Supporting Information

(C^C*) Cyclometalated Binuclear N-Heterocyclic Biscarbene Platinum(II) Complexes – Highly Emissive Phosphorescent Emitters

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List of Abbreviations

1D/2D-NMR	one-/twodimensional Nuclear Magnetic Resonance Spectroscopy
AcAc	Acetylacetonate, 2,4-Pentadione
B3LYP	Becke three-parameter exchange, Lee-Yang-Parr correlation functional
BCP	2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline
BP86	Becke 1988 exchange, Perdew86 correlation functional
CIE	Color coordinates, defined by an international commission (*CIE – Commission internationale de l'éclairage*)
COD	1,5-Cyclooctadiene
COSY	Homonuclear correlation spectroscopy
DFT	Density functional theory
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
ECP	Effective core potential
FMO	Frontier molecular orbital
HMBC	Heteronuclear multiple-bond correlation spectroscopy
HOMO	Highest occupied orbital
HSQC	Heteronuclear single-quantum correlation spectroscopy
Hz	Hertz
ILCT	Intraligand charge transfer
ITO	Indium-Tin-Oxide
KO^{t}Bu	Potassium *tert*-butanolate
LLCT	Interligand/ligand-to-ligand charge transfer
LUMO	Lowest unoccupied orbital
MLCT	Metal-to-ligand charge transfer
NHC	*N*-Heterocyclic carbene
NOESY	Nuclear Overhauser effect spectroscopy
OLED	organic light-emitting device/diode
PhOLED	Phosphorescent organic light-emitting device/diode
PMMA	Poly(methyl methacrylate)
SOC	Spin-orbit coupling
THF	Tetrahydrofuran

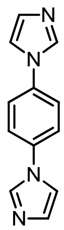
Experimental Details

Solvents of 99.5% purity were used throughout this study. 1,4-Dioxane and DMF were dried using standard techniques and stored under argon atmosphere over molecular sieve (4 Å). Dichloro(1,5-cyclooctadiene)platinum(II) was prepared differently from the literature procedure[1] as described in a previous report.[2] Dimesitoylmethane[3] was prepared according to literature procedure. Potassium tetrachloroplatinate(II) was obtained from Pressure Chemicals Co. All other chemicals were obtained from common suppliers and used without further purification. ^{1}H-, ^{13}C- and ^{195}Pt-NMR spectra were recorded on a Bruker AC 300 P, a Bruker DRX-500 or a Bruker Avance 600 spectrometer. ^{1}H and ^{13}C spectra were referenced internally using the resonances of the solvent (DMSO, $CDCl_3$). ^{195}Pt spectra were referenced externally using potassium tetrachloroplatinate(II) in perdeuterated water (-1617.2 ($PtCl_4^{2-}$), -2654.1 ($PtCl_2$)). Shifts are given in ppm, coupling constants *J* in Hz. Elemental analyses were performed by the microanalytical laboratory of our institute on a Hekatech EA 3000 Euro Vector elemental analyzer. Melting points have been determined using a Wagner and Munz PolyTherm A system and are not corrected. The photoluminescence of the complexes was measured in thin PMMA films doped with 2wt% emitter and/or in 100% emitter films. The 2wt% films were prepared by doctor blading a solution of emitter (2 mg/L) in a 10wt% PMMA solution in dichloromethane on a substrate with a 60 µm doctor blade. The film was dried and the emission was measured under nitrogen with a Hamamatsu Absolute PL Quantum Yield Measurement System C9920-02. The excitation was carried out at a wavelength of 355 – 370 nm (Xe-lamp with monochromator) and emission was detected with a calibrated CCD spectrometer. The phosphorescence decay was measured by excitation with pulses of a THG-NdYAG-Laser (355 nm, 1 ns) and time-resolved photon-counting in the Multi Channel Scaling (MCS)-Technique (Detector R928P from Hamamatsu, MCS Card P7888 from FAST Comtec).

For the production of the diode and testing an ITO substrate used as the anode was first cleaned by commercial detergents for the LCD-Production (Deconex® 20NS and 25ORGAN-ACID®) followed by immersion in a acetone/isopropanole-mixture in an ultrasonic bath. Afterwards the substrate is treated with ozone to remove residues of organic material. This treatment also improves the hole injection properties of the ITO substrate. Then the hole injection layer is spincoated from solution. This is followed by vacuum deposition of the various organic materials with rates of approximately 0.5-5 nm/min at 10^{-7}-10^{-9} mbar. Finally a layer of 0.75 nm lithium fluoride and a 100 nm aluminium electrode are deposited. All diodes are sealed with glass in an inert nitrogen atmosphere. For characterisation of the OLEDs the electroluminescence spectra were measured at various currents and voltages. The IV characteristic was measured in combination with the emitted light.

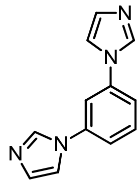
Synthesis

*1,4-Bis(imidazole)benzene (**1a**)*



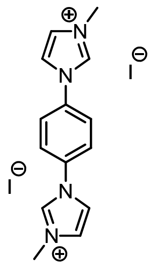
A dried schlenk tube was charged with 1,4-diiodobenzene (4.95 g, 15 mmol), imidazole (3.57 g, 52.5 mmol), potassium hydroxide (2.95 g, 52.5 mmol) and copper(I) oxide (0.43 g, 3 mmol) under an argon atmosphere. Dry DMSO was added through a septum after an additional degassing phase of the solids. The suspension was stirred for 48 hours at 130 °C. After cooling to room temperature the reaction mixture was poured into a water/ethyl acetate solution (1:3). Solids were filtered off and the phases separated. The aqueous phase was extracted with ethyl acetate (6x60 mL). The combined organic phases were washed with brine (50 mL) and dried over sodium sulfate. After concentration under reduced pressure the solid product was precipitated and washed with diethyl ether. Collecting the solid and drying under vacuum yielded the off-white product (1.55 g, 49.3%). ^{1}H-NMR ($CDCl_3$, 300.13 MHz): δ = 7.87 (s, 2H, NC*H*N), 7.51 (s, 4H, C$H_{arom.}$), 7.30 (t, J = 1.3 Hz, 2H, C$H_{arom.}$), 7.23 (s, 2H, C$H_{arom.}$) ppm. ^{13}C-NMR ($CDCl_3$, 75.475 MHz): δ = 136.4 (N*C*HN), 135.5 (C_i), 130.9 (CH$_{arom.}$), 122.8 (CH$_{arom.}$), 118.1 (CH$_{arom.}$) ppm. M.p. 208-210 °C. Anal. Calc. for $C_{12}H_{10}N_4$ (210.24 g mol^{-1}): C, 68.56; H, 4.79; N, 26.65. Found: C, 68.27; H, 4.98; N, 26.67 %.

*1,3-Bis(imidazole)benzene (**1b**)*



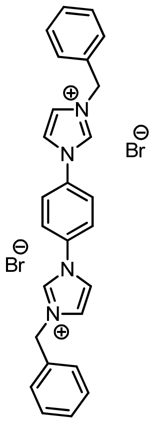
A dried schlenk tube was charged with 1,3-diiodobenzene (3.30 g, 10 mmol), imidazole (2.04 g, 30 mmol), potassium hydroxide (2.24 g, 40 mmol) and copper(I) oxide (0.29 g, 2 mmol) under an argon atmosphere. Dry DMSO was added through a septum after an additional degassing phase of the solids. The suspension was stirred for 48 hours at 120 °C. After cooling to room temperature the reaction mixture was poured into a water/ethyl acetate solution (1:3). Solids were filtered off and the phases separated. The aqueous phase was extracted with ethyl acetate (3x50 mL). The combined organic phases were washed with brine (50 mL) and dried over magnesium sulfate. The crude product was purified by flash chromatography with ethyl acetate yielding a pale brown crystalline solid (1.29 g, 61.3%). ^{1}H-NMR ($CDCl_3$, 300.13 MHz): δ = 7.93 (s, 2H, NC*H*N), 7.62 (t, *J* = 7.9 Hz, 1H, C$H_{arom.}$), 7.43 (s, 2H), 7.41 (s, 1H, C$H_{arom.}$), 7.33 (s, 2H, C$H_{arom.}$), 7.24 (s, 2H, C$H_{arom.}$) ppm. ^{13}C-NMR ($CDCl_3$, 75.475 MHz): δ = 138.7 (C_i), 135.5 (N*C*HN), 131.5 ($CH_{arom.}$), 131.0 ($CH_{arom.}$), 120.2 ($CH_{arom.}$), 118.1 ($CH_{arom.}$), 114.6 ($CH_{arom.}$) ppm. M.p. 129-131 °C. Anal. Calc. for $C_{12}H_{10}N_4$ (210.24 g mol^{-1}): C, 68.56; H, 4.79; N, 26.65. Found: C, 68.35; H, 4.74; N, 26.75 %.

*1,4-Bis(3-methylimidazolium)benzene iodide (**2a**)*



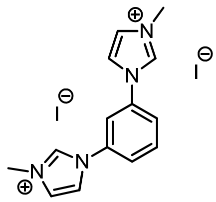
A sealed tube is charged with 1,4-bis(imidazole)benzene **1a** (1.05 g, 5 mmol) and iodomethane (1.9 mL, 30 mmol). After addition of 8 mL THF the tube is sealed and the reaction mixture stirred for 72 h at 100 °C. The generated solid is filtered off and washed with small portions of tetrahydrofuran and diethyl ether. After drying under vacuum an off-white solid is yielded (2.42 g, 98%). ^{1}H-NMR (d_6-DMSO, 300.13 MHz): δ = 9.90 (s, 2H, NC*H*N), 8.39 (s, 2H, C$H_{arom.}$), 8.10 (s, 4H, C$H_{arom.}$), 8.00 (s, 2H, C$H_{arom.}$), 3.98 (s, 6H, CH_3) ppm. ^{13}C-NMR (d_6-DMSO, 75.475 MHz): δ = 136.3 (N*C*HN), 135.2 (C_i), 124.6 (CH$_{arom.}$), 123.3 (CH$_{arom.}$), 120.9 (CH$_{arom.}$), 36.3 (CH$_3$) ppm. Dec. > ca. 300 °C. Anal. Calc. for $C_{14}H_{16}I_2N_4$ (494.12 g mol^{-1}): C, 34.03; H, 3.26; N, 11.34. Found: C, 33.94; H, 3.16; N, 11.33 %.

*1,4-Bis(3-benzylimidazolium)benzene bromide (**2b**)*



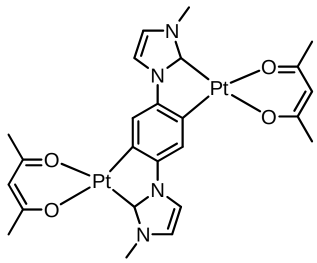
A sealed tube is charged with 1,4-bis(imidazole)benzene **1a** (0.51 g, 2.4 mmol) and benzylbromide (2.5 mL, 20.4 mmol). After addition of 8 mL THF the tube is sealed and the reaction mixture stirred for 48 h at 110 °C. The generated solid is filtered off and washed with small portions of tetrahydrofuran and diethyl ether. After drying under vacuum an off-white solid is yielded (1.25 g, 94%). ^{1}H-NMR (d_6-DMSO, 600.16 MHz): δ = 10.18 (s, 2H, NC*H*N), 8.45 (s, 2H, C$H_{arom.}$), 8.14 (s, 4H, C$H_{arom.}$), 8.10 (s, 2H, C$H_{arom.}$), 7.55 (d, J = 7.5 Hz, 4H, C$H_{arom.}$), 7.44 (m, 6H, C$H_{arom.}$), 5.54 (s, 4H, CH_2) ppm. ^{13}C-NMR (d_6-DMSO, 150.91 MHz): δ = 135.9 (C_i), 135.1 (NCHN), 134.2 (C_i), 128.9 (CH$_{arom.}$), 128.8 (CH$_{arom.}$), 128.5 (CH$_{arom.}$), 123.3 (CH$_{arom.}$), 121.6 (CH$_{arom.}$), 52.4 (CH$_2$) ppm. Dec. > ca. 345 °C. Anal. Calc. for $C_{26}H_{24}Br_2N_4$ (552.30 g mol^{-1}): C, 56.54; H, 4.38; N, 10.14. Found: C, 56.22; H, 4.45; N, 10.07 %.

*1,3-Bis(3-methylimidazolium)benzene iodide (**2c**)*



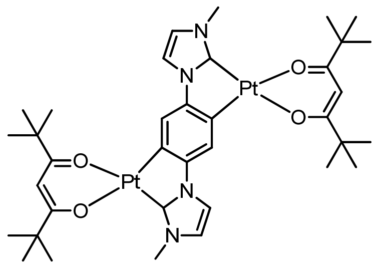
A sealed tube is charged with 1,3-bis(imidazole)benzene **1b** (0.42 g, 2 mmol) and iodomethane (1.2 mL, 8 mmol). After addition of 5 mL THF the tube is sealed and the reaction mixture stirred for 48 h at 100 °C. The generated solid is filtered off and washed with small portions of tetrahydrofuran and diethyl ether. After drying under vacuum an off-white solid is yielded (0.97 g, 98%). ^{1}H-NMR (d_6-DMSO, 600.16 MHz): δ = 9.90 (s, 2H, NC*H*N), 8.38 (s, 2H, C$H_{arom.}$), 8.31 (s, 1H, C$H_{arom.}$), 8.03 (s, 2H, C$H_{arom.}$), 8.00 (m, 3H, C$H_{arom.}$), 3.99 (s, 6H, CH_3) ppm. ^{13}C-NMR (d_6-DMSO, 150.91 MHz): δ = 136.4 (N*C*HN), 135.8 (C_i), 132.1 (CH$_{arom.}$), 124.8 (CH$_{arom.}$), 122.6 (CH$_{arom.}$), 121.0 (CH$_{arom.}$), 115.7 (CH$_{arom.}$), 36.3 (CH$_3$) ppm. M.p. 266-269 °C. Anal. Calc. for $C_{14}H_{16}I_2N_4$ (494.12 g mol^{-1}): C, 34.03; H, 3.26; N, 11.34. Found: C, 33.88; H, 3.19; N, 11.32 %.

*1,4-Bis{(SP-4)-[(3-methyl-1H-imidazol-2-ylidene-κC2)(pentan-2,4-dionato-κO2,κO4)platinum(II)] (κN1,κPt1,κN1‘,κPt1‘)benzene (**3a**)*



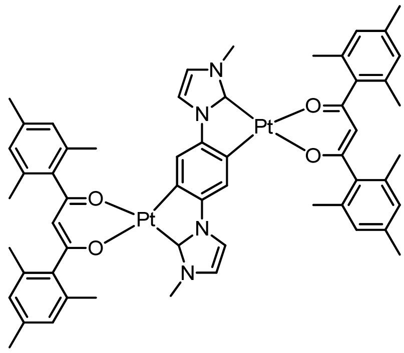
A dried and argon flushed schlenk tube was charged with 1,4-bis(3-methylimidazolium)benzene iodide **2a** (0.40 g, 0.8 mmol) and silver(I) oxide (0.20 g, 0.88 mmol). After addition of 20 mL dry 1,4-dioxane the reaction mixture was stirred under argon in the dark at room temperature for 48 h. Dichloro(1,5-cyclooctadiene)platinum(II) (0.75 g, 2 mmol) and 10 mL 2-butanone were added. The mixture was heated to 115 °C and stirred for another 54 h. Afterwards all volatiles were removed under reduced pressure. Potassium *tert*-butanolate (0.72 g, 6.4 mmol), acetylacetone (0.66 mL, 6.4 mmol) and 25 mL dry DMF were added under argon. After stirring for 28 h at room temperature and 14 h at 100 °C all volatiles were again removed under reduced pressure leaving the crude product, which was washed with water and purified by flash chromatography with methylene chloride/acetone 5/1. The product containing fraction was finally recrystallized from methylene chloride/tetrahydrofuran 1/1 solution and dried under vacuum to give a light-yellow solid (0.04 g, 6%). ^{1}H-NMR (d_6-DMSO, 300.13 MHz): δ = 7.77 (d, J = 2.0 Hz, 2H, NC*H*), 7.32 (d, J = 2.0 Hz, 2H, NC*H*), 7.21 (s, 2H, C$H_{arom.}$), 5.57 (s, 2H, OCC*H*), 3.98 (s, 6H, NCH_3), 2.05 (s, 6H, CCH_3), 1.92 (s, 6H, CCH_3) ppm. ^{13}C-NMR (d_6-DMSO, 150.927 MHz): δ = 184.1 (*C*O), 146.6 (N*C*N), 141.8 (Pt*C*), 121.6 (N*C*H), 118.8 (N*C*), 114.9 (N*C*H), 113.4 ($CH_{arom.}$), 101.7 (*C*H), 34.2 (NCH_3), 27.7 (C*C*H3) ppm. Dec. > ca. 310 °C. Anal. Calc. for $C_{24}H_{26}N_4O_4Pt_2$ (824.66 g mol^{-1}): C, 34.95; H, 3.18; N, 6.78. Found: C, 34.69; H, 3.15; N, 6.57 %.

*1,4-Bis{(SP-4)-[(3-methyl-1H-imidazol-2-ylidene-κC2)(2,2,6,6-tetramethylheptan-3,5-dionato-κO3,κO5)platinum(II)] (κN1,κPt1,κN1',κPt1')benzene (**3b**)*



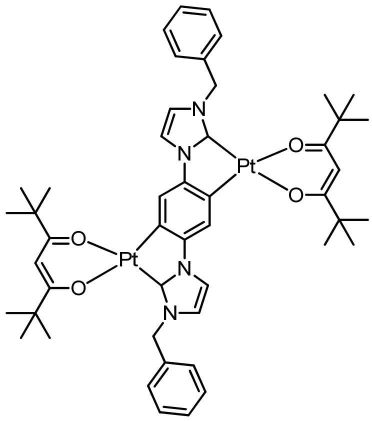
A dried and argon flushed schlenk tube was charged with 1,4-bis(3-methylimidazolium)benzene iodide **2a** (0.99 g, 2 mmol) and silver(I) oxide (0.70 g, 3 mmol). After addition of 30 mL dry 1,4-dioxane the reaction mixture was stirred under argon in the dark at room temperature for 72 h. Dichloro(1,5-cyclooctadiene)platinum(II) (1.87 g, 5 mmol) and 15 mL 2-butanone were added. The mixture was heated to 115 °C and stirred for another 96 h. Afterwards all volatiles were removed under reduced pressure. Potassium *tert*-butanolate (1.79 g, 16 mmol), 2,2,6,6-tetramethyl-3,5-heptanedione (2.95 g, 16 mmol) and 30 mL dry DMF were added under argon. After stirring for 3 days at room temperature and 24 h at 100 °C all volatiles were again removed under reduced pressure leaving the crude product, which was washed with water and purified by flash chromatography with methylene chloride. The product containing fraction was finally washed with diethyl ether to remove traces of the dione and dried under vacuum to give a light-yellow solid (0.33 g, 16%). ^{1}H-NMR ($CDCl_3$, 600.16 MHz): δ = 7.44 (*pseudo*-t, $J_{H,Pt}$ = 27.5 Hz, 2H, C$H_{arom.}$), 7.20 (d, J = 2.0 Hz, 2H, NC*H*), 6.77 (d, J = 2.0 Hz, 2H, NC*H*), 5.81 (s, 2H, OCC*H*), 4.09 (s, 6H, NCH_3), 1.33 (s, 18H, CCH_3), 1.21 (s, 18H, CCH_3) ppm. ^{13}C-NMR ($CDCl_3$, 150.91 MHz): δ = 194.4 (*C*O), 193.8 (*C*O), 149.3 (N*C*N), 142.5 (Pt*C*), 119.8 (N*C*H), 119.1 (N*C*), 114.3 (N*C*H), 113.5 (*C*$H_{arom.}$), 92.8 (OC*C*H), 42.0 (*C*CH_3), 41.4 (*C*CH_3), 35.1 (N*C*H_3), 28.8 (*C*H_3), 28.7 (*C*H_3), ppm. ^{195}Pt-NMR (CDCl3, 64.52 MHz): δ = -3402.7 (d, J = 52.0 Hz) ppm. Dec. > 275 °C. Anal. Calc. for $C_{36}H_{50}N_4O_4Pt_2$ (992.98 g mol^{-1}): C, 43.55; H, 5.08; N, 5.64. Found: C, 43.58; H, 5.31; N, 5.49 %.

1,4-Bis{(SP-4)-[(3-methyl-1H-imidazol-2-ylidene-κC2)(1,3-dimesitoylpropan-1,3-dionato-κO1,κO3)platinum(II)] (κN1,κPt1,κN1',κPt1')benzene (**3c**)



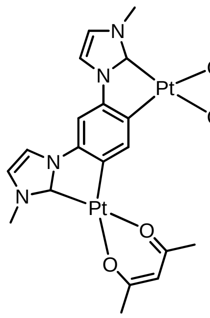
A dried and argon flushed schlenk tube was charged with 1,4-bis(3-methylimidazolium)benzene iodide **2a** (0.40 g, 0.8 mmol) and silver(I) oxide (0.19 g, 0.8 mmol). After addition of 20 mL dry 1,4-dioxane the reaction mixture was stirred under argon in the dark at room temperature for 48 h. Dichloro(1,5-cyclooctadiene)platinum(II) (0.75 g, 2 mmol) and 10 mL 2-butanone were added. The mixture was heated to 115 °C and stirred for another 48 h. Afterwards all volatiles were removed under reduced pressure. Potassium *tert*-butanolate (0.72 g, 6.4 mmol), dimesitoylmethane (1.97 g, 6.4 mmol) and 20 mL dry DMF were added under argon. After stirring for 64 h at room temperature and 7 h at 100 °C all volatiles were again removed under reduced pressure leaving the crude product, which was washed with water and purified by flash chromatography with methylene chloride/acetone. After drying under vacuum a light-yellow solid was obtained (0.21 g, 21%). ^{1}H-NMR ($CDCl_3$, 600.16 MHz): δ = 7.24 (s, 2H, $CH_{arom.}$), 7.14 (d, *J* = 2.0 Hz, 2H, NC*H*), 6.86 (s, 4H, $CH_{arom.}$), 6.82 (s, 4H, $CH_{arom.}$), 6.66 (d, *J* = 2.0 Hz, 2H, NC*H*), 5.64 (s, 2H, OCC*H*), 3.87 (s, 6H, NCH_3), 2.37 (s, 12H, CCH_3), 2.31 (s, 12H, CCH_3), 2.30 (s, 6H, CCH_3), 2.28 (s, 6H, CCH_3) ppm. ^{13}C-NMR ($CDCl_3$, 150.91 MHz): δ = 184.6 (*C*O), 183.9 (*C*O), 147.7 (N*C*N), 142.7 (Pt*C*), 139.9 (C_i), 139.4 (C_i), 137.4 (C_i), 137.2 (C_i), 134.3 (C_i), 133.7 (C_i), 128.2 ($CH_{arom.}$), 128.0 ($CH_{arom.}$), 120.0 (N*C*H), 118.5 (N*C*), 114.8 (N*C*H), 113.7 ($CH_{arom.}$), 107.2 (OC*C*H), 34.8 (NCH_3), 21.12 (CH_3), 21.08 (CH_3), 20.1 (CH_3), 19.5 (CH_3) ppm. ^{195}Pt-NMR (CDCl3, 64.52 MHz): δ = -3354.8 (s) ppm. M.p. 240-242 °C. Anal. Calc. for $C_{56}H_{58}N_4O_4Pt_2$ (1241.26 g mol^{-1}): C, 54.19; H, 4.71; N, 4.51. Found: C, 54.13; H, 4.87; N, 4.35 %.

*1,4-Bis{(SP-4)-[(3-benzyl-1H-imidazol-2-ylidene-κC2)(2,2,6,6-tetramethylheptan-3,5-dionato-κO3,κO5)platinum(II)] (κN1,κPt1,κN1‘,κPt1‘)benzene (**3d**)*



A dried and argon flushed schlenk tube was charged with 1,4-bis(3-methylimidazolium)benzene iodide **2b** (0.44 g, 0.8 mmol) and silver(I) oxide (0.19 g, 0.8 mmol). After addition of 20 mL dry 1,4-dioxane the reaction mixture was stirred under argon in the dark at room temperature for 48 h. Dichloro(1,5-cyclooctadiene)platinum(II) (0.75 g, 2 mmol) and 10 mL 2-butanone were added. The mixture was heated to 115 °C and stirred for another 48 h. Afterwards all volatiles were removed under reduced pressure. Potassium *tert*-butanolate (0.72 g, 6.4 mmol), 2,2,6,6-tetramethyl-3,5-heptanedione (1.18 g, 6.4 mmol) and 20 mL dry DMF were added under argon. After stirring for 2 days at room temperature and 6 h at 100 °C all volatiles were again removed under reduced pressure leaving the crude product, which was washed with water and purified by flash chromatography with methylene chloride. The product was dried under vacuum to give a light-yellow solid (57 mg, 6%). ^{1}H-NMR ($CDCl_3$, 600.16 MHz): δ = 7.50 (s, 2H, C$H_{arom.}$), 7.43 (d, J = 7.1 Hz, 4H, C$H_{arom.}$), 7.33 (t, J = 7.3 Hz, 4H, C$H_{arom.}$), 7.28 (t, J = 7.3 Hz, 2H, C$H_{arom.}$), 7.21 (d, J = 2.0 Hz, 2H, NC*H*), 6.71 (d, J = 2.0 Hz, 2H, NC*H*), 5.80 (s, 2H, C*H*), 5.79 (s, 4H, CH_2), 1.31 (s, 18H, CH_3), 1.03 (s, 18H, CH_3) ppm. ^{13}C-NMR ($CDCl_3$, 150.91 MHz): δ = 194.6 (*C*O), 193.9 (*C*O), 149.1 (N*C*N), 142.5 (Pt*C*), 137.0 (CH_2*C*), 128.7 (*C*$H_{arom.}$), 128.1 (*C*$H_{arom.}$), 127.9 (*C*$H_{arom.}$), 119.2 (N*C*), 118.4 (N*C*H), 115.0 (N*C*H), 113.5 (*C*$H_{arom.}$), 92.9 (*C*H), 51.1 (*C*H_2), 41.8 (*C*CH_3), 41.3 (*C*CH_3), 28.7 (*C*H_3), 28.4 (*C*H_3) ppm. ^{195}Pt-NMR (CDCl3, 64.52 MHz): δ = -3402.0 ppm. Dec. > 288 °C. Anal. Calc. for $C_{48}H_{58}N_4O_4Pt_2$ (1145.17 g mol^{-1}): C, 50.34; H, 5.10; N, 4.89. Found: C, 50.66; H, 5.22; N, 4.70 %.

*1,3-Bis{(SP-4)-[(3-methyl-1H-imidazol-2-ylidene-κC2)(pentan-2,4-dionato-κO2,κO4)platinum(II)] (κN1,κPt1,κN1‘,κPt1‘)benzene (**3e**)*



A dried and argon flushed schlenk tube was charged with 1,3-bis(3-methylimidazolium)benzene iodide **2c** (0.40 g, 0.8 mmol) and silver(I) oxide (0.19 g, 0.8 mmol). After addition of 20 mL dry 1,4-dioxane the reaction mixture was stirred under argon in the dark at room temperature for 48 h. Dichloro(1,5-cyclooctadiene)platinum(II) (0.75 g, 2 mmol) and 10 mL 2-butanone were added. The mixture was heated to 115 °C and stirred for another 48 h. Afterwards all volatiles were removed under reduced pressure. Potassium *tert*-butanolate (0.72 g, 6.4 mmol), acetylacetone (0.66 mL, 6.4 mmol) and 25 mL dry DMF were added under argon. After stirring for 60 h at room temperature and 16 h at 100 °C all volatiles were again removed under reduced pressure leaving the crude product, which was washed with water and purified by flash chromatography with methylene chloride/acetone. Drying under vacuum gave an off-white solid (0.06 g, 7%). ^{1}H-NMR (d_6-DMSO, 600.16 MHz): δ = 7.82 (s, 1H, C$H_{arom.}$), 7.66 (d, J = 2.0 Hz, 2H, NCH), 7.32 (d, J = 2.0 Hz, 2H, NCH), 7.25 (s, 1H, C$H_{arom.}$), 5.56 (s, 2H, OCCH), 3.98 (s, 6H, NCH_3), 1.99 (s, 6H, CCH_3), 1.92 (s, 6H, CCH_3) ppm. ^{13}C-NMR (d_6-DMSO, 150.91 MHz): δ = 184.6 (CO), 183.8 (CO), 147.4 (NCN), 142.3 (PtC), 134.7 (CH$_{arom.}$), 121.9 (NCH), 118.9 (C_i), 114.4 (NCH), 101.6 (OCCH), 96.2 (CH$_{arom.}$), 34.1 (NCH$_3$), 27.8 (CH$_3$), 27.4 (CH$_3$) ppm. ^{195}Pt-NMR (d_6-DMSO, 64.52 MHz): δ = -3416.3 ppm. M.p. > 320 °C. Anal. Calc. for $C_{24}H_{26}N_4O_4Pt_2$ (824.66 g mol^{-1}): C, 34.96; H, 3.18; N, 6.79. Found: C, 34.58; H, 3.02; N, 6.42 %.

Photoluminescence Data

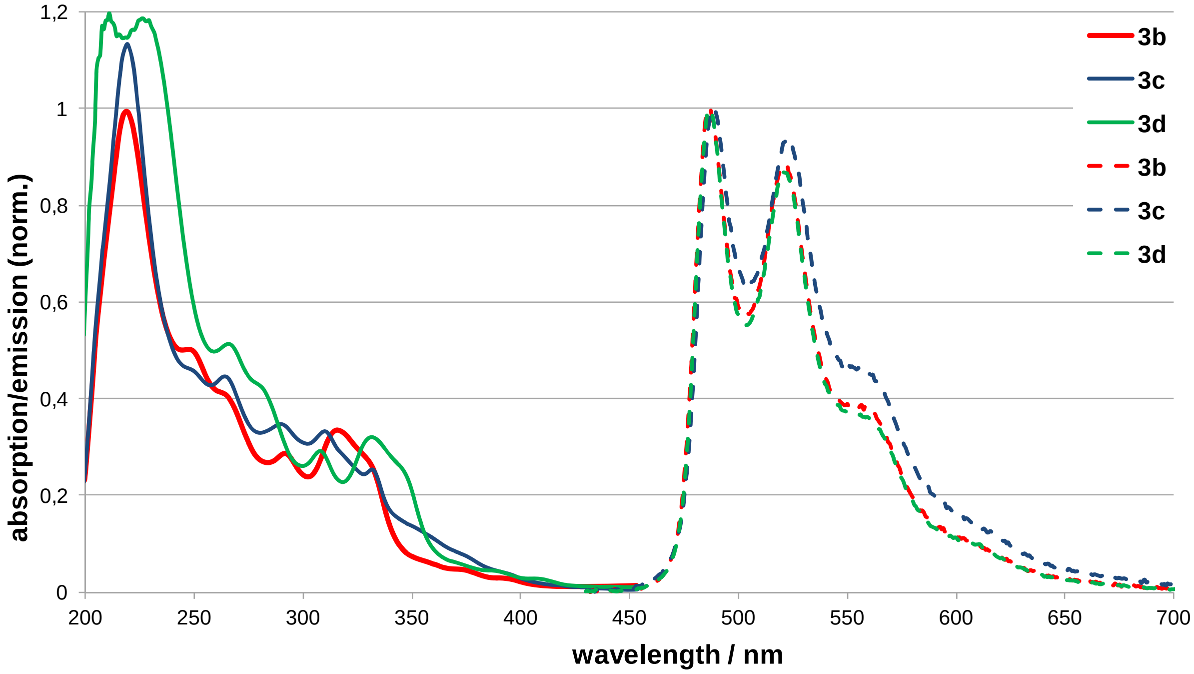


Figure S1. Absorption (left) and emission (right) spectra, 2wt% emitter in PMMA at room temperature.

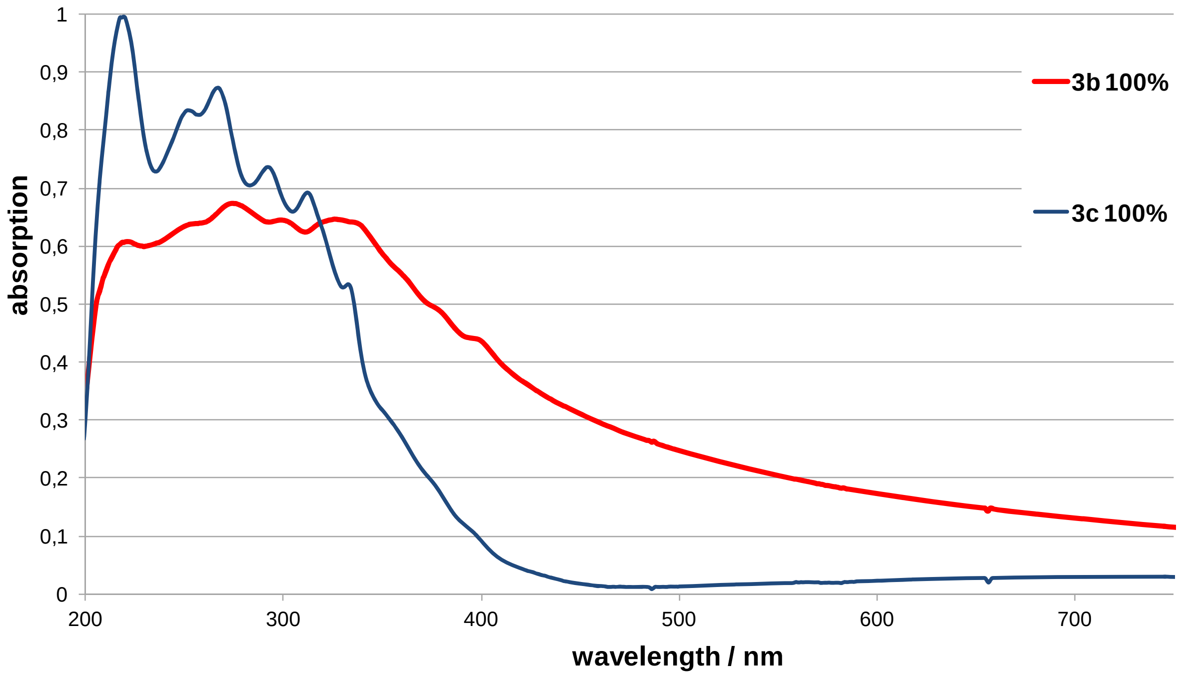


Figure S2. Absorption spectra for **3b** and **3c** as 100% films.

Device Data

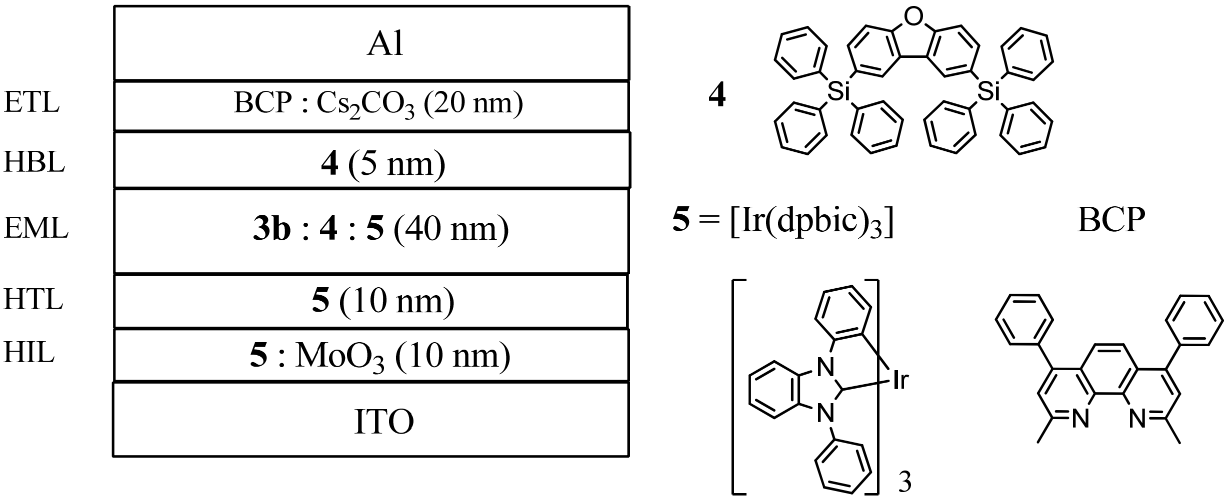


Figure S3. Device layout (left) and structure of **4** and **5** (right). ETL = electron-transport layer, HBL = hole-blocking layer, EML = emission layer, HTL = hole-transport layer, HIL = hole-injection layer. BCP = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline.

NMR Characterization

In the following section 2D NMR spectra (COSY, HSQC, HMBC for **3c**-**3e** and NOESY for **3d** and **3e**) are given.

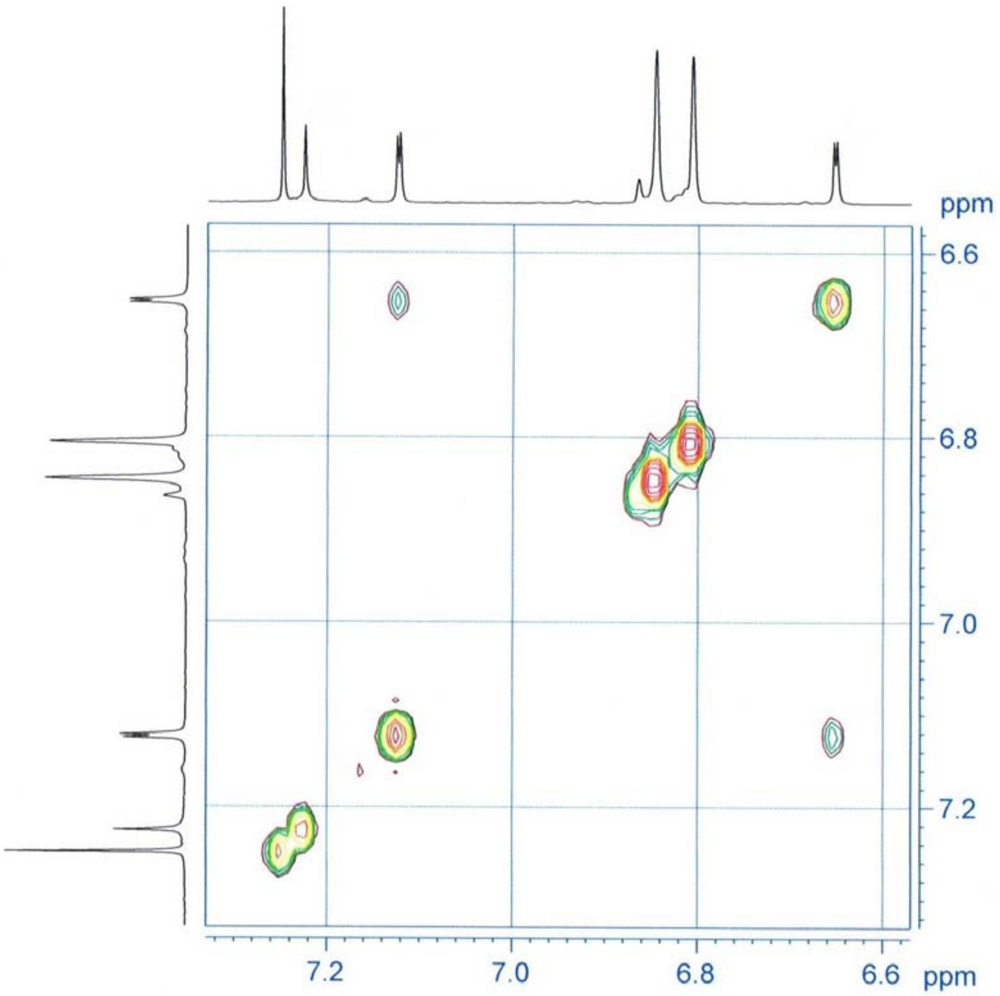


Figure S4. COSY spectrum of **3c** in $CDCl_3$.

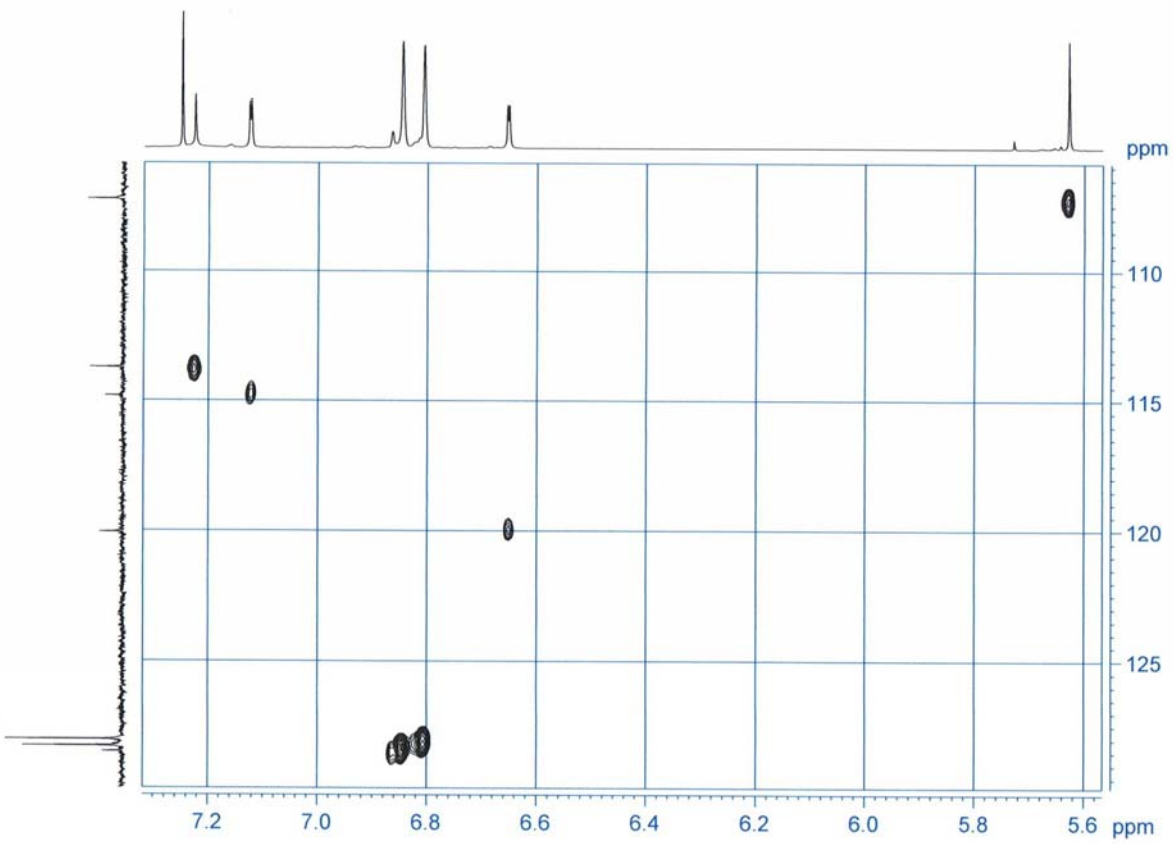


Figure S5. HSQC spectrum of **3c** in $CDCl_3$.

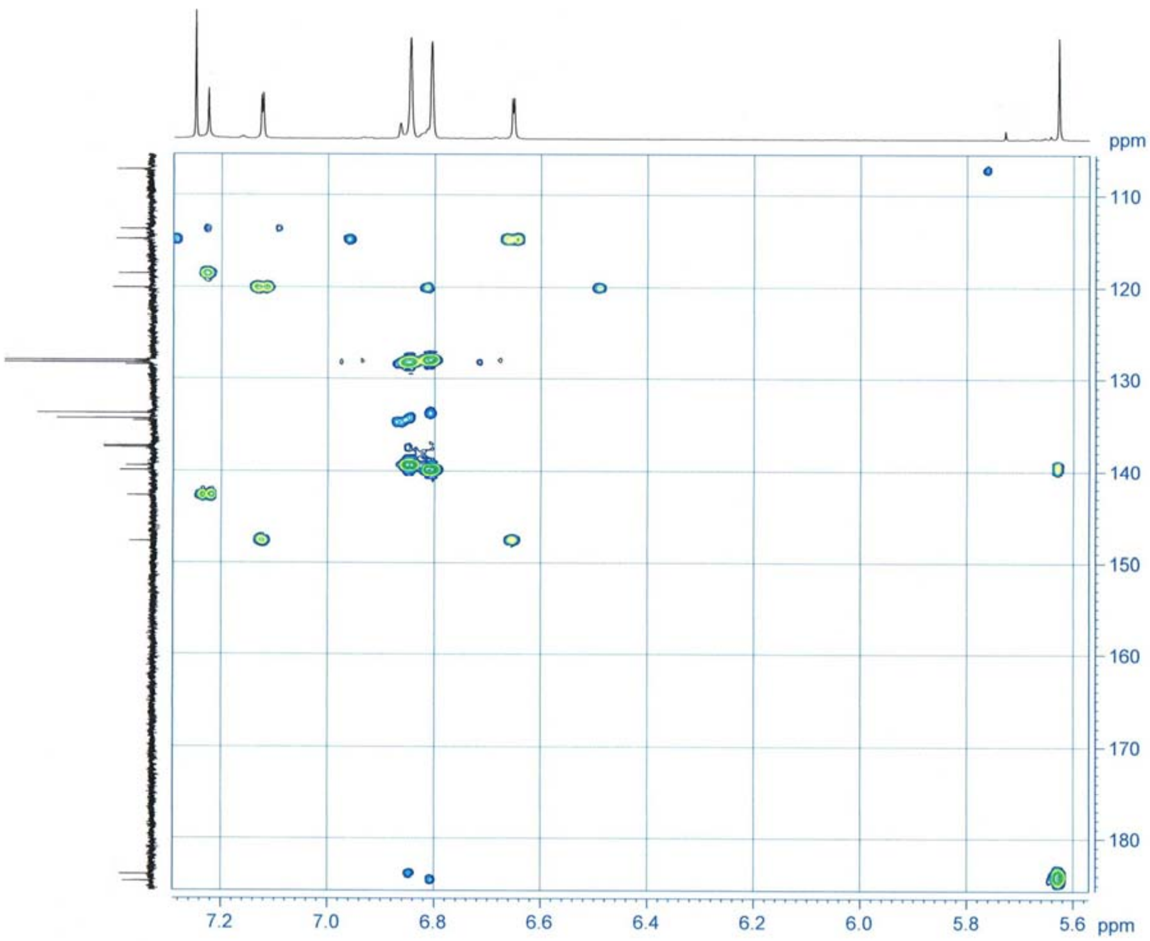


Figure S6. HMBC spectrum of **3c** in $CDCl_3$.

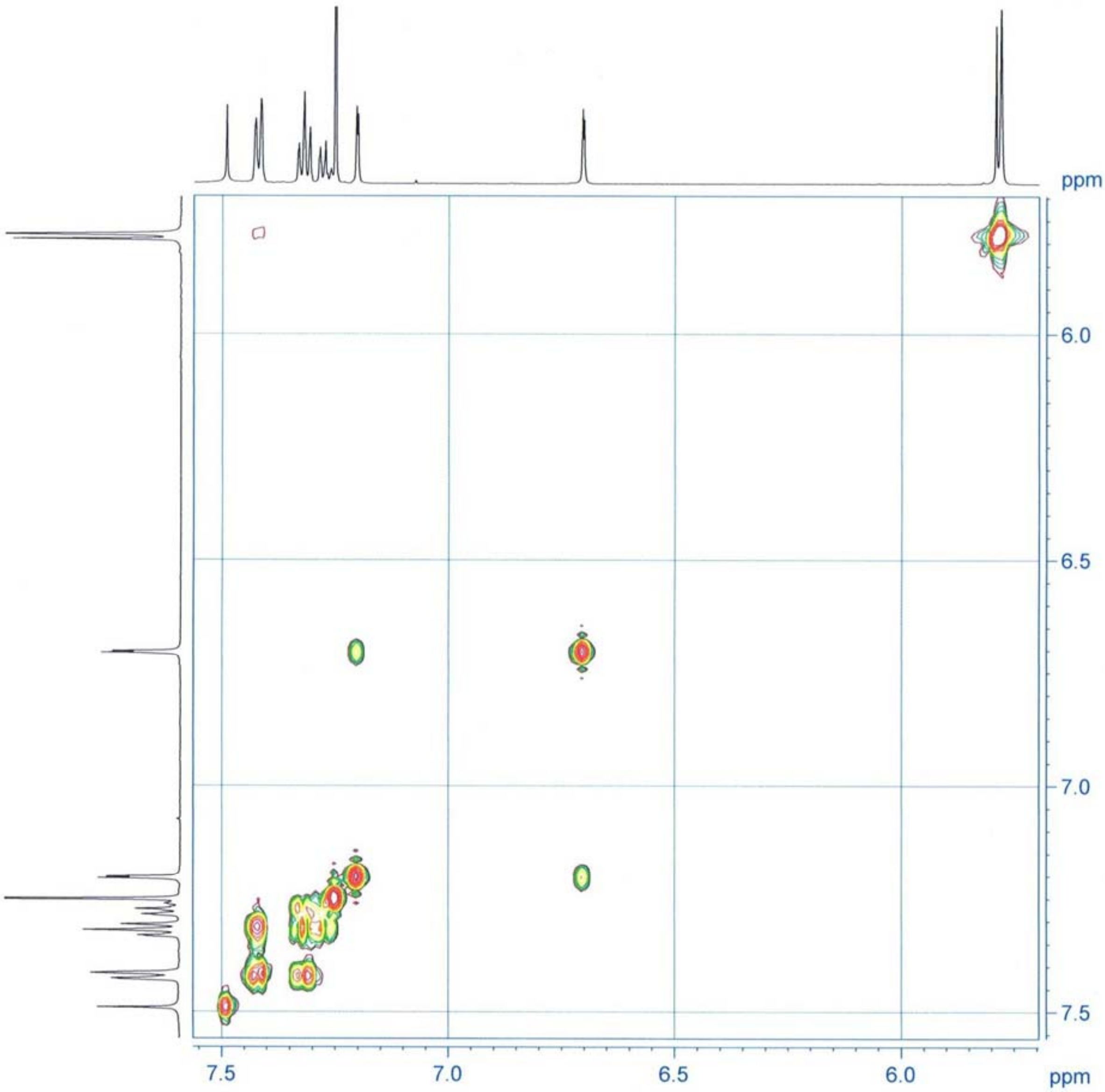


Figure S7. COSY spectrum of **3d** in $CDCl_3$.

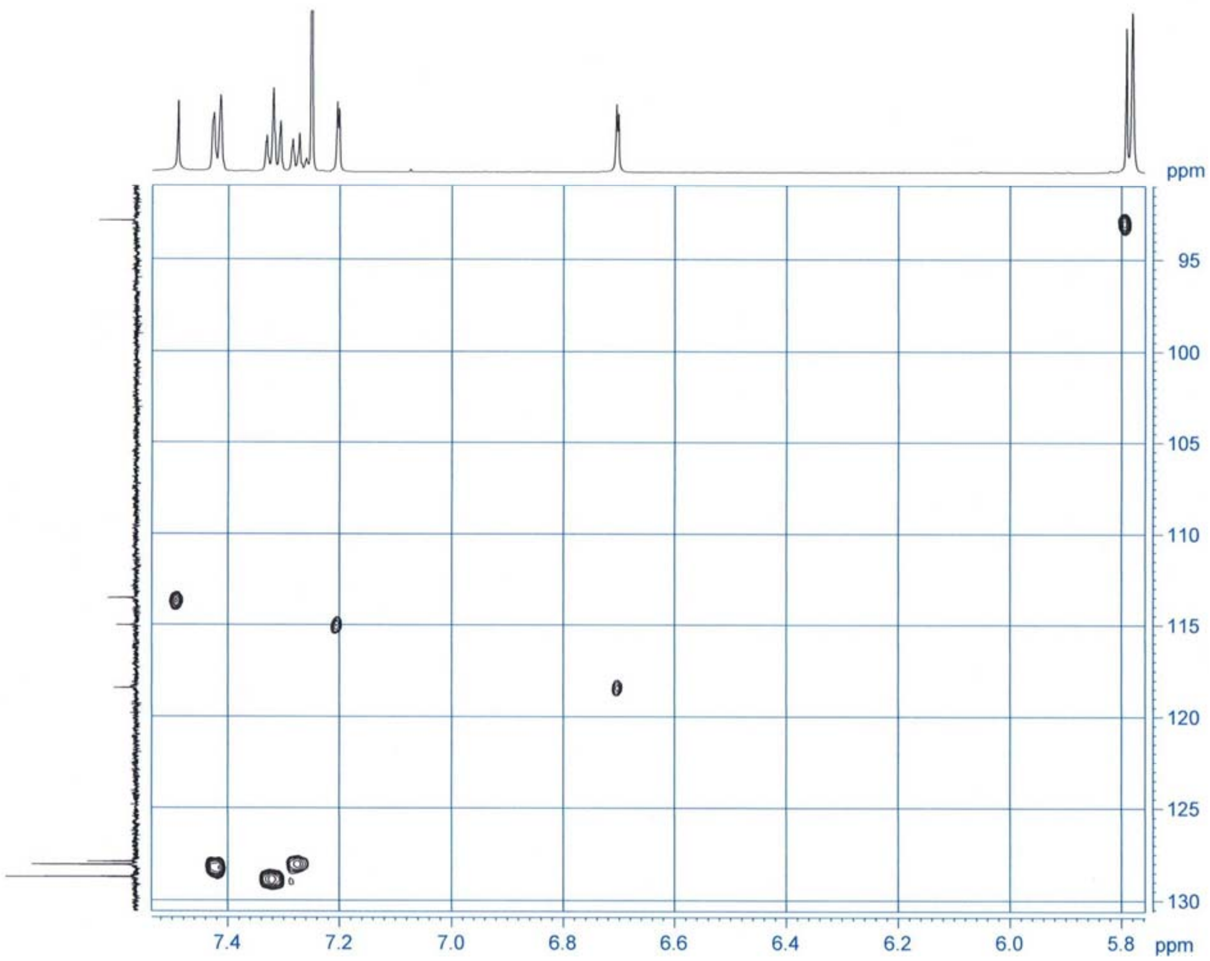


Figure S8. HSQC spectrum of **3d** in $CDCl_3$.

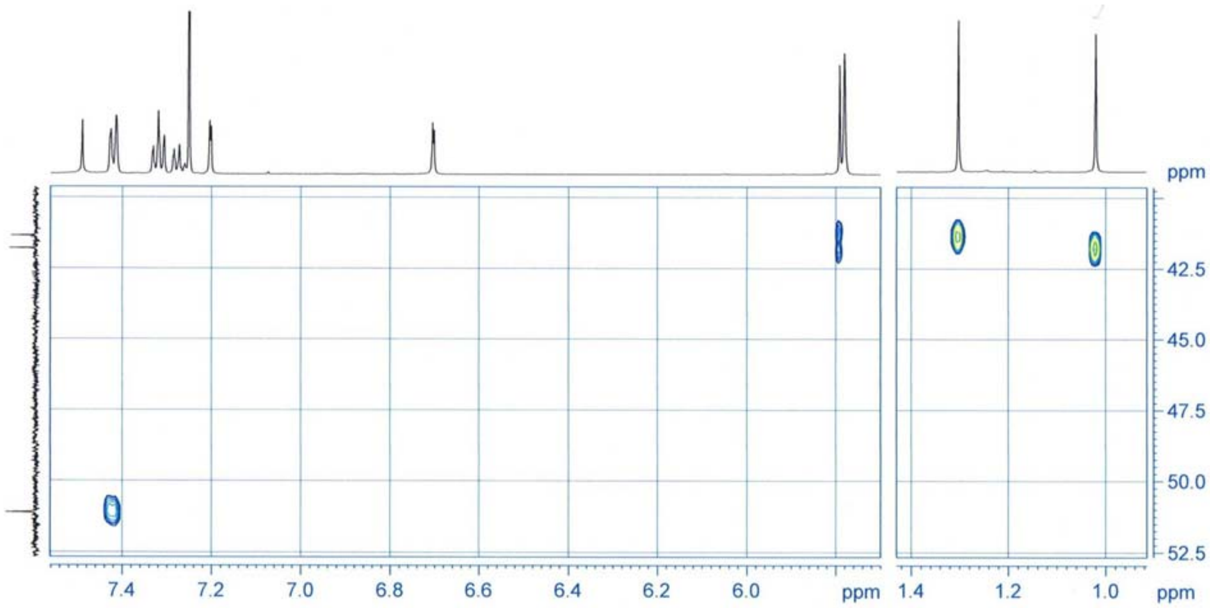


Figure S9a. HMBC spectrum of **3d** in $CDCl_3$.

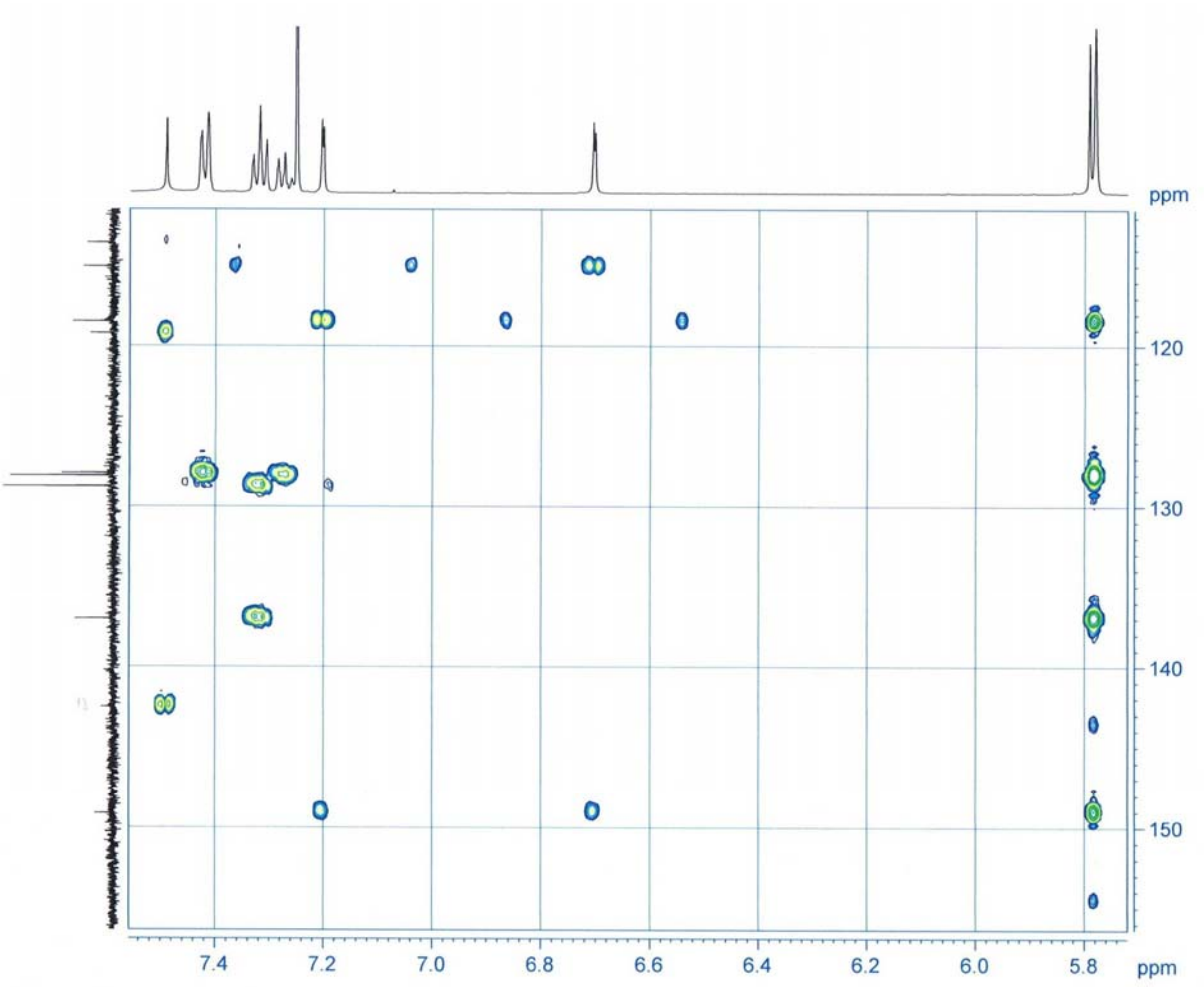


Figure S9b. HMBC spectrum of **3d** in $CDCl_3$.

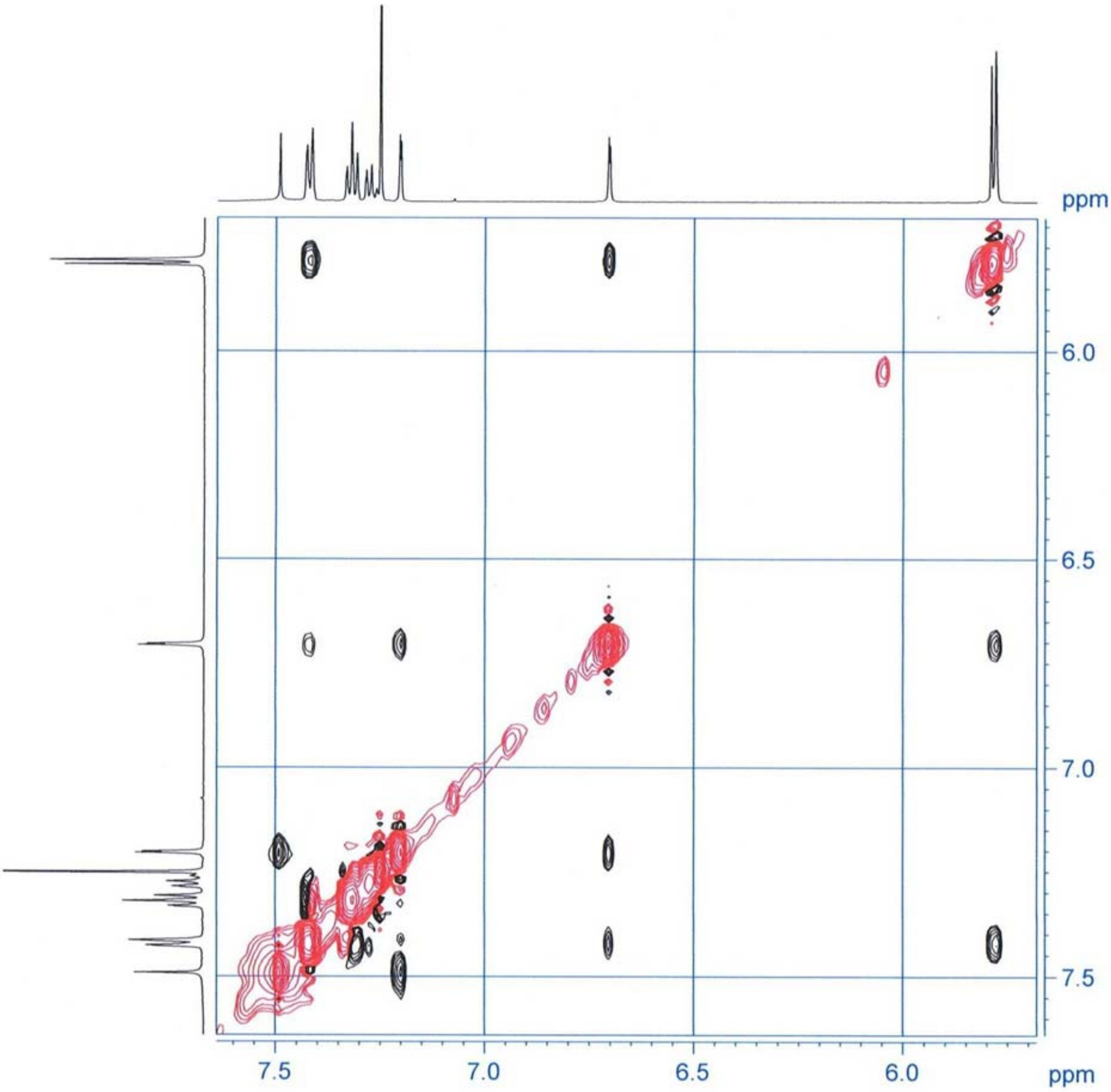


Figure S10. NOESY spectrum of **3d** in $CDCl_3$.

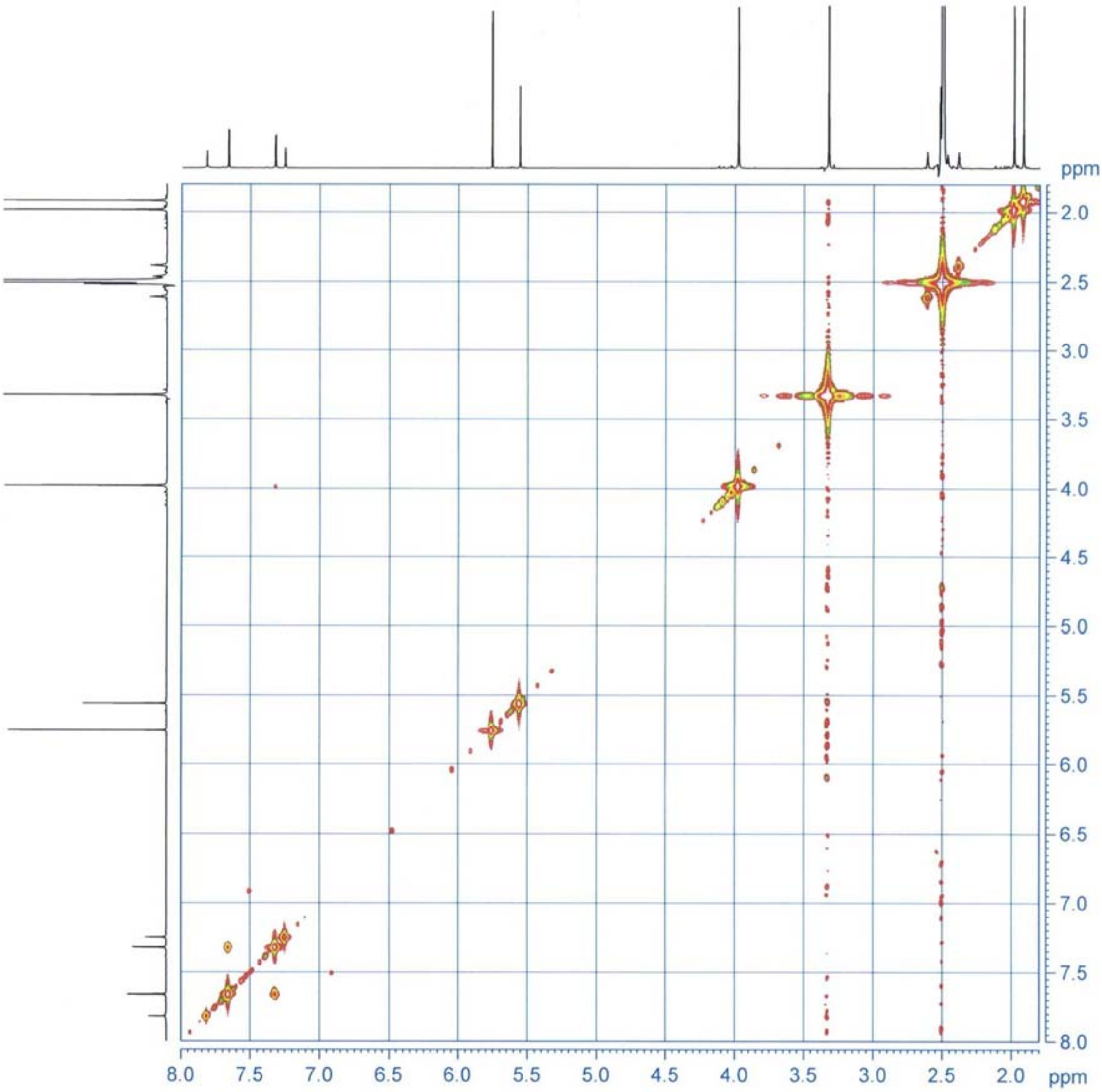


Figure S11. COSY spectrum of **3e** in DMSO-d_6.

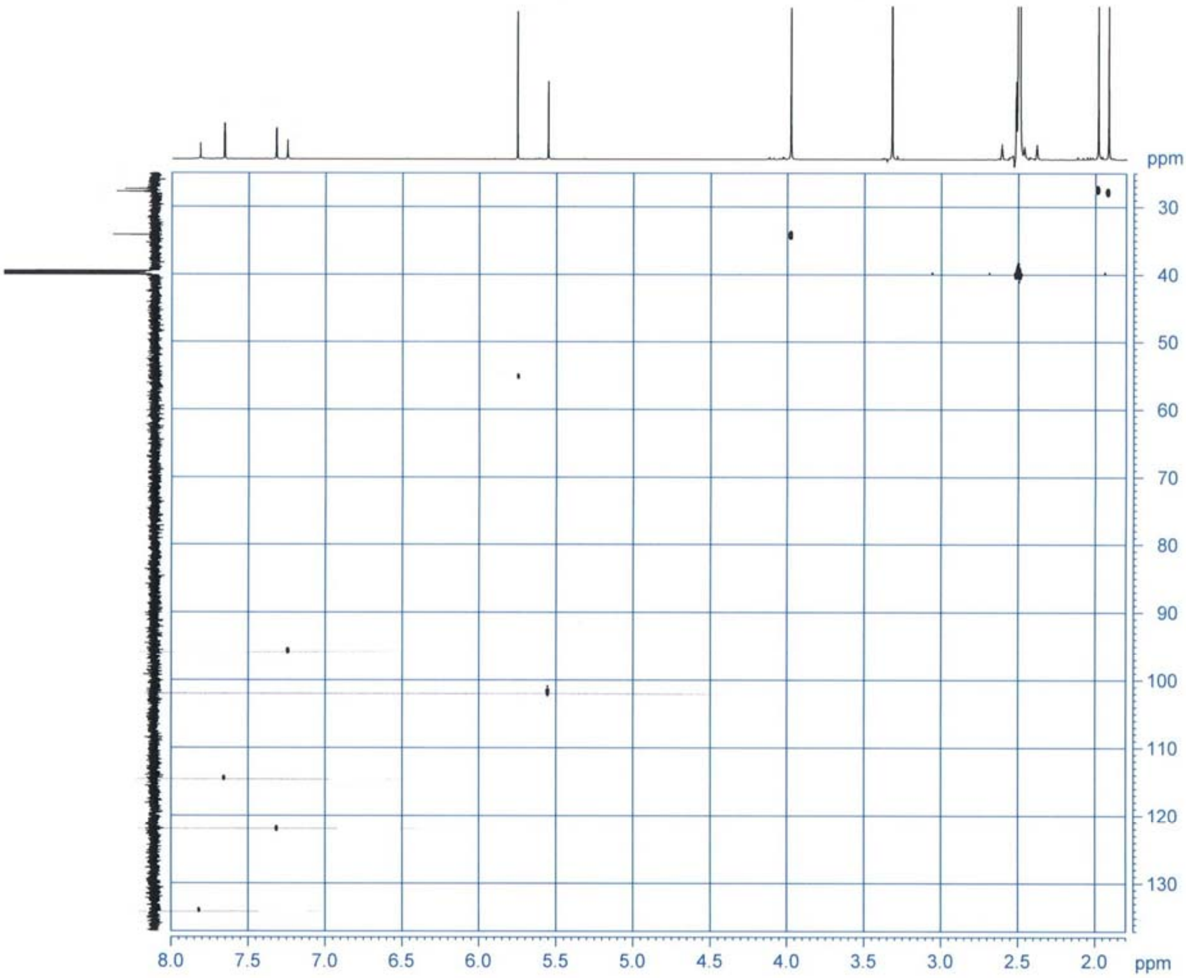


Figure S12. HSQC spectrum of **3e** in DMSO-d_6.

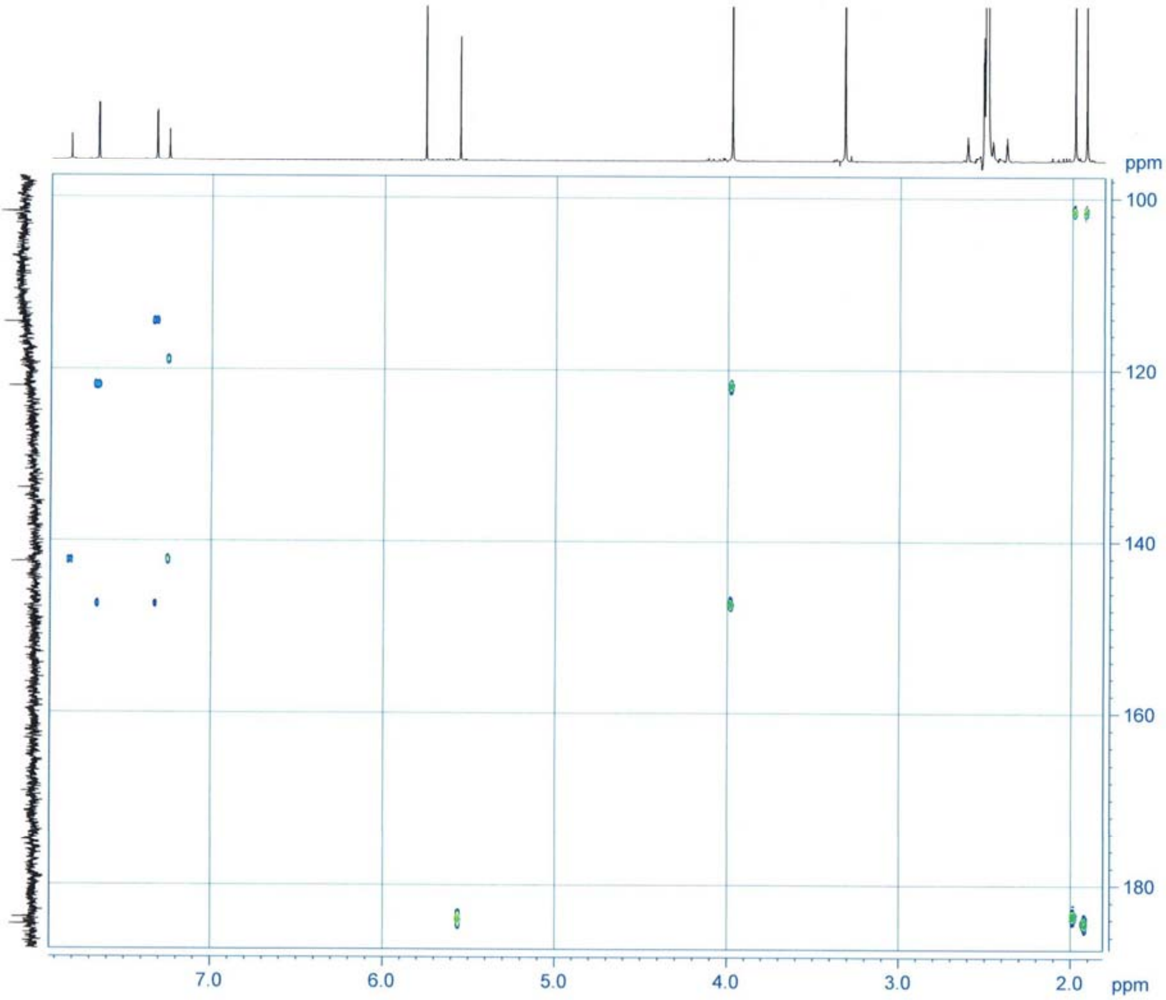


Figure S12. HMBC spectrum of **3e** in DMSO-d$_6$.

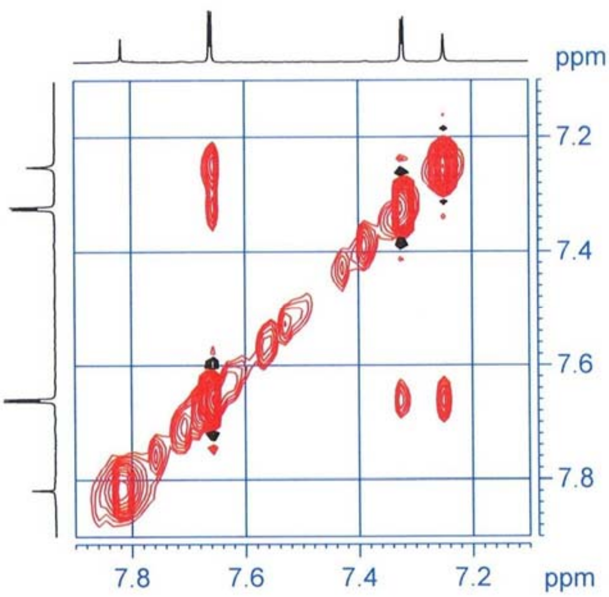


Figure S14. NOESY spectrum of **3e** in DMSO-d$_6$.

Solid-state structure determination

Preliminary examination and data collection were carried out on an area detecting system (Kappa-CCD; Nonius, FR590) using graphite monochromated Mo-Kα radiation (λ=0.71073 Å) with an Oxford Cryosystems cooling system at the window of a sealed fine-focus X-ray tube. The reflections were integrated. Raw data were corrected for Lorentz, polarization, decay and absorption effects. The absorption correction was applied using SADABS.[4] After merging the independent reflections were used for all calculations. The structure was solved by a combination of direct methods[5] and difference Fourier syntheses.[6] All non-hydrogen atom positions were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal positions using SHELXL riding model. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. Details of the structure determinations are given in the Supporting Information. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.[7] All calculations were performed with the programs COLLECT,[8] DIRAX,[9] EVALCCD,[10] SIR92,[5a] SIR97,[5b] SIR2004,[5c] SADABS,[4] PLATON[11] and the SHELXL-97 package.[6, 12] For the visualization Mercury[13] and ORTEP-III[14] were used.

Table S1. Crystallographic details for the salt **2b** and the complexes **3b** and **3c**.

Complex	**2b**	**3b**	**3c**
CCDC #	930701	930702	930703
empirical formula	C_{26} H_{24} Br_2 N_4	C_{36} H_{50} N_4 O_4 Pt_2	C_{56} H_{58} N_2 O_4 Pt_2
formula weight [g/mol]	552.31	992.28	1241.24
T [K]	198(2)	198(2)	198(2)
wavelength [Å]	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic
space group	P 21/c	P 21/n	P 21/n
a [Å]	12.301(3)	11.198(3)	11.342(2)
b [Å]	8.981(18)	12.003(2)	19.880(3)
c [Å]	11.865(2)	13.678(2)	12.6380(14)
α [°]	90	90	90
β [°]	112.87(3)	94.38(3)	101.411(9)
γ [°]	90	90	90
U [$Å^3$]	1207.7(4)	1833.1(6)	2793.3(8)
Z	2	2	2
D_{calc} [Mg/m^3]	1.519	1.799	1.476
μ(MoKα) [mm^{-1}]	3.377	7.665	5.047
crystal size [mm^3]	0.80x0.75x0.15	0.45x0.44x0.36	0.45x0.43x0.29
F(000)	556	964	1220
reflections collected	19823	37526	68874
independent reflections	2193 R_{int} = 0.059	3721 R_{int} = 0.040	5722 R_{int} = 0.050
Goodness-of-fit on F^2	1.051	1.152	1.113
R_1 [I>2σ(I)]	0.0359	0.0178	0.0286
wR_2	0.0685	0.0368	0.0659
data / restraints / parameters	2193/ 0 / 145	3721 / 0 / 215	5722 / 0 / 305

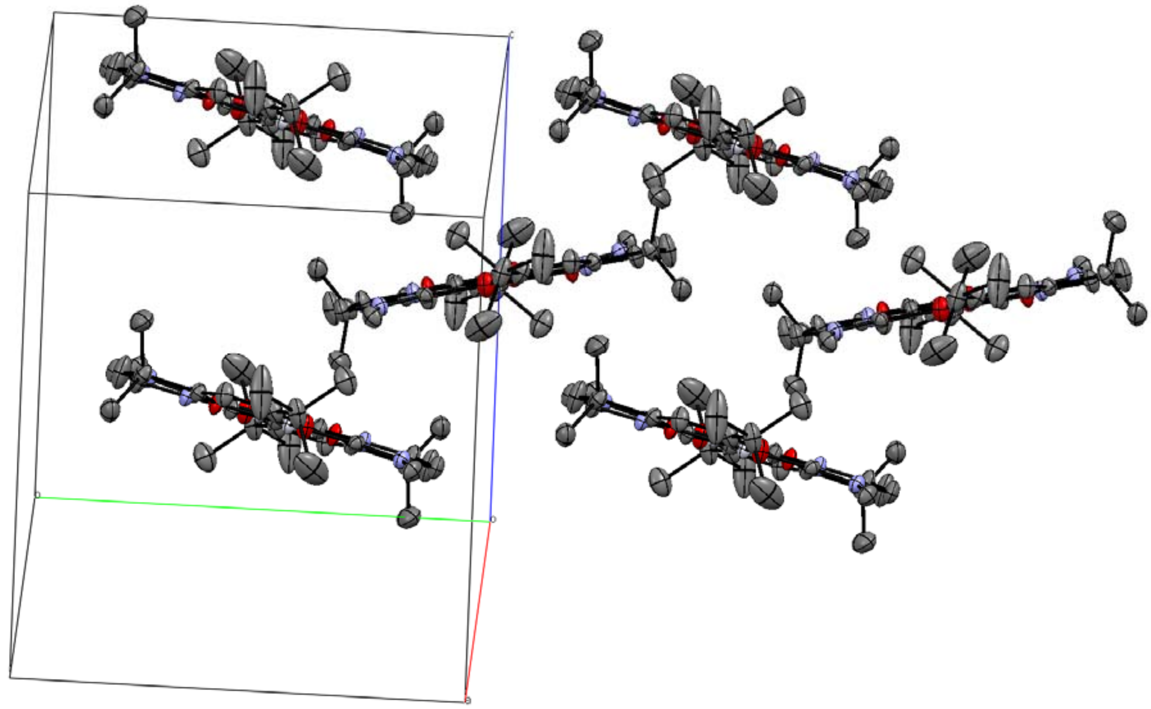


Figure S15. ORTEP plot of the molecule arrangement in complex **3b**. The shortest Pt-Pt distance is 6.058 Å. The molecules form two planes with an angle of 10.12 °.

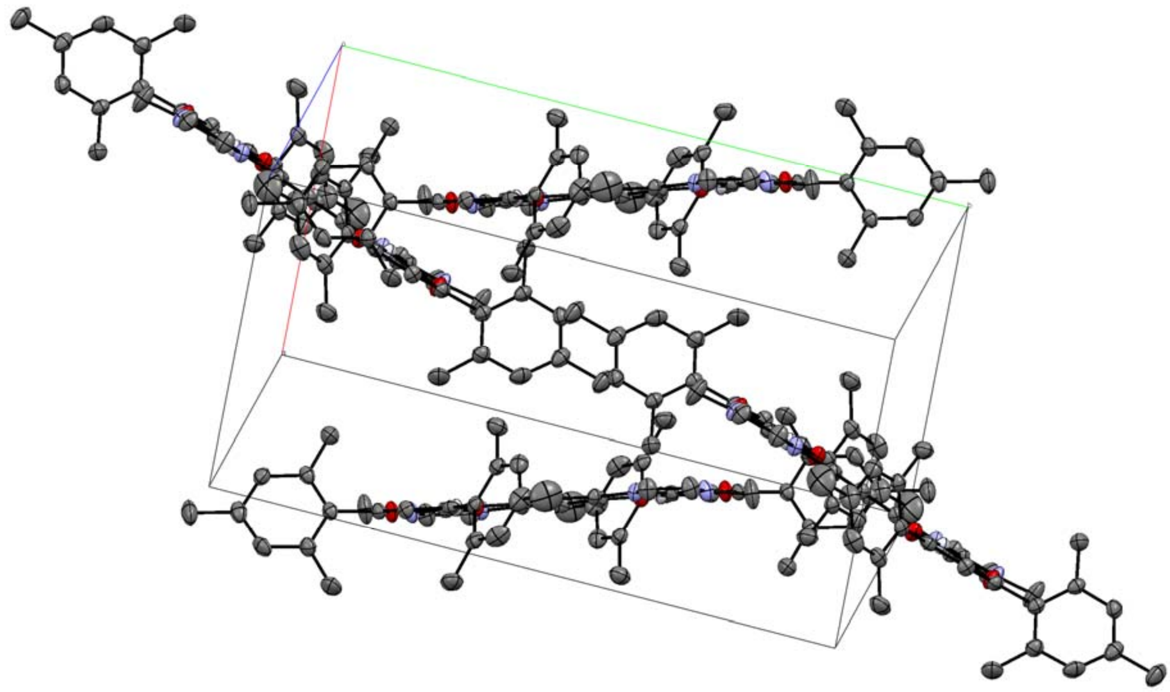


Figure S16. ORTEP plot of the molecule arrangement in complex **3c.** The shortest Pt-Pt distance is 8.716 Å. The molecules form two planes with an angle of 36.32 °.

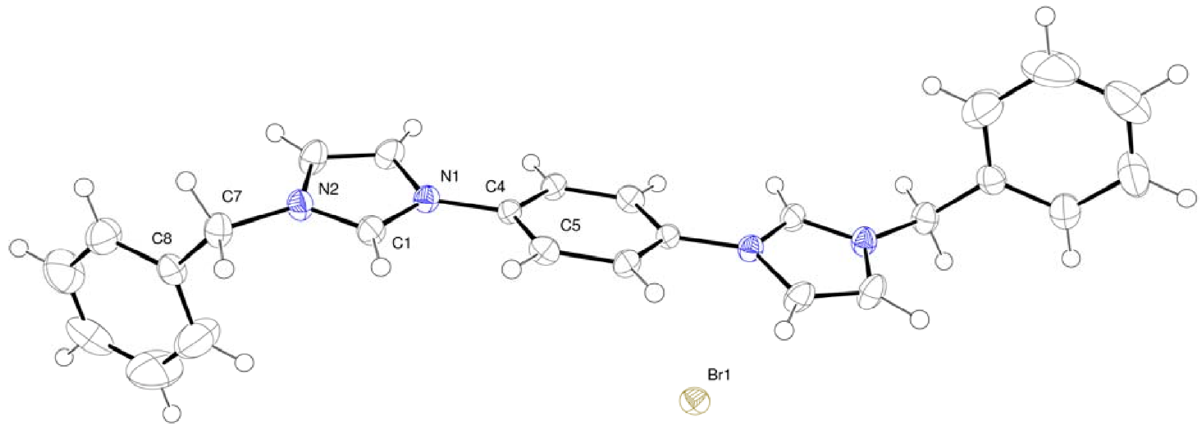


Figure S17. Solid-state structures of **2b**. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths [Å] and angles [°]: C1-N1 1.338(4); C1-N2 1.321(4); N1-C4 1.439(4); N2-C7 1.474(4); N2-C1-N1 108.5(3); C7-N2-C1 125.4(3); N1-C4-C5 119.8(3); N2-C1-N1-C4 178.7(3); C8-C7-N2-C1 -118.4(4); C1-N1-C4-C5 -9.1(5).

Quantum chemical Calculations

All calculations were performed with the Gaussian03 package.[15] The density functional hybrid model B3LYP[16] and the gradient-corrected density functional BP86[16b, 17] were used together with the 6-31G(d)[18] basis set. No symmetry or internal coordinate constraints were applied during optimizations. All reported intermediates were verified as true minima by the absence of negative eigenvalues in the vibrational frequency analysis. Harmonic force constants were calculated for all geometries in order to verify them as ground states. In all cases platinum was described using a decontracted Hay-Wadt(n+1) ECP and basis set.[19]
Approximate free energies were obtained through thermochemical analysis, using the thermal correction to Gibbs free energy as reported by Gaussian03. This takes into account zero-point effects, thermal enthalpy corrections, and entropy. All energies reported in this paper, unless otherwise noted, are free energies at standard conditions (T=298 K, p=1 atm), using unscaled frequencies. For visualization GaussView[20] and CYLview[21] were used.
B3LYP was used for the singlet and triplet ground state optimization. FMOs were computed on the singlet state while the spin densities were calculated on the optimized triplet ground state. Furthermore, BP86 was used to again optimize the complexes in the triplet ground state. The energies obtained from these calculations were then used for the emission wavelength prediction.

Table S2. Comparison of geometry data for **3b** and **3c** taken from solid-state determination and DFT calculations (B3LYP/6-31G(d)).

Bond lengths [Å] and Angles [°]	Complex **3b**		Complex **3c**	
	Xray	DFT	Xray	DFT
Pt(1)-C(1)	1.943(3)	1.966	1.955(4)	1.966
Pt(1)-C(5)	1.987(3)	2.005	1.980(4)	2.004
Pt(1)-O(1)	2.086(2)	2.161	2.075(3)	2.162
Pt(1)-O(2)	2.051(2)	2.090	2.046(3)	2.099
C(1)-Pt(1)-C(5)	80.40(12)	79.73	80.34(16)	79.93
O(1)-Pt(1)-O(2)	89.82(8)	87.72	90.10(11)	88.62
C(4)-N(1)-C(1)-Pt(1)	-4.1(4)	0.0	4.9(5)	-0.3
N(1)-C(1)-Pt(1)-O(1)	-174.1(2)	180.0	175.9(3)	-179.8

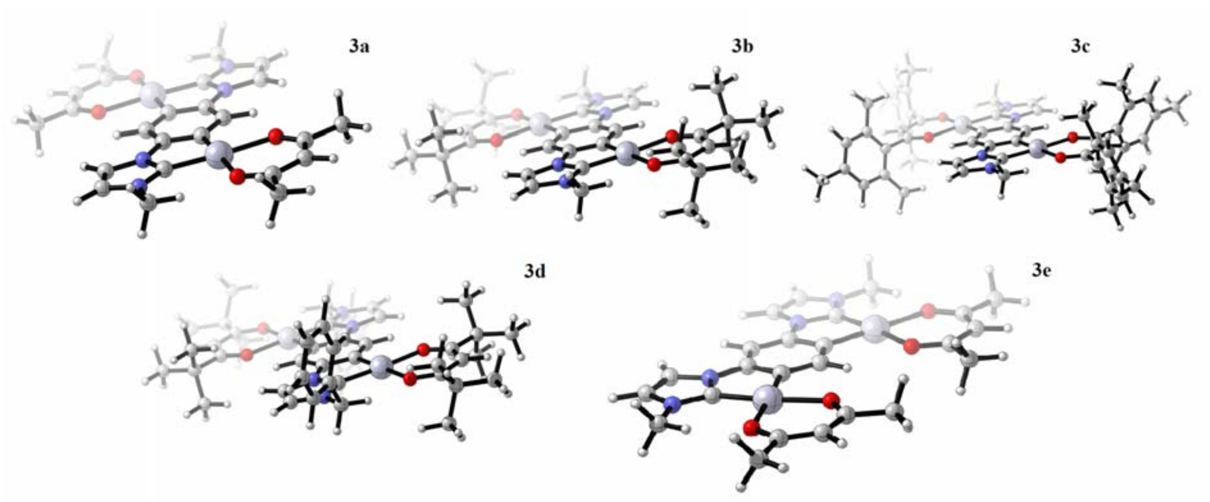


Figure S18. CYLview plot of the optimised singlet ground state structures (B3LYP/6-31G(d)).

In Figure S19 the calculated structure (left) of a possible isomer of **3e** with the second cyclometalation taking place at the position between the two imidazole fragments is shown. A strong twisting of the complex due to sterical repulsion is obvious and the reason for an energy difference of 21.9 kcal/mol to the thermodynamically more favoured complex **3e**. At the right side the calculated structure for **3e** with a dpm auxiliary ligand is depicted. Again the sterical hindrance is the reason, why this complex was not observed experimentally.

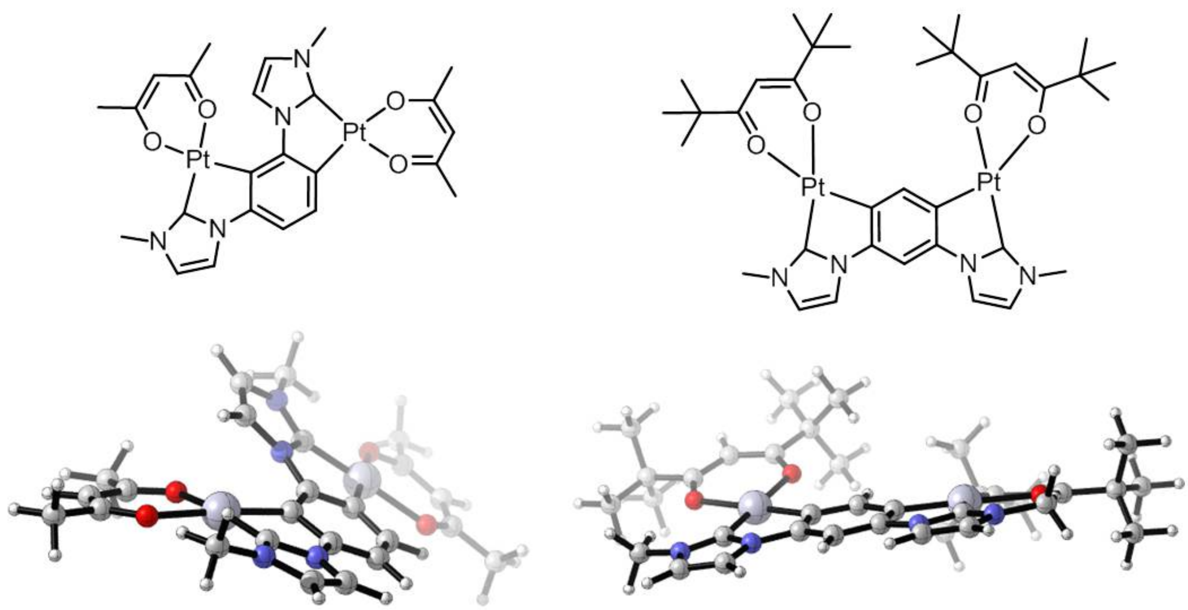
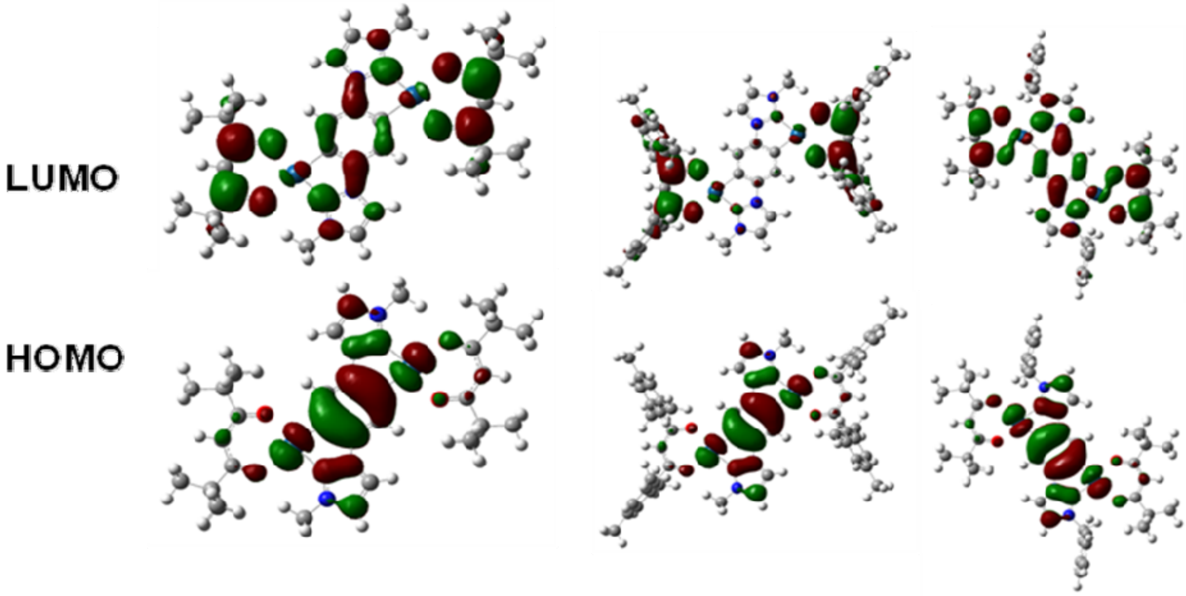


Figure S19. Possible but not favourable isomer of **3e** (left) and analogue to **3e** with dpm (right) as auxiliary ligand (B3LYP/6-31G(d)).

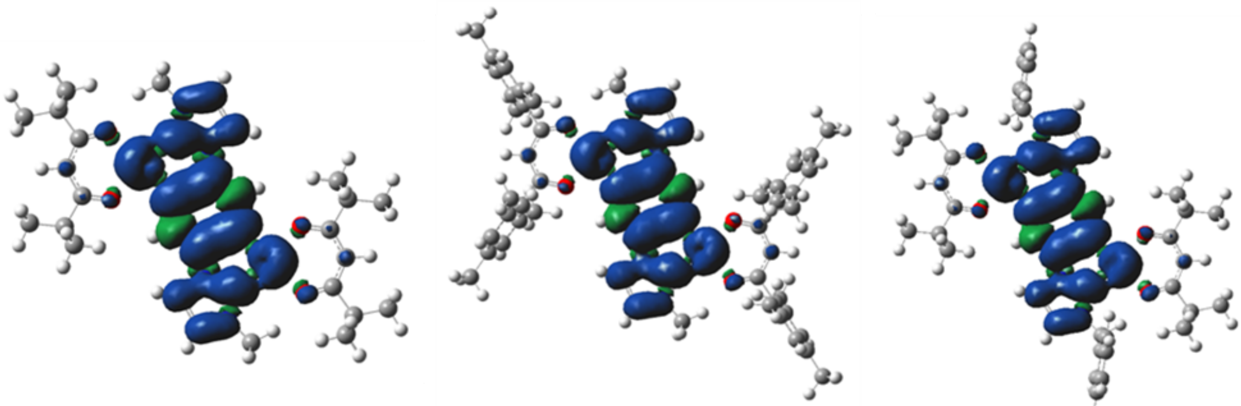
In Figure S20 the frontier molecular orbitals are shown for the optimized singlet state geometries.



3b 3c 3d

Figure S20. Frontier molecular orbitals of the emissive complexes computed on the singlet ground state (B3LYP/6-31G(d), isovalue = 0.02).

In Figure S21 the spin densities for **3b-d** are shown. The results of these calculation suggest a π-π* charge transfer during the emission process with a significant contribution of the metal d-orbitals.



3b 3c 3d

Figure S21. Spin densities computed on the first excited emitting triplet ground state (B3LYP/6-31G(d), isovalue = 0.02).

Table S3. Data for the wavelength prediction (BP86/6-31G(d)).

Complex	S-T gap [eV][a]	λ_{max} uncorr.[nm]	S-T gap corr. [eV][b]	λ_{max} corr.[nm][b]
3b	2.027	612	2.415	513
3c	2.035	609	2.423	512
3d	2.033	610	2.420	512

[a] Singlet ground state not optimized but geometry taken from the optimized triplet ground state. [b] Correction method taken from ref.[22]

In the following section the singlet ground state geometries for **3a-e** are given (B3LYP/6-31G(d)).

Coordinates for the optimized singlet ground state of **3a**. Free Energy ΔG = -1688.164157 H.

```
C   -0.67289   -1.24332    0.00009
C   -1.42851   -0.06767    0.00010
C   -0.71773    1.14745    0.00003
C    0.67288    1.24331    0.00001
C    1.42850    0.06766    0.00001
C    0.71772   -1.14745    0.00001
H   -1.18012   -2.20381    0.00014
H    1.18011    2.20381    0.00000
C    2.92963   -1.99299   -0.00023
C    1.37113   -3.63578   -0.00056
C    2.59835   -4.22212   -0.00088
C   -1.37112    3.63577   -0.00035
C   -2.92963    1.99300   -0.00020
C   -2.59834    4.22212   -0.00066
H    2.88326   -5.26266   -0.00119
H    0.38285   -4.06636   -0.00057
H   -0.38284    4.06635   -0.00029
H   -2.88323    5.26267   -0.00088
Pt   3.42665   -0.09177    0.00000
N    1.59198   -2.27203   -0.00010
N   -1.59198    2.27202   -0.00005
C    4.98931   -3.41835   -0.00069
H    5.27996   -3.98264    0.89141
H    5.28000   -3.98250   -0.89287
H    5.48667   -2.44833   -0.00061
C   -4.98930    3.41838   -0.00063
H   -5.27997    3.98270    0.89145
H   -5.27996    3.98252   -0.89284
H   -5.48668    2.44837   -0.00057
N    3.54667   -3.20184   -0.00071
N   -3.54666    3.20185   -0.00059
Pt  -3.42665    0.09178    0.00004
O   -3.69441   -1.98655    0.00051
O   -5.57522    0.30841   -0.00016
O    5.57520   -0.30841    0.00011
O    3.69442    1.98655    0.00028
C   -4.81325   -2.60311    0.00063
C   -6.09633   -2.03063    0.00026
C   -6.40649   -0.65917   -0.00010
C   -4.68540   -4.11424    0.00143
H   -4.11871   -4.43098    0.88469
H   -5.65437   -4.61956    0.00009
H   -4.11575   -4.43170   -0.87964
C   -7.86480   -0.23974   -0.00039
H   -8.06634    0.37940   -0.88238
H   -8.54935   -1.09156   -0.00091
H   -8.06688    0.37868    0.88200
H   -6.93394   -2.71841    0.00029
C    6.09635    2.03062    0.00034
C    6.40649    0.65916    0.00016
C    4.81327    2.60311    0.00046
C    4.68541    4.11424    0.00108
C    7.86479    0.23971   -0.00002
H    6.93396    2.71840    0.00045
H    8.54935    1.09153    0.00070
H    8.06669   -0.37834   -0.88270
H    8.06651   -0.37979    0.88167
H    4.11861    4.43107    0.88423
H    4.11589    4.43160   -0.88010
H    5.65438    4.61955   -0.00018
```

Coordinates for the optimized singlet ground state of **3b**. Free Energy ΔG = -2159.582045 H.

```
C   -0.82566    1.14573    0.00005
C   -1.42732   -0.11560    0.00006
C   -0.56580   -1.22860    0.00012
C    0.82566   -1.14573    0.00015
C    1.42732    0.11559    0.00012
C    0.56580    1.22859    0.00008
H   -1.44830    2.03525    0.00000
H    1.44829   -2.03525    0.00020
C    2.65016    2.34901   -0.00001
C    0.89444    3.77987    0.00014
C    2.03650    4.51837    0.00013
C   -0.89445   -3.77988    0.00017
```

C	-2.65016	-2.34901	-0.00000
C	-2.03651	-4.51837	0.00011
H	2.18590	5.58682	0.00017
H	-0.14053	4.08153	0.00022
H	0.14052	-4.08154	0.00028
H	-2.18591	-5.58682	0.00012
Pt	3.39017	0.52712	0.00003
N	1.28792	2.45546	0.00004
N	-1.28792	-2.45546	0.00011
C	4.51038	4.01887	-0.00024
H	4.73208	4.61308	-0.89277
H	4.73210	4.61391	0.89172
H	5.11675	3.11328	0.00012
C	-4.51039	-4.01887	-0.00040
H	-4.73203	-4.61297	-0.89301
H	-4.73216	-4.61402	0.89148
H	-5.11675	-3.11328	0.00004
N	3.10665	3.62709	0.00001
N	-3.10666	-3.62709	0.00004
Pt	-3.39017	-0.52712	0.00001
O	-3.92186	1.49422	0.00008
O	-5.50067	-0.99338	-0.00015
O	5.50066	0.99340	-0.00032
O	3.92184	-1.49422	0.00026
C	-5.10240	1.98581	0.00022
C	-6.30519	1.25847	0.00001
C	-6.45249	-0.14171	-0.00024
C	-5.10867	3.53477	0.00065
C	-7.86321	-0.78503	-0.00060
H	-7.21306	1.83745	0.00007
C	6.30518	-1.25845	-0.00018
C	6.45249	0.14172	-0.00053
C	5.10239	-1.98580	0.00031
C	5.10868	-3.53476	0.00098
C	7.86321	0.78503	-0.00114
H	7.21305	-1.83743	-0.00029
C	-7.98212	-1.66772	1.26335
H	-8.94725	-2.18856	1.27123
H	-7.18448	-2.41402	1.30008
H	-7.91851	-1.06042	2.17419
C	-7.98155	-1.66732	-1.26491
H	-8.94665	-2.18819	-1.27340
H	-7.91752	-1.05974	-2.17552
H	-7.18386	-2.41359	-1.30149
C	-9.01946	0.23103	-0.00068
H	-9.00334	0.87185	0.88792
H	-9.00313	0.87199	-0.88916
H	-9.97530	-0.30622	-0.00084
C	-6.51479	4.15925	0.00068
H	-7.08978	3.87603	-0.88807
H	-7.08995	3.87559	0.88917
H	-6.42690	5.25211	0.00096
C	-4.35278	4.00721	1.26435
H	-3.34814	3.57807	1.30191
H	-4.26959	5.10086	1.26869
H	-4.88284	3.70559	2.17573
C	-4.35246	4.00801	-1.26255
H	-4.26928	5.10166	-1.26619
H	-3.34781	3.57891	-1.30017
H	-4.88228	3.70696	-2.17427
C	4.35327	-4.00693	1.26505
H	3.34867	-3.57774	1.30291
H	4.27004	-5.10058	1.26961
H	4.88371	-3.70516	2.17615
C	4.35202	-4.00830	-1.26182
H	4.88157	-3.70755	-2.17379
H	4.26874	-5.10194	-1.26512
H	3.34739	-3.57912	-1.29924
C	6.51481	-4.15923	0.00062
H	7.08946	-3.87616	-0.88839
H	7.09029	-3.87540	0.88885
H	6.42693	-5.25210	0.00114
C	9.01944	-0.23104	-0.00182
H	9.00372	-0.87197	0.88670
H	9.00271	-0.87189	-0.89038
H	9.97529	0.30619	-0.00234
C	7.98244	1.66733	1.26308
H	8.94765	2.18801	1.27100
H	7.18493	2.41377	1.30010
H	7.91882	1.05980	2.17375
C	7.98125	1.66771	-1.26520
H	7.18360	2.41403	-1.30134
H	8.94638	2.18852	-1.27380
H	7.91695	1.06041	-2.17599

Coordinates for the optimized singlet ground state of **3c**. Free Energy ΔG = -2926.382176 H.

C	-0.89229	1.09726	-0.06413
C	-1.41472	-0.19899	-0.06145
C	-0.49186	-1.26168	-0.06603
C	0.89226	-1.09726	-0.06404
C	1.41469	0.19900	-0.06148
C	0.49184	1.26169	-0.06615
H	-1.56943	1.94644	-0.06577
H	1.56940	-1.94644	-0.06561
C	2.50837	2.50261	-0.07248
C	0.67306	3.82846	-0.07866
C	1.77135	4.63093	-0.08121
C	-0.67309	-3.82846	-0.07829
C	-2.50839	-2.50261	-0.07224
C	-1.77137	-4.63093	-0.08075
H	1.85902	5.70618	-0.08601
H	-0.37780	4.06972	-0.08117
H	0.37778	-4.06972	-0.08076
H	-1.85904	-5.70618	-0.08545
Pt	3.34814	0.72502	-0.05305
N	1.14243	2.52886	-0.07300
N	-1.14245	-2.52886	-0.07276
C	4.27086	4.28268	-0.07625
H	4.45914	4.87403	-0.97813
H	4.44475	4.90784	0.80536
H	4.94013	3.42255	-0.05409
C	-4.27089	-4.28267	-0.07586
H	-4.45923	-4.87387	-0.97783
H	-4.44471	-4.90798	0.80565
H	-4.94015	-3.42255	-0.05352
N	2.89212	3.80367	-0.07710
N	-2.89214	-3.80366	-0.07672
Pt	-3.34816	-0.72502	-0.05295

O	-3.99089	1.27229	-0.00647
O	-5.42167	-1.33752	-0.04990
O	5.42164	1.33753	-0.05011
O	3.99087	-1.27229	-0.00645
C	-5.20556	1.67173	0.02565
C	-6.36005	0.86884	0.02920
C	-6.41585	-0.53668	-0.00738
H	-7.31068	1.38965	0.06559
C	6.36003	-0.86884	0.02881
C	6.41582	0.53668	-0.00781
C	5.20554	-1.67173	0.02552
H	7.31067	-1.38964	0.06505
C	-7.77292	-1.19609	-0.01401
C	-8.29889	-1.67388	-1.23057
C	-8.48771	-1.36014	1.18735
C	-9.54880	-2.30018	-1.22451
C	-9.73245	-1.99897	1.14756
C	-10.28112	-2.47612	-0.04590
H	-9.96003	-2.65997	-2.16604
H	-10.28560	-2.12763	2.07619
C	-5.37551	3.16860	0.09027
C	-5.09146	3.83642	1.29875
C	-5.78520	3.89141	-1.04625
C	-5.24334	5.22511	1.35245
C	-5.91423	5.28180	-0.94877
C	-5.65071	5.96795	0.23961
H	-5.03807	5.73912	2.28981
H	-6.22837	5.84157	-1.82788
C	5.37552	-3.16858	0.09025
C	5.09145	-3.83632	1.29879
C	5.78530	-3.89148	-1.04617
C	5.24340	-5.22500	1.35261
C	5.91440	-5.28185	-0.94857
C	5.65086	-5.96792	0.23986
H	5.03810	-5.73894	2.29000
H	6.22859	-5.84169	-1.82763
C	7.77290	1.19608	-0.01472
C	8.29884	1.67346	-1.23144
C	8.48771	1.36053	1.18658
C	9.54876	2.29976	-1.22563
C	9.73247	1.99931	1.14654
C	10.28111	2.47607	-0.04710
H	9.95995	2.65925	-2.16728
H	10.28566	2.12825	2.07510
C	-6.07392	3.20204	-2.36299
H	-5.25456	2.53633	-2.65723
H	-6.98041	2.58722	-2.31045
H	-6.21530	3.93691	-3.16177
C	-4.64404	3.07438	2.52690
H	-5.36052	2.28735	2.79284
H	-3.68149	2.57892	2.36047
H	-4.54317	3.74344	3.38703
C	-5.77445	7.47276	0.31298
H	-6.07635	7.80223	1.31325
H	-4.81850	7.96393	0.08519
H	-6.51112	7.84994	-0.40454
C	-11.61414	-3.18857	-0.05960
H	-11.48655	-4.27577	0.03308
H	-12.25052	-2.86497	0.77105
H	-12.15726	-3.00603	-0.99346
C	-7.53810	-1.50612	-2.52759
H	-7.34413	-0.44838	-2.74470
H	-6.56187	-2.00142	-2.48401
H	-8.09889	-1.92525	-3.36867
C	-7.93302	-0.86839	2.50720
H	-6.91824	-1.24453	2.68169
H	-7.87540	0.22617	2.54027
H	-8.56297	-1.19596	3.34017
C	6.07409	-3.20224	-2.36297
H	5.25505	-2.53606	-2.65702
H	6.98096	-2.58796	-2.31065
H	6.21486	-3.93720	-3.16179
C	4.64398	-3.07422	2.52688
H	5.36044	-2.28717	2.79280
H	3.68143	-2.57878	2.36042
H	4.54311	-3.74325	3.38704
C	5.77466	-7.47272	0.31335
H	6.07613	-7.80213	1.31377
H	4.81885	-7.96396	0.08514
H	6.51169	-7.84988	-0.40382
C	7.53801	1.50528	-2.52839
H	7.34428	0.44745	-2.74529
H	6.56166	2.00037	-2.48483
H	8.09864	1.92440	-3.36958
C	7.93301	0.86926	2.50659
H	6.91849	1.24606	2.68123
H	7.87468	-0.22526	2.53977
H	8.56332	1.19652	3.33941
C	11.61414	3.18850	-0.06106
H	12.15719	3.00575	-0.99492
H	11.48658	4.27572	0.03140
H	12.25058	2.86507	0.76962

Coordinates for the optimized singlet ground state of **3d**. Free Energy ΔG = -2621.531156 H.

C	-0.49608	-1.30334	-0.22688
C	-1.40027	-0.28400	0.08354
C	-0.86169	0.99821	0.30111
C	0.49654	1.30277	0.22554
C	1.40072	0.28342	-0.08485
C	0.86216	-0.99880	-0.30239
H	-0.86418	-2.30989	-0.40217
H	0.86463	2.30930	0.40086
C	3.15496	-1.47835	-0.63933
C	1.84108	-3.30781	-0.87787
C	3.12977	-3.68973	-1.08183
C	-1.84051	3.30699	0.87770
C	-3.15441	1.47757	0.63896
C	-3.12911	3.68874	1.08255
H	3.55391	-4.65594	-1.30448
H	0.92482	-3.87527	-0.90270
H	-0.92427	3.87450	0.90231
H	-3.55319	4.65481	1.30590
Pt	3.39219	0.43767	-0.26383
N	1.87420	-1.95232	-0.60757
N	-1.87370	1.95163	0.60675
C	5.38926	-2.54711	-1.05041
H	5.65590	-2.94874	-2.03424
H	5.68975	-1.49768	-1.01322
C	-5.38845	2.54584	1.05278

H	-5.65389	2.94543	2.03777
H	-5.68893	1.49647	1.01388
N	3.92574	-2.55578	-0.93617
N	-3.92510	2.55482	0.93671
Pt	-3.39171	-0.43830	0.26277
O	-3.37672	-2.48310	-0.16769
O	-5.53661	-0.58289	0.46988
O	5.53716	0.58234	-0.47083
O	3.37702	2.48264	0.16578
C	-4.38227	-3.27191	-0.21588
C	-5.72421	-2.92261	0.01407
C	-6.22915	-1.64812	0.33600
C	-3.98808	-4.72792	-0.56817
C	-7.74832	-1.43718	0.56107
H	-6.44461	-3.71905	-0.06553
C	5.72444	2.92233	-0.01629
C	6.22954	1.64776	-0.33760
C	4.38247	3.27159	0.21354
C	3.98813	4.72769	0.56530
C	7.74872	1.43695	-0.56281
H	6.44474	3.71891	0.06287
C	-8.24290	-0.40070	-0.47432
H	-9.30522	-0.18239	-0.31100
H	-7.68307	0.53492	-0.40207
H	-8.13121	-0.78397	-1.49583
C	-7.94433	-0.88065	1.99031
H	-9.00517	-0.66849	2.16989
H	-7.61211	-1.60499	2.74367
H	-7.37749	0.04219	2.13710
C	-8.58921	-2.71803	0.41408
H	-8.51467	-3.14490	-0.59231
H	-8.29667	-3.48692	1.13783
H	-9.64489	-2.48223	0.59289
C	-5.17479	-5.70529	-0.62290
H	-5.69179	-5.77696	0.34058
H	-5.90599	-5.41939	-1.38720
H	-4.80995	-6.70787	-0.87547
C	-3.29636	-4.70475	-1.95126
H	-2.44915	-4.01397	-1.95355
H	-2.93434	-5.70736	-2.20972
H	-3.99460	-4.38596	-2.73449
C	-2.98647	-5.21771	0.50337
H	-2.62527	-6.22233	0.25174
H	-2.12897	-4.54354	0.57439
H	-3.45954	-5.26691	1.49151
C	2.98720	5.21732	-0.50694
H	2.12968	4.54321	-0.57834
H	2.62594	6.22203	-0.25576
H	3.46086	5.26626	-1.49481
C	3.29556	4.70480	1.94796
H	3.99330	4.38616	2.73170
H	2.93337	5.70746	2.20600
H	2.44834	4.01402	1.94986
C	5.17485	5.70502	0.62056
H	5.90547	5.41936	1.38549
H	5.69255	5.77630	-0.34257
H	4.80987	6.70770	0.87250
C	8.58942	2.71802	-0.41671
H	8.29665	3.48645	-1.14085
H	8.51498	3.14546	0.58944
H	9.64511	2.48229	-0.59556
C	7.94457	0.87960	-1.99175
H	9.00542	0.66750	-2.17140
H	7.37784	-0.04342	-2.13784
H	7.61210	1.60343	-2.74548
C	8.24369	0.40117	0.47310
H	7.68410	-0.53464	0.40145
H	9.30605	0.18305	0.30975
H	8.13203	0.78497	1.49441
C	6.06529	-3.34876	0.04541
C	6.84952	-4.46450	-0.26566
C	5.92268	-2.96913	1.38838
C	7.48327	-5.19344	0.74431
H	6.97038	-4.76364	-1.30491
C	6.55049	-3.69836	2.39710
H	5.31760	-2.10063	1.63728
C	7.33246	-4.81271	2.07766
H	8.09045	-6.05748	0.48768
H	6.43286	-3.39514	3.43397
H	7.82199	-5.37894	2.86547
C	-6.06600	3.34973	-0.04044
C	-6.85106	4.46388	0.27425
C	-5.92422	2.97382	-1.38455
C	-7.48646	5.19485	-0.73321
H	-6.97126	4.76017	1.31439
C	-6.55367	3.70508	-2.39077
H	-5.31851	2.10659	-1.63632
C	-7.33649	4.81778	-2.06769
H	-8.09428	6.05760	-0.47374
H	-6.43665	3.40474	-3.42854
H	-7.82730	5.38559	-2.85357

Coordinates for the optimized singlet ground state of **3e**. Free Energy ΔG = -1688.159140 H.

C	1.22142	-0.69956	0.00002
C	1.18182	-2.10741	-0.00004
C	-0.00000	-2.84254	0.00004
C	-1.18182	-2.10740	0.00015
C	-1.22143	-0.69956	0.00017
C	-0.00000	-0.01180	0.00012
H	0.00001	1.07260	0.00015
C	-3.52524	-1.80752	0.00024
C	-2.93383	-3.99410	0.00006
C	-4.29237	-3.92721	0.00000
H	-2.27269	-4.84575	0.00001
H	-5.03674	-4.70817	-0.00015
C	3.52523	-1.80752	-0.00019
C	2.93383	-3.99411	-0.00028
C	4.29237	-3.92721	-0.00033
H	2.27270	-4.84576	-0.00028
H	5.03675	-4.70817	-0.00034
N	-2.47950	-2.68859	0.00019
N	-4.64194	-2.57985	0.00012
N	2.47950	-2.68859	-0.00015
N	4.64194	-2.57984	-0.00030
C	6.01402	-2.08350	-0.00027
H	5.98796	-0.99350	-0.00020
H	6.53801	-2.44151	0.89190
H	6.53800	-2.44139	-0.89250
C	-6.01404	-2.08352	0.00001

H	-6.53788	-2.44129	-0.89235
H	-6.53815	-2.44167	0.89205
H	-5.98800	-0.99353	0.00022
H	-0.00001	-3.92947	0.00001
C	-6.82629	2.48376	-0.00067
C	-5.34219	2.16600	-0.00046
C	-4.42346	3.22843	-0.00064
H	-4.83744	4.23003	-0.00094
C	-3.02055	3.12808	-0.00035
C	-2.19530	4.40002	-0.00048
O	-5.06539	0.91966	0.00005
O	-2.32565	2.05788	-0.00009
C	2.19530	4.39999	0.00074
C	3.02058	3.12806	0.00026
C	4.42348	3.22842	-0.00000
H	4.83745	4.23003	-0.00004
C	5.34222	2.16600	-0.00002
C	6.82632	2.48372	0.00009
O	2.32567	2.05786	0.00024
O	5.06542	0.91966	-0.00001
Pt	-3.06236	0.09977	0.00022
Pt	3.06235	0.09977	-0.00005
H	7.29624	2.03509	0.88324
H	7.29688	2.03282	-0.88155
H	7.02752	3.55788	-0.00115
H	1.54509	4.40959	0.88291
H	1.54250	4.40863	-0.87950
H	2.81163	5.30255	-0.00058
H	-1.54331	4.40891	0.88037
H	-1.54426	4.40940	-0.88204
H	-2.81165	5.30256	0.00006
H	-7.02741	3.55794	-0.00107
H	-7.29651	2.03368	-0.88290
H	-7.29659	2.03440	0.88190

In the following section the triplet ground state geometries for the emissive complexes **3b-d** are given, which were used for the spin density calculations (B3LYP/6-31G(d)).

Coordinates for the optimized triplet ground state of **3b**. Free Energy ΔG = -2159.495115 H.

C	0.85979	1.16380	-0.00001
C	1.44593	-0.09233	-0.00002
C	0.53504	-1.26679	-0.00002
C	-0.85979	-1.16380	-0.00001
C	-1.44593	0.09233	-0.00000
C	-0.53504	1.26679	-0.00001
H	1.49244	2.04580	-0.00002
H	-1.49244	-2.04580	-0.00001
C	-2.63424	2.34275	0.00001
C	-0.86578	3.78527	0.00000
C	-2.01536	4.51276	0.00001
C	0.86578	-3.78527	-0.00005
C	2.63424	-2.34275	-0.00005
C	2.01536	-4.51276	-0.00007
H	-2.16365	5.58187	0.00002
H	0.16638	4.09470	-0.00001
H	-0.16638	-4.09470	-0.00004
H	2.16365	-5.58187	-0.00008
Pt	-3.36792	0.52160	0.00001
N	-1.24978	2.44740	0.00000
N	1.24978	-2.44740	-0.00004
C	-4.48630	4.02729	0.00007
H	-4.70912	4.62192	0.89257
H	-4.70911	4.62218	-0.89225
H	-5.09565	3.12388	-0.00006
C	4.48630	-4.02729	-0.00015
H	4.70909	-4.62228	0.89211
H	4.70913	-4.62181	-0.89271
H	5.09565	-3.12388	0.00009
N	-3.08555	3.63089	0.00001
N	3.08555	-3.63088	-0.00006
Pt	3.36792	-0.52160	-0.00003
O	3.92371	1.50581	-0.00002
O	5.47504	-1.00245	0.00006
O	-5.47504	1.00245	-0.00000
O	-3.92371	-1.50581	-0.00001
C	5.10742	1.98396	0.00005
C	6.30322	1.24214	0.00009
C	6.43489	-0.15838	0.00010
C	5.13219	3.53302	-0.00006
C	7.83871	-0.81622	0.00020
H	7.21740	1.81092	0.00012
C	-6.30322	-1.24214	-0.00002
C	-6.43489	0.15837	-0.00001
C	-5.10742	-1.98396	-0.00002
C	-5.13219	-3.53302	-0.00002
C	-7.83871	0.81622	-0.00003
H	-7.21740	-1.81092	-0.00003
C	7.94826	-1.69966	-1.26418
H	8.90828	-2.22980	-1.27239
H	7.14351	-2.43821	-1.30108
H	7.89040	-1.09141	-2.17474
C	7.94796	-1.69992	1.26442
H	8.90797	-2.23007	1.27274
H	7.88991	-1.09185	2.17509
H	7.14319	-2.43846	1.30099
C	9.00546	0.18782	0.00044
H	8.99591	0.82892	-0.88803
H	8.99579	0.82864	0.88910
H	9.95558	-0.35940	0.00042
C	6.54565	4.14086	-0.00039
H	7.11758	3.85067	0.88806
H	7.11712	3.85078	-0.88916
H	6.47045	5.23464	-0.00030
C	4.38168	4.01443	-1.26351
H	3.37173	3.59787	-1.30111
H	4.31170	5.10897	-1.26779
H	4.90769	3.70641	-2.17507
C	4.38219	4.01461	1.26363

H	4.31226	5.10916	1.26781
H	3.37223	3.59810	1.30167
H	4.90855	3.70668	2.17502
C	-4.38198	-4.01452	-1.26361
H	-3.37202	-3.59799	-1.30146
H	-4.31203	-5.10907	-1.26784
H	-4.90819	-3.70655	-2.17507
C	-4.38189	-4.01452	1.26353
H	-4.90805	-3.70654	2.17502
H	-4.31193	-5.10906	1.26776
H	-3.37194	-3.59798	1.30131
C	-6.54565	-4.14086	0.00003
H	-7.11731	-3.85075	0.88867
H	-7.11739	-3.85071	-0.88854
H	-6.47045	-5.23464	0.00001
C	-9.00546	-0.18783	-0.00010
H	-8.99583	-0.82874	-0.88870
H	-8.99586	-0.82883	0.88843
H	-9.95558	0.35940	-0.00009
C	-7.94807	1.69983	-1.26431
H	-8.90809	2.22998	-1.27258
H	-7.14331	2.43838	-1.30098
H	-7.89009	1.09171	-2.17493
C	-7.94815	1.69974	1.26431
H	-7.14339	2.43829	1.30108
H	-8.90817	2.22988	1.27256
H	-7.89022	1.09155	2.17489

Coordinates for the optimized triplet ground state of **3c**. Free Energy ΔG = -2926.295197 H.

C	-0.92674	1.11400	-0.08289
C	-1.43451	-0.17619	-0.07903
C	-0.45930	-1.29796	-0.08965
C	0.92674	-1.11401	-0.08287
C	1.43450	0.17618	-0.07909
C	0.45930	1.29795	-0.08973
H	-1.61335	1.95529	-0.08052
H	1.61335	-1.95530	-0.08048
C	2.49433	2.49360	-0.09365
C	0.64646	3.83167	-0.11508
C	1.75328	4.62268	-0.11638
C	-0.64647	-3.83168	-0.11485
C	-2.49434	-2.49361	-0.09342
C	-1.75329	-4.62270	-0.11607
H	1.84044	5.69846	-0.12611
H	-0.40185	4.08157	-0.12396
H	0.40184	-4.08159	-0.12376
H	-1.84045	-5.69847	-0.12574
Pt	3.32656	0.71705	-0.06234
N	1.10608	2.51785	-0.10089
N	-1.10608	-2.51787	-0.10071
C	4.24902	4.28676	-0.10276
H	4.44432	4.86242	-1.01385
H	4.41888	4.92725	0.76901
H	4.92049	3.42916	-0.06212
C	-4.24903	-4.28677	-0.10235
H	-4.44437	-4.86247	-1.01341
H	-4.41884	-4.92722	0.76945
H	-4.92050	-3.42916	-0.06172
N	2.87319	3.80416	-0.10304
N	-2.87320	-3.80417	-0.10271
Pt	-3.32656	-0.71706	-0.06218
O	-3.99102	1.28498	-0.00458
O	-5.39657	-1.34272	-0.05333
O	5.39656	1.34271	-0.05364
O	3.99102	-1.28499	-0.00466
C	-5.20729	1.67202	0.03495
C	-6.35467	0.85606	0.04065
C	-6.39679	-0.54854	-0.00226
H	-7.31022	1.36709	0.08411
C	6.35468	-0.85605	0.04043
C	6.39679	0.54854	-0.00257
C	5.20730	-1.67202	0.03483
H	7.31023	-1.36708	0.08388
C	-7.74793	-1.21980	-0.00613
C	-8.27362	-1.69827	-1.22265
C	-8.45726	-1.39326	1.19702
C	-9.51859	-2.33412	-1.21457
C	-9.69716	-2.04171	1.15901
C	-10.24591	-2.51921	-0.03418
H	-9.92996	-2.69423	-2.15592
H	-10.24626	-2.17775	2.08897
C	-5.39312	3.16657	0.10679
C	-5.10661	3.83243	1.31601
C	-5.81943	3.88926	-1.02345
C	-5.27260	5.21906	1.37647
C	-5.96225	5.27797	-0.91921
C	-5.69667	5.96203	0.26975
H	-5.06525	5.73145	2.31427
H	-6.28907	5.83792	-1.79352
C	5.39313	-3.16656	0.10679
C	5.10672	-3.83232	1.31609
C	5.81934	-3.88936	-1.02342
C	5.27271	-5.21893	1.37667
C	5.96217	-5.27806	-0.91907
C	5.69669	-5.96200	0.26997
H	5.06545	-5.73124	2.31453
H	6.28891	-5.83809	-1.79336
C	7.74793	1.21981	-0.00654
C	8.27355	1.69824	-1.22310
C	8.45731	1.39330	1.19657
C	9.51853	2.33409	-1.21511
C	9.69722	2.04176	1.15848
C	10.24591	2.51921	-0.03476
H	9.92984	2.69418	-2.15648
H	10.24636	2.17782	2.08840
C	-6.11056	3.20235	-2.34094
H	-5.28447	2.55009	-2.64640
H	-7.00748	2.57414	-2.28314
H	-6.27002	3.93909	-3.13457
C	-4.64204	3.06998	2.53753
H	-5.34861	2.27489	2.80601
H	-3.67599	2.58448	2.36205
H	-4.54111	3.73669	3.39947
C	-5.83628	7.46500	0.35137
H	-6.17437	7.78320	1.34381
H	-4.87762	7.96644	0.16048
H	-6.55208	7.84173	-0.38704
C	-11.57364	-3.24150	-0.04641
H	-11.43699	-4.32906	0.02691

H	-12.20407	-2.93634	0.79563
H	-12.12741	-3.04785	-0.97179
C	-7.51804	-1.52085	-2.52142
H	-7.33258	-0.46103	-2.73581
H	-6.53803	-2.00901	-2.48236
H	-8.07833	-1.94151	-3.36204
C	-7.90240	-0.90158	2.51683
H	-6.88243	-1.26635	2.68498
H	-7.85784	0.19341	2.55539
H	-8.52468	-1.24095	3.35084
C	6.11035	-3.20256	-2.34100
H	5.28423	-2.55035	-2.64646
H	7.00726	-2.57434	-2.28334
H	6.26976	-3.93938	-3.13458
C	4.64226	-3.06975	2.53758
H	5.34885	-2.27463	2.80593
H	3.67619	-2.58427	2.36214
H	4.54140	-3.73637	3.39959
C	5.83631	-7.46497	0.35172
H	6.17470	-7.78306	1.34411
H	4.87759	-7.96642	0.16119
H	6.55189	-7.84179	-0.38686
C	7.51790	1.52079	-2.52182
H	7.33241	0.46096	-2.73616
H	6.53790	2.00897	-2.48273
H	8.07816	1.94141	-3.36249
C	7.90253	0.90165	2.51643
H	6.88256	1.26643	2.68461
H	7.85797	-0.19333	2.55502
H	8.52485	1.24105	3.35039
C	11.57363	3.24151	-0.04707
H	12.12738	3.04778	-0.97245
H	11.43699	4.32907	0.02616
H	12.20408	2.93642	0.79498

Coordinates for the optimized triplet ground state of **3d**. Free Energy ΔG = -2621.443024 H.

C	-0.51440	-1.33773	-0.23604
C	-1.40694	-0.32151	0.06757
C	-0.84313	1.03475	0.29223
C	0.52233	1.32711	0.21157
C	1.41495	0.31071	-0.09128
C	0.85123	-1.04572	-0.31509
H	-0.88979	-2.34235	-0.40480
H	0.89771	2.33168	0.38056
C	3.14929	-1.47144	-0.63699
C	1.83358	-3.32206	-0.86980
C	3.12833	-3.68781	-1.06611
C	-1.82388	3.30757	0.86446
C	-3.13979	1.45761	0.62766
C	-3.11731	3.67067	1.07407
H	3.55576	-4.65452	-1.28267
H	0.92425	-3.89961	-0.89584
H	-0.91500	3.88600	0.88644
H	-3.54413	4.63520	1.30120
Pt	3.37159	0.44486	-0.27060
N	1.84822	-1.95525	-0.60275
N	-1.83938	1.94272	0.58755
C	5.38503	-2.55398	-1.02855
H	5.66306	-2.96391	-2.00624
H	5.68797	-1.50509	-0.99820
C	-5.37108	2.53036	1.06778
H	-5.62682	2.89772	2.06839
H	-5.67326	1.48278	1.00171
N	3.92239	-2.55848	-0.92825
N	-3.91150	2.54178	0.93290
Pt	-3.36316	-0.45640	0.25031
O	-3.36085	-2.51295	-0.18158
O	-5.50744	-0.59203	0.45580
O	5.51619	0.58055	-0.47490
O	3.36751	2.50385	0.14867
C	-4.37119	-3.29218	-0.23183
C	-5.71218	-2.93028	-0.00604
C	-6.20696	-1.65298	0.31517
C	-3.99031	-4.75249	-0.58193
C	-7.72524	-1.42931	0.53189
H	-6.43929	-3.72008	-0.08927
C	5.71793	2.92313	-0.03395
C	6.21413	1.64401	-0.34569
C	4.37690	3.28471	0.19198
C	3.99454	4.74692	0.53244
C	7.73223	1.42140	-0.56502
H	6.44389	3.71477	0.04135
C	-8.20440	-0.38671	-0.50486
H	-9.26572	-0.15962	-0.34729
H	-7.63725	0.54411	-0.42806
H	-8.09006	-0.76952	-1.52622
C	-7.92494	-0.87395	1.96114
H	-8.98509	-0.65349	2.13454
H	-7.60336	-1.60267	2.71489
H	-7.35153	0.04383	2.11358
C	-8.57650	-2.70237	0.37737
H	-8.49934	-3.12812	-0.62928
H	-8.29552	-3.47501	1.10170
H	-9.63106	-2.45721	0.54986
C	-5.18646	-5.71821	-0.63966
H	-5.70752	-5.78376	0.32204
H	-5.91209	-5.42616	-1.40693
H	-4.83052	-6.72456	-0.88984
C	-3.29441	-4.73710	-1.96297
H	-2.43987	-4.05535	-1.96363
H	-2.94203	-5.74353	-2.21977
H	-3.98702	-4.41154	-2.74839
C	-2.99712	-5.25112	0.49330
H	-2.64594	-6.25987	0.24419
H	-2.13239	-4.58635	0.56587
H	-3.47341	-5.29368	1.48018
C	3.00041	5.23707	-0.54583
H	2.13642	4.57085	-0.61366
H	2.64814	6.24710	-0.30354
H	3.47640	5.27345	-1.53310
C	3.29912	4.74008	1.91378
H	3.99239	4.42078	2.70118
H	2.94550	5.74777	2.16384
H	2.44548	4.05722	1.91937
C	5.18959	5.71436	0.58323
H	5.91613	5.42792	1.35174
H	5.70982	5.77449	-0.37927
H	4.83263	6.72183	0.82735
C	8.58115	2.69800	-0.42728

H	8.29519	3.46261	-1.15815
H	8.50757	3.13381	0.57533
H	9.63551	2.45347	-0.60199
C	7.92829	0.85079	-1.98875
H	8.98846	0.63162	-2.16366
H	7.35708	-0.07034	-2.12864
H	7.60164	1.57001	-2.74938
C	8.21734	0.39130	0.48136
H	7.65185	-0.54142	0.41689
H	9.27859	0.16474	0.32250
H	8.10587	0.78500	1.49890
C	6.04914	-3.34721	0.08090
C	6.85037	-4.45542	-0.21407
C	5.87707	-2.96863	1.42100
C	7.47227	-5.17722	0.80837
H	6.99350	-4.75436	-1.25057
C	6.49273	-3.69102	2.44188
H	5.25755	-2.10693	1.65759
C	7.29247	-4.79740	2.13836
H	8.09282	-6.03531	0.56390
H	6.35196	-3.38864	3.47614
H	7.77281	-5.35806	2.93577
C	-6.06349	3.36828	0.00984
C	-6.88001	4.44422	0.37401
C	-5.90630	3.06290	-1.35059
C	-7.53204	5.20549	-0.59990
H	-7.01124	4.68666	1.42667
C	-6.55216	3.82465	-2.32308
H	-5.27473	2.22694	-1.64146
C	-7.36742	4.89804	-1.95036
H	-8.16389	6.03796	-0.30172
H	-6.42273	3.57876	-3.37367
H	-7.87114	5.48953	-2.71018

In the following section the triplet ground state geometries for **3a-e** are given, which were used for the emission wavelength prediction (BP86/6-31G(d)).

Coordinates for the optimized triplet ground state of **3a**. Free Energy ΔG = -1688.293405 H.

C	0.70546	1.26939	0.00003
C	1.44489	0.08391	-0.00005
C	0.69804	-1.19448	0.00004
C	-0.70546	-1.26939	0.00014
C	-1.44489	-0.08391	0.00020
C	-0.69804	1.19448	0.00019
H	1.23454	2.22840	-0.00004
H	-1.23455	-2.22840	0.00015
C	-2.93497	1.98192	0.00039
C	-1.36184	3.66042	0.00045
C	-2.61054	4.23029	0.00064
C	1.36184	-3.66042	0.00009
C	2.93496	-1.98192	-0.00018
C	2.61054	-4.23029	-0.00001
H	-2.90519	5.27764	0.00079
H	-0.37293	4.10972	0.00040
H	0.37293	-4.10972	0.00025
H	2.90519	-5.27763	0.00002
Pt	-3.40505	0.08660	0.00023
N	-1.56156	2.27840	0.00032
N	1.56156	-2.27840	-0.00001
C	-5.00368	3.41867	0.00100
H	-5.30417	3.98282	0.90145
H	-5.30442	3.98426	-0.89846
H	-5.49592	2.43463	0.00031
C	5.00368	-3.41866	-0.00036
H	5.30441	-3.98363	0.89950
H	5.30419	-3.98344	-0.90042
H	5.49592	-2.43462	-0.00032
N	-3.55780	3.20937	0.00060
N	3.55780	-3.20937	-0.00015
Pt	3.40505	-0.08660	-0.00028
O	3.65325	2.00140	-0.00034
O	5.54953	-0.32516	-0.00042
O	-5.54953	0.32515	0.00016
O	-3.65325	-2.00140	0.00008
C	4.78473	2.62002	-0.00044
C	6.07281	2.03495	-0.00032
C	6.38570	0.65973	-0.00029
H	6.91981	2.72685	-0.00030
C	-6.07280	-2.03495	-0.00053
C	-6.38570	-0.65973	-0.00036
C	-4.78473	-2.62002	-0.00005
H	-6.91981	-2.72686	-0.00085
C	-7.84704	-0.23753	-0.00104
H	-8.05300	0.38482	-0.89074
H	-8.53668	-1.09658	0.00052
H	-8.05289	0.38814	0.88633
C	-4.66091	-4.13506	0.00156
H	-4.10088	-4.46138	0.89675
H	-5.64070	-4.63863	-0.00868
H	-4.08130	-4.46172	-0.88078
C	7.84704	0.23752	0.00009
H	8.05280	-0.38782	-0.88754
H	8.53668	1.09657	-0.00125
H	8.05310	-0.38515	0.88954
C	4.66091	4.13505	-0.00109
H	4.08800	4.46169	0.88567
H	5.64075	4.63863	0.00205
H	4.09413	4.46141	-0.89195

Coordinates for the optimized triplet ground state of **3b**. Free Energy ΔG = -2159.687480 H.

C	0.86260	1.16612	-0.00007
C	1.44660	-0.10278	-0.00008

C	0.53919	-1.27260	-0.00005
C	-0.86260	-1.16612	-0.00003
C	-1.44660	0.10278	-0.00002
C	-0.53919	1.27260	-0.00004
H	1.50608	2.05184	-0.00009
H	-1.50609	-2.05183	-0.00001
C	-2.65410	2.34149	0.00003
C	-0.87771	3.80363	-0.00003
C	-2.04237	4.53002	0.00001
C	0.87771	-3.80364	-0.00004
C	2.65410	-2.34149	-0.00007
C	2.04237	-4.53002	-0.00004
H	-2.19920	5.60665	0.00002
H	0.16059	4.12264	-0.00008
H	-0.16059	-4.12264	-0.00001
H	2.19920	-5.60665	-0.00003
Pt	-3.36983	0.52331	0.00003
N	-1.25408	2.45889	-0.00001
N	1.25408	-2.45889	-0.00005
C	-4.52006	4.02493	0.00019
H	-4.75109	4.62141	0.90033
H	-4.75114	4.62182	-0.89966
H	-5.12372	3.10483	0.00002
C	4.52006	-4.02493	-0.00016
H	4.75110	-4.62195	0.89961
H	4.75115	-4.62126	-0.90038
H	5.12372	-3.10482	0.00019
N	-3.11248	3.63910	0.00005
N	3.11248	-3.63911	-0.00003
Pt	3.36983	-0.52331	-0.00010
O	3.88897	1.50957	-0.00019
O	5.47466	-1.01653	0.00000
O	-5.47467	1.01652	0.00006
O	-3.88896	-1.50958	-0.00002
C	5.08382	1.99710	-0.00020
C	6.28783	1.25435	-0.00001
C	6.43451	-0.14958	0.00008
C	5.10016	3.55029	-0.00022
C	7.84842	-0.79597	0.00038
H	7.20747	1.83522	0.00008
C	-6.28783	-1.25436	0.00003
C	-6.43451	0.14958	0.00007
C	-5.08382	-1.99710	-0.00002
C	-5.10017	-3.55029	-0.00011
C	-7.84843	0.79598	0.00015
H	-7.20746	-1.83522	0.00003
C	7.96745	-1.68144	-1.26747
H	8.93753	-2.21193	-1.27125
H	7.15857	-2.42886	-1.30628
H	7.90915	-1.06894	-2.18566
C	7.96691	-1.68149	1.26827
H	8.93692	-2.21209	1.27238
H	7.90832	-1.06899	2.18643
H	7.15791	-2.42882	1.30675
C	9.00600	0.22460	0.00066
H	8.98992	0.87000	-0.89592
H	8.98906	0.87049	0.89687
H	9.97033	-0.31605	0.00127
C	6.51630	4.16201	-0.00052
H	7.09325	3.87106	0.89573
H	7.09279	3.87117	-0.89710
H	6.43831	5.26466	-0.00041
C	4.34529	4.03033	-1.26738
H	3.33243	3.59724	-1.30858
H	4.26109	5.13285	-1.26666
H	4.88084	3.72954	-2.18630
C	4.34583	4.03031	1.26726
H	4.26165	5.13283	1.26660
H	3.33297	3.59725	1.30886
H	4.88174	3.72950	2.18596
C	-4.34563	-4.03025	-1.26750
H	-3.33277	-3.59718	-1.30892
H	-4.26145	-5.13277	-1.26689
H	-4.88140	-3.72939	-2.18627
C	-4.34551	-4.03041	1.26715
H	-4.88120	-3.72966	2.18600
H	-4.26133	-5.13293	1.26639
H	-3.33265	-3.59734	1.30853
C	-6.51631	-4.16199	-0.00008
H	-7.09298	-3.87116	0.89639
H	-7.09308	-3.87102	-0.89645
H	-6.43834	-5.26465	-0.00018
C	-9.00603	-0.22457	0.00019
H	-8.98958	-0.87019	-0.89623
H	-8.98949	-0.87023	0.89657
H	-9.97035	0.31611	0.00025
C	-7.96723	1.68150	-1.26771
H	-8.93726	2.21206	-1.27161
H	-7.15827	2.42886	-1.30636
H	-7.90881	1.06901	-2.18589
C	-7.96711	1.68146	1.26804
H	-7.15815	2.42882	1.30663
H	-8.93714	2.21203	1.27204
H	-7.90862	1.06895	2.18620

Coordinates for the optimized triplet ground state of **3c**. Free Energy ΔG = -2926.484187 H.

C	-0.92551	1.11627	-0.11573
C	-1.43003	-0.18999	-0.10867
C	-0.46562	-1.30137	-0.12418
C	0.92550	-1.11628	-0.11568
C	1.43003	0.18999	-0.10879
C	0.46561	1.30136	-0.12435
H	-1.62669	1.95750	-0.11724
H	1.62668	-1.95751	-0.11716
C	2.51541	2.49586	-0.13947
C	0.65733	3.85061	-0.15359
C	1.77766	4.64237	-0.15706
C	-0.65734	-3.85062	-0.15316
C	-2.51542	-2.49587	-0.13903
C	-1.77767	-4.64238	-0.15647
H	1.87277	5.72608	-0.16698
H	-0.39816	4.10821	-0.15998
H	0.39815	-4.10822	-0.15961
H	-1.87278	-5.72609	-0.16627
Pt	3.32533	0.71854	-0.09163
N	1.11299	2.53187	-0.14182
N	-1.11299	-2.53188	-0.14148
C	4.28389	4.28604	-0.13976

H	4.48520	4.87984	-1.04828
H	4.46108	4.91371	0.75074
H	4.94958	3.40989	-0.11330
C	-4.28389	-4.28605	-0.13892
H	-4.48524	-4.88019	-1.04721
H	-4.46104	-4.91339	0.75182
H	-4.94959	-3.40990	-0.11274
N	2.89940	3.81368	-0.14797
N	-2.89941	-3.81369	-0.14737
Pt	-3.32533	-0.71854	-0.09133
O	-3.93020	1.27934	0.00366
O	-5.38083	-1.35737	-0.10277
O	5.38083	1.35735	-0.10319
O	3.93020	-1.27935	0.00351
C	-5.16010	1.69277	0.05926
C	-6.31818	0.87499	0.05413
C	-6.38265	-0.52929	-0.02226
H	-7.27803	1.39588	0.12381
C	6.31818	-0.87499	0.05397
C	6.38265	0.52929	-0.02255
C	5.16010	-1.69276	0.05915
H	7.27802	-1.39587	0.12371
C	-7.74134	-1.18737	-0.03710
C	-8.24488	-1.70502	-1.25868
C	-8.49163	-1.31263	1.15859
C	-9.50375	-2.33036	-1.26278
C	-9.74412	-1.95412	1.10734
C	-10.26939	-2.47024	-0.08991
H	-9.89793	-2.71788	-2.21176
H	-10.32383	-2.05486	2.03450
C	-5.31450	3.18431	0.17665
C	-4.79954	3.84030	1.32956
C	-5.94365	3.93602	-0.84989
C	-4.94114	5.23403	1.43703
C	-6.04917	5.33223	-0.70118
C	-5.55814	6.00262	0.43188
H	-4.56235	5.73458	2.33832
H	-6.52677	5.91252	-1.50188
C	5.31451	-3.18430	0.17661
C	4.79967	-3.84023	1.32960
C	5.94352	-3.93605	-0.84997
C	4.94128	-5.23396	1.43712
C	6.04906	-5.33225	-0.70122
C	5.55817	-6.00259	0.43192
H	4.56259	-5.73447	2.33847
H	6.52657	-5.91258	-1.50195
C	7.74135	1.18737	-0.03745
C	8.24486	1.70495	-1.25907
C	8.49166	1.31269	1.15821
C	9.50372	2.33030	-1.26323
C	9.74414	1.95418	1.10691
C	10.26939	2.47023	-0.09039
H	9.89788	2.71777	-2.21224
H	10.32387	2.05497	2.03405
C	-6.48404	3.28428	-2.10928
H	-5.80049	2.50953	-2.49760
H	-7.45855	2.79096	-1.93478
H	-6.63491	4.03804	-2.90150
C	-4.14082	3.06265	2.45216
H	-4.78186	2.22997	2.79593
H	-3.18847	2.60606	2.13054
H	-3.93923	3.71760	3.31704
C	-5.66296	7.50848	0.55769
H	-5.84260	7.81627	1.60333
H	-4.72982	8.00708	0.23000
H	-6.48284	7.91116	-0.06235
C	-11.60678	-3.18134	-0.11472
H	-11.48051	-4.27997	-0.05563
H	-12.24202	-2.87963	0.73632
H	-12.16151	-2.97027	-1.04645
C	-7.45693	-1.56683	-2.54617
H	-7.25166	-0.50525	-2.77922
H	-6.47464	-2.06561	-2.47313
H	-8.00701	-2.00251	-3.39752
C	-7.96784	-0.78194	2.47961
H	-6.93832	-1.13083	2.67752
H	-7.93550	0.32297	2.49529
H	-8.60799	-1.11140	3.31604
C	6.48372	-3.28433	-2.10946
H	5.79984	-2.50997	-2.49798
H	7.45799	-2.79053	-1.93499
H	6.63498	-4.03819	-2.90151
C	4.14106	-3.06253	2.45223
H	4.78216	-2.22987	2.79594
H	3.18871	-2.60591	2.13065
H	3.93950	-3.71745	3.31714
C	5.66303	-7.50845	0.55781
H	5.84340	-7.81614	1.60334
H	4.72963	-8.00705	0.23084
H	6.48245	-7.91122	-0.06278
C	7.45689	1.56669	-2.54654
H	7.25161	0.50509	-2.77952
H	6.47460	2.06547	-2.47352
H	8.00696	2.00232	-3.39793
C	7.96790	0.78208	2.47928
H	6.93837	1.13093	2.67717
H	7.93562	-0.32283	2.49505
H	8.60804	1.11164	3.31568
C	11.60678	3.18133	-0.11525
H	12.16150	2.97019	-1.04697
H	11.48052	4.27997	-0.05625
H	12.24203	2.87969	0.73580

Coordinates for the optimized triplet ground state of **3d**. Free Energy ΔG = -2621.626130 H.

C	-0.53566	-1.32381	-0.25517
C	-1.41700	-0.29369	0.08174
C	-0.83986	1.04554	0.33576
C	0.53567	1.32384	0.25504
C	1.41701	0.29372	-0.08185
C	0.83987	-1.04552	-0.33584
H	-0.93223	-2.32637	-0.44702
H	0.93223	2.32640	0.44688
C	3.14457	-1.47475	-0.68374
C	1.80753	-3.32754	-0.95339
C	3.11189	-3.69646	-1.16315
C	-1.80749	3.32749	0.95361
C	-3.14455	1.47474	0.68373
C	-3.11184	3.69638	1.16355

H	3.53991	-4.66762	-1.40109
H	0.88859	-3.90532	-0.99330
H	-0.88855	3.90526	0.99354
H	-3.53985	4.66750	1.40163
Pt	3.37171	0.42281	-0.27630
N	1.82739	-1.96274	-0.65486
N	-1.82738	1.96274	0.65486
C	5.38450	-2.57612	-1.06192
H	5.69218	-3.00703	-2.03227
H	5.69334	-1.51674	-1.03686
C	-5.38445	2.57607	1.06224
H	-5.69206	3.00697	2.03262
H	-5.69331	1.51669	1.03718
N	3.91479	-2.56867	-1.00636
N	-3.91474	2.56861	1.00659
Pt	-3.37170	-0.42279	0.27618
O	-3.35708	-2.46866	-0.19506
O	-5.51280	-0.53119	0.51709
O	5.51279	0.53123	-0.51739
O	3.35712	2.46870	0.19489
C	-4.38415	-3.24872	-0.24204
C	-5.72486	-2.88124	0.01999
C	-6.21759	-1.60630	0.37417
C	-4.01622	-4.70685	-0.63129
C	-7.73492	-1.38838	0.62996
H	-6.46230	-3.67669	-0.06229
C	5.72490	2.88125	-0.02022
C	6.21761	1.60633	-0.37444
C	4.38419	3.24876	0.24180
C	4.01629	4.70688	0.63107
C	7.73497	1.38832	-0.63004
H	6.46235	3.67669	0.06213
C	-8.24292	-0.33214	-0.38601
H	-9.30763	-0.10373	-0.19453
H	-7.66692	0.60452	-0.31493
H	-8.15612	-0.70759	-1.42206
C	-7.90278	-0.84782	2.07403
H	-8.96621	-0.61912	2.27175
H	-7.56887	-1.59351	2.81849
H	-7.31335	0.07088	2.22550
C	-8.58525	-2.66729	0.47963
H	-8.53083	-3.08282	-0.54269
H	-8.28076	-3.45384	1.19333
H	-9.64519	-2.42797	0.68251
C	-5.22483	-5.66351	-0.68537
H	-5.72961	-5.74806	0.29385
H	-5.96986	-5.34542	-1.43667
H	-4.88045	-6.67506	-0.96825
C	-3.34534	-4.66573	-2.02950
H	-2.48482	-3.97678	-2.03300
H	-2.99363	-5.67500	-2.31294
H	-4.05855	-4.32363	-2.80154
C	-3.00162	-5.23609	0.41566
H	-2.65201	-6.24552	0.13032
H	-2.12912	-4.56658	0.49026
H	-3.46328	-5.30516	1.41758
C	3.00169	5.23617	-0.41587
H	2.12918	4.56668	-0.49048
H	2.65211	6.24559	-0.13050
H	3.46335	5.30525	-1.41778
C	3.34542	4.66575	2.02929
H	4.05861	4.32358	2.80131
H	2.99375	5.67502	2.31276
H	2.48486	3.97684	2.03276
C	5.22492	5.66352	0.68515
H	5.96995	5.34542	1.43644
H	5.72970	5.74805	-0.29408
H	4.88056	6.67508	0.96803
C	8.58535	2.66722	-0.47985
H	8.28105	3.45360	-1.19381
H	8.53074	3.08300	0.54235
H	9.64531	2.42778	-0.68246
C	7.90295	0.84751	-2.07401
H	8.96639	0.61876	-2.27159
H	7.31352	-0.07120	-2.22539
H	7.56912	1.59309	-2.81862
C	8.24282	0.33223	0.38615
H	7.66680	-0.60442	0.31513
H	9.30755	0.10377	0.19485
H	8.15589	0.70784	1.42214
C	6.00347	-3.35739	0.08643
C	6.80859	-4.48558	-0.16033
C	5.78029	-2.95184	1.41982
C	7.38396	-5.20002	0.90391
H	6.99090	-4.80456	-1.19465
C	6.34862	-3.66861	2.48204
H	5.15445	-2.07267	1.61610
C	7.15262	-4.79438	2.22732
H	8.01001	-6.07552	0.69718
H	6.16771	-3.34537	3.51340
H	7.59789	-5.35164	3.05919
C	-6.00351	3.35737	-0.08604
C	-6.80859	4.48557	0.16084
C	-5.78050	2.95186	-1.41947
C	-7.38409	5.20004	-0.90331
H	-6.99076	4.80453	1.19519
C	-6.34896	3.66866	-2.48161
H	-5.15470	2.07268	-1.61586
C	-7.15292	4.79443	-2.22676
H	-8.01010	6.07555	-0.69647
H	-6.16817	3.34545	-3.51299
H	-7.59829	5.35171	-3.05856

Coordinates for the optimized triplet ground state of **3e**. Free Energy ΔG = -1688.284455 H.

C	1.22836	-0.67019	0.00016
C	1.18755	-2.15453	0.00049
C	0.00000	-2.89042	0.00032
C	-1.18755	-2.15453	-0.00011
C	-1.22836	-0.67019	-0.00025
C	0.00000	0.01299	-0.00010
H	0.00000	1.10709	-0.00021
C	-3.52349	-1.78425	-0.00077
C	-2.94003	-4.01734	-0.00037
C	-4.30667	-3.92089	-0.00073
H	-2.29043	-4.88819	-0.00009
H	-5.06501	-4.70129	-0.00080
C	3.52349	-1.78425	0.00092
C	2.94003	-4.01734	0.00152
C	4.30667	-3.92089	0.00183

H	2.29043	-4.88819	0.00165
H	5.06501	-4.70128	0.00227
N	-2.45526	-2.70647	-0.00041
N	-4.65377	-2.57044	-0.00099
N	2.45526	-2.70647	0.00097
N	4.65377	-2.57044	0.00147
C	6.02555	-2.06731	0.00160
H	5.98911	-0.96718	0.00115
H	6.55778	-2.42153	0.90197
H	6.55821	-2.42224	-0.89823
C	-6.02555	-2.06731	-0.00140
H	-6.55777	-2.42202	-0.90158
H	-6.55822	-2.42175	0.89862
H	-5.98911	-0.96718	-0.00155
H	0.00000	-3.98645	0.00051
C	-6.82944	2.47430	-0.00076
C	-5.34062	2.15883	-0.00001
C	-4.41789	3.22618	0.00185
H	-4.83966	4.23517	0.00274
C	-3.00587	3.13678	0.00273
C	-2.19014	4.42002	0.00493
O	-5.06268	0.89943	-0.00120
O	-2.29260	2.06502	0.00191
C	2.19013	4.42002	-0.00307
C	3.00586	3.13678	-0.00191
C	4.41788	3.22618	-0.00160
H	4.83965	4.23517	-0.00219
C	5.34062	2.15884	-0.00064
C	6.82944	2.47430	-0.00053
O	2.29259	2.06502	-0.00133
O	5.06268	0.89943	0.00012
Pt	-3.04746	0.10063	-0.00051
Pt	3.04746	0.10063	0.00007
H	7.30534	2.02199	0.88846
H	7.30549	2.02185	-0.88938
H	7.03253	3.55710	-0.00063
H	1.53293	4.43947	0.88453
H	1.53351	4.43822	-0.89113
H	2.82167	5.32275	-0.00350
H	-1.53386	4.43771	0.89325
H	-1.53260	4.43997	-0.88241
H	-2.82167	5.32275	0.00563
H	-7.03254	3.55709	0.00043
H	-7.30474	2.02303	-0.89061
H	-7.30610	2.02080	0.88722

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