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Electronic Supplementary Information

Green Light-Emitting Electrochemical Cells Based on Platinum (II) Complexes with a Carbazole-Appended Carbene Ligand

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1. EXPERIMENTAL

1.1. Materials and reagents

The starting material [{Pt(μ-Cl)(η^3-2-Me-C_3H_4)}$_2$][1] was prepared following the literature procedure. 9-(4-bromo-phenyl)-9H-carbazole (**A**) (AOBC Chem); Iodomethane (Scharlau); imidazole, potassium carbonate, copper (I) oxide and potassium hexafluorophosphate (Sigma-Aldrich); silver (I) oxide and 2-(2-(diphenylphosphino)ethyl)pyridine (Strem Chemicals); triphenylphosphine (Fluka); were purchased from the indicated chemical companies.

1.2. Physical Measurements and Instrumentation

IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR Spectrometer (ATR in the range 250-4000 cm^{-1}). Mass spectral analyses were performed with a Microflex MALDI-TOF Bruker or an Autoflex III MALDI-TOF Bruker instruments. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS analyzer. ^{1}H, ^{1}H{^{31}P}, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{195}Pt{^{1}H} NMR spectra were recorded on Bruker Avance 400 MHz instrument using the standard references: $SiMe_4$ for ^{1}H and ^{13}C, 85 % H_3PO_4 for ^{31}P and Na_2PtCl_6 in D_2O for ^{195}Pt. δ and J are given in ppm and Hz, respectively, and assignments are based on ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC and HMBC experiments. Molar conductances were carried out on a Philips PW9509 conductimeter in acetone solution (5×10^{-4} M). UV-visible spectra were recorded on a Unicam UV4 spectrophotometer. Steady-state photoluminescence spectra were recorded on a Jobin-Yvon Horiba Fluorolog FL-3-11 Tau 3 spectrofluorimeter. Phosphorescence lifetimes were recorded with a Fluoromax phosphorimeter accessory containing a UV xenon flash tube. Quantum yields measurements were carried out using the Hamamatsu Absolute PL Quantum Yield Measurement System C11347-11. PL films were prepared by drop-

casting solutions 5 wt % complex in PMMA (10^{-2} M or 10^{-3} M for **5**, CH_2Cl_2) onto a quartz slide and allowing the solvent to evaporate. PL spectra and PLQY values of the active thin films were obtained using a Xe lamp and a monochromator as excitation source at 340 nm and an integrated sphere coupled to a spectrometer (Hamamatsu C9920-02 with a Hamamatsu PMA-11 optical detector). All the measurements were conducted in air atmosphere.

1.3. X-ray Crystallography

Single crystals of **5-7** and **9** were obtained by slow diffusion of n-hexane (5-**7**) or pentane (**9**) into saturated CH_2Cl_2 solutions. The crystal data, data collection parameters, and structure solution and refinement details for the crystal structures determined are summarized in Table S1. Crystals were mounted at the end of quartz fibres. Data collection was carried out on a Bruker Smart Apex CCD diffractometer using graphite monochromated MoKα radiation (0.71073 Å). The diffraction frames were integrated using the SAINT package[2] and corrected for absorption with SADABS.[3] Structure solution, followed by full-matrix least-squares refinement (all data) was performed using SHELXL[4] under the WinGX package.[5] All non-hydrogen atoms were refined with anisotropic displacement parameters and refined without positional constraints, except as noted below. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *Ueq* value of the atoms they are linked to (1.5 times for methyl groups). Full-matrix least-squares refinement of these models against *F*2 converged to final residual indices given in Table S1.

CCDC Nos. 2151291-2151294 contain the supplementary crystallographic data for **5-7**·and **9**.

Table S1: Crystallographic data.

	5 · CH_2Cl_2	**6 · 0.75 CH_2Cl_2**	**7 · CH_2Cl_2**	**9 · C_5H_{12}**
Empirical formula	$C_{92}H_{76}Cl_4F_{12}N_8P_4Pt_2$	$C_{83.50}H_{71}Cl_3F_{12}N_8P_4Pt_2$	$C_{48}H_{40}Cl_2F_6N_3P_3Pt$	$C_{57}H_{52}F_6N_3P_3Pt$
Formula weight	2177.47	2034.89	1131.73	1181.01
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	P -1	C 2/c	P 2_1/c	P -1
a (Å)	9.8402(7)	48.516(2)	9.8679(7)	10.3398(5)
b (Å)	19.8457(14)	10.0725(4)	24.8302(16)	15.0320(7)
c (Å)	21.5454(15)	32.0266(13)	20.0686(13)	16.3589(8)
α (º)	90.4310(10)	90	90	100.9910(10)
β (º)	91.1710(10)	90.565(2)	101.7595(9)	92.9220(10)
γ (º)	98.1410(10)	90	90	98.2160(10)
Volume (Å^3)/Z	4164.0(5) / 2	15649.9(11) / 8	4814.0(6) / 4	2462.4(2) / 2
ρ (Mg/m^3)	1.737	1.727	1.561	1.593
μ (Mo-Kα) (mm^{-1})	3.642	3.837	3.185	3.012
F(000)	2152	8024	2240	1184
Crystal size (mm^3)	0.16 x 0.11 x 0.05	0.110 x 0.060 x 0.020	0.180 x 0.100 x 0.050	0.180 x 0.140 x 0.120
Theta range (º)	1.04 to 28.70	2.065 to 28.346	2.073 to 28.819	2.069 to 28.834
Reflections collected	51070	278162	59106	30744
Independent reflections [R(int)]	19538 [0.0706]	19522 [0.0549]	11781 [0.0900]	11651 [0.0296]
Final R_1, wR_2 [I>2sigma(I)]	0.0677, 0.1566	0.0463, 0.0972	0.1013, 0.2478	0.0353, 0.0900
R_1, wR_2 (all data)	0.1057, 0.1727	0.0502, 0.0987	0.1458, 0.2781	0.0401, 0.0938
GOF (F^2)	1.078	1.188	1.031	1.060
Largest diff. peak and hole/ e.Å^{-3}	6.009 and -3.037	3.250 and -2.270	6.106 and -2.839	2.587 and -2.268

1.4. Computational Methods.

Density functional calculations were performed using the M06 hybrid density functional[6] under the Gaussian09 package.[7] The SDD pseudopotential and associated basis set[8] was used for platinum, and the 6-31G(d)[9-10] basis set was used for all other atoms. Geometry optimisations for S_0 and T_1 were performed under no symmetry restrictions using the initial coordinates of models derived from X-ray data and in dichloromethane by using the polarizable continuum model (PCM) implemented Gaussian 09 package. Frequency calculations have been performed in order to determine the nature of the stationary points found (no imaginary frequencies for minima). Atomic coordinates (x, y, z) for the optimized structures are listed in a xyz file. The time-dependent density-functional (TD-DFT) calculations for singlets and triplets were also carried out in the presence of dichloromethane using the polarizable continuum model. Mulliken population analysis was carried out using Gaussian 09 package for interpretation purposes. Molekel, GaussView5 and ChemissianLab program packages were used for analysis and graphic representation of molecular structures and orbitals.

1.5. LECs fabrication and characterization

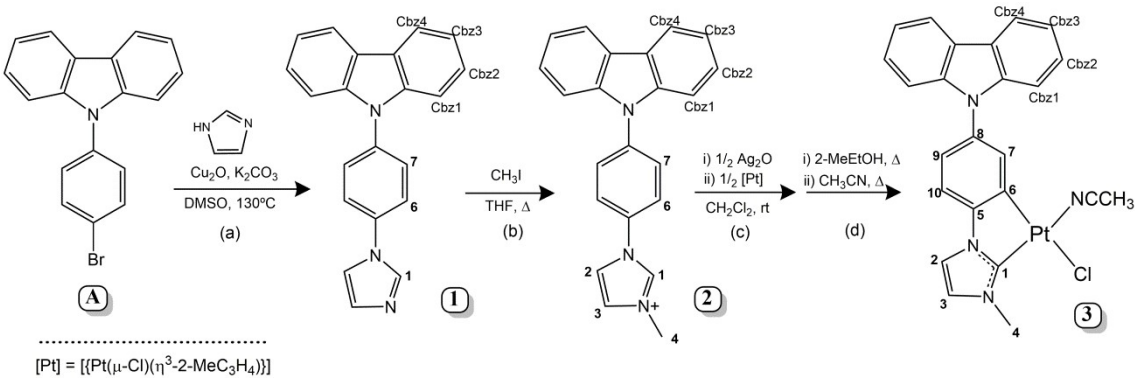
Solutions of emitter **5-9** were mixed in a molar ratio of 4:1 the ionic liquid (IL) 1-butyl-3-methyl-imidazolium-hexafluorophosphate ($BMIM^+PF_6^-$). The solvents used were acetonitrile (ACN) and dichloromethane (DCM) for emitter **7-9** and dichloroethane (DCE) for emitters **5-6**. The final concentration of the emitter in the solution was 20 mg/mL. Pre-patterned indium tin oxide (ITO)-coated glass plates were used as transparent conductive substrates. They were subsequently cleaned ultrasonically in soapy-water, water, and isopropanol baths. After drying, the substrates were placed in an UV-ozone cleaner (Jelight 42-220) for 20 min. The ITO substrates were first coated

with an 80-nm thick film of PEDOT:PSS (PEDOT = poly(3,4-ethylenedioxythiophene), PSS = polystyrenesulfonate) obtained at 4000 rpm for 60 seconds and annealed on a hotplate at 150°C for 10 minutes. The active layer solutions (emitter:IL) were then spin-coated. The films from both solutions of ACN and DCM were spun at 2000 rpm for 60 seconds. Films from DCM solutions were covered with a beaker for the first 10-15 seconds of spinning to reduce the fast solvent release and improve the morphology of the film. The films were annealed at 70°C for 15 minutes (**5-9**), at 70°C for 4 h (**7**) and at 90ºC for 1h (**9**). Resulting thicknesses of 90 nm and 120 nm were obtained, for layers processed from ACN and DCM, respectively. Finally, an Al electrode (100 nm) was thermally evaporated on top of the active layer using a shadow mask under inert atmosphere. The final active area of the cells was 6 mm^2. The thickness of the PEDOT:PSS and the active layers were determined with an Ambios XP-1 profilometer. The devices were measured by applying a pulsed current density (12.5 to 50 A m^{-2}) while monitoring the voltage and luminance versus time by using a True Color Sensor MAZeT (MTCSiCT sensor) with a Botest OLT OLED Lifetime-Test system. The applied pulsed current consisted of block waves at a frequency of 1000 Hz with a duty cycle of 50%. Hence, the average current density and voltage were obtained by multiplying the values by the time-on (0.5 s) and dividing by the total cycle time (1 s). Electroluminescence (EL) spectra were recorded by driving the cells with the Botest OLT system and an optical fibre connected to the Avant spectrometer AvaSpec – 2048L. The external quantum efficiency (EQE) of the devices was extracted from the current efficiency and the EL spectra. It was also calculated using the following equation:

$$EQE = \frac{b\varphi}{2n^2} \quad (1)$$

where *b* is the recombination efficiency (equals to 1 for ohmic contacts), *n* is the refractive index of glass and *φ* is the fraction of excitons that decay radiatively, approximated from the PLQY, as the studied complexes can harvest both singlet and triplet excitons.

1.6 Synthesis of 1-3.



Scheme S1: Synthesis of complex **1-3** and numerical scheme for NMR purposes

Synthesis of 9-[4-(1H-Imidazol-1-yl)phenyl]-9H-carbazole (1). Imidazole (180.7 mg, 2.653 mmol), potassium carbonate (489.0 mg, 3.538 mmol), and Cu_2O (25.3 mg, 0.177 mmol) were added to a solution of **A** (570.0 mg, 1.769 mmol) in dried and degassed DMSO (6 mL) under an argon atmosphere. After 48 h of reaction at 130ºC, the crude was cooled down to room temperature and treated with 60 mL of ethyl acetate. Then, the suspension was filtered through Celite and treated with H_2O (2 x 20 mL) and brine (2 x 20 mL). The organic layer was dried using anhydrous $MgSO_4$. The solvent was evaporated to dryness and treated with hexane (4 x 15 mL) to give **1** as a white solid. Yield: 508.5 mg, 92.9%. Anal. Calcd. for $C_{21}H_{15}N_3$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.24; H, 4.67; N, 13.23. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.41 (br s, 1H, H_1), 8.27 (br d, $^3J_{H\text{-}H}$ = 7.6, 2H, H_{cbz1}), 7.97 (ν_A, $^3J_{H\text{-}H}$ = 8.8, 2H, H_6), 7.90 (m, 1H, H_{imid}), 7.79

(ν_B, $^3J_{H\text{-}H}$ = 8.8, 2H, H_7), 7.49-7.44 (m, 2H, H_{cbz}), 7.41 (br d, 2H, H_{cbz}), 7.31 (m, 2H, H_{cbz2}), 7.18 (br s, 1H, H_{imid}).

Synthesis of 1-(4-(9H-Carbazol-9-yl)phenyl)-3-methyl-1*H*-imidazolium iodide (**2**). CH_3I (0.2 mL, 3.214 mmol) was added to a solution of **1** (549.7 mg, 1.777 mmol) in dried THF (10 mL) under an argon atmosphere. The mixture was refluxed for 24 hours and then it was cooled down to room temperature. Then, the solid was filtered and washed with hexane (5 x 10 mL) to give **2** as a white solid. Yield: 702.9 mg, 87.7%. Anal. Calcd for $C_{22}H_{18}N_3I$: C, 58.55; H, 4.02; N, 9.31. Found: C, 58.26; H, 3.81; N, 9.03. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.87 (br s, 1H, H_1), 8.42 (pt, 1H, H_{imid}), 8.30 (d, $^3J_{H\text{-}H}$ = 7.7, 2H, H_{cbz1}), 8.08 (ν_A, $^3J_{H\text{-}H}$ = 8.8, 2H, H_6), 8.02 (pt, 1H, H_{imid}), 7.99 (ν_B, $^3J_{H\text{-}H}$ = 8.8, 2H, H_7), 7.52-7.47 (m, 2H, H_{cbz}), 7.45 (br d, 2H, H_{cbz}), 7.35 (m, 2H, H_{cbz2}), 4.01 (s, 3H, CH_3).

Synthesis of [Pt(C^C*)Cl(NCCH$_3$)] (3). Ag_2O (77.0 mg, 0.332 mmol) was added to a suspension of **2** (300.0 mg, 0.665 mmol) in dried dichloromethane (30 mL) under an argon atmosphere and protected from light. After 3 hours of reaction at rt, [{Pt(μ-Cl)(η^3-2-Me-C_3H_4)}$_2$] (182.3 mg, 0.319 mmol) was added and the mixture was allowed to react for 3 hours to give a pale-yellow precipitate (AgI), which was separated by filtration under Argon through Celite. The resulting solution was evaporated to dryness to give a yellow residue, that was refluxed in 2-methoxyethanol (15 mL) for 3 hours. After cooling down to rt, the resulting solid was filtered and washed with dichloromethane (5 mL) and diethyl ether (5 mL). Then, it was treated with boiling acetonitrile (5 x 40 mL) and the suspension was filtered through Celite. The resulting solution was evaporated to dryness and the residue was washed with diethyl ether to give **3** as a yellow solid. Yield: 228.3 mg, 57.8%. Anal. Calcd. for $C_{24}H_{19}ClN_4Pt$: C, 48.53; H, 3.22; N, 9.43. Found: C, 48.18; H, 3.05; N, 8.93. ^{1}H NMR data for **3** (400

MHz, DMSO-d_6): δ = 8.57 (s, $^3J_{Pt-H}$ = 56.8, 1H, H_7), 8.23 (d, $^3J_{H-H}$ = 7.8, 2H, H_{cbz1}), 8.17 (d, $^3J_{H-H}$ = 1.9, 1H, H_2), 7.68 (d, $^3J_{H-H}$ = 8.2, 1H, H_{10}), 7.54 (d, $^3J_{H-H}$ = 1.9, 1H, H_3), 7.42 (m, 4H, H_{cbz}), 7.35 (dd, $^3J_{H-H}$ = 8.1, $^4J_{H-H}$ = 2.1, 1H, H_9), [7.30-7.23] (m, 2H, H_{Cbz2}), 4.18 (s, 3H, CH_3), 2.07 (s, 3H, CH_3CN).

1.7 NMR Spectroscopic data of 4-9.

[Pt(Cbz-C^C*)(Cl)(PPh$_3$)] (4). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.01-7.96 (m, 2H, H_{cbz1}), 7.63-7.54 (m, 6H, H_o(PPh_3)), 7.44 (m, 1H, H_2), 7.29-7.06 (m, 15H, H_m-H_p(PPh_3), 4H_{cbz}, H_9, H_{10}), 7.01 (m, 1H, H_3), 6.87-6.66 (m, 3H, H_7, 2H_{cbz}), 4.32 (s, 3H, CH_3). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ = 29.7 ($^1J_{P-Pt}$ = 2899.1).

[Pt(Cbz-C^C*)(PPh$_3$)(py)]PF$_6$ (5). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.44 (d, $^3J_{H-H}$ = 5.3, $^3J_{H-Pt}$ = 26.1, 2H, $H_{2'}$), 7.98 (d, $^3J_{H-H}$ = 6.8, 2H, H_{cbz1}), 7.67 (t, $^3J_{H-H}$ = 7.5, 1H, $H_{4'}$), 7.55-7.43 (m, 7H, H_2, H_o (PPh_3)), 7.35-7.27 (m, 4H, H_p (PPh_3), H_{10}), 7.24-7.06 (m, 13H, 2$H_{3'}$, 6H_m (PPh_3), 4H_{cbz}, H_9), 7.03 (br, 1H, H_3), 6.77 (m, $^3J_{H-Pt}$= 59.0, 1H, H_7), 6.73 (d, $^3J_{H-H}$ = 7.3, 2H, H_{cbz}), 2.90 (s, 3H, CH_3). ^{13}C{^{1}H} NMR plus HMBC and HSQC (101 MHz, CD_2Cl_2): δ = 171.5 (d, $^2J_{C-P}$ = 191.3, 1C, C_1), 152.4 (s, 2C, $C_{2'}$), 139.6 (s, 1C, $C_{4'}$), 139.1 (s, 1C, C_7), 135.0 (d, $^2J_{C-P}$ = 11.6, 6C, C_o (PPh_3)), 131.8 (d, $^3J_{C-P}$ = 2.4, 3C, C_p (PPh_3)), 129.1 (d, J_{C-P} = 10.8, 6C, C_m (PPh_3)), 127.8 (s, 2C, $C_{3'}$), 126.0 (s, 2C, C_{cbz}), 124.4 (br, 1C, C_3), 120.1 (s, 2C, C_{cbz1}), 119.8 (s, 2C, C_{cbz}), 112.6 (s, 1C, C_{10}), 109.9 (s, 2C, C_{cbz}), 35.8 (s, 1C, CH_3). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ = 29.0 ($^1J_{P-Pt}$ = 2914.2). ^{195}Pt{^{1}H} NMR (85.6MHz, CD_2Cl_2): δ = – 4271.0 (d).

[Pt(Cbz-C^C*)(P^N)]PF$_6$ (6). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.05 (d, $^3J_{H-H}$ = 5.3, 1H, $H_{6'}$), 8.04 (m, 2H, H_{cbz1}), 7.95 (t, $^3J_{H-H}$ = 7.8, 1H, $H_{4'}$), 7.70 (m, 2H, H_o (PPh_2)), 7.62 (d, $^3J_{H-H}$ = 7.9, 1H, $H_{3'}$), 7.54 (s, br, 1H, H_2), 7.48-7.28 (m, 8H, H_{10}, $H_{5'}$, 2H_{cbz}, 4H (PPh_2)), 7.24-7.15 (m, 5H, H_9, 4H_{cbz}), 7.12 (s, 1H, H_3), 7.01-6.73 (m, 4H (PPh_2)), 6.57 (m, $^3J_{H-Pt}$= 65.3, 1H, H_7), 3.75-3.69 (m, 1H, CH_2), 3.50-3.32 (m, 1H, CH_2), 3.26 (s, 3H, CH_3),

2.76-2.62 (m, 1H, CH_2), 2.41-2.25 (m, 1H, CH_2). $^{13}C\{^1H\}$ NMR plus HMBC and HSQC (101 MHz, CD_2Cl_2): δ 173.5 (s, 1C, C_1), 161.2 (d, $^3J_{C\text{-}P}$ = 3.5, 1C, $C_{2'}$), 153.6 (s, 1C, $C_{6'}$)), 141.3 (s, 1C, $C_{4'}$), 141.4 (s, 2C, C_{Cbz}), 138.1 (d, $^3J_{C\text{-}P}$ = 9.4, 1C, C_7), 134.8 (d, 2C, C_o (PPh_2)), 132.6 (d, C (PPh_2)), 131.5 (br, C (PPh_2)), 129.6 (d, C (PPh_2)), 129.2 (d, C (PPh_2)), 126.9 (s, 1C, $C_{3'}$), 126.1 (s, 2C, C_{Cbz}), 125.2 (s, 1C, $C_{5'}$), 124.3 (s, 1C, C_9), 124.1 (s, 1C, C_3), 120.6 (s, 2C, C_{Cbz1}), 120.1 (s, 2C, C_{Cbz}), 115.8 (s br, 1C, C_2), 112.8 (s, 1C, C_{10}), 110.1 (s, C (PPh_2)), 37.1 (s, 1C, CH_3), 36.8 (s, 1C, CH_2), 26.4 (d, $^1J_{C\text{-}P}$ = 36.3, 1C, CH_2). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 19.2 ($^1J_{P\text{-}Pt}$ = 2896.5). $^{195}Pt\{^1H\}$ NMR (85.6MHz, CD_2Cl_2): δ – 4208.6 (d).

[Pt(Cbz-C^C*)(dppm)]PF_6 (7). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.03 (m, 2H, H_{Cbz1}), 7.80-7.71 (m, 4H, H_o (Ph)), 7.69-7.52 (m, 11H, H_o (Ph), H_p (Ph), H_m (Ph), H_2), 7.50-7.42 (m, 3H, H_p (Ph), H_{10}), 7.37-7.30 (m, 5H, H_m (Ph), H_9), 7.29-7.25 (m, 1H, $^3J_{H\text{-}P}$ = 8.0, H_7), 7.23-7.15 (m, 4H; H_{Cbz}), 7.12 (s, br, 1H, H_3), 7.07-6.99 (m, 2H; H_{Cbz}), 4.82-4.66 (m, 2H, CH_2 dppm), 3.28 (s, 3H, H_4). $^{13}C\{^1H\}$ NMR plus HMBC and HSQC (100.6 MHz, CD_2Cl_2): δ 172.2 (C_1), 141.1 (s, 2C, C_{Cbz}), 137.7 (m, $^4J_{C\text{-}P}$= 11.3, $^4J_{C\text{-}P}$ = 4.0, C_7), 134.0-133.8 (m, 8C, C_o (Ph)), 133.4-133.2 (m, 4C, C_p (Ph)), 130.5 (d, 4C, $^3J_{C\text{-}P}$ = 10.9, H_m (Ph)), 130.2 (d, 4C, $^3J_{C\text{-}P}$ = 11.3, H_m (Ph)), 126.4 (s, 2C, C_{Cbz}), 125.7 (s, C_9), 124.1 (d, $^4J_{C\text{-}P}$ = 4.5, C_3), 123.7 (s, 2C, C_{Cbz}), 120.5 (s, 2C, C_{Cbz}), 120.3 (s, 2C, C_{Cbz}), 116.7 (s, br, C_2), 113. (d, $^4J_{C\text{-}P}$ = 3.9, C_{10}), 50.7-50.2 (m; *C*H_2 dppm), 39.10 (s, C_4). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ – 38.8 (ν_A, $J_{P\text{-}P}$ = 42, $^1J_{Pt\text{-}P}$= 2374.9; $P_{trans\ C1}$), – 39.4 (ν_B, $J_{P\text{-}P}$= 42, $^1J_{Pt\text{-}P}$= 1559.7, $P_{trans\ C6}$). $^{195}Pt\{^1H\}$ NMR (85.6MHz, CD_2Cl_2): δ – 4384 (dd).

[Pt(Cbz-C^C*)(dppe)]PF_6 (8). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.03 (d, 2H, $^3J_{H\text{-}H}$ = 7.6, H_{Cbz1}), 8.00-7.92 (m, 4H, H_o (Ph)), 7.70-7.58 (m, 11H, H_2, H_o (Ph), H_m (Ph), H_p (Ph)), 7.50-7.47 (dd, 1H, $^4J_{H\text{-}P}$ = 8.2, $^4J_{H\text{-}P}$ = 2.6, $^3J_{H\text{-}Pt}$ = 19.9, H_{10}), 7.42-7.36 (m, 2H; H_p (Ph)), 7.33-7.23 (m, 6H, H_7, H_9, H_m (Ph)), 7.21-7.15 (m, 2H, H_{Cbz2}), 7.13-7.08 (m,

2H; H_{Cbz3}), 7.03 (s, br, 1H, $^{3}J_{H\text{-}Pt}$ = 8.9, H_3), 6.82 (d, 2H, $^{3}J_{H\text{-}H}$ = 8.1; H_{Cbz4}), 3.07 (s, 3H, H_4), 2.43-2.19 (m, 4H, CH_2 dppe). $^{13}C\{^{1}H\}$ NMR plus HMBC and HSQC (100.6 MHz, CD_2Cl_2): δ 172.4 (C_1), 141.2 (s, 2C, C_{Cbz}), 138.2 (dd, $^{3}J_{C\text{-}P}$ = 9.6, $^{3}J_{C\text{-}P}$ = 2.4, $^{2}J_{C\text{-}Pt}$ = 48.4, C_7), 134.5-133.8 (m; 8C, C_o (Ph)), 133.1 (d, 2C, $^{4}J_{C\text{-}P}$ = 2.3, C_p (Ph)), 132.8 (d, 2C, $^{4}J_{C\text{-}P}$ = 2.3, C_p (Ph)), 132.3 (d, 4C, $^{3}J_{C\text{-}P}$ = 10.8, C_m (Ph)), 129.7 (d, 4C, $^{3}J_{C\text{-}P}$ = 11.0, C_m (Ph)), 129.0 (s, 1C, $^{2}J_{C\text{-}Pt}$ = 22.2, C (Ph)) 128.5, 126.7, 126.1 (s, 3C, C (Ph)), 126.0 (s, 2C, C_{Cbz3}), 125.3 (s, C_9), 124.8 (d, $^{4}J_{C\text{-}P}$ = 4.9, C_3), 123.5 (s, 2C, C_{Cbz}), 120.3 (s, 2C, C_{Cbz1}), 120.0 (s, 2C; C_{Cbz2}), 116.6 (s, C_2), 112.9 (d, $^{4}J_{C\text{-}P}$ = 3.8, $^{3}J_{C\text{-}Pt}$ = 26.8, C_{10}), 110.0 (s, 2C, C_{Cbz4}), 39.3 (s, C_4), 32.4-30.8 (m, *C*H_2 dppe). $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2): δ 50.4 (d, $^{2}J_{P\text{-}P}$= 6.3, $^{1}J_{Pt\text{-}P}$ = 2699.9, $P_{trans\ C1}$), 43.4 (d, $^{2}J_{P\text{-}P}$= 6.3, $^{1}J_{Pt\text{-}P}$ = 1964.2, $P_{trans\ C6}$). $^{195}Pt\{^{1}H\}$ NMR (85.6MHz, CD_2Cl_2): δ – 4983 (dd).

[Pt(Cbz-C^C*)(dppbz)]PF_6 (9). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.10 (m, 2H, H_{Cbz1}), 7.88-7.78 (m, 4H, H_o (Ph)), 7.62 (d, 1H, $^{3}J_{H\text{-}H}$ = 1.2, H_2), 7.59-7.54 (m, 4H, H_p (Ph), H_{BZ}), 7.52-7.44 (m, 6H, H_m (Ph), H_{10}, H_{BZ}), 7.42-7.30 (m, 6H, H_9, H_o (Ph), H_{BZ}), 7.27-7.20 (m, 4H, H_{Cbz}), 7.20-7.16 (m, 1H, $^{4}J_{H\text{-}P}$= 7.17, H_7), 7.14-7.07 (m, 2H, H_p (Ph)), 7.07-6.99 (m, 5H, H_3, H_m (Ph)), 6.99-6.94 (m, 2H, H_{Cbz}), 3.08 (s, 3H, H_4). $^{13}C\{^{1}H\}$ NMR plus HMBC and HSQC (100.6 MHz, CD_2Cl_2): δ 171.3 (C_1), 143.7-142.8 (m, C_{BZ}), 141.5 (s, 2C, C_{Cbz}), 140.6-139.6 (m, C_{BZ}), 138.4 (dd, $^{3}J_{C\text{-}P}$ = 9.1, $^{3}J_{C\text{-}P}$ = 2.5, $^{2}J_{C\text{-}Pt}$= 51.4, C_7), 134.1-133.4 (12C, C_o (Ph), C_{BZ}), 132.9 (d, 2C, $^{4}J_{C\text{-}P}$ = 2.3, C_p (Ph)), 132.4 (d, 2C, $^{4}J_{C\text{-}P}$ = 2.5, C_p (Ph)), 130.2 (d, 4C, $^{3}J_{C\text{-}P}$ = 11.0, C_m (Ph)), 129.5 (d, 4C, $^{3}J_{C\text{-}P}$ = 11.4, C_m (Ph)), 126.2 (s, 2C, C_{Cbz}), 125.6 (s, C_9), 125.1 (d, $^{4}J_{C\text{-}P}$= 4.5, $^{3}J_{C\text{-}Pt}$ = 30, C_3), 123.8 (s, 2C, C_{Cbz}), 120.5 (s, 2C, C_{Cbz}), 120.2 (s, 2C, C_{Cbz}), 116.8 (d, $^{4}J_{C\text{-}P}$ = 2.3, $^{3}J_{C\text{-}Pt}$ = 37.1, C_2), 113.0 (s, $^{4}J_{C\text{-}P}$ =3.8, $^{3}J_{C\text{-}Pt}$ = 27.9, C_{10}), 110.2 (s, 2C, C_{Cbz}), 39.3 (s, C_4). $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2): δ 47.0 (d, $^{2}J_{P\text{-}P}$= 4.4, $^{1}J_{Pt\text{-}P}$ = 2661.4, $P_{trans\ C1}$), 39.8 (d, $^{2}J_{P\text{-}P}$= 4.4, $^{1}J_{Pt\text{-}P}$= 1956.2, $P_{trans\ C6}$). $^{195}Pt\{^{1}H\}$ NMR (85.6MHz, CD_2Cl_2): δ – 4917 (dd).

2. MULTINUCLEAR NMR SPECTRA FOR CHARACTERIZATION

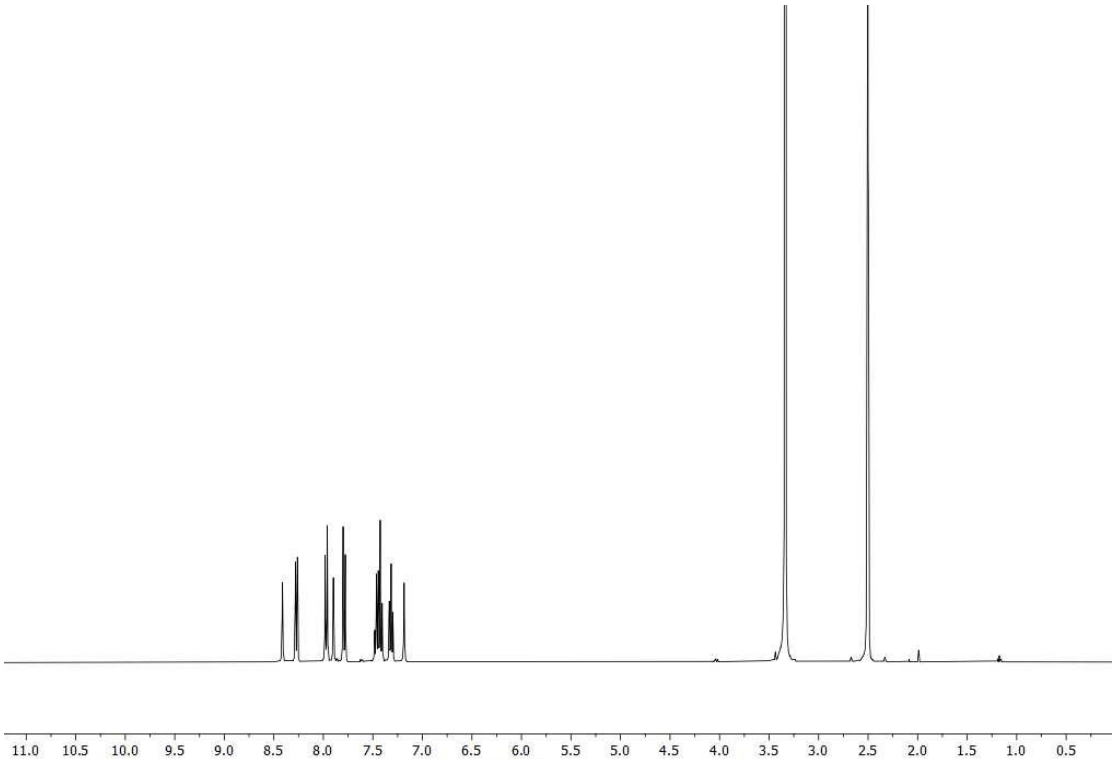
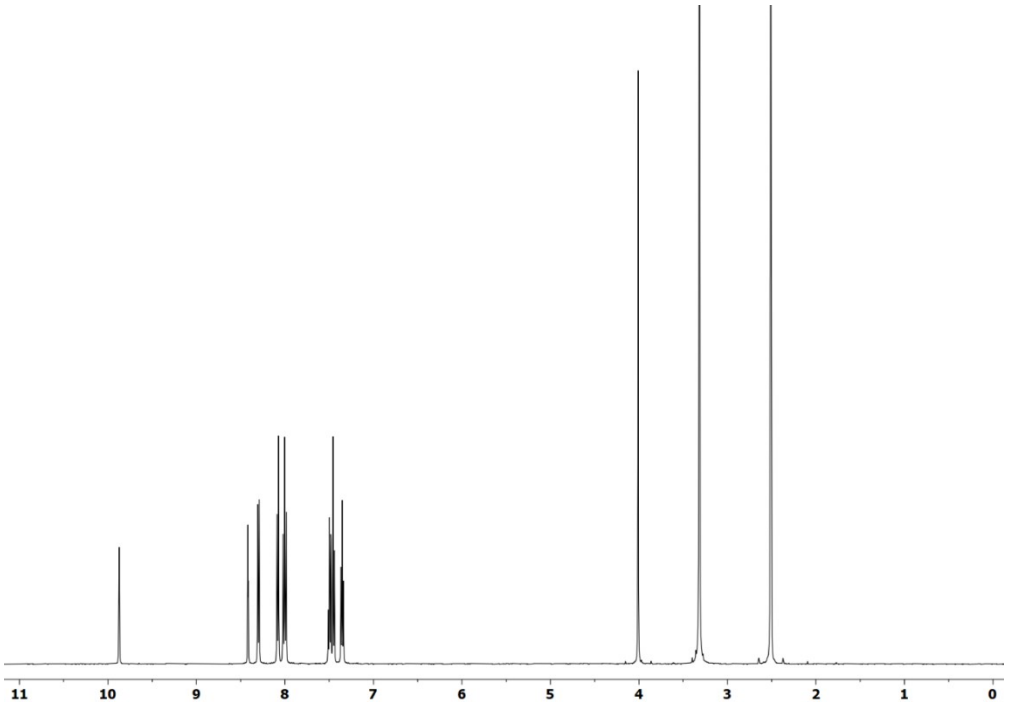
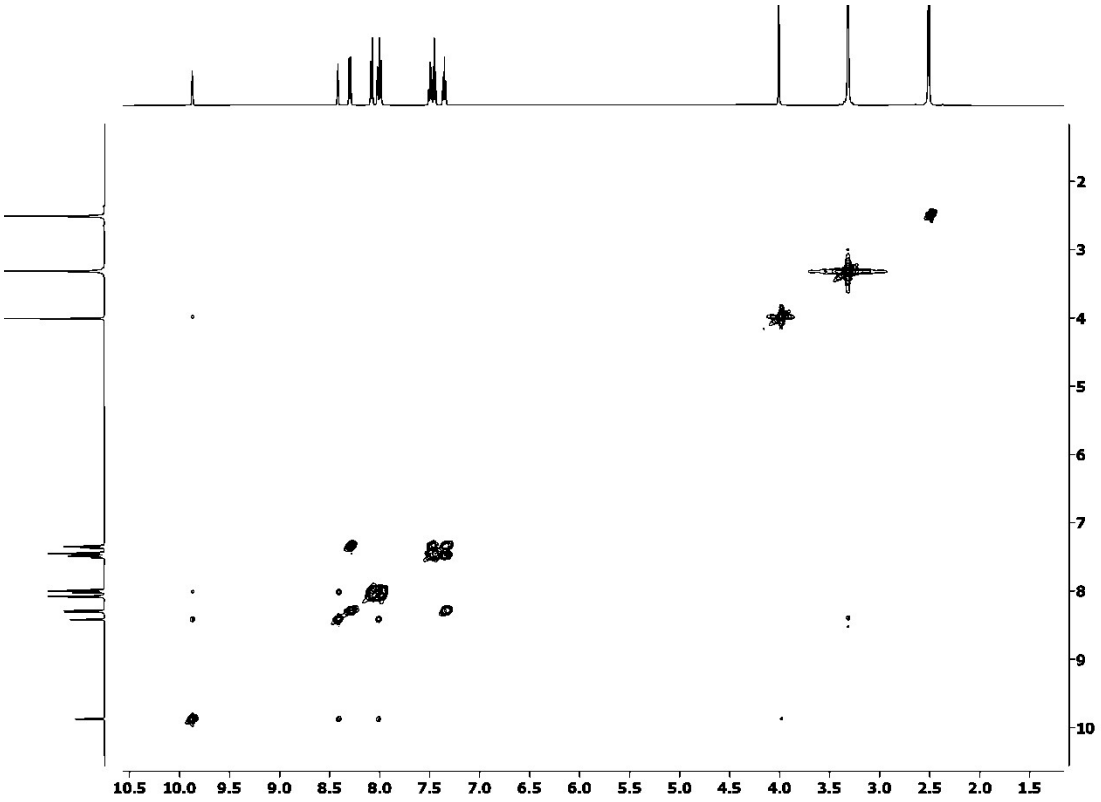


Figure S1. NMR spectra of **1** in DMSO-d_6. (a) ^{1}H, (b) ^{1}H -^{1}H COSY

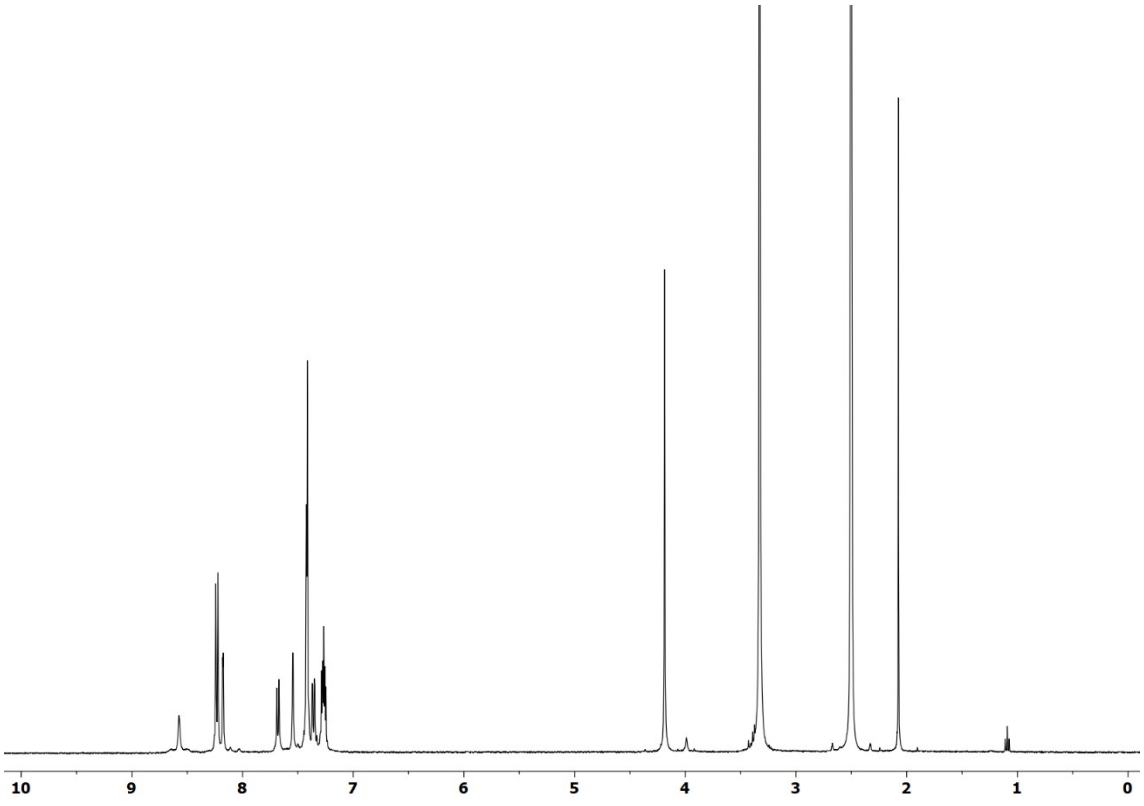


(a)

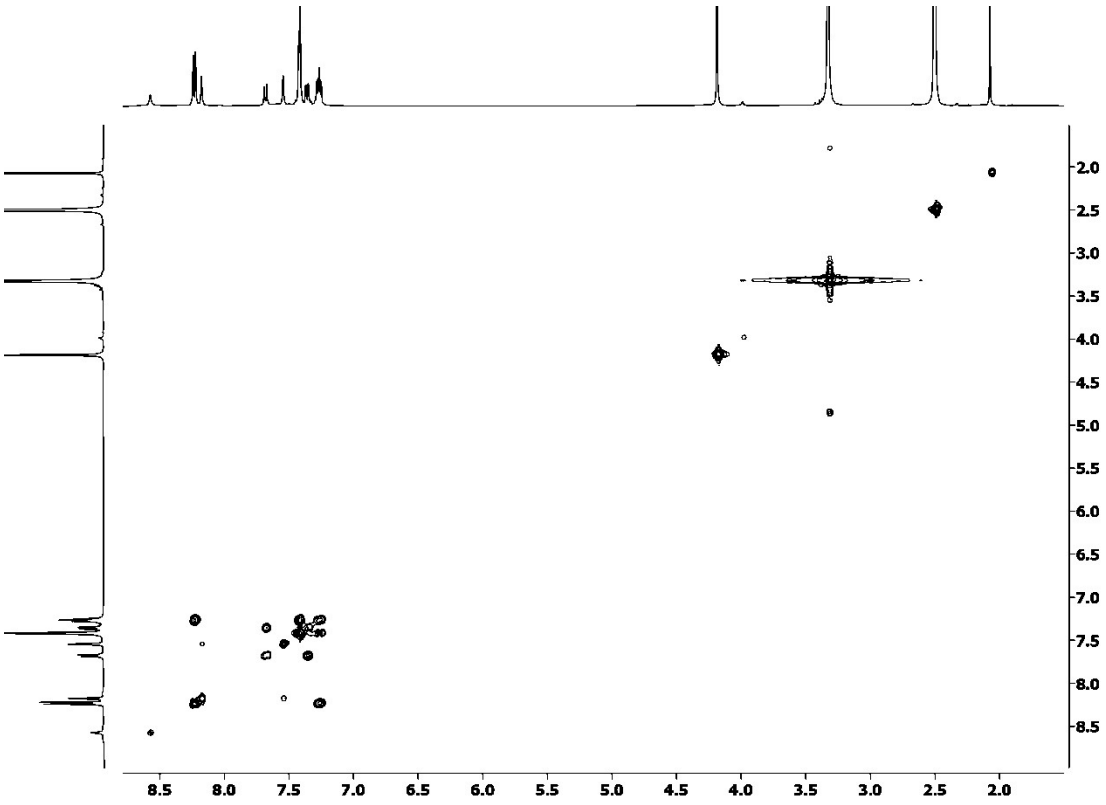


(b)

Figure S2. NMR spectra of **2** in DMSO-d_6. (a) ^{1}H, (b) ^{1}H -^{1}H COSY

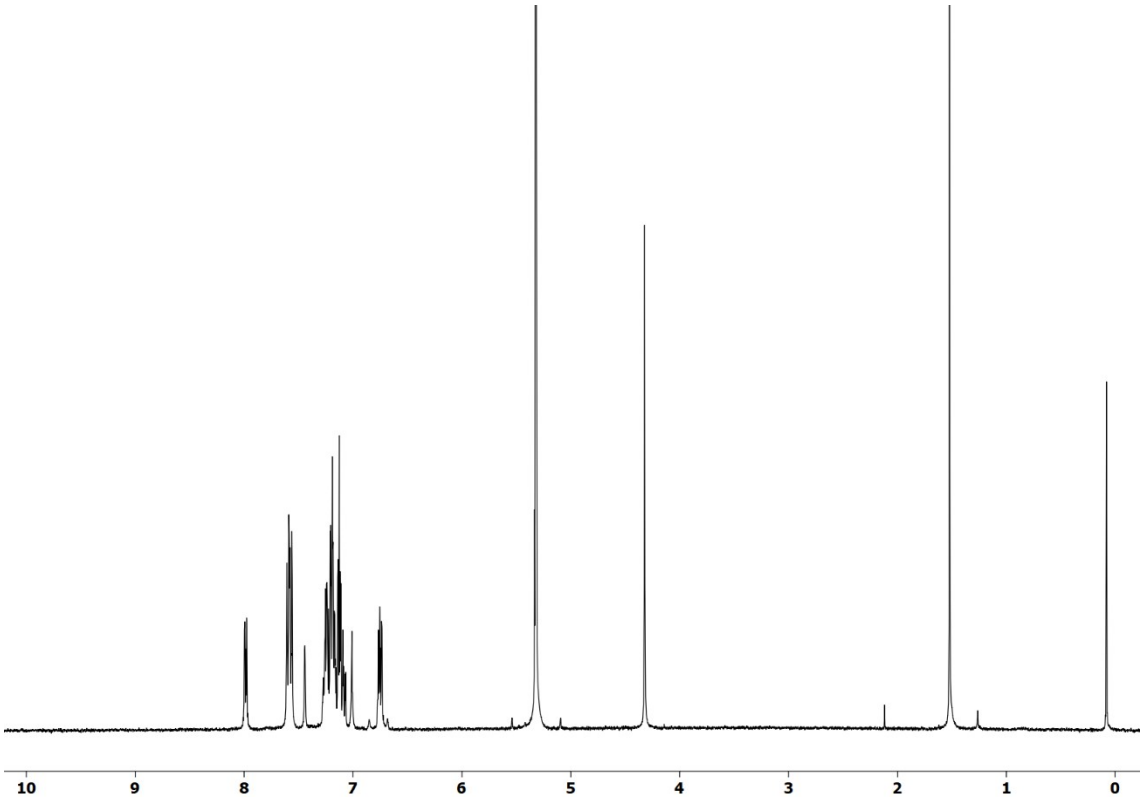


(a)

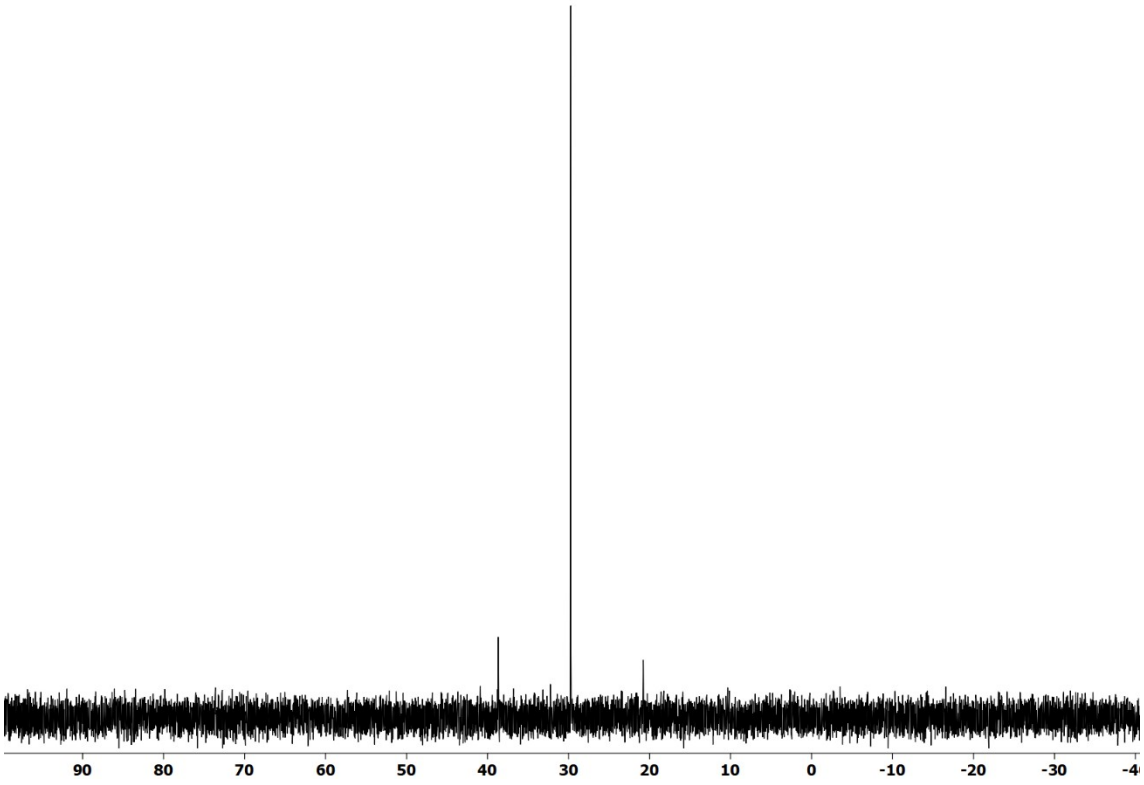


(b)

Figure S3: NMR spectrum of **3** in DMSO-d_6. (a) ^{1}H, (b) ^{1}H -^{1}H COSY

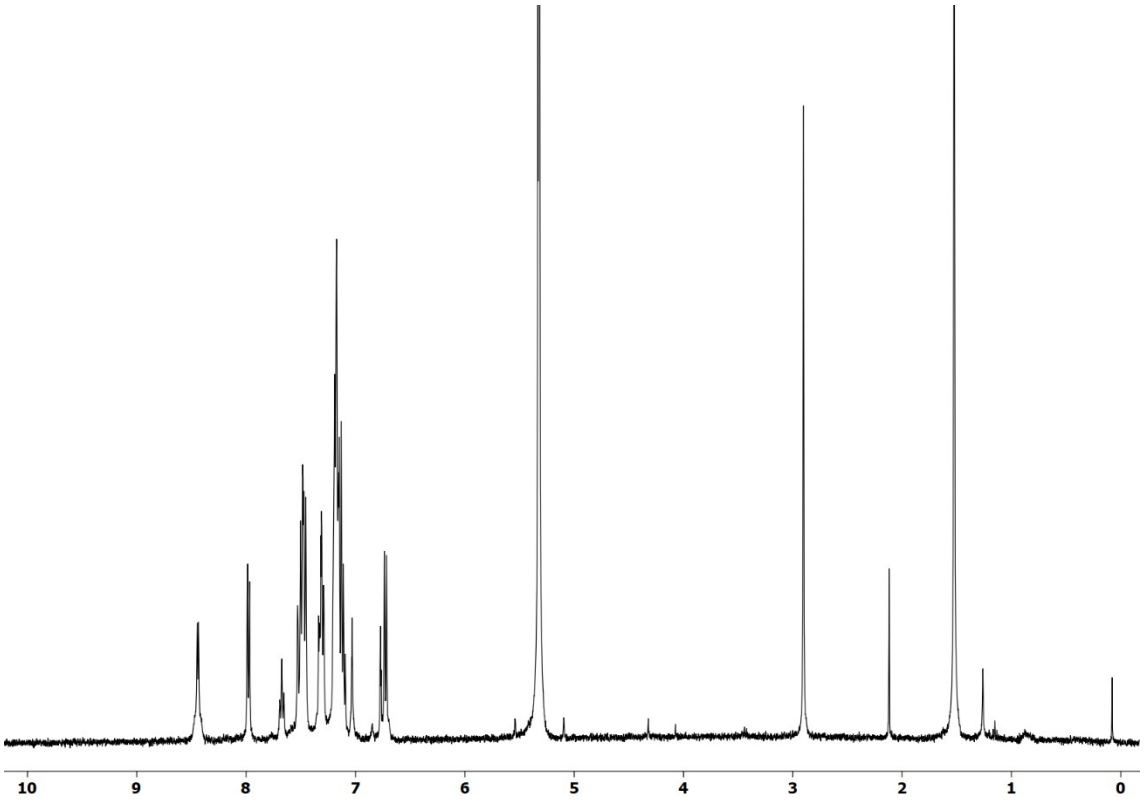


(a)

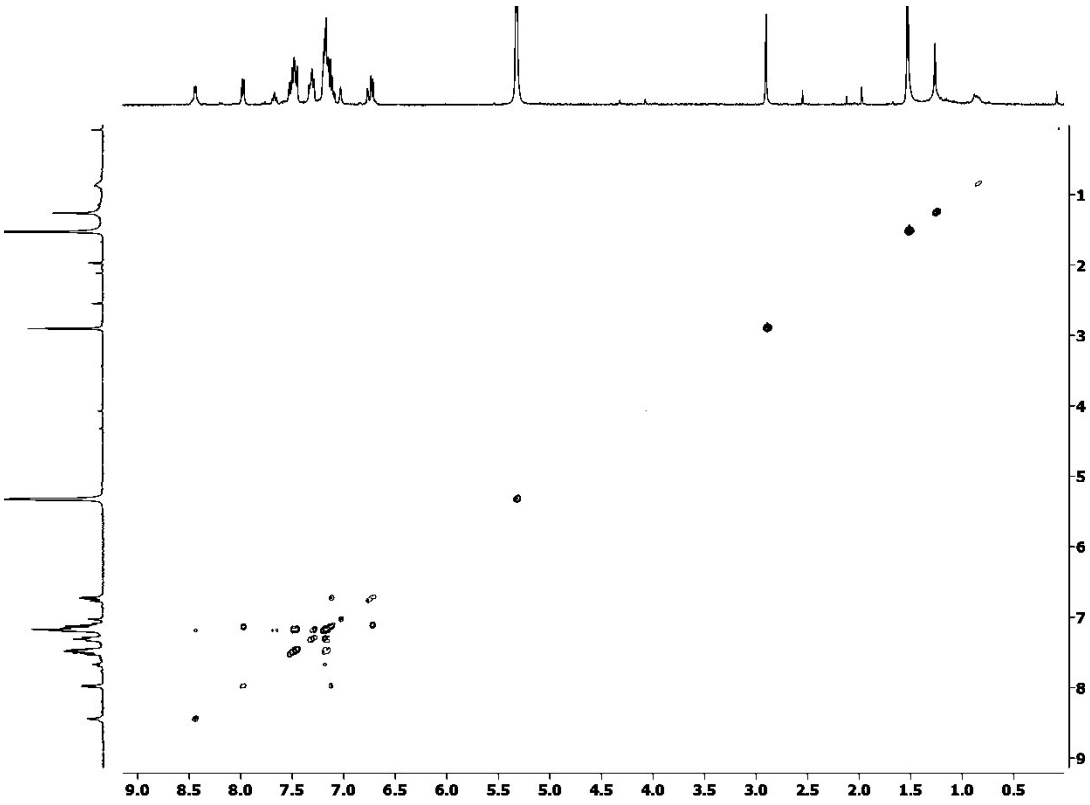


(b)

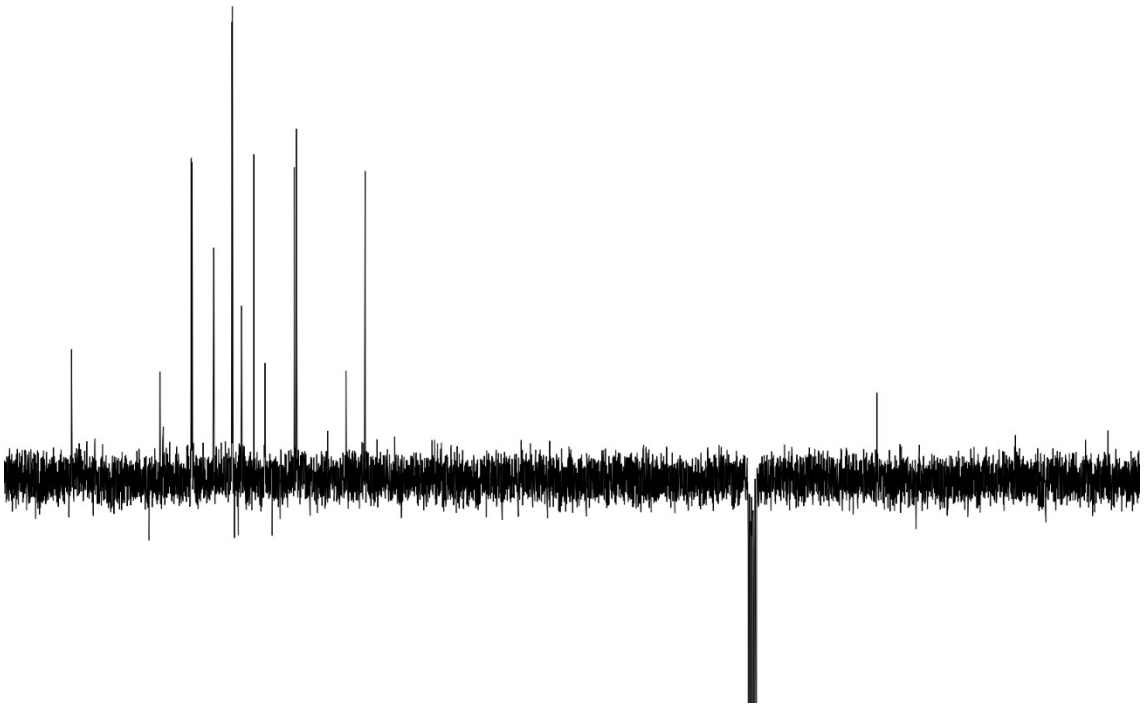
Figure S4: NMR spectrum of **4** in CD_2Cl_2. (a) ^{1}H, (b) $^{31}P\{1H\}$


10
9
8
7
6
5
4
3
2
1
0

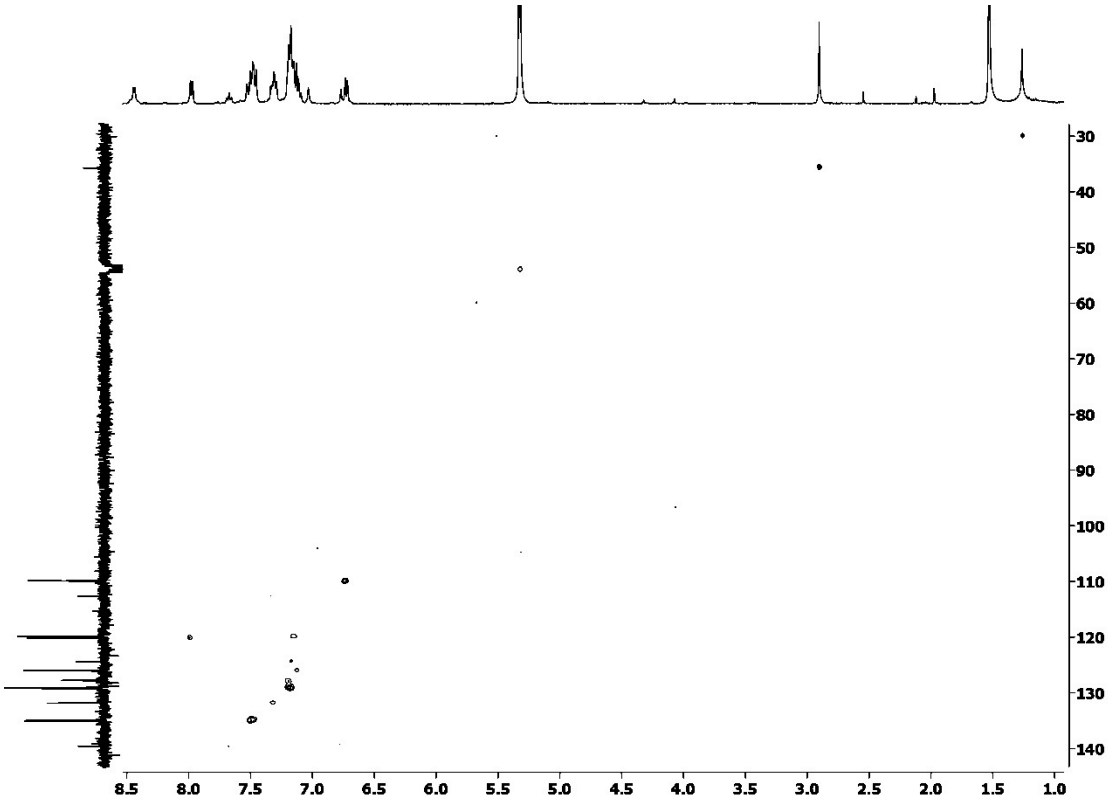
(a)


1
2
3
4
5
6
7
8
9
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

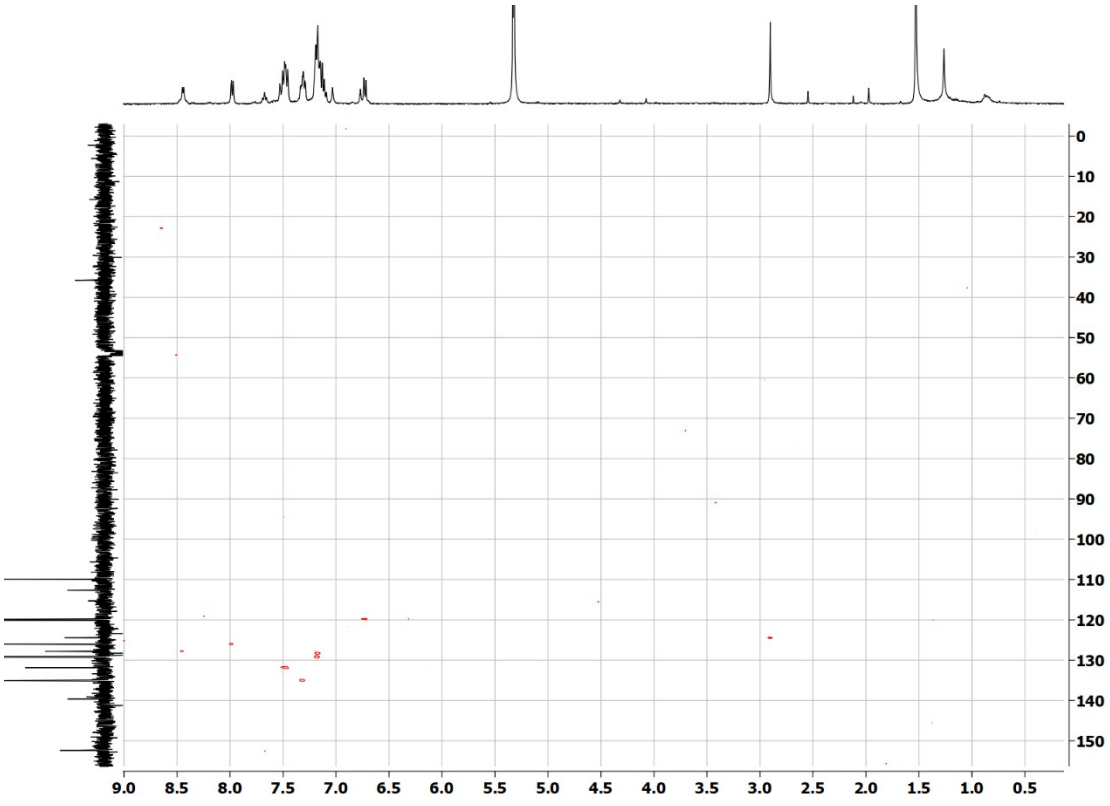
(b)



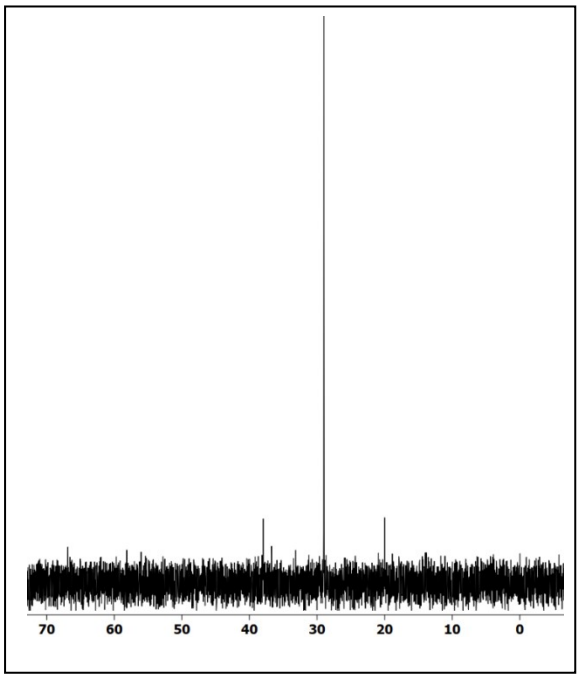
(c)

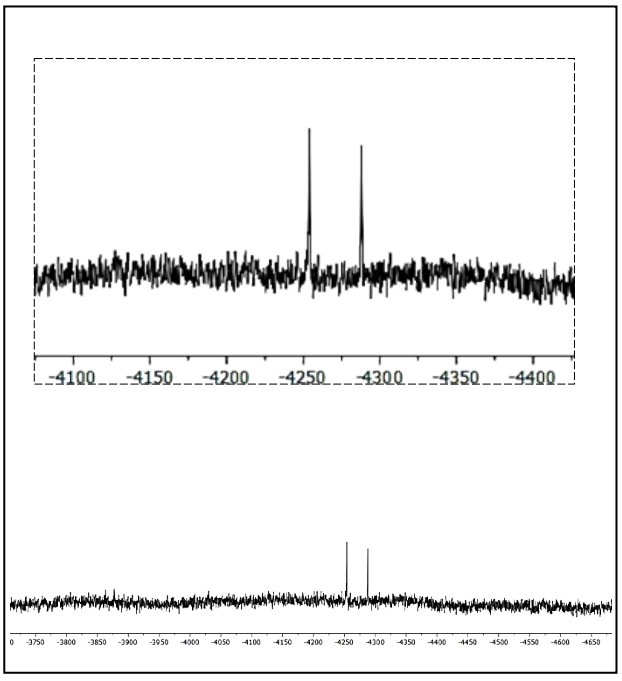

30
40
50
60
70
80
90
100
110
120
130
140
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

(d)



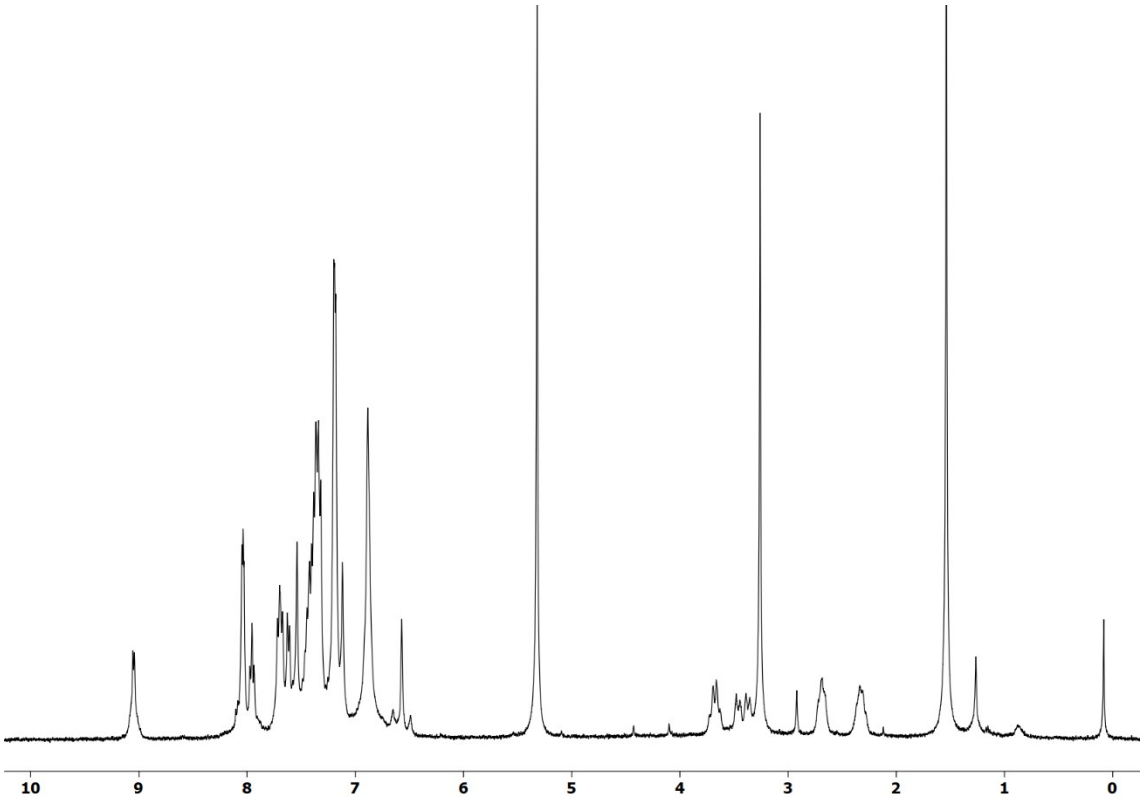
(e)



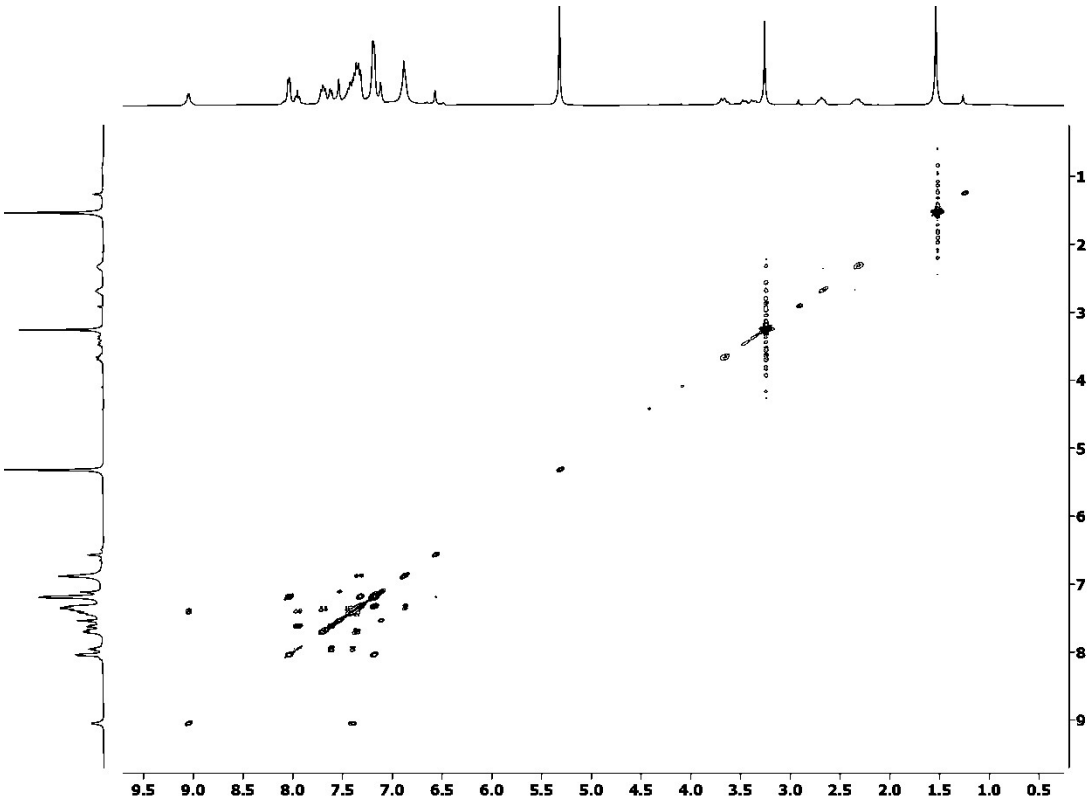


(f) (g)

Figure S5: NMR spectrum of **5** in CD_2Cl_2. (a) ^{1}H, (b) ^{1}H -^{1}H COSY, (c) ^{13}C {^{1}H} APT, (d) ^{1}H-^{13}C HSQC, (e) ^{1}H-^{13}C HMBC, (f) ^{31}P{^{1}H}, (g) ^{195}Pt{^{1}H}.


10
9
8
7
6
5
4
3
2
1
0

(a)


1
2
3
4
5
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7
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8.5
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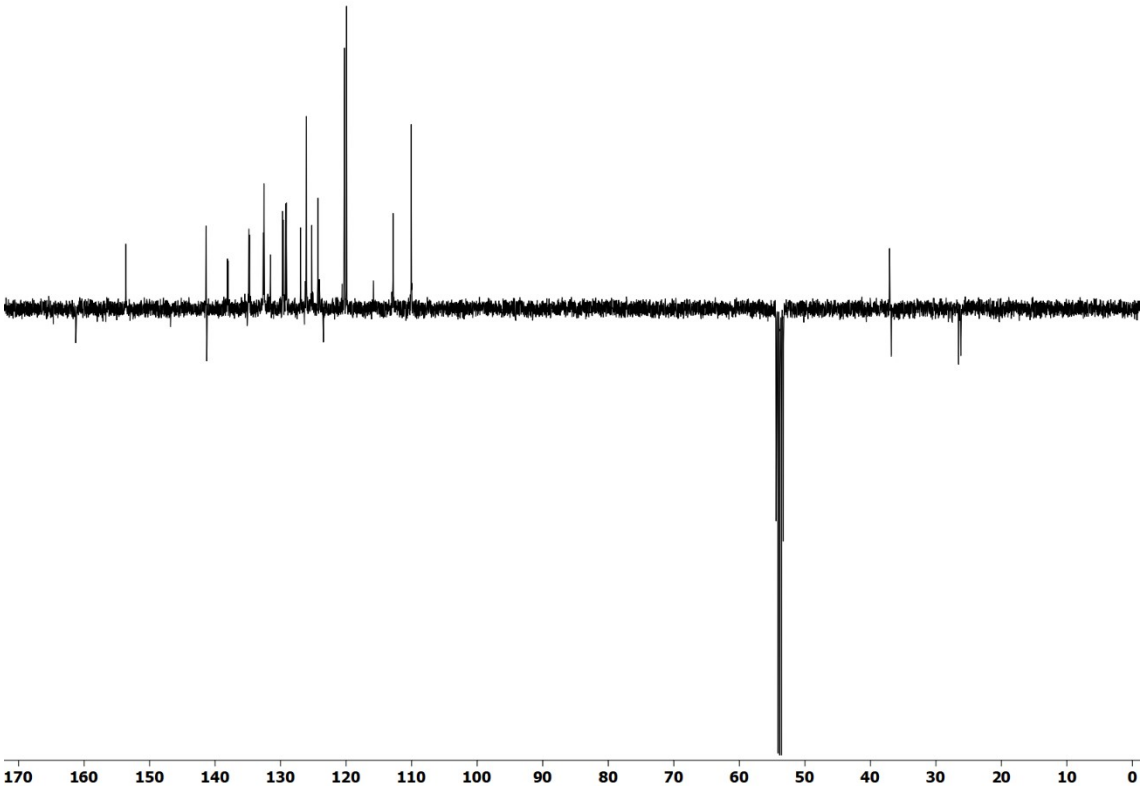
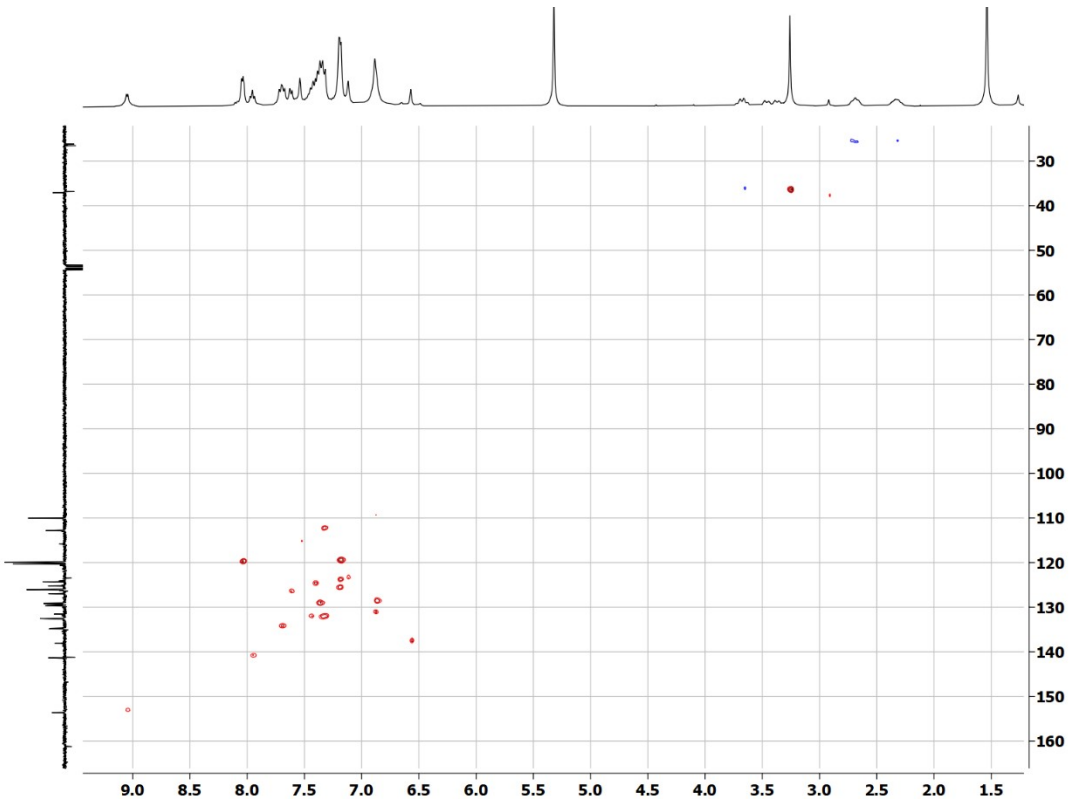
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

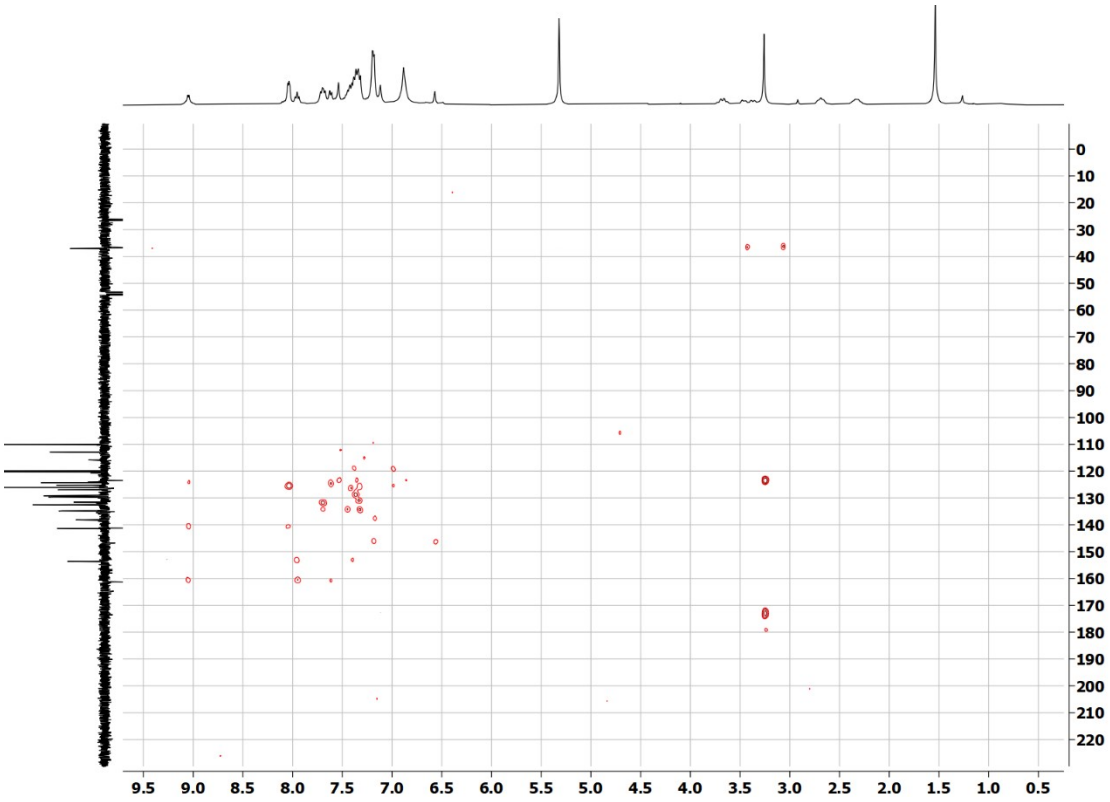
(b)


170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

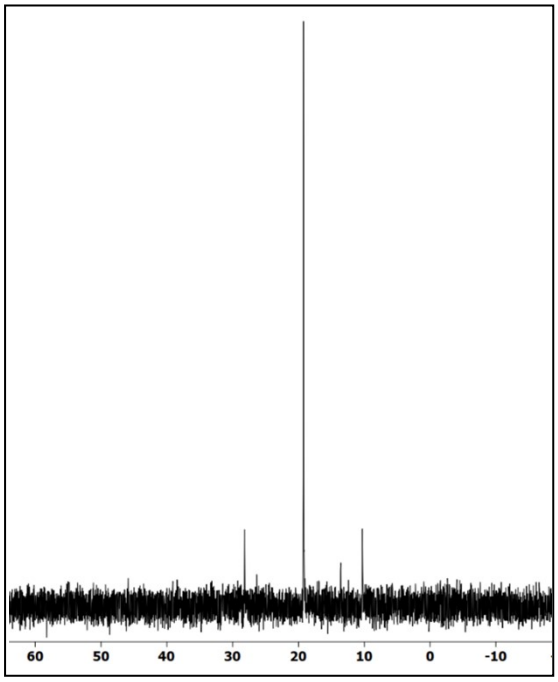
(c)


30 40 50 60 70 80 90 100 110 120 130 140 150 160
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5

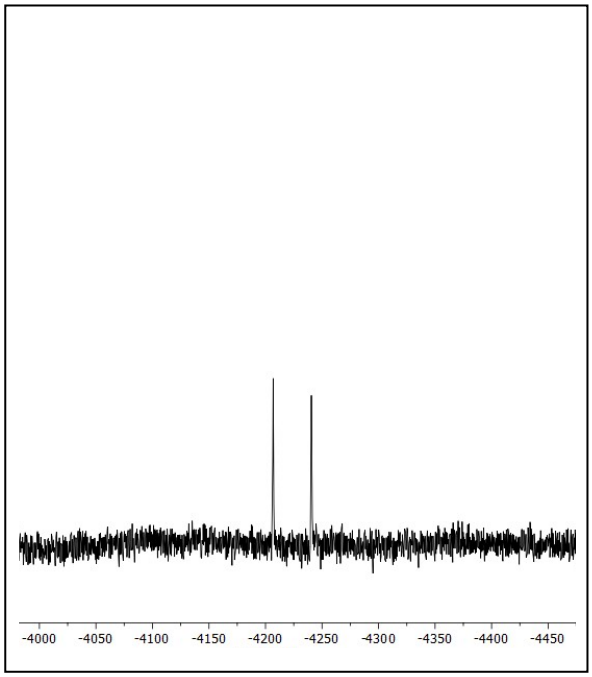
(d)



(e)

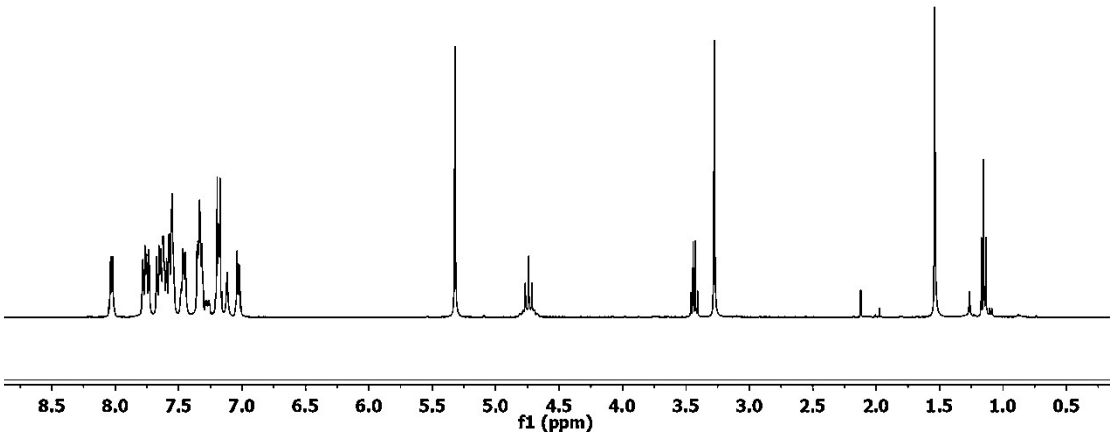


(f)

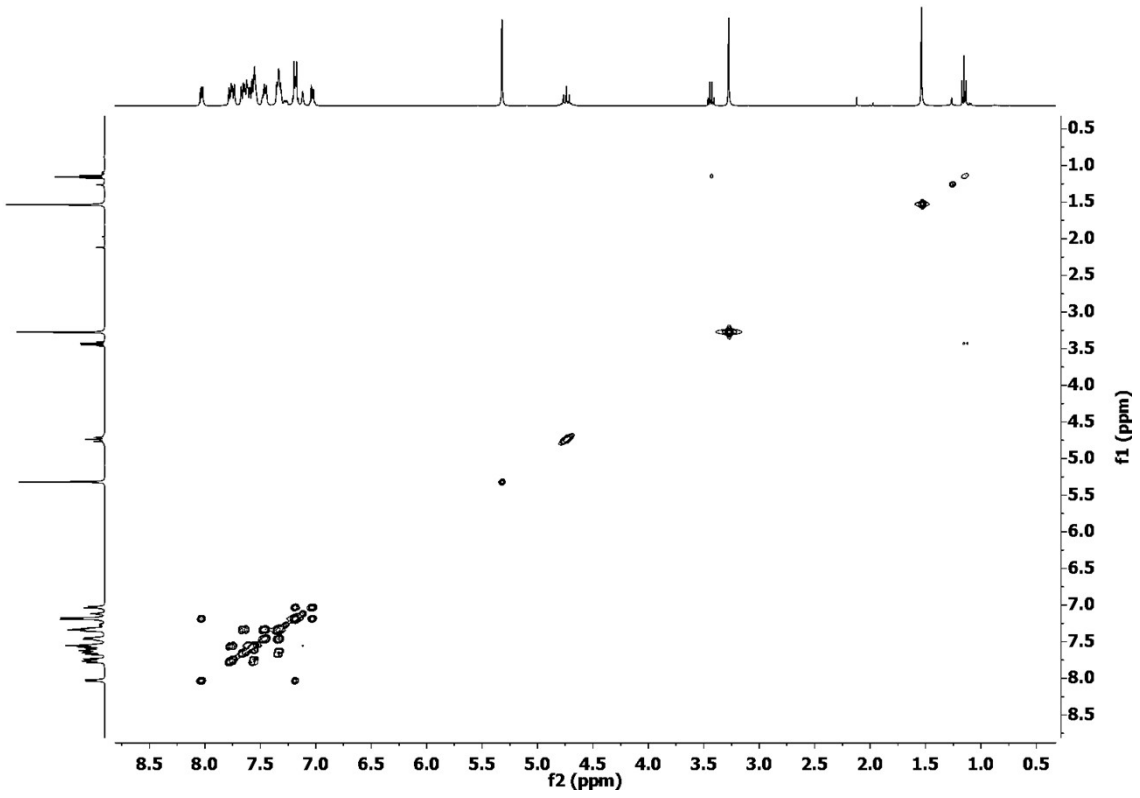


(g)

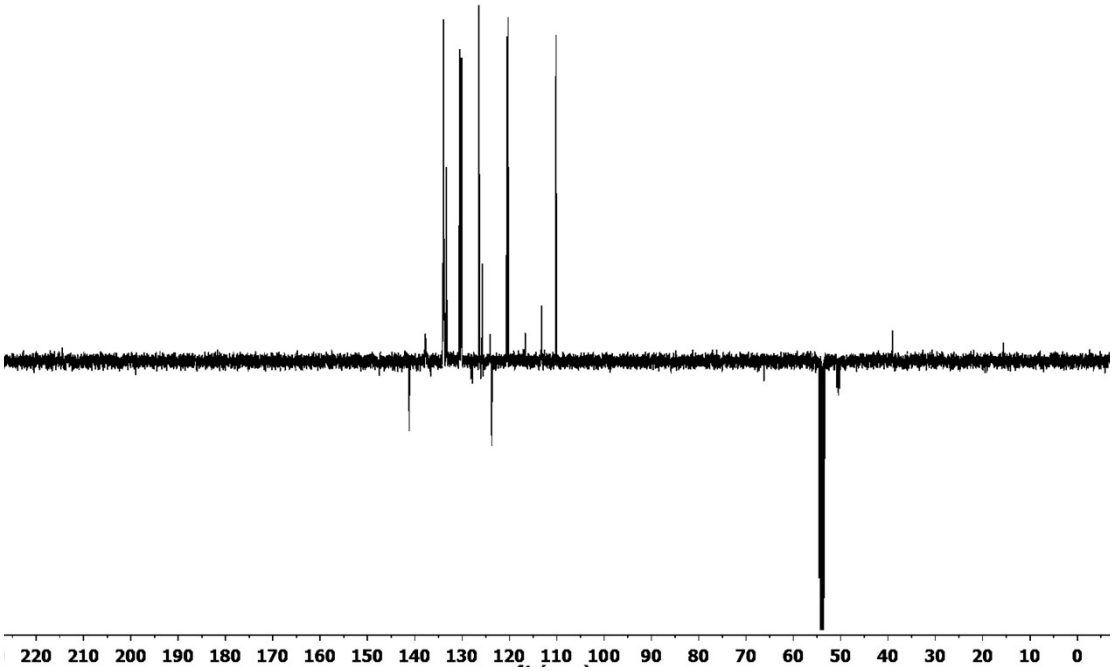
Figure S6: NMR spectrum of **6** in CD_2Cl_2. (a) ^{1}H, (b) ^{1}H -^{1}H COSY, (c) ^{13}C $\{^{1}H\}$ APT, (d) ^{1}H-^{13}C HSQC, (e) ^{1}H-^{13}C HMBC, (f) $^{31}P\{^{1}H\}$, (g) $^{195}Pt\{^{1}H\}$.


8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

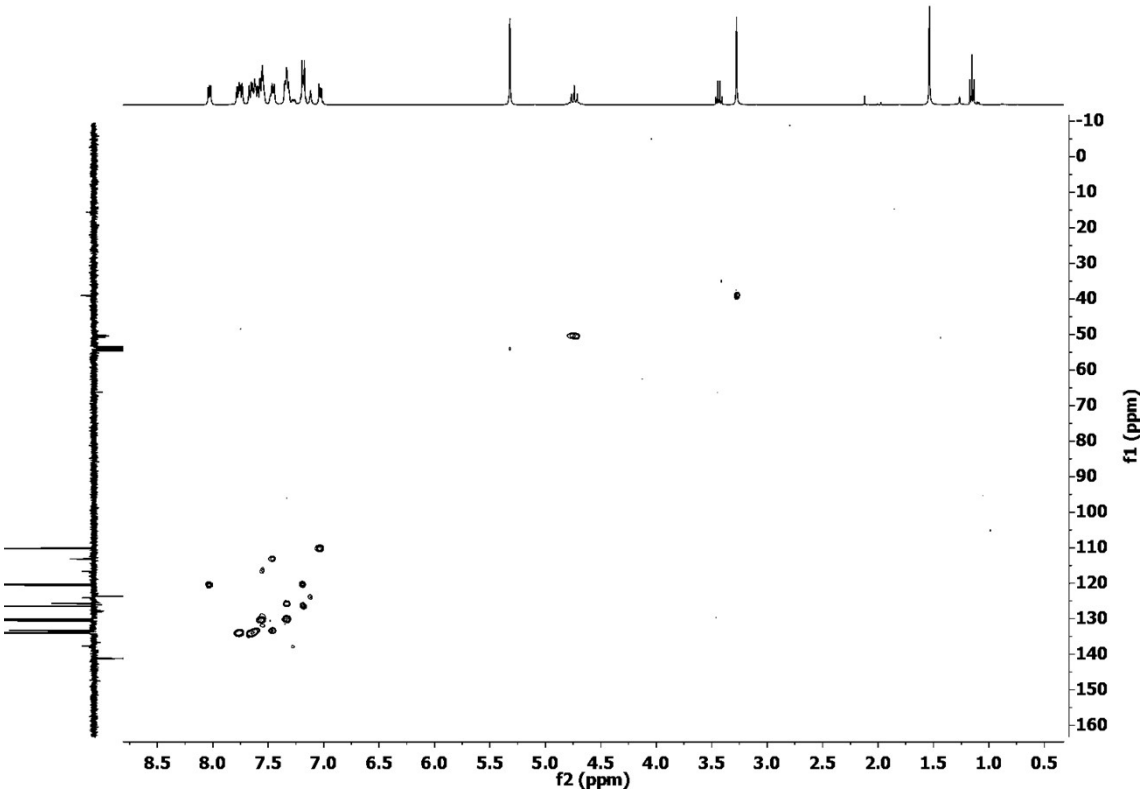
(a)


0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)

(b)


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

(c)


8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)
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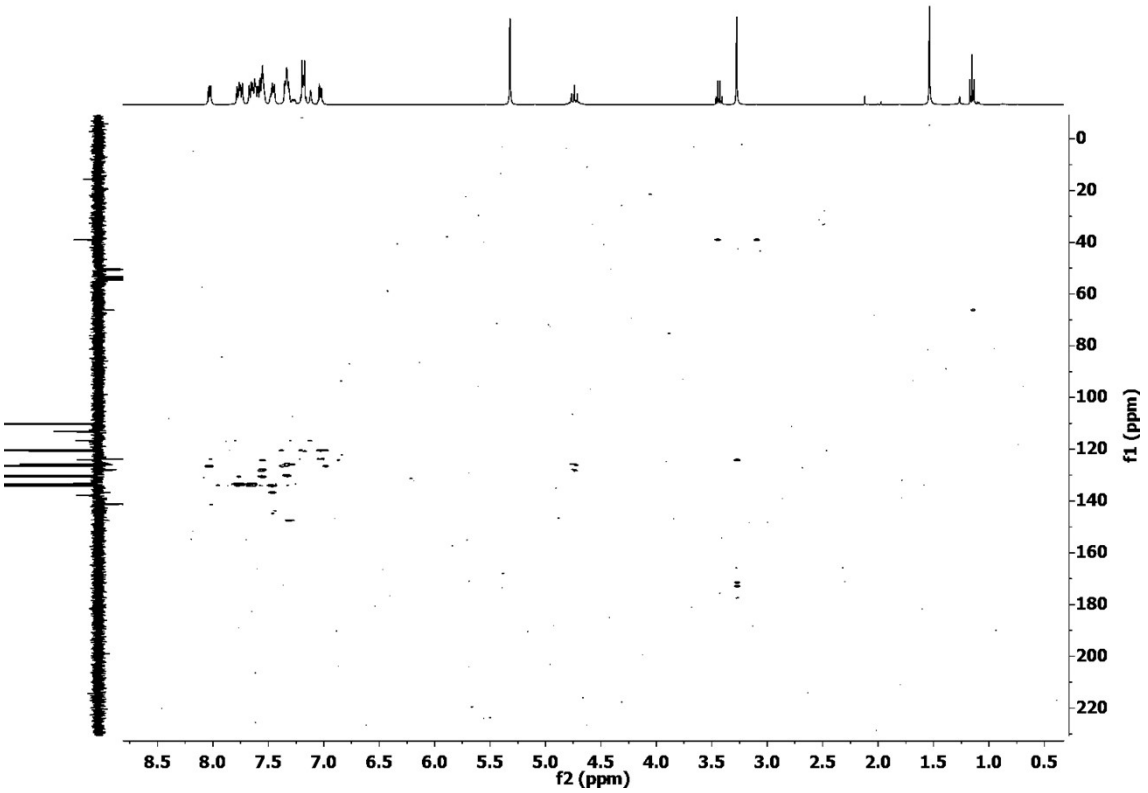
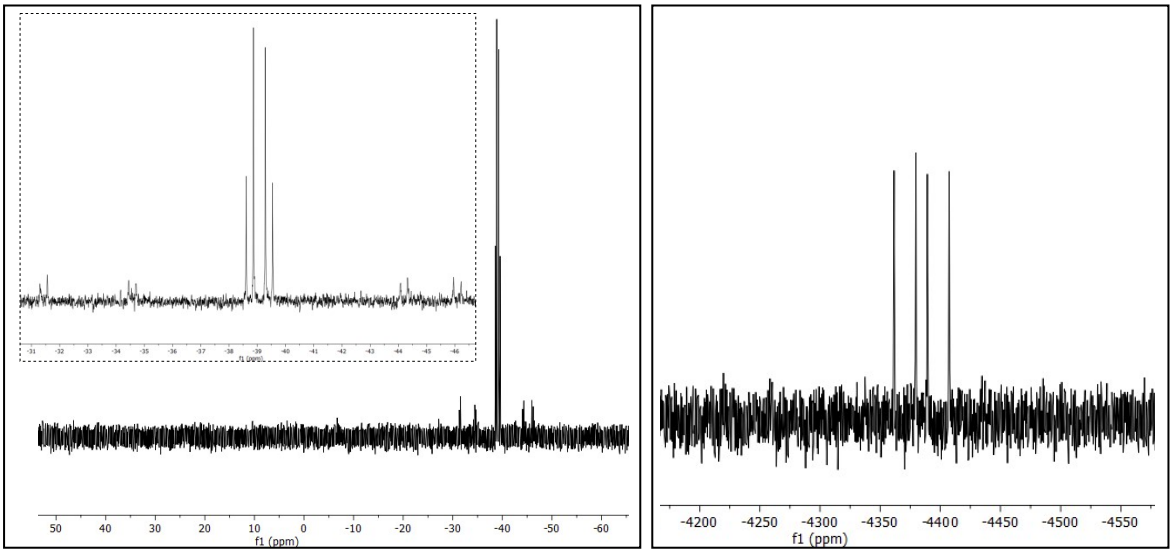
f1 (ppm)

(d)

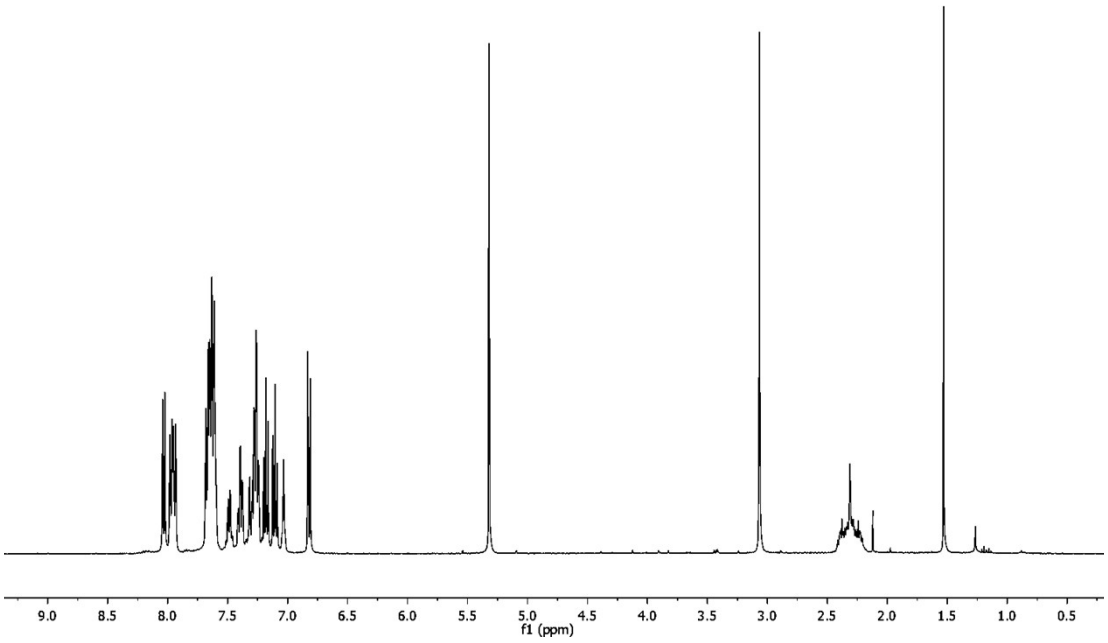


(e)

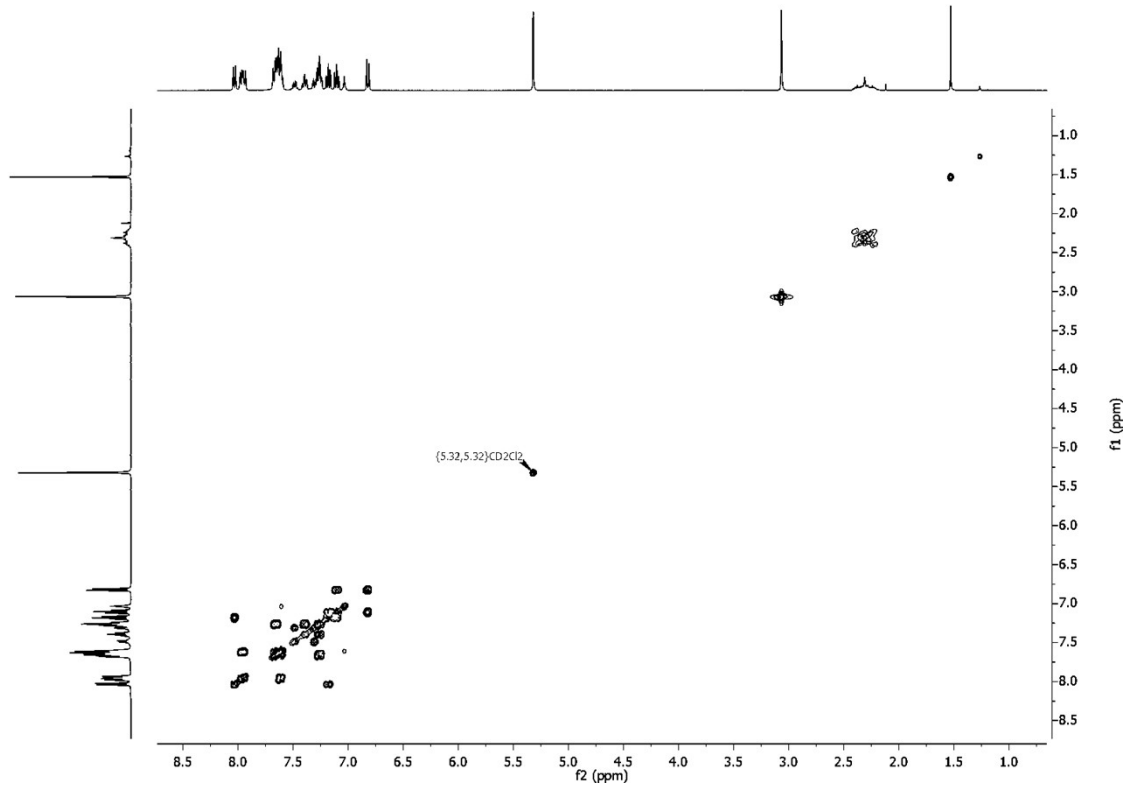


(f) (g)

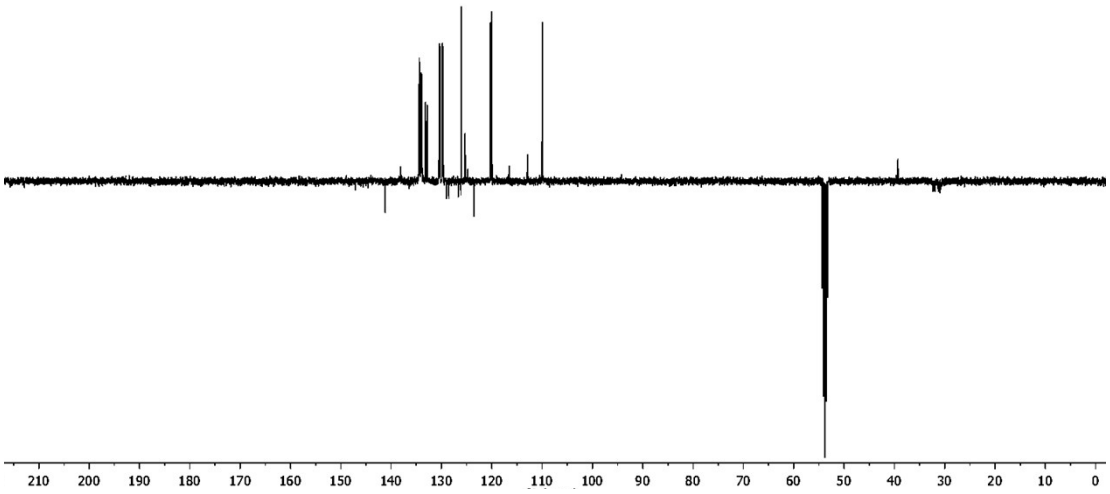
Figure S7: NMR spectrum of **7** in CD_2Cl_2. (a) ^{1}H, (b) ^{1}H -^{1}H COSY, (c) ^{13}C {^{1}H} APT, (d) ^{1}H-^{13}C HSQC, (e) ^{1}H-^{13}C HMBC, (f) ^{31}P{^{1}H}, (g) ^{195}Pt{^{1}H}.


9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

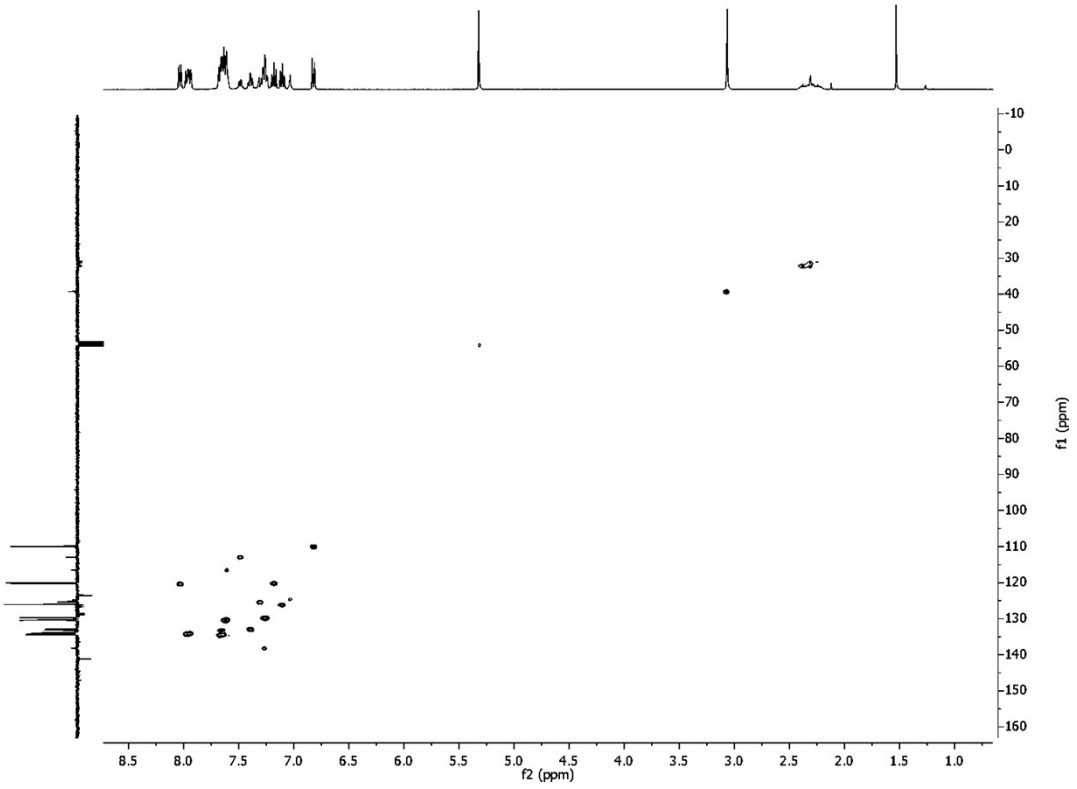
(a)


{5.32,5.32}CD2Cl2
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f2 (ppm)
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5
f1 (ppm)

(b)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

(c)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f2 (ppm)
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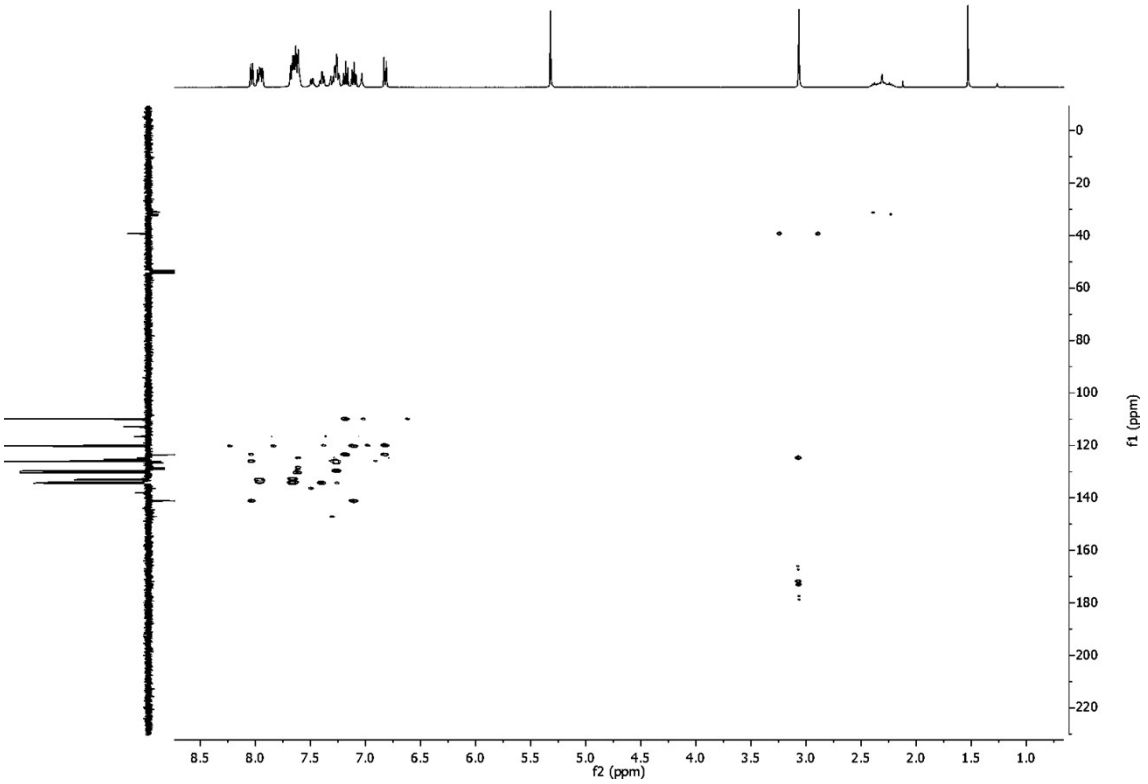
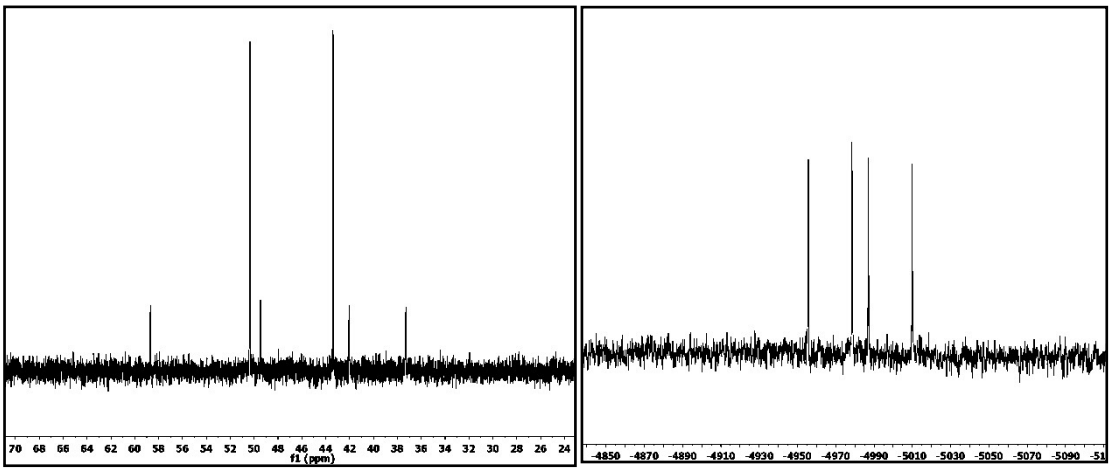
f1 (ppm)

(d)

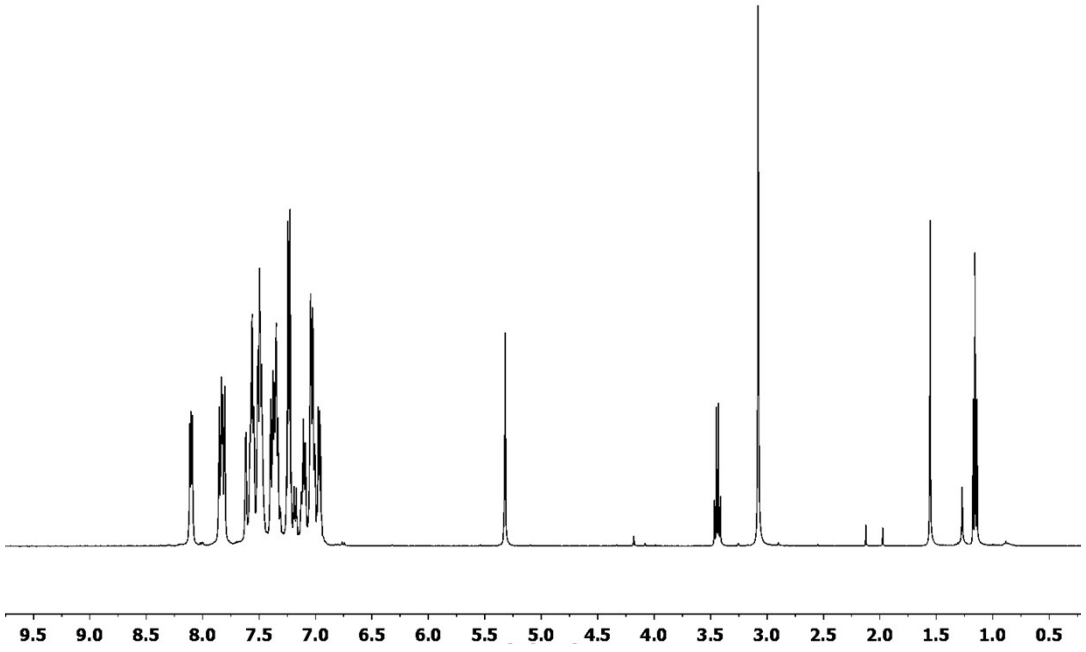


(e)

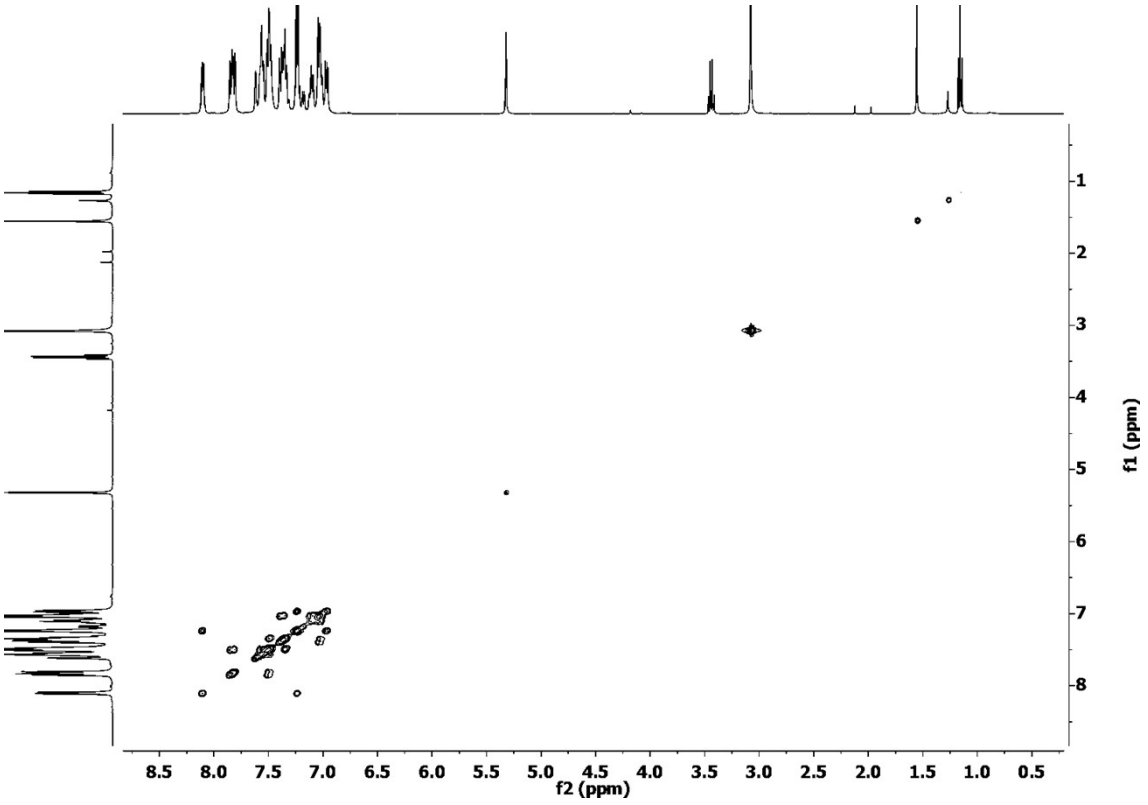


(f) (g)

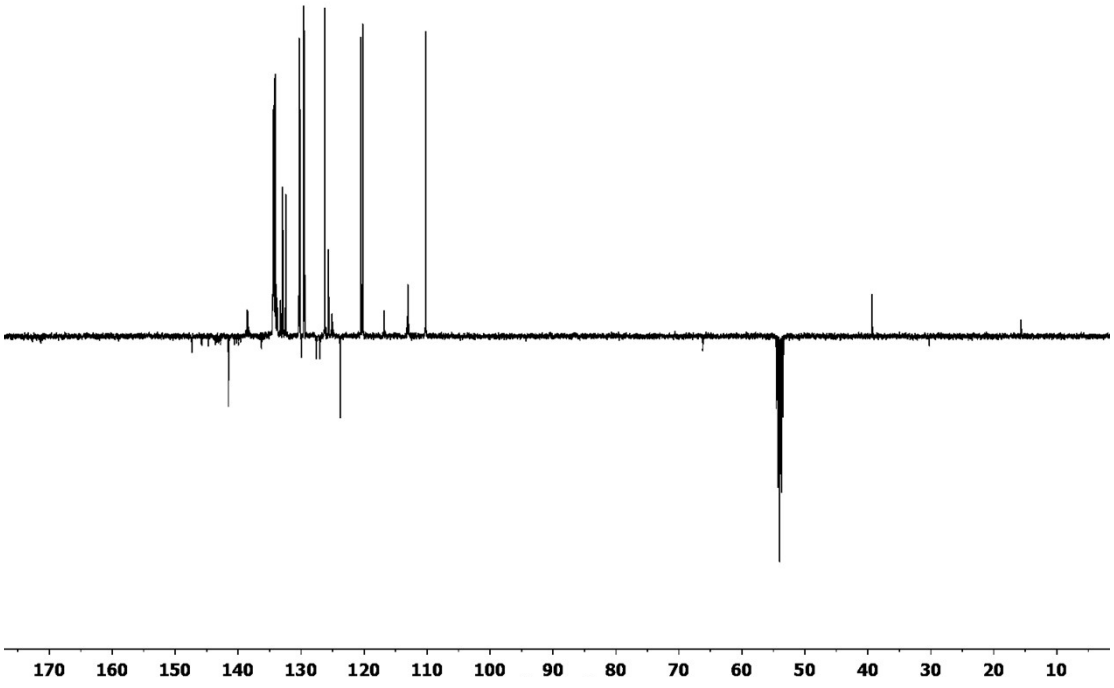
Figure S8: NMR spectrum of **8** in CD_2Cl_2. (a) ^{1}H, (b) ^{1}H -^{1}H COSY, (c) ^{13}C {^{1}H} APT, (d) ^{1}H-^{13}C HSQC, (e) ^{1}H-^{13}C HMBC, (f) ^{31}P{^{1}H}, (g) ^{195}Pt{^{1}H}.


9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

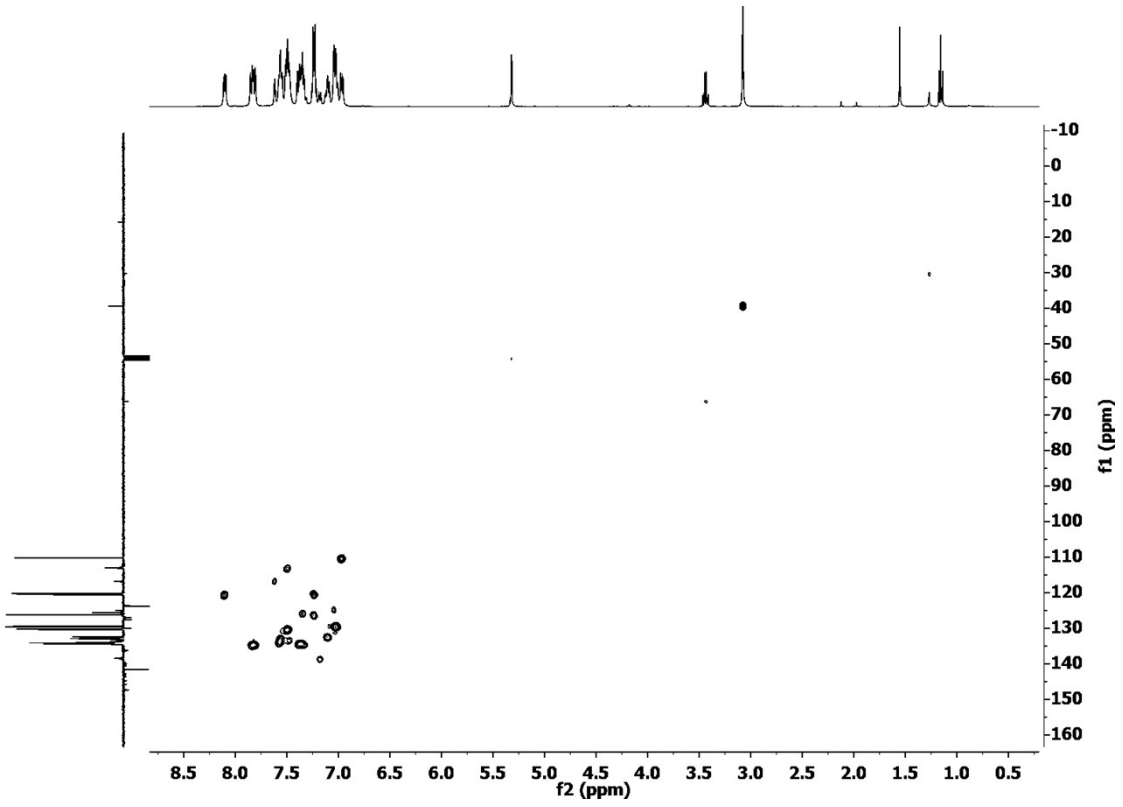
(a)


1
2
3
4
5
6
7
8
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)

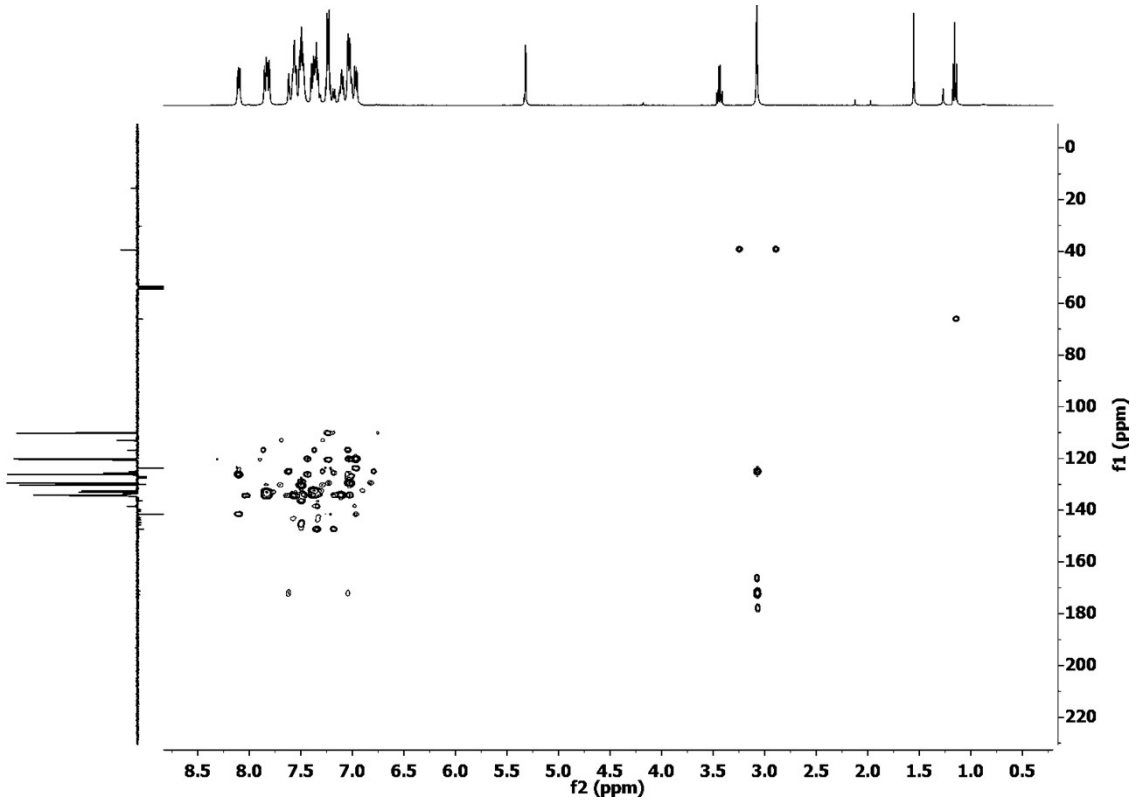
(b)


170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

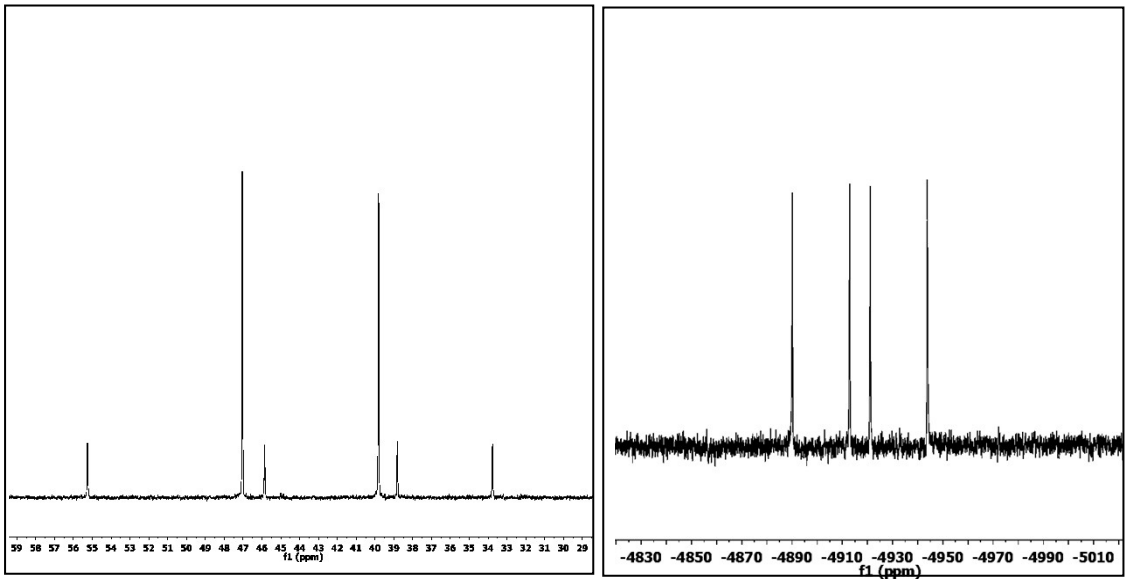
(c)


-10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)

(d)



(e)



(f) (g)

Figure S9: NMR spectrum of **9** in CD_2Cl_2. (a) ^{1}H, (b) ^{1}H -^{1}H COSY, (c) ^{13}C {^{1}H} APT, (d) ^{1}H-^{13}C HSQC, (e) ^{1}H-^{13}C HMBC, (f) ^{31}P{^{1}H}, (g) ^{195}Pt{^{1}H}.

3. X-RAY MOLECULAR STRUCTURES

Table S2: Selected bond parameters for 5-7 and 9.

Bond Lengths (Å)	**5 (X= N4)**	**6 (X= N4)**	**7 (X=P2)**	**9 (X= P2)**
Pt-C(1)	2.033(9)	2.029(5)	2.029(12)	2.054(4)
Pt-C(8)	2.045(9)	2.023(4)	2.048(16)	2.073(4)
Pt-P(1)	2.307(2)	2.283(1)	2.279(3)	2.2819(9)
Pt-X	2.109(7)	2.114(4)	2.324(3)	2.3110(4)
Angles (º)				
C(1)-Pt-C(8)	79.9(4)	79.8(2)	78.6(5)	79.56(15)
C(8)-Pt-P(1)	95.9(3)	97.8(1)	100.9(4)	96.06(11)
P(1)-Pt-X	89.6(2)	88.7(1)	71.37(10)	82.51(3)
X-Pt-C(1)	94.6(3)	95.3(2)	109.2(3)	102.91(11)

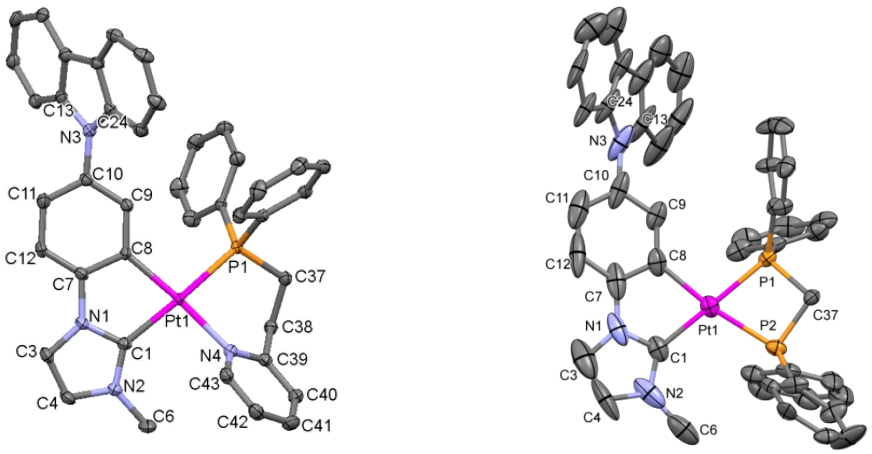


Figure S10. Molecular structures of the cationic complexes **6** (left) and **7** (right). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, solvent molecules and PF_6^- have been omitted for clarity.

4. PHOTOPHYSICAL PROPERTIES AND THEORETICAL CALCULATIONS

Table S3: Absorption Data for compounds **5-9** (solutions 5 x 10^{-5}M).

Comp	λ abs / nm (10^3 ε M^{-1} cm^{-1})
5	237 (62.3), 262 (33.1), 283 (23.2), 294 (22.8), 309 (12.3), 326 (7.1), 342 (5.3), 367 (0.8) **CH_2Cl_2**
6	237 (70.0), 261 (33.8), 285 (20.6), 295 (21.6), 315 (13.3), 330 (9.7), 341 (7.8), 370 (1.1) **CH_2Cl_2**
7	239 (87.8), 261 (43.1), 286 (30.7), 293 (31.0), 313 (14.1), 328 (11.3), 342 (9.5), 380 (1.2) **CH_2Cl_2**
8	237 (73.1), 285 (26.4), 293 (25.9), 313 (12.8), 329 (9.7), 341 (7.9), 374 (1.3) **CH_2Cl_2**
9	235 (61.0), 258 (34.8), 283 (20.3), 293 (18.6), 314 (9.7), 343 (5.3), 375 (1.1) **CH_2Cl_2**
	233 (78.6), 257 (41.0), 284 (26.8), 292 (26.0), 315 (11.0), 340 (6.5) 370 (0.9) **MeCN**
	257 (40.2), 284 (26.4), 292 (25.8), 316 (10.3), 340 (6.4), 370 (0.9) **MeOH**
	248 (48.8), 259 (41.6), 284 (27.1), 293 (26.5), 317 (10.6), 340 (6.8), 375 (0.8) **THF**

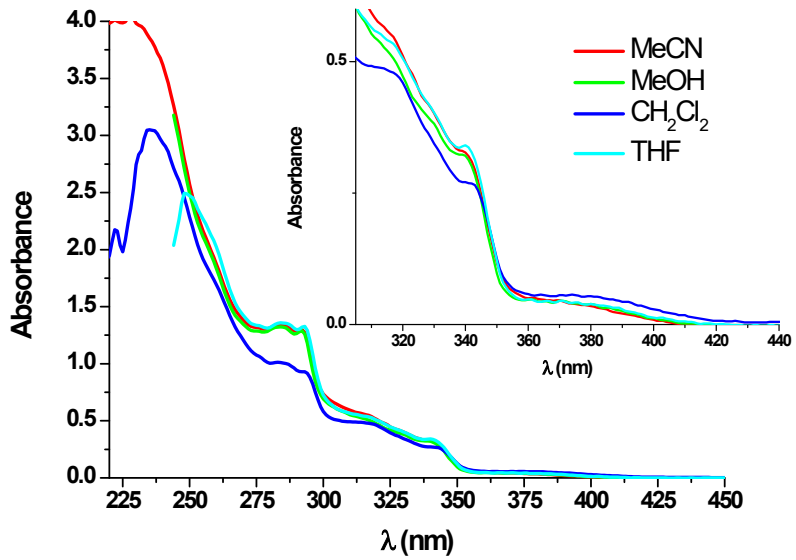


Figure S11: UV-Vis spectra of **9** in different solvents at 5x10^{-5}M.

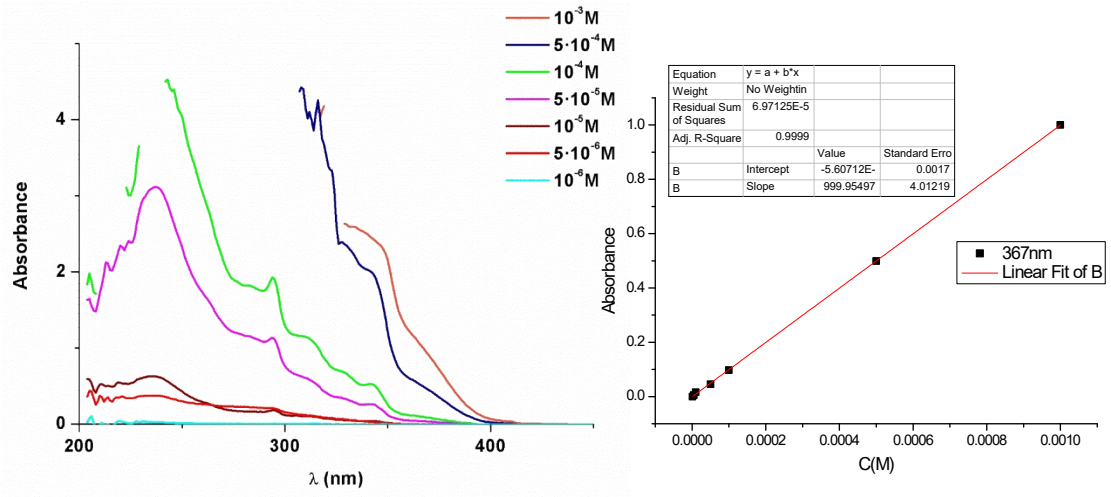


Figure S12. UV-Vis absorption spectra of **5** in CH_2Cl_2 at several concentrations at r.t (left). Linear fit representation of the absorbance at 367 nm vs concentration (right).

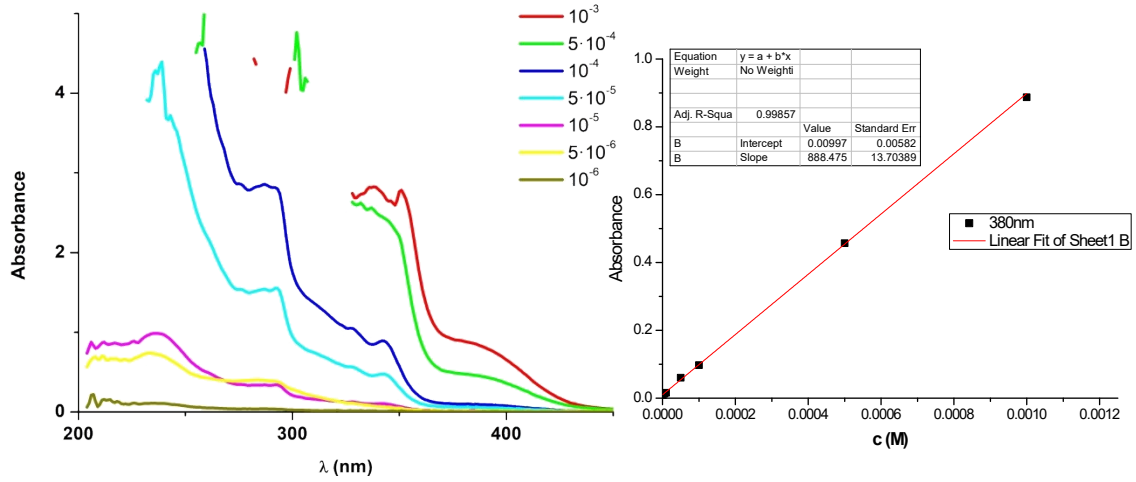


Figure S13. UV-Vis absorption spectra of **7** in CH_2Cl_2 at several concentrations at r.t (left). Linear fit representation of the absorbance at 380 nm vs concentration (right).

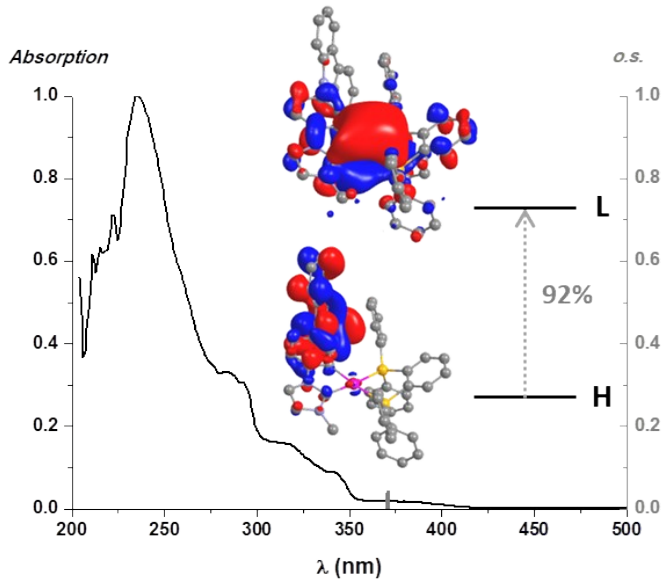


Figure S14: UV-vis absorption spectra, S_1 calculated transitions in CH_2Cl_2 (bars) and molecular orbital plots (isovalue 0.003) for **9**.

Table S4: Selection of the lowest-energy vertical singlet and triplet excitations calculated by TD-DFT for **5**, **7** and **9** at the Ground State in solution of CH_2Cl_2

Comp	State	λ_{exc} (nm)	o.s.	Transition (% contrib.)*	Assignment
5	S1	361.95	0.049	H → L (69); H → L+1 (21)	LL'CT, IL, LMCT
	T1	429.25	0.0	H → L (24); H-2 → L (22) H → L+1 (13); H-2 → L+1 (13)	LL'CT, IL, LMCT
	T2	406.59	0.0	H-1 → L+7 (31); H-1 → L+6 (25) H → L+14 (14)	
	T3	368.72	0.0	H → L+7 (38); H → L+6 (26) H → L+8 (11)	
7	S1	386.52	0.046	H → L (92)	IL, LL'CT, LMCT
	T1	449.25	0.0	H → L (50); H-2→ L (26)	IL, LL'CT, LMCT
	T2	407.69	0.0	H-1→ L+6 (48); H → L+14 (13)	
	T3	369.37	0.0	H→ L+6 (58); H→ L+5 (11)	
9	S1	371.30	0.041	H → L (92)	LL'CT, IL, LMCT
	T1	431.40	0.0	H → L (39); H-2→ L (28)	IL, LL'CT, LMCT
	T2	408.00	0.0	H-1 → L+6 (22); H-1→ L+5 (19) H → L+14 (13); H-1→ L+8 (11)	
	T3	371.77	0.0	(11 transitions below 10%)	

* transitions with contributions ≤ 10% were not included

Table S5: Population Analysis (%) of MOs in the Ground State in solution of CH_2Cl_2

MO	eV			Pt			NHC [Cbz]			PPh_3/py (5); P^P (7, 9)		
	5	**7**	**9**	**5**	**7**	**9**	**5**	**7**	**9**	**5**	**7**	**9**
L+14	0.10	0.04	0.05	0	0	0	[99]	97[96]	98[96]	1/0	3	2
L+8	-0.79		-0.74	7		6	45[13]		62[19]	47/1		32
L+7	-0.81			1			50[48]			47/2		
L+6	-0.87	-0.91	-0.95	16	19	25	41[33]	71[70]	40[33]	36/7	10	35
L+5		-0.92	-0.98		5	3		30[28]	27[25]		65	70
L+1	-1.65			18			23[1]			7 / 52		
L	**-1.78**	**-1.98**	**-1.90**	**18**	**29**	**26**	**32[1]**	**43[1]**	**39[1]**	**8 / 42**	**28**	**35**
H	**-5.91**	**-5.93**	**-5.95**	**1**	**1**	**1**	**99[83]**	**99[77]**	**99[82]**	**0/0**	**0**	**0**
H-1	-6.29	-6.37	-6.34	0	0	0	[99]	[100]	[99]	1/0	0	1
H-2	-6.78	-6.82	-6.84	24	21	19	75[10]	78[12]	80[11]	1/0	1	1

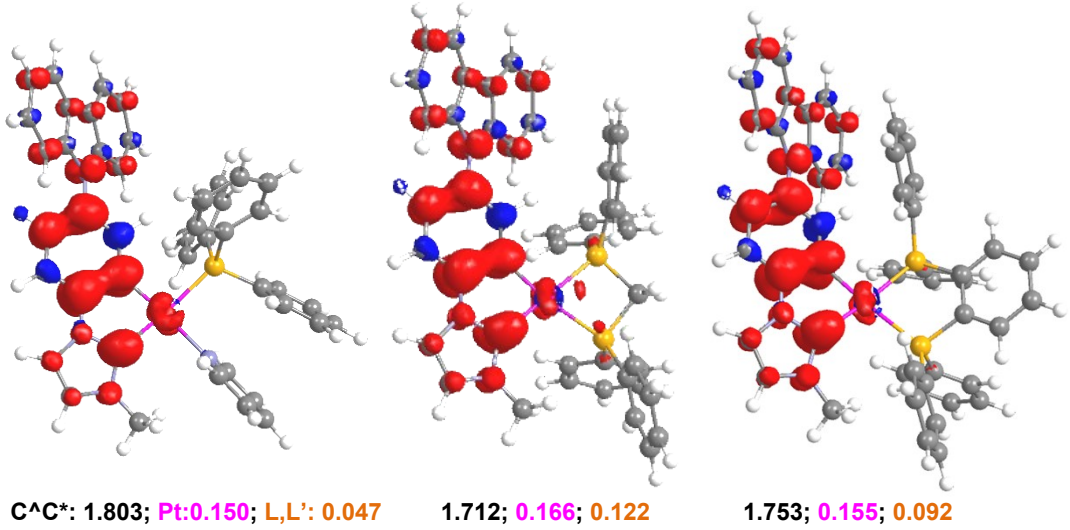


Figure S15. Spin-density distribution plots (isovalue 0.002) calculated in solution of CH_2Cl_2 for the T_1 states of **5** (left), **7** (center) and **9** (right).

Table S6: Photophysical data for **5-9** in solid state with λ_{exc} = 340 nm at 298 K

Comp.	λ_{em}(nm)	τ(μs)	Φ	k_r	k_{nr}
5	452, 476_{max}	2.5	0.07	2.8×10^4	3.7×10^5
6	470, 490_{max}	1.7	0.02	1.2×10^4	5.7×10^5
7	494_{sh}, 522_{max}	25.5	0.43	1.7×10^4	2.2×10^4
8^S	464_{sh}, 490_{max}	13.0	0.04	3.1×10^3	7.4×10^4
9^S	488_{sh}, 508_{max}	19.6	0.27	1.4×10^4	3.7×10^4

$k_r = \Phi/\tau_{exp}$ and $k_{nr} = (1 - \Phi)/\tau_{exp}$

5. LIGHT-EMITTING ELECTROCHEMICAL CELLS

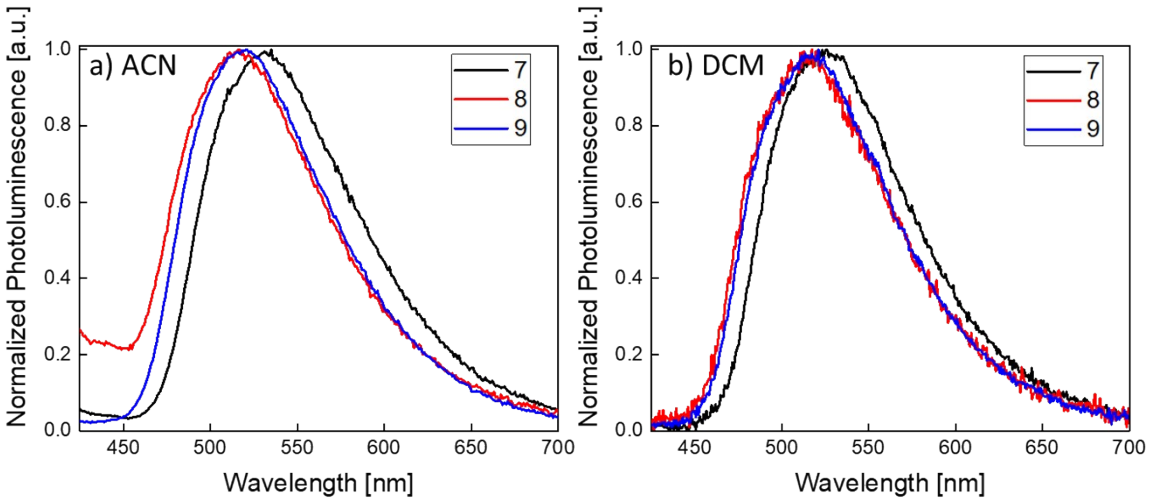


Figure S16. Photoluminescence spectra of the active layers (iTMC:IL), where iTMC are emitters **7** (black curve), **8** (red curve) and **9** (blue curve) in (a) ACN and (b) DCM.

Table S7. Maximum theoretical EQE calculated from the PLQY using Eq. S1 for emitters **7-9** in ACN and DCM.

Emitter in ACN	**EQE [%]**
7	2.44
8	1.77
9	3.11
Emitter in DCM	**EQE [%]**
7	2.66
8	1.33
9	2.44

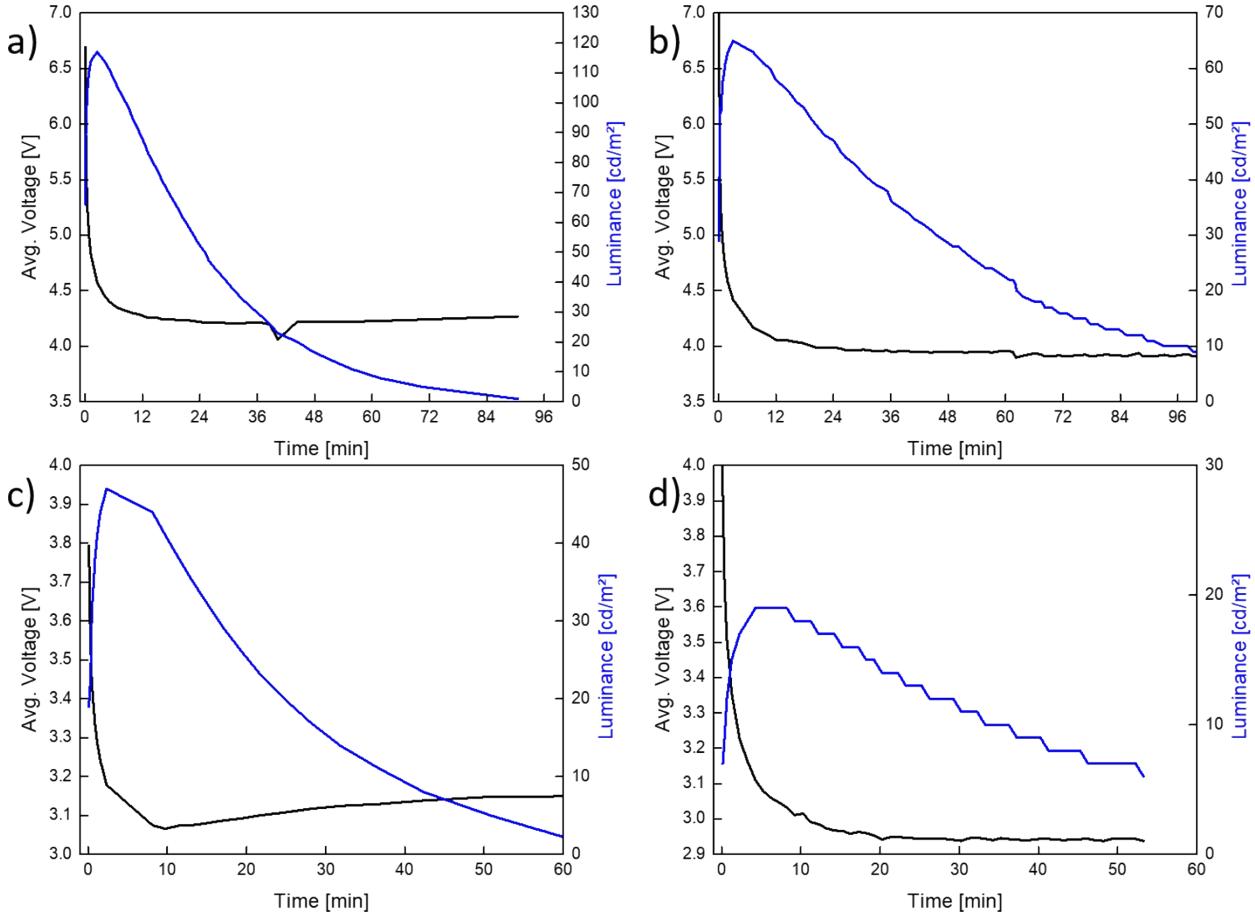


Figure S17. Time-dependence of the voltage (black curve) and luminance (blue curve) of LEC devices ITO/PEDOT:PSS/**7**:IL(4:1)/Al driven at a pulsed current with an average current density of samples processed from DCM (a) at 25 A m^{-2} and (b) at 12.5 A m^{-2}, and samples processed from ACN at (c) at 25 A m^{-2} and (d) at 12.5 A m^{-2}

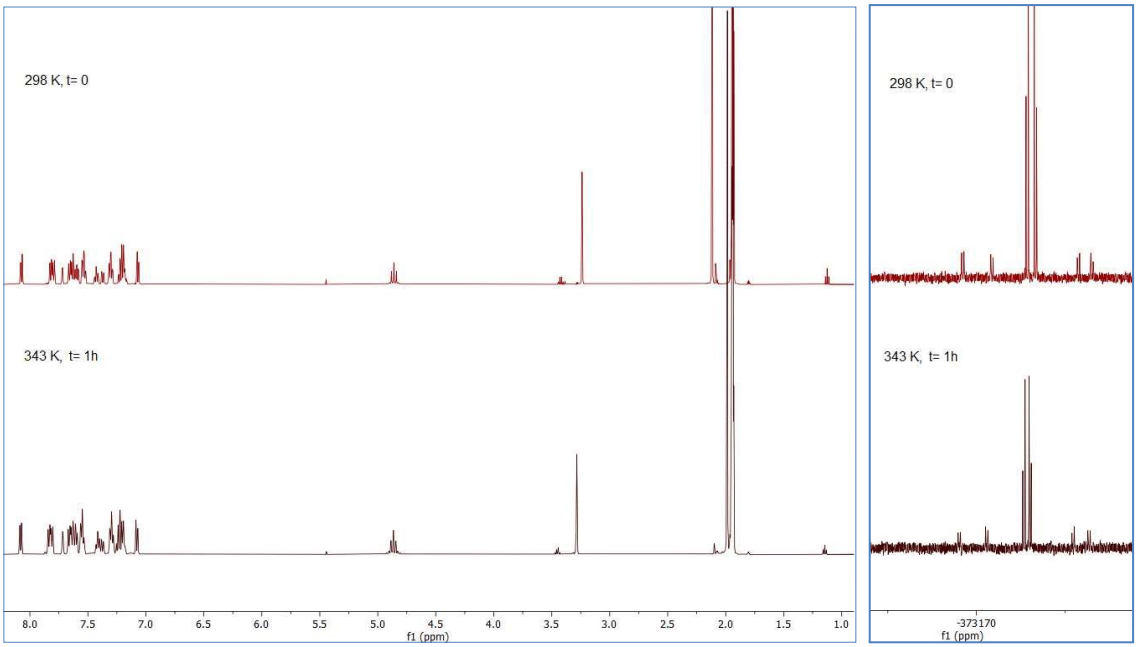


Figure S18. ^{1}H (left) and $^{31}P\{^{1}H\}$(right) NMR spectra of **7** in MeCN-d_3 (T= 25ºC and t = 0, top; T= 70ºC and t = 1 h, bottom)

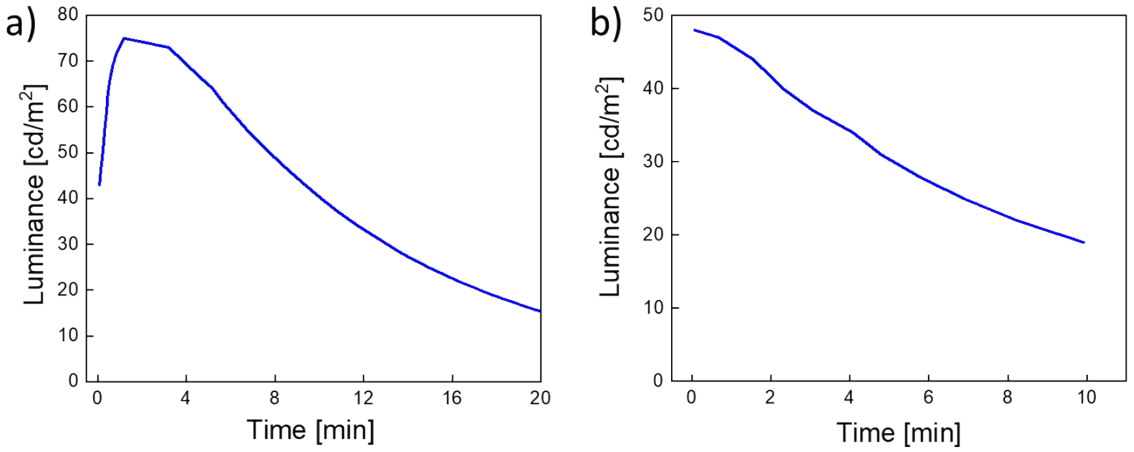


Figure S19. a) Time-dependence of the luminance of a LEC device ITO/PEDOT:PSS/**7**:IL(4:1)/Al in ACN with a longer annealing time (4 h) at the same temperature (70ºC). b) Time-dependence of the luminance of a LEC device ITO/PEDOT:PSS/**9**:IL(4:1)/Al in ACN with a higher temperature annealing process (90ºC) at a longer time (1 h).

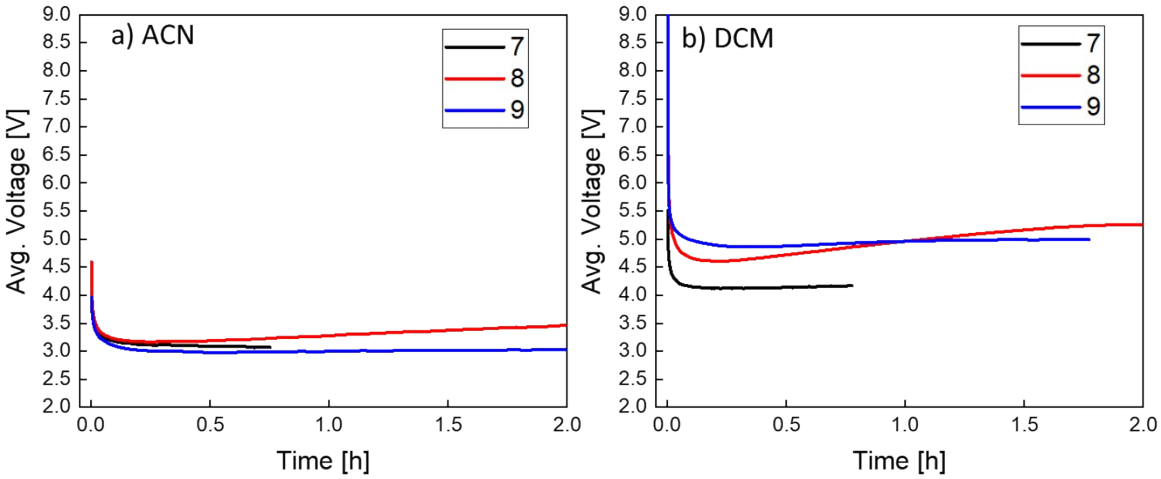


Figure S20. Time-dependence of the voltage of LEC devices ITO/PEDOT:PSS/iTMC:IL(4:1)/Al, where iTMC are emitters **7** (black curve), **8** (red curve) and **9** (blue curve) in (a) ACN and (b) DCM driven at a pulsed current with an average current density of 50 A m^{-2}.

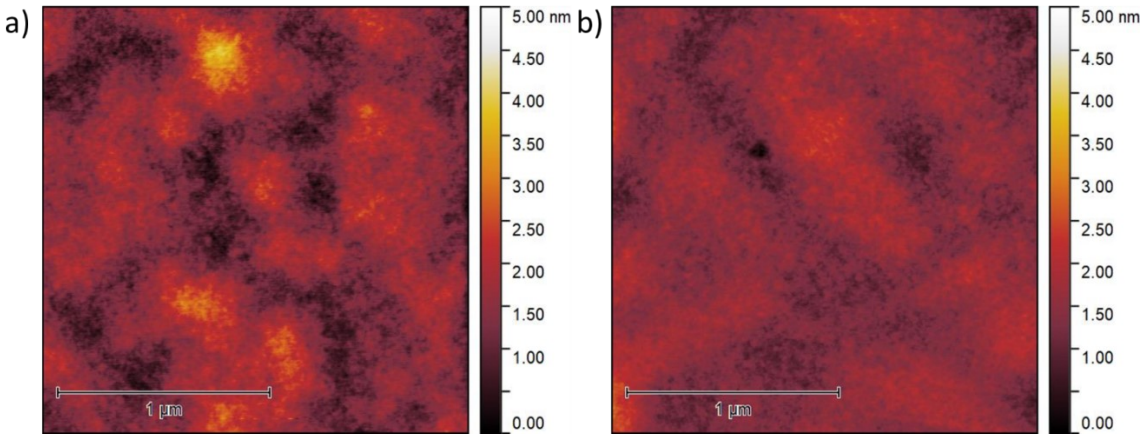


Figure S21. AFM images (2 µm x 2 µm) of the active film using emitter **7** processed from a) ACN and b) DCM.

Table S8. CIE coordinates of LEC devices ITO/PEDOT:PSS/iTMC:IL(4:1)/Al, where iTMC are emitters **7-9** in ACN and DCM.

ACN	**7**	**8**	**9**	**DCM**	**7**	**8**	**9**
X	0.3164	0.2991	0.2765	**X**	0.3129	0.3129	0.3075
Y	0.5866	0.5943	0.5754	**Y**	0.6081	0.6158	0.6054

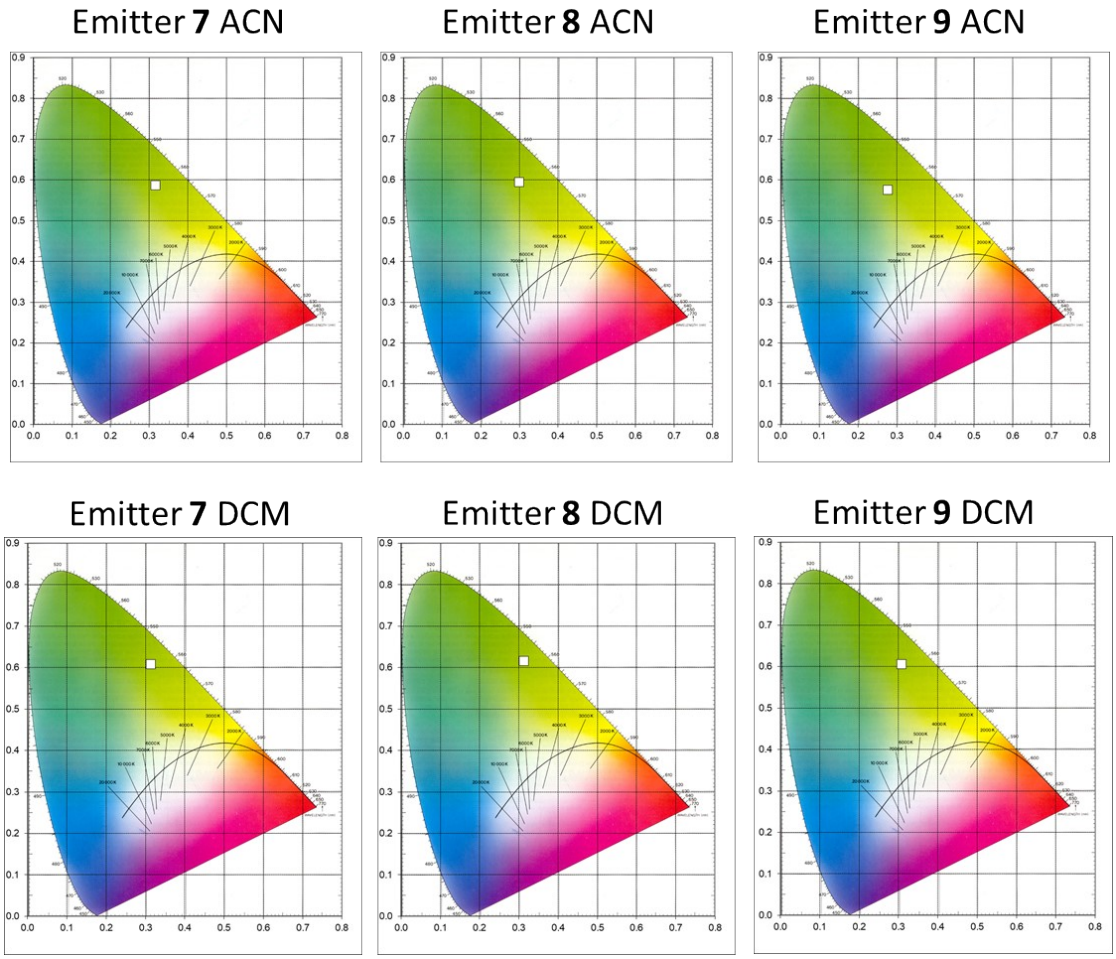


Figure S22. CIE coordinate plots of LEC devices ITO/PEDOT:PSS/iTMC:IL(4:1)/Al, where iTMC are emitters **7-9** in ACN and DCM. The white square indicates the emission coordinates.

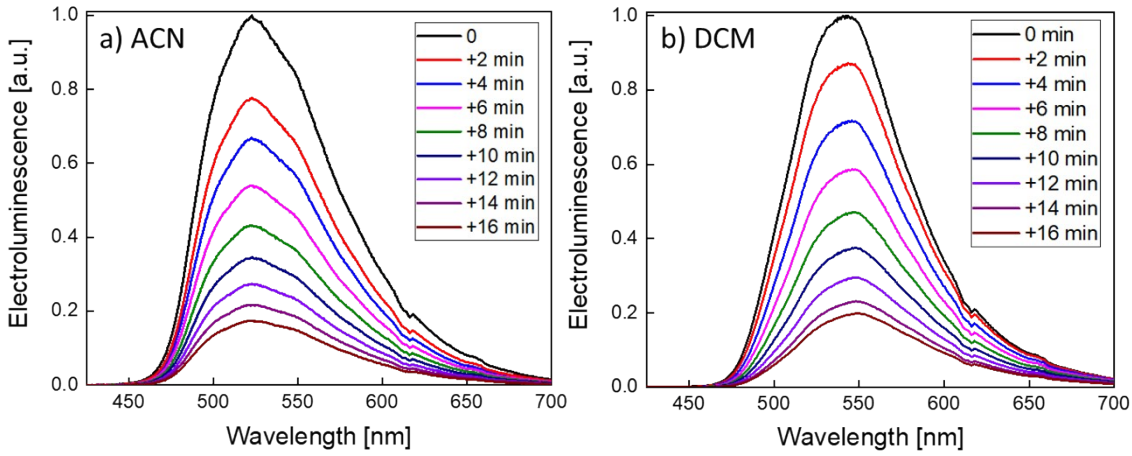


Figure S23. Electroluminescence spectra over time of LEC devices ITO/PEDOT:PSS/**7**:IL(4:1)/Al in a) ACN and b) DCM.

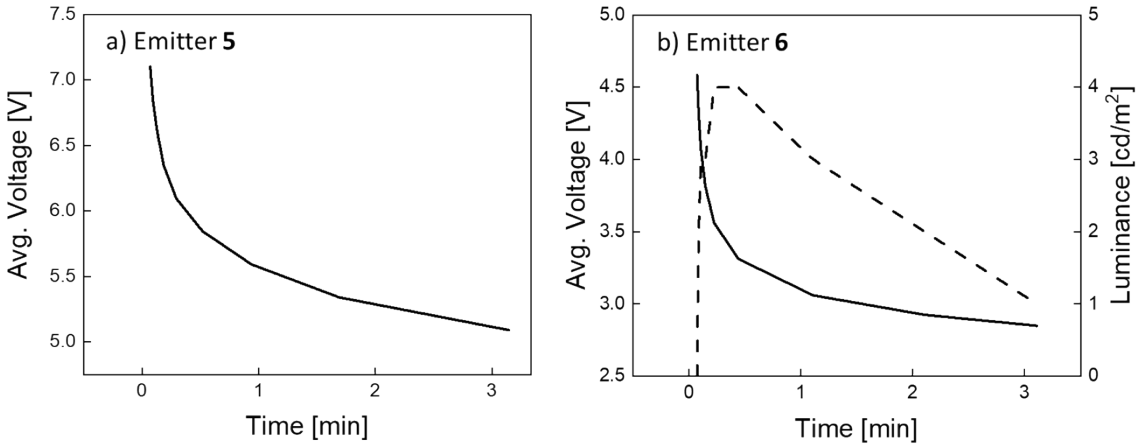


Figure S24. (a) Time-dependence of the voltage of a LEC device ITO/PEDOT:PSS/**5**:IL(4:1)/Al. (b) Time-dependence of the voltage (line) and luminance (dashed line) of a LEC device ITO/PEDOT:PSS/**6**:IL(4:1)/Al.

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