

ELECTRONIC SUPPLEMENTARY INFORMATION

Deprotonated diaminocarbene platinum complexes for thermoresponsive luminescent silicone materials: both catalysts and luminophores

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1. Experimental

1.1 Materials

Quinoline, isoquinoline, pyridine, and 4-picoline *N*-oxides, $K_2[PtCl_4]$, xylyl isocyanide, methanesulfonic acid, vinyl-terminated polymethylhydrosiloxane **PDMS-v** ($M_n = 28000$, vinyl group concentration $8.6 \cdot 10^{-5} \text{ mol} \cdot \text{g}^{-1}$) and polydimethylsiloxane-*co*-polymethylhydrosiloxane **PDMS-co-PMHS** (viscosity 25–35 cSt, hydride group concentration $3.5 \cdot 10^{-3} \text{ mol} \cdot \text{g}^{-1}$) were obtained from commercial sources. Ureas **1a**, **1b**¹ and complex **2** (*cis*-[PtCl₂(CNXyl)₂])² were prepared as previously reported. All solvents (CH₂Cl₂, CHCl₃, toluene, MeCN) were obtained from commercial sources and purified according to conventional methods prior to use.

1.2 Instrumentation and measurements

¹H, ¹³C, and ¹⁹⁵Pt NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer operating at room temperature (RT) at 400, 101, and 86 MHz for ¹H, ¹³C, and ¹⁹⁵Pt NMR spectra, respectively, using CDCl₃. The chemical shifts are given in δ -values [ppm]. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad; coupling constants, *J*, are reported in Hertz (Hz). Melting points were determined in open capillary tubes on Electrothermal IA 9300 series Digital Melting Point Apparatus. High-resolution mass-spectra (HR-MS) were measured on Bruker Maxis HR-MS-ESI-qTOF using ESI. The most intense peak in the isotopic pattern is reported. Infrared spectra ($4000\text{--}400 \text{ cm}^{-1}$) were recorded on a Shimadzu FTIR 8400S instrument in KBr pellets. The C, H, and N elemental analyses were carried out on a Euro EA 3028 HT CHNSO analyzer.

X-ray diffraction data were collected at a SuperNova diffractometer using Cu-K α ($\lambda = 0.154184 \text{ nm}$) radiation. The structures have been solved with the ShelXT³ structure solution program using Intrinsic Phasing and refined with the ShelXL⁴ refinement package incorporated in the OLEX2 program package⁵ using Least Squares minimization. The carbon-bound H atoms were placed in calculated positions. Empirical absorption correction was applied in CrysAlisPro

⁶ program complex using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. X-ray crystallographic data and structural refinement parameters for complexes **3a**, **3b**, and **3d** are summarized in Tables S1. Supplementary crystallographic data have been deposited at Cambridge Crystallographic Data Centre (CCDC 2102394, 2102396, 2102399) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

The UV-vis absorption spectra were recorded on a Shimadzu UV-2500 UV/VIS spectrophotometer in a quartz cuvette with 1.0 mm in CH₂Cl₂ solution at room temperature. Concentration of complexes **3a–d** are 3.5–3.8·10⁻⁵ M and concentration of ligands **1a–d** are 1.2–1.5·10⁻⁴ M.

Luminescence spectra were recorded on a Fliorolog-3 (Horiba Jobin Yvon) instrument at RT. Quantum luminescence yields were determined on the same instrument with the help of direct measurement using an integrating sphere. NanoLED (pulse duration 1.1 ns, repetition rate 50 kHz) was used as an excitation source to carry out lifetime measurements. In case of silicone rubbers luminescence measurements were performed for thin rubber sheets. Fluorescence microscopy images and confocal microscopy image were obtained on a Leica DM4000 B and Leica DMRX A microscopes, respectively.

TGA was performed on a *ca.* 6 mg sample of **3d** by using a Netzsch TG 209 F1 Libra thermal analyzer. The sample was dried under a vacuum at 50 °C before being heated from 40 to 450 °C at a heating rate of 10 K min⁻¹. A flow rate of 10 mL min⁻¹ of dry argon was used to purge the sample.

1.3 Synthetic work

1.3.1 Preparation of starting ureas **1c** and **1d**

A mixture of the corresponding azine-*N*-oxide (2 mmol), dimethyl cyanamide (3 mmol) and acetonitrile (1 mL, 10.0 mmol) was stirred at room temperature for 2 min, and then MsOH (288 mg, 3 mmol) was added dropwise within 3 min. The reaction mixture was stirred at 60 °C

for 3 h, cooled, diluted with saturated aq. Na₂CO₃ (2 mL) and aq. NaCl (5 mL), and extracted with EtOAc (4 × 10 mL). Combined organic fractions were dried with anhydrous Na₂SO₄, filtered, and concentrated on a rotary evaporator. The crude product was purified by column chromatography on silica gel using ethyl acetate/hexane mixture as an eluent.

1,1-Dimethyl-3-(quinolin-2-yl)urea 1c. White powder; 59% yield (253 mg); mp 128–129 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.32 (d, *J* = 8.8 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 7.76 (t, *J* = 8.4 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.51 (br s, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 3.10 (s, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 154.94, 152.45, 146.71, 138.07, 129.71, 127.57, 126.83, 125.79, 124.44, 114.06, 36.54. HR-MS (ESI), *m/z*: [M+H]⁺: calc. for C₁₂H₁₄N₃O 216.1131; found 216.1133. Anal. calcd. for C₁₂H₁₄N₃O C 66.96, H 6.09, N 19.52; found: C 66.82 H 6.10, N 19.91.

3-(Isoquinolin-1-yl)-1,1-dimethylurea 1d. Yellow powder; 51% yield (220 mg); mp 114–115 °C. ¹H NMR (400 MHz, CDCl₃): 14.42 (s, 1H), 8.66 (d, *J* = 8.0 Hz, 1H), 7.72 – 7.60 (m, 1H), 7.59 – 7.44 (m, 2H), 7.22 – 7.04 (m, 1H), 6.63 (d, *J* = 6.8 Hz, 1H), 3.35 (s, 3H), 3.06 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 165.97, 156.68, 136.65, 132.17, 127.01, 126.64, 126.33, 126.26, 126.11, 108.27, 37.42, 35.25. HR-MS (ESI), *m/z*: [M+H]⁺: calc. for C₁₂H₁₄N₃O 216.1131; found 216.1132. Anal. calcd. for C₁₂H₁₄N₃O C 66.96, H 6.09, N 19.52; found: C 67.05 H 6.14, N 19.89.

1.3.2 Preparation of Pt(II) complexes 3a–d

Triethanolamine (0.36 mmol, 0.40 mL) was added to a mixture of the corresponding urea (0.30 mmol) and *cis*-[PtCl₂(CNXyl)₂] (0.30 mmol, 160 mg) in CHCl₃ (5 mL). The reaction mixture was stirred at 35 °C for 24 h. After that, the reaction mixture was filtered to remove a small amount of undissolved material and evaporated to dryness at 45 °C *in vacuo*. Complexes **3a** and **3b** were dissolved in 1,2-dichloroethane (1 mL) and diluted with pentane (1 mL),

whereas complexes **3c** and **3d** were dissolved in chloroform (4 mL) and diluted with MeOH (20 mL). The formed precipitate was collected by filtration and dried in air at RT.

All complexes are solids; melting points were not determined due to decomposition at 200–250 °C.

Complex 3a. Yellow powder; 78% yield (155 mg). IR (KBr, selected bands, cm^{-1}): $\nu(\text{C}\equiv\text{N})$ 2199 (s), $\nu(\text{C}=\text{O})$ 1712 (s), $\nu(\text{C}=\text{N})$ 1609 (s). ^1H NMR (400 MHz, CDCl_3): δ 9.39 – 9.24 (m, 1H), 7.86 – 7.78 (m, 1H), 7.14 (t, $J = 7.6$ Hz, 1H), 7.05 – 6.87 (m, 4H), 6.78 (d, $J = 7.6$ Hz, 1H), 6.65 (d, $J = 7.6$ Hz, 1H), 6.16 (t, $J = 7.6$ Hz, 1H), 3.22 (s, 3H), 3.16 (s, 3H), 2.28 (s, 6H), 2.24 (d, $J = 2.0$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 156.84, 154.09, 150.79, 149.03, 146.13, 141.43, 134.41, 128.90, 128.65, 127.86, 127.36, 127.32, 127.29, 123.15, 115.16, 108.02, 38.21, 36.54, 19.68, 19.43, 18.41. ^{195}Pt NMR (86 MHz, CDCl_3): δ –3807.10. HR-MS (ESI), m/z : $[\text{M}-\text{Cl}]^+$: calc. for $\text{C}_{26}\text{H}_{28}\text{ClN}_5\text{OPt}$ 621.1936; found 621.1935. Anal. calcd. for $\text{C}_{27}\text{H}_{30}\text{ClN}_5\text{OPt} + 0.5 \text{C}_2\text{H}_4\text{Cl}_2$ (1,2-dichloroethane, recrystallization solvent) C 45.90, H 4.28, N 9.91; found: C 46.12 H 4.40, N 9.52.

Complex 3b. Light yellow powder; 90% yield (181 mg). IR (KBr, selected bands, cm^{-1}): $\nu(\text{C}\equiv\text{N})$ 2197 (s), $\nu(\text{C}=\text{O})$ 1712 (s), $\nu(\text{C}=\text{N})$ 1614 (s). ^1H NMR (400 MHz, CDCl_3): δ 9.12 (d, $J = 6.4$ Hz, 1H), 7.13 (t, $J = 7.6$ Hz, 1H), 6.99 (d, $J = 7.6$ Hz, 2H), 6.83 – 6.74 (m, 2H), 6.71 (s, 1H), 6.64 (d, $J = 7.2$ Hz, 1H), 6.15 (t, $J = 7.6$ Hz, 1H), 3.22 (s, 3H), 3.16 (s, 3H), 2.42 (s, 3H), 2.27 (s, 6H), 2.24 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 156.62, 154.32, 154.02, 150.86, 149.15, 145.28, 134.40, 128.83, 128.68, 127.85, 127.34, 127.26, 123.07, 116.81, 107.84, 38.25, 36.54, 21.88, 19.70, 19.44, 18.42. ^{195}Pt NMR (86 MHz, CDCl_3): δ –3808.40. HR-MS (ESI), m/z : $[\text{M}-\text{Cl}]^+$: calc. for $\text{C}_{27}\text{H}_{30}\text{ClN}_5\text{OPt}$ 635.2093; found 635.2077. Anal. calcd. for $\text{C}_{26}\text{H}_{28}\text{ClN}_5\text{OPt}$ C 48.32, H 4.51, N 10.44; found: C 48.74 H 4.38, N 9.98.

Complex 3c. Light yellow powder; 80% yield (170 mg). IR (KBr, selected bands, cm^{-1}): $\nu(\text{C}\equiv\text{N})$ 2196 (s), $\nu(\text{C}=\text{O})$ 1701 (s), $\nu(\text{C}=\text{N})$ 1614 (s). ^1H NMR (400 MHz, CDCl_3): δ 9.24 (d, $J =$

6.8 Hz, 1H), 8.17 (d, $J = 8.8$ Hz, 1H), 7.88 – 7.74 (m, 2H), 7.64 – 7.58 (m, 1H), 7.31 (d, $J = 6.8$ Hz, 1H), 7.17 – 7.11 (m, 1H), 7.03 – 6.98 (m, 2H), 6.82 (d, $J = 7.6$ Hz, 1H), 6.68 (d, $J = 7.6$ Hz, 1H), 6.20 (t, $J = 7.6$ Hz, 1H), 3.26 (s, 3H), 3.24 (s, 3H), 2.30 (s, 6H), 2.27 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 156.46, 155.66, 150.91, 150.77, 138.72, 137.66, 134.44, 132.49, 128.86, 128.61, 128.18, 127.91, 127.75, 127.37, 127.26, 127.05, 125.38, 123.25, 116.70, 114.89, 38.62, 36.55, 19.65, 19.50, 18.45. ^{195}Pt NMR (86 MHz, CDCl_3): δ –3797.28. HR-MS (ESI), m/z : $[\text{M}-\text{Cl}]^+$: calc. for $\text{C}_{30}\text{H}_{30}\text{ClN}_5\text{OPt}$ 671.2093; found 671.2096. Anal. calcd. for $\text{C}_{30}\text{H}_{30}\text{ClN}_5\text{OPt} + 0.5 \text{CHCl}_3$ C 47.77, H 4.01, N 9.13; found: C 47.84 H 4.13, N 9.10.

Complex 3d. Yellow powder; 77% yield (164 mg). IR (KBr, selected bands, cm^{-1}): $\nu(\text{C}\equiv\text{N})$ 2194 (s), $\nu(\text{C}=\text{O})$ 1694 (s), $\nu(\text{C}=\text{N})$ 1619 (s). ^1H NMR (400 MHz, CDCl_3): δ 9.48 (d, $J = 8.8$ Hz, 1H), 8.18 (d, $J = 8.8$ Hz, 1H), 7.74 (m, 2H), 7.46 (t, $J = 7.2$ Hz, 1H), 7.15 (t, $J = 7.6$ Hz, 1H), 7.06 (d, $J = 8.8$ Hz, 1H), 7.00 (d, $J = 7.6$ Hz, 2H), 6.83 (d, $J = 6.8$ Hz, 1H), 6.62 (d, $J = 7.2$ Hz, 1H), 6.27 (t, $J = 7.2$ Hz, 1H), 3.26 (s, 4H), 3.24 (s, 3H), 2.34 (s, 3H), 2.31 (s, 6H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 157.78, 154.10, 150.09, 148.24, 145.86, 142.15, 134.61, 131.07, 128.92, 128.64, 128.15, 127.72, 127.57, 127.37, 127.28, 126.66, 125.29, 124.54, 123.22, 108.74, 38.35, 36.59, 19.88, 19.82, 18.53. ^{195}Pt NMR (86 MHz, CDCl_3): –3688.36. HR-MS (ESI), m/z : $[\text{M}-\text{Cl}]^+$: calc. for $\text{C}_{30}\text{H}_{30}\text{ClN}_5\text{OPt}$ 671.2093; found 671.2098. Anal. calcd. for $\text{C}_{30}\text{H}_{30}\text{ClN}_5\text{OPt} + 0.5 \text{CHCl}_3$ C 50.96, H 4.28, N 9.90; found: C 50.79 H 4.34, N 9.68.

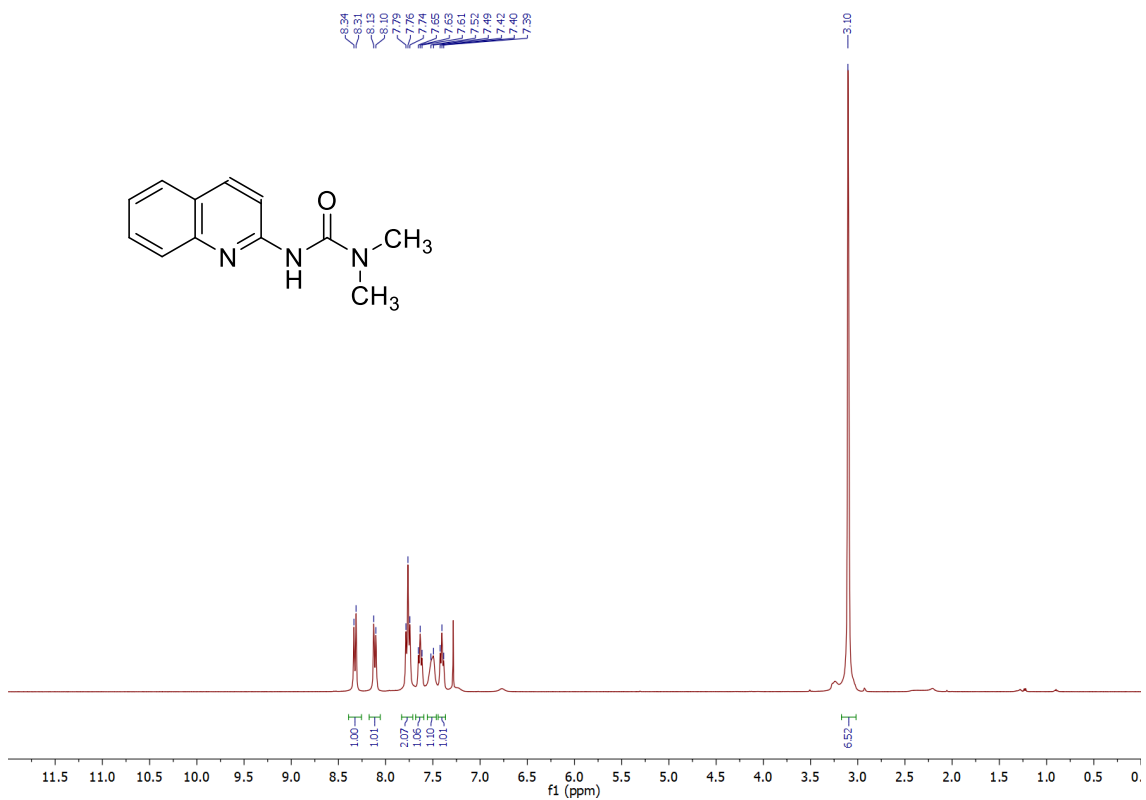


Figure S1. ¹H NMR spectrum of urea **1c**.

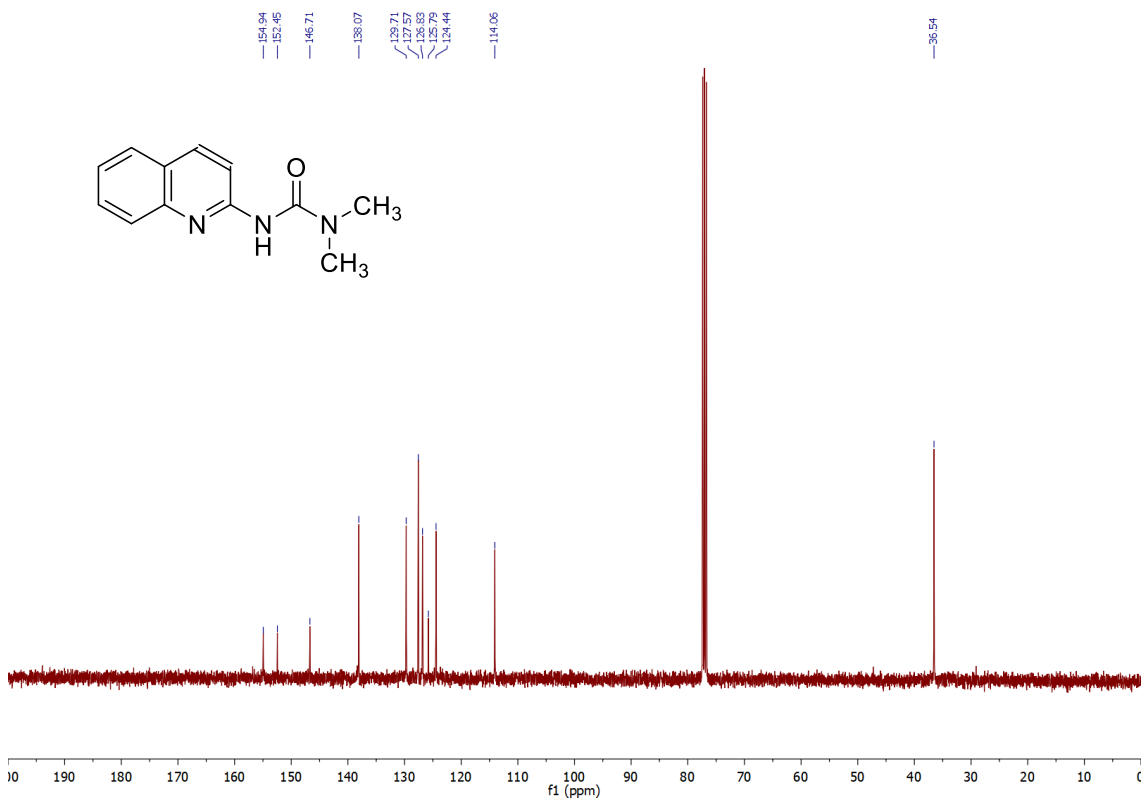


Figure S2. ¹³C NMR spectrum of urea **1c**.

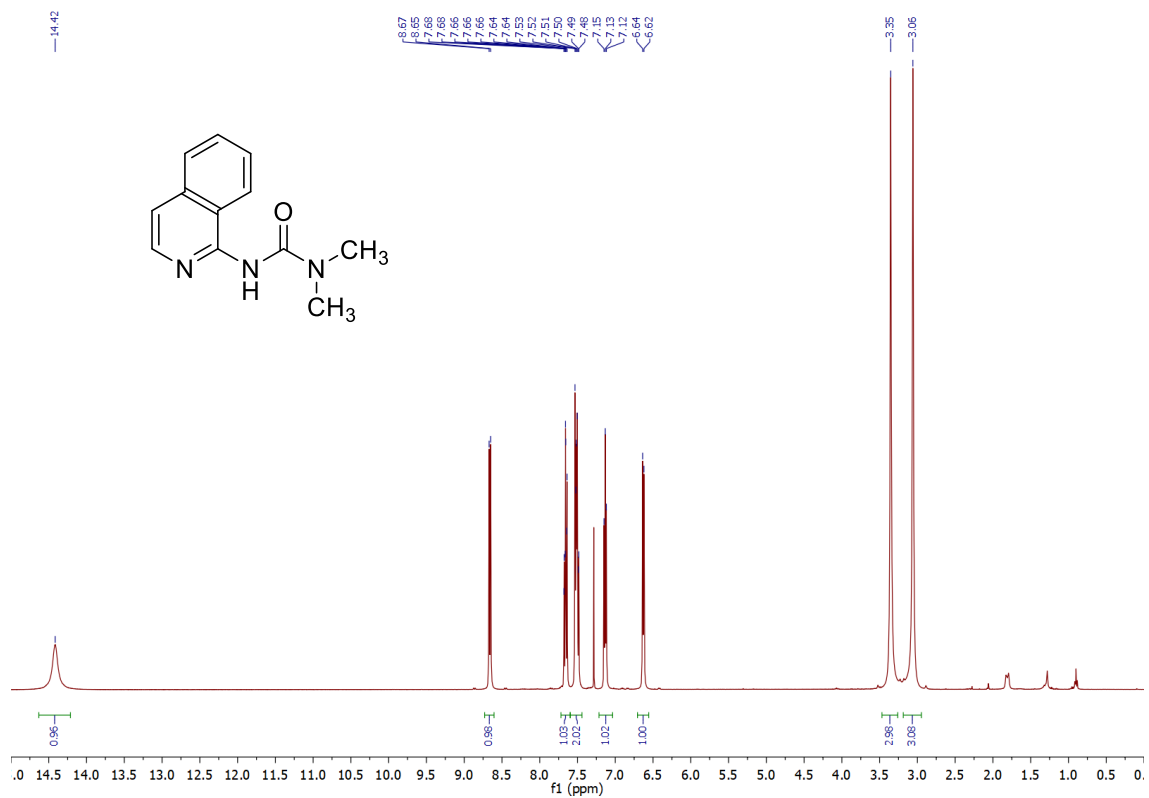


Figure S3. ¹H NMR spectrum of urea **1d**.

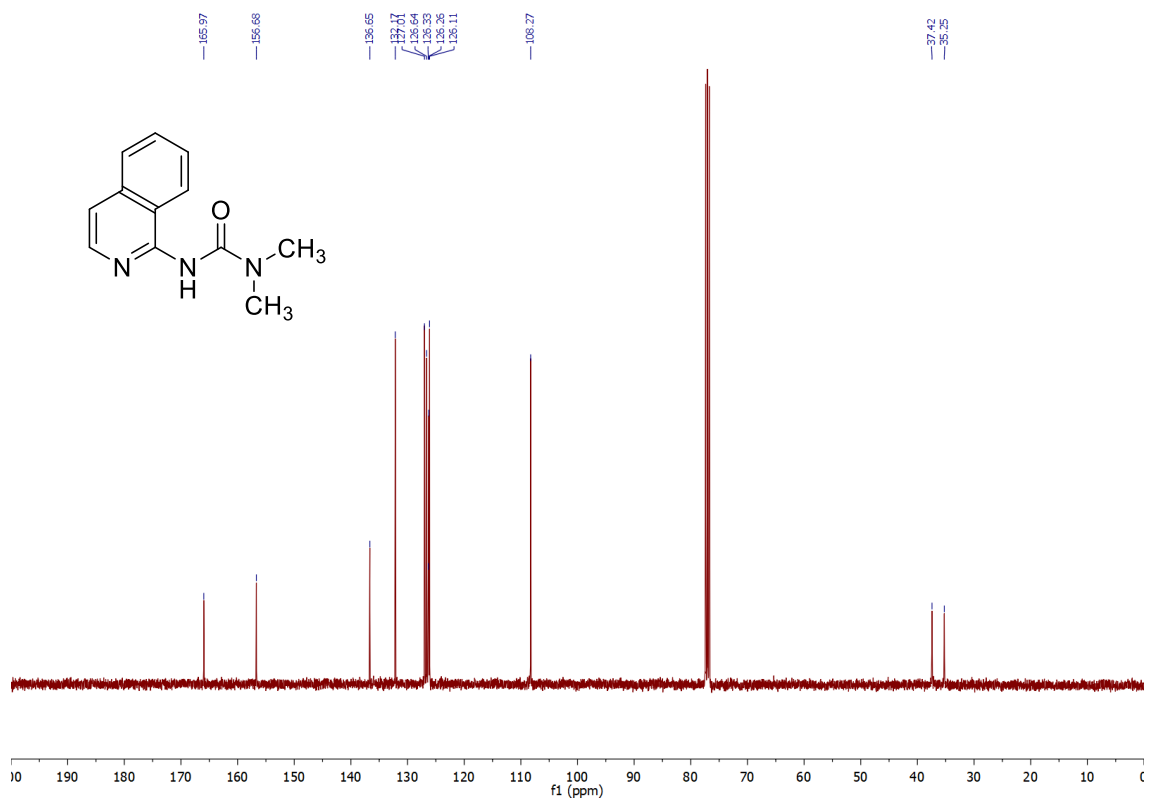


Figure S4. ¹³C NMR spectrum of urea **1d**.

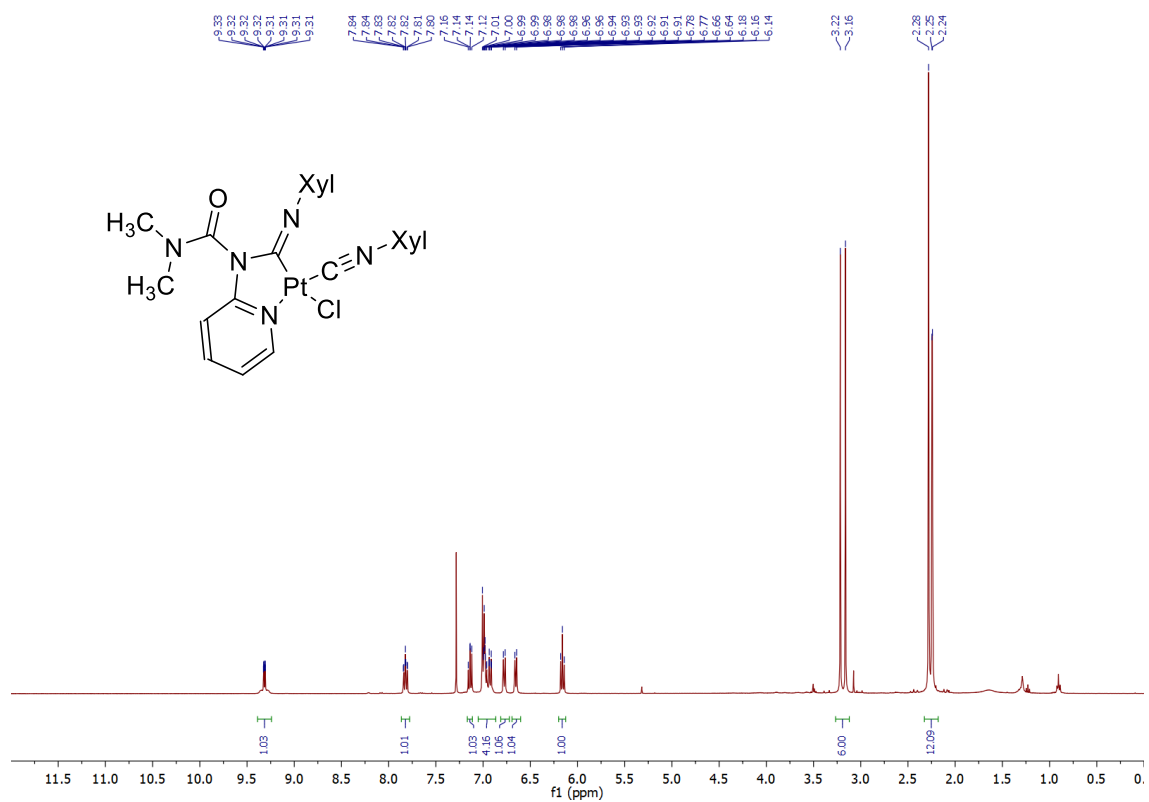


Figure S5. ^1H NMR spectrum of complex **3a**.

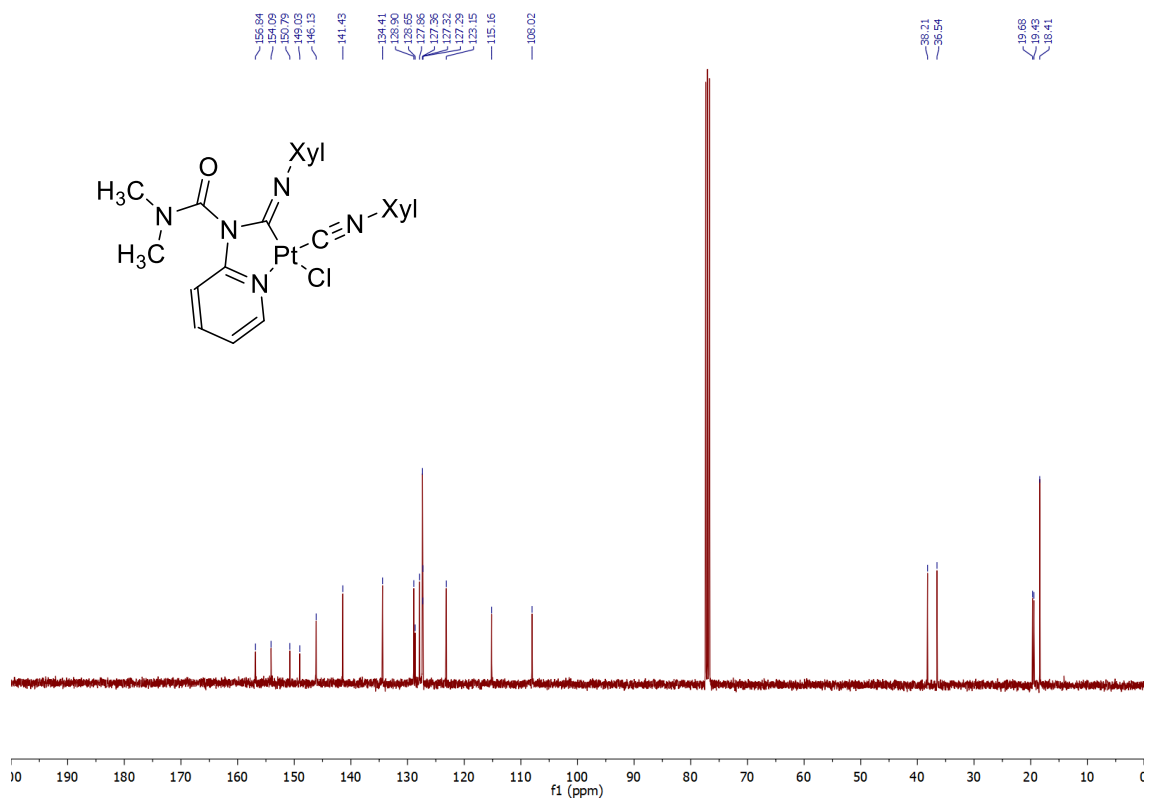


Figure S6. ^{13}C NMR spectrum of complex **3a**.

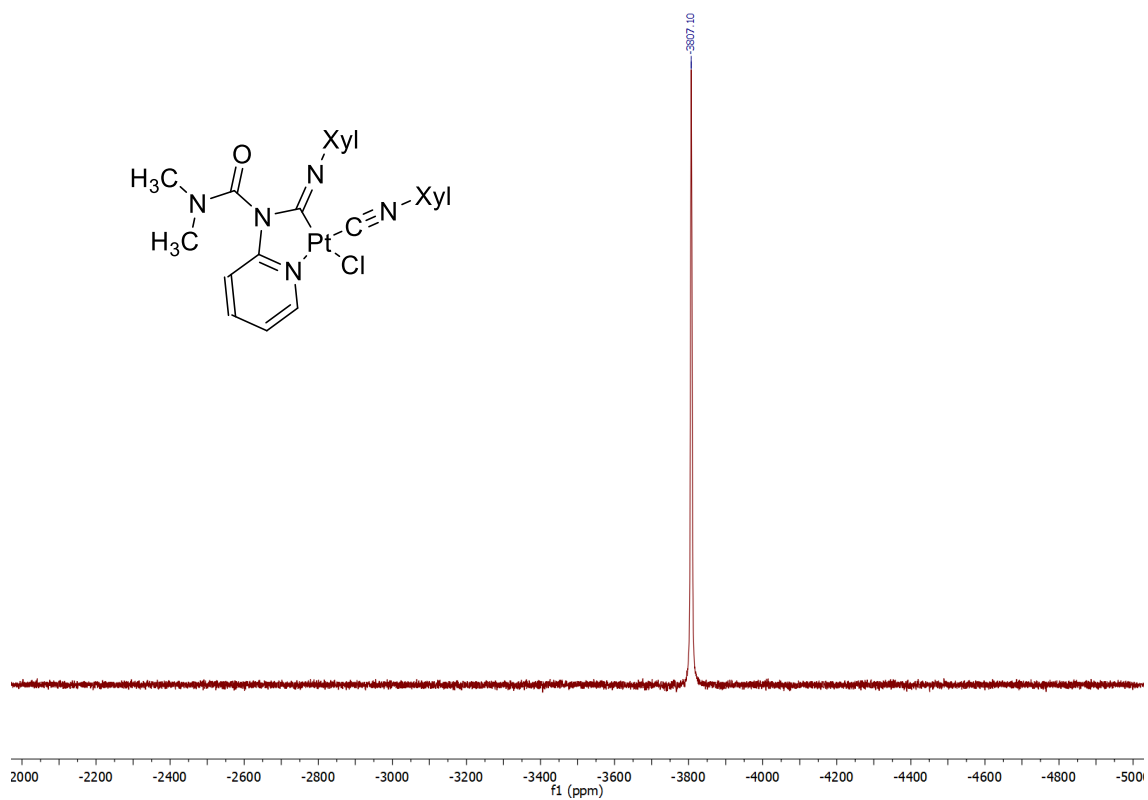


Figure S7. ^{195}Pt NMR spectrum of complex **3a**.

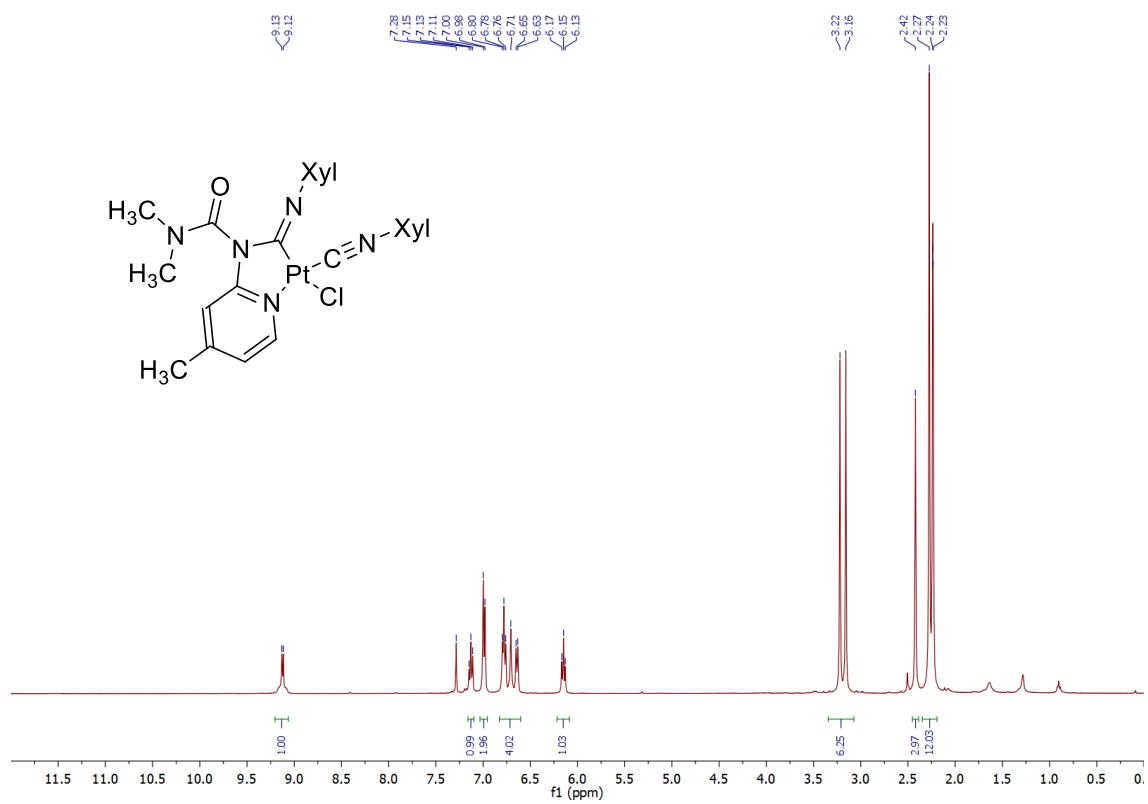


Figure S8. ^1H NMR spectrum of complex **3b**.

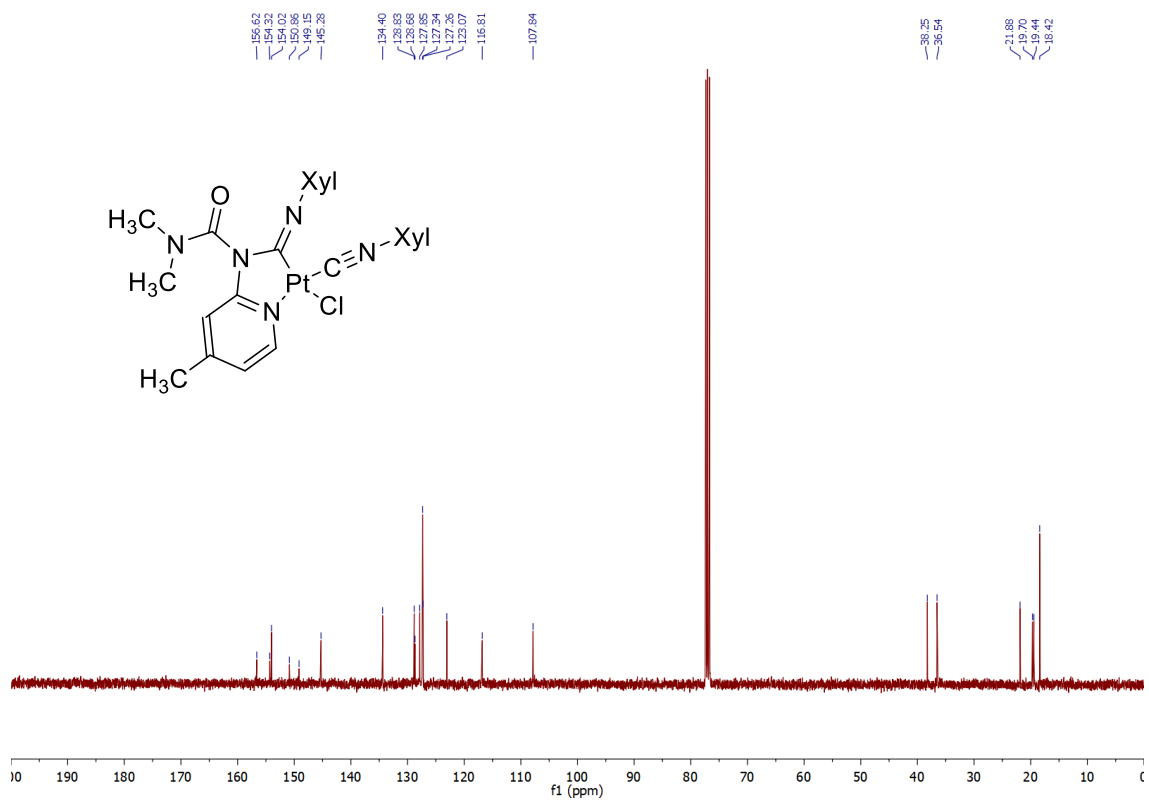


Figure S9. ¹³C NMR spectrum of complex **3b**.

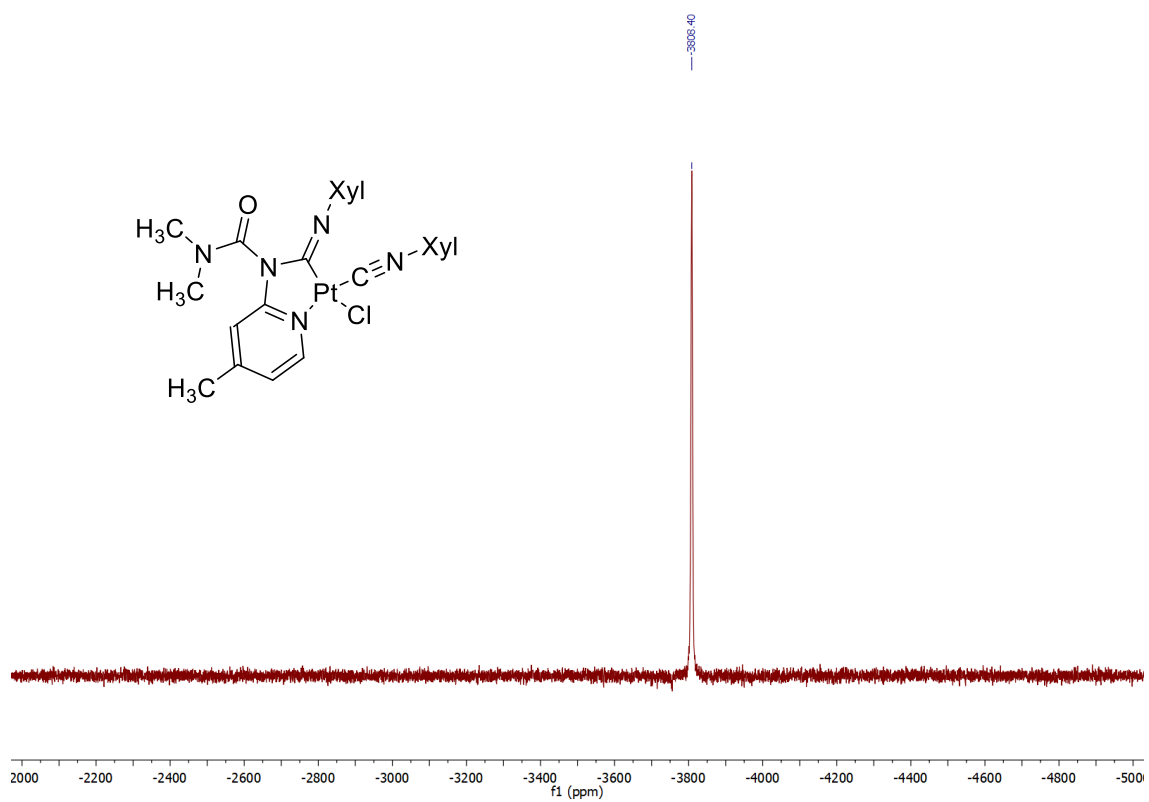


Figure S10. ¹⁹⁵Pt NMR spectrum of complex **3b**.

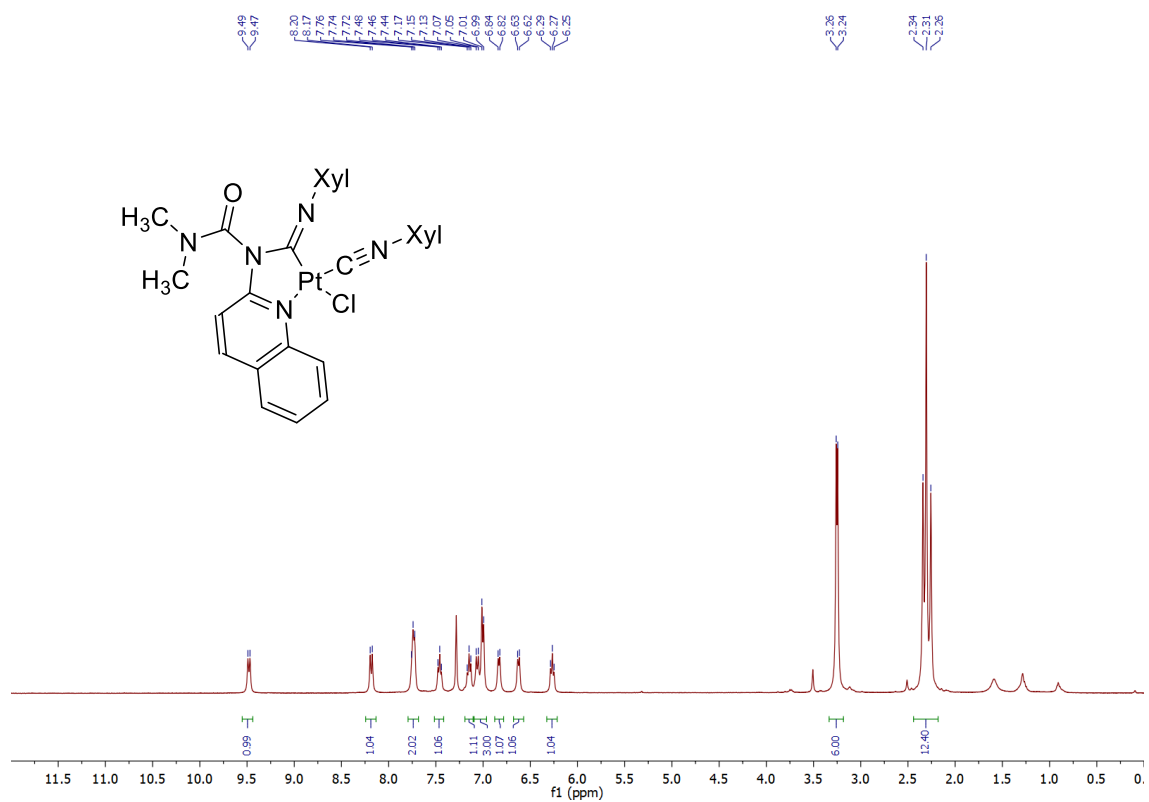


Figure S11. ¹H NMR spectrum of complex **3c**.

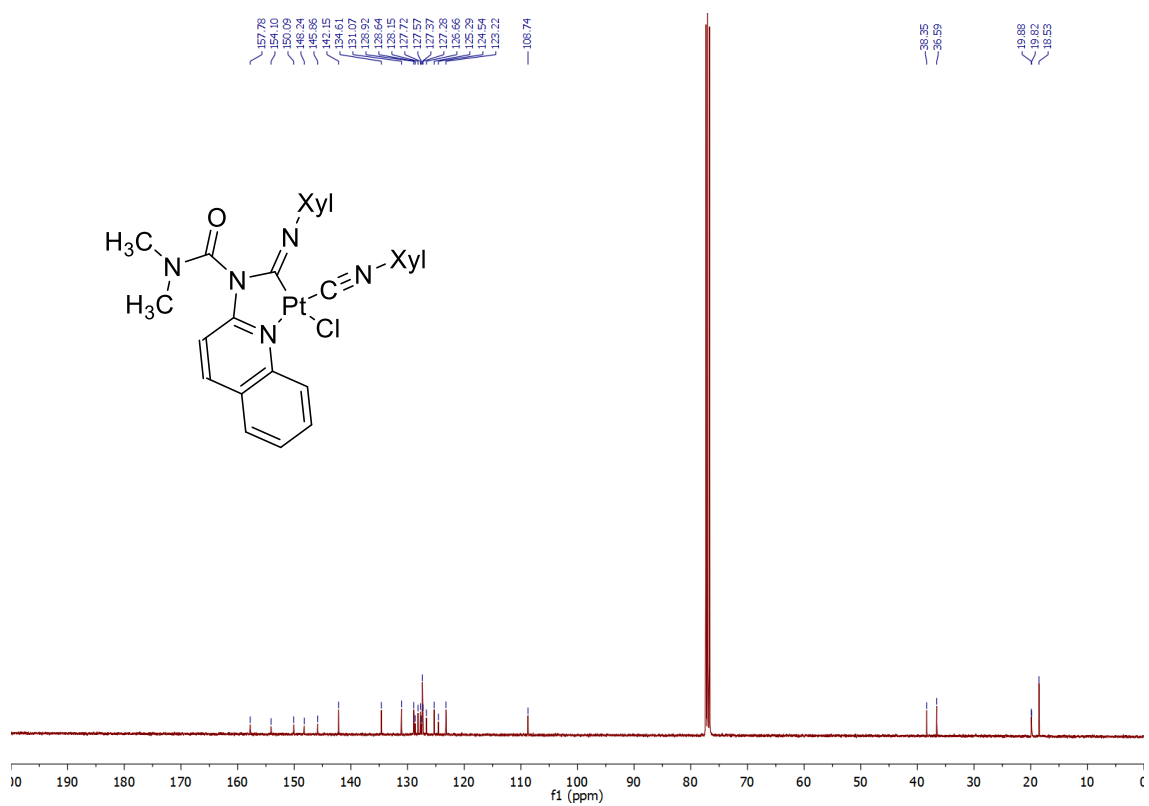


Figure S12. ¹³C NMR spectrum of complex **3c**.

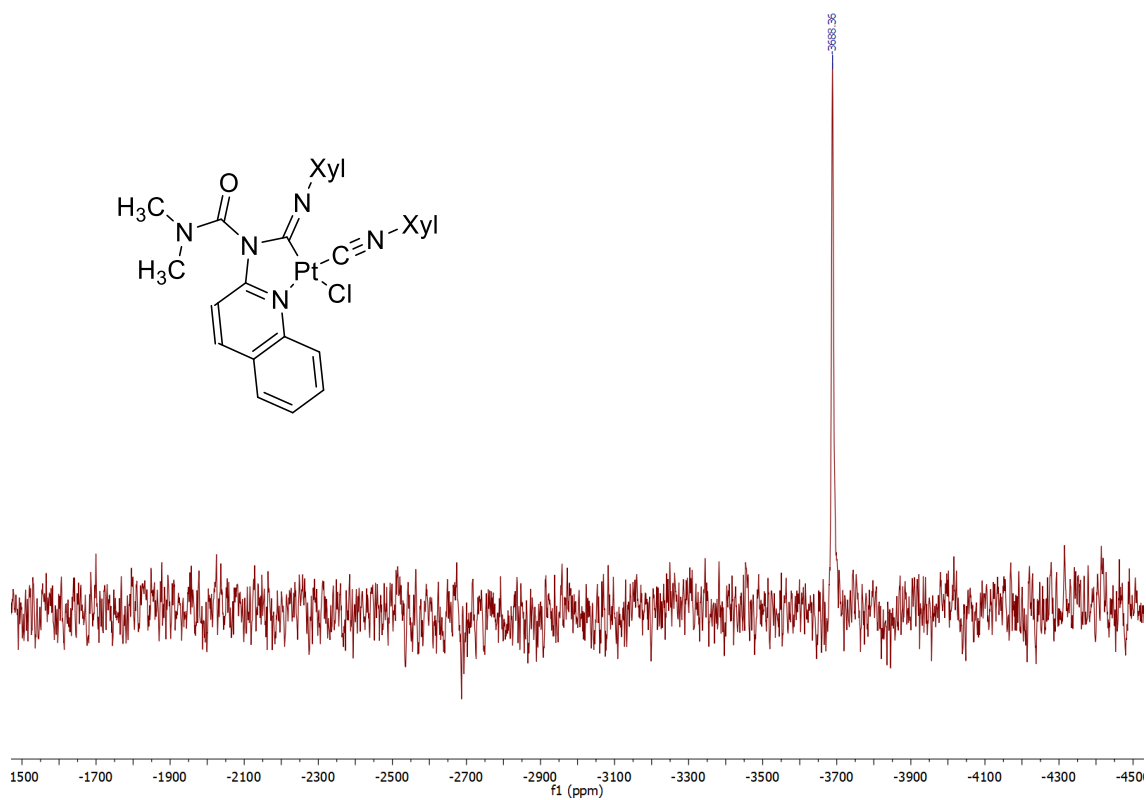


Figure S13. ^{195}Pt NMR spectrum of complex 3c.

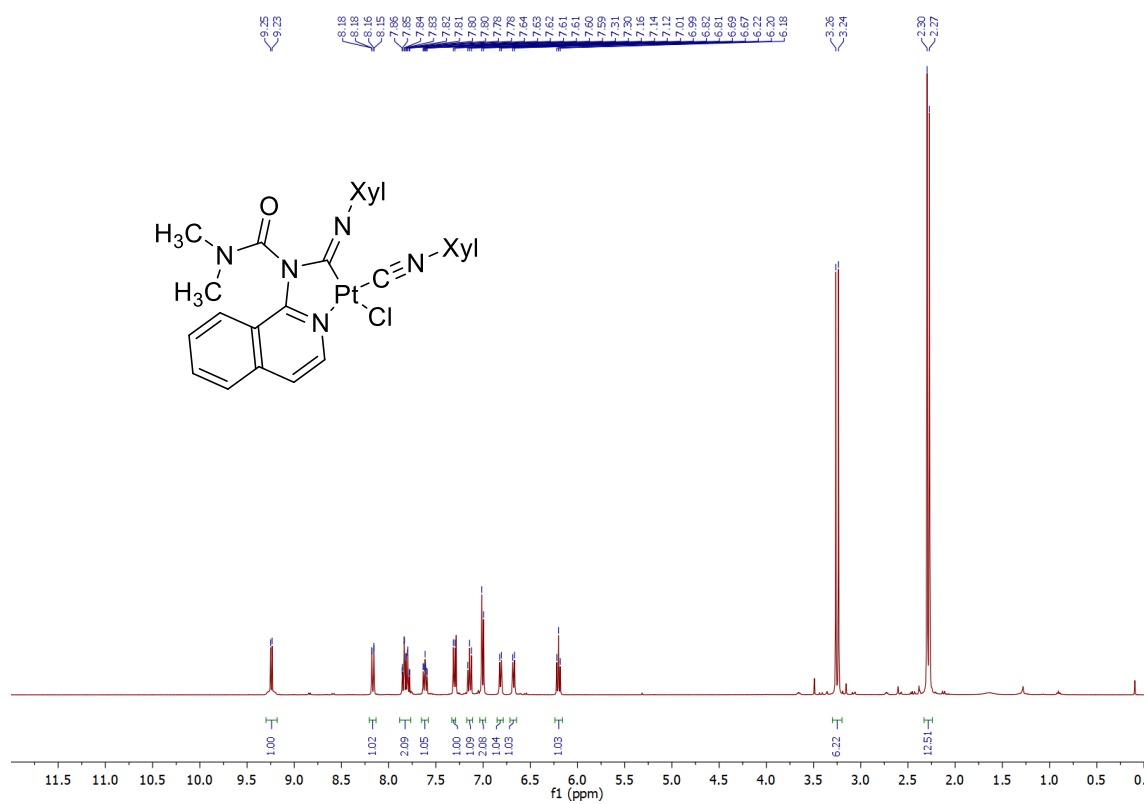
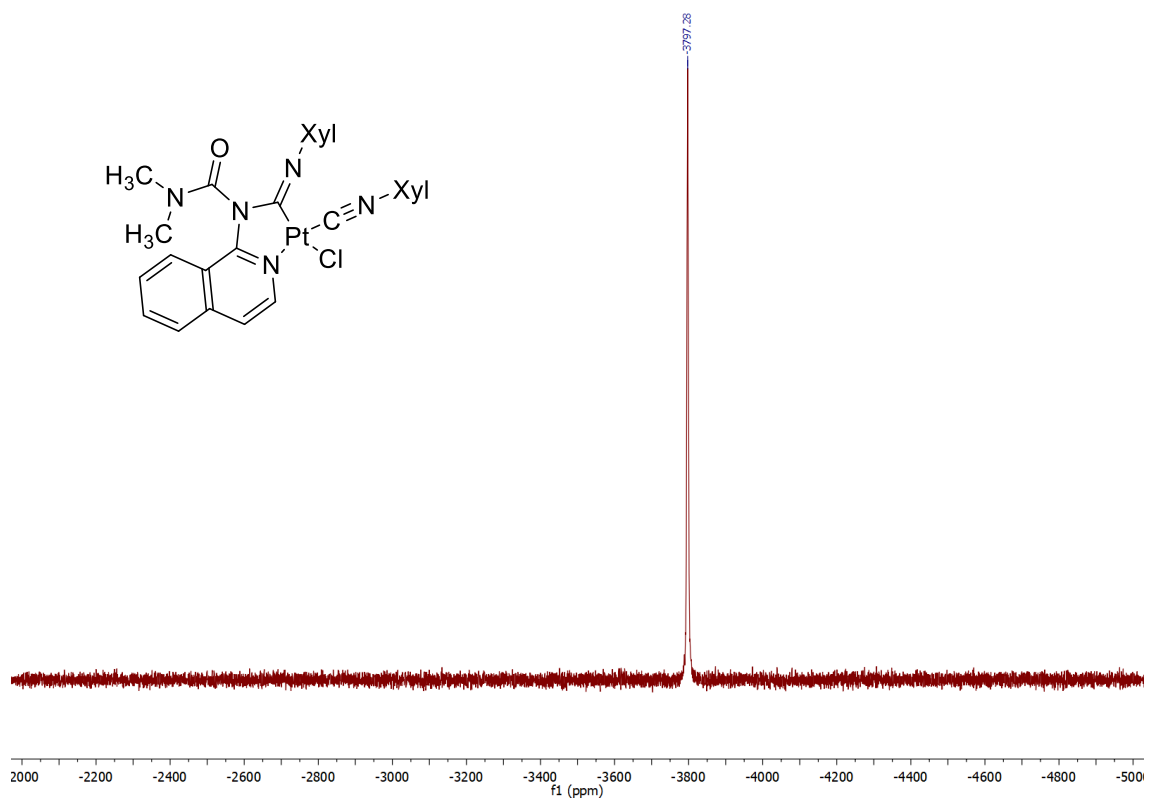
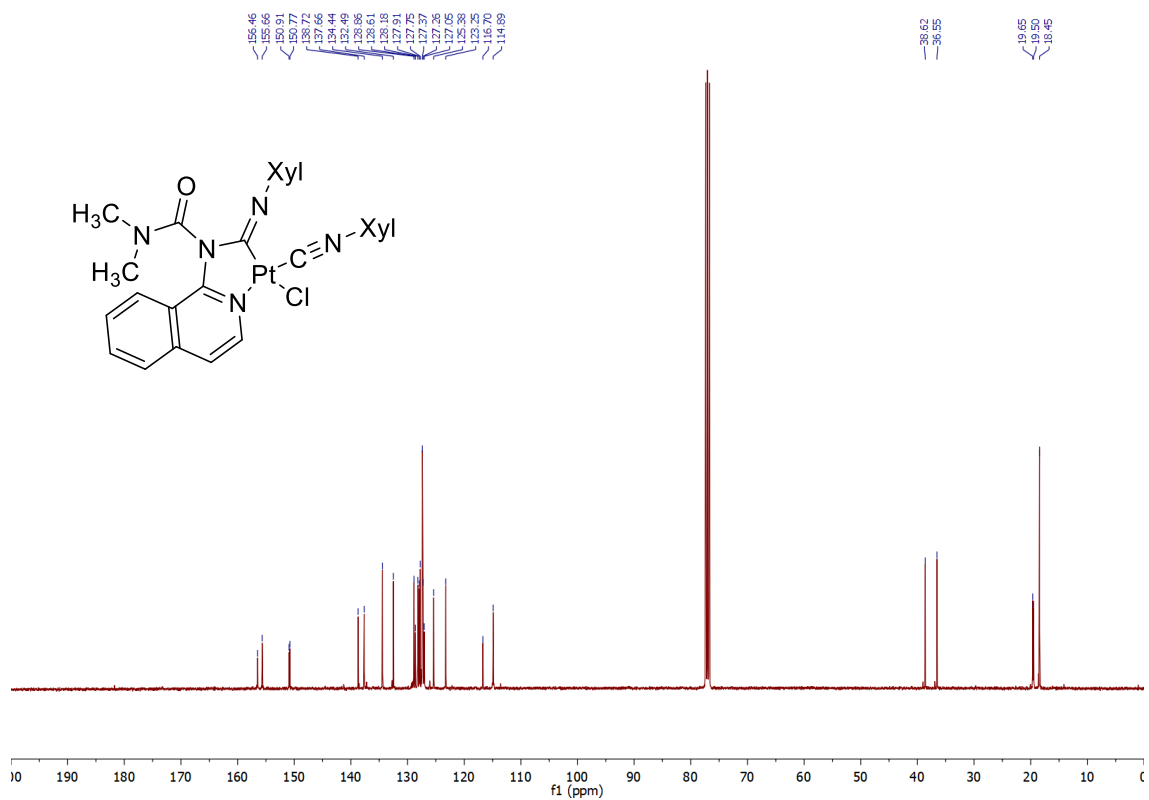


Figure S14. ^1H NMR spectrum of complex 3d.



1.4 Catalytic tests of the polymer system

The cross-linking system included components I and II. *Component I*: a calculated amount of platinum catalyst was diluted in CH₂Cl₂ and added to polymer **PDMS-v**; the mixture was then stirred and dried under vacuum at RT to remove the solvent. *Component II*: **PDMS-co-PMHS** and the corresponding vinyl-containing polymer were mixed in mass ratio 1 to 6.4 (w/w) and carefully stirred. The amounts required were calculated to ensure a specific ratio of hydride to vinyl groups (3:1) in the reaction mixture.

Component I (0.5 mL) was placed in an aluminum vessel, component II (0.5 mL) was added, and the mixture was stirred with a glass stick for 30 sec. The mixture was then placed in a thermostat at a certain temperature until the dry cured product was obtained. The total catalyst concentration in the resulting silicone rubber was 1.0×10^{-3} , 1.0×10^{-4} or 1.0×10^{-5} mol·L⁻¹.

The curing time (τ_{curing}) was defined as the time that passed between mixing Components I and II and the moment when the cross-linked rubber was obtained. The curing times were measured as dry-to-touch times according to ASTM D1640 ⁷: the criteria are no mark is left when the film is touched by a finger. Visual measurements were performed five times for each sample.

1.5 Swelling of silicone rubbers

For swelling measurements, a representative sample of silicone rubber (ca. 0.1 g) was weighed for evaluating the initial dry weight (m_{unex}) and then the sample was swollen for 6 h in a Soxhlet extractor using toluene. The sample was then gently wiped to remove liquid solvent from its surface, whereupon weighed immediately (m_{s}). It was then dried overnight at RT and then at 60 °C until the constant weight (ca. 3 h), and weighed again (m_{ex}). The soluble fraction (w_{sol}) and the volume fraction of the polymer in the swollen sample (v) were calculated as follows:

$$w_{\text{sol}}(\%) = \frac{m_{\text{unex}} - m_{\text{ex}}}{m_{\text{unex}}} \times 100 \quad (1)$$

$$v = \left[1 + \frac{m_s - m_{ex}}{m_{ex}} \times \frac{\rho_p}{\rho_s} \right]^{-1} \quad (2),$$

where ρ_s and ρ_p are the solvent (toluene, 0.865 g/cm³) and polymer (**PDMS-v**, 0.965 g/cm³) densities, respectively.

Cross-link density (ρ_{cross}) was calculated according to the Flory–Rehner equation ⁸:

$$\rho_{cross} = -\frac{1}{V_s} \cdot \frac{\ln(1-v) + v + \chi v^2}{v^{\frac{1}{3}} - \frac{v}{2}} \quad (3),$$

where V_s is molar volume of the solvent (toluene, 106.3 cm³/mol), χ is the Flory–Huggins polymer–solvent interaction parameter (0.465 for polydimethylsiloxane–toluene ⁹).

Average molecular weight of the rubber segment between cross-links (M_c) was calculated as follows ⁸:

$$M_c = \frac{\rho_p}{\rho_{cross}} \quad (4)$$

The swelling experiments were performed 10 times.

2. X-ray data for complexes **3a**, **3b**, and **3d**

Table S1. Crystal data and structure refinement parameters for complexes **3a**, **3b**, and **3d**.

Compound	3a	3b	3d
Identification code	BSC-355	BSC-450	BSC-461
CCDC number	2102394	2102396	2102399
Empirical formula	C ₂₆ H _{28.71} ClN ₅ O _{1.36} Pt	C ₂₇ H ₃₀ ClN ₅ OPt	C ₃₀ H ₃₀ ClN ₅ OPt
Formula weight	663.49	671.10	707.13
Temperature, K	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	tetragonal
Space group	I2/a	P2 ₁ /c	P4 ₃ 2 ₁ 2
a, Å	19.0902(3)	7.55950(10)	14.11700(10)
b, Å	12.0056(2)	29.0139(4)	14.11700(10)
c, Å	22.7916(3)	11.9767(2)	27.4755(3)
α , °	90	90	90

β , °	101.9090(10)	101.3680(10)	90
γ , °	90	90	90
Volume, Å ³	5111.16(14)	2575.32(7)	5475.58(10)
Z	8	4	8
ρ_{calc} , cm ³	1.724	1.731	1.716
μ , mm ⁻¹	11.469	11.378	10.742
F(000)	2604.0	1320.0	2784.0
Crystal size, mm ³	0.17 × 0.15 × 0.11	0.2 × 0.14 × 0.1	0.19 × 0.18 × 0.12
Radiation	Cu K α (λ = 1.54184)	CuK α (λ = 1.54184)	CuK α (λ = 1.54184)
2 Θ range for data collection, °	7.928 to 139.974	6.092 to 140.848	7.04 to 153.49
Index ranges	$-23 \leq h \leq 22$, $-13 \leq k \leq 14$, $-27 \leq l \leq 27$	$-9 \leq h \leq 7$ $-35 \leq k \leq 34$ $-14 \leq l \leq 14$	$-17 \leq h \leq 17$ $-17 \leq k \leq 17$ $-34 \leq l \leq 32$
Reflections collected	28786	14904	93936
Independent reflections	4833 [$R_{\text{int}} = 0.0414$ $R_{\text{sigma}} = 0.0255$]	4890 [$R_{\text{int}} = 0.0393$, $R_{\text{sigma}} = 0.0408$]	5721 [$R_{\text{int}} = 0.0777$ $R_{\text{sigma}} = 0.0218$]
Data/restraints/parameters	4833/0/319	4890/0/323	5721/0/349
Goodness-of-fit on F^2	1.154	1.098	1.045
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0364$ $wR_2 = 0.1015$	$R_1 = 0.0281$, $wR_2 = 0.0697$	$R_1 = 0.0354$ $wR_2 = 0.0822$
Final R indexes [all data]	$R_1 = 0.0400$ $wR_2 = 0.1048$	$R_1 = 0.0317$ $wR_2 = 0.0717$	$R_1 = 0.0372$ $wR_2 = 0.0832$
Largest diff. peak/hole/ eÅ ⁻³	1.84/-2.73	1.16/-1.27	0.87/-1.23
			-0.017(12)

Table S2. Selected bond lengths and angles for complexes **3a**, **3b**, and **3d**.

Parameter	3a	3b	3d
Pt1–Cl1, Å	2.3968(12)	2.3925(9)	2.3807(19)
Pt1–N1, Å	2.042(4)	2.043(3)	2.039(7)
Pt1–C6, Å	1.991(4)	2.003(4)	1.996(8)
Pt1–C15, Å	1.923(5)	1.909(4)	1.911(9)
C6–N2, Å	1.424(6)	1.413(5)	1.431(11)
C6–N3, Å	1.270(6)	1.270(5)	1.279(11)
C24–N2, Å	1.464(6)	1.453(5)	1.471(13)
C24–N5, Å	1.337(5)	1.347(5)	1.293(14)
C6–Pt1–N1, °	81.36(17)	81.36(14)	80.8(3)
N2–C6–N3, °	113.4(4)	113.5(3)	113.6(7)

3. TG/DTG data

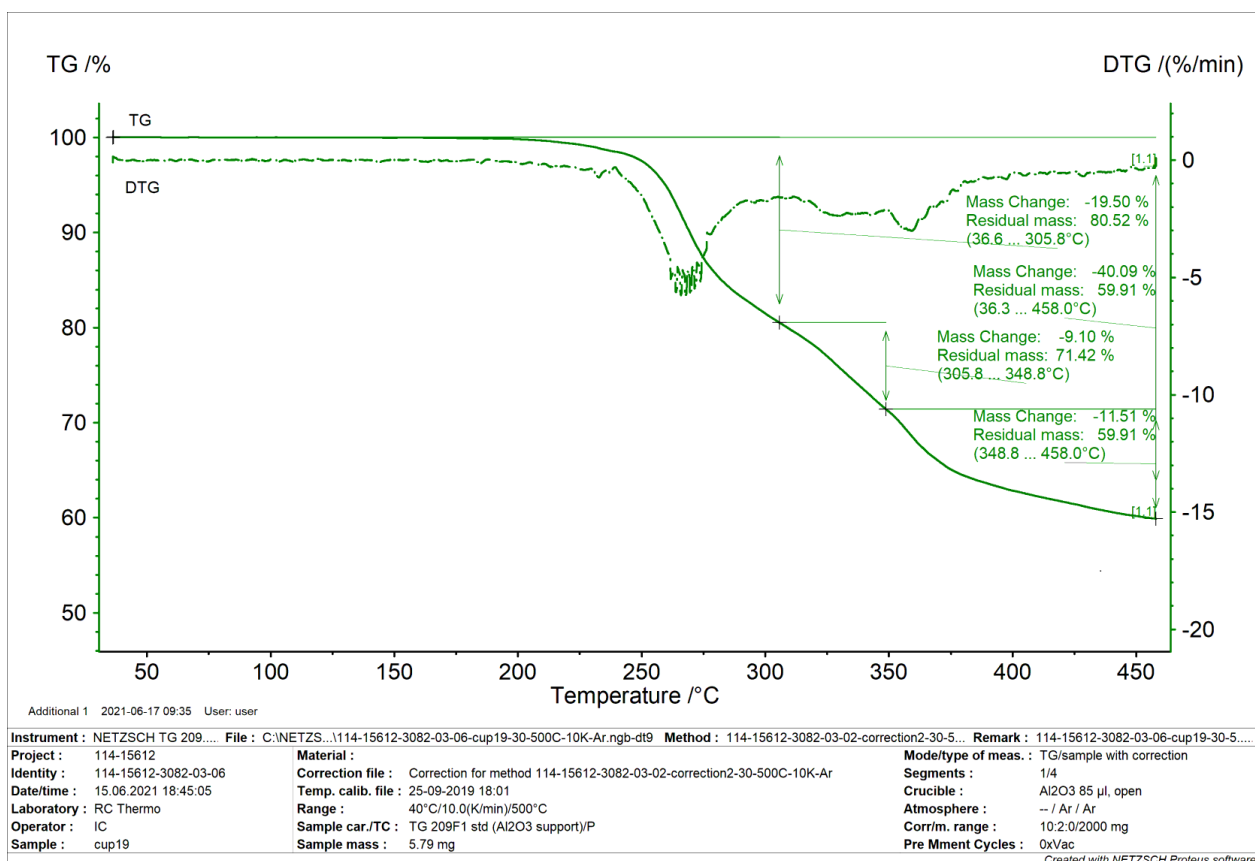


Figure S17. TG/DTG curves of complex **3d**.

4. Properties of the silicone rubbers obtained with **3d**

Table S3. Luminescent properties of silicone rubbers **PDMS-v/PDMS-co-PMHS** obtained with **3d** at 100 and 120 °C ($C_{\text{catalyst}} = 1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$).

Form	Lifetime, ns	Quantum yield, %	λ_{em} , nm (at 360 nm)	λ_{em} , nm (at 460 nm)	λ_{abs} , nm
Complex (solid)	51.7 (441 nm); 754.6 (576 nm)	0.2 (excitation 450–470 nm)	417; 438	547; 576	—
Complex (solution)	640 (555 nm) 640 (590 nm)	0.25	558; 591 (λ_{em} 312 nm)	558; 591 (λ_{em} 420 nm)	460

Silicone rubber obtained at 100 °C	4.4 (394nm); 3.9 (535 nm)	4.0 (excitation 350–370 nm)	534; 574	534; 574	367–466
Silicone rubber obtained at 120 °C	4.9 (400 nm); 4.7 (538 nm)	0.5 (excitation 350–370 nm)	401	538; 578	341, 359, 464

Table S4. Swelling experiments on silicone rubbers **PDMS-*v*/PDMS-*co*-PMHS** obtained with **3d** at various temperatures (in toluene; $C_{\text{catalyst}} = 1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$).

Temperature of curing, °C	M_c , g/mol	w_{sol} , %	ν
80	17000	9.1	0.17
100	12500	7.0	0.19
120	11200	7.0	0.20
140	9200	4.8	0.22

5. HRESI⁺ mass spectrometry data for a CHCl₃ extract from the silicone rubber obtained with 3d

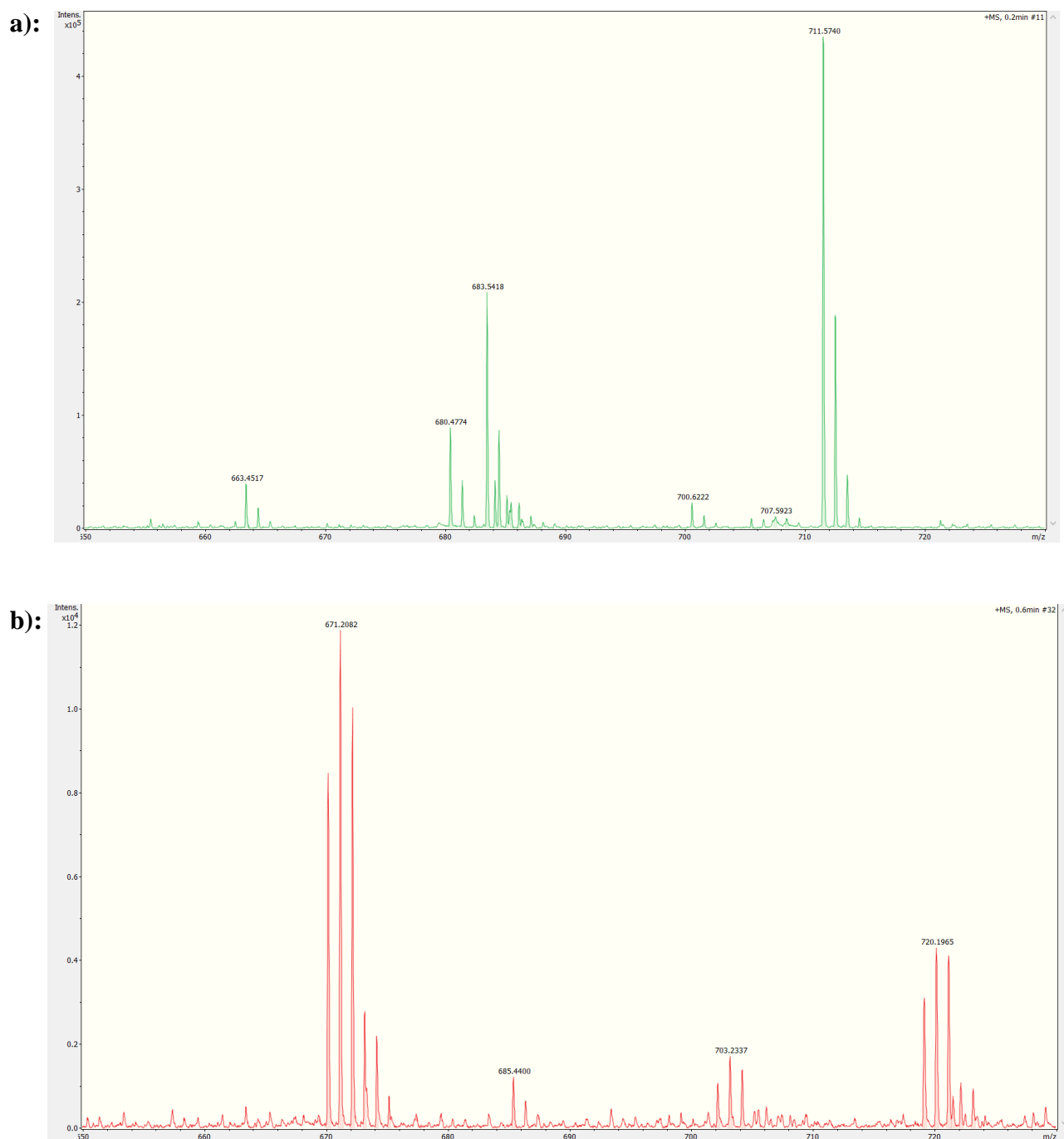


Figure S18. a) Fragment of HRESI⁺ mass spectrometry data for a CHCl₃ extract from the silicone rubber obtained with **3d** at 100 °C ($C_{\text{catalyst}} = 1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$). b) Fragment of HRESI⁺ mass spectrometry data for complex **3d** (for comparison). m/z for **3d** $[\text{M}-\text{Cl}]^+$: calc. for C₃₀H₃₀ClN₅OPt 671.2093; found 671.2098.

6. UV spectra and luminescence properties of the ligands, complexes, and silicone rubbers obtained with **3d**

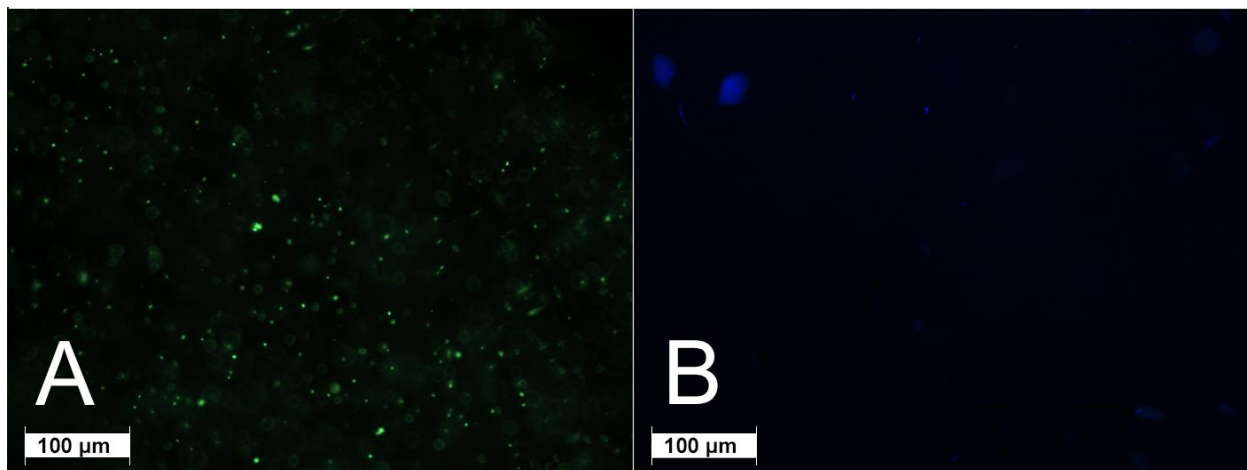


Figure S19. Fluorescence microscopy images of silicone rubber **PDMS-v/PDMS-co-PMHS** obtained with **3d** at 100 °C (A) and 120 °C (B) ($C_{\text{catalyst}} = 1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$).

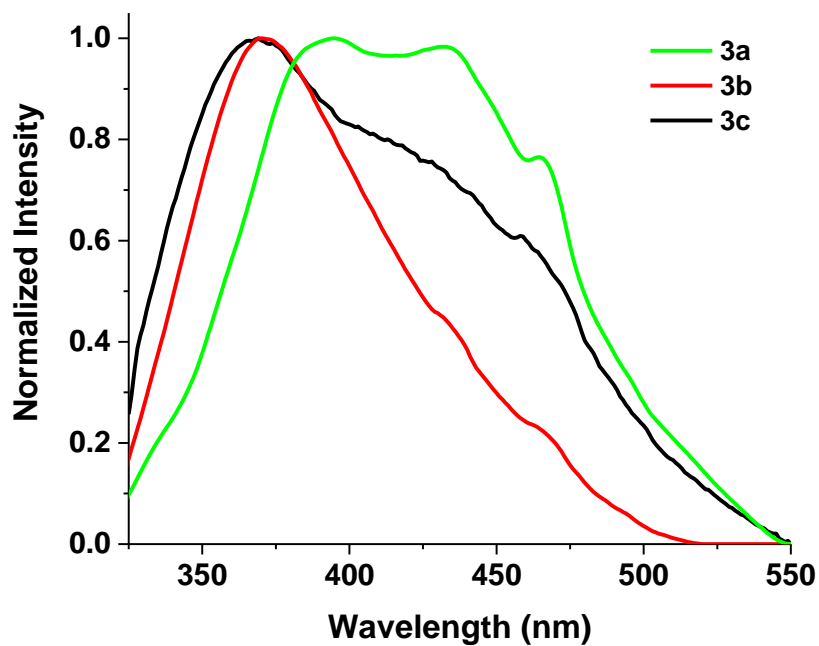


Figure S20. Solid state luminescence spectra of complexes **3a–c**.

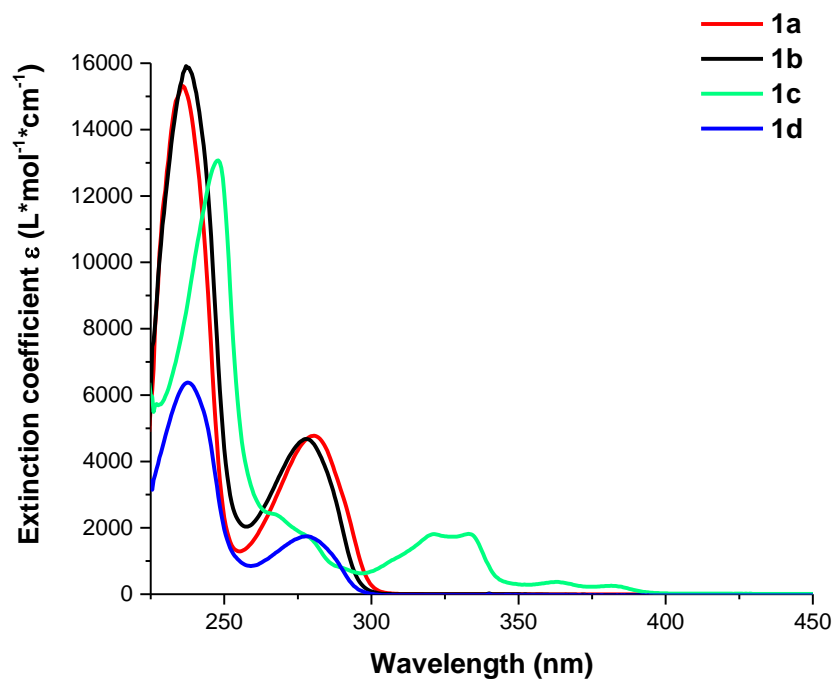


Figure S21. UV spectra of ureas **1a–d** in CH₂Cl₂ solution.

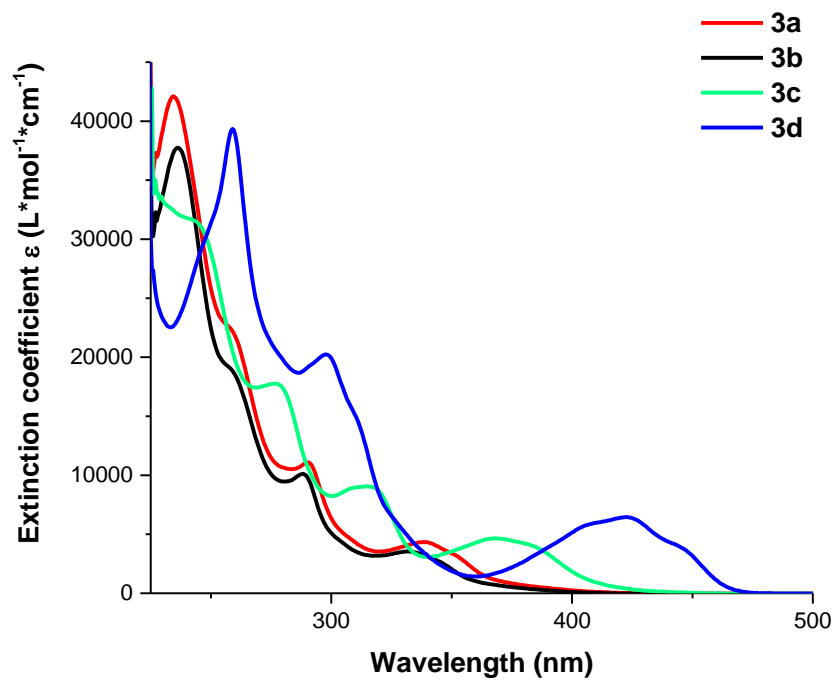


Figure S22. UV spectra of complexes **3a–d** in CH₂Cl₂ solution.

7. References

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