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Supporting Information

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Supporting Information



Scheme S1. Overview of the synthesis of ligand and metal complex precursors.

Synthesis of ligands and metal complex precursors

Synthesis of 1-bromooctane (3)^[1]

CH ₃ (CH ₂) ₇ OH	+	HBr		•	CH ₃ (CH ₂) ₇ Br
			H ₂ SO ₄		
			6 h. 96 °C		
C ₈ H ₁₈ O					C ₈ H ₁₇ Br
130.23 g/mol	80).91 g/mol			193.13 g/mol

In a 250 mL round-bottom flask equipped with reflux condenser, 48% hydrobromic acid (60 g, 0.74 mol) and concentrated sulphuric acid (11 mL, 20.16 g, 0.21 mol) were dissolved in noctanol (30 mL, 24.6 g, 0.19 mol). The clear solution was heated to 100 °C for 6 h. After cooling to room temperature, water (60 mL) was added, the organic phase separated, and extracted with 10% aqueous sodium hydrogen carbonate (90 mL). The aqueous phase was extracted with dichloromethane (2×20 mL), the combined organic phases dried over sodium sulphate, and the solvent removed under vacuum. The resulting yellow oil was distilled under vacuum and the main fraction with boiling point 81 °C (10^{-2} mbar) collected to obtain the product as a colourless liquid. Yield: 55% (20.35 g, 0.11 mol). **IR** (ATR): $\tilde{\nu}$ = 2957, 2925, 2855, 1465 cm⁻¹; ¹H NMR (400.40 MHz, CDCl₃): 3.41 (t, 2H, ${}^{3}J = 6.9$ Hz, CH₂Br), 1.85 (quin, 2H, ${}^{3}J = 6.7$ Hz, $CH_2CH_2CH_2Br$), 1.42 (quin, 2H, ³J = 7.5 Hz, $CH_2CH_2CH_2CH_2Br$), 1.32-1.27 (m, 8H, $(CH_2)_4CH_3$, 0.88 (t, 3H, ${}^{3}J = 7.1$ Hz, CH₃) ppm; ${}^{13}C$ NMR (100.68 MHz, CDCl₃): $\delta = 34.21$ (CH₂Br), 33.02 (CH₂CH₂Br), 31.92 (CH₂CH₂CH₃), 29.27 (CH₂(CH₂)₂CH₃), 28.90 (CH₂(CH₂)₃CH₃), 28.35 (CH₂(CH₂)₂Br), 22.78 (CH₂CH₃), 14.23 (CH₃) ppm; Elemental analysis (%) calcd. for C₈H₁₇Br: C 49.75, H 9.87; found (%): C 51.76, H 9.29; due to trace amounts of *n*-octanol which remained after the distillation, no accurate CHN analysis results could be obtained.





Synthesis of 1-bromodecane (4)^[1]

CH ₃ (CH ₂) ₉ OH	+	HBr	>	CH ₃ (CH ₂) ₉ Br
			H_2SO_4	
			5 h, 120 °C	
C ₁₀ H ₂₂ O				C ₁₀ H ₂₁ Br
158.28 g/mol		80.91 g/mol		221.18 g/mol

In a 250 mL round-bottom flask, 1-decanol (32 mL, 26.4 g, 0.17 mol) was cooled in ice and then, concentrated sulphuric acid (6 mL, 0.11 mol) and 48% hydrobromic acid (52.4 g, 0.64 mol) were added. The mixture was headed to reflux for 5 h and then carefully diluted with water (50 mL). The organic phase was separated and carefully washed with ice-cold concentrated sulphuric acid (2×10 mL) to removed remaining 1-decanol as well as other impurities. Then, it was washed with a mixture of methanol and water (2:1 v/v, 20 mL), water (2×10 mL), 5% aqueous sodium hydrogen carbonate (20 mL), and again water (10 mL). The organic phase was then dried over sodium sulphate and the solvent removed under vacuum. The resulting yellow liquid was distilled under vacuum (10⁻³ mbar) and the main fraction boiling at 91 °C collected to obtain the product as a colourless liquid. Yield: 62% (23.46 g, 0.11 mol). IR (ATR): $\tilde{\nu}$ = 2957, 2934, 2884, 1466 cm⁻¹; ¹**H NMR** (400.40 MHz, CDCl₃): $\delta = 3.41$ (t, 2H, ³J = 6.9 Hz, CH₂Br), 1.85 (quin, 2H, ${}^{3}J = 7.0$ Hz, CH₂CH₂CH₂Br), 1.42 (quin, 2H, ${}^{3}J = 7.4$ Hz, $CH_2CH_2CH_2CH_2Br$), 1.28-1.27 (m, 12H, (CH_2)₆CH₃), 0.88 (t, 3H, ${}^{3}J = 7.0$ Hz, CH_3) ppm; ¹³C **NMR** (100.68 MHz, CDCl₃): $\delta = 34.20$ (CH₂Br), 33.00 (CH₂CH₂Br), 32.03 (CH₃CH₂CH₂), 29.65 (CH₂), 29.60 (CH₂), 29.44 (CH₂), 28.92 (CH₂(CH₂)₂CH₂Br), 28.34 (CH₂CH₂CH₂Br), 22.82 (CH₃CH₂), 14.25 (CH₃) ppm; Elemental analysis (%) calcd. for C₁₀H₂₁Br: C 54.30, H 9.57; found (%):C 54.21, H 9.61.





Synthesis of *n*-octylmagnesium bromide (5)^[2]

CH ₃ (CH ₂) ₇ Br	+	Mg	>	CH ₃ (CH ₂) ₇ MgBr
C ₈ H ₁₇ Br 193.13 g/mol			a) I ₂ , RT b) Et ₂ O, RT c) 1 h, 30 °C	C ₈ H ₁₇ BrMg 217.43 g/mol

In a three-neck round-bottom flask equipped with a dropping funnel, anhydrous magnesium chips (1.34 g, 55.0 mmol) were mixed with a few crystals of iodine and kept under argon overnight. The, anhydrous and peroxide-free diethyl ether (10 mL) was added. The dropping funnel was charged with a solution of 1-bromooctane (8.75 mL, 9.71 g, 50 .3 mmol) in diethyl ether (10 mL) and a few drops carefully added to the magnesium chips in diethyl ether. When the solution started to boil, dropwise addition was slowly continued. After complete addition, the reaction mixture was heated to reflux for 1 h and then a sample taken and titrated with 1 M oxalic acid (2 mL) using phenolphthalein as an indicator. The resulting approx. 2 M solution of the Grignard reactant was then directly used in the next step.

Synthesis of *n*-decylmagnesium bromide (6)^[2]

CH ₃ (CH ₂) ₉ Br	+	Mg		CH ₃ (CH ₂) ₉ MgBr
C ₁₀ H ₂₁ Br			a) Et ₂ O, RT	C ₁₀ H ₂₁ BrMg
221.18 g/mol			b) 1 h, 30 °C	245.49

In a three-neck round-bottom flask equipped with a dropping funnel, anhydrous magnesium chips (521 mg, 21.4 mmol) were layered with anhydrous peroxide-free diethyl ether (15 mL). Then, the dropping funnel was charged with a solution of 1-bromodecane (5 mL, 5.35 g, 24.2 mmol) in diethyl ether (10 mL). A small amount of this solution (approx. 0.7 mL) was added to the magnesium chips until the diethyl ether started to boil. Then, the remaining 1-bromodecane was added dropwise and the reaction mixture heated to reflux for 1 h. The resulting solution of the Grignard reactant was then directly used in the next step.

Synthesis of 1-(pyridin-2-yl)nonan-1-one (8)^[2]



In a three-neck round-bottom flask equipped with a dropping funnel, 2-cyanopyridine (2.08 g, 20 mmol) was dissolved in anhydrous diethyl ether (40 mL) under argon and cooled to -15 °C with a mixture of sodium chloride and ice. Then, 2 M n-octylmagnesium bromide (20 mL, 40 mmol) was slowly added. The solution turned dark and stirring was continued at -15 °C for 1.5 h. The reaction was then warmed to room temperature over 4.5 h and quenched by added of 2 M hydrochloric acid (15 mL). After stirring at 0 °C for 15 min, the resulting yellow solution was adjusted with 2 M aqueous sodium hydroxide (approx. 15 mL) to pH 8-9. The organic phase was then separated, dried over sodium sulphate, and the solvent removed under vacuum. The resulting solid material was purified by column chromatography on silica using a mixture of petrol ether und ethyl acetate (9:1 v/v) as the eluent. After removal of the solvent under vacuum, the product was obtained as a yellow oil. Yield: 72% (3.16 g, 14.4 mmol). **IR** (ATR): $\tilde{\nu} = 2961, 2925, 2854, 1703 \text{ (C=O)}, 1697, 1258, 1087, 1008, 795, 788 \text{ cm}^{-1}; {}^{1}\text{H NMR} (500.13)$ MHz, CDCl₃): $\delta = 8.65$ (ddd, 1H, ${}^{3}J = 4.8$ Hz, ${}^{4}J = 1.7$ Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, ${}^{3}J = 1.7$ Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, ${}^{3}J = 1.7$ Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, ${}^{3}J = 1.7$ Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, ${}^{3}J = 1.7$ Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, ${}^{3}J = 1.7$ Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, ${}^{3}J = 1.7$ Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, ${}^{3}J = 1.7$ Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, ${}^{3}J = 1.7$ Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, ${}^{3}J = 1.7$ Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, {}^{3}J = 1.7 Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, {}^{3}J = 1.7 Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, {}^{3}J = 1.7 Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, {}^{3}J = 1.7 Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, {}^{3}J = 1.7 Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, {}^{3}J = 1.7 Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, {}^{3}J = 1.7 Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, {}^{3}J = 1.7 Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, {}^{3}J = 1.7 Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, {}^{3}J = 1.7 Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, {}^{3}J = 1.7 Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, {}^{3}J = 1.7 Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, {}^{3}J = 1.7 Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, {}^{3}J = 1.7 Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, {}^{3}J = 1.7 Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, {}^{3}J = 1.7 Hz, ${}^{5}J = 0.9$ Hz, H6), 8.01 (td, 1H, {}^{5}J = 0.9 Hz, H6), 8.01 (td, 1H, {}^{5}J = 0.9 Hz, H6), 8.01 (td, 1H, {}^{5}J = 0.9 7.8 Hz, ${}^{4}J = 1.2$ Hz, H3), 7.80 (dt, 1H, ${}^{3}J = 7.7$ Hz, ${}^{4}J = 1.7$ Hz, H4), 7.43 (ddd, 1H, ${}^{3}J = 7.6$ Hz, ${}^{3}J = 4.8$ Hz, ${}^{4}J = 1.3$ Hz, H5), 3.18 (t, 2H, ${}^{3}J = 7.3$ Hz, C(CH₂)=O), 1.70 (quin, 2H, ${}^{3}J = 7.3$ Hz, C(CH₂CH₂)O), 1.38-1.21 (m, 10H, CH₃CH₂), 0.85 (t, 3H, ${}^{3}J = 7.0$ Hz, CH₃) ppm; ${}^{13}C$ NMR $(125.76 \text{ MHz}, \text{CDCl}_3): \delta = 202.31 (C=O), 153.68 (C2), 148.99 (C6), 136.94 (C4), 127.04 (C5),$ 121.85 (C3), 37.82 (C(CH₂)O), 31.96 (CH₂CH₂CH₃), 29.80 (CH₃(CH₂)₂CH₂) 29.56 (CH₃(CH₂)₃CH₂), 29.47 (CH₃(CH₂)₄CH₂), 29.29 (CH₃(CH₂)₅CH₂), 24.10 (CH₃(CH₂)₆CH₂), 22.76 (CH₃CH₂) 14.20 (CH₃) ppm; **MS** (ASAP): $m/z = 220.1691 [M+H]^+$; Elemental analysis (%) calcd. for C₁₄H₂₁NO: C 76.67, H 9.65, N 6.39; found (%): C 76.57, H 9.94, N 6.36.



S8

Synthesis of 1-(pyridin-2-yl)undecan-1-one (9)^[2]



In a three-neck round-bottom flask equipped with a dropping funnel, 2-cyanopyridine (2.08 g, 20 mmol) was dissolved in anhydrous diethyl ether (40 mL) under argon and cooled to -15 °C with a mixture of sodium chloride and ice. Then, *n*-decylmagnesium bromide (15 mL, 30 mmol) was slowly added. The resulting yellow solution was stirred at -15 °C for 2 h and then warmed to room temperature over 4 h. After quenching with 2 M hydrochloric acid (11 mL), stirring was continued at 0 °C for 15 min. Then, 2 M aqueous sodium hydroxide (10 mL) was added to adjust the mixture to pH 8-9. The organic phase was separated, dried over sodium sulphate, and the solvent removed under vacuum. The resulting solid material was purified by column chromatography on silica using a mixture of petrol ether und ethyl acetate (9:1 v/v) as the eluent. After removal of the solvent under vacuum, the product was obtained as a yellow oil. Yield: 67% (3.25 g, 13.13 mmol). **IR** (ATR): $\tilde{\nu}$ = 3250, 2923, 2853, 1703 (C=O), 1693, 1584, 1463, 1436, 995 cm⁻¹; ¹**H NMR** (400.40 MHz, CDCl₃): $\delta = 8.68$ (ddd, 1H, ³J = 4.8 Hz, ⁴J = 1.7 Hz, ${}^{5}J = 0.9$ Hz, H6), 8.03 (td, 1H, ${}^{3}J = 7.8$ Hz, ${}^{4}J = 1.7$ Hz, H3), 7.84 (dt, 1H, ${}^{3}J = 7.7$ Hz, ${}^{4}J = 1.7$ Hz, H4), 7.47 (ddd, 1H, ${}^{3}J = 7.6$ Hz, ${}^{3}J = 4.8$ Hz, ${}^{4}J = 1.3$ Hz, H5), 3.21 (t, 2H, ${}^{3}J = 7.5$ Hz, CH₂CH₂CO), 1.72 (quin, 2H, ${}^{3}J = 7.4$ Hz, CH₂CH₂CO), 1.41-1.25 (m, 14H, (CH₂)₇CH₃), 0.85 (t, 3H, ${}^{3}J = 6.9$ Hz, CH₃) ppm; ${}^{13}C$ NMR (100.68 MHz, CDCl₃): $\delta = 202.32$ (C(CH₂)=O), 153.69 (C2), 148.99 (C6), 137.02 (C4), 127.08 (C5), 121.92 (C3), 37.88 (C(CH₂)=O), 32.04 (CH₂CH₂CH₃), 29.83 (CH₂), 29.80 (CH₂), 29.67 (CH₂), 29.63 (CH₂), 29.50 (CH₂), 28.46 (CH₂), 24.14 (C(CH₂CH₂)=O), 22.82 (CH₃CH₂) 14.24 (CH₃) ppm; Elemental analysis (%) calcd. for C₁₆H₂₅NO: C 77.68, H 10.19, N 5.66; found (%): C 77.82, H 10.38, N 5.62.



Synthesis of *n*-dodecyl isothiocyanate (12)^[3]

Attention!!! Thiophosgene is a malodorous, highly volatile, and extremely toxic liquid. It should only be handeled in a well-ventilated fume hood by experienced personnel. Particular care has to be taken when opening the original bottle due to significant overpressure inside. In a 250 mL round-bottom flask equipped with a reflux condenser, thiophosgene (0.7 mL, 1.04 g, 9 mmol) was dissolved in chloroform (15 mL). Then, a solution of dodecylamine (1.85 g, 10 mmol) in chloroform (10 mL) was slowly added via syringe. After complete addition, water (5 mL) was slowly added, followed by 1 M aqueous sodium hydroxide (24 mL). Stirring at room temperature was continued for 3 h and then, chloroform (10 mL) and *n*-pentane (20 mL) added. The organic phase was separated and the aqueous phase extracted with chloroform (2×25 mL) and n-pentane (2×25 mL). The combined organic phases were dried over sodium sulphate and the solvent removed under vacuum to obtain the product as a yelloworange oil. Yield: 86% (1.96 g, 8.6 mmol). ¹**H NMR** (500.13 MHz, DMSO- d_6): $\delta = 3.64$ (t, 2H, ${}^{3}J = 6.5$ Hz, CH₂N), 1.62 (quin, 2H, ${}^{3}J = 7.0$ Hz, CH₂CH₂CH₂NCS), 1.25 (s, 18H, (CH₂)₉CH₃), 0.86 (t, 3H, ${}^{3}J = 6.7$ Hz, CH₂CH₃) ppm; ${}^{13}C$ NMR (125.76 MHz, DMSO- d_{6}): $\delta = 127.82$ (C=S), 45.18 (CH₂NCS), 31.77 (CH₂CH₂CH₃), 29.58 (CH₂CH₂NCS), 29.54 (CH₂), 29.50 (CH₂), 29.49 (CH₂), 29.31 (CH₂), 29.19 (CH₂), 26.82 (CH₂CH₂CH₂NCS), 22.57 (CH₂CH₃), 14.43 (CH₃) ppm; Elemental analysis (%) calcd. for C₁₃H₂₅NS: C 68.66, H 11.08, N 6.16, S 14.10; found (%): C 68.95, H 10.62, N 6.93, S 13.88.



Synthesis of *N*-methylhydrazine carbothioamide (15)^[4]

H ₃ C-N=C=S	+ NH ₂ NH ₂ ·	H ₂ O Isopropanol RT, 0.5 h	$\overset{S}{\overset{H}{_3}C-NH-\overset{H}{C}-NH-NH_2}$
C ₂ H ₃ NS	N ₂ H ₆	O	C ₂ H ₇ N ₃ S
73.11 g/mol	50.06 g/	′mol	105.16 g/mol

In a 100 mL round-bottom flask, hydrazine hydrate (2 mL, 2.06 g, 41 mmol) was dissolved in isopropanol (20 mL). Then, methyl isothiocyanate (1.51 g, 21 mmol) was slowly added, leading to immediate formation of a white precipitate. After stirring at room temperature for 1 h, the solid material was collected by filtration, washed with isopropanol (3×5 mL) and dried under vacuum to obtain the product as a white solid. Yield: 64% (1.43 g, 13.5 mmol). **IR** (ATR): \tilde{v} = 3283, 3196 (NH), 3139, 2964, 2935, 1564, 1507, 1463, 1267, 1171, 1057, 1027, 971, 912, 751 (C=S) cm⁻¹; ¹H NMR (500.13 MHz, DMSO-*d*₆): δ = 8.55 (s, 1H, N*H*NH₂), 7.80 (s, 1H, CH₃N*H*), 4.41 (s, 2H, NHNH₂), 1.03 (d, ³*J* = 4.9 Hz, 3H, CH₃) ppm; ¹³C NMR (125.76 MHz, DMSO-*d*₆): δ = 182.43 (*C*=S), 30.65 (*C*H₃) ppm; **Elemental analysis** (%) calcd. for C₂H₇N₃S: C 22.84, H 6.71, N 39.96, S 30.49; found (%): C 22.70, H 6.61, N 41.55, S 31.55.







Synthesis of N-dodecylhydrazine carbothioamide (16)^[4]

$$H_{3}C(CH_{2})_{11}NCS + NH_{2}NH_{2} H_{2}O \xrightarrow[RT, 1 h]{} H_{3}C(H_{2}C)_{11} - NH - C'_{11} + NH_{2}NH_{2}O \xrightarrow[RT, 1 h]{} H_{3}C(H_{2}C)_{11} - NH - C'_{11} + NH_{2}O \xrightarrow[RT, 1 h]{} H_{1}O(H_{2}C)_{11} - NH - C'_{11}O(H_{2}C)_{11} + NH_{2}O \xrightarrow[RT, 1 h]{} H_{1}O(H_{2}C)_{11} - NH - C'_{11}O(H_{2}C)_{11} + NH_{2}O \xrightarrow[RT, 1 h]{} H_{1}O(H_{2}C)_{11} - NH - C'_{11}O(H_{2}C)_{11} + NH_{2}O \xrightarrow[RT, 1 h]{} H_{1}O(H_{2}C)_{11} - NH - C'_{11}O(H_{2}C)_{11} - NH_{2}O \xrightarrow[RT, 1 h]{} H_{1}O(H_{2}C)_{11} - NH_{2}O \xrightarrow[RT, 1 h]{} H_{1}O(H_{2}O)_{11} - NH_{2}$$

In a 100 mL round-bottom flask, hydrazine hydrate (0.5 mL, 0.516 g, 10.3 mmol) was dissolved in isopropanol (30 mL). Then, dodecyl isothiocyanate (1.35 mg, 6 mmol) was added dropwise. The yellow solution gradually turned colourless and a solid material started to precipitate. After stirring at room temperature for 60 min, the resulting colourless product was filtered off, washed with isopropanol (3x5 mL) and dried under vacuum. Yield: 49% (765 mg, 2.95 mmol). **IR** (ATR): $\tilde{v} = 3264$ (NH₂), 2915 (CH₂), 2849 (CH₂), 1562, 1555, 1471 cm⁻¹; ¹**H NMR** (500.13 MHz, DMSO-*d*₆): $\delta = 8.52$ (s, 1H, N*H*NH₂), 7.77 (s, 1H, C₁₂H₂₅N*H*), 4.41(s, 2H, NHN*H*₂), 3.42 (q, 2H, ³*J* = 6.9 Hz, CH₂CH₂NH), 1.50-1.46 (quin, 2H, ³*J* = 6.8 Hz, CH₂CH₂CH₂NH), 1.24 (s, 18H, (CH₂)₉CH₃), 0.85 (t, 3H, ³*J* = 6.8 Hz, CH₂CH₃) ppm; ¹³C **NMR** (125.76 MHz, DMSO*d*₆): $\delta = 181.14$ (*C*=S), 42.85 (*C*H₂NH), 31.30 (*C*H₂CH₂NH), 29.11 (*C*H₂CH₂CH₃), 29.07 (*C*H₂), 29.03 (*C*H₂), 29.02 (*C*H₂), 28.84 (*C*H₂), 28.72 (*C*H₂), 26.35 (*C*H₂CH₂CH₂NH), 22.10 (*C*H₂CH₃), 13.96 (*C*H₃) ppm; **Elemental analysis** (%) calcd. for C₁₃H₂₉N₃S: C 60.18, H 11.27, N 16.20, S 12.36; found (%): C 60.29, H 11.55, N 16.25, S 11.97.





Synthesis of *N*-phenylhydrazine carbothioamide (17)^[4]



In a 100 mL round-bottom flask, hydrazine hydrate (2 mL, 2.06 g, 41 mmol) was dissolved in isopropanol (20 mL). Then, phenyl isothiocyanate (2.5 mL, 2.84 g, 21 mmol) was added dropwise, leading to immediate formation of a white precipitate. After stirring at room temperature for 30 min, the solid material was collected by filtration, washed with isopropanol (3×5 mL) and dried under vacuum to obtain the product as a white solid. Yield: 82% (2.74 g, 16.40 mmol). **IR** (ATR): $\tilde{v} = 3301$, 3155, 3103, 2943, 1596, 1546, 1521, 1447, 1282, 1218, 1192, 1068, 966, 913, 895, 737 (C=S) cm⁻¹; ¹H NMR (500.13 MHz, DMSO-*d*₆): $\delta = 9.81$ (m, 1H, N*H*NH₂), 9.11 (s, 1H, C₆H₅N*H*), 7.66-7.53 (m, 2H, H2/H6), 7.37-7.28 (m, 2H, H3/H5), 7.09 (t, 1H, ³*J* = 7.3 Hz, H4), 4.80 (s, 2H, NHN*H*₂) ppm; ¹³C NMR (125.76 MHz, DMSO-*d*₆): $\delta = 179.88$ (*C*=S), 139.74 (C1), 128.51 (C2/C6), 124.51 (C3/C5), 123.91 (C4) ppm; **Elemental analysis** (%) calcd. for C₇H₉N₃S: C 50.28, H 5.42, N 25.13, S 19.17; found (%): C 50.18, H 5.19, N 23.29, S 19.39.





Synthesis of *N*-phenyl-2-(pyridin-2-ylmethylen)hydrazin-1-carbothioamide HL_{py}^{H,Ph} (20) [5,6]



N-Phenylhydrazine carbothioamide (539 mg, 3.22 mmol) und pyridine-2-carbaldehyde (0.35 mL, 394 mg, 4.24 mmol) were mixed in ethanol (30 mL). Then, glacial acetic acid (0.25 mL) was added and the suspension heated to 85 °C for 4 h. After cooling to room temperature, the resulting solid was filtered off, washed with ethanol (2×10 mL) and diethyl ether (2×5 mL), and dried under vacuum to obtain the product as a colourless solid. Yield: 71% (582 mg, 2.27 mmol). **IR** (ATR): $\tilde{v} = 1740$, 1549, 1465, 1369, 1219, 1191, 694, 666 cm⁻¹; ¹**H NMR** (400.40 MHz, DMSO-*d*₆): $\delta = 12.02$ (s, 1H, CHNN*H*), 10.25 (s, 1H, C₆H₅N*H*), 8.59 (d, 1H, ³*J* = 4.8 Hz, H6), 8.44 (d, H3, ³*J* = 8.0 Hz, H3), 8.20 (s, 1H, *CHN*), 7.85 (dt, 1H, ³*J* = 7.7 Hz, ⁴*J* = 1.3 Hz, H4), 7.55 (d, 2H, ³*J* = 7.6 Hz, H2′/H6′), 7.41-7.37 (m, 3H, H3′/H5′, H5), 7.23 (t, 1H, ³*J* = 7.4 Hz, H4′) ppm; ¹³C **NMR** (100.68 MHz, DMSO-*d*₆): $\delta = 176.42$ (*C*=S), 153.17 (C2), 149.35 (C6), 143.08 (*C*H=N), 138.95 (C1′), 136.49 (C4), 128.11 (C3′/C5′), 126.10 (C4′), 125.55 (C2′/C6′), 124.25 (C5), 120.62 (C3) ppm; **Elemental analysis** (%) calcd. for C₁₃H₁₂N₄S: C 60.91, H 4.72, N 21.86, S 12.51; found (%): C 60.79, H 4.81, N 21.99, S 12.45.







SynthesisofN-methyl-2-(1-(pyridin-2-yl)ethyliden)hydrazin-1-carbothioamideHL_{py}CH3,CH3 (21) ^[5, 6]



In a round-bottom flask, *N*-methylhydrazine carbothioamide (500 mg, 4.75 mmol) was dissolved in methanol (30 mL) with heating to 70 °C. Then, 2-acetylpyridine (0.56 mL, 605.7 mg, 5 mmol) was added and the clear solution heated to 70 °C for 4 h. After cooling to room temperature, the solvent was partially removed under vacuum. The resulting pale-yellow solid was filtered off, washed with methanol (2×5 mL) and diethyl ether (2×5 mL), and finally dried under vacuum. Yield: 57% (572 mg, 2.75 mmol). **IR** (ATR): \tilde{v} = 3281, 3228 (NH), 1535 (C=N), 1495, 1473, 1458, 1433, 1419, 1408, 1230, 1148, 1073, 1035, 779 (C-S) cm⁻¹; ¹H NMR (500.13 MHz, DMSO-*d*₆): δ = 10.34 (s, 1H, C(CH₃)NN*H*), 8.62 (q, 1H, ³*J* = 4.4 Hz, CH₃N*H*), 8.58 (ddd, 1H, ³*J* = 4.8 Hz, ⁴*J* = 1.8 Hz, ⁵*J* = 1.0 Hz, H6), 8.42 (td, 1H, ³*J* = 8.1 Hz, ⁴*J* = 1.1 Hz, H3), 7.82 (ddd, 1H, ³*J* = 8.2 Hz, ³*J* = 7.4 Hz, ⁴*J* = 1.8 Hz, H4), 7.38 (ddd, 1H, ³*J* = 7.6 Hz, ³*J* = 4.8 Hz, ⁴*J* = 1.3 Hz, H5), 3.05 (d, 3H, ³*J* = 4.6 Hz, CH₃NH), 2.38 (s, 3H, C(CH₃)N) ppm; ¹³C NMR (125.76 MHz, DMSO-*d*₆): δ = 179.16 (C=S), 155.22 (C2), 148.93 (C6), 148.32 (C(CH₃)=N), 136.77 (C4), 124.35 (C5), 121.24 (C3), 31.64 (CH₃NH), 12.57 (C(CH₃)=N) ppm; **Elemental analysis** (%) calcd. for C₉H₁₂N₄S: C 51.90, H 5.81, N 26.90, S 15.40; found (%): C 51.44, H 5.94, N 26.59, S 15.84.



S22

Synthesis of *N*-dodecyl-2-(1-(pyridin-2-yl)ethyliden)hydrazin-1-carbothioamide HL_{py}^{CH3,(CH2)11CH3} (22) ^[5, 6]



In a 100 mL round-bottom flask, N-dodecyl-2-(1-(pyridin-2-yl)ethyliden)hydrazin-1carbothioamid (350 mg, 1.35 mmol) was dissolved in ethanol (15 mL) with heating to 50 °C. Then, 2-acetylpyridine (0.2 mL, 216 mg, 1.78 mmol) and glacial acetic acid (0.1 mL) were added and the yellow solution heated to reflux for 5 h. After cooling to room temperature, the solvent was removed under vacuum and the resulting material recrystallized from a mixture of ethanol and water (3:1 v/v). The resulting pale-yellow product was washed with diethyl ether $(2 \times 5 \text{ mL})$ and then dried under vacuum. Yield: 62% (303 mg, 0.84 mmol). **IR** (ATR): $\tilde{\nu} = 3330$, 3211, 2916, 2851, 1532, 1498, 1467, 1458, 1434, 1265, 1243, 1220, 1199, 778 cm⁻¹; ¹H NMR $(500.13 \text{ MHz}, \text{DMSO-}d_6)$: $\delta = 10.24$ (s, 1H, C(CH₃)NNH), 8.64 (t, ${}^{3}J = 5.8 \text{ Hz}, 1H, C_{12}H_{25}NH)$, 8.59-8.57 (m, 1H, H6), 8.39 (d, 1H, ${}^{3}J = 8.1$ Hz, H3), 7.81 (dt, 1H, ${}^{3}J = 8.0$ Hz, ${}^{4}J = 1.8$ Hz, H4), 7.39 (ddd, 1H, ${}^{3}J = 7.5$ Hz, ${}^{3}J = 4.9$ Hz, ${}^{4}J = 1.4$ Hz, H5), 3.58 (q, 2H, ${}^{3}J = 8.0$ Hz, CH₂NH), 2.38 (s, 3H, C(CH₃)NNH), 1.61-1.58 (m, 2H, CH₂CH₂(CH₂)₉CH₃), 1.29-1.23 (m, 18H, $(CH_2)_9CH_3$), 0.85 (t, 3H, $^3J = 6.9$ Hz, CH_2CH_3) ppm; ^{13}C NMR (125.76 MHz, DMSO- d_6): δ =177.80 (C=S), 154.72 (C2), 148.47 (C6), 147.88 (C(CH₃)=N), 136.31 (C4), 123.88 (C5), 120.75 (C3), 43.73 (CH₂NH), 31.76 (CH₂CH₂CH₃), 29.04 (CH₂), 29.01 (CH₂), 28.98 (CH₂). 28.79 (CH₂), 28.70 (CH₂), 28.66 (CH₂), 26.82 (NH(CH₂)₂CH₂), 22.57 (CH₂CH₃), 14.43 (CH₃), 12.58 (C(CH₃)=N) ppm; Elemental analysis (%) calcd. for C₂₀H₃₄N₄S: C 66.25, H 9.45, N 15.45, S 8.84; found (%): C 66.04, H 9.65, N 15.07, S 8.76.



S24

Synthesis of *N*-phenyl-2-(1-(pyridin-2-yl)ethyliden)hydrazin-1-carbothioamide HL_{py}^{CH3,Ph} (23)^[5,6]



In a 100 mL round-bottom flask, N-phenylhydrazine carbothioamide (500 mg, 3.00 mmol) was dissolved in ethanol (15 mL). Then, glacial acetic acid (0.25 mL) and 2-acetylpyridine (0.35 mL, 324 mg, 3.12 mmol) were added and the solution heated to 85 °C for 4 h. After cooling to room temperature, the resulting pale-yellow precipitate was filtered off, washed with ethanol (2 mL) and dried under vacuum. After recrystallization from a mixture of acetonitrile and ethanol (2:1 v/v, 40 mL), the product was obtained as a yellow solid. Yield: 23% (186 mg, 0.69 mmol). **IR** (ATR): $\tilde{\nu}$ = 3298, 3239, 3051, 1514 (C=N), 1495, 1484, 1466, 1458, 1436, 1419, 1395, 1361, 1299, 1263, 1186, 1156, 1146, 781 (C=S), 739 cm⁻¹; ¹H NMR (500.13 MHz, DMSO- d_6): $\delta = 10.67$ (s, 1H, C(CH₃)NNH), 10.19 (s, 1H, C₆H₅NH), 8.60 (ddd, 1H, ³J = 4.0 Hz, ${}^{4}J = 1.8$ Hz, ${}^{5}J = 0.9$ Hz, H6), 8.54 (d, 1H, ${}^{3}J = 8.1$ Hz, H3), 7.81 (ddd, 1H, ${}^{3}J = 8.1$ Hz, ${}^{3}J$ = 7.6 Hz, ${}^{4}J$ = 1.8 Hz, H4), 7.56 (dd, 2H, ${}^{3}J$ = 8.4 Hz, ${}^{4}J$ = 1.2 Hz, H2⁻/H6⁻), 7.42-7.37 (m, 3H, H3[′]/H5[′], H5), 7.25-7.21 (m, 1H, H4[′]), 2.08 (s, 3H, CH₃) ppm; ¹³C NMR (125.76 MHz, DMSO d_6): $\delta = 177.26$ (C=S), 154.51 (C2), 149.19 (C6), 148.48 (C(CH_3)=N), 139.14 (C1²), 136.37 (C4), 128.10 (C3⁻/C5⁻), 126.18 (C4⁻), 125.55 (C2⁻/C6⁻), 124.11 (C5), 121.24 (C3), 12.48 (CH₃) ppm; Elemental analysis (%) calcd. for C₁₄H₁₄N₄S: C 62.20, H 5.22, N 20.72, S 11.86; found (%): C 61.87, H 4.83, N 20.63, S 11.50.



Synthesis of *N*-methyl-2-(1-(pyridin-2-yl)nonyliden)hydrazin-1-carbothioamide HL_{py}^{(CH2)7CH3,CH3} (24) ^[5, 6]



In a 100 mL round-bottom flask, N-methylhydrazine carbothioamide (193 mg, 1.84 mmol) was dissolved in ethanol (10 mL). Then, a mixture of glacial acetic acid (0.12 mL) und 1-(pyridin-2-yl)nonan-1-one (424 mg, 1.93 mmol) in ethanol (1 mL) were added and the mixture heated to 85 °C for 5 h. After cooling to room temperature, the resulting pale-yellow solid was filtered off, washed with ethanol (2×5 mL), and dried under vacuum. Yield: 51% (424 mg, 1.38 mmol). **IR** (ATR): $\tilde{\nu}$ = 3375, 3319 (NH), 2922, 2851, 1543 (C=N), 1536, 1502, 1463, 1431, 1414, 1375, 1336, 1286, 1232, 1204, 1161, 1128, 1107, 1051, 787 (C=S), 737 cm⁻¹; ¹H NMR (500.13 MHz, DMSO- d_6): $\delta = 10.50$ (s, 1H, C(CH₂)NNH)), 8.58-8.56 (m, 2H, H6, CH₃NH), 8.37 (dt, 1H, ³J = 8.1 Hz, ${}^{4}J = 1.0$ Hz, H3), 7.80 (ddd, 1H, ${}^{3}J = 8.1$ Hz, ${}^{3}J = 7.4$ Hz, ${}^{4}J = 1.8$ Hz, H4), 7.37 (ddd, 1H, ${}^{3}J = 7.4$ Hz, ${}^{3}J = 4.8$ Hz, ${}^{4}J = 1.2$ Hz, H5), 3.06-3.02 (m, 5H, C(CH₂)=N, CH₃NH), 1.39-1.22 (m, 12H, $(CH_2)_6$), 0.82 (t, 3H, ${}^{3}J = 6.9$ Hz, CH_2CH_3) ppm; ¹³C NMR (125.76 MHz, DMSO- d_6): $\delta = 179.16$ (C=S), 154.99 (C2), 152.24 (C6), 148.95 (C(CH₂)=N), 136.79 (C4), 124.21 (C5), 121.57 (C3), 31.71 (CH₂CH₂CH₃), 31.63 (CH₃NH), 29.45 (CH₂), 29.29 (CH₂), 29.07 (CH₂), 26.20 (C(CH₂)=N), 24.78 (CH₂CH₂C=N), 22.54 (CH₂CH₃), 14.41 (CH₃) ppm; **Elemental analysis** (%) calcd. for C₁₆H₂₆N₄S: C 62.71, H 8.55, N 18.28, S 10.46; found (%): C 62.90, H 8.79, N 17.18, S 10.49.



S28

Synthesis of *N*-methyl-2-(1-pyridin-2-yl)undecyliden)hydrazin-1-carbothiamide HL_{py}^{(CH2)9CH3,CH3} (25) ^[5, 6]



In a 100 mL round-bottom flask, *N*-methylhydrazine carbothioamide (194.1 mg, 1.85 mmol) was dissolved in ethanol (10 mL) and then, a mixture of glacial acetic acid (0.12 mL) und 1-(pyridin-2-yl)undecan-1-one (471 mg, 1.90 mmol) in ethanol (1 mL) added. The yellow mixture was heated to 85 °C for 5 h. After cooling to +4 °C for 3 d, the resulting pale-yellow solid was filtered off, washed with ice-cold ethanol (2×2 mL), and dried under vacuum. Yield: 84% (521.2 mg, 1.56 mmol). **IR** (ATR): $\tilde{\nu}$ = 3360, 3132, 2954, 2917, 2848, 1535 (C=N), 1469, 1436, 1400, 1374, 1287, 1236, 1221, 1106, 1043, 781 (C=S), 719 cm⁻¹; ¹H NMR (400.40 MHz, DMSO- d_6): $\delta = 13.98$ (s, 1H, C(CH₂)NNH), 10.43 (s, 2H, CH₃NH), 8.76-8.74 (m, 1H, H6), 8.58-8.51 (m, 5H, H3), 8.34 (d, 2H, ${}^{3}J = 8.0$ Hz, H3), 8.05 (dt, 2H, ${}^{3}J = 7.8$ Hz, ${}^{4}J = 1.6$ Hz, H4), 7.81-7.77 (m, 3H, H4), 7.53 (m, 1H, H5), 7.38-7.35 (m, 2H, H5), 3.05-3.01 (m, 12H, CH₃NH, C(CH₂)=N), 2.75-2.71(m, 2H, CH₂), 1.58-1.51 (m, 2H, CH₂), 1.42-1.20 (m, 47H, CH₂), 0.84 (t, 9H, CH₃) ppm; The compound is present as a mixture of several isomers. Thus, a complete assignment and integration was not possible for all signals; ¹³C NMR (100.68 MHz, DMSO d_6): $\delta = 178.73$ (C=S), 154.59 (C2), 151.06 (C6), 148.65 (C(CH_2)=N), 136.60 (C4), 123.99 (C5), 121.27 (C3), 31.40 (CH₂CH₂CH₃), 31.32 (CH₃NH), 29.04 (CH₂), 28.95 (CH₂), 28.80 (CH₂), 25.82 (C(CH₂CH₂)=N), 24.46 (C(CH₂)=N), 22.22 (CH₂CH₃), 14.10 (CH₃); Elemental analysis (%) calcd for C₁₈H₃₀N₄S: C 64.63, H 9.04, N 16.75, S 9.59; found (%): C 65.12, H 9.27, N 16.09, S 9.01.



Synthesis of *N*-phenyl-2-(1-(pyridin-2-yl)nonyliden)hydrazin-1-carbothioamide HL_{py}^{(CH2)7CH3,Ph} (26) ^[5, 6]



N-Phenylhydrazine carbothioamide (250 mg, 1.25 mmol) was dissolved in ethanol (9 mL) and then, glacial acetic acid (0.12 mL) and 1-(pyridin-2-yl)nonan-1-one (351 mg, 1.6 mmol) added and the clear solution heated to 85 °C for 5 h. After cooling to +4 °C for 3 d, resulting yellow precipitate was filtered off, washed with ethanol (2 mL) and dried under vacuum. Yield: 44% (244.5 mg, 0.66 mmol). **IR** (ATR): $\tilde{\nu} = 3100, 2925, 2858, 1597, 1547$ (C=N), 1537, 1507, 1497, 1475, 1457, 1438, 1417, 1371, 1345, 1251, 1182, 1156, 1129, 1092, 1070, 750 (C=S) cm⁻¹; ¹H **NMR** (500.13 MHz, DMDO- d_6): $\delta = 10.84$ (s, 1H, C(CH₂)NNH), 10.16 (s, 1H, C₆H₅NH), 8.60 (ddd, 1H, ${}^{3}J = 4.8$ Hz, ${}^{4}J = 1.8$ Hz, ${}^{5}J = 1.0$ Hz, H6), 8.48 (d, 1H, ${}^{3}J = 8.0$ Hz, H3), 7.81 (ddd, 1H, ${}^{3}J = 8.1$ Hz, ${}^{3}J = 7.7$ Hz, ${}^{4}J = 1.8$ Hz, H4), 7.57 (dd, 2H, ${}^{3}J = 8.2$ Hz, ${}^{4}J = 1.2$ Hz, H2⁻/H6⁻), 7.40–7.33 (m, 3H, H3²/H5², H5), 7.24-7.21 (m, 1H, H4²), 3.11 (t, 2H, ${}^{3}J = 7.6$ Hz, C(CH₂)=N), 1.45 (quin, 2H, ³*J* = 7.5 Hz, C(CH₂CH₂)=N), 1.36–1.24 (m, 2H, C(CH₂CH₂)=N), 1.29–1.24 (m, 8H, CH₂), 0.84 (m, 3H, CH₃) ppm; ¹³C NMR (125.76 MHz, DMDO- d_6): $\delta = 177.23$ (C=S), 154.28 (C2), 151.97 (C6), 148.51 (C(CH₂)=N)), 139.15 (C1[']), 136.46 (C4), 128.11 (C3[']/C5[']), 126.14 (C4⁻), 125.53 (C2⁻/C6⁻), 124.96 (C5), 121.59 (C3), 31.26 (CH₂CH₂CH₃), 29.05 (CH₂), 28.83 (CH₂), 28.63 (CH₂), 25.87 (C(CH₂CH₂)=N), 24.66 (C(CH₂CH₂)=N), 22.09 (CH₂CH₃), 13.97 (CH₃) ppm; Elemental analysis (%) calcd for C₂₁H₂₈N₄S: C 68.44, H 7.66, N 15.20, S 8.70; found (%): C 68.47, H 7.94, N 14.96, S 8.92.



Synthesis of *N*-phenyl-2-(1-(2-pyridyl)undecyliden)hydrazin-1-carbothioamide HL_{py}^{(CH2)9CH3,Ph} (27) ^[5, 6]



N-Phenylhydrazine carbothioamide (410.1 mg, 2.45 mmol) was dissolved in ethanol (30 mL) and then, a mixture of glacial acetic acid (0.25 mL) and 1-(pyridin-2-yl)undecan-1-one (676.62 mg, 2.74 mmol) in ethanol (5 mL) added. The resulting yellow solution was heated to 80 °C for 5 h, the solvent then partially removed under vacuum and the remaining solution cooled to +4°C for 2 d. The yellow solid which had precipitated was recrystallized from ethanol (20 mL), washed with ice-cold ethanol (2×2 mL) and dried under vacuum. Yield: 66% (645 mg, 1.63 mmol). **IR** (ATR): $\tilde{\nu}$ = 3334 (NH), 2955, 2917, 2850, 1519 (C=N), 1468, 1451, 1420, 1372, 1458, 1181, 1100, 782 (C=S), 720 cm⁻¹; ¹**H NMR** (500.13 MHz, DMSO- d_6): $\delta = 10.83$ (s, H, C(CH₂)NNH), 10.15 (s, 1H, C₆H₅NH), 8.59 (ddd, 1H, ${}^{3}J = 4.9$ Hz, ${}^{4}J = 1.8$ HZ, ${}^{5}J = 1.0$ Hz, H6), 8.48 (d, 1H, ${}^{3}J = 8.1$ Hz, 1H, H3), 7.80 (ddd, 1H, ${}^{3}J = 8.1$ Hz, ${}^{3}J = 7.4$ Hz, ${}^{4}J = 1.8$ Hz, H4), 7.55 (dd, 2H, ${}^{3}J = 8.2$ Hz, ${}^{4}J = 1.4$ Hz, H2′/H6′), 7.40–7.36 (m, 3H, H3′/H5′, H5), 7.22 (m, 1H, H4'), 3.11 (t, 2H, ${}^{3}J = 7.6$ Hz, C(CH₂)=N), 1.45 (quin, 2H, ${}^{3}J = 7.9$ Hz, C(CH₂CH₂)=N), 1.35 (quin, 2H, ${}^{3}J = 7.3$ Hz, C(CH₂CH₂CH₂)=N), 1.23 (m, 12H, (CH₂)₆CH₃), 0.84 (t, 3H, ${}^{3}J =$ 6.9 Hz, CH_3) ppm; ¹³C NMR (125.76 MHz, DMSO- d_6): $\delta = 177.22$ (C=S), 154.29 (C2), 151.99 (C6), 148.47 (C(CH₂)=N), 139.15 (C1[′]), 136.44 (C4), 128.19 (C3[′]/C5[′]), 126.13 (C4[′]), 124.93 (C2[′]/C6[′]), 123.99 (C5), 121.58 (C3), 31.29 (CH₂CH₂CH₃), 29.03 (CH₂), 28.97 (CH₂), 28.87 (CH₂), 28.71 (CH₂), 28.69 (CH₂), 25.87 (CH₂), 24.65 (C(CH₂CH₂)=N), 22.10 (CH₂CH₃), 13.97 (*C*H₃) ppm; **Elemental analysis** (%) calcd. for C₂₃H₃₂N₄S: C 69.66, H 8.13, N 14.13, S 8.09; found (%): C 70.73, H 8.59, N 13.59, S 7.34.


Synthesis of *N*-phenyl-2-(quinolin-2-ylmethylen)hydrazin-1-carbothioamide HL_{quin}^{H,Ph} (30) ^[5, 6]



N-Phenylhydrazine carbothioamide (503.2 mg, 3.00 mmol) and quinoline-2-carbaldehyde (497.3 mg, 3.16 mmol) were dissolved in ethanol (50 mL). Then, glacial acetic acid (0.5 mL) was added and the yellow solution heated to 80 °C for 5 h. The solvent was partially removed under vacuum and the remaining solution stored at + 4 °C for 3 d. The pale-yellow solid which had precipitated was filtered off, washed with ice-cold ethanol (2×10 mL), and dried under vacuum. Yield: 47% (428.4 mg, 1.40 mmol). **IR** (ATR): $\tilde{v} = 1740$, 1543, 1521, 1365, 1234, 1215, 1183, 1098, 827, 756 (C=S) cm⁻¹; ¹**HNMR** (400.40 MHz, DMSO-*d*₆): $\delta = 12.19$ (s, 1H, CHNN*H*), 10.82 (s, 1H, C₆H₅N*H*), 8.62 (d, 1H, ³*J* = 8.4 Hz, H3), 8.39 (d, 1H, ³*J* = 8.4 Hz, H4), 8.34 (s, 1H, C*H*N), 8.11-7.99 (m, 2H, H5, H8), 7.79 (t, 1H, ³*J* = 7.3 Hz, H7), 7.61 (t, 1H, ³*J* = 7.3 Hz, H6), 7.56 (d, 2H, ³*J* = 7.8 Hz, H2′/H6′), 7.43 (t, 2H, ³*J* = 7.8 Hz, 2H, H3′/H5′), 7.25 (t, ³*J* = 7.3 Hz, 1H, H4′) ppm; ¹³C **NMR** (100.68 MHz, DMSO-*d*₆): $\delta = 176.58$ (*C*=S), 153.78 (C2), 147.37 (C8a), 143.08 (*C*H=N), 138.96 (C1′), 136.24 (C4′), 129.96 (C7), 128.82 (C8), 118.45 (C3) ppm; **Elemental analysis** (%) calcd. for C₁₇H₁₄N₄S: C 66.64, H 4.61, N 18.29, S 10.47; found (%): C 66.05, H 4.57, N 18.65, S 10.60.



Synthesis of *N*-phenyl-2-(quinolin-2-ylethylen)hydrazin-1-carbothioamide HL_{quin}^{CH3,Ph} (31) ^[5, 6]



In a 100 mL round-bottom flask, N-phenylhydrazine carbothioamide (234.6 mg, 1.40 mmol) and 1-(quinolin-2-yl)ethan-1-one (236.3 mg, 1.38 mmol) were dissolved in ethanol (30 mL), glacial acetic acid added (0.25 mL) and the yellow solution heated to 85 °C for 6 h. After cooling to +4 °C for 1 h, resulting yellow precipitate was filtered off, washed with ice-cold ethanol (2×10 mL), and dried under vacuum. Yield: 46% (209 mg, 0.65 mmol). IR (ATR): $\tilde{\nu}$ = 3159, 1521, 1493, 1448, 1257, 1183, 1127, 1082, 942, 829, 750, 705 cm⁻¹; ¹H NMR (400.40 MHz, DMSO- d_6): $\delta = 10.75$ (s, 1H, C(CH₃)NNH), 10.31 (s, 1H, C₆H₅NH), 8.73 (d, 1H, ³J = 8.8 Hz, H3), 8.34 (d, 1H, ${}^{3}J = 8.7$ Hz, H4), 8.03 (d, 1H, ${}^{3}J = 8.4$ Hz, H8), 8.00 (d, 1H, ${}^{3}J = 7.8$ Hz, H5), 7.78 (ddd, 1H, ${}^{3}J = 8.4$ Hz, ${}^{3}J = 6.9$ Hz, ${}^{4}J = 1.4$ Hz, H7), 7.62 (ddd, 1H, ${}^{3}J = 8.1$ Hz, ${}^{3}J = 6.8$ Hz, ${}^{4}J = 1.4$ Hz, H6), 7.56 (d, 2H, ${}^{3}J = 7.6$ Hz, H2[′]/H6[′]), 7.41 (t, 2H, ${}^{3}J = 7.8$ Hz, H3[']/H5[']), 7.25 (t, 1H, ${}^{3}J = 7.4$ Hz, H4[']), 2.61 (s, 3H, CH₃) ppm; ${}^{13}C$ NMR (100.68 MHz, DMSO- d_6): $\delta = 177.43$ (C=S), 154.75 (C2), 149.14 (C8a), 146.74 (C(CH₃)=N), 138.19 (C1²), 135.92 (C4), 129.74 (C7), 129.15 (C8), 128.16 (C3⁻/C5⁻), 127.86 (C5), 127.76 (C6), 127.13 (C2[′]/C6[′]), 126.44 (C4[′]), 125.70 (C4a), 119.19 (C3), 12.24 (CH₃) ppm; **Elemental analysis** (%) calcd. for C₁₈H₁₆N₄S: C 67.47, H 5.03, N 17.49, S 10.01; found (%): C 67.30, H 4.92, N 17.98, S 9.74.



Synthesis of [PdCl₂(cod)] (32) ^[7]



Palladium(II) chloride (1679 mg, 9.47 mmol) was suspended in methanol (30 mL) and then 1,5-cyclooctadien (4.6 mL, 4.05 g, 37.35 mmol) added. The reaction mixture was stirred at room temperature for 72 h, during which a yellow precipitate formed, which was filtered off, washed with methanol (2×10 mL) und diethyl ether (2×5 mL) and dried under vacuum. **Yield**: 82% (2.22 g, 7.77 mmol). ¹**H NMR** (500.13 MHz, CDCl₃): δ = 6.32–6.31 (m, 4H, C*H*), 2.94–2.91 (m, 4H, C*H*₂), 2.60–2.56 (m, 4H, C*H*₂) ppm; ¹³C NMR (125.67 MHz, CDCl₃): δ = 116.79 (CH₂), 31.12 (*C*H) ppm; **Elemental analysis** (%): Calcd. for C₈H₁₂N₄PdCl₂: C 33.66, H 4.24; found (%): C 33.58, H 4.44.





Spectral data for metal semithiocarbazone complexes





IR (ATR)

[PdCl(L_{py}^{CH3,CH3})] (35) ^{6, 11, 12}



¹³C NMR (125.76 MHz, DMSO-*d*₆)



IR (ATR)

[PdCl(L_{py}^{CH3,Ph})] (36) ^{6, 11, 12}



¹³C NMR (125.76 MHz, DMSO-*d*₆)



IR (ATR)

[PdCl(L_{py}^{(CH2)7CH3,Ph})] (37) ^[6, 8, 9]





IR (ATR)

[PdCl(L_{py}^{(CH2)9CH3,Ph})] (38) ^[6, 8, 9]



S49



IR (ATR)

$[PtCl(L_{py}^{H,Ph})] (39)^{[6, 8, 9]}$



¹³C NMR (125.76 MHz, DMSO-*d*₆)



IR (ATR)





¹⁹⁵Pt NMR (107.51 MHz, DMSO-*d*₆)



IR (ATR)

[PtCl(L_{py}^{CH3,(CH2)11CH3})] (41) ^[6, 8, 9]



¹³C NMR (125 MHz, CDCl₃, ppm)

Due to low signal intensity, the peaks of C=S and py-C2 were not identified.



¹⁹⁵Pt NMR (107.5 MHz, CDCl₃)



IR (ATR)

[PtCl(L_{py}^{CH3,Ph})] (42) ^[6, 8, 9]



NMR (125.76 MHz, DMSO-*d*₆)



¹⁹⁵Pt NMR (107.51 MHz, DMSO-*d*₆)



IR (ATR)

[PtCl(L_{py}^{(CH2)7CH3,CH3})] (43) ^[6, 8, 9]



¹³C NMR (125.76 MHz, DMSO-*d*₆)



¹⁹⁵Pt NMR (107.51 MHz, DMSO-*d*₆)



IR (ATR)

[PtCl(L_{py}^{(CH2)7CH3,Ph})] (44) ^[6, 8, 9]





IR (ATR)

[PtCl(L_{py}^{(CH2)9CH3,CH3})] (45) ^[6, 8, 9]



S63



¹⁹⁵Pt NMR (107.51 MHz, DMSO-*d*₆)



IR (ATR)

[PtCl(L_{py}^{(CH2)9CH3,Ph})] (46) ^[6, 8, 9]



¹³C NMR (125.76 MHz, DMSO-*d*₆)



¹⁹⁵Pt NMR (107.51 MHz, DMSO-*d*₆)



IR (ATR)

[PdCl(Lquin^{H,Ph})] (47) ^[6, 8, 9]





IR (ATR)

[PdCl(Lquin^{CH3,Ph})] (48) ^[6, 8, 9]





IR (ATR)
$[PtCl(L_{quin}^{H,Ph})] (49)^{[6, 8, 9]}$



¹³C NMR (125.76 MHz, DMSO-*d*₆)



¹⁹⁵Pt NMR (107.51 MHz, DMSO-*d*₆)



IR (ATR)

[PtCl(Lquin^{CH3,Ph})] (50) ^[6, 8, 9]



S73



¹⁹⁵Pt NMR (107.51 MHz, DMSO-*d*₆)



IR (ATR)

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