Experimental Procedures

Synthesis of **1**:

Zinc acetate (0.493g, 2.68 mmol) was dissolved in tetrahydrofuran (65 mL) by the addition of TMEDA (0.61 mL, 4.02 mmol). Bis(trimethylsilyl)selenide (1.16 mL, 6.36 mmol) was then added at 0°C, and the resulting clear, colorless solution was stirred for 15 minutes. 200 mL of cold (-25°C) pentane was then added, and the reaction mixture was stored at -78°C to avoid decomposition of the complex, as demonstrated by the formation of $Se(SiMe_3)_2$ after overnight storage in THF at 0°C Single colorless, needle-like crystals suitable for X-ray crystallography formed from the reaction solution at -78°C after 3 days. Yield 92%; ^{1}H NMR ($CDCl_3$, 223K): δ 0.43(s) ($-SiMe_3$), δ 2.62(s) (NCH_2), δ 2.53(s) (NCH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 223K): δ 6.09 ($-SiMe_3$), δ 56.29 (NCH_2), δ 48.25 (NCH_3), ^{29}Si NMR ($CDCl_3$, 223K) δ 6.34, ^{77}Se NMR ($CDCl_3$, 223K) δ -512. Attempts to obtain elemental analysis were unsuccessful due to the thermal instability of the complex, evidenced by a slight yellowing of the pure crystalline solid after storage at room temperature in an inert atmosphere for 24 hours. The solid, however, can be stored at low temperature (-40°C) for extended periods.

Synthesis of **2**:

Cadmium acetate (0.25 g, 1.09 mmol) was dissolved in THF (35 mL) with P*n*Pr$_3$ (0.65 mL, 3.27 mmol), followed by the addition of $PhSeSiMe_3$ (0.27 mL, 1.09 mmol). The resulting colorless solution was cooled to -78°C and added to a freshly prepared solution of **1** (0.54 mmol) with excess TMEDA, also at -78°C. Upon warming to room temperature, a pale yellow solution was obtained. Reduction of the volume by ~50%, followed by the addition

of Et_2O (6 mL) and cooling to -30°C produced pale yellow needle-like crystals suitable for X-ray crystallographic analysis. Yield 60%.

Synthesis of **3**:

A solution of the tellurolate analogue of **1**, (*N,N'*-tmeda)Zn($TeSiMe_3$)$_2$, synthesized *via* the addition of Te($SiMe_3$)$_2$ (0.46 mL, 2.18 mmol) to a solution of TMEDA (0.24 mL, 1.62 mmol) and Zn(OAc)$_2$ (o.20 g, 1.09 mmol) in 70 mL THF at -78°C, was prepared. This solution was immediately added to a pale yellow solution of cadmium acetate (0.50 g, 2.18 mmol), PEt_3 (0.96 mL, 6.54 mmol), and $PhTeSiMe_3$ (0.50 mL, 2.18 mmol), also at -78°C. The reaction is allowed to warm slowly to -5°C overnight, yielding a bright yellow solution with a small amount of a bright yellow crystalline solid. The solution was filtered and stored undisturbed at room temperature in the absence of light, from which bright yellow single crystals suitable for X-ray crystallography form after three days. Yield 32%.

Characterization of 1-3

Elemental analysis calculated for $C_{74}H_{126}N_{10}O_2Zn_5Cd_{11}Se_{19}$: C, 20.88; H, 2.99. Found: C, 21.49, H, 2.33.

Elemental analysis calculated for $C_{70}H_{118}N_{10}OZn_5Cd_{11}Te_{19}$: C, 16.42, H, 2.33. Found: C, 15.67, H, 1.79.

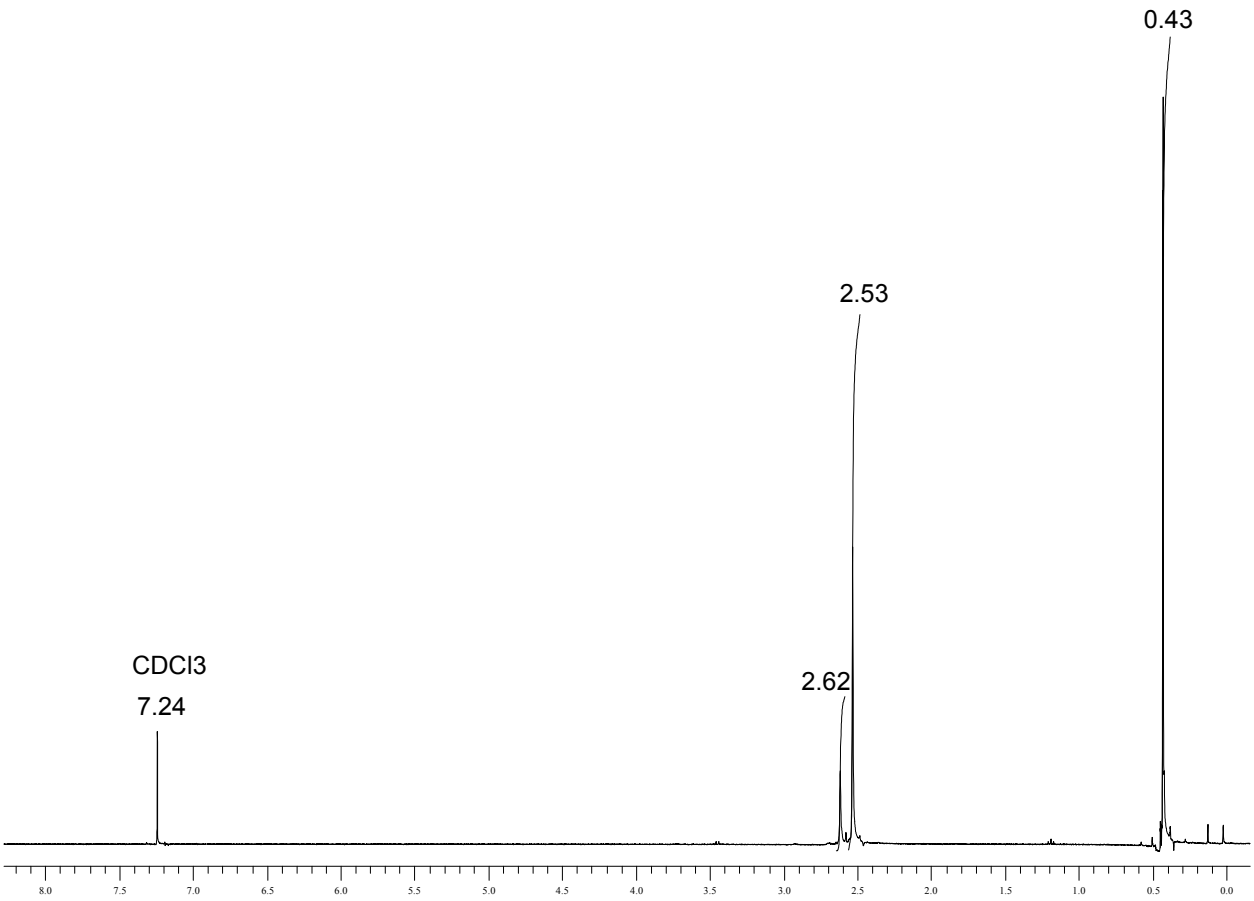

Figure S1. ^{1}H NMR spectrum of complex **1** in $CDCl_3$.