Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Synthesis and Structures of *N*-Arylcyano-β-diketiminate Zinc Complexes and Adducts, their Application in Ring-Opening Polymerization of L-lactide

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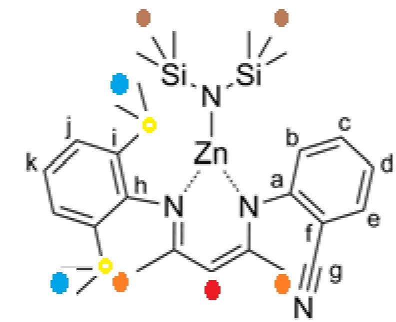
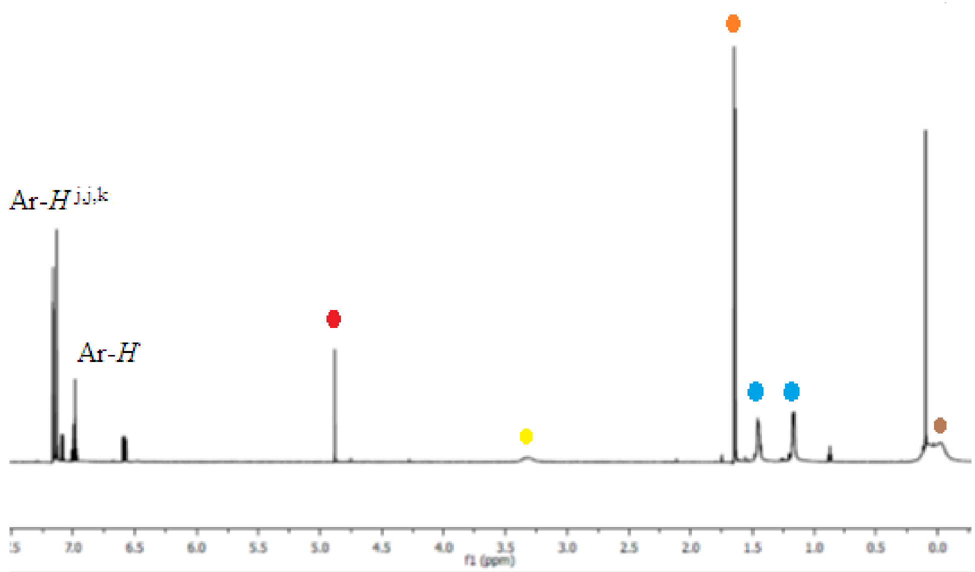
1. Synthesis and Characterization of compounds

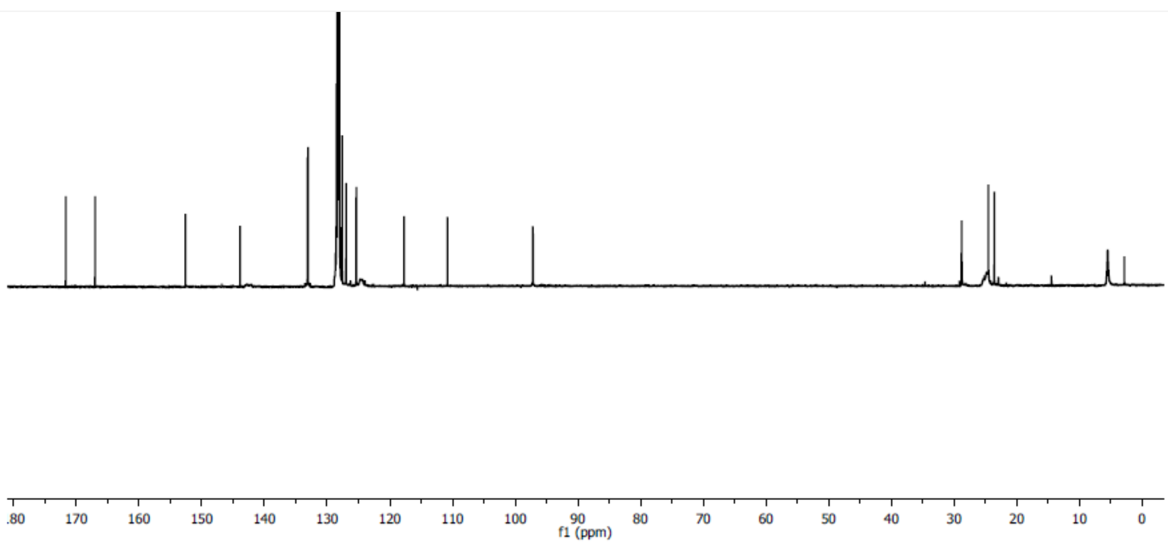
Preparation of $ZnL_1N(SiMe_3)_2$, 1.

$Zn\{N(SiMe_3)_2\}_2$ (128.9 mg, 278.1 mmol) and L_1H (100 mg, 278.1 mmol) were dissolved in toluene and stirred at 80 °C for 12 h. Evaporation of the solvent yielded a pale yellow, air-sensitive solid, that was washed with 3-4 ml cold pentane, and dried *in vacuo.* Yield: 110 mg (188.3 mmol, 68 %). Single crystals for X-ray crystallography were grown by layering pentane onto a toluene solution of compound (**1**) at-30 °C.





^{1}H NMR (600 MHz, C_6D_6, 299 K)



^{13}C {1H} (100 MHz, C_6D_6, 299 K)

^{1}H NMR (600 MHz, C_6D_6, 299 K): δ/ppm = 0.03 (bd, 18H, N(Si*Me*$_3$)$_2$), 1.16 (d, J = 1.16 Hz, 6H, CH(C*H*$_3$)$_2$), 1.46 (d, 6H, J = 1.16 Hz, CH(C*H*$_3$)$_2$), 1.64 (s, 3H, *Me*), 1.65 (s, 3H, *Me*), 3.33 (bs, 2H, C*H*(CH$_3$)$_2$), 4.88 (s, 1H, C*H*), 6.59 (m, 1H, Ar-*H*), 6.99 (m, 2H, Ar-*H*), 7.09 (m, 1H, Ar-*H*), 7.13 (m, 3H, Ar-*H* [j,j,k]).

^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 299 K): δ/ppm = 5.22 (N(Si(*C*H$_3$)$_3$)$_2$), 23.58 (CH(*C*H$_3$)$_2$), 24.51 (CH(*C*H$_3$)$_2$), 24.79 (*Me*), 28.77 (*C*H(CH$_3$)$_2$), 97.22 (*C*H), 110.77 (Ar-*C*), 117.67 (*C*≡N), 125.34 (Ar-*CH*), 126.98 (Ar-*CH*), 127.59 (Ar-*CH*), 128.06 (Ar-*C*), 128.51 (Ar-*C*), 133.05 (Ar-*CH*), 133.13 (Ar-*CH*), 143.87 (Ar-*C*), 152.59 (Ar-*C*), 167.01 (*C*=N), 171.69 (*C*=N).

GCOSY (600 MHz / 600 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{1}H) = 1.16/ 3.33 (CH(C*H*$_3$)$_2$/ C*H*(CH$_3$)$_2$), 3.33/ 1.16, 1.46 (C*H*(CH$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$), 6.59/ 6.99, 7.09 (Ar-*H*/ Ar-*H*, Ar-*H*), 6.99/ 6.59 (Ar-*H*/ Ar-*H*), 7.09/ 6.59, 6.99 (Ar-*H*/ Ar-*H*, Ar-*H*).

^{13}C-GHSQC (600 MHz / 100 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{13}C) = 0.03/ 5.22 (N(Si(C*H*$_3$)$_3$)$_2$/ N(Si(*C*H$_3$)$_3$)$_2$), 1.16/ 23.58 (CH(C*H*$_3$)$_2$/ CH(*C*H$_3$)$_2$), 1.46/ 24.51 (CH(C*H*$_3$)$_2$/ CH(*C*H$_3$)$_2$), 1.64/ 24.79 (*Me*/ *Me*), 1.65/ 24.79 (*Me*/ *Me*), 3.33/ 28.77 (C*H*(CH$_3$)$_2$/ *C*H(CH$_3$)$_2$), 4.88/ 97.22 (C*H*/ *C*H), 6.59/ 125.34 (Ar-*H*/ Ar-*C*H), 6.99/ 127.59, 133.05 (Ar-*H*/ Ar-*C*H, Ar-*C*H), 7.09/ 133.13 (Ar-*H*/ Ar-*C*H), 7.13/ 126.98 (Ar-*H*/ Ar-*C*H).

^{1}H, ^{13}C-GHMQC (600 MHz / 100 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{13}C) = 0.03/ 5.22 (N(Si(C*H*$_3$)$_3$)$_2$/ N(Si(*C*H$_3$)$_3$)$_2$), 1.16/ 23.58, 24.79, 143.87 (CH(C*H*$_3$)$_2$/ CH(*C*H$_3$)$_2$, *C*H, Ar-*C*), 1.46/ 24.5, 24.79, 143.87, 152.59 (CH(C*H*$_3$)$_2$/ CH(*C*H$_3$)$_2$, *C*H, Ar-*C*, Ar-*C*), 1.64/ 97.22, 167.01 (*Me*/ C*H*, *C*=N), 1.65/ 97.22, 171.69 (*Me*/ C*H*, *C*=N), 4.88/ 24.79, 143.87, 152.59, 167.01, 171.69 (C*H*/ *Me*, Ar-*C*, Ar-*C*, *C*=N, *C*=N), 6.59/ 110.77, 127.59 (Ar-*H*/ Ar-*C*, Ar-*C*H), 6.99/ 127.59, 133.05 (Ar-*H*/ Ar-*C*H, Ar-*CH*), 6.99/ 117.67, 125.34, 133.13, 152.59 (Ar-*H*/ *C*≡N, Ar-*CH*, Ar-*CH*, Ar-*C*), 7.09/ 117.67, 133.13, 152.59 (Ar-*H*/ *C*≡N, Ar-*CH*, Ar-*C*), 7.13/ 23.58, 24.51, 125.34, 143.87 (Ar-*H*/ CH(*C*H$_3$)$_2$, CH(*C*H$_3$)$_2$, Ar-*CH*, Ar-*C*).

^{29}Si, {^{1}H} (75 MHz, C_6D_6, 299 K): δ = 0.05 ppm.

DPFGNOE (600 MHz, C_6D_6, 299 K): δ ($^1H_{ir}$) / δ ($^1H_{res}$) = 1.16/ 1.46, 1.64, 1.65, 3.33, 7.13 (CH(C*H*$_3$)$_2$/ CH(C*H*$_3$)$_2$, *Me*, *Me*, C*H*(CH$_3$)$_2$, Ar-*H*), 1.46/ 3.33, 7.13 (CH(C*H*$_3$)$_2$/ C*H*(CH$_3$)$_2$, Ar-*H*), 1.64/ 3.33, 4.88, 6.59 (*Me/* C*H*(CH$_3$)$_2$, C*H*, Ar-*H*), 6.59/ 6.99, 7.09 (Ar-*H/* Ar-*H,* Ar-*H*), 6.99/ 7.09 (Ar-*H/* Ar-*H*), 7.13/ 1.16, 1.46 (Ar-*H/* CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$).

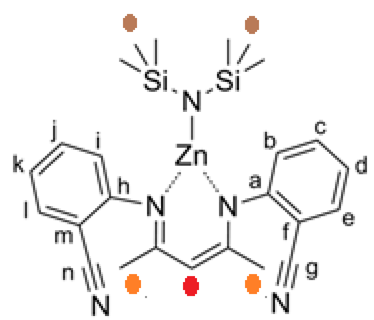
1D TOCSY (600 MHz, C_6D_6, 299 K): δ ($^1H_{ir}$) / δ ($^1H_{res}$) = 1.16/ 1.46, 3.33 ($CH(C\mathit{H}_3)_2$/ $CH(C\mathit{H}_3)_2$, $C\mathit{H}(CH_3)_2$), 1.46/ 1.16, 3.33 ($CH(C\mathit{H}_3)_2$/ $CH(C\mathit{H}_3)_2$, $C\mathit{H}(CH_3)_2$), 6.59/ 6.99, 7.09 (Ar-*H*/ Ar-*H*, Ar-*H*).

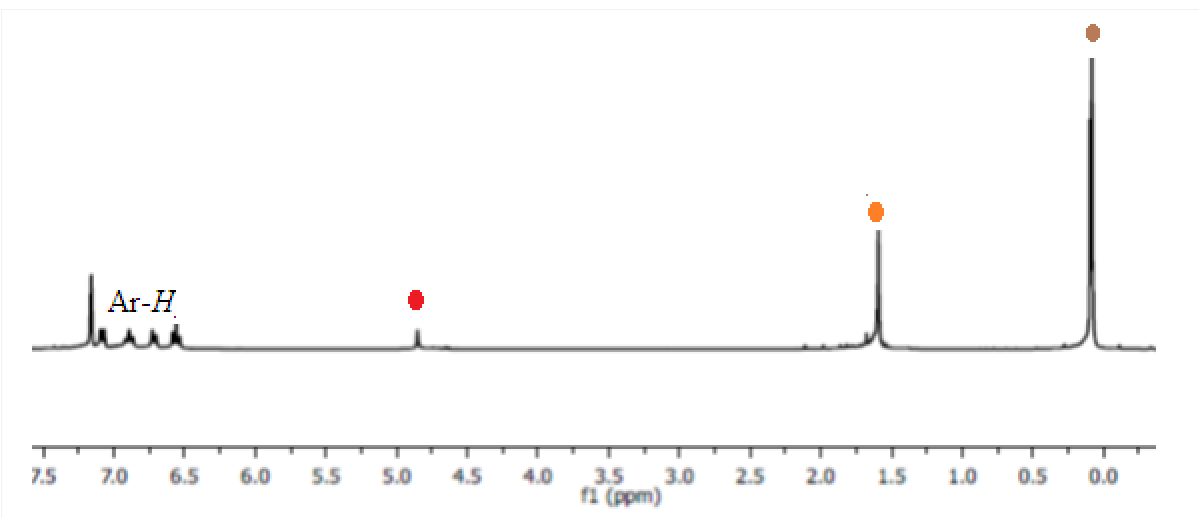
IR (KBr): ν/cm^{-1} = 2225 (ν (C≡N), s).

Elemental analysis (%) $C_{30}H_{46}N_4Si_2Zn$ (M = 584.2640 g/mol): calculated C 61.67, H 7.94, N 9.59; found C 62.13, H 7.47, N 9.54.

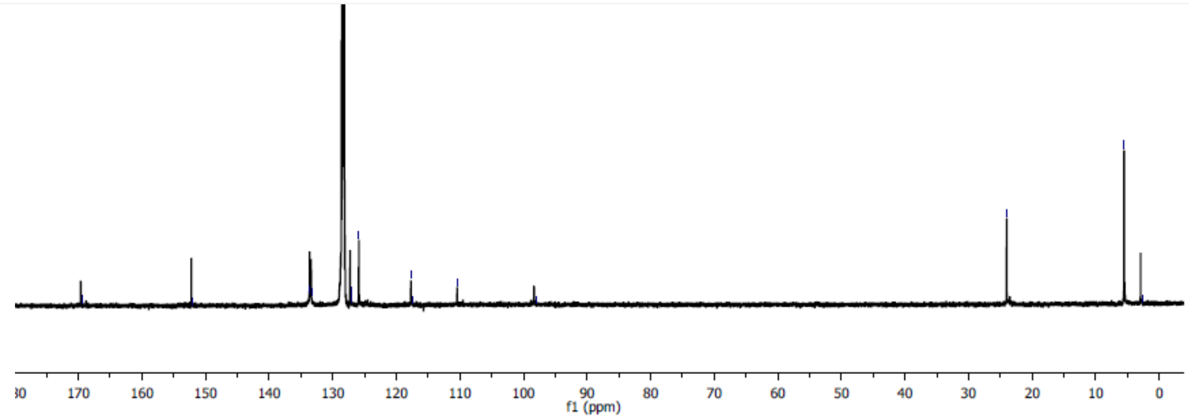
Preparation of $ZnL_2N(SiMe_3)_2$, 2.

$Zn\{N(SiMe_3)_2\}_2$ (154.3 mg, 332.9 mmol) and L_2H (100 mg, 332.9 mmol) were dissolved in toluene and stirred at 80 °C for 12 h. Evaporation of the solvent yielded a yellow, air-sensitive solid, that was washed with 5 ml cold pentane, and dried *in vacuo*. Yield: 131 mg (249.5 mmol, 75 %). Single crystals for X-ray crystallography were grown by layering pentane onto a toluene solution of compound (**2**) at-30 °C.





^{1}H NMR (600 MHz, C_6D_6, 299 K)



^{13}C {1H} (100 MHz, C_6D_6, 299 K)

^{1}H NMR (600 MHz, C_6D_6, 299 K): δ/ppm = 0.00 (s, 18H, N(Si*Me*$_3$)$_2$), 1.59 (s, 6H, *Me*), 4.85 (s, 1H, C*H*), 6.54 (m, 2H, Ar-*H*), 6.70 (m, 2H, Ar-*H*), 6.89 (m, 2H, Ar-*H*), 7.09 (m, 2H, Ar-*H*).

^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 299 K): δ/ppm = 5.24 (N(Si(*C*H$_3$)$_3$)$_2$), 23.73 (*Me*), 97.76 (*C*H), 110.15 (Ar-*C*), 117.42 (*C*≡N), 125.59 (Ar-*C*H), 126.67 (Ar-*C*H), 126.98 (Ar-*C*), 126.79 (Ar-*C*), 133.02 (Ar-*C*H), 133.38 (Ar-*C*H), 151.86 (Ar-*C*), 169.13 (*C*=N).

GCOSY (600 MHz / 600 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{1}H) = 6.54/ 6.89, 7.09 (Ar-C*H*/ Ar-C*H*, Ar-C*H*), 6.70/ 6.89 (Ar-C*H*/ Ar-C*H*), 6.89/ 6.54, 6.70 (Ar-*H*/ Ar-*H*, Ar-*H*), 7.09/ 6.54 (Ar-*H*/ Ar-*H*).

^{13}C-GHSQC (600 MHz / 100 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{13}C) = 0.00/ 5.24 (N(Si(C*H*$_3$)$_3$)$_2$/ N(Si(*C*H$_3$)$_3$)$_2$), 1.59/ 23.73 (*Me*/ *Me*), 4.85/ 97.76 (C*H*/ *C*H), 6.54/ 125.59 (Ar-*H*/ Ar-*C*H), 6.70/ 126.67 (Ar-*H*/ Ar-*C*H), 6.89/ 133.02 (Ar-*H*/ Ar-*C*H), 7.09/ 133.38 (Ar-*H*/ Ar-*C*H).

^{1}H, ^{13}C-GHMQC (600 MHz / 100 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{13}C) = 0.00/ 5.24 (N(Si(C*H*$_3$)$_3$)$_2$/ N(Si(*C*H$_3$)$_3$)$_2$), 1.59/ 97.76, 169.13 (*Me*/ *C*H, *C*=N), 4.85/ 23.73 (C*H*/ *Me*), 6.54/ 110.15, 126.67 (Ar-*H*/ Ar-*C*, Ar-*C*H).

^{29}Si, {^{1}H} (75 MHz, C_6D_6, 299 K): δ = - 0.05 ppm.

DPFGNOE (600 MHz, C_6D_6, 299 K): δ ($^{1}H_{ir}$) / δ ($^{1}H_{res}$) = 1.59/ 14.85 (*Me*/ C*H*), 6.54/ 7.09 (Ar-*H/* Ar-*H*).

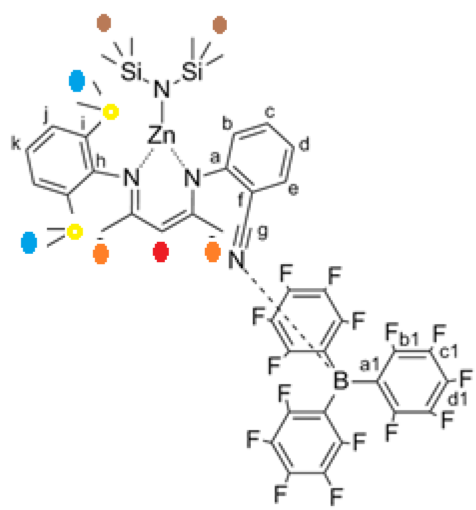
1D TOCSY (600 MHz, C_6D_6, 299 K): δ ($^1H_{ir}$) / δ ($^1H_{res}$) = 1.59/ 14.85 (*Me*/ C*H*), 6.54/ 6.70, 6.89, 7.09 (Ar-*H*/ Ar-*H*, Ar-*H*, Ar-*H*).

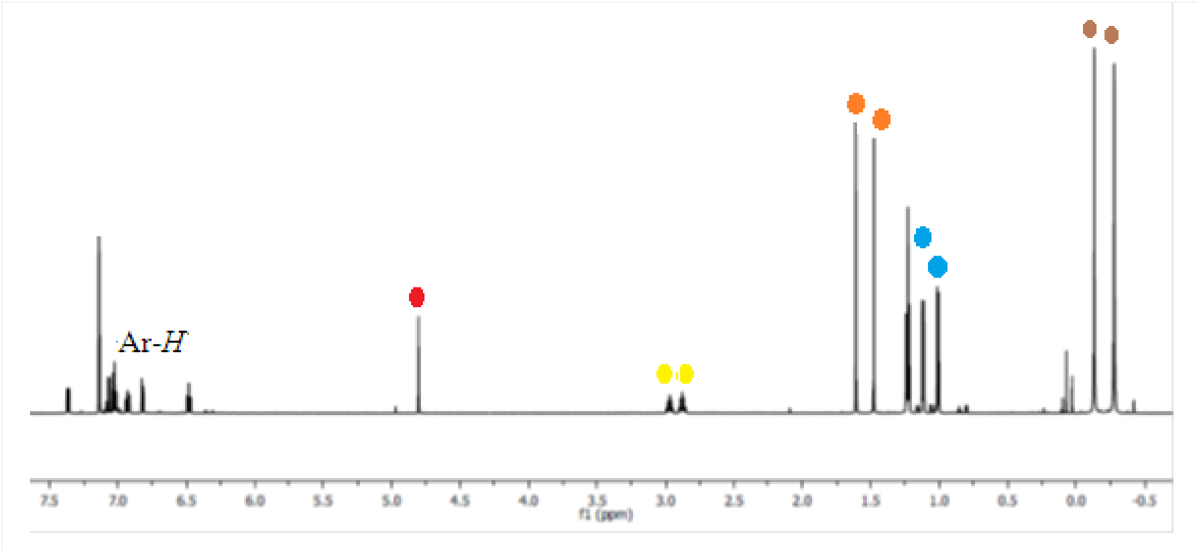
IR (KBr): ν/cm^{-1} = 2226 (ν (C≡N), s).

Elemental analysis (%) $C_{25}H_{33}N_5Si_2Zn$ (M = 525.1140 g/mol): calculated C 57.18, H 6.33, N 13.34; found C 57.23, H 6.01, N 13.21.

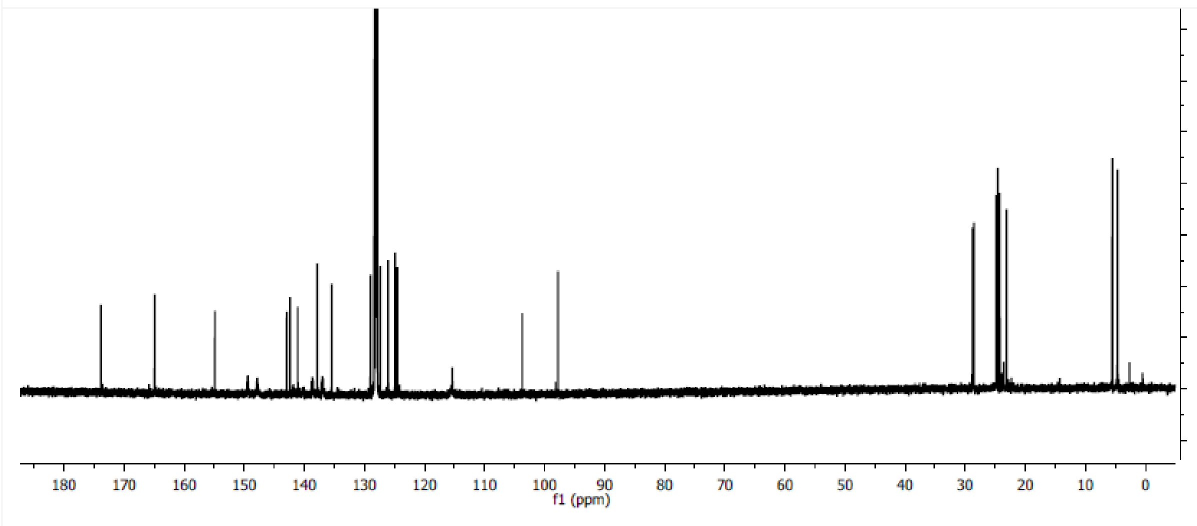
Preparation of ZnL$_1$N(SiMe$_3$)$_2$ * B(C$_6$F$_5$)$_3$, 3.

1 eq of Tris(pentafluorophenyl)borane (17.6 mg in 2 mL of toluene, 34.2 mmol) was added to a toluene solution of **1** (20 mg, 34.2 mmol). The reaction mixture was stirred for 10 min, filtered and dried several hours under vacuum. Compound **3** was isolated as bright yellow solid in 81 % yield.





^{1}H NMR (600 MHz, C_6D_6, 299 K)



^{13}C {1H} (100 MHz, C_6D_6, 299 K)

^{1}H NMR (600 MHz, C_6D_6, 299 K): δ/ppm = 0.11 (s, 9H, N(Si*Me*$_3$)$_2$), 0.25 (s, 9H, N(Si*Me*$_3$)$_2$), 1.03 (d, J = 1.14 Hz, 3H, CH(C*H*$_3$)$_2$), 1.15 (d, J = 1.14 Hz, 3H, CH(C*H*$_3$)$_2$), 1.25 (m, 6H, CH(C*H*$_3$)$_2$), 1.50 (s, 3H, *Me*), 1.63 (s, 3H, *Me*), 2.9 (s, 1H, C*H*(CH$_3$)$_2$), 2.99 (s, 1H, C*H*(CH$_3$)$_2$), 4.83 (s, 1H, C*H*), 6.50 (m, 1H, Ar-*H*^{d}), 6.85 (m, 1H, Ar-*H*), 6.95 (m, 1H, Ar-*H*), 7.05 (m, 2H, Ar-*H*), 7.10 (m, 1H, Ar-*H*), 7.38 (m, 1H, Ar-*H*^{e}).

^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 299 K): δ/ppm = 4.61 (N(Si*Me*$_3$)$_2$), 5.47(N(Si*Me*$_3$)$_2$), 23.04 (*Me*), 24.23 (*Me*), 24.53 (CH(C*H*$_3$)$_2$), 24.57 (CH(C*H*$_3$)$_2$), 24.70 (CH(*C*H$_3$)$_2$), 24.77 (CH(*C*H$_3$)$_2$), 28.52 (*C*H(CH$_3$)$_2$), 28.72 (*C*H(CH$_3$)$_2$), 97.73 (*C*H), 103.72 (Ar-*C*), 115.32

(*C*≡N), 124.49 (Ar-*C*H), 124.87 (Ar-*C*H), 126.04 (Ar-*C*H^{d}), 127.28 (Ar-*C*H), 128.95 (Ar-*C*H), 135.53 (Ar-*C*H^{e}), 137.04 (Ar^{F5}-*C*), 137.89 (Ar-*C*H), 138.56 (Ar^{F5}-*C*), 140.13 (Ar^{F5}-*C*), 141.02 (Ar-*C*), 141.79 (Ar^{F5}-*C*), 142.35 (Ar-*C*), 142.87 (Ar-*C*), 147.78 (Ar^{F5}-*C*), 149.40 (Ar^{F5}-*C*), 154.83 (Ar-*C*), 165.02 (*C*=N), 173.85 (*C*=N).

GCOSY (600 MHz / 600 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{1}H) = 1.03/ 2.9, 2.99 (CH(C*H*$_3$)$_2$ / C*H*(CH$_3$)$_2$, C*H*(CH$_3$)$_2$), 1.15/ 2.9, 2.99 (CH(C*H*$_3$)$_2$/ C*H*(CH$_3$)$_2$, C*H*(CH$_3$)$_2$), 1.25/ 2.9, 2.99 (CH(C*H*$_3$)$_2$/ C*H*(CH$_3$)$_2$, C*H*(CH$_3$)$_2$), 2.9/ 1.03, 1.15, 1.25 (C*H*(CH$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$), 2.99/ 1.03, 1.15, 1.25 (C*H*(CH$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$), 4.83/ 1.50, 1.63 (C*H*/ *Me*, *Me*), 6.50/ 6.85, 7.38 (Ar-*H*^{d}/ Ar-*H*, Ar-*H*^{e}), 6.85/ 6.95 (Ar-*H*/ Ar-*H*), 6.95/ 6.85 (Ar-*H*/ Ar-*H*), 7.05/ 7.10 (Ar-*H*/ Ar-*H*), 7.10/ 7.05 (Ar-*H*/ Ar-*H*), 7.38/ 6.50 (Ar-*H*^{e}/ Ar-*H*^{d}).

^{13}C-GHSQC (600 MHz / 100 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{13}C) = 0.25/ 4.61 (N(Si*Me*$_3$)$_2$ / N(Si*Me*$_3$)$_2$), 0.11/ 5.47 (N(Si*Me*$_3$)$_2$ / N(Si*Me*$_3$)$_2$), 1.03/ 24.53 (CH(C*H*$_3$)$_2$/ CH(*C*H$_3$)$_2$), 1.15/ 24.57 (CH(C*H*$_3$)$_2$/ CH(*C*H$_3$)$_2$), 1.25/ 24.70, 24.77 (CH(C*H*$_3$)$_2$/ CH(*C*H$_3$)$_2$, CH(*C*H$_3$)$_2$), 1.50/ 23.04 (*Me*/ *Me*), 1.63/ 24.23 (*Me*/ *Me*), 2.9/ 28.52 (C*H*(CH$_3$)$_2$/ *C*H(CH$_3$)$_2$), 2.99/ 28.72 (C*H*(CH$_3$)$_2$/ *C*H(CH$_3$)$_2$), 4.83/ 97.73 (C*H*/ *C*H), 6.50/ 126.04 (Ar-C*H*^{d}/ Ar-*C*H^{d}), 6.85/ 128.95 (Ar-C*H*/ Ar-*C*H), 6.95/ 137.89 (Ar-C*H*/ Ar-*C*H), 7.05/ 124.49, 124.87 (Ar-C*H*/ Ar-*C*H, Ar-*C*H), 7.10/ 127.28 (Ar-C*H*/ Ar-*C*H), 7.38/ 135.53 (Ar-C*H*^{e}/ Ar-*C*H).

^{1}H, ^{13}C-GHMQC (600 MHz / 100 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{13}C) = 0.25/ 4.61 (N(Si*Me*$_3$)$_2$ / N(Si*Me*$_3$)$_2$), 0.11/ 5.47 (N(Si*Me*$_3$)$_2$ / N(Si*Me*$_3$)$_2$), 1.03/ 24.53, 24.57, 28.52, 141.02 (CH(C*H*$_3$)$_2$/ CH(*C*H$_3$)$_2$, CH(*C*H$_3$)$_2$, *C*H(CH$_3$)$_2$, Ar-*C*), 1.15/ 24.53, 28.52, 142.35 (CH(C*H*$_3$)$_2$/ CH(*C*H$_3$)$_2$, *C*H(CH$_3$)$_2$, Ar-*C*), 1.25/ 24.70, 24.77, 28.52, 141.02, 142.35 (CH(C*H*$_3$)$_2$/ CH(*C*H$_3$)$_2$, CH(*C*H$_3$)$_2$, *C*H(CH$_3$)$_2$, Ar-*C*, Ar-*C*), 1.50/ 97.73, 165.02 (*Me*/ *C*H, *C*=N), 1.63/ 97.73, 173.85 (*Me*/ *C*H, *C*=N), 2.9/ 24.70, 24.77, 124.49, 141.02, 142.87 (C*H*(CH$_3$)$_2$/ CH(*C*H$_3$)$_2$, CH(*C*H$_3$)$_2$, Ar-*C*H, Ar-*C*, Ar-*C*), 2.99/ 24.53, 24.57, 124.87, 142.35 (C*H*(CH$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, Ar-*C*H, Ar-*C*), 4.83/ 23.04, 24.23, 142.87, 154.83, 165.02, 173.85 (C*H*/ *Me*, *Me*, Ar-*C*, Ar-*C*, *C*=N, *C*=N), 6.50/ 103.72, 128.95 (Ar-C*H*^{d}/ Ar-*C*, Ar-*C*H), 6.85/ 103.72, 126.04 (Ar-C*H*/ Ar-*C*, Ar-*C*H^{d}), 6.95/ 135.53, 154.83 (Ar-C*H*/ Ar-*C*H^{e}, Ar-*C*), 7.05/ 28.52, 28.72, 124.49, 124.87, 141.02, 142.35, 142.87 (Ar-C*H*/ *C*H(CH$_3$)$_2$, *C*H(CH$_3$)$_2$, Ar-*C*H, Ar-*C*H, Ar-*C*, Ar-*C*, Ar-*C*), 7.10/ 141.02 (Ar-C*H*/ Ar-*C*), 7.38/ 115.32, 154.83 (Ar-C*H*^{e}/ *C*≡N, Ar-*C*).

DPFGNOE (600 MHz, C_6D_6, 299 K): δ ($^1H_{ir}$) / δ ($^1H_{res}$) = 0.11/ 0.25, 1.25, 2.9, 2.99, 6.85 (N(Si*Me*$_3$)$_2$/ N(Si*Me*$_3$)$_2$, CH(C*H*$_3$)$_2$, C*H*(CH$_3$)$_2$, C*H*(CH$_3$)$_2$, Ar-C*H*), 0.25/ 0.11, 1.25, 2.9, 2.99, 6.85 (N(Si*Me*$_3$)$_2$/ N(Si*Me*$_3$)$_2$, CH(C*H*$_3$)$_2$, C*H*(CH$_3$)$_2$, C*H*(CH$_3$)$_2$, Ar-C*H*), 1.03/ 1.15, 1.25, 1.63, 2.9, 6.95 (CH(C*H*$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, C*H*(CH$_3$)$_2$, Ar-C*H*), 1.15/ 1.03, 1.25, 1.63, 2.99, 6.95 (CH(C*H*$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, C*H*(CH$_3$)$_2$, Ar-C*H*), 1.63/ 2.9, 2.99, 6.95 (C*H/* C*H*(CH$_3$)$_2$, C*H*(CH$_3$)$_2$, Ar-*H*), 1.50/ 4.83 (*Me*/ C*H*), 1.63/ 0.11, 0.25, 4.83, (*Me*/ N(Si*Me*$_3$)$_2$, N(Si*Me*$_3$)$_2$, C*H*), 4.83/ 1.50, 1.63 (C*H*/ *Me*, *Me*), 7.38/ 6.50 (Ar-H^e/ Ar-H^d).

1D TOCSY (600 MHz, C_6D_6, 299 K): δ ($^1H_{ir}$) / δ ($^1H_{res}$) = 0.11/ 0.25 (N(Si*Me*$_3$)$_2$/ N(Si*Me*$_3$)$_2$), 0.25/ 0.11 (N(Si*Me*$_3$)$_2$/ N(Si*Me*$_3$)$_2$), 1.03/ 1.25, 2.9 (CH(C*H*$_3$)$_2$/ CH(C*H*$_3$)$_2$, C*H*(CH$_3$)$_2$), 1.15/ 1.25, 2.99 (CH(C*H*$_3$)$_2$/ CH(C*H*$_3$)$_2$, C*H*(CH$_3$)$_2$), 1.25/ 1.03, 1.15, 2.9, 2.99 (CH(C*H*$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, C*H*(CH$_3$)$_2$, C*H*(CH$_3$)$_2$), 2.9/ 1.03, 1.25 (C*H*(CH$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$), 2.99/ 1.15, 1.25 (C*H*(CH$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$), 4.83/ 1.50, 1.63 (C*H/ Me*, *Me*), 6.50/ 6.85, 6.95, 7.38 (Ar-H^d/ Ar-*H*, Ar-*H*, Ar-H^e), 6.85/ 6.50, 6.95 7.38 (Ar-*H*/ Ar-H^d, Ar-*H*, Ar-H^e), 6.95/ 6.50, 6.85, 7.38 (Ar-*H*/ Ar-H^d, Ar-*H*, Ar-H^e), 7.38/ 6.50, 6.85, 6.95 (Ar-H^e/ Ar-H^d, Ar-*H*, Ar-*H*).

^{19}F NMR (564 MHz, C_6D_6, 299 K): δ -162.89 (m, 4F, m-C_6F_5), -155.67 (m, 2F, p-C_6F_5), -133.64 (m, 4F, o-C_6F_5) ppm.

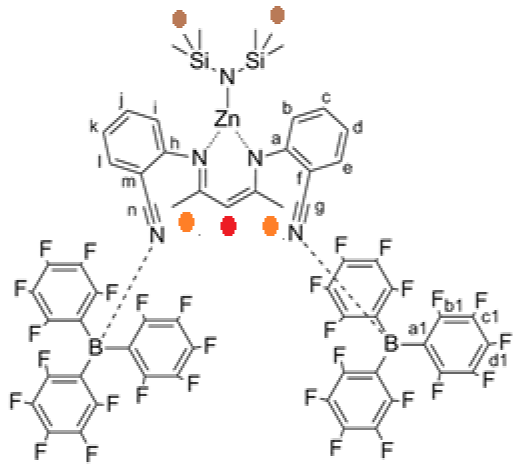
^{11}B NMR (192 MHz, C_6D_6, 299 K): δ -9.74 ppm.

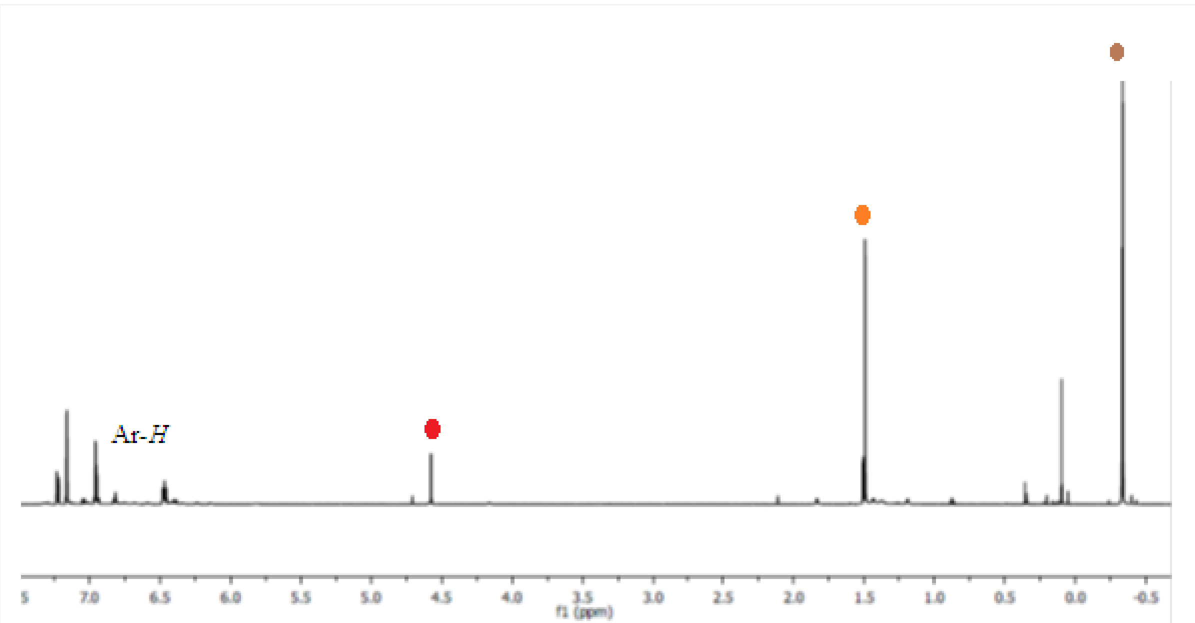
IR (KBr): ν/cm^{-1} = 2305 (ν (C≡N), s).

Elemental analysis (%) $C_{48}H_{46}BF_{15}N_4Si_2Zn$ (M = 1096.2437 g/mol): calculated C 52.59 H 4.23, N 5.11; found C 52.60, H 4.33, N 5.10.

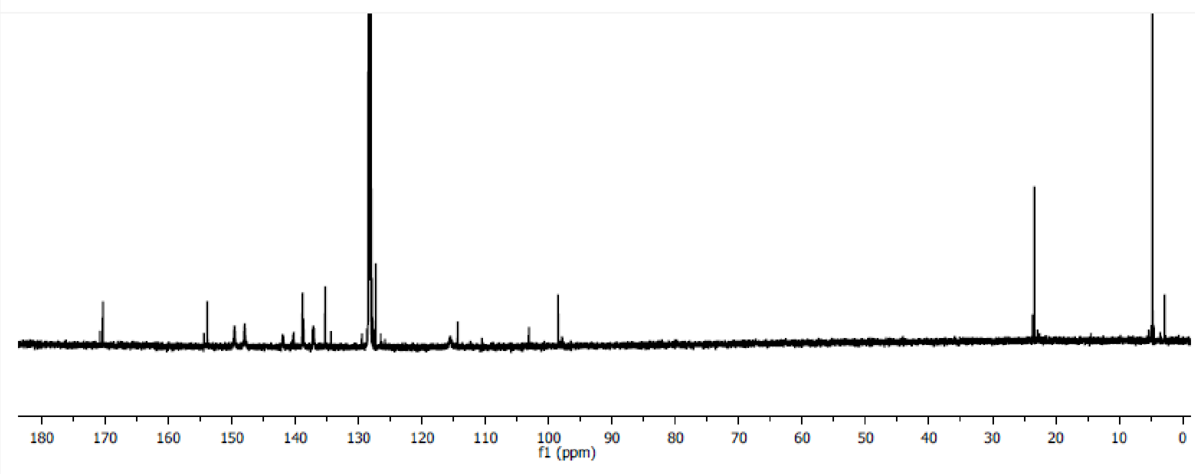
Preparation of $ZnL_2N(SiMe_3)_2$ * 2$B(C_6F_5)_3$, 4.

2 eq of Tris(pentafluorophenyl)borane (39 mg in 1 mL of toluene, 76.2 mmol) was added to a toluene solution of **2** (20 mg, 38 mmol). The reaction mixture was stirred for 10 min, filtered and dried several hours under vacuum. Compound **4** was isolated as bright yellow solid in 83 % yield. Single crystals for X-ray crystallography were grown by layering pentane onto a toluene solution of compound (**4**) at-30 °C.





^{1}H NMR (600 MHz, C_6D_6, 299 K)



^{13}C {1H} (100 MHz, C_6D_6, 299 K)

^{1}H NMR (600 MHz, C_6D_6, 299 K): δ/ppm = 0.33 (s, 18H, N(Si*Me*$_3$)$_2$), 1.50 (s, 6H, *Me*), 4.57 (s, 1H, C*H*), 6.48 (m, 2H, Ar-H^{b}), 6.95 (m, 4H, Ar-$H^{c,d}$), 7.23 (m, 2H, Ar-H^{e}).

^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 299 K): δ/ppm = 4.85 (N(Si(*C*H$_3$)$_3$)$_2$), 23.38 (*Me*), 98.51 (*C*H), 114.48 (*C*≡N), 115.48 (Ar-*C*), 127.34 (Ar-*C*H^{b}), 127.87 (Ar-*C*), 128.51 (Ar-*C*), 135.28 (Ar-*C*H^{e}), 137.09 (Ar^{F5}-*C*), 138.63 (Ar-*C*H), 138.71 (Ar^{F5}-*C*), 140.24 (Ar^{F5}-*C*), 141.93 (Ar^{F5}-*C*), 147.96 (Ar^{F5}-*C*), 149.70 (Ar^{F5}-*C*), 153.88 (Ar-*C*), 170.38 (*C*=N).

GCOSY (600 MHz / 600 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{1}H) = 1.50/ 4.57 (*Me*/ C*H*), 4.57/ 1.50 (C*H*/ *Me*), 6.48/ 6.95, 7.23 (Ar-H^{b}/ Ar-$H^{c,d}$, Ar-H^{e}), 6.95/ 6.48 (Ar-$H^{c,d}$/ Ar-H^{b}), 7.23/ 6.48, 6.95 (Ar-H^{e}/ Ar-H^{b}, Ar-$H^{c,d}$).

^{13}C-GHSQC (600 MHz / 100 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{13}C) = 0.33/ 4.85 (N(Si(C*H*$_3$)$_3$)$_2$/ N(Si(*C*H$_3$)$_3$)$_2$), 1.50/ 23.38 (*Me*/ *Me*), 4.85/ 98.51 (C*H*/ *C*H), 6.48/ 127.34 (Ar-H^{b}/ Ar-*C*H^{b}), 6.95/ 127.87, 138.63 (Ar-$H^{c,d}$/ Ar-*C*H, Ar-*C*H), 7.23/ 135.28 (Ar-H^{e}/ Ar-*C*H^{e}).

^{1}H, ^{13}C-GHMQC (600 MHz / 100 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{13}C) = 0.33/ 4.85 (N(Si(C*H*$_3$)$_3$)$_2$/ N(Si(*C*H$_3$)$_3$)$_2$), 1.50/ 98.51, 170.38 (*Me*/ *C*H, *C*=N), 4.85/ 23.38, 153.88, 170.38 (C*H*/ *Me,* Ar-*C*, *C*=N), 6.48/ 127.87 (Ar-H^{b}/ Ar-*C*H), 6.95/ 135.28, 153.88 (Ar-$H^{c,d}$/ Ar-*C*H^{e}, Ar-*C*), 7.23/ 114.48, 138.63, 153.88 (Ar-H^{e}/ *C*≡N, Ar-*C*H, Ar-*C*).

DPFGNOE (600 MHz, C_6D_6, 299 K): δ ($^{1}H_{ir}$) / δ ($^{1}H_{res}$) = 0.33/ 7.23 (N(Si*Me*$_3$)$_2$/ Ar-H^{e}), 1.50/ 4.57 (*Me*/ *C*H), 6.48/ 6.95, 7.23 (Ar-H^{b}/ Ar-$H^{c,d}$, Ar-H^{e}), 6.95/ 6.48, 7.23 (Ar-$H^{c,d}$/ Ar-H^{b}, Ar-H^{e}), 7.23/ 6.48, 6.95 (Ar-H^{e}/ Ar-H^{b}, Ar-$H^{c,d}$).

1D TOCSY (600 MHz, C_6D_6, 299 K): δ ($^{1}H_{ir}$) / δ ($^{1}H_{res}$) = 1.50/ 4.57 (*Me*/ *C*H), 6.48/ 6.95, 7.23 (Ar-H^{b}/ Ar-$H^{c,d}$, Ar-H^{e}), 6.95/ 6.48, 7.23 (Ar-$H^{c,d}$/ Ar-H^{b}, Ar-H^{e}), 7.23/ 6.48, 6.95 (Ar-H^{e}/ Ar-H^{b}, Ar-$H^{c,d}$).

^{19}F NMR (564 MHz, C_6D_6, 299 K): δ -162.79 (m, 4F, m-C_6F_5), -155.22 (m, 2F, p-C_6F_5), -133.87 (m, 4F, o-C_6F_5) ppm.

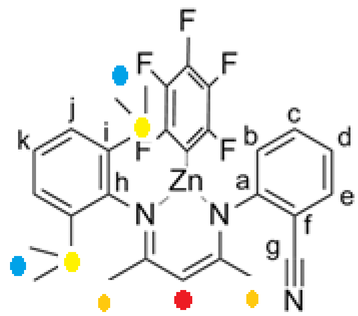
^{11}B NMR (192 MHz, C_6D_6, 299 K): δ -8.62 ppm.

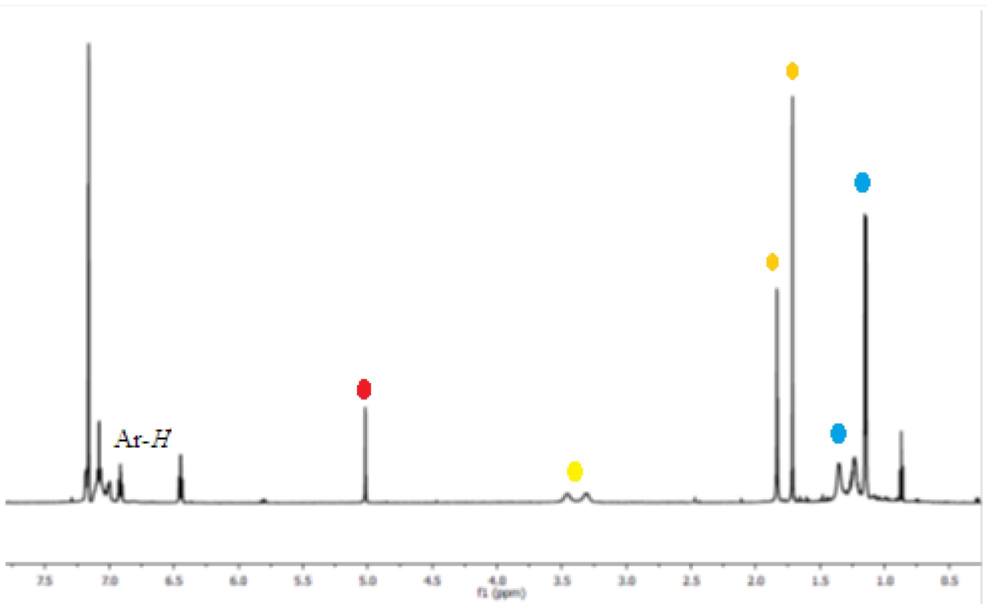
IR (KBr): ν/cm^{-1} = 2301 (ν (C≡N), s).

Elemental analysis (%) $C_{61}H_{33}B_2F_{30}N_5Si_2Zn$ (M = 1549.0733 g/mol): calculated C 47.30;, H 2.15, N 4.52; found C 47.41, H 1.65, N 4.18.

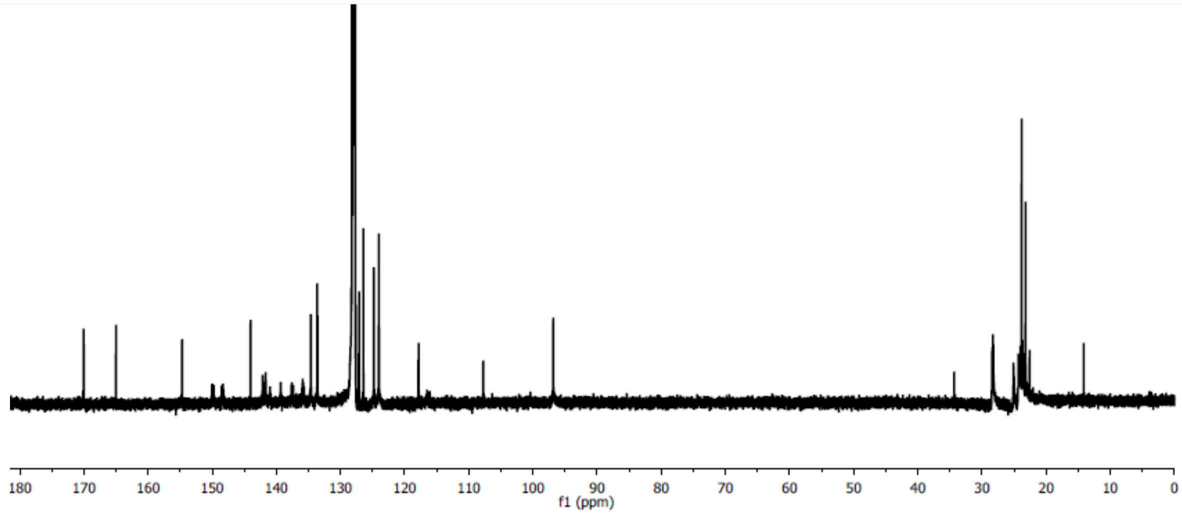
Preparation of $ZnL_1C_6F_5$, 5.

$ZnL_1N(SiMe_3)_2$ (**1**) (50 mg, 85.6 mmol) and $HB(C_6F_5)_2$ (29.6 mg, 85.6 mmol) were dissolved in toluene and stirred at 80 º C for 12 h. The color of the solution was changed from yellow to orange. Evaporation of the solvent yielded pale orange, air-sensitive solid, that was washed several times with 2 ml cold pentane, and dried few hours under vacuum. Yield: 23.3 mg (39.4 mmol, 46 %). Single crystals for X-ray crystallography were grown by layering pentane onto a toluene solution of compound (**5**) at room temperature.





^{1}H NMR (600 MHz, C_6D_6, 299 K)



^{13}C {1H} (100 MHz, C_6D_6, 299 K)

^{1}H NMR (600 MHz, C_6D_6, 299 K): δ/ppm = 1.14 (d, J = 1.15 Hz, 6H, CH(CH_3)$_2$), 1.23 (bs, 3H, CH(CH_3)$_2$), 1.36 (bs, 3H, CH(CH_3)$_2$), 1.72 (s, 3H, *Me*), 1.83 (s, 3H, *Me*), 3.31 (bs, 2H, C*H*(CH_3)$_2$), 3.45 (bs, 2H, C*H*(CH_3)$_2$), 5.02 (s, 1H, C*H*), 6.45 (t, 1H, Ar-H^d), 6.91 (t, 1H, Ar-H^c), 7.00 (d, 1H, Ar-H^b), 7.08 (m, 3H, Ar-$H^{j,k}$), 7.18 (d, 1H, Ar-H^e).

^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 299 K): δ/ppm = 23.21 (*Me*), 23.69 (*Me*), 23.81 (CH(*C*H_3)$_2$), 24.01 (CH(*C*H_3)$_2$), 24.31 (CH(*C*H_3)$_2$), 25.07 (CH(*C*H_3)$_2$), 28.28 (*C*H(CH_3)$_2$), 28.40 (*C*H(CH_3)$_2$), 96.71 (*C*H), 107.71 (Ar-*C*), 117.82 (*C*≡N), 124.02 (Ar-*C*H ^{j,k}), 124.80 (Ar-*C*H^d), 126.44 (Ar-*C*H^b), 127.10 (Ar-*C*), 128.19 (Ar-*C*), 133.61 (Ar-*C*H^e), 134.62 (Ar-*C*H^c), 135.88 (Ar^{F5}-*C*), 137.65 (Ar^{F5}-*C*), 139.32 (Ar^{F5}-*C*), 140.91 (Ar^{F5}-*C*), 141.68 (Ar-*C*), 142.14 (Ar-*C*), 144.01 (Ar-*C*), 148.28 (Ar^{F5}-*C*), 149.77 (Ar^{F5}-*C*), 154.70 (Ar-*C*), 165.00 (*C*=N), 170.03 (*C*=N).

GCOSY (600 MHz / 600 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{1}H) = 1.14/ 1.23, 1.36 (CH(CH_3)$_2$/ CH(CH_3)$_2$, CH(CH_3)$_2$), 3.31/ 1.14 (C*H*(CH_3)$_2$/ CH(CH_3)$_2$), 3.45/ 1.14 (C*H*(CH_3)$_2$/ CH(CH_3)$_2$), 6.45/ 6.91, 7.18 (Ar-H^d/ Ar-H^c, Ar-H^e), 6.91/ 6.45, 7.00, 7.18 (Ar-H^c/ Ar-H^d, Ar-H^b, Ar-H^e), 7.00/ 6.91 (Ar-H^b/ Ar-H^c), 7.18/ 6.45, 6.91 (Ar-H^e/ Ar-H^d, Ar-H^c).

^{13}C-GHSQC (600 MHz / 100 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{13}C) = 1.14/ 23.21, 23.81 (CH(CH_3)$_2$/ CH(*C*H_3)$_2$, CH(*C*H_3)$_2$), 1.23/ 24.31 (CH(CH_3)$_2$/ CH(*C*H_3)$_2$), 1.36/ 25.07 (CH(CH_3)$_2$/ CH(*C*H_3)$_2$), 1.72/ 23.69 (*Me/ Me*), 1.83/ 23.21 (*Me/ Me*), 3.31/ 28.28 (C*H*(CH_3)$_2$/ *C*H(CH_3)$_2$), 3.45/ 28.40 (C*H*(CH_3)$_2$/ *C*H(CH_3)$_2$), 5.02/ 96.71 (C*H*/ *C*H), 6.45/

124.80 (Ar-*H*^{d}/ Ar-*C*H^{d}), 6.91/ 134.62 (Ar-*H*^{c}/ Ar-*C*H^{c}), 7.00/ 126.44 (Ar-*H*^{b}/ Ar-*C*H^{b}), 7.08/ 124.02 (Ar-*H*^{j,k}/ Ar-*C*H^{j,k}), 7.18/ 133.61 (Ar-*H*^{e}/ Ar-*C*H^{e}).

^{1}H, ^{13}C-GHMQC (600 MHz / 100 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{13}C) = 1.14/ 28.28, 28.40, 141.68, 142.14 (CH(C*H*$_3$)$_2$/ *C*H(CH$_3$)$_2$, *C*H(CH$_3$)$_2$, Ar-*C*, Ar-*C*), 1.72/ 96.71, 170.03 (*Me*/ *C*H, *C*=N), 1.83/ 96.71, 165.00 (*Me*/ *C*H, *C*=N), 5.02/ 23.21, 23.69, 165.00, 170.03 (C*H*/ CH(*C*H$_3$)$_2$, CH(*C*H$_3$)$_2$, *C*=N, *C*=N), 6.45/ 107.71, 127.10 (Ar-*H*^{d}/ Ar-*C*, Ar-*C*), 6.91/ 133.61, 154.70 (Ar-*H*^{c}/ Ar-*C*H^{e}, Ar-*C*), 7.00/ 144.01 (Ar-*H*^{b}/ Ar-*C*), 7.18/ 154.70 (Ar-*H*^{e}/ Ar-*C*).

^{19}F NMR (564 MHz, C_6D_6, 299 K): δ -162.09 (m, 2F, m-C_6F_5), -156.17 (m, 1F, p-C_6F_5), -115.41 (m, 2F, o-C_6F_5) ppm.

DPFGNOE (600 MHz, C_6D_6, 299 K): δ ($^{1}H_{ir}$) / δ ($^{1}H_{res}$) = 1.14/ 1.72 (CH(C*H*$_3$)$_2$/ *Me*), 1.72/ 1.14, 5.02 (*Me*/ CH(C*H*$_3$)$_2$, C*H*), 5.02/ 1.72, 1.83 (C*H*/ *Me*, *Me*), 6.45/ 7.18 (Ar-*H*^{d}/ Ar-*H*^{e}), 6.91/ 7.00 (Ar-*H*^{c}/ Ar-*H*^{b}).

1D TOCSY (600 MHz, C_6D_6, 299 K): δ ($^{1}H_{ir}$) / δ ($^{1}H_{res}$) = 1.14/ 1.23, 1.36, 3.31, 3.45 (CH(C*H*$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, C*H*(CH$_3$)$_2$, C*H*(CH$_3$)$_2$), 6.45/ 6.91, 7.00, 7.18 (Ar-*H*^{d}/ Ar-*H*^{c}, Ar-*H*^{b}, Ar-*H*^{e}), 6.91/ 6.45, 7.00, 7.18 (Ar-*H*^{c}/ Ar-*H*^{d}, Ar-*H*^{b}, Ar-*H*^{e}).

IR (KBr): ν/cm^{-1} = 2249 (ν (C≡N), s).

HRMS (ESI + H^{+}): m/z calculated (for ($C_{30}H_{28}F_5N_3Zn$)($C_{24}H_{30}N_3$)): 949.3929 Found: 949.3931.

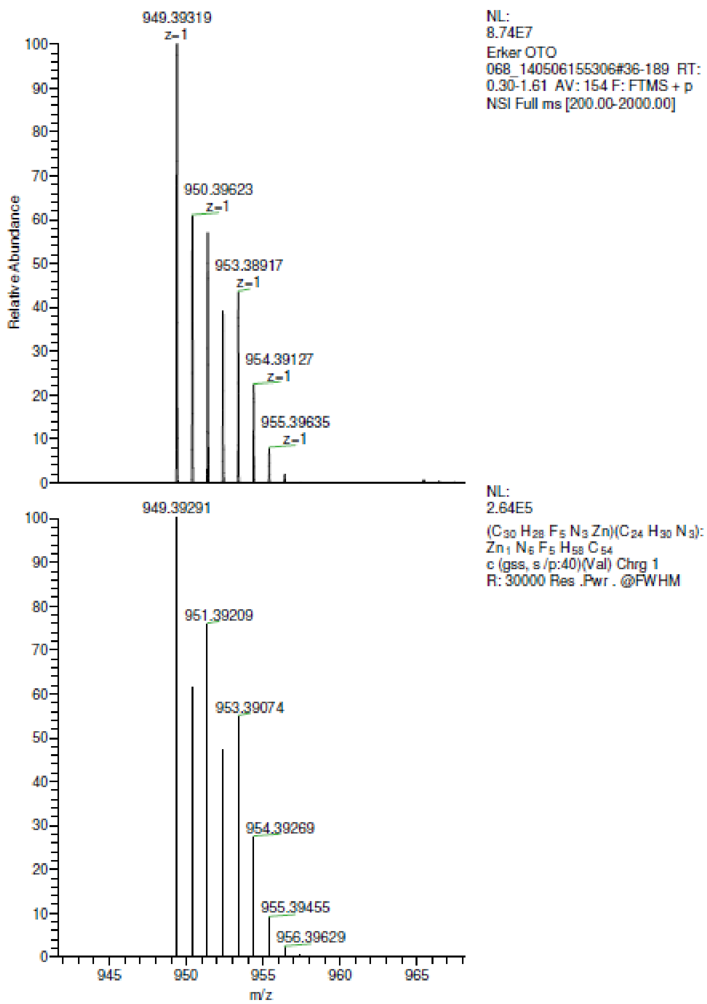
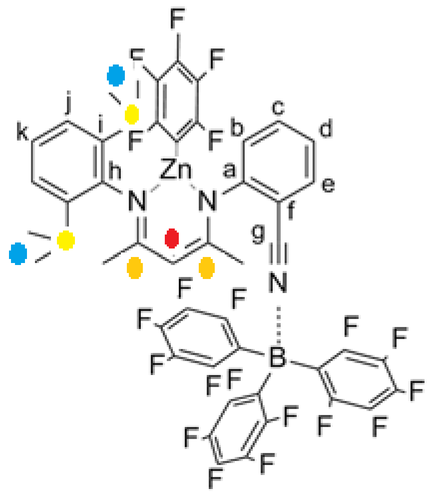
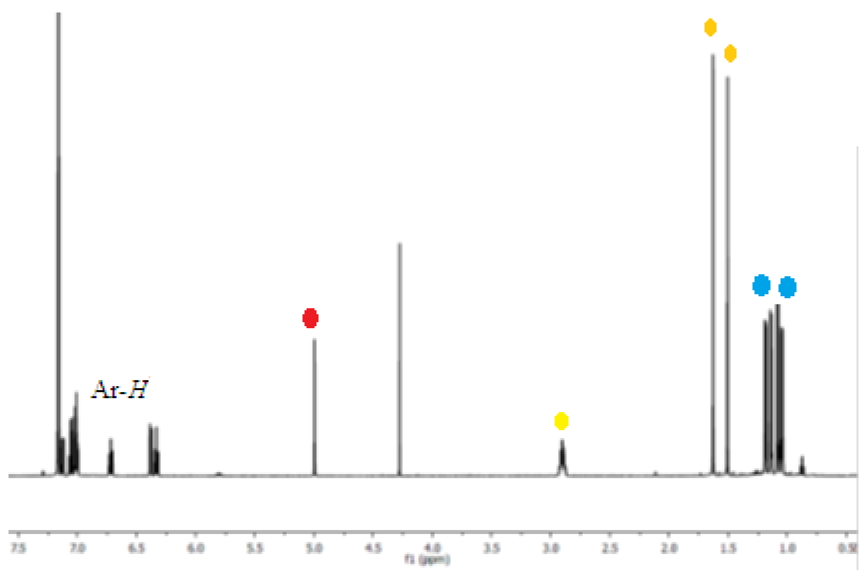


Figure S1. Experimental (above) and calculated (below) HRMS (ESI + H^+) spectra for $(C_{30}H_{28}F_5N_3Zn)(C_{24}H_{30}N_3)$

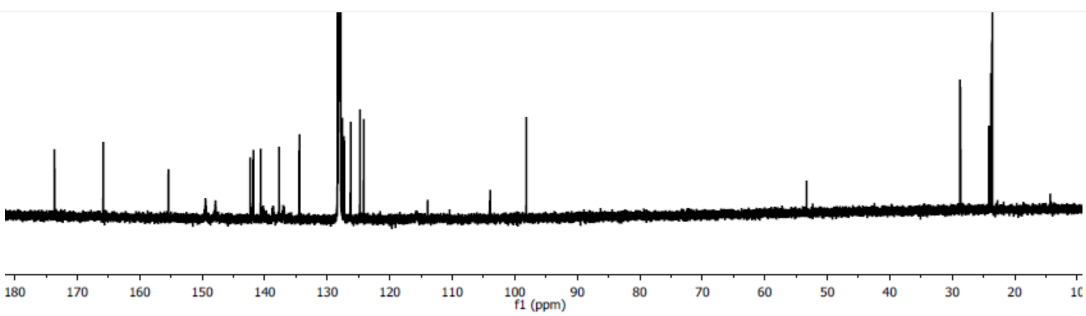
Preparation of $ZnL_1C_6F_5$* $B(C_6F_5)_3$, 6.

1 eq of Tris(pentafluorophenyl)borane (33.8 mg in 1 mL of toluene, 66 mmol) was added to a toluene solution of **5** (40 mg, 66 mmol). The reaction mixture was stirred for 20 min, filtered, washed with 3 ml cold pentane and dried under vacuum. Compound **6** was isolated as orange solid in 73 % yield.





^{1}H NMR (600 MHz, C_6D_6, 299 K)



^{13}C {1H} (100 MHz, C_6D_6, 299 K)

^{1}H NMR (600 MHz, C_6D_6, 299 K): δ/ppm = 1.05 (d, J = 1.05 Hz, 3H, $CH(CH_3)_2$), 1.09 (d, J = 1.08 Hz, 3H, $CH(CH_3)_2$), 1.14 (d, J = 1.14 Hz, 3H, $CH(CH_3)_2$), 1.19 (d, J = 1.18 Hz, 3H, $CH(CH_3)_2$), 1.51 (s, 3H, *Me*), 1.63 (s, 3H, *Me*), 2.90 (s, 1H, $CH(CH_3)_2$), 5.00 (s, 1H, C*H*), 6.33 (t, 1H, Ar-H^d), 6.39 (d, 1H, Ar-H^b), 6.72 (t, 1H, Ar-H^c), 7.00 (m, 2H, Ar-$H^{j,j}$), 7.04 (m, 1H, Ar-H^k), 7.12 (d, 1H, Ar-H^e).

^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 299 K): δ/ppm = 23.58 (*Me*), 23.60 ($CH(CH_3)_2$), 23.65 ($CH(CH_3)_2$), 23.82 ($CH(CH_3)_2$), 24.11 ($CH(CH_3)_2$), 28.67 ($CH(CH_3)_2$), 28.78 ($CH(CH_3)_2$), 98.16 (*C*H), 103.95 (Ar-C^f), 113.94 (*C*≡N), 124.17 (Ar-CH^j), 124.78 (Ar-CH^j), 126.27 (Ar-CH^d), 127.30 (Ar-CH^k), 127.59 (Ar-CH^b), 134.45 (Ar-CH^e), 137.01 (Ar^{F5}-*C*), 137.71 (Ar-CH^c), 138.65 (Ar^{F5}-*C*), 140.24 (Ar^{F5}-*C*), 140.65 (Ar-C^i), 141.84 (Ar-C^i), 141.89 (Ar^{F5}-*C*), 142.31 (Ar-C^h), 147.97 (Ar^{F5}-*C*), 149.44 (Ar^{F5}-*C*), 155.45 (Ar-C^a), 165.89 (*C*=N), 173.69 (*C*=N).

^{1}H-^{1}H GCOSY (600 MHz / 600 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{1}H) = 1.05/ 2.90 ($CH(CH_3)_2$/ $CH(CH_3)_2$), 1.09/ 2.90 ($CH(CH_3)_2$/ $CH(CH_3)_2$), 1.14/ 2.90 ($CH(CH_3)_2$/ $CH(CH_3)_2$), 1.19/ 2.90 ($CH(CH_3)_2$/ $CH(CH_3)_2$), 1.51/ 5.00 (*Me*/ C*H*), 2.90/ 1.05, 1.09, 1.14, 1.19, ($CH(CH_3)_2$/ $CH(CH_3)_2$, $CH(CH_3)_2$, $CH(CH_3)_2$, $CH(CH_3)_2$), 5.00/ 1.51, 1.63 (C*H/ Me, Me*), 6.33/ 6.72, 7.12 (Ar-H^d/ Ar-H^c, Ar-H^e), 6.39/ 6.72, 7.12 (Ar-H^b/ Ar-H^c, Ar-H^e), 6.72/ 6.33, 6.39, 7.12 (Ar-H^c/ Ar-H^d, Ar-H^b, Ar-H^e), 7.00/ 7.04 (Ar-$H^{j,j}$/ Ar-H^k), 7.04/ 7.00 (Ar-H^k/ Ar-$H^{j,j}$), 7.12/ 6.33 (Ar-H^e/ Ar-H^d).

^{13}C-GHSQC (600 MHz / 100 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{13}C) = 1.05/ 23.60 ($CH(CH_3)_2$/ $CH(CH_3)_2$), 1.09/ 23.65 ($CH(CH_3)_2$/ $CH(CH_3)_2$), 1.14/ 23.82 ($CH(CH_3)_2$/ $CH(CH_3)_2$), 1.19/ 24.11 ($CH(CH_3)_2$/ $CH(CH_3)_2$), 1.51/ 23.58 (*Me*/ CH_3), 1.63/ 23.58 (*Me*/ CH_3), 2.90/ 28.67, 28.78 ($CH(CH_3)_2$/ $CH(CH_3)_2$, $CH(CH_3)_2$), 5.00/ 98.16 (C*H/ C*H), 6.33/ 126.27 (Ar-H^d/ Ar-CH^d), 6.39/ 127.59 (Ar-H^b/ Ar-CH^b), 6.72/ 137.71 (Ar-H^c/ Ar-CH^c), 7.00/ 124.17, 124.78 (Ar-$H^{j,j}$/ Ar-CH^j, Ar-CH^j), 7.04/ 127.30 (Ar-H^k/ Ar-CH^k), 7.12/ 134.45 (Ar-H^e/ Ar-CH^e).

^{1}H, ^{13}C-GHMQC (600 MHz / 100 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{13}C) = 1.05/ 23.60, 28.67, 28.78, 141.84 ($CH(CH_3)_2$/ $CH(CH_3)_2$, $CH(CH_3)_2$, $CH(CH_3)_2$, Ar-C^i), 1.09/ 23.65, 28.67, 28.78, 140.65 ($CH(CH_3)_2$/ $CH(CH_3)_2$, $CH(CH_3)_2$, $CH(CH_3)_2$, Ar-C^i), 1.14/ 23.82, 28.67, 28.78, 141.84 ($CH(CH_3)_2$/ $CH(CH_3)_2$, $CH(CH_3)_2$, $CH(CH_3)_2$, Ar-C^i), 1.19/ 24.11, 28.67, 28.78, 140.65 ($CH(CH_3)_2$/ $CH(CH_3)_2$, $CH(CH_3)_2$, $CH(CH_3)_2$, Ar-C^i), 1.51/ 98.16, 165.89 (*Me*/ *C*H, *C*=N), 1.63/ 98.16, 173.69 (*Me*/ *C*H, *C*=N), 2.90/ 23.60, 23.65, 23.82, 24.11, 124.17, 124.78, 140.65, 141.84, 142.31 (C*H*(CH$_3$)$_2$/ CH(*C*H$_3$)$_2$, CH(*C*H$_3$)$_2$, CH(*C*H$_3$)$_2$, CH(*C*H$_3$)$_2$, Ar-*C*H^{j}, Ar-*C*H^{j}, Ar-*C*^{i}, Ar-*C*^{i}, Ar-*C*^{h}), 5.00/ 23.58, 141.84, 142.31, 155.45, 165.89, 173.69 (C*H*/ *Me,* Ar-*C*^{i}, Ar-*C*^{h}, Ar-*C*^{a}, *C*=N, *C*=N), 6.33/ 103.95, 134.45 (Ar-*H*^{d}/ Ar-*C*^{f}, Ar-*C*H^{e}), 6.39/ 103.95 (Ar-*H*^{b}/ Ar-*C*^{f}), 6.72/ 134.45, 155.45 (Ar-*H*^{c}/ Ar-*C*H^{e}, Ar-*C*^{a}), 7.00/ 28.67, 28.78, 124.17, 124.78, 141.84, 142.31 (Ar-*H*^{j,j}/ CH(*C*H$_3$)$_2$, CH(*C*H$_3$)$_2$, Ar-*C*H^{j}, Ar-*C*H^{j}, Ar-*C*^{i}, Ar-*C*^{h}), 7.04/ 140.65 (Ar-*H*^{k}/ Ar-*C*^{i}), 7.12/ 113.94, 137.71, 155.45 (Ar-*H*^{e}/ *C*≡N, Ar-*C*H^{c}, Ar-*C*^{a}).

DPFGNOE (600 MHz, C_6D_6, 299 K): δ ($^1H_{ir}$) / δ ($^1H_{res}$) = 1.05/ 1.09, 1.19, 2.90, 7.00 (CH(C*H*$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, C*H*(CH$_3$)$_2$, Ar-*H*^{j,j}), 1.09/ 1.05, 1.14, 2.90, 7.00 (CH(C*H*$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, C*H*(CH$_3$)$_2$, Ar-*H*^{j,j}), 1.14/ 1.09, 2.90, 7.00 (CH(C*H*$_3$)$_2$/ CH(C*H*$_3$)$_2$, C*H*(CH$_3$)$_2$, Ar-*H*^{j,j}), 1.19/ 1.05, 2.90, 7.00 (CH(C*H*$_3$)$_2$/ CH(C*H*$_3$)$_2$, C*H*(CH$_3$)$_2$, Ar-*H*^{j,j}), 1.51/ 2.90, 6.33 (*Me*/ C*H*(CH$_3$)$_2$, Ar-*H*^{j,j}), 1.63/ 1.09, 1.14, 1.19 (*Me*/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$), 2.90/ 1.05, 1.09, 1.14, 1.19, 1.63 (C*H*(CH$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, *Me*), 5.00/ 1.63 (C*H*/ *Me*), 6.33/ 6.39, 6.72, 7.12 (Ar-*H*^{d}/ Ar-*H*^{b}, Ar-*H*^{c}, Ar-*H*^{e}), 6.39/ 6.33, 6.72, 7.12 (Ar-*H*^{b}/ Ar-*H*^{d}, Ar-*H*^{c}, Ar-*H*^{e}), 6.72/ 6.33, 6.39, 7.12 (Ar-*H*^{c}/ Ar-*H*^{d}, Ar-*H*^{b}, Ar-*H*^{e}), 7.00/ 7.04 (Ar-*H*^{j,j}/ Ar-*H*^{k}), 7.04/ 7.00 (Ar-*H*^{k}/ Ar-*H*^{j,j}), 7.12/ 6.33, 6.39, 6.72 (Ar-*H*^{e}/ Ar-*H*^{d}, Ar-*H*^{b}, Ar-*H*^{c}).

1D TOCSY (600 MHz, C_6D_6, 299 K): δ ($^1H_{ir}$) / δ ($^1H_{res}$) = 1.05/ 1.09, 1.14, 1.19, 2.90 (CH(C*H*$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, C*H*(CH$_3$)$_2$), 1.09/ 1.05, 1.14, 1.19, 2.90 (CH(C*H*$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, C*H*(CH$_3$)$_2$), 1.14/ 1.05, 1.14, 1.19, 2.90 (CH(C*H*$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, C*H*(CH$_3$)$_2$), 1.19/ 1.05, 1.14, 1.19, 2.90 (CH(C*H*$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, C*H*(CH$_3$)$_2$), 2.90/ 1.05, 1.09, 1.14, 1.19 (C*H*(CH$_3$)$_2$/ CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$, CH(C*H*$_3$)$_2$), 5.00/ 1.51, 1.63 (C*H*/ *Me, Me*), 6.33/ 6.72 (Ar-*H*^{d}/ Ar-*H*^{c}), 6.39/ 6.33 (Ar-*H*^{b}/ Ar-*H*^{d}), 6.72/ 6.33, 6.39 (Ar-*H*^{c}/ Ar-*H*^{d}, Ar-*H*^{b}), 7.00/ 7.04 (Ar-*H*^{j,j}/ Ar-*H*^{k}), 7.04/ 7.00 (Ar-*H*^{k}/ Ar-*H*^{j,j}), 7.12/ 6.33 (Ar-*H*^{e}/ Ar-*H*^{c}).

^{19}F NMR (564 MHz, C_6D_6, 299 K): δ -162.75 (m, 6F, m-C_6F_5), -160.86 (m, 2F, m-C_6F_5), -155.54 (m, 3F, p-C_6F_5), -153.19 (m, 1F, p-C_6F_5), -134.23 (m, 6F, o-C_6F_5), -116.72 (m, 2F, o-C_6F_5) ppm.

^{19}F-^{19}F GCOSY (564 MHz / 564 MHz, C_6D_6, 299 K): δ (^{19}F)/ δ (^{19}F) = -162.75/ -155.54, -134.23 (m-C_6F_5/ p-C_6F_5, o-C_6F_5), -160.86/ -153.19, -116.72 (m-C_6F_5/ p-C_6F_5, o-C_6F_5), -

155.54/ -162.75, 134.23 (p-C_6F_5/ m-C_6F_5, o-C_6F_5), -153.19/ -160.86, -116.72 (p-C_6F_5/ m-C_6F_5, o-C_6F_5), -134.23/ -162.75, -155.54 (o-C_6F_5/ m-C_6F_5, p-C_6F_5), -116.72/ -160.86, -153.19 (o-C_6F_5/ m-C_6F_5, p-C_6F_5) ppm.

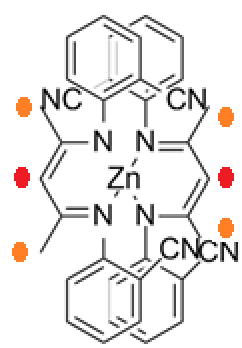
^{11}B NMR (192 MHz, C_6D_6, 299 K): δ -9.52 ppm.

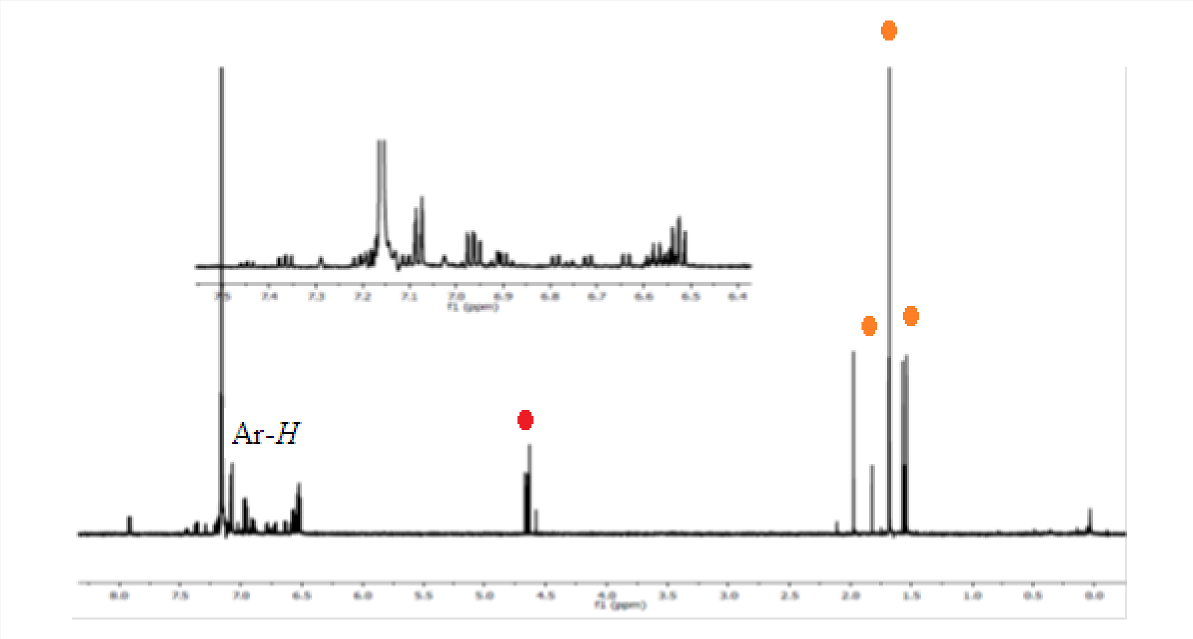
IR (KBr): ν/cm^{-1} = 2319 (ν (C≡N), s).

Elemental analysis (%) $C_{48}H_{28}BF_{20}N_3Zn$ * 0.5 C_5H_{12} : calculated C 53.25 H 3.01, N 3.69; found C 53.44, H 2.75, N 3.98.

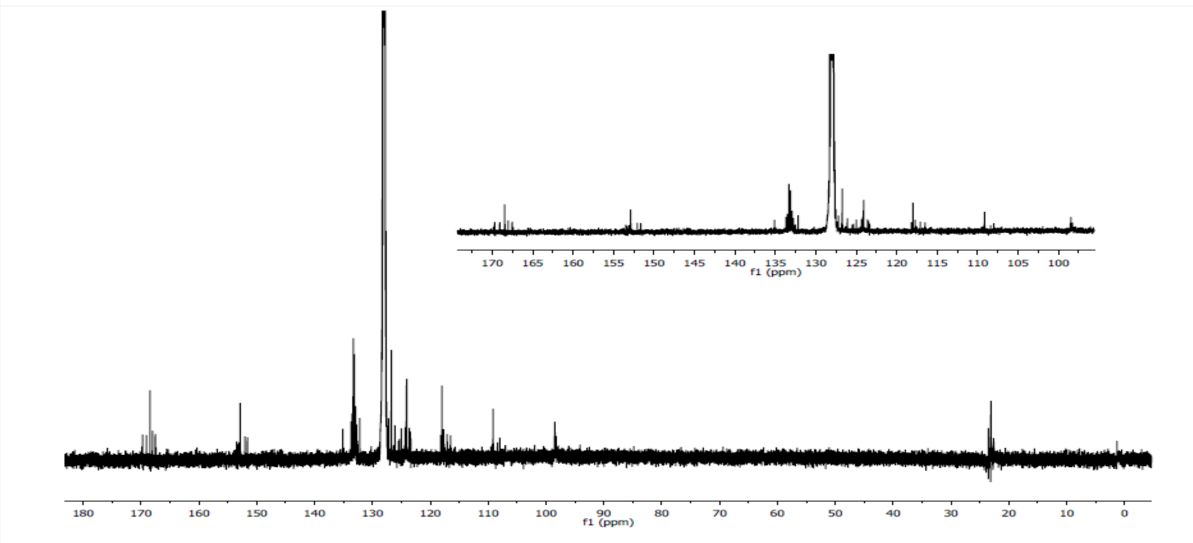
Preparation of ZnL_2, 7.

Diketimine L_2H (40 mg, 133.2 mmol) and Zn{N($SiMe_3$)$_2$}$_2$ (34.2 mg, 88.8 mmol) were reacted in toluene (5 ml) for 12 hours at 80 ^{o} C. The residue obtained after evaporation of the solvent was washed with pentane and dried under vacuum to yield yellow powder of **7** (36.5 mg, 62 %). Single crystals for X-ray crystallography were grown by layering pentane onto a toluene solution of compound (**7**) at-30 ^{o} C.





^{1}H NMR (600 MHz, C_6D_6, 299 K)



^{13}C {1H} (100 MHz, C_6D_6, 299 K)

^{1}H NMR (600 MHz, C_6D_6, 299 K): δ/ppm = 1.54 (s, 6H, *Me*), 1.55 (s, 3H, *Me*), 1.57 (s, 6H, *Me*), 1.68 (s, 18H, *Me*), 1.69 (s, 6H, *Me*), 1.82 (s, 3H, *Me*), 1.98 (s, 6H, *Me*), 4.58 (s, 1H, C*H*), 4.63 (s, 3H, C*H*), 4.65 (s, 2H, C*H*), 4.67 (s, 2H, C*H*), 6.51 (m, 2H, Ar-*H*), 6.53 (m, 3H, Ar-*H*), 6.54 (m, 3H, Ar-*H*), 6.55 (m, 1H, Ar-*H*), 6.56 (m, 4H, Ar-*H*), 6.58 (m, 2H, Ar-*H*), 6.59 (m, 1H, Ar-*H*), 6.63 (m, 1H, Ar-*H*), 6.64 (m, 1H, Ar-*H*), 6.71 (m, 1H, Ar-*H*), 6.72 (m, 1H, Ar-*H*), 6.75 (m, 1H, Ar-*H*), 6.76 (m, 1H, Ar-*H*), 6.78 (m, 1H, Ar-*H*), 6.79 (m, 1H, Ar-*H*), 6.88 (m, 1H, Ar-*H*), 6.90 (m, 1H, Ar-*H*), 6.91 (m, 1H, Ar-*H*), 6.92 (m, 1H, Ar-*H*), 6.95 (m, 1H, Ar-*H*), 6.96 (m, 3H, Ar-*H*), 6.98 (m, 2H, Ar-*H*), 7.02 (m, 2H, Ar-*H*), 7.07 (m, 5H, Ar-*H*), 7.09 (m, 5H, Ar-*H*), 7.10 (m, 1H, Ar-*H*), 7.11 (m, 1H, Ar-*H*), 7.13 (m, 2H, Ar-*H*), 7.15 (m, 2H, Ar-*H*), 7.17 (m, 2H, Ar-*H*), 7.18 (m, 1H, Ar-*H*), 7.19 (m, 1H, Ar-*H*), 7.21 (m, 1H, Ar-*H*), 7.22 (m, 1H, Ar-*H*), 7.29 (m, 2H, Ar-*H*), 7.37 (m, 1H, Ar-*H*), 7.45 (m, 1H, Ar-*H*), 7.91 (m, 2H, Ar-*H*).

^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 299 K): δ/ppm = 22.66 (*Me*), 22.71 (*Me*), 23.12 (*Me*), 23.45 (*Me*), 23.52 (*Me*), 98.27 (*C*H), 98.45 (*C*H), 98.52 (*C*H), 98.53 (*C*H), 107.99 (Ar-*C*), 108.39 (Ar-*C*), 108.40 (Ar-*C*), 109.13 (Ar-*C*), 109.19 (Ar-*C*), 116.48 (*C*≡N), 117.08 (*C*≡N), 117.6 (*C*≡N), 117.72 (*C*≡N), 118.00 (*C*≡N), 118.20 (*C*≡N), 123.35 (Ar), 123.48 (Ar-*C*H), 123.61 (Ar), 124.09 (Ar-*C*H), 124.18 (Ar), 124.24 (Ar), 124.35 (Ar), 125.00 (Ar-*C*H), 125.34 (Ar), 125.51 (Ar), 126.11 (Ar), 126.72 (Ar-*C*H), 126.78 (Ar), 127.21 (Ar), 132.17 (Ar-*C*H), 132.55 (Ar), 132.76 (Ar), 132.87 (Ar), 132.92 (Ar), 132.97 (Ar), 133.01 (Ar), 133.06 (Ar), 133.14 (Ar-*C*H), 133.32 (Ar-*C*H), 133.53 (Ar), 133.64 (Ar), 133.68 (Ar-*C*H), 135.12 (Ar), 151.62 (Ar), 152.07 (Ar), 152.88 (Ar), 153.05 (Ar), 153.29 (Ar), 153.48 (Ar), 167.39 (*C*=N), 167.53 (*C*=N), 168.04 (*C*=N), 168.45 (*C*=N), 169.07 (*C*=N), 169.71 (*C*=N), 169.84 (*C*=N).

GCOSY (600 MHz / 600 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{1}H) = 6.51/ 6.95, 6.96, 6.98, 7.07, 7.09 (Ar-*H*/ Ar-*H,* Ar-*H,* Ar-*H,* Ar-*H*), 6.55/ 6.78, 6.79 (Ar-*H*/ Ar-*H,* Ar-*H*), 6.56/ 6.71, 6.72 (Ar-*H*/ Ar-*H,* Ar-*H*), 6.58/ 7.18 (Ar-*H*/ Ar-*H*), 6.59/ 7.18 (Ar-*H*/ Ar-*H*), 6.63/ 7.22 (Ar-*H*/ Ar-*H*), 6.64/ 7.22 (Ar-*H*/ Ar-*H*), 6.71/ 6.53, 6.55, 6.56 (Ar-*H*/ Ar-*H,* Ar-*H,* Ar-*H*), 6.78/ 6.54, 6.58 (Ar-*H*/ Ar-*H,* Ar-*H*), 6.90/ 6.51, 6.54 (Ar-*H*/ Ar-*H,* Ar-*H*), 6.95/ 6.51, 6.54, 7.07, 7.09 (Ar-*H*/ Ar-*H,* Ar-*H,* Ar-*H,* Ar-*H*), 6.98/ 6.51, 6.54, 7.07, 7.09 (Ar-*H*/ Ar-*H,* Ar-*H,* Ar-*H,* Ar-*H*), 7.07/ 6.51, 6.54, 6.95, 6.98 (Ar-*H*/ Ar-*H,* Ar-*H,* Ar-*H,* Ar-*H*), 7.09/ 6.51, 6.54, 6.95, 6.98 (Ar-*H*/ Ar-*H,* Ar-*H,* Ar-*H,* Ar-*H*), 7.13/ 7.45 (Ar-*H*/ Ar-*H*), 7.17/ 6.56 (Ar-*H*/ Ar-*H*), 7.18/ 6.59, 7.91 (Ar-*H*/ Ar-*H,* Ar-*H*), 7.19/ 6.54 (Ar-*H*/ Ar-*H*), 7.22/ 6.54, 6.58, 6.63, 6.64 (Ar-*H*/ Ar-*H,* Ar-*H,* Ar-*H,* Ar-*H*), 7.45/ 7.13 (Ar-*H*/ Ar-*H*), 7.91/ 7.15, 7.18 (Ar-*H*/ Ar-*H,* Ar-*H*).

^{13}C-GHSQC (600 MHz / 100 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{13}C) = 1.68/ 23.12 (*Me*/ *Me*), 1.68/ 23.45 (*Me*/ *Me*), 1.68/ 23.52 (*Me*/ *Me*), 4.63/ 98.27 (C*H*/ *C*H), 4.65/ 98.45 (C*H*/ *C*H), 4.67/ 98.52 (C*H*/ *C*H), 6.51/ 123.48, 125.00 (Ar-*H*/ Ar-*C*H*,* Ar-*C*H), 6.53/ 124.09 (Ar-*H*/

Ar-*C*H), 6.58/ 125.00 (Ar-*H*/ Ar-*C*H), 6.95/ 126.72 (Ar-*H*/ Ar-*C*H), 6.96/ 133.14, 133.32 (Ar-*H*/ Ar-*C*H, Ar-*C*H), 7.07/ 132.17, 133.68 (Ar-*H*/ Ar-*C*H, Ar-*C*H).

^{1}H, ^{13}C-GHMQC (600 MHz / 100 MHz, C_6D_6, 299 K): δ (^{1}H)/ δ (^{13}C) = 4.63/ 22.66, 22.7, 98.45 (C*H*/ *Me*, *Me*, *C*H), 7.17/ 98.45 (Ar-*H*/ *C*H).

DPFGNOE (600 MHz, C_6D_6, 299 K): δ ($^1H_{ir}$) / δ ($^1H_{res}$) = 1.54/ 1.55, 1.57 (*Me*/ *Me*, *Me*), 1.55/ 1.54, 1.57 (*Me*/ *Me*, *Me*), 1.57/ 1.54, 1.55 (*Me*/ *Me*, *Me*), 1.68/ 1.69, 4.63 (*Me*/ *Me*, *Me*), 1.69/ 1.68, 4.63 (*Me*/ *Me*, C*H*), 4.63/ 1.68, 4.65, 4.67 (C*H*/ *Me*, C*H*, C*H*), 4.65/ 1.68, 4.63, 4.67 (C*H*/ *Me*, C*H*, C*H*), 4.67/ 1.68, 4.63, 4.65 (C*H*/ *Me*, C*H*, C*H*).

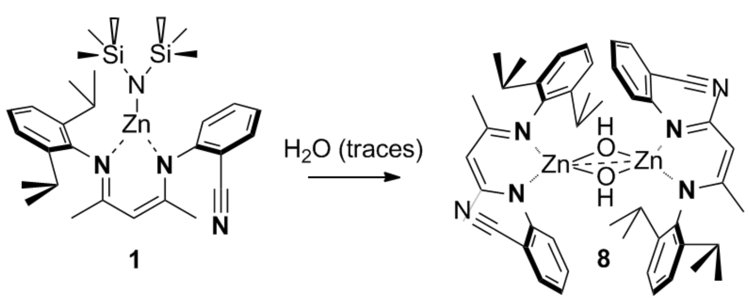
1D TOCSY (600 MHz, C_6D_6, 299 K): δ ($^1H_{ir}$) / δ ($^1H_{res}$) = 1.54/ 1.55, 1.57 (*Me*/ *Me*, *Me*), 1.55/ 1.54, 1.57 (*Me*/ *Me*, *Me*), 1.57/ 1.54, 1.55 (*Me*/ *Me*, *Me*), 1.68/ 1.69 (*Me*/ *Me*), 1.69/ 1.68 (*Me*/ *Me*), 4.63/ 4.65, 4.67 (C*H*/ C*H*, C*H*), 4.65/ 4.63, 4.67 (C*H*/ C*H*, C*H*), 4.67/ 4.63, 4.65 (C*H*/ C*H*, C*H*).

IR (KBr): ν/cm^{-1} = 2226 (ν (C≡N), s).

Elemental analysis (%) (M = 662.1885 g/mol): calculated C 68.73, H 4.55, N 16.87; found C 68.42, H 4.25, N 16.52.

2. $Zn_2(L_1)_2(OH)_2$ (1^a)

$Zn_2(L_1)_2(OH)_2$ (1^a). Zinc amide complex **1** with a long stay in a toluene solution was spotted to decompose to bimetallic zinc complex $Zn_2(L_1)_2(OH)_2$ (**1^a**), single crystals of this compound suitable for X-ray diffraction were obtained, but only in quantities insufficient for further characterization.



Scheme S1. Synthesis of **$Zn_2(L_1)_2(OH)_2$ (1^a)**

1^a crystallizes in the triclinic space group $P\bar{1}$ as a hydroxide-bridged centrosymmetric dimer (Scheme S1, Figure S2). The Zn-O bond lengths are almost identical (Zn1-O1 1.969(1);

Zn1-O1* 1.966(1) Å) as was previously observed for [Mes*nacnac*Zn(μ-OH)]$_2$,[1] whereas terminal OH groups show shorter Zn-O bond lengths (1.85-1.90 Å).[1] The Zn_2O_2 metallacycle in **1^a** is planar (dihedral angle Zn1-O1-Zn1*-O1* is -0.0(1)^o) with the Zn···Zn distance 3.002(1) Å, while in [Mes*nacnac*Zn(μ-OH)]$_2$ the distance between two atoms of zinc is 2.909 Å.[1] Zn-N bond lengths within the complex **1^a** are slightly larger compared to the starting amide zinc complex **1** (Figure 1, Figure S2). Four-coordinate zinc **1^a** adopts distorted tetrahedral geometry (O1-Zn1-N1 115.5(1)^o, O1*-Zn1-N2 121.1(1)^o, N1-Zn1-N2 97.2(1)^o).

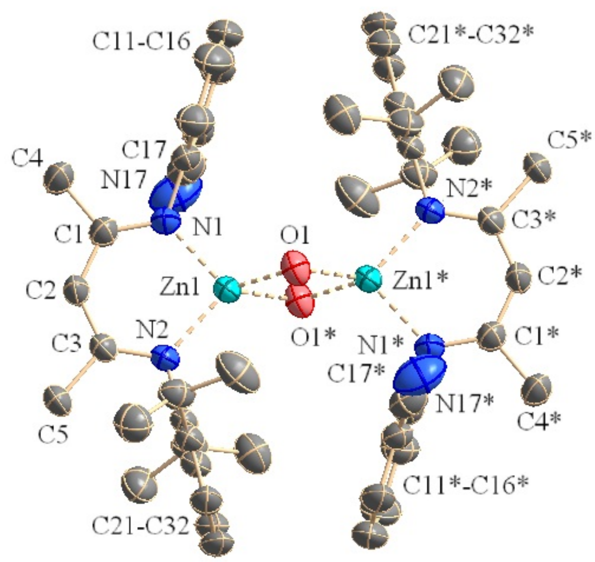


Figure S2. X-ray crystal structure of **1^a** with thermal ellipsoids drawn at the 50 % probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1-O1 1.969(1), Zn1-O1* 1.966(1), Zn1-Zn1* 3.002(1), Zn1-N1 1.997(2), Zn1-N2 1.989(2), O1-O1* 2.544(1), O1-Zn1-O1* 80.6(1), N1-Zn1-N2 97.2(1), O1-Zn1-N1 115.5(1), O1*-Zn1-N2 121.1(1), Zn1-O1-Zn1*-O1* -0.0(1).

3. Crystallography Characterization.

X-Ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution SHELXS-

97 (G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

The crystal data and refinement of **1**, **1**[a], **2**, **4**, **5** and **7** are summarized below.

X-ray crystal structure analysis of 1 (erk7483): formula $C_{30}H_{46}N_4Si_2Zn$, M = 584.26, pale yellow crystal, 0.14 x 0.11 x 0.03 mm, a = 10.6036(1), b = 17.0996(2), c = 19.1825(3) Å, α = 71.047(1), β = 81.865(1), γ = 89.954(1)°, V = 3252.7(1) Å^3, ρ_{calc} = 1.193 gcm^{-3}, μ = 0.852 mm^{-1}, empirical absorption correction (0.890 ≤ T ≤ 0.974), Z = 4, triclinic, space group P-1 (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 29851 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 13167 independent (R_{int} = 0.047) and 10493 observed reflections [I>2σ(I)], 691 refined parameters, R = 0.051, wR2 = 0.122, max. (min.) residual electron density 0.53 (-0.42) e.Å^{-3}, the hydrogens were calculated and refined as riding atoms.

X-ray crystal structure analysis of 2 (erk7466): formula $C_{50}H_{66}N_{10}Si_4Zn_2$, M = 1050.23, colorless crystal, 0.23 x 0.2 x 0.15 mm, a = 10.3795(3), b = 11.2101(4), c = 15.3836(6) Å, α = 75.093(1), β = 80.392(2), γ = 71.743(2)°, V = 1635.4(1) Å^3, ρ_{calc} = 1.066 gcm^{-3}, μ = 0.842 mm^{-1}, empirical absorption correction (0.829 ≤ T ≤ 0.884), Z = 1, triclinic, space group P-1 (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 12752 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 6468 independent (R_{int} = 0.042) and 5746 observed reflections [I>2σ(I)], 306 refined parameters, R = 0.057, wR2 = 0.136, max. (min.) residual electron density 0.46 (-0.47) e.Å^{-3}, the hydrogens were calculated and refined as riding atoms.

X-ray crystal structure analysis of 4 (erk7454): formula $C_{61}H_{33}B_2F_{30}N_5Si_2Zn$, M = 1549.09, pale yellow, 0.40 x 0.30 x 0.15 mm, a = 24.0692(3), b = 16.8248(3), c = 15.9161(3) Å, β = 93.334(1)°, V = 6434.5(2) Å^3, ρ_{calc} = 1.599 gcm^{-3}, μ = 0.551 mm^{-1}, empirical absorption correction (0.809 ≤ T ≤ 0.922), Z = 4, monoclinic, space group C2/c (No. 15), λ = 0.71073 Å, T = 273(2) K, ω and φ scans, 21499 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 5538 independent (R_{int} = 0.050) and 4537 observed reflections

[I>2σ(I)], 495 refined parameters, R = 0.061, wR2 = 0.164, max. (min.) residual electron density 0.35 (-0.25) e.Å^{-3}, the hydrogens were calculated and refined as riding atoms.

X-ray crystal structure analysis of 5 (erk7521): formula $C_{60}H_{56}N_6F_{10}Zn_2$, M = 1181.85, pale yellow crystal, 0.18 x 0.08 x 0.06 mm, a = 9.7839(1), b = 28.2012(3), c = 20.4432(3) Å, β = 91.327(1)°, V = 5639.1(1) Å^3, ρ_{calc} = 1.392 gcm^{-3}, μ = 0.928 mm^{-1}, empirical absorption correction (0.850 ≤ T ≤ 0.946), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 30909 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 11342 independent (R_{int} = 0.054) and 8289 observed reflections [I>2σ(I)], 715 refined parameters, R = 0.057, wR2 = 0.120, max. (min.) residual electron density 0.37 (-0.42) e.Å^{-3}, the hydrogens were calculated and refined as riding atoms.

X-ray crystal structure analysis of 7 (erk7511): formula $C_{38}H_{30}N_8Zn$, M = 664.07, yellow crystal, 0.16 x 0.07 x 0.03 mm, a = 9.7928(3), b = 11.3155(4), c = 16.9990(6) Å, α = 72.961(1), β = 83.413(2), γ = 68.922(2)°, V = 1680.4(1) Å^3, ρ_{calc} = 1.312 gcm^{-3}, μ = 0.770 mm^{-1}, empirical absorption correction (0.886 ≤ T ≤ 0.977), Z = 2, triclinic, space group P-1 (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 14852 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 5751 independent (R_{int} = 0.045) and 5251 observed reflections [I>2σ(I)], 428 refined parameters, R = 0.049, wR2 = 0.121, max. (min.) residual electron density 0.62 (-0.36) e.Å^{-3}, the hydrogens were calculated and refined as riding atoms.

X-ray crystal structure analysis of 1[a] (erk7487): formula $C_{48}H_{58}N_6O_2Zn_2$, M = 881.74, pale yellow crystal, 0.15 x 0.12 x 0.07 mm, a = 9.7845(3), b = 10.2261(4), c = 12.4486(4) Å, α = 101.950(2), β = 104.633(2), γ = 104.712(1)°, V = 1115.6(7) Å^3, ρ_{calc} = 1.312 gcm^{-3}, μ = 1.120 mm^{-1}, empirical absorption correction (0.850 ≤ T ≤ 0.925), Z = 1, triclinic, space group P-1 (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 14401 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 4478 independent (R_{int} = 0.037) and 4207 observed reflections [I>2σ(I)], 271 refined parameters, R = 0.032, wR2 = 0.085, max. (min.) residual electron density 0.23 (-0.38) e.Å^{-3}, the hydrogen at O1 atom was refined freely, but with O-H distance restraints (DFIX and fixed U-value); others were calculated and refined as riding atoms.

4. ^{1}H NMR spectra of PLLA formation.

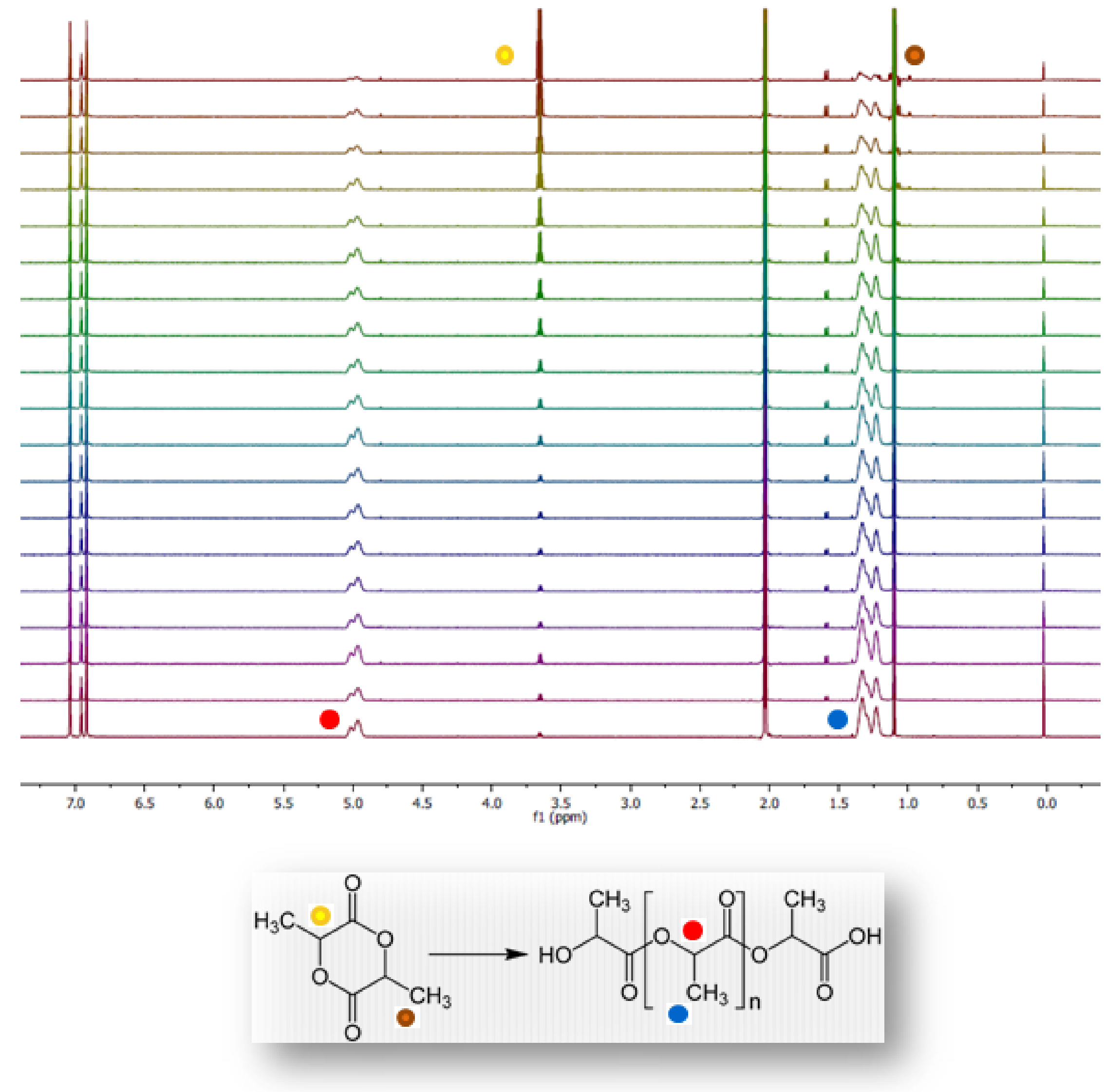


Figure S7. ^{1}H NMR spectra of PLLA formation in $C_6D_6CD_3$ ([LA]/[**1**] = 250)

5. [1]H NMR spectra of partially dissociated complex 2.

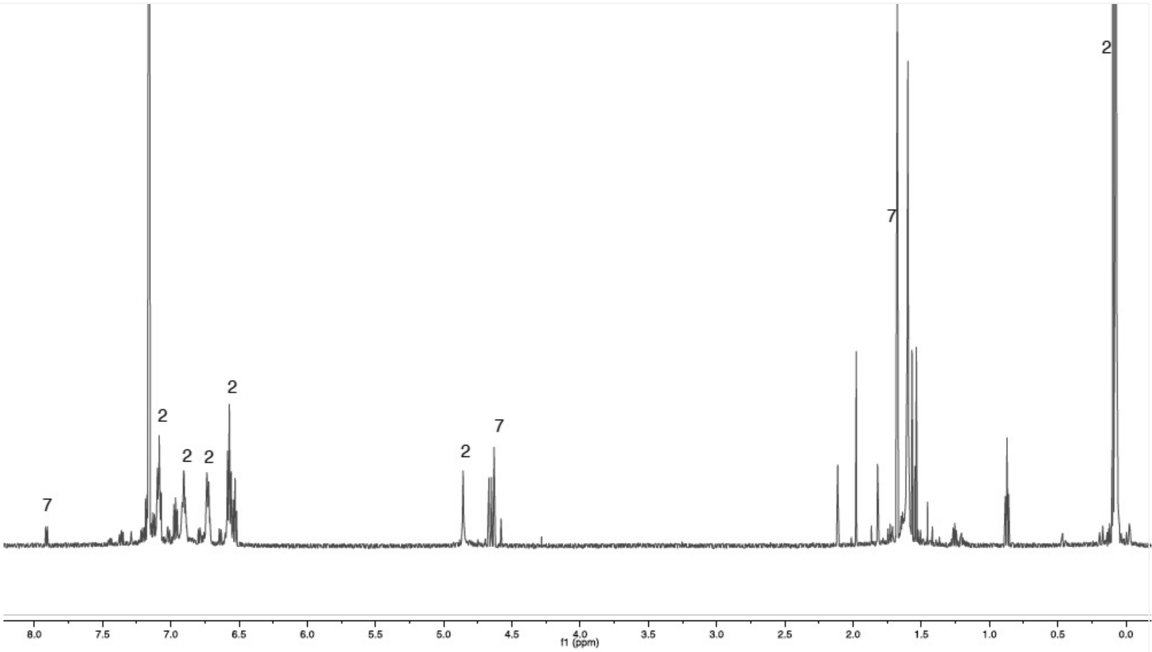


Figure S8. [1]H NMR spectra of partially dissotiated complex **2** (see signals of compound **2** and signals of compound **7**).

6. [1]H NMR spectrum of PLLA

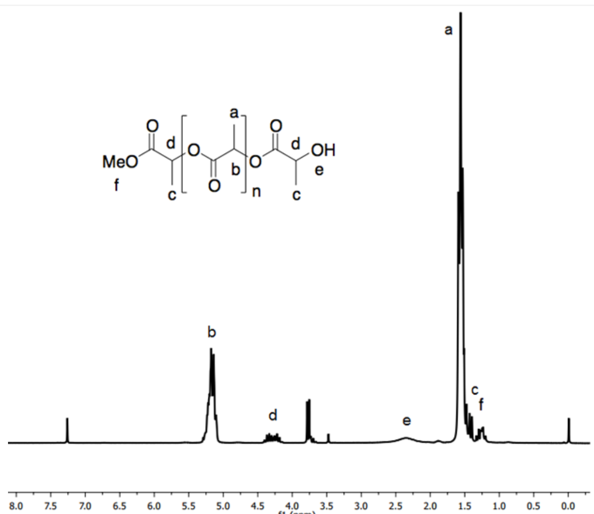


Figure S9. [1]H NMR spectrum (200 MHz, $CDCl_3$) of the oligomer product obtained from a reaction between L-LA and **1** at room temperature.

7. MALDI-TOF spectrum of PLLA

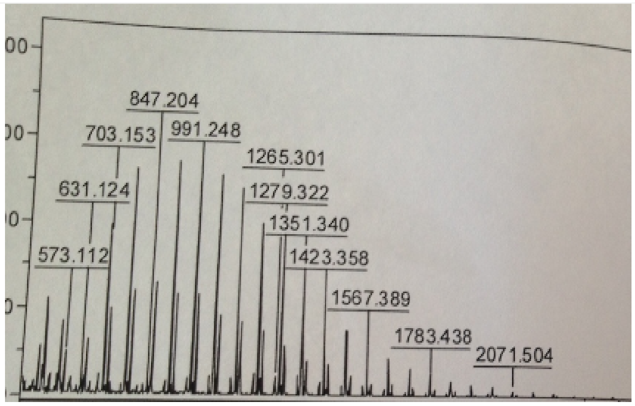


Figure S10. MALDI-TOF spectrum of the oligomer product obtained from a reaction between L-LA and **1** at room temperature.

8. PLLA SEC characterization

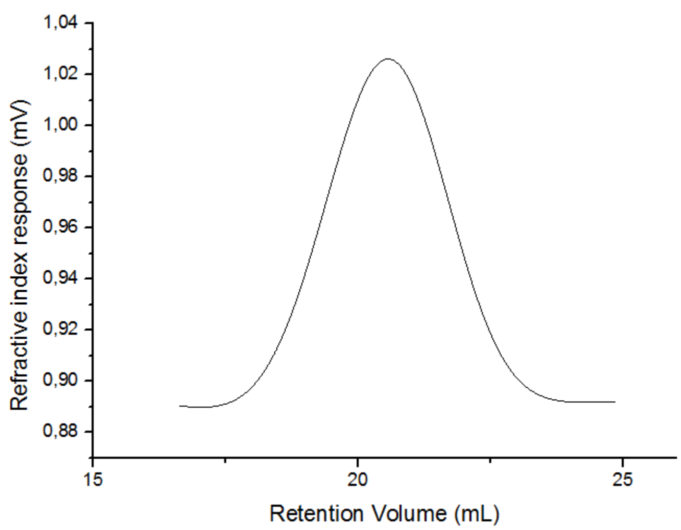


Figure S11. GPC traces of polymer produced using **1** at 25 °C. See Entry 1, Table 2 (manuscript).

References

1 (*a*) S. Schulz, J. Spielmann, D. Blaser and C. Wolper, *Chem. Commun.*, 2011, **47**, 2676-2678; (*b*) S. S. Al-Juaid, N. H. Buttrus, C. Eaborn, P. B. Hitchcock, A. T. L. Roberts, J. D. Smith and A. C. Sullivan, *Chem. Commun.*, 1986, 908. (c) G. Anantharaman and K. Elango, *Organometallics*, 2007, **26**, 1089.