Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting information for:

Comparing a Series of 8-Quinolinolato Complexes of Aluminium, Titanium and Zinc as Initiators for the Ring-Opening Polymerization of rac-Lactide

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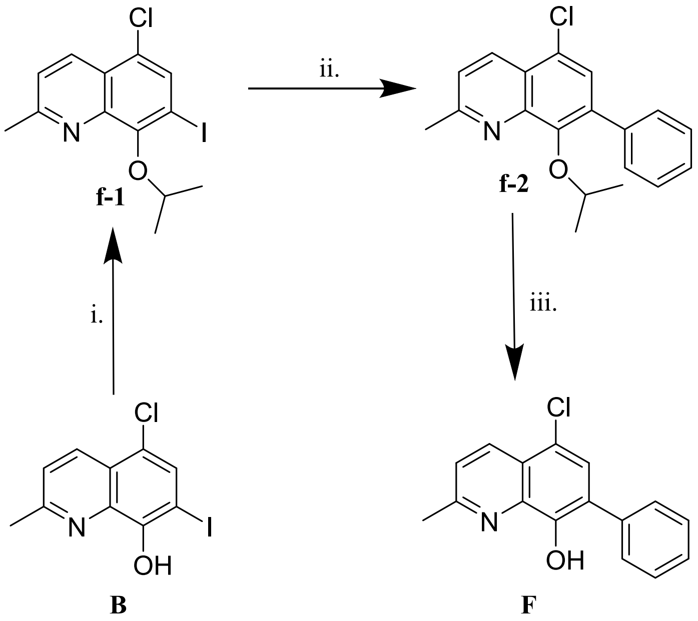
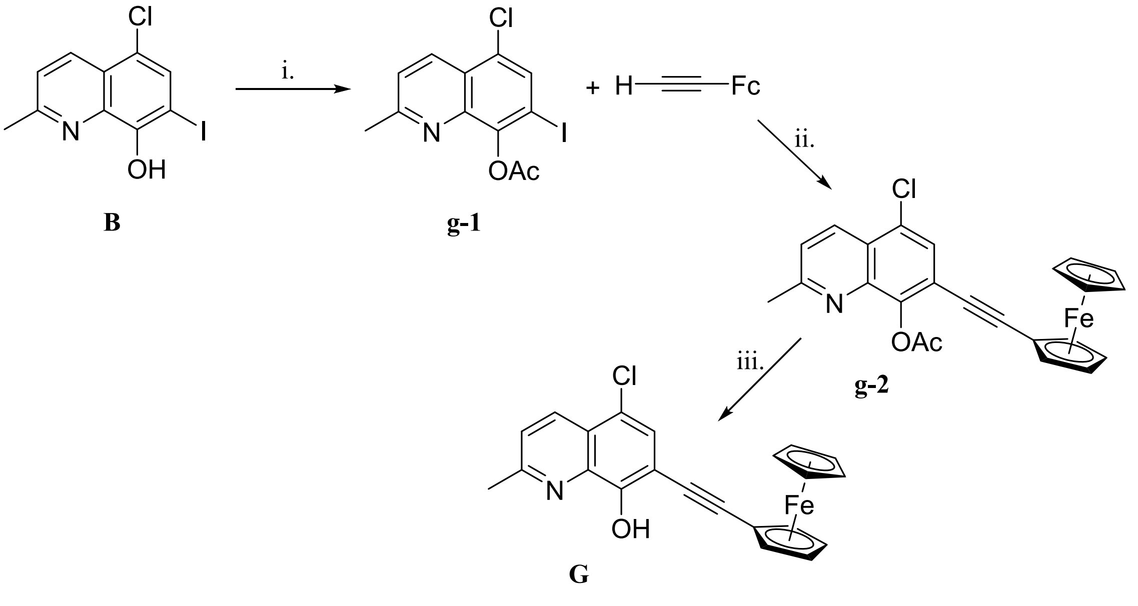


Scheme S1: Synthetic pathway to achieving pro-ligand, compound **F**. Reagents and conditions: i. 2-bromopropane, potassium carbonate, DMSO, 298 K, 16 h, 79 % ii. Phenyl boronic acid, Pd(PPh_3)$_4$, sodium carbonate (aq), toluene, ethanol, 373 K, 40 h, 88 % iii. Boron trichloride, methylene chloride, 220 K, 2 h, 82 %.



Scheme S2: Synthetic route to achieving compound **G**. Reagents and conditions: i. acetic anhydride, 410 K, 5 h, 90 % ii. CuI (5 %), Pd(PPh_3)$_2$$Cl_2$ (5 %), NEt_3, THF, 298 K, 12 h, 85 % iii. NEt_3/H_2O, 370 K, 6 h, 89 %.

^{1}H NMR spectra of Aluminium, Titanium and Zinc 8-Quinolinolato Complexes

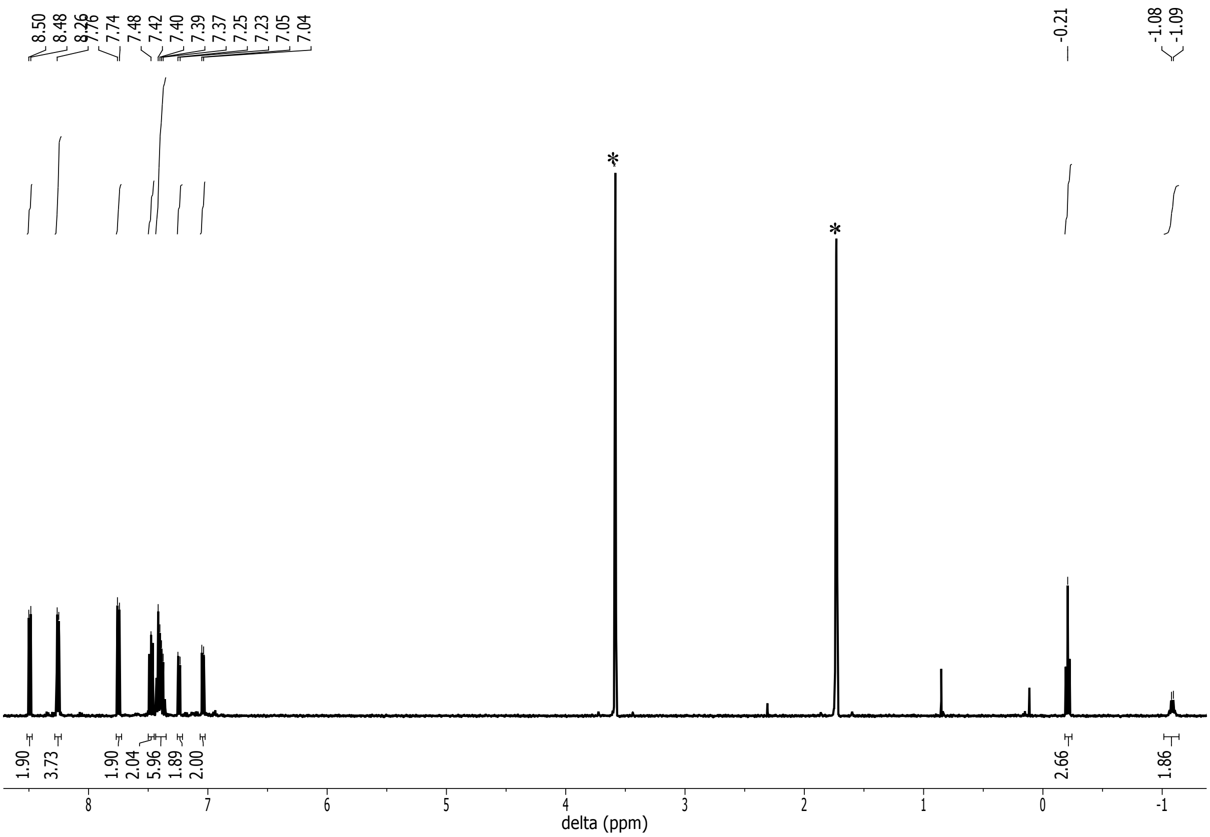


Figure S1: ^{1}H NMR spectrum of compound **Al-E** in THF-d_8; residual solvent peaks marked with asterisks.

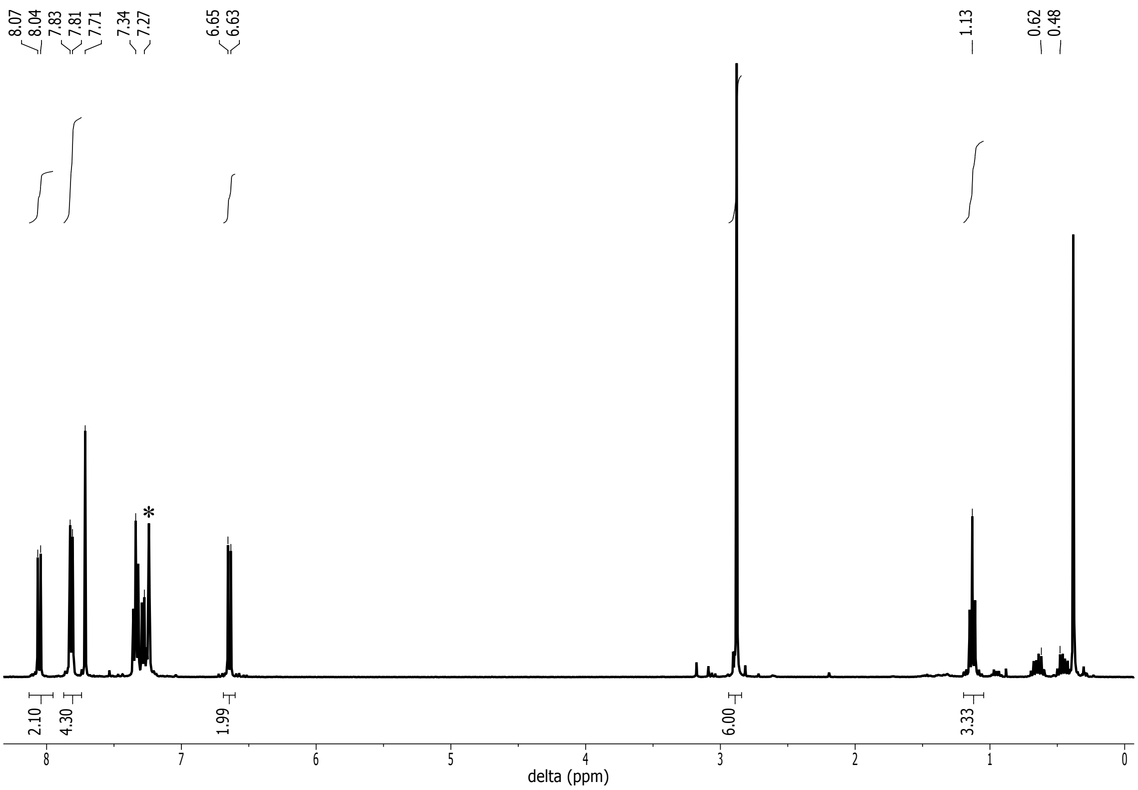


Figure S2: ^{1}H NMR spectrum of compound **Al-F** in benzene-d_8; residual solvent and grease peaks marked with asterisks.

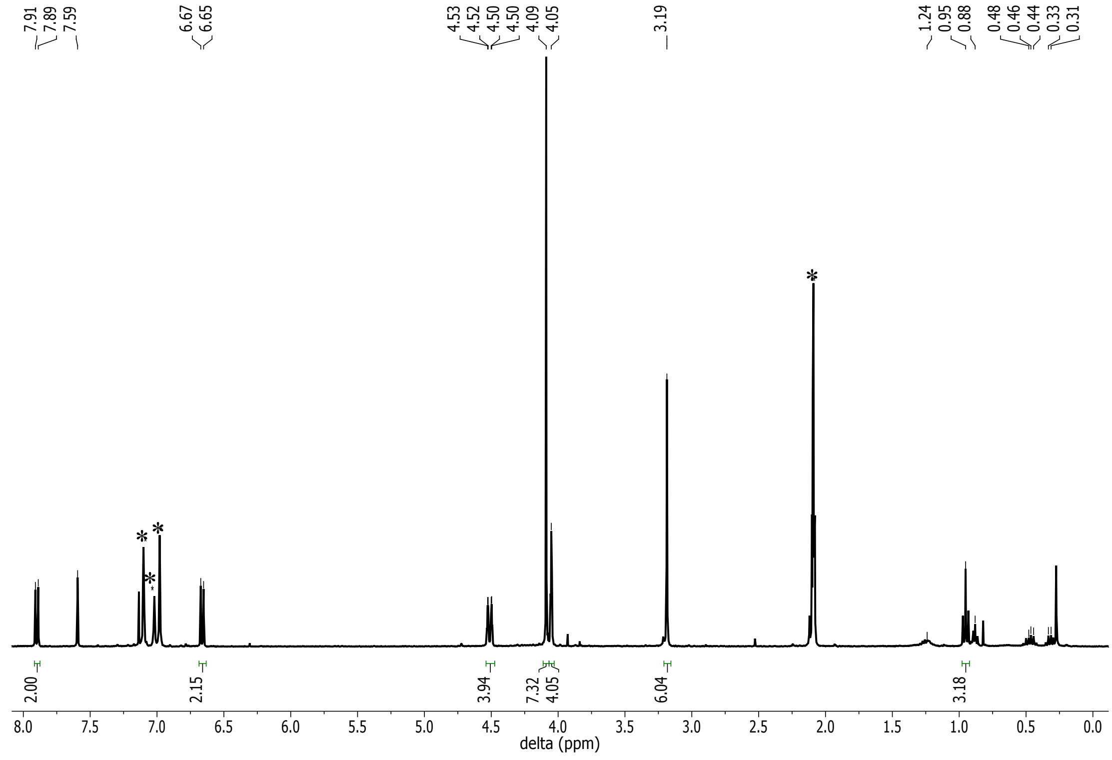


Figure S3: ^{1}H NMR spectrum of compound **Al-G** in toluene-d_8; residual solvent peaks marked with asterisks.

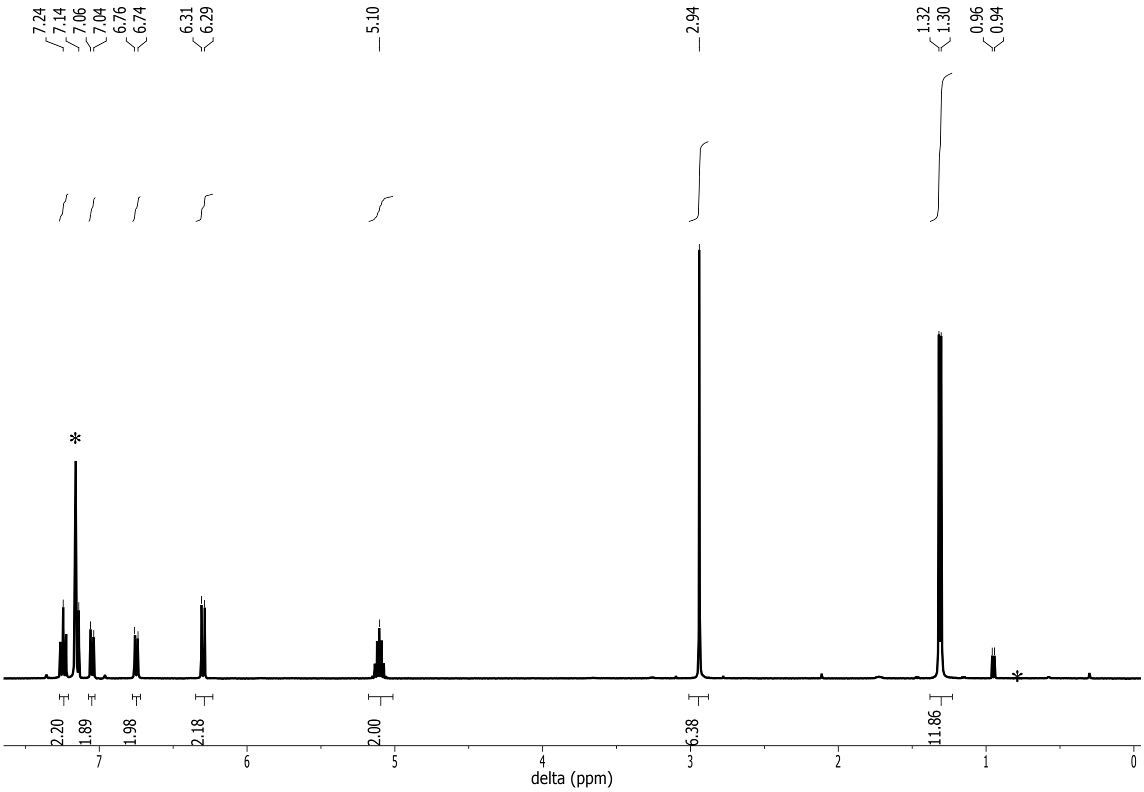


Figure S4: ^{1}H NMR spectrum of compound **Ti-D** in benzene-d_6; residual solvent peaks marked with asterisks.

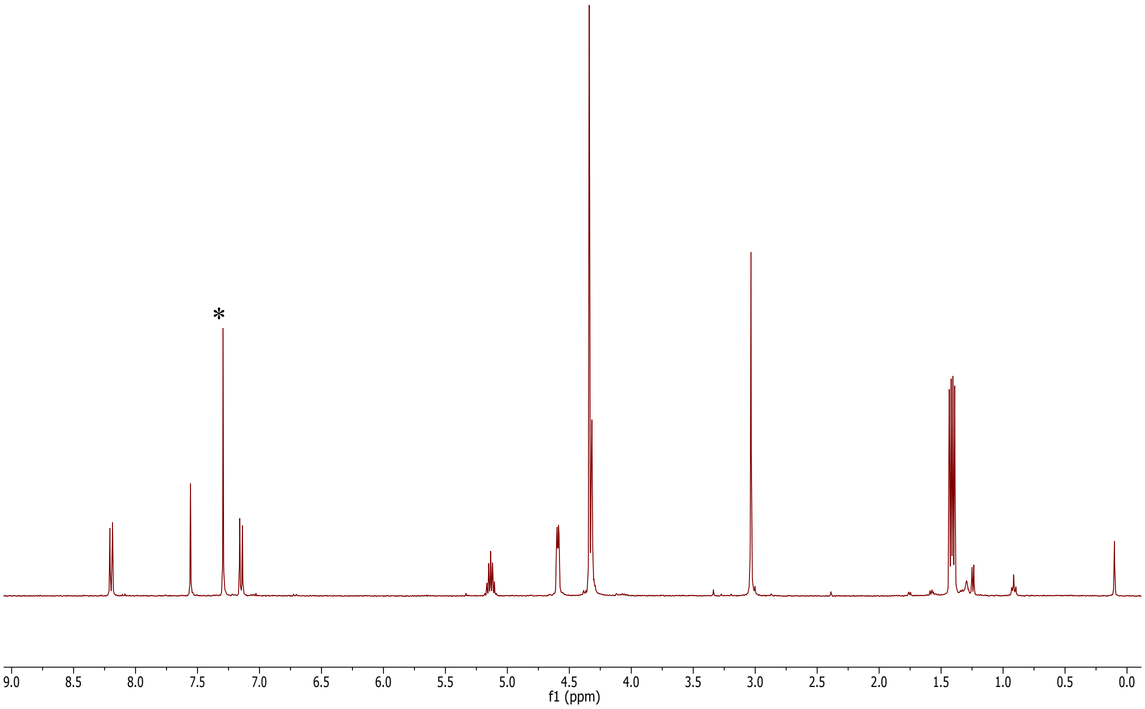


Figure S5: ^{1}H NMR spectrum of compound **Ti-G** in C*D*Cl$_3$; residual solvent peaks marked with asterisks.

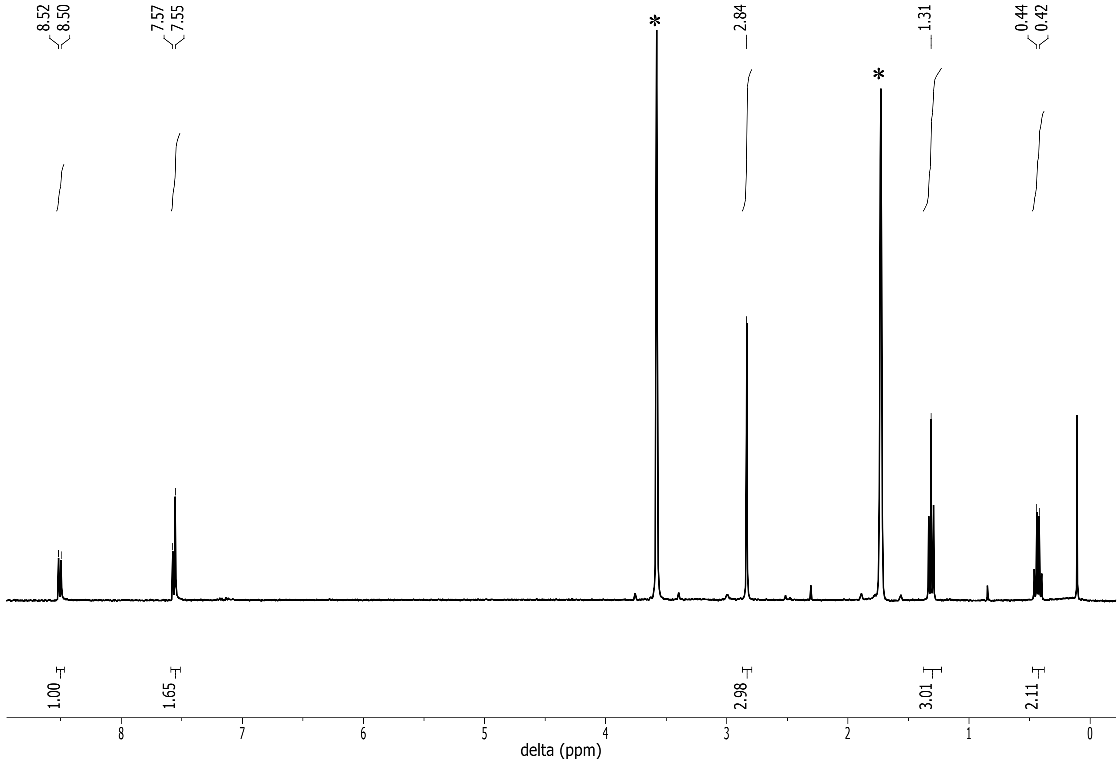


Figure S6: ¹H NMR spectrum of compound **Zn-A** in THF-d_8; residual solvent peaks marked with asterisks.

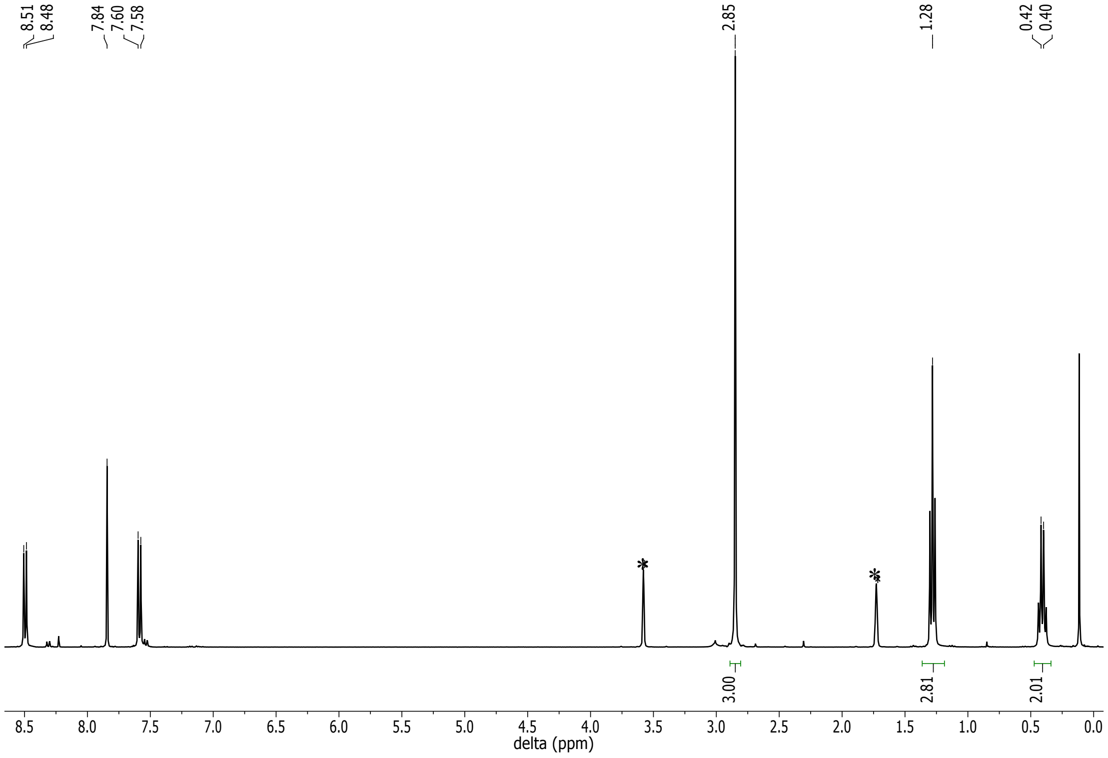


Figure S7: ¹H NMR spectrum of compound **Zn-B** in THF-d_8; residual solvent peaks marked with asterisks.

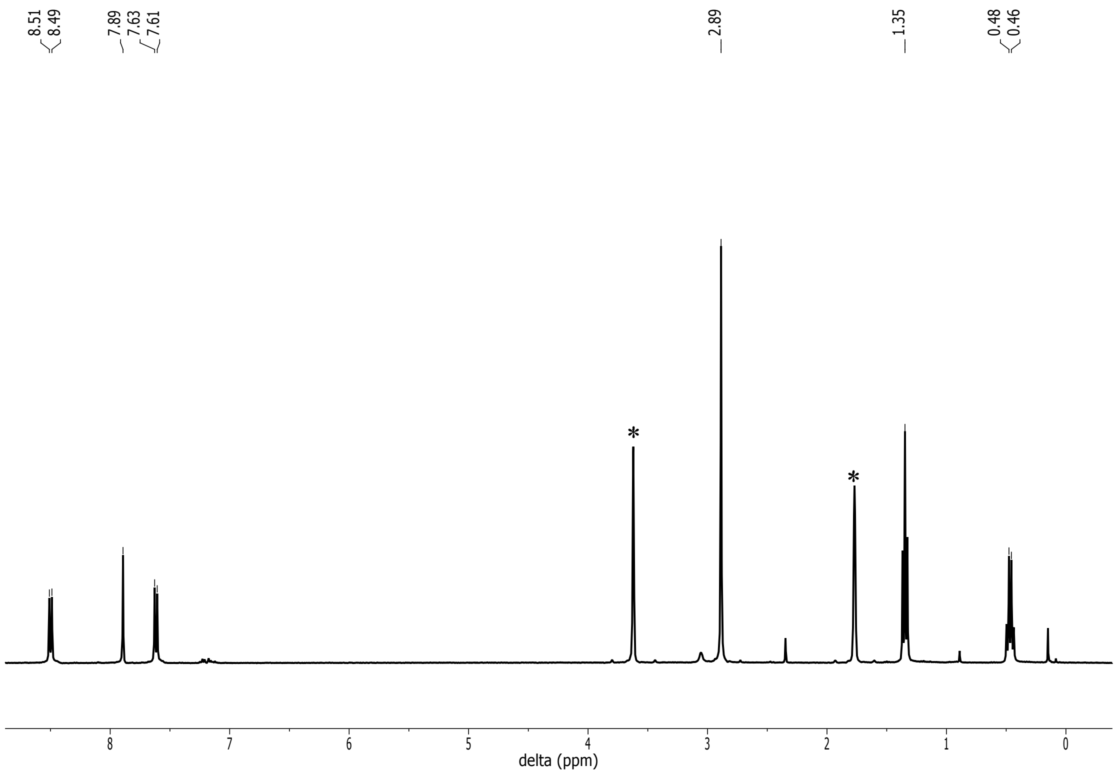


Figure S8: ^{1}H NMR spectrum of compound **Zn-C** in THF-d_8; residual solvent peaks marked with asterisks.

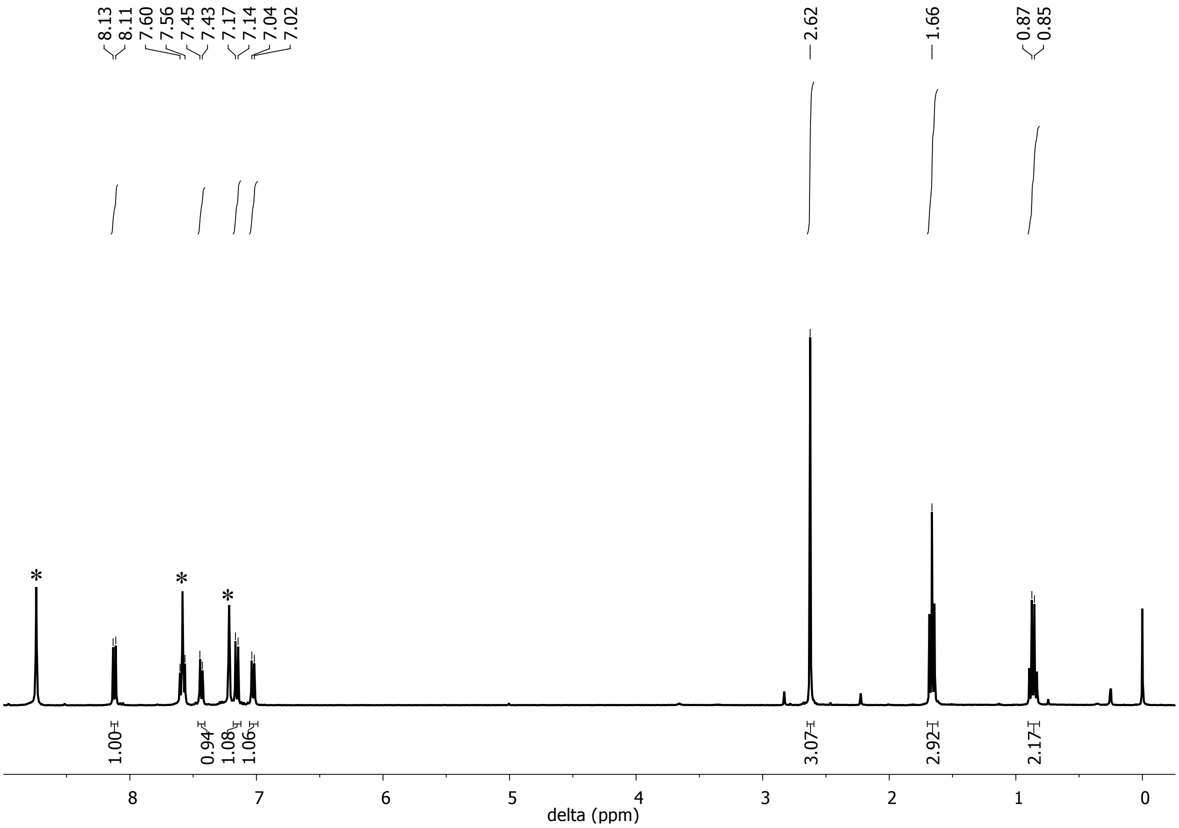


Figure S9: ^{1}H NMR spectrum of compound **Zn-D** in pyridine-d_5; residual solvent peaks marked with asterisks.

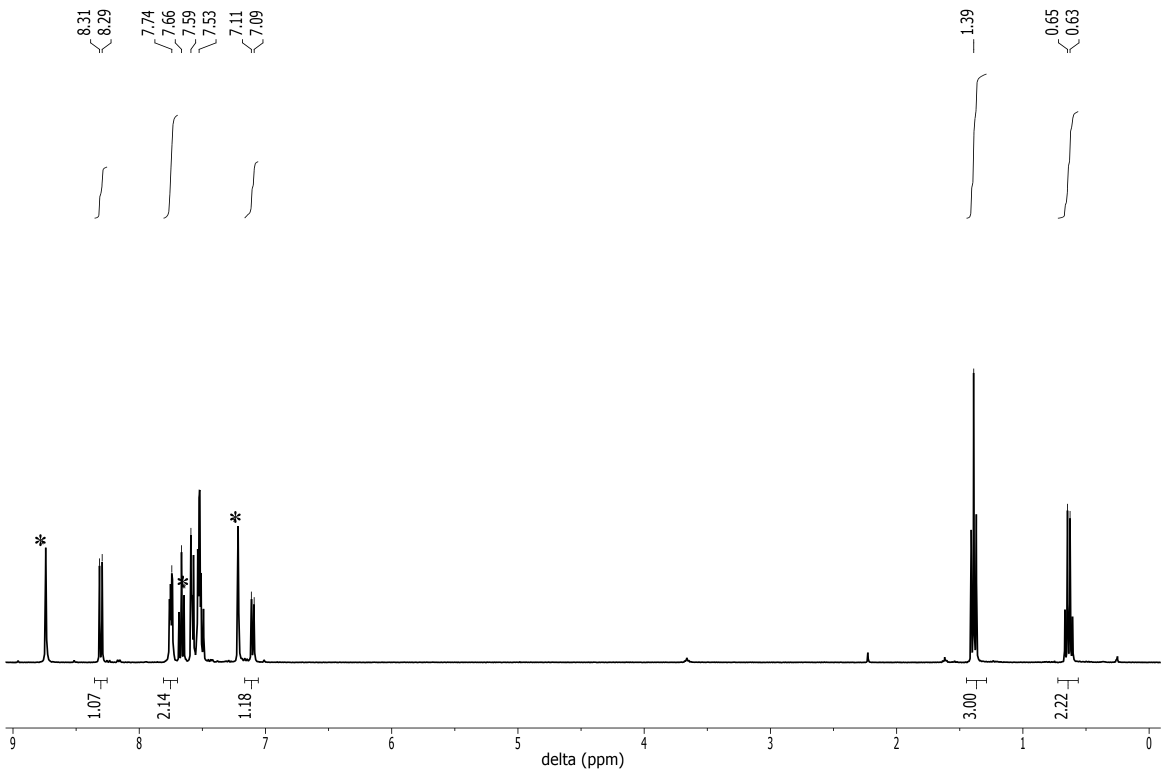


Figure S10: ^{1}H NMR spectrum of compound **Zn-E** in pyridine-d_5; residual solvent peaks marked with asterisks.

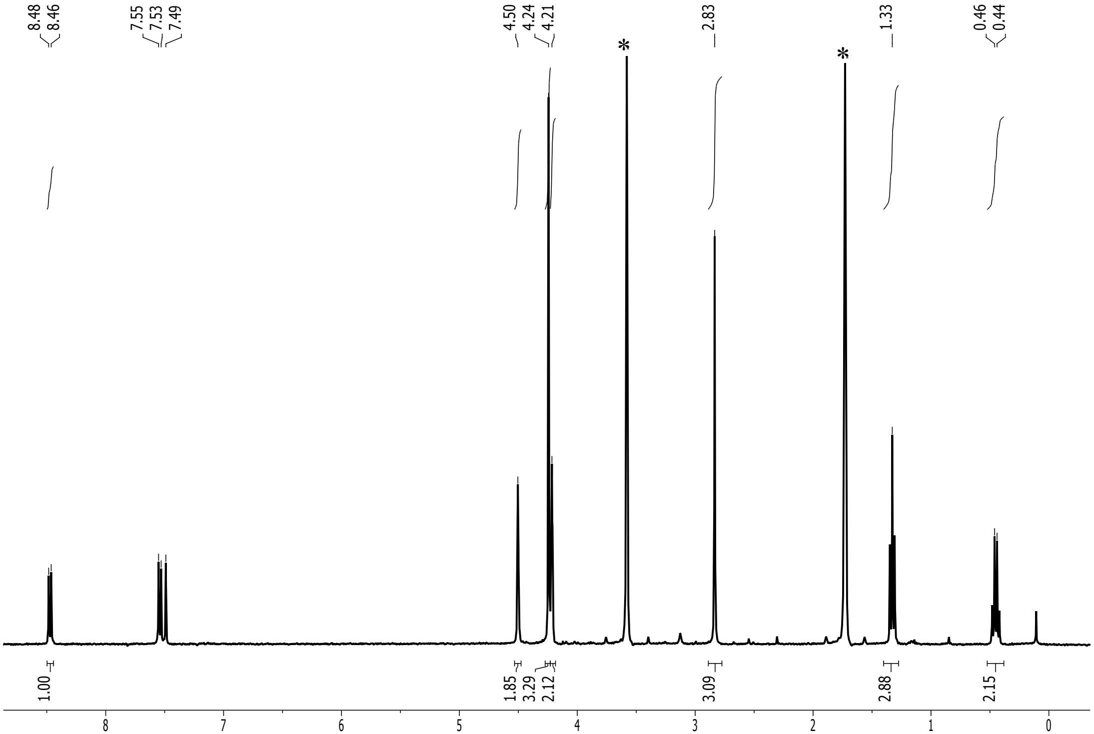


Figure S11: ^{1}H NMR spectrum of compound **Zn-G** in THF-d_8; residual solvent peaks marked with asterisks.

X-ray Crystallography Data

The X-ray crystal structure of Al-E

The C60-based toluene solvent molecule in the structure of **Al-E** (Fig. S12) was found to be disordered. Three orientations were identified of *ca*. 53, 33 and 14% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

The X-ray crystal structure of Zn-A

The structure of **Zn-A** (Fig. S13) has a centre of symmetry at the middle of the Zn_2O_2 ring.

The X-ray crystal structure of Zn-D

The structure of **Zn-D** is shown in Fig. S14.

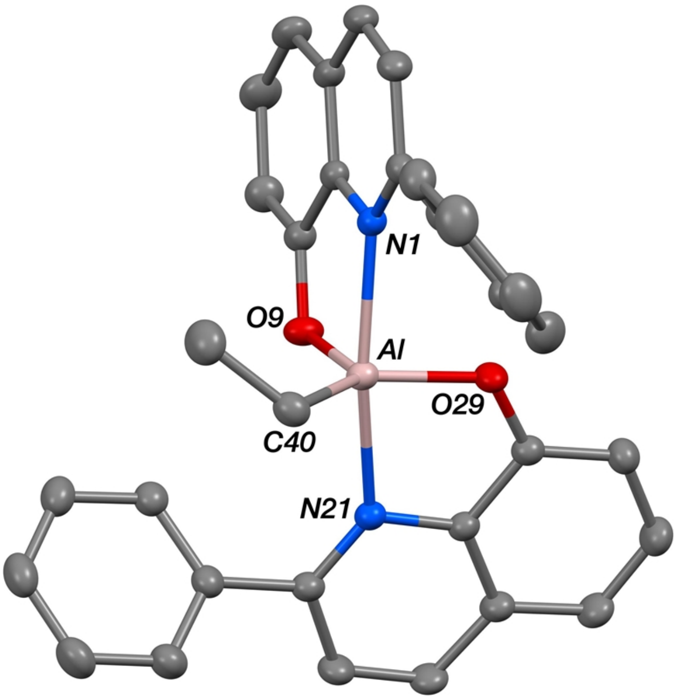


Fig. S12 The crystal structure of **Al-E** (50% probability ellipsoids).

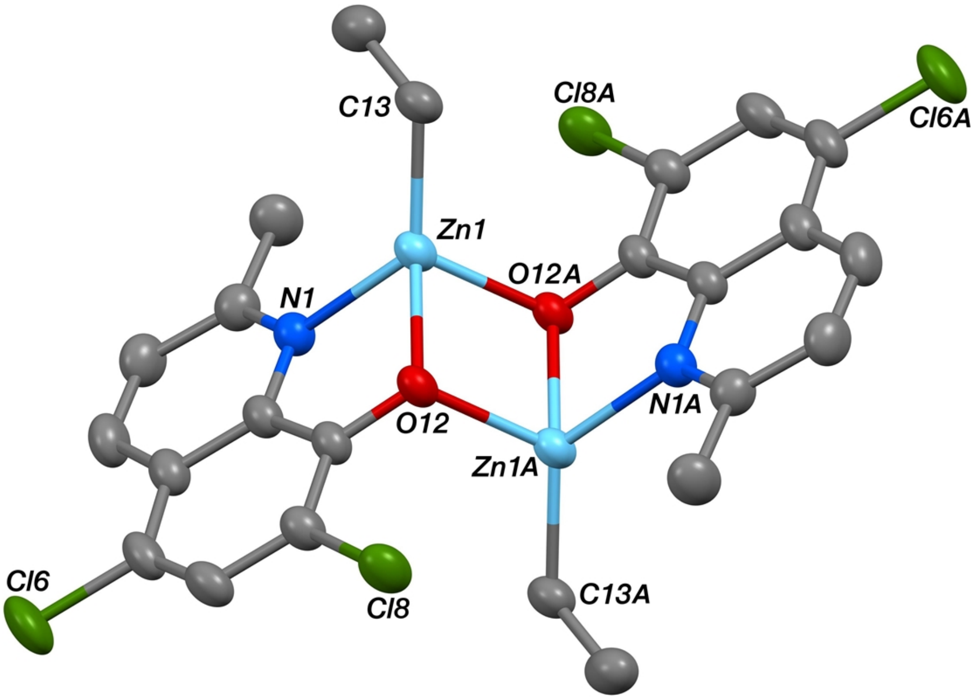


Fig. S13 The crystal structure of the C_i-symmetric complex **Zn-A** (50% probability ellipsoids).

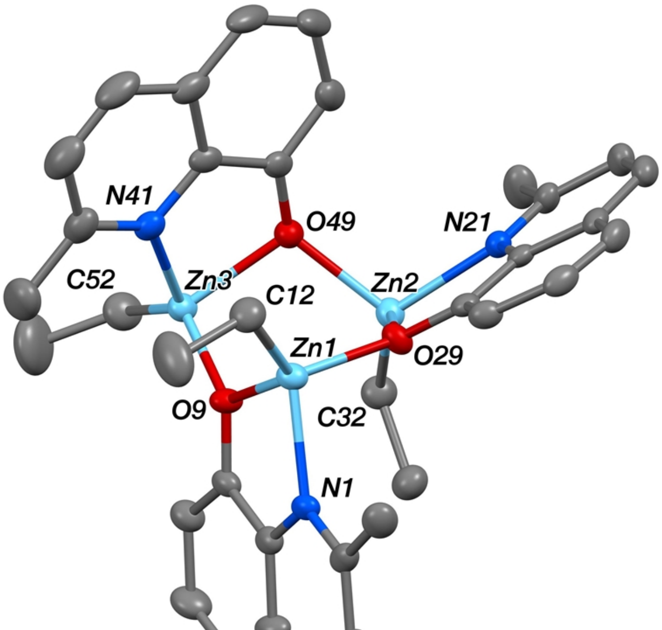


Fig. S14 The crystal structure of **Zn-D** (50% probability ellipsoids).

Crystal data for **Al-E**: $C_{32}H_{25}AlN_2O_2{\cdot}2(C_7H_8)$, M = 680.79, monoclinic, $C2/c$ (no. 15), a = 25.8123(7), b = 21.5571(4), c = 14.7290(4) Å, β = 116.529(3)°, V = 7332.8(4) Å^3, Z = 8, D_c = 1.233 g cm^{-3}, μ(Mo-Kα) = 0.097 mm^{-1}, T = 173 K, yellow blocks, Oxford Diffraction Xcalibur 3 diffractometer; 12412 independent measured reflections (R_{int} = 0.0242), F^2 refinement,[1] R_1(obs) = 0.0544, wR_2(all) = 0.1677, 9301 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 65°], 487 parameters. CCDC 1043547

Crystal data for **Zn-A**: $C_{24}H_{22}Cl_4N_2O_2Zn_2$, M = 642.98, orthorhombic, $Pbca$ (no. 61), a = 7.72046(6), b = 15.77008(11), c = 20.25661(15) Å, V = 2466.29(3) Å^3, Z = 4 [C_i symmetry], D_c = 1.732 g cm^{-3}, μ(Cu-Kα) = 6.595 mm^{-1}, T = 173 K, pale yellow tablets, Oxford Diffraction Xcalibur PX Ultra diffractometer; 2429 independent measured reflections (R_{int} = 0.0281), F^2 refinement,[1] R_1(obs) = 0.0273, wR_2(all) = 0.0787, 2214 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 145°], 155 parameters. CCDC 1043548

Crystal data for **Zn-D**: $C_{36}H_{39}N_3O_3Zn_3{\cdot}C_7H_8$, M = 849.94, triclinic, P-1 (no. 2), a = 11.8656(5), b = 12.3476(6), c = 14.4868(7) Å, α = 80.956(4), β = 69.131(4), γ = 78.832(4)°, V = 1936.67(17) Å^3, Z = 2, D_c = 1.458 g cm^{-3}, μ(Mo-Kα) = 1.886 mm^{-1}, T = 173 K, yellow blocks, Agilent Xcalibur 3E diffractometer; 7619 independent measured reflections (R_{int} = 0.0181), F^2 refinement,[1] R_1(obs) = 0.0323, wR_2(all) = 0.0738, 6378 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 57°], 477 parameters. CCDC 1043549

Polymerization Data

Representative Molecular weight versus percentage conversion graphs for PLA formed using aluminium, titanium and zinc 8-quinolinolato complexes:

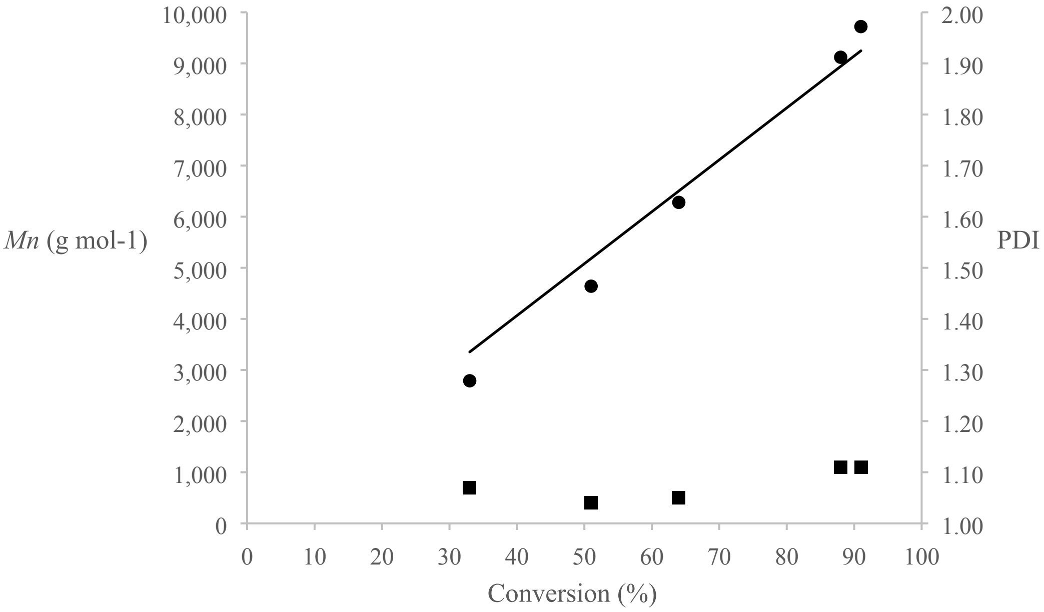


Figure S15: Plots of M_n versus % conversion (black circles) and PDI (black squares) using initiator **Al-E**; 1:1:100 [**Al-E**]:[iPrOH]:[LA], 1.0 M [LA], 298 K.

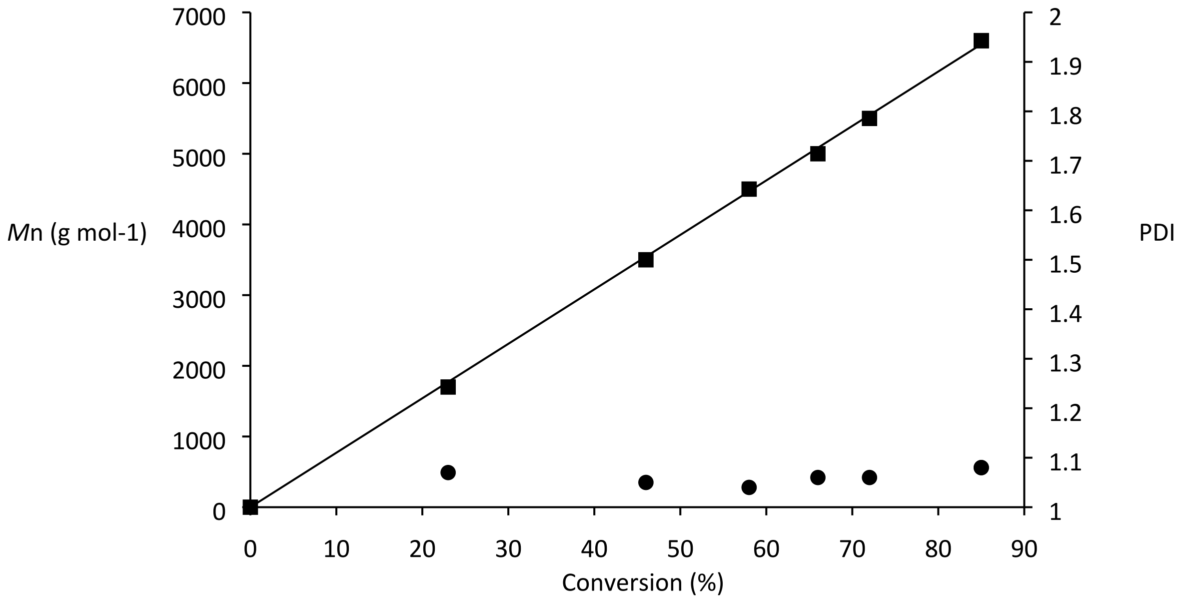


Figure S16: Plots of M_n versus % conversion (black squares) and PDI (black circles) using initiator **Ti-G**; 1:100 [**Ti-G**]:[LA], 1.0 M [LA], 298 K.

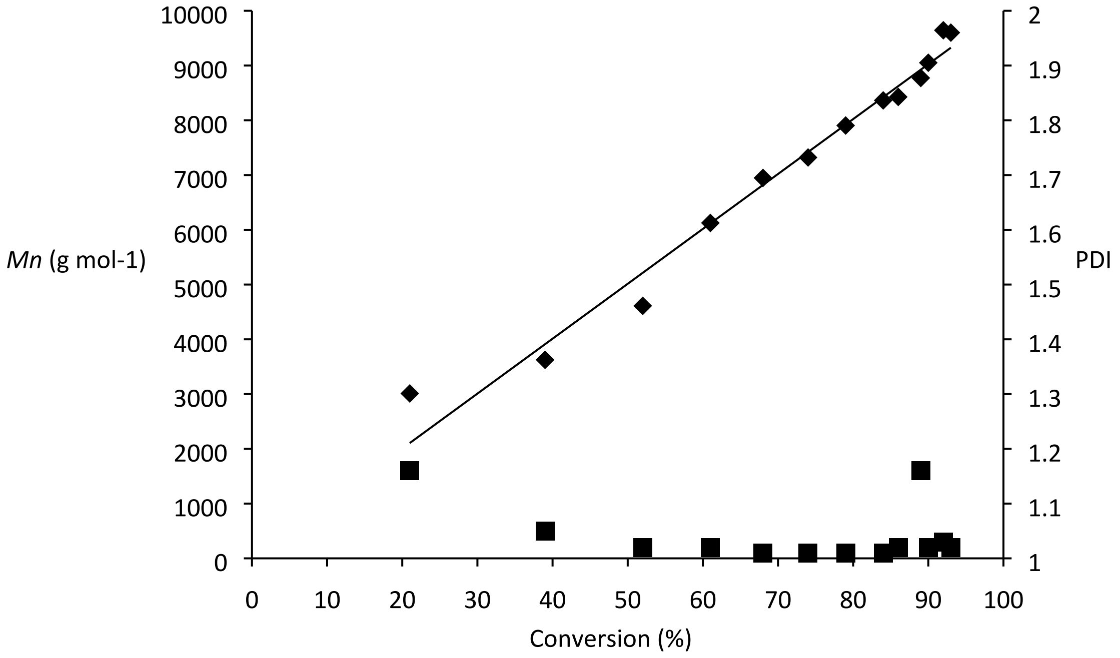


Figure S17: Plots of M_n versus % conversion (black diamonds) and PDI (black squares) using initiator **Zn-A**; 1:1:100 [**Zn-A**]:[iPrOH]:[LA], 1.0 M [LA], 298 K.

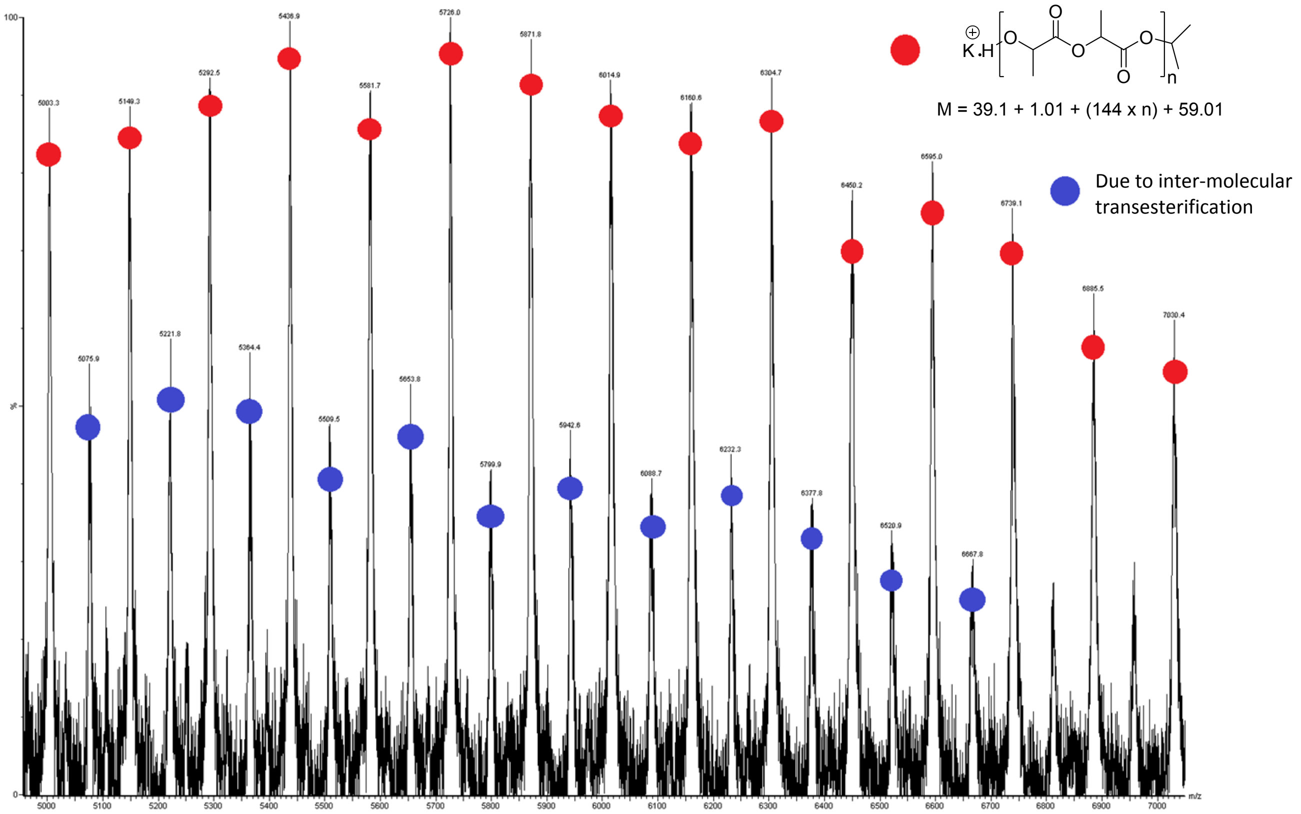


Figure S18: MALDI-ToF spectrum of the PLA produced using initiator Al-G.

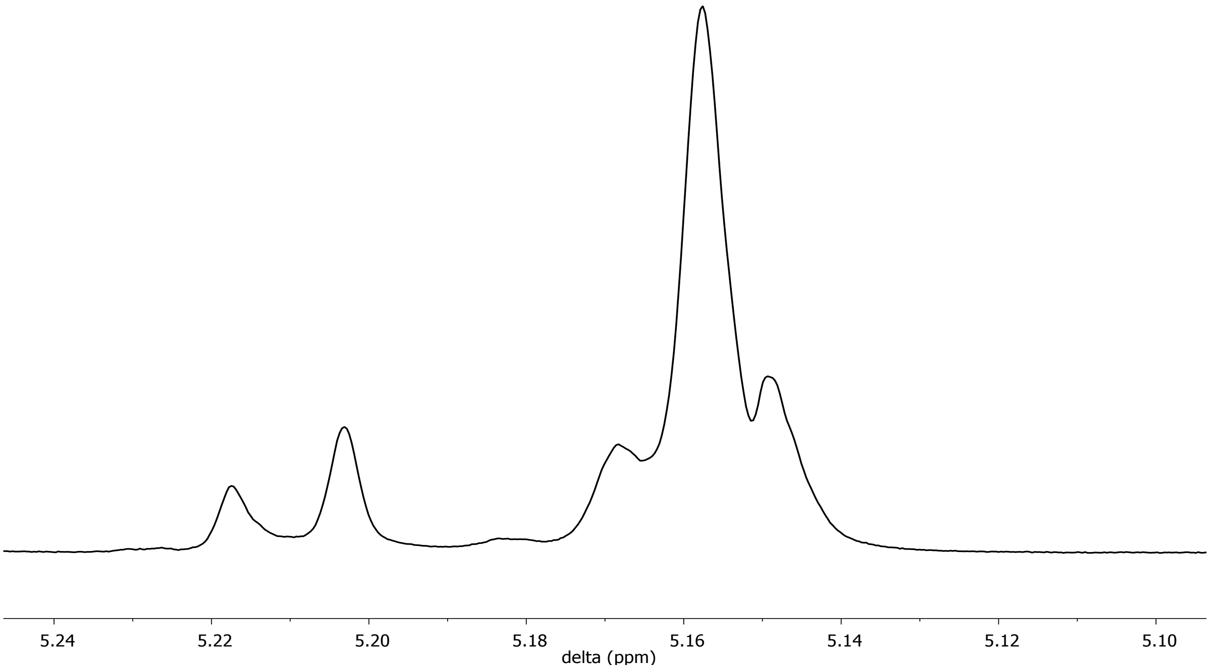


Figure S19: The methyne region of the $^1H\{^1H\}$ NMR spectrum of PLA in $CDCl_3$. Reagents and conditions: 1 :1:100 [**Al-F**]:[iPrOH]:[LA], 1.0 M [LA], 348 K ($P_i = 0.75$).

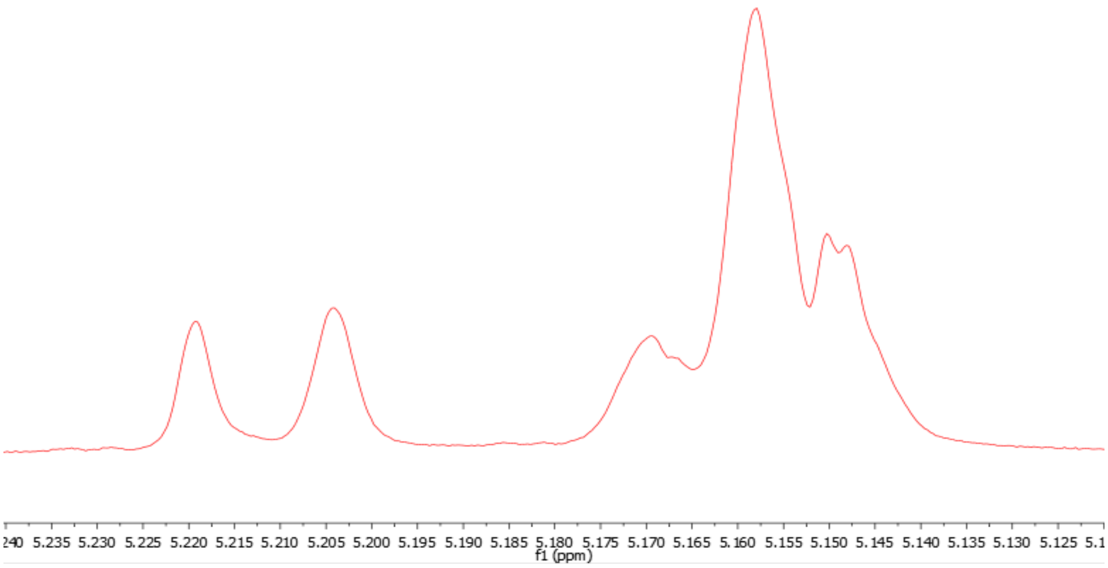


Figure S20: The methyne region of the $^1H\{^1H\}$ NMR spectrum of PLA in $CDCl_3$. Reagents and conditions: 1:100 [**Ti-B**]:[LA], 1.0 M [LA], 348 K ($P_i = 0.65$).

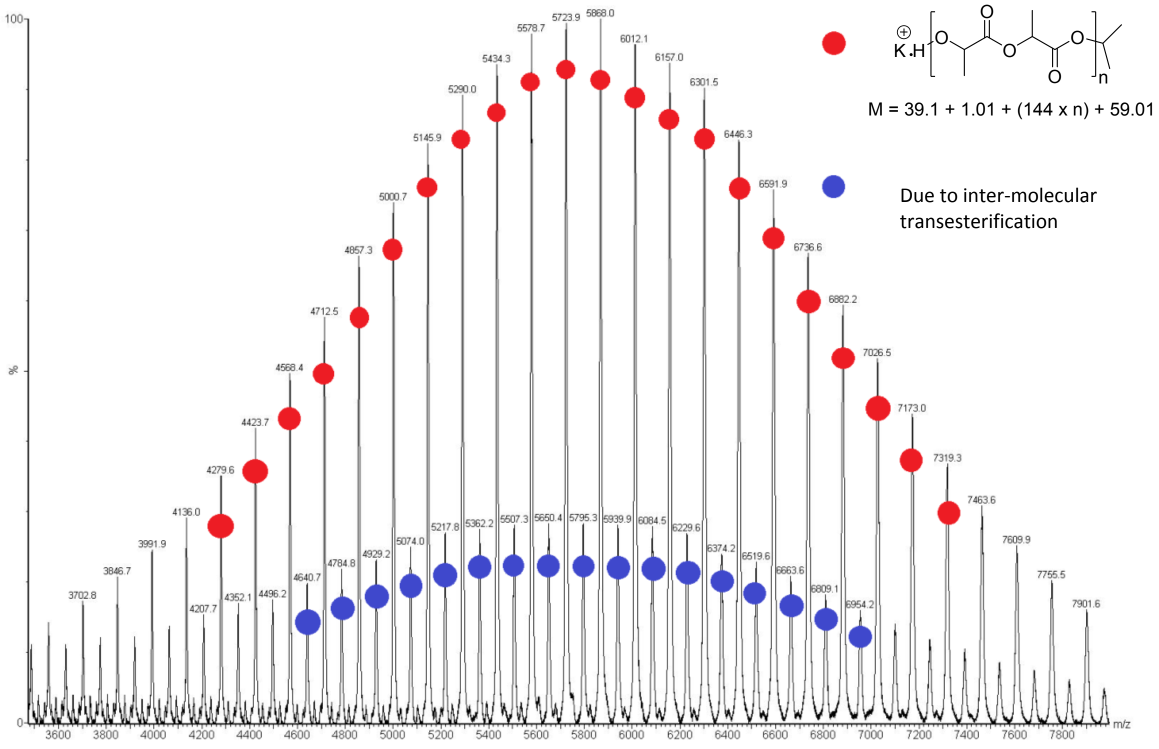


Figure S21: MALDI-ToF spectrum of the PLA produced using initiator **Zn-A**.

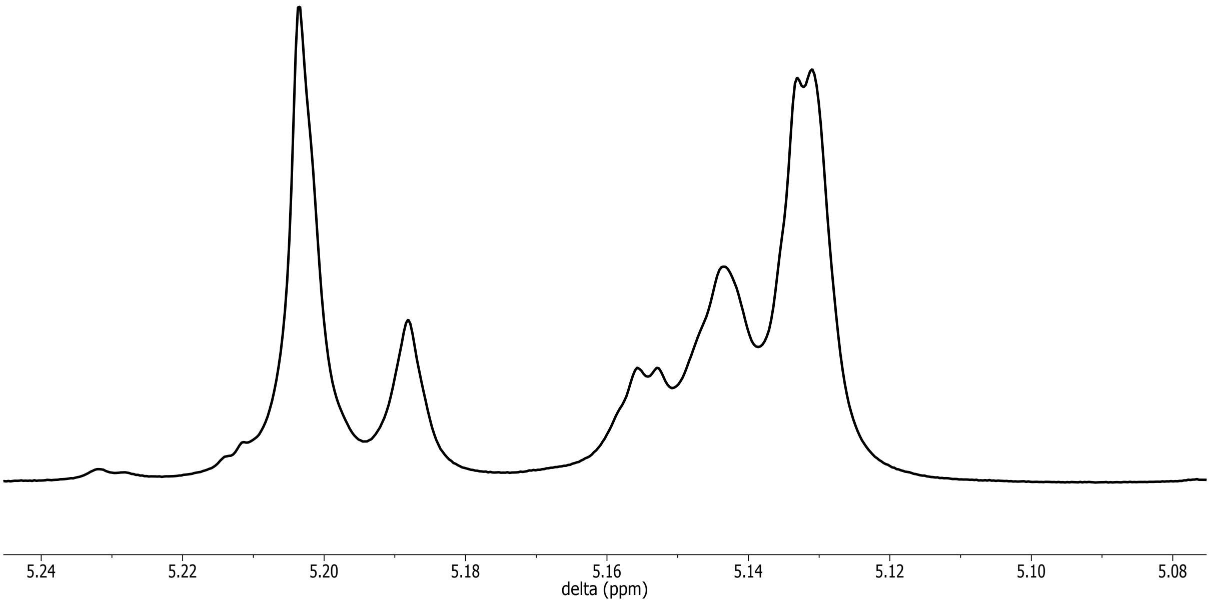


Figure S22: The methyne region of the $^{1}H\{^{1}H\}$ NMR spectrum of PLA in $CDCl_3$. Reagents and conditions: 1:1:100 [**Zn-E**]:[iPrOH]:[LA], 1.0 M [LA], 298 K ($P_s = 0.70$).

Experimental Section

2-Phenyl-8-hydroxyquinoline (E)[2]

Bromobenzene (6 mL, 57.8 mmol) was added dropwise to a stirred suspension of lithium metal (0.84 mg, 121.0 mmol) in diethyl ether (40 mL). After stirring for 1 h, a solution of 8-hydroxyquinoline (4.0 g, 27.6 mmol) in diethyl ether (80 mL) was added dropwise. The solution was heated at reflux for 1 h, cooled to 298 K and argon was bubbled through a water bubbler into the solution. Diethyl ether (80 mL) and water (40 mL) were added slowly, the resulting solution was neutralised with conc. HCl. The two phases were separated and the aqueous layer was then extracted with methylene chloride (3 x 50 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed *in vacuo*. The product was then purified by column chromatography (9:1 hexane:ethyl acetate, $R_f = 0.31$) to yield a white solid (3.23 g, 14.6 mmol, 53 %, lit. 56 %[2]).

^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.20 (dd, 1H, C*H*, $^3J_{HH}$=7.6 Hz, $^4J_{HH}$=1.2 Hz), 7.35 (dd, 1H, C*H*, $^3J_{HH}$=8.2 Hz, $^4J_{HH}$=1.2 Hz), 7.45 (t, 1H, C*H*, $^3J_{HH}$=8.0 Hz), 7.49 (m, 1H, C*H*), 7.55 (m, 2H, C*H*), 7.94 (d, 1H, C*H*, $^3J_{HH}$=8.6 Hz), 8.17 (dd, 2H, C*H*, $^3J_{HH}$=7.2 Hz, $^4J_{HH}$=1.6 Hz), 8.24 (d, 1H, C*H*, $^3J_{HH}$=8.6 Hz), 8.37 (bs, 1H, O*H*); Anal. Calc. ($C_{15}H_{11}NO$): C, 81.43 %; H, 5.01 %; N, 6.33 % Found: C, 81.49 %; H, 5.04 %; N, 6.32 %.

5-Chloro-7-iodo-8-isopropoxy-2-methylquinoline (f-1)

To a stirred solution of 5-chloro-7-iodo-8-hydroxy-2-methylquinoline (**B**) (2.00 g, 6.26 mmol) in DMSO (20 mL) was added potassium carbonate (1.06 g, 9.40 mmol) and 2-bromopropane (3.62 g, 26.30 mmol). The suspension was stirred overnight at 298 K, after which time a saturated solution of ammonium chloride (20 mL) was added. The reaction mixture was extracted with methylene chloride (3 x 100 mL) and the organic phases were combined and washed with solutions of NaOH (2 M, 100 ml), water (100 ml), brine (100 ml) and then dried (Na_2SO_4). The solvent was removed *in vacuo* and the crude product was purified by column chromatography (ethyl acetate:hexane = 25:75) (1.77 g, 4.9 mmol, 79 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.36 (d, 1H, C*H*, $^3J_{HH}$ = 8.7 Hz), 7.89 (s, 1H, C*H*), 7.38 (d, 1H, C*H*, $^3J_{HH}$ = 8.7 Hz), 5.35 (sept, 1H, C*H*(CH_3)$_2$, $^3J_{HH}$ = 6.2 Hz), 2.75 (s, 3H, C*H*$_3$), 1.44 (d, 6H, CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.2 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 159.0 (C^{IV}), 154.0 (*C*CH_3), 142.2 (C^{IV}), 134.4 (*C*H), 133.6 (*C*H), 125.8 (C^{IV}), 125.6 (C^{IV}), 123.1 (*C*H), 91.7 (C^{IV}), 78.3 (O*C*H), 25.6 (*C*H_3), 23.1 (CH(*C*H_3)$_2$); Anal. Calc. ($C_{13}H_{13}ClINO$): C, 43.18 %; H, 3.62 %; N, 3.87 % Found: C, 43.24 %; H, 3.71 %; N, 3.93 %.

5-Chloro-8-isopropoxy-2-methyl-7-phenylquinoline (f-2)

To a Schlenk tube charged with 5-chloro-7-iodo-8-isopropoxyquinaldine (**f-1**) (0.50 g, 1.39 mmol), phenylboronic acid (0.20 g, 1.60 mmol) and $Pd(PPh_3)_4$ (48 mg, 41 μmol) was added toluene (20 ml), Na_2CO_3 (2 M, 18 mL) and ethanol (3 mL). The reaction mixture was heated at reflux (373 K) for 40 h after which time the solution was cooled and extracted with ether (3 x 20 mL). The organic phases were collected, dried (Na_2SO_4), and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (ethyl acetate:hexane = 5:95) to yield the product as a white powder (0.38 g, 1.2 mmol, 88 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.40 (d, 1H, C*H*, $^3J_{HH}$ = 8.6 Hz), 7.69 (d, 1H, C*H*, $^3J_{HH}$ = 8.6 Hz), 7.60 (s, 1H, C*H*), 7.34-7.48 (m, 5H, C*H*), 4.56 (sept, 1H, C*H*(CH_3)$_2$, $^3J_{HH}$ = 6.2 Hz), 2.79 (s, 3H, C*H*$_3$), 1.08 (d, 6H, CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.2 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 159.2 (C^{IV}), 150.0 (C^{IV}), 144.2 (C^{IV}), 138.3 (C^{IV}), 135.2 (C^{IV}), 133.2 (*C*H), 130.2 (*C*H), 128.2 (*C*H), 127.9 (C*H*), 127.6 (*C*H), 125.5 (C^{IV}), 124.9 (C^{IV}), 122.7 (*C*H), 77.6 (OC*H*(CH_3)$_2$), 25.8 (*C*H_3), 22.5 (CH(*C*H_3)$_2$); Anal. Calc. ($C_{19}H_{18}ClNO$): C, 73.19 %; H, 5.82 %; N, 4.49 %. Found: C, 73.20 %; H, 5.93 %; N, 4.53 %.

5-Chloro-8-hydroxy-2-methyl-7-phenylquinoline (F)

To a stirred solution of 5-chloro-8-isopropoxy-2-methyl-7-phenylquinoline (**f-2**) (0.50 g, 1.60 mmol) in methylene chloride (10 mL) was added boron trichloride (1.0 M in CH_2Cl_2, 6.50 mL, 6.41 mmol) at 195 K. The reaction mixture was stirred at 195 K for 2 h, warmed to 298 K and stirred for a further 2 h. Ethanol (25 mL) was added and the mixture was stirred for 16 h. The solvent was removed *in* *vacuo* and the resulting residue washed with water. The product was then extracted with diethyl ether (3 x 25 mL) to yield a yellow solid (0.35 g, 1.2 mmol, 82 %).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.40 (d, 1H, C*H*, $^3J_{HH}$ = 8.8 Hz), 7.69 (d, 1H, C*H*, $^3J_{HH}$ = 7.6 Hz), 7.63 (s, 1H, C*H*), 7.35-7.54 (m, 5H, C*H*), 2.77 (s, 3H, C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ (ppm): 158.1 (C^{IV}), 147.5 (C^{IV}), 138.6 (C^{IV}), 136.9 (*C*H), 133.49 (*C*H), 129.4 (*C*H), 128.6 (*C*H), 128.0 (*C*H), 127.6 (*C*H), 123.7 (*C*H), 123.4 (*C*^{IV}), 123.1 (C^{IV}), 120.6 (*C*H), 25.0 (*C*H$_3$); Anal. Calc. ($C_{16}H_{12}ClNO$): C, 71.25 %; H, 4.48 %; N, 5.19 % Found: C, 70.95 %; H, 4.63 %; N, 5.02 %.

8-Acetoxy-5-chloro-7-iodo-2-methylquinoline (g-1)[3]

5-Chloro-7-iodo-8-hydroxy-2-methylquinolinate (**B**) (4.00 g, 12.50 mmol) was dissolved in acetic anhydride (120 mL). The solution was heated at reflux for 5 h, after which time the solvent was removed *in vacuo*. The residue was stirred in saturated sodium hydrogen carbonate (20 mL) after which the product was extracted into methylene chloride (3 x 20 mL). The organic washings were dried (MgSO$_4$) and the solvent was removed *in vacuo* to yield a brown solid (4.13 g, 11.40 mmol, 91 %).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.35 (d, 1H, C*H*, ^{3}J$_{HH}$=8.8 Hz), 7.89 (s, 1H, C*H*), 7.39 (d, 1H, C*H*, $^3J_{HH}$=8.8 Hz), 2.71 (s, 3H, COC*H*$_3$), 2.52 (s, 3H, C*H*$_3$); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ (ppm): 168.7 (CH$_3$*C*OOR), 161.1 (C^{IV}), 148.1 (C^{IV}), 141.4 (C^{IV}), 133.8 (*C*H), 133.4 (*C*H), 129.4 (C^{IV}), 125.6 (C^{IV}), 123.9 (*C*H), 90.2 (C^{IV}), 25.8 (*C*H$_3$), 21.2 (*C*H$_3$COOR); Anal. Calc. ($C_{12}H_9ClINO_2$): C, 39.86 %; H, 2.51 %; N, 3.87 % Found: C, 39.87 %; H, 2.47 %; N, 3.78 %.

8-Acetoxy-5-chloro-7-(2'-ethynylferrocene)-2-methylquinoline (g-2)

8-Acetoxy-5-chloro-7-iodo-2-methylquinoline (**g-1**) (1.41 g, 3.91 mmol) and ethynylferrocene (945 mg, 4.5 mmol) were dissolved in THF (25 mL) and triethylamine (10 mL). Copper iodide (37 mg, 5 %) and Pd(PPh$_3$)$_2$Cl$_2$ (135 mg, 5 %) were added sequentially to the solution. The reaction was stirred under argon at room temperature for 20 h. The solvent was removed *in vacuo* and the product was purified by column chromatography (methylene chloride, R$_f$ = 0.33) to yield a pale orange solid (85 %, 3.30 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.35 (d, 1H, C*H*, $^3J_{HH}$=8.8 Hz), 7.62 (s, 1H, C*H*), 7.36 (d, 1H, C*H*, $^3J_{HH}$=8.8 Hz), 4.52 (t, 2H, Cp(C*H*)C≡C, $^3J_{HH}$=1.9 Hz), 4.28 (t, 2H, Cp(C*H*)C≡C, $^3J_{HH}$=1.9 Hz), 4.24 (s, 5H, Cp(C*H*)), 2.73 (s, 3H, COCH_3), 2.56 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 169.1 (CH_3*C*OOR), 161.0 (C^{IV}), 147.2 (C^{IV}), 141.7 (C^{IV}), 133.2 (*C*H), 128.5 (C^{IV}), 127.9 (*C*H), 125.3 (C^{IV}), 123.6 (*C*H), 118.4 (C^{IV}), 96.9 (C≡C), 80.2 (C≡C), 71.9 (Cp(*C*H)C≡C), 70.4 (Cp(*C*H)), 69.6 (Cp(*C*H)C≡C), 64.2 (Cp(C^{IV})C≡C), 25.8 (*C*H_3), 21.0 (*C*H_3COOR); IR (cm^{-1}): 2217.0 (C≡C, very weak), 1762.0 (C=O); Anal. Calc. ($C_{24}H_{18}ClFeNO_2$): C, 64.97 %; H, 4.09 %; N, 3.16 % Found: C, 64.90 %; H, 4.06 %; N, 3.15 %.

5-Chloro-7-(2'ethynylferrocene) -8-hydroxy-2-methylquinoline (G)

8-Acetoxy-5-chloro-7-(2'-ethynylferrocene)-2-methylquinoline (**g-2**) (1.47 g, 3.30 mmol), triethylamine (120 mL) and water (10 mL) were heated at reflux (363 K) for 6 h. The solvent was removed i*n vacuo* and the brown residue was dissolved in methylene chloride (50 mL) and washed with water (3 x 50 mL). The organic layer was dried (Na_2SO_4) and the solvent was removed *in vacuo* to yield a red/brown solid. This was then purified by column chromatography (methylene chloride, R_f= 0.4) (1.18 g, 2.94 mmol, 89 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.33 (d, 1H, C*H*, $^3J_{HH}$=8.6 Hz), 7.52 (s, 1H, C*H*), 7.38 (d, 1H, C*H*, $^3J_{HH}$=8.6 Hz), 4.56 (t, 2H, Cp(C*H*)C≡C, $^3J_{HH}$=1.4 Hz), 4.27 (s, 5H, Cp(C*H*)), 4.25 (t, 2H, Cp(C*H*)C≡C, $^3J_{HH}$=1.4 Hz), 2.74 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm): 158.5 (C^{IV}), 152.3 (C^{IV}), 138.1 (C^{IV}), 133.6 (*C*H), 129.0 (*C*H), 124.3 (C^{IV}), 123.8 (*C*H), 120.4 (C^{IV}), 106.6 (C^{IV}), 95.2 (C≡C), 80.6 (C≡C), 71.9 (Cp(*C*H)), 70.4 (Cp(*C*H)C≡C), 69.2 (Cp(*C*H)C≡C), 65.1 (Cp(C^{IV})C≡C), 25.1 (*C*H_3); IR (cm^{-1}): 3350.5 (O-H, broad), 2210 (C≡C); Anal. Calc. ($C_{22}H_{16}ClFeNO$): C, 65.78 %; H, 4.02 %; N, 3.49 % Found: C, 65.66 %; H, 3.95 %; N, 3.42 %.

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