Supporting Information

Structurally-defined potassium-mediated regioselective zincation of amino-and alkoxy-substituted pyridines

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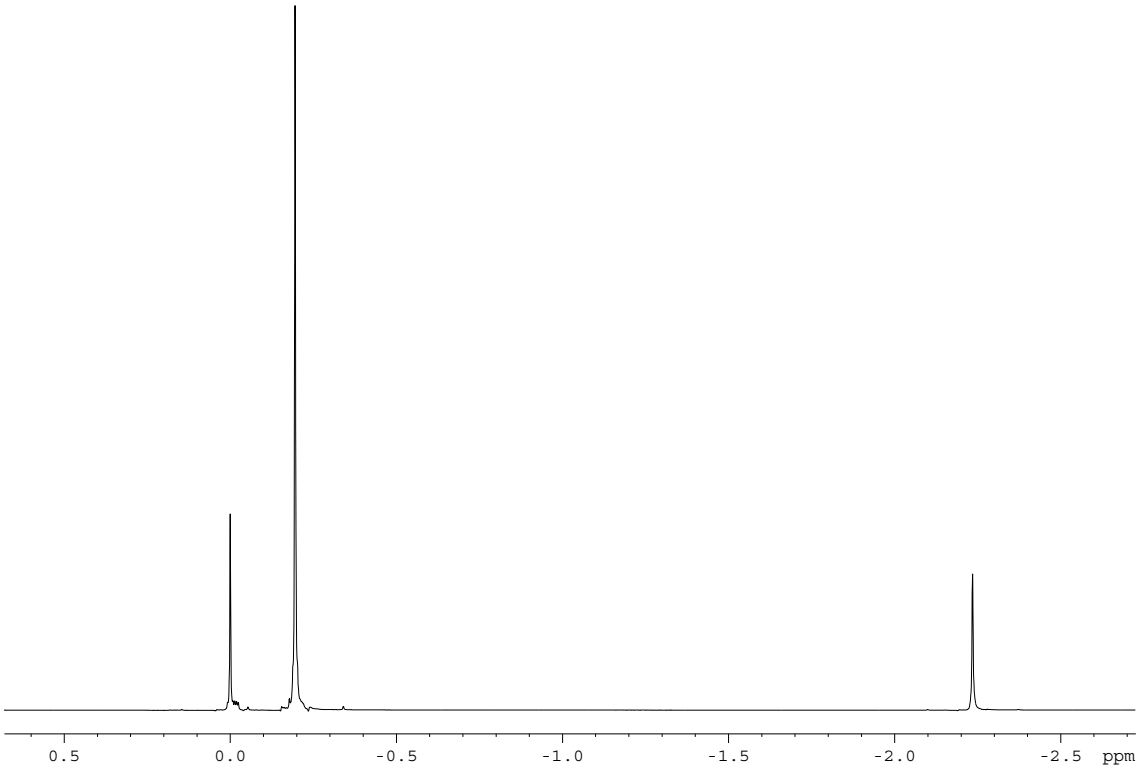
Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer. All ^{13}C NMR spectra were proton decoupled. Hexane and toluene were distilled from sodium-benzophenone. All crystal structures were measured at 123 K on a Nonius Kappa CCD instrument with 0.71073 Å graphite monochromated radiation. Structures were solved by direct methods (SHELXS or SIR) and refined to convergence against F^2 using SHELXL97. Full details are given in the associated cif files. All synthetic work was carried out under an inert argon atmosphere.

Synthesis of $KCH_2Si(CH_3)_3$

2.75 g (25 mmol) of KOtBu was dissolved in 50 mL of hexane in a Schlenk tube. To this solution, 25 mL (25 mmol) of 1M $LiCH_2Si(CH_3)_3$ solution was added, and the reaction mixture was left to stir overnight to form an off-white suspension. The solid was filtered, washed with hexane (2 x 20 mL) and dried under vacuum to afford a white solid (2.80 g, 93 % yield).



^{1}H NMR (400.13 MHz, 298K, deuterated THF):

δ -0.20 [9H, s, 3 x CH_3], -2.24 [2H, s, CH_2-K]

As far as we can ascertain there is no literature procedure for the synthesis of $KCH_2Si(CH_3)_3$. There is a literature citation for the synthesis of the bis-silyl analogue, $KCH[Si(CH_3)_3]_2$,[a] and for the compound [(PMDETA)K(μ-R)K(μ-R)$_2$K(μ-R)K(PMDETA)], where R = $CH[Si(CH_3)_3]_2$[b].

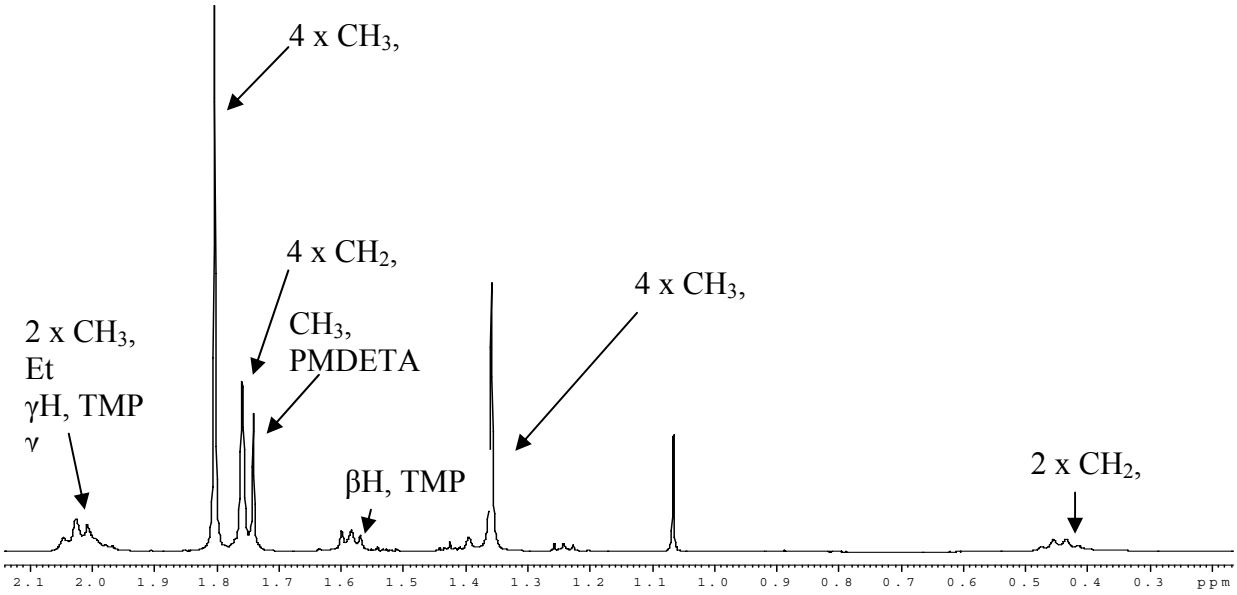
a) P. B. Hitchcock, M. F. Lappert, W-P Leung, L. Diansheng and T. Shun, *J. Chem. Soc., Chem. Commun*., 1993, 1386-1387.

b) W. M. Boesveld, P. B. Hitchcock, M. F. Lappert, D-S. Liu and S. Tian, *Organometallics*, 2000, *19*, 4030-4035.

Synthesis of [(PMDETA)K(TMP)(Et)Zn(Et)] (1)

0.24 g (2 mmol) of $KCH_2Si(CH_3)_3$ was suspended in 10 mL of hexane. 0.84 mL (4 mmol) of PMDETA was added to afford a clear orange solution. 0.34 mL (2mmol) of TMPH was added, followed by 2 mL (2 mmol) of 1M Et_2Zn. The Schlenk tube was

next placed in the freezer (-28°C) overnight to afford colourless crystals (0.58 g, 61 % yield).



^{1}H NMR (400.13 MHz, 298K, C_6D_6): δ 2.06 – 1.98 [8H, m, 2 x CH_3 of Et and γH TMP], 1.81 [12H, s, 4 x CH_3, PMDETA], 1.77 [11H, m, 4 x CH_2 and 1x CH_3 PMDETA], 1.58 [4H, m, βH TMP], 1.36 [12H, s, 4 x CH_3 TMP], 0.47 [4H, 2 x CH_2 of Et].

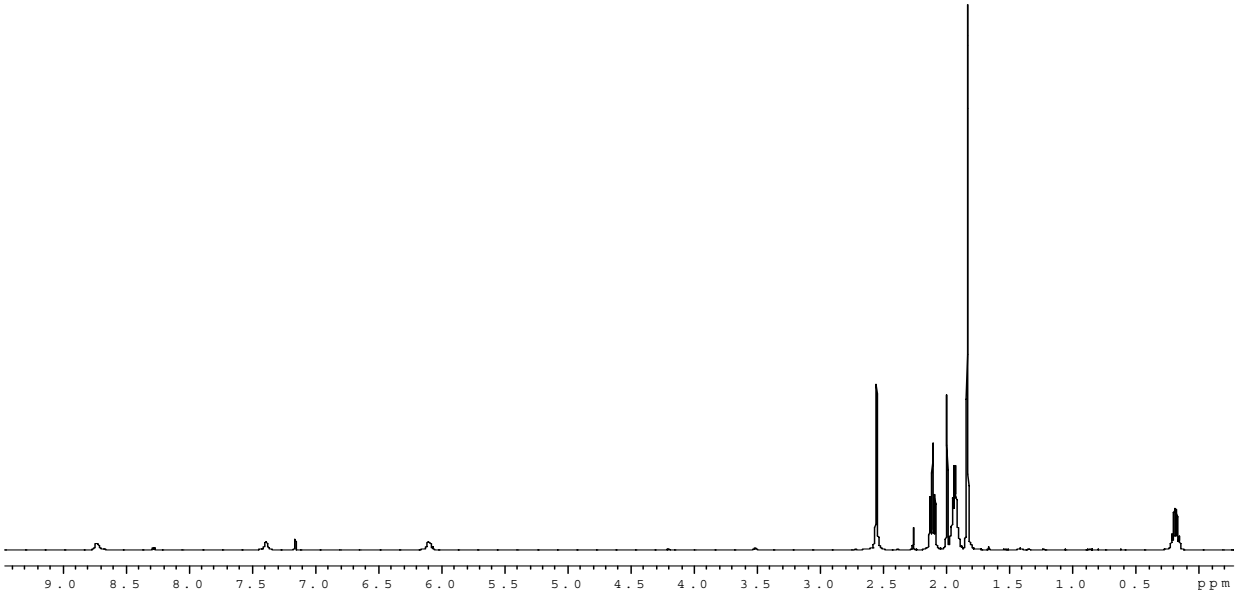
^{13}C{^{1}H} NMR (100.62 MHz, 298K, C_6D_6)**:** δ 56.92 [2 x CH_2 of PMDETA], 55.21 [2 x CH_2 of PMDETA], 45.20 [4 x CH_3 of PMDETA], 41.64 [1 x CH_3 of PMDETA], 41.20 [2 x βC of TMP], 35.11 [4 x CH_3 of TMP], 20.77 [1 x γC of TMP], 15.08 [2 x CH_3 of Et], 8.99 [2 x CH_2 of Et]

Calculated Microanalysis for $C_{22}H_{51}KN_4Zn$: C = 55.49 % H = 10.80 % N= 11.77 %
Experimental Microanalysis: C = 55.49 % H = 11.09 % N = 11.39 %

Synthesis of [{PMDETA.K[2-Zn(Et)$_2$-4-Me$_2$N-C$_5$H$_3$N]}$_2$] (2)

0.24 g (2 mmol) of $KCH_2Si(CH_3)_3$ was suspended in 10 mL of hexane. 0.84 mL (4 mmol) of PMDETA was added to afford a clear orange solution. 0.34 mL (2mmol) of TMPH was added, followed by 2 mL (2 mmol) of 1M Et_2Zn. 0.244 g (2 mmol) of 4-(dimethylamino)-pyridine was added to form a yellow solution. After 4 hr the solution

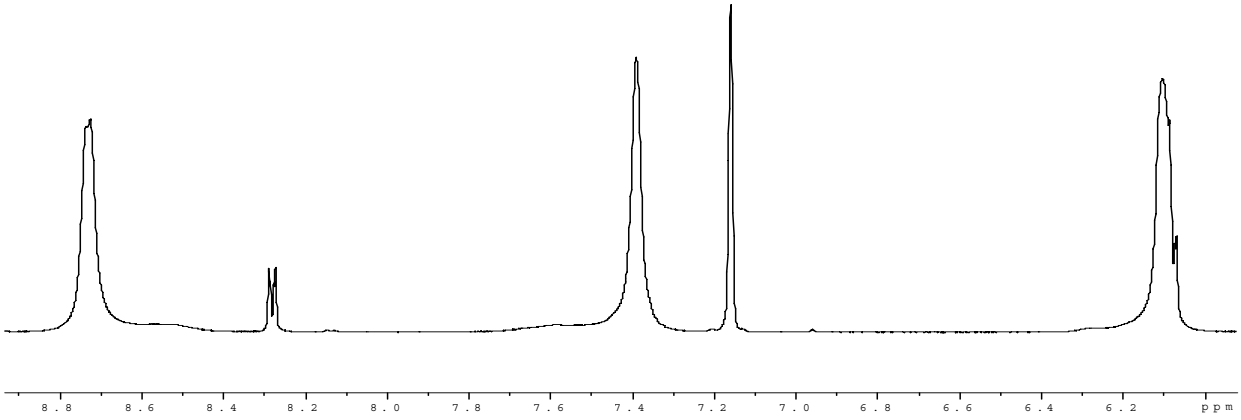
turned cloudy and 2 mL of THF was added to form a clear solution. The Schlenk tube was next placed in the freezer (-28°C) for 3 hrs to afford colourless crystals (0.48 g, 53 % yield).

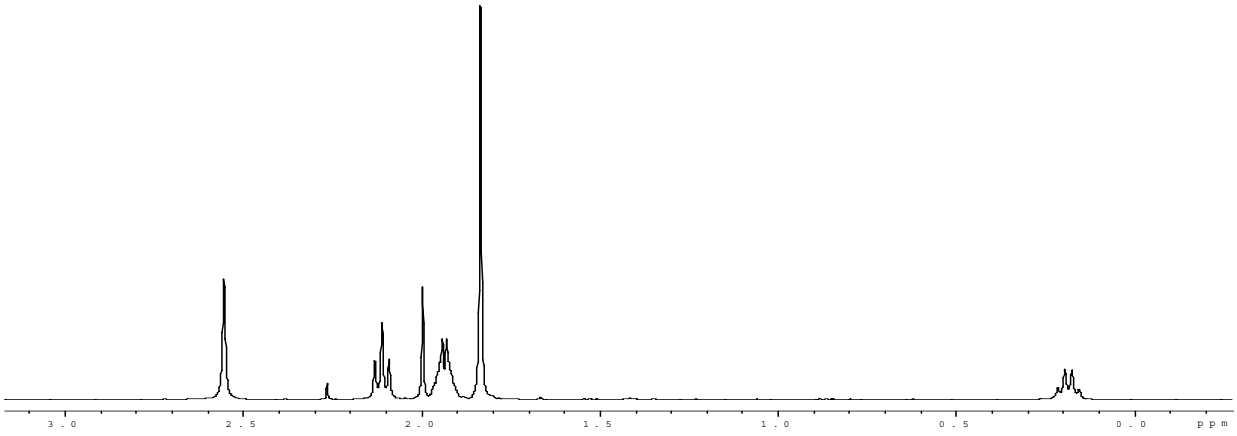


^{1}H NMR (400.13 MHz, 298K, C_6D_6):

δ 8.74 [1H, broad singlet], δ 7.41 [1H, broad singlet, aromatic H], 6.09 [1H, broad singlet, aromatic H], 2.55 [6H, s, 2 x N-CH_3] 2.13 [6H, t, J = 7.8 Hz, 2 x CH_3 of Et], 2.01 [3H, s, CH_3 of PMDETA], 1.96 [8H, m, 4 x CH_2 of PMDETA], 1.88 [s, 12H, 4 x CH_3 of PMDETA], 0.22 [4H, q, J = 7.8 Hz, 2 x CH_2 of Et].

Small amount of free DMAP at δ 8.29, 6.28 and 2.27 ppm.





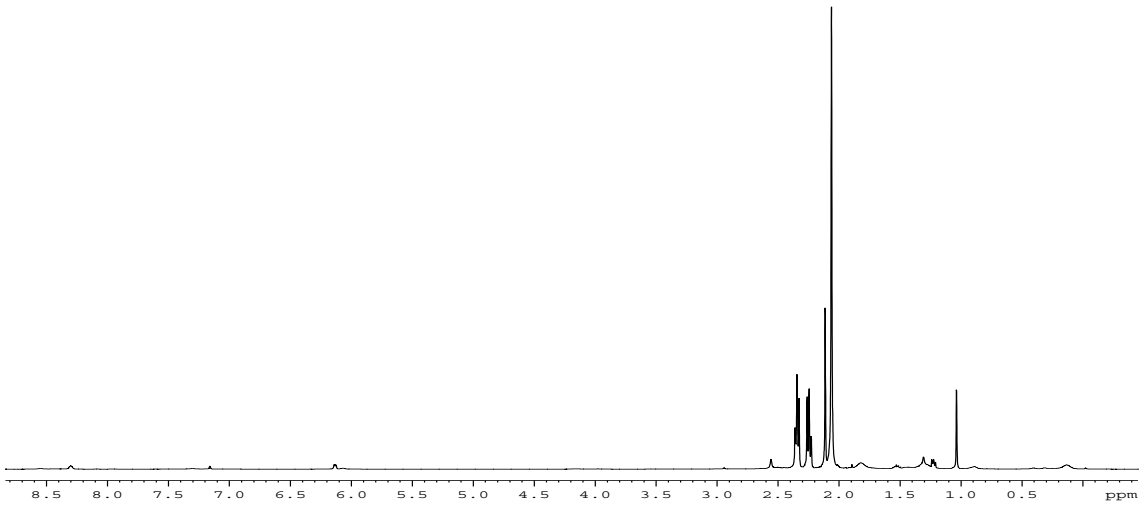
$^{13}C\{^{1}H\}$ NMR (100.62 MHz, 298K, C_6D_6):

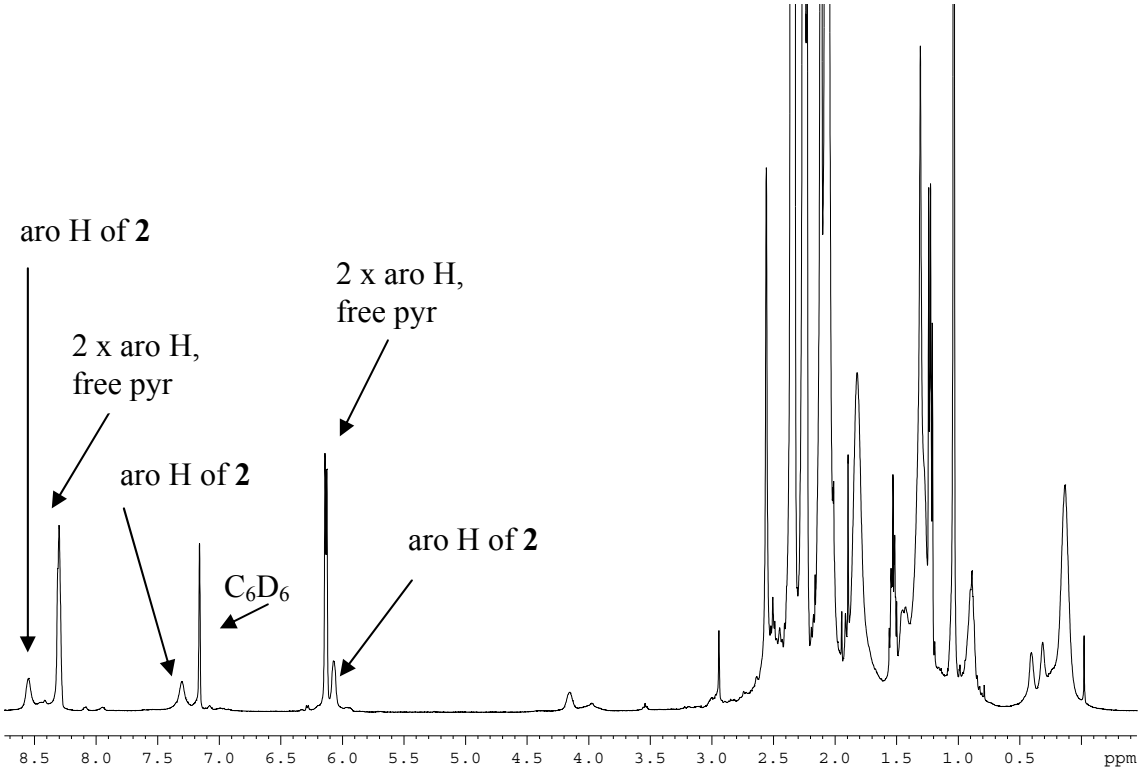
δ 154.11 [aromatic C] 150.64 [aromatic C], 150.32 [aromatic C at δ^H 8.74], 119.60 [aromatic C at δ^H 7.41], 103.58 [aromatic C at δ^H 6.09], 57.53 [2 x CH_2 of PMDETA], 56.11 [2 x CH_2 of PMDETA], 45.78 [4 x CH_3 of PMDETA], 42.25 [1 x CH_3 of PMDETA], 38.57 [2 x N-CH_3 of DMAP], 16.57 [2 x CH_3 of Et], 5.90 [2 x CH_2 of Et]

Calculated Microanalysis $C_{40}H_{84}K_2N_{10}Zn_2$: C = 52.56 % H = 9.26 % N = 15.32 %
Experimental Microanalysis: C = 52.56 % H = 9.02 % N = 16.35 %

Checking the filtrate of the reaction by ^{1}H NMR spectroscopy revealed the presence of some DMAP starting material and a further amount of **2**. No other metallated products were detected.

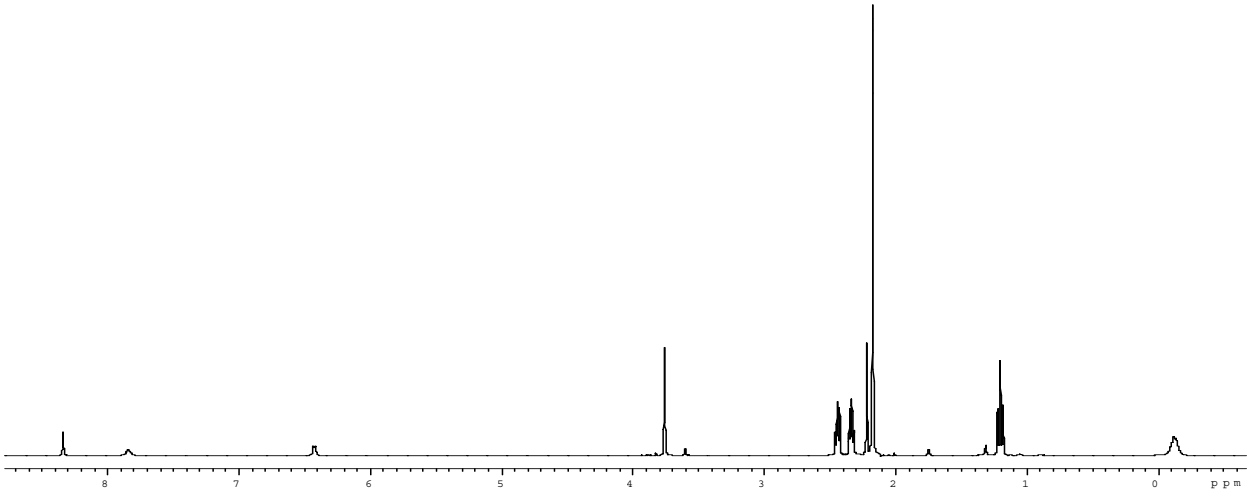
^{1}H NMR spectra of filtrate solution in deuterated benzene, highlighting the aromatic resonances:





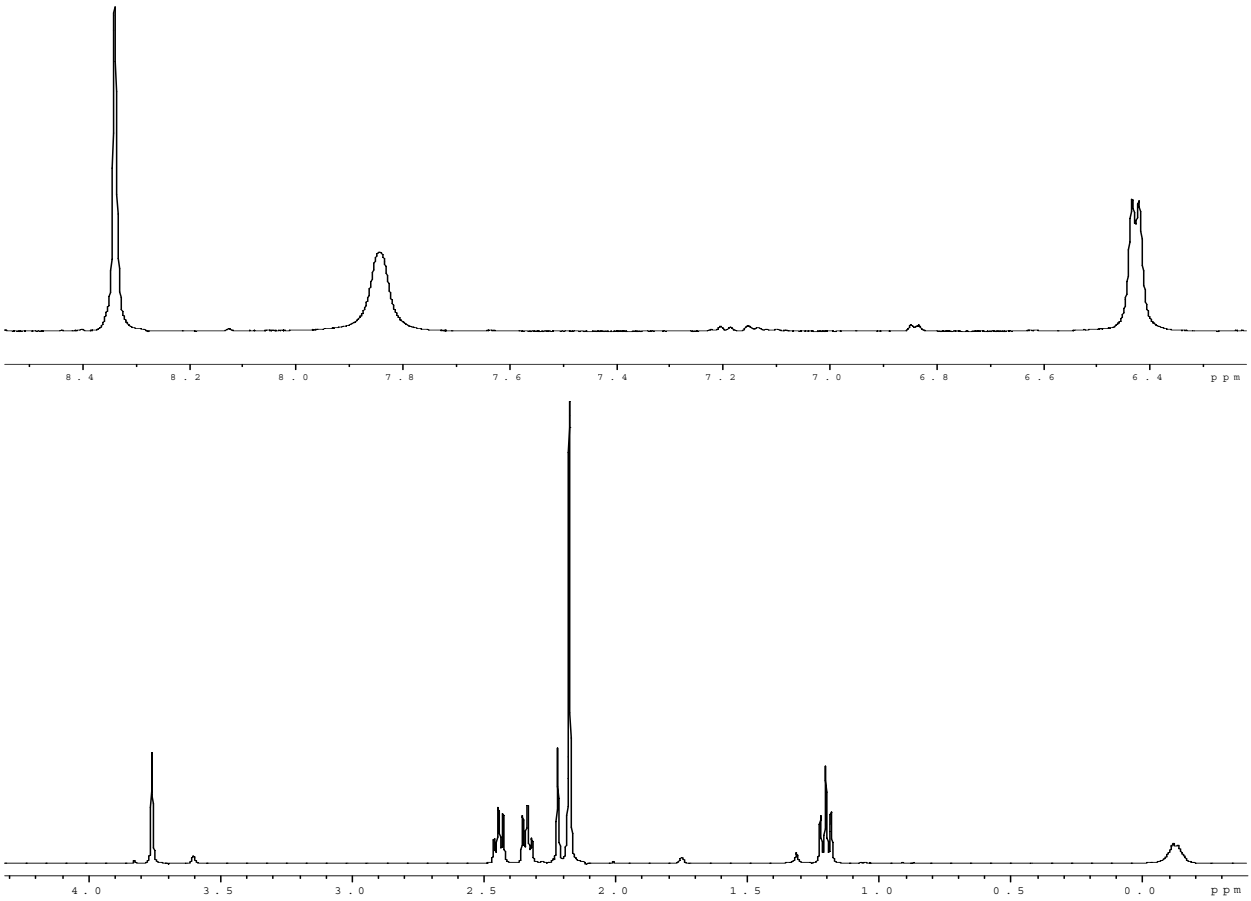
Synthesis of [catena-{PMDETA.K[3-Zn(Et)$_2$-4-MeO-C$_5$H$_3$N]}$_\infty$] (3)

0.24 g (2 mmol) of $KCH_2Si(CH_3)_3$ was suspended in 10 mL of hexane. 0.84 mL (4 mmol) of PMDETA was added to afford a clear orange solution. 0.34 mL (2mmol) of TMPH was added, followed by 2 mL (2 mmol) of 1M Et_2Zn. 0.20 mL (2 mmol) of 4-methoxypyridine was added to form a yellow solution, which turned into a suspension within 5 minutes. After 2 hr the solvent was removed *in vacuo* and 20 mL of toluene was added to form a clear orange solution. The Schlenk tube was next placed in the fridge (-4^{o}C) overnight to afford colourless crystals (0.46 g, 52 % yield)



^{1}H NMR (400.13 MHz, 298K, deuterated THF):

δ 8.34 [1H, broad singlet], δ 7.84 [1H, broad doublet, aromatic H], 6.43 [1H, broad doublet, aromatic H], 3.76 [3H, s, O-CH_3] 2.44 [4H, m, 2 x CH_2 of PMDETA] 2.37 [4H, m, 2 x CH_2 of PMDETA] 2.22 [3H, s, CH_3 of PMDETA], 2.18 [12H, s, 4 x CH_3 of PMDETA], 1.21 [6H, t, J = 8.0 Hz, 2 x CH_3 of Et], 0.22 [4H, m, 2 x CH_2 of Et]



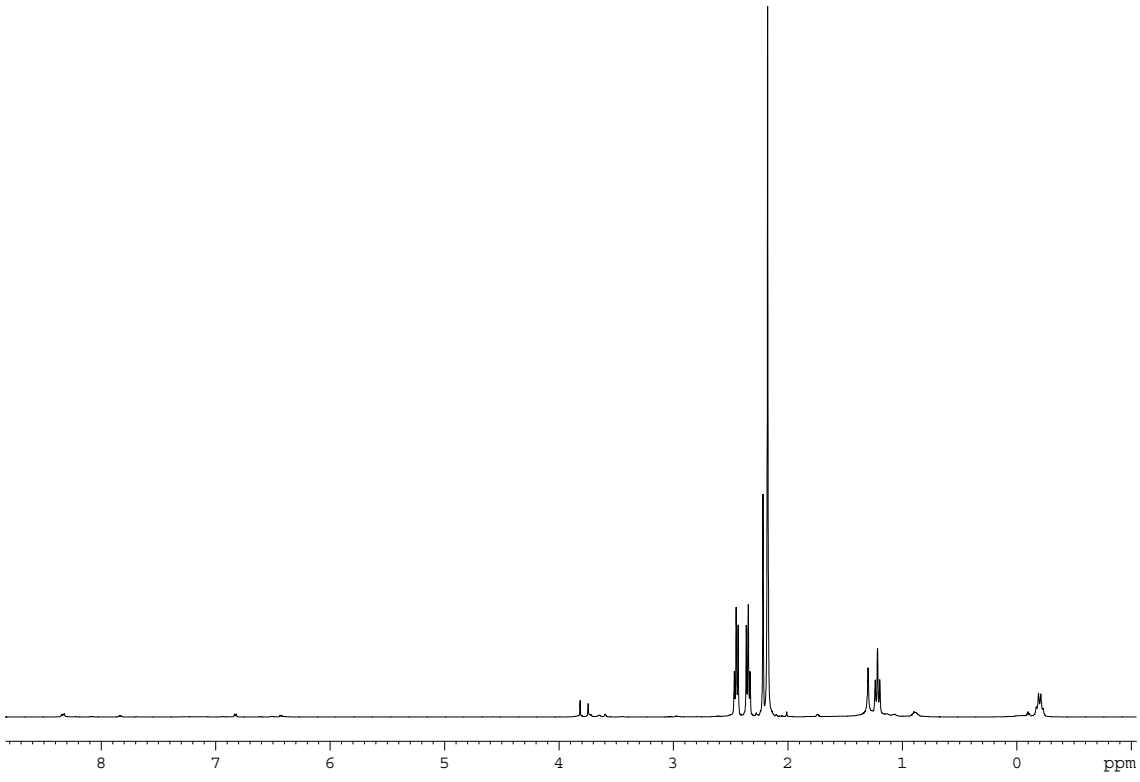
$^{13}C\{^{1}H\}$ NMR (100.62 MHz, 298K, deuterated THF):

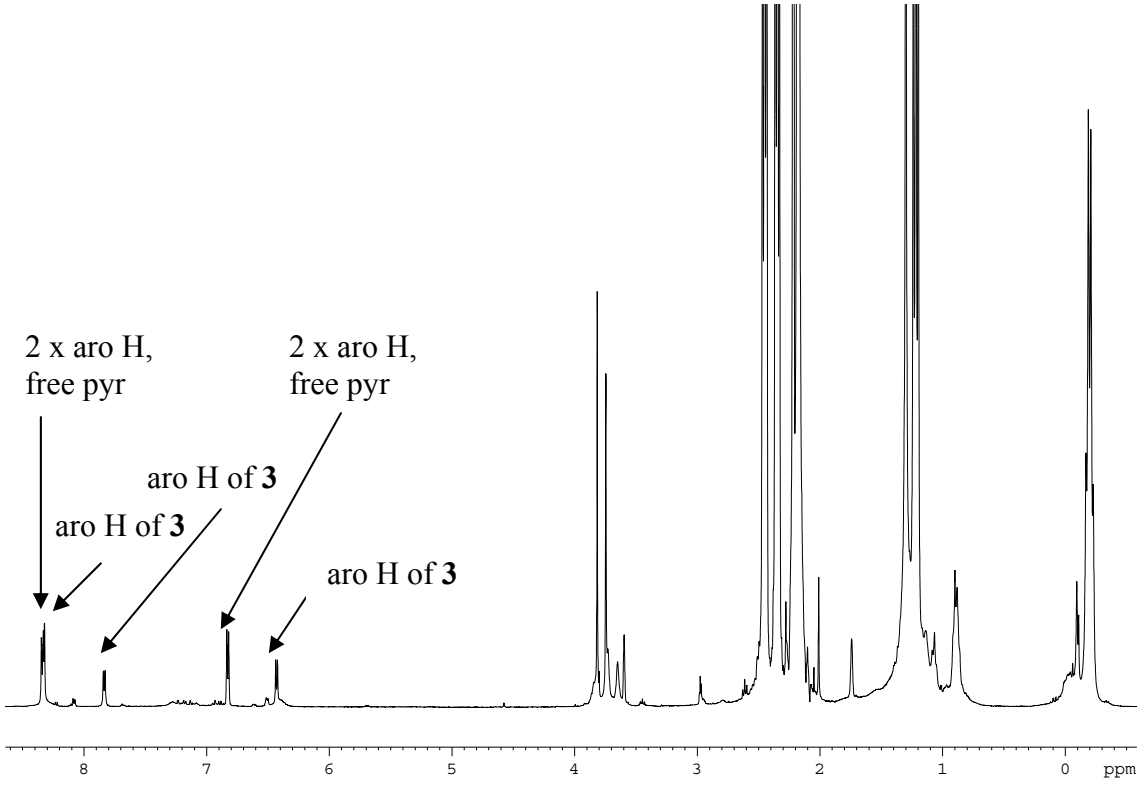
δ 172.09 [aromatic C] 158.58 [aromatic C at δ^{H} 8.43], 144.36 [aromatic C at δ^{H} 7.84], 128.63 [aromatic C], 108.42 [aromatic C at δ^{H} 6.43], 57.47 [2 x CH_2 of PMDETA], 56.16 [2 x CH_2 of PMDETA], 52.73 [1 x O-CH_3], 44.94 [4 x CH_3 of PMDETA], 42.02 [1 x CH_3 of PMDETA], 14.20 [2 x CH_3 of Et], 4.61 [2 x CH_2 of Et]

Calculated Microanalysis for $C_{19}H_{39}KN_4OZn$: C = 51.39 % H = 8.85 % N = 12.62%
Experimental Microanalysis: C = 51.39 % H = 8.99 % N = 12.41 %

Checking the filtrate of the reaction by ^{1}H NMR spectroscopy revealed mainly the presence of some 4-methoxypyridine starting material and a further amount of **3**.

^{1}H NMR spectra of filtrate solution in deuterated THF, highlighting the aromatic resonances:




2 x aro H,
free pyr
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