Supporting Information for:

Cyclotrimerisation of isocyanates catalysed by low-coordinate Mn(II) and Fe(II) *m*-terphenyl complexes

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General Procedures

All of the compounds prepared herein are air and moisture sensitive; therefore, all reactions and manipulations were performed by using standard Schlenk line and glovebox equipment under an atmosphere of purified argon or nitrogen. The hexane used was isohexane purchased from Fisher Scientific (contains <5% *n*-hexane); it was dried by passing through a column of activated 4 Å molecular sieves. THF and toluene were freshly distilled over sodium benzophenone ketyl (THF) or molten potassium (toluene) under nitrogen. All solvents were degassed *in vacuo* and stored over a potassium mirror (isohexane, toluene) or activated 4 Å molecular sieves (THF) prior to use. Benzene-d_6 was dried over potassium, and THF-d_8 was dried over CaH_2. Both were degassed with three freeze/pump/thaw cycles prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were collected on Bruker DPX 300, AV 400, DPX 400, AV(III)400, AV(III)400HD, AV(III)500 and AV(III)600 spectrometers. Chemical shifts are quoted in ppm relative to TMS. UV/visible absorption spectra were obtained in a Young's tap modified 10 mm quartz cell using a Perkin Elmer Lambda 5 spectrophotometer, with 1 nm data spacing. IR spectra were recorded as solutions in toluene using a solution cell on a Bruker Alpha FTIR instrument. Elemental analyses were performed by Mr. Stephen Boyer at London Metropolitan University. $(2,6\text{-Mes}_2C_6H_3)_2Mn$[1] and $(2,6\text{-Mes}_2C_6H_3)_2Fe$[1] were prepared following the procedures described in the literature.[1] All the isocyanates are commercially available and were transferred directly into the glovebox after which 4 Å molecular sieves were added with the exception of 3,5-dimethoxyphenyl isocyanate which was dried overnight under vacuum. Mass spectra were measured by the departmental service at the University of Nottingham and at the EPSRC National Mass Spectrometry Facility, Swansea University.

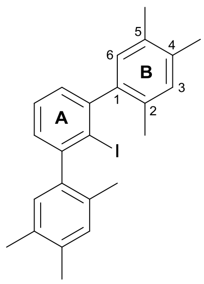
Table S1. Reaction of isocyanates with manganese(II) and iron(II) complexes.[a]

Entry	Isocyanate	Cat. (mol%)	T (°C)	Time (h)	Conv. (%)[b]
20	EtN=C=O	None	60	48	7
21	PhN=C=O	3 (5)	60	48	0
22	PhN=C=O	4 (5)	60	48	0
23	*p*-$MeC_6H_4N{=}C{=}O$	3 (10)	50	48	0
24	*p*-$MeC_6H_4N{=}C{=}O$	4 (10)	50	48	0
25	3,5-$(OMe)_2C_6H_3N{=}C{=}O$	3 (5)	60	48	0
26	3,5-$(OMe)_2C_6H_3N{=}C{=}O$	4 (5)	60	48	0
27	CyN=C=O	3 (5)	60	48	0
28	CyN=C=O	4 (5)	60	48	0
29	^{i}PrN=C=O	3 (5)	60	48	0
30	^{i}PrN=C=O	4 (5)	60	48	0
31	^{t}BuN=C=O	3 (5)	80[c]	48	0
32	^{t}BuN=C=O	4 (5)	80[c]	48	0

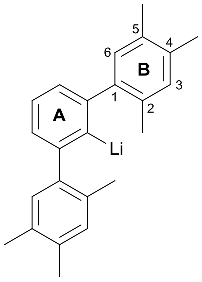
[a] Reaction conditions: 0.6 mL of C_6D_6. [b] Determined by ^{1}H NMR spectroscopy. [c] Reactions performed in toluene-d_8.

Synthesis of ($2,6\text{-}Tmp_2C_6H_3^-$) Ligand (Tmp = $2,4,5\text{-}Me_3C_6H_2^-$):

$2,6\text{-}Tmp_2C_6H_3I$ (7). To activated magnesium turnings (3.00 g, 125 mmol) suspended in THF (100 mL) a solution of 1-bromo-2,4,5-trimethylbenzene (20.0 g, 100 mmol) in THF (100 mL) was added dropwise with vigorous stirring. The reaction mixture was heated at reflux overnight, then allowed to cool to room temperature and filtered to give a solution of TmpMgBr (~20 g, 100 mmol) in THF. A solution of 1,3-dichlorobenzene (4.5 mL, 40.0 mmol) in THF (200 mL) was cooled to –78 °C and ^{n}BuLi (20 mL of 2.5 M in hexane, 50.0 mmol) was added dropwise and stirred for 2 h. To this mixture TmpMgBr (~20 g, 100 mmol) was added dropwise at –78 °C after which the solution was left to warm to room temperature with stirring overnight. The solution was heated at reflux for 4 h, then cooled to 0 °C and iodine (12.0 g, 50.0 mmol) was added slowly over 1 hour resulting in a dark yellow solution. The reaction mixture was poured onto aqueous Na_2SO_3 (5% wt, 200 mL) and extracted into Et_2O (200 mL). The organic layer was washed with Na_2SO_3 solution (5% wt, 3 x 100 mL) and brine (100 mL), then dried over $MgSO_4$. The solvent was removed *in vacuo* leaving an orange oily solid of crude product. Recrystallisation from ethanol (200 mL) resulted in a white crystalline powder of pure product (5.40 g, 31%). Anal. Calcd (%) for $C_{24}H_{25}I$ (440.37): C 65.46, H 5.72; found C 65.38, H 5.69. MS (ESI) *m/z*: calcd for $C_{24}H_{25}INa$ $[M+Na]^+$ 463.0893, found: 463.0886 (err [ppm] = 1.50). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.38 (t, ^3J(H,H) = 7.4 Hz, 1H, Ph^{Ap}), 7.14 (d, ^3J(H,H) = 7.4 Hz, 2H, Ph^{Am}), 7.05 (s, 2H, Ph^{B3}), 6.92 (s, 2H, Ph^{B6}), 2.30 (s, 6H, Me^4), 2.27 (s, 6H, Me^2), 2.06 (s, 6H, Me^5). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ 147.6 (Ph^{Am}), 142.9 (Ph^{B2}), 136.0 (Ph^{B5}), 133.5 (Ph^{B4}), 132.7 (Ph^{B1}), 131.1 (Ph^{B3}), 130.1 (Ph^{B6}), 128.9 (Ph^{Am}), 127.7 (Ph^{Ap}), 106.9 (Ph^{Aipso}), 19.5 (Me^4), 19.3 (Me^5), 19.3 (Me^2).



[2,6-Tmp$_2$C$_6$H$_3$Li]$_2$ (8). 2,6-Tmp$_2$C$_6$H$_3$I (4.96 g, 10.0 mmol) was dried *in vacuo* overnight (*ca.* 16 h). Hexane (100 mL) was added and the white suspension cooled to 0 °C, ^{n}BuLi (4.4 mL of 2.5 M in hexane, 11.0 mmol) was added dropwise with vigorous stirring then left to warm to room temperature. The pale yellow solution was filtered resulting in a pale yellow solid of pure product (2.94 g, 77%). Anal. Calcd (%) for $C_{24}H_{25}Li$ (320.40): C 89.97 H 7.86; found C 89.69 H 7.73. ^1H NMR (400 MHz, THF-*d*^{8}, 25 °C): δ 7.07 (s, 2H, Ph^{B3}), 6.89 (s, 2H, Ph^{B6}), 6.81 (m, 3H, Ph$^{A(m+p)}$), 2.25 (s, 6H, CH_3), 2.21 (s, 6H, CH_3), 2.20 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, THF-*d*^{8}, 25 °C): δ 156.3 (Ar), 152.9 (Ar), 151.3 (Ar), 132.9 (Ar), 132.7 (Ar), 132.3 (Ar), 132.2 (Ph^{B3}), 131.7 (Ph^{B6}), 123.2 (Ph^{Am}), 121.5 (Ph^{Ap}), 20.7 (Me), 19.5 (Me), 19.3 (Me). $^7Li\{^1H\}$ NMR (155 MHz, C_6D_6, 25 °C): δ 1.86 (s).



Synthesis of Complexes 1 and 2:

(2,6-Tmp$_2$C$_6$H$_3$)$_2$Mn(THF) (1). To a mixture of [2,6-Tmp$_2$C$_6$H$_3$Li]$_2$ (500 mg, 0.780 mmol) and $MnBr_2$ (168 mg, 0.780 mmol), were added toluene (20 mL) and THF (5 mL) with stirring resulting in a light yellow solution which was stirred for 16 h. The solvent was removed *in vacuo* resulting in an off white solid which was extracted into toluene (2 × 10 mL), concentrated *in vacuo* and stored at –30 °C for 1 day. This resulted in the precipitation of pale pink crystals suitable for X–ray diffraction (170 mg, 30%). Anal. Calcd (%) for

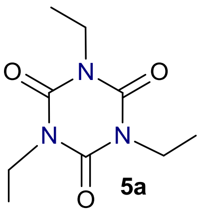
$C_{52}H_{58}OMn$ (753.96): C 82.84, H 7.75; found C 82.66, H 7.55. μ_{eff} (Evans, C_6D_6, 25 ºC) = 5.59 μB. MS (EI) *m/z* (%): 682.3 (100) $[M+H-THF]^+$. UV/Vis (THF): strong absorption between 200 and 400 nm (ε > 900 dm^3 mol^{-1} cm^{-1}). The ^1H NMR spectrum showed very broad signals which could not be readily assigned.

$(2,6\text{-}Tmp_2C_6H_3)_2Fe(THF)$ (2). To a mixture of $[2,6\text{-}Tmp_2C_6H_3Li]_2$ (500 mg, 0.780 mmol) and $FeCl_2(THF)_{1.5}$ (182 mg, 0.780 mmol), were added toluene (20 mL) and THF (5 mL) with stirring resulting in a dark brown solution which was stirred for 16 h. The solvent was removed *in vacuo* resulting in a brown solid which was extracted into hexane (2 × 10 mL), concentrated *in vacuo* and stored at –30 °C for 24 h resulting in the precipitation of yellow crystals suitable for X–ray diffraction (150 mg, 25%). Anal. Calcd (%) for $C_{52}H_{58}OFe$ (754.86): C 82.74, H 7.74; found C 82.63, H 7.62. μ_{eff} (Evans, C_6D_6, 25 ºC) = 5.58 μB. MS (EI) *m/z* (%): 683.4 (91) $[M+H-THF]^+$, 314.3 (100) $(Tmp_2C_6H_3+H)^+$. UV/Vis (THF): strong absorption between 200 and 400 nm (ε > 1200 $dm^3mol^{-1}cm^{-1}$); shoulder at 385 (ε = 194 $dm^3mol^{-1}cm^{-1}$). The ^1H NMR spectrum showed very broad signals which could not be readily assigned.

Standard procedure for the catalytic cyclotrimerisation of isocyanates: In a Young's NMR tube 5 mol% (10.0 mg) of the catalyst **1-4** was dissolved in C_6D_6 (0.6 mL) in a glove-box, the corresponding isocyanate was then added. The reaction was either carried out at room temperature and monitored by ^1H NMR spectroscopy or heated to 60 °C; the samples were maintained at 60 °C for 14 h and ^1H NMR spectroscopy was performed at the final time. Conversion was quantified by integration of ^1H NMR spectra. For the catalysis with 2 mol% and 0.5 mol% 5.0 mg of catalyst **1** was used.

Standard procedure for the scaled-up catalytic cyclotrimerisation of isocyanates: In a Schlenk flask, 5 mol% of **3** (10.0 mg, 0.0147 mmol) and the corresponding isocyanate were dissolved in toluene (5 mL) and stirred at room temperature for 3 h (**5a**) or heated at 60 °C for 14 h (**5b-d**). The solvent was removed *in vacuo* and the residue was dissolved in dichloromethane and filtered through a short silica plug. Elimination of the volatiles *in vacuo* enabled the isolation of the corresponding isocyanurates.

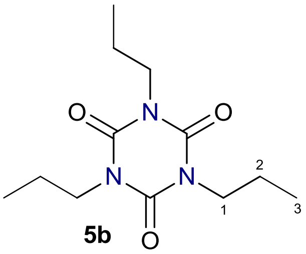
1,3,5-tri(ethyl)-isocyanurate (5a). The isocyanurate was identified by comparison of its spectroscopic data with those reported in the literature.[2] Selected spectroscopic data:



5a

MS (GC-EI) *m/z*: calcd for $C_9H_{15}N_3O_3$ $[M]^+$ 213.1108, found: 213.1106 (err [ppm] = 0.94). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.95 (q, $^3J(H,H)$ = 7.1 Hz, 6H, CH_2), 1.25 (t, $^3J(H,H)$ = 7.1 Hz, 9H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ 148.8 (C=O), 38.3 (CH_2), 13.3 (CH_3).

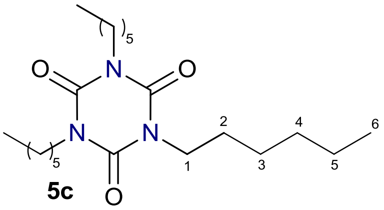
1,3,5-tri(^{n}propyl)-isocyanurate (5b). The isocyanurate was identified by comparison of its spectroscopic data with those reported in the literature.[3] Selected spectroscopic data:



5b

MS (GC-EI) *m/z*: calcd for $C_{12}H_{21}N_3O_3$ $[M]^+$ 255.1577, found: 255.1572 (err [ppm] = 2.17). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.88-3.81 (m, 6H, CH_2^1), 1.74-1.62 (m, 6H, CH_2^2), 0.94 (t, $^3J(H,H)$ = 7.5 Hz, 9H, CH_3^3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ 149.2 (C=O), 44.6 (CH_2^1), 21.3 (CH_2^2), 11.2 (CH_3^3).

1,3,5-tri(^{n}hexyl)-isocyanurate (5c). The isocyanurate was identified by comparison of its spectroscopic data with those reported in the literature.[4] Selected spectroscopic data:

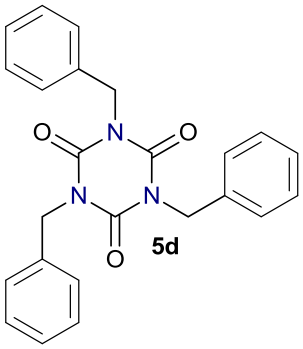


5c

MS (ESI) *m/z*: calcd for $C_{21}H_{40}N_3O_3$ $[M+H]^+$ 382.3064, found: 382.3070 (err [ppm] = 1.60). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 3.96-3.77 (m, 6H, CH_2^1), 1.66-1.58 (m, 6H, CH_2^2), 1.40-1.24 (m, 18H, CH_2^{3+4+5}), 0.94-0.79 (m, 9H, CH_3^6). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C): δ 149.2 (C=O), 43.2 (CH_2^1), 31.5 (CH_2), 27.9 (CH_2^2), 26.5 (CH_2), 22.7 (CH_2), 14.2 (CH_3^6).

1,3,5-tri(benzyl)-isocyanurate (5d).

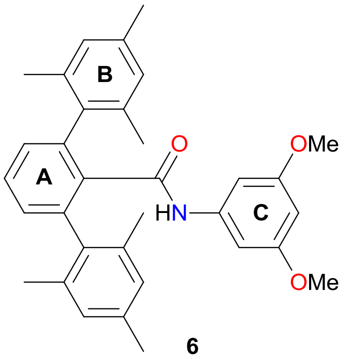
The isocyanurate was identified by comparison of its spectroscopic data with those reported in the literature. [4] Selected spectroscopic data:



5d

MS (ESI) *m/z*: calcd for $C_{24}H_{21}N_3O_3Na$ $[M+Na]^+$ 422.1475, found 422.1468 (err [ppm] = 1.60). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.49 (d, ^3J(H,H) = 7.1 Hz, 6H, Ph^{o}), 7.42-7.27 (m, 9H, Ph^{m+p}), 5.07 (s, 6H, CH_2).$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 25 °C): δ 149.2 (C=O), 135.9 (Ph^{i}), 129.2 (Ph^{o}), 128.8 (Ph^{m}), 128.3 (Ph^{p}), 46.4 (CH$_2$).

(2,6-MesC$_6$H$_3$)C(=O)NH(3,5-(OMe)$_2$C$_6$H$_3$) (6).



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3,5-Dimethoxyphenyl isocyanate, (8.0 mg, 0.045 mmol) was added to a yellow solution of $(2,6\text{-}Mes_2C_6H_3)_2Fe$ (**4**) (30.5 mg, 0.045 mmol) in toluene (4 mL). The reaction was monitored by IR spectroscopy. After stirring for 12 h at room temperature no reaction was observed. The solution was then heated to 60 °C and stirred for 16 h observing a colour change to dark red and a complete consumption of the isocyanate *via* IR spectroscopy. The solvent was evaporated to dryness under vacuum to yield a yellow solid. This mixture was redissolved in “wet” Et_2O and separated by silica gel column chromatography. The solvent was then evaporated to yield colourless crystals. ^1H NMR indicates a mixture 42:58 of **6** and protonated ligand ($2,6\text{-}Mes_2C_6H_4$) respectively. Single crystals for X-ray diffraction studies were grown from a hexane solution at –30 °C. MS (ESI) *m/z*: calcd for $C_{33}H_{34}NO$ $[M-H]^-$ 492.2544, found 492.2538 (err [ppm] = 1.20). IR (Toluene) ν/cm^{-1}: 3557 (s, N-H), 1676 (s, C=O). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.56 (t, ^3J(H,H) = 7.6 Hz, 1H, Ph^{Ap}), 7.21 (d, ^3J(H,H) = 7.6 Hz, 2H, Ph^{Am}), 6.96 (s, 4H, Ph^{Bm}), 6.11 (t, ^4J(H,H) = 2.3 Hz, 1H, Ph^{Cp}), 5.97 (d, ^4J(H,H) = 2.3 Hz, 2H, Ph^{Co}), 5.32 (s, 1H, NH), 3.65 (s, 6H, OCH_3), 2.30 (s, 6H, CH_3^{Bp}), 2.12 (s, 12H, CH_3^{Bo}). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ 166.2 (C=O), 160.8 (Ph^{Cm}), 141.1 (Ph^{Bo}), 139.2 (Ph^{Ao}), 138.9 (Ph^{Bi}), 138.7 (Ph^{Ci}), 137.2 (Ph^{Bp}), 135.9 (Ph^{Ai}), 130.0 (Ph^{Ap}), 129.2 (Ph^{Am}), 128.2 (Ph^{Bm}), 99.5 (Ph^{Co}), 96.9 (Ph^{Cp}), 55.4 (OCH$_3$), 21.2 (CH$_3^{Bp}$), 20.8 (CH$_3^{Bo}$).

Mercury Drop Test: **3** (5.0 mg, 0.5 mol%) in C_6D_6 (0.6 mL) was added to two separate Young's NMR tubes and to one of these a drop of mercury was added. Ethyl isocyanate (116 µL, 1.47 mmol) was added to each tube and the reactions were monitored by ^{1}H NMR. Both reactions were found to reach >90% conversion after 2 days at room temperature.

Cyclotrimerisation with Radical Trap: **1** (10.0 mg, 5 mol%) in C_6D_6 (0.6 mL) was added to two separate Young's NMR tubes and to one of these an excess of cumene was added (9.3 µL, 0.0665 mmol). *n*-Propyl isocyanate (25 µL, 0.266 mmol) was added to each tube and the reactions were monitored by ^{1}H NMR. Both reactions were found to reach >80% conversion after 7 h at room temperature.

Cyclotrimerisation with Mixed Isocyanates: In a Young's NMR tube was added **3** (10.0 mg, 5 mol%) in C_6D_6 (0.6 mL). The isocyanates were added and the reactions were monitored by ^{1}H NMR and GC-MS after 16 h at r.t. See Table S2 for amounts and ratios of the isocyanates used.

General Procedure for Kinetic NMR Experiments: In a Young's NMR tube the catalyst **3** was dissolved in C_6D_6 so that the total volume was 600 µL and was then frozen at –30 °C. Ethyl isocyanate was then added and the sample was cooled to –78 °C to prevent the reaction from initiating. The sample was transferred to the NMR spectrometer at 25 °C and monitored by ^{1}H NMR. Experiments for rate order determination were performed at variable concentrations of catalyst (**3**) and ethyl isocyanate while keeping the other reagent concentration constant. Reaction rates were determined by least-squares fit of ethyl isocyanate concentration versus time, and the rate data is plotted respect to reagent concentration to determine rate orders (Figures S1-S4).

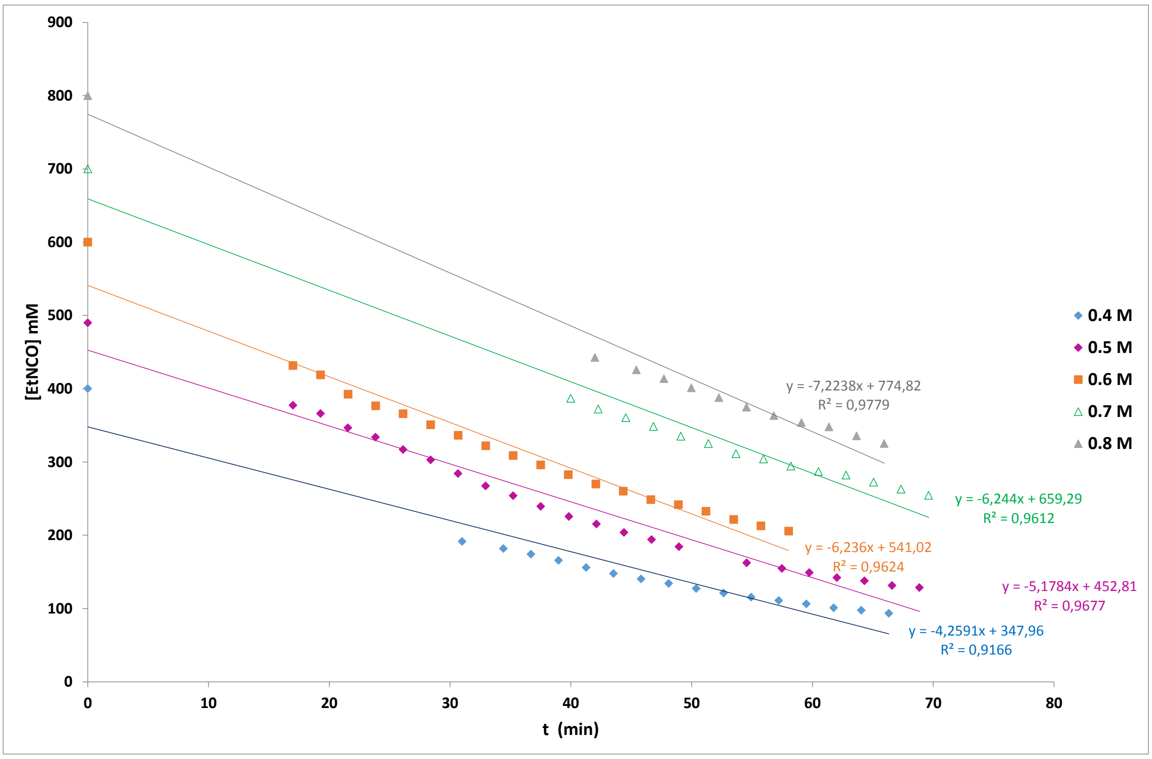


Figure S1. Initial rates obtained when the ethyl isocyanate concentration is varied.

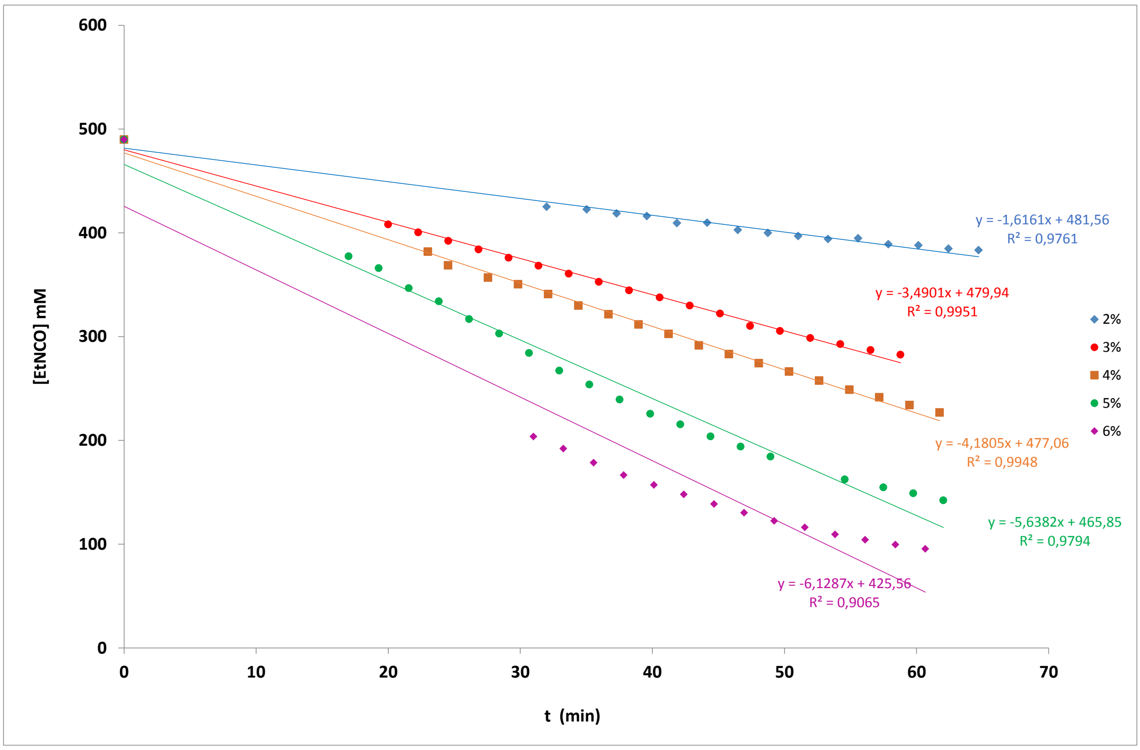


Figure S2. Initial rates obtained when the catalyst (**3**) concentration is varied.

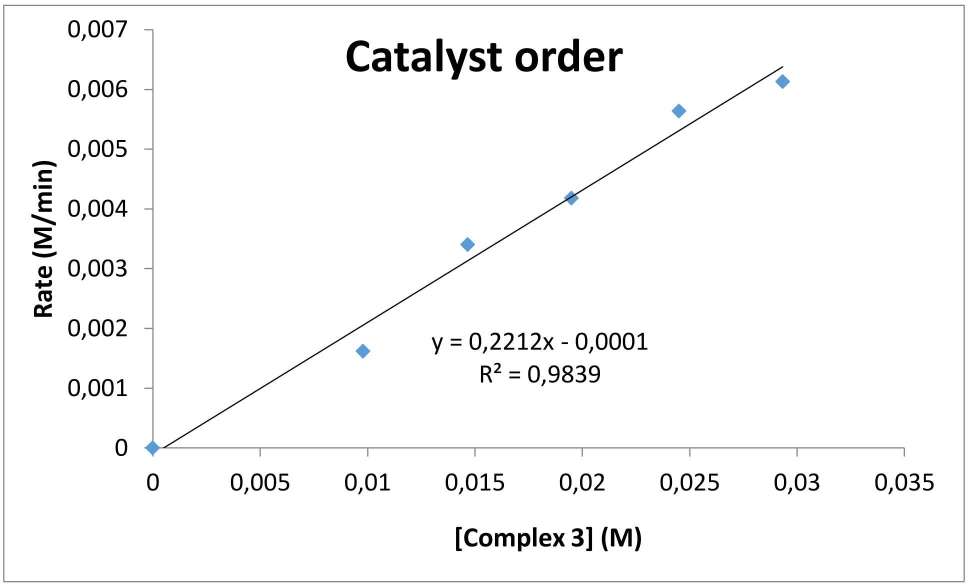


Figure S3. Plot of reaction rate (M/min) *vs.* catalyst **3** concentration (M) showing first-order kinetics**.**

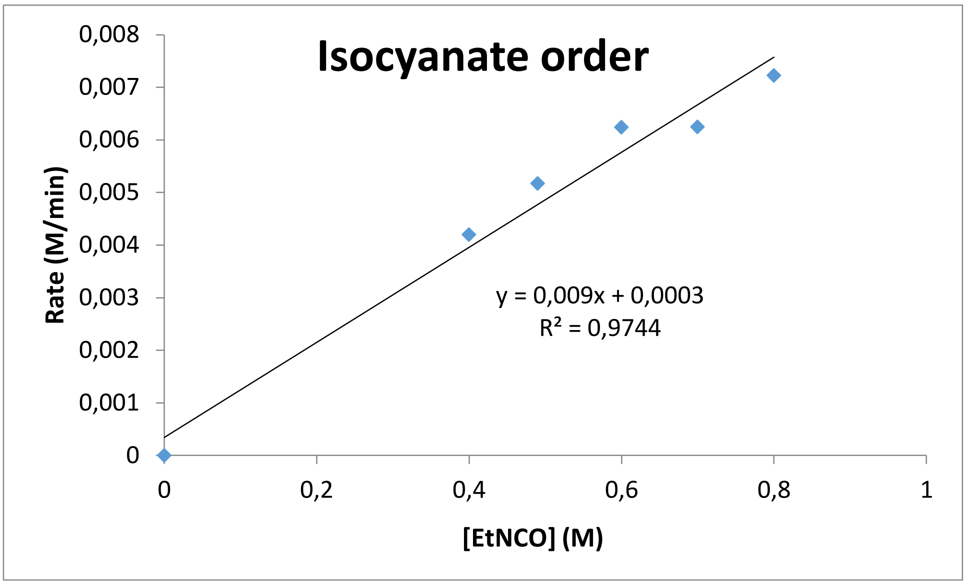


Figure S4. Plot of reaction rate (M/min) *vs.* Ethyl isocyanate concentration (M) showing first-order kinetics**.**

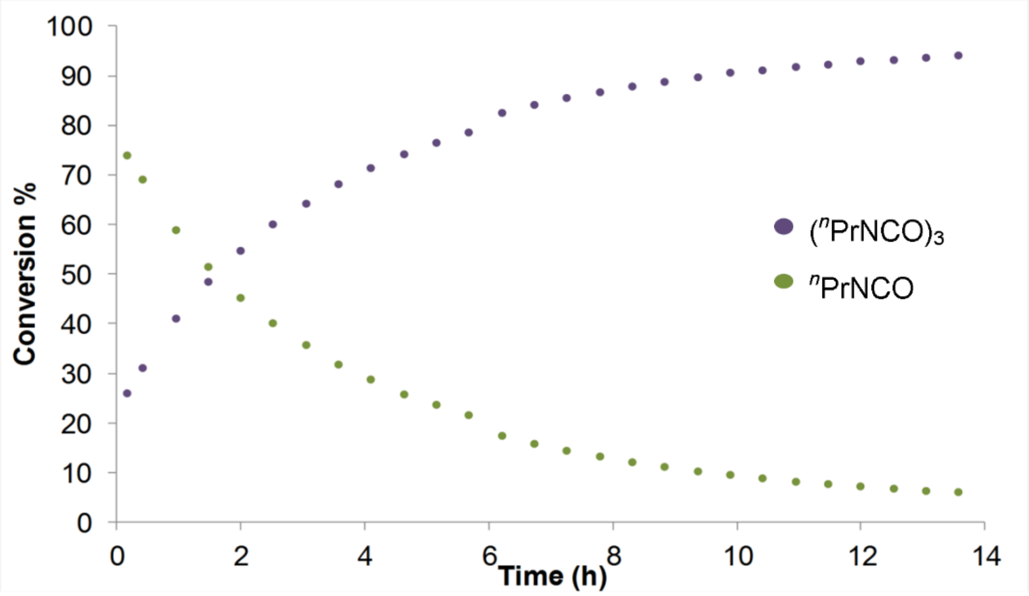


Figure S5. Conversion (%) *vs.* time (h) for the cyclotrimerisation of ^{n}PrNCO with 5 mol% of **3** in C_6D_6 at 60 °C.

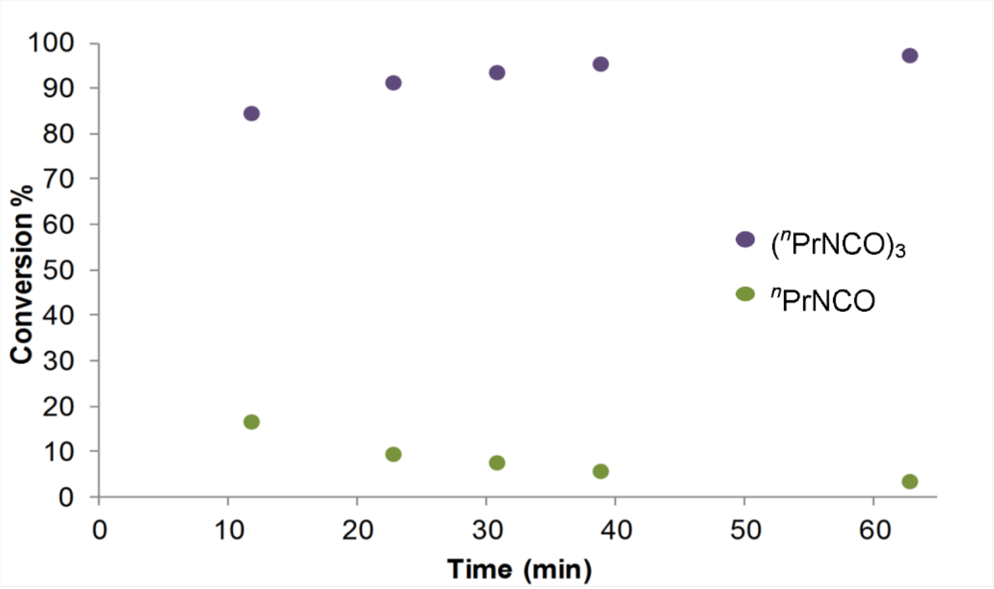


Figure S6. Conversion (%) *vs.* time (min) for the cyclotrimerisation of ^{n}PrNCO with 5 mol% of **1** in C_6D_6 at rt.

^{1}H NMR Spectra for Isocyanurates 5a-d:

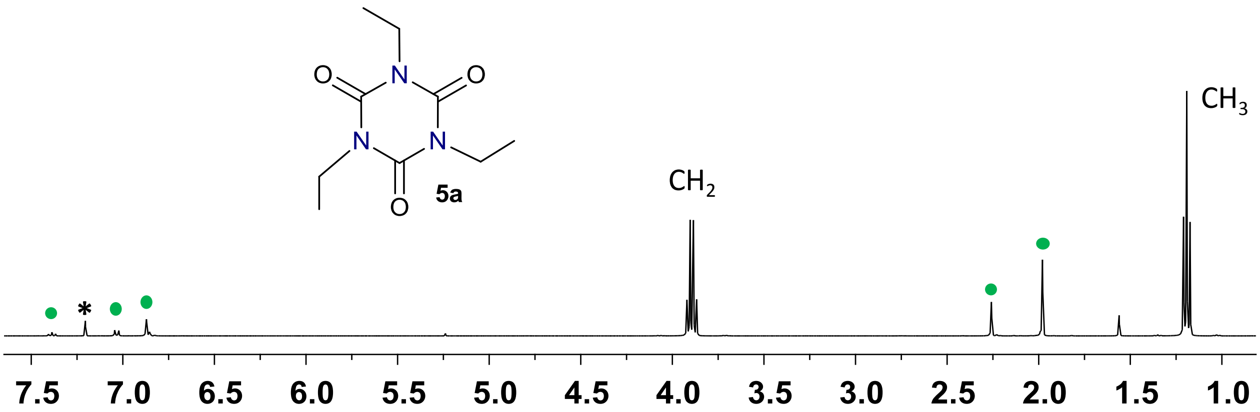


Figure S7. ^{1}H NMR of 1,3,5-tri(ethyl)-isocyanurate (**5a**) in $CDCl_3$ at rt. The asterisk (*) denotes $CDCl_3$. Green circle indicates protonated ligand (2,6-$Tmp_2C_6H_4$).

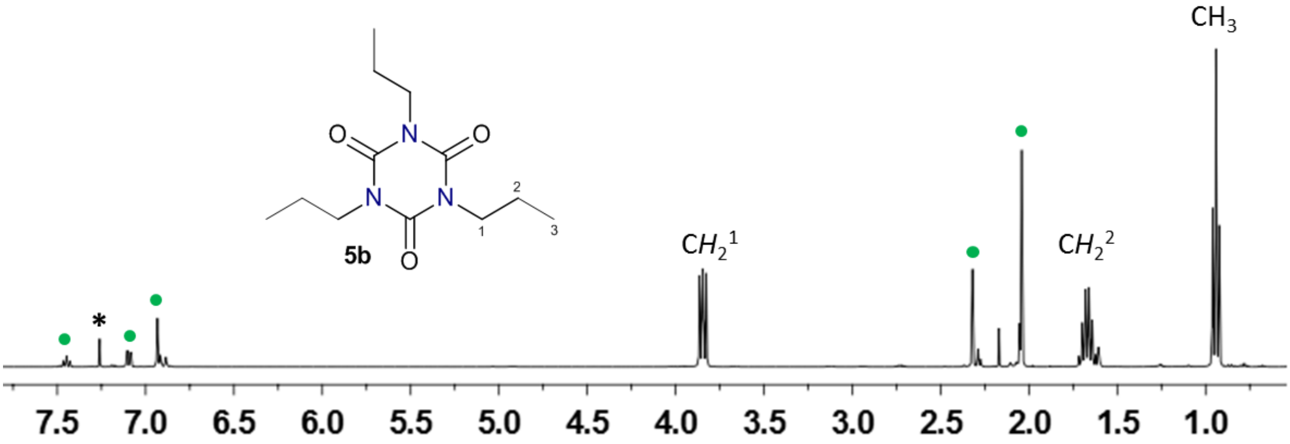


Figure S8. ^{1}H NMR of 1,3,5-tri(^{n}propyl)-isocyanurate (**5b**) in $CDCl_3$ at rt. The asterisk (*) denotes $CDCl_3$. Green circle indicates protonated ligand (2,6-$Tmp_2C_6H_4$).

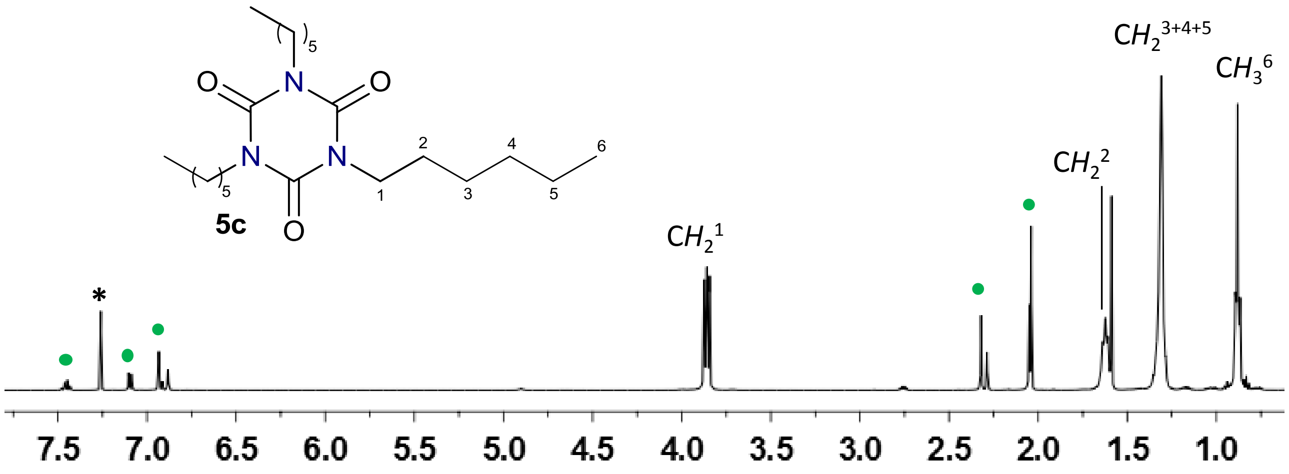


Figure S9. ^{1}H NMR of 1,3,5-tri(^{n}hexyl)-isocyanurate (**5c**) in $CDCl_3$ at rt. The asterisk (*) denotes $CDCl_3$. Green circle indicates protonated ligand (2,6-$Tmp_2C_6H_4$).

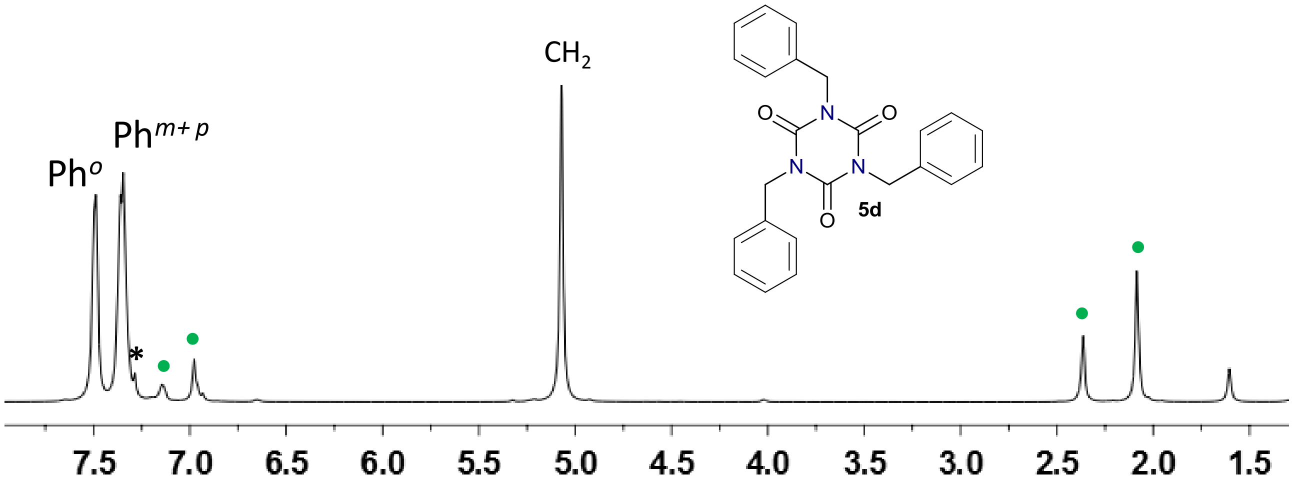


Figure S10. ^{1}H NMR of 1,3,5-tri(benzyl)-isocyanurate (**5d**) in $CDCl_3$ at rt. The asterisk (*) denotes $CDCl_3$. Green circle indicates protonated ligand (2,6-$Tmp_2C_6H_4$).

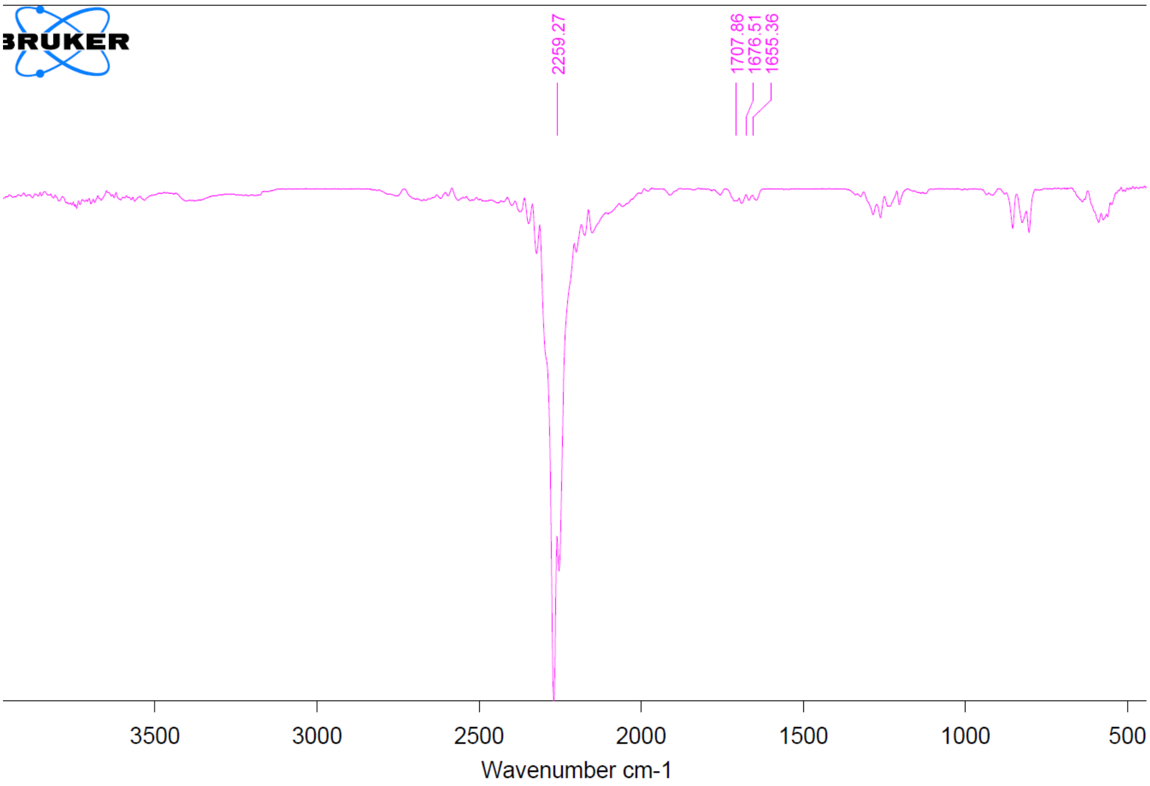


Figure S11. IR spectrum of the reaction between complex **4** with one equivalent of 3,5-dimethoxyphenyl isocyanate after 12 h at room temperature in toluene.

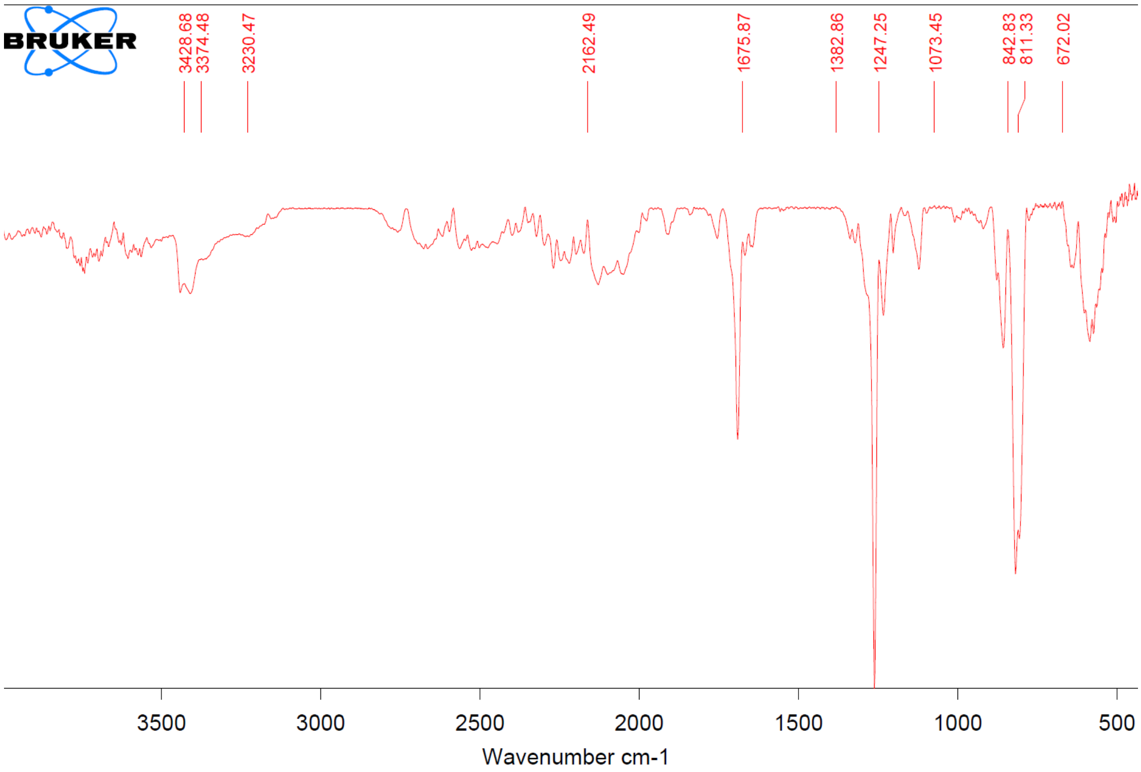


Figure S12. IR spectrum of the reaction between complex **4** with one equivalent of 3,5-dimethoxyphenyl isocyanate after 12 h at room temperature and 16 h at 60 °C in toluene.

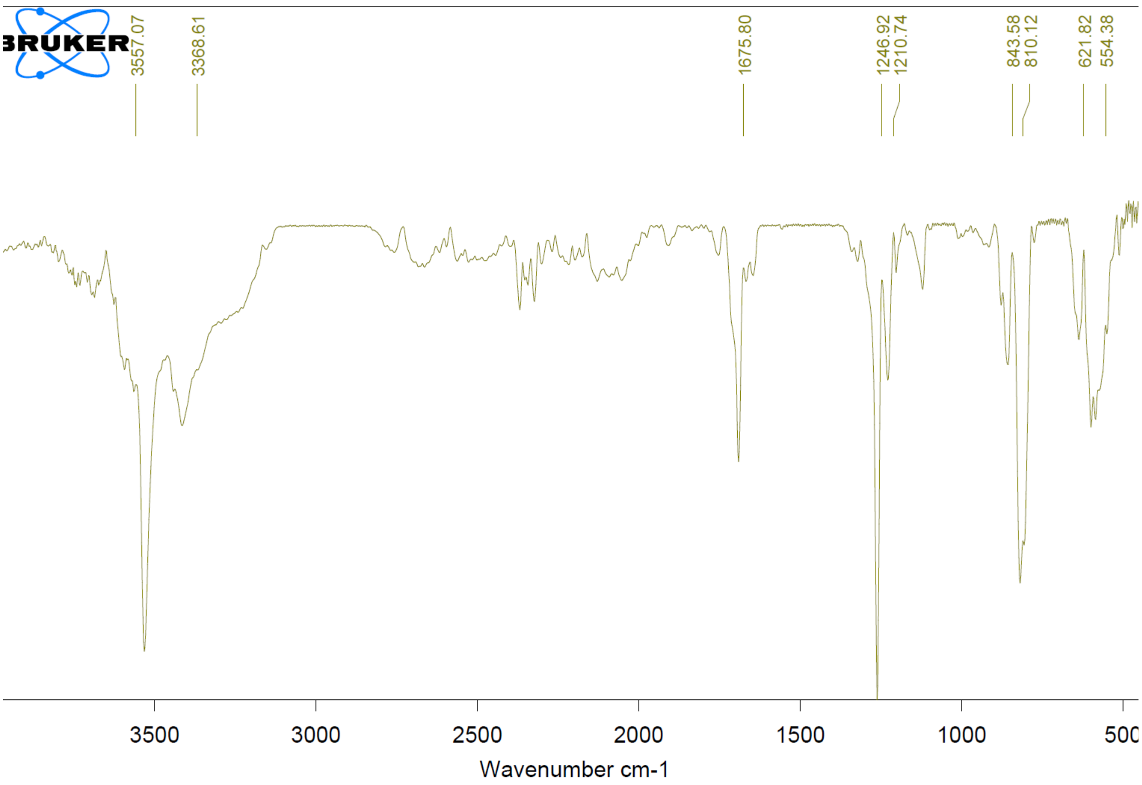


Figure S13. IR spectrum of the reaction between complex **4** with one equivalent of 3,5-dimethoxyphenyl isocyanate after 12 h at room temperature and 16 h at 60 °C and addition of two equivalents of water in toluene.

Table S2. Reactions performed with a mixture of isocyanates with precatalyst **3** (5 mol%).

Entry	Ratio of EtNCO:RNCO	R	EtNCO	RNCO
1	1:2	p-MeC$_6$H$_4$	23 µL, 0.294 mmol	74 µL, 0.588 mmol
2	2:1	p-MeC$_6$H$_4$	47 µL, 0.588 mmol	37 µL, 0.294 mmol
3	1:2	^{i}Pr	23 µL, 0.294 mmol	58 µL, 0.588 mmol
4	2:1	^{i}Pr	47 µL, 0.588 mmol	29 µL, 0.294 mmol

GC-MS Data:

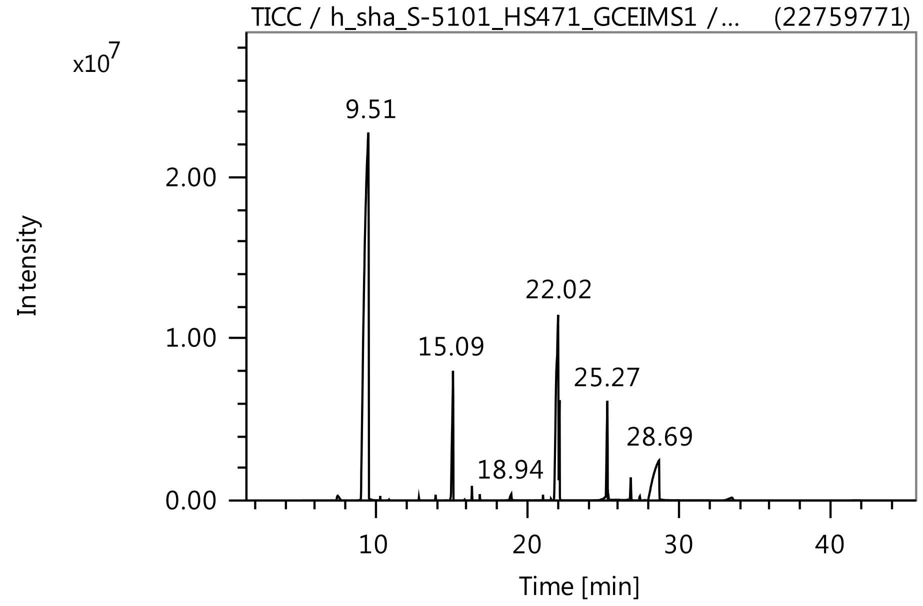
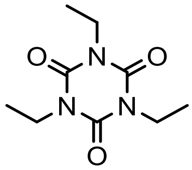
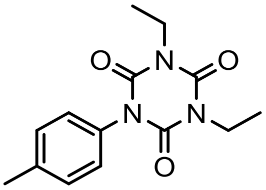
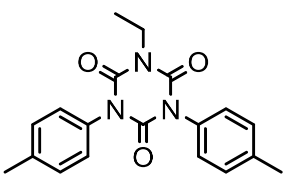


Figure S14. GC-MS trace for the reaction of EtNCO with 2 eq. of *p*-MeC$_6$H$_4$NCO with **3** (5 mol%). NB peak at 25.27 min due to protonated ligand: Tmp$_2$C$_6$H$_4$.

Table S3. GC-MS results for the reaction of EtNCO with 2 eq. of *p*-MeC$_6$H$_4$NCO with **3** (5 mol%).

Compound	*m/z*	Time (min)	Normalised area (%)
p-MeC$_6$H$_4$N=C=O	133.05	9.51	66
	213.11	15.09	7
	275.13	22.02	17
	337.14	28.69	10

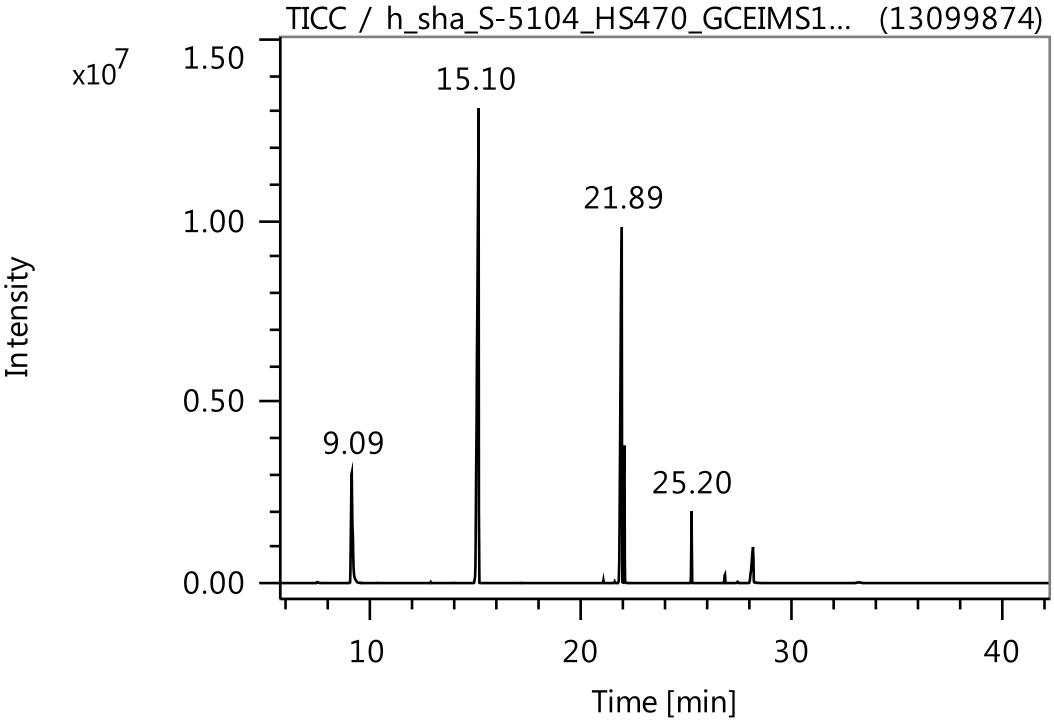
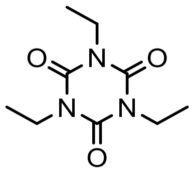
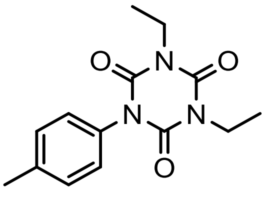
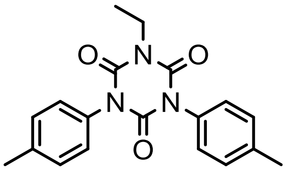


Figure S15. GC-MS trace for the reaction of 2 eq. of EtNCO with *p*-MeC_6H_4NCO with **3** (5 mol%) NB peak at 25.20 min due to protonated ligand $Tmp_2C_6H_4$.

Table S4. GC-MS results for the reaction of 2 eq. of EtNCO with *p*-MeC_6H_4NCO with **3** (5 mol%).

Compound	*m/z*	Time (min)	Normalised area (%)
p-$MeC_6H_4N=C=O$	133.05	9.09	12
	213.11	15.10	51
	275.13	21.89	33
	337.14	28.12	4

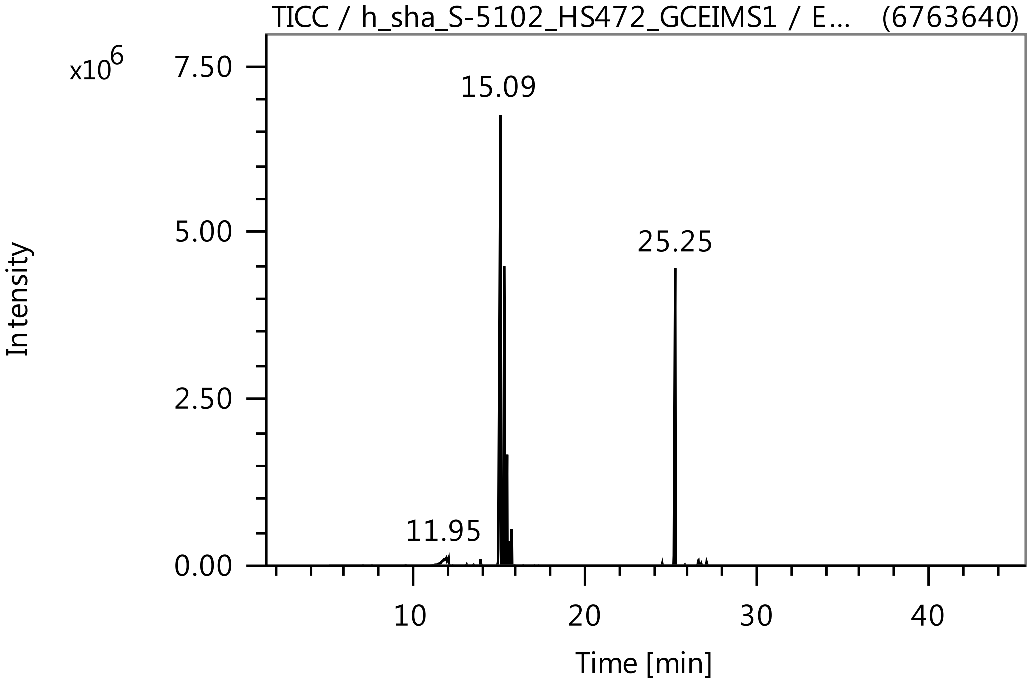
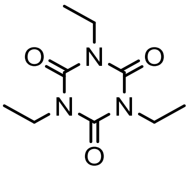
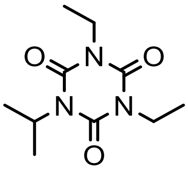
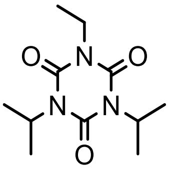
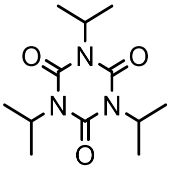


Figure S16. GC-MS trace for the reaction of EtNCO with 2 eq. of ^{i}PrNCO with **3** (5 mol%) NB peak at 25.25 min due to protonated ligand $Tmp_2C_6H_4$.

Table S5. GC-MS results for the reaction of EtNCO with 2 eq. of ^{i}PrNCO with **3** (5 mol%).

Compound	*m/z*	Time (min)	Normalised area (%)
	213.11	15.23	88
	227.16	15.30	10
	241.18	15.47	>1
	255.19	15.59	>0.1

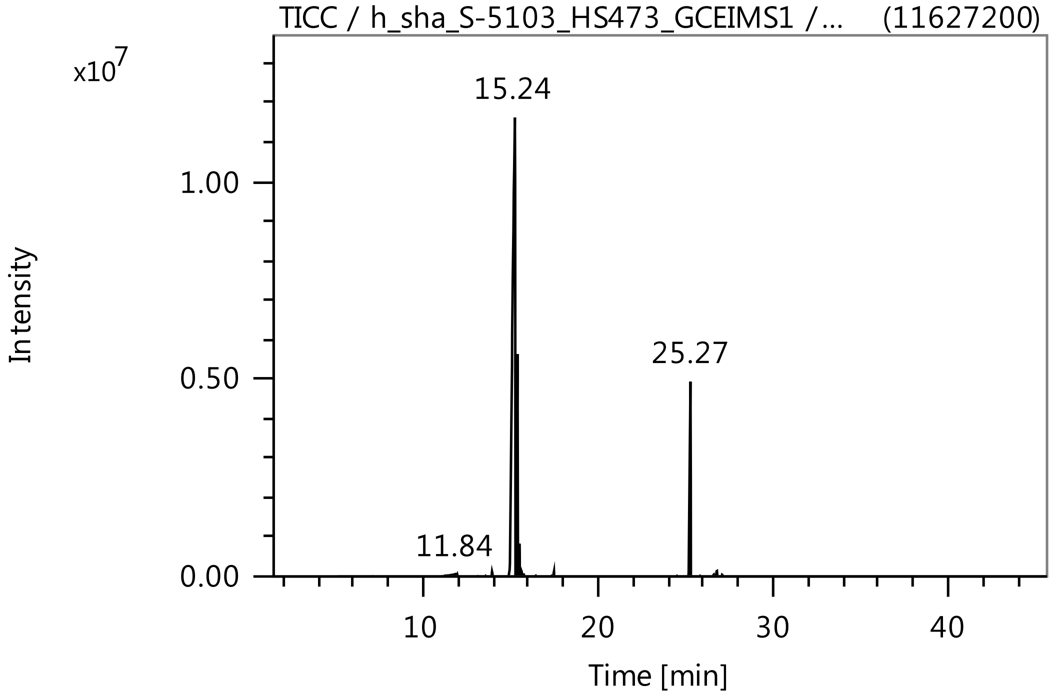
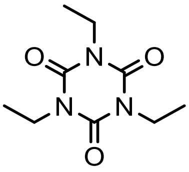
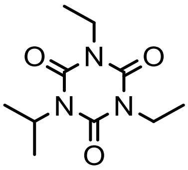
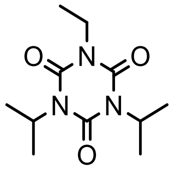
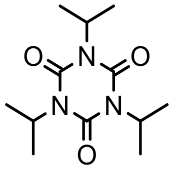


Figure S17. GC-MS trace for the reaction of 2 eq. of EtNCO with ^{i}PrNCO with **3** (5 mol%). NB peak at 25.27 min due to protonated ligand $Tmp_2C_6H_4$.

Table S6. GC-MS results for the reaction of 2 eq. of EtNCO with ^{i}PrNCO with **3** (5 mol%).

Compound	*m/z*	Time (min)	Normalised area (%)
	213.11	15.08	64
	227.16	15.39	29
	241.18	15.50	6
	255.19	15.62	1

X-ray Structure Analyses

Additional structures

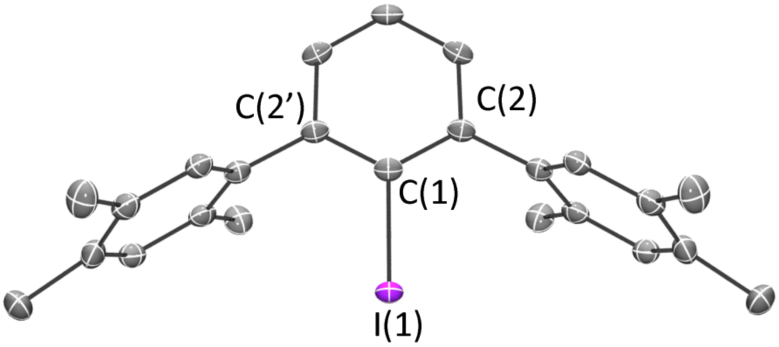


Figure S18. Molecular structure of 2,6-Tmp$_2$C$_6$H$_3$I (**7**) with anisotropic thermal parameters set at 50% probability. Hydrogen atoms have been omitted for clarity.

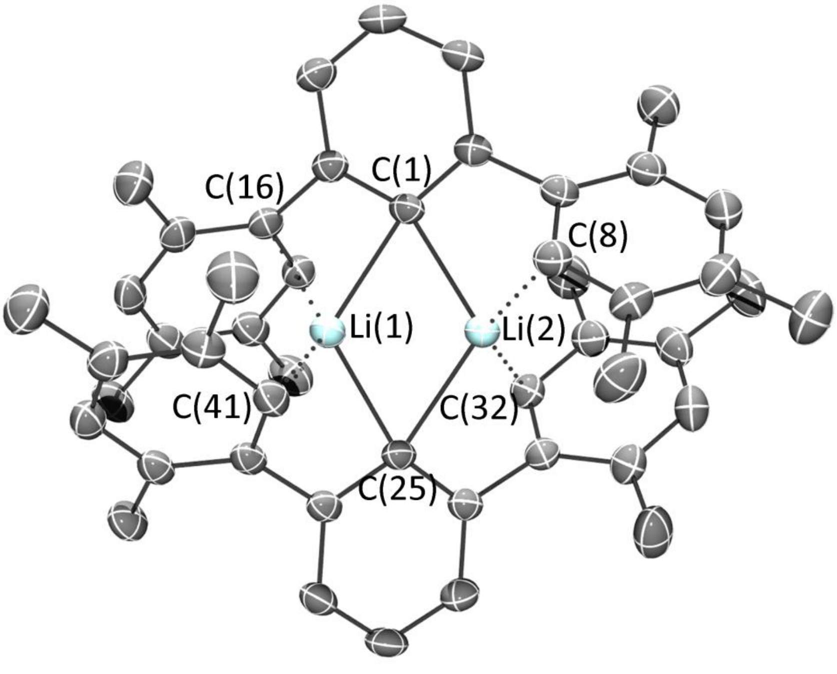


Figure S19. Molecular structure of [2,6-Tmp$_2$C$_6$H$_3$Li]$_2$ (**8**) with anisotropic thermal parameters set at 50% probability. Hydrogen atoms have been omitted for clarity.

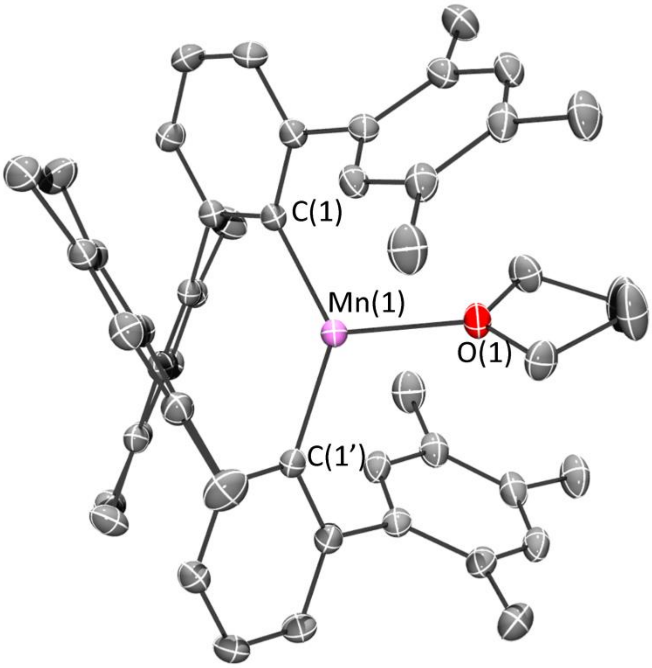


Figure S20. Molecular structure of (2,6-Tmp$_2$C$_6$H$_3$)$_2$Mn(THF) (**1**) with anisotropic thermal parameters set at 50% probability. Hydrogen atoms have been omitted for clarity.

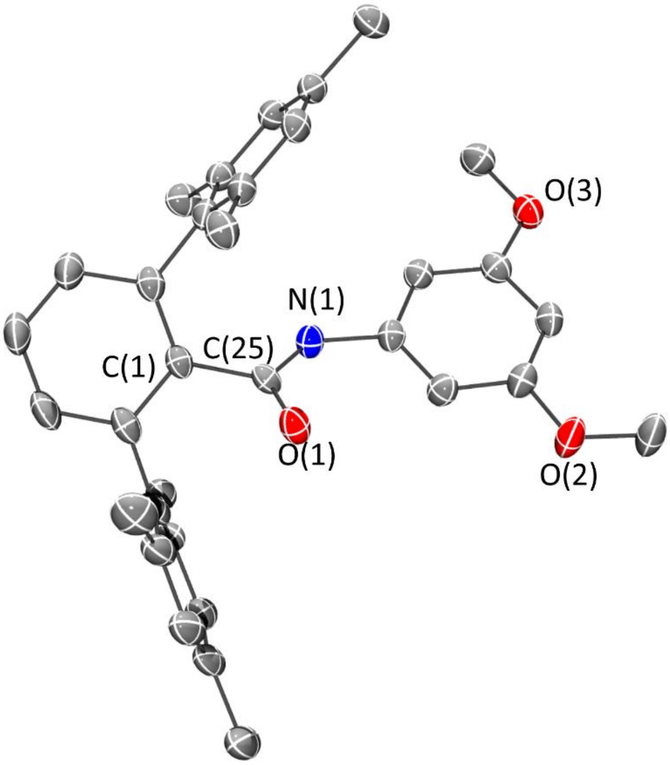


Figure S21. Molecular structure of (2,6-Mes$_2$C$_6$H$_3$)C(=O)NH(3,5-(OMe)$_2$C$_6$H$_3$) (**6**) with anisotropic thermal parameters set at 50% probability. Hydrogen atoms, disordered Mes substituent and solvent of recrystallisation have been omitted for clarity.

Crystallographic Methods

Under a flow of nitrogen, crystals suitable for analysis by X-ray diffraction were quickly removed from the crystallisation vessel and covered in YR-1800 perfluoropolyether oil. Crystals were mounted on a MiTeGen MicroMount™ and cooled rapidly in a cold stream of nitrogen using an Oxford Cryostreams open flow cryostat.[5] Single crystal X-ray diffraction data were collected on an Agilent SuperNova diffractometer (mirror-monochromated Cu-Kα radiation source; λ = 1.54184 Å; ω scans), equipped with either an Atlas, AtlasS2 or TitanS2 detector. Cell parameters were refined from the observed positions of all strong reflections in each data set and absorption corrections were applied using a Gaussian numerical method with beam profile correction (CrysAlisPro).[6] The structures were solved either by direct or iterative methods and all non-hydrogen atoms refined by full-matrix least-squares on all unique F^2 values with anisotropic displacement parameters. Hydrogen atoms were refined with constrained geometries and riding thermal parameters. Programs used include CrysAlisPro[6] (control of Supernova, data integration and absorption correction), SHELXL[7] (structure refinement), SHELXS[8] (structure solution), OLEX2[9] (molecular graphics). CIF files were checked using checkCIF[10] by Dr William Lewis and Prof. Alexander Blake at the University of Nottingham Crystal Structure Service. CCDC-1500842-1500845 and -1515783 contains the supplementary data for **1**, **2**, **6**-**8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for $(2,6\text{-Tmp}_2C_6H_3)_2Mn(THF)$ (1):

$C_{52}H_{58}OMn$ (M = 753.92 g/mol): orthorhombic, space group *Ccce* (no. 68), a = 18.67834(16) Å, b = 21.44845(18) Å, c = 21.13621(17) Å, V = 8467.62(12) Å^3, Z = 8, T = 120(2) K, μ(CuKα) = 2.798 mm^{-1}, D_{calc} = 1.183 g/cm^3, 16280 reflections measured (7.542° ≤ 2Θ ≤ 148.53°), 4254 unique (R_{int} = 0.0184, R_{sigma} = 0.0146) which were used in all calculations. The final R_1 was 0.0301 (I > 2σ(I)) and wR_2 was 0.0839 (all data).

Crystal data for $(2,6\text{-Tmp}_2C_6H_3)_2Fe(THF)$ (2):

$C_{52}H_{58}FeO$ (M = 754.83 g/mol): orthorhombic, space group *Pnna* (no. 52), a = 18.6528(2) Å, b = 43.7692(5) Å, c = 10.50646(11) Å, V = 8577.65(17) Å^3, Z = 8, T = 120(2) K, μ(CuKα) = 3.079 mm^{-1}, D_{calc} = 1.169 g/cm^3, 50578 reflections measured (8.08° ≤ 2Θ ≤ 148.422°), 8631 unique (R_{int} = 0.0316, R_{sigma} = 0.0206) which were used in all calculations. The final R_1 was 0.0456 (I > 2σ(I)) and wR_2 was 0.1067 (all data).

Crystal data for (2,6-Mes$_2$C$_6$H$_3$)C(=O)NH(3,5-(OMe)$_2$C$_6$H$_3$) (6):

$C_{36}H_{42}NO_3$ (*M* =536.70 g/mol): monoclinic, space group *C2/c* (no. 15), *a* = 31.251(2) Å, *b* = 12.6345(10) Å, *c* = 16.0331(12) Å, *β* = 99.824(7)°, *V* = 6237.8(8) Å^3, *Z* = 8, *T* = 120(2) K, μ(CuKα) = 0.558 mm^{-1}, D_{calc} = 1.143 g/cm^3, 20065 reflections measured (7.564° ≤ 2Θ ≤ 149.91°), 6245 unique (R_{int} = 0.0557, R_{sigma} = 0.0670) which were used in all calculations. The final R_1 was 0.0587 (I > 2σ(I)) and wR_2 was 0.1692 (all data).

Crystal data for 2,6-Tmp$_2$C$_6$H$_3$I (7):

$C_{24}H_{25}I$ (*M* = 440.34 g/mol): orthorhombic, space group *Pnma* (no. 62), *a* = 5.8071(4) Å, *b* = 27.443(2) Å, *c* = 12.2554(8) Å, *V* = 1953.1(3) Å^3, *Z* = 4, *T* = 120(2) K, *μ*(CuKα) = 12.877 mm^{-1}, D_{calc} = 1.498 g/cm^3, 4826 reflections measured (7.9° ≤ 2Θ ≤ 148.798°), 1976 unique (R_{int} = 0.0411, R_{sigma} = 0.0435) which were used in all calculations. The final R_1 was 0.0471 (I > 2σ(I)) and wR_2 was 0.1261 (all data).

Crystal data for [2,6-Tmp$_2$C$_6$H$_3$Li]$_2$ (8):

$C_{48}H_{50}Li_2$ (*M* = 640.76 g/mol): tetragonal, space group $P4_32_12$ (no. 96), *a* = 12.4731(2) Å, *c* = 48.7421(15) Å, *V* = 7583.3(4) Å^3, *Z* = 8, *T* = 120(2) K, *μ*(CuKα) = 0.460 mm^{-1}, D_{calc} = 1.122 g/cm^3, 31941 reflections measured (7.316° ≤ 2Θ ≤ 148.73°), 7589 unique (R_{int} = 0.0423, R_{sigma} = 0.0327) which were used in all calculations. The final R_1 was 0.0375 (I > 2σ(I)) and wR_2 was 0.0951 (all data).

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10. http://checkcif.iucr.org/