Developing Catalytic Applications of Cooperative Bimetallics: Competitive Hydroamination/Trimerization Reactions of Isocyanates Catalysed by Sodium Magnesiates

Alberto Hernán-Gómez, Tyne D. Bradley, Alan R. Kennedy, Zoe Livingstone, Stuart D. Robertson, and Eva Hevia*

WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK, G1 1XL. E-mail: eva.hevia@strath.ac.uk

General Experimental Conditions All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane and THF were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. [NaMg $(CH_2SiMe_3)_3$] (**1**),[1] was prepared according to literature procedure. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer operating at 400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C and 155.50 MHz. Elemental analyses were obtained using a Perkin Elmer 2400 elemental analyzer; however; due to the extreme air-sensitivity of compounds **3-(THF)$_2$** and **4-(\|THF)$_3$** satisfactory analyses could only be obtained for organic compounds **2a-2i** and **5a-d**.

Crystallography. Crystallographic data was collected at 123(2)K on Oxford Diffraction Diffractometers with Mo-Kα radiation (λ= 0.71073 Å). Structures were solved using SHELXS-97,[2] and refined to convergence on F^2 against all independent reflections by the full-matrix least squares method using the SHELXL-97 program.[2] Selected crystallographic data are presented in Table S1 and full details in cif format (CCDC 940855-940858) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Selected crystallographic and refinement parameters.

1. S. E. Baillie, W. Clegg, P. Garcia-Alvarez, E. Hevia, A. R. Kennedy, J. Klett, L. Russo, *Chem. Commum*. 2011, **47**, 388.
2 G.M. Sheldrick, *Acta Crystallogr*., 2007, **A64**, 112.

	2a	**3-(THF)$_2$**	**4-(THF)$_3$**	**5a**
Empirical formula	$C_{17}H_{20}N_2O$	$C_{44}H_{46}MgN_3NaO_2$	$C_{63}H_{81}MgN_6NaO_6$	$C_{24}H_{21}N_3O_3$
FW	268.35	696.14	1065.64	399.44
Crystal system	Triclinic	Monoclinic	Rhombohedral	Hexagonal
Space group	P1	P2(1)/c	R3	R3c
a (Å)	6.0329(5)	9.4286(3)	20.8559(6)	12.6655(19)
b (Å)	7.7817(7)	39.1553(19)	20.8559(6)	12.6655(19)
c (Å)	9.0003(7)	10.2035(3)	11.8574(4)	26.761(5)
α (^{o})	115.116(8)	90	90	90
β (^{o})	101.212(7)	97.029(3)	90	90
γ (^{o})	99.162(7)	90	120	120
V (Å^3)	361.11(5)	3738.6(2)	4466.6	3717.7(11)
Z	1	4	3	6
μ (mm^{-1})	0.077	0.101	0.092	0.072
Measured reflections	3468	20985	23200	2894
Unique reflections	2806	8131	5471	1477
R_{int}	0.0087	0.0284	0.0274	0.0234
R [on *F*, obs rflns only]	0.0307	0.0546	0.0344	0.0511
wR [on F^2, all data]	0.0761	0.1201	0.0870	0.1443
GoF	1.026	1.027	1.077	1.028
Largest diff. peak/hole (e Å^{-3})	0.234/-0.175	0.420/-0.487	0.241/-0.267	0.192/-0.306

Synthesis of [(THF)NaMg(NPh$_2$)$_3$(THF)] [3-(THF)$_2$]. To a solution of [NaMg(CH$_2$SiMe$_3$)$_3$] (**1**) (0.62g, 2 mmol) in hexane (10 mL), NHPh$_2$ (1.01 g, 6 mmol) was added and the resulting white suspension was stirred for one hour. THF (4 ml) was added affording a colourless solution which was transferred to the freezer (-28 °C). After 24 hours a crop of colourless crystals of **3-(THF)**2 was obtained, which were isolated and stored in a glove box (1.10 g, 80 %). ^{1}H NMR (298 K, d$_8$-THF) δ6.99 (m, 12H, Ph), 6.79 (dd, 12H, Ph), 6.26(d, 6H, Ph), 3.61 (m, 8H, OC*H*$_2$, THF), 1.77 (m, 8H, C*H*$_2$, THF). ^{13}C {^{1}H} NMR (298 K, d$_8$-THF) δ159.4 [*C*$_{ipso}$, Ph], 129.7 [*C*H, Ph], 123.1 [*C*H, Ph], 115.9 [*C*H, Ph], 69.2 (O*C*H$_2$,THF), 27.2 (*C*H$_2$, THF).

Synthesis of [(THF)$_3$NaMg{(*t*BuN)C(NPh$_2$)(=O)}$_3$] [4-(THF)$_3$]. To a solution of [(THF)NaMg(NPh$_2$)$_3$(THF)] [**3-(THF)$_2$**] (0.69 g, 1 mmol) in THF (4mL), *t*BuN=C=O was added (0.34 ml, 3 mmol). The resulting solution was stirred for one hour at room temperature. Hexane (1mL) was then introduced. The resulting pale yellow solution was placed in the freezer (-28^{o}C). After 24 hours, a crop of colourless crystals were isolated and stored in the glove box (0.66 g, 62 %). ^{1}H NMR (298K, C$_6$D$_6$) δ7.42 (d, 6H, Ar(*H*), Ph), 7.10 (m, 6H, Ar(*H*), Ph), 6.84 (m,3H, Ar(*H*), Ph), 3.27 (m, 12H, OC*H*$_2$, THF], 1.44 [s, 18H, C*H*$_3$, ^{t}Bu], 1.28 [m, 12H, C*H*$_2$, THF]. ^{13}C NMR{^{1}H} (298K, C$_6$D$_6$,) δ163.2 (N*C*(=O)N), 146.0 [*C*$_{ipso}$, NPh$_2$], 129.0, 122.0, 121.9 [*C*H, Ph], 67.5 [O*C*H$_2$, THF], 51.4 [*C*(CH$_3$)$_3$], 32.1 [C(*C*H$_3$)$_3$], 25.3 [*C*H$_2$, THF].

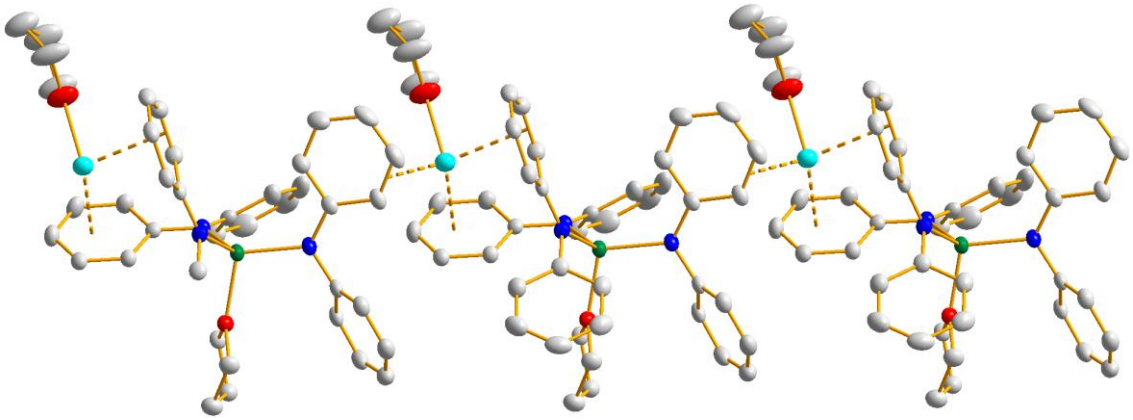


Figure S1a.Asymmetric unit of **3-(THF)$_2$** (thermal ellipsoids are shown at the 50% probability level, hydrogen atoms omitted for clarity).

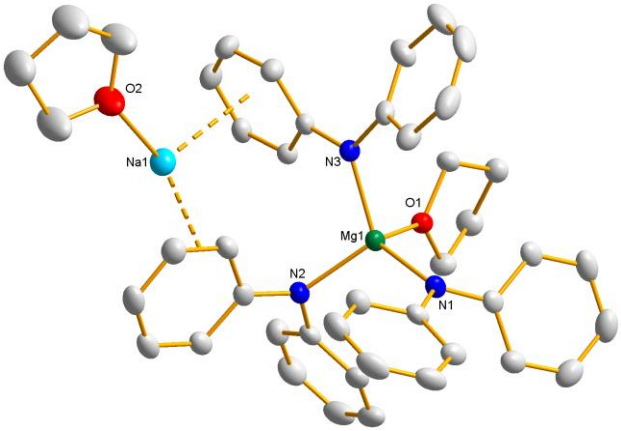


Figure S1b. Extended polymeric structure of **3-(THF)$_2$**(thermal ellipsoids are shown at the 50% probability level, hydrogen atoms omitted for clarity).

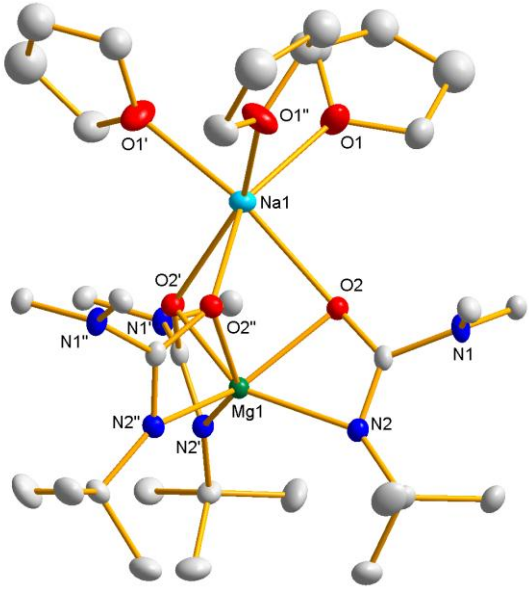


Figure S2.Molecular structure of **4-(THF)$_3$** (thermal ellipsoids are shown at the 50% probability level, hydrogen atoms, aromatic C, except C ipso, and minor disorder components in THF molecules omitted for clarity).

General procedure for hydroamination reactions of isocyanates at NMR tube scale. Catalytic reactions were performed in an NMR scale using the following standard procedure. An NMR tube was charged in the glove box with 1.1 mmol of amine, 1 mmol of isocyanate, a 10 mol% of ferrocene (0.018g, 0.1 mmol), which was employed as an internal standard and 2 mL of C_6D_6. The initial ratio of starting materials was determined by integration of their resonances in the ^{1}H NMR spectrum. Using standard Schlenk techniques, 2 mol%[3] of precatalyst **1** (6.2 mg, 0.02 mmol) was introduced. Reactions times were measured from this point. Yields were determined by integration of the products resonances relative to the resonance of the internal standard in the ^{1}H NMR spectrum. See Table 1 in manuscript for details.

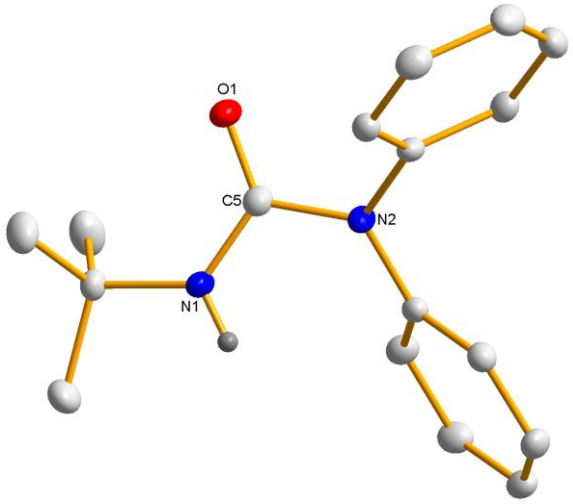


Figure S3.Molecular structure of **2a** (thermal ellipsoids are shown at the 50% probability level, hydrogen atoms except NH omitted for clarity).

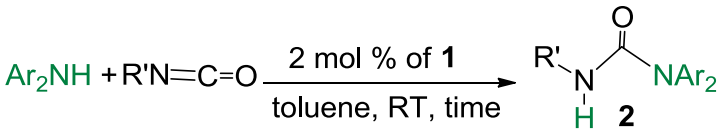
General procedure for preparative scale synthesis of ureas 2a-K. An oven dried Schlenk tube was charged sodium magnesiate **1** (0.0062 mg, 0.02 mmol, 2 mol%) and Toluene (2 mL). The relevant amine (1.1 mmol) and isocyanate (1 mmol) were added and the mixture was stirred at room temperature for 30 minutes, the toluene was removed in vacuo[4] and the crude dissolved in dichloromethane (100 mL). Washing the organic solution with water (3 x 10 mL), drying over magnesium sulfate and removing the solvent under reduced pressure gave a crude colourless product. Purification by flash column

[3] Note that the spectra showed in Figure S4 correspond to a catalytic hydroamination reaction where 5 mol% of **1** was employed.

4 Due to their volatility, for ureas **2g** and **2h** toluene was not removed under vacuum. The work-up procedure was followed using a mixture of toluene/dichloromethane.

chromatography upon silica gel using a 75:25 chromatography hexane: ethylacetate eluent system[5] gave ureas **2a-i** were isolated as white solids.

Table S2. Catalytic Formation of Ureas **2a-k**



Entry	Ar_2NH	R'	Time(h)	Product	Yield (%)[a]
1	Ph_2NH	*t*Bu	0.25	**2a**	79 (97)
2	Ph_2NH	Cy	0.25	**2b**	85(98)
3	Ph_2NH	Ad	0.25	**2c**	81(90)
4	$pTol_2NH$	*t*Bu	0.25	**2d**	83(99)
5	$pTol_2NH$	Cy	0.25	**2e**	80(98)
6	$pTol_2NH$	Ad	0.25	**2f**	87(92)
7	Ph(Me)NH	*t*Bu	0.25	**2g**	86(99)
8	Ph(Me)NH	Ad	0.25	**2h**	81(99)
9	Py_2NH	*t*Bu	3	**2i**	(11)
10	Py_2NH	Cy	3	**2j**	55(58)
11	Py_2NH	Ad	3	**2k**	(5)
12	$(SiMe_3)_2NH$	Cy	24	-	0

[a]Values showed in brackets correspond to the yields determined by ^{1}H NMR using ferrocene as an internal standard.

Characterization of [(NH*t*Bu)C(=O)NPh$_2$] (2a). Yield :0.211 g, 79%. Anal. Calcd. for $C_{17}H_{20}N_2O$: C, 76.09; H, 7.51; N, 10.44. Found: C, 76.17; H, 7.47; N, 10.41. ^{1}H NMR (298K, C_6D_6) δ7.18 (d, *J* = 8.0 Hz, 4H, Ph), 7.02 (t, *J* = 8 Hz, 4H, Ph), 6.87 (t, *J* = 8 Hz, 2H, Ph), 4.35 (s, 1H, N*H*), 1.24 (s, 9H, C*H*$_3$, ^{t}Bu). ^{13}C NMR {^{1}H} (298K, C_6D_6) δ154.8 (N*C*(=O)N), 144.2 (*C*$_{ipso}$, NPh_2), 129.3, 127.5, 125.5 (*C*H, Ph), 50.9 (*C*$(CH_3)_3$), 29.14 (C(*C*$H_3)_3$). Molecular structure of **2a** was determined by X-ray crystallography, see Figure S3 and CIF file for details.

Characterization of [(NHCy)C(=O)NPh$_2$] (2b). Yield :0.25 g, 85%. Anal. Calcd. for $C_{19}H_{22}N_2O$: C, 77.52; H, 7.53; N, 9.52 Found: C, 77.52; H, 7.79; N, 9.60. ^{1}H NMR (298K, C_6D_6) δ7.22 (d, *J* = 8 Hz, 4H, Ph), 7.04 (t, *J* = 8 Hz, 4H, Ph), 6.88 (t, *J* = 8 Hz, 4H, Ph) 4.27 (s, 1H, N*H*), 3.94-3.87 (m, 1H, Cy), 1.84-1.80 (m, 2H, Cy), 1.41-1.27 (m, 3H, Cy), 1.17-1.06 (m, 2H, Cy), 0.89-0.68 (m, 3H, Cy). ^{13}C NMR {^{1}H} (298K, C_6D_6) δ154.9 (N*C*(=O)N), 144.1 (*C*$_{ipso}$, NPh_2), 129.3, 127.5, 125.6 (*C*H, Ph), 49.4 (*C*H, Cy), 33.4, 25.7, 25.0 (*C*H_2, Cy).

5 In the case of **2j**, purification by flash column chromatography upon silica gel was carried out using a neat chromatography ethylacetate as an eluent.

Characterization of [(NHAd)C(=O)NPh$_2$] (2c). Yield :0.28 g, 81%. Anal. Calcd. for $C_{23}H_{26}N_2O$: C, 79.73; H, 7.56; N, 8.09. Found: C, 79.51; H, 7.45; N, 8.30. ^{1}H NMR (298K, C_6D_6) δ7.21 (d, *J* = 8 Hz, 4H, Ph), 7.04 (t, *J* = 8 Hz, 4H, Ph), 6.89 (t, *J* = 8 Hz, 2H, Ph), 4.27 (s, 1H, N*H*), 1.96 (m, 6H, Ad), 1.88 (m, 3H, Ad), 1.54-1.46 (m, 6H, Ad). ^{13}C NMR {^{1}H} (298K, C_6D_6) δ154.3 (N*C*(=O)N), 144.2 (C_{ipso}, NPh$_2$), 129.3, 127.5, 125.4 (*C*H, Ph), 51.5 (*C*, Ad), 42.2, 36.6 (*C*H$_2$, Ad), 29.9 (*C*H, Ad).

Characterization of [(NH*t*Bu)C(=O)N(*p*Tol)$_2$] (2d). Yield :0.245 g, 83%. Anal. Calcd. for $C_{19}H_{24}N_2O$: C, 76.99; H, 8.16; N, 9.45. Found: C, 77.06; H, 8.28; N, 9.25. ^{1}H NMR (298K, C_6D_6) δ7.17 (d, *J* = 8.0 Hz, 4H, *p*Tol), 6.87 (d, *J* = 8 Hz, 4H, *p*Tol), 4.44 (s, 1H, N*H*), 2.02 (s, 6H, *p*Tol), 1.28 (s, 9H, C*H*$_3$, ^{t}Bu). ^{13}C NMR {^{1}H} (298K, C_6D_6) δ155.0 (N*C*(=O)N), 141.8 (C_{ipso}, N*p*Tol$_2$), 135.0, 129.9, 127.4 (*C*H, *p*Tol), 50.8 (*C*(CH$_3$)$_3$), 29.2 (C(*C*H$_3$)$_3$), 20.8 (CH$_3$, *p*Tol).

Characterization of [(NHCy)C(=O)N(*p*Tol)$_2$] (2e). Yield :0.257 g, 80%. Anal. Calcd. for $C_{21}H_{26}N_2O$: C, 78.22; H, 8.13; N, 8.69. Found: C, 79.63; H, 8.19; N, 7.71. ^{1}H NMR (298K, C_6D_6) δ7.21 (d, *J* = 8 Hz, 4H, Ph), 6.90 (d, *J* = 8 Hz, 4H, Ph), 4.36 (s, 1H, N*H*), 3.96-3.93 (m, 1H, Cy), 2.03 (s, 6H, *p*Tol) 1.90-1.85 (m, 2H, Cy), 1.44-1.29 (m, 3H, Cy), 1.19-1.08 (m, 2H, C*H*$_2$, Cy), 0.91-0.73 (m, 3H, Cy). ^{13}C NMR {^{1}H} (298K, C_6D_6) δ155.2 (N*C*(=O)N), 141.7 (C_{ipso}, N*p*Tol$_2$), 135.1, 130.0, 127.5 (*C*H, *p*Tol), 49.5 (*C*H, Cy), 33.6, 25.8, 25.1 (*C*H$_2$, Cy), 20.8 (CH$_3$, *p*Tol).

Characterization of [(NHAd)C(=O)N(*p*Tol)$_2$] (2f). Yield :0.327 g, 87%. Anal. Calcd. for $C_{25}H_{30}N_2O$: C, 80.17; H, 8.07; N, 7.48. Found: C, 80.15; H, 8.17; N, 7.50. ^{1}H NMR (298K, C_6D_6) δ7.20 (d, *J* = 8 Hz, 4H, *p*Tol), 6.89 (d, *J* = 8 Hz, 4H, *p*Tol), 4.36 (s, 1H, N*H*), 2.03 (s, 6H, *p*Tol), 2.01-2.00 (m, 6H, Ad), 1.88 (m, 3H, Ad), 1.55-1.47 (m, 6H, Ad). ^{13}C NMR {^{1}H} (298K, C_6D_6) δ154.6 (N*C*(=O)N), 141.9 (C_{ipso}, NPh$_2$), 134.9, 129.9, 127.5 (*C*H, Ph), 51.4 (*C*, Ad), 42.4, 36.6 (CH$_2$, Ad), 29.9 (*C*H, Ad), 20.8 (*C*H$_3$, *p*Tol).

Characterization of [(NH*t*Bu)C(=O)N(Me)Ph] (2g). Yield :0.177 g, 86%. ^{1}H NMR (298K, C_6D_6) δ7.02 (t, *J* = 8.0 Hz, 4H, Ph), 6.95 (d, *J* = 8 Hz, 2H, Ph), 6.90 (t, *J* = 8 Hz, 1H, Ph), 4.24 (s, 1H, N*H*), 3.14 (s, 3H, NCH$_3$) 1.23 (s, 9H, C*H*$_3$, ^{t}Bu). ^{13}C NMR {^{1}H} (298K, C_6D_6) δ155.9 (N*C*(=O)N), 145.0 (C_{ipso}, NPh), 129.9, 127.2, 126.5 (*C*H, Ph), 50.6 (*C*(CH$_3$)$_3$), 36.7 (NCH$_3$) 29.3 (C(*C*H$_3$)$_3$). MS (ESI): m/z = 207.1 [M + H$^+$]

Characterization of [(NHAd)C(=O)N(Me)Ph] (2h). Yield :0.23 g, 81%. ^{1}H NMR (298K, C_6D_6) δ7.04-6.98 (m, 4H, Ph), 6.91-6.88 (m, 1H, Ph), 4.17 (s, 1H, N*H*), 3.16 (s, 3H, NMe), 1.97-1.96 (m, 6H, Ad), 1.87 (m, 3H, Ad), 1.54-1.46 (m, 6H, Ad). ^{13}C NMR {^{1}H} (298K, C_6D_6) δ155.5 (N*C*(=O)N), 145.2 (C_{ipso},

NPh_2), 129.8, 127.3, 126.3 (*C*H, Ph), 51.1 (*C*, Ad), 42.4 (CH_2, Ad), 36.7 (CH_2, Ad; NCH_3), 30.0 (*C*H, Ad). MS (ESI): m/z = 285.1 [M + H^+]

Characterization of [(NH*t*Bu)C(=O)N(Py)$_2$] (2i). Yield: 11% (determined by ^{1}H NMR). ^{1}H NMR (298K, [D_8]THF) δ9.90 (s, 1H, N*H*), 8.34-8.33 (m, 2H, NPy), 7.57 (t, *J* = 8 Hz, 2H, NPy), 7.03 (t, *J* = 8 Hz, 2H, NPy), 6.76-6.71 (m, 2H, NPy), 1.39 (s, 9H, CH_3, ^{t}Bu). ^{13}C NMR {^{1}H} (298K, [D_8]THF) δ156.3 (C_{ipso}, NPy) 154.4 (N*C*(=O)N), 138.5, 120.6, 120.4 (*C*H, Ph), 51.1 (*C*$(CH_3)_3$), 29.4 (C(*C*$H_3)_3$).

Characterization of [(NHCy)C(=O)N(Py)$_2$] (2j). Yield :0.163 g, 55%. Anal. Calcd. for $C_{17}H_{20}N_4O$: C, 68.89; H, 6.80; N, 18.90. Found: C, 68.57; H, 6.80; N, 18.69. ^{1}H NMR (298K, C_6D_6) δ10.03 (s, 1H, N*H*), 8.16-8.14 (m, 2H, NPy), 6.99 (t, *J* = 8 Hz, 2H, NPy), 6.67 (d, J = 8 Hz, 2H, NPy), 6.48 (t, *J* = 8 Hz, 2H, NPy), 4.11-4.02 (m, 1H, Cy), 2.02-1.98 (m, 2H, Cy), 1.58-1.53 (m, 2H, Cy), 1.30-1.27 (m, 3H, CH_2, Cy), 1.17-1.04 (m, 3H, Cy). ^{13}C NMR {^{1}H} (298K, C_6D_6) δ155.8 (C_{ipso}, NPy) 154.8 (N*C*(=O)N), 147.8, 137.7, 120.1, 119.8 (*C*H, NPy), 49.2 (*C*H, Cy), 33.4, 26.1, 24.9 (*C*H_2, Cy).

Characterization of [(NHAd)C(=O)N(Py)$_2$] (2k). Yield: 5% (determined by ^{1}H NMR). ^{1}H NMR (298K, [D_8]THF) δ9.82 (s, 1H, N*H*), 8.34-8.33 (m, 2H, NPy), 7.58 (t, *J* = 8 Hz, 2H, NPy), 7.03 (t, *J* = 8 Hz, 2H, NPy), 6.76-6.71 (m, 2H, NPy), 2.11 (m, 6H, Ad). ^{13}C NMR {^{1}H} (298K, [D_8]THF) δ156.3 (C_{ipso}, NPy) 153.9 (N*C*(=O)N), 138.5, 120.7, 120.4 (*C*H, NPy), 51.8 (*C*, Ad), 42.8 (*C*H_2, Ad), 37.5 (*C*H_2, Ad).

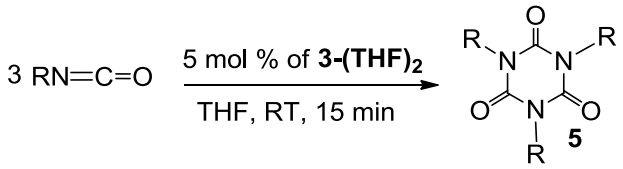
General procedure for preparative scale synthesis of isocyanurates 5a-d. An oven dried Schlenk tube was charged under argon with the relevant isocyanate RNCO (4 mmol), sodium magnesiate **3-(THF)$_2$** (0.14g, 0.20 mmol, 5 mol%) and THF (4 mL). The reaction mixture was allowed to stir at room temperature for 15 minutes affording a white precipitate. The resulting precipitate was filtered, washed with toluene (hexane in the case of *o*TolNCO), and dried *in vacuo* to afford the isocyanurate as a white solid. See Table S2 for details. Spectroscopic data for products **5a-d** matched those previously reported.[6]
It should be noted that the same conversion of *p*TolNCO to isocyanurate **5a** was observed when the reactions were carried out under the same conditions as the hydroamination reactions, using equimolar amounts of $NHPh_2$ and the relevant isocyanate along with a 5 mol% of homoleptic alkyl magnesiate **1**. However, when the reaction was carried out in the absence of amine, **5a** was obtained in a modest 10% yield, indicating that **1** has a much lower catalytic activity in this trimerization process than tris(amido)magnesiate **3**. These findings suggest that under hydroamination reaction conditions, the role

6 .a) J. Shi , Z. Guo, X. Wei, D. Liu, M. F. Lappert, *Synlett*, 2011, **13**, 1937-1939. b) L. Lunazzi, M. Mancinelli, and A. Mazzanti, *J. Org. Chem.*, 2012, **77**, 3373-3380.

of the amine is to generate in situ active species **3** which can then undergo subsequent insertion reactions with *p*TolNCO to give **5a** (see Scheme 2, cycle B). The high selectivity observed in this process is remarkable, considering that under these conditions there is a large excess of amine present, which could facilitate protonolysis of some of the insertion intermediates giving rise to the formation of byproducts. This is a well-known problem in cyclotrimerization processes.[7] Supporting this interpretation on the role of the amine, the reaction of *p*TolNCO with **1** (5 mol%) in the presence of 15 mol% of $NHPh_2$ afforded **5a** in a 81% yield.

Isocyanurates find widespread application in polymer chemistry, enhancing the physical properties of polyurethanes and coating materials.[7] Thus, recently several catalysts for the trimerization of isocyanates have been developed including Lewis acids or organometallic complexes. Some of the main hurdles faced by this catalytic transformation are the need of severe reaction conditions, limited selectivity with formation of byproducts as well as limited functional group tolerance.[7] Here sodium magnesiate **3** can effectively promote the trimerization of arylisocyanates at room temperature in a selective manner without forming other oligomers.

Table S3. Catalytic Formation of Isocyanurates **5a-d**[a]



Entry	RN=C=O	Product	Yield (%)[b]
1	*p*TolNCO	**5a**	75
2	*p*(OMe)C_6H_4NCO	**5b**	83
3	*p*(Cl)C_6H_4NCO	**5c**	74
4	*o*TolNCO	**5d**	70
5	2,6(Me)$_2C_6H_3$NCO	-	0

[a]Conditions: isocyanate (4 mmol), **3-(THF)$_2$** (0.20 mmol), THF (4 mL). [b] Isolated yields.

Characterization of 1,3,5-tris(4-methylphenyl)-1,3,5-triazinane-2,4,6-trione (5a). Yield: 0.396 g, 75%.Anal. Calcd. for $C_{24}H_{21}N_3O_3$: C, 72.16; H, 5.30; N, 10.52. Found: C, 71.90; H, 5.05; N, 10.63. ^{1}H NMR (298K, $CDCl_3$) δ7.25 (m, 4H, Ar*H*, *p*Tol), 2.37 (s, 9H, C*H*$_3$, *p*Tol). ^{13}C NMR {^{1}H} (298K, $CDCl_3$) δ148.8 (*C*=O), 139.2 (C_{ipso}, *p*Tol), 131.0, 129.9, 128.0 (*C*, *p*Tol), 21.9 (*C*H$_3$, *p*Tol). Molecular structure of **5a** was determined by X-ray crystallography, see Figure S4 and CIF file for details.

7 H. A. Duong, M. J. Cross, J. Louie, *Org. Lett.* 2004, **6**, 4679.

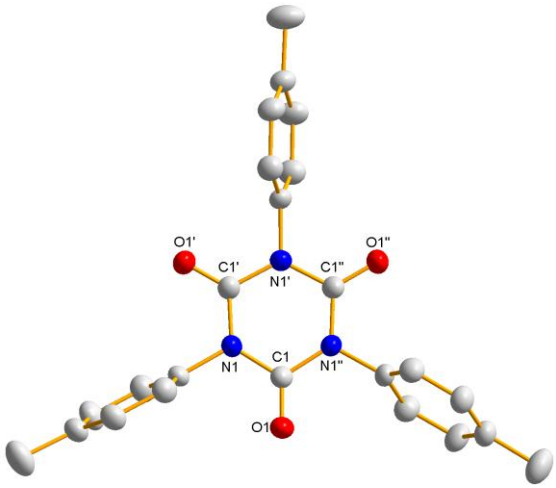


Figure S4.Molecular structure of **5a** (thermal ellipsoids are shown at the 50% probability level, hydrogen atoms omitted for clarity).

Characterization of [(THF)$_3$NaMg{(*p*N)C(NPh$_2$)(=O)}$_3$]. To a solution of [(THF)NaMg(NPh$_2$)$_3$(THF)] [**3-(THF)$_2$**] (0.14 g, 0.20 mmol) in THF (1mL), *p*TolN=C=O was added (0.13 g ml, 1 mmol). The resulted suspension was stirred for fifteen minutes at room temperature and filtered in order to remove **5a** from the solution. The filtrate was studied by ^{1}H and ^{13}C NMR spectroscopy revealing the formation of the metal tris(ureido) complex generated by insertion of a organic heterocumulene molecule in each Mg-N bond of **3-(THF)$_2$**

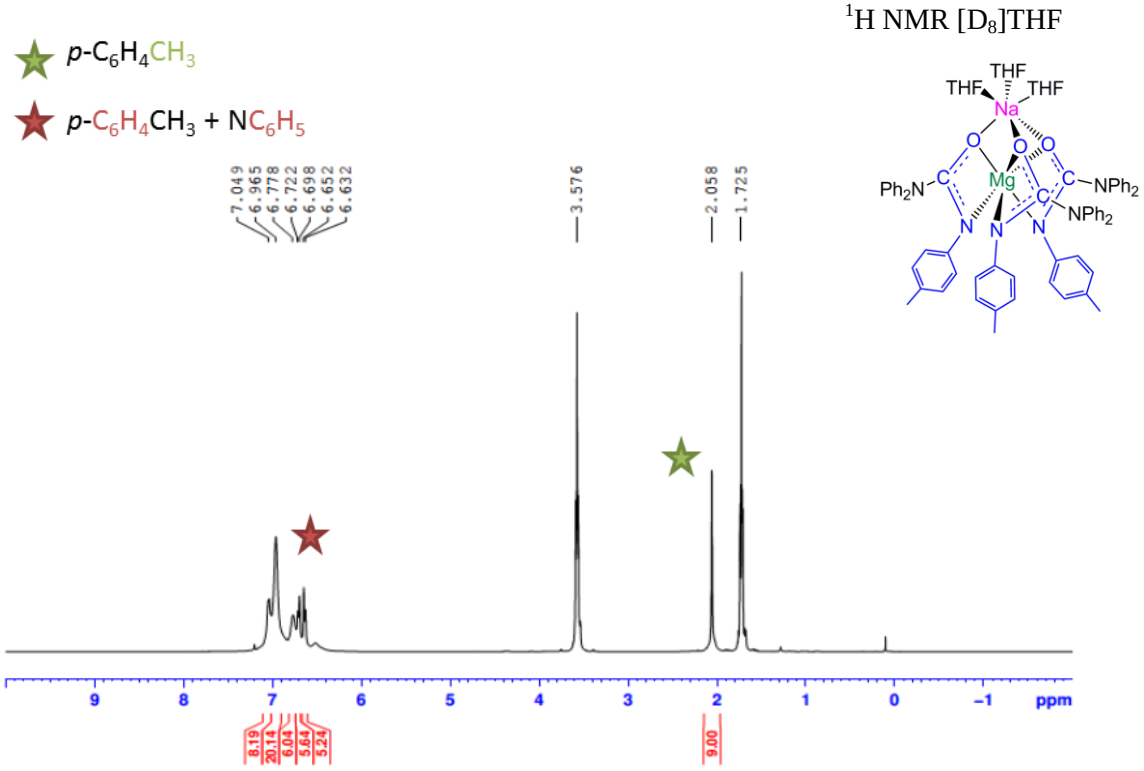


Figure S5a. ^{1}H NMR spectrum in [D$_8$]THF of *p*TolNCO and [(THF)NaMg(NPh$_2$)$_3$(THF)] **[3-(THF)$_2$]** (20 mol%).

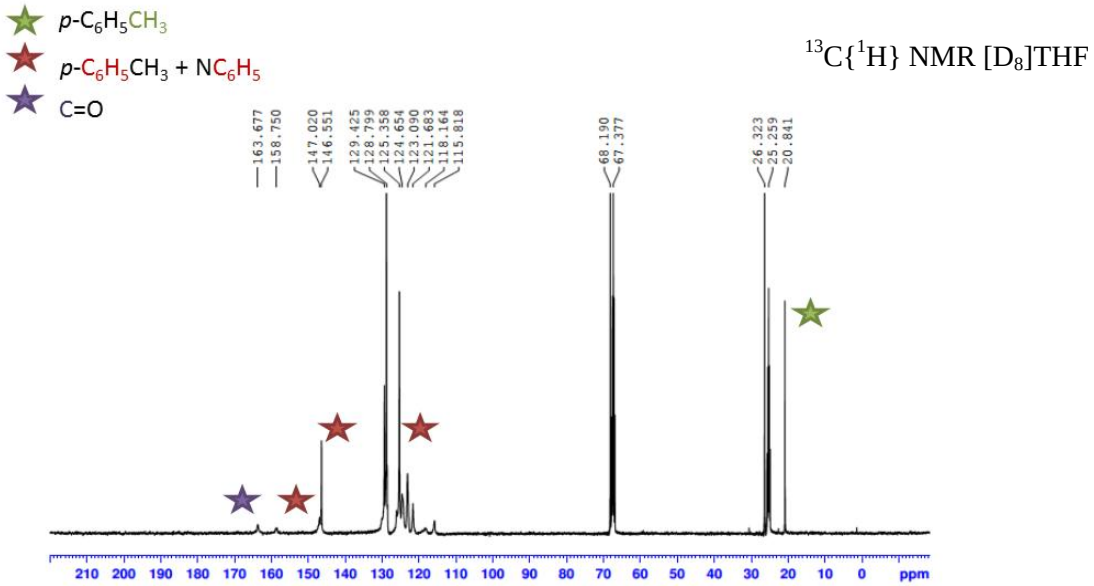


Figure S5b. ^{13}C NMR spectrum in $[D_8]THF$ of *p*TolNCO and $[(THF)NaMg(NPh_2)_3(THF)]$ **[3-(THF)$_2$]** (20 mol%).

Characterization of 1,3,5-tris(4-methoxyphenyl)-1,3,5-triazinane-2,4,6-trione (5b). Yield: 0.496 g, 83%.Anal. Calcd. for $C_{24}H_{21}N_3O_6$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.22; H, 4.47; N, 8.87. ^1H NMR (298K, $CDCl_3$) δ7.26 (d, J =8.8Hz, 6H, Ar*H*, *p*-PhOMe) 6.96 (d, J =8.8Hz, 6H, Ar*H*, *p*-PhOMe), 3.80 (s, 9H, O*CH*$_3$). ^{13}C NMR {^1H} (298K, $CDCl_3$) δ 159.88 (*C*=O), 149.09, 129.39, 126.29, 114.55 (*C*, *p*-PhOMe), 55.45 (O*C*H$_3$, *p*-PhOMe).

Characterization of 1,3,5-tris(4-Chlorophenyl)-1,3,5-triazinane-2,4,6-trione (5c). Yield: 0.453 g, 74%.Anal. Calcd. for $C_{21}H_{12}Cl_3N_3O_3$: C, 54.75; H, 2.63; N, 9.12. Found: C, 55.37; H, 3.13; N, 8.52. ^1H NMR (298K, $CDCl_3$) δ7.45 (d, J = 8.8Hz, 6H, Ar*H*, *p*-PhCl), 7.29 (d, J =8.8Hz, 6H, Ar*H*, *p*-PhCl). ^{13}C NMR {^1H} (298K, $CDCl_3$) δ 148.08 (*C*=O), 135.54, 131.69, 129.67 (**C**, *p*-PhCl).

Characterization of 1,3,5-tris(2-methylphenyl)-1,3,5-triazinane-2,4,6-trione (5d). Yield: 0.37 g, 70%.Anal. Calcd. for $C_{24}H_{21}N_3O_3$: C, 72.16; H, 5.30; N, 10.52. Found: C, 71.91; H, 5.13; N, 9.99. ^1H NMR (298K, $CDCl_3$) *anti* + *syn*, δ7.40−7.30 (m, 12H, Ar*H*, *o*Tol), 2.34 (s, 3H, C*H*$_3$, *o*Tol), 2.33 (s, 6H, C*H*$_3$, *o*Tol), 2.32, (s, 9H, C*H*$_3$, *o*Tol).^{13}C NMR {^1H} (298K, $CDCl_3$) *anti* δ 147.94 (3 *C*=O), 135.85, 135.66, 132.73, 131.18, 129.74, 128.60, 128.53, 127.19, 127.13 (*C*, *o*Tol), 17.36 (*C*H$_3$, *p*Tol); *syn*: 147.98, 135.50, 132.73, 131.14, 129.74, 128.66, 127.25 (*C*, *o*Tol), 17.36 (*C*H$_3$, *p*Tol).

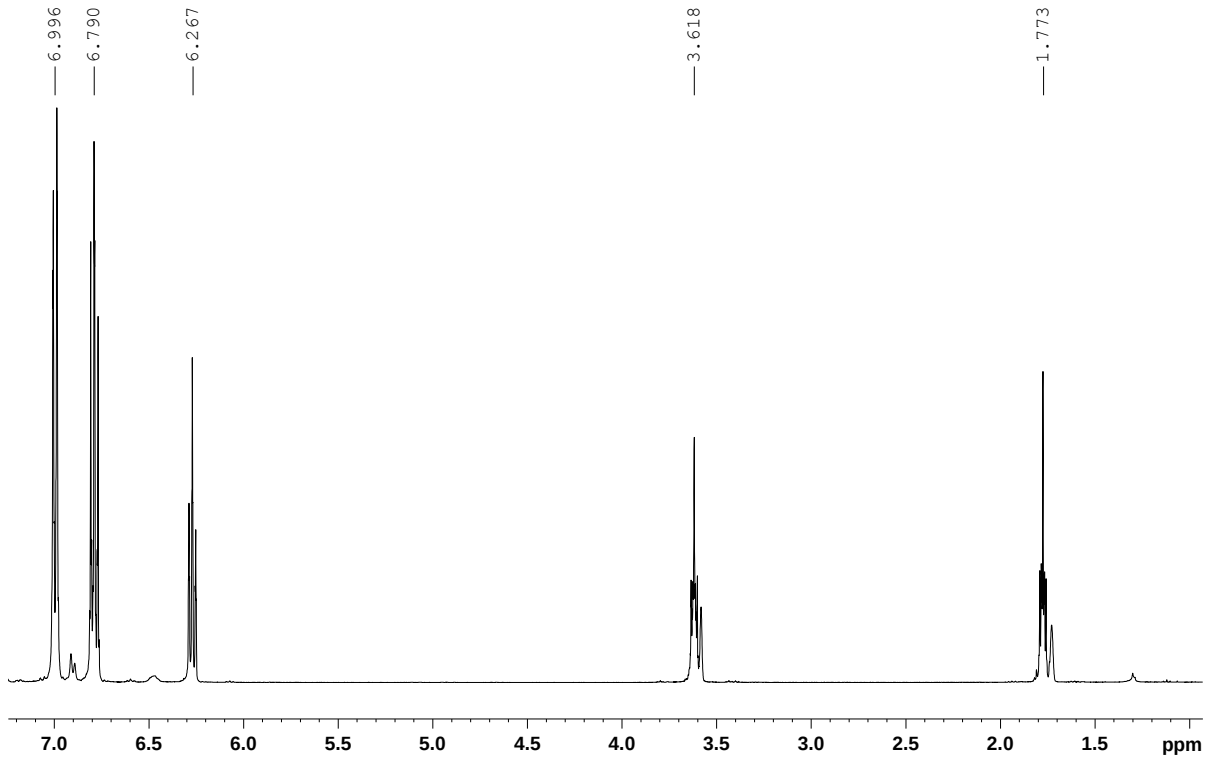


Figure S6. ^{1}H NMR spectrum of **3-(THF)$_2$** in D$_8$-THF solution.

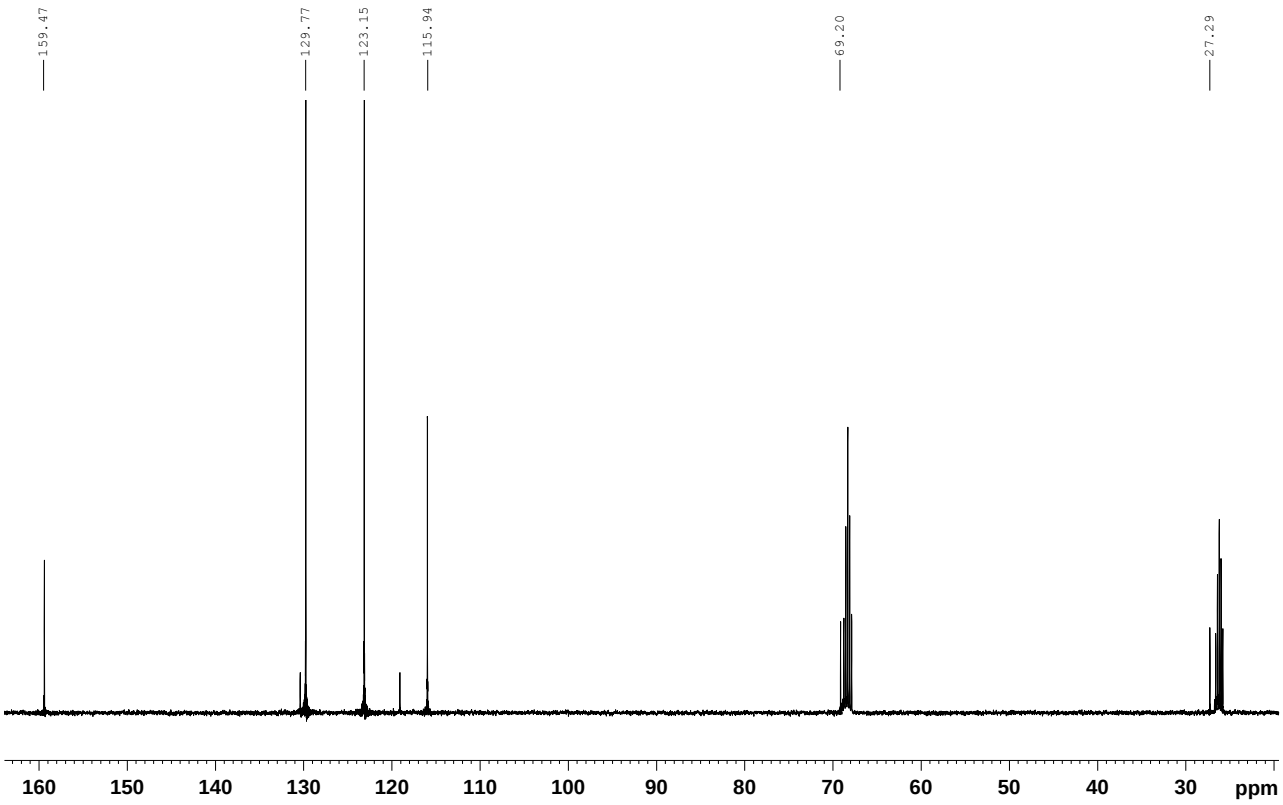


Figure S7. ^{13}C{^{1}H} NMR spectrum of **3-(THF)$_2$** in D$_8$-THF solution.

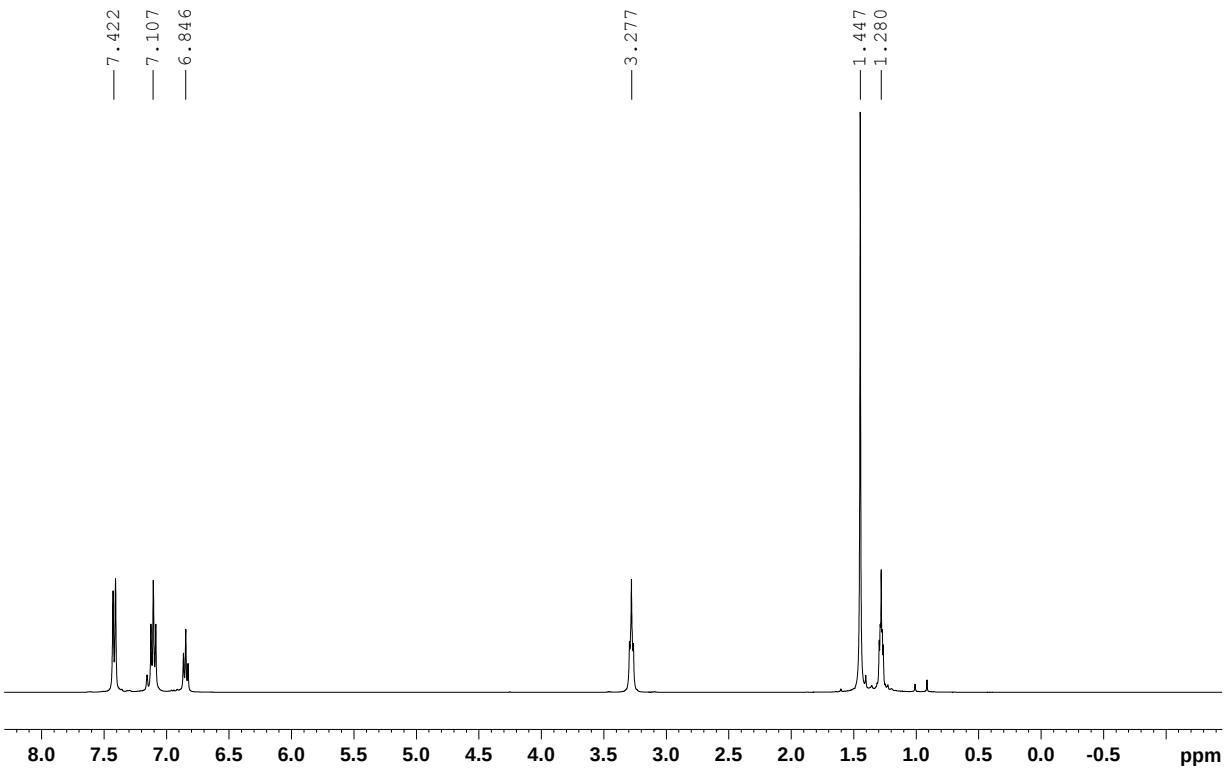


Figure S8. ^{1}H NMR spectrum of **4-(THF)$_3$** in C_6D_6 solution.

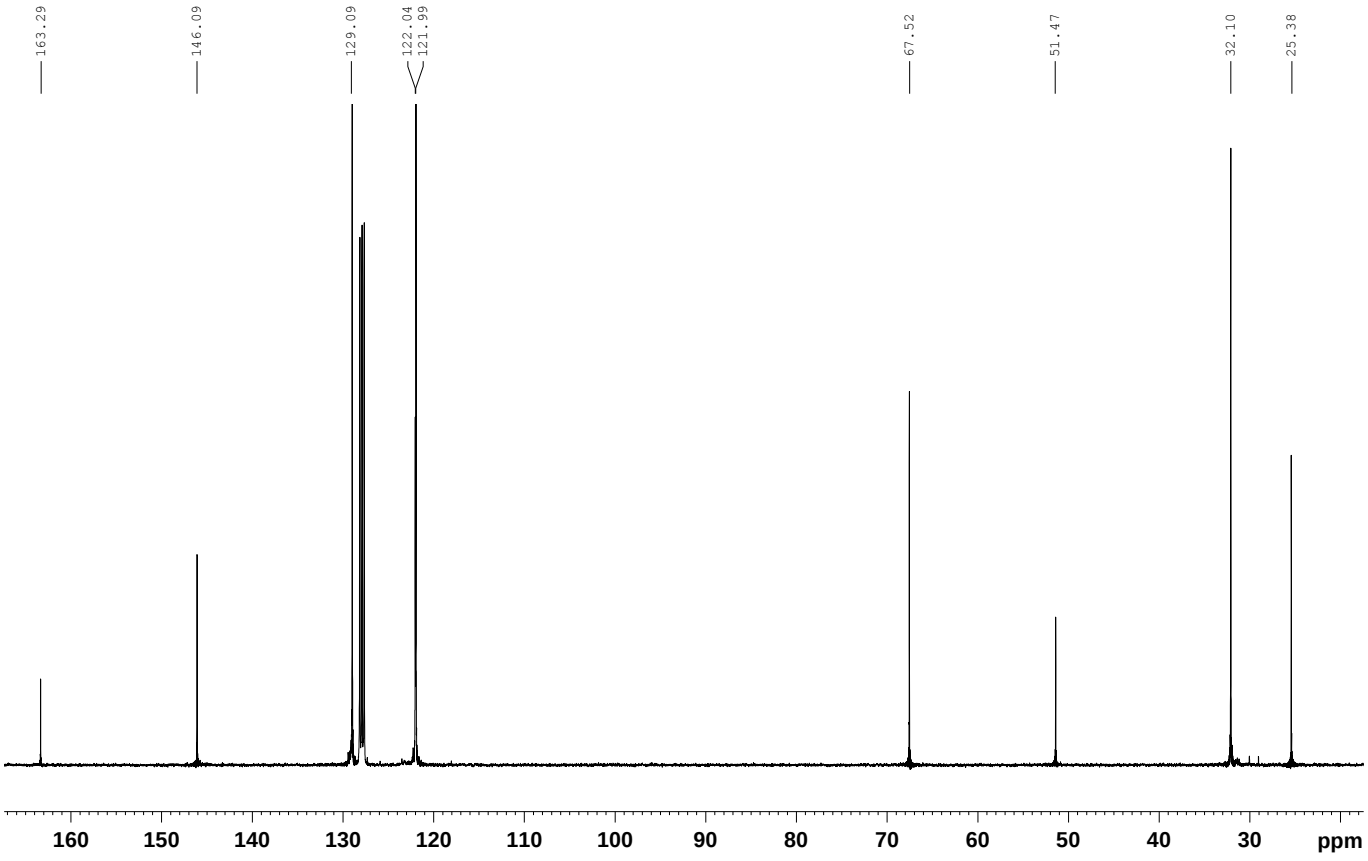


Figure S9. ^{13}C{^{1}H} NMR spectrum of **4-(THF)$_3$** in C_6D_6 solution.