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Highly efficient cyclotrimerization of isocyanates by N-Heterocyclic Olefins under bulk condition

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Contents

1. Materials, reagents, and methods.

All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, a high-vacuum line, or an argon-filled glovebox. Toluene and benzene were refluxed over sodium/potassium alloy, followed by distillation under nitrogen atmosphere; hexane, flurobenzene and dichloromethane were refluxed over CaH_2, followed by distillation under nitrogen atmosphere. Benzene-d_6 was dried over molecular sieves 4 Å, DMF was dried by CaH_2, followed by reduce pressure distillation under nitrogen atmosphere. All solvents were stored over molecular sieves 4 Å. NMR spectra were recorded on a Bruker Avance II 500 (500 MHz, ^{1}H; 126 MHz, ^{13}C) instrument at RT. Chemical shifts for ^{1}H and ^{13}C spectra were referenced to internal solvent resonances and are reported as parts per million relatives to $SiMe_4$. Air sensitive NMR samples were conducted in Teflon-valve sealed J. Young-type NMR tubes.

Isocyanates, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), and 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) were purchased from Energy Chemical. Ammonium hydroxide, potassium bis(trimethylsilyl)amide (KHMDS, 1.0 M solution in THF) and benzil were purchased from Titan. Iodomethane, isobutyraldehyde were purchased from Energy Chemical. Potassium hydride (30 wt. % dispersion in mineral oil) was purchased from Alfa Aesar. All Chemicals were used as received. **NHO1-3** were synthesized according to literatures.[1-3]

General procedure for cyclotrimerization in toluene: Under an argon atmosphere, 1.0 mmol PhNCO was added to an oven dried round bottom flask containing NHO solution in toluene and equipped with a magnetic stir bar. The reaction was stirred at room temperature (RT) up to quantitative precipitate was observed. The resulting precipitate was filtered, washed with hexane, and dried *in vacuo* to afford the isocyanurate as a white solid. Spectrums of products were compared to reported data.[4-11]

General procedure for the cyclotrimerization of isocyanates under solvent-free condition: Under an argon atmosphere, 10.0 mmol PhNCO was added to an oven dried round bottom flask containing **NHO3** solution in dry toluene (100 μL) and a magnetic stir bar. The reaction was stirred at RT until the solution was solidified. The resulting products was dried *in vacuo* to afford the isocyanurate as a white solid.

General procedure for cyclotrimerization of diisocyanates in DMF: Under an argon atmosphere, 4.0 mmol diisocyanate was added to an oven dried round bottom flask containing 19 mL dry DMF and equipped with a magnetic stir bar. After 10 minutes, **NHO3** solution in DMF (1.0 mL) was added to above-mentioned round bottom flask. The reaction was stirred at RT until a gel is formed. The resulting products are purged with methanol und subsequently washed with Ethanol, THF and chloroform for one day each, followed by a treatment with ethanol for 3 days, where the solvent was replaced every day.

X-ray Crystallographic Analysis of INT_{39}: Single crystals were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at 120 °C/10−6 Torr for 24h) after decanting the mother liquor. A crystal was then mounted on a thin glass fiber and transferred into the cold nitrogen stream of a Bruker APEX-II CCD diffractometer. The structures were solved by direct methods and refined using the Bruker SHELXTL program library by full-matrix least-squares on F2 for all reflections (SHELXTL, Version 6.12; Bruker Analytical X-ray Solutions: Madison, WI, 2001).

2. Synthesis and characterization of intermediates

2.1 Synthesis and characterization of 2-(1,3-dimethyl-1,3-dihydro-2*H*-benzoimidazol-2-ylidene)-*N*^{1},*N*^{3}-di-*m*-tolylmalonamide (INT_{13}): Under an argon atmosphere, 1.0 mmol isocyanates **3** was added to an oven dried round bottom flask containing **NHO1** solution in dry toluene (0.5 mmol, 5 mL) at -36 °C (in the freezer of glovebox). After 5 minutes, the resulting precipitate was filtrated and washed with hexane, then dried *in vacuo* to afford **INT_{13}** as a white solid. ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.61 (s, 2H, CON*H*), 7.13 – 7.04 (m, 6H, Ar-*H*), 6.83 (dd, *J* = 6.1, 3.1 Hz, 2H, Ar-*H*), 6.70 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 6.48 (dd, *J* = 6.0, 3.2 Hz, 2H, Ar-*H*), 3.08 (s, 6H, N*Me*), 2.13 (s, 6H, Ar-*Me*). ^{13}C NMR (126 MHz, C_6D_6) δ 151.3, 138.1, 130.0, 129.4, 128.6, 128.5, 128.0, 127.9, 127.9, 127.7, 127.7, 127.5, 127.5, 127.2, 70.9, 34.2, 21.3.

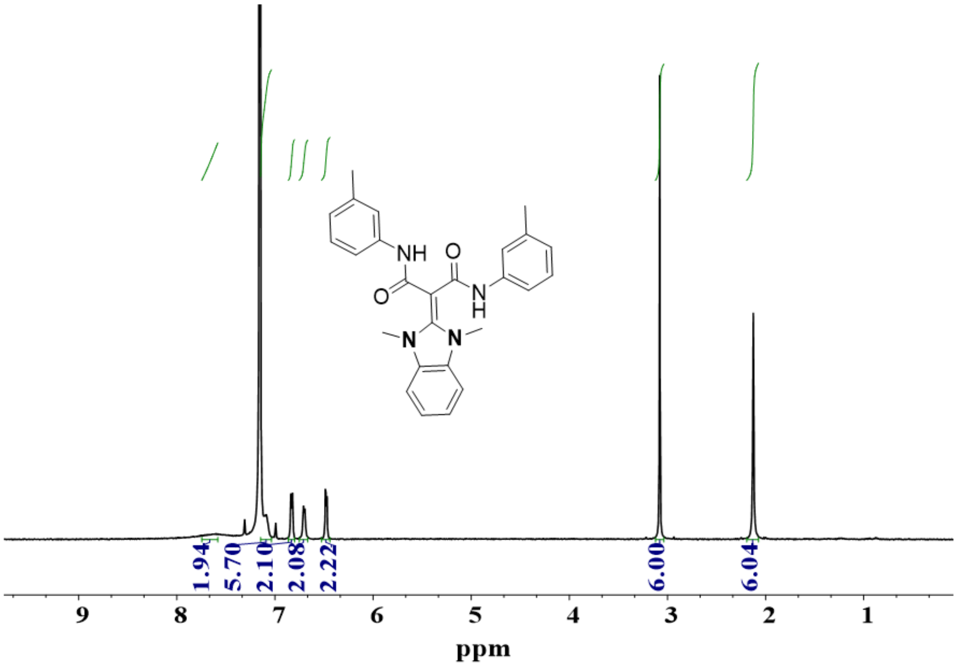


Fig S1. ^{1}H NMR spectrum of **INT$_{13}$** (500 MHz, Benzene-d_6).

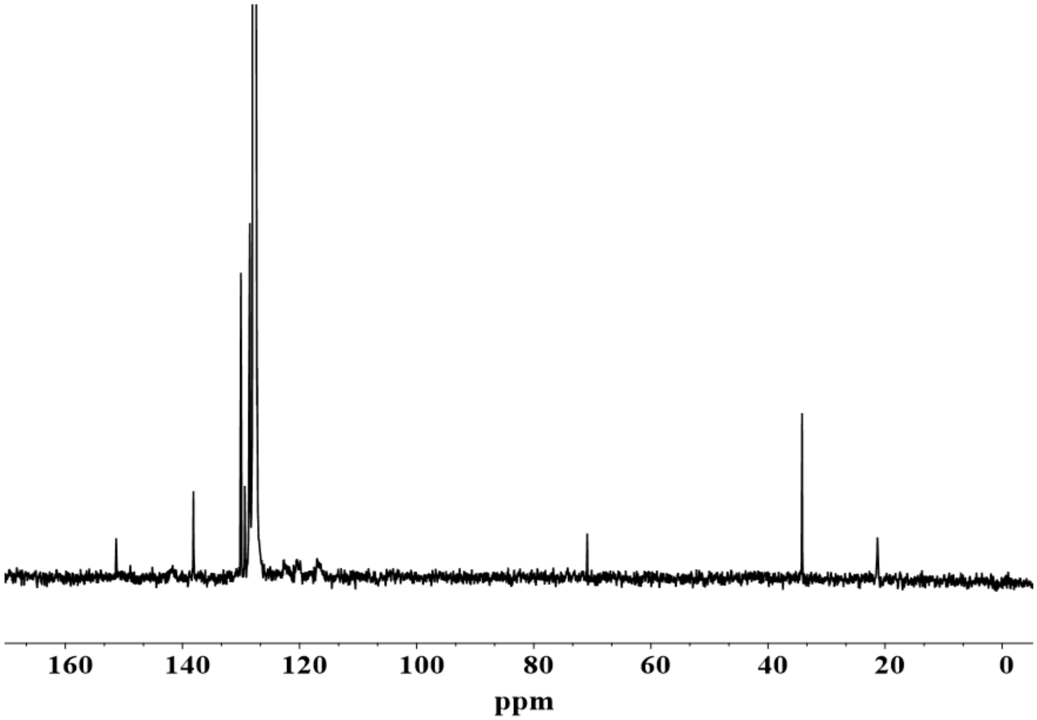
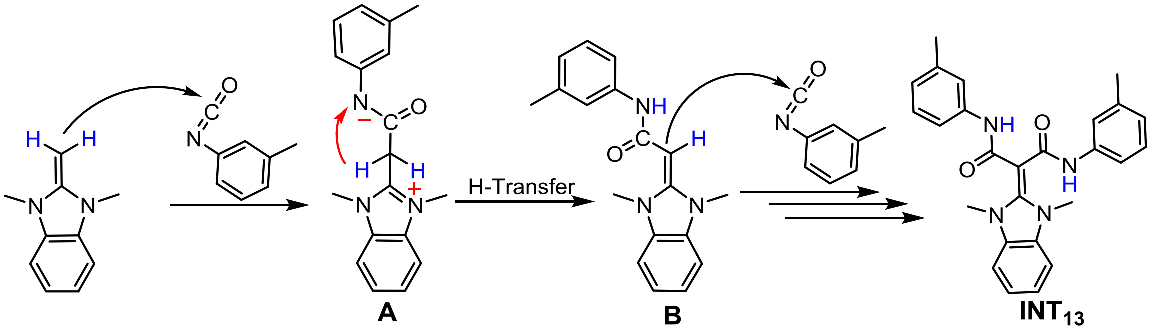


Fig S2. ^{13}C NMR spectrum of **INT$_{13}$** (126 MHz, Benzene-d_6).



Scheme S1. Pathway for the reaction of isocyanate **3** with **NHO1**.

2.2 Synthesis and characterization of 2-(1,3-dimethyl-4,5-diphenyl-1,3-dihydro-2*H*-imidazol-2-ylidene)-*N*-(*m*-tolyl)propanamide (INT$_{23}$). Under an argon atmosphere, 1.0 mmol **3** was added to an oven dried round bottom flask containing **NHO2** solution in dry toluene (1.0 mmol, 5 mL) at -36 °C (in the freezer of glovebox). The reaction was kept at -36 °C for 2 h. Then 3 mL dry hexane was added, the resulting precipitate was filtrated and dried *in vacuo* to afford the **INT$_{23}$** as yellow solid. ^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.95 (s, 1H, CON*H*), 7.89 (d, *J* = 8.1 Hz, 1H, Ar-*H*), 7.31 (s, 1H, Ar-*H*), 7.27 (t, *J* = 7.8 Hz, 1H, Ar-*H*), 6.96 – 6.90 (m, 9H, Ar-*H*), 6.84 – 6.78 (m, 2H, Ar-*H*), 2.97 (s, 6H, N*Me*), 2.28 (s, 3H, C*Me*), 2.00 (s, 3H, *Me*). ^{13}C NMR (126 MHz, C_6D_6) δ 164.8, 158.0, 142.7, 138.0, 129.4, 129.2, 129.0, 128.6, 128.5, 128.2, 127.9, 127.7, 127.5, 121.3, 119.2, 115.8, 60.2, 36.0, 21.5, 16.1. (These spectrums contains a small amount of hexane and toluene.)

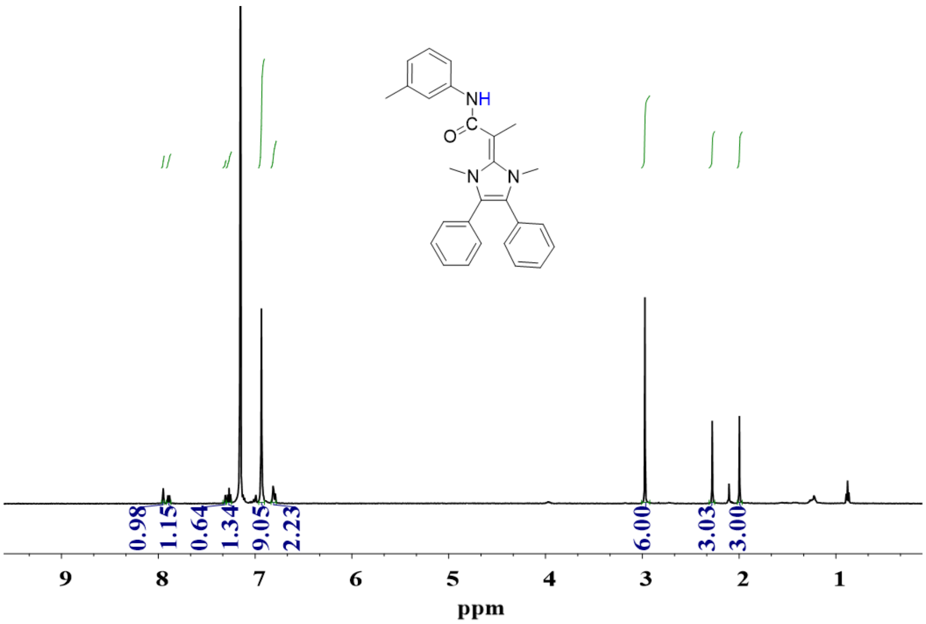


Fig S3. ^{1}H NMR spectrum of **INT$_{23}$** (500 MHz, Benzene-*d*$_6$).

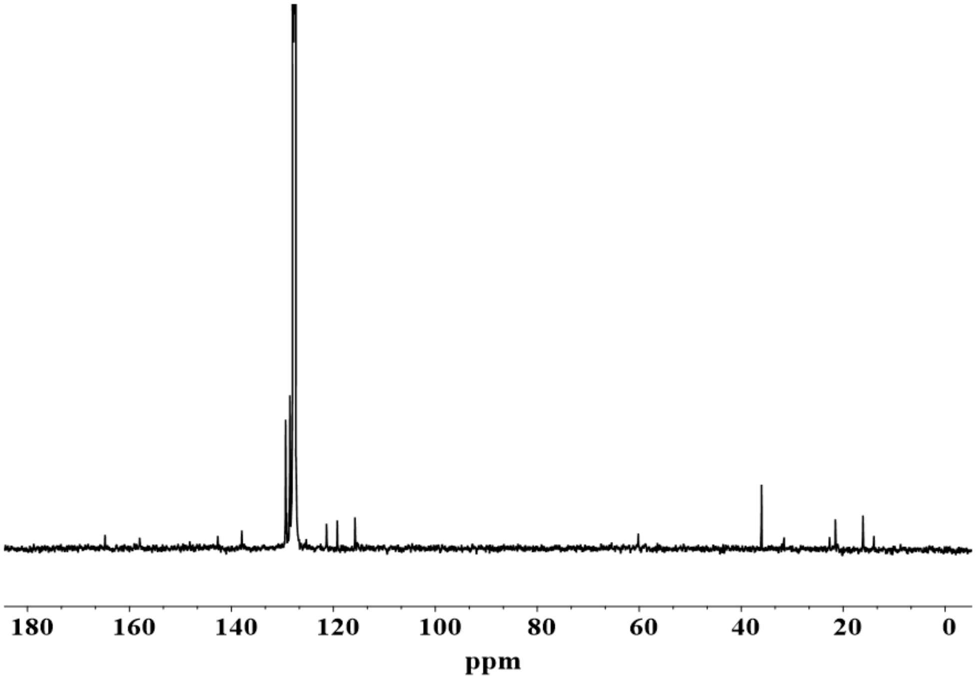
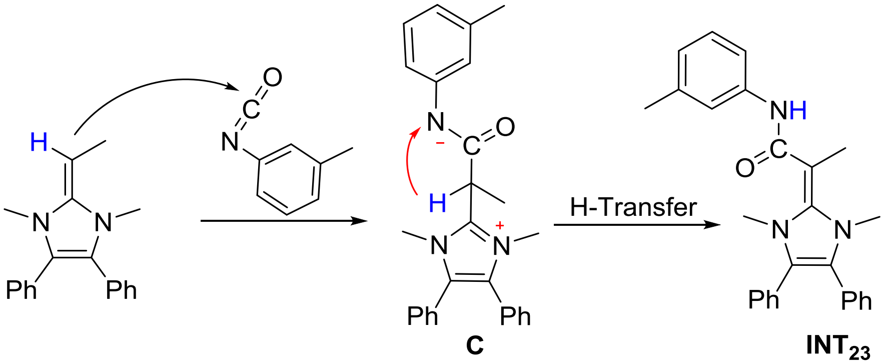


Fig S4. ^{13}C NMR spectrum of **INT$_{23}$** (126 MHz, Benzene-d_6).



Scheme S2. Pathway for the reaction of isocyanate **3** with **NHO2**.

2.3 Synthesis and characterization of (2-(1,3-dimethyl-4,5-diphenyl-1*H*-imidazol-3-ium-2-yl)-2-methylpropanoyl)(4-fluorophenyl)ami-de (INT$_{39}$). Under an argon atmosphere, 1.0 mmol **9** was added to an oven dried round bottom flask containing **NHO3** solution in dry toluene (1.0 mmol, 5 mL) at -36 °C (in the freezer of glovebox).

The reaction was kept at -36 °C for 12 h. Then 2 mL dry hexane was added, the resulting precipitate was filtrated and dried *in vacuo* to afford the **INT39** as off-white solid. And the single crystals were obtained by diffusion of hexane into a fluorobenzene solution. ^{1}H NMR (500 MHz, Benzene-d_6) δ 8.40 – 8.32 (m, 2H, Ar-*H*), 7.08 – 7.02 (m, 3H, *Ph*), 6.86 – 6.81 (m, 4H, *Ph*), 6.75 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 6.63 (d, *J* = 7.0 Hz, 3H, *Ph*), 3.14 (s, 6H, N*Me*), 1.86 (s, 6H, *Me*). ^{13}C NMR (126 MHz, Benzene-d_6) δ 171.77, 157.87, 154.91, 151.02, 148.60, 131.40, 131.27, 131.00 – 130.53 (m), 130.42, 129.33, 128.97, 128.55, 126.06, 125.21 – 124.95 (m), 115.85 (d, *J* = 23.0 Hz), 114.12 (d, *J* = 20.4 Hz), 49.10, 34.69, 27.06. (These spectrums contains a small amount of fluorobenzene.)

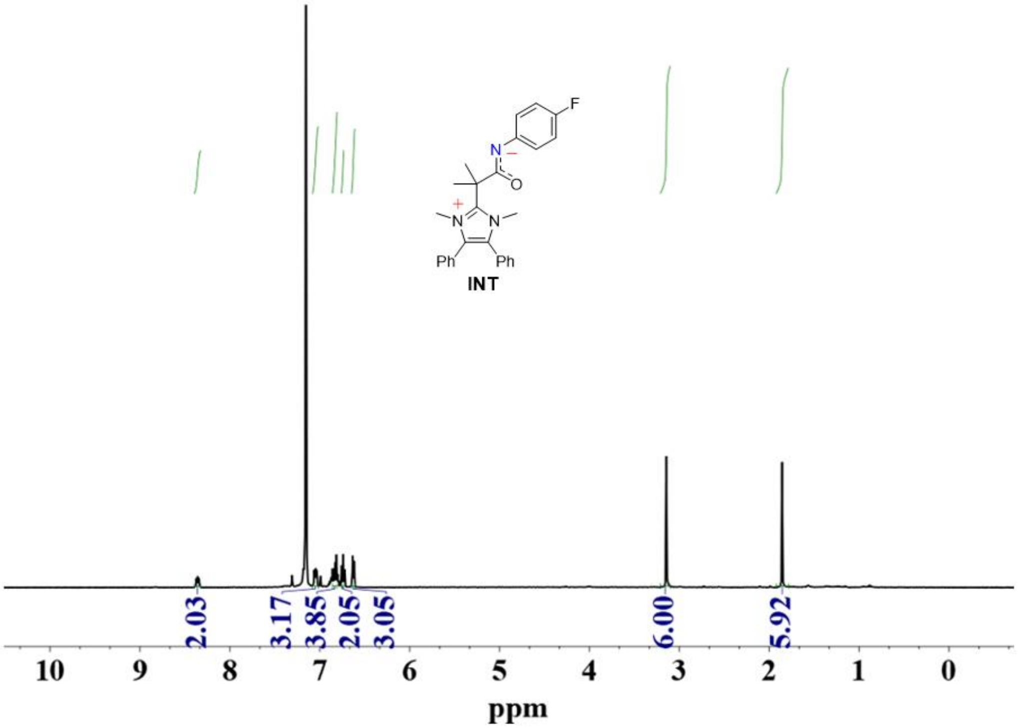


Fig S5. ^{1}H NMR spectrum of **INT39** (500 MHz, Benzene-d_6).

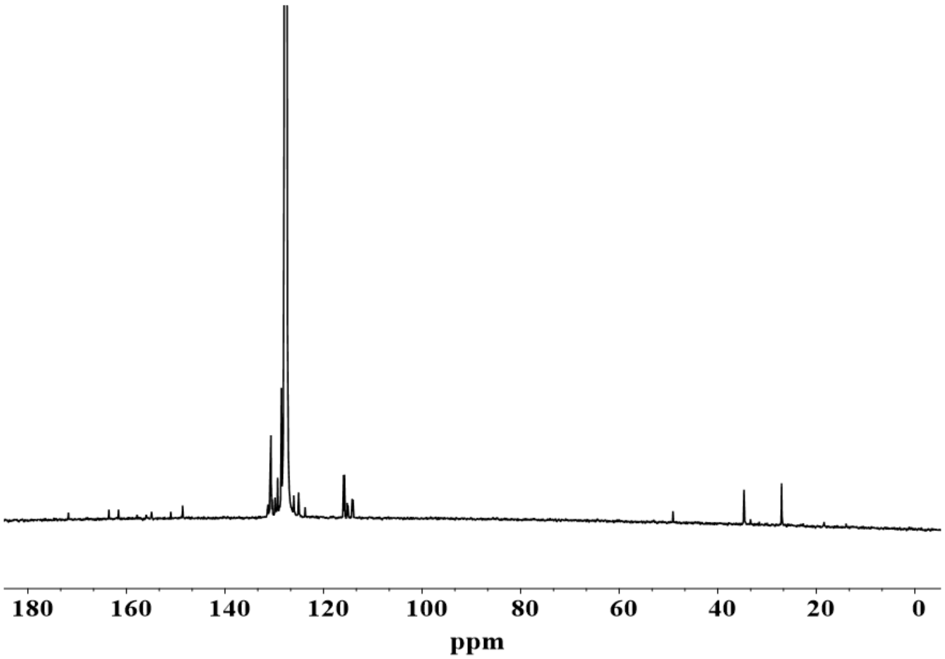


Fig S6. ^{13}C NMR spectrum of **INT$_{39}$** (126 MHz, Benzene-d_6).

3. In-situ NMR reactions.

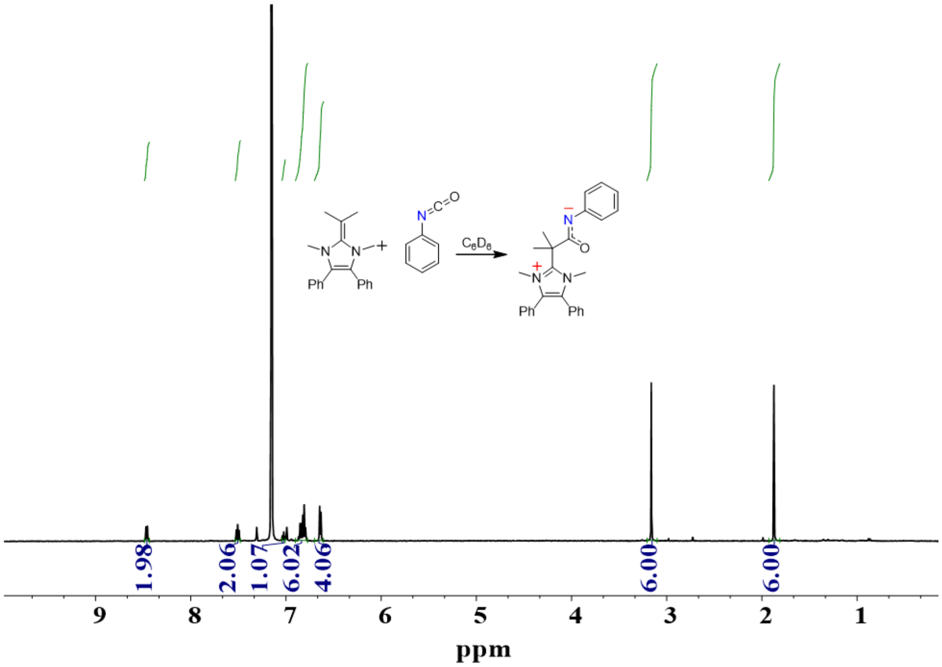


Fig S7. ^{1}H NMR spectrum of reaction of **1**: **NHO3 =** 1:1 (500 MHz, Benzene-d_6).

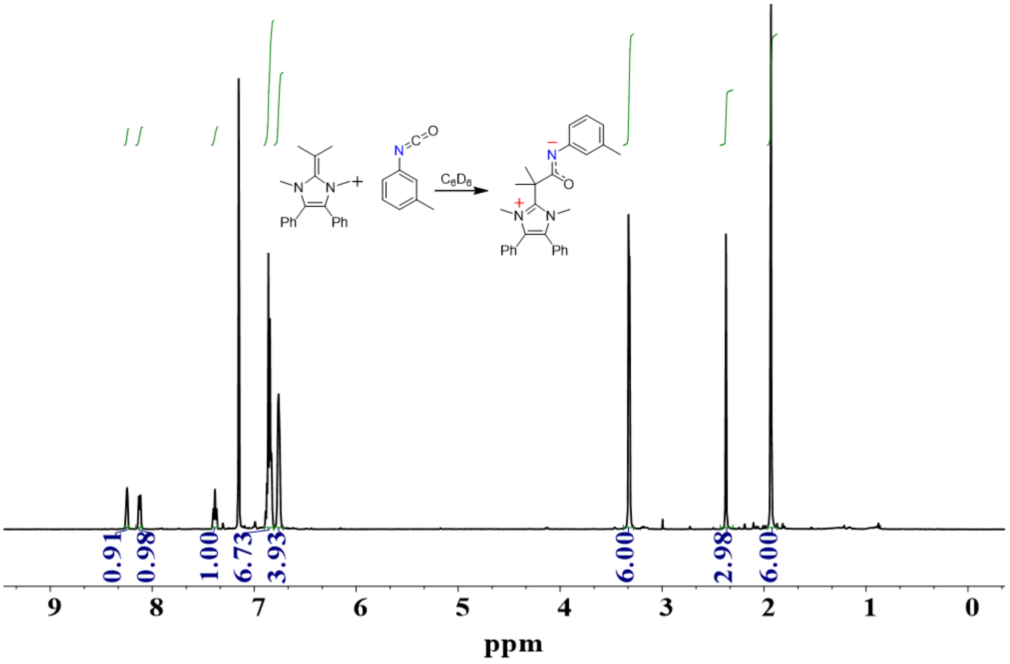


Fig S8. ^{1}H NMR spectrum of reaction of **3**: **NHO3 =** 1:1 (500 MHz, Benzene-*d*$_6$).

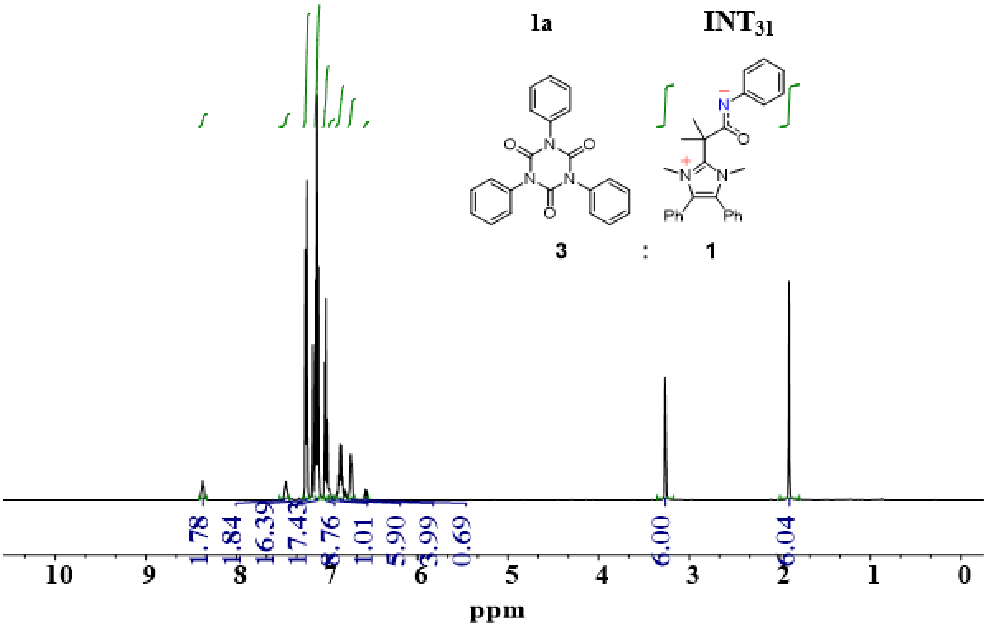


Fig S9. ^{1}H NMR spectrum of reaction of **1**: **NHO3 =** 10:1 (500 MHz, Benzene-*d*$_6$).

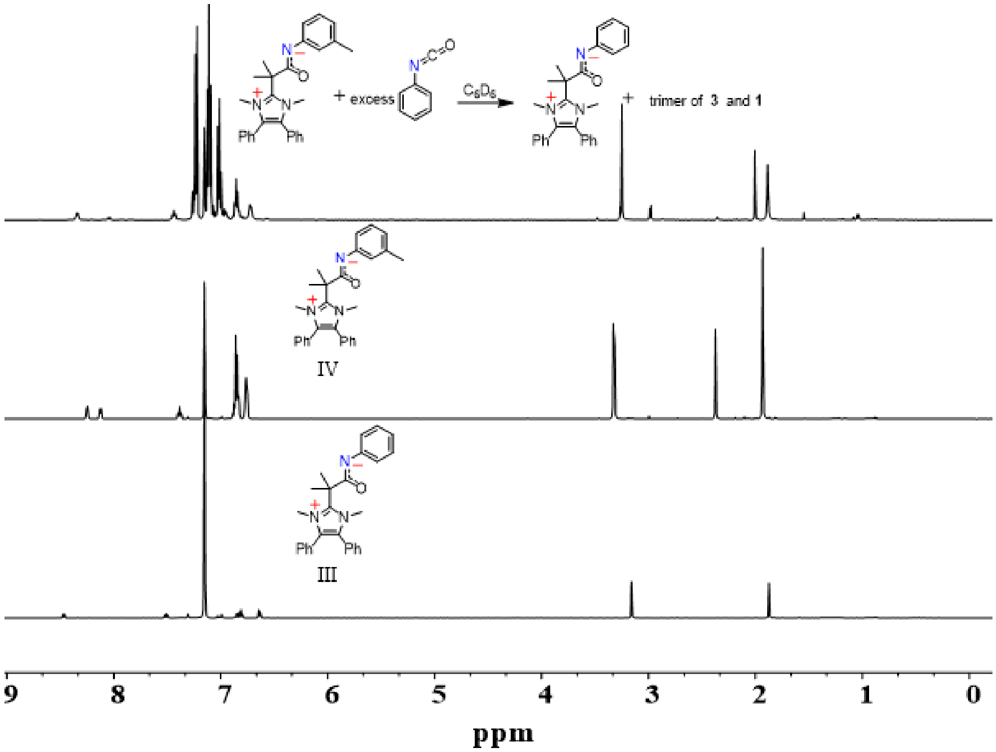


Fig S10. ^{1}H NMR spectrum of reaction of **INT**$_{33}$: **1 =** 1:10 (500 MHz, Benzene-d_6).

4. Selected Data for the cyclotrimerization of isocyanates

Table S1. NHO-catalyzed cyclotrimerization of isocyanates.[a]

Run	RNCO	NHO	RNCO:NHO	Time/min	Product.[b]	Yield. [c](%)
1	**1**	**NHO1**	100	1440	**1a**	0
2	**3**	**NHO1**	100	1440	**3a**	0
3	**1**	**NHO2**	100	3	**1a**	98
4	**3**	**NHO2**	100	3	**3a**	97
5	**5**	**NHO2**	100	5	**5a**	98

[a] Condition: carried out in toluene at RT; $[RNCO]_0 = 1.0$ M. [b] Cyclotrimer product. [c] Isolated yield.

Table S2. The cyclotrimerization of isocyanates catalyzed by NHOs in toluene.[a]

Run	RNCO	RNCO:**NHO3**	Time/min	Product [b]	Yield.[e](%)
1	**1**	100	<1	**1a**	97
2	**1**	2500	<1	**1a**	98
3	**2**	100	30	**2a**	90
4	**3**	100	<1	**3a**	95
5	**4**	100	30	**4a**	94
6	**5**	100	2	**5a**	97
7	**6**	100	3	**6a**	97
8	**7**	100	3	**7a**	96
9	**8**	100	3	**8a**	95
10	**9**	100	1440	**9a**	0
11	**10**	100	5	**10a**	95
12	**11**	100	48h	**11a**	92
13	**12**	100	96h	**12a**	90
14[c]	**1**	100	48h	**1a**	0
15[d]	**1**	100	3h	**1a**	80

[a] Condition: carried out in toluene at RT; $[RNCO]_0 = 1.0$ M. [b] Cyclotrimer product. [c] DBU was used. [d] MTBD was used as catalyst. [e] Isolated yield.

Table S3. The cyclotrimerization of isocyanates catalyzed by intermediates.[a]

Run	RNCO	Catalyst	RNCO:Cata	Product.[b]	Time/min	Yield.[c](%)
1	**1**	**INT$_{13}$**	100	**1a**	1440	0
2	**1**	**INT$_{23}$**	100	**1a**	3	98
3	**3**	**INT$_{23}$**	100	**3a**	5	98
4	**5**	**INT$_{23}$**	100	**5a**	5	97
5	**1**	**INT$_{39}$**	200	**1a**	2	95

[a] Condition: carried out in toluene at RT; $[RNCO]_0 = 1.0$ M. [b] Cyclotrimer product. [c] Isolated yield.

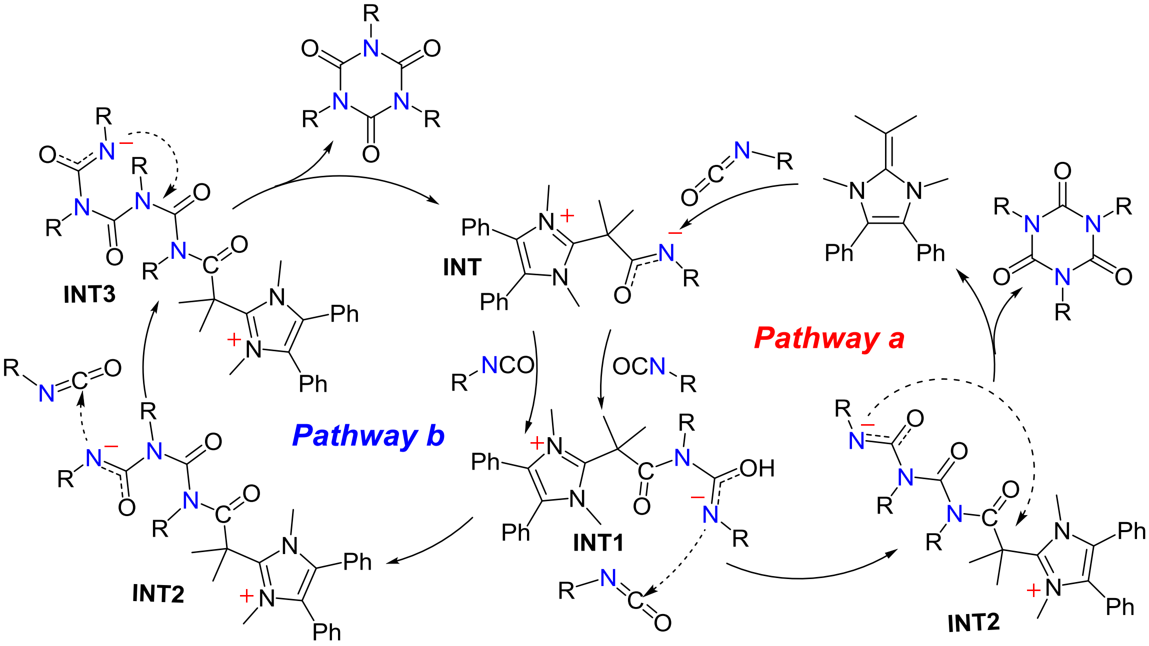
Table S4. The cyclotrimerization of diisocyanates catalyzed by NHO3.[a]

Run	RNCO	Solvent	RNCO:NHO	Time/min	Product	Yield.[b](%)

1	**15**	DMF	100	120	**P1**	90
2	**16**	DMF	100	2880	**P2**	79
3	**17**	DMF	100	120	**P3**	85

[a] Condition: carried out in DMF at RT; $[RNCO]_0 = 0.2$ M. [b] Isolated yield.

5. Two possible catalytic pathways.



Scheme S3. Proposed catalytic mechanism for cyclotrimerization of isocyanates catalyzed by **NHO3.**

6. The cyclotrimerization of diisocyanates.

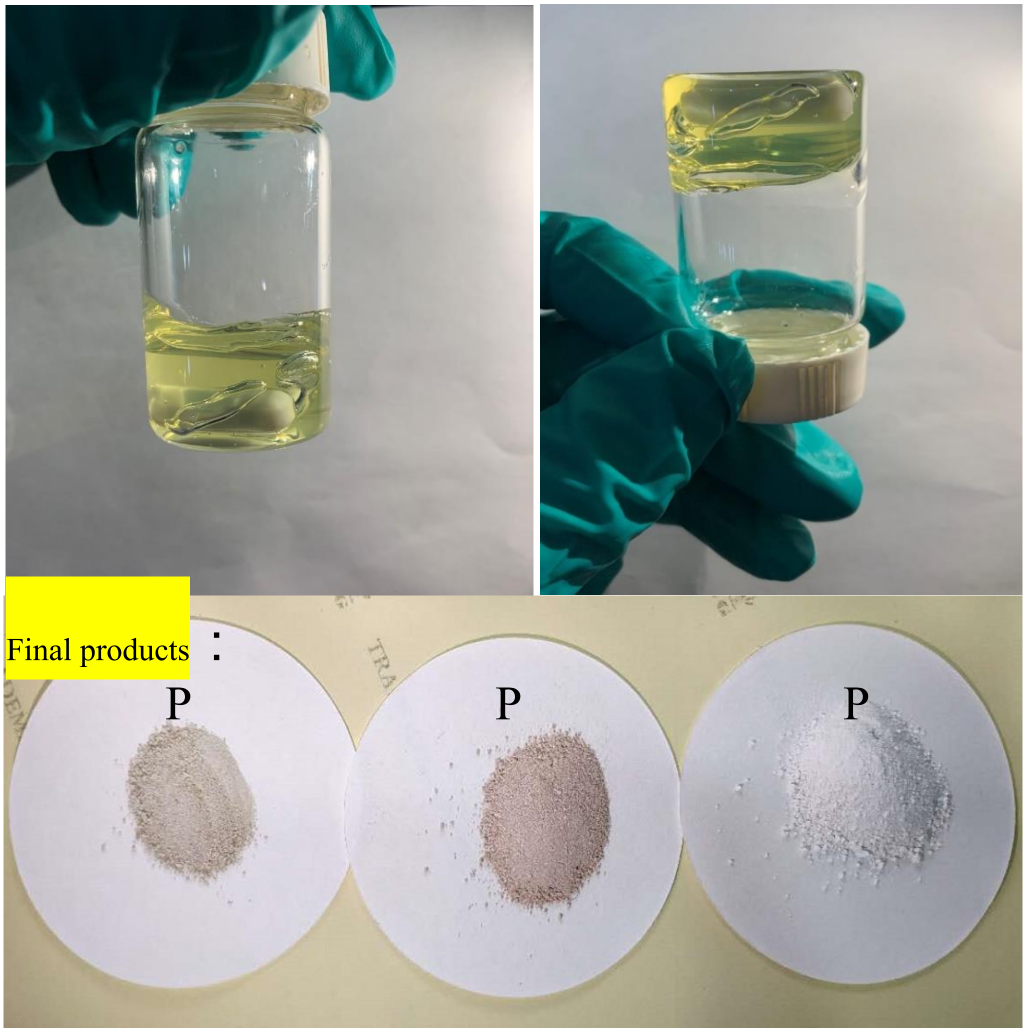
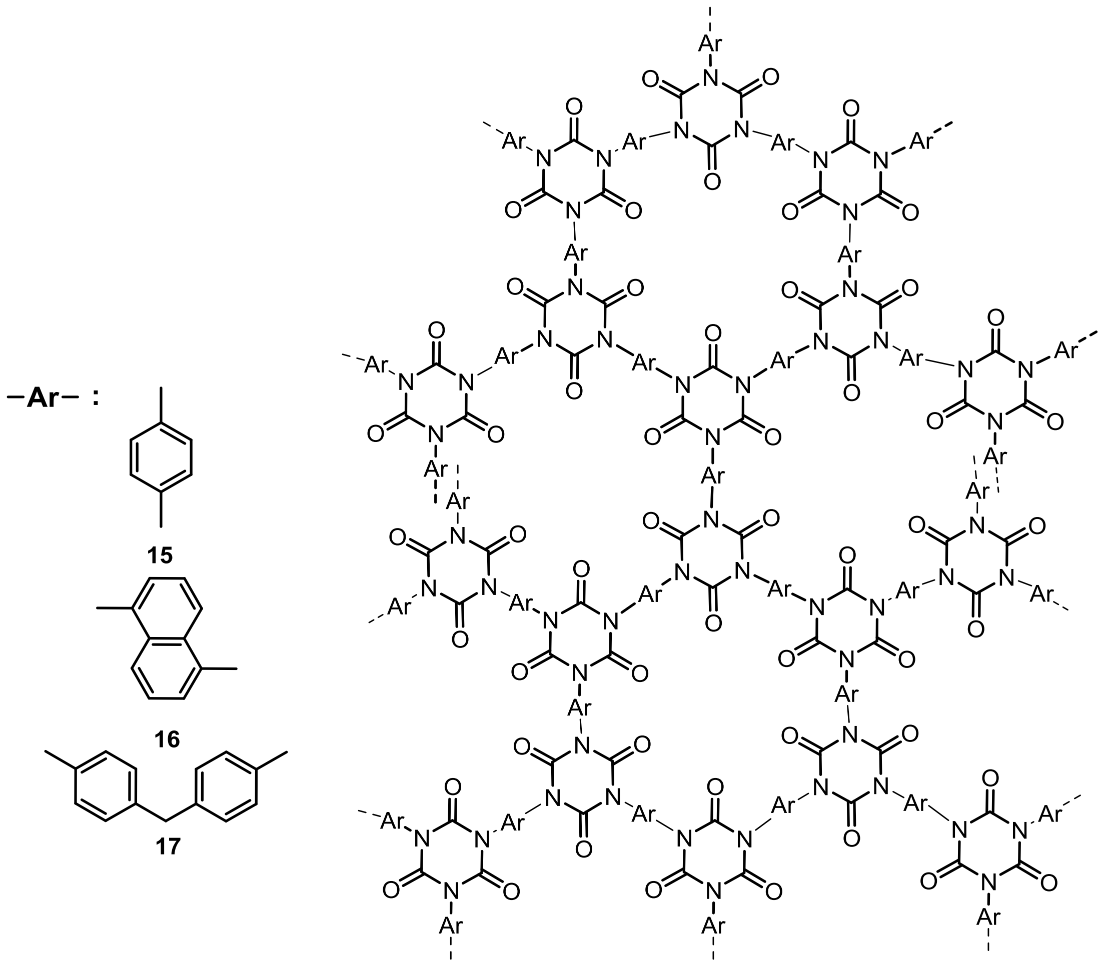


Fig S11. Reaction vials of cyclotrimerization of diisocyanates and final products.



Scheme S4. Structure of microporous polyisocyanurates.

7. ^{1}H NMR spectrum of cyclotrimerization products

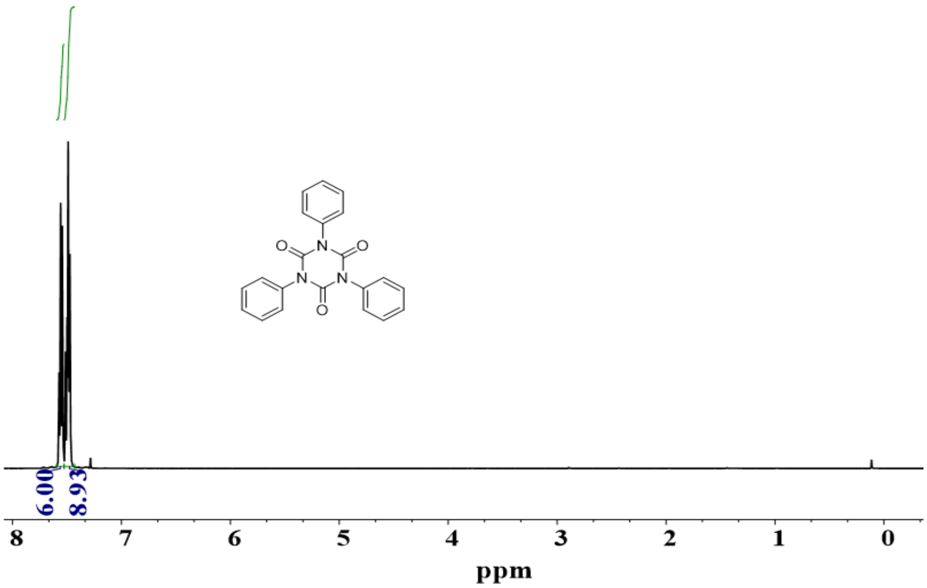


Fig S12. ^{1}H NMR spectrum of **1a** (500 MHz, chloroform-*d*).

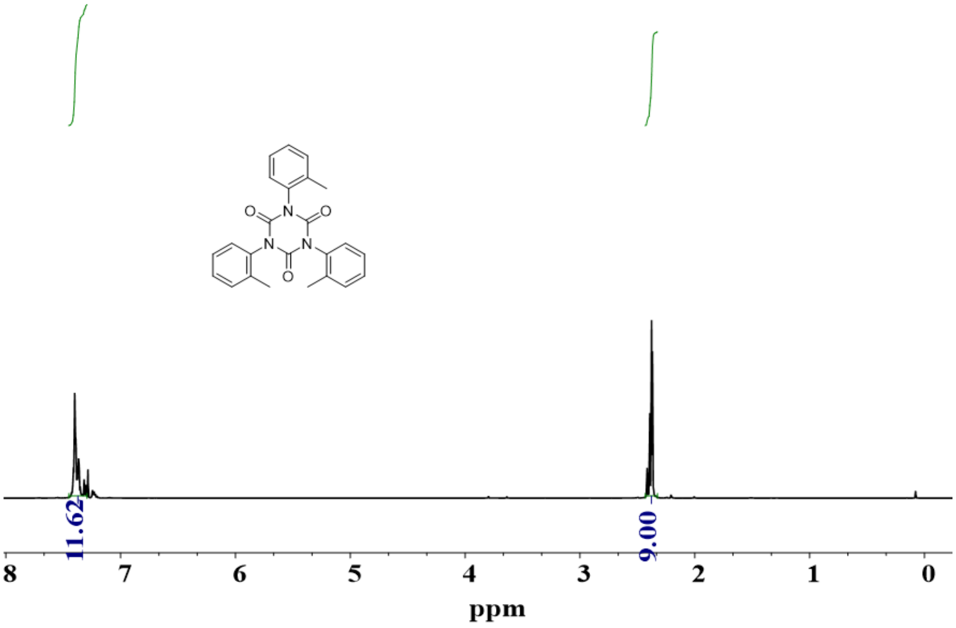


Fig S13. ^{1}H NMR spectrum of **2a** (500 MHz, chloroform-*d*).

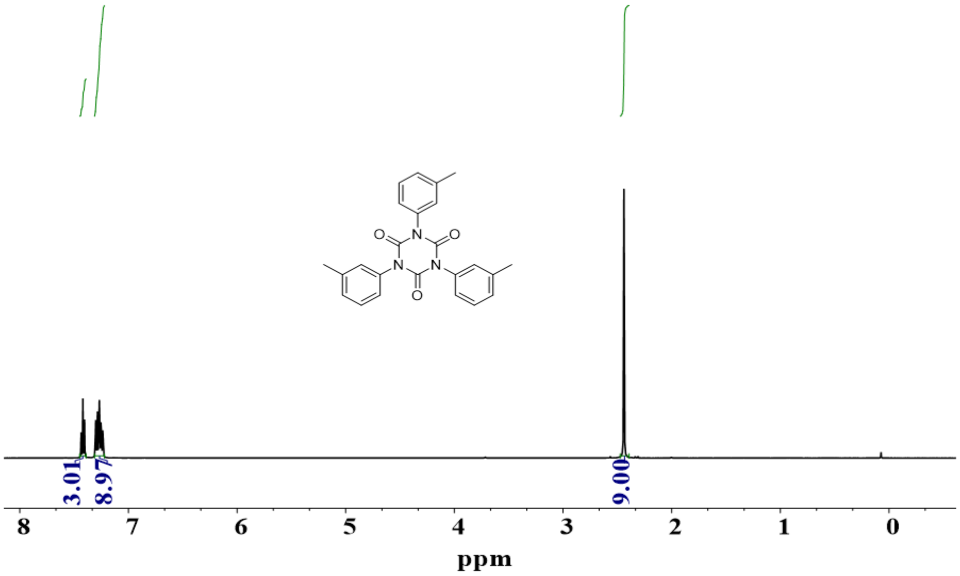


Fig S14. ^{1}H NMR spectrum of **3a** (500 MHz, chloroform-*d*).

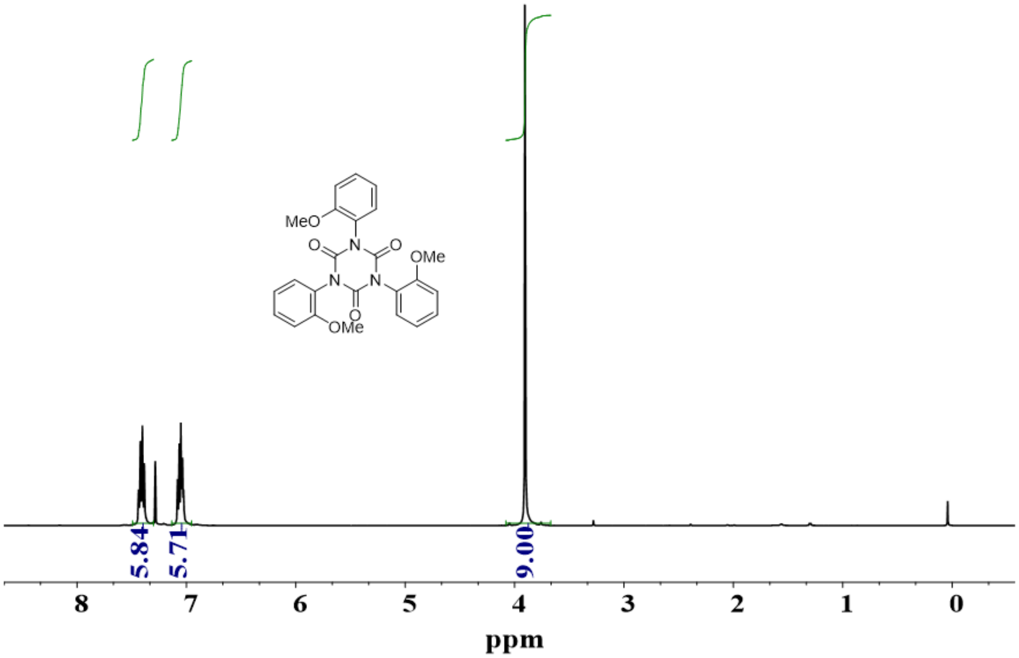


Fig S15. ^{1}H NMR spectrum of **4a** (500 MHz, chloroform-*d*).

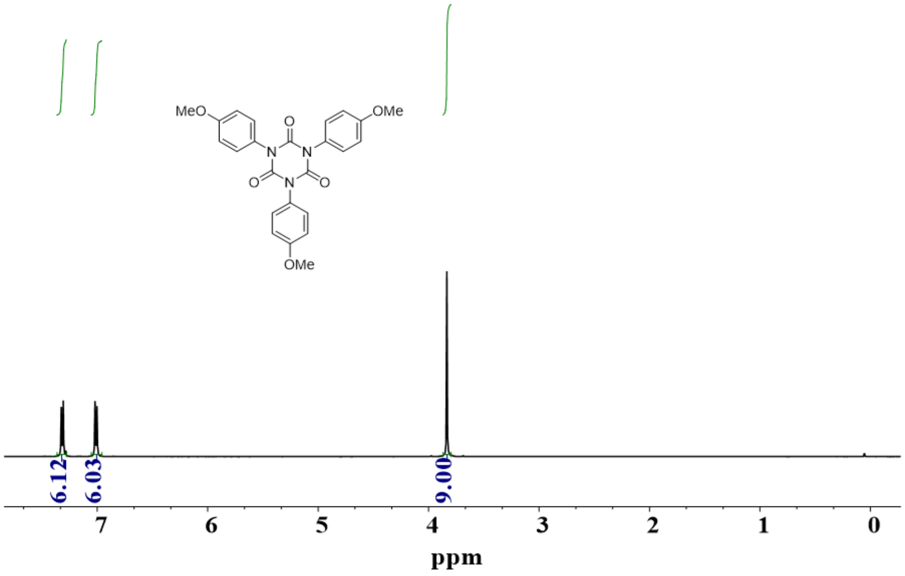


Fig S16. ^{1}H NMR spectrum of **5a** (500 MHz, chloroform-*d*).

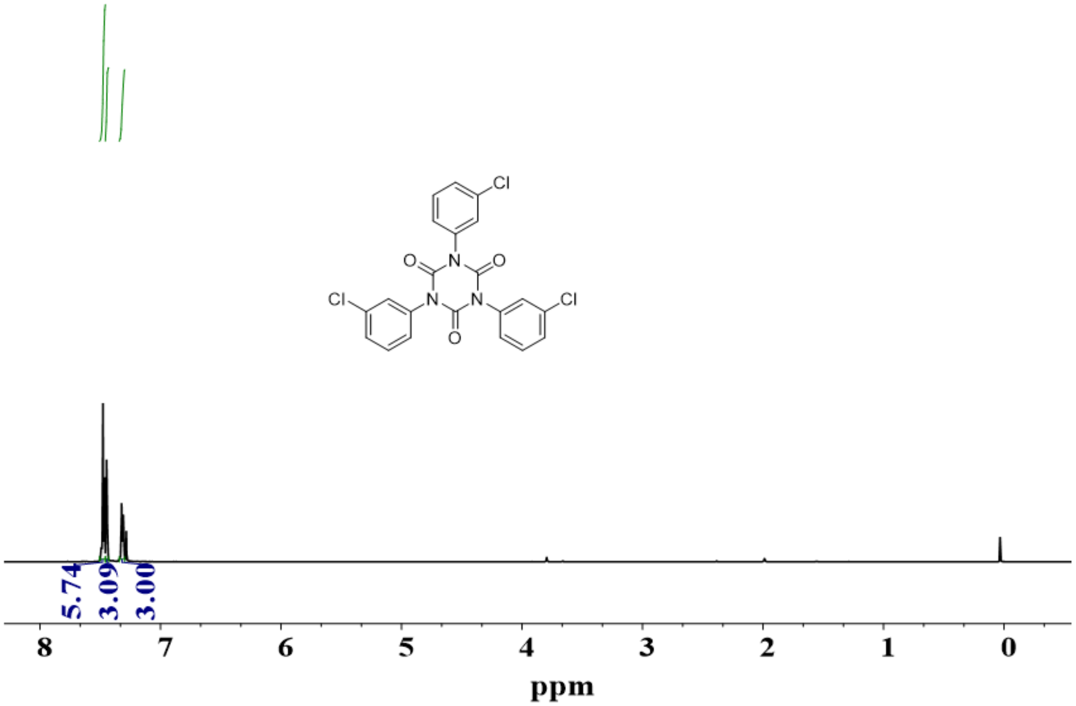


Fig S17. ^{1}H NMR spectrum of **6a** (500 MHz, chloroform-*d*).

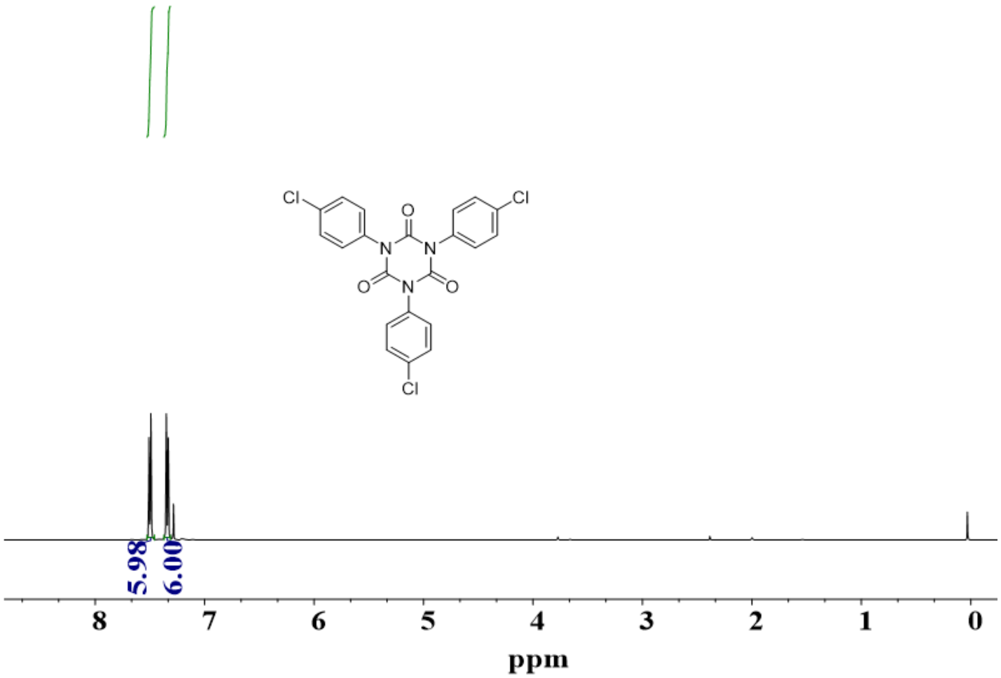


Fig S18. ^{1}H NMR spectrum of **7a** (500 MHz, chloroform-*d*).

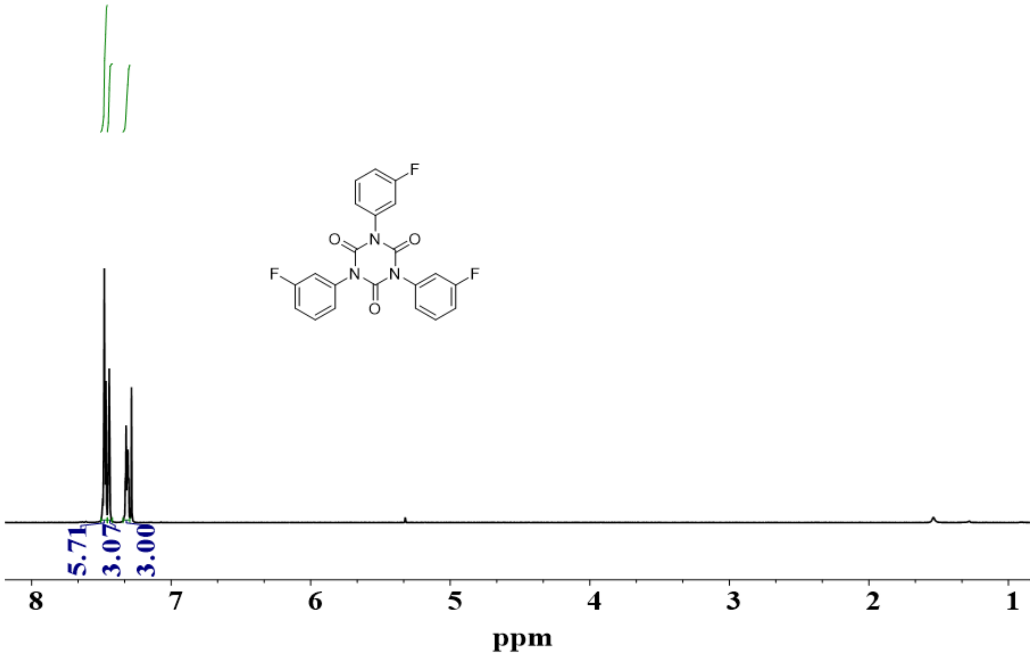


Fig S19. ^{1}H NMR spectrum of **8a** (500 MHz, chloroform-*d*).

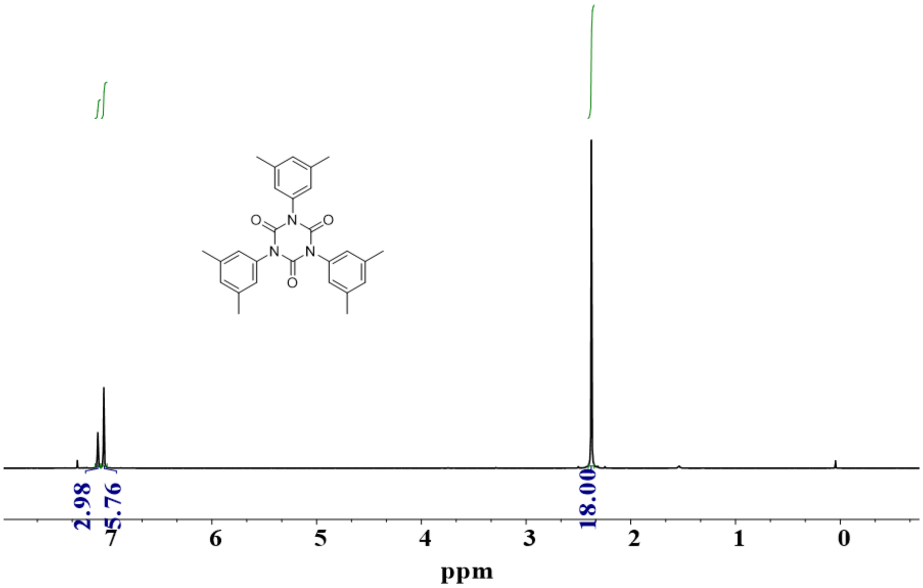


Fig S20. ^{1}H NMR spectrum of **10a** (500 MHz, chloroform-*d*).

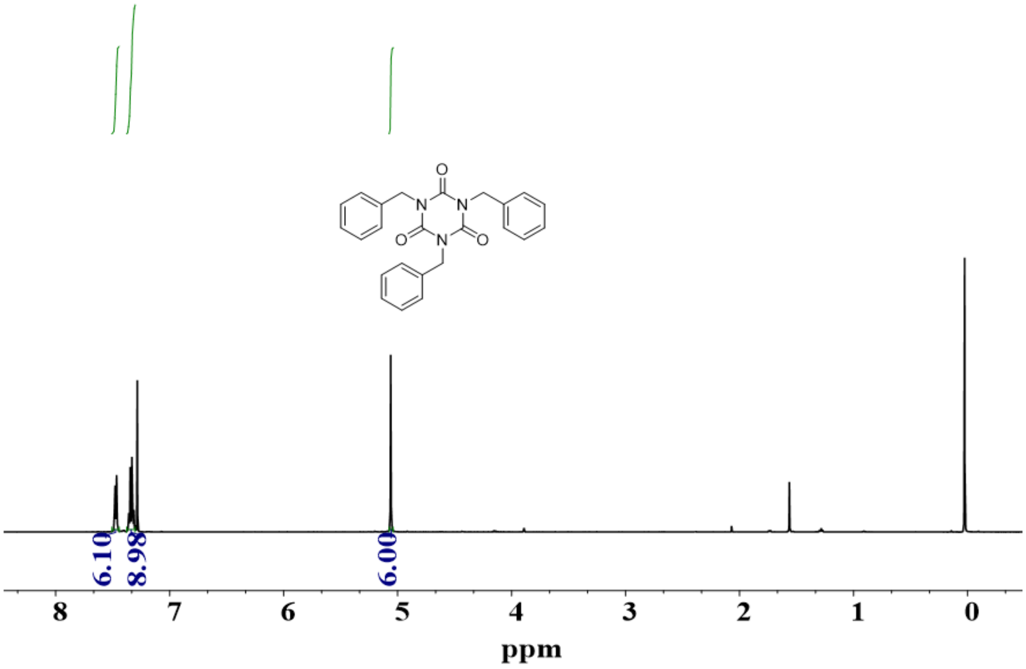


Fig S21. ^{1}H NMR spectrum of **11a** (500 MHz, chloroform-*d*).

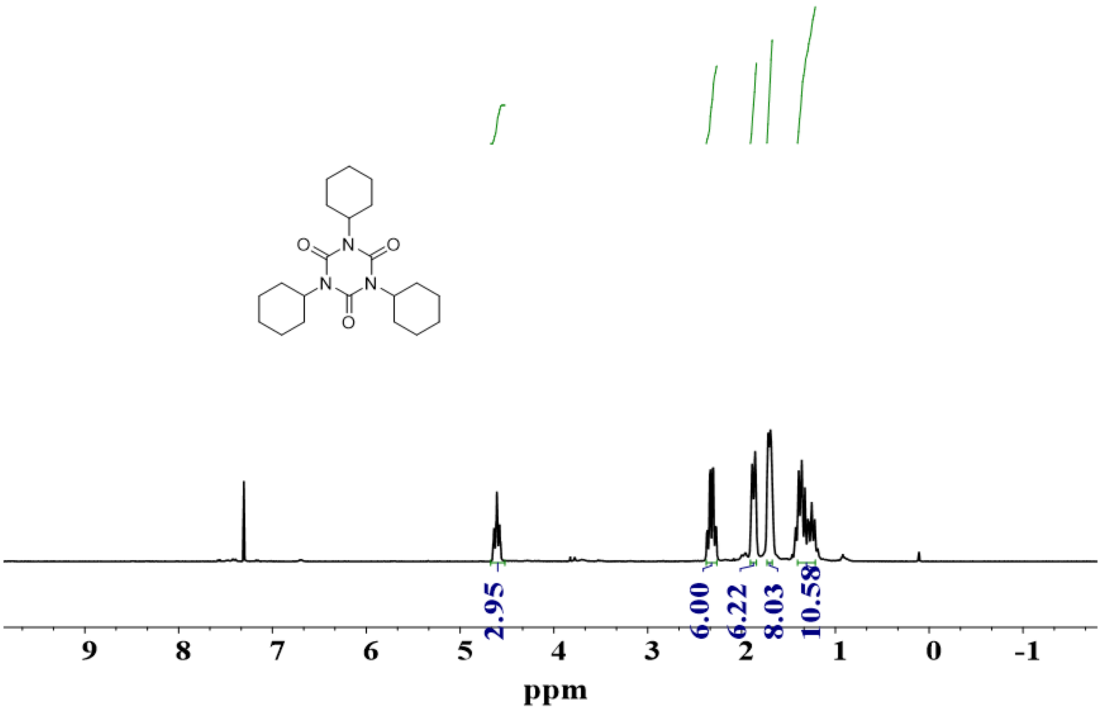


Fig S22. ^{1}H NMR spectrum of **12a** (500 MHz, chloroform-*d*).

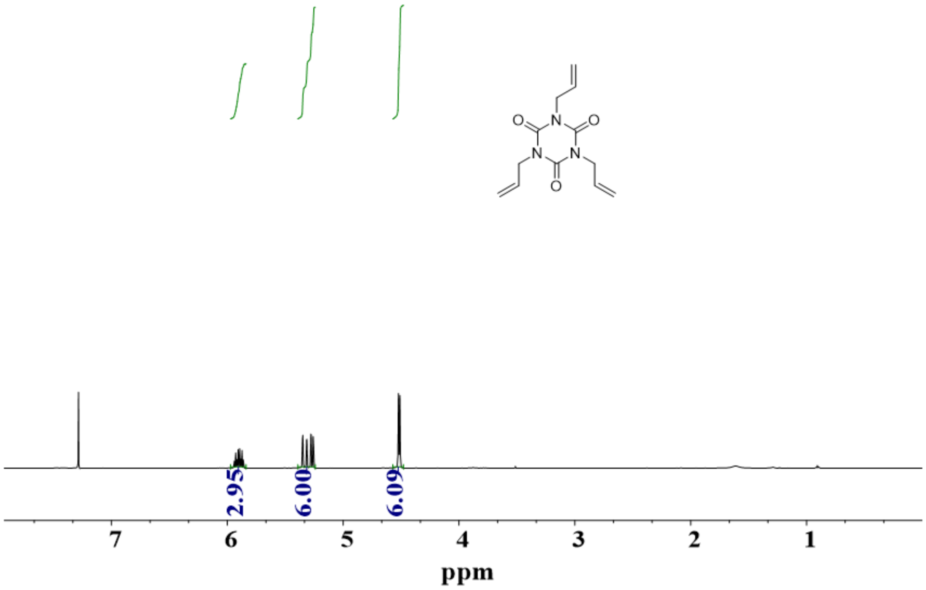


Fig S23. ^{1}H NMR spectrum of **13a** (500 MHz, chloroform-*d*).

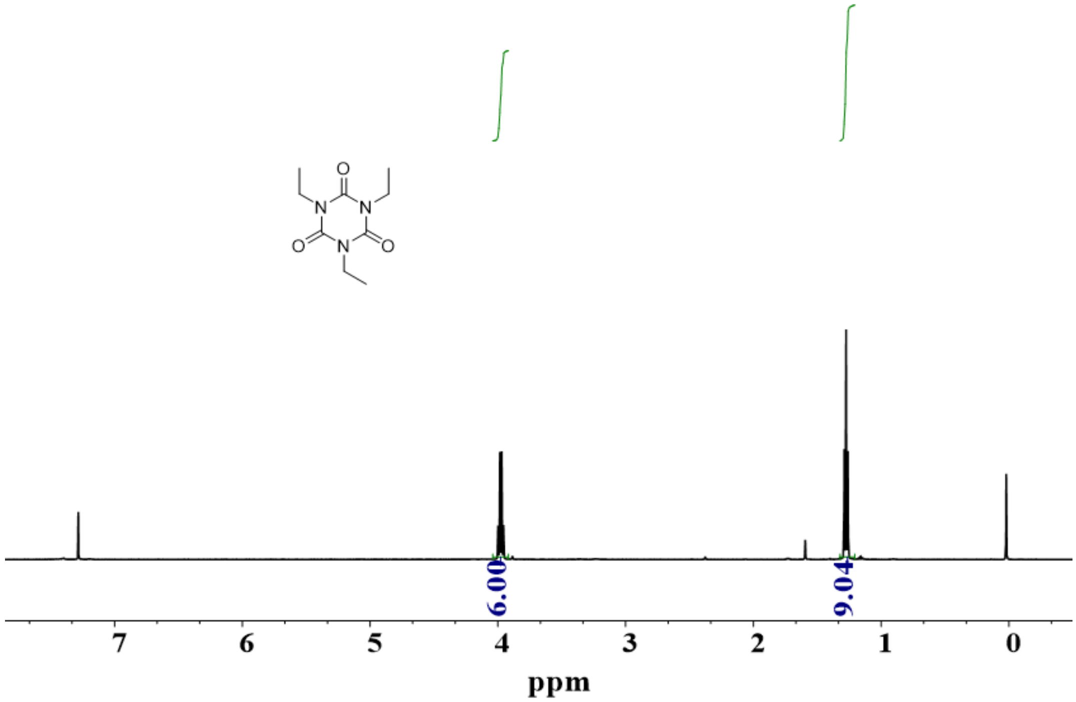


Fig S24. ^{1}H NMR spectrum of **14a** (500 MHz, chloroform-*d*).

8. X-ray diffraction data

Table S5. Crystal data and structure refinement for INT$_{39}$·C6H5F.

Compound	**INT$_{39}$·C_6H_5F**
Empirical formula	$C_{33}H_{31}F_2N_3O$
Formula weight	523.63
Temperature	273(2) K
Wavelength, Å	0.71073
Crystal system,	Triclinic
Space group	*P*-1
a, Å	10.2304(11)
b, Å	10.8156(11)
c, Å	13.0482(14)
α, deg.	84.556(2)
β, deg.	73.203(2)
γ, deg.	88.712(2)
V, Å^3	1375.9(3)
Z	2
D_{calc}, g/cm^3	1.264
Absorption coefficient, mm^{-1}	0.086
F(000)	452
Crystal size, mm	0.26 x 0.24 x 0.20
θ range, deg.	1.64 to 26.38
Limiting indices	$-12 \le h \le 12$
	$-13 \le k \le 10$
	$-15 \le l \le 16$
Reflections collected / unique	7943
Independent reflns	5475
	[*R*(int) = 0.0178]
Absorption correction	None
Data/restraints/para's	5475 / 0 / 356
Goodness-of-fit on F^2	1.059
Final *R* indices	*R*1 = 0.0574
[I>2σ (I)] [a]	w*R*2 = 0.1541

R indices (all data) [a]	*R*1 = 0.0832, w*R*2 = 0.1808
peak$_{max}$/hole$_{min}$ (e Å^{-3})	0.545/ -0.324

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S6. Bond lengths [Å] for INT$_{39}$·C_6H_5F.

C(1)-O(1)	1.256(3)	C(16)-C(21)	1.393(3)
C(1)-N(1)	1.312(3)	C(16)-C(17)	1.396(3)
C(1)-C(2)	1.565(3)	C(17)-C(18)	1.383(3)
C(2)-C(7)	1.518(3)	C(18)-C(19)	1.393(4)
C(2)-C(4)	1.534(3)	C(19)-C(20)	1.382(4)
C(2)-C(3)	1.542(3)	C(20)-C(21)	1.384(3)
C(5)-N(3)	1.470(3)	C(22)-C(23)	1.393(3)
C(6)-N(2)	1.465(3)	C(22)-C(27)	1.397(3)
C(7)-N(2)	1.348(3)	C(22)-N(1)	1.412(3)
C(7)-N(3)	1.348(3)	C(23)-C(24)	1.385(3)
C(8)-C(9)	1.361(3)	C(24)-C(25)	1.363(3)
C(8)-N(2)	1.390(3)	C(25)-C(26)	1.368(4)
C(8)-C(10)	1.477(3)	C(25)-F(1)	1.371(3)
C(9)-N(3)	1.393(3)	C(26)-C(27)	1.382(3)
C(9)-C(16)	1.478(3)	C(28)-C(29)	1.377(4)
C(10)-C(15)	1.386(3)	C(28)-C(33)	1.386(4)
C(10)-C(11)	1.400(3)	C(29)-C(30)	1.377(4)
C(11)-C(12)	1.377(4)	C(30)-F(2)	1.344(3)

C(12)-C(13)	1.380(4)	C(30)-C(31)	1.371(4)
C(13)-C(14)	1.362(4)	C(31)-C(32)	1.362(4)
C(14)-C(15)	1.392(4)	C(32)-C(33)	1.377(5)
O(1)-C(1)-N(1)	131.6(2)	C(17)-C(18)-C(19)	120.1(2)
O(1)-C(1)-C(2)	113.82(18)	C(20)-C(19)-C(18)	119.8(2)
N(1)-C(1)-C(2)	114.55(18)	C(19)-C(20)-C(21)	120.2(2)
C(7)-C(2)-C(4)	109.04(19)	C(20)-C(21)-C(16)	120.6(2)
C(7)-C(2)-C(3)	114.37(18)	C(23)-C(22)-C(27)	116.8(2)
C(4)-C(2)-C(3)	109.0(2)	C(23)-C(22)-N(1)	127.17(19)
C(7)-C(2)-C(1)	105.87(17)	C(27)-C(22)-N(1)	116.03(19)
C(4)-C(2)-C(1)	115.06(17)	C(24)-C(23)-C(22)	121.5(2)
C(3)-C(2)-C(1)	103.53(19)	C(25)-C(24)-C(23)	119.2(2)
N(2)-C(7)-N(3)	106.61(19)	C(24)-C(25)-C(26)	122.0(2)
N(2)-C(7)-C(2)	124.19(18)	C(24)-C(25)-F(1)	118.7(2)
N(3)-C(7)-C(2)	129.2(2)	C(26)-C(25)-F(1)	119.3(2)
C(9)-C(8)-N(2)	106.7(2)	C(25)-C(26)-C(27)	118.4(2)
C(9)-C(8)-C(10)	130.2(2)	C(26)-C(27)-C(22)	122.2(2)
N(2)-C(8)-C(10)	123.08(19)	C(29)-C(28)-C(33)	121.1(3)
C(8)-C(9)-N(3)	106.79(19)	C(28)-C(29)-C(30)	117.0(3)
C(8)-C(9)-C(16)	129.9(2)	F(2)-C(30)-C(31)	118.3(3)
N(3)-C(9)-C(16)	123.32(18)	F(2)-C(30)-C(29)	118.6(3)
C(15)-C(10)-C(11)	118.7(2)	C(31)-C(30)-C(29)	123.2(3)

C(15)-C(10)-C(8)	121.3(2)	C(32)-C(31)-C(30)	118.5(3)
C(11)-C(10)-C(8)	119.9(2)	C(9)-N(3)-C(5)	122.91(18)
C(12)-C(11)-C(10)	120.6(2)	C(31)-C(32)-C(33)	120.6(3)
C(11)-C(12)-C(13)	120.1(3)	C(32)-C(33)-C(28)	119.5(3)
C(14)-C(13)-C(12)	120.0(3)	C(1)-N(1)-C(22)	120.34(18)
C(13)-C(14)-C(15)	120.9(3)	C(7)-N(2)-C(8)	110.07(17)
C(10)-C(15)-C(14)	119.7(2)	C(7)-N(2)-C(6)	126.37(19)
C(21)-C(16)-C(17)	118.9(2)	C(8)-N(2)-C(6)	123.4(2)
C(21)-C(16)-C(9)	121.1(2)	C(7)-N(3)-C(9)	109.80(17)
C(17)-C(16)-C(9)	120.00(19)	C(7)-N(3)-C(5)	125.76(18)
C(18)-C(17)-C(16)	120.4(2)		

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