

2015

Cocatalyst Binding Effects in Organocatalytic Ring-Opening Polymerization of L-Lactide

Oleg I. Kazakov
University of Rhode Island

Matthew K. Kiesewetter
University of Rhode Island, mkiesewetter@chm.uri.edu

Follow this and additional works at: https://digitalcommons.uri.edu/chm_facpubs

**The University of Rhode Island Faculty have made this article openly available.
Please let us know how Open Access to this research benefits you.**

This is a pre-publication author manuscript of the final, published article.

Terms of Use

This article is made available under the terms and conditions applicable towards Open Access Policy Articles, as set forth in our [Terms of Use](#).

Citation/Publisher Attribution

Kazakov, O. I., & Kiesewetter, M. K. (2015). Cocatalyst Binding Effects in Organocatalytic Ring-Opening Polymerization of L-Lactide. *Macromolecules*, 48(17), 6121-6126. doi: 10.1021/acs.macromol.5b01140
Available at: <http://dx.doi.org/10.1021/acs.macromol.5b01140>

This Article is brought to you for free and open access by the Chemistry at DigitalCommons@URI. It has been accepted for inclusion in Chemistry Faculty Publications by an authorized administrator of DigitalCommons@URI. For more information, please contact digitalcommons@etal.uri.edu.

Supporting Information for *Cocatalyst Binding Effects in Organocatalytic Ring-Opening Polymerization of L-Lactide*

Oleg I. Kazakov and Matthew K. Kiesewetter*

Department of Chemistry, University of Rhode Island, Kingston, RI 02881 USA

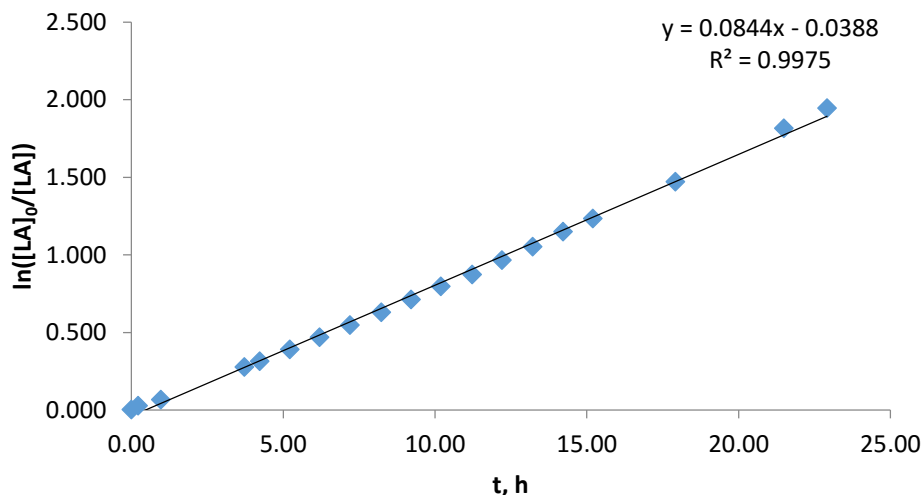


Figure S1. First order evolution of [LA] versus time in the **1**/HMTETA catalyzed ROP of LA from benzyl alcohol in CDCl_3 . $[\text{LA}]_0 = 0.5$ mmol; $[\text{HMTETA}]_0 = [\mathbf{1}]_0 = 0.025$ mmol; $[\text{benzyl alcohol}]_0 = 0.010$ mmol.

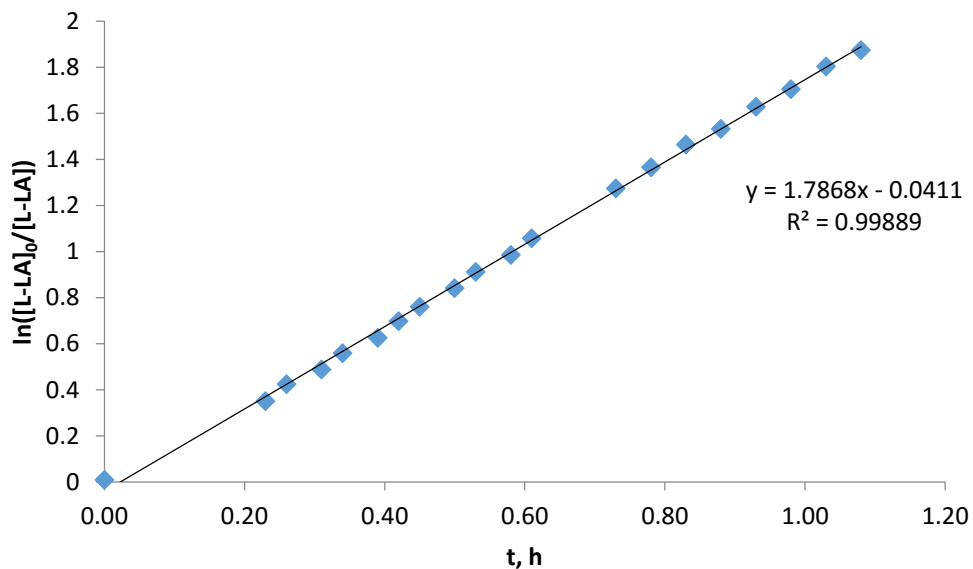


Figure S2. First order evolution of [LA] versus time in the **1**/Me₆TREN catalyzed ROP of LA from benzyl alcohol in CDCl_3 . $[\text{LA}]_0 = 0.5$ mmol; $[\text{Me}_6\text{TREN}]_0 = [\mathbf{1}]_0 = 0.050$ mmol; $[\text{benzyl alcohol}]_0 = 0.010$ mmol.

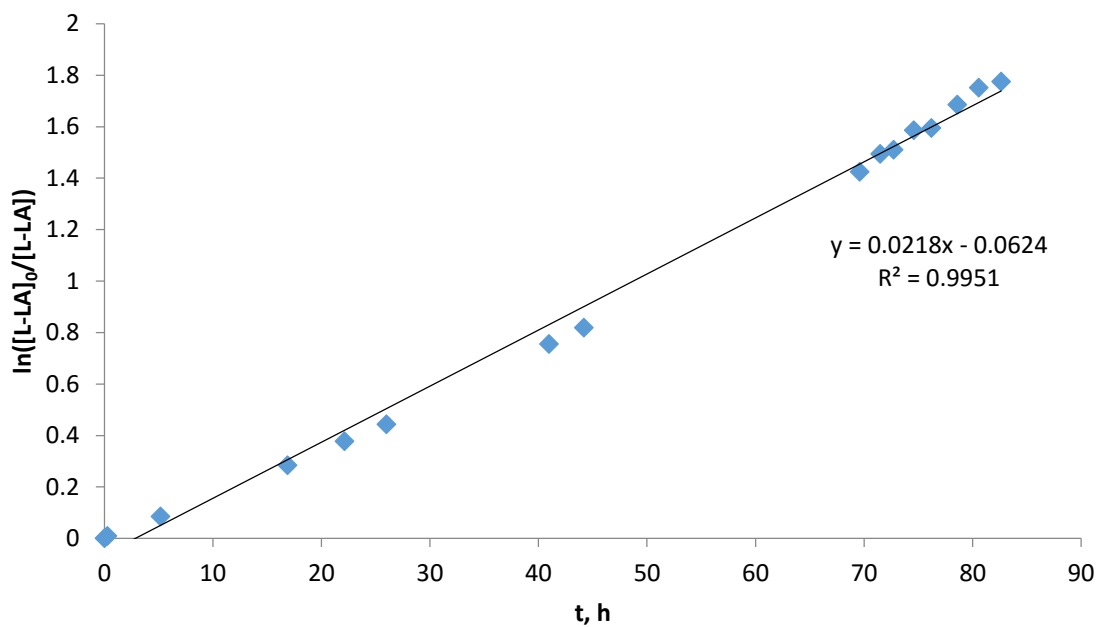
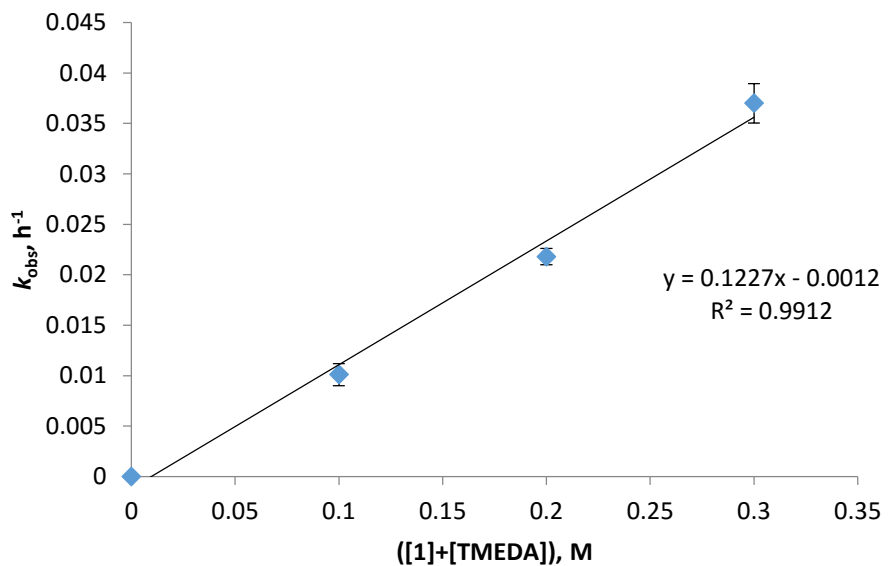
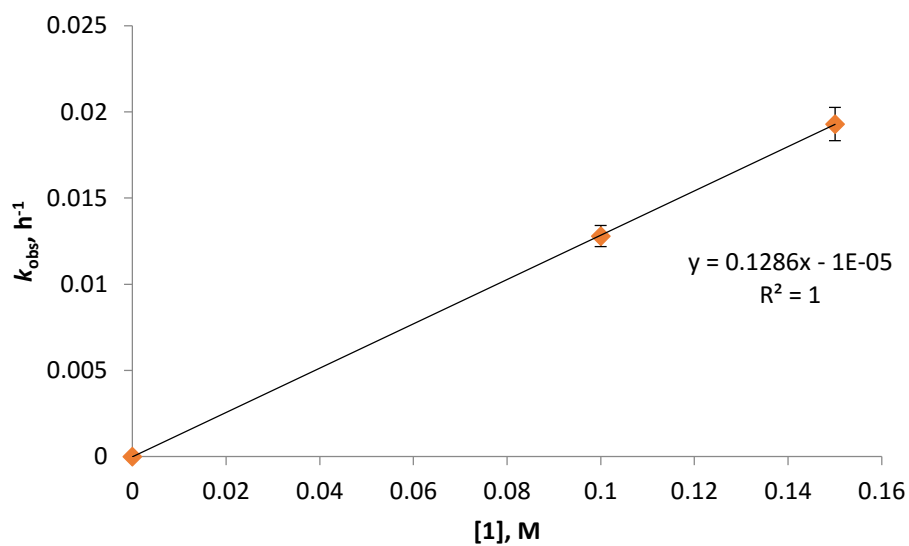


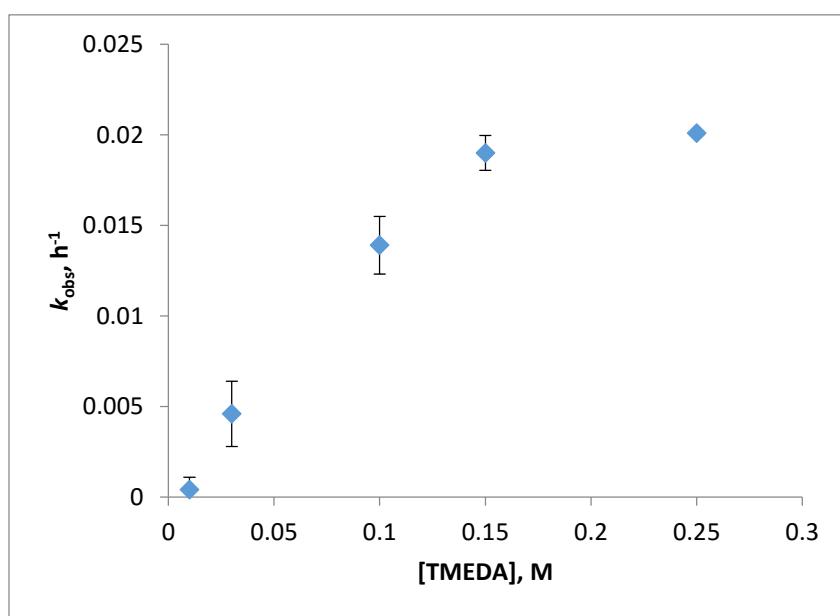
Figure S3. First order evolution of [LA] versus time in the **1**/TMEDA catalyzed ROP of LA from benzyl alcohol in CDCl_3 . $[\text{LA}]_0 = 0.5 \text{ mmol}$; $[\text{TMEDA}]_0 = [\mathbf{1}]_0 = 0.050 \text{ mmol}$; $[\text{benzyl alcohol}]_0 = 0.010 \text{ mmol}$.



A)



B)



C)

Figure S4. Observed rate constant (k_{obs}) vs concentration plots for the **1**/TMEDA catalyzed ROP of L-LA: A) $[\mathbf{1}] = [\text{TMEDA}]$, B) $[\mathbf{1}] > [\text{TMEDA}]$, $[\text{TMEDA}] = 0.05 \text{ M}$, C) k_{obs} vs $[\text{TMEDA}]$, $[\mathbf{1}] = 0.05 \text{ M}$ (bottom).

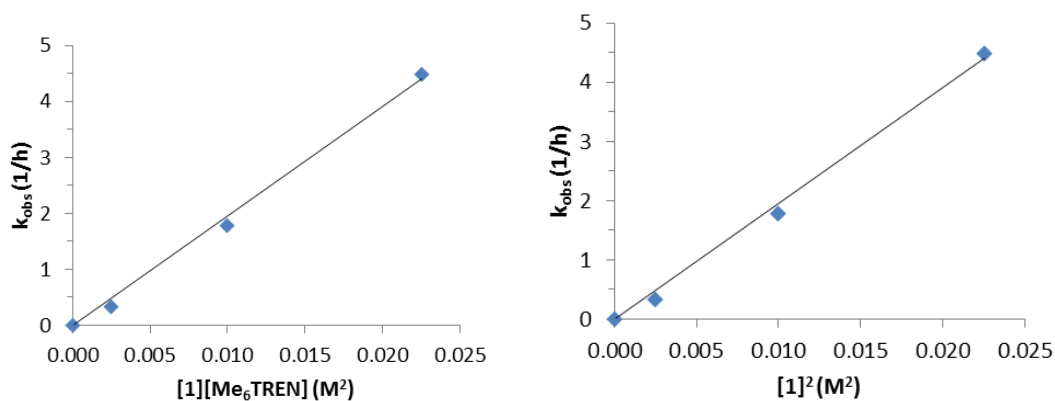


Figure S5. (left) Observed rate constant (k_{obs}) vs $[1][\text{Me}_6\text{TREN}]$, and (right) observed rate constant (k_{obs}) vs $[1]^2$ for the $1/\text{Me}_6\text{TREN}$ catalyzed ROP of L-LA.

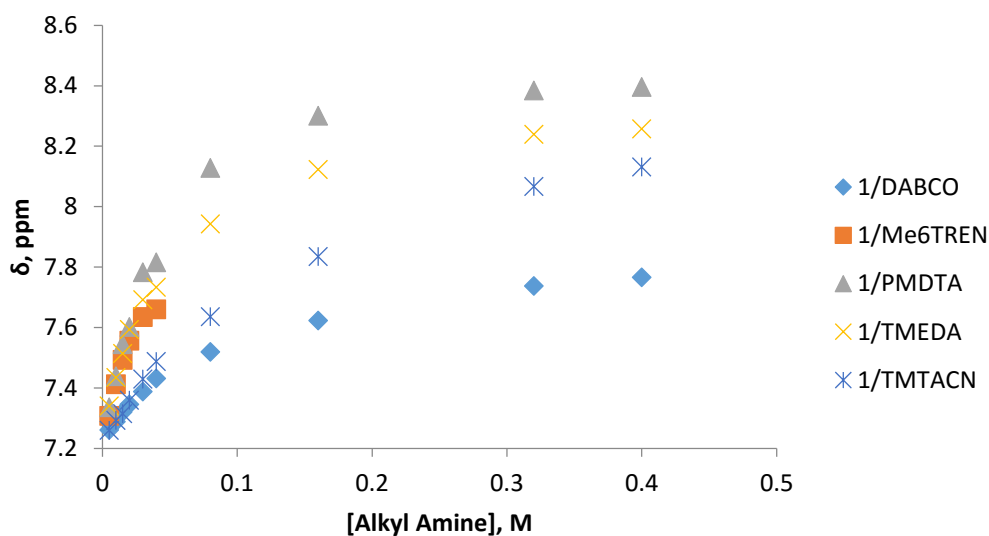


Figure S6. Binding curves for the association of **1** with alkylamine cocatalysts. The curve fitting method was used to extract binding constants, see Experimental Section. The chemical shift is of the *ortho*-protons of **1**.

Equation used for binding studies.¹⁻³

$$\delta_{\text{obs}} = \delta_{\text{H}} - (\Delta\delta/2[\text{H}]_o) \{ [\text{H}]_o + [\text{G}]_o + 1/\text{K} - (([\text{H}]_o + [\text{G}]_o + 1/\text{K})^2 - 4[\text{H}]_o[\text{G}]_o)^{1/2} \}$$

Where: δ_{obs} is the observed chemical shift of the TU in the presence of base
 δ_{H} is the chemical shift of free TU in the absence of base
 $\Delta\delta$ is the difference in the chemical shift of host and complex, ($\Delta\delta = \delta_{\text{C}} - \delta_{\text{H}}$)
 K is the binding constant, K_{eq}

The binding constants were determined by fitting the binding curve with the quadratic form of the binding equation shown above (K_{eq} and $\Delta\delta$ variables).¹⁻² The value of the binding constants determined from curve fitting are within experimental error of those

determined from the slope of the linear (Lineweaver-Burke) forms of the binding equation.⁴⁻⁵

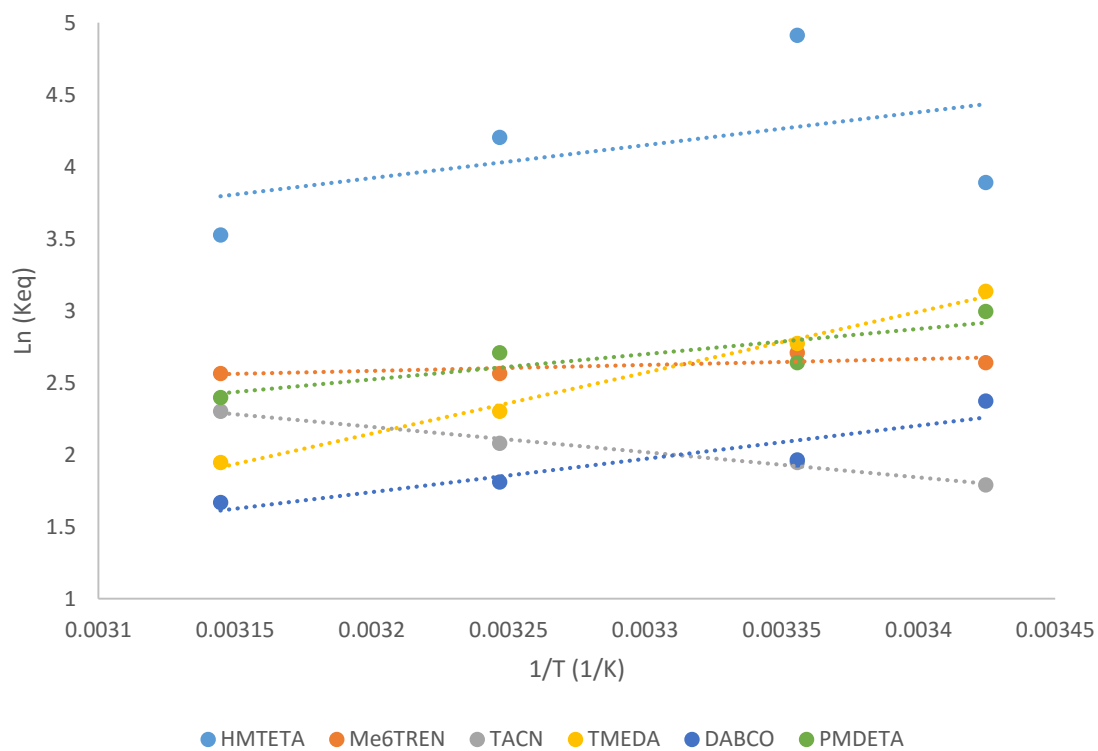


Figure S7. Temperature dependent binding.

Computational Images of Cocatalyst Complexes.

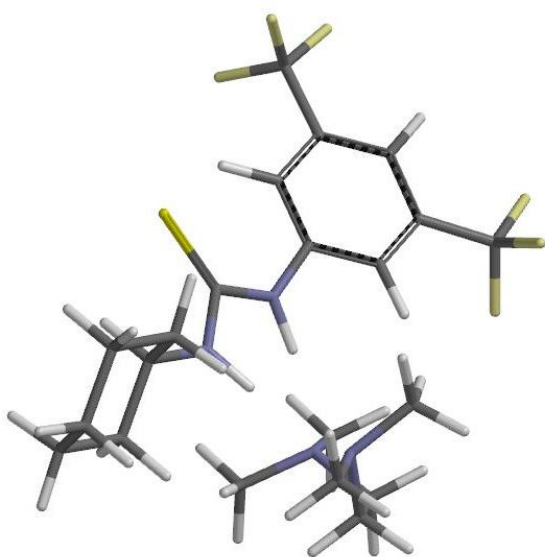


Figure S7. 1 + TMEDA. See Experimental Section for computational details and below for optimized coordinates.

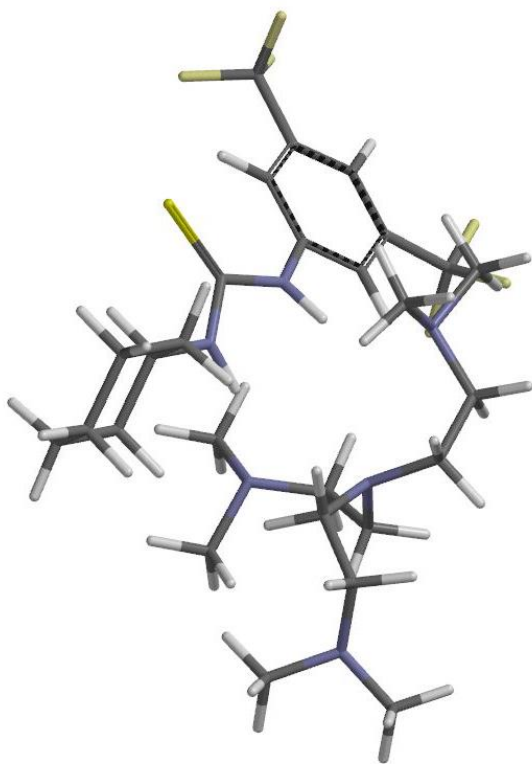


Figure S8. **1** + Me₆TREN. See Experimental Section for computational details and below for optimized coordinates.

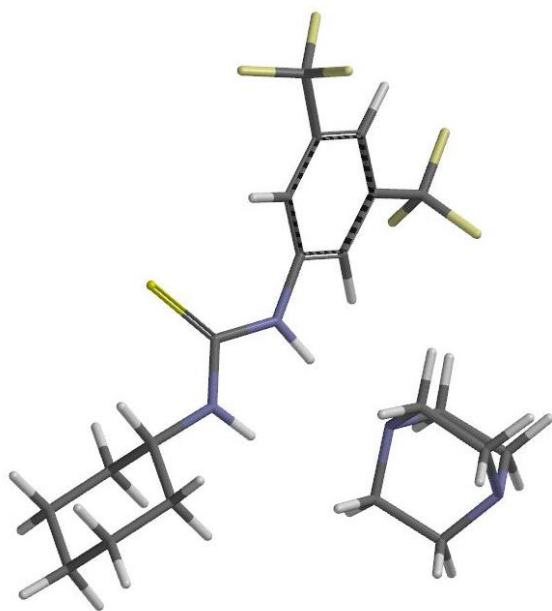


Figure S8. **1** + DABCO. See Experimental Section for computational details and below for optimized coordinates.

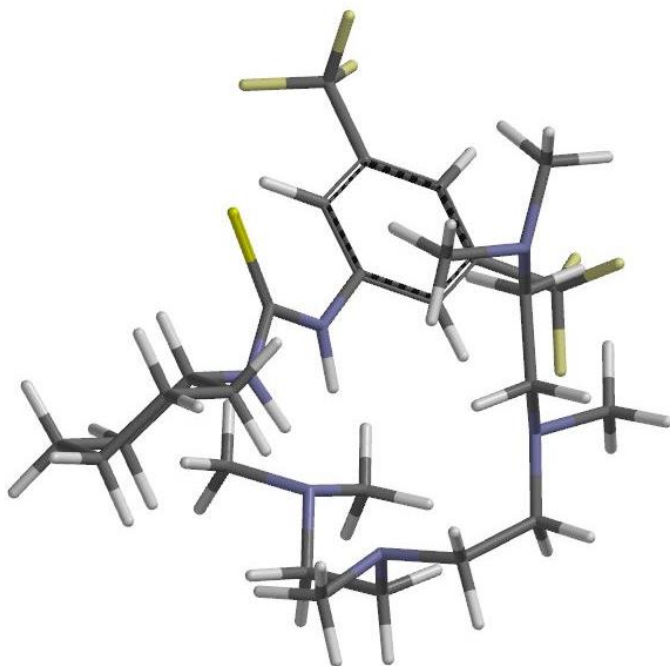


Figure S9. **1 + HMTETA.** See Experimental Section for computational details and below for optimized coordinates.

Optimized Energies and Atomic Coordinates:

1 + HMTETA

		Cartesian Coordinates (Angstroms)		
Atom		X	Y	Z
1 C	C16	0.9894109	-1.4727979	-0.8215657
2 S	S1	0.6430497	-3.1250735	-0.7542201
3 N	N2	2.2567399	-0.9719702	-0.8520693
4 H	H10	2.3673275	0.0235565	-0.6697293
5 N	N3	0.0487468	-0.4735353	-0.8389453
6 H	H27	0.3951613	0.4802393	-0.9934503
7 C	C17	-1.3536643	-0.5391003	-0.7540792
8 C	C18	-4.1633420	-0.3832505	-0.6479231
9 C	C19	-1.9865385	0.5674783	-0.1699250
10 C	C20	-2.1363603	-1.5750872	-1.2837411
11 C	C21	-3.5270611	-1.4876128	-1.2149658
12 C	C22	-3.3773418	0.6461909	-0.1317388
13 H	H28	-1.3716619	1.3511466	0.2606122
14 H	H30	-1.6591248	-2.4294477	-1.7419244
15 H	H33	-5.2436517	-0.3196712	-0.6245901
16 C	C23	3.4701700	-1.7767561	-0.9681170
17 C	C24	5.5695445	-2.1977026	-2.3280808
18 C	C25	5.5868573	-2.5902270	0.1753813
19 C	C26	6.4142148	-2.1636308	-1.0458813
20 C	C27	4.3109634	-1.7460253	0.3199323
21 C	C28	4.2993162	-1.3453127	-2.1899404
22 H	H36	5.2810725	-3.2358982	-2.5429145
23 H	H37	5.3070792	-3.6475100	0.0713954
24 H	H38	6.7954007	-1.1439239	-0.8892658

25 H H39	4.5881530	-0.7059347	0.5478426
26 H H40	4.5825388	-0.2874051	-2.0865219
27 H H41	3.1194264	-2.8008227	-1.1250681
28 H H42	6.1596642	-1.8546386	-3.1858855
29 H H43	6.1865864	-2.5166078	1.0900585
30 H H44	7.2930945	-2.8102422	-1.1530313
31 H H45	3.7014172	-2.1056411	1.1552688
32 H H46	3.6812193	-1.4246690	-3.0915252
33 C C29	-4.0219879	1.8357875	0.5235128
34 C C30	-4.3547243	-2.6287743	-1.7476187
35 F F1	-5.5818693	-2.2155149	-2.1391270
36 F F2	-3.7685601	-3.2213670	-2.8097864
37 F F3	-4.5413966	-3.5874171	-0.8127692
38 F F4	-5.2949743	2.0148487	0.1170267
39 F F5	-4.0544452	1.7135871	1.8754090
40 F F6	-3.3459894	2.9820225	0.2594708
41 N N1	2.6702447	2.5108853	-0.0118602
42 C C1	2.6570347	2.9767424	1.3897007
43 H H4	3.2432810	3.9126873	1.4845602
44 H H5	3.1977183	2.2290948	1.9783196
45 C C13	2.0303958	3.4807450	-0.9151633
46 C C3	4.0732986	2.3157114	-0.3913989
47 H H3	4.5422410	1.5921227	0.2811281
48 H H11	4.1548068	1.9264769	-1.4083824
49 C C4	1.7418670	2.9416491	-2.3207297
50 H H12	2.5907757	2.3487832	-2.6729730
51 H H13	1.6614474	3.8004166	-3.0132225
52 C C5	1.3082839	3.2790767	2.0514547
53 H H14	0.8102258	4.0953529	1.5175889
54 H H15	1.5640309	3.6946784	3.0481068
55 N N4	0.5390989	2.1003618	-2.4028408
56 N N5	0.3383679	2.1868039	2.1794641
57 C C7	0.5648099	1.2835707	-3.6206611
58 H H17	-0.3264400	0.6517953	-3.6579922
59 H H21	1.4424875	0.6313873	-3.6100076
60 H H22	0.5926992	1.8941239	-4.5403678
61 C C8	-0.6814797	2.9130532	-2.3783385
62 H H18	-0.7233249	3.6257529	-3.2220017
63 H H23	-0.7539024	3.4803785	-1.4475546
64 H H24	-1.5575433	2.2633073	-2.4307914
65 C C11	0.8643401	1.1098113	3.0334914
66 H H32	1.0817197	1.4774447	4.0546627
67 H H34	1.8121501	0.7804380	2.6016355
68 C C12	-0.9051967	2.7439296	2.7220489
69 H H1	-1.2482672	3.5624784	2.0830226
70 H H19	-0.7831571	3.1389513	3.7484449
71 H H47	-1.6979603	1.9967027	2.7363261
72 H H48	1.0878049	3.7985586	-0.4684969
73 H H49	2.6541594	4.3908863	-1.0099409
74 H H7	4.6567605	3.2541004	-0.3405876
75 C C2	-0.0642334	-0.1064021	3.1496429
76 H H6	-0.2826709	-0.5014797	2.1411538
77 H H8	-1.0186322	0.2058965	3.5825641
78 N N6	0.4913164	-1.1243020	4.0439486
79 C C6	1.5968539	-1.8693305	3.4473450
80 H H9	2.4082860	-1.1931472	3.1644554
81 H H16	1.2996867	-2.4454297	2.5515433
82 H H20	1.9997711	-2.5700019	4.1857611
83 C C9	-0.5421762	-2.0403384	4.5146340

84 H H2	-0.1055393	-2.7459537	5.2285419
85 H H25	-1.0128186	-2.6285078	3.7041436
86 H H26	-1.3292775	-1.4814082	5.0312808

1+ TACN

Atom	Cartesian Coordinates (Angstroms)		
	X	Y	Z
1 N N1	-3.9631626	-2.3050019	-1.2539444
2 C C1	-4.8886767	-2.7814741	-2.2730449
3 H H3	-5.5106800	-3.5872821	-1.8699328
4 H H4	-4.3243359	-3.1905683	-3.1182340
5 H H5	-5.5550754	-1.9903955	-2.6683066
6 C C2	-4.6096232	-1.8619147	-0.0203063
7 H H6	-5.6039747	-2.3225152	0.0330960
8 H H7	-4.7757403	-0.7694037	-0.0149363
9 C C3	-3.8746646	-2.2736638	1.2660706
10 H H8	-3.8345144	-3.3724584	1.3112164
11 H H9	-4.5039855	-1.9550676	2.1068505
12 C C4	-2.9845535	-1.3540467	-1.7997892
13 H H10	-2.7762733	-0.5859165	-1.0547378
14 H H11	-3.4073089	-0.8360211	-2.6780426
15 C C5	-1.6507800	-1.9842827	-2.2135349
16 H H12	-1.1336123	-1.2736685	-2.8697925
17 H H13	-1.8429327	-2.8933942	-2.8147716
18 N N2	-2.5174451	-1.7051403	1.4518723
19 N N3	-0.7363163	-2.2714848	-1.0950480
20 C C6	-1.4589247	-2.7161697	1.2812582
21 H H16	-1.6359694	-3.5752216	1.9584852
22 H H17	-0.5164651	-2.2576495	1.6011561
23 C C7	-1.2717620	-3.2679231	-0.1336680
24 H H18	-0.5711350	-4.1095125	-0.0553601
25 H H19	-2.2159496	-3.6737321	-0.5068160
26 C C9	-2.3824622	-1.1029927	2.7873490
27 H H1	-2.4718091	-1.8446681	3.6018546
28 H H20	-3.1523584	-0.3409928	2.9316040
29 H H21	-1.4072375	-0.6139913	2.8755968
30 C C10	-0.3709184	1.6522465	0.3890683
31 N N4	-1.7127224	1.4628076	0.5120385
32 H H24	-2.0527609	0.5029743	0.5790606
33 N N5	0.3114036	0.4779938	0.1573701
34 H H23	-0.2268353	-0.3721215	-0.0515139
35 S S1	0.3784710	3.1575981	0.5371844
36 C C11	1.7128331	0.2948509	0.1134650
37 C C12	4.4596054	-0.3015849	-0.0435930
38 C C13	2.5710317	1.1149817	-0.6330972
39 C C14	2.2432870	-0.8095529	0.7840138
40 C C15	3.6013244	-1.1177585	0.6858338
41 C C16	3.9322063	0.8202717	-0.6889279
42 H H22	2.1729769	1.9686009	-1.1632310
43 H H26	1.5910922	-1.4331372	1.3862344
44 H H29	5.5147685	-0.5351550	-0.1154477
45 C C17	-2.7057116	2.5371246	0.5439967
46 C C18	-4.4297349	3.8392205	-0.7904108
47 C C19	-4.7568961	3.4715049	1.6987798
48 C C20	-5.4518274	3.6477860	0.3404729
49 C C21	-3.7303318	2.3278134	1.6697620

50 C C22	-3.4024262	2.6982701	-0.8204078
51 H H25	-3.9029409	4.7934909	-0.6477641
52 H H30	-4.2443530	4.4054508	1.9697636
53 H H31	-6.0635677	2.7572660	0.1300492
54 H H32	-4.2580361	1.3728265	1.5166967
55 H H33	-3.9058246	1.7560227	-1.0849440
56 H H34	-2.1403753	3.4499352	0.7527893
57 H H35	-4.9412813	3.9077456	-1.7585613
58 H H36	-5.4983013	3.2842202	2.4854917
59 H H37	-6.1436403	4.4987462	0.3773559
60 H H38	-3.2086290	2.2558407	2.6319109
61 H H39	-2.6431580	2.8818684	-1.5896707
62 C C23	4.8568765	1.7480689	-1.4331844
63 C C24	4.0915529	-2.3847066	1.3275451
64 F F1	5.3363983	2.7196332	-0.6264127
65 F F2	5.9269385	1.0900910	-1.9361994
66 F F3	4.2354730	2.3572002	-2.4653152
67 F F4	3.6783539	-3.4756434	0.6285434
68 F F5	3.6082901	-2.5308782	2.5819912
69 F F6	5.4354727	-2.4444453	1.3964676
70 C C8	0.5642315	-2.6952970	-1.6307742
71 H H2	0.9890776	-1.8953792	-2.2459015
72 H H14	0.4902535	-3.6060394	-2.2524422
73 H H15	1.2628477	-2.8976087	-0.8149270

1 + Me₆TREN

Atom	Cartesian Coordinates (Angstroms)		
	X	Y	Z
1 C C16	-0.3565532	-1.9654632	0.2387363
2 S S1	-1.1207598	-3.4475029	0.4941631
3 N N2	0.9719516	-1.8466738	-0.0174063
4 H H10	1.3074932	-0.9566372	-0.3934779
5 N N3	-0.9757238	-0.7252759	0.3006581
6 H H27	-0.3722192	0.0499826	0.5924125
7 C C17	-2.3084752	-0.3440481	0.0937992
8 C C18	-4.9143951	0.6752252	-0.3453424
9 C C19	-2.5400110	1.0365476	-0.0393070
10 C C20	-3.4058028	-1.2145768	-0.0150334
11 C C21	-4.6815944	-0.6950182	-0.2357005
12 C C22	-3.8227716	1.5347176	-0.2418054
13 H H28	-1.7038945	1.7235529	0.0202816
14 H H30	-3.2512939	-2.2800549	0.0797111
15 H H33	-5.9121122	1.0599851	-0.5086353
16 C C23	1.9047760	-2.9753131	-0.0214730
17 C C24	3.9118105	-4.0150346	-1.1615347
18 C C25	3.5684324	-4.3331403	1.3300990
19 C C26	4.5990173	-4.1959931	0.1998898
20 C C27	2.5911907	-3.1492103	1.3452993
21 C C28	2.9328753	-2.8305365	-1.1526160
22 H H36	3.3649591	-4.9328453	-1.4169447
23 H H37	3.0021816	-5.2645983	1.1939824
24 H H38	5.2411063	-3.3255996	0.3987345
25 H H39	3.1309476	-2.2249158	1.5961858
26 H H40	3.4964247	-1.8965405	-1.0226784
27 H H41	1.2995863	-3.8676532	-0.2122285

28 H H42	4.6595808	-3.8707964	-1.9502402
29 H H43	4.0723748	-4.4156428	2.3001553
30 H H44	5.2591200	-5.0710342	0.1762892
31 H H45	1.8230726	-3.2920537	2.1125161
32 H H46	2.4117507	-2.7557165	-2.1139955
33 C C29	-3.9911292	3.0223452	-0.3838011
34 C C30	-5.8441155	-1.6536240	-0.2865727
35 F F1	-6.9221760	-1.1022743	-0.8889782
36 F F2	-5.5367901	-2.7824334	-0.9584769
37 F F3	-6.2325557	-2.0272279	0.9540142
38 F F4	-5.2849372	3.3972487	-0.3886396
39 F F5	-3.3818722	3.6903011	0.6312191
40 F F6	-3.4330444	3.4828813	-1.5279053
41 N N1	2.6712172	1.5729156	0.5387792
42 C C1	2.4560060	2.2769173	1.8008238
43 H H4	2.9756586	3.2532645	1.8337622
44 H H5	2.9036435	1.6771309	2.5998396
45 C C13	2.4717650	2.4043496	-0.6619079
46 C C3	3.9041124	0.7766860	0.5408367
47 H H3	3.8188353	0.0434604	1.3526992
48 H H11	3.9299761	0.1963593	-0.3851796
49 C C4	1.3290279	1.9414201	-1.5757468
50 H H12	1.1942213	2.7081642	-2.3651848
51 H H13	0.4026557	1.9235519	-0.9922123
52 C C5	0.9979294	2.5652812	2.1696056
53 H H14	0.5474077	3.2436689	1.4341452
54 H H15	1.0343664	3.1274073	3.1237948
55 C C6	5.2465570	1.5178999	0.7283457
56 H H6	5.9922056	0.8054275	1.1358054
57 H H16	5.1170011	2.2891301	1.4946283
58 N N4	1.4987514	0.6069992	-2.1665485
59 N N5	0.1108668	1.3975211	2.2981623
60 N N6	5.7523458	2.1697795	-0.4862453
61 C C7	2.6255564	0.5539074	-3.0974384
62 H H17	2.7280786	-0.4630850	-3.4868588
63 H H21	3.5582265	0.8182945	-2.5967624
64 H H22	2.4975802	1.2371232	-3.9578844
65 C C8	0.2784606	0.2019085	-2.8696812
66 H H18	0.0455305	0.8600357	-3.7268575
67 H H23	-0.5735378	0.2176121	-2.1878272
68 H H24	0.3922826	-0.8189360	-3.2462111
69 C C9	6.3856359	1.2148333	-1.3900349
70 H H9	6.6921431	1.7228455	-2.3095486
71 H H25	5.6870614	0.4206208	-1.6679526
72 H H26	7.2800528	0.7354826	-0.9471517
73 C C10	6.6751609	3.2558425	-0.1697362
74 H H20	7.5785419	2.9141576	0.3701598
75 H H29	6.1713257	4.0042144	0.4494834
76 H H31	7.0001824	3.7443355	-1.0935897
77 C C11	0.6890679	0.3261788	3.1143348
78 H H2	-0.0559571	-0.4643574	3.2360790
79 H H32	0.9924531	0.6695158	4.1201041
80 H H34	1.5535040	-0.1122512	2.6122861
81 C C12	-1.1598265	1.8303244	2.8902341
82 H H1	-1.6168627	2.6163775	2.2837463
83 H H19	-1.0278637	2.2212039	3.9152612
84 H H47	-1.8559628	0.9887315	2.9319240
85 H H48	2.2310503	3.4327438	-0.3603208
86 H H49	3.4117858	2.4835209	-1.2165070

1 + DABCO

Atom	Cartesian Coordinates (Angstroms)		
	X	Y	Z
1 C C16	1.2089310	-1.5514649	-0.1404124
2 S S1	0.8434249	-3.1945276	-0.1898216
3 N N2	2.4839571	-1.0697456	-0.1091368
4 H H10	2.5995125	-0.0695143	-0.2185575
5 N N3	0.2805404	-0.5364245	-0.1334519
6 H H27	0.6405493	0.4273059	-0.1680656
7 C C17	-1.1231022	-0.6064949	-0.1231761
8 C C18	-3.9363673	-0.4603232	-0.0478571
9 C C19	-1.8078393	0.4069801	-0.8032659
10 C C20	-1.8601259	-1.5672325	0.5860731
11 C C21	-3.2515290	-1.4878668	0.6055873
12 C C22	-3.1983255	0.4888863	-0.7479374
13 H H28	-1.2475707	1.1302262	-1.3853439
14 H H30	-1.3468037	-2.3653039	1.1036452
15 H H33	-5.0167641	-0.4085715	-0.0159565
16 C C23	3.6965505	-1.8707133	-0.2670929
17 C C24	5.4163840	-2.7844409	-1.8990332
18 C C25	6.1208369	-2.1025689	0.4379769
19 C C26	6.5465478	-2.2095660	-1.0337670
20 C C27	4.8250903	-1.2914282	0.5990594
21 C C28	4.1212951	-1.9734941	-1.7429378
22 H H36	5.2260834	-3.8256228	-1.6051630
23 H H37	5.9612217	-3.1111195	0.8431719
24 H H38	6.8160151	-1.2103320	-1.4057236
25 H H39	5.0145221	-0.2480021	0.3004993
26 H H40	4.2744714	-0.9583744	-2.1393945
27 H H41	3.4393165	-2.8710308	0.0937622
28 H H42	5.7153918	-2.8097876	-2.9532068
29 H H43	6.9195667	-1.6499140	1.0368580
30 H H44	7.4472147	-2.8280928	-1.1219844
31 H H45	4.5093513	-1.2703692	1.6483144
32 H H46	3.3067623	-2.4256999	-2.3177468
33 C C29	-3.8628339	1.6414512	-1.4475148
34 C C30	-4.0248454	-2.4831993	1.4323407
35 F F1	-5.3007159	-2.6062559	1.0033055
36 F F2	-3.4637370	-3.7081607	1.4066213
37 F F3	-4.0813457	-2.1009652	2.7308812
38 F F4	-5.2067203	1.5672760	-1.4105526
39 F F5	-3.5085914	2.8255572	-0.8790857
40 F F6	-3.4904649	1.7191521	-2.7451072
41 N N1	1.7151695	4.6739524	1.2927295
42 C C1	1.3708245	3.7165088	2.3580458
43 H H1	0.5246207	4.1222409	2.9221435
44 H H4	2.2209661	3.6473364	3.0450267
45 C C2	0.5816590	4.7728135	0.3582372
46 H H3	-0.2885464	5.1329969	0.9165792
47 H H7	0.8213070	5.5280997	-0.3977503
48 C C3	2.8906327	4.1757897	0.5619933
49 H H2	3.1281182	4.8907931	-0.2329674
50 H H9	3.7438368	4.1539792	1.2483343

51 C C4	1.0234908	2.3222680	1.7437244
52 H H5	-0.0134969	2.0350674	1.9452258
53 H H11	1.6649400	1.5290914	2.1428162
54 C C5	2.5997029	2.7557482	-0.0261382
55 H H12	3.2678858	2.0048223	0.4133317
56 H H13	2.7378696	2.7304746	-1.1127498
57 C C6	0.2926558	3.3842379	-0.2965406
58 H H6	0.4519217	3.4090504	-1.3802941
59 H H14	-0.7396619	3.0674558	-0.1226144
60 N N5	1.2031124	2.3573292	0.2707544

1 + PMDETA

Atom	Cartesian Coordinates (Angstroms)		
	X	Y	Z
1 C C16	0.9400661	-1.6040524	-0.1443843
2 S S1	0.6157847	-3.2162549	0.2401523
3 N N2	2.2057303	-1.1049881	-0.2575092
4 H H10	2.3141278	-0.0911790	-0.2229078
5 N N3	-0.0108788	-0.6399799	-0.3807524
6 H H27	0.3343899	0.2770472	-0.6868464
7 C C17	-1.4092661	-0.6787211	-0.2598552
8 C C18	-4.2218703	-0.4910748	-0.1243812
9 C C19	-2.0383473	0.5523458	-0.0232264
10 C C20	-2.2035871	-1.8246631	-0.4249482
11 C C21	-3.5913786	-1.7169660	-0.3403202
12 C C22	-3.4281184	0.6437516	0.0248336
13 H H28	-1.4219558	1.4304084	0.1326002
14 H H30	-1.7344506	-2.7785990	-0.6159406
15 H H33	-5.3010874	-0.4212929	-0.0872832
16 C C23	3.4183721	-1.9007813	-0.0703383
17 C C24	5.7270086	-2.4321396	-0.9765603
18 C C25	5.2956182	-2.5397073	1.5180724
19 C C26	6.3278211	-2.2347944	0.4230170
20 C C27	4.0166113	-1.7098841	1.3349931
21 C C28	4.4496489	-1.6002796	-1.1700992
22 H H36	5.4894708	-3.4951540	-1.1209284
23 H H37	5.0368427	-3.6067652	1.4842987
24 H H38	6.6714782	-1.1951208	0.5269876
25 H H39	4.2444625	-0.6444970	1.4896057
26 H H40	4.7079942	-0.5325104	-1.1504086
27 H H41	3.1001953	-2.9429187	-0.1617691
28 H H42	6.4607054	-2.1711481	-1.7482931
29 H H43	5.7220720	-2.3553794	2.5108448
30 H H44	7.2138715	-2.8683412	0.5475669
31 H H45	3.2636358	-1.9894235	2.0795107
32 H H46	4.0035875	-1.8023337	-2.1506696
33 C C29	-4.0458593	1.9966866	0.2443854
34 C C30	-4.4263740	-2.9663093	-0.4550219
35 F F1	-5.6740186	-2.6933512	-0.9032544
36 F F2	-3.8798602	-3.8647042	-1.3008540
37 F F3	-4.5643934	-3.5810240	0.7412260
38 F F4	-5.3903503	1.9704658	0.1667490
39 F F5	-3.7241858	2.5068657	1.4596089
40 F F6	-3.6055217	2.8959611	-0.6722761
41 N N1	2.8609581	2.3232232	0.1154391

42 C C1	2.8324698	2.8795208	1.4825166
43 H H4	3.3972421	3.8318341	1.5240012
44 H H5	3.3833560	2.1789626	2.1187197
45 C C13	2.1499982	3.1758319	-0.8518909
46 C C3	4.2707428	2.1880077	-0.2664492
47 H H3	4.7820072	1.5175267	0.4301727
48 H H11	4.3692558	1.7649898	-1.2679621
49 C C4	1.8813542	2.4867485	-2.1994069
50 H H12	2.6878678	1.7830710	-2.4216918
51 H H13	1.9043376	3.2447585	-3.0040595
52 C C5	1.4701625	3.1761508	2.1151257
53 H H14	0.9893280	4.0149546	1.5984064
54 H H15	1.6979940	3.5487139	3.1362736
55 N N4	0.6135739	1.7393036	-2.2390926
56 N N5	0.5113127	2.0753433	2.1537552
57 C C7	0.6267775	0.7602926	-3.3320572
58 H H17	-0.3204841	0.2153006	-3.3448300
59 H H21	1.4317413	0.0383152	-3.1681518
60 H H22	0.7680299	1.2284546	-4.3219965
61 C C8	-0.5242007	2.6520569	-2.4038536
62 H H18	-0.4622074	3.2210297	-3.3488124
63 H H23	-0.5689471	3.3689083	-1.5800036
64 H H24	-1.4605974	2.0905281	-2.3978799
65 C C11	1.0194452	0.9197221	2.8888881
66 H H2	0.2541795	0.1394243	2.9140273
67 H H32	1.2893103	1.1646713	3.9346331
68 H H34	1.8998185	0.5035958	2.3953640
69 C C12	-0.7404767	2.5366942	2.7525669
70 H H1	-1.1437064	3.3791766	2.1825798
71 H H19	-0.6162055	2.8633433	3.8027732
72 H H47	-1.4825717	1.7356678	2.7315969
73 H H48	1.1920571	3.4624643	-0.4169104
74 H H49	2.7141533	4.1115312	-1.0283118
75 H H7	4.8012259	3.1582719	-0.2578458

1 + TMEDA

Atom	Cartesian Coordinates (Angstroms)		
	X	Y	Z
1 C C16	1.1570678	1.2675919	0.0222826
2 S S1	0.9494085	2.9278905	-0.1958706
3 N N2	2.3798598	0.6712669	0.0681768
4 H H10	2.4168497	-0.3418869	-0.0773393
5 N N3	0.1397676	0.3487417	0.1844900
6 H H27	0.4285296	-0.5907202	0.4873435
7 C C17	-1.2463911	0.4684560	0.0007023
8 C C18	-4.0591293	0.4444004	-0.3149723
9 C C19	-1.9394608	-0.7225780	-0.2674805
10 C C20	-1.9850429	1.6566730	0.1120983
11 C C21	-3.3702227	1.6287463	-0.0599405
12 C C22	-3.3234370	-0.7358615	-0.4065835
13 H H28	-1.3856709	-1.6495293	-0.3627610
14 H H30	-1.4722421	2.5833396	0.3279167
15 H H33	-5.1343914	0.4411501	-0.4313642
16 C C23	3.6490887	1.3944767	-0.0070741
17 C C24	6.0307823	1.4967964	0.8554797

18 C C25	5.5076252	2.2557995	-1.5057231
19 C C26	6.5519716	1.6083247	-0.5845087
20 C C27	4.1672180	1.5070433	-1.4515880
21 C C28	4.6921368	0.7433315	0.9151919
22 H H36	5.8905068	2.5048970	1.2687728
23 H H37	5.3486534	3.2986839	-1.1992757
24 H H38	6.7925174	0.6028516	-0.9597954
25 H H39	4.2967586	0.4965878	-1.8645439
26 H H40	4.8532592	-0.3016587	0.6106266
27 H H41	3.4402613	2.4057996	0.3544496
28 H H42	6.7684484	0.9975785	1.4947389
29 H H43	5.8759867	2.2893798	-2.5376754
30 H H44	7.4864250	2.1809629	-0.6053528
31 H H45	3.4120860	2.0149830	-2.0592718
32 H H46	4.3094525	0.7201953	1.9423092
33 C C29	-3.9890580	-2.0548644	-0.6841672
34 C C30	-4.1151725	2.9351552	0.0475203
35 F F1	-5.4541487	2.7654965	-0.0240372
36 F F2	-3.8500760	3.5608646	1.2160605
37 F F3	-3.7646131	3.7875439	-0.9398024
38 F F4	-5.3327373	-1.9729156	-0.6611308
39 F F5	-3.6323375	-2.5501557	-1.8920969
40 F F6	-3.6250475	-2.9925675	0.2316921
41 N N1	2.4744326	-2.4736675	-0.7590856
42 C C1	1.4257689	-2.6453258	-1.7682042
43 H H4	1.4777839	-3.6292553	-2.2680308
44 H H5	1.5248856	-1.8680463	-2.5305927
45 C C13	2.4072905	-3.4928987	0.2970583
46 C C3	3.7886831	-2.5355159	-1.4060932
47 H H3	3.8584624	-1.7634978	-2.1766666
48 H H11	4.5778705	-2.3578008	-0.6696665
49 C C4	1.1151918	-3.5298157	1.1183454
50 H H12	1.2566766	-4.3107199	1.8900617
51 H H13	0.2841926	-3.8723424	0.4923204
52 N N4	0.7107028	-2.2572025	1.7318656
53 C C7	1.7242025	-1.7384717	2.6566403
54 H H17	1.3706376	-0.7971667	3.0857834
55 H H21	2.6553437	-1.5311150	2.1275283
56 H H22	1.9358424	-2.4377437	3.4850554
57 C C8	-0.5607377	-2.4327048	2.4463774
58 H H18	-0.4708125	-3.1394883	3.2900595
59 H H23	-1.3335598	-2.8056676	1.7693349
60 H H24	-0.8937992	-1.4696026	2.8423802
61 H H48	2.5410912	-4.5074014	-0.1261331
62 H H49	3.2616450	-3.3258903	0.9616365
63 H H7	3.9791157	-3.5137009	-1.8831872
64 H H51	0.4370790	-2.5424611	-1.3193358

SI References

- (1) Webb, J. E. A.; Crossley, M. J.; Turner, P.; Thordarson, P. *J. Am. Chem. Soc.* **2007**, *129*, 7155.
- (2) Thordarson, P. *Chem. Soc. Rev.* **2011**, *40*, 1305.
- (3) Deranleau, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 4044.

- (4) Horman, I.; Dreux, B. *Anal. Chem.* **1983**, *55*, 1219.
- (5) Peters, S. J.; Stevenson, C. D. *J. Chem. Educ.* **2004**, *81*, 715.