A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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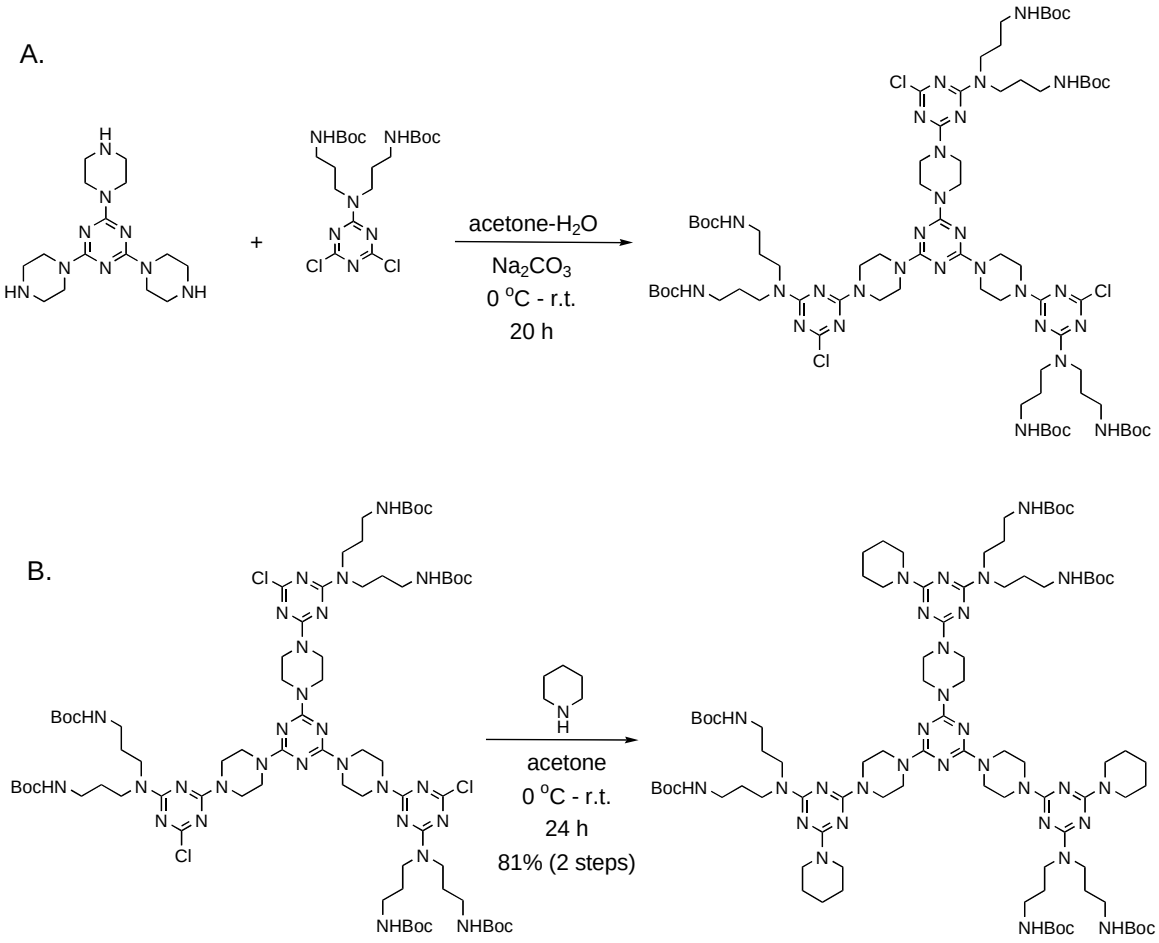
LARGE SCALE, GREEN SYNTHESIS OF A GENERATION-1 MELAMINE (TRIAZINE) DENDRIMER



Submitted by Abdellatif Chouai, Vincent J. Venditto, and Eric E. Simanek.[1]
Checked by Brian C. Vanderplas and John A. Ragan.

1. Procedure

A. *G1-[N(CH$_2$CH$_2$CH$_2$NHBoc)$_2$]$_6$-Cl$_3$*. In a 4-L, 4-necked, jacketed reaction vessel equipped with a 250-mL addition funnel, temperature probe, static N_2 and mechanical stirrer, 2-[3,3'-di-(*tert*-butoxycarbonyl)-aminodipropylamine]-4,6-dichloro-1,3,5-triazine (73.0 g, 0.152 mol, 3.5 equiv) (Note 1) is dissolved in acetone (1 L) (Note 2) and cooled to 0 °C (Note 3). Separately, a chilled solution of 1,3,5-[*tris*-piperazine]-triazine (14.5 g, 43.5 mmol, 1.0 equiv) (Note 4) in H_2O (500 mL) is prepared and treated with a solution of sodium carbonate (46.1 g, 0.435 mol, 10 equiv)

(Note 5) in 250 mL of H_2O. This solution is left to stir at 0 °C for 30 min. The resulting aqueous solution is added in a dropwise fashion to the acetone solution at 0 °C over a period of 2 h. The white suspension obtained after complete addition is left to stir at 0 °C for 2.5 h before warming gradually to 21 °C, and then stirred for an additional 20 h (Note 6). The white solid is collected by filtration on a 15 cm-diameter Büchner funnel. The reaction vessel is rinsed with 500 mL water, which is subsequently used to wash the filter cake (Notes 7 and 8). The wet solids are transferred back to the rinsed reaction vessel and dissolved in CH_2Cl_2 (1.5 L) (Note 9), washed with water (3 x 200 mL) (Note 10), a saturated, aqueous solution of sodium chloride (1 x 1.5 L) (Note 11), and then dried with 230 g sodium sulfate (Note 12). Following filtration, the solvent is removed using a rotary evaporator at 30 °C (Note 8) and dried under vacuum (Note 13) to yield an off-white crude material (76.1 g) (Note 14). This material is used in the next step without further purification (Note 15, 16, and 17).

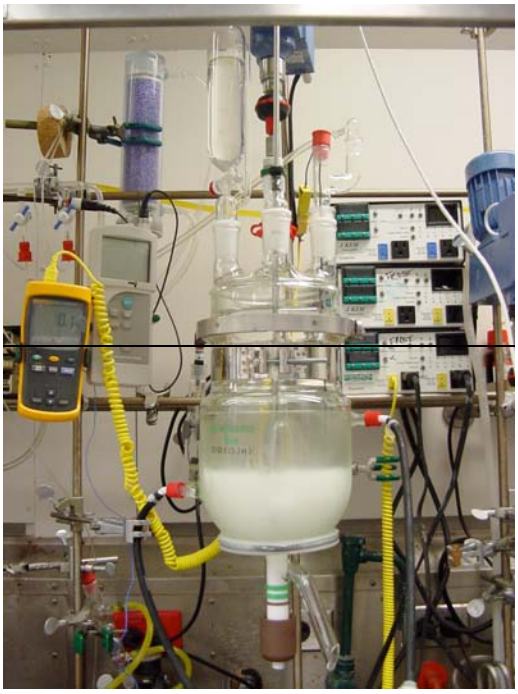
B. G1-[N(CH$_2$CH$_2$CH$_2$NHBoc)$_2$]$_6$-Piperidine$_3$. In a 4-L, 4-necked, jacketed reaction vessel (Note 3) equipped with a temperature probe, static N_2 inlet, glass stopper and mechanical stirrer, G1-[N(CH$_2$CH$_2$CH$_2$NHBoc)$_2$]$_6$-Cl$_3$ (74.8 g, 43.5 mmol, 1.0 equiv) (Note 18) is suspended in acetone (3 L) (Note 2) and left to stir at 0 °C for 1 h. Piperidine (79.3 mL, 68.4 g, 803 mmol, 18.5 equiv) (Note 19) is added in a single portion and the mixture is stirred at 0 °C for 4 h. A white suspension started to form after 30 min. The mixture is warmed to 21 °C and stirred for an additional 20 h, at which time the reaction was judged to be complete by HPLC (Note 20). The resulting suspension is filtered, washed with acetone (100 mL), and air dried overnight to afford 97.3 g of a white solid (Note 21). The white solid is dissolved in CH_2Cl_2 (1000 mL) (Notes 9 and 22), transferred to a 2-L separatory funnel and washed with a 5% HCl solution (4 x 300 mL) (Notes 23 and 24), 5% NaOH solution (1 x 300 mL) (Note 25), and a saturated, aqueous solution of sodium chloride (1 x 300 mL) (Note 11). The organic phase is dried over sodium sulfate (108 g) (Note 12) and the solvent is removed on a rotary evaporator at 30 °C (Note 8) to afford an off-white solid that is dried in a vacuum oven for 96 h (Note 13) to provide 67.4 g of the title product (86% yield over two steps) (Notes 26, 27 and 28).

2. Notes

1. The building block, 2-[3,3'-di-(*tert*-butoxycarbonyl)-aminodipropylamine]-4,6-dichloro-1,3,5,-triazine, was prepared by the reaction of cyanuric chloride with 3,3'-di-(*tert*-butoxycarbonyl)-aminodipropylamine in acetone-water. This procedure is described in the preceding *Organic Syntheses* preparation.

2. Acetone was obtained from J. T. Baker and used as received.

3. All reactions were performed in a 4-L jacketed reaction vessel (see photograph below). Temperature was controlled via circulating coolant through the vessel jacket. The submitters performed all reactions in standard round-bottomed glassware in a walk-in cold room with a temperature of 0 °C. The checkers utilized the jacketed reactor for convenience, but believe that standard glassware with ice-bath cooling could be used with equal success.



4. The core, 1,3,5-[*tris*-piperazine]-triazine, was prepared in two steps from the reaction of cyanuric chloride with *N*-(*tert*-butoxycarbonyl)-piperazine in tetrahydrofuran followed by deprotection using 6N hydrochloric acid in methanol. This procedure is described in the preceding preparation.

5. Sodium carbonate was purchased from J. T. Baker.

6. Monitoring the reaction mixture by TLC (SiO_2, 20:1 CH_2Cl_2:CH_3OH) confirmed that the reaction was complete. Furthermore, a

ninhydrin test showed that all of the 1,3,5-[*tris*-piperazine]-triazine had been consumed (this material appears as a purple spot at the baseline).

7. The mother liquor was concentrated to a volume of approximately 700 mL and the precipitated solids were collected. HPLC analysis showed this second crop to be almost entirely unreacted $C_3N_3[N(CH_2CH_2CH_2NHBoc)_2]Cl_2$ and was therefore discarded.

8. All solvent evaporations were performed using a rotary evaporator at a vacuum pressure of 75–200 mmHg.

9. Dichloromethane was obtained from J. T. Baker and used as received.

10. Separations were fast with sharp phase interfaces. The first aqueous wash was hazy, subsequent washes were clear. HPLC confirmed there was essentially no product in the aqueous washes. The submitters reported a thick emulsion during the extraction; this discrepancy may be related to their collection of a second crop of solids from the mother liquors (see Note 7).

11. Sodium chloride was purchased from J. T. Baker.

12. Anhydrous sodium sulfate was purchased from Sigma-Aldrich.

13. All products were dried in a vacuum oven at 38 °C, 200 mmHg pressure with a slow nitrogen sweep.

14. TLC and HPLC analysis of this material showed the presence of the desired product.

15. A small amount of the Step A product was purified for spectral characterization using column chromatography on silica gel eluting with 10% EtOAc:CH_2Cl_2 to give first the unreacted starting material $C_3N_3[N(CH_2CH_2CH_2NHBoc)_2]Cl_2$ as a white solid followed by (50:50) EtOAc:CH_2Cl_2 to give the product as a white solid.

16. The exact melting point for this compound could not be measured. The submitters report that the product formed a viscous oil, which stuck to wall of the melting tube at 87–90 °C and then become less viscous at 212–216 °C, where it proceeded to fall to the bottom of the melting tube and boil. The checkers also observed no sharp melting point, and found the material to gradually soften to a viscous oil at 112–118 °C.

17. The product has the following characteristics: TLC R_f = 0.28 (Silica Gel 60 F254, EMD Chemicals, Inc., 20:1 CH_2Cl_2:CH_3OH); IR (KBr pellet) cm^{-1}: 3375, 2976, 2931, 1713, 1571, 1539, 1493, 1437, 1390, 1367, 1248, 1167, 1081, 1041, 999, 983, 880, 801, 620, 465; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.44 (s, 54 H, C(C**H**$_3$)$_3$), 1.75 (m, 12 H, NCH$_2$C**H**$_2$), 3.08 (m, 12

H, C**H**$_2$NHBoc), 3.57 (m, 12 H, Boc-NC**H**$_2$), 3.82 (m, 24 H, C**H**$_2$, piperazine), 4.84 (br, 3 H, N**H**), 5.58 (br, 3 H, N**H**); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.0 (s, $NCH_2\mathbf{C}H_2$), 28.1 (s, $NCH_2\mathbf{C}H_2$), 28.6 (s, $C(\mathbf{C}H_3)_3$), 28.7 (s, $C(\mathbf{C}H_3)_3$), 37.0 (s, $\mathbf{C}H_2$NHBoc), 38.0 (s, $\mathbf{C}H_2$NHBoc), 42.9 (s, $\mathbf{C}H_2$), 43.1 (s, $\mathbf{C}H_2$), 43.6 (s, $\mathbf{C}H_2$, piperazine), 44.1 (s, $\mathbf{C}H_2$), 79.1 (s, $\mathbf{C}(CH_3)_3$), 79.5 (s, $\mathbf{C}(CH_3)_3$), 156.1 (s, **C**(O)), 156.4 (s, **C**(O)), 164.6 (s, C_3N_3), 165.2 (s, C_3N_3), 165.4 (s, C_3N_3), 169.6 (s, C_3N_3); HRMS (Thermo LTQ FT Ultra): Calcd for (M+H): 1660.8746. Found: 1660.87555. Anal calcd for $C_{72}H_{120}Cl_3N_{27}O_{12}$: C, 52.02; H, 7.28; N, 22.75; Cl, 6.40. Found: C, 52.14; H, 7.30; N, 22.63; Cl, 6.48.

18. Molar amount assumed based on a 100% yield in Step A.

19. Piperidine was purchased from Acros Chemical Co., Inc. and used as received.

20. Starting material and final product are resolved in the submitter's TLC system (SiO_2, 5% CH_3OH:CH_2Cl_2), but the intermediate mono- and bis-piperidine adducts are not distinguishable from product. The following HPLC system gives baseline resolution of starting material, product, and the mono- and bis-piperidine intermediates: Halo C18 column, 4.6 x 50 mm, 2.7 μm, 50 °C, 1.5 mL/min, 280 nm UV detection. Mobile phase: 95/5 0.5% $HClO_4$/acetonitrile, gradient to 5/95 $HClO_4$/acetonitrile over 3 minutes, isocratic hold for 4 min, gradient to 95/5 0.5% $HClO_4$/acetonitrile over 7 min. R_t of G1-$[N(CH_2CH_2CH_2NHBoc)_2]_6$-$Cl_3$ = 4.07 min; R_t of G1-$[N(CH_2CH_2CH_2NHBoc)_2]_6$-$Cl_2$ + $piperidine_1$ = 3.91 min; R_t of G1-$[N(CH_2CH_2CH_2NHBoc)_2]_6$-Cl + $piperidine_2$ = 3.76 min; R_t of G1-$[N(CH_2CH_2CH_2NHBoc)_2]_6$-$Piperidine_3$ = 3.59 min.

21. TLC analysis of the crude compound showed one spot under UV-lamp; however, after a ninhydrin stain a second spot was observed at the baseline corresponding to the presence of piperidine.

22. The checkers noted that if the crude product is dried overnight in a vacuum oven at this stage (38 °C, 200 mmHg, N_2-sweep), the material requires approximately twice as much dichloromethane to redissolve (ca. 20 mL/g). However, if it is air-dried, the solubility described in the current procedure is observed (10 mL/g). This suggests that during drying a less-soluble, anhydrous solid form is generated.

23. Hydrochloric acid was reagent-grade and obtained from Sigma-Aldrich.

24. After four extractions with 5% HCl, a ninhydrin stain confirmed the disappearance of piperidine.

25. Sodium hydroxide was purchased from Fisher Scientific.

26. The exact melting point for this compound could not be measured. The submitters report that the product started to decompose at 206–210 °C and turned brownish yellow. Then a liquid was observed at 210–214 °C, which later began to boil at 216 °C. The checkers also observed no sharp melting point, but observed a gradual softening of the solids from 75–100 °C, followed by a gradual change to a viscous oil from 110–122 °C.

27. The product has the following characteristics: TLC R_f = 0.36 (Silica Gel 60 $F_{254,}$ EMD Chemicals, Inc., 20:1 CH_2Cl_2:CH_3OH); IR (KBr pellet) cm^{-1}: 2975, 2931, 2853, 1717, 1530, 1487, 1434, 1366, 1293, 1249, 1173, 997; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.42 (s, 54 H, C(C**H**$_3$)$_3$), 1.56 (br, 12 H, C_5**H**$_{10}$N, β-H), 1.62 (br, 6 H, C_5**H**$_{10}$N, γ-H), 1.71 (br, 12 H, NCH_2C**H**$_2$), 3.06 (br, 12 H, C**H**$_2$NHBoc), 3.59 (br, 12 H, C**H**$_2$, Boc-NC**H**$_2$), 3.73 (br, 12 H, C_5**H**$_{10}$N, α-H), 3.80 (br, 24 H, C**H**$_2$, piperazine), 5.26 (br, 6 H, N**H**); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.1 (**C**$_5$H$_{10}$N, γ -C), 26.0 (**C**$_5$H$_{10}$N, β-C), 27.8 (s, NCH_2**C**H_2), 28.7 (s, C(**C**H_3)$_3$), 37.4 (s, **C**H_2NHBoc), 41.9 (**C**$_5$H$_{10}$N, α-C), 43.2 (s, Boc-N**C**H_2), 43.4 (s, Boc-N**C**H_2), 44.4 (s, **C**H_2, piperazine), 79.1 (s, **C**(CH_3)$_3$), 156.2 (s, **C**(O)), 165.1 (s, C_3N_3), 165.5 (s, C_3N_3), 166.1 (s, C_3N_3); HRMS (Thermo LTQ FT Ultra) [M+H] calcd for $C_{87}H_{150}N_{30}O_{12}$: 1808.2120. Found: 1808.20932. Anal. Calcd for $C_{87}H_{150}N_{30}O_{12}$: C, 57.78; H, 8.36; N, 23.24. Found: C, 57.45; H, 8.10; N, 22.90.

28. In a run performed on approximately 2/3 scale (50.3 g of the dichlorotriazine and 10.0 g of *tris*-piperazine-triazine), an 87% overall yield for the two steps was obtained.

Safety and Waste Disposal Information

All hazardous materials should be handled and disposed of in accordance with “Prudent Practices in the Laboratory”; National Academy Press; Washington, DC, 1995.

3. Discussion

In the past two decades, dendrimer syntheses have attracted the attention of numerous research groups worldwide.[2] Dendrimers are monodisperse macromolecules possessing a regular treelike array of

branching units. Dendrimers consist of a core unit, building blocks, and a large number of functional groups at the surface. Synthesizing monodisperse macromolecules demands a high level of synthetic control, which is achieved through stepwise fashion via a convergent or a divergent approach.[3] Because of their unique size and globular shape, dendrimers have potential uses in drug delivery, energy harvesting and conversion, catalysis, and optics.[4]

A variety of new dendrimers have been reported which incorporate a wide range of functionalities including ethers,[5] amides,[6] esters,[7] and alkynes[8]. Of the many examples of dendrimers that are described today, only five are commercially available. This limitation is due to the difficulties associated with producing large quantities. Not all of these materials are single chemical entities: some are mixtures. A further obstacle resides in the usage of sophisticated building blocks, and/or expensive chemical substances, and/or excess reagents, and/or complicated purification procedures. Our research is aimed at the development of an environmentally benign process and scaleable synthesis of a first generation (G1) melamine dendrimer that circumvent many of the barriers listed above.

The synthesis is performed in two steps by means of a divergent route, utilizing a "process friendly" solvent and without column chromatography. The building block, 2-[3,3'-di-(*tert*-butoxycarbonyl)-aminodipropylamine]-4,6-dichloro-1,3,5-triazine, is treated with 1,3,5-[*tris*-piperazine]-triazine in acetone-water and in presence of potassium carbonate to afford the G1-chloride intermediate. Subsequent treatment of the G1-chloride with excess piperidine affords the amino-functionalized G1 dendrimer in 81% overall yield. Preparation of both building blocks are described in the preceding *Organic Syntheses* procedure.

We have developed a simple and efficient strategy to produce multi-gram quantities of a G1-amine terminated dendrimer. This green and scalable synthesis can be extended to higher generations of dendrimers.[9]

1. Department of Chemistry, Texas A&M University, College Station, TX 77843.

2. (a) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. Angew. Chem. 1990, 102, 119-157. (b) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons*; Wiley-VCH Publishers: New York, NY, 2001. (c) Fréchet, J. M. J.; Tomalia, D. A.; *Dendrimers and Other*

Dendritic Polymers Molecules; Wiley-VCH Publishers: New York, NY, 2001. (d) Inoue, K. *Prog. Polym. Sci.* **2000**, *25*, 453-571. (e) Hecht, S.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 74-91.

3. (a) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J.* **1985**, *17*, 117-132. (b) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638-7647.

4. (a) Jiang, D.-L.; Aida, T. *Nature (London*) **1997**, *388*, 454-456. (b) Knapen, J. W. J.; Van der Made, A. W.; de Wilde, J. C.; Van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; Van Koten, G. *Nature (London*) **1994**, *372*, 659-663. (c) Percec, V.; Cho, C. G.; Pugh, C.; Tomazos, D. *Macromolecules* **1992**, *25*, 1164-1176. (d) Jansen, J. F. G. A.; de Brabander-Van den Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *266*, 1226-1229. (e) Hawker, C. J.; Fréchet, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2459-2469. (f) Tang, M.; Redemann, C. T.; Szoka, F. C. *Bioconjugate Chem.* **1996**, *7*, 703-714. (g) Malik, N.; Wiwattanapatapee, R.; Klopsch, R.; Lorenz, K.; Frey, H.; Weener, J. W.; Meijer, E. W.; Paulus, W.; Duncan, R. *J. Controlled Release* **2000**, *65*, 133-148.

5. Nlate, S.; Ruiz, J.; Sartor, V.; Navarro, R.; Blais, J. C.; Astruc, D. *Chem.-Eur. J.* **2000**, *6*, 2544-2553.

6. Brouwer, A. J.; Mulders, S. J. E.; Liskamp, R. M. J. *Eur. J. Org. Chem.* **2001**, 1903-1915.

7. Peng, Z.; Pan, Y.; Xu, B.; Zhang, J. *J. Am. Chem. Soc.* **2000**, *122*, 6619-6623.

8. Moore, J. S.; Xu, Z. *Macromolecules* **1991**, *24*, 5893-5894.

9. (a) Crampton, H.; Hollink, E.; Perez, L. M.; Simanek, E. E. *New J. Chem.***2007**, *31*, 1283-1290. (b**)** Chouai, A.; Simanek, E.E.; *J. Org. Chem.* **2008**, *73*, 2357-2366**.**

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

2-[3,3'-Di-(*tert*-butoxycarbonyl)-aminodipropylamine]-4,6-dichloro-1,3,5-triazine; 12-Oxa-2,6,10-triazatetradecanoic acid, 6-(4,6-dichloro-1,3,5-triazin-2-yl)-13,13-dimethyl-11-oxo-, 1,1-dimethylethyl ester; (947602-03-1)

1,3,5-[Tris-piperazine]-triazine: 1,3,5-Triazine, 2,4,6-tri-1-piperazinyl-; (19142-26-8)

G1-[$N(CH_2CH_2CH_2NHBoc)_2]_6$-$Cl_3$; (1016650-75-1)

G1-[$N(CH_2CH_2CH_2NHBoc)_2]_6$-$Piperidine_3$; (1016650-76-2)

Eric E. Simanek was born in 1969 in Tuscola, IL. He obtained a B.S. in Chemistry in 1991 from the University of Illinois at Urbana-Champaign while working in the laboratories of the late Dr. Kenneth L. Rinehart, Jr. After completing doctoral studies with Dr. George M. Whitesides at Harvard University in 1997, he joined Dr. Chi-Huey Wong's laboratory at The Scripps Research Institute. Since joining Texas A&M University in 1998, he has risen through the ranks to Professor of Chemistry. His interests lie in drug delivery and K-20 education.

Abdellatif Chouai was born in 1971 in Morocco. He earned a B.S. in Chemistry in 1995 from the University of Sidi Mohamed Ben Abdellah, Morocco, and a Ph.D. in Organic Chemistry from University of Houston in 2003 under Dr. Randolph P. Thummel. He joined Dr. Kim R. Dunbar's group at Texas A&M University as a postdoctoral research associate where he worked on reversible DNA biosensors complexes and bimetallic complexes as photodynamic therapy agents. He then moved to a research scientist position in 2006 in Dr. Simanek's laboratory. His research focused on an industrial scale production of triazine-based dendrimers and application in drug delivery. Currently, Dr. Chouai holds a professional development chemist position with BASF Corporation.

Vincent J. Venditto was born in 1981 in Philadelphia, PA. He earned a B.S. in Chemistry from Gettysburg College in 2003 and began working in the laboratory of Dr. Martin W. Brechbiel in the Radioimmune and Inorganic Chemistry Section of the National Cancer Institute within the NIH. After two years at the NIH, Vincent joined Dr. Simanek's laboratory at Texas A&M University to pursue a graduate degree in chemistry. His graduate work focuses on the synthesis of triazine-based dendrimers as drug carriers for a range of therapeutic applications.

Brian Vanderplas was born and raised in St. Louis, Missouri. Following a tour of duty in the US Army he attended Southwest Missouri State University where he received a B.S. in Chemistry in 1983. He was then employed by Sigma Chemical Company in St. Louis as a Production Chemist, and in 1986 moved to Pfizer Global Research & Development in Groton, Connecticut where he is currently a Senior Scientist in the Chemical Research & Development group. He is a 2008 recipient of the ACS Technical Achievements in Organic Chemistry Award.

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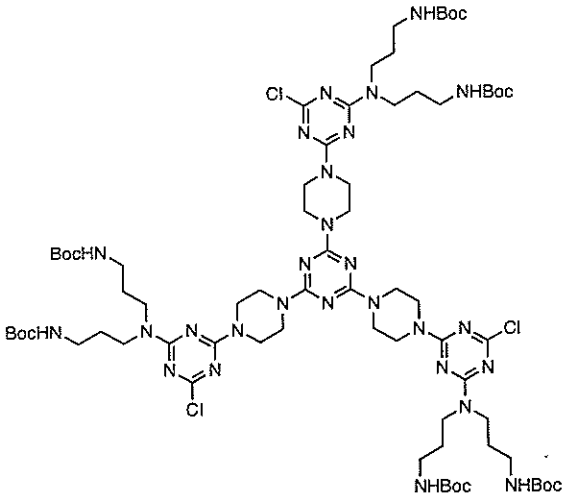

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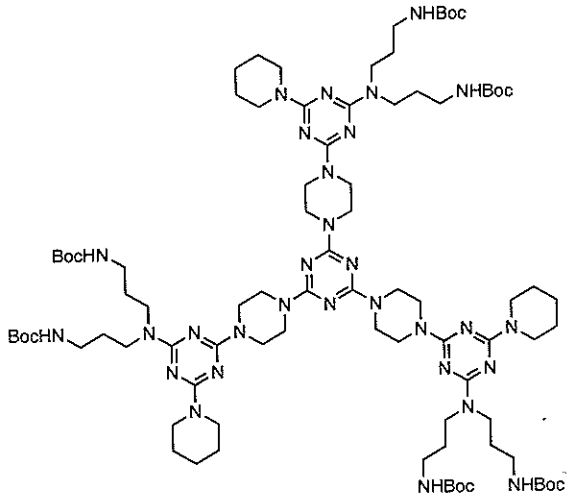

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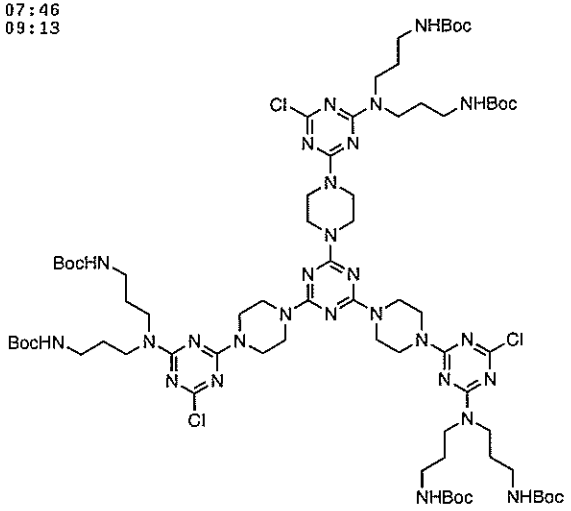
FT size 32768
Total time 1 minute



Filename: 113697-131-1_h1.fid

unityb: 080710

GAINS_SAMPLE_REFERENCE: 113697-131-1
GAINS_USER_ID: vanderplas
GAINS_INSTRUMENT: unityb
GAINS_EXPERIMENT_TIME: 07/10/2008 15:07:46
GAINS_END_TIME: 07/10/2008 15:09:13

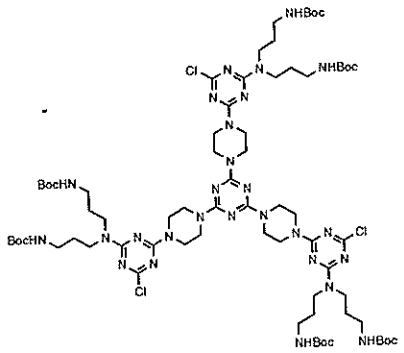
Org Syn #3182 Step A

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
File: 113697-131-1_h1
UNITYplus-500

PULSE SEQUENCE
Pulse 45.0 degrees
Acq. time 2.410 sec
Width 6799.3 Hz
16 repetitions
OBSERVE H1, 399.9506330 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 minute

Filename: 080710/113697-131-1_h1.fid

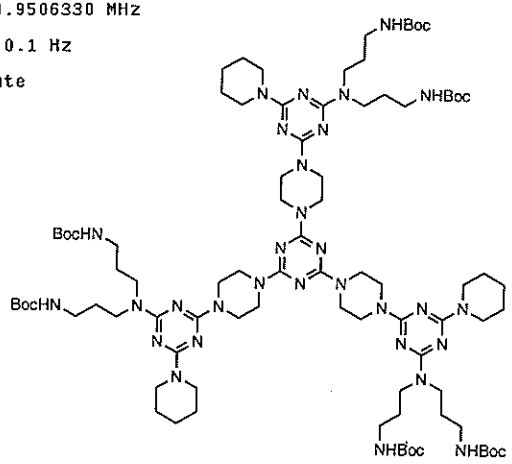
unityb



GAINS_SAMPLE_REFERENCE: 113697-149-3
GAINS_USER_ID: vanderplas
GAINS_INSTRUMENT: unityb
GAINS_EXPERIMENT_TIME: 07/10/2008 12:59:30
GAINS_END_TIME: 07/10/2008 13:01:00

Org Syn #3182 Step B

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
File: 113697-149-3_h1
UNITYplus-500
PULSE SEQUENCE
Pulse 45.0 degrees
Acq. time 2.410 sec
Width 6799.3 Hz
16 repetitions
OBSERVE H1, 399.9506330 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 minute



Filename: 113697-149-3_h1.fid
unityb: 080710

7.246
5.282
5.255
3.805
3.738
3.725
3.589
3.058
2.143
1.717
1.703
1.689
1.622
1.565
1.556
1.467
1.419
1.368
1.318
1.259

14 12 10 8 6 4 2 -0 ppm

3.16 39.93 56.92

GAINS_SAMPLE_REFERENCE: 113697-149-3
GAINS_USER_ID: vanderplas
GAINS_INSTRUMENT: unityb
GAINS_EXPERIMENT_TIME: 07/10/2008 12:59:30
GAINS_END_TIME: 07/10/2008 13:01:00

Org Syn #3182 Step B

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
File: 113697-149-3_h1
UNITYplus-500

PULSE SEQUENCE
Pulse 45.0 degrees
Acq. time 2.410 sec
Width 6799.3 Hz
16 repetitions
OBSERVE H1, 399.9506330 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 minute

Filename: 080710/113697-149-3_h1.fid

unityb