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Synthesis of Anthropomorphic Molecules: The NanoPutians

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Described here are the synthetic details en route to an array of 2-nm-tall anthropomorphic molecules in monomeric, dimeric, and polymeric form. These anthropomorphic figures are called, as a class, NanoPutians. Using tools of chemical synthesis, the ultimate in designed miniaturization can be attained while preparing the most widely recognized structures: those that resemble humans.

1. Introduction

Using tools of chemical synthesis, the ultimate in designed miniaturization can be attained. Beyond the molecular-sized domain there is no conceivable entity upon which to tailor architectures that could have programmed cohesive interactions between the individual building blocks. It is at this size region that synthetic chemists have been inherently captivated; however, their fascination is rarely shared by the layperson. The masses view chemical structures as difficult-to-grasp abstractions formulated by complex algorithms, except when molecules resemble macroscopic objects such as C_{60}. Arguably, the most widely recognized structures are those that resemble humans.[1] Here we describe the synthetic details en route to an array of 2 nm-tall anthropomorphic molecules, both in monomeric and polymeric form.[2,3]

Accepted common names such as "cubane", "dodecahedrane", "housane", and "chair-form" describe the constitution or conformation of cycloalkanes while "buckminsterfullerene" expresses chemical structure by its relation to the artisan that built macroscopic analogues. Utilizing such a license, the anthropomorphic molecules here are dubbed, as a class, NanoPutians, following the lead of the Lilliputians in Jonathan Swift's classic, *Gulliver's Travels*. More descriptive names follow here for each molecule type. Likewise, references to "head", "tail", "northwest region", and "warhead", for instance, are used by synthetic chemists to describe moieties or functions within a target molecule. In the same vein, we extend the concept to body-part-like descriptions such as "head", "neck", and "legs". Furthermore, realizing that many molecule types, for example, terpenes, are routinely drawn in nonequilibrium conformations to enhance their rapid cognitive classification, nonequilibrium conformations are shown here for some structures. However, the liberties we take with the nonequilibrium conformational drawings are only minor when representing the main structural portions; conformational license is only used, in some cases, with the NanoPutians' head dressings.

2. Results and Discussion

2.1. Synthesis of NanoKid. The first of the NanoPutians was prepared via a separate synthesis of the top and bottom body-portions followed by adjoining at the "waist", thereby constituting a convergent synthetic approach. The top-half was made as shown in Scheme 1.

1,4-Dibromobenzene was iodinated in good yield.[4] 3,3-Dimethylbutyne was then coupled to **1** to give **2**. Formylation[5] of **2** was accomplished by lithium−halogen exchange followed by quenching with DMF to afford the aldehyde **3**. The aldehyde was protected as the acetal using 1,2-ethanediol in a presence of a catalytic amount of *p*-toluenesulfonic acid with azeotropic removal of the water via a Dean−Stark trap. Attempts to couple **4** to alkynes (vide infra) gave a low yield (<10%) of the desired products due to the poor reactivity of the bromoarene in the presence of the sterically encumbering ortho moiety. The bromide was therefore exchanged with an iodide by lithium−halogen exchange and quenching with 1,2-diiodoethane to afford **5** as the top-body portion.

For the preparation of the lower-body segment, nitroaniline was brominated to afford **6** that was further converted to the diazonium salt and reduced to remove the diazo moiety (Scheme 2). Conversion of the nitro group to the amine afforded **8**.[6] Sandmeyer reaction was then used to make the diazonium salt followed by iodination[7] to afford the dibromoiodobenzene **9**. This latter compound was coupled to trimethylsilylacetylene (TMSA) via a Pd/Cu mixed catalyst[8] to give **10**. Analogous coupling of the dibromoarene **10** to 2 equiv of 1-pentyne afforded **11**. Compound **11** was then desilylated in

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(1) Hoffmann, R.; Laszlo, P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1.

(2) Chanteau, S. H.; Ruths, T.; Tour, J. M. *J. Chem. Educ.* **2003**, *80*, 395−400.

(3) An education outreach program has been established based on 3-D animations of anthropomorphic figures called NanoKids. See: http://nanokids.rice.edu.

(4) Harold, H.; Harada, K.; Du, C.-J. F. *J. Org. Chem.* **1985**, *50*, 3104.

(5) Meegalla, S. K.; Rodrigo, R. *J. Org. Chem.* **1991**, *56*, 1882.

(6) Garden, S. J.; Torres, J. C.; Ferreira, A. A.; Silva, R. B.; Pinto, A. C. *Tetrahedron Lett.* **1997**, *38*, 1501.

(7) Harold, H.; Vinod, T. K. *J. Org. Chem.* **1991**, *56*, 5630.

(8) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467.

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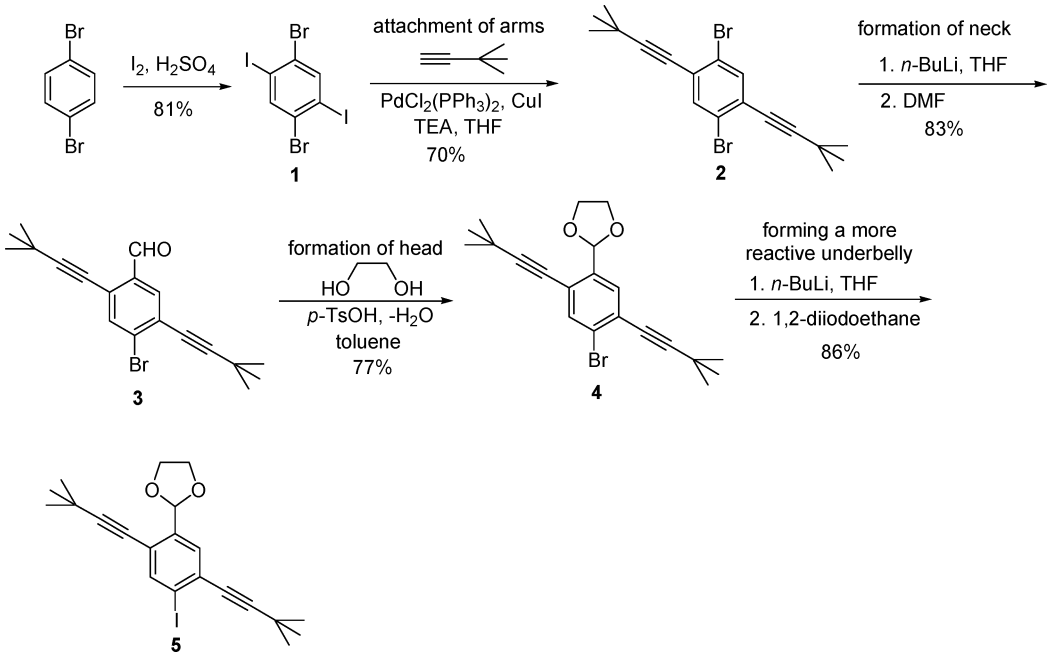
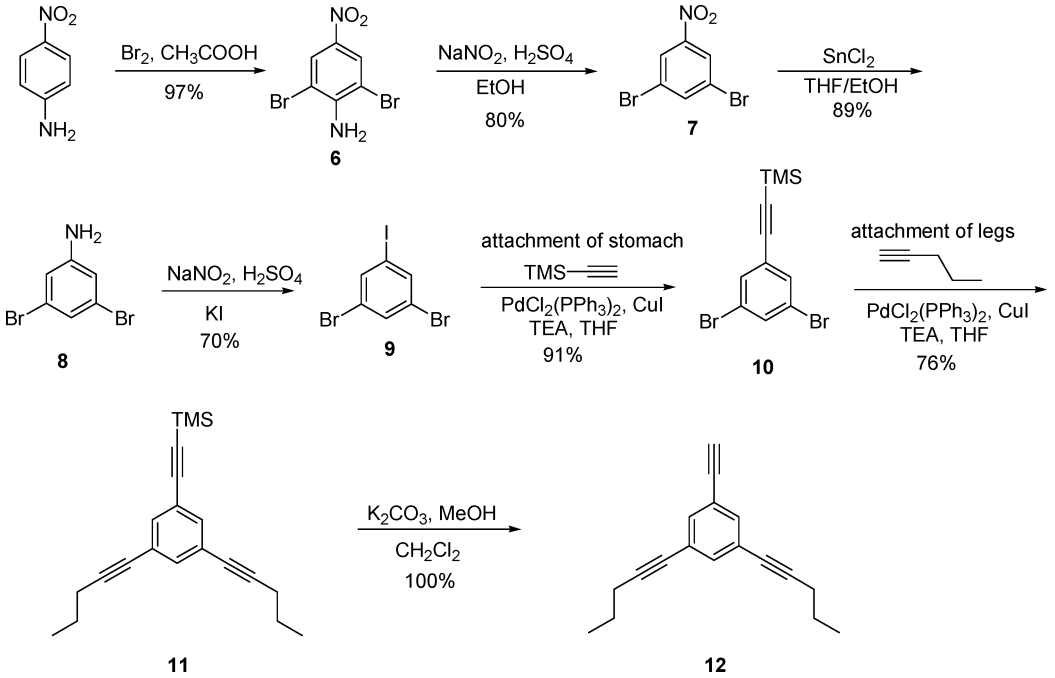
SCHEME 1. Synthesis of a NanoPutian's Upper Body[a]



[a] TEA = triethylamine.

SCHEME 2. Synthesis of NanoPutian's Lower Body



alkaline methanol to yield the lower half, **12**, of the NanoPutian.

The last step in the synthesis involves the coupling of the top and bottom portions. This was accomplished by once again using the Pd/Cu-catalyzed protocol[8] to afford NanoKid (**13**), each with the structure shown in Scheme 3.

2.2. Synthesis of the NanoProfessional NanoPutians. NanoKid (**13**) can now serve as the "progenitor" of the NanoProfessionals.

A facile procedure using microwave irradiation[9−12] was used for the head-conversion reactions. NanoKid (**13**) with an excess of a 1,2- or 1,3-diol, in the presence of a catalytic amount of *p*-toluenesulfonic acid, was irradiated for a few minutes, after which time a new NanoPutian was generated (Figure 1 and Table 1).

This includes NanoAthlete (**14**), NanoPilgrim (**15**), NanoGreenBeret (**16**), NanoJester (**17**), NanoMonarch

(9) A Sharp Carousel microwave oven (model RC510C) was used
(10) Moghaddam, F. M.; Sharifi, A. *Synth. Commun.* **1995**, *25*, 2457.
(11) Kalita, D. J.; Borah, R.; Sarma, J. C. *Tetrahedron Lett.* **1998**, *39*, 4573.
(12) Perio, B.; Dozias, M.-J.; Jacquault, P.; Hamelin, J. *Tetrahedron Lett.* **1997**, *38*, 7867.

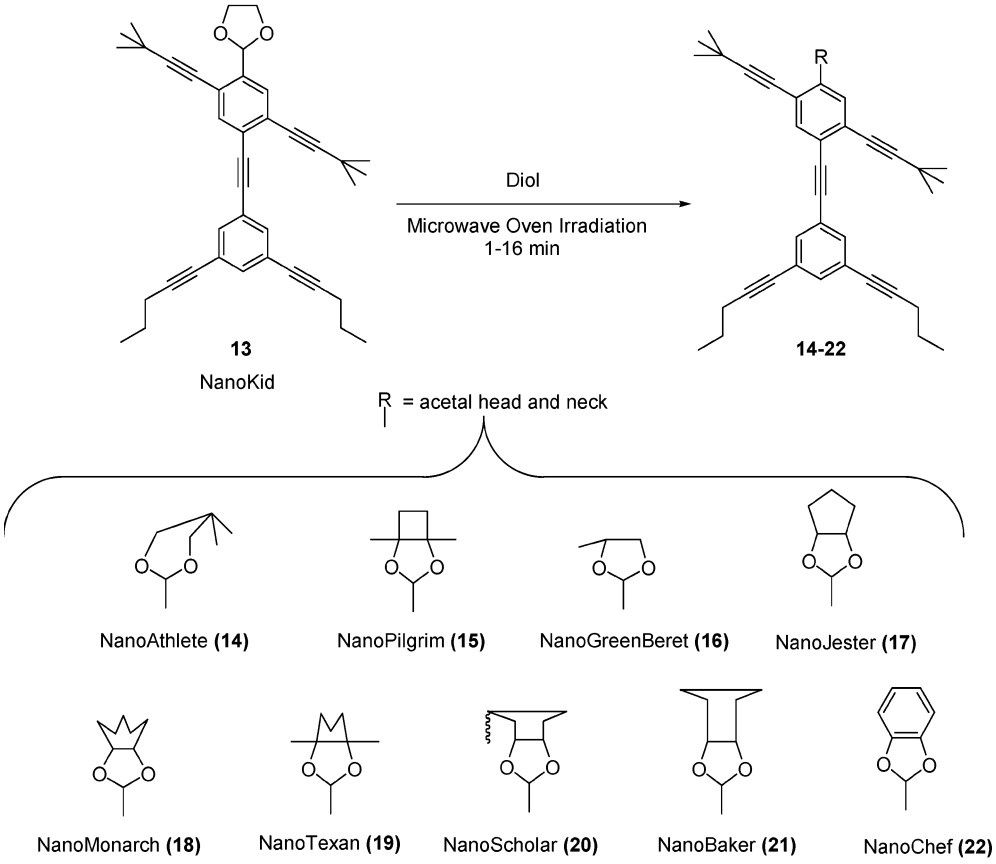
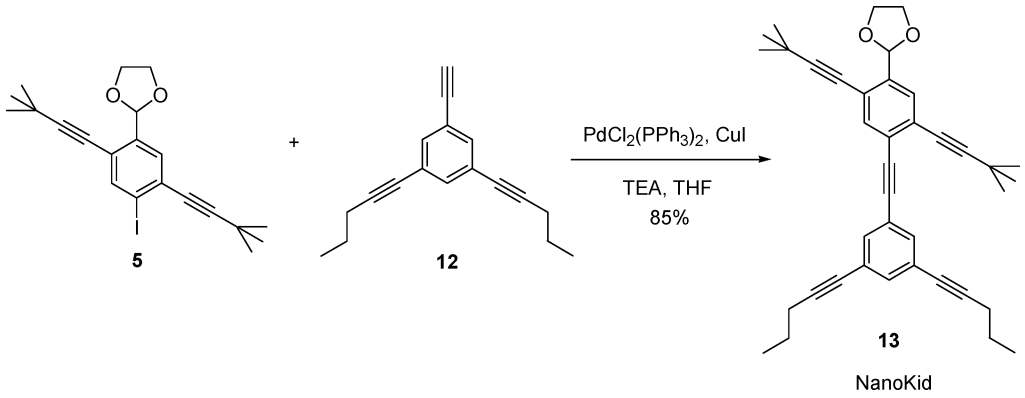


FIGURE 1. NanoKid (**13**) was treated with a series of 1,2- or 1,3-diols in the presence of catalytic acid and microwave oven-irradiation to effect acetal exchange and hence head conversion to afford a series of new NanoPutians, termed NanoProfessionals. See Table 1 for the specific diol used and the yield for each head conversion.

SCHEME 3. Coupling of the Upper and Lower Body Segments To Complete the Synthesis of the NanoPutian, NanoKid (13)

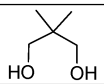
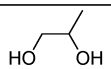
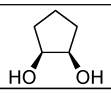
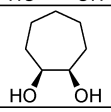
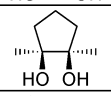
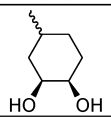
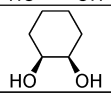
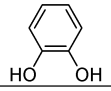


(**18**), NanoTexan (**19**) NanoScholar (**20**), and NanoBaker (**21**). By using this microwave irradiation method, longer reaction times are obviated. Decomposition resulted when the NanoChef (**22**) synthesis was attempted under the microwave conditions (Table 1, entry 9). This was probably due to phenol−aldehyde-like polymerization involving the electron-rich catechol and the aldehyde-based oxonium intermediate. Rather, a procedure employing catechol and chlorotrimethylsilane was efficacious,[13] albeit low yielding. The NanoPutians were characterized using spectroscopic and mass spectrometric analysis.

In a separate combinatorial experiment, we sought to make the entire NanoPutian population at once by starting with NanoKid (**13**) and adding all the appropriate diols (except catechol) in a single flask to generate **14**−**21** in one microwave oven reaction. Indeed, the conversion proceeded as planned in 4 min and the formation of **14**−**21** was confirmed by mass spectrometric analysis of the reaction mixture where the mass of each NanoPutian was detected. However, since a few of the figures have the same molecular weight, further confirmation was obtained using ^{1}H NMR peak matching of the mixture against the individual NanoPutian spectra that had previously been obtained.

(13) Chan, T. H.; Brook, M. A.; Chaly, T. *Synthesis* **1983**, 203.

TABLE 1. Conversion of NanoKid (13) into the NanoProfessionals 14−22 Using Microwave Irradiation in the Presence of Selected Diols

Entry	Diol[a]	Equiv. of Diol	Irradiation (min)	NanoPutian	Yield (%)	Diastereomeric ratio[b]
1		20	7	**14**	91	---
2		11	13	**15**	25[d]	55 : 45
3		100	1	**16**	85	1 : 1
4		20	7	**17**	94	10 : 3
5		5	10	**18**	87	10 : 3
6		9	9	**19**	24[d]	3.2 : 1
7		20	16	**20**	90	17 : 12 : 12 : 9
8		15	10	**21**	84	1.6 : 1
9[c]		22	---	**22**	9[d]	---

[a] The cyclic diols for entries 5 and 7 were prepared by catalytic OsO_4 dihydroxylation of the corresponding cycloalkenes. The diols for entries 2 and 6 were prepared by reductive pinacol coupling of the 1,4- and 1,5-diketones with SmI_2 and $Mg/TiCl_4$, respectively. [b] Ratios determined by ^1H NMR using the diastereotopic acetal protons that were consistently well-separated. [c] NanoChef (**22**) was synthesized using chlorotrimethylsilane (5 equiv) in dichloromethane. [d] Yields based on recovered NanoKid (**13**) for entries 2, 6, and 9 were 33%, 58%, and 20%, respectively.

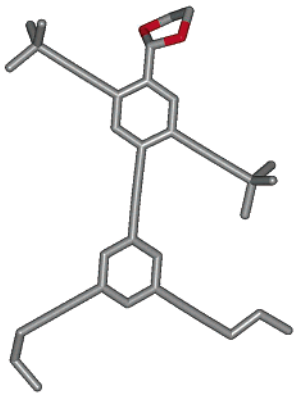


FIGURE 2. NanoKid (**13**) in its energy-minimized conformation that was determined using molecular mechanics (Spartan).

The stick figure drawn for **13** in Scheme 3 is similar to a molecular mechanics energy-minimized form of **13** in Figure 2. The rigidity of the backbone molecular structure causes the conformation to be quite similar to the visually recognizable form drawn.

2.3. Synthesis of the NanoToddler. Following the same route as for NanoKid (**13**), but using a truncated lower half (**24**), NanoToddler (**25**) was synthesized (Scheme 4).

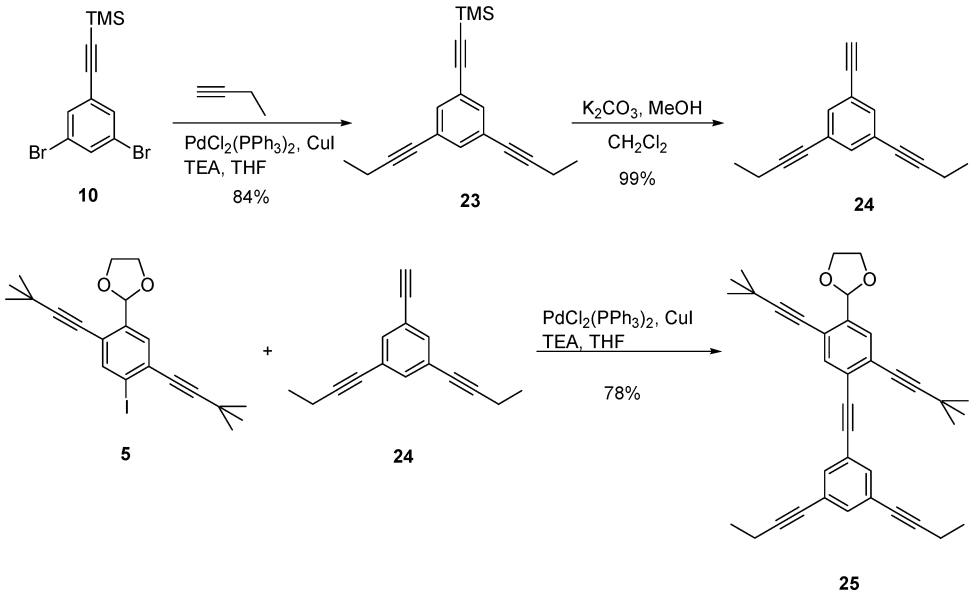
1-Butyne was coupled to **10** to give **23** in good yield, followed by deprotection with potassium carbonate and methanol. Compounds **5** and **24** were then coupled to afford the NanoToddler **(25)** in 78% yield.

2.4. Synthesis of a Standing Array. As described in Scheme 5, 3-butyn-1-ol was converted to the mesylate[14] **26** and then converted to the thiolacetate **27** using the cesium salt.[15] The free alkyne **27** was then coupled[8] to **10** to furnish **28**. The trimethylsilyl group was removed, and then the resulting free alkyne **29** was coupled to **5**. The NanoKid with protected thiol feet, **30**, was obtained then permitted to self-assemble on a gold surface (Figure 3).

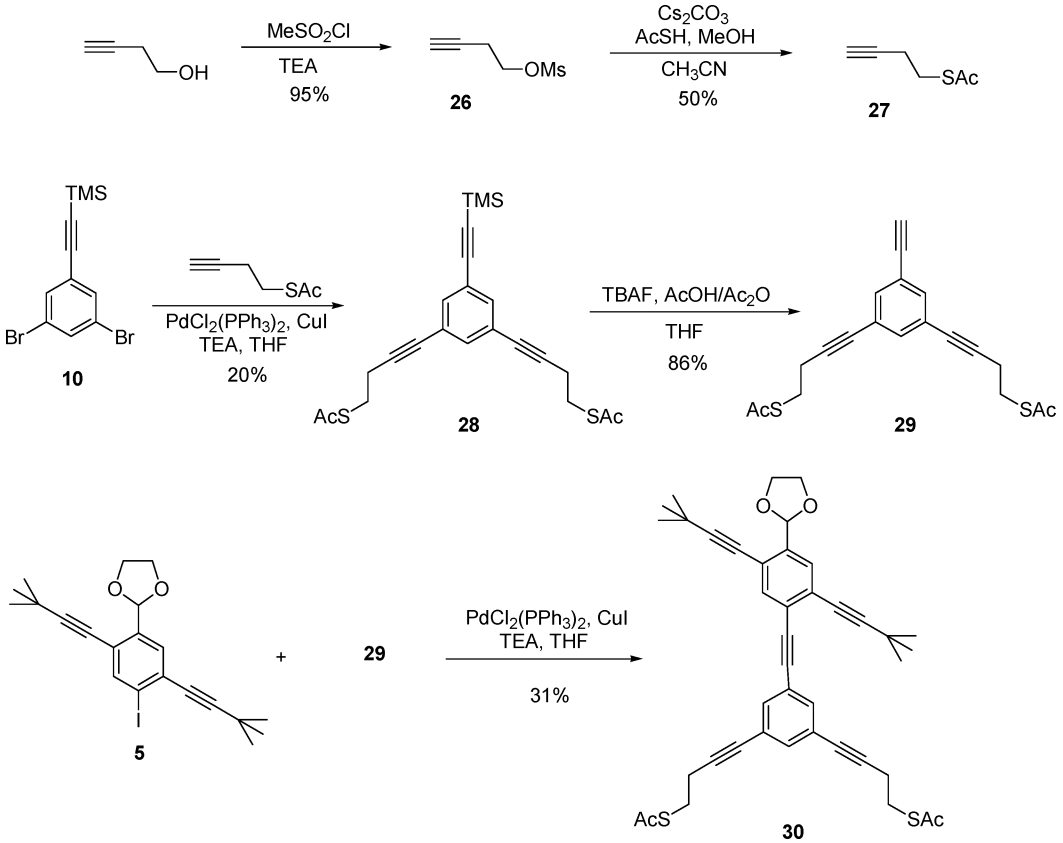
The acetyl protecting groups were removed by a solution of ammonium hydroxide in THF to give the free thiols or thiolates. A gold-plated substrate (Si/Cr/Au) was then dipped into this solution, and after incubating for 4 days, the resultant surface was rinsed and the thickness was measured by ellipsometry. This compound formed a

(14) Journet, M.; Rouillard, A.; Cai, D.; Larsen, R. D. *J. Org. Chem* **1997**, *62*, 8630.
(15) Kellogg, R. M.; Strijtveen, B. *J. Org. Chem.* **1986**, *51*, 3664.

SCHEME 4. Synthesis of NanoToddler (25)



SCHEME 5. Synthesis of the NanoKid with Thiol Feet, in Protected Form, To Be Used as Surface Adhesion Moieties



self-assembled monolayer (SAM) with an ellipsometrically measured thickness of 1.97 nm compared to a calculated thickness of 2.11 nm along the surface normal; the difference was indicative of the routinely observed sp^3-sulfur hybridization and intermolecular interaction-induced tilt angle from the surface normal.

2.5. Synthesis of NanoBalletDancers. Scheme 6 outlines the synthesis of the NanoBalletDancers. 2,5-Dibromoaniline was diiodinated.[16] The resulting aniline **31** was then diazotized and reduced. Compound **32** was coupled to 3,3-dimethylbutyne to furnish **33**, which was then treated with *tert*-butyllithium and DMF to afford the aldehyde. This reaction is not chemoselective as it yields equal amounts of the two aldehyde products, **34** and **35**. After separation on silica gel, **34** was protected with ethylene glycol to give **36**.

(16) Wilson, J. G.; Hunt, F. C. *Aust. J. Chem.* **1983**, *36*, 2317.

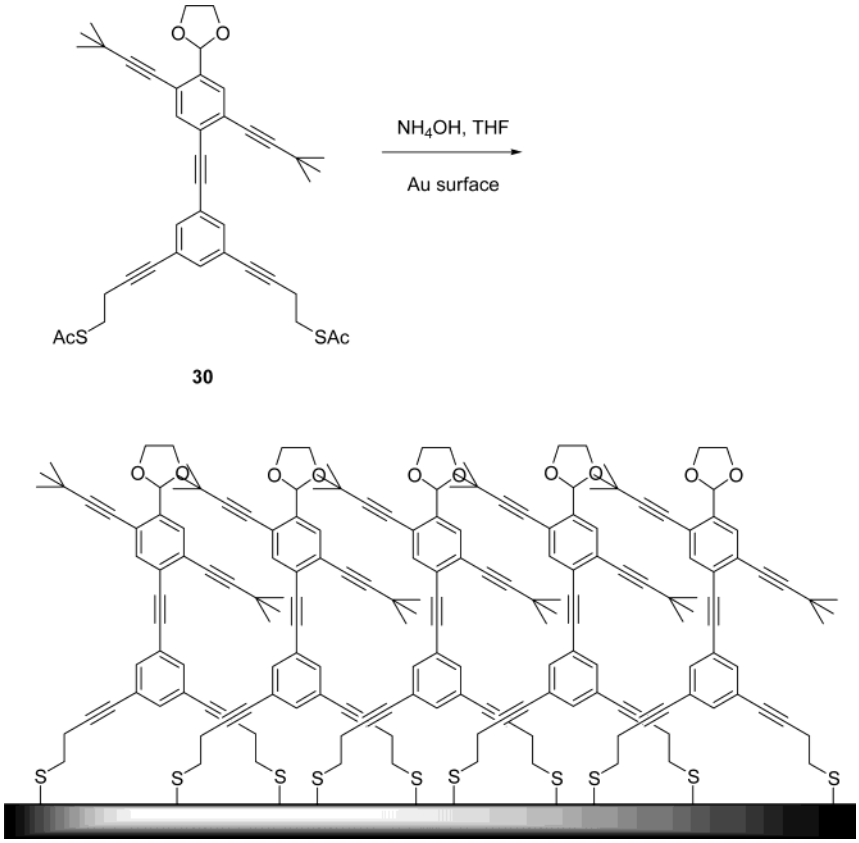
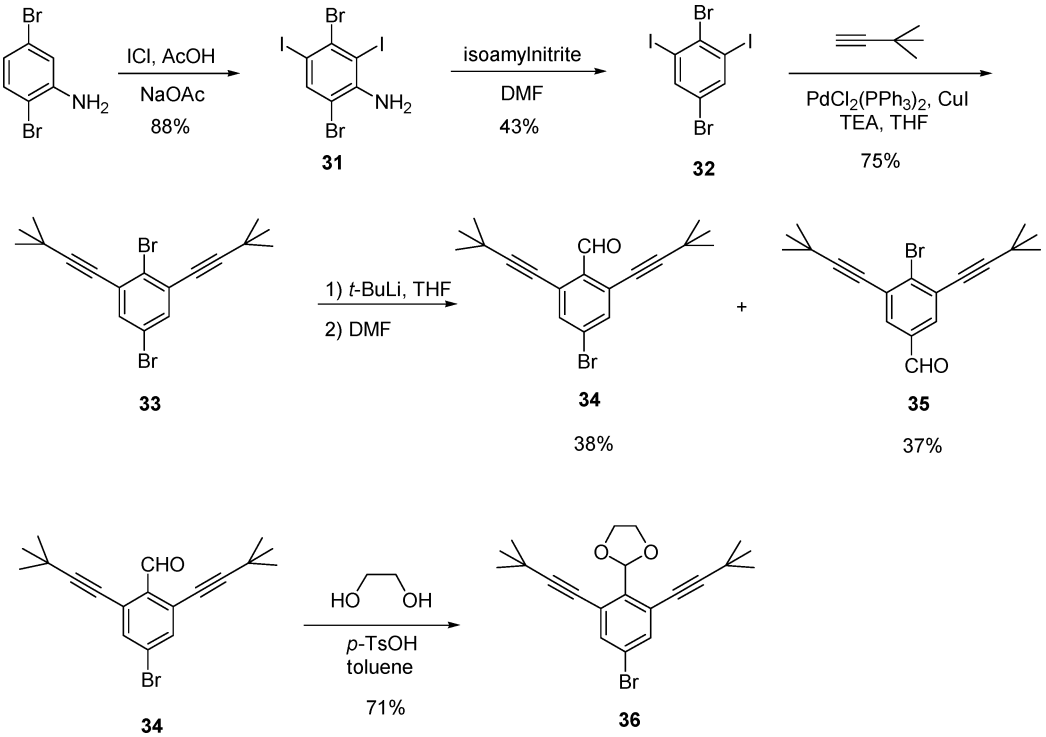


FIGURE 3. Self-assembly of **30** on a gold surface. Surface packing is greater than represented here since monolayer coverage was achieved.

SCHEME 6. Synthesis of the NanoBalletDancers' Upper Body

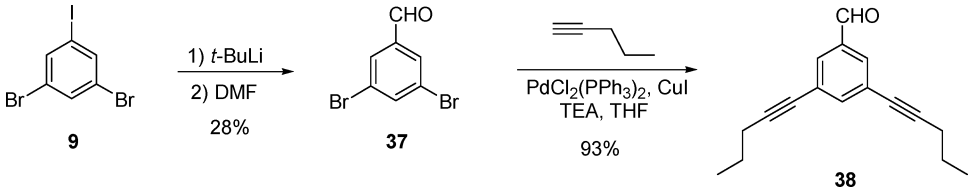


The bottom half was obtained by formylation of dibromoiodobenzene **(9)** to give **37** (Scheme 7). Activation of the bromides by the aldehyde for the Sonogashira[8] coupling permitted an excellent yield in the cross-coupling to afford **38**.

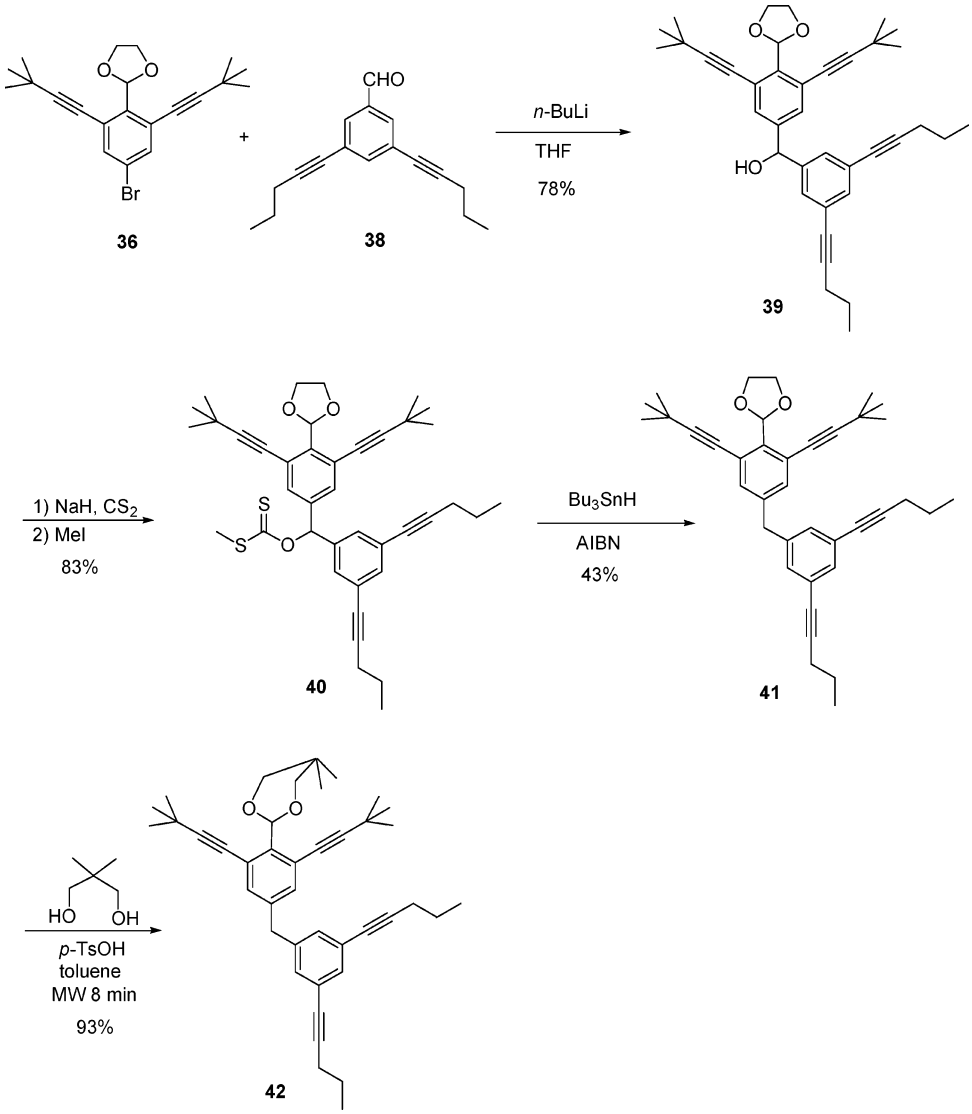
Compound **36** was lithiated and quenched with the aldehyde **38** to give the alcohol **39** (Scheme 8). Following a procedure by Hart,[17] the alcohol was converted to the

(17) Hart, D. J.; Kanai, K. *J. Org. Chem.* **1982**, *47*, 1555.

SCHEME 7. Synthesis of the NanoBalletDancers' Lower Body



SCHEME 8. Last Synthetic Steps toward the NanoBalletDancers



xanthate **40**. Reduction with tri-*n*-butyltin hydride in the presence of a catalytic amount of AIBN afforded the NanoBalletDancer **41** in fair yield. The synthesis of a second dancer was carried out by microwave-induced acetal exchange to furnish the NanoBalletDancer **42**.

2.6. Synthesis of a NanoPutian Chain. In an effort to unite the NanoPutians into an extended "hand-holding" chain, an AB-polymer target was sought (Figure 4).

The synthesis of the NanoPutians with "hand" moieties for the chain starts with the coupling of dibromodiiodobenzene (**1**) to the protected alkyne **43** (Scheme 9) (obtained by treatment of 3-butyn-1-ol with *tert*-butyldimethylsilyl chloride) to afford **44** in excellent yield. As before, the aldehyde moiety was added via lithiation followed by quenching with DMF to furnish **45**.

Sonogashira[8] coupling of the aldehyde **45** with the lower body half **12** was accomplished in excellent yield to afford **46** (Scheme 10). Acetal formation using the conventional method of azeotropic removal of water with a Dean−Stark trap gave a poor yield of 6%. However, using chlorotrimethylsilane[13] followed by the deprotection of the alcohols using TBAF furnished **47**, the hydroxyl-tipped NanoKid, in 36% over the two steps. Some removal of the TBS-protecting group occurred in the first step. Compound **47** appears to be sensitive to moisture and possibly light; hence, it should be used immediately or stored appropriately. Using the same procedure, the

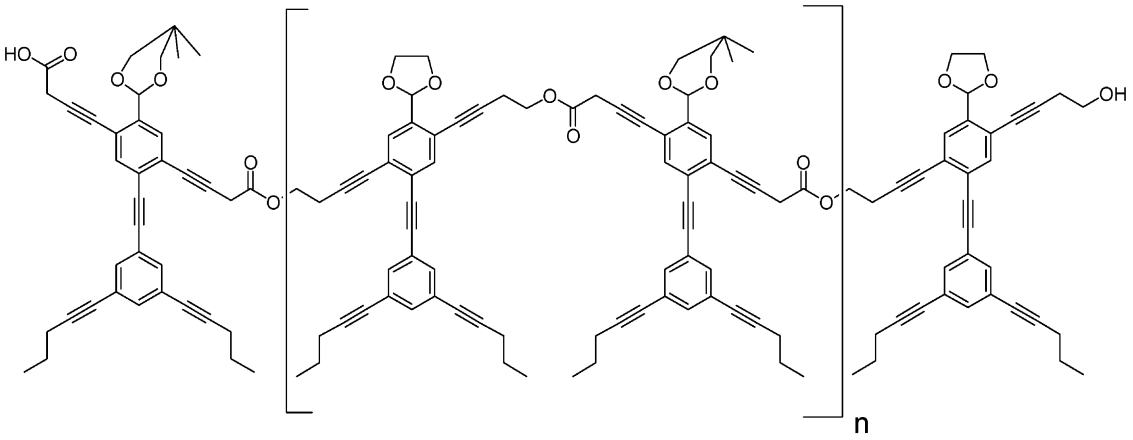
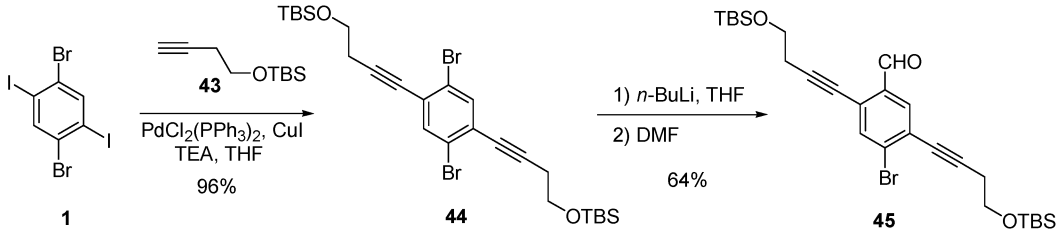


FIGURE 4. AB-polymer configuration of the NanoPutian chain.

SCHEME 9. Synthesis of the Upper Part of the NanoPutian Chain



aldehyde **46** was converted to **48**, the hydroxyl-tipped NanoAthlete, in good yield. Here again, a majority of the TBS protecting groups were removed in the acetalization step. To have an ester linkage between **47** and **48**, one of the two compounds needed to be oxidized. However, several attempts to oxidize the alcohols failed to cleanly afford the diacid. To circumvent the oxidation problem, the structure of the target polymer was modified; the ester linkage was replaced by a carbonate moiety (Scheme 11).

Following a procedure by Konakahara,[18] the *p*-nitrophenylchloroformate (**49**) was synthesized using diphosgene and Hünig's base. This chloroformate was then coupled to the alcohol **48** to give **50** in very good yield.[19−22] Finally, by reaction with **47**, three compounds were obtained. The dimers **51** and **52** were afforded in 21% and 23% yield, respectively, although they could not be conclusively distinguished between each other by NMR. The third compound was the polymer **53**. The regioisomeric pairs of hetero-dimers have differing arm directions. If we let a dash, "−", be the arrangement of arms within a single NanoPutian while the double-headed arrow, "↔", is the bonding pattern between any two NanoPutians, then the arm directions in these products are as follows: **51** is down−up↔up−down, **52** is up−down↔up−down, and AB-polymer **53** consists of three regioisomeric bonding patterns, namely down−up↔up−down, up−down↔up−down, and up−down↔down−up (Scheme 11). In **51** there is a mirror plane between the two parts of the dimer (except the heads). In **52**, there is an axis of symmetry down the middle of the dimer (except for the heads). **51** (less polar) and **52** were the only two non-baseline spots by TLC using 1:1 EtOAc/hexane. Compounds **51** and **52**, after flash chromatography, had $M_n = 775$ and 745 with $M_w = 800$ and 765, respectively, by size-exclusion chromatography (SEC) relative to polystyrene. Their actual molecular weights of 1130.5 were confirmed by mass spectrometry (MALDI) for each. The silica gel chromatographic baseline material consisted of higher oligomers and polymers which were then flushed from the chromatography column using EtOAc. LDI-MS showed a range of peaks centered around 47 500 which corresponds to the 42-mer, while the SEC showed **53** to have $M_n = 23\,500$ and a $M_w = 36\,600$, relative to polystyrene.

Summary

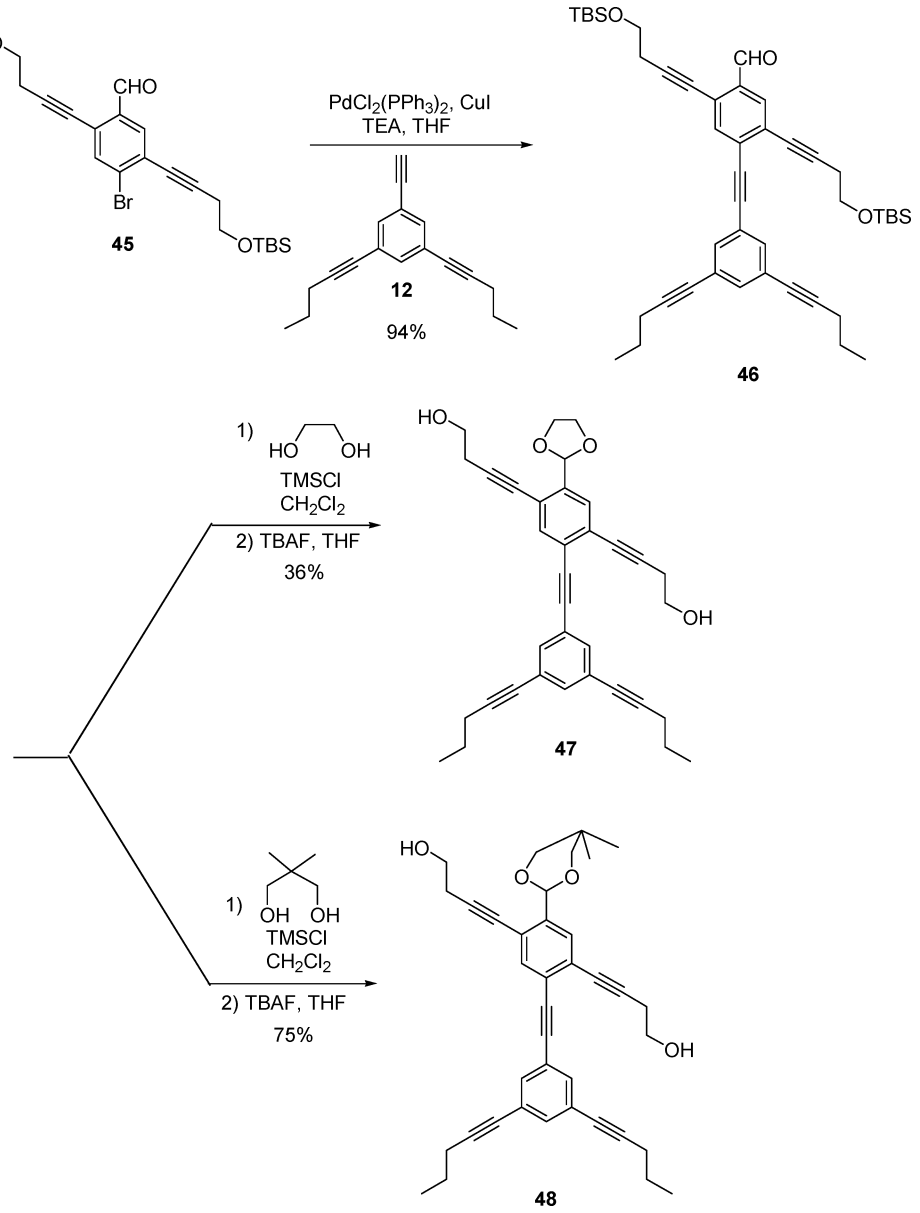
In conclusion, a series of monomeric, dimeric, and polymeric anthropomorphic molecules have been synthesized. These anthropomorphic entities are dubbed NanoPutians, as a class. Furthermore, they are assigned common names based on their individual anthropomorphic designs. These represent the ultimate in anthropomorphic design miniaturization.

Experimental Section

2,5-Bis(3,3-dimethylbutynyl)-1,4-dibromobenzene (2). See the Pd/Cu general procedure (Supporting Information). To a solution of 2,5-dibromo-1,4-diiodobenzene (4.29 g, 8.79 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.379 g, 0.541 mmol), and copper(I) iodide (0.206 g, 1.08 mmol) in

(18) Konakahara, T.; Ozaki, T.; Sato, K.; Gold, B. *Synthesis* **1993**, 103.
(19) Castano, A. M.; Mendez, M.; Ruano, M.; Echavarren, A. M. *J. Org. Chem* **2001**, *66*, 589.
(20) Molander, G. A.; Quirmbach, M. S.; Silva, L. F.; Spencer, K. C.; Balsells, J. *Org. Lett.* **2001**, *3*, 2257.
(21) Lee, C. B.; Chou, T.-C.; Zhang, X.-G.; Wang, Z.-G.; Kuduk, S. D.; D., C. M.; Stachel, S. J.; Danishefski, S. J. *J. Org. Chem* **2000**, *65*, 6525.
(22) Hanazawa, T.; Okamoto, S.; Sata, F. *Org. Lett.* **2000**, *2*, 2369.

SCHEME 10. Synthesis of the NanoPutians for the Chain

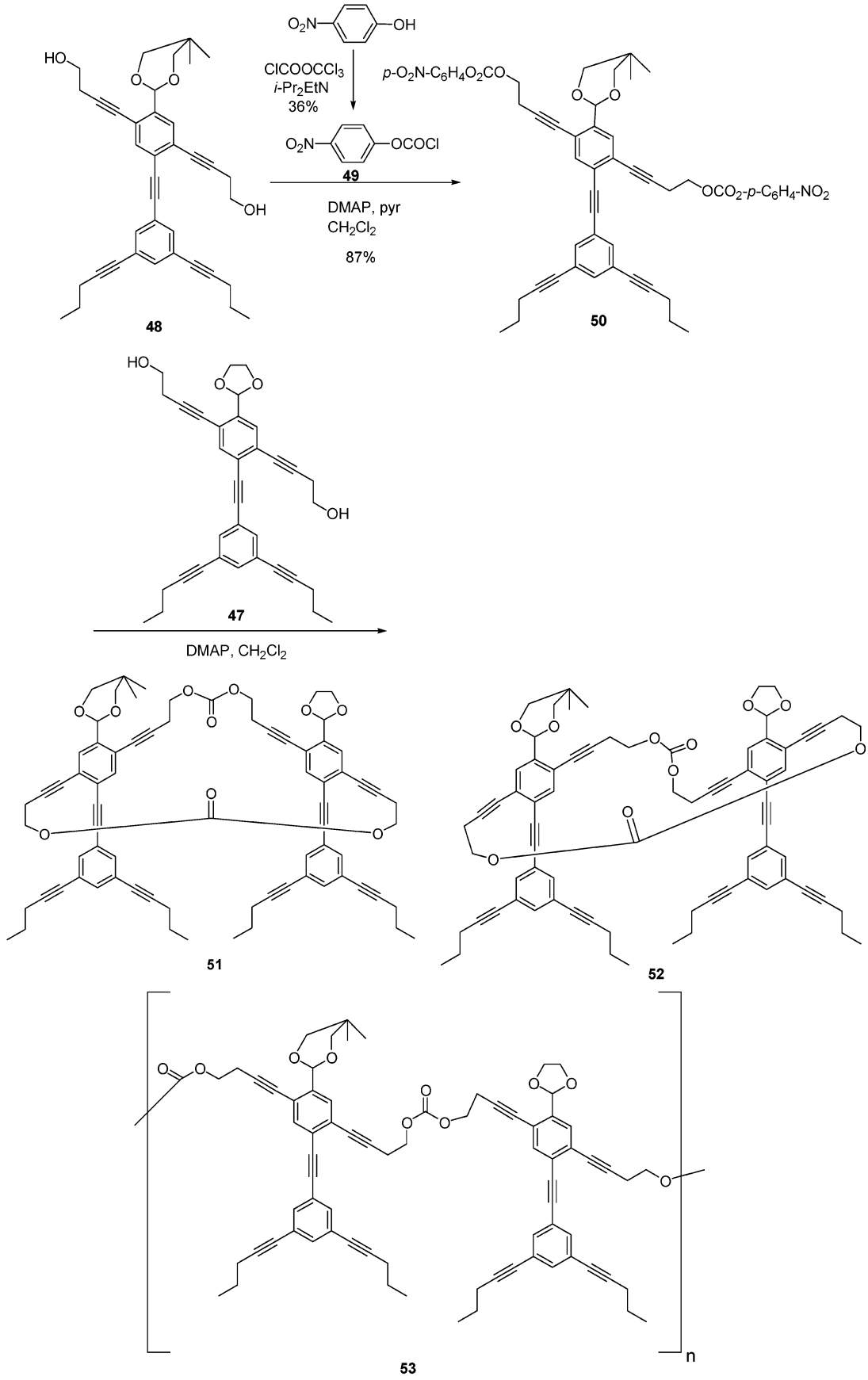


THF (40 mL) were added Et_3N (20 mL) and cold (0 °C) 3,3-dimethyl-1-butyne (2.22 mL, 18.03 mmol). The mixture was stirred at 23 °C for 20 h in a screwcap vial. Purification by flash chromatography (silica gel, hexanes) afforded 2.43 g (70% yield) of the title compound as a white solid. Mp: 154−158 °C. IR (KBr): 2969, 2922, 2896, 2864, 2243, 2208, 1463, 1359, 1264, 1200, 1061 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (s, 2 H), 1.34 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.8, 126.3, 123.7, 106.0, 30.7, 28.4. HRMS: calcd for $C_{18}H_{20}Br_2$ 393.9932, found 393.9917.

2,5-Bis(3,3-dimethylbutynyl)-4-bromobenzaldehyde (3). To a solution of 2,5-bis(3,3-dimethylbutynyl)-1,4-dibromobenzene (2.43 g, 6.135 mmol) in THF (30 mL) cooled to −78 °C under nitrogen was added dropwise *n*-BuLi (2.48 M, 2.72 mL). The reaction mixture was allowed to stir at −78 °C for 1 h. To this mixture was added DMF (0.48 mL, 6.135 mmol) predried over molecular sieves. The reaction mixture was allowed to stir for another 1 h and then warmed to room temperature for 4 h. It was then diluted with water and extracted with Et_2O. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and evaporated. Purification by flash chromatography (silica gel, hexanes/CH_2Cl_2 1/1) afforded 1.77 g (83% yield) of the title compound as a white solid. Mp: 98−102 °C. IR (KBr): 2967, 2926, 2897, 2865, 2837, 2735, 2239, 2213, 1699, 1586, 1520, 1466, 1380, 1362, 1010 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 10.31 (s, 1 H), 7.76 (s, 1 H), 7.58 (s, 1 H), 1.28 (s, 9 H), 1.27 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.0, 136.2, 134.1, 131.1, 130.7, 126.6, 125.9, 107.8, 105.7, 77.1, 73.6, 30.5, 28.2, 28.1. HRMS: calcd for $C_{19}H_{21}OBr$ 344.0776, found 344.0772.

2,5-Bis(3,3-dimethylbutynyl)-4-(1,3-dioxolane)bromobenzene (4). To a round-bottom flask equipped with a Dean−Stark trap for azeotropic removal of the water were added 2,5-(3',3'-dimethylbutynyl)-4-bromobenzenaldehyde (16.14 g, 46.746 mmol), ethylene glycol (5.20 mL, 93.49 mmol), *p*-toluenesulfonic acid (0.133 g, 0.701 mmol), and toluene (50 mL). The reaction mixture was heated to reflux for 3 d. It was then diluted with water. The pH was adjusted to 10 with 50% NaOH, and the solution was extracted with ether. The combined organic phases were dried over $MgSO_4$, filtered, and evaporated. Purification by flash chromatography (silica gel, hexanes/CH_2Cl_2 60/40) afforded 13.98 g (77% yield) of the title compound as a white solid. Mp: 128−134 °C. IR (KBr): 2968, 2927, 2898, 2866, 2240, 1594, 1533, 1470, 1398, 1363, 1268, 1075 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 1 H), 7.56 (s, 1 H), 6.06 (s, 1 H), 4.17 (m, 2 H), 4.03 (m, 2 H), 1.34 (s, 9

SCHEME 11. Reaction Products of the Hydroxyl-Tipped NanoKid (47) with the Activated Biscarbonate-Tipped NanoAthlete (50) To Form a Regioisomeric Pair of Hetero-Dimers 51 and 52 and an AB-Polymer (53) Consisting of Three Regioisomeric Bonding Patterns (Only One is Shown)



H), 1.32 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 135.4, 130.4, 125.6, 125.2, 123.6, 105.7, 104.7, 101.3, 77.9, 75.1, 65.4, 30.7, 28.3, 28.2. HRMS: calcd for $C_{21}H_{25}O_2Br$ 388.1038, found 388.1032. Anal. Calcd: C, 64.78; H, 6.47. Found: C, 64.91; H, 6.57.

2,5-Bis(3,3-dimethylbutynyl)-4-(1,3-dioxolane)iodobenzene (5). To a solution of 2,5-bis(3,3-dimethylbutynyl)-4-(1,3-dioxolane)bromobenzene (0.51 g, 1.310 mmol) in THF (25 mL) cooled to −78 °C under nitrogen was added dropwise *n*-BuLi (2.48 M, 0.57 mL). The reaction mixture was allowed to stir at −78 °C for 30 min. To this solution was added a solution of 1,2-diiodoethane (0.554 g, 1.965 mmol) in THF (10 mL). The reaction mixture was allowed to warm to rt overnight. It was diluted with a saturated solution of sodium bicarbonate and extracted with ether. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and evaporated in vacuo. Purification by flash chromatography (silica gel, CH_2Cl_2/hexanes 1/1) afforded 0.49 g (86% yield) of the title product as a white solid. Mp: 172−178 °C. IR (KBr): 2967, 2926, 2896, 2866, 2236, 1531, 1465, 1397, 1362, 1267, 1074 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1 H), 7.51 (s, 1 H), 6.05 (s, 1 H), 4.16 (m, 2 H), 4.03 (m, 2 H), 1.35 (s, 9 H), 1.32 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7, 138.5, 129.6, 129.2, 123.5, 105.6, 103.9, 101.4, 101.3, 81.7, 74.8, 65.4, 30.8, 30.7, 28.3, 28.3. HRMS: calcd for $C_{21}H_{25}IO_2$ 436.0899, found 436.0895.

3,5-Dibromoiodobenzene (9). 3,5-Dibromoaniline (13.0 g, 51.8 mmol) was dissolved in concentrated sulfuric acid (100 mL) at 50 °C. After the solution was cooled to 0 °C, sodium nitrite (7.15 g, 103.62 mmol) was added portionwise with continuous stirring, maintaining the temperature below 5 °C. The reaction mixture was allowed to stir at 0 °C for 2 h. The solution was poured onto ice, and KI (25.80, 155.43 mmol) in 125 mL of water was added. The mixture was then heated to 80 °C for 15 min. The solid was removed by filtration and washed with cold water. Recrystallization from ethanol gave an orange solid (13.20 g, 70% yield). Mp: 120−126 °C. IR (KBr): 3095, 3061, 1547, 1398, 1096 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 1.7 Hz, 2 H), 7.65 (t, J = 1.7 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 133.6, 123.4, 94.4 ppm. HRMS: calcd for $C_6H_3Br_2I$ 359.7646, found 359.7652.

3,5-Dibromo(trimethylsilylethynyl)benzene (10). See the Pd/Cu general procedure (Supporting Information). To a solution of 3,5-dibromoiodobenzene (13.20 g, 36.484 mmol), bis-(triphenylphosphine)palladium(II) dichloride (1.023 g, 1.46 mmol),and copper(I) iodide (0.694 g, 3.644 mmol) in THF (130 mL) were added Et_3N (40 mL) and trimethylsilylacetylene (5.19 mL, 36.484 mmol). The mixture was stirred at rt for 2 d. Purification by flash chromatography (silica gel, hexanes) afforded 11.0 g (91% yield) of the title compound as a clear liquid. IR (NaCl): 3074, 2960, 2898, 2167, 1578, 1540, 1419, 1402, 1250, 1103 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (t, J = 1.8 Hz, 1 H), 7.59 (d, J = 1.8 Hz, 2 H), 0.25 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.2, 133.33, 126.5, 122.5, 101.6, 97.6, −0.3. HRMS: calcd for $C_{11}H_{12}Br_2Si$ 331.9056, found 331.9053.

3,5-(1′-Pentynyl)-1-(trimethylsilylethynyl)benzene (11). See the Pd/Cu general procedure (Supporting Information). To a solution of bis(triphenylphosphine)palladium(II) dichloride (0.926 g, 1.32 mmol), copper(I) iodide (0.628 g, 3.30 mmol) in THF (100 mL), and Et_3N (70 mL) were added 3,5-dibromo-(trimethylsilylethynyl)benzene (11.0 g, 33.12 mmol) via a cannula and 1-pentyne (6.86 mL, 69.56 mmol). The mixture was heated to 75 °C for 3 d. After the mixture was checked by TLC, additional bis(triphenylphosphine)palladium(II) dichloride (0.502 g, 0.716 mmol), copper(I) iodide (0.304 g, 1.59 mmol), THF (40 mL), Et_3N (20 mL), and 1-pentyne (3.26 mL, 33.12 mmol) were added. The reaction mixture was allowed to stir for another 20 h at 80 °C. Purification by flash chromatography (silica gel, hexanes) afforded 6.89 g of the title compound as a clear liquid and 2.86 g of the monocoupled product. This monocoupled product was taken to a reaction flask with bis(triphenylphosphine)palladium(II) dichloride (0.188 g, 0.269 mmol), copper(I) iodide (0.102 g, 0.538 mmol), 1-pentyne (1.2 mL, 12.17 mmol), and Et_3N (30 mL) in THF (40 mL). The mixture was stirred at 70 °C for 3 d. After the same purification method as above, it afforded 0.84 g of the product. The overall yield for this reaction is 76%. IR (NaCl): 2963, 2934, 2902, 2872, 2836, 2233.6, 2155, 1581, 1460, 1413, 1250, 1171 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 1.5 Hz, 2 H), 7.36 (t, J = 1.5 Hz, 1 H), 2.36 (t, J = 7.0 Hz, 4 H), 1.63 (sext, J = 7.2 Hz, 4 H), 1.04 (t, J = 7.3 Hz, 6 H), 0.25 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.4, 133.8, 124.4, 123.3, 103.7, 94.9, 91.2, 79.4, 22.1, 21.3, 13.5, −0.2. HRMS: calcd for $C_{21}H_{26}Si$ 306.1804, found 306.1806.

3,5-(1′-Pentynyl)-1-ethynylbenzene (12). See the general alkyne deprotection procedure (Supporting Information). To a solution of 3,5-(1-pentynyl)-1-(trimethylsilylethynyl)benzene (1.729 g, 5.649 mmol) in MeOH (40 mL) and CH_2Cl_2 (40 mL) was added K_2CO_3 (7.80 g, 56.49 mmol). The solution was stirred at 23 °C for 2 h. The reaction afforded 1.32 g (100% yield) of the title compound as a yellow oil. IR (NaCl): 3295, 2963, 2933, 2872, 2835, 2234, 1582, 1461, 1415, 1380, 1340. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (s, 3 H), 3.06 (s, 1 H), 2.37 (t, J = 7.0 Hz, 4 H), 1.62 (sext, J = 7.2 Hz, 4 H), 1.05 (t, J = 7.4 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.8, 133.9, 124.6, 122.3, 91.5, 82.3, 79.2, 77.7, 22.0, 21.3, 13.5. HRMS: calcd for $C_{18}H_{18}$ 234.1408, found 234.1406.

NanoKid (13). See the Pd/Cu general procedure (Supporting Information). To a solution of 2,5-bis(3,3-dimethylbutynyl)-4-(1,3-dioxolane)iodobenzene (3.93 g, 9.017 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.253 g, 0.361 mmol), and copper(I) iodide (0.137 g, 0.721 mmol) in THF (40 mL) were added Et_3N (20 mL) and 3,5-(1-pentynyl)-1-ethynylbenzene (2.07 g, 8.846 mmol) in THF (20 mL) via a cannula. The mixture was stirred at 25 °C for 16 h and at 34 °C for 1 h. Purification by flash chromatography (silica gel, hexanes/CH_2Cl_2 60/40) afforded 4.31 g of the title compound as a yellow oil but was contaminated with 12% of 2,5-bis(3,3-dimethylbutynyl)-4-(1,3-dioxolane)iodobenzene. This contaminated material was re-subjected to the reaction by adding 3,5-(1-pentynyl)-1-ethynylbenzene (0.299 g, 1.278 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.034 g, 0.048 mmol), copper(I) iodide (0.020 g, 0.105 mmol), TEA (10 mL), and THF (60 mL). The mixture was allowed to stir at 50 °C for another 2 d. Purification by flash chromatography (silica gel, hexanes/CH_2Cl_2 60/40) afforded 4.17 g (85% yield) of the title compound as a sticky yellow solid. IR (NaCl, $CHCl_3$): 2966, 2931, 2897, 2869, 2230, 1581, 1474, 1454, 1398 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (s, 1 H), 7.53 (s, 1 H), 7.46 (d, J = 1.5 Hz, 2 H), 7.38 (t, J = 1.5 Hz, 1 H), 6.11 (s, 1 H), 4.19 (m, 2 H), 4.05 (m, 2 H), 2.38 (t, J = 7.0 Hz, 4 H), 1.60 (sext, J = 7.2 Hz, 4 H), 1.37 (s, 9 H), 1.34 (s, 9 H), 1.05 (t, J = 7.2 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 135.4, 134.2, 133.6, 129.5, 125.7, 125.5, 124.5, 123.5, 122.3, 105.0, 104.2, 101.4, 92.0, 91.3, 88.4, 79.4, 77.8, 75.5, 65.5, 31.0, 30.8, 28.3, 22.1, 21.3, 13.5. HRMS: calcd for $C_{39}H_{42}O_2$ 542.3185, found 542.3183. Anal. Calcd: C, 86.30; H, 7.80. Found: C, 86.27; H, 7.82.

NanoAthlete (14). In a small vial, NanoKid (**13**) (0.243 g, 0.448 mmol), *p*-toluenesulfonic acid monohydrate (0.003 g, 0.014 mmol), 2,2-dimethyl-1,3-propanediol (0.932 g, 8.956 mmol), and $MgSO_4$ (0.113 g, 0.939 mmol) were subjected to microwave irradiation for 7 min. The reaction mixture was then diluted with a saturated solution of $NaHCO_3$ and extracted with ether. The combined organic phases were dried over $MgSO_4$, filtered, and evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/CH_2Cl_2 60/40) afforded 239 mg (91% yield) of the title compound as a yellow sticky solid. IR (NaCl, $CHCl_3$): 2965, 2930, 2900, 2867, 2228, 1580, 1455, 1401, 1384, 1362, 1267, 1108 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1 H), 7.53 (s, 1 H), 7.47 (d, J = 1.5 Hz, 2 H), 7.38 (t, J = 1.5 Hz, 1 H), 5.69 (s, 1 H), 3.80 (d, J = 11 Hz, 2 H), 3.64 (d, J = 11 Hz, 2 H), 2.38 (t, J = 7.0 Hz, 4 H), 1.62 (sext, J = 7.2 Hz, 4 H), 1.37 (s, 9 H), 1.36 (s, 9 H), 1.34 (s, 3 H), 1.05 (t, J = 7.2 Hz, 6 H), 0.81 (s, 3 H). ^{13}C NMR (100

MHz, $CDCl_3$): δ 138.9, 135.0, 134.1, 133.5, 129.3, 125.9, 125.3, 124.5, 123.5, 121.5, 104.4, 104.1, 99.7, 91.8, 91.2, 88.5, 79.4, 77.9, 77.9, 75.6, 31.0, 30.9, 30.2, 28.2, 28.2, 23.2, 22.0, 21.8, 21.3, 13.4. HRMS: calcd for $C_{42}H_{48}O_2$ 584.3654, found 584.3648. Anal. Calcd: C, 86.26; H, 8.27. Found: C, 86.19; H, 8.25.

NanoPilgrim (15). In a small vial, NanoKid (**13**) (136 mg, 0.251 mmol), *p*-toluenesulfonic acid monohydrate (3 mg, 0.013 mmol), 1,2-dimethyl-1,2-cyclobutanediol (320 mg, 2.759 mmol), and $MgSO_4$ (60 mg, 0.501 mmol) were subjected to microwave irradiation for 13 min. The reaction mixture was purified flash chromatography (silica gel, hexanes/CH_2Cl_2 60/40) to afford 38 mg (25% yield, 33% yield based on recovered starting material) of the title compound as a sticky yellow oil. The product was inseparable from a small amount of the aldehyde. The product was obtained as an inseparable 45:55 mixture of diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 0.45 H), 7.60 (s, 0.55 H), 7.53 (s, 0.55 H), 7.52 (s, 0.45 H), 7.46 (d, J = 1.4 Hz, 4 H), 7.37 (t, J = 1.4 Hz, 2 H), 6.47 (s, 0.55 H), 6.21 (s, 0.45 H), 2.38 (t, J = 7.0 Hz, 8 H), 2.21 (pseudo pent, J = 5.4 Hz, 4 H), 2.00 (pseudo q, J = 5.4 Hz, 2 H), 1.85 (pseudo q, J = 5.4 Hz, 2 H), 1.61 (sext, J = 7.2 Hz, 8 H), 1.39−1.35 (m, 36 H), 1.05 (m, 24 H). HRMS: calcd for $C_{43}H_{48}O_2$ 596.3654, found 596.3649.

NanoGreenBeret (16). In a small vial, NanoKid (**13**) (0.206 g, 0.380 mmol), *p*-toluenesulfonic acid monohydrate (0.014 g, 0.075 mmol), 1,2-propanediol (2.78 mL, 37.69 mmol), and $MgSO_4$ (0.500 g, 4.15 mmol) were subjected to microwave irradiation for 1 min. The reaction mixture was then diluted with a saturated solution of $NaHCO_3$ and extracted with ether. The combined organic phases were dried over $MgSO_4$, filtered, and evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/CH_2Cl_2 60/40) afforded 179 mg (85% yield) of the title compound as a sticky yellow solid. The product was obtained as an inseparable 1:1 mixture of diastereoisomers. IR (KBr): 2966, 2231, 1585, 1532, 1451, 1380 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 0.5 H), 7.60 (s, 0.5 H), 7.53 (s, 2 H), 7.47 (t, J = 1.2 Hz, 4 H), 7.38 (t, J = 1.2 Hz, 2 H), 6.23 (s, 0.5 H), 6.13 (s, 0.5 H), 4.45 (pseudo sext, J = 6.1 Hz, 0.5 H), 4.35 (m, 1 H), 4.13 (dd, J = 6.5, 7.4 Hz, 0.5 H), 3.63 (t, J = 7.4 Hz, 0.5 H), 3.58 (dd, J = 6.5, 7.4 Hz, 0.5 H), 2.38 (t, J = 7.0 Hz, 8 H), 1.60 (sext, J = 7.3 Hz, 8 H), 1.42 (d, J = 6.1 Hz, 3 H), 1.372 (s, 4.5 H), 1.366 (s, 4.5 H), 1.36 (s, 3 H), 1.34 (s, 4.5 H), 1.33 (s, 4.5 H), 1.05 (t, J = 7.3 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 138.3, 135.3, 134.2, 133.5, 129.6, 129.4, 125.7, 125.7, 125.7, 125.5, 124.5, 123.5, 122.4, 122.2, 105.0, 104.9, 104.1, 101.4, 100.6, 92.0, 91.3, 88.4, 88.4, 79.4, 77.8, 75.6, 75.5, 73.7, 72.5, 72.1, 71.3, 31.0, 30.8, 28.2, 22.0, 21.3, 18.4, 18.2, 13.4. HRMS: calcd for $C_{40}H_{44}O_2$ 556.3341, found 556.3341. Anal. Calcd: C, 86.29; H, 7.97. Found: C, 86.16; H, 8.03.

NanoJester (17). In a small vial, NanoKid (**13**) (0.254 g, 0.468 mmol), *p*-toluenesulfonic acid monohydrate (0.003 g, 0.014 mmol), *cis*-cyclopentanediol (0.974 g, 9.54 mmol), and $MgSO_4$ (0.113 g, 0.936 mmol) were subjected to microwave irradiation for 6.5 min. The reaction mixture was then diluted with a saturated solution of $NaHCO_3$ and extracted with ether. The combined organic phases were dried over $MgSO_4$, filtered, and evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/CH_2Cl_2 60/40) afforded 257 mg (94% yield) of the title compound as a sticky yellow oil. The product was obtained as an inseparable 10:3 mixture of diastereomers. IR (NaCl, $CHCl_3$): 2965, 2869, 2231, 1581, 1491, 1457, 1403, 1362 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): (major) δ 7.69 (s, 1 H), 7.52 (s, 1 H), 7.43 (d, J = 1.5 Hz, 2 H), 7.39 (t, J = 1.5 Hz, 1 H), 5.94 (s, 1 H), 4.65 (d, J = 3.5 Hz, 2 H), 2.38 (t, J = 7.0 Hz, 4 H), 2.10 (m, 2 H), 2.07 (m, 2 H), 1.62 (sext, J = 7.2 Hz, 4 H), 1.49 (m, 2 H), 1.39 (s, 9 H), 1.34 (s, 9 H), 1.05 (t, J = 7.4 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): (major) δ 137.2, 134.9, 134.1, 133.4, 129.3, 125.7, 125.7, 124.5, 123.4, 122.4, 104.7, 104.0, 101.6, 100.0, 91.2, 88.4, 81.9, 79.3, 77.8, 75.3, 33.0, 30.9, 30.7, 30.7, 28.14, 28.10, 22.0, 21.2, 13.3. HRMS: calcd for $C_{42}H_{46}O_2$ 582.3498, found 582.3491. Anal. Calcd: C, 86.55; H, 7.96. Found: C, 86.74; H, 7.88.

NanoMonarch (18). In a small vial, NanoKid (**13**) (99 mg, 0.182 mmol), *p*-toluenesulfonic acid monohydrate (0.004 g, 0.021 mmol), *cis*-1,2-cycloheptanediol (0.109 g, 0.838 mmol), and $MgSO_4$ (0.044 g, 0.365 mmol) were subjected to microwave irradiation for 10 min. The reaction mixture was then diluted with a saturated solution of $NaHCO_3$ and extracted with ether. The combined organic phases were dried over $MgSO_4$, filtered, and evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/CH_2Cl_2 60/40) afforded 97 mg (87% yield) of the title compound as a yellow sticky oil. The product was obtained as a 10:3 ratio of diastereomers. IR (NaCl, $CHCl_3$): 2967, 2932, 2867, 2231, 1581, 1454, 1411, 1361 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): (major) δ 7.67 (s, 1 H), 7.51 (s, 1 H), 7.47 (d, J = 1.5 Hz, 2 H), 7.38 (t, J = 1.5 Hz, 1 H), 6.08 (s, 1 H), 4.31 (m, 2 H), 2.38 (t, J = 7.0 Hz, 4 H), 2.04−1.64 (m, 8 H), 1.60 (sext, J = 7.2 Hz, 4 H), 1.37 (s, 9 H), 1.34 (s, 9 H), 1.32 (m, 2 H), 1.05 (t, J = 7.2 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 135.1, 134.2, 133.5, 129.7, 125.8, 125.7, 124.5, 123.5, 122.5, 104.7, 104.0, 99.8, 91.2, 88.5, 80.2, 79.9, 79.4, 77.9, 75.5, 31.0, 30.8, 30.4, 28.23, 28.20, 24.2, 22.0, 21.3, 13.4. HRMS: calcd for $C_{44}H_{50}O_2$ 610.3811, found 610.3811. Anal. Calcd: C, 86.51; H, 8.25. Found: C, 86.50; H, 8.29.

NanoTexan (19). In a small vial, NanoKid (**13**) (59 mg, 0.109 mmol), *p*-toluenesulfonic acid monohydrate (few crystals), 1,2-dimethyl-1,2-cyclopentanediol (130 mg, 1.0 mmol), and $MgSO_4$ (50 mg, 0.748 mmol) were subjected to microwave irradiation for 9 min. The reaction mixture was purified flash chromatography (silica gel, hexanes/CH_2Cl_2 60/40) to afford 34 mg (24% yield, 58% yield based on recovered starting material) of the title compound as a sticky yellow oil. The desired product was inseparable from a small amount of the parent aldehyde. The product was obtained as an inseparable 1:3.2 mixture of diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$): (major) δ 7.70 (s, 1 H), 7.51 (s, 1 H), 7.46 (d, J = 1.5 Hz, 2 H), 7.37 (t, J = 1.5 Hz, 1 H), 6.06 (s, 1 H), 2.38 (t, J = 7.0 Hz, 4 H), 2.16 (m, 2 H), 1.64 (sext, J = 7.0 Hz, 4 H), 1.39−1.34 (m, 28 H), 1.06 (t, J = 7.3 Hz, 6 H). HMRS: calcd for $C_{44}H_{50}O_2$ 610.3811, found 610.3811.

NanoScholar (20). In a small vial, NanoKid (**13**) (92 mg, 0.170 mmol), *p*-toluenesulfonic acid monohydrate (few crystals), 4-methyl-*cis*-1,2-cyclohexanediol (443 mg, 3.408 mmol), and $MgSO_4$ (41 mg, 0.341 mmol) were subjected to microwave irradiation for 16 min. The reaction mixture was purified flash chromatography (silica gel, hexanes/CH_2Cl_2 60/40) to afford 93 mg (90% yield) of the title compound as a sticky yellow oil. The product was obtained as an inseparable 17:12:12:9 mixture of diastereomers. IR (NaCl, $CHCl_3$): 2967, 2869, 2232, 1582, 1456, 1362, 1265, 1103 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): (four isomers) δ 7.67 (s, 1 H), 7.66 (s, 1 H), 7.56 (s, 1 H), 7.55 (s, 1 H), 7.52 (m, 4 H), 7.47 (m, 8 H), 7.38 (m, 4 H), 6.43 (s, 1 H), 6.42 (s, 1 H), 6.16 (s, 1 H), 6.15 (s, 1 H), 4.30 (m, 8 H), 2.38 (t, J = 7.0 Hz, 16 H), 2.28 (m, 4 H), 2.0−1.7 (m, 12 H), 1.63 (sext, J = 7.0 Hz, 16 H), 1.55−1.45 (m, 4 H), 1.37−1.32 (m, 72 H), 1.30−1.15 (m, 8 H), 1.05 (t, J = 7.3 Hz, 24 H), 0.95 (m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): (four isomers) δ 140.9, 140.8, 139.2, 139.1, 135.4, 135.4, 134.4, 133.8, 129.6, 129.4, 129.2, 125.9, 125.8, 125.8, 125.7, 125.4, 124.8, 123.7, 122.8, 122.2, 105.5, 105.4, 105.3, 104.3, 104.2, 101.1, 99.9, 99.8, 92.1, 92.0, 91.5, 88.7, 79.6, 78.2, 77.4, 76.7, 76.1, 76.0, 75.8, 75.8, 75.5, 74.8, 74.6, 74.3, 73.4, 38.9, 36.0, 35.8, 35.5, 34.9, 31.8, 31.2, 31.1, 31.0, 30.6, 29.9, 29.4, 29.3, 29.1, 28.6, 28.5, 27.0, 26.9, 26.7, 26.5, 26.5, 25.5, 22.9, 22.4, 22.4, 22.3, 22.0, 21.8, 21.5, 14.3, 13.7. HMRS: calcd for $C_{44}H_{50}O_2$ 610.3811, found 610.3812. Anal. Calcd: C, 86.51; H, 8.25. Found: C, 86.36; H, 8.27.

NanoBaker (21). In a small vial, NanoKid (**13**) (128 mg, 0.236 mmol), *p*-toluenesulfonic acid monohydrate (few crystals), *cis*-1,2-cyclohexanediol (411 mg, 3.54 mmol), and $MgSO_4$ (116 mg, 0.964 mmol) were subjected to microwave irradiation for 10 min. The reaction mixture was purified flash chromatography (silica gel, hex/CH_2Cl_2 60/40) to afford 118 mg (84% yield) of the title compound as a sticky yellow oil. The product was obtained as an inseparable 1:1.63 mixture of diastereo-

mers. IR (NaCl, $CHCl_3$): 2969, 2869, 2253, 1582, 1456, 1363, 1266, 1153 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): (major) δ 7.68 (s, 1 H), 7.52 (s, 1 H), 7.46 (m, 2 H), 7.37 (m, 1 H), 6.15 (s, 1 H), 4.30 (m, 1 H), 4.20 (m, 1 H), 2.38 (t, J = 6.9 Hz, 4 H), 1.87−1.70 (m, 4 H), 1.69−1.58 (m, 8 H), 1.37 (s, 9 H), 1.36 (s, 9 H), 1.05 (t, J = 7.3 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) (two isomers) δ 140.7, 138.9, 135.20, 135.17, 134.2, 133.6, 129.2, 128.94, 125.7, 125.6, 125.6, 125.2, 124.5, 123.5, 122.6, 122.0, 105.3, 105.1, 104.1, 104.0, 100.7, 99.6, 91.9, 91.8, 91.2, 88.5, 79.4, 78.0, 77.2, 75.7, 75.6, 75.1, 74.6, 31.0, 30.8, 28.3, 28.2, 28.3, 27.1, 22.1, 21.3, 21.1, 20.7, 13.5. HMRS: calcd for $C_{43}H_{48}O_2$ 596.3654, found 596.3654.

NanoChef (22). To 100 mL round-bottom flask equipped with a condenser were added NanoKid (223 mg, 0.411 mmol), catechol (0.998 g, 9.063 mmol), and $MgSO_4$ (0.498 g, 4.137 mmol). The atmosphere was removed and replaced with nitrogen. To the flask were added trimethylsilyl chloride (0.26 mL, 2.05 mmol) and freshly distilled CH_2Cl_2. The mixture was allowed to stir at reflux for 42 h. A 5% solution of $NaHCO_3$ was added, and the reaction mixture was extracted with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and filtered, and the solvent was evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/CH_2Cl_2 60/40) afforded 23 mg (9% yield, 20% recovered) of the title product as a white solid. Mp: 117−124 °C. IR (KBr): 2966, 2929, 2900, 2867, 2225, 1580, 1481, 1350, 1230, 1022 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1 H), 7.60 (s, 1 H), 7.47 (d, J = 1.5 Hz, 2 H), 7.40 (t, J = 1.5 Hz, 1 H), 7.22 (s, 1 H), 6.89 (m, 4 H), 2.39 (t, J = 7.0 Hz, 4 H), 1.62 (sext, J = 7.2 Hz, 4 H), 1.35 (s, 9 H), 1.29 (s, 9 H), 1.05 (t, J = 7.2 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 136.2, 135.7, 134.4, 133.6, 129.8, 126.8, 125.9, 124.6, 123.3, 122.2, 121.7, 108.6, 108.0, 106.0, 104.9, 92.7, 91.4, 88.1, 79.4, 75.0, 30.9, 30.7, 28.3, 22.1, 21.3, 13.5. HRMS: calcd for $C_{43}H_{42}O_2$ 590.3185, found 590.3178.

Mixture of NanoPutians 14−21. In a small vial, NanoKid (163 mg, 0.30 mmol) was mixed with *cis*-1,2-dimethyl-1,2-cyclopentanediol (78 mg, 0.60 mmol), *cis*-cyclopentane-1,2-diol (61 mg, 0.60 mmol), *cis*-1,2-dimethylcyclobutane-1,2-diol (69 mg, 0.60 mmol), *cis*-cycloheptane-1,2-diol (78 mg, 0.60 mmol), 4-methyl-*cis*-1,2-cyclohexanediol (78 mg, 0.60 mmol), *cis*-1,2-cyclohexanediol (69 mg, 0.60 mmol), 1,2-propanediol (0.044 mL, 0.60 mmol), 2,2-dimethyl-1,3-propanediol (62 mg, 0.60 mmol), *p*-toluenesulfonic acid monohydrate (few crystals), and $MgSO_4$ (130 mg, 1.08 mmol). The reaction mixture was subjected to microwave irradiation for 4 min. The crude reaction mixture was purified by flash chromatography (silica gel, hexanes/CH_2Cl_2 66/33), which afforded 161 mg of a mixture of all the NanoPutians **14**−**21**. This was confirmed by mass spectrometric analysis of the reaction mixture where the mass of each NanoPutian was detected. However, since a few of the figures have the same molecular weight, further confirmation was obtained using ^1H NMR peak matching of the mixture against the individual NanoPutian spectra referenced above.

3,5-(1′-Butynyl)-1-(trimethylsilylethynyl)benzene (23). See the Pd/Cu general procedure (Supporting Information). A solution of 3,5-dibromo(trimethylsilylethynyl)benzene **(10)** (1.91 g, 5.75 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.202 g, 0.288 mmol), copper(I) iodide (0.109 g, 0.575 mmol) in THF (30 mL), and Et_3N (15 mL) was cooled to −70 °C. To this solution was added cold (−70 °C) 1-butyne (3 mL, 37.63 mmol). The mixture was allowed to warm to room temperature and heated to 74 °C for 2 d. After the mixture was checked by TLC, more of the cold 1-butyne (2.4 mL, 30.10 mmol) was added. The reaction mixture was allowed to stir for another 2 d. Purification by flash chromatography (silica gel, hexanes) afforded 1.34 g (84% yield) of the title compound as a clear liquid. IR (NaCl): 2976, 2938, 2241, 2161, 1581, 1455, 1414, 1316, 1250 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 1.5 Hz, 2 H), 7.35 (t, J = 1.5 Hz, 1 H), 2.40 (q, J = 7.5 Hz, 4 H), 1.22 (t, J = 7.5 Hz, 6 H), 0.24 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.4, 133.8, 124.4, 123.4, 103.7, 94.9, 92.6, 78.5, 13.8, 13.0, −0.2. HRMS: calcd for $C_{19}H_{22}Si$ 278.1491, found 278.1486.

3,5-(1′-Butynyl)-1-ethynylbenzene (24). See the general alkyne deprotection procedure (Supporting Information). To a solution of **23** (0.450 g, 1.616 mmol) in MeOH (20 mL) and CH_2Cl_2 (20 mL) was added K_2CO_3 (2.21 g, 15.98 mmol). The solution was stirred at 23 °C for 2 h. The reaction afforded 0.65 g (99% yield) of the title compound as a yellow oil. The compound was too unstable to attain its complete characterization data, and it was immediately used in the next step. IR (KBr): 3301, 2978, 2937, 2240, 1582, 1454, 1316 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 3 H), 3.05 (s, 1 H), 2.40 (q, J = 7.5 Hz, 4 H), 1.22 (t, J = 7.5 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.0, 134.2, 124.7, 122.6, 93.1, 82.6, 78.6, 77.9, 14.0, 13.3. HRMS: calcd for $C_{16}H_{14}$ 206.1096, found 206.1094.

NanoToddler (25). See the Pd/Cu general procedure (Supporting Information). To a solution of **5** (0.49 g, 1.123 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.039 g, 0.056 mmol), copper(I) iodide (0.021 g, 0.112 mmol) in THF (20 mL) were added Et_3N (20 mL) and **24** (0.253 g, 1.228 mmol) in THF (20 mL) via a cannula. The mixture was stirred at 80 °C for 42 h. Purification by flash chromatography (silica gel, hexanes/CH_2Cl_2 60/40) afforded 0.45 g (78% yield) of the title compound as a yellow oil. IR (NaCl): 2970, 2895, 2236, 1581, 1474, 1455, 1397, 1316, 1266, 1202, 1107 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (s, 1 H), 7.53 (s, 1 H), 7.46 (d, J = 1.4 Hz, 2 H), 7.38 (t, J = 1.4 Hz, 1 H), 6.11 (s, 1 H), 4.18 (m, 2 H), 4.05 (m, 2 H), 2.40 (q, J = 7.5 Hz, 4 H), 1.37 (s, 9 H), 1.34 (s, 9 H), 1.23 (t, J = 7.5 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 135.4, 134.2, 133.5, 129.5, 125.7, 125.6, 124.5, 123.4, 122.3, 105.0, 104.2, 101.4, 92.7, 92.0, 88.4, 78.5, 77.7, 75.5, 65.4, 31.0, 30.8, 28.23, 28.22, 13.8, 13.0. HRMS: calcd for $C_{37}H_{38}O_2$ 514.2872, found 514.2869. Anal. Calcd: C, 86.34; H, 7.44. Found: C, 86.24; H, 7.58.

3,5-(4′-Thiolacetyl-1′-butynyl)-1-(trimethylsilylethynyl)-benzene (28). See the Pd/Cu general procedure (Supporting Information). To a solution of bis(triphenylphosphine)palladium(II) dichloride (0.438 g, 0.625 mmol), copper(I) iodide (0.238 g, 1.25 mmol) in THF (15 mL) were added Et_3N (20 mL) a solution of **10** (2.07 g, 6.25 mmol) in THF (15 mL) and a solution of **27** (1.68 g, 13.12 mmol) in THF (20 mL) via a cannula. The mixture was stirred at 75 °C for 4 d. The solvent was evaporated in vacuo. The residue was diluted with NH_4Cl and extracted with Et_2O. The combined organic phases were dried over $MgSO_4$, filtered, and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, CH_2Cl_2) afforded a mixture of starting material, mono- and decoupled products. This mixture was resubmitted to the same amount of reagents and then heated to 80° C for 4 d. Purification by flash chromatography (silica gel, hexanes/CH_2Cl_2 50/50) afforded 0.531 g (20% yield) of the title compound as a yellow sticky liquid. IR (KBr): 2959, 2248, 2156, 1693, 1581, 1414, 1354, 1250, 1133 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 1.5 Hz, 2 H), 7.35 (t, J = 1.5 Hz, 1 H), 3.09 (t, J = 7.0 Hz, 4 H), 2.68 (t, J = 7.0 Hz, 4 H), 2.36 (s, 3 H), 0.24 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.5, 134.6, 134.4, 124.0, 123.7, 103.6, 95.6, 88.9, 80.5, 30.8, 28.5, 20.6, 0.0. HRMS: calcd for $C_{23}H_{26}O_2S_2Si$ 426.1144, found 426.1146.

3,5-(4′-Thiolacetyl-1′-butynyl)-1-(ethynyl)benzene (29). To a solution of **27** (0.531 g, 1.25 mmol) in THF (5 mL) were added a mixture of acetic anhydride (0.47 mL, 4.99 mmol) and acetic acid (0.286 mL, 4.94 mmol) and TBAF (1 M, 2.99 mmol). This solution was stirred at rt for 35 min. The reaction mixture was diluted with water and extracted with ether. The combined organic phases were dried over $MgSO_4$ and filtered, and the solvent was evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/CH_2Cl_2 30/70) afforded 0.379 g (86% yield) of the title compound as a yellow oil. IR (KBr): 3304, 2253, 1690, 1583, 1434, 1355, 1133 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 1.5 Hz, 2 H), 7.40 (t, J = 1.5 Hz, 1 H), 3.11(t, J = 7.0 Hz, 4 H), 3.07 (s, 1 H), 2.68 (t, J = 7.0 Hz, 4 H), 2.37 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6,

135.1, 134.6, 124.2, 122.8, 89.2, 82.3, 80.4, 78.3, 30.9, 28.5, 20.7. HRMS: calcd for $C_{20}H_{18}O_2S_2$ 354.0748, found 354.0748.

NanoKid with Thiolacetate Feet (30). See the Pd/Cu general procedure (Supporting Information). To a solution of the free alkyne **29** (0.379 g, 1.070 mmol), **5** (0.467 g, 1.017 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.038 g, 0.0535 mmol), and copper(I) iodide (0.020 g, 0.107 mmol) in THF (20 mL) was added Et_3N (10 mL). This solution was stirred at rt for 20 h. Purification by flash chromatography (silica gel, CH_2Cl_2) afforded 0.224 g (31% yield) of the title compound as a sticky yellow oil. IR (KBr, $CDCl_3$): 2971, 2898, 2253, 1690, 1582, 1474, 1456, 1400, 1359, 1134, 1107 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (s, 1 H), 7.52 (s, 1 H), 7.47 (d, J = 1.5 Hz, 2 H), 7.38 (t, J = 1.5 Hz, 1 H), 6.11 (s, 1 H), 4.19 (m, 2 H), 4.05 (m, 2 H), 3.11 (t, J = 7.0 Hz, 4 H), 2.69 (t, J = 7.0 Hz, 4 H), 2.37 (s, 6 H), 1.36 (s, 9 H), 1.33 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 138.7, 135.7, 134.6, 134.2, 129.7, 125.9, 125.7, 124.2, 123.9, 122.6, 105.3, 104.5, 101.6, 91.9, 89.0, 88.9, 80.5, 78.0, 75.7, 65.7, 53.6, 31.2, 31.0, 30.8, 28.5, 28.49, 28.47, 20.6. HRMS: calcd for $C_{41}H_{42}O_4S_2$ 662.2525, found 662.2525.

3,6-Dibromo-2,4-diiodoaniline (31). In a 500 mL round-bottom flask equipped with an addition funnel were stirred 2,5-dibromoaniline (9.52 g, 37.96 mmol), sodium acetate (6.85 g, 83.50 mmol), and acetic acid (60 mL) at rt. To this suspension was slowly added ICl (4.26 mL, 83.50 mmol) in acetic acid (15 mL). The mixture was heated to 80 °C for 5 h, diluted with water, and stirred for an additional 1 h after which it was allowed to stand overnight. The suspension was filtered and washed with a saturated solution of sodium bisulfite and water. After drying, it afforded a brown solid. NMR showed a mixture of product and mono-iodinated byproduct in a 1:0.3 ratio. The mixture was mixed with sodium acetate (6.85 g, 83.50 mmol) and acetic acid (80 mL). To this suspension was added slowly ICl (2.9 mL, 56.94 mmol) in acetic acid (20 mL). The mixture was heated to 80 °C for 18 h, diluted with water, and stirred for an additional 1 h after which it was allowed to stand overnight. The suspension was filtered and washed with a saturated solution of sodium bisulfite and water. After drying, it afforded a brown solid (16.80 g, 88% yield). Mp: 136−148 °C. IR (KBr): 3489, 2925, 2854, 1597 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1 H), 5.65 (br s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 141.1, 135.6, 105.3, 90.2, 82.9 ppm. HRMS: calcd for $C_6H_3Br_2I_2N$ 500.6722, found 500.6721.

2,5-Dibromo-1,3,diiodobenzene (32). Isoamylnitrite (5.4 mL, 40.1 mmol) and DMF (20 mL) were heated to 65 °C. To this mixture was slowly added **31** (16.80 g, 33.42 mmol) in DMF (80 mL). The reaction mixture was stirred for 24 h, diluted with HCl (1 M, 60 mL), and extracted with $CHCl_3$. The combined organic phases were dried over $MgSO_4$, filtered, and evaporated in vacuo. The NMR of the crude product showed a mixture of starting material and product. The crude was subjected to the same reaction for 2 d at 70 °C. The reaction mixture was diluted with HCl (1 M, 60 mL) and water. The light brown solid was filtered and recrystallized from ethanol, and after purification by flash chromatography (silica gel, hexanes), it afforded 7.07 g (43% yield) of the title compound as a white solid. Mp: 126−130 °C. IR (KBr): 3071, 1531, 1517, 1388, 1370, 1351 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 135.5, 121.8, 100.4 ppm. HRMS: calcd for $C_6H_2Br_2I_2$ 485.6613, found 485.6612.

2,6-Bis(3′,3′-dimethylbutynyl)-1,4-dibromobenzene (33). See the Pd/Cu general procedure (Supporting Information). To a solution of **32** (1.78 g, 3.650 mmol), bis(triphenylphosphine)-palladium(II) dichloride (0.256 g, 0.365 mmol), and copper(I) iodide (0.139 g, 0.730 mmol) in THF (50 mL) were added Et_3N (15 mL) and 3,3-dimethyl-1-butyne (0.99 mL, 8.03 mmol). The mixture was stirred at rt for 1 d. Purification by flash chromatography (silica gel, hexanes) afforded 1.08 g (75% yield) of the title compound as a white solid. Mp: 124−138 °C. IR (KBr): 2969, 2927, 2899, 2866, 2226, 1558, 1544, 1393, 1362, 1272, 1224, 1202 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (s, 2 H), 1.34 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.3, 128.4, 127.8, 119.8, 105.1, 86.5, 30.9, 28.5 ppm. HRMS: calcd for $C_{18}H_{20}Br_2$ 393.9932, found 393.9938.

4-Bromo-2,6-(3′,3′-dimethylbutynyl)benzaldehyde (34) and 4-Bromo-3,5-(3′,3′-dimethylbutynyl)benzaldehyde (35). To **33** (4.47 g, 11.28 mmol) in THF (50 mL) cooled to −78 °C under nitrogen was dropwise added *t*-BuLi (1.7 M, 13.94 mL). The reaction mixture was allowed to stir at −78 °C for 30 min. To this mixture was added DMF (1.75 mL, 22.56 mmol) predried over molecular sieves. The reaction mixture was allowed to warm to rt overnight. It was then diluted with water and extracted with Et_2O. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and evaporated. Purification by flash chromatography (silica gel, hexanes/CH_2Cl_2 75/25) afforded 1.47 g (38% yield) of **34** and 1.45 g (37% yield) of **35** as white solids. Less polar product **34**. Mp: 97−100 °C. IR (KBr): 2968, 2924, 2898, 2864, 2758, 2230, 1706, 1554, 1475, 1454, 1390, 1362, 1264 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 10.54 (s, 1 H), 7.54 (s, 2 H), 1.35 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5, 135.7, 135.2, 127.7, 126.8, 107.2, 75.5, 30.8, 28.6 ppm. HRMS: calcd for $C_{19}H_{21}$-BrO 344.0776, found 344.0779. More polar product **35**. Mp: 102−114 °C. IR (KBr): 2969, 2928, 2901, 2867, 2816, 1781, 2704, 2231, 1707, 1569, 1456, 1426, 1379, 1361, 1263 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 9.90 (s, 1 H), 7.76 (s, 2 H), 1.36 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 135.7, 135.8, 132.0, 128.2, 105.5, 77.7, 30.9, 28.6 ppm. HRMS: calcd for $C_{19}H_{21}BrO$ 344.0776, found 344.0774.

3,5-Bis(3′,3′-dimethylbutynyl)-4-(1″,3″-dioxolane)-1-bromobenzene (36). To a round-bottom flask equipped with a Dean−Stark trap for azeotropic removal of the water were added **34** (1.52 g, 4.40 mmol), ethylene glycol (1.47 mL, 26.41 mmol), *p*-toluenesulfonic acid (0.042 g, 0.22 mmol), and toluene (100 mL). The reaction mixture was heated to reflux for 1 d. It was then diluted with aq K_2CO_3. The solution was extracted with ether. The combined organic phases were dried over $MgSO_4$, filtered, and evaporated. Purification by flash chromatography (silica gel, hexanes/CH_2Cl_2 60/40) afforded 1.22 g (71% yield) of the title compound as a white solid. Mp: 96−98 °C. IR (KBr): 2966, 2926, 2891, 2221, 1560, 1411, 1383, 1220, 1256, 1102, 1080 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.47 (s, 2 H), 6.31 (s, 1 H), 4.29 (m, 2 H), 4.06 (m, 4 H), 1.32 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 135.8, 126.1, 122.2, 104.7, 102.2, 76.1, 66.4, 31.1, 28.4 ppm. HRMS: calcd for $C_{21}H_{25}BrO_2$ 388.1038, found 388.1030.

3,5-Dibromobenzadehyde (37). To 3,5-dibromoiodobenzene (6.037 g, 16.686 mmol) in THF (50 mL) cooled to −78 °C under nitrogen was dropwise added *n*-BuLi (2.39 M, 7.68 mL). The reaction mixture was allowed to stir at −78 °C for 30 min. To this mixture was added DMF (1.55 mL, 20.023 mmol) predried over molecular sieves. The reaction mixture was allowed to warm to rt overnight. It was then diluted with water and extracted with Et_2O. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and evaporated. Purification by flash chromatography (silica gel, hexanes/CH_2-Cl_2 50/50) afforded 1.25 g (28% yield) of the title compound as a white solid. Mp: 86−90 °C. IR (KBr): 3064, 2844, 1697, 1556, 1384, 1190 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 9.91 (s, 1 H), 7.95 (d, J = 1.6 Hz, 2 H), 7.92 (t, J = 1.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 139.8, 139.1, 131.4, 124.2 ppm. HRMS: calcd for $C_7H_4Br_2O$ 263.8609, found 263.8602.

3,5-Bis(pentynyl)benzaldehyde (38). See the Pd/Cu general procedure (Supporting Information). To a solution of **37** (2.60 g, 9.855 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.691 g, 0.985 mmol), and copper(I) iodide (0.375 g, 1.971 mmol) in THF (50 mL) were added Et_3N (20 mL) and 1-pentyne (5.83 mL, 59.13 mmol). The mixture was stirred at 80 °C for 2 d. Purification by flash chromatography (silica gel, hexanes/CH_2Cl_2 50/50) afforded 2.19 g (93% yield) of the title compound as a yellow liquid. IR (KBr): 2965, 2934, 2873, 2234, 1702, 1591, 1448, 1384, 1339, 1153 cm^{-1}. ^1H NMR (400 MHz,

$CDCl_3$): δ 9.93 (s, 1 H), 7.77 (d, J = 1.5 Hz, 2 H), 7.64 (s, 1 H), 2.40 (t, J = 4.3 Hz, 4 H), 1.64 (sext, J = 2.8 Hz, 4 h), 1.06 (t, J = 7.4 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 140.0, 136.6, 131.6, 125.6, 92.7, 79.2, 22.2, 21.6, 13.7 ppm. HRMS: calcd for $C_{17}H_{18}O$ 238.1358, found 238.1359.

39. To a solution of **36** (1.747 g, 4.487 mmol) in THF (25 mL) at −78 °C was dropwise added *n*-BuLi (2.39 M, 2.44 mL). The reaction mixture was stirred for 30 min. Then **38** (1.176 g, 4.936 mmol) was added. The reaction mixture was allowed to warm to rt. It was then diluted with aq NaOH and extracted with Et_2O. The combined organic phases were dried over $MgSO_4$, filtered, and evaporated. Purification by flash chromatography (silica gel, CH_2Cl_2) afforded 1.97 g (78% yield) of the title compound as a white sticky solid. Mp: 64−80 °C. IR (KBr): 3446, 2966, 2931, 2899, 2870, 2228, 1589, 1456, 1390, 1362, 1259, 1202, 1088 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (t, J = 1.5 Hz, 1 H), 7.30 (s, 2 H), 7.24 (d, J = 1.3 Hz, 2 H), 6.36 (s, 1 H), 5.62 (d, J = 2.7 Hz, 1 H), 4.31 (m, 2 H), 4.07 (m, 2 H), 2.37 (t, J = 7.0 Hz, 4 H), 2.18 (d, J = 2.7 Hz, 1 H), 1.62 (sext, J = 7.3 Hz, 4 H), 1.32 (s, 18 H), 1.04 (t, J = 7.3 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 143.4, 137.5, 134.2, 131.2, 129.2, 124.6, 103.5, 102.4, 91.2, 80.2, 74.8, 66.3, 31.2, 28.4, 22.3, 21.6, 13.7 ppm. HRMS: calcd for $C_{38}H_{44}O_3$ 548.3290, found 548.3290.

40. Using a three-neck round-bottom flask, **39** (0.195 g, 0.346 mmol) was dissolved in 10 mL of THF. To this solution were added NaH (71 mg, 1.778 mmol) and a few crystals of imidazole. After warming to 60 °C for 30 min, the solution turned milky yellow-orange. CS_2 (0.13 mL, 2.13 mmol) was added. After 30 min at 60 °C, MeI (0.13 mL, 2.13 mmol) was added. The milky yellow solution was stirred for another 30 min after which it was quenched with brine and extracted with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$, filtered, and evaporated. Purification by flash chromatography (silica gel, CH_2Cl_2/hexanes 33/66 then CH_2Cl_2) afforded 0.188 g (83% yield) of the title compound as a white sticky solid. IR (KBr): 2967, 2930, 2900, 2871, 2225, 1590, 1452, 1428, 1362, 1198, 1089, 1059 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 1 H), 7.38 (t, J = 1.4 Hz, 1 H), 7.29 (s, 2 H), 7.22 (d, J = 1.3 Hz, 2 H), 6.36 (s, 1 H), 4.30 (m, 2 H), 4.06 (m, 2 H), 2.59 (s, 3 H), 2.37 (t, J = 7.0 Hz, 4 H), 1.62 (sext, J = 7.3 Hz, 4 H), 1.32 (s, 18 H), 1.04 (t, J = 7.3 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.7, 139.2, 138.9, 138.4, 134.8, 132.0, 129.7, 124.8, 124.7, 103.9, 102.3, 91.6, 83.3, 79.9, 66.3, 31.1, 28.4, 22.3, 21.6, 13.7. HRMS: calcd for $C_{40}H_{46}O_3S_2$ 638.2888, found 638.2887.

NanoBalletDancer (41). To a solution of **40** (1.86 mg, 0.2849 mmol) were added a few crystals of 2,2'-azabis(2-methylpropionitrile) in toluene (7 mL) and tri-*n*-butyltin hydride (0.196 mL, 0.728 mmol). This solution was heated to 80 °C for 3 h. The solvent was evaporated in vacuo, and the residue was diluted with water and extracted with ether. The combined organic phases were dried over $MgSO_4$, filtered, and evaporated. Purification by flash chromatography (silica gel, CH_2Cl_2/hex 50/50) afforded 0.103 g of the product mixed with some starting material. The mixture was resubmitted to the same amount of reagents for 7 h. The solvent was evaporated in vacuo, and the residue was diluted with water and extracted with ether. The combined organic phases were dried over $MgSO_4$, filtered, and evaporated. Purification by flash chromatography (silica gel, CH_2Cl_2/hexanes 50/50) afforded 67 mg (43% yield) of the title compound as a sticky white solid. IR (KBr): 2969, 2901, 2872, 2252, 1587, 1457, 1391, 1088 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (s, 1 H), 7.15 (s, 2 H), 7.07 (d, 2 H), 6.36 (s, 1 H), 4.31 (m, 2 H), 4.06 (m, 2 H), 3.79 (s, 2 H), 2.37 (t, J = 7.0 Hz, 4 H), 1.62 (sext, J = 7.3 Hz, 4 H), 1.32 (s, 18 H), 1.04 (t, J = 7.3 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 140.5, 136.5, 134.1, 132.8, 131.3, 124.5, 124.4, 103.2, 102.5, 90.9, 80.3, 66.3, 40.7, 31.2, 28.4, 22.3, 21.6, 13.7. HRMS: calcd for $C_{38}H_{44}O_2$ 532.3341, found 532.3331.

NanoBalletDancer (42). In a small vial, **41** (59 mg, 0.108 mmol), *p*-toluenesulfonic acid monohydrate (few crystals), 2,2-dimethyl-1,3-propanediol (0.225 mg, 2.158 mmol), and $MgSO_4$ (0.58 mg, 0.482 mmol) were subjected to microwave irradiation for 8 min. The reaction mixture was then diluted with a saturated solution of $NaHCO_3$ and all solvent was evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/CH_2Cl_2 66/33) afforded 59 mg (93% yield) of the title compound as a white solid. Mp: 146−150 °C. IR (KBr): 2963, 2929, 2867, 2838, 2220, 1587, 1457, 1423, 1392, 1364, 1338, 1266, 1099 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (s, 1 H), 7.15 (s, 2 H), 7.05 (s, 2 H), 6.00 (s, 1 H), 3.81 (d, J = 11.1 Hz, 2 H), 3.77 (s, 2 H), 3.61 (d, J = 11.1 Hz, 2 H), 2.37 (t, J = 7.0 Hz, 4 H), 1.62 (sext, J = 7.3 Hz, 4 H), 1.49 (s, 3 H), 1.34 (s, 18 H), 1.04 (t, J = 7.3 Hz, 6 H), 0.80 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6, 140.1, 136.4, 134.2, 132.7, 131.3, 124.4, 123.7, 102.7, 102.1, 90.8, 80.3, 78.7, 77.8, 40.7, 31.1, 30.7, 28.4, 24.6, 22.3, 22.2, 21.6, 13.7. HRMS: calcd for $C_{41}H_{50}O_2$ 574.3811, found 574.3813. Anal. Calcd: C, 85.67; H, 8.77. Found: C, 85.56; H, 8.78.

2,5-Bis(4-*tert*-butyldimethylsiloxy-1′-butynyl)-1,4-dibromobenzene (44). See the Pd/Cu general procedure (Supporting Information). To a solution of 2,5-dibromo-1,4-diiodobenzene (19.84 g, 40.687 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.856 g, 1.22 mmol), and copper(I) iodide (0.620 g, 3.25 mmol) in THF (50 mL) were added Et_3N (50 mL) and **43** (17.98 g, 97.65 mmol) in THF (50 mL) via a cannula. The mixture was stirred at rt for 1 d. Purification by flash chromatography (silica gel, hexanes/CH_2Cl_2 60/40) afforded 23.36 g (96% yield) of the title compound as a soft white solid: IR (KBr in $CHCl_3$) 3309, 3018, 2955, 2931, 2884, 2857, 2400, 2234, 1470, 1387, 1355, 1256, 1216, 1107 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 2 H), 3.84 (t, J = 7.1 Hz, 4 H), 2.69 (t, J = 7.1 Hz, 4 H), 0.92 (s, 18 H), 0.10 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.4, 126.6, 123.6, 95.2, 79.3, 61.8, 26.1, 24.3, 18.6, −5.0 ppm. HRMS: calcd for $C_{26}H_{40}Br_2O_2Si_2$ 583.0699, found 583.0704.

2,5-Bis(4-*tert*-butyldimethylsiloxy-1′-butynyl)-4-bromobenzaldehyde (45). To a solution of **44** (10.14 g, 16.895 mmol) in THF (80 mL) cooled to −78 °C under nitrogen was added dropwise *n*-BuLi (2.53 M, 6.67 mL). The reaction mixture was allowed to stir at −78 °C for 30 min. To this mixture was added DMF (1.37 mL, 17.74 mmol) predried over molecular sieves. The reaction mixture was allowed to warm to rt overnight. It was then diluted with water and extracted with Et_2O. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and evaporated. Purification by flash chromatography (silica gel, hexanes/$CHCl_3$ 20/80) afforded 5.94 g (64% yield) of the title compound as a white solid. Mp: 78−82 °C. IR (KBr): 2953, 2929, 2886, 2856, 2230, 1695, 1588, 1525, 1471, 1383, 1255, 1107 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.41 (s, 1 H), 7.90 (s, 1 H), 7.73 (s, 1 H), 3.85 (m, 4 H), 2.70 (m, 4 H), 0.92 (s, 18 H), 0.10 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 136.9, 134.8, 131.7, 131.3, 127.1, 126.3, 97.7, 95.3, 79.5, 76.9, 61.8, 61.6, 26.09, 26.06, 24.3, 18.5, −5.04, −5.08 ppm. HRMS: calcd for $C_{27}H_{41}BrO_3Si_2$ 548.1778, found 548.1776.

46. See the Pd/Cu general procedure (Supporting Information). To a solution of **45** (2.04 g, 3.72 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.261 g, 0.372 mmol), and copper(I) iodide (0.142 g, 0.744 mmol) in THF (15 mL) were added via cannula Et_3N (20 mL) and **12** (1.48 g, 6.32 mmol) in THF (25 mL). The mixture was stirred at 70 °C for 1 d. Purification by flash chromatography (silica gel, hexanes/$CHCl_3$ 25/75) afforded 2.46 g (94% yield) of the title compound as a yellow oil. IR (KBr): 3371, 2958, 2931, 2857, 2233, 1783, 1696, 1585, 1467, 1386, 1334, 1255, 1105 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.45 (s, 1 H), 7.93 (s, 1 H), 7.61 (s, 1 H), 7.45 (d, J = 1.5 Hz, 2 H), 7.43 (t, J = 1.5 Hz, 1 H), 3.87 (t, J = 7.1 Hz, 4 H), 2.74 (m, 4 H), 2.39 (t, J = 7.0 Hz, 4 H), 1.62 (sext, J = 7.2 Hz, 4 H), 1.05 (t, J = 7.3 Hz, 6 H), 0.92 (s, 9 H), 0.88 (s, 9 H), 0.10 (s, 6 H), 0.07 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 136.6, 135.3, 135.0, 133.8, 130.7, 130.6, 126.2, 125.0, 123.1, 96.9, 95.8, 94.4, 91.9, 87.9, 79.6, 79.5, 62.0, 61.7,

26.1, 24.3, 22.3, 21.6, 18.6, 18.5, 13.7, −5.05, −5.09. No signal for the molecular ion could be obtained by HRMS.

47. In a flask equipped with a condenser was dissolved a solution of the aldehyde **46** (1.58 g, 2.25 mmol), ethylene glycol (1 mL, 17.98 mmol), and TMSCl (1.75 mL, 13.68 mmol, distilled over CaH_2) in 100 mL of CH_2Cl_2. This solution was heated to reflux for 20 h after which aq NaOH was added until the solution was basic. The mixture was extracted with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and filtered and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/EtOAc 40/60) afforded a mixture of the product as well as the TBS-protected **47**. The mixture was submitted to a TBS-deprotection with TBAF (4.0 mL, 4.0 mmol) in THF (40 mL) for 25 min. The reaction mixture was diluted with water and extracted with Et_2O. The combined organic phases were dried over $MgSO_4$ and filtered, and the solvent was evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/EtOAc 25/75) afforded 417 mg (36% yield) of the title compound as a white solid. This compound is light and moisture sensitive, and it should be used immediately or stored under nitrogen in the freezer. Mp: 115−116 °C. IR (KBr): 3372, 2961, 2931, 2873, 2230, 1601, 1581, 1485, 1461, 1387, 1341, 1167, 1078, 1044 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1 H), 7.54 (s, 1 H), 7.45 (d, J = 1.5 Hz, 2 H), 7.39 (t, J = 1.5 Hz, 1 H), 6.17 (s, 1 H), 4.14−4.04 (m, 4 H), 3.83 (m, 4 H), 2.81 (t, J = 6.2 Hz, 2 H), 2.70 (t, J = 6.2 Hz, 2 H), 2.38 (t, J = 7.0 Hz, 4 H), 2.04 (m, 1 H), 1.62 (sext, J = 7.2 Hz, 4 H), 1.05 (t, J = 7.3 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 135.5, 134.9, 133.7, 129.4, 126.2, 125.4, 124.9, 123.3, 122.2, 101.6, 94.9, 92.9, 92.8, 91.7, 88.1, 81.25, 79.6, 65.6, 61.3, 61.2, 24.5, 24.3, 22.3, 21.6, 13.7. HRMS: calcd for $C_{35}H_{34}O_4$ 518.2457, found 518.2460.

48. To a flask equipped with a condenser was added a solution of the aldehyde **46** (1.97 g, 2.80 mmol), 2,2-dimethyl-1,3-propanediol (2.33 g, 22.42 mmol), TMSCl (1.79 mL, 134.01 mmol, distilled over CaH_2) in CH_2Cl_2 (150 mL). The solution was heated to reflux for 18 h after which time aq NaOH was added until the solution became basic. The mixture was extracted with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and filtered, and the solvent was evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/EtOAc 50/50) afforded a mixture of the product as well as the bis-TBS-protected ether. The mixture was submitted to a TBS-deprotection with TBAF (3.25 mL, 3.25 mmol) in THF (60 mL) for 20 min. The reaction mixture was diluted with water and extracted with Et_2O. The combined organic phases were dried over $MgSO_4$ and filtered, and the solvent wasevaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/EtOAc 50/50) afforded 1.17 g (75% yield) of the title compound as a white solid. Mp: 110−111 °C. IR (KBr): 3436, 2963, 2936, 2873, 2251, 1582, 1466, 1386, 1097 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 1 H), 7.54 (s, 1 H), 7.45 (d, J = 1.5 Hz, 2 H), 7.39 (t, J = 1.5 Hz, 1 H), 5.67 (s, 1 H), 3.84−3.76 (m, 6 H), 3.66 (d, J = 10.9 Hz, 2 H), 2.78 (t, J = 6.2 Hz, 2 H), 2.73 (t, J = 6.2 Hz, 2 H), 2.38 (t, J = 7.0 Hz, 4 H), 1.62 (sext, J = 7.2 Hz, 4 H), 1.31 (s, 3 H), 1.05 (t, J = 7.3 Hz, 6 H), 0.80 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.4, 135.6, 134.8, 133.7, 130.0, 125.9, 125.7, 124.8, 123.3, 121.5, 99.5, 93.1, 92.7, 92.6, 91.7, 88.2, 81.3, 79.6, 79.2, 78.0, 61.2, 30.5, 24.34, 24.28, 23.3, 22.3, 22.0, 21.5, 14.4. HRMS: calcd for $C_{38}H_{40}O_4$ 560.2927, found 560.2928.

50. To a solution of the alcohol **48** (1.17 g, 2.09 mmol) and DMAP (40 mg, 0.334 mmol) in CH_2Cl_2 (20 mL) cooled to 0 °C were added pyridine (0.85 mL, 10.44 mmol) and a 0 °C solution of *p*-nitrophenylchloroformate (1.66 g, 8.22 mmol) in CH_2Cl_2 (10 mL). This yellow milky solution was stirred at 0 °C for 1.25 h after which a solution of saturated aq $NaHCO_3$ was slowly added to quench the reaction. The mixture was extracted with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and filtered and the solvent evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/EtOAc 50/50) afforded 1.61 g (87% yield) of the title compound as a white sticky solid. Mp: 23−58 °C. IR (KBr): 2964, 2253, 1767, 1595, 1528, 1469, 1385, 1350, 1218, 1165, 1097 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.29 (m, 2 H), 8.25 (M, 2 H), 7.80 (s, 1 H), 7.57 (s, 1 H), 7.43 (d, J = 1.5 Hz, 2 H), 7.39 (m, 2 H), 7.37 (t, J = 1.5 Hz, 1 H), 7.35 (m, 2 H), 5.72 (s, 1 H), 4.51 (dt, J = 6.6, 2.0 Hz, 4 H), 3.76 (d, J = 11.1 Hz, 2 H), 3.68 (d, J = 10.9 Hz, 2 H), 2.99 (m, 4 H), 2.35 (t, J = 7.0 Hz, 4 H), 1.60 (sext, J = 7.2 Hz, 4 H), 1.31 (s, 3 H), 1.04 (t, J = 7.3 Hz, 6 H), 0.78 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 155.5, 152.6, 152.4, 145.7, 145.5, 139.5, 135.8, 134.8, 133.7, 130.3, 126.0, 125.7, 125.6, 125.4, 124.8, 123.3, 122.0, 121.9, 121.4, 99.5, 92.8, 91.7, 90.9, 90.6, 87.9, 81.2, 79.5, 79.2, 78.0, 66.9, 30.5, 23.3, 22.3, 22.0, 21.5, 20.5, 20.4, 13.7. MALDI MS (dithranol, Ag): calcd for $C_{52}H_{46}N_2O_{12}$ 890.3, found 890.

Synthesis of Dimers 51 and 52 and Polymer 53. Compounds **47** (113.9 mg, 0.2196 mmol) and **50** (195.7 mg, 0.2196 mmol) were carefully weighed into a round-bottom flask, and DMAP (67 mg, 0.549 mmol) was added. After removal of the oxygen, CH_2Cl_2 (5 mL) was added, and the solution was stirred at rt for 21 h after which a solution of $NaHCO_3$ was added to quench the reaction. The mixture was extracted with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and filtered, and the solvent was evaporated in vacuo. Purification by flash chromatography (silica gel, hexanes/EtOAc 50/50 then EtOAc) afforded **51** and **52**, 56 mg (23%) and 52 mg (21%) (the two isomers could not be clearly distinguished between each other although they were separable), and 42 mg of **53**. Compounds **51** or **52** (the less polar of the two, blue spot on TLC under UV irradiation). IR (KBr): 2962, 2933, 2905, 2872, 2234, 1748, 1581, 1464, 1401, 1337, 1267, 1097 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 1 H), 7.51 (s, 1 H), 7.43 (s, 1 H), 7.42 (d, J = 1.5 Hz, 2 H), 7.39 (s, 1 H), 7.37 (t, J = 1.5 Hz, 2 H), 7.35 (d, J = 1.5 Hz, 2 H), 5.96 (s, 1 H), 5.55 (s, 1 H), 4.33 (m, 8 H), 3.93 (m, 4 H), 3.64 (s, 2 H), 3.55 (d, J = 10.2 Hz, 1 H), 3.38 (d, J = 10.2 Hz, 1 H), 2.88 (m, 8 H), 2.36 (m, 8 H), 1.60 (m, 8 H), 1.17 (s, 3 H), 1.04 (m, 12 H), 0.72 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ155.2, 155.1, 139.8, 139.2, 135.9, 135.2, 134.6, 134.5, 134.0, 133.9, 133.7, 129.8, 129.7, 126.1, 125.5, 125.3, 125.1, 124.8, 124.6, 124.5, 123.7, 123.6, 122.3, 121.7, 101.4, 99.3, 92.5, 92.2, 91.8, 91.4, 91.2, 91.1, 88.7, 81.0, 79.8, 79.7, 78.8, 78.0, 66.2, 66.1, 66.0, 65.5, 65.4, 30.2, 23.2, 22.31, 22.29, 22.26, 22.0, 21.5, 20.5, 20.4, 20.2, 13.7. MALDI (dithranol, Ag): calcd for $C_{75}H_{70}O_{10}$ 1130.5, found 1130.4. GPC (THF, PS): M_n = 775, M_w = 800. **51** or **52** (the more polar of the two, gray-black spot on TLC under UV irradiation). IR (KBr): 2963, 2933, 2872, 2250, 1746, 1581, 1464, 1401, 1269, 1096 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 1 H), 7.48 (s, 1 H), 7.43 (d, J = 1.3 Hz, 2 H), 7.39 (t, J = 1.4 Hz, 4 H), 7.35 (t, J = 1.5 Hz, 1 H), 7.32 (t, J = 1.5 Hz, 1 H), 6.01 (s, 1 H), 5.61 (s, 1 H), 4.39−4.30 (m, 8 H), 3.98−3.90 (m, 4 H), 3.68 (s, 2 H), 3.57 (d, J = 10.2 Hz, 1 H), 3.52 (d, J = 10.2 Hz, 1 H), 2.95−2.81 (m, 8 H), 2.38 (m, 8 H), 1.60 (m, 8 H), 1.21 (s, 3 H), 1.07 (m, 12 H), 0.76 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 155.0, 139.6, 139.1, 135.9, 135.4, 134.7, 134.5, 133.94, 133.91, 133.7, 130.0, 129.9, 126.1, 125.7, 125.6, 125.5, 124.5, 123.8, 123.6, 121.6, 121.1, 101.5, 99.4, 92.7, 92.3, 92.1, 91.5, 91.4, 91.2, 88.4, 88.1, 80.8, 80.7, 79.9, 79.8, 79.3, 79.2, 78.0, 66.3, 66.2, 66.0, 65.9, 65.5, 30.3, 29.9, 23.3, 22.32, 22.26, 22.1, 21.6, 21.2, 20.5, 20.4, 14.4, 13.7. MALDI (dithranol, Ag): calcd for $C_{75}H_{70}O_{10}$ 1130.5, found 1130.5. GPC (THF, PS): M_n = 745, M_w = 765. **53** (blue tailing spot on TLC under UV irradiation). IR (KBr): 2965, 2934, 2873, 2253, 1746, 1581, 1463, 1402, 1256 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (br s, 1 H), 7.62 (br s, 1 H), 7.54 (t, J = 1.5 Hz, 1 H), 7.52 (t, J = 1.4 Hz, 1 H), 7.44 (m, 4 H), 7.39 (br t, 2 H), 6.10 (s, 0.5 H), 6.08 (s, 0.5 H), 5.67 (br t, 1 H), 4.39−4.30 (m, 8 H), 4.15−4.03 (m, 4 H), 3.76 (dd, J = 10.9, 3.67 Hz, 2 H), 3.66 (d, J = 10.7 Hz, 1 H), 2.93−2.82 (m, 8 H), 2.38 (m, 8 H), 1.60 (m, 8 H), 1.21 (d, J = 4.0 Hz, 3 H), 1.07 (m, 12 H), 0.80 (d, J = 4.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 154.8, 154.8, 139.5, 139.1, 136.0, 135.6, 134.74, 133.72, 130.3, 130.1, 126.1, 125.8, 125.7, 125.5, 124.83, 124.81, 123.4, 122.2, 121.5, 101.4, 99.5,

92.9, 92.7, 91.7, 90.7, 88.1, 87.9, 81.0, 79.6, 78.9, 78.0, 65.9, 65.8, 65.7, 30.4, 29.9, 23.3, 22.3, 22.0, 21.5, 21.2, 20.4, 13.7. LDI MS: a broad peak centered at 47,536. GPC (THF, PS): M_n = 23,500, M_w = 36,600.

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Supporting Information Available: General procedures and preparations of **1**, **6**−**8**, the diols, **26**, **27**, **43**, and **49**, as well as copies of ^{1}H and ^{13}C NMR spectra of most compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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