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Synthesis of Extended, π-Conjugated Isoindolin-1-ones

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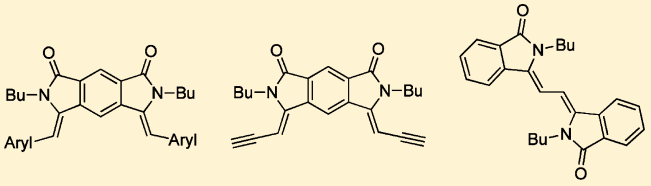
Supporting Information

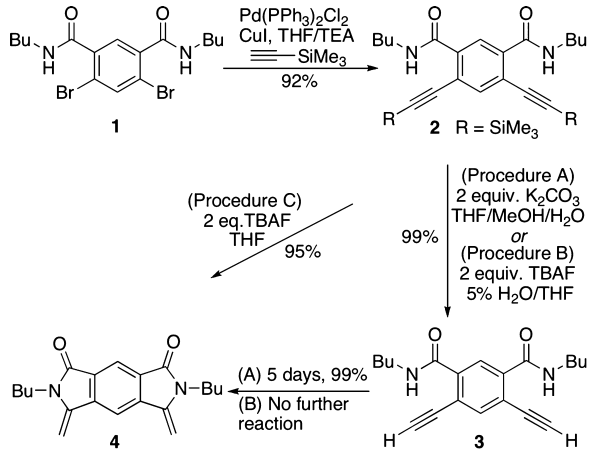
ABSTRACT: The synthesis and characterization of extended, conjugated molecules containing isoindolinone units was explored. Nucleophilic cyclizations between an amide and an alkyne were found to be an efficient method of producing the desired isoindolin-1-ones in high yields. A variety of derivatives were synthesized, demonstrating that a number of structural alterations could be made while maintaining good regio- and stereospecificity in the cyclized product.



Isoindolinone ring systems are frequently observed in natural products and are integral components of many pharmaceuticals.[1−4] In fact, while a handful of methods exist for their formation,[5−8] methodology for the synthesis of π-extended isoindolinone systems are limited in number and applicability to larger systems.[9−11] In addition, little is known about their electronic properties. Recent work with related structures hints at the potential utility of these molecular units toward the formation of organic photovoltaic (OPV) and organic field-effect transistor (OFET) components.[12−14] As we are interested in the incorporation of isoindolinone units into conjugated oligomers for the aforementioned applications, a method for their synthesis is desired that allows for conjugation length and structural complexity to be varied in a relatively facile manner. Cyclization reactions are particularly interesting for the synthesis of nitrogen heterocycles, as evidenced by several key papers in this field. Larock and co-workers showed that cyclization of *o*-(1-alkynyl)benzamides using electrophiles such as I_2 and ICl is an effective strategy to form both 5- and 6-membered lactams.[6,15] Friedel−Crafts acylation of ethynyl benzamides was found to effectively bring about the formation of alkylidene isoindolinones in either *E* or *Z* configurations.[16] Alabugin used base to explore the interplay between 5-exo and 6-endo cyclizations of hydrazides and alkynyl groups in the formation of *N*-aminolactams and benzopyridazinones,[17] and a recent discovery of Li and co-workers demonstrates the utility of I_2-induced cyclizations of nitrone-alkynes toward the formation of simple iodinated isoindolinones.[18] We report herein that intramolecular, nucleophilic cyclizations can be performed using mild conditions in high yields between an aryl amide and an adjacent alkynyl moiety to give a variety of π-extended, isoindolinone containing products that can easily be envisaged as building blocks for conjugated oligomers.

Our initial efforts focused on investigating a simple system in which more than one cyclization could be performed in the same molecule with a single synthetic operation, Scheme 1. Diamide **1** is available in a few steps from commercially available starting material and is easily transformed via a Sonogashira reaction into diyne **2**,[19] which serves as a model

Scheme 1



monomer unit, in 92% yield. While strong bases such as LHMDS and *n*-BuLi have been used to induce a similar cyclization,[20] reports of functional group-tolerant conditions that facilitate this transformation are rare but the group of Jacobi, in their efforts to synthesize chlorins and corrins, found that mild base can be an effective method of forming cyclic enamides.[21] Upon treatment with K_2CO_3 (procedure A), removal of the trimethylsilyl protective group to give terminal acetylene **3** and intramolecular cyclization provided lactam **4** quantitatively after 5 days as a result of 5-exo-ring closure, a structural assignment that was confirmed via the geminal coupling constant of the vinyl protons.[22] Because of the extended reaction time, the use of tetrabutylammonium fluoride (TBAF) to initiate cyclization was then explored as these conditions will remove silyl protective groups and are compatible with a range of functionality.[23] Upon treatment with TBAF in THF/H_2O (procedure B), terminal diyne **3** was produced directly in 10 min in quantitative yield, although even

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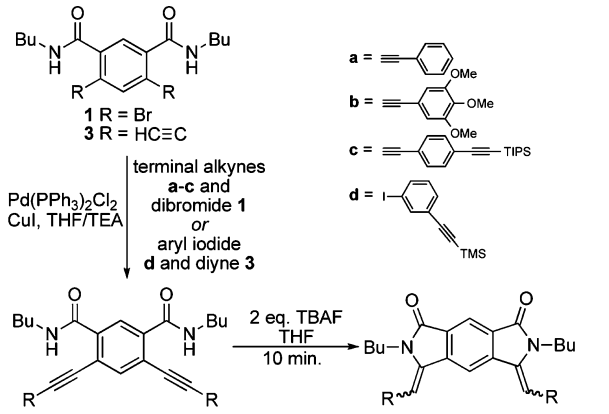
after several days of reaction, isoindolinone **4** was not produced. However, performing the reaction in anhydrous THF (procedure C) instead of THF/H_2O mixtures led immediately to the production of the desired product **4** as a stable, crystalline solid. The two methods (B and C) are conveniently complementary; for some synthetic routes the isolation of the terminal alkyne **3** is advantageous for subsequent chain extension reactions but it is often convenient to have a quick method to form the desired isoindolinone product. While detailed mechanistic studies are ongoing, Alabugin's work and our observations in Scheme 1 indicate that the first step is likely deprotonation of the amide,[17] followed by attack at the triple bond to form the cycle. Protonation of the resulting anion then leads to the product. The addition of water, as in procedure B, serves to decrease the basicity of the fluoride anion, thereby disfavoring the deprotonation and therefore the cyclization.[24] Encouraged by these early results, we set out to explore the scope of this approach toward the formation of more extended π-systems.[25]

A small series of diynes was therefore synthesized in an analogous manner to compound **2**, via a Sonogashira reaction between either dibromide **1** and various terminal alkynes, or diyne **3** and an aryl halide, Scheme 2. We initially extended the

Scheme 2

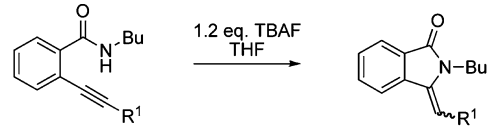


5a R = C_6H_5 99% **Z,Z-6a** R = C_6H_5 95%
5b R = 3,4,5-tri(OMe)C_6H_2 39% **Z,Z-6b** R = 3,4,5-tri(OMe)C_6H_2 79%
5c R = 4-(TIPSC≡C)C_6H_4 51% **Z,Z-6c** R = 4-(HC≡C)C_6H_4
Z,E-6c R = 4-(HC≡C)C_6H_4 77%
E,E-6c R = 4-(HC≡C)C_6H_4 (overall)
5d R = 3-(TMSC≡C)C_6H_4 40% **Z,Z-6d** R = 3-(HC≡C)C_6H_4 88%

conjugation length by appending a simple phenyl group on the alkyne, diyne **5a**. Compound **5a** was subsequently cyclized using TBAF to give *Z,Z*-**6a** as the sole product in 95% yield.[26] Substitution of the pendant aryl rings with methoxy groups in the 3,4,5-positions, as for **5b**, again did not hinder the reaction and derivative *Z,Z*-**6b** was isolated in 79% yield with ≤10% of other isomers produced. The conjugated structure was further extended by the placement of a silyl protected alkynyl moiety in either the *para*- and *meta*-positions of the phenyl ring, compounds **5c** and **5d**, respectively. Surprisingly, when diyne **5c** was exposed to the standard cyclization conditions, three products were produced as an inseparable mixture in a combined yield of 77%. NOE spectroscopy identified the products as the *ZZ*/*ZE*/*EE*-isomers of **6c** isolated in a 10:8:1 ratio.[27,28] Conversely, when *meta*-substituted **5d** was subjected to the same cyclization conditions, only the isoindolinone *Z,Z*-**6d** was produced as the main product, with <5% of other isomers being formed.

Intrigued by the disparity in product ratios between **6c** and **6d**, compounds **7** and **8** were synthesized via a Sonogashira reaction between *N*-butyl-2-iodobenzamide and the corresponding terminal acetylene[29] to determine the generality of this observation, Scheme 3.

Scheme 3



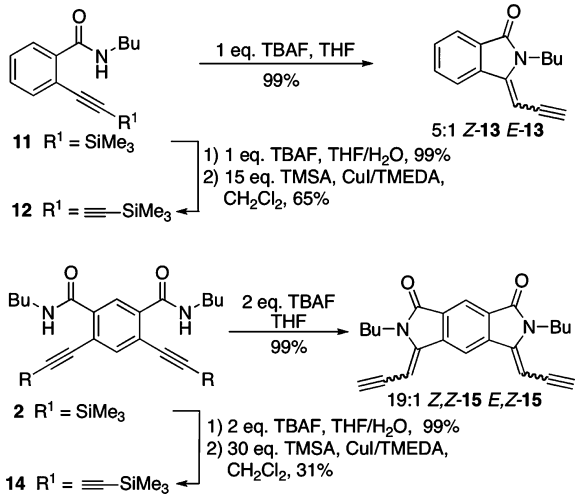
7 R^1 = 4-(TIPSC≡C)C_6H_4 → ***Z*-9** R^1 = 4-(HC≡C)C_6H_4 + ***E*-9** R^1 = 4-(HC≡C)C_6H_4 69%

8 R^1 = 3-(TIPSC≡C)C_6H_4 → ***Z*-10** R^1 = 3-(HC≡C)C_6H_4 86%

Cyclizations of these monoynes **7** and **8** were carried out with 1.2 equiv of TBAF. The *para*- derivative **7** gave a mixture of two isomers, *Z*-**9** and *E*-**9** in a ratio of 1:2, quite dissimilar to the ratio of products found for the cyclization of compound **5c**. However, cyclization of the *meta*- derivative **8**, again gave only one product, *Z*-**10**, in excellent yield. While derivatives *Z*-**9** and *E*-**9** possess different R_f values on silica, their isomerization in the presence of mild acid prevented isolation via flash chromatography and were therefore characterized as a mixture.

At this point, we decided to open up the structural possibilities by attempting cyclization with a butadiyne unit instead of an ethynyl unit, Scheme 4. To the best of our

Scheme 4



knowledge, anionic cyclizations between an amide and a butadiyne moiety have never been attempted. For amide **12**, the butadiyne was put into place via removal of the TMS group on **11** with TBAF in THF/H_2O, followed by oxidative coupling with excess trimethylsilylacetylene (TMSA) to give the protected butadiyne **12** in 65% yield.[30] The standard cyclization conditions were then applied to give a mixture of vinylic products **13** in a 5:1 ratio. The two peaks that appear in the vinylic region of the ^{1}H NMR spectrum of **13** are both coupled to the terminal acetylene proton, with J = 3 Hz, corresponding to a four-bond coupling, confirming the formation of a 5-membered ring. A NOESY experiment revealed that the main product was *Z*-**13** due to the presence of through-space coupling between the vinyl and aromatic protons. NOESY

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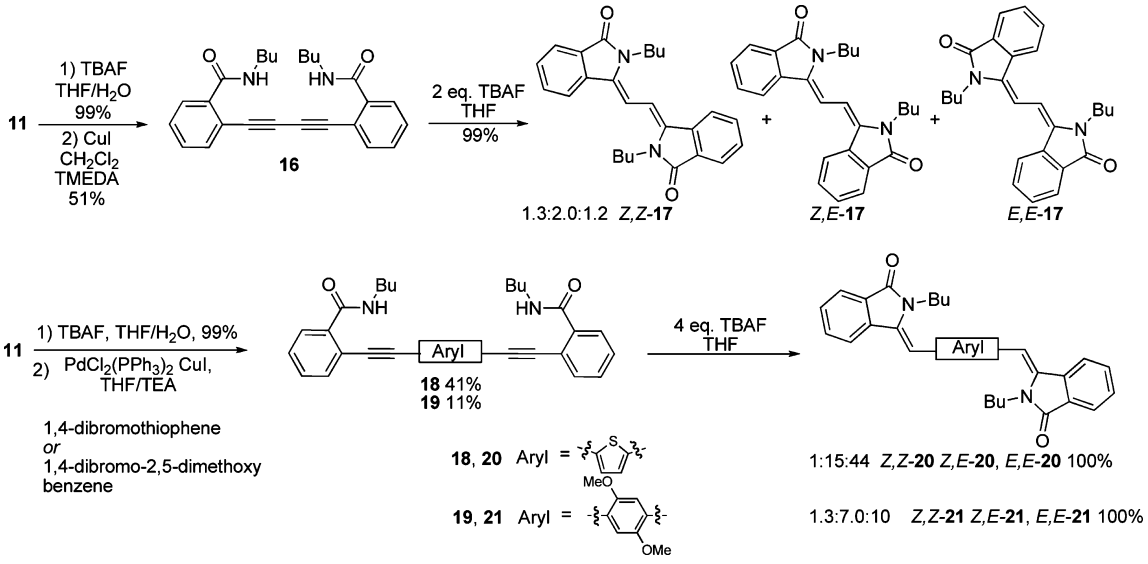
Scheme 5



correlations between the vinyl proton and the butyl group confirmed the identity of the minor isomer as *E*-**13**.

The more extended tetrayne system **14** was then synthesized to determine if more than one butadiyne cyclization could be performed in a single step. From diyne **2**, compound **14** was synthesized in 31% yield in an analogous manner to diyne **12**, via removal of the silyl group followed by oxidative coupling with excess trimethylsilylacetylene. Cyclization was induced with 2 equiv of TBAF. Again, the reaction proceeded in excellent yields to give a mixture of mainly two products as an inseparable mixture, which a NOESY experiment revealed to be isoindolinone **15** with a 19:1 *Z,Z* to *E,Z* ratio.[31] As diene **15** proved to be unstable, complicating purification and characterization, future studies will focus on discovering how to stabilize the conjugated core and producing this compound as a single isomer.[32]

Our initial success with the formation of these isoindolinone derivatives led us to further test the capabilities of this cyclization toward the formation of other extended networks with novel conjugation pathways. In addition, the results we have presented so far indicate that isomer formation is highly dependent on structure. The diyne **16** was therefore designed and synthesized through deprotection and an oxidative coupling reaction of amide **11**,[33] Scheme 5. Cyclization of **16** proceeded smoothly in high yield to provide conjugated diene **17** as a mixture of three isomers of the five-membered ring lactam, *ZZ*/*ZE*/*EE*, in a 1.3:2.0:1.2 ratio.[34] This experiment is the first example in this study where almost no *Z*/*E* selectivity is observed, with each individual cyclization in **16** proceeding close to 50% *Z* and 50% *E*. Intrigued by this incongruent result, an aryl group was inserted to provide diynes **18** and **19** to determine if the cyclizations in these systems generally proceed with less selectivity than the examples in Schemes 1−4. Upon cyclization of the derivative with a simple thiophene group, **20**, the *Z,Z*, *Z,E*, and *E,E* isomers were formed in a 1:15:44 ratio. Similar mixtures were produced with methoxy-substituted **21**, with a *ZZ*/*ZE*/*EE* ratio of 1.3:7.0:10. In both cases, the *E,E* isomers are greatly favored, indicating how different these derivatives behave under our cyclization reaction conditions. Future studies will focus on determining how to influence the isomer ratio in a controlled manner as the diene motifs in **17**, **20**, and **21** are particularly suitable for our continuing interest in isoindolinone-containing oligomers. Treatment with acid seems like a particularly reasonable method,[35] as putting the crude reaction mixture through a mildly acidic silica plug caused the isomer ratios for **20** and **21** to change in favor of the *Z,Z* and *Z,E* isomers and experiments involving acid-induced isomerization will be performed in the future.[36]

In conclusion, we have synthesized a number of isoindolinone derivatives with extended π-conjugation using 5-*exo* ring closures. While products can generally be isolated in excellent yields as stable crystalline solids, isomer formation is very sensitive to structure.

EXPERIMENTAL SECTION

Procedure A: General Deprotection. Arylsilylacetylene was dissolved in 10:5:1 THF/MeOH/H_2O. 1.2 equiv of K_2CO_3 per equiv of silyl group was added and the solution stirred for 30−90 min at rt. NH_4Cl_{satd} was added, the solution extracted with Et_2O, dried over $MgSO_4$, and filtered, and solvent removed.

Procedure B: General Deprotection. Arylsilylacetylene was dissolved in 20:1 THF/H_2O and cooled to 0 °C. 1.2 equiv of tetrabutylammonium fluoride (TBAF) per equiv of silyl group was added and the solution stirred for 5−10 min at 0 °C. NH_4Cl_{satd} was added, the solution extracted with Et_2O, dried over $MgSO_4$, and filtered, and solvent removed.

Procedure C: General Cyclization. Arylamide was dissolved in anhydrous THF and cooled to 0 °C. 1−1.5 equiv of TBAF per equiv of amide was added and the solution stirred for 5−10 min. NH_4Cl_{satd} was added, the solution extracted with Et_2O, dried over $MgSO_4$, and filtered, and solvent removed. The product was purified by flash chromatography (SiO_2) or recrystallization.

Procedure D: General Sonogashira. Under N_2, 1 equiv of aryl halide was dissolved in 25:1 anhyd THF/triethylamine (TEA), and the solution was degassed with N_2. 1−3 equiv of alkyne per equiv of alkyl halide was added, followed by 2.5−6 mol % of CuI and 2.5−5 mol % of $Pd(PPh_3)_2Cl_2$. The solution was heated to 70 °C until TLC indicated complete reaction. NH_4Cl_{satd} was added, the solution extracted with Et_2O, dried over $MgSO_4$, and filtered, and solvent removed. The product was purified by flash chromatography (SiO_2).

Procedure E. Deprotected alkyne was dissolved in CH_2Cl_2. 15 equiv of trimethylsilylacetylene per alkyne was added followed by a solution of 2:2.5 equiv of CuI/TMEDA in CH_2Cl_2. The solution was stirred for 2−3 h at rt. NH_4Cl_{satd} was added, the mixture extracted with Et_2O, dried over $MgSO_4$, and filtered, and solvent removed. The

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product was purified by flash chromatography (SiO_2) using 1:1 hexanes/EtOAc.

N^1,N^3-Dibutyl-4,6-dibromoisophthalamide (1). 4,6-Dibromoisophthalic acid[37] (757 mg, 2.34 mmol) was dissolved in 20 mL of benzene and $SOCl_2$ (8.50 mL, 117 mmol). After 5 h of reflux, solvent was removed and 10 mL DCM was added, followed by pyridine (0.50 mL, 6.2 mmol) and *n*-butylamine (0.68 mL, 6.9 mmol). The solution was stirred at rt for 18 h, concentrated under reduced pressure, followed by addition of water and extraction using Et_2O. The product was purified by elution through a silica plug (2:1 DCM/EtOAc): yield 853 mg (84%); white solid; mp 174−176 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.63 (s, 1H), 6.00 (br t, 2H), 3.45 (dt, J = 4.2, 5.4 Hz, 4H), 1.61 (m, 4H), 1.42 (m, 4H), 0.96 (t, J = 5.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.2, 137.5, 137.3, 129.6, 121.2, 40.1, 31.5, 20.3, 13.9; IR (film, KBr) 3248, 2958, 1643, 1301 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{22}Br_2N_2O_2Na$ $[M + Na]^+$ 454.9940, found 454.9942.

N^1,N^3-Dibutyl-4,6-bis[(trimethylsilyl)ethynyl]isophthalamide (2). Prepared by procedure D using **1** and trimethylsilylacetylene: orange solid; mp 198−201 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.68 (s, 1H), 7.27 (br, 2H), 3.48 (dt, J = 4.2, 5.4 Hz, 4H), 1.61 (m, 4H), 1.42 (m, 4H), 0.96 (t, J = 5.4 Hz, 6H), 0.28 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) 164.9, 139.4, 136.3, 131.5, 121.5, 104.0, 101.9, 40.2, 31.8, 20.5, 13.9, 0.2; IR (film, KBr) 3245, 2960, 2160, 1639, 1249 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{40}N_2O_2Si_2Na$ $[M + Na]^+$ 491.2541, found 491.2529.

N^1,N^3-Dibutyl-4,6-diethynylisophthalamide (3). Prepared by procedure A or B using **2**: orange solid; mp 93−96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, J = 0.6 Hz, 1H), 7.72 (s, 1H), 6.90 (br t, 2H), 3.53 (s, 2H), 3.46 (dt, J = 5.7, 6.9 Hz, 4H), 1.60 (m, 4H), 1.42 (m, 4H), 0.95 (t, J = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 165.2, 139.6, 137.8, 130.1, 120.8, 85.3, 80.6, 40.1, 31.5, 20.3, 13.9; IR (film, KBr) 3296, 2960, 2105, 1665, 1066 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{24}N_2O_2Na$ $[M + Na]^+$ 347.1730, found 347.1731.

2,6-Dibutyl-3,5-dimethylene-2,3,5,6-tetrahydropyrrolo[3,4-*f*]isoindole-1,7-dione (4). Prepared by procedure C using **2**: orange-yellow solid; mp 116−119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 0.8 Hz, 1H), 7.92 (d, J = 0.8 Hz, 1H), 5.32 (d, J = 2.8 Hz, 2H), 4.97 (d, J = 2.8 Hz, 2H), 3.79 (t, J = 7.2 Hz, 4H), 1.67 (m, 4H), 1.39 (m, 4H), 0.96 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.0, 141.5, 139.7, 130.8, 118.5, 111.5, 90.3, 39.6, 30.4, 20.4, 13.9; IR (film, KBr) 2959, 1699, 1639, 1393 cm^{-1}; HRMS (ASAP) calcd for $C_{20}H_{25}N_2O_2$ $[M + H]^+$ 325.1916, found 325.1913.

N^1,N^3-Dibutyl-4,6-bis(phenylethynyl)isophthalamide (5a). Prepared by procedure D using **1** and phenylacetylene: yield 99%; brown solid; mp 137−140 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (d, J = 0.6 Hz, 1H), 7.83 (d, J = 0.3 Hz, 1H), 7.54 (m, 4H), 7.41 (m, 6H), 7.02 (br t, 2H), 3.51 (dt, J = 5.7, 7.2 Hz, 4H), 1.59 (m, 4H), 1.39 (m, 4H), 0.88 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 165.6, 138.2, 136.3, 131.8, 130.8, 129.6, 128.8, 122.0, 97.3, 86.4, 40.2, 31.8, 20.4, 13.9 (one carbon signal missing); IR (film, KBr) 3399, 2961, 1643, 1261 cm^{-1}; HRMS (ASAP) calcd for $C_{32}H_{33}N_2O_2$ $[M + H]^+$ 477.2542, found 477.2523.

N^1,N^3-Dibutyl-4,6-bis[(3,4,5-trimethoxyphenyl)ethynyl]-isophthalamide (5b). Prepared by procedure D using **1** and 1-ethynyl-3,4,5-trimethoxybenzene:[38] yield 39%; yellow solid; mp 200−202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.82 (s, 1H), 7.00 (br t, 2H), 6.76 (s, 4H), 3.89 (s, 6H), 3.88 (s, 12H), 3.51 (dt, J = 4.5, 5.4 Hz, 4H), 1.61 (m, 4H), 1.41 (m, 4H), 0.89 (t, J = 5.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 165.6, 153.4, 140.1, 138.1, 136.1, 130.7, 122.1, 116.8, 109.1, 97.4, 85.5, 61.2, 56.4, 40.2, 31.8, 20.4, 13.9; IR (film, KBr) 3243, 2957, 1632, 1238 cm^{-1}; HRMS (ESI) calcd for $C_{38}H_{44}N_2O_8Na$ $[M + Na]^+$ 679.2990, found 679.2979.

N^1,N^3-Dibutyl-4,6-bis[4-((triisopropylsilyl)ethynyl)phenyl]-isophthalamide (5c). Prepared by procedure D using **1** and 4-triisopropylsilylethynyl-1-ethynylbenzene:[30] yield 51%; yellow solid; mp 200 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 2.4 Hz, 1H), 7.79 (d, J = 1.6 Hz, 1H), 7.49 (d, J = 8.0 Hz, 4H), 7.45 (d, J = 8.0 Hz, 4H), 7.00 (br t, 2H), 3.48 (q, J = 6.4 Hz, 4H), 1.58 (m, 4H), 1.39 (m, 4H), 1.14 (s, 42H), 0.89 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 165.6, 138.2, 136.5, 132.3, 131.6, 130.5, 124.7, 121.8, 121.6, 106.3, 96.7, 94.0, 87.9, 40.2, 31.8, 20.3, 18.8, 13.9, 11.4; IR (film, KBr) 3250, 2958, 2154, 1640 cm^{-1}; HRMS (APCI) calcd for $C_{54}H_{73}N_2O_2Si_2$ $[M + H]^+$ 837.5205, found 837.5213.

N^1,N^3-Dibutyl-4,6-bis[3-((trimethylsilyl)ethynylphenyl)-ethynyl]isophthalamide (5d). Prepared by procedure D using **3** and 3-trimethylsilylethynyl-1-iodobenzene:[39] yield 40%; orange solid; mp 143−146 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (d, J = 0.6 Hz, 1H), 7.80 (d, J = 0.6 Hz, 1H), 7.65 (td, J = 0.6, 1.5 Hz, 2H), 7.48 (tt, J = 1.2, 7.5 Hz, 4H), 7.33 (td, J = 0.6, 7.8 Hz, 2H), 6.89 (br t, 2H), 3.51 (dt, J = 5.7, 6.9 Hz, 4H), 1.61 (m, 4H), 1.41 (m, 4H), 0.91 (t, J = 7.2 Hz, 6H), 0.26 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) 165.6, 138.3, 136.7, 135.2, 132.8, 131.6, 130.5, 128.7, 124.1, 122.2, 121.8, 103.7, 96.2, 95.8, 86.8, 40.2, 31.9, 20.4, 13.9, 0.01; IR (film, KBr) 3254, 2957, 2160, 1640, 1250 cm^{-1}; HRMS (ESI) calcd for $C_{42}H_{49}N_2O_2Si_2$ $[M + H]^+$ 669.3333, found 669.3339.

(3*Z*,5*Z*)-3,5-Dibenzylidene-2,6-dibutyl-2,3,5,6-tetrahydropyrrolo[3,4-*f*]isoindole-1,7-dione (6a). Prepared by procedure C using **5a**: yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, J = 0.9 Hz, 1H), 8.08 (d, J = 1.2 Hz, 1H), 7.39 (m, 10H), 6.93 (s, 2H), 3.68 (m, 4H), 1.21 (m, 4H), 0.86 (m, 4H), 0.62 (t, J = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 167.7, 141.7, 134.7, 134.6, 129.6, 129.4, 128.3, 128.0, 118.9, 110.4, 108.0, 41.6, 30.3, 19.8, 13.6; IR (film, KBr) 2958, 1716, 1683, 1064 cm^{-1}; HRMS (ASAP) calcd for $C_{32}H_{33}N_2O_2$ $[M + H]^+$ 477.2542, found 477.2540.

(3*Z*,5*Z*)-2,6-Dibutyl-3,5-bis(3,4,5-trimethoxybenzylidene)-2,3,5,6-tetrahydropyrrolo[3,4-*f*]isoindole-1,7-dione (6b). Prepared by procedure C using **5b**: yellow solid; mp 79−82 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, J = 0.6 Hz, 1H), 8.04 (d, J = 0.9 Hz, 1H), 6.87 (s, 2H), 6.59 (d, J = 0.0.6 Hz, 4H), 3.89 (d, J = 0.8 Hz, 18H), 3.74 (m, 4H), 1.31 (m, 4H), 0.96 (m, 4H), 0.68 (t, J = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 167.7, 153.2, 141.7, 138.1, 134.6, 130.1, 129.4, 119.0, 110.2, 107.9, 106.9, 61.2, 56.4, 41.8, 30.6, 19.9, 13.7; IR (film, KBr) 2957, 1712, 1126 cm^{-1}; HRMS (ESI) calcd $C_{38}H_{44}N_2O_8Na$ $[M + Na]^+$ 679.2990, found 679.3002.

(3*Z*,5*Z*)-2,6-Dibutyl-3,5-bis(4-ethynylbenzylidene)-2,3,5,6-tetrahydropyrrolo[3,4-*f*]isoindole-1,7-dione (*Z*,*Z*-6c, *Z*,*E*-6c, and *E*,*E*-6c). Prepared by procedure C using **5c**: yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) ***Z*,*Z*-6c**: δ 8.31 (d, J = 0.8 Hz, 1H), 8.07 (d, J = 0.8 Hz, 1H), 7.54 (d, J = 8.0 Hz, 4H), 7.34 (d, J = 8.0 Hz, 4H), 6.86 (s, 2H), 3.70 (m, 4H), 3.17 (s, 2H), 0.65 (t, J = 7.6 Hz, 6H); ***Z*,*E*-6c**: δ 8.29 (d, J = 0.8 Hz, 1H), 7.63 (d, J = 0.8 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 6.58 (s, 1H), 6.30 (s, 1H), 3.91 (t, J = 7.6 Hz, 2H), 3.63 (m, 2H), 3.17 (s, 1H), 3.16 (s, 1H), 0.62 (t, J = 7.2 Hz, 3H); ***E*,*E*-6c**: δ 8.28 (d, J = 0.8 Hz, 1H), 7.88 (d, J = 0.8 Hz, 1H), 7.32 (d, J = 8.0 Hz, 4H), 7.16 (d, J = 8.0 Hz, 4H), 6.39 (s, 2H), 3.84 (t, J = 7.2 Hz, 4H), 3.23 (s, 2H); overlapping signals: 1.73 (m), 1.44 (m), 1.17 (m), 1.00 (m), 0.89 (m) (33 protons); ^{13}C NMR (75 MHz, $CDCl_3$) ***Z*,*Z*-6c**: δ 167.7, 141.7, 135.3, 135.2, 132.0, 129.6, 121.8, 119.2, 110.6, 107.0, 83.3, 78.5, 41.6, 30.2, 19.8, 13.6; one signal missing. ***Z*,*E*-6c**: δ 167.5, 165.5, 141.0, 138.1, 136.5, 135.8, 135.2, 135.0, 132.6, 131.9, 129.9, 129.7, 129.5, 129.5, 129.2, 122.1, 121.7, 118.9, 114.2, 110.7, 107.0, 83.3, 78.7, 78.5, 41.6, 39.8, 30.5, 30.2, 20.5, 19.7, 14.0, 13.6; ***E*,*E*-6c**: two very small signals assigned to this isomer: δ 132.7 and 131.6; IR (film, KBr) 3296, 3239, 2959, 1712 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{32}N_2O_2Na$ $[M + Na]^+$ 547.2356, found 547.2314.

(3*Z*,5*Z*)-2,6-Dibutyl-3,5-bis(3-ethynylbenzylidene)-2,3,5,6-tetrahydropyrrolo[3,4-*f*]isoindole-1,7-dione (6d). Prepared by procedure C using **5d**: orange solid; mp 90−93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.06 (s, 1H), 7.50 (m, 4H), 7.38 (m, 4H), 6.85 (s, 2H), 3.65 (m, 4H), 3.13 (s, 2H), 1.24 (m, 4H), 0.92 (m, 4H), 0.66 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 167.6, 141.6, 135.2, 135.0, 133.0, 131.6, 130.0, 129.6, 128.4, 122.4, 119.1, 110.6, 106.6, 83.0, 78.2, 41.7, 30.3, 19.8, 13.6; IR (film, KBr) 3296, 2958, 1712, 1397 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{33}N_2O_2$ $[M + H]^+$ 525.2542, found 525.2545.

***N*-Butyl-2[(4-((triisopropylsilyl)ethynyl)phenyl)ethynyl]-benzamide (7).** Prepared by procedure D using *N*-butyl-2-iodobenzamide[40] and 4-triisopropylsilylethynyl-1-ethynylbenzene:[30] yield 63%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (m, 1H), 7.59 (m, 1H), 7.47 (m, 6H), 7.18 (br t, 1H), 3.51 (dt, J = 7.2, 5.6

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Hz, 2H), 1.58 (m, 2H), 1.40 (m, 2H), 1.14 (s, 21H), 0.88 (t, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) 166.5, 136.3, 133.6, 132.3, 131.4, 130.5, 130.1, 129.2, 124.4, 122.1, 119.4, 106.4, 95.0, 93.7, 89.4, 40.1, 31.8, 20.4, 18.8, 13.9, 11.4; IR (film, KBr) 2865, 2153, 1652, 1464 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{39}NOSiNa$ [M + Na]$^+$ 480.2693, found 480.2677.

***N*-Butyl-2[3-((triisopropylsilyl)ethynyl)phenyl)ethynyl]-benzamide (8).** Prepared by procedure D using *N*-butyl-2-iodobenzamide[40] and 3-triisopropylsilylethynyl-1-ethynylbenzene:[30] yield 98%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (m, 1H), 7.62 (t, J = 1.2 Hz, 1H), 7.59 (m, 1H), 7.47 (m, 4H), 7.33 (t, J = 8.0 Hz, 1H), 7.22 (br t, 1H), 3.51 (dt, J = 7.2, 5.6, 2H), 1.59 (m, 2H), 1.40 (m, 2H), 1.14 (s, 21H), 0.88 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.5, 136.3, 135.0, 133.6, 132.6, 131.3, 130.5, 130.1, 129.2, 128.7, 124.3, 122.5, 119.3, 105.8, 94.5, 92.2, 88.2, 40.1, 31.8, 20.4, 18.8, 13.9, 11.4; IR (film, KBr) 2941, 2162, 1652, 1464 cm^{-1}; HRMS (ASAP) calcd for $C_{30}H_{40}NOSi$ [M + H]$^+$ 458.2879, found 458.2871.

2-Butyl-3-(4-ethynylbenzilidene)isoindolin-1-one (*Z*-9, *E*-9). Prepared by procedure C using **7**. Crude ratio 1:2 of *Z*:*E*, but after silica plug the ratios changed to 1:0.4 of *Z*:*E*: yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) ***Z*-9**: δ 7.85 (dt, J = 7.5, 0.9 Hz, 1H), 7.73 (d, J = 7.5 Hz, 1H), 7.61 (dd, J = 7.8, 1.2 Hz, 1H), 7.51 (m, 3H), 7.33 (m, 2H), 6.71 (s, 1H), 3.66 (t, J = 7.5 Hz, 2H), 3.15 (s, 1H), 1.19 (m, 2H), 0.89 (m, 2H), 0.64 (t, J = 7.2 Hz, 3H); ***E*-9**: δ 7.83 (dt, J = 7.5, 0.9 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.43 (m, 3H), 7.33 (m, 2H), 6.47 (s, 1H), 3.88 (t, J = 7.5 Hz, 2H), 3.17 (s, 1H), 1.73 (m, 2H), 1.45 (m, 2H), 0.99 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 168.9, 166.7, 138.4, 137.0, 136.2, 135.9, 135.5, 134.9, 132.5, 132.1, 131.9, 131.6, 129.8, 129.7, 129.6, 129.3, 128.6, 123.5, 123.4, 123.2, 121.6, 121.4, 119.4, 109.2, 105.5, 83.5, 83.5, 78.3, 78.2, 41.3, 39.4, 30.6, 30.3, 20.5, 19.8, 14.0, 13.7; IR (film, KBr) 3293, 2921, 2359, 1701, 1094 cm^{-1}; HRMS (ASAP) calcd for $C_{21}H_{20}NO$ [M + H]$^+$ 302.1545, found 302.1544.

2-Butyl-3-(3-ethynylbenzilidene)isoindolin-1-one (*Z*-10). Prepared by procedure C using **8**: yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (td, J = 7.5, 0.9 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.59 (tdd, J = 7.5, 0.6 Hz, 1H), 7.50 (m, 2H),7.45 (m, 1H), 7.34 (m, 2H), 6.68 (s, 1H), 3.61 (m, 2H), 3.11 (s, 1H), 1.19 (m, 2H), 0.89 (m, 2H), 0.64 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 168.8, 138.3, 135.6, 135.5, 133.2, 132.0, 131.3, 130.1, 129.3, 128.6, 128.3, 123.4, 122.3, 119.4, 105.1, 83.2, 77.9, 41.4, 30.4, 19.8, 13.6; IR (film, KBr) 3293, 2958, 1707, 1654, 1095 cm^{-1}; HRMS (ASAP) calcd for $C_{21}H_{20}NO$ [M + H]$^+$ 302.1545, found 302.1538.

***N*-Butyl-2-((trimethylsilyl)ethynyl)benzamide (11).** Prepared by procedure D using *N*-butyl-2-iodobenzamide[40] and trimethylsilylacetylene: yield 1.8 g (97%); orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (m, 1H), 7.67 (br s, 1H), 7.53 (m, 1H), 7.41 (m, 2H), 3.49 (dt, J = 7.2, 5.6 Hz, 2H), 1.63 (m, 2H), 1.44 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H), 0.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 135.6, 134.2, 130.4, 130.3, 129.3, 119.3, 103.8, 101.7, 40.1, 31.8, 20.5, 14.0, 0.1; IR (film, KBr) 3393, 2958, 2157, 1652 cm^{-1}; HRMS (ASAP) cald for $C_{16}H_{24}NOSi$ [M + H]$^+$ 274.1627, found 274.1629.

***N*-Butyl-2((trimethylsilyl)buta-1,3-diynyl)benzamide (12).** Prepared first by procedure B using **11** to give *N*-butyl-2-ethynylbenzamide followed by procedure E: yellow solid; mp 79−81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.6, 1.6 Hz, 1H), 7.55 (dd, J = 7.6, 1.6 Hz, 1H), 7.42 (m, 2H), 6.85 (br s, 1H), 3.50 (dt, J = 7.2, 5.6 Hz, 2H), 1.64 (m, 2H), 1.48 (m, 2H), 0.99 (t, J = 7.2 Hz, 3H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 138.1, 134.6, 130.5, 130.0, 129.9, 118.0, 93.7, 87.0, 80.0, 74.3, 40.1, 31.6, 20.4, 14.1, −0.3; IR (film, KBr) 3284, 2959, 2204, 2102, 1643, 1251 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{23}NOSiNa$ [M + Na]$^+$ 320.1441, found 320.1438.

***N*-Butyl-3-(prop-2-ynylidene)isoindolin-1-one (*Z*-13, *E*-13).** Prepared by procedure C using **12**: dark brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) ***Z*-13**: δ 7.82 (ddd, J = 7.6, 1.6, 0.8 Hz, 1H), 7.56 (m, 3H), 5.63 (d, J = 2.8 Hz, 1H), 4.19 (m, 2H), 3.35 (d, J = 2.8 Hz, 1H), 1.75 (m, 2H), 1.40 (m, 2H), 0.96 (t, J = 7.6 Hz, 3H); ***E*-13**: δ 8.55 (dt, J = 7.6 Hz, 0.8 Hz, 1H), 7.84 (ddd, J = 7.6, 1.2, 0.8 Hz, 1H), 7.56 (m, 2H), 5.42 (d, J = 2.8 Hz, 1H), 3.76 (m, 2H), 3.52 (d, J = 2.8 Hz, 1H), 1.64 (m, 2H), 0.96 (t, J = 7.6 Hz, 3H), one buried signal for *E* isomer in alkyl region; ^{13}C NMR (75 MHz, $CDCl_3$) ***Z*-13**: δ 167.6, 143.6, 136.7, 132.1, 130.1, 128.2, 123.5, 119.2, 84.8, 83.0, 79.7, 40.7, 32.0, 19.9, 14.1; ***E*-13**: δ 166.4, 145.3, 134.9, 132.5, 130.3, 129.6, 123.9, 123.3, 85.8, 85.4, 80.7, 39.3, 30.4, 20.3, 13.9; IR (film, KBr) 2959, 1709, 1636, 1074 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{15}NONa$ [M + Na]$^+$ 248.1046, found 248.1040.

***N*^{1},*N*^{3}-Dibutyl-4,6-bis((trimethylsilyl)buta-1,3-diynyl)-benzamide (14).** Prepared first by procedure B using **2**, followed by procedure E: orange solid; mp 166−168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.69 (s, 1H), 6.65 (br t, 2H), 3.48 (dt, J = 6.8, 5.6 Hz, 4H), 1.62 (m, 4H), 1.45 (m, 4H), 0.98 (t, J = 7.2 Hz, 6H), 0.24 (s, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 140.2, 138.7, 130.4, 120.7, 95.4, 86.7, 81.9, 72.3, 40.2, 31.5, 20.4, 14.0, −0.4; IR (film, KBr) 3249, 2959, 2211, 2103, 1641, 1250 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{40}N_2O_2Si_2Na$ [M + Na]$^+$ 539.2521, found 539.2506.

***N*^{2},*N*^{6}-Dibutyl-3,5-di(prop-2-ynylidene)-2,3,5,6-tetrahydropyrrolo[3,4-*f*]isoindole-1,7-dione (*Z*,*Z*-15, *Z*,*E*-15).** Prepared by procedure C using **14**: dark red solid; ^{1}H NMR (300 MHz, $CDCl_3$) ***Z*,*Z*-15**: δ 8.25 (d, J = 0.9 Hz, 1H), 7.80 (d, J = 0.9 Hz, 1H), 5.74 (d, J = 3.0 Hz, 2H), 4.21 (m, 4H), 3.44 (d, J = 3.0 Hz, 2H), 1.75 (m, 4H), 1.40 (m, 4H), 0.96 (t, J = 7.5 Hz, 6H); ***Z*,*E*-15**: 8.85 (d, J = 1.2 Hz, 1H), 8.26 (d, J = 0.9 Hz, 1H), 5.52 (d, J = 3.0 Hz, 1H), 3.72 (t, 7.5 Hz, 4H), 3.66 (d, J = 3.0 Hz, 1H); five signals for isomer Z,E are buried (1 alkynyl, 1 alkenyl, 3 alkyl); ^{13}C NMR (100 MHz, $CDCl_3$) ***Z*,*Z*-15**: δ 166.2, 142.8, 140.1, 129.7, 119.2, 110.1, 86.3, 84.9, 79.3, 41.1, 32.0, 20.0, 14.0; IR (film, KBr) 2959, 1709, 1622, 1259 cm^{-1}.[41]

***N*,N′-Dibutyl-2,2′-(buta-1,3-diyne-1,4-diyl)bisbenzamide (16).** Prepared by procedure B using **11** to form *N*-butyl-2-ethynylbenzamide (139 mg, 0.691 mmol), which was dissolved in CH_2Cl_2 (30 mL), and a solution of TMEDA (3.5 mL) and CuI (162 mg, 0.851 mmol) was added. After 20 min at rt, NH_4Cl_{satd} was added, the solution extracted with Et_2O, dried over $MgSO_4$, and filtered, and solvent removed. Recrystallized from Et_2O: white solid; mp 126−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 8.0, 1.6 Hz, 2H), 7.59 (dd, J = 7.6, 1.6 Hz, 2H), 7.45 (m, 4H), 6.72 (br t, 2H), 3.52 (dt, J = 7.2, 5.6 Hz, 4H), 1.66 (m, 4H), 1.49 (m, 4H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.3, 138.3, 134.5, 130.5, 130.1, 129.7, 118.1, 81.5, 78.6, 40.1, 31.7, 20.4, 14.0; IR (film, KBr) 3293, 2917, 2384, 1642, 1384, cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{28}N_2O_2Na$ [M + Na]$^+$ 423.2043, found 423.2025.

3,3′-(Ethane-1,2-diylidene)bis(2-butylisoindolin-1-one) (*E*,*Z*-17), (*Z*,*Z*-17), (*E*,*E*-17). Prepared by procedure C using **16**. Crude ratio of 1.3:2.0:1.2 for *ZZ*/*EZ*/*EE* but after silica plug ratio changed to 1.0:2.9:1.7: orange solid; mp 118−119 °C; ^{1}H NMR (300 MHz, $CDCl_3$) ***E*,*Z*-17**: δ 8.08 (d, J = 7.8 Hz, 1 H), 7.80 (dt, J = 7.8, 0.6 Hz, 1H), 7.11 (d, J = 12.6 Hz, 1H), 6.66 (d, J = 12.6 Hz, 1H) 4.14 (m, 2H), 3.89 (m, 2H); ***E*,*E*-17**: δ 6.84 (s, 1H), 4.21 (m, 2H); ***Z*,*Z*-17**: δ 6.92 (s, 1H), 3.98 (m, 2H); overlapping signals: 8.0 (m, 3H), 7.94 (m, 3H), 7.66 (m, 8H), 1.86 (m, 12H), 1.56 (m, 12H), 1.07 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) 168.0, 167.9, 166.3, 166.2, 138.0, 137.9, 137.3, 137.0, 135.4, 135.3, 134.8, 134.7, 132.2, 132.1, 132.0, 130.3, 130.2, 129.4, 129.4, 129.2, 129.1, 127.8, 127.8, 124.1, 124.1, 123.8, 123.8, 123.2, 119.3, 118.9, 105.9, 104.5, 101.4, 100.0, 42.0, 41.9, 39.6, 39.5, 32.1, 31.8, 31.0, 30.8, 20.6, 20.5, 20.5, 20.5, 14.1, 14.1, 14.0, 14.0 (2 signals missing); IR (film, KBr) 2917, 2383, 1692, 1384, cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{28}N_2O_2Na$ [M + Na]$^+$ 423.2043, found 423.2032.

***N*,N′-Dibutyl-2,2′-[2,5-thiophenebis(2,1-ethynediyl)]-bisbenzamide (18).** Prepared by procedure B using **11** to form *N*-butyl-2-ethynylbenzamide followed by procedure D using 1,4-dibromothiophene: orange solid; mp 126−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (m, 2H), 7.60 (m, 2H), 7.46 (m, 4H), 7.21 (s, 2H), 6.91 (br t, 2H), 3.52 (q, J = 6.4H, 4H) 1.63 (m, 4H), 1.44 (m, 4H), 0.92 (t, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.6, 136.7, 133.4, 132.7, 130.5, 129.9, 129.6, 124.5, 118.9, 92.8, 87.5, 40.1, 31.8, 20.4, 13.9; IR (film, KBr) 2957, 1642, 1534 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{30}N_2O_2SNa$ [M + Na]$^+$ 505.1920, found 505.1898.

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***N,N′*-Dibutyl-2,2′-[1,4-(2,5-dimethoxy)phenylenebis(2,1-ethynediyl)]bisbenzamide (19).** Prepared first by procedure B using **11** to form *N*-butyl-2-ethynylbenzamide, followed by procedure D using 1,4-diiodo-2,5-dimethoxybenzene:[42] orange solid; mp 123−129 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (m, 2H), 7.74 (br t, 2H), 7.63 (m, 2H), 7.46 (m, 2H), 7.05 (s, 2H), 3.92 (s, 6H), 3.51 (dt, J = 5.7, 7.2 Hz, 4H), 1.59 (m, 4H), 1.38 (m, 4H), 0.88 (t, J = 7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 166.0, 154.2, 135.6, 133.6, 130.5, 130.5, 129.3, 119.4, 115.3, 113.3, 93.8, 91.7, 56.6, 40.1, 31.9, 20.4, 14.0; IR (film, KBr) 3283, 2957, 2203, 1642 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{37}N_2O_4$ $[M + H]^+$ 537.2753, found 537.2753.

3,3′-(2,5-Thiophenebis(methanyl-1-ylidene))bis(2-butylisoindolin-1-one) (*E,Z*-20), (*E,E*-20), (*Z,Z*-20). Prepared by procedure C using **18**. Crude ratio of 1:15:44 for *ZZ*/*ZE*/*EE* but after silica plug ratio changed to 1:2:1: orange solid; mp 174−178 °C; ^{1}H NMR (300 MHz, $CDCl_3$) ***E,Z*-20**: δ 7.14 (dd, J = 3.6, 0.9 Hz, 1H), 7.04 (dd, J = 3.6, 0.9 Hz, 1H), 6.67 (s, 1H), 6.37 (s, 1H), 4.00 (t, J = 7.5 Hz, 2H), 3.88 (t, J = 7.5 Hz, 2H); ***E,E*-20**: 7.18 (d, J = 0.3 Hz, 2H), 6.42 (s, 2H), 3.89 (t, J = 7.5, 4H); ***Z,Z*-20**: 6.99 (d, J = 0.3 Hz, 2H), 6.64 (s, 2H), 3.98 (t, J = 7.5 Hz, 4H); overlapping signals: 7.86 (m), 7.76 (m), 7.61 (tt, J = 7.5, 1.5 Hz), 7.46 (m) for a total of 24H, 1.73 (m, 6H), 1.44 (m, 12H), 1.13 (m, 6H), 1.00 (dt, 7.5, 1.2 Hz, 9H), 0.80 (dt, 7.5, 3 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 168.8, 168.8, 166.6, 138.8, 138.8, 138.3, 138.2, 138.2, 138.1, 136.3, 136.2, 134.8, 134.8, 132.1, 131.8, 131.7, 130.5, 130.5, 129.8, 129.8, 129.4, 129.2, 129.0, 128.8, 128.4, 128.3, 128.2, 123.6, 123.5, 123.4, 123.3, 119.5, 101.5, 101.3, 98.1, 98.0, 41.3, 41.3, 39.5, 39.5, 31.0, 30.9, 30.6, 20.5, 20.0, 20.0, 14.0, 13.9, 13.9 (11 signals missing); IR (film, KBr) 2917, 2347, 1702, 1652, 1384 cm^{-1}; HRMS (ASAP) calcd for $C_{30}H_{31}N_2O_2S$ $[M + H]^+$ 483.2106, found 483.2107.

3,3′-(1,4-(2,5-Dimethoxy)phenelenebis(methanlyl-1-ylidene))bis(2-butylisoindolin-1-one) (*E,Z*-21), (*E,E*-21), (*Z,Z*-21). Prepared by procedure C using **19**. Crude ratio of 1.3:7.0:10 for *ZZ*/*EZ*/*EE* and after silica plug ratio changed to 1:4:3: orange solid; mp 181−186 °C; ^{1}H NMR (300 MHz, $CDCl_3$) ***E,Z*-21**: δ 7.11 (s, 1H), 6.89 (s, 1H), 6.72 (s, 1 H), 6.51 (s, 1H), 3.82 (s, 3H), 3.78 (s, 3H); ***E,E*-21**: 7.17 (s, 2H), 6.55 (s, 2H), 3.77 (s, 6H); ***Z,Z*-21**: 6.84 (s, 2H), 6.68 (s, 2H), 3.84 (s, 3H). Overlapping signals: 7.60 (24H), 3.92 (m, 12H), 1.78 (m, 6H), 1.48 (m, 6H), 1.27 (m, 8H), 1.00 (m, 16H), 0.73 (t, J = 7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 169.1, 169.0, 166.6, 166.6, 151.7, 151.4, 151.4, 151.2, 151.1, 140.0, 138.5, 136.3, 135.6, 135.2, 132.3, 132.2, 132.1, 132.1, 132.0, 131.3, 131.2, 130.7, 129.4, 129.1, 128.7, 128.6, 128.5, 128.3, 124.6, 124.6, 124.4, 124.3, 123.4, 123.4, 123.2, 123.1, 119.8, 119.7, 114.6, 114.3, 114.0, 113.8, 106.6, 106.5, 102.9, 102.8, 56.4, 56.3, 56.2, 56.1, 41.3, 41.3, 40.0, 39.5, 30.7, 30.4, 30.3, 29.8, 20.5, 20.4, 20.0, 19.9, 14.0, 13.9, 13.9, 13.8 (2 signals missing); IR (film, KBr) 2959, 1699, 1471 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{37}N_2O_4$ $[M + H]^+$ 537.2753, found 537.2756.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental methods, ^{1}H and ^{13}C NMR spectra for all new compounds, and NOESY spectra for cyclized products. This material is available free of charge via the Internet at http://pubs.acs.org.

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