JOC The Journal of Organic Chemistry

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Gold(I)-Catalyzed Polycyclizations of Polyenyne-Type Anilines Based on Hydroamination and Consecutive Hydroarylation Cascade

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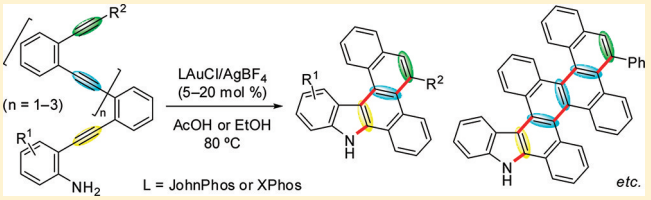
Supporting Information

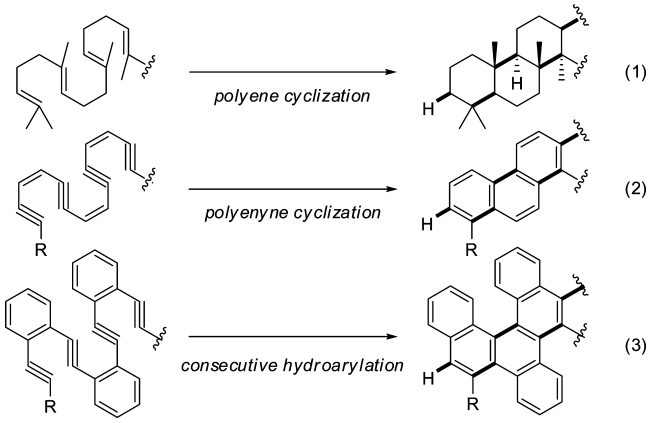
ABSTRACT: A hydroamination−double hydroarylation cascade using aniline derivatives bearing a trienyne moiety as the substrate was efficiently promoted by a gold(I) catalyst to produce benzo[*a*]naphtho[2,1-*c*]carbazole derivatives in good yields. This reaction is applicable to various substituted trienyne-type anilines, including 2,3-diethynylthiophene derivatives. The reaction of anilines bearing a tetraenyne and pentaenyne moiety allows direct construction of highly fused carbazoles by tetra- and pentacyclization, respectively, through hydroamination and consecutive hydroarylation without producing any theoretical waste products from the substrates.



INTRODUCTION

Polyene cyclization based on biogenetic conversion of squalenes into polycyclic triterpenoids enables direct construction of complex polycyclic molecules in a single operation (Scheme 1, eq 1).[1] Recent progress in this area including

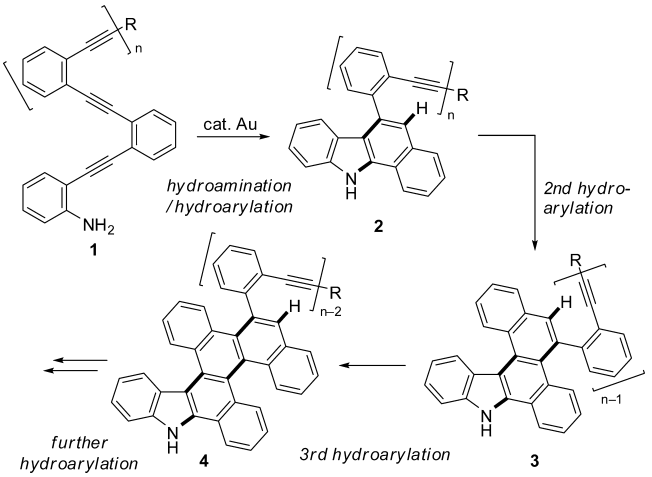
Scheme 1. Cascade Cyclization of Polyene and Polyenyne Derivatives



catalytic enantio-controlled polyene cyclization[2] has made this transformation a more powerful tool in organic synthesis. However, consecutive cyclization of polyenynes to form highly fused aromatic compounds (eq 2) is unknown as far as we are aware. This is partly because of the digonal bonding of the sp-hybridized carbons of enynes in the ground state, which restricts them from being in an appropriate orientation for polycyclization. A related reaction, anionic Bergman cyclization of enediynes, was reported for construction of a fused benzene ring.[3,4] Recently, Liu and co-workers reported ruthenium- or platinum-catalyzed naphthalene formation from 2,3-diethynylbenzenes via nucleophilic addition of methoxide onto activated alkyne, which was followed by 6-*endo*-*dig* cyclization to construct a single benzene ring.[5,6] In contrast, catalytic consecutive hydroarylation to form multiple benzene rings has not been reported.

We expected that consecutive hydroarylation (Scheme 1, eq 3) would be a promising approach to polyenyne-type cyclization. Recently, we found that highly alkynophilic gold salts promote a 5-*endo*-*dig*-hydroamination/6-*endo*-*dig* hydroarylation[7,8] cascade of anilines-derived diynes **1** (n = 0) to give aryl-annulated[*a*]-carbazoles **2** (n = 0) (Scheme 2),[9−12] which constitute an

Scheme 2. Synthetic Strategy Based on Hydroamination and Consecutive Hydroarylation



Received: September 2, 2011
Published: September 27, 2011

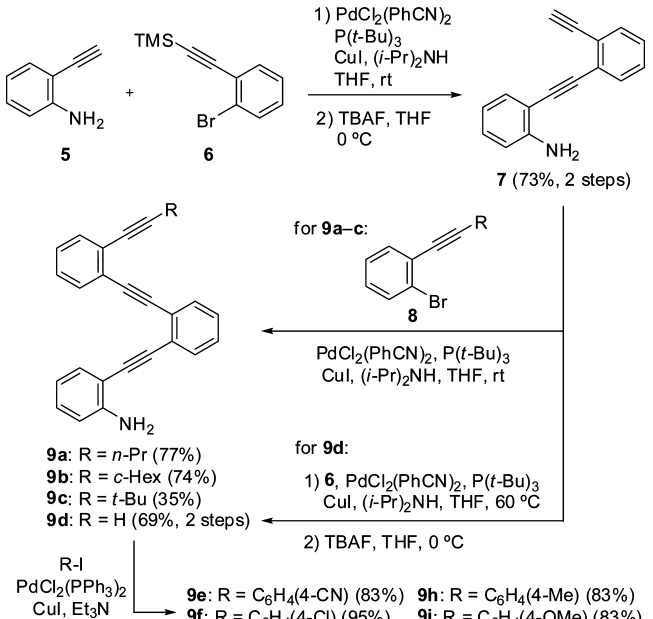
   dx.doi.org/10.1021/jo2018119 | *J. Org. Chem.* 2011, 76, 9068–9080

important class of compounds for their diverse biological activities.[13] Based on this chemistry, introduction of another alkyne moiety to the substrates might allow the second hydroarylation leading to benzo[*a*]naphtho[2,1-*c*]carbazoles **3** (n = 1). Although hydroarylation of the carbazole benzene ring onto alkyne is unprecedented, we anticipated the nitrogen atom at the *para*-position would accelerate this transformation. If the third and further hydroarylation successfully proceeded from **3**, polycyclization products such as **4** would be obtained. In these cases, hydroarylation with a simple naphthalene ring of **3**/**4** as well as activation of the appropriate alkyne in each step among several alkynes are challenging issues in this strategy. Here we report our study on the synthesis of highly fused carbazoles based on gold-catalyzed 5-*endo*-*dig* hydroamination and consecutive 6-*endo*-*dig* hydroarylation cascade using polyenyne-type anilines (n = 1–3).

RESULTS AND DISCUSSION

Synthesis of Polyenyne-Type Anilines. The requisite trienyne-type substrates **9** for construction of benzo[*a*]naphtho[2,1-*c*]carbazoles **3** (n = 1) were prepared in a straightforward manner as shown in Scheme 3. Sonogashira

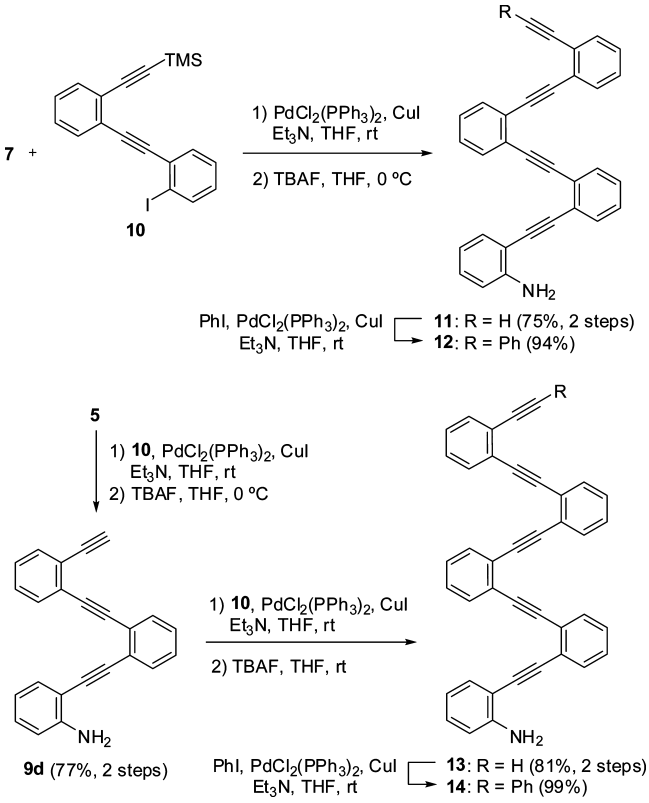
Scheme 3. Preparation of Trienyne-Type Substrates 9



coupling of 2-ethynylaniline **5**[14] with protected 1-bromo-2-ethynylbenzene **6**[15] followed by cleavage of the trimethylsilyl group with tetra-*n*-butylammonium fluoride (TBAF) afforded dienyne-type aniline **7** in 73% yield. A further coupling reaction with 1-bromo-2-ethynylbenzenes **8**, which have an alkyl substituent at the alkyne terminus, gave the trienyne-type anilines **9a–c**. By comparison, the second coupling–deprotection sequence of dienyne-type aniline **7** with 1-bromo-2-ethynylbenzene **6** led to the corresponding terminal alkyne **9d**, which was converted to aryl-substituted substrates **9e–i** in good yields by coupling with a series of aryl iodides. Other trienyne-type anilines were also prepared in a similar manner (see the Experimental Section).

Tetraenyne-type aniline **12** was easily prepared by a 2 + 2 approach with dienyne-type aniline **7** (Scheme 4). A cross-coupling

Scheme 4. Preparation of Tetra- and Pentaenyne-Type Substrates 12 and 14

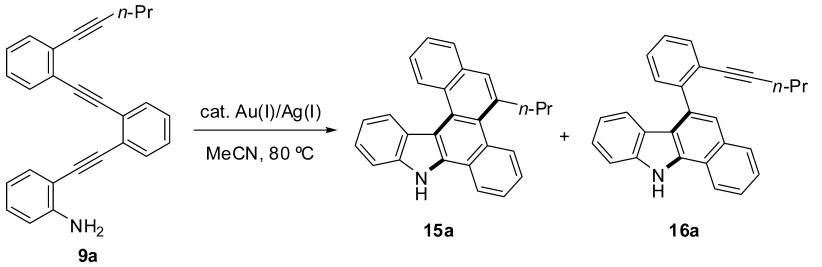


reaction with dienyne-type halide **10**, TBAF treatment, and coupling with iodobenzene gave **12** in good overall yield. Pentaenyne-type aniline **14** was synthesized by a 1 + 2 + 2 approach, which repeated the coupling–deprotection sequence starting from ethynylaniline **5** with dienyne-type halide **10**, followed by arylation at the terminal alkyne of **13**. This afforded the desired pentaenyne-type substrate **14** in good yield. The required polyenyne-type anilines with the desired number of enyne units could be prepared using the protected dienyne synthon **10** in an short synthesis starting from either mono- or dienyne-type aniline (**5** or **7**).

Tricyclization through Hydroarylation with Carbazole Ring. Following synthesis of the polyenyne substrates, the gold-catalyzed tricyclization through the second hydroarylation with carbazole benzene ring was investigated (Table 1). Treatment of trienyne-type aniline **9a** with 5 mol % of Ph_3PAuCl/AgOTf in MeCN at 80 °C produced the double cyclization product **16a** in only 28% yield (entry 1). A considerable amount of the starting material was recovered (53%). Fortunately, increased loading (20 mol %) of the catalyst resulted in formation of the desired tricyclization product, benzo[*a*]naphtho[2,1-*c*]carbazole derivative **15a**, in 49% yield (entry 2). Among the several silver salts tested for activation of the gold complex (entries 2–8), tetrafluoroborate was the most promising, producing **15a** in 77% yield (entry 8). However, decreasing the loading of the catalyst to 5 mol % was not successful (entry 9). The relatively lower electron density of the benzene ring of the carbazole intermediate compared with the indole 3 position would be problematic. In contrast, use of the gold–phosphine catalyst JohnPhosAuCl (Figure 1) in the presence of $AgBF_4$ exhibited improved turnover to give **15a** in 68% yield with a 5 mol % catalyst loading (entry 11).

dx.doi.org/10.1021/jo2018119 | J. Org. Chem. 2011, 76, 9068–9080

Table 1. Optimization of Reaction Conditions for Tricyclization



9a 15a 16a

entry	catalyst	loading (mol %)	time (h)	yield (%) 15a	yield (%) 16a	recovery (%)
1	$Ph_3PAuCl/AgOTf$	5	2		28	53
2	$Ph_3PAuCl/AgOTf$	20	1	49		
3	$Ph_3PAuCl/AgNTf_2$	20	4	55		
4	$Ph_3PAuCl/AgSbF_6$	20	2.5	72		
5	$Ph_3PAuCl/AgOTs$	20	1	60		
6	$Ph_3PAuCl/AgPF_6$	20	1	58		
7	$Ph_3PAuCl/AgClO_4$	20	3	55		
8	$Ph_3PAuCl/AgBF_4$	20	1.5	77		
9	$Ph_3PAuCl/AgBF_4$	5	4		29	43
10	JohnPhosAuCl/$AgBF_4$	20	0.5	65		
11	JohnPhosAuCl/$AgBF_4$	5	4.5	68		
12[a]	JohnPhosAuCl/$AgBF_4$	5	0.5	73		

[a]AcOH was used as the solvent.

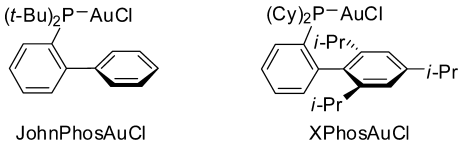
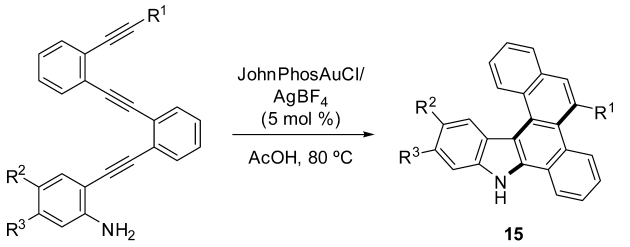


Figure 1. Screened gold–phosphine catalysts.

Acetic acid (AcOH) was the solvent of choice for the tricyclization to afford **15a** with a slightly improved yield (73%) within 30 min (entry 12), presumably due to the promoted proto-deauration.

Using the optimized conditions described in entry 12 (5 mol % JohnPhosAuCl/$AgBF_4$ in AcOH, Table 1), the tricyclization was extended to other types of substrates (Table 2). Replacement of the *n*-propyl group with a cyclohexyl group at the alkyne terminus (as R^1) was tolerated (entries 1 and 2). However, the sterically hindered *tert*-butyl group completely interrupted the third cyclization to give the double cyclization product **16c** in 72% yield (entry 3). The reaction of terminal alkyne derivative **9d** was also unsuccessful and gave a complex mixture of unidentified products (entry 4). By contrast, all the aryl-substituted trienyne-type substrates **9e–i** produced the desired tricyclization products in 47–77% yields (entries 5–9). Relatively low yields of the reaction using **9h** and **9i** bearing a 4-methyl- or 4-methoxyphenyl group (entries 8 and 9) can be attributed to the predominant coordination of the electron-rich aryl substituted alkyne to the gold complex, which somewhat hinders the first and/or second cyclization step. The substitution effect at the aniline part was also investigated (entries 10–13). The reaction of **9j** and **9k** bearing a methyl and chloro substitution at the *para*-position of the amino group (as R^2) gave the corresponding tricyclization products **15j** (66% yield) and **15k** (68% yield), respectively. As anticipated, a cyano group at the same position significantly decreased the reactivity to afford the tricyclization product **15l** in only 14% yield with a complex mixture of unidentified products (entry 12).

Table 2. Reaction of Various Trienyne-Type Substrates[a]



9 15

entry	subst	R^1	R^2	R^3	time (h)	yield (%)
1	**9a**	*n*-Pr	H	H	0.5	73
2	**9b**	*c*-Hex	H	H	24	70
3	**9c**	*t*-Bu	H	H	24	–[b]
4	**9d**	H	H	H	3	–[c]
5	**9e**	C_6H_4(4-CN)	H	H	0.5	77
6	**9f**	C_6H_4(4-Cl)	H	H	1	68
7	**9g**	Ph	H	H	0.5	63
8	**9h**	C_6H_4(4-Me)	H	H	0.75	60
9	**9i**	C_6H_4(4-OMe)	H	H	1	47
10	**9j**	*n*-Pr	Me	H	0.5	66
11	**9k**	*n*-Pr	Cl	H	0.5	68
12	**9l**	*n*-Pr	CN	H	1	14
13	**9m**	*n*-Pr	H	Cl	0.5	52

[a]All reactions were carried out using JohnPhosAuCl (5 mol %) and $AgBF_4$ (5 mol %) in AcOH at 80 °C. [b]Double cyclization product **16c** was obtained in 72% yield. [c]A mixture of unidentified products was obtained.

This was presumably because of the decreased nucleophilicity at the reaction site(s) as well as the activation/coordination ability of gold catalysts for the nitrile functionality.[16] Tricyclization of 3-chloro-substituted aniline derivative **9m** resulted in **15m** in 52% yield (entry 13).

dx.doi.org/10.1021/jo2018119 | J. Org. Chem. 2011, 76, 9068–9080

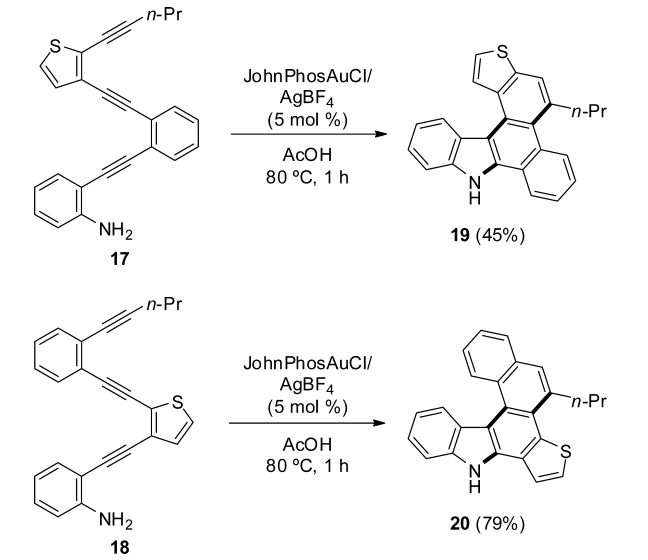
As shown in Scheme 5, exposure of the plausible intermediate **16a** to the optimized reaction conditions afforded **15a**

Scheme 5. Reaction of the Intermediate 16a

in 90% yield, the same product formed by tricyclization of **9a**. Combined with the reaction using insufficient loading of the catalyst to produce **16a** with recovered starting material (Table 1, entries 1 and 9), this result strongly supports the reaction pathway occurs through hydroamination and stepwise hydroarylation/proto-deauration (Scheme 2).

Next, the reaction of thiophene derivatives **17** and **18** was investigated (Scheme 6). The reactivity of trienyne-type aniline

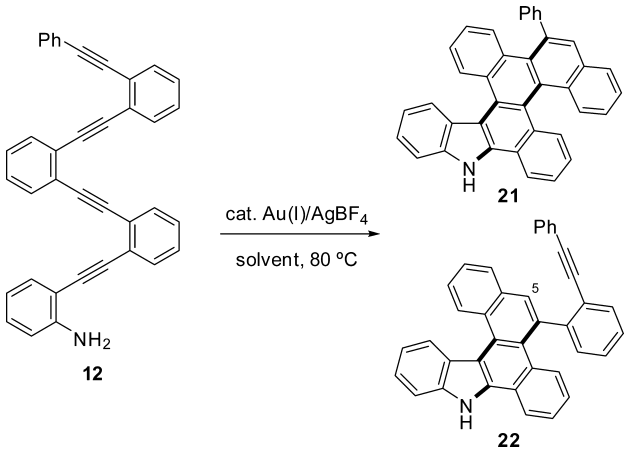
Scheme 6. Reaction of Thiophene Derivatives



17 bearing a thiophene ring at the distal position from the aniline moiety was relatively low, and the tricyclization product **19** was obtained in a moderate yield (45%). By contrast, aniline **18** bearing a thiophene ring at the central position of the molecule produced the corresponding fused thiophene **20** in 79% yield under the standard reaction conditions.

Polycyclization through Hydroarylation with the Naphthalene Ring. Tetracyclization of the tetraenyne-type aniline **12** (Table 3) through hydroarylation with the newly formed simple naphthalene ring was investigated next. To our delight, the reaction of **12** under the optimized conditions for tricyclization in AcOH produced the desired benzo[*a*]chryseno[5,6-*c*]carbazole derivative **21** in 38% yield. Formation of diastereomers based on the rotational barrier of the fused ring system was not observed. Increasing the catalyst loading to 20 mol % somewhat improved the yield (55%, entry 2). Changing the reaction solvent to ethanol (EtOH) led to a better result (78% yield, entry 3). However, decreasing the catalyst loading was not successful in this case and produced the tricyclization intermediate **22** as the major product (entries 4 and 5). The sterically more

Table 3. Optimization of Reaction Conditions for Tetracyclization



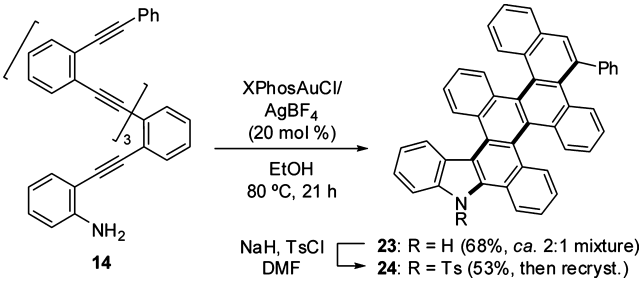
					yield (%)	
entry	Au(I) catalyst	loading (mol %)	solvent	time (h)	**21**	**22**
1	JohnPhosAuCl	5	AcOH	24	38	
2	JohnPhosAuCl	20	AcOH	3	55	
3	JohnPhosAuCl	20	EtOH	3	78	
4	JohnPhosAuCl	10	EtOH	29	12[a]	58[a]
5	JohnPhosAuCl	5	EtOH	24		61
6	XPhosAuCl	10	EtOH	1	86	
7	XPhosAuCl	5	EtOH	24	65[a]	22[a]
8	XPhosAuCl	5	AcOH	14	61	
9	XPhosAuCl	7.5	EtOH	3	86	

[a]Determined by ^{1}H NMR.

hindered catalyst XPhosAuCl (Figure 1) was then tested in the reaction. Treatment of **12** with XPhosAuCl/$AgBF_4$ (10 or 7.5 mol %) in EtOH showed clean conversion within 1−3 h to give **21** in 86% yield (entries 6 and 9).[17] This result suggests that the 5-position of benzo[*a*]naphtho[2,1-*c*]carbazole derivatives of the same type as **22** has sufficient reactivity for the gold(I)-catalyzed intramolecular hydroarylation of alkynes.

Finally, pentacyclization of **14** through hydroamination and quadruple hydroarylation cascade (Scheme 7) was investigated.

Scheme 7. Application to Pentacyclization



In this case, the fourth hydroarylation with the naphthalene moiety of the benzo[*a*]chryseno[5,6-*c*]carbazoles like **21** (Table 3) was tested. Reaction of **14** with XPhosAuCl/$AgBF_4$ (20 mol %) in EtOH for 21 h produced a highly fused carbazole **23** having a benzo[*a*]naphtho[1′,2′:11,12]chryseno-[5,6-*c*]carbazole skeleton in 68% yield. Interestingly, this was produced as a 2:1 mixture of stereoisomers, the isomeric ratio of which was increased to 3:1 when the isolated isomeric mixture of **23** (2:1) was heated under reflux in xylene for 10 h

dx.doi.org/10.1021/jo2018119 | *J. Org. Chem.* 2011, 76, 9068−9080

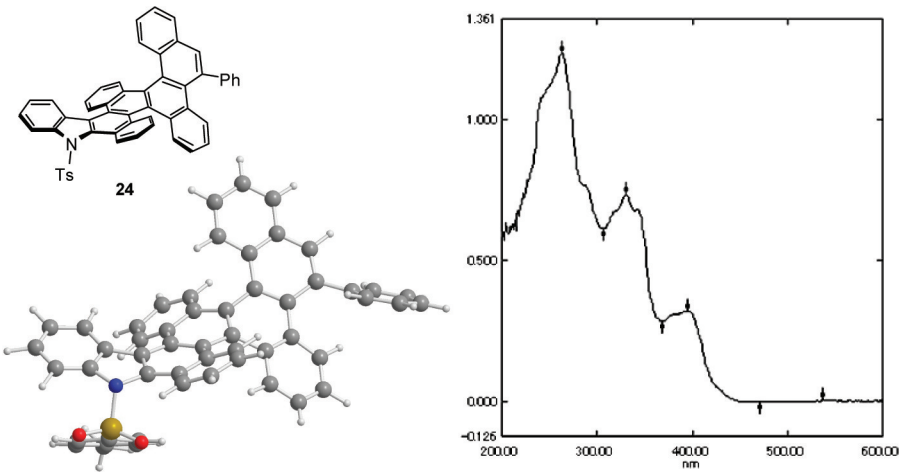


Figure 2. Crystal structure (benzene molecules as the solvent were omitted for clarity) and UV/vis spectra of **24**.

in the absence of any reagents and catalysts. Fortunately, tosylation of **23** followed by recrystallization led to isolation of the major isomer. X-ray analysis of the tosylate major isomer **24** has shown that this compound has an unprecedented polynaphthalene helix structure (Figure 2). UV/vis spectra of **24** (λ_{max} = 263, 331, 395 nm, $CHCl_3$) is in good coincidence with those of related polyaromatic hydrocarbon and carbazole structures.[18] From these observations, gold-catalyzed polycyclization of enyne-type substrates shows significant potential for construction of highly fused aromatic ring systems.

■ CONCLUSION

A gold-catalyzed cascade cyclization of polyenyne-type anilines for atom-economical synthesis of highly fused carbazoles was developed. The reaction of trienyne-type anilines produced benzo[*a*]naphtho[2,1-*c*]carbazoles through hydroarylation with the carbazole benzene ring. The gold catalysts promote the third and fourth hydroarylation with simple naphthalene rings to afford benzene-fused chryseno[5,6-*c*]- and naphtho-[1′,2′:11,12]chryseno[5,6-*c*]carbazoles, respectively. This is the first example of consecutive hydroarylation cascade, the polyenyne version of biogenetic polyene cyclization, in which the newly formed benzene ring(s) participates in the next cyclization to form multiple benzene rings. Synthesis and evaluation of the absorption properties of other fused aromatic ring systems are now underway.

■ EXPERIMENTAL SECTION

General Methods. ^{1}H NMR spectra were recorded at 400 or 500 MHz. ^{13}C NMR spectra were recorded at 100 or 125 MHz. Internal references were used for $CDCl_3$ in ^{1}H and ^{13}C NMR spectra. Data are presented as follows: chemical shift (in ppm on the δ scale relative to δTMS = 0), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (*J*/Hz) and number of protons. Melting points were measured by a hot stage melting point apparatus and are uncorrected. For column chromatography, silica gel (45−75 μm) and amino silica gel (100−200 mesh) were employed. The compounds **5**,[14] **6**,[15] **7**,[9b] 1-bromo-2-(cyclohexylethynyl)benzene (**8a**),[19] and **S3**[20] were synthesized according to the literature procedures. Other reagents are commercially available, which were used without further purification.

*1-Bromo-2-(cyclohexylethynyl)benzene (**8b**).* A mixture of 1-bromo-2-iodobenzene (0.26 mL, 2.0 mmol), CuI (9.5 mg, 0.05 mmol), $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol), Et_3N (1.4 mL, 10 mmol), and ethynylcyclohexane (0.77 mL, 6.0 mmol) in THF (4 mL) was stirred at room temperature for 2 h under argon. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography over silica gel with hexane to afford **8b** (0.40 g, 76% yield): colorless oil containing homodimer of ethynylcyclohexane (ca. 10%). IR (neat): 2228 (C≡C) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.35−1.47 (m, 4H), 1.60−1.64 (m, 2H), 1.77−1.84 (m, 2H), 1.87−1.90 (m, 2H), 2.65−2.70 (m, 1H), 7.10 (ddd, *J* = 7.7, 7.7, 1.7 Hz, 1H), 7.21 (ddd, *J* = 7.7, 7.7, 1.1 Hz, 1H), 7.42 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 24.6, 26.0 (2C), 29.7, 32.4 (2C), 79.5, 99.5, 125.6, 126.1, 126.8, 128.5, 132.2, 133.2. HRMS (FAB) calcd for $C_{14}H_{15}Br$ [M$^+$] 262.0352; found: 262.0349.

*1-Bromo-2-(3,3-dimethylbut-1-yn-1-yl)benzene (**8c**).* By a procedure identical to that described for the preparation of **8b**, 1-bromo-2-iodobenzene (0.51 mL, 4.0 mmol) was converted into **8c** (0.32 g, 33% yield) using 3,3-dimethylbut-1-yne (1.4 mL, 12 mmol): colorless oil. IR (neat): 2243 (C≡C) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.35 (s, 9H), 7.09 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.21 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 28.2, 30.8 (3C), 78.0, 103.6, 125.7, 126.0, 126.8, 128.5, 132.2, 133.0. HRMS (FAB) calcd for $C_{12}H_{14}Br$ [MH$^+$] 237.0279; found: 237.0271.

*2-[(2-{[2-(Pent-1-yn-1-yl)phenyl]ethynyl}phenyl)ethynyl]aniline (**9a**).* To a solution of **8a** (1.1 g, 5.2 mmol) in THF (10 mL) were successively added diisopropylamine (3.6 mL, 26 mmol), CuI (0.059 g, 0.31 mmol), $PdCl_2(PhCN)_2$ (0.12 g, 0.31 mmol), P(*t*-Bu)$_3$ (0.15 mL, 0.62 mmol), and **7** (1.3 g, 6.0 mmol) at room temperature under argon. The mixture was stirred at room temperature for 10 h. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography over silica gel with hexane−EtOAc (10:1) to afford **9a** (1.4 g, 77% yield) as an orange oil. IR (neat): 3480 (NH), 3380 (NH), 2210 (C≡C) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.96 (t, *J* = 7.2 Hz, 3H), 1.54−1.57 (m, 2H), 2.36 (t, *J* = 7.2 Hz, 2H), 4.40 (br s, 2H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.67 (dd, *J* = 8.6, 8.6 Hz, 1H), 7.11 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.23−7.34 (m, 4H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 6.9 Hz, 1H), 7.53−7.59 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.5, 21.6, 22.1, 79.4, 90.5, 92.1 (2C), 93.7, 95.4, 107.5, 114.0, 117.4, 125.1, 125.3, 125.8, 126.7, 127.2, 127.6, 128.1, 128.2, 129.9, 131.4, 131.86, 131.93, 132.2, 132.3, 148.4. HRMS (FAB) calcd for $C_{27}H_{21}N$ [M$^+$] 359.1674; found: 359.1669.

*2-[(2-{[2-(Cyclohexylethynyl)phenyl]ethynyl}phenyl)ethynyl]-aniline (**9b**).* By a procedure identical to that described for the preparation of **9a**, **7** (0.27 g, 1.23 mmol) was converted into **9b** (0.29 g, 74% yield) using **8b** (0.26 g, 0.99 mmol): pale brown solid; mp 129−131 °C. IR (neat): 3479 (NH), 3379 (NH), 2211 (C≡C) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.24−1.26 (m, 3H), 1.45−1.50 (m, 3H), 1.68−1.72 (m, 2H), 1.74−1.78 (m, 2H), 2.58−2.62 (m, 1H), 4.39 (br s, 2H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.67 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.11 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.25−7.31 (m, 4H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.44

dx.doi.org/10.1021/jo2018119 | *J. Org. Chem.* 2011, 76, 9068−9080

(d, J = 7.4 Hz, 1H), 7.53−7.60 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 24.6, 25.9 (2C), 29.7, 32.5 (2C), 79.3, 90.6, 92.1, 92.1, 93.7, 99.6, 107.5, 114.0, 117.4, 125.2, 125.3, 125.9, 126.8, 127.2, 127.6, 128.1, 128.2, 129.9, 131.3, 131.8, 131.9, 132.2 (2C), 148.4. Anal. Calcd for $C_{30}H_{25}N$: C, 90.19; H, 6.31; N, 3.51. Found: C, 90.07; H, 6.31; N, 3.53.

*2-[(2-{[2-(3,3-Dimethylbut-1-yn-1-yl)phenyl]ethynyl}phenyl)-ethynyl]aniline (**9c**).* By a procedure identical to that described for the preparation of **9a**, **7** (0.20 g, 0.92 mmol) was converted into **9c** (0.099 g, 35% yield) using **8c** (0.18 g, 0.76 mmol): orange oil. IR (neat): 3478 (NH), 3384 (NH), 2210 (C≡C) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.18 (s, 9H), 4.30 (br s, 2H), 6.53 (d, J = 8.3 Hz, 1H), 6.57 (dd, J = 8.5, 8.5 Hz, 1H), 7.00 (dd, J = 7.3, 7.3 Hz, 1H), 7.15−7.19 (m, 4H), 7.28 (d, J = 6.8 Hz, 1H), 7.34 (d, J = 7.1 Hz, 1H), 7.46−7.49 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.1, 30.9 (3C), 77.2, 77.8, 90.6, 92.00, 92.03, 93.7, 103.6, 107.4, 113.9, 117.4, 125.1, 125.3, 125.8, 126.6, 127.2, 127.6, 128.11, 128.14, 129.9, 131.3, 131.6, 131.9, 132.1, 148.3. HRMS (FAB) calcd for $C_{28}H_{23}N$ [M$^+$] 374.1909; found: 374.1902.

*2-({2-[(2-Ethynylphenyl)ethynyl]phenyl}ethynyl)aniline (**9d**).* To a solution of **6** (0.19 g, 0.76 mmol) in THF (5 mL) were successively added diisopropylamine (0.53 mL, 3.8 mmol), CuI (8.7 mg, 0.045 mmol), $PdCl_2(PhCN)_2$ (17 mg, 0.045 mmol), P(t-Bu)$_3$ (22 μL, 0.091 mmol), and **7** (0.20 g, 0.91 mmol) at room temperature under argon. The mixture was stirred at 60 °C for 16 h. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. To the residue were added THF (5 mL) and TBAF (1 M solution in THF; 0.91 mL, 0.91 mmol) at 0 °C. The mixture was stirred at 0 °C for 0.5 h and quenched by addition of saturated aqueous NH_4Cl and brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by column chromatography on silica gel with hexane−EtOAc (10:1) to afford **9d** (0.17 g, 69% yield in two steps): brown oil. IR (neat): 3480 (NH), 3377 (NH), 3295 (C≡CH), 2250 (C≡C), 2210 (C≡C) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.25 (s, 1H), 4.39 (br s, 2H), 6.67 (d, J = 8.3 Hz), 6.69 (dd, J = 7.6, 7.6 Hz), 7.13 (dd, J = 7.7, 7.7 Hz, 1H), 7.29−7.40 (m, 5H), 7.56−7.61 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 81.6, 82.0, 90.5, 91.4, 92.7, 93.6, 107.6, 114.1, 117.6, 124.7, 124.9, 125.8, 126.0, 127.7, 128.2, 128.4, 128.5, 129.9, 131.5, 132.0, 132.3, 132.5, 132.6, 148.3. HRMS (FAB) calcd for $C_{24}H_{16}N$ [MH$^+$] 318.1277; found: 318.1283.

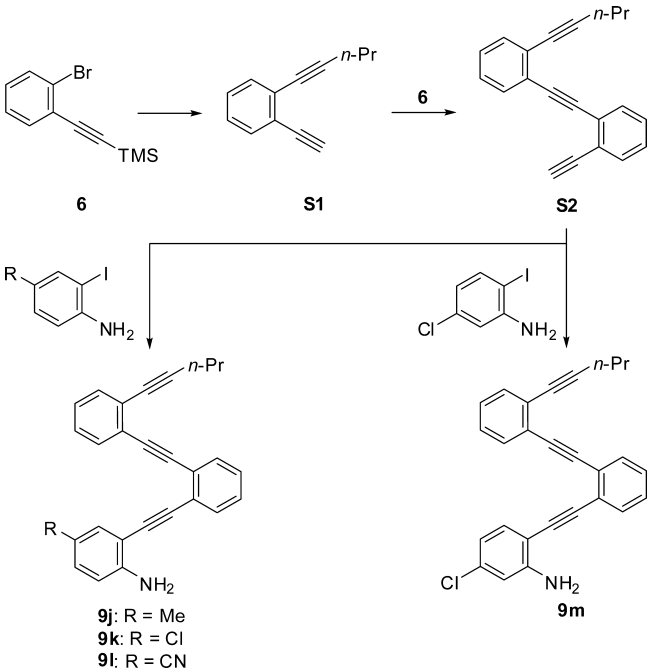
*4-{[2-({2-[(2-Aminophenyl)ethynyl]phenyl}ethynyl)phenyl]-ethynyl}benzonitrile (**9e**).* A mixture of **9d** (0.16 g, 0.49 mmol), CuI (2.3 mg, 0.012 mmol), $PdCl_2(PPh_3)_2$ (8.4 mg, 0.012 mmol), Et_3N (0.33 mL, 2.4 mmol), and p-iodobenzonitrile (0.11 g, 0.47 mmol) in THF (1.0 mL) was stirred at room temperature for 1 h under argon. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography over silica gel with hexane−EtOAc (5:1) to afford **9e** (0.16 g, 83% yield) as a pale yellow solid: mp 166−167 °C. IR (neat): 3460 (NH), 3364 (NH), 2221 (C≡C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.35 (br s, 2H), 6.60 (d, J = 8.0 Hz, 1H), 6.62 (dd, J = 7.4, 7.4 Hz, 1H), 7.07 (dd, J = 7.7, 7.7 Hz, 1H), 7.30−7.37 (m, 5H), 7.50 (s, 4H), 7.57−7.64 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 90.7, 91.4, 92.2, 92.3, 93.1, 93.5, 107.4, 111.4, 114.0, 117.5, 118.5, 124.7, 124.9, 125.8, 127.7, 127.8, 128.4, 128.5, 128.8, 129.9, 131.6, 131.8 (2C), 132.0 (2C), 132.1 (3C), 132.2, 132.4, 148.2. Anal. Calcd for $C_{31}H_{18}N_2$: C, 88.97; H, 4.34; N, 6.69. Found: C, 88.69; H, 4.33; N, 6.59.

*2-{[2-({2-[(4-Chlorophenyl)ethynyl]phenyl}ethynyl)phenyl]-ethynyl}aniline (**9f**).* By a procedure identical to that described for the preparation of **9e**, **9d** (0.16 g, 0.51 mmol) was converted into **9f** (0.20 g, 95% yield) using p-chloroiodobenzene (0.12 g, 0.49 mmol): white solid; mp 104−106 °C. IR (neat): 3475 (NH), 3378 (NH), 2210 (C≡C) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.38 (br s, 2H), 6.62 (d, J = 8.6 Hz, 1H), 6.64 (dd, J = 8.0, 8.0 Hz, 1H), 7.08 (dd, J = 6.9, 6.9 Hz, 1H), 7.22 (d, J = 8.6 Hz, 2H), 7.28−7.36 (m, 5H), 7.39 (d, J = 8.6 Hz, 2H), 7.56−7.60 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 89.0, 90.7, 91.6, 91.7, 92.9, 93.6, 107.5, 114.0, 117.5, 121.5, 124.9, 125.5, 125.6, 125.8, 127.7, 128.2, 128.3, 128.4, 128.6 (2C), 129.9, 131.5, 131.8, 132.0, 132.2, 132.3, 132.9 (2C), 134.4, 148.3. Anal. Calcd for $C_{30}H_{18}ClN$: C, 84.20; H, 4.24; N, 3.27. Found: C, 84.24; H, 4.24; N, 3.22.

*2-[(2-{[2-(Phenylethynyl)phenyl]ethynyl}phenyl)ethynyl]aniline (**9g**).* By a procedure identical to that described for the preparation of **9e**, **9d** (0.16 g, 0.50 mmol) was converted into **9g** (0.18 g, 94% yield) using iodobenzene (54 μL, 0.48 mmol): brown oil. IR (neat): 3481 (NH), 3382 (NH), 2251 (C≡C), 2212 (C≡C) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.41 (br s, 2H), 6.63 (d, J = 8.0 Hz, 1H), 6.65 (dd, J = 6.6, 6.6 Hz, 1H), 7.09 (dd, J = 7.7, 7.7 Hz, 1H), 7.24−7.35 (m, 8H), 7.50 (dd, J = 7.2, 2.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.60 (dd, J = 9.2, 9.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 88.1, 90.6, 91.9, 92.8, 93.6, 94.0, 107.5, 114.0, 117.5, 123.1, 125.0, 125.5, 125.8, 126.0, 127.7, 128.0, 128.2 (2C), 128.3 (2C), 128.4, 129.9, 131.5, 131.7 (2C), 131.8, 132.0, 132.3, 132.3, 148.3. HRMS (FAB) calcd for $C_{30}H_{19}N$ [M$^+$] 393.1517; found: 393.1525.

*2-[(2-{[2-(p-Tolylethynyl)phenyl]ethynyl}phenyl)ethynyl]aniline (**9h**).* By a procedure identical to that described for the preparation of **9e**, **9d** (0.19 g, 0.61 mmol) was converted into **9h** (0.20 g, 83% yield) using p-iodotoluene (0.13 g, 0.58 mmol): pale brown crystals; mp 100−102 °C. IR (neat): 3483 (NH), 3378 (NH), 2212 (C≡C) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.33 (s, 3H), 4.41 (br s, 2H), 6.63 (d, J = 8.0 Hz, 1H), 6.65 (dd, J = 7.4, 7.4 Hz, 1H), 7.07−7.10 (m, 3H), 7.24−7.40 (m, 7H), 7.55−7.62 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.5, 87.5, 90.6, 91.9, 92.7, 93.6, 94.3, 107.5, 114.0, 117.5, 120.0, 124.99, 125.04, 125.4, 125.8, 126.2, 127.7, 127.8, 128.3, 129.0 (2C), 129.9, 131.4, 131.6 (2C), 131.7, 132.0, 132.2, 132.3, 138.6, 148.3. Anal. Calcd for $C_{31}H_{21}N$: C, 91.37; H, 5.19; N, 3.44. Found: C, 91.15; H, 5.19; N, 3.44.

*2-{[2-({2-[(4-Methoxyphenyl)ethynyl]phenyl}ethynyl)phenyl]-ethynyl}aniline (**9i**).* By a procedure identical to that described for the preparation of **9e**, **9d** (0.21 g, 0.65 mmol) was converted into **9i** (0.22 g, 83% yield) using p-iodoanisole (0.15 g, 0.62 mmol): orange oil. IR (neat): 3472 (NH), 3379 (NH), 2212 (C≡C) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.79 (s, 3H), 4.42 (br s, 2H), 6.63 (d, J = 8.0 Hz, 1H), 6.65 (dd, J = 7.2, 7.2 Hz, 1H), 6.79 (d, J = 8.6 Hz, 2H), 7.09 (dd, J = 7.2, 7.2 Hz, 1H), 7.27−7.36 (m, 5H), 7.43 (d, J = 8.6 Hz, 2H), 7.57−7.60 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.3, 86.9, 90.6, 92.0, 92.6, 93.6, 94.2, 107.5, 113.9 (2C), 114.0, 115.2, 117.5, 125.1, 125.2, 125.8, 126.3, 127.6, 127.7, 128.26, 128.29, 129.9, 131.5, 131.6, 132.0, 132.2, 132.3, 133.2 (2C), 148.4, 159.7. HRMS (FAB) calcd for $C_{31}H_{21}NO$ [M$^+$] 423.1623; found: 423.1622.



*1-Ethynyl-2-(pent-1-yn-1-yl)benzene (**S1**).* To a solution of **6** (1.9 g, 7.7 mmol) in THF (15 mL) were successively added diisopropylamine (5.4 mL, 38 mmol), CuI (44 mg, 0.23 mmol), $PdCl_2(PhCN)_2$ (88 mg, 0.23 mmol), P(t-Bu)$_3$ (0.11 mL, 0.46 mmol), and pent-1-yne (1.1 mL, 11 mmol) at room temperature under argon. The mixture

dx.doi.org/10.1021/jo2018119 | J. Org. Chem. 2011, 76, 9068−9080

was stirred at room temperature for 24 h. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The residue was dissolved in THF (15 mL), and TBAF (1 M solution in THF; 9.2 mL, 9.2 mmol) was added to the mixture at 0 °C. The mixture was stirred at 0 °C for 0.5 h and quenched by addition of saturated aqueous NH_4Cl and brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by column chromatography over silica gel with hexane−EtOAc (100:1) to afford **S1** quantitatively as an orange oil. IR (neat): 2251 (C≡C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ: 1.08 (t, J = 6.9 Hz, 3H), 1.64−1.67 (m, 2H), 2.45 (t, J = 6.9 Hz, 2H), 3.27 (s, 1H), 7.19−7.27 (m, 2H), 7.40 (d, J = 7.4 Hz, 1H), 7.47 (d, J = 7.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.5, 21.6, 22.1, 79.2, 80.4, 82.4, 94.9, 124.4, 127.1 (2C), 128.4, 131.9, 132.4. HRMS (FAB) calcd for $C_{13}H_{12}$ [MH^+] 169.1017; found: 169.1016.

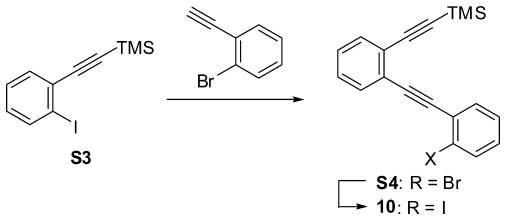
*1-Ethynyl-2-{[2-(pent-1-yn-1-yl)phenyl]ethynyl}benzene (**S2**).* To a solution of **6** (1.0 g, 4.0 mmol) in THF (10 mL) were successively added diisopropylamine (2.8 mL, 20 mmol), CuI (23 mg, 0.12 mmol), $PdCl_2(PhCN)_2$ (46 mg, 0.12 mmol), P(*t*-Bu)$_3$ (0.058 mL, 0.24 mmol), and **S1** (0.70 g, 4.2 mmol) at room temperature under argon. The mixture was stirred at room temperature for 18 h. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The residue was dissolved in THF (10 mL), and TBAF (1 M solution in THF; 4.2 mL, 4.2 mmol) was added to the mixture at 0 °C. The mixture was stirred at 0 °C for 1 h and quenched by addition of saturated aqueous NH_4Cl and brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by column chromatography over silica gel with hexane−EtOAc (100:1) to afford **S2** (0.94 g, 88% yield in two steps) as an orange oil. IR (neat): 2226 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.05 (t, J = 7.4 Hz, 3H), 1.63−1.70 (m, 2H), 2.46 (t, J = 7.4 Hz, 2H), 3.33 (s, 1H), 7.24−7.35 (m, 4H), 7.43−7.44 (m, 1H), 7.53−7.55 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.6, 21.7, 22.2, 79.5, 81.1, 82.2, 91.0, 92.6, 94.8, 124.5, 125.5, 126.49, 126.53, 127.2, 127.9, 128.1, 128.4, 131.9, 132.0, 132.2, 132.6. HRMS (FAB) calcd for $C_{21}H_{16}$ [M^+] 268.1252; found: 268.1248.

*4-Methyl-2-[(2-{[2-(pent-1-yn-1-yl)phenyl]ethynyl}phenyl)-ethynyl]aniline (**9j**).* By a procedure identical to that described for the preparation of **9a**, 2-iodo-4-methylaniline (0.14 g, 0.62 mmol) was converted into **9j** (0.20 g, 88% yield) using **S2** (0.20 g, 0.74 mmol): pale brown oil. IR (neat): 3465 (NH), 3378 (NH), 2197 (C≡C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ: 0.97 (t, J = 7.2 Hz, 3H), 1.53−1.60 (m, 2H), 2.20 (s, 3H), 2.37 (t, J = 6.9 Hz, 2H), 4.26 (br s, 2H), 6.57 (d, J = 8.6 Hz, 1H), 6.93 (d, J = 8.6 Hz, 1H), 7.20−7.33 (m, 5H), 7.44 (d, J = 6.9 Hz, 1H), 7.55−7.57 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.5, 20.2, 21.6, 22.1, 79.4, 90.8, 92.1 (2C), 93.4, 95.4, 107.6, 114.2, 125.2, 125.3, 125.9, 126.65, 126.72, 127.2, 127.5, 128.1, 128.2, 130.8, 131.3, 131.9, 132.1, 132.2 (2C), 146.1. HRMS (FAB) calcd for $C_{28}H_{24}N$ [$MH]^+$ 374.1909; found: 374.1910.

*4-Chloro-2-[(2-{[2-(pent-1-yn-1-yl)phenyl]ethynyl}phenyl)-ethynyl]aniline (**9k**).* By a procedure identical to that described for the preparation of **9a**, 4-chloro-2-iodoaniline (0.16 g, 0.69 mmol) was converted into **9k** (0.20 g, 74% yield) using **S2** (0.19 g, 0.73 mmol): yellow oil. IR (neat): 3482 (NH), 3381 (NH), 2204 (C≡C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ: 0.96 (t, J = 7.4 Hz, 3H), 1.54−1.57 (m, 2H), 2.36 (t, J = 7.2 Hz, 2H), 4.40 (br s, 2H), 6.56 (d, J = 8.6 Hz, 1H), 7.05 (dd, J = 8.6, 2.3 Hz, 1H), 7.27−7.31 (m, 5H), 7.45 (d, J = 8.0 Hz, 1H), 7.52−7.60 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.5, 21.6, 22.1, 79.4, 89.1, 91.9, 92.2, 94.6, 95.5, 108.8, 115.1, 121.7, 125.1, 125.3, 126.7, 127.3 (2C), 128.0, 128.2, 128.3, 129.8, 131.0, 131.4, 131.9, 132.2, 132.3, 147.0. HRMS (FAB) calcd for $C_{27}H_{21}ClN$ [MH^+] 394.1363; found: 394.1358.

*4-Amino-3-[(2-{[2-(pent-1-yn-1-yl)phenyl]ethynyl}phenyl)-ethynyl]benzonitrile (**9l**).* By a procedure identical to that described for the preparation of **9a**, 4-amino-3-iodobenzonitrile (0.16 g, 0.66 mmol) was converted into **9l** (0.25 g, 99% yield) using **S2** (0.21 g, 0.79 mmol): pale brown solid; mp 137−138 °C. IR (neat): 3476 (NH), 3364 (NH), 2220 (C≡C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ: 0.95 (t, J = 7.4 Hz, 3H), 1.52−1.55 (m, 2H), 2.35 (t, J = 6.9 Hz, 2H), 4.92 (br s, 2H), 6.62 (d, J = 8.6 Hz, 1H), 7.27−7.36 (m, 5H), 7.46 (d, J = 7.4 Hz, 1H), 7.51 (d, J = 6.9 Hz, 1H), 7.58−7.60 (m, 2H), 7.65 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.4, 21.5, 22.0, 79.3, 87.8, 91.8, 92.2, 95.2, 95.7, 99.7, 107.8, 113.7, 119.4, 124.8, 124.9, 125.3, 126.7, 127.3, 128.3, 128.4, 128.5, 131.5, 132.0, 132.1, 132.3, 133.3, 136.0, 151.4. Anal. Calcd for $C_{28}H_{20}N_2$: C, 87.47; H, 5.24; N, 7.29. Found: C, 87.56; H, 5.46; N, 7.29.

*5-Chloro-2-[(2-{[2-(pent-1-yn-1-yl)phenyl]ethynyl}phenyl)-ethynyl]aniline (**9m**).* By a procedure identical to that described for the preparation of **9a**, 5-chloro-2-iodoaniline (0.16 g, 0.62 mmol) was converted into **9m** (0.20 g, 84% yield) using **S2** (0.20 g, 0.74 mmol): pale yellow oil. IR (neat): 3481 (NH), 3383 (NH), 2250 (C≡C), 2204 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.96 (t, J = 7.3 Hz, 3H), 1.51−1.60 (m, 2H), 2.36 (t, J = 7.1 Hz, 2H), 4.47 (br s, 2H), 6.63−6.65 (m, 2H), 7.23−7.35 (m, 5H), 7.44−7.46 (m, 1H), 7.49−7.61 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.5, 21.5, 22.1, 79.4, 89.5, 92.0, 92.1, 94.4, 95.5, 106.0, 113.7, 117.6, 125.1 (2C), 125.5, 126.7, 127.2, 127.8, 128.2, 128.3, 131.3, 131.9, 132.1, 132.3, 132.8, 135.5, 149.2. HRMS (FAB) calcd for $C_{27}H_{20}ClN$ [M^+] 393.1284; found: 393.1288.



*({2-[(2-Bromophenyl)ethynyl]phenyl}ethynyl)trimethylsilane (**S4**).* A mixture of **S3** (2.9 g, 9.7 mmol), CuI (46 mg, 0.24 mmol), $PdCl_2(PPh_3)_2$ (0.17 g, 0.24 mmol), Et_3N (6.8 mL, 49 mmol), and 1-bromo-2-ethynylbenzene (2.1 g, 12 mmol) in THF (20 mL) was stirred at room temperature for 1 h under argon. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography over silica gel with hexane−EtOAc (100:1) to afford **S4** (3.41 g, quant) as a colorless oil. IR (neat): 2156 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.26 (s, 9H), 7.18 (ddd, J = 7.7, 7.7, 1.5 Hz, 1H), 7.27−7.32 (m, 3H), 7.50−7.52 (m, 1H), 7.56−7.63 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 0.0 (3C), 91.7, 92.5, 98.8, 103.4, 125.4, 125.51, 125.54, 125.6, 126.9, 128.18, 128.21, 129.5, 132.1, 132.4, 132.5, 133.6. HRMS (FAB) calcd for $C_{19}H_{17}BrSi$ [M^+] 352.0283; found: 352.0290.

*({2-[(2-Iodophenyl)ethynyl]phenyl}ethynyl)trimethylsilane (**10**).* To a stirred solution of **S4** (4.8 g, 14 mmol) in anhydrous Et_2O (70 mL) was added dropwise a solution of *n*-BuLi (1.6 M in hexane; 9.8 mL, 16 mmol) at −78 °C under argon. The reaction mixture was stirred at −78 °C for 1 h, and a solution of I_2 (4.8 g, 19 mmol) in anhydrous Et_2O (80 mL) was added dropwise to the mixture. The reaction mixture was stirred at −78 °C for 3 h, then warmed to room temperature, and stirred overnight. The mixture was quenched by the addition of 5% aqueous $Na_2S_2O_3$, washed with H_2O (3×), dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by column chromatography over silica gel with hexane−EtOAc (100:1) to afford **10** (5.1 g, 94% yield) as a colorless oil. IR (neat): 2159 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.26 (s, 9H), 7.01 (ddd, J = 7.7, 7.7, 1.7 Hz, 1H), 7.30−7.32 (m, 3H), 7.52−7.59 (m, 3H), 7.88 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 0.0 (3C), 91.7, 95.1, 98.8, 100.7, 103.4, 125.4, 125.6, 127.7, 128.2, 129.4, 129.9, 131.7, 132.1, 132.4, 132.8, 138.7. HRMS (FAB) calcd for $C_{19}H_{18}ISi$ [MH^+] 401.0222; found: 401.0229.

*2-{[2-({2-[(2-Ethynylphenyl)ethynyl]phenyl}ethynyl)phenyl]-ethynyl}aniline (**11**).* A mixture of **10** (1.0 g, 2.6 mmol), CuI (12 mg, 0.064 mmol), $PdCl_2(PPh_3)_2$ (45 mg, 0.064 mmol), Et_3N (1.8 mL, 13 mmol), and **7** (0.58 g, 2.7 mmol) in THF (5.0 mL) was stirred at room temperature for 3 h under argon. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography over silica gel with hexane−EtOAc (5:1) to afford 2-[(2-{[2-({2-[(trimethylsilyl)ethynyl]phenyl}ethynyl)phenyl]ethynyl}phenyl)ethynyl]aniline (**S5**) (0.95 g, 77% yield) as a brown amorphous solid.

dx.doi.org/10.1021/jo2018119 | *J. Org. Chem.* 2011, 76, 9068−9080

Compound **S5**: IR (neat): 3485 (NH), 3382 (NH), 2252 (C≡C), 2211 (C≡C), 2158 (C≡C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ: 0.23 (s, 9H), 4.43 (br s, 2H), 6.64 (d, J = 8.0 Hz, 1H), 6.65 (dd, J = 8.0, 8.0 Hz, 1H), 7.09 (dd, J = 7.7, 7.7 Hz, 1H), 7.17−7.35 (m, 7H), 7.46−7.48 (m, 2H), 7.56−7.63 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 0.0 (3C), 90.6, 91.9, 92.0, 92.7, 93.0, 93.7, 98.7, 103.5, 107.5, 114.1 (2C), 117.5, 125.1, 125.5, 125.8, 125.9, 126.0, 127.7, 128.0, 128.20 (2C), 128.22, 128.3, 129.9, 131.5, 132.0, 132.1, 132.15, 132.18, 132.3, 132.6, 148.4. HRMS (FAB) calcd for $C_{35}H_{28}NSi$ [MH^+] 490.1991; found: 490.1991.

To a solution of **S5** (0.94 g, 1.9 mmol) in THF (4.0 mL) was added TBAF (1 M solution in THF; 2.3 mL, 2.3 mmol) at 0 °C. The mixture was stirred at 0 °C for 2.5 h and quenched by addition of saturated aqueous NH_4Cl and brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by column chromatography over silica gel with hexane−EtOAc (5:1) to afford **11** (0.79 g, 98% yield) as a brown oil.

Compound **11**: IR (neat): 3480 (NH), 3380 (NH), 3293 (C≡CH), 2248 (C≡C), 2210 (C≡C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ: 3.18 (s, 1H), 4.41 (br s, 2H), 6.62 (d, J = 8.0 Hz, 1H), 6.64 (dd, J = 6.3, 6.3 Hz, 1H), 7.08 (dd, J = 7.7, 7.7 Hz, 1H), 7.25−7.33 (m, 7H), 7.47−7.51 (m, 2H), 7.58−7.62 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 81.4, 82.0, 90.7, 91.8, 92.0, 92.2, 92.8, 93.6, 107.4, 114.0, 117.5, 124.4, 125.0, 125.3, 125.7, 125.8, 126.1, 127.6, 128.0, 128.2, 128.26, 128.29, 128.4, 129.9, 131.4, 131.9, 132.2, 132.40, 132.42, 132.5, 132.6, 148.3. HRMS (FAB) calcd for $C_{32}H_{20}N$ [MH^+] 418.1596; found: 418.1588.

*2-({2-[(2-{[2-(Phenylethynyl)phenyl]ethynyl}phenyl)ethynyl]-phenyl}ethynyl)aniline (**12**).* A mixture of **11** (0.78 g, 1.9 mmol), CuI (8.5 mg, 0.045 mmol), $PdCl_2(PPh_3)_2$ (31 mg, 0.045 mmol), Et_3N (1.2 mL, 8.9 mmol), and iodobenzene (0.20 mL, 1.8 mmol) in THF (4.0 mL) was stirred at room temperature for 2 h under argon. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography over silica gel with hexane−EtOAc (5:1) to afford **12** (0.83 g, 94% yield) as a brown amorphous solid. IR (neat): 3475 (NH), 3379 (NH), 2211 (C≡C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ: 4.42 (s, 2H), 6.61 (d, J = 8.6 Hz, 1H), 6.64 (dd, J = 8.6, 8.6 Hz, 1H), 7.08 (dd, J = 7.7, 7.7 Hz, 1H), 7.19−7.34 (m, 10H), 7.51−7.61 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 88.3, 90.5, 91.8, 92.1, 92.7, 93.0, 93.7 (2C), 107.5, 114.0, 117.5, 123.2, 125.0, 125.4, 125.6, 125.68, 125.71, 126.0, 127.6, 127.9, 128.12, 128.14, 128.18, 128.25 (3C), 128.3, 129.8, 131.3, 131.6 (2C), 131.7, 131.9, 132.1, 132.2, 132.3, 132.5, 148.3. HRMS (FAB) calcd for $C_{38}H_{24}N$ [MH^+] 494.1909; found: 494.1915.

*Synthesis of 2-({2-[(2-Ethynylphenyl)ethynyl]phenyl}ethynyl)-aniline (**9d**) from **5**.* A mixture of **10** (1.6 g, 4.0 mmol), CuI (19 mg, 0.10 mmol), $PdCl_2(PPh_3)_2$ (0.070 g, 0.10 mmol), Et_3N (2.8 mL, 20 mmol), and **5** (0.56 g, 4.8 mmol) in THF (10 mL) was stirred at room temperature for 3 h under argon. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography over silica gel with hexane−EtOAc (10:1) to afford 2-[(2-[(2-[(trimethylsilyl)-ethynyl]phenyl)ethynyl]phenyl)ethynyl]aniline (1.2 g, 79% yield) as a brown oil. To a solution of this compound (1.2 g, 3.2 mmol) in THF (6 mL) was added TBAF (1 M solution in THF; 3.8 mL, 3.8 mmol) at 0 °C. The mixture was stirred at 0 °C for 0.5 h and quenched by addition of saturated aqueous NH_4Cl and brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by column chromatography over silica gel with hexane−EtOAc (5:1) to afford **9d** (1.0 g, 77% yield in two steps) as a brown oil.

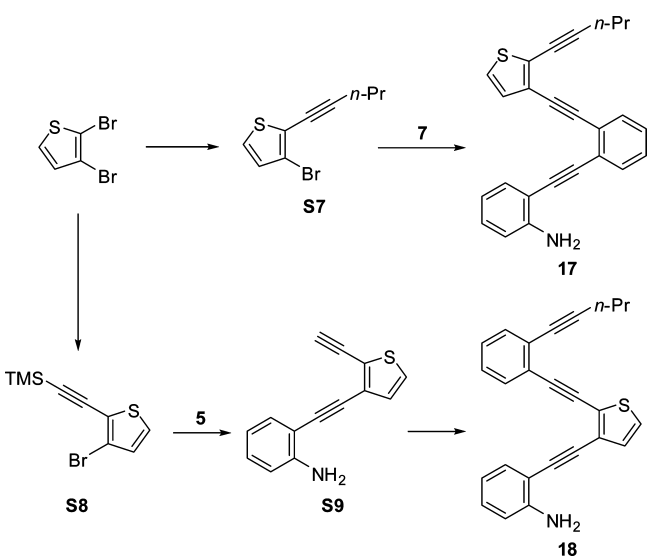
*2-[(2-{[2-({2-[(2-Ethynylphenyl)ethynyl]phenyl}ethynyl)phenyl]-ethynyl}phenyl)ethynyl]aniline (**13**).* A mixture of **10** (2.2 g, 5.5 mmol), CuI (26 mg, 0.14 mmol), $PdCl_2(PPh_3)_2$ (97 mg, 0.14 mmol), Et_3N (3.8 mL, 28 mmol), and **9d** (2.1 g, 6.6 mmol) in THF (10 mL) was stirred at room temperature for 5.5 h under argon. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography over silica gel with hexane−EtOAc (7:1) to afford 2-({2-[(2-{[2-({2-[(trimethylsilyl)ethynyl]phenyl}ethynyl)phenyl]-ethynyl}phenyl)ethynyl]phenyl}ethynyl)aniline (**S6**) (2.7 g, 83% yield) as a pale brown amorphous solid.

Compound **S6**: IR (neat): 3484 (NH), 3384 (NH), 2210 (C≡C), 2158 (C≡C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ: 0.23 (s, 9H), 4.43 (br s, 2H), 6.63 (d, J = 7.4 Hz, 1H), 6.65 (dd, J = 6.9, 6.9 Hz, 1H), 7.09 (dd, J = 7.4, 7.4 Hz, 1H), 7.20−7.35 (m, 9H), 7.50−7.59 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 0.0 (3C), 90.6, 91.9, 92.18, 92.24, 92.3, 92.8, 93.0, 93.7, 98.6, 103.5, 107.6, 114.1, 117.5, 125.0, 125.4, 125.5, 125.6, 125.7, 125.8, 126.0, 126.1, 127.7, 128.0, 128.06, 128.09, 128.18 (2C), 128.24, 128.3, 129.9, 131.4, 131.9, 132.0, 132.1, 132.2 (2C), 132.4, 132.4, 132.5, 148.3. HRMS (FAB) calcd for $C_{43}H_{32}NSi$ [MH^+] 590.2304; found: 590.2297.

To a solution of **S6** (2.7 g, 4.5 mmol) in THF (10 mL) was added TBAF (1 M solution in THF; 5.4 mL, 5.4 mmol) at 0 °C. The mixture was stirred at 0 °C for 0.5 h and quenched by addition of saturated aqueous NH_4Cl and brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by column chromatography over silica gel with hexane−EtOAc (5:1) to afford **13** (2.3 g, 97% yield) as a brown amorphous solid.

Compound **13**: IR (neat): 3476 (NH), 3381 (NH), 2252 (C≡C), 2210 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.19 (s, 1H), 4.43 (br s, 2H), 6.62−6.67 (m, 2H), 7.09 (dd, J = 7.8, 7.8 Hz, 1H), 7.22−7.27 (m, 6H), 7.32−7.36 (m, 3H), 7.47−7.64 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 81.3, 82.1, 90.5, 91.8, 91.9, 92.16, 92.22, 92.7, 93.0, 93.7, 107.5, 114.0, 117.5, 124.4, 124.9, 125.47, 125.51, 125.6, 125.7, 126.0, 126.3, 127.6, 128.0, 128.08, 128.13 (2C), 128.2 (2C), 128.4, 129.8, 131.3, 131.9, 132.2, 132.27, 132.28, 132.32, 132.4, 132.5 (2C), 148.3. HRMS (FAB) calcd for $C_{40}H_{24}N$ [MH^+] 518.1909; found: 518.1904.

*2-{[2-({2-[(2-{[2-(Phenylethynyl)phenyl]ethynyl}phenyl)ethynyl]-phenyl}ethynyl)phenyl]ethynyl}aniline (**14**).* A mixture of **13** (0.31 g, 0.60 mmol), CuI (2.7 mg, 0.014 mmol), $PdCl_2(PPh_3)_2$ (10 mg, 0.014 mmol), Et_3N (0.40 mL, 2.8 mmol), and iodobenzene (0.064 mL, 0.57 mmol) in THF (1.2 mL) was stirred at room temperature for 6 h under argon. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography over silica gel with hexane−EtOAc (5:1) to afford **14** (0.29 g, 99% yield) as a brown amorphous solid. IR (neat): 3479 (NH), 3380 (NH), 2252 (C≡C), 2212 (C≡C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ: 4.40 (s, 2H), 6.62 (d, J = 8.6 Hz, 1H), 6.64 (dd, J = 7.4, 7.4 Hz, 1H), 7.08 (dd, J = 7.7, 7.7 Hz, 1H), 7.20−7.28 (m, 11H), 7.33 (d, J = 6.3 Hz, 1H), 7.50−7.58 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 88.4, 90.5, 91.9, 92.2, 92.3, 92.4, 92.7, 92.9, 93.6, 93.7, 107.6, 114.0, 117.5, 123.3, 125.0, 125.4, 125.55, 125.65, 125.66, 125.7, 125.9, 127.6, 127.9, 128.02, 128.05, 128.07, 128.09, 128.13, 128.15, 128.22 (2C), 128.3, 129.8, 131.3, 131.7 (2C), 131.7, 131.9, 132.0, 132.1, 132.21, 132.24, 132.3, 132.47, 132.48, 148.3. HRMS (FAB) calcd for $C_{46}H_{28}N$ [MH^+] 594.2222; found: 594.2227.



dx.doi.org/10.1021/jo2018119 | J. Org. Chem. 2011, 76, 9068−9080

*3-Bromo-2-(pent-1-yn-1-yl)thiophene (**S7**).* To a solution of 2,3-dibromothiophene (0.52 mL, 4.6 mmol) in Et_3N (6 mL) were successively added CuI (54 mg, 0.28 mmol), $PdCl_2(PPh_3)_2$ (0.10 g, 0.15 mmol), and pent-1-yne (0.52 mL, 5.5 mmol) at room temperature under argon. The mixture was stirred at 80 °C for 18 h. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography over silica gel with hexane−EtOAc (400:1) to afford **S7** (0.56 g, 53% yield) as an orange oil. IR (neat): 2250 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.07 (t, J = 7.3 Hz, 3H), 1.64−1.67 (m, 2H), 2.45 (t, J = 7.0 Hz, 2H), 6.92 (d, J = 5.4 Hz, 1H), 7.10 (d, J = 5.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.5, 21.8, 21.9, 72.4, 98.8, 114.9, 121.7, 125.7, 129.8. HRMS (FAB) calcd for C_9H_9BrS [M^+] 227.9608; found: 227.9606.

*2-[(2-{[2-(Pent-1-yn-1-yl)thiophen-3-yl]ethynyl}phenyl)ethynyl]-aniline (**17**).* To a solution of **S7** (0.55 g, 2.4 mmol) in THF (5 mL) were successively added diisopropylamine (1.7 mL, 12 mmol), CuI (27 mg, 0.14 mmol), $PdCl_2(PhCN)_2$ (0.55 g, 0.14 mmol), P(t-Bu)$_3$ (0.070 mL, 0.29 mmol), and **7** (0.54 g, 2.5 mmol) at room temperature under argon. The mixture was stirred at room temperature for 15 h. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography over silica gel with hexane−EtOAc (10:1) to afford **17** (0.77 g, 88% yield) as a brown oil. IR (neat): 3421 (NH), 3377 (NH), 2209 (C≡C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ: 0.98 (t, J = 7.4 Hz, 3H), 1.53−1.56 (m, 2H), 2.34 (t, J = 7.2 Hz, 2H), 4.43 (br s, 2H), 6.68 (d, J = 7.4 Hz, 1H), 6.68 (dd, J = 7.4, 7.4 Hz, 1H), 7.06−7.14 (m, 3H), 7.27−7.34 (m, 2H), 7.38 (d, J = 8.0 Hz, 1H), 7.56 (dd, J = 6.6, 6.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.5, 21.8, 21.9, 73.0, 87.6, 90.6, 91.8, 93.7, 99.8, 107.6, 114.1, 117.5, 124.7, 125.0, 125.3, 125.8, 127.6, 127.8, 128.2, 129.6, 129.9, 131.3, 131.9, 132.3, 148.4. HRMS (FAB) calcd for $C_{25}H_{19}NS$ [M]$^+$ 365.1238; found: 365.1236.

*[(3-Bromothiophen-2-yl)ethynyl]trimethylsilane (**S8**).* To a solution of 2,3-dibromothiophene (0.52 mL, 4.6 mmol) in Et_3N (6 mL) were successively added CuI (54 mg, 0.28 mmol), $PdCl_2(PPh_3)_2$ (0.10 g, 0.15 mmol), and TMS−acetylene (0.76 mL, 5.5 mmol) at room temperature under argon. The mixture was stirred at 80 °C for 16 h. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography over silica gel with hexane−EtOAc (400:1) to afford **S8** (0.67 g, 57% yield) as an orange oil. IR (neat): 2149 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.27 (s, 9H), 6.93 (dd, J = 5.4, 0.5 Hz, 1H), 7.17 (dd, J = 5.4, 0.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 0.0 (3C), 95.7, 103.7, 116.9, 121.0, 127.2, 130.2; HRMS (FAB) calcd for $C_9H_{11}BrSSi$ [M^+] 257.9534; found: 257.9534.

*2-[(2-Ethynylthiophen-3-yl)ethynyl]aniline (**S9**).* To a solution of **S8** (1.2 g, 4.8 mmol) in THF (12 mL) were successively added diisopropylamine (3.3 mL, 24 mmol), CuI (55 mg, 0.29 mmol), $PdCl_2(PhCN)_2$ (0.11 g, 0.29 mmol), P(t-Bu)$_3$ (0.14 mL, 0.57 mmol), and **5** (0.67 g, 5.7 mmol) at room temperature under argon. The mixture was stirred at 60 °C for 16 h. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The residue was dissolved in THF (10 mL), and TBAF (1 M solution in THF; 5.7 mL, 5.7 mmol) was added to the mixture at 0 °C. The mixture was stirred at 0 °C for 0.5 h and quenched by addition of saturated aqueous NH_4Cl and brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by column chromatography over silica gel with hexane−EtOAc (5:1) to afford **S9** (0.43 g, 40% yield in two steps) as a brown oil. IR (neat): 3376 (NH), 3299 (NH), 3015 (C≡CH), 2199 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.62 (s, 1H), 4.41 (br s, 2H), 6.69−6.73 (m, 2H), 7.07 (d, J = 5.0 Hz, 1H), 7.15 (dd, J = 7.8, 7.8 Hz, 1H), 7.21 (d, J = 5.5 Hz, 1H), 7.36 (dd, J = 7.8, 1.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 76.6, 85.2, 88.9, 90.4, 107.3, 114.3, 117.8, 124.0, 126.6, 128.3, 129.0, 130.0, 131.8, 148.0. HRMS (FAB) calcd for $C_{14}H_9NS$ [M^+] 223.0456; found: 223.0464.

*2-[(2-{[2-(Pent-1-yn-1-yl)phenyl]ethynyl}thiophen-3-yl)ethynyl]-aniline (**18**).* A mixture of **S9** (0.11 g, 0.51 mmol), CuI (2.3 mg, 0.012 mmol), $PdCl_2(PPh_3)_2$ (8.5 mg, 0.012 mmol), Et_3N (0.34 mL, 2.4 mmol), and 1-bromo-2-iodobenzene (0.062 mL, 0.49 mmol) in THF (1.0 mL) was stirred at room temperature for 2 h under argon. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography over silica gel with hexane−EtOAc (5:1) to afford 2-[(2-[(2-bromophenyl)ethynyl]thiophen-3-yl)ethynyl]aniline (0.15 g, 81% yield) as an orange oil. To a solution of this compound (0.14 g, 0.38 mmol) in piperidine (1 mL) were successively added CuI (7.3 mg, 0.038 mmol), $PdCl_2(PPh_3)_2$ (27 mg, 0.038 mmol), and pent-1-yne (0.11 mL, 1.1 mmol) at room temperature under argon. The mixture was stirred at 80 °C for 13 h and quenched by the addition of saturated aqueous NH_4Cl at room temperature. The aqueous mixture was extracted with EtOAc, and the layers were separated. The organic layer was washed with brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by column chromatography over silica gel with hexane−EtOAc (10:1) to afford **18** (0.10 g, 59% yield in two steps) as an orange oil. IR (neat): 3482 (NH), 3379 (NH), 2198 (C≡C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ: 1.00 (t, J = 7.2 Hz, 3H), 1.56−1.64 (m, 2H), 2.38 (t, J = 6.9 Hz, 2H), 4.40 (s, 2H), 6.68 (d, J = 6.6 Hz, 1H), 6.69 (dd, J = 6.6, 6.6 Hz, 1H), 7.10−7.14 (m, 2H), 7.21−7.29 (m, 3H), 7.36 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 6.6 Hz, 1H), 7.52 (d, J = 6.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.6, 21.6, 22.1, 79.3, 85.5, 89.5, 90.4, 95.7, 96.3, 107.5, 114.1, 117.6, 125.0, 125.5, 126.4, 126.7, 126.9, 127.3, 128.4, 129.0, 129.9, 131.7, 131.8, 132.0, 148.2. HRMS (FAB) calcd for $C_{25}H_{20}NS$ [MH^+] 366.1316; found: 366.1316.

*General Procedure for Synthesis of Fused Carbazoles by Tricyclization: Synthesis of 6-Propyl-11H-benzo[a]naphtho[2,1-c]-carbazole (**15a**) (Table 1, Entry 12) and 6-[2-(Pent-1-ynyl)phenyl]-11H-benzo[a]carbazole (**16a**) (Table 1, Entry 1).* To a stirred solution of aniline **9a** (70 mg, 0.19 mmol) in AcOH (0.57 mL) under argon was added a suspension of JohnPhosAuCl (5.1 mg, 9.7 μmol, 5 mol %) and $AgBF_4$ (1.9 mg, 9.7 μmol, 5 mol %) in AcOH (0.4 mL) at room temperature. The mixture was stirred at 80 °C for 0.5 h. The reaction mixture was diluted with EtOAc, washed with saturated aqueous NH_4Cl and brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by column chromatography over amino silica gel with hexane/Et_2O (1:1) to afford **15a** (51 mg, 73% yield). On the other hand, the reaction of **9a** (47 mg, 0.13 mmol) with Ph_3PAuCl (3.3 mg, 6.6 μmol, 5 mol %)/AgOTf (1.7 mg, 6.6 μmol, 5 mol %) in MeCN (0.7 mL) for 2 h gave **16a** (13 mg, 28% yield).

Compound **15a**: a brown amorphous solid. IR (neat): 3422 (NH) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ: 1.01 (t, J = 7.2 Hz, 3H), 1.88−1.96 (m, 2H), 3.43 (t, J = 8.0 Hz, 2H), 7.20 (dd, J = 7.2, 7.2 Hz, 1H), 7.38 (dd, J = 7.7, 7.7 Hz, 1H), 7.51−7.61 (m, 5H), 7.76 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 6.9 Hz, 1H), 8.41 (d, J = 8.6 Hz, 1H), 8.60 (d, J = 8.0 Hz, 1H), 8.88 (br s, 1H), 8.97 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.3, 24.7, 39.6, 111.2, 113.9, 119.5, 120.8, 122.1, 123.2, 123.6, 124.2, 125.0, 125.2, 125.4, 125.7, 126.1, 126.4, 126.5, 127.8, 128.38, 128.43, 129.1, 130.3, 131.9, 134.8, 137.6, 138.7. HRMS (FAB) calcd for $C_{27}H_{21}N$ [M^+] 359.1674; found: 359.1665.

Compound **16a**: a brown amorphous solid. IR (neat): 3440 (NH), 2252 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.32 (t, J = 7.6 Hz, 3H), 0.83−0.92 (m, 2H), 1.85 (t, J = 6.6 Hz, 2H), 7.02 (dd, J = 7.8, 7.8 Hz, 1H), 7.19 (d, J = 6.9 Hz, 1H), 7.34 (dd, J = 7.8, 7.8 Hz, 1H), 7.42−7.47 (m, 2H), 7.52−7.57 (m, 4H), 7.59−7.66 (m, 2H), 8.00 (d, J = 8.2 Hz, 1H), 8.18 (d, J = 8.2 Hz, 1H), 8.86 (br s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 12.6, 21.1, 21.4, 79.9, 93.6, 110.6, 117.5, 119.6, 120.26, 120.30, 121.2, 122.0, 124.0, 124.1, 124.4, 125.27, 125.32, 127.4, 127.5, 128.9, 130.0, 132.0, 132.2, 134.9, 135.2, 138.6, 143.2. HRMS (FAB) calcd for $C_{27}H_{21}N$ [M^+] 359.1674; found: 359.1676.

*6-Cyclohexyl-11H-benzo[a]naphtho[2,1-c]carbazole (**15b**) (Table 2, Entry 2).* By a procedure similar to that described for the preparation of **15a**, **9b** (52 mg, 0.13 mmol) was converted into **15b** (36 mg, 70% yield) as a pale brown amorphous solid by treatment with JohnPhosAuCl (3.5 mg, 6.5 μmol) and $AgBF_4$ (1.3 mg, 6.5 μmol) in AcOH (0.81 mL) at 80 °C for 24 h. IR (neat): 3422 (NH) cm^{-1}.

dx.doi.org/10.1021/jo2018119 | J. Org. Chem. 2011, 76, 9068−9080

^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.41−1.45 (m, 3H), 1.79−1.91 (m, 5H), 2.09−2.12 (m, 2H), 3.72−3.75 (m, 1H), 7.22 (dd, J = 7.4, 7.4 Hz, 1H), 7.39 (dd, J = 7.4, 7.4 Hz, 1H), 7.51 (dd, J = 7.7, 7.7 Hz, 1H), 7.56−7.61 (m, 4H), 7.83 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 7.4 Hz, 1H), 8.39 (d, J = 8.6 Hz, 1H), 8.43 (d, J = 8.0 Hz, 1H), 8.96 (d, J = 8.0 Hz, 1H), 9.01 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 26.4, 27.3 (2C), 36.4 (2C), 42.9, 111.2, 113.8, 119.5, 120.9, 122.2, 122.7, 123.1, 123.6, 124.2, 124.8, 125.2, 125.5, 125.6, 126.4, 126.6, 127.4, 128.2, 128.8, 128.9, 129.9, 131.9, 134.6, 138.7, 143.4. HRMS (FAB) calcd for $C_{30}H_{25}N$ [M^+] 399.1987; found: 399.1993.

*6-[2-(3,3-Dimethylbut-1-yn-1-yl)phenyl]-11H-benzo[a]carbazole (**16c**) (Table 2, Entry 3).* By a procedure similar to that described for the preparation of **15a**, **9c** (47 mg, 0.13 mmol) was converted into biscyclization product **16c** (33 mg, 72% yield) as a pale yellow amorphous solid by treatment with JohnPhosAuCl (3.4 mg, 6.3 μmol) and $AgBF_4$ (1.2 mg, 6.3 μmol) in AcOH (0.78 mL) at 80 °C for 24 h. IR (neat): 3430 (NH), 2250 (C≡C) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.56 (s, 9H), 7.03 (dd, J = 7.7, 7.7 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.32 (dd, J = 7.7, 7.7 Hz, 1H), 7.42−7.44 (m, 2H), 7.51−7.61 (m, 6H), 7.98 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H), 8.87 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 27.4, 30.0 (3C), 78.4, 102.0, 110.5, 117.6, 119.6, 120.2, 120.3, 121.2, 122.3, 124.1, 124.3, 124.4, 125.25, 125.31, 127.4, 127.5, 128.9, 129.8, 131.6, 132.0, 134.7, 135.3, 138.5, 143.5. HRMS (FAB) calcd for $C_{28}H_{23}N$ [M^+] 373.1830; found: 373.1833.

*4-(11H-Benzo[a]naphtho[2,1-c]carbazol-6-yl)benzonitrile (**15e**) (Table 2, Entry 5).* By a procedure similar to that described for the preparation of **15a**, **9e** (51 mg, 0.12 mmol) was converted into **15e** (39 mg, 77% yield) as a yellow solid by treatment with JohnPhosAuCl (3.3 mg, 6.1 μmol) and $AgBF_4$ (1.2 mg, 6.1 μmol) in AcOH (0.76 mL) at 80 °C for 0.5 h: mp 199−200 °C. IR (neat): 3353 (NH), 2227 (C≡N) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.16 (dd, J = 8.0, 8.0 Hz, 1H), 7.29 (dd, J = 7.7, 7.7 Hz, 1H), 7.47 (dd, J = 7.4, 7.4 Hz, 1H), 7.54 (dd, J = 7.4, 7.4 Hz, 1H), 7.60−7.73 (m, 9H), 8.01 (d, J = 8.6 Hz, 1H), 8.19 (d, J = 7.4 Hz, 1H), 8.48 (d, J = 8.0 Hz, 1H), 9.09 (s, 1H), 9.10 (d, J = 7.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 110.4, 111.5, 113.4, 119.1, 119.7, 120.8, 122.4, 122.8, 123.1, 124.5 (2C), 125.05, 125.09, 125.9, 127.1, 127.4, 127.5, 128.3, 128.8, 129.2, 129.8, 130.1, 130.2 (2C), 131.5, 132.5 (2C), 135.4, 136.4, 138.7, 150.1. HRMS (FAB) calcd for $C_{31}H_{19}N_2$ [MH^+] 419.1548; found: 419.1549.

*6-(4-Chlorophenyl)-11H-benzo[a]naphtho[2,1-c]carbazole (**15f**) (Table 2, Entry 6).* By a procedure similar to that described for the preparation of **15a**, **9f** (51 mg, 0.12 mmol) was converted into **15f** (35 mg, 68% yield) as brown crystals by treatment with JohnPhosAuCl (3.3 mg, 6.0 μmol) and $AgBF_4$ (1.2 mg, 6.0 μmol) in AcOH (0.75 mL) at 80 °C for 1 h: mp 172−174 °C. IR (neat): 3427 (NH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.18 (dd, J = 7.7 Hz, 1H), 7.28 (dd, J = 7.7, 7.7 Hz, 1H), 7.42−7.45 (m, 5H), 7.53 (dd, J = 7.4, 7.4 Hz, 1H), 7.63−7.66 (m, 3H), 7.73 (s, 1H), 7.81 (d, J = 8.6 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 8.48 (d, J = 8.0 Hz, 1H), 9.04 (s, 1H), 9.08 (d, J = 8.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 111.3, 113.5, 119.6, 120.6, 122.3, 123.1, 123.6, 124.4, 124.5, 124.6, 125.2, 125.8, 126.9, 127.2, 127.3, 128.3, 128.7, 129.0 (2C), 129.7, 129.86, 129.88, 130.8 (2C), 131.7, 132.9, 135.4, 137.2, 138.7, 143.9. HRMS (FAB) calcd for $C_{30}H_{18}ClN$ [M^+] 427.1128; found: 427.1135.

*6-Phenyl-11H-benzo[a]naphtho[2,1-c]carbazole (**15g**) (Table 2, Entry 7).* By a procedure similar to that described for the preparation of **15a**, **9g** (51 mg, 0.13 mmol) was converted into **15g** (32 mg, 63% yield) as a brown amorphous solid by treatment with JohnPhosAuCl (3.5 mg, 6.4 μmol) and $AgBF_4$ (1.3 mg, 6.4 μmol) in AcOH (0.64 mL) at 80 °C for 0.5 h. IR (neat): 3423 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.11 (dd, J = 7.8, 7.8 Hz, 1H), 7.27 (dd, J = 7.8, 7.8 Hz, 1H), 7.37−7.52 (m, 7H), 7.58−7.67 (m, 3H), 7.77 (s, 1H), 7.82 (d, J = 8.7 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H), 8.49 (d, J = 8.2 Hz, 1H), 9.06 (br s, 1H), 9.08 (d, J = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.3, 113.6, 119.6, 120.4, 122.3, 123.2, 123.9, 124.3, 124.38, 124.42, 125.4, 125.7, 126.8, 126.9, 127.2, 127.3, 128.3, 128.6, 128.8 (2C), 129.6 (2C), 129.7, 130.0, 130.1, 131.8, 135.4, 138.5, 138.7, 145.4. HRMS (FAB) calcd for $C_{30}H_{19}N$ [M^+] 393.1517; found: 393.1520.

*6-(p-Tolyl)-11H-benzo[a]naphtho[2,1-c]carbazole (**15h**) (Table 2, Entry 8).* By a procedure similar to that described for the preparation of **15a**, **9h** (49 mg, 0.12 mmol) was converted into **15h** (29 mg, 60% yield) as a pale brown solid by treatment with JohnPhosAuCl (3.3 mg, 6.0 μmol) and $AgBF_4$ (1.2 mg, 6.0 μmol) in AcOH (0.75 mL) at 80 °C for 0.75 h: mp 241−243 °C. IR (neat): 3428 (NH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.44 (s, 3H), 7.12 (dd, J = 7.4, 7.4 Hz, 1H), 7.22−7.27 (m, 3H), 7.38 (d, J = 7.4 Hz, 2H), 7.43 (dd, J = 7.7, 7.7 Hz, 1H), 7.46 (dd, J = 7.4, 7.4 Hz, 1H), 7.60 (m, 3H), 7.75 (s, 1H), 7.88 (d, J = 8.6 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 7.4 Hz, 1H), 8.48 (d, J = 8.0 Hz, 1H), 9.03 (s, 1H), 9.06 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.2, 111.3, 113.5, 119.5, 120.5, 122.3, 123.2, 124.1, 124.3, 124.3, 125.4, 125.6, 126.8, 127.1, 127.2, 128.3, 128.6, 129.4 (2C), 129.5 (2C), 129.7, 130.0, 130.19, 130.20, 131.9, 135.4, 136.5, 138.5, 138.7, 142.6. HRMS (FAB) calcd for $C_{31}H_{21}N$ [M^+] 407.1674; found: 407.1671.

*6-(4-Methoxyphenyl)-11H-benzo[a]naphtho[2,1-c]carbazole (**15i**) (Table 2, Entry 9).* By a procedure similar to that described for the preparation of **15a**, **9i** (58 mg, 0.14 mmol) was converted into **15i** (27 mg, 47% yield) as white crystals by treatment with JohnPhosAuCl (3.7 mg, 6.9 μmol) and $AgBF_4$ (1.4 mg, 6.9 μmol) in AcOH (0.86 mL) at 80 °C for 1 h: mp 293−295 °C. IR (neat): 3419 (NH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.89 (s, 3H), 6.97 (d, J = 8.6 Hz, 2H), 7.15 (dd, J = 7.7, 7.7 Hz, 1H), 7.27 (dd, J = 8.0 Hz, 1H), 7.41−7.46 (m, 3H), 7.51 (dd, J = 7.4, 7.4 Hz, 1H), 7.57−7.68 (m, 3H), 7.75 (s, 1H), 7.90 (d, J = 9.2 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 8.49 (d, J = 8.0 Hz, 1H), 9.02 (s, 1H), 9.07 (d, J = 8.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 55.3, 111.3, 113.5, 114.3 (2C), 119.5, 120.5, 122.3, 123.2, 124.2, 124.2, 124.3, 124.4, 125.3, 125.6, 126.8, 126.9, 127.2, 128.3, 128.5, 129.7, 129.8, 130.2, 130.6 (2C), 131.9, 135.4, 138.0, 138.2, 138.7, 158.8. HRMS (FAB) calcd for $C_{31}H_{21}NO$ [M^+] 423.1623; found: 423.1630.

*14-Methyl-6-propyl-11H-benzo[a]naphtho[2,1-c]carbazole (**15j**) (Table 2, Entry 10).* By a procedure similar to that described for the preparation of **15a**, **9j** (57 mg, 0.15 mmol) was converted into **15j** (37 mg, 66% yield) as a pale brown amorphous solid by treatment with JohnPhosAuCl (4.1 mg, 7.6 μmol) and $AgBF_4$ (1.5 mg, 7.6 μmol) in AcOH (0.76 mL) at 80 °C for 0.5 h. IR (neat): 3426 (NH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.99 (t, J = 7.4 Hz, 3H), 1.88−1.91 (m, 2H), 2.46 (s, 3H), 3.40 (t, J = 7.7 Hz, 2H), 7.17 (dd, J = 6.3, 6.3 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.50−7.53 (m, 3H), 7.58 (dd, J = 7.4, 7.4 Hz, 1H), 7.73 (s, 1H), 7.90 (d, J = 8.0, 8.0 Hz, 1H), 8.03 (dd, J = 7.2, 2.0 Hz, 1H), 8.19 (s, 1H), 8.56 (dd, J = 7.7, 2.0 Hz, 1H), 8.77 (s, 1H), 8.95 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.3, 21.8, 24.7, 39.5, 110.8, 113.6, 120.8, 122.1, 123.1, 123.4, 124.9, 124.9, 125.5, 125.58, 125.63, 126.0, 126.3, 126.5, 127.7, 128.3, 128.5, 128.6, 129.2, 130.2, 131.8, 135.0, 137.0, 137.6. HRMS (FAB) calcd for $C_{28}H_{23}N$ [M^+] 373.1830; found: 373.1832.

*14-Chloro-6-propyl-11H-benzo[a]naphtho[2,1-c]carbazole (**15k**) (Table 2, Entry 11).* By a procedure similar to that described for the preparation of **15a**, **9k** (51 mg, 0.13 mmol) was converted into **15k** (35 mg, 68% yield) as a pale brown solid by treatment with JohnPhosAuCl (3.5 mg, 6.5 μmol) and $AgBF_4$ (1.3 mg, 6.5 μmol) in AcOH (0.65 mL) at 80 °C for 0.5 h: mp 191−192 °C. IR (neat): 3438 (NH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.01 (t, J = 7.4 Hz, 3H), 1.89−1.92 (m, 2H), 3.39 (t, J = 8.0 Hz, 2H), 7.28 (dd, J = 8.6, 2.3 Hz, 1H), 7.39 (d, J = 8.6 Hz, 1H), 7.53−7.62 (m, 4H), 7.75 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 6.9 Hz, 1H), 8.35 (s, 1H), 8.54 (d, J = 9.2 Hz, 1H), 8.81 (d, J = 8.0 Hz, 1H), 8.89 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.3, 24.7, 39.4, 112.0, 113.3, 120.8, 121.8, 122.6, 123.9, 124.2, 124.9, 125.4 (2C), 125.8, 126.3, 126.4, 126.6, 126.7, 127.5, 128.0, 128.4, 128.7, 130.5, 131.9, 135.6, 136.9, 137.5. HRMS (FAB) calcd for $C_{27}H_{20}ClN$ [M^+] 393.1284; found: 393.1292.

*6-Propyl-11H-benzo[a]naphtho[2,1-c]carbazole-14-carbonitrile (**15l**) (Table 2, Entry 12).* By a procedure similar to that described for the preparation of **15a**, **9l** (52 mg, 0.13 mmol) was converted into **15l** (7.4 mg, 14% yield) as a brown amorphous solid by treatment with JohnPhosAuCl (3.6 mg, 6.7 μmol) and $AgBF_4$ (1.3 mg, 6.7 μmol) in AcOH (0.65 mL) at 80 °C for 1 h: mp 267−269 °C. IR (neat): 3301 (NH), 2222 (C≡N) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 0.96

dx.doi.org/10.1021/jo2018119 | J. Org. Chem. 2011, 76, 9068−9080

(t, J = 7.4 Hz, 3H), 1.83−1.86 (m, 2H), 3.44 (t, J = 8.0 Hz, 2H), 7.64−7.71 (m, 2H), 7.73−7.83 (m, 3H), 7.88 (d, J = 8.6 Hz, 1H), 7.91 (s, 1H), 8.06 (d, J = 8.0 Hz, 1H), 8.61 (s, 1H), 8.66 (t, J = 8.6 Hz, 2H), 8.77 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 14.0, 24.0, 38.8, 100.7, 111.9, 113.1, 120.5, 121.9, 122.6, 123.9, 124.1, 125.2, 125.6, 126.1, 126.2, 126.37, 126.43, 126.6, 126.7, 126.9, 127.1, 127.7, 127.8, 129.9, 131.4, 136.5, 137.2, 140.9. HRMS (FAB) calcd for $C_{28}H_{20}N_2$ [M$^+$] 384.1621; found: 384.1621.

*13-Chloro-6-propyl-11H-benzo[a]naphtho[2,1-c]carbazole (**15m**) (Table 2, Entry 13).* By a procedure similar to that described for the preparation of **15a**, **9m** (50 mg, 0.13 mmol) was converted into **15m** (26 mg, 52% yield) as a brown amorphous solid by treatment with JohnPhosAuCl (3.5 mg, 6.4 μmol) and $AgBF_4$ (1.3 mg, 6.4 μmol) in AcOH (0.80 mL) at 80 °C for 0.5 h. IR (neat): 3427 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.02 (t, J = 7.3 Hz, 3H), 1.90−1.94 (m, 2H), 3.40 (t, J = 8.0 Hz, 2H), 7.12 (dd, J = 8.7, 1.8 Hz, 1H), 7.47−7.60 (m, 5H), 7.76 (s, 1H), 7.91 (d, J = 7.8 Hz, 1H), 8.06 (d, J = 7.8 Hz, 1H), 8.25 (d, J = 8.7 Hz, 1H), 8.56 (d, J = 8.2 Hz, 1H), 8.81 (d, J = 8.2 Hz, 1H), 8.88 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 24.7, 39.5, 111.0, 113.5, 119.9, 120.8, 121.8, 123.7, 123.9, 125.2, 125.4, 125.8 (2C), 126.3, 126.5, 126.6, 127.6, 128.0, 128.4, 128.6, 129.7, 130.3, 131.8, 135.1, 137.6, 139.1. HRMS (FAB) calcd for $C_{27}H_{20}ClN$ [M$^+$] 393.1284; found: 393.1277.

*5-Propyl-10H-benzo[a]thieno[3′,2′:3,4]benzo[1,2-c]carbazole (**19**) (Scheme 6).* By a procedure similar to that described for the preparation of **15a**, **17** (65 mg, 0.18 mmol) was converted into **19** (29 mg, 45% yield) as a brown amorphous solid by treatment with JohnPhosAuCl (4.8 mg, 8.8 μmol) and $AgBF_4$ (1.8 mg, 8.8 μmol) in AcOH (1.1 mL) at 80 °C for 1 h. IR (neat): 3429 (NH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.01 (t, J = 7.2 Hz, 3H), 1.91−1.93 (m, 2H), 3.43 (t, J = 8.0 Hz, 2H), 7.25 (dd, J = 7.7, 7.7 Hz, 1H), 7.37 (dd, J = 7.7, 7.7 Hz, 1H), 7.47 (d, J = 5.7 Hz, 1H), 7.51−7.57 (m, 3H), 7.91 (s, 1H), 8.05 (d, J = 6.3 Hz, 1H), 8.33 (d, J = 5.7 Hz, 1H), 8.44 (d, J = 8.0 Hz, 1H), 8.59 (d, J = 7.4 Hz, 1H), 8.88 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.3, 24.9, 39.7, 111.2, 113.5, 119.6, 120.1, 120.7, 122.0, 122.8, 122.9, 124.0, 125.03, 125.04, 125.2, 125.5, 126.7, 126.8, 128.4, 130.8, 132.8, 134.4, 136.7, 138.6, 138.7. HRMS (FAB) calcd for $C_{25}H_{19}NS$ [M$^+$] 365.1238; found: 365.1245.

*Propyl-10H-naphtho[2,1-c]thieno[3,2-a]carbazole (**20**) (Scheme 6).* By a procedure similar to that described for the preparation of **15a**, **18** (45 mg, 0.12 mmol) was converted into **20** (36 mg, 79% yield) as brown crystals by treatment with JohnPhosAuCl (3.4 mg, 6.2 μmol) and $AgBF_4$ (1.2 mg, 6.2 μmol) in AcOH (0.77 mL) at 80 °C for 1 h: mp 158−160 °C. IR (neat): 3429 (NH) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.19 (t, J = 7.3 Hz, 3H), 1.91−1.95 (m, 2H), 3.50 (t, J = 7.8 Hz, 2H), 7.23 (dd, J = 7.8, 7.8 Hz, 1H), 7.42 (dd, J = 7.3, 7.3 Hz, 1H), 7.54 (dd, J = 7.6, 7.6 Hz, 1H), 7.58−7.63 (m, 2H), 7.68 (d, J = 5.5 Hz, 1H), 7.72 (s, 1H), 7.74 (d, J = 5.5 Hz, 1H), 7.93 (d, J = 7.8 Hz, 1H), 8.54 (d, J = 8.2 Hz, 1H), 8.73 (br s, 1H), 9.17 (d, J = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 24.3, 38.9, 111.1, 114.4, 118.8, 119.1, 123.3, 123.5, 123.9, 124.4, 125.1, 125.6, 126.0, 126.47, 126.54, 126.7, 127.4, 128.57, 128.61, 131.7, 134.5, 135.3, 136.5, 138.6. Anal. Calcd for $C_{25}H_{19}NS$: C, 82.15; H, 5.24; N, 3.83. Found: C, 82.04; H, 5.37; N, 3.82.

*1-Phenyl-11H-benzo[a]chryseno[5,6-c]carbazole (**21**) (Table 3, Entry 9) and 6-[2-(Phenylethynyl)phenyl]-11H-benzo[a]naphtho-[2,1-c]carbazole (**22**) (Table 3, Entry 5).* To a stirred solution of aniline **12** (57 mg, 0.11 mmol) in ethanol (0.52 mL) under argon was added a suspension of XPhosAuCl (6.2 mg, 8.6 μmol, 7.5 mol %) and $AgBF_4$ (1.7 mg, 8.6 μmol, 7.5 mol %) in ethanol (0.2 mL) at room temperature. The mixture was stirred at 80 °C for 3 h. The reaction mixture was diluted with EtOAc, washed with saturated aqueous NH_4Cl and brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by column chromatography over amino silica gel with hexane/Et_2O (1:1) to afford **21** (49 mg, 86% yield). On the other hand, the reaction of **12** (73 mg, 0.15 mmol) with JohnPhosAuCl (3.9 mg, 7.4 μmol, 5 mol %)/$AgBF_4$ (1.4 mg, 7.4 μmol, 5 mol %) in EtOH (0.93 mL) for 24 h gave **22** (45 mg, 61% yield).

Compound **21**: yellow solid; mp >300 °C. IR (neat): 3427 (NH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.09−7.17 (m, 2H), 7.25 (dd, J = 7.7, 7.7 Hz, 1H), 7.31 (dd, J = 7.7, 7.7 Hz, 1H), 7.40−7.57 (m, 9H), 7.71 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.6 Hz, 1H), 7.91 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 8.6 Hz, 1H), 8.08 (d, J = 8.6 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H), 8.57 (d, J = 8.0 Hz, 1H), 9.08 (br s, 1H), 9.09 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.4, 113.0, 119.9, 120.6, 120.7, 122.6, 123.2, 124.5, 124.6 (2C), 124.6, 125.0, 125.1, 125.7, 125.9, 126.1, 126.8, 127.2, 127.3, 127.9, 128.3, 128.8, 128.9, 129.2, 129.4, 129.7, 130.00, 130.04, 130.3, 130.7, 130.8, 131.2, 131.3, 132.3, 135.7, 137.5, 138.7, 145.1. HRMS (FAB) calcd for $C_{38}H_{23}N$ [M$^+$] 493.1830; found 493.1821.

Compound **22**: pale brown amorphous solid. IR (neat): 3426 (NH), 2336 (C≡C) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.14 (d, J = 6.9 Hz, 2H), 6.33 (dd, J = 7.8, 7.8 Hz, 2H), 6.76 (dd, J = 7.8, 7.8 Hz, 1H), 7.12 (dd, J = 7.8, 7.8 Hz, 1H), 7.30 (dd, J = 7.8, 7.8 Hz, 1H), 7.39−7.67 (m, 8H), 7.82 (s, 1H), 7.84 (dd, J = 8.7, 2.7 Hz, 2H), 7.98−8.04 (m, 2H), 8.54 (d, J = 8.2 Hz, 1H), 8.85 (s, 1H), 9.12 (dd, J = 4.1, 4.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 88.7, 92.4, 111.3, 113.9, 119.7, 120.5, 121.9, 122.4, 123.1, 123.2, 124.3, 124.6, 124.8, 125.2, 125.6, 125.7, 126.7, 127.18 (2C), 127.21 (2C), 127.3, 127.4, 128.1, 128.5, 128.79, 128.81, 129.1, 129.7, 130.7 (2C), 130.8, 131.8, 132.6, 135.6, 137.0, 138.8, 147.7. HRMS (FAB) calcd for $C_{38}H_{23}N$ [M$^+$] 493.1830; found 493.1824.

*6-Phenyl-15H-benzo[a]naphtho[1′,2′:11,12]chryseno[5,6-c]-carbazole (**23**) (Scheme 7).* To a stirred solution of aniline **14** (0.34 g, 0.57 mmol) in ethanol (2.5 mL) under argon was added a suspension of XPhosAuCl (81 mg, 0.11 mmol, 20 mol %) and $AgBF_4$ (23 mg, 0.11 mmol, 20 mol %) in ethanol (1.5 mL) at room temperature. The mixture was stirred at 80 °C for 21 h. The reaction mixture was diluted with EtOAc, washed with saturated aqueous NH_4Cl and brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by column chromatography on silica gel with hexane/EtOAc (5:1) to afford **23** (ca. 2:1 isomeric mixture, 0.23 g, 68% yield) as a yellow solid: mp >300 °C. IR (neat): 3441 (NH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: (for both isomers) 6.89 (dd, J = 7.4, 7.4 Hz, 0.7H), 6.95 (dd, J = 7.4, 7.4 Hz, 0.3H), 7.03−7.06 (m, 1H), 7.23−7.42 (m, 4.7H), 7.45−7.58 (m, 5.6H), 7.63−7.79 (m, 3.3H), 7.89 (d, J = 8.0 Hz, 0.7H), 8.00−8.07 (m, 4.3H), 8.15 (dd, J = 7.7, 7.7 Hz, 0.7H), 8.22 (d, J = 8.0 Hz, 0.3H), 8.25 (d, J = 8.0 Hz, 0.7H), 8.74−8.80 (m, 2.7H), 9.10−9.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: [all the signals (<1.0C) for both isomers] 111.3, 111.5, 113.0, 113.7, 119.5, 120.1, 120.5, 120.7, 120.9, 121.0, 122.0, 122.6, 123.0, 123.5, 123.9, 124.0, 124.1, 124.2, 124.3, 124.6, 124.77, 124.79, 124.9, 125.25, 125.33, 125.35 (ca. 1C), 125.42, 125.8, 125.9, 126.1, 126.3, 126.46, 126.52, 126.7, 126.78, 126.83, 126.9, 127.36, 127.38, 127.42, 127.7, 127.8, 127.9, 127.99, 128.03, 128.1, 128.18, 128.20, 128.22, 128.25, 128.27, 128.39, 128.44, 128.5, 128.67, 128.72, 128.9, 129.0, 129.1, 129.3, 129.39, 129.43, 129.60, 129.62, 129.7, 129.9, 130.0, 130.6, 130.77, 130.79, 130.9, 131.0, 131.3, 131.37, 131.43, 131.6, 131.8, 132.1, 132.7, 133.3, 133.8, 135.5, 136.2, 136.4, 137.0, 137.6, 138.7, 139.3, 143.98, 144.03, 144.8. HRMS (FAB) calcd for $C_{46}H_{27}N$ [M$^+$] 593.2143; found 593.2134.

*6-Phenyl-15-tosyl-15H-benzo[a]naphtho[1′,2′:11,12]chryseno-[5,6-c]carbazole (**24**) (Scheme 7).* To a solution of **23** (0.23 g, 0.38 mmol) in DMF (1.0 mL) was added NaH (60% dispersion in mineral oil; 0.046 g, 1.2 mmol) at 0 °C. After being stirred at the same temperature for 20 min, TsCl (0.22 mg, 1.2 mmol) was added to the mixture and the stirring was continued for 23 h at room temperature. The reaction mixture was diluted with EtOAc, washed with saturated aqueous NH_4Cl and brine, dried over Na_2SO_4, filtrated, and concentrated in vacuo. The residue was purified by column chromatography over silica gel with hexane/EtOAc (5:1) to afford **24** (ca. 5:1 isomeric mixture, 0.15 g, 53% yield) as a yellow solid, which was recrystallized from chloroform/hexane to give the single isomer of **24** as a yellow solid: mp >300 °C. IR (neat): 1370 (S═O), 1175 (S═O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.12 (s, 3H), 6.86 (d, J = 8.6 Hz, 2H), 6.96 (dd, J = 7.7, 7.7 Hz, 1H), 7.17−7.41 (m, 10H), 7.47−7.49 (m, 2H), 7.54 (dd, J = 7.4, 7.4 Hz, 1H), 7.70 (dd, J = 7.7, 7.7 Hz, 3H), 7.99−8.05 (m, 5H), 8.16 (d, J = 8.6 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.41 (d, J = 8.6 Hz, 1H), 8.63 (d, J = 8.6 Hz, 1H), 8.66 (d, J = 8.6 Hz, 1H), 9.01 (d, J = 8.6 Hz, 1H). ^{13}C NMR

dx.doi.org/10.1021/jo2018119 | J. Org. Chem. 2011, 76, 9068−9080

(125 MHz, $CDCl_3$) δ: 21.3, 120.1, 123.0, 124.0, 124.1, 124.9, 124.99, 125.02, 125.3, 125.5, 125.6, 125.8, 126.3, 126.62, 126.64, 126.7, 126.8, 126.9, 127.0, 127.7 (4C), 127.8, 128.25, 128.30, 128.35, 128.38 (4C), 128.45, 128.47, 128.54, 128.8, 129.2, 129.8, 130.0, 130.1, 130.3, 130.46, 130.51, 130.6, 131.7, 132.4 (2C), 132.7, 133.4, 137.6, 140.2, 142.6, 144.5, 144.6. HRMS (FAB) calcd for $C_{53}H_{33}NO_2S$ [M^+] 747.2232; found 747.2231.

■ ASSOCIATED CONTENT

Supporting Information

ORTEP diagram of **24**, ^1H and ^{13}C NMR spectra of all new compounds, and a crystallographic information file (CIF) for **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas "Integrated Organic Synthesis" (H.O. and K.T.) and the Targeted Proteins Research Program from the Ministry of Education, Culture, Sports, Science and Technology of Japan, as well as the Program for Promotion of Fundamental Studies in Health Sciences of the National Institute of Biomedical Innovation (NIBIO). We thank Dr. Koji Tsukamoto (School of Pharmacy, Hyogo University of Health Sciences) for instruction of X-ray analysis and valuable discussions.

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