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Gold(I)-Catalyzed Regioselective Inter-/Intramolecular Addition Cascade of Di- and Triynes for Direct Construction of Substituted Naphthalenes

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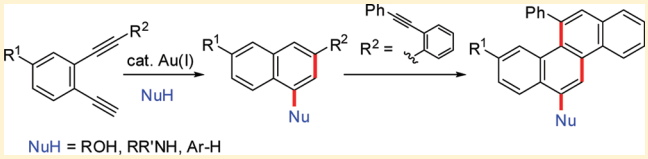
Supporting Information

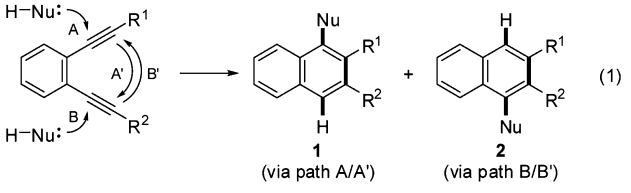
ABSTRACT: The gold-catalyzed cascade intermolecular addition−intramolecular carbocyclization reaction of dialkynylbenzenes was developed. In this reaction, regioselective addition of an external nucleophile toward the terminal alkyne and subsequent 6-*endo*-*dig* cyclization proceeded to give the 1,3-disubstituted naphthalenes in good yields. The direct synthesis of disubstituted chrysenes via a gold-catalyzed addition and double cyclization cascade using a triyne-type substrate was also achieved.



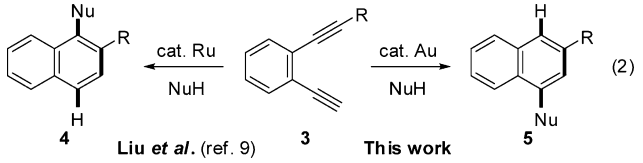
INTRODUCTION

In recent years, atom-economical efficient transformations have attracted attention in view of environmentally benign syntheses.[1] Cascade reactions involving such transformations are especially useful for step-economical direct syntheses of complex molecules reducing formation of waste products.[2] Intra- or intermolecular addition reactions to alkynes, which are being explored due to recent significant advances in the development of alkynophilic π-acidic catalysts such as gold complexes,[3,4] are important primary reactions for such strategies.[5]

As part of our program toward direct syntheses of useful heterocyclic compounds, we have been engaged in the development of gold-catalyzed intramolecular hydroamination/hydroarylation cascade of dienyne-type anilines for synthesis of aryl-annulated carbazoles.[6] We successfully applied this reaction to polyenyne-type anilines to produce highly fused carbazoles by consecutive hydroarylation.[7] In these intramolecular reaction cascades, the alkyne that participates in the first nucleophilic addition (hydroamination) among the several alkynes can be predicted from the substrate structures. By contrast, when applying this method to intermolecular reactions using external nucleophiles, the regioselectivity issue arises, i.e. which of the two regioisomeric products **1** and **2** predominates (eq 1). Recently,



Liu and co-workers reported ruthenium-catalyzed naphthalene formation via nucleophilic addition/insertion cascade of dialkynylbenzenes to afford 1,2-disubstituted naphthalene derivatives.[8] The nucleophilic addition of external nucleophiles to diynes **3** bearing internal and terminal alkyne moieties regioselectively proceeds at the internal alkyne to produce **4** (eq 2).



During our studies on intramolecular reaction cascades using carbamate **6** for investigation of double hydroarylation, we observed unexpected formation of naphthalene derivatives **7** (43%) and **8a** (41%) both bearing an ethoxy group (Scheme 1). Formation of **7** can be explained by gold-catalyzed intermolecular addition of ethanol toward the propargylamine moiety of **6** followed by 6-*endo*-*dig* cyclization. The naphthalene **8a** lacking the aminomethyl group would be formed by a gold-catalyzed retro-Mannich reaction to furnish gold acetylide **A** followed by the same reaction sequence (ethanol addition and 6-*endo*-*dig* cyclization).[9] Addition of ethanol proceeded exclusively at the terminal alkyne moiety of the intermediate **B**. Hence, we expected that diynes bearing terminal and internal alkynes would be promising substrates for a regioselective gold-catalyzed inter/intramolecular addition cascade of dialkynylbenzenes with external nucleophiles (eq 2).[8] In this paper, the cascade cyclization of di- and triyne derivatives, which provides convenient access to 1,3-disubstituted naphthalene derivatives,[10] benzofuran, benzothiophene, and chrysenes, is described.[11] Mechanistic consideration on the naphthalene formation is also presented.

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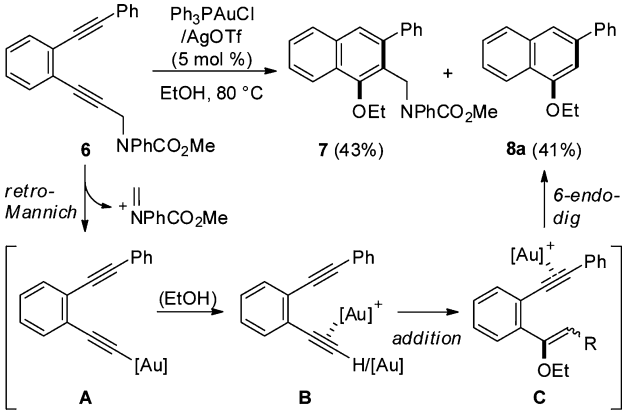
Scheme 1. Unexpected Regioselective Formation of 1-Ethoxy-3-phenylnaphthalenes



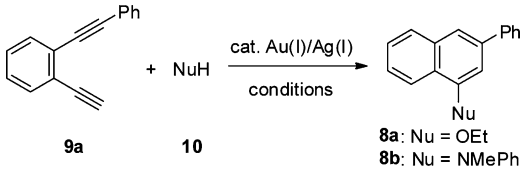
RESULTS AND DISCUSSION

Naphthalene Synthesis. Initially, we investigated the reaction of **9a** under the conditions shown in Scheme 1. When dialkynylbenzene **9a** was treated with 5 mol % of Ph_3PAuCl/AgOTf in EtOH (**10a**) at 80 °C for 1.5 h, naphthalene derivative **8a** was obtained in 36% yield (Table 1, entry 1). As expected, addition of EtOH regioselectively proceeded at the terminal alkyne of **9a**.[12] The reaction at lower temperature (rt) or use of $AgNTf_2$ instead of AgOTf was less effective (entries 2 and 3). Use of a bulky and electron-donating phosphine ligand (XPhos or JohnPhos) considerably decreased the yields (entries 4 and 5). Use of an *N*-heterocyclic carbene (NHC) ligand IPr [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] in place of PPh_3 exhibited more efficient conversion to **8a** (44%, entry 6). Decreasing the loading of EtOH improved the yields slightly (48–50%, entries 9 and 10), probably by suppressing side reactions with excess EtOH.[13] Interestingly, the most efficient conversion was observed by decreasing the loading of catalyst (2 mol %, entry 11). When using *N*-methylaniline (PhNHMe) as the external nucleophile, the desired product **8b** formed by nucleophilic carbon–nitrogen bond formation was obtained in an excellent yield (93%, entry 12). Use of IPrAuCl or AgOTf alone proved unsuccessful (entries 13 and 14). The reaction with AuCl bearing no ligand gave **8b** in only 5% yield (entry 15).

Using the optimized conditions described in entries 11 and 12 [2 mol % IPrAuCl/AgOTf and 1.1 equiv of NuH in 1,2-dichloroethane (DCE), Table 1], the reaction scope with various substrates and nucleophiles was investigated (Table 2). The use of aliphatic alcohols resulted in desired products **8c** and **8d** in moderate yields (65% and 64%, respectively). As the nitrogen nucleophiles, the electron density of the aniline benzene had a small influence on reactivity (**8b, 8e** and **8f**; 92%–quant). Similarly, the reaction with *N*-benzylaniline and the protected hydrazine derivative gave the desired products **8g** and **8h** in good yields (78% and 77%, respectively). Use of heteroaromatic rings such as indole and pyrrole as carbon nucleophiles afforded the desired biaryl products formed via nucleophilic C–C bond formation in moderate to good yields (**8i–k**).[14] For diynes, the internal alkyne bearing an alkyl group (R^2 = propyl) resulted in the desired product **8l** in 68% yield. Moreover, a range of substituents (R^1 and R^2) were tolerated, including benzene rings bearing an electron-withdrawing or -donating group (**8m** and **8n**; 86% and 90%, respectively).

Mechanistic Consideration. A plausible catalytic cycle of the gold-catalyzed naphthalene formation is shown in Scheme 2. As described previously, this reaction would proceed through a stepwise pathway including (1) intermolecular nucleophilic addition to **9a** onto terminal alkyne or gold acetylide as depicted in **A**, (2) protodeauration of **B**, (3) intramolecular nucleophilic addition of the resulting enol ether/enamine-type intermediate **C**, and (4) aromatization of **D** involving protodeauration (1,3-proton shift and/or intermolecular protonation) leading to the naphthalenes **8**. To support this catalytic cycle including

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst (mol %)	NuH (**10**)[c]	solvent[b]	*T* (°C)	time (h)	yield (%)
1	Ph_3PAuCl/AgOTf (5)	(EtOH)	EtOH	80	1.5	36
2	Ph_3PAuCl/AgOTf (5)	(EtOH)	EtOH	rt	26	11
3	Ph_3PAuCl/$AgNTf_2$ (5)	(EtOH)	EtOH	80	0.5	30
4	XPhosAuCl/$AgNTf_2$ (5)	(EtOH)	EtOH	rt	0.5	15
5	JohnPhosAuCl/$AgNTf_2$ (5)	(EtOH)	EtOH	rt	24	<6
6	IPrAuCl/AgOTf (5)	(EtOH)	EtOH	80	1	44
7	IPrAuCl/$AgNTf_2$ (5)	(EtOH)	EtOH	80	0.25	36
8	IPrAuCl/$AgNTf_2$ (5)	(EtOH)	EtOH	rt	2	31
9	IPrAuCl/AgOTf (5)	(EtOH)	AcOH/EtOH	80	1	48
10	IPrAuCl/AgOTf (5)	EtOH (**10a**)	DCE	50	4	50
11[d]	**IPrAuCl/AgOTf (2)**	**EtOH (10a)**	**DCE**	**50**	**2**	**61**
12[d]	**IPrAuCl/AgOTf (2)**	**PhNHMe (10b)**	**DCE**	**50**	**7**	**93**
13[d]	IPrAuCl (2)	PhNHMe (**10b**)	DCE	50	24	nr
14[d]	AgOTf (2)	PhNHMe (**10b**)	DCE	50	24	nr
15[d]	AuCl (2)	PhNHMe (**10b**)	DCE	50	22	5

[a]Reactions were carried out using **9a** (0.1 mmol) and **10** (1.1 equiv). [b]DCE = 1,2-dichloroethane. [c]PhNHMe = *N*-methylaniline. [d]0.17 mmol of **9a** was used.

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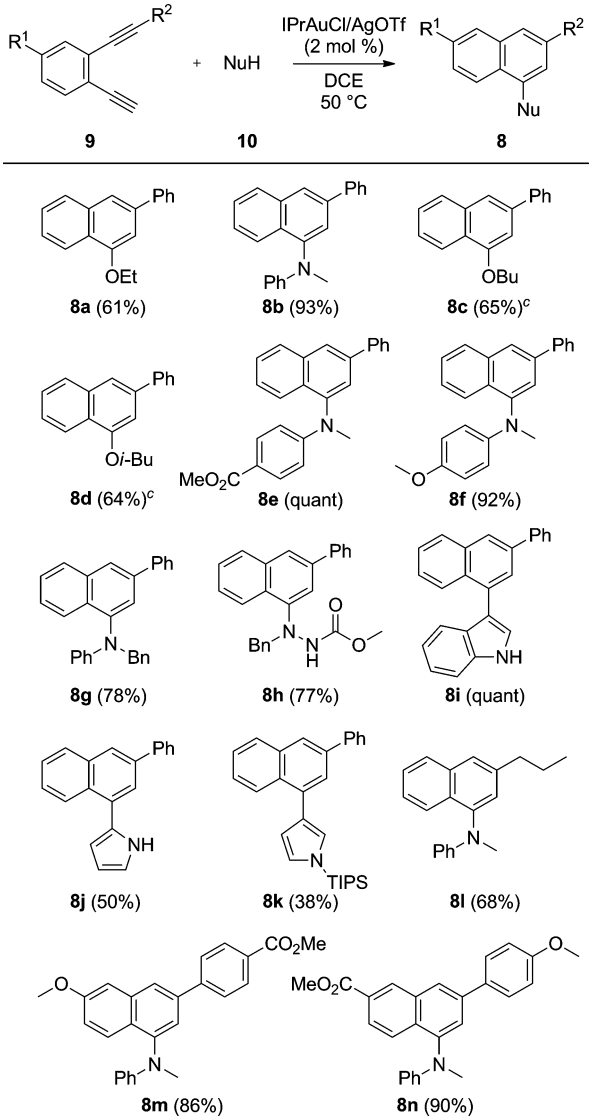
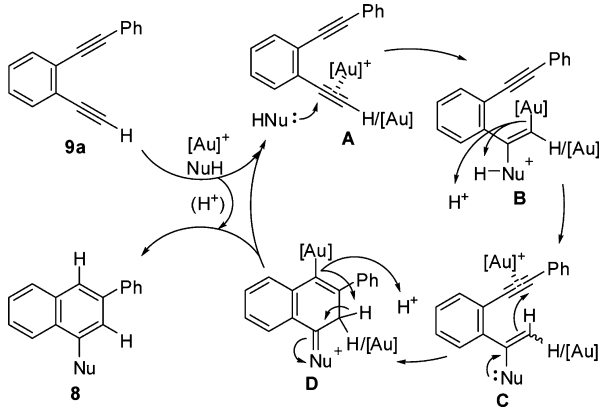
Table 2. Substrate Scope[a,b]



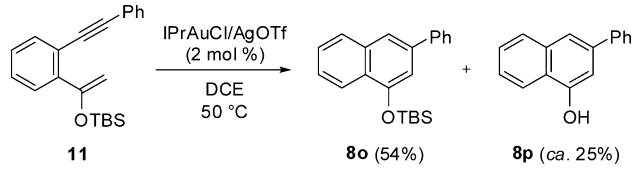
[a]Unless otherwise stated, the reaction was carried out using **9** (0.17 mmol) and **10** (1.1 equiv). [b]DCE = 1,2-dichloroethane. [c]5.0 equiv of **10c** (BuOH) or **10d** (*i*-BuOH) was used.

Scheme 2. A Plausible Catalytic Cycle



intermediacy of **C**, we prepared a related silyl enol ether **11** and subjected to the cyclization conditions (Scheme 3). As we expected, clean conversion to the corresponding naphthol

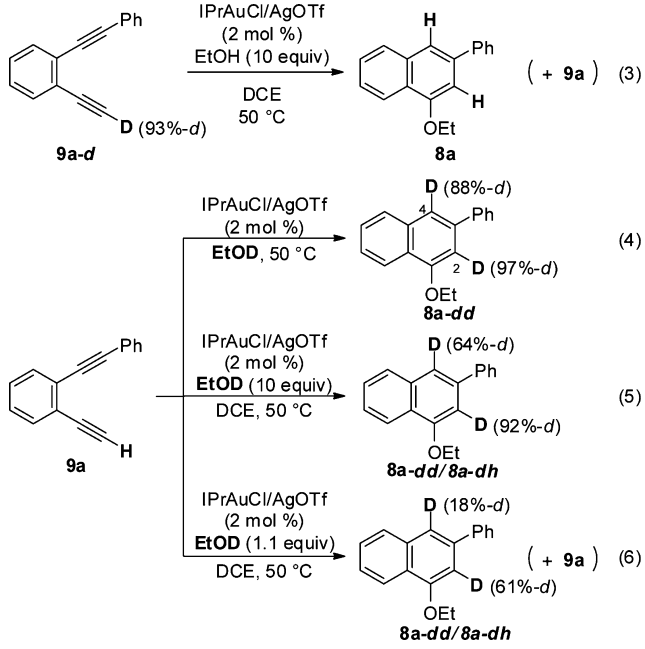
Scheme 3. Reaction of the Silyl Enol Ether 11



derivatives **8o** and **8p** as the silyl ether and alcohol forms, respectively, was observed.

To obtain further mechanistic insights especially on the gold acetylide formation, we next conducted deuterium-labeling experiments (Scheme 4). The reaction of the labeled substrate

Scheme 4. Isotopic Labeling Experiments



9a-*d* (93%-*d*) with EtOH (10 equiv) under the standard conditions gave the corresponding naphthalene derivative **8a** with a loss of deuterium labeling (≤10%-*d*, Scheme 4, eq 3). This suggests that gold acetylide is efficiently generated in the reaction. Isolation of the unlabeled substrate **9a** with a decreased deuterium content (<20%-*d*) from the reaction mixture before completion indicates that the D−H exchange by protonation of the gold acetylide is also promoted, presumably with cogenerated $EtODH^+$ or $EtOH_2^+$. Similarly, when the reaction of the unlabeled substrate **9a** was carried out in excess EtOD (Scheme 4, eq 4), a high deuterium incorporation (88−97%) was observed at the 2- and 4-positions of **8a**. Interestingly, the reaction with a decreased amount of EtOH (10 equiv, Scheme 4, eq 5), we observed a significant decrease of the deuterium incorporation at the 4-position (64%-*d*). When the reaction was conducted using 1.1 equiv of EtOD (Scheme 4, eq 6), deuterium contents at the 4- and 2-position dropped to 18% and 61%, respectively.

The deuterium experiments using unlabeled **9a** using EtOD (Scheme 4, eqs 4−6) provide important information on the reaction mechanism (Scheme 5). Thus, the reaction of the π-complex **A-*h*** with EtOD before H−D exchange would produce **8a-*dh*** bearing a hydrogen atom at the 4-position through preferential 1,3-proton shift from **D-*dh*** (Scheme 5, eq 7).[15]

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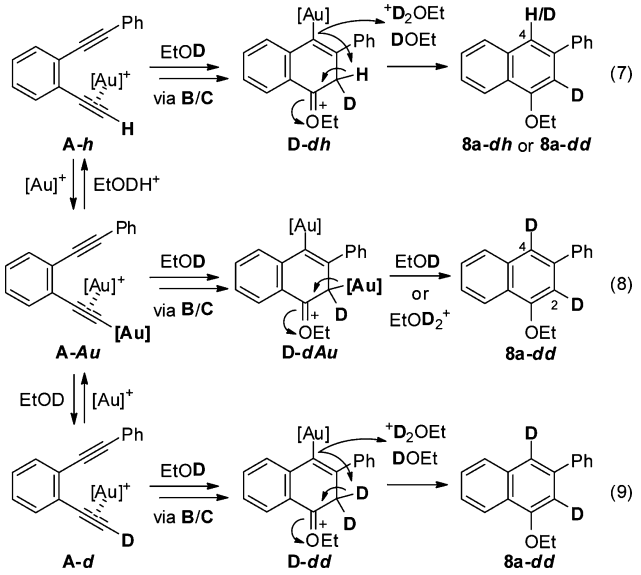
On the other hand, decomposition of **D-*dh*** by EtOD/$EtOD_2^+$ (instead of 1,3-proton shift) will afford **8a-*dd*** (Scheme 5, eq 7).

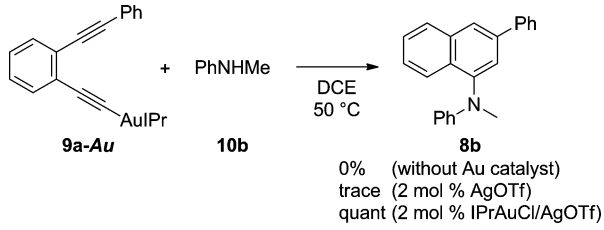
Scheme 5. Proposed Mechanism by the Experimental Results



The reaction after gold acetylide formation (Scheme 5, eq 8) or deuterium incorporation (Scheme 5, eq 9) furnishes **8a-*dd*** bearing two deuteriums at the 2- and 4-positions via deauration. Considering the lower deuterium incorporation at the 4-position when using a decreased amount of EtOD (18–64%-*d*, eqs 5 and 6 in Scheme 4) compared with the case using excess EtOD (88%-*d*, Scheme 4, eq 4), it is reasonable that both of the pathways (Scheme 5, eq 7) and (eq 8)/(eq 9) would be involved: an increased amount of EtOD accelerates the intermolecular reaction of **D-*dh*** (eq 7) with EtOD/$EtOD_2^+$ over 1,3-shift, as well as the H–D exchange from **A-*h*** to **A-*d***. Relatively lower deuterium content (61%-*d*) at the 2-position in the case using 1.1 equiv of EtOD (Scheme 4, eq 6) can be rationalized by two possibilites: relatively unfavorable 1,3-deuterium shift over 1,3-proton shift from **D-*dh*** (Scheme 5, eq 7) in the more dominated pathway and nucleophilic addition of cogenerated EtOH which should not be negligible here. Overall, interconversion between the terminal alkynes and gold acetylides would be one of the important factors for the regioselective intermolecular nucleophilic addition to the terminal alkyne moiety in addition to the steric reason.

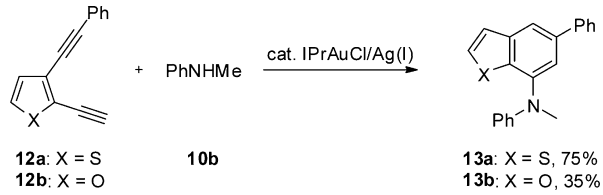
The remaining unsolved problem was the possibility of the intermolecular nucleophilic addition onto the gold acetylide **A-*Au*** (Scheme 5, eq 8). Thus, we prepared gold acetylide complex **9a-*Au*** according to the reported procedure[16] and examined its reactivity. When **9a-*Au*** was treated under the standard cyclization conditions using **10b** (1.1 equiv) without the gold catalyst, only gradual decomposition of **9a-*Au*** was observed without producing the naphthalene **8b** (Scheme 6). Similarly, addition of the AgOTf (2 mol %) did not promote the reaction. In sharp contrast, addition of the gold catalyst IPrAuCl/AgOTf (2 mol %) to **9a-*Au*** in DCE sufficiently promoted the naphthalene formation to afford **8b** quantatively. Thus, the gold acetylide complex **9a-*Au*** has proven to have sufficient reactivity toward the intermolecular nucleophilic addition. This is good accordance with the well-documented dual activation mechanism in gold-catalyzed cycloisomerization of 1,5-enynes and 1,5-allenynes, supported by calculations and tracking experiments.[17]

Scheme 6. Conversion of Gold Acetylide Complex 9a-*Au*



Application to Construction of Other Fused Rings. Next, the reaction of heteroaromatic ring derivatives **12a** and **12b** was investigated (Scheme 7). When thiophene **12a** was treated with 5 mol % of IPrAuCl/AgOTf and 1.1 equiv of *N*-methylaniline (**10b**) in DCE at 80 °C for 4 h, the benzothiophene derivative **13a** was obtained in 75% yield. A limitation of the reaction can be seen in synthesis of aminobenzofuran derivative **13b** in low yield (35%) by using an increased amount (10 mol %) of IPrAuCl/AgOTf.

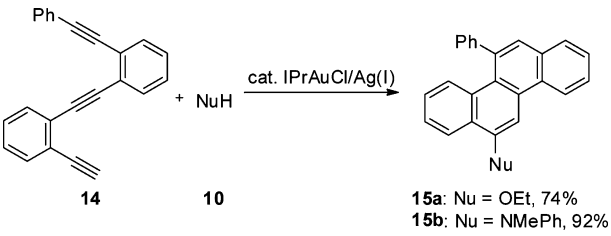
Scheme 7. Reaction of Heteroaromatic Compounds[a]



[a]Reaction conditions: **12** (0.16 mmol), **10b** (1.1 equiv), IPrAuCl/AgOTf (5 mol % for **13a**; 10 mol % for **13b**), DCE, 80 °C.

Finally, biscyclization of triyne-type substrate **14** through intermolecular nucleophilic addition and intramolecular double carbocyclization cascade was investigated (Scheme 8). When the triyne **14** was treated with 5 mol % of IPrAuCl/$AgNTf_2$ in EtOH at 80 °C for 1 h, the chrysene derivative **15a** was obtained in 74% yield.[18] An improved result was obtained using *N*-methylaniline as the external nucleophile (92%). From these observations, the inter-/intramolecular nucleophilic addition cascade is also useful for atom-economical syntheses of not only the 1,3-disubstituted naphthalenes but also the corresponding fused naphthalenes.

Scheme 8. Application to Consecutive Cyclization[a]



[a]Reaction conditions: (for **15a**) **14** (0.09 mmol), IPrAuCl/$AgNTf_2$ (5 mol %), EtOH (solvent), 80 °C; (for **15b**) **14** (0.11 mmol), **10b** (1.1 equiv), IPrAuCl/$AgNTf_2$ (10 mol %), DCE, 80 °C.

■ CONCLUSION

We developed a novel gold-catalyzed cascade reaction for direct construction of naphthalenes. The reaction of di- and trialkynylbenzene derivatives produced the 1,3-disubstituted

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naphthalenes and disubstituted chrysenes, respectively, through regioselective intermolecular addition of an external nucleophile such as alcohols, amines, and heteroarenes followed by (consecutive) *6-endo-dig* carbocyclization(s).

EXPERIMENTAL SECTION

General Methods. All reactions under argon atmosphere were performed using syringe−septum cap techniques and all glassware was dried in an oven at 80 °C for 2 h prior to use. For flash chromatography, silica gel or NH_2 silica gel was employed. Thin-layer chromatography was performed on TLC silica gel 60 F_{254} (layer thickness 0.25 mm), which was developed using standard visualizing agents: UV fluorescence (254 nm) and anisaldehyde with heating. Melting points were measured by a hot-stage melting point apparatus (uncorrected). In ^{1}H NMR spectra, chemical shifts are reported in δ (ppm) relative to TMS as internal standard. In ^{13}C NMR spectra, chemical shifts are referenced to the residual solvent signal. ^{1}H NMR spectra are tabulated as follows: chemical shift, multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), number of protons, and coupling constant(s). Magnetic sector-based mass spectrometer was used for exact mass (HRMS) measurement.

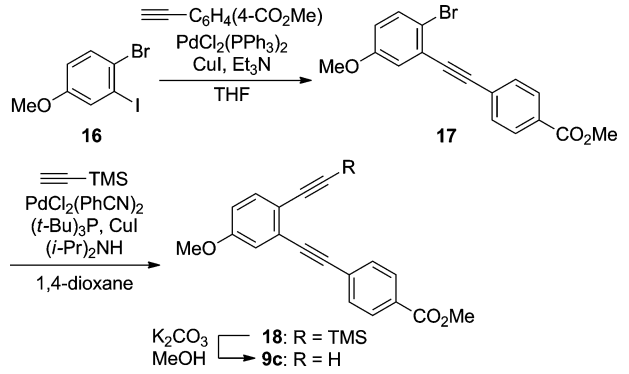
Preparation of Starting Materials. 1-Ethynyl-2-(phenylethynyl)-benzene (**9a**),[6a] 1-ethynyl-2-(pent-1-ynyl)benzene (**9b**),[19] methyl 4-(methylamino)benzoate (**10e**),[20] and *N*-benzylaniline (**10g**)[21] were prepared according to the literature.

Methyl 4-[(2-Bromo-5-methoxyphenyl)ethynyl]benzoate (17). To a stirred suspension of **16**[22] (775 mg, 2.48 mmol), methyl 4-ethynylbenzoate (476 mg, 2.97 mmol), $PdCl_2(PPh_3)_2$ (43.5 mg, 0.06 mmol), and CuI (11.8 mg, 0.06 mmol) in THF (8 mL) under argon was added Et_3N (1.7 mL, 12.4 mmol). After being stirred at rt for 4 h, the reaction mixture was diluted with EtOAc and filtered through a short pad of silica gel. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel (hexane/EtOAc = 50/1) to afford **17** (841 mg, 98%) as colorless crystals: mp 105−106 °C; IR (neat) 2360 (C≡C), 1709 (C═O), 1274 (OCH_3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.93 (s, 3H), 6.79 (dd, J = 9.2, 2.9 Hz, 1H), 7.09 (d, J = 2.9 Hz, 1H), 7.49 (d, J = 9.2 Hz, 1H), 7.63−7.65 (m, 2H), 8.03−8.04 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.3, 55.6, 90.9, 92.7, 116.5, 117.0, 117.9, 125.4, 127.5, 129.6 (2C), 129.9, 131.6 (2C), 133.2, 158.5, 166.5. Anal. Calcd for $C_{17}H_{13}BrO_3$: C, 59.16; H, 3.68. Found: C, 59.16; H, 3.80.

Methyl 4-[[5-Methoxy-2-[(trimethylsilyl)ethynyl]phenyl]-ethynyl]benzoate (18). The coupling of **17** and trimethylsilylacetylene was carried out according to the method reported as follows:[23] to a stirred suspension of **17** (690 mg, 2.00 mmol), $PdCl_2(PhCN)_2$ (23.0 mg, 0.06 mmol), and CuI (7.6 mg, 0.04 mmol) in 1,4-dioxane (2 mL) under argon were added diisopropylamine (0.8 mL, 6.00 mmol), trimethylsilylacetylene (0.3 mL, 2.20 mmol), and tri-*tert*-butylphosphine (30 μL, 0.12 mmol). After being stirred at rt for 3 h, the reaction mixture was diluted with EtOAc and filtered through a short pad of silica gel. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel (hexane/EtOAc = 50/1) to afford **18** (776.7 mg, quant) as colorless crystals: mp 73 °C; IR (neat) 2362, 2148 (C≡C), 1718 (C═O), 1308 ($SiCH_3$), 1268, 1231 (OCH_3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.25 (s, 9H), 3.83 (s, 3H), 3.93 (s, 3H), 6.85 (dd, J = 8.6, 2.9 Hz, 1H), 7.03 (d, J = 2.9 Hz, 1H), 7.43 (d, J = 8.6 Hz, 1H), 7.61−7.62 (m, 2H), 8.02−8.04 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.0 (3C), 52.1, 55.4, 91.0, 92.3, 97.0, 103.2, 115.3, 116.2, 118.3, 126.7, 127.8, 129.4 (2C), 129.6, 131.5 (2C), 133.6, 159.2, 166.5; HRMS (FAB) calcd for $C_{22}H_{22}O_3Si$ (M^+) 362.1338, found 362.1335.

Methyl 4-[(2-Ethynyl-5-methoxyphenyl)ethynyl]benzoate (9c) (Scheme 9). To the solution of **18** (294.9 mg, 0.80 mmol) in MeOH (8 mL) was added K_2CO_3 (331.7 mg, 2.40 mmol). After being stirred at rt for 4.5 h, the mixture was diluted with Et_2O and filtered through a short pad of silica gel. The filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel (hexane) to afford **9c** (154.9 mg, 67%) as orange crystals: mp 113−115 °C; IR (neat) 3267 (C≡CH), 2208 (C≡C), 1720 (C═O), 1275, 1232

Scheme 9. Preparation of 9c



(500 MHz, $CDCl_3$) δ 3.29 (s, 1H), 3.84 (s, 3H), 3.93 (s, 3H), 6.87 (dd, J = 8.5, 2.6 Hz, 1H), 7.06 (d, J = 2.6 Hz, 1H), 7.46 (d, J = 8.5 Hz, 1H), 7.61−7.63 (m, 2H), 8.02−8.03 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.3, 55.5, 79.9, 82.0, 90.7, 92.4, 115.5, 116.4, 117.3, 127.7, 127.0, 129.5 (2C), 129.8, 131.7 (2C), 134.0, 159.5, 166.5. Anal. Calcd for $C_{19}H_{14}O_3$: C, 78.61; H, 4.86. Found: C, 78.42; H, 4.66.

Methyl 3-Bromo-4-[(trimethylsilyl)ethynyl]benzoate (20). Compound **19** was prepared through diazotization and iodination of the corresponding amine according to the reported method.[24] To a stirred suspension of **19**[25] (1.02 g, 3.00 mmol), $PdCl_2(PPh_3)_2$ (52.6 mg, 0.08 mmol) and CuI (14.3 mg, 0.08 mmol) in THF (10 mL) under argon were added Et_3N (2.1 mL, 15.0 mmol) and trimethylsilylacetylene (0.5 mL, 3.60 mmol). After stirring at rt for 12 h, the reaction mixture was diluted with EtOAc and filtered through a short pad of silica gel. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel (hexane) to afford **20** (939 mg, quant) as a yellow oil. All spectral data were in good agreement with those reported.[26]

Methyl 3-[(4-Methoxyphenyl)ethynyl]-4-[(trimethylsilyl)-ethynyl]benzoate (21). The coupling of **20** and 1-ethynyl-4-methoxybenzene was carried out according to the method reported as follows:[23] to a stirred suspension of **20** (636 mg, 2.00 mmol), $PdCl_2(PhCN)_2$ (23.0 mg, 0.06 mmol) and CuI (7.6 mg, 0.04 mmol) in 1,4-dioxane (2 mL) were added diisopropylamine (0.8 mL, 6.00 mmol), 1-ethynyl-4-methoxybenzene (0.3 mL, 2.20 mmol) and tri-*tert*-butylphosphine (30 μL, 0.12 mmol). After stirring at rt overnight, the reaction mixture was diluted with EtOAc and filtered through a short pad of silica gel. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel (hexane) to afford **21** (750.7 mg, quant) as a yellow oil: IR (neat) 2252 (C≡C), 2209 (C≡C), 1723 (C═O), 1320 ($SiCH_3$), 1289, 1247 (OCH_3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.28 (s, 9H), 3.84 (s, 3H), 3.92 (s, 3H), 6.88−6.90 (m, 2H), 7.49−7.51 (m, 2H), 7.54 (d, J = 8.0 Hz, 1H), 7.88 (dd, J = 8.0, 1.7 Hz, 1H), 8.16 (d, J = 1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.0 (3C), 52.4, 55.4, 86.3, 94.5, 101.9, 103.0, 114.1 (2C), 115.2, 126.8, 128.3, 129.5, 129.7, 132.4, 132.7, 133.4 (2C), 160.1, 166.1; HRMS (FAB) calcd for $C_{22}H_{22}O_3Si$ (M^+) 362.1338, found 362.1337.

Methyl 4-Ethynyl-3-[(4-methoxyphenyl)ethynyl]benzoate (9d) (Scheme 10). To a stirred solution of **21** (262 mg, 0.70 mmol) in MeOH (7 mL) was added K_2CO_3 (300 mg, 2.20 mmol). After being stirred at rt for 2 h, the mixture was neutralized with saturated aqueous citric acid and diluted with EtOAc. The organic layer was separated, washed with water and brine, and dried over $MgSO_4$. The solvent was removed in vacuo and the residue was chromatographed on silica gel (hexane) to afford the title compound **9d** (114.8 mg, 55%) as colorless crystals: mp 133−134 °C; IR (neat) 3252 (C≡CH), 2209 (C≡C), 1729 (C═O), 1286, 1247 (OCH_3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.50 (s, 1H), 3.83 (s, 3H), 3.93 (s, 3H), 6.88−6.90 (m, 2H), 7.50−7.52 (m, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.90 (dd, J = 8.0, 1.7 Hz, 1H), 8.18 (d, J = 1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.4, 55.3, 81.7, 83.7, 85.9, 94.6, 114.1 (2C), 114.9, 127.0,

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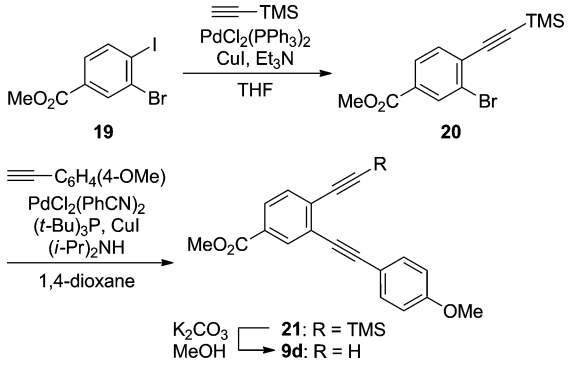
Scheme 10. Preparation of 9d

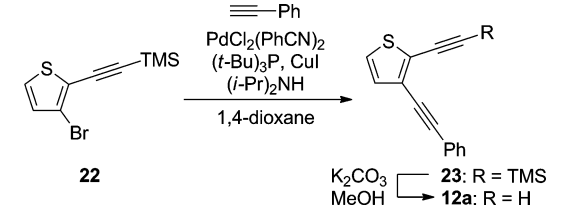


128.2, 128.4, 130.1, 132.58, 132.64, 133.4 (2C), 160.1, 165.9; HRMS (FAB) calcd for $C_{19}H_{14}O_3$ (M^+) 290.0943, found 290.0942.

Trimethyl[[3-(phenylethynyl)thiophen-2-yl]ethynyl]silane (23). The coupling of **22**[7] and ethynylbenzene was carried out according to the method reported as follows:[23] to a stirred suspension of **22** (714 mg, 2.75 mmol), $PdCl_2(PhCN)_2$ (63.4 mg, 0.17 mmol), and CuI (31.5 mg, 0.17 mmol) in 1,4-dioxane (5.5 mL) were added diisopropylamine (1.9 mL, 13.7 mmol), ethynylbenzene (0.4 mL, 3.3 mmol), and tri-*tert*-butylphosphine (80 μL, 0.33 mmol). After being stirred at rt for 6 h, the reaction mixture was diluted with EtOAc and filtered through a short pad of silica gel. The filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel (hexane) to afford **23** (705 mg, 91%) as a pale yellow oil; IR (neat) 2144 (C≡C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.28 (s, 9H), 7.05 (d, *J* = 5.4 Hz, 1H), 7.16 (d, *J* = 5.4 Hz, 1H), 7.33−7.36 (m, 3H), 7.52−7.54 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.0 (3C), 83.9, 93.7, 96.6, 103.7, 123.3, 126.1, 126.2, 127.7, 128.4, 128.5 (2C), 129.3, 131.7 (2C); HRMS (FAB) calcd for $C_{17}H_{17}SSi$ (MH^+) 281.0815, found 281.0804.

2-Ethynyl-3-(phenylethynyl)thiophene (12a) (Scheme 11). To a stirred solution of **23** (671.9 mg, 2.40 mmol) in MeOH (24 mL)

Scheme 11. Preparation of 12a



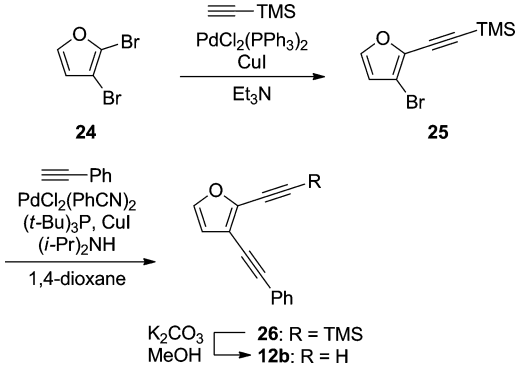
was added K_2CO_3 (993 mg, 7.20 mmol). After being stirred at rt for 5 h, the mixture was diluted with Et_2O and filtered through a short pad of silica gel. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel (hexane) to afford **12a** (457 mg, 92%) as an amber oil: IR (neat) 3299 (C≡CH), 2248 (C≡C), 2102 (C≡C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.62 (s, 1H), 7.07 (d, *J* = 5.2 Hz, 1H), 7.20 (d, *J* = 5.2 Hz, 1H), 7.33−7.36 (m, 3H), 7.54−7.55 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 76.0, 83.3, 85.3, 93.5, 122.9, 124.7, 126.4, 127.9, 128.3 (2C), 128.5, 129.5, 131.7 (2C); HRMS (FAB) calcd for $C_{14}H_9S$ (MH^+) 209.0419, found 209.0416.

[(3-Bromofuran-2-yl)ethynyl]trimethylsilane (25). The coupling **24** and trimethylsilylacetylene was carried out according to the reported method as follows:[7] to a stirred suspension of **24** (1.00 g, 4.40 mmol), $PdCl_2(PPh_3)_2$ (101 mg, 0.14 mmol) and CuI (52.7 mg, 0.28 mmol) in Et_3N (5.9 mL) under argon was added trimethylsilylacetylene (0.73 mL, 5.30 mmol). After being stirred at 80 °C overnight, the reaction mixture was diluted with EtOAc and filtered through a short pad of silica gel. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel (hexane) to afford **25** (627 mg, 58%) as an amber oil: IR (neat) 2158 (C≡C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.27 (s, 9H), 6.45 (d, *J* = 1.8 Hz, 1H), 7.28 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.0 (3C), 92.2, 104.5, 106.6, 114.8, 136.8, 143.9; HRMS (FAB) calcd for $C_9H_{12}BrOSi$ (MH^+) 242.9835, found 242.9826.

Trimethyl[[3-(phenylethynyl)furan-2-yl]ethynyl]silane (26). The coupling **25** and ethynylbenzene was carried out according to the method reported as follows:[23] to a stirred suspension of **25** (355 mg, 1.46 mmol), $PdCl_2(PhCN)_2$ (33.6 mg, 0.09 mmol) and CuI (16.7 mg, 0.09 mmol) in 1,4-dioxane (3 mL) under argon were added diisopropylamine (1.0 mL, 7.30 mmol), ethynylbenzene (0.17 mL, 1.60 mmol), and tri-*tert*-butylphosphine (40 μL, 0.18 mmol). After being stirred at rt for 6 h, the reaction mixture was diluted with EtOAc and filtered through a short pad of silica gel. The filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel (hexane) to afford **26** (313 mg, 81%) as a dark amber oil: IR (neat) 2252 (C≡C), 2157 (C≡C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.29 (s, 9H), 6.48 (d, *J* = 1.7 Hz, 1H), 7.30 (d, *J* = 1.7 Hz, 1H), 7.33−7.35 (m, 3H), 7.50−7.51 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.0 (3C), 80.8, 93.4, 95.1, 104.6, 113.47, 113.51, 113.7, 123.6, 128.6 (2C), 131.9 (2C), 143.26, 143.29; HRMS (FAB) calcd for $C_{17}H_{17}OSi$ (MH^+) 265.1043, found 265.1039.

2-Ethynyl-3-(phenylethynyl)furan (12b) (Scheme 12). To the solution of **26** (268 mg, 1.00 mmol) in MeOH (10 mL) was added

Scheme 12. Preparation of 12b



K_2CO_3 (451 mg, 3.0 mmol). After being stirred at rt for 1.5 h, the mixture was diluted with Et_2O and filtered through a short pad of silica gel. The filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel (hexane) to afford **12b** (159 mg, 81%) as a dark amber oil: IR (neat) 3302 (C≡CH), 2253 (C≡C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.66 (s, 1H), 6.51 (d, *J* = 1.7 Hz, 1H), 7.34−7.35 (m, 4H), 7.52−7.53 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 72.8, 79.8, 85.7, 94.7, 113.3, 113.7, 122.9, 128.3 (2C), 128.6, 131.6 (2C), 139.0, 143.4; HRMS (FAB) calcd for $C_{14}H_9O$ (MH^+) 193.0648, found 193.0646.

1-(Deuterioethynyl)-2-(phenylethynyl)benzene (9a-*d*). 1-Ethynyl-2-(phenylethynyl)benzene (**9a-*d***) was prepared according to the reported method as follows:[16] *n*-butyllithium (1.5 M in hexane, 260 μL, 0.39 mmol) was added to a mixture of 1-ethynyl-2-(phenylethynyl)benzene (**9a**) (66.1 mg, 0.33 mmol) in anhydrous diethyl ether (16 mL) under argon atmosphere at −78 °C. After being stirred for 30 min, the reaction mixture was quenched with D_2O. The aqueous layer was extracted three times with dichloromethane. The organic layer was dried over $MgSO_4$ and filtrated. Evaporation of the solvent gave **9a-*d*** (73.0 mg, quant) as a colorless oil: IR (neat) 2585 (C≡CD), 2249 (C≡C), 2218 (C≡C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.36 (s, 0.07H), 7.27−7.38 (m, 5H), 7.54−7.57 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 81.1, 87.8, 92.1, 93.5, 123.2, 124.6, 126.3, 127.9, 128.3 (2C), 128.45, 128.48, 128.5, 131.8 (2C), 132.6; HRMS (FAB) calcd for $C_{16}H_{10}D$ (MH^+) 204.0918, found 204.0917.

Gold(I)-Catalyzed Naphthalene Formation by Intermolecular/Intramolecular Addition Cascade. *General Procedure: Synthesis of 1-Ethoxy-3-phenylnaphthalene (**8a**) (Table 1, Entry 11).* To a stirred suspension of 1-ethynyl-2-(phenylethynyl)benzene (**9a**)

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(33.8 mg, 0.17 mmol), IPrAuCl (2.1 mg, 3.4 μmol), and AgOTf (0.9 mg, 3.4 μmol) in 1,2-dichloroethane (DCE) (0.9 mL) under argon was added ethanol (**10a**) (0.01 mL, 0.19 mmol), and the resulting mixture was stirred at 50 °C for 2 h. The reaction mixture was concentrated in vacuo. The residue was chromatographed on silica gel (hexane) to afford **8a** (25.5 mg, 61%) as pale yellow crystals: mp 78−81 °C; IR (neat) 1233 (OCH_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.58 (t, *J* = 6.9 Hz, 3H), 4.29 (q, *J* = 6.9 Hz, 2H), 7.05 (s, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.46−7.49 (m, 4H), 7.61 (s, 1H), 7.70 (d, *J* = 7.4 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.9, 63.8, 104.6, 118.2, 122.0, 124.9, 125.1, 126.8, 127.3, 127.4 (2C), 127.7, 128.8 (2C), 134.6, 138.9, 141.7, 155.1; HRMS (FAB) calcd for $C_{18}H_{17}O$ (MH^+) 249.1274, found 249.1278.

*N-Methyl-N,3-diphenylnaphthalen-1-amine (**8b**) (Table 1, Entry 12).* The diyne **9a** (22.6 mg, 0.11 mmol) was converted to **8b** (31.6 mg, 93%) by reaction with *N*-methylaniline (**10b**) (0.01 mL, 0.12 mmol) in the presence of IPrAuCl (1.4 mg, 2.2 μmol) and AgOTf (0.6 mg, 2.2 μmol) in DCE (0.6 mL) at 50 °C for 7 h: yellow oil; IR (neat) 1397 (NAr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.43 (s, 3H), 6.67 (d, *J* = 8.0 Hz, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 7.14−7.18 (m, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.39−7.51 (m, 4H), 7.67−7.69 (m, 3H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.99 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.3, 113.6 (2C), 117.3, 123.8, 124.3, 124.9, 126.4, 126.7, 127.3 (2C), 127.5, 128.8, 128.9 (2C), 129.0 (2C), 130.4, 135.4, 139.3, 140.5, 145.9, 150.1; HRMS (FAB) calcd for $C_{23}H_{20}N$ (MH^+) 310.1590, found 310.1583.

*1-Butoxy-3-phenylnaphthalene (**8c**) (Table 2).* The diyne **9a** (34.7 mg, 0.17 mmol) was converted to **8c** (30.8 mg, 65%) by reaction with 1-butanol (**10c**) (0.08 mL, 0.85 mmol) in the presence of IPrAuCl (2.1 mg, 3.4 μmol) and AgOTf (0.9 mg, 3.4 μmol) in DCE (0.9 mL) at 50 °C for 6 h: pale yellow needles; mp 49 °C; IR (neat) 1234 (OCH_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (t, *J* = 7.4 Hz, 3H), 1.62 (qt, *J* = 7.4, 7.4 Hz, 2H), 1.91−1.97 (m, 2H), 4.22 (t, *J* = 6.3 Hz, 2H), 7.05 (d, *J* = 1.1 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.44−7.51 (m, 4H), 7.60 (s, 1H), 7.69−7.71 (m, 2H), 7.83 (d, *J* = 7.4 Hz, 1H), 8.28 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 19.5, 31.4, 67.9, 104.6, 118.1, 122.0, 125.0, 125.1, 126.8, 127.3, 127.4 (2C), 127.7, 128.8 (2C), 134.6, 139.0, 141.7, 155.3; HRMS (FAB) calcd for $C_{20}H_{20}O$ (M^+) 276.1514, found 276.1514.

*1-Isobutoxy-3-phenylnaphthalene (**8d**).* The diyne **9a** (33.7 mg, 0.17 mmol) was converted to **8d** (29.3 mg, 64%) by reaction with isobutanol (**10d**) (0.08 mL, 0.83 mmol) in the presence of IPrAuCl (2.1 mg, 3.3 μmol) and AgOTf (0.9 mg, 3.3 μmol) in DCE (0.9 mL) at 50 °C for 24.5 h: yellow oil; IR (neat) 1230 (OCH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07 (t, *J* = 7.4 Hz, 3H), 1.44 (d, *J* = 6.3 Hz, 3H), 1.75−1.83 (m, 1H), 1.90−1.94 (m, 1H), 4.61−4.64 (m, 1H), 7.07 (d, *J* = 1.1 Hz, 1H), 7.35−7.39 (m, 1H), 7.44−7.49 (m, 4H), 7.59 (s, 1H), 7.68−7.70 (m, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.9, 19.3, 29.4, 75.3, 106.1, 118.0, 122.3, 125.0, 125.8, 126.7, 127.3, 127.5 (2C), 127.8, 128.8 (2C), 134.9, 139.0, 141.8, 154.3; HRMS (FAB) calcd for $C_{20}H_{21}O$ (MH^+) 277.1587, found 277.1577.

*Methyl 4-[Methyl(3-phenylnaphthalen-1-yl)amino]benzoate (**8e**).* The diyne **9a** (35.2 mg, 0.17 mmol) was converted to **8e** (71.1 mg, quant) by reaction with methyl 4-(methylamino)benzoate (**10e**)[20] (30.9 mg, 0.19 mmol) in the presence of IPrAuCl (2.2 mg, 3.5 μmol) and AgOTf (0.9 mg, 3.5 μmol) in DCE (0.9 mL) at 50 °C for 6 h: yellow oil; IR (neat) 1702 (C═O), 1397 (NAr), 1278 (OCH_3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.49 (s, 3H), 3.83 (s, 3H), 6.60 (d, *J* = 8.6 Hz, 2H), 7.41−7.51 (m, 5H), 7.70−7.72 (m, 4H), 7.84 (d, *J* = 9.2 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 1H), 8.06 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.2, 51.5, 112.0 (2C), 118.3, 123.2, 125.2, 125.4, 126.8, 126.9, 127.2 (2C), 127.7, 128.93, 128.94 (2C), 129.8, 131.2 (2C), 135.4, 139.3, 140.1, 144.2, 153.2, 167.3; HRMS (FAB) calcd for $C_{25}H_{22}NO_2$ (MH^+) 368.1645, found 368.1644.

*N-(4-Methoxyphenyl)-N-methyl-3-phenylnaphthalen-1-amine (**8f**).* The diyne **9a** (34.5 mg, 0.17 mmol) was converted to **8f** (53.0 mg, 92%) by reaction with 4-methoxy-*N*-methylaniline (**10f**) (25.7 mg, 0.19 mmol) in the presence of IPrAuCl (2.1 mg, 3.4 μmol) and AgOTf (0.9 mg, 3.4 μmol) in DCE (0.9 mL) at 50 °C for 24 h: yellow oil; IR (neat) 1285 (NAr), 1242 (OCH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (s, 3H), 3.74 (s, 3H), 6.67−6.70 (m, 2H), 6.75−6.78 (m, 2H), 7.33−7.51 (m, 5H), 7.60 (d, *J* = 1.7 Hz, 1H), 7.67−7.69 (m, 2H), 7.92−7.93 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 41.1, 55.7, 114.5 (2C), 116.1 (2C), 123.5, 123.6, 124.0, 126.1, 126.5, 127.3 (2C), 127.5, 128.7, 128.8 (2C), 130.1, 135.3, 139.2, 140.7, 144.9, 146.9, 152.4; HRMS (FAB) calcd for $C_{24}H_{21}NO$ (M^+) 339.1623, found 339.1622.

*N-Benzyl-N,3-diphenylnaphthalen-1-amine (**8g**).* The diyne **9a** (33.6 mg, 0.17 mmol) was converted to **8g** (50.1 mg, 78%) by reaction with *N*-benzylaniline (**10g**)[21] (0.03 mL, 0.18 mmol) in the presence of IPrAuCl (2.0 mg, 3.3 μmol) and AgOTf (0.9 mg, 3.3 μmol) in DCE (0.9 mL) at 50 °C for 4 h: yellow crystals; mp 128−131 °C; IR (neat) 1336 (NAr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.07 (s, 2H), 6.64−6.66 (m, 2H), 6.70−6.74 (m, 1H), 7.08−7.13 (m, 2H), 7.22−7.24 (m, 1H), 7.30−7.53 (m, 9H), 7.62−7.64 (m, 2H), 7.73 (d, *J* = 2.0 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.99 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 57.1, 114.1 (2C), 117.6, 123.9, 124.7, 126.2, 126.4, 126.6, 126.9, 127.0 (2C), 127.3 (2C), 127.5, 128.6 (2C), 128.87 (2C), 128.94, 128.95 (2C), 130.2, 135.6, 139.15, 139.16, 140.5, 144.5, 149.5. Anal. Calcd for $C_{29}H_{23}N$: C, 90.35; H, 6.01; N, 3.63. Found: C, 90.56; H, 6.06; N, 3.61.

*Methyl 2-Benzyl-2-(3-phenylnaphthalen-1-yl)hydrazinecarboxylate (**8h**).* The diyne **9a** (33.4 mg, 0.17 mmol) was converted to **8h** (48.8 mg, 77%) by reaction with methyl 2-benzylhydrazinecarboxylate (**10h**) (32.7 mg, 0.18 mmol) in the presence of IPrAuCl (2.0 mg, 3.3 μmol) and AgOTf (0.9 mg, 3.3 μmol) in DCE (0.8 mL) at 50 °C for 2 h: pale yellow crystals; mp 137 °C; IR (neat) 1712 (C═O), 1246 (OCH_3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.62 (s, 3H), 4.71 (br s, 2H), 6.49 (br s, 1H), 7.31 (dd, *J* = 6.7, 1.7 Hz, 1H), 7.34−7.39 (m, 5H), 7.47 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.52−7.54 (m, 3H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.83 (s, 1H), 7.89−7.90 (m, 1H), 8.41−8.43 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.3 (br), 60.0 (br), 117.1 (br), 123.2, 123.5, 126.0, 126.5, 127.36 (2C), 127.38, 127.7, 127.8 (2C), 128.46 (2C), 128.53, 128.8 (2C), 129.1 (2C), 134.9, 136.2 (br), 138.1, 141.0, 146.3 (br), 155.8 (br); HRMS (FAB) calcd for $C_{25}H_{23}N_2O_2$ (MH^+) 383.1754, found 383.1760.

*3-(3-Phenylnaphthalen-1-yl)-1H-indole (**8i**).* The diyne **9a** (32.8 mg, 0.16 mmol) was converted to **8i** (52.9 mg, quant) by reaction with indole (**10i**) (20.6 mg, 0.18 mmol) in the presence of IPrAuCl (2.0 mg, 3.2 μmol) and AgOTf (0.8 mg, 3.2 μmol) in DCE (0.8 mL) at 50 °C for 2 h. For column chromatography, NH_2 silica gel (hexane/EtOAc = 50/1) was employed: dark yellow oil; IR (neat) 3468 (NH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13−7.15 (m, 1H), 7.26−7.30 (m, 1H), 7.37−7.40 (m, 3H), 7.49−7.53 (m, 5H), 7.76−7.78 (m, 2H), 7.89 (d, *J* = 1.7 Hz, 1H), 7.97 (d, *J* = 8.6 Hz, 1H), 8.07−8.08 (m, 2H), 8.33 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 111.3, 116.6, 120.1, 120.3, 122.5, 123.6, 125.0, 125.8, 126.2, 126.4, 127.32, 127.35, 127.5 (2C), 127.7, 128.6, 128.8 (2C), 131.8, 133.5, 134.3, 136.1, 138.2, 141.1; HRMS (FAB) calcd for $C_{24}H_{18}N$ (MH^+) 320.1434, found 320.1431.

*2-(3-Phenylnaphthalen-1-yl)-1H-pyrrole (**8j**).* The diyne **9a** (33.1 mg, 0.16 mmol) was converted to **8j** (21.4 mg, 50%) by reaction with pyrrole (**10j**) (0.01 mL, 0.18 mmol) in the presence of IPrAuCl (2.1 mg, 3.3 μmol) and AgOTf (0.9 mg, 3.3 μmol) in DCE (0.8 mL) at 50 °C for 26 h. For column chromatography, NH_2 silica gel (hexane) was employed: dark brown oil; IR (neat) 3349 (NH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44 (dd, *J* = 5.7, 2.8 Hz, 1H), 6.56−6.57 (m, 1H), 6.99−7.00 (m, 1H), 7.38−7.40 (m, 1H), 7.47−7.54 (m, 4H), 7.73−7.74 (m, 2H), 7.78 (d, *J* = 1.7 Hz, 1H), 7.93−7.94 (m, 1H), 8.00 (s, 1H), 8.29 (d, *J* = 8.6 Hz, 1H), 8.46 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 109.55, 109.64, 118.5, 125.3, 125.6, 125.8, 126.38, 126.38, 127.4 (2C), 127.5, 128.7, 128.9 (2C), 130.5, 130.6, 132.1, 134.4, 138.2, 140.8; HRMS (FAB) calcd for $C_{20}H_{16}N$ (MH^+) 270.1277, found 270.1276.

*3-(3-Phenylnaphthalen-1-yl)-1-(triisopropylsilyl)-1H-pyrrole (**8k**).* The diyne **9a** (30.4 mg, 0.15 mmol) was converted to **8k** (24.4 mg,

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38%) by reaction with 1-(triisopropylsilyl)-1*H*-pyrrole (**10k**) (0.04 mL, 0.16 mmol) in the presence of IPrAuCl (1.9 mg, 3.0 μmol) and AgOTf (0.8 mg, 3.0 μmol) in DCE (0.8 mL) at 50 °C for 6 h: amber oil; IR (neat) 2867, 2946 (CH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17 (d, *J* = 7.4 Hz, 18H), 1.51−1.53 (m, 3H), 6.64 (dd, *J* = 2.9, 1.4 Hz, 1H), 6.91−6.93 (m, 1H), 7.02−7.03 (m, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.45−7.48 (m, 4H), 7.76−7.77 (m, 3H), 7.91−7.94 (m, 2H), 8.34 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.8 (3C), 17.9 (6C), 112.5, 123.5, 124.2, 124.3, 125.2, 125.6, 125.9, 126.1, 126.3, 127.2, 127.5 (2C), 128.5, 128.8 (2C), 131.3, 134.3, 135.6, 138.2, 141.4; HRMS (FAB) calcd for $C_{29}H_{36}NSi$ (MH^+) 426.2612, found 426.2603.

*N-Methyl-N-phenyl-3-propylnaphthalen-1-amine (**8l**).* 1-Ethynyl-2-(pent-1-ynyl)benzene (**9b**) (26.0 mg, 0.15 mmol) was converted to **8l** (29.1 mg, 68%) by reaction with *N*-methylaniline (**10b**) (0.02 mL, 0.17 mmol) in the presence of IPrAuCl (1.9 mg, 3.1 μmol) and AgOTf (0.8 mg, 3.1 μmol) in DCE (0.8 mL) at 50 °C for 10 h: yellow oil; IR (neat) 1396 (NAr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.2 Hz, 3H), 1.70−1.73 (m, 2H), 2.72 (t, *J* = 7.4 Hz, 2H), 3.38 (s, 3H), 6.61 (d, *J* = 8.6 Hz, 2H), 6.71 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.13−7.17 (m, 2H), 7.23−7.24 (m, 1H), 7.33−7.38 (m, 1H), 7.45 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.56 (s, 1H), 7.82 (dd, *J* = 9.5, 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 24.4, 38.0, 40.2, 113.4, 117.0, 123.6, 125.2, 125.4, 126.2, 126.8, 127.1, 127.9, 128.9, 129.6, 131.8, 135.2, 141.1, 145.1, 150.1; HRMS (FAB) calcd for $C_{20}H_{22}N$ (MH^+) 276.1747, found 276.1745.

*Methyl 4-[7-Methoxy-4-[methyl(phenyl)amino]naphthalen-2-yl]-benzoate (**8m**).* Methyl 4-[(2-ethynyl-5-methoxyphenyl)ethynyl]-benzoate (**9c**) (49.4 mg, 0.17 mmol) was converted to **8m** (57.8 mg, 86%) by reaction with *N*-methylaniline (**10b**) (0.02 mL, 0.19 mmol) in the presence of IPrAuCl (2.1 mg, 3.4 μmol) and AgOTf (0.9 mg, 3.4 μmol) in DCE (0.9 mL) at 50 °C for 7 h: orange crystals; mp 150−151 °C; IR (neat) 1713 (C═O), 1391 (NAr), 1276, 1231 (OCH_3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.43 (s, 3H), 3.94 (s, 6H), 6.66 (d, *J* = 8.0 Hz, 2H), 6.74 (t, *J* = 7.4 Hz, 1H), 7.10 (dd, *J* = 9.2, 2.9 Hz, 1H), 7.15−7.19 (m, 2H), 7.26 (d, *J* = 2.9 Hz, 1H), 7.51 (d, *J* = 1.7 Hz, 1H), 7.75−7.78 (m, 3H), 7.93 (d, *J* = 1.1 Hz, 1H), 8.12 (dd, *J* = 6.8, 1.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.3, 52.1, 55.4, 106.8, 113.7 (2C), 117.4, 119.6, 122.1, 123.7, 125.5, 126.2, 127.1 (2C), 128.97 (2C), 129.04, 130.1 (2C), 136.6, 138.7, 145.1, 146.2, 149.9, 158.4, 166.9. Anal. Calcd for $C_{26}H_{23}NO_3$: C, 78.57; H, 5.83; N, 3.52. Found: C, 78.30; H, 5.85; N, 3.42.

*Methyl 7-(4-Methoxyphenyl)-5-[methyl(phenyl)amino]-2-naphthoate (**8n**).* Methyl 4-ethynyl-3-[(4-methoxyphenyl)ethynyl]benzoate (**9d**) (49.8 mg, 0.17 mmol) was converted to **8n** (60.8 mg, 90%) by reaction with *N*-methylaniline (**10b**) (0.02 mL, 0.19 mmol) in the presence of IPrAuCl (2.1 mg, 3.4 μmol) and AgOTf (0.9 mg, 3.4 μmol) in DCE (0.9 mL) at 50 °C for 10 h: colorless crystals; mp 133 °C; IR (neat) 1710 (C═O), 1368 (NAr), 1259, 1240 (OCH_3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.44 (s, 3H), 3.87 (s, 3H), 3.98 (s, 3H), 6.67 (d, *J* = 8.6 Hz, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 7.00−7.03 (m, 2H), 7.16−7.19 (m, 2H), 7.62−7.63 (m, 2H), 7.73 (d, *J* = 1.7 Hz, 1H), 7.90 (d, *J* = 9.2 Hz, 1H), 7.96 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.03 (s, 1H), 8.69 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.3, 52.2, 55.4, 113.8 (2C), 114.4 (2C), 117.7, 124.1, 124.6, 125.3, 126.9, 128.2, 128.3 (2C), 129.0 (2C), 131.7, 132.1, 132.4, 134.6, 139.8, 145.9, 149.8, 159.6, 167.1. Anal. Calcd for $C_{26}H_{23}NO_3$: C, 78.57; H, 5.83; N, 3.52. Found: C, 78.33; H, 5.74; N, 3.48.

*tert-Butyldimethyl[(3-phenylnaphthalen-1-yl)oxy]silane (**8o**) (Scheme 3).* *tert*-Butyldimethyl[[1-(2-(phenylethynyl)phenyl)vinyl]oxy]-silane (**11**)[27] (51.2 mg, 0.15 mmol) was converted to **8o** (27.8 mg, 54%) and **8p** containing some impurities (8.4 mg, ca. 25%) by reaction in the presence of IPrAuCl (1.9 mg, 3.1 μmol) and AgOTf (0.8 mg, 3.1 μmol) in DCE (0.8 mL) at 50 °C for 24 h. The spectral data for **8p** was matched those presented in the literature.[28] Compound **8o**: orange oil; IR (neat) 1296 (Si-CH_3), 1100 (Si−O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.33 (s, 6H), 1.12 (s, 9H), 7.13 (d, *J* = 1.4 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.43−7.51 (m, 5H), 7.66−7.68 (m, 3H), 7.84 (t, *J* = 4.6 Hz, 1H), 8.18 (d, *J* = 4.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −4.14, 18.5, 25.9, 112.4, 119.0, 122.5, 125.2, 126.6, 127.1, 127.3 (3C), 128.0, 128.8 (2C), 135.1, 138.9, 141.3, 152.1; HRMS (FAB) calcd for $C_{22}H_{26}OSi$ (M) 334.1753, found 334.1753.

*N-Methyl-N,5-diphenylbenzo[b]thiophen-7-amine (**13a**) (Scheme 7).* 2-Ethynyl-3-(phenylethynyl)thiophene (**12a**) (34.1 mg, 0.16 mmol) was converted to **13a** (38.7 mg, 75%) by reaction with *N*-methylaniline (**10b**) (0.02 mL, 0.18 mmol) in the presence of IPrAuCl (5.1 mg, 8.2 μmol) and AgOTf (2.1 mg, 8.2 μmol) in DCE (0.8 mL) at 80 °C for 4 h: amber oil; IR (neat) 1366 (NAr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.44 (s, 3H), 6.84−6.86 (m, 3H), 7.20−7.23 (m, 3H), 7.34 (t, *J* = 6.8 Hz, 1H), 7.39−7.40 (m, 2H), 7.43−7.45 (m, 3H), 7.63−7.64 (m, 2H), 7.88 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 39.7, 116.4 (2C), 118.9, 119.2, 120.6, 124.5, 124.9, 127.2, 127.4 (2C), 128.8 (2C), 129.0 (2C), 135.9, 139.4, 141.1, 142.0, 143.7, 148.4; HRMS (FAB) calcd for $C_{21}H_{18}NS$ (MH^+) 316.1154, found 316.1152.

*N-Methyl-N,5-diphenylbenzofuran-7-amine (**13b**) (Scheme 7).* 2-Ethynyl-3-(phenylethynyl)furan (**9c**) (31.6 mg, 0.16 mmol) was converted to **13b** (17.2 mg, 35%) by reaction with *N*-methylaniline (**10b**) (0.02 mL, 0.18 mmol) in the presence of IPrAuCl (10.2 mg, 20 μmol) and AgOTf (4.2 mg, 20 μmol) in DCE (0.8 mL) at 80 °C for 27 h: amber oil; IR (neat) 1369 (NAr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.49 (s, 3H), 6.81 (d, *J* = 1.7 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 7.22−7.24 (m, 3H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 1.7 Hz, 1H), 7.42 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.57−7.58 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 39.7, 107.1, 115.7, 116.0 (2C), 119.2, 120.2, 127.0, 127.4 (2C), 128.7 (2C), 128.9 (2C), 129.8, 133.3, 137.5, 141.4, 145.4, 148.6, 148.9; HRMS (FAB) calcd for $C_{21}H_{18}NO$ (MH^+) 300.1383, found 300.1384.

*12-Ethoxy-5-phenylchrysene (**15a**) (Scheme 8).* 1-Ethynyl-2-[[2-(phenylethynyl)phenyl]ethynyl]benzene (**14**) (27.1 mg, 0.09 mmol) was converted to **15a** (23.2 mg, 74%) by reaction with ethanol (**10a**) in the presence of IPrAuCl (2.8 mg, 4.5 μmol) and $AgNTf_2$ (1.8 mg, 4.5 μmol) in ethanol (0.9 mL) under reflux for 1 h: pale yellow crystals: mp 147−148 °C; IR (neat) 1230 (OCH_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.68 (t, *J* = 6.9 Hz, 3H), 4.49 (q, *J* = 6.9 Hz, 2H), 7.11−7.14 (m, 1H), 7.40−7.47 (m, 6H), 7.65−7.67 (m, 2H), 7.59−7.62 (m, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.92 (d, *J* = 6.3 Hz, 1H), 8.00 (s, 1H), 8.44 (dd, *J* = 8.0, 1.1 Hz, 1H), 8.66 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.9, 63.8, 98.6, 121.9, 122.5, 123.0, 125.0, 125.4, 126.1, 126.6, 126.8, 127.0, 128.42, 128.44, 128.7, 128.8 (2C), 129.0 (2C), 129.5, 130.9, 131.6, 131.7, 138.3, 145.7, 153.8; HRMS (FAB) calcd for $C_{26}H_{21}O$ (MH^+) 349.1587, found 349.1583.

*N-Methyl-N,11-diphenylchrysen-6-amine (**15b**) (Scheme 8).* 1-Ethynyl-2-[[2-(phenylethynyl)phenyl]ethynyl]benzene (**14**) (31.9 mg, 0.11 mmol) was converted to **15b** (39.4 mg, 92%) by reaction with *N*-methylaniline (**10b**) (0.01 mL, 0.12 mmol) in the presence of IPrAuCl (6.5 mg, 12 μmol) and $AgNTf_2$ (4.1 mg, 12 μmol) in DCE (0.6 mL) under reflux for 24 h: pale yellow powder: mp 172−175 °C; IR (neat) 1346 (NAr); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.54 (s, 3H), 6.75−6.77 (m, 3H), 7.13 (t, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.43−7.52 (m, 5H), 7.61−7.66 (m, 2H), 7.84 (s, 1H), 7.89 (d, *J* = 9.2 Hz, 1H), 7.94 (d, *J* = 7.4 Hz, 1H), 7.98 (d, *J* = 8.6 Hz, 1H), 8.62 (d, *J* = 8.0 Hz, 1H), 8.69 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.3, 113.7 (2C), 117.4, 120.6, 123.1, 123.9, 124.9, 126.2, 126.5, 126.7, 126.9, 127.0, 128.4, 128.96 (2C), 129.01 (2C), 129.1 (2C), 129.4, 129.7, 130.5, 130.9, 131.2, 131.5, 132.3, 138.2, 144.6, 145.5, 150.0; HRMS (FAB) calcd for $C_{31}H_{24}N$ (MH^+) 410.1903, found 410.1901.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and compound characterization data including NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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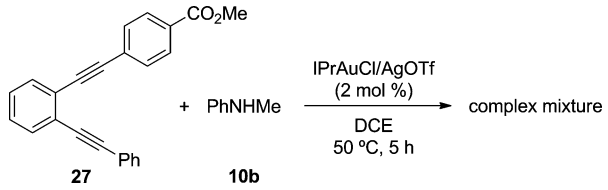

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