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Gold-Catalyzed Furan/Yne Cyclizations for the Regiodefined Assembly of Multisubstituted Protected 1-Naphthols

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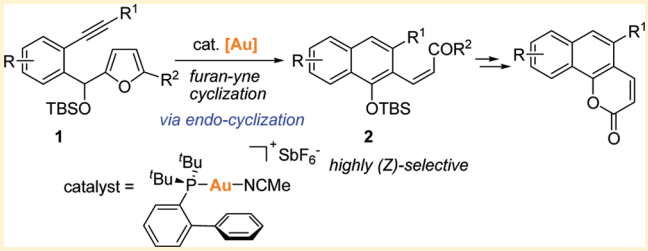
Supporting Information

ABSTRACT: The gold(I)-catalyzed intramolecular cycloisomerization of furan/ynes bearing a silyloxy or allyloxy group has been developed, which provides a highly efficient access to protected 1-naphthol derivatives with enal or enone moiety. The method offers several advantages such as high stereoselectivities, mild reaction conditions, and easily accessible starting materials. In addition, the naphthyl products could be further transformed into the important benzocoumarins in a one-pot procedure.



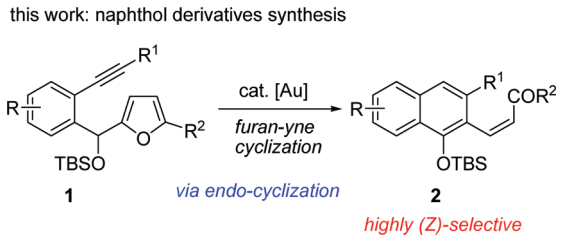
INTRODUCTION

Naphthol and its protected derivatives represent an important structural motif as they occur widely in numerous natural products with biological activities and in pharmaceuticals.[1] For example, they can be found in furomollugin,[1a] mollugin,[1a,b] naphthohydroquinones,[1c] dioncophylline E,[1d] *anti*-cancer agents of (+)-gossypol,[1e] and bactericidal antibiotic drugs of rifampicin, which are used to treat mycobacterium infections, including tuberculosis and Hansen's disease.[1f] Therefore, the development of new and efficient methodologies for the synthesis of naphthol derivatives are highly attractive. However, only limited reports for the preparation of these compounds have been known, such as metal[2a,b] or Lewis acid[2c] catalyzed ring-opening of oxabicyclic alkenes,[2] multicomponent reactions,[3] annulations of phthalides with acrylates,[4] reactions of allenoates with organozinc reagents,[5] copper-catalyzed cascade reactions of 3-(2-halophenyl)-3-oxopropanoates,[6] Pd-catalyzed annulation of alkynes with *ortho*-ester-containing phenylboronic acids,[7] and Pd-catalyzed hydroxylation of aryl halides.[8] These methods usually require high temperature and/or a prolonged reaction time. Thus, the development of synthetic routes that allows the facile assembly of multisubstituted naphthols in a regioselective manner under mild reaction conditions still remains an important objective.

RESULTS AND DISCUSSION

Recently, we have developed a series furan/yne cyclizations via gold-catalyzed[9,10] *endo*-type cyclizations of internal alkynes leading to aromatic compounds bearing enal or enone functionalities with excellent stereoselectivity.[11] In these reactions, the furan rings were introduced into the substrates through metal or Lewis acid catalyzed Friedel–Crafts reactions. On the basis of these results, we hypothesized that 2-furylcarbinol derivatives bearing an (*o*-alkynyl)phenyl moiety would be effective for the general synthesis of functionalized naphthols via gold-catalyzed reaction (Scheme 1). In this design, the furan moiety could be easily introduced through nucleophilic addition of 2-furanyllithium to an aldehyde.[12] Herein, we report our success in gold-catalyzed cycloisomerization of furan/ynes **1** to highly functionalized 1-naphthols **2** protected with a TBS group with high (*Z*)-stereoselectivity. It is noted that although the cyclization of furan/ynes has been proven to be a versatile method for phenol synthesis via *exo*-cyclization of terminal alkynes as reported by Hashmi et al.[13] (Scheme 2), there is still a lack of a general synthetic method for naphthol derivatives in this system. It is also noted that there is no report for the ring-opening cyclization of furan/ynes with an *o*-arylalkynyl-related skeleton to generate benzo-fused carbocycles.[14] We also report the further transfomations of naphthalenes **2** to benzocoumarins in a one-pot procedure.

Scheme 1



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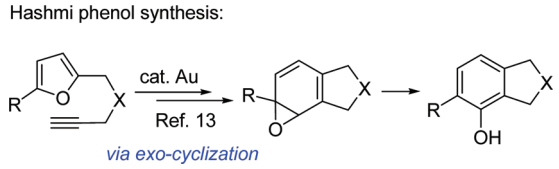
Scheme 2

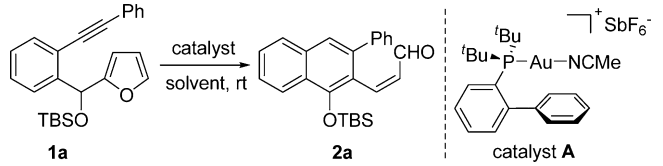


The requisite substrates of TBS-protected (*o*-alkynyl)phenyl 2-furylcarbinols **1** could be easily prepared in good to high yields through addition of the corresponding furanyllithium reagents to (*o*-alkynyl)benzaldehydes[12] followed by ether formation with TBSCl. Compound **1a** was selected as a model substrate to probe the feasibility of the intramolecular furan/yne cyclization reaction. It was found that the frequently used cationic gold(I) complexes such as PPh_3AuNTf_2, PPh_3AuBF_4, PPh_3AuSbF_6, or PPh_3AuOTf only led to a complicated reaction mixture (Table 1, entries 1−4). To our delight, when 2 mol % of Echavarren's catalyst (**A**)[15] with a bulky biarylphosphine ligand (Johnphos) was used as the catalyst, the desired 1-naphthyl TBS ether **2a** with an enal moiety could be isolated in a high yield of 89% in toluene for 2 h at room temperature (entry 5). X-ray crystallographic analysis of compound **2a** unambiguously confirmed the structure of 1,2,3-trisubstituted naphthalene **2**.[16] Apparently, the furan ring was opened during the catalytic process. It is interesting to note that **2a** was formed with high stereoselectivity (*Z*/*E* = 50:1). The reaction could also be well performed in THF to generate **2a** in 90% yield; however, the product was often contaminated with small amounts of colored impurities (entry 6). In DCM, only 32% yield of **2a** with lower stereoselectivity was obtained (entry 7). A decrease of the catalyst loading to 0.2 mol % afforded 75% of **2a** (entry 8). The above results indicated that the nature of the ligand on the gold(I) complex has an important influence on the reaction process. Control experiments with PPh_3AuCl or $AgSbF_6$ could not gave the desired naphthalene product **2a** (entries 9 and 10). When $PtCl_2$ was used as catalyst, 84% of the strating material was recovered after stirring at 80 °C for 12 h (entry 11). Nonprotected 2-furylcarbinol such as furan-2-yl(2-(phenylethynyl)phenyl)-methanol only resulted in a complicated mixture at room temperature for 0.5 h using several gold catalysts under the conditions as shown in Table 1, entries 3−5.

Next, we investigated the scope of this intramolecular cycloisomerization to naphthol derivatives. The results revealed that this methodology provides rapid access to a wide range of multisubstituted 1-naphthol derivatives with high stereoselectivities (Table 2). As shown in Table 2, the reactions are compatible with arylalkynes bearing common functional groups on the aromatic ring, including electron-withdrawing *p*-chloro (**2b**) and *o*-bromo (**2c**) groups and electron-rich *p*-methyl (**2d**), 3,5-dimethoxy (**2e**), and 1-naphthyl (**2f**) groups. The corresponding products could be obtained in good to high yields of 62−91%. Among these reactions, the sterically demanding cases of **2c** (*o*-bromo) and **2f** (1-naphthyl) afforded lower yields of 62−64%. A thienyl group was also suitable in this cyclization reaction, furnishing **2g** in 84% yield. 1-Cyclohexenyl tethered alkynes underwent the reaction readily to generate the naphthyl ether **2h** in 74% yield. The reaction with the alkyl-substituted alkyne such as cyclopropyl (**2i**) or *n*-butyl (**2j**) required a longer reaction time at room temperature. However, heating the reaction mixture to 50 °C could reduce the reaction time to 2−3 h. Introducing the synthetically valuable fluoro, bis(methoxy) or methylenedioxy groups on the parent phenyl ring did not influence the efficiency of this cyclization reaction, high yields were achieved in all cases (**2k**-**2m**). When an R^2 group on the furan ring is alkyl or phenyl group, the enone products **2n** and **2o** were formed in 78% and 97% yields, respectively, with exclusively (*Z*)-configuration of the double bond. The reaction has also been successfully extended to furan/yne **1p** without the fused aromatic ring to give the Indane derivative **2p** in 59% yield.

Interestingly, deprotection of the naphthalene **2a** by TBAF led to the quantitive formation of unstable lactol **3**, which can be readily converted to benzocoumarin **4** by PDC oxidation in a one-pot procedure (Scheme 3, eq 1). The reaction could be

Table 1. Optimization Studies for the Formation of 1-Naphthyl TBS Ether 2a



1a **2a** catalyst **A**

entry	catalyst (mol %)	solvent	time (h)	yield[a] (%) of **2a**
1	PPh_3AuNTf_2 (5)	DCM	1	
2	PPh_3AuBF_4 (5)	DCM	1.5	
3	PPh_3AuSbF_6 (5)	DCM	1	
4	PPh_3AuOTf (5)	THF	1	
5	**A** (2)	toluene	2	89 (50:1)
6	**A** (2)	THF	1	90 (39:1)[b]
7	**A** (2)	DCM	4	32 (5.3:1)
8	**A** (0.2)	toluene	15	75 (50:1)[c]
9	PPh_3AuCl (5)	toluene	2	*d*
10	$AgSbF_6$ (5)	toluene	6	*e*
11	$PtCl_2$ (10)	toluene	12	*f*

[a]0.2 mmol scale. [Substrate] = 0.1 M. All yields are isolated yields. The ratios of *Z*/*E* isomers are shown in parentheses, which were determined by ^{1}H NMR. [b]Contaminated with small amounts of colored impurities. [c]5 mmol scale. [Substrate] = 1.0 M. [d]91% of **1a** was recovered. [e]90% of **1a** was recovered. [f]The reaction was carried out at 80 °C, and 84% of **1a** was recovered.

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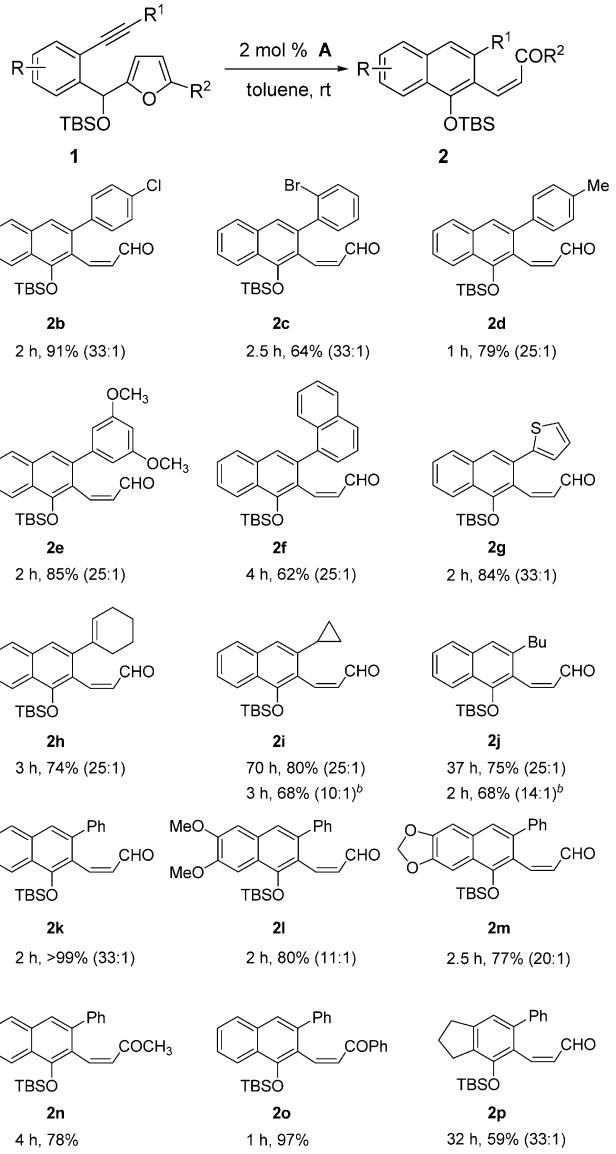
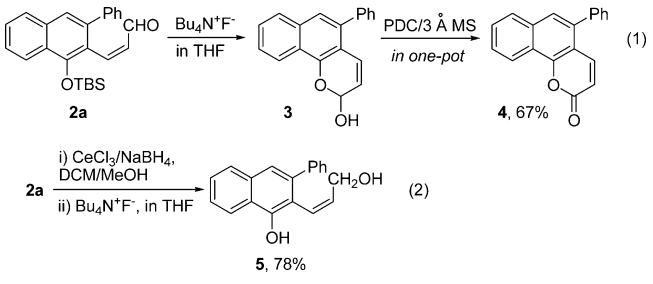
Table 2. Gold-Catalyzed Formation of Naphthol Derivatives 2[a]



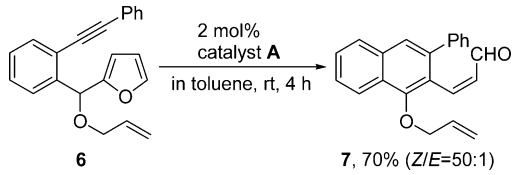
[a]Isolated yields. The ratios of *Z*/*E* isomers are shown in parentheses, which were determined by ^{1}H NMR. [b]50 °C.

Scheme 3



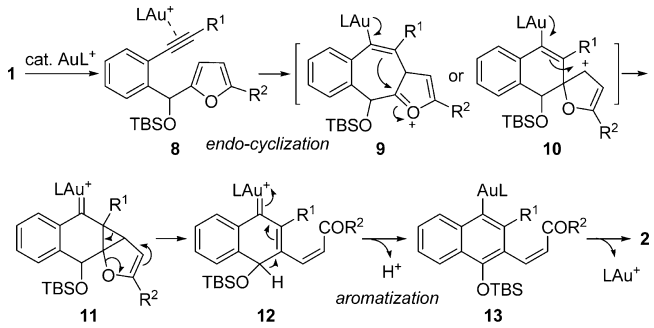
conveniently carried out by addition of 3 Å molecular sieves, PDC and TBAF successively to a THF solution of **2a** followed by stirring the mixture overnight. Compound **4** exhibits a blue fluorescence in organic solvents. Benzocoumarins are an important class of naturally occurring substances,[17] and they are also known as fluorescent-active materials.[18] Our method provides a facile route for functionalized benzocoumarins. When **2a** was reduced to an alcohol by Luche reduction followed by deprotection, naphthol **5** could be obtained in 78% overall yield (Scheme 3, eq 2). When TBS-protecting group was replaced by an allyl group, the desired cyclization also proceeded smoothly to afford enal **7** in 70% yield (*Z*/*E* = 50:1) (Scheme 4).

Scheme 4



We propose the following reaction mechanism for this cyclization reaction (Scheme 5).[11,13l] Initial coordination of the

Scheme 5



gold catalyst to the triple bond affords intermediate **8**. This is followed by intramolecular nucleophilic attack of the C-3 on the furan ring to the triple bond in a highly regioselective 7-*endo-dig* manner to give a cation **9**, which isomerizes to a cyclopropyl gold carbenoid **11**.[19] Alternatively, the cyclization may also proceed via attack of C-2 on the furan ring[20] to yield a spiro cycle **10**, from which rearrangement would give the same intermediate **11**. Ring-opening of **11** followed by deprotonation and deauration leads to naphthalene **2** with a *Z*-enone or enal moiety. The preferred *endo*-selectivity for all reactions may be attributed to the formation of stable aromatic products. It should be noted that the *endo*-type cyclization in furan/yne cycloisomerization is rare.[11,20]

In summary, we have developed an efficient gold(I)-catalyzed intramolecular cyclizations of furan/ynes bearing a silyloxy or allyloxy group in the α-position of the furan ring, which provides a rapid access to functionalized 1-naphthol derivatives with an enal or enone moiety under mild reaction conditions. The products could be further transformed to the important benzocoumarin derivatives. Further investigation of this cycloisomerization in related reaction systems and its application toward polyaromatic compounds is in progress.

EXPERIMENTAL SECTION

Typical Procedure for the Synthesis of TBS-Protected (*o*-Alkynyl)phenyl-2-furylcarbinols (1). To a solution of furan (0.48 mL, 6.5 mmol) in THF (10 mL) at 0 °C was added *n*-BuLi (2.5 mL, 2.4 M in hexanes, 6.0 mmol). After the solution was stirred at the same temperature for 2 h, a THF (5 mL) solution of 2-(phenylethynyl)-benzaldehyde (1.0 g, 5 mmol) was added at −78 °C. The resulting

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solution was warmed to room temperature and stirred for 1 h. The mixture was quenched with saturated ammonium chloride solution. The reaction mixture was extracted with ethyl acetate, washed with saturated NaCl solution, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate/CH_2Cl_2 = 5:1:1) to afford furan-2-yl(2-(phenylethynyl)phenyl)methanol.

To a solution of the above alcohol in DCM (20 mL) were added imidazole (0.68 g, 10 mmol) and TBSCl (1.1 g, 7.5 mmol). The mixture stirred at room temperature for 1 h before addition of a saturated ammonium chloride solution. The reaction mixture was extracted with ethyl acetate, washed with saturated NaCl solution, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate =20:1) to afford *tert*-butyl(furan-2-yl(2-(phenylethynyl)-phenyl)methoxy)dimethylsilane (**1a**) in 79% overall yield as a light yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.05 (s, 3H), 0.08 (s, 3H), 0.91 (s, 9H), 6.01 (d, J = 3.0 Hz, 1H), 6.24−6.26 (m, 1H), 6.36 (s, 1H), 7.27−7.50 (m, 9H), 7.78 (d, J = 7.5 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −5.1, −5.0, 18.3, 25.8, 68.4, 86.9, 94.4, 106.9, 110.1, 120.8, 123.2, 126.7, 127.3, 128.3, 128.4, 128.6, 131.4, 131.7, 141.9, 143.7, 156.5; HRMS (EI) calcd for $C_{25}H_{28}O_2Si$ 388.1859, found 388.1856.

***tert*-Butyl((2-((4-chlorophenyl)ethynyl)phenyl)(furan-2-yl)-methoxy)dimethylsilane (1b):** yield 60%; brown oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.05 (s, 3H), 0.07 (s, 3H), 0.91 (s, 9H), 5.99 (d, J = 2.4 Hz, 1H), 6.25 (s, 1H), 6.31 (s, 1H), 7.25−7.41 (m, 7H), 7.47 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −5.1, −5.0, 18.3, 25.8, 68.4, 87.9, 93.3, 106.9, 110.2, 120.5, 121.7, 126.7, 127.3, 128.7, 128.8, 131.7, 132.6, 134.3, 141.9, 143.8, 156.5; HRMS (EI) calcd for $C_{25}H_{27}{}^{35}ClO_2Si$ 422.1469, found 422.1468.

((2-((2-Bromophenyl)ethynyl)phenyl)(furan-2-yl)methoxy)-(*tert*-butyl)dimethylsilane (1c): yield 64%; yellow solid; mp 64−66 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.07 (s, 3H), 0.08 (s, 3H), 0.91 (s, 9H), 6.02 (d, J = 3.0 Hz, 1H), 6.21−6.23 (m, 1H), 6.48 (s, 1H), 7.13−7.18 (m, 1H), 7.24−7.32 (m, 3H), 7.39−7.60 (m, 4H), 7.81 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ −4.98, −4.86, 18.3, 25.8, 68.3, 91.5, 92.6, 107.0, 110.0, 120.4, 125.2, 125.4, 126.8, 127.0, 127.3, 129.0, 129.4, 132.0, 132.4, 133.3, 142.0, 144.0, 156.3; HRMS (EI) calcd for $C_{25}H_{27}{}^{79}BrO_2Si$ 466.0964, found 466.0967.

***tert*-Butyl(furan-2-yl(2-(*p*-tolylethynyl)phenyl)methoxy)-dimethylsilane (1d):** yield 87%; yellow solid; mp 65−68 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.05 (s, 3H), 0.07 (s, 3H), 0.91 (s, 9H), 2.36 (s, 3H), 6.01 (d, J = 2.8 Hz, 1H), 6.24 (s, 1H), 6.35 (s, 1H), 7.15 (d, J = 7.6 Hz, 2H), 7.25 (t, J = 7.6 Hz, 1H), 7.33−7.40 (m, 4H), 7.47 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ −5.08, −5.0, 18.4, 21.5, 25.8, 68.3, 86.3, 94.6, 106.8, 110.1, 120.1, 121.0, 126.6, 127.2, 128.4, 129.1, 131.3, 131.6, 138.5, 141.9, 143.6, 156.5; HRMS (EI) calcd for $C_{26}H_{30}O_2Si$ 402.2015, found 402.2012.

***tert*-Butyl((2-((3,5-dimethoxyphenyl)ethynyl)phenyl)(furan-2-yl)methoxy)dimethylsilane (1e):** yield 81%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.05 (s, 3H), 0.08 (s, 3H), 0.91 (s, 9H), 3.80 (s, 6H), 6.01 (d, J = 2.4 Hz, 1H), 6.26 (d, J = 1.6 Hz, 1H), 6.34 (s, 1H), 6.47 (d, J = 1.6 Hz, 1H), 6.62 (d, J = 1.6 Hz, 2H), 7.27 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 0.4 Hz, 1H), 7.40 (t, J = 7.2 Hz, 1H), 7.48 (d, J = 7.2 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ −5.1, −5.0, 18.4, 25.8, 55.3, 68.3, 86.5, 94.4, 101.7, 106.9, 109.2, 110.1, 120.6, 124.5, 126.6, 127.3, 128.7, 131.6, 141.9, 143.8, 156.4, 160.5; HRMS (EI) calcd for $C_{27}H_{32}O_4Si$ 448.2070, found 448.2074.

***tert*-Butyl(furan-2-yl(2-(naphthalen-1-ylethynyl)phenyl)-methoxy)dimethylsilane (1f):** yield 56%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.08 (s, 3H), 0.11 (s, 3H), 0.92 (s, 9H), 6.01 (d, J = 3.6 Hz, 1H), 6.23−6.24 (m, 1H), 6.52 (s, 1H), 7.28−7.35 (m, 2H), 7.40−7.45 (m, 2H), 7.48−7.56 (m, 2H), 7.60−7.62 (m, 1H), 7.69−7.71 (m, 1H), 7.80−7.85 (m, 3H), 8.27−8.29 (m, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −5.0, −4.9, 18.4, 25.8, 68.6, 91.8, 92.5, 107.2, 110.1, 120.9, 121.0, 125.3, 126.3, 126.4, 126.77, 126.81, 127.4, 128.3, 128.7, 128.8, 130.4, 132.0, 133.1, 133.2, 142.0, 143.6, 156.4. HRMS (EI) calcd for $C_{29}H_{30}O_2Si$: 438.2015, found 438.2012.

***tert*-Butyl(furan-2-yl(2-(thiophene-2-ylethynyl)phenyl)-methoxy)dimethylsilane (1g):** yield 66%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.05 (s, 3H), 0.08 (s, 3H), 0.91 (s, 9H), 6.05 (d, J = 2.4 Hz, 1H), 6.25−6.26 (m, 1H), 6.29 (s, 1H), 6.99−7.01 (m, 1H), 7.22−7.46 (m, 6H), 7.77 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −5.1, −5.0, 18.3, 25.8, 68.4, 87.6, 90.7, 106.9, 110.0, 120.5, 123.2, 126.7, 127.1, 127.3, 127.4, 128.7, 131.4, 131.7, 142.0, 143.7, 156.2; HRMS (EI) calcd for $C_{23}H_{26}O_2SSi$ 394.1423, found 394.1421.

***tert*-Butyl((2-(cyclohexenylethynyl)phenyl)(furan-2-yl)-methoxy)dimethylsilane (1h):** yield 80%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.04 (s, 3H), 0.05 (s, 3H), 0.90 (s, 9H), 1.55−1.68 (m, 4H), 2.13−2.18 (m, 4H), 5.96−5.97 (m, 1H), 6.15 (s, 1H), 6.25 (s, 2H), 7.18−7.38 (m, 4H), 7.71 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −5.1, −5.0, 18.3, 21.5, 22.3, 25.75, 25.81, 29.1, 68.3, 84.3, 96.4, 106.7, 110.0, 120.7, 121.4, 126.6, 127.1, 128.0, 131.4, 135.0, 141.8, 143.4, 156.5; HRMS (EI) calcd for $C_{25}H_{32}O_2Si$ 392.2172, found 392.2175.

***tert*-Butyl((2-(cyclopropylethynyl)phenyl)(furan-2-yl)-methoxy)dimethylsilane (1i):** yield 73%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.03 (s, 3H), 0.05 (s, 3H), 0.68−0.76 (m, 2H), 0.83−0.87 (m, 2H), 0.90 (s, 9H), 1.40−1.44 (m, 1H), 5.93 (d, J = 3.2 Hz, 1H), 6.18 (s, 1H), 6.24−6.25 (m, 1H), 7.16−7.33 (m, 4H), 7.68 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −5.1, −5.0, 0.2, 8.7, 8.8, 18.3, 25.8, 68.2, 73.1, 98.8, 106.7, 110.0, 121.5, 126.5, 127.1, 127.6, 131.5, 141.7, 143.6, 156.7; HRMS (EI) calcd for $C_{22}H_{28}O_2Si$ 352.1859, found 352.1862.

***tert*-Butyl(furan-2-yl(2-(hex-1-ynyl)phenyl)methoxy)-dimethylsilane (1j):** yield 55%; yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.04 (s, 3H), 0.05 (s, 3H), 0.90−0.96 (m, 12H), 1.40−1.56 (m, 4H), 2.40 (t, J = 6.9 Hz, 2H), 5.92 (d, J = 3.0 Hz, 1H), 6.23−6.26 (m, 2H), 7.16−7.35 (m, 4H), 7.70 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −5.1, −5.0, 13.6, 18.3, 19.2, 21.9, 25.8, 30.8, 68.3, 78.1, 95.5, 106.7, 110.0, 121.7, 126.6, 127.1, 127.7, 131.6, 141.8, 143.5, 156.7; HRMS (EI) calcd for $C_{23}H_{32}O_2Si$ 368.2172, found 368.2166.

***tert*-Butyl((5-fluoro-2-(phenylethynyl)phenyl)(furan-2-yl)-methoxy)dimethylsilane (1k):** yield 83%; yellow solid; mp 69−71 °C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.05 (s, 3H), 0.09 (s, 3H), 0.91 (s, 9H), 6.04 (d, J = 3.3 Hz, 1H), 6.24−6.26 (m, 1H), 6.30 (s, 1H), 6.93−6.99 (m, 1H), 7.32−7.35 (m, 4H), 7.42−7.52 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ −5.1, −5.0, 18.3, 25.8, 68.1 (d, J = 1.1 Hz), 85.9, 94.2 (d, J = 1.8 Hz), 107.1, 110.2, 113.9 (d, J = 23.9 Hz), 114.7 (d, J = 22.6 Hz), 116.8 (d, J = 3.3 Hz), 123.1, 128.4, 131.4, 133.5 (d, J = 8.1 Hz), 142.1, 146.7 (d, J = 8.1 Hz), 155.7, 162.8 (d, J = 248.9 Hz); HRMS (EI) calcd for $C_{25}H_{27}FO_2Si$ 406.1764, found 406.1761.

***tert*-Butyl((4,5-dimethoxy-2-(phenylethynyl)phenyl)(furan-2-yl)methoxy)dimethylsilane (1l):** yield 74%; brown oil; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.090 (s, 3H), 0.094 (s, 3H), 0.92 (s, 9H), 3.88 (s, 3H), 3.91 (s, 3H), 6.01 (d, J = 3.3 Hz, 1H), 6.24−6.26 (m, 1H), 6.31 (s, 1H), 6.97 (s, 1H), 7.28−7.34 (m, 5H), 7.43−7.46 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ −5.1, −5.0, 18.3, 25.7, 55.78, 55.83, 68.2, 86.9, 92.9, 106.6, 109.5, 110.0, 112.6, 113.6, 123.3, 128.0, 128.3, 131.2, 137.3, 141.9, 147.8, 149.5, 156.5; HRMS (EI) calcd for $C_{27}H_{32}O_4Si$ 448.2070, found 448.2075.

***tert*-Butyl(furan-2-yl(6-(phenylethynyl)benzo[*d*][1,3]dioxol-5-yl)methoxy)dimethylsilane (1m):** yield 70%; brown solid; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) 0.06 (s, 3H), 0.08 (s, 3H), 0.91 (s, 9H), 5.97 (d, J = 1.2 Hz, 1H), 6.00 (d, J = 1.2 Hz, 1H), 6.06 (d, J = 3.3 Hz, 1H), 6.25−6.27 (m, 1H), 6.31 (s, 1H), 6.91 (s, 1H), 7.21 (s, 1H), 7.23−7.34 (m, 4H), 7.44−7.47 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ −5.1, −5.0, 18.3, 25.8, 68.3, 87.0, 92.9, 101.4, 106.5, 107.3, 110.0, 110.8, 113.8, 123.3, 128.1, 128.4, 131.3, 139.4, 141.9, 146.6, 148.3, 156.4; HRMS (EI) calcd for $C_{26}H_{28}O_4Si$ 432.1757, found 432.1755.

***tert*-Butyldimethyl((5-methylfuran-2-yl)(2-(phenylethynyl)-phenyl)methoxy)silane (1n):** (5-Methylfuran-2-yl)lithium was used instead of 2-furanyllithium: yield 71%; yellow oil; ^{1}H NMR (400 MHz,

$CDCl_3$, $SiMe_4$) δ 0.18 (s, 3H), 0.21 (s, 3H), 1.04 (s, 9H), 2.34 (s, 3H), 5.94−5.96 (m, 2H), 6.43 (s, 1H), 7.36−7.38 (m, 1H), 7.44−7.50 (m, 4H), 7.58−7.60 (m, 3H), 7.90−7.92 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −4.96, −4.93, 13.6, 18.4, 25.9, 68.4, 87.1, 94.4, 106.1, 107.8, 120.8, 123.4, 126.7, 127.1, 128.2, 128.3, 128.5, 131.4, 131.6, 144.0, 151.5, 154.7; HRMS (EI) calcd for $C_{26}H_{30}O_2Si$ 402.2015, found 402.2014.

***tert*-Butyldimethyl((2-(phenylethynyl)phenyl)(5-phenylfuran-2-yl)methoxy)silane (1o):** (5-Phenylfuran-2-yl)lithium was used instead of 2-furanyllithium: yield 77%; yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.10 (s, 3H), 0.14 (s, 3H), 0.94 (s, 9H), 6.00 (d, J = 3.3 Hz, 1H), 6.41 (s, 1H), 6.53 (d, J = 3.3 Hz, 1H), 7.22−7.51 (m, 11H), 7.62 (d, J = 7.5 Hz, 2H), 7.83 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −4.9, 18.4, 25.8, 68.5, 87.0, 94.7, 105.8, 109.0, 120.9, 123.2, 123.6, 126.6, 127.0, 127.3, 128.25, 128.31, 128.6, 131.0, 131.5, 131.6, 143.7, 153.1, 156.4; HRMS (EI) calcd for $C_{31}H_{32}O_2Si$ 464.2172, found 464.2178.

***tert*-Butyl(furan-2-yl(2-(phenylethynyl)cyclopent-1-enyl)-methoxy)dimethylsilane (1p):** yield 57%; brown oil; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.11 (s, 6H), 0.92 (s, 9H), 1.85−1.95 (m, 2H), 2.37−2.68 (m, 4H), 5.89 (s, 1H), 6.22 (m, 1H), 6.29−6.30 (m, 1H), 7.28−7.33 (m, 4H), 7.42−7.45 (m, 2H); ^{13}C NMR (74.5 MHz, $CDCl_3$, Me_4Si) δ −5.1, −4.9, 18.3, 22.4, 25.8, 31.2, 36.7, 66.7, 85.2, 94.5, 105.7, 110.0, 120.3, 123.5, 128.0, 128.3, 131.4, 141.6, 150.8, 155.6; HRMS (EI) calcd for $C_{24}H_{30}O_2Si$ 378.2015, found 378.2016.

Typical Procedure for Au(I)-Catalyzed Cyclization Reactions of TBS-Protected (*o*-Alkynyl)phenyl 2-Furylcarbinols 1 to Naphthol Derivatives 2. To a solution of *tert*-butyl(furan-2-yl(2-(phenylethynyl)phenyl)methoxy)dimethylsilane (**1a**) (77.7 mg, 0.2 mmol) in toluene (2 mL) was added gold catalyst (acetonitrile)[(2-biphenyl)di-*tert*-butylphosphine]gold(I) hexafluoroantimonate (3.08 mg, 0.004 mmol). The resulting solution was stirred at room temperature for 2 h. Then the solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel (petroleum/ethyl acetate = 20:1) to afford 69 mg of the product 3-(1-(*tert*-Butyldimethylsilyloxy)-3-phenylnaphthalen-2-yl) acrylaldehyde (**2a**) in 89% yield (Z/E = 50:1) as a yellow solid. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.09 (s, 6H), 1.07 (s, 9H), 6.10 (dd, J = 11.2, 8.4 Hz, 1H), 7.31 (d, J = 11.6 Hz, 1H), 7.38−7.43 (m, 5H), 7.52−7.55 (m, 3H), 7.82−7.84 (m, 1H), 8.15−8.17 (m, 1H), 9.75 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −3.0, 18.4, 26.0, 120.3, 123.0, 123.8, 125.6, 127.0, 127.37, 127.38, 127.7, 128.2, 129.9, 130.6, 134.4, 139.6, 140.3, 145.4, 149.3, 194.0. Minor isomer: ^{1}H NMR(400 MHz, $CDCl_3$, Me_4Si) 6.23 (dd, J = 16.6, 8.4 Hz, 1H), 9.53 (d, J = 8.0 Hz, 1H); HRMS (EI) calcd for $C_{25}H_{28}O_2Si$ 388.1859, found 388.1862.

(*Z*)-3-(1-(*tert*-Butyldimethylsilyloxy)-3-(4-chlorophenyl)-naphthalen-2-yl)acrylaldehyde (2b): yield 91% (Z/E = 33:1); red oil. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.06 (s, 6H), 1.05 (s, 9H), 6.09 (dd, J = 11.6, 8.2 Hz, 1H), 7.26 (d, J = 11.2 Hz, 1H), 7.29−7.31 (m, 2H), 7.37−7.39 (m, 2H), 7.48−7.53 (m, 3H), 7.79−7.82 (m, 1H), 8.12−8.15 (m, 1H), 9.71 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −3.0, 18.4, 26.0, 120.0, 122.9, 123.8, 125.8, 127.1, 127.5, 127.8, 128.4, 130.9, 131.2, 133.6, 134.3, 138.3, 138.8, 145.0, 149.5, 193.7. Minor isomer: ^{1}H NMR(400 MHz, $CDCl_3$, Me_4Si) 6.23 (dd, J = 16.4, 7.6 Hz, 1H), 9.52 (d, J = 8.0 Hz, 1H); HRMS (EI) calcd for $C_{25}H_{27}{}^{35}ClO_2Si$: 422.1469, found 422.1465.

(*Z*)-3-(3-(2-Bromophenyl)-1-(*tert*-butyldimethylsilyloxy)-naphthalen-2-yl)acrylaldehyde (2c): yield 64% (Z/E = 33:1); yellow oil. Major isomer: ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.09 (s, 3H), 0.11 (s, 3H), 1.05 (s, 9H), 5.95 (dd, J = 11.4, 8.3 Hz, 1H), 7.19−7.40 (m, 5H), 7.52−7.55 (m, 2H), 7.63 (d, J = 8.3 Hz, 1H), 7.79−7.82 (m, 1H), 8.14−8.17 (m, 1H), 9.64 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ −3.2, −3.0, 18.4, 26.0, 120.6, 122.5, 123.7, 123.8, 125.8, 127.3, 127.37, 127.42, 127.8, 129.4, 130.7, 131.2, 132.6, 134.2, 138.9, 141.1, 144.3, 149.2, 194.0. Minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) 9.48 (d, J = 7.8 Hz, 1H); IR (neat) 3054, 2956, 2930, 1679, 1376, 1258, 1105, 826, 732 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{27}{}^{79}BrO_2Si$ 466.0964, found 466.0967.

(*Z*)-3-(1-(*tert*-Butyldimethylsilyloxy)-3-*p*-tolylnaphthalen-2-yl)acrylaldehyde (2d): yield 79% (Z/E = 25:1); yellow oil. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.15 (s, 6H), 1.14 (s, 9H), 2.49 (s, 3H), 6.17 (dd, J = 10.8, 8.2 Hz, 1H), 7.29−7.41 (m, 5H), 7.57−7.61 (m, 3H), 7.87−7.90 (m, 1H), 8.22−8.24 (m, 1H), 9.82 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −3.0, 18.4, 21.1, 26.0, 120.4, 122.9, 123.7, 125.5, 126.9, 127.3, 127.7, 128.9, 129.8, 130.6, 134.4, 137.2, 137.4, 139.6, 145.6, 149.3, 194.0. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) 9.61 (d, J = 8.0 Hz, 1H); IR (neat) 2955, 2930, 2858, 1679, 1490, 1374, 1258, 1090, 827, 751, 704 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{30}O_2Si$ 402.2015, found 402.2013.

(*Z*)-3-(1-(*tert*-Butyldimethylsilyloxy)-3-(3,5-dimethoxyphenyl)naphthalen-2-yl)acrylaldehyde (2e): yield 85% (Z/E = 25:1); yellow solid. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.06 (s, 6H), 1.05 (s, 9H), 3.80 (s, 6H), 6.11 (dd, J = 11.2, 8.0 Hz, 1H), 6.48 (t, J = 2.4 Hz, 1H), 6.52 (m, 2H), 7.32 (d, J = 11.6 Hz, 1H), 7.48−7.55 (m, 3H), 7.80−7.82 (m, 1H), 8.12−8.15 (m, 1H), 9.75 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −3.1, 18.4, 26.0, 55.3, 99.3, 108.2, 120.1, 122.6, 123.8, 125.6, 127.1, 127.4, 127.7, 130.5, 134.3, 139.5, 142.3, 145.5, 149.2, 160.4, 194.0. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) 6.34 (dd, J = 16.2, 7.6 Hz, 1H), 9.54 (d, J = 7.6 Hz, 1H); HRMS (EI) calcd for $C_{27}H_{32}O_4Si$ 448.2070, found 448.2069.

(*Z*)-3-(8′-(*tert*-Butyldimethylsilyloxy)-1,6′-binaphthyl-7′-yl)-acrylaldehyde (2f): yield 62% (Z/E = 25:1); red oil. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.10 (s, 6H), 1.04 (s, 9H), 5.87 (dd, J = 11.2, 8.0 Hz, 1H), 7.03 (d, J = 11.2 Hz, 1H), 7.32−7.36 (m, 1H), 7.40−7.47 (m, 3H), 7.49−7.57 (m, 4H), 7.79−7.81 (m, 1H), 7.87−7.90 (m, 2H), 8.19−8.22 (m, 1H), 9.72 (d, J = 8.0 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ −3.2, −3.0, 18.4, 26.0, 121.5, 123.6, 123.8, 125.2, 125.66, 125.72, 125.9, 126.3, 127.3, 127.4, 127.4, 127.7, 128.2, 128.3, 130.5, 131.8, 133.4, 134.4, 137.9, 138.1, 144.6, 149.1, 193.7. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) 6.02 (dd, J = 16.4, 7.8 Hz, 1H), 9.36 (d, J = 7.8 Hz, 1H); IR (neat) 2955, 2930, 2858, 1679, 1377, 1260, 1107, 828, 779, 735 cm^{-1}; HRMS (MALDI/DHB) calcd for $C_{29}H_{31}O_2Si$ $[M + H]^+$ 439.2088, found 439.2093.

(*Z*)-3-(1-(*tert*-Butyldimethylsilyloxy)-3-(thiophene-2-yl)-naphthalen-2-yl)acrylaldehyde (2g): yield 84% (Z/E = 33:1); yellow oil. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.32 (s, 6H), 1.31 (s, 9H), 6.47 (dd, J = 11.2, 8.0 Hz, 1H), 7.34−7.38 (m, 2H), 7.62−7.63 (m, 1H), 7.71−7.79 (m, 3H), 7.95 (s, 1H), 8.06−8.08 (m, 1H), 8.38 (d, J = 7.2 Hz, 1H), 9.99 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −3.0, 18.4, 26.0, 120.0, 123.4, 123.8, 125.9, 126.2, 127.2, 127.4, 127.5, 127.8, 128.1, 131.3, 131.8, 134.2, 141.7, 145.1, 149.4, 194.0. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) 6.73 (dd, J = 16.4, 8.4 Hz, 1H), 9.87 (d, J = 8.4 Hz, 1H); HRMS (EI) calcd for $C_{23}H_{26}O_2SSi$ 394.1423, found 394.1421.

(*Z*)-3-(1-(*tert*-Butyldimethylsilyloxy)-3-cyclohexenylnaphthalen-2-yl)acrylaldehyde (2h): yield 74% (Z/E = 25:1); yellow oil. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.15 (s, 6H), 1.11 (s, 9H), 1.72−1.75 (m, 4H), 2.21−2.22 (m, 4H), 5.84 (s, 1H), 6.21 (dd, J = 11.2, 8.2 Hz, 1H), 7.40 (s, 1H), 7.49−7.55 (m, 2H), 7.65 (d, J = 11.2 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 9.66 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −2.9, 18.5, 21.9, 22.8, 25.5, 26.0, 30.3, 120.0, 120.9, 123.5, 125.1, 126.7, 127.0, 127.5, 129.1, 130.4, 134.7, 138.2, 142.9, 145.5, 149.2, 193.5. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) 6.99 (dd, J = 16.4, 8.4 Hz, 1H), 9.74 (d, J = 7.6 Hz, 1H); IR (neat) 2931, 2858, 2360, 1676, 1373, 1264, 1104, 829, 734, 702 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{32}O_2Si$: 392.2172, found 392.2171.

(*Z*)-3-(1-(*tert*-Butyldimethylsilyloxy)-3-cyclopropylnaphthalen-2-yl)acrylaldehyde (2i). yield 80% (Z/E = 25:1); yellow solid. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.20 (s, 6H), 0.90−0.91 (m, 2H), 1.11−1.17 (m, 11H), 2.00−2.07 (m, 1H), 6.39 (dd, J = 11.2, 8.0 Hz, 1H), 7.33 (s, 1H), 7.52−7.60 (m, 2H), 7.83−7.87 (m, 2H), 8.17 (d, J = 8.0 Hz, 1H), 9.76 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −3.1, 7.8, 14.5, 18.3, 25.9, 118.3, 122.3, 123.5, 124.8, 126.4, 126.9, 127.2, 130.9, 134.5, 139.6, 145.1, 148.6, 194.2. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) 7.18

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(dd, J = 16.2, 8.0 Hz, 1H), 9.89 (d, J = 8.0 Hz, 1H); IR (neat) 2955, 2930, 2858, 1679, 1379, 1256, 1011, 827, 780, 736 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{28}O_2Si$ 352.1859, found 352.1860.

(*Z*)-3-(3-Butyl-1-(*tert*-butyldimethylsilyloxy)naphthalen-2-yl)acrylaldehyde (2j): yield 68% (Z/E = 14:1); yellow solid. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.06 (s, 6H), 0.93 (t, J = 7.6 Hz, 3H), 1.03 (s, 9H), 1.12−1.42 (m, 2H), 1.58−1.64 (m, 2H), 2.71 (t, J = 7.6 Hz, 2H), 6.24 (dd, J = 11.2, 8.4 Hz, 1H), 7.37 (s, 1H), 7.40−7.49 (m, 2H), 7.57 (d, J = 10.8 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 9.57 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −3.1, 13.9, 18.4, 22.6, 26.0, 32.5, 33.9, 121.0, 121.2, 123.6, 124.8, 126.3, 126.9, 127.1, 131.4, 134.6, 139.1, 144.8, 148.7, 194.1. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) 6.80 (dd, J = 16.0, 8.0 Hz, 1H), 9.75 (d, J = 8.0 Hz); IR (neat) 2956, 2930, 2859, 1682, 1375, 1258, 1107, 1022, 830, 781, 748 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{32}O_2Si$ 368.2172, found 368.2169.

(*Z*)-3-(1-(*tert*-Butyldimethylsilyloxy)-7-fluoro-3-phenylnaphthalen-2-yl)acrylaldehyde (2k): yield >99% (Z/E = 33:1); yellow solid. Major isomer: ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.08 (s, 6H), 1.05 (s, 9H), 6.08 (dd, J = 11.1, 8.4 Hz, 1H), 7.26−7.41 (m, 7H), 7.51 (s, 1H), 7.72−7.83 (m, 2H), 9.71 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ −3.0, 18.4, 25.9, 107.5 (d, J = 22.6 Hz), 117.7 (d, J = 25.4 Hz), 121.2, 122.8 (d, J = 0.8 Hz), 127.5, 127.9 (d, J = 8.5 Hz), 128.2, 129.9, 130.3 (d, J = 8.5 Hz), 130.9, 131.3 (d, J = 2.7 Hz), 138.9 (d, J = 2.7 Hz), 140.0, 145.0, 148.7 (d, J = 5.4 Hz), 160.6 (d, J = 246.9 Hz), 193.6. Minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) 6.23 (dd, J = 16.2, 7.8 Hz, 1H), 9.51 (d, J = 7.8 Hz, 1H); HRMS (EI) calcd for $C_{25}H_{27}FO_2Si$ 406.1764, found 406.1767.

(*Z*)-3-(1-(*tert*-Butyldimethylsilyloxy)-6,7-dimethoxy-3-phenylnaphthalen-2-yl)acrylaldehyde (2l): yield 80% (Z/E = 11:1); yellow solid. Major isomer: ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.08 (s, 6H), 1.05 (s, 9H), 4.01 (s, 3H), 4.03 (s, 3H), 6.06 (dd, J = 11.1, 8.4 Hz, 1H), 7.11 (s, 1H), 7.27−7.43 (m, 8H), 9.73 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ −2.94, −2.89, 18.4, 25.9, 55.9, 70.5, 102.8, 106.2, 118.8, 121.6, 122.2, 127.1, 128.0, 129.9, 130.3, 130.5, 138.0, 140.5, 145.8, 148.2, 149.2, 150.6, 194.1. Minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) 6.21 (dd, J = 16.4, 8.1 Hz, 1H), 9.48 (d, J = 7.5 Hz, 1H); HRMS (EI) calcd for $C_{27}H_{32}O_4Si$ 448.2070, found 448.2067.

(*Z*)-3-(5-(*tert*-Butyldimethylsilyloxy)-7-phenylnaphtho[2,3-*d*][1,3]dioxol-6-yl)acrylaldehyde (2m): yield 77% (Z/E = 20:1); white solid. Major isomer: ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.20 (s, 6H), 1.17 (s, 9H), 6.14−6.21 (m, 3H), 7.21 (s, 1H), 7.39−7.54 (m, 8H), 9.83 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ −3.0, 18.4, 26.0, 100.3, 101.3, 103.8, 119.2, 122.3, 123.7, 127.2, 128.1, 129.9, 130.4, 131.9, 138.3, 140.4, 145.6, 147.7, 148.68, 148.72, 194.0. Minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) 6.29 (dd, J = 16.4, 8.4 Hz, 1H), 9.61 (d, J = 8.1 Hz, 1H); HRMS (EI) calcd for $C_{26}H_{28}O_4Si$ 432.1757, found 432.1760.

(*Z*)-4-(1-(*tert*-Butyldimethylsilyloxy)-3-phenylnaphthalen-2-yl)but-3-en-2-one (2n): yield 78%; yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.10 (s, 6H), 1.07 (s, 9H), 1.86 (s, 3H), 6.13 (d, J = 12.3 Hz, 1H), 6.92 (d, J = 12.3 Hz, 1H), 7.35−7.39 (m, 5H), 7.46−7.50 (m, 3H), 7.78−7.81 (m, 1H), 8.10−8.14 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ −3.0, 18.4, 26.0, 28.6, 122.4, 122.9, 123.4, 125.3, 126.9, 127.09, 127.12, 127.8, 128.0, 129.8, 132.7, 134.2, 138.2, 139.1, 140.8, 148.8, 199.9; HRMS (MALDI/DHB) calcd for $C_{26}H_{31}O_2Si$ $[M + H]^+$ 403.2088, found 403.2098.

(*Z*)-3-(1-(*tert*-Butyldimethylsilyloxy)-3-phenylnaphthalen-2-yl)-1-phenylprop-2-en-1-one (2o): yield 97%; yellow solid; mp 88−89 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.40 (s, 6H), 1.34 (s, 9H), 6.98 (dd, J = 12.0, 1.2 Hz, 1H), 7.26−7.30 (m, 1H), 7.38−7.67 (m, 11H), 7.77 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 1H), 8.30 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −3.1, 18.6, 26.1, 122.8, 123.0, 123.2, 124.8, 126.4, 126.5, 127.0, 127.59, 127.61, 128.1, 130.1, 131.9, 134.1, 137.5, 139.4, 141.2, 149.1, 191.2; HRMS (EI) calcd for $C_{31}H_{32}O_2Si$ 464.2172, found 464.2170.

(*Z*)-3-(4-(*tert*-Butyldimethylsilyloxy)-6-phenyl-2,3-dihydro-1*H*-inden-5-yl)acrylaldehyde (2p): yield 59% (Z/E = 33:1); yellow solid. Major somer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.09 (s, 6H), 0.95 (s, 9H), 2.06−2.13 (m, 2H), 2.90−2.97 (m, 4H), 5.94 (dd, J = 11.2, 8.2 Hz, 1H), 6.93 (s, 1H), 7.20−7.36 (m, 6H), 9.63 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −3.1, 18.4, 25.4, 25.9, 31.2, 33.4, 120.0, 122.6, 127.1, 128.1, 129.9, 130.4, 134.1, 140.8, 141.7, 145.9, 147.6, 149.3, 193.9. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) 6.21 (dd, J = 16.4, 7.6 Hz,1H), 9.42 (d, J = 8.0 Hz, 1H); HRMS (EI) calcd for $C_{24}H_{30}O_2Si$ 378.2015, found 378.2020.

Synthesis of Benzocoumarin 4. To a solution of (*Z*)-3-(1-(*tert*-butyldimethylsilyloxy)-3-phenylnaphthalen-2-yl)-acrylaldehyde (**2a**) (117 mg, 0.3 mmol) in THF were added 3 Å MS (75 mg), PDC (451.4 mg, 1.2 mmol), and TBAF (0.3 mL, 0.3 mmol, 1.0 M in THF) successively, and the mixture was stirred overnight. After the reaction was complete as monitored by thin-layer chromatography, the mixture was filtered and the filter cake was washed with acetone. The solvent was evaporated and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford 5-phenyl-2*H*-benzo[*h*]chromen-2-one **4** (55.0 mg, 67%) as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 6.42 (dd, J = 10.0, 1.6 Hz, 1H), 7.41−7.53 (m, 5H), 7.61−7.64 (m, 3H), 7.83−7.88 (m, 2H), 8.54 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 113.2, 115.3, 122.3, 122.4, 124.6, 127.0, 127.8, 128.0, 128.6, 129.1, 129.8, 134.3, 136.9, 138.2, 142.6, 151.9, 160.7; HRMS (EI) calcd for $C_{19}H_{12}O_2$ 272.0837, found 272.0836.

Synthesis of 1-Naphthol Derivative 5. To a solution of (*Z*)-3-(1-(*tert*-butyldimethylsilyloxy)-3-phenylnaphthalen-2-yl)-acrylaldehyde (**2a**) (117 mg, 0.3 mmol) in DCM (2 mL) and MeOH (2 mL) were added $CeCl_3{\cdot}7H_2O$ (335 mg, 0.9 mmol) and $NaBH_4$ (34 mg, 0.9 mmol) successively at 0 °C. The resulting solution was warmed to room temperature and stirred for 3 h. The mixture was quenched with water and extracted with ether. The combined organic phase was washed with brine solution and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford (*Z*)-3-(1-(*tert*-butyldimethylsilyloxy)-3-phenylnaphthalen-2-yl)-prop-2-en-1-ol (107.9 mg, 92%) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 0.19 (s, 6H), 1.16 (s, 9H), 1.33 (bs, 1H), 3.91 (d, J = 6.4 Hz, 2H), 5.85 (dt, J = 11.2, 2.8 Hz, 1H), 6.54 (d, J = 11.2 Hz, 1H), 7.36−7.54 (m, 8H), 7.83−7.85 (m, 1H), 8.19−8.21 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ −3.1, 18.6, 26.1, 60.4, 122.4, 122.6, 123.2, 125.1, 126.3, 126.9, 127.1, 127.5, 127.6, 127.8, 129.8, 132.2, 133.7, 139.9, 141.4, 148.8; HRMS (EI) calcd for $C_{25}H_{30}O_2Si$ 390.2015, found 390.2018.

To a solution of above alcohol (105 mg, 0.27 mmol) in THF (2.7 mL) was added TBAF (0.27 mmol, 0.27 mL, 1.0 M solution in THF) at 0 °C. The resulting solution was warmed to room temperature and stirred for 1 h. The mixture was quenched with water and extracted with ether. The combined organic phase was washed with brine solution and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 3:1:1) to afford (*Z*)-2-(3-hydroxyprop-1-enyl)-3-phenylnaphthalen-1-ol **5** (63 mg, 85%) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 2.43 (bs, 1H), 4.03 (d, J = 6.4 Hz, 2H), 6.00 (dt, J = 11.2, 7.6 Hz, 1H), 6.31 (d, J = 11.2 Hz, 1H), 6.73 (s, 1H), 7.30−7.46 (m, 8H), 7.73−7.75 (m, 1H), 8.23−8.25 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 59.7, 115.4, 120.7, 122.6, 123.6, 125.4, 126.8, 127.1, 127.4, 127.5, 127.9, 129.6, 133.1, 133.6, 139.5, 141.0, 148.3; HRMS (ESI) calcd for $C_{19}H_{15}O_2$ $[M - H]^-$ 275.1078, found 275.10717.

2-(Allyloxy(2-(phenylethynyl)phenyl)methyl)furan (6). Compound **6** was prepared by the reaction of the corresponding alcohol with allyl bromide using NaH as base: ^{1}H NMR ($CDCl_3$, Me_4Si, 300 MHz) δ 4.08 (d, J = 5.7 Hz, 2H), 5.20 (d, J = 10.5 Hz, 1H), 5.32 (dd, J = 17.6, 1.5 Hz, 1H), 5.93−6.02 (m, 1H), 6.07 (s, 1H), 6.13 (d, J = 3.0 Hz, 1H), 6.27−6.29 (m, 1H), 7.26−7.40 (m, 6H), 7.42−7.53 (m, 3H), 7.75 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, Me_4Si) δ 70.00, 73.75, 86.74, 94.49, 108.60, 110.10, 117.45, 122.06, 123.06, 126.74, 127.64, 128.34, 128.37, 128.65, 131.42, 131.93, 134.37, 140.86, 142.56, 153.85; HRMS (ESI) calcd for $C_{22}H_{18}O_2Na$ $[M + Na]^+$ 337.1204, found 337.1199.

(*Z*)-3-(1-(Allyloxy)-3-phenylnaphthalen-2-yl)acrylaldehyde (7): yield 70% (Z/E = 50:1); white soild. Major isomer: ^{1}H NMR (400

MHz, $CDCl_3$, Me_4Si) δ 4.38 (dd, J = 5.6, 0.8 Hz, 2H), 5.24 (dd, J = 10.8, 0.8 Hz, 1H), 5.39 (dd, J = 17.2, 0.8 Hz, 1H), 5.98−6.08 (m, 1H), 6.13 (dd, J = 11.4, 8.0 Hz, 1H), 7.24 (d, J = 11.2 Hz, 1H), 7.25−7.43 (m, 5H), 7.54−7.57 (m, 2H), 7.66 (s, 1H), 7.84−7.87 (m, 1H), 8.17−8.19 (m, 1H), 9.81 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$, Me_4Si) δ 74.58, 117.79, 122.92, 122.94, 125.06, 126.67, 127.05, 127.59, 127.65, 128.03, 128.26, 129.88, 130.36, 133.09, 134.60, 139.71, 139.99, 142.70, 153.11, 193.49. Minor isomer: ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 6.79 (dd, J = 16.0, 8.0 Hz, 1H), 9.50 (d, J = 7.6 Hz, 1H); HRMS (ESI) calcd for $C_{22}H_{18}O_2Na$ $[M + Na]^+$ 337.1204, found 337.1203.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallography of compound **2a** and spectroscopic characterization of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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