Et_3N-promoted sequential reactions for the synthesis of 6*H*-benzo[*c*]chromenes

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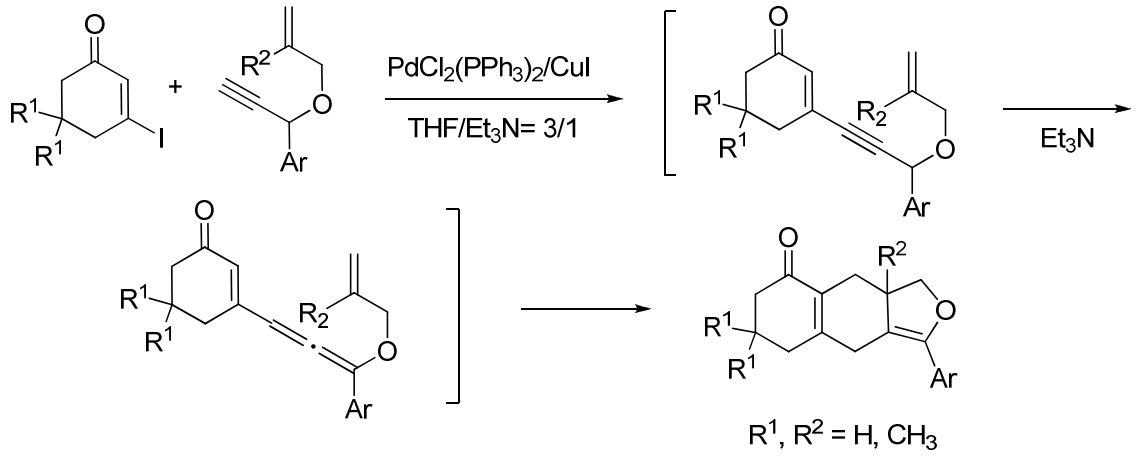
Abstract
An interesting Et_3N-promoted sequential reaction consisting of propargyl-allenyl isomerizations, intramolecular [4+2] cycloaddition and aromatization has been developed, providing a facile method for synthesis of 6*H*-benzo[*c*]chromenes under mild conditions in moderate yields.

Keywords: Sequential reaction, propargyl-allenyl isomerization, intramolecular [4+2] cycloaddition, aromatization, 6*H*-benzo[*c*]chromene

Introduction

6*H*-Benzo[*c*]chromenes are an important class of heterocycles due to their applications as bioactive compounds[1] and photoswitches in photochemical reactions.[2] Previous reports for the synthesis of 6*H*-benzo[*c*]chromenes are few, and these approaches usually present some limitations in terms of regioselectivity, need for forcing reaction conditions or complex starting materials.[3] Therefore, development of a synthetically useful methodology for 6*H*-benzo[*c*]chromenes using acyclic readily available starting materials attracted our attention and interest.

Recently, Huang reported a Pd-catalyzed coupling and base-induced propargyl-allenyl isomerization, intramolecular [4+2] cycloaddition reaction providing an efficient synthesis of polycyclic compounds containing a 2,3-dihydrofuran unit (Scheme 1).[4]



Scheme 1

In the reaction shown in Scheme 1, a conjugated enyne with an electron-withdrawing group was used as an efficient diene in an intramolecular [4+2] cycloaddition through propargyl-allenyl isomerization. We proposed that this kind of conjugated enyne might be used as an efficient synthon in the construction of 6*H*-benzo[*c*]chromenes. Retrosynthetically, 6*H*-benzo[*c*]chromenes could be prepared by intramolecular [4+2] cycloaddition and aromatization of conjugated enynes which in turn could be obtained conveniently by a Sonogashira coupling between alkynes and vinyl iodides (Figure 1).

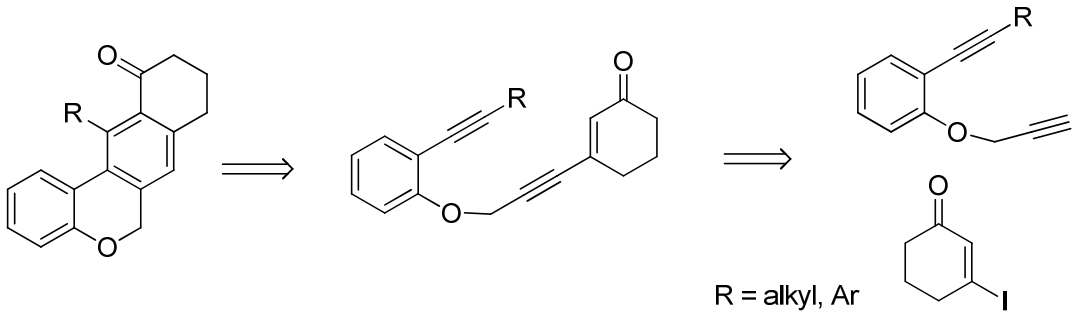


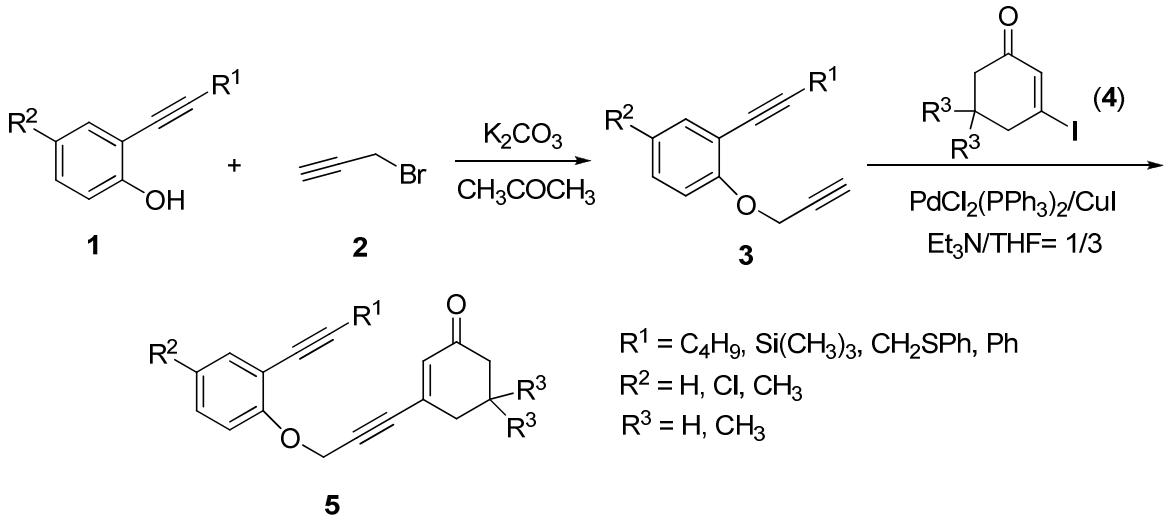
Figure 1

According to the above synthetic route, herein we wish to report an efficient synthesis of 6*H*-benzo[*c*]chromenes from acyclic enyne substrates in moderate yields.

Results and Discussion

Synthesis of enynes. The synthetic route to conjugated enynes **5** is outlined in Scheme 2. Compounds **3** were synthesized from 2-(alkynyl)phenols[5] and 3-bromoprop-1-yne **2** in acetone

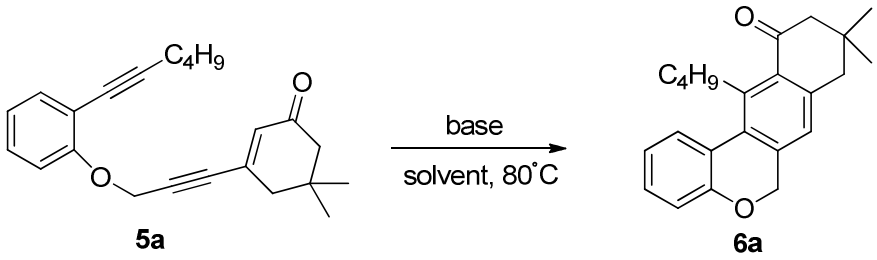
using K_2CO_3 as the base. Conjugated enynes **5** were conveniently obtained by a Sonogashira coupling between alkynes **3** and vinyl iodides **4**. [6]



Scheme 2

Effect of base and solvent. In order to find the most efficient reaction conditions, we initially examined the cyclization reaction of **5a** usiong various bases and solvents and the results are summarized in Table 1.

Table 1. Optimization of reaction conditions for the cyclization of **5a**[a]



Entry	Solvent	Base	t(h)	Yield (%)[b]
1	DMSO	Et_3N	24	25
2[c]	DMSO	DBU	72	11
3[c]	DMSO	NaH	72	-[d]
4	DMSO	*i*-Pr_2NH	24	-[d]
5[c]	DMSO	*t*-BuOK	48	-[d]
6	Toluene	Et_3N	24	-[d]
7	CH_3CN	Et_3N	70	35
8	$ClCH_2CH_2Cl$	Et_3N	80	22
9	DMA	Et_3N	48	40

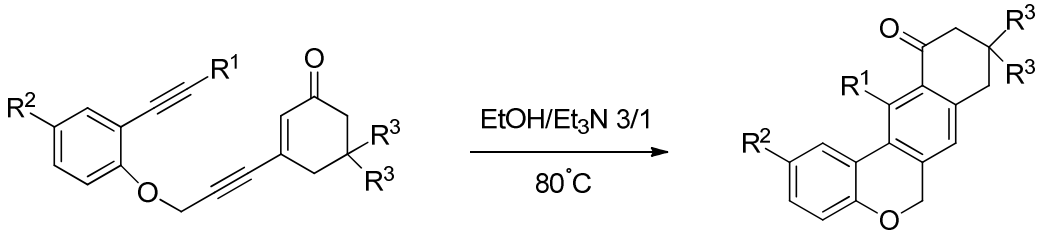
10	EtOH	Et_3N	24	66
11	CH_3OH	Et_3N	24	-[d]
12	*t*-BuOH	Et_3N	24	55
13	*n*-BuOH	Et_3N	35	45

[a] The reaction was carried out using **5a** (0.18 mmol) in 1.5 mL of solvent and 0.5 mL of base. [b] Isolated yields. [c] Reactions were carried out at rt. [d] No product was obtained.

In an initial experiment, we observed the formation of 6*H*-benzo[*c*]chromene **6a** when the reaction was performed in DMSO using Et_3N as the base (Table 1, entry 1). Further screening revealed that strong organic inorganic bases were not suitable for the transformation (Table 1, entries 2-5). Next, we examined the effect of solvent on this reaction (Table 1, entries 6-13). A better yield was obtained when EtOH was used as the solvent. The reaction seem to give much more competitive yields with shorter reaction time when protic solvents were used (entries 10, 12-13 Table 1).

Cyclization of enynes 5 to 6*H*-benzo[*c*]chromenes 6. With the optimized reaction conditions in hand (Table 1, entry 10), the scope and the limitations were examined (Table 2). From the results in Table 2, it is evident that the reaction proceeded smoothly to afford 6*H*-benzo[*c*]chromenes in moderate yields when R^1 was an alkyl or an aryl group (Table 2, entries 1-10).[7]

Table 2. Cyclization of enynes **5** to 6*H*-benzo[*c*]chromenes **6**



5 **6**

Entry	$R^1/R^2/R^3$	Time(h)	Product	Yield(%)[a]
1	C_4H_9/H/CH_3, **5a**	24	**6a**	66
2	C_4H_9/H/H, **5b**	22	**6b**	55
3	TMS/H/CH_3, **5c**	48	**6c**	45
4	TMS/H/H, **5d**	48	**6d**	40
5	$PhSCH_2$/H/H, **5e**	20	**6e**	50
6	Ph/H/CH_3, **5f**	24	**6f**	35
7	Ph/Cl/H, **5g**	28	**6g**	33
8	Ph/CH_3/CH_3, **5h**	28	**6h**	40

[a] Isolated yield based on **5**.

Conclusions

In summary, we have developed an efficient method for the synthesis of 6*H*-benzo[*c*]chromenes in moderate yields under mild conditions using acyclic substrate. These 6*H*-benzo[*c*]chromenes bearing carbonyl functional groups may be converted to other interesting and useful structural units in organic synthesis. Further studies into the scope and synthetic applications of this transformation are being carried out in our laboratory.

Experimental Section

General. All ^{1}H- and ^{13}C-NMR spectra were measured in $CDCl_3$ and recorded on a Brucker Avance III 500 MHz (125 MHz) spectrometer with TMS as the internal standard. Chemical shifts are expressed in ppm and *J* values are given in Hz. IR spectra were run on a Thermo Nicolet 6700 spectrometer. EIMS were determined with a Thermo ITQ 1100 mass spectrometer. HRMS were performed on a Waters GCT Premier instrument. Melting points were measured using CRC-1 melting point instrument and are uncorrected. Solvents were distilled before use.

Synthesis of (3)

To a solution of 2-(hex-1-ynyl)phenol **1a** (348 mg, 2 mmol) and 3-bromoprop-1-yne **2** (285.6 mg, 2.4 mmol) in 5 mL of Me_2CO was added K_2CO_3 (414 mg, 3 mmol). The resulting mixture was stirred at rt until the reaction was completed (monitored by TLC). The solvent was evaporated, a saturated solution of NaCl (20 mL) was added, the aqueous layer was extracted with Et_2O (3 x 20 mL) and the organic layer was dried over anhydrous $MgSO_4$. After filtration and evaporation, the residue was purified by flash chromatography (eluent: EtOAc/petroleum ether = 1/50) to afford **3**.

2-(Hex-1-ynyl)-1-(prop-2-ynyloxy)benzene (3a). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (dd, *J* 7.6 Hz, *J* 1.7 Hz, 1H, Ar-H), 7.23 (dt, *J* 7.80 Hz, *J* 1.7 Hz, 1H, Ar-H), 7.00 (d, *J* 8.2 Hz, 1H, Ar-H), 6.93 (dt, *J* 7.4 Hz, *J* 0.9 Hz, 1H, Ar-H), 4.77 (d, *J* 2.4 Hz, 2H, -OCH_2), 2.50 (t, *J* 2.4 Hz, 1H, alkyne-H), 2.46 (t, *J* 7.1 Hz, 2H, ArCH_2), 1.64-1.58 (m, 2H, -CH_2), 1.54-1.47 (m, 2H, -CH_2), 0.95 (t, *J* 7.2 Hz, 3H, -CH_3).

2-(Trimethylsilylethynyl)-1-(prop-2-ynyloxy)benzene (3b). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (dd, *J* 7.6 Hz, *J* 1.7 Hz, 1H, Ar-H), 7.29 (dt, *J* 7.9 Hz, *J* 1.6 Hz, 1H, Ar-H), 7.02 (d, *J* 8.2 Hz, 1H, Ar-H), 6.95 (dt, *J* 7.4 Hz, *J* 0.7 Hz, 1H, Ar-H), 4.78 (d, *J* 2.4 Hz, 2H, -OCH_2), 2.53 (t, *J* 2.4 Hz, 1H, alkyne-H), 0.28 (s, 9H, -$Si(CH_3)_3$).

2-(2-Phenylsulfenylmethylethynyl)-1-(prop-2-ynyloxy)benzene (3c). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55-7.53 (m, 2H, Ar-H), 7.34-7.31 (m, 3H, Ar-H), 7.27-7.22 (m, 2H, Ar-H), 7.00 (d, *J* 8.3 Hz, 1H, Ar-H), 6.92 (dt, *J* 7.5 Hz, *J* 0.6 Hz, 1H, Ar-H), 4.72 (d, *J* 2.4 Hz, 2H, -OCH_2), 3.88 (s,

2H, -SCH_2), 2.50 (t, *J* 2.4 Hz, 1H, alkyne-H).

2-(Phenylethynyl)-1-(prop-2-ynyloxy)benzene (3d). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56-7.54 (m, 2H, Ar-H), 7.50 (dd, *J* 7.6 Hz, *J* 1.6 Hz, 1H, Ar-H), 7.34-7.28 (m, 4H, Ar-H), 7.05 (d, *J* 8.3 Hz, 1H, Ar-H), 6.99 (dt, *J* 7.4 Hz, *J* 0.7 Hz,1H, Ar-H), 4.80 (d, *J* 2.4 Hz, 2H, -OCH_2), 2.53 (t, *J* 2.4 Hz, 1H, alkyne-H).

4-Chloro-2-(phenylethynyl)-1-(prop-2-ynyloxy)benzene (3e). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56-7.54 (m, 2H, Ar-H), 7.48 (d, *J* 2.6 Hz, 1H, Ar-H), 7.36-7.34 (m, 3H, Ar-H), 7.26-7.24 (m, 1H, Ar-H), 6.99 (d, *J* 8.8 Hz, 1H, Ar-H), 4.80 (d, *J* 2.4 Hz, 2H, -OCH_2), 2.54 (t, *J* 2.4 Hz, 1H, alkyne-H).

4-Methyl-2-(phenylethynyl)-1-(prop-2-ynyloxy)benzene (3f). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56-7.54 (m, 2H, Ar-H), 7.35-7.32 (m, 4H, Ar-H), 7.11-7.09 (m, 1H, Ar-H), 6.96 (d, *J* 8.5 Hz, 1H, Ar-H), 4.79 (d, *J* 2.4 Hz, 2H, -OCH_2), 2.52 (t, *J* 2.4 Hz, 1H, alkyne-H), 2.30 (s, 3H, -CH_3).

Synthesis of enynes (5)

To a solution of 2-(hex-1-ynyl)-1-(prop-2-ynyloxy)benzene **3a** (424 mg, 2.0 mmol) and 3-iodo-5,5-dimethylcyclohex-2-enone **4a** (500 mg, 2.0 mmol) in THF (3 mL) was added CuI (19 mg. 0.001 mmol) and $PdCl_2(PPh_3)_2$ (70 mg, 0.001 mmol), Et_3N (1 mL) was then added under a N_2 atmosphere at rt and the mixture was stirred until reaction was complete (monitored by TLC). The reaction was quenched with saturated aqueous NH_4Cl, extracted with Et_2O, and dried over anhydrous $MgSO_4$. After evaporation, chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/20) afforded **5a**.

3-(3-(2-(Hex-1-ynyl)phenoxy)prop-1-ynyl)-5,5-dimethylcyclohex-2-enone (5a). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (dd, *J* 7.5 Hz, *J* 1.7 Hz, 1H, Ar-H), 7.24 (td, *J* 7.9 Hz, *J* 1.7 Hz, 1H, Ar-H), 6.98-6.93 (m, 2H, Ar-H), 6.18 (t, *J* 1.7 Hz, 1H, vinyl-H), 4.95 (s, 2H, -OCH_2), 2.47 (t, *J* 7.0 Hz, 2H, -CH_2), 2.29 (d, *J* 1.6 Hz, 2H, cyclohex-2-enone-CH_2), 2.24 (s, 2H, cyclohex-2-enone-CH_2), 1.63-1.58 (m, 2H, -CH_2), 1.52-1.48 (m, 2H, -CH_2), 1.03 (s, 6H, -2CH_3), 0.95 (t, *J* 7.3 Hz, 3H, -CH_3); ^{13}C NMR(125 MHz, $CDCl_3$): δ 198.79, 157.89, 140.18, 133.84, 132.05, 128.63, 121.84, 114.52, 113.62, 95.23, 94.06, 86.50, 76.29, 57.48, 51.03, 43.93, 33.70, 30.85, 28.06, 22.00, 19.44, 13.66.

3-(3-(2-(Hex-1-ynyl)phenoxy)prop-1-ynyl)cyclohex-2-enone (5b). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* 7.5 Hz, *J* 1.6 Hz, 1H, Ar-H), 7.23 (td, *J* 7.9 Hz, *J* 1.7 Hz, 1H, Ar-H), 6.98-6.93 (m, 2H, Ar-H), 6.18 (s, 1H, vinyl-H), 4.95 (s, 2H, -OCH_2), 2.47 (t, *J* 7.0 Hz, 2H, -CH_2), 2.41-2.38 (m, 4H, cyclohex-2-enone-CH_2), 2.03-1.99 (m, 2H, cyclohex-2-enone-CH_2), 1.63-1.58 (m, 2H, -CH_2), 1.52-1.48 (m, 2H, -CH_2), 0.95 (t, *J* 7.3 Hz, 3H, -CH_3); ^{13}C NMR(125 MHz, $CDCl_3$): δ 198.46, 157.87, 142.35, 133.85, 133.07, 128.63, 121.84, 114.53, 113.64, 95.24, 94.43, 86.29, 76.29, 57.46, 37.28, 30.86, 30.11, 22.47, 22.01, 19.45, 13.66.

5,5-Dimethyl-3-(3-(2-((trimethylsilyl)ethynyl)phenoxy)prop-1-ynyl)cyclohex-2-enone (5c). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* 7.8 Hz, *J* 1.6 Hz, 1H, Ar-H), 7.28 (td, *J* 7.9 Hz, *J* 1.6 Hz, 1H, Ar-H), 6.97-6.94 (m, 2H, Ar-H), 6.18 (t, *J* 1.6 Hz, 1H, vinyl-H), 4.94 (s, 2H, -OCH_2), 2.29 (d, *J* 1.6 Hz, 2H, cyclohex-2-enone-CH_2), 2.24 (s, 2H, cyclohex-2-enone-CH_2), 1.04 (s, 6H,

-2CH_3), 0.26 (s, 9H, -Si(CH_3)$_3$); ^{13}C NMR(125 MHz, $CDCl_3$): δ 198.74, 158.42, 140.10, 134.18, 132.01, 129.73, 121.79, 113.68, 113.64, 100.76, 99.20, 93.87, 86.57, 57.54, 51.02, 43.94, 33.68, 28.04, 0.01.

3-(3-(2-((Trimethylsilyl)ethynyl)phenoxy)prop-1-ynyl)cyclohex-2-enone (5d). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* 7.5 Hz, *J* 1.5 Hz, 1H, Ar-H), 7.28 (td, *J* 7.9 Hz, *J* 1.6 Hz, 1H, Ar-H), 6.98-6.94 (m, 2H, Ar-H), 6.18 (s, 1H, vinyl-H), 4.96 (s, 2H, -OCH_2), 2.42-2.38 (m, 4H, cyclohex-2-enone-CH_2), 2.03-1.99 (m, 2H, cyclohex-2-enone-CH_2), 0.26 (s, 9H, -Si(CH_3)$_3$); ^{13}C NMR(125 MHz, $CDCl_3$): δ 198.42, 158.38, 142.26, 134.20, 133.04, 129.72, 121.81, 113.76, 113.66, 100.77, 99.19, 94.24, 86.34, 57.53, 37.25, 30.08, 22.45, 0.01.

3-(3-(2-(3-(Phenylthio)prop-1-ynyl)phenoxy)prop-1-ynyl)cyclohex-2-enone (5e). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* 7.7 Hz, 2H, Ar-H), 7.34-7.22 (m, 5H, Ar-H), 6.97-6.92 (m, 2H, Ar-H), 6.16 (s, 1H, vinyl-H), 4.89 (s, 2H, -OCH_2), 3.88 (s, 2H, -SCH_2), 2.39-2.36 (m, 4H, cyclohex-2-enone-CH_2), 2.00-1.97 (m, 2H, cyclohex-2-enone-CH_2); ^{13}C NMR(125 MHz, $CDCl_3$): δ 198.43, 158.07, 142.25, 135.36, 133.91, 133.10, 130.48, 129.41, 128.88, 126.88, 121.76, 113.47, 113.37, 94.18, 89.87, 86.39, 79.57, 57.31, 37.24, 30.06, 24.06, 22.43.

5,5-Dimethyl-3-(3-(2-(phenylethynyl)phenoxy)prop-1-ynyl)cyclohex-2-enone (5f). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.51 (m, 3H, Ar-H), 7.35-7.29 (m, 4H, Ar-H), 7.02 (t, *J* 7.9 Hz, 2H, Ar-H), 6.19 (t, *J* 1.5 Hz, 1H, vinyl-H), 5.00 (s, 2H, -OCH_2), 2.28 (d, *J* 1.5 Hz, 2H, cyclohex-2-enone-CH_2), 2.23 (s, 2H, cyclohex-2-enone-CH_2), 1.02 (s, 6H, -2CH_3); ^{13}C NMR(125 MHz, $CDCl_3$): δ 198.75, 158.03, 140.10, 133.70, 132.09, 131.64, 129.54, 128.30, 128.27, 123.46, 121.96, 113.86, 113.75, 93.95, 93.91, 86.65, 85.37, 57.64, 51.03, 43.92, 33.69, 28.05.

3-(3-(4-Chloro-2-(phenylethynyl)phenoxy)prop-1-ynyl)cyclohex-2-enone (5g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.53 (m, 2H, Ar-H), 7.49 (d, *J* 2.6 Hz, 1H, Ar-H), 7.36-7.34 (m, 3H, Ar-H), 7.27-7.25 (m, 1H, Ar-H), 6.96 (d, *J* 8.7 Hz, 1H, Ar-H), 6.18 (s, 1H, vinyl-H), 4.97 (s, 2H, -OCH_2), 2.41-2.38 (m, 4H, cyclohex-2-enone-CH_2), 2.01-1.99 (m, 2H, cyclohex-2-enone-CH_2); ^{13}C NMR(125 MHz, $CDCl_3$): δ 198.03, 156.58, 142.00, 133.28, 133.12, 131.71, 129.26, 128.64, 128.37, 126.88, 122.94, 115.53, 114.94, 95.03, 93.61, 86.72, 84.05, 57.84, 37.27, 30.07, 22.45.

5,5-Dimethyl-3-(3-(4-Methyl-2-(phenylethynyl)phenoxy)prop-1-ynyl)cyclohex-2-enone (5h). ^{1}H NMR(500 MHz, $CDCl_3$): δ 7.56-7.54 (m, 2H, Ar-H), 7.35-7.32 (m, 4H, Ar-H), 7.10 (dd, *J* 8.0 Hz, *J* 2.0 Hz, 1H, Ar-H), 6.92 (d, *J* 8. 0 Hz, 1H, Ar-H), 6.19 (t, *J* 1.7 Hz, 1H, vinyl-H), 4.97 (s, 2H, -OCH_2), 2.30 (s, 3H, -CH_3), 2.28 (d, *J* 1.7 Hz, 2H, cyclohex-2-enone-CH_2), 2.23 (s, 2H, cyclohex-2-enone-CH_2), 1.03 (s, 6H, -2CH_3); ^{13}C NMR(125 MHz, $CDCl_3$): δ 198.83, 155.98, 140.22, 134.04, 132.00, 131.61, 131.49, 130.14, 128.27, 128.21, 123.48, 114.08, 113.59, 94.21, 93.60, 86.51, 85.53, 57.91, 51.01, 43.91, 33.68, 28.04, 20.36.

Synthesis of (6)

To a solution of 3-(3-(2-(hex-1-ynyl)phenoxy)-prop-1-ynyl)-5,5-dimethyl- cyclohex-2-enone **5a** (60 mg, 0.18 mmol) in EtOH (1.5 mL) was added Et_3N (0.5 mL) under a N_2 atmosphere. Then the reaction mixture was warmed to 80 °C and stirred until reaction was completed (monitored

by TLC). The solvent was then evaporated and chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/15) afforded **6a**.

12-Butyl-9,9-dimethyl-9,10-dihydro-6*H*-naphtho[2,3-c]chromen-11(8*H*)-one (6a). Solid, mp 86-88 °C; ^{1}H NMR(500 MHz, $CDCl_3$): δ 7.72 (d, *J* 7.5 Hz, 1H, Ar-H), 7.28-7.25 (m, 1H, Ar-H), 7.09 (t, *J* 7.0 Hz, 2H, Ar-H), 6.93 (s, 1H, Ar-H) , 4.88 (s, 2H, -OCH_2), 3.39 (s, 2H, -CH_2), 2.86 (s, 2H, -CH_2), 2.54 (s, 2H, -CH_2), 1.60 (s, 2H, -CH_2), 1.46-1.40 (m, 2H, -CH_2), 1.09 (s, 6H, -2CH_3), 0.94 (t, *J* 7.5 Hz, 3H, -CH_3); ^{13}C NMR (125MHz, $CDCl_3$): δ 200.23, 156.88, 143.54, 142.93, 139.89, 131.72, 129.52, 128.80, 128.35, 124.07, 123.76, 121.68, 117.50, 70.09, 55.17, 45.16, 33.85, 33.09, 30.33, 28.14, 22.88, 13.78; MS(70eV, EI) *m/z* (%): 334(M^+, 100); HRMS: Calcd for $C_{23}H_{26}O_2$: 334.1933. Found: 334.1922; IR ν_{max} (cm^{-1}): 2957, 1687, 1458, 1221, 1025, 761.

12-Butyl-9,10-dihydro-6*H*-naphtho[2,3-c]chromen-11(8*H*)-one (6b). Solid, mp 90-92 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, *J* 7.0 Hz, 1H, Ar-H), 7.27-7.24 (m, 1H, Ar-H), 7.08 (t, *J* 7.0 Hz, 2H, Ar-H), 6.95 (s, 1H, Ar-H) , 4.87 (s, 2H, -OCH_2), 3.36 (s, 2H, -CH_2), 2.93 (t, *J* 6.5 Hz, 2H, -CH_2), 2.69 (t, *J* 6.5 Hz, 2H, -CH_2), 2.10-2.07 (m, 2H, -CH_2), 1.61-1.60 (m, 2H, -CH_2), 1.46-1.41 (m, 2H, -CH_2), 0.94 (t, *J* 7.0z, 3H, -CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.25, 156.91, 145.21, 142.92, 139.65, 132.87, 129.59, 128.84, 128.32, 124.08, 123.05, 121.70, 117.54, 70.08, 41.46, 33.92, 31.17, 30.36, 22.91, 22.69, 13.82; MS(70eV, EI) *m/z* (%): 306(M^+, 100); HRMS: Calcd for $C_{21}H_{22}O_2$: 306.1620. Found: 306.1610; IR ν_{max} (cm^{-1}): 2952, 1669, 1461, 1216, 1030, 750.

9,9-Dimethyl-12-(trimethylsilyl)-9,10-dihydro-6*H*-naphtho[2,3-c]chromen-11(8*H*)-one (6c). Solid, mp 142-144 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (dd, *J* 8.0 Hz, *J* 1.5 Hz, 1H, Ar-H), 7.28-7.26 (m, 1H, Ar-H), 7.07-7.04 (m, 2H, Ar-H), 6.97 (s, 1H, Ar-H) , 4.94 (s, 2H, -OCH_2), 2.83 (s, 2H, -CH_2), 2.54 (s, 2H, -CH_2), 1.11 (s, 6H, -2CH_3), 0.13 (s, 9H, -Si(CH_3)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.93, 155.95, 141.78, 141.47, 141.16, 139.85, 138.35, 129.71, 129.63, 127.15, 125.61, 121.92, 117.04, 69.88, 52.98, 44.22, 33.47, 28.34, 3.84; MS(70eV, EI) *m/z* (%): 350(M^+, 2); HRMS: Calcd for $C_{22}H_{26}O_2Si$: 350.1702. Found: 350.1718; IR ν_{max} (cm^{-1}): 2953. 1673, 1249, 876, 760.

12-(Trimethylsilyl)-9,10-dihydro-6*H*-naphtho[2,3-c]chromen-11(8*H*)-one (6d). Solid, mp 158-160 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (dd, *J* 8.0 Hz, *J* 1.5 Hz, 1H, Ar-H), 7.29-7.25 (m, 1H, Ar-H), 7.07-7.04 (m, 2H, Ar-H), 7.01 (s, 1H, Ar-H), 4.94 (s, 2H, -OCH_2), 2.93 (t, *J* 5.5 Hz, 2H, -CH_2), 2.70 (t, *J* 5.5 Hz, 2H, -CH_2), 2.17-2.10 (m, 2H, -CH_2), 0.14 (s, 9H, -Si(CH_3)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.88, 155.93, 143.35, 142.27, 142.06, 139.46, 138.44, 129.61, 129.60, 127.07, 124.88, 121.85, 116.99, 69.82, 39.36, 30.37, 22.99, 3.80; MS(70eV, EI) *m/z* (%): 322(M^+, 1.5); HRMS: Calcd for $C_{20}H_{22}O_2Si$: 322.1389. Found: 322.1402; IR ν_{max} (cm^{-1}): 2942, 1679, 1246, 866,758.

12-(Phenylthiomethyl)-9,10-dihydro-6*H*-naphtho[2,3-c]chromen-11(8*H*)-one (6e). Solid, mp 90-92 °C; ^{1}H NMR(500 MHz, $CDCl_3$): δ 8.12 (dd, *J* 8.0 Hz, *J* 1.5 Hz, 1H, Ar-H), 7.26-6.99 (m, 9H, Ar-H), 5.39(br, 1H, -SCH_2), 4.87 (s, 2H, -OCH_2), 4.65(br, 1H, -SCH_2), 2.93 (t, *J* 6.0 Hz, 2H, -CH_2), 2.70 (t, *J* 6.0 Hz, 2H, -CH_2), 2.12-2.06 (m, 2H, -CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.18, 156.90, 145.29, 139.64, 136.81, 135.74, 132.99, 130.41, 129.70, 129.34, 128.78, 128.76,

126.19, 124.37, 123.22, 122.15, 117.52, 69.80, 41.02, 35.00, 30.85, 22.64; MS(70eV, EI) *m/z* (%): 372(M^+, 22); HRMS: Calcd for $C_{24}H_{20}O_2S$: 372.1184. Found: 372.1206; IR ν_{max} (cm^{-1}): 2950, 1682, 1436, 1026, 751.

9,9-Dimethyl-12-phenyl-9,10-dihydro-6*H*-naphtho[2,3-c]chromen-11(8*H*)-one (6f). Solid, mp 190-192 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.35 (m, 3H, Ar-H), 7.11-7.10 (m, 3H, Ar-H), 7.05-7.01 (m, 1H, Ar-H), 6.96 (dd, *J* 8.0 Hz, *J* 1.0 Hz, 1H, Ar-H), 6.50 (td, *J* 8.0 Hz, *J* 1.5 Hz, 1H, Ar-H), 6.41 (dd, *J* 8.0 Hz, *J* 1.5 Hz, 1H, Ar-H), 4.97 (s, 2H, -OCH_2), 2.91 (s, 2H, -CH_2), 2.43 (s, 2H, -CH_2), 1.09 (s, 6H, -2CH_3); ^{13}C NMR (125MHz, $CDCl_3$): δ 198.39, 156.50, 142.71, 141.02, 139.81, 139.22, 131.61, 129.01, 128.81, 128.59, 128.45, 128.40, 126.91, 125.34, 123.12, 121.16, 117.14, 69.41, 54.58, 44.70, 33.65, 28.25; MS(70eV, EI) *m/z* (%): 354(M^+, 100); HRMS: Calcd for $C_{25}H_{22}O_2$: 354.1620. Found: 354.1631; IR ν_{max} (cm^{-1}): 2956, 1693, 1460, 1225, 1049, 759, 698.

2-Chloro-12-phenyl-9,10-dihydro-6*H*-naphtho[2,3-c]chromen-11(8*H*)-one (6g). Solid, mp 184-186 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43-7.40 (m, 3H, Ar-H), 7.13 (s, 1H, Ar-H), 7.10-7.08 (m, 2H, Ar-H), 6.99 (dd, *J* 8.5 Hz, *J* 2.0 Hz, 1H, Ar-H), 6.87 (d, *J* 8.50 Hz, 1H, Ar-H), 6.25 (d, *J* 2.5 Hz, 1H, Ar-H), 4.97 (s, 2H, -OCH_2), 3.01 (t, *J* 6.0 Hz, 2H, -CH_2), 2.59 (t, *J* 7.0 Hz, 2H, -CH_2), 2.17-2.11 (m, 2H, -CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.04, 154.98, 145.09, 140.40, 140.34, 138.52, 132.71, 128.80, 128.77, 128.64, 128.39, 127.64, 127.34, 126.25, 124.75, 124.34, 118.24, 69.42, 40.81, 30.70, 22.85; MS(70eV, EI) *m/z* (%): 360(M^+, 100); HRMS: Calcd for $C_{23}H_{17}ClO_2$: 360.0917. Found: 360.0908; IR ν_{max} (cm^{-1}): 2957, 1685, 1479, 1023, 818, 699.

2,9,9-Trimethyl-12-phenyl-9,10-dihydro-6H-naphtho[2,3-c]chromen-11(8H)-one (6h). solid, mp 198-200 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-7.36 (m, 3H, Ar-H), 7.11-7.08 (m, 3H, Ar-H), 6.84 (s, 2H, Ar-H), 6.09 (s, 1H, Ar-H), 4.94 (s, 2H, -OCH_2), 2.92 (s, 2H, -CH_2), 2.44 (s, 2H, -CH_2), 1.83 (s, 3H, -CH_3), 1.09 (s, 6H, -2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.44, 154.22, 142.61, 141.22, 139.73, 139.20, 131.37, 130.11, 129.63, 129.12, 128.96, 128.62, 128.33, 126.74, 125.38, 122.61, 116.51, 69.42, 54.56, 44.68, 33.66, 28.24, 20.72; MS(70eV, EI) *m/z* (%): 368(M^+, 100); HRMS: Calcd for $C_{26}H_{24}O_2$: 368.1776. Found: 368.1780; IR ν_{max} (cm^{-1}):2969, 1687, 1492, 1230, 1045, 817, 699.

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References and Notes

1. Devlin, J. P. Can. J. Chem. 1975, 53, 343. (b) Devlin, J. P. Can. J. Chem. 1975, 53, 350. (c) Stewart, P. B.; Devlin, J. P.; Freter, K. R. *Fed. Proc.* **1974**, *33*, 762. (d) Gaoni, Y.; Mechoulam, R. *J. Am. Chem. Soc.* **1971**, *93*, 217. (e) Bowd, A.; Swann, D. A.; Turnbull, J. H. *J. Chem. Soc., Chem. Commun.* **1975**, 797. (f) Kogan, N. M.; Rabinowitz, R.; Levi, P.; Gibson, D.; Sandor, P.; Schlesinger, M.; Mechoulam, R. *J. Med. Chem.* **2004**, *47*, 3800.
2. Huang, C.-G.; Beveridge, K. A.; Wan, P. *J. Am. Chem. Soc.* **1991**, *113*, 7676. (b) Shi, Y.; Wan, P. *J. Chem. Soc., Chem. Commun.* **1995**, 1217. (c) Shi, Y.; Wan, P. *Chem. Commun.* **1997**, 273.
3. Huang, C.-G.; Beveridge, K. A.; Wan, P. *J. Am. Chem. Soc*. **1991**,*113*, 7676. (b) Terao, Y.; Wakui, H.; Nomoto, M.; Satoh, T.; Miura, M.; Nomura, M. *J. Org. Chem*. **2003**, *68*, 5236. (c) Bajracharya, G. B.; Daugulis, O. *Org. Lett.* **2008**, *10*, 4625. (d) Wang, B.; Li, M.; Xu, S.; Song, H.; Wang, B. *J. Org. Chem.* **2006**, *71*, 8291. (e) Jana, R.; Chatterjee, I.; Samanta, S.; Ray, J. K. *Org. Lett.* **2008**, *10*, 4795.
4. Shen, R.; Huang, X. *Org. Lett*. **2008**, *10*, 3283.
5. Kimura, M.; Ezoe, A.; Mori, M.; Tamaru, Y. *J. Am. Chem. Soc.* **2005**, *127*, 201. (b) Arcadi, A.; Cacchi, S.; Rosario, M. D.; Fabrizi, G.; Marinelli, F. *J. Org. Chem.* **1996**, *61*, 9280.
6. Barnier J. P., Blanco L. *Synth. Commun.* **2003**, *33*, 2487.
7. At present, the reason for the lower yield is not clear. Some polymerization may occur during the reaction due to the high reactivity of the intermediate. Mostly, only one reaction product could be identified during the reaction using thin layer chromatography.

