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Divergent Strategy for the Diastereoselective Synthesis of the Tricyclic 6,7-Diaryltetrahydro-6*H*-benzo[*c*]chromene Core via Pt(IV)-Catalyzed Cycloaddition of *o*-Quinone Methides and Olefin Ring-Closing Metathesis

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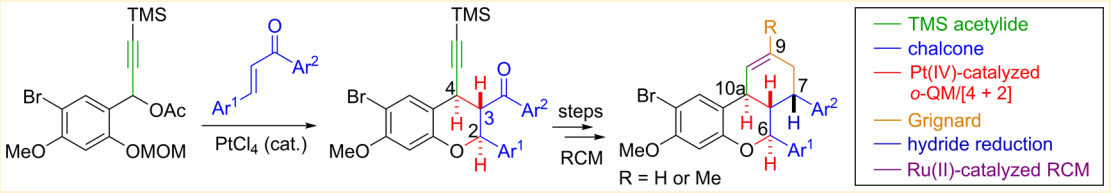
Supporting Information



ABSTRACT: A divergent strategy for the synthesis of the tricyclic 6,7-diaryltetrahydro-6*H*-benzo[*c*]chromene core was successfully developed. The 2,3-trans, 2,4-cis trisubstituted chroman moiety was formed via highly efficient and stereoselective Pt(IV)-catalyzed cycloaddition reactions of the corresponding quinone methides with chalcones. Subsequent steps provided the common diene alcohol, which underwent $BF_3{\cdot}Et_2O$-mediated Et_3SiH reduction and olefin ring-closing metathesis (RCM) using Ru(II) catalysts. The sequence of the final two steps provided a handle to diversify the stereochemical outcomes at C6 as well as C10a.

INTRODUCTION

The tricyclic tetrahydro- and hexahydro-6*H*-benzo[*c*]-chromenes are the cores of naturally occurring as well as synthetic compounds, many of which display a wide range of interesting and important biological activities.[1−9] Palodesangrens, a group of natural Diels−Alder products isolated from *Brosimum rubescens* Taubert, possess the common tetracyclic tetrahydrobenzo[*c*]pyranochromenone **1**, which also features a unique tricyclic tetrahydro-6*H*-benzo[*c*]chromene core structure with two aryl substituents at C6 and C7 (**2**, Figure 1).[10] Although several elegant approaches have been successfully developed for the total synthesis of some tetrahydro- as well as hexahydro-6*H*-benzo[*c*]chromenes such as (+)-machaeriol A (**3**), (+)-machaeriol B (**4**),[11] (−)-nabilone (**5**),[12] (+)-conicol (**6**),[13] and Δ^9-*cis*- and Δ^9-*trans*-tetrahydrocannabinols (Δ^9-THC, **7a**,**b**),[14] among others,[15] those toward the synthesis of the more complex tricyclic core of palodesangrens with four contiguous stereocenters at C6, C6a, C7, and C10a, to the best of our knowledge, have never been reported.

The tricyclic core **2** can be considered as a 3,4-cyclohexenyl-fused chroman derivable from a 3,4-functionalized chroman. In recent years, we have investigated and reported the use of *p*-toluenesulfonic acid immobilized on silica (PTS-Si) as well as $PtCl_4$ as the mediator/catalyst for the generation and [4 + 2] cycloaddition reactions of *o*-quinone methides (*o*-QMs) to prepare functionalized chromans and others.[16] Herein we report, for the first time, the stereoselective synthesis of the 6,7-diaryltetrahydro-6*H*-benzo[*c*]chromene structurally related to the tricyclic core of palodesangrens.

RESULTS AND DISCUSSION

Initially, we first considered the simplified tricyclic compound **8**, where the substituent at C9 was a hydrogen atom instead of a methyl group. In addition, to facilitate the quinone methide chemistry, a methoxy group was placed at C3 while bromine was present at C2.[16] Thus, our approach toward the synthesis of **8** where both Ar groups at C6 and C7 were 4-methoxyphenyl can be outlined retrosynthetically as shown in Scheme 1. While it is plausible to form **8** via an intramolecular [4 + 2] cycloaddition reaction of the diacetate precursor **9**, the aldol condensation between benzaldehyde **10** and ketone **11** failed. The presence of an Ar group at the allylic position of **11** renders the proton at that position more acidic; the preformed

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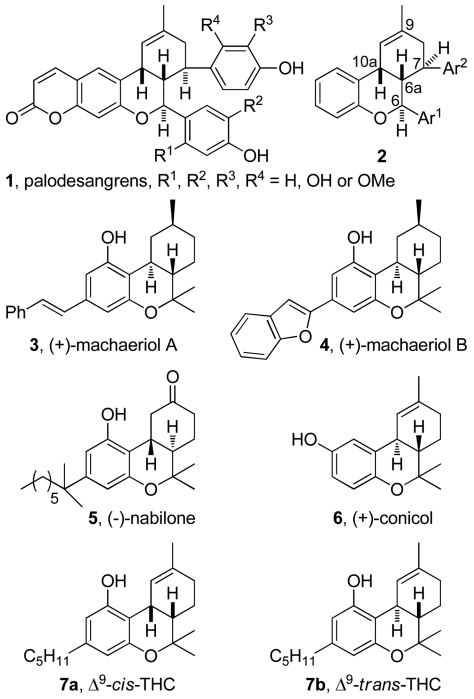
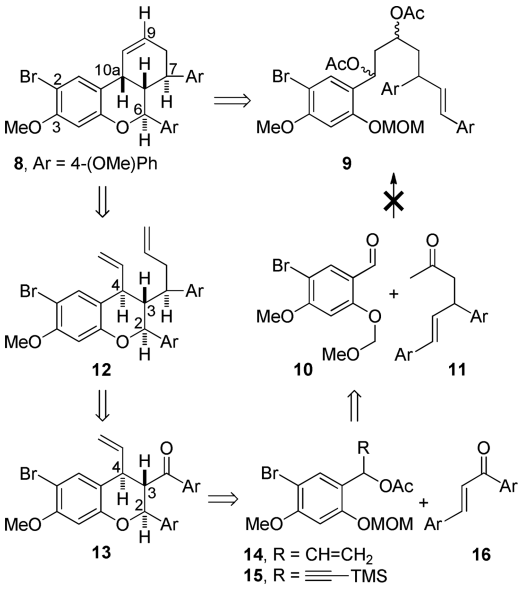


Figure 1. General structures of palodesangrens (**1**), the tricyclic core **2**, and some natural and synthetic tricyclic tetrahydro- as well as hexahydro-6*H*-benzo[*c*]chromenes **3**−**7**.

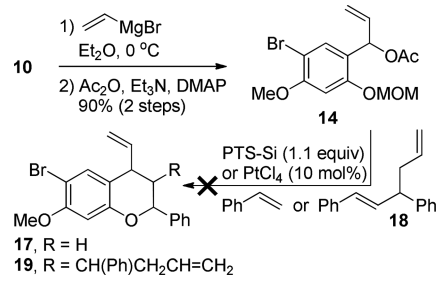
Scheme 1. Retrosynthetic Analysis of the Simplified Tricyclic Compound 8



enolate of **11** under basic conditions may be quenched by this proton, presumably via proton transfer.[17] Thus, the intermolecular [4 + 2] cycloaddition reaction was considered as a means to install the requisite 2,3-*trans* 2,4-*cis* chroman core of **8**. The olefin moiety of the cyclohexenyl ring of **8** could arise from the diene **12** via ring-closing metathesis (RCM).[18] The allyl group of the diene **12** could be installed by allylation followed by reduction (or vice versa) of the ketone functional group in **13**. As the quinone methide precursor, the corresponding benzyl acetates **14** and **15** could be prepared from the aldehyde **10** prior to its [4 + 2] cycloaddition reaction with the chalcone **16**.

Formation of Chroman. The acetate **14**, prepared in two steps from **10**, was first considered as the quinone methide precursor to prepare **8** (Scheme 2). However, **14** did not

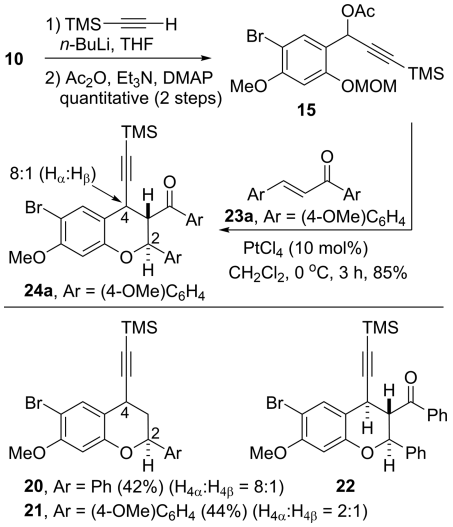
Scheme 2. Attempted Synthesis of the Chromans 17 and 19



provide the corresponding product **17** from the anticipated [4 + 2] cycloaddition reactions with simple styrene; decomposition of **14** as well as the allylic alcohol (the intermediate prior to acetylation) was observed under both PTS-Si and $PtCl_4$ conditions.[19] Similarly, the [4 + 2] cycloaddition reactions of **14** with the diene **18**[20] did not proceed to furnish the desired 2,3,4-trisubstituted chroman **19**.

Due to the apparently low stability of **14** under the PTS-Si/$PtCl_4$-mediated [4 + 2] cycloaddition reaction conditions, the benzyl acetate **15** bearing a TMS-protected acetylene moiety as a masked vinyl group[21] was then considered. The benzyl acetate **15** was prepared in a straightforward manner from the aldehyde **10** via TMS acetylide addition followed by acetylation in quantitative yield over two steps (Scheme 3). With the

Scheme 3. Synthesis of the Ketone Chroman 24a



benzyl acetate **15** in hand, its [4 + 2] cycloaddition reactions with styrene and 4-vinylanisole were carried out using PTS-Si; moderate yields (42−44%) of the desired chromans **20** and **21** were obtained, each as a mixture of inseparable 2,4-cis and 2,4-trans diastereomers.[22] The corresponding ketone chroman **22** from a similar reaction using (*E*)-chalcone under $PtCl_4$ catalysis was also produced, presumably in low yield, as evidenced by the ^1H NMR of the semipurified product.[23] Nevertheless, the results suggested that the $PtCl_4$-catalyzed [4 + 2] cycloaddition

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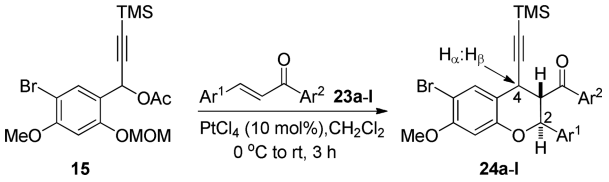
Table 1. $PtCl_4$-Catalyzed [4 + 2] Cycloaddition Reactions between Benzyl Acetate 15 and Various Chalcones 23a–l[a]



entry	chalcone	Ar^1	Ar^2	product	H_α:H_β	yield (%)[b]
1	**23a**	$(4\text{-OMe})C_6H_4$	$(4\text{-OMe})C_6H_4$	**24a**	8:1	85
2	**23b**	$(3,4\text{-(OMe)}_2)C_6H_3$	$(4\text{-OMe})C_6H_4$	**24b**	8:1	56
3	**23c**	$(3,4,5\text{-(OMe)}_3)C_6H_2$	$(4\text{-OMe})C_6H_4$	**24c**	7:1	41
4	**23d**	$(4\text{-OMe})C_6H_4$	$(3\text{-OMe})C_6H_4$	**24d**	>99:1	60
5	**23e**	$(3,4\text{-(OMe)}_2)C_6H_3$	$(3\text{-OMe})C_6H_4$	**24e**	>99:1	68
6	**23f**	$(3,4,5\text{-(OMe)}_3)C_6H_2$	$(3\text{-OMe})C_6H_4$	**24f**	6:1	44
7	**23g**	$(4\text{-OMe})C_6H_4$	$(3,4\text{-(OMe)}_2)C_6H_3$	**24g**	8:1	98
8	**23h**	$(3,4\text{-(OMe)}_2)C_6H_3$	$(3,4\text{-(OMe)}_2)C_6H_3$	**24h**	9:1	70
9	**23i**	$(3,4,5\text{-(OMe)}_3)C_6H_2$	$(3,4\text{-(OMe)}_2)C_6H_3$	**24i**	5:1	38
10	**23j**	$(4\text{-OMe})C_6H_4$	$(3,4,5\text{-(OMe)}_3)C_6H_2$	**24j**	>99:1	53
11	**23k**	$(3,4\text{-(OMe)}_2)C_6H_3$	$(3,4,5\text{-(OMe)}_3)C_6H_2$	**24k**	>99:1	42
12	**23l**	$(3,4,5\text{-(OMe)}_3)C_6H_2$	$(3,4,5\text{-(OMe)}_3)C_6H_2$	**24l**	5:1	41

[a]Unless otherwise noted, the reactions were performed using $PtCl_4$ (10 mol %) and chalcone **23a–l** (2 equiv) in CH_2Cl_2 as solvent. [b]Isolated yields.

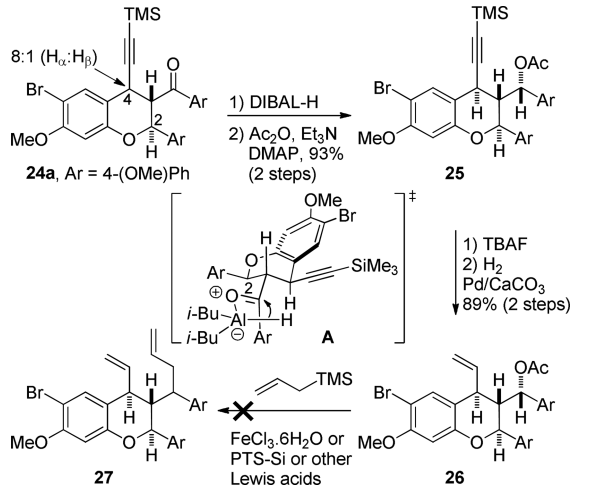
reaction between the benzyl acetate **15** as a quinone methide precursor and a chalcone as a dienophile was feasible. After some experimentation, upon reaction with chalcone **23a** containing a 4-methoxy substituent on each aromatic ring, the benzyl acetate **15** gave the corresponding ketone chroman **24a** in 85% yield as an inseparable 8:1 mixture of 2,4-cis and 2,4-trans diastereomers.[22] Presumably, the ratio of 2,4-cis to 2,4-trans reflected the endo preference at the transition state of the [4 + 2] cycloaddition.[16]

The scope of the [4 + 2] cycloaddition reactions between the benzyl acetate **15** and various substituted chalcones **23a–l** was investigated. Chalcones **23a–l** with different numbers and substitution patterns of the methoxy group were used; the results are summarized in Table 1.

Moderate to excellent yields (up to 98%) and C2–C4 diastereoselectivity favoring the cis form (5:1 to >99:1) could be obtained from these [4 + 2] cycloaddition reactions. In general, chalcones containing 4-methoxyphenyl group(s) gave good yields and C2–C4 diastereoselectivity for each series (entries 1, 4, 7, and 10). Those chalcones containing 3,4,5-trimethoxyphenyl group(s) as Ar^1, on the other hand, gave lower yields (38–53%, entries 3, 6, 9, and 12) and C2–C4 diastereoselectivity (5:1). It should be noted that chalcones containing 3,5-dimethoxyphenyl group(s), as either Ar^1 or Ar^2, did not appreciably undergo the [4 + 2] cycloaddition reactions (<12%).[24] Due to the better yields, the ketone chromans **24a,e,g,h** were chosen for the subsequent steps.

Installation of the Diene. With chroman **24a** in hand, we then investigated a sequence of (1) desilylation of the TMS group, (2) Lindlar hydrogenation of the terminal alkyne to the corresponding olefin, and (3) allylation of the ketone (or alcohol/acetate) moiety via a Hosomi–Sakurai-type reaction. Cleavage of the TMS group on the TMS-acetylene moiety using *n*-Bu_4NF (TBAF) led to a product from the chroman ring opening. Thus, the ketone was first reduced using DIBAL-H to the alcohol, which was acetylated under standard conditions to give the acetate **25** in 93% yield over two steps as a single diastereomer (Scheme 4).[25] Stereoselectivity of the DIBAL-H reduction could be accounted for by the approach of the reagent, presumably from the less hindered side of the ketone,

Scheme 4. Attempted Synthesis of the Diene 27



as shown in **A**. Subsequent TBAF-mediated desilylation followed by hydrogenation of the terminal acetylene using Lindlar's catalyst produced the corresponding olefin **26** in 89% yield over two steps. However, allylation of **26** or its *N*-tosylated amine, under various conditions, did not proceed to give the desired diene **27**.[20,26]

At this point, allylation of the ketone via allyl Grignard followed by reduction of the corresponding tertiary alcohol using Et_3SiH was considered as an alternative to provide the diene **27**. After some experimentation, it was found that desilylation of **24a** could be smoothly affected by Cs_2CO_3 in methanol[27] to furnish the corresponding ketone alkyne **28** in 91% yield as a single diastereomer (Scheme 5). Isomerization at C4 of the minor diastereomer may occur concomitantly under these basic conditions. Hydrogenation of **28** with Lindlar's catalyst at 300 psi of hydrogen gas[28] using a Paar apparatus provided the ketone olefin, which was then treated with allyl Grignard in a diethyl ether (Et_2O):THF (2:1) solvent mixture to provide the diene alcohol **29** in 82% yield over two steps as a 2:1 inseparable mixture of two diastereomers.[29] Reduction of

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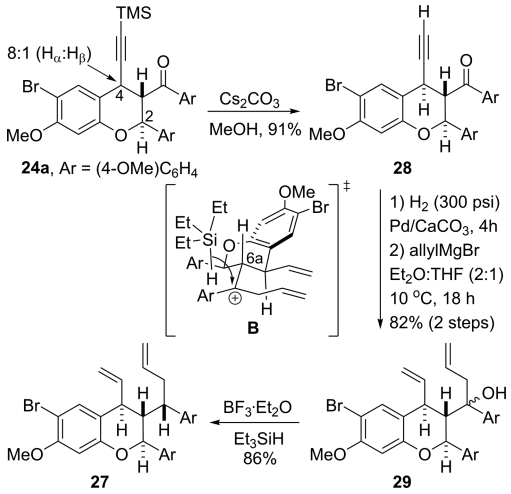
Scheme 5. Synthesis of the Diene 27

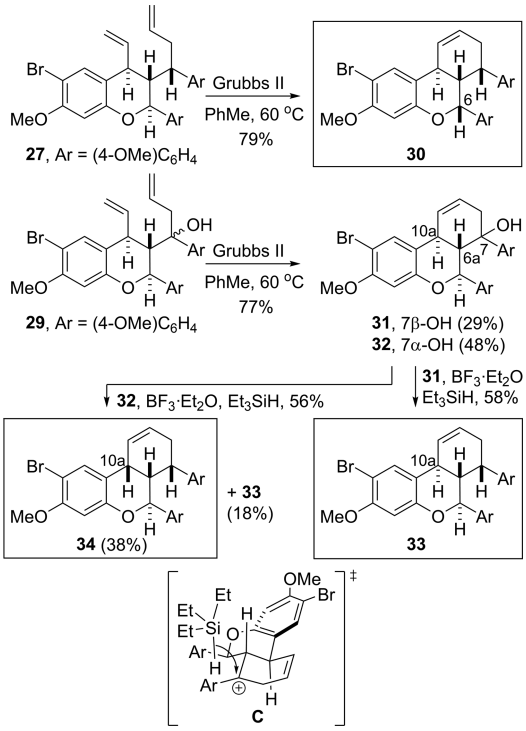


the hydroxy group of the diene alcohol **29** could be effectively performed by using Et_3SiH in the presence of $BF_3{\cdot}Et_2O$[30,31] to furnish the desired diene **27** in 86% yield as a single diastereomer, presumably via the transition state **B**, which delivered the hydride from Et_3SiH syn to the C6a proton.

Ring-Closing Metathesis. With the diene **27** in hand, we next performed the RCM using the second-generation Grubbs ruthenium catalyst. After some experimentation, it was found that RCM of the diene **27** could be best carried out in toluene at 60 °C for 18 h, giving the desired tricyclic compound **30** in 79% yield as a single diastereomer. Surprisingly, from careful NMR analysis of **30**, the unanticipated epimerization at the 6-position of the tetrahydro-6*H*-benzo[*c*]chromene (C2 of the chroman) took place under the RCM reaction conditions (Scheme 6).[25] Addition of 1,4-benzoquinone to suppress isomerization under the RCM conditions did not improve the outcome of the reactions.[32] Thus, as an alternative, the sequence of alcohol reduction by Et_3SiH and RCM was investigated. When the diene alcohol **29** was subjected to the RCM conditions, a separable diastereomeric mixture of the tricyclic alcohols **31** and **32** was obtained in 29% and 48% yields, respectively.[33] The alcohol **31** (7*β*-OH) then underwent $BF_3{\cdot}Et_2O$-mediated Et_3SiH reduction to provide the tricyclic product **33**[25] ($H_{10a\alpha}$) as a single diastereomer in 58% yield. Interestingly, when the alcohol **32** (7*α*-OH) underwent such reduction, a separable mixture of **33** and **34**[25] ($H_{10a\beta}$) was obtained in 18% and 38% yields, respectively. It should be noted that, under the reaction conditions, **34** was formed as a result of reduction at C7 as well as epimerization at C10a. This $BF_3{\cdot}Et_2O$-mediated Et_3SiH reduction at C7 for both alcohols **31** and **32** was stereoselective, presumably due to the presence of the more rigid cyclohexenyl ring fused with the chroman system (transition state **C**), resulting in the delivery of the hydride syn to the C6a proton on the adjacent carbon. Thus, the sequence of $BF_3{\cdot}Et_2O$-mediated Et_3SiH reduction and RCM of the diene alcohol **29** serves as a handle to provide differently stereodefined tricyclic products. In other words, generation of a specific diastereomer of the desired tricyclic product (**30**, **33**, and **34**) from the common diene alcohol **29** is under the reaction sequence control.

Scope of the Strategy. The developed strategy was then applied to the synthesis of other 6,7-diaryltetrahydro-6*H*-benzo[*c*]chromenes from the corresponding chromans **24e,g,h**

Scheme 6. Synthesis of the Tricyclic 6,7-Diaryltetrahydro-6*H*-benzo[*c*]chromenes 30, 33, and 34



(Scheme 7). With the exception of the diene **37a** from the reduction of the diene alcohol **36a** (3-OMePh as the Ar^2), the other corresponding intermediates **35a–c**, **36a–c**, **37b,c**, **39a–c**, and **40a–c** could be prepared in moderate to excellent yields en route to the desired tricyclic compounds **38b,c**, **41b,c**, and **42a–c** (Table 2).[34] It should be noted that the $BF_3{\cdot}Et_2O$-mediated Et_3SiH reduction of **36a** (Ar^1 = 3,4-$(OMe)_2$Ph; Ar^2 = 3-OMePh) gave no desired product **37a**; only a mixture of unidentifiable compounds could be obtained. Hence, without **37a**, the subsequent Grubbs II RCM could not be performed to yield the tricyclic product **38a**. In addition, when the tricyclic alcohol **39a** underwent the $BF_3{\cdot}Et_2O$-mediated Et_3SiH reduction, the expected tricyclic product **41a** was not obtained. The tricyclic compound **42a**, with concomitant 10a-isomerization, was produced from the reaction instead. Interestingly, when **40a** was subjected to this reduction, **42a**, one of the expected products, was obtained in low yield (15%) along with the nonreduced product with 10a,6a-isomerization **43**[35] (Figure 2) in 19% yield. Interestingly, when **40c** (Ar^1 = Ar^2 = 3,4-$(OMe)_2$Ph) underwent the $BF_3{\cdot}Et_2O$-mediated Et_3SiH reduction, only the tricyclic product **42c** with 10a-isomerization was obtained; no **41c** was observed.

Lindlar hydrogenation followed by methallylation of the ketone alkyne **28** could install the requisite methyl group at C9 and furnish the corresponding alcohol **44** in 75% yield over two steps. After some experimentation, subsequent RCM of **44** using Grubbs II catalyst under various conditions proceeded more sluggishly than those of other similar dienes (**29**, **37b,c**, **39a–c**, and **40a–c**) to give a separable mixture of the corresponding tricyclic alcohols **45** (7*β*-OH) and **46** (7*α*-OH) in 26% and 30% yields, respectively.[34] When the catalyst was changed to Hoveyda–Grubbs II, better yields of both **45** (35%) and **46** (38%) could be obtained. In the final step, hydride reduction of the alcohol **45** furnished the desired

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Scheme 7. Scope of the Developed Chemistry to Prepare Diverse Tricyclic 6,7-Diaryltetrahydro-6*H*-benzo[*c*]chromenes 38b,c, 41b,c, 42a−c, and 47

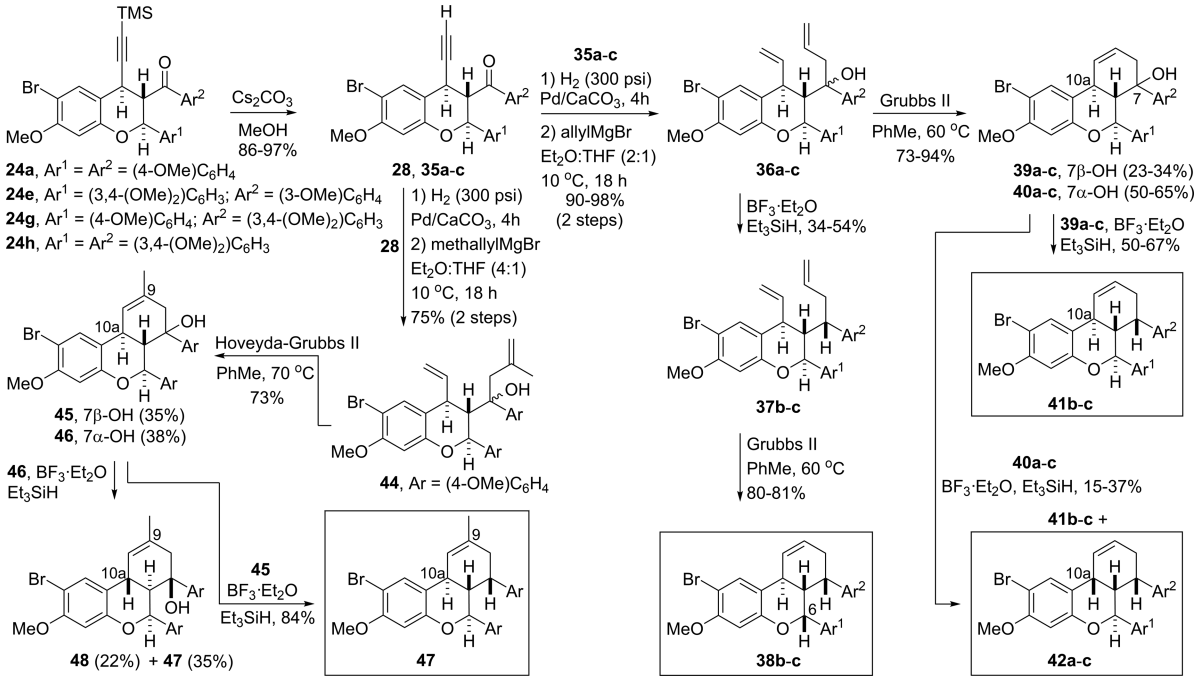

Table 2. Scope of the Currently Developed Strategy

entry	TMS alkyne	ketone alkyne[a]	diene alcohol[a]	diene[a]	tricyclic product[a]	tricyclic alcohols[a]	tricyclic products[a]
1	**24e**	**35a** (86)	**36a** (98)	**37a** (0)	**38a** (0)	**39a** (26)	**42a** (19)
						40a (65)	**42a** (15), **43**[b]
2	**24g**	**35b** (97)	**36b** (90)	**37b** (54)	**38b** (81)	**39b** (23)	**41b** (50, 18)[c]
						40b (50)	**42b** (27)
3	**24h**	**35c** (88)	**36c** (93)	**37c** (34)	**38c** (80)	**39c** (34)	**41c** (67)
						40c (60)	**42c** (37)

[a]Values in parentheses are the isolated yields. [b]19% of **43** was obtained. [c]The first value refers to the yield from **39b**, while the second value refers to the yield from **40b**.

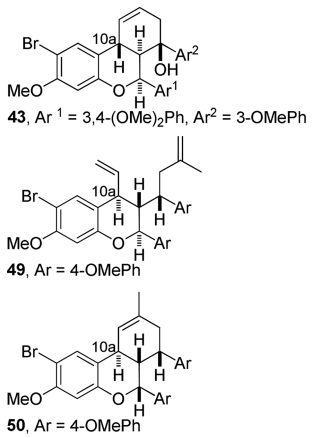

Figure 2. Nonreduced tricyclic product **43**, diene **49**, and tricyclic product **50**.

product **47** ($H_{10a\alpha}$) in 84% yield as a single isomer while the alcohol **46** furnished a separable mixture of **47** and the nonreduced 10a,6a-isomerized tricyclic alcohol **48**[35] ($H_{10a\beta}$) in 35% and 22% yields, respectively. It should be noted that, while **44** could undergo the hydride reduction to give the corresponding diene **49**, its subsequent RCM, under various RCM conditions, did not proceed to furnish the corresponding tricyclic product **50**.

■ CONCLUSION

A synthetic approach for the tricyclic 6,7-diaryltetrahydro-6*H*-benzo[*c*]chromenes has been successfully developed employing simple benzaldehydes and acetophenones as building blocks. The skeleton of the tricyclic system comprises two units of benzaldehyde derivatives (one as the chroman aromatic ring and the other as the aryl group (Ar^1) on C6), one unit of acetophenone (as the aryl group (Ar^2) on C7), and one three-carbon (allylic) unit (as part of the cyclohexene ring). The chroman moiety was assembled first via a highly efficient and stereoselective [4 + 2] cycloaddition reaction between the *o*-QMs derived from the TMS-protected acetylene benzyl acetate and chalcones. Subsequent reactions on the TMS-protected alkyne group converted such a moiety to the corresponding olefin. The requisite allylic moiety was then added to the ketone via the Grignard reaction. The sequence of the remaining two steps of Grubbs RCM and BF_3·Et_2O-mediated Et_3SiH reduction on the resulting diene alcohol could be exploited to provide the final different tricyclic products in a stereodefined manner. Thus, through eight steps starting from the benzaldehyde building block **10**, the desired complex

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tricyclic 6,7-diaryltetrahydro-6*H*-benzo[*c*]chromenes containing four contiguous stereocenters could be obtained in good overall yields (up to 43%). Applications of the developed method have been further investigated for the total synthesis of palodesangrens, and the results will be reported in due course.

EXPERIMENTAL SECTION

General Experimental Methods. Unless otherwise noted, reactions were run in oven-dried round-bottomed flasks. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl or purified by the solvent purification system, while dichloromethane (CH_2Cl_2) was also purified by the solvent purification system prior to use. All other compounds were used as received from the suppliers; PTS-Si (*p*-TsOH immobilized on silica) employed in these experiments possessed a surface area of 500 m^2/g, as indicated by the supplier. The crude reaction mixtures were concentrated under reduced pressure by removing organic solvents on a rotary evaporator. Column chromatography was performed using silica gel 60 (particle size 0.06−0.2 mm; 70−230 mesh ASTM). Analytical thin-layer chromatography (TLC) was performed with silica gel 60 F_{254} aluminum sheets. Chemical shifts for ^1H nuclear magnetic resonance (NMR) spectra are reported in parts per million (ppm, δ) downfield from tetramethylsilane. Splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br), doublet of doublets (dd), doublet of triplets (dt), and doublet of doublets of doublets (ddd). Resonances for infrared (IR) spectra are reported in wavenumbers (cm^{-1}). Low-resolution (LRMS) mass spectra were obtained using either electron ionization (EI) or time of flight (TOF), while high-resolution (HRMS) mass spectra were obtained using TOF via atmospheric-pressure chemical ionization (APCI) or electrospray ionization (ESI). Melting points are uncorrected.

1-(5-Bromo-4-methoxy-2-(methoxymethoxy)phenyl)allyl Acetate (14). Allylmagnesium chloride (1.6 M in THF, 0.33 mL, 0.52 mmol) was added to a solution of benzaldehyde **10** (0.110 g, 0.40 mmol) in THF (2 mL) at 0 °C. The reaction mixture was stirred for 4 h and then was quenched with saturated NH_4Cl (2 mL). The resulting mixture was extracted with EtOAc (3 × 2 mL), and the combined organic layers were washed with water (3 × 2 mL) and brine (5 mL), dried over Na_2SO_4, and filtered. The filtrate was evaporated (aspirator then vacuum) to give a crude product, which was used in the next step without further purification.

A solution of the benzyl alcohol and *N*,*N*-dimethylaminopyridine (DMAP; 0.073 g, 0.6 mmol) in dichloromethane (DCM; 2 mL) was cooled in an ice bath for 10 min before Et_3N (0.08 mL, 0.6 mmol) and Ac_2O (0.06 mL, 0.6 mmol) were added successively. The mixture was warmed to room temperature, at which it was stirred for 2 h. The reaction mixture was quenched with water (2 mL), the resulting mixture was extracted with DCM (3 × 2 mL), and the combined organic phases were washed with water (3 × 2 mL) and brine (2 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a crude product, which was purified by column chromatography on silica (15−20% EtOAc/hexanes) to give the desired product **14** as a colorless oil (0.125 g, 0.36 mmol, 90% over two steps). ^1H NMR (300 MHz, $CDCl_3$): δ 2.11 (s, 3H), 3.48 (s, 3H), 3.88 (s, 3H), 5.205 (dt, J = 10.4, 1.3 Hz, 1H), 5.207 (s, 2H), 5.23 (dt, J = 17.1, 1.3 Hz, 1H), 5.97 (ddd, J = 17.1, 10.4, 5.5 Hz, 1H), 6.58 (dt, J = 5.5, 1.3 Hz, 1H), 6.74 (s, 1H), 7.47 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 56.1, 56.3, 69.8, 94.7, 99.6, 103.4, 116.2, 121.7, 131.6, 135.6, 154.6, 156.3, 167.7. TOF-HRMS: calcd for $C_{14}H_{17}{}^{79}BrNaO_5$ ($M + Na^+$) 367.0152, found 367.0147; calcd for $C_{14}H_{17}{}^{81}BrNaO_5$ ($M + Na^+$) 369.0133, found 369.0133.

1-(5-Bromo-4-methoxy-2-(methoxymethoxy)phenyl)-3-(trimethylsilyl)prop-2-yn-1-yl Acetate (15). To a solution of ethynyltrimethylsilane (3.50 mL, 24.0 mmol) in THF (20 mL) was slowly added *n*-BuLi (1.55 M, 12.9 mL, 20 mmol) at −78 °C. The mixture was then warmed to 0 °C, at which it was stirred for 2 h. A solution of benzaldehyde **10** (2.20 g, 8.00 mmol) in THF (20 mL) was added to the TMS acetylide solution at 0 °C. The mixture was warmed to room temperature, and the reaction mixture was stirred for 18 h. The resulting mixture was quenched with saturated NH_4Cl (20 mL). The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined organic phases were washed with water (3 × 20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a crude product which was used in the next step without further purification.

A solution of the benzyl alcohol and DMAP (1.50 g, 12.0 mmol) in DCM (40 mL) was cooled in an ice bath for 10 min before Et_3N (1.70 mL, 12.0 mmol) and Ac_2O (1.20 mL, 12.0 mmol) were added successively. The mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with water (10 mL), and the resulting mixture was extracted with DCM (3 × 20 mL). The combined organic phases were washed with water (3 × 20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a crude product which was purified by column chromatography on silica (15−20% EtOAc/hexanes) to give the desired product **15** as a white solid (3.31 g, 8.00 mmol, 100% over two steps). Mp (EtOAc/hexanes):: 79.4−80.2 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 0.20 (s, 9H), 2.08 (s, 3H), 3.48 (s, 3H), 3.89 (s, 3H), 5.20 (br s, 2H), 6.71 (s, 1H), 6.74 (s, 1H), 7.79 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.28, 21.0, 56.2, 56.4, 60.1, 92.0, 94.7, 99.4, 101.1, 103.4, 119.5, 133.0, 154.9, 157.2, 169.4. IR (UATR): ν_{max} 2960, 2180, 1743, 1218, 843 cm^{-1}. LRMS (EI): m/z (rel intensity) 416 (1.45) $[C_{17}H_{23}{}^{81}BrO_5Si]^+$, 414 (1.16) $[C_{17}H_{23}{}^{79}BrO_5Si]^+$, 312 (92), 310 (87), 73 (100). TOF-HRMS: calcd for $C_{17}H_{23}{}^{79}BrNaO_5Si$ ($M + Na^+$) 437.0390, found 437.0379; calcd for $C_{17}H_{23}{}^{81}BrNaO_5Si$ ($M + Na^+$) 439.0372, found 439.0366.

General Procedure for the PTS-Si-Mediated Generation of *o*-QM and the [4 + 2] Cycloaddition Reaction. To a stirred solution of benzyl acetate **15** (1.0 equiv) in toluene (5 mL/mmol) was added the corresponding styrene (10 equiv) or its derivative (2 equiv in the case of 4-methoxystyrene) at room temperature. The resulting mixture was stirred at 0 °C for 10 min, and then PTS-Si (1.1 equiv) was added. The mixture was then slowly warmed to room temperature. The reaction mixture was stirred until the starting material was consumed, as indicated by TLC (typically 1−4 h). At that time, PTS-Si was filtered off and the resulting mixture was concentrated under reduced pressure to give a crude product mixture which was further purified by PTLC (10% EtOAc/hexanes) to furnish the desired product.

((6-Bromo-7-methoxy-2-phenylchroman-4-yl)ethynyl)-trimethylsilane (20). Following the general procedure for the PTS-Si-mediated *o*-QM/[4 + 2] cycloaddition reaction, benzyl acetate **15** (0.029 g, 0.070 mmol) furnished the chroman product **20** as an 8:1 (2,4-*cis*:2,4-*trans*) inseparable mixture of diastereomers as a colorless oil (0.012 g, 0.029 mmol, 42%). ^1H NMR (300 MHz, $CDCl_3$): δ 0.17 (s, 9H, minor), 0.18 (s, 9H, major), 2.17 (dt, J = 13.7, 11.8 Hz, 1H, major), 2.21−2.28 (m, 2H, minor), 2.46 (ddd, J = 13.7, 5.3, 1.9, 1H, major), 3.74 (t, J = 4.5 Hz, 1H, minor), 3.83 (s, 3H, major), 3.84 (s, 3H, minor), 4.07 (ddd, J = 11.8, 5.3, 0.9 Hz, 1H, major), 5.00 (dd, J = 11.8, 1.9 Hz, 1H, major), 5.34 (dd, J = 9.0, 3.0, 1H, minor), 6.46 (s, 1H), 6.51 (s, 1H, minor), 7.31−7.45 (m, 5H), 7.66 (d, J = 0.9 Hz, 1H, major). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.0 (major), 0.1 (minor), 27.0 (minor), 29.3 (major), 35.6 (minor), 36.8 (major), 56.2 (minor), 56.3 (major), 75.0 (minor), 78.0 (major), 86.9 (major), 100.9 (major), 101.1 (minor), 102.6 (major), 106.3 (major), 107.9 (minor), 114.7 (major), 125.9 (minor), 126.1 (major), 128.1 (minor), 128.4 (major), 128.7 (major), 132.7 (major), 133.3 (minor), 140.2 (major), 140.5 (minor), 154.2 (minor), 154.3 (major), 155.8 (major). TOF-HRMS: calcd for $C_{21}H_{23}{}^{79}BrNaO_2Si$ ($M + Na^+$) 437.0543, found 437.0537; calcd for $C_{21}H_{23}{}^{81}BrO_2Si$ ($M + Na^+$) 439.0525, found 439.0519.

((6-Bromo-7-methoxy-2-(4-methoxyphenyl)chroman-4-yl)-ethynyl)trimethylsilane (21). Following the general procedure for the PTS-Si-mediated *o*-QM/[4 + 2] cycloaddition reaction, benzyl acetate **15** (0.042 g, 0.100 mmol) furnished the chroman product **21** as a 2:1 (2,4-*cis*:2,4-*trans*) inseparable mixture of diastereomers as a colorless oil (0.019 g, 0.044 mmol, 44%). ^1H NMR (300 MHz, $CDCl_3$): δ 0.17 (s, 9H, minor), 0.19 (s, 9H, major), 2.18−2.26 (m, 2H, minor), 2.19 (dt, J = 13.7, 11.8 Hz, 1H, major), 2.42 (ddd, J = 13.7, 5.4, 1.9 Hz, 1H, major), 3.75 (t, J = 4.4 Hz, 1H, minor), 3.82 (s, 3H), 3.83 (s, 3H, major), 3.84 (s, 3H, minor), 4.06 (ddd, J = 11.8, 5.4,

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J. Org. Chem. 2017, 82, 2672−2688

1.0 Hz, 1H, major), 4.95 (dd, J = 11.8, 1.9, 1H, major), 5.29 (dd, J = 8.4, 3.8 Hz, 1H, minor), 6.44 (s, 1H, major), 6.49 (s, 1H, minor), 6.93 (d, J = 8.6 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H, minor), 7.35 (d, J = 8.6 Hz, 2H, major), 7.43 (s, 1H, minor), 7.65 (d, J = 1.0 Hz, 1H, major). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.0 (major), 0.1 (minor), 27.2, (minor), 29.4 (major), 35.4 (minor), 36.6 (major), 55.3, 56.2 (minor), 56.3 (major), 74.7 (minor), 77.8 (major), 86.8 (major), 86.9 (minor), 101.0 (major), 101.1, (minor), 102.4 (minor), 102.5 (major), 106.4 (major), 108.0 (minor), 114.1, 114.7 (major), 114.8 (minor), 127.4 (minor), 127.5 (major), 132.3 (major), 132.6 (minor), 132.7 (major), 133.3 (minor), 154.3 (minor), 154.4 (major), 155.7, 159.5 (minor), 159.7 (major). TOF-HRMS: calcd for $C_{22}H_{25}{}^{79}BrNaO_3Si$ (M + Na^+) 467.0649, found 467.0638; calcd for $C_{22}H_{25}{}^{81}BrNaO_3Si$ (M + Na^+) 469.0631, found 469.0622.

General Procedure for the $PtCl_4$-Catalyzed Generation of *o*-QM and the [4 + 2] Cycloaddition Reaction with Chalcones 23a–l. To a stirred solution of benzyl acetate **15** (1.0 equiv) in DCM (10 mL/mmol) was added chalcone **23a–l** (2 equiv) at room temperature. The resulting mixture was stirred at 0 °C for 10 min, and then $PtCl_4$ (10 mol %) was added. The mixture was then slowly warmed to room temperature. The reaction mixture was stirred until the starting material was consumed, as indicated by TLC (typically 2–4 h). At that time, the reaction mixture was concentrated under reduced pressure to give a crude product mixture which was further purified by PTLC (20–40% EtOAc/hexanes) to furnish the desired products **24a–l**.

(6-Bromo-7-methoxy-2-(4-methoxyphenyl)-4-((trimethylsilyl)ethynyl)chroman-3-yl)(4-methoxyphenyl)-methanone (24a). Following the general procedure for the $PtCl_4$-catalyzed *o*-QM/[4 + 2] cycloaddition reaction using chalcone **23a**, benzyl acetate **15** (0.200 g, 0.482 mmol) furnished the corresponding chroman **24a** as a 8:1 (2,4-*cis*:2,4-*trans*) inseparable mixture of diastereomers as a yellow sticky gum (0.237 g, 0.410 mmol, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.07 (s, 9H, major), 0.11 (s, 9H, minor), 3.69 (s, 3H, major), 3.76 (s, 3H, minor), 3.80 (s, 3H, major), 3.82 (s, 3H, minor), 3.83 (s, 3H, major), 3.84 (s, 3H, minor), 4.11 (dd, J = 11.0, 10.0 Hz, 1H, major), 4.38 (dd, J = 11.0, 0.9 Hz, 1H, major), 5.12 (d, J = 10.0 Hz, 1H, major), 5.56 (d, J = 9.1 Hz, 1H, minor), 6.49 (s, 1H, major), 6.50 (s, 1H, minor), 6.73 (d, J = 8.7 Hz, 2H, major), 6.76 (d, J = 8.9 Hz, 2H, major), 6.86 (d, J = 8.7 Hz, 2H, minor), 6.91 (d, J = 8.9 Hz, 2H, minor), 7.26 (d, J = 8.7 Hz, 2H, major), 7.398 (d, J = 8.7 Hz, 2H, minor), 7.400 (s, 1H, minor), 7.69 (d, J = 0.9 Hz, 1H, major), 7.81 (d, J = 8.9 Hz, 2H, major), 7.83 (d, J = 8.9 Hz, 2H, minor). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.4 (major), −0.2 (minor), 31.8 (minor), 33.9 (major), 48.2 (minor), 50.7 (major), 55.1 (major), 55.2 (minor), 55.4 (major), 55.5 (minor), 56.2 (minor), 56.3 (major), 76.1 (minor), 80.0 (major), 89.1 (major), 100.7 (major), 100.9 (minor), 102.5 (minor), 102.8 (major), 103.2 (minor), 104.0 (major), 113.4 (major), 113.85 (major), 113.90 (minor), 113.95 (minor), 114.1 (minor), 114.4 (major), 128.5 (major), 128.8 (minor), 129.4 (minor), 129.7 (major), 130.1 (minor), 130.2, (minor), 130.8 (major), 131.0 (major), 131.4 (minor), 132.5 (minor), 132.8 (major), 153.8 (major), 155.8 (major), 159.5 (minor), 159.7 (major), 163.6 (major), 194.2 (minor), 198.9 (major). IR (UATR): ν_{max} 2959, 2838, 2175, 1666, 1600, 1249, 839 cm^{-1}. LRMS (EI): m/z (rel intensity) 580 (19) $[C_{30}H_{31}{}^{81}BrO_5Si]^+$, 578 (17) $[C_{30}H_{31}{}^{79}BrO_5Si]^+$, 268 (21), 135 (100). TOF-HRMS: calcd for $C_{30}H_{32}{}^{79}BrO_5Si$ (M + H^+) 579.1197, found 579.1180; calcd for $C_{30}H_{32}{}^{81}BrO_5Si$ (M + H^+) 581.1182, found 581.1144.

(6-Bromo-2-(3,4-dimethoxyphenyl)-7-methoxy-4-((trimethylsilyl)ethynyl)chroman-3-yl)(4-methoxyphenyl)-methanone (24b). Following the general procedure for the $PtCl_4$-catalyzed *o*-QM/[4 + 2] cycloaddition reaction using chalcone **23b**, benzyl acetate **15** (0.021 g, 0.050 mmol) furnished chroman **24b** as a 8:1 (2,4-*cis*:2,4-*trans*) inseparable mixture of diastereomers as a yellow solid (0.017 g, 0.028 mmol, 56%). Mp (EtOAc/hexanes): 74.5–76.6 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.06 (s, 9H, major), 0.11 (s, 9H, minor), 3.768 (s, 3H, major), 3.774 (s, 3H, major), 3.81 (s, 3H, major), 3.83 (s, 3H, minor), 3.84 (s, 3H, major), 3.856 (s, 3H, minor), 3.862 (s, 3H, minor), 4.14 (dd, J = 11.0, 10.0 Hz, 1H, major), 4.39 (dd, J = 11.0, 1.0, 1H, major), 5.11 (d, J = 10.0, 1H, major), 5.55 (d, J = 9.2 Hz, 1H, minor), 6.51, (s, 1H, major), 6.52 (s, 1H, minor), 6.70 (d, J = 8.2 Hz, 1H, major), 6.79 (d, J = 8.9 Hz, 2H, major), 6.84 (d, J = 1.9 Hz, 1H, major), 6.89 (dd, J = 8.2, 1.9 Hz, 1H, major), 6.98 (d, J = 2.0 Hz, 1H, minor), 7.04 (dd, J = 8.3, 2.0 Hz, 1H, minor), 7.41 (s, 1H, minor), 7.49 (d, J = 8.3 Hz, 1H, minor), 7.70 (d, J = 1.0 Hz, 1H, major), 7.75 (d, J = 8.9 Hz, 2H, major), 7.84 (d, J = 8.9 Hz, 2H, minor). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.4 (major), −0.2 (minor), 31.8 (minor), 33.9 (major), 48.1 (minor), 50.6 (major), 55.4 (major), 55.5 (minor), 55.79 (major), 55.80 (major), 55.9 (minor), 56.2 (minor), 56.3 (major), 80.2 (major), 89.1 (major), 100.7 (major), 101.0 (minor), 102.9 (major), 104.0 (major), 110.0 (major), 110.9 (major), 111.1 (minor), 113.5 (major), 114.0 (minor), 114.1 (minor), 114.4 (major), 120.2 (major), 129.9 (major), 130.2 (minor), 130.7 (major), 131.0 (major), 132.6 (major), 132.9 (minor), 148.9 (major), 149.2 (major), 153.7 (major), 155.8 (major), 163.7 (major), 198.9 (major). IR (UATR): ν_{max} 2959, 2835, 2172, 1598, 1259, 1160 cm^{-1}. LRMS (EI): m/z (rel intensity) 610 (0.2) $[C_{31}H_{33}{}^{81}BrO_6Si]^+$, 608 (0.2) $[C_{31}H_{33}{}^{79}BrO_6Si]^+$, 195 (100). TOF-HRMS: calcd for $C_{31}H_{33}{}^{79}BrNaO_6Si$ (M + Na^+) 631.1120, found 631.1117; calcd for $C_{31}H_{33}{}^{81}BrNaO_6Si$ (M + Na^+) 633.1107, found 633.1117.

(6-Bromo-2-(3,4,5-trimethoxyphenyl)-7-methoxy-4-((trimethylsilyl)ethynyl)chroman-3-yl)(4-methoxyphenyl)-methanone (24c). Following the general procedure for the $PtCl_4$-catalyzed *o*-QM/[4 + 2] cycloaddition reaction using chalcone **23c**, benzyl acetate **15** (0.021 g, 0.050 mmol) furnished chroman **24c** as a 7:1 (2,4-*cis*:2,4-*trans*) inseparable mixture of diastereomers as a yellow sticky gum (0.013 g, 0.021 mmol, 41%). ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.04 (s, 9H, major), 0.12 (s, 9H, minor), 3.70 (s, 3H, major), 3.74 (s, 6H, major), 3.80 (s, 3H, minor), 3.81 (s, 3H, major), 3.83 (s, 6H, minor), 3.85 (s. 3H, major), 3.86 (s, 3H, minor), 3.94 (s, 3H, minor), 4.13 (dd, J = 11.0, 10.0 Hz, 1H, major), 4.42 (dd, J = 11.0, 1.0 Hz, 1H, major), 5.06 (d, J = 10.0 Hz, 1H, major), 5.53 (d, J = 9.2 Hz, 1H, minor), 6.52 (s, 1H, major), 6.54 (s, 2H, major), 6.68 (s, 2H, minor), 6.79 (d, J = 8.9 Hz, 2H, major), 6.93 (d, J = 8.9, 2H, minor), 7.13 (s, 1H, minor), 7.41 (s, 1H, minor), 7.71 (d, J = 1.0 Hz, 1H, major), 7.74 (d, J = 8.9 Hz, 2H, major), 7.85 (d, J = 8.9 Hz, 2H, minor). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.4 (major), −0.2 (minor), 31.7 (minor), 33.6 (major), 47.9 (minor), 50.7 (major), 55.4 (major), 55.5 (minor), 56.1 (major), 56.2 (minor), 56.25 (minor), 56.31 (major), 60.65 (major), 60.68 (minor), 76.8 (minor), 80.5 (major), 89.0 (major), 91.4 (minor), 100.7 (major), 100.9 (minor), 103.1 (major), 104.0 (major), 104.5 (major), 104.9 (minor), 106.7 (minor), 113.4 (major), 114.0 (minor), 114.3 (major), 130.2 (minor), 130.6 (major), 131.0 (major), 132.7 (major), 132.8 (major), 134.7 (minor), 138.1 (minor), 153.2 (major), 155.5 (major), 155.8 (major), 156.1 (minor), 163.7 (major), 191.0 (minor), 198.7 (major). IR (UATR): ν_{max} 2959, 2175, 1664, 1596, 1125 cm^{-1}. LRMS (EI): m/z (rel intensity) 641 (19) $[C_{32}H_{36}{}^{81}BrO_7Si]^+$, 639 (20) $[C_{32}H_{36}{}^{79}BrO_7Si]^+$, 328 (26), 135 (100). TOF-HRMS: calcd for $C_{32}H_{35}{}^{79}BrNaO_7Si$ (M + Na^+) 661.1228, found 661.1240; calcd for $C_{32}H_{35}{}^{81}BrNaO_7Si$ (M + Na^+) 663.1213, found 663.1232.

(6-Bromo-7-methoxy-2-(4-methoxyphenyl)-4-((trimethylsilyl)ethynyl)chroman-3-yl)(3-methoxyphenyl)-methanone (24d). Following the general procedure for the $PtCl_4$-catalyzed *o*-QM/[4 + 2] cycloaddition reaction using chalcone **23d**, benzyl acetate **15** (0.021 g, 0.050 mmol) furnished chroman **24d** as a single diastereomer as a white sticky gum (0.018 g, 0.030 mmol, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.05 (s, 9H), 3.72 (s, 3H), 3.78 (s, 3H), 3.86 (s, 3H), 4.15 (dd, J = 11.0, 10.1 Hz, 1H), 4.41 (dd, J = 11.0, 1.1 Hz, 1H), 5.14 (d, J = 10.1 Hz, 1H), 6.52 (s, 1H), 6.76 (d, J = 8.7 Hz, 2H), 7.02 (ddd, J = 8.1, 2.6, 0.9 Hz, 1H), 7.18–7.22 (m, 1H), 7.23–7.30 (m, 3H), 7.31–7.36 (m, 1H), 7.72 (d, J = 1.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.5, 34.0, 51.5, 55.2, 55.3, 56.3, 80.0, 89.3, 100.7, 102.9, 103.7, 112.2, 113.9, 114.2, 119.8, 121.2, 128.5, 129.2, 129.5, 132.5, 139.3, 153.7, 155.8, 159.5, 160.0, 200.9. IR (UATR): ν_{max} 2959, 2837, 2172, 1674, 1488, 1250, 1152 cm^{-1}. LRMS (EI): m/z (rel intensity) 580 (1) $[C_{30}H_{31}{}^{81}BrO_5Si]^+$, 578 (1) $[C_{30}H_{31}{}^{79}BrO_5Si]^+$, 165 (100). TOF-HRMS: calcd for

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J. Org. Chem. 2017, 82, 2672–2688

$C_{30}H_{31}{}^{79}BrNaO_5Si$ (M + Na^+) 601.1016, found 601.1020; calcd for $C_{30}H_{31}{}^{81}BrNaO_5Si$ (M + Na^+) 603.1001, found 603.0992.

(6-Bromo-2-(3,4-dimethoxyphenyl)-7-methoxy-4-((trimethylsilyl)ethynyl)chroman-3-yl)(3-methoxyphenyl)-methanone (24e). Following the general procedure for the $PtCl_4$-catalyzed *o*-QM/[4 + 2] cycloaddition reaction using chalcone **23e**, benzyl acetate **15** (0.021 g, 0.050 mmol) furnished chroman **24e** as a single diastereomer as a yellow sticky gum (0.021 g, 0.034 mmol, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.06 (s, 9H), 3.76 (s, 6H), 3.78 (s, 3H), 3.84 (s, 3H), 4.17 (dd, *J* = 11.0, 10.0 Hz, 1H), 4.40 (dd, *J* = 11.0, 1.0 Hz, 1H), 5.09 (d, *J* = 10.0 Hz, 1H), 6.51 (s, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 6.84 (d, *J* = 2.0 Hz, 1H), 6.89 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.01 (ddd, *J* = 8.1, 2.6, 0.8 Hz, 1H), 7.18 (d, *J* = 1.6 Hz, 1H), 7.22 (dd, *J* = 8.1, 7.8 Hz, 1H), 7.34 (br d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 1.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.5, 33.9, 51.4, 55.3, 55.80, 55.81, 56.3, 80.3, 89.2, 100.7, 103.0, 103.8, 110.0, 110.9, 112.5, 114.2, 121.1, 129.2, 129.7, 132.9, 139.3, 148.9, 149.3, 153.7, 155.9, 159.5, 200.8. IR (UATR): ν_{max} 2958, 2837, 2176, 1674, 1262, 1151 cm^{-1}. LRMS (EI): *m*/*z* (rel intensity) 610 (20) $[C_{31}H_{33}{}^{81}BrO_6Si]^+$, 608 (18) $[C_{31}H_{33}{}^{79}BrO_6Si]^+$, 475 (71), 298 (78), 135 (100). TOF-HRMS: calcd for $C_{31}H_{33}{}^{79}BrNaO_6Si$ (M + Na^+) 631.1122, found 631.1103; calcd for $C_{31}H_{33}{}^{81}BrNaO_6Si$ (M + Na^+) 633.1107, found 633.1112.

(6-Bromo-2-(3,4,5-trimethoxyphenyl)-7-methoxy-4-((trimethylsilyl)ethynyl)chroman-3-yl)(3-methoxyphenyl)-methanone (24f). Following the general procedure for the $PtCl_4$-catalyzed *o*-QM/[4 + 2] cycloaddition reaction using chalcone **23f**, benzyl acetate **15** (0.021 g, 0.050 mmol) furnished chroman **24f** as a 6:1 (2,4-*cis*:2,4-*trans*) inseparable mixture of diastereomers as a yellow sticky gum (0.014 g, 0.022 mmol, 44%). ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.04 (s, 9H, major), 0.13 (s, 9H, minor), 3.70 (s, 3H, major), 3.73 (s, 6H, major), 3.76 (s, 3H, major), 3.80 (s, 3H, minor), 3.83 (s, 3H, minor), 3.84 (s, 6H, minor), 3.85 (s, 3H, major), 4.17 (dd, *J* = 11.0, 10.0 Hz, 1H, major), 4.24 (dd, *J* = 9.3, 5.3 Hz, 1H, minor), 4.43 (dd, *J* = 11.0, 1.0 Hz, 1H, major), 5.04 (d, *J* = 10.0 Hz, 1H, major), 5.52 (d, *J* = 9.3 Hz, 1H, minor), 6.52 (s, 1H, major), 6.53 (s, 2H, major), 6.69 (s, 2H, minor), 7.01 (ddd, *J* = 8.1, 2.5, 1.0 Hz, 1H, major), 7.12 (ddd, *J* = 7.8, 2.6, 1.0 Hz, 1H, minor), 7.14 (s, 1H, minor), 7.17 (dd, *J* = 2.5, 1.4 Hz, 1H, major), 7.23 (dd, *J* = 8.1, 7.8 Hz, 1H, major), 7.34 (ddd, *J* = 7.8, 1.4, 1.0 Hz, 1H, major), 7.34−7.42 (m, 3H, minor), 7.44 (ddd, *J* = 7.8, 1.3, 1.0 Hz, 1H, minor), 7.71 (d, *J* = 1.0 Hz, 1H, major). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.4 (major), −0.2 (minor), 31.7 (minor), 33.7 (major), 48.6 (minor), 51.6 (major), 55.3 (major), 55.4 (minor), 56.1 (major), 56.2 (minor), 56.3 (minor), 56.4 (major), 60.70 (major), 60.73 (minor), 80.6 (major), 89.2 (major), 100.8 (major), 101.0 (minor), 102.9 (minor), 103.0 (major), 103.3 (major), 103.8 (major), 104.6 (major), 105.0 (minor), 112.5 (major), 114.0 (minor), 114.2 (major), 119.6 (major), 119.8 (minor), 120.2 (minor), 120.9 (major), 129.2 (major), 129.8 (minor), 132.6 (major), 132.7 (major), 132.9 (minor), 137.9 (minor), 138.4 (minor), 139.5 (major), 153.25 (major), 153.28 (major), 153.5 (major), 153.6 (minor), 155.9 (major), 156.2 (minor), 159.5 (major), 160.2 (minor), 195.6 (minor), 200.6 (major). IR (UATR): ν_{max} 2957, 2839, 2167, 1657, 1263, 1123, 842 cm^{-1}. LRMS (EI): *m*/*z* (rel intensity) 640 (24) $[C_{32}H_{35}{}^{81}BrO_7Si]^+$, 638 (21) $[C_{32}H_{35}{}^{79}BrO_7Si]^+$, 505 (57), 503 (64), 328 (82), 297 (50), 135 (100). TOF-HRMS: calcd for $C_{32}H_{35}{}^{79}BrNaO_7Si$ (M + Na^+) 661.1228, found 661.1234; calcd for $C_{32}H_{35}{}^{81}BrNaO_7Si$ (M + Na^+) 663.1213, found 663.1203.

(6-Bromo-7-methoxy-2-(4-methoxyphenyl)-4-((trimethylsilyl)ethynyl)chroman-3-yl)(3,4-dimethoxyphenyl)-methanone (24g). Following the general procedure for the $PtCl_4$-catalyzed *o*-QM/[4 + 2] cycloaddition reaction using chalcone **23g**, benzyl acetate **15** (0.021 g, 0.050 mmol) furnished chroman **24g** as a 8:1 (2,4-*cis*:2,4-*trans*) inseparable mixture of diastereomers as a yellow sticky gum (0.030 g, 0.049 mmol, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.07 (s, 9H, major), 0.12 (s, 9H, minor), 3.70 (s, 3H, major), 3.78 (s, 3H, minor), 3.83 (s, 3H, minor), 3.84 (s, 3H, major), 3.85 (s, 3H, major), 3.87 (s, 3H, major), 3.90 (s, 3H, major), 3.93 (s, 3H, minor), 4.11 (dd, *J* = 11.0, 10.0 Hz, 1H, major), 4.21 (dd, *J* = 9.0, 5.3 Hz, 1H, minor), 4.39 (dd, *J* = 11.0, 1.0 Hz, 1H, major), 5.14 (d, *J* = 10.0 Hz, 1H, major), 5.56 (d, *J* = 9.0 Hz, 1H, minor), 6.50 (s, 1H, major), 6.51 (s, 1H, minor), 6.70−6.79 (m, 3H, major), 6.86 (d, *J* = 8.4 Hz, 1H, major), 6.87 (d, *J* = 8.7 Hz, 2H, minor), 7.22−7.31 (m, 3H, major), 7.40 (dd, *J* = 8.4, 1.8 Hz, 1H, major), 7.48 (dd, *J* = 8.4, 2.0 Hz, 1H, minor), 7.70 (d, *J* = 1.0 Hz, 1H, major). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.4 (major), −0.2 (minor), 32.0 (minor), 34.0 (minor), 48.1 (minor). 50.6, 55.1, 55.2 (minor), 55.8, 55.9 (minor), 56.0, 56.1 (minor), 56.2 (minor), 56.3, 76.2 (minor), 80.1, 89.1, 100.7, 100.9 (minor), 102.5 (minor), 102.9, 103.2 (minor), 103.9, 109.7, 109.9 (minor), 110.1, 110.3 (minor), 113.87, 113.93 (minor), 114.3, 122.1 (minor), 123.6, 128.5, 128.8 (minor), 129.6 (minor), 129.7, 131.1, 131.4 (minor), 132.5, 132.8 (minor), 148.7, 149.4 (minor), 153.47, 153.52 (minor), 153.7, 153.78 (minor), 155.80, 156.0 (minor), 159.6 (minor), 159.7, 194.3 (minor), 199.0. IR (UATR): ν_{max} 2959, 2838, 2172, 1663, 1514, 1248, 1151, 1023, 842 cm^{-1}. LRMS (EI): *m*/*z* (rel intensity) 610 (18) $[C_{31}H_{33}{}^{81}BrO_6Si]^+$, 608 (1) $[C_{31}H_{33}{}^{79}BrO_6Si]^+$, 298 (30), 165 (100). TOF-HRMS: calcd for $C_{31}H_{33}{}^{79}BrNaO_6Si$ (M + Na^+) 631.1122, found 631.1107; calcd for $C_{31}H_{33}{}^{81}BrNaO_6Si$ (M + Na^+) 633.1107, found 633.1088.

(6-Bromo-2-(3,4-dimethoxyphenyl)-7-methoxy-4-((trimethylsilyl)ethynyl)chroman-3-yl)(3,4-dimethoxyphenyl)-methanone (24h). Following the general procedure for the $PtCl_4$-catalyzed *o*-QM/[4 + 2] cycloaddition reaction using chalcone **23h**, benzyl acetate **15** (0.021 g, 0.050 mmol) furnished chroman **24h** as a 9:1 (2,4-*cis*:2,4-*trans*) inseparable mixture of diastereomers as a yellow sticky gum (0.023 g, 0.035 mmol, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.06 (s, 9H, major), 0.12 (s, 9H, minor), 3.78 (s, 3H, major), 3.79 (s, 3H, major), 3.85 (s, 6H, major), 3.87 (s, 3H, minor), 3.88 (s, 3H, minor), 3.90 (s, 3H, major), 3.94 (s, 3H, minor), 4.13 (dd, *J* = 11.0, 10.0 Hz, 1H, major), 4.03 (dd, *J* = 11.0, 0.9 Hz, 1H, major), 5.12 (d, *J* = 10.0 Hz, 1H, major), 5.55 (d, *J* = 9.3 Hz, 1H, minor), 6.52 (s, 1H, major), 6.53 (s, 1H, minor), 6.70 (d, *J* = 8.1 Hz, 1H, major), 6.75 (d, *J* = 8.5 Hz, 1H, major), 6.81−6.93 (m, 2H, major), 6.98 (d, *J* = 1.9 Hz, 1H, minor), 7.04 (dd, *J* = 8.3, 1.9 Hz, 1H, minor), 7.42 (dd, *J* = 8.4, 2.0 Hz, 1H, major), 7.49 (dd, *J* = 8.5, 1.9 Hz, 1H, minor), 7.71 (d, *J* = 0.9 Hz, 1H, major). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.4 (major), −0.2 (minor), 32.0 (minor), 33.9 (major), 47.9 (minor), 50.5 (major), 55.8 (major), 55.85 (major), 55.90 (minor), 56.0 (major), 56.1 (minor), 56.2 (minor), 56.3 (major), 80.2 (major), 89.1 (major), 100.7 (major), 101.0 (minor), 102.6 (minor), 103.0 (major), 103.9 (major), 109.7 (major), 109.9 (minor), 110.0 (major), 110.1 (major), 110.3 (minor), 110.8 (minor), 110.9 (major), 111.1 (minor), 114.1 (minor), 114.3 (major), 120.08 (major), 120.14 (minor), 122.1 (minor), 123.6 (major), 129.6 (minor), 130.0 (major), 131.1 (major), 131.7 (minor), 132.6 (minor), 132.9 (major), 148.8 (major), 148.9 (major), 149.2 (major), 153.6 (major), 153.7 (major), 155.8 (major), 194.2 (minor), 198.9 (major). IR (UATR): ν_{max} 2958, 2838, 2172, 1515, 1262, 1150 cm^{-1}. LRMS (EI): *m*/*z* (rel intensity) 640 (8) $[C_{32}H_{35}{}^{81}BrO_7Si]^+$, 638 (5) $[C_{32}H_{35}{}^{79}BrO_7Si]^+$, 165 (100). TOF-HRMS: calcd for $C_{32}H_{35}{}^{79}BrNaO_7Si$ (M + Na^+) 661.1228, found 661.1244; calcd for $C_{32}H_{35}{}^{81}BrNaO_7Si$ (M + Na^+) 663.1213, found 663.1219.

(6-Bromo-7-methoxy-2-(3,4,5-trimethoxyphenyl)-4-((trimethylsilyl)ethynyl)chroman-3-yl)(3,4-dimethoxyphenyl)-methanone (24i). Following the general procedure for the $PtCl_4$-catalyzed *o*-QM/[4 + 2] cycloaddition reaction using chalcone **23i**, benzyl acetate **15** (0.021 g, 0.050 mmol) furnished chroman **24i** as a 5:1 (2,4-*cis*:2,4-*trans*) inseparable mixture of diastereomers as a yellow sticky gum (0.013 g, 0.019 mmol, 38%). ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.05 (s, 9H, major), 0.12 (s, 9H, minor), 3.70 (s, 3H, major), 3.75 (s, 6H, major), 3.81 (s, 3H, minor), 3.84 (s, 6H, minor), 3.85 (s, 3H, major), 3.86 (s, 3H, major), 3.89 (s, 3H, major), 3.95 (s, 3H, minor), 4.12 (dd, *J* = 11.0, 10.0 Hz, 1H, major), 4.25 (dd, *J* = 9.1, 5.3 Hz, 1H, minor), 4.43 (dd, *J* = 11.0, 0.9 Hz, 1H, major), 5.08 (d, *J* = 10.0 Hz, 1H, major), 5.53 (d, *J* = 9.1 Hz, 1H, minor), 6.53 (s, 1H, major), 6.54 (s, 1H, minor), 6.56 (s, 2H, major), 6.69 (s, 2H, minor), 6.75 (d, *J* = 8.5 Hz, 1H, major), 6.87 (d, *J* = 8.4 Hz, 1H, minor), 7.27 (d, *J* = 1.9 Hz, 1H, major), 7.41 (dd, *J* = 8.5, 1.9 Hz, 1H, major), 7.51 (dd, *J* = 8.4, 1.8 Hz, 1H, minor), 7.71 (d, *J* = 0.9 Hz, 1H, major). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.4 (major), −0.2 (minor), 31.9 (minor), 33.7 (major), 47.8 (major), 50.7 (major), 55.85 (major), 55.92 (minor), 56.05 (major), 56.07 (major), 56.10 (minor), 56.26 (minor), 56.31

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J. Org. Chem. 2017, 82, 2672−2688

(major), 60.66 (major), 60.69 (minor), 76.8 (minor), 80.5 (major), 89.1 (major), 91.4 (minor), 100.7 (major), 100.9 (minor), 102.7 (minor), 103.1 (major), 103.9 (major), 104.4 (major), 104.8 (major), 109.6 (major), 110.0 (minor), 110.1 (major), 110.3 (minor), 114.0 (minor), 114.3 (major), 122.1 (minor), 123.4 (major), 129.6 (minor), 131.2 (major), 132.6 (major), 132.86 (minor), 132.92 (major), 134.6 (minor), 138.2 (minor), 148.8 (major), 153.17 (major), 153.23 (minor), 153.5 (major), 153.6 (major), 155.8 (major), 156.1 (minor), 194.1 (minor), 198.7 (major). IR (UATR): ν_{max} 2958, 2174, 1664, 1593, 1263, 1126 cm^{-1}. LRMS (EI): *m/z* (rel intensity) 670 (15) $[C_{33}H_{37}{}^{81}BrO_8Si]^+$, 668 (16) $[C_{33}H_{37}{}^{79}BrO_8Si]^+$, 358 (23), 165 (100). TOF-HRMS: calcd for $C_{33}H_{37}{}^{79}BrNaO_8Si$ (M + Na^+) 691.1333, found 691.1335; calcd for $C_{33}H_{37}{}^{81}BrNaO_8Si$ (M + Na^+) 693.1319, found 693.1302.

(6-Bromo-7-methoxy-2-(4-methoxyphenyl)-4-((trimethylsilyl)ethynyl)chroman-3-yl)(3,4,5-trimethoxyphenyl)methanone (24j). Following the general procedure for the $PtCl_4$-catalyzed *o*-QM/[4 + 2] cycloaddition reaction using chalcone **23j**, benzyl acetate **15** (0.021 g, 0.050 mmol) furnished chroman **24j** as a single diastereomer as a pale yellow solid (0.017 g, 0.027 mmol, 53%). Mp (EtOAc/hexanes): 134.6–136.9 °C. ^1H NMR (300 MHz, $CDCl_3$): δ −0.07 (s, 9H), 3.72 (s, 3H), 3.82 (s, 6H), 3.845 (s, 3H), 3.851 (s, 3H), 4.06 (dd, *J* = 11.0, 10.0 Hz, 1H), 4.40 (dd, *J* = 11.0, 0.8 Hz, 1H), 5.14 (d, *J* = 10.0 Hz, 1H), 6.51 (s, 1H), 6.77 (d, *J* = 8.3 Hz, 2H), 6.92 (s, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 0.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.4, 34.0, 51.4, 55.2, 56.2, 56.3, 60.8, 80.0, 89.3, 100.7, 103.0, 103.7, 105.9, 114.0, 114.1, 128.4, 129.8, 132.5, 133.2, 142.7, 152.7, 153.7, 155.9, 159.9, 199.7. IR (UATR): ν_{max} 2958, 2172, 1668, 1249, 1150 cm^{-1}. LRMS (EI): *m/z* (rel intensity) 640 (9) $[C_{32}H_{35}{}^{81}BrO_7Si]^+$, 638 (9) $[C_{32}H_{35}{}^{79}BrO_7Si]^+$, 195 (100), 178 (49). TOF-HRMS: calcd for $C_{32}H_{35}{}^{79}BrNaO_7Si$ (M + Na^+) 661.1228, found 661.1210; calcd for $C_{32}H_{35}{}^{81}BrNaO_7Si$ (M + Na^+) 663.1213, found 663.1198.

(6-Bromo-2-(3,4-dimethoxyphenyl)-7-methoxy-4-((trimethylsilyl)ethynyl)chroman-3-yl)(3,4,5-trimethoxyphenyl)methanone (24k). Following the general procedure for the $PtCl_4$-catalyzed *o*-QM/[4 + 2] cycloaddition reaction using chalcone **23k**, benzyl acetate **15** (0.021 g, 0.050 mmol) furnished chroman **24k** as a single diastereomer as a yellow sticky gum (0.014 g, 0.021 mmol, 42%). ^1H NMR (300 MHz, $CDCl_3$): δ −0.06 (s, 9H), 3.78 (s, 3H), 3.79 (s, 3H), 3.82 (s, 6H), 3.86 (s, 3H), 4.09 (dd, *J* = 11.0, 10.0 Hz, 1H), 4.41 (dd, *J* = 11.0, 1.0 Hz, 1H), 5.12 (d, *J* = 10.0 Hz, 1H), 6.53 (s, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.86 (d, *J* = 1.8 Hz, 1H), 6.91 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.94 (s, 1H), 7.70 (d, *J* = 1.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.4, 34.0, 51.3, 55.8, 55.9, 56.2, 56.4, 60.9, 80.2, 89.3, 100.8, 103.1, 103.8, 106.0, 110.0, 111.1, 114.2, 120.0, 130.1, 132.6, 133.2, 142.9, 149.0, 152.8, 153.6, 155.9, 199.6. IR (UATR): ν_{max} 2957, 2837, 2173, 1668, 1580, 1126 cm^{-1}. LRMS (EI): *m/z* (rel intensity) 670 (11) $[C_{33}H_{37}{}^{81}BrO_8Si]^+$, 668 (10) $[C_{33}H_{37}{}^{79}BrO_8Si]^+$, 195 (100). TOF-HRMS: calcd for $C_{33}H_{37}{}^{79}BrNaO_8Si$ (M + Na^+) 691.1333, found 691.1345; calcd for $C_{33}H_{37}{}^{81}BrNaO_8Si$ (M + Na^+) 693.1319, found 693.1318.

(6-Bromo-7-methoxy-2-(3,4,5-trimethoxyphenyl)-4-((trimethylsilyl)ethynyl)chroman-3-yl)(3,4,5-trimethoxyphenyl)methanone (24l). Following the general procedure for the $PtCl_4$-catalyzed *o*-QM/[4 + 2] cycloaddition reaction using chalcone **23l**, benzyl acetate **15** (0.021 g, 0.050 mmol) furnished chroman **24l** as a 5:1 (2,4-*cis*:2,4-*trans*) inseparable mixture of diastereomers as a yellow sticky gum (0.015 g, 0.021 mmol, 41%). ^1H NMR (300 MHz, $CDCl_3$): δ −0.44 (s, 9H, major), 0.13 (s, 9H, minor), 3.72 (s, 3H, major), 3.75 (s, 6H, major), 3.82 (s, 6H, major), 3.85 (s, 6H, minor), 3.856 (s, 3H, major), 3.861 (s, 3H, major), 3.88 (s, 6H, minor), 3.92 (s, 3H, minor), 4.08 (dd, *J* = 11.0, 10.0 Hz, 1H, major), 4.43 (dd, *J* = 11.0, 1.0 Hz, 1H, major), 5.08 (d, *J* = 10.0 Hz, 1H, major), 5.51 (d, *J* = 8.6 Hz, 1H, minor), 6.54 (s, 1H, major), 6.56 (s, 2H, major), 6.69 (s, 2H, minor), 6.94 (s, 2H, major), 7.10 (s, 2H, minor), 7.44 (s, 1H, minor), 7.71 (d, *J* = 1.0 Hz, 1H, major). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.4 (major), −0.2 (minor), 31.7 (minor), 33.7 (major), 48.2 (minor), 51.4 (major), 56.1 (major), 56.2 (major), 56.29 (minor), 56.34 (major), 56.4 (minor), 60.7 (major), 60.85 (major), 60.92 (minor), 80.4 (major), 89.2 (major), 100.7 (major), 100.9 (minor), 103.2 (major), 103.8 (major), 104.4 (major), 104.9 (minor), 105.7 (minor), 105.9 (major), 113.9 (minor), 114.1 (major), 131.7 (minor), 132.6 (major), 132.9 (minor), 133.0 (major), 133.3 (major), 134.5 (minor), 138.3 (minor), 142.9 (minor), 152.8 (major), 153.28 (major), 153.31 (major), 153.4 (major), 153.5 (minor), 155.9 (major), 156.1 (minor), 194.5, (minor), 199.4 (major). IR (UATR): ν_{max} 2941, 28.8, 2176, 1668, 1582, 1124, 842 cm^{-1}. LRMS (EI): *m/z* (rel intensity) 700 (17) $[C_{34}H_{39}{}^{81}BrO_9Si]^+$, 698 (13) $[C_{34}H_{39}{}^{79}BrO_9Si]^+$, 388 (22), 195 (100). TOF-HRMS: calcd for $C_{34}H_{43}{}^{79}BrNO_9Si$ (M + NH_4^+) 716.1885, found 716.1873; calcd for $C_{34}H_{43}{}^{81}BrNO_9Si$ (M + NH_4^+) 718.1872, found 718.1867.

(6-Bromo-7-methoxy-2-(4-methoxyphenyl)-4-((trimethylsilyl)ethynyl)chroman-3-yl)(4-methoxyphenyl)-methyl Acetate (25). Diisobutylaluminum hydride (DIBAL-H; 1.0 M in toluene, 0.17 mL, 0.17 mmol) was added to a solution of chroman **24a** (0.076 g, 0.13 mmol) in toluene (2 mL) at 0 °C. The reaction mixture was stirred at that temperature for 1 h. The mixture was then quenched with water (0.1 mL) and 15% NaOH (0.1 mL) sequentially at −78 °C. The reaction mixture was warmed to room temperature, and water (0.3 mL) was added. Na_2SO_4 was then added, and the mixture was filtered through Celite. The filtrate was evaporated (aspirator then vacuum) to give a crude product, which was used in the next step without further purification.

A solution of the benzyl alcohol and DMAP (0.024 g, 0.20 mmol) in DCM (1.5 mL) was cooled in an ice bath for 10 min before Et_3N (28 μL, 0.20 mmol) and Ac_2O (19 μL, 0.20 mmol) were added successively. The mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with water (2 mL), and the resulting mixture was extracted with DCM (3 × 2 mL). The combined organic phases were washed with water (3 × 2 mL) and brine (2 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a crude product which was purified by column chromatography on silica (15–30% EtOAc/hexanes) to give the desired product **25** as a white solid (0.075 g, 0.12 mmol, 93%). ^1H NMR (300 MHz, $CDCl_3$): δ 0.14 (s, 9H), 2.92 (td, *J* = 8.1, 4.4 Hz, 1H), 3.73–3.78 (m, 1H), 3.77 (s, 3H), 3.79 (s, 3H), 3.80 (s, 3H), 4.90 (d, *J* = 8.1 Hz, 1H), 5.97 (d, *J* = 4.4 Hz, 1H), 6.41 (s, 1H), 6.73 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 0.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.0, 21.1, 30.3, 47.4, 55.2, 55.4, 56.2, 74.6, 78.1, 87.8, 100.7, 102.9, 106.4, 113.6, 113.8, 114.4, 127.5, 129.0, 129.8, 130.2, 133.4, 153.5, 155.7, 156.0, 159.7, 167.7. TOF-HRMS: calcd for $C_{32}H_{35}{}^{79}BrNaO_6Si$ (M + Na^+) 645.1278, found 645.1285; calcd for $C_{32}H_{35}{}^{81}BrNaO_6Si$ (M + Na^+) 647.1264, found 647.1250.

(6-Bromo-7-methoxy-2-(4-methoxyphenyl)-4-vinylchroman-3-yl)(4-methoxyphenyl)methyl Acetate (26). To a solution of chroman TMS acetylide **25** (0.075 g, 0.12 mmol) in THF (2 mL) was added tetrabutylammonium fluoride (TBAF; 0.059 g, 0.18 mmol) at 0 °C, and the reaction mixture was kept at this temperature for 3 h. The reaction mixture was quenched with water (2 mL), and the resulting mixture was extracted with EtOAc (3 × 2 mL). The combined organic phases were washed with water (3 × 2 mL) and brine (2 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a crude product, which was used in the next step without further purification.

A suspension of the chroman alkyne and Pd on $CaCO_3$ (0.051 g, 0.024 mmol) in DCM (7 mL) was stirred at room temperature under an H_2 atmosphere. After the mixture was stirred for 24 h, the palladium catalyst was removed by filtration through Celite and the filtrate was concentrated under reduced pressure to give the crude product, which was further purified by column chromatography on silica (15–30% EtOAc/hexanes) to give the desired product **26** as a white sticky gum (0.059 g, 0.11 mmol, 89%). ^1H NMR (300 MHz, $CDCl_3$): δ 2.09 (s, 3H), 2.66–2.75 (m, 1H), 3.27 (t, *J* = 8.3 Hz, 1H), 3.75 (s, 3H), 3.77 (s, 3H), 3.82 (s, 3H), 4.97 (dd, *J* = 16.9, 1.3 Hz, 1H), 5.03 (dd, *J* = 9.9, 1.3 Hz, 1H), 5.12 (d, *J* = 6.8 Hz, 1H), 5.41 (ddd, *J* = 16.9, 9.9, 8.3 Hz, 1H), 5.92 (d, *J* = 5.4 Hz, 1H), 6.69 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 7.18 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.0,

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J. Org. Chem. 2017, 82, 2672–2688

41.7, 48.0, 55.2, 55.3, 56.2, 74.5, 77.3, 100.9, 102.7, 113.5, 113.7, 116.3, 117.1, 127.3, 128.4, 130.7, 131.0, 133.9, 140.0, 154.1, 155.3, 158.8, 159.3, 169.7. TOF-HRMS: calcd for $C_{29}H_{29}{}^{79}BrNaO_6$ (M + Na^+) 575.1040, found 575.1038; calcd for $C_{29}H_{29}{}^{81}BrNaO_6$ (M + Na^+) 577.1024, found 577.1037.

General Procedure for the Desilylation Using Cs_2CO_3 in Methanol. To a solution of ketone chroman TMS acetylide **24** (1.0 equiv) in 1/1 THF/MeOH (20 mL $mmol^{-1}$) was added Cs_2CO_3 (2.0 equiv) at 0 °C, and the reaction mixture was stirred at a temperature between 5 and 9 °C until the starting material was consumed, as indicated by TLC (typically 3−4 h). Water and EtOAc were added, and the mixture was concentrated under reduced pressure. The residue was extracted with EtOAc, and the combined organic phases were washed with water and brine, dried over $NaSO_4$, filtered, and concentrated under reduced pressure to give a crude product, which was further purified by column chromatography on silica to give the desilylated product.

(6-Bromo-4-ethynyl-7-methoxy-2-(4-methoxyphenyl)-chroman-3-yl)(4-methoxyphenyl)methanone (28). Following the general procedure for the desilylation using Cs_2CO_3, ketone chroman TMS acetylide **24a** (0.075 g, 0.13 mmol) was converted to the corresponding ketone chroman alkyne **28**, which was obtained as a pale yellow solid (0.060 g, 0.12 mmol, 91%). Mp (EtOAc/hexanes): 167.6−168.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.11 (d, J = 2.4 Hz, 1H), 3.70 (s, 3H), 3.81 (s, 3H), 3.85 (s, 3H), 4.11 (dd, J = 11.0, 10.0 Hz, 1H), 4.45 (ddd, J = 11.0, 2.4, 1.0 Hz, 1H), 5.07 (d, J = 10.0 Hz, 1H), 6.51 (s, 1H), 6.72 (d, J = 8.7 Hz, 2H), 6.78 (d, J = 8.9 Hz, 2H), 7.24 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 8.9 Hz, 2H), 7.72 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 32.4, 50.5, 55.1, 55.3, 56.2, 72.1, 80.2, 82.2, 100.7, 102.9, 113.5, 113.8, 114.0, 128.4, 129.4, 130.6, 130.7, 132.4, 153.8, 155.8, 159.7, 163.6, 198.5. IR (UATR): ν_{max} 3292, 2937, 2170, 1664, 1599, 1260, 1154, 1030 cm^{-1}. LRMS (EI): m/z (rel intensity) 508 (9) $[C_{27}H_{24}{}^{81}BrO_5]^+$, 506 (14) $[C_{27}H_{24}{}^{79}BrO_5]^+$, 135 (100). TOF-HRMS: calcd for $C_{27}H_{24}{}^{79}BrO_5$ (M + H^+) 507.0802, found 507.0784; calcd for $C_{27}H_{24}{}^{81}BrO_5$ (M + H^+) 509.0785, found 509.0791.

(6-Bromo-2-(3,4-dimethoxyphenyl)-4-ethynyl-7-methoxy-chroman-3-yl)(3-methoxyphenyl)methanone (35a). Following the general procedure for the desilylation using Cs_2CO_3, ketone chroman TMS acetylide **24e** (0.188 g, 0.309 mmol) was converted to the corresponding ketone chroman alkyne **35a**, which was obtained as a yellow sticky gum (0.143 g, 0.266 mmol, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.16 (d, J = 2.4 Hz, 1H), 3.75 (s, 6H), 3.76 (s, 3H), 3.84 (s, 3H), 4.17 (dd, J = 10.6, 9.9 Hz, 1H), 4.47 (ddd, J = 10.6, 2.4, 0.7 Hz, 1H), 5.02 (d, J = 9.9 Hz, 1H), 6.52 (s, 1H), 6.68 (d, J = 8.2 Hz, 1H), 6.81 (d, J = 1.8 Hz, 1H), 6.86 (dd, J = 8.2, 1.8 Hz, 1H), 6.99 (dd, J = 8.2, 1.8 Hz, 1H), 7.17 (d, J = 1.8 Hz, 1H), 7.20 (dd, J = 8.2, 7.8 Hz, 1H), 7.29 (br d, J = 7.8 Hz, 1H), 7.73 (d, J = 0.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 32.4, 51.4, 55.3, 55.79, 55.81, 56.3, 72.2, 80.4, 82.1, 100.8, 103.2, 110.0, 110.9, 112.4, 113.8, 119.7, 120.2, 120.9, 129.2, 129.4, 132.5, 139.1, 148.9, 149.3, 153.7, 155.9, 159.4, 200.3. IR (UATR): ν_{max} 3288, 2937, 2836, 1672, 1595, 1262, 1152, 1026 cm^{-1}. LRMS (EI): m/z (rel intensity) 538 (18) $[C_{28}H_{25}{}^{81}BrO_6]^+$, 536 (19) $[C_{28}H_{25}{}^{79}BrO_6]^+$, 403 (35), 401 (37). TOF-HRMS: calcd for $C_{28}H_{26}{}^{79}BrO_6$ (M + H^+) 537.0907, found 537.0912; calcd for $C_{28}H_{26}{}^{81}BrO_6$ (M + H^+) 539.0888, found 539.0878.

(6-Bromo-4-ethynyl-7-methoxy-2-(4-methoxyphenyl)-chroman-3-yl)(3,4-dimethoxyphenyl)methanone (35b). Following the general procedure for the desilylation using Cs_2CO_3, ketone chroman TMS acetylide **24g** (0.103 g, 0.170 mmol) was converted to the corresponding ketone chroman alkyne **35b**, which was obtained as a yellow sticky gum (0.089 g, 0.165 mmol, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.13 (d, J = 2.4 Hz, 1H), 3.70 (s, 3H), 3.84 (s, 6H), 3.89 (s, 3H), 4.11 (dd, J = 11.0, 10.1 Hz, 1H), 4.46 (ddd, J = 11.0, 2.4, 1.0 Hz, 1H), 5.08 (d, J = 10.1 Hz, 1H), 6.51 (s, 1H), 6.73 (d, J = 8.9 Hz, 2H), 6.74 (d, J = 8.5 Hz, 1H), 7.248 (d, J = 8.9 Hz, 2H), 7.249 (d, J = 2.0 Hz, 1H), 7.36 (dd, J = 8.5, 2.0 Hz, 1H), 7.72 (d, J = 1.0, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 32.5, 50.5, 55.1, 55.8, 55.9, 56.2, 72.2, 80.1, 82.2, 100.7, 102.9, 109.7, 110.1, 113.8, 113.9, 123.5, 128.4, 129.4, 130.8, 132.4, 148.6, 153.4, 153.7, 155.8, 159.7, 198.5. IR (UATR): ν_{max} 3290, 2922, 2852, 1661, 1514, 1262 cm^{-1}. LRMS (EI): m/z (rel intensity) 554 (13) $[C_{29}H_{29}{}^{81}BrO_6]^+$, 552 (14) $[C_{29}H_{29}{}^{79}BrO_6]^+$, 374 (16), 372, (20), 165 (100). TOF-HRMS: calcd for $C_{29}H_{29}{}^{79}BrNaO_6$ (M + Na^+) 575.1040, found 575.1036; calcd for $C_{29}H_{29}{}^{81}BrNaO_6$ (M + Na^+) 577.1021, found 577.1025.

(6-Bromo-2-(3,4-dimethoxyphenyl)-4-ethynyl-7-methoxy-chroman-3-yl)(3,4-dimethoxyphenyl)methanone (35c). Following the general procedure for the desilylation using Cs_2CO_3, ketone chroman TMS acetylide **24h** (0.321 g, 0.502 mmol) was converted to the corresponding ketone chroman alkyne **35c**, which was obtained as a yellow sticky gum (0.252 g, 0.442 mmol, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.14 (d, J = 2.4 Hz, 1H), 3.77 (s, 3H), 3.78 (s, 3H), 3.84 (s, 6H), 3.89 (s, 3H), 4.13 (t, J = 10.5 Hz, 1H), 4.46 (br d, J = 10.5 Hz, 1H), 5.07 (d, J = 10.5 Hz, 1H), 6.52 (s, 1H), 6.68 (d, J = 8.1 Hz, 1H), 6.73 (d, J = 8.5 Hz, 1H), 6.88−6.91 (m, 2H), 7.26 (d, J = 1.2 Hz, 1H), 7.38 (dd, J = 8.5 Hz, 1H), 7.73 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 50.5, 55.76, 55.81, 55.9, 56.3, 72.2, 80.3, 82.2, 100.7, 103.1, 109.7, 110.0, 110.1, 110.9, 113.9, 119.9, 123.4, 129.7, 130.8, 132.5, 148.7, 148.9, 149.2, 153.60, 153.65, 155.8, 198.5. IR (UATR): ν_{max} 2936, 1661, 1593, 1515, 1260, 1148, 1021 cm^{-1}. LRMS (EI): m/z (rel intensity) 568 (17) $[C_{29}H_{27}{}^{81}BrO_7]^+$, 566 (17) $[C_{29}H_{27}{}^{79}BrO_7]^+$, 165 (100). TOF-HRMS: calcd for $C_{29}H_{27}{}^{79}BrNaO_7$ (M + Na^+) 589.0832, found 589.0821; calcd for $C_{29}H_{27}{}^{81}BrNaO_7$ (M + Na^+) 591.0817, found 591.0805.

General Procedure for the Lindlar Hydrogenation and Allyl Grignard Addition. A suspension of ketone chroman alkyne (1 equiv) and Pd on $CaCO_3$ (30 mol %) in DCM (30 mL $mmol^{-1}$) was stirred at room temperature under an H_2 atmosphere (300 psi). After the mixture was stirred for 5 h, the palladium catalyst was removed by filtration through Celite and the filtrate was concentrated under reduced pressure to give the crude corresponding ketone chroman alkene product, which was used in the next step without further purification.

To a solution of the ketone chroman alkene in 1/2 THF/Et_2O (20 mL $mmol^{-1}$) was added allylmagnesium bromide (1.0 M in Et_2O, 2.5 equiv) at 0 °C. The mixture was stirred and slowly warmed to 10 °C, at which it was stirred for an additional 18 h. The reaction mixture was quenched with saturated NH_4Cl. The resulting mixture was extracted with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a crude product, which was further purified by column chromatography on silica (0−30% EtOAc/hexanes) to give the desired diene alcohol product.

1-(6-Bromo-7-methoxy-2-(4-methoxyphenyl)-4-vinylchroman-3-yl)-1-(4-methoxyphenyl)but-3-en-1-ol (29). Following the general procedure for the Lindlar hydrogenation and allyl Grignard addition, ketone chroman alkyne **28** (0.070 g, 0.14 mmol) was converted to the corresponding diene alcohol **29**, which was obtained as a 2:1 inseparable mixture of diastereomers as a white sticky gum (0.063 g, 0.11 mmol, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.32 (s, 1H, minor), 2.40 (s, 1H, major), 2.40−2.49 (m, 1H, minor), 2.58−2.66 (m, 1H, major), 2.78 (d, J = 7.1 Hz, 1H, major), 3.02 (dd, J = 13.7, 5.5 Hz, 1H, minor), 3.51−3.60 (m, 1H, major), 3.74 (s, 3H, major), 3.81 (s, 3H, major), 3.88 (s, 3H, major), 4.53−4.71 (m, 2H, major), 4.96−5.20 (m, 3H, major), 5.46−5.64 (m, 2H, major), 6.53 (s, 1H, minor), 6.56, (s, 1H, major), 6.73 (d, J = 8.8 Hz, 2H, major), 6.74 (d, J = 8.9 Hz, 2H, minor), 6.88 (d, J = 9.0 Hz, 2H, minor), 6.89 (d, J = 8.7 Hz, 2H, major), 6.96 (d, J = 9.0 Hz, 2H, minor), 6.99 (d, J = 8.7 Hz, 2H, major), 7.11 (s, 1H, minor), 7.14 (s, 1H, major), 7.39 (d, J = 8.8 Hz, 2H, major), 7.42 (d, J = 8.9 Hz, 2H, minor). ^{13}C NMR (75 MHz, $CDCl_3$): δ 37.4, 37.8 (minor), 42.2, (minor), 42.4 (major), 54.0 (major), 55.1 (major), 55.2 (major), 56.1 (major), 74.4 (minor), 74.5 (major), 78.0 (minor), 78.3 (major), 100.7 (minor), 100.8 (major), 102.6 (major), 102.7 (minor), 113.4 (minor), 113.45 (major), 113.51 (minor), 113.6 (major), 113.68 (minor), 113.70 (major), 117.5 (major), 118.0 (minor), 120.0 (major), 120.2 (minor), 126.7 (major), 126.8 (minor), 127.2 (major), 127.5 (minor), 133.1 (major), 133.2 (minor), 133.4 (minor), 133.6 (major), 133.69 (minor), 133.71 (major), 136.4 (minor), 136.7 (major), 141.8, (minor), 142.0 (major), 153.1 (major), 153.3 (minor), 155.17 (minor), 155.22 (major), 158.3

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(major), 158.4 (minor), 158.48 (major), 158.53 (minor). IR (UATR): ν_{max} 3547, 2935, 1610, 1510 1247, 1153 cm^{-1}. LRMS (EI): *m/z* (rel intensity) 552 (1) $[C_{30}H_{31}{}^{81}BrO_5]^+$, 550 (1) $[C_{30}H_{31}{}^{79}BrO_5]^+$, 376 (16), 374 (17), 135 (100), 121 (30). TOF-HRMS: calcd for $C_{30}H_{31}{}^{79}BrNaO_5$ ($M + Na^+$) 573.1247, found 573.1262; calcd for $C_{30}H_{31}{}^{81}BrNaO_5$ ($M + Na^+$) 575.1232, found 575.1203.

1-(6-Bromo-2-(3,4-dimethoxyphenyl)-7-methoxy-4-vinylchroman-3-yl)-1-(3-methoxyphenyl)but-3-en-1-ol (36a). Following the general procedure for the Lindlar hydrogenation and allyl Grignard addition, ketone alkyne **35a** (0.106 g, 0.198 mmol) was converted to the corresponding diene alcohol **36a**, which was obtained as a 3:1 inseparable mixture of diastereomers as a yellow sticky gum (0.113 g, 0.194 mmol, 98%). ^1H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 1H, minor), 2.44 (s, 1H, major), 2.65−2.71 (m, 1H), 2.74−2.83 (m, 1H), 3.01 (dd, *J* = 13.9, 5.6 Hz, 1H, minor), 3.57 (d, *J* = 8.3 Hz, 1H, minor), 3.64 (d, *J* = 8.3 Hz, 1H, major), 3.72 (s, 3H), 3.80 (s, 3H), 3.81 (s, 3H), 3.86 (s, 3H), 4.62−4.78 (m, 2H), 5.03−5.26 (m, 3H), 5.39−5.63 (m, 2H), 6.55 (s, 1H, minor), 6.57 (s, 2H, major), 6.60−6.74 (m, 2H), 6.75−6.84 (m, 1H), 6.97−7.10 (m, 2H), 7.12 (s, 1H, minor), 7.18 (s, 1H, major), 7.22−7.32 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 37.7 (major), 37.9 (minor), 42.4 (minor), 43.1 (major), 53.8 (major), 53.9 (minor), 55.1 (major), 55.2 (major), 55.70 (major), 55.73 (minor), 55.8 (major), 56.2 (major), 74.6 (minor), 75.1 (major), 78.3 (minor), 78.7 (major), 100.7 (minor), 100.8 (major), 102.8 (major), 109.3 (major), 109.4 (minor), 110.7 (major), 110.8 (minor), 111.8 (major), 112.2 (minor), 112.6 (major), 112.7 (minor), 113.7 (minor), 113.9 (major), 117.8 (major), 118.0 (major), 118.1 (minor), 118.3 (major), 118.7 (minor), 120.1 (major), 120.4 (minor), 129.1 (minor), 129.3 (major), 132.9 (major), 133.1 (minor), 133.7 (major), 133.9 (minor), 134.1 (major), 141.9 (minor), 142.1 (major), 146.2 (major), 146.6 (major), 147.8 (major), 148.6 (major), 153.3 (major), 153.4 (minor), 155.3 (major), 159.7 (minor), 159.8 (major). IR (UATR): ν_{max} 3546, 2937, 1607, 1515, 1257, 1144, 1027 cm^{-1}. LRMS (EI): *m/z* (rel intensity) 582 (1) $[C_{31}H_{33}{}^{81}BrO_6]^+$, 580 (1) $[C_{31}H_{33}{}^{79}BrO_6]^+$, 178 (84), 135 (100). TOF-HRMS: calcd for $C_{31}H_{33}{}^{79}BrNaO_6$ ($M + Na^+$) 603.1353, found 603.1348; calcd for $C_{31}H_{33}{}^{81}BrNaO_6$ ($M + Na^+$) 605.1338, found 605.1340.

1-(6-Bromo-7-methoxy-2-(4-methoxyphenyl)-4-vinylchroman-3-yl)-1-(3,4-dimethoxyphenyl)but-3-en-1-ol (36b). Following the general procedure for the Lindlar hydrogenation and allyl Grignard addition, ketone alkyne **35b** (0.089 g, 0.166 mmol) was converted to the corresponding diene alcohol **36b**, which was obtained as a 2:1 inseparable mixture of diastereomers as a yellow sticky gum (0.086 g, 0.149 mmol, 90%). ^1H NMR (300 MHz, $CDCl_3$): δ 2.35−2.50 (m, 1H), 2.59−2.67 (m, 1H), 2.75−2.83 (m, 1H), 2.97−3.07 (m, 1H, minor), 3.55−3.64 (m, 1H), 3.74 (s, 3H), 3.88 (s, 6H), 3.89 (s, 3H), 4.57−4.74 (m, 2H), 4.96−5.25 (m, 3H), 5.35−5.67 (m, 2H), 6.53 (s, 1H, minor), 6.56 (s, 1H, major), 6.65−6.79 (m, 2H), 6.79−6.90 (m, 1 Hz), 6.90−7.06 (m, 4H), 7.06−7.10 (m, 1H, minor), 7.11 (s, 1H, minor), 7.15 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 37.6 (major), 37.9 (minor), 42.2 (minor), 42.8 (major), 53.87 (major), 53.92 (minor), 55.1 (major), 55.78 (minor), 55.81 (major), 56.0 (major), 56.1 (major), 74.3 (minor), 74.8 (major), 78.1 (minor), 78.5 (major), 100.7 (minor), 100.9 (major), 102.6 (major), 109.6 (major), 109.9 (minor), 110.4 (minor), 110.7 (major), 113.5 (major), 113.6 (minor), 113.7 (minor), 113.8 (major), 117.6 (major), 117.8 (minor), 118.3 (major), 118.7 (minor), 120.1 (major), 120.3 (minor), 126.7 (major), 129.1 (minor), 133.06 (major), 133.14 (minor), 133.4 (minor), 133.57 (major), 133.63 (major), 133.7 (minor), 136.9 (minor), 137.3 (major), 141.8 (minor), 142.0 (major), 147.9 (major), 148.0 (minor), 148.8 (minor), 148.9 (major), 153.2 (major), 153.3 (major), 155.2 (major), 158.3 (major), 158.4 (minor). IR (UATR): ν_{max} 3546, 2935, 2835, 1610, 1512, 1252, 1151, 1028 cm^{-1}. LRMS (EI): *m/z* (rel intensity) 582 (0.3) $[C_{31}H_{33}{}^{81}BrO_6]^+$, 580 (1) $[C_{31}H_{33}{}^{79}BrO_6]^+$, 165 (100). TOF-HRMS: calcd for $C_{31}H_{33}{}^{79}BrNaO_6$ ($M + Na^+$) 603.1353, found 603.1338; calcd for $C_{31}H_{33}{}^{81}BrNaO_6$ ($M + Na^+$) 605.1338, found 605.1347.

1-(6-Bromo-2-(3,4-dimethoxyphenyl)-7-methoxy-4-vinylchroman-3-yl)-1-(3,4-dimethoxyphenyl)but-3-en-1-ol (36c). Following the general procedure for the Lindlar hydrogenation and allyl Grignard addition, ketone alkyne **35c** (0.375 g, 0.661 mmol) was converted to the corresponding diene alcohol **36c**, which was obtained as a 4:1 inseparable mixture of diastereomers as a yellow sticky gum (0.376 g, 0.614 mmol, 93%). ^1H NMR (300 MHz, $CDCl_3$): δ 2.38−2.51 (m, 1H), 2.66 (s, 1H, major), 2.80 (d, *J* = 7.3 Hz, 1H), 3.05 (dd, *J* = 13.9, 5.6 Hz, 1H, minor), 3.57−3.66 (m, 1H), 3.73 (s, 3H, minor), 3.74 (s, 3H, major), 3.82 (s, 3H, major), 3.88 (s, 3H, major), 3.885 (s, 3H), 3.889 (s, 3H), 3.394 (s, 3H, minor), 4.61−4.78 (m, 2H), 5.04−5.27 (m, 3H), 5.45−5.69 (m, 2H), 6.54, (s, 1H, minor), 6.57 (s, 1H, major), 6.58−6.68 (m, 2H), 6.71 (d, *J* = 8.4 Hz, 1H, major), 6.72 (d, *J* = 8.4 Hz, 1H, minor), 6.837 (d, *J* = 8.5 Hz, 1H, minor), 6.844 (d, *J* = 8.3 Hz, 1H, major), 6.96 (dd, *J* = 8.4, 2.1 Hz, 1H, major), 6.99−7.04 (m, 1H, major), 7.10 (d, *J* = 2.0 Hz, 1H, minor), 7.13 (s, 1H, minor), 7.18 (s, 1H, major), 7.28 (s, 1H, minor).^{13}C NMR (75 MHz, $CDCl_3$): δ 37.7 (major), 37.9 (minor), 42.1 (minor), 42.9 (major), 54.0, (minor), 54.1 (major), 55.7 (major), 55.80 (major), 55.83 (minor), 55.9 (major), 56.0 (major), 56.2 (major), 74.4 (minor), 75.1 (major), 78.1 (major), 78.4 (major), 100.6 (minor), 100.9 (major), 102.8 (major), 109.3 (minor), 109.4 (major), 109.7 (major), 109.9 (minor), 110.5 (minor), 110.7 (major), 110.8 (major), 113.8 (minor), 113.9 (major), 117.8 (major), 117.9 (major), 118.0 (major), 118.1 (major), 118.4 (major), 118.8 (minor), 120.2 (major), 120.4 (minor), 133.1 (major), 133.2 (minor), 133.6 (major), 133.7 (minor), 133.9 (minor), 134.2 (major), 136.9 (major), 137.2 (major), 141.9 (minor), 142.1 (major), 147.8 (major), 147.9 (minor), 148.0 (major), 148.1 (minor), 148.6 (major), 148.7 (minor), 148.8 (minor), 148.9 (major), 153.3 (major), 153.4 (minor), 155.3 (major). IR (UATR): ν_{max} 3534, 2935, 1608, 1514, 1256, 1144, 1025 cm^{-1}. TOF-HRMS: calcd for $C_{32}H_{35}{}^{79}BrNaO_7$ ($M + Na^+$) 633.1458, found 633.1445; calcd for $C_{32}H_{35}{}^{81}BrNaO_7$ ($M + Na^+$) 635.1444, found 635.1437.

General Procedure for the $BF_3{\cdot}Et_2O$-Mediated Et_3SiH Reduction. A solution of alcohol (1.0 equiv) in DCM (10 mL $mmol^{-1}$) was cooled in an ice bath for 5 min. At this time, Et_3SiH (10 equiv) and $BF_3{\cdot}Et_2O$ (1.5 equiv) were added to the reaction mixture successively. The stirring was continued (for the time and temperature indicated for each substrate). When the reaction was complete, water was added to quench the reaction. The aqueous layer was extracted with DCM, and the combined organic phases were washed with water and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a crude product, which was further purified by PTLC to give the desired product.

6-Bromo-7-methoxy-2-(4-methoxyphenyl)-3-(1-(4-methoxyphenyl)but-3-en-1-yl)-4-vinylchroman (27). Following the general procedure for the $BF_3{\cdot}Et_2O$-mediated Et_3SiH reduction at 0 °C for 2 h, diene alcohol **29** (0.016 g, 0.029 mmol) furnished the diene **27** as a yellow sticky gum (0.013 g, 0.025 mmol, 86%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.82−1.93 (m, 1H), 1.95−2.07 (m, 1H), 2.20 (dt, *J* = 6.8, 1.7 Hz, 1H), 2.70 (ddd, *J* = 10.1, 6.8, 5.6 Hz, 1H), 3.11−3.16 (m, 1H), 3.73 (s, 3H), 3.85 (s, 3H), 3.86 (s, 3H), 4.62 (dd, *J* = 17.0, 2.1 Hz, 1H), 4.68 (dd, *J* = 10.2, 2.1 Hz, 1H), 4.78 (dt, *J* = 17.0, 1.5 Hz, 1H), 5.17 (dt, *J* = 10.1, 1.3 Hz, 1H), 5.17−5.30 (m, 2H), 5.98 (ddd, *J* = 17.0, 10.2, 5.5 Hz, 1H), 6.42 (s, 1H), 6.62 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 6.83 (s, 1H), 6.98 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 39.6, 41.8, 42.1, 46.3, 55.2, 55.3, 56.2, 74.6, 100.6, 102.1, 113.0, 113.8, 115.3, 115.6, 117.2, 126.4, 129.6, 132.4, 134.4, 137.1, 142.9, 154.9, 155.2, 157.9, 158.8. IR (UATR): ν_{max} 2932, 2836, 1610, 1511, 1246, 1156 cm^{-1}. LRMS (EI): *m/z* (rel intensity) 536 (7) $[C_{30}H_{31}{}^{81}BrO_4]^+$, 543 (5) $[C_{30}H_{31}{}^{79}BrO_4]^+$, 253 (100), 161 (95). TOF-HRMS: calcd for $C_{30}H_{35}{}^{79}BrNO_4$ ($M + NH_4^+$) 552.1744, found 552.1742; calcd for $C_{30}H_{31}{}^{81}BrNO_4$ ($M + NH_4^+$) 554.1729, found 554.1729.

6-Bromo-3-(1-(3,4-dimethoxyphenyl)but-3-en-1-yl)-7-methoxy-2-(4-methoxyphenyl)-4-vinylchroman (37b). Following the general procedure for the $BF_3{\cdot}Et_2O$-mediated Et_3SiH reduction at 0 °C for 1 h, diene alcohol **36b** (0.086 g, 0.148 mmol) furnished the diene **37b** as a yellow sticky gum (0.045 g, 0.080 mmol, 54%).^1H NMR (300 MHz, $CDCl_3$): δ 1.77−1.88 (m, 1H), 1.95−2.10 (m, 1H), 2.20 (dt, *J* = 7.1, 1.5 Hz, 1H), 2.68 (ddd, *J* = 10.2, 7.1, 5.2 Hz, 1H), 3.08−3.13 (m, 1H), 3.70 (s, 3H), 3.81 (s, 3H), 3.85 (s, 3H), 3.86 (s, 3H), 4.63 (dd, *J* = 17.0, 2.0 Hz, 1H), 4.70 (dd, *J* = 10.2, 2.0 Hz, 1H),

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J. Org. Chem. 2017, 82, 2672−2688

4.78 (dt, J = 15.0, 1.4 Hz, 1H), 5.18 (dt, J = 10.2, 1.5 Hz, 1H), 5.18–5.53 (m, 2H), 5.99 (ddd, J = 17.0, 10.2, 5.5 Hz, 1H), 6.29 (d, J = 1.9 Hz, 1H), 6.41 (dd, J = 8.3, 1.9 Hz, 1H), 6.44 (s, 1H), 6.62 (d, J = 8.3 Hz, 1H), 6.85 (s, 1H), 6.98 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 39.4, 41.8, 42.6, 46.5, 55.3, 55.7, 55.9, 56.2, 74.6, 100.6, 102.3, 110.7, 112.6, 113.9, 115.4, 115.7, 117.2, 120.5, 126.4, 132.4, 134.5, 134.8, 137.0, 142.9, 147.3, 148.1, 155.0, 155.2, 158.8. IR (UATR): ν_{max} 2934, 2835, 1513, 1249, 1156, 1029, 832 cm^{-1}. LRMS (EI): m/z (rel intensity) 566 (5) $[C_{31}H_{33}{}^{81}BrO_5]^+$, 564 (4) $[C_{31}H_{33}{}^{79}BrO_5]^+$, 191 (100). TOF-HRMS: calcd for $C_{31}H_{33}{}^{79}BrNaO_5$ (M + Na$^+$) 587.1404, found 587.1379; calcd for $C_{31}H_{33}{}^{81}BrNaO_5$ (M + Na$^+$) 589.1389, found 589.1390.

6-Bromo-2-(3,4-dimethoxyphenyl)-3-(1-(3,4-dimethoxyphenyl)but-3-en-1-yl)-7-methoxy-4-vinylchroman (37c). Following the general procedure for the $BF_3{\cdot}Et_2O$-mediated Et_3SiH reduction at 0 °C for 2 h, diene alcohol **36c** (0.030 g, 0.049 mmol) furnished the diene **37c** as a yellow sticky gum (0.010 g, 0.017 mmol, 34%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.75–1.86 (m, 1H), 1.99–2.12 (m, 1H), 2.18 (br d, J = 7.1 Hz, 1H), 2.69 (ddd, J = 10.2, 7.1, 5.0 Hz, 1H), 3.06–3.11 (m, 1H), 3.69 (s, 3H), 3.81 (s, 3H), 3.86 (s, 3H), 3.93 (s, 3H), 3.97 (s, 3H), 4.63 (dd, J = 17.0, 2.0 Hz, 1H), 4.71 (dd, J = 10.2, 2.0 Hz, 1H), 4.78 (dt, J = 17.0, 1.4 Hz, 1H), 5.20 (dt, J = 10.2, 1.3 Hz, 1H), 5.22–5.34 (m, 2H), 6.00 (ddd, J = 17.0, 10.2, 5.5 Hz, 1H), 6.29 (d, J = 1.9 Hz, 1H), 6.42 (dd, J = 8.2, 1.9 Hz, 1H), 6.47 (s, 1H), 6.63 (d, J = 8.2 Hz, 1H), 6.85 (s, 1H), 6.95 (d, J = 8.2 Hz, 1H), 7.03–7.10 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 39.5, 41.9, 42.5, 46.6, 55.7, 55.8, 55.9, 56.1, 56.2, 74.5, 100.6, 102.3, 108.7, 110.7, 111.2, 112.7, 115.4, 115.7, 117.3, 117.5, 120.4, 132.9, 134.5, 134.8, 137.1, 142.9, 147.4, 148.1, 148.3, 149.2, 155.0, 155.1. IR (UATR): ν_{max} 2935, 1609, 1514, 1257, 1160, 1142, 1027 cm^{-1}. LRMS (EI): m/z (rel intensity) 596 (6) $[C_{32}H_{35}{}^{81}BrO_6]^+$, 594 (3) $[C_{32}H_{35}{}^{79}BrO_6]^+$, 191 (100). TOF-HRMS: calcd for $C_{32}H_{35}{}^{79}BrNaO_6$ (M + Na$^+$) 617.1509, found 617.1500; calcd for $C_{32}H_{35}{}^{81}BrNaO_6$ (M + Na$^+$) 619.1495, found 619.1486.

General Procedure for the Ring-Closing Metathesis. Grubbs II catalyst (10 mol %) or Hoveyda–Grubbs II catalyst (8 mol %) was added to a solution of the corresponding diene (1 equiv) in toluene (100 mL mmol^{-1}). Then, the mixture was heated at 60 °C (or 70 °C in the case of Hoveyda–Grubbs II catalyst) for 18 h. The reaction mixture was evaporated under reduced pressure. The residue was purified by PTLC (50/2/48 DCM/MeOH/hexanes) to give the desired cyclic product.

(6β,6aβ,7β,10aα)-2-Bromo-3-methoxy-6,7-bis(4-methoxyphenyl)-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromene (30). Following the general procedure for the ring-closing metathesis using Grubbs II as catalyst (10 mol %), diene **27** (0.013 g, 0.025 mmol) was converted to the corresponding tricyclic product **30**, which was obtained as a white sticky gum (0.010 g, 0.020 mmol, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.13–2.25 (m, 1H), 2.65–2.85 (m, 2H), 3.26 (dd, J = 7.0, 3.1 Hz, 1H), 3.64 (s, 6H), 3.78 (s, 3H), 3.80–3.85 (br m, 1H), 5.28 (d, J = 4.4 Hz, 1H), 5.94 (ddt, J = 10.1, 4.8, 2.5 Hz, 1H), 6.31–6.44 (m, 6H), 6.72 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 8.7 Hz, 2H), 7.56 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.3, 35.0, 39.4, 42.8, 55.1, 56.1, 81.7, 101.4, 101.7, 112.9, 113.1, 117.9, 127.8, 127.9, 129.4, 130.3, 131.1, 134.7, 153.8, 155.2, 157.6, 159.0. IR (UATR): ν_{max} 2909, 2835, 1608, 1512, 1247, 1149, 828 cm^{-1}. LRMS (EI): m/z (rel intensity) 508 (64) $[C_{28}H_{27}{}^{81}BrO_4]^+$, 506 (66) $[C_{28}H_{27}{}^{79}BrO_4]^+$, 253 (89), 121 (100). TOF-HRMS: calcd for $C_{28}H_{27}{}^{79}BrNaO_4$ (M + Na$^+$) 529.0985, found 529.0980; calcd for $C_{28}H_{27}{}^{81}BrNaO_4$ (M + Na$^+$) 531.0969, found 531.0949.

(6β,6aβ,7β,10aα)-2-Bromo-7-(3,4-dimethoxyphenyl)-3-methoxy-6-(4-methoxyphenyl)-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromene (38b). Following the general procedure for the ring-closing metathesis using Grubbs II as catalyst (10 mol %), diene **37b** (0.045 g, 0.080 mmol) was converted to the corresponding tricyclic product **38b**, which was obtained as a pale brown sticky gum (0.035 g, 0.065 mmol, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.14–2.26 (m, 1H), 2.71 (ddd, J = 12.5, 3.9, 3.9 Hz, 1H), 2.73–2.85 (m, 1H), 3.24 (dd, J = 7.0, 3.9 Hz, 1H), 3.63, (s, 3H), 3.67 (s, 3H), 3.71 (s, 3H), 3.78 (s, 3H), 3.83–3.92 (m, 1H), 5.28 (d, J = 3.9 Hz, 1H), 5.95 (ddt, J = 10.1, 4.8, 2.5 Hz, 1H), 6.34–6.46 (m, 7H), 6.73, (d, J = 8.7 Hz, 2H), 7.57 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.5, 34.9, 39.7, 42.8, 55.1, 55.6, 55.9, 56.1, 81.6, 101.4, 101.7, 110.8, 112.4, 112.9, 117.9, 121.2, 127.5, 128.0, 129.3, 130.2, 131.0, 135.5, 147.2, 147.9, 153.8, 155.2, 159.0. IR (UATR): ν_{max} 2932, 2834, 1608, 1513, 1255, 1146, 1028 cm^{-1}. LRMS (EI): m/z (rel intensity) 539 (96) $[C_{29}H_{30}{}^{81}BrO_5]^+$, 537 (100) $[C_{29}H_{30}{}^{79}BrO_5]^+$, 374 (32), 372 (38), 283 (45), 121 (85). TOF-HRMS: calcd for $C_{29}H_{29}{}^{79}BrNaO_5$ (M + Na$^+$) 559.1091, found 559.1101; calcd for $C_{29}H_{29}{}^{81}BrNaO_5$ (M + Na$^+$) 561.1072, found 561.1074.

(6β,6aβ,7β,10aα)-2-Bromo-6,7-bis(3,4-dimethoxyphenyl)-3-methoxy-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromene (38c). Following the general procedure for the ring-closing metathesis using Grubbs II as catalyst (10 mol %), diene **37c** (0.010 g, 0.017 mmol) was converted to the corresponding tricyclic product **38c**, which was obtained as a yellow sticky gum (0.008 g, 0.013 mmol, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.16–2.28 (m, 1H), 2.66–2.87 (m, 2H), 3.25 (dd, J = 7.0, 3.1 Hz, 1H), 3.59 (s, 3H), 3.67 (s, 3H), 3.71 (s, 3H), 3.72 (s, 3H), 3.79 (s, 3H), 3.90–3.99 (m, 1H), 5.26 (d, J = 4.6 Hz, 1H), 5.97 (ddt, J = 10.2, 4.5, 2.5 Hz, 1H), 6.32–6.50 (m, 8H), 7.58 (d, J = 0.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.7, 34.9, 39.8, 42.9, 55.67, 55.70, 55.90, 55.95, 56.1, 81.9, 101.5, 101.9, 110.7, 112.2, 112.5, 117.8, 121.2, 121.4, 127.7, 128.1, 130.2, 131.6, 135.5, 147.3, 148.0, 148.1, 148.8, 153.7, 155.3. IR (UATR): ν_{max} 2925, 1606, 1516, 1257, 1144, 1026 cm^{-1}. LRMS (EI): m/z (rel intensity) 568 (33) $[C_{30}H_{31}{}^{81}BrO_6]^+$, 566 (36) $[C_{30}H_{31}{}^{79}BrO_6]^+$, 178 (87), 151 (76), 57(100). TOF-HRMS: calcd for $C_{30}H_{31}{}^{79}BrNaO_6$ (M + Na$^+$) 589.1196, found 589.1193; calcd for $C_{30}H_{31}{}^{81}BrNaO_6$ (M + Na$^+$) 591.1181, found 591.1176.

2-Bromo-3-methoxy-6,7-bis(4-methoxyphenyl)-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromen-7-ol (31 and 32). Following the general procedure for the ring-closing metathesis using Grubbs II as catalyst (10 mol %), diene alcohol **29** (0.065 g, 0.118 mmol) was converted to the corresponding tricyclic product **31**, which was obtained as a brown oil (0.018 g, 0.034 mmol, 29%), and the corresponding tricyclic product **32**, which was obtained as a brown oil (0.030 g, 0.057 mmol, 48%).

(6α,6aβ,7β,10aα)-2-Bromo-3-methoxy-6,7-bis(4-methoxyphenyl)-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromen-7-ol (31). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.81 (br s, 1H), 2.53–2.72 (m, 3H), 3.36 (br d, J = 10.7 Hz, 1H), 3.74 (s, 3H), 3.81 (s, 3H), 3.86 (s, 3H), 4.66 (d, J = 10.4 Hz, 1H), 6.03–6.13 (m, 1H), 6.30 (dd, J = 10.2, 1.9 Hz, 1H), 6.34 (s, 1H), 6.87 (d, J = 8.9 Hz, 2H), 7.00 (d, J = 8.7 Hz, 2H), 7.34 (d, J = 8.9 Hz, 2H), 7.38 (d, J = 8.7 Hz, 2H), 7.45 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.3, 44.0, 48.9, 55.2, 55.3, 56.2, 74.4, 79.8, 101.1, 102.1, 113.2, 114.3, 118.1, 127.0, 127.2, 128.0, 129.4, 129.8, 132.6, 136.1, 154.1, 154.9, 158.9, 160.2. IR (UATR): ν_{max} 3563, 2906, 2836, 1609, 1511, 1247 cm^{-1}. LRMS (EI): m/z (rel intensity) 524 (11) $[C_{28}H_{27}{}^{81}BrO_5]^+$, 522 (11) $[C_{28}H_{27}{}^{79}BrO_5]^+$, 374 (15), 372 (14), 135 (100). TOF-HRMS: calcd for $C_{28}H_{28}{}^{79}BrO_5$ (M + H$^+$) 523.1115, found 523.1090; calcd for $C_{28}H_{28}{}^{81}BrO_5$ (M + H$^+$) 525.1096, found 525.1097.

(6α,6aβ,7α,10aα)-2-Bromo-3-methoxy-6,7-bis(4-methoxyphenyl)-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromen-7-ol (32). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.15–2.30 (m, 2H), 2.42 (t, J = 10.2 Hz, 1H), 2.64–2.77 (m, 1H), 3.67 (s, 3H), 3.69 (s, 3H), 3.69–3.72 (m, 1H), 3.75 (s, 3H), 5.04 (d, J = 10.2 Hz, 1H), 5.97 (ddt, J = 10.2, 5.0, 2.5 Hz, 1H), 6.38 (s, 1H), 6.39–6.45 (m, 7H), 6.86 (d, J = 8.1 Hz, 2H), 7.45 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 34.0, 43.4, 52.5, 55.1, 55.2, 56.3, 72.5, 81.4, 102.6, 102.8, 112.9, 113.2, 123.9, 125.0, 126.2, 126.3, 127.6, 128.1, 134.7, 136.1, 154.8, 155.0, 158.0, 158.3. IR (UATR): ν_{max} 3503, 2930, 2835, 1608, 1512, 1247 cm^{-1}. LRMS (EI): m/z (rel intensity) 524 (3) $[C_{28}H_{27}{}^{81}BrO_5]^+$, 522 (3) $[C_{28}H_{27}{}^{79}BrO_5]^+$, 149 (92), 69 (100). TOF-HRMS: calcd for $C_{28}H_{28}{}^{79}BrO_5$ (M + H$^+$) 523.1115, found 523.1094; calcd for $C_{28}H_{28}{}^{81}BrO_5$ (M + H$^+$) 525.1096, found 525.1104.

(6α,6aβ,7β,10aα)-2-Bromo-3-methoxy-6,7-bis(4-methoxyphenyl)-6a,7,8,10a-tetrahydro-6*H*-benzo[c]chromene (33). Following the general procedure for the $BF_3{\cdot}Et_2O$-mediated Et_3SiH reduction at 0 °C for 30 min, tricyclic alcohol **31** (0.014 g, 0.034

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J. Org. Chem. 2017, 82, 2672–2688

mmol) furnished the corresponding tricyclic product **33** as a yellow sticky gum (0.010 g, 0.020 mmol, 58%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.18−2.29 (m, 1H), 2.41 (td, J = 10.9, 3.2 Hz, 1H), 2.58−2.75 (m, 1H), 2.95 (dd, J = 7.0, 3.2 Hz, 1H), 3.46 (br d, J = 10.9 Hz, 1H), 3.75 (s, 3H), 3.78 (s, 3H), 3.88 (s, 3H), 4.48 (d, J = 10.9 Hz, 1H), 6.07 (ddd, J = 9.8, 4.3, 2.5 Hz, 1H), 6.29−6.36 (m, 1H), 6.36 (s, 1H), 6.77 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 1.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.9, 33.1, 36.8, 41.9, 55.2, 55.4, 56.1, 81.1, 101.1, 101.7, 113.3, 114.3, 118.1, 127.7, 128.6, 129.7, 129.8, 130.0, 130.7, 133.9, 154.5, 154.8, 158.4, 160.1. IR (UATR): ν_{max} 2909, 2830, 1610, 1513, 1250, 1155, 830 cm^{-1}. LRMS (EI): m/z (rel intensity) 508 (44) $[C_{28}H_{27}{}^{81}BrO_4]^+$, 506 (37) $[C_{28}H_{27}{}^{79}BrO_4]^+$, 253 (100), 121 (91). TOF-HRMS: calcd for $C_{28}H_{27}{}^{79}BrNaO_4$ (M + Na$^+$) 529.0985, found 529.0972; calcd for $C_{28}H_{27}{}^{81}BrNaO_4$ (M + Na$^+$) 531.0969, found 531.0967.

(6*α*,6a*β*,7*β*,10a*β*)-2-Bromo-3-methoxy-6,7-bis(4-methoxyphenyl)-6a,7,8,10a-tetrahydro-6*H*-benzo[c]chromene (34). Following the general procedure for the $BF_3{\cdot}Et_2O$-mediated Et_3SiH reduction at 0 °C for 30 min, tricyclic alcohol **32** (0.052 g, 0.010 mmol) furnished the corresponding tricyclic product **33** (0.009 g, 0.018 mmol, 18%) and the corresponding tricyclic product **34** as a white solid (0.019 g, 0.038 mmol, 38%). Mp (EtOAc/hexanes): 157.3−159.7 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.14−2.27 (m, 1H), 2.40−2.55 (m, 1H), 2.87−2.96 (m, 1H), 3.24−3.33 (m, 1H), 3.70 (s, 3H), 3.71 (s, 3H), 3.76 (s, 3H), 3.76−3.83 (m, 1H), 4.87 (d, J = 10.2 Hz, 1H), 5.76−5.83 (m, 1H), 5.84−5.92 (m, 1H), 6.39 (s, 1H), 6.44 (d, J = 8.7 Hz, 2H), 6.47 (d, J = 8.6 Hz, 2H), 6.56 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 7.39 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.9, 39.9, 40.4, 42.3, 55.19, 55.21, 56.2, 77.03, 100.9, 102.3, 113.1, 113.2, 119.1, 125.6, 127.5, 129.4, 130.2, 131.1, 132.7, 135.1, 154.9, 155.0, 156.9, 159.4. IR (UATR): ν_{max} 3001, 2907, 1610, 1514, 1247 cm^{-1}. LRMS (EI): m/z (rel intensity) 508 (13) $[C_{28}H_{27}{}^{81}BrO_7]^+$, 506 (12) $[C_{28}H_{27}{}^{79}BrO_4]^+$, 253 (100). TOF-HRMS: calcd for $C_{28}H_{31}{}^{79}BrNO_4$ (M + NH_4^+) 524.1431, found 524.1434; calcd for $C_{28}H_{31}{}^{81}BrNO_4$ (M + NH_4^+) 526.1415, found 526.1434.

2-Bromo-6-(3,4-dimethoxyphenyl)-3-methoxy-7-(3-methoxyphenyl)-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromen-7-ol (39a and 40a). Following the general procedure for the ring-closing metathesis using Grubbs II as catalyst (10 mol %), diene alcohol **36a** (0.533 g, 0.917 mmol) was converted to the corresponding tricyclic product **39a**, which was obtained as a red sticky gum (0.130 g, 0.238 mmol, 26%), and the corresponding tricyclic product **40a**, which was obtained as a yellow sticky gum (0.332 g, 0.596 mmol, 65%).

(6*α*,6a*β*,7*β*,10a*α*)-2-Bromo-6-(3,4-dimethoxyphenyl)-3-methoxy-7-(3-methoxyphenyl)-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromen-7-ol (39a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.02 (br s, 1H), 2.55−2.75 (m, 3H), 3.45 (br d, J = 10.2 Hz, 1H), 3.75 (s, 3H), 3.80 (s, 3H), 3.92 (s, 3H), 3.93 (s, 3H), 4.66 (d, J = 10.2 Hz, 1H), 6.05−6.14 (m, 1H), 6.28−6.36 (m, 1H), 6.36 (s, 1H), 6.81−6.86 (m, 1H), 6.92 (d, J = 1.9 Hz, 1H), 6.96 (d, J = 8.3 Hz, 1H), 6.99−7.07 (m, 3H), 7.22−7.29 (m, 1H), 7.47 (d, J = 0.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.3, 43.6, 48.8, 55.2, 55.9, 56.0, 56.2, 74.4, 80.2, 101.1, 102.2, 111.3, 111.7, 112.1, 113.0, 118.1, 118.4, 121.0, 126.8, 128.0, 128.8, 129.4, 132.5, 145.9, 149.2, 149.8, 154.0, 154.9, 159.3. IR (UATR): ν_{max} 3546, 2935, 1607, 1514, 1489, 1260, 1159, 1026 cm^{-1}. LRMS (EI): m/z (rel intensity) 554 (16) $[C_{29}H_{29}{}^{81}BrO_6]^+$, 552 (15) $[C_{29}H_{29}{}^{79}BrO_6]^+$, 151 (64), 135 (100). TOF-HRMS: calcd for $C_{29}H_{29}{}^{79}BrNaO_6$ (M + Na$^+$) 575.1024, found 575.1033; calcd for $C_{29}H_{29}{}^{81}BrNaO_6$ (M + Na$^+$) 577.1024, found 577.1016.

(6*α*,6a*β*,7*α*,10a*α*)-2-Bromo-6-(3,4-dimethoxyphenyl)-3-methoxy-7-(3-methoxyphenyl)-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromen-7-ol (40a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.17−2.28 (m, 1H), 2.32 (s, 1H), 2.45 (t, J = 10.0 Hz, 1H), 2.66−2.77 (m, 1H), 3.60 (s, 6H), 3.67−3.73 (m, 1H), 3.75 (s, 3H), 3.76 (s, 3H), 5.04 (d, J = 10.0 Hz, 1H), 5.96 (ddt, J = 7.7, 5.0, 2.5 Hz, 1H), 6.10 (d, J = 1.9 Hz, 1H), 6.21 (dd, J = 8.2, 1.9 Hz, 1H), 6.37−6.45 (m, 1H), 6.41 (s, 1H), 6.47 (d, J = 8.2 Hz, 2H), 6.51−6.63 (m, 2H), 6.83 (t, J = 8.2 Hz, 1H), 7.46 (d, J = 0.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 33.9, 43.3, 51.9, 54.7, 55.1, 55.7, 56.2, 72.7, 81.5, 102.6, 110.7, 111.2, 111.7, 117.7, 118.8, 123.4, 125.1, 125.9, 127.7, 128.3, 134.8, 145.9, 147.7, 147.8, 154.7, 154.9, 158.7. IR (UATR): ν_{max} 3503, 2939, 1605, 1487, 1260, 1140, 1026 cm^{-1}. LRMS (EI): m/z (rel intensity) 554 (16) $[C_{29}H_{29}{}^{81}BrO_6]^+$, 552 (19) $[C_{29}H_{29}{}^{79}BrO_6]^+$, 151 (89), 135 (100). TOF-HRMS: calcd for $C_{29}H_{29}{}^{79}BrNaO_6$ (M + Na$^+$) 575.1039, found 575.1028; calcd for $C_{29}H_{29}{}^{81}BrNaO_6$ (M + Na$^+$) 577.1024, found 577.1016.

2-Bromo-7-(3,4-dimethoxyphenyl)-3-methoxy-6-(4-methoxyphenyl)-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromen-7-ol (39b and 40b). Following the general procedure for the ring-closing metathesis using Grubbs II as catalyst (10 mol %), diene alcohol **36b** (0.057 g, 0.103 mmol) was converted to the corresponding tricyclic product **39b**, which was obtained as a yellow oil (0.013 g, 0.024 mmol, 23%), and the corresponding tricyclic product **40b**, which was obtained as a yellow oil (0.028 g, 0.052 mmol, 50%).

(6*α*,6a*β*,7*β*,10a*α*)-2-Bromo-7-(3,4-dimethoxyphenyl)-3-methoxy-6-(4-methoxyphenyl)-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromen-7-ol (39b). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.82 (br s, 1H), 2.59−2.74 (m, 3H), 3.42 (br d, J = 10.5 Hz, 1H), 3.75 (s, 3H), 3.86 (s, 3H), 3.87 (s, 3H), 3.89 (s, 3H), 4.69 (d, J = 10.5 Hz, 1H), 6.10 (ddd, J = 9.9, 6.6, 3.3 Hz, 1H), 6.28−6.35 (m, 1H), 6.35 (s, 1H), 6.83 (d, J = 9.0 Hz, 1H), 6.96−7.05 (m, 4H), 7.38 (d, J = 8.6 Hz, 2H), 7.46 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.4, 44.1, 48.9, 55.4, 55.87, 55.92, 56.2, 74.4, 79.9, 101.2, 102.1, 110.0, 110.5, 114.3, 118.2, 118.3, 126.9, 128.1, 129.4, 129.8, 132.6, 136.8, 148.3, 148.4, 154.1, 155.0, 160.3. IR (UATR): ν_{max} 3548, 2932, 1609, 1512, 1256 cm^{-1}. LRMS (EI): m/z (rel intensity) 554 (13) $[C_{29}H_{29}{}^{81}BrO_6]^+$, 552 (14) $[C_{29}H_{29}{}^{79}BrO_6]^+$, 374 (16), 372, (20), 165 (100). TOF-HRMS: calcd for $C_{29}H_{29}{}^{79}BrNaO_6$ (M + Na$^+$) 575.1040, found 575.1036; calcd for $C_{29}H_{29}{}^{81}BrNaO_6$ (M + Na$^+$) 577.1021, found 577.1025.

(6*α*,6a*β*,7*α*,10a*α*)-2-Bromo-7-(3,4-dimethoxyphenyl)-3-methoxy-6-(4-methoxyphenyl)-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromen-7-ol (40b). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.18−2.29 (m, 2H), 2.42 (t, J = 10.1 Hz, 1H), 2.67−2.78 (m, 1H), 3.60 (br s, 3H), 3.68 (s, 3H), 3.68−3.74 (m, 1H), 3.758 (s, 3H), 3.764 (s, 3H), 5.05 (d, J = 10.1 Hz, 1H), 5.98 (ddt, J = 10.2, 5.0, 2.5 Hz, 1H), 6.39 (s, 1H), 6.39−6.49 (m, 7H), 6.60 (br d, J = 8.0 Hz, 1H), 7.46 (d, J = 0.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 34.0, 43.3, 52.8, 55.2, 55.4, 55.8, 56.3, 72.5, 80.2, 102.7, 102.9, 108.8, 110.4, 113.1, 117.6, 123.9, 125.0, 126.2, 127.5, 128.0, 134.8, 136.7, 147.5, 148.1, 154.8, 155.0, 158.4. IR (UATR): ν_{max} 3503, 2935, 1608, 1514, 1254, 1141 cm^{-1}. LRMS (EI): m/z (rel intensity) 554 (30) $[C_{29}H_{29}{}^{81}BrO_6]^+$, 552 (27) $[C_{29}H_{29}{}^{79}BrO_6]^+$, 165 (100). TOF-HRMS: calcd for $C_{29}H_{29}{}^{79}BrO_6$ (M + Na$^+$) 575.1040, found 575.1040; calcd for $C_{29}H_{29}{}^{81}BrO_6$ (M + Na$^+$) 577.1021, found 577.1005.

2-Bromo-6,7-bis(3,4-dimethoxyphenyl)-3-methoxy-6a,7,8,10a-tetrahydro-6*H*-benzo[c]chromen-7-ol (39c and 40c). Following the general procedure for the ring-closing metathesis using Grubbs II as catalyst (10 mol %), diene alcohol **36c** (0.114 g, 0.191 mmol) was converted to the corresponding tricyclic product **39c**, which was obtained as a yellow oil (0.038 g, 0.065 mmol, 34%), and the corresponding tricyclic product **40c**, which was obtained as a yellow sticky gum (0.067 g, 0.115 mmol, 60%).

(6*α*,6a*β*,7*β*,10a*α*)-2-Bromo-6,7-bis(3,4-dimethoxyphenyl)-3-methoxy-6a,7,8,10a-tetrahydro-6*H*-benzo[c]chromen-7-ol (39c). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.96 (br s, 1H), 2.55−2.74 (m, 3H), 3.46 (br d, J = 10.6 Hz, 1H), 3.76 (s, 3H), 3.86 (s, 3H), 3.89 (s, 3H), 3.91 (s, 3H), 3.93 (s, 3H), 4.68 (d, J = 10.6 Hz, 1H), 6.06−6.15 (m, 1H), 6.30−6.37 (m, 1H), 6.37 (s, 1H), 6.83 (d, J = 9.0 Hz, 1H), 6.92 (d, J = 1.8 Hz, 1H), 6.94 (d, J = 8.3 Hz, 1H), 6.97−7.04 (m, 3H), 7.47 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.4, 43.9, 48.9, 55.8, 55.9, 56.0, 56.2, 74.2, 80.3, 101.1, 102.1, 110.2, 110.5, 111.1, 111.5, 118.2, 118.4, 121.1, 126.7, 128.2, 129.3, 132.7, 136.8, 148.3, 148.4, 149.3, 149.9, 154.0, 155.0. IR (UATR): ν_{max} 3510, 2933, 1607, 1512, 1260, 1159, 1026 cm^{-1}. LRMS (EI): m/z (rel intensity) 584 (4) $[C_{30}H_{31}{}^{81}BrO_7]^+$, 582 (4) $[C_{30}H_{31}{}^{79}BrO_7]^+$, 165 (100). TOF-HRMS: calcd for $C_{30}H_{31}{}^{79}BrNaO_7$ (M + Na$^+$) 605.1145, found 605.1143; calcd for $C_{30}H_{31}{}^{81}BrNaO_7$ (M + Na$^+$) 607.1130, found 607.1128.

(6*α*,6a*β*,7*α*,10a*α*)-2-Bromo-6,7-bis(3,4-dimethoxyphenyl)-3-methoxy-6a,7,8,10a-tetrahydro-6*H*-benzo[c]chromen-7-ol (40c). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.21 (br s, 1H), 2.19−2.31 (m,

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J. Org. Chem. 2017, 82, 2672−2688

1H), 2.44 (t, J = 10.4 Hz, 1H), 2.68−2.80 (m, 1H), 3.60 (s, 3H), 3.65 (br s, 3H), 3.65−3.71 (m, 1H), 3.76 (s, 3H), 3.77 (s, 6H), 5.03 (d, J = 9.8 Hz, 1H), 5.95−6.03 (m, 1H), 6.02 (d, J = 2.0 Hz, 1H), 6.11 (dd, J = 8.2, 2.0 Hz, 1H), 6.38−6.49 (m, 4H), 6.49−6.60 (br m, 2H), 7.47 (d, J = 0.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 33.9, 43.3, 52.8, 55.3, 55.4, 55.8, 55.9, 56.3, 72.4, 81.5, 102.7, 102.8, 108.9, 110.2, 110.3, 110.7, 117.7, 119.1, 123.9, 125.0, 126.2, 127.6, 135.2, 136.8, 147.4, 147.90, 147.95, 148.0, 154.8, 155.0. IR (UATR): ν_{max} 3506, 2937, 1606, 1516, 1259, 1140, 1026 cm^{-1}. LRMS (EI): m/z (rel intensity) 584 (6) $[C_{30}H_{31}{}^{81}BrO_7]^+$, 582 (5) $[C_{30}H_{31}{}^{79}BrO_7]^+$, 165 (100). TOF-HRMS: calcd for $C_{30}H_{31}{}^{79}BrNaO_7$ (M + Na$^+$) 605.1145, found 605.1139; calcd for $C_{30}H_{31}{}^{81}BrNaO_7$ (M + Na$^+$) 607.1130, found 607.1124.

(6α,6aβ,7β,10aα)-2-Bromo-7-(3,4-dimethoxyphenyl)-3-methoxy-6-(4-methoxyphenyl)-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromene (41b). Following the general procedure for the BF_3·Et_2O-mediated Et_3SiH reduction at −10 to −5 °C for 4 h, tricyclic alcohol **39b** (0.015 g, 0.027 mmol) furnished the corresponding tricyclic product **41b** as a white sticky gum (0.007 g, 0.014 mmol, 50%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.20−2.33 (m, 1H), 2.44 (td, J = 10.8, 3.2 Hz, 1H), 2.61−2.76 (m, 1H), 2.96 (dd, J = 6.9, 3.2 Hz, 1H), 3.48−3.58 (br m, 1H), 3.75 (s, 3H), 3.78 (s, 3H), 3.85 (s, 3H), 3.87 (s, 3H), 4.52 (d, J = 10.8 Hz, 1H), 6.08 (ddt, J = 10.0, 4.4, 2.4 Hz, 1H), 6.31−6.38 (br m, 1H), 6.36 (s, 1H), 6.54 (d, J = 1.9 Hz, 1H), 6.69 (dd, J = 8.3, 1.9 Hz, 1H), 6.75 (d, J = 8.3 Hz, 1H), 7.02 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 8.7 Hz, 2H), 7.50 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 32.2, 33.1, 37.3, 41.8, 55.4, 55.8, 55.9, 56.2, 81.1, 101.2, 101.8, 110.9, 112.5, 114.3, 118.1, 120.6, 127.6, 128.6, 129.8, 130.1, 130.7, 134.5, 147.9, 148.3, 154.5, 154.9, 160.2. IR (UATR): ν_{max} 2909, 2835, 1610, 1514, 1250, 1146 cm^{-1}. LRMS (EI): m/z (rel intensity) 538 (71) $[C_{29}H_{29}{}^{81}BrO_5]^+$, 536 (59) $[C_{29}H_{29}{}^{79}BrO_5]^+$, 283 (64), 121 (100). TOF-HRMS: calcd for $C_{29}H_{29}{}^{79}BrNaO_5$ (M + Na$^+$) 559.1091, found 559.1086; calcd for $C_{29}H_{29}{}^{81}BrNaO_5$ (M + Na$^+$) 561.1075, found 561.1075.

(6α,6aβ,7β,10aα)-2-Bromo-6,7-bis(3,4-dimethoxyphenyl)-3-methoxy-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromene (41c). Following the general procedure for the BF_3·Et_2O-mediated Et_3SiH reduction at 0 °C for 18 h, tricyclic alcohol **39c** (0.010 g, 0.017 mmol) furnished the corresponding tricyclic product **41c** as a yellow oil (0.007 g, 0.012 mmol, 67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.22−2.32 (m, 1H), 2.43 (td, J = 10.8, 3.2 Hz, 1H), 2.62−2.75 (m, 1H), 2.99 (dd, J = 6.9, 3.2 Hz, 1H), 3.51−3.60 (br m, 1H), 3.76 (s, 3H), 3.77 (s, 3H), 3.85 (s, 3H), 3.92 (s, 3H), 3.95 (s, 3H), 4.51 (d, J = 10.8 Hz, 1H), 6.09 (ddt, J = 9.9, 4.4, 2.4 Hz, 1H), 6.32−6.38 (br m, 1H), 6.38 (s, 1H), 6.56 (d, J = 1.8 Hz, 1H), 6.69 (dd, J = 8.3, 1.8 Hz, 1H), 6.74 (d, J = 8.3 Hz, 1H), 6.93 (d, J = 1.8 Hz, 1H), 6.97 (d, J = 8.2 Hz, 1H), 7.25 (dd, J = 8.2, 1.8 Hz, 1H), 7.51 (d, J = 0.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 32.2, 33.1, 37.3, 41.8, 55.8, 55.9, 56.0, 56.1, 56.2, 81.5, 101.1, 101.8, 110.8, 111.2, 111.6, 112.7, 118.0, 120.8, 121.7, 127.5, 128.7, 129.7, 130.9, 134.5, 147.9, 148.3, 149.4, 149.7, 154.4, 154.9. IR (UATR): ν_{max} 2934, 1608, 1515, 1263, 1157, 1027 cm^{-1}. LRMS (EI): m/z (rel intensity) 568 (50) $[C_{30}H_{31}{}^{81}BrO_6]^+$, 566 (53) $[C_{30}H_{31}{}^{79}BrO_6]^+$, 313 (61), 151 (100). TOF-HRMS: calcd for $C_{30}H_{31}{}^{79}BrNaO_6$ (M + Na$^+$) 589.1196, found 589.1181; calcd for $C_{30}H_{31}{}^{81}BrNaO_6$ (M + Na$^+$) 591.1181, found 591.1175.

(6α,6aβ,7β,10aβ)-2-Bromo-6-(3,4-dimethoxyphenyl)-3-methoxy-7-(3-methoxyphenyl)-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromene (42a). Following the general procedure for the BF_3·Et_2O-mediated Et_3SiH reduction at 10 °C for 18 h, tricyclic alcohol **39a** (0.028 g, 0.050 mmol) furnished the corresponding tricyclic product **42a** as a pale yellow sticky gum (0.005 g, 0.010 mmol, 19%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.15−2.27 (m, 1H), 2.46−2.62 (m, 1H), 2.92−3.02 (m, 1H), 3.26−3.36 (m, 1H), 3.58 (s, 3H), 3.67 (s, 3H), 3.77 (s, 3H), 3.82 (s, 3H), 4.86 (d, J = 10.2 Hz, 1H), 5.77−5.84 (m, 1H), 5.84−5.93 (m, 1H), 6.14 (s, 1H), 6.30 (d, J = 1.8 Hz, 1H), 6.41 (d, J = 8.2 Hz, 1H), 6.42 (s, 1H), 6.48 (dd, J = 8.2, 2.3 Hz, 1H), 6.59 (d, J = 8.1 Hz, 1H), 6.70 (dd, J = 8.1, 1.8 Hz, 1H), 6.89 (t, J = 8.2 Hz, 1H), 7.40 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.4, 40.1, 41.0, 42.6, 54.8, 55.1, 55.7, 56.2, 77.4, 100.9, 102.4, 109.4, 109.9, 110.1, 113.5, 118.9, 119.5, 121.4, 125.5, 128.2, 130.5, 131.2, 132.8, 144.5, 148.4, 149.2, 155.0, 158.8. IR (UATR): ν_{max} 2923, 2853, 1607, 1443, 1264, 1159, 1050 cm^{-1}. LRMS (EI): m/z (rel intensity) 538 (28) $[C_{29}H_{29}{}^{81}BrO_5]^+$, 536 (25) $[C_{29}H_{29}{}^{79}BrO_5]^+$, 283 (100), 151 (37). TOF-HRMS: calcd for $C_{29}H_{29}{}^{79}BrNaO_5$ (M + Na$^+$) 559.1091, found 559.1103; calcd for $C_{29}H_{29}{}^{81}BrNaO_5$ (M + Na$^+$) 561.1075, found 561.1092.

(6α,6aβ,7β,10aβ)-2-Bromo-7-(3,4-dimethoxyphenyl)-3-methoxy-6-(4-methoxyphenyl)-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromene (42b). Following the general procedure for the BF_3·Et_2O-mediated Et_3SiH reduction at −20 °C for 24 h, tricyclic alcohol **40b** (0.023 g, 0.041 mmol) furnished the corresponding tricyclic product **41b** (0.004 g, 0.007 mmol, 18%) and the corresponding tricyclic product **42b** as a white solid (0.006 g, 0.012 mmol, 27%). Mp (EtOAc/hexanes): 221.5−223.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.16−2.29 (br m, 1H), 2.40−2.54 (br m, 1H), 2.92−3.00 (br m, 1H), 3.71 (s, 3H), 3.72 (s, 3H), 3.76 (s, 3H), 3.79 (s, 3H), 3.80−3.86 (br m, 1H), 4.88 (d, J = 10.2 Hz, 1H), 5.77−5.85 (m, 1H), 5.85−5.93 (m, 1H), 6.18 (dd, J = 8.3, 1.6 Hz, 1H), 6.22 (d, J = 1.6 Hz, 1H), 6.40 (s, 1H), 6.42 (d, J = 8.3 Hz, 1H), 6.49 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 7.40 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.0, 40.0, 40.7, 42.5, 55.2, 55.5, 56.0, 56.2, 77.1, 100.9, 102.3, 110.1, 113.2, 118.9, 119.0, 125.5, 129.5, 130.2, 131.2, 132.7, 135.8, 146.5, 148.2, 155.0, 155.1, 159.4. IR (UATR): ν_{max} 2908, 2835, 1515, 1248, 1158 cm^{-1}. LRMS (EI): m/z (rel intensity) 538 (26) $[C_{29}H_{29}{}^{81}BrO_5]^+$, 536 (31) $[C_{29}H_{29}{}^{79}BrO_5]^+$, 283 (100). TOF-HRMS: calcd for $C_{29}H_{29}{}^{79}BrNaO_5$ (M + Na$^+$) 559.1091, found 559.1096; calcd for $C_{29}H_{29}{}^{81}BrNaO_5$ (M + Na$^+$) 561.1075, found 561.1075.

(6α,6aβ,7β,10aβ)-2-Bromo-6,7-bis(3,4-dimethoxyphenyl)-3-methoxy-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromene (42c). Following the general procedure for the BF_3·Et_2O-mediated Et_3SiH reduction at 20 °C for 18 h, tricyclic alcohol **40c** (0.067 g, 0.115 mmol) furnished the corresponding tricyclic product **42c** as a yellow sticky gum (0.024 g, 0.043 mmol, 37%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.18−2.29 (br m, 1H), 2.43−2.59 (br m, 1H), 2.70−2.98 (br m, 1H), 3.26−3.36 (br m, 1H), 3.64 (s, 3H), 3.73 (s, 3H), 3.77 (s, 3H), 3.78 (s, 3H), 3.81 (s, 3H), 4.87 (d, J = 10.2 Hz, 1H), 5.77−5.85 (m, 1H), 5.85−5.94 (m, 1H), 6.16 (dd, J = 8.0, 1.6 Hz, 1H), 6.30 (d, J = 1.6 Hz, 1H), 6.37 (d, J = 1.8 Hz, 1H), 6.40 (d, J = 8.0 Hz, 1H), 6.41 (s, 1H), 6.53 (d, J = 8.1 Hz, 1H), 6.63 (dd, J = 8.1, 1.8 Hz, 1H), 7.40 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.8, 40.0, 40.8, 42.6, 55.3, 55.5, 55.9, 56.1, 56.2, 100.9, 102.4, 110.3, 110.4, 110.8, 118.8, 118.9, 121.3, 125.6, 130.7, 131.2, 132.7, 135.8, 146.6, 148.2, 148.5, 149.1, 155.0. IR (UATR): ν_{max} 2926, 1613, 1504, 1263, 1155, 1029 cm^{-1}. LRMS (EI): m/z (rel intensity) 568 (24) $[C_{30}H_{31}{}^{81}BrO_6]^+$, 566 (21) $[C_{30}H_{31}{}^{79}BrO_6]^+$, 313 (100), 175 (30), 151 (27). TOF-HRMS: calcd for $C_{30}H_{31}{}^{79}BrNaO_6$ (M + Na$^+$) 589.1196, found 589.1194; calcd for $C_{30}H_{31}{}^{81}BrNaO_6$ (M + Na$^+$) 591.1181, found 591.1179.

(6α,6aα,7β,10aβ)-2-Bromo-6-(3,4-dimethoxyphenyl)-3-methoxy-7-(3-methoxyphenyl)-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromen-7-ol (43). Following the general procedure for the BF_3·Et_2O-mediated Et_3SiH reduction at 0 °C for 18 h, tricyclic alcohol **40a** (0.069 g, 0.125 mmol) furnished the corresponding tricyclic product **42a** (0.010 g, 0.019 mmol, 15%) and the corresponding tricyclic alcohol **43** as a pale yellow oil (0.013 g, 0.024 mmol, 19%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (d, J = 2.1 Hz, 1H), 2.17−2.29 (m, 1H), 2.39−2.51 (m, 1H), 2.94 (dd, J = 4.3 Hz, 1H), 3.64 (s, 3H), 3.82 (s, 3H), 3.84 (s, 3H), 3.85 (s, 3H), 3.86−3.92 (m, 1H), 5.30 (d, J = 4.3 Hz, 1H), 5.80 (ddt, J = 10.1, 4.8, 2.5 Hz, 1H), 6.19 (d, J = 2.0 Hz, 1H), 6.34 (br d, J = 10.1 Hz, 1H), 6.46 (s, 1H), 6.48 (dd, J = 8.4, 2.0 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 6.89 (dd, J = 8.1, 2.7 Hz, 1H), 7.04−7.12 (m, 2H), 7.39 (t, J = 8.1 Hz, 1H), 7.60 (d, J = 0.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.4, 44.1, 45.4, 55.3, 55.6, 55.9, 56.2, 73.3, 76.5, 100.9, 102.1, 110.8, 111.5, 111.8, 112.0, 117.5, 117.6, 119.6, 125.6, 125.8, 129.9, 130.1, 131.5, 148.0, 148.8, 149.3, 153.8, 155.4, 160.0. IR (UATR): ν_{max} 3545, 2923, 1607, 1442, 1259, 1147, 1025 cm^{-1}. LRMS (EI): m/z (rel intensity) 554 (13) $[C_{29}H_{29}{}^{81}BrO_6]^+$, 552 (10) $[C_{29}H_{29}{}^{79}BrO_6]^+$, 151 (100), 135 (95). TOF-HRMS: calcd for $C_{29}H_{29}{}^{79}BrNaO_6$ (M + Na$^+$) 575.1039, found 575.1042; calcd for $C_{29}H_{29}{}^{81}BrNaO_6$ (M + Na$^+$) 577.1024, found 577.1021.

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J. Org. Chem. 2017, 82, 2672−2688

1-(6-Bromo-7-methoxy-2-(4-methoxyphenyl)-4-vinylchroman-3-yl)-1-(4-methoxyphenyl)-3-methylbut-3-en-1-ol (44). Following the general procedure for the Lindlar hydrogenation and allyl Grignard addition (while using methallyl Grignard instead), ketone alkyne **28** (0.170 g, 0.335 mmol) was converted to the corresponding diene alcohol **44**, which was obtained as a 1.4:1 inseparable mixture of diastereomers as a white sticky gum (0.142 g, 0.251 mmol, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 3H), 2.54 (s, 1H, minor), 2.56 (s, 1H, major), 2.58−2.71 (m, 2H), 2.75−2.83 (m, 1H, minor), 2.88−2.96 (m 1H, major), 3.46 (d, J = 8.3 Hz, 1H, minor), 3.73 (s, 3H), 3.76 (s, 3H, minor), 3.80 (s, 6H, major), 3.86 (s, 3H, minor), 3.87 (s, 3H, major), 4.48−4.59 (m, 2H, minor), 4.64−4.73 (m, 2H), 4.78−4.88 (m, 2H), 5.02−5.21 (m, 1H), 5.23 (s, 1H), 5.68 (s, 1H, minor), 6.50 (s, 1H, minor), 6.55 (s, 1H, major), 6.71 (d, J = 8.8 Hz, 2H, major), 6.78 (d, J = 8.7 Hz, 2H, minor), 6.83 (d, J = 8.8 Hz, 2H, minor), 6.87 (d, J = 8.8 Hz, 2H, major), 6.93 (d, J = 8.8 Hz, 2H, major), 7.06 (d, J = 8.8 Hz, minor), 7.07 (s, 1H, minor), 7.18 (s, 1H, major), 7.31 (d, J = 8.7 Hz, 2H, minor), 7.38 (d, J = 8.8 Hz, 2H, major). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.2 (major), 24.4 (minor), 37.8 (major), 38.3 (minor), 46.6 (minor), 47.2 (major), 54.3 (major), 55.0 (minor), 55.1 (major), 56.1 (major), 74.8 (major), 75.0 (minor), 77.5 (minor), 78.2 (major), 100.8 (major), 102.56 (major), 102.62 (minor), 113.0 (minor), 113.39 (major), 113.44 (major), 113.7 (minor), 113.8 (major), 116.1 (major), 116.2 (minor), 118.0 (major), 118.5 (minor), 126.7 (major), 127.0 (major), 127.1 (minor), 127.4 (minor), 133.3 (minor), 133.50 (minor), 133.54 (major), 133.6 (minor), 136.2 (minor), 136.8 (major), 141.8 (major), 141.88 (minor), 141.91 (minor), 142.1(major), 153.2 (major), 153.5 (minor), 155.0 (minor), 155.1 (major), 158.2 (major), 158.3 (major), 158.38 (minor), 158.42 (minor). IR (UATR): ν_{max} 3526, 2934, 1610, 1510, 1248 cm^{-1}. LRMS (EI): m/z (rel intensity) 566 (0.4) $[C_{31}H_{33}{}^{81}BrO_5]^+$, 564 (0.4) $[C_{31}H_{33}{}^{79}BrO_5]^+$, 376 (3), 374 (3), 135 (100), 121 (16). TOF-HRMS: calcd for $C_{31}H_{33}{}^{79}BrNaO_5$ (M + Na$^+$) 587.1404, found 587.1408; calcd for $C_{31}H_{35}{}^{81}BrNaO_5$ (M + Na$^+$) 589.1385, found 589.1383.

2-Bromo-3-methoxy-6,7-bis(4-methoxyphenyl)-9-methyl-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromen-7-ol (45). Following the general procedure for the ring-closing metathesis using Hoveyda−Grubbs II catalyst (8 mol %) at 70 °C, diene alcohol **44** (0.370 g, 0.650 mmol) furnished the corresponding tricyclic alcohol **45** as a pale yellow sticky gum (0.123 g, 0.227 mmol, 35%) and **46** as a pale yellow sticky gum (0.132 g, 0.247 mmol, 38%).

(6*α*,6a*β*,7*β*,10a*α*)-2-Bromo-3-methoxy-6,7-bis(4-methoxyphenyl)-9-methyl-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromen-7-ol (45). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.80 (br s, 1H), 1.89 (br s, 3H), 2.41−2.61 (m, 3H), 3.27 (br d, J = 10.6 Hz, 1H), 3.74 (s, 3H), 3.82 (s, 3H), 3.86 (s, 3H), 4.65 (d, J = 10.6 Hz, 1H), 6.01 (br s, 1H), 6.34 (s, 1H), 6.87 (d, J = 8.7 Hz, 2H), 7.00 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 8.7 Hz, 2H), 7.46 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.0, 36.2, 48.6, 48.9, 55.2, 55.3, 56.1, 74.6, 79.8, 101.1, 102.0, 113.2, 114.3, 118.7, 121.2, 127.2, 129.4, 129.7, 132.6, 135.7, 136.2, 154.0, 154.8, 158.9, 160.2. IR (UATR): ν_{max} 3557, 2907, 2836, 1609, 1512, 1247, 1161, 1033, 831 cm^{-1}. LRMS (EI): m/z (rel intensity) 538 (5) $[C_{29}H_{29}{}^{81}BrO_5]^+$, 536 (5) $[C_{29}H_{29}{}^{79}BrO_5]^+$, 388 (16), 136 (17), 135 (100). TOF-HRMS: calcd for $C_{29}H_{29}{}^{79}BrNaO_5$ (M + Na$^+$) 559.1091, found 559.1073; calcd for $C_{29}H_{29}{}^{81}BrO_5$ (M + Na$^+$) 561.1075, found 561.1063.

(6*α*,6a*β*,7*α*,10a*α*)-2-Bromo-3-methoxy-6,7-bis(4-methoxyphenyl)-9-methyl-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromen-7-ol (46). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.60 (br s, 1H), 1.84 (br s, 3H), 2.09 (br d, J = 18.5 Hz, 1H), 2.35 (t, J = 10.2 Hz, 1H), 2.66 (br d, J = 18.5 Hz, 1H), 3.60−3.65 (m, 1H), 3.65 (s, 3H), 3.69 (s, 3H), 3.76 (s, 3H), 5.04 (d, J = 10.2 Hz, 1H), 6.11 (br s, 1H), 6.38 (s, 1H), 6.39−6.46 (m, 6H), 6.87 (br d, J = 8.1 Hz, 2H), 7.46 (d, J = 0.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.5, 34.0, 48.2, 52.3, 55.10, 55.13, 56.2, 72.9, 81.4, 102.5, 102.7, 112.8, 113.2, 118.7, 124.2, 126.2, 127.5, 128.1, 133.9, 134.7, 136.0, 154.8, 154.9, 157.9, 158.3. IR (UATR): ν_{max} 3503, 2909, 2835, 1608, 1512, 1247, 1178, 825 cm^{-1}. LRMS (EI): m/z (rel intensity) 538 (8) $[C_{29}H_{29}{}^{81}BrO_5]^+$, 536 (8) $[C_{29}H_{29}{}^{79}BrO_5]^+$, 135 (100). TOF-HRMS: calcd for $C_{29}H_{29}{}^{79}BrNaO_5$ (M + Na$^+$) 559.1091, found 559.1092; calcd for $C_{29}H_{29}{}^{81}BrNaO_5$ (M + Na$^+$) 561.1075, found 561.1075.

(6*α*,6a*β*,7*β*,10a*α*)-2-Bromo-3-methoxy-6,7-bis(4-methoxyphenyl)-9-methyl-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromene (47). Following the general procedure for the $BF_3{\cdot}Et_2O$-mediated Et_3SiH reduction at −20 °C for 3.5 h, tricyclic alcohol **45** (0.023 g, 0.043 mmol) furnished the corresponding tricyclic alcohol **47** as a white sticky gum (0.019 g, 0.036 mmol, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.86 (br s, 3H), 2.07 (br d, J = 18.2 Hz, 1H), 2.33 (td, J = 10.9, 3.2 Hz, 1H), 2.61 (br d, J = 18.2 Hz, 1H), 2.95 (dd, J = 6.9, 3.2 Hz, 1H), 3.46 (br d, J = 10.9 Hz, 1H), 3.74 (s, 3H), 3.78 (s, 3H), 3.88 (s, 3H), 4.48 (d, J = 10.9 Hz, 1H), 6.04 (br s, 1H), 6.35 (s, 1H), 6.76 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 0.8 HZ, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.7, 32.0, 37.3, 37.8, 42.1, 55.2, 55.4, 56.1, 81.1, 101.0, 101.6, 113.3, 114.3, 118.6, 121.9, 129.7, 130.0, 130.9, 134.0, 154.0, 154.4, 154.7, 158.4, 160.1. IR (UATR): ν_{max} 2907, 2835, 1610, 1511, 1247, 1158 cm^{-1}. LRMS (EI): m/z (rel intensity) 522 (31) $[C_{29}H_{29}{}^{81}BrO_4]^+$, 520 (27) $[C_{29}H_{29}{}^{79}BrO_4]^+$, 253 (100), 121 (58). TOF-HRMS: calcd for $C_{29}H_{30}{}^{79}BrO_4$ (M + H$^+$) 521.1322, found 521.1313; calcd for $C_{29}H_{30}{}^{81}BrO_4$ (M + H$^+$) 523.1306, found 523.1313.

(6*α*,6a*α*,7*β*,10a*β*)-2-Bromo-3-methoxy-6,7-bis(4-methoxyphenyl)-9-methyl-6a,7,8,10a-tetrahydro-6*H*-benzo[*c*]chromen-7-ol (48). Following the general procedure for the $BF_3{\cdot}Et_2O$-mediated Et_3SiH reduction at 10 °C for 1.5 h, tricyclic alcohol **46** (0.060 g, 0.110 mmol) furnished the corresponding tricyclic product **47** (0.020 g, 0.039 mmol, 35%) and the corresponding tricyclic alcohol **48** as a white sticky gum (0.013 g, 0.024 mmol, 22%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20 (d, J = 2.2 Hz, 1H), 1.73 (br s, 3H), 2.06 (br d, J = 18.2 Hz, 1H), 2.37 (br d, J = 18.2 Hz, 1H), 2.83 (dd, J = 11.7, 4.3 Hz, 1H), 3.75 (s, 3H), 3.75−3.80 (m, 1H), 3.80 (s, 3H), 3.88 (s, 3H), 5.28 (d, J = 4.3 Hz, 1H), 6.03 (br s, 1H), 6.44 (s, 1H), 6.68−6.77 (m, 4H), 6.99 (d, J = 8.7 Hz, 2H), 7.39 (d, J = 8.7 Hz, 2H), 7.61 (d, J = 0.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.3, 28.3, 45.4, 49.1, 55.25, 55.33, 56.2, 73.4, 76.5, 100.9, 102.0, 114.0, 114.1, 118.2, 119.7, 126.3, 128.7, 130.1, 131.2, 133.3, 138.1, 153.9, 155.3, 158.7, 159.9. IR (UATR): ν_{max} 3552, 2933, 2836, 1609, 1511, 1248 cm^{-1}. LRMS (EI): m/z (rel intensity) 538 (2) $[C_{29}H_{29}{}^{81}BrO_5]^+$, 536 (1) $[C_{29}H_{29}{}^{79}BrO_5]^+$, 388 (16), 386 (17), 135 (100). TOF-HRMS: calcd for $C_{29}H_{29}{}^{79}BrNaO_5$ (M + Na$^+$) 559.1091, found 559.1085; calcd for $C_{29}H_{29}{}^{81}BrNaO_5$ (M + Na$^+$) 561.1075, found 561.1096.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b03086.

^{1}H and ^{13}C NMR spectra for all new compounds, NOE results of compounds **27**, **30**−**34**, and **48** and discussion of the assignment of stereochemistry (PDF)

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Notes

The authors declare no competing financial interest.

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(23) From the reaction, peaks on the ^{1}H NMR could be clearly interpreted to be in accordance with the structure of the chroman ketone **22**. Unfortunately, purification of **22** from the remaining amount of the (*E*)-chalcone proved to be difficult; it was not possible to obtain **22** in a spectroscopically pure form. Thus, the exact yield of **22** could not be determined. In addition, when other α,β-unsaturated ketones (alkyl substituted as well as (*E*)-1-phenylhexa-1,5-dien-3-one ($PhCH{=}CHCOCH_2CH{=}CH_2$)) were employed in the $PtCl_4$-catalyzed cycloaddition reactions with either **14** or **15**, no corresponding desired products could be obtained. Only decomposition of **14** or **15** was observed with complete recovery of the α,β-unsaturated ketones.
(24) This is in agreement with our previous findings of different reaction modes of quinone methides. For chalcones containing 3,5-dimethoxyphenyl group(s), the corresponding diarylmethane(s) could be isolated as the product(s) from the reaction(s) between the quinone methide and these electron-rich aromatics. For more details, see: Tangdenpaisal, K.; Phakhodee, W.; Ruchirawat, S.; Ploypradith, P. *Tetrahedron* **2013**, *69*, 933−941.
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(34) The stereochemical assignment of all intermediates and final products followed that of **27**−**34**.

(35) For compounds **43** and **48**, the relative stereochemistry was also established on the basis of the NOE enhancements (or the lack thereof) and the coupling constants (J values) of the protons on the adjacent carbons. The presence of the hydroxy group was confirmed by mass spectrometry.

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