JOC The Journal of Organic Chemistry

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$Sc(OTf)_3$ Catalyzed [4 + 2]-Annulation Reaction between Electron-Rich Phenols and Donor−Acceptor Cyclopropanes: Synthesis of Polysubstituted Dihydronaphthols

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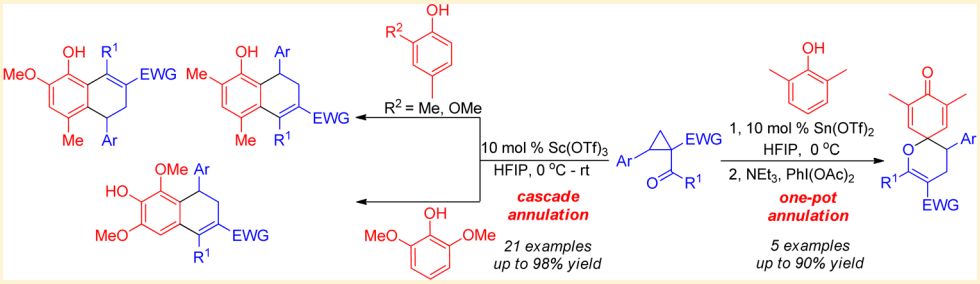
Supporting Information



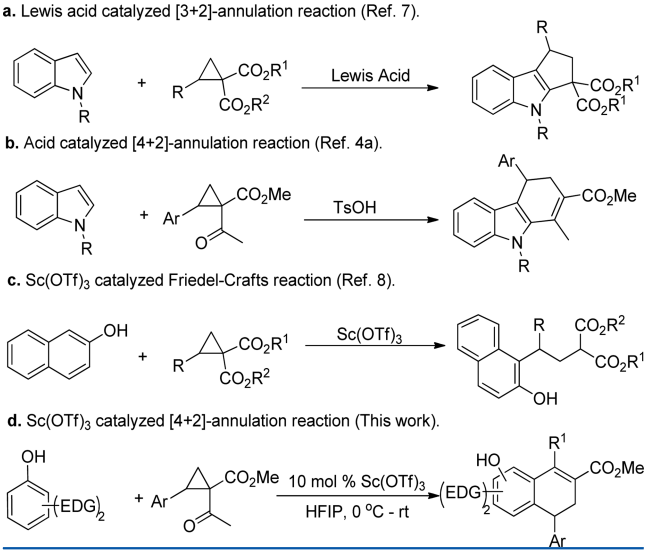
ABSTRACT: On the basis of the Lewis acid-catalyzed Friedel−Crafts alkylation between 1-acyl-2-arylcyclopropanecarboxylate esters and electron-rich phenols, a $Sc(OTf)_3$ catalyzed cascade [4 + 2]-annulation reaction was developed for the direct synthesis of polysubstituted dihydronaphthols from phenols. In this reaction, the structure of products is dominated by the directing effect of the substituent groups on phenols. Meanwhile, a one-pot Friedel−Crafts alkylation/oxidative cyclization reaction was also developed for the synthesis of *spiro*-fused 2,5-cyclohexadienones.

INTRODUCTION

In the past decades, donor−acceptor cyclopropanes (D−A cyclopropanes) attracted widespread attention because of their versatility in organic synthesis.[1] Among them, 1-acyl-2-arylcyclopropanecarboxylate ester has been intensively studied. As useful as other D−A cyclopropanes, 1-acyl-2-arylcyclopropanecarboxylate esters could be used as homo-Michael acceptors in the ring-opening reactions[2] and as three-carbon zwitterion equivalents in the [3 + *n*]-annulation reactions.[3,4] Beyond that, 1-acyl-2-arylcyclopropanecarboxylate esters could also be used as C4 building blocks in [4 + *n*]-annulation reactions.[5] It is noteworthy that most of these [4 + *n*]-annulation reactions are achieved via sequential ring opening/cyclization. Therefore, searching for new ring-opening reactions of 1-acyl-2-arylcyclopropane-carboxylate ester is necessary for developing other useful annulation reactions.

According to the previous reports on D−A cyclopropanes, Lewis acid catalyzed Friedel−Crafts alkylation between D−A cyclopropanes and electron-rich arenes is an efficient ring-opening approach for D−A cyclopropanes. On the basis of this method, many reactions between indole derivatives and D−A cyclopropanes have been developed (Scheme 1a).[6,7] For 1-acyl-2-arylcyclopropanecarboxylate ester, its [4 + 2]-annulation reaction with indole was developed by Gu in 2016 (Scheme 1b).[5a] However, to the best of our knowledge, the Friedel−Crafts reaction between phenols and D−A cyclopropanes has not been reported. Until recently, Biju and co-workers developed the Friedel−Crafts reaction between 2-naphthols and 2-arylcyclopropanecarboxylate 1,1-diesters (Scheme 1c).[8] In view of our interest in D−A cyclopropanes and the reactive characteristics of 1-acyl-2-arylcyclopropanecarboxylate ester,[9] we investigated the Friedel−Crafts alkylation between 1-acyl-2-arylcyclopropanecarboxylate

Scheme 1. Reactions between D−A Cyclopropanes and Phenols or Indoles



Received: October 23, 2016
Published: December 20, 2016

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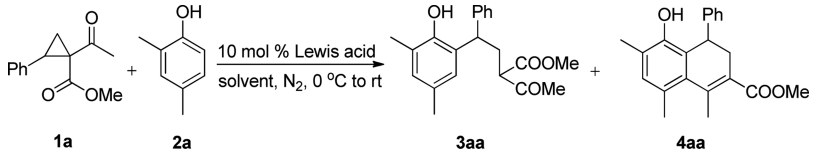
DOI: 10.1021/acs.joc.6b02566
J. Org. Chem. 2017, 82, 1013−1023

Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3aa 4aa

	1a:2a	Lewis acid	solvent (mL)	time (h)	product (yield %)[b]
1	2:1	$Sc(OTf)_3$	DCM (1.5)	24	**3aa** (16)
2	2:1	$Sn(OTf)_2$	DCM (1.5)	24	**3aa** (21)
3	2:1	$Sn(OTf)_2$	HFIP (1.5)	24	**4aa** (40)
4	2:1	$In(OTf)_3$	HFIP (1.5)	24	**4aa** (54)
5	2:1	$Sc(OTf)_3$	HFIP (1.5)	24	**4aa** (65)
6	2:1	$Sc(OTf)_3$[c]	HFIP (1.5)	72	**4aa** (55)
7	2:1	$Sc(OTf)_3$	HFIP (3.0)	24	**4aa** (78)
8	1.5:1	$Sc(OTf)_3$	HFIP (3.0)	24	**4aa** (60)
9	1:2[d]	$Sc(OTf)_3$	HFIP (3.0)	8	**4aa** (61)
10	1:2[d,e]	$Sc(OTf)_3$	HFIP (3.0)	8	**4aa** (61)

[a]Unless otherwise noted, 0.3 mmol of **1a**, 0.15 mmol of **2a**, and 0.015 mmol of Lewis acid were successively added to HFIP at 0 °C. Then, the temperature was allowed to rise to room temperature naturally. [b]Isolated yield of major product. [c]$Sc(OTf)_3$ (5 mol %) was used. [d]**1a** (0.1 mmol) was used. [e]The reaction mixture was maintained at 0 °C.

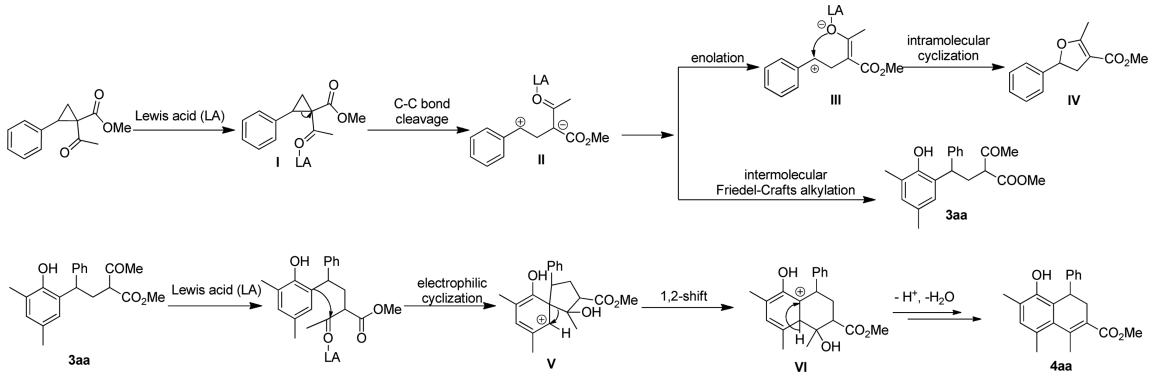
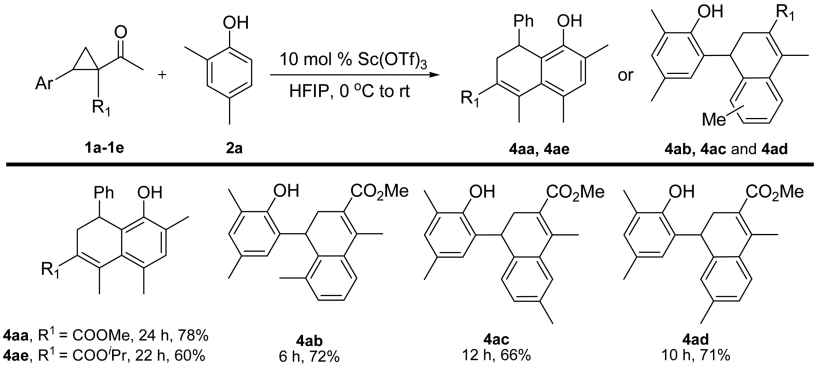


Figure 1. Plausible mechanism for the [4 + 2]-annulation reaction.

Scheme 2. Synthesis of 7,8-Dihydro-1-naphthols and Dihydronaphthalene from 2,4-Dimethylphenol via [4 + 2]-Annulation Reaction[a]



[a]Unless otherwise noted, 0.3 mmol of **1**, 0.15 mmol of **2a**, and 0.015 mmol of $Sc(OTf)_3$ were successively added into 3 mL of HFIP at 0 °C. Then, the temperature was allowed to rise to room temperature naturally.

ester and phenols and further developed a $Sc(OTf)_3$ catalyzed [4 + 2]-annulation reaction (Scheme 1d).

RESULTS AND DISCUSSION

At the beginning of our work, we concentrated on the Friedel−Crafts alkylation between 1-acyl-2-arylcyclopropanecarboxylate esters and phenols. To avoid the unmanageable regioselectivity, 2,4-dimethylphenol (**2a**) and methyl 1-acetyl-2-phenylcyclopropanecarboxylate (**1a**) were used to optimize the reaction conditions, and the results are summarized in Table 1. When 10 mol % of $Sc(OTf)_3$ as catalyst was used, the Friedel−Crafts alkylation occurred at the C-6 position of phenol **2a**, and the product **3aa** was obtained in 16% yield as an inseparable mixture of diastereoisomers in dichloromethane (DCM) (Table 1, entry 1). When $Sc(OTf)_3$ was replaced by $Sn(OTf)_2$, the yield of product **3aa** increased slightly (Table 1, entry 2). Analysis of the

DOI: 10.1021/acs.joc.6b02566
J. Org. Chem. 2017, 82, 1013−1023

byproducts disclosed that most of cyclopropane **1a** had isomerized to 4,5-dihydrofurans (Figure 1IV).[10] This suggested that isomerization of cyclopropane **1a** is faster than the Friedel−Crafts alkylation under these conditions. To suppress the isomerization of cyclopropane **1a**, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was employed as the solvent. We expected that the hydrogen bonding interaction between HFIP and the acetyl group on cyclopropane **1a** would inhibit the isomerization. Unexpectedly, when the reaction was carried out in HFIP, alkylation product **3aa** was formed first and further transformed into the dihydronaphthol **4aa** (Table 1, entry 3). We speculated that dihydronaphthol **4aa** derived from alkylation product **3aa** via an intramolecular electrophilic cyclization[11] (Figure 1), and the keto-carbonyl on ring-opening product **3aa** was probably activated further by HFIP because of its high acidity and strong hydrogen-bond-donating property.[12] We then turned our attention to this [4 + 2]-annulation reaction. Screening of Lewis acids disclosed that $Sc(OTf)_3$ is the best catalyst for this reaction (Table 1, entries 3−5). When the catalyst loading was reduced to 5 mol %, the reaction rate slowed, and the yield decreased (Table 1, entry 6). Fortunately, when the reactant concentration reduced, the yield increased to 78% (Table 1, entry 7). Subsequently, we optimized the ratios of reactants and reaction temperature, but the yield was not improved (Table 1, entries 8−10). Finally, the conditions in entry 7 (Table 1) were identified as the optimal conditions.

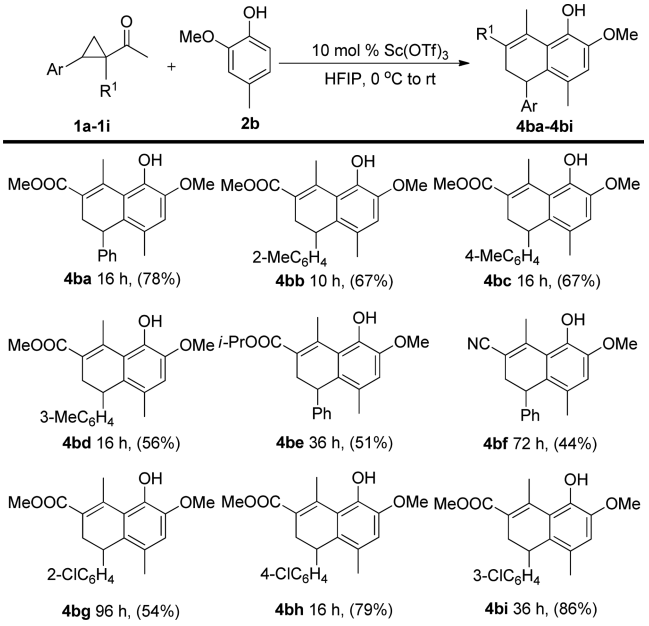
After the optimal reaction conditions were established, a substrate scope was investigated. At first, several cyclopropanes were screened under the optimized reaction conditions (Scheme 2). For methyl 1-acetyl-2-chlorophenylcyclopropanecarboxylate esters (**1g**, **1h**, and **1i**) and methyl 1-cyano-2-phenylcyclopropanecarboxylate (**1f**), the expected products were not obtained. Cyclopropane **1e** gave the 5,6-dihydro-1-naphthol **4ae** in 60% yield. Surprisingly, when cyclopropanes (**1b**, **1c**, and **1d**) bearing methylphenyl at the C-2 position were used, the electrophilic cyclization of the ring-opening product occurred at the aromatic ring of the cyclopropane rather than the phenols. Dihydronaphthalenes (**4ab**−**4ad**) (Scheme 2) were obtained in moderate yield. It is clear the regioselectivity of the electrophilic cyclization is dominated by an electronic effect. Thus, it can be seen that more electron-rich phenols are needed for the synthesis of dihydronaphthols via this [4 + 2]-annulation reaction.

For 2-methoxyl-4-methylphenol (**2b**), this protocol was found to be tolerant of cyclopropanes with both electron-withdrawing and electron-donating groups on the aryl, and several 5,6-dihydro-1-naphthols (**4ba**−**4bi**) (Scheme 3) were prepared in moderate to good yields. The cyclopropanes with alkylphenyl at the C-2 position gave yields lower than the ones with chlorophenyl at the C-2 position. It might be because the more reactive cyclopropanes are more prone to isomerization.

To synthesize the dihydro-2-naphthols, 2,6-dimethoxyphenol (**2c**) was employed in this reaction. Just as expected, the reaction occurred smoothly under the optimal conditions, but the yield was unsatisfactory. To increase the yield, the ratio between the cyclopropane and phenol was adjusted. At last, a series of 7,8-dihydro-1-naphthols (**4ca**−**4cj**) (Scheme 4) were prepared in high yield. So far, we developed an efficient method for the synthesis of 5,6-dihydronaphthols and 7,8-dihydronaphthols directly from electron-rich 2,4- or 2,6-disubstituted phenols. Simple hydrogenation of the products offered the useful tetrahydronaphthols (Scheme 5). The relative configuration of the hydrogenation product **7cc** was determined by NOE experiment (Supporting Information).

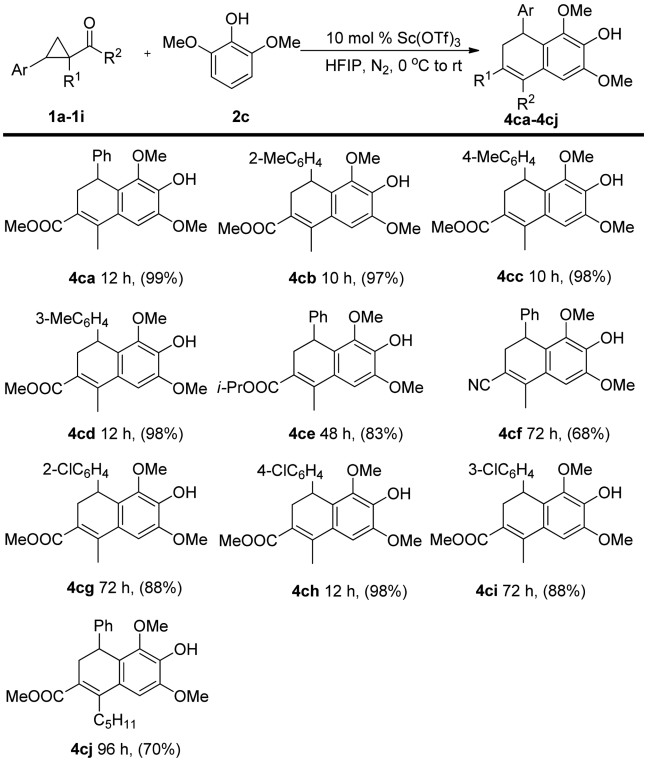
The above [4 + 2]-annulation reactions have clearly demonstrated that Lewis acid catalyzed Friedel−Crafts alkylation between 1-acyl-2-arylcyclopropanecarboxylate esters and electron-rich phenols is an efficient ring-opening method. This

Scheme 3. Synthesis of 5,6-Dihydro-1-naphthols from 2-Methoxyl-4-methylphenol via [4 + 2]-Annulation Reaction[a]



[a]Unless otherwise noted, 0.3 mmol of **1**, 0.15 mmol of **2b**, and 0.015 mmol of $Sc(OTf)_3$ were successively added into 3 mL of HFIP at 0 °C. Then, the temperature was allowed to rise to room temperature naturally.

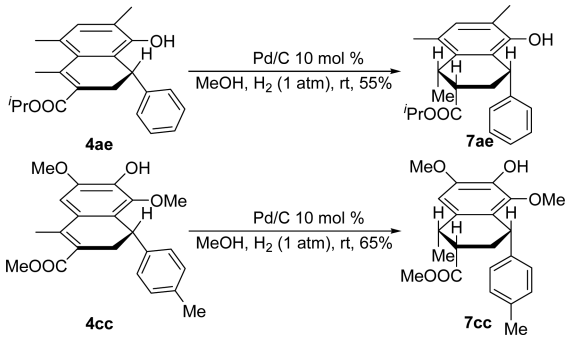
Scheme 4. Synthesis of 7,8-Dihydro-2-naphthols from 2,4-Dimethoxyphenols via [4 + 2]-Annulation Reaction[a]



[a]Unless otherwise noted, 0.4 mmol of **1**, 0.15 mmol of **2c**, and 0.015 mmol of $Sc(OTf)_3$ were successively added into 3 mL of HFIP at 0 °C. Then, the temperature was allowed to rise to room temperature naturally.

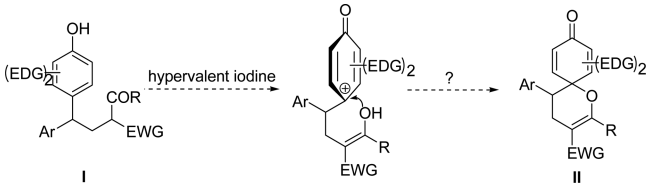
DOI: 10.1021/acs.joc.6b02566
J. Org. Chem. 2017, 82, 1013−1023

Scheme 5. Hydrogenation of the Dihydronaphthols



provides the opportunity for development of other annulation reactions. As shown in Scheme 6, if the ring-opening product **I**

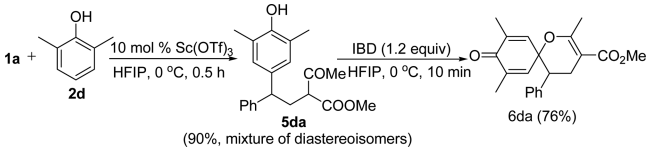
Scheme 6. Friedel−Crafts Alkylation between D−A Cyclopropane and 2,6-Dimethyl Phenol



is oxidized with iodobenzene diacetate (IBD), the *spiro*-fused 2,5-cyclohexadienone **II** may be obtained via intramolecular oxidative cyclization.[13] According to this idea, we attempted to combine the Lewis acid-catalyzed Friedel−Crafts alkylation and oxidative cyclization in one pot.

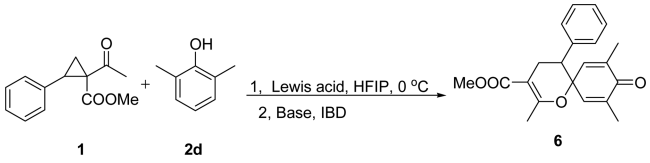
At first, we prepared the ring-opening product **5da** (Scheme 7) and investigated its oxidative cyclization in HFIP with IBD at

Scheme 7. Stepwise Synthesis of *Spiro*-Fused 2,5-Cyclohexadienone



0 °C. The reaction occurred quickly and offered the *spiro*-fused 2,5-cyclohexadienone **6da** (Scheme 7) in several minutes with high yield. Then, we attempted to synthesize the *spiro*-fused 2,5-cyclohexadienone by a one-pot procedure. When $Sc(OTf)_3$ was used as the catalyst, cyclopropane **1a** and phenol **2d** reacted smoothly. After 0.5 h, phenol **2d** was consumed completely, and IBD was added. When the ring-opening product **5da** disappeared in several minutes, the reaction mixture became complex, and the cyclization product **6da** was not detected (Table 2, entry 1). This result suggested that, under these conditions, the enolization of *β*-ketoester is slow. Therefore, Et_3N was added to accelerate the enolization, and product **6da** was obtained in high yield (Table 2, entry 2). According to these results, further optimization of reaction conditions was carried out. Screening of Lewis acids and bases demonstrated that $Sn(OTf)_2$ was the best catalyst, and Et_3N was the most suitable base (Table 2, entry 4). Using this one-pot procedure, several *spiro*-fused 2,5-cyclohexadienones (Scheme 8) were prepared conveniently in moderate to good yields.

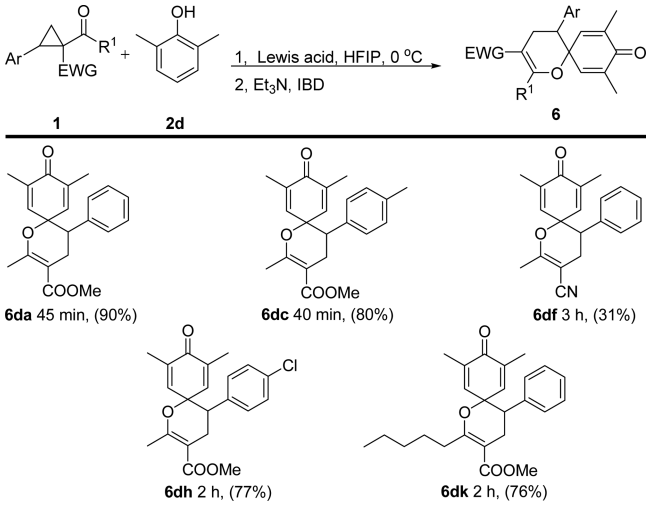
Table 2. Optimization of the Conditions for the One-Pot Reaction[a]



	Lewis acid	base	time (min)	yield (%)[b]
1	$Sc(OTf)_3$		30	complex
2	$Sc(OTf)_3$	NEt_3	30	80
3	$Sc(OTf)_3$	DBU	30	75
4	$Sn(OTf)_2$	NEt_3	45	90
5	$Hf(OTf)_4$	NEt_3	20	87
6	$In(OTf)_3$	NEt_3	30	20

[a]The reaction was carried out with **1a** (0.22 mmol), 2,6-dimethylphenol **2d** (0.2 mmol), and Lewis acid (0.02 mmol) in HFIP (2 mL) at 0 °C. After **2d** was consumed completely, the base (0.08 mmol) was added first, and after 5 min, IBD (0.24 mmol) was added. [b]Isolated yield.

Scheme 8. Synthesis of *Spiro*-Fused 2,5-Cyclohexadienones via One-Pot Reaction[a]



CONCLUSION

In summary, Lewis acid-catalyzed Friedel−Crafts alkylation between 1-acyl-2-arylcyclopropanecarboxylate esters and electron-rich phenols was investigated; this ring-opening approach was combined with electrophilic cyclization and oxidative cyclization, respectively. A $Sc(OTf)_3$ catalyzed cascade [4 + 2]-annulation reaction and a one-pot Friedel−Crafts alkylation/oxidative cyclization reaction were developed. Using these reactions, polysubstituted dihydronaphthols and *spiro*-fused 2,5-cyclohexadienones could be directly prepared from phenols.

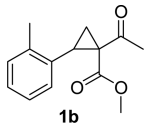
EXPERIMENTAL SECTION

General. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Analytical thin-layer chromatography (TLC) was performed on silica gel plates with GF-254 indicator, and the compounds were visualized by irradiation with UV light. Flash chromatography was carried out utilizing silica gel 200−300 mesh. ^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR. Chemical shifts were reported as δ values in ppm and calibrated from residual solvent peaks ($CDCl_3$: δ 7.26 for ^1H NMR, δ 77.00 for ^{13}C NMR) or

DOI: 10.1021/acs.joc.6b02566
J. Org. Chem. 2017, 82, 1013−1023

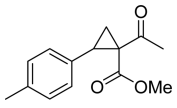
tetramethylsilane (δ 0 for 1 H NMR). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), br (broad peak), and m (complex multiplet). IR spectra were recorded on a FT-IR instrument and are reported in wave numbers (cm^{-1}). HRMS was performed on an FT-ICRMS mass instrument (ESI).

Preparation of D−A Cyclopropanes (1b−1j). D−A cyclopropanes (**1b−1j**) used in this work were prepared according to the reported method A[14] or B.[15]



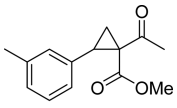
1b

*Methyl 1-Acetyl-2-(o-tolyl)cyclopropane-1-carboxylate (**1b**).* This compound was prepared according to method A. Colorless oil (453 mg, 39% yield); R_f = 0.43 (EtOAc/petroleum ether = 1/8); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.05 (m, 4H), 3.25 (s, 3H), 3.22 (t, J = 8.8 Hz, 1H), 2.49 (s, 3H), 2.36 (dd, J = 8.4, 4.8 Hz, 1H), 2.27 (s, 3H), 1.75 (dd, J = 9.2, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 168.6, 138.7, 132.9, 129.6, 127.6, 127.5, 125.3, 51.7, 43.6, 34.8, 29.5, 21.4, 19.2; IR (KBr) 3020, 2951, 1719, 1696, 1437, 1262, 1091, 917, 731 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{16}O_3Na$ $[M + Na]^+$ 255.0992, found 255.0997.



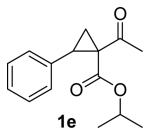
1c

*Methyl 1-Acetyl-2-(p-tolyl)cyclopropane-1-carboxylate (**1c**).* This compound was prepared according to method A and obtained as an inseparable diastereoisomeric mixture (dr = 2.6/1). Colorless oil (488 mg, 42% yield); R_f = 0.42 (EtOAc/petroleum ether = 1/8); The following characterization data is for the major diastereoisomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09−7.04 (m, 4H), 3.36 (s, 3H), 3.23 (t, J = 8.4 Hz, 1H), 2.44 (s, 3H), 2.29 (s, 3H), 2.21 (dd, J = 8.0, 4.4 Hz, 1H), 1.72 (dd, J = 9.2, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 168.7, 136.9, 131.6, 128.7, 128.5, 51.8, 44.6, 35.4, 29.5, 21.6, 21.0; IR (KBr) 3012, 2953, 2256, 1731, 1700, 1519, 1438, 1262, 1123, 912, 733 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{16}O_3Na$ $[M + Na]^+$ 255.0992, found 255.0988.



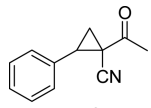
1d

*Methyl 1-Acetyl-2-(m-tolyl)cyclopropane-1-carboxylate (**1d**).* This compound was prepared according to method A and obtained as an inseparable diastereoisomeric mixture (dr = 4:1). Colorless oil (407 mg, 35% yield); R_f = 0.43 (EtOAc/petroleum ether = 1/8); The following characterization data is for the major diastereoisomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, J = 7.2 Hz, 1H), 7.07−6.93 (m, 3H), 3.36 (s, 3H), 3.24 (t, J = 8.4 Hz, 1H), 2.45 (s, 3H), 2.31 (s, 3H), 2.22 (dd, J = 8.0, 4.4 Hz, 1H), 1.73 (dd, J = 9.2, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 168.6, 137.6, 134.7, 129.4, 128.1, 127.9, 125.5, 51.8, 44.5, 35.5, 29.5, 21.6, 21.2; IR (KBr) 3015, 2952, 1732, 1719, 1609, 1438, 1123, 911, 734 cm^{-1}; HRMS (ESI) m/z calcdfor $C_{14}H_{17}O_3$ $[M + H]^+$ 233.1172, found 233.1175.



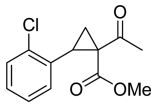
1e

*Isopropyl 1-Acetyl-2-phenylcyclopropane-1-carboxylate (**1e**).* This compound was prepared according to method B. Colorless oil (924 mg, 75% yield); R_f = 0.50 (EtOAc/petroleum ether = 1/8); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.17 (m, 5H), 4.79−4.66 (m, 1H), 3.27 (t, J = 8.4 Hz, 1H), 2.45 (s, 3H), 2.21 (dd, J = 8.0, 4.4 Hz, 1H), 1.69 (dd, J = 8.8, 4.4 Hz, 1H), 0.92 (d, J = 6.0 Hz, 3H), 0.80 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 167.5, 134.8, 128.9, 128.0, 127.3, 68.8, 44.7, 35.1, 29.5, 21.2, 21.1, 21.0; IR (KBr) 3031, 2981, 2937, 1698, 1454, 1313, 1259, 1105, 910, 698 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{18}O_3Na$ $[M + Na]^+$ 269.1148, found 269.1150.



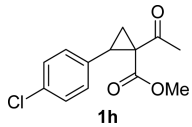
1f

*1-Acetyl-2-phenylcyclopropane-1-carbonitrile (**1f**).* This compound was prepared according to method B. Waxy solid (860 mg, 93% yield); R_f = 0.33 (EtOAc/petroleum ether = 1/8); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.31 (m, 3H), 7.28−7.22 (m, 2H), 3.12 (t, J = 8.8 Hz, 1H), 2.57 (s, 3H), 2.19 (dd, J = 9.2, 5.2 Hz, 1H), 2.10 (dd, J = 8.4, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 133.0, 128.7, 128.5, 118.3, 38.3, 30.2, 29.4, 24.6; IR (KBr) 3061, 3007, 1715, 1450, 1355, 1288, 1131, 1082, 779, 732 cm^{-1}; HRMS (ESI) m/z calcd for $C_{12}H_{11}NONa$ $[M + Na]^+$ 208.0733, found 208.0735.



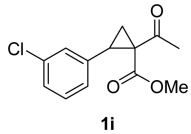
1g

*Methyl 1-Acetyl-2-(2-chlorophenyl)cyclopropane-1-carboxylate (**1g**).* This compound was prepared according to method A. Colorless oil (581 mg, 46% yield); R_f = 0.43 (EtOAc/petroleum ether = 1/8); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.30 (m, 1H), 7.26−7.07 (m, 3H), 3.36 (s, 3H), 3.26 (t, J = 8.8 Hz, 1H), 2.53 (s, 3H), 2.26 (dd, J = 8.4, 4.4 Hz 1H), 1.90 (dd, J = 9.2, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 168.5, 136.2, 133.0, 129.5, 129.1, 128.7, 126.2, 51.9, 43.2, 34.9, 29.8, 21.0; IR (KBr): 3008, 2952, 1732, 1697, 1438, 1324, 1212, 1132, 743 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{13}ClO_3Na$ $[M + Na]^+$ 275.0445, found 275.0451.



1h

*Methyl 1-Acetyl-2-(4-chlorophenyl)cyclopropane-1-carboxylate (**1h**).* This compound was prepared according to method A and obtained as an inseparable diastereoisomeric mixture (dr = 1.8/1). Colorless oil (480 mg, 38% yield); R_f = 0.36 (EtOAc/petroleum ether = 1/8), The following characterization data is for the major diastereoisomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 3.40 (s, 3H), 3.24 (t, J = 8.4 Hz, 1H), 2.45 (s, 3H), 2.19 (dd, J = 8.0, 4.4 Hz, 1H), 1.72 (dd, J = 9.2, 4.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 168.5, 133.4, 132.3, 130.1, 128.3, 52.1, 44.5, 34.4, 29.6, 21.6; IR (KBr) 3008, 2953, 1732, 1701, 1496, 1438, 1324, 836, 734 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{13}ClO_3Na$ $[M + Na]^+$ 275.0445, found 275.0441.



1i

*Methyl 1-Acetyl-2-(3-chlorophenyl)cyclopropane-1-carboxylate (**1i**).* This compound was prepared according to method A and obtained as an inseparable diastereoisomeric mixture (dr = 6/1). Colorless oil (341 mg, 27% yield); R_f = 0.36 (EtOAc/petroleum ether = 1/8). The

DOI: 10.1021/acs.joc.6b02566
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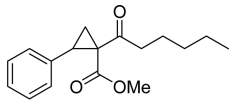
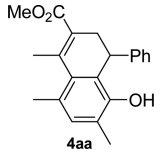
following characterization data is for the major diastereoisomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.14 (m, 3H), 7.10−7.03 (m, 1H), 3.41 (s, 3H), 3.24 (t, J = 8.4 Hz, 1 H), 2.45 (s, 3H), 2.20 (dd, J = 8.4, 4.8 Hz, 1H), 1.72 (dd, J = 9.2, 4.8 Hz, 1H) (major diastereomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 168.3, 137.0, 133.9, 129.3, 128.8, 127.5, 126.9, 52.0, 44.3, 34.3, 29.4, 21.4; IR (KBr) 3054, 2953, 1731, 1700, 1436, 1212, 1122, 797, 695 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{14}ClO_3$ $[M + H]^+$ 253.0626, found 253.0631.



1j

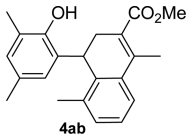
*Methyl 1-Hexanoyl-2-phenylcyclopropane-1-carboxylate (**1j**).* This compound was prepared according to method B. Colorless oil (1.098 g, 80% yield); R_f = 0.52 (EtOAc/petroleum ether = 1/8); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.21 (m, 3H), 7.20−7.15 (m, 2H), 3.34 (s, 3H), 3.28 (t, J = 8.4 Hz, 1H), 2.95−2.84 (m, 1H), 2.73−2.60 (m, 1H), 2.20 (dd, J = 8.0, 4.8 Hz, 1H), 1.67 (dd, J = 9.2, 4.8 Hz, 3H), 1.65−1.54 (m, 2H), 1.39−1.21 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4, 168.8, 135.0, 128.7, 128.1, 127.3, 51.9, 44.5, 41.7, 34.6, 31.3, 23.7, 22.4, 21.3, 13.9; IR (KBr) 2954, 2930, 2864, 1735, 1697, 1437, 1324, 1158, 697 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{22}O_3Na$ $[M + Na]^+$ 297.1461, found 297.1458.

General Procedure for the Annulation Reaction between 2,4-Disubstituted Phenols (2a and 2b) and D−A Cyclopropanes. Under a nitrogen atmosphere, a stirring solution of cyclopropane **1** (0.3 mmol, 2 equiv) and phenol **2a** or **2b** (0.15 mmol, 1 equiv) in HFIP (3 mL) was cooled by the mixture of ice and water for 10 min. Then, $Sc(OTf)_3$ (0.015 mmol, 10 mol %) was added, and the reaction temperature was allowed to rise to room temperature naturally. The reaction was monitored by TLC analysis. When the generated ring-opening intermediate disappeared, the solvent was removed in vacuo, and the residue was purified by flash column chromatography on silica gel to give the product **4**.



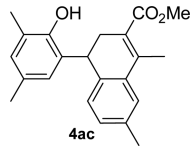
4aa

*Methyl 5-Hydroxy-1,6,8-trimethyl-4-phenyl-3,4-dihydronaphthalene-2-carboxylate (**4aa**).* Colorless oil (37.7 mg, 78% yield); R_f = 0.42 (EtOAc/petroleum ether = 1/8); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.19 (td, J = 7.6, 1.2 Hz, 1H), 6.91−6.85 (m, 2H), 6.70 (s, 1H), 4.54 (s, 1H), 4.35 (dd, J = 12.8, 6.8 Hz, 1H), 3.74 (s, 3H), 2.94−2.77 (m, 2H), 2.50 (s, 3H), 2.23 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 149.6, 141.4, 138.7, 136.3, 129.9, 129.6, 128.9, 127.9, 127.8, 126.9, 126.5, 125.7, 125.3, 123.6, 51.5, 38.7, 31.0, 20.6, 16.3, 16.0; IR (KBr) 3487, 2951, 2922, 1703, 1615, 1483, 1435, 1194, 907, 734 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{22}O_3Na$ $[M + Na]^+$ 345.1461, found 345.1456.



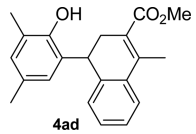
4ab

*Methyl 4-(2-Hydroxy-3,5-dimethylphenyl)-1,5-dimethyl-3,4-dihydronaphthalene-2-carboxylate (**4ab**).* White solid (36.3 mg, 72% yield); mp 137−139 °C; R_f = 0.40 (EtOAc/petroleum ether = 1/6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.6 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 7.2 Hz, 1H), 6.72 (s, 1H), 5.99 (s, 1H), 4.74 (s, 1H), 4.63 (d, J = 7.2 Hz, 1H), 3.67 (s, 3H), 3.09 (d, J = 16.8 Hz, 1 H), 2.83−2.74 (m, 1H), 2.52 (d, J = 2.4 Hz, 3H), 2.22 (s, 3H), 2.10 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 149.1, 142.3, 136.9, 136.8, 135.7, 131.1, 129.3, 128.7, 127.4, 127.3, 126.5, 123.1, 123.0, 121.7, 51.3, 32.0, 30.6, 20.7, 19.1, 16.6, 15.8; IR (KBr) 3481, 2949, 2920, 1693, 1617, 1482, 1265, 1192, 1047, 737 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{24}O_3Na$ $[M + Na]^+$ 359.1618, found 359.1623.



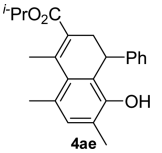
4ac

*Methyl 4-(2-Hydroxy-3,5-dimethylphenyl)-1,7-dimethyl-3,4-dihydronaphthalene-2-carboxylate (**4ac**).* White solid (27.8 mg, 66% yield); mp 141−143 °C; R_f = 0.52 (EtOAc/petroleum ether = 1/8); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1 H), 7.02 (d, J = 7.6 Hz, 1H), 6.88 (s, 1H), 6.79 (s, J = 8.0 Hz, 1H), 6.71 (s, 1H), 4.46 (s, 1H), 4.28 (dd, J = 12.4, 7.2 Hz, 1H), 3.75 (s, 3H), 2.94−2.73 (m, 2H), 2.50 (s, 3H), 2.37 (s, 3H), 2.24 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 149.6, 141.5, 136.4, 136.2, 135.5, 129.9, 129.6, 129.5, 128.1, 127.8, 126.3, 126.2, 124.4, 125.7, 123.7, 51.5, 38.8, 31.2, 21.3, 20.6, 16.3, 16.0; IR (KBr) 3442, 2924, 1709, 1604, 1436, 1231, 1058, 820 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{24}O_3Na$ $[M + Na]^+$ 359.1618, found: 359.1624.



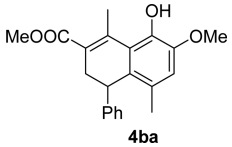
4ad

*Methyl 4-(2-Hydroxy-3,5-dimethylphenyl)-1,6-dimethyl-3,4-dihydronaphthalene-2-carboxylate (**4ad**).* Colorless oil (35.8 mg, 71% yield); R_f = 0.42 (EtOAc/petroleum ether = 1/8); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 6.88 (s, 1H), 6.70 (d, J = 15.6 Hz 1H), 4.48 (s, 1H), 4.30 (dd, J = 12.4, 7.2 Hz, 1H), 3.74 (s, 3H), 2.98−2.79 (m, 2H), 2.50 (s, 3H), 2.26 (s, 3H), 2.25 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 149.6, 141.7, 139.2, 138.5, 133.7, 130.0, 129.6, 128.1, 127.9, 127.7, 127.3, 125.5, 124.6, 123.7, 51.4, 39.0, 31.2, 21.3, 20.6, 16.3, 16.0; IR (KBr) 3479, 2949, 2919, 1707, 1607, 1482, 1435, 1223, 1054, 819, 738 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{24}O_3Na$ $[M + Na]^+$ 359.1618, found 359.1621.



4ae

*Isopropyl 5-Hydroxy-1,6,8-trimethyl-4-phenyl-3,4-dihydronaphthalene-2-carboxylate (**4ae**).* White solid (31.5 mg, 60% yield); mp 108−110 °C; R_f = 0.47 (EtOAc/petroleum ether = 1/8); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.49 (m, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.18 (td, J = 7.6, 1.20 Hz, 1H), 6.90 (s, 1 H), 6.86 (d, J = 7.6 Hz, 1H), 6.78 (s, 1H), 5.17−5.06 (m, 1H), 4.46 (s, 1H), 4.33 (dd, J = 13.6, 6.8 Hz, 1H), 2.93−2.71 (m, 2H), 2.47 (d, J = 1.2 Hz, 3H), 2.25 (s, 3H), 2.23 (s, 3H), 1.29 (d, J = 5.2 Hz, 3H), 1.27 (d, J = 4.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 149.8, 139.9, 138.5, 136.3, 130.0, 129.8, 128.8, 128.2, 127.8, 126.9, 126.8, 126.3, 125.3, 123.8, 67.7, 39.2, 31.1, 21.9, 20.6, 16.2, 16.0; IR (KBr): 3475, 2979, 2925, 1699, 1686, 1612, 1483, 1374, 1183, 1034, 911, 735 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{26}O_3Na$ $[M + Na]^+$ 373.1774, found 373.1776.



4ba

DOI: 10.1021/acs.joc.6b02566
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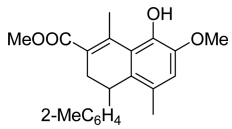
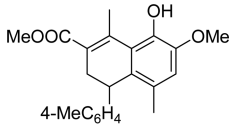
*Methyl 8-Hydroxy-7-methoxy-1,5-dimethyl-4-phenyl-3,4-dihydronaphthalene-2-carboxylate (**4ba**).* Red solid (39.6 mg, 78% yield); mp 164−166 °C; R_f = 0.43 (EtOAc/petroleum ether = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.11 (m, 3H), 6.99 (d, J = 7.2 Hz, 2H), 6.68 (s, 1H), 6.04 (s, 1H), 4.14 (d, J = 4.8 Hz, 1H), 3.91 (s, 3H), 3.65 (s, 3H), 3.17 (dd, J = 16.0, 1.6 Hz, 1H), 2.68−2.55 (m, 1H), 2.55 (d, J = 2.4 Hz, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 145.3, 144.1, 142.5, 141.6, 130.8, 128.0, 127.8, 126.0, 125.6, 123.9, 123.6, 112.8, 56.2, 51.3, 39.0, 32.5, 19.8, 19.2; IR (KBr) 3516, 2949, 2846, 1702, 1602, 1587, 1479, 1465, 1312, 1193, 910, 731 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{23}O_4$ $[M + H]^+$ 339.1591, found 339.1595.



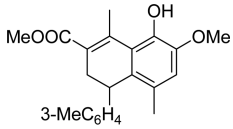
4bb

*Methyl 8-Hydroxy-7-methoxy-1,5-dimethyl-4-(o-tolyl)-3,4-dihydronaphthalene-2-carboxylate (**4bb**).* Yellow solid (35.4 mg, 67% yield); mp 168−170 °C; R_f = 0.41 (EtOAc/petroleum ether = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 7.2 Hz, 1H), 7.05 (td, J = 7.6, 1.2 Hz, 1H), 6.91 (t, J = 7.2 Hz, 1H), 6.65 (s, 1H), 6.52 (d, J = 7.6 Hz, 1H), 6.07 (s, 1H), 4.28 (d, J = 6.8 Hz, 1H), 3.90 (s, 3H), 3.63 (s, 3H), 3.01−2.95 (m, 1H), 2.65−2.58 (m, 4H), 2.51 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 145.2, 144.0, 142.4, 139.2, 135.3, 131.7, 130.2, 128.0, 126.0, 125.6, 124.5, 123.5, 113.0, 56.2, 51.2, 35.9, 30.6, 19.7, 19.4, 18.9; IR (KBr): 3502, 2948, 1704, 1602, 1479, 1433, 1278, 1193, 1034, 902 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{24}O_4Na$ $[M + Na]^+$ 375.1567, found 375.1562.



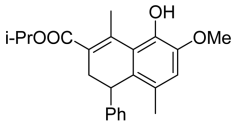
4bc

*Methyl 8-Hydroxy-7-methoxy-1,5-dimethyl-4-(p-tolyl)-3,4-dihydronaphthalene-2-carboxylate (**4bc**).* Red oil (35.4 mg, 67% yield); R_f = 0.40 (EtOAc/petroleum ether = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 6.67 (s, 1H), 6.03 (s, 1H), 4.10 (d, J = 5.2 Hz, 1H), 3.90 (s, 3H), 3.65 (s, 3H), 3.15 (dd, J = 16.0, 1.6 Hz, 1H), 2.69−2.57 (m, 1H), 2.55 (d, J = 2.4 Hz, 1H), 2.26 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 145.2, 144.2, 142.4, 138.4, 135.3, 130.9, 128.7, 127.6, 125.5, 123.8, 123.6, 112.7, 56.2, 51.3, 38.6, 32.4, 21.0, 19.8, 19.2; IR (KBr) 3507, 2948, 1704, 1586, 1478, 1444, 1280, 1231, 1192, 1163, 737 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{24}O_4Na$ $[M + Na]^+$ 375.1567, found: 375.1564.



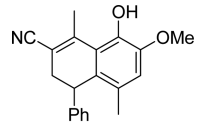
4bd

*Methyl 8-Hydroxy-7-methoxy-1,5-dimethyl-4-(m-tolyl)-3,4-dihydronaphthalene-2-carboxylate (**4bd**).* Yellow solid (29.6 mg, 56% yield); mp 170−172 °C; R_f = 0.41 (EtOAc/petroleum ether = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (t, J = 7.6 Hz, 1 H), 6.92 (d, J = 7.6 Hz, 1H), 6.82 (s, 1H), 6.76 (d, J = 7.6 Hz, 1H), 6.67 (s, 1H), 6.03 (s, 1H), 4.09 (d, J = 4.8 Hz, 1H), 3.91 (s, 3H), 3.65 (s, 3H), 3.15 (dd, J = 16.0, 1.6 Hz, 1H), 2.68−2.57 (m, 1H), 2.55 (d, J = 2.4 Hz, 3H), 2.25 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 145.3, 144.2, 142.4, 141.5, 137.3, 131.0, 128.6, 127.8, 126.8, 125.6, 124.8, 123.9, 123.7, 112.8, 56.2, 51.2, 39.0, 32.5, 21.5, 19.8, 19.2; IR (KBr) 3504, 2948, 1703, 1604, 1478, 1444, 1280, 1192, 1166, 737 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{24}O_4Na$ $[M + Na]^+$ 375.1567, found: 375.1561.



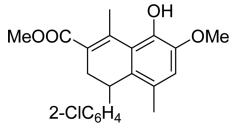
4be

*Isopropyl 8-Hydroxy-7-methoxy-1,5-dimethyl-4-phenyl-3,4-dihydronaphthalene-2-carboxylate (**4be**).* Yellow oil (24.2 mg, 44% yield); R_f = 0.46 (EtOAc/petroleum ether = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 6.8 Hz, 2H), 7.15−7.09 (m, 1H), 7.00 (d, J = 7.2 Hz, 2H), 6.67 (s, 1H), 6.02 (s, 1H), 5.01−4.91 (m, 1H), 4.12 (d, J = 4.8 Hz, 1H), 3.91 (s, 3H), 3.17 (dd, J = 15.6, 1.6 Hz, 1H), 2.64−2.56 (m, 1 H), 2.50 (d, J = 2.4 Hz, 3H), 2.10 (s, 3H), 1.21 (d, J = 6.4 Hz, 3H), 1.15 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 145.3, 142.5, 142.4, 141.5, 130.9, 127.9, 127.7, 125.9, 125.6, 124.6, 124.0, 112.6, 67.3, 56.2, 39.0, 32.4, 21.9, 21.8, 19.7, 19.2; IR (KBr) 3512, 2978, 1697, 1602, 1587, 1479, 1280, 1107, 1030, 914 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{23}H_{26}O_4Na$ $[M + Na]^+$ 389.1723, found 389.1725.



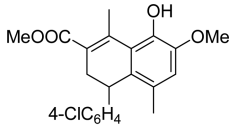
4bf

*8-Hydroxy-7-methoxy-1,5-dimethyl-4-phenyl-3,4-dihydronaphthalene-2-carbonitrile (**4bf**).* Yellow solid (20.2 mg, 44% yield); mp 147−148 °C; R_f = 0.32 (EtOAc/petroleum ether = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.14 (m, 3H), 6.97−6.85 (m, 2H), 6.70 (s, 1H), 6.12 (s, 1H), 4.18 (d, J = 4.8 Hz, 6H), 3.91 (s, 3H), 2.91−2.82 (m, 1H), 2.69 (dd, J = 15.6, 1.2 Hz, 1H), 2.60 (d, J = 2.8 Hz, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 145.4, 142.6, 140.8, 129.5, 128.4, 127.5, 126.5, 126.4, 120.4, 119.9, 113.9, 104.1, 56.2, 38.5, 33.7, 21.5, 19.3; IR (KBr) 3513, 2951, 2202, 1587, 1480, 1273, 1205, 1103, 1033, 895, 739 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{20}H_{20}NO_2$ $[M + H]^+$ 306.1489, found 306.1487.



4bg

*Methyl 4-(2-Chlorophenyl)-8-hydroxy-7-methoxy-1,5-dimethyl-3,4-dihydronaphthalene-2-carboxylate (**4bg**).* Red oil (30.2 mg, 54% yield); R_f = 0.41 (EtOAc/petroleum ether = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, J = 8.0, 1.2 Hz, 1H), 7.08 (td, J = 7.6, 1.6 Hz, 1H), 6.97 (td, J = 7.6, 0.8 Hz, 1H), 6.66 (s, 1H), 6.59 (dd, J = 7.6, 1.6 Hz, 1H), 6.06 (s, 1H), 4.56 (d, J = 6.4 Hz, 1H), 3.90 (s, 3H), 3.63 (s, 3H), 3.18−3.10 (m, 1H), 2.66−2.58 (m, 4H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 145.5, 143.5, 142.5, 138.5, 133.5, 130.3, 129.7, 129.4, 127.5, 126.4, 125.7, 124.3, 123.6, 113.0, 56.2, 51.3, 36.2, 30.3, 19.6, 18.9; IR (KBr) 3503, 2948, 1705, 1588, 1479, 1441, 1311, 1277, 1193, 902, 738 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{21}ClO_4Na$ $[M + Na]^+$ 395.1021, found 395.1017.



4bh

*Methyl 4-(4-Chlorophenyl)-8-hydroxy-7-methoxy-1,5-dimethyl-3,4-dihydronaphthalene-2-carboxylate (**4bh**).* Yellow solid (44.2 mg, 79% yield); mp 126−128 °C; R_f = 0.41 (EtOAc/petroleum ether = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4

DOI: 10.1021/acs.joc.6b02566
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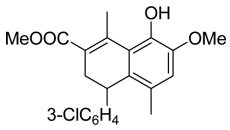
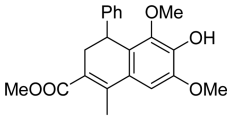
Hz, 2H), 6.68 (s, 1H), 6.06 (s, 1H), 4.12−4.03 (m, 1H), 3.91 (s, 3H), 3.66 (s, 3H), 3.12 (dd, J = 16.0, 1.6 Hz, 1H), 2.67−2.58 (m, 1H), 2.53 (d, J = 2.4 Hz, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 145.5, 144.1, 142.6, 140.1, 131.7, 130.2, 129.1, 128.1, 125.5, 123.7, 123.4, 112.8, 56.2, 51.4, 38.4, 32.4, 19.8, 19.1; IR (KBr) 3509, 2949, 2845, 1703, 1586, 1479, 1444, 1312, 1193, 1100, 906, 733 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{21}ClO_4Na$ [M + Na]$^+$ 395.1021, found 395.1026.



4bi

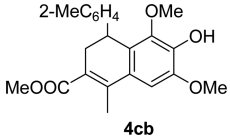
*Methyl 4-(3-Chlorophenyl)-8-hydroxy-7-methoxy-1,5-dimethyl-3,4-dihydronaphthalene-2-carboxylate (**4bi**).* White solid (44.7 mg, 80% yield); mp134−136 °C; R_f = 0.42 (EtOAc/petroleum ether = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13−7.10 (m, 2H), 6.96 (s, 1H), 6.91−6.86 (m, 1H), 6.68 (s, 1H), 6.07 (s, 1H), 4.10 (d, J = 4.8 Hz, 1H), 3.91 (s, 3H), 3.67 (s, 3H), 3.14 (dd, J = 16.0, 1.6 Hz, 1H), 2.67−2.58 (m, 1H), 2.55 (d, J = 2.4 Hz, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 145.5, 144.2, 143.9, 142.6, 133.8, 129.9, 129.3, 127.9, 126.3, 126.0, 125.5, 123.7, 123.3, 112.9, 56.2, 51.4, 38.8, 32.3, 19.8, 19.2; IR (KBr) 3504, 2948, 1702, 1593, 1477, 1280, 1193, 1103, 1035, 910 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{22}ClO_4$ [M + H]$^+$ 373.1201, found 373.1208.

General Procedure for the [4 + 2]-Annulation Reaction between 2,6-Dimethoxy Phenol (2c) and D−A Cyclopropanes. Under the nitrogen atmosphere, a stirring solution of cyclopropane **1** (0.4 mmol, 2.7 equiv) and phenol **2c** (0.15 mmol, 1 equiv) in HFIP (3 mL) was cooled by a mixture of ice and water for 10 min. Then, $Sc(OTf)_3$ (0.015 mmol, 10 mol %) was added, and the reaction temperature was allowed to rise to room temperature naturally. The reaction was monitored by TLC analysis. When the generated ring-opening intermediate disappeared, the solvent was removed in vacuo, and the residue was purified by flash column chromatography on silica gel to give the product **4**.



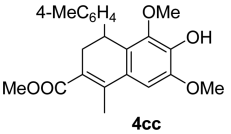
4ca

*Methyl 6-Hydroxy-5,7-dimethoxy-1-methyl-4-phenyl-3,4-dihydronaphthalene-2-carboxylate (**4ca**).* Colorless solid (52.6 mg, 99% yield); mp 128−130 °C; R_f = 0.41 (EtOAc/petroleum ether = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−7.14 (m, 2H), 7.14−7.08 (m, 1H), 7.03 (d, J = 7.2 Hz, 1H), 6.94 (s, 1H), 5.72 (s, 1H), 4.48 (d, J = 6.8 Hz, 1H), 3.96 (s, 3H), 3.67 (s, 3H), 3.54 (s, 3H), 3.08 (d, J = 16.4 Hz, 1H), 2.86−2.73 (m, 1H), 2.48 (d, J = 2.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 146.2, 143.9, 143.5, 142.0, 139.5, 128.1, 128.0, 127.6, 126.1, 125.9, 121.5, 104.3, 60.6, 56.3, 51.3, 35.1, 32.3, 16.5; IR (KBr) 3523, 3401, 2949, 2839, 1699, 1606, 1500, 1452, 1320, 1260, 1050, 910, 834 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{22}O_5Na$ [M + Na]$^+$ 377.1359, found 377.1352.



4cb

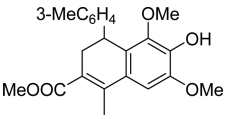
*Methyl 6-Hydroxy-5,7-dimethoxy-1-methyl-4-(o-tolyl)-3,4-dihydronaphthalene-2-carboxylate (**4cb**).* Red oil (53.6 mg, 97% yield); R_f = 0.43 (EtOAc/petroleum ether = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 7.6 Hz, 1H), 7.06−7.00 (m, 1H), 6.96 (s, 1H), 6.92 (t, J = 7.2 Hz, 1H), 6.55 (d, J = 7.6 Hz, 1H), 5.69 (s, 1H), 4.70 (dd, J = 7.6, 2.0 Hz, 1H), 3.96 (s, 3H), 3.65 (s, 3H), 3.37 (s, 3H), 2.86 (d, J = 16.0 Hz, 1H), 2.83−2.74 (m, 1H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 146.2, 143.7, 141.9, 141.2, 139.6, 134.9, 130.3, 128.4, 127.7, 126.6, 126.0, 125.6, 121.2, 104.1, 60.2, 56.3, 51.3, 31.2, 30.7, 19.6, 16.5; IR (KBr) 3400, 2949, 2837, 1702, 1606, 1572, 1456, 1318, 1259, 1204, 1110, 913 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{24}O_5Na$ [M + Na]$^+$ 391.1516, found 391.1524.



4cc

*Methyl 6-Hydroxy-5,7-dimethoxy-1-methyl-4-(p-tolyl)-3,4-dihydronaphthalene-2-carboxylate (**4cc**).* Yellow oil (54.1 mg, 98% yield); R_f = 0.42 (EtOAc/petroleum ether = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, J = 8.0 Hz, 2H), 6.85 (s, 1H), 6.84 (d, J = 8.0 Hz, 2H), 5.63 (s, 1H), 4.37 (d, J = 7.2 Hz, 1H), 3.88 (s, 3H), 3.60 (s, 3H), 3.49 (s, 3H), 2.98 (d, J = 16.4 Hz, 1H), 2.79−2.64 (m, 1H), 2.41 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 146.1, 143.8, 142.0, 140.4, 139.5, 135.5, 128.8, 128.0, 127.4, 126.1, 121.6, 104.3, 60.7, 56.3, 51.3, 34.7, 32.4, 21.0, 16.5; IR (KBr) 3524, 3403, 2949, 1700, 1607, 1574, 1500, 1456, 1320, 1259, 1109, 911 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{24}O_5Na$ [M + Na]$^+$ 391.1516, found 391.1518.

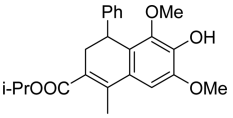
*Methyl 6-Hydroxy-5,7-dimethoxy-1-methyl-4-(m-tolyl)-3,4-dihydronaphthalene-2-carboxylate (**4cd**).* Yellow oil (54.1 mg, 98%



4cd

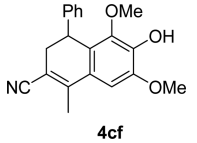
yield); R_f = 0.43 (EtOAc/petroleum ether = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (t, J = 7.6 Hz, 1H), 6.95−6.91 (m, 2H), 6.87 (s, 1H), 6.77 (d, J = 7.6 Hz, 1H), 5.71 (s, 1H), 4.44 (d, J = 6.0 Hz, 1H), 3.96 (s, 3H), 3.68 (s, 3H), 3.55 (s, 3H), 3.07 (dd, J = 16.8, 0.8 Hz, 1H), 2.83−2.74 (m, 1H), 2.49 (d, J = 2.0 Hz, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 146.1, 143.9, 143.4, 142.1, 139.5, 137.5, 128.4, 128.1, 127.9, 126.9, 125.9, 124.6, 121.5, 104.3, 60.6, 56.3, 51.3, 35.1, 32.4, 21.5, 16.5; IR (KBr) 3401, 2948, 2837, 1701, 1606, 1501, 1456, 1259, 1109, 913 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{24}O_5Na$ [M + Na]$^+$ 391.1516, found 391.1524.

*Isopropyl 6-Hydroxy-5,7-dimethoxy-1-methyl-4-phenyl-3,4-dihydronaphthalene-2-carboxylate (**4ce**).* Yellow oil (47.6 mg, 83% yield);



4ce

R_f = 0.43 (EtOAc/petroleum ether = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19−7.15 (m, 2H), 7.05 (d, J = 7.2 Hz, 1H), 6.91 (s, 1H), 5.68 (s, 1H), 5.06−4.95 (m, 1H), 4.46 (d, J = 6.4 Hz, 1H), 3.95 (s, 3H), 3.57 (s, 3H), 3.07 (d, J = 16.0 Hz, 1H), 2.82−2.73 (m, 1H), 2.44 (d, J = 2.4 Hz, 3H), 1.24 (d, J = 6.0 Hz, 3H), 1.21 (d, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 146.1, 143.9, 143.5, 140.6, 139.3, 128.2, 128.0, 127.5, 126.0, 125.8, 122.5, 104.2, 67.4, 60.6, 56.3, 35.1, 32.3, 21.9, 21.8, 16.4; IR (KBr) 3401, 2979, 1696, 1499, 1452, 1319, 1258, 1106, 1042, 700 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{26}O_5Na$ [M + Na]$^+$ 405.1672, found 405.1675.



4cf

*6-Hydroxy-5,7-dimethoxy-1-methyl-4-phenyl-3,4-dihydronaphthalene-2-carbonitrile (**4cf**).* Yellow solid (32.8 mg, 68% yield); mp 166−167 °C; R_f = 0.34 (EtOAc/petroleum ether = 1/2); ^{1}H NMR

DOI: 10.1021/acs.joc.6b02566
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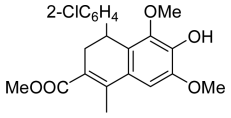
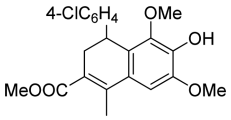
(400 MHz, $CDCl_3$) δ 7.24−7.13 (m, 3H), 7.00−6.93 (m, 2H), 6.82 (s, 1H), 5.77 (s, 1H), 4.52 (d, J = 7.2 Hz, 1H), 3.96 (s, 3H), 3.53 (s, 3H), 3.01−2.90 (m, 1H), 2.70 (d, J = 16.4 Hz, 1H), 2.41 (d, J = 2.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 146.4, 144.3, 142.7, 140.5, 128.4, 127.3, 126.6, 125.3, 125.2, 119.9, 103.6, 102.4, 60.6, 56.3, 34.8, 33.1, 18.6; IR (KBr) 3387, 2939, 2200, 1604, 1573, 1501, 1451, 1326, 1115, 700 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{20}NO_3$ $[M + H]^+$ 322.1438, found 322.1435.



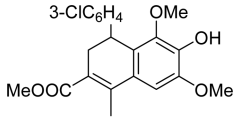
4cg

*Methyl 4-(2-Chlorophenyl)-6-hydroxy-5,7-dimethoxy-1-methyl-3,4-dihydronaphthalene-2-carboxylate (**4cg**).* Red oil (51.3 mg, 88% yield); R_f = 0.41 (EtOAc/petroleum ether = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, J = 7.6, 1.2 Hz, 1H), 7.06 (td, J = 7.6, 1.6 Hz, 1H), 7.01−6.93 (m, 2H), 6.56 (dd, J = 8.0, 1.6 Hz, 1H), 5.72 (s, 1H), 4.94 (d, J = 6.8 Hz, 1H), 3.97 (s, 3H), 3.66 (s, 3H), 3.49 (s, 3H), 3.03 (d, J = 16.8 Hz, 1H), 2.83−2.73 (m, 1H), 2.52 (d, J = 2.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 146.5, 143.9, 141.6, 140.2, 139.8, 133.2, 129.6, 129.4, 128.6, 127.4, 126.4, 125.1, 121.4, 104.2, 60.4, 56.3, 51.3, 32.0, 30.3, 16.4; IR (KBr) 3400, 2945, 2838, 1703, 1572, 1501, 1458, 1434, 1319, 1258, 1109, 1046, 754 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{22}ClO_5$ $[M + H]^+$ 389.1150, found 389.1146.



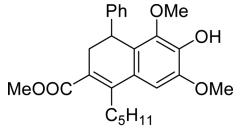
4ch

*Methyl 4-(4-Chlorophenyl)-6-hydroxy-5,7-dimethoxy-1-methyl-3,4-dihydronaphthalene-2-carboxylate (**4ch**).* Yellow oil (57.1 mg, 98% yield); R_f = 0.44 (EtOAc/petroleum ether = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 6.92 (s, 1H), 5.79 (s, 1H), 4.44 (d, J = 6.4 Hz, 1H), 3.95 (s, 3H), 3.69 (s, 3H), 3.58 (s, 3H), 3.03 (d, J = 16.4 Hz, 1H), 2.85−2.73 (m, 1H), 2.47 (d, J = 2.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 146.3, 143.8, 141.9, 139.6, 131.7, 128.9, 128.2, 128.2, 127.8, 125.3, 121.3, 104.2, 60.6, 56.3, 51.4, 34.5, 32.2, 16.5; IR (KBr) 3519, 3399, 2949, 1700, 1501, 1457, 1322, 1108, 1050, 911, 733 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{22}ClO_5$ $[M + H]^+$ 389.1150, found 389.1155.



4ci

*Methyl 4-(3-Chlorophenyl)-6-hydroxy-5,7-dimethoxy-1-methyl-3,4-dihydronaphthalene-2-carboxylate (**4ci**).* Yellow oil (51.3 mg, 88% yield); R_f = 0.42 (EtOAc/petroleum ether = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14−7.08 (m, 2H), 7.00 (s, 1H), 6.93 (s, 1H), 6.92−6.87 (m, 1H), 5.78 (s, 1H), 4.45 (d, J = 6.0 Hz, 1H), 3.96 (s, 3H), 3.70 (s, 3H), 3.59 (s, 3H), 3.05 (d, J = 16.4 Hz, 1H), 2.84−2.74 (m, 1H), 2.49 (d, J = 2.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 146.4, 145.7, 143.9, 142.0, 139.6, 133.9, 129.3, 127.9, 127.8, 126.3, 125.8, 124.9, 121.3, 104.3, 60.6, 56.3, 51.4, 34.9, 32.1, 16.5; IR (KBr) 3402, 2946, 1701, 1573, 1500, 1321, 1108, 1051, 914, 737 cm^{-1}; HRMS (ESI) m/z calcdfor $C_{21}H_{22}ClO_5$ $[M + H]^+$ 389.1150, found 389.1147.

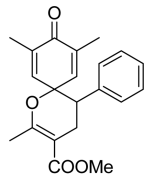


4cj

*Methyl 6-Hydroxy-5,7-dimethoxy-1-pentyl-4-phenyl-3,4-dihydronaphthalene-2-carboxylate (**4cj**).* Yellow oil (43.1 mg, 70% yield); R_f = 0.48 (EtOAc/petroleum ether = 1/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, J = 7.2 Hz, 2H), 7.13−7.08 (m, 1H), 7.02 (d, J = 7.2 Hz, 2H), 6.96 (s, 1H), 5.71 (s, 1H), 4.47 (d, J = 6.4 Hz, 1H), 3.95 (s, 3H), 3.66 (s, 3H), 3.54 (s, 3H), 3.14−3.04 (m, 1H), 3.01 (dd, J = 16.4, 1.6 Hz, 1H), 2.87−2.76 (m, 2H), 1.70−1.43 (m, 2H), 1.39−1.31 (m, 4H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 146.5, 146.2, 144.1, 143.3, 139.5, 128.0, 127.7, 126.6, 126.5, 126.1, 121.0, 104.2, 60.6, 56.3, 51.3, 35.1, 32.6, 32.1, 29.3, 29.1, 22.5, 14.1; IR (KBr) 3403, 2954, 1705, 1570, 1502, 1459, 1323, 1197, 915, 700 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{30}O_5Na$ $[M + Na]^+$ 433.1985, found 433.1980.

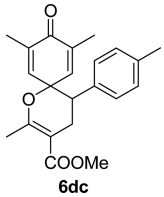
Procedure for the Synthesis of *Spiro*-Fused 2,5-Cyclohexadienones (6da). Under a nitrogen atmosphere, a stirring solution of cyclopropane **1** (0.22 mmol, 1.1 equiv) and phenol **2d** (0.2 mmol, 1 equiv) in HFIP (2 mL) was cooled by a mixture of ice and water for 10 min. Then, $Sc(OTf)_3$ (0.02 mmol, 10 mol %) was added. The reaction was monitored by TLC analysis. After the phenol was consumed completely, the solvents were removed in vacuo, and the residue was purified by flash column chromatography to afford the product **5da**. Then, the product **5da** was dissolved in HFIP (2 mL), and iodobenzene diacetate (IBD, 0.24 mmol) was added under zero degrees. About 10 min later, **5da** was consumed completely. The solvents were removed in vacuo, and the residue was purified by flash column chromatography to afford the product **6da**.

One-Pot Procedure for the Synthesis of *Spiro*-Fused 2,5-Cyclohexadienones (6da, 6dc, 6df, 6dh, and 6dk). Under a nitrogen atmosphere, a stirring solution of cyclopropane **1** (0.22 mmol, 1.1 equiv) and phenol **2d** (0.2 mmol, 1 equiv) in HFIP (2 mL) was cooled by a mixture of ice and water for 10 min. Then, $Sn(OTf)_2$ (0.02 mmol, 10 mol %) was added. The reaction was monitored by TLC analysis. After the phenol was consumed completely, NEt_3 (0.08 mmol) was added. About 5 min later, iodobenzene diacetate (IBD, 0.24 mmol) was added, and stirring continued for 10 min. Then, the solvents were removed in vacuo, and the residue was purified by flash column chromatography to afford the *spiro*-fused 2,5-cyclohexadienones **6**.



6da

*Methyl 2,8,10-Trimethyl-9-oxo-5-phenyl-1-oxaspiro[5.5]undeca-2,7,10-triene-3-carboxylate (**6da**).* Yellow oil (57.5 mg, 85% yield); R_f = 0.40 (EtOAc/petroleum ether = 1/8); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.15 (m, 3H), 7.07−7.01 (m, 2H), 6.70 (d, J = 1.6 HZ, 1H), 6.55 (d, J = 1.6 Hz, 1H), 3.72 (s, 3H), 3.12 (dd, J = 11.2, 5.6 Hz, 1H), 2.81−2.63 (m, 2H), 2.35 (s, 3H), 1.86 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 168.1, 162.6, 142.6, 138.0, 137.6, 136.5, 136.4, 128.6, 127.8, 127.6, 101.2, 76.2, 51.2, 47.1, 26.5, 20.0, 15.9, 15.4; IR (KBr) 3030, 2950, 1711, 1629, 1434, 1378, 1284, 1078, 1010, 734 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{22}O_4Na$ $[M + Na]^+$ 361.1410, found: 361.1408.



6dc

*Methyl 2,8,10-Trimethyl-9-oxo-5-(p-tolyl)-1-oxaspiro[5.5]undeca-2,7,10-triene-3-carboxylate (**6dc**).* Yellow solid (56.4 mg, 80% yield); mp 93−95 °C; R_f = 0.45 (EtOAc/petroleum ether = 1/8); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H),

DOI: 10.1021/acs.joc.6b02566
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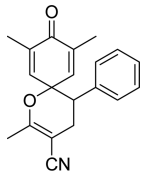
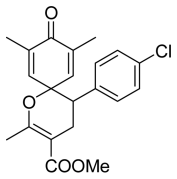
6.69 (s, 1H), 6.55 (s, 1H), 3.73 (s, 3H), 3.08 (dd, J = 11.6, 6.0 Hz, 2H), 2.78−2.71 (m, 1H), 2.70−2.60 (m, 1H), 2.35 (s, 3H), 2.26 (s, 3H), 1.86 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 168.2, 162.6, 142.8, 137.5, 137.2, 136.7, 136.4, 135.0, 128.6, 128.5, 101.2, 76.2, 51.2, 46.7, 26.7, 21.0, 20.1, 16.0, 15.5; IR (KBr) 2950, 1711, 1628, 1434, 1379, 1230, 1077, 1010, 963, 734 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{25}O_4$ $[M + H]^+$ 353.1747, found 353.1749.



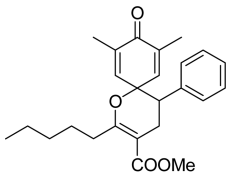
6df

*2,8,10-Trimethyl-9-oxo-5-phenyl-1-oxaspiro[5.5]undeca-2,7,10-triene-3-carbonitrile (**6df**).* Yellow oil (18.9 mg, 31% yield); R_f = 0.45 (EtOAc/petroleum ether = 1/6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.17 (m, 3H), 7.04−6.97 (m, 2H), 6.64 (dd, J = 3.2, 1.6 Hz, 1H), 6.51 (dd, J = 3.2, 1.6 Hz 1H), 3.14 (J = 11.6, 5.6 Hz, 1H), 2.77−2.67 (m, 1H), 2.59−2.51 (m, 1H), 2.20 (t, J = 1.2 Hz, 3H), 1.88 (d, J = 1.6 Hz, 3H), 1.69 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.3, 164.4, 141.4, 138.3, 137.0, 136.7, 135.2, 128.6, 128.1, 119.2, 82.9, 46.3, 26.9, 19.8, 16.0, 15.4; IR (KBr) 2924, 2208, 1702, 1642, 1445, 1386, 1244, 1104, 1014, 914, 734, 701 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{20}NO_2$ $[M + H]^+$ 306.1489, found 306.1494.



6dh

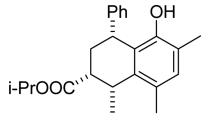
*Methyl 5-(4-Chlorophenyl)-2,8,10-trimethyl-9-oxo-1-oxaspiro[5.5]undeca-2,7,10-triene-3-carboxylate (**6dh**).* Yellow oil (57.4 mg, 77% yield); R_f = 0.35 (EtOAc/petroleum ether = 1/8); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.66 (q, J = 1.2 Hz, 1H), 6.53 (q, J = 1.6 Hz, 1H), 3.74 (s, 3H), 3.09 (dd, J = 11.2, 5.6 Hz, 1H), 2.75 (ddd, J = 17.2, 5.6, 1.2 Hz, 1H), 2.66−2.57 (m, 1H), 2.35 (s, 3H), 1.87 (d, J = 1.6 Hz, 3H), 1.72 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.6, 168.0, 162.7, 142.2, 137.9, 136.7, 136.6, 136.2, 133.5, 129.9, 128.1, 101.0, 75.8, 51.3, 46.5, 26.6, 20.0, 16.0, 15.5; IR (KBr) 2950, 1710, 1643, 1630, 1493, 1434, 1378, 1228, 1013, 731 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{21}ClO_4Na$ $[M + Na]^+$ 395.1021, found: 395.1017.



6dj

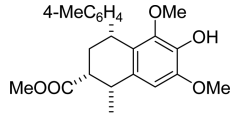
*Methyl 8,10-Dimethyl-9-oxo-2-pentyl-5-phenyl-1-oxaspiro[5.5]undeca-2,7,10-triene-3-carboxylate (**6dj**).* White solid (60.0 mg, 76% yield); mp 96−98 °C; R_f = 0.50 (EtOAc/petroleum ether = 1/8); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.16 (m, 3H), 7.06−7.01 (m, 2H), 6.70−6.63 (m, 1H), 6.54 (dd, J = 6.8, 1.2 Hz, 1H), 3.73 (s, 3H), 3.09 (dd, J = 11.6, 5.6 Hz, 1H), 2.88−2.62 (m, 4H), 1.86 (d, J = 1.2 Hz, 3H), 1.69 (d, J = 1.2 Hz, 1H), 1.65−1.55 (m, 2H), 1.37−1.31 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.8, 167.9, 166.6, 142.8, 138.2, 137.5, 136.7, 136.3, 128.7, 127.8, 127.6, 100.8, 75.9, 51.2, 47.3, 32.9, 31.7, 27.4, 26.7, 22.4, 15.9, 15.4, 14.0; IR (KBr) 2953, 1710, 1649, 1625, 1433, 1229, 1170, 1060, 771, 701 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{30}O_4Na$ $[M + Na]^+$ 417.2036, found 417.2039.

Procedure for the Hydrogenation of Dihydronaphthol 4ae and 4cc. A mixture of dihydronaphthol (**4ae** or **4cc**) and 10 mol % of Pd/C (10%) in 2 mL of methanol was stirred under a hydrogen atmosphere (1 atm) at room temperature for several hours. The reaction was monitored by TLC. When the starting material was consumed completely, Pd/C was removed by filtration, and the filtrate was concentrated. The residue was purified by flash chromatography to afford the product.



7ae

*Isopropyl 5-Hydroxy-1,6,8-trimethyl-4-phenyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**7ae**).* Colorless oil (10.5 mg, 55% yield); R_f = 0.40 (EtOAc/petroleum ether = 1/8); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.14 (m, 2H), 7.12−7.03 (m, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.87 (s, 1H), 6.79 (s, 1H), 5.13−5.02 (m, 1H), 4.30 (s, 1H), 4.25−3.77 (m, 1H), 3.49−3.40 (m, 1H), 3.01−2.92 (m, 1H), 2.24 (s, 4H), 2.18 (s, 3H), 1.29 (d, J = 7.2 Hz, 3H), 1.26 (d, J = 4.4 Hz, 3H), 1.25 (d, J = 4.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 149.6, 141.9, 130.1, 129.7, 129.2, 126.8, 67.7, 44.1, 35.5, 29.7, 26.8, 21.9, 21.8, 20.5, 19.4, 15.9; IR (KBr) 3518, 2974, 2924, 1726, 1484, 1377, 1201, 1106, 758 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{32}NO_3$ $[M + NH_4]^+$ 370.2377, found 370.2376.



7cc

*Methyl 6-Hydroxy-5,7-dimethoxy-1-methyl-4-(p-tolyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**7cc**).* Colorless oil (50.6 mg, 65% yield); R_f = 0.33 (EtOAc/petroleum ether = 1/4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 7.6 Hz, 2H), 6.46 (s, 1H), 5.31 (s, 1H), 4.08 (dd, J = 10.8, 8.0 Hz, 1H), 3.88 (s, 3H), 3.69 (s, 3H), 3.34−3.27 (m, 1H), 3.16 (s, 3H), 2.89−2.80 (m, 1H), 2.40−2.32 (m, 1H), 2.30 (s, 3H), 1.96−1.84 (m, 1H), 1.26 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 146.5, 146.1, 145.4, 137.4, 134.9, 134.0, 128.9, 126.8, 124.6, 105.9, 58.8, 56.1, 51.5, 43.7, 41.4, 35.7, 30.5, 21.0, 19.3; IR (KBr) 3456, 2947, 1732, 1614, 1497, 1459, 1286, 1238, 1167, 1101, 911, 818 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{30}NO_5$ $[M + NH_4]^+$ 388.2118, found 388.2119.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02566.

Crystallographic information for **4ab** (CIF)
Crystallographic information for **4ba** (CIF)
Crystallographic information for **4ca** (CIF)
^{1}H NMR and ^{13}C NMR spectra for all new compounds (PDF)

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DOI: 10.1021/acs.joc.6b02566
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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the Chinese National Foundation of Natural Science (NSFC) (Grants 21202070 and 21402073) and the Fundamental Research Funds for the Central Universities (Grant lzujbky-2016-54).

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DOI: 10.1021/acs.joc.6b02566
J. Org. Chem. 2017, 82, 1013−1023