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Synthetic studies on nemorosone via enantioselective intramolecular cyclopropanation

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ABSTRACT

This Letter describes synthetic studies of nemorosone via enantioselective intramolecular cyclopropanation. For the total synthesis of nemorosone, three potential intermediates were evaluated through the efficiency of three sequential reactions, namely, their intramolecular cyclopropanation, dimethylation of the resultant cyclopropanes, and ring-opening reaction of the alkylated cyclopropanes. As a result, α-diazomethyl ketone **10c** was found to be the most suitable. The enantioselective intramolecular cyclopropanation to construct the bicyclo[3.3.1]nonane core and preparation of the compound with all the correct stereogenic centers of nemorosone are also described.

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Polycyclic polyprenylated acylphloroglucinols (PPAPs) have diverse and complex structures with intriguing biological activities including cytotoxicity against several human cancer cell lines. PPAPs feature a highly oxygenated and densely substituted bicyclo[3.3.1]nonane-2,4,9-trione or bicyclo[3.2.1]octane-2,4,8-trione core incorporating C_5H_9 or $C_{10}H_{17}$ (prenyl, geranyl, etc.) side chains.[1] PPAPs have been divided into type-A, B, and C. Typical type-A PPAPs include hyperforin,[2] adhyperforin,[3] and nemorosone[4] (Fig. 1). Such PPAPs might suffer from further cyclizations involving the -diketone and the alkene in side-chain alkenes to afford furano-fused compounds such as garsubellin,[5] furohyperforin,[6] and hyperibone G.[7] The fascinating and wide-ranging biological activities of PPAPs have made them attractive synthetic targets, and many synthetic studies[8] including total syntheses[9] have been reported thus far. We report herein synthetic studies on nemorosone via enantioselective intramolecular cyclopropanation that could also be utilized to synthesize other type-A PPAPs.

We have reported the construction of the bicyclo[3.3.1]nonane derivative **4** (Scheme 1) including the common scaffold that can be found in type-A PPAPs.[10] The key reaction in our approach to **4** is the intramolecular cyclopropanation (IMCP) of α-diazo-β-keto ester **1** and subsequent regioselective ring-opening reaction of the methoxycyclopropane **3**. This approach could be enantioselective when a chiral bisoxazoline ligand is used instead of **2**, and enantio-enriched **4** and its derivatives are expected to be obtained.[11]

Our retrosynthetic analysis of type-A PPAPs is shown in Scheme 2. To synthesize type-A PPAPs from **4**, prenyl groups must be introduced at C3, C5, and C7 of **4**, and alkyl groups at C8. Allyl groups at C3, C5, and C7 can be converted to prenyl groups via cross-metathesis with 2-methyl-2-butene in a late stage.[12] Therefore, compound **5** (Scheme 2) would be a potential substrate for the cross-metathesis. Compound **5** was expected to be obtained by the oxidation of compound **6**. Compound **6** could be prepared from compound **7**, which was thought to be obtained from the ring-opening reaction of compound **8**. Hence, we decided to prepare three α-diazo-β-keto compounds **10a–c** ($R^4 = CO_2Et$, SO_2Ph, H) to examine their IMCP, subsequent alkylation of the cyclopropanes **9**, and ring-opening reaction of the alkylated cyclopropanes **8**. Then, we intended to select one among **10a–c** on the basis of the overall yield from **10** to **7** to pursue the enantioselective preparation of **7** and further transformation toward enantioselective total synthesis of nemorosone.

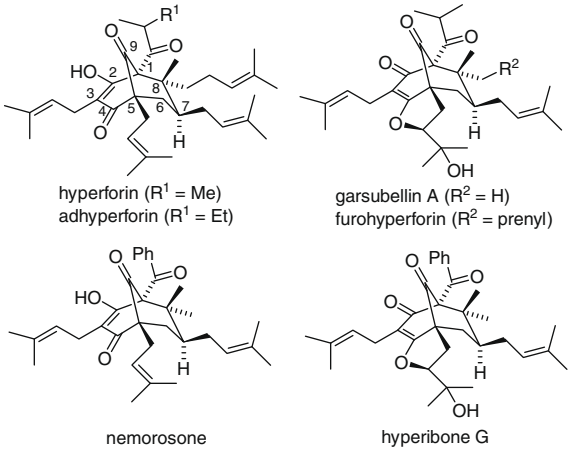

Figure 1. Structures of some type-A PPAPs.

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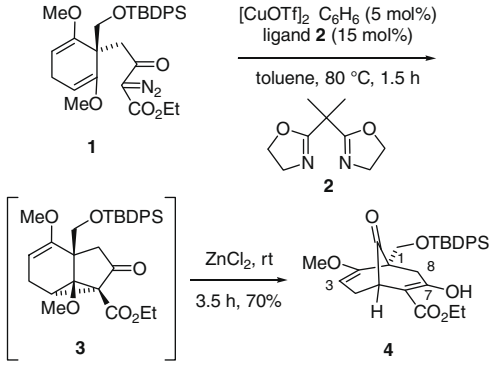
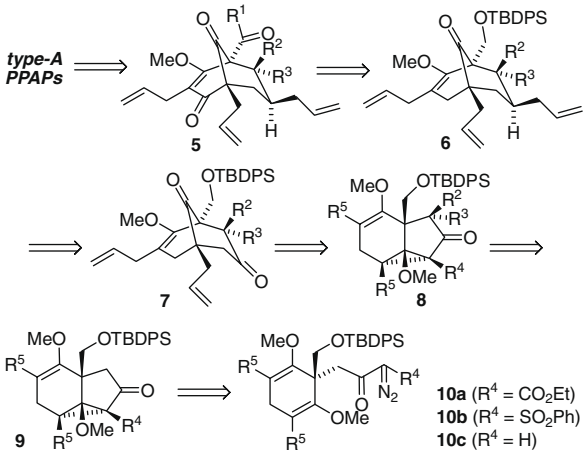
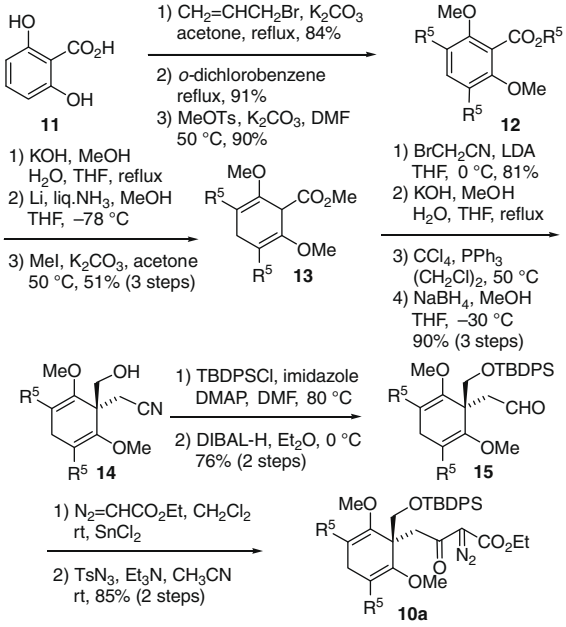
We first prepared α-diazo-β-keto ester **10a** (Scheme 3) by an easy two-step procedure from aldehyde **15**. 2,6-Dihydroxybenzoic acid **11** were allylated with allylbromide and potassium carbonate followed by Claisen rearrangement and O-methylation to afford allyl ester **12**. Compound **12** was hydrolyzed to the carboxylic acid, followed by Birch reduction and methylation of the product to afford methyl ester. The enolate generated by the treatment of **13** with LDA was subjected to reaction with bromoacetonitrile, followed by the hydrolysis of the methyl ester, formation of the acid chloride, and reduction to afford alcohol **14**. Compound **14** was converted to the corresponding TBDPS ether, followed by reduction with DIBAL to afford aldehyde **15**. Compound **15** was subjected to reaction with ethyl diazoacetate and $SnCl_2$[13] to afford the β-keto ester, and this in turn was successfully converted to α-diazo-β-keto ester **10a** via a diazotransfer reaction.



Scheme 1. Intramolecular cyclopropanation (IMCP) of α-diazo-β-keto ester **1** and the subsequent ring-opening reaction.



Scheme 2. Retrosynthetic analysis of type-A PPAPs (R^5 = allyl).



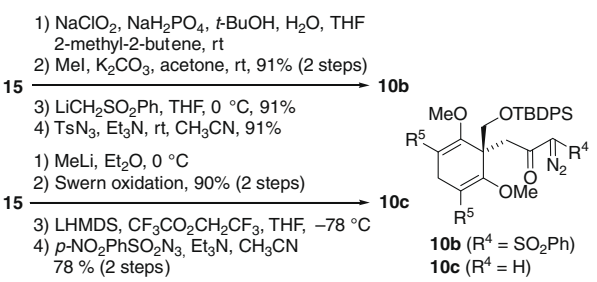
Scheme 3. Preparation of α-diazo-β-keto ester **10a** from 2,6-dihydroxybenzoic acid **11** (R^5 = allyl).

Other substrates for the IMCP, **10b** and **10c**, were prepared as shown in Scheme 4. The former was prepared by the reaction of a dianion of methyl phenyl sulfone with the methyl ester, which was prepared from **15** via Pinnick oxidation and methylation. The latter was prepared by a modified Danheiser's protocol using the methyl ketone,[14] which was obtained by the addition of methyllithium to **15** and subsequent Swern oxidation.[15]

With **10a–c** in hand, we applied their IMCP, subsequent dimethylation in C8, and the ring-opening reaction, respectively. The results of the three reactions are summarized in Table 1. The IMCP of **10a** afforded **9a** in 40% yield and dimethylation of **9a** proceeded with 43% yield, and the ring-opening reaction of **8a** afforded **7a** in 55% yield. Extensive optimization did not improve the yields of the three reactions. In the case of **10b**, the yields of IMCP and dimethylation were 57% and 69%, respectively, which were better than those of **10a**. Interestingly, the ring-opening reaction of **8b** resulted in no reactions or decomposition of **8b** under any acidic conditions. The reactions attempted using nucleophiles under basic and neutral conditions (Li_2S, LiI, NaCl) gave the same results. Although it has been reported that the steric repulsion between the *cis*-substituents on a cyclopropane accelerates its ring-opening reaction,[16] we speculate that this is not the case and rather, a bulky phenylsulfonyl group could prevent the cyclopropane in **8b** from reacting with the reagent.

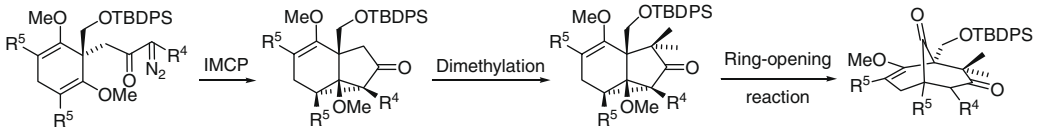
IMCP of α-diazomethyl ketone **10c** proceeded at room temperature to afford **9c** in 97% yield. This result suggests that the slow reaction rate and low yield of the IMCPs of **10a** and **10b** can be attributed to the steric hindrance around the metal–carbene center. Dimethylation of **9c** with iodomethane afforded **8c** in 74% yield, and the ring-opening reaction of **8c** under the conditions listed in Table 1 successfully afforded **7c** in 95% yield. On the basis of the results described above, we decided to examine the enantioselective intramolecular cyclopropanation of **10c** and further transformation from **7c**.

The enantioselective IMCPs of **10c** are summarized in Table 2. The catalytic asymmetric IMCP (CAIMCP) using $Rh_2(5R\text{-MEPY})_4$[17] afforded the desired product **9c** in 74% yield; however, interestingly, it was formed as a racemic mixture. CAIMCP with bisoxazoline ligand **A**[18a] (Fig. 2) and CuOTf proceeded quite smoothly at



Scheme 4. Preparation of **10b** and **10c** (R^5 = allyl).

Table 1
Transformation from **10a–c** to **7a–c** (R^5 = allyl)

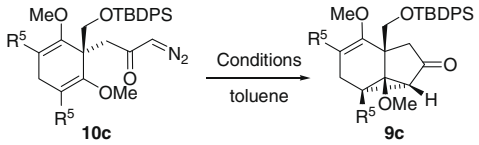


10a (R^4 = CO_2Et) **9a** (R^4 = CO_2Et) **8a** (R^4 = CO_2Et) **7a** (R^4 = CO_2Et)[a]
10b (R^4 = SO_2Ph) **9b** (R^4 = SO_2Ph) **8b** (R^4 = SO_2Ph) **7b** (R^4 = SO_2Ph)
10c (R^4 = H) **9c** (R^4 = H) **8c** (R^4 = H) **7c** (R^4 = H)

Entry	**10**	IMCP Conditions	Yield[b] (%)	Dimethylation Conditions	Yield[b] (%)	Ring-opening reaction Conditions	Yield[b] (%)
1	**10a**	CuOTf (20 mol %), ligand **2** (30 mol %) toluene, 60 °C, 17 h	40 (**9a**)	MeI, KH, THF, 0 °C, 12 h	43 (**8a**)	PPTS, $(CH_2Cl)_2$, 50 °C, 12 h	55 (**7a**)
2	**10b**	CuOTf (20 mol %), ligand **2** (30 mol %) toluene, 50 °C, 10 h	57 (**9b**)	MeI, KH, THF, −20 °C, 2 days	69 (**8b**)	See text	0 (**7b**)
3	**10c**	CuOTf (10 mol %), ligand **2** (15 mol %) toluene, rt, 12 h	97 (**9c**)	MeI, ^{t}BuOK, THF/HMPA = 6:1, −78 °C, 6 h	74 (**8c**)	2 N HCl, THF, rt, 12 h	95 (**7c**)

[a] Compound **7a** exists as the enol form.
[b] Isolated yields.

Table 2
Enantioselective preparation of **10c** (R^5 = allyl)

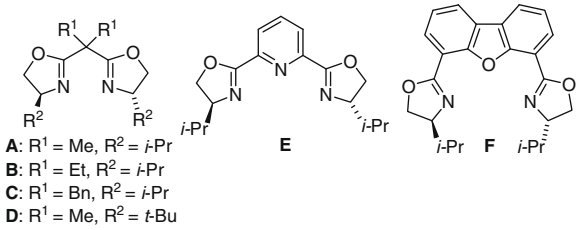


10c **9c**

Entry	Catalyst[a]	Temp (°C)	Time (h)	Yield[c] (%)	ee[d] (%)
1	Rh_2(5*R*-MEPY)$_4$[b]	rt	1 min	74	0
2	**A** + CuOTf	rt	0.2	97	59
3	**A** + CuOTf	0	3.5	70	62
4	**A** + CuOTf[e]	−20	48	39 (29% conv.)[f]	77
5	**B** + CuOTf	rt	1	100	46
6	**C** + CuOTf	rt	1 min	87	36
7	**D** + CuOTf	rt	1 min	75	−37
8	**E** + CuOTf	rt, 50	0.5, 40	91	6
9	**F** + CuOTf	rt, 50, 70	1.5, 1.5, 48	63 (26% conv.)[f]	0
10	**A** + $CuBF_4$	rt	1 min	69	62
11	**A** + $CuBF_4$	0	0.4	99	71
12	**A** + $CuBF_4$	−20	18	48 (66% conv.)[f]	79
13	**A** + $CuBF_4$	−50	12	0	—
14	**A** + $CuBF_4$[e]	−20	1	58	75
15	**A** + $CuBF_4$[e]	−30	16	69 (84% conv.)[f]	80
16	**A** + $CuBF_4$[e]	−40	18	15 (15% conv.)[f]	80

[a] **A-F** are chiral ligands in Figure 2. Ligand (15 mol %) and CuOTf (10 mol %) were used unless otherwise noted.
[b] 10 mol % of Rh_2(5*R*-MEPY)$_4$ was used in CH_2Cl_2.
[c] Isolated yields.
[d] ee determined by HPLC. The absolute configuration has not been determined.
[e] 100 mol % of CuX (X = OTf or BF_4) and 150 mol % of **A** were used.
[f] Yields based on the recovered starting materials.

room temperature to afford **9c** in 97% yield with 59% ee (entry 2). CAIMCP with ligand **A** at 0 °C reduced the yield to 70%; however, it improved the ee slightly to 62% (entry 3). The ee was further increased to 77% in the reaction with a stoichiometric amount of catalyst at −20 °C; however, the reaction proceeded sluggishly and the yield was 39% (at 29% conversion) (entry 4). CAIMCP with ligand **B**[18b] proceeded quantitatively (entry 5), and interestingly, the CAIMCPs with more bulky ligands **C**[11a] and **D**[18a] completed within 1 min (entries 6 and 7). Although the yields in entries 5–7 were good, the ee of **9c** did not increase. CAIMCPs with tridentate



A: R^1 = Me, R^2 = *i*-Pr
B: R^1 = Et, R^2 = *i*-Pr
C: R^1 = Bn, R^2 = *i*-Pr
D: R^1 = Me, R^2 = *t*-Bu

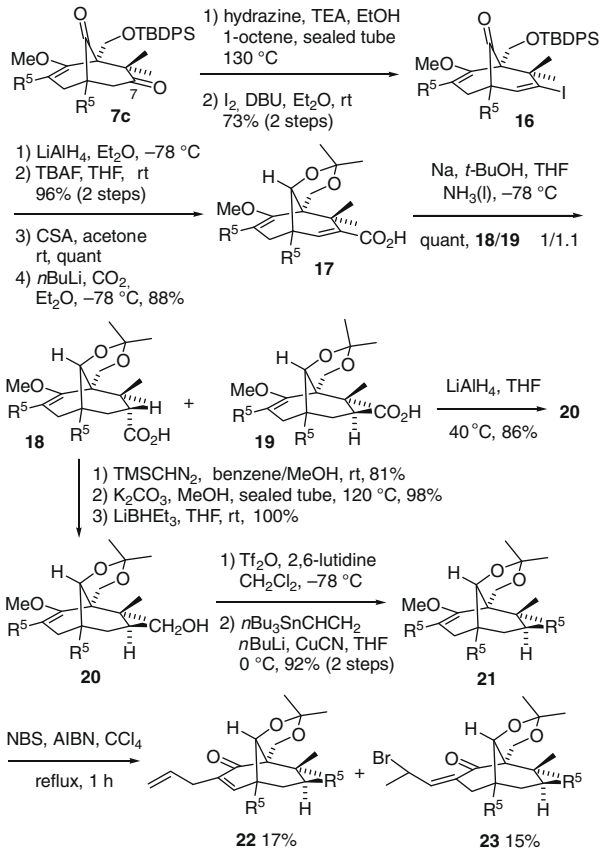
Figure 2. Structures of ligands **A–F**.

ligands **E**[18c] and **F**[18d] were also attempted (entries 8 and 9); however, the reactions were slow and the ee of **9c** was very low. Use of $CuBF_4$ accelerated the reaction (entries 10–16). Thus, the reaction completed in 1 min at room temperature (69%, 62% ee, entry 10) and in 0.4 h at 0 °C (99%, 71% ee, entry 11). The reaction using $CuBF_4$ at −20 °C, however, did not complete (48% at 66% conv.), but afforded **9c** with 79% ee (entry 12). The reaction at −50 °C did not proceed (entry 13). The reaction with a stoichiometric amount of catalyst at −20 °C completed in 1 h to afford **9c** with 58% yield and 75% ee (entry 14). The reactions were carried out at −30 °C and at −40 °C, too, affording **9c** with 69% yield (at 84% conv., 80% ee) (entry 15) and 15% yield (at 15% conv., 80% ee) (entry 16), respectively.

As described above, CAIMCP of **10c** has some characteristic features. First, the results in Table 2 suggest that it is relatively fast. This fact is well explained by the reactive electron-rich methoxyalkene in **10c**. Second, although we have found that a bulky bisoxazoline ligand effectively improves enantioselectivity in the CAIMCP of α-diazo-β-keto sulfones,[11] in the case of **10c**, the ee of entry 2 is higher than those of entries 5–7. The results in entries 2 and 5–7 indicate that less bulky ligand **A** is more effective for the CAIMCP of **10c**. In addition, it should be noted that the CAIMCP with ligand **D** (entry 7) exhibited reversal enantioselectivity when compared with the other entries. The CAIMCP with $CuBF_4$ afforded the product with almost the same ee as the one obtained with using CuOTf, however, the reaction with $CuBF_4$ proceeded faster than with CuOTf. The above-mentioned characteristic features of the CAIMCP of **10c** would be beneficial for designing a new chiral bisoxazoline ligand effective for the CAIMCP of **10c**. Determination of the absolute structure of the product and further optimization of the enantioselectivity are now in progress.

Further transformation of **7c** is shown in Scheme 5. We successfully introduced an allyl group into the C7 position of ketone **7c**. Thus, ketone **7c** was converted to alkenyl iodide **16** via a hydrazone under Barton's conditions,[19] followed by stereoselective reduction with $LiAlH_4$ from the less hindered side,[20] removal of a TBDPS group, acetonide formation of the resultant diol, lithiation via halogen–metal exchange, and subsequent trapping with carbon dioxide to afford carboxylic acid **17**. 1,4-Reduction of **17** or its ester form hardly occurred under several reaction conditions; however, it was finally realized by Birch reduction. Although the product was a mixture of diastereomers, **18** and **19**, we found that the methyl ester of **18** was converted to the desired isomer by epimerization under the basic conditions, and subsequent reduction gave alcohol **20** with the correct C7 configuration. The desired isomer **19**, the stereochemistry of which was confirmed by NOE correlations, was converted to **20** by reduction with $LiAlH_4$. Alcohol **20** was converted to the corresponding triflate, which was subjected to a coupling reaction with a divinylcuprate[21] to successfully afford **21**. Further transformation of **21** was difficult; however, after several attempts, we found that the reaction of **21** with NBS under the conditions for allylic bromination[22] afforded **22** and **23**. As the yield of **22** was only 17%, further efforts are being continued to improve the yield.

In summary, we prepared three α-diazo-β-keto compounds **10a–c** and evaluated their three sequential transformations, namely, the IMCP of **10a–c**, dimethylation at the C8 position of the cyclopropanes **9a–c**, and ring-opening reaction to afford two bicycle[3.3.1]nonane compounds **7a** and **7c**. We found that α-diazomethyl ketone **10c** would be the most suitable intermediate for the total synthesis of nemorosone. We also examined the enantioselective intramolecular cyclopropanation of **10c** using some chiral catalysts, and found that the CAIMCP with the chiral bisoxazoline ligand A effectively afforded the enantio-enriched compound **9c** with 48% yield (66% conv.) and 79% ee. Moreover, the reaction with a stoichiometric amount of catalyst afforded the same product with 69% yield (84% conv.) and 80% ee. Although the CAIMCP of **10c** requires further optimization, some information about the relationships between the structure of the chiral bisoxazoline ligand and the ee of the product were obtained through this study. We have also succeeded in preparing the compound with all the correct stereogenic centers of nemorosone. Further elaboration toward the enantioselective total synthesis of nemorosone is now underway and will be reported in due course.



Scheme 5. Transformation from **7c** to **22** (R^5 = allyl).

Acknowledgments

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