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AN INTRAMOLECULAR NUCLEOPHILE-CATALYZED ALDOL-LACTONIZATION (NCAL) REACTION OF *S*-ARYL-(*E*)-6-OXOHEX-2-ENETHIOATE WITH *N,N*-4-DIMETHYLAMINOPYRIDINE *N*-OXIDE

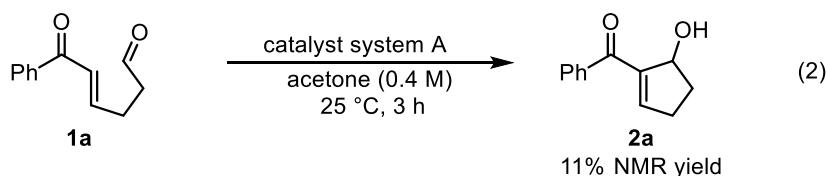
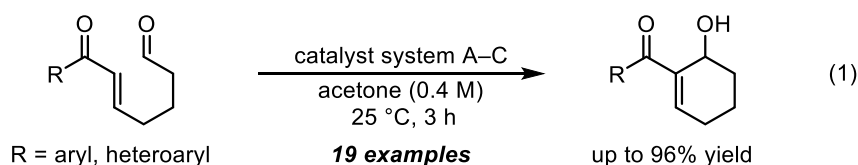
Hiroki Mandai,* Keita Shimowaki, Kohei Hongo, Koichi Mitsudo, and Seiji Suga*

Division of Applied Chemistry, Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530; E-mail: mandai@cc.okayama-u.ac.jp, suga@cc.okayama-u.ac.jp

Abstract – We have developed an intramolecular nucleophile-catalyzed aldol-lactonization (NCAL) reaction of *S*-aryl-(*E*)-6-oxohex-2-enethiolate with *N,N*-4-dimethylaminopyridine *N*-oxide (DMAPO) to afford densely functionalized bicyclic β -lactones in moderate yield. This unique transformation may be explained in terms of nucleophilic substitution of the *S*-aryl moiety by DMAPO, followed by 1,4-addition of aryl thiolate to generate a zwitterionic enolate and an intramolecular C–C bond-forming reaction (aldol-lactonization).

The construction of densely functionalized carbocycles has been a challenging topic in organic synthesis.¹ One option for accessing such molecules is through the use of intramolecular Morita-Baylis-Hillman (MBH) reactions² or their products³ from easily accessible starting materials. However, these reactions, especially with the use of α,β -unsaturated carbonyls having an (*E*)-olefin (versus (*Z*)-olefin) in the intramolecular MBH reaction, are extremely slow⁴ due to steric repulsion between the reactant and a nucleophilic catalyst.⁵ To address this reactivity issue, several organocatalytic methods including enantioselective variants have been developed to enhance the rate of the reaction by using a nucleophilic catalyst in combination with a co-catalyst.⁶ Very recently, we also reported an extremely fast intramolecular MBH reaction by the combination of a catalytic amount of a nucleophilic catalyst (*N,N*-4-dimethylaminopyridine, 4-pyrrolidinopyridine, or tributylphosphine) and 1,3-diphenyl-2-thiourea as a co-catalyst (eq. 1).⁷ Under these catalytic systems A–C, the reaction proceeded smoothly to give various six-membered ring MBH adducts in good to excellent yield (up to 96% yield) within 3 hours. However, when catalytic system A was applied to **1a** for the construction of a five-membered ring system,

only a trace amount of **2a** was obtained (11% NMR yield, eq. 2). Thus, we were strongly motivated to explore the intramolecular MBH reaction for constructing a five-membered system, and eventually found an unexpected rearrangement reaction from *S*-aryl-(*E*)-6-oxohex-2-enethioate to afford densely functionalized fused bicyclic β -lactones in moderate yields. The reaction should proceed via an intramolecular nucleophile-catalyzed aldol-lactonization (NCAL) reaction.⁸ In this paper, we report the details of the development of a NCAL reaction with *S*-aryl-(*E*)-6-oxohex-2-enethioate by *N,N*-4-dimethylaminopyridine *N*-oxide (DMAPO).



catalyst system

(A) 5 mol% DMAP and 10 mol% 1,3-diphenyl-2-thiourea

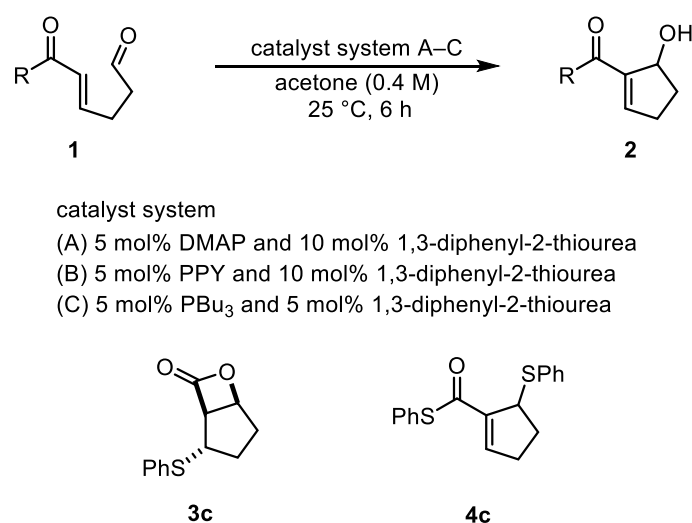
(B) 5 mol% PPY and 10 mol% 1,3-diphenyl-2-thiourea

(C) 5 mol% PBU₃ and 5 mol% 1,3-diphenyl-2-thiourea

We began by exploring an optimal substrate for an intramolecular MBH reaction for constructing a five-membered carbocycle (Table 1). For comparison to the previous results with **1a** (**2a** obtained in NMR yield of 11%, eq. 2), the reactions with selected substrates **1b–e** were carried out using catalyst system A–C in acetone (0.4 M) at 25 °C for 6 h (entries 1–4). Unfortunately, in most cases, the reaction did not proceed⁹ and recovery of the unreacted starting material was confirmed. However, the reaction of **1c** with catalyst system A or B delivered a trace amount of MBH adduct **2c** along with two other products (entries 1, 3, 4 vs 2). On the basis of a precise analysis of the byproducts using various spectroscopy modalities, these were identified as **3c** and **4c**, which were obtained in respective yields of 15% and 11% yield. Interestingly, **3c** has a fused β -lactone skeleton with three continuous stereogenic centers, and consisted of a single diastereomer. Presumably, it was directly derived from **1c** though an intramolecular nucleophile-catalyzed aldol-lactonization (NCAL) reaction. Generally, NCAL reactions and their enantioselective variants, which involve the *in-situ* generation of ketene through the activation of a carboxylic acid by Mukaiyama's reagent, are known to generate bicyclic β -lactone.⁸ Very recently, during the preparation of this manuscript, Birman also reported an enantioselective NCAL-type reaction with α,β -unsaturated thioesters catalyzed by chiral homobenzotetramisole (HBTM), followed by

decarboxylation for the synthesis of 2-substituted thiochromenes.¹⁰ As illustrated in entry 2 in Table 1, such a unique transformation from the simple starting material **1c** to construct a densely functionalized β -lactone **3c** is of great interest in synthetic organic chemistry. Thus, we sought to develop an efficient method for the synthesis of fused β -lactone through an intramolecular NCAL-type process using α,β -unsaturated thioesters.

Table 1. Seeking the optimal substrate for the intramolecular MBH reaction



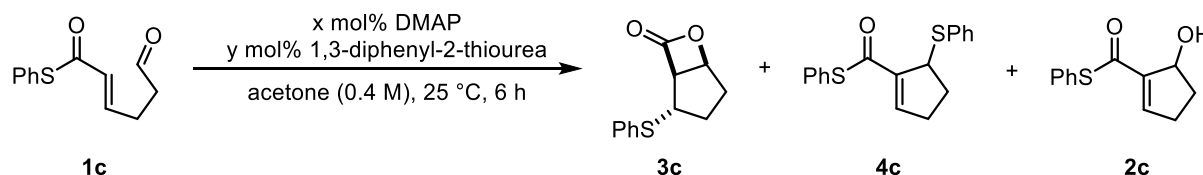
Entry	R	Substrate	Product	NMR yield of 2 (%) ^a		
				System A	System B	System C
1	OPh	1b	2b	N.D.	N.D.	N.D.
2	SPh	1c	2c	8	5	trace
3	OEt	1d	2d	N.D.	N.D.	N.D.
4	SEt	1e	2e	N.D.	N.D.	N.D.

^aYields were determined by ¹H NMR analysis using mesitylene as an internal standard.

To improve the yield of **3c**, we began by seeking the optimal catalyst loading (for both DMAP and thiourea) for an intramolecular NCAL reaction of **1c** as a model substrate in acetone (0.4 M) for 6 h (Table 2). As a result, in the absence of either DMAP or thiourea, the reactions did not afford any products compared to the combination of DMAP and thiourea (entries 2 and 3 vs 1). Although further increases in the amounts of both catalysts (50 mol% each) increased the yield of β -lactone (35% yield, entry 4), stoichiometric amounts of both catalysts were somewhat less efficient (28% yield, entry 5). In all

cases, none or only a trace amount of the MBH adduct **2c** was obtained, and we decided to use 50 mol% of both DMAP and thiourea as optimal catalyst loadings for further screening of the reaction conditions.

Table 2. Effects of catalyst loading of DMAP and thiourea in an intramolecular NCAL reaction of **1c**

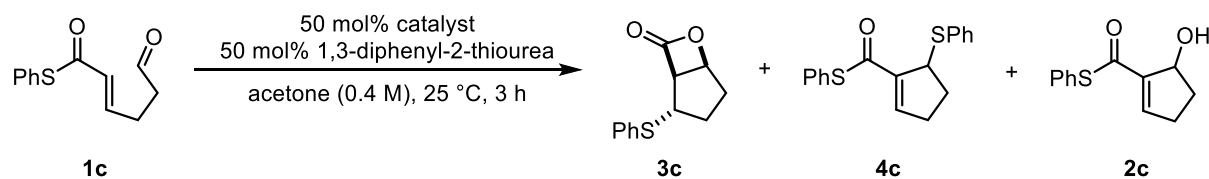


Entry	DMAP	Thiourea	NMR yield (%) ^a		
	x (mol%)	y (mol%)	3c	4c	2c
1 ^b	5	10	15	11	8
2	5	none	trace	trace	trace
3	none	10	N.D. ^c	N.D. ^c	N.D. ^c
4	50	50	35	trace	trace
5	100	100	28	trace	trace

^aYields were determined by ¹H NMR analysis using mesitylene as an internal standard.

^bSame data as in entry 2, Table 1. ^cNot detected.

Next, a series of nucleophilic catalysts, which are generally used in MBH-type reactions, in combination with 50 mol% of thiourea were tested in an intramolecular NCAL reaction of **1c** in acetone (0.4 M) for 3 h (Table 3). The use of 4-pyrrolidinopyridine (PPY),¹¹ which is a more nucleophilic catalyst than DMAP, gave **3c** in 16% yield (entry 2 vs entry 1). On the other hand, the use of 1,4-diazabicyclo[2.2.2]octane (DABCO), *N*-methylimidazole (NMI), triphenylphosphine, or tributylphosphine only afforded a mixture of β -lactone **3c** and the MBH adduct **2c** (entries 3–6). Finally, the use of 50 mol% of DMAPO¹² and 50 mol% of thiourea resulted in a significant increase in the yield of **3c** (53% yield, entry 7). Subsequently, we found that the co-catalyst (thiourea) was not necessary because 50 mol% of DMAPO, by itself, afforded **3c** in 55% yield (entry 8 vs 7). With the use of 10 mol% of DMAPO without thiourea, this reaction proceeded (30% yield of **3c**, entry 9), but it is not efficient enough regardless of the complete consumption of **1c**. Thus, the optimal catalyst and its loading amount in this reaction are currently thought to be DMAPO and 50 mol%.

Table 3. Effects of a nucleophilic catalyst in an intramolecular NCAL reaction of **1c**

Entry	Catalyst	NMR yield (%) ^a		
		3c	4c	2c
1	DMAP	23	3	trace
2	PPY	16	3	trace
3	DABCO	trace	trace	18
4	NMI	5	trace	4
5	PPh ₃	8	trace	3
6	PBu ₃	14	trace	N.D.
7	DMAPO	53	trace	trace
8 ^b	DMAPO	55	trace	trace
9 ^{b,c}	DMAPO	30	trace	trace

^aYields were determined by ¹H NMR analysis using mesitylene as an internal standard. ^bWithout thiourea. ^c10 mol% of DMAPO was used.

Our work to this point revealed that 50 mol% of DMAPO facilitated an intramolecular NCAL reaction of **1c**. Thus, we set out to explore the effectiveness of a series of *N*-oxides as a nucleophilic catalyst (Figure 1). The reaction promoted by 50 mol% of 4-pyrrolidinopyridine (PPYO) for 1.5 h was almost identical to that with DMAPO (51% NMR yield with PPYO vs 55% NMR yield with DMAPO), whereas other *N*-oxides resulted in no reaction or the formation of a complex mixture. Finally, we selected 50 mol% of DMAPO in acetone (0.4 M) at 25 °C as the optimal conditions.

A variety of substrates with different *S*-aryl units were subjected to an intramolecular NCAL reaction (Figure 2). The β-lactone **3c** with a phenyl group, which was derived from model substrate **1c**, was isolated in 49% yield. The reaction of an electron-deficient *S*-aryl unit (*p*-FC₆H₄S and *p*-BrC₆H₄S) **1f** and **1g** gave **3f** and **3g** in 31% and 48% yield, respectively, whereas that of an electron-enriched substrate (*p*-MeOC₆H₄S) proceeded slowly to afford **3h** in 34% yield (10 h). The nucleophilic substitution of the *p*-MeOC₆H₄S unit by DMAPO in the initial step of the NCAL process may be rather slow due to the leaving ability of thiolate. Furthermore, the reaction of **1i** with a sterically demanding *S*-aryl unit

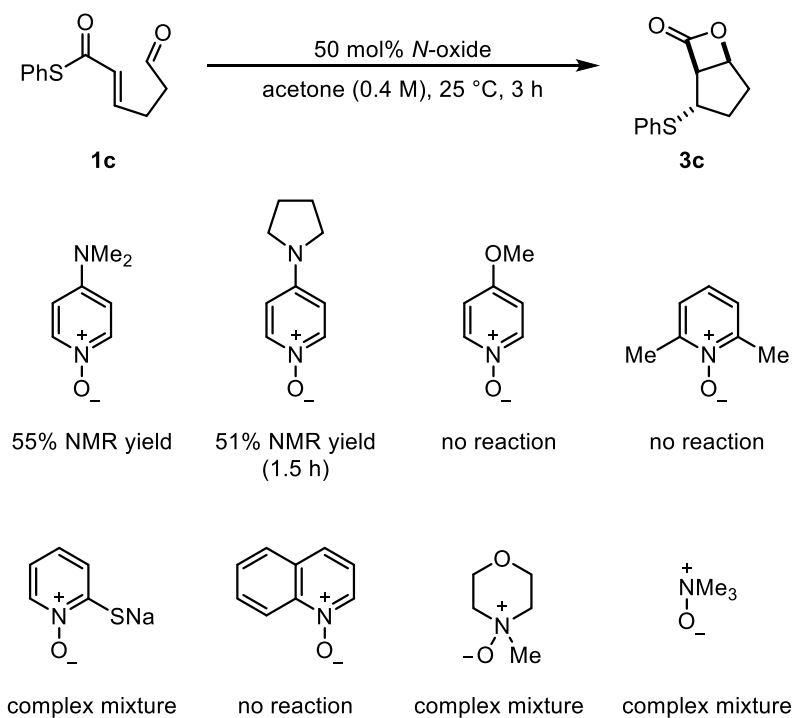


Figure 1. The intramolecular NCAL reactions of **1c** catalyzed by various *N*-oxides

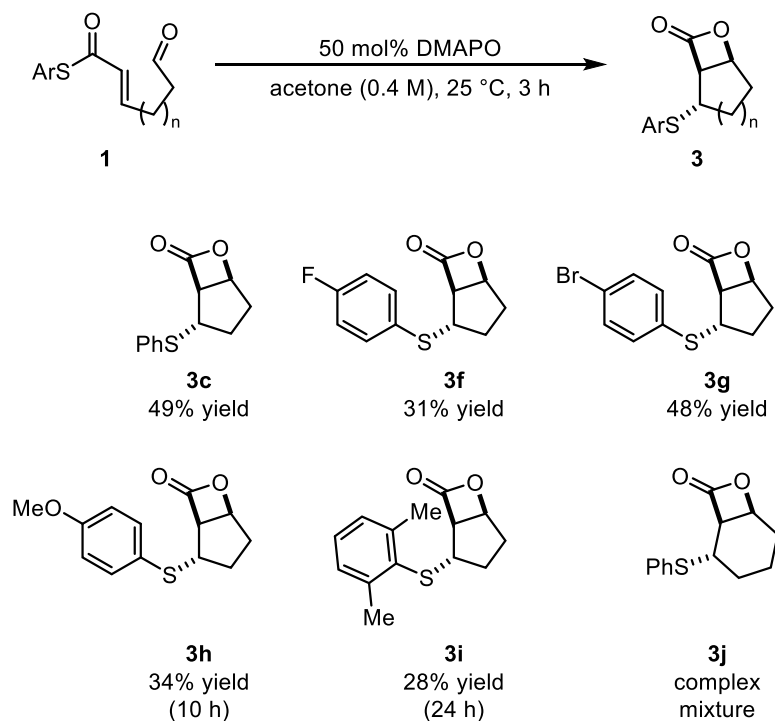


Figure 2. The intramolecular NCAL reactions of various *S*-Ar substrates

(2,6-di-MeC₆H₃S) was more sluggish and gave **3i** in 28% yield after 24 h. The reaction of substrate **1j** that affords six-membered ring **3j** somewhat resulted in complex mixture. Although the desired β -lactones **3c**, **3f–i** were obtained in low to moderate yields due to the formation of unidentified byproducts, to the best of our knowledge, this is the first example of a DMAPO-catalyzed C–C bond-forming reaction and the synthesis of highly functionalized bicyclic β -lactones from an easily accessible starting material such as **1**.

A proposed mechanism for the NCAL reaction of **1c**, inspired by Romo's studies,⁸ is as follows. First, nucleophilic displacement of the *S*-Aryl unit by DMAPO gives an activated ester **i**, which is followed by the 1,4-addition of thiolate (PhS⁻)¹³ to generate zwitterionic enolate **ii**. An intramolecular C–C bond-forming reaction (aldol-lactonization) then proceeds to give densely functionalized bicyclic β -lactone **3c**. This mechanism may be reasonable and consistent with the relative stereochemistry of the product.

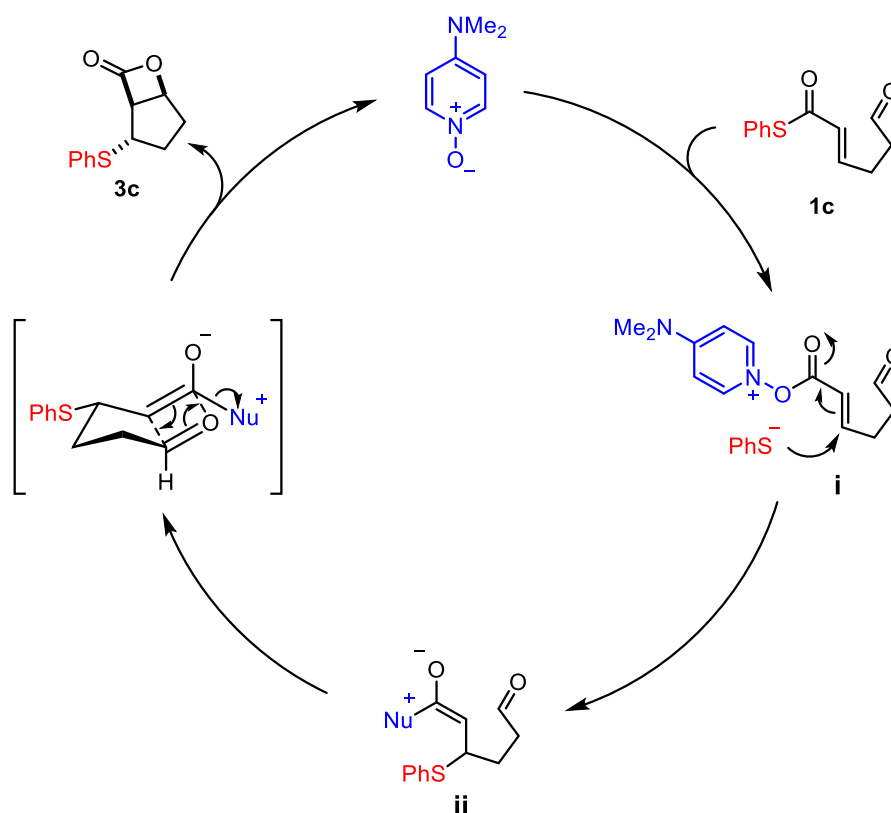


Figure 3. A plausible reaction mechanism of the NCAL reaction of **1c** with DMAPO

In summary, we have developed a simple protocol for the synthesis of densely functionalized bicyclic β -lactones in moderate yield via an NCAL reaction. This unique transformation can be performed with

easily accessible *S*-aryl-(*E*)-6-oxohex-2-enethiolate and commercially available DMAPO. It does not require stoichiometric amounts of a condensation agent (e.g., Mukaiyama's reagent) and base, which are typically required for the *in-situ* generation of a ketene in the NCAL reaction. The reaction presumably involves nucleophilic displacement of the *S*-aryl moiety by DMAPO, followed by the 1,4-addition of aryl thiolate to generate zwitterionic enolate and an intramolecular C–C bond-forming reaction (aldol-lactonization). Since the efficiency of the reaction was still moderate due to the formation of several unidentified byproducts, further tuning of the catalyst or reaction conditions to improve the reaction efficiency is now underway.

EXPERIMENTAL

All melting points were determined using a Yanaco MP-S3 micro melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. NMR spectra were recorded on a JEOL ECS-400 series, operating at 400 MHz for ¹H NMR and at 100 MHz for ¹³C NMR. Chemical shifts in CDCl₃ are reported on the δ scale relative to CHCl₃ (7.26 ppm) as an internal reference for ¹H-NMR. For ¹³C NMR, chemical shifts are reported on the δ scale relative to CHCl₃ (77.16 ppm) as an internal reference. Column chromatography was performed with silica gel 60N (spherical, neutral, 40–50 μm) purchased from KANTO CHEMICAL. Optical rotations were measured on a HORIBA Model SEPA-300 High-sensitive polarimeter. High-resolution FAB mass spectra (HRMS) were measured on a JEOL JMS-700 MStation or Agilent 6520 Accurate Mass Q-TOF LC/MS (ESI-MS) at the Mass Spectrometry Facility (Okayama University). 4-(Dimethylamino)pyridine *N*-oxide (DMAPO), and 1,3-diphenyl-2-thiourea were purchased from Tokyo Chemical Industry Co., Ltd. 4-(Dimethylamino)pyridine (DMAP) and 4-pyrrolidinopyridine (PPY) were purchased from Wako Pure Chemical Industries, Ltd. Unless otherwise noted, all materials were purchased from commercial suppliers and used without further purification.

General procedure for nucleophilic-catalyzed aldol lactonization (NCAL)

To a solution of *S*-aryl-(*E*)-6-oxohex-2-enethiolate (0.20 mmol) in acetone (0.5 mL) was added DMAPO (50 mol%) at 25 °C. After being stirred for 3 h, the reaction mixture was quenched with saturated aqueous NH₄Cl (1 mL) and diluted with EtOAc (7 mL). The organic layer was separated, dried over MgSO₄, and concentrated *in vacuo*. Purification of the crude product by flash column chromatography on silica gel using toluene as an eluent gave the desired product.

6-Oxa-2-(phenylthio)-bicyclo[3.2.0]heptan-7-one (3c).

According to the general procedure, product **3c** was obtained (21.1 mg, 95.8 μmol , 49% yield) as a pale yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41–7.26 (m, 5H), 5.09 (t, $J = 3.6$ Hz, 1H), 4.04 (d, $J = 4.8$ Hz, 1H), 3.89 (d, $J = 3.6$ Hz, 1H), 2.32–2.19 (m, 2H), 2.17–2.09 (m, 1H), 2.08–1.99 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.1, 133.6, 131.9, 129.5, 127.9, 77.9, 61.3, 46.5, 28.8, 28.7; **IR** (neat) 3057, 2868, 1967, 1481, 1248, 1115, 741 cm^{-1} ; **TLC** R_f 0.65 (toluene/EtOAc = 10/1), 0.35 (toluene); **HRMS** (FAB) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{13}\text{O}_2\text{S}$: 221.0630, found: 221.0656.

6-Oxa-2-(4-fluorophenylthio)-bicyclo[3.2.0]heptan-7-one (3f).

According to the general procedure, product **3f** was obtained (14.6 mg, 61.3 μmol , 31% yield) as a pale yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.46 (ddt, $J = 8.4, 5.0, 2.5$ Hz, 2H), 7.05 (tt, $J = 8.4, 2.5$ Hz, 2H), 5.09 (t, $J = 4.0$ Hz, 1H), 3.94 (d, $J = 5.6$ Hz, 1H), 3.85 (d, $J = 4.0$ Hz, 1H), 2.29–2.19 (m, 2H), 2.16–1.96 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.0, 162.9 (d, $J = 248.2$ Hz), 135.0 (d, $J = 8.6$ Hz), 128.6 (d, $J = 3.8$ Hz), 116.7 (d, $J = 22.0$ Hz), 77.8, 61.2, 47.5, 28.8, 28.6; **IR** (neat) 3071, 2868, 1965, 1489, 1223, 1123, 746 cm^{-1} ; **TLC** R_f 0.35 (toluene); **HRMS** (FAB) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{12}\text{FO}_2\text{S}$: 239.0536, found: 239.0539.

6-Oxa-2-(4-bromophenylthio)-bicyclo[3.2.0]heptan-7-one (3g).

According to the general procedure, product **3g** was obtained (18.4 mg, 61.5 μmol , 48% yield) as a brown oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.46 (dt, $J = 8.9, 2.2$ Hz, 2H), 7.23 (dt, $J = 8.9, 2.2$ Hz, 2H), 5.09 (t, $J = 4.0$ Hz, 1H), 4.01 (d, $J = 5.6$ Hz, 1H), 3.86 (d, $J = 4.0$ Hz, 1H), 2.32–2.20 (m, 2H), 2.16–1.97 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.8, 133.2, 132.9, 132.6, 122.0, 77.8, 61.2, 46.5, 28.8, 28.6; **IR** (neat) 2934, 2382, 1823, 1248, 1009, 804 cm^{-1} ; **TLC** R_f 0.37 (toluene); **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{12}\text{BrO}_2\text{S}$: 298.9736, found: 298.9746.

6-Oxa-2-(4-methoxyphenylthio)-bicyclo[3.2.0]heptan-7-one (3h).

According to the general procedure, product **3h** was obtained (17.3 mg, 69.1 μmol , 34% yield) as a pale yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 (dt, $J = 9.0, 2.6$ Hz, 2H), 6.88 (dt, $J = 9.0, 2.6$ Hz, 2H), 5.08 (t, $J = 3.3$ Hz, 1H), 3.88–3.86 (m, 1H), 3.85 (d, $J = 3.3$ Hz, 1H), 3.82 (s, 3H), 2.24–1.97 (m, 4H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.4, 160.2, 135.6, 123.7, 115.1, 77.9, 61.2, 55.5, 48.0, 28.8, 28.5; **IR** (neat) 3065, 2916, 2847, 1967, 1115, 745 cm^{-1} ; **TLC** R_f 0.35 (toluene); **HRMS** (FAB) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3\text{SNa}$: 273.0555, found: 273.0556.

6-Oxa-2-(2,6-dimethylphenylthio)-bicyclo[3.2.0]heptan-7-one (3i).

According to the general procedure, product **3i** was obtained (17.0 mg, 68.4 μmol , 28% yield) as a brown solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.20–7.09 (m, 3H), 5.11–5.08 (m, 1H), 3.84 (d, $J = 5.5$ Hz, 1H), 3.64 (dd, $J = 3.8, 0.8$ Hz, 1H), 2.50 (s, 6H), 2.29–2.21 (m, 2H), 2.21–2.10 (m, 1H), 1.95–1.86 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.5, 143.6, 131.0, 129.3, 128.7, 78.1, 61.2, 45.7, 29.1, 28.9, 22.2; **IR** (KBr) 2963, 2938, 1813, 1460, 1292, 878 cm^{-1} ; **TLC** R_f 0.50 (toluene/EtOAc = 15/1); **HRMS** (FAB) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{17}\text{O}_2\text{S}$: 249.0944, found: 249.0952; mp 70.9–72.0 $^\circ\text{C}$.

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REFERENCES AND NOTES

1. S. K. Armstrong, *J. Chem. Soc., Perkin Trans. 1*, 1998, 371; L. Yet, *Chem. Rev.*, 2000, **100**, 2963; R. H. Grubbs, *Tetrahedron*, 2004, **60**, 7117; S. P. Nolan and H. Clavier, *Chem. Soc. Rev.*, 2010, **39**, 3305; C. A. Leverett, V. C. Purohit, and D. Romo, *Angew. Chem. Int. Ed.*, 2010, **49**, 9479.
2. V. Singh and S. Batra, *Tetrahedron*, 2008, **64**, 4511.
3. P. Xie and Y. Huang, *Org. Biomol. Chem.*, 2015, **13**, 8578.
4. F. Roth, P. Gyax, and G. Frater, *Tetrahedron Lett.*, 1992, **33**, 1045.
5. W. D. Teng, R. Huang, C. K. W. Kwong, M. Shi, and P. H. Toy, *J. Org. Chem.*, 2006, **71**, 368.
6. Y. Wei and M. Shi, *Chem. Rev.*, 2013, **113**, 6659; D. Basavaiah, K. V. Rao, and R. J. Reddy, *Chem. Soc. Rev.*, 2007, **36**, 1581; D. Basavaiah, B. S. Reddy, and S. S. Badsara, *Chem. Rev.*, 2010, **110**, 5447.
7. H. Mandai, K. Shimowaki, K. Mitsudo, and S. Suga, *Asian J. Org. Chem.*, 2014, **3**, 437.
8. G. S. Cortez, R. L. Tennyson, and D. Romo, *J. Am. Chem. Soc.*, 2001, **123**, 7945; G. S. Cortez, S. H. Oh, and D. Romo, *Synthesis*, 2001, 1731; S. H. Oh, G. S. Cortez, and D. Romo, *J. Org. Chem.*, 2005, **70**, 2835; K. A. Morris, K. M. Arendt, S. H. Oh, and D. Romo, *Org. Lett.*, 2010, **12**, 3764.
9. There are previous examples of the MBH reaction of **1d** and **1e** using a DMAP/DMAP•HCl or PMe_3 system to afford MBH adducts in good yield. See: G. E. Keck and D. S. Welch, *Org. Lett.*, 2002, **4**,

[3687](#).

10. N. A. Ahlemeyer and V. B. Birman, [Org. Lett., 2016, 18, 3454](#).
11. W. Steglich and G. Höfle, [Tetrahedron Lett., 1970, 11, 4727](#).
12. For recent selected examples of DMAPO-catalyzed transformations, see: K. Ishihara and Y. Lu, [Chem. Sci., 2016, 7, 1276](#); K. Yoshida, H. Suzuki, H. Inoue, K. Matsui, Y. Fujino, Y. Kanoko, Y. Itatsu, and K.-i. Takao, [Adv. Synth. Catal., 2016, 358, 1886](#); K. Yoshida, Y. Fujino, Y. Itatsu, H. Inoue, Y. Kanoko, and K.-i. Takao, [Tetrahedron Lett., 2016, 57, 627](#); I. Shiina, H. Ushiyama, Y. Yamada, Y. Kawakita, and K. Nakata, [Chem. Asian J., 2008, 3, 454](#); I. Shiina, A. Sasaki, T. Kikuchi, and H. Fukui, [Chem. Asian J., 2008, 3, 462](#).
13. Y. Fukata, T. Okamura, K. Asano, and S. Matsubara, [Org. Lett., 2014, 16, 2184](#).