Note

An Efficient Method for the Synthesis of 2′,3′-Nonsubstituted Cycloalkane-1,3-dione-2-spirocyclopropanes Using (2-Bromoethyl)-diphenylsulfonium Trifluoromethanesulfonate

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An efficient and practical synthesis of 2′,3′-nonsubstituted cyclohexane-1,3-dione-2-spirocyclopropanes using a sulfonium salt was achieved. The reaction of 1,3-cyclohexanediones and (2-bromoethyl)diphenylsulfonium trifluoromethanesulfonate with powdered K_2CO_3 in EtOAc at room temperature (r.t.) provided the corresponding spirocyclopropanes in high yields. The synthetic method was also applied to 1,3-cyclopentanedione, 1,3-cycloheptanedione, 1,3-indanedione, acyclic 1,3-diones, ethyl acetoacetate, and Meldrum's acid.

Key words cyclopropane; sulfonium salt; spiro compound; 1,3-cyclohexanedione; double alkylation

Cyclopropanes are extremely versatile building blocks in organic synthesis because of the high reactivity arising from their strong ring strain.[1,2] Ring-opening cyclization of doubly activated cyclopropanes has emerged as a powerful method for the synthesis of a variety of carbo- and heterocyclic compounds.[3–6] Recently, we demonstrated the formation of indole skeletons by employing the ring-opening cyclization of the doubly activated spirocyclopropanes, 2′-arylcyclohexane-1,3-dione-2-spirocyclopropanes **1**, with primary amines[7] (Chart 1). The reaction proceeded regioselectively at room temperature (r.t.) to give 2-aryltetrahydroindol-4-ones **2**, one of which was easily converted to the 4-hydroxyindole derivative **3**. We also reported acid-catalyzed ring-opening cyclization of spirocyclopropanes **1** to 2-aryltetrahydro-1-benzofuran-4-ones **4** and its application to the synthesis of 4-hydroxybenzofuran **5**.[8] In order to achieve syntheses of indole and benzofuran natural products and also to further our understanding of the reaction mechanisms, we need to investigate the ring-opening cyclization of 2′,3′-nonsubstituted cyclohexane-1,3-dione-2-spirocyclopropanes. However, very few methods for their synthesis have been reported.[9,10] These circumstances have led us to develop a novel, efficient, and practical method for preparing 2′,3′-nonsubstituted spirocyclopropanes. Herein, we report the synthetic method for 2′,3′-nonsubstituted cyclohexane-1,3-dione-2-spirocyclopropanes using 2-bromoethylsulfonium salt.

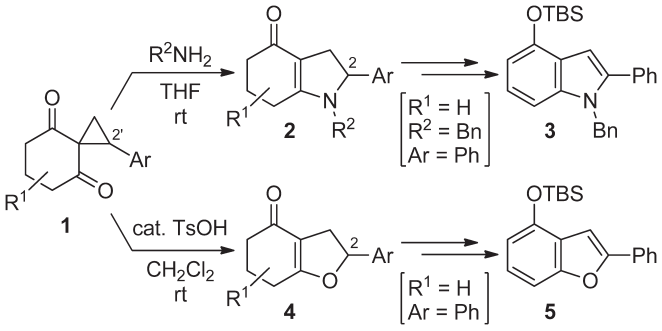

Chart 1. Synthesis of Indole **3** and Benzofuran **5** from Spirocyclopropanes **1**

Results and Discussion

Rh(II)-catalyzed cyclopropanation of alkenes with diazo compounds is widely employed for the synthesis of a variety of doubly activated cyclopropanes, but it is not suitable for application to spiro systems.[11] Furthermore, it requires an unpractical ethene gas.[12]

2,3-Nonsubstituted 1,1-diacylcyclopropanes can be prepared from 1,3-dicarbonyl compounds by double alkylation using 1,2-dibromoethane. For example, the reaction of acetylacetone (**6a**) and 1,2-dibromoethane with potassium carbonate in dimethyl sulfoxide (DMSO) afforded the corresponding cyclopropane **7a** in 61% yield[13] (Chart 2). The conversion of 1-phenyl-1,3-butanedione (**6b**) into cyclopropane **7b** was also conducted in the same manner.[14] Therefore, we initially examined the reaction of 1,3-cyclohexanedione (**8a**) and 1,2-dibromoethane under the same reaction conditions (Chart 3). However, 2′,3′-nonsubstituted spirocyclopropane **1a** was not detected; instead, *O*-alkylation product **9**[15] was obtained in 36% yield.

As an alternative double alkylation approach, the synthetic method using a sulfonium salt in place of 1,2-dibromoethane has been developed. In 2012, Lin and colleagues reported a

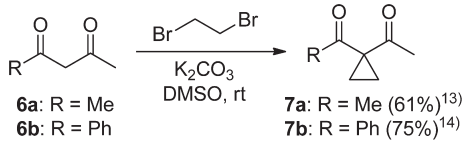

Chart 2. Synthesis of Cyclopropanes **7a** and **b** with 1,2-Dibromoethane

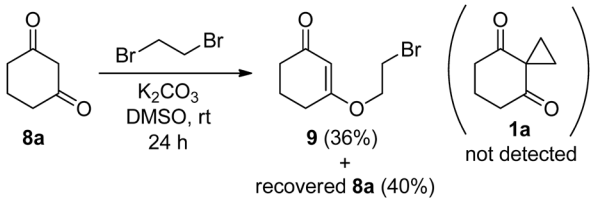

Chart 3. Reaction of 1,3-Cyclohexanedione (**8a**) and 1,2-Dibromoethane

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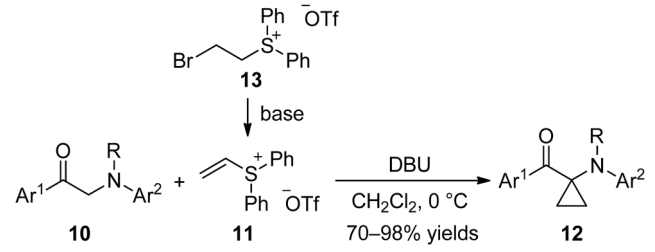


Chart 4. Synthesis of 1,1-Cyclopropane Aminoketones **12** with Vinyl Sulfonium Salt **11** Derived from **13**

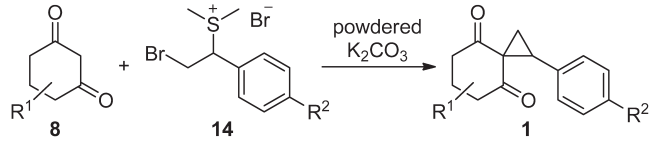


Chart 5. Reaction of 1,3-Cyclohexanediones **8** and Sulfonium Salts **14** with Powdered K_2CO_3 in EtOAc at Room Temperature

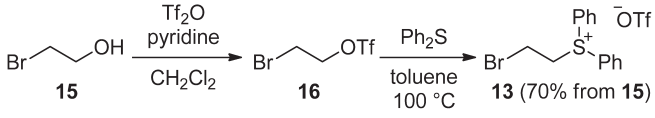
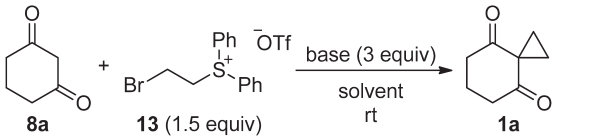


Chart 6. Preparation of Sulfonium Salt **13** from 2-Bromoethanol (**15**)

simple and efficient access to 1,1-cyclopropane aminoketones **12** *via* the reaction of *α*-aminoacetophenones **10** and vinylsulfonium salt **11** in the presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU)[16] (Chart 4). The vinylsulfonium salt **11** was prepared from (2-bromoethyl)diphenylsulfonium trifluoromethanesulfonate (**13**)[17–21] by eliminating the hydrogen bromide with a base such as silver(I) oxide,[17,18] potassium bicarbonate,[19,22] or sodium hydride (NaH).[20] Recently, we developed a simple preparation of 2′-arylcyclohexane-1,3-dione-2-spirocyclopropanes **1** from 1,3-cyclohexanediones **8** directly using (1-aryl-2-bromoethyl)dimethylsulfonium bromides **14**, which were converted into the corresponding vinylsulfonium salt *in situ*[23] (Chart 5). Therefore, we envisioned that the reaction of 1,3-cyclohexanediones **8** using **13** with an appropriate base would provide 2′,3′-nonsubstituted spirocyclopropanes.

The sulfonium salt **13** was prepared using a slightly modified procedure, originally reported by Aggarwal and colleagues[22] (Chart 6). The conversion of 2-bromoethanol (**15**) into triflate **16** with trifluoromethanesulfonic anhydride and pyridine in CH_2Cl_2 followed by treatment with diphenyl sulfide in toluene at reflux afforded the sulfonium salt **13** in 70% overall yield. First, we investigated the reaction of **8a** with 1.5 eq of **13** using 3 eq of DBU in CH_2Cl_2 at r.t. The reaction did not complete even after 24 h, and gave the corresponding spirocyclopropane **1a** in only 19% yield (Table 1, entry 1). When NaH was used in CH_2Cl_2, the reaction for 15 h afforded **1a** in 72% yield (entry 2). Changing the base to $KHCO_3$ resulted in a similar reaction rate (17 h) and increased the product yield to 84% (entry 3). Next, we investigated powdered potassium carbonate as a base[23] (Chart 5). Remarkably, the use of powdered K_2CO_3 enhanced the reaction rate (1.5 h) and afforded **1a** in 84% yield (entry 4). Switching the solvent from CH_2Cl_2 to *N*,*N*-dimethylformamide (DMF) improved the reaction rate (1 h), although a considerable decrease in the product yield was observed (72% yield, entry 5). Delightfully, the reaction in EtOAc for 1.5 h gave **1a** in 87% yield (entry 6). The use of granular K_2CO_3 slightly decreased the product yield (83% yield) and gave irreproducible conversion (entry 7). We next optimized the amount of sulfonium salt **13**. Using 1.2 eq of **13** led to a slight drop in the product yield (84% yield, entry 8), and the use of 2.0 eq of **13** appreciably diminished the product yield (81% yield, entry 9). Thus, we achieved the direct synthesis of spirocyclopropane **1a** from **8a** using 1.5 eq of sulfonium salt **13** and 3 eq of powdered K_2CO_3 in EtOAc.

Table 1. Reaction of 1,3-Cyclohexanedione (**8a**) with Sulfonium Salt **13**[a]



Entry	Base	Solvent	Time (h)	Yield (%)
1	DBU	CH_2Cl_2	24	19[b]
2	NaH	CH_2Cl_2	15	72
3	Powdered $KHCO_3$	CH_2Cl_2	17	84
4	Powdered K_2CO_3	CH_2Cl_2	1.5	84
5	Powdered K_2CO_3	DMF	1	72
6	Powdered K_2CO_3	EtOAc	1.5	87
7	Granular K_2CO_3	EtOAc	1.5	83[c]
8[d]	Powdered K_2CO_3	EtOAc	1.5	84
9[e]	Powdered K_2CO_3	EtOAc	1.5	81

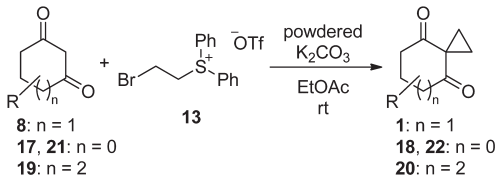
a) All reactions were performed on a 0.5 mmol scale with 1.5 eq of sulfonium salt **13** and 3 eq of base. *b*) The starting material **8a** was recovered in 30% yield. *c*) Irreproducible yield. *d*) 1.2 eq of sulfonium salt **13** and 2.4 eq of powdered K_2CO_3 were used. *e*) 2.0 eq of sulfonium salt **13** and 4.0 eq of powdered K_2CO_3 were used.

With the optimal conditions in hand, we investigated the reaction with a variety of 1,3-cyclohexanediones **8b**–**h** with 1.5 eq of sulfonium salt **13** (Table 2). High yields of spirocyclopropanes **1b**–**h** (80–88% yields) were consistently obtained in the reactions of dimedone (**8b**), 5-methyl-, 5-isopropyl- and 5-phenylcyclohexane-1,3-diones (**8c**–**e**), spiro[2.5]octane-5,7-dione (**8f**), and 4,4-dimethyl- and 4-methylcyclohexane-1,3-dione (**8g**, **h**) (entries 1–7). We next turned our attention to the reaction of 5- and 7-membered carbocycles with **13**. The reaction of 1,3-cyclopentanedione (**17**) and 1,3-cycloheptanedione (**19**) afforded the corresponding spirocyclopropanes **18** and **20** in 77 and 71% yields, respectively (entries 8, 9). The present protocol was found to be applicable to 1,3-indanedione (**21**), affording the corresponding spirocyclopropane **22**[24] in 86% yield (entry 10).

In addition, the synthesis of acyclic 1,3-dione-derived cyclopropanes using the present protocol was examined (Chart 7). The reaction of acetylacetone (**6a**) with 1.5 equiv of sulfonium salt **13** using powdered K_2CO_3 in EtOAc provided the corresponding cyclopropane **7a** in 79% yield. The use of 1-phenyl-1,3-butanedione (**6b**) afforded cyclopropane **7b** in 83% yield. Since the yields of **7a**, **b** were higher than those in Chart 2,[13,14] these results clearly demonstrate that the present synthetic method using the sulfonium salt **13** is also effective for the synthesis of acyclic 1,3-dione-derived cyclopropanes.

Finally, we investigated the synthesis of cyclopropanecarboxylates (Chart 8). The reaction of ethyl acetoacetate (**23**) with sulfonium salt **13** and powdered K_2CO_3 in EtOAc for 1.5 h gave ethyl 1-acetylcyclopropanecarboxylate (**24**) in only 71% yield. On the other hand, the reaction of dimethyl malo-

Table 2. Synthesis of Spirocyclopropanes **1**[a)]



Entry	Substrate	Product	Time (h)	Yield (%)
1	**8b**	**1b**	1.5	88
2	**8c**	**1c**	1.5	84
3	**8d**	**1d**	1.5	87
4	**8e**	**1e**	1.5	85
5	**8f**	**1f**	1.5	88
6	**8g**	**1g**	1.5	81
7	**8h**	**1h**	1.5	80
8	**17**	**18**	1.5	77
9	**19**	**20**	2	71
10	**21**	**22**	1.5	86

a) All reactions were performed on a 0.5 mmol scale with 1.5 eq of sulfonium salt **13** and 3 eq of powdered K_2CO_3 in EtOAc.

nate (**25**) with **13** for 4 h gave dimethyl 1,1-cyclopropanedicarboxylate (**26**) in only 49% yield, and some decomposition products.[25)] Interestingly, the use of Meldrum's acid (**27**) afforded the corresponding spirocyclopropane **28** in 80% yield. We speculate that the higher acidity of Meldrum's acid (**27**: pK_a 7.3, in DMSO at 25°C)[26)] than that of dimethyl malonate (**25**: pK_a 15.9, in DMSO at 25°C) is the reason for the success of the reaction.

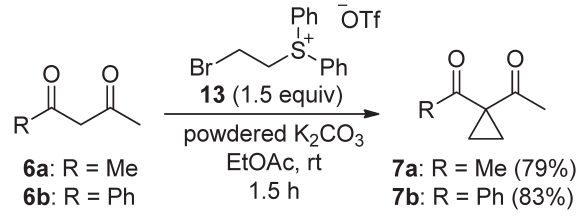


Chart 7. Synthesis of Cyclopropanes **7a** and **b** with Sulfonium Salt **13**

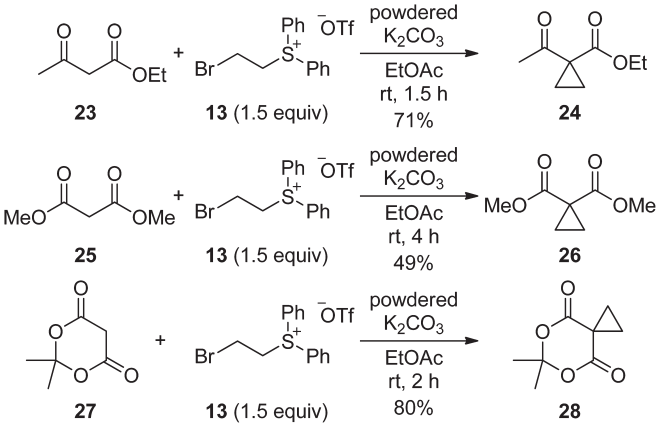


Chart 8. Reaction of Ethyl Acetoacetate (**23**), Dimethyl Malonate (**25**), and Meldrum's Acid (**27**) with Sulfonium Salt **13**

In summary, we have developed an efficient procedure for the synthesis of 2′,3′-nonsubstituted cyclohexane-1,3-dione-2-spirocyclopropanes. The reaction of 1,3-cyclohexanediones and (2-bromoethyl)diphenylsulfonium trifluoromethanesulfonate with powdered K_2CO_3 in EtOAc at r.t. provided the corresponding spirocyclopropanes in high yields. The present protocol was also found to be applicable to 1,3-cyclopentanedione, 1,3-cycloheptanedione, 1,3-indanedione, acyclic 1,3-diones, ethyl acetoacetate, and Meldrum's acid.

Experimental

General Melting points are uncorrected. IR spectra were recorded on a JASCO FT/IR-460 Plus spectrophotometer and absorbance bands are reported in wavenumber (cm^{-1}). All NMR spectra were recorded using a JEOL JNM-ECX400P spectrometer. ^{1}H-NMR spectra were recorded at 400 MHz. Chemical shifts are reported relative to internal standard (tetramethylsilane at δ_H 0.00 or $CDCl_3$ at δ_H 7.26). Data are presented as follows: chemical shift (δ, ppm), multiplicity (s=singlet, d=doublet, t=triplet, quint=quintet, m=multiplet), coupling constant and integration. ^{13}C-NMR spectra were recorded at 100 MHz. The following internal reference was used ($CDCl_3$ at δ_C 77.0). All ^{13}C-NMR spectra were determined with complete proton decoupling. High-resolution (HR) mass spectra were determined with JEOL JMS-GCmate II instrument. Column chromatography was performed on Silica Gel 60 PF_{254} (Nacalai Tesque, Inc., Kyoto, Japan) and Kanto silica gel 60 N (63–210 mesh) under pressure. Analytical TLC was carried out on Merck Kieselgel 60 F_{254} plates. Visualization was accomplished with UV light and phosphomolybdic acid stain solution followed by heating.

All reagents such as 1,3-cyclohexanedione (**8a**) and its derivatives **8b**, **c**, **e**, and **g**, 1,3-cyclopentanedione (**17**), 1,3-cy-

cloheptanedione (**19**), 1,3-indanedione (**21**), acetylacetone (**6a**), 1-phenyl-1,3-dutanedione (**6b**), ethyl acetoacetate (**23**), dimethyl malonate (**25**), Meldrum's acid (**27**), and powdered K_2CO_3 are commercially available and were purchased from suppliers such as Sigma-Aldrich Co., U.S.A., Tokyo Chemical Industry Co., Ltd., Tokyo, Japan, Wako Pure Chemical Industries, Ltd., Osaka, Japan and Nacalai Tesque, Inc. Dehydrated DMSO CH_2Cl_2, toluene, DMF, and EtOAc were purchased from Wako Pure Chemical Industries, Ltd. 5-Isopropylcyclohexane-1,3-dione (**8d**),[27] spiro[2.5]octane-5,7-dione (**8f**),[28] and 4-methylcyclohexane-1,3-dione (**8h**)[29] were prepared according to literature procedures.

Preparation of (2-Bromoethyl)diphenylsulfonium Trifluoromethanesulfonate (13) from 2-Bromoethanol (15) (Chart 6) A solution of triflic anhydride (1.81 mL, 11 mmol) in CH_2Cl_2 (5 mL) was added to a solution of pyridine (0.88 mL, 11 mmol) in CH_2Cl_2 (5 mL) at −20°C. After stirring for 10 min, 2-bromoethanol (**15**) (0.71 mL, 10 mmol) was added to the mixture and the reaction mixture was stirred at −20°C for 15 min. The precipitate was removed by filtration and washed with Et_2O (10 mL). The combined filtrates were concentrated *in vacuo*, and the residue was diluted with hexane (30 mL). The precipitate was removed by filtration and washed with Et_2O (5 mL). The combined filtrates were concentrated *in vacuo* to provide crude product **16** (2.38 g), which was used in the next step without further purification.

Diphenyl sulfide (6.90 g, 18.5 mmol) was added to a solution of crude product **16** in toluene (9 mL) at r.t. The reaction mixture was then heated at 100°C and stirred for 7 h. The solution was allowed to cool to r.t. and Et_2O (20 mL) was added, resulting in the formation of a white precipitate. The mixture was stirred at r.t. overnight and the precipitate was collected by suction, washed with Et_2O (3 mL) and dried *in vacuo* to provide **13** (3.10 g, 70%) as a white solid: mp 85.0–86.0°C (lit.,[17] mp 86.5–88.0°C); IR (KBr, cm^{-1}) ν 3065, 2986, 1448, 1274, 1149, 1032, 755, 638; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.13–8.09 (m, 4H), 7.81–7.70 (m, 6H), 4.93–4.87 (m, 2H), 3.71–3.67 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 135.3, 131.9, 131.1, 122.7, 48.5, 24.0.

Typical Procedure for the Synthesis of Spirocyclopropanes 1: Spiro[2.5]octane-4,8-dione (1a) (Table 1, Entry 6) Powdered K_2CO_3 (207 mg, 1.5 mmol) and 1,3-cyclohexanedione (**8a**) (56 mg, 0.50 mmol) were added to a suspension of sulfonium salt **13** (332 mg, 0.75 mmol) in EtOAc (5 mL). After stirring at r.t. for 1.5 h, the reaction was quenched with water (10 mL) and the whole mixture was extracted with EtOAc (2×10 mL). The combined organic layer was washed with brine (10 mL) and dried over anhydrous $MgSO_4$. The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography (silica gel, 30% EtOAc in hexane) to provide **1a** (60 mg, 87%) as a colorless oil; IR (film, cm^{-1}) ν 2956, 1682, 1330, 1162, 1026, 956; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.67 (t, J=6.4 Hz, 4H), 2.14 (quint, J=6.4 Hz, 2H), 1.77 (s, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 206.9, 40.8, 39.5, 27.6, 18.0; HR-MS electron ionization (EI) *m/z* Calcd for $C_8H_{10}O_2$ (M^+) 138.0681. Found 138.0668.

6,6-Dimethylspiro[2.5]octane-4,8-dione (1b)[9] (Table 2, Entry 1) According to the typical procedure for the synthesis of **1a**, **1b** was prepared from dimedone (**8b**) (70 mg, 0.50 mmol) for 1.5 h. The crude product was purified by column chromatography (silica gel, 30% EtOAc in hexane) to provide **1b** (73 mg, 88%) as a colorless oil: IR (film, cm^{-1}) ν 2957, 2871, 1710, 1683, 1469, 1404, 1371, 1335, 1320, 1291, 1181, 1145, 1123, 1082, 987, 918; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.56 (s, 4H), 1.76 (s, 4H), 1.13 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 206.8, 53.2, 39.6, 30.3, 28.5, 27.3.

6-Methylspiro[2.5]octane-4,8-dione (1c) (Table 2, Entry 2) According to the typical procedure for the synthesis of **1a**, **1c** was prepared from 5-methylcyclohexane-1,3-dione (**8c**) (63 mg, 0.50 mmol) for 1.5 h. The crude product was purified by column chromatography (silica gel, 40% EtOAc in hexane) to provide **1c** (64 mg, 84%) as a colorless oil: IR (film, cm^{-1}) ν 2958, 1683, 1321, 1165, 950; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.80–2.71 (m, 2H), 2.44–2.34 (m, 3H), 1.76 (s, 4H), 1.15 (d, J=6.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 206.7, 47.5, 40.1, 27.7, 27.4, 25.4, 21.0; HR-MS (EI) *m/z* Calcd for $C_9H_{12}O_2$ (M^+) 152.0837. Found 152.0835.

6-Isopropylspiro[2.5]octane-4,8-dione (1d) (Table 2, Entry 3) According to the typical procedure for the synthesis of **1a**, **1d** was prepared from 5-isopropylcyclohexane-1,3-dione (**8d**)[27] (77 mg, 0.50 mmol) for 1.5 h. The crude product was purified by column chromatography (silica gel, 20% EtOAc in hexane) to provide **1d** (78 mg, 87%) as a colorless oil; IR (film, cm^{-1}) ν 2962, 2879, 1683, 1332, 1160, 1082; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.75 (dd, J=16.5, 3.2 Hz, 2H), 2.43 (dd, J=16.5, 11.9 Hz, 2H), 2.05 (m, 1H), 1.75 (s, 4H), 1.68 (m, 1H), 0.97 (d, J=6.4 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 207.1, 43.5, 40.1, 36.2, 31.5, 27.7, 27.4, 19.2; HR-MS (EI) *m/z* Calcd for $C_{11}H_{16}O_2$ (M^+) 180.1150. Found 180.1154.

6-Phenylspiro[2.5]octane-4,8-dione (1e) (Table 2, Entry 4) According to the typical procedure for the synthesis of **1a**, **1e** was prepared from 5-phenylcyclohexane-1,3-dione (**8e**) (94 mg, 0.50 mmol) for 1.5 h. The crude product was purified by column chromatography (silica gel, 30% EtOAc in hexane) to provide **1e** (91 mg, 85%) as a white solid: mp 117.0–118.0°C; IR (KBr, cm^{-1}) ν 1675, 1333, 1163, 768, 703; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.37 (t, J=7.3 Hz, 2H), 7.29 (d, J=7.3 Hz, 1H), 7.24 (d, J=7.3 Hz, 2H), 3.54 (tt, J=11.4, 4.1 Hz, 1H), 2.99 (dd, J=16.9, 4.1 Hz, 2H), 2.87 (dd, J=16.9, 11.4 Hz, 2H), 1.89–1.77 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 206.0, 141.8, 129.0, 127.3, 126.5, 46.9, 40.4, 35.7, 28.1; HR-MS (EI) *m/z* Calcd for $C_{14}H_{14}O_2$ (M^+) 214.0994. Found 214.0967.

Dispiro[2.2.2.2]decane-4,10-dione (1f) (Table 2, Entry 5) According to the typical procedure for the synthesis of **1a**, **1f** was prepared from spiro[2.5]octane-5,7-dione (**8f**)[28] (69 mg, 0.50 mmol) for 1.5 h. The crude product was purified by column chromatography (silica gel, 30% EtOAc in hexane) to provide **1f** (72 mg, 88%) as a white solid: mp 30.5–32.0°C; IR (KBr, cm^{-1}) ν 2362, 1685, 1320, 1136, 1084; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.54 (s, 4H), 1.79 (s, 4H), 0.54 (s, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 206.1, 48.5, 40.6, 27.4, 12.5, 10.5; HR-MS (EI) *m/z* Calcd for $C_{10}H_{12}O_2$ (M^+) 164.0837. Found 164.0860.

5,5-Dimethylspiro[2.5]octane-4,8-dione (1g) (Table 2, Entry 6) According to the typical procedure for the synthesis of **1a**, **1g** was prepared from 4,4-dimethylcyclohexane-1,3-dione (**8g**) (70 mg, 0.50 mmol) for 1.5 h. The crude product was purified by column chromatography (silica gel, 20% EtOAc in hexane) to provide **1g** (67 mg, 81%) as a colorless oil; IR (film, cm^{-1}) ν 2966, 2361, 1684, 1329, 1058; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.69 (t, J=6.9 Hz, 2H), 1.98 (t, J=6.9 Hz, 2H), 1.75–1.69 (m, 4H), 1.22 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 210.8, 207.3,

43.0, 38.9, 35.5, 31.8, 27.3, 24.6; HR-MS (EI) *m/z* Calcd for $C_{10}H_{14}O_2$ (M^+) 166.0994. Found 166.0972.

5-Methylspiro[2.5]octane-4,8-dione (1h) (Table 2, Entry 7) According to the typical procedure for the synthesis of **1a**, **1h** was prepared from 4-methylcyclohexane-1,3-dione (**8h**)[29] (63 mg, 0.50 mmol) for 1.5 h. The crude product was purified by column chromatography (silica gel, 20% EtOAc in hexane) to provide **1h** (61 mg, 80%) as a colorless oil; IR (film, cm^{-1}) *v* 2362, 1683, 1331, 756; ^{1}H-NMR (400 MHz, $CDCl_3$) *δ*: 2.78 (dt, *J*=18.3, 4.1 Hz, 1H), 2.68–2.54 (m, 2H), 2.20 (m, 1H), 1.93–1.65 (m, 5H), 1.24 (d, *J*=6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) *δ*: 208.4, 207.3, 43.6, 40.1, 38.9, 27.8, 26.9, 26.2, 15.3; HR-MS (EI) *m/z* Calcd for $C_9H_{12}O_2$ (M^+) 152.0837. Found 152.0832.

Spiro[2.4]heptane-4,7-dione (18) (Table 2, Entry 8) According to the typical procedure for the synthesis of **1a**, **18** was prepared from 1,3-cyclopentanedione (**17**) (49 mg, 0.50 mmol) for 1.5 h. The crude product was purified by column chromatography (silica gel, 60% EtOAc in hexane) to provide **18** (48 mg, 77%) as a white solid: mp 135.0–136.0°C; IR (KBr, cm^{-1}) *v* 3099, 1701, 1427, 1343, 1130, 1115, 924; ^{1}H-NMR (400 MHz, $CDCl_3$) *δ*: 2.85 (s, 4H), 1.79 (s, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) *δ*: 212.6, 38.9, 35.5, 26.7; HR-MS (EI) *m/z* Calcd for $C_7H_8O_2$ (M^+) 124.0524. Found 124.0488.

Spiro[2.6]nonane-4,9-dione (20) (Table 2, Entry 9) According to the typical procedure for the synthesis of **1a**, **20** was prepared from 1,3-cycloheptanedione (**19**) (63 mg, 0.50 mmol) for 2 h. The crude product was purified by column chromatography (silica gel, 20% EtOAc in hexane) to provide **20** (54 mg, 71%) as a colorless oil: IR (film, cm^{-1}) *v* 2937, 1680, 1454, 1330, 1298, 1110; ^{1}H-NMR (400 MHz, $CDCl_3$) *δ*: 2.74–2.71 (m, 4H), 2.01–1.97 (m, 4H), 1.49 (s, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) *δ*: 207.5, 43.2, 41.7, 23.1, 21.7; HR-MS (EI) *m/z* Calcd for $C_9H_{12}O_2$ (M^+) 152.0837. Found 152.0852.

Spiro[cyclopropane-1,2′-(2*H*)-indene]-1′,3′-dione (22)[24] (Table 2, Entry 10) According to the typical procedure for the synthesis of **1a**, **22** was prepared from 1,3-indanedione (**21**) (73 mg, 0.50 mmol) for 1.5 h. The crude product was purified by column chromatography (silica gel, 40% EtOAc in hexane) to provide **22** (74 mg, 86%) as a white solid: mp 94.0–95.0°C; IR (KBr, cm^{-1}) *v* 3047, 1712, 1600, 1361, 1204, 1069, 788; ^{1}H-NMR (400 MHz, $CDCl_3$) *δ*: 7.97 (dd, *J*=5.6, 3.2 Hz, 2H), 7.82 (dd, *J*=5.6, 3.2 Hz, 2H), 1.78 (s, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) *δ*: 199.2, 142.1, 134.8, 122.5, 35.7, 20.4.

1,1-Diacetylcyclopropane (7a) (Chart 7) According to the typical procedure for the synthesis of **1a**, **7a** was prepared from acetylacetone (**6a**) (49 mg, 0.50 mmol) for 1.5 h. The crude product was purified by column chromatography (silica gel, 40% EtOAc in hexane) to provide **7a** (50 mg, 79%) as a colorless oil; IR (film, cm^{-1}) *v* 2368, 2330, 1689, 1365, 761; ^{1}H-NMR (400 MHz, $CDCl_3$) *δ*: 2.23 (s, 6H), 1.48 (s, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) *δ*: 203.9, 43.2, 27.7, 17.4.

1-Acetyl-1-benzoylcyclopropane (7b) (Chart 7) According to the typical procedure for the synthesis of **1a**, **7b** was prepared from 1-phenyl-1,3-butanedione (**6b**) (81 mg, 0.50 mmol) for 1.5 h. The crude product was purified by column chromatography (silica gel, 20% EtOAc in hexane) to provide **7b** (78 mg, 83%) as a colorless oil; IR (film, cm^{-1}) *v* 2368, 2335, 1672, 1324, 1135, 1006; ^{1}H-NMR (400 MHz, $CDCl_3$) *δ*: 7.93 (d, *J*=7.3 Hz, 2H), 7.59 (t, *J*=7.3 Hz, 1H), 7.48 (t, *J*=7.3 Hz, 2H), 2.06 (s, 3H), 1.62–1.59 (m, 2H), 1.52–1.49 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) *δ*: 203.9, 196.4, 136.7, 133.5, 128.9, 128.8, 41.9, 29.2, 17.1.

Ethyl 1-Acetylcyclopropanecarboxylate (24) (Chart 8) According to the typical procedure for the synthesis of **1a**, **24** was prepared from ethyl acetoacetate (**23**) (65 mg, 0.50 mmol) for 1.5 h. The crude product was purified by column chromatography (silica gel, 10% EtOAc in hexane) to provide **24** (55 mg, 71%) as a colorless oil; IR (film, cm^{-1}) *v* 2931, 2860, 2360, 1734, 1714, 1542, 1457, 755; ^{1}H-NMR (400 MHz, $CDCl_3$) *δ*: 4.21 (q, *J*=3.4 Hz, 2H), 2.47 (s, 3H), 1.47 (s, 4H), 1.29 (t, *J*=3.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) *δ*: 203.1, 171.0, 61.2, 35.1, 29.8, 19.1, 14.1.

Dimethyl 1,1-Cyclopropanedicarboxylate (26) (Chart 8) According to the typical procedure for the synthesis of **1a**, **26** was prepared from dimethyl malonate (**25**) (66 mg, 0.50 mmol) for 4 h. The crude product was purified by column chromatography (silica gel, 10% EtOAc in hexane) to provide **26** (39 mg, 49%) as a colorless oil; IR (film, cm^{-1}) *v* 3227, 1732, 1443, 1322, 1218, 1136, 755; ^{1}H-NMR (400 MHz, $CDCl_3$) *δ*: 3.75 (s, 6H), 1.47 (s, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) *δ*: 170.2, 52.6, 27.8, 16.7.

6,6-Dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (28) (Chart 8) According to the typical procedure for the synthesis of **1a**, **28** was prepared from Meldrum's acid (**27**) (72 mg, 0.50 mmol) for 2 h. The crude product was purified by column chromatography (silica gel, 30% EtOAc in hexane) to provide **28** (68 mg, 80%) as a white solid, which was directly identical to the commercial sample supplied by Tokyo Chemical Industry Co., Ltd. mp 60.5–61.5°C; IR (KBr, cm^{-1}) *v* 2368, 1775, 1742, 1400, 1340, 1200, 1047, 970 856, 730; ^{1}H-NMR (400 MHz, $CDCl_3$) *δ*: 1.99 (s, 4H), 1.82 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) *δ*: 168.1, 105.1, 27.6, 24.1, 23.9.

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