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Diphenylparabanic Acid as a Synthon for the Synthesis of α-Diketones and α-Ketocarboxylic Acids

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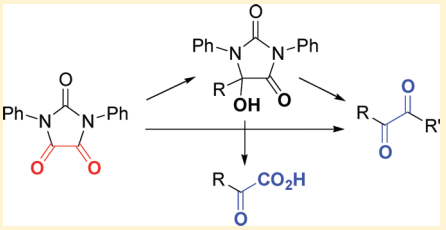
Supporting Information

ABSTRACT: Diphenylparabanic acid was found to react with >2 equiv of organolithiums at −78 °C to effectively give the corresponding symmetrical α-diketones. However, upon treatment with 1 equiv of organolithium, the parabanic acid gave mainly 5-substituted 5-hydroxyimidazolidine-2,4-diones. On the other hand, Grignard reagents were less reactive toward the parabanic acid at low temperature, and selectively gave the corresponding 5-hydroxyimidazolidine-2,4-diones even if more than 1 equiv of the reagents was used. A tandem process in which the parabanic acid was first reacted with a Grignard reagent and then reacted in one-pot with an organolithium effectively gave the unsymmetrical α-diketone. 5-Substituted 5-hydroxyimidazolidine-2,4-diones were useful as versatile precursors for preparing α-ketocarboxylic acids as well as unsymmetrical α-diketones.

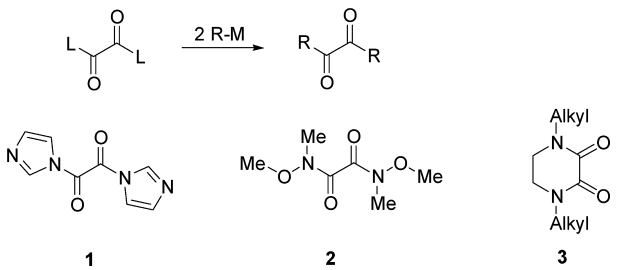


INTRODUCTION

α-Diketones, an important class of compounds as versatile intermediates for organic synthesis, can be synthesized by various methods, such as the oxidation of acetylenic compounds,[1−5] acyloins[6] or enamines,[7] the base-mediated homologation of dimethyldihydropyrazines,[8] and the nucleophilic substitution (addition−elimination) of oxalic acid derivatives.[9−12] Among these methods, the latter shows a considerably wide scope for the synthesis of dialkyl-, diaryl-, and unsymmetrically substituted α-diketones, though it could be made even more versatile with the development of a new effective synthon.

α-Diketone synthons that have been described thus far include oxalyldiimidazole (**1**),[9] oxalamide of *N*,*O*-dimethylhydroxylamine (**2**),[10] *N*,*N*′-dialkylpiperazine-2,3-diones (**3**)[11] and oxalyl chloride (Chart 1).[12] Each synthon offers characteristic advantages and disadvantages. Oxalamide **1** reacts even with sterically crowded aromatic Grignard reagents to give α-diketones at low temperature, while its effectiveness for the synthesis of unsymmetrical α-diketones is unclear. Oxalamide **2** undergoes nucleophilic substitution with Grignard reagents to give the corresponding α-ketoamides in low to high yields, as well as double nucleophilic substitution with aromatic organolithiums to give α-diketones in moderate yields. However, there have been no reports of the synthesis of unsymmetrical α-diketones from **2**. Cyclic oxalamide **3** undergoes double nucleophilic substitution with organolithiums or Grignard reagents to give the corresponding α-diketones in good yields, while there have been no reports of single substitution. The reaction of oxalyl chloride with organocopper reagents is apparently limited to the synthesis of ω,ω′-disubstituted hexa-1,5-diyne-3,4-diones.

Chart 1. Oxalamide Derivatives as α-Diketone Synthons



We report here that readily available diphenylparabanic acid (*N*,*N*′-diphenylimidazolidine-2,4,5-trione) (**4**)[13] acts as a new synthon[14] to effectively prepare symmetrical and unsymmetrical α-diketones **5** and **6**, and provides stable precursors **7**, which can be successively transformed to α-ketocarboxylic acids **8** as well as α-diketones **5** and **6** (Scheme 1).

RESULTS AND DISCUSSION

1. Reaction of Diphenylparabanic acid with Organolithiums or Grignard Reagents: Formation of Symmetrical α-Diketones or 5-Substituted 5-Hydroxyimidazolidine-2,4-diones. Diphenylparabanic acid **4** is an oxalic acid derivative that has the characteristics of an α-diketone synthon as follows. First, **4** is formally a cyclic imide of oxalic acid, so that the carbons of−CO−CO− would be more electron-deficient, and thus more reactive, toward nucleophiles than simple oxalamides **1**−**3**. Second, a fixed cisoid −CO−CO− structure presumably stabilizes the metal salt of monoadduct **7** produced from organolithium or Grignard reagent by forming a chelate, so that it preferably inhibits side reactions such as a

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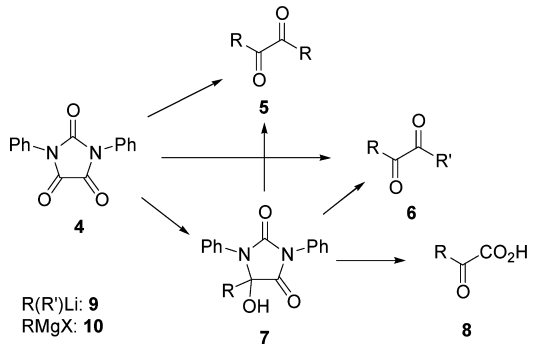
Scheme 1. Synthesis of α-Diketones 5 and 6, 5-Substituted 5-Hydroxyimidazolidine-2,4-diones 7 and α-Ketocarboxylic Acids 8



double nucleophilic attack on the same carbon. Third, it may be possible to isolate intermediate, a certain cyclic hemiaminal, **7** produced by the reaction of **4** with a nucleophile, since it has been reported that certain *N*,*N*′,5-trisubstituted 5-hydroxyimidazolidine-2,4-diones are isolable.[15]

First, we treated diphenylparabanic acid **4** with >2 equiv of phenyllithium (**9a**) in THF at −78 °C for 3 h. A usual workup of the reaction mixture gave 1,2-diphenylethane-1,2-dione (**5a**), as expected, in 84% isolated yield along with *N*,*N*′-diphenylurea. Similar treatment of **4** with 1-naphthyllithium (**9b**) or 2-naphthyllithium (**9c**) gave the corresponding 1,2-diarylethane-1,2-diones **5b** and **5c** in good yields, as shown in Table 1. These results suggest that, as expected, aryllithium **9**

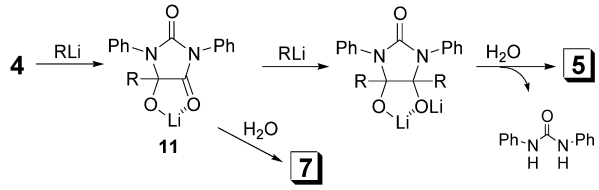
Table 1. Synthesis of α-Diketones 5 or 5-Substituted 5-Hydroxyimidazolidine-2,4-diones 7 by the Reaction of Diphenylparabanic Acid (4) with Organolithiums 9[a]

Organolithium **9** R		Product Yield / %		Organolithium **9** R		Product Yield / %	
9a		**5a** **7a** [b]	84 73 [b]	**9e**		**7e**	90
9b		**5b**	84	**9f**	Bu	**5f**	62
9c		**5c**	89	**9g**		**5g** **7g** [c]	77 85 [c]
9d		**7d**	96	**9h**		**5h**	87

[a]Unless otherwise stated, all of the reactions were carried out by using 2.0−2.5 equiv of organolithium **9** in THF at −78 °C for 1−3 h. [b]1.1 equiv of **9a** was used. [c]1.1 equiv of **9g** was used.

attacked a −CO−CO− of **4** to initially produce lithium salt **11**, in which a remaining carbonyl was presumably coordinated with Li^+ and subsequently reacted with the second aryllithium (Scheme 2). In fact, when **4** was treated with 1 equiv of phenyllithium **9a** as a representative compound at −78 °C, 1:1 adduct, that is, 5-hydroxy-*N*,*N*′,5-triphenylimidazolidine-2,4-dione (**7a**), was obtained in 73% yield together with a trace amount of **5a**. In contrast to the results with **9a**−**c**, the reaction of **4** with 9-anthryllithium (**9d**), even with the use of >2 equiv, did not give the desired α-diketone **5d**, and instead gave 1:1 adduct **7d**. Sterically congested 2,4,6-trimethylphenyllithium (**9e**) also gave only 1:1 adduct **7e** (Table 1).

Scheme 2. Reaction of Diphenylparabanic Acid with Organolithiums



BuLi (**9f**), as a representative alkyllithium, also gave α-diketone **5f**, though the isolated yield was somewhat low (62%). We also attempted to synthesize hexa-1,5-diyne-3,4-diones, since they have only been synthesized by the reaction of oxalyl chloride with copper acetylides.[11] Treatment of **4** with >2 equiv of (4-methylphenyl)ethynyllithium (**9g**) at −78 °C gave the desired diynedione **5g** in 77% yield, while the reaction of **4** with 1 equiv of **9g** gave 1:1 adduct **7g** in 85% yield. Notably, benzothiophen-2-yllithium (**9h**), as a representative heteroaromatic lithium reagent, effectively underwent addition to **4** to give α-diketone **5h**. These results are summarized in Table 1.

Next, we investigated the reactivity of **4** with Grignard reagents **10**. When **4** was treated with >1 equiv of phenylmagnesium bromide (**10a**) in THF at −78 °C for 1 h, only 1:1 adduct **7a** was selectively obtained. A use of excess **10** and/or a prolonged reaction time at −78 °C had little effect on the production of α-diketone **5a**. Various Grignard reagents **10b**, **10c** and **10i**−**k** were found to react similarly with **4** to give the corresponding 5-substituted 5-hydroxyimidazolidine-2,4-diones **7b**, **7c** and **7i**−**k** in high yields, as shown in Table 2. However, at higher

Table 2. Synthesis of 5-Substituted 5-Hydroxyimidazolidine-2,4-diones 7 by the Reaction of Diphenylparabanic Acid (4) with Grignard Reagents 10[a]

Grignard reagent R		Product Yield / %		Grignard reagent R		Product Yield / %	
10a		**7a**	97	**10i**		**7i**	98
10b		**7b**	94	**10j**	Et	**7j**	90
10c		**7c**	95	**10k**	*tert*-Bu	**7k**	93

[a]Reactions were carried out in THF at −78 °C for 1 h.

temperature (room temp), 2 equiv of **10a** reacted with **4** to give hydroxydiphenylacetic acid (**12a**) in high yield, but not **5a**. These results suggest that Grignard reagents were not sufficiently reactive to cause double nucleophilic attack to two carbons of **4**, though the initially formed Mg salt **13** could not retain its structure at room temperature and presumably exposed a reactive α-ketoamide moiety, as illustrated in Scheme 3.

2. Synthesis of Unsymmetrical α-Diketones and α-Ketocarboxylic Acids. The results described in the previous section suggest that the tandem reaction of **4** would proceed with the use of two different organometallic reagents to give unsymmetrical α-diketone **6**. There are two possible types of tandem method: the addition of organolithium **9** to a solution of magnesium salt **13** prepared from **4** and Grignard reagent **10**, and the successive addition of organolithium **9** to an initially prepared solution of lithium salt **11**. Thus, we examined these two types of reactions using Grignard reagent

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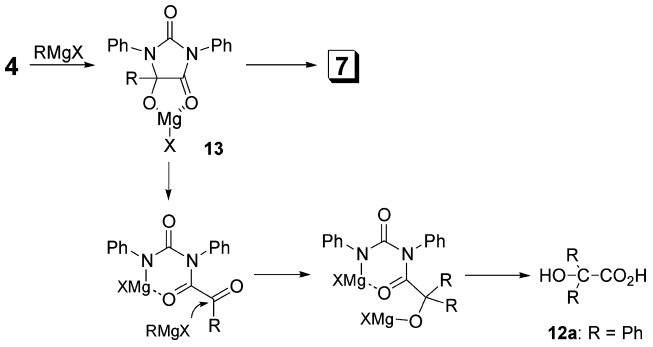
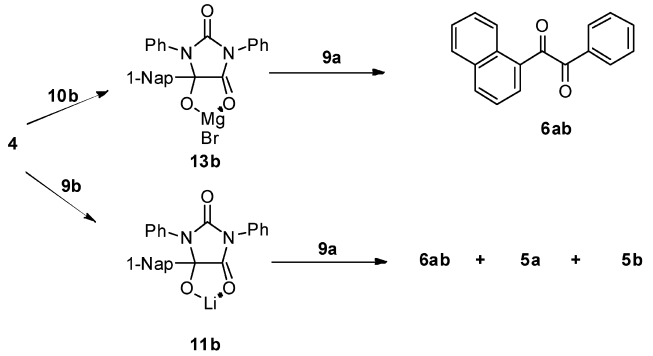
Scheme 3. Reaction of Diphenylparabanic Acid with Grignard Reagents 10



10b, and organolithiums **9a** and **9b** as representative reagents. When **4** was first treated with 1.5 equiv of Grignard reagent **10b** in THF at −78 °C for 1 h, and successively treated in one-pot with organolithium **9a** at −78 °C for 1 h, unsymmetrical α-diketone **6ab** was obtained in 90% yield. On the other hand, a tandem reaction with a combination of two organolithiums was less effective for synthesizing unsymmetrical α-diketones **6**: treatment of **4** with 1.1 equiv of **9b** and then with **9a** in THF at −78 °C gave the desired **6ab** in only 44% yield along with a small amount of symmetrical α-diketone **5a** and **5b** (Scheme 4).

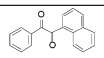
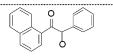
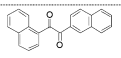
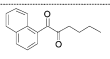
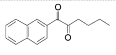
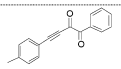
Scheme 4. Synthesis of Unsymmetrical α-Diketone 6ab by a Tandem Reaction



We further attempted to use 5-substituted 5-hydroxyimidazolidine-2,4-diones **7** as a versatile precursor for the synthesis of unsymmetrical α-diketones **6**. When **7a** was treated with >2 equiv of **9b** in THF at −78 °C for 1 h, unsymmetrical α-diketone **6ab** was obtained in 99% yield. The inverse combination, that is, the addition of **9a** to **7b**, also gave **6ab** in 88% yield, as shown in Table 3. Other representative combinations of **7** and **9** also gave the expected unsymmetrical α-diketones **6** in high yields, as shown in Table 3.

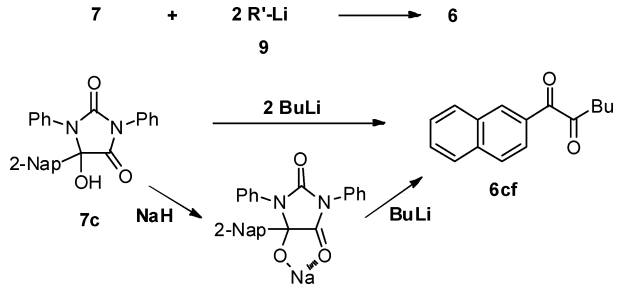
The synthetic method that uses precursor **7** as described above would be useful as a library for the synthesis of unsymmetrical α-diketones **6**, though it requires more than 2 equiv of organolithium reagent **9**: half of **9** is consumed just to form a lithium salt **11**. Thus, we attempted to use an inexpensive sodium salt of **7** instead of **11** for the synthesis of **6**. A representative reaction sequence was as follows. Precursor **7c** was treated with NaH in THF to give a sodium salt, which was then treated in one-pot with 1.2 equiv of BuLi **9f** at −78 °C for 1 h. After workup, unsymmetrical α-diketone **6cf** was obtained in 92% yield (Scheme 5).

Table 3. Synthesis of Unsymmetrical α-Diketones 6 by the Reaction of 5-Substituted 5-Hydroxyimidazolidine-2,4-diones 7 with Organolithium 9[a]

Combination	Unsymmetrical α-diketone		Product Yield / %
7a + **9b**	**6ab**		99
7b + **9a**	**6ab**		88
7b + **9c**	**6bc**		83
7b + **9f**	**6bf**		91
7c + **9f**	**6cf**		97
7g + **9a**	**6ag**		98
7k + **9a**	**6ak**		62

[a]Reactions were carried out using 2.3 equiv of organolithium **9** in THF at −78 °C for 1 h.

Scheme 5. Synthesis of Unsymmetrical α-Diketones 6 from 5-Substituted 5-Hydroxyimidazolidine-2,4-diones 7



Finally, we investigated whether or not hydroxyimidazolidinediones **7** could be effectively hydrolyzed to the corresponding α-ketocarboxylic acids **8**. When **7a** was heated in NaOH/H_2O-MeOH at 50 °C for 1 h, the hydrolysis of **7a** proceeded to give 2-oxo-2-phenylethanoic acid **8a** in 89% yield together with diphenylurea after acidification. Similarly, hydroxyimidazolidinediones **7b–e**, **7g**, **7i** and **7k** were effectively hydrolyzed to the corresponding α-ketocarboxylic acids **8b–e**, **8g**, **8i** and **8k**, as shown in Table 4.

CONCLUSION

Diphenylparabanic acid **4** was found to react with >2 equiv of organolithiums at −78 °C to effectively give the corresponding symmetrical α-diketones **5**, though **4** gave mainly 5-substituted 5-hydroxyimidazolidine-2,4-diones **7** when treated with 1 equiv of organolithiums. On the other hand, Grignard reagents were less reactive toward **4** at low temperature, and selectively gave **7** even if more than 1 equiv of the reagents were used. A tandem reaction of **4** by the successive addition of two different organolithiums gave an unsymmetrical α-diketone **6** in moderate yields. However, a tandem process in which **4** was first reacted with a Grignard reagent and then with an organolithium was effective for producing an unsymmetrical α-diketone **6**. 5-Substituted 5-hydroxyimidazolidine-2,4-diones

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Table 4. Synthesis of α-Ketocarboxylic Acids 8 from 5-Substituted 5-Hydroxyimidazolidine-2,4-diones 7[a]

Imidazolidine-2,4-dione		α-Ketocarboxylic acid Yield / %		Imidazolidine-2,4-dione		α-Ketocarboxylic acid Yield / %	
7a		**8a**	98	**7e**		**8e**	39 [b]
7b		**8b**	94	**7g**		**8g**	80 [c]
7c		**8c**	89	**7i**		**8i**	84
7d		**8d**	78	**7k**		**8k**	96

[a]Reactions were carried out by using 4 M NaOH in H_2O/MeOH at 50 °C for 1 h. [b]*N*-Phenyl-2-(2,4,6-trimethylphenyl)-2-oxoacetamide (**14**) was concomitantly produced in 54% yield. [c]**8g** was isolated as a lactone form, 5-(4-methylphenyl)furan-2,3-dione.

7 were useful as versatile precursors for preparing unsymmetrical α-diketones **6** and α-ketocarboxylic acids **8**.

Finally, synthon **4** could be easily modified to a copolymer with *N*-phenyl-*N*′-(4-vinylphenyl)parabanic acid and styrene, and further studies of this process are now underway.

EXPERIMENTAL SECTION

Preparation of Diphenylparabanic Acid (4). According to the procedure reported,[13] **4** was prepared as follows, though CH_2Cl_2 was used as a solvent instead of diethyl ether. Oxalyl chloride (12.0 mL, 0.14 mol) was added dropwise to a solution of *N*,*N*′-diphenylurea (25.2 g, 0.12 mol) in CH_2Cl_2 (400 mL) and refluxed for 1.5 h. The reaction mixture was washed with sat. aq. NaCl, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was crystallized from CH_2Cl_2–hexane to give **4** as colorless needles (31.5 g, 99% yield).

4: colorless needles melted at 208.0–209.0 °C (from CH_2Cl_2–hexane). (lit.,[13] 202 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.44–7.51 (m, 6H), 7.52–7.58 (m, 4H) ppm.

Synthesis of 1,2-Diphenylethane-1,2-dione (5a) by the Reaction of Diphenylparabanic Acid (4) with Phenyllithium (9a). *Typical Procedure.* A solution of **4** (1.02 g, 3.83 mmol) in dry THF (5 mL) was added to a solution of phenyllithium (**9a**) (1.13 M in THF, 7.80 mL, 8.81 mmol, 2.30 equiv) in dry THF (5 mL) at −78 °C under a N_2 atmosphere and stirred for 1 h. The reaction mixture was poured into sat. aq. NH_4Cl and then extracted with AcOEt. The organic layer was washed with sat. aq. NaCl, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was rinsed with $CHCl_3$ and *N*,*N*′-diphenylurea was removed by filtration. The filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel and eluted with hexane-AcOEt (4:1) to give **5a** as a yellow solid (675 mg, 84% yield).

5a: yellow needles melted at 96.5–97.0 °C (from AcOEt–hexane) (lit.,[16] 95–97 °C from AcOEt–hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.52 (dd, *J* = 8.2 and 7.3 Hz, 4H), 7.66 (t, *J* = 7.3 Hz, 2H), 7.98 (d with fine coupling, *J* = 8.2 Hz, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 129.0 (×2), 129.9 (×2), 133.0, 134.9, 194.5 ppm. IR (KBr): $\tilde{\nu}$ 3063, 1677, 1660, 1594, 1579 cm^{-1}. Mass (*m*/*z*, %): 210 (M^+, 6), 105 (100), 77 (54). HRMS (ESI): 233.0583, calcd for $C_{14}H_{10}O_2Na$ $[M + Na]^+$ 233.0579.

According to the procedure described above, **4** was reacted with 1-naphthyllithium (**9b**), 2-naphthyllithium (**9c**), butyllithium (**9f**), (4-methylphenyl)ethynyllithium (**9g**), or benzothiophen-2-yllithium (**9h**) to give the corresponding symmetrical α-diketones **5b** (84%), **5c** (89%), **5f** (62%), **5g** (77%) and **5h** (87%): organolithiums **9b** and **9c** were prepared by the metal–halogen exchange reaction of the corresponding bromide with butyllithium, while **9g** and **9h** were prepared by the lithiation of (4-methylphenyl)ethyne or benzothiophene with butyllithium.

5b: yellow granules melted at 192.0–194.0 °C (from CH_2Cl_2) (lit.,[17] 192–194 °C from AcOEt–hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.47 (dd, *J* = 8.2 and 7.3 Hz, 2H), 7.63 (ddd, *J* = 8.2, 7.1, and 1.1 Hz, 2H), 7.75 (ddd, *J* = 8.5, 7.1, and 1.4 Hz, 2H), 7.95 (d with fine coupling, *J* = 8.2 Hz, 2H), 8.02 (dd, *J* = 7.3 and 1.1 Hz, 2H), 8.12 (d, *J* = 8.2 Hz, 2H), 9.36 (d, *J* = 8.5 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 124.4, 126.0, 127.1, 128.8, 128.9, 129.4, 131.1, 134.1, 135.0, 135.8, 196.9 ppm. IR (KBr): $\tilde{\nu}$ 3055, 1662, 1571 cm^{-1}. Mass (*m*/*z*, %): 310 (M^+, 10), 156 (11), 155 (100), 128 (10), 127 (96), 126 (18). HRMS (ESI): 333.0901, calcd for $C_{22}H_{14}O_2Na$ $[M + Na]^+$ 333.0892.

5c: colorless needles melted at 160.0–161.0 °C (from CH_2Cl_2) (lit.,[18] 156–157 °C from AcOEt-hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.55 (dd with fine coupling, *J* = 8.0 and 7.1 Hz, 2H), 7.65 (dd with fine coupling, *J* = 8.0 and 7.1 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 8.7 Hz, 2H), 8.16 (d with fine coupling, *J* = 8.7 Hz, 2H), 8.46 (s, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 123.7, 127.1, 127.9, 129.1, 129.5, 129.9, 130.4, 132.3, 133.6, 136.4, 194.7 ppm. IR (KBr): $\tilde{\nu}$ 3061, 1664, 1628, 1596 cm^{-1}. Mass (*m*/*z*, %): 310 (M^+, 12), 156 (12), 155 (100), 127 (85), 126 (15). HRMS (ESI): 333.0901, calcd for $C_{22}H_{14}O_2Na$ $[M + Na]^+$ 333.0892.

5f: yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.92 (t, *J* = 7.3 Hz, 6H), 1.30–1.38 (m, 4H), 1.53–1.60 (m, 4H), 2.74 (t, *J* = 7.3 Hz, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 13.7, 22.2, 25.1, 35.7, 200.1 ppm. (lit.,[3a] 100 MHz, $CDCl_3$ δ_C 13.8, 22.2, 25.1, 35.8, 200.2 ppm). IR (liquid film): $\tilde{\nu}$ 2961, 1713 cm^{-1}. Mass (*m*/*z*, %): 170 (M^+, 7), 85 (100), 71 (12), 57 (66).

5g: orange columns melted at 154.5–156.0 °C (from CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 2.42 (s, 6H), 7.23 (d, *J* = 8.1 Hz, 4H), 7.60 (d, *J* = 8.1 Hz, 4H) ppm.; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.9, 86.2, 100.8, 116.1, 129.6 (×2), 133.9 (×2), 142.9, 172.6 ppm. IR (KBr): $\tilde{\nu}$ 3033, 2190, 1659, 1603, 1508 cm^{-1}. Mass (*m*/*z*, %): 286 (M^+, 0.8), 230 (37), 144 (11), 143 (100), 115 (13), 89 (11). HRMS (ESI): 309.0894 calcd for $C_{20}H_{14}O_2Na$ $[M + Na]^+$ 309.0892.

5h: yellow needles melted at 236.0–236.5 °C (from CH_2Cl_2) (lit.,[19] 239–240 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.44 (dd, *J* = 8.5 and 6.8 Hz, 2H), 7.53 (dd, *J* = 8.5 and 6.8 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 4H), 8.32 (s, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 123.0, 125.4, 126.9, 128.7, 135.4, 138.8, 139.0, 143.8, 184.3 ppm. IR (KBr): $\tilde{\nu}$ 1647, 1592 cm^{-1}. Mass (*m*/*z*, %): 322 (M^+, 19), 162 (11), 161 (100), 133 (31), 89 (55). HRMS (ESI): 345.0002, calcd for $C_{18}H_{10}O_2S_2Na$ $[M + Na]^+$ 345.0020.

Synthesis of 5-Hydroxy-*N*,*N*′,5-triphenylimidazolidine-2,4-dione (7a) by the Reaction of Diphenylparabanic Acid (4) with Phenyllithium (9a). A solution of **4** (1.00 g, 3.76 mmol) in dry THF (5 mL) was added dropwise to a solution of phenyllithium (**9a**) (1.1 equiv) in dry THF under a N_2 atmosphere at −78 °C and stirred for 1 h. The reaction mixture was poured into sat. aq. NH_4Cl and then extracted with AcOEt. The organic layer was washed with sat. aq. NaCl, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was crystallized from $CHCl_3$ to give **7a** (174 mg, 13%). The filtrate was concentrated in vacuo, and chromatograped on silica gel with hexane–AcOEt (4:1) to further give **7a** (772 mg, 60%) as a yellow solid. Total yield of **7a** was 73%.

7a: colorless granules melted at 208.0–209.0 °C (from $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 4.20 (s, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.23–7.28 (m, 2H), 7.34–7.52 (m, 12H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 88.5, 125.4 (×2), 126.6, 126.6 (×2), 127.4 (×2), 128.8, 128.9 (×2), 129.0 (×2), 129.4 (×3), 131.9, 135.2, 136.3, 153.4, 170.9 ppm. IR (KBr): $\tilde{\nu}$ 3378, 3062, 3034, 1779, 1706, 1596 cm^{-1}. Mass (*m*/*z*, %): 344 (M^+, 23), 225 (26), 197 (15), 119 (34), 105 (100), 91 (12), 77 (37). HRMS (ESI): 367.1073, calcd for $C_{21}H_{16}N_2O_3Na$ $[M + Na]^+$ 367.1059. Anal. Calcd for $C_{21}H_{16}N_2O_3$: C, 73.24; H, 4.68; N, 8.13. Found: C, 73.06; H, 4.67; N, 8.14.

Synthesis of 5-(9-Anthryl)-5-hydroxy-*N*,*N*′-diphenylimidazolidine-2,4-dione (7d). BuLi (1.63 M in hexane, 5.30 mL, 8.64 mmol) was added to a solution of 9-bromoanthracene (2.44 g, 9.49 mmol) in dry THF (20 mL) at −78 °C under a N_2 atmosphere and stirred for

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30 min. To the thus-prepared solution of 9-anthryllithium, a solution of **4** (1.00 g, 3.76 mmol) in dry THF (10 mL) was added dropwise under a N_2 atmosphere at −78 °C and stirred for 1 h. The reaction mixture was poured into sat. aq. NH_4Cl and then extracted with AcOEt. The organic layer was washed with sat. aq. NaCl, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by chromatography on silica gel and eluted with hexane-AcOEt (4:1) to give **7d** (1.61 g, 96%) as a yellow solid.

7d: yellow granules melted at 192.0−194.0 °C (from CH_2Cl_2−hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 4.15 (s, 1H), 7.09−7.19 (m, 6H), 7.27−7.31 (m, 1H), 7.42 (t with fine coupling, J = 7.3 Hz, 1H), 7.45−7.61 (m, 6H), 7.88 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 9.2 Hz, 1H), 8.03 (d, J = 8.2 Hz, 1H), 8.40 (d, J = 9.2 Hz, 1H), 8.46 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 90.3, 122.4, 123.9, 124.6, 124.8, 125.9, 125.9 (×2), 126.0, 127.4, 128.4, 128.7, 129.0 (×2), 129.1 (×2), 129.2, 129.2 (×2), 129.6, 130.0, 130.9, 131.5, 131.8, 132.0, 132.1, 133.6, 154.1, 171.8 ppm. IR (KBr): $\tilde{\nu}$ 3461, 3046, 1778, 1726, 1624, 1597 cm^{-1}. Mass (35 eV, m/z, %): 444 (M^+, 1), 325 (18), 206 (16), 205 (100), 177 (33), 119 (12). HRMS (ESI): 467.1376, calcd for $C_{29}H_{20}N_2O_3Na$ $[M + Na]^+$ 467.1372.

Synthesis of 5-Hydroxy-5-(2,4,6-trimethylphenyl)-*N*,*N*′-diphenylimidazolidine-2,4-dione (7e). BuLi (1.64 M in hexane, 5.30 mL, 8.69 mmol) was added to a solution of 1-bromo-2,4,6-trimethylbenzene (1.41 mL, 9.42 mmol) in dry THF (5 mL) at −78 °C under a N_2 atmosphere and stirred for 30 min. To the thus-prepared solution of 2,4,6-trimethylphenyllithium in dry THF, a solution of **4** (1.02 g, 3.83 mmol) in dry THF (5 mL) was added dropwise under a N_2 atmosphere at −78 °C and stirred for 1.5 h. The reaction mixture was poured into sat. aq. NH_4Cl and then extracted with AcOEt. The organic layer was washed with sat. aq. NaCl, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was crystallized from hexane−AcOEt to give **7e** (1.06 g, 72%) as colorless granules. The filtrate was concentrated in vacuo and chromatographed on silica gel with hexane−AcOEt (4:1) to further give **7e** (275 mg, 18%) as a colorless solid. Total yield of **7e** was 90%.

7e: colorless granules melted at 170.0−171.0 °C (from CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 2.16 (s, 3H), 2.23 (s, 3H), 2.35 (s, 3H), 3.92 (s, 1H), 6.72 (s, 1H), 6.85 (s, 1H), 7.11−7.17 (m, 2H), 7.24−7.30 (m, 3H), 7.37−7.44 (m, 1H), 7.38−7.52 (m, 4H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 20.3, 20.8, 24.7, 90.6, 125.8 (×2), 126.8 (×2), 127.1, 128.6, 128.9 (×2), 128.9, 129.3 (×2), 131.1, 131.8, 132.5, 134.8, 135.4, 137.8, 139.9, 153.2, 170.8 ppm. IR (KBr): $\tilde{\nu}$ 3356, 3065, 2973, 2924, 1783, 1715, 1598 cm^{-1}. Mass (m/z, %): 386 (M^+, 1), 212 (14), 148 (11), 147 (100), 119 (19), 93 (44), 91 (14), 77 (10). HRMS (ESI): 409.1527, calcd for $C_{24}H_{22}N_2O_3Na$ $[M + Na]^+$ 409.1528.

Synthesis of 5-Hydroxy-5-(4-methylphenylethynyl)-*N*,*N*′-diphenylimidazolidine-2,4-dione (7g). BuLi (1.61 M in hexane, 2.50 mL, 4.03 mmol) was added to a solution of 4-methylphenylacetylene (0.57 mL, 4.5 mmol) in dry THF (5 mL) at −78 °C under a N_2 atmosphere and stirred for 30 min. To the solution of 2-(4-methylphenyl)ethynyllithium in dry THF, a solution of **4** (1.02 g, 3.83 mmol) in dry THF (5 mL) was added dropwise under N_2 atmosphere at −78 °C and stirred for 1 h. The reaction mixture was poured into sat. aq. NH_4Cl and then extracted with AcOEt. The organic layer was washed with sat. aq. NaCl, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was crystallized from CH_2Cl_2−hexane to give **7g** (1.25 g, 85%) as a colorless solid.

7g: colorless granules melted at 168.0−169.0 °C (from CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 2.32 (s, 3H), 4.85 (s, 1H), 7.07 (d, J = 7.8 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 7.33−7.39 (m, 2H), 7.40−7.47 (m, 6H), 7.65 (d, J = 7.8 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.5, 80.5, 80.7, 90.0, 117.1, 126.1 (×2), 126.9 (×2), 128.0, 128.5, 129.1 (×6), 130.9, 131.9 (×2), 133.7, 140.2, 152.4, 167.9 ppm. IR (KBr): $\tilde{\nu}$ 3387, 2227, 1787, 1728, 1596 cm^{-1}. Mass (m/z, %): 382 (M^+, 0.6), 266 (50), 119 (100), 116 (17), 115 (19), 91 (52), 64 (20), 63 (12). HRMS (ESI): 405.1221, calcd for $C_{24}H_{18}N_2O_3Na$ $[M + Na]^+$ 405.1215. Anal. Calcd for $C_{24}H_{18}N_2O_3$: C, 75.38; H, 4.74; N, 7.33. Found: C, 75.03; H, 4.49; N, 7.30.

Synthesis of 5-Hydroxy-*N*,*N*′,5-triphenylimidazolidine-2,4-dione (7a) by the Reaction of *N*,*N*′-Diphenylparabanic Acid (4) with Phenylmagnesium Bromide (10a). *Typical Procedure.* To the solution of phenylmagnesium bromide (**10a**), which was prepared from bromobenzene (11.3 mmol) and Mg (13.0 mmol) in dry THF, a solution of **4** (2.01 g, 7.55 mmol) in dry THF (10 mL) was added dropwise over 5 min at −78 °C and stirred for 1 h. The reaction mixture was poured into sat. aq. NH_4Cl and extracted with AcOEt. The reaction mixture was poured into sat. aq. NH_4Cl and then extracted with AcOEt. The organic layer was washed with sat. aq. NaCl, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was chromatograped on silica gel and eluted with hexane−AcOEt (4:1) to give **7a** (2.53 g, 97%) as colorless granules.

According to the procedure described above, the reaction of diphenylparabanic acid (**4**) with 1-naphthylmagnesium bromide (**10b**), 2-naphthylmagnesium bromide (**10c**), 1-pyrenylmagnesium bromide (**10i**), ethylmagnesium chloride (**10j**) or tert-butylmagnesium chloride (**10k**) gave the corresponding 5-substituted 5-hydroxyimidazolidine-2,4-diones **7b** (94%), **7c** (95%), **7i** (98%), **7j** (90%) and **7k** (93%).

7b: colorless granules melted at 191.0−192.0 °C (from CH_2Cl_2−hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.64 (s, 1H), 7.02−7.18 (m, 5H), 7.29−7.57 (m, 8H), 7.78−7.97 (m, 4H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 87.4 (br), 121.6 (br), 125.1, 125.4 (×2), 125.9, 126.8 (br), 127.1 (×2), 127.8 (br), 128.4 (br), 128.7 (×3), 128.8, 129.4, 129.4, 129.8 (br), 130.2 (br), 130.8, 131.8, 133.8 (br), 134.6 (br), 153.4, 170.9 ppm. IR (KBr): $\tilde{\nu}$ 3383, 3094, 3058, 3019, 1784, 1726, 1596 cm^{-1}. Mass (m/z, %): 394 (M^+, 6), 275 (23), 156 (13), 155 (100), 127 (43), 119 (25), 91 (10). HRMS (ESI): 417.1230, calcd for $C_{25}H_{18}N_2O_3Na$ $[M+Na]^+$ 417.1215.

7c: colorless needles melted at 204.0−205.0 °C (from CH_2Cl_2−hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 4.69 (s, 1H), 7.14 (t, J = 7.3 Hz, 1H), 7.22 (dd, J = 8.2 and 7.3 Hz, 2H), 7.38−7.55 (m, 10H), 7.80−7.86 (m, 3H), 8.11 (s with fine coupling, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 88.5, 123.6, 125.3 (×2), 126.4, 126.5, 126.7, 127.1, 127.3 (×2), 127.7, 128.6 (×2), 128.7, 128.8 (×2), 129.2 (×2), 131.8, 132.7, 133.1, 133.7, 135.1, 153.3, 170.7 ppm. IR (KBr): $\tilde{\nu}$ 3350, 3063, 1785, 1723, 1596 cm^{-1}. Mass (m/z, %): 394 (M^+, 4), 275 (22), 156 (13), 155 (100), 127 (63), 126 (10), 119 (16), 77 (13). HRMS (ESI): 417.1224, calcd for $C_{25}H_{18}N_2O_3Na$ $[M + Na]^+$ 417.1215. Anal. Calcd for $C_{25}H_{18}N_2O_3$: C, 76.13; H, 4.60; N, 7.10. Found: C, 75.90; H, 4.37; N, 7.10.

7i: pale yellow granules melted at 218.5−219.5 °C (from $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 4.74 (s, 1H), 6.95−7.03 (m, 3H), 7.13−7.17 (m, 2H), 7.41−7.53 (m, 3H), 7.57 (d, J = 7.3 Hz, 2H), 7.95 (d, J = 8.7 Hz, 1H), 7.99 (d, J = 8.2 Hz, 1H), 8.03 (dd, J = 7.8 and 7.3 Hz, 2H), 8.07 (d, J = 9.2 Hz, 1H), 8.16 (d, J = 7.3 Hz, 1H), 8.21 (d with fine coupling, J = 7.8 Hz, 2H), 8.36 (br-s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 124.5, 124.6, 125.1, 125.8, 126.1 (×2), 126.2 (×4), 126.3 (×2), 127.0, 127.2 (×2), 128.5, 128.6 (×3), 128.6, 129.1 (br), 129.3 (×3), 130.1, 131.1, 131.3, 132.6, 133.6, 153.8, 171.8 ppm. IR (KBr): $\tilde{\nu}$ 3380, 3044, 1780, 1722, 1597 cm^{-1}. Mass (35 eV, m/z, %): 468 (M^+, 2), 349 (20), 230 (18), 229 (100), 201 (46), 119 (11). HRMS (ESI): 491.1388, calcd for $C_{31}H_{20}N_2O_3Na$ $[M + Na]^+$ 491.1372. Anal. Calcd for $C_{31}H_{20}N_2O_3$: C, 79.47; H, 4.30; N, 5.98. Found: C, 79.15; H, 4.15; N, 5.99.

7j: colorless amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.84 (t, J = 7.3 Hz, 3H), 1.87 (dq, J = 14.4 and 7.3 Hz, 1H), 2.06 (dq, J = 14.4 and 7.3 Hz, 1H), 4.33 (s, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.35−7.47 (m, 7H), 7.55 (d, J = 8.2 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 7.3, 27.3, 89.1, 126.1 (×2), 126.2 (×2), 127.3, 128.3, 129.0 (×4), 130.8, 133.6, 153.5, 171.8 ppm. IR (KBr): $\tilde{\nu}$ 3388, 3065, 2974, 2939, 2882, 1781, 1714, 1596 cm^{-1}. Mass (m/z, %): 296 (M^+, 60), 268 (16), 267 (100), 149 (11), 120 (62), 119 (31), 93 (29), 91 (20), 77 (36), 57 (12). HRMS (ESI): 297.1258, calcd for $C_{17}H_{17}N_2O_3$ $[M + H]^+$ 297.1239.

7k: colorless granules melted at 145.0−146.0 °C (from AcOEt−hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.98 (s, 9H), 4.14 (s, 1H), 7.29 (t, J = 7.3 Hz, 1H), 7.32−7.38 (m, 5H), 7.40−7.45 (m, 2H), 7.51 (d, J = 7.8 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 24.9 (×3), 40.2, 91.9, 126.2 (×2), 127.5, 127.8 (×2), 128.3, 128.8 (×2), 129.0

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(×2), 131.1, 136.1, 153.8, 171.9 ppm. IR (KBr): $\tilde{\nu}$ 3421, 3065, 2963, 2874, 1775, 1711, 1597 cm^{-1}. Mass (*m*/*z*, %): 324 (M^+, 4), 269 (17), 268 (100), 267 (94), 120 (56), 119 (34), 92 (11), 91 (22), 77 (28), 57 (29). HRMS (ESI): 347.1380, calcd for $C_{19}H_{20}N_2O_3Na$ $[M + Na]^+$ 347.1372.

Synthesis of 1-Naphthyl-2-phenylethane-1,2-dione (6ab) by the Reaction of 5-Hydroxy-*N*,*N*′,5-triphenylimidazolidine-2,4-dione (7a) with 1-Naphthyllithium (9b). *Typical Procedure.* To the solution of 1-naphthyllithium (**9b**) prepared from BuLi (1.63 M in hexane, 4.10 mL, 6.68 mmol) and 1-bromonaphthalene in dry THF (10 mL), a solution of 5-hydroxy-*N*,*N*′,5-triphenylimidazolidine-2,4-dione (**7a**) (1.01 g, 2.93 mmol) in dry THF (5 mL) was added dropwise under a N_2 atmosphere at −78 °C and stirred for 1 h. The reaction mixture was poured into sat. aq. NH_4Cl and then extracted with AcOEt. The organic layer was washed with sat. aq. NaCl, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was dissolved in $CHCl_3$ (15 mL) including Et_3N (catalytic amount), stirred at 50 °C for 30 min and concentrated in vacuo. The residue was rinsed with $CHCl_3$ to remove N,N′-diphenylurea by filtration and the filtrate was concentrated in vacuo. The residue was chromatographed on silica gel and eluted with hexane−AcOEt (4:1) to give **6ab** (753 mg, 99% yield) as a yellow solid.

6ab: pale-yellow granules melted at 103.0−104.0 °C (from CH_2Cl_2) (lit.,[20] 101.5−102 °C). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.44−7.54 (m, 3H), 7.58−7.68 (m, 2H), 7.74 (ddd, *J* = 8.6, 6.8, and 1.3 Hz, 1H), 7.91 (dd, *J* = 7.3 and 1.2 Hz, 1H), 7.93 (d with fine coupling, *J* = 8.3 Hz, 1H), 8.03 (d with fine coupling, *J* = 8.3 Hz, 2H), 8.11 (d, *J* = 8.2 Hz, 1H), 9.31 (d with fine coupling, *J* = 8.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 124.4, 125.9, 127.1, 128.5, 128.7, 129.0 (×2), 129.4, 129.9 (×2), 130.9, 133.3, 134.0, 134.7, 135.0, 135.9, 194.5, 197.1 ppm. IR (KBr): $\tilde{\nu}$ 3065, 1673, 1661, 1594, 1572 cm^{-1}. Mass (*m*/*z*, %): 260 (M^+, 9), 156 (11), 155 (100), 127 (68), 126 (14), 105 (17), 77 (29). HRMS (ESI): 283.0740, calcd for $C_{18}H_{12}O_2Na$ $[M + Na]^+$ 283.0735.

According to the procedure described above, unsymmetrical diketones **6ab**, **6bc**, **6bf**, **6cf**, **6ag** and **6ak** were synthesized by the reaction of 5-hydroxy-5-(1-naphthyl)-*N*,*N*′-diphenylimidazolidine-2,4-dione (**7b**) with phenyllithium (**9a**), **7b** with 2-naphtyllithium (**9c**), **7b** with butyllithium (**9f**), 5-hydroxy-5-(2-naphthyl)-*N*,*N*′-diphenylimidazolidine-2,4-dione (**7c**) with butyllithium (**9f**), 5-hydroxy-5-(4-methylphenyl)ethynyl-*N*,*N*′-diphenylimidazolidine-2,4-dione (**7g**) with **9a**, 5-tert-butyl-5-hydroxy-*N*,*N*′-diphenylimidazolidine-2,4-dione (**7k**) with phenyllithium (**9a**), respectively. The yields were 88% for **6ab** (from **7b** with **9a**), 83% for **6bc**, 91% for **6bf**, 97% for **6cf**, 98% for **6ag**, and 62% for **6ak**.

6bc: yellow granules melted at 140.0−141.5 °C (from CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.46 (dd, *J* = 8.0 and 7.6 Hz, 1H), 7.53 (dd, *J* = 8.2 and 7.1 Hz, 1H), 7.60−7.66 (m, 2H), 7.76 (dd with fine coupling, *J* = 8.7 and 6.9 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.92−7.98 (m, 3H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.14 (dd with fine coupling, *J* = 8.7 and 1.6 Hz, 1H), 8.48 (s, 1H), 9.37 (d, *J* = 8.7 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 123.9, 124.4, 126.0, 127.1, 127.1, 127.9, 128.8, 128.8, 129.1, 129.4 (×2), 129.9, 130.7, 131.0, 132.4, 133.4, 134.1, 135.2, 135.9, 136.3, 194.7, 197.1 ppm. IR (KBr): $\tilde{\nu}$ 3380, 3044, 1780, 1722, 1597 cm^{-1} Mass (*m*/*z*, %): 310 (M^+, 11), 156 (12), 155 (100), 128 (11), 127 (97), 126 (20). HRMS (ESI): 333.0898, calcd for $C_{22}H_{14}O_2Na$ $[M + Na]^+$ 333.0892.

6bf: yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ_H 0.97 (t, *J* = 7.3 Hz, 3H), 1.41−1.50 (m, 2H), 1.71−1.78 (m, 2H), 2.97 (t, *J* = 7.4 Hz, 2H), 7.53 (dd, *J* = 8.2 and 7.3 Hz, 1 H), 7.59 (ddd, *J* = 8.2, 6.9, and 1.1 Hz, 1H), 7.68 (ddd, *J* = 8.5, 6.9, and 1.4 Hz, 1 H), 7.87 (dd, *J* = 7.3 and 1.4 Hz, 1H), 7.92 (d with fine coupling, *J* = 8.2 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 1 H), 8.96 (d, *J* = 8.5 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 13.8, 22.4, 25.1, 38.6, 124.2, 125.7, 126.9, 128.1, 128.7, 129.0, 131.1, 133.6, 134.1, 135.3, 195.6, 204.0 ppm. IR (liquid film): $\tilde{\nu}$ 2959, 1710, 1666 cm^{-1}. Mass (*m*/*z*, %): 240 (M^+, 89), 197 (16), 169 (19), 157 (11), 156 (100), 155 (99), 128 (95), 127 (97), 126 (94), 101 (44), 85 (16), 77 (50), 76 (14), 75 (25), 74 (12), 57 (31), 51 (14). HRMS (ESI): 263.1037, calcd for $C_{16}H_{16}O_2Na$ $[M + Na]^+$ 263.1048.

6cf: yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ_H 0.96 (t, *J* = 7.3 Hz, 3H), 1.39−1.48 (m, 2H), 1.69−1.77 (m, 2H), 2.94 (t, *J* = 7.3 Hz, 2H), 7.57 (dd, *J* = 8.2 and 6.9 Hz, 1H), 7.64 (dd, *J* = 8.2 and 6.9 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 8.03 (dd, *J* = 8.7 and 1.8 Hz, 1H), 8.51 (s with fine coupling, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 13.8, 22.3, 25.0, 38.6, 124.2, 127.0, 127.9, 128.9, 129.2, 129.4, 130.0, 132.3, 133.5, 136.2, 192.5, 203.7 ppm. IR (liquid film):$\tilde{\nu}$ 2959, 1711, 1668, 1626 cm^{-1}. Mass (*m*/*z*, %): 240 (M^+, 7), 156 (12), 155 (100), 127 (66), 126 (12). HRMS (ESI): 263.1061, calcd for $C_{16}H_{16}O_2Na$ $[M + Na]^+$ 263.1048.

6ag: yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ_H 2.40 (s, 3H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.51−7.57 (m, 4H), 7.67 (t with fine coupling, *J* = 7.3 Hz, 1H), 8.08 (d with fine coupling, *J* = 7.3 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.9, 87.1, 100.1, 116.1, 128.9 (×2), 129.6 (×2), 130.5 (×2), 131.7, 133.7 (×2), 134.8, 142.7, 178.6, 188.6 ppm. IR (liquid film): $\tilde{\nu}$Z 2186, 1679, 1657, 1601 cm^{-1}. Mass (*m*/*z*, %): 248 (M^+, 2), 192 (27), 144 (11), 143 (100), 115 (13), 105 (58), 77 (55). HRMS (ESI): 271.0738, calcd for $C_{17}H_{12}O_2Na$ $[M + Na]^+$ 271.0735.

6ak: yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.31 (s, 9H), 7.50 (dd, *J* = 7.9 and 7.4 Hz, 2H), 7.64 (t with fine coupling, *J* = 7.4 Hz, 1H), 7.83 (d with fine coupling, *J* = 7.9 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 26.2 (×3), 42.6, 128.9 (×2), 129.5 (×2), 132.9, 134.5, 195.4, 210.9 ppm. (lit.,[3a] 100 MHz, $CDCl_3$ δ_C 26.2, 42.6, 128.9, 129.5, 132.8, 134.5, 195.4, 210.9 ppm). IR (liquid film): $\tilde{\nu}$ 2969, 1704, 1676, 1597 cm^{-1}. Mass (*m*/*z*, %): 190 (M^+, 3), 105 (100), 77 (51), 57 (23).

Synthesis of 2-Oxo-2-naphthylethanoic Acid (8c) from 5-Hydroxy-5-(2-naphthyl)-*N*,*N*′-diphenylimidazolidine-2,4-dione (7c). *Typical Procedure.* NaOH in H_2O (4 M, 3 mL) was added to a solution of 5-hydroxy-5-(2-naphthyl)-*N*,*N*′-diphenylimidazolidine-2,4-dione (**7c**) (1.16 g, 2.94 mmol) in MeOH (10 mL) at room temperature and heated 50 °C for 1 h. The reaction mixture poured into H_2O and extracted with AcOEt to give organic layer including *N*,*N*′-diphenylurea. The thus-obtained aqueous layer was acidified with 1N HCl, and then extracted with AcOEt. The AcOEt solution was washed with sat. aq. NaCl, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was crystallized from hexane−CH_2Cl_2 to give **8c** (525 mg, 89% yield) as a yellow solid.

8c: yellow granules melted at 92.0−93.0 °C (from AcOEt−hexane) (lit.,[21] 92− 93 °C from xylene). ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.59 (dd with fine coupling, *J* = 8.2 and 6.9 Hz, 1H), 7.68 (dd with fine coupling, *J* = 8.2 and 6.9 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.7 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 8.18 (d with fine coupling, *J* = 8.7 Hz, 1H), 8.95−9.17 (m, 1H), 9.09 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 124.4, 127.2, 127.8, 128.9, 129.0, 130.0, 130.3, 132.2, 135.2, 136.5, 163.3, 184.3 ppm. IR (KBr): $\tilde{\nu}$ 3062, 3006, 2964, 1747, 1653, 1616, 1588 cm^{-1}. HRMS (ESI negative): 199.0345, calcd for $C_{12}H_7O_3$ $[M - H]^-$ 199.0395.

According to the procedure described above, 5-substituted 5-hydroxyimidazolidine-2,4-diones (**7a**, **7b**, **7d**, **7e**, **7i** and **7k**) were individually hydrolyzed to give the corresponding α-ketocarboxylic acids **8a** (98%), **8b** (94%), **8d** (78%), **8e** (39%), **8i** (84%), and **8k** (96%): for hydrolysis of **7e**, **8e** was produced along with 2-oxo-*N*-phenyl-2-(2,4,6-trimethylphenyl)acetamide (**14**) (54%). Hydroxyimidazolidinedione **7g** was similarly hydrolyzed to give 5-(4-methylphenyl)furan-2,3-dione in 80% yield instead of the expected keto carboxylic acid (**8g**).

8a: yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.53 (dd, J = 8.2 and 7.6 Hz, 2H), 7.70 (td, J = 7.6 and 1.1 Hz, 1H), 8.23 (dd, J = 8.2 and 1.1 Hz, 2H), 9.77 (s, 1H) ppm. (lit.,[21] $CDCl_3$, δ_H 7.51 (t, J = 7.8 Hz, 2H), 7.65 (t, J = 7.8 Hz, 1H), 8.14 (d, J = 7.8 Hz, 2H), 12.47 (s, 1H) ppm). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 129.0 (x2), 130.9 (x2), 131.7, 135.6, 163.8, 184.9 ppm. IR (liquid film): $\tilde{\nu}$ 3496, 1741, 1686, 1596 cm^{-1}. HRMS (ESI negative): 299.0570, calcd for $C_{16}H_{11}O_6$ $[2M-H]^-$ 299.0556.

8b: colorless needles melted at 102.0−103.0 °C (from CH_2Cl_2−hexane) (lit.,[22] 112−114 °C). ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.51−7.62 (m, 2H), 7.68 (dd, *J* = 8.2 and 6.9 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 7.3 Hz, 1H), 8.32 (d, *J* = 6.9 Hz, 1H), 8.93 (d, *J* = 8.7 Hz, 1H), 10.51−11.06 (m, 1H) ppm. ^{13}C NMR (125 MHz,

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$CDCl_3$): δ_C 124.3, 125.3, 127.1, 127.2, 128.9, 129.5, 131.0, 133.8, 134.9, 136.5, 165.4, 187.0 ppm. IR (KBr): $\tilde{\nu}$Z 3142, 1701, 1681, 1573 cm^{-1}. HRMS (ESI negative): 199.0346, calcd for $C_{12}H_7O_3$ $[M - H]^-$ 199.0395.

8d: pale yellow solid melted at >300 °C. ^1H NMR (500 MHz, DMSO-d_6): δ_H 7.49−7.56 (m, 4H), 8.07−8.15 (m, 2H), 8.18−8.27 (m, 2H), 8.64 (s, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 125.7 (×2), 126.1 (×2), 126.4 (×2), 127.9, 128.0 (×2), 128.5 (×2), 130.8 (×2), 136.4, 169.1, 203.6 ppm. IR (KBr): $\tilde{\nu}$ 3399, 3052, 1673, 1645 cm^{-1}. HRMS (ESI negative): 249.0534, calcd for $C_{16}H_9O_3$ $[M - H]^-$ 249.0552.

8e: pale yellow columns melted at 119.0−120.0 °C (from CH_2Cl_2−hexane) (lit.,[23] 118.8−119.4 °C from hexane). ^1H NMR (500 MHz, $CDCl_3$): δ_H 2.25 (s, 6H), 2.30 (s, 3H), 6.89 (s, 2H), 10.4 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 19.6 (×2), 21.2, 129.1 (×2), 131.6, 136.4 (×2), 141.5, 163.4, 192.0 ppm. IR (KBr): $\tilde{\nu}$ 3042, 2961, 2926, 1721, 1692, 1609 cm^{-1}. HRMS (ESI negative): 191.0695, calcd for $C_{11}H_{11}O_3$ $[M - H]^-$ 191.0708.

14: colorless needles melted at 136.0−137.5 °C (from CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ_H 2.23 (s, 6H), 2.31 (s, 3H), 6.90 (s, 2H), 7.19 (t with fine coupling, J = 7.4 Hz, 1H), 7.39 (dd with fine coupling, J = 8.7 and 7.4 Hz, 2H), 7.70 (d with fine coupling, J = 8.7 Hz, 2H), 8.87 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 19.5 (×2), 21.2, 119.6 (×2), 125.2, 128.7 (×2), 129.2 (×2), 132.6, 135.6 (×2), 136.6, 140.4, 158.0, 197.3 ppm. IR (KBr): $\tilde{\nu}$ 3287, 3135, 3060, 3018, 2975, 2920, 1685, 1674, 1674, 1600, 1542 cm^{-1}. Mass (m/z, %): 267 (M^+, 3), 148 (11), 147 (100), 119 (17), 91 (10). HRMS (ESI): 268.1324, calcd for $C_{17}H_{18}NO_2$ $[M + H]^+$ 268.1338, 290.1154, calcd for $C_{17}H_{17}NO_2Na$ $[M + Na]^+$ 290.1157. Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.09; H, 6.29; N, 5.13.

5-(4-Methylphenyl)furan-2,3-dione as a Cyclized Form of 8g. Colorless needles were melted at 142.5− 144.0 °C (from $CHCl_3$) (lit.,[24] 136−137 °C (decom.)). ^1H NMR (500 MHz, $CDCl_3$): δ_H 2.45 (s, 3H), 7.15 (s, 1H), 7.32 (d, J = 8.2 Hz, 2H), 7.92 (d, J = 8.2 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.8, 95.3, 128.1 (×2), 129.8 (×2), 130.6, 145.6 (×2), 162.6, 187.6 ppm. IR (KBr): $\tilde{\nu}$ 1700, 1604 cm^{-1}. Mass (m/z, %): 188 (M^+, 1), 162 (11), 161 (100), 119 (17).

8i: orange granules melted at 183.0−185.0 °C (from AcOEt−hexane) (lit.,[25] 170−172 °C from ethanol). ^1H NMR (500 MHz, $CDCl_3$): δ_H 8.09−8.15 (m, 2H), 8.23 (d, J = 8.2 Hz, 1H), 8.28 (d, J = 8.7 Hz, 1H), 8.31−8.38 (m, 3H), 8.90 (d, J = 8.2 Hz, 1H), 9.17 (d, J = 9.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, 123.8, 123.9, 124.0, 124.2, 124.9, 126.8, 127.2, 127.3, 127.6, 130.3, 130.9, 131.4 (×2), 131.5, 132.3, 136.4, 161.5, 186.4 ppm. IR (KBr): $\tilde{\nu}$ 3466, 3013, 1712, 1666, 1592 cm^{-1}. HRMS (ESI negative): 273.0600, calcd for $C_{18}H_9O_3$ $[M - H]^-$ 273.0552.

8k: colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ_H 1.34 (s, 9H), 7.81−8.47 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 25.6 (×3), 42.5, 164.2, 202.0 ppm. (lit.,[26] 100 MHz, $CDCl_3$, 25.6 (×3), 42.5, 163.7, 201.9 ppm. IR (liquid film): $\tilde{\nu}$ 3538, 2977, 1717 cm^{-1}. HRMS (ESI negative): 259.1185, calcd for $C_{12}H_{19}O_6$ $[2M - H]^-$ 259.1182.

■ ASSOCIATED CONTENT

Supporting Information

^1H NMR/^{13}C NMR spectra of **5g**, **7a**, **7b**, **7c**, **7d**, **7e**, **7g**, **7i**, **7j**, **7k**, **6bc**, **6bf**, **6cf**, **6ag** and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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