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Selectfluor-Mediated Simultaneous Cleavage of C−O and C−C Bonds in α,β-Epoxy Ketones Under Transition-Metal-Free Conditions: A Route to 1,2-Diketones

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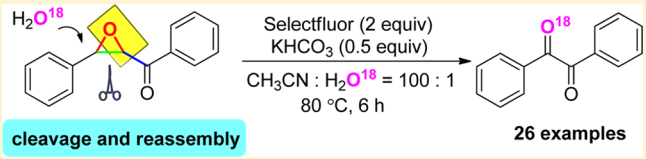
Supporting Information

ABSTRACT: Selectfluor-mediated simultaneous cleavage of C−O and C−C bonds in α,β-epoxy ketones has been successfully achieved under transition-metal-free conditions. The reaction gives 1,2-diketone compounds in moderate to good yields involving a ring-opening/benzoyl rearrangement/C−C bond cleavage sequence under oxidative conditions.



Carbon−carbon bonds represent the most ubiquitous chemical bond in organic molecules. However, achieving efficient and selective cleavage of carbon−carbon single bonds for chemical transformations remains one of the most challenging tasks faced by chemists.[1] In the past few decades, transition-metal-mediated reactions have been widely adopted to accomplish this goal (e.g., transition-metal-catalyzed oxidative addition, β-carbon elimination, and decarbonylation reactions, and so forth).[1,2] Recently, the cleavage of C−C single bonds under transition-metal-free conditions has received increasing attention because such procedures generally have obvious advantages in terms of cost, nontoxicity, and environmental compatibility.[3] Therefore, it is highly desirable to develop facile and transition-metal-free approaches for C−C single bond cleavage.

Epoxide derivatives are a class of three-membered cyclic ethers that can serve as important and versatile building blocks in organic synthesis.[4] To date, the dominant research on the application of epoxides in organic synthesis generally focuses on ring-opening reactions via facile C−O bond cleavage.[4] However, reactions involving the C−C bond cleavage of epoxide motifs are much more difficult and have been less documented due to the harsh conditions required.[5−8] Several limited examples are (1) Lewis acid-catalyzed cycloaddition reactions of epoxide derivatives with certain dipolar reagents involving carbonyl ylide or 1,4-dipole intermediates (Scheme 1a),[6] (2) iron-promoted tandem reaction of styrene oxides with anilines to give 3-arylquinolines involving C−C bond cleavage (Scheme 1b),[7] and (3) copper-catalyzed aniline-assisted oxidative cleavage of C−C bonds in epoxides leading to aryl ketones (Scheme 1c).[8] As part of our ongoing research interest on C−C bond cleavage,[9a] we present herein Selectfluor-mediated simultaneous cleavage of C−O and C−C bonds in α,β-epoxy ketones leading to 1,2-diketone compounds in moderate to good yields under transition-metal-free conditions (Scheme 1d).[10,11]

Our findings originated from our recent research interest in Cu(0)/Selectfluor system-mediated tandem reactions.[9] When we subjected α,β-epoxy ketone **1a** to the Cu(0)/Selectfluor system (Cu(0) powder: 5 mol %; Selectfluor: 2.0 equiv) in acetonitrile at 80 °C for 6 h, an unexpected product, 1,2-diketone **2a**, was obtained in 53% yield (entry 1, Table 1). 1,2-Diketone compounds serve as important biologically active candidates as well as synthetic intermediates for various chemical transformations.[10,12] Our particular interest in the novel transformation of α,β-epoxy ketones to 1,2-diketones as well as the curiosity of the mechanism for the C−C bond cleavage stimulated us to further optimize the reaction conditions (Table 1). It was found that the employment of other Lewis acid catalysts, such as CuBr, $CuCl_2·2H_2O$, $PdCl_2$, $FeCl_3$, Ph_3PAuCl, and $Ph_3PAuNTf_2$, did not significantly improve the yield of **2a** (entries 2−7, Table 1). Surprisingly, the reaction gave an even better result when no transition-metal catalyst was used (entry 8, Table 1). The employment of 2 equiv of Selectfluor was indispensable, otherwise, the conversion of **1a** to **2a** would be low (entry 9, Table 1). A range of other oxidants were investigated and all displayed lower effectiveness than Selectfluor (entries 10−14, Table 1), demonstrating the unique role of Selectfluor in the reaction. Note that the addition of 0.5 equiv of $KHCO_3$ slightly increased the yield of **2a** (67%, entry 15, Table 1). However, other base additives, such as K_2CO_3, Na_2CO_3, $NaHCO_3$, and Et_3N, could not increase the yield of **2a** (entries 16−19, Table 1). A series of solvents were screened for the reaction, 100:1 (v/v) acetonitrile−water has proven to be the best choice for the transformation (entries 15, 24, 26, 27 vs 20, Table 1). An attempt to conduct the reaction at a lower temperature only gave a reduced yield of **2a** (50 °C, 47%, entry 25, Table 1). The addition of several strong Lewis acids, such as $Zn(OTf)_2$,

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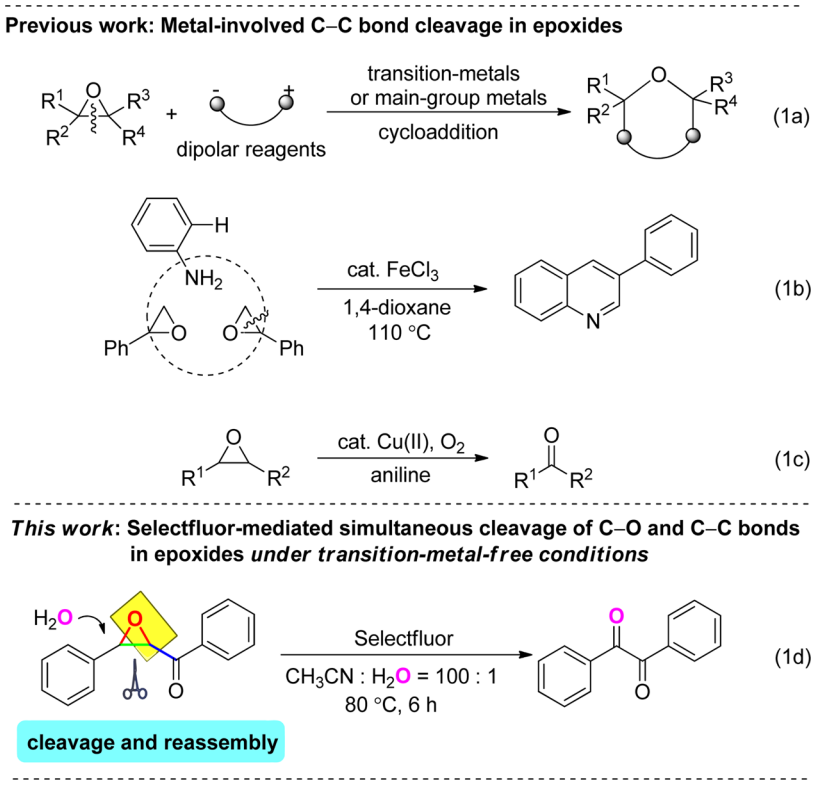
Scheme 1. Reactions Involving C−C Bond Cleavage in Epoxide Derivatives



$In(OTf)_3$, and $Yb(OTf)_3$, to the reaction mixture did not increase the yield of **2a** (entries 21−23, Table 1).

With the optimized reaction conditions established, we began to investigate the generality and scope of this method for the synthesis of diketones (Table 2). As seen from Table 2, a wide range of *α,β*-epoxy ketones **1** bearing aryl rings with various substitution patterns (*ortho*-, *meta*-, or *para*-) were able to undergo C−C bond cleavage and reassemble into diketones **2** in moderate to good yields (40−85%, entries 1−26, Table 2). It was found that both electron-donating and -withdrawing substituents in the aryl ring of *α,β*-epoxy ketones **1** were compatible with the reaction conditions, among which include methyl, halo (F, Cl, Br), aryl, and nitro groups. Note that epoxy ketone **1l** bearing a heterocycle was also well-tolerated under the reaction conditions, and the corresponding diketone was obtained in 57% yield (entry 12, Table 2). It seemed that the steric hindrance on the aryl ring of **1** had no obvious effect on the reaction outcome. For example, epoxy ketone **1o** possessing a large [1,1′-biphenyl]-2-yl group also worked well to give the desired product in moderate yield (61%, **2o**, entry 15, Table 2). Epoxy ketone **1m** derived from aryl aldehyde and aliphatic ketone was also a suitable substrate for the reaction (63%, **2i**, entry 13, Table 2), whereas epoxy ketone **1za** derived from aliphatic aldehyde and acetophenone failed to give the desired product (entry 27, Table 2). The inertness of **1w** may be ascribed to the large steric hindrance of the *t*-butyl group to allow the reaction as well as the requirement for nonenolizable substrates in the present reaction.

When we subjected aryloxiranyl carboxylates **3** to the standard reaction conditions, the reaction only gave a trace amount of 1,2-dicarbonyl compounds **4**, whereas a mixture of diketo ester **5** and its hydrate form **5′** were isolated as the predominant products (R = H, **5a**/**5′a**: 85%; R = 4-Cl, **5b**/**5′b**: 77%; Scheme 2).[13] Although these reactions failed to give 1,2-dicarbonyl compounds **4**, the formation of diketo ester **5** led us to speculate that 1,2,3-trione might be an intermediate for the generation of diketone **2** from *α,β*-epoxy ketones **1**.

To test the above speculation, we synthesized 1,2,3-trione **6** according to the reported procedure.[13] Note that there is also an equilibrium between **6** and its hydrate form **6′**. When the mixture of **6** and **6′** was subjected to the standard reaction conditions, **2a** was indeed produced in 62% yield (eq 1, Scheme 3), thus confirming that 1,2,3-trione was an intermediate for the formation of **2**. In addition, an O^{18}-labeling experiment was conducted using CH_3CN-H_2O^{18} (100:1, v/v) as the solvent and mono-O^{18}-incorporated product **2a**-O^{18} was obtained in 81% yield (eq 2, Scheme 3; see also the Supporting Information), suggesting that one of the oxygen atoms in **2a** originated from water. Furthermore, the addition of TEMPO, a radical scavenger,[14] to the reactants showed no effect on the final outcome (eq 3, Scheme 3), suggesting that no radical pathway was involved in the reaction.

On the basis of the above mechanistic studies and previous reports,[15−18] a plausible mechanism for the Selectfluor-mediated simultaneous cleavage of C−O and C−C bonds in epoxy ketone **1a** leading to diketone **2a** is depicted in Scheme 4. It was reported that Selectfluor could serve as an efficient Lewis acid catalyst for the hydrolysis of acetals, dithia-acetals, and tetrahydropyranyl ethers[15] as well as for the ring-opening of epoxides with thiocyanates.[16] Thus, for the first step, the reaction may undergo ring-opening of **1a** with water promoted by Selectfluor, leading to an intermediate **I**.[16] Subsequent oxidation of **I** by Selectfluor gave 1,2,3-trione intermediate **6**.[13,17] Then, **6** may undergo a 1,2-Wagner−Meerwein-type rearrangement of a benzoyl group through F^+- or H^+-assisted activation of the carbonyl group in **6** to yield intermediate **II**.[18] Finally, a carbon monoxide was released from intermediate **II** followed by a proton abstraction with a base from resulting

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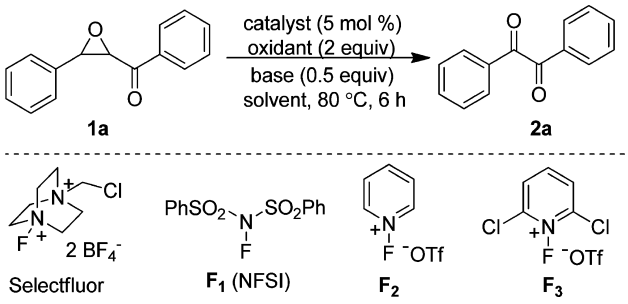
Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	oxidant	base	solvent	yield (%)
1	Cu(0)	Selectfluor		CH_3CN	53
2	CuBr	Selectfluor		CH_3CN	47
3	$CuCl_2·2H_2O$	Selectfluor		CH_3CN	43
4	$PdCl_2$	Selectfluor		CH_3CN	49
5	$FeCl_3$	Selectfluor		CH_3CN	51
6	Ph_3PAuCl	Selectfluor		CH_3CN	52
7	$Ph_3PAuNTf_2$	Selectfluor		CH_3CN	50
8		Selectfluor		CH_3CN	64
9		Selectfluor		CH_3CN	43[b]
10		F_1		CH_3CN	34
11		F_2		CH_3CN	19
12		F_3		CH_3CN	0
13		$PhI(OAc)_2$		CH_3CN	trace
14		DDQ		CH_3CN	40
15		Selectfluor	$KHCO_3$	CH_3CN	67
16		Selectfluor	K_2CO_3	CH_3CN	56
17		Selectfluor	Na_2CO_3	CH_3CN	51
18		Selectfluor	$NaHCO_3$	CH_3CN	54
19		Selectfluor	Et_3N	CH_3CN	trace
20		Selectfluor	$KHCO_3$	$CH_3CN:H_2O$ = 100:1	83
21	$Zn(OTf)_2$	Selectfluor	$KHCO_3$	$CH_3CN:H_2O$ = 100:1	80
22	$In(OTf)_3$	Selectfluor	$KHCO_3$	$CH_3CN:H_2O$ = 100:1	79
23	$Yb(OTf)_3$	Selectfluor	$KHCO_3$	$CH_3CN:H_2O$ = 100:1	83
24		Selectfluor	$KHCO_3$	solvent[c]	<20
25		Selectfluor	$KHCO_3$	$CH_3CN:H_2O$ = 100:1	47[d]
26		Selectfluor	$KHCO_3$	$CH_2Cl_2:H_2O$ = 100:1	trace
27		Selectfluor	$KHCO_3$	toluene:H_2O = 100:1	trace

[a]Reaction conditions: **1a** (0.3 mmol), catalyst (0.015 mmol), oxidant (0.6 mmol), base (0.15 mmol) in 3 mL of solvent at 80 °C for 6 h unless otherwise noted. [b]The reaction was conducted in the presence of 1 equiv of Selectfluor. [c]1,4-Dioxane, DMF, THF, toluene, and CH_2Cl_2 were used as the solvent, respectively. [d]The reaction was performed at 50 °C.

intermediate **III** to afford 1,2-diketone **2a**.[18] An attempt to detect the released CO by a CO gas sensor was indeed successful (see the Supporting Information).

In summary, we have realized a Selectfluor-mediated simultaneous cleavage of C−O and C−C in *α,β*-epoxy ketones under transition-metal-free conditions. The present protocol provides an efficient route to access 1,2-diketone compounds from easily available *α,β*-epoxy ketones. Mechanistic studies disclosed that the reaction may proceed via an interesting ring opening/benzoyl arrangement/C−C bond cleavage sequence and that Selectfluor plays a unique role in the reaction.

EXPERIMENTAL SECTION

General Information. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a spectrometer at 25 °C in $CDCl_3$ at 500 (or 400) MHz and 125 (or 100) MHz, respectively, with TMS as the internal standard. Chemical shifts (δ) are expressed in ppm, and coupling constants J are given in Hz. The IR spectra were recorded on an FT-IR spectrometer. GC-MS experiments were performed with an EI source, high resolution mass spectra (HRMS) were obtained on a TOF MS instrument with an EI or ESI source. Elemental analysis was performed on an EA-1110 instrument. The CO gas sensor used was an MOT 200-A model.

The *α,β*-epoxy ketones (**1a**−**w**)[19] and the oxiranyl carboxylates (**3a**, **b**)[20] were prepared according to the reported literature.

*General Procedure for the Synthesis of 1,2-Diketones **2** from Epoxy Ketones **1** Mediated by Selectfluor.* To a 15 mL Schlenk flask were added epoxy ketones **1** (0.3 mmol), Selectfluor (106.3 mg, 0.3 mmol, 1 equiv), $KHCO_3$ (15.0 mg, 0.15 mmol), and a mixture of CH_3CN/H_2O (3 mL; $CH_3CN:H_2O$ = 100:1 (v/v)). Then, the resulting mixture was stirred at 80 °C for 2 h. To the flask was added another 1 equiv of Selectfluor, and the reaction mixture was stirred at 80 °C for another 4 h. After being cooled to room temperature, the mixture was filtered with Celite, and the filtrate was evaporated in vacuum. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1, v/v) as the eluent to give pure **2**.

*1,2-Diphenyl-ethane-1,2-dione (**2a**).*[21] Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a pale yellow solid (52.3 mg, 83%); mp 94−96 °C (lit.[21] mp 95−97 °C); IR (KBr) ν

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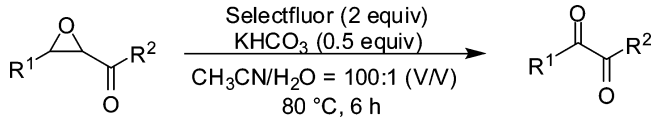
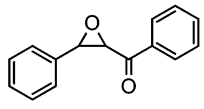
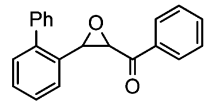
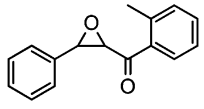
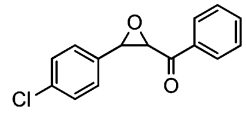
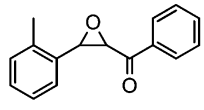
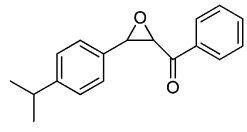
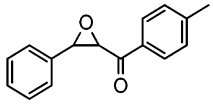
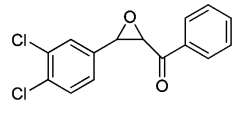
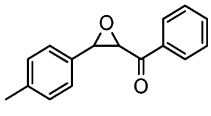
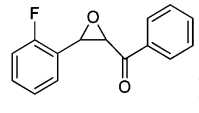
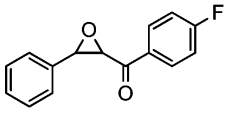
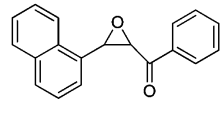
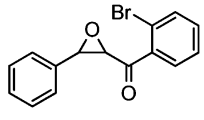
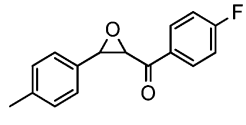
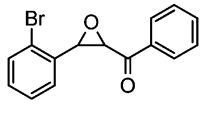
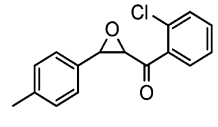
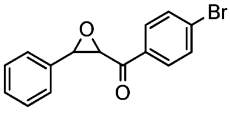
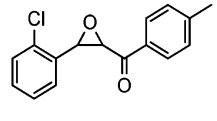
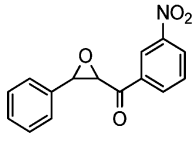
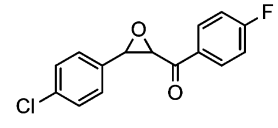
Table 2. Selectfluor-Mediated Oxidative Cleavage and Reassembly of 1 into 2[a]



1 2

entry	substrate	product	yield (%)	entry	substrate	product	yield (%)
1	 **1a**	**2a**	83	15	 **1o**	**2o**	61
2	 **1b**	**2b**	55	16	 **1p**	**2p**	80
3	 **1c**	**2b**	71	17	 **1q**	**2q**	59
4	 **1d**	**2d**	75	18	 **1r**	**2r**	43
5	 **1e**	**2d**	61	19	 **1s**	**2s**	73
6	 **1f**	**2f**	77	20	 **1t**	**2t**	51
7	 **1g**	**2g**	57	21	 **1u**	**2u**	68
8	 **1h**	**2g**	85	22	 **1v**	**2v**	60
9	 **1i**	**2i**	73	23	 **1w**	**2v**	77
10	 **1j**	**2j**	80	24	 **1x**	**2x**	73

[a]Reaction conditions: **1** (0.3 mmol), Selectfluor (0.6 mmol), $KHCO_3$ (0.15 mmol) in CH_3CN/H_2O mixture (3 mL; CH_3CN/H_2O = 100:1 (v/v) at 80 °C for 6 h.

1657 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.00 (d, J = 7.5 Hz, 4H), 7.68 (t, J = 7.5 Hz, 2H), 7.53 (t, J = 7.5 Hz, 4H); MS (EI, 70 eV) m/z (%) 210 (20) [M^+], 105 (100).

1-Phenyl-2-o-tolyl-ethane-1,2-dione (**2b**).[22] Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a pale yellow solid (37.0 mg, 55%, from **1b**; 47.8 mg, 71%, from **1c**); mp 55−57 °C (lit.[22]

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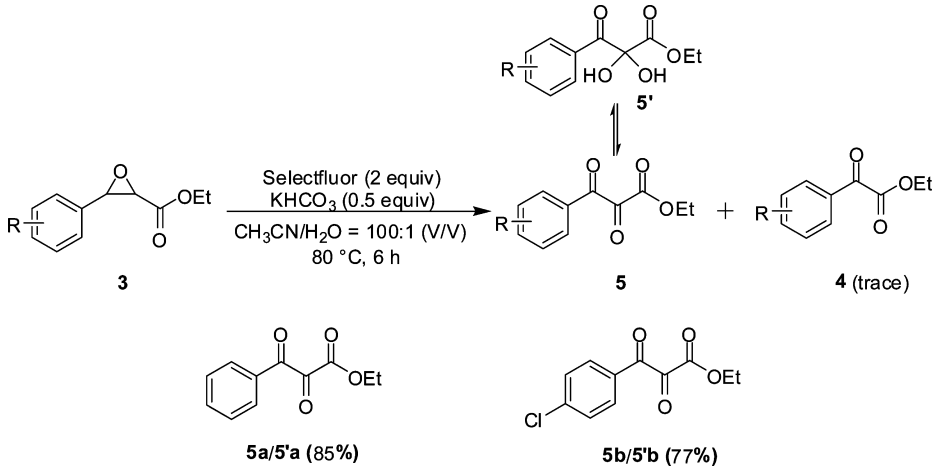
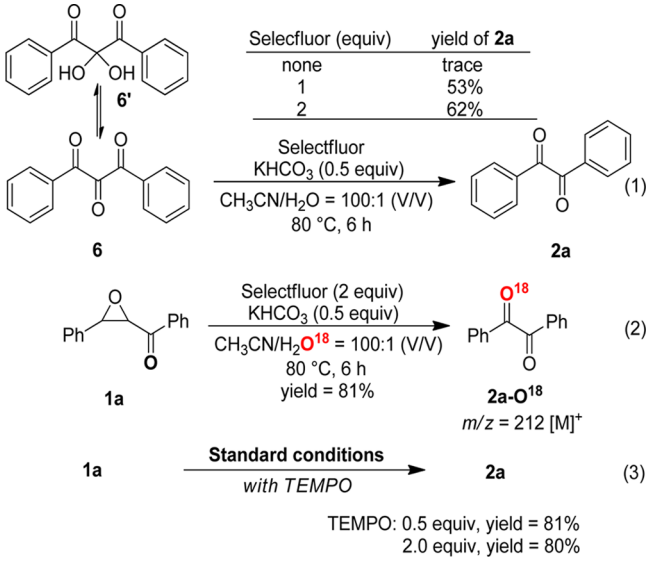
Scheme 2. Reaction of Ethyl 3-Aryloxirane-2-carboxylates 3 under the Standard Conditions



Scheme 3. Mechanistic Studies



mp 56–57 °C); IR (KBr) ν 1672 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.00–7.98 (m, 2H), 7.69–7.65 (m, 2H), 7.55–7.50 (m, 3H), 7.37–7.29 (m, 2H), 2.73 (s, 3H); MS (EI, 70 eV) m/z (%) 224 (3) [M$^+$], 119 (100).

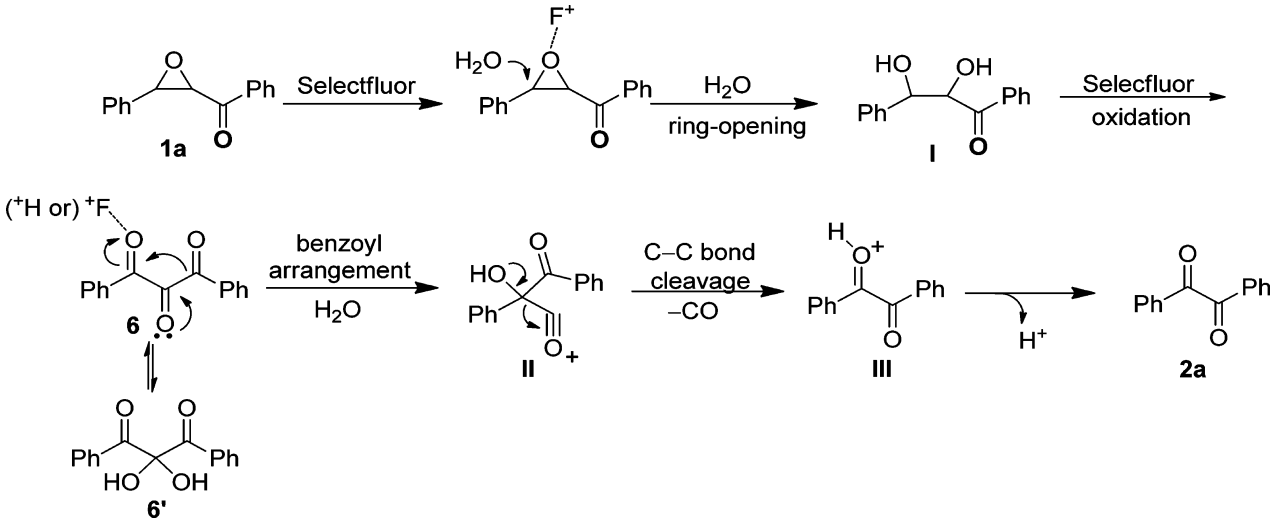
1-Phenyl-2-p-tolylethane-1,2-dione (**2d**).[23] Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a pale yellow solid (50.5 mg, 75%, from **1d**; 41.1 mg, 61%, from **1e**); mp 29–30 °C (lit.[23] mp 30–31 °C); IR (KBr) ν 1674 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.98 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.66 (t, J = 7.5 Hz, 1H), 7.53–7.50 (m, 2H), 7.32 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H); MS (EI, 70 eV) m/z (%) 224 (3) [M$^+$], 119 (100).

1-(4-Fluorophenyl)-2-phenylethane-1,2-dione (**2f**).[24] Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a pale yellow solid (52.7 mg, 77%); mp 64–66 °C (lit.[24] mp 66–68 °C); IR (KBr) ν 1667 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04 (dd, J_1 = 9.0 Hz, J_2 = 5.5 Hz, 2H), 7.99 (d, J = 7.5 Hz, 2H), 7.69 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 8.0 Hz, 2H), 7.21 (t, J = 8.5 Hz, 2H); MS (EI, 70 eV) m/z (%) 228 (3) [M$^+$], 105 (100).

1-(2-Bromophenyl)-2-phenyl-1,2-ethanedione (**2g**).[25] Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a pale yellow solid (49.4 mg, 57%, from **1g**; 73.7 mg, 85%, from **1h**); mp 39–40 °C (lit.[25] mp 40–41 °C); IR (KBr) ν 1675 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.08–8.06 (m, 2H), 7.83–7.80 (m, 1H), 7.68–7.26 (m, 6H); MS (EI, 70 eV) m/z (%) 288 (3) [M$^+$], 105 (100).

1-(4-Bromophenyl)-2-phenylethane-1,2-dione (**2i**).[22] Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a pale

Scheme 4. Proposed Mechanism



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yellow solid (63.3 mg, 73%); mp 82−84 °C (lit.[22] mp 86−87 °C); IR (KBr) ν 1670 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.98 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 2H), 7.86 (d, J = 8.5 Hz, 2H), 7.69−7.68 (m, 3H), 7.56 (t, J = 8.0 Hz, 2H); MS (EI, 70 eV) m/z (%) 288 (1) [M^+], 105 (100).

*1-(3-Nitrophenyl)-2-phenyl-1,2-ethanedione (**2j**).*[26] Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a pale yellow solid (61.2 mg, 80% from **1j**; 30.6 mg, 40% from **1k**); mp 118−120 °C (lit.[26] mp 119−121 °C); IR (KBr) ν 1674 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.83 (t, J = 2.0 Hz, 1H), 8.53−8.50 (m, 1H), 8.34−8.31 (m, 1H), 8.03−8.00 (m, 2H), 7.77−7.70 (m, 2H), 7.58−7.54 (m, 2H); MS (EI, 70 eV) m/z (%) 255 (3) [M^+], 105 (100).

*1-Phenyl-2-(2-thienyl)-1,2-dione (**2l**).*[21] Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a pale yellow solid (37.0 mg, 57%); mp 59−61 °C (lit.[21] mp 62−63 °C); IR (KBr) ν 1649 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.06−8.04 (m, 2H), 7.85−7.81 (m, 2H), 7.69−7.64 (m, 1H), 7.54−7.50 (m, 2H), 7.21−7.18 (m, 1H); MS (EI, 70 eV) m/z (%) 216 (3) [M^+], 105 (100).

*1-Phenylpropane-1,2-dione (**2m**).*[27] Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a yellow oil (28.0 mg, 63%); IR (neat) ν 1674 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.03 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 2H), 7.68−7.64 (m, 1H), 7.53−7.50 (m, 2H), 2.54 (s, 3H); MS (EI, 70 eV) m/z (%) 148 (4) [M^+].

*1-(3-Methylphenyl)-2-phenyl-1,2-ethanedione (**2n**).*[28] Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a yellow solid (42.4 mg, 63%); mp 54−56 °C (lit.[28] mp 56−57 °C); IR (KBr) ν 1672 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.98 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.67 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H); MS (EI, 70 eV) m/z (%) 224 (3) [M^+], 119 (100).

*1-[1,1′-Biphenyl]-2-yl-2-phenyl-1,2-ethanedione (**2o**).* Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a pale yellow solid (52.4 mg, 61%); mp 78−80 °C; IR (KBr) ν 1672 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.96 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 7.79−7.78 (m, 2H), 7.67−7.64 (m, 1H), 7.57−7.54 (m, 2H), 7.42 (dd, J_1 = 7.5 Hz, J_2 = 0.5 Hz, 1H), 7.38−7.35 (m, 2H), 7.22−7.20 (m, 2H), 7.07−7.04 (m, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 195.7, 191.4, 143.6, 139.8, 135.2, 133.9, 132.9, 132.8, 130.6, 130.5, 129.8, 128.3, 128.1, 128.0, 127.7; MS (EI, 70 eV) m/z (%) 286 (3) [M^+], 105 (100); HRMS (EI) for $C_{20}H_{14}O_2$ [M^+] calcd 286.0994, found 286.0986; Anal. Calcd for $C_{20}H_{14}O_2$, C 83.90, H 4.93; found, C 83.68, H 4.97.

*1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (**2p**).*[26] Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a pale yellow solid (58.7 mg, 80%); mp 72−75 °C (lit.[26] mp 75−76 °C); IR (KBr) ν 1668 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.98 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 2H), 7.94 (dd, J_1 = 7.0 Hz, J_2 = 2.0 Hz, 2H), 7.69 (t, J = 7.0 Hz, 1H), 7.56−7.50 (m, 4H); MS (EI, 70 eV) m/z (%) 244 (2) [M^+], 105 (100).

*1-(4-Isopropylphenyl)-2-phenylethane-1,2-dione (**2q**).*[29] Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a pale yellow liquid (44.6 mg, 59%); IR (KBr) ν 1673 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.00−7.98 (m, 2H), 7.92 (d, J = 8.5 Hz, 2H), 7.66 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 3.04−2.96 (m, 1H), 1.29 (d, J = 7.0 Hz, 6H); $^{13}C\{^1H\}$ ($CDCl_3$, 125 MHz) δ 194.8, 194.3, 156.8, 134.8, 133.2, 131.0, 130.2, 129.9, 129.0, 127.2, 34.5, 23.5; MS (EI, 70 eV) m/z (%) 252 (4) [M^+], 105 (100).

*1-(3,4-Dichlorophenyl)-2-phenylethane-1,2-dione (**2r**).* Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a pale yellow solid (36.1 mg, 43%); mp 97−99 °C; IR (KBr) ν 1664 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.10 (d, J = 2.0 Hz, 1H), 7.98(dd, J_1 = 8.0 Hz, J_2 = 0.5 Hz, 2H), 7.82 (dd, J_1 = 8.5 Hz, J_2 = 1.0 Hz, 1H), 7.72−7.69 (m, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.55 (t, J = 8.0 Hz, 2H); $^{13}C\{^1H\}$ ($CDCl_3$, 125 MHz) δ 193.1, 191.8, 139.8, 135.3 (2C), 134.0, 132.6, 131.6, 131.2, 130.0, 129.2, 128.8; HRMS (EI) for $C_{14}H_8Cl_2O_2$ [M^+] calcd 277.9901, found 277.9910; Anal. Calcd for $C_{14}H_8Cl_2O_2$, C 60.24, H 2.89; found, C 60.42, H 2.92.

*1-(2-Fluorophenyl)-2-phenylethane-1,2-dione (**2s**).*[26] Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a pale yellow solid (49.9 mg, 73%); mp 60−62 °C (lit.[26] mp 63−64 °C); IR (KBr) ν 1682 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.09−8.05 (m, 1H), 8.00−7.98 (m, 2H), 7.70−7.64 (m, 2H), 7.56−7.53 (m, 2H), 7.38−7.35 (m, 1H), 7.16−7.12 (m, 1H); $^{13}C\{^1H\}$ ($CDCl_3$, 125 MHz) δ 193.1, 191.9, 162.9 (d, J = 257.5 Hz), 136.8 (d, J = 8.8 Hz), 134.7, 132.1 (d, J = 2.5 Hz), 130.8 (d, J = 1.3 Hz), 129.9, 129.0, 125.0 (d, J = 3.8 Hz), 122.4 (d, J = 10.0 Hz), 116.7 (d, J = 21.3 Hz); MS (EI, 70 eV) m/z (%) 228 (3) [M^+], 105 (100).

*1-(Naphthalen-1-yl)-2-phenylethane-1,2-dione (**2t**).*[30] Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a pale yellow solid (39.8 mg, 51%); mp 99−100 °C (lit.[30] mp 101.5−102 °C); IR (KBr) ν 1651 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.35 (d, J = 9.0 Hz, 1H), 8.11 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 7.5 Hz, 2H), 7.95−7.93 (m, 2H), 7.77−7.74 (m, 1H), 7.68−7.62 (m, 2H), 7.54−7.46 (m, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 197.1, 194.5, 135.9, 135.0, 134.7, 134.0, 133.3, 130.9, 129.9, 129.4, 129.0, 128.8, 128.6, 127.1, 125.8, 124.4; MS (EI, 70 eV) m/z (%) 260 (4) [M^+], 105 (100).

*1-(4-Fluorophenyl)-2-(p-tolyl)ethane-1,2-dione (**2u**).* Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a white solid (49.4 mg, 68%); mp 89−91 °C; IR (KBr) ν 1672 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.96−7.92 (m, 2H), 7.79 (dd, J_1 = 2.0 Hz, J_2 = 8.0 Hz, 2H), 7.24 (dd, J_1 = 2.0 Hz, J_2 = 8.0 Hz, 2H), 7.12−7.08 (m, 2H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 192.8, 191.9, 165.7 (d, J = 256 Hz), 145.4, 131.7 (d, J = 10.0 Hz), 129.5, 129.0, 128.9, 115.3 (d, J = 22.0 Hz); MS (EI, 70 eV) m/z (%) 242 (2) [M^+], 119 (100); HRMS (EI) for $C_{15}H_{11}FO_2$ [M^+] calcd 242.0743, found 242.0752; Anal. Calcd for $C_{15}H_{11}FO_2$, C 74.37, H 4.58; found, C 74.60, H 4.52.

*1-(2-Chlorophenyl)-2-p-tolylethane-1,2-dione (**2v**).*[31] Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a pale yellow solid (46.6 mg, 60%); mp 80−81 °C (lit.[31] mp 82−83 °C); IR (KBr) ν 1673 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.96−7.91 (m, 3H), 7.57−7.35 (m, 5H), 2.47 (s, 3H); MS (EI, 70 eV) m/z (%) 258 (2) [M^+], 119 (100).

*1-(4-Chlorophenyl)-2-(4-fluorophenyl)-1,2-ethanedione (**2x**).*[24] Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a white solid (57.5 mg, 73%); mp 143−145 °C (lit.[24] mp 144−146 °C); IR (KBr) ν 1662 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.04−7.99 (m, 2H), 7.94−7.91 (m, 2H), 7.51−7.48 (m, 2H), 7.22−7.19 (m, 2H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ 192.5, 192.0, 166.9 (d, J = 257.0 Hz), 141.8, 132.8 (d, J = 10.0 Hz), 131.2 (d, J = 2.0 Hz), 129.5, 129.34, 129.31, 116.5 (d, J = 22.0 Hz); MS (EI, 70 eV) m/z (%) 262 (4) [M^+], 123 (100).

*1-(4-Bromophenyl)-2-(4-methylphenyl)-1,2-dione (**2y**).* Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a pale yellow solid (64.6 mg, 71%); mp 131−133 °C; IR (KBr) ν 1664 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.85−7.84 (m, 4H), 7.68−7.66 (m, 2H), 7.33 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 193.6, 193.5, 146.5, 132.4, 131.9, 131.3, 130.43, 130.38, 130.1, 129.8, 22.0; MS (EI, 70 eV) m/z (%) 302 (1) [M^+], 119 (100); HRMS (EI) for $C_{15}H_{11}BrO_2$ [M^+] calcd 301.9942, found 301.9934; Anal. Calcd for $C_{15}H_{11}BrO_2$, C 59.43, H 3.66; found, C 59.26, H 3.62.

*1-(4-Bromophenyl)-2-(4-fluorophenyl)ethane-1,2-dione (**2z**).* Purified by column chromatography (petroleum ether/EtOAc, 10:1) as a pale yellow solid (69.1 mg, 75%); mp 160−162 °C; IR (KBr) ν 1663 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.04−8.00 (m, 2H), 7.86−7.83 (m, 2H), 7.69−7.66 (m, 2H), 7.23−7.17 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 192.8, 192.0, 166.9 (d, J = 257.0 Hz), 132.8 (d, J = 10.0 Hz), 132.5, 131.6, 131.3, 130.7, 129.3 (d, J = 3.0 Hz), 116.5 (d, J = 22.0 Hz); MS (EI, 70 eV) m/z (%) 306 (2) [M^+], 123 (100); HRMS (EI) for $C_{14}H_8BrFO_2$ [M^+] calcd 305.9692, found 305.9683; Anal. Calcd for $C_{14}H_8BrFO_2$, C 54.75, H 2.63; found, C 54.56, H, 2.67.

Procedure for the Synthesis of Diketo Ester 5 (5′) from Oxiranyl Carboxylates 3 Mediated by Selectfluor. The procedure is the same as for the preparation of **2**.

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*2,3-Dioxo-3-phenyl-propionic Acid Ethyl Ester (**5a**; Equilibrium with Its Hydrate Form **5′a**, **5a**:**5′a** = 1:4).*[13] Purification by column chromatography (petroleum ether/EtOAc, 6:1) as a yellow oil (52.6 mg, 85%); IR (neat) ν 3423 (OH), 1749 (C═O), 1693 (COOR) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) for **5a** δ 8.01 (dd, J_2 = 8.0 Hz, J_1 = 1.0 Hz, 2H), 7.74−7.71 (m, 1H), 7.58−7.55 (m, 2H), 4.44 (q, J = 7.0 Hz, 2H), 1.40 (t, J = 7.0 Hz, 3H); ^1H NMR ($CDCl_3$, 500 MHz) for **5′a** δ 8.09 (dd, J_2 = 7.5 Hz, J_1 = 2.5 Hz, 2H), 7.66−7.62 (m, 1H), 7.51−7.47 (m, 2H), 4.23 (q, J = 7.0 Hz, 2H), 1.10 (t, J = 7.0 Hz, 3H).

*3-(4-Chloro-phenyl)-2,3-dioxo-propionic Acid Ethyl Ester (**5b**; Equilibrium with Its Hydrate Form **5′b**, **5b**:**5′b** = 1:6).* Purification by column chromatography (petroleum ether/EtOAc, 6:1) as a pale white solid (55.6 mg, 77%); mp 83−85 °C; IR (neat) ν 3464 (OH), 1743 (C═O), 1694 (COOR) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) for **5b** δ 7.99−7.96 (m, 2H), 7.55−7.53 (m, 2H), 4.44 (q, J = 7.0 Hz, 2H), 1.41 (t, J = 7.0 Hz, 3H); ^1H NMR ($CDCl_3$, 500 MHz) for **5′b** δ 8.05−8.03 (m, 2H), 7.48−7.45 (m, 2H), 4.23 (q, J = 7.0 Hz, 2H), 1.13 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) for **5b** and **5′b** δ 190.7, 188.7, 175.0, 169.7, 142.4, 141.4, 131.6, 131.4, 130.0, 129.7, 129.2, 100.1, 91.8, 63.4, 63.0, 14.0, 13.7.

Mechanistic Studies. *Subjection of **6** and **6′** Mixture to the Standard Reaction Conditions.* **6** and its hydrate form **6′** were prepared according to the reported literature.[13] To a 15 mL Schlenk flask were added a mixture of **6** and **6′** (**6**:**6′** = 1:2, 75.1 mg, 0.3 mmol), Selectfluor (106.3 mg, 0.3 mmol, 1 equiv), $KHCO_3$ (15.0 mg, 0.15 mmol), and a mixture of CH_3CN-H_2O (3 mL; CH_3CN-H_2O = 100:1 (v/v)). Then, the resulting mixture was stirred at 80 °C for 2 h. To the flask was added another 1 equiv of Selectfluor, and the reaction mixture was stirred at 80 °C for another 4 h. After being cooled to room temperature, the mixture was filtered with Celite, and the filtrate was evaporated in a vacuum. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1, v/v) as the eluent to give pure **2a** (39.1 mg, 62%).

O^{18}-Labeling Experiment. To a 15 mL Schlenk flask were added a mixture of **1a** (0.3 mmol), Selectfluor (106.3 mg, 0.3 mmol, 1 equiv), and $KHCO_3$ (15.0 mg, 0.15 mmol) and a mixture of CH_3CN-H_2O^{18} (3 mL; CH_3CN-H_2O^{18} = 100:1 (v/v)). Then, the resulting mixture was stirred at 80 °C for 2 h. To the flask was added another 1 equiv of Selectfluor, and the reaction mixture was stirred at 80 °C for another 4 h. After being cooled to room temperature, the mixture was filtered with Celite, and the filtrate was evaporated in vacuum. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1, v/v) as the eluent to give pure **2a**-O^{18} (51.5 mg, 81%).

*Effect of Radical Scavenger TEMPO on the Formation of **2a**.* To a 15 mL Schlenk flask were added a mixture of **1a** (0.3 mmol), Selectfluor (106.3 mg, 0.3 mmol, 1 equiv), $KHCO_3$ (15.0 mg, 0.15 mmol), and TEMPO (0.15 or 0.6 mmol) and a mixture of CH_3CN-H_2O (3 mL; CH_3CN-H_2O = 100:1 (v/v)). Then, the resulting mixture was stirred at 80 °C for 2 h. To the flask was added another 1 equiv of Selectfluor, and the reaction mixture was stirred at 80 °C for another 4 h. After being cooled to room temperature, the mixture was filtered with Celite, and the filtrate was evaporated in vacuum. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (10:1, v/v) as the eluent to give pure **2a** (TEMPO: 0.5 equiv: 51.1 mg, 81% or TEMPO: 2.0 equiv: 50.4 mg, 80%).

■ ASSOCIATED CONTENT

Supporting Information

Charts for mechanistic studies as well as copies of ^1H NMR and ^{13}C NMR spectra of the products. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00857.

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Notes

The authors declare no competing financial interest.

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