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AIBN-Catalyzed Oxidative Cleavage of *gem*-Disubstituted Alkenes with O_2 as an Oxidant

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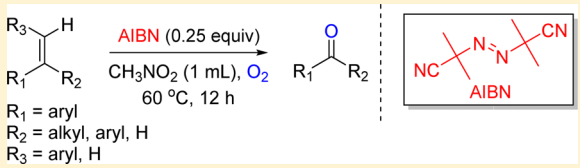
Supporting Information

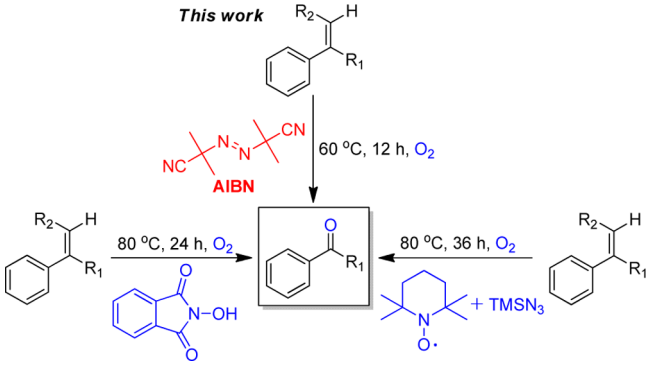
ABSTRACT: A 2,2-azobis(isobutyronitrile) (AIBN) catalyzed oxidative cleavage of *gem*-disubstituted alkenes with molecular oxygen as the oxidant has been described. Carbonyl compounds were obtained as the desired products in high yield under mild conditions. Based on previous documents and current experimental results, a relatively reasonable mechanism is proposed.



Oxidative cleavage of alkenes to the carbonyl compounds is an important transformation in organic synthesis.[1] A variety of protocols have been reported, including traditional methods,[2] transition-metal-catalyzed methods,[3] special oxidants oxidized method,s[4] and photochemical methods.[5] However, the aforementioned methods always suffer from several drawbacks, such as overstoichiometric amounts of oxidants, toxic metals, and too much byproducts. Therefore, it is imperative to find some green and efficient methods.

Compared to the strong oxidants used previously, oxygen has drawn considerable attention over the past few years due to its stable, inexpensive and environmental-friendly properties.[6] Therefore, molecular oxygen is considered as a green oxidant for the cleavage of olefinic bond.[7] Excitingly, great progress has been made regarding this area (Scheme 1). The NHPI (*N*-hydroxyphthalimide)-catalyzed oxidative cleavage of C=C bond with molecular oxygen as an oxidant was reported in 2012.[8] Recently, the TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl)-catalyzed oxygenation of alkene was also reported,[9] which further emphasized the importance of aerobic oxygenation in this area. The development of other protocols for the aerobic oxygenation of alkene is still urgently required. Herein, we reported a convenient and efficient method for the cleavage of *gem*-disubstituted alkenes catalyzed by AIBN with O_2 as the oxidant. Compared to other works, we employed shorter time and lower temperature in our reaction system.

Scheme 1. Aerobic Oxygenation of Alkenes



As a starting point of this work, 1,1-diphenylethylene (**1a**) was chosen as the substrate to optimize the reaction conditions. First, different kinds of solvents (1 mL) were tested under O_2 for 12 h at 60 °C. The results indicated that the solvents (Table 1, entries 1−9) had great influence on the reaction yield, and CH_3NO_2 (nitromethane) was the best solvent for this transformation.

Regarding the amount of AIBN, we found that catalytic amount (0.25 equiv) (Table 1, entries 10−12) showed better reactivity. Moreover, temperature also has great influence on the reaction system. The results showed that yield decreased with the increase or decrease of reaction temperature (Table 1, entries 13 and 14), this might be attributed to the significant influence of temperature on decomposition rate of AIBN.[10] In the absence of the AIBN, only a trace amount of oxidative cleavage product was obtained (Table 1, entry 15). This transformation would not occur under Ar atmosphere, and only 32% yield was gained when it was performed in air (Table 1, entries 16 and 17), which showed the importance of O_2 in this system.

Having established the optimum reaction conditions, the applicability of this optimized system was further investigated. Different kinds of alkenes were used as substrates, and their corresponding products and yields are summarized in Table 2. Substituents bearing either electron-withdrawing groups, such as CF_3 (**1b**), F (**1c**), Cl (**1d**), CN (**1e**), $COCH_3$ (**1f**), or CHO (**1g**), or electron-donating groups, such as CH_3 (**1h**) or OMe (**1i**), at the para-position of the aryl group could be smoothly transformed into the corresponding diaryl ketones with good to excellent yields (**2b−i**). However, a strongly electron-donating group like OH (**1j**) showed a relatively lower yield of 41% (**2j**). When one benzene ring of the substrate was substituted by the

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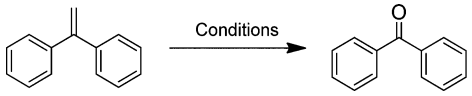
Table 1. Oxidative Cleavage of Diphenyl Ethylene[a]



1a 2a

entry	AIBN (equiv)	temp (°C)	solvent	yield[b] (%)
1	1	60	MeCN	45
2	1	60	toluene	25
3	1	60	DMA	48
4	1	60	DME	44
5	1	60	DMF	24
6	1	60	THF	12
7	1	60	EtOH	25
8	1	60	CH_3NO_2	75
9	1	60	$CHCl_3$	8
10	0.5	60	CH_3NO_2	80
11	0.25	60	CH_3NO_2	91
12	0.2	60	CH_3NO_2	72
13	0.25	80	CH_3NO_2	78
14	0.25	40	CH_3NO_2	trace
15		60	CH_3NO_2	trace
16[c]	0.25	60	CH_3NO_2	trace
17[d]	0.25	60	CH_3NO_2	32

[a]Reactions were carried out with **1a** (0.25 mmol) and solvent (1 mL) for 12 h. [b]GC yield using diphenyl as an internal standard. [c]Under an Ar atmosphere. [d]Under an air atmosphere.

F and the other by the Cl atom at the *para*-position (**1k**), the desired product can be obtained with a high yield (**2k**). Substrates substituted at the meta-position (**1l**, **1m**) can also react well in our system (**2l**, **2m**). A moderate yield of 55% was obtained when the 1,2,3-trifluoro-4-(1-phenylvinyl)benzene (**1n**) was employed as the substrate; this may be come from the strong inductive effect of F atoms. The 2-(1-phenylvinyl)-naphthalene (**1o**) could also proceed smoothly and gave a high yield of 85% (**2o**). Surprisingly, substrates with tricyclic ring are well tolerated under the optimized reaction conditions (**2p**, **2q**). Furthermore, the α-alkylarylalkenes were also good substrates and oxidized to the corresponding ketones in high yields ranging from 64% to 90% (**2r**−**2t**).

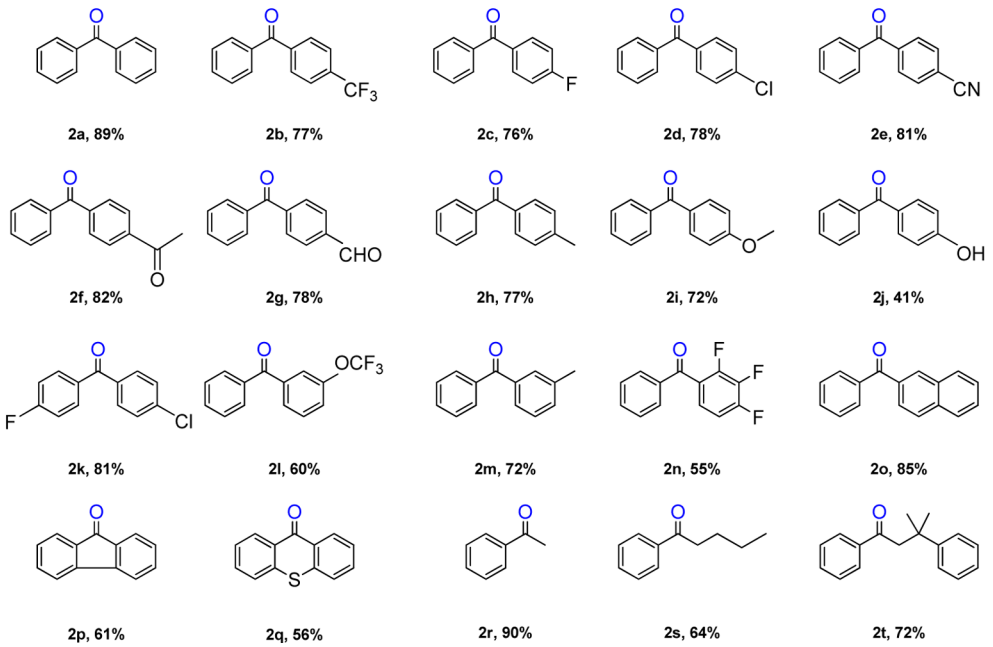
When some single-substituted (phenyl) alkenes were investigated, the aldehydes were obtained as the main products under the optimized conditions. Various functional groups substituted at the *para*-position of the substrates, such as Br, Cl, CH_3, C_4H_9, and ester, oxidized to the corresponding aldehydes in moderate yields (**4a**−**e**) (Table 3). However, vinyl-naphthalene (**3f**) could not react well under the above conditions. By decreasing the volume of solvent and shortening reaction time, we got a moderate yield of the special substrate. 4-Vinylpyridine is not applicable in our system, and only a trace amount of the product was formed (**4g**). For the alkyl olefins, this transformation is limited (**4h**).

1,2-Disubstituted alkenes are less effective under the conditions, such as *cis*-stilbene, and the product was obtained in only 42% yield (**6a**). On the other hand, the α,β-unsaturated ketone (**5b**) and allyl chloride (**5c**) could not get the corresponding products under the optimized conditions (Scheme 2).

To compare the activity of geminal diarylalkene and single-substituted alkene in this oxidation process, 1-(1-phenylvinyl)-4-vinylbenzene (**7a**) was employed as the reactant (Scheme 3).

Table 2. AIBN-Catalyzed Oxidative Cleavage of Substituted Geminal Diarylalkenes[a]

1a - 1t 2a - 2t



[a]Reactions were carried out using alkene (0.25 mmol), AIBN (0.25 equiv), and CH_3NO_2 (1 mL) at 60 °C under O_2 for 12 h.

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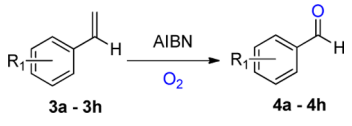
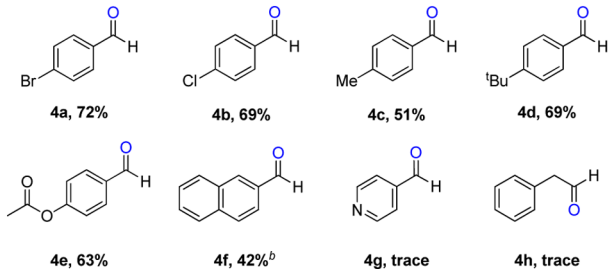
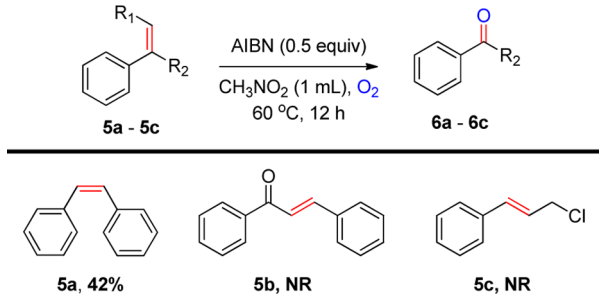
Table 3. AIBN-Catalyzed Oxidative Cleavage of the Single-Substituted Alkenes[a]



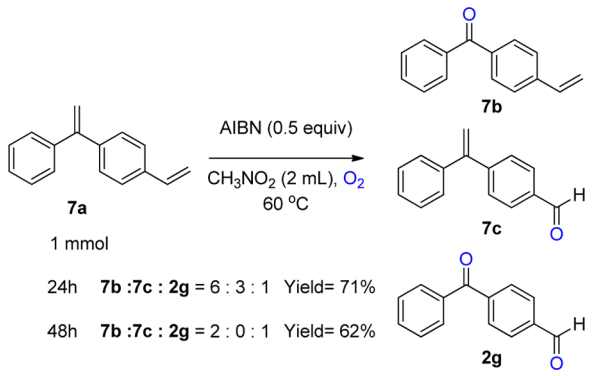


[a]Reactions were carried out using alkene (0.25 mmol), AIBN (0.25 equiv), and CH_3NO_2 (1 mL) at 60 °C under O_2 for 12 h. [b]Vinylnaphthalene (0.25 mmol), AIBN (0.25 equiv), CH_3NO_2 (0.2 mL), 60 °C, O_2 (1 atm), 5 h.

Scheme 2. Investigation the Activity of 1,2-Disubstituted Alkenes



Scheme 3. Comparison of the Activity



The products **7b**, **7c**, and **2g** were obtained with a mole ratio of 6:3:1 under the indicated condition. When we extended the reaction time to 48 h, the **7c** was completely transformed to **2g**, causing the mole ratio of **7b** to **2g** to change to 2:1. The result indicated that geminal diarylalkene was easier to oxidize than the single-substituted alkene.

The activity ratio among geminal diarylalkene (ethene-1,1-diyldibenzene (**1a**)), single-substituted alkene (styrene (**8a**)), and α-methyl styrene (prop-1-en-2-ylbenzene (**1r**)) are shown in Scheme 4. It shows that when the **1a** and **8a** were reacted under the same conditions, the desired product **2a** could be obtained with a high yield of 83%; however, only a trace amount of **6a** was formed, which showed the higher reactivity of geminal diarylalkene compared to the single-substituted alkene. It also shows that α-methylstyrene is more reactive than the single-substituted alkene. Also, the competition experiment was done between **1a** and **1r** by using GC yield as the standard. To summarize, the reactivity order is geminal diarylalkene > α-methylstyrene > single-substituted alkene.

To highlight the utility of these transformations, the oxidative cleavage reaction of prop-1-en-2- ylbenzene (**1r**) was successfully scaled to 5 mmol and the yield reached as high as 61% (**2r**) (Scheme 5).

Futhermore, to shed light on the plausible mechanism of this oxidative process, we designed the following experiment (Scheme 6). The result showed that this oxidation was completely inhibited by the BHT (2,6-ditertbutyl-4-methylphenol),[11] which is a typical radical-trapping reagent. This might suggest that this transformation underwent a radical initiation pathway.

Based on the literature and our experimental results,[12] we proposed that AIBN-catalyzed oxidative cleavage of *gem*-disubstituted alkenes may proceed through the process shown in Scheme 7. First, radical **A** is generated from AIBN through heating and desorption of nitrogen. The 2-cyano-2-propylperoxyl radical **B** is generated from radical **A** by adding to the styrene derivative. The adduct radical can then be trapped by dioxygen to give the corresponding peroxyl radical **C**. Subsequently, the intermediate **D** may be produced with the elimination of radical **A** to complete the catalytic cycle. Finally, the corresponding carbonyl product is produced by the opening loop of dioxetane **D**.[13]

In summary, we have developed an efficient method for the oxidative cleavage of *gem*-disubstituted alkenes. AIBN was employed as the catalyst, and oxygen was used as the oxidant to promote the oxidation reaction. What's more, this method represented a relatively good selectivity for the oxidation of geminal diaryl alkene compared to the single-substituted alkene.

EXPERIMENTAL SECTION

General Procedure A. AIBN (10.3 mg, 25 mol %) and alkene (0.25 mmol) (if solid) were added to a 25 mL oven-dried Schlenk tube. The tube was then evacuated and filled with oxygen (this procedure was repeated three times). The alkene (0.25 mmol) (if liquid) and CH_3NO_2 (1 mL) were added under flow of oxygen. The mixture was stirred at 60 °C for 12 h and then cooled to room temperature. The reaction mixture was diluted with Et_2O, concentrated, and purified by silica gel chromatography eluting with petroleum ether and ethyl acetate to get the pure product.

General Procedure B for the preparation of 1b–o[14] and 7a.[14] $Pd(PPh_3)_4$ (3 mol %) and arylboronic acids (7.5 mmol) were added to a 25 mL oven-dried Schlenk tube. The tube was then evacuated and filled with dry argon (this procedure was repeated three times). Acetic acid (15 mol %), phenylacetylene (5.0 mmol), and 1,4-dioxane (5 mL) were added under flow of dry argon. The mixture was stirred at 80 °C for 12 h and then cooled to room temperature. The reaction mixture was diluted with Et_2O, concentrated, and purified by silica gel chromatography eluting with petroleum ether and ethyl acetate to get the pure product.

General Procedure C for the Preparation of 1p,[15] 1q,[15] 1s.[15] In a two-necked, round-bottomed flask under argon was prepared a solution of Ph_3PMeBr (0.91 equiv, 1.42 g, 4.55 mmol) and *n*-BuLi (0.91 equiv, 1.82 mL of 2.5 M solution, 4.55 mmol) in Et_2O (0.34 M, 11.38 mL). After the reaction mixture was stirred for 4 h at 0 °C, a solution of ketone [1 equiv, 5 mmol in Et_2O (2.2 M, 2.28 mL)] was added. The reaction mixture was stirred at reflux overnight and filtered. The resulting solution was poured into water and extracted with Et_2O (3 × 30 mL). The combined organic phases were dried over

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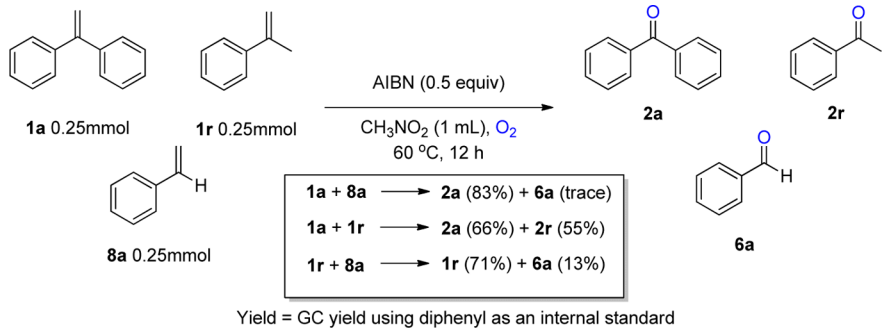
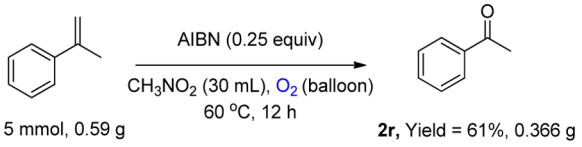
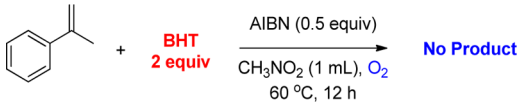
Scheme 4. Investigation of the Selectivity



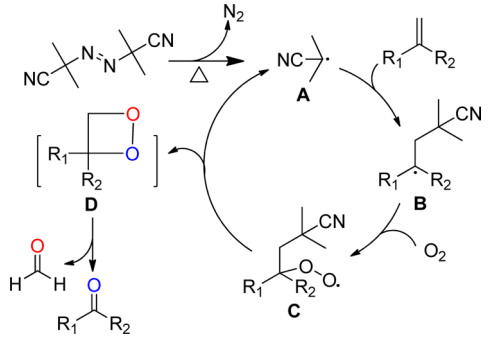
Scheme 5. Large-Scale Synthesis of Acetophenone



Scheme 6. Investigation of the Mechanism



Scheme 7. Possible Mechanism for this Reaction



$MgSO_4$, concentrated in vacuum, and purified by flash chromatography to afford pure alkene.

Benzophenone (2a).[8] Following general procedure A, colorless liquid (89%, 40.5 mg): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 4H), 7.57 (t, J = 7.4 Hz, 2H), 7.46 (t, J = 7.7 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.6, 137.5, 132.3, 129.9, 128.2.

Phenyl(4-(trifluoromethyl)phenyl)methanone (2b).[16] Following general procedure A, pale yellow solid (77%, 48 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.0 Hz, 2H), 7.84–7.71 (m, 4H), 7.66–7.61 (m, 1H), 7.55–7.46 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 140.7, 136.7, 133.7(q, J = 32.6 Hz), 133.1, 130.1, 130.0, 128.5, 125.3 (q, J = 3.7 Hz), 123.7 (q, J = 272.5 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ −63.0; mp 110–112 °C (lit.[31a] mp 112–114 °C).

(4-Fluorophenyl)(phenyl)methanone (2c).[8] Following general procedure A, pale yellow solid (76%, 38 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.82 (m, 2H), 7.80–7.73 (m, 2H), 7.64–7.56 (m, 1H), 7.54–7.46 (m, 2H), 7.21–7.12 (m, 2H); ^{13}C NMR (151 MHz, CDCl3) δ 195.2, 165.3 (d, J = 254.2 Hz), 137.4, 133.7 (d, J = 3.0 Hz), 132.6 (d, J = 9.2 Hz), 132.4, 129.8, 128.3, 115.4 (d, J = 21.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −105.9; mp 46–48 °C (lit.[31b] mp 49 °C).

(4-Chlorophenyl)(phenyl)methanone (2d).[16] Following general procedure A, yellow solid (78%, 42 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.71 (m, 4H), 7.64–7.57 (m, 1H), 7.55–7.42 (m, 4H); ^{13}C NMR (151 MHz, CDC_3) δ 195.4, 138.8, 137.2, 135.8, 132.6, 131.4, 129.9, 128.6, 128.4; mp 72–74 °C (lit.[31c] mp 73–74 °C).

4-Benzoylbenzonitrile (2e).[17] Following general procedure A, yellow solid (81%, 42 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.86 (m, 2H), 7.79 (m, 4H), 7.69–7.61 (m, 1H), 7.54–7.50 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0, 141.2, 136.3, 133.3, 132.2, 130.2, 130.0, 128.6, 118.0, 115.6; mp 113–115 °C (lit.[31d] mp 115–116 °C).

1-(4-Benzoylphenyl)ethanone (2f).[16] Following general procedure A, white solid (82%, 46 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 2H), 7.92–7.76 (m, 4H), 7.63 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 2.68 (s, 3H); ^{13}C NMR (151 MHz,$CDCl_3$) δ 197.5, 195.9, 141.3, 139.5, 136.9, 132.9, 130.1, 130.0, 128.4, 128.1, 26.9; mp 80–82 °C (lit.[31e] mp 83–84 °C).

4-Benzoylbenzaldehyde (2g).[18] Following general procedure A, white solid (78%, 41 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.04–7.99 (m, 2H), 7.93 (d, J = 8.2 Hz, 2H), 7.81 (dd, J = 5.2, 3.3 Hz, 2H), 7.67–7.61 (m, 1H), 7.51 (dd, J = 10.6, 4.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.8, 191.6, 142.5, 138.4, 136.7, 133.1, 130.3, 130.1, 129.5, 128.5; mp 61–63 °C (lit.[31f] mp 62–65 °C).

Phenyl(*p*-tolyl)methanone (2h).[8] Following general procedure A, white solid (77%, 38 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.76 (m, 2H), 7.75–7.69 (m, 2H), 7.61–7.55 (m, 1H), 7.52–7.44 (m, 2H), 7.28 (d, J = 7.9 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.5, 143.2, 137.9, 134.9, 132.1, 130.3, 129.9, 128.9, 128.2, 21.6; mp 53–55 °C (lit.[31g] mp 55–58 °C).

(4-Methoxyphenyl)(phenyl)methanone (2i).[8] Following general procedure A, white solid (72%, 38 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.80 (m, 2H), 7.78–7.72 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.00–6.93 (m, 2H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 163.2, 138.2, 132.5, 131.8, 130.1, 129.7, 128.2, 113.5, 55.5; mp 63–64 °C (lit.[31h] mp 60–62 °C).

(4-Hydroxyphenyl)(phenyl)methanone (2j).[19] Following general procedure A, yellow solid (41%, 20 mg): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85–7.70 (m, 4H), 7.57 (m, 1H), 7.50–7.44 (m, 2H), 6.94–6.90 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.2, 160.2, 138.1, 133.0, 132.1, 129.9, 129.8, 128.2, 115.2; mp 128–130 °C (lit.[31i] mp 130–132 °C).

(4-Chlorophenyl)(4-fluorophenyl)methanone (2k).[19] Following general procedure A, white solid (81%, 47 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.79 (m, 2H), 7.76–7.70 (m, 2H), 7.50–7.44 (m, 2H), 7.22–7.14 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.9, 165.5 (d, J = 254.8 Hz), 138.9, 135.7, 133.4 (d, J = 3.2 Hz), 132.5 (d, J = 9.2 Hz), 131.23, 128.7, 115.6 (d, J = 21.9 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ −105.4; mp 112–114 °C (lit.[31j] mp 114–115 °C).

Phenyl(3-(trifluoromethoxy)phenyl)methanone (2l). Following general procedure A, pale yellow liquid (60%, 40 mg): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (dd, J = 5.1, 3.3 Hz, 2H), 7.72 (d, J = 7.7 Hz, 1H), 7.63 (dd, J = 20.1, 12.6 Hz, 2H), 7.51 (m, 3H), 7.44 (dd, J = 8.2, 1.1 Hz, 1H).; ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.0, 149.1, 139.4, 136.8, 132.9, 130.0, 129.8, 128.5, 128.3, 124.7, 122.3, 121.3, 120.4(d, J = 258.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −57.9; HRMS calcd for $C_{14}H_9F_3O_2$ (M^+) 266.0555, found 266.0558.

Phenyl(*m*-tolyl)methanone (2m).[16] Following general procedure A, pale yellow solid (72%, 35 mg): ^{1}H NMR (600 MHz, $CDCl_3$)

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δ 7.80 (d, J = 7.9 Hz, 2H), 7.57−7.63 (m, 3H), 7.47 (t, J = 7.7 Hz, 2H), 7.34−7.40 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.9, 138.1, 137.7, 137.6, 133.1, 132.3, 130.4, 130.0, 128.2, 128.1, 127.3, 21.4; mp 155−158 °C (lit.[31k] mp 159−160 °C).

Phenyl(2,3,4-trifluorophenyl)methanone (2n). Following general procedure A, pale yellow liquid (55%, 33 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.75 (m, 2H), 7.67−7.60 (m, 1H), 7.54−7.46 (m, 2H), 7.39−7.29 (m, 1H), 7.11 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 153.2 (ddd, J = 255.8, 10.1, 3.1 Hz), 149.8 (ddd, J = 257.1, 10.8, 3.7 Hz), 140.0 (dt, J = 254.2, 15.4 Hz), 136.9, 133.9, 129.7 (t, J = 7.6 Hz), 128.7, 125.9, 124.9 (ddd, J = 8.2, 4.6, 3.3 Hz), 112.67 (dd, J = 17.8, 3.8 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ −128.4 (dd, J = 20.2, 10.4 Hz), −131.6 (dd, J = 21.3, 10.4 Hz), −158.9 (t, J = 20.7 Hz); HRMS calcd for $C_{13}H_7F_3O$ (M^+) 236.0449, found 236.0450.

Naphthalen-2-yl(phenyl)methanone (2o).[20] Following general procedure A, white solid (85%, 49 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.97−7.83 (m, 6H), 7.65−7.58 (m, 2H), 7.57−7.47 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.7, 137.9, 135.2, 134.8, 132.3, 132.2 131.8, 130.1, 129.4, 128.4−128.1 (m), 127.8, 126.8, 125.8; mp 81−83 °C (lit.[31l] mp 80−81 °C).

9*H*-Fluoren-9-one (2p).[21] Following general procedure A, pale yellow solid (61%, 28 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.3 Hz, 2H), 7.52−7.46 (m, 4H), 7.29 (t, J = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 144.4, 134.7, 134.1, 129.0, 124.3, 120.3; mp 81−83 °C (lit.[31m] mp 83−85 °C).

9*H*-Thioxanthen-9-one (2q).[22] Following general procedure A, pale yellow solid (56%, 30 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, J = 8.1, 1.4 Hz, 2H), 7.64−7.56 (m, 4H), 7.48−7.48 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.9, 137.2, 132.2, 129.8, 129.2, 126.3, 125.9; mp 81−83 °C (lit.[31n] mp 80−81 °C).

Acetophenone (2r).[8] Following general procedure A, colorless liquid (90%, 27 mg): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.8 Hz, 2H), 2.54 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.8, 136.9, 132.9, 128.4, 128.1, 26.4.

1-Phenylpentan-1-one (2s).[8] Following general procedure A, colorless liquid (64%, 26 mg): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98−7.91 (m, 2H), 7.56−7.51 (m, 1H), 7.44 (dd, J = 10.6, 5.0 Hz, 2H), 3.00−2.94 (m, 2H), 1.72−1.68 (m, 2H), 1.45−1.35 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.5, 137.1, 132.8, 128.49, 128.0, 38.3, 26.5, 22.5, 13.9.

3-Methyl-1,3-diphenylbutan-1-one (2t).[23] Following general procedure A, colorless liquid (72%, 43 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.79 (m, 2H), 7.51−7.47(m, 1H), 7.39−7.37 (m, 4H), 7.31−7.26 (m, 2H), 7.18−7.13 (m, 1H), 3.31 (s, 2H), 1.50 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.0, 148.8, 138.1, 132.6, 128.4, 128.1, 128.0, 125.8, 125.4, 50.9, 37.5, 29.1.

4-Bromobenzaldehyde (4a).[24] Following general procedure A, colorless liquid (72%, 33 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.78−7.74 (m, 2H), 7.70−7.66 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.0, 135.1, 132.4, 130.9, 129.7.

4-Chlorobenzaldehyde (4b).[24] Following general procedure A, colorless liquid (69%, 24 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 140.9, 134.7, 130.9, 129.5.

4-Methylbenzaldehyde (4c).[24] Following general procedure A, colorless liquid (51%, 15.3 mg): ^{1}H NMR (600 MHz,$CDCl_3$) δ 9.94 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.9, 145.5, 134.2, 129.8, 129.7, 21.8.

4-*tert*-Butylbenzaldehyde (4d).[25] Following general procedure A, colorless liquid (69%, 28 mg): ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.07 (s, 1H), 7.91 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 1.44 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.0, 158.4, 134.1, 129.7, 126.0, 35.3, 31.1.

4-Formylphenyl Acetate (4e).[26] Following general procedure A, colorless liquid (63%, 26 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.94−7.91 (m, 2H), 7.30−7.27 (m, 3H), 2.34 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.9, 168.7, 155.3, 134. 0, 131.2, 122.4, 21.2.

2-Naphthaldehyde (4f).[27] Following general procedure A, colorless liquid (42%, 16.4 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (s, 1H), 8.33 (s, 1H), 8.01−7.89 (m, 4H), 7.66−7.57 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 136.4, 134.6, 134.1, 132.6, 129.5, 129.1, 129.0, 128.1, 127.1, 122.7.

Benzaldehyde (6a).[28] Following general procedure A, colorless liquid (42%, 22.3 mg): ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.87 (dd, J = 8.1, 1.1 Hz, 2H), 7.65−7.59 (m, 1H), 7.52 (t, J = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 136.4, 134.4, 129.7, 129.0.

1-(1-Phenylvinyl)-4-vinylbenzene (7a): colorless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, J = 8.2 Hz, 2H), 7.37 (dd, J = 15.5, 6.9 Hz, 7H), 6.77 (dd, J = 17.6, 10.9 Hz, 1H), 5.81 (d, J = 17.6 Hz, 1H), 5.50 (d, J = 17.8 Hz, 3H), 5.30 (d, J = 10.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.7, 141.4, 140.9, 137.0, 136.4, 128.5, 128.3, 128.2, 127.7, 126.0, 114.2, 113.9. HRMS calcd for $C_{16}H_{14}$ (M^+) 206.1096, found 206.1098.

Phenyl(4-vinylphenyl)methanone (7b).[29] Following general procedure A, colorless liquid (42.6%, 88.6 mg, 24 h) (41.3%, 85.9 mg, 48 h): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88−7.71 (m, 4H), 7.64−7.56 (m, 1H), 7.54−7.44 (m, 4H), 6.78 (dd, J = 17.6, 10.9 Hz, 1H), 5.89 (d, J = 17.6 Hz, 1H), 5.40 (d, J = 10.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.2, 141.5, 137.8, 136.7, 136.0, 132.3, 130.5, 129.9, 128.2, 126.0, 116.6.

4-(1-Phenylvinyl)benzaldehyde (7c).[30] Following general procedure A, colorless liquid (21.3%, 44.7 mg, 24 h): ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.85 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 5.3 Hz, 3H), 7.32−7.28 (m, 2H), 5.58 (d, J = 6.9 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.8, 149.2, 147.6, 140.6, 135.6, 129.7, 128.8, 128.4, 128.2, 128.1, 116.5.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, ^{13}C, and ^{19}F NMR spectra for the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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