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Photocatalytic One-Pot Synthesis of Homoallyl Ketones via a Norrish Type I Reaction of Cyclopentanones

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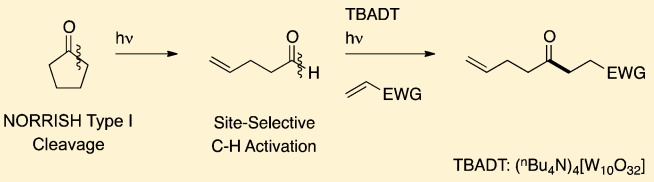
Supporting Information

ABSTRACT: A photocatalytic synthesis of homoallyl ketones was achieved via a one-pot procedure starting from a Norrish Type I reaction of cyclopentanones, followed by a decatungstate-catalyzed hydroacylation of electron-deficient olefins by the resulting 4-pentenals. The site-selective formyl H-abstraction in the second step can be explained by radical polar effects in the transition state.

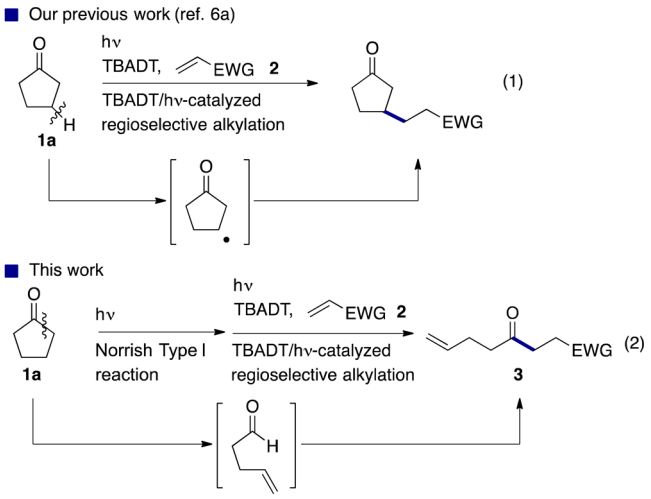


Homoallyl ketones are an important class of compounds that are found in a wide range of natural products, and also serve as useful building blocks.[1,2] They are typically synthesized either by carbanion-based[3] or transition metal-catalyzed approaches,[4] whereas the radical-based options are rare.[5]

During the course of our study on the regioselective C−H alkylation of cyclopentanones with electron-deficient olefins (Scheme 1, eq 1),[6] which uses a decatungstate photocatalyst ($(^nBu_4N)_4W_{10}O_{32}$, TBADT),[7,8] we observed the formation of a small amount of 4-pentenal as a byproduct derived via a Norrish Type I reaction when using a 310 nm irradiation wavelength. This led us to envision a one-pot synthesis of homoallyl ketones that could be based on the combination of a Norrish Type I reaction[9,10] of cyclopentanones[11,12] and the subsequent photocatalytic conversion of formyl C−H to C−C bond (Scheme 1, eq 2).[13] This second step is based on the known capability of excited TBADT to homolytically cleave the formyl C−H bond to form an acyl radical, which has an affinity for addition to electron-deficient alkenes.[14] This reaction, however, would require site-selectivity at the formyl C−H among the 3 weak C−H bonds of pentenals (viz. formyl, allylic, and oxoallylic positions), and we are confident that oxoallylic C−H would not be chosen in light of our recent work.[6a]

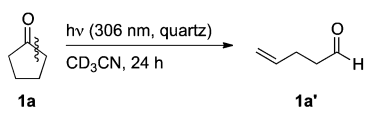
A one-pot option would depend on the consistent use of the same wavelength (ca. 306 nm) of light for the 2 steps. However, the existence of cyclopentanone and TBADT as the absorbing species in each step would necessitate an examination into whether the presence of TBADT in the Norrish Type I reaction would have a negative effect. This led us to examine the effect of TBADT in the Norrish Type I reaction of cyclopentanone **1a** (Scheme 2). During photoirradiation using phosphor-coated lamps (15 W × 6) through a quartz tube, **1a** was converted to 4-pentenal **1a′** in a 98% yield, but only 12% of **1a′** was formed in the presence of 4 mol % of TBADT. Increasing the amount of TBADT to 10 mol % almost completely suppressed the formation of **1a′** (2%). Obviously,

Scheme 1. Concept: Photocatalytic One-Pot Synthesis of Homoallyl Ketones 3 from Cyclopentanone 1a and Electron-Deficient Olefins 2



TBADT = $(^nBu_4N)_4W_{10}O_{32}$

Scheme 2. Effect of TBADT in the Norrish Type I Reaction of Cyclopentanone 1a



TBADT	**1a** (%)	**1a'** (%)
none	2	98
4 mol%	88	12
10 mol%	98	2

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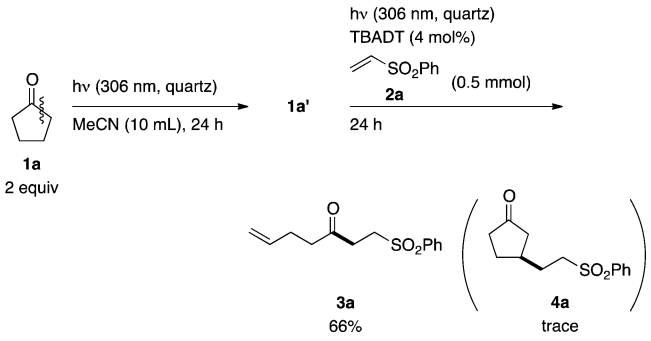
TBADT prevents the Norrish Type I reaction of cyclopentanone **1a** by absorbing the light.

On the basis of the above results, we then carried out a photocatalytic one-pot reaction of cyclopentanone **1a** with phenyl vinyl sulfone **2a** as a model reaction wherein TBADT and **2a** were added at the second step (Scheme 3). Irradiation

Scheme 3. Photocatalytic One-Pot Reaction of Cyclopentanone 1a and Phenyl Vinyl Sulfone 2a

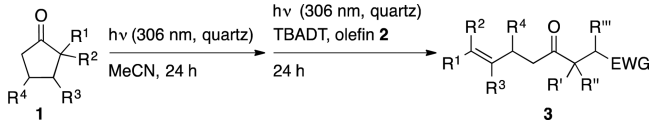


of an acetonitrile solution of **1a** (1 mmol) using phosphor-coated lamps (15 W × 6) through a quartz tube for 24 h gave 4-pentenal **1a′**. Without the isolation of **1a′**, phenyl vinyl sulfone **2a** (0.5 mmol) and TBADT (4 mol %) were then added to the reaction mixture, with stirring continued for another 24 h under irradiation. After concentration of the reaction mixture, silica gel chromatography gave the desired homoallyl ketone **3a** in a 66% isolated yield. It should be noted that in the crude product, NMR detected only a trace amount of *β*-alkylated cyclopentanone **4a**.

To elucidate the generality of a one-pot synthesis of homoallyl ketones, we examined the reaction between a variety of cyclopentanones **1** with electron-deficient olefins **2** under TBADT/*hν* conditions. The results are summarized in Table 1. In a similar manner, the reaction of cyclopentanone **1a** with acrylonitrile **2b** gave cyano-functionalized butenyl ketone **3b** in a 68% yield (Table 1, entry 2). The reaction of **1a** with *t*-butyl acrylate **2c** gave **3c** in a 58% yield (Table 1, entry 3). The reaction of **1a** with dimethyl maleate **2d** or dibutyl maleate **2e** proceeded well to give the expected products **3d** and **3e** in yields of 67 and 49% yield, respectively (Table 1, entries 4 and 5). Cyclic olefins such as cyclopentenone **2f** and cyclohexenone **2g** were also applicable to this system to afford the corresponding 1,4-diketones **3f** and **3g** in yields of 51 and 58%, respectively (Table 1, entries 6 and 7). Tetra-substituted olefin **2h** was also effective for this reaction to give **3h** with a quaternary carbon next to a carbonyl (Table 1, entry 8).

When 2-methylcyclopentanone **1b** was treated with acrylonitrile **2b**, a Norrish Type I reaction proceeded only between the C1−C2 bond to give **3i** in a 66% yield as a mixture of diastereomeric isomers (*E*/*Z* = 71/29) (Table 1, entry 9). In this reaction, the initial *α*-cleavage of ketone **1b** proceeded site-selectively to form a more stable secondary radical, which agreed with the results of previous work.[13a] The reaction of 2-hexylcyclopentanone **1c** with **2b** gave **3j** in a 59% yield (Table 1, entry 10).[11] In contrast, the reaction of 3-methylcyclopentanone **1d** with **2b** was not regioselective, and gave a 79/21 mixture of two types of homoallyl ketones, **3k** and **3k′**, in a 78% yield (Table 1, entry 11). The reaction of **1d** with **2d** also proceeded with a similar selectivity in the ring cleavage to give **3l** and **3l′** (Table 1, entry 12). The observed regioselectivity

Table 1. One-Pot Synthesis of Homoallyl Ketones from Cyclopentanones 1 and Electron-Deficient Olefins 2[a]



entry	ketone **1**	olefin **2**	product **3**	yield[b]
1	**1a**	**2a**	**3a**	66%
2	**1a**	**2b**	**3b**	68%
3	**1a**	**2c**	**3c**	58%
4	**1a**	**2d**	**3d**	67%
5	**1a**	**2e**	**3e**	49%
6	**1a**	**2f**	**3f**	51%
7	**1a**	**2g**	**3g**	58%
8	**1a**	**2h**	**3h**	55%
9	**1b**	**2b**	**3i**	66% (*E*/*Z* = 71/29)[c]
10	**1c**	**2b**	**3j**	59% (*E*/*Z* = 74/26)[d]
11	**1d**	**2b**	**3k**, **3k′**	78% (**3k**:**3k′** = 79:21)[c]
12	**1d**	**2d**	**3l**, **3l′**	40% (**3l**:**3l′** = 80:20)[c]
13	**1e**	**2g**	**3m**	60%
14	**1e**	**2i**	**3n**	84%
15	**1f**	**2b**	**3o**	54%

[a]**1** (1 mmol), **2** (0.5 mmol), TBADT (4 mol %), MeCN (10 mL), irradiation by a 15 W × 6 phosphor-coated lamp. [b]Yields of product isolated after flash chromatography on SiO_2. If necessary, further purification was made by preparative HPLC. [c]Determined by GC analysis. [d]Determined by ^{13}C NMR.

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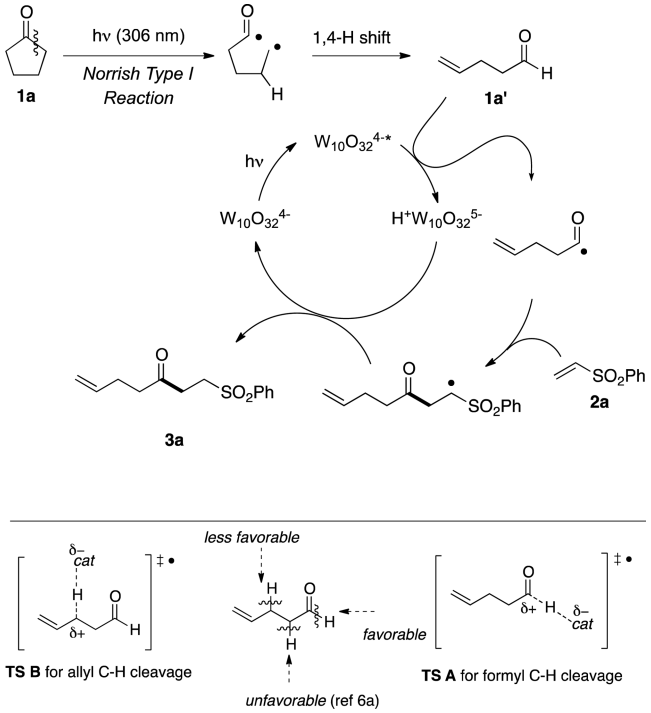
can be rationalized by the faster reaction rate of a 1,4-H shift in the biradical obtained by the Norrish Type I reaction of **1d**. When the reaction of 2,2-dimethylcyclopentanone **1e** with cyclohexenone **2g** was carried out, a regioselective Norrish Type I reaction took place to give **3m** as the sole product in a 60% yield (Table 1, entry 13).[13e] The reaction of **1e** and methyl vinyl ketone **2i** proceeded likewise to give **3n** in an 84% yield (Table 1, entry 14). Norcamphor **1f** also reacted with **2b** to afford the corresponding homoallyl ketone **3o** as the sole product in a 54% yield (Table 1, entry 15).[13a,b]

A plausible reaction mechanism for the photocatalytic one-pot synthesis is outlined in Scheme 4, using the reaction of

Scheme 4. Mechanism of a One-Pot Synthesis of Homoallyl Ketones under TBADT/*hν* Conditions



cyclopentanone **1a** with vinyl sulfone **2a** as a model reaction. Under irradiation conditions, the Norrish Type I reaction of **1a** proceeds to give 4-pentenal **1a′**. Then, excited polyoxotungstate anion ($W_{10}O_{32}^{4-*}$) abstracts the formyl hydrogen from **1a′**. The thus-formed acyl radical then undergoes addition to an electron-deficient olefin to form an adduct radical.[14] Back-hydrogen atom transfer from the reduced form of the decatungstate anion to the radical then occurs to give the desired product **3a**, while restoring the starting TBADT catalyst. The observed site-selectivity favoring formyl C−H cleavage rather than allylic C−H cleavage may be accounted for by the enhanced radical polar effect in the transition state **A** of the H-abstraction by decatungstate.

In summary, using the same cyclopentanones and electron-deficient alkenes, for which we have previously shown the *β*-alkylation of cyclopentanones,[6a] the ring-opening alkylation of cyclopentanones leading to homoallyl ketones is now available. The judicious combination of photoirradiation conditions and photocatalysts is the key to the success in controlling these two useful reaction courses.

EXPERIMENTAL SECTION

General Information. Photoinduced reactions were carried out by using 15 W × 6 phosphor-coated lamp with emission maximum at 306 nm (SANKYO DENKI, GL15E).[15] Products were purified by flash chromatography on silica gel and, if necessary, were further purified by preparative HPLC using $CHCl_3$ as an eluent. ^1H NMR spectra were recorded at 300, 400, or 500 MHz and referenced to the solvent peak at 7.26 ppm. ^{13}C NMR spectra were recorded at 75 or 100 MHz and referenced to the solvent peak at 77.16 ppm. Splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; dd, double doublet; dt, double triplet; q, quartet; sext, sextet; m, multiplet. Infrared spectra are reported in reciprocal centimeters. HRMS data were obtained by EI, CI, or ESI using a double-focusing mass spectrometer or an orbitrap mass spectrometer. Tetrakis-(tetrabutylammonium) decatungstate (TBADT, $(^nBu_4N)_4W_{10}O_{32}$) was prepared according to a published procedure,[16] and CH_3CN was purchased from Nacalai Tesque, Inc. and distilled from CaH_2 before use.

Typical Procedure for Synthesis of 3a. A magnetic stirring bar, cyclopentanone (**1a**; 84.1 mg, 1 mmol), and acetonitrile (10 mL) were placed in a quartz tube under nitrogen atmosphere. The reaction mixture was irradiated by phosphor-coated lamps (15 W × 6) for 24 h. Then, tetrabutylammonium decatungstate (TBADT, 66.4 mg, 0.02 mmol) and phenyl vinyl sulfone (**2a**; 84.1 mg, 0.5 mmol) were added into the reaction mixture under nitrogen atmosphere and kept stirring another 24 h with irradiation by phosphor-coated lamp (15W × 6). After the reaction, the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 5/1) to give 82.8 mg of 1-(phenylsulfonyl)-hept-6-en-3-one (**3a**, 66%).

*1-(Phenylsulfonyl)hept-6-en-3-one (**3a**).* Colorless oil (82.8 mg, 66%); ^1H NMR (400 MHz, $CDCl_3$) δ 2.25−2.31 (m, 2H), 2.53 (t, J = 6.8 Hz, 2H), 2.87−2.91 (m, 2H), 3.35−3.39 (m, 2H), 4.94−5.01 (m, 2H), 5.68−5.77 (m, 1H), 7.54−7.59 (m, 2H), 7.64−7.68 (m, 1H), 7.88−7.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.6, 35.1, 41.9, 50.6, 115.8, 128.0, 129.5, 134.0, 136.5, 139.0, 205.4; IR (neat) 1149, 1308, 1641, 1717 cm^{-1}; MS m/z (relative intensity) 197 ([M − CH_2 = $CHCH_2CH_2]^+$, 34), 143 (20), 125 (100), 111 (21), 110 (73), 95 (15), 83 (48), 77 (34), 55 (59); HRMS (EI) m/z calcd for $C_9H_9O_3S$ ([M − CH_2 = $CHCH_2CH_2]^+$) 197.0272; found, 197.0263.

*4-Oxooct-7-enenitrile (**3b**).* Colorless oil (46.5 mg, 68%); ^1H NMR (400 MHz, $CDCl_3$) δ 2.36 (q, 2H), 2.54−2.60 (m, 4H), 2.80 (t, J = 7.6 Hz, 2H), 4.99−5.07 (m, 2H), 5.74−5.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.4, 27.6, 37.9, 41.5, 115.9, 119.1, 136.5, 205.5; IR (neat) 1642, 1718, 2250 cm^{-1}; CIMS m/z (relative intensity) 138 ([M + H]$^+$, 100), 137 (1), 111 (1), 109 (1), 82 (2); HRMS (CI) m/z calcd for $C_8H_{12}ON$ ([M + H]$^+$) 138.0913; found, 138.0918.

*tert-Butyl 4-oxooct-7-enoate (**3c**).* Colorless oil (61.0 mg, 58%); ^1H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 2.29−2.34 (m, 2H), 2.46−2.55 (m, 4H), 2.64 (t, J = 6.4 Hz, 2H), 4.93−5.02 (m, 2H), 5.73−5.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.8, 28.2, 29.2, 37.4, 41.9, 80.7, 115.3, 137.2, 172.1, 208.4; IR (neat) 1156, 1642, 1720 cm^{-1}; MS m/z (relative intensity) 212 ([M]$^+$, 11), 211 (84), 210 (38), 193 (41), 192 (39), 183 (23), 182 (15), 173 (31), 165 (14), 164 (13), 155 (41), 138 (13), 98 (15), 83 (33), 57 (100), 55 (27); HRMS (CI) m/z calcd for $C_{12}H_{21}O_3$ ([M + H]$^+$) 213.1485; found, 213.1486.

*Dimethyl 2-(pent-4-enoyl)succinate (**3d**).* Colorless oil (76.5 mg, 67%); ^1H NMR (400 MHz, $CDCl_3$) δ 2.31−2.36 (m, 2H), 2.67−2.75 (m, 1H), 2.78−2.86 (m, 2H), 2.95−3.01 (m, 1H), 3.66 (s, 3H), 3.73 (s, 3H), 3.98 (dd, J = 6.0, 8.0 Hz, 1H), 4.96−5.05 (m, 2H), 5.73−5.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.4, 32.2, 42.0, 52.2, 52.9, 53.8, 115.5, 136.8, 168.9, 171.9, 203.2; IR (neat) 1642, 1736 cm^{-1}; MS m/z (relative intensity) 197 ([M-OMe]$^+$, 17), 196 (42), 169 (13), 168 (13), 164 (14), 145 (15), 137 (17), 136 (11), 114 (33), 113 (35), 83 (100), 55 (86); HRMS (EI) m/z calcd for $C_{10}H_{13}O_4$ ([M-OMe]$^+$) 197.0814; found, 197.0804.

*Dibutyl 2-(pent-4-enoyl)succinate (**3e**).* Colorless oil (76.7 mg, 49%); ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (dt, J = 1.6, 7.2 Hz, 6H), 1.35 (sext, J = 8.0 Hz, 4H), 1.54−1.61 (m, 4H), 2.28−2.36 (m, 2H),

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2.65−2.75 (m, 1H), 2.78−2.87 (m, 2H), 2.93−3.00 (m, 1H), 3.95−3.98 (m, 1H), 4.04 (t, J = 6.4 Hz, 2H), 4.11 (dt, J = 0.8, 6.8 Hz, 2H), 4.94−5.06 (m, 2H), 5.73−5.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 13.8, 19.2, 19.2, 27.5, 30.5, 30.6, 32.5, 42.1, 54.0, 65.0, 65.7, 115.5, 136.8, 168.5, 171.6, 203.4; IR (neat) 1642, 1715 cm^{-1}; MS m/z (relative intensity) 239 ([M − OBu]$^+$, 28), 238 (45), 211 (11), 182 (27), 156 (23), 137 (19), 136 (23), 101 (15), 100 (50), 83 (100), 81 (22), 69 (33), 57 (35), 55 (77); HRMS (EI) m/z calcd for $C_{13}H_{19}O_4$ ([M − OBu]$^+$) 239.1283; found, 239.1291.

*3-(Pent-4-enoyl)cyclopentanone (**3f**).* Colorless oil (42.4 mg, 51%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.93−2.03 (m, 1H), 2.16−2.39 (m, 6H), 2.45−2.71 (m, 3H), 3.20−3.28 (m, 1H), 4.96−5.06 (m, 2H), 5.74−5.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.1, 27.6, 37.6, 40.2, 40.8, 47.9, 115.7, 136.9, 209.9, 216.8; IR (neat) 1641, 1711, 1744 cm^{-1}; MS m/z (relative intensity) 167 ([M − H]$^+$, 20), 149 (43), 111 (13), 95 (29), 83 (49), 81 (61), 69 (100), 57 (38), 55 (55); HRMS (EI) m/z calcd for $C_{10}H_{14}O_2$ ([M − H]$^+$) 166.0994; found, 166.0992.

*3-(Pent-4-enoyl)cyclohexanone (**3g**).* Colorless oil (52.3 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62−1.77 (m, 2H), 2.01−2.09 (m, 2H), 2.27−2.41 (m, 5H), 2.49−2.67 (m, 3H), 2.83−2.88 (m, 1H), 4.97−5.06 (m, 2H), 5.74−5.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.0, 27.4, 27.6, 40.2, 41.0, 42.5, 50.3, 115.6, 136.9, 210.0, 210.1; IR (neat) 1641, 1713 cm^{-1}; MS m/z (relative intensity) 180 ([M]$^+$, 19), 126 (12), 125 (35), 120 (12), 98 (18), 97 (92), 85 (10), 83 (77), 69 (32), 55 (100); HRMS (EI) m/z calcd for $C_{11}H_{16}O_2$ ([M]$^+$) 180.1150; found, 180.1147.

*2-(1-(Pent-4-enoyl)cyclohexyl)malononitrile (**3h**).* Colorless oil (63.4 mg, 55%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40−2.00 (m, 8H), 2.00−2.15 (m, 2H), 2.40 (q, J = 7.0 Hz, 2H), 2.70 (t, J = 7.0 Hz, 2H), 4.05 (s, 1H), 4.95−5.15 (m, 2H), 6.75−6.90 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 24.5, 27.5, 27.9, 29.8, 36.8, 54.8, 111.3, 116.0, 136.2, 207.9; IR (neat) 3080, 2935, 2255, 1706, 1641, 1458 cm^{-1}; Anal. Calcd for $C_{14}H_{18}N_2O$: C, 73.01; H, 7.88; N, 12.16. Found: C, 73.0; H, 7.8; N, 12.2.

*4-Oxonon-7-enenitrile (**3i**).* Colorless oil (51.6 mg, 66%), mixture of E/Z = 71/29; E isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.62−1.65 (m, 3H), 2.27−2.31 (m, 2H), 2.49−2.52 (m, 2H), 2.57−2.60 (m, 2H), 2.78−2.80 (m, 2H), 5.38 (dt, J = 15.5, 6.0 Hz, 1H) 5.44−5.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.4, 18.0, 26.7, 37.9, 42.3, 119.2, 126.6, 128.9, 205.9. Z isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.62−1.65 (m, 3H), 2.33−2.38 (m, 2H), 2.49−2.52 (m, 2H), 2.57−2.60 (m, 2H), 2.78−2.80 (m, 2H), 5.31 (dt, J = 10.5, 7.5 Hz, 1H), 5.47−5.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 21.3, 26.7, 37.9, 42.2, 119.2, 125.7, 128.1, 205.9; IR (neat) 1719, 2249 cm^{-1}; MS m/z (relative intensity) 151 ([M]$^+$, 20), 36 (29), 123 (12), 108 (23), 97 (59), 94 (46), 82 (85), 69 (100), 55 (45); HRMS (ESI) m/z calcd for $C_9H_{13}ONNa$ ([M + Na]$^+$) 174.0889; found, 174.0859.

*4-Oxotetradec-7-enenitrile (**3j**).* Colorless oil (64.0 mg, 59%), mixture of E/Z = 74/26; E isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, 3H, J = 7.0 Hz), 0.24−0.33 (m, 8H), 1.94−1.98 (m, 2H), 2.27−2.31 (m, 2H), 2.51 (t, 2H, J = 7.0 Hz), 2.58 (t, 2H, J = 6.5 Hz), 2.79 (t, 2H, J = 7.0 Hz), 5.35 (dtt, 1H, J = 15.5, 6.5, 1.0 Hz), 5.45 (dtt, 1H, J = 15.0, 7.0, 1.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.3, 14.1, 22.6, 26.7, 28.8, 29.4, 31.7, 32.5, 37.8, 42.4, 119.1, 127.6, 132.2, 205.8. Z isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, 3H, J = 7.5 Hz), 0.24−0.33 (m, 8H), 2.00−2.04 (m, 2H), 2.31−2.36 (m, 2H), 2.50 (t, 2H, J = 6.5 Hz), 2.58 (t, 2H, J = 6.5 Hz), 2.80 (t, 2H, J = 7.5 Hz), 5.28 (dtt, 1H, J = 10.5, 7.5, 1.0 Hz), 5.40−5.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.3, 14.1, 21.6, 27.2, 29.0, 29.6, 31.7, 31.8, 37.8, 42.4, 119.1, 127.0, 131.8, 205.8; IR (neat) 1719, 2250 cm^{-1}; MS m/z (relative intensity) 221 ([M]$^+$, 3), 178 (5), 167 (11), 149 (29), 137 (15), 136 (14), 124 (62), 109 (18), 96 (37), 95 (45), 83 (37), 82 (100), 81 (65), 69 (94), 68 (37), 67 (45), 57 (23), 55 (57), 54 (58); HRMS (EI) m/z calcd for $C_{14}H_{23}NO$ ([M]$^+$) 221.1780; found, 221.1782.

*6-Methyl-4-oxooct-7-enenitrile (**3k**).* Colorless oil (62.5 mg, 78%), from inseparable mixture (**3k**/**3k**′ = 71/29); ^{1}H NMR (400 MHz, $CDCl_3$, signals of **3k**) δ 1.01 (d, J = 6.8 Hz, 3H), 2.52−2.59 (m, 4H), 2.67−2.81 (m, 3H), 4.92−5.00 (m, 2H), 5.65−5.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, signals of **3k**) δ 11.4, 20.0, 33.7, 37.8, 49.1, 113.8, 119.1, 142.3, 205.3; IR (neat) 1641, 1718, 2250 cm^{-1}; MS m/z (relative intensity) 152 ([M + H]$^+$, 15), 136 (10), 97 (17), 82 (57), 69 (100), 55 (36), 54 (37), 53 (18); HRMS (ESI) m/z calcd for $C_9H_{13}ONNa$ ([M + Na]$^+$) 174.0889; found, 174.0889.

*7-Methyl-4-oxooct-7-enenitrile (**3k**′).*[17] Colorless oil, from inseparable mixture (**3k**/**3k**′ = 71/29); ^{1}H NMR (400 MHz, $CDCl_3$, signals of **3k**′) δ 1.72 (s, 3H), 2.28−2.32 (m, 2H), 2.54−2.61 (m, 4H), 2.69−2.83 (m, 2H), 4.64 (s, 1H), 4.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, signals of **3k**′) δ 11.4, 22.7, 31.3, 37.8, 40.6, 110.7, 119.1, 143.9, 205.7.

*Dimethyl 2-(3-methylpent-4-enoyl)succinate (**3l**).* Colorless oil (48.4 mg, 40%), from inseparable mixture (**3l**/**3l**′ = 72/28), mixture of two diastereomers, dr = 53/47; ^{1}H NMR (400 MHz, $CDCl_3$, signals of **3l**) δ 0.97−1.01 (m, 6H), 2.57−3.25 (m, 10H), 3.65 (s, 6H), 3.71 (s, 6H), 3.93−3.97 (m, 2H), 4.90−5.00 (m, 4H), 5.67−5.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, signals of **3l**) δ 19.4, 19.7, 32.0, 32.1, 32.7, 32.7, 49.2, 49.3, 52.1, 52.1, 52.8, 52.8, 54.3, 54.3, 113.3, 113.3, 142.5, 142.6, 168.8, 168.9, 171.9, 202.6, 202.7; IR (neat) 1643, 1738 cm^{-1}; MS m/z (relative intensity) 242 ([M]$^+$, 5), 211 (43), 210 (63), 183 (51), 182 (22), 151 (49), 150 (22), 145 (54), 114 (37), 113 (72), 97 (80), 96 (24), 69 (100), 55 (45); HRMS (EI) m/z calcd for $C_{11}H_{15}O_4$ ([M − OMe]$^+$) 211.0970; found, 211.0967.

*Dimethyl 2-(4-methylpent-4-enoyl)succinate (**3l**′).* Colorless oil, from inseparable mixture (**3l**/**3l**′ = 72/28); ^{1}H NMR (400 MHz, $CDCl_3$, signals of **3l**′) δ 1.72 (s, 3H), 2.28−2.32 (m, 2H), 2.57−3.25 (m, 4H), 3.65 (s, 3H), 3.71 (s, 3H), 3.93−3.97 (m, 1H), 4.65 (s, 1H), 4.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, signals of **3l**′) δ 22.7, 31.0, 32.2, 41.1, 52.1, 52.9, 53.8, 110.3, 144.2, 168.9, 171.9, 203.4.

*3-(5-Methylhex-4-enoyl)cyclohexanone (**3m**).* Colorless oil (62.5 mg, 60%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60 (s, 3H), 1.70 (s, 3H), 1.70−1.80 (m, 2H), 2.00−2.20 (m, 2H), 2.25−2.55 (m, 8H), 2.80−2.90 (m, 1H), 5.00−5.10 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.5, 22.2, 24.8, 25.5, 27.2, 40.8, 41.0, 42.4, 50.2, 122.3, 132.9, 210.0, 210.3; IR (neat) 2931, 1714 cm^{-1}; Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.9; H, 9.7.

*9-Methyldec-8-ene-2,5-dione (**3n**).* Colorless oil (76.5 mg, 84%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60 (s, 3H), 1.65 (s, 3H), 2.15 (s, 3H), 2.15−2.25 (m, 2H), 2.40−2.55 (m, 2H), 3.60−3.70 (m, 4H), 5.05 (t, J = 6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.5, 22.3, 25.5, 29.8, 36.0, 36.7, 42.6, 122.6, 132.5, 207.1, 209.1; IR (neat) 2920, 1714 cm^{-1}; Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.4; H, 10.0.

*5-(Cyclopent-2-en-1-yl)-4-oxopentanenitrile (**3o**).* Colorless oil (43.2 mg, 54%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33−1.41 (m, 1H), 2.10−2.18 (m, 1H), 2.30−2.37 (m, 2H), 2.43−2.61 (m, 4H), 2.77−2.81 (m, 2H), 3.08−3.16 (m, 1H), 5.61−5.63 (m, 1H), 5.76−5.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.4, 30.0, 31.9, 38.2, 41.0, 48.7, 119.1, 131.9, 133.4, 205.8; IR (neat) 1614, 1714, 2250 cm^{-1}; MS m/z (relative intensity) 163 ([M]$^+$, 8), 109 (88), 98 (29), 85 (25), 83 (39), 82 (27), 81 (58), 79 (38), 67 (89), 66 (100), 54 (25); HRMS (EI) m/z calcd for $C_{10}H_{13}NO$ ([M]$^+$) 163.0997; found, 163.1005.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01850.

^{1}H and ^{13}C NMR charts of products (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Chen, F.; Mudryk, B.; Cohen, T. *Tetrahedron* **1994**, *50*, 12793. (b) Dechoux, L.; Jung, L.; Stambach, J. F. *Synlett* **1994**, *1994*, 965. (c) Antonioletti, R.; Magnanti, S.; Scettri, A. *Tetrahedron Lett.* **1994**, *35*, 2619. (d) Hutton, T. K.; Muir, K.; Procter, D. J. *Org. Lett.* **2002**, *4*, 2345. (e) Koganemaru, Y.; Kitamura, M.; Narasaka, K. *Chem. Lett.* **2002**, 784.

(2) Ferrer, S.; Muratore, M. E.; Echavarren, A. M. *ChemCatChem* **2015**, *7*, 228.

(3) (a) Yan, X.-X.; Liang, C.-G.; Zhang, Y.; Hong, W.; Cao, B.-X.; Dai, L.-X.; Hou, X.-L. *Angew. Chem., Int. Ed.* **2005**, *44*, 6544. (b) Clive, D. L. J.; Pham, M. P. *J. Org. Chem.* **2009**, *74*, 1685. (c) Wen, Y.; Huang, L.; Jiang, H.; Chen, H. *J. Org. Chem.* **2012**, *77*, 2029. (d) Trost, B. M.; Xu, J.; Schmidt, T. *J. Am. Chem. Soc.* **2009**, *131*, 18343. (e) Huo, X.; Yang, G.; Liu, D.; Liu, Y.; Gridnev, I. D.; Zhang, W. *Angew. Chem., Int. Ed.* **2014**, *53*, 6776.

(4) (a) Tsuji, J.; Minami, I.; Shimizu, I. *Chem. Lett.* **1983**, 1325. (b) Katritzky, A. R.; Huang, Z.; Fang, Y. *J. Org. Chem.* **1999**, *64*, 7625. (c) Higashino, T.; Sakaguchi, S.; Ishii, Y. *Org. Lett.* **2000**, *2*, 4193. (d) Morita, M.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **2006**, *71*, 6285. (e) Ketcham, J. M.; Biannic, B.; Aponick, A. *Chem. Commun.* **2013**, *49*, 4157. (f) Gómez-Suárez, A.; Gasperini, D.; Vummaleti, S. V. C.; Poater, A.; Cavallo, L.; Nolan, S. P. *ACS Catal.* **2014**, *4*, 2701.

(5) (a) Ryu, I.; Yamazaki, H.; Kusano, K.; Ogawa, A.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 8558. (b) Fusano, A.; Fukuyama, T.; Nishitani, S.; Inouye, T.; Ryu, I. *Org. Lett.* **2010**, *12*, 2410. (c) Sumino, S.; Ui, T.; Ryu, I. *Org. Lett.* **2013**, *15*, 3142.

(6) (a) Okada, M.; Fukuyama, T.; Yamada, K.; Ryu, I.; Ravelli, D.; Fagnoni, M. *Chem. Sci.* **2014**, *5*, 2893. Also, see the case of nitriles (b) Yamada, K.; Okada, M.; Fukuyama, T.; Ravelli, D.; Fagnoni, M.; Ryu, I. *Org. Lett.* **2015**, *17*, 1292.

(7) For recent work on TBADT-catalyzed reaction, see (a) Ryu, I.; Tani, A.; Fukuyama, T.; Ravelli, D.; Fagnoni, M.; Albini, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 1869. (b) Ravelli, D.; Albini, A.; Fagnoni, M. *Chem. - Eur. J.* **2011**, *17*, 572. (c) Montanaro, S.; Ravelli, D.; Merli, D.; Fagnoni, M.; Albini, A. *Org. Lett.* **2012**, *14*, 4218. (d) Ryu, I.; Tani, A.; Fukuyama, T.; Ravelli, D.; Montanaro, S.; Fagnoni, M. *Org. Lett.* **2013**, *15*, 2554. (e) Qrareya, H.; Ravelli, D.; Fagnoni, M.; Albini, A. *Adv. Synth. Catal.* **2013**, *355*, 2891.

(8) For reviews on decatungstate photocatalysis, see (a) Hill, C. L. *Synlett* **1995**, *1995*, 127. (b) Tanielian, C. *Coord. Chem. Rev.* **1998**, *178*−*180*, 1165. (c) Hill, C. L. *J. Mol. Catal. A: Chem.* **2007**, *262*, 2. (d) Tzirakis, M. D.; Lykakis, I. N.; Orfanopoulos, M. *Chem. Soc. Rev.* **2009**, *38*, 2609. (e) Protti, S.; Fagnoni, M.; Ravelli, D. *ChemCatChem* **2015**, *7*, 1516.

(9) Norrish, R. G. W.; Bamford, C. H. *Nature* **1936**, *138*, 1016.

(10) (a) Turro, N. J.; Ramamurthy, V.; Scaiano, J. C. *Modern Molecular Photochemistry of Organic Molecules*; University Science Books: Sausalito, CA, 2010. (b) *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P. S., Eds.; CRC Press: Boca Raton, FL, 1995.

(11) (a) Tai, H.-M.; Huang, M.-H.; Yang, C.-C. *J. Chin. Chem. Soc.* **2003**, *50*, 441. (b) Itagaki, N.; Iwabuchi, Y. *Chem. Commun.* **2007**, 1175. (c) Albini, A.; Fagnoni, M. *Photochemically-Generated Intermediates in Synthesis*; John Wiley & Sons: Hoboken, NJ, 2013; pp 131−167.

(12) Baum, A. A. *Tetrahedron Lett.* **1972**, *13*, 1817.

(13) For the Norrish Type I photocleavage of cyclopentanones, see (a) Meinwald, J.; Chapman, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3218. (b) Dalton, J. C.; Pond, D. M.; Weiss, D. S.; Lewis, F. D.; Turro, N. J. *J. Am. Chem. Soc.* **1970**, *92*, 2564. (c) Badcoc, C. C.; Rickborn, B.; Pritchard, G. O. *Chem. Ind.* **1970**, 1053. (d) Dalton, J. C.; Dawes, K.; Turro, N. J.; Weiss, D. S.; Barltrop, J. A.; Coyle, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 7213. (e) Morton, D. R.; Turro, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 3947. (f) Mueller-Remmers, P. L.; Mishra, P. C.; Jug, K. *J. Am. Chem. Soc.* **1984**, *106*, 2538. (g) Cossy, J.; Pete, J.-P. *Bull. Soc. Chim. Fr.* **1988**, 989.

(14) (a) Esposti, S.; Dondi, D.; Fagnoni, M.; Albini, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 2531. (b) Fagnoni, M.; Bonassi, F.; Palmieri, A.; Protti, S.; Ravelli, D.; Ballini, R. *Adv. Synth. Catal.* **2014**, *356*, 753. (c) Kawamoto, T.; Uehara, S.; Hirao, H.; Fukuyama, T.; Matsubara, H.; Ryu, I. *J. Org. Chem.* **2014**, *79*, 3999. For a review on acyl radicals, see (d) Chatgilialoglu, C.; Crich, D.; Komatsu, M.; Ryu, I. *Chem. Rev.* **1999**, *99*, 1991.

(15) Sankyo Denki: http://www.sankyo-denki.co.jp/e2_09.html.

(16) Protti, S.; Ravelli, D.; Fagnoni, M.; Albini, A. *Chem. Commun.* **2009**, 7351.

(17) Molander, G. A.; Dowdy, E. D. *J. Org. Chem.* **1998**, *63*, 8983.

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