Visible Light Induced Cyclopropanation of Dibromomalonates with Alkenes via Double-SET by Photoredox Catalysis

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**Scheme S1.** Reactions of 2a with 3t, 3u, and 3v under Condition A

**Scheme S2.** Effect of radical scavenger

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Detailed discussion on other possibilities of reaction pathways

Although the above results fitted well with our initially proposed mechanism as shown in Scheme 3, some other possibilities of reaction pathways should also be considered. One alternative mechanism could be envisaged that the initially formed radical intermediate 5 could abstract hydrogen from the solvent (MeOH) or the Hunig base to form 1. Then the *in situ* formed 1 might undergo deprotonation by the amine to afford the bromomalonate carbanion 6 which would undergo intermolecular Michael addition and intramolecular nucleophilic substitution (pathway A), or it might also be possible to undergo atom-transfer, deprotonation by the amine, and intramolecular nucleophilic substitution to afford the final product (pathway B) (Scheme S4).

![Scheme S4. Bromomalonate 1 involved mechanism](image)

To explore these possibilities, we firstly tried to isolate or detect 1 from the reaction mixture before the reaction was completed. Disapprovingly, all attempts failed (Scheme S5).

![Scheme S5. Detecting or isolating bromomalonate 1](image)

Then this reaction was carried out using aprotic solvent (benzene) under strictly anhydrous conditions. 4aa was isolated in an 80% yield, which might be considered
as negative evidence for the hypothesis that 5 abstracted hydrogen from the solvent (MeOH) to form 1, since it is hard to abstract hydrogen from benzene. However, the possibility for the transformation of 6 into 1 could not be fully ruled out, since this might not be the rate-determining step.

Notably, the reaction of 1 with 3a with or without light proceeded smoothly to form 4aa in much lower yields (Scheme S6). If the reaction of 2a with 3a proceeded mainly via intermediate 1, the final yield of 4aa should be no more than 75% (Scheme S6) which is the yield of reaction with pure 1 as the starting material. However, an isolated yield as high as 92% (entry 5, Table 1) was afforded. This might be a proof showing the impossibility of the above hypothesis.

**Scheme S6.** Reactions of 1 with 3a under Condition A with and without visible light

Finally, the reactions under Condition A using 1 instead of 2a with and without TEMPO were studied. As shown in Scheme S7, the isolated yields of 4aa in both cases became much lower. If this reaction proceeded mainly via intermediate 1, the addition of 5 equiv. of TEMPO should decrease the final yield to at least 50% (Scheme S7) which is the yield of reaction with pure 1 as the starting material. However, an isolated yield as high as 80% (Scheme S2) was afforded. This might not support the above mechanism.
Scheme S7. The photocyclopropanation of 1 with and without TEMPO under Condition A

Additionally, a carbone intermediate involved mechanism (Scheme S8) was explored. The result of reaction of 2a with 3u under Condition A (Scheme S1) negativized this proposal, since 3u is a typical reactant in such a carbone involved cyclopropanation. Then a reported carbone precursor was employed to check the possibility of carbone-involved mechanism, but also showed negative results (Scheme S9).

Scheme S8. Carbone intermediate involved mechanism
Scheme S9. Reaction of carbone precursor with 3a
Experimental Section

The sunlight induced photoreactions were carried out by exposing the reaction tube to direct solar illumination in the daytime from 9:00 to 16:00 in a sunny day. A picture for the setup of this reaction is shown in Figure S1.

Figure S1. A picture for the setup of sunlight induced reaction.
The visible light induced photoreactions were carried out using a 23W household lamp at a distance of 3-5 cm with the reactor. A picture for the setup of this reaction is shown in Figure S2.

![Figure S2. A picture for the setup of visible light induced reaction.](image)

**General information**

All reactions were carried out using a pyrex reactor. IR spectra were recorded on a Avatar 360 FT-IR spectrometer. $^1$H (400 MHz), $^{13}$C (100 MHz), and $^{19}$F (376 MHz) NMR spectra of samples in CDCl$_3$ were recorded on an AVANCE III 400 spectrometer. MS (EI, 70 eV) determinations were carried out on a HP 5973 spectrometer. MS (ESI) determinations were carried out on an Agilent 1100 LC/MSD SL spectrometer. HRMS (EI, 70 eV) determinations were carried out on a Water GCT CA176 spectrometer. HRMS (ESI) determinations were carried out on a Bruker
Daltonics APEXIII™ ESI-FTICRMS spectrometer. Compound 3a, 3h, 3t, 3u and Z-8 was commercial available. Compounds 2b, 3a, 3b, 3c, 3d, 3e, 3f, 3g, 3i, 3j, 3k, 3l, 3m, 3n, 3o, 3p, 3q, 3r, 3s, 3t and E-8 were prepared according to literature procedures.

Synthesis of Diisopropyl dibromomalonate (2c)

Diisopropyl malonate (1.9 mL, 10.0 mmol) was added into a 100 mL three-necked flask. Then a solution of bromine (1.2 mL, 23.4 mmol) in carbon tetrachloride (10 mL) was added dropwise. The resulting reaction mixture was refluxed for 48 hours, and then cooled to room temperature, quenched by 5% Na₂CO₃ solution, and extracted with ethyl acetate (30 mL x 3). The combined organic layer was dried over MgSO₄. Filtration, concentration, and purification by flash chromatography on silica gel (eluent: petroleum ether→ethyl acetate/petroleum ether = 1/100) afforded 2c as a liquid (690 mg, 20%); ¹H NMR (400 MHz, CDCl₃) δ 5.21-5.08 (m, 2 H), 1.32 (d, J = 6.4 Hz, 12 H); ¹³C NMR (100 MHz, CDCl₃) δ 162.6, 72.9, 51.9, 21.1; IR (neat) 1747 cm⁻¹; MS (ESI) m/z 369 (M+Na⁺); HRMS (ESI) calcd for C₉H₁₄Br₂NaO₄ 366.9151, found 366.9163.

Typical Procedure I for the photoreaction under Condition A.

Synthesis of diethyl 2,2-dicyano-3-(4-methoxycarbonylphenyl)cyclopropane-1,1-dicarboxylate (4ab)

2a (38 μL, 0.20 mmol), 3b (86 mg, 0.41 mmol), Ru(bpy)₃Cl₂·6H₂O (2 mg, 0.0027 mmol), Pr₂NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) were added to a dry 25 mL pyrex reaction flask. The mixture was irradiated by a 23W household lamp at rt in the open air. The photoreaction was completed after 4 h as
monitored by TLC (eluent: petroleum ether/ethyl acetate = 10/1). The solvent was removed and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1→15/1→10/1) to afforded 4ab as a solid (73 mg, 98%); mp 68.1-69.9 °C (ethyl acetate/petroleum ether). 1H NMR (400 MHz, CDCl3) δ 8.08 (d, J = 8.8 Hz, 2 H), 7.48 (d, J = 8.8 Hz, 2 H), 4.44 (q, J = 7.2 Hz, 2 H), 4.30-4.19 (m, 2 H), 3.99 (s, 1 H), 3.93 (s, 3 H), 1.40 (t, J = 7.2 Hz, 3 H), 1.20 (t, J = 7.2 Hz, 3 H); 13C NMR (100 MHz, CDCl3) δ 165.9, 162.7, 160.8, 132.0, 131.2, 130.1, 128.9, 111.4, 109.4, 64.5, 63.7, 52.3, 46.0, 39.4, 16.2, 13.8, 13.5; IR (neat) 2253, 1745, 1720, 1612, 1440 cm⁻¹; MS (EI, 70 eV) m/z 370 (M⁺, 0.51), 266 (100); HRMS (EI, 70 eV) calcd for C19H18N2O6 370.1165, found 370.1160.

The following compounds were prepared according to Typical Procedure I.

(1) Diethyl 2,2-dicyano-3-(4-trifluoromethylphenyl)cyclopropane-1,1-dicarboxylate (4ac)

The reaction of 2a (38 μL, 0.20 mmol), 3c (92 mg, 0.41 mmol), Ru(bpy)3Cl2·6H2O (2 mg, 0.0027 mmol), Pr2NEt (68 μL, 0.41 mmol), and anhydrous methanol (10 mL) afforded 4ac as a solid (73 mg, 96%); mp 148.9-151.3 °C (ethyl acetate/petroleum ether). 1H NMR (400 MHz, CDCl3) δ 7.68 (d, J = 8.4 Hz, 2 H), 7.54 (d, J = 8.4 Hz, 2 H), 4.44 (q, J = 7.2 Hz, 2 H), 4.32-4.21 (m, 2 H), 4.00 (s, 1 H), 1.39 (t, J = 7.2 Hz, 3 H), 1.21 (t, J = 7.2 Hz, 3 H); 13C NMR (100 MHz, CDCl3) δ 162.6, 160.7, 131.6 (q, J = 32.9 Hz), 131.3, 129.4, 125.9 (q, J = 3.6 Hz), 123.4 (q, J = 270.7 Hz), 111.4, 109.4, 64.6, 63.8, 46.1, 39.1, 16.2, 13.7, 13.4; 19F NMR (376 MHz, CDCl3) δ -63.4 ppm; IR (neat) 2250, 1741,1321 cm⁻¹; MS (EI, 70 eV) m/z 380 (M⁺, 1.52), 209 (100); HRMS (EI, 70 eV) calcd for C18H15N2O4F3 380.0984, found 380.0979.

(2) Diethyl 2,2-dicyano-3-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate (4ad)
The reaction of 2a (38 μL, 0.20 mmol), 3d (80 mg, 0.40 mmol), Ru(bpy)_3Cl_2·6H_2O (2 mg, 0.0027 mmol), Pr_2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ad as a solid (66 mg, 92%); mp 113.0-114.2 °C (ethyl acetate/petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 8.29 (d, J = 8.8 Hz, 2 H), 7.62 (d, J = 8.8 Hz, 2 H), 4.46 (q, J = 6.8 Hz, 2 H), 4.33-4.22 (m, 2 H), 4.02 (s, 1 H), 1.41 (t, J = 6.8 Hz, 3 H), 1.25 (t, J = 6.8 Hz, 3 H); ^13C NMR (100 MHz, CDCl_3) δ 162.6, 160.5, 148.4, 134.2, 130.2, 124.2, 111.1, 109.2, 64.9, 64.1, 46.1, 38.9, 16.3, 13.9, 13.6; IR (neat) 2256, 1744, 1610, 1528, 1351 cm⁻¹; MS (EI, 70 eV) m/z 357 (M⁺), 257 (100); HRMS (EI, 70 eV) calcd for C_{17}H_{15}N_3O_6 357.0961, found 357.0964.

(3) Diethyl 2,2-dicyano-3-(3-nitrophenyl)cyclopropane-1,1-dicarboxylate (4ae)

The reaction of 2a (38 μL, 0.20 mmol), 3e (78 mg, 0.39 mmol), Ru(bpy)_3Cl_2·6H_2O (2 mg, 0.0027 mmol), Pr_2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ae as a solid (60 mg, 84%); mp 109.5-110.4 °C (ethyl acetate/petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 8.33-8.25 (m, 2 H), 7.80 (d, J = 7.6 Hz, 1 H), 7.66 (t, J = 7.2 Hz, 1 H), 4.46 (q, J = 6.8 Hz, 2 H), 4.37-4.25 (m, 2 H), 4.04 (s, 1 H), 1.41 (t, J = 6.8 Hz, 3 H), 1.28 (t, J = 6.8 Hz, 3 H); ^13C NMR (100 MHz, CDCl_3) δ 162.5, 160.6, 148.4, 135.0, 130.4, 129.4, 124.6, 124.2, 111.1, 109.2, 64.8, 64.2, 46.1, 38.8, 16.4, 13.9, 13.6; IR (neat) 2253, 1744, 1537 cm⁻¹; MS (EI, 70 eV) m/z 357 (M⁺, 1.08), 257 (100); HRMS (EI, 70 eV) calcd for C_{17}H_{15}N_3O_6 357.0961, found 357.0957.

(4) Diethyl 2,2-dicyano-3-(2-nitrophenyl)cyclopropane-1,1-dicarboxylate (4af)
The reaction of 2a (38 μL, 0.20 mmol), 3f (83 mg, 0.42 mmol), Ru(bpy)3Cl2·6H2O (2 mg, 0.0027 mmol), Pr2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4af as a solid (61 mg, 85%); mp 73.1-74.3 °C (ethyl acetate/petroleum ether). 1H NMR (400 MHz, CDCl3) δ 8.26 (d, J = 8.0 Hz, 1 H), 7.80-7.69 (m, 2 H), 7.65 (t, J = 7.2 Hz, 1 H), 4.46 (q, J = 7.2 Hz, 2 H), 4.36 (s, 1 H), 4.17 (q, J = 6.8 Hz, 2 H), 1.41 (t, J = 6.8 Hz, 3 H), 1.19 (t, J = 6.8 Hz, 3 H); 13C NMR (100 MHz, CDCl3) δ 162.8, 160.7, 149.1, 134.0, 130.9, 130.7, 125.6, 123.3, 110.9, 110.0, 64.5, 63.8, 45.1, 40.0, 16.9, 13.8, 13.4; IR (neat) 2253, 1741, 1534 cm⁻¹; MS (ESI) m/z 380 (M+Na⁺); HRMS (ESI) calcd for C17H15N3NaO6 380.0853, found 380.0859.

(5) Diethyl 2,2-dicyano-3-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate (4ag)

The reaction of 2a (38 μL, 0.20 mmol), 3g (71 mg, 0.41 mmol), Ru(bpy)3Cl2·6H2O (2 mg, 0.0027 mmol), Pr2NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ag as a solid (63 mg, 95%); mp 73.3-75.2 °C (ethyl acetate/petroleum ether). 1H NMR (400 MHz, CDCl3) δ 7.43-7.35 (m, 2 H), 7.11 (t, J = 8.4 Hz, 2 H), 4.43 (q, J = 6.8 Hz, 2 H), 4.31-4.20 (m, 2 H), 3.93 (s, 1 H), 1.39 (t, J = 6.8 Hz, 3 H), 1.22 (t, J = 6.8 Hz, 3 H); 13C NMR (100 MHz, CDCl3) δ 163.2 (d, J = 248.9 Hz), 162.8, 160.9, 130.8 (d, J = 8.8 Hz), 123.1 (d, J = 3.6 Hz), 116.2 (d, J = 21.9 Hz), 111.6, 109.6, 64.5, 63.7, 46.3, 39.2, 16.2, 13.8, 13.5; 19F NMR (376 MHz, CDCl3) δ -111.0 ppm; IR (neat) 2253, 1744, 1516 cm⁻¹; MS (EI, 70 eV) m/z 330 (M⁺, 0.32), 159 (100); HRMS (EI, 70 eV) calcd for C17H15F2O4 330.1016, found S12
(6) Diethyl 2,2-dicyano-3-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate (4ah)\(^{17}\)

\[
\begin{array}{c}
\text{EtOOC} \quad \text{COOEt} \\
\text{Br} \quad \text{Br} \\
2a
\end{array}
\begin{array}{c}
\text{Cl} \\
\text{CN} \\
3h
\end{array}
\begin{array}{c}
\text{EtOOC} \quad \text{COOEt} \\
\text{Br} \quad \text{Br} \\
2 \text{ (equiv.)}
\end{array}
\begin{array}{c}
\text{air (1 atm)} \\
\text{visible light}
\end{array}
\begin{array}{c}
1 \text{ mol\% Ru(bpy)\textsubscript{3}Cl\textsubscript{2}·6H\textsubscript{2}O} \\
\text{Pr\textsubscript{2}NEt (2 equiv.)} \\
\text{MeOH, rt, 3.5 h, 95%}
\end{array}
\begin{array}{c}
\text{EtOOC} \quad \text{COOEt} \\
\text{CN} \quad \text{CN} \\
4ah
\end{array}
\]

The reaction of 2a (38 \(\mu\)L, 0.20 mmol), 3h (70 mg, 0.37 mmol), Ru(bpy)\textsubscript{3}Cl\textsubscript{2}·6H\textsubscript{2}O (2 mg, 0.0027 mmol), Pr\textsubscript{2}NEt (66 \(\mu\)L, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ah as a solid (66 mg, 95\%); mp 85.0-87.0 °C\(^{17}\) (ethyl acetate/petroleum ether). \(^1H\) NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.39 (d, \(J = 8.0\) Hz, 2 H), 7.33 (d, \(J = 8.0\) Hz, 2 H), 4.43 (q, \(J = 6.4\) Hz, 2 H), 4.31-4.20 (m, 2 H), 3.92 (s, 1 H), 1.39 (t, \(J = 6.4\) Hz, 3 H), 1.22 (t, \(J = 6.4\) Hz, 3 H).

(7) Diethyl 2,2-dicyano-3-phenylcyclopropane-1,1-dicarboxylate (4aa)\(^{18}\)

\[
\begin{array}{c}
\text{EtOOC} \quad \text{COOEt} \\
\text{Br} \quad \text{Br} \\
2a
\end{array}
\begin{array}{c}
\text{CN} \\
\text{CN} \\
3a
\end{array}
\begin{array}{c}
\text{EtOOC} \quad \text{COOEt} \\
\text{Br} \quad \text{Br} \\
2 \text{ (equiv.)}
\end{array}
\begin{array}{c}
\text{air (1 atm)} \\
\text{visible light}
\end{array}
\begin{array}{c}
1 \text{ mol\% Ru(bpy)\textsubscript{3}Cl\textsubscript{2}·6H\textsubscript{2}O} \\
\text{Pr\textsubscript{2}NEt (2 equiv.)} \\
\text{MeOH, rt, 5 h, 92%}
\end{array}
\begin{array}{c}
\text{EtOOC} \quad \text{COOEt} \\
\text{CN} \quad \text{CN} \\
4aa
\end{array}
\]

The reaction of 2a (38 \(\mu\)L, 0.20 mmol), 3a (62 mg, 0.41 mmol), Ru(bpy)\textsubscript{3}Cl\textsubscript{2}·6H\textsubscript{2}O (2 mg, 0.0027 mmol), Pr\textsubscript{2}NEt (66 \(\mu\)L, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4aa as a solid (64 mg, 92\%); mp 71.0-72.0 °C\(^{18}\) (ethyl acetate/petroleum ether). \(^1H\) NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.44-7.34 (m, 5 H), 4.42 (q, \(J = 7.2\) Hz, 2 H), 4.29-4.18 (m, 2 H), 3.96 (s, 1 H), 1.38 (t, \(J = 7.2\) Hz, 3 H), 1.19 (t, \(J = 7.2\) Hz, 3 H).

(8) Diethyl 2,2-dicyano-3-(4-methylphenyl)cyclopropane-1,1-dicarboxylate (4ai)\(^{19}\)

\[
\begin{array}{c}
\text{EtOOC} \quad \text{COOEt} \\
\text{Br} \quad \text{Br} \\
2a
\end{array}
\begin{array}{c}
\text{CN} \\
\text{CN} \\
3i
\end{array}
\begin{array}{c}
\text{EtOOC} \quad \text{COOEt} \\
\text{Br} \quad \text{Br} \\
2 \text{ (equiv.)}
\end{array}
\begin{array}{c}
\text{air (1 atm)} \\
\text{visible light}
\end{array}
\begin{array}{c}
1 \text{ mol\% Ru(bpy)\textsubscript{3}Cl\textsubscript{2}·6H\textsubscript{2}O} \\
\text{Pr\textsubscript{2}NEt (2 equiv.)} \\
\text{MeOH, rt, 2.5 h, 95%}
\end{array}
\begin{array}{c}
\text{EtOOC} \quad \text{COOEt} \\
\text{CN} \quad \text{CN} \\
4ai
\end{array}
\]

The reaction of 2a (38 \(\mu\)L, 0.20 mmol), 3i (69 mg, 0.41 mmol),
Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_3^2$NEt (66 μL, 0.41 mmol), and anhydrous methanol (10 mL) afforded 4ai as a solid (64 mg, 95%); mp 77.0-79.0 °C $^{19}$ (ethyl acetate/petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.25 (d, $J = 8.0$ Hz, 2 H), 7.20 (d, $J = 8.0$ Hz, 2 H), 4.41 (q, $J = 6.8$ Hz, 2 H), 4.31-4.19 (m, 2 H), 3.93 (s, 1 H), 2.35 (s, 2 H), 1.38 (t, $J = 6.8$ Hz, 3 H), 1.21 (t, $J = 6.8$ Hz, 3 H).

(9) Diethyl 2,2-dicyano-3-(3-methylphenyl)cyclopropane-1,1-dicarboxylate (4aj)

The reaction of 2a (38 μL, 0.20 mmol), 3j (68 mg, 0.40 mmol), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_3^2$NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4aj as a solid (62 mg, 95%); mp 95.2-96.1 °C (ethyl acetate/petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32-7.12 (m, 4 H), 4.42 (q, $J = 7.2$ Hz, 2 H), 4.29-4.19 (m, 2 H), 3.93 (s, 1 H), 2.35 (s, 2 H), 1.38 (t, $J = 7.2$ Hz, 3 H), 1.20 (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.0, 161.0, 138.8, 130.3, 129.4, 128.9, 127.1, 125.5, 111.9, 109.6, 64.3, 63.5, 46.2, 40.0, 21.2, 16.0, 13.9, 13.5; IR (neat) 2253, 1744, 1217 cm$^{-1}$; MS (EI, 70 eV) m/z 326 (M$^+$, 4.42), 154 (100); HRMS (EI, 70 eV) calcd for C$_{18}$H$_{18}$N$_2$O$_4$ 326.1267, found 326.1263.

(10) Diethyl 2,2-dicyano-3-(2-methylphenyl)cyclopropane-1,1-dicarboxylate (4ak)

The reaction of 2a (38 μL, 0.20 mmol), 3k (69 mg, 0.41 mmol), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_3^2$NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ak as a liquid (63 mg, 96%); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, $J = 7.2$ Hz, 1 H), 7.33-7.26 (m, 2 H), 7.22-7.16 (m, 1 H), 4.44 (q, $J = 7.2$ Hz, 2 H), 4.22 (q, $J$
= 7.2 Hz, 2 H), 3.87 (s, 1 H), 2.42 (s, 3 H), 1.39 (t, J = 7.2 Hz, 3 H), 1.16 (t, J = 7.2 Hz, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.1, 161.2, 138.4, 131.0, 129.5, 127.2, 126.2, 126.0, 112.1, 109.8, 64.3, 63.5, 46.0, 39.6, 19.4, 16.2, 13.9, 13.4; IR (neat) 2250, 1744, 1464, 1372 cm\(^{-1}\); MS (El, 70 eV) m/z 326 (M\(^{+}\), 2.4), 154 (100); HRMS (El, 70 eV) calcd for C\(_{18}\)H\(_{18}\)N\(_2\)O\(_4\) 326.1267, found 326.1265.

(11) Diethyl 2,2-dicyano-3-(4-ethylphenyl)cyclopropane-1,1-dicarboxylate (4al)

The reaction of 2a (38 \(\mu\)L, 0.20 mmol), 3l (74 mg, 0.41 mmol), Ru(bpy)\(_3\)Cl\(_2\)-6H\(_2\)O (2 mg, 0.0027 mmol), Pr\(_2\)NEt (66 \(\mu\)L, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4al as a solid (64 mg, 94%); mp 69.3-71.2 °C (ethyl acetate/petroleum ether). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.28 (d, J = 8.4 Hz, 2 H), 7.22 (d, J = 8.4 Hz, 2 H), 4.42 (q, J = 6.8 Hz, 2 H), 4.31-4.19 (m, 2 H), 3.93 (s, 1 H), 2.65 (q, J = 7.2 Hz, 2 H), 1.38 (t, J = 6.8 Hz, 3 H), 1.23-1.17 (m, 6 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.2, 161.2, 146.0, 128.7, 128.6, 124.3, 111.9, 109.8, 64.4, 63.5, 46.3, 40.1, 28.5, 16.3, 15.2, 13.9, 13.6; IR (neat) 2247, 1744 cm\(^{-1}\); MS (El, 70 eV) m/z 340 (M\(^{+}\), 2.91), 225 (100); HRMS (El, 70 eV) calcd for C\(_{19}\)H\(_{20}\)N\(_2\)O\(_4\) 340.1423, found 340.1420.

(12) Diethyl 2,2-dicyano-3-(4-isopropylphenyl)cyclopropane-1,1-dicarboxylate (4am)

The reaction of 2a (38 \(\mu\)L, 0.20 mmol), 3m (76 mg, 0.39 mmol), Ru(bpy)\(_3\)Cl\(_2\)-6H\(_2\)O (2 mg, 0.0027 mmol), Pr\(_2\)NEt (66 \(\mu\)L, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4am as a solid (68 mg, 96%); mp 83.6-84.6 °C (ethyl acetate/petroleum ether). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.32-7.21 (m, 4 H), 4.40 (q, J
= 7.6 Hz, 2 H), 4.30-4.18 (m, 2 H), 3.93 (s, 1 H), 2.96-2.85 (m, 1 H), 1.37 (t, J = 6.8 Hz, 3 H), 1.29-1.12 (m, 9 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.1, 161.1, 150.6, 128.7, 127.1, 124.4, 111.9, 109.8, 64.3, 63.5, 46.3, 40.1, 33.8, 23.7, 16.3, 13.9, 13.5; IR (neat) 2250, 1747, 1613, 1522, 1464 cm\(^{-1}\); MS (EI, 70 eV) m/z 354 (M\(^+\), 5.12), 84 (100); HRMS (EI, 70 eV) calcd for C\(_{20}\)H\(_{22}\)N\(_2\)O\(_4\) 354.1580, found 354.1576.

(13) Diethyl 2,2-dicyano-3-(4-phenylphenyl)cyclopropane-1,1-dicarboxylate (4an)

\[
\begin{align*}
\text{EtOOC} & \quad \text{COOEt} \\
\text{Br} & \quad \text{Br} \\
2\text{a} & \quad 2 \text{equiv.} \\
\end{align*}
\]

The reaction of 2a (38 \(\mu\)L, 0.20 mmol), 3n (94 mg, 0.41 mmol), Ru(bpy)\(_3\)Cl\(_2\)-6H\(_2\)O (2 mg, 0.0027 mmol), Pr\(_2\)NEt (68 \(\mu\)L, 0.41 mmol), and anhydrous methanol (10 mL) afforded 4an as a solid (69 mg, 89%); mp 100.8-102.1 °C (ethyl acetate/petroleum ether). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.65-7.52 (m, 4 H), 7.47-7.41 (m, 4 H), 7.40-7.34 (m, 1 H), 4.43 (q, J = 6.8 Hz, 2 H), 4.32-4.21 (m, 2 H), 4.00 (s, 1 H), 1.39 (t, J = 6.8 Hz, 3 H), 1.21 (t, J = 6.8 Hz, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.0, 161.0, 142.5, 139.7, 129.2, 128.9, 127.9, 127.7, 127.1, 126.1, 111.8, 109.7, 64.5, 63.6, 46.4, 39.9, 16.4, 13.9, 13.6; IR (neat) 2247, 1744, 1214 cm\(^{-1}\); MS (EI, 70 eV) m/z 388 (M\(^+\), 5.88), 216 (100); HRMS (EI, 70 eV) calcd for C\(_{23}\)H\(_{20}\)N\(_2\)O\(_4\) 388.1423, found 388.1425.

(14) Diethyl 2,2-dicyano-3-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (4ao)\(^\dagger\)

\[
\begin{align*}
\text{EtOOC} & \quad \text{COOEt} \\
\text{Br} & \quad \text{Br} \\
2\text{a} & \quad 2 \text{equiv.} \\
\end{align*}
\]

The reaction of 2a (38 \(\mu\)L, 0.20 mmol), 3o (73 mg, 0.40 mmol), Ru(bpy)\(_3\)Cl\(_2\)-6H\(_2\)O (2 mg, 0.0027 mmol), Pr\(_2\)NEt (68 \(\mu\)L, 0.41 mmol), and anhydrous methanol (10 mL) afforded 4ao as a solid (48 mg, 70%); mp 75.0-77.0 °C\(^\dagger\) (ethyl

\(\dagger\)
acetate/petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29 (d, $J = 8.4$ Hz, 2 H), 6.91 (d, $J = 8.4$ Hz, 2 H), 4.42 (q, $J = 7.2$ Hz, 2 H), 4.31-4.20 (m, 2 H), 3.91 (s, 1 H), 3.81 (s, 3 H), 1.38 (t, $J = 7.2$ Hz, 3 H), 1.23 (t, $J = 7.2$ Hz, 3 H).

(15) **Diethyl 2,2-dicyano-3-(3-methoxyphenyl)cyclopropane-1,1-dicarboxylate (4ap)**

\[ \text{EtOOC} \text{Br} \text{Br} \rightarrow \text{EtOOC} \text{CO} \text{Et} + 2 \text{ equiv.} \]

The reaction of 2a (38 μL, 0.20 mmol), 3p (73 mg, 0.40 mmol), \( \text{Ru(bpy)}_3 \text{Cl}_2 \cdot 6\text{H}_2\text{O} \) (2 mg, 0.0027 mmol), \( \text{Pr}^2\text{NEt} \) (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ap as a liquid (58 mg, 85%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34-7.28 (m, 1 H), 6.97-6.89 (m, 3 H), 4.43 (q, $J = 6.8$ Hz, 2 H), 4.31-4.19 (m, 2 H), 3.95 (s, 1 H), 3.81 (s, 3 H), 1.39 (t, $J = 6.8$ Hz, 3 H), 1.21 (t, $J = 6.8$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.9, 161.0, 159.8, 130.1, 128.5, 120.8, 115.3, 114.2, 111.8, 109.7, 64.4, 63.6, 55.3, 46.3, 39.9, 16.2, 13.9, 13.5; IR (neat) 2250, 1741, 1601, 1583, 1464 cm$^{-1}$; MS (EI, 70 eV) m/z 342 (M+, 3.73), 84 (100); HRMS (EI, 70 eV) calcd for C$_{18}$H$_{18}$N$_2$O$_5$ 342.1216, found 342.1214.

(16) **Diethyl 2,2-dicyano-3-(2-methoxyphenyl)cyclopropane-1,1-dicarboxylate (4aq)**

\[ \text{EtOOC} \text{Br} \text{Br} \rightarrow \text{EtOOC} \text{CO} \text{Et} + 2 \text{ equiv.} \]

The reaction of 2a (38 μL, 0.20 mmol), 3q (75 mg, 0.41 mmol), \( \text{Ru(bpy)}_3 \text{Cl}_2 \cdot 6\text{H}_2\text{O} \) (2 mg, 0.0027 mmol), \( \text{Pr}^2\text{NEt} \) (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4aq as a liquid (55 mg, 80%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42-7.34 (m, 1 H), 7.24 (d, $J = 8.0$ Hz, 1 H), 7.00-6.89 (m, 2 H), 4.42 (q, $J = 7.2$ Hz, 2 H), 4.32-4.22 (m, 2 H), 3.91 (s, 3 H), 3.83 (s, 1 H), 1.39 (t, $J = 7.2$ Hz, 3 H), 1.24 (t,
\[ J = 7.2 \text{ Hz, } 3 \text{ H}; \] \[ ^{13}\text{C NMR (100 MHz, CDCl}_3 \delta 163.2, 161.5, 158.2, 131.0, 128.6, 120.5, 115.9, 112.3, 110.9, 110.1, 64.1, 63.3, 55.6, 46.2, 39.6, 16.9, 13.9, 13.5; IR (neat) 2253, 1744, 1601, 1494, 1464 \text{ cm}^{-1}; MS (EI, 70 \text{ eV}) m/z 342 (M^+, 10.53), 227 (100); HRMS (EI, 70 \text{ eV}) \text{ calcd for } \text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_5 342.1216, \text{ found 342.1219.}

(17) **Diethyl 2,2-dicyano-3-(4-ethoxyphenyl)cyclopropane-1,1-dicarboxylate (4ar)**

\[
\text{EtOOC} \quad \text{COOEt} \\
\text{Br} \quad \text{Br} \\
\text{2a} \quad \text{+} \quad \text{EtO} \quad \text{O} \\
\text{CN} \quad \text{CN} \\
\text{3r} \quad \text{2 (equiv.)} \quad \text{Ru(bpy)}_3\text{Cl}_2 \cdot 6\text{H}_2\text{O (2 mg, } 0.0027 \text{ mmol)} \quad \text{Pr}_2\text{NEt (66 } \mu\text{L, 0.40 mmol)} \quad \text{air (1 atm)} \quad \text{visible light} \quad \text{MeOH, rt, 4 h, 81%} \quad \text{4ar}
\]

The reaction of 2a (38 } \mu\text{L, 0.20 mmol), 3r (80 mg, 0.40 mmol), Ru(bpy)_3Cl_2\cdot6H_2O (2 mg, 0.0027 mmol), Pr_2NEt (66 } \mu\text{L, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ar as a solid (58 mg, 81%); mp 69.3-71.2 °C (ethyl acetate/petroleum ether). \(^1\text{H NMR (400 MHz, CDCl}_3 \delta 7.28 (d, } J = 8.8 \text{ Hz, 2 H), 6.89 (d, } J = 8.8 \text{ Hz, 2 H), 4.42 (q, } J = 7.2 \text{ Hz, 2 H), 4.31-4.20 (m, 2 H), 4.03 (q, } J = 6.8 \text{ Hz, 2 H), 3.91 (s, 1 H), 1.44-1.35 (m, 6 H), 1.22 (t, } J = 7.2 \text{ Hz, 3 H); } ^{13}\text{C NMR (100 MHz, CDCl}_3 \delta 163.1, 161.1, 159.8, 130.1, 118.7, 114.9, 111.9, 109.9, 64.4, 63.6, 63.5, 46.3, 39.9, 16.4, 14.6, 13.9, 13.6; IR (neat) 2251, 1743, 1612, 1517, 1474 \text{ cm}^{-1}; MS (EI, 70 \text{ eV}) m/z 356 (M^+, 17.8), 170 (100); HRMS (EI, 70 \text{ eV}) \text{ calcd for } \text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_5 356.1372, \text{ found 356.1373.}

(18) **Diethyl 2,2-dicyano-3-(4-acetoxyphenyl)cyclopropane-1,1-dicarboxylate (4as)**

\[
\text{EtOOC} \quad \text{COOEt} \\
\text{Br} \quad \text{Br} \\
\text{2a} \quad \text{+} \quad \text{AcO} \quad \text{O} \\
\text{CN} \quad \text{CN} \\
\text{3s} \quad \text{2 (equiv.)} \quad \text{Ru(bpy)}_3\text{Cl}_2 \cdot 6\text{H}_2\text{O (2 mg, } 0.0027 \text{ mmol)} \quad \text{Pr}_2\text{NEt (66 } \mu\text{L, 0.40 mmol)} \quad \text{air (1 atm)} \quad \text{visible light} \quad \text{MeOH, rt, 4 h, 77%} \quad \text{4as}
\]

The reaction of 2a (38 } \mu\text{L, 0.20 mmol), 3s (82 mg, 0.40 mmol), Ru(bpy)_3Cl_2\cdot6H_2O (2 mg, 0.0027 mmol), Pr_2NEt (66 } \mu\text{L, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4as as a liquid (57 mg, 77%); \(^1\text{H NMR (400 MHz, CDCl}_3 \delta 7.40 (d, } J = 8.8 \text{ Hz, 2 H), 7.15 (d, } J = 8.8 \text{ Hz, 2 H), 4.42 (q, } J = 6.8 \text{ Hz, 2 H),}}
4.30-4.18 (m, 2 H), 3.94 (s, 1 H), 2.30 (s, 3 H), 1.38 (t, \( J = 6.8 \) Hz, 3 H), 1.20 (t, \( J = 6.8 \) Hz, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 168.8, 162.8, 160.9, 151.5, 129.9, 124.6, 122.3, 111.6, 109.6, 64.5, 63.7, 46.3, 39.4, 21.0, 16.3, 13.9, 13.5; IR (neat) 2250, 1744, 1510, 1464 cm\(^{-1}\); HRMS (ESI) calcld for C\(_{19}\)H\(_{18}\)N\(_2\)NaO\(_6\) 393.1063, found 393.1051.

(19) Dimethyl 3-phenyl-2,2-dicyanocyclopropane-1,1-dicarboxylate (4ba)\(^{17}\)

The reaction of \( 2b \) (58 mg, 0.20 mmol), \( 3a \) (65 mg, 0.40 mmol), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_2$NEt (68 \( \mu \)L, 0.41 mmol), and anhydrous methanol (10 mL) afforded \( 4ba \) as a solid (55 mg, 96%); mp 125.0-126.0 °C\(^{17}\) (ethyl acetate/petroleum ether). \(^1\)H NMR (400 MHz, CDCl$_3$) \( \delta \) 7.45-7.39 (m, 3 H), 7.38-7.33 (m, 2 H), 3.98 (s, 4 H), 3.78 (s, 3 H).

(20) Diisopropyl 3-phenyl-2,2-dicyanocyclopropane-1,1-dicarboxylate (4ca)

The reaction of \( 2c \) (70 mg, 0.20 mmol), \( 3a \) (63 mg, 0.40 mmol), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_2$NEt (66 \( \mu \)L, 0.40 mmol), and anhydrous methanol (10 mL) afforded \( 4ca \) as a liquid (63 mg, 93%); \(^1\)H NMR (400 MHz, CDCl$_3$) \( \delta \) 7.44-7.34 (m, 5 H), 5.30-5.18 (m, 1 H), 5.14-5.02 (m, 1 H), 3.94 (s, 1 H), 1.42-1.32 (m, 6 H), 1.19 (d, \( J = 6.8 \) Hz, 6 H); \(^{13}\)C NMR (100 MHz, CDCl$_3$) \( \delta \) 162.7, 160.7, 129.5, 128.9, 128.8, 127.3, 111.9, 109.7, 72.8, 72.0, 46.2, 39.8, 21.5, 21.3, 21.2, 21.0, 15.8; IR (neat) 2241, 1738, 1500, 1467 cm\(^{-1}\); MS (ESI) \( m/z \) 363 (M+Na$^+$); HRMS (ESI) calcld for C\(_{19}\)H\(_{20}\)N\(_2\)NaO\(_4\) 363.1315, found 363.1327.

(21) Triethyl (2,3-trans)-2-cyano-3-phenylcyclopropane-1,1,2-tricarboxylate (trans-9)\(^{20}\) from Z-8
The reaction of 2a (38 μL, 0.20 mmol), Z-8 (78 mg, 0.40 mmol), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_2$NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded trans-9 as a liquid (42 mg, 60%) with recovered Z-8 as white solid (28 mg, 35%); trans-9: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40-7.27 (m, 5 H), 4.39-4.25 (m, 4 H), 4.14 (q, $J$ = 6.8 Hz, 2 H), 3.94 (s, 1 H), 1.39 (t, $J$ = 6.8 Hz, 3 H), 1.31 (t, $J$ = 6.8 Hz, 3 H), 1.10 (t, $J$ = 6.8 Hz, 3 H).

**Typical Procedure II for the photoreaction under Condition B.**

**Synthesis of diethyl 2,2-dicyano-3-(4-methoxycarbonylphenyl)cyclopropane-1,1-dicarboxylate (4ab)**

The reaction of 2a (66 mg, 0.20 mmol), E-8 (85 mg, 0.42 mmol), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_2$NEt (53 mg, 0.41 mmol), and anhydrous methanol (10 mL) afforded trans-9 as a liquid (46 mg, 62%) with recovered E-8 as white solid (32 mg, 38%); trans-9: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41-7.31 (m, 5 H), 4.42-4.22 (m, 4 H), 4.14 (q, $J$ = 6.8 Hz, 2 H), 3.94 (s, 1 H), 1.39 (t, $J$ = 6.8 Hz, 3 H), 1.31 (t, $J$ = 6.8 Hz, 3 H), 1.10 (t, $J$ = 6.8 Hz, 3 H).
0.0027 mmol), Pr\textsubscript{2}NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) were added to a dry 25 mL pyrex reaction tube. The mixture was irradiated by sunlight at rt in the open air. The photoreaction was completed after 4 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 10/1). The solvent was removed and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1→15/1→10/1) to afforded 4ab as a solid (73 mg, 98%).

The following compounds were prepared according to Typical Procedure I.

(1) Diethyl 2,2-dicyano-3-(4-trifluoromethylphenyl)cyclopropane-1,1-dicarboxylate (4ac)

The reaction of 2a (38 μL, 0.20 mmol), 3c (91 mg, 0.41 mmol), Ru(bpy)\textsubscript{3}Cl\textsubscript{2}·6H\textsubscript{2}O (2 mg, 0.0027 mmol), Pr\textsubscript{2}NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ac as a solid (75 mg, 98%).

(2) Diethyl 2,2-dicyano-3-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate (4ad)

The reaction of 2a (38 μL, 0.20 mmol), 3d (82 mg, 0.41 mmol), Ru(bpy)\textsubscript{3}Cl\textsubscript{2}·6H\textsubscript{2}O (2 mg, 0.0027 mmol), Pr\textsubscript{2}NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ad as a solid (65 mg, 91%).

(3) Diethyl 2,2-dicyano-3-(3-nitrophenyl)cyclopropane-1,1-dicarboxylate (4ae)
The reaction of 2a (38 μL, 0.20 mmol), 3e (81 mg, 0.41 mmol), Ru(bpy)₃Cl₂·6H₂O (2 mg, 0.0027 mmol), Pr₃NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ae as a solid (58 mg, 81%).

(4) Diethyl 2,2-dicyano-3-(2-nitrophenyl)cyclopropane-1,1-dicarboxylate (4af)

The reaction of 2a (38 μL, 0.20 mmol), 3f (82 mg, 0.41 mmol), Ru(bpy)₃Cl₂·6H₂O (2 mg, 0.0027 mmol), Pr₃NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4af as a solid (60 mg, 84%).

(5) Diethyl 2,2-dicyano-3-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate (4ag)

The reaction of 2a (38 μL, 0.20 mmol), 3g (69 mg, 0.40 mmol), Ru(bpy)₃Cl₂·6H₂O (2 mg, 0.0027 mmol), Pr₃NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ag as a solid (64 mg, 97%).

(6) Diethyl 2,2-dicyano-3-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate (4ah)

The reaction of 2a (38 μL, 0.20 mmol), 3h (77 mg, 0.41 mmol), Ru(bpy)₃Cl₂·6H₂O (2 mg, 0.0027 mmol), Pr₃NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ah as a solid (66 mg, 95%).

(7) Diethyl 2,2-dicyano-3-phenylcyclopropane-1,1-dicarboxylate (4aa)
The reaction of 2a (38 μL, 0.20 mmol), 3a (62 mg, 0.41 mmol), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_2$NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4aa as a solid (61 mg, 97%).

(8) Diethyl 2,2-dicyano-3-(4-methylphenyl)cyclopropane-1,1-dicarboxylate (4ai)

The reaction of 2a (38 μL, 0.20 mmol), 3i (71 mg, 0.42 mmol), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_2$NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ai as a solid (63 mg, 96%).

(9) Diethyl 2,2-dicyano-3-(3-methylphenyl)cyclopropane-1,1-dicarboxylate (4aj)

The reaction of 2a (38 μL, 0.20 mmol), 3j (69 mg, 0.41 mmol), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_2$NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4aj as a solid (62 mg, 95%).

(10) Diethyl 2,2-dicyano-3-(2-methylphenyl)cyclopropane-1,1-dicarboxylate (4ak)

The reaction of 2a (38 μL, 0.20 mmol), 3k (70 mg, 0.42 mmol),
Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_2$NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ak as a liquid (64 mg, 98%).

(11) Diethyl 2,2-dicyano-3-(4-ethylphenyl)cyclopropane-1,1-dicarboxylate (4al)

![Chemical reaction diagram]

The reaction of 2a (38 μL, 0.20 mmol), 3l (74 mg, 0.41 mmol), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_2$NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4al as a solid (65 mg, 95%).

(12) Diethyl 2,2-dicyano-3-(4-isopropylphenyl)cyclopropane-1,1-dicarboxylate (4am)

![Chemical reaction diagram]

The reaction of 2a (38 μL, 0.20 mmol), 3m (82 mg, 0.42 mmol), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_2$NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4am as a solid (68 mg, 96%).

(13) Diethyl 2,2-dicyano-3-(4-phenylphenyl)cyclopropane-1,1-dicarboxylate (4an)

![Chemical reaction diagram]

The reaction of 2a (38 μL, 0.20 mmol), 3n (94 mg, 0.41 mmol), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_2$NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4an as a solid (70 mg, 90%).

(14) Diethyl 2,2-dicyano-3-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (4ao)
The reaction of 2a (38 μL, 0.20 mmol), 3o (74 mg, 0.40 mmol), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_2$NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ao as a solid (58 mg, 85%).

(15) **Diethyl 2,2-dicyano-3-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (4ap)**

The reaction of 2a (38 μL, 0.20 mmol), 3p (74 mg, 0.40 mmol), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_2$NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ap as a liquid (58 mg, 85%).

(16) **Diethyl 2,2-dicyano-3-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (4aq)**

The reaction of 2a (38 μL, 0.20 mmol), 3q (74 mg, 0.40 mmol), Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_2$NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4aq as a liquid (54 mg, 79%).

(17) **Diethyl 2,2-dicyano-3-(4-ethoxyphenyl)cyclopropane-1,1-dicarboxylate (4ar)**
The reaction of 2a (38 μL, 0.20 mmol), 3r (82 mg, 0.41 mmol), Ru(bpy)₃Cl₂·6H₂O (2 mg, 0.0027 mmol), Pr₂NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ar as a solid (58 mg, 81%).

(18) Diethyl 2,2-dicyano-3-(4-acetoxyphenyl)cyclopropane-1,1-dicarboxylate (4as)

The reaction of 2a (38 μL, 0.20 mmol), 3s (85 mg, 0.40 mmol), Ru(bpy)₃Cl₂·6H₂O (2 mg, 0.0027 mmol), Pr₂NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4as as a liquid (57 mg, 77%).

(19) Dimethyl 3-phenyl-2,2-dicyanocyclopropane-1,1-dicarboxylate (4ba)¹⁷

The reaction of 2b (58 mg, 0.20 mmol), 3a (62 mg, 0.40 mmol), Ru(bpy)₃Cl₂·6H₂O (2 mg, 0.0027 mmol), Pr₂NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ba as a solid (54 mg, 95%).

(20) Diisopropyl 3-phenyl-2,2-dicyanocyclopropane-1,1-dicarboxylate (4ca)

The reaction of 2c (70 mg, 0.20 mmol), 3a (61 mg, 0.40 mmol),
Ru(bpy)$_3$Cl$_2$·6H$_2$O (2 mg, 0.0027 mmol), Pr$_2$NEt (66 μL, 0.40 mmol), and anhydrous methanol (10 mL) afforded 4ca as a liquid (63 mg, 93%).
NMR Spectra
References


