Supporting Information

Photochemical and Additive-free Coupling Reaction of α-Cumyl α-Ketoesters via Intermolecular C-H Bond Activation

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1. General Methods

NMR spectra were recorded on a JEOL ECS-400 spectrometer at 400 MHz for 1H-NMR and 100.4 MHz for 13C-NMR and on a JEOL ECA-500 at 125.8 MHz for 13C-NMR. Chemical shifts were reported in the scale relative to CHCl3 (7.26 ppm for 1H-NMR), CH3OH (3.31 ppm for 1H-NMR), CDCl3 (77.16 ppm for 13C-NMR), and CD3OD (49.00 ppm for 13C-NMR) as an internal reference. MS spectrum was taken on a Bruker Daltonics micrOTOF-QII (ESI). Column chromatography was performed with silica gel 60 (40-50 μm) purchased from KANTO CHEMICAL Co. Anhydrous THF, Et2O, CH2Cl2, toluene, DMF, and methanol were purchased from KANTO CHEMICAL Co. and purified by Glass Contour Solvent Dispensing System.
2. Scheme S1: Preparation of Substrates 13

\[
\begin{align*}
\text{R}^+\text{COOH} & \xrightarrow{\text{Cl}_3\text{C} = \text{O} - \text{O} - \text{Ph}} \text{R}^+\text{COO} - \text{Ph} & \text{R} = \text{C(CH}_3\text{)}_3 \quad \text{13a: 27\%} \\
\text{R}^+\text{COOH} & \xrightarrow{\text{pyridine (2.5 eq.)} \quad \text{MsCl (1.2 eq.)} \quad \text{THF, rt}} \text{R}^+\text{COO} - \text{Ph} & \text{R} = \text{CH}_2\text{CH}_3 \quad \text{13g: 32\%}
\end{align*}
\]

\[
\begin{align*}
\text{R}^+\text{COOH} & \xrightarrow{\text{pyridine (2.5 eq.)} \quad \text{MsCl (1.2 eq.)} \quad \text{THF, rt}} \text{R}^+\text{COO} - \text{Ph} & \text{13b: 31\%}
\end{align*}
\]

\[
\begin{align*}
\text{R}^+\text{COOH} & \xrightarrow{\text{pyridine (2.5 eq.)} \quad \text{MsCl (1.2 eq.)} \quad \text{THF, rt}} \text{R}^+\text{COO} - \text{Ph} & \text{13c: 50\%}
\end{align*}
\]

\[
\begin{align*}
\text{R}^+\text{COOH} & \xrightarrow{\text{pyridine (2.5 eq.)} \quad \text{MsCl (1.2 eq.)} \quad \text{THF, rt}} \text{R}^+\text{COO} - \text{Ph} & \text{R} = \text{C}_6\text{H}_5 \quad \text{13d: 18\%} \\
& & \text{R} = \text{2-thienyl} \quad \text{13e: 36\%} \\
& & \text{R} = \text{CH(CH}_3\text{)}_2 \quad \text{13f: 40\%}
\end{align*}
\]
3. Experimental Section for Preparation of 13

1) Experimental Procedures

Synthesis of 13g (Typical procedure for synthesis of 13a and 13g)

To a solution of NaH (60 % dispersion in mineral oil, 105 mg, 9.61 mmol) in diethylether (9.5 ml) was added \(\alpha,\alpha\)-dimethyl benzenemethanol (3.04 g, 22.3 mmol) at 0 \(^\circ\)C. After stirring for 40 min at room temperature, trichloroacetonitrile (2.0 ml, 20.0 mmol) was added at 0 \(^\circ\)C. The reaction mixture was stirred for 3 h at room temperature and concentrated \textit{in vacuo}. Hexane (2.5 ml) and MeOH (0.1 ml) were added to the resulting residue. The mixture was filtered through Celite\textsuperscript{®} and concentrated \textit{in vacuo} to give S1\textsuperscript{1} (4.85 g, 78%).

To a solution of S1 (1.11 g, 3.94 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (4.9 ml) was added 2-oxobutanoic acid (208.4 mg, 2.04 mmol), and the mixture was stirred for 10 h. The reaction mixture was filtered through Celite\textsuperscript{®} and concentrated \textit{in vacuo}. The residue was purified by silica gel column chromatography to give 13g (142.7 mg, 32%) as a colorless oil.

Synthesis of 13f (Typical procedure for synthesis of 13b, 13c, 13d, 13e, and 13f)

To a solution of 3-methyl-2-oxo-butanoic acid sodium salt (1.03 g, 7.47 mmol) in THF (9.8 ml) were added \(\alpha,\alpha\)-dimethoxy benzenemethanol (2.05 g, 15.0 mmol) and pyridine (1.55 ml, 18.7 mmol). The mixture was cooled to 0 \(^\circ\)C, and methanesulfonyl chloride (700 \(\mu\)L, 8.97 mmol) was added. The reaction mixture was stirred for 25 min at room temperature before quenching with distilled water at 0 \(^\circ\)C. The resulting mixture was extracted with diethylether twice. The combined organic layers were washed with brine, dried over MgSO\textsubscript{4}, and concentrated \textit{in vacuo}. Further purification was carried out by silica gel column chromatography to give 13f (699.7 mg, 40%) as a colorless oil.

2) Compounds Data

**Compound 13a**

![Chemical structure of 13a]

**Yield:** 129.6 mg (27%), a colorless oil (from 250 mg of 3,3-dimethyl-2-oxobutanoic acid)

\(\textsuperscript{1}H\) NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 1.23 (s, 9H), 1.87 (s, 6H), 7.29 (m, 1H), 7.36 (m, 2H), 7.41 (m, 2H); \(\textsuperscript{13}C\) NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 25.9 (3C), 28.5 (2C), 42.7, 84.9, 124.5 (2C), 127.6, 128.5 (2C), 144.5, 163.1, 202.1; IR (cm\textsuperscript{-1}): 2976, 1734, 1712, 1300, 1244, 1140, 1050, 999; HRMS-ESI \((m/z)\): [M+Na]\textsuperscript{+} calcd for C\textsubscript{15}H\textsubscript{20}NaO\textsubscript{3}, 271.1310; found 271.1306.

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Compound 13b

Yield: 110.8 mg (31%), a colorless oil (from 200 mg of 3,3-dimethyl-2-oxobutanoic acid)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.18 (s, 9 H), 3.03 (t, \(J = 7.4\) Hz, 2H), 4.47 (t, \(J = 7.4\) Hz, 2H), 7.22-7.25 (m, 3H), 7.31 (m, 2H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 25.7 (3C), 35.0, 42.7, 66.1, 127.0, 128.8 (2C), 129.0 (2C), 137.1, 163.9, 202.1; IR (cm\(^{-1}\))): 2969, 1737, 1719, 1290, 1238, 1052, 1008; HRMS-ESI (m/z): [M+Na]\(^+\) calcd for C\(_{14}\)H\(_{18}\)NaO\(_3\), 257.1154; found 257.1150.

Compound 13c

Yield: 92.5 mg (50%), a colorless oil (from 94.2 mg of 3,3-dimethyl-2-oxobutanoic acid)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.21 (s, 9 H), 1.64 (d, \(J = 6.5\) Hz, 3H), 6.03 (q, \(J = 6.5\) Hz, 1H), 7.29-7.40 (m, 5H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 22.1, 25.8 (3C), 42.9, 74.4, 126.4 (2C), 128.5, 128.8 (2C), 140.4, 163.5, 202.2; IR (cm\(^{-1}\))): 2976, 1734, 1721, 1286, 1240, 1048, 1004; HRMS-ESI (m/z): [M+Na]\(^+\) calcd for C\(_{14}\)H\(_{18}\)NaO\(_3\), 257.1154; found 257.1153.

Compound 13d

Yield: 325.5 mg (18%), a pale yellow oil (from 996.9 mg of \(\alpha\)-oxo-benzeneacetic acid)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.95 (s, 6H), 7.31 (m, 1H), 7.39 (m, 2H), 7.49 (m, 4H), 7.64 (m, 1H), 7.94 (m, 2H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 28.6 (2C), 85.4, 124.5 (2C), 127.7, 128.6 (2C), 129.0 (2C), 130.1 (2C), 132.5, 134.9, 144.5, 163.0, 186.5; IR (cm\(^{-1}\))): 3056, 2963, 1738, 1686, 1593, 1451, 1213, 1178; HRMS-ESI (m/z): [M+Na]\(^+\) calcd for C\(_{17}\)H\(_{16}\)NaO\(_3\), 291.0997; found 291.0995.

Compound 13e

Yield: 71.0 mg (36%), a pale yellow oil (from 103.8 mg of \(\alpha\)-oxo-2-thiopheneacetic acid)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.94 (s, 6H), 7.16 (m, 1H), 7.29 (m, 1H), 7.37 (t, \(J = 7.4\) Hz, 2H), 7.45 (br d, \(J = 7.4\) Hz, 2H), 7.78 (br d, \(J = 4.6\) Hz, 1H), 7.98 (br d, \(J = 3.7\) Hz, 1H); \(^1^3\)C NMR (100
MHz, CDCl$_3$) $\delta$ 28.6 (2C), 85.5, 124.5 (2C), 127.7, 128.6 (2C), 128.7, 137.1, 137.2, 139.3, 144.4, 160.8, 177.3; IR (cm$^{-1}$): 1730, 1663, 1410, 1209, 1136, 1056; HRMS-ESI ($m/z$): [M+Na]$^+$ calcd for C$_{15}$H$_{14}$NaO$_3$S, 297.0561; found 297.0563.

**Compound 13f**

![Compound 13f](image)

**Yield:** 699.7 mg (40%), a colorless oil (from 1.03 g of 3-methyl-2-oxo-butanoic acid sodium salt)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.13 (d, $J$ = 6.9 Hz, 6H), 1.87 (s, 6H), 3.18 (septet, $J$ = 6.9 Hz, 1H), 7.28 (m, 1H), 7.33-7.42 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 17.1 (2C), 28.4 (2C), 36.9, 84.8, 124.5 (2C), 127.6, 128.6 (2C), 144.5, 161.3, 198.9; IR (cm$^{-1}$): 2976, 1726, 1273, 1140, 1028; HRMS-ESI ($m/z$): [M+Na]$^+$ calcd for C$_{14}$H$_{18}$NaO$_3$, 257.1154; found 257.1158.

**Compound 13g**

![Compound 13g](image)

**Yield:** 142.7 mg (32%), a colorless oil (from 208.4 mg of 2-oxo-butanoic acid)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.11 (t, $J$ = 7.2 Hz, 3H), 1.87 (s, 6H), 2.80 (q, $J$ = 7.2 Hz, 2H) 7.29 (m, 1H), 7.33-7.42 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 7.07, 28.4 (2C), 32.7, 84.7, 124.4 (2C), 127.6, 128.6 (2C), 144.5, 160.4, 195.9; IR (cm$^{-1}$): 2980, 1725, 1272, 1139, 1096, 1031; HRMS-ESI ($m/z$): [M+Na]$^+$ calcd for C$_{13}$H$_{16}$NaO$_3$, 243.0997; found 243.1000.
4. Experimental Section for Irradiation of 13 in MeOH

1) Experimental Procedures

Photo-reaction of 13f (Typical procedure for photo-reaction of 13a~13g)

A degassed 80 mM solution of 13f in MeOH (700 µl) was irradiated with 365 nm LED lamp (OMRON ZUV-C20H, ZUV-H20MB, ZUV-L8H) as described previously. Irradiation was continued until starting material was consumed (3 h for 13f). The crude material was purified by silica gel column chromatography to give 14f (10.2 mg, 68%) as a colorless oil.

2) Compounds Data

Compound 14a

Yield: 8.5 mg (54%), a colorless oil (from 13.9 mg of 13a)

\[^1\mathrm{H}\text{ NMR} (400 \text{ MHz}, \text{CDCl}_3) \delta 1.01 (s, 9\text{H}), 1.80 (s, 3\text{H}), 1.89 (s, 3\text{H}), 3.64 (\text{br s}, 1\text{H}), 3.75 (d, J = 11.0 \text{ Hz}, 1\text{H}), 4.09 (d, J = 11.0 \text{ Hz}, 1\text{H}), 7.27 (m, 1\text{H}), 7.32-7.37 (m, 2\text{H}), 7.42-7.46 (m, 2\text{H}); \[^1\text{C}\text{ NMR} (100 \text{ MHz}, \text{CDCl}_3) \delta 25.9 (3\text{C}), 27.7, 29.4, 36.6, 63.9, 82.7, 84.7, 124.7 (2\text{C}), 127.5, 128.4 (2\text{C}), 144.7, 174.3; \text{IR (cm}^{-1}) \): 3488, 2976, 2952, 1718, 1367, 1267, 1122, 1101; \text{HRMS-ESI (m/z)}: [M+Na]^+ \text{calcd for C}_{16}\text{H}_{24}\text{NaO}_4, 303.1572; \text{found} 303.1571.

Compound 14b

Yield: 0.5 mg (3%), a colorless oil (from 13.1 mg of 13b)

\[^1\text{H}\text{ NMR} (400 \text{ MHz}, \text{CDCl}_3) \delta 0.90 (s, 9\text{H}), 1.98 (dd, J = 11.0, 2.8 \text{ Hz}, 1\text{H}), 3.02 (t, J = 7.1 \text{ Hz}, 2\text{H}), 3.61 (d, J = 0.9 \text{ Hz}, 1\text{H}), 3.67 (dd, J = 11.0, 2.8 \text{ Hz}, 1\text{H}), 3.92 (td, J = 11.0, 0.9 \text{ Hz}, 1\text{H}), 4.47 (t, J = 7.1 \text{ Hz}, 2\text{H}), 7.22-7.25 (m, 3\text{H}), 7.29-7.34 (m, 2\text{H}); \[^1\text{C}\text{ NMR} (125 \text{ MHz}, \text{CDCl}_3) \delta 25.7 (3\text{C}), 35.1, 36.5, 63.8, 66.8, 83.2, 126.9, 128.8 (2\text{C}), 129.0 (2\text{C}), 137.4, 175.5; \text{IR (cm}^{-1}) \): 3502, 2957, 1723, 1267, 1211, 1123; \text{HRMS-ESI (m/z)}: [M+Na]^+ \text{calcd for C}_{15}\text{H}_{22}\text{NaO}_4, 289.1416; \text{found} 289.1418.

**Compound 14c**

![Chemical structure of compound 14c]

**Yield:** 1.5 mg (10%) as a mixture of two diastereomers (dr = 1:1), a colorless oil (from 13.1 mg of 13c)

$^1$H NMR (400 MHz, CDCl$_3$, mixture of 2 diastereomers) $\delta$ 0.88 (s, 9H), 1.02 (s, 9H), 1.626 (d, $J$ = 6.7 Hz, 3H), 1.632 (d, $J$ = 6.7 Hz, 3H), 1.99 (dd, $J$ = 11.2, 2.8 Hz, 1H), 2.08 (dd, $J$ = 11.2, 2.8 Hz, 1H), 3.66 (d, $J$ = 0.9 Hz, 1H), 3.67 (d, $J$ = 0.9 Hz, 1H), 3.72 (dd, $J$ = 11.2, 2.8 Hz, 2H), 4.02 (td, $J$ = 11.2, 0.9 Hz, 1H), 4.03 (td, $J$ = 11.2, 0.9 Hz, 1H), 5.988 (q, $J$ = 6.7 Hz, 1H), 5.993 (q, $J$ = 6.7 Hz, 1H), 7.28-7.41 (m, 10H);

$^{13}$C NMR (125 MHz, CDCl$_3$, mixture of two diastereomers) $\delta$ 21.9, 22.4, 25.7 (3C), 25.9 (3C), 36.6, 36.7, 63.7, 63.8, 75.0, 75.4, 82.9 (2C), 126.0 (2C), 126.8 (2C), 128.2, 128.5, 128.7 (4C), 140.5, 140.8, 174.96, 175.03; IR (cm$^{-1}$): 3503, 2956, 2929, 1718, 1266, 1207, 1122, 1060; HRMS-ESI ($m/z$): [M+Na]$^+$ calcd for C$_{15}$H$_{22}$NaO$_4$, 289.1416; found 289.1405.

**Compound 14d**

![Chemical structure of compound 14d]

**Yield:** 4.2 mg (25%), a colorless oil (from 15.0 mg of 13d)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.75 (s, 3H), 1.83 (s, 3H), 3.81 (d, $J$ = 11.3 Hz, 1H), 4.07 (br s, 1H), 4.37 (d, $J$ = 11.3 Hz, 1H), 7.18-7.27 (m, 5H), 7.35-7.42 (m, 3H), 7.58-7.62 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 28.4, 28.6, 68.2, 79.5, 85.0, 124.3 (2C), 125.7 (2C), 127.5, 128.4 (3C), 128.6 (2C), 138.4, 144.6, 172.5; IR (cm$^{-1}$): 3474, 2980, 1728, 1267, 1230, 1131, 1101, 1075; HRMS-ESI ($m/z$): [M+Na]$^+$ calcd for C$_{18}$H$_{20}$NaO$_4$, 323.1259; found 323.1261.

**Compound 14f**

![Chemical structure of compound 14f]

**Yield:** 10.2 mg (68%), a colorless oil (from 13.1 mg of 13f)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (d, $J$ = 6.9 Hz, 3H), 0.94 (d, $J$ = 6.9 Hz, 3H), 1.81 (s, 3H), 1.86 (s, 3H), 2.06 (septet, $J$ = 6.9 Hz, 1H), 2.06 (m, 1H), 3.40 (br d, $J$ = 1.8 Hz, 1H) 3.76 (d, $J$ = 11.0 Hz, 1H), 3.88 (br m, 1H), 7.27 (m, 1H), 7.32-7.37 (m, 2H), 7.40-7.43 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 16.5, 17.2, 27.9, 28.9, 32.7, 66.7, 80.9, 84.3, 124.6 (2C), 127.6, 128.4 (2C), 144.8, 174.4; IR (cm$^{-1}$):
3485, 2969, 1727, 1270, 1225, 1134, 1102, 1077, 1031; HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₅H₂₄NaO₄, 289.1416; found 289.1412.

**Compound 14g**

![Chemical structure of Compound 14g](image)

**Yield:** 2.1 mg (15%), a colorless oil (from 12.3 mg of 13g)

\(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 0.89 (t, \(J = 7.8\) Hz, 3H), 1.64 (m, 1H), 1.76 (m, 1H), 1.81 (s, 3H), 1.84 (s, 3H), 2.11 (dd, \(J = 10.1, 3.5\) Hz, 1H), 3.47 (s, 1H), 3.63 (dd, \(J = 11.0, 3.5\) Hz, 1H), 3.88 (dd, \(J = 11.0, 10.1\) Hz, 1H), 7.28 (m, 1H), 7.33-7.41 (m, 4H); \(^13\)C NMR (100 MHz, CDCl₃) \(\delta\): 7.39, 28.1, 28.9, 68.0, 78.9, 84.3, 124.5 (2C), 127.6, 128.5 (2C), 144.9, 174.1; IR (cm⁻¹): 3464, 2980, 2931, 1731, 1249, 1134, 1102, 1067; HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₄H₂₀NaO₄, 275.1259; found 275.1251.
5. Experimental Section for coupling reaction of 13 with various partners

1) Experimental Procedures

Photo-chemical synthesis of 16f (Typical procedure for photo-reaction of 13d, 13f, and 13g)

A degassed 80 mM solution of 13f in 1-butanol (700 µl) was irradiated with 365 nm LED lamp (OMRON ZUV-C20H, ZUV-H20MB, ZUV-L8H) as described previously. Irradiation was continued until starting material was consumed (20 min). The crude material was purified by silica gel column chromatography to give 16f (5.7 mg, 33%) as a colorless oil. The dimers 15f and alcohol 17f was obtained in some cases as a mixture (52% and 5% respectively in the case of the reaction with 1-butanol). The yields of 15f and 17f were determined by 1H-NMR, unless otherwise noted. The dimers 15f were formed as diastereomeric mixtures, and combined yield of two diastereomers was shown.

2) Compounds Data

Compound 15f

[Diastereomer A] 1H NMR (400 MHz, CDCl₃) δ 0.92 (d, J = 6.9 Hz, 6H), 1.08 (d, J = 6.9 Hz, 6H), 1.77 (s, 6H), 1.78 (s, 6H), 2.34 (septet, J = 6.9 Hz, 2H), 3.87 (s, 2H), 7.21-7.35 (m, 6H), 7.44 (m, 4H); 13C NMR (100 MHz, CDCl₃) δ 18.5 (2C), 19.3 (2C), 27.6 (2C), 28.2 (2C), 33.2 (2C), 84.01 (2C), 84.6 (2C), 125.18 (4C), 127.5 (2C), 128.2 (4C), 144.8 (2C), 173.45 (2C).

[Diastereomer B] 1H NMR (400 MHz, CDCl₃) δ 0.84 (d, J = 6.9 Hz, 6H), 1.01 (d, J = 6.9 Hz, 6H), 1.82 (s, 6H), 1.86 (s, 6H), 2.39 (septet, J = 6.9 Hz, 2H), 3.72 (s, 2H), 7.21-7.35 (m, 6H), 7.48 (m, 4H); 13C NMR (100 MHz, CDCl₃) δ 18.2 (2C), 18.9 (2C), 27.4 (2C), 28.2 (2C), 34.7 (2C), 83.96 (2C), 84.9 (2C), 125.23 (4C), 127.7 (2C), 128.3 (4C), 144.6 (2C), 173.48 (2C).

IR (mixture, cm⁻¹): 3472, 2976, 2938, 2879, 1718, 1385, 1247, 1134, 1101, 1077; HRMS-ESI (mixture, m/z): [M+Na]^+ calcd for C_{28}H_{38}NaO_{6}, 493.2566; found 493.2551.

Compound 16f

Yield: 5.7 mg (33%, d.r. = 1.6:1), a colorless oil (from 13.1 mg of 13f)
15f (52%) and 17f (5%) were also obtained.

[Major diastereomer] $^1$H NMR (400 MHz, CDCl$_3$) δ 0.92 (d, $J = 6.9$ Hz, 3H), 0.94 (d, $J = 6.9$ Hz, 3H), 0.96 (t, $J = 6.9$ Hz, 3H), 1.32-1.48 (m, 2H), 1.56-1.71 (m, 2H), 1.83 (s, 3H), 1.86 (s, 3H), 2.00 (d, $J = 6.4$ Hz, 1H), 2.23 (septet, $J = 6.9$ Hz, 1H), 3.40 (s, 1H), 3.81 (ddd, $J = 10.6$, 6.4, 1.4 Hz, 1H), 7.29 (m, 1H), 7.35 (m, 2H), 7.42 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 14.2, 16.4, 17.7, 20.0, 28.0, 28.7, 32.6, 33.7, 74.4, 82.8, 84.4, 124.9 (2C), 127.7, 128.4 (2C), 144.5, 173.8; IR (cm$^{-1}$): 3474, 2961, 2928, 2873, 1722, 1451, 1385, 1243, 1136, 1101, 1017; HRMS-ESI (m/z): [M+Na]$^+$ calcd for C$_{18}$H$_{28}$NaO$_4$, 331.1885; found 331.1885.

[Minor diastereomer] $^1$H NMR (400 MHz, CDCl$_3$) δ 0.93 (d, $J = 6.9$ Hz, 3H), 0.95 (t, $J = 7.4$ Hz, 3H), 0.97 (d, $J = 6.9$ Hz, 3H), 1.19-1.28 (m, 1H), 1.36-1.46 (m, 1H), 1.56-1.71 (m, 2H), 1.85 (s, 3H), 1.87 (s, 3H), 2.15 (septet, $J = 6.9$ Hz, 1H), 3.36 (s, 1H), 3.85 (td, $J = 11.0$, 1.8 Hz, 1H), 7.28 (m, 1H), 7.36 (m, 2H), 7.44 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 14.2, 16.7, 17.1, 19.4, 28.2, 28.6, 32.9, 33.6, 73.3, 82.1, 84.8, 124.9 (2C), 127.7, 128.5 (2C), 144.5, 174.4; IR (cm$^{-1}$): 3499, 2960, 2935, 2873, 1721, 1385, 1245, 1136, 1077; HRMS-ESI (m/z): [M+Na]$^+$ calcd for C$_{18}$H$_{28}$NaO$_4$, 331.1885; found 331.1885.

Compound 17f

![Compound 17f](image)

$^1$H NMR (400 MHz, CDCl$_3$) δ 0.85 (d, $J = 6.9$ Hz, 3H), 1.06 (d, $J = 6.9$ Hz, 3H), 1.81 (s, 3H), 1.84 (s, 3H), 2.16 (septet doublet, $J = 6.9$, 3.2 Hz, 1H), 2.66 (d, $J = 5.9$ Hz, 1H), 4.01 (dd, $J = 5.9$, 3.2 Hz, 1H), 7.27 (m, 1H), 7.32-7.39 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 15.8, 19.3, 28.1, 28.9, 32.2, 75.1, 83.6, 124.5 (2C), 127.6, 128.5 (2C), 145.0, 173.9; IR (cm$^{-1}$): 3505, 2967, 2932, 1718, 1385, 1253, 1100; HRMS-ESI (m/z): [M+Na]$^+$ calcd for C$_{14}$H$_{20}$NaO$_3$, 259.1310; found 259.1311.

Compound 18f

![Compound 18f](image)

Yield: 1.4 mg (8%), a colorless oil (from 13.1 mg of 13f)

15f (64%) and 17f (5%) were also obtained.

$^1$H NMR (400 MHz, CDCl$_3$) δ 0.80 (d, $J = 6.9$ Hz, 3H), 1.08 (d, $J = 6.9$ Hz, 3H), 1.10 (s, 3H), 1.43 (s, 3H), 1.876 (s, 3H), 1.879 (s, 3H), 2.36 (septet, $J = 6.9$ Hz, 1H), 2.77 (s, 1H), 3.48 (s, 1H), 7.31 (m, 1H), 7.37 (m, 2H), 7.45 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 17.9, 18.5, 24.4, 27.0, 27.5, 27.9, 31.9, 74.1, 82.8, 84.8, 125.1, 128.0, 128.4, 144.0, 174.7; IR (cm$^{-1}$): 3492, 2977, 2935, 2917, 1718, 1385, 1253, 1128, 1101, 1030; HRMS-ESI (m/z): [M+Na]$^+$ calcd for C$_{17}$H$_{26}$NaO$_4$, 317.1729; found
Compound 19f

Yield: 7.0 mg (38%), a colorless oil (from 13.1 mg of 13f)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.87 (d, $J = 6.9$ Hz, 3H), 1.08 (d, $J = 6.9$ Hz, 3H), 1.63 (s, 3H), 1.67 (s, 3H), 2.15 (septet, $J = 6.9$ Hz, 1H), 2.92 (d, $J = 13.8$ Hz, 1H), 3.14 (s, 1H), 3.15 (d, $J = 13.8$ Hz, 1H), 7.23-7.31 (m, 10H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 16.4, 17.6, 27.3, 28.3, 36.4, 42.9, 80.3, 84.1, 124.7 (2C), 126.7, 127.5, 128.1 (2C), 128.4 (2C), 130.5 (2C), 137.2, 145.0, 174.6; IR (cm$^{-1}$): 3502, 3025, 2969, 2935, 1722, 1262, 1203, 1136, 1029; HRMS-ESI ($m/z$): [M+Na]$^+$ calcd for C$_{21}$H$_{26}$NaO$_3$, 349.1780; found 349.1788.

Compound 20f

Yield: 7.2 mg (40%), a colorless oil (from 13.1 mg of 13f)

$^{15}$f (20%) and $^{17}$f (1.0 mg, 8% isolated yield) were also obtained.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.89 (d, $J = 6.9$ Hz, 3H), 0.93 (d, $J = 6.9$ Hz, 3H), 1.05-1.39 (m, 5H), 1.48-1.89 (m, 6H), 1.85 (s, 3H), 1.87 (s, 3H), 2.14 (septet, $J = 6.9$ Hz, 1H), 3.24 (s, 1H), 7.26-7.31 (m, 1H), 7.33-7.38 (m, 2H), 7.42-7.46 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 16.4 17.5, 26.5, 26.71, 26.72, 26.8, 27.6, 27.9, 28.5, 32.2, 43.4, 81.7, 83.8, 125.1 (2C), 127.7, 128.3 (2C), 144.6, 175.4; IR (cm$^{-1}$): 3516, 2976, 2928, 2848, 1718, 1444, 1382, 1252, 1226, 1133; HRMS-ESI ($m/z$): [M+Na]$^+$ calcd for C$_{20}$H$_{30}$NaO$_3$, 341.2093; found 341.2088.

Compound 21f

Yield: 13.2 mg (73%), a colorless oil (from 13.1 mg of 13f)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (d, $J = 6.9$ Hz, 3H), 0.96 (d, $J = 6.9$ Hz, 3H), 1.19 (s, 9H), 1.81 (s,
6H), 2.10 (septet, $J = 6.9$ Hz, 1H), 3.22 (s, 1H), 3.47 (d, $J = 8.3$ Hz, 1H), 3.65 (d, $J = 8.3$ Hz, 1H), 7.25 (m, 1H), 7.33 (m, 2H), 7.43 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 16.6, 17.4, 27.6 (3C), 28.45, 28.49, 33.0, 67.0, 73.3, 79.9, 83.4, 124.7 (2C), 127.2, 128.3 (2C), 145.6, 173.9; IR (cm$^{-1}$): 3533, 2975, 2931, 2880, 1735, 1469, 1365, 1234, 1197, 1178, 1136, 1101; HRMS-ESI (m/z): [M+Na]$^+$ calcd for C$_{19}$H$_{30}$NaO$_4$, 345.2042; found 345.2034.

**Compound 22f**

![Compound 22f](image)

**Yield:** 7.6 mg (40%), a colorless oil (from 13.1 mg of 13f)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.94 (d, $J = 6.9$ Hz, 3H), 1.05 (d, $J = 6.9$ Hz, 3H), 1.76 (s, 3H), 1.82 (s, 3H), 2.24 (septet, $J = 6.9$ Hz, 1H), 3.42 (s, 1H), 4.14 (d, $J = 8.7$ Hz, 1H), 4.25 (d, $J = 8.7$ Hz, 1H), 6.91 (br d, $J = 8.3$ Hz, 2H), 6.98 (br t, $J = 7.4$ Hz, 1H), 7.22-7.35 (m, 7H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 16.5, 17.2, 27.7, 28.9, 32.9, 72.6, 79.4, 84.1, 114.7 (2C), 121.2, 124.6 (2C), 127.5, 128.4 (2C), 129.6 (2C), 144.9, 158.7, 173.4; IR (cm$^{-1}$): 3516, 2976, 2935, 2873, 1736, 1600, 1497, 1245, 1135; HRMS-ESI (m/z): [M+Na]$^+$ calcd for C$_{21}$H$_{26}$NaO$_4$, 365.1729; found 365.1728.

**Compound 23f**

![Compound 23f](image)

**Yield:** 9.1 mg (50%, d.r. = 1:1), a colorless oil (from 13.1 mg of 13f).

[Diastereomer A] $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.93 (d, $J = 6.9$ Hz, 3H), 1.06 (d, $J = 6.9$ Hz, 3H), 1.82 (s, 3H), 1.87 (s, 3H), 1.96 (septet, $J = 6.9$ Hz, 1H), 3.34 (s, 1H), 3.59 (dd, $J = 11.5$, 10.3 Hz, 1H), 3.59-3.87 (m, 4H), 3.89 (dd, $J = 11.5$, 2.3 Hz, 1H), 7.28 (m, 1H), 7.34 (m, 2H), 7.43 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 17.1, 17.5, 28.1, 28.7, 32.6, 66.55, 66.62, 67.4, 77.7, 80.5, 84.4, 124.8 (2C), 127.5, 128.3 (2C), 144.9, 173.0; IR (cm$^{-1}$): 3505, 2969, 2880, 1730, 1270, 1239, 1220, 1135, 1117, 1101, 1076; HRMS-ESI (m/z): [M+Na]$^+$ calcd for C$_{18}$H$_{26}$NaO$_5$, 345.1678; found 345.1678.

[Diastereomer B] $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.90 (d, $J = 6.9$ Hz, 3H), 0.97 (d, $J = 6.9$ Hz, 3H), 1.85 (s, 3H), 1.86 (s, 3H), 2.04 (septet, $J = 6.9$ Hz, 1H), 3.41 (s, 1H), 3.57 (td, $J = 11.4$, 2.9 Hz, 1H), 3.68-3.88 (m, 6H), 7.28 (m, 1H), 7.35 (m, 2H), 7.44 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 16.3, 17.3, 28.1, 28.7, 31.7, 66.6, 67.1, 67.6, 79.4, 80.4, 84.6, 124.9 (2C), 127.7, 128.4 (2C), 144.5, 172.4; IR (cm$^{-1}$): 3505, 2969, 2880, 1730, 1270, 1239, 1220, 1135, 1117, 1101, 1076; HRMS-ESI (m/z): [M+Na]$^+$ calcd for C$_{18}$H$_{26}$NaO$_5$, 345.1678; found 345.1678.
Compound 24f

Yield: 4.4 mg (23%), a colorless oil (from 13.1 mg of 13f)

15f (2.7 mg, 20% isolated yield) and 17f (2.5 mg, 19% isolated yield) were also obtained.

1H NMR (400 MHz, CDCl3) δ 0.87 (d, J = 6.9 Hz, 3H), 0.95 (d, J = 6.9 Hz, 3H), 1.46-1.55 (m, 2H), 1.62-1.75 (m, 6H), 1.80 (s, 3H), 1.82 (s, 3H), 2.09 (septet, J = 6.9 Hz, 1H), 3.24 (s, 1H), 3.50 (d, J = 9.2 Hz, 1H), 3.70 (d, J = 9.2 Hz, 1H), 3.94 (m, 1H), 7.26 (m, 1H), 7.33 (m, 2H), 7.41 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 16.5, 17.3, 23.77, 23.80, 28.2, 28.6, 32.2, 32.4, 33.0, 73.8, 80.1, 82.5, 83.5, 124.6 (2C), 127.3, 128.3 (2C), 145.5, 173.9; IR (cm⁻¹): 3523, 2964, 2876, 1734, 1449, 1384, 1366, 1239, 1173, 1136, 1102; HRMS-ESI (m/z): [M+Na]+ calcd for C20H30NaO4, 357.2042; found 357.2051.

Compound 25d

Yield: 11.0 mg (55%), a colorless oil (from 15.0 mg of 13g)

[Major rotamer]: 1H NMR (400 MHz, CDCl3) δ 1.74 (s, 3H), 1.76 (s, 3H), 2.06 (s, 3H), 2.82 (d, J = 14.3 Hz, 1H), 4.23 (d, J = 14.3 Hz, 1H), 5.71 (brs, 1H), 7.03-7.13 (m 2H), 7.18-7.22 (m, 3H), 7.30-7.42 (m, 3H), 7.57-7.62 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 22.0, 27.9, 29.0, 39.3, 57.6, 80.3, 83.7, 124.3 (2C), 125.8 (2C), 127.2, 128.1, 128.28 (2C), 128.34 (2C), 140.2, 145.2, 171.9, 174.2; IR (cm⁻¹): 3485, 2979, 1726, 1623, 1496, 1448, 1406, 1258, 1137, 1102, 1076; HRMS-ESI (m/z): [M+Na]+ calcd for C21H25NNaO4, 378.1681; found 378.1682.

Compound 25f

Yield: 15.3 mg (85%), a colorless oil (from 13.1 mg of 13f)

[Major rotamer]: 1H NMR (400 MHz, CDCl3) δ 0.86 (d, J = 6.7 Hz, 3H), 0.97 (d, J = 6.7 Hz, 3H),
1.79 (s, 3H), 1.86 (s, 3H), 2.06 (m, 1H), 2.07 (s, 3H), 2.93 (s, 3H), 3.58 (d, $J = 14.0$ Hz, 1H), 3.85 (d, $J = 14.0$ Hz, 1H), 4.60 (s, 1H), 7.23-7.47 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 16.1, 17.4, 22.1, 26.9, 28.9, 35.5, 39.1, 55.3, 81.2, 83.6, 125.0 (2C), 127.5, 128.3 (2C), 145.2, 173.1, 174.4; IR (cm$^{-1}$): 3502, 3326, 2973, 2935, 2876, 1719, 1630, 1406, 1256, 1136, 1102, 1031; HRMS-ESI (m/z): [M+Na]$^+$ calcd for C$_{18}$H$_{27}$NNaO$_4$, 344.1838; found 344.1835.

**Compound 25g**

\[
\text{Yield: 8.9 mg (52%), a colorless oil (from 12.3 mg of 13g)}
\]

[Major rotamer]: $^1$H NMR (400 MHz, CDCl$_3$) δ 0.87 (t, $J = 7.4$ Hz, 3H), 1.66 (dq, $J = 13.8$, 7.4 Hz, 1H), 1.82 (s, 3H), 1.83 (m, 1H), 1.84 (s, 3H), 2.10 (s, 3H), 3.02 (s, 3H), 3.62 (d, $J = 14.0$ Hz, 1H), 3.77 (d, $J = 14.0$ Hz, 1H), 4.30 (s, 1H), 7.24-7.44 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 7.6, 22.1, 27.6, 28.6, 30.6, 39.1, 55.7, 79.3, 83.8, 124.7 (2C), 127.5, 128.4 (2C), 145.2, 172.8, 174.1; IR (cm$^{-1}$): 3504, 3403, 2976, 2932, 1723, 1628, 1496, 1448, 1405, 1366, 1273, 1247, 1174, 1134, 1101; HRMS-ESI (m/z): [M+Na]$^+$ calcd for C$_{17}$H$_{25}$NNaO$_4$, 330.1681; found 330.1680.

**Compound 26f**

\[
\text{Yield: 14.5 mg (84%), a colorless oil (from 13.1 mg of 13f)}
\]

$^1$H NMR (400 MHz, CDCl$_3$) δ 0.88 (d, $J = 6.9$ Hz, 3H), 0.95 (d, $J = 6.9$ Hz, 3H), 1.78 (s, 3H), 1.83 (s, 3H), 1.94 (s, 3H), 2.07 (septet, $J = 6.9$ Hz, 1H), 3.20 (br d, $J = 13.3$ Hz, 1H), 3.41 (s, 1H), 4.11 (dd, $J = 13.3$, 8.3 Hz, 1H), 5.69 (br m, 1H), 7.27 (m, 1H), 7.33 (m, 2H), 7.39 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 16.4, 17.2, 23.5, 27.6, 28.4, 34.0, 44.6, 79.4, 84.5, 124.8 (2C), 127.7, 128.4 (2C), 144.4, 170.2, 174.3; IR (cm$^{-1}$): 3499, 3319, 2973, 2935, 1727, 1654, 1545, 1449, 1385, 1368, 1274, 1240, 1179, 1133, 1102; HRMS-ESI (m/z): [M+Na]$^+$ calcd for C$_{17}$H$_{25}$NNaO$_4$, 330.1681; found 330.1681.
Compound 27f

**Yield:** 5.6 mg (31%, d.r. = 1:1), a colorless oil (from 13.1 mg of 13f)

[Diastereomer A] ¹H NMR (400 MHz, CDCl₃) δ 0.88 (d, J = 6.9 Hz, 3H), 0.95 (d, J = 6.9 Hz, 3H), 1.84 (s, 6H), 2.17 (m, 2H), 2.25-2.37 (m, 3H), 3.44 (s, 1H), 4.01 (dd, J = 9.0, 5.2 Hz, 1H), 5.88 (br s, 1H), 7.27-7.38 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 16.5, 17.3, 21.4, 28.0, 28.1, 30.2, 32.4, 59.0, 81.9, 85.2, 124.7 (2C), 128.0, 128.6, 144.1, 173.2, 178.0; IR (cm⁻¹): 3381, 3246, 2969, 2935, 1692, 1465, 1389, 1243, 1132, 1102; HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₈H₂₅NNaO₄, 342.1681; found 342.1682.

[Diastereomer B] ¹H NMR (400 MHz, CDCl₃) δ 0.97 (d, J = 6.9 Hz, 6H), 1.85 (s, 3H), 1.88 (s, 3H), 2.00-2.43 (m, 5H), 3.22 (s, 1H), 4.05 (dd, J = 7.6, 4.8 Hz, 1H), 5.22 (br s, 1H), 7.31 (m, 1H), 7.36-7.43 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 17.0, 17.5, 21.7, 27.9, 28.3, 29.9, 33.5, 57.9, 81.0, 84.9, 124.9 (2C), 128.2, 128.7 (2C), 143.8, 173.4, 178.6; IR (cm⁻¹): 3501, 3208, 2973, 2929, 1693, 1386, 1368, 1274, 1245, 1133, 1101; HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₈H₂₅NNaO₄, 342.1681; found 342.1685.

Compound 28f

**Yield:** 10.6 mg (57%, d.r. = 1:1), a colorless oil (from 13.1 mg of 13f)

[Diastereomer A, including impurities] ¹H NMR (400 MHz, CDCl₃) δ 0.79 (d, J = 6.9 Hz, 3H), 1.80 (s, 3H), 1.82 (s, 3H), 2.17 (m, 1H), 2.27-2.41 (m, 4H), 2.88 (s, 3H), 3.28 (s, 1H), 3.81 (dd, J = 7.6, 4.4 Hz, 1H), 7.29 (m, 1H), 7.33-7.36 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 16.2, 16.9, 19.6, 27.7, 28.0, 30.1, 31.2, 33.0, 66.0, 82.7, 85.3, 124.7 (2C), 127.9, 128.6 (2C), 144.1, 173.8, 176.1; IR (cm⁻¹): 3505, 2976, 2938, 2880, 1722, 1676, 1449, 1388, 1274, 1240, 1131, 1101; HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₉H₂₇NNaO₄, 356.1838; found 356.1841.

[Diastereomer B, including impurities] ¹H NMR (400 MHz, CDCl₃) δ 0.92 (d, J = 6.9 Hz, 3H), 1.91 (s, 3H), 1.94 (s, 3H), 2.03-2.25 (m, 4H), 2.44 (m, 1H), 2.76 (s, 3H), 3.32 (s, 1H), 4.05 (dd, J = 7.6, 4.4 Hz, 1H), 7.33 (m, 1H), 7.37 (dd, J = 7.4, 7.8 Hz, 2H), 7.49 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 16.7, 17.4, 20.3, 27.0, 28.2, 29.9, 30.0, 35.1, 63.8, 80.4, 85.7, 125.5 (2C), 128.2, 128.5 (2C), 143.4, 173.6, 176.7; IR (cm⁻¹): 3502, 3388, 2980, 2935, 1717, 1679,
1471, 1450, 1386, 1368, 1274, 1240, 1130, 1101; HRMS-ESI (m/z): [M+Na]^+ calcd for C_{19}H_{27}NNaO_{4}, 356.1838; found 356.1834.

**Compound 29f**

![Compound 29f](image)

**Yield:** 3.9 mg (21%), a colorless oil (from 13.1 mg of 13f)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.83 (d, \(J = 6.9\) Hz, 3H), 0.97 (d, \(J = 6.9\) Hz, 3H), 1.79 (s, 3H), 1.79-1.94 (m, 2H), 1.84 (s, 3H), 2.13 (septet, \(J = 6.9\) Hz, 1H), 2.34 (dd, \(J = 8.3, 7.8\) Hz, 2H), 3.23 (d, \(J = 13.8\) Hz, 1H), 3.29 (ddd, \(J = 10.1, 7.6, 6.4\) Hz, 1H), 3.58 (ddd, \(J = 10.1, 8.0, 6.0\) Hz, 1H), 3.72 (s, 1H), 4.05 (dd, \(J = 13.8\) Hz, 1H), 7.27 (m 1H), 7.34 (dd, \(J = 7.8, 7.4\) Hz, 2H), 7.44 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 16.2, 17.3, 18.5, 26.8, 28.8, 30.9, 34.9, 49.55, 49.60, 80.7, 84.3, 125.0 (2C), 127.7, 128.3 (2C), 144.7, 174.3, 176.6; IR (cm\(^{-1}\)): 3502, 2969, 2935, 1718, 1685, 1423, 1385, 1273, 1252, 1132, 1102; HRMS-ESI (m/z): [M+Na]^+ calcd for C_{19}H_{27}NNaO_{4}, 356.1838; found 356.1842.

6. **Table S1**: Irradiation of \(\alpha\)-ketoester 13f in various solvents

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Recovery (%)a</th>
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<tr>
<td>1</td>
<td>acetone</td>
<td>1</td>
<td>77</td>
</tr>
<tr>
<td>2</td>
<td>benzene</td>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>t-BuOH</td>
<td>1</td>
<td>69</td>
</tr>
<tr>
<td>4</td>
<td>CH(_3)CN</td>
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</tr>
<tr>
<td>5</td>
<td>t-BuOAc</td>
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<td>44</td>
</tr>
<tr>
<td>6</td>
<td>CF(_3)Ph</td>
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<td>59</td>
</tr>
</tbody>
</table>

a) NMR yield are shown.

7. Experimental Section for Irradiation of 13f with \(N,N\)-dimethylacetamide in benzene

**Photo-reaction of 13f with 50 eq. of \(N,N\)-dimethylacetamide**

To a degassed 127 mM solution of 13f in benzene (440 \(\mu\)l) was added degassed \(N,N\)-dimethylacetamide (260 \(\mu\)L, 2.81 mmol). The resulting solution (700 \(\mu\)l) was irradiated for 20 min with 365 nm LED lamp (OMRON ZUV-C20H, ZUV-H20MB, ZUV-L8H). The crude material was purified by silica gel column chromatography to give 25f (15.6 mg, 87%) as a colorless oil and 15f (1.0 mg, 8%) as a colorless oil.
Photo-reaction of 13f with 15 eq. of N,N-dimethylacetamide
To a degassed 90.0 mM solution of 13f in benzene (622 μl) was added degassed N,N-dimethylacetamide (78 μL, 0.84 mmol). The resulting solution (700 μl) was irradiated for 50 min with 365 nm LED lamp. The crude material was purified by silica gel column chromatography to give 25f (14.9 mg, 83%) as a colorless oil and a mixture of 15f (15%) and 17f (1%) (total 2.0 mg, the yields were calculated from $^1$H-NMR).

Photo-reaction of 13f with 5 eq. of N,N-dimethylacetamide
To a degassed 83.1 mM solution of 13f in benzene (674 μl) was added degassed N,N-dimethylacetamide (26 μL, 0.28 mmol). The resulting solution (700 μl) was irradiated for 60 min with 365 nm LED lamp. The crude material was purified by silica gel column chromatography to give 25f (12.1 mg, 67%) as a colorless oil and a mixture of 15f (15%) and 17f (1%) (total 2.2 mg, the yields were calculated from $^1$H-NMR).

8. Experimental Section for Synthesis of 33
Synthesis of 31

![Synthesis of 31](image)

To a degassed 160 mM solution of 13f in acetone (350 μl) was added a degassed 2.40 M solution of N-[2-(dimethylamino)-2-oxoethyl]-carbamic acid 1,1-dimethyl ester (30, 350 μL, 0.840 mmol). The resulting solution (700 μl) was irradiated for 50 min with 365 nm LED lamp (OMRON ZUV-C20H, ZUV-H20MB, ZUV-L8H) as described previously. The crude material was purified by silica gel column chromatography to give 31 (14.3 mg, 58%) as a colorless oil.

[Major rotamer]: $^1$H NMR (400 MHz, CDCl$_3$) δ 0.84 (d, $J = 6.7$ Hz, 3H), 0.97 (d, $J = 6.7$ Hz, 3H), 1.45 (s, 9H), 1.79 (s, 3H), 1.84 (s, 3H), 2.09 (septet, $J = 6.7$ Hz, 1H), 2.92 (s, 3H), 3.50 (d, $J = 13.8$ Hz, 1H), 3.90 (m, 2H), 3.95 (s, 1H), 4.05 (m, 1H), 5.51 (br s, 1H), 7.26-7.45 (m 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 16.1, 17.3, 26.8, 28.5 (3C), 28.7, 35.2, 36.3, 42.7, 54.4, 79.8, 80.7, 84.1, 125.0 (2C), 127.7, 128.3 (2C), 144.8, 155.8, 170.2, 174.1; IR (cm$^{-1}$): 3419, 2970, 2935, 1715, 1653, 1487, 1367, 1252, 1168, 1134, 1102; HRMS-ESI (m/z): [M+Na]$^+$ calcd for C$_{23}$H$_{36}$N$_2$NaO$_6$, 459.2471; found 459.2467.
Synthesis of 33

To a solution of 31 (12.9 mg, 29.5 μmol) in CH₂Cl₂ (430 μl) was added i-Pr₃SiH (30.1 μl, 146 μmol) and trifluoroacetic acid (1.29 ml) at 0 °C. After stirring for 1 h at room temperature, the reaction mixture was diluted with toluene and concentrated in vacuo to give the corresponding amino acid (11.0 mg). The resulting residue was used for the next step without further purification.

To a solution of the amino acid in toluene (2.95 ml) was added triethylamine (12.3 µl, 88.5 µmol), molecular sieves 4Å (100 mg), and HBTU (16.8 mg, 44.3 μmol) sequentially at room temperature. After refluxing for 17 h in toluene, the reaction mixture was filtered through Celite® and concentrated in vacuo. Further purification was carried out by silica gel column chromatography to give 33 (3.2 mg, 49%) as a white amorphous solid.

1H NMR (400 MHz, CD₃OD) δ 0.99 (d, J = 6.9 Hz, 3H), 1.03 (d, J = 6.9 Hz, 3H), 2.16 (septet, J = 6.9 Hz, 1H), 3.06 (s, 3H), 3.28 (m, 1H), 3.46 (d, J = 15.2 Hz, 1H), 4.13 (d, J = 16.1 Hz, 1H), 4.35 (d, J = 15.2 Hz, 1H); 13C NMR (100 MHz, CD₃OD) δ 16.2, 17.5, 36.6, 37.4, 46.6, 53.4, 80.5, 172.6, 177.9; IR (cm⁻¹): 3321, 2965, 2925, 1735, 1654, 1522, 1469, 1221, 1162, 1087; HRMS-ESI (m/z): [M+Na]⁺ calcd for C₉H₁₆N₂NaO₃, 223.1059; found 223.1059.

9. Experimental Section for Deprotection of DMeBn group

To a solution of 14f (7.7 mg, 28.9 μmol) in CH₂Cl₂ (294 μl) was added i-Pr₃SiH (28.0 μl, 137 μmol) and trifluoroacetic acid (6.0 μl). After stirring for 40 min, the mixture was concentrated in vacuo to give the corresponding carboxylic acid (6.4 mg). To a solution of the carboxylic acid in MeOH-Et₂O (300 μl, v/v = 1) was added a solution of 2.0 M TMSCHN₂ in Et₂O (54.0 μl, 108 μmol). After stirring for 5 min, the reaction mixture was concentrated in vacuo. Further purification was carried out by silica gel column chromatography to give S2 (3.9 mg, 89%) as a colorless oil.

1H NMR (400 MHz, CDCl₃) δ 0.85 (d, J = 6.9 Hz, 3H), 0.93 (d, J = 6.9 Hz, 3H), 2.00 (septet, J = 6.9 Hz, 1H), 2.08 (br s, 1H), 3.43 (br s, 1H), 3.73 (dd, J = 11.0, 2.3 Hz, 1H), 3.80 (m, 1H), 3.83 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 16.4, 17.4, 32.7, 53.2, 66.5, 81.4, 176.1; IR (cm⁻¹): 3474, 2966, 1734, 1225, 1163, 1139, 1080; HRMS-ESI (m/z): [M+Na]⁺ calcd for C₇H₁₄NaO₄, 185.0790; found 185.0792.
13d

**1H NMR Spectroscopy**
- Domain: 1H
- Experiment: proton.xlsx
- Frequency: 400.2822 MHz
- Offset: 5 ppm
- Sweep: 7.50 MHz
- Points: 16384
- Scans: 8
- Temperature: 21.8°C
- Solvent: CHLOROFORM-D

**13C NMR Spectroscopy**
- Domain: 13C
- Experiment: carbon.xlsx
- Frequency: 100.00248 MHz
- Offset: 10.0 ppm
- Sweep: 31.65666 kHz
- Points: 32768
- Scans: 110
- Temperature: 21.5°C
- Solvent: CHLOROFORM-D

**Chemical Structures**

**13d**
13e

\[ \text{S23} \]
(a mixture of diastereomer A and B)
S46
X: Domain = 1H
Experiment = proton.jsp
X Freq = 401.2822[MHz]
X Offset = 5[ppm]
X Sweep = 7-53012[kHz]
X Points = 16384
Scans = 8
Temp. Get = 21.9[dC]
Solvent = CHLOROFORM-D

S2

X: parts per Million : Proton

X: Domain = 13C
Experiment = carbon.jsp
X Freq = 100.90248[MHz]
X Offset = 100.0[ppm]
X Sweep = 31.56566[kHz]
X Points = 32768
Scans = 1024
Temp. Get = 21.7[dC]
Solvent = CHLOROFORM-D

S2

X: parts per Million7: Carbon13