Supporting Information

Organophotoredox/Copper Hybrid Catalysis for Regioselective Allylic Aminodecarboxylation of $\beta,\gamma$-Unsaturated Carboxylic Acids

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1. General method

$^1$H and $^{13}$C NMR spectra were recorded on JEOL JNM-LA 500, JEOL ECX500 (500 MHz for $^1$H NMR, 125 MHz for $^{13}$C NMR), and JEOL ECS400 (400 MHz for $^1$H NMR, 100 MHz for $^{13}$C NMR) spectrometer. Chemical shifts were reported in ppm on the $\delta$ scale relative to residual CHCl$_3$ ($\delta = 7.26$ for $^1$H NMR and $\delta = 77.16$ for $^{13}$C NMR) as an internal reference. Coupling constant ($J$) are reported in Hertz unit (Hz). Multiplicities are described with standard following abbreviations: s = singlet, br = broad, d = doublet, t = triplet, q = quadruplet, m = multiplet. Column chromatographies were performed with silica gel 60 (40–63 $\mu$m, purchased from Kanto Chemical Co., Inc.) or by Biotage® Isolera$^{\text{TM}}$ One 3.0 with pre-packed column of Biotage® SNAP Ultra. ESI-mass spectra were measured on a Shimadzu LCMS-2020 spectrometer (for LRMS), and a JEOL JMS-T100LC AccuTOF spectrometer (for HRMS). Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. Gel permeation chromatography (GPC) was performed on a recycling preparative HPLC LC9210 NEXT system, Japan Analytical Industry Co., Ltd. All solvents and reagents were used without further purification (purchased from Aldrich, Tokyo Chemical Industry Co., Ltd. (TCI), Kanto Chemical Co., Inc., and Wako Pure Chemical Industries, Ltd.). Allylic aminodecarboxylation reactions were carried out in dry and degassed solvents under argon atmosphere. 2,2-dimethyl-3-butenoic acid (1e), (E)-non-3-enoic acid (1g) and 1-cyclohexene acetic acid (1h) are commercially available.

2. Preparation of substrates

Procedure A :

The disubstituted-3-enoic acid were synthesized using a reported procedure.$^1$ In a round bottom flask was placed at 0 °C, 5.6 equiv. of diisopropylamine in dry THF (Conc. = 0.2 mol/L) under argon. Then a solution of $n$BuLi in hexane (5.6 equiv.) was added dropwise at 0 °C. After 15 min. stirring at 0°C, 1 equiv. of acid was added dropwise. After 30 min., 11.0 equiv. of haloalkane was added and the solution was allowed to warm to room temperature slowly overnight. The mixture was acidified with aqueous HCl solution (1 M) and was extracted with EtO (3 times). The combined organic phases were dried over Na$_2$SO$_4$, filtrated and the solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using pentane/EtOAc as eluent (9:1 to 8:2).

(E)-2,2-dimethylnon-3-enoic acid (1a)

Prepared according to the procedure A from non-3-enoic acid and iodomethane.

Light yellow oil; yield: 173 mg (94%).

IR (KBr) cm$^{-1}$ 2927, 1701, 1470, 1364, 1287, 1166, 972.

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta = 5.62$ (d, $J = 15.5$ Hz, 1 H), 5.54 (dt, $J = 6.0$, 16.0 Hz, 1 H), 2.02 (q, $J = 6.5$ Hz, 2 H), 1.40 – 1.32 (m, 2 H), 1.30 (s, 6 H), 1.31 – 1.19 (m, 4 H), 0.88 (t, $J = 6.5$ Hz, 3 H).

$^{1}$ Duong, H.A.; Gilligan, R.E.; Cooke, M.L.; Phipps, R.J.; Gaunt, M.J. Angew. Chem. Int. Ed. 2011, 50, 463
$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta = 183.9, 133.7, 129.7, 44.0, 32.7, 31.5, 29.1, 25.1, 22.6, 14.2.$

LRMS (ESI) : $m/z = 185 \ [M + H]^+$

**(E)-2,2-diethylnon-3-enoic acid (1b)**

![Image](https://via.placeholder.com/150)

Prepared according to the procedure A from (E)-2,2-dimethylnon-3-enoic acid and iodoethane.

Colorless oil ; 600 mg (57%).

IR (KBr) cm$^{-1}$ 2957, 2927, 2873, 1698, 1455, 1405, 1276, 1196, 970.

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta = 5.55 - 5.49$ (m, 2 H), 2.09 - 2.02 (m, 2 H), 1.77 - 1.68 (m, 4 H), 1.41 - 1.34 (m, 2 H), 1.34 - 1.24 (m, 4 H), 0.88 (t, $J = 7.0$ Hz, 3 H), 0.83 (t, $J = 7.5$ Hz, 6.0 H).

$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta = 183.1, 131.4, 130.8, 52.2, 33.0, 31.5, 29.2, 28.4, 22.6, 14.2, 8.8.$

LRMS (ESI) : $m/z = 213 \ [M + H]^+$

**(E)-1-(hept-1-en-1-yl)cyclopentane-1-carboxylic acid (1c)**

![Image](https://via.placeholder.com/150)

Prepared according to the procedure A from (E)-2,2-dimethylnon-3-enoic acid and 1,4-diiodobutane.

Purification by GPC.

Colorless oil; yield : 146 mg (14%).

IR (KBr) cm$^{-1}$ 2965, 2565, 1700, 1457, 666, 613.

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta = 5.60$ (d, $J = 15.0$ Hz, 1 H), 5.54 (dt, $J = 6.5$, 15.5 Hz, 1 H), 2.22 - 2.10 (m, 2 H), 2.02 (q, $J = 7.0$ Hz, 2 H), 1.77 - 1.69 (m, 2 H), 1.69 - 1.61 (m, 4 H), 1.41 - 1.32 (m, 2 H), 1.32 - 1.20 (m, 4 H), 0.88 (t, $J = 7.5$ Hz, 3 H).

$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta = 183.3, 131.3, 130.6, 55.9, 35.7, 32.7, 31.5, 29.1, 24.0, 22.6, 14.2.$

LRMS (ESI) : $m/z = 211 \ [M + H]^+$

**(E)-4-(hept-1-en-1-yl)tetrahydro-2H-pyran-4-carboxylic acid (1d)**

![Image](https://via.placeholder.com/150)

To a solution of diisopropylamine (309 $\mu$L, 2.2 mmol) in THF (5 mL) was added n-BuLi (1.4 mL, 2.2 mmol, 1.57 M in hexane) at 0 $^\circ$C. After the mixture was stirred for 30 min, methyl (E)-non-3-enoate (170 mg, 1 mmol) was added to the mixture at 0 $^\circ$C and the mixture was stirred at 0 $^\circ$C for another 30 min. 1-Bromo-2-(2-bromoethoxy)ethane (150 $\mu$L, 1.2 mmol) was added to the mixture at 0 $^\circ$C. The reaction was allowed to warm to room temperature over 18 h, then quenched with sat. NaHCO$_3$aq, extracted with AcOEt, dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by a flash chromatography on silica gel (SiO$_2$, EtOAc / Hexane = 1:9) to give colorless oil as methyl ester (43.8 mg, 18%). The product was hydrolyzed by
2M-NaOH aq. (180 μL, 0.36 mmol) in MeOH (1 mL) at 60 °C for 4 h. The reaction mixture was diluted with 2M-NaOH aq. and washed with Et₂O. The aqueous layer was separated and acidified by HCl aq. to adjust pH to 1~2, then extracted with EtOAc, dried over Na₂SO₄ and concentrated to give pale yellow oil as the title compound (1d).

Pale yellow oil; yield : 37 mg (16% over 2 steps).

IR (KBr) cm⁻¹ 2957, 2926, 2856, 1699, 1443, 1244, 1107, 1028, 631, 680.

¹H NMR (CDCl₃, 500 MHz) δ = 5.62 (dt, J = 7, 15.0 Hz, 1 H), 5.42 (dt, J = 1.5, 15.5 Hz, 1 H), 3.80 (dt, J = 4.0, 11.5 Hz, 2 H), 3.62 - 3.54 (m, 2 H), 2.17 – 2.09 (m, 2 H), 2.04 (q, J = 7.0 Hz, 2 H), 1.77 – 1.68 (m, 2 H), 1.41 – 1.33 (m, 2 H), 1.33 – 1.20 (m, 5 H), 0.88 (t, J = 7.0 Hz, 3 H).

¹³C NMR (CDCl₃, 125 MHz) δ = 180.8, 132.7, 131.8, 65.2, 46.3, 33.7, 32.7, 31.4, 28.9, 22.6, 14.2.

LRMS (ESI) : m/z = 227 [M + H]+

(E)-5-methylhex-3-enoic acid (1f)

To a solution of diisopropylamine (15 mmol, 3 equiv.) in THF (2 0 mL) was added n-BuLi (15 mmol, 3 equiv.) at 0 °C. The mixture was stirred for 30 min, tert-butyl but-3-enoate (5 mmol, 1 equiv.) was added to the mixture at 0 °C and the mixture was stirred at 0 °C for another 30 min. Iodomethane (20 mmol, 4 equiv.) was added to the mixture at 0 °C. The reaction was allowed to warm to room temperature over 4 h, then quenched with sat. NaHCO₃aq, extracted with AcOEt, dried over Na₂SO₄ and concentrated in vacuo. The crude residue was purified by a flash chromatography on silica gel (EtOAc/hexane = 1:9) to give the desired ester tert-butyl 2,2-dimethylbut-3-enoate as colorless oil (244 mg, 29%).

¹H NMR (500 MHz, CDCl₃) δ = 6.01 (dd, J = 10.9 Hz, 17.8 Hz, 1 H), 5.11-5.01 (m, 2 H), 1.43 (s, 9 H), 1.26 (s, 6 H).

To a solution of but-3-en-1-ylbenzene (11.7 mmol, 3 equiv.) and tert-butyl 2,2-dimethylbut-3-enoate (3.89 mmol, 1 equiv.) in CH₂Cl₂ (15 mL) was added Grubbs 2nd generation catalyst (0.195 mmol, 5 mol%). The mixture was refluxed for 16 h. The reaction was concentrated then diluted with hexane and filtrated by Celite. The filtrate was concentrated. To the residue was added 4 M HCl in dioxane (4 mL). The mixture was stirred at room temperature overnight. Then the reaction mixture was concentrated, basified by NaOHaq (50 mL) then washed with Et₂O (two times). The separated aqueous layer was acidified by HClaq and extracted with AcOEt, dried over Na₂SO₄, concentrated, purified by column chromatograph on silica (EtOAc/hexane = 1/4) and GPC (6 cycles) to give the desired product (1f).

White foam; yield : 46 mg (5%).
\[ ^1H \text{NMR (500 MHz, CDCl}_3) \delta = 7.27 - 7.24 (m, 2H), 7.18 - 7.12 (m, 3H), 5.64 - 5.54 (m, 2H), 2.67 (t, J = 7.4 Hz, 2H), 2.32 (dt, J = 8.0 Hz, 7.4 Hz, 2H), 1.27 (s, 6H). \]
\[ ^13C \text{NMR (125 MHz, CDCl}_3) \delta = 183.1, 141.7, 134.7, 128.6, 128.5, 128.2, 125.8, 43.9, 35.8, 34.3, 25.0. \]
LRMS (ESI) : \[ m/z = 219 [M + H]^+ \]

3-methylbut-3-enoic acid (1i)

The 3-methylbut-3-enoic acid (1i) was synthesized using a reported procedure. In a round bottom flask was placed a solution of 3-methylbut-3-en-1-ol (9.28 mmol, 1 equiv.) in acetone (46 mL, conc. = 0.2 mol/L). At 0°C, Jones’ reagent (2.68 mol/L, 12.99 mmol, 1.4 equiv.) was added and the reaction mixture was stirred at 0°C for 1 h. The reaction mixture was washed with 2 M NaOH. The aqueous layer was acidified with HCl and extracted with Et2O (three times). The combined organic phases were dried over Na2SO4, filtrated, and the solvent was removed under vacuum. The residual oil was purified by distillation (bp 88-90°C (20 mmHg)).

Colorless oil ; yield 162 mg (16%).

\[ ^1H \text{NMR (CDCl}_3, 400 MHz) \delta = 4.96 (s, 1H), 4.89 (s, 1H), 3.09 (s, 2H), 1.84 (s, 3H). \]

Data are in accordance with the literature.2

(E)-5-methylhex-3-enoic acid (1j)

The (E)-5-methylhex-3-enoic acid (1j) was synthesized using a reported procedure. In a round bottom flask was placed a solution of pyrrolidine (0.29 mmol, 1 mol%) and acetic (0.29 mmol, 1 mol%) in DMSO (0.73 mL) under argon. The mixture was stirred at room temperature for 5 min, after which time a solution of malonic acid (29 mmol, 1 equiv.) and isovaleraldehyde (29 mmol, 1 equiv.) in DMSO (14.5 mL) was added. The reaction mixture was stirred at room temperature for 20 min and then at 100°C for 16 h. Once cooled to room temperature, the reaction mixture was diluted with H2O and extracted with Et2O (three times). The combined organic phases were washed with H2O, dried over Na2SO4, filtrated, and the solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using pentane/EtOAc as eluent (7:3).

Colorless oil ; yield : 2.9 g (78%).

IR (KBr) cm\(^{-1}\) 2961, 1713, 1466, 1416, 1364, 1289, 1222, 1051, 970.

\[ ^1H \text{NMR (CDCl}_3, 500 MHz) \delta = 5.56 (dd, J = 6.5, 15.5 Hz, 1H), 5.47 (dtd, J = 0.5, 6.5, 15.5 Hz, 1H), 3.06 (d, J = 7.0 Hz, 2H), 2.35 – 2.25 (m, 1H), 0.99 (d, J = 6.5 Hz, 6H). \]
\[ ^13C \text{NMR (CDCl}_3, 125 MHz) \delta = 179.2, 142.4, 118.0, 37.9, 31.1, 22.3. \]

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LRMS (ESI) : $m/z = 127 \ [M + H]^+$
Data are in accordance with the literature.4

3. General procedure for the photocatalytic aminodecarboxylation of 3-alkenoic acids

Procedure B : One equivalent of 3-alkenoic acid in degassed CH$_3$CN (Conc. = 0.1 mol/L) was added into a 4 mL vial equipped with a Teflon coated magnetic stirring bar. The vial was sealed with a septum-cap and the internal atmosphere exchanged with argon via three repeated cycle of vacuum-refill. Then 5 mol% of 9-mesityl-10-methylacridinium perchlorate was added followed by 10 mol% of CuOAc, 10 mol% of (R,R)-Me-DuPHOS, 3 equiv. of azodicarboxylate and 25 mol% of DBU. The vial was irradiated with blue LEDs (Aldrich® micro photochemical reactor, 100-240 V, 435-445 nm) under vigorous stirring at 4°C (cold room). After 24 hours the solvent was removed under vacuum. The crude mixture was purified by flash chromatography on silica gel provided the desired product (eluent pentane/EtOAc).

4. Compound caracterization data

Di-tert-butyl 1-(2-methylnon-2-en-4-yl)hydrazine-1,2-dicarboxylate (2a)

Prepared according to the procedure B from (E)-2,2-dimethylnon-3-enoic acid (1a) and di-tert-butyl azodicarboxylate.

A mixture of rotamers.

Colorless oil ; yield : 61 mg (78%).

$R_f = 0.42$ (pentane/EtOAc, 9:1)

IR (KBr) cm$^{-1}$ 3267, 2930, 1699, 1456, 1366, 1244, 1160, 1049, 865, 730.

$^1$H NMR (CDCl$_3$, 400 MHz, 50°C) $\delta = 6.22 – 5.89$ (br s, NH, 1 H), 5.06 (d, $J = 8.5$ Hz, 1 H), 4.89 – 4.60 (br m, 1 H), 1.76 – 1.58 (m, 6 H), 1.45 (s, 18 H), 1.39 – 1.14 (br m, 8 H), 0.87 (t, $J = 5.6$ Hz, 3 H).

$^{13}$C NMR (CDCl$_3$, 125 MHz, 50°C) $\delta = 154.9, 123.9, 80.7, 55.5, 33.3, 31.8, 28.4, 28.2, 25.7, 25.6, 22.6, 18.5, 14.0$.

LRMS (ESI) : $m/z = 393 \ [M + Na]^+$

HRMS (ESI) : $m/z \ [M + Na]^+$ calcd for C$_{20}$H$_{38}$N$_2$O$_4$Na 393.2729; found : 393.2728

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Di-tert-butyl 1-(3-ethyldec-3-en-5-yl)hydrazine-1,2-dicarboxylate (2b)

Prepared according to the procedure B from (E)-2,2-diethylnon-3-enoic acid (1b) and di-tert-butyl azodicarboxylate.

A mixture of rotamers.

Colorless foam; yield: 72 mg (68%).

\[ R_f = 0.38 \text{ (pentane/EtOAc, 9:1)} \]

IR (KBr) cm\(^{-1}\) 2966, 1702, 1366, 1162, 1022, 755.

\[ ^1H \text{ NMR (CDCl}_3, 500 \text{ MHz, 50°C)} \delta = 6.07 - 5.69 \text{ (br s, NH, 1 H), 5.03 (d, } J = 9.0 \text{ Hz, 1 H), 4.87 - 4.73 \text{ (br m, 1 H), 2.10 (q, } J = 7.5 \text{ Hz, 2 H), 2.03 (q, } J = 7 \text{ Hz, 2 H), 1.70 - 1.22 \text{ (m, 8 H), 1.46 (s, 18 H), 0.99 (t, } J = 7.5 \text{ Hz, 3 H), 0.97 (t, } J = 7.5 \text{ Hz, 3 H), 0.88 (t, } J = 6.0 \text{ Hz, 3 H).} \]

\[ ^13C \text{ NMR (CDCl}_3, 125 \text{ MHz, 50°C)} \delta = 154.9, 121.7, 80.9, 54.8, 33.6, 31.9, 29.1, 28.5, 28.4, 25.9, 24.1, 22.7, 14.1, 13.4, 12.9. \]

LRMS (ESI): \( m/z = 421 \) [M + Na]+

HRMS (ESI): \( m/z \) [M + Na]+ calcd for C\(_{22}\)H\(_{42}\)N\(_2\)O\(_4\)Na 421.3042; found: 421.3021

Di-tert-butyl 1-(1-cyclopentylideneheptan-2-yl)hydrazine-1,2-dicarboxylate (2c)

Prepared according to the procedure B from (E)-1-(hept-1-en-1-yl)cyclopentane-1-carboxylic acid (1c) and di-tert-butyl azodicarboxylate.

A mixture of rotamers.

Colorless foam; yield: 40 mg (75%).

\[ R_f = 0.37 \text{ (pentane/EtOAc, 9:1)} \]

IR (KBr) cm\(^{-1}\) 3266, 2957, 1701, 1455, 1366, 1253, 1162, 1048, 1020, 864, 758.

\[ ^1H \text{ NMR (CDCl}_3, 500 \text{ MHz, 50°C)} \delta = 6.08 - 5.93 \text{ (br s, NH, 1 H), 5.19 (d, } J = 8.5 \text{ Hz, 1 H), 4.72 - 4.54 \text{ (br m, 1 H), 2.42 - 2.08 \text{ (br m, 4 H), 1.72 - 1.51 \text{ (m, 5 H), 1.45 (s, 18 H), 1.35 - 1.06 \text{ (br m, 7 H), 0.87 (t, } J = 5.5 \text{ Hz, 3 H).} \]

\[ ^13C \text{ NMR (CDCl}_3, 125 \text{ MHz, 50°C)} \delta = 155.1, 130.6, 119.1, 80.8, 56.9, 33.8, 33.3, 31.9, 29.4, 28.5, 28.4, 26.5, 26.3, 25.9, 22.8, 14.1. \]

LRMS (ESI): \( m/z = 419 \) [M + Na]+

HRMS (ESI): \( m/z \) [M + Na]+ calcd for C\(_{22}\)H\(_{40}\)N\(_2\)O\(_4\)Na 419.2886; found: 419.2898
**Di-tert-butyl 1-(1-(tetrahydro-4H-pyran-4-ylidene)heptan-2-yl)hydrazine-1,2-dicarboxylate (2d)**

![Structural formula of compound 2d]

Prepared according to the procedure B from (E)-4-(hept-1-en-1-yl)tetrahydro-2H-pyran-4-carboxylic acid (1d) and di-tert-butyl azodicarboxylate.

A mixture of rotamers.

White foam; yield: 47 mg (76%).

\[ R_f = 0.24 \text{ (pentane/EtOAc, 9:1)} \]

IR (KBr) cm\(^{-1}\): 3313, 2977, 2857, 1801, 1456, 1367, 1251, 1049, 854, 759.

\(^1\)H NMR (CDCl\(_3\), 500 MHz, 50°C) \( \delta = 6.05 - 5.93 \) (br s, 1 H, NH), 5.15 (d, J = 8.5 Hz, 1 H), 4.85 – 4.74 (br m, 1 H), 3.89 – 3.57 (br m, 4 H), 2.48 – 2.26 (br m, 2H), 2.25 – 2.15 (br m, 2 H), 1.56 – 1.48 (br m, 4 H), 1.47 (s, 9 H), 1.46 (s, 9 H), 1.33 – 1.23 (br m, 4 H), 0.88 (t, J = 6.5 Hz, 3 H).

\(^13\)C NMR (CDCl\(_3\), 125 MHz, 50°C) \( \delta = 154.8, 122.3, 83.7, 81.1, 69.6, 68.9, 54.2, 37.1, 33.2, 31.8, 30.8, 28.4, 28.3, 28.1, 25.9, 22.7, 14.1 \).

LRMS (ESI): \( m/z = 435 [M + Na]^+ \)

HRMS (ESI): \( m/z [M + Na]^+ \) calcd for C\(_{22}\)H\(_{40}\)N\(_2\)O\(_5\)Na 435.2835; found: 435.2811

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**Di-tert-butyl 1-(3-methylbut-2-en-1-yl)hydrazine-1,2-dicarboxylate (2e)**

![Structural formula of compound 2e]

Prepared according to the procedure B from 2,2-dimethylbut-3-enolic acid (1e) and di-tert-butyl azodicarboxylate.

A mixture of rotamers.

White foam; yield: 35 mg (44%).

\[ R_f = 0.41 \text{ (pentane/EtOAc, 9:1)} \]

IR (KBr) cm\(^{-1}\): 3319, 2977, 1705, 1455, 1366, 1254, 1157.

\(^1\)H NMR (CDCl\(_3\), 500 MHz, 50°C) \( \delta = 6.10 - 5.75 \) (br m, 1 H, NH), 4.97 (t, J = 7.0 Hz, 1 H), 3.79 (d, J = 6.0 Hz, 2 H), 1.47 (s, 3 H), 1.40 (s, 3 H), 1.21 (s, 9 H), 1.21 (s, 9 H).

\(^13\)C NMR (CDCl\(_3\), 100 MHz, 50°C) \( \delta = 155.5, 136.7, 119.4, 81.2, 47.4, 28.4, 25.8, 17.9 \).

LRMS (ESI): \( m/z = 323 [M + Na]^+ \)

HRMS (ESI): \( m/z [M + Na]^+ \) calcd for C\(_{15}\)H\(_{28}\)N\(_2\)O\(_4\)Na 323.1947; found: 323.1938

Data are in accordance with the literature.

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Di-tert-butyl 1-(5-methyl-1-phenylhex-4-en-3-yl)hydrazine-1,2-dicarboxylate (2f)

\[
\text{CO}_2\text{Bu}
\]
\[
\text{Ph}
\]
\[
\text{Me}
\]

Prepared according to the procedure B from (E)-2,2-dimethyl-6-phenylhex-3-enoic acid (1f) and di-tert-butyl azodicarboxylate.

A mixture of rotamers.

Pale foam; yield: 39 mg (58%).

R_f = 0.40 (pentane/EtOAc, 9:1)

IR (KBr) cm⁻¹ 3267, 2977, 2930, 1703, 1455, 1392, 1366, 1250, 1160, 699, 654.

¹H NMR (CDCl₃, 500 MHz, 50°C) δ = 7.32 – 7.23 (m, 2 H), 7.23 – 7.12 (m, 3 H), 6.05 – 5.80 (br m, 1 H), 5.13 (d, J = 9.0 Hz, 1 H), 4.89 – 4.69 (br m, 1 H), 2.86 – 2.56 (br m, 2 H), 2.09 – 1.91 (br m, 1 H), 1.72 (s, 3 H), 1.64 (s, 3 H), 1.71 – 1.59 (br m, 1 H), 1.47 (s, 9 H), 1.46 (s, 9 H).

¹³C NMR (CDCl₃, 125 MHz, 50°C) δ = 155.9, 155.0, 142.5, 135.9, 128.6, 128.4, 125.8, 123.5, 81.1, 55.4, 35.1, 32.6, 28.4, 28.4, 25.8, 18.7.

LRMS (ESI) : m/z = 427 [M + Na]^+

HRMS (ESI) : m/z [M + Na]^+ calcd for C₂₃H₃₆N₂O₄Na 427.2573 ; found : 427.2566

Di-tert-butyl 1-(oct-1-en-3-yl)hydrazine-1,2-dicarboxylate (2g)

\[
\text{CO}_2\text{Bu}
\]
\[
\text{Me}
\]

Prepared according to the procedure B from 3-nonenolic acid (1g) and di-tert-butyl azodicarboxylate.

A mixture of rotamers.

Colorless oil; yield: 19 mg (29%).

R_f = 0.35 (pentane/EtOAc, 9:1)

IR (KBr) cm⁻¹ 3303, 2929, 1705, 1456, 1392, 1157, 601.

¹H NMR (CDCl₃, 500 MHz, 50°C) δ = 6.10-5.88 (br s, NH, 1 H), 5.88 – 5.73 (m, 1 H), 5.19 – 5.08 (br m, 2 H), 4.59 – 4.44 (br m, 1 H), 1.74 – 1.99 (br m, 1 H), 1.46 (s, 18 H), 1.40 – 1.22 (br m, 7 H), 0.88 (br m, 3 H).

¹³C NMR (CDCl₃, 125 MHz, 50°C) δ = 155.1, 137.1, 116.4, 81.3, 60.4, 31.8, 31.5, 28.4, 28.4, 25.9, 22.7, 14.1.

LRMS (ESI) : m/z = 365 [M + Na]^+

HRMS (ESI) : m/z [M + Na]^+ calcd for C₁₈H₃₆N₂O₄Na 365.2416 ; found : 365.2419
Di-tert-butyl 1-(cyclohex-1-en-1-ylmethyl)hydrazine-1,2-dicarboxylate (2h)

Prepared according to the procedure B from 1-cyclohexene-1-acetic acid (1h) and di-tert-butyl azodicarboxylate.
A mixture of rotamers.
Colorless foam; yield: 23 mg (56%).
Rf = 0.34 (pentane/EtOAc, 9:1)
IR (KBr) cm⁻¹ 2930, 1699, 1366, 1156, 759.
¹H NMR (CDCl₃, 500 MHz, 50°C) δ = 6.32 – 5.86 (br s, NH, 1 H), 5.60 – 5.45 (br m, 1 H), 4.06 – 3.73 (br m, 2 H), 2.09 – 1.97 (br m, 2 H), 1.96 – 1.83 (br m, 2 H), 1.68 – 1.52 (br m, 4 H), 1.46 (s, 18 H).
¹³C NMR (CDCl₃, 100 MHz, 50°C) δ = 155.7, 133.4, 125.1, 81.2, 56.2, 28.4, 26.6, 25.3, 22.8, 22.5.
LRMS (ESI): m/z = 349 [M + Na]⁺
HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₇H₃₀N₂O₄Na 349.2103; found: 349.2105

Di-tert-butyl 1-(2-methylallyl)hydrazine-1,2-dicarboxylate (2i)

Prepared according to the procedure B from 3-methylbut-3-enioic acid (1i) and di-tert-butyl azodicarboxylate.
A mixture of rotamers.
Colorless foam; yield: 37 mg (60%).
Rf = 0.31 (pentane/EtOAc, 9:1)
IR (KBr) cm⁻¹ 2930, 1699, 1366, 1156, 759.
¹H NMR (CDCl₃, 500 MHz, 50°C) δ = 6.36 – 6.07 (br s, NH, 1 H), 4.87 (s, 1 H), 4.81 (s, 1 H), 4.07 – 3.87 (br m, 2 H), 1.73 (s, 3 H), 1.47 (s, 9 H), 1.47 (s, 9 H).
¹³C NMR (CDCl₃, 100 MHz, 50°C) δ = 155.6, 140.9, 112.9, 81.4, 81.3, 53.5, 29.9, 28.4, 20.3.
LRMS (ESI): m/z = 309 [M + Na]⁺
HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₄H₂₆N₂O₄Na 309.1790; found: 309.1799

Di-tert-butyl (E)-1-(4-methylpent-2-en-1-yl)hydrazine-1,2-dicarboxylate (2j)

Prepared according to the procedure B from (E)-5-methylhex-3-enioic acid (1j) and di-tert-butyl azodicarboxylate.
A mixture of rotamers.
Colorless foam; yield: 31 mg (51%).


Rf = 0.33 (pentane/EtOAc, 9:1)
IR (KBr) cm⁻¹: 3326, 2977, 1707, 1652, 1541, 1365, 1152.

¹H NMR (CDCl₃, 500 MHz, 50°C) δ = 6.39 – 6.11 (br s, NH, 1 H), 5.56 (dd, J = 6.5, 15.5 Hz, 1 H), 5.40 (dd, J = 1.0, 6.5, 15.5 Hz, 1 H), 4.05 – 3.91 (br m, 2 H), 2.35 – 2.23 (m, 1 H), 1.47 (s, 9 H), 1.46 (s, 9 H), 0.98 (d, J = 7.0 Hz, 6 H).
¹³C NMR (CDCl₃, 125 MHz, 50°C) δ = 155.4, 141.9, 121.5, 81.2, 53.1, 51.5, 30.9, 28.3, 22.4.

LRMS (ESI): m/z = 337 [M + Na]⁺
HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₆H₃₀N₂O₄Na 337.2103; found: 337.2106

Di-tert-buty1 1-(1-(tert-butoxycarbonyl)-2,5-dihydro-1H-pyrrol-2-yl)hydrazine-1,2-dicarboxylate (2k)

Prepared according to the procedure B from tert-buty1 2,5-dihydro-1H-pyrrole-1-carboxylate (1k) and di-tert-buty1 azodicarboxylate.
A mixture of rotamers.
Yellow foam; yield: 76 mg (72%).
Rf = 0.35 (pentane/EtOAc, 8:2)
IR (KBr) cm⁻¹: 3314, 2978, 1707, 1478, 1418, 1391, 1327, 1244, 1164, 896, 635.
¹H NMR (CDCl₃, 500 MHz, 50°C) δ = 6.73 – 6.53 (br m, 1 H), 6.21 – 5.89 (br m, 2 H), 5.84 – 5.59 (br m, 1 H), 4.21 – 3.95 (br m, 2 H), 1.47 (s, 18 H), 1.44 (s, 9 H).
¹³C NMR (CDCl₃, 125 MHz, 50°C) δ = 155.9, 120.2, 111.9, 83.7, 81.6, 52.8, 28.4, 28.2.

LRMS (ESI): m/z = 422 [M + Na]⁺
HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₉H₃₅N₃O₆Na 422.2267; found: 422.2265

Diisopropyl 1-(2-methylnon-2-en-4-yl)hydrazine-1,2-dicarboxylate (4a)

Prepared according to the procedure B from (E)-2,2-dimethylnon-3-enoic acid (1a) and diisopropyl azodicarboxylate.
A mixture of rotamers.
Colorless foam; yield: 25 mg (68%).
Rf = 0.35 (pentane/EtOAc, 9:1)
IR (KBr) cm⁻¹: 2927, 2359, 1715, 1385, 1109, 762.
¹H NMR (CDCl₃, 500 MHz, 50°C) δ = 6.17 – 6.02 (br s, NH, 1 H), 5.06 (d, J = 8.0 Hz, 1 H), 5.01 – 4.88 (br m, 2 H), 4.87 – 4.69 (m, 1 H), 1.70 (s, 3 H), 1.67 (s, 3 H), 1.49 – 1.02 (m, 20 H), 0.87 (t, J = 6.5 Hz, 3 H).
$^{13}$C NMR (CDCl$_3$, 125 MHz, 50°C) δ = 156.4, 155.6, 136.1, 123.4, 69.9, 69.5, 55.6, 33.2, 31.8, 25.8, 22.8, 22.2, 22.2, 22.1, 18.7, 14.2.

LRMS (ESI) : $m/z = 365$ [M + Na]$^+$

HRMS (ESI) : $m/z$ [M + Na]$^+$ calcd for C$_{18}$H$_{34}$N$_2$O$_4$Na 365.2416; found: 365.2438

**Diethyl 1-(2-methylnon-2-en-4-yl)hydrazine-1,2-dicarboxylate (5a)**

![Diethyl 1-(2-methylnon-2-en-4-yl)hydrazine-1,2-dicarboxylate (5a)](image)

Prepared according to the procedure B from (E)-2,2-dimethylnon-3-enio acid (1a) and diethyl azodicarboxylate.

A mixture of rotamers.

Colorless foam; yield: 24 mg (52%).

R$_f$ = 0.31 (pentane/EtOAc, 9:1)

IR (KBr) cm$^{-1}$ 2932, 1708, 1412, 1222, 1061, 667.

$^1$H NMR (CDCl$_3$, 500 MHz, 50°C) δ = 6.26 – 6.00 (br s, NH, 1 H), 5.06 (d, $J = 9.0$ Hz, 1 H), 4.85 – 4.71 (br m, 1 H), 4.18 (q, $J = 7.0$ Hz, 4 H), 1.70 (s, 3 H), 1.68 (s, 3 H), 1.47 – 1.16 (m, 14 H), 0.87 (t, $J = 6.5$ Hz, 3 H).

$^{13}$C NMR (CDCl$_3$, 125 MHz, 50°C) δ = 156.8, 156.0, 136.2, 123.1, 62.4, 62.0, 55.9, 33.1, 31.8, 25.8, 22.7, 18.7, 14.6, 14.6, 14.2.

LRMS (ESI) : $m/z = 337$ [M + Na]$^+$

HRMS (ESI) : $m/z$ [M + Na]$^+$ calcd for C$_{16}$H$_{30}$N$_2$O$_4$Na 337.2103; found: 337.2090

**Bis(2-methoxyethyl) 1-(2-methylnon-2-en-4-yl)hydrazine-1,2-dicarboxylate (6a)**

![Bis(2-methoxyethyl) 1-(2-methylnon-2-en-4-yl)hydrazine-1,2-dicarboxylate (6a)](image)

Prepared according to the procedure B from (E)-2,2-dimethylnon-3-enio acid (1a) and bis(2-methoxyethyl) azodicarboxylate.

A mixture of rotamers.

Colorless foam; yield: 21 mg (60%).

R$_f$ = 0.28 (pentane/EtOAc, 1:1)

IR (KBr) cm$^{-1}$ 3284, 2927, 1757, 1714, 1519, 1455, 1245, 1128, 1067, 850, 759.

$^1$H NMR (CDCl$_3$, 400 MHz, 50°C) δ = 6.59 – 6.29 (br s, NH, 1 H), 5.05 (d, $J = 8.8$ Hz, 1 H), 4.92 – 4.67 (br m, 1 H), 4.39 – 4.14 (br m, 4 H), 3.68 – 3.50 (br m, 4 H), 3.39 (s, 3 H), 3.36 (s, 3 H), 1.70 (s, 3 H), 1.68 (s, 3 H), 1.44 – 1.17 (m, 8 H), 0.87 (t, $J = 6.8$ Hz, 3 H).
Dibenzyl 1-(2-methylnon-2-en-4-yl)hydrazine-1,2-dicarboxylate (7a)

From (E)-2,2-dimethylnon-3-enoic acid (1a) and dibenzyl azodicarboxylate. CuOAc-DuPHOS was replaced by Bi(OAc)₃.
A mixture of rotamers.
Colorless foam; yield: 18 mg (38%).
Rf = 0.21 (pentane/ EtOAc, 9:1)
IR (KBr) cm⁻¹ 2926, 2361, 1709, 1407, 1217, 1049, 600.

5. Procedures for the post-functionalization of the product (2a)

 tert-butyl (2-methylnon-2-en-4-yl)carbamate (8)

 tert-butyl (2-methylnon-2-en-4-yl)carbamate (8) was synthesized using a reported procedure.⁶
In a round bottom flask were placed, 1.0 equiv. of di-tert-butyl 1-(2-methylnon-2-en-4-yl)hydrazine-1,2-dicarboxylate (2a) and 2.5 equiv. of Cs₂CO₃ in CH₃CN (conc. = 0.175 mol/L) under argon. At room temperature, 2.0 equiv. of methyl bromoacetate was added. The mixture was heated to 50°C for 18 h. The reaction was quenched with NH₄Claq and was extracted with EtOAc (3 times). The combined organic phases were dried over Na₂SO₄, filtrated and the solvent was removed under vacuum. The crude was placed in a round bottom flask in CH₃CN (conc. = 0.18 mol/L). Then 3.0 equiv. of Cs₂CO₃ was added at room temperature. The mixture was heated at reflux for 16 h. The reaction was quenched with NH₄Claq and was extracted with EtOAc (3 times). The combined organic phases were dried over Na₂SO₄, filtrated and the

solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using pentane/EtOAc as eluent (98:2 to 95:5).

White foam; yield: 21 mg (42% over 2 steps).

A mixture of rotamers.

Rf = 0.51 (pentane/EtOAc, 9:1)

IR (KBr) cm⁻¹: 3419, 2284, 1055, 782, 601.

$^1$H NMR (CDCl₃, 500 MHz, 50°C) δ = 4.93 (d, J = 8.5 Hz, 1 H), 4.44 – 4.28 (br m, 1 H), 4.28 – 4.15 (br m, 1 H), 1.69 (s, 3 H), 1.68 (s, 3 H), 1.43 (s, 9 H), 1.39 – 1.19 (br m, 8 H), 0.87 (t, J = 7.0 Hz, 3 H).

$^{13}$C NMR (CDCl₃, 125 MHz, 50°C) δ = 155.5, 134.6, 126.5, 79.1, 49.4, 36.7, 31.9, 28.6, 25.7, 25.5, 22.8, 18.5, 14.1.

LRMS (ESI): m/z = 278 [M + Na]^+

HRMS (ESI): m/z [M + Na]^+ calcd for C₁₅H₂₉NO₂Na 278.2096; found: 278.2077

**tert-butyl (1-hydroxyheptan-2-yl)carbamate (9)**

A solution of tert-butyl (2-methylnon-2-en-4-yl)carbamate (8, 1 equiv., 0.08 mmol) in CH₂Cl₂ (1 mL) was cooled to -78 °C, followed by bubbling of the ozone for 5 min with stirring. After the reaction color changed to blue, the oxygen was bubbling to remove the ozone. CH₃OH (0.5 mL) and NaBH₄ (3 equiv) were added to the mixture at -78 °C. Then the reaction mixture was allowed to warm to room temperature for 1 h. The solvents were removed *in vacuo* and the residue was purified by a flash chromatography on silica gel (pentane/EtOAc, 6:4).

White foam; yield: 10 mg (60%).

Rf = 0.18 (pentane/EtOAc, 9:1)

A mixture of rotamers.

IR (KBr) cm⁻¹: 3853, 3585, 3346, 2929, 2359, 1684, 1508, 1457, 1365, 1251, 1061, 670.

$^1$H NMR (CDCl₃, 500 MHz, 50°C) δ = 4.62 – 4.42 (br s, 1 H, NH), 3.70 – 3.52 (br m, 2 H), 3.57 – 3.51 (br m, 1 H), 2.15 – 1.89 (br m, 1 H), 1.46 (s, 9 H), 1.43 – 1.24 (br m, 8 H), 0.90 (t, J = 6.5 Hz, 3 H).

$^{13}$C NMR (CDCl₃, 125 MHz, 50°C) δ = 156.7, 79.8, 66.3, 53.3, 31.9, 31.8, 28.6, 25.8, 22.7, 14.0.

LRMS (ESI): m/z = 232.1 [M + H]^+ 254.1 [M + Na]^+

HRMS (ESI): m/z [M + Na]^+ calcd for C₁₂H₂₅NO₃Na 254.1732; found: 254.1716
2,2,6,6-tetramethyl-1-((2-methylnon-2-en-4-yl)oxy)piperidine (11)

General procedure for the photocatalytic decarboxylation and allylation from (E)-2,2-dimethylnon-3-enoic acid (1a) and di-tert-butyl azodicarboxylate with the addition of 3 equiv. of TEMPO.
Orange foam ; yield : 22 mg (58%).
Rf = 0.63 (pentane/EtOAc, 95:5)
IR (KBr) cm⁻¹ 2871, 1774, 1459, 1375, 1248, 1154, 1048, 957, 865.
¹H NMR (CDCl₃, 500 MHz) δ = 5.11 – 5.03 (m, 1 H), 4.33 (td, J = 4.0, 8.5 Hz, 1 H), 1.63 (s, 3 H), 1.62 (s, 3 H), 1.44 – 1.35 (m, 4 H), 1.35 – 1.17 (m, 10 H), 1.15 (s, 6 H), 1.08 (s, 6 H), 0.87 (t, J = 7.0 Hz, 3 H).
¹³C NMR (CDCl₃, 100 MHz) δ = 132.5, 129.1, 80.6, 60.3, 40.6, 39.5, 35.1, 32.3, 31.7, 27.9, 25.9, 25.2, 22.8, 20.7, 18.7, 17.6, 17.2, 14.1.
LRMS (ESI) : m/z = 296 [M + H]⁺
HRMS (ESI) : m/z [M + H]⁺ calcd for C₁₉H₃₈NO 296.2875 ; found : 296.2890

6. General procedure for the photocatalytic decarboxylation and allylation of (1a), (1e) and (1g) in the absence of CuOAc/ligand

Procedure C : procedure B in the absence of CuOAc and ligand.

Di-tert-butyl (E)-1-(2-methylnon-3-en-2-yl)hydrazine-1,2-dicarboxylate (3a)

Prepared according to procedure C from (E)-2,2-dimethylnon-3-enoic acid (1a) and di-tert-butyl azodicarboxylate.
The crude mixture was purified by flash chromatography on silica gel (eluent : pentane/EtOAc, 9/1) provided the mixture of two inseparable regioisomers 2a and 3a (ratio (2a) : (3a) = 80 :20).
¹H NMR (CDCl₃, 400 MHz, 50°C) δ = 6.28 – 5.89 (br m, 0.8 H, NH, 2a), 5.86 – 5.75 (br m, 0.2 H, NH, 3a),
5.66 (d, J = 14.8 Hz, 0.2 H, 3a), 5.43 (dt, J = 6.4, 16.0 Hz, 0.2 H, 3a), 5.06 (d, J = 8.8 Hz, 0.8 H, 2a),
4.94 – 4.57 (br m, 0.8 H, 2a), 2.00 (q, J = 7.2 Hz, 0.4 H, 3a), 1.79 – 1.58 (m, 6 H, 2a, 3a), 1.54 – 1.03 (m, 25.6 H,
2a, 3a), 0.93 – 0.80 (m, 3H, 2a, 3a).
Di-tert-butyl 1-(2-methylbut-3-en-2-yl)hydrazine-1,2-dicarboxylate (3e)

From 2,2-dimethylbut-3-enoic acid (1e) and di-tert-butyl azodicarboxylate under general procedure for the photocatalytic decarboxylation and allylation in the absence of CuOAc and ligand.
The crude mixture was purified by flash chromatography on silica gel (eluent : pentane/EtOAc = 9/1) provided the mixture of two inseparable regioisomers 2e and 3e (ratio (2e) : (3e) = 85 : 15).
$^1$H NMR (500 MHz, CDCl$_3$, 50°C) $\delta = 6.49 – 6.08$ (br m, 1.7 H, NH, 2e), $6.01 – 5.91$ (br m, 0.3 H, NH, 3e), 5.21 (t, $J = 7.0$ Hz, 1.3 H, 2e), 5.11 – 5.00 (m, 0.4 H, 3e), 4.99 – 4.93 (m, 0.2 H, 3e), 1.73 (s, 3 H, 2e, 3e), 1.65 (s, 3 H, 2e, 3e), 1.46 (s, 18 H, 2e, 3e).

Di-tert-butyl (E)-1-(oct-2-en-1-yl)hydrazine-1,2-dicarboxylate (3g)

From 3-nonenoic-acid (1g) and di-tert-butyl azodicarboxylate under general procedure for the photocatalytic decarboxylation and allylation in the absence of CuOAc and ligand.
Mixture of separable regioisomers (2g) and (3g) (ratio (2g) : (3g) = 7:3).
Colorless oil ; yield : 29 mg (49%).
R$_f$ = 0.35 (pentane/AcOEt, 9:1)
IR (KBr) cm$^{-1}$ 3321, 2925, 1716, 1456, 1393, 1367, 1254, 1155, 629.
$^1$H NMR (400 MHz, CDCl$_3$, 50°C) $\delta = 6.36-5.93$ (br s, 1 H, NH), 5.64 – 5.53 (br m, 1 H), 5.49 – 5.37 (br m, 1 H), 4.11 – 3.86 (br m, 2 H), 2.02 (q, $J = 7.2$ Hz, 2 H), 1.46 (s, 18 H), 1.38 – 1.26 (br m, 6 H), 0.88 (t, $J = 7.2$ Hz, 3 H).
$^{13}$C NMR (125 MHz, CDCl$_3$, 50°C) $\delta = 155.4, 135.2, 124.5, 81.3, 61.5, 32.4, 31.5, 29.9, 29.0, 28.4, 22.6, 14.1.$
HRMS (ESI) : $m/z$ [M + Na]$^+$ calced for C$_{18}$H$_{34}$N$_2$O$_4$Na 365.2416 ; found : 365.2407
7. Ligand screening and enantioselectivity investigation

-Ligand screening:

\[
\begin{array}{cccc}
\text{Entry}^a & \text{[Cu(I)]} & \text{Ligand} & \text{Yield [%]}^b \\
1 & \text{CuOAc} & (R,R)-\text{Me-DuPHOS} & 78 \\
2 & \text{CuOAc} & \text{X-PHOS} & 73 \\
3 & \text{CuMes} & (R,R)-\text{Me-DuPHOS} & 61 \\
4 & \text{CuMes} & \text{X-PHOS} & 52 \\
5 & \text{CuMes} & (S)-\text{PHANEPHOS} & 44 \\
6 & \text{CuMes} & (R)-\text{DM-SEGPHOS} & 33 \\
7 & \text{CuMes} & (R)-\text{BINAP} & 29 \\
8 & \text{CuMes} & (S,S)-\text{DIPAMP} & 2 \\
9 & \text{CuMes} & (R,R)-\text{Me-BPE} & \text{traces} \\
10 & \text{CuMes} & 2,2^\prime\text{-methylenebis}[(4S)-4\text{-tert}-\text{butyl}-2\text{-oxazoline}] & \text{traces} \\
\end{array}
\]

\text{Entry}^a: \text{Reaction conditions: } 1\text{a} (0.2 \text{ mmol}), \text{Metal} (0.02 \text{ mmol}), \text{Mes-Acr}^+\text{-Me} (0.01 \text{ mmol}), \text{Ligand} (0.02 \text{ mmol}), \text{DTBAD} (0.6 \text{ mmol}), \text{DBU} (0.05 \text{ mmol}), \text{CH}_3\text{CN} (2 \text{ mL}), 4^\circ\text{C}, \text{Blue LEDs, 24 h.}^b \text{Yields refer to isolated products.}
- Enantioselectivity investigation:

Di-tert-butyl 1-(1-((4-methoxybenzoyl)oxy)heptan-2-yl)hydrazine-1,2-dicarboxylate (12)

A solution of di-tert-butyl 1-(2-methylnon-2-en-4-yl)hydrazine-1,2-dicarboxylate (2a) (27 mg, 0.08 mmol) in CH₂Cl₂ (1 mL) was cooled to -78 °C, followed by bubbling of the ozone for 5 min with stirring. After the reaction color changed to blue, the oxygen was bubbling to remove the ozone. MeOH (0.5 mL) and NaBH₄ (3 equiv) were added to the mixture at -78 °C. Then the reaction mixture was allowed to warm to room temperature for 1 h. The solvents were removed in vacuo and the residue was purified by a flash chromatography on silica gel (EtOAc / hexane = 1:4 to 1:2). The obtained intermediate was dissolved in THF (1 mL) and added p-anisic acid (1.2 equiv), triphenylphosphone (1.5 equiv) and diethyl azodicarboxylate (2.2 mol/L in toluene, 1.5 equiv) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, then quenched with sat. NaHCO₃ aq, extracted with EtOAc, dried over Na₂SO₄ and concentrated. The residue was purified by a flash chromatography on silica gel (EtOAc / hexane = 1:4) to give the title compound. Colorless oil; yield (37% over 2 steps).

IR (KBr) cm⁻¹ 3316, 2977, 2932, 2861, 1713, 1586, 1513, 1457, 1392, 1367, 1257, 1168, 1104, 1030, 849, 770, 597.

¹H NMR (500 MHz, CDCl₃) δ 7.96 (d, J = 8.0 Hz, 2 H), 6.87 (d, J = 8.0 Hz, 2 H), 6.40-5.80 (br m, 1 H), 4.58-4.25 (m, 2 H), 4.24-3.92 (m, 1 H), 3.83 (s, 3 H), 1.70-1.40 (br m, 12 H), 1.40-1.17 (br m, 14 H), 0.87 (br s, 3 H).

¹³C NMR (125 MHz, CDCl₃) δ 166.7, 156.3, 156.3, 155.5, 131.9, 122.4, 113.7, 80.9, 64.1, 57.4, 55.5, 31.9, 28.2, 28.1, 25.9, 22.6, 14.2.

HRMS (ESI) m/z [M+Na]⁺ calc. for C₂₅H₄₀N₂O₇Na 503.2728, found 503.2719.

Chiral separation condition

Column: IA3
Eluting solvent: n-hexane : IPA = 9 : 1
Flow rate: 1.0 mL/min
Compound concentration: 0.1 mg/mL
Inject volume: 5 µL
Retention time: 11.5 min and 24.6 min
Peak area %: 50.1 : 49.9
8. $^1$H and $^{13}$C NMR spectra
Ph

Me

Me

1f

CO₂H

Ph

CO₂H

Ph

CO₂H

Ph
Me

\[
\text{fBuO}_2\text{CO}_2\text{Bu} \quad \text{N} \quad \text{NH} \\
\text{2d}
\]
N\text{^*}NH
CO_2\text{Bu}^-

2h

\[
\text{\begin{align*}
\text{N} & \text{^*NH} \\
\text{CO}_2\text{Bu}^- & \\
\end{align*}}
\]