Phosphine-Catalyzed Doubly Stereoconvergent γ-Additions of Racemic Heterocycles to Racemic Allenoates: The Catalytic Enantioselective Synthesis of Protected α,α-Disubstituted α-Amino Acid Derivatives

Marcin Kalek and Gregory C. Fu*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

Supporting Information

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I. General Information

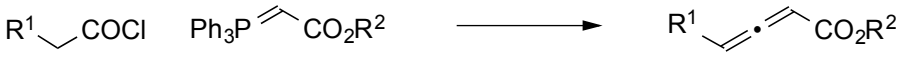
Unless otherwise noted, all materials were purchased from commercial suppliers and used as received. Anhydrous diisopropyl ether was purchased from Sigma-Aldrich. Catalyst **1** was synthesized according to a published procedure.[1]

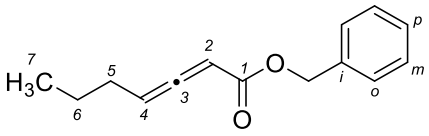
^{1}H and ^{13}C NMR spectroscopic data were collected on a Varian 500 MHz or a Bruker 400 MHz spectrometer at ambient temperature. The chemical shifts are reported in ppm, relative to solvent peaks. Assignment of the NMR signals was accomplished on the basis of 2D correlation experiments (atom-labeling scheme is arbitrary). High-resolution mass spectra (HRMS) were recorded on a Jeol MS Route (EI, FAB) or an Agilent G220A (ESI/APCI) mass spectrometer. IR spectra were recorded on a Perkin Elmer Spectrum BX FT-IR spectrometer. Optical rotations were measured on a Jasco P-2000 polarimeter at 589 nm (sodium D line). HPLC analyses were carried out on an Agilent 1100 series system with Daicel CHIRALPAK columns (4.6 × 250 mm, particle size 5 μm).

II. Preparation of Substrates

The yields have not been optimized.

Synthesis of allenoates

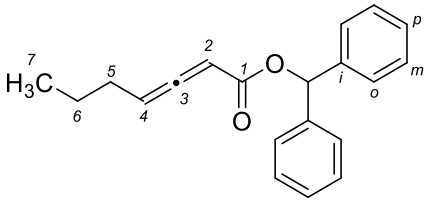




(±)-Benzyl hepta-2,3-dienoate.[2] A solution of benzyl 2-(triphenylphosphanylidene)acetate[3] (4.11 g, 10 mmol) in dichloromethane (anhydrous, 80 mL) was cooled to 0 °C in an ice bath under an atmosphere of nitrogen. Triethylamine (1.52 mL, 1.11 g, 11 mmol) was added, and then valeroyl chloride (1.30 mL, 1.33 g, 11 mmol) was added dropwise. The reaction mixture was stirred at rt for 4 h. Next, hexane (80 mL) was added. After 10 min, the precipitate was filtered off, and then the filtrate was concentrated under reduced pressure to one-third of its original volume. The mixture was filtered again, and the filtrate was concentrated under reduced pressure. The product was purified by column chromatography (silica gel, hexanes:diethyl ether / 100:0→85:15). The product was obtained as a colorless oil (1.95 g, 90% yield).[4]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40 – 7.31 (m, 5H, -C_6H_5), 5.66 – 5.61 (m, 2H, *H2*, *H4*), 5.20 and 5.16 (*AB*, *J* = 12.5 Hz, 2H, OCH_2Ph), 2.12 (m, 2H, *H5*), 1.49 (m, 2H, *H6*), 0.94 (t, *J* = 7.5 Hz, 3H, *H7*).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 212.8 (*C3*), 166.3 (*C1*), 136.2 (C_i), 128.6 (C_m), 128.3 (C_p), 128.2 (C_o), 95.5 (*C4*), 88.1 (*C2*), 66.6 (OCH_2Ph), 29.6 (*C5*), 22.1 (*C6*), 13.6 (*C7*).



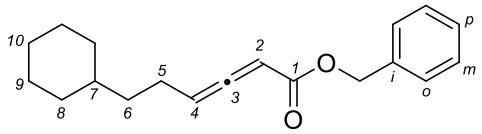
(±)-Benzhydryl hepta-2,3-dienoate. The title compound was prepared from valeroyl chloride and benzhydryl 2-(triphenylphosphanylidene)acetate following the same procedure as for (±)-benzyl hepta-2,3-dienoate. The product was purified by column chromatography (silica gel, hexanes:diethyl ether / 100:0→85:15), which furnished a colorless oil (83% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39 – 7.26 (m, 10H, -C_6H_5), 6.94 (s, 1H, OC*H*Ph_2), 5.72 – 5.63 (m, 2H, *H2*, *H4*), 2.15 (m, 2H, *H5*), 1.52 (m, 2H, *H6*), 0.96 (t, *J* = 7.4 Hz, 3H, *H7*).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 213.0 (*C3*), 165.4 (*C1*), 140.5, 140.4 (C_i), 128.6, 128.5 (C_m), 127.95, 127.94 (C_p), 127.2 (C_o), 95.5 (*C4*), 88.3 (*C2*), 77.1 ($OCHPh_2$), 29.6 (*C5*), 22.2 (*C6*), 13.7 (*C7*).

FT-IR (neat): 3064, 3031, 2959, 2931, 2872, 1959, 1716, 1495, 1455, 1415, 1246, 1148, 1002, 864, 795, 746 cm^{-1}.

HRMS (FAB): *m*/*z* 291.1371 ($[M+H-H_2]^+$, $C_{20}H_{19}O_2^+$ calcd. 291.1385).



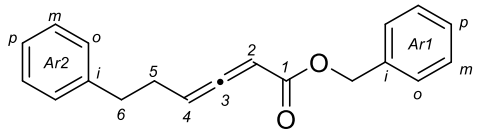
(±)-Benzyl 6-cyclohexylhexa-2,3-dienoate. The title compound was prepared from 4-cyclohexylbutanoyl chloride and benzyl 2-(triphenylphosphanylidene)acetate following the same procedure as for (±)-benzyl hepta-2,3-dienoate. The product was purified by column chromatography (silica gel, hexanes:diethyl ether/100:0→85:15), which furnished a colorless oil (72% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 – 7.28 (m, 5H, -C_6H_5), 5.67 – 5.60 (m, 2H, *H2*, *H4*), 5.20 and 5.16 (*AB*, *J* = 12.7 Hz, 2H, OCH_2Ph), 2.14 (m, 2H, *H5*), 1.75 – 0.89 (m, 13H, *H6* – *H10*).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.8 (*C3*), 166.3 (*C1*), 136.2 (C_i), 128.6 (C_m), 128.24 (C_p), 128.16 (C_o), 96.0 (*C4*), 88.2 (*C2*), 66.5 (OCH_2Ph), 37.1, 36.4, 33.3, 26.8, 26.4, 25.0 (*C5* – C*10*).

FT-IR (neat): 2922, 2850, 1960, 1723, 1448, 1417, 1256, 1148, 1003, 886, 799, 735 cm^{-1}.

HRMS (FAB): *m*/*z* 285.1844 ($[M+H]^+$, $C_{19}H_{25}O_2^+$ calcd. 285.1855).



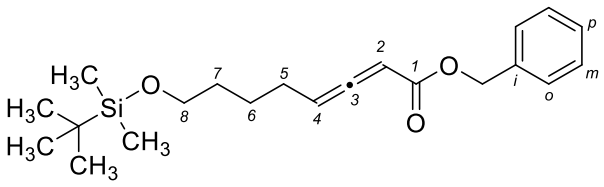
(±)-Benzyl 6-phenylhexa-2,3-dienoate. The title compound was prepared from 4-phenylbutanoyl chloride and benzyl 2-(triphenylphosphanylidene)acetate following the same procedure as for (±)-benzyl hepta-2,3-dienoate. The product was purified by column chromatography (silica gel, hexanes:diethyl ether/10:0→8:2), which furnished a colorless oil (51% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 – 7.17 (m, 10H, 2×-C_6H_5), 5.71 – 5.62 (m, 2H, *H2*, *H4*), 5.19 (s, 2H, OCH_2Ph), 2.79 (td, *J* = 7.4, 3.2 Hz, 2H, *H6*), 2.46 (m, 2H, *H5*).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.7 (*C3*), 166.1 (*C1*), 141.0 (C_i^{Ar2}), 136.2 (C_i^{Ar1}), 128.7, 128.57, 128.54 (C_m^{Ar1}, C_m^{Ar2}, C_o^{Ar2}), 128.3 (C_p^{Ar1}), 128.2 (C_o^{Ar1}), 126.3 (C_p^{Ar2}), 95.1 (*C4*), 88.6 (*C2*), 66.6 (OCH_2Ph), 35.2 (*C6*), 29.2 (*C5*).

FT-IR (neat): 3029, 2944, 1960, 1713, 1497, 1455, 1418, 1248, 1150, 1002, 871, 798, 748 cm^{-1}.

HRMS (FAB): *m*/*z* 279.1392 ($[M+H]^+$, $C_{19}H_{19}O_2^+$ calcd. 279.1385).



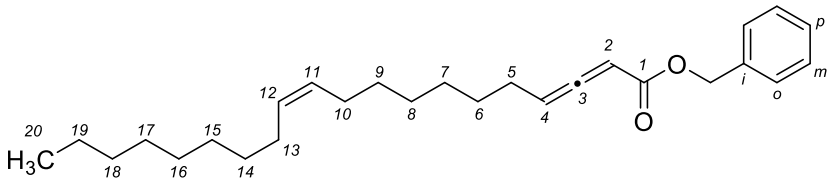
(±)-Benzyl 8-((*tert*-butyldimethylsilyl)oxy)octa-2,3-dienoate. The title compound was prepared from 6-((*tert*-butyldimethylsilyl)oxy)hexanoyl chloride and benzyl 2-(triphenylphosphanylidene)acetate following the same procedure as for (±)-benzyl hepta-2,3-dienoate. The product was purified by column chromatography (silica gel, hexanes:diethyl ether / 10:0→9:1), which furnished a colorless oil (83% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40 – 7.29 (m, 5H, -C_6H_5), 5.66 – 5.61 (m, 2H, *H2*, *H4*), 5.19 and 5.16 (*AB*, *J* = 12.4 Hz, 2H, OCH_2Ph), 3.59 (t, *J* = 6.2 Hz, 2H, *H8*), 2.16 (m, 2H, *H5*), 1.59 – 1.47 (m, 4H, *H6*, *H7*), 0.89 (s, 9H, $(CH_3)_3$C), 0.04 (s, 6H, $(CH_3)_2$Si).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 212.8 (*C3*), 166.2 (*C1*), 136.2 (C_i), 128.6 (C_m), 128.27 (C_p), 128.23 (C_o), 95.6 (*C4*), 88.3 (*C2*), 66.6 (OCH_2Ph), 62.9 (*C8*), 32.2 (*C7*), 27.4 (*C5*), 26.1 ($(CH_3)_3$C), 25.3 (*C6*), 18.5 ($(CH_3)_3C$), –5.1 ($(CH_3)_2$Si).

FT-IR (neat): 2929, 2857, 1960, 1724, 1456, 1417, 1256, 1150, 1103, 1006, 836, 776 cm^{-1}.

HRMS (ESI / APCI): *m*/*z* 361.2197 ([M+H]$^+$, $C_{21}H_{32}O_3Si^+$ calcd. 361.2194).



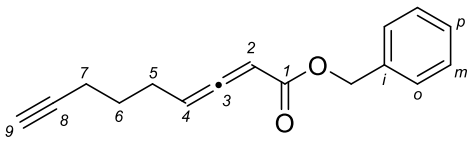
(±)-Benzyl (*Z*)-icosa-2,3,11-trienoate. The title compound was prepared from oleoyl chloride and benzyl 2-(triphenylphosphanylidene)acetate following the same procedure as for (±)-benzyl hepta-2,3-dienoate. The product was purified by column chromatography (silica gel, hexanes:diethyl ether / 10:0→9:1), which furnished a colorless oil (86% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 – 7.27 (m, 5H, -C_6H_5), 5.69 – 5.58 (m, 2H, *H2*, *H4*), 5.42 – 5.28 (m, 2H, *H11*, *H12*), 5.20 and 5.17 (*AB*, *J* = 12.5 Hz, 2H, OCH_2Ph), 2.14 (m, 2H, *H5*), 2.09 – 1.94 (m, 4H, *H10*, *H13*), 1.46 (m, 2H, *H6*), 1.40 – 1.20 (m, 18H, *H7* – *H9*, *H14* – *H19*), 0.89 (t, *J* = 7.1 Hz, 3H, *H20*).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.8 (*C3*), 166.2 (*C1*), 136.2 (C_i), 130.2, 129.8 (*C11*, *C12*), 128.6 (C_m), 128.24 (C_p), 128.17 (C_o), 95.7 (*C4*), 88.2 (*C2*), 66.5 (OCH_2Ph), 32.0, 29.9, 29.8, 29.7, 29.47, 29.46, 29.1, 29.0, 28.9, 27.6, 27.4, 27.3 (*C5* – *C10*, *C13* – *C18*), 22.8 (*C19*), 14.3 (*C20*).

FT-IR (neat): 2925, 2853, 1960, 1718, 1456, 1254, 1148, 1003, 871, 735 cm^{-1}.

HRMS (EI): *m*/*z* 396.3044 ([M]$^+$, $C_{27}H_{40}O_2^+$ calcd. 396.3028).



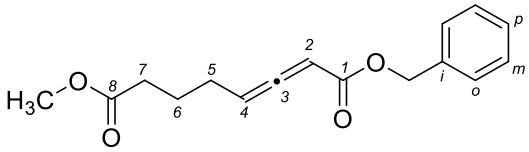
(±)-Benzyl nona-2,3-dien-8-ynoate. The title compound was prepared from hept-6-ynoyl chloride and benzyl 2-(triphenylphosphanylidene)acetate following the same procedure as for (±)-benzyl hepta-2,3-dienoate. The product was purified by column chromatography (silica gel, hexanes:diethyl ether / 10:0→8:2), which furnished a colorless oil (77% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 – 7.29 (m, 5H, -C_6H_5), 5.69 – 5.59 (m, 2H, *H2*, *H4*), 5.20 and 5.16 (*AB*, *J* = 12.7 Hz, 2H, OCH_2Ph), 2.31 – 2.21 (m, 4H, *H5*, *H7*), 1.95 (t, *J* = 2.8 Hz, *H9*), 1.69 (m, 2H, *H6*).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.8 (*C3*), 166.0 (*C1*), 136.1 (C_i), 128.7 (C_m), 128.31 (C_p), 128.29 (C_o), 94.8 (*C4*), 88.6 (*C2*), 83.8 (*C8*), 68.9 (*C9*), 66.7 (OCH_2Ph), 27.5 (*C6*), 26.4 (*C5*), 17.8 (*C7*).

FT-IR (neat): 3294, 2945, 2116, 1959, 1716, 1454, 1418, 1256, 1151, 1002, 873, 797, 737 cm^{-1}.

HRMS (ESI / APCI): *m*/*z* 241.1216 ([M+H]$^+$, $C_{16}H_{17}O_2^+$ calcd. 241.1224).



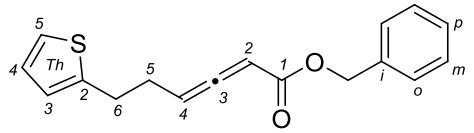
(±)-1-Benzyl 8-methyl octa-2,3-dienedioate. The title compound was prepared from methyl 6-chloro-6-oxohexanoate and benzyl 2-(triphenylphosphanylidene)acetate following the same procedure as for (±)-benzyl hepta-2,3-dienoate. The product was purified by column chromatography (silica gel, hexanes:diethyl ether / 8:2→5:5), which furnished a colorless oil (73% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42 – 7.28 (m, 5H, -C_6H_5), 5.68 – 5.58 (m, 2H, *H2*, *H4*), 5.18 (s, 2H, OCH_2Ph), 3.66 (s, 3H, CH_3O), 2.37 (td, *J* = 7.4, 1.2 Hz, 2H, *H7*), 2.19 (m, 2H, *H5*), 1.80 (m, 2H, *H6*).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.7 (*C3*), 173.8 (*C8*), 166.0 (*C1*), 136.1 (C_i), 128.6 (C_m), 128.29 (C_p), 128.27 (C_o), 94.7 (*C4*), 88.6 (*C2*), 66.7 (OCH_2Ph), 51.7 (CH_3O), 33.1 (*C7*), 26.9 (*C5*), 23.9 (*C6*).

FT-IR (neat): 2951, 1960, 1731, 1437, 1420, 1371, 1246, 1151, 1003, 878, 737 cm^{-1}.

HRMS (ESI / APCI): *m*/*z* 275.1269 ([M+H]$^+$, $C_{16}H_{19}O_4^+$ calcd. 275.1278).



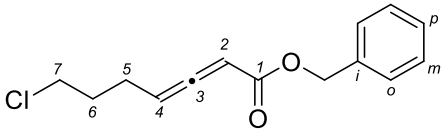
(±)-Benzyl 6-(thiophen-2-yl)hexa-2,3-dienoate. The title compound was prepared from 4-(thiophen-2-yl)butanoyl chloride and benzyl 2-(triphenylphosphanylidene)acetate following the same procedure as for (±)-benzyl hepta-2,3-dienoate. The product was purified by column chromatography (silica gel, hexanes:diethyl ether / 100:0→85:15), which furnished a colorless oil (60% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 – 7.28 (m, 5H, -C_6H_5), 7.13 (dd, J = 5.1, 1.2 Hz, 1H, $H5^{Th}$), 6.92 (dd, J = 5.1, 3.4 Hz, 1H, $H4^{Th}$), 6.81 (dq, J = 3.4, 1.2 Hz, 1H, $H3^{Th}$), 5.76 – 5.63 (m, 2H, *H2*, *H4*), 5.19 (s, 2H, OCH_2Ph), 2.99 (m, 2H, *H6*), 2.52 (m, 2H, *H5*).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.7 (*C3*), 166.0 (*C1*), 143.6 ($C2^{Th}$), 136.1 (C_i), 128.7 (C_m), 128.3 (C_p), 128.2 (C_o), 126.9 ($C4^{Th}$), 124.8 ($C3^{Th}$), 123.5 ($C5^{Th}$), 94.6 (*C4*), 88.9 (*C2*), 66.6 (OCH_2Ph), 29.5 (*C5*), 29.2 (*C6*).

FT-IR (neat): 3066, 3031, 2945, 1960, 1718, 1437, 1419, 1254, 1150, 1002, 870, 850, 825, 798, 764 cm^{-1}.

HRMS (ESI/APCI): *m*/*z* 285.0941 ([M+H]$^+$, $C_{17}H_{17}O_2S^+$ calcd. 285.0944).



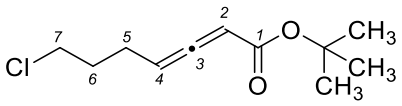
(±)-Benzyl 7-chlorohepta-2,3-dienoate. The title compound was prepared from 5-chloropentanoyl chloride and benzyl 2-(triphenylphosphanylidene)acetate following the same procedure as for (±)-benzyl hepta-2,3-dienoate. The product was purified by column chromatography (silica gel, hexanes:diethyl ether/10:0→8:2), which furnished a colorless oil (96% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 – 7.29 (m, 5H, -C_6H_5), 5.71 – 5.60 (m, 2H, *H2*, *H4*), 5.20 and 5.17 (*AB*, J = 12.4 Hz, 2H, OCH_2Ph), 3.57 (t, J = 6.5 Hz, 2H, *H7*), 2.31 (m, 2H, *H5*), 1.93 (m, 2H, *H6*).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.7 (*C3*), 165.9 (*C1*), 136.0 (C_i), 128.7 (C_m), 128.4 (C_p), 128.3 (C_o), 94.2 (*C4*), 88.9 (*C2*), 66.8 (OCH_2Ph), 43.9 (*C7*), 31.3 (*C6*), 24.6 (*C5*).

FT-IR (neat): 3033, 2957, 1961, 1713, 1498, 1456, 1418, 1374, 1256, 1150, 1003, 848, 798, 736 cm^{-1}.

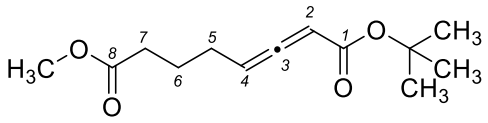
HRMS (FAB): *m*/*z* 251.0843 ([M+H]$^+$, $C_{14}H_{16}ClO_2^+$ calcd. 251.0839).



(±)-*Tert*-butyl 7-chlorohepta-2,3-dienoate.[5] The title compound was prepared from 5-chloropentanoyl chloride and *tert*-butyl 2-(triphenylphosphanylidene)acetate following the same procedure as for (±)-benzyl hepta-2,3-dienoate. The product was purified by column chromatography (silica gel, hexanes:diethyl ether/97:3→80:20), which furnished a colorless oil (73% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.59 – 5.50 (m, 2H, *H2*, *H4*), 3.62 (t, J = 6.6 Hz, 2H, *H7*), 2.33 – 2.27 (m, 2H, *H5*), 2.00 – 1.88 (m, 2H, *H6*).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 212.0 (*C3*), 165.4 (*C1*), 93.6 (*C4*), 90.6 (*C2*), 81.1 ($C(CH_3)_3$), 44.0 (*C7*), 31.4 (*C6*), 28.2 ($C(CH_3)_3$), 24.6 (*C5*).



(±)-1-(*Tert*-butyl) 8-methyl octa-2,3-dienedioate. The title compound was prepared from methyl 6-chloro-6-oxohexanoate and *tert*-butyl 2-(triphenylphosphanylidene)acetate following the same procedure as for (±)-benzyl hepta-2,3-dienoate. The product was purified by column chromatography (silica gel, hexanes:ethyl acetate/95:5→85:15), which furnished a colorless oil (53% yield).

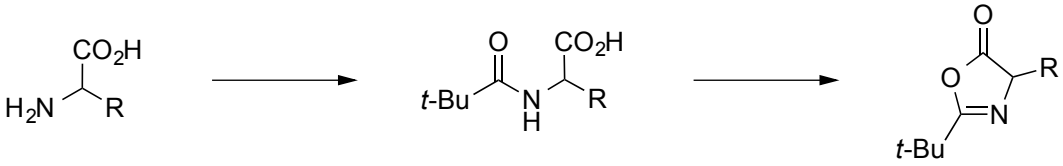
^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.58 – 5.48 (m, 2H, *H2*, *H4*), 3.66 (s, 3H, CH_3O), 2.40 (t, *J* = 7.6 Hz, 2H, *H7*), 2.17 (m, 2H, *H5*), 1.80 (m, 2H, *H6*), 1.47 (s, 9H, C(CH_3)$_3$).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.0 (*C3*), 173.9 (*C8*), 165.5 (*C1*), 94.2 (*C4*), 90.4 (*C2*), 81.0 (*C*(CH$_3$)$_3$), 51.7 (*C*H$_3$O), 33.1 (*C7*), 28.2 (C(*C*H$_3$)$_3$), 27.0 (*C5*), 24.0 (*C6*).

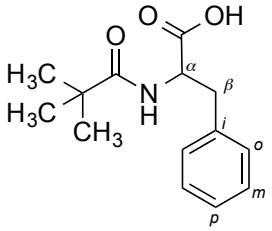
FT-IR (neat): 2978, 2952, 1960, 1738, 1705, 1368, 1281, 1256, 1146, 961, 879, 853, 802 cm^{-1}.

HRMS (FAB): *m*/*z* 241.1434 ([M+H]$^+$, $C_{13}H_{21}O_4^+$ calcd. 241.1435).

Synthesis of 1,3-oxazol-5(4*H*)-ones



When an enantiopure amino acid was used as the starting material, the resulting 1,3-oxazol-5(4*H*)-one was produced as a racemate or underwent complete racemization upon storage at –20 °C within days to weeks.

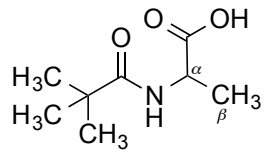


(±)-Pivaloylphenylalanine. A solution of NaOH (2.00 g, 50 mmol) in water (50 mL) was cooled to 0 °C in an ice bath. (±)-Phenylalanine (3.30 g, 20 mmol) was added, and the mixture was stirred until it became homogeneous. A solution of trimethylacetyl chloride (2.71 mL, 2.65 g, 22 mmol) in 1,4-dioxane (20 mL) was added dropwise, and the reaction mixture was stirred at r.t. for 16 h. The reaction mixture was then extracted with diethyl ether (3 × 25 mL), and the organic layers were discarded. The aqueous layer was cooled to 0 °C in an ice bath, and then it was acidified to pH = 2 (measured with pH paper) by the dropwise addition of aqueous HCl (1 M) with stirring. The resulting heterogeneous mixture was extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over anhydrous Mg_2SO_4 and then filtered. The solvent was removed under reduced pressure, and then the residue was dried under high

vacuum to afford the product as a white solid (containing a trace of pivalic acid), which was used in the next step without further purification (4.74 g, 95% yield).[6]

^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.24 (b, 1H, CO_2H), 7.35 – 7.21 (m, 3H, H_m, H_p), 7.19 – 7.12 (m, 2H, H_o), 6.09 (d, J = 7.3 Hz, 1H, NH), 4.85 (dt, J = 7.3, 6.0 Hz, 1H, $H\alpha$), 3.26 (dd, J = 14.0, 5.6 Hz, 1H, $H\beta$), 3.14 (dd, J = 14.0, 6.2 Hz, 1H, $H\beta'$), 1.13 (s, 9H, (CH_3)$_3$C).

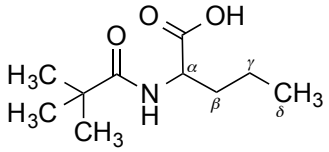
^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.1 (*C*ONH), 175.4 (CO_2H), 135.8 (C_i), 129.5 (C_o), 128.8 (C_m), 127.4 (C_p), 53.2 (Cα), 38.9 ((CH$_3$)$_3$*C*), 37.2 (Cβ), 27.4 ((*C*H$_3$)$_3$C).



(±)-Pivaloylalanine.[7] The title compound was prepared from (±)-alanine following the same procedure as for (±)-pivaloylphenylalanine. The product was obtained as a white solid (65% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.82 (b, 1H, CO_2H), 6.25 (d, J = 7.1 Hz, 1H, NH), 4.55 (quintet, J = 7.1 Hz, 1H, $H\alpha$), 1.46 (d, J = 7.2 Hz, 2H, $H\beta$), 1.22 (s, 9H, (CH_3)$_3$C).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.3 (*C*ONH), 176.7 (CO_2H), 48.4 ($C\alpha$), 38.8 ((CH$_3$)$_3$*C*), 27.5 ((*C*H$_3$)$_3$C), 18.1 ($C\beta$).



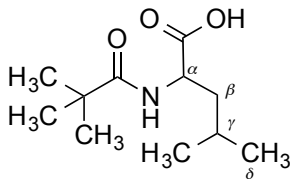
(±)-2-Pivalamidopentanoic acid. The title compound was prepared from (±)-norvaline following the same procedure as for (±)-pivaloylphenylalanine. The product was obtained as a white solid (99% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.12 (b, 1H, CO_2H), 6.14 (d, J = 7.0 Hz, 1H, NH), 4.57 (m, 1H, $H\alpha$), 1.89 (m, 1H, $H\beta$), 1.70 (m, 1H, $H\beta'$), 1.38 (m, 2H, $H\gamma$), 1.22 (s, 9H, (CH_3)$_3$C), 0.95 (t, J = 7.3 Hz, 3H, $H\delta$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.2 (*C*ONH), 176.8 (CO_2H), 52.4 ($C\alpha$), 38.9 ((CH$_3$)$_3$*C*), 34.2 ($C\beta$), 27.5 ((*C*H$_3$)$_3$C), 18.7 ($C\gamma$), 13.8 ($C\delta$).

FT-IR (neat): 3352, 2963, 1730, 1628, 1529, 1201 cm^{-1}.

HRMS (ESI / APCI): m/z 200.1295 ([M–H]$^-$, $C_{10}H_{18}NO_3^-$ calcd. 200.1292).



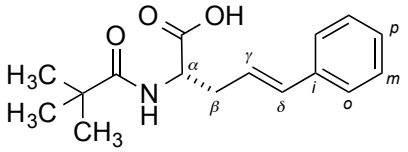
(±)-Pivaloylleucine. The title compound was prepared from (±)-leucine following the same procedure as for (±)-pivaloylphenylalanine. The product was obtained as a white solid (91% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.99 (d, J = 7.6 Hz, 1H, N*H*), 4.57 (m, 1H, *Hα*), 1.82 – 1.55 (m, 3H, *Hβ*, *Hβ′*, *Hγ*), 1.23 (s, 9H, (CH_3)$_3$C), 0.96 (t, J = 6.7 Hz, 6H, *Hδ*).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.5 (*C*ONH), 176.6 (*C*O$_2$H), 51.1 (*Cα*), 41.0 (*Cβ*), 38.9 ((CH$_3$)$_3$*C*), 27.5 ((*C*H$_3$)$_3$C), 25.1 (*Cγ*), 23.0, 22.1 (*Cδ*, *Cδ′*).

FT-IR (neat): 3378, 2959, 2871, 1725, 1624, 1540, 1369, 1267, 1203, 1149, 935 cm^{-1}.

HRMS (ESI/APCI): *m*/*z* 214.1452 ([M–H]$^-$, $C_{11}H_{20}NO_3^-$ calcd. 214.1448).



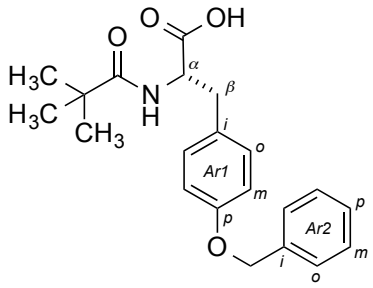
(*S*,*E*)-5-Phenyl-2-pivalamidopent-4-enoic acid. The title compound was prepared from (*S*,*E*)-2-amino-5-phenylpent-4-enoic acid (*L*-styrylalanine) following the same procedure as for (±)-pivaloylphenylalanine. The product was obtained as a white solid (81% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.36 – 7.22 (m, 5H, -C$_6$*H*$_5$), 6.49 (d, J = 15.8 Hz, 1H, *Hδ*), 6.23 (d, 1H, J = 7.3 Hz, N*H*), 6.10 (dt, J = 15.8, 7.5 Hz, 1H, *Hγ*), 4.69 (m, 1H, *Hα*), 2.83 (m, 1H, *Hβ*), 2.75 (m, 1H, *Hβ′*), 1.19 (s, 9H, (C*H*$_3$)$_3$C).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.5 (*C*ONH), 174.9 (*C*O$_2$H), 136.8 (C_i), 134.8 (*Cδ*), 128.8 (C_m), 127.8 (C_p), 126.4 (C_o), 123.6 (*Cγ*), 52.0 (*Cα*), 38.9 ((CH$_3$)$_3$*C*), 35.2 (*Cβ*), 27.5 ((*C*H$_3$)$_3$C).

FT-IR (neat): 3350, 2965, 1727, 1620, 1517, 1203, 966, 740 cm^{-1}.

HRMS (ESI/APCI): *m*/*z* 274.1451 ([M–H]$^-$, $C_{16}H_{20}NO_3^-$ calcd. 274.1448).



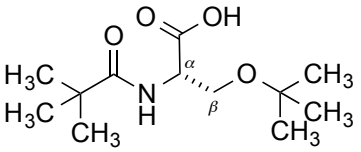
(*S*)-3-(4-(Benzyloxy)phenyl)-2-pivalamidopropanoic acid. The title compound was prepared from (*S*)-*N*-benzyltyrosine following the same procedure as for (±)-pivaloylphenylalanine. The product was obtained as a white solid (37% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42 (m, 2H, H_o^{Ar2}), 7.38 (m, 2H, H_m^{Ar2}), 7.32 (m, 1H, H_p^{Ar2}), 7.07 (m, 2H, H_o^{Ar1}), 6.91 (m, 2H, H_m^{Ar1}), 6.01 (d, J = 7.3 Hz, 1H, N*H*), 5.04 (s, 2H, OCH_2Ph), 4.81 (dt, J = 7.3, 5.8 Hz 1H, *Hα*), 3.19 (dd, J = 14.2, 5.8 Hz, 1H, *Hβ*), 3.10 (dd, J = 14.2, 5.8 Hz, 1H, *Hβ′*), 1.14 (s, 9H, (CH_3)$_3$C).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 178.9 (*C*ONH), 176.5 (*C*O_2H), 158.1 (C_p^{Ar1}), 137.0 (C_i^{Ar2}), 130.6 (C_o^{Ar1}), 129.2 (C_i^{Ar1}), 128.7 (C_m^{Ar2}), 128.1 (C_p^{Ar2}), 127.6 (C_o^{Ar2}), 115.2 (C_m^{Ar1}), 70.2 (OCH_2Ph), 53.3 (*Cα*), 38.9 ((CH_3)$_3$*C*), 36.4 (*Cβ*), 27.5 ((*C*H_3)$_3$C).

FT-IR (neat): 2965, 1727, 1613, 1512, 1242, 1026, 834, 734 cm^{-1}.

HRMS (ESI/APCI): *m*/*z* 354.1714 ([M–H]$^-$, $C_{21}H_{24}NO_4^-$ calcd. 354.1710).



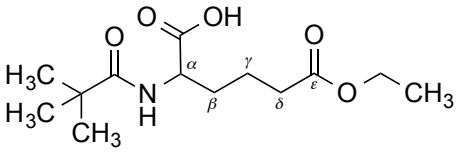
(*S*)-*O*-(*tert*-Butyl)-*N*-pivaloylserine. The title compound was prepared from (*S*)-O-(*tert*-butyl)-serine (*L*-O-(*tert*-butyl)-serine) following the same procedure as for (±)-pivaloylphenylalanine. The product was obtained as a white solid (91% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.53 (d, J = 7.1 Hz, 1H, N*H*), 4.61 (ddd, J = 7.1, 5.1, 3.8 Hz, 1H, *Hα*), 3.90 (dd, J = 9.0, 3.8 Hz, 1H, *Hβ*), 3.55 (dd, J = 9.0, 5.1 Hz, 1H, *Hβ′*), 1.23, 1.20 (2×s, 2×9H, (CH_3)$_3$C, (CH_3)$_3$CO).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.4 (*C*ONH), 173.6 (*C*O_2H), 74.6 ((CH_3)$_3$*C*O), 61.2 (*Cβ*), 52.7 (*Cα*), 38.9 ((CH_3)$_3$*C*), 27.51, 27.49 ((*C*H_3)$_3$C, (CH_3)$_3$CO).

FT-IR (neat): 3455, 2973, 1745, 1631, 1520, 1365, 1195, 1100, 940, 883 cm^{-1}.

HRMS (ESI/APCI): *m*/*z* 244.1557 ([M–H]$^-$, $C_{12}H_{22}NO_4^-$ calcd. 244.1554).



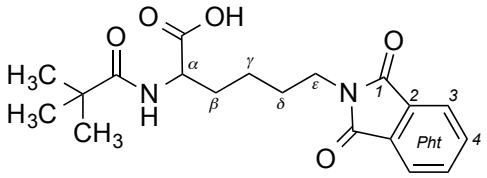
(±)-6-Ethoxy-6-oxo-2-pivalamidohexanoic acid. (±)-2-Amino-6-ethoxy-6-oxohexanoic acid[8] (1.89 g, 10 mmol) and triethylamine (4.99 mL, 3.64 g, 36 mmol) were dissolved in a mixture of water (25 mL) and 1,4-dioxane (25 mL). The solution was cooled to 0 °C in an ice bath, and a solution of trimethylacetyl chloride (1.35 mL, 1.33 g, 11 mmol) in 1,4-dioxane (13 mL) was added dropwise. The reaction mixture was stirred at r.t. for 1 h. Next, the 1,4-dioxane was removed under reduced pressure, and the aqueous residue was cooled to 0 °C in an ice bath. The mixture was acidified to pH = 2 (measured with pH paper) by the dropwise addition of aqueous HCl (1 M) with stirring. The resulting heterogeneous mixture was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over anhydrous Mg_2SO_4 and then filtered. The solvent was removed under reduced pressure, and then the residue was dried under high vacuum to afford the product as a white solid (containing a trace of pivalic acid), which was used in the next step without further purification (2.70 g, 99% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.07 (b, 1H, CO_2H), 6.43 (d, J = 7.1 Hz, 1H, N*H*), 4.53 (dt, J = 7.1, 5.1 Hz, 1H, *Hα*), 4.13 (q, J = 7.1 Hz, 2H, CH_3CH_2O), 2.36 (td, J = 7.1, 2.8 Hz, 2H, *Hδ*), 1.95 (m, 1H, *Hβ*), 1.76 (m, 1H, *Hβ′*), 1.69 (m, 2H, *Hγ*), 1.25 (t, J = 7.1 Hz, 3H, CH_3CH_2O), 1.23 (s, 9H, $(CH_3)_3C$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.8 (*C*ONH), 175.8 (*Cε*), 173.8 (CO_2H), 60.9 (CH_3CH_2O), 52.4 (*Cα*), 39.0 ($(CH_3)_3C$), 33.7 (*Cδ*), 31.2 (*Cβ*), 27.6 ($(CH_3)_3C$), 20.6 (*Cγ*), 14.4 (CH_3CH_2O).

FT-IR (neat): 3355, 2967, 1733, 1627, 1531, 1367, 1198, 1030 cm^{-1}.

HRMS (ESI/APCI): *m*/*z* 272.1506 ([M–H]$^-$, $C_{13}H_{22}NO_5^-$ calcd. 272.1503).



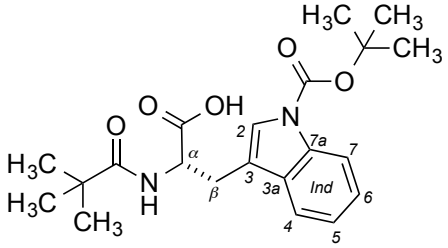
(*S*)-6-(1,3-Dioxoisoindolin-2-yl)-2-pivalamidohexanoic acid. The title compound was prepared from (*S*)-1-carboxy-5-(1,3-dioxoisoindolin-2-yl)pentan-1-aminium chloride (*L*-N^{ε}-phtaloyllysine hydrochloride)[9] following the same procedure as for (±)-6-ethoxy-6-oxo-2-pivalamidohexanoic acid. The product was obtained as a white solid (97% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.81 (m, 2H, $H3^{Pht}$), 7.70 (m, 2H, $H4^{Pht}$), 6.33 (d, J = 7.5 Hz, 1H, N*H*), 4.51 (m, 1H, *Hα*), 3.68 (t, J = 7.1 Hz, 2H, *Hε*), 1.96 (m, 1H, *Hβ*), 1.83 (m, 1H, *Hβ′*), 1.71 (m, 2H, *Hδ*), 1.40 (m, 2H, *Hγ*), 1.19 (s, 9H, $(CH_3)_3C$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.5 (*C*ONH), 175.8 (CO_2H), 168.7 ($C1^{Pht}$), 134.1 ($C4^{Pht}$), 132.1 ($C2^{Pht}$), 123.4 ($C3^{Pht}$), 52.4 (*Cα*), 38.8 ($(CH_3)_3C$), 37.3 (*Cε*), 31.1 (*Cβ*), 28.2 (*Cδ*), 27.5 ($(CH_3)_3C$), 22.6 (*Cγ*).

FT-IR (neat): 3398, 2959, 1712, 1624, 1526, 1398, 1368, 1189, 1045, 720 cm^{-1}.

HRMS (ESI/APCI): *m*/*z* 359.1616 ([M–H]$^-$, $C_{19}H_{23}N_2O_5^-$ calcd. 359.1612).



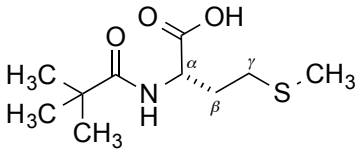
1-(*tert*-Butoxycarbonyl)-N^{α}-pivaloyl-*L*-tryptophan. The title compound was prepared from 1-(*tert*-butoxycarbonyl)-*L*-tryptophan following the same procedure as for (±)-6-ethoxy-6-oxo-2-pivalamidohexanoic acid. The product was obtained as a white solid (97% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (d, J = 7.8 Hz, 1H, $H7^{Ind}$), 7.55 (d, J = 7.7 Hz, 1H, $H4^{Ind}$), 7.42 (s, 1H, $H2^{Ind}$), 7.31 (t, J = 7.8 Hz, 1H, $H6^{Ind}$), 7.21 (t, J = 7.7 Hz, 1H, $H5^{Ind}$), 6.23 (d, J = 7.0 Hz, 1H, N*H*), 4.86 dt, J = 7.0, 5.6 Hz, *Hα*), 3.36 (dd, J = 15.1, 5.6 Hz, 1H, *Hβ*), 3.29 (dd, J = 15.1, 5.6 Hz, 1H, *Hβ′*), 1.65 (s, 9H, $(CH_3)_3CO$), 1.13 (9H, s, $(CH_3)_3C$).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.2 (*C*ONH), 174.4 (*C*O_2H), 149.7 (O(*C*=O)N), 135.4 (*C7a*^{Ind}), 130.7 (*C3a*^{Ind}), 124.8 (*C2*^{Ind}), 124.4 (*C6*^{Ind}), 122.8 (*C5*^{Ind}), 119.1 (*C4*^{Ind}), 115.4 (*C7*^{Ind}), 115.1 (*C3*^{Ind}), 83.9 ((CH$_3$)$_3$*C*O), 52.7 (*Cα*), 38.9 ((CH$_3$)$_3$*C*), 28.3 ((*C*H$_3$)$_3$CO), 27.4 ((*C*H$_3$)$_3$C), 26.7 (*Cβ*).

FT-IR (neat): 3345, 2974, 1734, 1642, 1522, 1453, 1371, 1257, 1159, 1086, 768, 747 cm^{-1}.

HRMS (ESI/APCI): *m*/*z* 387.1929 ([M–H]$^-$, $C_{21}H_{27}N_2O_5^-$ calcd. 387.1925).



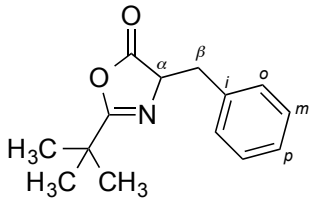
(±)-Pivaloylmethionine. The title compound was prepared from (±)-methionine following the same procedure as for (±)-pivaloylphenylalanine. The product was obtained as a white solid (97% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.62 (d, *J* = 7.1 Hz, 1H, N*H*), 4.66 (td, *J* = 7.1, 5.1, 1H, *Hα*), 2.59 (m, 2H, *Hγ*), 2.23 (m, 1H, *Hβ*), 2.12 (s, 3H, SC*H*$_3$), 2.09 (m, 1H, *Hβ′*), 1.23 (s, 9H, (C*H*$_3$)$_3$C).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.8 (*C*ONH), 175.0 (*C*O_2H), 52.3 (*Cα*), 38.9 ((CH$_3$)$_3$*C*), 30.5 (*Cβ*), 30.2 (*Cγ*), 27.5 ((*C*H$_3$)$_3$C), 15.6 (SCH$_3$).

FT-IR (neat): 3345, 2966, 2913, 1730, 1631, 1526, 1437, 1202 cm^{-1}.

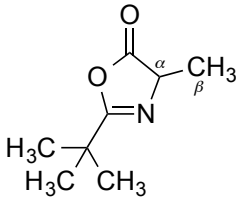
HRMS (ESI/APCI): *m*/*z* 232.1015 ([M–H]$^-$, $C_{10}H_{18}NO_3S^-$ calcd. 232.1012).



(±)-4-Benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one.[10] A solution of (±)-pivaloylphenylalanine (1.25 g, 5.0 mmol) in dichloromethane (anhydrous, 50 mL) was cooled to 0 °C in an ice bath under an atmosphere of nitrogen. EDC·HCl (1.05 g, 5.5 mmol) was added in one portion, and the reaction mixture was stirred at 0° C for 1 h. Next, the reaction mixture was diluted with dichloromethane (50 mL), and this solution was washed successively with water (50 mL), aqueous $NaHCO_3$ (saturated, 50 mL), water (50 mL), and aqueous NaCl (saturated, 50 mL). The organic layer was dried over anhydrous Mg_2SO_4 and filtered, and then the solvent was removed under reduced pressure. The residue was concentrated under high vacuum to afford the product as a colorless oil, suitable for the use in the phosphine-catalyzed γ-addition without further purification (1.10 g, 95% yield).[11]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.28 – 7.14 (m, 5H, -C$_6$*H*$_5$), 4.47 (t, *J* = 5.0 Hz, 1H, *Hα*), 3.27 (dd, *J* = 13.8, 5.2 Hz, 1H, *Hβ*), 3.18 (dd, *J* = 13.8, 4.7 Hz, 1H, *Hβ′*), 1.05 (s, 9H, (C*H*$_3$)$_3$C).

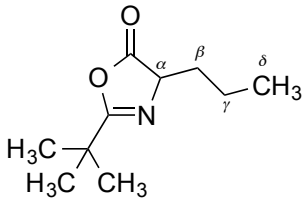
^{13}C NMR ($CDCl_3$, 125 MHz): δ 178.5 (*C*=O), 172.1 (*C*=N), 134.6 (*C*$_i$), 130.1 (*C*$_o$), 128.3 (*C*$_m$), 127.4 (*C*$_p$), 65.7 (*Cα*), 36.9 (*Cβ*), 34.1 ((CH$_3$)$_3$*C*), 26.5 ((*C*H$_3$)$_3$C).



(±)-2-(*tert*-Butyl)-4-methyloxazol-5(4*H*)-one.[12] The title compound was prepared from (±)-pivaloylalanine following the same procedure as for (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one. The product was obtained as a colorless oil (78% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): 4.20 (q, J = 7.6 Hz, 1H, *Hα*), 1.46 (d, J = 7.8 Hz, 2H, *Hβ*), 1.28 (s, 9H, $(CH_3)_3C$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.9 (*C*=O), 171.8 (*C*=N), 60.7 (*Cα*), 34.2 ($(CH_3)_3C$), 26.9 ($(CH_3)_3C$), 17.0 (*Cβ*).



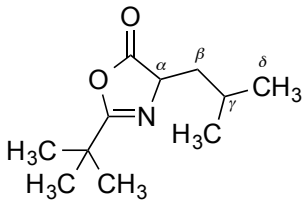
(±)-2-(*tert*-Butyl)-4-propyloxazol-5(4*H*)-one. The title compound was prepared from (±)-2-pivalamidopentanoic acid following the same procedure as for (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one. The product was obtained as a colorless oil (88% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): 4.17 (dd, J = 6.6, 5.7 Hz, 1H, *Hα*), 1.87 (m, 1H, *Hβ*), 1.73 (m, 1H, *Hβ′*), 1.38 (m, 2H, *Hγ*), 1.27 (s, 9H, $(CH_3)_3C$), 0.93 (t, J = 7.4 Hz, 3H, *Hδ*).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.4 (*C*=O), 171.8 (*C*=N), 64.8 (*Cα*), 34.3 ($(CH_3)_3C$), 33.2 (*Cβ*), 26.9 ($(CH_3)_3C$), 18.2 (*Cγ*), 13.8 (*Cδ*).

FT-IR (neat): 2965, 2936, 2876, 1824, 1668, 1482, 1464, 1366, 1300, 1272, 1167, 1123, 1089, 1066, 1048, 1022, 893 cm^{-1}.

HRMS (ESI/APCI): *m*/*z* 184.1333 ($[M+H]^+$, $C_{10}H_{18}NO_2^+$ calcd. 184.1333).



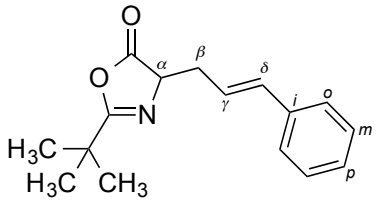
(±)-2-(*tert*-Butyl)-4-isobutyloxazol-5(4*H*)-one. The title compound was prepared from (±)-pivaloylleucine following the same procedure as for (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one. The product was obtained as a colorless oil (84% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): 4.17 (dd, J = 8.0, 6.1 Hz, 1H, *Hα*), 1.95 (m, 1H, *Hγ*), 1.77 (m, 1H, *Hβ*), 1.57 (m, 1H, *Hβ′*), 1.28 (s, 9H, $(CH_3)_3C$), 0.97, 0.95 (2×d, J = 8.8 Hz, 6H, *Hδ*, *Hδ′*).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.9 (*C*=O), 171.5 (*C*=N), 63.6 (*Cα*), 40.6 (*Cβ*), 34.3 ($(CH_3)_3C$), 26.9 ($(CH_3)_3C$), 25.1 (*Cγ*), 22.7, 22.5 (*Cδ*, *Cδ′*).

FT-IR (neat): 2961, 2873, 1824, 1668, 1464, 1367, 1305, 1278, 1167, 1135, 1101, 1064, 1027, 893 cm^{-1}.

HRMS (ESI/APCI): *m*/*z* 198.1488 ($[M+H]^+$, $C_{11}H_{20}NO_2^+$ calcd. 198.1489).



2-(*tert*-Butyl)-4-cinnamyloxazol-5(4*H*)-one. The title compound was prepared from (*S*,*E*)-5-phenyl-2-pivalamidopent-4-enoic acid following the same procedure as for (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one. The product was obtained as a white solid (75% yield). The product underwent racemization upon storage at –20 °C.

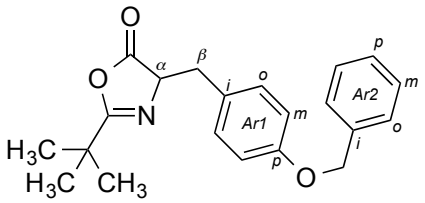
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33 – 7.19 (m, 5H, -C_6H_5), 6.51 (d, *J* = 16.2 Hz, 1H, *Hδ*), 6.05 (dt, *J* = 16.2, 7.5 Hz, 1H, *Hγ*), 4.34 (t, *J* = 5.6 Hz, 1H, *Hα*), 2.86 (m, 1H, *Hβ*), 2.74 (m, 1H, *Hβ′*), 1.25 (s, 9H, $(CH_3)_3C$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 178.6 (*C*=O), 172.3 (*C*=N), 136.8 (C_i), 135.1 (*Cδ*), 128.7 (C_m), 127.7 (C_p), 126.3 (C_o), 122.1 (*Cγ*), 65.1 (*Cα*), 34.34 ($(CH_3)_3C$), 34.30 (*Cβ*), 26.9 ($(CH_3)_3C$).

FT-IR (neat): 2975, 1820, 1667, 1480, 1310, 1268, 1164, 1084, 1069, 1025, 969, 894, 738 cm^{-1}.

HRMS (ESI/APCI): *m*/*z* 258.1491 ($[M+H]^+$, $C_{16}H_{20}NO_2^+$ calcd. 258.1489).

HPLC analysis of the product: CHIRALPAK AD-H column; hexanes:2-propanol/99:1, 1.0 mL/min flow-rate; retention times: 6.7 min, 7.5 min.



4-(4-(Benzyloxy)benzyl)-2-(*tert*-butyl)oxazol-5(4*H*)-one. The title compound was prepared from (*S*)-3-(4-(benzyloxy)phenyl)-2-pivalamidopropanoic acid following the same procedure as for (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one. The product was obtained as a colorless oil (52% yield). The product underwent racemization upon storage at –20 °C.

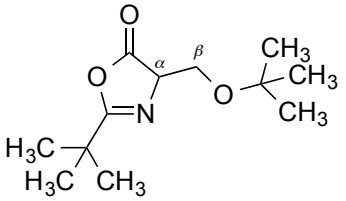
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39 (m, 2H, H_o^{Ar2}), 7.36 (m, 2H, H_m^{Ar2}), 7.31 (m, 1H, H_p^{Ar2}), 7.08 (m, 2H, H_o^{Ar1}), 6.86 (m, 2H, H_m^{Ar1}), 5.03 (s, 2H, OCH_2Ph), 4.43 (t, *J* = 4.9 Hz, 1H, *Hα*), 3.21 (dd, *J* = 14.0, 4.9 Hz, 1H, *Hβ*), 3.12 (dd, *J* = 14.0, 4.9 Hz, 1H, *Hβ′*), 1.06 (s, 9H, $(CH_3)_3C$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 178.7 (*C*=O), 171.9 (*C*=N), 158.1 (C_p^{Ar1}), 137.1 (C_i^{Ar2}), 131.1 (C_o^{Ar1}), 128.7 (C_m^{Ar2}), 128.1 (C_p^{Ar2}), 127.5 (C_o^{Ar2}), 127.0 (C_i^{Ar1}), 114.7 (C_m^{Ar1}), 70.1 (OCH_2Ph), 66.0 (*Cα*), 36.1 (*Cβ*), 34.1 ($(CH_3)_3C$), 26.6 ($(CH_3)_3C$).

FT-IR (neat): 2971, 2876, 1813, 1672, 1609, 1511, 1467, 1382, 1306, 1270, 1239, 1178, 1159, 1094, 1056, 1031, 1005, 893, 831, 758, 727 cm^{-1}.

HRMS (ESI/APCI): *m*/*z* 338.1754 ($[M+H]^+$, $C_{21}H_{24}NO_3^+$ calcd. 338.1751).

HPLC analysis of the product: CHIRALPAK IC column; hexanes:2-propanol/99.5:0.5, 1.0 mL/min flow-rate; retention times: 16.6 min, 17.5 min.



4-(*tert*-Butoxymethyl)-2-(*tert*-butyl)oxazol-5(4*H*)-one. The title compound was prepared from (*S*)-*O*-(*tert*-butyl)-*N*-pivaloylserine following the same procedure as for (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one. The product was obtained as a colorless oil (84% yield). The product underwent racemization upon storage at –20 °C.

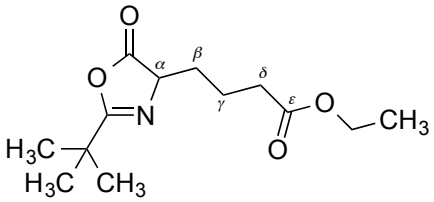
^{1}H NMR ($CDCl_3$, 400 MHz): 4.22 (t, J = 2.9 Hz, 1H, $H\alpha$), 3.77 (d, J = 2.9 Hz, 2H, $H\beta$), 1.28 (s, 9H, $(CH_3)_3C$), 1.11 (s, 9H, $(CH_3)_3CO$).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.0 (C=O), 172.8 (C=N), 73.5 ($(CH_3)_3CO$), 66.3 ($C\alpha$), 60.3 ($C\beta$), 34.3 ($(CH_3)_3C$), 27.4 ($(CH_3)_3CO$), 26.9 ($(CH_3)_3C$).

FT-IR (neat): 2975, 2935, 2873, 1825, 1672, 1482, 1462, 1365, 1311, 1285, 1195, 1093, 1077, 1002, 897 cm^{-1}.

HRMS (ESI/APCI): m/z 228.1595 ($[M+H]^+$, $C_{12}H_{22}NO_3^+$ calcd. 228.1595).

HPLC analysis of the product: CHIRALPAK AD-H column; hexanes:2-propanol/99.7:0.3, 1.0 mL/min flow-rate; retention times: 11.4 min, 13.0 min.



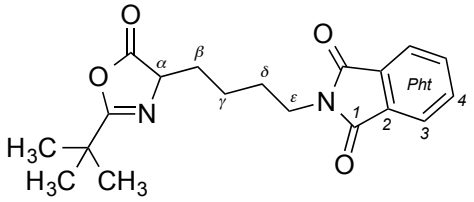
(±)-Ethyl 4-(2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)butanoate. The title compound was prepared from (±)-6-ethoxy-6-oxo-2-pivalamidohexanoic acid following the same procedure as for (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one. The product was obtained as a colorless oil (79% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.17 (t, J = 5.7 Hz, 1H, $H\alpha$), 4.12 (q, J = 7.2 Hz, 2H, CH_3CH_2O), 2.35 (t, J = 7.4 Hz, 2H, $H\delta$), 1.95 (m, 1H, $H\beta$), 1.83 – 1.67 (m, 3H, $H\beta'$, $H\gamma$), 1.28 (s, 9H, $(CH_3)_3C$), 1.25 (t, J = 7.2 Hz, 3H, CH_3CH_2O).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.1 (C=O), 173.0, 172.1 (C=N, $C\varepsilon$), 64.7 ($C\alpha$), 60.6 (CH_3CH_2O), 34.4 ($(CH_3)_3C$), 33.9 ($C\delta$), 30.7 ($C\beta$), 26.9 ($(CH_3)_3C$), 20.7 ($C\gamma$), 14.4 (CH_3CH_2O).

FT-IR (neat): 2977, 1821, 1733, 1668, 1481, 1463, 1369, 1299, 1167, 1089, 1075, 1023, 894 cm^{-1}.

HRMS (ESI/APCI): m/z 256.1546 ($[M+H]^+$, $C_{13}H_{22}NO_4^+$ calcd. 256.1544).



2-(4-(2-(*tert*-Butyl)-5-oxo-4,5-dihydrooxazol-4-yl)butyl)isoindoline-1,3-dione. The title compound was prepared from (*S*)-6-(1,3-dioxoisoindolin-2-yl)-2-pivalamidohexanoic acid following the same procedure as for (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one. The product was obtained as a white solid (84% yield). The product underwent racemization upon storage at –20 °C.

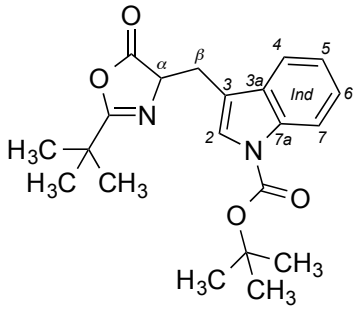
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.83 (m, 2H, $H3^{Pht}$), 7.71 (m, 2H, $H4^{Pht}$), 4.17 (dd, J = 5.9, 6.7 Hz, 1H, $H\alpha$), 3.68 (t, J = 7.3 Hz, 2H, $H\varepsilon$), 1.95 (m, 1H, $H\beta$), 1.81 (m, 1H, $H\beta'$), 1.72 (m, 2H, $H\delta$), 1.43 (m, 2H, $H\gamma$), 1.27 (9H, s, $(CH_3)_3C$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 179.2 (C=O), 172.0 (C=N), 168.5 ($C1^{Pht}$), 134.1 ($C4^{Pht}$), 132.2 ($C2^{Pht}$), 123.3 ($C3^{Pht}$), 64.7 ($C\alpha$), 37.6 ($C\varepsilon$), 34.3 ($(CH_3)_3C$), 30.8 ($C\beta$), 28.3 ($C\delta$), 26.9 ($(CH_3)_3C$), 22.4 ($C\gamma$).

FT-IR (neat): 2974, 2937, 1819, 1772, 1713, 1668, 1466, 1437, 1397, 1367, 1042, 893, 720.

HRMS (ESI/APCI): m/z 343.1645 ($[M+H]^+$, $C_{19}H_{23}N_2O_4^+$ calcd. 343.1653).

HPLC analysis of the product: CHIRALPAK AD-H column; hexanes:2-propanol/90:10, 1.0 mL/min flow-rate; retention times: 10.6 min, 15.4 min.



***tert*-Butyl 3-((2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)methyl)-1*H*-indole-1-carboxylate**. The title compound was prepared from 1-(*tert*-butoxycarbonyl)-N^{α}-pivaloyl-*L*-tryptophan following the same procedure as for (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one. The product was obtained as a white solid (84% yield). The product underwent racemization upon storage at –20 °C.

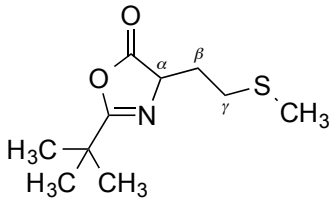
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10 (d, J = 8.1 Hz, 1H, $H7^{Ind}$), 7.60 (d, J = 7.7 Hz, 1H, $H4^{Ind}$), 7.43 (s, 1H, $H2^{Ind}$), 7.29 (m, 1H, $H6^{Ind}$), 7.23 (m, 1H, $H5^{Ind}$), 4.53 (t, J = 5.0, 1H, $H\alpha$), 3.38 (dd, J = 14.4, 5.0 Hz, 1H, $H\beta$), 3.25 (dd, J = 14.4, 5.0 Hz, 1H, $H\beta'$), 1.65 (s, 9H, $(CH_3)_3CO$), 1.01 (9H, s, $(CH_3)_3C$).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.4 (C=O), 172.1 (C=N), 149.5 (O(C=O)N), 135.1 ($C7a^{Ind}$), 130.4 ($C3a^{Ind}$), 124.7 ($C2^{Ind}$), 124.5 ($C6^{Ind}$), 122.4 ($C5^{Ind}$), 119.9 ($C4^{Ind}$), 115.0 ($C7^{Ind}$), 113.8 ($C3^{Ind}$), 83.7 ($(CH_3)_3CO$), 65.5 ($C\alpha$), 34.0 ($(CH_3)_3C$), 28.2 ($(CH_3)_3CO$), 26.3 ($(CH_3)_3C$, $C\beta$; overlapped).

FT-IR (neat): 2976, 2933, 1818, 1735, 1670, 1453, 1370, 1256, 1159, 1085, 894, 768, 746 cm^{-1}.

HRMS (ESI/APCI): m/z 371.1965 ($[M+H]^+$, $C_{21}H_{27}N_2O_4^+$ calcd. 371.1966).

HPLC analysis of the product: CHIRALPAK AD-H column; hexanes:2-propanol/97:3, 1.0 mL/min flow-rate; retention times: 9.2 min, 10.4 min.



(±)-2-(*tert*-Butyl)-4-(2-(methylthio)ethyl)oxazol-5(4*H*)-one. The title compound was prepared from (±)-pivaloylmethionine following the same procedure as for (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one. The product was obtained as a colorless oil (84% yield).

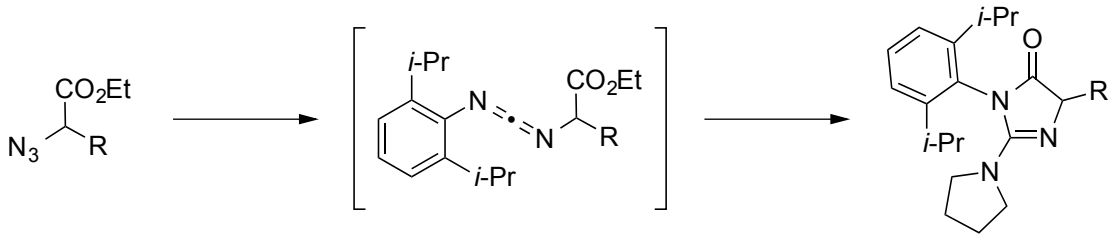
^{1}H NMR ($CDCl_3$, 400 MHz): 4.32 (t, J = 6.9 Hz, 1H, $H\alpha$), 2.63 (t, J = 7.1 Hz, 2H, $H\gamma$), 2.20 (m, 1H, $H\beta$), 2.09 (s, 3H, SCH_3), 2.07 (m, 1H, $H\beta'$), 1.29 (s, 9H, $(CH_3)_3C$).

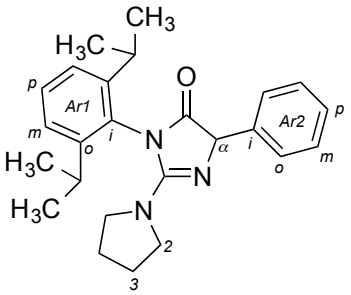
^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.4 (C=O), 172.4 (C=N), 73.5 ($(CH_3)_3CO$), 66.3 ($C\alpha$), 34.4 ($(CH_3)_3C$), 30.0 ($C\beta$), 29.9 ($C\gamma$), 26.9 ($(CH_3)_3C$), 15.2 (SCH_3).

FT-IR (neat): 2974, 2918, 2873, 1818, 1663, 1458, 1297, 1255, 1161, 1102, 1070, 1044, 894 cm^{-1}.

HRMS (ESI/APCI): m/z 216.1048 ($[M+H]^+$, $C_{10}H_{18}NO_2S^+$ calcd. 216.1053).

Synthesis of 3,5-dihydro-4*H*-imidazol-4-ones





(±)-3-(2,6-Diisopropylphenyl)-5-phenyl-2-(pyrrolidin-1-yl)-3,5-dihydro-4*H*-imidazol-4-one. A solution of PPh_3 (2.62 g, 10 mmol) in dichloromethane (anhydrous, 10 mL) was added to a solution of (±)-ethyl 2-azido-2-phenylacetate[13] (2.05 g, 10 mmol) in dichloromethane (anhydrous, 30 mL) under an atmosphere of nitrogen; evolution of gas started shortly after the addition. The reaction mixture was stirred at r.t. for 16 h. Next, 2,6-diisopropylphenyl isocyanate was added via syringe, and the resulting mixture was stirred at r.t. for 2 h. The

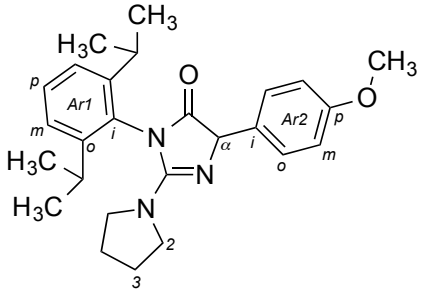
solvent was then removed under reduced pressure, and the residue was dissolved in THF (anhydrous, 40 mL) under an atmosphere of nitrogen. Pyrrolidine (1.00 mL, 0.85 g, 12 mmol) was added via syringe, and the reaction mixture was stirred at r.t. for 24 h. The solvent was then removed under reduced pressure, and the residue was purified by chromatography (silica gel, hexanes:diethyl ether / 5:5→2:8). The product was further purified by recrystallization from hexanes, which furnished a white crystalline solid (2.22 g, 57%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 – 7.16 (m, 8H, -$C_6H_3^{Ar1}$, -$C_6H_5^{Ar2}$), 5.30 (s, 1H, *Hα*), 3.26 – 3.05 (m, 4H, *H2*), 2.98, 2.78 (2×sep, *J* = 7.0 Hz, 2H, C*H*(CH_3)$_2$), 1.81 – 1.71 (m, 4H, *H3*), 1.23 (d, *J* = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.20, 0.87 (2×d, *J* = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 181.5 (*C*=O), 156.4 (*C*=N), 147.5, 147.0 (C_o^{Ar1}), 137.9 (C_i^{Ar2}), 130.5 (C_i^{Ar1}), 130.2 (C_p^{Ar1}), 128.6 (C_m^{Ar2}), 127.7 (C_p^{Ar2}), 127.1 (C_o^{Ar2}), 124.3, 124.1 (C_m^{Ar1}), 69.9 (*Cα*), 47.9 (*C2*), 29.0, 28.9 (*C*H(CH_3)$_2$)), 25.4 (*C3*), 25.0, 24.6, 23.1, 22.8 (CH(*C*H$_3$)$_2$).

FT-IR (neat): 2963, 2869, 1741, 1615, 1449, 1428, 1349, 1184, 1156, 909, 809, 733 cm^{-1}.

HRMS (ESI / APCI): *m*/*z* 390.2544 ([M+H]$^+$, $C_{25}H_{32}N_3O^+$ calcd. 390.2540).



(±)-3-(2,6-Diisopropylphenyl)-5-(4-methoxyphenyl)-2-(pyrrolidin-1-yl)-3,5-dihydro-4*H*-imidazol-4-one. The title compound was prepared from (±)-ethyl 2-azido-2-(4-methoxyphenyl)acetate[14] following the same procedure as for (±)-3-(2,6-diisopropylphenyl)-5-phenyl-2-(pyrrolidin-1-yl)-3,5-dihydro-4*H*-imidazol-4-one. The product was purified by column chromatography (silica gel, hexanes:diethyl ether / 4:6→0:10), followed by recrystallization from hexanes, and was obtained as a white crystalline solid (62% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 – 7.35 (m, 3H, H_p^{Ar1}, H_o^{Ar2}), 7.23, 7.18 (2×d, *J* = 7.7 Hz, 2H, H_m^{Ar1}), 6.90 (m, 2H, H_m^{Ar2}), 5.25 (s, 1H, *Hα*), 3.80 (s, 3H, OC*H*$_3$), 3.23 – 3.03 (m, 4H, *H2*), 2.96, 2.78 (2×sep, *J* = 6.9 Hz, 2H, C*H*(CH_3)$_2$), 1.83 – 1.68 (m, 4H, *H3*), 1.22 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.20 and 0.91 (2×d, *J* = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$).

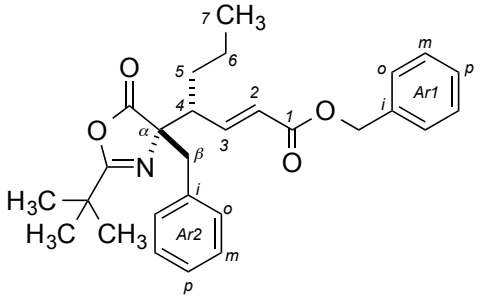
^{13}C NMR ($CDCl_3$, 100 MHz): δ 181.8 (*C*=O), 159.3 (C_p^{Ar2}), 156.3 (*C*=N), 147.4, 147.0 (C_o^{Ar1}), 130.6 (C_i^{Ar1}), 130.2 (C_p^{Ar1}), 130.0 (C_i^{Ar2}), 128.2 (C_o^{Ar2}), 124.3, 124.1 (C_m^{Ar1}), 114.1 (C_m^{Ar2}), 68.7 (*Cα*), 55.4 (OCH_3), 47.9 (*C2*), 29.0, 28.9 (*C*H(CH_3)$_2$)), 25.3 (*C3*), 25.0, 24.7, 23.1, 22.8 (CH(*C*H$_3$)$_2$).

FT-IR (neat): 2963, 2869, 1740, 1616, 1510, 1498, 1425, 1350, 1301, 1247, 1169, 1033, 909, 827, 794, 731 cm^{-1}.

HRMS (ESI / APCI): *m*/*z* 420.2654 ([M+H]$^+$, $C_{26}H_{34}N_3O_2^+$ calcd. 420.2646).

III. γ-Addition of 1,3-Oxazol-5(4*H*)-ones to Allenoates

General Procedure A. An oven-dried 20-mL vial was charged with catalyst **1** (6.8 mg, 0.018 mmol, 5%; or, 13.6 mg, 0.036 mmol, 10%), 2-chloro-6-methylphenol (4.2 μL, 5.0 mg, 0.035 mmol, 10%), and the 1,3-oxazol-5(4*H*)-one (0.35 mmol). The vial was capped with a PTFE-lined septum cap and evacuated/back-filled with nitrogen (3 cycles). Diisopropyl ether (anhydrous; 3.5 mL) was added via syringe, and then the vial was cooled to 0 °C. Next, the allenoate (0.42 mmol, 1.2 equiv) was added via syringe, and then the reaction mixture was stirred at 0 °C for 24 h. To deactivate the catalyst, a solution of *tert*-butyl hydroperoxide (5.0-6.0 M in decane; 50 μL) was added. The resulting mixture was stirred at 0 °C for 10 min, and then it was allowed to warm to r.t. The mixture was concentrated under reduced pressure, and the product was purified by column chromatography.



Benzyl (*R*,*E*)-4-((*S*)-4-benzyl-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)hept-2-enoate (Table 2, entry 1). The title compound was prepared according to General Procedure A from (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one (81 mg, 0.35 mmol) and (±)-benzyl hepta-2,3-dienoate (91 mg, 0.42 mmol), using 5% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 14:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/95:5→90:10), the title compound was isolated as a mixture of diastereomers (colorless oil, 138 mg, 88% yield) in 92% ee (major diastereomer).

HPLC analysis of the product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/98:2, 1.0 mL/min flow-rate; retention times: 6.2 min (minor), 8.4 min (major).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR (major diastereomer, $CDCl_3$, 400 MHz): δ 7.45 – 7.29 (m, 5H, -$C_6H_5^{Ar1}$), 7.26 – 7.13 (m, 3H, H_m^{Ar2}, H_p^{Ar2}), 7.05 (m, 2H, H_o^{Ar2}), 6.94 (dd, *J* = 15.7, 10.5 Hz, 1H, *H3*), 6.04 (d, *J* = 15.7 Hz, 1H, *H2*), 5.24 and 5.20 (*AB*, *J* = 12.2 Hz, 2H, OCH_2Ph), 3.02 (d, *J* = 13.1 Hz, 1H, *Hβ*), 2.93 (d, *J* = 13.1 Hz, 1H, *Hβ'*), 2.70 (td, *J* = 10.5, 2.9 Hz, 1H, *H4*), 1.38 – 1.08 (m, 4H, *H5*, *H6*), 0.96 (s, 9H, $(CH_3)_3C$), 0.85 (t, *J* = 7.1 Hz, 3H, *H7*).

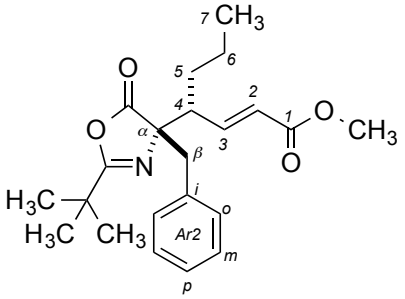
^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 180.2 (*C*=O), 170.2 (*C*=N), 165.8 (*C1*), 147.2 (*C3*), 136.0 (C_i^{Ar1}), 134.3 (C_i^{Ar2}), 130.5 (C_o^{Ar2}), 128.7 (C_m^{Ar1}), 128.5 (C_m^{Ar2}), 128.4 (C_p^{Ar1}), 128.1 (C_o^{Ar1}), 127.3 (C_p^{Ar2}), 125.1 (*C2*), 76.3 (*Cα*), 66.5 (OCH_2Ph), 48.9 (*C4*), 42.2 (*Cβ*), 33.9 ($(CH_3)_3C$), 31.0 (*C5*), 26.5 ($(CH_3)_3C$), 20.5 (*C6*), 13.8 (*C7*).

FT-IR (major diastereomer, neat): 2956, 1953, 1876, 1806, 1721, 1667, 1452, 1264, 1217, 993, 892, 731, 701 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 92% ee): –34.8 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 448.2481 ($[M+H]^+$, $C_{28}H_{34}NO_4^+$ calcd. 448.2483).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 13:1 dr. The product was isolated as a mixture of diastereomers (colorless oil, 144 mg, 92% yield) in 92% ee (major diastereomer).



Methyl (*R*,*E*)-4-((*S*)-4-benzyl-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)hept-2-enoate (Table 2, entry 2). The title compound was prepared according to General Procedure A from (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one (81 mg, 0.35 mmol) and (±)-methyl hepta-2,3-dienoate (59 mg, 0.42 mmol), using 5% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 14:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/95:5→90:10), the title compound was isolated as a mixture of diastereomers (colorless oil, 105 mg, 81% yield) in 92% ee (major diastereomer).

HPLC analysis of the product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/98:2, 1.0 mL/min flow-rate; retention times: 6.9 min (minor), 8.5 min (major).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR (major diastereomer, $CDCl_3$, 500 MHz): δ 7.26 – 7.14 (m, 3H, H_m, H_p), 7.05 (m, 2H, H_o), 6.89 (dd, J = 15.7, 10.5 Hz, 1H, *H3*), 5.99 (d, J = 15.7 Hz, 1H, *H2*), 3.77 (s, 3H, CO_2CH_3), 3.01 (d, J = 13.2 Hz, 1H, *Hβ*), 2.93 (d, J = 13.2 Hz, 1H, *Hβ′*), 2.69 (td, J = 10.5, 2.8 Hz, 1H, *H4*), 1.36 – 1.09 (m, 4H, *H5*, *H6*), 0.97 (s, 9H, $(CH_3)_3C$), 0.85 (t, J = 7.0 Hz, 3H, *H7*).

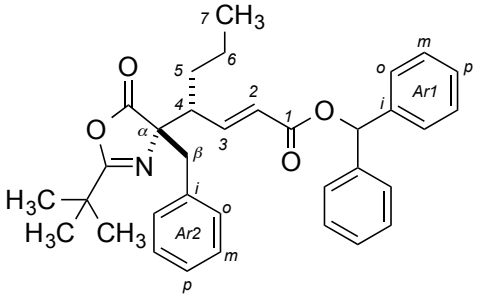
^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 180.2 (*C*=O), 170.3 (*C*=N), 166.4 (*C1*), 146.8 (*C3*), 134.2 (C_i), 130.5 (C_o), 128.1 (C_m), 127.3 (C_p), 125.1 (*C2*), 76.3 (*Cα*), 51.8 (CO_2CH_3), 48.9 (*C4*), 42.2 (*Cβ*), 33.9 ($(CH_3)_3C$), 31.0 (*C5*), 26.5 ($(CH_3)_3C$), 20.4 (*C6*), 13.8 (*C7*).

FT-IR (major diastereomer, neat): 2961, 2873, 1811, 1721, 1669, 1452, 1434, 1346, 1295, 1269, 1223, 1176, 1145, 1106, 1028, 987, 900, 786, 734, 698 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 92% ee): –29.9 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 372.2174 ($[M+H]^+$, $C_{22}H_{30}NO_4^+$ calcd. 372.2170).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 14:1 dr. The product was isolated as a mixture of diastereomers (colorless oil, 104 mg, 80% yield) in 91% ee (major diastereomer).



Benzhydryl (*R*,*E*)-4-((*S*)-4-benzyl-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)hept-2-enoate (Table 2, entry 3). The title compound was prepared according to General Procedure A from (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one (81 mg, 0.35 mmol) and (±)-benzhydryl hepta-2,3-dienoate (123 mg, 0.42 mmol), using 5% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 11:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/9:1), the title compound was isolated as a mixture of diastereomers (white solid, 148 mg, 81% yield) in 89% ee (major diastereomer).

HPLC analysis of the product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/98:2, 1.0 mL/min flow-rate; retention times: 5.8 min (minor), 7.9 min (major).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR (major diastereomer, $CDCl_3$, 500 MHz): δ 7.40 – 7.27 (m, 10H, -$C_6H_5^{Ar1}$), 7.23 – 7.15 (m, 3H, H_m^{Ar2}, H_p^{Ar2}), 7.05 (m, 2H, H_o^{Ar2}), 7.00 – 6.93 (m, 2H, *H3*, OC*H*Ph_2), 6.11 (d, *J* = 15.6 Hz, 1H, *H2*), 3.01 and 2.95 (*AB*, *J* = 13.2 Hz, *Hβ*, *Hβ'*), 2.72 (td, *J* = 10.5, 2.9 Hz, 1H, *H4*), 1.37 – 1.09 (m, 4H, *H5*, *H6*), 0.94 (s, 9H, (CH_3)$_3$C), 0.86 (t, *J* = 7.1 Hz, 3H, *H7*).

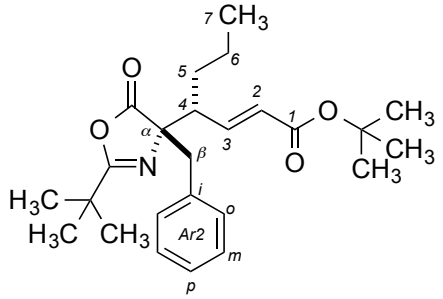
^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 180.2 (*C*=O), 170.2 (*C*=N), 165.0 (*C1*), 147.7 (*C3*), 140.29, 140.28 (C_i^{Ar1}), 134.2 (C_i^{Ar2}), 130.5 (C_o^{Ar2}), 128.69, 128.66 (C_m^{Ar1}, C_m^{Ar2}), 128.11, 128.10 (C_p^{Ar1}), 127.3 (C_o^{Ar1}, C_p^{Ar2}), 125.1 (*C2*), 77.1 (OCHPh$_2$), 76.2 (*Cα*), 49.0 (*C4*), 42.2 (*Cβ*), 33.9 ((CH$_3$)$_3$*C*), 30.9 (*C5*), 26.5 ((*C*H$_3$)$_3$C), 20.5 (*C6*), 13.8 (*C7*).

FT-IR (major diastereomer, neat): 3059, 3028, 2966, 2925, 2868, 1809, 1724, 1664, 1496, 1455, 1364, 1292, 1259, 1217, 1168, 1143, 985, 900, 731, 696 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 88% ee): –32.4 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 524.2793 ([M+H]$^+$, $C_{34}H_{38}NO_4^+$ calcd. 524.2796).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 10:1 dr. The product was isolated as a mixture of diastereomers (white solid, 153 mg, 84% yield) in 89% ee (major diastereomer).



***tert*-Butyl (*R*,*E*)-4-((*S*)-4-benzyl-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)hept-2-enoate** (Table 2, entry 4). The title compound was prepared according to General Procedure A from (±)-

4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one (81 mg, 0.35 mmol) and (±)-*tert*-butyl hepta-2,3-dienoate (77 mg, 0.42 mmol), using 10% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in >20:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/95:5→90:10), the title compound was isolated in 80% ee (colorless oil, 110 mg, 76% yield).

HPLC analysis of the product: CHIRALPAK IC column; hexanes:2-propanol/98:2, 1.0 mL/min flow-rate; retention times: 4.5 min (minor), 5.6 min (major).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24 – 7.16 (m, 3H, H_m, H_p), 7.07 (m, 2H, H_o), 6.77 (dd, *J* = 15.7, 10.5 Hz, 1H, *H3*), 5.89 (d, *J* = 15.6 Hz, 1H, *H2*), 3.03 (d, *J* = 13.2 Hz, 1H, *Hβ*), 2.94 (d, *J* = 13.2 Hz, 1H, *Hβ′*), 2.66 (td, *J* = 10.5, 2.8 Hz, 1H, *H4*), 1.51 (s, 9H, $CO_2C(CH_3)_3$), 1.35 – 1.12 (m, 4H, *H5*, *H6*), 0.97 (s, 9H, $(CH_3)_3C$), 0.86 (t, *J* = 7.0 Hz, 3H, *H7*).

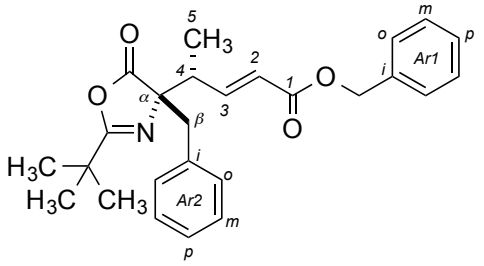
^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.3 (*C*=O), 170.1 (*C*=N), 165.4 (*C1*), 145.2 (*C3*), 134.4 (C_i), 130.5 (C_o), 128.1 (C_m), 127.3, 127.2 (*C2*, C_p), 80.8 ($CO_2C(CH_3)_3$), 76.3 (*Cα*), 48.8 (*C4*), 42.2 (*Cβ*), 33.9 ($(CH_3)_3C$), 31.0 (*C5*), 28.3 ($CO_2C(CH_3)_3$), 26.5 ($(CH_3)_3C$), 20.5 (*C6*), 13.8 (*C7*).

FT-IR (neat): 2975, 2934, 2873, 1815, 1716, 1667, 1456, 1367, 1298, 1231, 1145, 1065, 1029, 990, 896, 733, 700 cm^{-1}.

$[\alpha]^{25}_D$ (80% ee): –20.7 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 414.2639 ($[M+H]^+$, $C_{25}H_{36}NO_4^+$ calcd. 414.2639).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in >20:1 dr. The product was isolated in 83% ee (colorless oil, 104 mg, 72% yield).



Benzyl (*R*,*E*)-4-((*S*)-4-benzyl-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)pent-2-enoate (Table 2, entry 5). The title compound was prepared according to General Procedure A from (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one (81 mg, 0.35 mmol) and (±)-benzyl penta-2,3-dienoate (79 mg, 0.42 mmol), using 5% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in >20:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/93:7→85:15), the title compound was isolated in 97% ee (colorless oil, 142 mg, 97% yield).

HPLC analysis of the product: CHIRALPAK IC column; hexanes:2-propanol/97:3, 1.0 mL/min flow-rate; retention times: 7.9 min (minor), 10.8 min (major).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 – 7.31 (m, 5H, $-C_6H_5^{Ar1}$), 7.24 – 7.17 (m, 3H, H_m^{Ar2}, H_p^{Ar2}), 7.07 (m, 2H, H_o^{Ar2}), 7.04 (dd, *J* = 15.9, 9.6 Hz, 1H, *H3*), 6.04 (d, *J* = 15.9 Hz, 1H, *H2*), 5.22 and 5.19 (*AB*, *J* = 12.5 Hz, 2H, OCH_2Ph), 3.04 and 2.99 (*AB*, *J* = 13.1 Hz, 2H, *Hβ*), 2.89 (dq, *J* = 9.6, 6.8 Hz, 1H, *H4*), 1.03 (d, *J* = 6.8 Hz, 3H, *H5*), 0.97 (s, 9H, $(CH_3)_3C$).

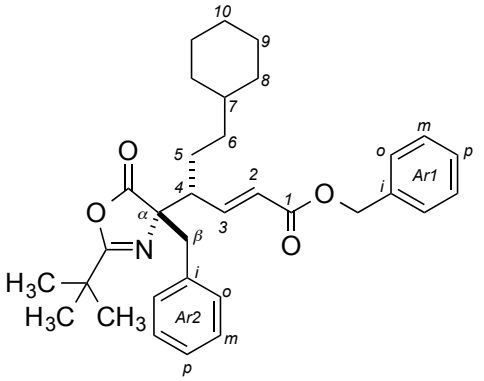
^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.8 (*C*=O), 170.5 (*C*=N), 166.0 (*C1*), 148.1 (*C3*), 136.0 (C_i^{Ar1}), 134.3 (C_i^{Ar2}), 130.5 (C_o^{Ar2}), 128.7 (C_m^{Ar1}), 128.5 (C_m^{Ar2}), 128.4 (C_p^{Ar1}), 128.1 (C_o^{Ar1}), 127.3 (C_p^{Ar2}), 123.7 (*C2*), 76.1 (*Cα*), 66.5 (OCH_2Ph), 43.1 (*C4*), 42.0 (*Cβ*), 33.9 ($(CH_3)_3C$), 26.5 ($(CH_3)_3C$), 14.9 (*C5*).

FT-IR (neat): 2974, 1815, 1721, 1666, 1455, 1378, 1343, 1293, 1261, 1226, 1176, 1149, 982, 896, 732 cm^{-1}.

$[\alpha]^{25}_D$ (97% ee): –19.1 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 420.2168 ([M+H]$^+$, $C_{26}H_{30}NO_4^+$ calcd. 420.2175).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in >20:1 dr. The product was isolated in 94% ee (colorless oil, 134 mg, 91% yield).



Benzyl (*R*,*E*)-4-((*S*)-4-benzyl-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)-6-cyclohexylhex-2-enoate (Table 2, entry 6). The title compound was prepared according to General Procedure A from (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one (81 mg, 0.35 mmol) and (±)-benzyl 6-cyclohexylhexa-2,3-dienoate (119 mg, 0.42 mmol), using 5% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 20:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/95:5→90:10), the title compound was isolated in 90% ee (colorless oil, 153 mg, 85% yield).

HPLC analysis of the product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/99:1, 1.0 mL/min flow-rate; retention times: 5.6 min (minor), 7.4 min (major).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 – 7.30 (m, 5H, -$C_6H_5^{Ar1}$), 7.24 – 7.15 (m, 3H, H_m^{Ar2}, H_p^{Ar2}), 7.05 (m, 2H, H_o^{Ar2}), 6.92 (dd, *J* = 15.7, 10.5 Hz, 1H, *H3*), 6.02 (d, *J* = 15.7 Hz, 1H, *H2*), 5.24 and 5.20 (*AB*, *J* = 12.4 Hz, 2H, OCH_2Ph), 3.01 and 2.93 (*AB*, *J* = 13.5 Hz, 2H, *Hβ*, *Hβ′*), 2.64 (m, 1H, *H4*), 1.76 – 0.71 (m, 24H, *H5* – *H10*, $(CH_3)_3C$).

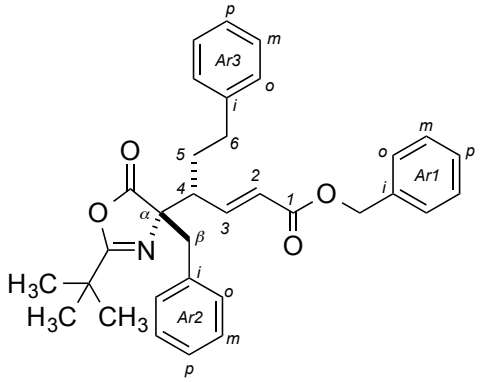
^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.2 (*C*=O), 170.2 (*C*=N), 165.8 (*C1*), 147.4 (*C3*), 136.0 (C_i^{Ar1}), 134.3 (C_i^{Ar2}), 130.5 (C_o^{Ar2}), 128.7 (C_m^{Ar1}), 128.5 (C_m^{Ar2}), 128.4 (C_p^{Ar1}), 128.1 (C_o^{Ar1}), 127.3 (C_p^{Ar2}), 125.1 (*C2*), 76.3 (*Cα*), 66.5 (OCH_2Ph), 49.4 (*C4*), 42.2 (*Cβ*), 37.5, 35.0, 33.9, 33.7, 32.9, 26.7, 26.53, 26.46, 26.4, 26.3 (*C5* – *C10*, $(CH_3)_3C$, $(CH_3)_3C$).

FT-IR (neat): 2923, 2851, 1814, 1724, 1666, 1455, 1301, 1267, 1222, 1162, 1143, 1100, 1067, 986, 896, 733 cm^{-1}.

$[\alpha]^{25}_D$ (90% ee): –30.2 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 516.3104 ([M+H]$^+$, $C_{33}H_{42}NO_4^+$ calcd. 516.3109).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 20:1 dr. The product was isolated in 90% ee (colorless oil, 157 mg, 87% yield).



Benzyl (*R*,*E*)-4-((*S*)-4-benzyl-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)-6-phenylhex-2-enoate (Table 2, entry 7). The title compound was prepared according to General Procedure A from (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one (81 mg, 0.35 mmol) and (±)-benzyl 6-phenylhexa-2,3-dienoate (117 mg, 0.42 mmol), using 5% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 9:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/9:1), the title compound was isolated as a mixture of diastereomers (colorless oil, 169 mg, 95% yield) in 88% ee (major diastereomer).

HPLC analysis of the product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/99:1, 1.0 mL/min flow-rate; retention times: 7.4 min (minor), 9.6 min (major).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR (major diastereomer, $CDCl_3$, 400 MHz): δ 7.45 – 7.02 (m, 15H, 3×-C_6H_5), 6.98 (dd, *J* = 15.6, 10.4 Hz, 1H, *H3*), 6.05 (d, *J* = 15.6 Hz, 1H, *H2*), 5.26 and 5.22 (*AB*, *J* = 12.4 Hz, 2H, OCH_2Ph), 3.00 and 2.93 (*AB*, *J* = 12.9 Hz, 2H, *Hβ*, *Hβ'*), 2.77 – 2.61 (m, 2H, *H4*, *H6*), 2.43 (dt, *J* = 14.1, 8.4 Hz, 1H, *H6'*), 1.66 (m, 2H, *H5*), 0.94 (s, 9H, $(CH_3)_3$C).

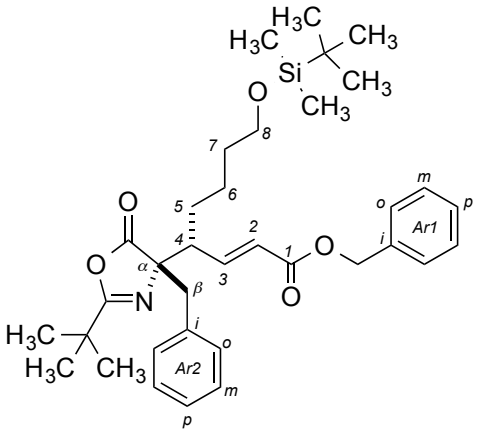
^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 179.9 (*C*=O), 170.4 (*C*=N), 165.7 (*C1*), 146.7 (*C3*), 140.7 (C_i^{Ar3}), 136.0 (C_i^{Ar1}), 134.1 (C_i^{Ar2}), 130.5 (C_o^{Ar2}), 128.8, 128.6, 128.50, 128.44 (C_o^{Ar1}, C_o^{Ar3}, C_m^{Ar1}, C_m^{Ar3}), 128.47 (C_p^{Ar1}), 128.1 (C_m^{Ar2}), 127.3 (C_p^{Ar2}), 126.3 (C_p^{Ar3}), 125.7 (*C2*), 76.1 (*Cα*), 66.6 (OCH_2Ph), 48.5 (*C4*), 42.1 (*Cβ*), 33.9 ($(CH_3)_3C$), 33.3 (*C6*), 30.1 (*C5*), 26.5 ($(CH_3)_3C$).

FT-IR (neat, major diastereomer): 3030, 2981, 2973, 1813, 1721, 1666, 1496, 1455, 1345, 1297, 1266, 1223, 1190, 1149, 1095, 986, 896, 733 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 88% ee): –31.0 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 510.2640 ($[M+H]^+$, $C_{33}H_{36}NO_4^+$ calcd. 510.2639).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 9:1 dr. The product was isolated as a mixture of diastereomers (colorless oil, 169 mg, 95% yield) in 90% ee (major diastereomer).



Benzyl (*R*,*E*)-4-((*S*)-4-benzyl-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)-8-((*tert*-butyldimethylsilyl)oxy)oct-2-enoate (Table 2, entry 8). The title compound was prepared according to General Procedure A from (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one (81 mg, 0.35 mmol) and (±)-benzyl 8-((*tert*-butyldimethylsilyl)oxy)octa-2,3-dienoate (152 mg, 0.42 mmol), using 5% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 18:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/93:7→85:15), the title compound was isolated as a mixture of diastereomers (colorless oil, 182 mg, 88% yield) in 89% ee (major diastereomer).

HPLC analysis of the product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/99:1, 1.0 mL/min flow-rate; retention times: 6.0 min (minor), 8.9 min (major).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR (major diastereomer, $CDCl_3$, 400 MHz): δ 7.44 – 7.29 (m, 5H, -$C_6H_5^{Ar1}$), 7.25 – 7.13 (m, 3H, H_m^{Ar2}, H_p^{Ar2}), 7.05 (m, 2H, H_o^{Ar2}), 6.94 (dd, *J* = 15.7, 10.4 Hz, 1H, *H3*), 6.04 (d, *J* = 15.7 Hz, 1H, *H2*), 5.23 and 5.20 (*AB*, *J* = 12.4 Hz, 2H, OCH_2Ph), 3.54 (td, *J* = 6.3, 1.3 Hz, 2H, *H8*), 3.02 (d, *J* = 13.1 Hz, 1H, *Hβ*), 2.93 (d, *J* = 13.1 Hz, 1H, *Hβ'*), 2.68 (td, *J* = 10.4, 3.1 Hz, 1H, *H4*), 1.56 – 1.12 (m, 6H, *H5*, *H6*, *H7*), 0.96 (s, 9H, (CH_3)$_3$C), 0.87 (s, 9H, (CH_3)$_3$CSi), 0.02 (s, 6H, (CH_3)$_2$Si).

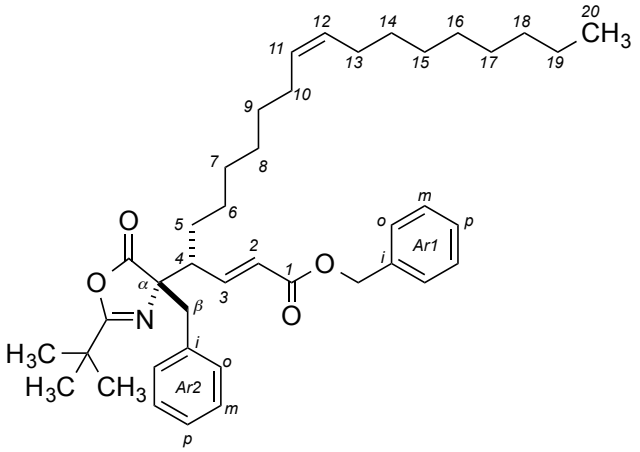
^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 180.2 (*C*=O), 170.3 (*C*=N), 165.7 (*C1*), 147.1 (*C3*), 136.0 (C_i^{Ar1}), 134.2 (C_i^{Ar2}), 130.5 (C_o^{Ar2}), 128.7 (C_m^{Ar1}), 128.5 (C_m^{Ar2}), 128.4 (C_p^{Ar1}), 128.1 (C_o^{Ar1}), 127.3 (C_p^{Ar2}), 125.2 (*C2*), 76.3 (*Cα*), 66.5 (OCH_2Ph), 62.8 (*C8*), 49.2 (*C4*), 42.2 (*Cβ*), 33.9 ((CH$_3$)$_3$C), 32.5 (*C7*), 28.7 (*C5*), 26.5 ((*C*H$_3$)$_3$C), 26.1 ((CH$_3$)$_3$CSi), 23.6 (*C6*), 18.5 ((CH$_3$)$_3$CSi), –5.2 ((*C*H$_3$)$_2$Si).

FT-IR (major diastereomer, neat): 2951, 2863, 1809, 1724, 1672, 1494, 1445, 1347, 1254, 1096, 982, 894, 845, 776, 734, 699 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 88% ee): –32.1 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 592.3447 ([M+H]$^+$, $C_{35}H_{50}NO_5Si^+$ calcd. 592.3453).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 17:1 dr. The product was isolated as a mixture of diastereomers (colorless oil, 176 mg, 85% yield) in 89% ee (major diastereomer).



Benzyl (*R*,2*E*,11*Z*)-4-((*S*)-4-benzyl-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)icosa-2,11-dienoate (Table 2, entry 9). The title compound was prepared according to General Procedure A from (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one (81 mg, 0.35 mmol) and (±)-benzyl (*Z*)-icosa-2,3,11-trienoate (167 mg, 0.42 mmol), using 5% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 10:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/95:5→90:10), the title compound was isolated as a mixture of diastereomers (colorless oil, 189 mg, 86% yield) in 91% ee (major diastereomer).

HPLC analysis of the product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/99:1, 1.0 mL/min flow-rate; retention times: 6.0 min (minor), 9.9 min (major).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR (major diastereomer, $CDCl_3$, 500 MHz): δ 7.42 – 7.31 (m, 5H, -$C_6H_5^{Ar1}$), 7.23 – 7.15 (m, 3H, H_m^{Ar2}, H_p^{Ar2}), 7.05 (m, 2H, H_o^{Ar2}), 6.94 (dd, *J* = 15.7, 10.5 Hz, 1H, *H3*), 6.03 (d, *J* = 15.7 Hz, 1H, *H2*), 5.39 – 5.27 (m, 2H, *H11*, *H12*), 5.25 and 5.20 (*AB*, *J* = 12.4 Hz, 2H, OCH_2Ph), 3.02 (d, *J* = 13.2 Hz, 1H, *Hβ*), 2.93 (d, *J* = 13.2 Hz, 1H, *Hβ'*), 2.68 (td, *J* = 10.5, 2.2 Hz, 1H, *H4*), 2.03 – 1.95 (m, 4H, *H10*, *H13*), 1.37 – 1.08 (m, 22H, *H5 – H9*, *H14 – H19*), 0.96 (s, 9H, $(CH_3)_3C$), 0.85 (t, *J* = 7.0 Hz, 3H, *H20*).

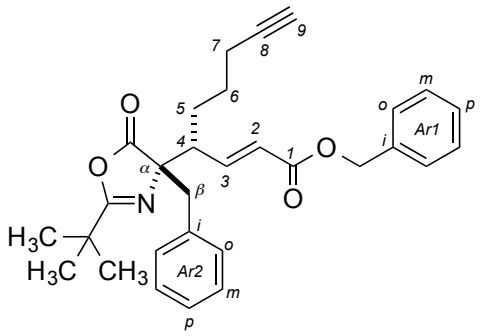
^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 180.2 (*C*=O), 170.2 (*C*=N), 165.8 (*C1*), 147.3 (*C3*), 136.0 (C_i^{Ar1}), 134.3 (C_i^{Ar2}), 130.5 (C_o^{Ar2}), 130.2, 129.8 (*C11*, *C12*), 128.7 (C_m^{Ar1}), 128.5 (C_m^{Ar2}), 128.4 (C_p^{Ar1}), 128.1 (C_o^{Ar1}), 127.3 (C_p^{Ar2}), 125.1 (*C2*), 76.3 (*Cα*), 66.5 (OCH_2Ph), 49.2 (*C4*), 42.2 (*Cβ*), 33.9 ($(CH_3)_3C$), 32.1, 29.9, 29.8, 29.7, 29.47, 29.45, 29.3, 29.2, 28.9, 27.4, 27.31, 27.28 (*C5 – C10*, *C13 – C18*), 26.5 ($(CH_3)_3C$), 22.8 (*C19*), 14.3 (*C20*).

FT-IR (major diastereomer, neat): 2925, 2853, 1817, 1729, 1667, 1452, 1372, 1345, 1297, 1261, 1220, 1150, 1096, 1065, 985, 894, 729, 696 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 91% ee): –27.9 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 628.4357 ($[M+H]^+$, $C_{41}H_{58}NO_4^+$ calcd. 628.4361).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 11:1 dr. The product was isolated as a mixture of diastereomers (colorless oil, 195 mg, 89% yield) in 91% ee (major diastereomer).



Benzyl (*R*,*E*)-4-((*S*)-4-benzyl-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)non-2-en-8-ynoate (Table 2, entry 10). The title compound was prepared according to General Procedure A from (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one (81 mg, 0.35 mmol) and (±)-benzyl nona-2,3-dien-8-ynoate (95 mg, 0.42 mmol), using 5% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 15:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/93:7→85:15), the title compound was isolated as a mixture of diastereomers (colorless oil, 146 mg, 88% yield) in 95% ee (major diastereomer).

HPLC analysis of the product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/99:1, 1.0 mL/min flow-rate; retention times: 8.8 min (minor), 14.0 min (major).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR (major diastereomer, $CDCl_3$, 400 MHz): δ 7.45 – 7.29 (m, 5H, -$C_6H_5^{Ar1}$), 7.26 – 7.13 (m, 3H, H_m^{Ar2}, H_p^{Ar2}), 7.05 (m, 2H, H_o^{Ar2}), 6.94 (dd, *J* = 15.7, 10.4 Hz, 1H, *H3*), 6.04 (d, *J* = 15.7 Hz, 1H, *H2*), 5.24 and 5.20 (*AB*, *J* = 12.6 Hz, 2H, OCH_2Ph), 3.02 (d, *J* = 13.2 Hz, 1H, *Hβ*), 2.95 (d, *J* = 13.2 Hz, 1H, *Hβ'*), 2.71 (td, *J* = 10.4, 4.0 Hz, 1H, *H4*), 2.15 (qd, *J* = 6.6, 2.7 Hz, 2H, *H7*), 1.93 (t, *J* = 2.7 Hz, *H9*), 1.58 – 1.31 (m, 4H, *H5*, *H6*), 0.97 (s, 9H, (CH_3)$_3$C).

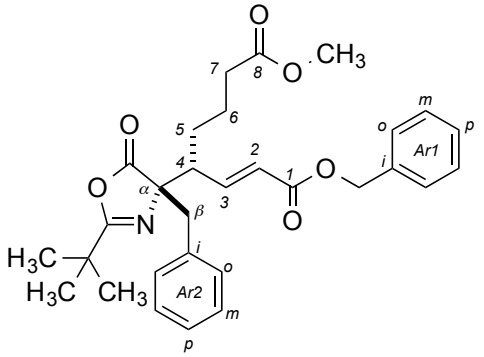
^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 180.0 (*C*=O), 170.4 (*C*=N), 165.7 (*C1*), 146.7 (*C3*), 135.9 (C_i^{Ar1}), 134.1 (C_i^{Ar2}), 130.5 (C_o^{Ar2}), 128.7 (C_m^{Ar1}), 128.53 (C_m^{Ar2}), 128.48 (C_p^{Ar1}), 128.1 (C_o^{Ar1}), 127.4 (C_p^{Ar2}), 125.5 (*C2*), 83.4 (*C8*), 76.1 (*Cα*), 69.1 (*C9*), 66.6 (OCH_2Ph), 48.7 (*C4*), 42.1 (*Cβ*), 33.9 ((CH_3)$_3$*C*), 28.0 (*C6*), 26.5 ((CH_3)$_3$C), 26.1 (*C5*), 18.3 (*C7*).

FT-IR (major diastereomer, neat): 3298, 3064, 2973, 2934, 2871, 2117, 1813, 1721, 1667, 1496, 1455, 1378, 1347, 1301, 1262, 1222, 1188, 1151, 1096, 989, 897, 787, 733 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 95% ee): –36.4 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 472.2489 ([M+H]$^+$, $C_{30}H_{34}NO_4^+$ calcd. 472.2483).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 14:1 dr. The product was isolated as a mixture of diastereomers (colorless oil, 145 mg, 88% yield) in 95% ee (major diastereomer).



1-Benzyl 8-methyl (*R*,*E*)-4-((*S*)-4-benzyl-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)oct-2-enedioate (Table 2, entry 11). The title compound was prepared according to General Procedure A from (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one (81 mg, 0.35 mmol) and (±)-1-benzyl 8-methyl octa-2,3-dienedioate (115 mg, 0.42 mmol), using 5% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 14:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/80:20→60:40), the title compound was isolated as a mixture of diastereomers (white solid, 149 mg, 84% yield) in 96% ee (major diastereomer).

HPLC analysis of the product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/9:1, 1.0 mL/min flow-rate; retention times: 10.4 min (minor), 16.9 min (major).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR (major diastereomer, $CDCl_3$, 400 MHz): δ 7.45 – 7.29 (m, 5H, -$C_6H_5^{Ar1}$), 7.28 – 7.13 (m, 3H, H_m^{Ar2}, H_p^{Ar2}), 7.05 (m, 2H, H_o^{Ar2}), 6.92 (dd, *J* = 15.7, 10.5 Hz, 1H, *H3*), 6.05 (d, *J* = 15.7 Hz, 1H, *H2*), 5.23 and 5.20 (*AB*, *J* = 12.5 Hz, 2H, OCH_2Ph), 3.65 (s, 3H, OCH_3), 3.01 (d, *J* = 13.1 Hz, 1H, *Hβ*), 2.93 (d, *J* = 13.1 Hz, 1H, *Hβ'*), 2.69 (td, J = 10.5, 3.3 Hz, 1H, *H4*), 2.25 (m, 2H, *H7*), 1.69 – 1.23 (m, 4H, *H5*, *H6*), 0.95 (s, 9H, $(CH_3)_3C$).

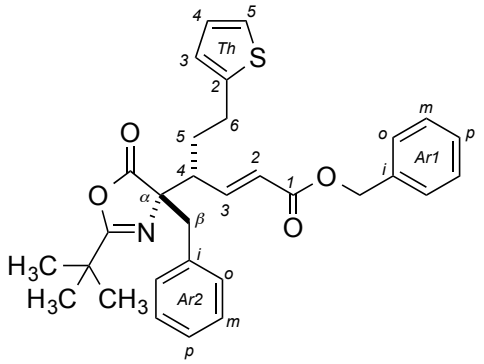
^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 180.0 (*C*=O), 173.5 (*C8*), 170.4 (*C*=N), 165.6 (*C1*), 146.4 (*C3*), 135.9 (C_i^{Ar1}), 134.1 (C_i^{Ar2}), 130.5 (C_o^{Ar2}), 128.7, 128.54 (C_m^{Ar1}, C_m^{Ar2}), 128.47 (C_p^{Ar1}), 128.1 (C_o^{Ar1}), 127.4 (C_p^{Ar2}), 125.6 (*C2*), 76.1 (*Cα*), 66.6 (OCH_2Ph), 51.7 (OCH_3), 48.9 (*C4*), 42.1 (*Cβ*), 33.9 ($(CH_3)_3C$), 33.7 (*C7*), 28.3 (*C5*), 26.5 ($(CH_3)_3C$), 22.7 (*C6*).

FT-IR (major diastereomer, neat): 2973, 1813, 1735, 1724, 1669, 1457, 1296, 1263, 1223, 1174, 1149, 1097, 988, 896, 733 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 96% ee): –31.8 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 506.2532 ($[M+H]^+$, $C_{30}H_{36}NO_6^+$ calcd. 506.2538).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 14:1 dr. The product was isolated as a mixture of diastereomers (white solid, 157 mg, 89% yield) in 96% ee (major diastereomer).



Benzyl (*R*,*E*)-4-((*S*)-4-benzyl-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)-6-(thiophen-2-yl)hex-2-enoate (Table 2, entry 12). The title compound was prepared according to General Procedure A from (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one (81 mg, 0.35 mmol) and (±)-benzyl 6-(thiophen-2-yl)hexa-2,3-dienoate (119 mg, 0.42 mmol), using 5% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 7:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/9:1), the title compound was isolated as a mixture of diastereomers (colorless oil, 164 mg, 91% yield) in 89% ee (major diastereomer).

HPLC analysis of the product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/99:1, 1.0 mL/min flow-rate; retention times: 10.2 min (minor), 14.6 min (major).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR (major diastereomer, $CDCl_3$, 400 MHz): δ 7.45 – 7.30 (m, 5H, -$C_6H_5^{Ar1}$), 7.26 – 7.13 (m, 3H, H_m^{Ar2}, H_p^{Ar2}), 7.12 (dd, *J* = 5.2, 1.2 Hz, 1H, $H5^{Th}$), 7.05 (m, 2H, H_o^{Ar2}), 6.96 (dd, *J* = 15.7, 10.3 Hz, 1H, *H3*), 6.91 (dd, *J* = 5.2, 3.5 Hz, 1H, $H4^{Th}$), 6.74 (m, 1H, $H3^{Th}$), 6.06 (d, *J* = 15.7 Hz, 1H, *H2*), 5.25 and 5.21 (*AB*, *J* = 12.4 Hz, 2H, OCH_2Ph), 3.00 and 2.94 (*AB*, *J* = 13.2 Hz, 2H, *Hβ*, *Hβ′*), 2.89 – 2.62 (m, 3H, *H4*, *H6*), 1.79 – 1.63 (m, 2H, *H5*), 0.96 (s, 9H, $(CH_3)_3C$).

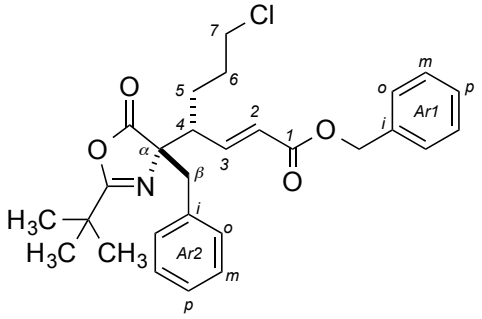
^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 179.8 (*C*=O), 170.5 (*C*=N), 165.6 (*C1*), 146.2 (*C3*), 143.4 ($C2^{Th}$), 135.9 (C_i^{Ar1}), 134.1 (C_i^{Ar2}), 130.5 (C_o^{Ar2}), 128.8 (C_m^{Ar1}), 128.52 (C_o^{Ar1}), 128.49 (C_p^{Ar1}), 128.1 (C_m^{Ar2}), 127.4 (C_p^{Ar2}), 127.0 ($C4^{Th}$), 125.9 (*C2*), 124.6 ($C3^{Th}$), 123.5 ($C5^{Th}$), 76.0 (*Cα*), 66.6 (OCH_2Ph), 48.1 (*C4*), 42.0 (*Cβ*), 33.9 ($(CH_3)_3C$), 30.5 (*C5*), 27.4 (*C6*), 26.5 ($(CH_3)_3C$).

FT-IR (neat, major diastereomer): 3034, 2972, 2925, 2253, 1953, 1876, 1811, 1726, 1664, 1495, 1452, 1206, 1085, 985, 902, 734, 701 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 89% ee): –37.9 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 516.2203 ($[M+H]^+$, $C_{31}H_{34}NO_4S^+$ calcd. 516.2204).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 7:1 dr. The product was isolated as a mixture of diastereomers (colorless oil, 152 mg, 84% yield) in 89% ee (major diastereomer).



Benzyl (*R*,*E*)-4-((*S*)-4-benzyl-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)-7-chlorohept-2-enoate (Table 2, entry 13). The title compound was prepared according to General Procedure A from (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one (81 mg, 0.35 mmol) and (±)-benzyl 7-chlorohepta-2,3-dienoate (105 mg, 0.42 mmol), using 5% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 12:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/90:10→85:15), the title compound was isolated as a mixture of diastereomers (colorless oil, 146 mg, 86% yield) in 95% ee (major diastereomer).

HPLC analysis of the product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/99:1, 1.0 mL/min flow-rate; retention times: 9.9 min (minor), 15.4 min (major).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR (major diastereomer, $CDCl_3$, 400 MHz): δ 7.47 – 7.29 (m, 5H, -$C_6H_5^{Ar1}$), 7.30 – 7.14 (m, 3H, H_m^{Ar2}, H_p^{Ar2}), 7.06 (m, 2H, H_o^{Ar2}), 6.93 (dd, *J* = 15.7, 10.4 Hz, 1H, *H3*), 6.05 (d, *J* = 15.7 Hz, 1H, *H2*), 5.23 and 5.21 (*AB*, *J* = 12.4 Hz, 2H, OCH_2Ph), 3.47 (m, 2H, *H7*), 3.02 (d, *J* = 13.2 Hz, 1H, *Hβ*), 2.95 (d, *J* = 13.2 Hz, 1H, *Hβ′*), 2.71 (m, 1H, *H4*), 1.74 (m, 1H, *H6*), 1.64 (m, 1H, *H6′*), 1.46 (m, 2H, *H5*), 0.97 (s, 9H, (CH_3)$_3$C).

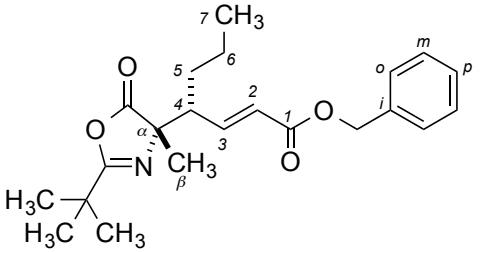
^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 179.9 (*C*=O), 170.6 (*C*=N), 165.6 (*C1*), 146.3 (*C3*), 135.9 (C_i^{Ar1}), 134.0 (C_i^{Ar2}), 130.5 (C_o^{Ar2}), 128.8 (C_m^{Ar1}), 128.54 (C_m^{Ar2}), 128.51 (C_p^{Ar1}), 128.2 (C_o^{Ar1}), 127.4 (C_p^{Ar2}), 125.7 (*C2*), 76.1 (*Cα*), 66.7 (OCH_2Ph), 48.5 (*C4*), 44.3 (*C7*), 42.1 (*Cβ*), 33.9 ((CH$_3$)$_3$*C*), 30.3 (*C6*), 26.5 ((*C*H$_3$)$_3$C), 26.4 (*C5*).

FT-IR (major diastereomer, neat): 2972, 1813, 1772, 1667, 1455, 1300, 1262, 1223, 1184, 1146, 1095, 987, 896, 733 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 95% ee): –34.1 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 482.2087 ([M+H]$^+$, $C_{28}H_{33}ClNO_4^+$ calcd. 482.2093).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 11:1 dr. The product was isolated as a mixture of diastereomers (colorless oil, 145 mg, 86% yield) in 94% ee (major diastereomer).



Benzyl (*R*,*E*)-4-((*S*)-2-(*tert*-butyl)-4-methyl-5-oxo-4,5-dihydrooxazol-4-yl)hept-2-enoate (Table 3, entry 1). The title compound was prepared according to General Procedure A from (±)-2-(*tert*-butyl)-4-methyloxazol-5(4*H*)-one (54 mg, 0.35 mmol) and (±)-benzyl hepta-2,3-dienoate (91 mg, 0.42 mmol), using 10% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in >20:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/93:7→85:15), the title compound was isolated in 90% ee (colorless oil, 99 mg, 76% yield).

HPLC analysis of the product: CHIRALPAK AD-H column; hexanes:2-propanol/99.5:0.5, 1.0 mL/min flow-rate; retention times: 10.1 min (major), 13.7 min (minor).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 – 7.29 (m, 5H, -C_6H_5), 6.80 (dd, *J* = 15.7, 10.5 Hz, 1H, *H3*), 5.96 (d, *J* = 15.7 Hz, 1H, *H2*), 5.21 and 5.17 (*AB*, *J* = 12.5 Hz, 2H, OCH_2Ph), 2.50 (td, *J* = 10.5, 2.9 Hz, 1H, *H4*), 1.32 (s, 3H, *Hβ*), 1.30 – 1.22 (m, 2H, *H5*), 1.26 (s, 9H, (CH_3)$_3$C), 1.20 – 1.03 (m, 2H, *H6*), 0.83 (t, *J* = 7.1 Hz, 3H, *H7*).

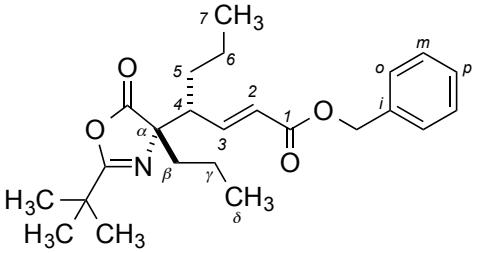
^{13}C NMR ($CDCl_3$, 100 MHz): δ 181.2 (*C*=O), 170.4 (*C*=N), 165.7 (*C1*), 146.9 (*C3*), 136.0 (C_i), 128.7, 128.5 (C_m, C_o), 128.2 (C_p), 125.2 (*C2*), 71.1 (*Cα*), 66.5 (OCH_2Ph), 49.3 (*C4*), 34.2 ((CH_3)$_3$*C*), 30.7 (*C5*), 27.0 ((CH_3)$_3$C), 22.8 (*Cβ*), 20.5 (*C6*), 13.8 (*C7*).

FT-IR (neat): 3034, 2961, 2920, 2873, 1814, 1721, 1664, 1455, 1367, 1346, 1297, 1264, 1215, 1168, 1139, 1075, 1024, 894, 791, 734, 696 cm^{-1}.

$[\alpha]^{25}_D$ (90% ee): –76.8 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 372.2170 ([M+H]$^+$, $C_{22}H_{30}NO_4^+$ calcd. 372.2170).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in >20:1 dr. The product was isolated in 92% ee (colorless oil, 103 mg, 79% yield).



Benzyl (*R*,*E*)-4-((*S*)-2-(*tert*-butyl)-5-oxo-4-propyl-4,5-dihydrooxazol-4-yl)hept-2-enoate (Table 3, entry 2). The title compound was prepared according to General Procedure A from (±)-2-(*tert*-butyl)-4-propyloxazol-5(4*H*)-one (64 mg, 0.35 mmol) and (±)-benzyl hepta-2,3-dienoate (91 mg, 0.42 mmol), using 5% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 17:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/95:5→90:10), the title compound was isolated as a mixture of diastereomers (colorless oil, 117 mg, 84% yield) in 92% ee (major diastereomer).

HPLC analysis of the product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/99.7:0.3, 1.0 mL/min flow-rate; retention times: 14.8 min (minor), 15.9 min (major).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR (major diastereomer, $CDCl_3$, 400 MHz): δ 7.43 – 7.30 (m, 5H, -C_6H_5), 6.81 (dd, *J* = 15.7, 10.5 Hz, 1H, *H3*), 5.94 (d, *J* = 15.7 Hz, 1H, *H2*), 5.21 and 5.17 (*AB*, *J* = 12.3 Hz, 2H, OCH_2Ph), 2.51 (td, *J* = 10.5, 2.8 Hz, 1H, *H4*), 1.77 – 1.58 (m, 2H, *Hβ, Hβ′*), 1.27 (s, 9H, (CH_3)$_3$C), 1.32 – 0.92 (m, 6H, *H5*, *H6*, *Hγ*), 0.85 (t, *J* = 7.6 Hz, 3H, *H7*), 0.82 (t, *J* = 7.1 Hz, 3H, *Hδ*).

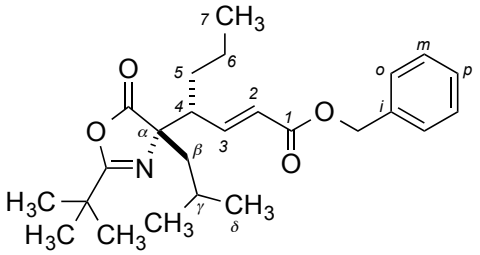
^{13}C NMR (major diastereomer, $CDCl_3$, 125 MHz): δ 180.8 (*C*=O), 170.7 (*C*=N), 165.8 (*C1*), 147.2 (*C3*), 136.0 (C_i), 128.7, 128.5 (C_m, C_o), 128.4 (C_p), 124.8 (*C2*), 75.2 (*Cα*), 66.5 (OCH_2Ph), 49.1 (*C4*), 37.8 (*Cβ*), 34.3 ((CH_3)$_3$*C*), 30.6 (*C5*), 27.1 ((CH_3)$_3$C), 20.4 (*C6*), 17.0 (*Cγ*), 13.9, 13.8 (*C7*, *Cδ*).

FT-IR (major diastereomer, neat): 2991, 2873, 1811, 1721, 1667, 1458, 1367, 1344, 1297, 1264, 1220, 1171, 1142, 1049, 1024, 889, 745, 696 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 92% ee): –59.6 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 400.2480 ([M+H]$^+$, $C_{24}H_{34}NO_4^+$ calcd. 400.2483).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 15:1 dr. The product was isolated as a mixture of diastereomers (colorless oil, 116 mg, 83% yield) in 90% ee (major diastereomer).



Benzyl (*R*,*E*)-4-((*S*)-2-(*tert*-butyl)-4-isobutyl-5-oxo-4,5-dihydrooxazol-4-yl)hept-2-enoate (Table 3, entry 3). The title compound was prepared according to General Procedure A from (±)-2-(*tert*-butyl)-4-isobutyloxazol-5(4*H*)-one (69 mg, 0.35 mmol) and (±)-benzyl hepta-2,3-dienoate (91 mg, 0.42 mmol), using 10% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in >20:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/95:5→90:10), the title compound was isolated in 80% ee (colorless oil, 123 mg, 85% yield).

HPLC analysis of the product: CHIRALPAK AD-H column; hexanes:2-propanol/99.7:0.3, 1.0 mL/min flow-rate; retention times: 9.7 min (major), 11.3 min (major).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 – 7.29 (m, 5H, -C_6H_5), 6.75 (dd, *J* = 15.6, 10.5 Hz, 1H, *H3*), 5.91 (d, *J* = 15.6 Hz, 1H, *H2*), 5.21 and 5.17 (*AB*, *J* = 12.2 Hz, 2H, OCH_2Ph), 2.47 (td, *J* = 10.5, 3.4 Hz, 1H, *H4*), 1.79 (dd, *J* = 14.0, 5.7 Hz, 1H, *Hβ*), 1.62 (dd, *J* = 14.0, 6.9 Hz, 1H, *Hβ′*), 1.46 – 1.02 (m, 5H, *H5*, *H6*, *Hγ*), 1.26 (s, 9H, (CH_3)$_3$C), 0.85 (d, *J* = 6.7 Hz, 3H, *Hδ*), 0.83 (t, *J* = 7.4 Hz, 3H, *H7*), 0.79 (d, *J* = 6.9 Hz, 3H, *Hδ′*).

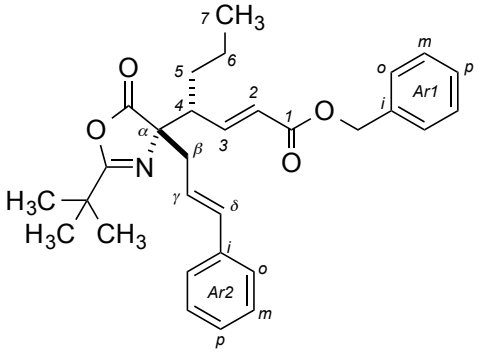
^{13}C NMR ($CDCl_3$, 100 MHz): δ 181.3 (*C*=O), 170.1 (*C*=N), 165.7 (*C1*), 147.2 (*C3*), 136.0 (C_i), 128.7, 128.5 (C_o, C_m), 128.4 (C_p), 125.1 (*C2*), 74.4 (*Cα*), 66.5 (OCH_2Ph), 50.1 (*C4*), 44.4 (*Cβ*), 34.3 ((CH_3)$_3$*C*), 30.0 (*C5*), 27.0 ((CH_3)$_3$C), 25.0 (*Cγ*), 24.2, 23.2 (*Cδ*, *Cδ′*), 20.5 (*C6*), 13.8 (*C7*).

FT-IR (neat): 2960, 2873, 1815, 1724, 1667, 1457, 1370, 1343, 1296, 1266, 1221, 1173, 1144, 1059, 1027, 988, 893, 740 cm^{-1}.

$[\alpha]^{25}_{D}$ (80% ee): –70.3 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 414.2641 ($[M+H]^+$, $C_{25}H_{36}NO_4^+$ calcd. 414.2639).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in >20:1 dr. The product was isolated in 81% ee (colorless oil, 119 mg, 82% yield).



Benzyl (*R*,*E*)-4-((*S*)-2-(*tert*-butyl)-4-cinnamyl-5-oxo-4,5-dihydrooxazol-4-yl)hept-2-enoate (Table 3, entry 4). The title compound was prepared according to General Procedure A from 2-(*tert*-butyl)-4-cinnamyloxazol-5(4*H*)-one (90 mg, 0.35 mmol) and (±)-benzyl hepta-2,3-dienoate (91 mg, 0.42 mmol), using 5% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in >20:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/95:5→90:10), the title compound was isolated in 92% ee (colorless oil, 139 mg, 84% yield).

HPLC analysis of the product: CHIRALPAK IC column; hexanes:2-propanol/99:1, 1.0 mL/min flow-rate; retention times: 8.2 min (minor), 9.2 min (major).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 – 7.32 (m, 5H, -$C_6H_5^{Ar1}$), 7.30 – 7.16 (m, 5H, -$C_6H_5^{Ar2}$), 6.89 (dd, *J* = 15.7, 10.4 Hz, 1H, *H3*), 6.41 (d, *J* = 15.9 Hz, 1H, *Hδ*), 6.00 (d, *J* = 15.7 Hz, 1H, *H2*), 5.85 (dt, *J* = 15.9, 7.6 Hz, 1H, *Hγ*), 5.24 and 5.19 (*AB*, *J* = 12.4 Hz, 2H, OCH_2Ph), 2.69 – 2.58 (m, 2H, *H4*, *Hβ*), 2.53 (dd, *J* = 13.5, 7.6 Hz, 1H, *Hβ′*), 1.43 – 1.08 (m, 4H, *H5*, *H6*), 1.20 (s, 9H, (CH_3)$_3$C), 0.85 (t, *J* = 7.0 Hz, 3H, *H7*).

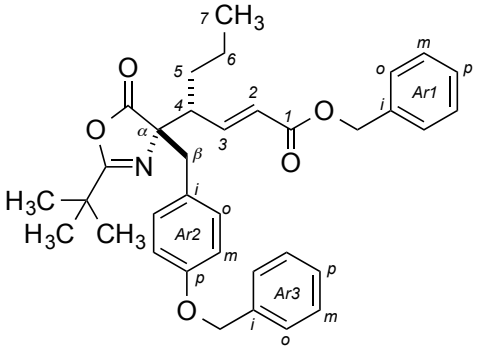
^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.2 (*C*=O), 170.9 (*C*=N), 165.7 (*C1*), 146.9 (*C3*), 136.7 (C_i^{Ar2}), 136.0 (C_i^{Ar1}), 135.8 (*Cδ*), 128.73, 128.66, 128.5 (C_o^{Ar1}, C_m^{Ar1}, C_m^{Ar2}), 128.4 (C_p^{Ar1}), 127.8 (C_p^{Ar2}), 126.3 (C_o^{Ar2}), 125.1 (*C2*), 122.2 (*Cγ*), 74.5 (*Cα*), 66.5 (OCH_2Ph), 48.5 (*C4*), 39.3 (*Cβ*), 34.3 ((CH_3)$_3$*C*), 30.9 (*C5*), 27.0 ((CH_3)$_3$C), 20.4 (*C6*), 13.8 (*C7*).

FT-IR (neat): 2962, 1815, 1722, 1666, 1457, 1297, 1266, 1220, 1173, 1146, 1026, 989, 970, 895, 744 cm^{-1}.

$[\alpha]^{25}_{D}$ (92% ee): –15.8 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 474.2638 ($[M+H]^+$, $C_{30}H_{36}NO_4^+$ calcd. 474.2639).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 17:1 dr. The product was isolated in 89% ee (colorless oil, 133 mg, 80% yield).



Benzyl (*R*,*E*)-4-((*S*)-4-(4-(benzyloxy)benzyl)-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)hept-2-enoate (Table 3, entry 5). The title compound was prepared according to General Procedure A from 4-(4-(benzyloxy)benzyl)-2-(*tert*-butyl)oxazol-5(4*H*)-one (118 mg, 0.35 mmol) and (±)-benzyl hepta-2,3-dienoate (91 mg, 0.42 mmol), using 5% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 13:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/9:1→8:1), the title compound was isolated as a mixture of diastereomers (white solid, 169 mg, 87% yield) in 90% ee (major diastereomer).

HPLC analysis of the product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/97:3, 1.0 mL/min flow-rate; retention times: 9.2 min (minor), 14.5 min (major).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR (major diastereomer, $CDCl_3$, 400 MHz): δ 7.44 – 7.27 (m, 10H, -$C_6H_5^{Ar1}$, -$C_6H_5^{Ar3}$), 6.99 – 6.88 (m, 3H, H_o^{Ar2}, *H3*), 6.81 (m, 2H, H_m^{Ar2}), 6.02 (d, *J* = 15.7 Hz, 1H, *H2*), 5.23 and 5.19 (*AB*, *J* = 12.5 Hz, 2H, CO_2CH_2Ph), 5.01 (s, 2H, OCH_2Ph), 2.96 (d, *J* = 13.3 Hz, 1H, *Hβ*), 2.87 (d, *J* = 13.3 Hz, 1H, *Hβ′*), 2.68 (td, *J* = 10.5, 2.9 Hz, 1H, *H4*), 1.37 – 1.07 (m, 4H, *H5*, *H6*), 0.98 (s, 9H, $(CH_3)_3$C), 0.84 (t, *J* = 7.0 Hz, 3H, *H7*).

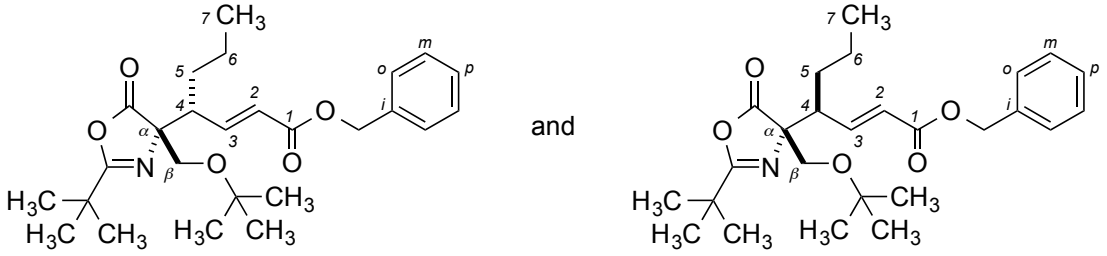
^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 180.3 (*C*=O), 170.2 (*C*=N), 165.8 (*C1*), 158.1 (C_p^{Ar2}), 147.3 (*C3*), 137.1 (C_i^{Ar3}), 136.0 (C_i^{Ar1}), 131.6 (C_o^{Ar2}), 128.74, 128.69, 128.5, 128.4, 128.0 (C_o^{Ar1}, C_m^{Ar1}, C_m^{Ar3}, C_p^{Ar1}, C_p^{Ar3}), 127.5 (C_o^{Ar3}), 126.6 (C_i^{Ar2}), 125.0 (*C2*), 114.6 (C_m^{Ar2}), 76.4 (*Cα*), 70.0 (OCH_2Ph), 66.5 (CO_2CH_2Ph), 48.8 (*C4*), 41.4 (*Cβ*), 33.9 (($CH_3)_3C$), 31.0 (*C5*), 26.6 (($CH_3)_3C$), 20.4 (*C6*), 13.8 (*C7*).

FT-IR (major diastereomer, neat): 3059, 3028, 2691, 2626, 1809, 1721, 1664, 1507, 1445, 1372, 1297, 1225, 1168, 1149, 987, 897, 838, 737, 698 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 90% ee): –25.4 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 554.2904 ($[M+H]^+$, $C_{35}H_{40}NO_5^+$ calcd. 554.2901).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 14:1 dr. The product was isolated as a mixture of diastereomers (white solid, 161 mg, 83% yield) in 90% ee (major diastereomer).



Benzyl (*R*,*E*)-4-((*R*)-4-(*tert*-butoxymethyl)-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)hept-2-enoate and the other diastereomer (Table 3, entry 6). The title compounds were prepared according to General Procedure A from 4-(*tert*-butoxymethyl)-2-(*tert*-butyl)oxazol-5(4*H*)-one (80 mg, 0.35 mmol) and (±)-benzyl hepta-2,3-dienoate (91 mg, 0.42 mmol), using 10% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 4:1 dr. The product was purified by flash chromatography (silica gel, hexanes:ethyl acetate/95:5→90:10) and the diastereomers were isolated separately: major diastereomer (colorless oil, 88 mg, 57% yield) in 88% ee; minor diastereomer (colorless oil, 27 mg, 17% yield) in 88% ee.

HPLC analysis of the product (major diastereomer): CHIRALPAK AD-H column; hexanes:2-propanol/99:1, 1.0 mL/min flow-rate; retention times: 4.6 min (minor), 5.0 min (major).

^{1}H NMR (major diastereomer, $CDCl_3$, 400 MHz): δ 7.43 – 7.29 (m, 5H, -C_6H_5), 6.88 (dd, *J* = 15.7, 10.5 Hz, 1H, *H3*), 5.93 (d, *J* = 15.7 Hz, 1H, *H2*), 5.22 and 5.17 (*AB*, *J* = 12.2 Hz, 2H, OCH_2Ph), 3.47 (d, *J* = 8.7 Hz, 1H, *Hβ*), 3.41 (d, *J* = 8.7 Hz, 1H, *Hβ'*), 2.58 (td, *J* = 10.5, 2.7 Hz, 1H, *H4*), 1.28 (s, 9H, (CH_3)$_3$CO), 1.26 – 1.08 (m, 4H, *H5*, *H6*), 1.06 (s, 9H, (CH_3)$_3$C), 0.82 (t, *J* = 6.8 Hz, 3H, *H7*).

^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 179.9 (*C*=O), 171.5 (*C*=N), 165.7 (*C1*), 147.0 (*C3*), 136.0 (C_i), 128.7, 128.5 (C_o, C_m), 128.4 (C_p), 124.2 (*C2*), 76.2 (*Cα*), 73.6 ((CH$_3$)$_3$CO), 66.5 (OCH_2Ph), 64.7 (*Cβ*), 45.7 (*C4*), 34.2 ((CH$_3$)$_3$*C*), 30.8 (*C5*), 27.4, 27.1 ((*C*H$_3$)$_3$C, (*C*H$_3$)$_3$CO), 20.1 (*C6*), 13.7 (*C7*).

FT-IR (major diastereomer, neat): 2973, 1820, 1723, 1672, 1457, 1365, 1262, 1176, 1097, 1019, 900, 741 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 88% ee): –23.2 (c = 1.0, $CHCl_3$).

HRMS (major diastereomer): *m*/*z* 444.2746 ([M+H]$^+$, $C_{26}H_{38}NO_5^+$ calcd. 444.2745).

HPLC analysis of the product (minor diastereomer): CHIRALPAK AD-H column; hexanes:2-propanol/99:1, 1.0 mL/min flow-rate; retention times: 5.1 min (minor), 5.5 min (major).

^{1}H NMR (minor diastereomer) ($CDCl_3$, 400 MHz): δ 7.40 – 7.30 (m, 5H, -C_6H_5), 6.78 (dd, *J* = 15.7, 10.4 Hz, 1H, *H3*), 5.88 (d, *J* = 15.7 Hz, 1H, *H2*), 5.20 and 5.14 (*AB*, *J* = 12.4 Hz, 2H, OCH_2Ph), 3.57 and 3.55 (*AB*, *J* = 8.7 Hz, 2H, *Hβ*, *Hβ'*), 2.62 (m, 1H, *H4*), 1.46 – 1.11 (m, 4H, *H5*, *H6*), 1.26 (s, 9H, (CH_3)$_3$CO), 1.08 (s, 9H, (CH_3)$_3$C), 0.86 (t, *J* = 7.1 Hz, 3H, *H7*).

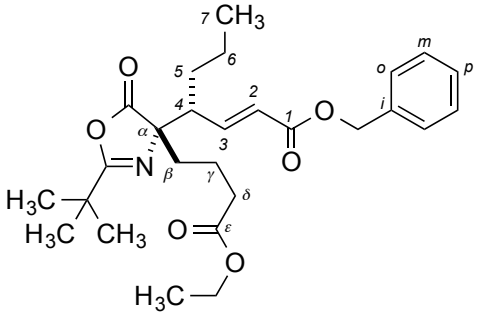
^{13}C NMR (minor diastereomer) ($CDCl_3$, 100 MHz): δ 179.0 (*C*=O), 171.8 (*C*=N), 165.6 (*C1*), 146.0 (*C3*), 136.0 (C_i), 128.7, 128.43 (C_o, C_m), 128.39 (C_p), 124.6 (*C2*), 76.1 (*Cα*), 73.7 ((CH$_3$)$_3$CO), 66.5 (OCH_2Ph), 64.3 (*Cβ*), 45.6 (*C4*), 34.2 ((CH$_3$)$_3$*C*), 30.3 (*C5*), 27.4, 27.0 ((*C*H$_3$)$_3$C, (*C*H$_3$)$_3$CO), 20.5 (*C6*), 13.9 (*C7*).

FT-IR (minor diastereomer, neat): 2972, 1820, 1723, 1670, 1456, 1365, 1264, 1195, 1175, 1145, 1094, 1019, 901, 741 cm^{-1}.

$[\alpha]^{25}_D$ (minor diastereomer, 88% ee): –20.9 (c = 1.0, $CHCl_3$).

HRMS (minor diastereomer): *m*/*z* 444.2746 ([M+H]$^+$, $C_{26}H_{38}NO_5^+$ calcd. 444.2745).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 3:1 dr. The product was purified by flash chromatography (silica gel, hexanes:diethyl ether/95:5→90:10), and the diastereomers were isolated separately: major diastereomer (colorless oil, 88 mg, 57% yield) in 89% ee; minor diastereomer (colorless oil, 25 mg, 16% yield) in 91% ee.



Benzyl (*R*,*E*)-4-((*S*)-2-(*tert*-butyl)-4-(4-ethoxy-4-oxobutyl)-5-oxo-4,5-dihydrooxazol-4-yl)hept-2-enoate (Table 3, entry 7). The title compound was prepared according to General Procedure A from (±)-ethyl 4-(2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)butanoate (89 mg, 0.35 mmol) and (±)-benzyl hepta-2,3-dienoate (91 mg, 0.42 mmol), using 10% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 17:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/90:10→85:15), the title compound was isolated (colorless oil, 121 mg, 73% yield) in 88% ee.

HPLC analysis of the product: CHIRALPAK IC column; hexanes:2-propanol/93:7, 1.0 mL/min flow-rate; retention times: 8.5 min (major), 10.7 min (minor).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 – 7.29 (m, 5H, -C_6H_5), 6.79 (dd, *J* = 15.7, 10.5 Hz, 1H, *H3*), 5.94 (d, *J* = 15.7 Hz, 1H, *H2*), 5.21 and 5.17 (*AB*, *J* = 12.4 Hz, 2H, OCH_2Ph), 4.09 (q, *J* = 7.1 Hz, 2H, CH_3CH_2O), 2.52 (td, *J* = 10.5, 2.8 Hz, 1H, *H4*), 2.32 – 2.17 (m, 2H, *Hδ*), 1.82 – 1.64 (m, 2H, *Hβ*), 1.49 – 1.02 (m, 6H, *H5*, *H6*, *Hγ*), 1.27 (s, 9H, $(CH_3)_3C$), 1.22 (t, *J* = 7.2 Hz, 3H, CH_3CH_2O), 0.82 (t, *J* = 7.1 Hz, 3H, *H7*).

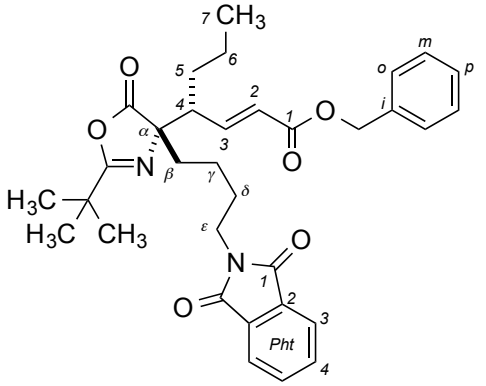
^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.4 (*C*=O), 172.7 (*Cε*), 171.0 (*C*=N), 165.7 (*C1*), 146.9 (*C3*), 136.0 (C_i), 128.7, 128.5 (C_m, C_o), 128.4 (C_p), 125.0 (*C2*), 74.9 (*Cα*), 66.5 (OCH_2Ph), 60.5 (CH_3CH_2O), 48.9 (*C4*), 35.0 (*Cβ*), 34.4 ($(CH_3)_3C$), 33.9 (*Cδ*), 30.5 (*C5*), 28.4 (*Cδ*), 27.1 ($(CH_3)_3C$), 20.4 (*C6*), 19.2 (*Cγ*), 14.3 (CH_3CH_2O), 13.8 (*C7*).

FT-IR (major diastereomer, neat): 2963, 2874, 1815, 1729, 1667, 1456, 1372, 1265, 1027, 894, 738, 695 cm^{-1}.

$[\alpha]^{25}_D$ (88% ee): –41.5 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 472.2692 ([M+H]$^+$, $C_{27}H_{38}NO_6^+$ calcd. 472.2694).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in >20:1 dr. The product was isolated (colorless oil, 124 mg, 75% yield) in 87% ee.



Benzyl (*R*,*E*)-4-((*S*)-2-(*tert*-butyl)-4-(4-(1,3-dioxoisoindolin-2-yl)butyl)-5-oxo-4,5-dihydrooxazol-4-yl)hept-2-enoate (Table 3, entry 8). The title compound was prepared according to General Procedure A from 2-(4-(2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)butyl)isoindoline-1,3-dione (120 mg, 0.35 mmol) and (±)-benzyl hepta-2,3-dienoate (91 mg, 0.42 mmol), using 10% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 19:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/95:5→90:10), the title compound was isolated as a mixture of diastereomers (colorless oil, 152 mg, 78% yield) in 85% ee (major diastereomer).

HPLC analysis of the product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/80:20, 0.5 mL/min flow-rate; retention times: 19.4 min (major), 20.3 min (minor).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR (major diastereomer, $CDCl_3$, 400 MHz): δ 7.85 – 7.78 (m, 2H, $H3^{Pht}$), 7.73 – 7.67 (m, 2H, $H4^{Pht}$), 7.44 – 7.26 (m, 5H, -C_6H_5), 6.77 (dd, J = 15.7, 10.5 Hz, 1H, *H3*), 5.92 (d, J = 15.6 Hz, 1H, *H2*), 5.20 and 5.16 (*AB*, J = 12.5 Hz, 2H, OCH_2Ph), 3.61 (td, J = 6.9, 1.4 Hz, 2H, *Hε*), 2.50 (td, J = 10.5, 2.9 Hz, 1H, *H4*), 1.82 – 1.53 (m, 4H, *Hβ*, *Hδ*), 1.30 – 0.94 (m, 6H, *H5*, *H6*, *Hγ*), 1.24 (s, 9H, (CH_3)$_3$C), 0.81 (t, J = 6.8 Hz, 3H, *H7*).

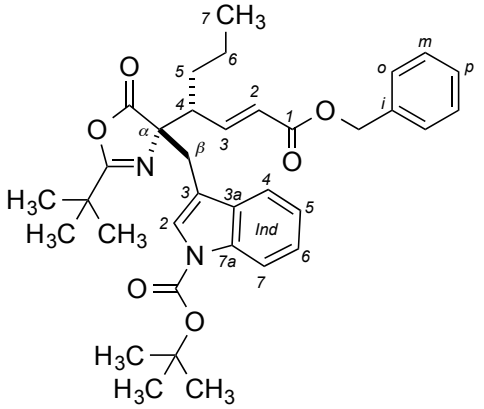
^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 180.6 (*C*=O), 170.9 (*C*=N), 168.4 ($C1^{Pht}$), 165.7 (*C1*), 147.0 (*C3*), 136.0 (C_i), 134.0 ($C4^{Pht}$), 132.2 ($C2^{Pht}$), 128.7, 128.5 (C_m, C_o), 128.4 (C_p), 125.0 (*C2*), 123.3 ($C3^{Pht}$), 74.9 (*Cα*), 66.5 (OCH_2Ph), 49.0 (*C4*), 37.7 (*Cε*), 35.3 (*Cβ*), 34.3 ((CH_3)$_3$*C*), 30.6 (*C5*), 28.4 (*Cδ*), 27.0 ((CH_3)$_3$C), 21.2 (*Cγ*), 20.4 (*C6*), 13.8 (*C7*).

FT-IR (major diastereomer, neat): 3028, 2956, 2930, 2868, 1811, 1773, 1716, 1668, 1455, 1393, 1372, 1295, 1265, 1220, 1172, 1145, 1026, 894, 720, 697 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 85% ee): –25.8 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 559.2801 ([M+H]$^+$, $C_{33}H_{39}N_2O_6^+$ calcd. 559.2803).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 15:1 dr. The product was isolated as a mixture of diastereomers (colorless oil, 157 mg, 80% yield) in 89% ee (major diastereomer).



***Tert*-butyl 3-(((*S*)-4-((*R*,*E*)-1-(benzyloxy)-1-oxohept-2-en-4-yl)-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)methyl)-1*H*-indole-1-carboxylate** (Table 3, entry 9). The title compound was prepared according to General Procedure A from *tert*-butyl 3-((2-(tert-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)methyl)-1*H*-indole-1-carboxylate (129 mg, 0.35 mmol) and (±)-benzyl hepta-2,3-dienoate (91 mg, 0.42 mmol), using 10% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 17:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/95:5→90:10), the title compound was isolated as a mixture of diastereomers (colorless oil, 175 mg, 85% yield) in 87% ee (major diastereomer).

HPLC analysis of the product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/93:7, 1.0 mL/min flow-rate; retention times: 8.0 min (minor), 12.3 min (major).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR (major diastereomer, $CDCl_3$, 400 MHz): δ 8.07 (d, *J* = 7.8 Hz, 1H, *H7*^{Ind}), 7.54 (d, *J* = 7.9 Hz, 1H, *H4*^{Ind}), 7.45 – 7.17 (m, 8H, -C$_6$*H*$_5$, *H2*^{Ind}, *H5*^{Ind}, *H6*^{Ind}), 7.02 (dd, *J* = 15.7, 10.5 Hz, 1H, *H3*), 6.08 (d, *J* = 15.7 Hz, 1H, *H2*), 5.23 (s, 2H, OC*H*$_2$Ph), 3.14 (d, *J* = 13.8 Hz, 1H, *Hβ*), 3.02 (d, *J* = 13.8 Hz, 1H, *Hβ'*), 2.75 (td, *J* = 10.5, 2.8 Hz, 1H, *H4*), 1.64 (s, 9H, (C*H*$_3$)$_3$CO), 1.39 – 1.10 (m, 4H, *H5*, *H6*), 0.94 – 0.79 (m, 12H, (C*H*$_3$)$_3$C), *H7*).

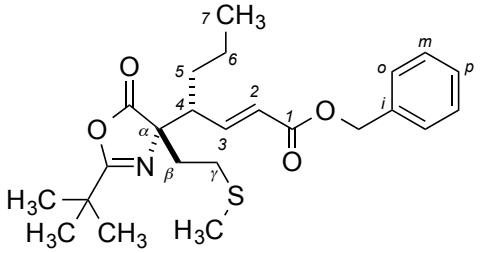
^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 180.2 (*C*=O), 170.7 (*C*=N), 165.8 (*C1*), 149.5 (O(*C*=O)N), 147.2 (*C3*), 136.0 (*C*$_i$), 135.2 (*C7a*^{Ind}), 130.5 (*C3a*^{Ind}), 128.8, 128.5 (*C*$_m$, *C*$_o$, *C*$_p$; overlapped), 125.2, 125.1 (*C2*, *C2*^{Ind}), 124.5 (*C6*^{Ind}), 122.4 (*C5*^{Ind}), 120.5 (*C4*^{Ind}), 115.0 (*C7*^{Ind}), 113.5 (*C3*^{Ind}), 83.8 ((CH$_3$)$_3$CO), 77.5 (*Cα*), 66.5 (OCH$_2$Ph), 48.8 (*C4*), 33.9 ((CH$_3$)$_3$*C*), 31.6 (*Cβ*), 31.2 (*C5*), 28.3 ((*C*H$_3$)$_3$CO), 26.3 ((*C*H$_3$)$_3$C), 20.4 (*C6*), 13.8 (*C7*).

FT-IR (major diastereomer, neat): 2974, 2932, 1815, 1734, 1666, 1453, 1367, 1309, 1258, 1221, 1160, 1107, 1016, 991, 897, 747 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 87% ee): –11.6 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 587.3109 ([M+H]$^+$, $C_{35}H_{43}N_2O_6^+$ calcd. 587.3116).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 19:1 dr. The product was isolated as a mixture of diastereomers (colorless oil, 185 mg, 90% yield) in 87% ee (major diastereomer).



Benzyl (*R*,*E*)-4-((*S*)-2-(*tert*-butyl)-4-(2-(methylthio)ethyl)-5-oxo-4,5-dihydrooxazol-4-yl)hept-2-enoate (Table 3, entry 10). The title compound was prepared according to General Procedure A from (±)-2-(*tert*-butyl)-4-(2-(methylthio)ethyl)oxazol-5(4*H*)-one (75 mg, 0.35 mmol) and (±)-benzyl hepta-2,3-dienoate (91 mg, 0.42 mmol), using 10% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 20:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/90:10→85:15), the title compound was isolated in 81% ee (colorless oil, 127 mg, 84% yield).

HPLC analysis of the product: CHIRALPAK AD-H column; hexanes:2-propanol/99.7:0.3, 1.0 mL/min flow-rate; retention times: 21.6 min (major), 25.6 min (minor).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 – 7.30 (m, 5H, -C_6H_5), 6.79 (dd, *J* = 15.7, 10.5 Hz, 1H, *H3*), 5.95 (d, *J* = 15.7 Hz, 1H, *H2*), 5.22 and 5.18 (*AB*, *J* = 12.3 Hz, 2H, OCH_2Ph), 2.53 (td, *J* = 10.5, 3.0 Hz, 1H, *H4*), 2.31 (m, 1H, *Hβ*), 2.21 (m, 1H, *Hβ′*), 2.06 (m, 2H, *Hγ*), 2.03 (s, 3H, SCH_3), 1.27 (s, 9H, (CH_3)$_3$C), 1.30 – 1.05 (m, 4H, *H5*, *H6*), 0.84 (t, *J* = 7.0 Hz, 3H, *H7*).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.5 (*C*=O), 171.4 (*C*=N), 165.6 (*C1*), 146.7 (*C3*), 136.0 (C_i), 128.7, 128.6 (C_m, C_o), 128.4 (C_p), 125.3 (*C2*), 74.0 (*Cα*), 66.5 (OCH_2Ph), 49.4 (*C4*), 34.7, 34.4 ((CH_3)$_3$*C*, *Cγ*), 30.6 (*C5*), 28.5 (*Cβ*), 27.1 ((CH_3)$_3$C), 20.4 (*C6*), 15.2 (SCH_3), 13.8 (*C7*).

FT-IR (neat): 2961, 1814, 1722, 1663, 1457, 1298, 1264, 1221, 1171, 1146, 1013, 894, 743 cm^{-1}.

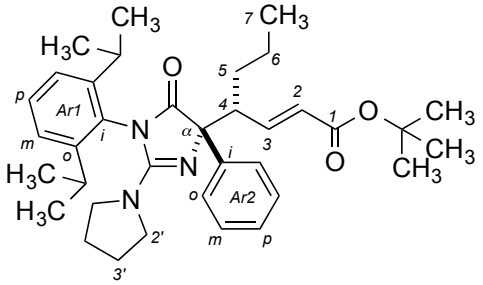
$[\alpha]^{25}_D$ (81% ee): –57.1 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 432.2204 ([M+H]$^+$, $C_{24}H_{34}NO_4S^+$ calcd. 432.2204).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in >20:1 dr. The product was isolated in 82% ee (colorless oil, 121 mg, 80% yield).

IV. γ-Addition of 2-Amino-3,5-dihydro-4*H*-imidazol-4-ones to Allenoates

General Procedure B. An oven-dried 20-mL vial was charged with catalyst **1** (11.7 mg, 0.030 mmol, 10%), 2-fluoro-6-methoxyphenol (3.5 μL, 4.3 mg, 0.030 mmol, 10%), and the 2-amino-3,5-dihydro-4*H*-imidazol-4-one (0.30 mmol). The vial was capped with a PTFE-lined septum cap and evacuated/back-filled with nitrogen (3 cycles). Toluene (anhydrous, 3.00 mL) was added via syringe, and then the vial was cooled to 10 °C. Next, the allenoate (0.45 mmol, 1.5 equiv) was added via syringe, and then the reaction mixture was stirred at 10 °C for 24 h. To deactivate the catalyst, a solution of *tert*-butyl hydroperoxide (5.0-6.0 M in decane; 50 μL) was added. The resulting mixture was stirred at 10 °C for 10 min, and then it was allowed to warm to r.t. The mixture was concentrated under reduced pressure, and the product was purified by column chromatography.



***Tert*-butyl (*R*,*E*)-4-((*R*)-1-(2,6-diisopropylphenyl)-5-oxo-4-phenyl-2-(pyrrolidin-1-yl)-4,5-dihydro-1*H*-imidazol-4-yl)hept-2-enoate** (Table 4, entry 1). The title compound was prepared according to General Procedure B from (±)-3-(2,6-diisopropylphenyl)-5-phenyl-2-(pyrrolidin-1-yl)-3,5-dihydro-4*H*-imidazol-4-one (117 mg, 0.30 mmol) and (±)-*tert*-butyl hepta-2,3-dienoate (82 mg, 0.45 mmol), using 10% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 20:1 dr. After purification by flash chromatography (silica gel, hexanes:ethyl acetate/95:5→85:15), the title compound was isolated in 90% ee (white solid, 135 mg, 79% yield).

HPLC analysis of the product: CHIRALPAK IC column; hexanes:2-propanol/99:1, 1.0 mL/min flow-rate; retention times: 6.6 min (major), 8.0 min (minor).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (m, 2H, H_o^{Ar2}), 7.34 (t, J = 7.8 Hz, 1H, H_p^{Ar1}), 7.28 – 7.05 (m, 5H, H_m^{Ar1}, H_m^{Ar2}, H_p^{Ar2}), 6.82 (dd, J = 15.8, 10.1 Hz, 1H, *H3*), 5.64 (d, J = 15.8 Hz, 1H, *H2*), 3.24 – 2.95 (m, 6H, *H4*, *H2′*, C*H*$(CH_3)_2$), 2.28 (sep, J = 7.1 Hz, 1H, C*H*$(CH_3)_2$), 1.80 – 1.70 (m, 4H, *H3′*), 1.58 – 1.17 (m, 4H, *H5*, *H6*), 1.41 (s, 9H, C(C*H*$_3)_3$), 1.27, 1.23, 0.96, 0.51 (4×d, J = 6.8; 7.0; 7.2; 7.1 Hz, 12H, CH(C*H*$_3)_2$), 0.88 (t, J = 7.4 Hz, 3H, *H7*).

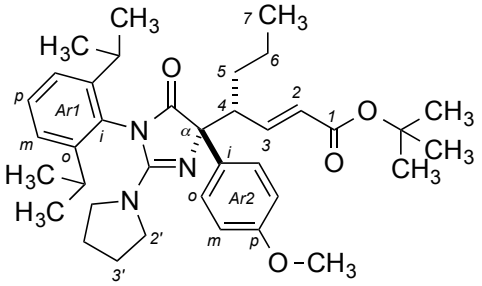
^{13}C NMR ($CDCl_3$, 100 MHz): δ 183.3 (*C*=O), 166.0 (*C1*), 154.4 (*C*=N), 147.9 (*C3*), 147.5, 147.2 (C_o^{Ar1}), 141.1 (C_i^{Ar2}), 130.8 (C_i^{Ar1}), 130.0 (C_p^{Ar1}), 127.7 (C_m^{Ar2}), 127.0 (C_p^{Ar2}), 126.7 (C_o^{Ar2}), 125.2 (*C2*), 124.1 (C_m^{Ar1}), 79.9 (*C*$(CH_3)_3$), 76.2 (*Cα*), 51.3 (*C4*), 47.9 (*C2′*), 31.7 (*C5*), 29.2, 28.4 (*C*H$(CH_3)_2$), 28.3 (C$(CH_3)_3$), 25.3 (*C3′*, CH$(CH_3)_2$; overlapped), 23.9, 23.0, 22.7 (CH$(CH_3)_2$), 20.9 (*C6*), 14.3 (*C7*).

FT-IR (neat): 2962, 2870, 1713, 1615, 1447, 1418, 1349, 1308, 1256, 1227, 1160, 985, 912, 728 cm^{-1}.

$[\alpha]^{25}_D$ (90% ee): –56.0 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 572.3849 ([M+H]$^+$, $C_{36}H_{50}N_3O_3^+$ calcd. 572.3847).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in >20:1 dr. The product was isolated in 91% ee (white solid, 129 mg, 75% yield).



***Tert*-butyl (*R*,*E*)-4-((*R*)-1-(2,6-diisopropylphenyl)-4-(4-methoxyphenyl)-5-oxo-2-(pyrrolidin-1-yl)-4,5-dihydro-1*H*-imidazol-4-yl)hept-2-enoate** (Table 4, entry 2). The title compound was prepared according to General Procedure B from (±)-3-(2,6-diisopropylphenyl)-5-(4-methoxyphenyl)-2-(pyrrolidin-1-yl)-3,5-dihydro-4*H*-imidazol-4-one (126 mg, 0.30 mmol) and (±)-*tert*-butyl hepta-2,3-dienoate (82 mg, 0.45 mmol), using 10% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 7:1 dr. After purification by flash chromatography (silica gel, hexanes:ethyl acetate/95:5→85:15), the title compound was isolated as a mixture of diastereomers (white solid, 101 mg, 56% yield) in 91% ee (major diastereomer).

HPLC analysis of the product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/96:4, 1.0 mL/min flow-rate; retention times: 7.1 min (major), 10.1 min (minor).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR (major diastereomer, $CDCl_3$, 400 MHz): δ 7.62 (m, 2H, H_o^{Ar2}), 7.35 (t, J = 7.9 Hz, 1H, H_p^{Ar1}), 7.21, 7.08 (2×d, J = 7.9 Hz, 2H, H_m^{Ar1}), 6.86 – 6.77 (m, 3H, *H3*, H_m^{Ar2}), 5.48 (d, J = 15.4 Hz, 1H, *H2*), 3.78 (s, 3H, CH_3O), 3.20 – 2.91 (m, 6H, *H4*, *H2′*, C*H*(CH_3)$_2$), 2.30 (sep, J = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 1.80 – 1.69 (m, 4H, *H3′*), 1.59 – 1.17 (m, 4H, *H5*, *H6*), 1.42 (s, 9H, C(CH_3)$_3$), 1.27, 1.23, 0.97, 0.56 (4×d, J = 7.4; 7.2; 7.3; 6.8 Hz, 12H, CH(CH_3)$_2$), 0.87 (t, J = 7.2 Hz, 3H, *H7*).

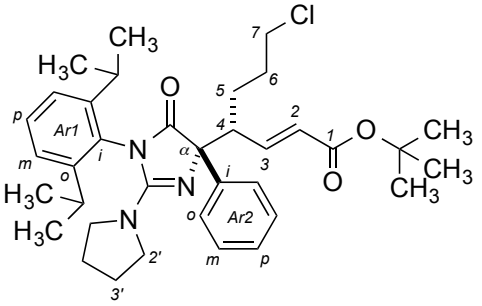
^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 183.4 (*C*=O), 165.9 (*C1*), 158.7 (C_p^{Ar2}), 154.4 (*C*=N), 148.0 (*C3*), 147.5, 147.2 (C_o^{Ar1}), 133.4 (C_i^{Ar2}), 130.8 (C_i^{Ar1}), 129.9 (C_p^{Ar1}), 127.8 (C_o^{Ar2}), 125.1 (*C2*), 124.0 (C_m^{Ar1}), 113.2 (C_m^{Ar2}), 79.9 (*C*(CH_3)$_3$), 75.8 (*Cα*), 55.4 (OCH_3), 51.6 (*C4*), 47.9 (*C2′*), 31.7 (*C5*), 29.2, 28.4 (*C*H(CH_3)$_2$), 28.3 (C(*C*H_3)$_3$), 25.3 (*C3′*, CH(*C*H_3)$_2$; overlapped), 24.0, 23.0, 22.7 (CH(*C*H_3)$_2$), 21.0 (*C6*), 14.3 (*C7*).

FT-IR (major diastereomer, neat): 2963, 2871, 1714, 1617, 1508, 1463, 1423, 1349, 1306, 1248, 1161, 1036, 913, 732 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 92% ee): –24.6 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 602.3958 ([M+H]$^+$, $C_{37}H_{52}N_3O_4^+$ calcd. 602.3953).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 7:1 dr. The product was isolated as a mixture of diastereomers (white solid, 110 mg, 61% yield) in 93% ee (major diastereomer).



***T*ert-butyl (*R*,*E*)-7-chloro-4-((*R*)-1-(2,6-diisopropylphenyl)-5-oxo-4-phenyl-2-(pyrrolidin-1-yl)-4,5-dihydro-1*H*-imidazol-4-yl)hept-2-enoate** (Table 4, entry 3). The title compound was prepared according to General Procedure B from (±)-3-(2,6-diisopropylphenyl)-5-phenyl-2-(pyrrolidin-1-yl)-3,5-dihydro-4*H*-imidazol-4-one (117 mg, 0.30 mmol) and (±)-*tert*-butyl 7-chlorohepta-2,3-dienoate (98 mg, 0.45 mmol), using 10% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 13:1 dr. After purification by flash chromatography (silica gel, hexanes:ethyl acetate/95:5→85:15), the title compound was isolated as a mixture of diastereomers (white solid, 166 mg, 91% yield) in 89% ee (major diastereomer).

HPLC analysis of the product (major diastereomer): CHIRALPAK AD-H column; hexanes:2-propanol/98:2, 1.0 mL/min flow-rate; retention times: 4.6 min (major), 5.8 min (minor).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR (major diastereomer, $CDCl_3$, 400 MHz): δ 7.71 (m, 2H, H_o^{Ar2}), 7.35 (t, J = 8.0 Hz, 1H, H_p^{Ar1}), 7.28 – 7.15 (m, 4H, H_m^{Ar1}, H_m^{Ar2}), 7.07 (m, 1H, H_p^{Ar2}), 6.81 (dd, J = 15.8, 10.1 Hz, 1H, *H3*), 5.47 (d, J = 15.8 Hz, 1H, *H2*), 3.51 (m, 2H, H7), 3.23 – 2.96 (m, 6H, *H4*, *H2′*, C*H*$(CH_3)_2$), 2.26 (sep, J = 7.0 Hz, 1H, C*H*$(CH_3)_2$), 1.83 – 1.62 (m, 8H, *H5*, *H6*, *H3′*), 1.41 (s, 9H, C(CH_3)$_3$), 1.29, 1.23, 0.96, 0.48 (4×d, J = 7.0; 7.2; 6.8; 7.0 Hz, 12H, CH(CH_3)$_2$).

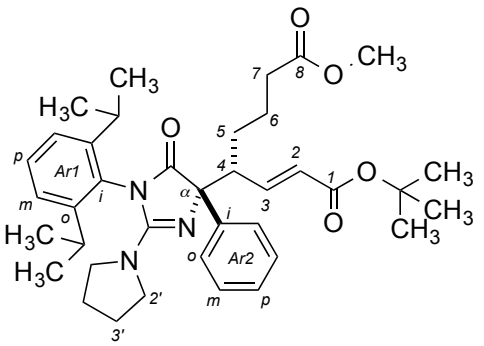
^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 183.1 (*C*=O), 165.6 (*C1*), 154.5 (*C*=N), 147.9 (*C3*), 147.08, 147.05 (C_o^{Ar1}), 140.9 (C_i^{Ar2}), 130.7 (C_i^{Ar1}), 130.0 (C_p^{Ar1}), 127.9 (C_m^{Ar2}), 127.2 (C_p^{Ar2}), 126.7 (C_o^{Ar2}), 125.7 (*C2*), 124.2, 124.1 (C_m^{Ar1}), 80.1 (*C*$(CH_3)_3$), 76.0 (*Cα*), 51.1 (*C4*), 47.9 (*C2′*), 45.2 (*C7*), 30.8 (*C6*), 29.3, 28.4 (CH(CH$_3$)$_2$), 28.3 (C(*C*H$_3$)$_3$), 27.1 (*C5*), 25.4 (CH(*C*H$_3$)$_2$), 25.3 (*C3′*), 23.9, 23.0, 22.6 (CH(*C*H$_3$)$_2$).

FT-IR (major diastereomer, neat): 2965, 2869, 1713, 1615, 1447, 1420, 1349, 1310, 1250, 1162, 1141, 910, 728 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 89% ee): –44.6 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 606.3462 ([M+H]$^+$, $C_{36}H_{49}ClN_3O_3^+$ calcd. 606.3457).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 17:1 dr. The product was isolated as a mixture of diastereomers (white solid, 163 mg, 90% yield) in 94% ee (major diastereomer).



1-(*Tert*-butyl) 8-methyl (*R*,*E*)-4-((*R*)-1-(2,6-diisopropylphenyl)-5-oxo-4-phenyl-2-(pyrrolidin-1-yl)-4,5-dihydro-1*H*-imidazol-4-yl)oct-2-enedioate (Table 4, entry 4). The title compound was prepared according to General Procedure B from (±)-3-(2,6-diisopropylphenyl)-5-phenyl-2-(pyrrolidin-1-yl)-3,5-dihydro-4*H*-imidazol-4-one (117 mg, 0.30 mmol) and (±)-1-(*tert*-butyl) 8-methyl octa-2,3-dienedioate (108 mg, 0.45 mmol), using 10% of (*R*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 16:1 dr. After purification by flash chromatography (silica gel, hexanes:diethyl ether/80:20→50:50), the title compound was isolated as a mixture of diastereomers (white solid, 131 mg, 69% yield) in 94% ee (major diastereomer).

HPLC analysis of the product (major diastereomer): CHIRALPAK AD-H column; hexanes:2-propanol/95:5, 1.0 mL/min flow-rate; retention times: 4.3 min (major), 6.0 min (minor).

For the purpose of NMR, IR, and optical rotation analysis, a sample of pure major diastereomer was obtained by column chromatography.

^{1}H NMR (major diastereomer, $CDCl_3$, 400 MHz): δ 7.71 (m, 2H, H_o^{Ar2}), 7.34 (t, J = 7.9 Hz, 1H, H_p^{Ar1}), 7.29 – 7.16 (m, 4H, H_m^{Ar1}, H_m^{Ar2}), 7.07 (m, 1H, H_p^{Ar2}), 6.79 (dd, J = 15.6, 10.0 Hz, 1H, *H3*), 5.50 (d, J = 15.6 Hz, 1H, *H2*), 3.65 (s, 3H, OCH_3), 3.21 – 2.92 (m, 6H, *H4*, *H2′*, $CH(CH_3)_2$), 2.34 – 2.19 (m, 3H, *H7*, $CH(CH_3)_2$), 1.80 – 1.46 (m, 8H, *H5*, *H6*, *H3′*), 1.41 (s, 9H, $C(CH_3)_3$), 1.27, 1.23, 0.95, 0.51 (4×d, J = 6.9; 7.0; 6.8; 6.8 Hz, 12H, $CH(CH_3)_2$).

^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 183.0 (*C*=O), 173.9 (*C8*), 165.7 (*C1*), 154.4 (*C*=N), 147.4, 147.1 (C_o^{Ar1}), 147.0 (*C3*), 140.9 (C_i^{Ar2}), 130.7 (C_i^{Ar1}), 130.0 (C_p^{Ar1}), 127.9 (C_m^{Ar2}), 127.2 (C_p^{Ar2}), 126.7 (C_o^{Ar2}), 125.8 (*C2*), 124.1 (C_m^{Ar1}), 80.0 ($C(CH_3)_3$), 76.0 (*Cα*), 51.6 (OCH_3), 51.4 (*C4*), 47.9 (*C2′*), 34.3 (*C7*), 29.2, 28.9 ($CH(CH_3)_2$), 28.4 (*C5*), 28.3 ($C(CH_3)_3$), 25.3 (*C3′*, $CH(CH_3)_2$; overlapped), 23.9 ($CH(CH_3)_2$), 23.2 (*C6*), 23.0, 22.7 ($CH(CH_3)_2$).

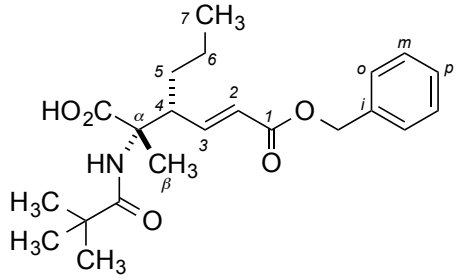
FT-IR (major diastereomer, neat): 2966, 2870, 1739, 1715, 1617, 1447, 1420, 1365, 1349, 1254, 1165, 1144, 911, 729 cm^{-1}.

$[\alpha]^{25}_D$ (major diastereomer, 94% ee): –47.7 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 630.3905 ($[M+H]^+$, $C_{38}H_{52}N_3O_5^+$ calcd. 630.3902).

The second run was performed with (*S*)–**1**. ^{1}H NMR analysis of the unpurified reaction mixture showed that the product was formed in 20:1 dr. The product was isolated as a mixture of diastereomers (white solid, 141 mg, 75% yield) in 95% ee (major diastereomer).

V. Derivatization of the Products



Hydrolysis: (2*S*,3*R*,*E*)-6-(benzyloxy)-2-methyl-6-oxo-2-pivalamido-3-propylhex-4-enoic acid (eq 5). Benzyl (*R*,*E*)-4-((*S*)-2-(*tert*-butyl)-4-methyl-5-oxo-4,5-dihydrooxazol-4-yl)hept-2-enoate (0.15 mmol, 56 mg; Table 3, entry 1; >20:1 dr, 90% ee; from (*R*)–**1**) was stirred in aqueous HCl (1.0 M, 12 mL) at 80 °C for 6 h. Next, the reaction mixture was allowed to cool to r.t., and then it was extracted with diethyl ether (3 × 5 mL). The combined organic layers were dried over anhydrous Mg_2SO_4 and filtered, and then the solvent was removed under reduced pressure. The residue was dried under high vacuum to afford the product (colorless oil, 55 mg, 95% yield, >20:1 dr, 90% ee).

HPLC analysis of the product: CHIRALPAK AD-H column; 0.1% trifluoroacetic acid in hexanes:2-propanol/95:5, 1.0 mL/min flow-rate; retention times: 9.7 min (minor), 12.0 min (major).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 – 7.30 (m, 5H, -C_6H_5), 6.76 (dd, *J* = 15.7, 10.4 Hz, 1H, *H3*), 6.06 (s, 1H, N*H*), 5.97 (d, *J* = 15.7 Hz, 1H, *H2*), 5.18 (m, 2H, OCH_2Ph), 3.05 (td, *J* = 10.4, 2.6 Hz, 1H, *H4*), 1.57 (s, 3H, *Hβ*), 1.54 – 1.12 (m, 4H, *H5*, *H6*), 1.19 (s, 9H, (CH_3)$_3$C), 0.88 (t, *J* = 7.2 Hz, 3H, *H7*).

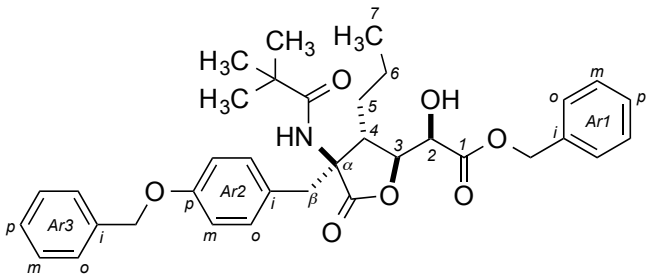
^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.9 (*C*ONH), 174.5 (*C*O_2H), 165.8 (*C1*), 147.2 (*C3*), 136.0 (C_i), 128.7, 128.3 (C_m, C_o), 128.4 (C_p), 125.1 (*C2*), 66.5 (OCH_2Ph), 62.9 (*Cα*), 48.0 (*C4*), 39.3 ((CH_3)$_3$*C*), 30.7 (*C5*), 27.5 ((*C*H_3)$_3$C), 21.0 (*C6*), 20.9 (*Cβ*), 14.0 (*C7*).

FT-IR (neat): 3399, 2959, 2872, 1723, 1624, 1518, 1457, 1379, 1266, 1224, 1157, 986, 736, 697 cm^{-1}.

$[\alpha]^{25}_D$ (90% ee): +24.4 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 388.2135 ([M-H]$^-$, $C_{22}H_{30}NO_5^-$ calcd. 388.2129).

The second run was performed starting from benzyl (*S*,*E*)-4-((*R*)-2-(*tert*-butyl)-4-methyl-5-oxo-4,5-dihydrooxazol-4-yl)hept-2-enoate (>20:1 dr, 92% ee; from (*S*)–**1**). The product was isolated in >20:1 dr (colorless oil, 57 mg, 98% yield, 91% ee).



Diastereoselective dihydroxylation/lactonization: Benzyl (*R*)-2-((2*S*,3*S*,4*S*)-4-(4-(benzyloxy)benzyl)-5-oxo-4-pivalamido-3-propyltetrahydrofuran-2-yl)-2-hydroxyacetate (eq

6). $NaIO_4$ (32 mg, 0.15 mmol) and aqueous H_2SO_4 (1.0 M, 4 drops) were added to water (deionized, 80 μL), and the mixture was stirred until it was homogeneous. $RuCl_3 \cdot 2H_2O$ (3 small crystals) was added, followed by ethyl acetate (160 μL). After 5 min of stirring at rt, acetonitrile was added (320 μL), and the mixture was cooled to 0 °C in an ice-water bath. A solution of benzyl (*R*,*E*)-4-((*S*)-4-(4-(benzyloxy)benzyl)-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)hept-2-enoate (55 mg, 0.10 mmol; Table 3, entry 5; 14:1 dr, 90% ee; from (*R*)–**1**) in ethyl acetate (240 μL), pre-cooled to 0 °C, was added, and the reaction mixture was stirred for 5 min at 0 °C (a longer reaction time leads to the formation of over-oxidation products). The reaction was quenched by the addition of aqueous $Na_2S_2O_3$ (saturated, 500 μL), followed by aqueous $NaHCO_3$ (saturated, 500 μL). The mixture was extracted with ethyl acetate (3 × 1 mL), and the combined organic layers were dried over anhydrous $MgSO_4$. The organic layer was filtered, the solvent was removed under reduced pressure, and the product was purified by chromatography (silica gel, hexanes:ethyl acetate/70:30→50:50). The title compound was isolated in >10:1 ratio of the major diastereomer to the sum of the other diastereomers (white solid, 44 mg, 76%, 91% ee).

HPLC analysis of the product: CHIRALPAK IC column; hexanes:2-propanol/65:35, 1.0 mL/min flow-rate; retention times: 16.9 min (minor), 24.7 min (major).

^{1}H NMR (major diastereomer, $CDCl_3$, 400 MHz): δ 7.46 – 7.29 (m, 10H, -$C_6H_5^{Ar1}$, -$C_6H_5^{Ar3}$), 7.10 (m, 2H, H_o^{Ar2}), 6.93 (m, 2H, H_m^{Ar2}), 5.80 (s, 1H, N*H*), 5.31 and 5.21 (2×d, *J* = 12.2 Hz, 2H, CO_2CH_2Ph), 5.05 – 5.01 (m, 2H, OCH_2Ph), 4.33 – 4.23 (m, 2H, *H2*, *H3*), 3.61 (m, 1H, *H4*), 3.30 (d, *J* = 7.7 Hz, O*H*), 3.09 (d, *J* = 14.0 Hz, 1H, *Hβ*), 2.92 (d, *J* = 14.0 Hz, 1H, *Hβ′*), 1.86 (m, 1H, *H5*), 1.56 – 1.34 (m, 3H, *H5′*, *H6*), 1.07 (s, 9H, $(CH_3)_3C$), 0.97 (t, *J* = 7.1 Hz, 3H, *H7*).

^{13}C NMR (major diastereomer, $CDCl_3$, 100 MHz): δ 178.2 (*C*ONH), 174.1 (*C*=O), 171.3 (*C1*), 158.6 (C_p^{Ar2}), 136.8 (C_i^{Ar3}), 135.0 (C_i^{Ar1}), 131.7 (C_o^{Ar2}), 128.84, 128.81, 128.74, 128.68, 128.2 (C_o^{Ar1}, C_m^{Ar1}, C_m^{Ar3}, C_p^{Ar1}, C_p^{Ar3}), 127.7 (C_o^{Ar3}), 125.1 (C_i^{Ar2}), 115.2 (C_m^{Ar2}), 81.8 (*C3*), 70.13, 70.06 (*C2*, OCH_2Ph), 68.1 (CO_2CH_2Ph), 61.9 (*Cα*), 41.0 (*C4*), 39.0 ($(CH_3)_3C$), 35.6 (*Cβ*), 28.7 (*C5*), 27.4 ($(CH_3)_3C$), 21.0 (*C6*), 14.5 (*C7*).

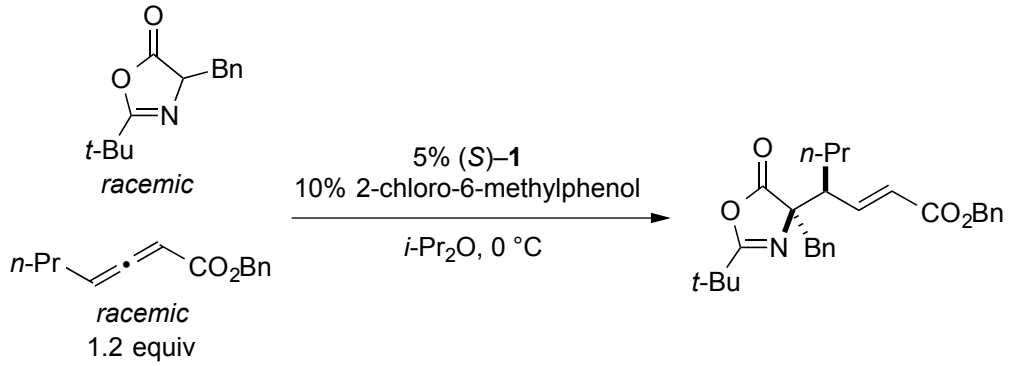
FT-IR (neat): 3381, 2960, 2871, 1778, 1749, 1660, 1611, 1516, 1455, 1246, 1179, 1139, 1117, 1025, 752, 697 cm^{-1}.

$[\alpha]^{25}_D$ (91% ee): +48.4 (c = 1.0, $CHCl_3$).

HRMS (ESI/APCI): *m*/*z* 588.2961 ($[M+H]^+$, $C_{35}H_{42}NO_7^+$ calcd. 588.2956).

The second run was performed starting from benzyl (*S*,*E*)-4-((*R*)-4-(4-(benzyloxy)benzyl)-2-(*tert*-butyl)-5-oxo-4,5-dihydrooxazol-4-yl)hept-2-enoate (13:1 dr, 90% ee; from (*S*)–**1**). The product was isolated in >10:1 ratio of the major diastereomer to the sum of the other diastereomers (white solid, 43 mg, 73%, >98% ee).

VI. Mechanistic Studies



Enantiomeric excess of the substrates and of the product during the course of the reaction (Table 2, entry 1). In a nitrogen-filled glovebox, stock solutions in diisopropyl ether (anhydrous) of (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one (0.36 M, 220 μL, 0.080 mmol), (*S*)–**1** (0.01 M, 400 μL, 0.004 mmol, 5%), and 2-chloro-6-methylphenol (1.00 M, 80 μL, 0.0080 mmol) were mixed in an oven-dried vial. Next, 1-fluorotetradecane (internal standard; 21.3 μL, 17.3 mg, 0.080 mmol) was added, and the resulting mixture was cooled to 0 °C. A stock solution of (±)-benzyl hepta-2,3-dienoate (0.96 M in anhydrous diisopropyl ether, 100 μL, 0.096 mmol), pre-cooled to 0 °C, was added, and the resulting reaction mixture was stirred at 0 °C. Aliquots (~50 μL) were taken from the reaction mixture at different reaction times and were immediately quenched by addition into vials that contained a solution of *tert*-butyl hydroperoxide (5.0-6.0 M in decane; 5 μL). After the aliquots were concentrated under reduced pressure, the composition of each of the aliquots was determined by ^{1}H NMR analysis. Pure samples of the unreacted substrates and of the product were obtained by preparative TLC (silica gel; hexanes:ethyl acetate/9:1), and their ee was determined by chiral HPLC or SFC analysis: product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/98:2, 1.0 mL/min flow-rate, retention times: 6.2 min (major), 8.4 min (minor); oxazol-5(4*H*)-one: CHIRALPAK AD-H column; hexanes:2-propanol/99.7:0.3, 1.0 mL/min flow-rate, retention times: 8.8 min, 9.5 min; allenoate: SFC/CHIRALPAK AD-H column; CO_2:2-propanol/98:2, 3.5 mL/min flow-rate, 100 bar outlet pressure, retention times: 6.7 min (major), 8.1 min (minor).

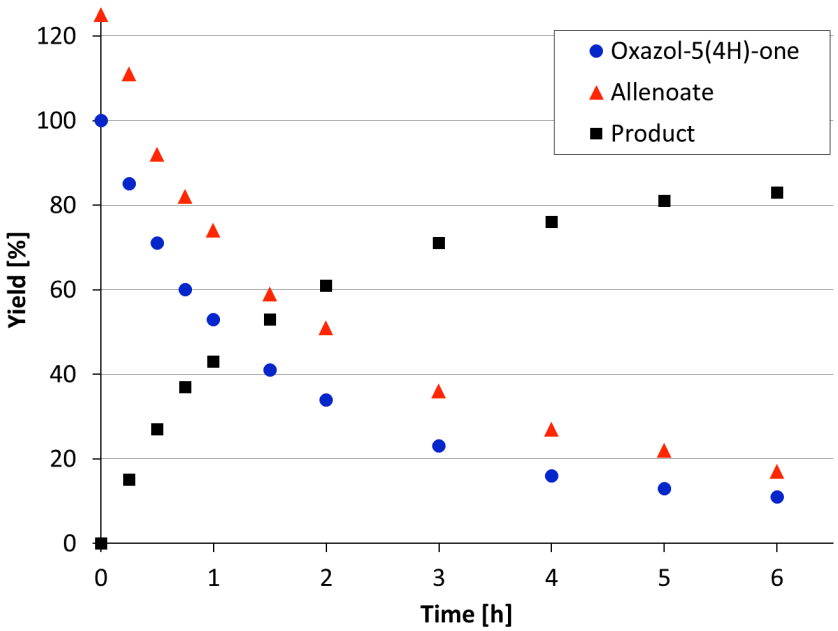


Figure S1. Composition of the reaction mixture as a function of time.

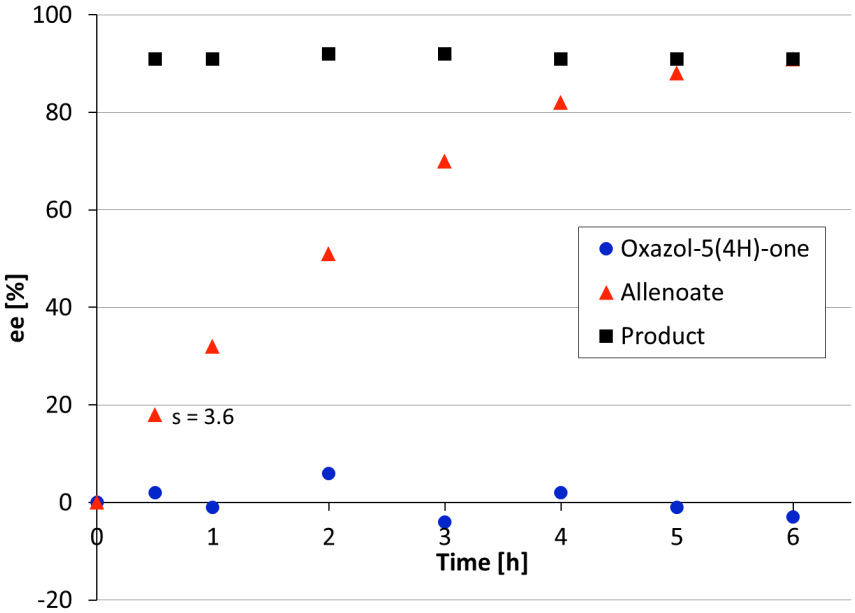
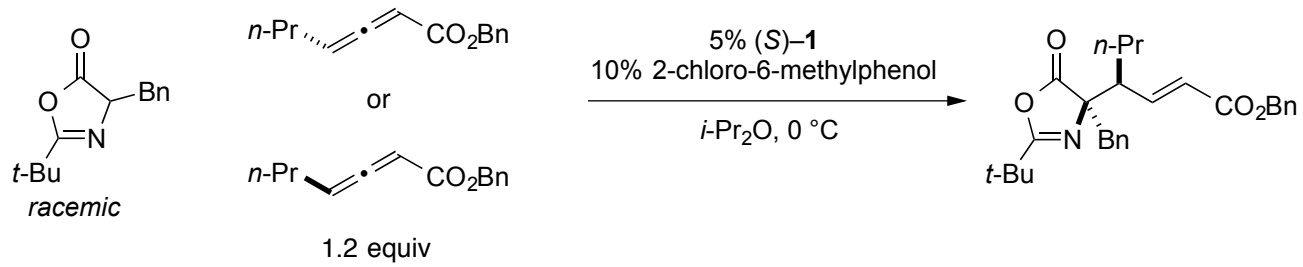


Figure S2. Enantiomeric excess of the substrates and of the product as a function of time. The initial selectivity factor for the kinetic resolution of the allenoate (calculated for the 30-min timepoint) is 3.6.



Reactions with enantiopure allenoates. The enantiomers of (±)-benzyl hepta-2,3-dienoate were separated (>98% ee) by preparative HPLC: CHIRALPAK AD-H column (21 × 250 mm, particle size 5 μm); hexanes:2-propanol/98:2, 10.0 mL/min flow-rate, retention times: 13.4 min, 17.1 min. After the separation, the enantiomeric allenoates were passed through a short plug of silica, using hexanes:diethyl ether/9:1 as the eluent. Fast-moving enantiomer: $[\alpha]^{25}_{D}$= +123 (c = 1.0, $CHCl_3$), (*S*)-configuration according to the Brewster rule;[15] slow-moving enantiomer: $[\alpha]^{25}_{D}$= –119 (c = 1.0, $CHCl_3$), (*R*)-configuration.

In a nitrogen-filled glovebox, diisopropyl ether (anhydrous) stock solutions of (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one (0.36 M, 220 μL, 0.080 mmol), (*S*)–**1** (0.01 M, 400 μL, 0.004 mmol, 5%), and 2-chloro-6-methylphenol (1.00 M, 80 μL, 0.0080 mmol) were mixed in an oven-dried vial. Next, 1-fluorotetradecane (internal standard; 21.3 μL, 17.3 mg, 0.080 mmol) was added, and the resulting mixture was cooled to 0 °C. A stock solution of benzyl (*S*)-hepta-2,3-dienoate (0.96 M in anhydrous diisopropyl ether, 100 μL, 0.096 mmol), pre-cooled to 0 °C, was added, and the resulting reaction mixture was stirred at 0 °C. Aliquots (~50 μL) were taken from the reaction mixture at different reaction times and were immediately quenched by addition into vials that contained a solution of *tert*-butyl hydroperoxide (5.0-6.0 M in decane; 5 μL). After the aliquots were concentrated under reduced pressure, the composition of each of the aliquots was determined by ^{1}H NMR analysis. Pure samples of the unreacted substrates and of the product were obtained by preparative TLC (silica gel; hexanes:ethyl acetate/9:1), and their ee was determined by chiral HPLC or SFC analysis: product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/98:2, 1.0 mL/min flow-rate, retention times: 6.2 min (major), 8.4 min (minor); allenoate: SFC/CHIRALPAK AD-H column; CO_2:2-propanol/98:2, 3.5 mL/min flow-rate, 100 bar outlet pressure, retention times: 6.7 min (major), 8.1 min (minor).

The reaction with benzyl (*R*)-hepta-2,3-dienoate was carried out in a similar manner, also with (*S*)–**1**.

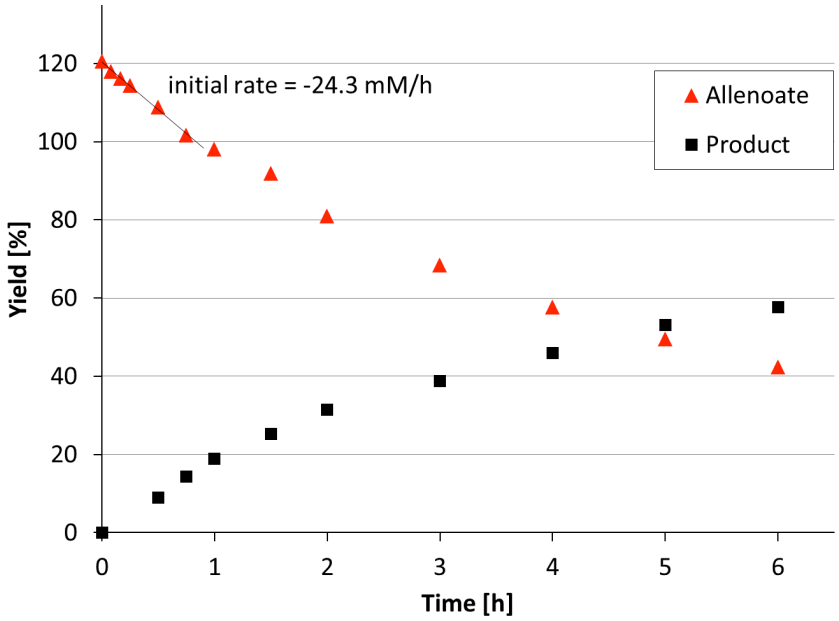


Figure S3. Consumption of benzyl (*S*)-hepta-2,3-dienoate and formation of the product using (*S*)–**1**.

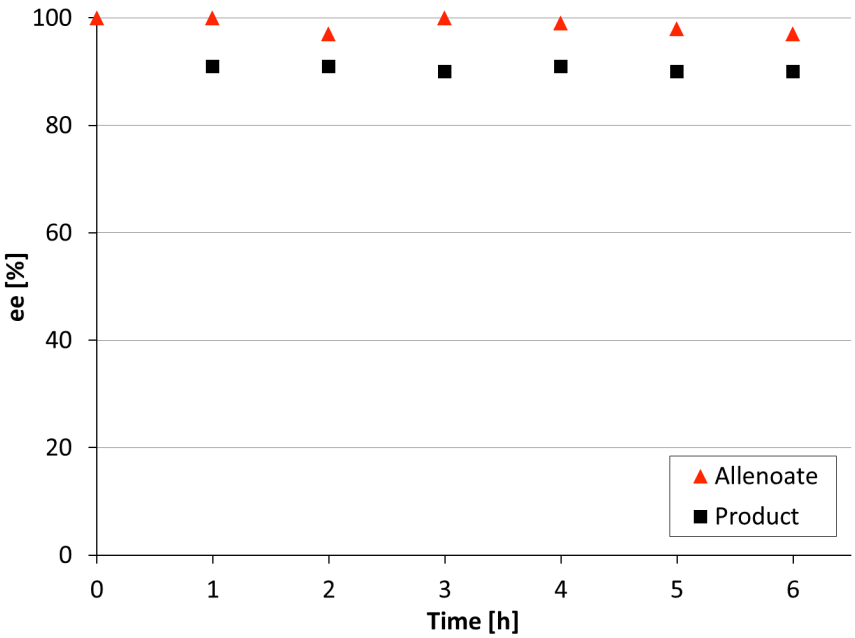


Figure S4. Enantiomeric excess of benzyl hepta-2,3-dienoate and of the product in the reaction of benzyl (*S*)-hepta-2,3-dienoate using (*S*)–**1**.

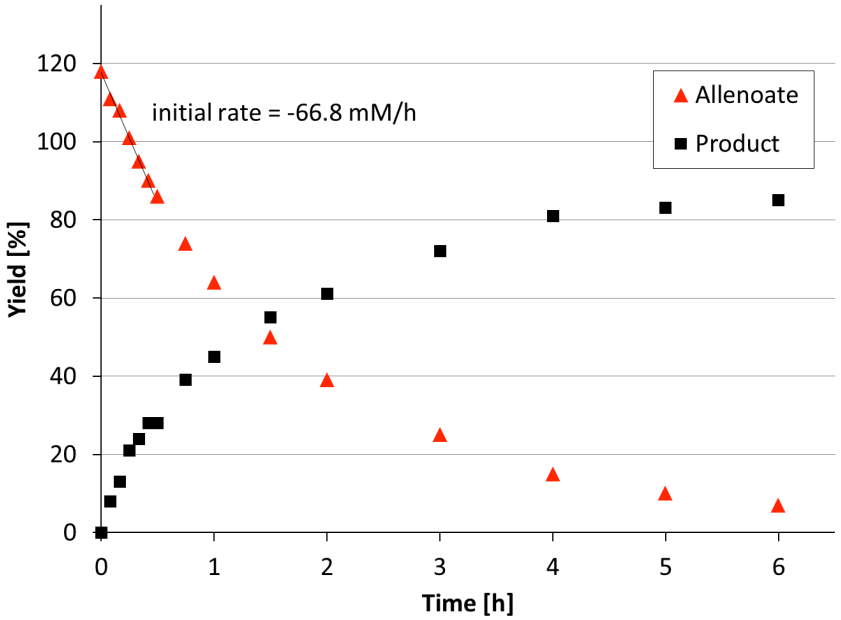


Figure S5. Consumption of benzyl (*R*)-hepta-2,3-dienoate and formation of the product using (*S*)–**1**.

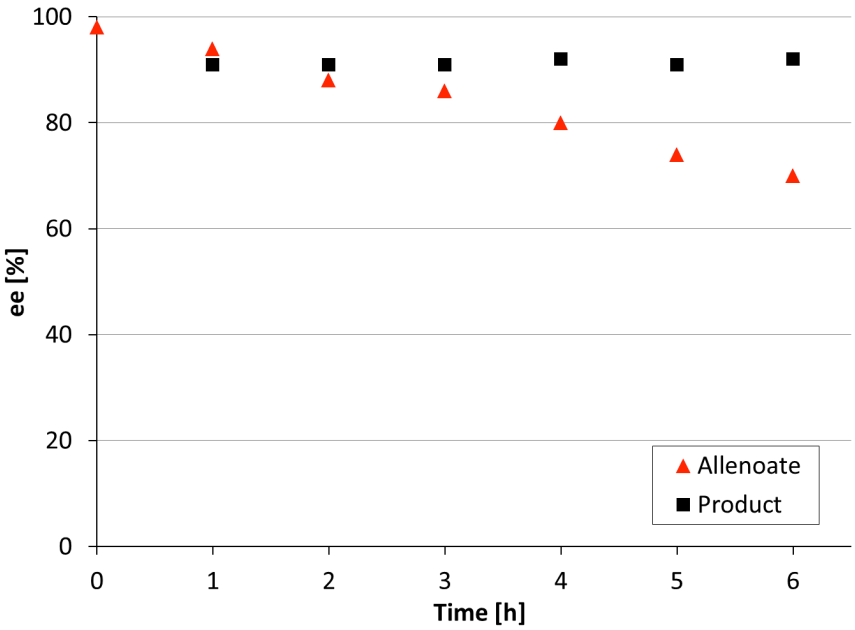
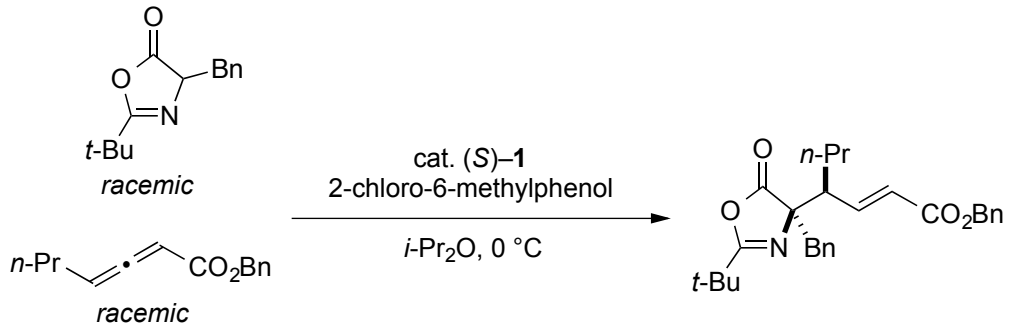


Figure S6. Enantiomeric excess of benzyl hepta-2,3-dienoate and of the product in the reaction of benzyl (*R*)-hepta-2,3-dienoate using (*S*)–**1**.

The relative rates of reaction of the two enantiomers of benzyl hepta-2,3-dienoate calculated on the basis of the initial rates is 2.7. This is in a qualitative agreement with the value of 3.6 obtained in the direct competition experiment (kinetic resolution) described above.



Determination of the rate law. The rate law was determined by the method of initial rates, following the formation of product up to ~20% conversion of the limiting reagent/formation of the product. Racemic allenoate and racemic nucleophile were used. The reactions were carried out with a total volume of 500 μL (neglecting the volume of the internal standard).

In a nitrogen-filled glovebox, appropriate amounts of diisopropyl ether (anhydrous) stock solutions of (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one (0.50 M), (*S*)–**1** (0.025 M), 2-chloro-6-methylphenol (0.10 M), and diisopropyl ether (anhydrous) were mixed in an oven-dried vial. Next, 1-fluorotetradecane (internal standard; 13.4 μL, 10.8 mg, 0.050 mmol) was added, and the mixture was cooled to 0 °C. An appropriate amount of a stock solution of (±)-benzyl hepta-2,3-dienoate (0.50 M) in diisopropyl ether (anhydrous), pre-cooled to 0 °C, was added, and the reaction mixture was stirred at 0 °C. Aliquots (~50 μL) were taken from the reaction mixture every 5 min over a 30-min period and were immediately quenched by addition into vials that contained a solution of *tert*-butyl hydroperoxide (5.0-6.0 M in decane; 5 μL). After the aliquots were concentrated under reduced pressure, the composition of each of the aliquots was determined by ^{1}H NMR analysis.

Order in allenoate. Initial concentrations: 5.0 mM (±0.5 mM) in (*S*)–**1**; 10 mM (±1 mM) in 2-chloro-6-methylphenol; 100 mM (±10 mM) in nucleophile; 49-222 mM in allenoate.

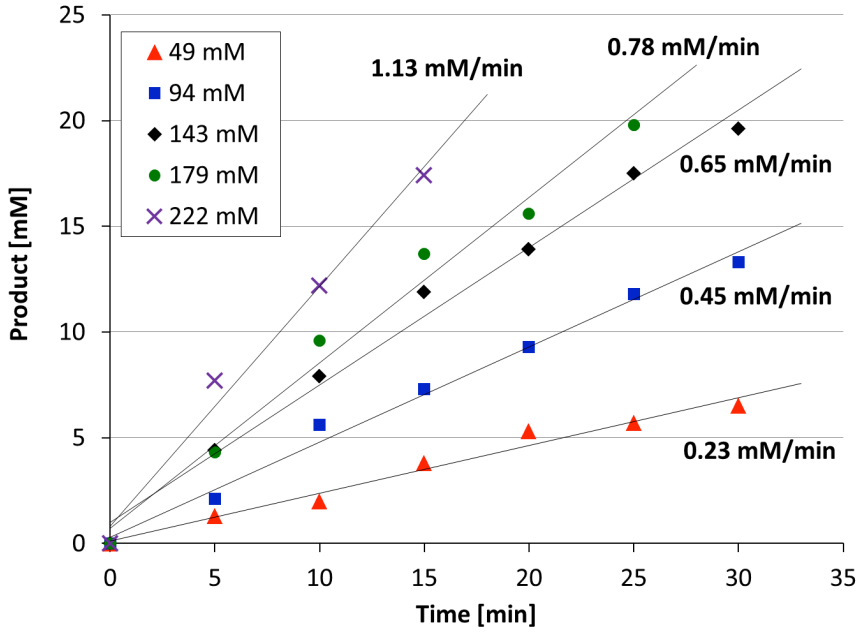


Figure S7. Initial rates with varying initial concentrations of the allenoate.

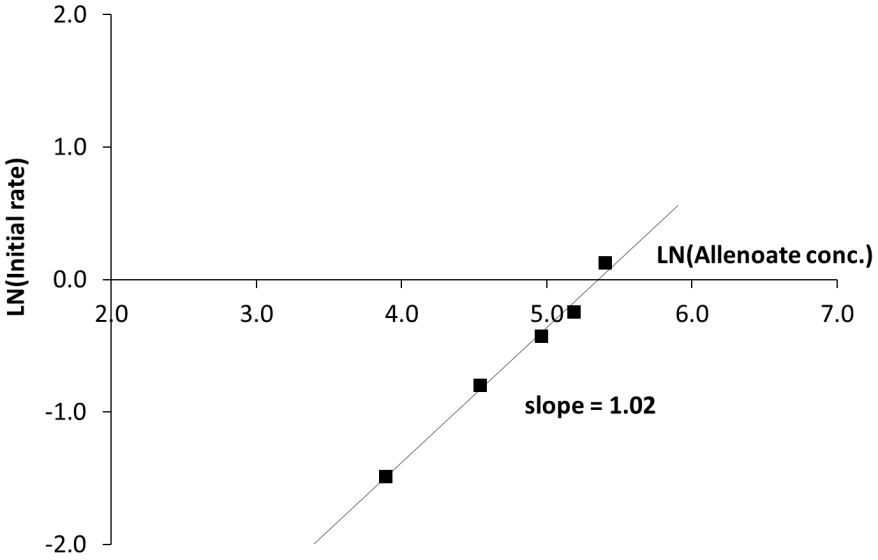


Figure S8. Plot of ln(initial rate) vs. ln([allenoate]).

Order in nucleophile. Initial concentrations: 5.0 mM (±0.5 mM) in (*S*)–**1**; 10 mM (±1 mM) in 2-chloro-6-methylphenol; 41-232 mM in nucleophile; 100 mM (±10 mM) in allenoate.

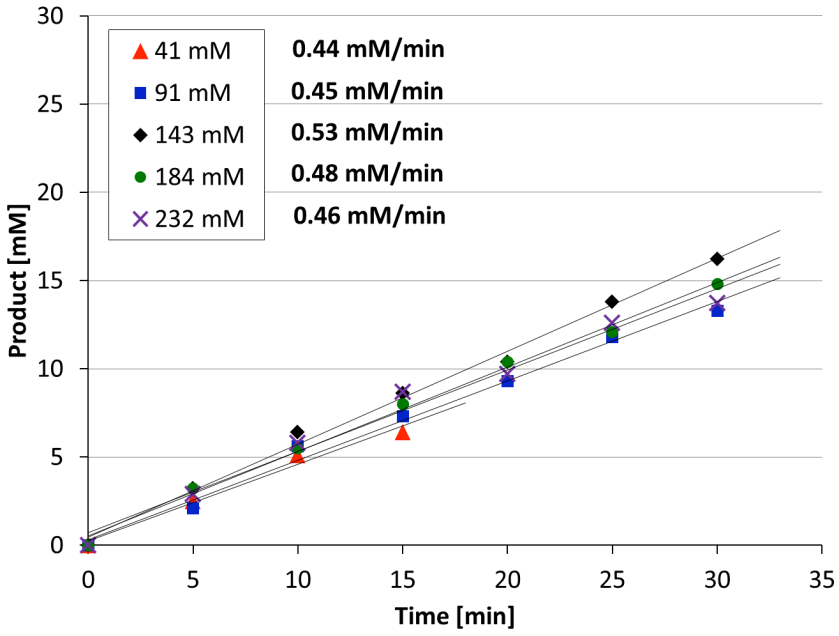


Figure S9. Initial rates with varying initial concentrations of the nucleophile.

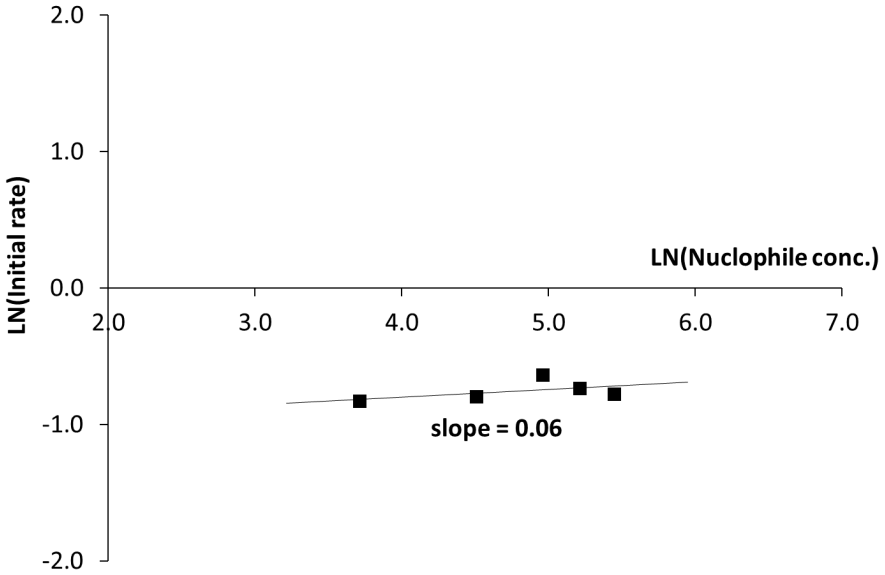


Figure S10. Plot of ln(initial rate) vs. ln([nucleophile]).

Order in catalyst. Initial concentrations: 2.5-12.5 mM (±0.25-1.25 mM) in (*S*)–**1**; 10 mM (±1 mM) in 2-chloro-6-methylphenol; 100 mM (±10 mM) in nucleophile; 100 mM (±10 mM) in allenoate.

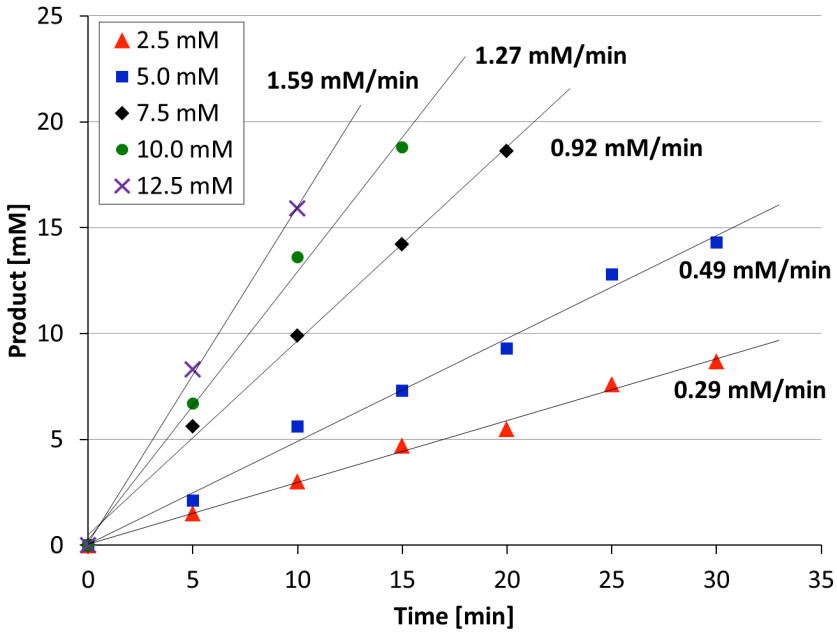


Figure S11. Initial rates with varying initial concentrations of the catalyst.

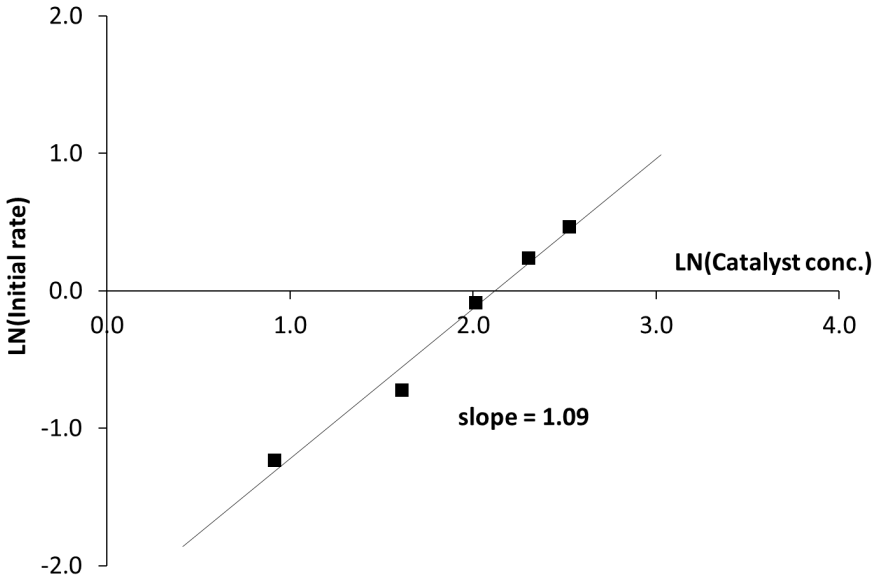


Figure S12. Plot of ln(initial rate) vs. ln([catalyst]).

Order in 2-chloro-6-methylphenol. Initial concentrations: 5.0 mM (±0.5 mM) in (*S*)–**1**; 5-25 mM (±0.5-2.5 mM) in 2-chloro-6-methylphenol; 100 mM (±10 mM) in nucleophile; 100 mM (±10 mM) in allenoate.

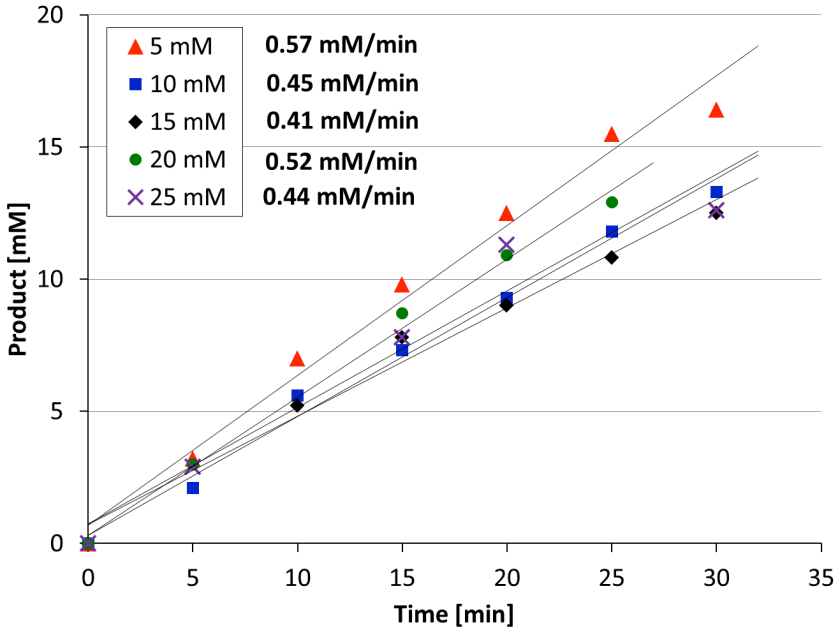


Figure S13. Initial Initial rates with varying initial concentrations of 2-chloro-6-methylphenol.

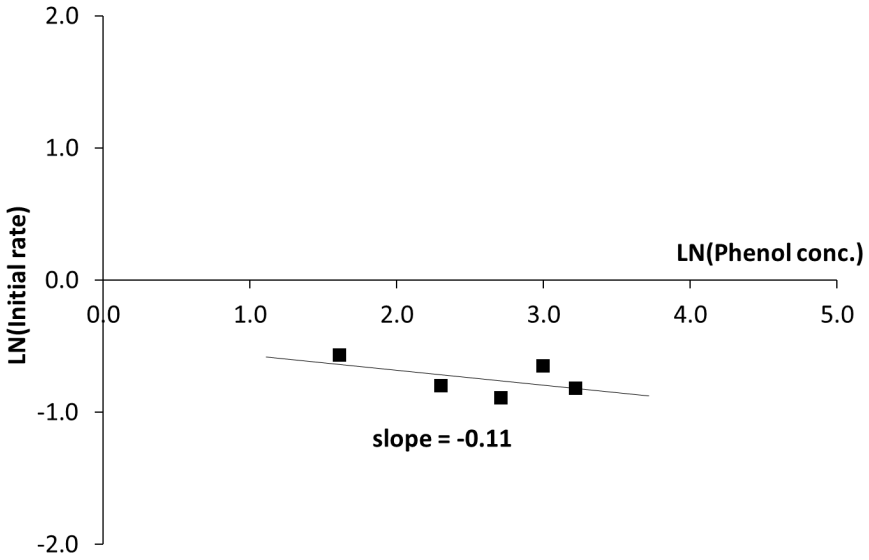
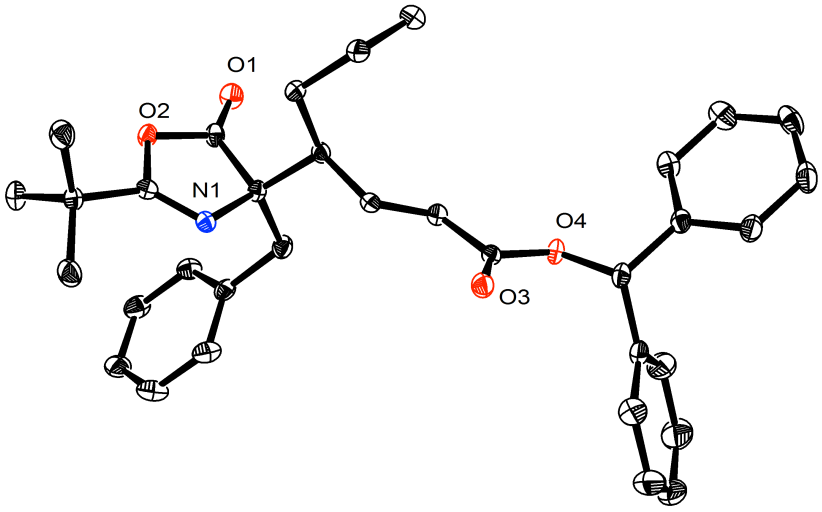


Figure S14. Plot of ln(initial rate) vs. ln([2-chloro-6-methylphenol]).

Determination of the catalyst resting state. In a nitrogen-filled glovebox, diisopropyl ether (anhydrous) stock solutions of (±)-4-benzyl-2-(*tert*-butyl)oxazol-5(4*H*)-one (0.36 M, 220 μL, 0.080 mmol), (*S*)–**1** (0.01 M, 400 μL, 0.004 mmol, 5%), and 2-chloro-6-methylphenol (1.00 M, 80 μL, 0.008 mmol) were mixed in an oven-dried 5 mm NMR tube equipped with a PTFE-lined septum cap. Next, 1-fluorotetradecane (internal standard; 21.3 μL, 17.3 mg, 0.080 mmol) was added. A sealed capillary tube, containing a solution of H_3PO_4 (^{31}P NMR external standard; 2% w/w in D_2O), was inserted into the NMR tube. The NMR tube was capped, removed from the glovebox, and inserted into the NMR magnet with the probe temperature set to 5 °C. After 10 min, the NMR tube was removed from the magnet, and a stock solution of (±)-benzyl hepta-2,3-dienoate (0.96 M in anhydrous diisopropyl ether, 100 μL, 0.096 mmol), pre-cooled to 0 °C in an ice-water bath, was added via syringe. The NMR tube was shaken to ensure complete mixing of the solution and returned into the magnet. ^{31}P NMR (^{1}H-decoupled) and ^{1}H NMR (with the suppression of solvent peaks) spectra were taken alternately every 15 min over the first 2 h, and then every 30 min over the following 3 h. After a total reaction time of 5 h, the conversion reached >80% (determined by ^{1}H NMR spectroscopy), and the reaction was quenched by an injection of *tert*-butyl hydroperoxide solution (5.0-6.0 M in decane; 50 μL). Over the entire duration of the reaction, the only ^{31}P NMR signal observed was the one corresponding to the free phosphine catalyst (δ 6.0). A sample of the reaction product was isolated through preparative TLC (silica gel; hexanes:ethyl acetate/9:1), and it was determined to have 91% ee, similar to the preparative reactions at 0 °C described above. HPLC analysis of the product (major diastereomer): CHIRALPAK IC column; hexanes:2-propanol/98:2, 1.0 mL/min flow-rate, retention times: 6.2 min (major), 8.4 min (minor).

VII. X-Ray Crystallographic Data, including Determination of Stereochemistry



(Table 2, entry 3; obtained with (*S*)-**1**)

X-ray quality crystals were grown by slow evaporation of a solution of the compound in hexanes. A suitable crystal was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Photon diffractometer with filtered Cu-Kα radiation at a temperature of 100 K. Using Olex2,[16] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package[17] using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S–1. Crystal data and structure refinement for crystal_01.

Identification code	crystal_01	
Empirical formula	$C_{34}H_{37}NO_4$	
Formula weight	523.64	
Temperature	100.15 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 15.8254(4) Å	α= 90°.
	b = 6.0257(2) Å	β= 115.5408(13) °.
	c = 16.6449(5) Å	γ = 90 °.
Volume	1432.13(7) $Å^3$	
Z	2	
Density (calculated)	1.214 Mg/m^3	
Absorption coefficient	0.624 mm^{-1}	
F(000)	560	
Crystal size	0.24 x 0.2 x 0.18 mm^3	
Theta range for data collection	2.942 to 79.184°.	
Index ranges	-20<=h<=20, -7<=k<=7, -21<=l<=21	
Reflections collected	34506	
Independent reflections	6107 [R(int) = 0.0460]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7542 and 0.6876	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6107 / 1 / 356	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0298, wR2 = 0.0653	
R indices (all data)	R1 = 0.0339, wR2 = 0.0672	
Absolute structure parameter	0.04(7)	
Largest diff. peak and hole	0.142 and -0.177 $e/Å^{-3}$	

Table S–2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for crystal_01. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-8172(1)	-9995(2)	-6851(1)	21(1)
O(2)	-9229(1)	-7648(2)	-7816(1)	17(1)
O(3)	-6700(1)	-17(2)	-4037(1)	20(1)
O(4)	-5811(1)	-2551(2)	-3019(1)	17(1)
N(1)	-9178(1)	-4722(2)	-6929(1)	14(1)
C(1)	-8584(1)	-8280(3)	-6979(1)	16(1)
C(2)	-9540(1)	-5536(3)	-7704(1)	14(1)
C(3)	-8517(1)	-6386(3)	-6347(1)	14(1)
C(4)	-8813(1)	-7156(3)	-5619(1)	19(1)
C(5)	-9847(1)	-7659(3)	-5980(1)	17(1)
C(6)	-10205(1)	-9736(3)	-6318(1)	21(1)
C(7)	-11165(1)	-10121(3)	-6678(1)	25(1)
C(8)	-11774(1)	-8447(4)	-6712(1)	26(1)
C(9)	-11424(1)	-6373(3)	-6362(1)	28(1)
C(10)	-10466(1)	-5994(3)	-5997(1)	23(1)
C(11)	-7484(1)	-5574(3)	-5931(1)	15(1)
C(12)	-7178(1)	-4887(3)	-6661(1)	16(1)
C(13)	-6188(1)	-3914(3)	-6300(1)	19(1)
C(14)	-5429(1)	-5511(4)	-5704(1)	26(1)
C(15)	-7310(1)	-3694(3)	-5290(1)	15(1)
C(16)	-6752(1)	-3876(3)	-4426(1)	16(1)
C(17)	-6456(1)	-1917(3)	-3838(1)	15(1)
C(18)	-5291(1)	-809(3)	-2401(1)	17(1)
C(19)	-5726(1)	-327(3)	-1768(1)	20(1)
C(20)	-6189(1)	1661(4)	-1822(1)	29(1)
C(21)	-6583(2)	2111(4)	-1237(2)	38(1)
C(22)	-6512(2)	570(5)	-595(1)	40(1)
C(23)	-6057(2)	-1427(5)	-543(1)	38(1)
C(24)	-5659(1)	-1869(4)	-1124(1)	29(1)
C(25)	-4279(1)	-1557(3)	-1942(1)	17(1)
C(26)	-3618(1)	-72(3)	-1363(1)	22(1)
C(27)	-2673(1)	-637(4)	-962(1)	26(1)
C(28)	-2382(1)	-2679(4)	-1133(1)	27(1)
C(29)	-3029(1)	-4168(3)	-1694(1)	26(1)
C(30)	-3980(1)	-3611(3)	-2098(1)	21(1)
C(31)	-10256(1)	-4562(3)	-8558(1)	16(1)
C(32)	-10969(1)	-6365(3)	-9080(1)	22(1)
C(33)	-9730(1)	-3733(4)	-9089(1)	25(1)
C(34)	-10756(1)	-2634(3)	-8354(1)	24(1)

Table S–3. Bond lengths [Å] and angles [°] for crystal_01.

O(1)-C(1)	1.191(2)
O(2)-C(1)	1.3793(19)
O(2)-C(2)	1.4056(19)
O(3)-C(17)	1.208(2)
O(4)-C(17)	1.3584(19)
O(4)-C(18)	1.451(2)
N(1)-C(2)	1.264(2)
N(1)-C(3)	1.471(2)
C(1)-C(3)	1.525(2)
C(2)-C(31)	1.503(2)
C(3)-C(4)	1.547(2)
C(3)-C(11)	1.554(2)
C(4)-C(5)	1.511(2)
C(5)-C(6)	1.389(3)
C(5)-C(10)	1.394(3)
C(6)-C(7)	1.391(3)
C(7)-C(8)	1.380(3)
C(8)-C(9)	1.389(3)
C(9)-C(10)	1.388(3)
C(11)-C(12)	1.546(2)
C(11)-C(15)	1.498(2)
C(12)-C(13)	1.532(2)
C(13)-C(14)	1.525(3)
C(15)-C(16)	1.328(2)
C(16)-C(17)	1.476(2)
C(18)-C(19)	1.515(2)
C(18)-C(25)	1.516(2)
C(19)-C(20)	1.387(3)
C(19)-C(24)	1.388(3)
C(20)-C(21)	1.390(3)
C(21)-C(22)	1.385(4)
C(22)-C(23)	1.386(4)
C(23)-C(24)	1.387(3)
C(25)-C(26)	1.398(2)
C(25)-C(30)	1.389(3)
C(26)-C(27)	1.391(3)
C(27)-C(28)	1.386(3)
C(28)-C(29)	1.378(3)
C(29)-C(30)	1.400(3)
C(31)-C(32)	1.537(2)
C(31)-C(33)	1.536(2)
C(31)-C(34)	1.524(2)
C(1)-O(2)-C(2)	105.37(13)

C(17)-O(4)-C(18)	117.28(14)
C(2)-N(1)-C(3)	106.77(13)
O(1)-C(1)-O(2)	122.05(15)
O(1)-C(1)-C(3)	130.97(15)
O(2)-C(1)-C(3)	106.94(13)
O(2)-C(2)-C(31)	113.10(14)
N(1)-C(2)-O(2)	117.15(14)
N(1)-C(2)-C(31)	129.73(15)
N(1)-C(3)-C(1)	103.75(12)
N(1)-C(3)-C(4)	110.51(13)
N(1)-C(3)-C(11)	113.04(13)
C(1)-C(3)-C(4)	111.22(14)
C(1)-C(3)-C(11)	106.83(13)
C(4)-C(3)-C(11)	111.21(13)
C(5)-C(4)-C(3)	113.02(13)
C(6)-C(5)-C(4)	121.64(16)
C(6)-C(5)-C(10)	118.67(16)
C(10)-C(5)-C(4)	119.67(17)
C(5)-C(6)-C(7)	120.26(17)
C(8)-C(7)-C(6)	120.64(18)
C(7)-C(8)-C(9)	119.68(18)
C(10)-C(9)-C(8)	119.66(18)
C(9)-C(10)-C(5)	121.07(18)
C(12)-C(11)-C(3)	111.11(13)
C(15)-C(11)-C(3)	112.95(13)
C(15)-C(11)-C(12)	109.50(14)
C(13)-C(12)-C(11)	114.05(13)
C(14)-C(13)-C(12)	113.55(16)
C(16)-C(15)-C(11)	122.72(16)
C(15)-C(16)-C(17)	121.68(16)
O(3)-C(17)-O(4)	123.76(15)
O(3)-C(17)-C(16)	127.08(15)
O(4)-C(17)-C(16)	109.09(14)
O(4)-C(18)-C(19)	110.09(13)
O(4)-C(18)-C(25)	107.13(14)
C(19)-C(18)-C(25)	113.90(13)
C(20)-C(19)-C(18)	120.40(17)
C(20)-C(19)-C(24)	119.41(17)
C(24)-C(19)-C(18)	120.20(17)
C(19)-C(20)-C(21)	120.4(2)
C(22)-C(21)-C(20)	119.9(2)
C(21)-C(22)-C(23)	119.76(19)
C(22)-C(23)-C(24)	120.2(2)
C(23)-C(24)-C(19)	120.2(2)
C(26)-C(25)-C(18)	118.11(16)

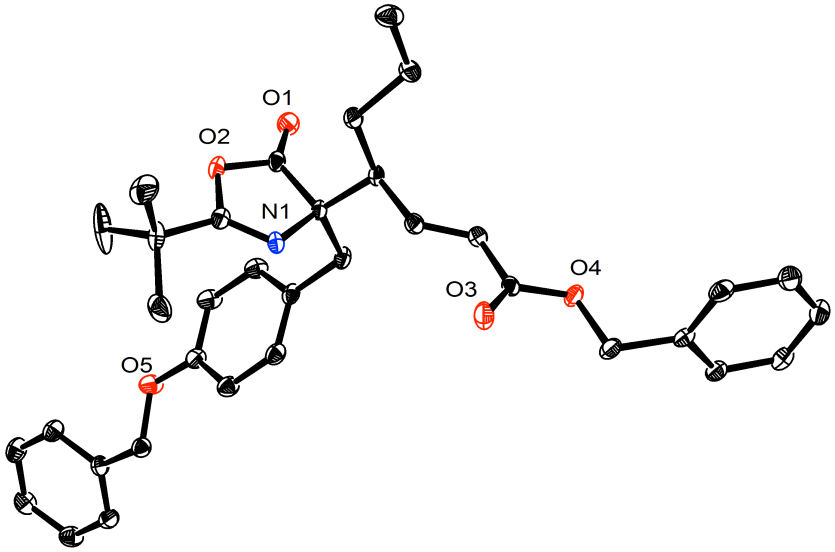
C(30)-C(25)-C(18)	122.78(15)
C(30)-C(25)-C(26)	119.07(16)
C(27)-C(26)-C(25)	120.27(19)
C(28)-C(27)-C(26)	120.13(18)
C(29)-C(28)-C(27)	120.13(18)
C(28)-C(29)-C(30)	120.01(19)
C(25)-C(30)-C(29)	120.38(17)
C(2)-C(31)-C(32)	109.19(14)
C(2)-C(31)-C(33)	107.23(14)
C(2)-C(31)-C(34)	109.78(14)
C(33)-C(31)-C(32)	110.71(14)
C(34)-C(31)-C(32)	109.87(15)
C(34)-C(31)-C(33)	110.02(15)

Table S–4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for crystal_01. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	24(1)	14(1)	22(1)	1(1)	7(1)	3(1)
O(2)	19(1)	14(1)	14(1)	-1(1)	4(1)	2(1)
O(3)	18(1)	20(1)	18(1)	-1(1)	5(1)	2(1)
O(4)	17(1)	19(1)	11(1)	-1(1)	2(1)	-2(1)
N(1)	13(1)	15(1)	14(1)	1(1)	5(1)	0(1)
C(1)	16(1)	15(1)	14(1)	3(1)	4(1)	-1(1)
C(2)	15(1)	12(1)	17(1)	1(1)	8(1)	0(1)
C(3)	15(1)	14(1)	12(1)	0(1)	4(1)	0(1)
C(4)	19(1)	22(1)	14(1)	1(1)	6(1)	-2(1)
C(5)	21(1)	20(1)	14(1)	1(1)	9(1)	-2(1)
C(6)	23(1)	18(1)	24(1)	-1(1)	13(1)	0(1)
C(7)	27(1)	24(1)	28(1)	-8(1)	16(1)	-8(1)
C(8)	21(1)	34(1)	29(1)	-5(1)	16(1)	-4(1)
C(9)	27(1)	26(1)	39(1)	-1(1)	22(1)	3(1)
C(10)	28(1)	20(1)	29(1)	-4(1)	19(1)	-3(1)
C(11)	13(1)	15(1)	14(1)	0(1)	4(1)	2(1)
C(12)	16(1)	18(1)	14(1)	-2(1)	6(1)	1(1)
C(13)	18(1)	23(1)	19(1)	-3(1)	9(1)	-2(1)
C(14)	18(1)	34(1)	24(1)	-2(1)	9(1)	3(1)
C(15)	12(1)	17(1)	16(1)	-1(1)	6(1)	0(1)
C(16)	15(1)	17(1)	15(1)	0(1)	6(1)	0(1)
C(17)	12(1)	20(1)	13(1)	0(1)	6(1)	0(1)
C(18)	16(1)	18(1)	14(1)	-3(1)	4(1)	-4(1)
C(19)	16(1)	25(1)	15(1)	-5(1)	4(1)	-4(1)
C(20)	26(1)	31(1)	30(1)	-5(1)	11(1)	1(1)
C(21)	30(1)	43(1)	44(1)	-16(1)	19(1)	1(1)
C(22)	29(1)	64(2)	33(1)	-19(1)	20(1)	-9(1)
C(23)	38(1)	56(2)	27(1)	-1(1)	20(1)	-7(1)
C(24)	32(1)	34(1)	24(1)	1(1)	15(1)	1(1)
C(25)	16(1)	24(1)	11(1)	2(1)	5(1)	-3(1)
C(26)	21(1)	27(1)	16(1)	-3(1)	7(1)	-5(1)
C(27)	19(1)	39(1)	16(1)	0(1)	3(1)	-8(1)
C(28)	16(1)	40(1)	21(1)	12(1)	4(1)	0(1)
C(29)	23(1)	26(1)	27(1)	9(1)	10(1)	3(1)
C(30)	19(1)	21(1)	21(1)	2(1)	6(1)	-1(1)
C(31)	16(1)	17(1)	14(1)	2(1)	4(1)	1(1)
C(32)	21(1)	21(1)	17(1)	0(1)	2(1)	-1(1)
C(33)	23(1)	31(1)	20(1)	8(1)	8(1)	1(1)
C(34)	22(1)	23(1)	23(1)	1(1)	4(1)	7(1)

Table S–5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for crystal_01.

	x	y	z	U(eq)
H(4A)	-8454	-8504	-5328	22
H(4B)	-8652	-5983	-5160	22
H(6)	-9793	-10897	-6304	25
H(7)	-11403	-11551	-6902	30
H(8)	-12430	-8711	-6973	32
H(9)	-11839	-5220	-6373	33
H(10)	-10229	-4576	-5755	28
H(11)	-7080	-6845	-5595	18
H(12A)	-7211	-6203	-7029	20
H(12B)	-7627	-3774	-7053	20
H(13A)	-6055	-3483	-6808	23
H(13B)	-6163	-2553	-5957	23
H(14A)	-5479	-6909	-6022	39
H(14B)	-5509	-5800	-5161	39
H(14C)	-4812	-4851	-5545	39
H(15)	-7612	-2314	-5511	18
H(16)	-6539	-5305	-4181	19
H(18)	-5324	568	-2749	20
H(20)	-6238	2722	-2262	35
H(21)	-6900	3476	-1279	46
H(22)	-6776	879	-190	47
H(23)	-6016	-2497	-109	46
H(24)	-5340	-3231	-1080	35
H(26)	-3815	1328	-1243	27
H(27)	-2227	378	-569	32
H(28)	-1736	-3053	-864	32
H(29)	-2829	-5572	-1806	31
H(30)	-4425	-4644	-2482	25
H(32A)	-10646	-7583	-9222	33
H(32B)	-11444	-5731	-9632	33
H(32C)	-11272	-6931	-8717	33
H(33A)	-9391	-4971	-9197	38
H(33B)	-9285	-2574	-8749	38
H(33C)	-10179	-3124	-9660	38
H(34A)	-11218	-1998	-8912	37
H(34B)	-10297	-1494	-8018	37
H(34C)	-11073	-3169	-7999	37



(Table 3, entry 5; obtained with (*S*)-**1**)

X-ray quality crystals were grown by slow evaporation of a solution of the compound in hexanes. A suitable crystal was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Photon diffractometer with filtered Cu-Kα radiation at a temperature of 100 K. Using Olex2,[16] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package[17] using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S–6. Crystal data and structure refinement for crystal_02.

Identification code	crystal_02	
Empirical formula	$C_{35}H_{39}NO_5$	
Formula weight	553.67	
Temperature	100.05 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.6834(4) Å	α= 90°.
	b = 16.2787(7) Å	β= 90 °.
	c = 21.3864(9) Å	γ = 90 °.
Volume	3023.1(2) $Å^3$	
Z	4	
Density (calculated)	1.217 Mg/m^3	
Absorption coefficient	0.644 mm^{-1}	
F(000)	1184	
Crystal size	0.84 x 0.24 x 0.2 mm^3	
Theta range for data collection	3.412 to 70.193°.	
Index ranges	-10<=h<=10, -19<=k<=19, -26<=l<=25	
Reflections collected	73998	
Independent reflections	5754 [R(int) = 0.0594]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.5075	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5754 / 0 / 374	
Goodness-of-fit on F^2	1.138	
Final R indices [I>2sigma(I)]	R1 = 0.0373, wR2 = 0.0922	
R indices (all data)	R1 = 0.0375, wR2 = 0.0923	
Absolute structure parameter	0.06(2)	
Largest diff. peak and hole	0.192 and -0.346 $e/Å^{-3}$	

Table S–7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for crystal_02. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-15294(2)	-11208(1)	1545(1)	23(1)
O(2)	-16726(1)	-10072(1)	1688(1)	19(1)
O(3)	-11589(2)	-7938(1)	-282(1)	25(1)
O(4)	-9546(1)	-8741(1)	-484(1)	19(1)
O(5)	-14185(2)	-8895(1)	4170(1)	25(1)
N(1)	-15179(2)	-9059(1)	1313(1)	15(1)
C(1)	-15419(2)	-10478(1)	1500(1)	17(1)
C(2)	-14313(2)	-9831(1)	1248(1)	15(1)
C(3)	-13915(2)	-10023(1)	554(1)	16(1)
C(4)	-15378(2)	-10180(1)	160(1)	19(1)
C(5)	-15024(2)	-10575(1)	-472(1)	23(1)
C(6)	-16434(2)	-10620(1)	-896(1)	27(1)
C(7)	-13032(2)	-9316(1)	278(1)	17(1)
C(8)	-11658(2)	-9355(1)	6(1)	17(1)
C(9)	-10962(2)	-8603(1)	-261(1)	16(1)
C(10)	-8740(2)	-8011(1)	-721(1)	20(1)
C(11)	-7469(2)	-8298(1)	-1139(1)	17(1)
C(12)	-5970(2)	-8374(1)	-914(1)	19(1)
C(13)	-4806(2)	-8670(1)	-1298(1)	21(1)
C(14)	-5130(2)	-8891(1)	-1910(1)	24(1)
C(15)	-6615(2)	-8797(1)	-2142(1)	26(1)
C(16)	-7774(2)	-8502(1)	-1762(1)	22(1)
C(17)	-16444(2)	-9232(1)	1568(1)	16(1)
C(18)	-17727(2)	-8665(1)	1762(1)	22(1)
C(19)	-17055(2)	-7808(1)	1874(1)	32(1)
C(20)	-18472(4)	-8979(2)	2364(1)	55(1)
C(21)	-18902(2)	-8636(2)	1227(1)	35(1)
C(22)	-12847(2)	-9793(1)	1658(1)	18(1)
C(23)	-13171(2)	-9541(1)	2325(1)	17(1)
C(24)	-13735(2)	-10103(1)	2764(1)	21(1)
C(25)	-14084(2)	-9868(1)	3370(1)	24(1)
C(26)	-13843(2)	-9056(1)	3558(1)	20(1)
C(27)	-13293(2)	-8482(1)	3129(1)	22(1)
C(28)	-12973(2)	-8731(1)	2520(1)	20(1)
C(29)	-13728(2)	-8121(1)	4420(1)	19(1)
C(30)	-13960(2)	-8150(1)	5118(1)	18(1)
C(31)	-12899(2)	-7764(1)	5506(1)	22(1)
C(32)	-13112(3)	-7752(1)	6153(1)	26(1)
C(33)	-14391(3)	-8125(1)	6413(1)	26(1)
C(34)	-15439(2)	-8525(1)	6029(1)	27(1)
C(35)	-15221(2)	-8541(1)	5385(1)	22(1)

Table S–8. Bond lengths [Å] and angles [°] for crystal_02.

O(1)-C(1)	1.198(2)
O(2)-C(1)	1.373(2)
O(2)-C(17)	1.413(2)
O(3)-C(9)	1.213(2)
O(4)-C(9)	1.338(2)
O(4)-C(10)	1.469(2)
O(5)-C(26)	1.369(2)
O(5)-C(29)	1.425(2)
N(1)-C(2)	1.470(2)
N(1)-C(17)	1.259(2)
C(1)-C(2)	1.524(2)
C(2)-C(3)	1.554(2)
C(2)-C(22)	1.548(2)
C(3)-C(4)	1.545(2)
C(3)-C(7)	1.503(2)
C(4)-C(5)	1.528(2)
C(5)-C(6)	1.526(3)
C(7)-C(8)	1.328(2)
C(8)-C(9)	1.481(2)
C(10)-C(11)	1.495(2)
C(11)-C(12)	1.393(2)
C(11)-C(16)	1.399(2)
C(12)-C(13)	1.388(3)
C(13)-C(14)	1.387(3)
C(14)-C(15)	1.389(3)
C(15)-C(16)	1.381(3)
C(17)-C(18)	1.504(2)
C(18)-C(19)	1.531(3)
C(18)-C(20)	1.529(3)
C(18)-C(21)	1.535(3)
C(22)-C(23)	1.510(2)
C(23)-C(24)	1.398(3)
C(23)-C(28)	1.394(3)
C(24)-C(25)	1.385(3)
C(25)-C(26)	1.398(3)
C(26)-C(27)	1.393(3)
C(27)-C(28)	1.394(3)
C(29)-C(30)	1.509(2)
C(30)-C(31)	1.389(3)
C(30)-C(35)	1.389(3)
C(31)-C(32)	1.396(3)
C(32)-C(33)	1.382(3)
C(33)-C(34)	1.387(3)

C(34)-C(35)	1.391(3)
C(1)-O(2)-C(17)	105.60(13)
C(9)-O(4)-C(10)	115.13(14)
C(26)-O(5)-C(29)	117.81(14)
C(17)-N(1)-C(2)	107.23(14)
O(1)-C(1)-O(2)	121.94(16)
O(1)-C(1)-C(2)	131.07(16)
O(2)-C(1)-C(2)	106.98(14)
N(1)-C(2)-C(1)	103.58(13)
N(1)-C(2)-C(3)	112.11(13)
N(1)-C(2)-C(22)	109.43(13)
C(1)-C(2)-C(3)	109.80(13)
C(1)-C(2)-C(22)	110.14(14)
C(22)-C(2)-C(3)	111.49(13)
C(4)-C(3)-C(2)	111.77(13)
C(7)-C(3)-C(2)	109.50(14)
C(7)-C(3)-C(4)	109.36(14)
C(5)-C(4)-C(3)	112.75(15)
C(6)-C(5)-C(4)	112.61(16)
C(8)-C(7)-C(3)	126.45(16)
C(7)-C(8)-C(9)	119.81(16)
O(3)-C(9)-O(4)	123.34(16)
O(3)-C(9)-C(8)	124.69(16)
O(4)-C(9)-C(8)	111.97(15)
O(4)-C(10)-C(11)	107.76(14)
C(12)-C(11)-C(10)	120.78(16)
C(12)-C(11)-C(16)	119.01(16)
C(16)-C(11)-C(10)	120.21(16)
C(13)-C(12)-C(11)	120.47(16)
C(14)-C(13)-C(12)	120.01(17)
C(13)-C(14)-C(15)	119.79(17)
C(16)-C(15)-C(14)	120.32(17)
C(15)-C(16)-C(11)	120.35(17)
O(2)-C(17)-C(18)	114.49(14)
N(1)-C(17)-O(2)	116.52(15)
N(1)-C(17)-C(18)	128.98(16)
C(17)-C(18)-C(19)	108.60(15)
C(17)-C(18)-C(20)	109.92(16)
C(17)-C(18)-C(21)	107.78(16)
C(19)-C(18)-C(21)	109.99(16)
C(20)-C(18)-C(19)	109.6(2)
C(20)-C(18)-C(21)	110.9(2)
C(23)-C(22)-C(2)	113.14(14)
C(24)-C(23)-C(22)	121.38(16)
C(28)-C(23)-C(22)	121.07(16)

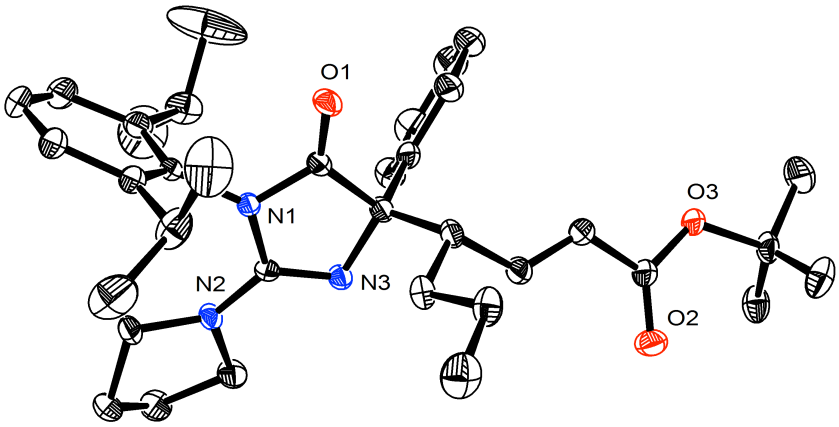
C(28)-C(23)-C(24)	117.51(16)
C(25)-C(24)-C(23)	121.63(17)
C(24)-C(25)-C(26)	119.81(17)
O(5)-C(26)-C(25)	115.08(16)
O(5)-C(26)-C(27)	125.13(17)
C(27)-C(26)-C(25)	119.79(17)
C(26)-C(27)-C(28)	119.22(17)
C(23)-C(28)-C(27)	122.00(16)
O(5)-C(29)-C(30)	107.77(14)
C(31)-C(30)-C(29)	119.21(16)
C(31)-C(30)-C(35)	119.01(16)
C(35)-C(30)-C(29)	121.77(16)
C(30)-C(31)-C(32)	120.67(18)
C(33)-C(32)-C(31)	119.88(18)
C(32)-C(33)-C(34)	119.71(17)
C(33)-C(34)-C(35)	120.36(19)
C(30)-C(35)-C(34)	120.33(18)

Table S–9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for crystal_02. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	25(1)	22(1)	22(1)	3(1)	3(1)	-2(1)
O(2)	14(1)	24(1)	18(1)	2(1)	4(1)	-1(1)
O(3)	26(1)	21(1)	28(1)	2(1)	12(1)	2(1)
O(4)	13(1)	19(1)	24(1)	1(1)	4(1)	-2(1)
O(5)	35(1)	27(1)	14(1)	-1(1)	2(1)	-11(1)
N(1)	13(1)	20(1)	12(1)	0(1)	0(1)	4(1)
C(1)	14(1)	24(1)	12(1)	0(1)	1(1)	-1(1)
C(2)	11(1)	18(1)	14(1)	0(1)	2(1)	1(1)
C(3)	14(1)	19(1)	14(1)	0(1)	4(1)	0(1)
C(4)	18(1)	23(1)	14(1)	-2(1)	2(1)	-2(1)
C(5)	26(1)	25(1)	16(1)	-4(1)	3(1)	-3(1)
C(6)	35(1)	28(1)	17(1)	-1(1)	-2(1)	-9(1)
C(7)	18(1)	20(1)	13(1)	-1(1)	1(1)	0(1)
C(8)	18(1)	18(1)	15(1)	-1(1)	1(1)	0(1)
C(9)	15(1)	22(1)	11(1)	-4(1)	0(1)	-1(1)
C(10)	15(1)	19(1)	25(1)	1(1)	2(1)	-4(1)
C(11)	15(1)	16(1)	20(1)	2(1)	0(1)	-5(1)
C(12)	18(1)	20(1)	18(1)	2(1)	0(1)	-5(1)
C(13)	14(1)	23(1)	26(1)	4(1)	0(1)	-3(1)
C(14)	24(1)	26(1)	24(1)	0(1)	8(1)	-3(1)
C(15)	30(1)	30(1)	18(1)	0(1)	3(1)	-8(1)
C(16)	18(1)	27(1)	21(1)	2(1)	-5(1)	-6(1)
C(17)	15(1)	22(1)	12(1)	2(1)	-1(1)	0(1)
C(18)	16(1)	30(1)	20(1)	7(1)	6(1)	6(1)
C(19)	23(1)	35(1)	37(1)	-11(1)	-2(1)	12(1)
C(20)	62(2)	57(2)	45(1)	26(1)	42(1)	35(1)
C(21)	19(1)	38(1)	49(1)	0(1)	-9(1)	6(1)
C(22)	12(1)	26(1)	18(1)	1(1)	1(1)	1(1)
C(23)	10(1)	26(1)	16(1)	1(1)	-2(1)	1(1)
C(24)	24(1)	22(1)	18(1)	2(1)	-4(1)	-3(1)
C(25)	30(1)	24(1)	16(1)	4(1)	-4(1)	-7(1)
C(26)	20(1)	26(1)	13(1)	1(1)	-1(1)	-4(1)
C(27)	23(1)	23(1)	19(1)	1(1)	0(1)	-5(1)
C(28)	18(1)	25(1)	17(1)	3(1)	1(1)	-4(1)
C(29)	19(1)	21(1)	18(1)	0(1)	1(1)	-2(1)
C(30)	17(1)	18(1)	18(1)	1(1)	0(1)	3(1)
C(31)	20(1)	24(1)	23(1)	-1(1)	1(1)	-4(1)
C(32)	31(1)	27(1)	20(1)	-2(1)	-4(1)	-3(1)
C(33)	34(1)	27(1)	16(1)	2(1)	2(1)	2(1)
C(34)	25(1)	33(1)	23(1)	6(1)	5(1)	-2(1)
C(35)	18(1)	27(1)	21(1)	2(1)	-3(1)	-1(1)

Table S–10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for crystal_02.

	x	y	z	U(eq)
H(3)	-13253	-10525	540	19
H(4A)	-16081	-10543	397	22
H(4B)	-15915	-9652	90	22
H(5A)	-14209	-10253	-684	27
H(5B)	-14623	-11137	-403	27
H(6A)	-16153	-10888	-1290	40
H(6B)	-16810	-10064	-981	40
H(6C)	-17245	-10938	-689	40
H(7)	-13503	-8791	300	20
H(8)	-11124	-9863	-16	20
H(10A)	-8314	-7688	-369	24
H(10B)	-9463	-7658	-958	24
H(12)	-5743	-8223	-495	23
H(13)	-3787	-8722	-1141	26
H(14)	-4340	-9105	-2170	29
H(15)	-6833	-8937	-2564	31
H(16)	-8785	-8437	-1924	26
H(19A)	-16249	-7840	2194	48
H(19B)	-17872	-7438	2016	48
H(19C)	-16613	-7599	1483	48
H(20A)	-19007	-9498	2280	82
H(20B)	-19212	-8572	2518	82
H(20C)	-17674	-9070	2681	82
H(21A)	-18409	-8415	851	53
H(21B)	-19768	-8284	1346	53
H(21C)	-19280	-9193	1141	53
H(22A)	-12349	-10340	1659	22
H(22B)	-12114	-9397	1471	22
H(24)	-13882	-10659	2643	26
H(25)	-14485	-10259	3657	28
H(27)	-13138	-7927	3252	26
H(28)	-12608	-8336	2228	24
H(29A)	-14357	-7676	4235	23
H(29B)	-12632	-8013	4321	23
H(31)	-12020	-7506	5329	27
H(32)	-12378	-7489	6414	32
H(33)	-14553	-8107	6852	31
H(34)	-16311	-8789	6207	32
H(35)	-15938	-8822	5126	27



(Table 4, entry 1; obtained with (*S*)-**1**)

X-ray quality crystals were grown by slow evaporation of a solution of the compound in hexanes. A suitable crystal was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Photon diffractometer with filtered Cu-Kα radiation at a temperature of 100 K. Using Olex2,[16] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package[17] using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S–11. Crystal data and structure refinement for crystal_03.

Identification code	crystal_03	
Empirical formula	$C_{36}H_{49}N_3O_3$	
Formula weight	571.78	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 11.3063(4) Å	α = 90 °.
	b = 17.1064(6) Å	β = 90 °.
	c = 17.5636(6) Å	γ = 90 °.
Volume	3397.0(2) $Å^3$	
Z	4	
Density (calculated)	1.118 Mg/m^3	
Absorption coefficient	0.553 mm^{-1}	
F(000)	1240	
Crystal size	0.18 x 0.16 x 0.1 mm^3	
Theta range for data collection	3.607 to 79.180°.	
Index ranges	-14<=h<=14, -21<=k<=21, -21<=l<=22	
Reflections collected	87604	
Independent reflections	7330 [R(int) = 0.1050]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.7204	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7330 / 0 / 387	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0904	
R indices (all data)	R1 = 0.0379, wR2 = 0.0922	
Absolute structure parameter	-0.01(8)	
Largest diff. peak and hole	0.217 and -0.211 $e/Å^{-3}$	

Table S–12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for crystal_03. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-3812(1)	10540(1)	1918(1)	25(1)
O(2)	-539(1)	6916(1)	2302(1)	33(1)
O(3)	970(1)	7784(1)	2214(1)	25(1)
N(1)	-5102(1)	9818(1)	1184(1)	17(1)
N(2)	-5907(1)	8777(1)	421(1)	20(1)
N(3)	-4070(1)	8680(1)	1016(1)	19(1)
C(1)	-4057(1)	9954(1)	1564(1)	19(1)
C(2)	-3303(1)	9219(1)	1432(1)	19(1)
C(3)	-5034(1)	9056(1)	864(1)	16(1)
C(4)	-2219(2)	9457(1)	955(1)	22(1)
C(5)	-2090(2)	9183(1)	217(1)	29(1)
C(6)	-1114(2)	9407(1)	-223(1)	39(1)
C(7)	-280(2)	9910(1)	73(1)	39(1)
C(8)	-413(2)	10192(1)	805(1)	36(1)
C(9)	-1375(2)	9967(1)	1245(1)	29(1)
C(10)	-2952(1)	8898(1)	2232(1)	21(1)
C(11)	-4053(2)	8663(1)	2689(1)	23(1)
C(12)	-3799(2)	8515(1)	3528(1)	29(1)
C(13)	-4871(2)	8221(2)	3964(1)	41(1)
C(14)	-2107(2)	8223(1)	2186(1)	22(1)
C(15)	-939(2)	8280(1)	2247(1)	24(1)
C(16)	-178(2)	7578(1)	2254(1)	24(1)
C(17)	1907(2)	7207(1)	2388(1)	26(1)
C(18)	3033(2)	7680(1)	2258(2)	42(1)
C(19)	1793(2)	6976(1)	3215(1)	35(1)
C(20)	1872(2)	6517(1)	1849(1)	32(1)
C(21)	-5733(2)	8022(1)	34(1)	27(1)
C(22)	-6831(2)	7959(1)	-462(1)	33(1)
C(23)	-7779(2)	8334(1)	29(1)	31(1)
C(24)	-7149(2)	9033(1)	387(1)	26(1)
C(25)	-5910(1)	10440(1)	1003(1)	18(1)
C(26)	-6799(2)	10630(1)	1522(1)	23(1)
C(27)	-7571(2)	11234(1)	1327(1)	30(1)
C(28)	-7466(2)	11612(1)	633(1)	37(1)
C(29)	-6555(2)	11424(1)	139(1)	36(1)
C(30)	-5740(2)	10840(1)	321(1)	25(1)
C(31)	-4664(2)	10690(1)	-180(1)	34(1)
C(32)	-4986(4)	10494(2)	-992(2)	71(1)
C(33)	-3828(3)	11367(2)	-123(3)	100(2)
C(34)	-6920(2)	10210(1)	2276(1)	34(1)
C(35)	-6478(3)	10726(2)	2924(1)	57(1)
C(36)	-8190(2)	9937(2)	2422(2)	53(1)

Table S–13. Bond lengths [Å] and angles [°] for crystal_03.

O(1)-C(1)	1.212(2)
O(2)-C(16)	1.207(2)
O(3)-C(16)	1.347(2)
O(3)-C(17)	1.479(2)
N(1)-C(1)	1.377(2)
N(1)-C(3)	1.421(2)
N(1)-C(25)	1.438(2)
N(2)-C(3)	1.345(2)
N(2)-C(21)	1.472(2)
N(2)-C(24)	1.472(2)
N(3)-C(2)	1.461(2)
N(3)-C(3)	1.293(2)
C(1)-C(2)	1.537(2)
C(2)-C(4)	1.540(2)
C(2)-C(10)	1.558(2)
C(4)-C(5)	1.386(3)
C(4)-C(9)	1.389(3)
C(5)-C(6)	1.401(3)
C(6)-C(7)	1.377(3)
C(7)-C(8)	1.382(3)
C(8)-C(9)	1.388(3)
C(10)-C(11)	1.535(2)
C(10)-C(14)	1.501(2)
C(11)-C(12)	1.523(2)
C(12)-C(13)	1.520(3)
C(14)-C(15)	1.329(2)
C(15)-C(16)	1.479(2)
C(17)-C(18)	1.525(3)
C(17)-C(19)	1.510(3)
C(17)-C(20)	1.515(3)
C(21)-C(22)	1.521(3)
C(22)-C(23)	1.518(3)
C(23)-C(24)	1.527(2)
C(25)-C(26)	1.396(2)
C(25)-C(30)	1.393(2)
C(26)-C(27)	1.396(2)
C(26)-C(34)	1.512(3)
C(27)-C(28)	1.384(3)
C(28)-C(29)	1.385(3)
C(29)-C(30)	1.396(3)
C(30)-C(31)	1.524(3)
C(31)-C(32)	1.510(3)
C(31)-C(33)	1.497(3)

C(34)-C(35)	1.525(4)
C(34)-C(36)	1.532(3)
C(16)-O(3)-C(17)	120.28(14)
C(1)-N(1)-C(3)	107.45(13)
C(1)-N(1)-C(25)	121.81(13)
C(3)-N(1)-C(25)	128.75(13)
C(3)-N(2)-C(21)	118.68(14)
C(3)-N(2)-C(24)	128.19(14)
C(24)-N(2)-C(21)	111.71(13)
C(3)-N(3)-C(2)	106.84(13)
O(1)-C(1)-N(1)	125.76(15)
O(1)-C(1)-C(2)	128.89(15)
N(1)-C(1)-C(2)	105.34(13)
N(3)-C(2)-C(1)	105.20(13)
N(3)-C(2)-C(4)	111.48(14)
N(3)-C(2)-C(10)	112.32(13)
C(1)-C(2)-C(4)	107.86(13)
C(1)-C(2)-C(10)	107.07(13)
C(4)-C(2)-C(10)	112.43(13)
N(2)-C(3)-N(1)	120.94(14)
N(3)-C(3)-N(1)	114.86(14)
N(3)-C(3)-N(2)	124.17(14)
C(5)-C(4)-C(2)	120.21(16)
C(5)-C(4)-C(9)	118.93(17)
C(9)-C(4)-C(2)	120.83(17)
C(4)-C(5)-C(6)	120.38(19)
C(7)-C(6)-C(5)	120.1(2)
C(6)-C(7)-C(8)	119.63(19)
C(7)-C(8)-C(9)	120.4(2)
C(8)-C(9)-C(4)	120.5(2)
C(11)-C(10)-C(2)	110.91(13)
C(14)-C(10)-C(2)	112.62(14)
C(14)-C(10)-C(11)	110.12(14)
C(12)-C(11)-C(10)	113.36(14)
C(13)-C(12)-C(11)	113.08(16)
C(15)-C(14)-C(10)	124.91(16)
C(14)-C(15)-C(16)	121.28(16)
O(2)-C(16)-O(3)	125.16(16)
O(2)-C(16)-C(15)	124.50(16)
O(3)-C(16)-C(15)	110.33(14)
O(3)-C(17)-C(18)	102.30(14)
O(3)-C(17)-C(19)	108.23(15)
O(3)-C(17)-C(20)	111.85(15)
C(19)-C(17)-C(18)	110.70(18)
C(19)-C(17)-C(20)	113.25(17)

C(20)-C(17)-C(18)	109.96(17)
N(2)-C(21)-C(22)	102.56(15)
C(23)-C(22)-C(21)	102.80(15)
C(22)-C(23)-C(24)	103.60(16)
N(2)-C(24)-C(23)	103.26(14)
C(26)-C(25)-N(1)	119.08(15)
C(30)-C(25)-N(1)	117.77(15)
C(30)-C(25)-C(26)	123.12(16)
C(25)-C(26)-C(27)	117.54(17)
C(25)-C(26)-C(34)	121.75(15)
C(27)-C(26)-C(34)	120.70(17)
C(28)-C(27)-C(26)	120.59(19)
C(27)-C(28)-C(29)	120.45(18)
C(28)-C(29)-C(30)	120.91(19)
C(25)-C(30)-C(29)	117.23(18)
C(25)-C(30)-C(31)	121.66(17)
C(29)-C(30)-C(31)	120.97(18)
C(32)-C(31)-C(30)	113.0(2)
C(33)-C(31)-C(30)	109.56(19)
C(33)-C(31)-C(32)	112.9(3)
C(26)-C(34)-C(35)	110.46(19)
C(26)-C(34)-C(36)	112.09(19)
C(35)-C(34)-C(36)	111.0(2)

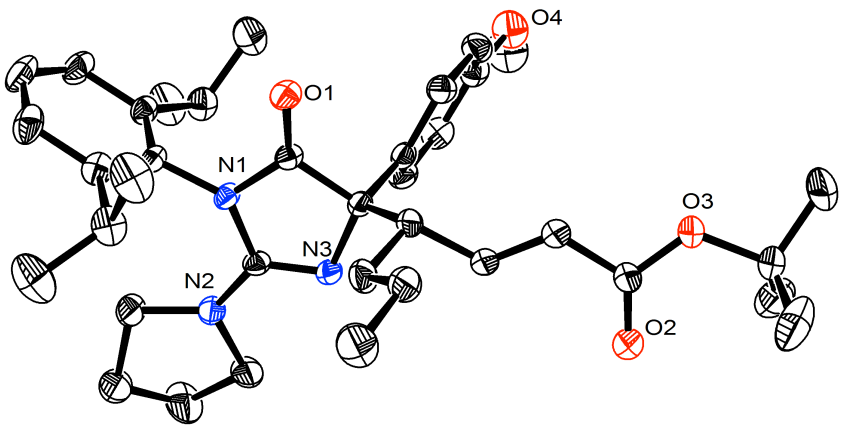
Table S–14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for crystal_03. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	21(1)	20(1)	34(1)	-9(1)	-5(1)	-1(1)
O(2)	22(1)	21(1)	56(1)	6(1)	3(1)	1(1)
O(3)	16(1)	22(1)	37(1)	6(1)	-3(1)	2(1)
N(1)	15(1)	15(1)	20(1)	-3(1)	-2(1)	1(1)
N(2)	18(1)	20(1)	23(1)	-6(1)	-6(1)	1(1)
N(3)	17(1)	17(1)	22(1)	-4(1)	-2(1)	1(1)
C(1)	15(1)	18(1)	23(1)	-1(1)	-1(1)	-1(1)
C(2)	16(1)	18(1)	23(1)	-4(1)	-2(1)	1(1)
C(3)	17(1)	16(1)	16(1)	-2(1)	1(1)	-2(1)
C(4)	16(1)	20(1)	29(1)	2(1)	0(1)	3(1)
C(5)	24(1)	32(1)	31(1)	-2(1)	4(1)	1(1)
C(6)	35(1)	46(1)	37(1)	2(1)	12(1)	4(1)
C(7)	24(1)	40(1)	53(1)	12(1)	14(1)	2(1)
C(8)	22(1)	31(1)	56(1)	6(1)	0(1)	-3(1)
C(9)	21(1)	27(1)	40(1)	0(1)	-1(1)	-1(1)
C(10)	16(1)	22(1)	23(1)	-3(1)	-4(1)	1(1)
C(11)	19(1)	30(1)	22(1)	-1(1)	-3(1)	3(1)
C(12)	30(1)	35(1)	23(1)	-1(1)	-4(1)	7(1)
C(13)	46(1)	52(1)	25(1)	6(1)	4(1)	3(1)
C(14)	20(1)	20(1)	26(1)	-3(1)	-3(1)	1(1)
C(15)	22(1)	18(1)	32(1)	0(1)	-5(1)	2(1)
C(16)	19(1)	22(1)	30(1)	3(1)	-2(1)	2(1)
C(17)	19(1)	28(1)	31(1)	0(1)	-5(1)	8(1)
C(18)	19(1)	47(1)	60(1)	2(1)	-4(1)	2(1)
C(19)	44(1)	34(1)	27(1)	0(1)	-4(1)	18(1)
C(20)	29(1)	38(1)	30(1)	-6(1)	-4(1)	12(1)
C(21)	29(1)	22(1)	30(1)	-10(1)	-6(1)	0(1)
C(22)	39(1)	28(1)	32(1)	-8(1)	-13(1)	-4(1)
C(23)	28(1)	27(1)	40(1)	-2(1)	-14(1)	-7(1)
C(24)	18(1)	24(1)	36(1)	-3(1)	-9(1)	0(1)
C(25)	16(1)	14(1)	24(1)	-1(1)	-5(1)	-1(1)
C(26)	19(1)	19(1)	30(1)	-1(1)	0(1)	1(1)
C(27)	22(1)	21(1)	48(1)	-1(1)	-2(1)	4(1)
C(28)	31(1)	22(1)	58(1)	8(1)	-14(1)	5(1)
C(29)	39(1)	29(1)	39(1)	14(1)	-13(1)	-3(1)
C(30)	26(1)	24(1)	24(1)	4(1)	-5(1)	-6(1)
C(31)	40(1)	37(1)	23(1)	3(1)	4(1)	-7(1)
C(32)	96(2)	87(2)	30(1)	-12(1)	-4(2)	6(2)
C(33)	89(3)	96(3)	117(3)	-62(2)	76(2)	-65(2)
C(34)	35(1)	35(1)	33(1)	5(1)	14(1)	14(1)
C(35)	64(2)	81(2)	28(1)	-4(1)	4(1)	14(2)
C(36)	48(1)	46(1)	65(2)	15(1)	31(1)	8(1)

Table S–15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for crystal_03.

	x	y	z	U(eq)
H(5)	-2667	8841	8	35
H(6)	-1027	9212	-726	47
H(7)	382	10062	-225	47
H(8)	157	10542	1009	44
H(9)	-1457	10163	1748	35
H(10)	-2549	9329	2514	25
H(11A)	-4651	9084	2645	28
H(11B)	-4395	8184	2463	28
H(12A)	-3155	8126	3571	35
H(12B)	-3519	9007	3764	35
H(13A)	-5119	7715	3757	61
H(13B)	-5520	8598	3913	61
H(13C)	-4667	8162	4503	61
H(14)	-2431	7717	2107	27
H(15)	-586	8783	2288	29
H(18A)	3072	7845	1724	63
H(18B)	3723	7356	2378	63
H(18C)	3027	8142	2588	63
H(19A)	1814	7446	3534	53
H(19B)	2450	6631	3354	53
H(19C)	1042	6702	3293	53
H(20A)	1159	6207	1947	48
H(20B)	2574	6191	1929	48
H(20C)	1860	6705	1322	48
H(21A)	-5690	7587	405	32
H(21B)	-5004	8025	-279	32
H(22A)	-6729	8245	-947	39
H(22B)	-7024	7406	-574	39
H(23A)	-8063	7967	425	38
H(23B)	-8460	8506	-284	38
H(24A)	-7235	9506	67	31
H(24B)	-7461	9144	902	31
H(27)	-8175	11387	1672	37
H(28)	-8022	12004	495	44
H(29)	-6484	11696	-330	43
H(31)	-4246	10225	34	40
H(32A)	-5510	10037	-998	106
H(32B)	-4266	10376	-1281	106
H(32C)	-5392	10940	-1225	106

H(33A)	-4172	11822	-379	151
H(33B)	-3077	11230	-367	151
H(33C)	-3689	11491	415	151
H(34)	-6405	9736	2257	41
H(35A)	-5670	10901	2814	86
H(35B)	-6482	10427	3400	86
H(35C)	-6996	11182	2976	86
H(36A)	-8708	10393	2474	80
H(36B)	-8216	9628	2892	80
H(36C)	-8458	9615	1994	80



(Table 4, entry 2; obtained with (*S*)-**1**)

X-ray quality crystals were grown by slow evaporation of a solution of the compound in hexanes. A suitable crystal was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Photon diffractometer with filtered Cu-Kα radiation at a temperature of 100 K. Using Olex2,[16] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package[17] using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S–16. Crystal data and structure refinement for crystal_04.

Identification code	crystal_04	
Empirical formula	$C_{37}H_{51}N_3O_4$	
Formula weight	601.80	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.3317(3) Å	α = 90 °.
	b = 11.0488(3) Å	β = 90 °.
	c = 31.0607(8) Å	γ = 90 °.
Volume	3545.67(17) $Å^3$	
Z	4	
Density (calculated)	1.127 Mg/m^3	
Absorption coefficient	0.575 mm^{-1}	
F(000)	1304	
Theta range for data collection	2.845 to 79.444°.	
Index ranges	-13<=h<=12, -13<=k<=13, -39<=l<=39	
Reflections collected	112215	
Independent reflections	7623 [R(int) = 0.0681]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7491 and 0.6922	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7623 / 0 / 406	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0448, wR2 = 0.1068	
R indices (all data)	R1 = 0.0520, wR2 = 0.1111	
Absolute structure parameter	-0.08(6)	
Largest diff. peak and hole	0.539 and -0.299 $e/Å^{-3}$	

Table S–17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for crystal_04. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	731(2)	6242(2)	2025(1)	28(1)
O(2)	-289(3)	2876(2)	42(1)	47(1)
O(3)	-699(3)	1388(2)	517(1)	51(1)
O(4)	4775(2)	1928(2)	1658(1)	43(1)
N(1)	1727(2)	7636(2)	1583(1)	22(1)
N(2)	2659(2)	8545(2)	951(1)	28(1)
C(1)	1171(2)	6529(2)	1680(1)	22(1)
C(2)	1266(2)	5773(2)	1267(1)	22(1)
N(3)	1786(2)	6604(2)	944(1)	25(1)
C(4)	2075(2)	7600(2)	1140(1)	22(1)
C(5)	3074(3)	8404(3)	500(1)	39(1)
C(6)	3861(4)	9552(3)	420(1)	57(1)
C(7)	3290(4)	10469(3)	723(1)	47(1)
C(8)	2964(3)	9743(2)	1123(1)	39(1)
C(9)	2042(2)	8459(2)	1926(1)	21(1)
C(10)	1147(2)	9343(2)	2043(1)	27(1)
C(11)	1430(3)	10042(3)	2407(1)	36(1)
C(12)	2543(3)	9833(3)	2642(1)	40(1)
C(13)	3420(3)	8963(3)	2516(1)	36(1)
C(14)	3198(2)	8260(2)	2151(1)	25(1)
C(15)	4164(2)	7306(2)	2009(1)	32(1)
C(16)	5556(3)	7787(3)	2030(1)	48(1)
C(17)	4024(3)	6148(3)	2273(1)	43(1)
C(18)	-106(2)	9529(3)	1795(1)	34(1)
C(19)	-381(3)	10866(3)	1710(1)	52(1)
C(20)	-1232(3)	8948(3)	2039(1)	46(1)
C(21)	-111(2)	5306(2)	1151(1)	26(1)
C(22)	-65(3)	4452(2)	779(1)	28(1)
C(23)	-452(3)	3313(2)	793(1)	34(1)
C(24)	-466(3)	2532(2)	405(1)	35(1)
C(25)	-1047(3)	6355(2)	1053(1)	30(1)
C(26)	-2460(3)	5961(2)	1031(1)	34(1)
C(27)	-3374(3)	7000(3)	913(1)	46(1)
C(28)	-905(4)	434(3)	189(1)	55(1)
C(29)	-2147(4)	720(4)	-50(1)	64(1)
C(30)	-1001(8)	-693(3)	465(1)	103(2)
C(31)	232(4)	324(3)	-114(1)	60(1)
C(32)	2217(2)	4738(2)	1363(1)	24(1)
C(33)	3440(2)	4727(2)	1184(1)	30(1)
C(34)	4333(3)	3813(3)	1275(1)	34(1)

C(35)	3990(3)	2885(2)	1551(1)	32(1)
C(36)	2771(3)	2889(2)	1739(1)	32(1)
C(37)	1899(2)	3801(2)	1647(1)	27(1)
C(38)	6039(3)	1901(4)	1477(1)	58(1)

Table S–18. Bond lengths [Å] and angles [°] for crystal_04.

O(1)-C(1)	1.208(3)
O(2)-C(24)	1.204(3)
O(3)-C(24)	1.333(3)
O(3)-C(28)	1.480(3)
O(4)-C(35)	1.373(3)
O(4)-C(38)	1.423(4)
N(1)-C(1)	1.384(3)
N(1)-C(4)	1.423(3)
N(1)-C(9)	1.437(3)
N(2)-C(4)	1.341(3)
N(2)-C(5)	1.474(3)
N(2)-C(8)	1.461(3)
C(1)-C(2)	1.533(3)
C(2)-N(3)	1.463(3)
C(2)-C(21)	1.556(3)
C(2)-C(32)	1.536(3)
N(3)-C(4)	1.293(3)
C(5)-C(6)	1.527(4)
C(6)-C(7)	1.505(5)
C(7)-C(8)	1.515(4)
C(9)-C(10)	1.393(3)
C(9)-C(14)	1.402(3)
C(10)-C(11)	1.401(4)
C(10)-C(18)	1.520(4)
C(11)-C(12)	1.381(4)
C(12)-C(13)	1.379(4)
C(13)-C(14)	1.393(3)
C(14)-C(15)	1.517(4)
C(15)-C(16)	1.534(4)
C(15)-C(17)	1.526(4)
C(18)-C(19)	1.527(4)
C(18)-C(20)	1.529(4)
C(21)-C(22)	1.494(3)
C(21)-C(25)	1.540(4)
C(22)-C(23)	1.322(4)
C(23)-C(24)	1.484(4)
C(25)-C(26)	1.525(4)
C(26)-C(27)	1.531(4)
C(28)-C(29)	1.515(6)
C(28)-C(30)	1.515(5)
C(28)-C(31)	1.510(6)
C(32)-C(33)	1.380(3)
C(32)-C(37)	1.399(3)

C(33)-C(34)	1.397(4)
C(34)-C(35)	1.384(4)
C(35)-C(36)	1.388(4)
C(36)-C(37)	1.382(4)
C(24)-O(3)-C(28)	121.4(2)
C(35)-O(4)-C(38)	117.6(3)
C(1)-N(1)-C(4)	106.88(18)
C(1)-N(1)-C(9)	119.49(17)
C(4)-N(1)-C(9)	132.56(19)
C(4)-N(2)-C(5)	117.6(2)
C(4)-N(2)-C(8)	130.0(2)
C(8)-N(2)-C(5)	112.3(2)
O(1)-C(1)-N(1)	125.6(2)
O(1)-C(1)-C(2)	128.6(2)
N(1)-C(1)-C(2)	105.86(17)
C(1)-C(2)-C(21)	108.43(19)
C(1)-C(2)-C(32)	106.60(17)
N(3)-C(2)-C(1)	104.82(18)
N(3)-C(2)-C(21)	112.61(18)
N(3)-C(2)-C(32)	111.36(19)
C(32)-C(2)-C(21)	112.50(19)
C(4)-N(3)-C(2)	107.18(18)
N(2)-C(4)-N(1)	121.0(2)
N(3)-C(4)-N(1)	114.9(2)
N(3)-C(4)-N(2)	124.1(2)
N(2)-C(5)-C(6)	102.8(2)
C(7)-C(6)-C(5)	104.3(2)
C(6)-C(7)-C(8)	104.1(3)
N(2)-C(8)-C(7)	103.2(2)
C(10)-C(9)-N(1)	119.1(2)
C(10)-C(9)-C(14)	123.1(2)
C(14)-C(9)-N(1)	117.6(2)
C(9)-C(10)-C(11)	117.2(2)
C(9)-C(10)-C(18)	122.0(2)
C(11)-C(10)-C(18)	120.8(2)
C(12)-C(11)-C(10)	120.6(3)
C(13)-C(12)-C(11)	120.9(2)
C(12)-C(13)-C(14)	120.7(3)
C(9)-C(14)-C(15)	121.6(2)
C(13)-C(14)-C(9)	117.4(2)
C(13)-C(14)-C(15)	121.0(2)
C(14)-C(15)-C(16)	111.4(2)
C(14)-C(15)-C(17)	111.3(2)
C(17)-C(15)-C(16)	110.9(2)
C(10)-C(18)-C(19)	112.1(2)

C(10)-C(18)-C(20)	109.9(2)
C(19)-C(18)-C(20)	110.5(2)
C(22)-C(21)-C(2)	111.1(2)
C(22)-C(21)-C(25)	110.0(2)
C(25)-C(21)-C(2)	111.74(19)
C(23)-C(22)-C(21)	124.5(2)
C(22)-C(23)-C(24)	121.9(2)
O(2)-C(24)-O(3)	124.9(3)
O(2)-C(24)-C(23)	125.2(2)
O(3)-C(24)-C(23)	109.9(2)
C(26)-C(25)-C(21)	113.2(2)
C(25)-C(26)-C(27)	112.7(2)
O(3)-C(28)-C(29)	108.0(3)
O(3)-C(28)-C(30)	101.9(2)
O(3)-C(28)-C(31)	111.9(3)
C(29)-C(28)-C(30)	113.1(4)
C(31)-C(28)-C(29)	111.7(3)
C(31)-C(28)-C(30)	109.7(4)
C(33)-C(32)-C(2)	121.0(2)
C(33)-C(32)-C(37)	117.5(2)
C(37)-C(32)-C(2)	121.5(2)
C(32)-C(33)-C(34)	122.0(2)
C(35)-C(34)-C(33)	119.5(2)
O(4)-C(35)-C(34)	124.7(3)
O(4)-C(35)-C(36)	115.9(2)
C(34)-C(35)-C(36)	119.4(2)
C(37)-C(36)-C(35)	120.5(2)
C(36)-C(37)-C(32)	121.1(2)

Table S–19. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for crystal_04. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

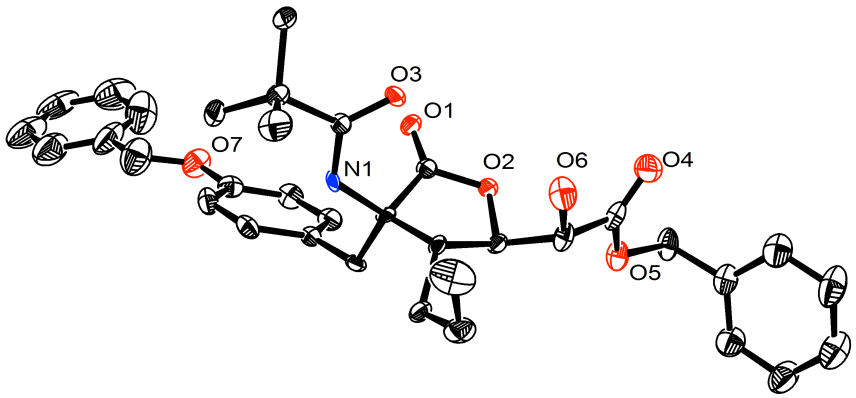
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	28(1)	33(1)	22(1)	0(1)	7(1)	-9(1)
O(2)	82(2)	32(1)	28(1)	1(1)	-8(1)	-12(1)
O(3)	99(2)	25(1)	30(1)	-1(1)	-11(1)	-16(1)
O(4)	32(1)	42(1)	56(1)	1(1)	-9(1)	9(1)
N(1)	23(1)	25(1)	17(1)	-3(1)	2(1)	-7(1)
N(2)	38(1)	26(1)	22(1)	0(1)	8(1)	-7(1)
C(1)	19(1)	26(1)	20(1)	0(1)	-1(1)	-5(1)
C(2)	27(1)	22(1)	18(1)	0(1)	-1(1)	-5(1)
N(3)	32(1)	24(1)	18(1)	1(1)	0(1)	-6(1)
C(4)	23(1)	26(1)	18(1)	1(1)	2(1)	-2(1)
C(5)	58(2)	32(1)	27(1)	3(1)	18(1)	-1(1)
C(6)	78(3)	43(2)	50(2)	7(2)	32(2)	-14(2)
C(7)	69(2)	37(2)	34(1)	4(1)	8(1)	-18(2)
C(8)	55(2)	32(1)	30(1)	0(1)	4(1)	-22(1)
C(9)	20(1)	25(1)	18(1)	-3(1)	4(1)	-8(1)
C(10)	21(1)	32(1)	28(1)	-2(1)	8(1)	-3(1)
C(11)	37(1)	37(2)	35(1)	-13(1)	14(1)	-2(1)
C(12)	48(2)	47(2)	26(1)	-15(1)	0(1)	-11(1)
C(13)	36(1)	43(2)	29(1)	-8(1)	-9(1)	-9(1)
C(14)	24(1)	27(1)	24(1)	-2(1)	-1(1)	-6(1)
C(15)	25(1)	34(1)	38(1)	-3(1)	-6(1)	0(1)
C(16)	26(1)	45(2)	72(2)	1(2)	-1(1)	-1(1)
C(17)	37(2)	35(2)	58(2)	3(1)	-15(1)	-1(1)
C(18)	22(1)	35(1)	45(2)	-2(1)	3(1)	-2(1)
C(19)	32(2)	39(2)	86(2)	10(2)	-3(2)	1(1)
C(20)	22(1)	44(2)	74(2)	3(2)	7(1)	-3(1)
C(21)	29(1)	22(1)	25(1)	2(1)	-5(1)	-7(1)
C(22)	35(1)	24(1)	24(1)	2(1)	-7(1)	-3(1)
C(23)	47(2)	27(1)	26(1)	2(1)	-8(1)	-7(1)
C(24)	47(2)	23(1)	33(1)	3(1)	-12(1)	-6(1)
C(25)	31(1)	23(1)	36(1)	0(1)	-8(1)	-5(1)
C(26)	34(1)	32(1)	37(1)	1(1)	-9(1)	-6(1)
C(27)	38(2)	42(2)	58(2)	2(1)	-10(1)	0(1)
C(28)	103(3)	29(2)	34(1)	-2(1)	-17(2)	-19(2)
C(29)	62(2)	75(3)	55(2)	-32(2)	3(2)	-19(2)
C(30)	225(7)	31(2)	53(2)	-2(2)	-15(3)	-38(3)
C(31)	81(3)	51(2)	49(2)	-14(2)	-24(2)	19(2)
C(32)	26(1)	25(1)	21(1)	-3(1)	-2(1)	-6(1)
C(33)	32(1)	34(1)	24(1)	-1(1)	3(1)	-4(1)
C(34)	27(1)	42(2)	32(1)	-3(1)	2(1)	1(1)

C(35)	29(1)	33(1)	34(1)	-3(1)	-8(1)	2(1)
C(36)	32(1)	30(1)	33(1)	4(1)	-6(1)	-3(1)
C(37)	24(1)	30(1)	26(1)	2(1)	-3(1)	-6(1)
C(38)	34(2)	61(2)	77(2)	-2(2)	-2(2)	16(2)

Table S–20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for crystal_04.

	x	y	z	U(eq)
H(5A)	2320	8359	304	47
H(5B)	3612	7671	462	47
H(6A)	4789	9415	484	68
H(6B)	3774	9822	117	68
H(7A)	2502	10841	599	56
H(7B)	3923	11115	790	56
H(8A)	3711	9707	1322	47
H(8B)	2212	10094	1276	47
H(11)	852	10665	2493	43
H(12)	2705	10297	2894	49
H(13)	4185	8841	2680	43
H(15)	3973	7103	1702	39
H(16A)	5611	8555	1873	72
H(16B)	6144	7197	1899	72
H(16C)	5802	7917	2331	72
H(17A)	4339	6288	2566	65
H(17B)	4531	5500	2138	65
H(17C)	3110	5910	2283	65
H(18)	-23	9112	1511	41
H(19A)	-592	11270	1982	79
H(19B)	-1114	10941	1512	79
H(19C)	386	11246	1583	79
H(20A)	-1043	8091	2090	70
H(20B)	-2026	9022	1869	70
H(20C)	-1348	9360	2316	70
H(21)	-456	4855	1405	31
H(22)	266	4747	513	33
H(23)	-730	2984	1060	40
H(25A)	-953	6981	1279	36
H(25B)	-802	6727	774	36
H(26A)	-2719	5626	1314	41
H(26B)	-2548	5309	815	41
H(27A)	-3201	7261	617	69
H(27B)	-3233	7680	1110	69
H(27C)	-4273	6724	936	69
H(29A)	-2840	877	158	96
H(29B)	-2386	30	-231	96
H(29C)	-2018	1437	-230	96
H(30A)	-251	-736	658	155

H(30B)	-1017	-1411	280	155
H(30C)	-1797	-662	637	155
H(31A)	271	1041	-299	91
H(31B)	129	-401	-292	91
H(31C)	1034	262	54	91
H(33)	3683	5361	994	36
H(34)	5169	3828	1148	40
H(36)	2534	2260	1932	38
H(37)	1069	3793	1779	32
H(38A)	5976	1905	1162	86
H(38B)	6488	1165	1571	86
H(38C)	6525	2613	1572	86



(eq 6; derived from the product obtained with (*S*)-**1**)

X-ray quality crystals were grown by slow evaporation of a solution of the compound in hexanes/dichloromethane. A suitable crystal was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Photon diffractometer with filtered Cu-Kα radiation at a temperature of 100 K. Using Olex2,[16] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package[17] using Least Squares minimization. The absolute stereochemistry was determined on the basis of a reference molecule and the absolute structure parameter.

Table S–21. Crystal data and structure refinement for crystal_05.

Identification code	crystal_05	
Empirical formula	$C_{35}H_{41}NO_7$	
Formula weight	587.69	
Temperature	100.15 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.3732(6) Å	α = 90°.
	b = 10.9685(8) Å	β = 90 °.
	c = 30.310(2) Å	γ = 90 °.
Volume	3116.2(4) $Å^3$	
Z	4	
Density (calculated)	1.253 Mg/m^3	
Absorption coefficient	0.703 mm^{-1}	
F(000)	1256	
Crystal size	0.24 x 0.19 x 0.02 mm^3	
Theta range for data collection	2.916 to 63.664°.	
Index ranges	-10<=h<=7, -11<=k<=12, -34<=l<=35	
Reflections collected	32639	
Independent reflections	5095 [R(int) = 0.1051]	
Completeness to theta = 63.664°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7420 and 0.5846	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5095 / 0 / 393	
Goodness-of-fit on F^2	1.145	
Final R indices [I>2sigma(I)]	R1 = 0.0716, wR2 = 0.1490	
R indices (all data)	R1 = 0.0892, wR2 = 0.1578	
Absolute structure parameter	0.17(15)	
Largest diff. peak and hole	0.580 and -0.301 $e/Å^{-3}$	

Table S–22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for crystal_05. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(3)	1580(4)	7335(3)	2012(1)	20(1)
O(1)	-948(4)	8021(3)	2562(1)	21(1)
O(2)	-2130(4)	7502(3)	1959(1)	20(1)
O(5)	-4701(4)	7724(4)	1311(1)	30(1)
O(6)	-1081(5)	7171(4)	1023(2)	35(1)
O(4)	-3037(5)	8934(4)	998(2)	37(1)
N(1)	710(5)	5761(4)	2406(2)	16(1)
O(7)	-1119(5)	6397(5)	4409(1)	38(1)
C(17)	1790(6)	6475(5)	2264(2)	17(1)
C(1)	-1221(6)	7262(5)	2294(2)	19(1)
C(28)	-494(6)	4961(5)	3330(2)	25(1)
C(2)	-765(5)	5916(5)	2270(2)	16(1)
C(27)	-289(7)	5251(6)	3769(2)	28(2)
C(3)	-1028(6)	5623(5)	1778(2)	17(1)
C(4)	-2299(6)	6441(5)	1674(2)	19(1)
C(6)	-3418(7)	7981(6)	1159(2)	29(2)
C(26)	-1215(7)	6061(6)	3973(2)	26(1)
C(8)	-853(7)	3981(6)	1173(2)	33(2)
C(23)	-1557(6)	5483(5)	3072(2)	17(1)
C(20)	4206(6)	7278(6)	2433(2)	27(1)
C(25)	-2308(7)	6581(6)	3732(2)	29(2)
C(10)	-5824(7)	8669(6)	1246(2)	33(2)
C(5)	-2408(7)	6894(6)	1202(2)	27(2)
C(19)	3277(7)	5545(7)	2884(2)	38(2)
C(18)	3283(6)	6127(5)	2424(2)	24(1)
C(12)	-6159(7)	9123(7)	437(2)	41(2)
C(22)	-1723(6)	5187(5)	2593(2)	19(1)
C(24)	-2458(6)	6308(5)	3288(2)	26(1)
C(16)	-7620(7)	7621(7)	783(2)	40(2)
C(9)	625(9)	4374(7)	1022(3)	51(2)
C(7)	-1169(6)	4284(5)	1656(2)	23(1)
C(15)	-8267(8)	7378(8)	384(2)	48(2)
C(30)	-318(9)	6229(10)	5150(3)	58(3)
C(11)	-6535(7)	8464(6)	813(2)	29(2)
C(29)	-115(9)	5841(9)	4669(3)	58(2)
C(21)	3864(7)	5228(6)	2084(2)	40(2)
C(35)	213(10)	5485(11)	5470(3)	72(3)
C(31)	-1019(10)	7293(11)	5254(3)	71(3)
C(32)	-1116(10)	7678(11)	5701(3)	75(3)
C(13)	-6842(8)	8884(9)	39(2)	53(2)
C(14)	-7887(8)	8010(8)	17(2)	48(2)
C(33)	-568(10)	6914(12)	6025(3)	68(3)
C(34)	79(10)	5828(12)	5899(3)	76(3)

Table S–23. Bond lengths [Å] and angles [°] for crystal_05.

O(3)-C(17)	1.230(6)
O(1)-C(1)	1.192(7)
O(2)-C(1)	1.350(7)
O(2)-C(4)	1.458(6)
O(5)-C(6)	1.319(8)
O(5)-C(10)	1.491(7)
O(6)-C(5)	1.390(8)
O(4)-C(6)	1.207(8)
N(1)-C(17)	1.350(7)
N(1)-C(2)	1.453(7)
O(7)-C(26)	1.373(7)
O(7)-C(29)	1.371(9)
C(17)-C(18)	1.529(8)
C(1)-C(2)	1.538(8)
C(28)-C(27)	1.383(9)
C(28)-C(23)	1.389(8)
C(2)-C(3)	1.545(8)
C(2)-C(22)	1.550(7)
C(27)-C(26)	1.387(9)
C(3)-C(4)	1.524(8)
C(3)-C(7)	1.521(8)
C(4)-C(5)	1.519(8)
C(6)-C(5)	1.528(9)
C(26)-C(25)	1.383(9)
C(8)-C(9)	1.521(10)
C(8)-C(7)	1.529(8)
C(23)-C(22)	1.496(8)
C(23)-C(24)	1.400(8)
C(20)-C(18)	1.531(8)
C(25)-C(24)	1.386(9)
C(10)-C(11)	1.488(9)
C(19)-C(18)	1.533(8)
C(18)-C(21)	1.525(9)
C(12)-C(11)	1.395(9)
C(12)-C(13)	1.391(10)
C(16)-C(15)	1.378(10)
C(16)-C(11)	1.378(9)
C(15)-C(14)	1.358(10)
C(30)-C(29)	1.530(11)
C(30)-C(35)	1.363(13)
C(30)-C(31)	1.376(14)
C(35)-C(34)	1.358(13)
C(31)-C(32)	1.422(13)

C(32)-C(33)	1.388(13)
C(13)-C(14)	1.372(11)
C(33)-C(34)	1.389(15)
C(1)-O(2)-C(4)	111.0(4)
C(6)-O(5)-C(10)	116.6(5)
C(17)-N(1)-C(2)	123.8(4)
C(29)-O(7)-C(26)	118.5(6)
O(3)-C(17)-N(1)	121.5(5)
O(3)-C(17)-C(18)	122.3(5)
N(1)-C(17)-C(18)	116.2(5)
O(1)-C(1)-O(2)	120.8(5)
O(1)-C(1)-C(2)	130.1(5)
O(2)-C(1)-C(2)	109.1(5)
C(27)-C(28)-C(23)	123.2(6)
N(1)-C(2)-C(1)	111.3(4)
N(1)-C(2)-C(3)	113.6(5)
N(1)-C(2)-C(22)	108.2(4)
C(1)-C(2)-C(3)	101.6(4)
C(1)-C(2)-C(22)	107.7(4)
C(3)-C(2)-C(22)	114.2(4)
C(28)-C(27)-C(26)	119.3(6)
C(4)-C(3)-C(2)	101.6(4)
C(7)-C(3)-C(2)	116.7(5)
C(7)-C(3)-C(4)	116.8(5)
O(2)-C(4)-C(3)	105.2(4)
O(2)-C(4)-C(5)	107.7(5)
C(5)-C(4)-C(3)	116.1(5)
O(5)-C(6)-C(5)	111.6(6)
O(4)-C(6)-O(5)	126.6(6)
O(4)-C(6)-C(5)	121.8(6)
O(7)-C(26)-C(27)	124.1(6)
O(7)-C(26)-C(25)	116.5(6)
C(25)-C(26)-C(27)	119.4(6)
C(9)-C(8)-C(7)	113.8(6)
C(28)-C(23)-C(22)	122.1(5)
C(28)-C(23)-C(24)	115.9(5)
C(24)-C(23)-C(22)	122.1(5)
C(26)-C(25)-C(24)	120.0(6)
C(11)-C(10)-O(5)	109.2(5)
O(6)-C(5)-C(4)	112.2(5)
O(6)-C(5)-C(6)	110.5(5)
C(4)-C(5)-C(6)	112.2(5)
C(17)-C(18)-C(19)	112.8(5)
C(20)-C(18)-C(17)	108.5(5)
C(20)-C(18)-C(19)	109.1(5)

C(21)-C(18)-C(17)	106.0(5)
C(21)-C(18)-C(20)	110.1(5)
C(21)-C(18)-C(19)	110.2(5)
C(13)-C(12)-C(11)	119.7(7)
C(23)-C(22)-C(2)	116.1(5)
C(25)-C(24)-C(23)	122.1(6)
C(11)-C(16)-C(15)	120.9(7)
C(3)-C(7)-C(8)	115.2(5)
C(14)-C(15)-C(16)	120.2(7)
C(35)-C(30)-C(29)	117.9(10)
C(35)-C(30)-C(31)	121.1(9)
C(31)-C(30)-C(29)	121.0(8)
C(12)-C(11)-C(10)	121.9(6)
C(16)-C(11)-C(10)	119.4(6)
C(16)-C(11)-C(12)	118.7(6)
O(7)-C(29)-C(30)	109.8(7)
C(34)-C(35)-C(30)	118.9(12)
C(30)-C(31)-C(32)	120.1(9)
C(33)-C(32)-C(31)	118.0(11)
C(14)-C(13)-C(12)	120.1(7)
C(15)-C(14)-C(13)	120.4(7)
C(34)-C(33)-C(32)	119.0(9)
C(35)-C(34)-C(33)	122.7(11)

Table S–24. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for crystal_05. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(3)	19(2)	13(2)	28(2)	5(2)	-3(2)	1(2)
O(1)	19(2)	21(2)	24(2)	-2(2)	-6(2)	0(2)
O(2)	19(2)	14(2)	26(2)	1(2)	-6(2)	1(2)
O(5)	21(2)	34(2)	34(2)	2(2)	-4(2)	13(2)
O(6)	25(2)	45(3)	35(3)	9(2)	6(2)	7(2)
O(4)	32(3)	32(3)	47(3)	5(2)	-6(2)	1(2)
N(1)	14(2)	13(2)	21(3)	7(2)	-3(2)	5(2)
O(7)	39(3)	52(3)	24(2)	-2(2)	2(2)	-5(2)
C(17)	14(3)	17(3)	19(3)	1(2)	2(2)	1(2)
C(1)	11(3)	19(3)	28(3)	3(3)	-1(2)	0(2)
C(28)	27(3)	17(3)	31(4)	4(3)	3(3)	4(3)
C(2)	7(3)	15(3)	25(3)	0(2)	-3(2)	-3(2)
C(27)	27(3)	31(3)	26(4)	9(3)	-1(3)	4(3)
C(3)	12(3)	17(3)	21(3)	-1(2)	-6(2)	2(2)
C(4)	17(3)	17(3)	24(3)	-3(3)	-7(3)	1(2)
C(6)	24(4)	41(4)	21(3)	-2(3)	-9(3)	2(3)
C(26)	28(4)	27(3)	23(3)	-1(3)	6(3)	-5(3)
C(8)	38(4)	26(3)	35(4)	-11(3)	-2(3)	-1(3)
C(23)	11(3)	18(3)	23(3)	2(2)	4(2)	1(2)
C(20)	17(3)	30(3)	33(3)	7(3)	-6(3)	-6(3)
C(25)	22(3)	29(3)	35(4)	0(3)	8(3)	4(3)
C(10)	32(4)	34(4)	32(4)	0(3)	-7(3)	20(3)
C(5)	21(3)	34(4)	25(3)	0(3)	-7(3)	7(3)
C(19)	25(4)	41(4)	48(4)	21(4)	-17(3)	-9(3)
C(18)	15(3)	25(3)	30(3)	3(3)	-3(3)	-2(3)
C(12)	23(4)	63(5)	38(4)	8(4)	4(3)	-2(4)
C(22)	17(3)	12(3)	28(3)	4(2)	-1(3)	-3(2)
C(24)	17(3)	24(3)	36(4)	2(3)	3(3)	1(3)
C(16)	32(4)	50(4)	37(4)	3(4)	2(3)	-5(4)
C(9)	56(5)	40(4)	58(5)	-17(4)	22(4)	5(4)
C(7)	24(3)	20(3)	26(3)	-5(3)	-10(3)	0(3)
C(15)	37(4)	70(6)	38(4)	3(4)	-6(3)	-15(4)
C(30)	44(5)	92(7)	37(5)	4(5)	-14(4)	-19(5)
C(11)	20(3)	39(4)	27(3)	-2(3)	2(3)	11(3)
C(29)	49(5)	80(7)	45(5)	4(5)	0(4)	3(5)
C(21)	21(3)	32(4)	68(5)	-8(4)	-2(3)	12(3)
C(35)	69(6)	97(8)	49(6)	16(5)	-14(5)	-33(6)
C(31)	62(6)	107(9)	44(5)	19(6)	10(5)	10(7)
C(32)	52(6)	93(8)	81(7)	-2(6)	16(5)	-24(6)
C(13)	34(4)	95(7)	29(4)	8(4)	-1(3)	1(5)
C(14)	34(4)	76(6)	35(4)	-4(4)	-2(3)	1(4)
C(33)	55(6)	121(9)	30(5)	-7(6)	6(4)	-51(6)
C(34)	65(7)	124(10)	40(6)	14(6)	-5(5)	-52(7)

Table S–25. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for crystal_05.

	x	y	z	U(eq)
H(6)	-1079	7897	935	53
H(1)	911	5168	2591	20
H(28)	120	4377	3198	30
H(27)	478	4899	3930	33
H(3)	-195	5952	1610	20
H(4)	-3199	6006	1755	23
H(8A)	-949	3090	1130	39
H(8B)	-1575	4385	985	39
H(20A)	4169	7679	2144	40
H(20B)	5195	7055	2501	40
H(20C)	3846	7836	2660	40
H(25)	-2956	7127	3870	34
H(10A)	-6536	8620	1486	39
H(10B)	-5388	9491	1252	39
H(5)	-2819	6215	1022	32
H(19A)	2709	6049	3085	57
H(19B)	4257	5488	2994	57
H(19C)	2861	4727	2866	57
H(12)	-5441	9733	453	50
H(22A)	-2731	5325	2510	23
H(22B)	-1522	4308	2552	23
H(24)	-3197	6693	3124	31
H(16)	-7926	7202	1040	48
H(9A)	800	4066	723	77
H(9B)	1344	4041	1224	77
H(9C)	683	5266	1022	77
H(7A)	-2153	4016	1724	28
H(7B)	-513	3806	1844	28
H(15)	-8981	6766	366	58
H(29A)	853	6071	4568	70
H(29B)	-209	4944	4644	70
H(21A)	3251	4505	2075	60
H(21B)	4834	4986	2168	60
H(21C)	3882	5615	1793	60
H(35)	670	4740	5396	86
H(31)	-1440	7770	5028	85
H(32)	-1543	8435	5776	91
H(13)	-6584	9326	-219	63
H(14)	-8348	7847	-255	58
H(33)	-635	7130	6328	82
H(34)	442	5304	6122	91

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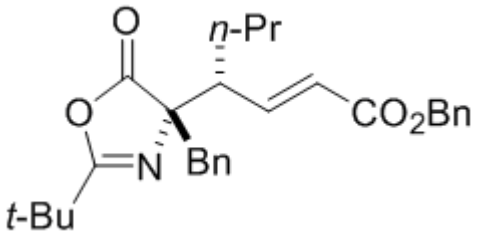
Table 2, entry 1

VIII. NMR Spectra



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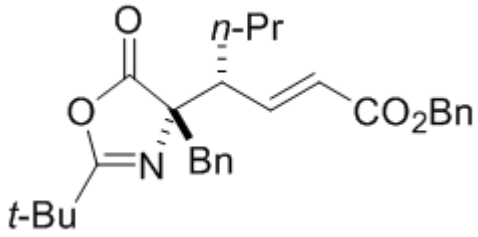

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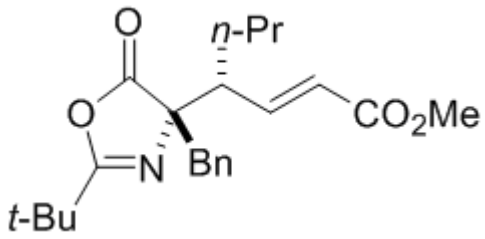

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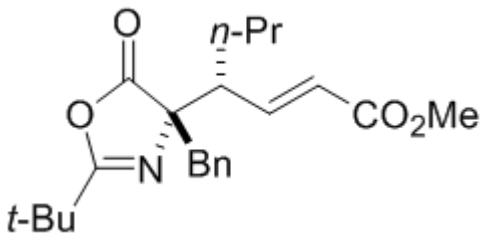

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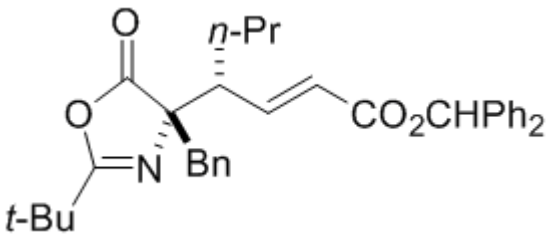

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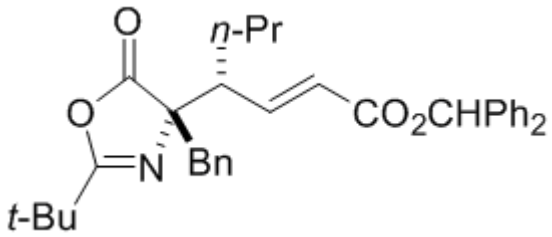

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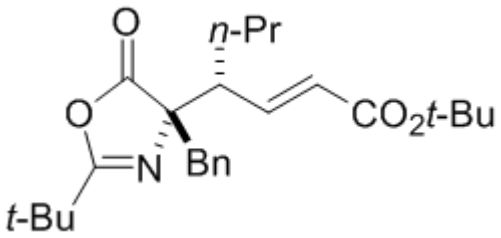

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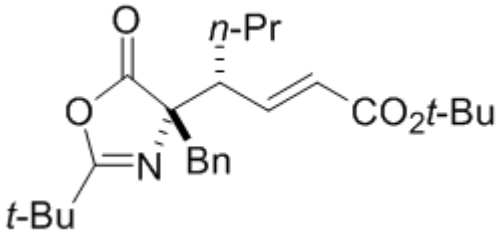

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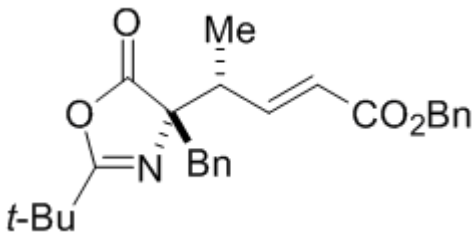

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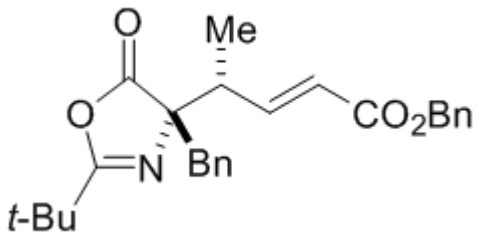

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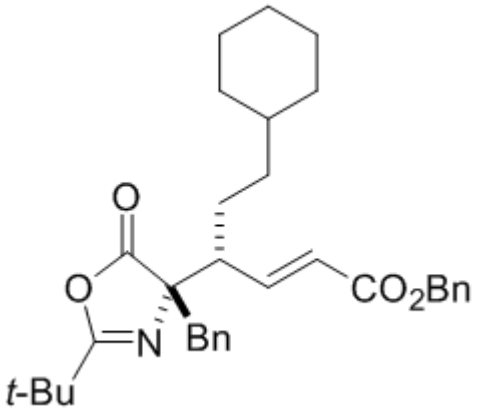

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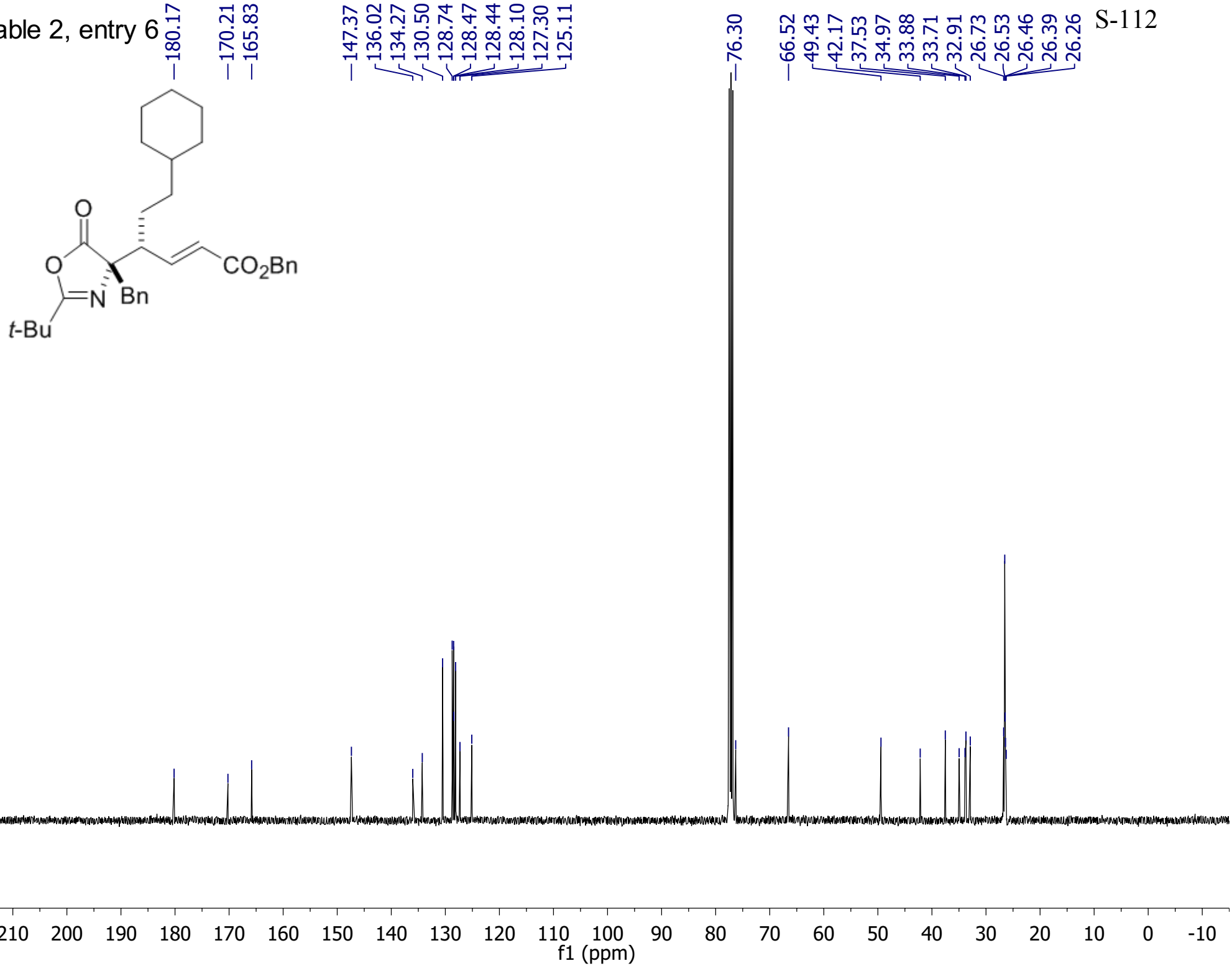

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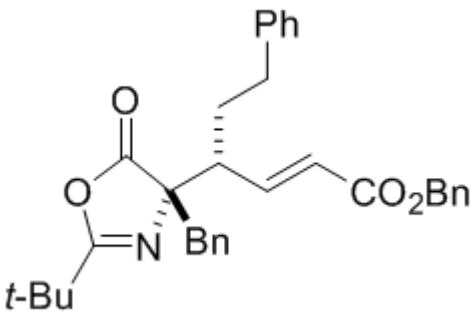

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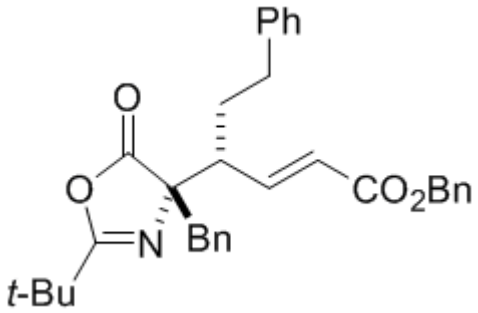

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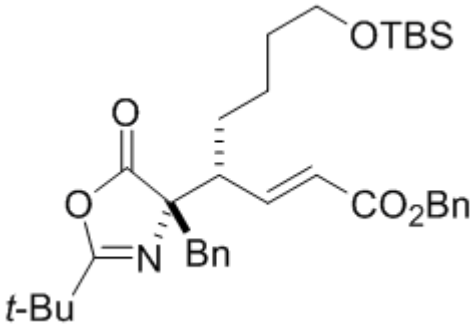

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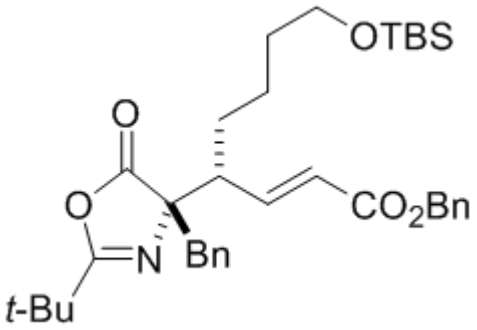

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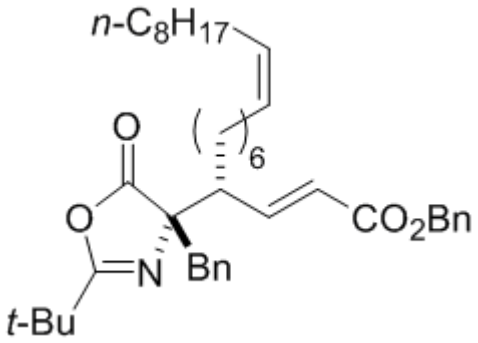

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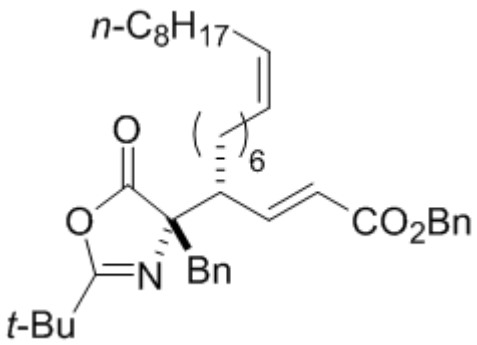

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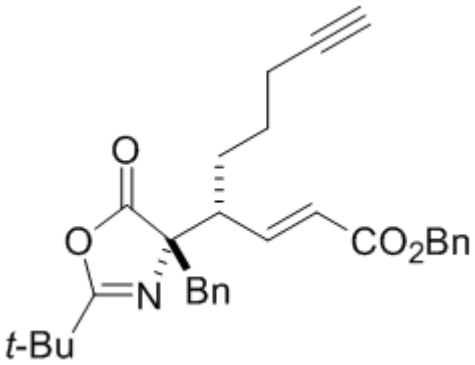

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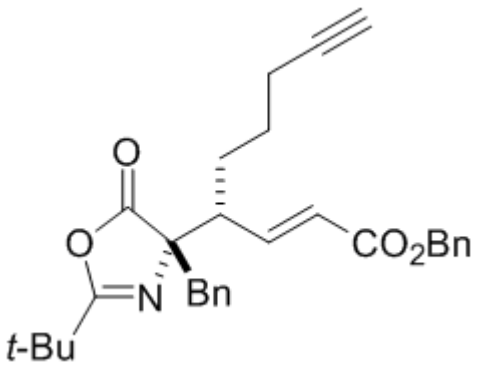

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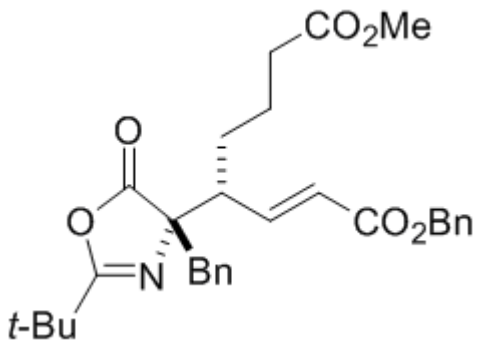

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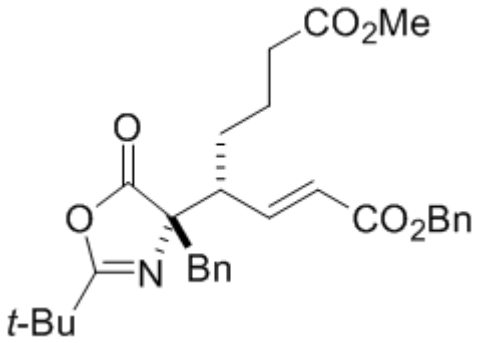

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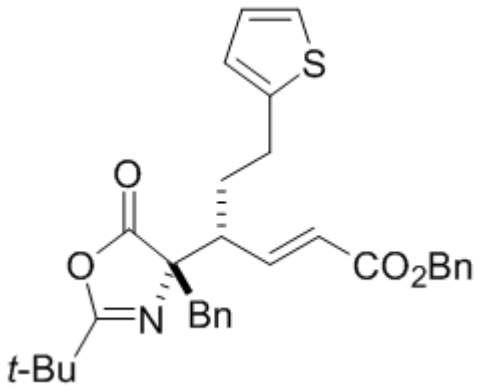

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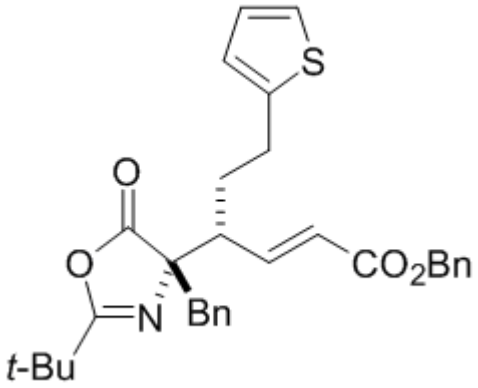

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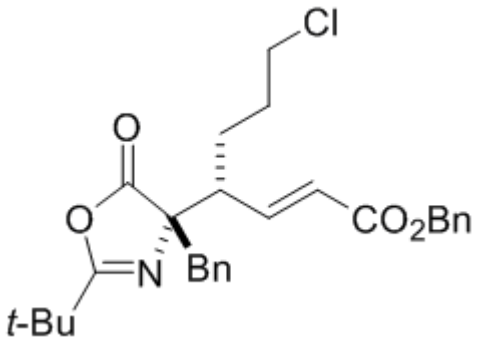
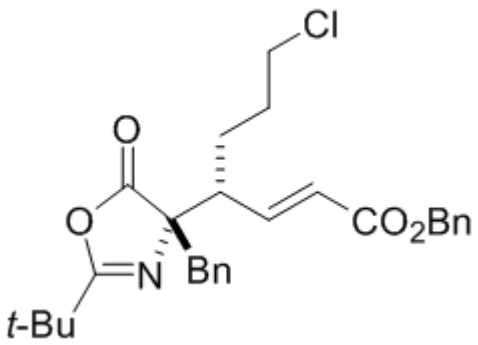


Table 2, entry 13



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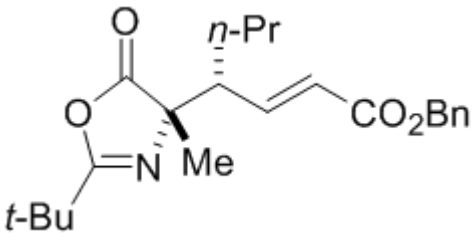
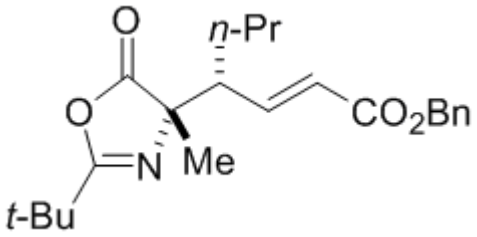


Table 3, entry 1



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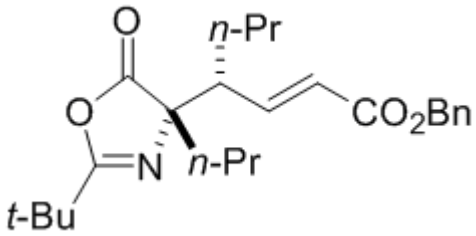

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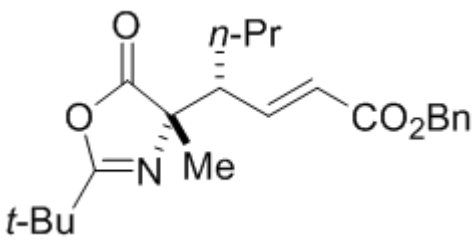

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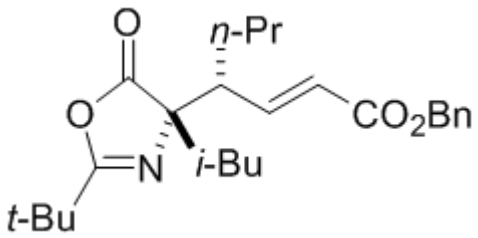

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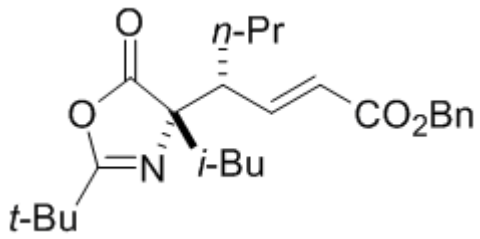

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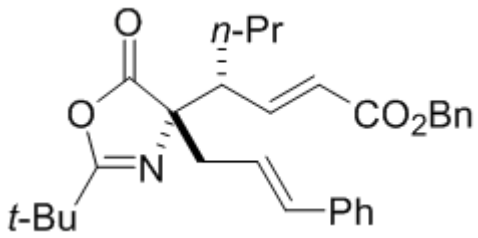

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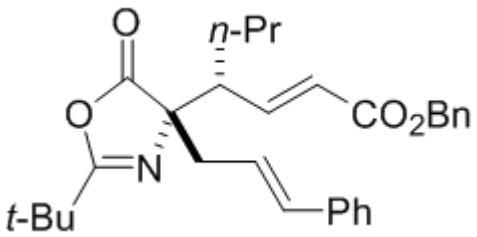
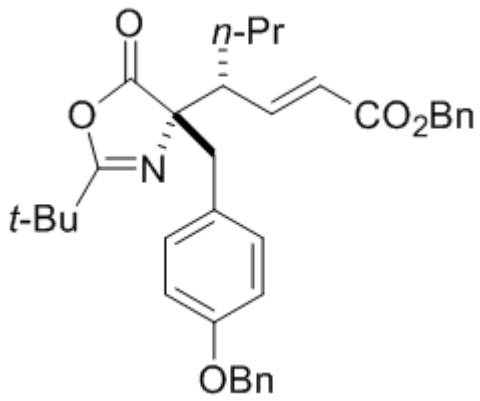


Table 3, entry 5



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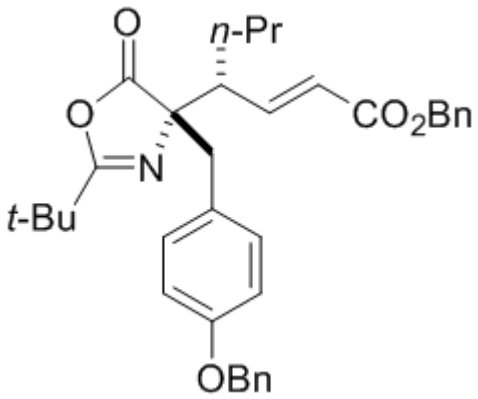


Table 3, entry 6 (major diast.)

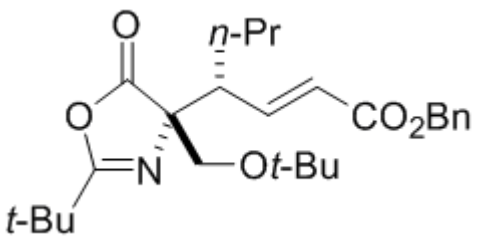


Table 3, entry 6
(major diast.)

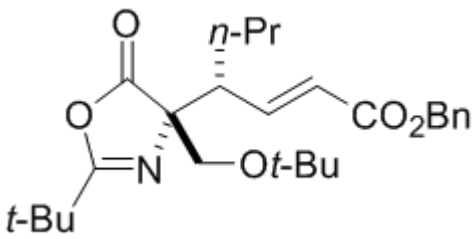


Table 3, entry 6 (minor diast.)

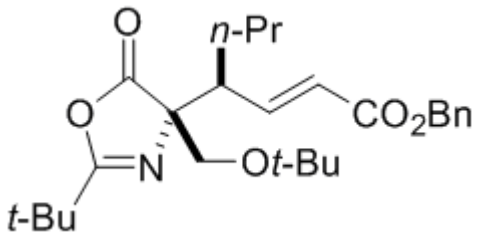


Table 3, entry 6
(minor diast.)

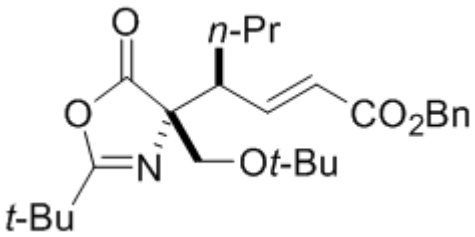
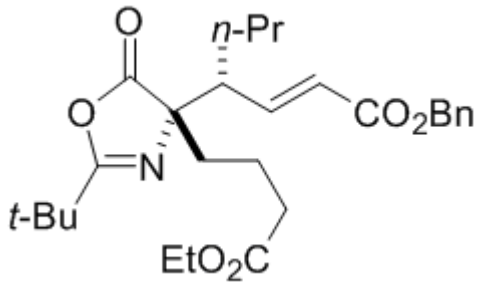


Table 3, entry 7



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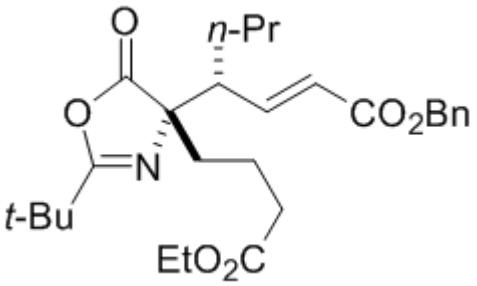

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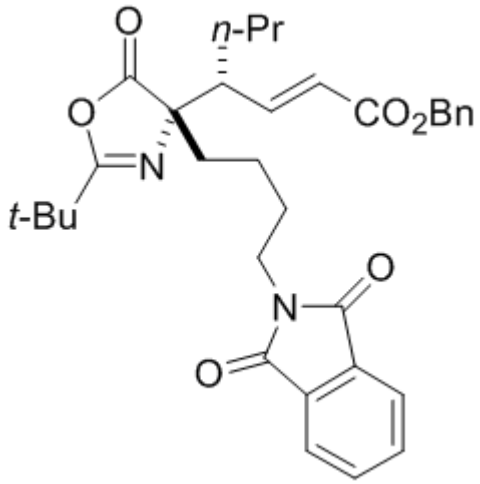

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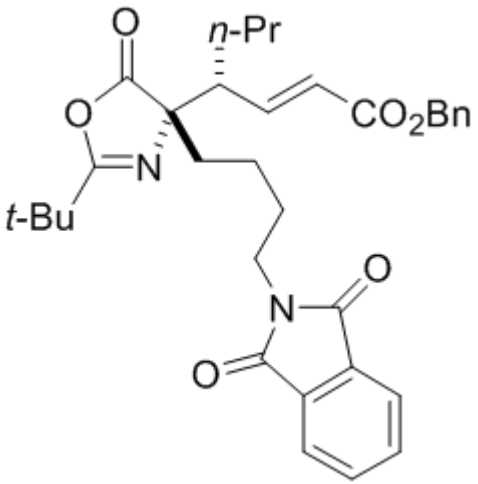

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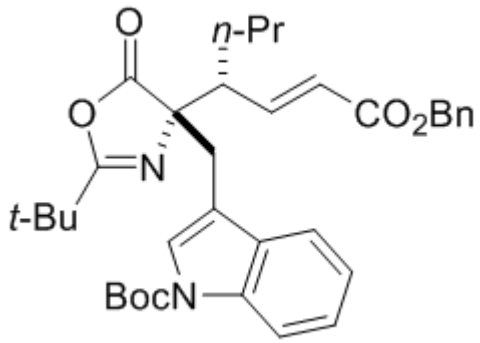

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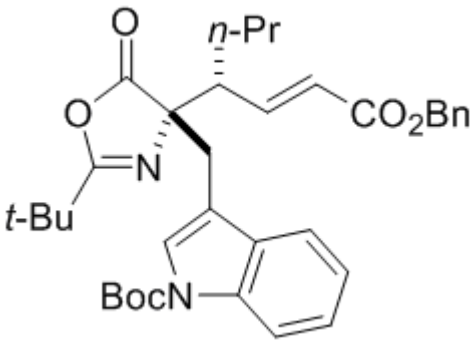
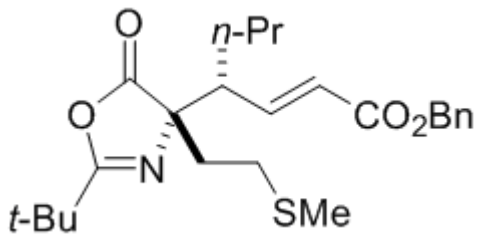


Table 3, entry 10



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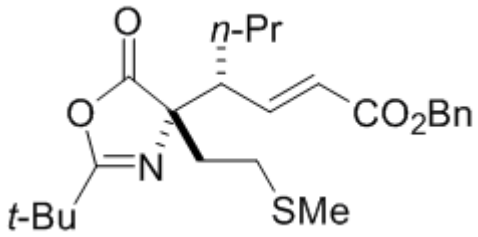


Table 4, entry 1

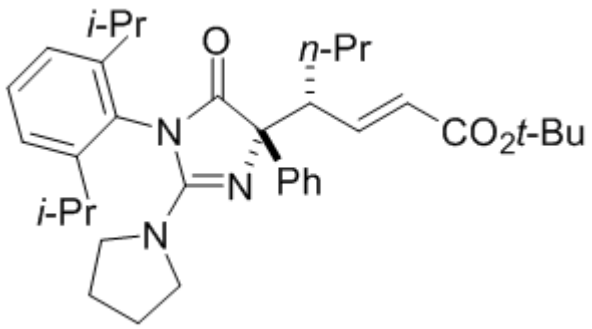


Table 4, entry 1

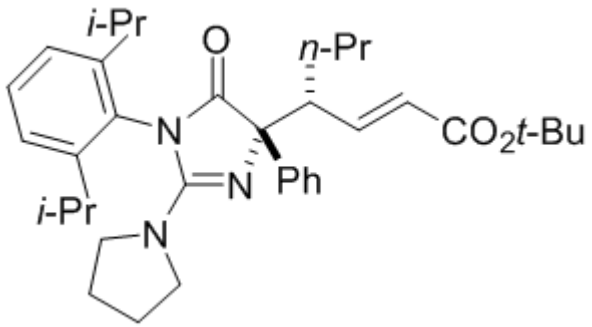
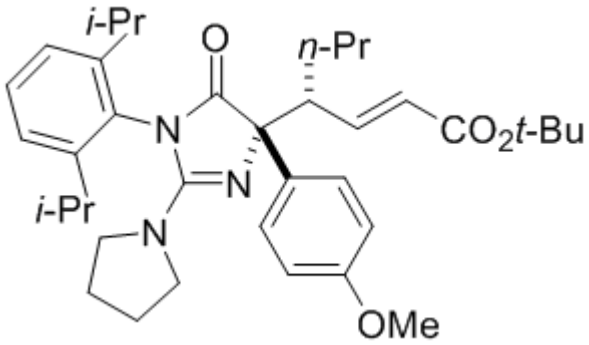


Table 4, entry 2



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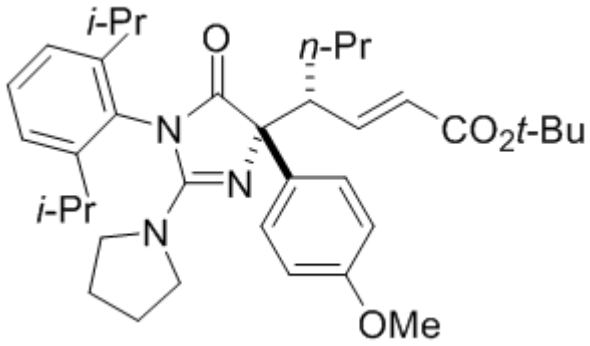


183.39
165.94
158.65
154.35
148.03
147.47
147.19
133.35
130.82
129.92
127.85
125.13
124.04
113.19
79.89
75.75
55.35
51.56
47.86
31.69
29.17
28.39
28.32
25.35
24.03
22.97
22.69
20.95
14.25

Table 4, entry 3

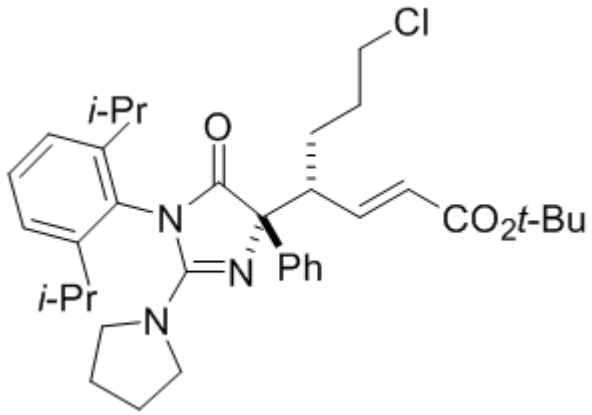
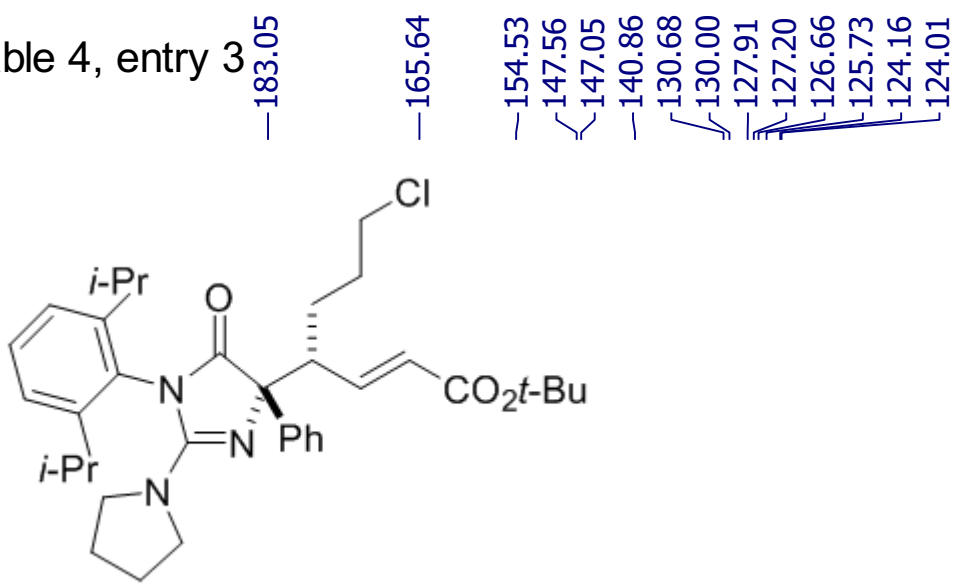


Table 4, entry 3



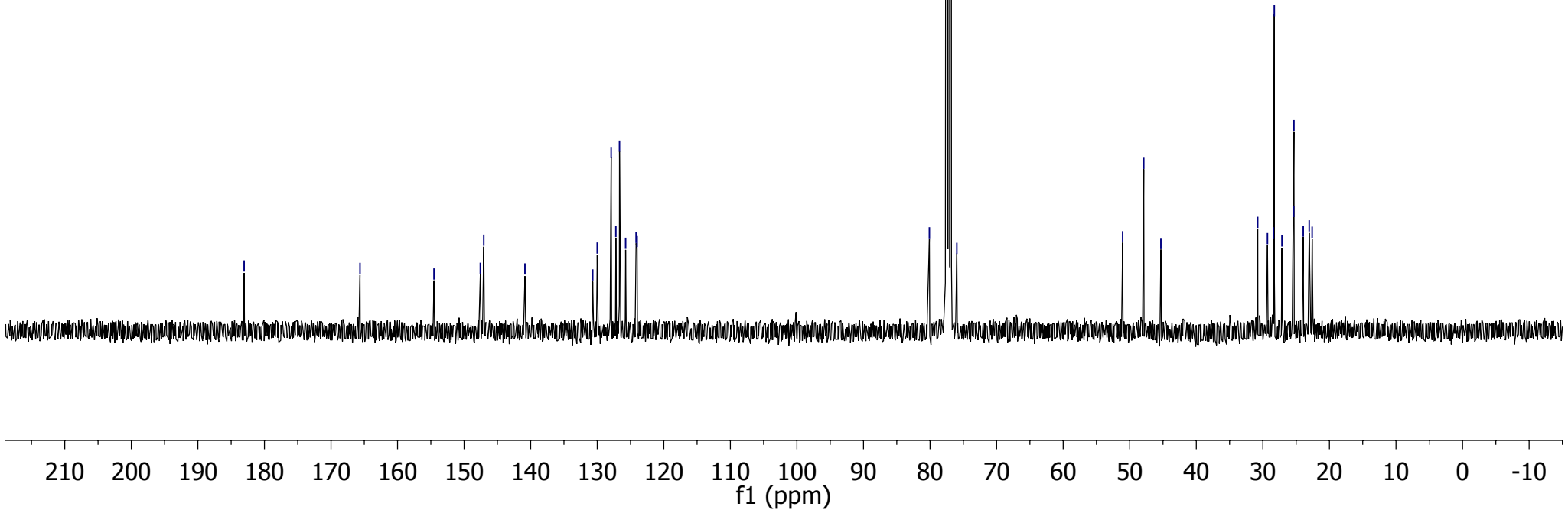


Table 4, entry 4

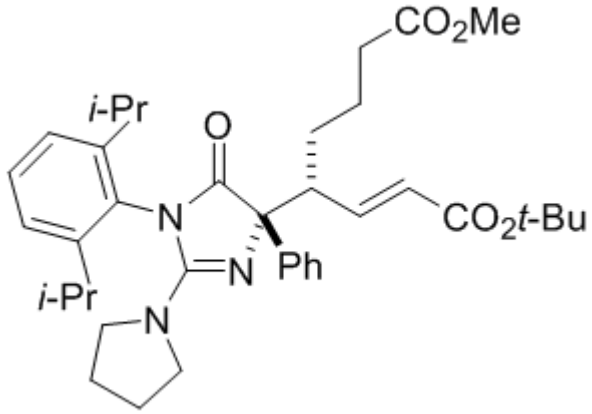
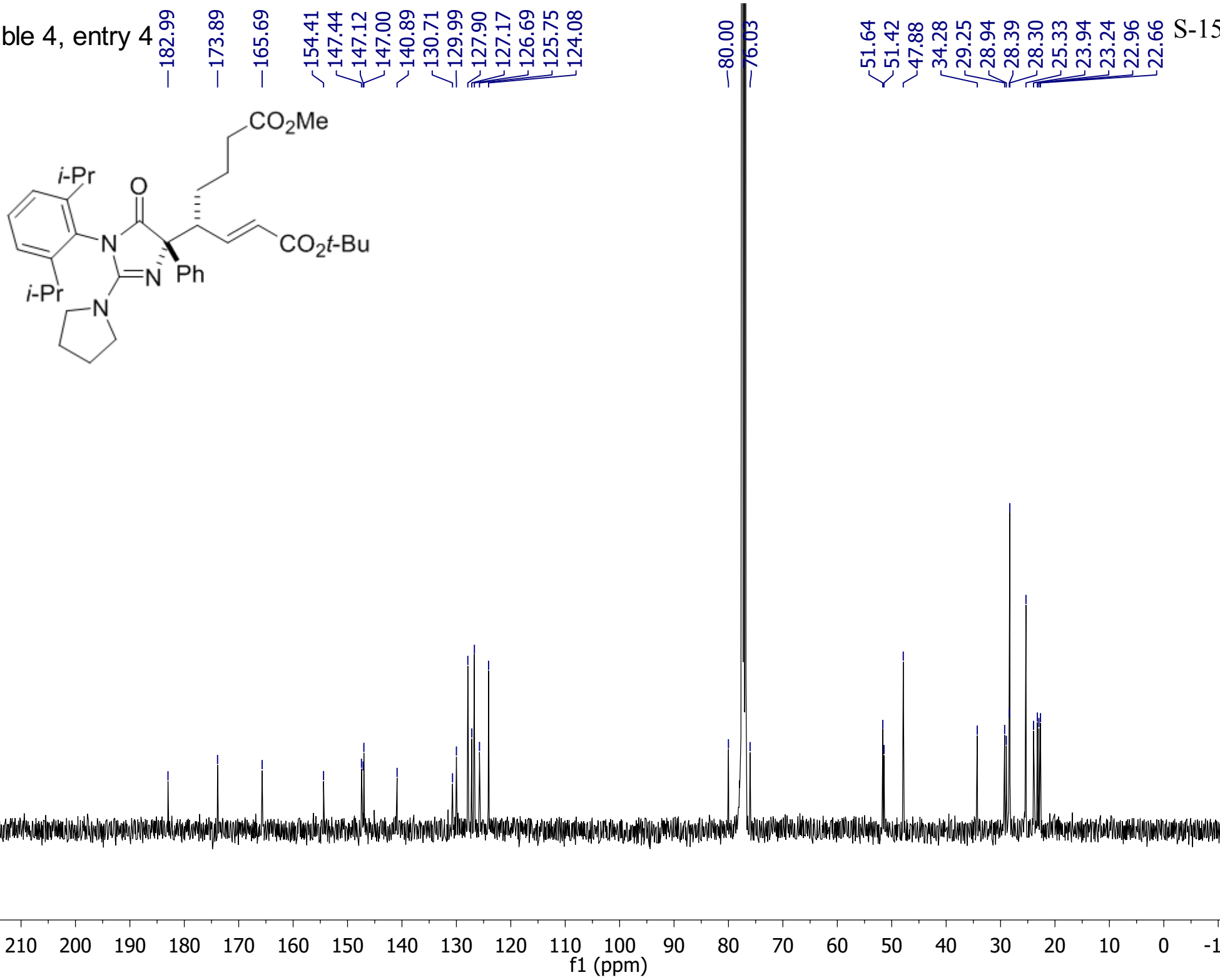
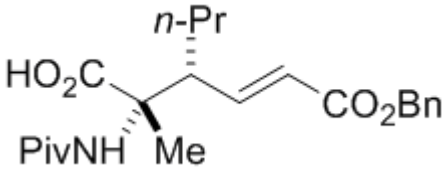


Table 4, entry 4

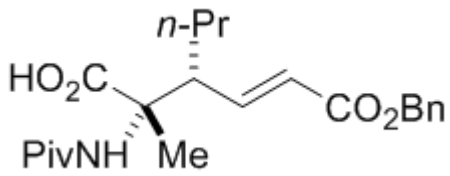


Eq 5


n-Pr
HO2C
CO2Bn
PivNH
Me

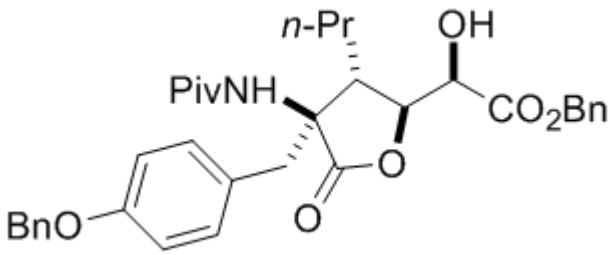
5.10
1.00
1.00
1.02
1.95
0.98
2.81
13.78
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

Eq 5


n-Pr
HO2C
CO2Bn
PivNH
Me

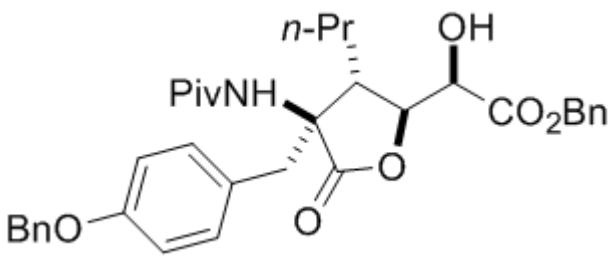
179.77
174.52
165.76
147.20
135.97
128.69
128.37
128.32
125.07
66.51
62.88
48.03
39.34
30.74
27.50
21.04
20.89
13.96
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Eq 6


n-Pr
OH
PivNH
CO2Bn
O
O
BnO

10.53
2.36
2.26
1.05
1.07
1.00
2.12
2.13
1.20
0.97
1.14
1.18
1.00
3.50
9.03
3.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

Eq 6


n-Pr
OH
PivNH
CO2Bn
O
O
BnO

178.23
174.00
171.31
158.64
136.86
135.01
131.65
128.84
128.81
128.74
128.68
128.19
127.65
125.13
81.85
70.13
70.05
68.11
61.85
41.03
38.97
28.68
27.39
21.02
14.50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)