Supporting Information-I

High-yielding Sequential One-pot Synthesis of Chiral and Achiral α-Substituted Acrylates via Metal-free Reductive Coupling Reaction

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General Methods: The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS (δ = 0) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.0) for ^{13}C NMR. *In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.* The coupling constants *J* are given in Hz. Column chromatography was performed using Acme's silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra were recorded on micromass ESI-TOF MS. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300 and Thermo Nicolet FT/IR-5700. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

Materials: All solvents and commercially available chemicals were used as received.

General Experimental Procedures for the Sequential One-pot Reactions:

Proline-catalyzed sequential one-pot TCRA/A/M reactions in one-pot: In an ordinary glass vial equipped with a magnetic stirring bar, was added 0.5 mmol of the aldehyde **3**, 0.5 mmol of CH-acid **1** and 0.5 mmol of Hantzsch ester **2a** in 1.7 mL of solvent, and then the catalyst L-proline **4** (0.1 mmol) was added and the reaction mixture was stirred at 25 °C for 2-12 h. To the crude reaction mixture added 2.5 equivalents of an Eschenmoser's salt **7b**; the reaction mixture was stirred at 65 °C for 12 h. After evaporation of the solvent, the crude reaction mixture was directly loaded onto a silica gel column with or without aqueous work-up and pure one-pot products **8** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

General procedure for the synthesis of product 9ua:

In an ordinary glass vial equipped with a magnetic stirring bar, to 0.2 mmol of the substrate **8ua** was added 1 mL of MeOH, and then the 30 µl of CH_3COCl was added, and the reaction mixture was stirred at 70 °C for 2 h. After evaporation of solvent, the pH was adjusted to 8 with aqueous $NaHCO_3$ solution, and then the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), and concentrated. Pure product **9ua** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

General procedure for the synthesis of product 10wa:

In an ordinary glass vial equipped with a magnetic stirring bar, to 0.3 mmol of the substrate **8wa** was added 1 mL of MeOH, and then the 2 drops of con. HCl was added, and the reaction mixture was stirred at 70 °C for 1 h. After evaporation of solvent, the pH was adjusted to 8 with aqueous $NaHCO_3$ solution, and then the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), and concentrated. Pure product **10wa** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

General procedure for the synthesis of product 11ha: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.5 mmol of the methyl 2-(2-nitrobenzyl)acrylate **8ha** was added 3 mL of acetic acid, and then the 3 mmol of Fe powder was added and the reaction mixture was stirred at 120 °C for 1h. The crude

reaction mixture was treated with saturated aqueous $NaHCO_3$ solution; then the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), and concentrated. Pure product **11ha** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

General procedure for the synthesis of product 11na: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.5 mmol of the methyl 2-methylene-5-(2-nitrophenyl)pentanoate **8na** was added 3 ml of acetic acid, and then the 3 mmol of Fe powder was added and the reaction mixture was stirred at 120 °C for 1h. The crude reaction mixture was treated with saturated aqueous $NaHCO_3$ solution; then the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), and concentrated.

To the above obtained compound (0.3 mmol), was added 1.2 equiv. of KO^tBu (0.36 mmol) in 1 mL dry THF, and the reaction mixture was stirred at 25 °C for 8 h. The crude reaction mixture was treated with saturated aqueous NH_4Cl solution; then the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), and concentrated. Pure products **11na** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

General procedure for the synthesis of product 12ga:

In an ordinary glass vial equipped with a magnetic stirring bar, to 0.5 mmol of the substrate **8ga** was added 15 mL of 1:1 mixture of ^{i}PrOH:THF, and then the 2.4 mL of 10% HCl was added and the reaction mixture was stirred at 50 °C for 12 h. After evaporation of solvent, the crude reaction mixture was treated with water, and then the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), and concentrated. Pure product **12ga** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

General procedure for the synthesis of product 13ga:

In an ordinary glass vial equipped with a magnetic stirring bar, to 1.2 mmol of the substrate **8ga** was added 3 mL of MeOH, and then the 2.8 mL of 10% NaOH (7.2 mmol) was added, and the reaction mixture was stirred at 70 °C for 7 h. After evaporation of solvent, the pH was adjusted to 8 with aqueous NH_4Cl solution, and then the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried

(Na_2SO_4), and concentrated. Pure product acrylic acid was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

To the above obtained product, was added 2.4 mL of 10% HCl in 1:1 mixture of ^{i}PrOH:THF (15 ml), and the reaction mixture was stirred at 50 °C for 12 h. After evaporation of solvent, the crude reaction mixture was treated with water, and then the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), and concentrated. Pure product **13ga** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

General procedure for the synthesis of products 14pa, 14xa:

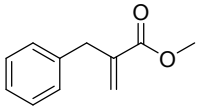
In an ordinary glass vial equipped with a magnetic stirring bar, to the 0.6 mmol of the substrate **8pa** was added 1.0 mL of dry MeOH, and then the 30 mole% of Pd under hydrogen atmosphere (1 atm) was added, and the reaction mixture was stirred at 25 °C for 5 h. After completion of reaction, crude reaction mixture filtered with celite pad. Pure product **14pa** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Similarly compound **14xa** obtained under same condition in EtOAc as solvent by using **8xa.**

General procedure for the synthesis of product 15ua:

In an ordinary glass vial equipped with a magnetic stirring bar, was added to 0.4 mmol of substrate **8ua,** *p*-TSA (30 mole%) in 1.0 mL of MeOH, and the reaction mixture was stirred at 25 °C for 1 h. After evaporation of solvent, the pH was adjusted to 8 with aqueous $NaHCO_3$ solution, and then the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), and concentrated. Pure product **15ua** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

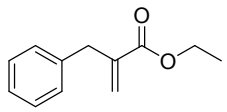
Methyl 2-benzylacrylate (8aa):[1] Purified by column chromatography using EtOAc/hexane (5:95) and isolated as colourless oil. IR (neat): ν_{max} 1722 (O–C=O), 1631, 1438, 1279, 1257, 1204, 1138, 949, 748, 702 and 604 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.33–7.23 (5H, m) [Ar-*H*]; 6.28 (1H, s), 5.50 (1H, s), 3.77 (3H, s, OC*H*$_3$), 3.68 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.4 (C, O-



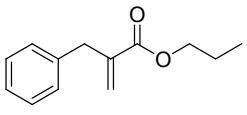
(**8aa**)

C=O), 140.1 (C), 138.7 (C), 129.0 (2 x CH), 128.4 (2 x CH), 126.4 (CH), 126.3 (CH_2), 51.9 (CH_3, O*C*H_3), 38.1 (CH_2, *C*H_2Ph); LCMS m/z 177.00 ($M+H^+$), calcd $C_{11}H_{12}O_2$ 176.08; Anal. calcd for $C_{11}H_{12}O_2$ (176.08): C, 74.98; H, 6.86. Found: C, 74.85; H, 6.81%.

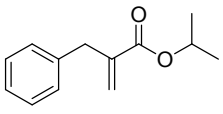
Ethyl 2-benzylacrylate (8ab):[1] Purified by column chromatography using EtOAc/hexane (5:95) and isolated as colourless oil. IR (neat): ν_{max} 1722 (O-C=O), 1438, 1396, 1276, 1204, 1138, 950, 752 and 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32–7.27 (2H, m), 7.23–7.20 (3H, m), 6.24 (1H, s), 5.46 (1H, q, *J* = 1.2 Hz), 4.19 (2H, q, *J* = 7.2 Hz), 3.64 (2H, s), 1.27 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.9 (C, O–C=O), 140.4 (C), 138.8 (C), 129.0 (2 x CH), 128.4 (2 x CH), 126.3 (CH), 125.9 (CH_2), 60.7 (CH_2), 38.1 (CH_2), 14.1 (CH_3); LCMS m/z 189.00 ($M–H^+$), calcd $C_{12}H_{14}O_2$ 190.10; Anal. calcd for $C_{12}H_{14}O_2$ (190.10): C, 75.76; H, 7.42. Found: C, 75.68; H, 7.49%.


(**8ab**)

***n*-Propyl 2-benzylacrylate (8ac):** Purified by column chromatography using EtOAc/hexane (5:95) and isolated as colourless oil. IR (neat): ν_{max} 2971, 1721 (O-C=O), 1397, 1274, 1197, 1136, 948, 752 and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30 (2H, t, *J* = 7.2 Hz), 7.24–7.21 (3H, m), 6.26 (1H, s), 5.47 (1H, s), 4.10 (2H, t, *J* = 6.8 Hz), 3.66 (2H, s), 1.69 (2H, sextet, *J* = 7.6 Hz), 0.93 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.0 (C, O–C=O), 140.4 (C), 138.8 (C), 129.0 (2 x CH), 128.4 (2 x CH), 126.3 (CH), 126.0 (CH_2), 66.4 (CH_2), 38.1 (CH_2), 22.0 (CH_2), 10.4 (CH_3); LCMS m/z 205.00 ($M+H^+$), calcd $C_{13}H_{16}O_2$ 204.11; Anal. calcd for $C_{13}H_{16}O_2$ (204.11): C, 76.44; H, 7.90. Found: C, 76.65; H, 7.96%.

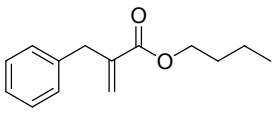

(**8ac**)

***iso*-Propyl 2-benzylacrylate (8ad):** Purified by column chromatography using EtOAc/hexane (5:95) and isolated as colourless oil. IR (neat): ν_{max} 2981, 1714 (O-C=O), 1375, 1275, 1204, 1142, 1107, 749, 701, 636 and 608 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.23–7.18 (2H, m), 7.14–7.11 (3H, m), 6.13 (1H, s), 5.35 (1H, s), 4.99–4.92 (1H, m), 3.55 (2H, s), 1.14 (6H, d, *J* = 6.0 Hz, 2 x C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.4 (C, O–C=O), 140.7 (C), 138.9 (C), 129.0 (2 x CH), 128.3 (2 x CH), 126.2 (CH_2), 125.7 (CH), 68.1 (CH), 38.0 (CH_2), 21.7 (2

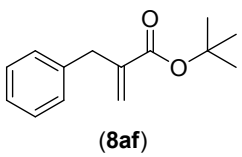

(**8ad**)

x CH_3); LCMS m/z 205.00 ($M+H^+$), calcd $C_{13}H_{16}O_2$ 204.12; Anal. calcd for $C_{13}H_{16}O_2$ (204.12): C, 76.44; H, 7.90. Found: C, 76.40; H, 7.85%.

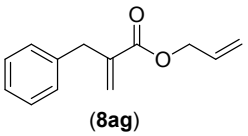
***n*-Butyl 2-benzylacrylate (8ae):** Purified by column chromatography using EtOAc/hexane (5:95) and isolated as colourless oil. IR (neat): ν_{max} 2962, 1720 (O-C=O), 1398, 1260, 1196, 1135, 1092, 1019, 798, 753 and 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.31 (2H, t, *J* = 7.2 Hz), 7.24–7.21 (3H, m), 6.25 (1H, s), 5.47 (1H, s), 4.15 (2H, t, *J* = 6.4 Hz), 3.65 (2H, s), 1.63 (2H, quintet, *J* = 6.8 Hz), 1.43–1.32 (2H, m), 0.93 (3H, t, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.0 (C, O–C=O), 140.4 (C), 138.8 (C), 129.0 (2 x CH), 128.4 (2 x CH), 126.3 (CH), 126.0 (CH_2), 64.6 (CH_2), 38.1 (CH_2), 30.6 (CH_2), 19.2 (CH_2), 13.7 (CH_3); LCMS m/z 219.00 ($M+H^+$), calcd $C_{14}H_{18}O_2$ 218.13; Anal. calcd for $C_{14}H_{18}O_2$ (218.13): C, 77.03; H, 8.31. Found: C, 77.13; H, 8.37%.


(**8ae**)

***tert*-Butyl 2-benzylacrylate (8af):**[2] Purified by column chromatography using EtOAc/hexane (5:95) and isolated as colourless oil. IR (neat): ν_{max} 2978, 1713 (O-C=O), 1393, 1368, 1308, 1256, 1216, 1141, 948, 850, 744 and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30 (2H, t, *J* = 7.2 Hz), 7.27–7.18 (3H, m), 6.15 (1H, s), 5.38 (1H, s), 3.60 (2H, s), 1.44 (9H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.2 (C, O–C=O), 141.7 (C), 139.1 (C), 129.0 (2 x CH), 128.3 (2 x CH), 126.2 (CH), 125.2 (CH_2), 80.7 (C), 38.2 (CH_2), 28.0 (3 x CH_3); LCMS m/z 217.00 ($M–H^+$), calcd $C_{14}H_{18}O_2$ 218.13; Anal. calcd for $C_{14}H_{18}O_2$ (218.13): C, 77.03; H, 8.31. Found: C, 77.22; H, 8.25%.

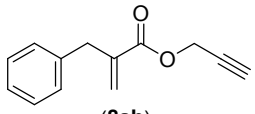

(**8af**)

Allyl 2-benzylacrylate (8ag): Purified by column chromatography using EtOAc/hexane (5:95) and isolated as yellow oil. IR (neat): ν_{max} 3028, 1720 (O-C=O), 1633, 1433, 1273, 1194, 1134, 986, 939, 819, 751, 702, 661 and 604 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20–7.19 (2H, m), 7.12–7.11 (3H, m), 6.19 (1H, s), 5.86–5.78 (1H, m), 5.39 (1H, s), 5.19 (1H, d, *J* = 17.2 Hz), 5.12 (1H, d, *J* = 10.4 Hz), 4.55 (2H, s), 3.56 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.4 (C, O–C=O), 140.1 (C), 138.6 (C), 132.0 (CH), 129.0 (2 x CH), 128.4 (2 x CH), 126.4 (CH_2), 126.3 (CH), 118.0 (CH_2), 65.3 (CH_2), 38.0 (CH_2); LCMS: m/z 201.00 ($M–H^+$),

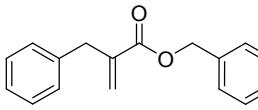

(**8ag**)

calcd $C_{13}H_{14}O_2$ 202.10; Anal. calcd for $C_{13}H_{14}O_2$ (202.10): C, 77.20, H, 6.98. Found: C, 77.32; H, 6.88%.

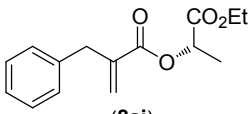
Prop-2-yn-1-yl 2-benzylacrylate (8ah): Purified by column chromatography using EtOAc/hexane (5:95) and isolated as yellow oil. IR (neat): ν_{max} 3297, 1724 (O-C=O), 1273, 1188, 1127, 998, 954, 746, 702 and 652 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30 (2H, t, *J* = 7.2 Hz), 7.25–7.19 (3H, m), 6.30 (1H, s), 5.52 (1H, s), 4.73 (2H, d, *J* = 2.0 Hz), 3.65 (2H, s), 2.47 (1H, br s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.0 (C, O–C=O), 139.5 (C), 138.3 (C), 129.1 (2 x CH), 128.4 (2 x CH), 127.3 (CH_2), 126.4 (CH), 77.6 (C), 74.9 (CH), 52.3 (CH_2), 37.9 (CH_2); LCMS: m/z 201.00 ($M+H^+$), calcd $C_{13}H_{12}O_2$ 200.08; Anal. calcd for $C_{13}H_{12}O_2$ (200.08): C, 77.98, H, 6.04. Found: C, 77.88; H, 6.12%.


(8ah)

Benzyl 2-benzylacrylate (8ai):[1] Purified by column chromatography using EtOAc/hexane (5:95) and isolated as colourless oil. IR (neat): ν_{max} 1719 (O-C=O), 1633, 1452, 1274, 1193, 1129, 952, 744, 669 and 612 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.44–7.31 (8H, m), 7.28–7.22 (2H, m), 6.34 (1H, s), 5.53 (1H, s), 5.21 (2H, s), 3.70 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.6 (C, O–C=O), 140.0 (C), 138.6 (C), 135.9 (C), 129.0 (2 x CH), 128.4 (2 x CH), 128.3 (2 x CH), 128.1 (CH), 128.0 (2 x CH), 126.6 (CH_2), 126.3 (CH), 66.4 (CH_2), 38.0 (CH_2); LCMS: m/z 253.00 ($M+H^+$), calcd $C_{17}H_{16}O_2$ 252.11; HRMS m/z 275.1049 (M+Na), calcd for $C_{17}H_{16}O_2Na$ 275.1048, Anal. calcd for $C_{17}H_{16}O_2$ (252.11): C, 80.93; H, 6.39. Found: C, 80.85; H, 6.35%.

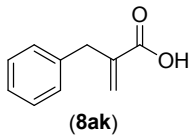

(8ai)

(*S*)-1-Ethoxy-1-oxopropan-2-yl 2-benzylacrylate (8aj): Purified by column chromatography using EtOAc/hexane (5:95) and isolated as colourless oil. **$[\alpha]_D^{25}$ = –10.69° (*c* = 0.30 g/100 mL, $CHCl_3$);** IR (neat): ν_{max} 2988, 1754 (O-C=O), 1724 (O-C=O), 1452, 1374, 1272, 1198, 1131, 1097, 1050, 753 and 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32–7.27 (2H, m), 7.23–7.21 (3H, m), 6.35 (1H, s), 5.54 (1H, s), 5.10 (1H, q, *J* = 7.2 Hz), 4.19 (2H, q, *J* = 7.2 Hz), 3.67 (2H, s), 1.50 (3H, d, *J* = 7.2 Hz), 1.25 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 170.7 (C, O-C=O), 166.1 (C, O–C=O), 139.4 (C), 138.5 (C), 129.0 (2 x CH), 128.4 (2 x CH), 127.2 (CH_2), 126.3 (CH), 69.0 (CH), 61.3 (CH_2), 37.9 (CH_2),


(8aj)

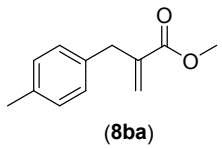
16.9 (CH_3), 14.0 (CH_3); LCMS: m/z 263.00 ($M+H^+$), calcd $C_{15}H_{18}O_4$ 262.12; Anal. calcd for $C_{15}H_{18}O_4$ (262.12): C, 68.68, H, 6.92. Found: C, 68.61; H, 6.95%.

2-Benzylacrylic acid (8ak):[3] Purified by simple acid/base workup and isolated as white solid. MP: 66-68 °C; IR (neat): ν_{max} 3059, 3027, 2888, 2828, 1692, 1628, 1437, 1292, 1225, 1156, 909, 734 and 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32 (2H, t, *J* = 7.2 Hz), 7.26–7.22 (3H, m), 6.40 (1H, s), 5.60 (1H, s), 3.65 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 172.3 (C, *C*O_2H), 139.5 (C), 138.4 (C), 129.0 (2 x CH), 128.6 (CH), 128.4 (2 x CH), 126.4 (CH_2), 37.5 (CH_2); LCMS: m/z 163.00 ($M+H^+$), calcd $C_{10}H_{10}O_2$ 162.07; Anal. calcd for $C_{10}H_{10}O_2$ (162.07): C, 74.06; H, 6.21. Found: C, 74.14; H, 6.28%.



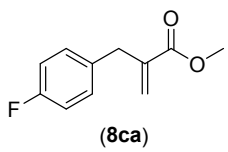
(**8ak**)

Methyl 2-(4-methylbenzyl)acrylate (8ba):[1] Purified by column chromatography using EtOAc/hexane (5:95) and isolated as colourless oil. IR (neat): ν_{max} 3008, 1722 (O-C=O), 1632, 1438, 1397, 1275, 1266, 1203, 1137, 948, 810 and 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.12 (4H, br s), 6.25 (1H, s), 5.49 (1H, s), 3.76 (3H, s), 3.62 (2H, s), 2.35 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.4 (C, O–C=O), 140.2 (C), 135.8 (C), 135.5 (C), 129.1 (2 x CH), 128.8 (2 x CH), 126.0 (CH_2), 51.8 (CH_3), 37.6 (CH_2), 21.0 (CH_3); LCMS: m/z 191.00 ($M+H^+$), calcd $C_{12}H_{14}O_2$ 190.10; Anal. calcd for $C_{12}H_{14}O_2$ (190.10): C, 75.76; H, 7.42. Found: C, 75.62; H, 7.35%.



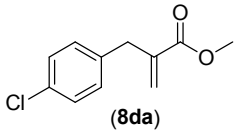
(**8ba**)

Methyl 2-(4-fluorobenzyl)acrylate (8ca):[1] Purified by column chromatography using EtOAc/hexane (8:92) and isolated as colourless oil. IR (neat): ν_{max} 3007, 1723 (O-C=O), 1510, 1439, 1275, 1266, 1222, 1138, 1018, 817 and 754 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.16 (2H, t, *J* = 8 Hz), 6.98 (2H, t, *J* = 8.4 Hz), 6.24 (1H, s), 5.47 (1H, s), 3.74 (3H, s), 3.60 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.2 (C, O–C=O), 161.5 (C, d, *J* = 243 Hz), 140.0 (C), 134.2 (C), 130.4 (2 x CH, d, *J* = 8.0 Hz), 126.3 (CH_2), 115.2 (2 x CH, d, *J* = 21 Hz), 51.9 (CH_3, OCH_3), 37.3 (CH_2); LCMS: m/z 195.00 ($M+H^+$), calcd $C_{11}H_{11}FO_2$ 194.07; Anal. calcd for $C_{11}H_{11}FO_2$ (194.07): C, 68.03; H, 5.71. Found: C, 68.12; H, 5.78%.

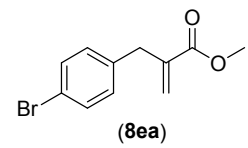


(**8ca**)

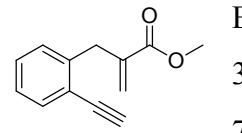
Methyl 2-(4-chlorobenzyl)acrylate (8da):[1] Purified by column chromatography using EtOAc/hexane (8:92) and isolated as colourless oil. IR (neat): ν_{max} 3008, 1721 (O-C=O), 1486, 1438, 1398, 1275, 1266, 1203, 1138, 1072, 1012, 797 and 754 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41 (2H, d, *J* = 7.2 Hz), 7.08 (2H, d, *J* = 6.8 Hz), 6.24 (1H, s), 5.49 (1H, s), 3.73 (3H, s), 3.58 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.0 (C, O–C=O), 139.4 (C), 137.6 (C), 131.4 (2 x CH), 130.6 (2 x CH), 126.5 (CH_2), 120.2 (C), 51.9 (CH_3), 37.5 (CH_2); LCMS: m/z 211.00 ($M+H^+$), calcd $C_{11}H_{11}ClO_2$ 210.04; Anal. calcd for $C_{11}H_{11}ClO_2$ (210.04): C, 62.72; H, 5.26. Found: C, 62.85; H, 5.33%.


(**8da**)

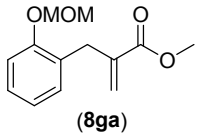
Methyl 2-(4-bromobenzyl)acrylate (8ea):[1] Purified by column chromatography using EtOAc/hexane (8:92) and isolated as colourless oil. IR (neat): ν_{max} 3006, 1722 (O-C=O), 1492, 1438, 1275, 1266, 1204, 1138, 1091 and 754 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26 (2H, d, *J* = 8 Hz), 7.13 (2H, d, *J* = 8.4 Hz), 6.24 (1H, s), 5.48 (1H, s), 3.73 (3H, s), 3.60 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.0 (C, O–C=O), 139.6 (C), 137.1 (C), 132.1 (C), 130.2 (2 x CH), 128.4 (2 x CH), 126.4 (CH_2), 51.8 (CH_3), 37.4 (CH_2); LCMS: m/z 255.00 ($M+H^+$), 257.00 ($M+2+H^+$), calcd $C_{11}H_{11}BrO_2$ 253.99; Anal. calcd for $C_{11}H_{11}BrO_2$ (253.99): C, 51.79; H, 4.35. Found: C, 51.65; H, 4.41%.


(**8ea**)

Methyl 2-(2-ethynylbenzyl)acrylate (8fa): Purified by column chromatography using EtOAc/hexane (8:92) and isolated as colourless oil. IR (neat): ν_{max} 3296, 3008, 1721 (O-C=O), 1632, 1439, 1396, 1274, 1204, 1140, 951, 757, 687 and 639 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.51 (1H, d, *J* = 7.2 Hz), 7.29 (1H, t, *J* = 7.2 Hz), 7.23-7.18 (2H, m), 6.26 (1H, s), 5.39 (1H, s), 3.84 (2H, s), 3.76 (3H, s), 3.24 (1H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.4 (C, O–C=O), 141.2 (C), 138.9 (C), 133.0 (CH), 129.5 (CH), 129.0 (CH), 126.6 (CH_2), 126.4 (CH), 122.2 (C), 82.1 (C), 81.1 (CH), 51.9 (CH_3), 36.1 (CH_2); LCMS: m/z 201.00 ($M+H^+$), calcd $C_{13}H_{12}O_2$ 200.08; HRMS m/z 201.0915 (M+H), calcd for $C_{13}H_{12}O_2H$ 201.0916, Anal. calcd for $C_{13}H_{12}O_2$ (200.08): C, 77.98; H, 6.04. Found: C, 77.85; H, 7.35%.

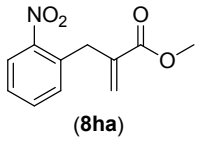

(**8fa**)

Methyl 2-(2-(methoxymethoxy)benzyl)acrylate (8ga): Purified by column chromatography using EtOAc/hexane (10:90) and isolated as oil. IR (neat): ν_{max} 1722 (O-C=O), 1493, 1439, 1237, 1203, 1149, 1106, 1079, 1046, 1003, 947, 924, 757, 660 and 628 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22–7.15 (2H, m), 7.10 (1H, d, *J* = 8 Hz), 6.96 (1H, t, *J* = 7.2 Hz), 6.22 (1H, d, *J* = 0.8 Hz), 5.35 (1H, d, *J* = 1.6 Hz), 5.18 (2H, s), 3.77 (3H, s), 3.67 (2H, s), 3.45 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.6 (C, O–C=O), 155.1 (C), 139.2 (C), 130.8 (CH), 127.7 (CH), 127.5 (C), 125.6 (CH_2), 121.6 (CH), 113.8 (CH), 94.1 (CH_2), 55.9 (CH_3), 51.8 (CH_3), 32.1 (CH_2); LCMS: m/z 237.00 ($M+H^+$), calcd $C_{13}H_{16}O_4$ 236.26; Anal. calcd for $C_{13}H_{16}O_4$ (236.26): C, 66.09; H, 6.83. Found: C, 66.15; H, 6.78%.



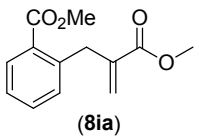
(**8ga**)

Methyl 2-(2-nitrobenzyl)acrylate (8ha):[4] Purified by column chromatography using EtOAc/hexane (20:80) and isolated as oil. IR (neat): ν_{max} 1720 (O-C=O), 1526, 1440, 1351, 1260, 1210, 1147, 955, 859, 819, 788, 747 and 624 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.93 (1H, d, *J* = 8.4 Hz), 7.54 (1H, t, *J* = 7.2 Hz), 7.41–7.35 (2H, m), 6.26 (1H, s), 5.40 (1H, s), 3.97 (2H, s), 3.73 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 166.8 (C, O–C=O), 149.4 (C), 138.1 (C), 133.5 (C), 133.0 (CH), 132.4 (CH), 127.8 (CH), 127.0 (CH_2), 124.9 (CH), 52.1 (CH_3), 34.8 (CH_2); LCMS: m/z 222.00 ($M+H^+$), calcd $C_{11}H_{11}NO_4$ 221.04; HRMS m/z 244.0584 (M+Na), calcd for $C_{11}H_{11}NO_4Na$ 244.0586, Anal. calcd for $C_{11}H_{11}NO_4$ (221.04): C, 59.73; H, 5.01; N, 6.33. Found: C, 59.65; H, 4.96; N, 6.38%.



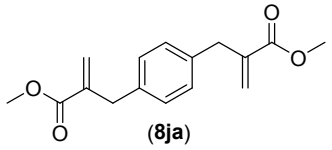
(**8ha**)

Methyl 2-(2-(methoxycarbonyl)allyl)benzoate (8ia):[5] Purified by column chromatography using EtOAc/hexane (20:80) and isolated as oil. IR (neat): ν_{max} 1722 (O-C=O), 1437, 1263, 1196, 1133, 1080, 951, 817, 756, 718 and 637 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.89 (1H, d, *J* = 8.0 Hz), 7.42 (1H, t, *J* = 8.0 Hz), 7.29–7.22 (2H, m), 6.17 (1H, s), 5.19 (1H, s), 4.00 (2H, s), 3.82 (3H, s), 3.72 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.5 (C, O–*C*=O), 167.3 (C, O-*C*=O), 140.0 (C), 139.9 (C), 131.9 (CH), 131.4 (CH), 130.7 (CH), 129.8 (C), 126.4 (CH), 125.5 (CH_2), 51.8 (CH_3), 51.8 (CH_3), 35.8 (CH_2); LCMS: m/z 235.00 ($M+H^+$), calcd $C_{13}H_{14}O_4$ 234.09; HRMS m/z 257.0789 (M+Na), calcd for $C_{13}H_{14}O_4Na$ 257.0790, Anal. calcd for $C_{13}H_{14}O_4$ (234.09): C, 66.66; H, 6.02. Found: C, 66.75; H, 6.11%.

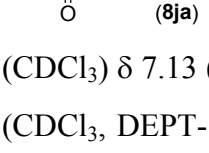


(**8ia**)

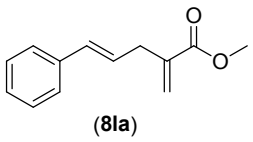
Dimethyl 2,2'-(1,4-phenylenebis(methylene))diacrylate (8ja): Purified by column chromatography using EtOAc/hexane (5:95) and isolated as oil. IR (neat): ν_{max} 2956, 1720 (O-C=O), 1631, 1511, 1438, 1303, 1269, 1024, 953, 846, 758 and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.13 (4H, br s), 6.22 (2H, s), 5.46 (2H, s), 3.73 (6H, s), 3.60 (4H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.3 (2 x C, O–*C*=O), 140.0 (2 x C), 136.6 (2 x C), 129.0 (4 x CH), 126.2 (2 x CH_2), 51.8 (2 x CH_3), 37.6 (2 x CH_2); LCMS: m/z 275.00 ($M+H^+$), calcd $C_{16}H_{18}O_4$ 274.12; Anal. calcd for $C_{16}H_{18}O_4$ (274.12): C, 70.06; H, 6.61. Found: C, 70.21; H, 6.58%.


(**8ja**)

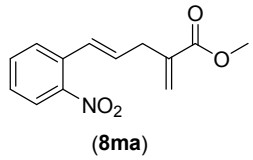
Dimethyl 2,2'-(1,3-phenylenebis(methylene))diacrylate (8ka): Purified by column chromatography using EtOAc/hexane (5:95) and isolated as oil. IR (neat): ν_{max} 2952, 1720 (O-C=O), 1630, 1440, 1395, 1205, 1139, 1024, 951, 758 and 649 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22 (1H, t, *J* = 7.6 Hz), 7.06–7.04 (3H, m), 6.22 (2H, s), 5.44 (2H, s), 3.73 (6H, s), 3.61 (4H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.3 (2 x C, O–*C*=O), 140.0 (2 x C), 138.7 (2 x C), 129.7 (CH), 128.4 (CH), 127.0 (2 x CH), 126.2 (2 x CH_2), 51.8 (2 x CH_3), 37.9 (2 x CH_2); LCMS: m/z 275.00 ($M+H^+$), calcd $C_{16}H_{18}O_4$ 274.12; HRMS m/z 297.1107 (M+Na), calcd for $C_{16}H_{18}O_4Na$ 297.1103; Anal. calcd for $C_{16}H_{18}O_4$ (274.12): C, 70.06; H, 6.61. Found: C, 70.21; H, 6.57%.


(**8ka**)

(*E*)-Methyl 2-methylene-5-phenylpent-4-enoate (8la):[6] Purified by column chromatography using EtOAc/hexane (5:95) and isolated as oil. IR (neat): ν_{max} 2963, 1726 (O-C=O), 1446, 1264, 1202, 1103, 1044, 818, 752 and 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38 (2H, d, *J* = 7.2 Hz), 7.32 (2H, t, *J* = 7.2 Hz), 7.27–7.21 (1H, m), 6.47 (1H, d, *J* = 16.0 Hz), 6.30–6.22 (2H, m), 5.66 (1H, s), 3.79 (3H, s), 3.24 (2H, d, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.3 (C, O–C=O), 139.1 (C), 137.2 (C), 132.0 (CH), 128.4 (2 x CH), 127.2 (CH), 126.6 (CH), 126.1 (2 x CH), 125.6 (CH_2), 51.9 (CH_3), 35.1 (CH_2); LCMS: m/z 203.00 ($M+H^+$), calcd $C_{13}H_{14}O_2$ 202.10; Anal. calcd for $C_{13}H_{14}O_2$ (202.10): C, 77.20; H, 6.98. Found: C, 77.35; H, 6.89%.

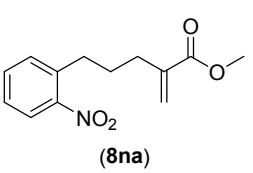

(**8la**)

(*E*)-Methyl 2-methylene-5-(2-nitrophenyl)pent-4-enoate (8ma): Purified by column chromatography using EtOAc/hexane (20:80) and isolated as yellow oil. IR (neat): ν_{max} 1721 (O-C=O), 1524, 1439, 1347, 1297, 1205, 1143, 966, 854, 816, 788 and 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.87 (1H, d, *J* = 8 Hz), 7.55 (1H, t, *J* = 7.6 Hz), 7.51 (1H, d, *J* = 7.6 Hz), 7.34 (1H, t, *J* = 8 Hz), 6.88 (1H, d, *J* = 15.6 Hz), 6.26–6.19 (1H, m), 6.24 (1H, s), 5.66 (1H, s), 3.77 (3H, s), 3.25 (2H, d, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.1 (C, O–*C*=O), 147.5 (C), 138.2 (C), 132.9 (CH), 132.8 (C), 132.3 (CH), 128.5 (CH), 127.7 (CH), 127.2 (CH), 126.3 (CH_2), 124.3 (CH), 51.9 (CH_3), 35.3 (CH_2); LCMS: m/z 248.00 ($M+H^+$), calcd $C_{13}H_{13}NO_4$ 247.08; HRMS m/z 270.0743 (M+Na), calcd for $C_{13}H_{13}NO_4Na$ 270.0742, Anal. calcd for $C_{13}H_{13}NO_4$ (247.08): C, 63.15; H, 5.30; N, 5.67. Found: C, 63.08; H, 5.26; N, 5.71%.



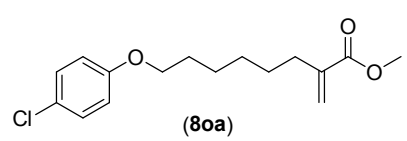
(**8ma**)

Methyl 2-methylene-5-(2-nitrophenyl)pentanoate (8na): Purified by column chromatography using EtOAc/hexane (20:80) and isolated as oil. IR (neat): ν_{max} 3008, 1720 (O-C=O), 1630, 1526, 1441, 1349, 1268, 1150, 951, 816, 750 and 661 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.87 (1H, d, *J* = 8 Hz), 7.50 (1H, t, *J* = 7.6 Hz), 7.35–7.30 (2H, m), 6.16 (1H, s), 5.56 (1H, s), 3.74 (3H, s), 2.89 (2H, t, *J* = 8 Hz), 2.39 (2H, t, *J* = 7.6 Hz), 1.83 (2H, quintet, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.4 (C, O–*C*=O), 149.2 (C), 139.7 (C), 136.9 (C), 132.8 (CH), 131.8 (CH), 127.0 (CH), 125.2 (CH_2), 124.6 (CH), 51.8 (CH_3), 32.4 (CH_2), 31.7 (CH_2), 29.2 (CH_2); LCMS: m/z 250.00 ($M+H^+$), calcd $C_{13}H_{15}NO_4$ 249.10; HRMS m/z 272.0899 (M+Na), calcd for $C_{13}H_{15}NO_4Na$ 272.0899; Anal. calcd for $C_{13}H_{15}NO_4$ (249.10): C, 62.64; H, 6.07; N, 5.62. Found: C, 62.51; H, 6.12; N, 5.58%.



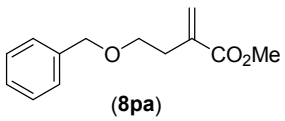
(**8na**)

Methyl 8-(4-chlorophenoxy)-2-methyleneoctanoate (8oa):[7] Purified by column chromatography using EtOAc/hexane (20:80) and isolated as oil. IR (neat): ν_{max} 2361, 1721 (O-C=O), 1492, 1286, 1244, 1199, 1148, 1003, 824 and 604 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.21 (2H, d, *J* = 9.2 Hz), 6.81 (2H, d, *J* = 8.8 Hz), 6.14 (1H, s), 5.53 (1H, s), 3.91 (2H, t, *J* = 6.4 Hz), 3.75 (3H, s), 2.31 (2H, t, *J* = 7.6 Hz), 1.77 (2H, quintet, *J* = 6.4 Hz), 1.54–1.45 (4H, m), 1.44–1.36 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-



(**8oa**)

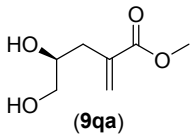
135) δ 167.8 (C, O–C=O), 157.7 (C), 140.6 (C), 129.2 (2 x CH), 125.3 (C), 124.6 (CH_2), 115.7 (2 x CH), 68.2 (CH_2), 51.8 (CH_3), 31.8 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 28.3 (CH_2), 25.8 (CH_2); LCMS: m/z 297.00 ($M+H^+$), calcd $C_{16}H_{21}ClO_3$ 296.12; HRMS m/z 319.1079 (M+Na), calcd for $C_{16}H_{21}ClO_3Na$ 319.1077; Anal. calcd for $C_{16}H_{21}ClO_3$ (296.12): C, 64.75; H, 7.13. Found: C, 64.75; H, 7.18%.



(8pa)

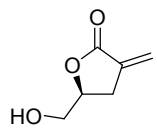
Methyl 4-(benzyloxy)-2-methylenebutanoate (8pa): Purified by column chromatography using EtOAc/hexane (5:95) and isolated as oil. IR (neat): ν_{max} 1722 (O-C=O), 1441, 1330, 1196, 1160, 1093, 816 735 and 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.39 – 7.28 (5H, m), 6.26 (1H, d, *J* = 1.2 Hz), 5.69 (1H, q, *J* = 1.2 Hz), 4.54 (2H, s), 3.76 (3H, s), 3.65 (2H, t, *J* = 6.4 Hz), 2.67 (2H, t, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.5 (C, O–C=O), 138.4 (C), 137.4 (C), 128.4 (2 x CH), 127.6 (2 x CH), 127.5 (CH), 126.7 (CH_2), 72.8 (CH_2), 68.7 (CH_2), 51.8 (CH_3), 32.3 (CH_2); LCMS m/z 221.00 ($M+H^+$), calcd $C_{13}H_{16}O_3$ 220.11; Anal. calcd for $C_{13}H_{16}O_3$ (220.11): C, 70.89; H, 7.32. Found: C, 70.81; H, 7.38%.

(*S*)-Methyl 4,5-dihydroxy-2-methylenepentanoate (9qa): Purified by column chromatography using EtOAc/hexane (35:65) and isolated as oil. **$[\alpha]_D^{25}$ = –2.01° (*c* = 0.20 g/100 mL, $CHCl_3$);** IR (neat): ν_{max} 3512, 3413, 1715 (O-C=O), 1442, 1315, 1207, 1091, 1035, 952, 864, 821 and 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.30 (1H, d, *J* = 1.2 Hz), 5.75 (1H, br s), 3.89 – 3.84 (1H, m), 3.80 (3H, s), 3.66 (1H, dd, *J* = 11.2, 3.6 Hz), 3.51 (1H, dd, *J* = 11.6, 6.4 Hz), 2.87 (1H, br s), 2.59 – 2.46 (2H, m); ^3C NMR ($CDCl_3$, DEPT-135) δ 168.4 (C, O–*C*=O), 136.6 (C), 128.4 (CH_2), 71.2 (CH), 66.0 (CH_2), 52.2 (CH_3), 36.2 (CH_2); LCMS m/z 161.00 ($M+H^+$), calcd $C_7H_{12}O_4$ 160.07; HRMS m/z 183.0633 (M+Na), calcd for $C_7H_{12}O_4Na$ 183.0633; Anal. calcd for $C_7H_{12}O_4$ (160.07): C, 52.49; H, 7.55. Found: C, 52.35; H, 7.51%.



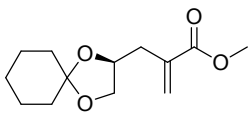
(9qa)

(*S*)-5-(Hydroxymethyl)-3-methylenedihydrofuran-2(3H)-one (10qa):[8] Purified by column chromatography using EtOAc/hexane (30:70) and isolated as oil. **$[\alpha]_D^{25}$ = +42.40° (*c* = 0.30 g/100 mL, $CHCl_3$);** IR (neat): ν_{max} 3460, 1757 (O-C=O), 1402, 1348, 1280, 1136, 1053, 1012, 951, 768 and 678 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.27 (1H, t, *J* = 3.2 Hz), 5.69 (1H, t, *J* = 2.8 Hz), 4.69 – 4.65 (1H, m), 3.93 (1H, dd, *J* = 12.4, 2.8 Hz), 3.68 (1H, dd, *J* = 12.8, 4.8 Hz), 3.05–2.98



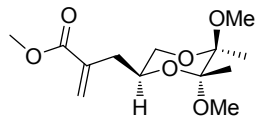
(10qa)

(1H, m), 2.92–2.84 (1H, m), 2.24 (1H, br s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 170.3 (C, O–C=O), 134.2 (C), 122.5 (CH_2), 77.2 (CH), 64.2 (CH_2), 28.8 (CH_2); LCMS m/z 129.00 ($M+H^+$), calcd for $C_6H_8O_3$ 128.00; HRMS m/z 129.0552 (M+H), calcd for $C_6H_8O_3H$ 129.0552; Anal. calcd for $C_6H_8O_3$ (128.00): C, 56.24; H, 6.29. Found: C, 56.32; H, 6.61%.


(**8ra**)

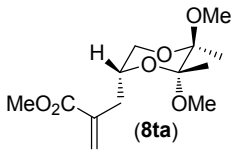
(*S*)-Methyl 2-(1,4-dioxaspiro[4.5]decan-2-ylmethyl)acrylate (8ra): Purified by column chromatography using EtOAc/hexane (20:80) and isolated as oil. **$[\alpha]_D^{25}$ = –16.05° (*c* = 0.20 g/100 mL, $CHCl_3$);** IR (neat): ν_{max} 2942, 1723 (O-C=O), 1443, 1365, 1279, 1230, 1202, 1044, 935 and 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.26 (1H, s), 5.70 (1H, s), 4.28 (1H, quintet, *J* = 6.4 Hz), 4.02 (1H, t, *J* = 6.8 Hz), 3.76 (3H, s), 3.60 (1H, t, *J* = 7.2 Hz), 2.64–2.52 (2H, m), 1.62–1.57 (8H, m), 1.42–1.35 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.4 (C, O–C=O), 136.5 (C), 127.6 (CH_2), 109.7 (C), 73.9 (CH), 68.6 (CH_2), 51.9 (CH_3), 36.7 (CH_2), 36.5 (CH_2), 35.2 (CH_2), 25.1 (CH_2), 24.0 (CH_2), 23.8 (CH_2); LCMS m/z 241.00 ($M+H^+$), calcd for $C_{13}H_{20}O_4$ 240.14; Anal. calcd for $C_{13}H_{20}O_4$ (240.14): C, 64.98; H, 8.39. Found: C, 64.78; H, 8.45%.

Methyl 2-(((2*S*,5*R*,6*R*)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxan-2-yl)methyl)acrylate


(**8sa**)

(8sa): Purified by column chromatography using EtOAc/hexane (30:70) and isolated as oil. **$[\alpha]_D^{25}$ = –175.74° (*c* = 0.42 g/100 mL, $CHCl_3$);** IR (neat): ν_{max} 1723 (O-C=O), 1441, 1375, 1209, 1123, 1040, 878 and 658 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.22 (1H, s), 5.69 (1H, s), 4.05–4.02 (1H, m), 3.74 (3H, s), 3.58–3.52 (1H, m), 3.44 (1H, dd, *J* = 11.2, 3.2 Hz), 3.27 (3H, s), 3.21 (3H, s), 2.47 –2.36 (2H, m), 1.28 (3H, s), 1.27 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.2 (C, O–C=O), 136.0 (C), 127.8 (CH_2), 99.2 (C), 98.0 (C), 65.8 (CH), 63.2 (CH_2), 51.9 (CH_3), 48.0 (CH_3), 47.8 (CH_3), 34.0 (CH_2), 17.8 (CH_3), 17.5 (CH_3); LCMS m/z 275.00 ($M+H^+$), calcd $C_{13}H_{22}O_6$ 274.14; HRMS m/z 297.1314 (M+Na), calcd for $C_{13}H_{22}O_6Na$ 297.1314; Anal. calcd for $C_{13}H_{22}O_6$ (274.14): C, 56.92; H, 8.08. Found: C, 56.85; H, 8.12%.

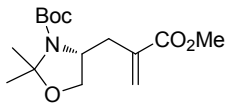
Methyl 2-(((2*R*,5*R*,6*R*)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxan-2-yl)methyl)acrylate



(**8ta**)

(8ta): Purified by column chromatography using EtOAc/hexane (30:70) and isolated as oil. **$[\alpha]_D^{25}$ = –127.13° (*c* = 0.33 g/100 mL, $CHCl_3$);** IR (neat): ν_{max} 2953, 1724 (O-C=O), 1635, 1443, 1374, 1207, 1123, 1040, 878 and 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.24 (1H, d, *J* = 1.2 Hz), 5.70 (1H, d, *J* = 0.8 Hz), 4.07–4.01 (1H, m), 3.75 (3H, s), 3.56 (1H, t, *J* = 11.2 Hz), 3.45 (1H, dd, *J* = 11.2, 3.2 Hz), 3.28 (3H, s), 3.22 (3H, s), 2.48 –2.37 (2H, m), 1.29 (3H, s), 1.28 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.2 (C, O–C=O), 136.0 (C), 127.9 (CH_2), 99.2 (C), 98.0 (C), 65.8 (CH), 63.2 (CH_2), 51.9 (CH_3), 47.8 (CH_3), 40.0 (CH_3), 34.0 (CH_2), 17.9 (CH_3), 17.6 (CH_3); LCMS m/z 275.00 ($M+H^+$), calcd for $C_{13}H_{22}O_6$ 274.14; Anal. calcd for $C_{13}H_{22}O_6$ (274.14): C, 56.92; H, 8.08. Found: C, 56.85; H, 8.15%.

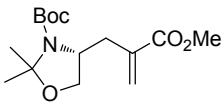
(*R*)-*tert*-Butyl 4-(2-(methoxycarbonyl)allyl)-2,2-dimethyloxazolidine-3-carboxylate



(**8ua** at 25 °C)

(8ua):[9] Purified by column chromatography using EtOAc/hexane (30:70) and isolated as oil. **$[\alpha]_D^{25}$ = –1.46° (*c* = 1.1 g/100 mL, $CHCl_3$);** IR (neat): ν_{max} 2980, 1696 (O–C=O), 1440, 1389, 1260, 1204, 1177, 1096, 954, 854 and 755 cm^{-1}; ^1H NMR ($CDCl_3$, 25 °C, 1:1 rotamers) δ 6.24 (1H, s), 6.19 (1H, s), 5.59 (1H, s), 5.55 (1H, s), 4.18 (1H, br s), 4.06 (1H, br s), 3.85 (2H, br s), 3.76 (2H, s), 3.74 (6H, s), 2.75-2.72 (2H, m), 2.56-2.42 (2H, m), 1.61 (3H, s), 1.55 (3H, s), 1.45 (24H, s); ^{13}C NMR ($CDCl_3$, DEPT-135, 25 °C, 1:1 rotamers) δ 167.3 (C, O–*C*=O), 167.1 (C, O-*C*=O), 152.2 (C, N-*C*=O), 151.9 (C, N-*C*=O), 137.6 (C), 137.3 (C), 128.2 (CH_2), 127.0 (CH_2), 94.0 (C), 93.4 (C), 80.0 (C), 79.8 (C), 66.5 (2 x CH_2), 56.6 (CH), 56.2 (CH), 51.8 (CH_3), 51.8 (CH_3), 36.4 (CH_2), 35.5 (CH_2), 28.3 (6 x CH_3), 27.6 (CH_3), 27.0 (CH_3), 24.4 (CH_3), 23.2 (CH_3); LCMS m/z 300.00 ($M+H^+$), calcd $C_{15}H_{25}NO_5$ 299.17; Anal. calcd for $C_{15}H_{25}NO_5$ (299.17): C, 60.18; H, 8.42; N, 4.68. Found: C, 60.25; H, 8.39; N, 4.63%.

(*R*)-*tert*-Butyl 4-(2-(methoxycarbonyl)allyl)-2,2-dimethyloxazolidine-3-carboxylate

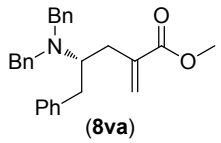


(**8ua** at 50 °C)

(8ua): Purified by column chromatography using EtOAc/hexane (30:70) and isolated as oil. IR (neat): ν_{max} 2980, 1696 (O–C=O), 1440, 1389, 1260, 1204, 1177, 1096, 954, 854 and 755 cm^{-1}; ^1H NMR ($CDCl_3$, 50 °C) δ 6.21 (1H, s), 5.56 (1H, s), 4.10 (1H, br s), 3.88 (1H, dd, *J* = 8.8,

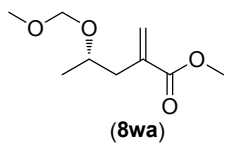
6.0 Hz), 3.78 (1H, d, *J* = 1.2 Hz), 3.75 (3H, s), 2.76 (1H, dd, *J* = 13.6, 5.2 Hz), 2.54 (1H, br s), 1.60 (3H, s), 1.47 (12H, s, 4 x CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135, 50 °C) δ 167.1 (C, O-*C*=O), 152.0 (C, N-*C*=O), 137.6 (C), 127.8 (CH_2), 94.0 (C), 79.8 (C), 66.5 (CH_2), 56.4 (CH), 51.6 (CH_3), 36.3 (CH_2), 28.3 (3 x CH_3), 27.0 (CH_3), 24.4 (CH_3).

(*S*)-Methyl 4-(dibenzylamino)-2-methylene-5-phenylpentanoate (8va): Purified by column chromatography using EtOAc/hexane (25:75) and isolated as yellow oil. **$[\alpha]_D^{25}$ = +14.05° (c = 1.82 g/100 mL, $CHCl_3$);** IR (neat): ν_{max} 2798, 1721 (O-C=O), 1494, 1270, 1075, 938, 817, 749, and 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.34–7.27 (13H, m), 7.13 (2H, d, *J* = 7.2 Hz), 6.29 (1H, s), 5.50 (1H, s), 3.85 (2H, d, *J* = 14.0 Hz), 3.66 (2H, d, *J* = 14 Hz), 3.55 (3H, s), 3.27–3.22 (1H, m), 3.14 (1H, dd, *J* = 13.6, 6.0 Hz), 2.72 (1H, dd, *J* = 14.0, 8.4 Hz), 2.59 (1H, dd, *J* = 13.6, 8.4 Hz), 2.40 (1H, dd, *J* = 13.6, 6.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.2 (C, O–*C*=O), 140.2 (C), 139.8 (2 x C), 138.8 (C), 129.2 (2 x CH), 128.6 (4 x CH), 128.1 (2 x CH), 128.0 (4 x CH), 126.7 (CH_2), 126.6 (2 x CH), 125.7 (CH), 58.2 (CH), 53.0 (2 x CH_2), 51.4 (CH_3), 35.1 (CH_2), 32.8 (CH_2); LCMS m/z 400.00 ($M+H^+$), calcd $C_{27}H_{29}NO_2$ 399.22; HRMS m/z 400.2276 (M+H), calcd for $C_{27}H_{29}NO_2H$ 400.2277; Anal. calcd for $C_{27}H_{29}NO_2$ (399.22): C, 81.17; H, 7.32; N, 3.51. Found: C, 81.08; H, 7.37; N, 3.58%.



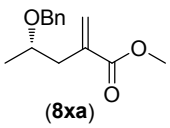
(**8va**)

(*S*)-Methyl 4-(methoxymethoxy)-2-methylenepentanoate (8wa): Purified by column chromatography using EtOAc/hexane (20:80) and isolated as oil. **$[\alpha]_D^{25}$ = +12.25° (*c* = 0.86 g/100 mL, $CHCl_3$);** IR (neat): ν_{max} 2971, 1723 (O-C=O), 1634, 1442, 1331, 1281, 1204, 1162, 1100, 1034, 947, 818 and 644 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.20 (1H, d, *J* = 1.6 Hz), 5.62 (1H, d, *J* = 1.2 Hz), 4.60 (2H, dd, *J* = 15.2, 6.8 Hz), 3.90–3.85 (1H, m), 3.74 (3H, s), 3.31 (3H, s), 2.53 (1H, dd, *J* = 13.6, 7.2 Hz), 2.44 (1H, dd, *J* = 5.6, 4.8 Hz), 1.16 (3H, d, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.5 (C, O–*C*=O), 137.3 (C), 127.4 (CH_2), 94.9 (CH_2), 71.7 (CH), 55.2 (CH_3), 51.8 (CH_3), 39.8 (CH_2), 20.2 (CH_3); LCMS: m/z 189.00 ($M+H^+$), calcd $C_9H_{16}O_4$ 188.10; Anal. calcd for $C_9H_{16}O_4$ (188.10): C, 57.43; H, 8.57. Found: C, 57.65; H, 8.49%.



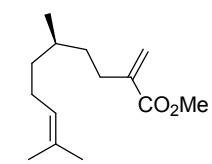
(**8wa**)

(*S*)-Methyl 4-(benzyloxy)-2-methylenepentanoate (8xa): Purified by column chromatography using EtOAc/hexane (20:80) and isolated as oil. **$[\alpha]_D^{25}$ = +14.89° (c = 0.33 g/100 mL, $CHCl_3$);** IR (neat): ν_{max} 1722 (O–C=O), 1442, 1330, 1224, 1196, 1161, 1093, 818 and 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33–7.25 (5H, m), 6.22 (1H, s), 5.65 (1H, s), 4.53 (2H, ABq, *J* = 12.0 Hz), 3.73 (1H, m), 3.72 (3H, s), 2.66 (1H, dd, *J* = 14.0, 6.8 Hz), 2.45 (1H, dd, *J* = 14.0, 6.0 Hz), 1.21 (3H, d, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.6 (C, O–*C*=O), 138.8 (C), 137.4 (C), 128.2 (2 x CH), 127.6 (3 x CH), 127.3 (CH_2), 73.5 (CH), 70.5 (CH_2), 51.8 (CH_3), 39.4 (CH_2), 19.5 (CH_3); LCMS: m/z 235.00 ($M+H^+$), calcd $C_{14}H_{18}O_3$ 234.13; HRMS m/z 235.1334 (M+H), calcd for $C_{14}H_{18}O_3H$ 235.1334; Anal. calcd for $C_{14}H_{18}O_3$ (234.13): C, 71.77; H, 7.74. Found: C, 71.65; H, 7.71%.



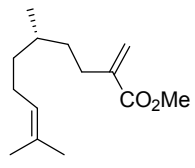
(8xa)

(*R*)-Methyl 5,9-dimethyl-2-methylenedec-8-enoate (8ya): Purified by column chromatography using EtOAc/hexane (5:95) and isolated as oil. **$[\alpha]_D^{25}$ = –3.93° (*c* = 0.56 g/100 mL, $CHCl_3$);** IR (neat): ν_{max} 2961, 1720 (O-C=O), 1441, 1270, 1200, 1151 and 754 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.11 (1H, s), 5.51 (1H, s), 5.08 (1H, t, *J* = 6.8 Hz), 3.74 (3H, s), 2.33 – 2.25 (2H, m), 2.01 – 1.92 (2H, m), 1.67 (3H, s), 1.59 (3H, s), 1.49 – 1.42 (2H, m), 1.39 – 1.25 (2H, m), 1.20 – 1.13 (1H, m), 0.90 (3H, d, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.8 (C, O–*C*=O), 141.1 (C), 131.1 (C), 124.8 (CH_2), 124.2 (CH), 51.7 (CH_3), 36.9 (CH_3), 35.6 (CH_3), 32.1 (CH_2), 29.4 (CH), 25.7 (CH_2), 25.5 (CH_3), 19.4 (CH_2), 17.6 (CH_2); LCMS: m/z 225.00 ($M+H^+$), calcd $C_{14}H_{24}O_2$ 224.18; Anal. calcd for $C_{14}H_{24}O_2$ (224.18): C, 74.95; H, 10.78. Found: C, 74.85; H, 10.71%.



(8ya)

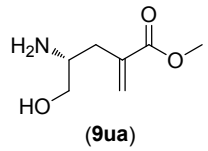
(*S*)-Methyl 5,9-dimethyl-2-methylenedec-8-enoate (8za): Purified by column chromatography using EtOAc/hexane (5:95) and isolated as oil. **$[\alpha]_D^{25}$ = +4.31° (*c* = 1.0 g/100 mL, $CHCl_3$);** IR (neat): ν_{max} 2959, 1725 (O-C=O), 1440, 1378, 1268, 1200, 1153, 755 and 649 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.10 (1H, s), 5.50 (1H, s), 5.08 (1H, t, *J* = 7.2 Hz), 3.73 (3H, s), 2.34 – 2.24 (2H, m), 2.00 – 1.91 (2H, m), 1.66 (3H, s), 1.58 (3H, s), 1.50 – 1.41 (2H, m), 1.39 – 1.24 (2H, m), 1.19 – 1.12 (1H, m), 0.89 (3H, d, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.8 (C, O–*C*=O), 141.1 (C), 131.0 (C), 124.8 (CH_2), 124.2



(8za)

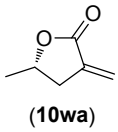
(CH), 51.7 (CH_3), 36.9 (CH_3), 35.6 (CH_3), 32.1 (CH_2), 29.4 (CH), 25.6 (CH_2), 25.4 (CH_3), 19.4 (CH_2), 17.6 (CH_2); LCMS: m/z 225.00 ($M+H^+$), calcd $C_{14}H_{24}O_2$ 224.18; Anal. calcd for $C_{14}H_{24}O_2$ (224.18): C, 74.95; H, 10.78. Found: C, 74.85; H, 10.71%.

(*R*)-Methyl 4-amino-5-hydroxy-2-methylenepentanoate (9ua): Purified by column chromatography using EtOAc/hexane (40:60) and isolated as oil. **$[\alpha]_D^{25}$ = +1.98° (*c* = 0.66 g/100 mL, MeOH);** IR (neat): ν_{max} 3394, 3278, 3198, 2957, 1694 (O-C=O), 1656, 1551, 1441, 1309, 1202, 1156, 1120, 882 and 786 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.40 (1H, s), 5.92 (1H, s), 3.83 – 3.75 (4H, m), 3.60 (1H, dd, *J* = 11.6, 6.0 Hz), 3.51 (1H, br s), 3.35 (1H, br s), 2.75 – 2.64 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 167.4 (C, O–C=O), 135.5 (C), 129.8 (CH_2), 61.2 (CH_2), 52.5 (CH), 51.9 (CH_3), 32.7 (CH_2); LCMS: m/z 160.00 ($M+H^+$), calcd $C_7H_{13}NO_3$ 159.08; Anal. calcd for $C_7H_{13}NO_3$ (159.08): C, 52.82; H, 8.23; N, 8.80. Found: C, 52.75; H, 8.28; N, 8.76%.



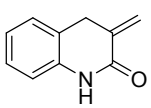
(**9ua**)

(*S*)-5-Methyl-3-methylenedihydrofuran-2(3H)-one (10wa):[10] Purified by column chromatography using EtOAc/hexane (10:90) and isolated as oil. **$[\alpha]_D^{25}$ = –20.56° (c = 0.40 g/100 mL, $CHCl_3$);** IR (neat): ν_{max} 1761 (O–C=O), 1438, 1394, 1339, 1259, 1203, 1162, 1087, 1037, 954, 872 and 797 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.24 (1H, s), 5.63 (1H, s), 4.70–4.65 (1H, m), 3.13–3.07 (1H, m), 2.57–2.52 (1H, m), 1.43 (3H, d, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 170.3 (C, O–*C*=O), 134.9 (C), 122.0 (CH_2), 73.9 (CH), 35.2 (CH_2), 22.0 (CH_3); LCMS: m/z 113.00 ($M+H^+$), calcd $C_6H_8O_2$ 112.05; Anal. calcd for $C_6H_8O_2$ (112.05): C, 64.27; H, 7.19. Found: C, 64.18; H, 7.25%.



(**10wa**)

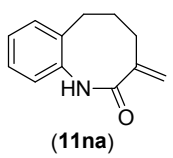
3-Methylene-3,4-dihydroquinolin-2(1H)-one (11ha):[11] Purified by column chromatography using EtOAc/hexane (30:70) and isolated as yellow oil. IR (neat): ν_{max} 3214, 1662, 1599, 1494, 1391, 1292, 1161, 1052, 958, 752 and 678 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.75 (1H, br s, N-*H*), 7.19–7.12 (2H, m), 6.98 (1H, t, *J* = 8 Hz), 6.92 (1H, d, *J* = 8 Hz), 6.31 (1H, s), 5.58 (1H, s), 3.84 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 165.8 (C, NH–C=O), 136.6 (C), 135.6 (C), 127.6 (CH), 127.5 (CH), 123.7 (CH_2), 123.0 (CH), 122.2 (C), 115.7 (CH), 33.8 (CH_2); LCMS: m/z 158.00 ($M–H^+$), calcd $C_{10}H_9NO$ 159.07; HRMS m/z 160.0760 (M+H), calcd for



(**11ha**)

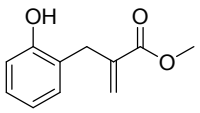
$C_{10}H_9NOH$ 160.0762; Anal. calcd for $C_{10}H_9NO$ (159.07): C, 75.45; H, 5.70; N, 8.80. Found: C, 75.32; H, 5.71, N, 8.85%.

3-Methylene-3,4,5,6-tetrahydrobenzo[b]azocin-2(1H)-one (11na): Purified by column chromatography using EtOAc/hexane (30:70) and isolated as oil. IR (neat): ν_{max} 3020, 1654, 1600, 1492, 1403, 1266, 1208, 1108, 946, 759 and 713 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.27 (1H, br s, N-*H*), 7.24–7.18 (3H, m), 7.09 (1H, t, *J* = 3.2 Hz), 5.59 (1H, s), 5.18 (1H, s), 2.77 (2H, t, *J* = 6 Hz), 2.31 (2H, t, *J* = 6.4 Hz), 1.86 – 1.83 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 171.8 (C, O–C=O), 142.9 (C), 137.0 (C), 136.7 (C), 130.4 (CH), 127.1 (CH), 126.9 (CH), 123.7 (CH), 121.6 (CH_2), 31.4 (CH_2), 30.6 (CH_2), 30.0 (CH_2); LCMS: m/z 188.00 ($M+H^+$), calcd $C_{12}H_{13}NO$ 187.10; HRMS m/z 210.0896 (M+Na), calcd for $C_{12}H_{13}NONa$ 210.0895; Anal. calcd for $C_{12}H_{13}NO$ (187.10): C, 76.98; H, 7.00, N, 7.48. Found: C, 76.85; H, 7.11, N, 7.56%.



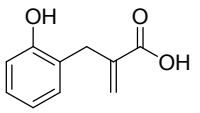
(**11na**)

Methyl 2-(2-hydroxybenzyl)acrylate (12ga):[12] Purified by column chromatography using EtOAc/hexane (30:70) and isolated as oil. IR (neat): ν_{max} 3379, 1718 (O–C=O), 1628, 1493, 1455, 1346, 1269, 1224, 1143, 1042, 952, 819, 757, and 674 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.17–7.13 (2H, m), 6.94–6.87 (2H, m), 6.25 (1H, s), 5.80 (1H, s), 3.79 (3H, s), 3.62 (2H, s), 1.46 (1H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 169.3 (C, O–*C*=O), 154.0 (C), 138.9 (C), 130.6 (CH), 128.2 (CH), 127.2 (CH_2), 125.4 (C), 120.8 (CH), 117.0 (CH), 52.2 (CH_3), 32.7 (CH_2); LCMS: m/z 193.00 ($M+H^+$), calcd $C_{11}H_{12}O_3$ 192.03; Anal. calcd for $C_{11}H_{12}O_3$ (192.03): C, 68.74; H, 6.29. Found: C, 68.85; H, 6.19%.



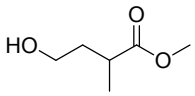
(**12ga**)

2-(2-Hydroxybenzyl)acrylic acid (13ga):[12] Purified by column chromatography using EtOAc/hexane (50:50) and isolated as oil. IR (neat): ν_{max} 3383, 1694 (CO_2H), 1629, 1492, 1455, 1353, 1232, 1175, 1148, 1096, 954, 835 and 723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.17–7.13 (2H, m), 6.92–6.89 (2H, m), 6.40 (1H, s), 5.83 (1H, s), 3.62 (2H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 173.0 (C, O–*C*=O), 153.7 (C), 138.3 (C), 130.7 (CH), 129.5 (CH_2), 128.2 (CH), 125.0 (C), 120.9 (CH), 116.8 (CH), 32.0 (CH_2); LCMS: m/z 179.00 ($M+H^+$), calcd $C_{10}H_{10}O_3$ 178.06; HRMS m/z 201.0528 (M+Na), calcd for $C_{10}H_{10}O_3Na$ 201.0528; Anal. calcd for $C_{10}H_{10}O_3$ (178.06): C, 67.41; H, 5.66. Found: C, 67.32; H, 5.71%.



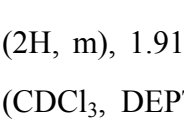
(**13ga**)

Methyl 4-hydroxy-2-methylbutanoate (14pa): Purified by column chromatography using EtOAc/hexane (20:80) and isolated as oil. IR (neat): ν_{max} 3416, 2975, 1734 (O-C=O), 1458, 1374, 1208, 1172, 1133, 1076, 1004, 847, 758 and 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.62 – 3.58 (5H, m), 2.61 – 2.56 (2H, m), 1.91–1.82 (1H, m), 1.65–1.57 (1H, m), 1.13 (3H, d, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 177.3 (C, O–*C*=O), 60.2 (CH_2), 51.6 (CH_3), 36.2 (CH), 36.2 (CH_2), 17.0 (CH_3); LCMS: m/z 133.00 ($M+H^+$), calcd $C_6H_{12}O_3$ 132.08; HRMS m/z 155.0684 (M+Na), calcd for $C_6H_{12}O_3Na$ 155.0684; Anal. calcd for $C_6H_{12}O_3$ (132.08): C, 54.53; H, 9.15. Found: C, 54.42; H, 9.10%.



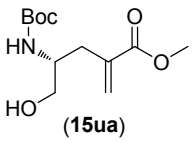
(14pa)

(4*S*)-Methyl 4-hydroxy-2-methylpentanoate (14xa): Purified by column chromatography using EtOAc/hexane (20:80) and isolated as oil. **$[\alpha]_D^{25}$ = +4.71° (*c* = 0.66 g/100 mL, $CHCl_3$);** IR (neat): ν_{max} 3527, 3502, 2974, 1769, 1734, 1459, 1378, 1259, 1195, 1135, 1088, 953, 843 and 737 cm^{-1}; ^1H NMR ($CDCl_3$, 1:1 diastereomers) δ 3.83 – 3.79 (2H, m), 3.66 (3H, s), 3.65 (3H, s), 2.73 – 2.68 (1H, m), 2.65 – 2.58 (1H, m), 1.89–1.73 (2H, m), 1.54–1.43 (2H, m), 1.27-1.15 (2H, m), 1.17–1.15 (12H, m, 4 x CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135, 1:1 diastereomers) δ 177.8 (C, O–C=O), 177.5 (C, O–C=O), 66.2 (CH), 65.7 (CH), 51.7 (2 x CH_3), 43.0 (CH_2), 42.9 (CH_2), 36.9 (CH), 36.2 (CH), 24.0 (CH_3), 23.7 (CH_3), 17.7 (CH_3), 17.4 (CH_3); LCMS: m/z 147.00 ($M+H^+$), calcd $C_7H_{14}O_3$ 146.09; Anal. calcd for $C_7H_{14}O_3$ (146.09): C, 57.51; H, 9.65. Found: C, 57.42; H, 9.71%.



(14xa)

(*R*)-Methyl 4-((tert-butoxycarbonyl)amino)-5-hydroxy-2-methylenepentanoate (15ua): Purified by column chromatography using EtOAc/hexane (30:70) and isolated as oil. **$[\alpha]_D^{25}$ = +10.87° (*c* = 0.36 g/100 mL, $CHCl_3$);** IR (neat): ν_{max} 3374, 2974, 1696 (O–C=O), 1631, 1518, 1442, 1256, 1197, 1055, 956, 814 and 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.29 (1H, s), 5.76 (1H, s), 5.05 (1H, br s), 3.79 (3H, s), 3.77–3.71 (1H, m), 3.59 (2H, br s), 3.15 (1H, br s), 2.62 – 2.48 (2H, m), 1.43 (9H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 168.3 (C, O–*C*=O), 156.0 (C, N–*C*=O), 136.5 (C), 128.7 (CH_2), 79.5 (C), 64.2 (CH_2), 52.6 (CH), 52.3 (CH_3), 33.2 (CH_2), 28.3 (3 x CH_3); LCMS: m/z 260.00 ($M+H^+$), calcd $C_{12}H_{21}NO_5$ 259.14; HRMS m/z



(15ua)

282.1319 (M+Na), calcd for $C_{12}H_{21}NO_5Na$ 282.1317; Anal. calcd for $C_{12}H_{21}NO_5$ (259.14): C, 55.58; H, 8.16; N, 5.40. Found: C, 55.62; H, 8.06; N, 5.36%.

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