Highly Diastereoselective Asymmetric Mannich Reactions of 1,3-Dicarbonyls with Acyl Imines

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Supporting Information

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General Information. All ^1H NMR, and ^{13}C NMR spectra were recorded using Varian Unity Plus 400 (93.94 kG, ^1H 400 MHz) spectrometer at ambient temperature in CDCl_3 . Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant, and integration. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR ESP spectrophotometer. High-resolution mass spectra were obtained in the Boston University Mass Spectrometry Laboratory on a Finnegan MAT-90 spectrometer. Optical rotations were recorded on an AUTOPOL III digital polarimeter at 589 nm, and were reported as $[\alpha]^{23}_{\text{D}}$ (concentration in grams/100 mL solvent). Analytical thin layer chromatography was performed using EMD 0.25 mm silica gel 60-F plates. Flash column chromatography was performed on Sorbent Technologies 60 Å silica gel. Chiral HPLC analysis was performed using an Agilent 1100 series HPLC with a diode array detector and either a (*R,R*)-Whelk-O 1 (Regis[®] Technologies Inc., 25cm× 4.6mm I.D.) column or a Chiralcel[®] OD (Chiral Technologies Inc., 24cm×4.6mm I.D.). All reactions were performed under nitrogen atmosphere, in oven dried glassware with magnetic stirring, unless otherwise noted. Reaction solvents were obtained from a dry solvent system (alumina) and used without further drying. All aryl substituted acyl imines (**7a-d**, **8a-b**) were prepared according to published procedure.¹ (+)-Cinchonine, quinine, quinidine, and other reagents were used as supplied by Sigma-Aldrich, Alfa Aesar, Lancaster, or Acros unless otherwise noted.

General Procedure for Asymmetric Mannich Reaction of Cyclic 1,3-Dicarbonyls (6a-6d) to Acyl Imines. In an oven dried 17×110 mm round bottom reaction vessel, (+)-cinchonine (8.00 mg, 0.025 mmol) was dissolved in 0.50 mL CH_2Cl_2 . The 1,3-dicarbonyl (**6a-6d**, 0.50 mmol) was added to catalyst solution and cooled down to appropriate reaction temperature. The acyl imine (1.00 equivalent, 0.50 mmol) in CH_2Cl_2 (0.50 mL) was added drop-wise to the reaction mixture. The solution was stirred at reaction

temperature and monitored by TLC (30% ethyl acetate in hexanes). Once the reaction is complete, the reaction mixture was flashed through a plug of silica gel and eluted with ethyl acetate (5 mL). The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography over silica gel (elution with 15%-40% ethyl acetate in hexanes) to afford Mannich products **10-15**, and **20-21** as white waxy solids.

Procedure for 17a (3-phenyl-propenyl) acyl aldimines and 17b (3-furyl-propenyl) acyl aldimine.

Hexamethyldisilazane (5.54 mL, 26 mmol) was placed under argon in a septum-stoppered 250 mL round bottom. Internal temperature of round bottom was cooled down to 0 °C for drop-wise addition of nBuLi in hexanes (1.60 M, 15.60 mL, 25 mmol). Reaction was stirred at room temperature for 15 minutes and cooled back down to 0 °C for slow addition of freshly distilled 3-aryl-propenal (25 mmol) in THF (10 mL). Reaction was stirred for 30 minutes at room temperature then concentrated under reduced pressure for addition of CH₂Cl₂ (25 mL). Reaction mixture was cooled down to 0 °C for slow addition of methyl chloroformate (125 mmol). Reaction was stirred for 3 hours at room temperature then concentrated under reduced pressure. To the concentrate, diethyl ether (50 mL) and toluene (10mL) were added; resulting in precipitation of LiCl salt that was filtered off quickly with sintered glass funnel over dry Na₂SO₄. The filtrate was dried under reduced pressure. Product comes off as air-sensitive orange solid which is used without further purification.

17a: [(E)-3-Phenyl-prop-2-en-(E)-ylidene]-carbamic acid methyl ester.

Yield: 90%. ¹H NMR (400 MHz, CDCl₃): δ 8.74 (d, *J* = 12.8 Hz, 1H), 7.54 (m, 2H), 7.41 (m, 3H), 7.22 (m, 1H), 7.21-6.94 (dd, *J* = 21.2 Hz, 1H), 3.87 (s, 3H). ¹³C NMR (75.0 MHz, CDCl₃): δ 172.9, 151.3, 134.4, 128.9, 128.5, 128.2, 126.4, 53.8. IR (neat, cm⁻¹): 3335, 3027, 2954, 1714, 1669, 1626, 1527, 1449, 1347, 1251, 1125, 1072, 970, 751, 693. HRMS: calc'd for (M+1)⁺ C₁₁H₁₂NO₂: 190.0823; found: 190.0853.

17b: [(E)-3-Furan-2-yl-prop-2-en-(E)-ylidene]-carbamic acid methyl ester.

Yield: 90%. ¹H NMR (400 MHz, CDCl₃): δ 8.70 (d, *J* = 9.2 Hz, 1H), 7.54 (d, *J* = 1.6 Hz, 1H), 7.13 (d, *J* = 15.2 Hz, 1H), 6.85 (dd, *J* = 16, 9.2 Hz, 1H), 6.70 (d, *J* = 3.6 Hz), 6.50 (dd, *J* = 3.4, 1.6 Hz, 1H), 3.86 (s, 3H). ¹³C NMR (75.0 MHz, CDCl₃): δ 172.5, 151.0, 145.7, 136.7, 124.0, 116.0, 112.7, 111.3, 53.6. IR (neat, cm⁻¹): 3326, 2956, 2252, 1715, 1624, 1520, 1447, 1358, 1211, 1175, 911, 735. HRMS: calc'd for (M)⁺ C₉H₉NO₃: 179.0582; found: 179.0540.

10a: (R)-1-((S)-Methoxycarbonylamino-phenyl-methyl)-2-oxo-cyclopentane carboxylic acid methyl ester

According to General Procedure, imine **7a** (benzylidene-carbamic acid methyl ester) was added to β -ketoester **6a** (2-oxo-cyclopentanecarboxylic acid methyl ester) and stirred at $-40\text{ }^{\circ}\text{C}$ for 6 hours to give Mannich product **10a**. **Yield:** 0.150 g (98%), **de:** 98%, **ee:** 90%; **HPLC Analysis**, t_r minor: 29.6 min., t_r major: 39.6 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 90:10, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.29–7.21 (m, 5H), 6.19 (d, $J = 7.7$ Hz, 1H), 5.15 (d, $J = 9.2$ Hz, 1H), 3.66 (s, 3H), 3.61 (s, 3H), 2.53–2.46 (m, 1H), 2.34 (s, 2H), 2.01–1.94 (m, 3H); **^{13}C NMR** (75.0 MHz, CDCl_3): δ 210.9, 169.7, 156.3, 137.9, 128.3, 127.9, 127.8, 64.4, 56.2, 52.1, 37.4, 30.5, 18.8; **IR (thin film, cm^{-1}):** 3333, 2955, 1733, 1537, 1454, 1357, 1231, 1142, 961, 758, 706; **HRMS:** calc'd for (M) $^+$ $\text{C}_{16}\text{H}_{19}\text{NO}_5$: 305.1263; found: 305.1299; $[\alpha]_D^{23} = -22.7^{\circ}$ ($c = 1.0$, CHCl_3).

10b: (R)-1-((S)-Methoxycarbonylamino-phenyl-methyl)-2-oxo-cyclopentane carboxylic acid ethyl ester

According to General Procedure, imine **7a** (benzylidene-carbamic acid methyl ester) was added to β -ketoester **6b** (2-oxo-cyclopentanecarboxylic acid ethyl ester) and stirred at $-40\text{ }^{\circ}\text{C}$ for 6 hours to give Mannich product **10b**. **Yield:** 0.159 g (96%), **de:** 96%, **ee:** 93%; **HPLC Analysis**, t_r minor: 21.5 min., t_r major: 33.1 min., [(*R,R*)-Whelk-O 1 column, Hexanes: IPA = 90:10, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.30–7.22 (m, 5H), 6.16 (d, $J = 8.4$ Hz, 1H), 5.16 (d, $J = 9.5$ Hz, 1H), 4.13–4.06 (m, 2H), 3.60 (s, 3H), 2.53–2.46 (m, 1H), 2.34–2.32 (m, 2H), 2.01–1.92 (m, 3H), 1.15 (t, $J = 6.9$ Hz, 3H); **^{13}C NMR** (75.0 MHz, CDCl_3): δ 211.1, 169.3, 156.4, 38.1, 128.3, 128.1, 127.8, 64.5, 61.8, 56.3, 52.2, 37.5, 30.7, 18.8, 13.8; **IR (thin film, cm^{-1}):** 3334, 2980, 1725, 1533, 1454, 1230, 1118, 1029, 952, 756, 706; **HRMS:** calc'd for ($\text{M}+\text{H}$) $^+$ $\text{C}_{17}\text{H}_{21}\text{NO}_5$: 319.1420; found: 320.1488; $[\alpha]_D^{23} = -10.3^{\circ}$ ($c = 1.0$, CHCl_3).

10c: [(S)-(S)-(1-Acetyl-2-oxo-cyclopentyl)-phenyl-methyl]-carbamic acid methyl ester

According to General Procedure, imine **7a** (benzylidene-carbamic acid methyl ester) was added to β -diketone **6c** (2-Acetyl-cyclopentanone) and stirred at -55°C for 2 hours to give Mannich product **10c**. **Yield:** 0.145 g (98%), **de** 98%, **ee:** 93%; **HPLC Analysis**, t_r minor: 22.42 min., t_r major: 28.9 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 90:10, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.35–7.20 (m, 5H), 6.69 (d, J = 9.5 Hz, 1H), 5.15 (d, J = 8.4 Hz, 1H), 3.60 (s, 3H), 2.59–2.61 (m, 1H), 2.33 (s, 3H), 2.16–2.13 (m, 2H), 1.77–1.70 (m, 3H); **^{13}C NMR** (75.0 MHz, CDCl_3): δ 213.1, 202.4, 155.9, 137.9, 128.5, 128.1, 127.9, 127.5, 73.5, 57.3, 52.3, 39.0, 25.5, 19.2; **IR (thin film, cm^{-1}):** 3385, 3354, 3021, 2970, 1711, 1530, 1240, 1195, 1149, 1054, 751, 703; **HRMS:** calc'd for ($\text{M}+\text{H}$) $^+$ $\text{C}_{16}\text{H}_{19}\text{NO}_4$: 289.1314; found: 290.1400; $[\alpha]_{\text{D}}^{23} = +71.7^{\circ}$ (c = 1.0, CHCl_3).

11a: (*R*)-1-((*S*)-Allyloxycarbonylamino-phenyl-methyl)-2-oxocyclopentane carboxylic acid methyl ester

According to General Procedure, imine **8a** (benzylidene-carbamic acid allyl ester) was added to β -ketoester **6a** (2-oxo-cyclopentanecarboxylic acid methyl ester) and stirred at -55°C for 2 hours to give Mannich product **11a**. **Yield:** 0.162 g (98%), **de:** 98%, **ee:** 90%; **HPLC Analysis**, t_r minor: 22.8 min., t_r major: 29.6 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 90:10, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.29–7.21 (m, 5H), 6.22 (d, J = 8.1 Hz, 1H), 6.87–6.85 (m, 1H), 5.28–5.24 (br, 1H), 5.16 (9.5 Hz, 2H), 3.66 (s, 3H), 2.53–2.47 (m, 1H), 2.35–2.31 (m, 2H), 2.04–1.92 (m, 3H); **^{13}C NMR** (75.0MHz, CDCl_3): δ 210.8, 169.8, 155.6, 137.9, 132.6, 128.4, 128.0, 127.9, 117.6, 65.7, 64.5, 56.2, 52.7, 37.5, 30.7, 18.8; **IR (thin film, cm^{-1}):** 3304, 3064, 2954, 1724, 1537, 1454, 1229, 1119, 1052, 934, 758, 707; **HRMS:** calc'd for (M) $^+$ $\text{C}_{18}\text{H}_{21}\text{NO}_5$: 331.1420; found: 331.1417; $[\alpha]_{\text{D}}^{23} = -19.6^{\circ}$ (c = 1.0, CHCl_3).

11b: (*R*)-1-((*S*)-Allyloxycarbonylamino-phenyl-methyl)-2-oxocyclopentane carboxylic acid ethyl ester

According to General Procedure, imine **8a** (benzylidene-carbamic acid allyl ester) was added to β -ketoester **6b** (2-oxo-cyclopentanecarboxylic acid ethyl ester) and stirred at -55°C for 2 hours to give Mannich product **11b**. **Yield:** 0.161 g (98%), **de** 99%, **ee:** 90%; **HPLC Analysis**, t_r minor: 16.9 min., t_r major: 24.9 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 90:10, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.32–7.15 (m, 5H), 6.19–6.17 (d, J = 9.2 Hz, 1H), 5.90–5.85 (m, 1H), 5.33–5.23 (m, 1H), 5.17 (d, J = 8.4 Hz, 2H), 4.13–4.06 (m, 2H), 2.51–2.48 (m, 1H), 2.33–2.31 (m, 2H), 2.01–1.92 (m, 3H), 1.15 (t, J = 6.9 Hz, 3H); **^{13}C NMR** (75.0 MHz, CDCl_3): δ 211.0, 155.5, 138.0, 132.5

128.3, 128.2, 128.0, 127.7, 125.6, 117.9, 117.5, 65.6, 61.7, 56.2, 37.5, 30.5, 18.8, 13.7; **IR (thin film, cm⁻¹):** 3334, 2979, 2929, 1732, 1523, 1454, 1227, 1142, 1031, 927, 757, 705; **HRMS:** calc'd for (M)⁺ C₁₉H₂₃NO₅: 345.1576; found: 345.1546; [α]_D²³ = - 8.3 ° (c = 1.0, CHCl₃).

11c: [(S)-(S)-(1-Acetyl-2-oxo-cyclopentyl)-phenyl-methyl]-carbamic acid allyl ester

According to General Procedure, imine **8a** (benzylidene-carbamic acid allyl ester) was added to β -diketone **6c** (2-Acetyl-cyclopentanone) and stirred at - 55 °C for 2 hours to give Mannich product **11c**. **Yield:** 0.155 g (98%), **de:** 99%, **ee:** 91%; **HPLC** analysis, *t_r* minor: 16.6 min., *t_r* major: 18.9 min., [(*R, R*)-Whelk-O 1 column, Hexanes:IPA = 90:10, 1.0 mL/min]; **¹H NMR** (400 MHz, CDCl₃): δ 7.31-7.19 m, 5H), 5.84-5.85 (m, 1H), 5.70 (d, *J* = 9.5 Hz, 1H), 5.27 (d, *J* = 8.4 Hz, 1H), 5.18 (d, *J* = 9.5 Hz, 2H), 4.48 (t, *J* = 5.6 Hz, 2H), 2.61-2.60 (m, 1H), 2.33 (s, 3H), 2.17-2.12 (m, 1H), 1.77-1.60 (m, 4H); **¹³C NMR** (75.0 MHz, CDCl₃): δ 212.9, 202.3, 155.2, 137.9, 132.3, 128.5, 127.9, 127.5, 117.9, 73.5, 65.9, 57.3, 39.0, 25.5, 19.2; **IR (thin film, cm⁻¹):** 3308, 1962, 1706, 1533, 1358, 1295, 1250, 1138, 1054 996, 758, 707; **HRMS:** calc'd for (M+H)⁺ C₁₈H₂₁NO₄: 315.1471; found: 316.1591; [α]_D²³ = + 85.4 ° (c = 1.0, CHCl₃).

12a: (R)-1-((S)-Methoxycarbonylamino-*m*-tolyl-methyl)-2-oxo-cyclopentanecarboxylic acid methyl ester

According to General Procedure, imine **7b** ((3-Methyl-benzylidene)-carbamic acid methyl ester) was added to β -ketoester **6a** (2-oxo-cyclopentanecarboxylic acid methyl ester) and stirred at - 55 °C for 4 hours to give Mannich product **12a**. **Yield:** 0.168 g (98%), **de:** 93%, **ee:** 96%; **HPLC Analysis**, *t_r* minor: 21.1 min., *t_r* major: 30.2 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **¹H NMR** (400 MHz, CDCl₃): δ 7.19-7.05 (m, 5H), 6.20 (d, *J* = 8.4 Hz, 1H), 5.09 (d, *J* = 8.4 Hz, 1H), 3.67 (s, 3H), 3.61 (s, 3H), 2.50-2.47 (m, 1H), 2.36-2.32 (m, 1H), 2.31 (s, 3H), 2.01-1.94 (m, 4H); **¹³C NMR** (75.0 MHz, CDCl₃): δ 210.7, 169.4, 156.2, 137.9, 137.7, 128.5, 128.1, 124.7, 58.1, 55.9, 52.5, 52.0, 37.2, 30.5, 21.2, 18.6, 18.1; **IR (thin film, cm⁻¹):** 3335, 2956, 1726, 1512, 1453, 1234, 1141, 1118, 1051, 757, 711; **HRMS:** calc'd for (M+H)⁺ C₁₇H₂₁NO₅: 319.1420; found: 320.1490; [α]_D²³ = - 20.9 ° (c = 1.0, CHCl₃).

12b: (R)-1-((S)-Methoxycarbonylamino-*m*-tolyl-methyl)-2-oxocyclopentane carboxylic acid ethyl ester

According to General Procedure, imine **7b** ((3-Methyl-benzylidene)-carbamic acid methyl ester) was added to β -ketoester **6b** (2-oxo-cyclopentanecarboxylic acid ethyl ester) and stirred at $-55\text{ }^{\circ}\text{C}$ for 4 hours to give Mannich product **12b**. **Yield:** 0.118 g (98%), **de:** 98%, **ee:** 92%; **HPLC Analysis**, t_r minor: 15.4 min., t_r major: 25.5 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.18-7.04 (m, 4H), 6.17 (d, $J = 8.4$ Hz, 1H), 5.10 (d, $J = 9.2$ Hz, 1H), 4.13-4.05 (m, 2H), 3.60 (s, 3H), 2.51-2.42 (m, 2H), 2.33 (s, 3H), 2.02-1.93 (m, 4H), 1.67 (t, $J = 6.6$ Hz, 3H); **^{13}C NMR** (75.0 MHz, CDCl_3): δ 211.1, 169.3, 156.4, 138.0, 137.9, 128.8, 128.6, 128.2, 125.1, 64.4, 61.8, 56.2, 52.2, 37.5, 30.8, 21.4, 18.8, 13.8; **IR (thin film, cm^{-1}):** 3340, 2958, 1723, 1512, 1461, 1230, 1141, 1118, 731, 711; **HRMS:** calc'd for $(\text{M})^+$ $\text{C}_{18}\text{H}_{23}\text{NO}_5$: 333.1576; found: 333.1559; $[\alpha]_D^{23} = -9.0^{\circ}$ ($c = 1.0$, CHCl_3).

12c: [(S)-(S)-(1-Acetyl-2-oxo-cyclopentyl)-*m*-tolyl-methyl]-carbamic acid methyl ester

According to General Procedure, imine **7b** ((3-Methyl-benzylidene)-carbamic acid methyl ester) was added to β -diketone **6c** (2-Acetyl-cyclopentanone) and stirred at $-55\text{ }^{\circ}\text{C}$ for 2 hours to give Mannich product **12c**. **Yield:** 0.149 g (98%), **de:** 94%, **ee:** 94%; **HPLC Analysis**, t_r minor: 14.5 min., t_r major: 16.6 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.18-7.14 (m, 1H), 7.04-6.98 (m, 3H), 5.66 (d, $J = 9.2$ Hz, 1H), 5.27 (d, $J = 8.8$ Hz, 1H), 3.59 (s, 3H), 2.62-2.61 (m, 1H), 2.32 (s, 3H), 2.29 (s, 3H), 2.16-2.11 (m, 1H), 1.78-1.58 (m, 4H); **^{13}C NMR** (75.0MHz, CDCl_3): δ 212.8, 202.2, 155.7, 137.9, 137.6, 128.5, 128.2, 127.9, 124.3, 76.4, 73.2, 57.1, 52.1, 38.8, 25.3, 21.2, 19.0 ; **IR (thin film, cm^{-1}):** 3329, 2958, 1705, 1532, 1358, 1243, 1196, 1143, 1055, 917, 757, 732; **HRMS:** calc'd for $(\text{M}+\text{H})^+$ $\text{C}_{17}\text{H}_{21}\text{NO}_4$: 303.1471; found: 304.1537; $[\alpha]_D^{23} = +83.3^{\circ}$ ($c = 1.0$, CHCl_3).

12d: [(S)-(S)-(3-Acetyl-2-oxo-tetrahydro-furan-3-yl)-*m*-tolyl-methyl]-carbamic acid methyl ester

According to General Procedure, imine **7b** ((3-Methyl-benzylidene)-carbamic acid methyl ester) was added to β -diketone **6d** (3-Acetyl-dihydro-furan-2-one) and stirred at -78°C for 2 hours to give Mannich product **12d**. **Yield:** 0.135 g (88%), **de:** 38%, **ee:** 91%, (major diastereomer); **HPLC Analysis**, t_r minor: 24.4 min., t_r major: 25.7 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.22-7.20 (m, 1H), 7.11-7.08 (m, 3H), 5.75 (d, $J = 9.9$ Hz, 1H), 5.04 (d, $J = 8.1$ Hz, 1H), 3.99-3.94 (m, 1H), 3.66-3.63 (m, 1H), 3.63 (s, 3H), 2.89-2.83 (m, 1H), 2.45 (s, 3H), 2.32 (s, 3H), 2.10-2.09 (m, 1H); **^{13}C NMR** (75.0 MHz, CDCl_3): δ 200.9, 173.1, 155.9, 138.6, 136.5, 129.3, 128.7, 127.9, 124.1, 66.8, 66.2, 56.7, 52.6, 25.5, 24.2, 21.5; **IR (thin film, cm^{-1}):** 3327, 2956, 2922 1760, 1716, 1537, 1361, 1248, 1170, 1028, 914, 733; **HRMS:** calc'd for $(\text{M}+\text{H})^+$ $\text{C}_{16}\text{H}_{19}\text{NO}_5$: 305.1263; found: 306.1309; **$[\alpha]_D^{23} = -6.1^{\circ}$** ($c = 1.0$, CHCl_3).

13a: (*R*)-1-((*S*)-Allyloxycarbonylamino-*m*-tolyl-methyl)-2-oxo-cyclopentanecarboxylic acid methyl ester

According to General Procedure, imine **8b** ((3-Methyl-benzylidene)-carbamic acid allyl ester) was added to β -ketoester **6a** (2-oxo-cyclopentanecarboxylic acid methyl ester) and stirred at -55°C for 2 hours to give Mannich product **13a**. **Yield:** 0.165 g (96%), **de:** 97%, **ee:** 92%; **HPLC analysis**, t_r minor: 16.7 min., t_r major: 22.2 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.19-7.15 (m, 2H), 7.08-7.05 (m, 3H), 6.23 (d, $J = 8.4$ Hz, 1H), 5.85 (br, 1H), 5.28-5.24 (m, 1H), 5.13 (dd, $J = 21.6, 9.2$ Hz, 2H), 4.95 (s, 2H), 3.67 (s, 3H), 2.52-2.47 (m, 1H), 2.36-2.33 (br, 1H), 2.31 (s, 3H), 2.03-1.94 (m, 4H); **^{13}C NMR** (75.0 MHz, CDCl_3): δ 210.8, 169.7, 155.5, 137.9, 137.8, 132.6, 128.7, 128.6, 128.2, 124.9, 117.5, 65.6, 64.4, 56.1, 52.6, 37.4, 30.5, 21.4, 18.7; **IR (thin film, cm^{-1}):** 3336, 2954, 1731, 1507, 1436, 1233, 1140, 1119, 1048, 917, 732; **HRMS:** calc'd for $(\text{M})^+$ $\text{C}_{19}\text{H}_{23}\text{NO}_5$: 345.1657; found: 345.1587; **$[\alpha]_D^{23} = -25.1^{\circ}$** ($c = 1.0$, CHCl_3).

13b: (*R*)-1-((*S*)-Allyloxycarbonylamino-*m*-tolyl-methyl)-2-oxo-cyclopentanecarboxylic acid ethyl ester

According to General Procedure, imine **8b** ((3-Methyl-benzylidene)-carbamic acid allyl ester) was added to β -ketoester **6b** (2-oxo-cyclopentanecarboxylic acid ethyl ester) and stirred at -55°C for 2 hours to give Mannich product **13b**. **Yield:** 0.177 g (98%), **de:** 98%, **ee:** 99%; **HPLC analysis**, t_r minor: 19.2 min., t_r major: 25.5 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.19-7.04

(m, 5H), 6.20 (d, $J = 8.8$ Hz, 1H), 5.87 (br, 1H), 5.28-5.24 (m, 1H), 5.18-5.11 (m, 2H), 4.50-4.49 (m, 2H), 4.10 (m, 2H), 2.50-2.47 (m, 2H), 2.30 (s, 3H), 2.00-1.92 (m, 4H), 1.85 (t, $J = 6.0$ Hz, 3H); ^{13}C NMR (75.0 MHz, CDCl_3): δ 210.9, 169.3, 155.5, 137.9, 137.9, 132.6, 128.8, 128.6, 128.2, 125.1, 117.50, 65.63, 64.4, 61.8, 56.2, 37.5, 30.6, 21.4, 18.8, 13.8; **IR** (thin film, cm^{-1}): 3339, 2978, 1722, 1529, 1641, 1229, 1139, 1118, 1048, 922, 711; **HRMS**: calc'd for $(\text{M})^+ \text{C}_{20}\text{H}_{25}\text{NO}_5$: 359.1733; found: 359.1719; $[\alpha]_{\text{D}}^{23} = -15.2^\circ$ ($c = 1.0$, CHCl_3).

13c: [(S)-(S)-(1-Acetyl-2-oxo-cyclopentyl)-*m*-tolyl-methyl]-carbamic acid allyl ester

According to General Procedure, imine **8b** ((3-Methyl-benzylidene)-carbamic acid allyl ester) was added to β -diketone **6c** (2-Acetyl-cyclopentanone) and stirred at -55°C for 2 hours to give Mannich product **13c**. **Yield**: 0.152 g (92%), **de**: 92%, **ee**: 98%; **HPLC Analysis**, t_{r} minor: 14.5 min., t_{r} major: 15.5 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; ^1H NMR (400 MHz, CDCl_3): δ 7.19-7.15 (m, 2H), 7.06-6.98 (m, 3H), 5.85 (br, 1H), 5.67 (d, $J = 9.9$ Hz, 1H), 5.27 (m, 1H), 5.18 (d, $J = 10.2$, 2H), 4.50-4.48 (m, 2H), 2.62-2.59 (m, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 2.17-1.12 (m, 1H), 1.78-1.52 (m, 4H); ^{13}C NMR (75.0 MHz, CDCl_3): δ 213.4, 202.7, 155.6, 138.5, 138.2, 132.7, 129.1, 128.7, 128.6, 124.9, 118.3, 73.9, 66.2, 57.7, 39.4, 29.9, 25.9, 21.8, 19.6; **IR** (thin film, cm^{-1}): 3331, 2598, 1700, 1607, 1533, 1360, 1238, 1142, 1050, 998, 917, 732; **HRMS**: calc'd for $(\text{M}+\text{H})^+ \text{C}_{19}\text{H}_{23}\text{NO}_4$: 329.1627; found: 330.1695; $[\alpha]_{\text{D}}^{23} = +70.5^\circ$ ($c = 1.0$, CHCl_3).

13d: [(S)-(S)-(3-Acetyl-2-oxo-tetrahydro-furan-3-yl)-*m*-tolyl-methyl]-carbamic acid allyl ester

According to General Procedure, imine **8b** ((3-Methyl-benzylidene)-carbamic acid allyl ester) was added to β -diketone **6d** (3-Acetyl-dihydro-furan-2-one) and stirred at -55°C for 2 hours to give Mannich product **13d**. **Yield**: 0.130 g (78%), **de**: 38%, **ee**: 99% (major diastereomer); **HPLC Analysis**, t_{r} minor: 19.3 min., t_{r} major: 20.5 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; ^1H NMR (400 MHz, CDCl_3): δ 7.22-7.20 (m, 1H), 7.12-7.09 (m, 3H), 5.85 (br, 1H), 5.76 (d, $J = 9.9$ Hz, 1H), 5.28-5.19 (m, 2H), 5.10 (d, $J = 8.0$ Hz, 1H), 4.52-4.49 (m, 2H), 3.97 (q, $J = 16.1, 8.3$ Hz, 1H), 3.72-3.66 (m, 2H), 2.90-2.84 (m, 1H), 2.45 (s, 3H), 2.32 (s, 3H), 2.14-2.03 (m, 1H); ^{13}C NMR (75.0 MHz, CDCl_3): δ 200.9, 173.1, 155.2, 138.6, 136.5, 132.2, 129.3, 128.7, 128.0, 124.2, 118.2, 66.8, 66.1, 56.7, 25.5, 24.2, 21.5; **IR** (thin film, cm^{-1}): 3327, 2923,

1760, 1716, 1533, 1376, 1242, 1168, 1027, 916, 732, 649; **HRMS**: calc'd for (M+H)⁺ C₁₈H₂₁NO₅: 331.1420; found: 331.1376; [α]_D²³ = - 14.2 ° (c = 1.0, CHCl₃).

14a: (R)-1-((S)-Furan-2-yl-methoxycarbonylamino-methyl)-2-oxo-cyclopentanecarboxylic acid methyl ester

According to General Procedure, imine **7c** (Furan-2-ylmethylene-carbamic acid methyl ester) was added to β -ketoester **6a** (2-oxo-cyclopentanecarboxylic acid methyl ester) and stirred at - 78 °C for 3 hours to give Mannich product **14a**. **Yield**: 0.145 g (98%), **de**: 99%, **ee**: 99%; **HPLC Analysis**, t_r minor: 22.6 min., t_r major: 23.1 min., [(R,R)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **¹H NMR** (400 MHz, CDCl₃): δ 7.29 (d, *J* = 1.1 Hz, 1H), 6.28 (dd, *J* = 2.9, 1.8 Hz, 1H), 6.21 (d, *J* = 2.9 Hz, 1H), 5.83 (d, *J* = 9.2 Hz, 1H), 5.35 (d, *J* = 9.9 Hz, 1H), 3.71 (s, 3H), 3.65 (s, 3H), 2.61-2.45 (m, 1H), 2.36-2.33 (m, 2H), 2.06-1.94 (m, 3H); **¹³C NMR** (75.0 MHz, CDCl₃): δ 210.6, 156.4, 151.2, 142.1, 110.5, 108.3, 63.9, 52.8, 52.4, 50.9, 37.6, 30.6, 29.6, 18.9; **IR (thin film, cm⁻¹)**: 3330, 2956, 1726, 1526, 1451, 1321 1240, 1142, 1042, 1011, 745; **HRMS**: calc'd for (M)⁺ C₁₄H₁₇NO₆: 295.1056; found: 295.1030; [α]_D²³ = - 41.8 ° (c = 1.0, CHCl₃).

14b: (R)-1-((S)-Furan-2-yl-methoxycarbonylamino-methyl)-2-oxo-cyclopentanecarboxylic acid ethyl ester

According to General Procedure, imine **7c** (Furan-2-ylmethylene-carbamic acid methyl ester) was added to β -ketoester **6b** (2-oxo-cyclopentanecarboxylic acid ethyl ester) and stirred at - 78 °C for 3 hours to give Mannich product **14b**. **Yield**: 0.151g (98%) **de**: 99%, **ee**: 99%; **HPLC Analysis**, t_r minor: 15.8, min., t_r major: 16.6 min., [(R,R)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **¹H NMR** (400 MHz, CDCl₃): δ 7.29 (d, *J* = 1.1 Hz, 1H), 6.28 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.22 (s, 2H), 5.80 (d, *J* = 9.2 Hz), 5.36 (d, *J* = 9.5 Hz, 1H), 4.21-4.11 (m, 2H), 3.64 (s, 3H), 2.61-2.54 (m, 1H), 2.36-2.32 (m, 2H), 2.05-1.93 (m, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (75.0 MHz, CDCl₃): 210.7, 156.3, 151.4, 141.9, 110.5, 108.3, 63.9, 61.9, 52.4, 50.9, 37.6, 30.7, 29.7, 18.9, 13.9; **IR (thin film, cm⁻¹)**: 3333, 2960, 1723, 1526, 1456, 1319, 1235, 1071, 1141, 1015, 743; **HRMS**: calc'd for (M)⁺ C₁₅H₁₉NO₆: 309.1212; found: 309.1238; [α]_D²³ = - 26.5 ° (c = 1.0, CHCl₃).

14c: [(S)-(S)-(1-Acetyl-2-oxo-cyclopentyl)-furan-2-yl-methyl]-carbamic acid methyl ester

According to General Procedure, imine **7c** (Furan-2-ylmethylene-carbamic acid methyl ester) was added to β -diketone **6c** (2-Acetyl-cyclopentanone) and stirred at -78°C for 3 hours to give Mannich product **14c**. **Yield:** 0.138 g (98%), **de:** 99%, **ee:** 99%; **HPLC Analysis**, t_r minor: 16.6 min., t_r major: 17.2 min., [(R,R)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.30 (d, $J = 1.1$ Hz, 1H), 6.28 (dd, $J = 2.9, 1.8$ Hz, 1H), 6.15 (d, $J = 2.9$ Hz, 1H), 5.77 (d, $J = 9.2$ Hz, 1H), 5.08 (d, $J = 8.8$ Hz, 1H), 3.64 (s, 3H), 2.67-2.64 (m, 1H), 2.31 (s, 3H), 2.26-2.17 (m, 1H), 2.09-2.02 (m, 1H), 1.75-1.59 (m, 3H); **^{13}C NMR** (75.0 MHz, CDCl_3): δ 212.3, 156.1, 150.9, 142.3, 119.6, 110.6, 108.2, 72.9, 52.6, 52.4, 38.5, 26.5, 25.7, 19.1; **IR (thin film, cm^{-1}):** 3321, 2959, 2242, 1708, 1532, 1244, 1141, 1052, 1010, 925, 739; **HRMS:** calc'd for $(\text{M}+\text{H})^+$ $\text{C}_{14}\text{H}_{15}\text{NO}_6$: 279.1107; found: 280.1159; $[\alpha]_D^{23} = +146.0^{\circ}$ ($c = 1.0$, CHCl_3).

15a: (R)-1-[(S)-(3-Fluoro-phenyl)-methoxycarbonylamino-methyl]-2-oxo-cyclopentanecarboxylic acid methyl ester

According to General Procedure, imine **7d** (3-Fluoro-benzylidene)-carbamic acid methyl ester) was added to β -ketoester **6a** (2-oxo-cyclopentanecarboxylic acid methyl ester) and stirred at -85°C for 2 hours to give Mannich product **15a**. **Yield:** 0.159 g (98%), **de:** 99%, **ee:** 90%; **HPLC Analysis**, t_r minor: 17.9 min., t_r major: 22.7 min., [(R,R)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.26–6.93 (m, 2H), 7.08-7.04 (m, 1H), 6.97-6.93 (m, 1H), 6.17 (s, 1H), 5.12 (d, $J = 8.1$ Hz, 1H), 3.67 (s, 3H), 3.61 (s, 3H), 2.49-2.48 (m, 1H), 2.35-2.34 (m, 2H), 1.95 (m, 3H); **^{13}C NMR** (75.0 MHz, CDCl_3): δ 210.7, 164.3, 156.3, 140.7, 129.9, 123.9, 115.2, 115.1, 114.9, 114.8, 55.9, 52.8, 52.3, 37.5, 30.9, 18.9; **IR (thin film, cm^{-1}):** 331, 2957, 1726, 1590, 1523, 1237, 1134, 1049, 918, 785, 705; **HRMS:** calc'd for $(\text{M})^+$ $\text{C}_{16}\text{H}_{18}\text{FNO}_5$: 323.1169; found 324.1270; ; $[\alpha]_D^{23} = -17.4^{\circ}$ ($c = 2.0$, CHCl_3).

15b: (R)-1-[(S)-(3-Fluoro-phenyl)-methoxycarbonylamino-methyl]-2-oxo-cyclopentanecarboxylic acid ethyl ester

According to General Procedure, imine **7d** (3-Fluoro-benzylidene)-carbamic acid methyl ester) was added to β -ketoester **6b** (2-oxo-cyclopentanecarboxylic acid ethyl ester) and stirred at -90°C for 3 hours to give Mannich product **15b**. **Yield:** 0.165 g (98%), **de:** 99%, **ee:** 92%; **HPLC** analysis, t_{r} minor: 14.9 min., t_{r} major: 20.7 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.23–7.21 (m, 1H), 7.10–7.06 (m, 2H), 6.96–6.92 (m, 1H), 6.15 (d, $J = 6.6$ Hz, 1H), 5.14 (d, $J = 8.4$ Hz, 1H), 4.14–4.07 (m, 2H), 3.60 (s, 3H), 2.49–2.48 (m, 1H), 2.34–2.31 (m, 2H), 2.10–1.94 (m, 3H), 1.16 (t, $J = 6.9$ Hz, 3H); **^{13}C NMR** (75.0 MHz, CDCl_3): δ 210.9, 164.3, 156.3, 140.8, 129.9, 124.0, 115.3, 115.0, 114.7, 61.9, 55.9, 52.3, 37.5, 30.9, 18.9, 13.7; **IR (thin film, cm^{-1}):** 3334, 2960, 1724, 1590, 1529, 1453, 1351, 1236, 1123, 11028, 782, 706; **HRMS** :calc'd for $(\text{M}+\text{H})^+$ $\text{C}_{17}\text{H}_{20}\text{FNO}_5$: 337.1326; found: 338.1377; $[\alpha]_{\text{D}}^{23} = -4.6^{\circ}$ ($c = 1.2$, CHCl_3).

15c: [(S)-(S)-(1-Acetyl-2-oxo-cyclopentyl)-(3-fluoro-phenyl)-methyl]-carbamic acid methyl ester

According to General Procedure, imine **7d** (3-Fluoro-benzylidene)-carbamic acid methyl ester) was added to β -diketone **6c** (2-Acetyl-cyclopentanone) and stirred at -78°C for 2 hours to give Mannich product **15c**. **Yield:** 0.150 g (98%) **de:** 99%, **ee:** 93%; **HPLC Analysis**, t_{r} minor: 13.5 min., t_{r} major: 15.8 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.26–7.24 (m, 1H), 6.99–6.92 (m, 3H), 5.67 (d, $J = 9.2$ Hz, 1H), 5.22 (br, 1H), 3.60 (s, 3H), 2.62–2.61 (m, 1H), 2.31 (s, 3H), 2.20–2.16 (m, 1H), 1.82–1.64 (m, 4H); **^{13}C NMR** (75.0 MHz, CDCl_3): δ 212.9, 164.3, 156.0, 140.8, 130.1, 123.3, 115.0, 114.8, 114.4, 73.4, 56.9, 52.4, 38.9, 25.6, 25.5, 19.2; **IR (thin film, cm^{-1}):** 3325, 2961, 1706, 1591, 1532, 1452, 1357, 1245, 11945, 1143, 732; **HRMS**: calc'd for $(\text{M})^+$ $\text{C}_{16}\text{H}_{18}\text{FNO}_4$: 307.1220; found: 307.1234; $[\alpha]_{\text{D}}^{23} = +1.17^{\circ}$ ($c = 1.0$, CHCl_3).

18a: (E)-(S)-2-Acetyl-3-methoxycarbonylamino-5-phenyl-pent-4-enoic acid allyl ester.

According to General Procedure, imine **17a** (3-Phenyl-allylidene)-carbamic acid methyl ester) was added to β -ketoester **16a** and stirred at -78°C for 2 hours to give Mannich product **18a**. **Yield:** 0.325 g (98%), **ee:** 95%; **HPLC** analysis, t_{r} major: 12.0 min, t_{r} minor: 13.6 min, [Chiralcel[®] OD Column, Hexanes : IPA = 90 : 10, 1.0 mL/min.]; **^1H NMR** (400 MHz, CDCl_3 , both isomers were reported): δ 7.33–7.19 (m, 10H), 6.60–6.55 (dd, $J = 8.8$, 3.2 Hz, 2H), 6.22–6.13 (m, 2H), 5.98 (d, $J = 9.2$ Hz, 1H), 5.88–5.80 (m, 2H), 5.75 (d, $J = 8$ Hz, 1H), 5.29 (d, $J = 17.2$ Hz, 2H), 5.21 (d, $J = 8.8$ Hz, 2H), 5.08 (m, 1H), 4.98 (m, 1H), 4.60 (m, 4H), 3.92 (d, $J = 4.4$ Hz, 1H), 3.87 (d, $J = 4.4$ Hz, 1H), 3.65 (s, 6H), 2.30 (s,

3H), 2.26 (s, 3H); ^{13}C NMR (75.0 MHz, CDCl_3 , both isomers were reported): δ 202.2, 201.2, 168.2, 167.2, 156.3, 156.1, 136.0, 135.9, 132.4, 132.2, 131.1, 131.0, 128.5, 128.4, 127.9, 127.8, 126.5, 126.5, 126.2, 126.0, 119.2, 119.1, 66.3, 66.1, 62.7, 62.4, 52.6, 52.2, 52.1, 30.2, 29.2; **IR** (neat, cm^{-1}): 3337, 2954, 1712, 1722, 1508, 1450, 1361, 1242, 1047, 750; **HRMS**: calc'd for $(\text{M})^+$ $\text{C}_{18}\text{H}_{21}\text{NO}_5$: 331.1420; found: 331.1420; $[\alpha]^{23}_{\text{D}} = -3.9^\circ$ ($c = 1.0$, CHCl_3).

18b: *(E)-(S)*-2-Acetyl-3-methoxycarbonylamino-5-phenyl-pent-4-enoic acid methyl ester.

According to General Procedure, imine **17a** (3-Phenyl-allylidene)-carbamic acid methyl ester) was added to β -ketoester **16b** and stirred at -78°C for 2 hours to give Mannich product **18b**. **Yield**: 0.295g (97%), **de**: 67%, **ee**: 92%; **HPLC Analysis**, t_{r} major: 10.7 min, t_{r} minor: 12.2 min, [Chiralcel[®] OD Column, Hexanes : IPA = 90 : 10, 1.0 mL/min]; ^1H NMR (400 MHz, CDCl_3 , major isomer was reported): δ 7.31-7.12 (m, 5H), 6.52 (d, $J = 8.8$ Hz, 1H), 6.16-6.11 (dd, $J = 16, 7.2$ Hz, 1H), 5.69 (d, $J = 8.8$ Hz, 1H), 4.90 (dd, $J = 14.8, 6.8$ Hz, 1H), 3.85 (d, $J = 6.8$ Hz, 1H), 3.69 (s, 3H), 3.60 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (75.0 MHz, CDCl_3): δ 202.3, 168.0, 156.2, 136.0, 132.4, 128.5, 127.9, 126.5, 126.2, 126.0, 62.2, 52.6, 52.2, 30.2; **IR** (thin film, cm^{-1}): 3363, 3003, 2960, 1750, 1701, 1519, 1444, 1356, 1302, 1228, 1047, 735; **HRMS**: calc'd for $(\text{M})^+$ $\text{C}_{16}\text{H}_{19}\text{NO}_5$: 305.1263; found: 305.1293; $[\alpha]^{23}_{\text{D}} = -22.7^\circ$ ($c = 1.0$, CHCl_3).

19a: *(E)-(S)*-2-Acetyl-5-furan-2-yl-3-methoxycarbonylamino-pent-4-enoic acid allyl ester.

According to General Procedure, imine **17b** (3-Furan-allylidene)-carbamic acid methyl ester) was added to β -ketoester **16a** and stirred at -78°C for 2 hours to give Mannich product **19a**. **Yield**: 0.325g (98%), **ee**: 90%; **HPLC Analysis**, t_{r} minor: 11.6 min, t_{r} major: 12.4 min, [Chiralcel[®] OD Column, Hexanes : IPA = 90 : 10, 1.0 mL/min.]; ^1H NMR (400 MHz, CDCl_3 , both isomers were reported): δ 7.27 (m, 2H), 6.35 (d, $J = 16$ Hz, 2H), 6.29 (m, 2H), 6.19 (t, $J = 4$ Hz, 2H), 6.04 (m, 2H), 5.92 (d, 9.2 Hz), 5.83 (m, 2H), 5.70 (d, $J = 9.2$ Hz), 5.25 (m, 2H), 5.17 (m, 2H), 5.02 (m, 1H), 4.91 (dd, $J = 14.8, 6.4$ Hz, 1H), 4.56 (m, 4H), 3.85 (d, $J = 5.2$ Hz, 1H), 3.81 (d, $J = 4$ Hz, 1H), 3.61 (s, 6H), 2.26 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (75.0 MHz, CDCl_3 , both isomers were reported): δ 202.5, 201.4, 168.5, 167.4, 156.7, 156.4, 151.8, 151.8, 142.5, 142.4, 131.4, 131.3, 124.9, 124.8, 120.9, 120.7, 119.5, 119.4, 111.6, 111.5, 109.2, 109.1, 66.6, 66.4, 62.9, 62.4, 52.7, 52.5, 52.4, 52.0, 30.6, 29.5; **IR** (neat, cm^{-1}): 3343, 2954, 1720, 1510, 1454, 1361, 1242, 1156, 1048, 964, 742. 700; **HRMS**: calc'd for $(\text{M})^+$ $\text{C}_{16}\text{H}_{19}\text{NO}_6$: 321.1212; found: 321.1199; $[\alpha]^{23}_{\text{D}} = -7.5^\circ$ ($c = 1.0$, CHCl_3).

19b: (*E*)-(*S*)-2-Acetyl-5-furan-2-yl-3-methoxycarbonylamino-pent-4-enoic acid methyl ester.

According to General Procedure, imine **17b** (3-Furan-allylidene)-carbamic acid methyl ester) was added to β -ketoester **16b** and stirred at -78°C for 2 hours to give Mannich product **19b**. **Yield:** 0.290g (98%), **ee:** 90%; **HPLC** analysis, t_r major: 25.6 min, t_r minor: 29.3 min, [Chiralcel[®] AD Column, Hexanes : IPA = 90 : 10, 1.0 mL/min.]; **¹H NMR** (400 MHz, CDCl₃, both isomers were reported): δ 7.26 (m, 2H), 6.35 (dd, J = 16, 2.4 Hz, 2H), 6.28 (m, 2H), 6.18 (m, 2H), 6.04 (m, 2H), 5.94 (d, J = 9.2 Hz), 5.73 (d, J = 8.8 Hz), 4.99 (m, 1H), 4.90 (m, 1H), 3.83 (d, J = 5.6 Hz, 1H), 3.79 (d, J = 4 Hz, 1H), 3.68 (s, 6H), 3.60 (s, 6H), 2.25 (s, 3H), 2.21 (s, 3H); **¹³C NMR** (75.0 MHz, CDCl₃, both isomers were reported): δ 202.6, 201.5, 169.2, 168.2, 156.6, 156.5, 151.8, 151.7, 142.5, 142.4, 124.9, 124.8, 120.9, 120.7, 111.6, 111.5, 109.3, 109.2, 62.8, 62.2, 52.9, 52.7, 52.5, 52.4, 30.5, 29.4; **IR** (neat, cm⁻¹): 3346, 2957, 1722, 1511, 1440, 1362, 1245, 1157, 1047, 743; **HRMS**: calc'd for (M)⁺ C₁₄H₁₇NO₆: 295.1056; found: 295.1050; [α]_D²³ = -5.7° (c = 1.0, CHCl₃).

20a: (*R*)-1-((*E*)-(*S*)-1-Methoxycarbonylamino-3-phenyl-allyl)-2-oxo-cyclopentanecarboxylic acid methyl ester

According to General Procedure, imine **17a** (3-Phenyl-allylidene)-carbamic acid methyl ester) was added to β -ketoester **6a** (2-oxo-cyclopentanecarboxylic acid methyl ester) and stirred at -78°C for 2 hours to give Mannich product **20a**. **Yield:** 0.160 g (98%), **de:** 90%, **ee:** 99%; **HPLC** analysis, t_r minor: 21.6 min., t_r major: 23.6 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **¹H NMR** (400 MHz, CDCl₃): δ 7.34-7.21 (m, 5H), 6.58 (d, J = 15.8 Hz, 1H), 6.17 (dd, J = 15.8, 7.7 Hz, 1H), 5.60 (d, J = 8.8 Hz, 1H), 4.68 (t, J = 8.7 Hz, 1H), 3.69 (s, 3H), 3.64 (s, 3H), 2.54-2.47 (m, 1H), 2.46-2.33 (m, 2H), 2.03 (br, 3H); **¹³C NMR** (75.0 MHz, CDCl₃): δ 211.8, 170.5, 156.5, 136.1, 133.9, 128.5, 128.0, 126.6, 124.7, 64.2, 55.1, 52.7, 52.3, 37.5, 31.4, 18.9; **IR** (thin film, cm⁻¹): 3334, 2955, 1726, 1508, 1449, 1233, 1192, 1148, 970, 753, 695; **HRMS**: calc'd for (M)⁺ C₁₈H₂₁NO₅: 331.1420 ; found: 331.1448; [α]_D²³ = -73.9° (c = 1.0, CHCl₃).

20b: (R)-1-((E)-(S)-1-Methoxycarbonylamino-3-phenyl-allyl)-2-oxo-cyclopentanecarboxylic acid ethyl ester

According to General Procedure, imine **17a** (3-Phenyl-allylidene)-carbamic acid methyl ester) was added to β -ketoester **6b** (2-oxo-cyclopentanecarboxylic acid ethyl ester) and stirred at -78°C for 2 hours to give Mannich product **20b**. **Yield:** 0.170 g (98%), **de:** 94%, **ee:** 98%; **HPLC** analysis, t_{r} minor: 16.9 min., t_{r} major: 19.5 min, [(R, R)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.34-7.21 (m, 5H), 6.58 (d, J = 15.8 Hz, 1H), 6.20 (dd, J = 15.8, 7.7 Hz, 1H), 5.59 (d, J = 8.1 Hz, 1H), 4.68 (t, J = 8.8 Hz, 1H), 3.64 (s, 3H), 2.54-2.47 (m, 1H), 2.39-2.38 (m, 2H), 2.15-2.12 (m, 1H), 2.11-1.97 (m, 2H), 1.23 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (75.0 MHz, CDCl_3): δ 211.9, 156.5, 136.1, 133.8, 128.5, 127.9, 126.6, 124.8, 64.1, 61.7, 55.1, 52.3, 37.5, 31.4, 29.6, 18.9, 13.9; **IR** (thin film, cm^{-1}): 3437, 2957, 1720, 1506, 1451, 1269, 1229, 1192, 909, 733, 647; **HRMS:** calc'd for $(\text{M}+\text{H})^+$ $\text{C}_{19}\text{H}_{23}\text{NO}_5$: 345.1576; found: 345.1540; $[\alpha]_{\text{D}}^{23} = -56.9^{\circ}$ (c = 1.0, CHCl_3).

20c: [(E)-(S)-1-((S)-1-Acetyl-2-oxo-cyclopentyl)-3-phenyl-allyl]-carbamic acid methyl ester

According to General Procedure, imine **17a** (3-Phenyl-allylidene)-carbamic acid methyl ester) was added to β -diketone **6c** (2-Acetyl-cyclopentanone) and stirred at -78°C for 2 hours to give Mannich product **20c**. **Yield:** 0.150 g (98%), **de:** 95%, **ee:** 99%; **HPLC Analysis**, t_{r} minor: 19.5 min., t_{r} major: 20.9 min, [(R,R)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.31-7.24 (m, 5H), 6.53 (d, J = 15.8 Hz, 1H), 6.01 (dd, J = 16.0, 6.4 Hz, 1H), 5.15-5.105 (m, 1H), 4.87 (d, J = 9.9 Hz, 1H), 3.65 (s, 3H), 2.59-2.56 (m, 1H), 2.32-2.23 (m, 3H), 1.95-1.89 (m, 1H), 1.86-1.84 (m, 1H); **^{13}C NMR** (75.0 MHz, CDCl_3): δ 213.4, 156.2, 135.8, 133.3, 128.6, 128.1, 126.6, 124.7, 72.68, 55.8, 52.4, 38.6, 29.6, 27.1, 26.0, 19.7; **IR** (thin film, cm^{-1}): 3328, 2956, 2927, 1702, 1527, 1358, 1449, 1238, 1196, 1144, 755; **HRMS:** calc'd for $(\text{M})^+$ $\text{C}_{18}\text{H}_{21}\text{NO}_4$: 315.1471; found: 315.1332; $[\alpha]_{\text{D}}^{23} = +63.6^{\circ}$ (c = 1.0, CHCl_3).

20d: [(E)-(S)-1-((S)-3-Acetyl-2-oxo-tetrahydro-furan-3-yl)-3-phenyl-allyl]-carbamic acid methyl ester

According to General Procedure, imine **17a** (3-Phenyl-allylidene)-carbamic acid methyl ester) was added to β -diketone **6d** (3-Acetyl-dihydro-furan-2-one) and stirred at -78°C for 2 hours to give Mannich product **20d**. **Yield:** 0.132 g (88%), **de:** 38%, **ee:** 98% (major diastereomer); **HPLC** analysis, t_{r} minor: 30.2 min., t_{r} major: 34.7 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.35-7.24 (m, 5H), 6.58 (d, $J = 15.0$ Hz, 1H), 6.15 (dd, $J = 15.8, 5.9$ Hz, 1H), 5.29 (t, 1H), 4.71 (d, $J = 8.7$, 1H), 4.39-4.26 (m, 2H), 4.16-4.07 (m, 1H), 3.67 (s, 3H), 2.85-2.73 (m, 1H), 2.44 (s, 3H), 2.33-2.21 (m, 1H); **^{13}C NMR** (75.0 MHz, CDCl_3): δ 175.5, 156.2, 136.1, 135.3, 128.7, 128.6, 128.5, 126.7, 122.9, 65.8, 63.8, 55.8, 52.5, 29.8, 26.2; **IR (thin film, cm^{-1}):** 3399, 2955, 2925, 1765, 1716, 1225, 1194, 1028, 972; **HRMS:** calc'd for $(\text{M})^+ \text{C}_{17}\text{H}_{19}\text{NO}_5$: 317.1263; found: 317.1230; **$[\alpha]_{\text{D}}^{23} = -43.2^{\circ}$** ($c = 1.0$, CHCl_3).

21a: (*R*)-1-((*E*)-(*S*)-3-Furan-2-yl-1-methoxycarbonylamino-allyl)-2-oxo-cyclopentanecarboxylic acid methyl ester

According to General Procedure, imine **17b** (3-Furan-allylidene)-carbamic acid methyl ester) was added to β -ketoester **6a** (2-oxo-cyclopentanecarboxylic acid methyl ester) and stirred at -78°C for 2 hours to give Mannich product **21a**. **Yield:** 0.158 g (98%) **de:** 99%, **ee:** 99%; **HPLC Analysis**, t_{r} minor: 25.8 min., t_{r} major: 27.2 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.31 (d, $J = 1.5$ Hz, 1H), 6.40 (d, $J = 15.7$ Hz, 1H), 6.34 (dd, $J = 3.3, 1.8$ Hz, 1H), 6.23 (d, $J = 3.3$ Hz, 1H), 6.07 (dd, $J = 15.6, 7.5$ Hz, 1H), 5.6 (br, 1H), 4.65 (t, $J = 8.6$ Hz, 1H), 3.69 (s, 3H), 3.63 (s, 3H), 2.56-2.49 (m, 1H), 2.40-2.34 (m, 3H), 2.13-2.08 (m, 1H); **^{13}C NMR** (75.0 MHz, CDCl_3): δ 211.6, 163.2, 156.6, 142.3, 123.2, 121.9, 111.3, 109.1, 64.0, 54.8, 52.7, 52.3, 37.5, 31.3, 29.7, 19.0; **IR (thin film, cm^{-1}):** 3339, 2956, 1725, 1514, 1455, 1236, 1151, 1014, 956, 736; **HRMS:** calc'd for $(\text{M}+\text{H})^+ \text{C}_{16}\text{H}_{19}\text{NO}_6$: 321.1212; found: 322.1301; **$[\alpha]_{\text{D}}^{23} = -39.1^{\circ}$** ($c = 0.8$, CHCl_3).

21b: (*R*)-1-((*E*)-(*S*)-3-Furan-2-yl-1-methoxycarbonylamino-allyl)-2-oxo-cyclopentanecarboxylic acid ethyl ester

According to General Procedure, imine **17b** (3-Furan-allylidene)-carbamic acid methyl ester) was added to β -ketoester **6b** (2-oxo-cyclopentanecarboxylic acid ethyl ester) and stirred at -85°C for 3 hours to give Mannich product **21b**. **Yield:** 0.165 g (98%), **de:** 98%, **ee:** 93%; **HPLC Analysis**, t_{r} minor: 18.2, t_{r} major: 19.9 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; **^1H NMR** (400 MHz, CDCl_3): δ 7.30 (d, $J =$

1.5 Hz, 1H), 6.39 (d, $J = 15.7$ Hz, 1H), 6.33 (dd, $J = 3.3, 1.8$ Hz, 1H), 6.22 (d, $J = 3.3$ Hz, 1H), 6.09 (dd, $J = 15.5, 7.5$ Hz, 1H), 5.58 (d, $J = 8.4$ Hz, 1H), 4.65 (t, $J = 7.8$ Hz, 1H), 4.19-4.11 (m, 2H), 3.63 (s, 3H), 2.55-2.48 (m, 1H), 2.39-2.36 (m, 2H), 2.12-2.07 (m, 1H), 2.02-1.97 (m, 2H), 1.21 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75.0 MHz, CDCl_3): δ 211.7, 151.7, 142.2, 123.3, 121.9, 111.3, 108.9, 61.8, 54.9, 53.5, 53.4, 52.3, 37.6, 31.4, 29.7, 19.0, 13.9; **IR** (thin film, cm^{-1}): 3356, 2959, 2361, 1723, 1514, 1232, 1150, 1018, 965; **HRMS**: calc'd for $(\text{M})^+$ $\text{C}_{17}\text{H}_{21}\text{NO}_6$: 335.1369; found: 335.1357; $[\alpha]_{\text{D}}^{23} = -24.3^\circ$ ($c = 0.5$, CHCl_3)

21c: [(E)-(S)-1-((S)-1-Acetyl-2-oxo-cyclopentyl)-3-furan-2-yl-allyl]-carbamic acid methyl ester

According to General Procedure, imine **17b** (3-Furan-allylidene)-carbamic acid methyl ester) was added to β -diketone **6c** (2-Acetyl-cyclopentanone) and stirred at -78°C for 2 hours to give Mannich product **21c**. **Yield**: 0.150 g (98%), **de**: 94%, **ee**: 98%; **HPLC Analysis**, t_{r} minor: 23.3, t_{r} major: 24.4 min., [(*R,R*)-Whelk-O 1 column, Hexanes:IPA = 85:15, 1.0 mL/min]; ^1H NMR (400 MHz, CDCl_3): δ 7.30 (s, 1H), 6.35-6.31 (m, 2H), 6.23(d, $J = 3.3$ Hz, 1H), 5.90 (dd, $J = 15.7, 6.5$ Hz, 1H), 5.14-5.10 (m, 1H), 4.80 (d, $J = 9.9$ Hz, 1H), 3.64 (s, 3H), 2.60-2.57 (m, 1H), 2.30-2.71 (m, 2H), 2.25 (s, 3H), 1.96-1.85 (m, 3H); ^{13}C NMR (75.0 MHz, CDCl_3): δ 211.6, 170.3, 156.6, 151.6, 142.3, 123.2, 121.9, 111.3, 109.1, 54.8, 52.7, 52.3, 37.5, 31.3, 29.6, 18.9; **IR** (thin film, cm^{-1}): 3327, 29657, 1707, 1527, 1357, 1241, 1147, 1012, 965, 921, 735; **HRMS**: calc'd for $(\text{M})^+$ $\text{C}_{16}\text{H}_{19}\text{NO}_5$: 305.1263 ; found: 305.1283; $[\alpha]_{\text{D}}^{23} = +71.3^\circ$ ($c = 1.0$, CHCl_3).

Figure 1: Transformation of Mannich Product **11a** to adduct **22** for determination of relative and absolute stereochemistry

To Mannich product **11a** (130 mg, 0.37 mmol, 90% ee) in dry THF was slowly added LiAlH₄ (414.9 mg, 10.9 mmol, 30.0 equivalents) at room temperature. The reaction was refluxed for 24 h under N₂. Reaction was diluted with CH₂Cl₂ (13.0 ml) at -78 °C. To the mixture, H₂O (0.4 mL), aqueous 1N NaOH (0.4 mL), and H₂O (1.5 mL) was added sequentially. The mixture was warmed to room temperature and filtered through Celite. Solvent was removed under reduced pressure to afford yellow oil. To the yellow oil, pyridine (5.5 mL) and acetic anhydride (3.0 mL) were added and reaction was stirred for 12 h at room temperature. Toluene (5.0 mL) was added to reaction and mixture was subjected to reduced pressure vacuum pump to yield product **22** (73.0 mg, 56.1 % yield) confirmed by ¹H-NMR. Comparison of the sign of optical rotation to compound **22** and **22'** (as reported by Sodeoka *et al.*²) confirmed the absolute stereochemistry of major diastereomer of Mannich product **11a** as the (2*R*,1*S*) enantiomer.

Figure 1: Relative Stereochemistry of **15a**: (*R*)-1-[(*S*)-(3-Fluoro-phenyl)-methoxycarbonylamino-methyl]-2-oxo-cyclopentanecarboxylic acid methyl ester

Crystals of compound **15a** suitable for x-ray analysis were obtained by slow evaporation from methylene chloride and hexanes.

Table 1. Crystal data and structure refinement for **15a**.

Identification code	15a	
Empirical formula	C ₁₅ H ₂₀ F N O ₅	
Formula weight	313.32	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.754(2) Å	α = 90°.
	b = 12.086(2) Å	β = 90°.
	c = 13.614(3) Å	γ = 90°.

Volume	1605.0(6) Å ³
Z	4
Density (calculated)	1.297 Mg/m ³
Absorption coefficient	0.104 mm ⁻¹
F(000)	664
Crystal size	0.40 x 0.10 x 0.05 mm ³
Theta range for data collection	2.25 to 30.53°.
Index ranges	-13<= <i>h</i> <=13, -17<= <i>k</i> <=16, -19<= <i>l</i> <=19
Reflections collected	27484
Independent reflections	4884 [R(int) = 0.0367]
Completeness to theta = 30.53°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9948 and 0.9595
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4884 / 0 / 280
Goodness-of-fit on F ²	1.016
Final R indices [<i>I</i> >2sigma(<i>I</i>)]	R1 = 0.0357, wR2 = 0.0935
R indices (all data)	R1 = 0.0435, wR2 = 0.0981
Absolute structure parameter	0.0(6)
Largest diff. peak and hole	0.244 and -0.188 e.Å ⁻³

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for **15a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	2974(1)	-1032(1)	987(1)	56(1)
O(1)	8305(1)	-193(1)	-2246(1)	42(1)
O(2)	6205(1)	2753(1)	-2907(1)	48(1)
O(3)	8117(1)	2325(1)	-2053(1)	38(1)
O(4)	7686(1)	2717(1)	399(1)	32(1)
O(5)	5577(1)	3532(1)	485(1)	38(1)
N(1)	5822(1)	2056(1)	-463(1)	25(1)
C(1)	6489(1)	1049(1)	-838(1)	24(1)
C(2)	6295(1)	1017(1)	-1979(1)	25(1)

C(3)	7135(1)	49(1)	-2460(1)	28(1)
C(4)	6236(1)	-533(1)	-3210(1)	35(1)
C(5)	5018(1)	253(1)	-3374(1)	37(1)
C(6)	4819(1)	804(1)	-2358(1)	32(1)
C(7)	6841(1)	2128(1)	-2381(1)	32(1)
C(8)	8676(2)	3406(1)	-2284(1)	49(1)
C(9)	5978(1)	5(1)	-319(1)	26(1)
C(10)	6838(1)	-923(1)	-230(1)	37(1)
C(11)	6380(2)	-1882(1)	241(1)	45(1)
C(12)	5069(2)	-1937(1)	644(1)	43(1)
C(13)	4251(1)	-1009(1)	567(1)	37(1)
C(14)	4664(1)	-41(1)	97(1)	30(1)
C(15)	6474(1)	2758(1)	164(1)	24(1)
C(16)	6125(2)	4330(2)	1169(2)	61(1)

Figure 2: Relative Stereochemistry of **15c**: [(*S*)-(*S*)-(1-Acetyl-2-oxo-cyclopentyl)-(3-fluoro-phenyl)-methyl]-carbamic acid methyl ester.

Crystals of compound **15c** suitable for x-ray analysis were obtained by slow evaporation from methylene chloride and hexanes.

Table 1. Crystal data and structure refinement for **15c**.

Identification code	15c	
Empirical formula	C ₁₆ H ₁₈ F N O ₄	
Formula weight	307.31	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.6137(19) Å	α = 90°.
	b = 11.512(2) Å	β = 90°.
	c = 13.536(3) Å	γ = 90°.

Volume	1498.1(5) Å ³
Z	4
Density (calculated)	1.363 Mg/m ³
Absorption coefficient	0.106 mm ⁻¹
F(000)	648
Crystal size	0.40 x 0.10 x 0.03 mm ³
Theta range for data collection	2.32 to 25.67°.
Index ranges	-11<=h<=11, -13<=k<=14, -12<=l<=16
Reflections collected	7386
Independent reflections	2839 [R(int) = 0.0406]
Completeness to theta = 25.67°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9974 and 0.9589
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2839 / 0 / 271
Goodness-of-fit on F ²	0.953
Final R indices [I>2sigma(I)]	R1 = 0.0380, wR2 = 0.0705
R indices (all data)	R1 = 0.0668, wR2 = 0.0778
Absolute structure parameter	2.2(9)
Largest diff. peak and hole	0.135 and -0.220 e.Å ⁻³

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for **15c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	6690(1)	11008(1)	3838(1)	52(1)
O(1)	1603(2)	9986(2)	7392(1)	39(1)
O(2)	3838(2)	7114(2)	8022(1)	46(1)
O(3)	2260(1)	7191(1)	4556(1)	28(1)
O(4)	4345(1)	6287(1)	4481(1)	29(1)
N(1)	4097(2)	7798(2)	5480(1)	24(1)
C(1)	3428(2)	8828(2)	5886(2)	25(1)
C(2)	3669(2)	8830(2)	7021(2)	26(1)
C(3)	2828(2)	9799(2)	7535(2)	29(1)

C(4)	3760(3)	10461(2)	8225(2)	35(1)
C(5)	5025(3)	9679(2)	8351(2)	35(1)
C(6)	5168(2)	9078(3)	7348(2)	31(1)
C(7)	3132(3)	7662(2)	7448(2)	32(1)
C(8)	1721(3)	7246(3)	7140(2)	40(1)
C(9)	3885(2)	9933(2)	5365(2)	24(1)
C(10)	3054(2)	10920(2)	5383(2)	35(1)
C(11)	3467(3)	11935(2)	4912(2)	42(1)
C(12)	4700(3)	11982(2)	4391(2)	37(1)
C(13)	5473(2)	10995(2)	4369(2)	34(1)
C(14)	5122(2)	9982(2)	4839(2)	27(1)
C(15)	3471(2)	7112(2)	4812(2)	23(1)
C(16)	3742(3)	5448(3)	3818(2)	40(1)

Figure 3: Relative Stereochemistry of **20c**: [(*E*)-(*S*)-1-((*S*)-1-Acetyl-2-oxo-cyclopentyl)-3-phenyl-allyl]-carbamic acid methyl ester

Crystals of compound **20c** suitable for x-ray analysis were obtained by slow evaporation from methylene chloride and hexanes.

Table 1. Crystal data and structure refinement for **20c**.

Identification code	20c	
Empirical formula	C ₁₈ H ₂₁ N O ₄	
Formula weight	315.36	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 6.3666(4) Å	α = 90°.
	b = 15.3404(9) Å	β = 90°.
	c = 17.1852(13) Å	γ = 90°.

Volume	1678.41(19) Å ³
Z	4
Density (calculated)	1.248 Mg/m ³
Absorption coefficient	0.088 mm ⁻¹
F(000)	672
Crystal size	0.40 x 0.10 x 0.05 mm ³
Theta range for data collection	1.78 to 28.28°.
Index ranges	-8<=h<=8, -20<=k<=20, -22<=l<=15
Reflections collected	12635
Independent reflections	4169 [R(int) = 0.0264]
Completeness to theta = 28.28°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9956 and 0.9656
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4169 / 0 / 292
Goodness-of-fit on F ²	1.018
Final R indices [I>2sigma(I)]	R1 = 0.0331, wR2 = 0.0785
R indices (all data)	R1 = 0.0455, wR2 = 0.0835
Absolute structure parameter	1.0(8)
Largest diff. peak and hole	0.177 and -0.157 e.Å ⁻³

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for **20c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	8617(1)	2714(1)	1781(1)	30(1)
O(2)	3778(2)	2189(1)	162(1)	36(1)
O(3)	3372(2)	309(1)	2247(1)	37(1)
O(4)	-43(2)	692(1)	2101(1)	33(1)
N(1)	2353(2)	1726(1)	2097(1)	23(1)
C(1)	4414(2)	2128(1)	2169(1)	21(1)
C(2)	4915(2)	2659(1)	1422(1)	19(1)
C(3)	7121(2)	3072(1)	1491(1)	20(1)
C(4)	7048(2)	3995(1)	1202(1)	26(1)

C(5)	4926(2)	4074(1)	804(1)	29(1)
C(6)	3517(2)	3452(1)	1268(1)	24(1)
C(7)	4876(2)	2031(1)	715(1)	23(1)
C(8)	6182(2)	1225(1)	761(1)	29(1)
C(9)	4634(2)	2672(1)	2894(1)	24(1)
C(10)	3224(2)	2788(1)	3450(1)	24(1)
C(11)	3587(2)	3264(1)	4184(1)	25(1)
C(12)	2092(3)	3213(1)	4775(1)	32(1)
C(13)	2455(3)	3598(1)	5494(1)	41(1)
C(14)	4290(3)	4041(1)	5632(1)	42(1)
C(15)	5775(3)	4119(1)	5048(1)	40(1)
C(16)	5411(2)	3737(1)	4327(1)	34(1)
C(17)	2039(2)	866(1)	2157(1)	24(1)
C(18)	-613(3)	-212(1)	2039(1)	46(1)

(±)-10a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.670	MM	1.4987	362.68723	4.03331	13.3971
2	35.604	MM	1.7692	1110.24854	10.45897	41.0108
3	45.091	MM	1.6397	273.42917	2.77929	10.1000
4	63.391	MM	2.2932	960.84674	6.98340	35.4921
Total s :				2707.21167	24.25497

10a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.620	MM	1.2454	358.50980	4.79763	4.8193
2	39.652	MM	2.2759	7080.46826	51.85069	95.1807
Total s :				7438.97806	56.64832

(±)-10b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.621	MF	0.9095	238.01205	4.36167	10.0152
2	24.698	FM	1.1401	976.18256	14.27098	41.761
3	36.557	MM	1.3467	261.79413	3.23983	11.0159
4	46.895	MM	1.7857	900.53088	8.40483	37.8928
Total s :				2376.51962	30.27732

10b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.471	MM	0.7081	111.72901	2.62996	3.1190
2	33.214	MM	1.6598	3470.50879	34.84883	96.8810
Total s :				3582.23780	37.47879

Signal 1: MWD1 A, Si g=250, 100 Ref=360, 100

(±)-10c

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.257	MF	0.9881	1441.24756	24.31108	22.6945
2	24.985	FM	1.1717	1402.40649	19.94769	22.0829
3	29.559	MM	1.5788	1757.01794	18.54817	27.6668
4	48.331	MM	2.2552	1749.96619	12.93293	27.5558
Total s :				6350.63818	75.73987

Signal 1: MWD1 A, Si g=250, 100 Ref=360, 100

10c

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.230	MM	0.7800	46.11024	9.85274e-1	3.3887
2	26.584	MM	1.2862	1314.61316	17.03484	96.6113
Total s :				1360.72340	18.02011

(±)-11a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.686	MM	1.0943	790.41083	12.03849	12.9949
2	28.064	MF	1.2867	2189.28809	28.35874	35.9935
3	31.961	FM	1.3324	822.40741	10.28702	13.5210
4	48.408	MM	1.8718	2280.34106	20.30438	37.4905
Total s :				6082.44739	70.98863

11a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.448	MM	0.8031	666.39783	13.82965	5.5000
2	28.926	MM	1.4888	1.14499e4	128.18004	94.5000
Total s :				1.21163e4	142.00969

Signal 1: MWD1 A, Si g=250, 100 Ref=360, 100

(±)-11b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.716	MF	0.6668	1224.53699	30.60925	11.6816
2	19.864	FM	0.8419	3981.01733	78.81196	37.9773
3	26.531	MM	0.9701	1195.53027	20.54030	11.4049
4	36.291	MM	1.4029	4081.53052	48.48949	38.9362
Totals :				1.04826e4	178.45099

Signal 1: MWD1 A, Si g=250, 100 Ref=360, 100

11b

Peak	RetTime	Type	Width	Area	Height	Area
1	16.914	MM	0.6363	59.46564	1.55752	5.1628
2	24.945	MM	1.0913	1092.34973	16.68331	94.8372
Totals :				1151.81537	18.24082

(±)-11c

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.629	MM	0.7037	325.27365	7.70394	34.0696
2	19.426	MM	0.7403	469.54358	10.57160	49.1806
3	24.699	MM	0.9982	94.92257	1.58492	9.9423
4	30.358	MM	1.8951	64.99271	5.71589e-1	6.8074
Total s :				954.73251	20.43205

11 c

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.568	MM	0.5926	71.58801	2.01355	4.0637
2	18.961	MM	0.7565	1690.06384	37.23217	95.9363
Total s :				1761.65186	39.24572

Signal 4: MWD1 D, Si g=230, 16 Ref=360, 100

(±)-12a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.189	MF	0.9462	817.71045	14.40404	10.3982
2	22.258	FM	1.1971	3110.05957	43.30022	39.5482
3	30.828	MM	1.3960	883.80023	10.55149	11.2386
4	39.907	MM	1.7218	3052.39331	29.54731	38.8149
Total s :				7863.96356	97.8030

Signal 4: MWD1 D, Si g=230, 16 Ref=360, 100

12a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.115	MM	1.0614	136.49564	2.14325	2.3246
2	30.185	MM	1.6174	5639.56836	58.11529	96.0459
3	42.197	MM	1.3986	95.67829	1.14016	1.6295
Total s :				5871.74229	61.39870

(±)-12b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.098	MF	0.5772	1169.40100	33.76773	12.1372
2	16.418	FM	0.7319	3665.70239	83.47158	38.0463
3	25.795	MM	1.0565	1253.61243	19.77708	13.0112
4	30.165	MM	1.1935	3546.13818	49.52059	36.8053
Totals :				9634.85400	186.53698

12b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.353	MM	0.6230	194.84410	5.21241	4.0878
2	25.469	MM	1.1859	4549.51123	63.93924	95.4492
3	31.493	MM	0.6787	22.06596	5.41851e-1	0.4629
Totals :				4766.42129	69.69349

Signal 4: MWD1 D, Si g=230, 16 Ref=360, 100

(±)-12c

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.717	MM	0.6176	225.68637	6.09070	4.3534
2	17.244	MM	0.7280	234.54956	5.36997	4.5244
3	19.599	MM	0.9922	2307.09863	38.75524	44.5035
4	32.847	MM	1.5188	2416.75391	26.51962	46.6187
Total s :				5184.08847	76.73553

Signal 4: MWD1 D, Si g=230, 16 Ref=360, 100

12c

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.489	MM	0.6198	54.89904	1.47627	3.2570
2	16.604	MM	0.7402	1630.67590	36.71873	96.7430
Total s :				1685.57494	38.19501

(±)-12d

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.360	MF	1.2262	131.81317	1.79163	2.9349
2	27.004	FM	1.2669	178.85742	2.35295	3.9823
3	44.602	MM	2.6948	2270.54224	14.04256	50.5545
4	66.757	MM	2.9614	1910.06567	10.74995	42.5283
Total s :				4491.27850	28.93709

12d

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.398	MF	0.7172	390.44058	9.07271	4.4095
2	25.666	FM	1.3660	8464.15820	103.27444	95.5905
Total s :				8854.59879	112.34715

(±)-13a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.932	MF	0.6919	1630.75830	39.28381	13.5364
2	19.476	FM	0.8510	4416.46777	86.49593	36.6598
3	23.392	MM	0.9013	1570.34473	29.03880	13.0350
4	32.488	MM	1.2533	4429.60596	58.90784	36.7688
Total s :				1.20472e4	213.72638

13a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.731	MM	0.6459	539.36633	13.91662	3.9558
2	20.308	MM	0.5775	26.90791	7.76539e-1	0.1973
3	22.197	MM	1.0112	1.29066e4	212.73425	94.6601
4	32.699	MM	0.8645	161.80061	3.11950	1.1867
Total s :				1.36347e4	230.54691

Signal 1: MWD1 A, Si g=250, 100 Ref=360, 100

(±)-13b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.901	MF	0.4681	2463.92261	87.72008	12.5201
2	14.398	MF	0.6028	7191.21729	198.83556	36.5412
3	19.807	MM	0.7535	2574.17188	56.93962	13.0803
4	24.912	MM	0.9730	7450.41309	127.61501	37.8583
Totals :				1.96797e4	471.11026

Signal 1: MWD1 A, Si g=250, 100 Ref=360, 100

13b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.224	MM	0.8495	1.00888e4	197.94032	99.4488
2	25.471	MM	0.6430	55.91658	1.44942	0.5512
Totals :				1.01447e4	199.38974

Signal 1: MWD1 A, Si g=250, 100 Ref=360, 100

(±)-13c

Peak #	RetTime [mi n]	Type	Width [mi n]	Area [mAU*s]	Height [mAU]	Area %
1	12.730	MF	0.4938	3176.26855	107.20261	21.7078
2	14.079	FM	0.5513	3296.08105	99.64565	22.5266
3	16.774	MM	0.7579	4030.47485	88.62774	27.5457
4	25.931	MM	1.0861	4129.12354	63.36296	28.2199
Total s :				1.46319e4	358.83895

Signal 1: MWD1 A, Si g=250, 100 Ref=360, 100

13c

Peak #	RetTime [mi n]	Type	Width [mi n]	Area [mAU*s]	Height [mAU]	Area %
1	14.542	MF	0.4567	136.05318	4.96502	1.8275
2	15.545	FM	0.5657	7308.67529	215.34677	98.1725
Total s :				7444.72847	220.31179

Signal 1: MWD1 A, Si g=250, 100 Ref=360, 100

(±)-13d

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.289	MF	0.7287	2668.33325	61.03114	44.8591
2	20.486	FM	0.8855	3279.91919	61.73569	55.1409
Totals :				5948.25244	122.76683

Signal 1: MWD1 A, Si g=250, 100 Ref=360, 100

13d

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.243	MM	0.9475	8803.78906	154.85773	100.0000
Totals :				8803.78906	154.85773

(±)-14a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.596	MF	0.9899	1055.70862	17.77388	10.8823
2	24.633	MF	1.7176	5069.39160	49.19081	52.2554
3	28.365	FM	1.6021	3576.08374	37.20102	36.8623
Total s :				9701.18396	104.16

14a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.112	MM	1.3911	7885.91504	94.47906	99.6079
2	29.630	MM	0.9357	31.04330	5.52963e-1	0.3921
Total s :				7916.95834	95.03202

Signal 4: MWD1 D, Si g=230, 16 Ref=360, 100

(±)-14b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.875	MF	0.6169	693.59100	18.73921	7.8489
2	17.939	MF	0.9067	4502.40967	82.76254	50.9510
3	20.825	FM	1.0127	3640.73633	59.91648	41.2000
Total s :				8836.73700	161.41824

Signal 1: MWD1 A, Si g=250, 100 Ref=360, 100

14b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.599	MM	0.7999	1.01249e4	210.95163	100.0000
Total s :				1.01249e4	210.95163

(±)-14c

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.600	MF	0.7876	896.56152	18.97254	16.3792
2	18.551	FM	0.9511	975.54291	17.09569	17.8221
3	24.853	MF	1.0103	1279.66040	21.11059	23.3781
4	26.207	FM	1.5502	2322.00391	24.96406	42.4206
Total s :				5473.76874	82.14288

14c

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.227	MM	0.8438	2.34517e4	463.22723	100.0000
Total s :				2.34517e4	463.22723

(±)-15a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.868	MM	0.5760	2576.00391	74.53156	26.6348
2	17.127	MF	0.5411	1547.49597	47.66442	16.0005
3	17.752	FM	0.7656	3314.96216	72.16737	34.2754
4	25.059	MM	1.0408	2233.09741	35.76070	23.0893
Total s :				9671.55945	230.12406

15a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.940	MM	0.8219	558.52148	11.32638	6.0174
2	22.736	MM	1.2269	8723.29199	118.49576	93.9826
Total s :				9281.81348	129.82213

Signal 4: MWD1 D, Si g=230, 16 Ref=360, 100

(±)-15b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.739	MF	0.4552	836.87189	30.63906	18.7000
2	12.417	FM	0.5071	796.43134	26.17621	17.7964
3	15.422	MM	0.6972	1378.01575	32.93994	30.7919
4	20.275	MM	0.9202	1463.93018	26.51349	32.7117
Total s :				4475.24915	116.2687

Signal 1: MWD1 A, Si g=250, 100 Ref=360, 100

15b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.896	MM	0.5500	178.40741	5.40636	4.4098
2	20.690	MM	0.9260	3867.30176	69.60434	95.5902
Total s :				4045.70917	75.0107

Signal 4: MWD1 D, Sig=230,16 Ref=360,100

(±)-16c

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.116	MF	0.3914	1782.39246	75.89680	30.0066
2	12.866	MF	0.4946	1174.58142	39.58142	19.7741
3	14.789	FM	0.5617	1795.98157	53.28949	30.2354
4	19.320	MM	0.7240	1187.03845	27.32456	19.9838
Total s :				5939.99390	196.09227

Signal 3: MWD1 C, Sig=210,8 Ref=360,100

16c

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.538	MM	0.5064	532.77753	17.53430	4.4476
2	15.783	MM	0.7170	1.14462e4	266.07397	95.5524
Totals :				1.19790e4	283.60828

Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.735	VV	0.5267	2.08569e4	604.31049	49.9781
2	12.107	VB	0.6662	2.08751e4	483.05063	50.0219
Total s :				4.17320e4	1087.36111

Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.705	MM	0.5698	5.41714e4	1584.60706	98.0015
2	12.246	MM	0.5803	1104.69751	31.72968	1.9985
Total s :				5.52761e4	1616.33673

Signal 3: MWD1 C, Si g=210, 8 Ref=360, 100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.072	VV	0.4968	6038.93506	186.99037	49.7615
2	12.242	VB	0.6537	6096.83350	143.48877	50.2385
Total s :				1.21358e4	330.47914

Signal 1: MWD1 A, Si g=250, 100 Ref=360, 100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.638	MF	0.4410	721.84009	27.28339	3.4980
2	12.465	FM	0.7399	1.99142e4	448.57898	96.5020
Total s :				2.06361e4	475.86237

	Retention Time	Peak Type	% Area	Area	Height	% Height
1	25.317	Unknown	50.24	3655254	40896	59.40
2	30.851	Unknown	49.76	3620380	27948	40.60

	Retention Time	Peak Type	% Area	Area	Height	% Height
1	25.577	Unknown	95.61	4198042	69142	94.94
2	29.317	Unknown	4.39	192925	3683	5.06

Signal 2: MWD1 B, Si g=254, 16 Ref=360, 100

(±)-20a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.188	MF	1.1078	8759.71875	131.79225	18.7190
2	23.998	MF	1.2466	9599.63770	128.34682	20.5139
3	27.399	FM	1.6541	1.46546e4	147.66241	31.3161
4	41.144	MM	2.0679	1.37818e4	111.07785	29.4509
Total s :				4.67958e4	518.87933

Signal 2: MWD1 B, Si g=254, 16 Ref=360, 100

20a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.613	MF	0.9948	1453.11743	24.34412	5.2263
2	23.576	FM	1.2601	2.63506e4	348.51273	94.7737
Total s :				2.78038e4	372.85685

(±)-20b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.494	MF	0.7438	1.39468e4	312.51794	19.0007
2	19.658	FM	1.0164	3.72284e4	610.47272	50.7186
3	31.121	MM	1.3895	2.22266e4	266.60947	30.2807
Totals :				7.34018e4	1189.60013

20b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.955	MM	0.6637	90.65255	2.27660	0.4402
2	19.478	MM	0.8566	2.04167e4	397.22656	99.1483
3	32.468	MM	1.0867	84.72912	1.29948	0.4115
Totals :				2.05921e4	400.80264

Signal 2: MWD1 B, Si g=254, 16 Ref=360, 100

(±)-20c

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.562	MF	0.9457	2308.73096	40.69028	24.7583
2	21.776	FM	1.0992	2580.10229	39.12102	27.6684
3	25.715	MM	1.4485	2167.31494	24.93661	23.2418
Total s :				9325.09180	125.43532

Signal 2: MWD1 B, Si g=254, 16 Ref=360, 100

20c

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.957	MM	1.0595	4.09370e4	643.98218	97.3145
2	34.501	MM	1.5952	1129.69946	11.80330	2.6855
Total s :				4.20667e4	655.78548

Signal 2: MWD1 B, Si g=254, 16 Ref=360, 100

(±)-20d

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.778	MF	0.8082	2547.36499	52.52938	12.4586
2	34.463	FM	2.1312	8728.67578	68.26219	42.6901
3	59.104	MM	3.8024	4829.83936	21.17041	23.6217
4	71.846	MM	4.0238	4340.73291	17.97939	21.2296
Total s :				2.04466e4	159.94137

Signal 2: MWD1 B, Si g=254, 16 Ref=360, 100

20d

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.254	MM	1.8137	43.57941	4.00472e-1	0.2048
2	34.688	MM	2.1932	6183.70117	46.99121	29.0592
3	61.197	MM	3.2064	735.68170	3.82399	3.4572
4	69.557	MM	4.0359	1.43167e4	59.12160	67.2788
Total s :				2.12797e4	110.33726

Signal 1: MWD1 A, Sig=250, 100 Ref=360, 100

(±)-21a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.844	BV	1.0728	1.09095e4	145.49484	15.8500
2	28.251	VV	1.3076	1.58012e4	164.35376	22.9570
3	31.659	VB	1.7071	2.33658e4	179.92741	33.9473
4	47.314	BB	2.0245	1.87531e4	123.15710	27.2457
Total s :				6.88296e4	612.93311

Signal 1: MWD1 A, Sig=250, 100 Ref=360, 100

21a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.200	MM	1.5372	5.32473e4	577.31757	100.0000
Total s :				5.32473e4	577.31757

(±)-21b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.657	VV	0.8968	2.27353e4	360.01080	18.4172
2	24.529	VV	1.0422	2.45421e4	330.55786	19.8808
3	28.591	VB	1.4560	3.96274e4	374.05304	32.1010
4	38.006	BB	1.7884	3.65413e4	281.50333	29.6010
Totals :				1.23446e5	1346.12503

21b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.170	MF	0.7296	536.35986	12.25310	3.6840
2	19.934	FM	0.8981	1.40228e4	260.22552	96.3160
Totals :				1.45591e4	272.47862

Signal 4: MWD1 D, Sig=230,16 Ref=360,100

(±)-21c

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.041	BV	0.7349	5769.84521	112.02627	11.9000
2	22.507	VV	1.0095	2.43196e4	347.94077	50.1578
3	25.815	VB	1.2083	8682.63281	105.26807	17.9074
4	35.267	BB	1.3667	9714.07422	96.47791	20.0347
Total s :				4.84862e4	661.71302

Signal 2: MWD1 B, Sig=254,16 Ref=360,100

21c

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.320	MF	0.8952	392.31689	7.30399	1.1480
2	24.440	FM	1.2218	3.28426e4	447.99194	96.1012
3	40.763	MM	1.9744	940.10840	7.93578	2.7509
Total s :				3.41750e4	463.23171	

References and Notes

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