Diastereoselective Synthesis of Cyclopropane Amino Acids Using Diazo Compounds Generated *In Situ*

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1. General Methods.

All chemicals were purchased from common chemical suppliers and used as delivered unless otherwise stated. THF and toluene were pre-dried over sodium wire and then purified by passing through a solvent drying column prior to use.¹ Dehydroamino acids **4**,² **5**³ and **6**⁴ were prepared according to literature procedures (see also supplementary material). Commercially available dehydroamino acid **7** was either used as delivered or prepared using a newly developed large-scale procedure (see supplementary material).

2. Characterisation of Tosylhydrazones.

Benzaldehyde tosylhydrazone.⁵

Colourless needles (91% yield); m.p. 127-128 °C (MeOH) (lit.,⁵ 128-129 °C); ¹H NMR (400 MHz, CDCl₃) δ 2.39 (3H, s, CH₃), 7.29-7.36 (5H, m, Aryl H), 7.52-7.57 (2H, m, Aryl H), 7.78 (1H, s, CHN), 7.89 (2H, d, *J* = 8.3 Hz, Aryl H), 8.29 (1H, br. s, NH); ¹³C NMR (100 MHz, CDCl₃) δ 21.6 (q), 127.3 (2d), 127.9 (2d), 128.6 (2d), 129.7 (2d), 130.4 (d), 133.1 (s), 135.2 (s), 144.3 (s), 147.9 (d).

p-Methoxybenzaldehyde tosylhydrazone.⁶

Colourless needles (83% yield); m.p. 110-112 °C (lit.,⁶ 110-112 °C, MeOH); ¹H NMR (400 MHz, CDCl₃) δ 2.39 (3H, s, ArCH₃), 3.80 (3H, s, OCH₃), 6.85 (2H, d, *J* = 8.7 Hz, Aryl H), 7.29 (2H, d, *J* = 8.3 Hz, Aryl H), 7.50 (2H, d, *J* = 8.7 Hz, Aryl H), 7.74 (1H, s, CHN), 7.87 (2H, d, *J* = 8.3 Hz, Aryl H), 8.24 (1H, br. s, NH); ¹³C NMR (100 MHz, CDCl₃) δ 21.6 (q), 55.4 (q), 114.2 (2d), 126.1 (s), 128.0 (2d), 129.0 (2d), 129.7 (2d), 135.5 (s), 144.2 (s), 148.4 (d), 165.5 (s).

***p*-Methylbenzaldehyde tosylhydrazone.**⁷

Colourless needles (73% yield); $R_f = 0.70$ (EtOAc/petroleum ether 1:4); m.p. 144-146 °C (MeOH) (lit.⁷ 147-149 °C); ¹H NMR (270 MHz, CDCl₃) δ 2.33 (3H, s, CH₃), 2.38 (3H, s, CH₃), 7.13 (2H, d, $J = 8.0$ Hz, Aryl H), 7.28 (2H, d, $J = 8.0$ Hz, Aryl H), 7.46 (2H, d, $J = 8.0$ Hz, Aryl H), 7.75 (1H, s, CH), 7.88 (2H, d, $J = 8.0$ Hz, Aryl H), 8.24 (1H, br. s, NH); ¹³C NMR (68 MHz, CDCl₃) δ 21.5 (q), 21.6 (q), 127.4 (2d), 127.9 (2d), 129.4 (2d), 129.7 (2d), 130.5 (s), 135.3 (s), 140.8 (s), 144.2 (s), 148.3 (d).

***p*-Fluorobenzaldehyde tosylhydrazone.**⁸

Colourless needles (95% yield); m.p. 133-134 °C (MeOH) (lit.,⁸ 134-136 °C); ¹H NMR (400 MHz, CDCl₃) δ 2.38 (3H, s, ArCH₃), 7.04 (2H, t, $J = 8.4$ Hz, Aryl H), 7.31 (2H, d, $J = 8.4$ Hz, Aryl H), 7.56 (2H, dd, $J = 8.4$ and $J_{H-F} = 5.5$ Hz, Aryl H), 7.77 (1H, s, NCH), 7.84 (2H, d, $J = 8.4$ Hz, Aryl H), 8.56 (1H, br. s, NH); ¹³C NMR (100 MHz, CDCl₃) δ 21.2 (q), 115.5 (2d, $J_{C-F} = 22.3$ Hz), 127.5 (2d), 128.8 (2d, $J_{C-F} = 8.4$ Hz), 129.4 (2d), 129.9 (s), 135.9 (s), 143.8 (s), 146.1 (d), 163.7 (s, $J_{C-F} = 250.0$ Hz); IR $\nu_{\max}/\text{cm}^{-1}$ 3437, 1643, 1602, 1511, 1167.

 β -Phenyl-cinnamaldehyde tosyl hydrazone.⁹

Colourless needles (90% yield); $R_f = 0.23$ (EtOAc/petroleum ether 1:4); m.p. 172-174 °C (MeOH) (lit.⁹ 174-175 °C); ¹H NMR (400 MHz, CDCl₃) δ 2.43 (3H, s, CH₃), 6.79 (1H, d, $J = 9.8$ Hz, NCHCH), 7.12 (2H, m, Aryl H), 7.21-7.40 (11H, m, Aryl H and NCHCH), 7.54 (1H, br. s, NH), 7.82 (2H, m, Aryl H); ¹³C NMR (100 MHz, CDCl₃) δ 21.7 (q), 123.0 (d), 127.8 (2d), 128.0 (2d), 128.4 (d), 128.5 (2d), 128.7 (2d), 128.9 (d), 129.8 (2d), 130.3 (2d), 135.6 (s), 138.1 (s), 140.6 (s), 144.2 (s), 148.2 (d), 150.5 (s).

3-[1-(*tert*-Butyl)-1,1-dimethylsilyl]oxybenzaldehyde.¹⁰

Imidazole (6.50 g, 95.5 mmol) and TBSCl (12 g, 79.6 mmol) were slowly added to a suspension of 3-hydroxybenzaldehyde (9.72 g, 79.6 mmol) in anhydrous CH₂Cl₂ (190 mL) at 0 °C. After the addition, the reaction was stirred at rt for 3 h. As phenol was still remaining (checked by TLC) another portion of TBSCl (1.80 g, 11.9 mmol) was added and the mixture was stirred for a further 16 h. The resultant mixture was washed with a 2% aq. solution of HCl (2 $\times$ 50 mL), water (2 $\times$ 50 mL), brine (2 $\times$ 50 mL) and then dried over MgSO₄. After filtration, the solvent was removed under reduced pressure to afford 3-[1-(*tert*-butyl)-1,1-dimethylsilyl]oxybenzaldehyde (18.23 g, 97%) as a colourless oil.¹¹ $R_f = 0.70$ (petroleum ether/EtOAc 3:1); ¹H NMR (400 MHz, CDCl₃) δ

0.23 (6 H, s, Si(CH₃)₂), 1.00 (9H, s, SiC(CH₃)₃), 7.11 (1H, dd, *J* = 7.8 and 2.4 Hz, Aryl H), 7.33 (1H, d, *J* = 2.4 Hz, Aryl H), 7.40 (1H, dd, *J* = 7.8 and 7.3 Hz, Aryl H), 7.48 (1H, d, *J* = 7.3 Hz, Aryl H), 9.96 (1H, s, CHO); ¹³C NMR (100 MHz, CDCl₃) δ -4.4 (2q), 18.3 (s), 25.7 (3q), 119.9 (d), 123.6 (d), 126.6 (d), 129.6 (d), 138.0 (s), 156.5 (s), 192.2 (d); GC-MS retention time 11.08 min, *m/z* (EI) 236 (M⁺, 8), 179 (100), 151 (40), 135 (7), 105 (4), 91 (7), 75 (8), 59 (5).

3-(*tert*-Butyl-dimethyl-silyloxy)-benzaldehyde tosylhydrazone 23.¹²

Colourless cubes (84% yield); m.p. 120-122 °C (MeOH) (lit.¹² 120-122 °C); ¹H NMR (400 MHz, CDCl₃) δ 0.19 (6H, s, Si(CH₃)₃), 0.98 (9H, s, SiC(CH₃)₃), 2.40 (3H, s, ArCH₃), 6.84 (1H, dd, *J* = 8.0 and 2.2 Hz, Aryl H), 7.08 (1H, d, *J* = 2.2 Hz, Aryl H), 7.12 (1H, d, *J* = 7.7 Hz, Aryl H), 7.19 (1H, dd, *J* = 8.0 and 7.7 Hz, Aryl H), 7.30 (2H, d, *J* = 8.2 Hz, Aryl H), 7.71 (1H, s, NCH), 7.88 (2H, d, *J* = 8.2 Hz, Aryl H), 8.21 (1H, br. s, NH); ¹³C NMR (100 MHz, CDCl₃) δ -4.4 (2q), 18.3 (s), 21.6 (q), 25.7 (3q), 118.3 (d), 121.0 (d), 122.5 (d), 128.1 (2d), 129.7 (d), 129.7 (2d), 134.7 (s), 135.4 (s), 144.3 (s), 147.8 (d), 156.0 (s); IR ν_{max}/cm⁻¹ 3177, 1576, 1438, 1361, 1331; MS *m/z* (CI with CH₄) 405 ([MH]⁺, 20), 390 (40), 107 (100). Anal Calc'd for C₂₀H₂₈N₂O₃SSi: C, 59.37; H, 6.98; N, 6.92; found C, 59.25; H, 6.80; N, 7.06.

2-Propenal tosylhydrazone 24.¹²

Yellow solid (68% yield); eluent petroleum ether/EtOAc 35:65, *R_f* = 0.29; m.p. 88-90 °C (petroleum ether/EtOAc) (lit.¹² 98-99 °C); ¹H NMR (400 MHz, CDCl₃) δ 2.43 (3H, s, CH₃), 5.52 (1H, d, *J* = 17.4 Hz, CHH=CH), 5.59 (1H, d, *J* = 9.9 Hz, CHH=CH), 6.40 (1H, dt, *J* = 17.4 and 9.9 Hz, CHH=CH), 7.28-7.36 (2H, m, Aryl H), 7.41 (1H, d, *J* = 9.9 Hz, CHN), 7.78-7.86 (2H, m, Aryl H), 8.06 (1H, br. s, NH); ¹³C NMR (100 MHz, CDCl₃) δ 21.7 (q), 125.2 (t), 127.9 (2d), 129.8 (2d), 133.2 (d), 135.3 (s), 144.3 (s), 149.8 (d); IR ν_{max}/cm⁻¹ 1597, 1344, 1158, 936, 809; MS *m/z* (ES) 225 ([MH]⁺, 100). Anal. Calc'd for C₁₀H₁₂N₂O₂S: C, 53.5; H, 5.4; N, 12.5. Found: C, 53.6; H, 5.5; N, 12.4.

3. Characterisation of Tosylhydrazone Sodium Salts.

Benzaldehyde tosylhydrazone sodium salt.¹³

Colourless powder; ¹H NMR (400 MHz, D₂O) δ 2.17 (3H, s, CH₃), 7.15-7.23 (5H, m, Aryl H), 7.35-7.40 (2H, m, Aryl H), 7.60 (2H, d, *J* = 8.4 Hz, Aryl H), 7.83 (1H, s, CHN); ¹³C NMR (100 MHz, D₂O) δ 20.7 (q), 126.6 (2d), 126.7 (2d), 128.8 (2d), 129.5 (2d), 129.6 (d), 135.8 (s), 139.2 (s), 142.8 (s), 145.9 (d); MS *m/z* (FAB) 297 ([MH]⁺, 84).

***p*-Methylbenzaldehyde tosylhydrazone sodium salt.**⁷

Pink solid; ¹H NMR (270 MHz, D₂O) δ 2.13 (3H, s, CH₃), 2.26 (3H, s, ArCH₂), 7.11 (2H, d, *J* = 8.0 Hz, Aryl H), 7.26 (2H, d, *J* = 8.0 Hz, Aryl H), 7.37 (2H, d, *J* = 8.0 Hz, Aryl H), 7.70 (2H, d, *J* = 8.0 Hz, Aryl H), 7.89 (1H, s, NCH); ¹³C NMR (75 MHz, D₂O) δ 20.3 (q), 20.5 (q), 126.4 (2d), 126.5 (2d), 129.2 (2d), 129.3 (2d), 132.7 (s), 139.2 (d), 142.5 (s), 146.0 (s); MS *m/z* (FAB) 311 ([MH]⁺, 41), 308 (25), 307 (100); HRMS (FAB, [MH]⁺): found 311.0834 C₁₅H₁₆N₂O₂SNa requires 311.0830.

***p*-Methoxybenzaldehyde tosylhydrazone sodium salt.**⁷

Colourless solid; ¹H NMR (270 MHz, D₂O) δ 2.20 (3H, s, ArCH₃), 3.65 (3H, s, OCH₃), 6.78 (2H, d, *J* = 8.0, Aryl H), 7.19 (2H, d, *J* = 8.0 Hz, Aryl H), 7.36 (2H, d, *J* = 8.0 Hz, Aryl H), 7.68 (2H, d, *J* = 8.0 Hz, Aryl H), 7.86 (1H, s, NCH); ¹³C NMR (75 MHz, D₂O) δ 20.4 (q), 55.2 (q), 113.9 (2d), 126.5 (2d), 127.8 (s), 128.7 (2d), 129.3 (2d), 139.3 (s), 142.4 (s), 145.6(d), 159.1 (s); MS *m/z* (FAB) 327 ([MH]⁺, 100), 298 (40); HRMS (FAB, [MH]⁺): found 327.0779 C₁₅H₁₆N₂O₃SNa requires 327.0799.

***p*-Fluorobenzaldehyde tosylhydrazone sodium salt.**¹²

Pink solid; ¹H NMR (400 MHz, *d*₆-DMSO) δ 2.27 (3H, s, ArCH₃), 7.05 (2H, t, *J* = 8.8 Hz and *J*_{H-F} = 8.8 Hz, Aryl H), 7.16 (2H, d, *J* = 8.0 Hz, Aryl H), 7.41 (2H, dd, *J* = 8.8 Hz and *J*_{H-F} = 6.6 Hz, Aryl H), 7.65 (2H, d, *J* = 8.0 Hz, Aryl H), 7.66 (1H, s, NCH); ¹³C NMR (100 MHz, *d*₆-DMSO) δ 21.4 (q), 115.5 (2d, *J*_{C-F} = 21.4 Hz), 126.9 (2d, *J*_{C-F} = 7.7 Hz), 127.1 (2d), 128.8 (2d), 135.4 (s), 136.6 (d), 139.2 (s), 144.4 (s), 161.4 (s, *J*_{C-F} = 241.6 Hz); IR ν_{max} /cm⁻¹ 1602, 1508, 1225, 1126, 1084, 1033, 952, 776; MS *m/z* (CI with CH₄) 315 ([MH]⁺, 12).

***β*-Phenyl-cinnamaldehyde tosylhydrazone sodium salt.**¹²

Pale orange solid; ¹H NMR (400 MHz, CD₃OD) δ 2.30 (3H, s, CH₃), 6.80 (1H, d, *J* = 10.0 Hz, CHCHN), 7.05-7.34 (10H, m, Aryl H), 7.43-7.51 (2H, m, Aryl H), 7.54 (1H, d, *J* = 10.0 Hz, CH=CHN) and 7.63-7.74 (2H, m, Aryl H); ¹³C NMR (75 MHz, CD₃OD) δ 20.0 (q), 123.9 (d), 126.8 (2d), 126.9 (2d), 127.1 (d), 127.2 (d), 127.9 (2d), 128.0 (2d), 128.5 (2d), 130.2 (2d), 139.6 (s), 140.7 (s), 141.8 (s), 142.0 (s), 143.4 (s), 144.1 (d); IR ν_{max} /cm⁻¹ 1062, 811, 764, 695; MS *m/z* (CI with CH₄) 384 ([MH-Me]⁺, 1), 323 (1), 307 (3), 221 (41), 206 (17), 193 (100), 91 (22); HRMS (CI, [MH-Ph+H]⁺) Found: 323.0834. Calc. for C₁₆H₁₆N₂O₂SNa 323.0830.

4. Synthesis and Characterisation of Dehydroaminoacids.

Methyl 2-[(*tert*-butoxycarbonyl)amino]acrylate **4**.²

EDCI (11.40 g, 59.5 mmol) was added under nitrogen to a mixture of *N*-(*tert*-butoxycarbonyl)-*DL*-serine methyl ester (12.42 g, 56.7 mmol) and CuCl (5.89 g, 59.48 mmol) in anhydrous CH₂Cl₂ (100 mL) at 0°C. After stirring at rt in a dark fume cupboard for 60 h, the solvent was removed under reduced pressure and the oily residue was dissolved in EtOAc (2 L), washed with water (2 × 400 mL) and brine (300 mL) and dried over Na₂SO₄. After filtration, the solvent was evaporated under reduced pressure to give a residue. The crude product was purified by flash chromatography (eluent petroleum ether/EtOAc 10:1) to give methyl 2-[(*tert*-butoxycarbonyl)amino]acrylate **4** (7.81 g, 69%) as a colourless oil. The product was stored at rt in a dark cupboard and polymerised after a few days; *R*_f = 0.80 (petroleum ether/EtOAc 10:1); ¹H NMR (400 MHz, CDCl₃) δ 1.49 (9H, s, C(CH₃)₃), 3.83 (3H, s, COOCH₃), 5.73 (1H, s, CHH), 6.16 (1H, s, CHH), 7.02 (1H, br. s, NH); ¹³C NMR (100 MHz, CDCl₃) δ 28.3 (3q), 52.9 (q), 80.8 (s), 105.2 (t), 131.4 (s), 152.6 (s), 164.5 (s).

4-Nitrobenzyl 2-[(*tert*-butoxycarbonyl)amino]-3-hydroxypropanoate.¹⁴

N-(*tert*-Butoxycarbonyl)-*DL*-serine (26.6 g, 130 mmol) was dissolved in MeOH (500 mL) and water (50 mL). The pH of this weakly acidic solution was adjusted to pH = 7 with a 20% aq. solution of cesium carbonate. The solvent was removed under reduced pressure give the *N*-(*tert*-butoxycarbonyl)-*DL*-serine cesium salt as a colourless viscous oil. 4-Nitrobenzyl bromide (39.2 g, 182 mmol) was added to a solution of the cesium salt in DMF (300 mL) and the resultant mixture stirred at rt for 24 h. Water (200 mL) and CH₂Cl₂ (500 mL) were added to the reaction mixture. The organic layer was separated and washed with water (4 × 200 mL), dried over Na₂SO₄, filtered and evaporated under reduced pressure to give a yellow oily residue, which solidified on standing. The crude material was recrystallised from EtOAc/hexane to give the ester 4-nitrobenzyl 2-[(*tert*-butoxycarbonyl)amino]-3-hydroxypropanoate (27.9 g, 63%) as colourless crystals. ¹H NMR (300 MHz, CDCl₃) δ 1.45 (9H, s, C(CH₃)₃), 2.44-2.56 (1H, m, OH), 3.94 (1H, ddd, *J* = 11.2, 5.5 and 3.5 Hz, CHHOH), 4.05 (1H, ddd, *J* = 11.0, 5.5 and 3.7 Hz, CHHOH), 4.40-4.52 (1H, m, CHNH), 5.28 (1H, d, *J* = 13.5 Hz, CHHAr), 5.35 (1H, d, *J* = 13.5 Hz, CHHAr), 5.51 (1H, br. d, *J* = 7.7 Hz, NH), 7.49-7.57 (2H, m, Aryl H), 8.18-8.26 (2H, m, Aryl H); ¹³C NMR (75 MHz, CDCl₃) δ 28.2 (3q), 55.7 (d), 63.3 (t), 65.7 (t), 80.5 (s), 123.8 (2d), 128.2 (2d), 142.5 (s), 147.7 (s), 155.7 (s), 170.6 (s);

IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3414, 3345, 1748, 1665, 1607, 1523, 1350, 1292, 856; MS m/z (CI) 341 ($[\text{MH}]^+$, 15), 285 (66), 267 (18), 241 (100), 160 (16), 136 (24), 122 (14) and 57 (54).

4-Nitrobenzyl 2-[(*tert*-butoxycarbonyl)amino]acrylate 5.¹⁴

EDCI (29.2 g, 152 mmol) was added under nitrogen to a mixture of 4-nitrobenzyl 2-[(*tert*-butoxycarbonyl)amino]-3-hydroxypropanoate (5.9 g, 76.1 mmol) and CuCl (753 mg, 7.61 mmol) in anhydrous CHCl_3 (700 mL) at rt. The mixture rapidly became a dark brown colour and was stirred for 17 h at rt. The reaction mixture was filtered through a celite® pad and washed with brine (700 mL), before the layers were separated and the aq. extracted with CHCl_3 (3×500 mL). The combined organic layers were dried over MgSO_4 , filtered and evaporated under reduced pressure to give 4-nitrobenzyl 2-[(*tert*-butoxycarbonyl)amino]acrylate (24.2 g, 99%) as an off white solid; $R_f = 0.70$ (petroleum ether/EtOAc 10:1); ^1H NMR (270 MHz, CDCl_3) δ 1.49 (9H, s, $\text{C}(\text{CH}_3)_3$), 5.36 (2H, s, COOCH_2), 5.83 (1H, s, $\text{CHH}=\text{CH}$), 6.25 (1H, s, $\text{CHH}=\text{CH}$), 6.99 (1H, br. s, NH), 7.50-7.58 (2H, m, Aryl H), 8.21-8.29 (2H, m, Aryl H); IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3426, 1735, 1712, 1640, 1606, 1515, 886, 840; MS m/z (CI with CH_4) 323 ($[\text{MH}]^+$, 2), 57 (100).

Methyl 2-[di(*tert*-butoxycarbonyl)amino]acrylate 6.¹⁵

To a solution of *N*-(*tert*-butoxycarbonyl)-*DL*-serine methyl ester (9.69 g, 44.2 mmol) in anhydrous MeCN (175 mL) was added DMAP (540 mg, 4.42 mmol) followed by di-*tert*-butyl dicarbonate (21.2 g, 97.2 mmol). The colourless solution was heated at gentle reflux under nitrogen for 8 h. After removal of the solvent, diethyl ether (200 mL) and water (100 mL) were added to the resultant residue. The aq. layer was acidified to pH = 1 with a saturated solution of aq. KHSO_4 and the layers were separated. The organic layer was washed with water (100 mL), a saturated solution of aq. KHSO_4 (3×100 mL), a saturated solution of aq. NaHCO_3 (3×100 mL) and brine (3×100 mL). The organic layer was separated and dried over Na_2SO_4 . After filtration, the solvent was evaporated under reduced pressure to give methyl 2-[di(*tert*-butoxycarbonyl)amino]acrylate (12.3 g, 93%) as a pale brown solid; $R_f = 0.40$ (petroleum ether/EtOAc 3:1); m.p. 54-55 °C (lit.,¹⁵ 52-52.5 °C); ^1H NMR (270 MHz, CDCl_3) δ 1.47 (18H, s, $2\text{C}(\text{CH}_3)_3$), 3.80 (3H, s, COOCH_3), 5.65 (1H, s, $\text{CHH}=\text{CH}$), 6.35 (1H, s, $\text{CHH}=\text{CH}$). m/z (ES) 324 ($[\text{MNa}]^+$, 98%), 302 (86), 287 (20), 272 (15), 246 (100).

Methyl 2-(acetylamino)acrylate 7.¹⁶

A mixture of serine methyl ester hydrochloride (12.5 g, 80.3 mmol), anhydrous sodium acetate (39.54 g, 482 mmol) and acetic anhydride (120 mL) was heated at reflux for 2 h. The volatiles were evaporated under reduced pressure and the residue was dissolved in Et_2O (200 mL). A

saturated aq. solution of NaHCO₃ (200 mL) was added and the biphasic mixture was stirred for 1 h. The organic layer was separated and washed with a saturated aq. solution of NaHCO₃ (40 mL). The organic layer was separated and dried over Na₂SO₄. After filtration, the solvent was removed under reduced pressure to give a 83:17 mixture of methyl 2-(diacetylamino)acrylate (9.05 g, 61%) and methyl 2-(acetylamino)acrylate (1.43 g, 12 %) as a yellow oil. Methyl 2-(diacetylamino)acrylate; ¹H NMR (400 MHz, CDCl₃) δ 2.36 (6H, s, 2 × CH₃CON), 3.83 (3H, s, COOCH₃), 5.81 (1H, s CHH), 6.60 (1H, s, CHH); ¹³C NMR (100 MHz, CDCl₃) δ 26.0 (2q), 53.0 (q), 128.1 (t), 137.3 (s), 163.4 (s), 172.2 (2s); GC-MS retention time 7.21 min., *m/z* (EI) 185 (M⁺, 1), 143 (56), 111 (32), 101 (100), 71 (20).

The crude reaction mixture was dissolved in MeOH (150 mL) and treated with triethylamine (1.57 mL, 11.3 mmol) and hydroquinone (0.19 g, 1.7 mmol). The reaction mixture was heated at reflux until all methyl 2-(diacetylamino)acrylate was consumed (followed by TLC and GC-MS). The solvent was removed under reduced pressure and the resultant solid was triturated in cyclohexane. The cyclohexane-acetic acid azeotropic mixture was evaporated under reduced pressure and the remaining solid was recrystallised in diethyl ether (165 mL) to give methyl 2-(acetylamino)acrylate (7.94 g, 70%) as colourless needles. ¹H NMR (400 MHz, CDCl₃) δ 2.14 (3H, s, CH₃CONH), 3.85 (3H, s, COOCH₃), 5.89 (1H, s CHH), 6.61 (1H, s, CHH), 7.74 (1H, br. s, NH); ¹³C NMR (100 MHz, CDCl₃) δ 24.7 (q), 53.0 (q), 108.8 (t), 130.9 (s), 164.7 (s), 168.9 (s); GC-MS retention time 7.05 min., *m/z* (EI) 143 (M⁺, 55), 111 (31), 101 (100), 71 (20).

5. Characterisation of Compounds from Table 1 - yields and ratios given in Table 1.

Methyl (1S*, 2R*)- and (1R*, 2R*)-1-[(*tert*-butoxycarbonyl)amino]-2-phenyl-1-cyclopropanecarboxylate 8 (Table 1, entries 1-5).¹⁷

***E*-8**; colourless solid; eluent petroleum ether/EtOAc 3:1, *R_f* = 0.52; m.p. 87-89 °C (petroleum ether/EtOAc) (lit.,¹⁷ 85-86 °C); ¹H NMR (400 MHz, CDCl₃) δ 1.49 (9H, s, C(CH₃)₃), 1.61 (1H, m, CHH), 2.18 (1H, dd, *J* = 8.4 and 5.5 Hz, CHH), 2.84 (1H, dd, *J* = 10.1 and 8.4 Hz, CHPh), 3.35 (3H, s, CH₃O), 5.33 (1H, br. s, NH), 7.07-7.51 (5H, m, Aryl H); ¹³C-NMR (100 MHz, CDCl₃) δ 20.3 (t), 28.4 (3q), 35.2 (d), 40.6 (s), 51.9 (q), 76.8 (s), 127.0 (d), 128.0 (2d), 129.3 (2d), 135.4 (s), 156.0 (s), 170.7 (s); IR ν_{max}/cm⁻¹ 3343, 2987, 1735, 1682, 1494, 1283, 1150, 700; GC-MS retention time 13.84 min., *m/z* (EI) 235 ([M- *t*-Bu]⁺, 5), 159 (35), 131 (36), 104 (13), 77 (8), 57 (100).

***Z*-8**; colourless solid; eluent petroleum ether/EtOAc 3:1, *R_f* = 0.48; m.p. 107-109 °C (petroleum ether/EtOAc); ¹H NMR (300 MHz, 124 °C, *d*₆-DMSO) δ 1.16 (9H, s, C(CH₃)₃), 1.63 (1H, dd, *J* =

8.3 and 5.7 Hz, CHH), 1.69 (1H, dd, $J = 9.7$ and 5.7 Hz, CHH), 2.92 (1H, dd, $J = 9.7$ and 8.3 Hz, CHPh), 3.65 (3H, s, CH₃O), 6.47 (1H, br. s, NH), 7.14-7.25 (5H, m, Aryl H); ¹³C NMR (75 MHz, 124°C, *d*₆-DMSO) δ 21.0 (t), 28.4 (3q), 32.2 (d), 39.9 (s), 52.4 (q), 78.7 (s), 126.8 (d), 128.0 (2d), 129.2 (2d), 136.1 (s), 155.6 (s), 172.9 (s); IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3368, 2986, 1722, 1691, 1505, 1287, 1243, 1158, 769, 697; GC-MS retention time 13.91 min., m/z (EI) 235 ([M- *t*-Bu]⁺, 7), 159 (45), 131 (47), 104 (15), 77 (9), 57 (100).

(1*R, 2*S**)- and (1*R**, 2*R**)-4-Nitrobenzyl 1-[(*tert*-butoxycarbonyl)amino]-2-phenyl-1-cyclopropanecarboxylate 9 (Table 1, entries 6-7).**

See experimental section in paper.

Methyl (1*R, 2*S**)- and (1*R**, 2*R**)-1-(acetylamino)-2-phenyl-1-cyclopropanecarboxylate 10 (Table 1, entries 10-12).**¹⁸

See experimental section in paper.

6. Characterisation of Compounds in Table 2 - yields and ratios given in Table 2.

Table 2, entry 1, compound 9 - see Table 1, entries 6-7.

Table 2, entry 2, compound 10 - see Table 1, entries 10-12.

(1*R, 2*S**)- and (1*R**, 2*R**)-4-Nitrobenzyl 1-[(*tert*-butoxycarbonyl)amino]-2-(4-methoxyphenyl)-1-cyclopropanecarboxylate 12 (Table 2, entry 3).**

***E*-12**; colourless solid; eluent petroleum ether/EtOAc 3:1, $R_f = 0.25$; m.p. 129-131 °C (EtOAc/petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 1.47 (9H, s, C(CH₃)₃), 1.63 (1H, dd, $J = 9.2$ and 5.5 Hz, CHHCCO₂), 2.17 (1H, dd, $J = 8.4$ and 5.5 Hz, CHHCCO₂), 2.85 (1H, dd, $J = 9.2$ and 8.4 Hz, ArCH), 3.75 (3H, s, ArOCH₃), 4.95 (2H, s, COOCH₂), 5.37 (1H, br. s, NH), 6.73 (2H, d, $J = 8.8$ Hz, Aryl H), 7.11 (2H, d, $J = 8.8$ Hz, Aryl H), 7.22 (2H, br. d, $J = 8.4$ Hz, Aryl H), 8.07 (2H, d, $J = 8.4$ Hz, Aryl H); ¹³C NMR (100 MHz, CDCl₃) δ 21.1 (t), 28.4 (3q), 35.1 (d), 41.4 (s), 55.2 (q), 65.2 (t), 80.2 (s), 113.5 (2d), 123.4 (2d), 127.2 (s), 128.3 (2d), 130.4 (2d), 142.9 (s), 147.5 (s), 156.0 (s), 158.8 (s), 170.0 (s); IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3242, 3126, 2977, 1701, 1610, 1515, 1454, 1390, 1366, 1344, 1249, 1150, 1058, 1037, 925, 852, 805, 701; MS m/z (EI) 443 ([MH]⁺, 30), 343 (19), 250 (70), 206 (100), 189 (90). Anal. Calc'd for C₂₃H₂₆N₂O₇: C, 62.43; H, 5.92; N, 6.33. Found: C, 62.44; H, 6.20; N, 6.48.

Z-12; minor product, could not be isolated; $R_f = 0.15$ (EtOAc/petroleum ether 1/3).

Methyl (1*R, 2*S**)- and (1*R**, 2*R**)-1-(acetylamino)-2-(4-methoxyphenyl)-1-cyclopropanecarboxylate 13 (Table 2, entry 4).**

E-13; colourless solid characterised from an enriched mixture of both diastereoisomers; EtOAc/petroleum ether 3:2, $R_f = 0.15$; ^1H NMR (400 MHz, CDCl_3) δ 1.58 (1H, dd, $J = 9.8$ and 5.9 Hz, CHHCCO_2), 2.04 (3H, s, CH_3CONH), 2.21 (1H, dd, $J = 8.8$ and 5.9 Hz, CHHCCO_2), 2.77 (1H, dd, $J = 9.8$ and 8.8 Hz, ArCH), 3.37 (3H, s, COOCH_3), 3.78 (3H, s, ArOCH), 6.40 (1H, br. s, NH), 6.81 (2H, d, $J = 8.8$ Hz, Aryl H), 7.26 (2H, d, $J = 8.8$ Hz, Aryl H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.7 (t), 23.3 (q), 34.3 (d), 40.6 (s), 52.0 (q), 55.2 (q), 113.5 (2d), 127.3 (s), 130.3 (2d), 158.7 (s), 170.1 (s), 171.2 (s); GC-MS retention time 15.25 min., m/z (EI) 263 (M^+ , 6), 231 (38), 220 (64), 189 (90), 160 (100), 145 (67), 134 (34), 91 (36).

Z-13; colourless solid characterised from an enriched mixture of both diastereoisomers; EtOAc/petroleum ether 3:2, $R_f = 0.20$; ^1H NMR (400 MHz, CDCl_3) δ 1.66 (1H, dd, $J = 7.9$ and 5.9 Hz, CHH), 1.85 (3H, s, CH_3CONH), 2.19 (1H, dd, $J = 9.5$ and 5.9 Hz, CHH), 2.90 (1H, dd, $J = 9.5$ and 7.9 Hz, ArCH), 3.74 (3H, s, COOCH_3), 3.81 (3H, s, ArOCH), 5.34 (1H, br. s, NH), 6.87 (2H, d, $J = 8.8$ Hz, Aryl H), 7.09 (2H, d, $J = 8.8$ Hz, Aryl H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.3 (t), 23.0 (q), 32.0 (d), 38.9 (s), 52.7 (q), 55.4 (q), 114.0 (2d), 126.1 (s), 129.8 (2d), 159.1 (s), 171.3 (s), 172.2 (s); IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3280, 1717, 1661, 1545, 1517, 1437, 1337, 1264, 1247, 1156, 1029, 838, 682; MS m/z (EI) 263 (M^+ , 12), 231 (45), 220 (85), 189 (78), 160 (100), 145 (42), 91 (40); HRMS: found 263.1155, $\text{C}_{14}\text{H}_{17}\text{NO}_4$ requires 263.1158.

(1*R, 2*S**)- and (1*R**, 2*R**)-4-Nitrobenzyl 1-[(*tert*-butoxycarbonyl)amino]-2-(4-methylphenyl)-1-cyclopropanecarboxylate 14 (Table 2, entry 5).**

E-14; colourless solid; eluent petroleum ether/EtOAc 3:1, $R_f = 0.35$; m.p. 146-147 °C (EtOAc/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 1.47 (9H, s, $\text{C}(\text{CH}_3)_3$), 1.63 (1H, dd, $J = 9.2$ and 5.5 Hz, CHHCCO_2), 2.19 (1H, dd, $J = 8.4$ and 5.5 Hz, CHHCCO_2), 2.21 (3H, s, ArCH₃), 2.87 (1H, dd, $J = 9.2$ and 8.4 Hz, ArCH), 4.91 and 4.96 (2H, AB System, $J_{\text{AB}} = 13.6$ Hz, COOCH_2), 5.46 (1H, br. s, NH), 7.02 (2H, d, $J = 8.2$ Hz, Aryl H), 7.08 (2H, d, $J = 8.2$ Hz, Aryl H), 7.19 (2H, br. d, $J = 8.8$ Hz, Aryl H), 8.05 (2H, d, $J = 8.8$ Hz, Aryl H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.1 (q), 21.1 (t), 28.4 (3q), 35.4 (d), 41.2 (s), 65.3 (t), 80.3 (s), 123.4 (2d), 128.2 (2d), 128.8 (2d), 129.3 (2d), 132.1 (s), 136.8 (s), 142.9 (s), 147.5 (s), 155.9 (s), 170.0 (s); IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3361, 1730, 1708, 1605, 1508, 1447, 1346, 1249, 1152, 1062, 932, 825, 735; MS m/z (EI) 427 ($[\text{MH}]^+$, 30), 371 (48), 327 (26), 234 (40), 190 (100), 173 (58), 144 (40), 137 (28), 117 (36), 90 (22), 78

(24); HRMS: found $[M-Boc]^+$ 325.1188, $C_{18}H_{17}N_2O_4$ requires 325.1188. Anal. Calc'd for $C_{23}H_{26}N_2O_6$: C, 64.78; H, 6.15; N, 6.57. Found: C, 64.71; H, 6.33; N, 6.69.

Z-14; minor product, could not be isolated; eluent petroleum ether/EtOAc 3:1, R_f = 0.25.

Methyl (1*R, 2*S**)- and (1*R**, 2*R**)-1-(acetylamino)-2-(4-methylphenyl)-1-cyclopropanecarboxylate 15 (Table 2, entry 6).**

E-15; colourless solid characterised from an enriched mixture of both diastereoisomers; EtOAc/petroleum ether 2:1, R_f = 0.20; 1H NMR (400 MHz, $CDCl_3$) δ 1.59 (1H, dd, J = 9.5 and 5.7 Hz, $CHHCCO_2$), 2.05 (3H, s, CH_3CONH), 2.23 (1H, dd, J = 8.4 and 5.7 Hz, $CHHCCO_2$), 2.31 (3H, s, $ArCH_3$), 2.78 (1H, dd, J = 9.5 and 8.4 Hz, $ArCH$), 3.36 (3H, s, $COOCH_3$), 6.31 (1H, br. s, NH), 7.08 (2H, d, J = 8.1 Hz, Aryl H), 7.22 (2H, d, J = 8.1 Hz, Aryl H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6 (t), 21.2 (q), 23.4 (q), 34.6 (d), 40.7 (s), 52.0 (q), 128.8 (2d), 129.1 (2d), 132.1 (s), 136.7 (s), 170.1 (s), 171.1 (s).

Z-15; colourless solid; EtOAc/petroleum ether 2:1, R_f = 0.25; m.p. 105-107 °C (EtOAc/petroleum ether); 1H NMR (400 MHz, $CDCl_3$) δ 1.70 (1H, dd, J = 8.0 and 5.9 Hz, $CHHCCO_2$), 1.85 (3H, s, CH_3CONH), 2.21 (1H, dd, J = 9.5 and 5.9 Hz, $CHHCCO_2$), 2.35 (3H, s, $ArCH_3$), 2.90 (1H, dd, J = 9.5 and 8.0 Hz, $ArCH$), 3.74 (3H, s, $COOCH_3$), 5.32 (1H, br. s, NH), 7.05 (2H, d, J = 7.9 Hz, Aryl H), 7.14 (2H, d, J = 7.9 Hz, Aryl H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.1 (q), 21.3 (t), 23.0 (q), 32.3 (d), 38.9 (s), 52.7 (q), 128.6 (2d), 129.3 (2d), 131.1 (s), 137.3 (s), 171.3 (s), 172.2 (s); IR ν_{max}/cm^{-1} 3317, 1720, 1661, 1527, 1439, 1368, 1335, 1271, 1206, 1167, 832, 689; MS m/z (EI) 247 (M^+ , 35), 215 (45), 204 (87), 173 (76), 144 (100), 117 (76), 91 (76); HRMS: found 247.1208, $C_{14}H_{17}NO_3$ requires 247.1208. Anal. Calc'd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 68.30; H, 7.30; N, 5.73.

(1*R, 2*S**)- and (1*R**, 2*R**)-4-Nitrobenzyl 1-[(*tert*-butoxycarbonyl)amino]-2-(4-fluorophenyl)-1-cyclopropanecarboxylate 16 (Table 2, entry 7).**

E-16; colourless crystal; eluent petroleum ether/EtOAc 3:1, R_f = 0.35; m.p. 103-104 °C (EtOAc/petroleum ether); 1H NMR (400 MHz, $CDCl_3$) δ 1.47 (9H, s, $C(CH_3)_3$), 1.66 (1H, dd, J = 9.8 and 5.6 Hz, $CHHCCO_2$), 2.15 (1H, dd, J = 8.3 and 5.6 Hz, $CHHCCO_2$), 2.90 (1H, dd, J = 9.8 and 8.3 Hz, $ArCH$), 4.92 and 4.98 (2H, AB System, J_{AB} = 13.2 Hz, $COOCH_2$), 5.45 (1H, br. s, NH), 6.89 (2H, dd, J_{H-F} = 8.8 Hz and J = 8.3 Hz, Aryl H), 7.19 (2H, d, J = 8.3 Hz, Aryl H), 7.32 (2H, br. d, J = 8.8 Hz, Aryl H), 8.10 (2H, d, J = 8.8 Hz, Aryl H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3 (t), 28.4 (3q), 35.1 (d), 41.0 (s), 65.4 (t), 80.4 (s), 115.0 (2d, J_{C-F} = 21.4 Hz), 123.6 (2d), 128.3 (2d), 128.7 (s), 131.0 (2d, J_{C-F} = 7.7 Hz), 142.8 (s), 147.6 (s), 155.9 (s), 162.0 (s, J_{C-F} =

244.7 Hz), 169.8 (s); IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3390, 1714, 1604, 1510, 1445, 1346, 1250, 1233, 1150, 1112, 1060, 922, 836, 771, 735; MS m/z (EI) 431 (M^+ , 34), 375 (90), 238 (32), 194 (100), 57 (92). Anal. Calc'd for $\text{C}_{22}\text{H}_{23}\text{FN}_2\text{O}_6$: C, 61.39; H, 5.39; N, 6.51. Found: C, 61.56; H, 5.74; N, 6.74.

Z-16; colourless crystals; eluent petroleum ether/EtOAc 3:1, $R_f = 0.25$; ^1H NMR (400 MHz, CDCl_3) δ 1.31 (9H, s, $\text{C}(\text{CH}_3)_3$), 1.71 (1H, m, CHHCCO_2), 2.12 (1H, m, CHHCCO_2), 3.04 (1H, m, ArCH), 4.73 (1H, br. s, NH), 4.92 and 4.98 (2H, AB System, $J_{\text{AB}} = 13.6$ Hz, COOCH_2), 7.01 (2H, dd, $J_{\text{H-F}} = 8.8$ Hz and $J = 8.4$ Hz, Aryl H), 7.19 (2H, d, $J = 8.4$ Hz, Aryl H), 7.54 (2H, d, $J = 8.1$ Hz, Aryl H), 8.21 (2H, d, $J = 8.1$ Hz, Aryl H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.0 (t), 28.1 (3q), 32.6 (d), 41.1 (s), 65.8 (t), 80.3 (s), 115.2 (2d, $J_{\text{C-F}} = 20.8$ Hz), 123.8 (2d), 128.1 (2d), 128.4 (s), 130.4 (2d, $J_{\text{C-F}} = 7.7$ Hz), 143.1 (s), 147.8 (s), 155.6 (s), 162.2 (s, $J_{\text{C-F}} = 246.0$ Hz), 172.1 (s).

Methyl (1*R, 2*S**)- and (1*R**, 2*R**)-1-(acetylamino)-2-(4-fluorophenyl)-1-cyclopropanecarboxylate 17 (Table 2, entry 8).**

E-17; colourless solid characterised from an enriched mixture of both diastereoisomers; EtOAc/petroleum ether 3:1, $R_f = 0.15$; ^1H NMR (400 MHz, CDCl_3) δ 1.60 (1H, dd, $J = 9.8$ and 5.8 Hz, CHHCCO_2), 2.06 (3H, s, CH_3CONH), 2.18 (1H, dd, $J = 8.3$ and 5.8 Hz, CHHCCO_2), 2.81 (1H, dd, $J = 9.8$ and 8.3 Hz, ArCH), 3.37 (3H, s, COOCH_3), 6.38 (1H, br. s, NH), 6.97 (2H, dd, $J_{\text{H-F}} = 8.8$ Hz and $J = 7.8$ Hz, Aryl H), 7.35 (2H, dd, $J = 7.8$ Hz and $J_{\text{H-F}} = 5.4$ Hz, Aryl H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.8 (t), 23.3 (q), 34.3 (d), 40.5 (s), 52.1 (q), 114.9 (2d, $J_{\text{C-F}} = 21.4$ Hz), 130.9 (2d, $J_{\text{C-F}} = 8.4$ Hz), 131.1 (s, $J_{\text{C-F}} = 3.1$ Hz), 162.0 (s, $J_{\text{C-F}} = 245.9$ Hz), 170.8 (s), 171.3 (s).

Z-17; colourless solid; EtOAc/petroleum ether 3:1, $R_f = 0.25$; m.p. 143-145 °C (EtOAc/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 1.68 (1H, dd, $J = 8.1$ and 5.9 Hz, CHHCCO_2), 1.82 (3H, s, CH_3CONH), 2.13 (1H, dd, $J = 9.3$ and 5.9 Hz, CHHCCO_2), 2.97 (1H, dd, $J = 9.3$ and 8.1 Hz, ArCH), 3.74 (3H, s, COOCH_3), 5.71 (1H, br. s, NH), 7.01 (2H, dd, $J = 8.8$ Hz and $J_{\text{H-F}} = 6.8$ Hz, Aryl H), 7.15 (2H, dd, $J = 8.8$ Hz and $J_{\text{H-F}} = 5.7$ Hz, Aryl H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.2 (t), 22.8 (q), 31.7 (d), 39.2 (s), 52.7 (q), 115.3 (2d, $J_{\text{C-F}} = 21.4$ Hz), 130.2 (s, $J_{\text{C-F}} = 2.3$ Hz), 130.3 (2d, $J_{\text{C-F}} = 7.6$ Hz), 162.2 (s, $J_{\text{C-F}} = 245.5$ Hz), 171.3 (s), 172.0 (s); IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3326, 1725, 1667, 1513, 1438, 1371, 1333, 1265, 1161, 1066, 982, 844, 824, 761; MS m/z (EI) 251 (M^+ , 34), 233 (36), 219 (47), 208 (81), 177 (42), 148 (100), 122 (39), 84 (23); HRMS: found 251.0950, $\text{C}_{13}\text{H}_{14}\text{FNO}_3$ requires 251.0958. Anal. Calc'd for $\text{C}_{13}\text{H}_{14}\text{FNO}_3$: C, 61.90; H, 5.90; N, 5.49. Found: C, 62.14; H, 5.62; N, 5.57.

(1*R, 2*S**)- and (1*R**, 2*R**)-4-Nitrobenzyl 1-[(*tert*-butoxycarbonyl)amino]-2-(2,2-diphenylvinyl)-1-cyclopropanecarboxylate 18 (Table 2, entry 9).**

E-18; yellow solid; eluent petroleum ether/EtOAc 3:1; m.p. 146-148 °C (EtOAc/petroleum ether); ¹H NMR (300 MHz at 55 °C, CDCl₃) δ 1.41 (9H, s, C(CH₃)₃), 1.55 (1H, dd, *J* = 9.3 and 5.4 Hz, CHHCCO₂), 1.97 (1H, dd, *J* = 8.1 and 5.4 Hz, CHHCCO₂), 2.14 (1H, dd, *J* = 9.3 and 8.1 Hz, Ph₂C=CHCH), 5.00 (1H, br. s, NH), 5.19 and 5.35 (2H, AB System, *J*_{AB} = 13.3 Hz, COOCH₂), 5.94 (1H, d, *J* = 9.3 Hz, Ph₂C=CH), 7.00-7.42 (10H, m, Aryl H), 7.41-7.49 (2H, m, Aryl H), 8.00-8.08 (2H, m, Aryl H); ¹³C NMR (75 MHz, CDCl₃) δ 21.6 (s), 25.3 (t), 28.2 (3q), 32.5 (d), 65.6 (t), 80.4 (s), 123.7 (2d), 124.1 (d), 127.2, 127.5, 127.5, 127.7, 127.9, 128.1, 128.4, 129.6, 130.1, 139.6, 141.6, 142.9, 145.2, 147.5, 147.9, 155.5 (s), 170.8 (s); IR ν_{max}/cm⁻¹ 1731, 1686, 1607, 1508, 1160, 845, 768, 739, 705, 699; MS *m/z* (CI with CH₄) 469 ([MH-NO₂]⁺, 1), 441 (3), 415 (64), 398 (12), 335 (34), 234 (100), 167 (80), 122 (42), 57 (66); HRMS (CI, [MH-Boc+H]⁺) found: 415.1657, C₂₅H₂₃N₂O₄ requires 415.1658.

Z-18; yellow solid; eluent petroleum ether/EtOAc 3:1; m.p. 112-113 °C (EtOAc/petroleum ether); ¹H NMR (300 MHz, 55 °C, CDCl₃) δ 1.42 (9H, s, C(CH₃)₃), 1.42 (1H, m, CHHCCO₂), 1.98 (1H, dd, *J* = 9.2 and 5.1 Hz, CHHCCO₂), 2.46 (1H, q, *J* = 9.2 Hz, Ph₂C=CHCH), 5.06 (1H, br. s, NH), 5.10 and 5.26 (2H, AB System, *J*_{AB} = 13.6 Hz, COOCH₂), 5.69 (1H, d, *J* = 9.2 Hz, Ph₂CCHCH), 7.15-7.35 (10H, m, Aryl H), 7.35-7.43 (2H, m, Aryl H), 8.11-8.19 (2H, m, Aryl H); ¹³C NMR (100 MHz, CDCl₃) δ 25.3 (t), 28.1 (s), 28.3 (3q), 30.1 (d), 65.5 (t), 80.5 (s), 123.8, 124.4, 127.6, 127.6, 127.6, 128.1, 128.4, 128.5, 130.0, 139.5, 142.1, 143.1, 147.7, 156.1, 171.7; IR ν_{max}/cm⁻¹ 1727, 1693, 1607, 1510, 1338, 1156, 844, 762, 737; MS *m/z* (CI with CH₄) 469 ([MH-NO₂]⁺, 1), 441 (3), 415 (64), 398 (10), 335 (28), 234 (100), 167 (84), 122 (52) and 57 (84); HRMS (CI, [MH-Boc+H]⁺) Found: 415.1657, C₂₅H₂₃N₂O₄ requires 415.1658.

Methyl (1*R, 2*S**)- and (1*R**, 2*R**)-1-(acetylamino)-2-(2,2-diphenylvinyl)-1-cyclopropanecarboxylate 19 (Table 2, entry 10).**

E-19; green solid; EtOAc/petroleum ether 7:3; ¹H NMR (400 MHz, CDCl₃) δ 1.53 (1H, dd, *J* = 9.1 and 5.3 Hz, CHHCCO₂), 2.04 (3H, s, CH₃CONH), 2.04 (1H, m, CHHCCO₂), 2.11 (1H, q, *J* = 9.1 Hz, Ph₂C=CHCH), 3.74 (3H, s, OCH₃), 6.02 (1H, d, *J* = 9.1 Hz, Ph₂C=CH), 6.05 (1H, br. s, NH), 7.18-7.44 (10H, m, Aryl H); ¹³C NMR (100 MHz, CDCl₃) δ 21.1 (q), 23.1 (t), 31.5 (d), 41.3 (s), 53.0 (q), 124.3 (d), 127.3 (d), 127.4 (d), 127.5 (d), 127.8 (d), 127.9 (d), 128.2 (d), 128.4 (d), 128.5 (d), 129.9 (d), 130.3 (d), 140.0 (s), 141.9 (s), 145.0 (s), 170.8 (s), 172.1 (s).

Z-19; pale green solid; EtOAc/petroleum ether 7:3; m.p. 71-74 °C (EtOAc/petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 1.33 (1H, dd, *J* = 7.5 and 5.4 Hz, CHHCCO₂), 2.04 (3H, s, COCH₃), 2.04 (1H, dd, *J* = 9.3 and 5.4 Hz, CHHCCO₂), 2.40 (1H, td, *J* = 9.3 and 7.5 Hz, Ph₂C=CHCH), 3.64 (3H, s, OCH₃), 5.60 (1H, d, *J* = 9.3 Hz, Ph₂C=CHCH), 6.10 (1H, br. s, NH) and 7.18-7.44

(10H, m, Aryl H); ^{13}C NMR (100 MHz, CDCl_3) δ 23.3 (q), 24.7 (t), 29.4 (d), 40.1 (s), 52.6 (q), 124.4 (d), 127.7 (2d), 127.7 (2d), 128.3 (2d), 128.4 (2d), 130.1 (2d), 139.4 (s), 142.1 (s), 146.4 (s), 171.5 (s), 171.8 (s); IR $\nu_{\text{max}}/\text{cm}^{-1}$ 1729, 1662, 1532, 1266, 1195, 1155, 765, 699; MS m/z (CI with CH_4) 336 ($[(\text{MH})]^+$, 100); Anal. Calc'd for $\text{C}_{21}\text{H}_{21}\text{NO}_3$: C, 75.2; H, 6.3; N, 4.2. Found: C, 75.2; H, 6.4; N, 4.3.

(1*R, 2*S**)- and (1*R**, 2*R**)-4-Nitrobenzyl 1-[(*tert*-butoxycarbonyl)amino]-2-(3-[1-(*tert*-butyl)-1,1-dimethylsilyl]oxyphenyl)-1-cyclopropanecarboxylate 20** (Table 2, entry 11).

See experimental section in paper.

Methyl (1*R, 2*S**)- and (1*R**, 2*R**)-1-(acetylamino)-2-(3-[1-(*tert*-butyl)-1,1-dimethylsilyl]oxyphenyl)-1-cyclopropanecarboxylate 21** (Table 2, entry 12).

E-21; colourless oil (7% yield); EtOAc/petroleum ether 1:1, R_f = 0.15; ^1H NMR (400 MHz, CDCl_3) δ 0.18 (6H, s, $\text{Si}(\text{CH}_3)_2$), 0.97 (9H, s, $\text{SiC}(\text{CH}_3)_3$), 1.59 (1H, dd, J = 9.9 and 5.5 Hz, CHHCCO_2), 2.05 (3H, s, CH_3CONH), 2.21 (1H, dd, J = 8.4 and 5.5 Hz, CHHCCO_2), 2.77 (1H, dd, J = 9.9 and 8.4 Hz, ArCH), 3.34 (3H, s, COOCH_3), 6.33 (1H, br. s, NH), 6.73 (1H, dd, J = 8.1 Hz and 1.8 Hz, Aryl H), 6.83 (1H, d, J = 1.8 Hz, Aryl H), 6.92 (1H, d, J = 7.7 Hz, Aryl H), 7.12 (1H, dd, J = 8.1 Hz and 7.7 Hz, Aryl H); ^{13}C NMR (100 MHz, CDCl_3) δ -4.3 (2q), 18.3 (s), 20.5 (t), 23.3 (q), 25.8 (3q), 34.4 (d), 40.7 (s), 51.9 (q), 118.9 (d), 121.1 (d), 122.3 (d), 129.0 (d), 136.8 (s), 155.5 (s), 170.0 (s), 171.1 (s); IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3289, 2931, 2858, 1737, 1662, 1532, 1487, 1436, 1334, 1277, 1151, 1005, 918, 833, 779, 693; MS m/z (EI) 363 (M^+ , 63), 306 (92), 245 (100), 232 (100), 204 (90); HRMS: found 363.1854, $\text{C}_{19}\text{H}_{29}\text{NO}_4\text{Si}$ requires 363.1866.

Z-21; colourless solid (37% yield); EtOAc/petroleum ether 1:1, R_f = 0.25; m.p. 110-112 °C (EtOAc/petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 0.19 (6H, s, $\text{Si}(\text{CH}_3)_2$), 0.98 (9H, s, $\text{SiC}(\text{CH}_3)_3$), 1.68 (1H, dd, J = 8.0 and 6.0 Hz, CHHCCO_2), 1.86 (3H, s, CH_3CONH), 2.22 (1H, dd, J = 9.5 and 6.0 Hz, CHHCCO_2), 2.88 (1H, dd, J = 9.5 and 8.0 Hz, ArCH), 3.75 (3H, s, COOCH_3), 5.31 (1H, br. s, NH), 6.63 (1H, d, J = 8.1 Hz, Aryl H), 6.77 (2H, m, Aryl H), 7.19 (1H, t, J = 7.9 Hz, Aryl H); ^{13}C NMR (100 MHz, CDCl_3) δ -4.3 (2q), 18.2 (s), 21.3 (t), 22.9 (q), 25.7 (3q), 32.3 (d), 39.0 (s), 52.7 (q), 119.2 (d), 120.4 (d), 121.9 (d), 129.5 (d), 135.9 (s), 155.9 (s), 171.2 (s), 172.1 (s); IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3299, 2959, 1742, 1665, 1602, 1542, 1489, 1270, 1249, 1159, 971, 921, 834, 781, 687; MS m/z (EI) 363 (M^+ , 32), 304 (100), 245 (72), 232 (71), 204 (70); HRMS: found 363.1862, $\text{C}_{19}\text{H}_{29}\text{NO}_4\text{Si}$ requires 363.1866. Anal. Calc'd for $\text{C}_{19}\text{H}_{29}\text{NO}_4\text{Si}$: C, 62.78; H, 8.04; N, 3.85. Found: C, 62.63; H, 8.39; N, 4.00.

(1*R**, 2*S**)- and (1*R**, 2*R**)-4-Nitrobenzyl 1-[(tert-butoxycarbonyl)amino]-2-vinyl-1-cyclopropanecarboxylate **22** (Table 2, entry 13).

E-22; colourless solid (26% yield); EtOAc/petrol 25:75, R_f = 0.31; m.p. 69-70 °C (EtOAc/petrol); ^1H NMR (300 MHz, CDCl_3) δ 1.41 (9H, s, $\text{C}(\text{CH}_3)_3$), 1.54 (1H, dd, J = 8.7 and 5.4 Hz, CHHCCO_2), 1.83 (1H, dd, J = 8.7 and 5.4 Hz, CHHCCO_2), 2.21 (1H, q, J = 8.7 Hz, $\text{CH}_2=\text{CHCH}$), 5.11 (1H, dd, J = 10.3 and 1.7 Hz, $\text{CHH}=\text{CH}$), 5.22 (1H, br. s, NH), 5.22 and 5.28 (2H, AB System, J_{AB} = 13.5 Hz, CCO_2CHHAr), 5.29 (1H, dd, J = 17.2 and 1.7 Hz, $\text{CHH}=\text{CH}$), 5.74 (1H, ddd, J = 17.2, 10.3 and 8.7 Hz, $\text{CH}_2=\text{CH}$), 7.46-7.54 (2H, m, Aryl H), 8.14-8.22 (2H, m, Aryl H); ^{13}C NMR (100 MHz, CDCl_3) δ 23.9 (t), 28.3 (3q), 34.8 (d), 40.8 (s), 65.5 (t), 80.3 (s), 118.2 (t), 123.7 (2d), 128.1 (2d), 133.3 (d), 143.2 (s), 147.8 (s), 155.7 (s), 170.5 (s); IR $\nu_{\text{max}}/\text{cm}^{-1}$ 1710, 1607, 1521, 1346, 1153, 994, 912, 845; MS m/z (ES) 363 ($[\text{MH}]^+$, 41), 348 (26), 307 (100), 263 (97), 136 (17); HRMS (ES, $[\text{MH}-\text{C}(\text{CH}_3)_3+\text{H}]^+$): found 307.0922. $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_6$ requires 307.0930.

Z-22; colourless solid (10% yield); EtOAc/petrol 25:75, R_f = 0.26; m.p. 117-119 °C (EtOAc/petrol); ^1H NMR (300 MHz at 55 °C, CDCl_3) δ 1.27 (1H, dd, J = 8.4 and 5.1 Hz, CHHCCO_2), 1.41 (9H, s, $\text{C}(\text{CH}_3)_3$), 1.92 (1H, dd, J = 8.4 and 5.1 Hz, CHHCCO_2), 2.43 (1H, q, J = 8.4 Hz, $\text{CH}_2=\text{CHCH}$), 4.91 (1H, br. s, NH), 5.24 (1H, d, J = 9.7 Hz, $\text{CHH}=\text{CH}$), 5.21 and 5.27 (2H, AB System, J_{AB} = 13.7 Hz, CCO_2CHHAr), 5.28 (1H, d, J = 17.2 Hz, $\text{CHH}=\text{CH}$), 5.57 (1H, ddd, J = 17.2, 9.7 and 8.4 Hz, $\text{CH}_2=\text{CH}$), 7.44-7.54 (2H, m, Aryl H), 8.15-8.23 (2H, m, Aryl H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.6 (t), 28.3 (3q), 31.9 (d), 39.4 (s), 65.7 (t), 80.4 (s), 118.9 (t), 123.9 (2d), 128.1 (2d), 133.4 (d), 143.1 (s), 147.8 (s), 156.0 (s), 172.2 (s); IR $\nu_{\text{max}}/\text{cm}^{-1}$ 1732, 1684, 1608, 1507, 1339, 1157, 913, 846; MS m/z (ES) 363 ($[\text{MH}]^+$, 35), 348 (17), 307 (89), 263 (100), 241 (6), 136 (15); HRMS (ES, $[\text{MH}-\text{C}(\text{CH}_3)_3+\text{H}]^+$): found 307.0922, $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_6$ requires 307.0930.

7. X-ray Crystallographic Data.

Methyl (1*R**, 2*R**)-1-(acetilamino)-2-(2,2-diphenylvinyl)-1-cyclopropanecarboxylate **Z-19**.

The cyclopropane crystallised from petroleum ether/EtOAc in the form of colourless blocks; crystallographic data is presented in Tables 4 and 5. A single crystal of the cyclopropane was coated in high-vacuum grease and mounted on a glass fibre. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$).¹⁹ Intensities were integrated²⁰ from several series of exposures, each exposure covering 0.3° in ω , and the total data set being a hemisphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.²¹ The structure was solved by direct methods and refined by least squares on weighted F^2 values for all reflections (see Table 4).²² All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters 1.2 times that of their parent atoms. Refinement proceeded smoothly to give the residuals. Complex neutral-atom scattering factors were used.²³

Table 4. Crystal data and structure refinement for Methyl (1R*, 2R*)-1-(acetylamino)-2-(2,2-diphenylvinyl)-1-cyclopropanecarboxylate Z-19.

Empirical formula	C ₂₁ H ₂₁ N O ₃	
Formula weight	335.39	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.6815(19) Å	$\alpha = 90^\circ$
	b = 20.478(4) Å	$\beta = 118.67(3)^\circ$
	c = 9.968(2) Å	$\gamma = 90^\circ$
Volume	1733.9(6) Å ³	
Z	4	
Density (calculated)	1.285 Mg/m ³	
Absorption coefficient	0.086 mm ⁻¹	
F(000)	712	
Crystal size	0.20 x 0.20 x 0.10 mm	
θ range for data collection	1.99 to 27.48°	
Index ranges	-11 ≤ h ≤ 12, -20 ≤ k ≤ 26, -12 ≤ l ≤ 12	

Reflections collected 12125

Independent reflections 3966 [$R_{\text{int}} = 0.0561$]

Completeness to $\theta = 27.48^\circ$ 99.8 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.993 and 0.879

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters 3966 / 0 / 231

Goodness-of-fit on F^2 $S = 0.948$

R indices [for 2441 reflections with $I > 2\sigma(I)$] $R_1 = 0.0487$, $wR_2 = 0.1012$

R indices (for all 3966 data) $R_1 = 0.0916$, $wR_2 = 0.1130$

Weighting scheme $w^{-1} = \sigma^2(F_o^2) + (aP)^2$,

where $P = [\max(F_o^2, 0) + 2F_c^2]/3$

$a = 0.0542$

Largest diff. peak and hole 0.278 and -0.209 $\text{e}\text{\AA}^{-3}$

Table 5. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for Methyl (1R*, 2R*)-1-(acetylamino)-2-(2,2-diphenylvinyl)-1-cyclopropanecarboxylate **Z-19**.

C(1)-C(2)	1.385(3)
C(1)-C(6)	1.394(2)
C(1)-H(1)	0.9500
C(2)-C(3)	1.382(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.377(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.392(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.390(2)
C(5)-H(5)	0.9500
C(6)-C(7)	1.490(2)
C(7)-C(14)	1.340(2)
C(7)-C(8)	1.492(2)
C(8)-C(9)	1.387(3)
C(8)-C(13)	1.388(3)
C(9)-C(10)	1.386(3)

C(9)-H(9)	0.9500
C(10)-C(11)	1.376(3)
C(10)-H(10)	0.9500
C(11)-C(12)	1.380(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.379(3)
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(14)-C(15)	1.476(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.500(2)
C(15)-C(17)	1.536(2)
C(15)-H(15)	1.0000
C(16)-C(17)	1.501(2)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-N(1)	1.427(2)
C(17)-C(18)	1.494(2)
C(18)-O(3)	1.210(2)
C(18)-O(2)	1.332(2)
C(19)-O(2)	1.447(2)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-O(1)	1.231(2)
C(20)-N(1)	1.345(2)
C(20)-C(21)	1.505(2)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
N(1)-H(1A)	0.868(19)
C(2)-C(1)-C(6)	121.29(17)
C(2)-C(1)-H(1)	119.4
C(6)-C(1)-H(1)	119.4
C(3)-C(2)-C(1)	120.28(18)
C(3)-C(2)-H(2)	119.9
C(1)-C(2)-H(2)	119.9

C(4)-C(3)-C(2)	119.39(18)
C(4)-C(3)-H(3)	120.3
C(2)-C(3)-H(3)	120.3
C(3)-C(4)-C(5)	120.23(18)
C(3)-C(4)-H(4)	119.9
C(5)-C(4)-H(4)	119.9
C(6)-C(5)-C(4)	121.26(17)
C(6)-C(5)-H(5)	119.4
C(4)-C(5)-H(5)	119.4
C(5)-C(6)-C(1)	117.51(16)
C(5)-C(6)-C(7)	121.05(15)
C(1)-C(6)-C(7)	121.44(15)
C(14)-C(7)-C(6)	121.51(15)
C(14)-C(7)-C(8)	120.76(16)
C(6)-C(7)-C(8)	117.70(14)
C(9)-C(8)-C(13)	118.54(17)
C(9)-C(8)-C(7)	121.59(17)
C(13)-C(8)-C(7)	119.87(17)
C(10)-C(9)-C(8)	120.68(19)
C(10)-C(9)-H(9)	119.7
C(8)-C(9)-H(9)	119.7
C(11)-C(10)-C(9)	119.8(2)
C(11)-C(10)-H(10)	120.1
C(9)-C(10)-H(10)	120.1
C(10)-C(11)-C(12)	120.18(19)
C(10)-C(11)-H(11)	119.9
C(12)-C(11)-H(11)	119.9
C(13)-C(12)-C(11)	119.8(2)
C(13)-C(12)-H(12)	120.1
C(11)-C(12)-H(12)	120.1
C(12)-C(13)-C(8)	120.9(2)
C(12)-C(13)-H(13)	119.5
C(8)-C(13)-H(13)	119.5
C(7)-C(14)-C(15)	127.34(16)
C(7)-C(14)-H(14)	116.3
C(15)-C(14)-H(14)	116.3
C(14)-C(15)-C(16)	118.92(15)

C(14)-C(15)-C(17)	117.87(15)
C(16)-C(15)-C(17)	59.24(11)
C(14)-C(15)-H(15)	116.3
C(16)-C(15)-H(15)	116.3
C(17)-C(15)-H(15)	116.3
C(15)-C(16)-C(17)	61.59(12)
C(15)-C(16)-H(16A)	117.6
C(17)-C(16)-H(16A)	117.6
C(15)-C(16)-H(16B)	117.6
C(17)-C(16)-H(16B)	117.6
H(16A)-C(16)-H(16B)	114.7
N(1)-C(17)-C(18)	116.86(15)
N(1)-C(17)-C(16)	118.58(14)
C(18)-C(17)-C(16)	114.85(15)
N(1)-C(17)-C(15)	118.66(14)
C(18)-C(17)-C(15)	116.20(14)
C(16)-C(17)-C(15)	59.17(12)
O(3)-C(18)-O(2)	123.92(16)
O(3)-C(18)-C(17)	123.39(16)
O(2)-C(18)-C(17)	112.64(15)
O(2)-C(19)-H(19A)	109.5
O(2)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
O(2)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(1)-C(20)-N(1)	121.84(16)
O(1)-C(20)-C(21)	122.14(17)
N(1)-C(20)-C(21)	116.03(15)
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(20)-N(1)-C(17)	120.64(14)
C(20)-N(1)-H(1A)	119.7(13)

C(17)-N(1)-H(1A)	119.6(13)
C(18)-O(2)-C(19)	115.15(14)

(1*S, 2*R**)-1-[(*tert*-Butoxycarbonyl)amino]-2-(2,2-diphenylvinyl)-1-cyclopropanecarboxylic Acid.**

The cyclopropane crystallised from chloroform/pentane by vapour diffusion to give single crystals; crystallographic data is presented in Tables 6 and 7. A single crystal of the cyclopropane was coated in high-vacuum grease and mounted on a glass fibre. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å). Intensities were integrated from several series of exposures, each exposure covering 0.3° in ω , and the total data set being a hemisphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements. The structure was solved by direct methods and refined by least squares on weighted F^2 values for all reflections (see Table 6). All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters 1.2 times that of their parent atoms. Refinement proceeded smoothly to give the residuals shown in Table 00. Complex neutral-atom scattering factors were used.

Table 6. Crystal data and structure refinement for (1*S**, 2*R**)-1-[(*tert*-Butoxycarbonyl)amino]-2-(2,2-diphenylvinyl)-1-cyclopropanecarboxylic Acid.

Empirical formula	$\text{C}_{24} \text{H}_{26} \text{Cl}_3 \text{N O}_4$	
Formula weight	498.81	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	$a = 12.425(3)$ Å	$\alpha = 90^\circ$
	$b = 18.223(5)$ Å	$\beta = 103.042(17)^\circ$
	$c = 11.601(2)$ Å	$\gamma = 90^\circ$
Volume	$2558.9(11)$ Å ³	

Z 4

Density (calculated) 1.295 Mg/m³

Absorption coefficient 0.387 mm⁻¹

F(000) 1040

Crystal size 0.2 x 0.2 x 0.05 mm

θ range for data collection 2.02 to 24.01°

Index ranges -14 ≤ h ≤ 9, -20 ≤ k ≤ 20, -13 ≤ l ≤ 12

Reflections collected 12277

Independent reflections 4000 [$R_{\text{int}} = 0.0381$]

Completeness to $\theta = 24.01^\circ$ 99.7 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.981 and 0.926

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters 4000 / 0 / 295

Goodness-of-fit on F^2 S = 1.067

R indices [for 2905 reflections with $I > 2\sigma(I)$] $R_1 = 0.0745$, $wR_2 = 0.1994$

R indices (for all 4000 data) $R_1 = 0.0991$, $wR_2 = 0.2216$

Weighting scheme $w^{-1} = \sigma^2(F_o^2) + (aP)^2$,

where $P = [\max(F_o^2, 0) + 2F_c^2]/3$

$a = 0.1057$

Largest diff. peak and hole 1.435 and -1.008 eÅ⁻³

Table 7. Bond lengths [Å] and angles [°] for (1*S**, 2*R**)-1-[(*tert*-Butoxycarbonyl)amino]-2-(2,2-diphenylvinyl)-1-cyclopropanecarboxylic Acid *E*-**25**.

C(1)-C(2)	1.383(5)
C(1)-C(6)	1.389(5)
C(1)-H(1)	0.9500
C(2)-C(3)	1.382(6)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.384(6)
C(3)-H(3)	0.9500
C(4)-C(5)	1.392(5)
C(4)-H(4)	0.9500
C(5)-C(6)	1.397(5)

C(5)-H(5)	0.9500
C(6)-C(7)	1.493(5)
C(7)-C(14)	1.338(5)
C(7)-C(8)	1.495(5)
C(8)-C(13)	1.396(6)
C(8)-C(9)	1.398(6)
C(9)-C(10)	1.395(6)
C(9)-H(9)	0.9500
C(10)-C(11)	1.370(7)
C(10)-H(10)	0.9500
C(11)-C(12)	1.375(7)
C(11)-H(11)	0.9500
C(12)-C(13)	1.388(6)
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(14)-C(15)	1.487(5)
C(14)-H(14)	0.9500
C(15)-C(16)	1.496(5)
C(15)-C(17)	1.538(5)
C(15)-H(15)	1.0000
C(16)-C(17)	1.505(5)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-N(1)	1.443(5)
C(17)-C(18)	1.499(5)
C(18)-O(1)	1.211(4)
C(18)-O(2)	1.321(5)
C(19)-O(3)	1.227(5)
C(19)-O(4)	1.332(5)
C(19)-N(1)	1.343(5)
C(20)-O(4)	1.488(4)
C(20)-C(22)	1.509(7)
C(20)-C(23)	1.512(6)
C(20)-C(21)	1.516(6)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800

C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
N(1)-H(1A)	0.9200
O(2)-H(2)	0.69(9)
C(24)-Cl(2)	1.704(6)
C(24)-Cl(1)	1.716(7)
C(24)-Cl(3)	1.737(5)
C(24)-H(24)	1.0000
C(2)-C(1)-C(6)	121.3(4)
C(2)-C(1)-H(1)	119.3
C(6)-C(1)-H(1)	119.3
C(3)-C(2)-C(1)	120.2(4)
C(3)-C(2)-H(2A)	119.9
C(1)-C(2)-H(2A)	119.9
C(2)-C(3)-C(4)	119.5(4)
C(2)-C(3)-H(3)	120.2
C(4)-C(3)-H(3)	120.2
C(3)-C(4)-C(5)	120.4(4)
C(3)-C(4)-H(4)	119.8
C(5)-C(4)-H(4)	119.8
C(4)-C(5)-C(6)	120.4(4)
C(4)-C(5)-H(5)	119.8
C(6)-C(5)-H(5)	119.8
C(1)-C(6)-C(5)	118.2(3)
C(1)-C(6)-C(7)	120.3(3)
C(5)-C(6)-C(7)	121.4(3)
C(14)-C(7)-C(6)	120.1(3)
C(14)-C(7)-C(8)	122.9(3)
C(6)-C(7)-C(8)	116.9(3)
C(13)-C(8)-C(9)	118.4(4)
C(13)-C(8)-C(7)	120.6(3)
C(9)-C(8)-C(7)	120.9(3)
C(10)-C(9)-C(8)	120.4(4)

C(10)-C(9)-H(9)	119.8
C(8)-C(9)-H(9)	119.8
C(11)-C(10)-C(9)	119.9(5)
C(11)-C(10)-H(10)	120.1
C(9)-C(10)-H(10)	120.1
C(10)-C(11)-C(12)	120.7(4)
C(10)-C(11)-H(11)	119.7
C(12)-C(11)-H(11)	119.7
C(11)-C(12)-C(13)	120.0(5)
C(11)-C(12)-H(12)	120.0
C(13)-C(12)-H(12)	120.0
C(12)-C(13)-C(8)	120.6(4)
C(12)-C(13)-H(13)	119.7
C(8)-C(13)-H(13)	119.7
C(7)-C(14)-C(15)	126.2(3)
C(7)-C(14)-H(14)	116.9
C(15)-C(14)-H(14)	116.9
C(14)-C(15)-C(16)	119.9(3)
C(14)-C(15)-C(17)	120.7(3)
C(16)-C(15)-C(17)	59.5(2)
C(14)-C(15)-H(15)	115.2
C(16)-C(15)-H(15)	115.2
C(17)-C(15)-H(15)	115.2
C(15)-C(16)-C(17)	61.7(2)
C(15)-C(16)-H(16A)	117.6
C(17)-C(16)-H(16A)	117.6
C(15)-C(16)-H(16B)	117.6
C(17)-C(16)-H(16B)	117.6
H(16A)-C(16)-H(16B)	114.7
N(1)-C(17)-C(18)	117.4(3)
N(1)-C(17)-C(16)	118.6(3)
C(18)-C(17)-C(16)	117.6(3)
N(1)-C(17)-C(15)	115.6(3)
C(18)-C(17)-C(15)	115.4(3)
C(16)-C(17)-C(15)	58.9(2)
O(1)-C(18)-O(2)	123.8(3)
O(1)-C(18)-C(17)	122.7(3)

O(2)-C(18)-C(17)	113.4(3)
O(3)-C(19)-O(4)	124.1(3)
O(3)-C(19)-N(1)	123.4(3)
O(4)-C(19)-N(1)	112.6(3)
O(4)-C(20)-C(22)	109.2(3)
O(4)-C(20)-C(23)	101.9(3)
C(22)-C(20)-C(23)	111.2(4)
O(4)-C(20)-C(21)	110.5(3)
C(22)-C(20)-C(21)	111.9(4)
C(23)-C(20)-C(21)	111.6(4)
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(20)-C(22)-H(22A)	109.5
C(20)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(20)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(20)-C(23)-H(23A)	109.5
C(20)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(20)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(19)-N(1)-C(17)	122.9(3)
C(19)-N(1)-H(1A)	106.6
C(17)-N(1)-H(1A)	106.6
C(18)-O(2)-H(2)	114(8)
C(19)-O(4)-C(20)	121.2(3)
Cl(2)-C(24)-Cl(1)	114.7(4)
Cl(2)-C(24)-Cl(3)	110.4(3)
Cl(1)-C(24)-Cl(3)	109.0(3)
Cl(2)-C(24)-H(24)	107.5

Cl(1)-C(24)-H(24) 107.5

Cl(3)-C(24)-H(24) 107.5

8. Spectra of new compounds.

File Name - db3705C.2
Author - BUCHHEIM
Sample ID - va/db3705
Content - bb14 recf. b.bressel
Creation Date - 26-JUN-2002 10:43:34
Revision Date - 26-JUN-2002 08:12:17
Spec Site - GK400
Spec Type - DELTA_NMR
Data Format - 1D COMPLEX
X - 13C
D1a Title - 13C
D1a Size - 32768
D1a Units - [ppm]
X_Center - 13C [ppm]
X_Sweep - 100.531568 [MHz]
X_Pulses - 25.1882188 [Hz]
X_Pulse - 3.6566667 [us]
Relaxation_Delay - 1.308896 [s]
Relaxation_Delay - 1.00
Pulse_Program - 28
Pulse_Program - CHOROPOR-D
Solvent - CDCl3
Spin_Site - 13[Hz]
Temp_Site - 24.9 [C]
Lock_Site - 24.9 [C]
Lock - ON
Lock_Strength - 678
Charger_Sample - 14
Irr_Width - 40 [us]
Experiment - single_pulse_dec

(Millions)

bb4014D.2
bb34d b.bressed

File Name = bb4014D.2
Author = b.bressed
Sample ID = bb34d
Content = b.bressed
Creation Date = 2-JUL-2002 23:48:35
Revision Date = 2-JUL-2002 23:43:58
Spec file = GZ400
Spec type = DEPTX_JMR
Data Format = 1D COMPLEX
Dimensions = 13C
D1a file = 32768
D1a file = 32768
D1a units = [ppm]
X_domain = 100 [ppm]
X_offset = 100 [ppm]
X_freq = 125.761688 [MHz]
X_sweep = 25.1891688 [Hz]
X_pulses = 11 [us]
X_pulse = 1.3008896 [s]
Relaxation_delay = 2 [s]
Solvent = CHLOROFORM-D
Solv. gain = 15 [Hz]
Solv. set = 23.2 [Hz]
Temp. set = 23.2 [Hz]
Lock = 733
Lock strength = 31
Changer. sample = 40 [us]
Experiment = dept_dec_exp

(Billions)

bb4014C.2
bb34d b.bressed

File Name = bb4014C.2
Author = b.bressed
Sample ID = bb34d
Content = b.bressed
Creation Date = 2-JUL-2002 23:36:24
Revision Date = 2-JUL-2002 23:31:26
Spec file = GZ400
Spec type = DEPTX_JMR
Data Format = 1D COMPLEX
Dimensions = 13C
D1a file = 32768
D1a file = 32768
D1a units = [ppm]
X_domain = 100 [ppm]
X_offset = 100 [ppm]
X_freq = 125.761688 [MHz]
X_sweep = 25.1891688 [Hz]
X_pulses = 11 [us]
X_pulse = 1.3008896 [s]
Relaxation_delay = 2 [s]
Solvent = CHLOROFORM-D
Solv. gain = 15 [Hz]
Solv. set = 23.2 [Hz]
Temp. set = 23.2 [Hz]
Lock = 733
Lock strength = 31
Changer. sample = 40 [us]
Experiment = dept_dec_exp

X : parts per Million : 13C

Z-18

0.94069

File Name	Author
16A207H.2	rc/L16207
Sample ID	ICL161505 S90C
Content	IAXI1505 19:53:14
Creation Date	15-NOV-2001 09:53:14
Revision Date	15-NOV-2001 09:53:14
Spc site	Eclipse+ 300
Spc Type	DELTA_INNR
Data Format	ID COMPLEX
Din size	1H
Din Units	12766
Obs start	[DPM]
X offset	5 [DPM]
X freq	299.946657 [Hz]
X points	32768
X sweep	6.00240096 [Hz]
X Pulse duration	3.1 [ms]
Pulse repetition rate	3.14308 [1/s]
Relaxation_delay	16
Scans	17
Recyrc_gain	CHROMPD
Revcyc	CHROMPD-D
RGWAVE	55 [dc]
Tend deg	LOCK ON
Lock state	868
Exp. strength	single-pulse-exp
Experiment	

14354H.2
LA1173C L. Adams

Z/E mix-19

X : parts per Million : 1H

File Name: 14354H.2
 Author: RUCM
 Sample ID: rc/LA14354
 Content: LA1173C
 Creation Date: 9-JUL-2002 22:01:27
 Revision Date: 9-JUL-2002 22:54:56
 Spec Site: GZ40C
 Spec Type: DELTA NMR
 Data Format: 1D COMPLEX
 Data Size: 16384
 Dim Title: 1H
 Dim Units: [ppm]
 X_domain: 10
 X_offset: 3.0
 X_freq: 300.1360971[MHz]
 X_sweep: 5.9980024[kHz]
 X_pulse: 8[us]
 X_acq_duration: 2.731128[s]
 X_processing_delay: 1.6
 Scans: 16
 Recor_gain: 16
 Solvent: CHLOROFORM-D
 Spu_gain: 15[MHz]
 Temp_set: 20.1[°C]
 Lock_strength: 689
 Changr_sample: 21
 Xpr_jdch: 40[us]
 Experiment: single_pulse_exp

* visible EtOAc

File Name	= hb5026C-2
Author	= BROCHEN
Sample ID	= va/hb5026
Content	= b5b3c7 - b5b3e1
Creation Date	= 21-01-2002 21:45:41
Modification Date	= 21-01-2002 21:48:12
Spec Size	= 262400
Spec Type	= EX200A_NMR
Data Format	= ID_COMPLEX
D1a File	= 13C
D1a Size	= 33768
D1a Units	= [ppm]
X_dosim1	= 13C
X_freq1	= 125.5351566 [MHz]
X_sweep	= 21.18891668 [kHz]
X_pulse	= 3.66666667 [us]
X_pulse_duration	= 1.3068896 [us]
Mixtimeout_delay	= 140
Recvr_gain	= 2700
Solvent	= CHLOROFORM-D
Acq1_get	= 14 [Hz]
Temp_size	= EX200_OPP
Temp_units	= 100C
Lock_size	= LOCK_ON
Lock_strength	= 67
Changer_sample	= 40 [us]
ir_gamma	=
Experiment	= Single_pulse_dec

JEOL

File Name = 1a1608_2
 Author = BOCHER
 Sample ID = FC/1a160
 Content = 1A11479
 Creation Date = 2-NOV-2001 14:46:13
 Revision Date = 2-NOV-2001 14:46:14
 Spec file = GX400
 Spec type = DELTA_NMR
 Data Format = 1D COMPLEX
 X = 1
 Dim 1 Size = 16384
 Dim 1 Unit = [ppm]
 X 1 Offset = 31000
 X 1 Range = 31000-784193 [Hz]
 X 1 Sweep = 8 [Hz]
 X 1 Pulse = 8 [us]
 X 1 Duration = 2.048 [s]
 Relaxation delay = 4 [s]
 Recycle gain = 16
 Solvent = CHLOROFORM-D
 Spin set = 11 [Hz]
 Temp set = 22.2 [C]
 Lock state = LOCK ON
 Lock strength = 792
 Changer sample = 17
 Irr pulse = 40 [us]
 Experiment = single_pulse_exp

Z/E mix (60/40)-22

9. References.

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