

Supporting information for

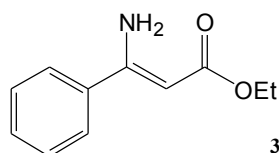
Efficient synthesis of β -amino- α,β -unsaturated carbonyl compounds

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General Experimental: Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz. Carbon-13 nuclear magnetic resonance ($^{13}\text{C-NMR}$) was recorded on Bruker Avance 300 spectrometer at 75 MHz. Chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (TMS) for all recorded NMR spectra. Low resolution Mass spectra were recorded on Finnigan Trace 2000 GC-MS spectrometer. Starting materials and reagents used in reactions were obtained commercially from Acros, Aldrich, Fluka and were used without purification, unless otherwise indicated.

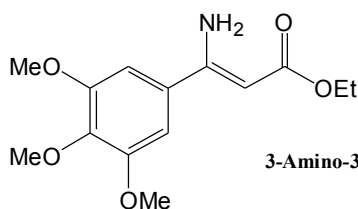
Experimental:

To a solution of 1,3- β -dicarbonyl compounds (1 mmol) and tetraethyl orthosilicate (2 mmol) in absolute ethanol (5 mL), ammonium acetate (4~5 mmol, 4~5 eq.) or (aryl) alkylammonium acetate (prepared in situ from equimolar amounts of aryl or alkylamine and acetic acid, 1.2~1.5 mmol) was added. The resulting mixture were then stirred at reflux under nitrogen for 3~48 hours. The reaction was monitored by thin layer chromatography. After removal of the solvents, the residue was chromatographed on silica gel or on basic alumina to afford the products.



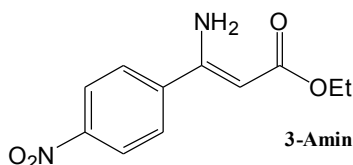
3-Amino-3-phenyl-acrylic acid ethyl ester

3-Amino-3-phenyl-acrylic acid ethyl ester: Colorless oil. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 7.45-7.38 (2H, m), 7.33-7.24 (3H, m), 4.85 (1H, s), 4.05 (2H, q, $J = 7.1$ Hz), 1.18 (3H, t, $J = 7.1$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 170.43, 160.57, 137.72, 130.20, 128.82, 126.19, 84.59, 58.90, 14.60. **GC-MS** (EI) m/z : 191.2 (M^+ , 69%), 162.1 (7), 146.0 (100), 119.0 (100), 104.1 (73), 103.1 (46), 91.1 (35), 77.1 (27).



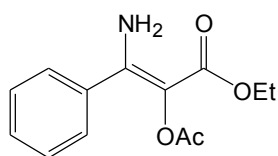
3-Amino-3-(3,4,5-trimethoxy-phenyl)-acrylic acid ethyl ester

3-Amino-3(3,4,5-trimethoxy-phenyl)-acrylic acid ethyl ester: pale yellow plate (EtOAc). mp 76~77 °C. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 6.70 (2H, s), 4.86 (1H, s), 4.10 (2H, q, $J = 7.2$ Hz), 3.80 (6H, s, OMe), 3.79 (3H, s, OMe), 1.24 (3H, t, $J = 7.2$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 170.25, 160.69, 153.34, 139.71, 133.32, 103.57, 84.21, 60.80, 58.87, 56.17, 14.55. **GC-MS** (EI) m/z : 280.9 (M^+ , 100%), 265.9 (7), 235.9 (88), 219.9 (20), 209.0 (91), 194.0 (75), 178.0 (46), 163.1 (41), 162.0 (37), 150.0 (24), 133.0 (27), 118.0 (26), 107.1 (16), 102.8 (25), 91.1 (16), 79.1 (23).



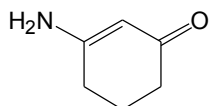
3-Amino-3-(4-nitro-phenyl)-acrylic acid ethyl ester

3-Amino-3-(4-nitro-phenyl)-acrylic acid ethyl ester: yellow plate (EtOAc). mp 92–93 °C. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 8.25 (2H, d, $J = 7.0$ Hz), 7.70 (2H, d, $J = 7.0$ Hz), 4.99 (1H, s), 4.18 (2H, q, $J = 7.1$ Hz), 1.30 (3H, t, $J = 7.1$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 170.22, 157.92, 149.21, 144.22, 127.67, 124.47, 87.62, 59.69, 14.86. **GC-MS** (EI) m/z: 236.0 (M^+ , 68%), 207.9 (21), 190.8 (100), 174.9 (10), 164.0 (98), 148.9 (74), 144.8 (97), 133.0 (14), 117.1 (36), 103.1 (27), 90.1 (31), 89.1 (52).



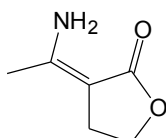
2-Acetoxy-3-amino-3-phenyl-acrylic acid ethyl ester

2-Acetoxy-3-amino-3-phenyl-acrylic acid ethyl ester: pale yellow syrup. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 7.59–7.52 (2H, m), 7.22–7.10 (3H, m), 4.06 (2H, q, $J = 7.1$ Hz), 2.05 (3H, s, Me), 1.03 (3H, t, $J = 7.1$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 162.60, 146.77, 142.47, 131.76, 129.59, 128.72, 128.18, 122.71, 60.75, 14.41, 13.71. **GC-MS** (EI) m/z: 232.1 ($\text{M}^+ - 17$, 5%), 231.1 ($\text{M}^+ - 17$, 80%), 215.9 (40), 185.1 (45), 183.7 (100), 169.9 (45), 158.0 (60), 144.0 (35), 130.0 (11), 117.0 (36), 116.0 (45), 104.0 (38), 89.0 (67), 81.0 (64).



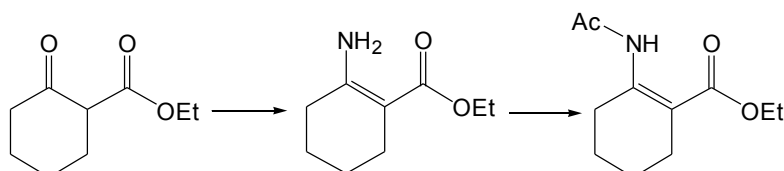
3-Amino-cyclohex-2-enone

3-Amino-cyclohex-2-enone: pale yellow solid (EtOAc). mp 111–112 °C. (Lit.⁵ mp 130–131 °C). $^1\text{H-NMR}$ (300MHz, CD_3OD): δ 5.03 (1H, s), 5.02 (2H, brs), 2.42 (2H, t, $J = 7.1$ Hz), 2.24 (2H, t, $J = 6.3$ Hz), 1.91 (2H, m). $^{13}\text{C-NMR}$ (75MHz, CD_3OD): δ 200.04, 173.60, 98.84, 36.55, 29.74, 23.37. **GC-MS** (EI) m/z: 111.1 (M^+ , 61%), 83.1 (100), 68.1 (9), 55.2 (59), 54.2 (36).



3-(1-Amino-ethylidene)-dihydro-furan-2-one

3-(1-Amino-ethylidene)-dihydro-furan-2-one: Pale brown syrup. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 4.21 (2H, t, $J = 7.9$ Hz), 2.75 (2H, t, $J = 7.9$ Hz), 1.87 (3H, s, Me). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 173.99, 155.27, 86.42, 65.11, 25.79, 20.26. **GC-MS** (EI) m/z: 127.1 (M^+ , 98%), 126.0 (26), 98.1 (39), 97.1 (27), 83.1 (35), 69.1 (100), 54.2 (27).

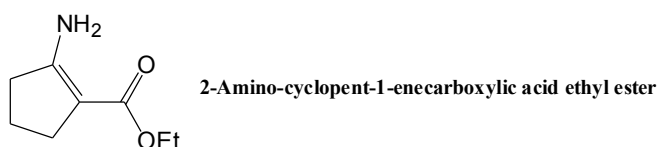


2-Acetylamino-cyclohex-1-enecarboxylic acid ethyl ester

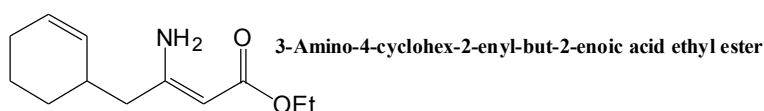
To a solution of 2-oxo-cyclohexanecarboxylic acid ethyl ester (1 mmol) and tetraethyl orthosilicate (2 mmol) in absolute ethanol (5 mL), ammonium acetate (4~5 mmol, 4~5 eq.) was added. The resulting mixture was then stirred at reflux under nitrogen overnight. After removal of the solvents, the residue was esterification with acetic anhydride (2 mmol) and pyridine (4 mmol) in THF (5 mL) for 5 hours. The reaction mixture was diluted with 1N HCl aqueous solution and extracted with ether. The solvents were removed and the residue was chromatographed on silica gel to afford the products (99%, two steps).

2-Amino-cyclohex-1-enecarboxylic acid ethyl ester: $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 4.13 (2H, q, $J = 7.1$ Hz), 2.30-2.15 (4H, m), 1.65-1.52 (4H, m), 1.27 (3H, t, $J = 7.1$ Hz). **GC-MS** (EI) m/z : 169.0 (M^+ , 99%), 167.9 (33), 140.0 (100), 124.0 (88), 122.0 (97), 113.1 (57), 112.0 (60), 96.1 (93), 95.1 (80), 94.1 (57), 81.1 (39), 79.0 (56), 77.1 (35), 69.1 (75), 67.1 (72), 55.2 (43).

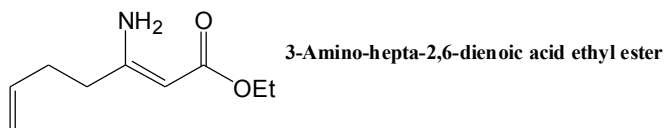
2-Acetylamino-cyclohex-1-enecarboxylic acid ethyl ester: White plate. mp 50–52 °C. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 11.54 (1H, brs), 4.11 (2H, q, $J = 7.1$ Hz), 2.98-2.82 (2H, m), 2.36-2.16 (2H, m), 2.04 (3H, s, CH_3), 1.68-1.45 (4H, m), 1.21 (3H, t, $J = 7.1$ Hz, Me). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 170.30, 168.99, 152.60, 104.58, 60.53, 28.81, 25.81, 24.52, 22.17, 22.04, 14.57. **GC-MS** (EI) m/z : 211.0 (M^+ , 18%), 165.0 (100), 150.0 (5), 140.1 (22), 137.1 (94), 123.1 (74), 113.1 (8), 109.1 (5), 96.2 (66), 79.2 (14), 69.2 (16), 67.2 (25), 54.2 (16), 43.2 (65).



2-Amino-cyclopent-1-enecarboxylic acid ethyl ester: Brown oil. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 4.14 (2H, q, $J = 7.1$ Hz), 2.51-2.41 (4H, m), 1.84-1.73 (2H, m), 1.24 (3H, t, $J = 7.1$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 168.22, 161.85, 95.39, 58.72, 35.17, 29.59, 20.86, 14.74. **GC-MS** (EI) m/z : 155.0 (M^+ , 92%), 154.0(80), 126.0 (97), 110.1 (96), 108.0 (100), 82.1 (98), 80.0 (88), 67.1 (36), 65.0 (25), 54.2 (66), 53.2 (73).

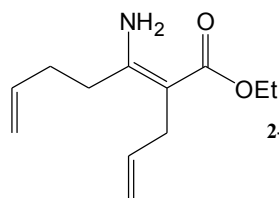


3-Amino-4-cyclohex-2-enoic acid ethyl ester: Yellow oil. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 5.67 (1H, ddd, $J = 3.4, 5.7, 12.6$ Hz), 5.47 (1H, dd, $J = 2.0, 12.6$ Hz), 4.47 (1H, s), 4.07 (2H, q, $J = 7.1$ Hz), 2.38-2.22 (1H, m), 2.10-1.85 (4H, m), 1.80-1.58 (2H, m), 1.54-1.38 (1H, m), 1.28-1.14 (1H, m), 1.20 (3H, t, $J = 7.1$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 170.03, 162.59, 130.17, 128.31, 84.38, 58.50, 43.09, 34.24, 28.67, 25.14, 21.04, 14.57. **GC-MS** (EI) m/z : 209.0 (M^+ , 16%), 180.1(6), 166.1 (15), 136.1 (15), 129.1 (100), 122.1 (16), 107.1 (7), 94.1 (12), 83.1 (37), 81.2 (63), 68.2 (11), 57.2 (86).



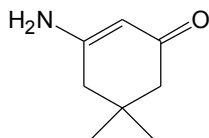
3-Amino-hepta-2,6-dienoic acid ethyl ester: Pale yellow oil. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 5.86-5.69 (1H, m), 5.04 (1H, dd, $J = 1.5, 17.2$ Hz), 4.98 (1H, dd, $J = 1.5, 11.6$ Hz), 4.50 (1H, s), 4.06 (2H, q, $J = 7.1$ Hz), 2.36-2.12 (4H, m), 1.22 (3H, t, $J = 7.1$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 170.48, 163.11, 136.84, 115.86, 83.51, 58.61, 35.74,

32.01, 14.61. **GC-MS** (EI) *m/z*: 169.1 (M^+ , 21%), 154.1 (5), 140.0 (23), 124.1 (32), 108.1 (6), 96.1 (100), 94.1 (46), 82.2 (46), 79.1 (24), 68.1 (23), 55.2 (37).



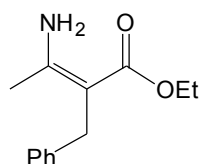
2-Allyl-3-amino-hepta-2,6-dienoic acid ethyl ester

2-Allyl-3-amino-hepta-2,6-dienoic acid ethyl ester: Yellow oil. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 5.90-5.74 (2H, m), 5.05 (1H, dd, $J = 1.3, 18.7$ Hz), 5.00 (1H, dd, $J = 1.3, 9.8$ Hz), 4.93 (1H, dd, $J = 1.5, 18.9$ Hz), 4.88 (1H, dd, $J = 1.5, 10.0$ Hz), 4.10 (2H, q, $J = 7.1$ Hz), 2.94 (2H, dt, $J = 1.5, 5.8$ Hz), 2.32-2.24 (4H, m), 1.23 (3H, t, $J = 7.1$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 170.72, 160.68, 138.68, 137.07, 115.70, 113.19, 91.56, 58.96, 33.12, 32.13, 30.93, 14.56. **GC-MS** (EI) *m/z*: 209.2 (M^+ , 25%), 180.1 (40), 168.2 (16), 167.2 (29), 154.0 (37), 136.2 (100), 134.1 (45), 126.1 (18), 122.1 (45), 120.1 (36), 108.1 (59), 106.1 (23), 95.1 (29), 94.1 (99).



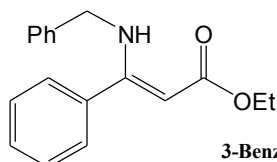
3-Amino-5,5-dimethyl-cyclohex-2-enone

3-Amino-5,5-dimethyl-cyclohex-2-enone: White solid (EtOAc). mp 159–160 °C. (Lit.^{15a} mp 168–169 °C). $^1\text{H-NMR}$ (300MHz, CD_3OD): δ 5.21 (1H, s), 4.88 (2H, brs), 2.28 (2H, s), 2.12 (2H, s), 1.07 (6H, s, Me). $^{13}\text{C-NMR}$ (75MHz, CD_3OD): δ 199.30, 171.92, 97.52, 50.51, 43.42, 34.05, 28.90. **GC-MS** (EI) *m/z*: 139.1 (M^+ , 22%), 124.0 (3), 111.1(5), 96.0 (7), 83.1 (100), 68.1 (8), 55.2 (39), 54.2 (17).



3-Amino-2-benzyl-but-2-enoic acid ethyl ester

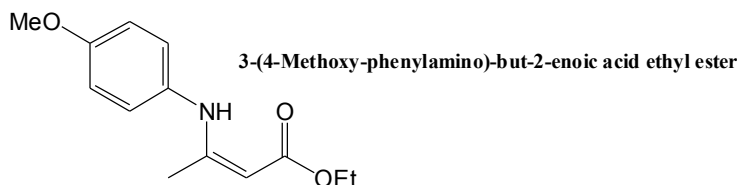
3-Amino-2-benzyl-but-2-enoic acid ethyl ester: Yellow syrup. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 7.20-7.00 (5H, m), 4.01 (2H, q, $J = 7.1$ Hz), 3.52 (2H, s), 1.83 (3H, s, Me), 1.09 (3H, t, $J = 7.1$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 171.07, 158.59, 143.16, 128.47, 128.21, 125.76, 93.39, 59.33, 33.03, 21.37, 14.89. **GC-MS** (EI) *m/z*: 218.9 (M^+ , 85%), 203.8 (6), 189.9 (37), 173.0 (78), 157.8 (17), 143.9 (100), 131.0 (75), 115.0 (14), 105.0 (24), 103.0 (39), 96.0 (41), 91.0 (67), 77.1 (36).



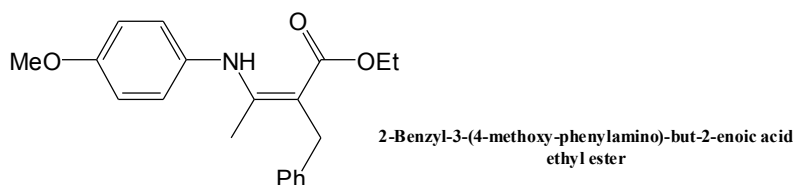
3-Benzylamino-3-phenyl-acrylic acid ethyl ester

3-Benzylamino-3-phenyl-acrylic acid ethyl ester: Yellow needle. mp 60–61 °C. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 7.40-7.02 (10H, m), 4.58 (1H, s), 4.15 (2H, d, $J = 6.5$ Hz), 4.06 (2H, q, $J = 7.1$ Hz), 1.17 (3H, t, $J = 7.1$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 170.78, 165.15, 139.68, 136.38, 129.67, 129.02, 128.79, 128.29, 127.60, 127.27, 86.76,

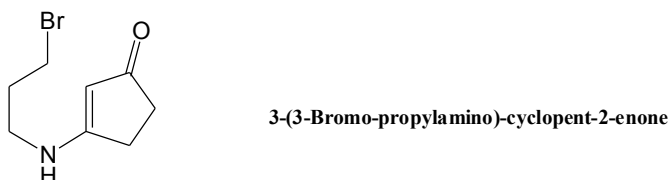
59.17, 48.76, 15.00. **GC-MS** (EI) m/z: 281.1 (M^+ , 65%), 280.1(63), 252.0 (37), 234.0 (72), 207.9 (87), 192.9 (43), 177.8 (10), 164.9 (8), 146.0 (22), 131.1 (22), 106.1 (58), 104.1 (76), 103.1 (51), 91.0 (100), 77.1 (41), 65.1 (52).



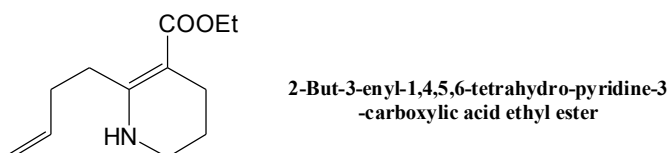
3-(4-Methoxy-phenylamino)-but-2-enoic acid ethyl ester: Brown oil. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 7.00 (2H, d, $J = 8.9$ Hz), 6.84 (2H, d, $J = 8.9$ Hz), 4.64 (1H, s), 4.13 (2H, q, $J = 7.1$ Hz), 3.78 (3H, s, OMe), 1.87 (3H, s, Me), 1.27 (3H, t, $J = 7.1$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 171.12, 160.61, 158.12, 132.81, 127.42, 114.85, 85.42, 59.23, 56.05, 20.67, 15.24. **GC-MS** (EI) m/z: 234.8 (M^+ , 66%), 219.9 (5), 188.8 (71), 173.8 (68), 159.8 (21), 147.6 (100), 145.8 (62), 132.0 (22), 118.0 (38), 107.0 (28), 92.0 (31), 76.8 (61).



2-Benzyl-3-(4-methoxy-phenylamino)-but-2-enoic acid ethyl ester: Brown syrup. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 7.28-7.11 (5H, m), 6.98 (2H, d, $J = 8.7$ Hz), 6.82 (2H, d, $J = 8.7$ Hz), 4.14 (2H, q, $J = 7.1$ Hz), 3.76 (3H, s, OMe), 3.71 (2H, s), 1.90 (3H, s, Me), 1.21 (3H, t, $J = 7.1$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 171.41, 159.13, 157.66, 143.05, 133.25, 128.54, 128.24, 127.36, 125.83, 114.61, 94.27, 59.52, 55.83, 33.27, 17.19, 14.94. **GC-MS** (EI) m/z: 325.0 (M^+ , 77%), 309.9 (14), 296.0 (12), 280.0 (20), 263.9 (6), 251.9 (100), 235.9 (59), 219.9 (45), 201.8 (11), 173.9 (74), 147.9 (99), 129.1 (22), 107.0 (41), 91.0 (82), 76.9 (83).

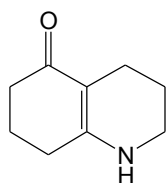


3-(3-Bromo-propylamino)-cyclopent-2-enone: Yellow oil. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 6.70-6.56 (1H, brs), 5.05 (1H, s), 3.45 (2H, t, $J = 6.2$ Hz), 3.33 (2H, t, $J = 6.1$ Hz), 2.66-2.54 (2H, m), 2.42-2.31 (2H, m), 2.14 (2H, quintet, $J = 6.2$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 205.33, 178.24, 99.16, 43.75, 34.02, 31.65, 30.87, 28.53. **GC-MS** (EI) m/z: 138.1 (M^+ -Br, 6%), 137.1 (M^+ -HBr, 100%), 136.1 (49), 109.1 (47), 108.1 (100), 94.1 (52), 81.1 (43), 80.1 (39).



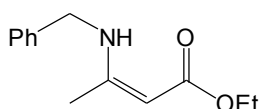
2-But-3-enyl-1,4,5,6-tetrahydro-pyridine-3-carboxylic acid ethyl ester: Brown oil. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 5.90-5.74 (1H, m), 5.00 (1H, dd, $J = 1.6, 15.6$ Hz), 4.91 (1H, dd, $J = 1.4, 10.2$ Hz), 4.28 (1H, brs), 4.06 (2H, q, $J = 7.1$ Hz), 3.17-3.08 (2H, m), 2.62 (2H, t, $J = 7.4$ Hz), 2.40-2.20 (4H, m), 1.80-1.65 (2H, m), 1.21 (3H, t, $J = 7.1$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 168.56, 156.58, 138.14, 114.88, 91.65, 58.66, 41.71, 34.38, 33.16, 22.88, 21.61, 14.68.

GC-MS (EI) *m/z*: 209.2 (M^+ , 29%), 194.1 (7), 180.1 (45), 164.1 (34), 152.1 (5), 136.0 (100), 122.1 (25), 120.1 (18), 108.1 (21), 94.1 (30).



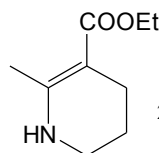
2,3,4,6,7,8-Hexahydro-1H-quinolin-5-one

2,3,4,6,7,8-Hexahydro-1H-quinolin-5-one: Yellow oil. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 5.92 (1H, brs), 3.19-3.13 (2H, m), 2.27-2.15 (6H, m), 1.98-1.75 (2H, m), 1.74-1.63 (2H, m). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 194.25, 160.88, 104.34, 41.75, 36.74, 29.50, 22.09, 21.41, 19.45. **GC-MS** (EI) *m/z*: 151.0 (M^+ , 93%), 136.0 (71), 123.0 (100), 108.0 (8), 95.1 (75), 94.1 (78), 80.1 (20), 67.1 (23), 55.2 (17), 53.2 (18).



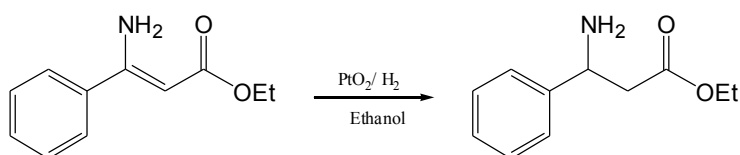
3-Benzylamino-but-2-enoic acid ethyl ester

3-Benzylamino-but-2-enoic acid ethyl ester: Yellow oil. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 7.26-7.15 (5H, m), 4.43 (1H, s), 4.27 (2H, d, $J = 6.2$ Hz), 3.98 (2H, q, $J = 7.1$ Hz), 1.77 (3H, s, Me), 1.13 (3H, t, $J = 7.1$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 170.58, 161.76, 138.80, 128.78, 127.33, 126.71, 83.27, 58.35, 46.77, 19.31, 14.65. **GC-MS** (EI) *m/z*: 218.9 (M^+ , 78%), 189.9 (72), 174.0 (56), 171.9 (77), 145.9 (84), 143.9 (49), 131.0 (37), 114.9 (7), 105.1 (48), 103.9 (52), 90.9 (100), 84.0 (32), 76.9 (23), 65.2 (74).



2-Methyl-1,4,5,6-tetrahydro-pyridine-3-carboxylic acid ethyl ester

2-Methyl-1,4,5,6-tetrahydro-pyridine-3-carboxylic acid ethyl ester: Pale yellow oil. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 4.12 (1H, brs), 4.03 (2H, q, $J = 7.1$ Hz), 3.15-3.08 (2H, m), 2.30 (2H, t, $J = 6.2$ Hz), 2.15 (3H, s, Me), 1.70 (2H, qui, $J = 6.2$ Hz), 1.18 (3H, t, $J = 7.1$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 169.18, 152.96, 92.08, 58.69, 41.86, 22.73, 21.86, 21.62, 14.80. **GC-MS** (EI) *m/z*: 169.0 (M^+ , 48%), 140.0 (64), 124.0 (100), 122.0 (8), 96.1 (97), 94.1 (28), 81.1 (14), 67.2 (9), 55.2 (25).



3-Amino-3-phenyl-propionic acid ethyl ester

Procedure for hydrogenation of 3-Amino-3-phenyl-acrylic acid ethyl ester:

To a solution of 3-Amino-3-phenyl-acrylic acid ethyl ester (1 mmol) in 4 mL of ethanol was added PtO_2 (5 mg). The resulting mixture was then degassed and purged three times with hydrogen. The mixture was then stirred under hydrogen (1 atm.) at room temperature for 20 hr. After filtration, the solvent was removed and the residue was chromatographed on silica gel to give hydrogenation product 3-amino-3-phenyl-propionic acid ethyl ester in 98% yield as a pale yellow syrup.

3-Amino-3-phenyl-propionic acid ethyl ester: Pale yellow syrup. $^1\text{H-NMR}$ (300MHz, CD_3COCD_3): δ 7.30-7.10 (5H, m), 4.31 (1H, m), 4.03 (2H, q, $J = 7.1$ Hz), 2.54 (2H, d, $J = 6.9$ Hz), 1.62 (2H, brs), 1.13 (3H, t, $J = 7.1$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 171.92, 144.72, 128.55, 127.31, 126.18, 60.41, 52.63, 44.20, 14.15. **GC-MS** (EI) m/z : 193.2 (M^+ , 22%), 164.1 (25), 146.0 (12), 119.1 (34), 107.2 (31), 106.0 (100) 104.1 (72), 91.1 (15), 79.1 (73), 77.0 (71).



Procedure to indolizidine derivative:

β -ketone ester (1mmol), bromopropylammonium acetate (1.2 mmol) and tetraethyl orthosilicate (2 mmol, 2.0 equiv.) in absolute ethanol (5 mL) were stirred at reflux. The reaction progress was monitored by thin-layer chromatography. The solvent was then removed under reduced pressure and the residue was dissolved in dichloromethane (5 mL) and iodine (1.2 mmol,) and Na_2CO_3 (3 mmol) was added. The resulting mixture was stirred at room temperature for 20 hours. The reaction was monitored by thin-layer chromatography. The reaction mixture was diluted with water (20 mL) and extracted with dichloromethane (3×10 mL). The organic phases were combined and washed with water and dried over anhydrous Na_2SO_4 . After removal of the solvent, the residue was chromatographed on silica gel to afford the pure products as pale yellow syrup (90% yield).

3-Iodomethyl-1,2,3,5,6,7-hexahydro-indolizine-8-carboxylic acid ethyl ester: $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 4.07 (2H, q, $J = 7.1$ Hz), 3.48-3.34 (1H, m), 3.31 (1H, dd, $J = 2.4, 10.4$ Hz), 3.23-3.10 (1H, m), 3.18 (1H, dd, $J = 6.9, 10.4$ Hz), 3.10-2.91 (3H, m), 2.40-2.20 (2H, m), 2.20-1.98 (1H, m), 1.90-1.70 (3H, m), 1.21 (3H, t, $J = 7.1$ Hz). $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 168.70, 158.56, 88.99, 63.23, 58.65, 42.97, 30.65, 27.91, 21.60, 21.48, 14.83, 10.44. **GC-MS** (EI) m/z : 335.1 (M^+ , 33%), 306.0 (16), 290.0 (31), 262.0 (10), 208.1 (36), 194.2 (100), 180.1 (21), 166.1 (24), 162.1 (19), 148.1 (42), 134.0 (72), 120.1 (45), 106.1 (15), 91.0 (8).