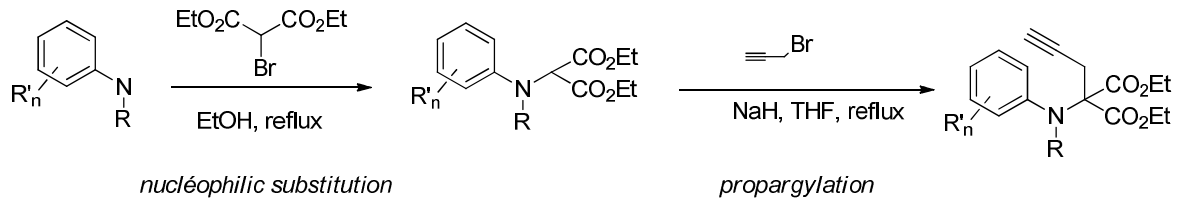
Gold-catalyzed formation of dihydroquinolines and indoles from *N*-aminophenyl propargyl malonates

1. General procedures

General procedure 5.1 : Synthesis of substrates from *N*-alkylanilines



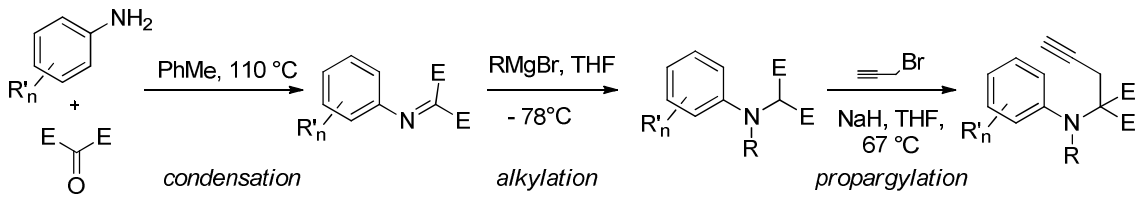
Condensation of N-*methylaniline on diethylbromomalonate :*

To a solution of *N*-methyl aniline (2 eq.) in ethanol (1M) was added diethylbromalonate (1 eq.). The reaction was then heated up to reflux overnight. After the complete consumption of the diethyl malonate (TLC), the reaction mixture was cooled to room temperature, concentrated under reduced pressure. The resulting crude material was dissolved in water and extracted with AcOEt (3x); then washed water (5x); dried over Magnesium sulfate and concentrated under reduced pressure to afford the pure malonate.

Propargylation of monoalkylated diethyl malonates:

To a solution of diethyl malonate (1 eq.) and propargyl bromide (3 eq.) in THF (0.25 M) was added portionwise NaH (2eq) at 0°C. The reaction was then heated up to relux overnight. After the complete consumption of the malonate (TLC), the reaction mixture was cooled to room temperature, quenched with a saturated solution of NH_4Cl, extracted with AcOEt (3x); washed with small amounts of water (5x); dried over Magnesium sulfate and concentrated under reduced pressure. Purification by flash column chromatography generally afforded the pure monoalkylated malonate.

General procedure 5.2 : Synthesis of substrates from anilines



Condensation of aniline on diethylketomalonate[2] *:*

To a solution of diethyl ketomalonate (1 equiv.) in toluene (0.5 M) was added the aniline (1 equiv.). The reaction was heated up to reflux in a Dean-Stark apparatus. After the complete consumption of the aniline (TLC), the reaction mixture was cooled to room temperature, concentrated under reduced pressure. The resulting crude material was used in the next step without further purification.

Alkylation of the imine[3] *:*

To a solution of the crude immine (1.0 equiv.) in THF (0.5 M.) at -78°C was added dropwise a solution of RMgBr (1.5 equiv.). After the complete consumption of the immine (TLC), the reaction mixture was quenched with a saturated aqueous NH_4Cl solution. The reaction mixture was allowed to warm to room temperature. Then the mixture was extracted with ethyl acetate (3 times), dried over Magnesium sulfate and concentrated under reduced pressure. The resulting malonate was used in the next step without further purification.

propargylation of monoalkylated diethyl malonates:

To a solution of diethyl malonate (1 equiv.) and propargyl bromide (3 equiv.) in THF (0.25 M) was added portionwise NaH (2equiv.) at 0°C. The reaction was then heated up to relux overnight. After the complete consumption of the malonate (TLC), the reaction mixture was cooled to room temperature, quenched with a saturated solution of NH_4Cl, extracted with AcOEt (3x); washed with small amounts of water (5x); dried over Magnesium sulfate and concentrated under reduced pressure. Purification by flash column chromatography (generally afforded the pure monoalkylated malonate).

General Procedure 5.3: Synthesis of 1,2-dihydroquinolines:

To a solution of the propargyl derivative in nitromethane (500 µl) was added the gold catalyst (0.01 equiv.). After the complete consumption of the starting material, the mixture was concentrated under reduced pressure. The resulting crude material was dissolved in CH_2Cl_2 and 5 % of *p*TSA was added to the solution. After the complete consumption of the methylene derivative, a saturated aqueous $NaHCO_3$ solution was added to the mixture. The solution was extracted with AcOEt (3 times); dried over Magnesium sulfate and concentrated under reduced pressure to afford the pure dihydroquinoline.

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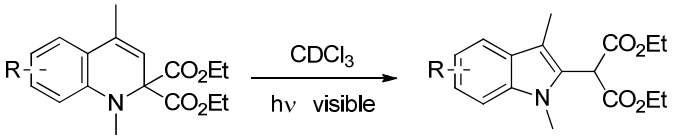
[2] Trost, B.M. ; Marrs, C.M., *J. Am. Chem. Soc.* **1993**, *115*, 6637.

[3] Niwa, Y.; Takayama, K.; Shimizu, M., *Tetrahedron Lett.*. **2001**, *42*,5473.

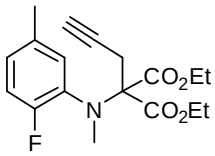
General procedure 5.4 : Isomerisation into indoles :



A solution of 0.1 mmol of dihydroquinoline in 500 ul of $CDCl_3$ in an NMR tube was left under the sunlight until the complete consumption of the dihydroquinoline. The reaction mixture was concentrated under reduced pressure. The resulting crude material was purified by column chromatography on silica gel (petroleum ether:ethyl acetate 90 : 10 as eluent) to afford the pure indole.

2. Preparation of the starting substrates

2-[(2-Fluoro-5-methyl-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester (5.39) $C_{18}H_{22}FO_4N$ **MW = 335.4g.mol^{-1}**



Procedure : see general procedure 5.2

Product: yellow oil.

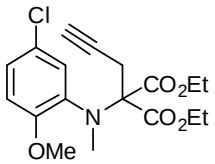
Yield: 11 % (m = 89 mg) over 3 steps

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.25 (d, *J* = 7.1 Hz, 1H), 6.94-6.83 (m, 2H), 4.30 (q, *J* = 7.1 Hz, 4H), 3.03 (s, 3H), 2.78 (d, *J* = 2.5 Hz, 2H), 2.07 (t, *J* = 2.5 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.6 (C x2), 158.6 (C) (d, *J* = 245.6 Hz), 134.3 (C), 133.598 (C) (d, *J* = 1.7 Hz), 131.301 (CH) (d, *J* = 2.2 Hz), 127.826 (CH) (d, *J* = 7.8 Hz), 116.0 (CH) (d, *J* = 21.2 Hz), 79.0 (C), 73.4 (C), 71.6 (CH), 61.7 (CH_2 x2), 40.1 (CH_3) (d, *J* = 3.4 Hz), 26.2 (CH_2), 20.6 (CH_3),14.2 (CH_3 x2)

HRMS: $C_{18}H_{22}FO_4N$ [M+Na$^+$]; calculated: 335.1533; found: 335.15

1,3-diethyl 2-[(5-chloro-2-methoxyphenyl)(methyl)amino]-2-(prop-2-yn-1-yl)propanedioate (5.41) $C_{18}H_{22}ClNO_5$ **MW = 367.3 g.mol^{-1}**



Procedure : see general procedure 5.2

Product: brown oil.

Yield: 13 % (m = 117 mg) over 3 steps

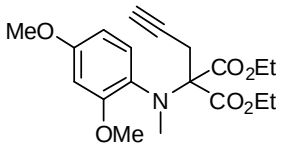
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37 (d, *J* = 2.5 Hz, 1H), 7.10 (dd, *J* = 2.5 Hz, *J* =

8.7 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 1H), 4.29 (dq, *J* = 2.5 Hz, *J* = 7.1 Hz, 4H), 3.74 (s, 3H), 2.98 (s, 3H), 2.74 (d, *J* = 2.5 Hz, 2H), 2.02 (t, *J* = 2.5 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.9 (2C), 156.0, 137.5, 130.7, 126.6, 125.2, 112.8, 79.2, 73.3, 71.5, 61.6 (2C), 55.6, 40.1, 26.0, 14.1 (2C).

HRMS: $C_{18}H_{22}ClNO_45$[M+Na^+]; calculated: 367.1187; found: 367.1187.

1,3-diethyl 2-[(2,4-dimethoxyphenyl)(methyl)amino]-2-(prop-2-yn-1-yl)propanedioate (5.42) $C_{19}H_{25}NO_6$ **MW = 363.4 g.mol^{-1}**



Procedure : see general procedure 5.2

Product: brown oil.

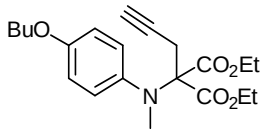
Yield: 46 % (m = 420 mg) over 3 steps

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.34 (d, *J* = 8.2 Hz, 1H), 6.40 (s, 1H), 6.39 (d, *J* = 8.2 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 4H), 3.79 (s, 3H), 3.73 (s, 3H) 2?98 (s, 3H), 2.67 (d, *J* = 2.5 Hz, 2H), 2.02 (t, *J* = 2.5 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.2 (2C), 159.1, 158.6, 132.1, 128.9, 103.9, 99.4, 79.7, 73.4, 71.2, 61.3 (2C), 55.4, 55.2, 40.2, 26.0, 14.2 (2C).

HRMS: $C_{19}H_{25}NO_6$[M+Na^+]; calculated: 363.1682; found: 362.1689

2-[(4-Butoxy-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester (5.49) $C_{21}H_{29}O_5N$ **MW = 375.5 g.mol^{-1}**



Procedure : see general procedure 5.2

Product: yellow oil.

Yield: 37 % (m = 351 mg) over 3 steps

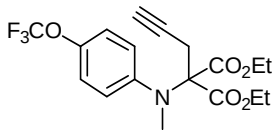
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.19 (d, *J* = 8.9 Hz, 2H), 6.80 (d, *J* = 8.9 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 4H), 3.93 (t, *J* = 6.5 Hz, 2H), 3.00 (s, 3H), 2.72 (d, *J* = 2.6 Hz, 2H), 2.09 (t, *J* = 2.6 Hz, 1H), 1.79-1.72 (m, 2H), 1.49 (q, *J* = 7.4 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 6H), 0.98 (t, *J* = 7.4 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.8 (C x2), 157.2 (C), 141.0 (C), 145.7 (C), 128.8 (CH x2), 114.5 (CH x2), 79.3 (C), 74.1 (C), 71.6 (CH), 67.9 (CH_2), 61.6 (CH_2 x2), 41.4 (CH_3), 31.4 (CH_2), 26.5 (CH_2), 19.3 (CH_2), 14.2 (CH_3 x2), 13.9 (CH_3)

HRMS: $C_{21}H_{29}O_5N$ [M+Na^+]; calculated: 375.2046; found: 375.2053

IR (CCl_4): ν (cm^{-1}) 3315, 2962, 2874, 1732, 1509, 1242, 1064

2-[Methyl-(4-trifluoromethoxy-phenyl)-amino]-2-prop-2-ynyl-malonic acid diethyl ester (5.51) $C_{18}H_{20}O_5NF_3$ **MW = 387.4 g.mol^{-1}**



Procedure : see general procedure 5.1

Product: yellow oil.

Yield: 31 % (m = 299 mg) over 3 steps

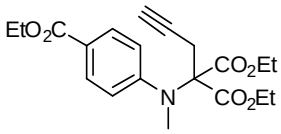
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.26 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 4H), 3.10 (s, 3H), 2.91 (d, *J* = 2.7 Hz, 2H), 2.13 (t, *J* = 2.7 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.5 (C x2), 147.5 (C), 145.7 (C) (q, *J* = 1.9 Hz), 126.8 (CH x2), 121.2 (CH x2), 120.5 (C) (q, *J* = 255.2 Hz), 78.9 (C), 73.9 (C), 71.9 (CH), 62.0 (CH_2 x2), 40.8 (CH_3), 26.5 (CH_2), 14.0 (CH_3 x2)

HRMS: $C_{18}H_{20}O_5NF_3$ [M+Na$^+$]; calculated: 387.1294; found: 387.1309

IR (CCl_4): ν (cm^{-1}) 3314, 2983, 2939, 1736, 1510, 1225, 1169, 1063

2-[(4-Ethoxycarbonyl-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester (5.53) $C_{20}H_{25}O_6N$ **MW = 375.4 g.mol^{-1}**



Procedure : see general procedure 5.2

Product: yellow oil.

Yield: 39 % (m = 365 mg) over 3 steps

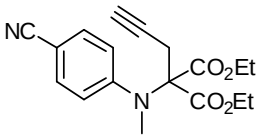
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.87 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 4H), 3.16 (s, 3H), 3.10 (d, *J* = 2.5 Hz, 2H), 2.06 (t, *J* = 2.5 Hz, 1H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.3 (C x2), 166.5 (C), 153.0 (C), 130.4 (CH), 122.8 (CH), 119.4 (CH), 78.8 (C), 73.8 (C), 92.0 (CH), 62.4 (CH_2 x2), 60.6 (CH_2), 40.0 (CH_3), 26.2 (CH_2), 14.4 (CH_3), 14.0 (CH_3 x2).

HRMS: $C_{20}H_{25}O_6N$ [M+Na$^+$]; calculated: 375.1682; found: 375.1671

IR (CCl_4): ν (cm^{-1}) 3314, 2982, 1963, 1740, 1713, 1607, 1519, 1261, 1190, 105

2-[(4-Cyano-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester (5.55) $C_{18}H_{20}O_4N_2$ **MW = 328.4 g.mol^{-1}**



Procedure : see general procedure 5.2

Product: yellow oil.

Yield: 25 % (m = 202 mg) over 3 steps

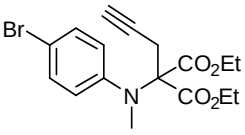
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.52 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 4H), 3.24 (s, 3H), 3.20 (d, *J* = 2.6 Hz, 2H), 2.13 (t, *J* = 2.6 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.9 (C x2), 152.8 (C), 132.7 (CH x2), 119.6 (CH x2), 118.9 (C), 112.7 (C) 78.4 (C), 73.7 (C), 72.3 (CH), 62.6 (CH_2 x2), 39.4 (CH_3), 26.2 (CH_2), 14.2 (CH_3 x2)

HRMS: $C_{18}H_{20}O_4N_2$ [M+Na$^+$]; calculated: 328.1423; found: 328.1431

IR (CCl_4): ν (cm^{-1}) 3313, 2984, 2224, 1743, 1607, 1517, 1232, 1057

2-[(4-Bromo-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester (5.61) $C_{17}H_{20}O_4NBr$ **MW = 382.2 g.mol^{-1}**



Procedure : see general procedure 5.2

Product: yellow oil.

Yield: 27 % (m = 261 mg) over 3 steps

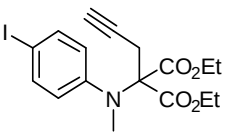
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 4H), 3.05 (s, 3H), 2.87 (d, *J* = 2.7 Hz, 2H), 2.09 (t, *J* = 2.7 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.5 (C x2), 147.9 (C), 131.7 (CH x2), 127.0 (CH x2), 117.4 (C), 78.9 (C), 73.8 (C), 71.9 (CH), 62.0 (CH_2 x2), 40.7 (CH_3), 26.4 (CH_2), 14.1 (CH_3 x2)

HRMS: $C_{17}H_{20}O_4NBr$ [M+Na$^+$]; calculated: 381.0576; found: 381.0571

IR (CCl_4): ν (cm^{-1}) 3314, 2983, 1732, 1493, 1187, 1063

2-[(4-Iodo-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester (5.63) $C_{17}H_{20}IO_4N$ **MW = 429.2 g.mol^{-1}**



Procedure : see general procedure 5.2

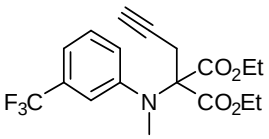
Product: yellow oil.

Yield: 17 % over 3 steps (m = 187 mg) over 3 steps

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 4H), 3.09 (s, 3H), 2.92 (d, *J* = 2.7 Hz, 2H), 2.13 (t, *J* = 2.7 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.5 (C x2), 148.6 (C), 137.7 (CH x2), 126.9 (CH x2), 87.9 (CH), 78.9 (C), 73.7 (C), 72.0 (CH), 62.0 (CH_2 x2), 40.64 (CH_2), 26.4 (CH_2), 14.9 (CH_3), 14.1 (CH_3 x2).

2-[Methyl-(3-trifluoromethyl-phenyl)-amino]-2-prop-2-ynyl-malonic acid diethyl ester (5.65) $C_{18}H_{20}O_4NF_3$ **MW = 371.4 g.mol^{-1}**



Procedure : see general procedure 5.2

Product: yellow oil.

Yield: 15 % (m = 151 mg) over 3 steps

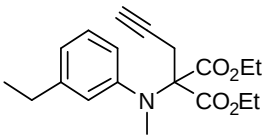
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 (s, 1H), 7.38-7.27 (m, 3H), 4.29 (dq, *J* = 7.0 Hz, *J* = 1.3 Hz, 4H), 3.11 (s, 3H), 2.94 (d, *J* = 2.5 Hz, 2H), 2.10 (t, *J* = 2.5 Hz, 1H), 1.27 (t, *J* = 7.0 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.4 (C x2), 149.5 (C), 131.2 (q, *J* = 31.8 Hz) (C), 129.1 (CH), 127.5 (CH), 124.1 (C) (q, *J* = 271.1 Hz), 121.1 (CH), 120.1 (CH), 78.7 (C), 73.8 (C), 72.0 (CH), 62.1 (CH_2 x2), 40.3 (CH_3), 26.5 (CH_2),14.0 (CH_3 x2).

HRMS: $C_{18}H_{20}O_4NF_3$ [M+Na^+]; calculated: 371.1344; found: 371.1347

IR (CCl_4): ν (cm^{-1}) 3314, 2983, 2939, 1736, 1586, 1476, 1229, 1063.

2-[(3-Ethyl-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester (5.68) $C_{19}H_{25}NO_4$ **MW = 331.4 g.mol^{-1}**



Procedure : see general procedure 5.2

Product: yellow oil.

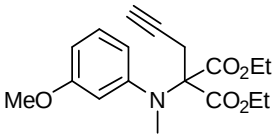
Yield: 27 % (m = 264 mg) over 3 steps

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.18 (t, *J* = 7.8 Hz, 1H), 7.06 (s, 1H), 7.99 (dd, *J* = 7.8 Hz, *J* = 1.7 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 4H), 3.07 (s, 3H), 2.83 (d, *J* = 2.7 Hz, 2H), 2.61 (q, *J* = 7.6 Hz, 2H), 2.09 (t, *J* = 2.7 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 6H), 1.22 (t, *J* = 7.6 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.8 (C x2), 148.5 (C), 144.8 (C), 128.6 (CH), 125.7 (CH), 124.4 (CH) 122.9 (CH), 79.3 (C), 74.0 (C), 71.6 (CH), 61.8 (CH_2 x2), 41.0 (CH_3), 28.8 (CH_2), 26.5 (CH_2), 15.4 (CH_3), 14.1 (CH_3 x2)

IR (CCl_4): ν (cm^{-1}) 3315, 2967, 2935, 1733, 1602, 1487, 1227, 1186, 1064.

2-[(3-Methoxy-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester (5.71) $C_{18}H_{23}O_5N$ **MW = 333.4 g.mol^{-1}**



Procedure : see general procedure 5.2

Product: yellow oil.

Yield: 27 % (m = 261 mg) over 3 steps

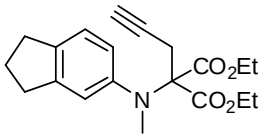
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.15 (t, *J* = 8.1Hz, 1H), 6.79 (t, *J* = 2.3 Hz, 1H), 6.73 (dd, *J* = 8.1 Hz, *J* = 1.8 Hz, 1H), 6.65 (dd, *J* = 8.1 Hz, *J* = 2.3Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 4H), 3.77(s, 1H), 3.06 (s, 3H), 2.87 (d, *J* = 2.7 Hz, 2H), 2.10 (t, *J* = 2.7 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 6H

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.7 (C x2), 159.9 (C), 149.9 (C), 129.3 (CH), 117.5 (CH), 111.6 (CH) 110.3 (CH), 79.2 (C), 73.2 (C), 71.8 (CH), 61.9 (CH_2 x2), 55.2 (CH_3), 41.0 (CH_3), 26.4 (CH_2),14.1 (CH_3 x2)

HRMS: $C_{18}H_{23}O_5N$ [M+Na$^+$]; calculated: 333.1576; found: 333.1581

IR (CCl_4): ν (cm^{-1}) 3314, 2983, 2939, 1736, 1599, 1488, 1227, 1064

1,3-diethyl 2-[(2,3-dihydro-1H-inden-5-yl)(methyl)amino]-2-(prop-2-yn-1-yl)propanedioate (5.74) $C_{20}H_{25}NO_4$ **MW = 343.4 g.mol^{-1}**



Procedure : see general procedure 5.2

Product: brown oil.

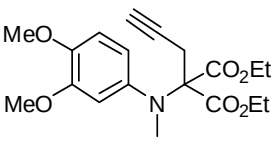
Yield: 20 % (m = 205 mg) over 3 steps

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.12-7.08 (m, 2H), 7.00 (dd, *J* = 2.0 Hz, *J* = 8.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 4H), 3.03 (s, 3H), 2.86 (t, *J* = 7.4 Hz, 4H), 2.78 (d, *J* = 2.6 Hz, 2H), 2.10-2.03 (m, 3H), 1.31 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.9 (2C), 146.7, 144.9, 141.3, 124.8, 124.3, 122.9, 79.4, 74.1, 71.6, 61.8 (2C), 41.4, 32.9, 32.4, 26.6, 25.6, 14.1 (2C).

HRMS: $C_{20}H_{25}NO_4$ [M+Na$^+$]; calculated: 343.1784; found: 343.1790.

2-[(3,4-Dimethoxy-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester (5.77) $C_{19}H_{25}O_6N$ **MW = 363.4 g.mol^{-1}**



Procedure : see general procedure 5.2

Product: yellow oil.

Yield: 13 % over 3 steps

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.96 (s, 1H), 6.76 (s, 2H), 4.30 (q, *J* = 7.1 Hz, 4H), 3.85 (s, 3H), 3.84 (s, 3H), 3.01 (s, 3H), 2.72 (d, *J* = 2.6 Hz, 2H), 2.10 (t, *J* = 2.6 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 6H)

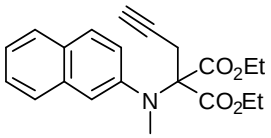
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.7 (C x2), 148.5 (C), 147.2 (C), 141.4 (C), 119.0 (CH), 112.2 (CH), 110.8 (CH), 79.4 (C), 74.1 (C), 71.8 (CH), 61.7 (CH_2 x2), 56.0 (CH_3), 55.9 (CH_3), 41.4 (CH_3), 26.5 (CH_2), 14.2 (CH_3 x2).

HRMS: $C_{19}H_{25}O_6N$ [M+Na^+]; calculated: 363.1682; found: 363.1681

IR (CCl_4): ν (cm^{-1}) 3314, 2983, 2957, 1733, 1510, 1239, 1185, 1034.

2-(Methyl-naphthalen-2-yl-amino)-2-prop-2-ynyl-malonic acid diethyl ester (5.80)

$C_{21}H_{23}O_4N$ **MW = 353.4 g.mol^{-1}**



Procedure : see general procedure 5.2

Product: yellow oil.

Yield: 50 % (440 mg) over 3 steps

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79-7.72 (m, 3H), 7.58 (d, *J* = 2.1 Hz, 1H), 7.47-7.38 (m, 3H), 4.33 (q, *J* = 7.1 Hz, 4H), 3.19 (s, 3H), 2.95 (d, *J* = 2.7 Hz, 2H), 2.13 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 6H)

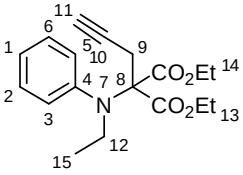
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.4 (C x2), 146.7 (C), 134.3 (C), 131.4 (C), 129.1 (CH), 128.1 (CH), 128.0 (CH), 126.7 (CH), 125.7 (CH x2), 122.9 (CH), 79.8 (C), 74.6 (C), 72.4 (CH), 62.5 (CH_2 x2), 41.6 (CH_3), 27.0 (CH_2), 14.7 (CH_3 x2)

HRMS: $C_{21}H_{23}O_4N$ [M+Na^+]; calculated: 353.1627; found: 353.1625

IR (CCl_4): ν (cm^{-1}) 3314, 2982, 2926, 1735, 1599, 1231, 1186, 1063.

2-(Ethyl-phenyl-amino)-2-prop-2-ynyl-malonic acid diethyl ester (5.87)

$C_{18}H_{23}O_4N$ **MW = 317.4 g.mol^{-1}**



Procedure : see general procedure 5.1 starting (with) 10 mmol of N-ethylanilin

Product: yellow oil.

Yield: 17 % (m = 540 mg) over 2 steps

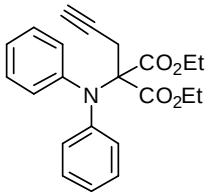
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.35-7.22 (m, 5H **aromatic H**), 4.33 (dq, *J* = 7.1 Hz, *J* = 1.6 Hz, 4H, **CH_2 esters**), 3.34 (q, *J* = 7.0 Hz, 2H, **H12**), 2.70 (d, *J* = 2.7Hz, 2H, **H9**), 2.08 (t, *J* = 2.7 Hz, 1H, **H11**), 1.35 (t, *J* = 7.1 Hz, 6H, **CH_3 esters**), 0.98 (t, *J* = 7.0Hz, 3H, **H15**)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.3 (C x2, **C=O esters**), 145.5 (C, **C4**), 129.8 (CH x2, **C3 and C5**), 128.7 (CH x2, **C2 and C6**), 126.3 (CH, **C1**), 79.4 (C, **C5**), 74.6 (C, **C8**), 71.5 (CH, **C11**), 61.6 (CH_2 x2, **esters**), 47.6 (CH_2, **C12**), 26.7 (CH_2, **C19**), 14.9 (CH_3, **C15**), 14.1 (CH_3 x2, **esters**)

HRMS: $C_{18}H_{23}O_4N$ [M+Na^+]; calculated: 317.1627; found: 317.1627

IR (CCl_4): ν (cm^{-1}) 3315, 2982, 2936, 1736, 1493, 1231

2-Diphenylamino-2-prop-2-ynyl-malonic acid diethyl ester (5.89) $C_{22}H_{23}O_4N$ **MW = 365.4 g.mol^{-1}**



Procedure : see general procedure 5.2

Product: yellow oil.

Yield: 36 % (m = 341 mg) over 3 steps

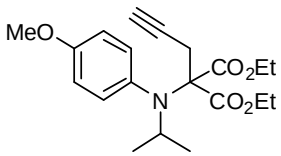
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.29 (t, *J* = 8.2 Hz, 4H), 7.09 (t, *J* = 8.2 Hz, 6H), 4.24 (q, *J* = 7.0 Hz, 4H), 3.10 (d, *J* = 2.0Hz, 2H), 2.05 (t, *J* = 2.0 Hz, 1H), 1.23 (t, *J* = 7.0 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.6 (C x2), 145.8 (C x2), 128.5 (CH x4), 125.0 (CH x4), 123.4 (CH x2), 78.8 (C), 73.0 (C), 71.8 (CH), 62.2 (CH_2 x2), 28.1 (CH_2), 13.9 (CH_3 x2).

HRMS: $C_{22}H_{23}O_4N$ [M+Na^+]; calculated: 365.1627; found: 365.1622

IR (CCl_4): ν (cm^{-1}) 3314, 3064, 2983, 2938, 1744, 1591, 1499, 1228, 1055

1,3-diethyl 2-[(4-methoxyphenyl)(propan-2-yl)amino]-2-(prop-2-yn-1-yl)propanedioate (5.92) $C_{20}H_{27}NO_5$ **MW = 361.4g.mol^{-1}**



Procedure : see general procedure 5.1

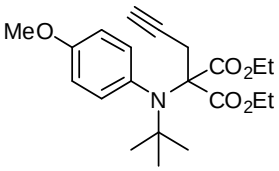
Product: brown oil.

Yield: 21 % (m = 189 mg) over 2 steps

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.12 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 4.33-4.21 (m, 4H), 3.80 (s, 3H), 3.75 (septuplet, *J* = 6.5 Hz, 1H), 2.66 (d, *J* = 1.7 Hz, 2H), 1.94 (t, *J* = 1.7 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 6H), 0.99 (d, *J* = 6.5 Hz, 6H).

HRMS: $C_{20}H_{27}NO_5$ [M+Na^+]; calculated: 361.1889; found: 361.1893

1,3-diethyl 2-[tert-butyl(4-methoxyphenyl)amino]-2-(prop-2-yn-1-yl)propanedioate (5.93) $C_{21}H_{29}NO_5$ **MW = 375.5 g.mol^{-1}**



Procedure : see general procedure 5.1

Product: brown oil.

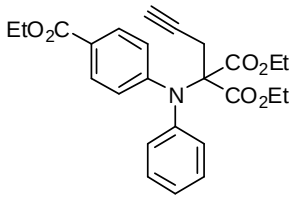
Yield: 12 % (m = 114.3 mg) over 2 steps

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.21 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8/.7 Hz, 2H), 4.27-4.23 (m, 4H), 3.80 (s, 3H), 2.53 (d, *J* = 1.7 Hz, 2H), 1.98 (t, *J* = 1.7 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 6H), 1.20 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 171.4 (2C), 157.9, 136.8, 135.4 (2C), 112.8 (2C), 79.5, 72.5, 71.4, 61.5 (2C), 57.7, 55.4, 31.1, 30.2 (3C), 14.0 (2C).

HRMS: $C_{21}H_{29}NO_5$ [M+Na$^+$]; calculated: 375.2046; found: 375.2050

Ethyl 4-((1-ethoxy-2-(ethoxycarbonyl)-1-oxopent-4-yn-2-yl)(phenyl)amino)benzoate (5.94) $C_{25}H_{27}NO_6$ **MW = g.mol^{-1}**



Procedure : see general procedure 5.2

Product: yellow oil.

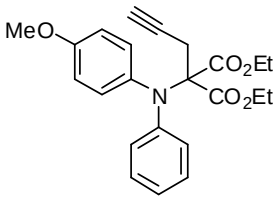
Purification: Flash chromatography (SiO_2 PE/ AcOEt : 85/15).

Yield: 35 % over 3 steps

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.78 (d, *J* = 8.7 Hz, 2H), 7.45-7.37(m, 2H), 6.55(d, *J* = 8.7 Hz, 1H), 4.30 (q, *J* = 6.9 Hz, 2H), 4.22(q, *J* = 7.1 Hz, 4H), 3.04 (s, 3H), 2.72 (d, *J* = 2.6 Hz, 2H), 2.00 (s, 1H), 1.34 (t, *J* = 7.0 Hz, 6H), 1.21(t, *J* = 7.1 Hz, 6H)

HRMS: $C_{25}H_{27}NO_6$[M+Na$^+$]; calculated: 437.1838; found: 437.1840

Diethyl 2-((4-methoxyphenyl)(phenyl)amino)-2-(prop-2-ynyl)malonate (5.97) $C_{18}H_{23}O_5N$ **MW = g.mol^{-1}**



Procedure : see general procedure 5.2

Product: yellow oil.

Purification: Flash chromatography (SiO_2 PE/ AcOEt : 85/15)

Yield: 43 % over 3 steps

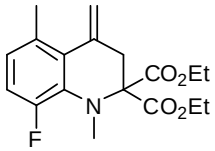
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.12 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 4H), 3.82 (s, 3H), 3.04 (s, 3H), 2.01 (t, *J* = 2.6 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.7 (C x2), 158.1 (C), 147.8(C), 137.0(C x2), 132.0(CH), 128.2 (CH), 120.0(CH), 119.0(CH), 114.4 (CH x2), 78.8 (C), 73.1 (C), 71.7 (CH), 61.2 (CH_2 x2), 55.5 (CH_3), 41.4 (CH_3), 28.2 (CH_2), 13.9 (CH_3 x2)

HRMS: $C_{18}H_{23}O_5N$ [M+Na^+]; calculated: 395.1733; found: 395.1736

3. Preparation of dihydroquinolines

8-Fluoro-1,4,5-trimethyl-*1H*-quinoline-2,2-dicarboxylic acid diethyl ester (5.40) $C_{18}H_{22}FNO_4$ **MW = 335.4 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown solid.

Reaction time: 1.5 h at 100 °C (cyclisation)

Yield: 85 % (m = 57 mg)

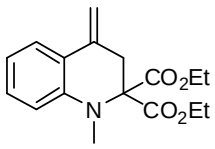
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.87 (dd, *J* = 13.7 Hz, *J* = 8.4 Hz, 1H), 6.62 (dd, *J* = 8.4 Hz, *J* = 4.6 Hz, 1H), 5.26 (s, 1H), 5.25 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 4H), 3.19 (d, *J* = 7.5 Hz, 3H), 3.04 (s, 2H), 2.37 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.4 (C x2), 149.8 (d, *J* = 240.8 Hz, C), 135.1 (d, *J* = 3.1 Hz, C), 132.9 (d, *J* = 6.7 Hz, C), 128.8 (d, *J* = 2.9 Hz, C), 126.2 (d, *J* = 3.2 Hz, C), 120.5 (d, *J* = 7.9 Hz, CH), 114.9 (d, *J* = 22.1 Hz, CH), 114.8 (CH2), 72.8 (C), 60.9 (CH_2 x2), 40.6 (CH_2), 38.9 (d, *J* = 13.7 Hz, CH_3), 20.2 (CH_3), 13.1 (CH_3 x2)

HRMS: $C_{18}H_{22}FNO_4$ [M+Na^+]; calculated: 335.1533; found: 335.1535

IR (CCl_4): ν (cm^{-1}) 2983, 1738, 1490, 1231

1-Methyl-4-methylene-3,4-dihydro-1H-quinoline-2,2-dicarboxylic acid diethyl ester (5.28) $C_{17}H_{21}O_4N$ **MW = 303.4 g.mol^{-1}**



Procedure : see general procedure 5.3 without isomerisation

Product: brown solid.

Reaction time: 3 h at 100 °C (cyclisation)

Yield: 99 % (m = 1.19 g)

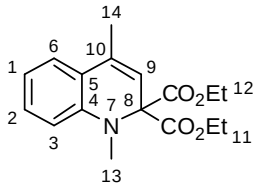
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.43 (dd, *J* = 7.9 Hz, *J* = 1.3 Hz, 1H), 7.22 (dt, *J* = 7.8 Hz, *J* = 1.3 Hz, 1H), 6.76-6.72 (m, 2H), 5.42 (s, 1H), 4.88 (s, 1H), 4.32-4.22 (m, 4H), 3.14 (s, 2H), 3.00 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.8 (C x2), 143.9 (C), 136.4 (C), 129.7 (CH), 124.4 (CH), 121.1 (C), 117.5 (CH), 112.3 (CH), 108.8 (CH_2), 73.3 (C), 62.0 (CH_2 x2), 38.4 (CH_2), 37.1 (CH_3), 14.1 (CH_3 x2).

HRMS: $C_{17}H_{21}O_4N$ [M+Na^+]; calculated: 303.1471; found: 303.1472

IR (CCl_4): ν (cm^{-1}) 2983, 1740, 1604, 1482, 1265, 1227, 1054.

1,4-Dimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester (5.29) $C_{17}H_{21}O_4N$ **MW = 303.4 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown solid.

Reaction time: 1.5 h at 100 °C (cyclisation). 1 h at room temperature (isomerisation)

Yield: 92 % (m = 139 mg)

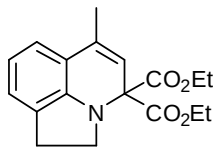
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.23 (td, *J* = 7.8 Hz, *J* = 1.5 Hz, 1H, **H1**), 7.18 (dd, *J* = 7.6 Hz, *J* = 1.4 Hz, 1H, **H6**), 6.77 (td, *J* = 7.5 Hz, *J* = 0.9 Hz, 1H, **H2**), 6.70 (d, *J* = 8.2 Hz, 1H, **H3**), 5.61 (q, *J* = 1.1 Hz, 1H, **H9**), 4.31 (q, *J* = 7.1 Hz, 4H, **CH_2 esters**), 3.05 (s, 3H, **H13**), 2.13 (d, *J* = 1.1 Hz, 3H, **H14**), 1.34 (t, *J* = 7.1 Hz, 6H, **CH_3 esters**).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 169.4 (C x2, **C=O esters**), 143.1 (C, **C4**), 132.2 (C, **C5**), 129.6 (CH, **aromatic**), 123.9 (CH, **aromatic**), 120.9 (C, **C10**), 117.4 (CH, **aromatic**), 116.9 (CH, **aromatic**), 110.5 (CH, **C9**), 73.9 (C, **C8**), 62.0 (CH_2 x2, **esters**), 35.9 (CH_3, **C13**), 18.8 (CH_3, **C14**), 14.1 (CH_3 x2, **esters**).

HRMS: $C_{17}H_{21}O_4N$ [M+Na^+]; calculated: 303.1471; found: 303.1475

IR (CCl_4): ν (cm^{-1}) 2982, 1737, 1604, 1482, 1227, 1056, 1039

6-Methyl-1,2-dihydro-pyrrolo*[3,2,1-ij]*quinoline-4,4-dicarboxylic acid diethyl ester (5.44) $C_{18}H_{21}O_4N$ **MW = 315.4 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown oil.

Reaction time: 18 h at 100 °C (cyclisation), 1 h at room temperature (isomerisation)

Yield: 99 %

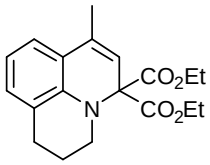
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.96 (d, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.59 (t, *J* = 7.5 Hz, 1H), 5.55 (s, 1H), 4.29-4.21 (m, 4H), 3.80 (t, *J* = 8.6 Hz, 2H), 3.09 (t, *J* = 8.6 Hz, 2H), 2.07 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.8 (C x2), 146.4 (C), 133.2 (C), 125.8 (CH), 124.8 (CH), 122.4 (C), 120.8 (C), 117.8 (CH), 115.3 (CH), 71.3 (C), 61.7 (CH_2 x2), 49.4 (CH_2), 28.1 (CH_2), 17.6 (CH_3), 14.1 (CH_3 x2)

HRMS: $C_{18}H_{21}O_4N$ [M+Na^+]; calculated: 315.1471; found: 315.1469

IR (CCl_4): ν (cm^{-1}) 2962, 1739, 1460, 1238, 1031

1-Methyl-6,7-dihydro-*5H*-pyrido*[3,2,1-ij]*quinoline-3,3-dicarboxylic acid diethyl ester (5.46) $C_{19}H_{23}O_4N$ **MW = 329.4 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown powder.

Reaction time: 30 min at 100 °C (cyclisation), 1 h at room temperature (isomerisation)

Yield: 94 %

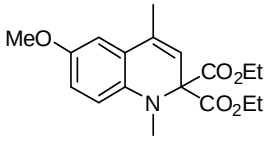
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.98 (d, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.59 (t, *J* = 7.5 Hz, 1H), 5.53 (s, 1H), 4.27 (q, *J* = 7.0 Hz, 4H), 3.39 (t, *J* = 5.2 Hz, 2H), 2.78 (t, *J* = 6.0 Hz, 2H), 2.07 (s, 3H), 2.04-1.99 (m, 2H), 1.31 (t, *J* = 7.0 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.3 (C x2), 139.1 (C), 132.3 (C), 129.9 (CH), 122.4 (CH), 121.6 (C), 120.1 (C), 116.6 (CH), 116.1 (CH), 73.6 (C), 62.0 (CH_2 x2), 47.1 (CH_2), 27.9 (CH_2), 21.4 (CH_2), 19.2 (CH_3), 14.2 (CH_3 x2).

HRMS: $C_{19}H_{23}O_4N$ [M+Na^+]; calculated: 329.1627; found: 329.1631

IR (CCl_4): ν (cm^{-1}) 2982, 2939, 1737, 1475, 1446, 1239

6-Methoxy-1,4-dimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester (5.48) $C_{18}H_{23}O_5N$ **MW = 333.4 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown solid.

Reaction time: 50 min. at 100 °C (cyclisation)

Yield: 95 % (m = 159 mg)

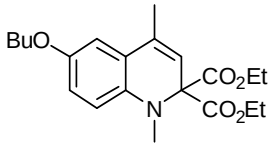
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.79-6.76 (m, 2H), 6.66 (d, *J* = 8.4 Hz, 1H), 5.63 (d, *J* = 1.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 2.99 (s, 3H), 2.08 (d, *J* = 1.3 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.5 (C x2), 151.9 (C), 137.6 (C), 132.1 (C), 122.4 (C), 118.4 (CH), 114.1 (CH), 111.4 (CH), 110.9 (CH), 73.7 (C), 61.9 (CH_2 x2), 55.9 (CH_3), 35.9 (CH_3), 18.8 (CH_3), 14.1 (CH_3 x2).

HRMS: $C_{18}H_{23}O_5N$ [M+Na^+]; calculated: 333.1576; found: 333.1581

IR (CCl_4): ν (cm^{-1}) 2983, 1738, 1492, 1264, 1225, 1039

6-Butoxy-1,4-dimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester (5.50) $C_{21}H_{29}O_5N$ **MW = 375.5 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown oil.

Reaction time: 1.5 h at 100 °C (cyclisation), 1 h at 40 °C (isomerisation)

Yield: 99 % (m = 187.0 mg)

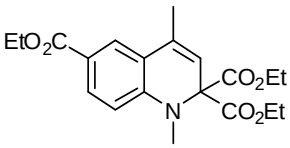
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.77 (d, *J* = 9.0 Hz, 1H), 6.76 (s, 1H), 6.58 (d, *J* = 9.0 Hz, 1H), 5.62 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 4H), 3.91 (t, 6.5 Hz, 2H), 2.98 (s, 3H), 2.07 (d, *J* = 6.3 Hz, 3H), 1.77-1.70 (m, 2H), 1.57-1.49 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 6H), 0.97 (t, *J* = 7.4 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.6 (C x2), 151.4 (C), 137.5 (C), 132.1 (C), 122.3 (C), 118.3 (CH), 114.9 (CH), 111.7 (CH) 111.3 (CH), 73.7 (C), 68.4 (CH_2), 62.3 (CH_2 x2), 35.9 (CH_3), 31.6 (CH_2), 19.3 (CH_3), 19.3 (CH_2), 14.1 (CH_3 x2), 13.9 (CH_3).

HRMS: $C_{21}H_{29}O_5N$ [M+Na^+]; calculated: 375.2046; found: 375.2041

IR (CCl_4): ν (cm^{-1}) 2962, 1736, 1498, 1224, 1036

1,4-Dimethyl-1H-quinoline-2,2,6-tricarboxylic acid triethyl ester (5.54) $C_{20}H_{25}O_6N$ **MW = 375.4 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown oil.

Reaction time: 4 h at 100 °C (cyclisation), 4 h at 40 °C (isomerisation)

Yield: 97 % (m = 181.9 mg)

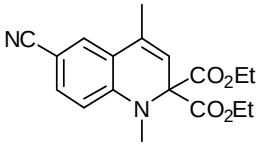
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88 (dd, *J* = 8.7 Hz, *J* = 2.0 Hz, 1H), 7.80 (d, *J* = 2.0 Hz, 1H), 6.64 (d, *J* = 8.7 Hz, 1H), 5.60 (d, *J* = 1.1 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 4H), 3.06 (s, 3H), 2.13 (d, *J* = 1.1 Hz, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 6H

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.7 (C x2), 166.8 (C), 146.9 (C), 132.0 (CH), 131.7 (CH), 125.6 (CH), 120.0 (C), 119.0 (C) 117.0 (CH), 109.8 (C), 74.0 (C), 62.3 (CH_2 x2), 60.4 (CH_2), 36.5 (CH_3), 18.9 (CH_3), 14.5 (CH_3), 14.1 (CH_3 x2)

HRMS: $C_{20}H_{25}O_6N$ [M+Na^+]; calculated: 375.1682; found: 375.1693

IR (CCl_4): ν (cm^{-1}) 2982, 1739, 1709, 1607, 1499, 1270, 1159, 1046.

6-Cyano-1,4-dimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester (5.56) $C_{18}H_{20}O_4N_2$ **MW = 328.4 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown oil.

Reaction time: at 100 °C (cyclisation), overnight at room temperature (isomerisation)

Yield: 94 % (m = 154.8 mg)

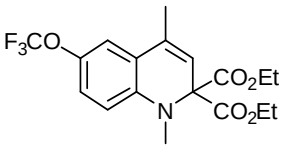
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44 (dd, *J* = 8.6 Hz, *J* = 1.7 Hz, 1H), 7.34 (d, *J* = 1.7 Hz, 1H), 6.64 (d, *J* = 8.6 Hz, 1H), 5.65 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 4H), 3.04 (s, 3H), 2.07 (d, *J* = 1.1 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.3 (C x2), 146.4 (C), 133.8 (C), 130.9 (C), 127.6 (C), 120.9 (C), 120.1 (CH),118.0 (CH), 110.6 (CH), 99.6 (C), 74.0 (C), 62.5 (CH_2 x2), 36.5 (CH_3), 18.7 (CH_3), 14.1 (CH_3 x2).

HRMS: $C_{18}H_{20}O_4N_2$ [M+Na^+]; calculated: 328.1423; found: 328.1407

IR (CCl_4): ν (cm^{-1}) 2983, 2939, 2222, 1740, 1605, 1499, 1227, 1162

1,4-Dimethyl-6-trifluoromethoxy-1H-quinoline-2,2-dicarboxylic acid diethyl ester (5.52) $C_{18}H_{20}O_5NF_3$ **MW = 387.4 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown oil.

Reaction time: 30 min at 100 °C (cyclisation), 48 h at room temperature (isomerisation)

Yield: 91 % (m = 175.4 mg)

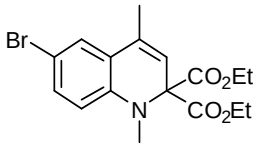
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.04 (dd, *J* = 8.9 Hz, *J* = 1.7 Hz, 1H), 6.97 (d, *J* = 1.7 Hz, 1H), 6.60 (d, *J* = 8.9 Hz, 1H), 5.64 (d, *J* = 1.1 Hz, 1H), 4.28 (dq, *J* = 7.1 Hz, *J* = 1.3 Hz, 4H), 3.01 (s, 3H), 2.07 (d, *J* = 1.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.0 (C x2), 141.8 (C), 140.7 (C) (q, *J* = 2.0 Hz), 131.4 (C), 122.2 (C), 121.8 (CH), 120.7 (C) (q, *J* = 254.0 Hz), 118.4 (CH), 117.2 (CH),110.9 (CH), 73.8 (C), 62.3 (CH_2 x2), 36.2 (CH_3), 18.7 (CH_3), 14.1 (CH_3 x2).

HRMS: $C_{18}H_{20}O_5NF_3$ [M+Na^+]; calculated: 387.1294; found: 387.1287

IR (CCl_4): ν (cm^{-1}) 2983, 2927, 1740, 1498, 1223, 1166.

6-Bromo-1,4-dimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester (5.62) $C_{17}H_{20}O_4NBr$ **MW = 382.2 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown solid.

Reaction time: 30 min at 100 °C (cyclisation), 1 h at room temperature (isomerisation)

Yield: 97 % (m = 184.4 mg)

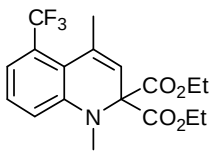
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.24 (d, *J* = 2.4 Hz, 1H), 7.20 (d, *J* = 2.4 Hz, 1H), 6.52 (d, *J* = 8.8 Hz, 1H), 5.60 (d, *J* = 1.2 Hz, 1H), 4.27 (q, *J* = 7.0 Hz, 4H), 2.98 (s, 3H), 2.06 (d, *J* = 1.2 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 6H)

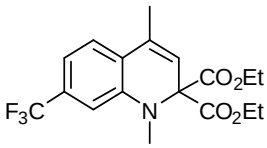
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.0 (C x2), 131.9 (CH), 126.6 (CH), 122.9 (C), 118.2 (CH), 112.3 (CH), 109.8 (C), 62.2 (CH_2 x2), 36.1 (CH_3), 18.7 (CH_3), 14.1 (CH_3 x2)

HRMS: $C_{17}H_{20}O_4NBr$ [M+Na^+]; calculated: 381.0576; found: 381.0570

IR (CCl_4): ν (cm^{-1}) 2983, 2938, 1738, 1489, 1263, 1226, 1046

1,4-Dimethyl-7-trifluoromethyl-*1H*-quinoline-2,2-dicarboxylic acid diethyl ester and 1,4-Dimethyl-5-trifluoromethyl-*1H*-quinoline-2,2-dicarboxylic acid diethyl ester (5.66 and 5.67) $C_{18}H_{20}O_4NF_3$ **MW = 371.4 g.mol^{-1}**





Procedure : see general procedure 5.3

Product: brown oil.

Reaction time: 5 h at 100 °C (cyclisation), 1.5 h at room temperature (isomerisation)

Yield: 90 % (m = 83.2 mg)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.63 (d, *J* = 7.0 Hz, 1H), 7.37 (t, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 7.8 Hz), 7.07 (s, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 5.28 (s, 1H), 5.08 (s, 1H), 4.30 (q, *J* = 6.8 Hz, 8H), 3.19 (s, 3H), 3.17 (s, 3H), 3.08 (s, 3H), 3.05 (s, 3H), 1.34-1.28 (m, 12H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.6 (C x2), 168.8 (C x2), 145.5 (C), 143.4 (C), 134.0 (C) (q, *J* = 9.1 Hz), 131.3 (CH) (q, *J* = 31.5 Hz), 129.6 (CH) (q, *J* = 27.6 Hz), 128.5 (CH), 124.9 (C) (q, *J* = 269.1 Hz), 124.4 (C) (q, *J* = 261.9 Hz), 124.1 (CH), 119.0 (CH), 116.3 (CH) (q, *J* = 5.4 Hz), 115.7 (CH) (q, *J* = 5.1 Hz), 114.9 (CH), 114.0 (CH) (q, *J* = 4.0 Hz), 106.9 (CH) (q, *J* = 4.0 Hz), 74.3 (C), 73.8 (C), 62.3 (CH_2 x4), 51.8 (CH_3), 36.9 (CH_3), 36.1 (CH_3), 18.7 (CH_3), 14.2 (CH_3 x2), 14.1 (CH_3 x2), 2 missing C signals.

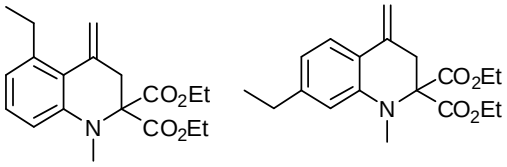
HRMS: $C_{18}H_{20}O_4NF_3$ [M+Na^+]; calculated: 371.1344; found: 371.1354

IR (CCl_4): ν (cm^{-1}) 2983, 2926, 1740, 1594, 1465, 1314, 1231, 1130, 1063

7-Ethyl-1-methyl-4-methylene-3,4-dihydro-*1H*-quinoline-2,2-dicarboxylic acid diethyl ester

and 5-Ethyl-1-methyl-4-methylene-3,4-dihydro-*1H*-quinoline-2,2-dicarboxylic acid diethyl ester (5.69 and 5.70)

$C_{19}H_{25}NO_4$ **MW = 331.4 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown oil.

Reaction time: 15 min at 100 °C (cyclisation)

Yield: 71 % (m = 93.6 mg)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.36 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.58 (t, *J* = 9.1 Hz, 1H), 6.57 (s, 1H), 5.37 (s, 1H), 5.18 (s, 2H), 4.82 (s, 1H), 4.31-4.21 (m, 12H), 3.13 (s, 2H), 3.07 (s, 2H), 3.02 (s, 3H), 3.00 (s, 3H), 2.79 (q, *J* = 7.5 Hz, 2H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.32-1.21 (m, 6H)

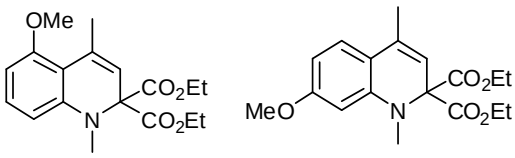
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.1 (C x2), 169.9 (C x2), 146.1 (C), 144.7 (C), 143.8 (C), 140.9 (C), 136.3 (C), 135.8 (C), 128.3 (CH), 124.4 (CH), 118.7 (CH), 117.3 (CH), 115.0 (CH), 111.8 (CH), 109.2 (C), 107.8 (CH_2), 74.0 (C), 73.4 (C), 62.0 (CH_2 x4), 40.1 (CH_2), 38.5 (CH_2), 37.2 (CH_3), 36.9 (CH_3), 29.35 (CH_2), 26.0 (CH_2), 16.1 (CH_3), 15.6 (CH_3), 14.2 (CH_3 x2), 14.1 (CH_3 x2)

IR (CCl_4): ν (cm^{-1}) 2967, 2935, 1739, 1609, 1464, 1230, 1050

7-Methoxy-1,4-dimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester

and 5-Methoxy-1,4-dimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester (5.72 and 5.73)

$C_{18}H_{23}O_5N$ **MW = 333.4 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown oil.

Reaction time: 30 min at 100 °C (cyclisation), 1 h at room temperature (isomerisation)

Yield: 93 % (m = 176.3 mg)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.03□□d, *J* = 8.3 Hz, 1H), 6.25 (dd, *J* = 8.3 Hz, *J* = 2.3 Hz, 1H), 6.21 (d, *J* = 2.3 Hz, 1H), 5.43 (s, 1H), 4.24 (q, *J* = 7.2 Hz, 4H), 3.78 (s, 3H), 2.98 (s, 3H), 2.04 (d, *J* = 1.3 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.4 (C x2), 161.2 (C), 144.6 (C), 132.0 (C), 125.0 (CH), 114.8 (C), 114.4 (CH), 101.4 (CH), 97.8 (CH), 73.9 (C), 62.0 (CH_2 x2), 55.2 (CH_3), 36.1 (CH_3), 18.9 (CH_3), 14.2 (CH_3 x2)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ7.11 (t, *J* = 8.3 Hz, 1H), 6.41 (d, *J* = 8.3 Hz, 1H), 6.34 (d, *J* = 8.3 Hz, 1H), 5.43 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 4H), 3.74 (s, 3H), 3.00 (s, 3H), 2.25 (d, *J* = 1.3 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 6H)

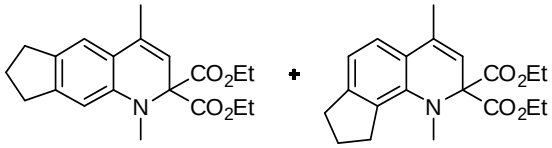
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.9 (C x2), 157.7 (C), 145.2 (C), 132.6 (C), 129.7 (CH), 117.2 (CH), 111.0 (C), 105.3 (CH), 102.4 (CH), 73.1 (C), 61.9 (CH_2 x2), 55.4 (CH_3), 36.7 (CH_3), 23.5 (CH_3), 14.1 (CH_3 x2)

HRMS: $C_{18}H_{23}O_5N$ [M+Na^+]; calculated: 333.1576; found: 333.1575

IR (CCl_4): ν (cm^{-1}) 2984, 1737, 1610, 1264, 1233, 1044

2,2-diethyl 1,4-dimethyl-*1H,2H,6H,7H,8H*-cyclopenta*[g]*quinoline-2,2-dicarboxylate and 2,2-diethyl 1,4-dimethyl-*1H,2H,7H,8H,9H*-cyclopenta*[h]*quinoline-2,2-dicarboxylate (5.75 et 5.76)

$C_{20}H_{25}O_4N$ **MW = 343.4 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown oil

Reaction time: 24 h at 100 °C (cyclisation), 1 h at room temperature (isomerisation)

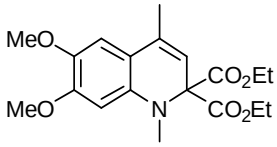
Yield: 90 %

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.05 (d, *J* = 8.1 Hz, 1H minor isomer), 7.00 (s, 1H major isomer), 6.59-6.56 (m, 1H minor isomer + 1H major isomer), 5.55 (s, 1H minor isomer), 5.50 (s, 1H major isomer), 4.24 (q, *J* = 7.1 Hz, 4 H minor isomer + 4H major isomer), 3.12 (t, *J* = 7.7 Hz, 2 H minor isomer), 3.00 (s, 3H minor isomer), 2.99 (s, 3H major isomer), 2.86 (t, *J* = 7.3 Hz, 2H major isomer), 2.82-2.74 (m, 2H minor isomer + 2H major isomer), 2.07-1.97 (m, 5H minor isomer + 5H major isomer), 1.28 (t, *J* = 7.1 Hz, 6 H minor isomer + 6H major isomer).

IR (CCl_4): ν (cm^{-1}) 2980, 2960, 2845, 1737, 1480, 1465, 1261, 1223.

6,7-Dimethoxy-1,4-dimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester (5.78)

$C_{19}H_{25}O_6N$ **MW = 363.4 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown oil.

Reaction time: 30 min at 100 °C (cyclisation), no isomerisation needed

Yield: 36 % (65.5 mg) (75% NMR-yield)

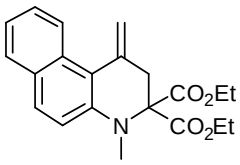
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.73 (s, 1H), 6.29 (s, 1H), 5.46 (s, 1H), 4.26 (dq, *J* = 7.0 Hz, *J* = 1.4 Hz, 4H), 3.91 (s, 3H), 3.82 (s, 3H), 3.01 (s, 3H), 2.06 (s, 3H), 1.29 (t, *J* = 7.0 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) δ169.7 (C x2), 150.5 (C), 141.0 (C), 138.6 (C), 131.8 (C), 114.9 (CH), 113.6 (C), 109.8 (CH), 96.6 (CH), 73.9 (C), 62.0 (CH_2 x2), 57.2 (CH_3), 56.0 (CH_3), 36.1 (CH_3), 18.9 (CH_3), 14.2 (CH_3 x2).

HRMS: $C_{19}H_{25}O_6N$ [M+Na^+]; calculated: 363.1682; found: 363.1674

IR (CCl_4): ν (cm^{-1}) 2983, 2936, 1737, 1508, 1464, 1232.

4-Methyl-1-methylene-1,4-dihydro-*2H*-benzo*[f]*quinoline-3,3-dicarboxylic acid diethyl ester (5.81) $C_{21}H_{23}O_4N$ **MW = 353.4 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: dark green oil.

Reaction time: 15 min at 100 °C (cyclisation)

Yield: 93 % (m = 164.1 mg)

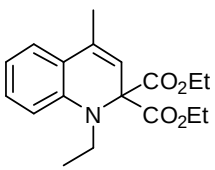
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.34 (d, *J* = 8.7 Hz, 1H), 7.76-7.70 (m, 2H), 7.40 (dt, *J* = 7.8 Hz, *J* = 1.2 Hz, 1H), 7.27-7.22 (m, 1H), 7.14 (d, *J* = 9.2 Hz, 1H), 5.55 (d, *J* = 1.2 Hz, 1H), 5.39 (s, 1H), 4.34-4.25 (m, 4H), 3.22 (s, 2H), 3.16 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 6H

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.1 (C x2), 141.7 (C), 135.0 (C), 130.5 (C), 129.3 (CH), 128.3 (CH), 127.6 (C), 126.6 (CH), 123.6 (CH), 122.0 (C), 115.9 (CH), 115.0 (C), 114.1 (CH), 74.5 (C), 62.2 (CH_2 x2), 39.7 (CH_3), 37.1 (CH_2), 14.0 (CH_3 x2)

HRMS: $C_{21}H_{23}O_4N$ [M+Na^+]; calculated: 353.1627; found: 353.1623

IR (CCl_4): ν (cm^{-1}) 2983, 1739, 1597, 1514, 1364, 1264, 1227, 1048.

1-Ethyl-4-methyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester (5.88) $C_{18}H_{23}O_4N$ **MW = 317.4 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown oil.

Reaction time: 20 min at 100 °C (cyclisation), 1 h at room temperature (isomerisation)

Yield: 97 % (164.3 mg)

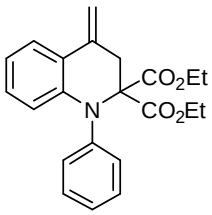
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.19-7.14 (m, 2H), 6.73-6.67 (m, 2H), 5.54 (s, 1H), 4.30 (m, 4H), 3.50 (q, *J* = 7.0 Hz, 2H), 2.08 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 6H), 1.18 (t, *J* = 7.1 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.3 (C x2), 135.9 (C), 128.4 (C), 126.3 (C), 122.0 (CH), 119.1 (CH), 119.0 (CH), 111.0 (C), 109.5 (CH), 62.1 (CH_2 x2), 49.5 (CH_2), 38.8 (CH_3), 15.1 (CH_3), 14.1 (CH_3 x2), 9.2 (CH_3).

HRMS: $C_{18}H_{23}O_4N$ [M+Na^+]; calculated: 317.1627; found: 317.1619

IR (CCl_4): ν (cm^{-1}) 2982, 1739, 1463, 1203, 1146, 1037

4-Methylene-1-phenyl-3,4-dihydro-1H-quinoline-2,2-dicarboxylic acid diethyl ester (5.90) $C_{22}H_{23}O_4N$ **MW = 365.4 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown oil.

Reaction time: 5 min at 100 °C (cyclisation)

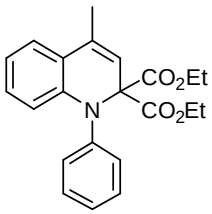
Yield: 59 %

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.46-7.43 (m, 2H), 7.37-7.34 (m, 2H), 7.28-7.22 (m, 1H), 6.91 (dt, *J* = 7.7 Hz, *J* = 1.5 Hz, 1H), 6.65 (t, *J* = 7.5 Hz, 1H), 6.14 (d, *J* = 8.3 Hz, 1H), 5.47 (d, *J* = 1.3 Hz, 1H), 4.00 (qq, *J* = 10.7 Hz, *J* = 7.1 Hz, 4H), 3.26 (s, 2H), 1.00 (t, *J* = 7.1 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.0 (C x2), 144.3 (C), 142.7 (C), 136.9 (C), 131.6 (CH x2), 129.9 (CH x2), 129.5 (CH), 128.0 (CH), 124.8 (CH), 120.3 (C), 118.1 (CH), 114.9 (CH), 109.3 (CH_2), 74.1 (C), 62.2 (CH_2 x2), 39.4 (CH_3), 14.0 (CH_3 x2)

HRMS: $C_{22}H_{23}O_4N$ [M+Na^+]; calculated: 365.1627; found: 365.1624

4-Methyl-1-phenyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester (5.91) $C_{22}H_{23}O_4N$ **MW = 365.4 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown oil.

Reaction time: 5 min at 100 °C (cyclisation), 1.5 h at room temperature (isomerisation)

Yield: 86 % (m = 161.8 mg)

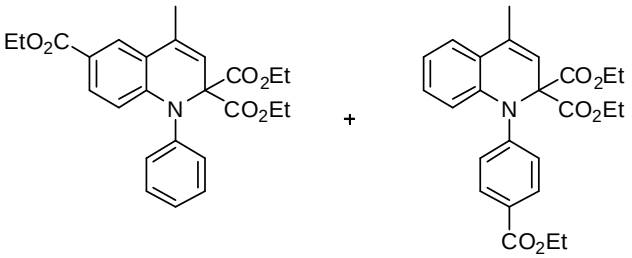
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.49 (dd, *J* = 8.7 Hz, *J* = 1.0 Hz, 2H), 7.36 (tt, *J* = 8.7 Hz, *J* = 2.1 Hz, 2H), 7.26 (tt, *J* = 7.3 Hz, *J* = 1.2 Hz, 1H), 7.20 (dd, *J* = 7.7 Hz, *J* = 1.5 Hz, 1H), 6.99 (dd, *J* = 7.7 Hz, *J* = 1.5 Hz, 1H), 6.75 (dt, *J* = 7.4 Hz, *J* = 1.1 Hz, 1H), 6.36 (dd, *J* = 8.3 Hz, *J* = 1.0 Hz, 1H), 5.72 (d, *J* = 1.3 Hz, 1H), 4.03 (q, *J* = 7.1 Hz, 4H), 2.17 (d, *J* = 1.3 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.5 (C x2), 143.0 (C), 142.9 (C), 131.7 (CH), 130.1 (CH x2), 129.3 (CH x2), 128.9 (CH), 126.9 (CH), 124.0 (CH), 121.9 (C), 118.3 (CH), 117.4 (CH), 115.2 (CH), 73.8 (C), 61.9 (CH_2 x2), 18.9 (CH_3), 13.8 (CH_3 x2)

HRMS: $C_{22}H_{23}O_4N$ [M+Na^+]; calculated: 365.1627; found: 365.1624

IR (CCl_4): ν (cm^{-1}) 2982, 1742, 1489, 1265, 1225, 1047

2,2,6-triethyl 4-methyl-1-phenyl-1,2-dihydroquinoline-2,2,6-tricarboxylate and 2,2-diethyl 1-[4-(ethoxycarbonyl)phenyl]-4-methyl-1,2-dihydroquinoline-2,2-dicarboxylate (5.95 and 5.96) $C_{25}H_{27}NO_6$ **MW = 437.5 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown oil.

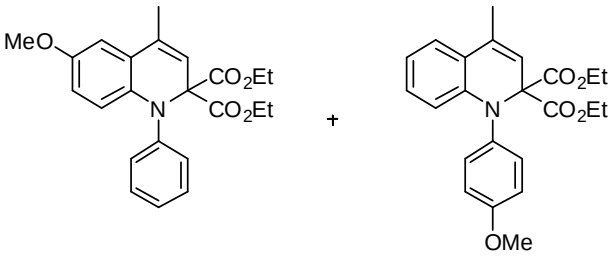
Reaction time: 0.5 h (cyclisation), 1 h at room temperature (isomerisation)

Yield: 95 % (NMR yield)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.00 (d, *J* = 8.7 Hz, 2H Major isomer), 7.89 (d, *J* = 2.0 Hz, 1H, major isomer), 7.65 (dd, *J* = 2.0 Hz, *J* = 8.7 Hz, 2H, minor isomer), 7.61-7.57 (m, 1H major isomer + 1H minor isomer), 7.39 (m, 2H minor isomer), 7.33 (m, 1H major isomer + 1H minor isomer), 7.22 (dd, *J* = 1.4 Hz, *J* = 7.7 Hz, 1H minor isomer=, 7.01 (m, 1H major isomer), 6.81 (dt, *J* = 1.0 Hz, *J* = 7.5 Hz, 1H major isomer), 6.52 (d, *J* = 8.2 Hz, 1H minor isomer), 6.27 (d, *J* = 8.7 Hz, 1H major isomer), 5.74-5.72 (m, 1H major isomer + 1H minor isomer), 4.48 (q, *J* = 7.2 Hz, 2H minor isomer), 4.42 (q, *J* = 7.2 Hz, 2H major isomer), 4.14-4.02 (m, 4H major isomer + 4H minor isomer), 2.31 (d, *J* = 1.3 Hz, 3H major isomer), 2.26 (d, *J* = 1.3 Hz, 3H minor isomer), 1.50 (t, *J* = 7.1 Hz, 3H minor isomer), 1.45 (t, *J* = 7.1 Hz, 3H major isomer), 1.18-1.13 (m, 6H major isomer + 6H minor isomer).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.2 (2C minor isomer), 168.8 (2C, major isomer), 166.7 (major isomer), 166.2 (minor isomer), 147.8 (minor isomer), 147.0 (major isomer), 142.0 (major isomer), 141.8 (minor isomer), 131.8 (major isomer), 131.4 (minor isomer), 130.7 (1C major isomer + 2C minor isomer), 130.3 (2C, major isomer), 129.6 (2C, major isomer), 128.9 (minor isomer), 128.0 (2C, minor isomer), 127.9 (major isomer), 127.7 (minor isomer), 126.0 (major isomer), 124.0 (minor isomer), 123.0 (minor isomer), 121.1 (major isomer), 120.0 (major isomer), 119.6 (minor isomer), 118.2 (minor isomer), 117.7 (major isomer), 116.5 (minor isomer), 114.4 (major isomer), 73.9 (major isomer), 73.5 (minor isomer), 62.2 (2C, minor isomer), 62.1 (2C, major isomer), 61.0 (minor isomer), 60.5 (major isomer), 18.9 (major isomer), 18.7 (minor isomer), 14.5 (major isomer), 14.4 (minor isomer), 13.8 (2C, minor isomer), 13.8 (2C, major isomer).

2,2-diethyl 6-methoxy-4-methyl-1-phenyl-1,2-dihydroquinoline-2,2-dicarboxylate and 2,2-diethyl 1-(4-methoxyphenyl)-4-methyl-1,2-dihydroquinoline-2,2-dicarboxylate (5.98 and 5.99) $C_{23}H_{25}NO_5$ **MW = 395.4 g.mol^{-1}**



Procedure : see general procedure 5.3

Product: brown oil.

Reaction time: 0.5 h (cyclisation), 1 h at room temperature (isomerisation)

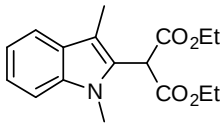
Yield: 96 % (NMR yield)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.45-7.40 (m, 2H both isomers), 7.27-6.51 (m, 5H both isomers), 6.36 (d, *J* = 7.6 Hz, 1H minor isomer), 6.24 (d, *J* = 7.7 Hz, 1H major isomer), 5.75 (s, 1H minor isomer), 5.68 (s, 1H major isomer), 4.02 (q, *J* = 6.9 Hz, 4H both isomers), 3.81 (s, 3H major isomer), 3.74 (s, 3H minor isomer), 2.14 (s, 3H both isomers), 1.09-1.01 (m, 6 H both isomers).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) major isomer only 169.1 (2C), 141.8, 140.7, 140.7, 131.4, 122.2, 121.8, 118.4 (2C), 117.2, 110.9 (2C), 73.8, 62.3 (2C), 36.2, 18.7, 14.1 (2C).

4. Synthesis of indoles

2-(1,3-Dimethyl-1H-indol-2-yl)-malonic acid diethyl ester (5.107) $C_{17}H_{21}O_4N$ **MW = 303.4 g.mol^{-1}**



Procedure : see general procedure 5.4

Product: pale oil.

Reaction time: 4 days

Yield: 85 % (m = 25 mg)

Purification: Flash Chromatography (SiO_2 PE/AcOEt : 90 : 10)

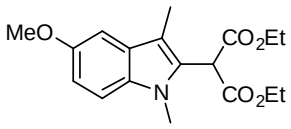
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) *δ* = 7.57 (d, *J* = 7.9 Hz, 1H), 7.35-7.27 (m, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 5.11 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 2.37 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.4 (C x2), 137.4 (C), 127.8 (C), 127.0 (C), 122.2 (CH), 119.0 (CH x2), 110.9 (C), 109.2 (CH), 62.1 (CH_2 x2), 49.6 (CH), 30.9 (CH_3), 14.1 (CH_3 x2), 9.0 (CH_3)

HRMS: $C_{17}H_{21}O_4N$ [M+Na$^+$]; calculated: 303.1471; found: 303.1468

IR (CCl_4): ν (cm^{-1}) 2983, 1739, 1472, 1206, 1146

2-(5-Methoxy-1,3-dimethyl-1H-indol-2-yl)-malonic acid diethyl ester (5.112) $C_{18}H_{23}O_5N$ **MW = 333.4 g.mol^{-1}**



Procedure : see general procedure 5.4

Product: brown solid.

Reaction time: 4 weeks

Yield: 88 % (m = 29 mg)

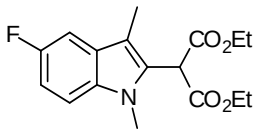
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.19 (d, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 2.3 Hz, 1H), 6.91 (dd, *J* = 8.8 Hz, *J* = 2.3 Hz, 1H), 5.05 (s, 1H), 4.29-4.23 (m, 4H), 3.88 (s, 3H), 3.72 (s, 3H), 2.99 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.4 (C x2), 153.9 (C), 132.8 (C), 128.0 (C), 127.6 (C), 112.4 (CH), 110.4 (C), 110.0 (CH), 100.8 (CH), 62.1 (CH_2 x2), 56.0 (CH_3), 49.7 (CH), 31.1 (CH_3), 14.1 (CH_3 x2), 9.1 (CH_3).

HRMS: $C_{18}H_{23}O_5N$ [M+Na^+]; calculated: 333.1576 ; found: 333.1571

IR (CCl_4): ν (cm^{-1}) 2984, 2939, 1739, 1490, 1299, 1145

2-(5-Fluoro-1,3-dimethyl-1H-indol-2-yl)-malonic acid diethyl ester (5.113) $C_{17}H_{20}O_4NF$ **MW = 321.3 g.mol^{-1}**



Procedure : see general procedure 5.4

Product: pale oil.

Reaction time: 7 days

Yield: 92 % (m = 29 mg)

Purification: Flash Chromatography (SiO_2 PE/AcOEt : 90 : 10)

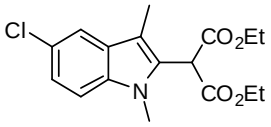
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.26-7.22 (m, 2H), 7.02 (td, *J* = 9.0 Hz, *J* = 2.5 Hz, 1H), 5.09 (s, 1H), 4.85-4.27 (m, 4H), 3.78 (s, 3H), 2.32 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.2 (C x2), 157.7 (d, *J* = 157.7 Hz, C), 134.0 (C), 128.7 (C), 128.0 (d, *J* = 10.0 Hz, C), 110.8 (d, *J* = 5.2 Hz, C), 110.5 (d, *J* = 26.3 Hz, CH), 109.8 (d, *J* = 9.8 Hz, CH), 103.8 (d, *J* = 23.2 Hz, CH), 62.2 (CH_2 x2), 49.7 (CH), 31.2 (CH_3), 14.1 (CH_3 x2), 9.0 (CH_3).

HRMS: $C_{17}H_{20}O_4NF$ [M+Na^+]; calculated: 321.1376; found: 321.1394

IR (CCl_4): ν (cm^{-1}) 2984, 1739, 1488, 1156.

2-(5-Chloro-1,3-dimethyl-1*H*-indol-2-yl)-malonic acid diethyl ester (5.114) $C_{17}H_{20}O_4NCl$ **MW = 337.8 g.mol^{-1}**



Procedure : see general procedure 5.4

Product: pale oil.

Reaction time: 4 weeks

Yield: 67 % (m = 23 mg)

Purification: Flash Chromatography (SiO_2 PE/AcOEt : 90 : 10)

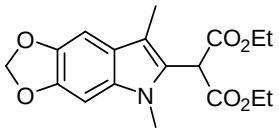
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.51 (d, *J* = 1.2 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.18 (dd, *J* = 8.7 Hz, *J* = 1.8 Hz, 1H), 5.05 (s, 1H), 4.31-4.22 (m, 4H), 3.73 (s, 3H), 2.28 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.2 (C x2), 135.8 (C), 128.8 (C), 128.5 (C), 124.8 (CH), 122.4 (C), 118.5 (CH), 110.6 (C), 110.3 (CH), 62.3 (CH_2 x2), 49. 6 (CH), 31.2 (CH_3), 14.1 (CH_3 x2), 9.0 (CH_3).

HRMS: $C_{17}H_{20}O_4NCl$ [M+Na$^+$]; calculated: : 337.1081; found: 337.1086

IR (CCl_4): ν (cm^{-1}) 2983, 1740, 1475, 1308, 1146

5-Methyl-8-methylene-7,8-dihydro-5*H*-[1,3]dioxolo[4,5-*g*]quinoline-6,6-dicarboxylic acid diethyl ester (5.115) $C_{18}H_{21}O_6N$ **MW = 347.4 g.mol^{-1}**



Procedure : see general procedure 5.4

Product: white solid.

Reaction time: 3 weeks

Yield: 88 % (m = 31 mg)

Purification: Flash Chromatography (SiO_2 PE/AcOEt : 80 : 20)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.92 (s, 1H), 6.76 (s, 1H), 5.92 (s, 2H), 5.00 (s, 1H), 4.29-4.21 (m, 4H), 3.66 (s, 3H), 2.24 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.6 (C x2), 144.2 (C), 141.5 (C), 131.7 (C), 124.4 (C), 120.6 (C), 109.9 (C), 99.5 (CH_2), 96.6 (CH), 89.3 (CH), 61.1 (CH_2 x2), 48.6 (CH), 30.2 (CH_3), 13.1 (CH_3 x2), 8.1 (CH_3)

HRMS: $C_{18}H_{21}O_6N$ [M+Na$^+$]; calculated: 347.1369; found: 347.1374

IR (CCl_4): ν (cm^{-1}) 2984, 1737, 1472, 1043