Gold(I)-Catalyzed Formation of Dihydroquinolines and Indoles from *N*-Aminophenyl propargyl malonates

Colombe Gronnier, Yann Odabachian, and Fabien Gagosz*

Laboratoire de Synthèse Organique, UMR 7652 CNRS / Ecole Polytechnique, 91128 Palaiseau, France.

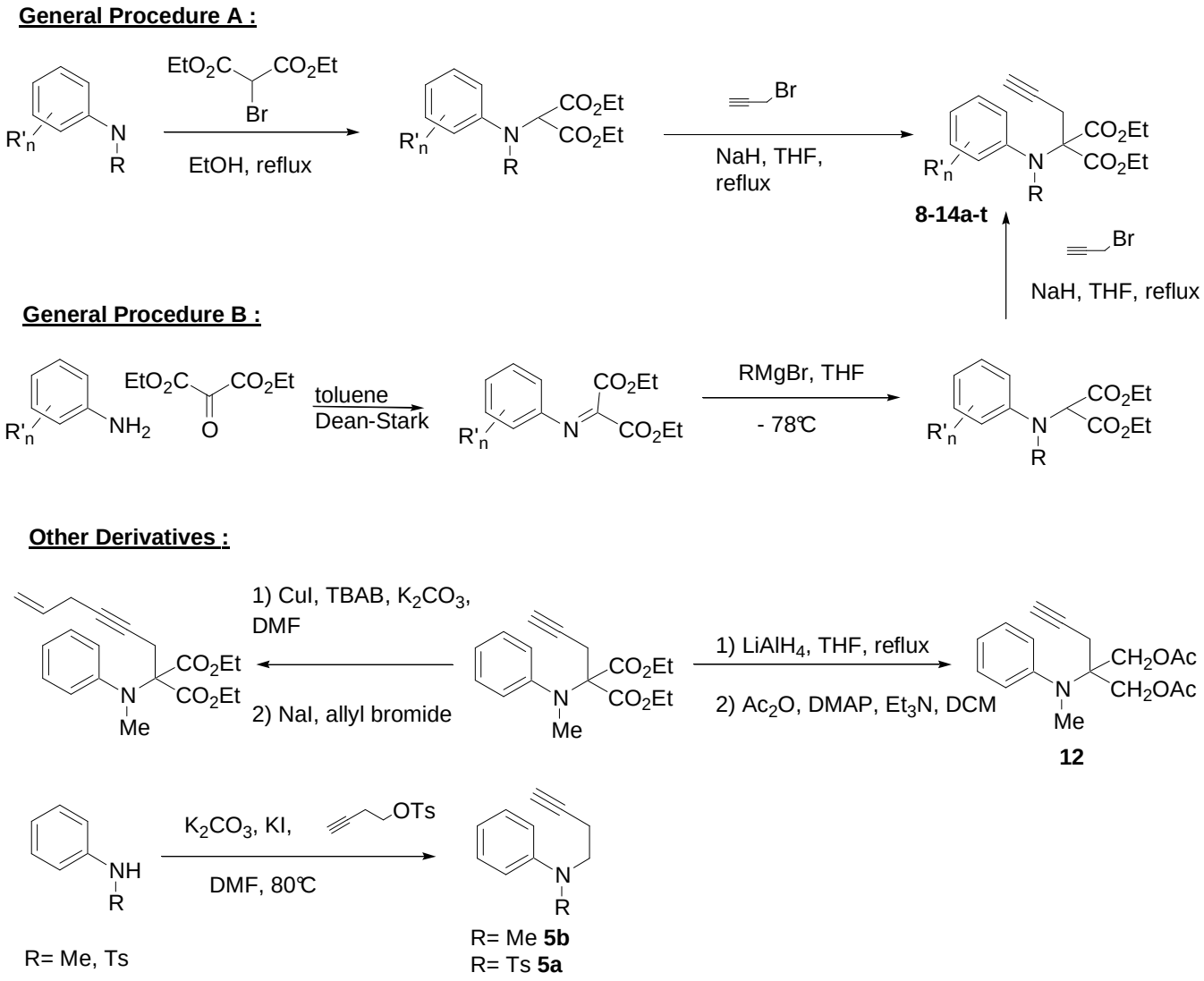
Supporting Information

General Information

All non-aqueous reactions, besides the catalysis, were performed under a positive pressure of argon using standard syringe-cannula/septa techniques. Commercially available reagents were used as received without further purification. Distilled solvents were dried over Na/benzophenone (THF) or CaH_2 (CH_2Cl_2) under N_2 gas. For chromatographic purification, technical-grade solvents were used. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) using *Merck Silica Gel 60 F254* plates and visualized by fluorescence quenching at 254 nm. In addition, TLC plates were stained using anisaldehyde solution (338 mL ethanol, 9.2 mL anisaldehyde, 3.8 mL acetic acid, 12.5 mL *conc.* H_2SO_4). Chromatographic purification of products was performed on *silica gel 60, 230–400 mesh* using a forced flow of eluent at 0.1–0.5 bar pressure. Concentration under reduced pressure was performed by rotary evaporation at RT using a water jet pump. Purified compounds were further dried on high vacuum. NMR-spectra were measured in the given solvent at RT on *Bruker Avance 400* (400.2 MHz, ^{1}H; 100.6 MHz, ^{13}C) instrument operating at the denoted spectrometer frequency given in mega Hertz (MHz) for the specified nucleus. Chemical shifts δ are given in parts per million (ppm) relative to tetramethylsilane (TMS) as an external standard for ^{1}H- and ^{13}C-NMR spectra and calibrated against the solvent residual peak. Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept. = septet, m = multiplet, or as combination of them. Coupling constants J are given in Hertz (Hz). Infrared spectra were recorded on a *Perkin-Elmer 1600 Fourier Transform Spectrophotometer* as solution in CCl_4 and are reported as absorption maxima in cm^{-1}. Melting points were measured with a *Reichert microscope apparatus* in open capillaries and are uncorrected. Mass spectra were obtained on a *Hewlett-Packard HP 5989B* spectrometer *via* direct injection. Ionization was obtained by chemical ionization with ammonia (CI, NH_3). High-resolution mass spectrometry with electrospray ionization (ESI-MS) was performed on a *JEOL GCmate II* spectrometer. Fragment signals are given in mass per charge number (m/z).

Starting Materials

Substrates for catalysis were synthesized according to the general synthetic routes described in the following scheme:



The chemical transformations mentioned in this scheme were performed as described in the following general procedures:

General procedure A :

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 complete consumption of the diethyl bromomalonate (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 MgSO4 and concentrated under reduced pressure to afford the pure *N*-methyl *N*-aryl aminomalonate.

Propargylation of monoalkylated diethyl malonates: To a solution of the aminomalonate (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 MgSO4 and concentrated under reduced pressure. Purification by flash column chromatography afforded the pure *N*-aminoaryl propargyl malonate.

General procedure B :

Condensation of aniline on diethylketomalonate[1] *:* To a solution of diethyl ketomalonate (1 eq.) in toluene (0.5 M) was added the aniline (1 eq.). The reaction was heated up to reflux in a Dean-Stark apparatus. After 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[2] *:* To a solution of the crude immine (1.0 eq.) in THF (0.5 M.) at -78°C was added dropwise a solution of RMgBr (1.5 eq.). After the complete consumption of the imine (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 (3x), dried over MgSO4 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 the aminomalonate (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 MgSO4 and concentrated under reduced pressure. Purification by flash column chromatography afforded the pure *N*-aminoaryl propargyl malonate.

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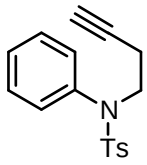
(1) Trost, B.M.; Marrs, C.M., *J. Am. Chem. Soc.* **1993**, *115*, 6637.
(2) Niwa, Y.; Takayama, K.; Shimizu, M., *Tetrahedron Lett.* **2001**, *42*, 5473.

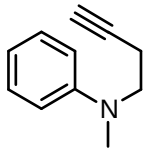
N-But-3-ynyl-4-methyl-N-phenyl-benzenesulfonamide **(5a)**



To a solution of N-tosylaniline (742 mg, 3 mmol, 1.5 eq.), the tosylate (448 mg, 2 mmol, 1 eq) and KI (33 mg, 0.2 mmol, 0.1 eq.) in DMF (4 ml) was added K_2CO_3 (818 mg, 6 mmol, 3 eq.). The mixture was heated to 90°C. After the complete consumption of the tosylate (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 $MgSO_4$ and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2 PE/AcOEt : 95/5) afforded 307 mg (50%) of the desired compound as a yellow solid.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.34-7.30 (m, 3H), 7.26 (d, *J* = 8.9 Hz, 2H), 7.07 (dd, *J* = 6.8 Hz, *J* = 3.0 Hz, 2H), 3.71 (t, *J* = 7.5 Hz, 2H), 2.43 (s, 3H), 2.39 (td, *J* = 7.5 Hz, *J* = 2.8 Hz, 2H), 1.96 (t, *J* = 2.6 Hz, 1H). **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 143.5 (C), 138.9 (C), 135.5 (C), 129.5 (CH x2), 129.2 (CH x2), 129.0 (CH x2), 128.2 (C), 127.7 (CH x2), 80.5 (C), 70.2 (CH), 49.8 (CH_2), 21.6 (CH_3), 19.3 (CH_2). F **IR** (CCl_4): ν (cm^{-1}) 3313, 2983, 1600, 1506, 1361, 1264, 1168. **MS** (EI): *m/z* 299 (M^+), 260, 154. **MS** (HRMS EI): *m/z* 299.0977 (Calcd. for $C_{17}H_{17}O_2NS$:299.0980).

But-3-ynyl-methyl-phenyl-amine **(5b)**

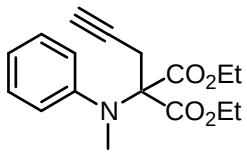


To a solution of N-methylaniline (320 ul, 3 mmol, 1.5 eq.), the tosylate (448 mg, 2 mmol, 1 eq) and KI (33 mg, 0.2 mmol, 0.1 eq.) in DMF (4 ml) was added K_2CO_3 (818 mg, 6 mmol, 3 eq.). The mixture was heated to 90°C. After the complete consumption of the tosylate (TLC), the reaction mixture was cooled to room temperature, quenched with a saturated solution of NH_4Cl, extracted with AcOEt (3x); washed with small amounts of water (5x); dried over $MgSO_4$ and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2 PE/AcOEt : 90/10) afforded 193 mg (60%) of the desired compound as a yellow oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.27 (t, *J* = 7.8 Hz, 2H), 6.76-6.74 (m, 3H), 3.60 (t, *J* = 7.3 Hz, 2H), 3.00 (s, 3H), 2.46 (td, *J* = 7.3 Hz, *J* = 2.6 Hz, 2H), 2.03 (t, *J* = 2.5 Hz, 1H). **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 148.4 (C), 129.3 (CH x2), 116.6 (CH), 112.2 (CH x2), 82.2 (C), 69.7 (C), 51.8 (CH_2), 38.4

(CH_3), 16.4 (CH_2). F **IR** (CCl_4): ν (cm^{-1}) 3313, 2888, 1599, 1505, 1357, 1117, 1037. **MS** (EI): *m/z* 159 (M^+),126, 120. **MS** (HRMS EI): *m/z* 159.1042 (Calcd. for $C_{11}H_{13}N$: 159.1048).

***2-(Methyl-phenyl-amino)-2-prop-2-ynyl-malonic acid diethyl ester* (8)**



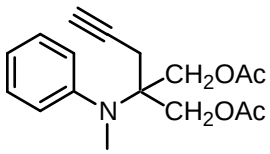
Following procedure A starting with 20 mmol of N-methylaniline.

Flash chromatography (SiO_2 PE/ AcOEt : 93/7)

Yield: 1.2 g (40%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.27 (t, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 4H), 3.08 (s, 3H), 2.85 (d, *J* = 2.5 Hz, 2H), 2.09 (t, *J* = 2.4 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 168.8 (C x2), 148.6 (C), 128.8 (CH x2), 125.8 (CH x2), 124.7 (CH), 79.2 (C), 73.9 (C), 71.7 (CH), 61.8 (CH_2 x2), 41.0 (CH_3), 26.5 (CH_2), 14.1 (CH_3 x2). F **IR** (CCl_4): ν (cm^{-1}) 3355, 2933, 2853, 1731, 1688, 1502, 1934, 1260, 1087. **MS** (EI): *m/z* 303 (M^+), 264, 228, 199, 190. **MS** (HRMS EI): *m/z* 303.1481 (Calcd. for $C_{17}H_{21}O_4N$: 303.1471).

***Acetic acid 2-acetoxymethyl-2-(methyl-phenyl-amino)-pent-4-ynyl ester* (12)**



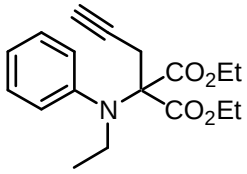
To a solution of $LiAlH_4$ (684 mg, 18 mmol, 6 eq.) in THF (10ml) at 0°C was added dropwise a solution of malonate **8** (909 mg, 3 mmol, 1.0 eq.) in THF (5 ml). The reaction was heated to reflux. After the complete consumption of the malonate (TLC). The reaction was quenched with an aqueous solution of Rochelle salts. The aqueous layer were was extracted twice with Et_2O. The combined organics layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The crude material was purified by Flash chromatography (SiO_2 PE/AcOEt: 60/40) to afford 420 mg (66 %) of the desired compound.

To a solution of previously prepared diol (420 mg, 2.0 mmol,1 eq.) in DCM were added sequentially Et_3N (8.0 mmol, 8 eq., 1.2 ml), Ac_20 (6.0 mmol, 3 eq., 0.6 ml) and DMAP (0.10 mmol, 0.05 eq.). The reaction was monitored by TLC. Upon reaction completion (approx. 15 min.), the reaction was quenched with water. The aqueous layer was extracted twice with DCM. The combined organics layers were washed with water twice, brine, dried over $MgSO_4$ and concentrated *in vacuo*. Flash column chromatography (SiO_2, PE/AcOEt: 90/10) of the residue afforded 340 mg (56%) of the desired diacetate

in yield as a colorless oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.29-7.25 (m, 2H), 7.23-7.21 (m, 2H), 7.15-7.21 (m, 1H), 4.26 (s, 4H), 2.92 (s, 3H), 2.50 (d, *J* = 2.7 Hz, 2H), 2.07 (t, *J* = 2.6 Hz, 1H), 2.04 (s, 6H). **^{13}C-NMR** (100.6 MHz, $CDCl_3$): 170.6 (C x2), 149.0 (C), 128.7 (CH x2), 128.4 (CH x2), 125.5 (CH), 79.9 (C), 71.6 (CH), 64.5 (CH_2 x2), 60.9 (C), 38.0 (CH_3), 22.9 (CH_2), 21.0 (CH_3 x2). F **IR** (CCl_4): ν (cm^{-1}) 3312, 2962, 1749, 1493, 1226, 1045. **MS** (EI): *m/z* 303 (M^+), 264, 230, 188, 144. **MS** (HRMS EI): *m/z* 303.1475 (Calcd. for $C_{17}H_{21}O_4N$: 303.1471).

2-(Ethyl-phenyl-amino)-2-prop-2-ynyl-malonic acid diethyl ester **(14a)**



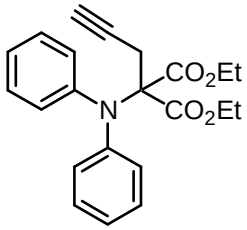
Following procedure A starting (with) 10 mmol of N-ethylaniline.

Flash chromatography (SiO_2 PE/ AcOEt : 93/7).

Yield: 538.8 mg (17%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.35-7.22 (m, 5H), 4.33 (dq, *J* = 7.1 Hz, *J* = 1.6 Hz, 4H), 3.34 (q, *J* = 7.0 Hz, 2H), 2.70 (d, *J* = 2.7Hz, 2H), 2.08 (t, *J* = 2.7 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 6H), 0.98 (t, *J* = 7.0Hz, 3H) **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 169.3 (C x2), 145.5 (C), 129.8 (CH x2), 128.7 (CH x2), 126.3 (CH), 79.4 (C), 74.6 (C), 71.5 (CH), 61.6 (CH_2 x2), 47.6 (CH_2), 26.7 (CH_2), 14.9 (CH_3), 14.1 (CH_3 x2). **F IR** (CCl_4): ν (cm^{-1}) 3315, 2982, 2936, 1736, 1493, 1231. **MS** (EI): *m/z* 317 (M^+), 278, 244, 216, 170. **MS** (HRMS EI): *m/z* 317.1627 (Calcd. for $C_{18}H_{23}O_4N$: 317.1627).

2-Diphenylamino-2-prop-2-ynyl-malonic acid diethyl ester **(14b)**

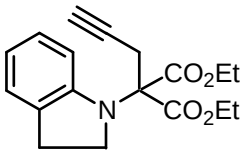


Following procedure B starting (with) 2.5 mmol of aniline with phenylmagnesium bromide. Flash chromatography (SiO_2 PE/ AcOEt : 93/7).

Yield: 341.1 mg (36%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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** (100.6 MHz, $CDCl_3$): δ 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). **F IR** (CCl_4): ν (cm^{-1}) 3314, 3064, 2983, 2938, 1744, 1591, 1499, 1228, 1055. **MS** (EI): *m/z* 365 (M^+), 326, 292, 264, 217, 180. **MS** (HRMS EI): *m/z* 365.1622 (Calcd. for $C_{22}H_{23}O_4N$: 365.1627).

2-(2,3-Dihydro-indol-1-yl)-2-prop-2-ynyl-malonic acid diethyl ester **(14c)**



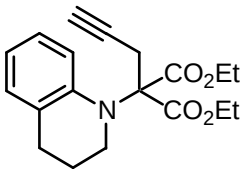
Following procedure B starting with 20 mmol of indoline.

Flash chromatography (SiO_2 PE/ AcOEt : 93/7).

Yield: 1.1 g (34%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.10 (d, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.52 (d, *J* = 6.5 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 4H), 3.76 (t, *J* = 7.1 Hz, 2H), 3.22 (d, *J* = 2.6 Hz, 2H), 3.05 (t, *J* = 8.3 Hz, 2H), 2.16 (t, *J* = 2.6 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 167.7 (C x2), 148.6 (C), 130.7 (C), 126.4 (CH), 124.3 (CH), 119.1 (CH), 111.1 (CH), 78.4 (C), 72.1 (CH), 71.2 (C), 62.1 (CH_2 x2), 50.5 (CH_2), 28.1 (CH_2), 26.0 (CH_2), 14.1 (CH_3 x2). F **IR** (CCl_4): ν (cm^{-1}) 3314, 2983, 1737, 1607, 1486, 1459, 1237, 1222, 1058. **MS** (EI): *m/z* 314 (M^+), 276, 239, 211, 167, 130. **MS** (HRMS EI): *m/z* 315.1485 (Calcd. for $C_{18}H_{21}O_4N$: 315.1471).

2-(3,4-Dihydro-2H-quinolin-1-yl)-2-prop-2-ynyl-malonic acid diethyl ester **(14d)**



Following procedure B starting with 20 mmol of 1,2,3,4-Tetrahydroquinoline.

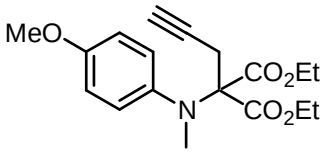
Flash chromatography (SiO_2 PE/ AcOEt : 93/7).

Yield: 1.2 g (38 %) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.02 (d, *J* = 7.3 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.53(d, *J* = 8.2 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 4H), 3.36 (t, *J* = 6.3 Hz, 2H), 3.26 (d, *J* = 2.6 Hz, 2H), 2.73 (t, *J* = 6.6 Hz, 2H), 2.06 (t, *J* = 2.6 Hz, 1H), 2.00 (tt, *J* = 6.6 Hz, *J* = 6.3 Hz, 2H), 1.25 (t, *J* = 6.5 Hz,

6H). **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 169.1 (C x2), 144.8 (C), 128.8 (C), 128.6 (CH), 125.9 (CH), 118.8 (CH), 114.8 (CH), 79.2 (C), 73.4 (C), 71.6 (CH), 62.2 (CH_2 x2), 47.3 (CH_2), 27.6 (CH_2), 25.8 (CH_2), 24.5 (CH_2), 14.0 (CH_3 x2). F **IR** (CCl_4): ν (cm^{-1}) 3314, 2940, 1740, 1495, 1299, 1230, 1197, 1053. **MS** (EI): *m/z* 329 (M^+), 290, 255, 182. **MS** (HRMS EI): *m/z* 329.1623 (Calcd. for $C_{19}H_{23}O_4$: 329.1627).

2-[(4-Methoxy-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester **(14e)**



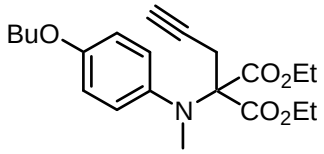
Following procedure B starting with 2.5 mmol of p-anisidine

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

Yield: 208 mg (28%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.9 Hz, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 4H), 3.79 (s, 3H), 3.00 (s, 3H), 2.72 (d, *J* = 2.6 Hz, 2H), 2.09 (t, *J* = 2.6 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 168.8 (C x2), 157.6 (C), 141.2 (C), 128.8 (C x2), 113.9 (C x2), 79.3 (C), 74.1 (C), 71.7 (CH), 61.6 (CH_2 x2), 55.4 (CH_3), 41.4 (CH_3), 26.5 (CH_2), 14.2 (CH_3 x2). F **IR** (CCl_4): ν (cm^{-1}) 3314, 2931, 1738, 1491, 1225, 1039. **MS** (EI): *m/z* 333 (M^+),297, 260, 232, 214, 190. **MS** (HRMS EI): *m/z* 333.1555(Calcd. for $C_{18}H_{23}O_5N$: 333.1576).

2-[(4-Butoxy-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester **(14f)**



Following procedure B starting (with) 2.5 mmol of p-butoxyaniline.

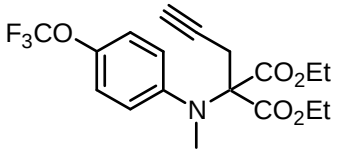
Flash chromatography (SiO_2 PE/ AcOEt : 85/15).

Yield: 350.8 mg (37%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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** (100.6 MHz, $CDCl_3$): δ 168.8 (C x2), 157.2 (C), 141.0 (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). **F IR** (CCl_4): ν (cm^{-1}) 3315, 2962, 2874, 1732, 1509, 1242, 1064. **MS** (EI): *m/z* 375 (M^+), 336, 302, 274, 230. **MS** (HRMS EI): *m/z* 375.2053 (Calcd. for $C_{21}H_{29}O_5N$: 375.2046).

2-[Methyl-(4-trifluoromethoxy-phenyl)-amino]-2-prop-2-ynyl-malonic acid diethyl ester **(14g)**



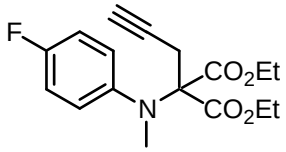
Following procedure B starting (with) 2.5 mmol of p-trifluoromethoxyaniline.

Flash chromatography (SiO_2 PE/ AcOEt : 90/10).

Yield: 299.2 mg (31%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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** (100.6 MHz, $CDCl_3$): δ 168.5 (C x2), 147.5 (C), 145.7 (q, *J* = 1.9 Hz, C), 126.8 (CH x2), 121.2 (CH x2), 120.5 (q, *J* = 255.2 Hz, C), 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). **F IR** (CCl_4): ν (cm^{-1}) 3314, 2983, 2939, 1736, 1510, 1225, 1169, 1063. **MS** (EI): *m/z* 387 (M^+), 348, 315, 286, 240. **MS** (HRMS EI): *m/z* 387.1309 (Calcd. for $C_{18}H_{20}O_5NF_3$: 387.1294).

2-[(4-Fluoro-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester **(14h)**



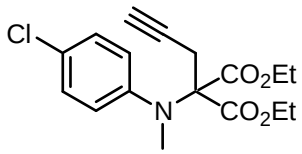
Following procedure A starting with 10 mmol of 4-fluoro-N-methylaniline.

Flash chromatography (SiO_2 PE/ AcOEt : 93/7).

Yield: 802 mg (50 %) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.27 (dd, *J* = 9.0 Hz, *J* = 5.0 Hz, 2H), 7.00 (t, *J* = 8.7 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 4H), 3.05 (s, 3H), 2.80 (d, *J* = 2.7 Hz, 2H), 2.12 (t, *J* = 2.6 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 168.6 (C x2), 160.3 (d, *J* = 244.9 Hz, C), 144.5 (C), 128.8 (d, *J* = 8.3 Hz, CH x2), 115.4 (d, *J* = 22.1 Hz, CH x2), 79.0 (C), 73.9 (C), 71.8 (CH), 61.8 (CH_2 x2), 41.2 (CH_3), 26.5 (CH_2), 14.1 (CH_3 x2). F **IR** (CCl_4): ν (cm^{-1}) 3314, 2983, 1733, 1509, 1264, 1233, 1064. **MS** (EI): *m/z* 321 (M^+), 282, 249, 220. **MS** (HRMS EI): *m/z* 321.1380 (Calcd. for $C_{17}H_{20}O_4NF$: 321.1376).

2-[(4-Chloro-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester **(14i)**



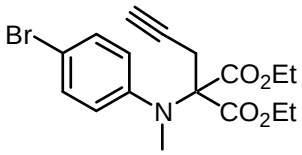
Following procedure B starting with 2.5 mmol of 4-chloroaniline.

Flash chromatography (SiO_2 PE/ AcOEt : 93/7).

Yield: 294 mg (35%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 7.1 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 4H), 3.04 (s, 3H), 2.85 (d, *J* = 2.6 Hz, 2H), 2.09 (t, *J* = 2.5 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 168.5 (C x2), 147.4 (C), 129.8 (C), 128.8 (CH x2), 126.9 (CH x2), 78.9 (C), 73.8 (C), 71.9 (CH), 61.9 (CH_2 x2), 40.8 (CH_3), 26.4 (CH_2), 14.1 (CH_3 x2). F **IR** (CCl_4): ν (cm^{-1}) 3314, 2983, 1735, 1488, 1229, 1190, 1064. **MS** (EI): *m/z* 337 (M^+),297, 263, 235, 225, 186. **MS** (HRMS EI): *m/z* 337.1070 (Calcd. for $C_{17}H_{20}O_4NCl$: 337.1081).

2-[(4-Bromo-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester **(14j)**



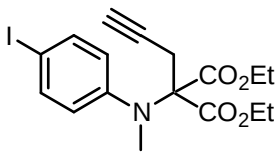
Following procedure B starting (with) 2.5 mmol of p-bromoaniline.

Flash chromatography (SiO_2 PE/ AcOEt : 93/7).

Yield: 261.2 mg (27%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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** (100.6 MHz, $CDCl_3$): δ 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). **F IR** (CCl_4): ν (cm^{-1}) 3314, 2983, 1732, 1493, 1187, 1063. **MS** (EI): *m/z* 381 (M^+), 344, 308, 280, 233, 198. **MS** (HRMS EI): *m/z* 381.0571 (Calcd. for $C_{17}H_{20}O_4NBr$: 381.0576).

2-[(4-Iodo-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester **(14k)**



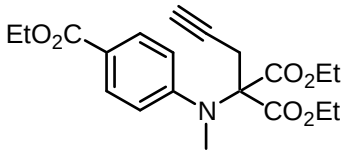
Following procedure B starting with 2.5 mmol of 4-iodoaniline.

Flash chromatography (SiO_2 PE/ AcOEt : 93/7).

Yield: 430 mg (44%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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** (100.6 MHz, $CDCl_3$): δ 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). F **IR** (CCl_4): ν (cm^{-1}) 3314, 2983, 2601, 1736, 1492, 1229, 1062. **MS** (EI): *m/z* 430 (M^+),392, 357, 281, 231, 203. **MS** (HRMS EI): *m/z* 430.0501 (Calcd. for $C_{17}H_{19}O_4NID$: 430.0500).

2-[(4-Ethoxycarbonyl-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester **(14l)**



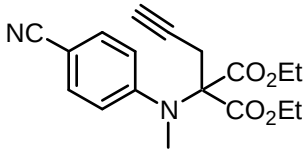
Following procedure B starting (with) 2.5 mmol of Ethyl-4-aminobenzoate.

Flash chromatography (SiO_2 PE/ AcOEt : 93/7).

Yield: 365.0 mg (39%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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** (100.6 MHz, $CDCl_3$): δ 168.3 (C x2), 166.5 (C), 153.0 (C), 130.4 (CH x2), 122.8 (C), 119.4 (CH x2), 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). **F IR** (CCl_4): ν (cm^{-1}) 3314, 2982, 1963, 1740, 1713, 1607, 1519, 1261, 1190, 1058. **MS** (EI): *m/z* 375 (M^+), 336, 302, 274, 228, 201. **MS** (HRMS EI): *m/z* 375.1671 (Calcd. for $C_{20}H_{25}O_6N$: 375.1682).

2-[(4-Cyano-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester **(14m)**



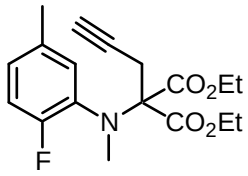
Following procedure B starting (with) 2.5 mmol of p-aminobenzonitrile.

Flash chromatography (SiO_2 PE/ AcOEt : 93/7).

Yield: 202.4 mg (25%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ7.52 (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** (100.6 MHz, $CDCl_3$): δ167.9 (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). **F IR** (CCl_4): ν(cm^{-1}) 3313, 2984, 2224, 1743, 1607, 1517, 1232, 1057. **MS** (EI): *m/z* 328 (M^+), 289, 255, 227, 217, 189. **MS** (HRMS EI): *m/z* 328.1431 (Calcd. for $C_{18}H_{20}O_4N_2$: 328.1423).

2-[(2-Fluoro-5-methyl-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester **(14n)**



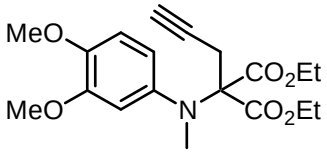
Following procedure B starting (with) 2.5 mmol of 2-fluoro-5-methylaniline.

Flash chromatography (SiO_2 PE/ AcOEt : 93/7).

Yield: 88.5 mg (11%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ7.25 (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), 2.77 (s, 3H), 2.07 (t, *J* = 2.5 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 6H) **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ168.6 (C x2), 158.6 (d, *J* = 245.6 Hz, C), 134.3 (C), 133.6 (d, *J* = 1.7 Hz, C), 131.4 (d, *J* = 2.2 Hz, CH), 127.8 (d, *J* = 7.8 Hz, CH), 116.0 (d, *J* = 21.2 Hz, CH), 79.0 (C), 73.4 (C), 71.6 (CH), 61.7 (CH_2 x2), 40.1 (d, *J* = 3.4 Hz, CH_3), 26.2 (CH_2), 20.6 (CH_3),14.2 (CH_3 x2). **MS** (EI): *m/z* 335 (M^+), 296, 262, 224, 188. **MS** (HRMS EI): *m/z* 335.1534 (Calcd. for $C_{18}H_{22}FO_4N$: 335.1533).

2-[(3,4-Dimethoxy-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester **(14o)**



Following procedure B starting (with) 2.5 mmol of 3-4-methoxyaniline.

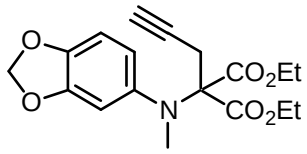
Flash chromatography (SiO_2 PE/ AcOEt : 80/20).

Yield: 281 mg (31 %) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ6.96 (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** (100.6 MHz, $CDCl_3$): δ168.7 (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). **F IR** (CCl_4): ν (cm^{-1}) 3314, 2983, 2957, 1733, 1510, 1239, 1185, 1034. **MS** (EI): *m/z* 363 (M^+), 324, 290, 262, 232, 201. **MS** (HRMS EI): *m/z* 363.1681 (Calcd. for $C_{19}H_{25}O_6N$: 363.1682).

2-(Benzo[1,3]dioxol-5-yl-methyl-amino)-2-prop-2-ynyl-malonic acid diethyl ester **(14p)**



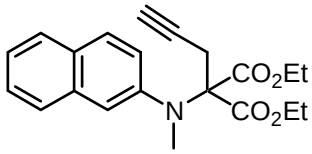
Following procedure B starting with 2.5 mmol of 3,4-(methylenedioxy)aniline.

Flash chromatography (SiO_2 PE/ AcOEt : 80/20).

Yield: 190 mg (22%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 6.82 (d, *J* = 1.9 Hz, 1H), 6.76 (dd, *J* = 8.3 Hz, *J* = 2.0 Hz, 1H), 6.70 (d, *J* = 8.3 Hz, 1H), 5.94 (s, 2H), 4.30 (q, *J* = 7.1 Hz, 4H), 2.98 (s, 3H), 2.75 (d, *J* = 2.6 Hz, 2H), 2.09 (d, *J* = 2.6 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 168.7 (C x2), 147.6 (C), 145.5 (C), 142.5 (C), 121.0 (CH), 108.9 (CH), 107.8 (CH), 101.3 (CH_2), 79.2 (C), 74.1 (C), 71.8 (CH), 61.7 (CH_2 x2), 41.5 (CH_3), 26.5 (CH_2), 14.2 (CH_3 x2). F **IR** (CCl_4): ν (cm^{-1}) 3315, 2983, 1737, 1472, 1169. **MS** (EI): *m/z* 347 (M^+), 274, 228. **MS** (HRMS EI): *m/z* 347.1371(Calcd. for $C_{18}H_{21}O_6N$:347.1369).

2-(Methyl-naphthalen-2-yl-amino)-2-prop-2-ynyl-malonic acid diethyl ester **(14q)**



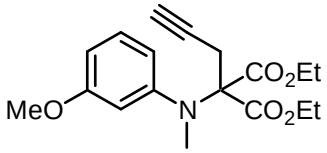
Following procedure B starting (with) 2.5 mmol of 2-aminonaphtalene.

Flash chromatography (SiO_2 PE/ AcOEt : 93/7).

Yield: 440.4 mg (50%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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 (t, *J* = 2.7 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 6H) **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 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). **F IR** (CCl_4): ν (cm^{-1}) 3314, 2982, 2926, 1735, 1599, 1231, 1186, 1063. **MS** (EI): *m/z* 353 (M^+), 314, 280, 253, 206. **MS** (HRMS EI): *m/z* 353.1625 (Calcd. for $C_{21}H_{23}O_4N$: 353.1627).

2-[(3-Methoxy-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester **(14r)**



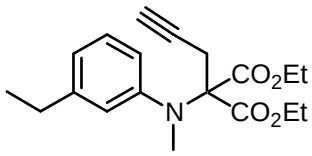
Following procedure B starting (with) 2.5 mmol of m-methoxyaniline.

Flash chromatography (SiO_2 PE/ AcOEt : 80/20).

Yield: 261.3 mg (27%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ7.15 (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, 3H), 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** (100.6 MHz, $CDCl_3$): δ168.7 (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). **F IR** (CCl_4): ν(cm^{-1}) 3314, 2983, 2939, 1736, 1599, 1488, 1227, 1064. **MS** (EI): *m/z* 333 (M^+), 294, 260, 232, 186. **MS** (HRMS EI): *m/z* 333.1581 (Calcd. for $C_{18}H_{23}O_5N$: 333.1576).

2-[(3-Ethyl-phenyl)-methyl-amino]-2-prop-2-ynyl-malonic acid diethyl ester **(14s)**



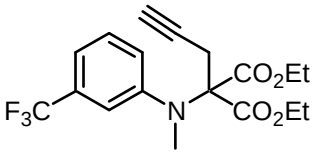
Following procedure B starting (with) 2.5 mmol of m-ethylaniline.

Flash chromatography (SiO_2 PE/ AcOEt : 93/7).

Yield: 277.9 mg (34%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ7.18 (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** (100.6 MHz, $CDCl_3$): δ168.8 (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). **F IR** (CCl_4): ν(cm^{-1}) 3315, 2967, 2935, 1733, 1602, 1487, 1227, 1186, 1064. **MS** (EI): *m/z* 331 (M^+), 292, 259, 230, 184. **MS** (HRMS EI): *m/z* 331.1778 (Calcd. for $C_{19}H_{21}O_4N$: 333.1784).

2-[Methyl-(3-trifluoromethyl-phenyl)-amino]-2-prop-2-ynyl-malonic acid diethyl ester **(14t)**



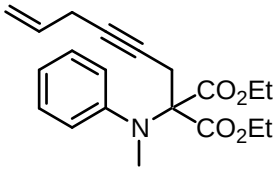
Following procedure B starting (with) 2.5 mmol of m-trifluoromethylaniline.

Flash chromatography (SiO_2 PE/ AcOEt : 93/7).

Yield: 140.7 mg (15%) of a yellowish oil.

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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** (100.6 MHz, $CDCl_3$): δ 168.4 (C x2), 149.5 (C), 131.2 (q, *J* = 31.8 Hz, C), 129.1 (CH), 127.5 (CH), 124.1 (q, *J* = 271.1 Hz, C), 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). **F IR** (CCl_4): ν (cm^{-1}) 3314, 2983, 2939, 1736, 1586, 1476, 1229, 1063. **MS** (EI): *m/z* 371 (M^+), 332, 298, 270, 224. **MS** (HRMS EI): *m/z* 371.1347 (Calcd. for $C_{18}H_{20}O_4NF_3$: 371.1344).

2-Hex-5-en-2-ynyl-2-(methyl-phenyl-amino)-malonic acid diethyl ester **(14u)**

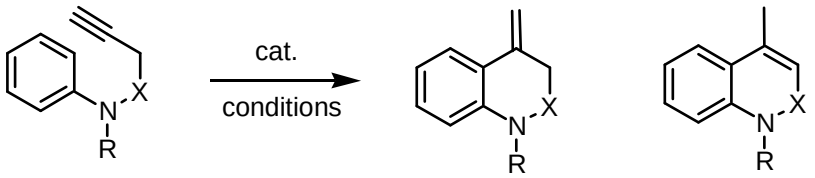


To a solution of compound **8** (303 mg, 1.0 mmol, 1eq) in DMF (1ml) were added K_2CO_3 (386 mg, 2.8 mmol, 2.8 eq.), TBAB (48 mg, 0.15 mmol, 0.15 eq.) and CuI (19 mg, 0.10 mmol, 0.10 eq) at room temperature. After 30 min, allyl bromide (860 ul, 10 mmol, 10 eq.) and NaI (120 mg, 0.8 mmol, 0.8 eq). The reaction mixture was stirred for 3 days. The reaction was quenched with water. Then the mixture was extracted with ethyl acetate (3x), dried over $MgSO_4$ and concentrated under reduced pressure. The crude material was purified by Flash chromatography (SiO_2 PE/AcOEt: 93/7) to afford 70 mg (23 %) of the desired compound.

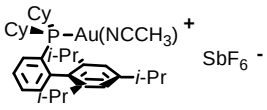
^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.25 (dd, *J* = 8.2 Hz, *J* = 7.0 Hz, 2H), 7.17 (dt, *J* = 8.6 Hz, *J* = 1.2 Hz, 2H), 7.07 (tt, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 5.78 (ddt, *J* = 17.0 Hz, *J* = 10.1 Hz, *J* = 5.1 Hz, 1H), 5.32 (ddd, *J* = 17.0 Hz, *J* = 3.6 Hz, *J* = 1.8 Hz, 1H), 5.09 (dt, *J* = 10.0 Hz, *J* = 1.7 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 4H), 3.07 (s, 3H), 2.94-2.92 (m, 2H), 2.88 (t, *J* = 2.3 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 169.0 (C x2), 146.9 (C), 132.8 (CH), 128.6 (CH x2), 125.5 (CH x2), 124.3 (CH), 115.9 (CH_2), 80.0 (C), 77.5 (C), 74.2 (C), 61.7 (CH_2 x2), 40.8 (CH_3), 26.9 (CH_2), 23.2 (CH_2), 14.1 (CH_3 x2). F **IR** (CCl_4): ν (cm^{-1}) 2983, 1734, 1493, 1263, 1227, 1192, 1063. **MS** (EI): *m/z* 343 (M^+), 263, 142, 218, 196, 164. **MS** (HRMS EI): *m/z* 343.1770 (Calcd. for $C_{20}H_{25}O_4N$: 343.1784).

Optimization of the catalytic system

The optimization was performed using model substrates **5a**, **5b**, **8** and **12**. Reaction conditions: 0.5 mmol of substrate in 500 µL of solvent with 0.5-1mol% of the catalyst. The reaction was monitored by ^{1}H NMR spectroscopy.



R= Ts	X= CH_2 **5a**	**7a**	**7'a**
R= Me	X= CH_2 **5b**	**7b**	**7'b**
R= Me	X= $C(CO_2Me)_2$ **8**	**9**	**10**
R= Me	X= $C(CH_2OAc)_2$ **12**	**13**	**13'**

C1: $Ph_3P-Au(NCCH_3)^+ SbF_6^-$ **C2**: 

substrate	cat.		solvent	temp.	time	yield	ratio
5a	**C1**	1 mol%	$CDCl_3$	rt	18h	0%	—
	C1	1 mol%	$CDCl_3$	60℃	18h	0%	—
	C2	1 mol%	$CDCl_3$	60℃	18h	0%	—
	C2	1 mol%	CD_3NO_2	100℃	18h	0%	—
5b	**C1**	1 mol%	$CDCl_3$	rt	18h	0%	—
	C1	1 mol%	$CDCl_3$	60℃	18h	0%	—
	C2	1 mol%	$CDCl_3$	60℃	18h	0%	—
	C2	1 mol%	CD_3NO_2	100℃	18h	0%	—
8	**C1**	1 mol%	$CDCl_3$	rt	18h	0%	—
	C1	1 mol%	$CDCl_3$	60℃	18h	0%	—
	C2	1 mol%	$CDCl_3$	60℃	18h	0%	—
	C2	1 mol%	CD_3NO_2	rt	18h	0%	—
	C2	1 mol%	CD_3NO_2	100℃	1.5h	92% *a*	**9**:**10**=2:1
	C2	0.5 mol%	CD_3NO_2	100℃	3h	99% *b*	**9**:**10**=1:0
12	**C2**	1 mol%	CD_3NO_2	100℃	3h	5% *c*	**13**:**13'**=1:0
					24h	52% *c*	**13**:**13'**=1:0

a isolated yield of **10** after isomerization of the mixture of **9** and **10** with pTsOH.
b isolated yield of **9**
c yield determined by ^{1}H NMR

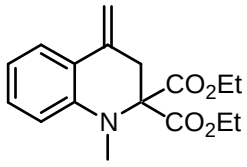
Catalysis

General Procedures C and D for the Au^{I}-Catalyzed transformations of substrates 8 and 14-u:

General Procedure C (*for the obtention of dihydroquinoline*): To a solution of the substrate (1 equiv.) in nitromethane (1M) was added XPhosAu($NCCH_3$)SbF_6 **6** (0.005 to 0.01 equiv.). The reaction mixture was heated at 100°C. Upon complete comsumption of the substrate, the mixture was concentrated under reduced pressure. The resulting crude material was dissolved in dichloromethane (0.1M) and pTsOH (0.05 equiv) was added to the solution. The reaction mixture was stirred at room temperature or at 40°C (depending on substrate) until complete isomerization of the *exo*-methylene tetrahydroquinoline (**9** and **15a-t**) into the corresponding dihydroquinoline (**10** and **16a-t**). A saturated aqueous $NaHCO_3$ solution was then added to the mixture. The organic layer was separated and the aqueous layer was extrated with AcOEt (3x). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure to afford the desired dihydroquinolines **9** and **16a-t** under pure form in most cases. If necessary, a rapid purification by flash column chromatography (SiO_2) was performed to remove impurities (note that dihydroquinolies **10** and **16a-t** were found to be unstable on silica).

General Procedure D (*for the obtention of the exo-methylene tetrahydroquinoline*): To a solution of the substrate (1 equiv.) in nitromethane (1M) was added XPhosAu($NCCH_3$)SbF_6 **6** (0.01 equiv.). The reaction mixture was heated at 100°C. Upon completion of the reaction, the mixture was evaporated. The residue was diluted with AcOEt and rapidly filtered through a pad of silica (AcOEt) to afford the desired compound.

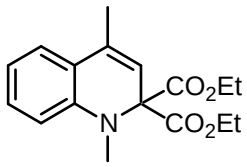
***1-Methyl-4-methylene-3,4-dihydro-1H-quinoline-2,2-dicarboxylic acid diethyl ester* (9)**



Following procedure D starting with 4 mmol (1.21 g) of **8**, 0.02 mmol (30.4 mg) of **6**.
Reaction time: 3 h (cyclisation).
Yield: 1.19 g (99%).
^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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** (100.6 MHz, $CDCl_3$): δ 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). F **IR** (CCl_4): ν (cm^{-1}) 2983, 1740, 1604, 1482, 1265, 1227, 1054. **MS** (EI): *m/z* 303 (M^+), 264, 229, 202, 157. **MS** (HRMS EI): *m/z* 303.1472 (Calcd. for $C_{17}H_{21}O_4N$: 303.1471).

1,4-Dimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester **(10)**



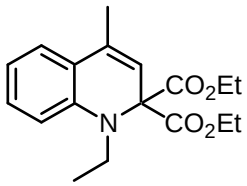
Following procedure C starting with 0.5 mmol (151 mg) of **8**, 0.005 mmol (3.8 mg) of **6**.

Reaction time: 1.5 h (cyclisation) / 1 h at rt (isomerisation).

Yield: 139 mg (92%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.23 (td, *J* = 7.8 Hz, *J* = 1.5 Hz, 1H), 7.18 (dd, *J* = 7.6 Hz, *J* = 1.4 Hz, 1H), 6.77 (td, *J* = 7.5 Hz, *J* = 0.9 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 5.61 (q, *J* = 1.1 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 4H), 3.05 (s, 3H), 2.13 (d, *J* = 1.1 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 6H). ***^{13}C*-NMR** (100.6 MHz, $CDCl_3$): δ 169.4 (C x2), 143.1 (C), 132.2 (C), 129.6 (CH), 123.9 (CH), 120.9 (C), 117.4 (CH), 116.9 (CH), 110.5 (CH), 73.9 (C), 62.0 (CH_2 x2), 35.9 (CH_3), 18.8 (CH_3), 14.1 (CH_3 x2). F **IR** (CCl_4): ν (cm^{-1}) 2982, 1737, 1604, 1482, 1227, 1056, 1039. **MS** (EI): *m/z* 303 (M^+), 230, 184. **MS** (HRMS EI): *m/z* 303.1475 (Calcd. for $C_{17}H_{21}O_4N$: 303.1471).

1-Ethyl-4-methyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester **(16a)**



Following procedure C starting with 0.54 mmol (171 mg) of **14a**, 0.005 mmol (3.8 mg) of **6**.

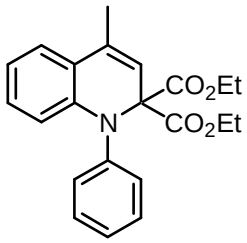
Reaction time: 20min (cyclisation) / 1h at room temperature (isomerisation).

Yield: 164 mg (97%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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, 3H) **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 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). **F IR** (CCl_4):

ν (cm^{-1}) 2982, 1739, 1463, 1203, 1146, 1037. **MS** (EI): *m/z* 317 (M^+), 292, 244, 198. **MS** (HRMS EI): *m/z* 317.1619 (Calcd. for $C_{18}H_{23}O_4N$: 317.1627).

4-Methyl-1-phenyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester **(16b)**



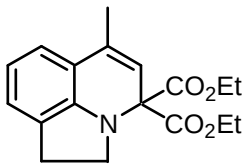
Following procedure C starting with 0.25 mmol (91 mg) of **16b**, 0.0025 mmol (1.9 mg) of **6**.

Reaction time: 0.5h (cyclisation), 1.5h at room temperature (isomerisation).

Yield: 78 mg (86%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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** (100.6 MHz, $CDCl_3$): δ 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). **F IR** (CCl_4): ν (cm^{-1}) 2982, 1742, 1489, 1265, 1225, 1047. **MS** (EI): *m/z* 365 (M^+), 292, 264, 218. **MS** (HRMS EI): *m/z* 365.1624 (Calcd. for $C_{22}H_{23}O_4N$: 365.1627).

6-Methyl-1,2-dihydro-pyrrolo[3,2,1-ij]quinoline-4,4-dicarboxylic acid diethyl ester **(16c)**



Following procedure C starting with 0.5 mmol (158 mg) of **14c**, 0.005 mmol (3.8 mg) of **6**.

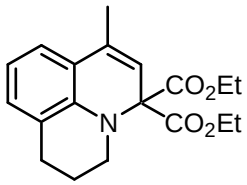
Reaction time: 18h (cyclisation) / 1h at room temperature (isomerisation).

Yield: 157 (99%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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** (100.6 MHz, $CDCl_3$): δ 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). **F IR** (CCl_4): ν (cm^{-1}) 2962, 1739, 1460, 1238, 1031. **MS** (EI): *m/z* 315 (M^+), 302, 242, 214. **MS** (HRMS EI): *m/z* 315.1469 (Calcd. for $C_{18}H_{21}O_4N$: 315.1471).

1-Methyl-6,7-dihydro-5H-pyrido[3,2,1-ij]quinoline-3,3-dicarboxylic acid diethyl ester **(16d)**



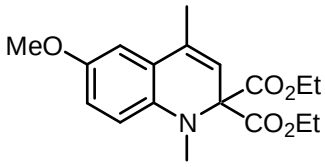
Following procedure C starting with 0.5 mmol (164 mg) of **15d,** 0.005 mmol (3.8 mg) of **6**.

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

Yield: 155 mg (94%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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** (100.6 MHz, $CDCl_3$): δ 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). **F IR** (CCl_4): ν (cm^{-1}) 2982, 2939, 1737, 1475, 1446, 1239. **MS** (EI): *m/z* 329 (M^+), 257, 229, 210, 183. **MS** (HRMS EI): *m/z* 329.1631 (Calcd. for $C_{19}H_{23}O_4N$: 329.1627).

6-Methoxy-1,4-dimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester **(16e)**



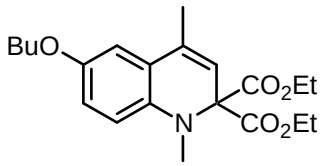
Following procedure C starting with 0.5 mmol (167 mg) of **16e**, 0.005 mmol (3.8 mg) of **6**.

Reaction time: 50 min (cyclisation).

Yield: 159 mg (95%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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** (100.6 MHz, $CDCl_3$): δ 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). F **IR** (CCl_4): ν (cm^{-1}) 2983, 1738, 1492, 1264, 1225, 1039. **MS** (EI): *m/z* 333 (M^+), 261, 231; 189. **MS** (HRMS EI): *m/z* 333.1581 (Calcd. for $C_{18}H_{23}O_5N$: 333.1576).

6-Butoxy-1,4-dimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester **(16f)**



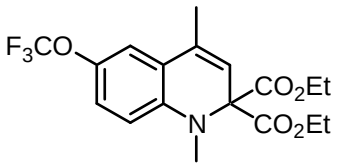
Following procedure C starting with 0.5 mmol (188 mg) of **14f,** 0.005 mmol (3.8 mg) of **6**.

Reaction time: 1.5h (cyclisation) / 1h at 40°C (isomerisation).

Yield: 187 mg (99%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ6.77 (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, 2H), 1.29 (t, *J* = 7.1 Hz, 6H), 0.97 (t, *J* = 7.4 Hz, 3H) **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ169.6 (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). **F IR** (CCl_4): ν (cm^{-1}) 2962, 1736, 1498, 1224, 1036. **MS** (EI): *m/z* 375 (M^+), 303, 275, 247, 217, 190. **MS** (HRMS EI): *m/z* 375.2041 (Calcd. for $C_{21}H_{29}O_5N$: 375.2046).

1,4-Dimethyl-6-trifluoromethoxy-1H-quinoline-2,2-dicarboxylic acid diethyl ester **(16g)**



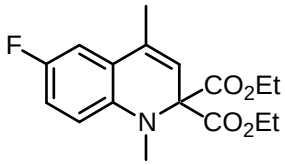
Following procedure C starting with 0.5 mmol (193 mg) of **14g,** 0.005 mmol (3.8 mg) of **6**.

Reaction time: 0.5h (cyclisation) / 48h at room temperature (isomerisation).

Yield: 175.4mg (91%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ7.04 (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** (100.6 MHz, $CDCl_3$): δ169.0 (C x2), 141.8 (C), 140.7 (C) (q, *J* = 2.0 Hz), 131.4 (C), 122.2 (C), 121.8 (CH), 120.7 (q, *J* = 254.0 Hz, C), 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). **F IR** (CCl_4): ν (cm^{-1}) 2983, 2927, 1740, 1498, 1223, 1166. **MS** (EI): *m/z* 387 (M^+), 314, 286, 267, 226. **MS** (HRMS EI): *m/z* 387.1287 (Calcd. for $C_{18}H_{20}O_5NF_3$: 387.1294).

6-Fluoro-1,4-dimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester **(16h)**



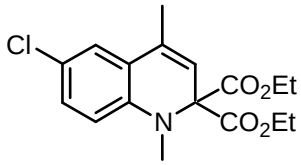
Following procedure C starting with 0.5 mmol (160.5 mg) of **14h**, 0.005 mmol (3.8 mg) of **6**.

Reaction time: 18h (cyclisation) / 1 h at room temperature (isomerisation).

Yield: 135 mg (84%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 6.91-6.84 (m, 2H), 6.57 (dd, *J* = 8.8 Hz, *J* = 4.5 Hz, 1H), 5.64 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 4H), 2.99 (s, 3H), 2.06 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 169.3 (C x2), 155.9 (d, *J* = 234.8 Hz, C), 139.5 (C), 131.6 (C), 122.3 (d, *J* = 7.3 Hz, C), 118.8 (CH), 115.3 (d, *J* = 21.4 Hz, CH), 111.3 (d, *J* = 7.5 Hz, CH), 110.7 (d, *J* = 23.7 Hz, CH), 73.7 (C), 62.1 (CH_2 x2), 36.1 (CH_3), 18.7 (CH_3), 14.1 (CH_3 x2). F **IR** (CCl_4): ν (cm^{-1}) 2982, 1738, 1495, 1223, 1048. **MS** (EI): *m/z* 321 (M^+), 230, 202. **MS** (HRMS EI): *m/z* 321.1363 (Calcd. for $C_{17}H_{20}O_4NF$: 321.1376).

6-Chloro-1,4-dimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester **(16i)**



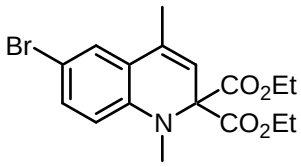
Following procedure C starting with 0.5 mmol (168.5 mg) of **14i**, 0.005 mmol (3.8 mg) of **6**.

Reaction time: 7h (cyclisation) / 1h at room temperature (isomerisation).

Yield: 143 mg (85%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.12 (dd, *J* = 8.7 Hz, *J* = 2.3 Hz, 1H), 7.07 (d, *J* = 2.2 Hz, 1H), 6.57 (d, *J* = 8.7 Hz, 1H), 5.62 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 4H), 2.98 (s, 3H), 2.06 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 168.0 (C x2), 140.7 (C), 130.4 (C), 127.9 (CH), 122.7 (CH), 121.5 (CH), 121.4 (C), 117.2 (CH), 110.8 (CH), 72.7 (C), 61.1 (CH_2 x2), 35.0 (CH_3), 17.7 (CH_3), 13.1 (CH_3 x2). F **IR** (CCl_4): ν (cm^{-1}) 2983, 1738, 1491, 1264, 1225. **MS** (EI): *m/z* 337 (M^+), 264, 235. **MS** (HRMS EI): *m/z* 337.1095 (Calcd. for $C_{17}H_{20}O_4NCl$: 337.1081).

6-Bromo-1,4-dimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester **(16j)**



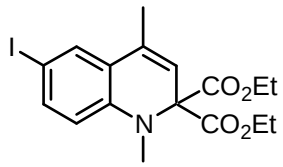
Following procedure C starting with 0.5 mmol (190 mg)of **14j**, 0.005 mmol (3.8 mg) of **6**.

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

Yield: 185 mg (97%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ7.24 (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** (100.6 MHz, $CDCl_3$): δ169.0 (C x2), 142.2 (C), 131.9 (CH), 131.4 (C), 126.6 (CH), 122.9 (C), 118.2 (CH), 112.3 (CH), 109.8 (C), 77.2 (C), 62.2 (CH_2 x2), 36.1 (CH_3), 18.7 (CH_3), 14.1 (CH_3 x2). **F IR** (CCl_4): ν (cm^{-1}) 2983, 2938, 1738, 1489, 1263, 1226, 1046. **MS** (EI): *m/z* 381 (M^+), 308, 280, 262, 229. **MS** (HRMS EI): *m/z* 381.0570 (Calcd. for $C_{17}H_{20}O_4NBr$: 381.0576).

6-Iodo-1,4-dimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester **(16k)**



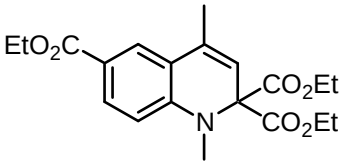
Following procedure C starting with 0.3 mmol (129 mg) of **14k**, 0.005 mmol (2.3 mg) of **6**.

Reaction time: 40 min (cyclisation) / 18 h at 40°C (isomerisation).

Yield: 125 mg (97%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ7.43 (dd, *J* = 8.6 Hz, *J* = 2.1 Hz, 1H), 7.35 (d, *J* = 2.0 Hz, 1H), 6.42 (d, *J* = 8.7 Hz, 1H), 5.57 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 4H), 2.97 (s, 3H), 2.04 (bs, 2H), 1.36 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 170.9 (C x2), 144.7 (C), 139.9 (CH), 134.2 (CH), 133.1 (C), 125.2 (C), 119.8 (CH), 114.9 (CH), 80.8 (C), 75.6 (C), 64.1 (CH_2 x2), 37.9 (CH_3), 20.4 (m, CH_3), 16.0 (CH_3 x2). F **IR** (CCl_4): ν (cm^{-1}) 2983, 1738, 1488, 1223, 1037. **MS** (EI): *m/z* 430 (M^+),357, 328, 230, 202. **MS** (HRMS EI): *m/z* 430.0492 (Calcd. for $C_{17}H_{19}O_4NID$: 430.0500).

1,4-Dimethyl-1H-quinoline-2,2,6-tricarboxylic acid triethyl ester **(16l)**



Following procedure C starting with 0.5 mmol (187 mg)of **14l,** 0.005 mmol (3.8 mg) of **6**.

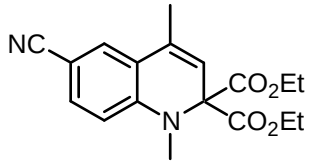
Reaction time: 4h (cyclisation) / 4h at 40°C (isomerisation).

Yield: 182 mg (97%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ7.88 (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** (100.6 MHz, $CDCl_3$): δ168.7 (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). **F IR** (CCl_4): ν (cm^{-1}) 2982, 1739, 1709, 1607, 1499, 1270, 1159, 1046. **MS** (EI): *m/z* 375 (M^+), 302, 274, 246. **MS** (HRMS EI): *m/z* 375.1693 (Calcd. for $C_{20}H_{25}O_6N$: 375.1682).

6-Cyano-1,4-dimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester **(16m)**



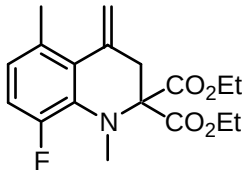
Following procedure C starting with 0.5 mmol (164 mg)of **14m,** 0.005 mmol (3.8 mg) of **6**.

Reaction time: 0.5h (cyclisation), overnight at rt (isomerisation).

Yield: 155 mg (94%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ7.44 (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** (100.6 MHz, $CDCl_3$): δ168.3 (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). **F IR** (CCl_4): ν (cm^{-1}) 2983, 2939, 2222, 1740, 1605, 1499, 1227, 1162. **MS** (EI): *m/z* 328 (M^+), 290, 255, 227, 182. **MS** (HRMS EI): *m/z* 328.1407 (Calcd. for $C_{18}H_{20}O_4N_2$: 328.1423).

8-Fluoro-1,4,5-trimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester **(16n)**



Following procedure D starting with 0.2 mmol (67 mg) of **14n**, 0.002 mmol (1.4 mg) of **6**.

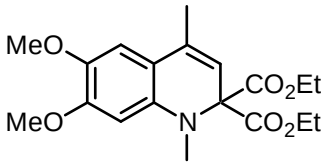
Reaction time: 1.5h at 100°C (cyclisation).

Yield: 57mg (85%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ6.87 (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** (100.6 MHz, $CDCl_3$): δ168.4 (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). F **IR** (CCl_4): ν (cm^{-1}) 2983, 1738, 1490, 1231. **MS** (EI): *m/z* 335 (M^+), 263, 234, 189. **MS** (HRMS EI): *m/z* 335.1535(Calcd. for $C_{18}H_{22}FNO_4$: 335.1533).

6,7-Dimethoxy-1,4-dimethyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester **(16o)**



Following procedure C starting with 0.5 mmol (131 mg) of **14o,** 0.005 mmol (3.8 mg) of **6**.

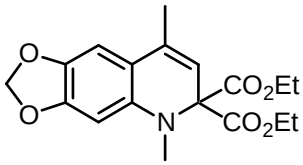
Reaction time: 0.5h (cyclisation), no isomerisation step required.

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

Yield: 136mg (75%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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** (100.6 MHz, $CDCl_3$): δ 169.7 (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). **F IR** (CCl_4): ν (cm^{-1}) 2983, 2936, 1737, 1508, 1464, 1232. **MS** (EI): *m/z* 363 (M^+), 290, 262, 244. **MS** (HRMS EI): *m/z* 363.1674 (Calcd. for $C_{19}H_{25}O_6N$: 363.1682).

5-Methyl-8-methylene-7,8-dihydro-5H-[1,3]dioxolo[4,5-g]quinoline-6,6-dicarboxylic acid diethyl ester **(16p)**



Following procedure C starting with 0.5 mmol (170 mg) of **14p**, 0.005 mmol (3.8 mg) of **6**.

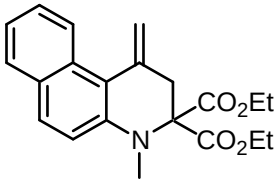
Reaction time: 20 min (cyclisation), no isomerisation step required.

Flash Chromatography (SiO_2, EP/AcOEt : 80/20)

Yield: 90.1 mg (53%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 6.69 (s, 1H), 6.35 (s, 1H), 5.87 (s, 2H), 5.46 (s, 1H), 4.25 (q, J = 7.1 Hz, 6H), 2.98 (s, 3H), 2.03 (s, 3H), 1.29 (t, J = 7.1 Hz, 6H). **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 168.7 (C x2), 147.5 (C), 138.5 (C), 138.4 (C), 131.0 (C), 113.9 (CH), 113.5 (C), 103.5 (CH), 99.8 (CH_2), 93.0 (CH), 72.9 (C), 60.9 (CH_2 x2), 35.4 (CH_3), 18.1 (CH_3), 13.1 (CH_3 x2). F **IR** (CCl_4): ν (cm^{-1}) 2939, 1737, 1482, 1145. **MS** (EI): *m/z* 347 (M^+), 274, 228. **MS** (HRMS EI): *m/z* 347.1371(Calcd. for $C_{18}H_{23}O_6N$:347.1369).

***4-Methyl-1-methylene-1,4-dihydro-2H-benzo[f]quinoline-3,3-dicarboxylic acid diethyl ester* (15q)**



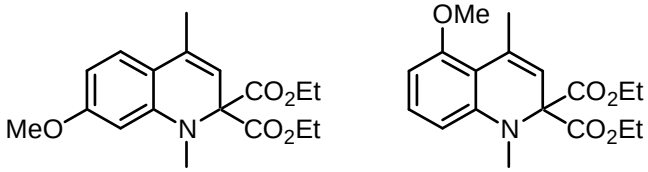
Following procedure D starting with 0.5 mmol (176 mg) of **14q**, 0.005 mmol (3.8 mg) of **6**.

Reaction time: 15min (cyclisation).

Yield: 164 mg (93%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ8.34 (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** (100.6 MHz, $CDCl_3$): δ170.1 (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). **F IR** (CCl_4): ν (cm^{-1}) 2983, 1739, 1597, 1514, 1364, 1264, 1227, 1048. **MS** (EI): *m/z* 353 (M^+), 282, 252, 234, 208. **MS** (HRMS EI): *m/z* 353.1623 (Calcd. for $C_{21}H_{23}O_4N$: 353.1627).

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* (16r and 16'r)**



Following procedure C starting with 0.5 mmol (167 mg) of **14r**, 0.005 mmol (3.8 mg) of **6**.

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

Yield: 154 mg (93%).

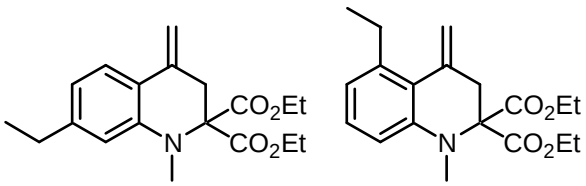
16r : ^{1}H-NMR (400.2 MHz, $CDCl_3$): δ7.03 (d, *J* = 8.3 Hz, 1H), 6.25 (dd, *J* = 8.3 Hz, *J* = 2.3 Hz, 1H), 6.21 (d, *J* = 2.3 Hz, 1H), 5.43 (s, 1H), 4.24 (q, *J* = 7.2 Hz, 4H), 3.78 (s, 3H), 2.98 (s, 3H), 2.04 (d, *J* = 1.3 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 6H) **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ169.4 (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)

16'r: ^{1}H-NMR (400.2 MHz, $CDCl_3$): 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** (100.6 MHz, $CDCl_3$): δ169.9 (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)

For the mixture of **16r** and **16'r**: **F IR** (CCl_4): ν (cm^{-1}) 2984, 1737, 1610, 1264, 1233, 1044. **MS** (EI): *m/z* 333 (M^+), 260, 232, 217, 189. **MS** (HRMS EI): *m/z* 333.1575 (Calcd. for $C_{18}H_{23}O_5N$: 333.1576).

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*** **(16s and 16's)**



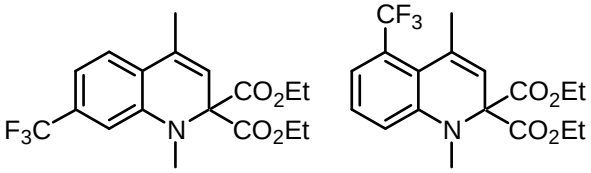
Following procedure C starting with 0.5 mmol (165.5 mg) of **14s**, 0.005 mmol (3.8 mg) of **6**.

Reaction time: 15min (cyclisation).

Yield: 117 mg (71%).

For the mixture of **16s** and **16's**: **^{1}H-NMR** (400.2 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.59-6.56 (m, 3H), 5.37 (s, 1H), 5.18 (s, 2H), 4.82 (s, 1H), 4.31-4.21 (m, 8H), 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, 18H) **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 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), 122.3 (C), 118.7 (CH), 118.7 (C), 117.3 (CH), 115.0 (CH_2), 111.8 (CH), 109.2 (CH), 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). **F IR** (CCl_4): ν (cm^{-1}) 2967, 2935, 1739, 1609, 1464, 1230, 1050. **MS** (EI): *m/z* 330 (M^+),291, 229, 170. **MS** (HRMS EI): *m/z* 331.1782 (Calcd. for $C_{19}H_{25}O_4N$: 331.1784).

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 esterv*** **(16t and 16't)**



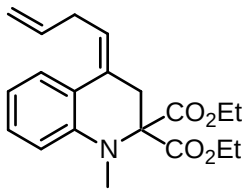
Following procedure C starting with 0.25 mmol (93 mg) of **14t**, 0.005 mmol (3.8 mg) of **6**.

Reaction time: 5h (cyclisation) / 1.5h at room temperature (isomerisation).

Yield: 83.2mg (90%).

For the mixture of **16t** and **16't**: **^{1}H-NMR** (400.2 MHz, $CDCl_3$): δ7.63 (d, *J* = 7.0 Hz, 1H), 7.37 (t, J = 8.2 Hz, 1H), 7.14 (d, J = 7.8 Hz), 7.07-7.02 (m, 3 H), 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** (100.6 MHz, $CDCl_3$): δ169.6 (C x2), 168.8 (C x2), 145.5 (C), 143.4 (C), 134.0 (q, *J* = 9.1 Hz, C), 131.3 (q, *J* = 31.5 Hz, C), 129.6 (q, *J* = 27.6 Hz, CH), 128.5 (CH), 124.9 (q, *J* = 269.1 Hz, C), 124.4 (C) (q, *J* = 261.9 Hz), 124.1 (CH), 123.6 (C), 119.0 (CH), 116.3 (q, *J* = 5.4 Hz, C), 115.7 (q, *J* = 5.1 Hz, C), 114.9 (CH), 114.0 (q, *J* = 4.0 Hz, CH), 106.9 (q, *J* = 4.0 Hz, CH), 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 non vivible C signals. **F IR** (CCl_4): ν(cm^{-1}) 2983, 2926, 1740, 1594, 1465, 1314, 1231, 1130, 1063. **MS** (EI): *m/z* 371 (M^+), 300, 271, 250, 226. **MS** (HRMS EI): *m/z* 371.1354 (Calcd. for $C_{18}H_{20}O_4NF_3$: 371.1344).

4-But-3-en-(Z)-ylidene-1-methyl-3,4-dihydro-1H-quinoline-2,2-dicarboxylic acid diethyl ester **(15u)**



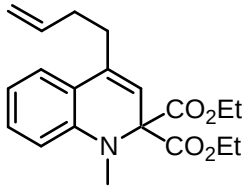
Following procedure D starting with 0.1 mmol (34.3 mg) of **14u**, 0.001 mmol (0.7 mg) of **6**.

Reaction time: 6h (cyclisation).

Yield: 28.1 mg (82%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ7.23-7.18 (m, 2H), 6.74-6.70 (m, 2H), 5.88 (ddt, *J* = 16.3 Hz, *J* = 10.2 Hz, *J* = 5.9 Hz, 1H), 5.38 (t, *J* = 7.5 Hz, 1H), 5.10 (dt, *J* = 17.2 Hz, *J* = 1.7 Hz, 1H), 5.04 (dt, *J* = 10.2 Hz, *J* = 1.3 Hz, 1H), 4.32-4.19 (m, 4H), 3.09 (t, *J* = 5.8 Hz, 2H), 3.04 (s, 2H), 3.01 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 170.0 (C x2), 144.4 (C), 137.0 (CH), 129.0 (C), 129.0 (CH), 127.3 (CH), 125.2 (CH), 121.3 (C), 116.5 (CH), 115.3 (CH_2), 111.6 (CH), 74.2 (C), 62.0 (CH_2 x2), 39.8 (CH_2), 36.6 (CH_3), 33.2 (CH_2), 14.2 (CH_3 x2). F **IR** (CCl_4): ν(cm^{-1}) 2983, 1738, 1228, 1095. **MS** (EI): *m/z* 343 (M^+),286, 270, 245. **MS** (HRMS EI): *m/z* 343.1801 (Calcd. for $C_{20}H_{25}O_4N$: 343.1784).

4-But-3-enyl-1-methyl-1H-quinoline-2,2-dicarboxylic acid diethyl ester **(16u)**



Following procedure C starting with 0.1 mmol (34.3 mg) of **14u**, 0.001 mmol (0.7 mg) of **6**.

Reaction time: 6h (cyclisation) / 18h at 40°C (isomerisation)

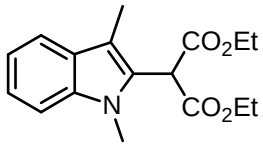
Yield: 28.1 mg (82%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 7.21-7.15 (m, 2H), 6.73 (td, *J* = 7.6 Hz, *J* = 1.5 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 5.91 (d, *J* = 8.0 Hz, 1H), 5.57 (s, 1H), 5.08 (ddd, *J* = 17.2 Hz, *J* = 3.3 Hz, *J* = 1.6 Hz, 1H), 5.00 (ddd, *J* = 10.2 Hz, *J* = 3.4 Hz, *J* = 1.6 Hz, 1H), 4.29-4.24 (m, 4H), 3.01 (s, 3H), 2.55 (dd, *J* = 9.3 Hz, *J* = 6.1 Hz, 2H), 2.35 (dd,*J* = 14.7 Hz, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ 169.8 (C x2), 143.4 (C), 137.9 (CH), 135.2 (C), 129.6 (CH), 123.5 (CH), 119.9 (C), 117.5 (CH), 116.7 (CH), 115.0 (CH_2), 111.0 (CH), 73.8 (C), 62.1 (CH_2 x2), 36.0 (CH_3), 32.2 (CH_2), 31.2 (CH_2), 14.2 (CH_3 x_2). F **IR** (CCl_4): ν (cm^{-1}) 2983, 1737, 1264, 1227. **MS** (EI): *m/z* 343 (M^+), 302, 271, 241. **MS** (HRMS EI): *m/z* 343.1771 (Calcd. for $C_{20}H_{25}O_4N$: 343.1784).

Isomerization into indoles

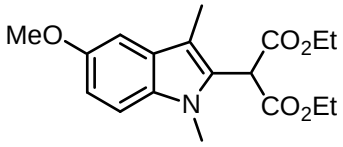
General Procedure E (***for the isomerization of the hydroquinolines into indoles***)**:** A solution of the dihydroquinoline (0.1 mmol) in $CDCl_3$ (500µL) in an NMR tube was exposed to sunlight. The transformation was monitored by ^1H NMR spectroscopy. Upon complete conversion of the dihydroquinoline, the reaction mixture was concentrated under reduced pressure and the resulting crude material was purified by Flash Chromatography to afford the pure indole.

2-(1,3-Dimethyl-1*H*-indol-2-yl)-malonic acid diethyl ester (11)



Following procedure E starting with 0.1 mmol (30 mg) of **10**.
Flash Chromatography (SiO_2 PE/AcOEt : 90/10)
Yield: 25 mg (85%).
^{1}H-NMR (400.2 MHz, $CDCl_3$): 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** (100.6 MHz, $CDCl_3$): δ 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). F **IR** (CCl_4): ν (cm^{-1}) 2983, 1739, 1472, 1206, 1146. **MS** (EI): *m/z* 303 (M^+), 228, 184. **MS** (HRMS EI): *m/z* 303.1468 (Calcd. for $C_{17}H_{21}O_4N$: 303.1471).

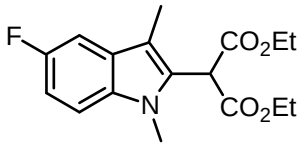
2-(5-Methoxy-1,3-dimethyl-1*H*-indol-2-yl)-malonic acid diethyl ester (20a)



Following procedure E starting with 0.1 mmol (33 mg) of **16e**.
Flash Chromatography (SiO_2 PE/AcOEt : 80/20)
Yield: 29 mg (88%).
^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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** (100.6 MHz, $CDCl_3$): δ 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). F **IR** (CCl_4): ν (cm^{-1}) 2984, 2939, 1739, 1490, 1299, 1145. **MS** (EI): *m/z* 333 (M^+), 260, 215. **MS** (HRMS EI): *m/z* 333.1571 (Calcd. for $C_{18}H_{23}O_5N$: 333.1576).

2-(5-Fluoro-1,3-dimethyl-1*H*-indol-2-yl)-malonic acid diethyl ester (20b)



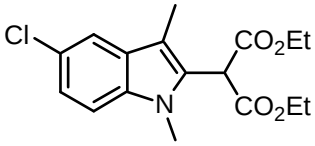
Following procedure E starting with 0.1 mmol (32 mg) of **16h**.

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

Yield: 29 mg (92%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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** (100.6 MHz, $CDCl_3$): δ 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). F **IR** (CCl_4): ν (cm^{-1}) 2984, 1739, 1488, 1156. **MS** (EI): *m/z* 321 (M^+), 275, 248, 220, 201. **MS** (HRMS EI): *m/z* 321.1394 (Calcd. for $C_{17}H_{20}O_4NF$: 321.1376).

2-(5-Chloro-1,3-dimethyl-1*H*-indol-2-yl)-malonic acid diethyl ester (20c)



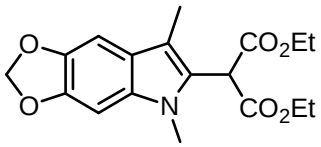
Following procedure E starting with 0.1 mmol (34 mg) of **16i**.

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

Yield: 23 mg (67%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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** (100.6 MHz, $CDCl_3$): δ 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). F **IR** (CCl_4): ν (cm^{-1}) 2983, 1740, 1475, 1308, 1146. **MS** (EI): *m/z* 337 (M^+), 263, 216, 176. **MS** (HRMS EI): *m/z* 337.1086 (Calcd. for $C_{17}H_{20}O_4NCl$: 337.1081).

5-Methyl-8-methylene-7,8-dihydro-5*H*-[1,3]dioxolo[4,5-*g*]quinoline-6,6-dicarboxylic acid diethyl ester (20d)



Following procedure E starting with 0.1 mmol (35 mg) of **16p**.

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

Yield: 31 mg (88%).

^{1}H-NMR (400.2 MHz, $CDCl_3$): δ 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** (100.6 MHz, $CDCl_3$): δ 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). F **IR** (CCl_4): ν (cm^{-1}) 2984, 1737, 1472, 1043. **MS** (EI): *m/z* 347 (M^+), 274, 246, 228, 202. **MS** (HRMS EI): *m/z* 347.1374(Calcd. for $C_{18}H_{21}O_6N$:347.1369).