



Supporting Information

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Organocatalytic, Asymmetric α -Halogeneration of 1,3-Dicarbonyl Compounds

Giuseppe Bartoli,* Marcella Bosco, Armando Carlone, Manuela Locatelli, Paolo Melchiorre,* and Letizia Sambri

Department of Organic Chemistry "A. Mangini",
Alma Mater Studiorum - Bologna University
v.le Risorgimento 4, I-40136 Bologna, Italy

e-mail: pm@ms.fci.unibo.it; giuseppe.bartoli@unibo.it

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General Methods. The ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts (δ) for ^1H and ^{13}C are given in ppm relative to residual signals of the solvents (CHCl_3). Coupling constants are given in Hz. Carbon types were determined from DEPT ^{13}C NMR experiments. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad signal. Purification of reaction products was carried out by flash chromatography (FC) on silica gel (230-400 mesh) according to the method of Still.¹ Optical rotations are reported as follows: $[\alpha]^{rt}_{\text{D}}$ (c in g per 100 mL, solvent).

¹ W. C. Still, M. Kahn, A. J. Mitra, *J. Org. Chem.* **1978**, *43*, 2923.

Materials. Commercial grade reagents and solvents were used without further purification; otherwise, where necessary, they were purified as recommended.²

β -keto esters **1a-g** and β -diketones **1h-i** were purchased from Aldrich or Lancaster and used as received.

Cinchona alkaloids derivatives such as Cinchonidine, Quinine, (DHQD)₂PHAL, (DHQ)₂PYR and (DHQ)₂AQN were purchased from Aldrich and used as received. Benzoylquinine (BQ) **4a** and Benzoylquinidine (BQd) **4b** were prepared according to standard literature procedures (Quinine or Quinidine / Et₃N / benzoylchloride / DCM / overnight, RT). N-chlorosuccinimide (NCS) **3a**, 1,3-dichloro-5,5-dimethylhydantoin **3b** and 2,3,4,5,6,6-hexachloro-2,4-cyclohexadien-1-one **3c** were purchased from Acros Organics and used as received.

5,7,7-trichloro-7H-quinolin-8-one **3d** and 2,2,4-trichloro-2H-naphthalen-1-one **3e** were prepared starting from 8-hydroxyquinoline and 1-naphthol, respectively, following the literature procedure (*t*-butylhypochlorite/DCM/RT, 3h).³

Determination of Enantiomeric Purity. Chiral HPLC analysis was performed on an Agilent 1100-series instrumentation. Daicel Chiralpak AD-H or AS-H columns with i-PrOH/hexane as the eluent were used.

Chiral GC analysis was performed on a Hewlett-Packard 5890 gas chromatography using a RT-BetaDEX-sm chiral column.

The enantiomeric excess (ee) of the products was determined by GC analysis for chloro compounds **2a-c**, **2e** and **2g-h** and by HPLC analysis for chloro compounds **2d**, **2f**, **2i** and for bromo compounds **7b** and **7f**. HPLC and GC traces were compared to racemic samples prepared with Et₃N as the catalyst.

Determination of Absolute Configuration. The absolute configurations of the optically active chloro compounds **2a-b**⁴ and **2e**⁴ were determined on the basis of the measured optical rotations that were compared with literature values. All other absolute configurations were assigned by analogy.

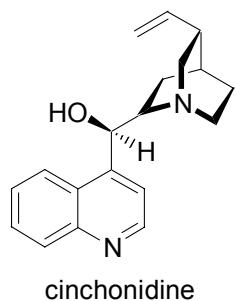
² W. L. F. Armarengo, D. D. Perrin, In *Purification of Laboratory Chemicals*, 4th ed.; Butterworth Heinemann: Oxford, 1996.

³ S. France, H. Wack, A. E. Taggi, A. M. Hafez, T. R. Wagerle, M. H. Shah, C. L. Dusich, T. Lectka, *J. Am. Chem. Soc.* **2004**, *126*, 4245.

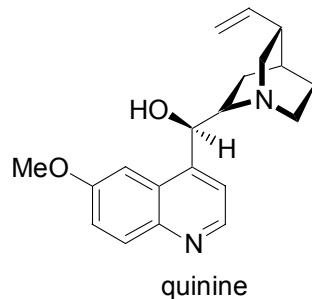
⁴ M. Marigo, N. Kumaragurubaran, K. A. Jørgensen, *Chem. Eur. J.* **2004**, *10*, 2133.

Structure of the Catalysts.

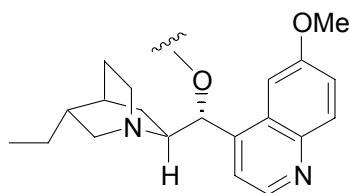
Cinchona alkaloids derivatives tested in Table 1.



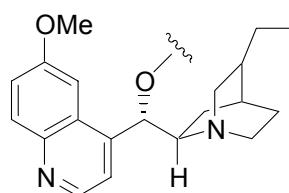
cinchonidine



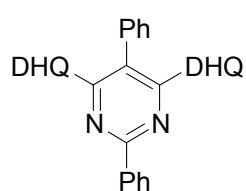
quinine



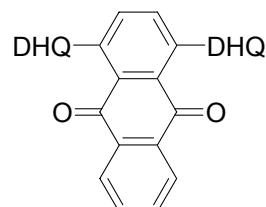
DHQ



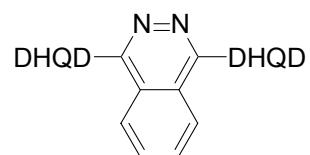
DHQD



(DHQ)₂PYR



(DHQ)₂AQN



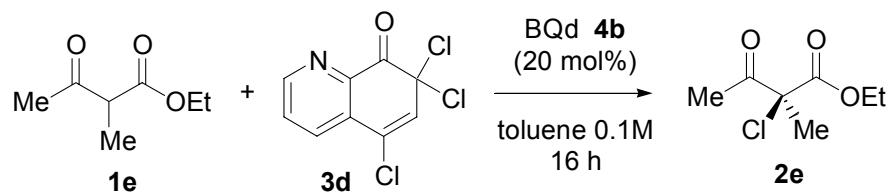
(DHQD)₂PHAL

Table S1. Screening results for the organocatalytic asymmetric chlorination of **1a** (not reported in Table 1).

Catalyst	Cl - donor	T [°C]	solvent	ee [%]
4a (BQ)	NCS	RT	toluene	60
A	NCS	RT	toluene	59
B	NCS	RT	toluene	60
C	NCS	RT	toluene	44
E	NCS	RT	toluene	46
F	NCS	RT	toluene	31
G	NCS	RT	toluene	40
4a (BQ)	3d	RT	toluene	79
4a (BQ)	3d	-78	toluene	95 (70) ^[a]
A	3d	RT	toluene	66
B	3d	-78	toluene	91
D	3d	-78	toluene	95
4a (BQ)	3d	-78	THF	91 (66) ^[a]
4a (BQ)	3d	-78	DCM	62 (25) ^[a]
4a (BQ)	3d	-78	TBME	95 (68) ^[a]

[a] Reaction time 24 h: number in parenthesis indicates conversion as determined by ¹H NMR spectroscopy of the crude mixture.

Table S2. Screening results for the organocatalytic asymmetric chlorination of **1e** in the presence of additives.^[a]



Additive [x equiv]	Conversion	ee [%]
None	22%	78
NaHCO ₃ (1)	45%	77
NaHCO ₃ (5)	46%	77
K ₂ CO ₃ (1)	15%	76
KHPO ₄ (1)	28%	75
8-hydroxyquinoline (1)	20%	76
HFIP (1)	23%	69
Proton sponge (1)	No reaction	-
NaHCO ₃ (1) ^[b]	63%	76

[a] Experimental conditions: open-air reactions run in undistilled toluene (0.1 M) for 16 h using a 1:1.2 ratio of **1e** to **3d** and 20 mol% of BQd **4b** as catalyst. [b] Reaction carried out in toluene 0.25 M.

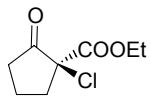
Experimental Procedures.

Synthesis of 5,7,7-trichloro-7*H*-quinolin-8-one (3d)³: To a solution of 8-hydroxyquinoline (725 mg, 5 mmol, 1 equiv) in CH₂Cl₂ (15 mL) was slowly added *t*-butylhypochlorite (2.3 mL, 3.6 equiv) at 0°C. The reaction was stirred at room temperature for 3 hours. After removal of the solvent under reduced pressure, 5 mL of Et₂O was added to the crude residue. The solid was collected by vacuum filtration and washed with 5 mL of cold hexane to afford product **3d** as a pale solid in 85% yield. ¹H NMR (CDCl₃): δ = 6.81 (s, 1H), 7.68 (dd, 1H, *J* = 4.8, 8.0), 8.10 (dd, 1H, *J* = 1.6, 8.0), 8.83 (dd, 1H, *J* = 1.6, 4.8); ¹³C NMR (CDCl₃): δ = 77.3 (C), 128.7 (CH), 129.4 (C), 130.9 (CH), 131.3 (C), 134.2 (CH), 143.7 (C), 151.7 (CH), 182.0 (C). Structure of compound **3d** was further confirmed by HMBC and HSQC experiments.

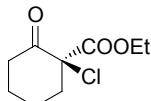
Synthesis of 5,5,7-tribromo-5*H*-quinolin-8-one (6): A 9/1 glacial acetic acid/distilled water solution (40 mL) was added to 8-hydroxyquinoline (290 mg, 2 mmol, 1 equiv). The yellow solution was cooled to 0°C in an ice bath and bromine (1.056 g, 6.6 mmol, 3.3 equiv) was added dropwise over 10 minutes. After 1 hour stirring, ice was added to the reaction causing the formation of a precipitate. The solution was carefully extracted with DCM (3 x 30 mL) and the organic layer was washed with a saturated solution of NaHCO₃ (4 x 30 mL), brine (1 x 30 mL), dried over MgSO₄, filtered and concentrated under reduced pressure to yield product **6** as a pale yellow solid. ¹H NMR (CDCl₃): δ = 7.69 (dd, 1H, *J* = 4.4, 8.4), 7.99 (s, 1H), 8.49 (dd, 1H, *J* = 1.6, 8.4), 8.87 (dd, 1H, *J* = 1.6, 4.4); ¹³C NMR (CDCl₃): δ = 46.9 (C), 121.8 (C), 128.1 (CH), 139.5 (C), 139.8 (CH), 141.6 (C), 147.4 (CH), 152.4 (CH), 174.7 (C). Structure of compound **6** was further confirmed by HMBC and HSQC experiments.

General Procedure for the Organocatalytic Asymmetric α-Halogenation of 1,3-Dicarbonyl Compounds. All the reactions were carried out in undistilled solvent without any precautions to exclude water. In an ordinary test tube equipped with a magnetic stirring bar, benzoylquinine BQ **4a** or benzoylquinidine BQd **4b** (0.02 mmol) was dissolved in 1.6 mL of toluene. After addition of the 1,3-dicarbonyl compound (0.4 mmol), the tube was closed with a rubber stopper and the mixture was stirred at the indicated temperature for 10 minutes. Then the freshly prepared halogenating agent **3d** or **6** (0.48 mmol) and

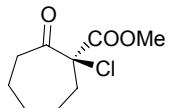
NaHCO_3 (0.4 mmol) were added and stirring was continued until GC and TLC analysis showed disappearance of the 1,3-dicarbonyl compound. Then the crude reaction mixture was diluted with hexane (5 mL) and filtered by suction. The organic phase was concentrated under reduced pressure and then flushed through a plug of silica, using hexane/ Et_2O 9/1 as the eluent. Solvent was removed in vacuo, and the residue was dissolved in an hexane/ Et_2O solution. After precipitation, the solid was filtered away and the organic phase concentrated to yield the pure halogenated product.



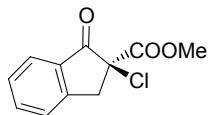
(*S*)-1-Chloro-2-oxo-cyclopentanecarboxylic acid ethyl ester (2a)⁴ - The reaction was carried out at -40°C for 24 h using 5 mol% of benzoylquinidine (**BQd**) **4b** following the general procedure. The title compound was isolated as a colourless oil in 98% yield. The ee was determined by GC analysis using a RT-BetaDEX-sm chiral column ($T_1 = 50^\circ\text{C}$; $T_2 = 210^\circ\text{C}$, rate = 4 $^\circ\text{C}/\text{min.}$; $\tau_R = 27.4$ min, $\tau_S = 27.6$ min). $[\alpha]^{rt}_{D} = -9.3^\circ$ ($c = 0.9$, CHCl_3 , 95% ee), lit.⁴ $[\alpha]^{rt}_{D} = -15.6^\circ$, (*S*)-**2a** ($c = 1.2$, CHCl_3 , 72% ee). ESI-MS m/z 191 [$\text{M}+\text{H}]^+$, 213 [$\text{M}+\text{Na}]^+$. ^1H NMR (CDCl_3): $\delta = 1.30$ (t, $J = 7.1$, 3H), 2.13 (m, 2H), 2.40 (m, 2H), 2.56 (m, 1H), 2.75 (m, 1H), 4.27 (q, $J = 7.1$, 2H); ^{13}C NMR (CDCl_3): $\delta = 14.0$ (CH_3), 19.1 (CH_2), 35.3 (CH_2), 38.4 (CH_2), 63.1 (CH_2), 69.6 (C), 167.2 (C), 206.1 (C).



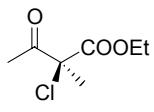
(*S*)-1-Chloro-2-oxo-cyclohexanecarboxylic acid ethyl ester (2b)⁴ - The reaction was carried out at -40°C for 40 h using 15 mol% of benzoylquinidine (**BQd**) **4b** following the general procedure. The title compound was isolated as a colourless oil in 83% yield. The ee was determined by GC analysis using a RT-BetaDEX-sm chiral column (isotherm 115°C ; $\tau_R = 36.4$ min, $\tau_S = 37.1$ min). $[\alpha]^{rt}_{D} = -22.8^\circ$ ($c = 2.0$, CHCl_3 , 96% ee), lit.⁴ $[\alpha]^{rt}_{D} = -10.9^\circ$, (*S*)-**2b** ($c = 1.2$, CHCl_3 , 76% ee). ESI-MS m/z 205 [$\text{M}+\text{H}]^+$, 227 [$\text{M}+\text{Na}]^+$. ^1H NMR (CDCl_3): $\delta = 1.31$ (t, $J = 7.1$, 3H), 1.74 (m, 2H), 1.91 (m, 2H), 2.14 (m, 1H), 2.43 (m, 1H), 2.83 (m, 2H), 4.30 (q, $J = 7.1$, 2H); ^{13}C NMR (CDCl_3): $\delta = 13.9$ (CH_3), 22.1 (CH_2), 26.7 (CH_2), 38.8 (CH_2), 39.6 (CH_2), 62.9 (CH_2), 73.5 (C), 167.2 (C), 199.6 (C).



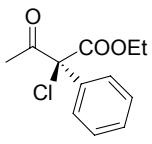
(S)-1-Chloro-2-oxo-cycloheptanecarboxylic acid methyl ester (2c) - The reaction was carried out following the general procedure at -40 °C for 52 h using 15 mol% of benzoylquinidine (BQd) **4b**. The title compound was isolated after filtration and flash chromatography (hexane - hexane/Et₂O 9/1) as a colourless oil in 48% yield. The ee was determined by GC analysis using a RT-BetaDEX-sm chiral column (isotherm 130 °C; τ_R = 24.6 min, τ_S = 25.2 min). $[\alpha]^{rt}_D$ = -13.2° (c = 1.1, CHCl₃, 90% ee). ESI-MS *m/z* 205 [M+H]⁺, 227 [M+Na]⁺. ¹H NMR (CDCl₃): 1.47-1.90 (m, 6H), 2.26-2.34 (m, 1H), 2.41-2.49 (m, 1H), 2.62-2.70 (m, 1H), 2.80-2.87 (m, 1H), 3.81 (s, 3H); ¹³C NMR (CDCl₃): δ = 24.6 (CH₂), 25.2 (CH₂), 28.9 (CH₂), 37.6 (CH₂), 40.5 (CH₂), 53.5 (CH₃), 75.9 (C), 168.5 (C), 202.3 (C).



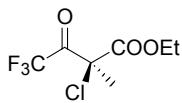
(S)-2-Chloro-1-oxo-indan-2-carboxylic acid methyl ester (2d) - The reaction was carried out at -78 °C for 36 h using 5 mol% of benzoylquinidine (BQd) **4b** following the general procedure. The title compound was isolated as a pale yellow oil in 80% yield. The ee was determined by HPLC analysis using a Chiraldpak AS-H column (80/20 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = 230 nm; τ_R = 9.5 min; τ_S = 10.2 min). $[\alpha]^{rt}_D$ = +12.0° (c = 0.25, CHCl₃, 93% ee). ESI-MS *m/z* 225 [M+H]⁺, 247 [M+Na]⁺. ¹H NMR (CDCl₃): δ = 3.74 (d, AB system, J = 22.4, 1H), 3.77 (s, 3H), 3.87 (d, AB system, J = 22.4, 1H), 7.35-7.47 (m, 3H), 7.50-7.55 (m, 1H); ¹³C NMR (CDCl₃): δ = 41.1 (CH₂), 54.0 (CH₃), 70.3 (C), 125.2 (CH), 125.5 (CH), 128.8 (CH), 130.7 (CH), 136.5 (C), 138.6 (C), 166.5 (C), 203.1 (C).



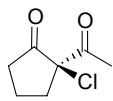
(S)-2-Chloro-2-methyl-3-oxo-butyric acid ethyl ester (2e)⁴ - The reaction was carried out following the general procedure at room temperature for 48 h using 20 mol% of benzoylquinidine (BQd) **4b**. The title compound was isolated after filtration and flash chromatography (hexane - hexane/Et₂O 9/1) as a colourless oil in 75% yield. The ee was determined by GC analysis using a RT-BetaDEX-sm chiral column (isotherm 75 °C; τ_S = 22.4 min; τ_R = 22.7 min). $[\alpha]^{rt}_D$ = +8.9° (c = 1.2, CHCl₃, 76% ee), lit.⁴ $[\alpha]^{rt}_D$ = +3.6°, (*S*)-**2e** (c = 1.0, CHCl₃, 77% ee). ESI-MS *m/z* 179 [M+H]⁺, 201 [M+Na]⁺. ¹H NMR (CDCl₃): δ = 1.29 (t, J = 7.2, 3H), 1.81 (s, 3H), 2.36 (s, 3H), 4.27 (q, J = 7.2, 2H); ¹³C NMR (CDCl₃): δ = 13.8 (CH₃), 24.2 (CH₃), 25.2 (CH₃), 63.0 (CH₂), 70.7 (C), 168.0 (C), 198.8 (C).



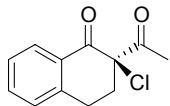
(S)-2-Chloro-3-oxo-2-phenyl-butyric acid ethyl ester (2f) - The reaction was carried out following the general procedure at -10 °C for 36 h using 15 mol% of benzoylquinidine (BQd) **4b**. The title compound was isolated as a pale yellow oil in 99% yield. The ee was determined by HPLC analysis using a Chiralpak AD-H column (98/2 hexane/i-PrOH; flow rate 0.75 mL/min; λ = 254 nm; τ_R = 8.6 min; τ_S = 8.9 min). $[\alpha]^{rt}_{D} = +21.4^\circ$ (c = 1.0, CHCl₃, 80% ee). ESI-MS m/z 241 [M+H]⁺, 263 [M+Na]⁺. ¹H NMR (600 MHz, CDCl₃): δ = 1.30 (t, J = 7.2, 3H), 2.33 (s, 3H), 4.31 (q, J = 7.2, 2H), 7.35-7.42 (m, 3H), 7.48-7.53 (m, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 13.8 (CH₃), 25.8 (CH₃), 63.3 (CH₂), 77.3 (C), 127.7 (CH, 2C), 128.4 (CH, 2C), 129.1 (CH), 133.9 (C), 170.0 (C), 197.5 (C).



(S)-2-Chloro-4,4,4-trifluoro-2-methyl-3-oxo-butyric acid ethyl ester (2g) - The reaction was carried out in TBME as the solvent at -78 °C for 52 h using 15 mol% of benzoylquinidine (BQd) **4b**. The title compound was isolated after filtration using pentane as solvent and flash chromatography (pentane - pentane/Et₂O 9/1) as a colourless oil in 44% yield (be careful, the product is volatile). The ee was determined by GC analysis using a RT-BetaDEX-sm chiral column (T_1 = 50 °C; T_2 = 210 °C, rate = 4 °C/min.; τ_S = 9.7 min; τ_R = 9.8 min). $[\alpha]^{rt}_{D} = +9.8^\circ$ (c = 1.47, CHCl₃, 89% ee). ESI-MS m/z 233 [M+H]⁺, 255 [M+Na]⁺. ¹H NMR (CDCl₃): δ = 1.30 (t, J = 7.2, 3H), 1.93 (s, 3H), 4.33 (q, J = 7.2, 2H); ¹³C NMR (CDCl₃): δ = 13.6 (CH₃), 23.8 (CH₃), 64.0 (CH₂), 65.8 (C), 118.9 (q, CF, J = 290 Hz), 165.9 (C).

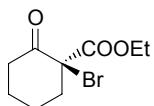


(R)-2-Acetyl-2-chloro-cyclopentanone (2h) - The reaction was carried out at -78 °C for 30 h using 5 mol% of benzoylquinidine (BQd) **4b** without NaHCO₃; the use of NaHCO₃ was avoided because no beneficial effect was observed under those conditions. The title compound was isolated as a colourless oil in 90% yield. The ee was determined by GC analysis using a RT-BetaDEX-sm chiral column (T_1 = 50 °C; T_2 = 210 °C, rate = 4 °C/min.; τ_S = 20.4 min; τ_R = 21.0 min). $[\alpha]^{rt}_{D} = +5.6^\circ$ (c = 0.25, CHCl₃, 51% ee). ESI-MS m/z 161 [M+H]⁺, 183 [M+Na]⁺. ¹H NMR (CDCl₃): δ = 2.02-2.15 (m, 2H), 2.17-2.27 (m, 1H), 2.30-2.38 (m, 1H), 2.48 (s, 3H), 2.48-2.58 (m, 1H), 2.78-2.86 (m, 1H); ¹³C NMR (CDCl₃): δ = 18.5 (CH₂), 27.1 (CH₃), 35.9 (CH₂), 36.3 (CH₂), 73.8 (C), 201.6 (C), 207.8 (C).



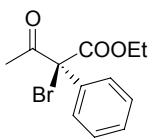
(R)-2-Acetyl-2-chloro-3,4-dihydro-2H-naphthalen-1-one (2i)

- The reaction was carried out at -40 °C for 48 h using 15 mol% of benzoylquinidine (BQd) **4b**; the use of NaHCO₃ was avoided because a lower enantiomeric excess was observed under those conditions. The title compound was isolated as a colourless oil in 74% yield. The ee was determined by HPLC analysis using a Chiralpak AS-H column (9/1hexane/*i*-PrOH; flow rate 0.75 mL/min; λ=254 nm; τ_R = 8.7 min; τ_S = 9.2 min). [α]^{rt}_D = +29.9° (c = 0.65, CHCl₃, 59% ee). ESI-MS *m/z* 223 [M+H]⁺, 245 [M+Na]⁺. ¹H NMR (CDCl₃): δ = 2.37-2.44 (m, 1H), 2.52 (s, 3H), 2.87-2.95 (m, 1H), 3.00-3.08 (m, 1H), 3.22-3.32 (m, 1H), 7.25-7.29 (m, 1H), 7.33-7.38 (m, 1H), 7.50-7.56 (m, 1H), 8.04-8.08 (m, 1H); ¹³C NMR (CDCl₃): δ = 25.5 (CH₂), 27.6 (CH₃), 33.4 (CH₂), 73.7 (C), 127.2 (CH), 128.7 (CH), 128.8 (CH), 130.0 (C), 134.5 (CH), 142.8 (C), 189.8 (C), 201.8 (C).



(S)-1-Bromo-2-oxo-cyclohexanecarboxylic acid ethyl ester (7b)⁴

- The reaction was carried out at -78 °C for 30 h using 10 mol% of benzoylquinidine (BQd) **4b** and freshly prepared brominating agent **6**, without using NaHCO₃. The title compound was isolated after careful filtration and flash chromatography (hexane - hexane/Et₂O 9/1) as a colourless oil in 82% yield. The ee was determined by HPLC analysis using a Chiralpak AD-H column (95/5 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ=214 nm; τ_S = 7.3 min; τ_R = 7.6 min). [α]^{rt}_D = -50.2° (c = 0.87, CHCl₃, 83% ee). ESI-MS *m/z* 249 [M+H]⁺, 271 [M+Na]⁺. ¹H NMR (CDCl₃): δ = 1.30 (t, *J* = 7.2, 3H), 1.69-1.97 (m, 4H), 2.18-2.26 (m, 1H), 2.42-2.50 (m, 1H), 2.83-2.95 (m, 2H), 4.29 (q, *J* = 7.2, 2H); ¹³C NMR (CDCl₃): δ = 13.8 (CH₃), 23.1 (CH₂), 26.7 (CH₂), 38.8 (CH₂), 40.5 (CH₂), 62.9 (CH₂), 67.5 (C), 167.5 (C), 199.1 (C).



(S)-2-Bromo-3-oxo-2-phenyl-butyric acid ethyl ester (7f)

- The reaction was carried out at -78 °C for 30 h using 15 mol% of benzoylquinidine (BQd) **4b** and freshly prepared brominating agent **6**, without using NaHCO₃. The title compound was isolated after careful filtration and flash chromatography (hexane - hexane/Et₂O 95/5) as a colourless oil in 67% yield. The ee was determined by HPLC analysis using a Chiralpak AS-H column (99/1 hexane/*i*-PrOH; flow rate 0.75 mL/min; λ = 254 nm; τ_s = 9.8 min; τ_R = 10.3 min). $[\alpha]^{rt_D} = -11.6^\circ$ (*c* = 1.12, CHCl₃, 84% ee). ESI-MS *m/z* 285 [M+H]⁺, 307 [M+Na]⁺. ¹H NMR (CDCl₃): δ = 1.31 (t, *J* = 7.2, 3H), 2.40 (s, 3H), 4.33 (q, *J* = 7.2, 2H), 7.36-7.40 (m, 3H), 7.48-7.53 (m, 2H); ¹³C NMR (CDCl₃): δ = 13.8 (CH₃), 26.4 (CH₃), 63.4 (CH₂), 71.2 (C), 128.4 (CH, 2C), 128.7 (CH, 2C), 129.1 (CH), 134.2 (C), 167.3 (C), 196.7 (C).