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# Supporting Information

# Enantioselective decarboxylation (- protonation) of ß-ketoesters with Pd - amino alcohol systems: successive metal- and organocatalysis

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**Synthesis of starting materials and characterization of intermediates and products.**

**1-Tetralone-2-carboxylic acid ethyl ester 7.** 1-tetralone (21.8 g, 149 mmol) was added dropwise to a stirred suspension of sodium hydride (60% dispersion in oil, 1.3 eq., 8.0 g, 0.2 mol) in dry diethyl carbonate (5.0 eq., 97.5 g, 100 ml, 825 mmol) under an atmosphere of argon. The reaction mixture was heated to reflux and white-violet solid was formed. After 1 hour at reflux, the mixture was cooled down to 5°C and 200 ml of 2-M hydrochloric acid was added dropwise while stirring. The solid dissolved and the phases were separated. Aqueous phase was extracted (2x) with toluene. The combined extracts were dried over $MgSO_4$ and evaporated *in vacuo* to give brown oil (30.2 g). This crude product was purified by flash chromatography (petrol ether/ethyl acetate, 9:1) to give 24.0 g (73% yield) of 2-carboethoxy-1-tetralone. The ratio keto to enol was approximately 1:2. The spectroscopic data were in agreement with those published elsewhere.[1] $^1$H NMR (500 MHz, $CDCl_3$): 1.28 (t, *J* = 7.1 Hz, Me, 3 H, ketone), 1.32 (t, *J* = 7.1 Hz, Me, 3 H, enol), 2.30-2.35 (m, H-C(3), 1 H, ketone), 2.40-2.50 (m, H-C(3), 1 H, ketone), 2.53-2.57 (m, H-C(3), 2 H, enol), 2.77-2.80 (m, H-C(4), 2 H, enol), 2.93-3.06 (m, H-C(4), 2 H, ketone), 3.57 (dd, *J* = 4.7, 10.5 Hz, H-C(2), 1 H, ketone), 4.12-4.31 (m, $OCH_2$, 2 H, ketone), 4.26 (q, *J* = 7.1 Hz, $OCH_2$, 2 H, enol), 7.14 (dd, *J* = 0.8, 7.2 Hz, H-C(5), 1 H, enol), 7.21 (d, *J* = 7.7 Hz, H-C(5), 1 H, ketone), 7.23-7.31 (m, H-C(6,7), 3 H, ketone and enol), 7.45 (td, *J* = 1.5, 7.9, H-C(7), 1 H, ketone), 7.78 (dd, *J* = 1.4, 7.5 Hz, H-C(8), 1 H, enol), 8.03 (dd, *J* = 1.1, 7.9 Hz, H-C(8), 1 H, ketone), 12.50 (s, OH, 1 H, enol). $^{13}$C NMR (125 MHz, $CDCl_3$): 14.2 (q, Me, ketone), 14.3 (q, Me, enol), 20.6 (t, C(3), enol), 26.4 (t, C(3), ketone), 27.6 (t, C(4), keto), 27.8 (t, C(4), enol), 54.6 (d, C(2), keto), 60.5 (t, OCH2, enol), 61.2 (t, OCH2, keto), 97.0 (s, C(2), enol), 124.3 (d, C(8), enol), 126.5 (d, C(6), enol), 126.9 (d, C(6), ketone), 127.4 (d, C(5), enol), 127.7 (d, C(8), ketone), 128.8 (d, C(5), ketone), 130.1 (s, C(4a), enol), 130.5 (d, C(7), enol), 131.8 (s, C(4a), ketone), 133.8 (d, C(7), ketone), 139.4 (s, C(8a), enol), 143.7 (s, C(8a), ketone), 165.0 (s, C(1), enol), 170.2 (s, OC=O, ketone), 172.7 (s, OC=O, enol), 193.2 (s, C(1), ketone).

**2-Methyl-1-tetralone-2-carboxylic acid ethyl ester 8.** Ethyl ester **7** (20 g, 92 mmol) was dissolved in toluene (500 ml) and an aqueous 50% NaOH solution (250 ml) was added dropwise under vigorous mechanical stirring. After stirring for one hour, three portions of tetrabutylammonium bromide (1g each, ca. 0.1 eq.) were added at intervals of 30 min. Then, methyl iodide (75 ml, 171 g, 13 eq.) was added dropwise within one hour and the mixture was stirred overnight. The mixture was cooled to 0°C and quenched with 2M aqueous HCl (440 ml). The organic phase was separated and the water phase was extracted three times with diethyl ether (3 x 200 ml). Combined organic extracts were washed with brine, dried over $MgSO_4$ and evaporated to give raw 2-methyl-2-carboethoxy-1-tetralone (19.5 g, 92% yield). GC (80°C, 2 min, 20°C/min, 300°C, 4 min, inj. 260°C, det. 260°, flow 1.5 ml/min): rt 9.9 min. GC-MS (80°C, 2 min, 20°C/min, 280°C, 8 min, inj. 250°C, flow 1 ml/min): rt 9.2 min. EI-MS: 232 (39, $M^+$), 217 (7, $M^+$-Me), 187 (5, $M^+$-OEt), 158 (100, $M^+$-COOEt), 131 (19), 118 (46), 90 (29). $^1$H NMR (500 MHz, $CDCl_3$):1.15 (t, *J* = 7.1 Hz, C*H*$_3$CH$_2$, 3 H), 1.49 (s, Me-C(2), 3 H), 2.00-2.06 (m, H-C(3), 1 H), 2.54-2.62 (m, H-C(3), 1 H), 2.90-3.06 (m, H-C(4), 2 H), 4.12 (qd, *J* = 1.9, 7.1 Hz, OCH$_2$, 2 H), 7.20 (d, 7.7 Hz, H-C(5), 1 H), 7.29 (dd, *J* = 7.5, 7.7 Hz, H-C(6), 1 H), 7.45 (dd, *J* = 1.4, 7.5 Hz, H-C(7), 1 H), 8.05 (dd, *J* = 1.4, 7.9 Hz, H-C(8), 1 H). $^{13}$C NMR (125 MHz, $CDCl_3$): 14.0 (q, *C*H$_3$CH$_2$), 20.6 (q, Me-C(2)), 26.0 (t, C(3)), 33.9 (t, C(4)), 53.8 (s, C(2)), 61.2 (t, *C*H$_2$CH$_3$), 126.7 (d, C(6)), 128.0 (d, C(8)), 128.7 (d, C(5)), 131.8 (s, C(4a)), 133.4 (d, C(7)), 143.1 (s, C(8a)), 172.8 (s, COOEt), 196.1 (s, C(1)).

**2-Methyl-1-tetralone-2-carboxylic acid benzyl ester 1** (from **8**). Benzyl ester **1** was prepared by transesterification with benzyl alcohol in the presence of tetraisopropyl titanate described by Seebach *et al.*[2] To a mixture of **8** (10 g, 43 mmol) and benzyl alcohol (37 ml, 357 mmol) was added titanium isopropoxide (12.8 ml, 43.3 mmol) and the mixture was heated at 120°C for 3 hours. The cooled mixture (<20°C) was quenched with 1M-HCl and extracted with ether/hexane (1:1). The organic extract was washed with saturated aqueous solution of sodium hydrogen carbonate and saturated sodium chloride solution, and dried with magnesium sulfate. The solvent was distilled off (65-75°C/0.05-0.1 torr) with Kugelrohr apparatus and the residue was purified by flash chromatography (petrol ether/acetone, 9:1) to give 7.1 g (56% yield) racemic benzyl 2-methyl-1-tetralone-2-carboxylate. GC (80°C, 2 min, 20°C/min, 300°C, 4 min, inj. 260°C, det. 260°, flow 1.5

ml/min): rt 12.9 min. GC-MS (80°C, 2 min, 20°C/min, 280°C, 8 min, inj. 250°C, flow 1 ml/min): rt 13.1 min. HP-5MS (30 m, 0.25 mm, 0.25 μm), EI-MS: 294 (14, $M^+$), 203 (10, $M^+$-Bn), 159 (51, $M^+$-COOBn), 145 (7), 141 (9), 131 (16), 118 (31), 91 (100), 65 (11). HPLC (rt 13.3 and 14.5 min). $^1$H NMR (500 MHz, $CDCl_3$): 1.52 (s, Me-C(2), 3 H), 2.02-2.08 (m, H-C(3), 1 H), 2.57-2.62 (m, H-C(3), 1 H), 2.78-2.99 (m, H-C(4), 2 H), 5.05 (d, 12.5 Hz, $OCH_2$, 1 H), 5.17 (d, 12.5 Hz, $OCH_2$, 1 H), 7.10-7.14 (m, 2 H), 7.17 (d, *J* = 7.7 Hz, 1 H), 7.23-7.25 (m, 3 H), 7.29-7.32 (m, 1 H), 7.43-7.47 (dd, *J* = 1.4, 6.5 Hz, H-C(7), 1 H), 8.06 (dd, *J* = 1.1, 7.9 Hz, H-C(8), 1 H). $^{13}$C NMR (125 MHz, $CDCl_3$): 20.5 (q, Me), 25.9 (t, C(3)), 33.9 (t, C(4)), 53.9 (s, C(2)), 66.7 (t, *C*$H_2$Ph), 126.8 (d, Ph), 127.6 (2d, Ph), 128.0 (d, C(5)), 128.0 (d, C(6)), 128.4 (2d, Ph), 128.7 (d, C(7)), 131.9 (s, Ph), 133.4 (d, C(8)), 135.6 (s, C(4a)), 143.1 (s, C(8a)), 172.8 (s, COO), 196.1 (s, C(1)). Anal. Calc. for $C_{19}H_{18}O_3$ (294.35): C 77.53, H 6.16, O 16.31; found: C 77.44, H 6.26, O 16.39.

**1-Tetralone-2-carboxylic acid benzyl ester 9.** The ethyl ester **7** (10.5 g, 48.1 mmol), benzyl alcohol (25 mL, 241 mmol) and toluene (250 mL) were stirred at 120°C for 2 days. Afterwards, toluene was evaporated and benzyl alcohol was distilled off at 150°C (1 Torr). Remained raw product was purified by Kügelrohr distillation (170-210°C at $10^{-4}$ Torr) to afford 8 g (28.5 mmol, 58% yield) of benzyl 1-tetralone-2-carboxylate. $^1$H NMR (500 MHz, $CDCl_3$): 2.32-2.35 (m, H-C(3), 1 H, ketone), 2.40-2.50 (m, H-C(3), 1 H, ketone), 2.53-2.57 (m, H-C(3), 2 H, enol), 2.78-2.84 (m, H-C(4), 2 H, enol), 2.93-3.06 (m, H-C(4), 2 H, ketone), 3.70 (dd, *J* = 4.7, 10.5 Hz, H-C(2), 1 H, ketone), 5.07-5.18 (m, OCH2, 2 H, ketone), 5.26 (q, *J* = 7.1 Hz, OCH2, 2 H, enol), 7.14 (dd, *J* = 0.8, 7.2 Hz, H-C(5), 1 H, enol), 7.21 (d, *J* = 7.7 Hz, H-C(5), 1 H, ketone), 7.13-7.56 (m, 8 H, ketone and enol), 7.81 (dd, *J* = 1.5, 7.4 Hz, H-C(8), 0.6 H, enol), 8.07 (dd, *J* = 1.0, 7.9 Hz, H-C(8), 0.4 H, ketone), 12.49 (s, OH, 0.6 H, enol).

**2-Methyl-1-tetralone-2-carboxylic acid benzyl ester 1** (from **9**). The solution of **9** (8 g, 28.5 mmol) in THF (150 mL) was cooled down to 0°C and solid potassium *tert*-butoxide (3.8 g, 34.2 mmol, 1.2 eq) was added portion wise over 15 min with magnetic stirring. Methyl iodide (4.9 g, 34.2 mmol, 1.2 eq.) was then added dropwise to the reaction mixture, and a stirring was continued for further 1.5 hour. The reaction mixture was diluted with EtOAc (100 mL), filtered through a pad of Celite, and concentrated under vacuum. The resulting oil was further purified by column chromatography (petrol

ether/acetone, 9:1) to give 7.8 g (93% yield) racemic benzyl 2-methyl-1-tetralone-2-carboxylate. TLC: $R_f$ 0.50. GC (80°C, 2 min, 20°C/min, 300°C, 4 min, inj. 250°C, det. 250°C, flow 1.5 ml/min): rt 12.9 min. GC-MS (80°C, 2 min, 10°C/min, 280°C, 8 min, inj. 250°C, flow 1 ml/min): rt 13.1 min. HP-5MS (30 m, 0.25 mm, 0.25 μm), EI-MS: 294 (14, $M^+$), 203 (10, $M^+$-Bn), 159 (51, $M^+$-COOBn), 145 (7), 141 (9), 131 (16), 118 (31), 91 (100), 77 (8), 65 (11). HPLC (rt 13.3 and 14.5 min). $^1$H NMR (500 MHz, $CDCl_3$): 1.52 (s, Me-C(2), 3 H), 2.02-2.08 (m, H-C(3), 1 H), 2.57-2.62 (m, H-C(3), 1 H), 2.78-2.99 (m, H-C(4), 2 H), 5.05 (d, $J$ = 12.5 Hz, $OCH_2$, 1 H), 5.17 (d, $J$ = 12.5 Hz, $OCH_2$, 1 H), 7.10-7.14 (m, 2 H), 7.17 (d, $J$ = 7.7 Hz, 1 H), 7.23-7.25 (m, 3 H), 7.29-7.32 (m, 1 H), 7.43-7.47 (dd, $J$ = 1.4, 6.5 Hz, H-C(7), 1 H), 8.06 (dd, $J$ = 1.1, 7.9 Hz, H-C(8), 1 H). $^{13}$C NMR (125 MHz, $CDCl_3$): 20.5 (q, Me), 25.9 (t, C(3)), 33.9 (t, C(4)), 53.9 (s, C(2)), 66.7 (t, *C*$H_2$Ph), 126.8 (d, Ph), 127.6 (2d, Ph), 128.0 (d, C(5)), 128.0 (d, C(6)), 128.4 (2d, Ph), 128.7 (d, C(7)), 131.9 (s, Ph), 133.4 (d, C(8)), 135.6 (s, C(4a)), 143.1 (s, C(8a)), 172.8 (s, COO), 196.1 (s, C(1)). Anal. Calc. for $C_{19}H_{18}O_3$ (294.35): C 77.53, H 6.16, O 16.31; found: C 77.47, H 6.21, O 16.31.

**2-Methyl-1-tetralone-2-carboxylic acid 2.** 2-Methyl-2-carbomethoxy-1-tetralone (17.4 g, 80 mmol) prepared by acylation of 1-tetralone with dimethyl carbonate and methylation with MeI in the presence of KOt-Bu by methods described above, was dissolved in methanol (250 mL) and cooled down to 0°C on ice-water bath. A pre-cooled aqueous solution of KOH (13.5 g in 110 mL water) was slowly poured into methanolic solution of 2-methyl-2-carbomethoxy-1-tetralone and the mixture was led to warm up to room temperature and stirred for two hours. Methanol was evaporated under reduced pressure at 0°C. The aqueous-methanolic phase was extracted with dichloromethane (5 x 40 mL), acidified with diluted HCl to pH 2 and again extracted with dichloromethane (5 x 50 mL). The organic extracts were washed with brine and dried over $MgSO_4$. The solvent was evaporated to 1/3 and the product was crystallized by adding a portion of hexane. The mother liquor was concentrated in vacuo and the pure white crystals of 2-carboxy-2-methyl-1-tetralone (11.6 g, 71% yield) were separated by filtration. The acid was unstable at room temperature and decomposed readily to the 2-methyl-1-tetralone and carbon dioxide. Therefore, it was stored in the freezer at -20°C, where it remained

stable for a period of weeks. TLC: $R_f$ 0. $^1$H NMR (500 MHz, $CDCl_3$):1.41 (s, Me-C(2), 3 H), 1.98-2.03 (m, H-C(3), 1 H), 2.45-2.49 (m, H-C(3), 1 H), 2.82-2.88 (m, H-C(4), 1 H), 2.95-3.01 (m, H-C(4), 1 H), 7.12 (d, *J* = 7.7 Hz, H-C(5), 1 H), 7.20 (dd, *J* = 7.4, 7.7 Hz, H-C(7), 1 H), 7.37 (ddd, *J* = 1.1, 7.4, 7.8 Hz, H-C(6), 1 H), 7.94 (d, *J* = 7.8 Hz, H-C(8), 1 H), 12.75 (brs, OH, 1 H). $^{13}$C NMR (125 MHz, $CDCl_3$): 20.4 (q, Me-C(2)), 25.6 (t, C(3)), 33.2 (t, C(4)), 53.4 (s, C(2)), 126.8 (d, C(6)), 128.0 (d, C(8)), 128.7 (d, C(5)), 131.8 (s, C(4a)), 133.7 (d, C(7)), 143.2 (s, C(8a)), 178.7 (s, COOH), 196.2 (s, C(1)).

**Diastereomeric salt of 2 and (-)-ephedrine.** 40 mg **2** and 33 mg (-)-ephedrine were dissolved in 0.4 mL pre-cooled dichloromethane and immediately transferred to NMR spectrometer with regulated temperature. $^1$H NMR (500 MHz, $CD_2Cl_2$, -20°C): signals belonging to the acid **2**: 1.39 and 1.41 (2 s, Me-C(2), 3 H), 1.91-1.96 and 2.45-2.50 (2 m, H-C(3), 2 H), 2.79 and 2.82 (2 brs, H-C(4), 1 H), 3.13-3.19 (m, H-C(4), 1 H), 7.19-7.35 (m, H-C(5,7), 2 H), 7.35-7.41 and 7.42-7.48 (2 m, H-C(6), 1 H), 7.82 and 7.93 (2 d, *J* = 7.7 and 7.8 Hz, H-C(8), 1 H); signals belonging to (-)-ephedrine: 0.83 (d, *J* = 6.5 Hz, Me-C, 3 H), 2.51 (s, Me-N, 3 H), 3.00-3.02 (m, H-C-Me, 1 H), 5.05 (s, H-C-Ph, 1 H), 7.19-7.34 (m, Ph, 5 H). $^{13}$C NMR (125 MHz, $CD_2Cl_2$, -20°C): signals belonging to the acid **2**: 22.5 and 22.7 (q, Me-C(2)), 27.8 and 27.9 (t, C(3)), 36.0 and 36.1 (t, C(4)), 56.6 and 56.7 (s, C(2)), 127.8 (d, C(6)), 128.0 (d, C(8)), 129.8 and 129.9 (d, C(5)), 133.5 and 133.6 (s, C(4a)), 133.8 and 133.9 (d, C(7)), 145.2 and 145.3 (s, C(8a)), 179.6 and 179.7 (s, COOH), 200.2 and 200.3 (s, C(1)); signals belonging to (-)-ephedrine: 10.7 (q, Me-C), 32.2 (q, Me-N), 61.8 (d, C-Me), 71.4 (d, C-Ph), 126.8, 127.2, 129.0 (3d, Ph), 142.3 (s, Ph).

**2-Methyl-1-tetralone 4.** TLC: $R_f$ 0.50. GC (80°C, 2 min, 20°C/min, 300°C, 4 min, inj. 260°C, det. 260°, flow 1.5 ml/min): rt 8.2 min. GC-MS (80°C, 2 min, 20°C/min, 280°C, 8 min, inj. 250°C, flow 1 ml/min): rt 7.5 min). HP-5MS (30 m, 0.25 mm, 0.25 μm), EI-MS: 160 (72), 145 (28), 131 (22), 118 (100), 90 (50), 77 (10), 63 (8), 51 (7), 39 (6). HPLC: 7.2 min (*R*)-**4** and 7.8 min (*S*)-**4**. $^1$H NMR (500 MHz, $CDCl_3$):1.25 (d, *J* = 6.8 Hz, Me-C(2), 3 H), 1.82-1.90 (m, H-C(2), 1 H), 2.15-2.20 (m, H-C(3), 1 H), 2.55-2.59 (m, H-C(3), 1 H), 2.92-3.05 (m, H-C(4), 2 H), 7.21 (d, *J* = 7.7 Hz, H-C(5), 1 H), 7.27 (dd, *J* = 7.4, 7.7 Hz, H-C(7), 1 H), 7.43 (dd, *J* = 7.4, 7.8 Hz, H-C(6), 1 H), 8.01 (d, 7.8 Hz, H-

C(8), 1 H). $^{13}$C NMR (125 MHz, $CDCl_3$): 15.2 (q, Me-C(2)), 28.6 (t, C(3)), 31.1 (t, C(4)), 42.4 (d, C(2)), 126.3 (d, C(6)), 127.0 (d, C(8)), 128.5 (d, C(5)), 132.1 (s, C(4a)), 133.9 (d, C(7)), 144.0 (s, C(8a)), 200.5 (s, C(1)). Anal. Calc. for $C_{11}H_{12}O$ (160.22): C 82.46, H 7.55, O 9.99; found: C 82.44, H 7.47, O 10.03.

**2-Methyl-1-tetralol (*cis*- and *trans*-2-methyl-1,2,3,4-tetrahydro-1-naphtol) 5.** GC (80°C, 2 min, 20°C/min, 300°C, 4 min, inj. 260°C, det. 260°, flow 1.5 ml/min): rt 7.9 and 8.0 min. GC-MS (rt 7.30 and 7.35 min), 80°C, 2 min, 20°C/min, 280°C, 8 min, inj. 250°C, flow 1ml/min, HP-5MS (30 m, 0.25 mm, 0.25 μm), EI-MS: 162 (22), 144 (64), 134 (25), 129 (54), 120 (88), 118 (100), 115 (19), 105 (11), 91 (42), 77 (12), 65 (12), 51 (8), 39 (7).

**2-Hydoxy-2-methyl-1-tetralone 6.** GC (80°C, 2 min, 20°C/min, 300°C, 4 min, inj. 260°C, det. 260°, flow 1.5 ml/min): rt 8.6 min. GC-MS (80°C, 2 min, 20°C/min, 280°C, 8 min, inj. 250°C, flow 1 ml/min): rt 7.8 min. EI-MS: 176 (23), 158 (45), 133 (30), 118 (100), 105 (23), 90 (56), 77 (20), 63 (10), 51 (8), 43 (46). $^1$H NMR (500 MHz, $CDCl_3$): 1.36 (s, Me-C(2), 3 H), 2.17-2.25 (m, H-C(3), 2 H), 3.00-3.10 (m, H-C(4), 2 H), 7.22 (d, $J$ = 7.8 Hz, H-C(5), 1 H), 7.31 (dd, $J$ = 7.4, 7.8 Hz, H-C(7), 1 H), 7.49 (ddd, $J$ = 1.4, 7.4, 7.8 Hz, H-C(6), 1 H), 8.01 (dd, $J$ = 1.2, 7.8 Hz, H-C(8), 1 H). $^{13}$C NMR (125 MHz, $CDCl_3$): 23.9 (q, Me-C(2)), 26.8 (t, C(3)), 35.9 (t, C(4)), 73.6 (s, C(2)), 126.9 (d, C(6)), 128.0 (d, C(8)), 129.0 (d, C(5)), 129.9 (s, C(4a)), 134.1 (d, C(7)), 143.4 (s, C(8a)). Anal. Calc. for $C_{11}H_{12}O_2$ (176.22): C 74.98, H 6.86, O 18.16; found: C 75.0, H 6.95, O 18.21.

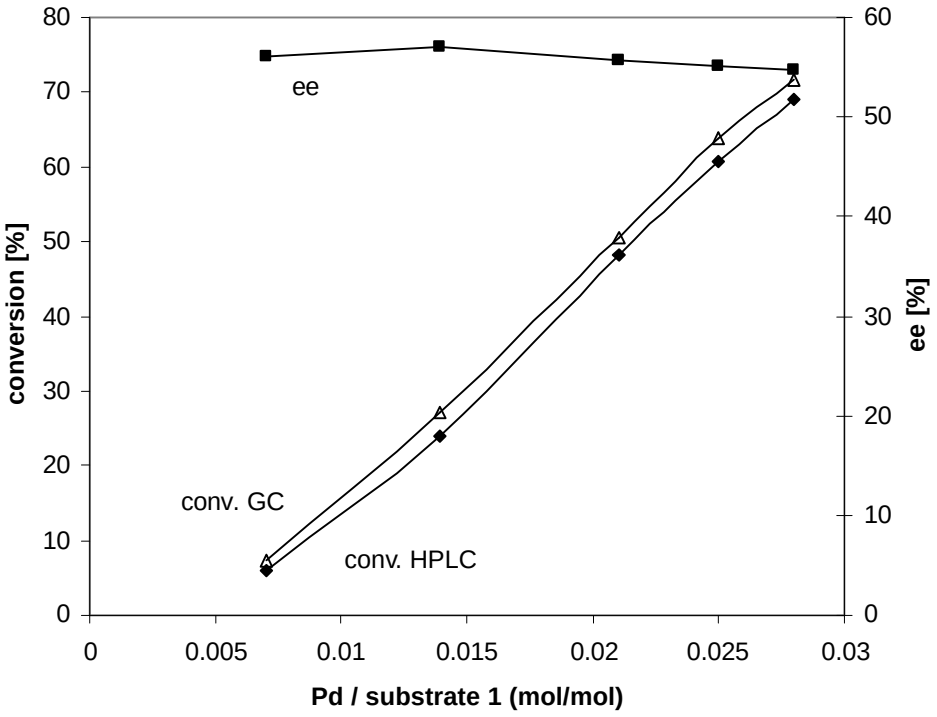


**Fig. 1** The influence of Pd to **1** molar ratio on the conversion of **1** and the enantioselectivity in **4**. Conditions: 20 mg of **1**, 1-4 mg 5wt-% Pd/C, 0.3 equiv. QN, 2 mL acetonitrile, 1 bar $H_2$, 90 min, room temperature.

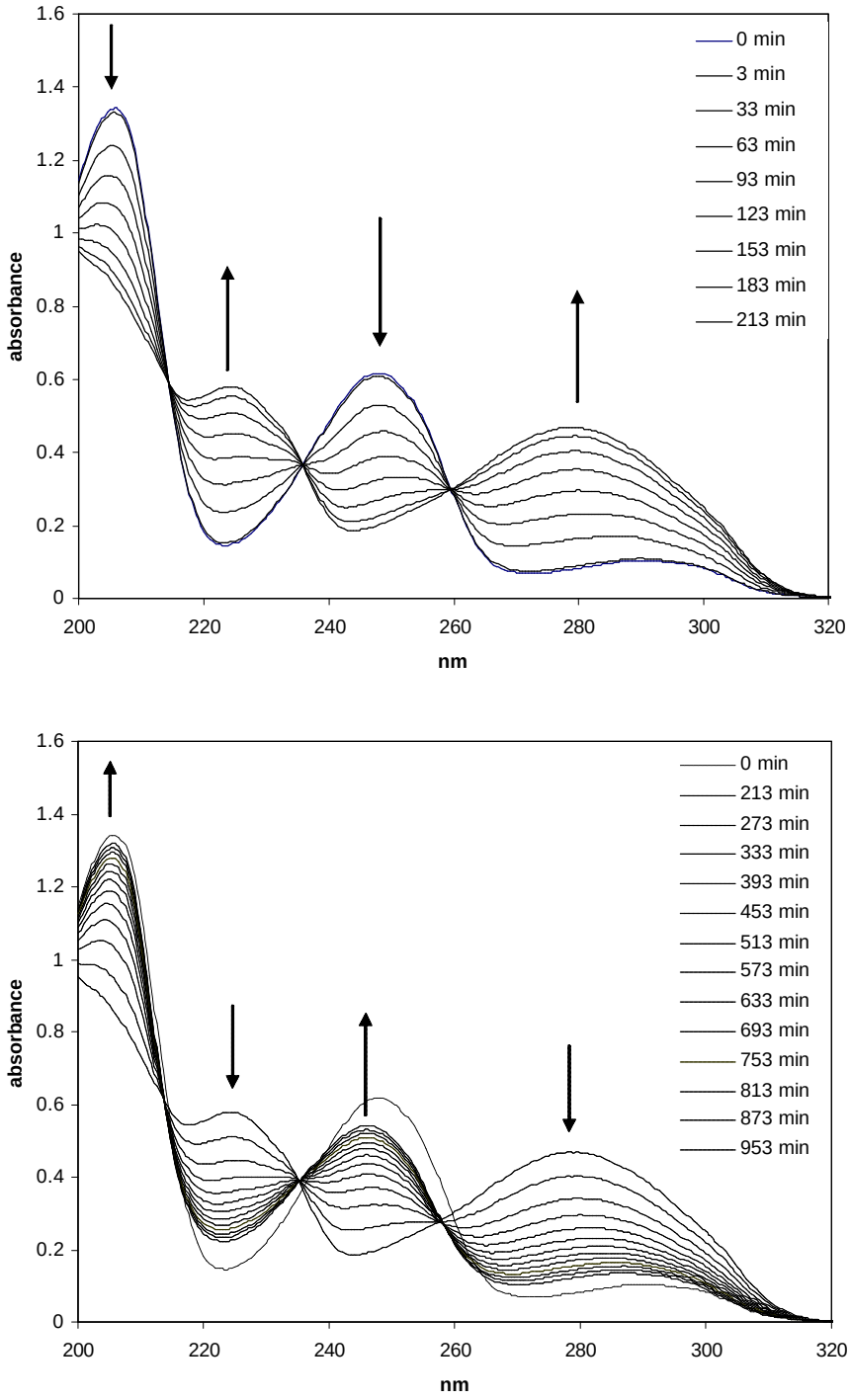


**Fig. 2** Continuous measurement of UV absorption spectra of ketoacid **2** (c = 5.0 x $10^{-5}$ mol/l in acetonitrile).

**Table 1** Results of UV spectroscopy measurements of ketoacid **2** in acetonitrile

| Concentration (mol/l) | $Abs^{246}$ (max) | $Abs^{246}$ (min) | T (min) (min) | T (max) (min) |
|---|---|---|---|---|
| $3.9 \times 10^{-2}$ | * | * | * | * |
| $2.5 \times 10^{-4}$ | 3 | 1.6 | 280 | 480** (1050) |
| $5.0 \times 10^{-5}$ | 0.65 | 0.19 | 210 | 953 |
| $1.0 \times 10^{-5}$ | 0.1 | 0.04 | 65 | 215 |
| $5.0 \times 10^{-6}$ | 0.04 | 0.02 | 19 | 70 |

$Abs^{246}$ (max, min) - maximum and minimum absorption at 246 nm, T (min, max) – time to reach minimum and maximum absorption at 246 nm, * - reaction does not oscilate, ** - after reaching the maximum, the band at 246 nm started to decrease again.

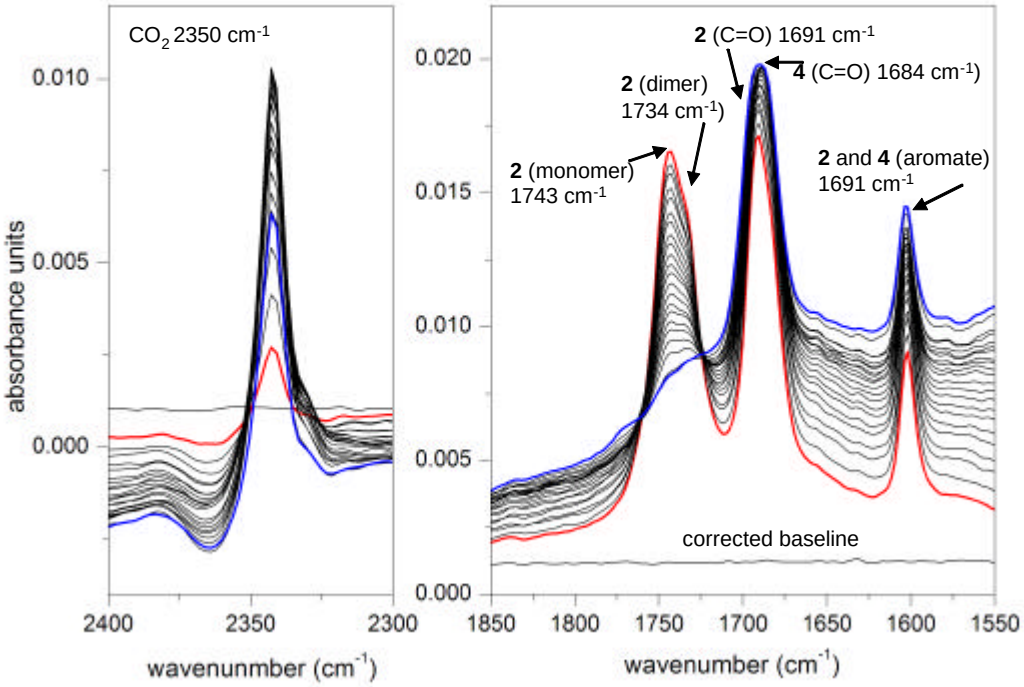


**Fig. 3** Decarboxylation of ketoacid **2** followed by *in-situ* ATR-IR spectroscopy. Conditions: 200 mg **2**, 20 mL AcCN (c = $4.9.10^{-2}$ M), stirred under argon at 50°C.

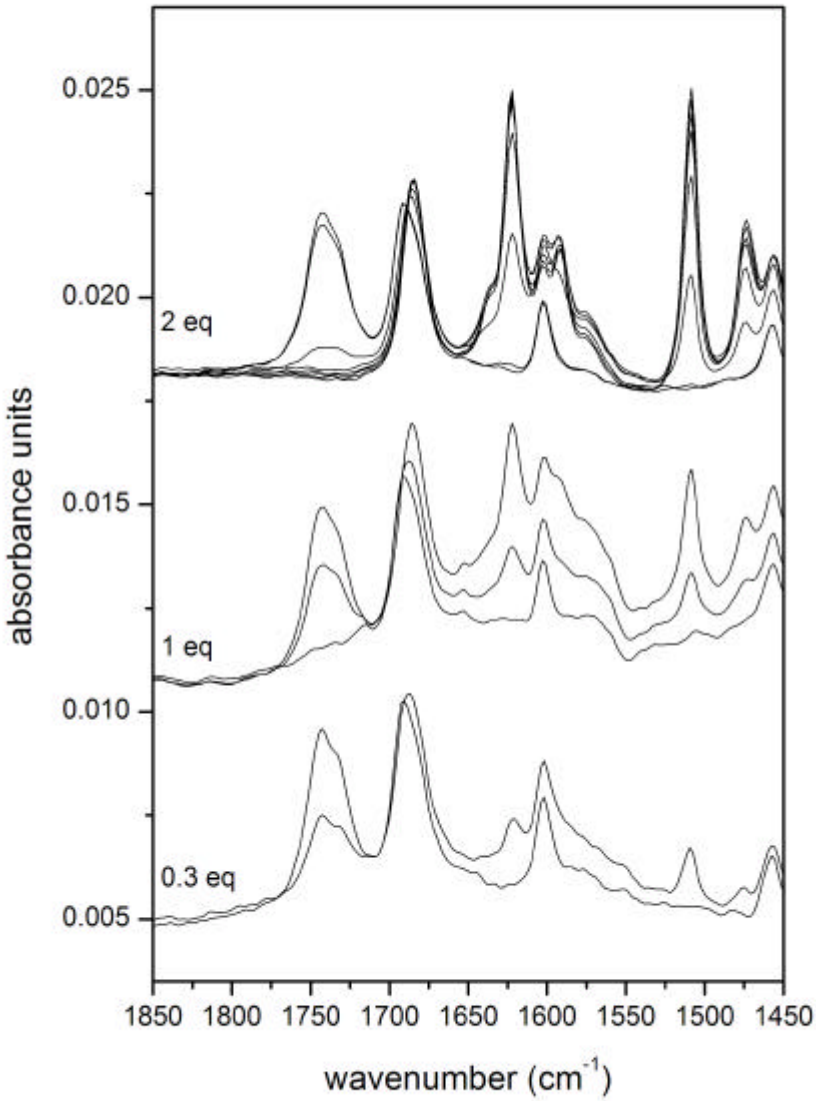


**Fig. 4** Decarboxylation of ketoacid **2** followed by *in-situ* ATR-IR spectroscopy. Conditions: 100 mg **2**, 20 mL AcCN ($c = 2.4.10^{-2}$ M), 0.3, 1.0, 2.0 equiv. QN, stirred under argon at 50°C.

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2. Seebach, D.; Hungerbühler, E.; Naef, R.; Schnurrenberger, P.; Wiedmann, B.; Züger, M. F. *Synthesis* **1982**, 138.