Electronic supplementary materials *Mendeleev Commun.*, 2015, **25**, 111−113

Synthesis of new ferrocene derivatives with rod-like structure

Vladimir N. Okulov, Damir A. Popov, Anastasia V. Panfilova,
Marina A. Dyadchenko, Dmitrii A. Lemenovskii and Victor P. Dyadchenko

Experimental part.

The following compounds were prepared in accordance with published procedures: 4-([1,1']biphenyl-4-yl)butanoic acid (**13**) [9], 4-iodosuccinanilic acid (**20**) [10], N-Boc-β-alanine [11], N^1-Boc-1,4-butanediamine [12] and 4'-ferrocenyl[1,1']biphenyl-4-amine (**30**) [13].

NMR spectra were recorded with VARIAN VXR-400 and Agilent 400-MR instruments (400 MHz for ^{1}H and 100 MHz for ^{13}C).

4-Ferrocenylsuccinanilic acid (2). A solution of 4-ferrocenylaniline (0.24 g, 0.87 mmol) and succinic anhydride (0.1 g, 1.0 mmol) in 10 ml of dichloromethane was refluxed for 1 h. The liberating precipitate was separated, washed with dichloromethane (2 x 25 ml) and air dried. Acid **2** (0.35 g, 93%) was obtained as orange crystalline substance.

^{1}H NMR (dmso-d$_6$, δ, ppm): 2.51-2.56 m. (4H, CH_2), 3.99 s. (5H, C_5H_5), 4.29 m. (2H, C_5H_4), 4.71 m. (2H, C_5H_4), 7.43-7.45 m. and 7.50-7.52 m. (4H, AA’BB’, C_6H_4), 9,93 s. (1H, NH), 12.17 broad signal (1H, COOH).

^{13}C NMR (dmso-d$_6$, δ, ppm): 28.8 (CH_2), 31.0 (CH_2), 65.9 (C_5H_4), 68.6 (C_5H_4), 69.3 (C_5H_5), 84.9 ($\mathbf{C_{Cp}}$-Ar), 118.9 (CH_{Ar}), 126.0 (CH_{Ar}), 133.3 ($\mathbf{C_{Ar}}$-C_5H_4), 137.3 ($\mathbf{C_{Ar}}$-NH), 169.9 (**C**(O)NH-Ar), 173.9 (COOH).

N-tert-Butoxycarbonyl-β-alanine 4-ferrocenylanilide (3). Dry triethylamine (0.27 g; 0.2 ml; 1.25 mmol) was added to a suspension of *N-tert*-butoxycarbonyl-β-alanine (0.19 g; 1 mmol) in 10 ml of dry toluene. The resulting solution was cooled to -18 ^{o}C and isobutyl chloroformate (0.117 g; 0.112 ml; 0.87 mmol) was added in 5 min by drops with a good stirring, which was continued at -18 ^{o}C for additional 30 min. A solution of 4-ferrocenylaniline (0.24 g; 0.87 mmol) in 15 ml of dry dichloromethane was added to a cold reaction mixture in 10 min. Stirring was continued at -18 ^{o}C for 1 h and then at ambient temperature overnight.

The reaction mixture was added to chloroform (70 ml) and the resulting solution was washed with saturated solution of $NaHCO_3$ (3 x 50 ml) and then thoroughly with water. The organic layer was dried over Na_2SO_4 and solvent was removed under reduced pressure. The residue was purified in the following manner. Petroleum ether, bp 70/100 ^{o}C (50 ml) was added, and the mixture was refluxed for 5 min with stirring. A precipitate was separated from a hot solution with sintered glass filter and the procedure of hot extraction was repeated. The precipitate was air dried which afforded 0.33 g (84%) of amide **3**.

^1H NMR (dmso-d_6, δ, ppm): 1.37 s. (9H, CH_3), 2.46 m. (2H, $\mathbf{CH_2}C(O)$), 3.19-3.24 m. (2H, $\mathbf{CH_2}NH$), 3.98 s. (5H, C_5H_5), 4.29 m. (2H, C_5H_4), 4.71 m. (2H, C_5H_4), 6.86 t. (1H, **NH**-BOC) 7.43-7.45 m. and 7.51-7.54 m. (4H, AA'BB', C_6H_4), 9.91 s. (1H, **NH**-Ar).

^{13}C NMR (dmso-d_6, δ, ppm): 28.2 (CH_3), 36.5 (CH_2), 36.8 (CH_2), 65.9 (C_5H_4), 68.6 (C_5H_4), 69.3 (C_5H_5), 77.6 (**C**Me_3), 84.9 ($\mathbf{C_{Cp}}$-Ar), 119.1 (CH_{Ar}), 126.0 (CH_{Ar}), 133.4 ($\mathbf{C_{Ar}}$-C_5H_4), 137.2 ($\mathbf{C_{Ar}}$-NH), 155.5 (**C**(O)OCMe_3), 169.2 (**C**(O)NH-Ar).

β-Alanine 4-ferrocenylanilide (4). Amide **3** (0.227 g; 0,51 mmol) was stirred with a solution of trifluoroacetic acid (2 ml) in dry dichloromethane (10 ml) for 1.5 h. Volatiles were removed under reduced pressure. Traces of trifluoroacetic acid were removed from the residue by adding of toluene with subsequent evaporation under reduced pressure. The same procedure was used for removal of traces of toluene using adding of dichloromethane and evaporation to dryness. The solid residue was dissolved in chloroform (100 ml) and washed with 0.25 M solution of NaOH. The organic layer was separated, washed with water and dried over Na_2SO_4. Evaporation of the solvent afforded 0.163 g (92%) of **4** as an orange powder.

^1H NMR (dmso-d_6, δ, ppm): 2.37 t., ^3J 6.44 Hz (2H, $\mathbf{CH_2}C(O)$), 3.83 t. ^3J 6.44 Hz (2H, $\mathbf{CH_2}NH_2$), 3.27 broad signal (2H, NH_2), 3.99 s. (5H, C_5H_5), 4.29 m. (2H, C_5H_4), 4.71 m. (2H, C_5H_4), 7.43-7.45 m. and 7.50-7.52 m. (4H, AA'BB', C_6H_4), 10.01 s. (1H, **NH**-Ar).

^{13}C NMR (dmso-d_6, δ, ppm): 38.2 (CH_2), 40.2 (CH_2), 65.8 (C_5H_4), 68.6 (C_5H_4), 69.3 (C_5H_5), 84.9 ($\mathbf{C_{Cp}}$-Ar), 119.1 (CH_{Ar}), 126.0 (CH_{Ar}), 133.3 ($\mathbf{C_{Ar}}$-C_5H_4), 137.2 ($\mathbf{C_{Ar}}$-NH), 170.4 (**C**(O)NH).

4-Ferrocenylbenzoic acid (6). Butyllithium (2.0 M solution of in hexane, 3.3 ml; 6.6 mmol) was added with stirring to a solution of 4-bromophenylferrocene (1.935 g; 5.67 mmol) in THF (20 ml) at -78 ^{o}C. The deep red reaction mixture quickly became yellow-orange. Stirring was continued for additional 30 min at -78 ^{o}C and then the reaction mixture was poured on solid carbon dioxide (7 g). After warming to ambient temperature 16% solution of HCl was added to pH 1, the mixture was extracted with ethyl acetate (3 portions of 15 ml) and the turbid extract was dried over sodium sulfate. Acid **6** was distributed between solution and precipitate. The solution of **6** in ethyl acetate was filtered. The precipitate remaining on filter was dissolved in THF and combined with solution in ethyl acetate. After removal of the solvent under reduced pressure acid **6** (1.639 g; 94%) was obtained as deep red powder, decomp. above 140 ^{o}C.

^{1}H NMR (dmso-d_6, δ, ppm): 4.02 s. (5H, C_5H_5), 4.42 m. (2H, C_5H_4), 4.88 m. (2H, C_5H_4), 7.63 -7.84 d (4H, AA'BB', C_6H_4); *cf.* [14].

4-Ferrocenylbenzoic acid N-[4-(tert-butoxycarbonylamino)butyl]amide (7). To a stirred mixture of **6** (0.20 g; 0.65 mmol) and dichloromethane (5 ml) were added successively at 0 ^{o}C: 3 drops of DMF and 0.1 ml (0.148 g; 1.16 mmol) of oxalyl chloride in argon purge. Stirring was continued at 0 ^{o}C for 5 min and at ambient temperature for 3.5 h. The solvent was removed from the resulting blood-reddish reaction mixture *in vacuo*. Anhydrous potassium carbonate (0.18 g; 1.3 mmol), N^1-Boc-1,4-butanediamine (0.147 g; 0.78 mmol), ethyl acetate (10 ml), 5 ml of water were added to the residue and the mixture was stirred at ambient temperature for 20 h. The resulting dark reaction mixture was extracted with ethyl acetate (3 x 5 ml). The extract was washed successively with saturated $NaHCO_3$ solution (2 x 10 ml), brine (2 x 10 ml) and dried with Na_2SO_4. Solvent was removed from the solution which gave **7** (0.265 g; 86%) as dark brown oil.

^{1}H NMR (dmso-d_6, δ, ppm): 1.36 s. (9H, CH_3), 1.39-1.44 m (2H, $\mathbf{CH_2}$-CH_2-NHBoc), 1.46-1.51 m. (2H, C(O)NH-CH_2-$\mathbf{CH_2}$), 2.93 m. (2H, $\mathbf{CH_2}$-NHBoc), 3.24 m. (2H, C(O)NH-$\mathbf{CH_2}$), 4.00 s. (5H, C_5H_5), 4.38 m. (2H, C_5H_4), 4.85 m. (2H, C_5H_4), 6.78 t. (^3J 5.5 Hz, 1H, **NH**Boc), 7.58-7.76 m. (4H, AA'BB', C_6H_4), 8.38 t. (J=5.5 Hz, 1H,CO**NH**).

^{13}C NMR (dmso-d_6, δ, ppm): 26.7 (CH_2), 27.9 (CH_2), 28.7 (CH_3), 39.8 (CH_2), 40.3 (CH_2), 66.9, 69.8, 83.8 (C_5H_4), 70.0 (C_5H_5), 69.6 (O**C**Me$_3$), 126.0 (C_{Ar}), 127.4 (C_{Ar}), 127.6 (C_{Ar}), 131.9 (C_{Ar}), 143.5 (C=O), 167.8 (C=O).

4-Ferrocenylbenzoic acid N-(4-aminobutyl)amide (8). A mixture of **7** (0.265 g; 0.56 mmol), dichloromethane (10 ml) and trifluoroacetic acid (3 ml) was stirred in argon purge for 2 h. Then all volatiles were removed under reduced pressure and the residue was dissolved in 10 ml of dichloromethane. The solution was washed with saturated solution of $NaHCO_3$ (2 portions of 10 ml), water (2 x10 ml) and dried over Na_2SO_4. After removal of the solvent **8** (0.189 g; 90%) was obtained as dark brown oil.

^{1}H NMR (dmso-d$_6$, δ, ppm): 1.39 m. (2H, CH$_2$), 1.53 m. (2H, CH$_2$), 2.60 m. (2H, **CH$_2$**-NH$_2$), 2.95 m. (2H, **CH$_2$**-NHC(O)), 4.00 s. (5H, C$_5$H$_5$), 4.38 m. (2H, C$_5$H$_4$), 4.85 m. (2H, C$_5$H$_4$), 7.57 -7.77 (4H, AA'BB', C$_6$H$_4$), 8.43 m. (1H,**NH**CO).

^{13}C NMR (dmso-d$_6$, δ, ppm): 27.1 (CH$_2$), 29.7 (CH$_2$), 39.9 (CH$_2$NH$_2$), 41.7 (**C**H$_2$NHCO), 66.7, 69.5 (C$_5$H$_4$), 69.7 (C$_5$H$_5$), 83.60 (C$_5$H$_4$-*ipso*), 125.8 (CH$_{Ar}$), 127.0 (CH$_{Ar}$), 131.9 (C$_{Ar}$), 143.1 (**C**$_{Ar}$-CO), 167.32 (CO).

It is noteworthy that a preparation of the starting 4-phenylbutyric acid (**12**) by the method published previously [8] requires many delicate manipulations on a stage of separation of the product. We propose a much more simple method of separation (see experimental part) which makes **12** readily available.

4-Phenylbutanoic acid (12) A mixture of aluminium chloride (150 g; 1,125 mol) and 342 ml of dry benzene heated to 50 °C on an oil bath and stirred at this temperature for 10 min. Then γ-butyrolactone (58 ml; 65.5 g; 0.76 mol) was added in 35 min and stirring at 50-60 °C was continued for 90 min. After cooling to ambient temperature the reaction mixture was poured into a mixture of 500 g of ice and 500 ml of conc. hydrochloric acid. The organic layer was separated, washed with water, dried over Na$_2$SO$_4$ and benzene was evaporated under reduced pressure. Water (500 ml) was added to an oily residue for removal of γ-butyrolactone and 4-phenylbutyric acid was extracted with chloroform. Then the product was converted into sodium salt by extraction of solution in chloroform with 5% solution of NaOH. Water solution of sodium salt was washed with chloroform and then carefully acidified by adding of conc. HCl to pH 9-10. The solution was evaporated under reduced pressure till water started to distill for removal of traces of chloroform. Water solution so prepared was filtered through a paper filter and then acidified with conc. HCl to pH 1-2. 4-Phenybutyric acid was separated as lower oily layer which crystallized gradually on standing for a night. Crystalline precipitate was separated, washed with water and dried on air for 2 days. Yield of 4-phenylbutyric acid (**12**) 119 g (96%), mp 43-45 °C, *cf* [15]: mp 47-48 °C.

^{1}H NMR (CDCl$_3$, δ, ppm): 1.97 quint., ^3J 7.55 Hz (2H, C**H**$_2$CH$_2$COOH), 2.37 t., ^3J 7.55 Hz (2H, C**H**$_2$COOH), 2.63 t., ^3J 7.55 Hz (2H, C**H$_2$**-Ar); 7.16 m. (5H, C$_6$H$_5$), 11.84 br. signal (1H, COO**H**).

^{13}C NMR (CDCl$_3$, δ, ppm): 26.19 (**C**H$_2$CH$_2$COOH), 33.27 (**C**H$_2$COOH), 34.99 (C**H$_2$**-Ar), 126.04 (***p*-C**, C$_6$H$_5$), 128.41 (***m*-C**, C$_6$H$_5$), 128.46 (***o*-C**, C$_6$H$_5$), 141.17 (***ipso*-C**, C$_6$H$_5$), 179.57 (**C**OOH).

4-(4-Iodophenyl)butanoic acid (14) – a modified procedure [7]. A mixture of **12** (85 g; 0.52 mol), periodic acid H_5IO_6 (36 g; 0.16 mol), iodine (79 g; 0.31 mol), 10 M H_2SO_4 (22 ml), glacial acetic acid (700 ml), water (150 ml) and dichloromethane (30 ml) was stirred at 75 ^oC for 18 h.

After cooling to ambient temperature the reaction mixture was poured into 500 ml of cold water and product was extracted with dichloromethane (4 portions of 200 ml). Organic layer was washed with water, 10% solution of sodium thiosulfate, dried over Na_2SO_4 and evaporated under reduced pressure. Red-brown oily residue was dissolved in 800 ml of 5% NaOH, charcoal (7 g) was added and the mixture was stirred overnight. The solution was filtered and acidified with conc. HCl to pH 2. A precipitate of **14** was separated by decantation. For removal of traces of charcoal acid **14** was dissolved in dichloromethane. This solution was washed twice with water, which lead to a migration of micelles containing charcoal into water layer. Organic layer was dried over Na_2SO_4 and the solvent was evaporated under educed pressure. The residue was dissolved in minimal volume of dichloromethane and the solution was filtered through 4 cm of silica gel. Filtrate was evaporated again. The oily residue readily crystallized on cooling and was recrystallized from petroleum ether – dichloromethane 1:1 mixture. A precipitate of **14** which was formed after cooling to -3 ^oC was separated and dried on air for 1 day (*protection from light*). Acid **14** (60.34g; 40%) was obtained, mp 87-88 ^oC, *cf.* [7]: mp 80-82 ^oC; [16]: mp 89-90.5 ^oC.

^1H NMR ($CDCl_3$, δ, ppm): 1.92 m. (2H, $C\mathbf{H_2}CH_2COOH$); 2.35 t. ^3J = 7.34 Hz (2H, $C\mathbf{H_2}COOH$); 2.60 t. ^3J = 7.82 Hz (2H, $C\mathbf{H_2}C_6H_4$); 6.91-6.93 m. and 7.57-7.60 m. (4H, AA'BB', C_6H_4).

4-(4'-Iodo[1,1']biphenyl-4-yl)butanoic acid (15). A mixture of 4-([1,1']biphenyl-4-yl)butanoic acid **13** (0.48 g; 2 mmol), periodic acid H_5IO_6 (0.091 g; 0.4 mmol), finely grinded iodine (0.204 g; 0.8 mmol), 10 M sulfuric acid (0.1 ml), water (1 ml), glacial acetic acid (3 ml) and 1 ml of chloroform was stirred at 65 ^oC for 18 h. After cooling to ambient temperature a precipitate of **15** was filtered off, washed thoroughly with a solution of Na_2SO_3 and air dried. Crystallization from 10 ml of acetic acid gave 0.5 g (68%) of **15** as microcrystalline substance, mp 142-146 ^oC. Calc. for $C_{16}H_{15}O_2I$, %: C 52.48, H 4.13. Found, %: C 52.70, H 4.24.

^{1}H NMR (dmso-d$_6$, δ, ppm): 1.80 m. (2H, **CH$_2$**CH$_2$COOH), 2.10 t. (2H, **CH$_2$**COOH), 2.22 t. (2H, **CH$_2$**C$_6$H$_4$), 7.26-7.28 and 7.55-7.57 m. (4H, AA'BB', C$_6$H$_4$), 7.44-7.46 and 7.77-7.79 m. (4H, AA'BB', C$_6$H$_4$).

^{13}C NMR (dmso-d$_6$,δ, ppm): 26.13 (**C**H$_2$CH$_2$COOH), 33.02 (**C**H$_2$COOH), 33.95 (**C**H$_2$C$_6$H$_4$), 93.31 (**C**-iodine), 126.39, 128.64, 128.97, 136.55, 137.57, 139.51, 141.32 (Ar, except C-iod), 174.18 (**C**OOH).

N-tert-Butoxycarbonyl-β-alanine 4-iodoanilide (16). Synthesis was carried out as described for **3** from *N-tert*-butoxycarbonyl-β-alanine (1.77g; 9.35 mmol) and 4-iodoaniline (2.04 g, 9.31 mmol). Yield of amide **16** 0.5 g (72%).

^{1}H NMR (CDCl$_3$, δ, ppm): 1.43 s. (9H, CH$_3$), 2.58 t. (2H, **CH$_2$**C(O)NH), 3.48 q. (2H, **CH$_2$**NH), 5.21 broad signal (1H, NH), 7.33-7.35 and 7.59-7.61 (AA'BB', 4H, C$_6$H$_4$), 8.24 broad signal (1H, ArN**H**CO).

^{13}C NMR (CDCl$_3$, δ, ppm): 28.4 (3C, CH$_3$), 36.4 (1C, CH$_2$), 37.8 (1C, CH$_2$), 79.8 (1C, **C**(CH$_3$)$_3$, 87.4 (1C, C$_{Ar}$-I), 121.6 (2C, CH$_{Ar}$), 137.7 (1C, C$_{Ar}$-NH), 137.8 (2C, CH$_{Ar}$), 156.5 (1C, CH2**C**(O)O), 169.7 (C, CH$_2$**C**(O)NH).

N-tert-Butoxycarbonyl-β-alanine N'-(4'-iodo[1,1']biphenyl-4-yl)amide (17). This compound was prepared by procedure described for **3**. Starting from *N-tert*-butoxycarbonyl-β-alanine (0.615 g; 3.25 mmol) and 4-iodobiphenylamine (0.836 g; 2.83 mmol) amide **17** (0.92 g; 70%) was obtained.

Calc. for C$_{20}$H$_{23}$IN$_2$O$_3$, %: C 51.51, H 4.97, N 6.01. Found, % : C 51.27, H 5.16, N 5.78.

^{1}H NMR (CDCl$_3$, δ, ppm): 1.43 s. (9H, CH$_3$), 2.62 t. (2H, **CH$_2$**COOH), 3.50 m. (2H, **CH$_2$**NH), 5.14 broad signal (1H, **NH**-BOC), 7.28-7.30 м. and 7.72-7.74 m. (4H, AA'BB', C$_6$H$_4$), 7.49-7.51 m. and 7.59-7.61 m. (4H, AA'BB', C$_6$H$_4$), 8.21 broad signal (1H, NH).

^{1}H NMR (dmso-d$_6$, δ, ppm): 1.37 s. (9H, CH$_3$), 2.49 t., ^{3}J 7 Hz (2H, **CH$_2$**COOH), 3.50 m. ^{3}J 7 Hz, ^{3}J 5.8 Hz (2H, **CH$_2$**NH), 6.87 t., ^{3}J 5.8 Hz (1H, **NH**-BOC), 7.43-7.45 m. and 7.76-7.78 m. (4H, AA'BB', C$_6$H$_4$), 7.58-7.61 and 7.67-7.70 (4H, AA'BB', C$_6$H$_4$), 10.05 s. (1H, NH).

^{13}C NMR (dmso-d$_6$, δ, ppm): 28.3 (CH$_3$), 36.5 (CH$_2$), 36.81 (CH$_2$), 77.6 (O**C**Me$_3$), 93.1 (C$_{Ar}$-I), 119.4 (CH$_{Ar}$), 126.7 (CH$_{Ar}$), 128.4 (CH$_{Ar}$), 133.4 (**C$_{Ar}$**-Ar), 137.6 (CH$_{Ar}$) 139.0 (**C$_{Ar}$**-NH), 139.2 (**C$_{Ar}$**-Ar), 155.6 (**C**(O)OCMe$_3$), 169.5 (**C**(O)NH-Ar).

β-Alanine 4-iodoanilide (18). Anilide **16** (0.5 g; 1.28 mmol) was stirred with a mixture of dry dichloromethane (25 ml) and trifluoroacetic acid (5 ml) for 2 h. Volatiles were removed *in vacuo*. Tracers of trifluoroacetic acid were removed from the residue by adding of toluene with subsequent evaporation under reduced pressure. The same procedure was used for removal of tracers of toluene using adding of dichloromethane and evaporation to dryness. 0.25 M solution of NaOH (15 ml) was added to the residue and **18** extracted with dichloromethane. After evaporation of the solvent **18** (0.335 g; 91%) was obtained as off-white powder, mp 115-119 ^{o}C.

^{1}H NMR ($CDCl_3$, δ, ppm): 1.52 broad signal (2H, NH_2); 2.44 m. (2H, CH_2), 3.09 m., (2H, CH_2), 7,32-7.34 m., 7,57-7,59 (4H, AA'BB', C_6H_4), 10,34 broad signal (1H, NHCO).

^{13}C NMR ($CDCl_3$, δ, ppm): 37.8 (1C, CH_2), 38.5 (1C, CH_2), 86.6 (1C, C_{Ar}-I), 121.6 (2C, CH_{Ar}), 137.7 (2C, CH_{Ar}), 138.3 (1C, C_{Ar}-NH), 171.2 (C, CH_2**C**(O)NH).

β-Alanine N-(4'-iodo[1,1']biphenyl-4-yl)amide (19). Amide **17** (0.92 g; 1,28 mmol) was stirred with a mixture of dry dichloromethane (50 ml) and trifluoroacetic acid (10 ml) for 1.5 h. Volatiles were removed under reduced pressure. Tracers of trifluoroacetic acid were removed from the residue by adding of toluene with subsequent evaporation under reduced pressure. The same procedure was used for removal of tracers of toluene using adding of dichloromethane and evaporation to dryness. The solid residue was washed with 0.25 M solution of NaOH (15 ml), white precipitate was separated, washed several times with water up to neutral reaction of washings and with cold ethanol (2 x 10 ml). The precipitate was dissolved in boiling ethanol (150 ml), the solution was filtered and placed at 4 ^{o}C for crystallization. This gave **19** (0.35 g; 75%) as off-white powder, mp 263 ^{o}C (decomp.). Calc. for $C_{15}H_{15}IN_2O$, %: C 49.2, H 4.13, N 7.65. Found, %: C 48.98, H 4.12, N 7.40.

^{1}H NMR ($CDCl_3$ + CF_3COOH, δ, ppm): 1.94 m. (2H, CH_2), 3.55 m. (2H, CH_2), 7.22-7.38 (4H, AA'BB', C_6H_4) and 7.53-7.81 (4H, AA'BB', C_6H_4).

^{13}C NMR ($CDCl_3$ + CF_3COOH, δ, ppm): 31.94 (**C**H_2C(O)NH), 37.24 (**C**H_2NH_2), 93.53 (**C**-iod), 122.39, 127.82, 128.75, 138.04 (Ar, except **C**-iod), 170.76 (**C**=O).

4-[N-(4'-Iodo[1,1']biphenyl-4-yl)amino]-4-oxobutanoic acid (21). A mixture of 4'-iodo[1,1']biphenyl-4-amine (1.7 g; 5.8 mmol), succinic anhydride (0.58 g; 5.8 mmol) and 50 ml of dichloromethane was stirred under reflux on water bath for 1 h. After cooling to ambient temperature a precipitate of **21** was separated, washed with dichloromethane and dried on air. Crystallization from 25 ml of glacial acetic acid gave 2 g (88%) of **21** as colorless crystals, mp 249-251 ^{o}C. Calc. for $C_{16}H_{14}O_3NI$ (%): C 48.22, H 3.62, N 3.43. Found (%): C 48.63, H 3.57, N 3.54.

^{1}H NMR (dmso-d_6, δ, ppm): 2.52-2.61 m. (4H, CH_2), 7.42-7.44 m. and 7.74-7.76 m. (4H, AA'BB', C_6H_4), 7.58-7.60 and 7.67-7.69 (4H, AA'BB', C_6H_4), 10.08 s. (1H, NH), 12.15 broad signal (1H, COOH).

^{13}C NMR (dmso-d$_6$, δ, ppm): 28.8 (CH$_2$), 31.1 (CH$_2$), 93.0 (C$_{Ar}$-I), 119.3 (CH$_{Ar}$), 126.8 (CH$_{Ar}$), 128.4 (CH$_{Ar}$), 133.4 (**C$_{Ar}$**-Ar), 137.6 (CH$_{Ar}$) 139.1 (**C$_{Ar}$**-NH), 139.2 (**C$_{Ar}$**-Ar), 170.2 (**C**(O)NH-Ar), 173.9 (COOH).

4'-Ferrocenyl[1,1']biphenyl-4-ol (22). A mixture of boroxine **9** (0.2 g; 0.23 mmol), 4-iodophenol (0.154 g; 0.7 mmol), potassium carbonate (0.29 g; 2.1 mmol), Pd(PPh$_3$)$_4$ (0.043 g; 0.035 mmol), DMF (10 ml) and 1 ml of water was stirred at 40 °C for 6 h in argon purge. After cooling to ambient temperature the reaction mixture was poured into a mixture of dichloromethane (25 ml) and water (25 ml) and was acidified to pH 3 with conc. HCl. Organic layer was separated, water layer was extracted with dichloromethane (3 x 20 ml). Combined organic extracts were washed thoroughly with water to remove DMF, dried over Na$_2$SO$_4$ and evaporated to dryness. The residue was subjected to column chromatography on silica gel. First (orange) and second (yellow) fractions were eluted with petroleum ether – dichloromethane 8:2 mixture and discarded. Subsequent elution with dichloromethane afforded phenol **22** (0.18 g; 72%) was obtained as orange solid.

^{1}H NMR (CDCl$_3$, δ, ppm): 4.05 s (5H, C$_5$H$_4$); 4.31 m (2H, C$_5$H$_4$); 4.65 m (2H, C$_5$H$_4$); 6.93-6.95 m (2H, ArH); 7.45-7.51 m (6H, ArH); *cf.* [**16**].

^{13}C NMR (CDCl$_3$,δ, ppm): 66.4, 68.9, 69.5, 85.2, 115.8, 126.4, 127.8, 132.9, 137.5, 138.3, 155.8; *cf.* [**16**].

4-(4'-Ferrocenyl[1,1']biphenyl-4-yl)butanoic acid (23). A mixture of boroxine **9** (0.370 g; 0.4 mmol), iodide **14** (0.373 g; 1.2 mmol), potassium carbonate (0.193 g; 1.35 mmol), Pd(PPh$_3$)$_4$ (0.017 g; 0.015 mmol), DMF (10 ml) and 1 ml of water was stirred at 60 °C for 12 h in argon purge. Acid **23** was isolated as described for **22**. Crude **23** was subjected to column chromatography on silica gel. First (orange) and second (yellow) fractions were eluted with benzene and discarded. Subsequent elution with ethyl acetate – benzene 1:1 mixture afforded 0.358 g (69%) of **23** as an orange powder. Calc. for C$_{26}$H$_{24}$O$_2$Fe, %: C 73.60, H 5.70. Found, %: C 73.45, H 5.84.

^{1}H NMR (dmso-d$_6$, δ, ppm): 2.01 quint., ^3J 7.50 Hz (2H, CH$_2$); 2.41 t. ^3J 7.50 Hz (2H, CH$_2$); 2.72 t. ^3J 7.50 Hz (2H, CH$_2$); 4.07 s. (5H, C$_5$H$_5$); 4.34 m. (2H, C$_5$H$_4$); 4.68 m. (2H, C$_5$H$_4$); 7.25 m. (4H, AA'BB', C$_6$H$_4$); 7.51 m. (4H, AA'BB', C$_6$H$_4$).

^{13}C NMR (dmso-d$_6$, δ, ppm): 26.15 (CH$_2$**C**H$_2$CH$_2$), 33.24 (**C**H$_2$COOH), 34.61 (**C**H-$_2$C$_6$H$_4$), 66.47 (2**C**, C$_5$H$_4$), 68.97 (2**C**, C$_5$H$_4$), 69.62 (5**C**, C$_5$H$_5$), 85.06 (**C$_{ipso}$**, C$_5$H$_4$), 126.44, 126.80, 128.31, 128.92, 138.18, 135.85, 138.72, 140.05 (Ar), 179.32 (**C**OOH).

MALDI-TOF calc for C$_{26}$H$_{24}$FeO$_2$ M$^+$ 424.1125; found M$^+$ 424.110.

4-[N-(4'-Ferrocenyl[1,1']biphenyl-4-yl)amino]-4-oxobutanoic acid (24).

Method 1. Synthesis was carried out as described for **22**, starting from boroxine **9** (0.209 g; 0.3 mmol) and 4-iodosuccinanilic acid (0.287 g; 0.9 mmol). The product was purified by column chromatography on silica gel. First (orange) and second (yellow) fractions were eluted with ethyl acetate – benzene 2:8 mixture and discarded. Acid **24** was eluted with ethanol – benzene 8:2 mixture. After evaporation of the eluate and drying of the residue over P_4O_{10} acid **27** (0.325 g; 80%) were obtained as orange solid. Calc. for $C_{26}H_{23}FeNO_3$, %: C 68.89, H 5.11, N 3.09. Found, %: C 68.98, H 5.31, N 3.10.

Method 2. A mixture of 4'-ferrocenyl[1,1']biphenyl-4-amine (0.39 g; 1.1 mmol), succinic anhydride (0.13 g; 1.3 mmol) and 25 ml of dichloromethane was stirred under reflux on water bath for 1 h. After cooling to ambient temperature a precipitate of **24** was separated, washed with dichloromethane and air dried. Yield 0.47 g (94%).

^{1}H NMR (dmso-d_6, δ, ppm): 2.53-2.62 m. (4H, CH_2), 4.00 s. (5H, C_5H_5), 4.33 m. (2H, C_5H_4), 4.79 m. (2H, C_5H_4), 7.57 m. (4H, C_6H_4), 7.63-7.65 m. and 7.69-7.71 m. (4H, AA'BB', C_6H_4), 10.07 s. (1H, NH), 12.16 broad signal (1H, COOH).

^{13}C NMR (dmso-d_6, δ, ppm): 28.8 (CH_2), 31.1 (CH_2), 66.2 (C_5H_4), 69.0 (C_5H_4), 69.4 (C_5H_5), 84.3 ($\mathbf{C_{Cp}}$-Ar), 119.3 (CH_{Ar}), 126.1 (CH_{Ar}), 126.3 (CH_{Ar}), 126.5 (CH_{Ar}), 134.3 ($\mathbf{C_{Ar}}$-C_5H_4), 137.0 ($\mathbf{C_{Ar}}$-NH), 137.8 ($\mathbf{C_{Ar}}$-Ar), 138.6 ($\mathbf{C_{Ar}}$-Ar), 170.1 (**C**(O)NH-Ar), 173.9 (COOH).

MALDI-TOF calc. for $C_{26}H_{23}FeNO_3$ M^+ 453.1027. Found M^+ 453.103.

β-Alanine (4'-ferrocenyl[1,1']biphenyl-4-yl)amide (25).

Method 1: A mixture of boroxine **9** (0.144 g; 0.167 mmol), iodoarene **18** (0.144 g; 0.5 mmol), potassium carbonate (0.069 g; 0.5 mmol), $Pd(PPh_3)_4$ (0.003 g; 0.0025 mmol), DMF (10 ml) and 1 ml of water was stirred at 60 ^{o}C for 12 h in argon purge. After cooling to ambient temperature the reaction mixture was poured into a mixture of dichloromethane (25 ml) and water (25 ml). Organic layer was separated, water layer was extracted with dichloromethane (3 x 25 ml). Combined organic extracts were washed thoroughly with water to remove DMF, dried over Na_2SO_4 and evaporated to dryness. The residue was subjected to column chromatography on silica gel. Crude **25** was subjected to column chromatography on silica gel with dichloromethane - methanol 1 : 1 mixture as eluent. First and second yellow bands were discarded, third yellow band gave 0.13 g (61%) of **25**.

Method 2: Amide **31** (0.393 g; 0,75 mmol) was stirred with a solution of trifluoroacetic acid (2 ml) in dry dichloromethane (15 ml) for 1.5 h. Volatiles were removed under reduced pressure. Traces of trifluoroacetic acid were removed from the residue by adding of toluene with subsequent evaporation under reduced pressure. The same procedure was used for removal of traces of toluene using adding of dichloromethane and evaporation to dryness. The solid residue was dissolved in chloroform (100 ml) and solution was washed thoroughly with 0.25 M NaOH. The organic layer was separated, washed with water and dried over Na_2SO_4. Evaporation of the solvent afforded 0.3 g (94%) of **25** as an orange powder.

^{1}H NMR (dmso-d_6, δ, ppm): 2.41 t., ^3J 6.7 Hz (2H, **CH_2**C(O)), 2,85 t., ^3J 6.7 Hz (2H, **CH_2**NH), 3.25 broad signal (2H, NH_2), 4.02 s. (5H, C_5H_5), 4.35 m. (2H, C_5H_4), 4.80 m. (2H, C_5H_4), 7.55-7.59 m. (4H, C_6H_4), 7.62-7.64 and 7.68-7.70 m. (4H, AA'BB', C_6H_4), 10.14 broad signal (1H, **NH**-Ar).

^{13}C NMR (dmso-d_6, δ, ppm): 38.2 (CH_2), 40.3 (CH_2), 66.2 (C_5H_4), 68.9 (C_5H_4), 69.3 (C_5H_5), 84.3 (**C_{Cp}**-Ar), 119.4 (CH_{Ar}), 126.0 (CH_{Ar}), 126.3 (CH_{Ar}), 126.4 (CH_{Ar}), 134.3 (**C_{Ar}**-Cp), 137.0 (**C_{Ar}**-NH), 137.7 (**C_{Ar}**-Ar), 138.5 (**C_{Ar}**-Ar), 170.6 (**C**(O)NH).

4-Ferrocenylethynyl-4'-nitro[1,1']biphenyl (26). Synthesis was carried out as described for **25** (*method 1*), starting from boroxine **11**, (0.15 g; 0.16 mmol) and 4-nitro-1-iodobenzene (0.12 g; 0.48 mmol). Crude **26** was subjected to column chromatography on silica gel with petroleum ether – chloroform 7:3 mixture as eluent. First (orange) and second (yellow) bands were discarded. Product **26** as a red band was collected. After evaporation of the eluate and drying of the residue *in vacuo* **26** (0.17 g; 86%) was obtained as red solid.

^{1}H NMR ($CDCl_3$, δ, ppm): 3.91 s. (5H, C_5H_5), 3.94 m. (2H, C_5H_4), 4.19 m. (2H, C_5H_4), 7.39 - 7.97 m. (8H, C_6H_4); *cf.* [18].

^{13}C NMR ($CDCl_3$, δ, ppm): 64.8, 69.0, 70.0, 71.5 (Cp), 85.2, 90.6 ($C\equiv C$), 124.2, 124.8, 127.2, 127.6, 132.0, 137.6, 146.8, 147.1 (C_6H_4-C_6H_4); *cf.* [18].

4'-Ferrocenylethynyl[1,1']biphenyl-4-amine (27). Synthesis was carried out as described for **25**, starting from boroxine **11**, (0.165 g; 0.5 mmol) and 4-iodoaniline (0.109 g; 0.5 mmol). The reaction mixture was stirred at 40 ^{o}C for 18 h and then poured into a mixture of chloroform (50 ml) and water (50 ml). Organic layer was washed thoroughly with water, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel with dichloromethane as eluent. Two first yellow bands were discarded, third (bright red) band gave 0.12 g (64%) of **27**.

^{1}H NMR ($CDCl_3$, δ, ppm): 3.63 br. (2H, NH_2), 4.21 m. (5H, C_5H_5 + 2H, C_5H_4), 7.41-7.65 m. (8H, two AA'BB', C_6H_4-C_6H_4).

^{13}C NMR ($CDCl_3$, δ, ppm): 65.2 (**C$_{cp}$**-Ar, C_5H_4), 68.8 (C_5H_4), 69.9 (C_5H_5), 71.4 (C_5H_4); 86.15, 89.18 (C≡C); 128.48, 128.60, 131.05, 131.96 (CH$_{Ar}$); 128.26 (**C$_{Ar}$**-C≡C), 130.39 (**C$_{Ar}$**-Ar), 132.14 (**C$_{Ar}$**-Ar); 134.02 (**C**-NH_2).

4'-Nitro[1,1']biphenyl-4-amine (29).

Preparation of reducing agent. Sodium (1.46 g; 0.0635 mol) was dissolved in methanol (133 ml) and dry hydrogen sulfide was passed through the solution until the last acquired yellow-green coloration (about 1 h). A drop of the solution must reveal pH 9-10 when being put on a wet indicator paper.

Reduction. The solution of reducing agent was added by drops but fast (in 15 min) with a good stirring to a refluxing suspension of 4,4'-dinitrobiphenyl (10.0 g; 0.041 mol) in 67 ml of anhydrous THF. After addition was complete stirring was continued for 12 h at ambient temperature.

The reaction mixture was poured into water (700 ml) and the resulting suspension was stirred for 30 min. Orange-red precipitate of **29** was separated by filtration and added to a solution of potassium hydroxide (11.2 g; 0.2 mol) in water (170 ml). The mixture was stirred at 80 ^{o}C for 4 h to remove elementary sulfur. Then a precipitate was separated, washed thoroughly with water till neutral reaction of washings and air dried yielding **29** (7.91 g; 90%), mp 201-204 ^{o}C. *Cf*. [19]: mp 203.5-204 °C.

^{1}H NMR ($CDCl_3$, δ, ppm): 3.81 broad signal ((2H, NH_2); 6.69-6.72 and 7.39-7.41 (4H, AA'BB', C$_6$**H$_4$**NH$_2$), 7.58-7.60 and 8.16-8.18 (4H, AA'BB', C$_6$**H$_4$**NO$_2$).

Compound is pure enough for most applications but can be additionally purified by recrystallization. For this a mixture 7.5 ml of acetone and 52 ml of 95% ethanol was used per 1 g of the substance which gave **32**, mp 203-204 °C. Calc. for $C_{12}H_{10}N_2O_2$ (%): C 67.28; H 4.70; N 13.08. Found (%): C 67.14; H 4.88; N 13.23.

N-tert-Butoxycarbonyl-β-alanine N-(4'-ferrocenyl[1,1']biphenyl-4-yl)amide (31).
Preparation was carried out as described for **16** from *N*-*tert*-butoxycarbonyl-β-alanine (0.19 g; 1 mmol) and 4'-ferrocenyl[1,1']biphenyl-4-amine (0.35 g; 1 mmol) This afforded **31** (0.48 g; 92%).

^{1}H NMR (dmso-d$_6$, δ, ppm): 1.37 s. (9H, CH_3), 2.47-2.51 m. (2H, **CH$_2$**C(O)), 3.20-3.25 m. (2H, **CH$_2$**NH), 4.02 s. (5H, C_5H_5), 4.35 m. (2H, C_5H_4), 4.80 m. (2H, C_5H_4), 6.86 t. (1H, **NH**-BOC), 7.55-7.60 m. (4H, C_6H_4), 7.62-7.64 and 7.67-7.69 m. (4H, AA'BB', C_6H_4), 10.01 s. (1H, **NH**-Ar).

^{13}C NMR (dmso-d$_6$, δ, ppm): 28.2 (CH_3), 36.5 (CH_2), 36.8 (CH_2), 66.2 (C_5H_4), 68.9 (C_5H_4), 69.3 (C_5H_5), 77.6 (O**C**Me$_3$), 84.3 (**C$_{Cp}$**-Ar), 119.4 (CH$_{Ar}$), 126.1 (CH$_{Ar}$), 126.3 (CH$_{Ar}$), 126.4 (CH_{Ar}), 134.4 ($\mathbf{C}_{\mathbf{Ar}}$-Cp), 137.0 ($\mathbf{C}_{\mathbf{Ar}}$-NH), 137.8 ($\mathbf{C}_{\mathbf{Ar}}$-Ar), 138.4 ($\mathbf{C}_{\mathbf{Ar}}$-Ar), 155.5 (**C**(O)$OCMe_3$), 169.4 (**C**(O)NH-Ar).

References

[9] C. Tan, B. M. Fung and G. Cho, *J. Am. Chem. Soc.*, 2002, **124**, 11827.

[10] F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masulo, M. Mausner and E. Sommer, *J. Am. Chem. Soc.*, 1959, **81**, 342.

[11] J. S. Stover, J. Shi, W. Jin, P. K. Vogt and D. L. Boger, *J. Am. Chem. Soc.*, 2009, **131**, 3342.

[12] D. Muller, I. Zeltser, G. Bitan and Ch. Gilon, *J. Org. Chem.*, 1997, **62**, 411.

[13] V. P. Dyadchenko, N. M. Belov, D. A. Lemenovskii, M. Yu. Antipin, K. A. Lyssenko, A. E. Bruce and M. R. M. Bruce, *J. Organomet. Chem.*, 2010, **695**, 304.

[14] N. Khan, A. Badshah, Bh. Lal, M. A. Malik, J. Raftery, P. O’Brien and A. A. Altah, *Polyhedron*, 2014, **69**, 40.

[15] W. E. Truce and C. E. Olson, *J. Am. Chem. Soc*., 1952, **74**, 4721.

[16] J. T. Plati, W. H. Strain and S. L. Warren, *J. Am. Chem. Soc.*, 1943, **65**, 1273.

[17] C. Imrie, P. Engelbrecht, C. Loubser, C. W McCleland, V. O Nyamori, R. Bogardi, D. C. Levendis, N. Tolom, J. Rooyen and N. Williams, *J. Organomet. Chem.*, 2002, **645**, 65.

[18] S. Quan-Ling, B. Yue-Guang, W. Yi-Bing, H. Li-Min and W. Lin-Hong, *Polyhedron*, 2007, **26**, 3153.

[19] D. W. Sherwood and M. Calvin, *J. Am. Chem. Soc.*, 1942, **64**, 1350.