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Microwave-promoted *N*-arylation of imidazole and amino acids in the presence of Cu₂O and CuO in poly(ethylene glycol)*

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Copper(I)-catalyzed *N*-arylation of imidazole with iodobenzene, its derivatives, and bromobenzene in poly(ethylene glycol) under microwave irradiation was studied. The influence of the following factors on the yield of arylation product was investigated: the nature of the source of copper and ligand, type of poly(ethylene glycol) (PEG) used, and substituents in iodoarene. An optimal catalytic system was selected: CuO/L-Hys/Cs₂CO₃/PEG-400, a possibility of recycling of copper-containing catalyst was demonstrated. *N*-Arylation of eight natural amino acids using catalysis with Cu₂O/Cs₂CO₃/PEG-400 and microwave irradiation was studied, the dependence of the reaction results on temperature, duration of the process, and the ratio of the starting reagents was found. The highest yields of the target products were reached in the case of leucine, valine, and phenylalanine.

Key words: catalysis, copper(I) compounds, aryl halides, imidazole, amino acids, poly(ethylene glycol).

Catalysis for the C(sp²)—N bond formation by univalent copper complexes is an intensively developing trend in modern synthetic organic chemistry, which already became a subject of several reviews and monographs.^{1–3} *N*-Arylation of imidazole is used as a model reaction for testing different catalytic systems. Aryl iodides and bromides were used to study catalytic properties of Cu₂O in the presence of various Schiff bases and oximes.⁴ Arylation with iodoarenes can be successfully effected using CuI and *N*¹,*N*²-dimethylcyclohexane-1,2-diamine.⁵ Amino acids such as proline and *N,N*-dimethylglycine^{6–10} are widely used as ligands in various copper-catalyzed amination reactions. In these reactions, DMSO is used as the solvent most frequently, however, in some case this is acetonitrile and dioxane. Non-natural amino acids such as pipercolic and pyrrololeucic^{11,12} can be also used. Of natural amino acid, histidine¹³ was used in a number of experiments, with some of them being performed in poly(ethylene glycols) (PEG) instead of DMSO. Another

work mentioned the use of mixtures of PEG—butyronitrile and PEG—*N*-methylpyrrolidone for arylation of imidazole in the presence of Cu₂O and 4,7-dimethoxyphenanthroline.¹⁴ Note that in the indicated works, the aspect of recyclability of the catalyst due to the use of PEG as the medium for carrying out the catalytic process was not developed. The multiple use of the catalyst due to the simplicity of isolation of reaction products from poly(ethylene glycols) was considered in the literature for the following examples: the amidation of aryl iodides (PEG-400) catalyzed by Cu₂O nanoparticles,¹⁵ the reaction of arylboronic acids with aryl bromides and even aryl chlorides in the system Cu/I₂ (PEG-400),¹⁶ the reactions of C—H-activation of triazoles and oxadiazoles with iodoarenes in the system Cu(nanoparticles)/PEG-400¹⁷, thiolation of aryl bromides and aryl iodides in the presence of CuI in PEG-1000 and a mixture of PEG—water.¹⁸ Microwave irradiation in the *N*-arylation of indole and benzimidazole in more high-molecular-weight PEG-3400 was also reported.¹⁹

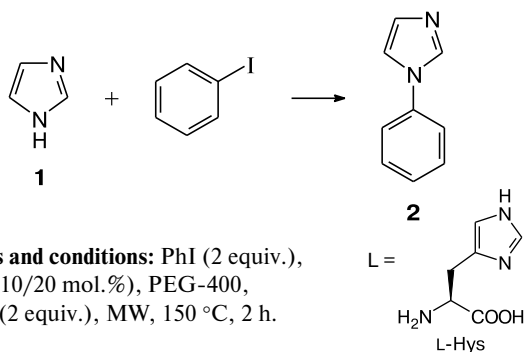
Based on the above-mentioned facts, we attempted to study a possibility of *N*-arylation of imidazole in poly(ethylene glycols) under influence of microwave irradiation. Initially, we selected the optimal source of copper in

* Dedicated to Academician of the Russian Academy of Sciences O. G. Sinyashin on the occasion of his 60th birthday.

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PEG-400, trying the following compounds: copper(I) oxide and copper(II) oxide, copper iodide, copper acetylacetonate, copper nanoparticles in the presence or in the absence of histidine; the latter was initially chosen as the ligand, which was successfully used in poly(ethylene glycol) (Scheme 1, Table 1). All the reactions were carried out under standard conditions: 10 mol.% of copper, 20 mol.% of histidine (in the case of its addition), 2 equiv. of aryl iodide and cesium carbonate used as a base, the concentration of imidazole in PEG-400 was 0.46 mol L^{-1} , the reactions were carried out for 2 h at $150 \text{ }^\circ\text{C}$, the conversion of imidazole (**1**) into *N*-phenylimidazole (**2**) was determined using ^1H NMR spectroscopy after treatment of the reaction mixture with diethyl ether and separation of the reaction product and unreacted imidazole from the catalyst and the base.

Scheme 1



The reaction time and temperature were optimized experimentally for several versions of catalytic systems. It was preliminarily found that an increase in temperature above $150 \text{ }^\circ\text{C}$ did not improve the result, an increase in the reaction time beyond 2 h can only insignificantly increase

the product yield. More interesting and important conclusions were drawn from the experiments on variation of the source of copper. It follows from the data in Table 1 that under the indicated conditions, the conversion of imidazole to the product was 52–83%, with the yields more than 70% being reached in the presence of the following catalytic systems: CuI/L-Hys (entry 1), CuO/L-Hys (entry 5), $\text{Cu}(\text{acac})_2$ /L-Hys (entry 8), and copper nanoparticles/L-His (entry 10). A special experiment (entry 6) showed that the use of 2 equiv. of iodobenzene is an important factor for the increase in the yield of the arylation product. The best result was reached in the case of application of the catalytic system $\text{Cu}(\text{acac})_2$ /L-Hys (83%, entry 8), however, in further experiments we used another system, CuO/L-Hys (entry 5), which gave a slightly lower yield of compound **2**, but did not contain an additional acetylacetonate ligand, which could neutralize the influence of the studied ligands on the efficiency of the arylation reaction.

Further, in the presence of the catalyst CuO/L-His (10/20 mol.%) we carried out a series of experiments to study the influence of the reaction medium on the efficiency of the arylation reaction (Table 2). A high conversion of the starting imidazole (above 70%) was observed for PEG-400 (entry 1), PEG-2000 (entry 2), and PEG-3400 (entry 5), with PEG-400 being found the most preferable. In the cases of completely or partially methylated poly(ethylene glycols), the conversion of imidazole was lower (entries 3 and 4). A mixture of PEG-400 and PEG-3400 turned out to be noticeably less efficient (entry 7) than PEG-400 and PEG-3400 separately. A two-fold decrease in the concentration of the starting compounds leads to a considerable decrease in the yield of compound **2** (entry 6). In the solvents in which the process cannot be carried out at a required temperature ($150 \text{ }^\circ\text{C}$), the conversion of imidazole was low (entries 8 and 9). Thus, the

Table 1. Optimization of copper source in arylation of imidazole

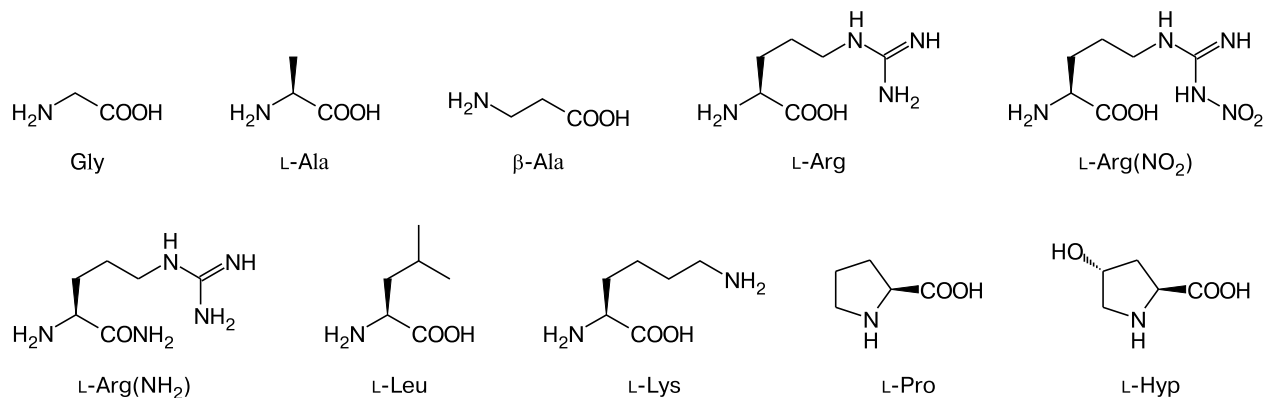
Entry	Source of copper	Ligand	Yield of 2 (%)
1	CuI	L-Hys	72
2	Cu_2O	—	52
3	Cu_2O	L-Hys	65
4	CuO	—	62
5	CuO	L-Hys	79
6*	CuO	L-Hys	50
7	$\text{Cu}(\text{acac})_2$	—	62
8	$\text{Cu}(\text{acac})_2$	L-Hys	83
9	Cu_{nano}	—	60
10	Cu_{nano}	L-Hys	79

* 1 equiv. of iodobenzene was used.

Table 2. Optimization of reaction medium in arylation of imidazole

Entry	Medium	Yield of 2 (%)
1	PEG-400	79
2	PEG-2000	70
3	$\text{PEG-2000}(\text{OMe})_2$	63
4	$\text{PEG-2000}(\text{OMe})(\text{OH})$	54
5	PEG-3400	75
6*	PEG-3400	45
7	PEG-400 + PEG-3400	54
8	H_2O	34
9	MeCN	33

* The reaction was carried with half as large concentrations of the starting compounds.



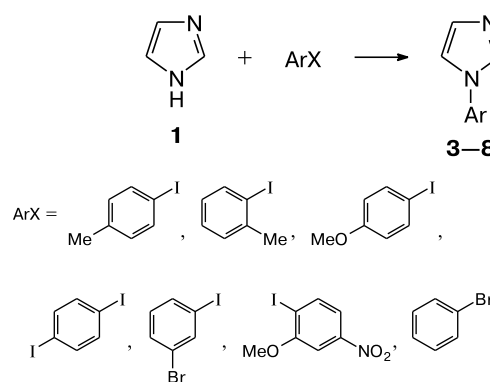
additional studies of the influence of the reaction medium justified the choice of PEG-400 for this process.

In the following step, we studied the influence of the ligand on the yield of the arylation product. Table 3 summarizes the data on 10 amino acids, which were compared with histidine in the standard arylation reaction of imidazole with iodobenzene (CuO/L, 0/20 mol.%).

It was found that the following catalysts provided conversion of imidazole comparable (above 70%) with that of histidine (entry 1): an equimolar mixture of histidine with glycine (entry 3), alanine hydrochloride (entry 6), or proline in the combination with copper iodide (entry 11). The latter catalytic system is described in details in the literature, including its use in PEG.¹⁸ The other α -amino acids provided slightly lower conversion of imidazole (56–67%), whereas β -alanine turned out to be even less efficient (entry 5). These experiments confirmed the right choice of histidine as the ligand in PEG medium.

The optimized conditions were used to study the reactivity of different aryl iodides containing electron-donating and electron-withdrawing substituents, including those in *ortho*-position, as well as bromobenzene (Scheme 2, Table 4). The reactions with 4-iodotoluene and 4-iodo-

Scheme 2



Reagents and conditions: CuO/L-Hys (10/20 mol.%), PEG-400, Cs₂CO₃ (2 equiv.), MW, 150 °C, 2 h.

anisole under the standard conditions provided very high yields of the arylation products 3 and 5 (entries 1 and 3), which were higher than in the model reaction with iodobenzene (79%). At the same time, in the reactions with 2-iodotoluene and 1-iodo-2-methoxy-4-nitrobenzene the

Table 3. Optimization of ligand in arylation of imidazole

Entry	Ligand	Yield 2 (%)
1	L-Hys	79
2	Gly	67
3	Gly + L-Hys (1 : 1)	72
4	L-Ala	63
5	β -Ala	50
6	L-AlaNH ₂ ·HCl	75
7	L-Arg	64
8	L-Arg(NO ₂)	62
9	L-Arg(NH ₂)	66
10	L-Lys·HCl	63
11*	L-Pro	80
12	L-Hyp	66
13	L-Leu	56

* CuI was used instead of CuO.

Table 4. Arylation of imidazole with aryl halides

Entry	Aryl halide	Product and its yield (%)
1	4-MeC ₆ H ₄ I	3 (90)
2	2-MeC ₆ H ₄ I	4 (27)
3	4-MeOC ₆ H ₄ I	5 (89)
4 ^a	4-MeOC ₆ H ₄ I	5 (50)
5 ^b	4-MeOC ₆ H ₄ I	5 (74)
6	1,4-I ₂ C ₆ H ₃	6 ^c (60)
7	3-BrC ₆ H ₄ I	7 ^d (65)
8	2-MeO-4-O ₂ NC ₆ H ₃ I	8 (38)
9	PhBr	2 (34)

^a PEG-3400 was used.

^b Proline was used instead of histidine as the ligand.

^c The product was 1-(4-iodophenyl)imidazole (6).

^d The product was 1-(3-bromophenyl)imidazole (7).

arylation products **4** and **8** were obtained in low yields (entries 2 and 8). Apart from that, the replacement of PEG-400 with PEG-3400, as well as the use of proline instead of histidine in the reactions with *p*-iodoanisole led to the decrease in the yields of the target product **5** (entries 4 and 5). The arylation of 1,4-diiodobenzene and 3-bromoiodobenzene gave fairly good yields of products **6** and **7** (entries 6 and 7), a slight decrease in the yields as compared to iodobenzene is probably due to the side reactions proceeding because of the presence of the second halogen atom.

Preliminary study of recyclability of the catalyst was carried out in two catalytic systems: CuO/L-Hys/Cs₂CO₃/PEG-400 and CuI/L-Pro/Cs₂CO₃/PEG-400 (Table 5). From the given data, it can be concluded that in the reactions in the presence of ligands (histidine and proline) the catalytic activity of copper decreases starting from the third cycle. More detailed conclusions will be made after further studies of these processes, however, in this study we demonstrated a principal possibility of the catalyst recovery.

In the reactions catalyzed by univalent copper involving amino acids with a primary amino group as ligands, they themselves undergo partial arylation. This process can be made a predominant, there are literature data describing conditions for the efficient *N*-arylation of amino acids. Thus, aryl iodides and aryl bromides were used to arylate amino acids in the presence of CuI in dimethoxyethane without addition of extra ligands.²⁰ Additional ligands were not used either in the amination of 4-iodo-, 4-bromo-, and 5-bromo-*N*-tosylindoles with amino acids in DMSO.²¹ The system CuI/KI was used for the arylation of amino acids and their esters with bromoarenes,²² the same catalyst was applied for the arylation of amino acids with aryl iodides and aryl bromides in DMF with microwave assistance.²³ Additional ligands are used seldom in these processes: thus, the reactions of aryl iodides and aryl bromides with amino acids in water in the presence of *N,N*-dimethylaminoethanol were catalyzed by an equimolar mixture of Cu : CuI,²⁴ a more traditional system

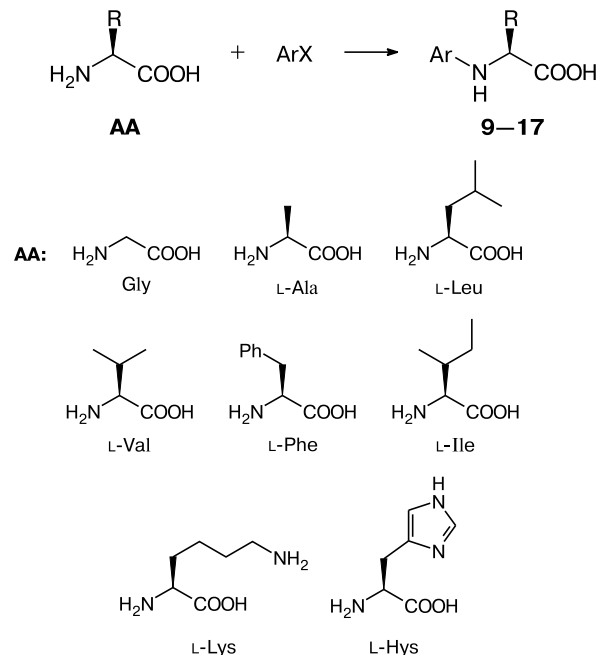
Table 5. Study of recyclability of catalyst in arylation of imidazole with iodobenzene (10 mol.% [Cu], 20 mol.% ligand, MW, 150 °C, 2 h)

Entry	Catalytic system	<i>N</i>	Yield of 2 (%)
1	I	1	79
2		2	87
3		3	54
4	II	1	78
5		2	71
6		3	52

Note. Catalytic systems: CuO/L-Hys/Cs₂CO₃/PEG-400 (I) and CuI/L-Pro/Cs₂CO₃/PEG-400 (II); *N* is the number of the catalytic cycles.

CuI/2-isobutyrylcyclohexanone was also used.²⁵ In the present study, we for the first time investigated arylation of eight amino acids (AA) in PEG (Scheme 3, Table 6).

Scheme 3



Reagents and conditions: 5 equiv. ArX, Cu₂O (10 mol.%), Cs₂CO₃ (3 equiv.), PEG-400, MW.

Based on the preliminarily obtained data, Cu₂O was used as a source of copper, the reactions were carried out with iodobenzene (1–5 equiv.) at a temperature of 100–150 °C and a concentration of amino acids of 0.46 mol L⁻¹. In a number of cases, the reaction time was varied within the range of 10–120 min. The studies resulted in finding the following specific features.

The reaction of a considerable excess of iodobenzene (5 equiv.) with the parent amino acid glycine gave arylation product **9** in only 10% yield (entry 1). Under the same conditions, alanine gave 57% of compound **10** (entry 2). When 2 equiv. of iodobenzene was used instead of 5 equiv. (entry 3) with even longer reaction time and higher temperature, the yield of arylation product **10** decreased almost by a factor of 2. Valine has proved even more active than alanine: its reaction with 2 equiv. of iodobenzene an increase in temperature from 100 to 150 °C initially led to a noticeable increase in the reaction rate (entries 4 and 5), then the rate of the process decreased, and the difference between the results of arylation after 30 min and after 2 h became insignificant (entries 6 and 7). The good choice of PEG-400 as a reaction medium was confirmed by the experiment in PEG-3400, which showed a two-fold decrease in the yield of compound **11** (entry 8). The higher

Table 6. *N*-Arylation of amino acids with aryl halides

Entry	Amino acid	ArX (n/equiv.)	T/°C	τ /min	Product and its yield (%)
1	L-Gly	PhI (5)	100	40	9 (10)
2	L-Ala	PhI (5)	100	40	10 (57)
3	L-Ala	PhI (2)	150	60	10 (30)
4	L-Val	PhI (2)	100	10	11 (15)
5	L-Val	PhI (2)	150	10	11 (43)
6	L-Val	PhI (2)	150	30	11 (51)
7	L-Val	PhI (2)	150	120	11 (57)
8*	L-Val	PhI (2)	150	60	11 (29)
9	L-Val	PhI (5)	100	120	11 (70)
10	L-Val	PhI (5)	150	60	11 (63)
11	L-Leu	PhI (1)	100	120	12 (41)
12	L-Leu	PhI (5)	100	15	12 (55)
13	L-Leu	PhI (5)	100	30	12 (88)
14	L-Phe	PhI (5)	100	120	13 (72)
15	L-Ile	PhI (5)	100	120	14 (59)
16	L-Lys	PhI (5)	150	60	—
17	L-Hys	PhI (5)	150	120	—
18	L-Leu	4-MeC ₆ H ₄ I	100	40	15 (41)
19	L-Leu	3-BrC ₆ H ₄ I	100	40	16 (60)
20	L-Leu	PhBr	100	120	—
21	L-Leu	PhBr	150	120	12 (60)
22	L-Leu	PhCl	150	60	—
23	L-Val	1,4-I ₂ C ₆ H ₄	150	60	17 (79)

* PEG-3400 was used instead of PEG-400.

yields of the target product **11** can be obtained using 5 equiv. of iodobenzene (entries **9** and **10**). Leucine turned to be the most active amino acid: even with 1 equiv. of iodobenzene, the yield of compound **12** was 41% (entry **11**), while in the presence of 5 equiv. of iodobenzene the product was obtained in 88% yield already after 30 min (entry **13**). Phenylalanine and isoleucine showed slightly lower activity (entries **14** and **15**). Lysine and histidine were absolutely inert (entries **16** and **17**), the latter result is a good confirmation of a rightful choice of this amino acid as a ligand in the *N*-arylation reactions of imidazole. 4-Iodotoluene (entry **18**) and 3-bromoiodobenzene (entry **19**) were also coupled with leucine. For arylation with bromobenzene, the reaction temperature was a decisive factor: at 100 °C the process did not take place (entry **20**), while at 150 °C the arylation was successful and gave compound **12** in 60% yield (entry **21**). Chlorobenzene did not give the product (entry **22**). Another amino acid, valine, was coupled with 1,4-diiodobenzene giving the product **17** (entry **23**) in the yield considerably higher than the yield of similar compound **11** obtained from iodobenzene (entry **10**).

In conclusion, the studies on catalytic *N*-arylation of imidazole showed that the optimal catalytic system in PEG-400 is CuO/L-Hys/Cs₂CO₃ when using 2 equiv. of aryl iodide and 2 equiv. of a base. The highest product yields reached 90% when aryl iodide contains electron-donating substituents in *para*-position. The studies of the

catalytic *N*-arylation of a number of amino acids showed that leucine, valine and phenylalanine containing more bulky hydrophobic substituents were the most active in the reactions catalyzed by Cu₂O/Cs₂CO₃ in PEG-400.

Experimental

All the experiments on Cu-catalyzed arylation of imidazole and amino acids were conducted using commercially available reagents. The reactions were carried out in a Biotage Initiator+ microwave reactor (600 W) in hermetically sealable vials suitable for the solution volume of 2 mL. ¹H NMR spectra were recorded on a Bruker Avance 300 spectrometer (300 MHz) in CDCl₃. Chemical shifts in the ¹H NMR spectra are given in the δ scale relative to Me₄Si as a reference. Dibromomethane was used as an internal standard in calculating yields of arylation products.

Catalytic *N*-arylation of imidazole (general procedure). Imidazole (0.23 mmol), aryl halide (0.46 mmol), CuO (1.8 mg, 10 mol.%), L-histidine (7.1 mg, 20 mol.%), cesium carbonate (150 mg, 0.46 mmol), and PEG-400 (0.5 mL) were placed into a vial equipped with a magnetic stirrer. The vial was hermetically sealed and kept in the microwave reactor at a temperature of 150 °C for 2 h. After the reaction reached completion, the mixture was diluted with water (1 mL), transferred into a separatory funnel, and extracted with cyclohexane or diethyl ether (3–5 times 10 mL each). The combined organic phases were concentrated *in vacuo* and analyzed by ¹H NMR. The spectra of compounds **2**, **3**, **5**, and **6** agree with those reported in the literature,²⁶ the spectra of compounds **4**, **7**, and **8** are identical to those reported in the corresponding publications.^{27–29}

Catalytic *N*-arylation of amino acids (general procedure). A corresponding amino acid (0.23 mmol), aryl halide (0.46–1.15 mmol), Cu₂O (3.3 mg, 10 mol.%), cesium carbonate (225 mg, 0.69 mmol), and PEG-400 (0.5 mL) were placed into a vial equipped with a magnetic stirrer. The vial was hermetically sealed and kept in the microwave reactor at a temperature of 100–150 °C for 0.5–2 h. After the reaction reached completion, the mixture was diluted with water (1 mL), treated with 1 *M* hydrochloric acid to adjust pH 1, transferred into a separatory funnel, and extracted with diethyl ether (3–5 times 10 mL each). The combined organic phases were concentrated *in vacuo* and analyzed by ¹H NMR. The spectra of compounds **9**–**14** corresponded to those reported in the literature.²⁵

(S)-4-Methyl-2-(*p*-tolylamino)pentanoic acid (15). ¹H NMR (CD₃OD), δ : 0.94 (d, 3 H, CH₃, ³*J* = 6.6 Hz); 0.98 (d, 3 H, CH₃, ³*J* = 6.6 Hz); 1.67 (t, 2 H, CH₂, ³*J* = 7.0 Hz); 1.78–1.92 (d, 1 H, CH); 2.20 (s, 3 H, CH₃); 3.97 (t, 1 H, CH, ³*J* = 7.1 Hz); 6.64 (d, 2 H, H_{Ph}(2), ³*J* = 7.6 Hz); 6.97 (d, 2 H, H_{Ph}(3), ³*J* = 7.6 Hz); the protons of the NH and COOH groups were not detected.

(S)-2-(3-Bromophenylamino)-4-methylpentanoic acid (16). ¹H NMR (CDCl₃), δ : 0.92 (d, 3 H, CH₃, ³*J* = 6.6 Hz); 0.96 (d, 3 H, CH₃, ³*J* = 6.6 Hz); 1.65 (t, 2 H, CH₂, ³*J* = 7.0 Hz); 1.72–1.87 (d, 1 H, CH); 2.20 (s, 3 H, CH₃); 3.97 (t, 1 H, CH, ³*J* = 7.1 Hz); 6.53 (d, 1 H, H_{Ph}(6), ³*J* = 7.1 Hz); 6.75 (br.s, 1 H, H_{Ph}(2)); 6.82 (d, 1 H, H_{Ph}(4), ³*J* = 7.6 Hz); 6.99 (t, 1 H, H_{Ph}(5), ³*J* = 7.9 Hz); the protons of the NH and COOH groups were not detected.

(S)-2-(4-Iodophenylamino)-3-methylbutanoic acid (17). ¹H NMR (CDCl₃), δ : 1.02 (d, 3 H, CH₃, ³*J* = 6.8 Hz); 1.03 (d, 3 H, CH₃, ³*J* = 6.9 Hz); 2.04–2.25 (d, 1 H, CH); 3.83 (d, 1 H, CH,

$^3J = 5.5$ Hz); 6.42 (d, 2 H, $H_{\text{ph}}(2)$, $^3J = 8.4$ Hz); 6.70 (br.s, 1 H, COOH); 7.43 (d, 2 H, $H_{\text{ph}}(3)$, $^3J = 8.4$ Hz), the proton of the NH group was not detected.

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