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Enantioselective rhodium-catalysed addition of boronic acids using C_2-symmetric aryl diphosphite ligands

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Abstract

The enantioselective rhodium-catalysed conjugate addition of aryl boronic acids to dehydroalanine derivatives has been successfully carried out in the presence of C_2-symmetric aryl diphosphite ligand (**R**,**R**,**R-4**) to prepare unnatural amino acid esters. The products have been obtained in up to 72% ee and with good isolated yield.

Keywords: C–C coupling; Amino acids; Boronic acids; Rhodium; Conjugate addition

1. Introduction

The rhodium-catalysed addition of boronic acids to organic electrophiles has emerged as important methodology for organic synthesis. An efficient transmetallation between boron and rhodium permits the addition of organoboronic acids to a range of activated alkenes [1], aldehydes [2], imines [3] and anhydrides [4]. The use of the enantiopure diphosphine ligand BINAP (**R**)-**1** enables an enantioselective addition to cyclic enones and activated acyclic *E*-alkenes [5]. Recent work by Hayashi et al. [6] has elucidated the key steps in the catalytic cycle and revealed that $[Rh(OH)(BINAP)]_2$ complexes are the most effective pre-catalysts for the enantioselective addition. The reason for the improved activity is in part due to the high oxophilicity of boron resulting in an acceleration in the rate of transmetallation. Previously, α-substituted activated alkenes had not customarily been employed as substrates owing to their low reactivity. However, Hayashi et al. [7] have reported that 1-nitrocyclohexene is a satisfactory substrate in the enantioselective addition affording products with high enantioselectivity and good diastereoselectivity controlled by protonation. In addition to this, work from our group has revealed a rhodium-catalysed conjugate addition of boronic acids to α,β-dehydroamino acid derivatives allowing rapid access to a wide range of substituted phenylalanine α-amino acids [8]. Li and coworker [9] first reported the analogous addition reaction using organotin and organobismuth reagents. The corresponding enantioselective reaction has been achieved by Reetz et al. [10] who reported one example of this type of transformation to prepare the naturally occurring amino acid phenylalanine. Importantly, Reetz noted that the BINAP-derived rhodium catalyst afforded excellent activity (100% conversion) but racemic product, whereas less-electron-rich diphosphonite ligands such as (**R**,**R**)-**2** afforded 37% ee increasing to 77% ee when 3,3′-dibromo-1,1′-binaphthyl-2,2′-diol-derived diphosphonite ligand (**R**,**R**)-**3** was used. In this case, enantioselectivity is influenced by facial selectivity and protonation. In this paper, we wish to present our studies on the enantioselective synthesis of amino acids by the addition of aryl boronic acids to dehydroalanine derivatives catalysed by a rhodium complex of an enantiopure diphosphite (**R**,**R**,**R**)-**4**. This ligand was first reported by Pringle and coworker [11] for nickel-catalysed hydrocyanations and has since been used in a variety of catalytic, enantioselective processes (Scheme 1).

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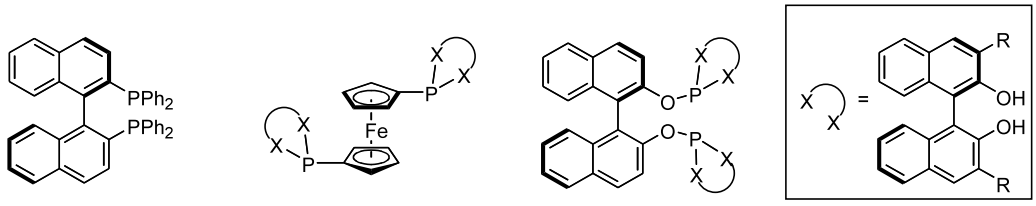


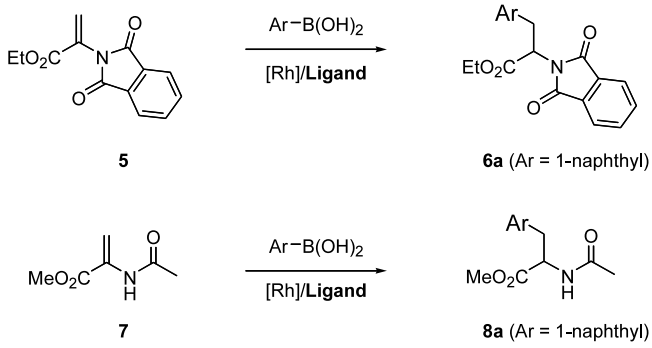
1 **2** (R = H) **4** (R = H)
3 (R = Br)

Scheme 1. Ligands for rhodium-catalysed addition of boronic acids.

2. Results and discussion

The ligands (**R**,**R**,**R**)-**4** and (**S**,**S**,**S**)-**4** were prepared in good yield by the literature methods [11]. Initial experiments examined the enantioselective addition of 1-naphthaleneboronic acid to α-phthalimidoacrylic ester (**5**) [12] and commercially available α-acetimidoacrylic ester (**7**); selected results are shown in Table 1. Disappointingly, there was no enantioselectivity using substrate **5**, although in the case of the (**R**)-**1**-derived rhodium complex (entry 1), isolated yields of product **6** were excellent. To investigate whether the observed low enantioselectivity is a direct result of product racemisation under the reaction conditions, a sample of (*S*)-L-*N*-phthalimidophenylalanine ethyl ester (**6b**) was subjected to the reaction conditions. Analysis of the recovered amino acid derivative showed no change in enantioselectivity to that of the starting substrate (Scheme 2).

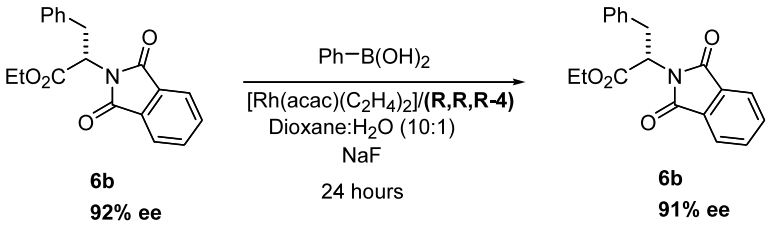
Table 1
Rhodium-catalysed synthesis of amino acid derivatives [a]



5 **6a** (Ar = 1-naphthyl)
7 **8a** (Ar = 1-naphthyl)

Entry	Enamide	Rh source	Ligand	Product	Yield (%) [b]	ee (%) [c]
1	**5**	$[Rh(OH)(COD)]_2$	(**R**)-**1**	**6a**	96	< 5
2	**5**	$[Rh(OH)(COD)]_2$	(**R**,**R**,**R**)-**4**	**6a**	6	< 5
3	**5**	$[Rh(acac)(C_2H_4)_2]$	(**R**,**R**,**R**)-**4**	**6a**	40	< 5
4	**7**	$[Rh(acac)(C_2H_4)_2]$	(**R**)-**1**	**8b**	81	< 5
5	**7**	$[Rh(acac)(C_2H_4)_2]$	(**R**,**R**,**R**)-**4**	**8a**	91	72 (*S*)
6	**7**	$[Rh(acac)(C_2H_4)_2]$	(**S**,**S**,**S**)-**4**	**8a**	86	71 (*R*)
7	**7**	$[Rh(acac)(C_2H_4)_2]$	(**R**,**R**,**R**)-**4**	**8a**	71 [d]	71 (*S*)
8	**7**	$[Rh(COE)_2Cl]_2$	(**R**,**R**,**R**)-**4**	**8a**	98	70 (*S*)
9	**7**	$[Rh(COD)Cl]_2$	(**R**,**R**,**R**)-**4**	**8a**	98	50 (*S*)
10	**7**	$[Rh(OH)(COD)]_2$	(**R**,**R**,**R**)-**4**	**8a**	67	36 (*S*)
11	**7**	$[Rh(acac)(C_2H_4)_2]$	–	**8a**	2	–
12	**7**	$[Rh(COE)_2Cl]_2$	–	**8a**	3	–
13	**7**	$[Rh(COD)Cl]_2$	–	**8a**	43	–
14	**7**	$[Rh(OH)(COD)]_2$	–	**8a**	30	–

[a] General conditions: Rh (3 mol%), ligand (3.3 mol%), enamide (0.5 mmol), boronic acid (2 mmol), NaF (1.5 mmol), dioxane (1.5 ml), H_2O (150 μl), 100 °C, 24 h.
[b] Isolated yield after flash chromatography.
[c] Determined by HPLC analysis using a chiral column (Chiralpak AD (10% 2-PrOH:hexane)).
[d] 2.5 equivalents of boronic acid used with no NaF was added.

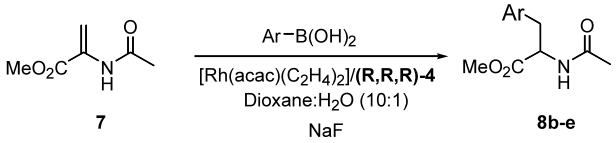


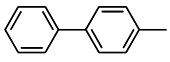
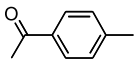
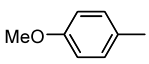
Scheme 2. Reaction conditions do not promote racemisation.

Better results in terms of enantioselectivity (up to 72% ee) were obtained when **7** was used as substrate (entries 5–9). It was noteworthy that the rhodium source had a significant influence on enantioselectivity. Pertinent to this is the reactivity of the rhodium source in the absence of ligand (entries 11–14). The highest enantioselectivities result from the use of $[Rh(acac)(C_2H_4)_2]$ and $[Rh(COE)_2Cl]_2$, both which are ineffective without added ligand. NMR experiments indicate that ligand exchange ((**R**,**R**,**R**)-**4**/$(C_2H_4)_2$) is complete within 10 min at 25 °C, whereas exchange of COD is slower. The significant catalytic activity of $[Rh(COD)Cl]_2$ and $[Rh(OH)(COD)]_2$ results in an increased proportion of racemic product thus lowering the overall enantioselectivity. The enantioselectivities obtained under optimised conditions were repeatable and as would be expected, the use of the opposite enantiomer of ligand (**S**,**S**,**S**)-**4** afforded a reversal in the sense of asymmetric induction (entry 6).

From the preceding results, the favoured pre-catalyst/ligand combination was revealed as $[Rh(acac)(C_2H_4)_2]$/(**R**,**R**,**R**)-**4**. Using the preferred conditions the scope of the process was explored with respect to the boronic acid (Table 2). In all cases, the reaction proceeded in good yield with modest but significant enantioselectivity. It was useful to note that both electron-rich and electron-deficient aryl boronic acids could be successfully employed using diphosphite ligand (**R**,**R**,**R**)-**4**. This

Table 2
Synthesis of amino acid derivatives from **7** [a]



Entry	Ar	Product	Yield [%][b]	ee [%][c]
1		**8b**	77	55 (S)
2		**8c**	79	48 (S)
3		**8d**	36	37 (S)
4		**8e**	73	56 (S)

[a]General conditions: Rh (3 mol%), ligand (3.3 mol%), enamide (0.5 mmol), boronic acid (2 mmol), NaF (1.5 mmol), dioxane (1.5 ml), H_2O (150 μl), 100 °C, 24 h.[b]Isolated yield after flash chromatography.[c]Determined by HPLC analysis using a chiral column (Chiralpak AD (10% 2-PrOH:hexane)).

is in contrast to [Rh(acac)((**R**)-**1**)] which is known to effect the hydrolysis of electron-rich arylboronic acids at 100 °C [6].

3. Conclusion

In summary, the use of enantiomerically pure diphosphite ligands has enabled the scope of the rhodium-catalysed addition of boronic acids to be extended to allow the preparation of enantioenriched amino acids. The enantioselectivity is sensitive to the choice of rhodium pre-catalyst and key structural elements of the substrate. The prospect of tuning the ligand backbone to increase the facial selectivity of the dehydroalanine derivatives is currently being explored.

4. Experimental

Reactions were performed under a dry nitrogen atmosphere. Anhydrous dioxane was purchased from Sigma Aldrich and used as purchased, water was deoxygenated by sparging with nitrogen for 30 min and all other reagents were used without further purification. Melting points were determined using a Büchi 535 melting point apparatus and are uncorrected. Infrared spectra (4000–600 cm^{-1}) were recorded on a Perkin–Elmer FT 1000 spectrometer with internal calibration. NMR spectra were recorded on a JEOL A-400 spectrometer or a Brucker DPX-300 spectrometer. Chemical shifts are reported in ppm, referenced to an internal $SiMe_4$ standard for ^{1}H- and ^{13}C-NMR. Mass spectra were recorded on a Finnigan MAT 8340 instrument at the University of Bath. Elemental analyses were performed with an Exeter analytical, Inc. CE-440 elemental analyser in the Chemistry Department at the University of Bath. High-performance liquid chromatography (HPLC) was performed on SP thermoSeparation products spectra SERIES system which uses chiral columns such as Chiralpak AD by Daicel Chemical Industry Ltd.

4.1. A typical procedure for the rhodium-catalysed 1,4 addition of boronic acids to dehydroalanine derivatives

An oven-dried Shlenk tube under nitrogen is charged with [Rh(acac)(C_2H_4)$_2$] (3.9 mg, 15 μmol), ligand (16 μmol), enamide **5** or **7** (0.5 mmol), boronic acid (2 mmol), NaF (63 mg, 1.5 mmol) and dioxane (1.5 ml). The mixture was stirred at room temperature (r.t.) for 30 min and water (150 μl) added. The mixture was then stirred under an atmosphere of nitrogen at 100 °C for 24 h. After cooling to r.t. the solution was dissolved in ethyl acetate (3 ml) and water (5 ml) added. The aqueous layer was separated and extracted with ethyl acetate (3 × 5 ml), the combined organics were washed with brine (10 ml), dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by silica gel column chromatography.

4.2. N-Phthalimido-3-(1-naphthyl)alanine ethyl ester (*6a*)

Colourless oil 96%; R_f (4:1, petrol:ethyl acetate) 0.38; m.p.: 87–90 °C; ν_{max} (Nujol) (cm^{-1}): 2924, 2852, 1773, 1744, 1711, 1597, 1462, 1386, 1276, 1251, 1199, 1103, 1028, 992, 945, 884, 798, 775, 720; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.28 (3H, t, $J = 7.2$), 3.90 (1H, dd, $J = 11.3$, 14.7), 4.17 (1H, dd, $J = 4.5$, 14.7), 4.29 (2H, qd, $J = 1.1$, 7.2), 5.31 (1H, dd, $J = 4.5$, 11.3), 7.22−7.26 (2H, m), 7.43−7.51 (2H, m), 7.65−7.69 (3H, m), 7.72−7.76 (2H, m), 7.81 (1H, d, $J = 8.7$), 8.10 (1H, d, $J = 8.7$); ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 167.7, 166.2, 132.8, 132.6, 131.7, 130.5, 130.3, 127.7, 126.6, 126.0, 125.2, 124.5, 124.0, 122.2, 121.8, 60.9, 51.6, 30.6, 12.9; HRMS (FAB^+) [MH^+]—Calc. for $C_{23}H_{20}NO_4$: *m/z*, 374.1392; Found: *m/z*, 374.1395. Anal. Calc. for $C_{23}H_{19}NO_4$: C, 73.98; H, 5.13; N, 3.75. Found: C, 73.6; H, 5.12; N, 3.75%.

4.3. N-Acetyl-3-(1-naphthyl)alanine methyl ester (*8a*)

Colourless solid 98%; R_f (petrol:ethyl acetate, 1:1) 0.20; m.p.: 90–91 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.91 (3H, s), 3.48 (1H, dd, $J = 6.6$, 14.1), 3.59 (1H, dd, $J = 6.3$, 14.1), 3.61 (3H, s), 5.01 (1H, m), 6.29 (1H, br d, $J = 7.9$), 7.22 (1H, app. d, $J = 6.8$), 7.36 (1H, app. d, $J = 8.3$), 7.45−7.56 (2H, m), 7.74 (1H, d, $J = 8.3$), 7.83 (1H, d, $J = 7.9$), 8.07 (1H, d, $J = 8.3$); ^{13}C-NMR (100.5 MHz, $CDCl_3$): δ 172.5, 170.0, 134.0, 132.6, 132.4, 129.0, 128.1, 127.5, 126.5, 126.0, 125.4, 123.7, 53.6, 52.6, 35.4, 23.4; ν_{max} (film) (cm^{-1}): 3430, 3310, 3017, 2954, 1741, 1669, 1512, 1437, 1374, 1215, 1130, 1022, 758, 668; HRMS (FAB^+) [MH^+]—Calc. for $C_{16}H_{18}NO_3$: *m/z*, 272.1287; Found: *m/z*, 272.1275 (100%). Calc. for $C_{15}^{13}CH_{18}NO_3$: *m/z*, 273.1320; Found: *m/z*, 273.1324 (18.1%). Anal. Calc. for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 71.2; H, 6.34; N, 5.04%.

4.4. N-Acetylphenylalanine methyl ester (*8b*)

Colourless oil 77%; R_f (petrol:ethyl acetate, 1:1) 0.22; m.p.: 66–68 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.98 (3H, s), 3.09 (1H, dd, $J = 5.7$, 13.8), 3.16 (1H, dd, $J = 6.0$, 13.8), 3.72 (3H, s), 4.88 (1H, m), 5.95 (1H, br d, $J = 6.4$), 7.07−7.10 (2H, m), 7.21−7.32 (3H, m); ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ 172.5, 170.0, 136.2, 129.6, 129.0, 127.5, 53.5, 52.7, 38.2, 23.5; ν_{max} (film) (cm^{-1}): 3287, 3064, 3029, 2953, 2848, 1743, 1657, 1544, 1437, 1374, 1274, 1218, 1178, 1129, 1080, 1031, 1012, 985, 756, 701; FABMS: *m/z*, 222.1 (100%, MH^+). Anal. Calc. for

$C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.0; H, 6.93; N, 6.15%.

4.5. *N*-Acetyl-3-(4-biphenyl)alanine methyl ester (**8c**)

Pale solid 79%; R_f (petrol:ethyl acetate, 1:1) 0.18; m.p.: 152–154 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.98 (3H, s), 3.11 (1H, dd, $J = 6.0, 13.9$), 3.19 (1H, dd, $J = 5.7, 13.9$), 3.72 (3H, s), 4.91 (1H, m), 6.25 (1H, br d, $J = 7.5$), 7.16 (2H, d, $J = 8.1$), 7.32 (1H, t, $J = 7.5$), 7.42 (2H, app. t, $J = 7.5$), 7.51 (2H, d, $J = 8.1$), 7.56 (2H, d, $J = 7.5$); ^{13}C-NMR (100.5 MHz, $CDCl_3$): δ 172.2, 169.9, 140.7, 140.1, 135.1, 129.8, 129.0, 127.5, 127.4, 127.1, 53.5, 52.7, 37.8, 23.5; υ_{max} (film) (cm^{-1}): 3348, 3029, 2954, 2358, 1752, 1653, 1533, 1488, 1437, 1375, 1217, 1172, 1129, 1007, 830, 761, 728, 695, 668; FABMS: *m*/*z*, 298.1 (100%, MH^+). Anal. Calc. for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.6; H, 6.39; N, 4.66%.

4.6. *N*-Acetyl-3-(4-acetylphenyl)alanine methyl ester (**8d**)

Colourless solid 36%; R_f (petrol:ethyl acetate, 1:2) 0.17; m.p.: softens at 125 °C and melts at 144–146 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.96 (3H, s), 2.55 (3H, s), 3.09 (1H, dd, $J = 6.0, 14.1$), 3.20 (1H, dd, $J = 6.0, 14.1$), 3.70 (3H, s), 4.88 (1H, dt, $J = 6.0, 7.8$), 6.18 (1H, br d, $J = 7.5$), 7.18 (2H, d, $J = 8.3$), 7.85 (2H, d, $J = 8.3$); ^{13}C-NMR (100.5 MHz, $CDCl_3$): δ 197.8, 171.9, 169.8, 141.8, 136.1, 129.7, 128.8, 53.3, 52.9, 38.3, 27.0, 23.5; υ_{max} (film) (cm^{-1}): 3286, 3076, 3016, 2959, 1746, 1678, 1608, 1549, 1216, 1183, 1126, 1017, 959, 832, 755, 666; FABMS: *m*/*z*, 264.1 (100%, MH^+). Anal. Calc. for $C_{14}H_{17}NO_4$: C, 63.87; H, 6.51; N, 5.32. Found: C, 63.5; H, 6.48; N, 5.08%.

4.7. *N*-Acetyl-3-(4-methoxyphenyl)alanine methyl ester (**8e**)

Colourless solid 73%; R_f (petrol:ethyl acetate, 1:1) 0.18; m.p.: 94 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.97 (3H, s), 3.00 (1H, dd, $J = 5.8, 13.8$), 3.07 (1H, dd, $J = 5.9, 13.8$), 3.71 (3H, s), 3.77 (3H, s), 4.82 (1H, m), 6.26 (1H, br d, $J = 7.8$), 6.82 (2H, d, $J = 8.7$), 7.01 (2H, d, $J = 8.7$); ^{13}C-NMR (100.5 MHz, $CDCl_3$): δ 172.3, 169.8, 158.7, 130.3, 127.9, 114.1, 55.5, 53.6, 52.6, 37.3, 23.5; υ_{max} (film) (cm^{-1}) 3431, 3019, 2955, 1743, 1675, 1612, 1513, 1438, 1374, 1250, 1216, 1178, 1128, 1035, 754, 669; FABMS: *m*/*z*, 252.1 (100%, MH^+). Anal. Calc. for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.2; H, 6.76; N, 5.37%.

4.8. Chiral HPLC

The enantiomeric excess was determined by HPLC using either Daicel Chiralcel OD or Chiralpak AD Columns (4.6×250 mm^2) at ambient temperature. The separation of mixtures under HPLC conditions is as follows: *N*-phthalimido-3-(1-naphthyl)alanine ethyl ester (**6a**) (AD, 1.0 ml min^{-1}, 10% 2-PrOH:hexane): (*S*) $t_1 = 13.7$ min, (*R*) $t_2 = 15.4$ min; *N*-acetyl-3-(1-naphthyl)alanine methyl ester (**8a**) (AD, 1.0 ml min^{-1}, 10% 2-PrOH:hexane): (*R*) $t_1 = 11.2$ min, (*S*) $t_2 = 14.1$ min; *N*-acetylphenylalanine methyl ester (**8b**) (AD, 1.0 ml min^{-1}, 10% 2-PrOH:hexane): (*R*) $t_1 = 10.2$ min, (*S*) $t_2 = 12.9$ min; *N*-acetyl-3-(4-biphenyl)alanine methyl ester (**8c**) (AD, 1.0 ml min^{-1}, 10% 2-PrOH:hexane): (*R*) $t_1 = 13.5$ min, (*S*) $t_2 = 21.5$ min; *N*-acetyl-3-(4-acetylphenyl)alanine methyl ester (**8d**) (AD, 1.0 ml min^{-1}, 10% 2-PrOH:hexane): (*R*) $t_1 = 32.2$ min, (*S*) $t_2 = 41.1$ min; *N*-acetyl-3-(4-methoxyphenyl)alanine methyl ester (**8e**) (OD, 1.0 ml min^{-1}, 10% 2-PrOH:hexane): (*R*) $t_1 = 13.9$ min, (*S*) $t_2 = 17.8$ min.

Configurations were established for *N*-acetyl-3-(1-naphthyl)alanine methyl ester (**8a**) and *N*-acetylphenylalanine methyl ester (**8b**) by chiral HPLC (Chiralcel OJ) and comparison to the literature values [13]. Other analogous products, which eluted in the same order by chiral HPLC (Chiralpak AD), were assigned the same absolute configuration. For example, (**R**,**R**,**R**)-**4** produced *N*-acetylphenylalanine and substituted *N*-acylphenylalanine derivatives which were eluted second by chiral HPLC (Chiralpak AD). All such products were assigned *S* absolute configuration. Configuration of *N*-phthalimido-3-(1-naphthyl)alanine ethyl ester was assigned by comparison of the HPLC (Chiralpak AD) elution times with those for a sample of *N*-phthalimidophenylalanine ethyl ester produced from L-phenylalanine ethyl ester [14].

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