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Enantioselective recognition of 1,2-aminoalcohols by the binol receptor dangled with pyrrole-2-carboxamide and its analogues

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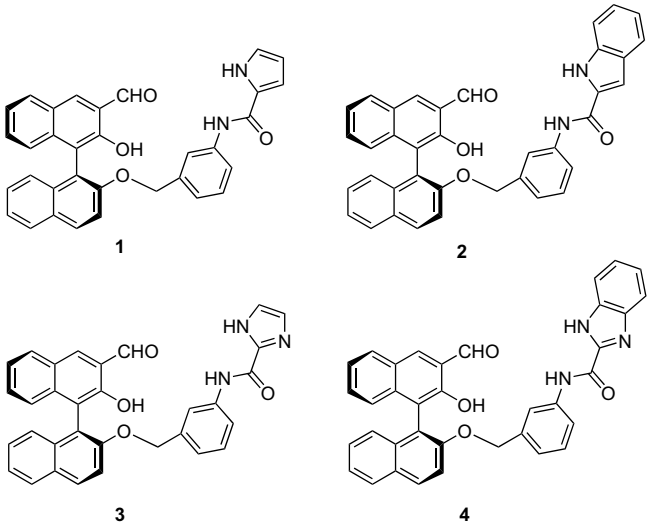
ABSTRACT

Novel binol receptor with pyrrole-2-carboxamide moiety and its analogues have been designed, synthesized, and used to enantioselectively recognize 1,2-aminoalcohols via multiple hydrogen bonding. The pyrrole-based binol receptor showed the highest enantioselectivity among the four receptors as determined by the ^{1}H NMR. The DFT calculation strongly supports complementary hydrogen bonding between alcoholic –OH and pyrrolyl groups.

1. Introduction

Over the years, there has been considerable interest in making stereoselective receptors for amines,[1] amino acids,[2] and aminoalcohols,[3] which are important materials in chirotechnology.[4] Although much progress has been made, it remains a challenge to develop highly stereoselective receptors for these substrates based on simple organic molecules. Recently, we reported organic binol based receptors that stereoselectively bind 1,2-aminoalcohols [5,6] and amino acids[7] via reversible imine formation[8] with multiple hydrogen bonding. These receptors are attractive because they convert L-amino acids to D-amino acids,[7] exhibit high stereoselectivity, and are effective extractants for the resolution of racemic 1,2-aminoalcohols.[6] The origin of the selectivity is well understood by molecular calculations on the imines. Based on our previous experience, the hydrogen bonding between the uryl[5] or guanidinium group[6] of the receptor and the –OH group of an aminoalcohol plays an important role in the stereoselectivity of the imines.

In this context, we have devoted efforts to synthesize binol receptors with other moieties that efficiently bind alcoholic –OH group by hydrogen bonding in pursuit of improving the efficiency of the stereoselective recognition. Pyrrole-2-carboxamide moiety has been studied for the recognition of anions such as F^-, OAc^-, and $H_2PO_4^-$.[9] Hence, we designed pyrrole-2-carboxamide dangled binol compound **1** and its analogues **2**–**4** (Scheme 1). Herein, we report the detailed synthetic procedures of those receptors, their stereoselectivities toward aminoalcohols, and also an insight into the hydrogen bonding mode between alcoholic –OH and pyrrole-2-carboxamide moiety based on the density functional theory (DFT) calculations.



Scheme 1. Binol compounds dangled with pyrrole-2-carboxamide and its analogues.

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2. Results and discussion

2.1. Synthesis of receptors 1–4

The synthesis of receptors **1**–**4** is described in Scheme 2. Using benzotriazol-1-yl-tripyrrolidinophosphonium hexafluorophosphate (PyBOP) as a coupling reagent, appropriate carboxylic acids were coupled to the amino group of (*S*)-3-hydroxymethyl-2-methoxymethoxy-2′-(3-aminobenzyloxy)-1,1′-binaphthol (**5**)[6] in dimethylformamide (DMF) and *N*-methyl morpholine (NMP) to obtain the corresponding amides in good yields. These amides were further treated with pyridinium chlorochromate (PCC) in methylene chloride, where the oxidation of hydroxymethyl produces the aldehyde, and the deprotection of methoxymethoxy (MOM) group under acidic conditions gave the final products. The optical purity of the final receptors **1**–**4** is considered to be the same with the starting material **5** in the above reaction conditions. The synthesized compounds were confirmed by spectroscopic and analytical data, which are in good agreement with the presented structures. All the receptors are freely soluble in solvents such as DMSO, $CHCl_3$, benzene, etc.

2.2. Enantioselective recognition of receptors for chiral aminoalcohols

Aldehyde **1** forms imines, **1**-*S*-*aal* and **1**-*R*-*aal*, with both enantiomers of chiral 1,2-aminoalcohols (*aal*). As they are in diastereomeric relations, the corresponding imine formation constants K_R and K_S are ideally not the same. Stereoselectivity (K_R/K_S) in the imine formation can be conveniently assessed by ^{1}H NMR spectrum of the solution containing **1** and 2 equiv racemic aminoalcohols, where **1** completely reacts with 1 equiv aminoalcohol, and K_R/K_S=([**1**-*R*-*aal*]/[**1**-*S*-*aal*])^2.[6]

Figure 1 shows the stereoselective imine formation of the receptor **1** for 2-aminopropanol (*ap*) as a representative. Figure 1a indicates the ^{1}H NMR spectrum for **1** in $CDCl_3$, where the peaks at 10.52 and 10.18 ppm are due to –OH and –CHO, respectively. The broad singlet at 9.45 ppm is assigned to pyrrole NH, and the singlet at 5.13 ppm to benzylic –CH_2–. The addition of (*S*)-*ap* to the $CDCl_3$ solution of **1** results in complete formation of the imine, **1**-*S*-*ap*, within minutes. This can be clearly noted by the appearance of the imine proton peak at 8.65 ppm and the disappearance of the aldehyde peak (Fig. 1b).

Similarly, but in different position, the imine proton peak of **1**-*R*-*ap* appears at 8.54 ppm on addition of (*R*)-*ap* (Fig. 1c). A noticeable discrimination between **1**-*S*-*ap* and **1**-*R*-*ap* is observed on diastereotopic benzylic –CH_2– signals; singlet for **1**-*S*-*ap* at 5.10 ppm and prominent doublet of doublet splitting pattern for **1**-*R*-*ap* centered at 5.05 ppm. This implies that **1**-*R*-*ap* is more rigid than **1**-*S*-*ap*, i.e., stronger hydrogen bonding interaction is assumed for **1**-*R*-*ap* between alcoholic –OH and pyrrole-2-amide moiety. The peak of pyrrole –NH– of **1**-*R*-*ap* experiences much more downfield shift than that of **1**-*S*-*ap*, which also supports the stronger hydrogen bonding of **1**-*R*-*ap*.

Figure 1d shows the ^{1}H NMR spectrum for a mixture of **1**-*R*-*ap* and **1**-*S*-*ap* formed by the addition of 2 equiv of racemic *ap* to the $CDCl_3$ solution of **1**. The ratio of **1**-*R*-*ap* and **1**-*S*-*ap* is conveniently obtained from the signals of the sharp singlet imine peaks. Integration of the two peaks provides the ratio of **1**-*R*-*ap*/**1**-*S*-*ap* as 2.33:1 at equilibrium. The same ratio has been obtained when either (*R*)-*ap* was added to **1**-*S*-*ap* or (*S*)-*ap* was added to **1**-*R*-*ap*. These indicate that the imine formation is a reversible thermodynamic process, and the imine formation constant for **1**-*R*-*ap* (K_R) is larger than that for **1**-*S*-*ap* (K_S) by a factor of 5.43 (2.33^2). We have compared the stereoselectivities (K_R/K_S) for the imine formation between receptors **1**–**4** and six representative aminoalcohols, 2-aminopropanol (*ap*), 2-amino-1-butanol (*ab*), 2-amino-3-methyl-1-butanol (*amb*), 2-amino-3-phenyl-1-propanol (*app*), 2-amino-2-phenylethanol (*ape*), and 2-amino-4-methyl-1-pentanol (*ampt*) following the above mentioned protocol. The results are tabulated in Table 1.

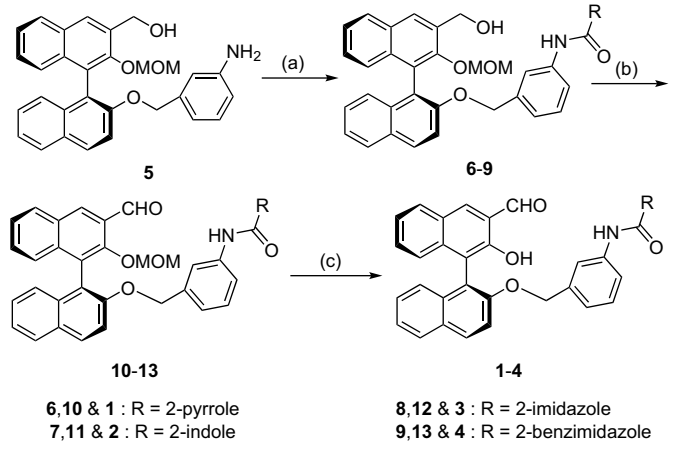
According to Table 1, the enantioselectivities of the pyrrole-based receptor **1** is higher than those of the others, and also apparently higher than those[5] of the previously reported uryl-based mother receptor. The imidazole based receptor **3** shows the selectivities comparable to those[5] of the uryl-based receptor. Additional phenyl rings in **2** and **4** produce unfavorable effect on the selectivities. The stereoselectivities for methylbenzylamine (*mba*) is negligible, which means that the hydrogen bonds perform an important role in stereoselective recognition of aminoalcohols and hence these receptors are tailored for aminoalcohols.

2.3. The DFT calculation for the enantioselective recognition of receptor 1

In order to further elucidate the origin of the structural preference of (*R*)-*ap* bound imine over (*S*)-*ap* bound imine, the density function theory (DFT) calculations were performed for the geometry optimization and vibrational analysis at the B3LYP/6-31G* level[10] followed by the single point energy calculation at the MPWB1K/6-31+G*//B3LYP/6-31G* level of theory[11] by using Gaussian 03 package.[12]

For each imine structure, two different patterns of hydrogen bonding are available: (i) both pyrrole NH and amide O participate to hold alcoholic OH group by hydrogen bonds (N–O mode, Scheme 3a) and (ii) both pyrrole NH and amide NH contribute to keep alcoholic oxygen closer by hydrogen bonds (N–N mode, Scheme 3b). The calculations were done for the four receptors bound by *ap* for both N–N and N–O modes, and the results are listed in Table 2.

Notably, the conformations with N–O mode are found to be more stable than those with N–N mode by 8.9 for **1**-*R*-*ap* and 9.4 kcal/mol for **1**-*S*-*ap*. In **1**-*R*-*ap* of N–O mode conformation, the hydrogen bond distance between alcoholic –OH and amide carbonyl oxygen is 1.86 Å, and that between alcoholic oxygen and pyrrole NH is 1.85 Å. Also, shorter hydrogen bond distance of 1.77 Å is detected between phenol –OH and imine nitrogen, which is especially called resonance assisted hydrogen bond (RAHB).[13] On the other hand, in **1**-*R*-*ap* of N–N mode conformation, the hydrogen bond distance between alcoholic –OH and amide NH is 2.23 Å, that between alcoholic –OH and pyrrole NH is 1.96 Å, and that of RAHB is 1.76 Å. Tighter hydrogen bonding and dipole contribute to the



Scheme 2. Reagents and conditions: (a) PyBOP, DMF, NMP, R-COOH, rt, 15 h; (b) PCC, CH_2Cl_2, rt, 5 h; (c) HCl, EtOH, reflux, 0.5 h.

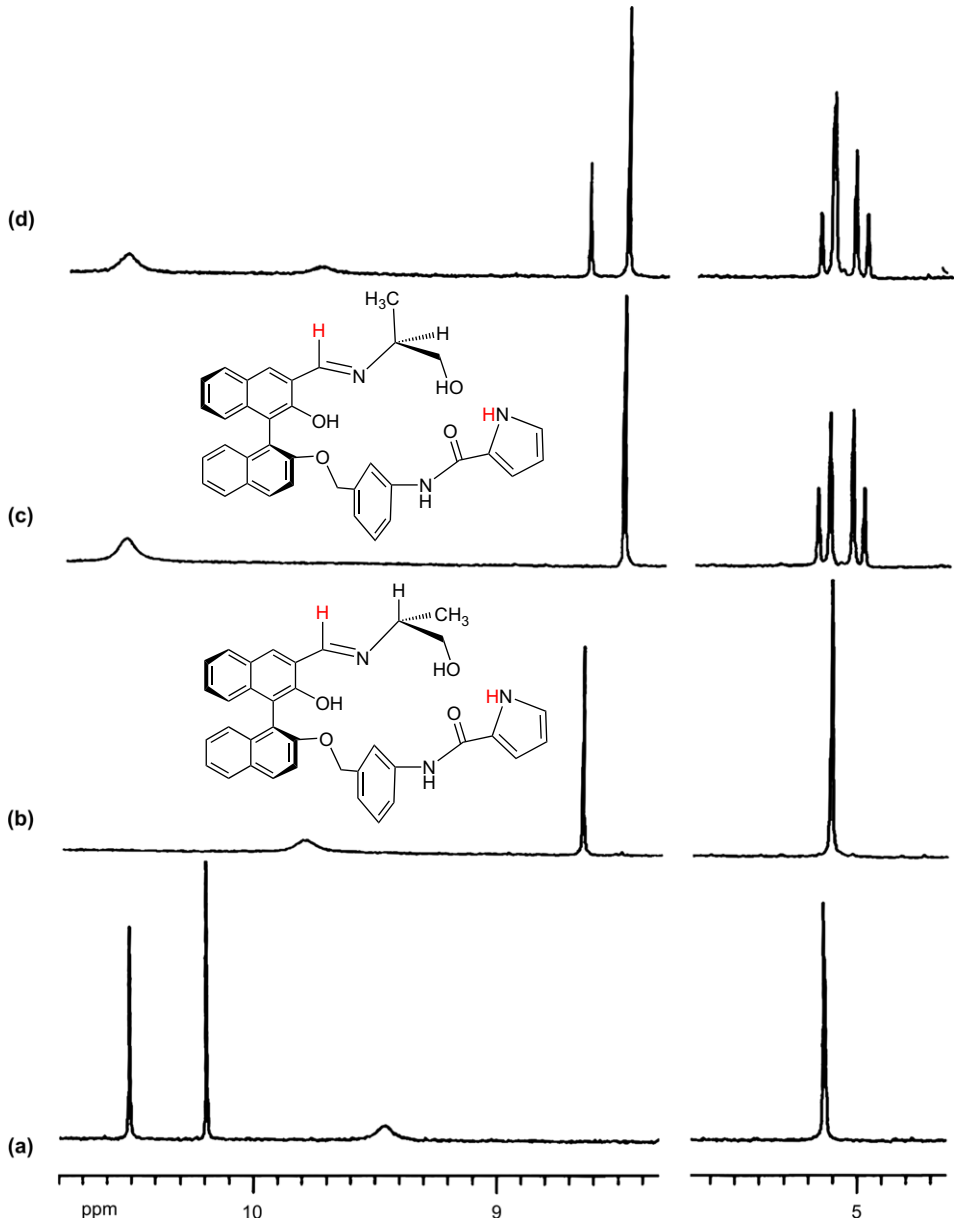


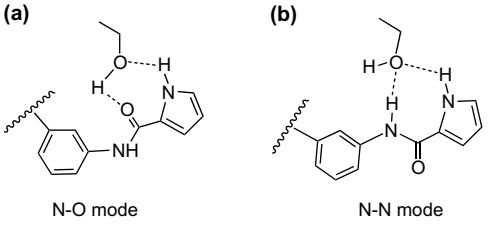
Figure 1. Partial ^{1}H NMR spectra in $CDCl_3$ of (a) **1**, (b) **1**-*S*-*ap*, (c) **1**-*R*-*ap*, and (d) mixture of **1**-*S*-*ap* and **1**-*R*-*ap* formed by the addition of 2 equiv of racemic *ap* to **1**.

thermodynamic stability of N–O mode over N–N mode conformations. Overall, complementary N–O hydrogen bonding mode between alcoholic –OH and pyrrole-2-carboxamide moiety appears to be more probable. Similar calculations on receptors **2**–**4** showed same trends.

Table 1
Stereoselective imine formation (K_R/K_S) between the receptors and aminoalcohols as determined by ^{1}H NMR in $CDCl_3$

Aminoalcohols	Receptors			
	1	**2**	**3**	**4**
mba	1.00	1.00	1.00	1.00
ap	5.42	2.56	4.41	3.31
ab	5.91	2.96	3.61	3.46
amb	7.68	2.86	4.28	4.20
app	8.51	2.75	3.03	2.28
ape	6.76	2.96	3.84	2.34
ampt	6.43	2.62	3.61	2.72

The thermodynamic preference for **1**-*R*-*ap* over **1**-*S*-*ap* is computed to be 2.2 kcal/mol at the MPWB1K/6-31+G*//B3LYP/6-31G* level (Table 2). It is in qualitative agreement with the experimentally observed selectivity. The energy-minimized conformations for **1**-*R*-*ap* and **1**-*S*-*ap* predicted by the DFT calculation are shown in Figure 2, where hydrogen bonding interactions are noted by dashed lines. The different dipoles and steric hindrances found in both



Scheme 3. Possible hydrogen bonding modes between aminoalcohol –OH and pyrrole-2-carboxamide groups.

Table 2
Computed relative energies (kcal/mol) and dipole moments (Debye) for N–O and N–N modes

	Rel energy[a]		Dipole[b]	
	N–O	N–N	N–O	N–N
1-*R*-*ap*	0.0	8.9	4.5	8.1
1-*S*-*ap*	2.2	11.6	4.6	8.2
2-*R*-*ap*	0.0	7.8	4.1	7.4
2-*S*-*ap*	2.1	10.6	4.1	7.1
3-*R*-*ap*	0.0	14.4	3.4	9.4
3-*S*-*ap*	2.4	20.9	3.7	9.4
4-*R*-*ap*	0.0	13.3	2.9	8.9
4-*S*-*ap*	2.1	19.5	3.1	8.2

[a] Computed at the MPWB1K/6-31+G*//B3LYP/6-31G* level.
[b] Computed at the B3LYP/6-31G* level.

structures would be the main contribution to the observed enantioselectivity.

The stereoselectivity, K_R/K_S, will be maximized in the condition that the whole imine complex is rigid by multiple hydrogen bondings. The lower stereoselectivities of **2** and **4** compared to **1** and **3** may be presumably due to the lower hydrogen bond donor capability and steric hindrance of the additional benzene moiety.[14]

3. Conclusion

In conclusion, four novel chiral binol receptors dangled with pyrrole-2-carboxamide analogues have been synthesized and studied on the enantioselecitve imine formation of aminoalcohols. Pyrrole-based receptor **1** showed the highest enantioselectivity toward the chiral aminoalcohols compared to the other three receptors. DFT calculation strongly supports complementary hydrogen bonding between alcoholic –OH and both pyrrole –NH– and amide=O. Large downfield chemical shift of the pyrrole –NH– peak upon imine formation with *R*-aminoalcohol supports the strong hydrogen bonding. This work demonstrates that pyrrole-2-carboxamide unit is an efficient motif for binding of alcoholic –OH groups that may be available in developing receptors for molecular recognitions.

4. Experimental

4.1. General

Imidazole-2-carboxylic acid and benzimidazole carboxylic acid were prepared according to the literature procedures.[15,16] All other chemicals were commercially available and used without further purifications. The solvents for dry reactions were dried with appropriate desiccants and distilled prior to use. NMR spectra were recorded on a BrukerAM 250 spectrometer in $CDCl_3$ solution containing tetramethylsilane as internal standard. Melting points were measured with Electrothermal IA 9000 digital melting point apparatus and are uncorrected. HRMS spectra were obtained on FAB mode. EA was determined using vario EL Elemental Analyser. For column chromatography, silica gel of 230–400 mesh was used.

4.2. (*S*)-3-Hydroxymethyl-2-methoxymethoxy-2′-(3-(1*H*-pyrrole-2-carboxamido)-benzyl)-1,1′-binaphthalene (6)

A mixture of the 2-pyrrole carboxylic acid (0.49 g, 4.4 mmol), PyBOP (2.3 g, 4.4 mmol), and *N*-methyl morpholine (NMP, 2 ml) in DMF (40 ml) was stirred at room temperature for 15 min. Amine **5** (2.0 g, 3.7 mmol) was added and the mixture was stirred over night. The mixture was hydrolyzed with water, extracted with ethyl acetate, and silica gel column chromatography (EA/Hexane, 1:1) afforded **6**. Isolated yield: 81% (mp 105 °C). ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm)=9.77 (br s, 1H), 8.20 (s, 1H), 8.04–7.84 (m, 5H), 7.52–7.00 (m, 7H), 6.74–6.38 (m, 5H), 6.12 (s, 1H), 5.00–4.90 (m, 3H), 4.66–4.51 (m, 4H), 3.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ (ppm)=162.7, 158.2, 157.2, 148.6, 141.4, 136.1, 132.5, 128.9, 128.3, 128.1, 127.6, 127.4, 125.7, 124.1, 123.3, 122.8, 122.3, 119.4, 119.3, 111.7, 95.7, 71.2, 64.9, 55.6. Anal. Calcd for $C_{35}H_{30}N_2O_5$: C, 75.25; H, 5.41; N, 5.01. Found: C, 75.34; H, 5.53; N, 4.92.

4.3. (*S*)-3-Hydroxymethyl-2-methoxymethoxy-2′-(3-(1*H*-indole-2-carboxamido)-benzyl)-1,1′-binaphthalene (7)

It was prepared similar to **6**, but with indole-2-carboxylic acid. Isolated yield: 86% (mp 158 °C). ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm)=10.55 (s, 1H), 9.04 (s, 1H), 7.95–7.77 (m, 8H), 7.47–7.07 (m, 11H), 6.80 (d, 1H), 5.18–5.04 (dd, 2H), 4.96 (d, 2H), 4.60 (q, 2H), 4.35 (br s, 1H), 3.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ (ppm)=160.5, 157.9, 156.7, 144.3, 141.5, 138.5, 136.1, 134.7, 131.2, 129.9, 129.8, 129.2, 128.7, 128.3, 128.0, 127.4, 126.0, 125.7, 124.1, 123.9, 122.8, 122.2, 120.1, 119.0, 115.6, 111.1, 97.6, 70.5, 65.5, 54.6; Anal. Calcd for $C_{39}H_{32}N_2O_5$: C, 76.96; H, 5.30; N, 4.60. Found: C, 76.85; H, 5.21; N, 4.71.

4.4. (*S*)-3-Hydroxymethyl-2-methoxymethoxy-2′-(3-(1*H*-imidazole-2-carboxamido)-benzyl)-1,1′-binaphthalene (8)

It was prepared similar to **6**, but with imidazole-2-carboxylic acid. Isolated yield: 76% (mp 70 °C). ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm)=12.55 (br s, 1H), 9.34 (s, 1H), 8.38 (s, 1H), 8.07–7.85 (m, 5H), 7.47–7.15 (m, 9H), 7.09 (s, 1H), 6.97 (d, 1H), 5.55 (br s, 1H), 5.23–4.90 (m, 4H), 4.62 (s, 2H), 2.99 (s, 3H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ (ppm)=163.0, 156.6, 154.0, 152.8, 141.8, 138.4, 137.4, 134.0, 134.1, 133.7, 131.9, 130.3, 129.3, 129.0, 128.6, 128.1, 126.9, 126.3, 125.7, 125.5, 125.1, 120.3, 118.7, 115.3, 99.3, 70.4, 61.5, 56.8.

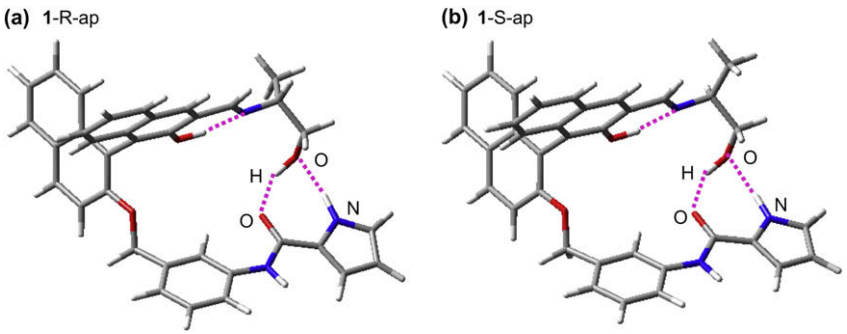


Figure 2. The energy-minimized geometries for **1**-*R*-*ap* and **1**-*S*-*ap* (N–O modes) at the B3LYP/6-31G* level. The pink dotted lines represent hydrogen bonding.

Anal. Calcd for $C_{34}H_{29}N_3O_5$: C, 72.97; H, 5.22; N, 7.51. Found: C, 72.81; H, 5.36; N, 7.43.

4.5. (*S*)-3-Hydroxymethyl-2-methoxymethoxy-2′-(3-(1*H*-benzo[*d*]imidazole-2-carboxamido)-benzyl)-1,1′-binaphthalene (9)

It was prepared similar to **6**, but with benzimidazole-2-carboxylic acid. Isolated yield: 81% (mp 246 °C). ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm)=12.01 (br s, 1H), 9.15 (s, 1H), 8.52 (s, 1H), 8.12–7.80 (m, 4H), 7.58–7.11 (m, 13H), 6.73 (d, 1H), 5.10–4.87 (m, 3H), 4.72–4.55 (m, 4H), 3.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ (ppm)=161.3, 158.3, 149.8, 145.5, 141.7, 138.9, 138.5, 136.1, 132.1, 129.8, 129.5, 129.0, 128.5, 128.0, 127.9, 120.4, 126.8, 125.7, 124.1, 123.6, 123.3, 120.5, 120.1, 119.5, 115.6, 115.3, 98.6, 74.8, 66.0, 58.4. Anal. Calcd for $C_{38}H_{31}N_3O_5$: C, 74.86; H, 5.13; N, 6.89. Found: C, 74.97; H, 5.01; N, 6.78.

4.6. (*S*)-2-Methoxymethoxy-2′-(3-(1*H*-pyrrole-2-carboxamido)-benzyl)-1,1′-binaphthyl-3-carboxaldehyde (10)

A mixture of **6** (2.0 g, 3.6 mmol) and pyridinium chlorochromate (PCC) (1.5 g, 7.2 mmol) was dissolved in methylene chloride and stirred for 5 h. The reaction mixture was filtered, and after evaporation and column chromatography with EA and hexane 1:2 mixture provided compound **10**. Isolated yield: 79% (mp 185 °C). ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm)=10.54 (s, 1H) 10.17 (br s, 1H), 8.46 (s, 1H), 8.89–7.74 (m, 4H), 7.37–7.01 (m, 10H), 6.83–6.72 (m, 3H), 6.18 (s, 1H), 5.01 (s, 2H), 4.68 (q, 2H), 2.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ (ppm)=194.1, 159.6, 158.5, 142.4, 137.4, 135.7, 134.5, 132.7, 132.3, 129.9, 129.4, 128.7, 128.1, 127.8, 127.1, 126.8, 125.7, 125.0, 124.6, 120.3, 120.1, 114.5, 112.6, 97.3, 73.5, 56.1. Anal. Calcd for $C_{35}H_{28}N_2O_5$: C, 75.52; H, 5.07; N, 5.03. Found: C, 75.43; H, 5.15; N, 5.12.

4.7. (*S*)-2-Methoxymethoxy-2′-(3-(1*H*-indole-2-carboxamido)-benzyl)-1,1′-binaphthyl-3-carboxaldehyde (11)

Same procedures as that of **10**. Isolated yield: 82% (mp 201 °C). ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm)=10.59 (s, 1H), 10.33 (br s, 1H), 8.53 (s, 1H), 8.11–7.63 (m, 6H), 7.47–7.10 (m, 13H), 6.87 (d, 1H), 5.14 (q, 2H), 4.77 (q, 2H), 2.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ (ppm)=192.5, 159.7, 158.5, 152.8, 145.2, 144.1, 139.5, 138.6, 135.9, 134.6, 134.1, 132.5, 131.2, 129.8, 128.9, 128.6, 126.5, 125.0, 124.5, 122.2, 121.6, 120.5, 120.1, 119.6, 119.2, 114.4, 108.0, 96.3, 71.2, 55.3. Anal. Calcd for $C_{39}H_{30}N_2O_5$: C, 77.21; H, 4.98; N, 4.62. Found: C, 77.14; H, 5.08; N, 4.69.

4.8. (*S*)-2-Methoxymethoxy-2′-(3-(1*H*-imidazole-2-carboxamido)-benzyl)-1,1′-binaphthyl-3-carboxaldehyde (12)

Same procedures as that of **10**. Isolated yield: 74% (mp 185 °C). ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm)=10.60 (s, 1H), 10.45 (br s, 1H), 8.79 (s, 1H), 8.01–7.84 (m, 4H), 7.35–7.16 (m, 9H), 6.73–6.58 (m, 3H), 6.35 (s, 1H), 5.13 (s, 2H), 4.75 (q, 2H), 3.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ (ppm)=195.4, 160.7, 159.4, 142.8, 139.9, 136.7, 135.1, 132.8, 132.2, 129.8, 129.1, 128.6, 128.2, 127.9, 127.3, 126.4, 125.2, 125.3, 124.9, 121.4, 120.5, 115.7, 112.9, 97.7, 74.1, 57.2. Anal. Calcd for $C_{34}H_{27}N_3O_5$: C, 73.24; H, 4.88; N, 7.54. Found: C, 73.31; H, 5.01; N, 7.44.

4.9. (*S*)-2-Methoxymethoxy-2′-(3-(1*H*-benzo[*d*]imidazole-2-carboxamido)-benzyl)-1,1′-binaphthyl-3-carboxaldehyde (13)

Same procedures as that of **10**. Isolated yield: 82% (mp 168 °C); ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm)=12.14 (br s, 1H), 10.60 (s, 1H), 9.4 (s, 1H), 8.61 (s, 1H), 8.01–7.90 (m, 4H), 7.65–7.19 (m, 13H), 6.91 (d, 1H), 5.16 (q, 2H), 4.76 (q, 2H), 2.96 (s, 3H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ (ppm)=194.3, 160.8, 159.0, 158.1, 152.8, 145.6, 144.0, 138.7, 136.9, 135.7, 133.5, 131.9, 130.0, 129.9, 129.6, 128.8, 128.4, 127.6, 126.8, 124.3, 123.6, 123.1, 122.5, 121.1, 120.6, 118.9, 116.1, 115.9, 97.5, 73.5, 57.6. Anal. Calcd for $C_{38}H_{29}N_3O_5$: C, 75.11; H, 4.81; N, 6.92. Found: C, 75.01; H, 4.73; N, 7.02.

4.10. (*S*)-2-Hydroxy-2′-(3-(1*H*-pyrrole-2-carboxamido)-benzyl)-1,1′-binaphthyl-3-carboxaldehyde (1)

To an ethanolic solution of **10** a few drops of concd hydrochloric acid was added and refluxed for 30 min. The solvent was evaporated and extracted with ethyl acetate to afford the desired receptor **1**. Isolated yield: 98% (mp 240 °C). ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm)=10.50 (s, 1H), 10.18 (s, 1H), 9.45 (br s, 1H), 8.30 (s, 1H), 7.99–7.87 (m, 3H), 7.48–7.16 (m, 10H), 7.00–6.71 (m, 4H), 6.35 (s, 1H), 5.12 (s, 2H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ (ppm)=196.9, 158.8, 154.0, 153.4, 138.3, 137.9, 130.3, 130.1, 129.7, 128.9, 128.2, 127.5, 126.7, 125.5, 124.8, 124.2, 124.0, 122.5, 122.4, 122.1, 119.2, 115.6, 110.1, 109.5, 70.8; HRMS (FAB) calcd for $C_{33}H_{24}N_2O_4$: 512.1736, found: 512.1731.

4.11. (*S*)-2-Hydroxy-2′-(3-(1*H*-indole-2-carboxamido)-benzyl)-1,1′-binaphthyl-3-carboxaldehyde (2)

It was prepared similar to receptor **1**. Isolated yield: 98% (mp 130 °C). ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm)=10.55 (s, 1H), 10.10 (s, 1H), 9.83 (s, 1H), 8.18 (1H, s), 7.94–7.73 (m, 4H), 7.46–7.15 (m, 15H), 6.98 (d, 1H), 5.09 (s, 2H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ (ppm)=196.9, 159.7, 154.0, 153.4, 138.3, 137.9, 136.9, 130.5, 130.3, 130.1, 129.7, 129.5, 128.9, 128.2, 127.5, 126.7, 125.4, 124.9, 124.8, 124.2, 122.0, 120.8, 115.4, 112.2, 103.1, 70.7; HRMS (FAB) calcd for $C_{37}H_{26}N_2O_4$: 562.1893, found: 562.1899.

4.12. (*S*)-2-Hydroxy-2′-(3-(1*H*-imidazole-2-carboxamido)-benzyl)-1,1′-binaphthyl-3-carboxaldehyde (3)

It was prepared similar to receptor **1**. Isolated yield: 75% (mp 110 °C); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 12.37 (br s, 1H), 10.51 (s, 1H), 10.12 (s, 1H), 9.14 (s, 1H), 8.28 (s, 1H), 7.97–7.86 (m, 3H), 7.63 (d, 1H), 7.45–7.11 (m, 11H), 6.83 (d, 1H), 5.09 (s, 2H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ 196.9, 156.8, 154.0, 153.4, 138.4, 138.0, 137.1, 133.7, 130.3, 130.1, 129.8, 129.5, 128.2, 127.5, 126.7, 125.3, 125.0, 124.3, 124.0, 122.0, 118.7, 118.6, 115.7, 70.8; HRMS (FAB) calcd for $C_{32}H_{23}N_3O_4$: 513. 1689, found: 513.1683.

4.13. (*S*)-2-Hydroxy-2′-(3-(1*H*-benzo[*d*]imidazole-2-carboxamido)-benzyl)-1,1′-binaphthyl-3-carboxaldehyde (4)

It was prepared similar to receptor **1**. Isolated yield: 98% (mp 145 °C). ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm)=12.31 (br s, 1H), 10.52 (s, 1H), 10.16 (s, 1H), 9.46 (s, 1H), 8.51 (s, 1H), 8.19–7.88 (m, 4H), 7.71–7.22 (m, 13H), 6.96 (d, 1H), 5.19 (s, 2H); ^{13}C NMR ($CDCl_3$, 63 MHz): δ (ppm)=194.7, 161.6, 159.8, 158.6, 151.5, 147.32, 146.1, 140.5, 138.9, 138.6, 136.9, 136.2, 132.7, 131.9, 129.9, 129.7, 128.7, 128.0, 126.6, 124.8, 123.7, 123.1, 122.8, 120.1, 116.5, 116.1, 72.6; HRMS (FAB) calcd for $C_{36}H_{25}N_3O_4$: 563.1845, found: 563.1840.

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