Supporting Information for:

Imidazolium-Functionalized BINOL as Multifunctional Receptor for Chromogenic and Chiral Anion Recognition

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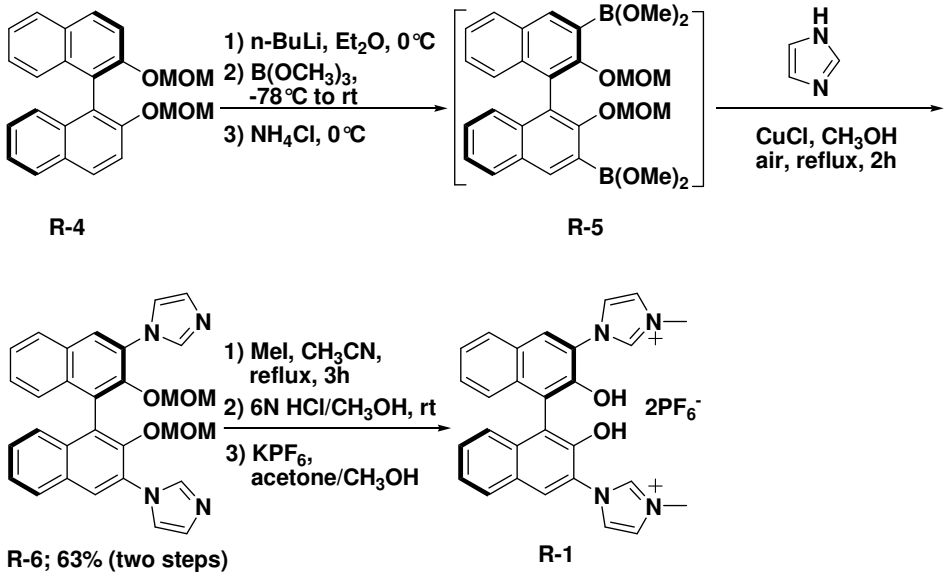
Experimental Section

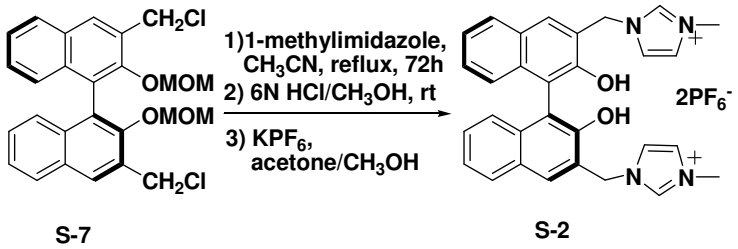
General remarks for experimental

^{1}H NMR, ^{13}C NMR spectra were measured on a Bruker AM400 NMR spectrometer. Proton Chemical shifts of NMR spectra were given in ppm relative to internals reference TMS (^{1}H, 0.00 ppm) and residual $CDCl_3$ (^{1}H, 7.26 ppm) as indicated. ESI-MS and HRMS spectral data were recorded on a Finnigan LCQ^{DECA} and a Bruker Daltonics Bio TOF mass spectrometer, respectively. Optical rotations were measured on a Perkin-Elmer 341 automatic polarimeter. Fluorescence emission spectra were obtained using FluoroMax-4 Spectrofluorophotometer (HORIBA Jobin Yvon) at 298 K. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. All the solvents were dried according to the standard methods prior to use. All of the solvents were either HPLC or spectroscopic grade in the optical spectroscopic studies.

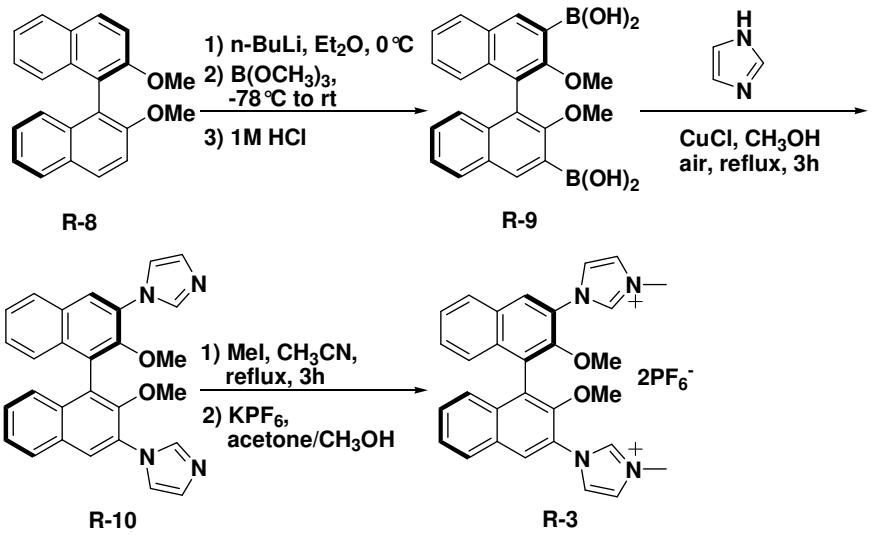
Synthesis and characterization of various compounds



Scheme S1. Synthesis of the 3, 3'-imidazolium-substituted BINOL **R-1**.



Scheme S2. Synthesis of the 3, 3'-imidazoliummethyl-substituted BINOL **S-2**.



Scheme S3. Synthesis of the 3, 3'-imidazolium-substituted Me-protected BINOL **R-3**.

Preparation and Characterization of R-3, 3'-Bis(1 *H*-Imidazol-1-yl)-2, 2'-dimethoxymethoxy-1, 1'-dinaphthyl [R-6]

A flame-dried three-necked flask was charged with TMEDA (4.5 mL, 30 mmol) and dry Et_2O (150 mL) under N_2. n-BuLi (2.2M in hexane, 13.6 mL, 30 mmol) was then slowly added over a period of 30 min. After the mixture was sitrred for another 30 min at the same temperature, **R-4** (3.74 g, 10 mmol) was added in one portion to this solution. The mixture was stirred for 3 h at 0□, $B(OMe_3)_3$ (6.8 mL, 60 mmol) was then added to the resulting light-brown by means of a syringe over a period of 30 min at -78□. The solution was allowed to warm to room temperature and was then stirred overnight. After being cooled to 0□, the reaction mixture was quenched with saturated aqueous NH_4Cl (50 mL) and extracted with diethyl ether. The combined diethyl ether extracts were washed with saturated aqueous NH_4Cl (2×50 mL) and with saturated aqueous NaCl (100 mL) and then dried over Na_2SO_4. The solvent was removed under reduced pressure to give **R-6** as colorless oil, which was used for the next reaction without further purification.

Compound **R-6** was added in one portion to a vigorously stirred mixture of imidazole (2.72 g, 40 mmol) and a catalytic amount of CuCl (99.0 mg, 1 mmol) in absolute methanol (150 mL). The mixture was then refluxed for 2 h under dry air. It was then passed through a pad of Celite, the filtrate was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/CH_3OH to give R-**6** (3.20 g, 63% two steps) as a pale yellow amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 2H), 7.97 (s, 2H), 7.92 (d, 2H, *J* = 8.4 Hz), 7.52 (ddd, 2H, *J* = 0.8, 1.2, 0.8 Hz), 7.46 (s, 2H), 7.37 (ddd, 2H, *J* = 1.2, 1.6, 1.2), 7.27 (d, 2H, *J* = 8.4 Hz), 7.18 (s, 2H), 4.39 (d, 2H, *J* = 6 Hz), 4.30 (d, 2H, *J* = 6 Hz), 2.50 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 137.9, 133.0, 130.7, 130.4, 129.8, 128.0, 127.6, 127.1, 126.5, 126.2, 125.3, 120.7, 98.8, 56.3; ESI-MS: m/z 507.6 $[M+H]^+$ (calcd 507.2).

Preparation and Characterization of R-3, 3'-Bis(3-methyl-1 *H*-Imidazolium-1-yl)-2, 2'-dihydroxy-1, 1'-dinaphthyl dihexafluorophosphate [R-1]

A solution of **R-6** (2.02 g, 4 mmol) and MeI (5 mL, 80 mmol) in acetonitrile (30 mL) was refluxed for 3 h. After cooling to the room temperature, the solvent was evaporated to dryness under reduced pressure. Under nitrogen, the residue was dissolved in methanol (10 mL) to which 6 N HCl (30 mL) was added. After the mixture was stirred at room temperature overnight, the solvent was removed under reduced pressure.

Acetone/methanol (10 mL/10 mL) were added to the residue, after stirring for 20 min at room temperature, KPF_6 (1.48 g, 8 mmol) was added to the reaction mixture. After another 24 h stirring at room temperature, the solvent was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/CH_3OH to give **R-1** (1.24 g, 42%) as a white solid.
$[\alpha]^{25}_D$ +22.7 (c 0.25, CH_3OH); ^1H NMR (600 MHz, D_2O : DMSO-d_6 = 9: 1) δ 9.25 (s, 2H), 8.35 (s, 2H), 8.10 (d, 2H, *J* = 8.4 Hz), 7.92 (s, 2H), 7.68 (s, 2H), 7.56 (t, 2H, *J* = 15 Hz), 7.47 (t, 2H, *J* = 15 Hz), 7.19 (d, 2H, *J* = 8.4 Hz), 4.04 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 147.9, 138.3, 134.4, 129.1, 128.6, 127.9, 126.9, 125.9, 125.0, 124.7, 124.3, 124.1; 31.2; HRMS calcd for $C_{28}H_{24}N_4O_2$ $[M\text{-}2PF_6^-\text{-}H]^{2+}$ 447.1816, found 447.1819.

Preparation and Characterization of S-3, 3'-Bis(3-methyl-1 *H*-Imidazoliummethyl)-2, 2'-dihydroxy-1, 1'-dinaphthyl dihexafluorophosphate [S-2]

S-7 was prepared according to the reported methods.[1] A solution of **S-7** (700 mg, 1.48 mmol) and 1-methylimidazole (1.20 mL, 15 mmol) in acetonitrile (30 mL) was refluxed for 72 h. After cooling to the room temperature, the solvent was evaporated to dryness under reduced pressure. Under nitrogen, the residue was dissolved in methanol (10 mL) to which 6 N HCl (30 mL) was added. After the mixture was stirred at room temperature for 24 h , the solvent was removed under reduced pressure. Acetone (30 mL) was added to the residue, after stirring for 20 min at room temperature, KPF_6 (552 mg, 3 mmol) was added to the reaction mixture. After another 24 h stirring at room temperature, the solvent was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/CH_3OH to give **S-2** (620 mg, 55%) as a pale yellow solid.
$[\alpha]^{25}_D$ +33 (c 0.25, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 9.31 (s, 2H), 8.97 (s, 2H), 8.07 (s, 2H), 7.91 (d, 2H, *J* = 8.4 Hz), 7.84 (s, 2H), 7.78 (s, 2H), 7.34 (t, 2H, *J* = 14.8 Hz), 7.25 (t, 2H, *J* = 14.8 Hz), 5.70-5.59 (m, 4H), 3.87 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.9, 136.8, 134.4, 131.0, 128.2, 128.1, 126.9, 124.0, 123.7, 123.5, 123.4, 122.7, 115.0, 49.1, 35.8; HRMS calcd for $C_{30}H_{27}N_4O_2$ $[M\text{-}2PF_6^-\text{-}H]^{2+}$ 475.2123, found 475.2117.

Preparation and Characterization of R-3, 3'-Bis(1 *H*-Imidazol-1-yl)-2, 2'-dimethoxy-1, 1'-dinaphthyl [R-10]

R-9 was synthesized from the **R-8** following the published procedure.[2] Compound **R-9** (4.02 g, 10 mmol) was added in one portion to a vigorously stirred mixture of imidazole (2.72 g, 40 mmol) and a catalytic amount of CuCl (99.0 mg, 1 mmol) in absolute methanol (150 mL). The mixture was then refluxed for 4 h under dry air. It was then passed through a pad of Celite, the filtrate was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/CH_3OH to give **R-10** (3.12 g, 70%) as a pale yellow amorphous solid.
^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 2H), 7.99 (s, 2H), 7.94 (d, 2H, *J* = 8.4 Hz), 7.54 (s, 2H), 7.50 (t, 2H, *J*=15.2 Hz), 7.35 (t, 2H, *J*=15.2 Hz), 7.27 (s, 2H), 7.19 (d, 2H, *J* = 8.4 Hz), 3.17 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 137.6, 132.9, 130.4, 130.3, 129.9, 128.1, 127.5, 126.6, 126.3, 125.6, 124.8, 120.3, 60.5; ESI-MS: m/z 446.5 $[M+H]^+$ (calcd 446.2).

Preparation and Characterization of R-3, 3'-Bis(3-methyl-1 *H*-Imidazolium-1-yl)-2, 2'-dimethoxy-1, 1'-dinaphthyl dihexafluorophosphate [R-3]

A solution of **R-10** (1.78 g, 4 mmol) and MeI (5 mL, 80 mmol) in acetonitrile (30 mL) was refluxed for 3 h. After cooling to the room temperature, the solvent was evaporated to dryness under reduced pressure. Under

nitrogen, acetone/methanol (10 mL/10 mL) were added to the residue, after stirring for 20 min at room temperature, KPF_6 (1.48 g, 8 mmol) was added to the reaction mixture. After another 24 h stirring at room temperature, the solvent was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/CH_3OH to give **R-3** (2.60 g, 85%) as a pale yellow solid.

$[\alpha]^{25}_D$ -15 (c 0.25, CH_3OH); ^1H NMR (400 MHz, DMSO-d_6) δ 9.71 (s, 2H), 8.58 (s, 2H), 8.24 (s, 2H), 8.17 (d, 2H, J = 8.4 Hz), 8.05 (s, 2H), 7.66 (t, 2H, J = 15.2 Hz), 7.54 (t, 2H, J = 15.2 Hz), 7.20 (d, 2H, J = 8.4 Hz), 4.04 (s, 6H), 3.24 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.3, 138.4, 133.8, 129.9, 129.3, 129.2, 128.2, 127.8, 127.3, 125.7, 125.4, 124.5, 124.2, 61.8, 36.9; HRMS calcd for $C_{30}H_{27}N_4O_2$ $[M-2PF_6^-H]^{2+}$ 475.2123, found 475.2114.

NMR Titration Method

All NMR experiments were performed on a Bruker AM400 NMR spectrometer at 298 K. A solution (2 mM) of receptors in DMSO-d_6 was titrated with aliquots from stock solution of tetrabutylammonium salts (10 mM) in the same solvent. The chemical shift changes of the C(2) proton of imidazolium units in receptors were monitored.

Preparation of fluorometric anion titration solutions.

Stock solutions (2 mM or 100 mM) of the tetrabutylammonium salts of $H_2PO_4^-$, $CH_3CO_2^-$, F^-, Cl^-, Br^-, and HSO_4^- in acetonitrile were prepared. Stock solutions (2 mM) of the tetrabutylammonium salts of amino acids in acetonitrile were prepared. Stock solutions of **R-1**, **S-2**, **R-3** (1 mM) were prepared in DMSO. Test solutions were prepared by placing 9-15 μL of the probe stock solution into a test tube, adding an appropriate aliquot of each anion stock, and diluting the solution to 3 mL with acetonitrile. For all measurements, excitation was at 290 nm; emission was measured at 370 nm.

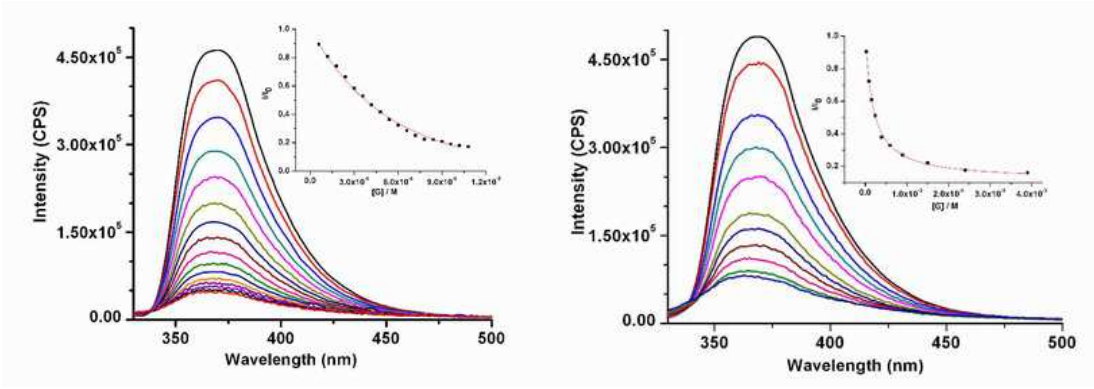


Figure S1. Fluorescent titrations of **R-1** (3 μM) with tetrabutyl ammonium salts of F^- (left) and Cl^- (right) in CH_3CN (λ_{ex} = 290 nm, excitation and emission slit: 1.5 nm), the equivalents of anion are 0-3.6 for F^-, and 0-2000 for Cl^-, respectively. Inset: the corresponding nonlinear curve fitting.

Table S1. Association constants (M^{-1}, for F^-: M^{-2}) of **R-1** with anions in CH_3CN.

		R-1	
Guest	Host:Guest	R	K (M^{-1})
F^-	1:2	0.9977	7.36×10^5
$CH_3CO_2^-$	1:1	0.9981	2.83×10^5
$H_2PO_4^-$	1:1	0.9961	2.46×10^5
HSO_4^-	1:1	0.9987	5140
Cl^-	1:1	0.9989	5286
Br^-	1:1	0.9996	1256

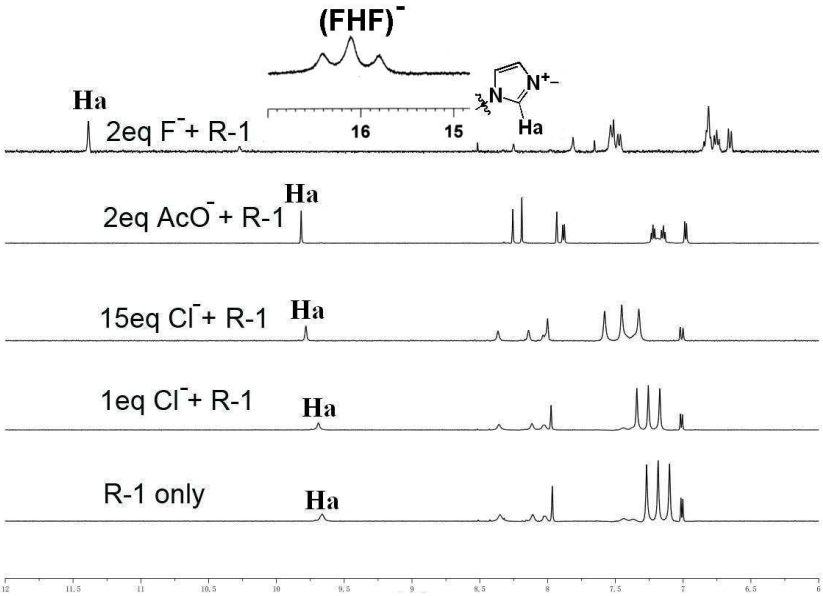


Figure S2. Partial ^1H NMR (300 MHz) spectra of **R-1** (2 mM) in the presence of anions in DMSO-d_6.

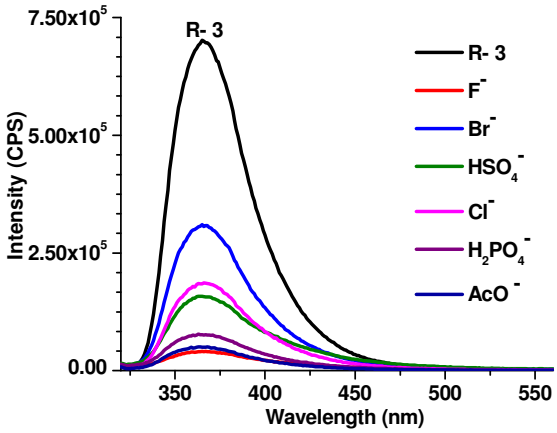


Figure S3. Fluorescent emission changes of **R-3** (3 μM) upon addition of tetrabutyl ammonium salts of $H_2PO_4^-$, $CH_3CO_2^-$, F^-, Cl^-, HSO_4^- and Br^- (100 equiv) in CH_3CN (excitation at 290 nm, excitation and emission slit: 1.5 nm).

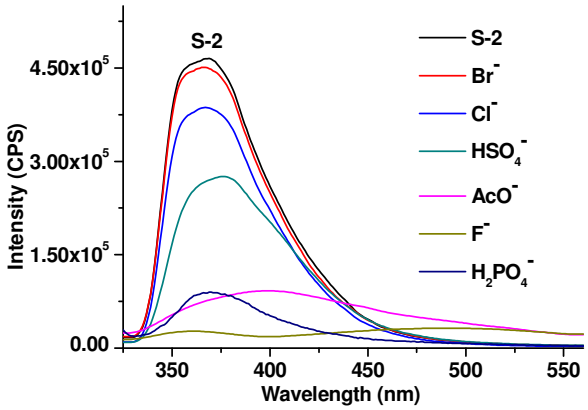


Figure S4. Fluorescent emission changes of **S-2** (3 μM) upon addition of tetrabutyl ammonium salts of $H_2PO_4^-$, $CH_3CO_2^-$, F^-, Cl^-, HSO_4^- and Br^- (100 equiv) in CH_3CN (excitation at 290 nm, excitation and emission slit: 1.5 nm).

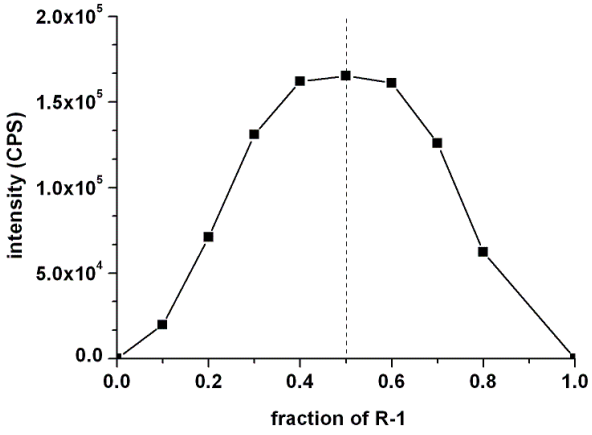
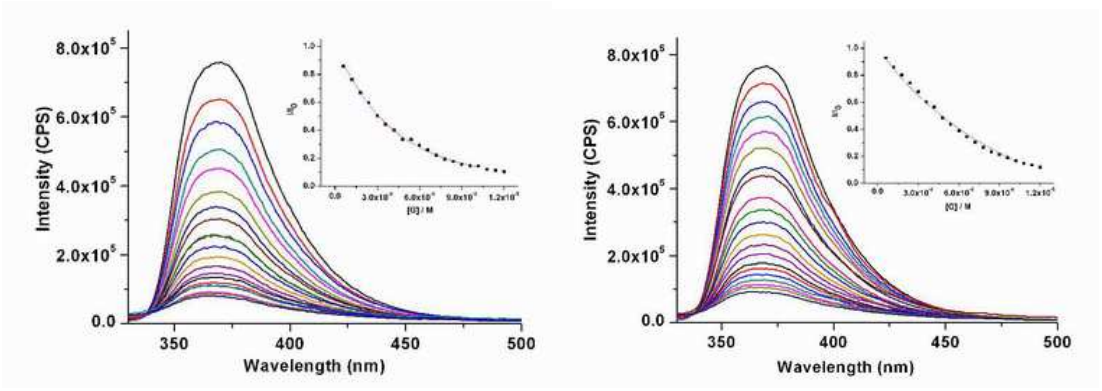


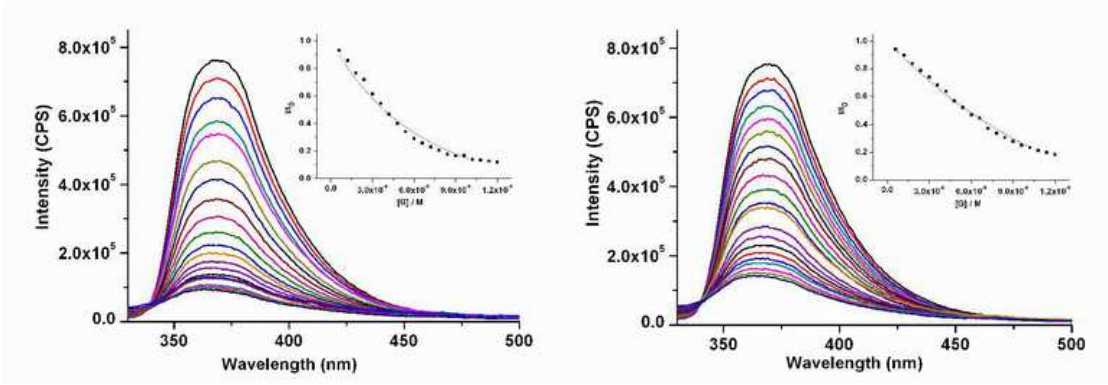
Figure S5. Job's plot of host **R-1/L-Ala** system at 370 nm. ([**R-1**]·[**L-Ala**] = 30 μM).

Figure S6-S9: the equivalents of anion are 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6, 3.8, 4.0. λ_{ex} = 290 nm, excitation and emission slit are both 3 nm.



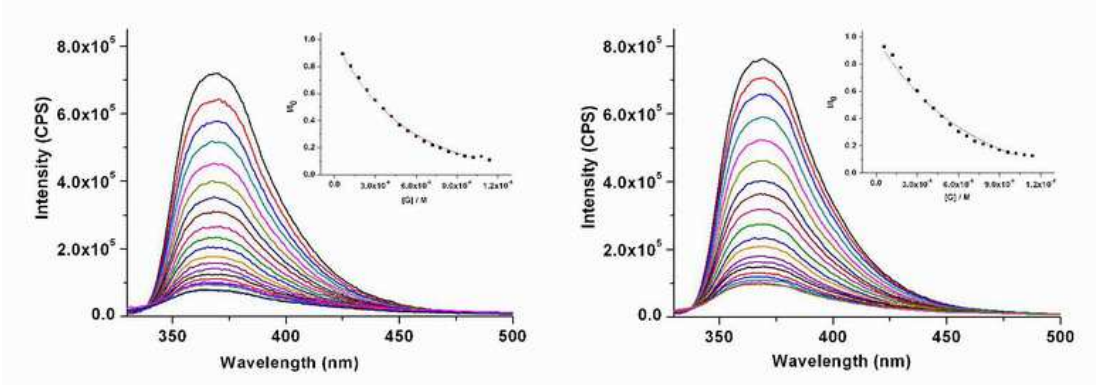
R = 0.9990, k = 4.55 × 10^5 M^{-1} R = 0.9972, k = 1.02 × 10^5 M^{-1}

Figure S6. Fluorescent titrations of **R-1** (3 μM) with tetrabutyl ammonium salts of L-Ala (left) and D-Ala (right) in CH_3CN. Inset: the corresponding nonlinear curve fitting.



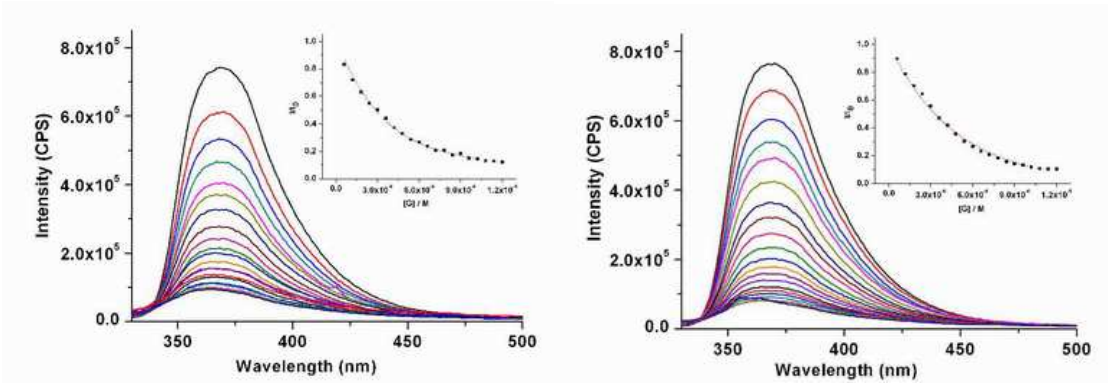
R = 0.9918, k = 2.12 × 10^5 M^{-1} R = 0.9963, k = 0.55 × 10^5 M^{-1}

Figure S7. Fluorescent titrations of **R-1** (3 μM) with tetrabutyl ammonium salts of L-Leu (left) and D-Leu (right) in CH_3CN. Inset: the corresponding nonlinear curve fitting.



R = 0.9984, k = 3.23 × 10^5 M^{-1} R = 0.9948, k = 1.93 × 10^5 M^{-1}

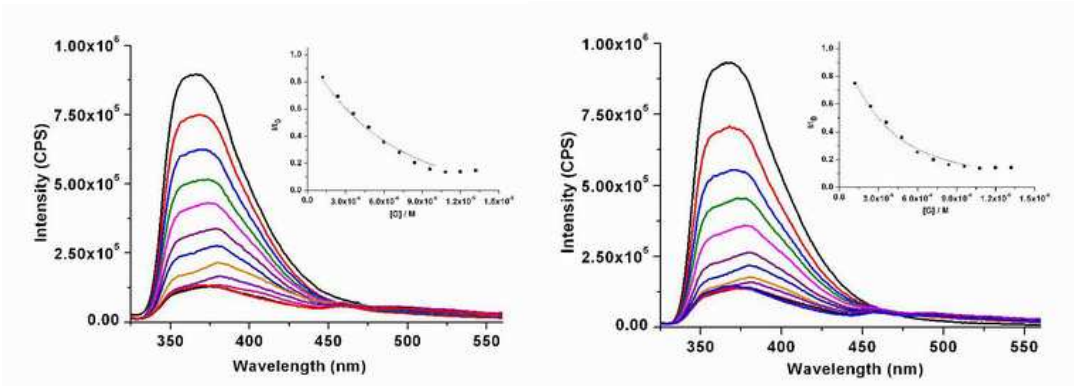
Figure S8. Fluorescent titrations of **R-1** (3 μM) with tetrabutyl ammonium salts of L-Phe (left) and D-Phe (right) in CH_3CN. Inset: the corresponding nonlinear curve fitting.



R = 0.9975, k = 7.31 × 10^5 M^{-1} R = 0.9975, k = 3.45 × 10^5 M^{-1}

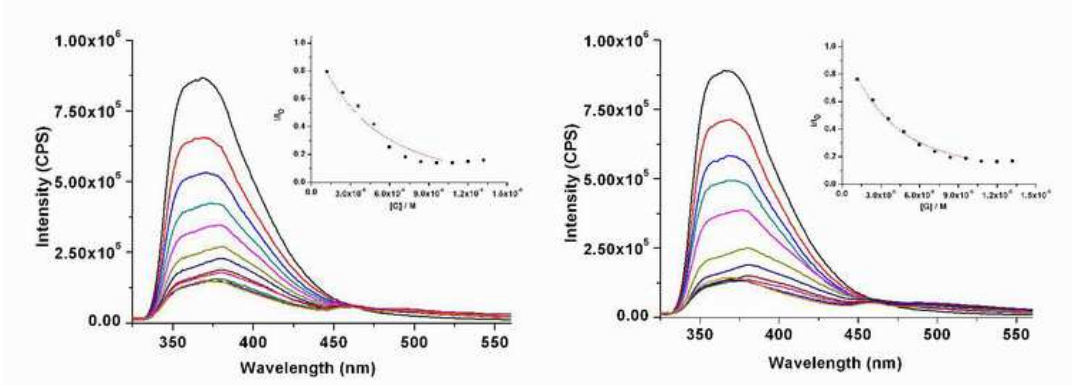
Figure S9. Fluorescent titrations of **R-1** (3 μM) with tetrabutyl ammonium salts of L-Ser (left) and D-Ser (right) in CH_3CN. Inset: the corresponding nonlinear curve fitting.

Figure S10-S13: the equivalents of anion are 0, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 4.4. λ_{ex} = 290 nm, excitation and emission slit are both 3 nm.



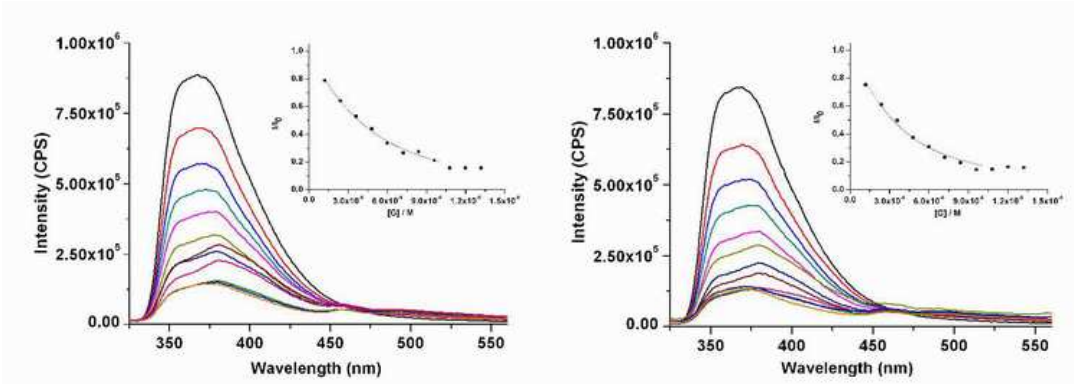
R = 0.9925, k = 2.13 × 10^5 M^{-1} R = 0.9942, k = 6.26 × 10^5 M^{-1}

Figure S10. Fluorescent titrations of **S-2** (3 μM) with tetrabutyl ammonium salts of L-Ala (left) and D-Ala (right) in CH_3CN. Inset: the corresponding nonlinear curve fitting.



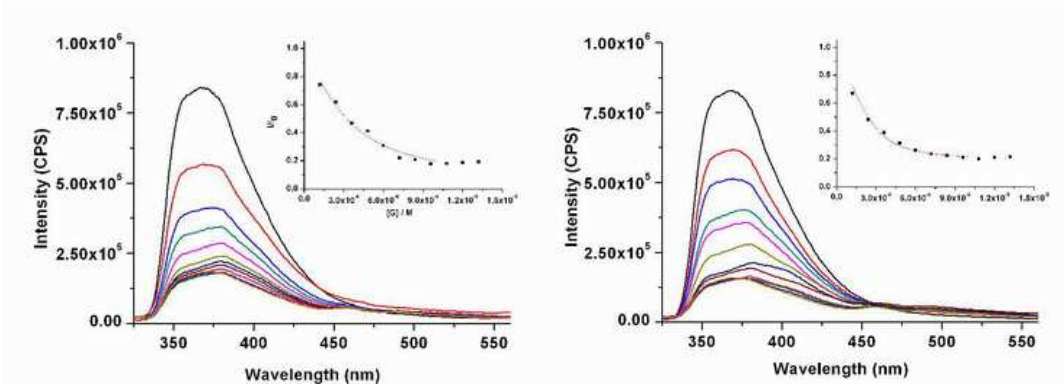
R = 0.9887, k = 3.96 × 10^5 M^{-1} R = 0.9962, k = 5.94 × 10^5 M^{-1}

Figure S11. Fluorescent titrations of **S-2** (3 μM) with tetrabutyl ammonium salts of L-Leu (left) and D-Leu (right) in CH_3CN. Inset: the corresponding nonlinear curve fitting.



R = 0.9963, k = 3.50 × 10^5 M^{-1} R = 0.9934, k = 5.26 × 10^5 M^{-1}

Figure S12. Fluorescent titrations of **S-2** (3 μM) with tetrabutyl ammonium salts of L-Phe (left) and D-Phe (right) in CH_3CN. Inset: the corresponding nonlinear curve fitting.



R = 0.9900, k = 8.03 × 10^5 M^{-1} R = 0.9893, k = 14.20 × 10^5 M^{-1}

Figure S13. Fluorescent titrations of **S-2** (3 μM) with tetrabutyl ammonium salts of L-Ser (left) and D-Ser (right) in CH_3CN. Inset: the corresponding nonlinear curve fitting.

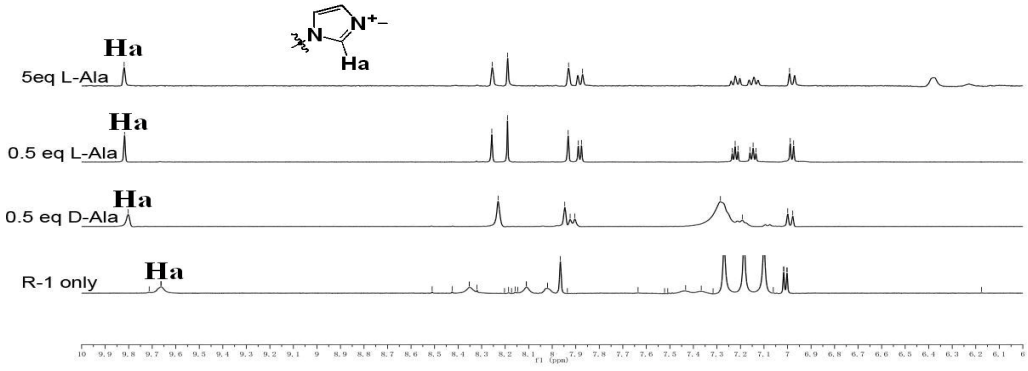


Figure S14. Partial ^1H NMR (300 MHz) spectra of **R-1** (2 mM) in the presence of amino acids in DMSO-d_6.

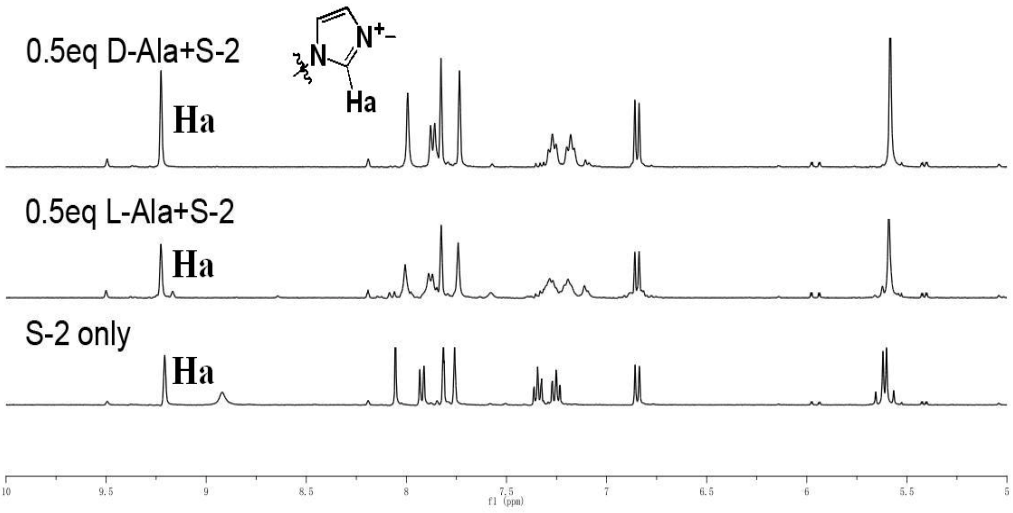
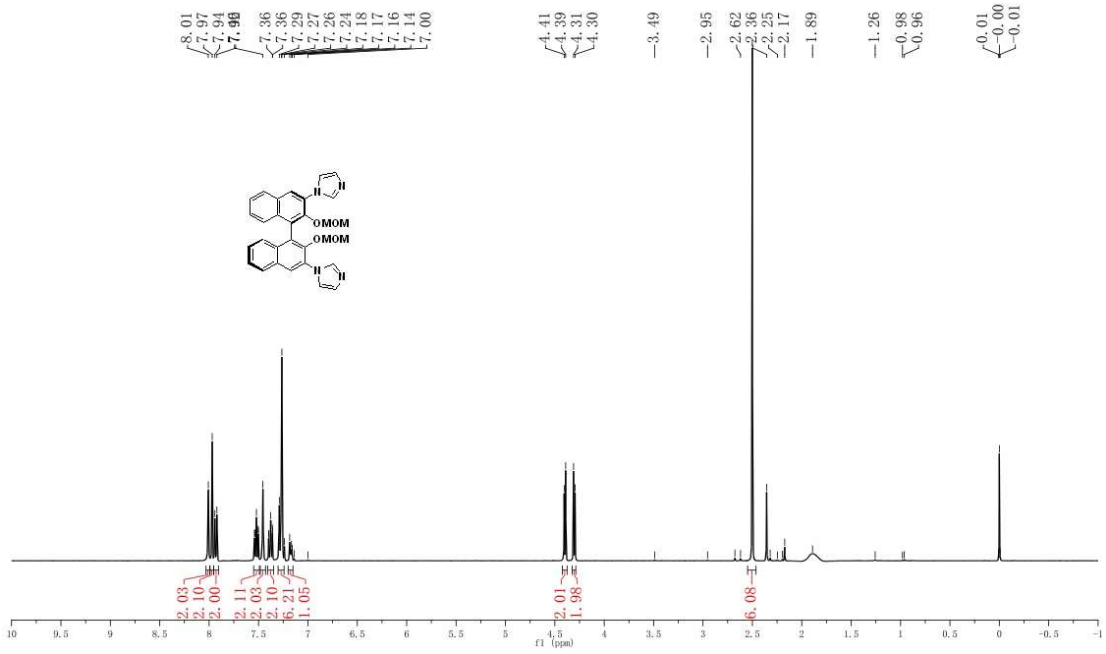
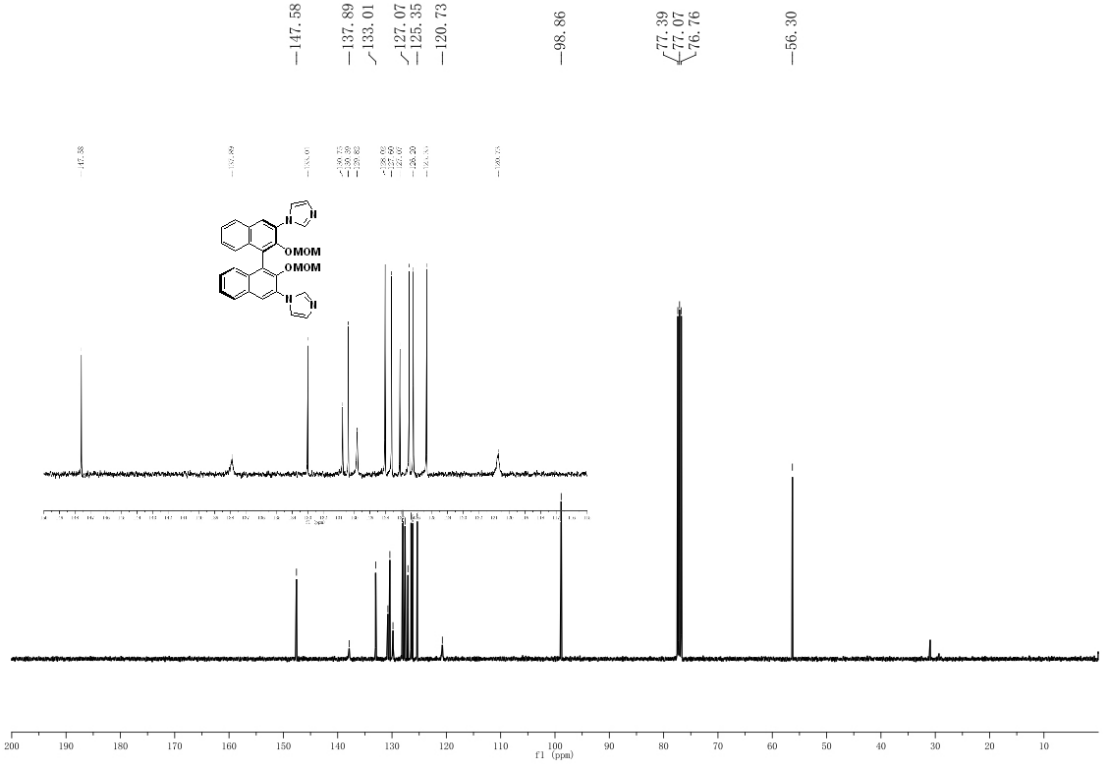


Figure S15. Partial ^{1}H NMR (300 MHz) spectra of **S-2** (5 mM) in the presence of amino acids in DMSO-d_6.

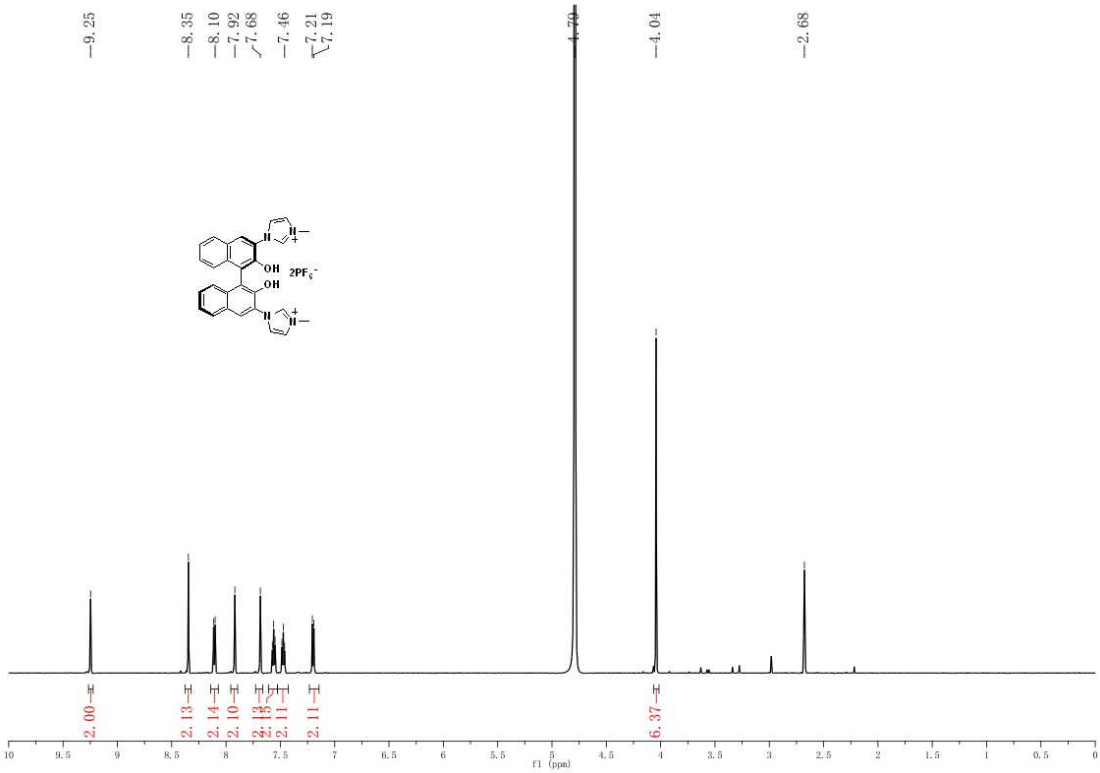
^{1}H-NMR Spectrum of **R-6** in $CDCl_3$ (400 MHz):



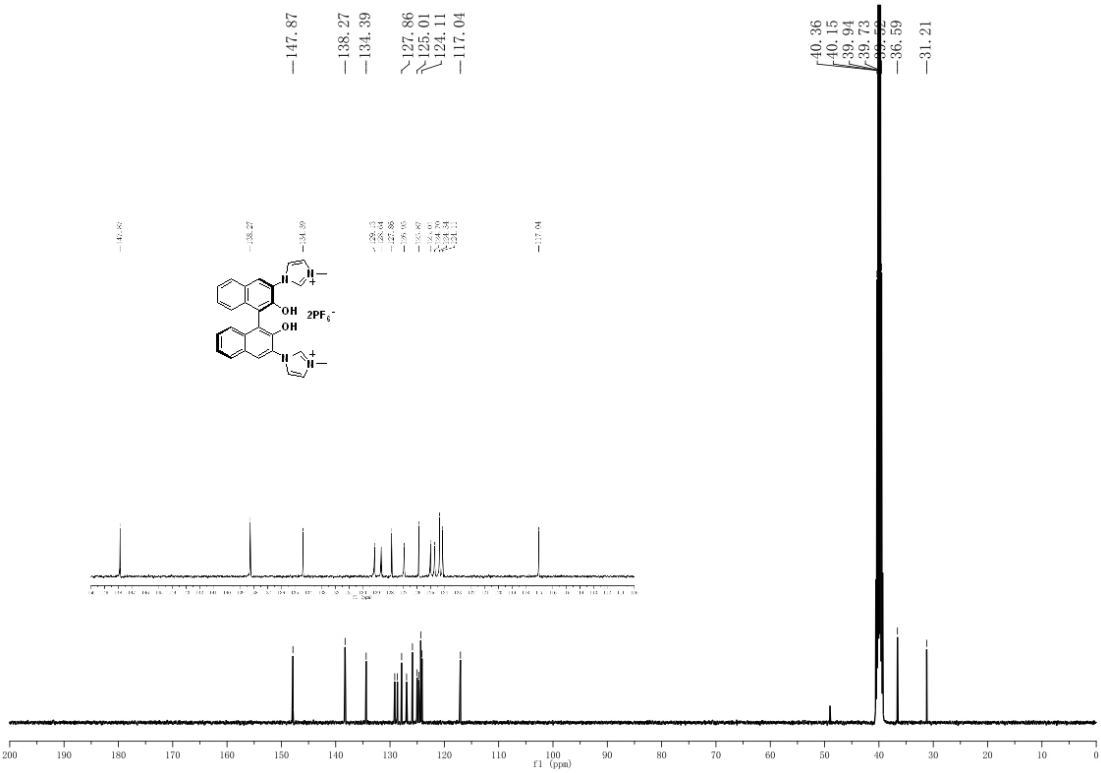
^{13}C-NMR Spectrum of **R-6** in $CDCl_3$ (100 MHz):



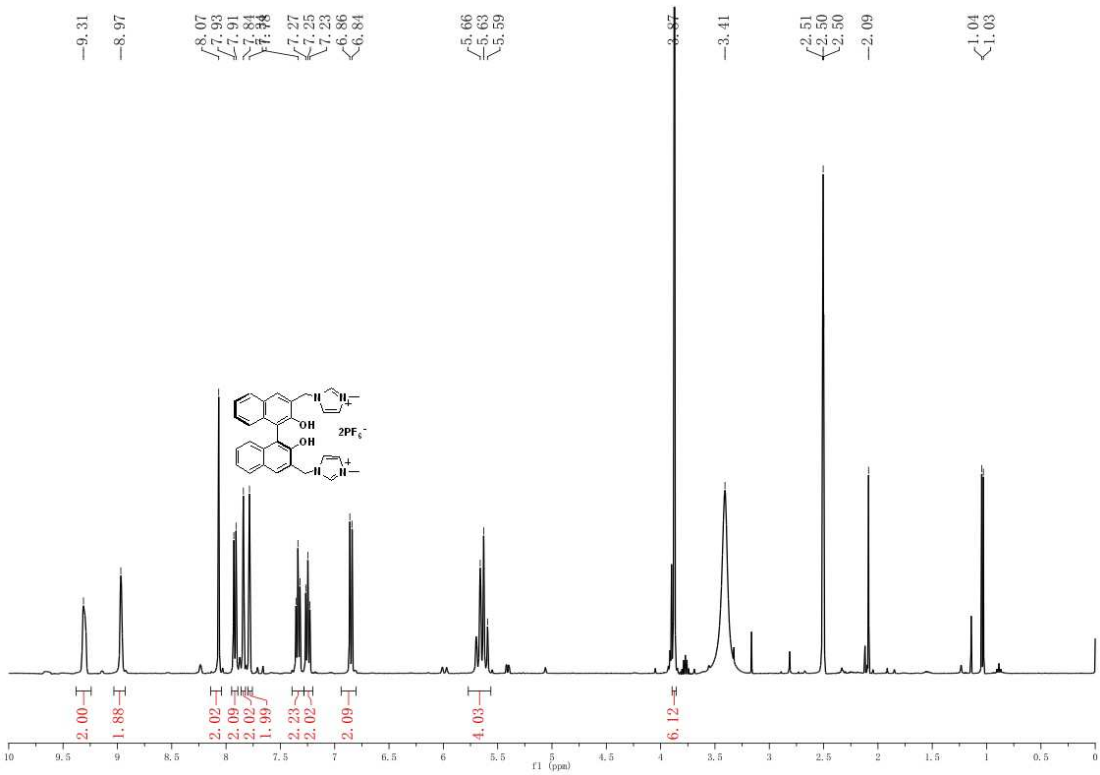
^{1}H-NMR Spectrum of **R-1** in D_2O:DMSO-d_6 = 9:1 (600 MHz):



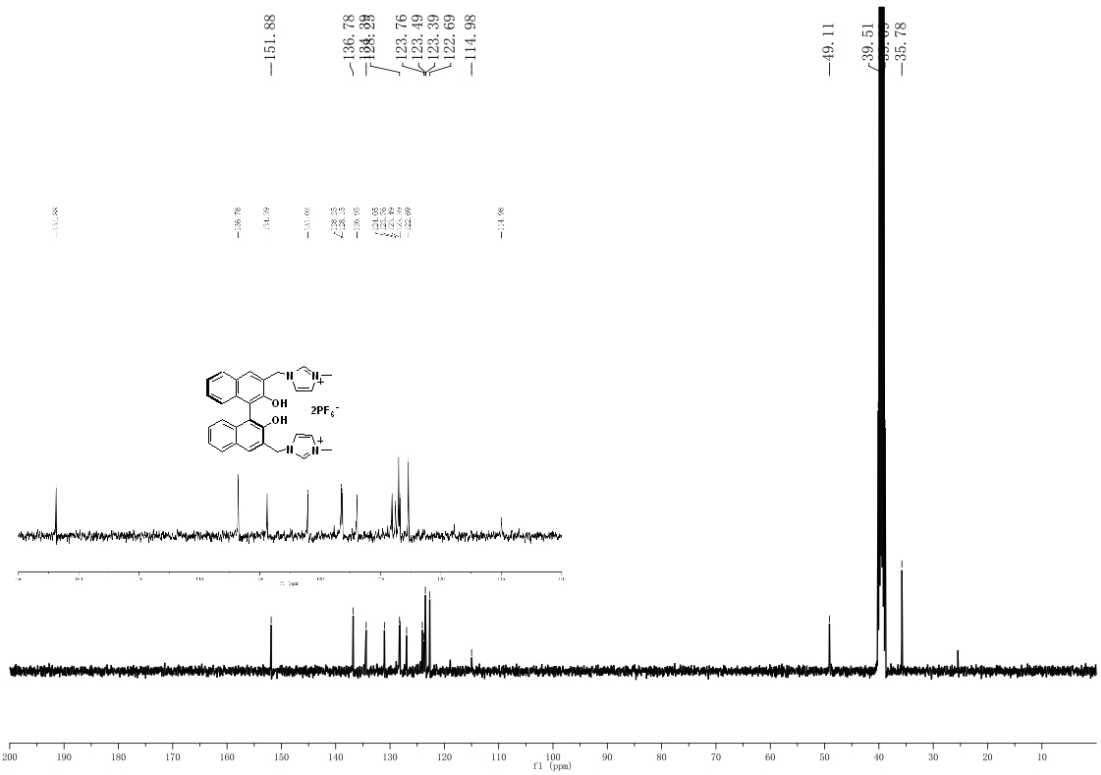
^{13}C-NMR Spectrum of **R-1** in D_2O:DMSO-d_6 = 9:1 (100 MHz):



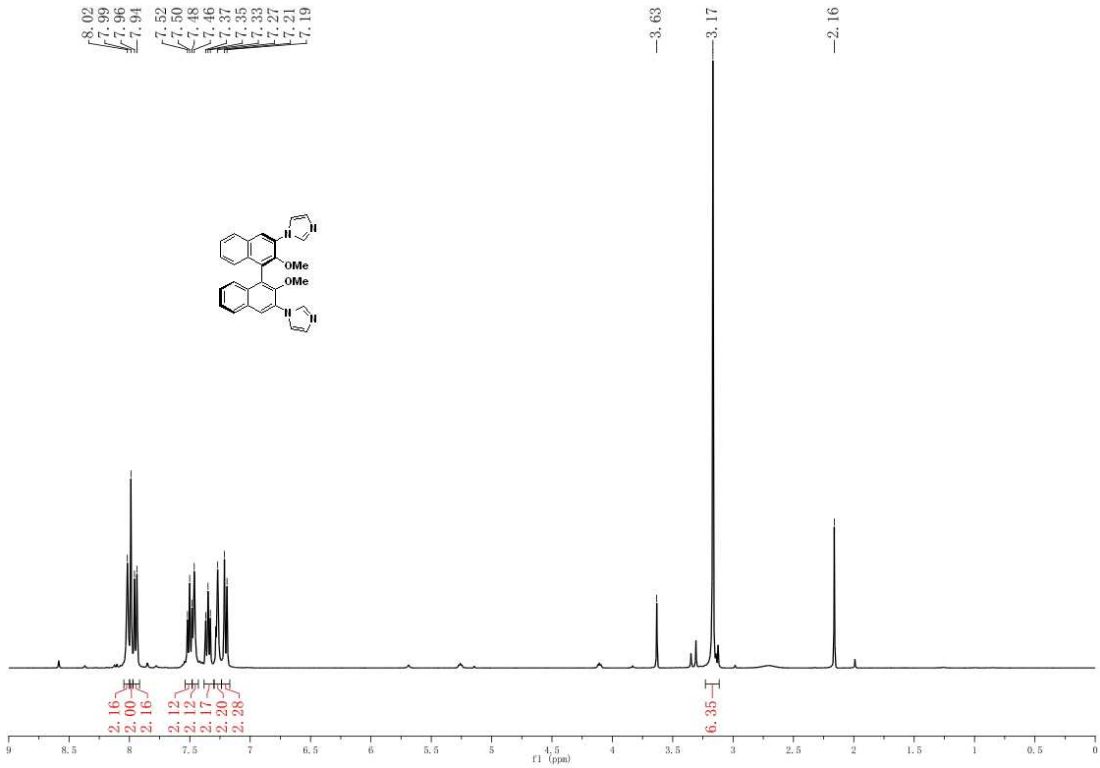
^{1}H-NMR Spectrum of **S-2** in DMSO-d_6 (400 MHz):



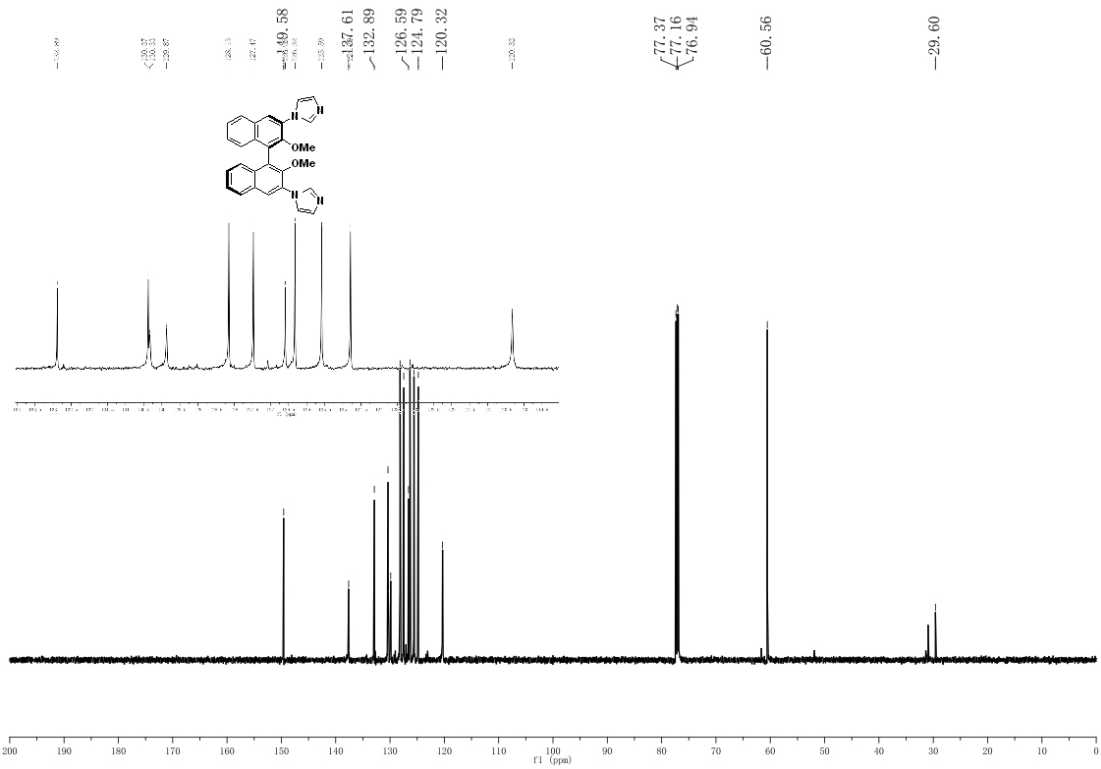
^{13}C-NMR Spectrum of **S-2** in DMSO-d_6 (100 MHz):



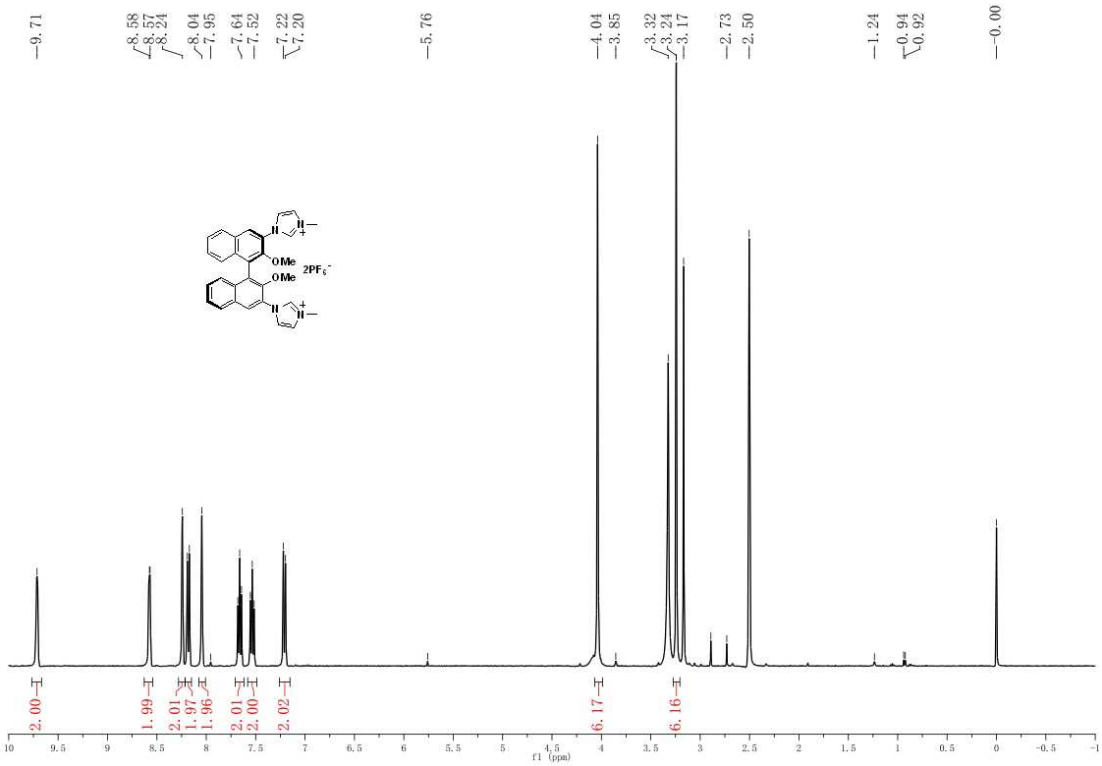
^{1}H-NMR Spectrum of **R-10** in $CDCl_3$ (400 MHz):



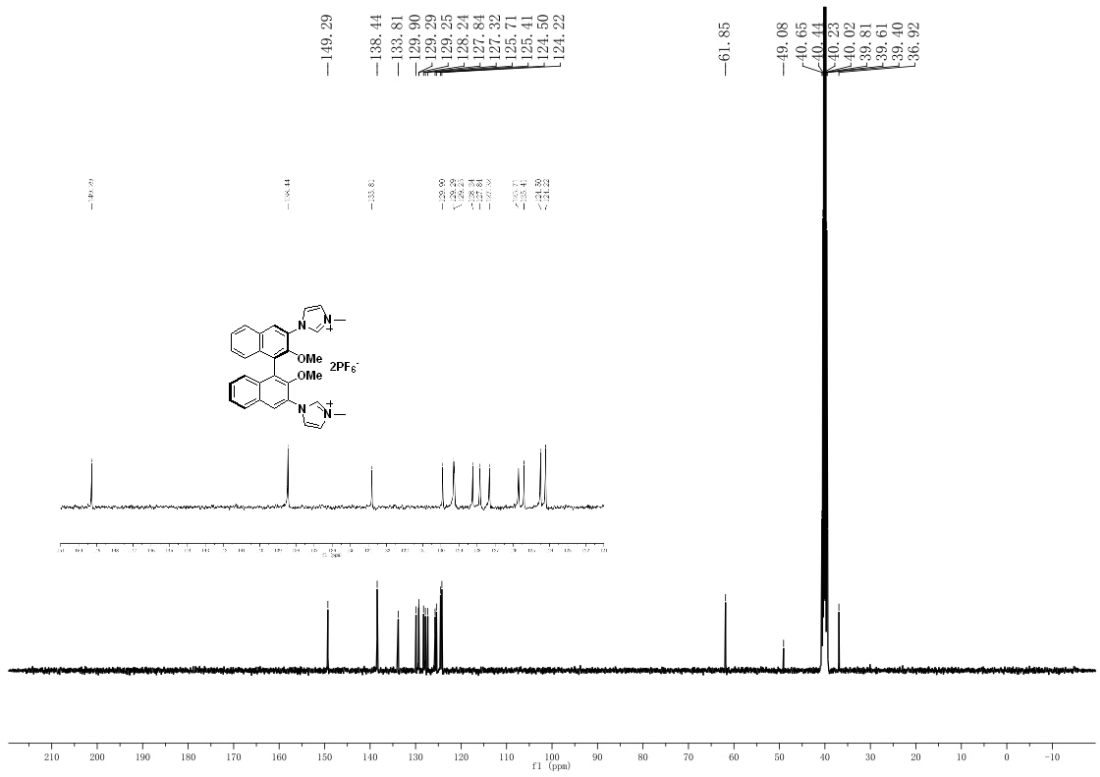
^{13}C-NMR Spectrum of **R-10** in $CDCl_3$ (100 MHz):



^{1}H-NMR Spectrum of **R-3** in DMSO-d_6 (400 MHz):



^{13}C-NMR Spectrum of **R-3** in DMSO-d_6 (100 MHz):



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[1]Hamashima, Y.; Sawada, D.; Nogami, H.; Kanai, M.; Shibasaki, M. *Tetrahedron.* **2001**, *57*, 805-814.

[2]Simonsen, K. B.; Gothelf, K. V.; Jorgensen, K. A. *J. Org. Chem.* **1998**, *63*, 7536-7538.