Supporting Information

Fluorescent Sensing of Guanine and Guanosine Monophosphate with Conjugated Receptors Incorporating Aniline and Naphthyridine Moieties

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Experimental

General. All reactions requiring anhydrous conditions were conducted in flame-dried apparatus under an inert atmosphere of argon using standard techniques. Syringes and needles for the transfer of reagents were dried at 100 ^{o}C and allowed to cool in a desiccator over P_2O_5 before use. All the reagents and solvents were reagent grade and used without further purification unless otherwise specified. Ethers were distilled from sodium benzophenone ketyl; (chlorinated) hydrocarbons, and amines from CaH_2. Reactions were monitored by TLC using aluminum plates pre-coated with a 0.25 mm layer of silica gel containing a fluorescent indicator. Kieselgel 60 (40–63 μm) and neutral aluminum oxide (50–200 μm) were used for column chromatography.

Melting points are uncorrected. Chemical shifts (δ) are given in parts per million (ppm) relative to δ_H 7.24 / δ_C 77.0 (central line of t) for $CHCl_3/CDCl_3$, δ_H 2.05 / δ_C 29.92 for $(CH_3)_2CO/(\underline{C}D_3)_2CO$, δ_H 3.31 / δ_C 49.0 CH_3OD/CD_3OD, and δ_H 2.49 (m) / δ_C 39.5 (m) for $(CH_3)_2SO/(CD_3)_2SO$. The splitting patterns are reported as s (singlet), d (doublet), t (triplet) q (quartet), m (multiplet) and br (broad). Coupling constants (*J*) are given in Hz. Distortionless enhancement polarization transfer (DEPT) spectra were taken to determine the types of carbon signals.

UV-vis titration studies. The stock solutions of receptor compound (1×10^{-5} M) and analyte (e.g. 9-decylguanine and GMP) (1×10^{-2} M) were prepared by using spectroscopic grade solvent (e.g. CH_2Cl_2) or deionized water. The stock solution (2 mL) of receptor compound was placed in a quartz cell (1 cm length), and the absorption spectrum was recorded at 298 K. The stock solution of analyte was introduced in an incremental fashion (2 μL corresponds to 1.0 equiv) via microsyringe; the mixture was shaken well, and the corresponding UV-vis curves were recorded.

Fluorescent titration studies. The fluorescence spectra were taken using the same samples employed in the UV-vis study, i.e. transferring the same cuvette from the UV-vis spectrophotometer to the fluorescence spectrophotometer for each incremental addition. The fluorescence spectra were taken as a function of the concentrations of analyte.

Based on 1:1 stoichiometry of complex, the apparent binding constant was calculated according to the following equation, and determined by nonlinear least squares curve fitting method.

$$y = f + [(d - f)/(2c)] \{K^{-1} + c + x - [(K^{-1} + c + x)^2 - 4cx)]^{0.5}\}$$

c: receptor concentration; d: maximum change of fluorescence intensity at saturation; f: initial fluorescence intensity; K: association constant; x: substrate concentration; y: fluorescence intensity.

Job's plot. Stock solutions of receptor compound and analyte were prepared in the same concentration (1×10^{-5} M). Sample solutions containing the receptor compound and guest molecule in different ratios (0:10 to 10:0) were made to maintain total volume of 2 mL. Changes of the absorbance or fluorescence intensity (I_{Fl}) were monitored as a function of molar ratio of the receptor. The complex concentration was calculated as follows:

[complex] = Δ absorbance (or Δ I_{Fl}) × X

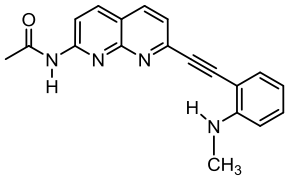
wherein Δ absorbance (or Δ I_{Fl}) is the absorbance (or fluorescence intensity) after adding analyte minus the absorbance (or $I_{o\ Fl}$) before adding any analyte, X is the molar ratio of the receptor.

^{1}H-NMR titration studies. The stock solution of receptor compound (2×10^{-3} M) and analyte (1×10^{-2} M) was prepared in deuterated solvents ($CDCl_3$ for the pyrene-hinged receptor **4** and 9-decylguanine; DMSO-d_6 for the guanidine-hinged receptor **5** and guanosine monophosphate free acid). The stock solution of receptor compound (0.5 mL) was placed in an NMR tube, and the NMR spectrum was recorded at 298 K. The analyte solution was introduced in an incremental fashion (10, 20, 30, 50, 70, 100, 250 μL; 50 μL corresponds to 1 equiv).

ESI–MS analysis. A mixture of receptor compound (**1**–**5**) and guest molecule (e.g. 9-decylguanine) in 1:1 molar ratio was dissolved in CH_2Cl_2, and the solvent was then removed under reduced pressure. The residue was diluted to ~1 μM in aqueous CH_3CN (50%) containing 0.1% of HOAc as the spray solvent for MS analysis.

Synthetic Procedures and Characterization of Compounds

2-Acetamido-7-[2-(methylamino)phenyl]ethynyl-1,8-naphthyridine (1)



According to the previously reported procedure,[5] compound **1** was prepared by Sonogashira coupling reaction (70–80 ^{o}C, 24 h) of 2-acetamido-7-chloro-1,8-naphthyridine (**6**)[s1, s2] (836 mg, 3.8 mmol) with 2-ethynyl-*N*-methylaniline (**7**)[5, s3] (390 mg, 3.0 mmol) in anhydrous DMF (36 mL) in the presence of Et_3N (7 mL) and co-catalysts $Pd(PPh_3)_2Cl_2$ (125 mg, 0.18 mmol) and CuI (36.5 mg, 0.19 mmol). $C_{19}H_{16}N_4O$; yellowish solid recrystallized from acetone, mp = 227.4 ^{o}C; TLC (MeOH/CH_2Cl_2 (1:99)) R_f = 0.15; λ_{max} (CH_2Cl_2) 399 nm (ε = 17500 $M^{-1}cm^{-1}$), 350 nm (ε = 18100 $M^{-1}cm^{-1}$); λ_{max} (DMSO) 402 nm (ε = 23900 $M^{-1}cm^{-1}$), 353 nm (ε = 22400 $M^{-1}cm^{-1}$); Fluorescence λ_{max} (CH_2Cl_2) 518 nm; λ_{max} (DMSO) 565 nm;

IR ν_{max} (KBr) 2200, 1691, 1612 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.96 (1 H, s), 8.51 (1 H, d, *J* = 8.0 Hz), 8.12 (1 H, d, *J* = 8.0 Hz), 8.03 (1 H, d, *J* = 8.0 Hz), 7.50 (1 H, d, *J* = 8.0 Hz), 7.40 (1 H, d, *J* = 8.0 Hz), 7.27 (1 H, t, *J* = 8.0 Hz), 6.63 (1 H, t, *J* = 8.0 Hz), 6.58 (1 H, d, *J* = 8.0 Hz), 2.91 (3 H, s), 2.34 (3 H, s), ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.7, 154.1, 153.9, 150.2, 146.2, 138.5, 136.1, 132.4, 131.0, 123.4, 119.1, 115.7, 115.5, 108.8, 105.0, 95.0, 89.0, 30.4, 25.4; HRMS calcd for $C_{19}H_{17}N_4O$: 317.1397, found: *m/z* 317.1462 $[M + H]^+$.

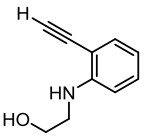
References:

(s1) Newkome, G. R.; Garbis, S. J.; Majestic, V. K.; Fronczek, F. R.; Chiari, G. *J. Org. Chem.* **1981**, *46*, 833–839.

(s2) Corbin, P. S.; Zimmerman, S. C.; Thiessen, P. A.; Hawryluk, N. A.; Murray, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 10475–10488.

(s3) Arcadi, A.; Cacchi, S.; Rosario, M. D.; Fabrizi, G.; Marinelli, F. *J. Org. Chem.* **1996**, *61*, 9280–9288.

2-(2-Ethynylphenylamino)ethanol (8).



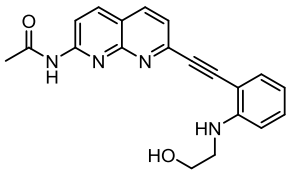
To a solution of 2-iodoaniline (7.8 g, 35.6 mmol) in 2-chloroethanol (60 mL, 447.1 mmol) was added K_2CO_3 (24 g, 173.7 mmol) under argon at room temperature. The mixture was stirred at 55 ^oC for 16 h. After evaporation in vacuo to remove 2-chloroethanol, the mixture was diluted with ice water and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by SiO_2 column chromatography (MeOH/CH_2Cl_2, 0:100 to 5:95) to afford 2-(2-iodophenylamino)ethanol (6.2 g, 66%). $C_8H_{10}INO$; colorless oil; TLC (CH_2Cl_2) R_f = 0.3; IR ν_{max} (neat) 3370, 1586, 1501 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.65 (1 H, d, *J* = 7.6 Hz), 7.19 (1 H, t, *J* = 7.6 Hz), 6.60 (1 H, d, *J* = 7.6 Hz), 6.45 (1 H, t, *J* = 7.6 Hz), 4.44 (1 H, s), 3.86 (2 H, t, 5.2 Hz), 3.35 (2 H, t, 5.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.4, 138.5, 128.9, 118.6, 110.5, 85.7, 60.7, 46.2; HRMS (ESI) calcd for $C_8H_{10}INO$: 263.9885, found: *m/z* 263.9883 $[M + H]^+$.

To a solution of the above-prepared iodide (928 mg, 3.53 mmol) in 1,4-dioxane (5 mL) were added NEt_3 (4 mL), $Pd(PPh_3)_2Cl_2$ (21 mg, 0.03 mmol) and CuI (6 mg, 0.03 mmol) under argon at room temperature. The mixture was degassed and stirred at 50 ^oC for 10 min; then ethynyltrimethylsilane (0.51 mL, 3.57 mmol) was added slowly. The mixture was stirred at 50 ^oC for 16 h. The catalysts were removed by filtration through a pad of Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by SiO_2 column chromatography (MeOH/CH_2Cl_2, 1:9) to afford

2-(2-(2-(trimethylsilyl)ethynyl)phenylamino)ethanol (748 mg, 81%). $C_{13}H_{19}NOSi$; yellow oil; TLC (CH_2Cl_2) R_f = 0.4; IR ν_{max} (neat) 3395, 2957, 2144, 1601, 1510 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.29 (1 H, d, *J* = 7.6 Hz), 7.17 (1 H, t, *J* = 7.6 Hz), 6.61 (2 H, m), 4.92 (1 H, s), 3.82 (1 H, t, *J* = 5.2 Hz), 3.34 (2 H, t, 5.2 Hz), 2.01 (1 H, s), 0.27 (9 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.5, 131.7, 129.6, 116.1, 109.3, 107.3, 101.6, 100.1, 61.0, 45.5, 0.5 (3 CH_3); HRMS (ESI) calcd for $C_{13}H_{20}NOSi$: 234.1314, found: *m*/*z* 234.1317 $[M + H]^+$.

To a solution of the above-prepared silane (748 mg, 3.21 mmol) in methanol (5 mL) was added K_2CO_3 (1 g, 7.24 mmol) under argon at room temperature. The mixture was stirred at room temperature for 2 h. The mixture was concentrated under reduced pressure, diluted with water, and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by SiO_2 column chromatography (MeOH/CH_2Cl_2, 0:100 to 2.5:97.5) to afford compound **8** (388 mg, 75%). $C_{10}H_{11}NO$; yellow oil; TLC (MeOH/CH_2Cl_2, 2.5:97.5) R_f = 0.25; IR ν_{max} (neat) 3401, 2937, 2881, 2094, 1601, 1511 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.32 (1 H, d, *J* = 7.6 Hz), 7.19 (1 H, t, *J* = 7.6 Hz), 6.64–6.59 (2 H, m), 4.91 (1 H, s), 3.79 (2 H, t, 5.2 Hz), 3.41 (1 H, s), 3.32 (2 H, t, 5.2 Hz), 2.47 (1 H, s),; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.7, 132.3, 129.9, 116.2, 109.5, 106.3, 83.0, 80.5, 61.0, 45.7; HRMS (ESI) calcd for $C_{10}H_{12}NO$: 162.0919, found: *m*/*z* 162.0926 $[M + H]^+$.

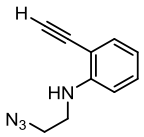
_N_-(2-(2-(2-(2-Hydroxyethylamino)phenyl)ethynyl)-1,8-naphthyridin-7-yl)acetamide (2)



To a solution of chloride **6** (330 mg, 1.80 mmol) in DMF (3 mL) and NEt_3 (3 mL) were added $Pd(PPh_3)_2Cl_2$ (40 mg, 0.06 mmol) and CuI (8 mg, 0.04 mmol) under argon at room temperature. The mixture was degassed and stirred at 80 °C for 10 min; then alkynyl compound **8** (300 mg, 1.86 mmol) in DMF (3 mL) was added slowly. The mixture was stirred at 80 °C for 16 h. The catalysts were removed by filtration through a pad of Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by SiO_2 column chromatography (MeOH/CH_2Cl_2, 2.5:97.5 to 1:9) to afford the desired receptor compound **2** (346 mg, 67%). $C_{20}H_{18}N_4O_2$; yellow solid, mp 182.7–183.4 °C; TLC (MeOH/CH_2Cl_2, 1:9) R_f = 0.3; UV-vis λ_{max} (CH_2Cl_2): 350 nm, 392 nm; ε = 17100, 16200; λ_{max} (DMSO): 353 nm, 395 nm; ε = 15300, 15500; FL λ_{max} 525 nm (CH_2Cl_2), 568 nm (DMSO); IR ν_{max} (neat) 3447, 2994, 2194, 1772, 1610, 1500 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz) δ 8.38 (1 H, d, *J* = 8.0 Hz), 8.23 (2 H, d, *J* = 8.0 Hz), 7.59 (1 H, d, *J* = 8.0 Hz), 7.35 (1 H, d, *J* = 8.0 Hz), 7.24 (1 H, t, *J* = 8.0 Hz), 6.72 (1 H, d, *J* = 8.0 Hz), 6.62 (1 H, t, *J* = 8.0 Hz), 3.82 (2 H, t, *J* = 5.6 Hz), 3.40 (2 H, t,

J = 5.6 Hz), 2.24 (3 H, s); ^{13}C NMR (CD_3OD, 100 MHz) δ 172.6, 156.2, 155.4, 151.7, 147.5, 140.1, 139.1, 134.1, 132.7, 124.8, 121.1, 117.3, 116.8, 111.1, 106.5, 95.3, 91.1, 61.5, 46.6, 24.6; ESI–HRMS calcd for $C_{20}H_{19}N_4O_2$: 347.1508, found: *m/z* 347.1508 $[M + H]^+$.

***N*-(2-Azidoethyl)-2-ethynylbenzenamine (9).**



To a solution of 2-(2-iodophenylamino)ethanol (7.38 g, 29.80 mmol) in anhydrous CH_2Cl_2 (74.4 mL) at 0 °C was added methanesulfonyl chloride (11.05 mL, 71.40 mmol), then triethylamine (19.90 mL, 71.40 mmol) was added dropwise. The mixture was stirred at 0 °C for 1 h, and then concentrated under reduced pressure. The residue was extracted with CH_2Cl_2 and water. The organic layer was dried over $MgSO_4$, filtered and concentrated to give the mesylation product.

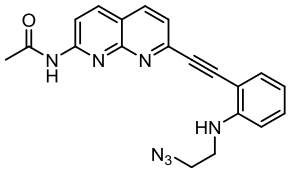
The crude mesylate in anhydrous DMF (75 mL) was treated with sodium azide (5.8 g, 89.2 mmol). The mixture was stirred at 80 °C for 2 h, and then concentrated under reduced pressure. The residue was extracted with CH_2Cl_2 and water. The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography (EtOAc/hexane = 1:19) to afford *N*-(2-azidoethyl)-2-iodobenzenamine (6.94g, 81%). $C_8H_9IN_4$; light yellow oil; TLC (EtOAc/Hexane = 1:19) R_f = 0.3; ν_{max} (neat) 3381, 2918, 2849, 2093, 1504 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (1 H, dd, *J* = 0.8, 7.6 Hz), 7.24 (1 H, dt, *J* = 1.2, 8.0 Hz), 6.56 (1 H, d, *J* = 8.0 Hz), 6.51 (1 H, t, *J* = 7.6 Hz), 4.41 (1 H, br s), 3.48 (1 H, t, *J* = 6.0, 5.6 Hz), 3.32 (1 H, t, *J* = 5.6, 6.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.1, 138.9, 129.2, 119.0, 110.3, 85.6, 49.8, 42.9; ESI–HRMS calcd for $C_8H_{10}IN_4$ $[M + H]^+$: 288.9950, found: *m/z* 288.9949.

To a solution of the-above prepared iodide (3.30 g, 11.45 mmol) in 1,4-dioxane (20 mL) and NEt_3 (20 mL) were added $Pd(PPh_3)_2Cl_2$ (0.80 g, 1.15 mmol) and CuI (0.22 g, 1.15 mmol) under argon at room temperature. The mixture was degassed and stirred at 50 °C for 20 min, and then ethynyltrimethysilane (4.07 mL, 28.63 mmol) was added dropwise over a period of 2 h. The mixture was stirred at 50 °C for another 1.5 h. The catalysts were removed by filtration through a Celite pad, and the filtrate was concentrated under reduced pressure. The residue was purified by SiO_2 column chromatography (EtOAc/hexane = 0:100 to 5:95) to afford the coupling product, *N*-(2-azidoethyl)-2-(2-(trimethylsilyl)ethynyl)benzenamine (2.21g, 75%). $C_{13}H_{18}N_4Si$; brown oil; TLC (EtOAc/hexane = 2.5:97.5) R_f = 0.32; ν_{max} (neat) 2958, 2144, 2101, 1511 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 (1 H, d, *J* = 7.2 Hz), 7.24 (1 H, t, *J* = 9.6, 8.0 Hz), 6.69 (1 H, t, *J* = 7.2 Hz), 6.59 (1 H, d, *J* = 8.4 Hz), 4.931 (1 H, br s), 3.53 (1 H, t, *J* = 5.6, 6.0 Hz), 3.38 (1 H, t, *J* = 5.6 Hz), 0.328 (3 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.4, 132.1, 130.0, 116.7, 109,3, 107,9, 101.5, 100.5, 50.4, 42.3, -0.1 (3 ×) ; ESI–HRMS

calcd for $C_{13}H_{19}N_4Si$ $[M + H]^+$.: 259.1377, found: *m/z* 259.1379.

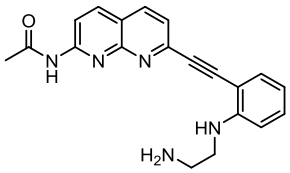
To a solution of the above-prepared coupling product (1.03 g, 3.99 mmol) in MeOH (10 mL) was added KF (1.62 g, 27.93 mmol) under argon at room temperature. The mixture was stirred at room temperature for 3 h, concentrated under reduced pressure, diluted with water, and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified by SiO_2 column chromatography (EtOAc/hexane = 5:95) to afford the title compound **9** (0.72 g, 97%). $C_{10}H_{10}N_4$; brown oil; TLC ((EtOAc/hexane = 5:95) R_f = 0.26; ν_{max} (neat) 3397, 2100, 1511 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.34 (1 H, d, *J* = 7.6 Hz), 7.21 (1 H, t, *J* = 7.6 Hz), 6.65 (1 H, t, *J* = 7.6 Hz), 6.60 (1 H, d, *J* = 7.6 Hz), 4.86 (1 H, s), 3.54 (2 H, t, 6.0 Hz), 3.44–3.39 (3 H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.3, 132.7, 130.2, 116.7, 109.3, 106.7, 83.1, 80.3, 50.4, 42.6; ESI–HRMS calcd for $C_{10}H_{11}N_4$ $[M + H]^+$: 187.0983, found: *m/z* 187.0984.

***N*-(2-(2-(2-(2-Azidoethylamino)phenyl)ethynyl)-1,8-naphthyridin-7-yl)acetamide (10)**



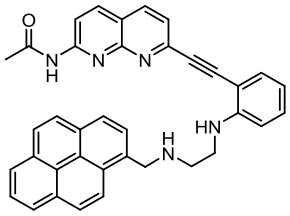
To a solution of chloride **6** (674 mg, 3.05 mmol) in DMF (10 mL) were added NEt_3 (10 mL), $Pd(PPh_3)_2Cl_2$ (310 mg, 0.44 mmol) and CuI (50 mg, 0.26 mmol) under argon at room temperature. The mixture was degassed and stirred at 80 °C for 10 min, and alkynyl compound **9** (682 mg, 3.66 mmol) was added slowly. The mixture was stirred at 80 °C for 16 h. The catalysts were removed by filtration through a pad of Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by SiO_2 column chromatography ($MeOH/CH_2Cl_2$, 5:95) to afford the desired receptor compound **10** (804 mg, 71%). $C_{20}H_{17}N_7O$; yellow solid, mp 176–178 °C; TLC ($MeOH/CH_2Cl_2$, 5:95) R_f = 0.3; IR ν_{max} (neat) 2924, 2854, 2198, 2100, 1695, 1597, 1501, 1318, 747 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.92 (1 H, s), 8.51 (1 H, d, *J* = 8.4 Hz), 8.11 (1 H, d, *J* = 8.4 Hz), 8.03 (1 H, d, *J* = 8.4 Hz), 7.51 (1 H, d, *J* = 8.4 Hz), 7.42 (1 H, d, *J* = 8.4 Hz), 7.24 (1 H, t, *J* = 8.0 Hz), 6.68 (1 H, t, *J* = 8.4 Hz), 6.63 (1 H, d, *J* = 8.4 Hz), 5.23 (1 H, t, *J* = 5.4 Hz), 3.52 (2 H, t, *J* = 5.4 Hz), 3.45 (2 H, q, *J* = 5.4 Hz), 2.29 (3 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.6, 154.2, 153.9, 148.4, 146.0, 138.4, 136.1, 132.8, 130.9, 123.5, 119.2, 116.6, 115.5, 109.3, 105.9, 95.1, 88.5, 50.5, 42.7, 25.3; HRMS (ESI) calcd for $C_{20}H_{17}N_7O$: 372.1573, found: *m/z* 372.1570 $[M + H]^+$.

***N*-(2-(2-(2-(2-Aminoethylamino)phenyl)ethynyl)-1,8-naphthyridin-7-yl)acetamide (3)**



To a solution of azide **10** (1.82 g, 4.90 mmol) in H_2O (4.0 mL) and THF (16.0 mL) was added PPh_3 (6.43 g, 24.5 mmol) under argon at room temperature. The mixture was stirred at room temperature for 4 h. The mixture was concentrated under reduced pressure to remove H_2O and THF. The residue was diluted with water, and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by SiO_2 column chromatography (MeOH/CH_2Cl_2, 5:95 to 2:8) to afford receptor compound **3** (1.62, 96%). $C_{20}H_{19}N_5O$; yellow solid, mp 250.2–251.9 °C; TLC (MeOH/CH_2Cl_2, 1:9) R_f = 0.16; UV-vis λ_{max} (CH_2Cl_2): 351 nm (ε = 4800) and 392 nm (ε = 4600); λ_{max} (DMSO): 353 nm (ε = 14500) and 406 nm (ε = 15100); FL λ_{max} 530 nm (CH_2Cl_2), λ_{max} 570 nm (DMSO); IR ν_{max} (neat) 2925, 2199 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz) δ 8.41 (1 H, d, *J* = 8.8 Hz), 8.29 (2 H, d, *J* = 8.4Hz), 7.65 (1 H, d, *J* = 8.0 Hz), 7.40 (1 H, dd, *J* = 1.2, 7.6 Hz), 7.28 (1 H, dt, *J* = 1.6, 8.4 Hz), 6.76 (1 H, d, 8.4 Hz), 6.65 (1 H, t, *J* = 7.6 Hz), 3.39 (2 H, t, *J* = 6.4 Hz), 2.93 (2 H, t, *J* = 5.6 Hz), 2.26 (3 H, s); ^{13}C NMR (CD_3OD, 100 MHz) δ 172.9, 156.5, 155.8, 151,9, 147.9, 140.3, 139.3, 134.5, 132.9, 124.9, 121.3, 117.4, 116.9, 111.2, 106.5, 95.3, 91.3, 46.8, 41.7, 24.5; HRMS (ESI) calcd for $C_{20}H_{20}N_5O$: 346.1668, found: *m*/*z* 346.1667 $[M + H]^+$.

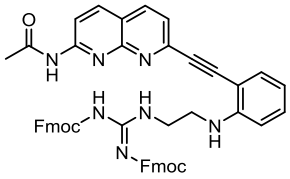
***N*-(2-(2-(2-(2-((Pyren-1-yl)methylamino)ethylamino)phenyl)ethynyl)-1,8-naphthyridin-7-yl)acetamide (4)**



A solution of amine **3** (50 mg, 0.14 mmol) and pyrene-1-carbaldehyde (67 mg, 0.29 mmol) in cosolvent MeOH/DMSO (1:1, 0.5 mL) was stirred under argon at room temperature for 30 min; and then $NaBH_3CN$ (27 mg, 0.44 mmol) was added quickly. The mixture was stirred at room temperature for 20 h, and then concentrated under reduced pressure. The residue was extracted with CH_2Cl_2 and water (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography (MeOH/CH_2Cl_2 = 2.5:97.5 to 5:95) to afford receptor compound **4** (49 mg, 60%). $C_{37}H_{29}N_5O$; UV-vis λ_{max} (CH_2Cl_2): 326 nm (ε = 20700), 344 nm (ε = 20700), 397 nm (ε = 8100); λ_{max} (DMSO): 330 nm (ε = 23800), 346 nm (ε = 31400), 399 nm (ε = 10900); FL λ_{max} 523 nm (CH_2Cl_2), 542 nm (DMSO); IR ν_{max} (neat) 2197, 1697, 1596, 1499, 746 cm^{-1}; ^1H NMR (CD_3Cl, 400 MHz) δ 9.19 (1 H, s), 8.10 (1 H, d, *J* = 9.2 Hz), 8.03 (2 H, dd, *J* = 9.2, 3.2 Hz,), 7.89–7.80 (4 H, m), 7.78–7.70 (3 H, m), 7.52 (1 H, d, *J* = 8.8 Hz), 7.21 (1 H, t, *J* = 6.8 Hz), 7.15 (1 H, d, *J* = 8.0 Hz), 6.69 (1 H, d, *J* = 8.4 Hz), 6.61 (1 H, t, *J* = 4.4 Hz), 5.55 (1 H, br s), 4.57 (2 H, s), 3.45 (2 H, s), 3.26 (2 H, d, *J* = 5.2 Hz), 2.10 (3 H, s); ^{13}C NMR

(CD_3Cl, 400 MHz) δ 170.0, 154.0, 153.6, 149.4, 145.5,138.1, 135.9, 132.6, 131.4, 131.0, 130.9, 130.3, 129.2, 128.0, 127.7, 127.4, 127.1, 125.9, 125.3, 125.2 (2 ×), 124.5, 124.4, 124.2, 122.6, 122.3, 118.8, 116.9, 115.2, 109.9, 106.0, 95.1, 89.2, 49.9, 47.4, 41.3, 24.7; ESI–HRMS calcd for $C_{37}H_{30}N_5O$: 560.2450, found: *m/z* 560.2451 $[M + H]^+$.

***N*-(2-(2-(2-(2-(2-(1,3-bis(fluorenylmethyloxycarbonyl))guanidine)aminoethylamino)phenyl)ethynyl)-1,8-naphthyridin-7-yl)acetamide (13).**

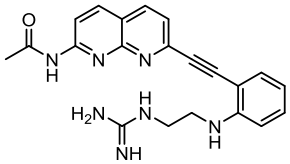


To a solution of *S*-methylisothiourea hemisulfate salt (100 mg, 0.718 mmol) in CH_2Cl_2 and saturated aqueous $NaHCO_3$ (7:3, 5 mL) was added fluorenylmethyloxycarbonyl chloride (Fmoc-Cl, 409 mg, 1.58 mmol). The mixture was stirred at room temperature for 16 h, diluted with water and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography (EtOAc/hexane = 5:95) to afford 1,3-bis(fluorenylmethyloxycarbony)-2-methyl-2-thiopseudourea (**12**) (347.7 mg, 95%). $C_{32}H_{26}N_2O_4S$; white solid; mp 95.3–98.6 °C; TLC (EtOAc/hexane = 5:95) R_f = 0.3; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 12.01 (1 H, br s), 7.79 (4 H, d, *J* = 6.0 Hz), 7.69 (2 H, br), 7.60 (2 H, br), 7.45 (4 H, t, *J* = 7.6 Hz), 7.36 (4 H, t, *J* = 7.2 Hz), 4.48 (4 H, d, *J* = 7.2 Hz), 4.38 (1 H, br), 4.28 (1 H, br), 2.52 (3 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.9, 161,1, 151.5, 143.6, 143.0, 141.2 (8 ×), 127.9 (2 ×), 127.8 (2 ×), 127.1 (4 ×), 125.2, 124.9, 120.0 (4 ×), 68.6, 68.5, 46.6 (2 ×), 14.7; ESI–HRMS calcd for $C_{32}H_{27}N_2O_4S$ $[M + H]^+$: 535.1696, found: *m/z* 535.1698.

To a solution of amine **3** (10 mg, 0.029 mmol), diisopropylethylamine (5.3 μL) and $HgCl_2$ (8.68 mg, 0.029 mmol) in anhydrous DMF (1 mL) was added a solution of the above-prepared thiopseudourea (15.6 mg, 0.029 mmol) in anhydrous DMF (790 μL, 0.037 M) over a period of 2 h at room temperature under an atmosphere of argon. The mixture was stirred for another 0.5 h at room temperature, concentrated under reduced pressure, and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated. The residue was purified by SiO_2 column chromatography ($MeOH/CH_2Cl_2$ = 0:100 to 5:95) to afford the Fmoc-protecting product **13** (17 mg, 70%). $C_{51}H_{41}N_7O_5$; TLC ($MeOH/CH_2Cl_2$ = 5:95) R_f = 0.33; ^{1}H NMR (CD_3Cl, 400 MHz) δ 11.89 (1 H, br s), 9.01 (1 H, d, *J* = 12 Hz), 8.65 (1 H, br s), 8.37 (1 H, d, *J* = 8.8 Hz), 7.93 (1 H, d, *J* = 8.8 Hz), 7.86 (1 H, d, *J* = 8.4 Hz), 7.76 (2 H, d, *J* = 7.2 Hz), 7.69 (4 H, d, *J* = 7.6 Hz), 7.46–7.21 (15 H, m), 5.36 (1 H, br s), 4.39 (3 H, m), 4.21 (2 H, d, *J* = 7.2 Hz), 4.03 (1 H, t, *J* = 7.2 Hz), 3.79 (2 H, q, *J* = 5.6 Hz), 3.59 (2 H, d, *J* = 5.6 Hz), 2.18 (3 H, s); ^{13}C NMR (CD_3Cl, 100 MHz) δ 169.6, 163.9, 156.4, 154.3, 154.2, 153.7, 149.5, 146.7, 144.1 (2 ×), 143.0 (2 ×), 141.2

(2 ×), 141.1 (2 ×), 127.9 (2 ×), 127.6 (2 ×), 127.2 (2 ×), 127.1 (2 ×), 125.3 (2 ×), 124.9 (2 ×), 123.6, 120.0 (2 ×), 119.9 (2 ×), 119.4, 116.7, 115.2, 110.0, 106.0, 95.3, 89.2, 68.4, 67.8, 47.0, 46.4, 41.9, 40.0, 24.9; ESI–HRMS calcd for $C_{51}H_{42}N_7O_5$ $[M + H]^+$: 832.3247, found: *m/z* 832.3257.

***N*-(2-(2-(2-(2-Guanidinoethylamino)phenyl)ethynyl)-1,8-naphthyridin-7-yl)acetamide (5).**



To a solution of compound **13** (49 mg, 0.06 mmol) in anhydrous DMF (0.5 mL) was added a solution of tetrabutylammonium fluoride (TBAF, 1.19 mmol, 0.1 M) in DMF (11.9 mL). The mixture was stirred at room temperature for 10 min, and then concentrated by rotary evaporation under reduced pressure. The residue was chromatographed on a reversed-phase column by elution with H_2O/MeOH (10:3) to afford the guanidine-hinged compound **5** (20 mg, 90%). $C_{21}H_{21}N_7O$; ^{1}H NMR (CD_3OD, 400 MHz) δ 8.40 (2 H, m), 7.70 (1 H, d, *J* = 8.4 Hz), 7.44 (1 H, dd, *J* = 1.2, 7.6 Hz), 7.32 (1 H, d, *J* = 1.6 Hz), 7.30 (1 H, t, *J* = 6.8 Hz), 6.80 (1 H, d, *J* = 8.4 Hz), 6.71 (1 H, t, *J* = 7.6 Hz), 4.58 (2 H, br), 3.56 (4 H, dd, *J* = 4.8, 7.2 Hz), 2.28 (3 H, s); ^{13}C NMR (CD_3OD, 100 MHz) δ 171.9, 158.2, 155.7, 154.8, 150.4, 146.7, 139.5, 138.6, 133.5, 132.1, 124.0, 120.4, 117.0, 116.2, 110.3, 105.9, 94.3, 90.1, 42.2, 41.0, 23.5; ESI–HRMS calcd for $C_{21}H_{22}N_7O$: 388.1886, found: *m/z* 388.1885 $[M + H]^+$.

Guanosine 5′-monophosphate free acid. A solution of guanosine 5′-monophosphate disodium salt hydrate (1.0 g, 2.5 mmol) in water and Dowex 50W×8 resin (2.0 g) were stirred at room temperature for 30 min. The resin was filtered, and the clear filtrate was concentrated under reduced pressure to afford the corresponding free acid GMP (690 mg, 99%). $C_{10}H_{14}N_5O_8P$; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 10.64 (1 H, br), 7.89 (1 H, s), 6.48 (2 H, br), 5.72 (1 H, d, *J* = 6.4 Hz), 4.48 (1 H, t, *J* = 6.0 Hz), 4.12–3.98 (2 H, m), 3.95 (1 H, m); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 156.7, 153.7, 151.5, 135.4, 116.6, 86.1, 83.15 (d, *J* = 8.10 Hz), 73.3, 70.6, 65.2 (d, *J* = 4.9 Hz); ESI–HRMS calcd for $C_{10}H_{14}N_5O_5$ $[M + H]^+$: 364.0658, found: *m/z* 364.0657.

Adenosine 5′-monophosphate free acid. A solution of adenosine 5′-monophosphate disodium salt hydrate (1.0 g, 2.6 mmol) in water and Dowex® 50W×8 resin (2.0 g) were stirred at room temperature for 30 min. The resin was filtered, and the clear filtrate was concentrated under reduced pressure to afford the corresponding free acid AMP (894 mg, 99%). $C_{10}H_{14}N_5O_7P$; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.36 (1 H, s), 8.17 (1 H, s), 7.46 (2 H,

br s), 5.93 (1 H, d, *J* = 5.6 Hz), 4.59 (1 H, t, *J* = 5.2 Hz), 4.19 (1 H, t, *J* = 3.2 Hz), 4.06 (2 H, m, *J* = 6 Hz), 3.95 (1 H, q, *J* = 6 Hz); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 156.7, 153.7, 151.5, 135.4, 116.6, 86.1, 83.15 (d, *J* = 8.10 Hz), 155.7, 152.2, 149.5, 139.5, 119.0, 87.1, 83.2 (d, *J* = 8 Hz), 73.4, 70.5, 65.3; ESI–HRMS calcd for $C_{10}H_{14}N_5O_5$ $[M + H]^+$: 348.0709, found: *m/z* 348.0710.

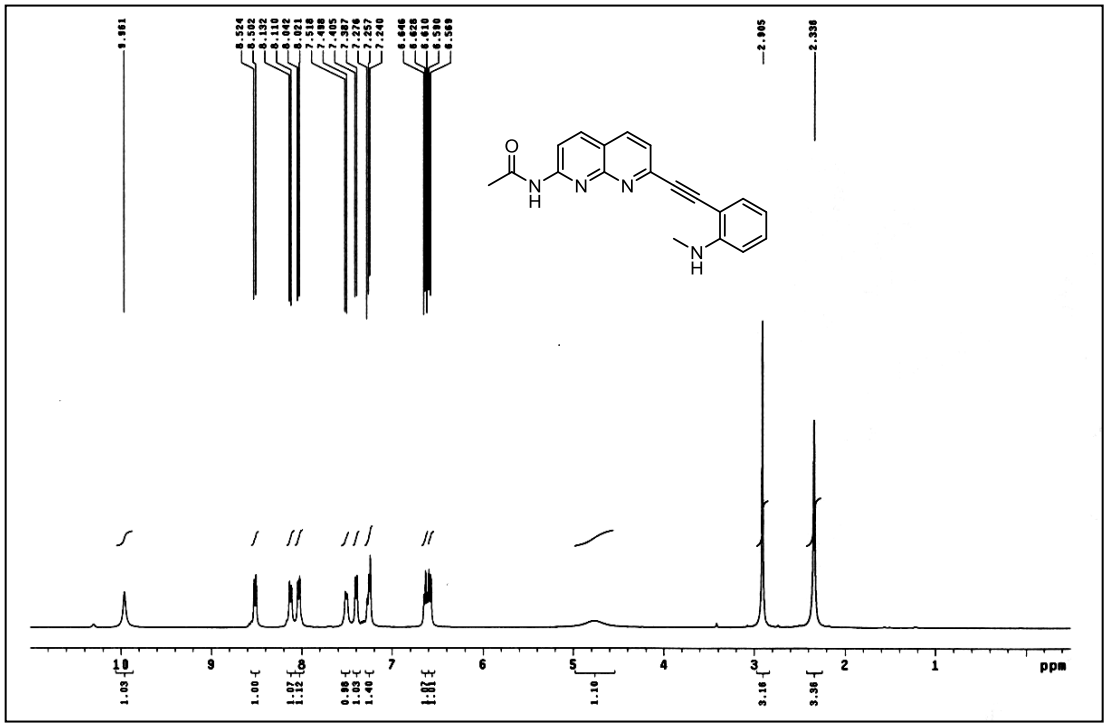


Figure S1. ^{1}H NMR spectrum of compound **1** ($CDCl_3$, 400 MHz)

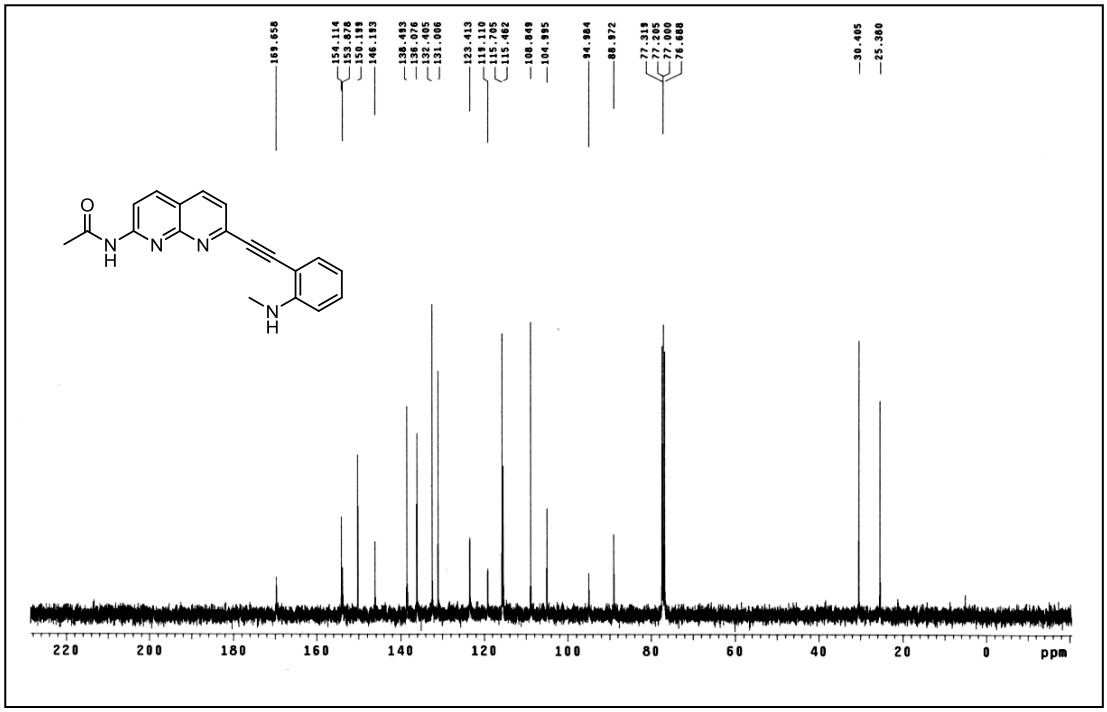


Figure S2. ^{13}C NMR spectrum of compound **1** ($CDCl_3$, 100 MHz)

(A) (B)

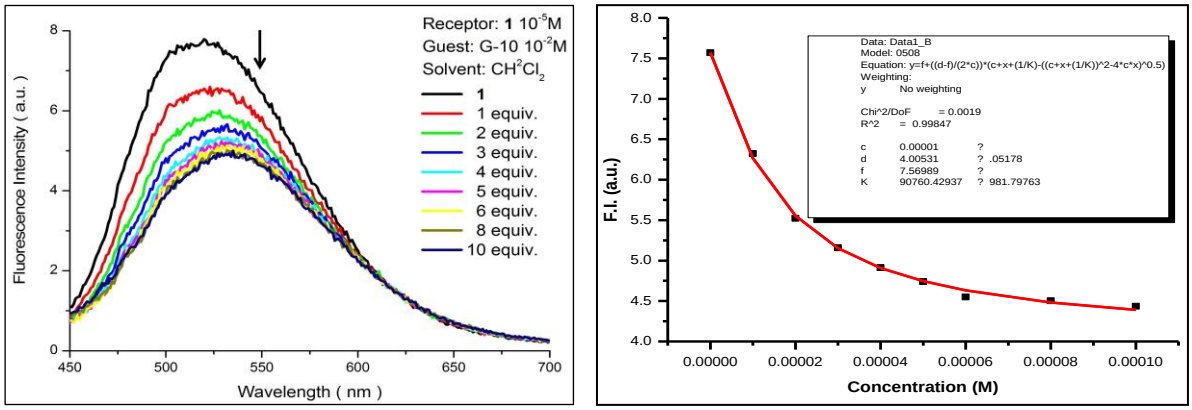


Figure S3. (A) Fluorescence titration of receptor **1** (1×10^{-5} M) upon incremental additions of 9-decylguanine (G10, 1×10^{-2} M) in CH_2Cl_2 solution. Excitation wavelength: 417 nm. (B) Binding isotherm of **1**–G10 obtained from the changes of intensity at the highest point of each curve (518–535 nm) in fluorescence titration; K_{ass} = 90800 ± 980 M^{-1} in CH_2Cl_2 solution using nonlinear least-squares curve-fitting method.[19]

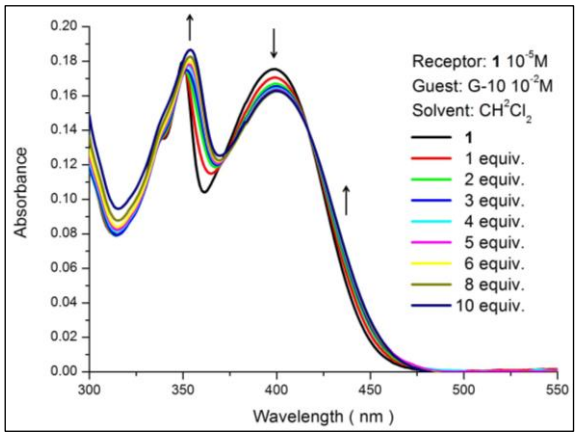


Figure S4. UV-vis titration of receptor **1** (1×10^{-5} M) upon incremental additions of 9-decylguanine (1×10^{-2} M) in CH_2Cl_2 solution.

(A) (B)

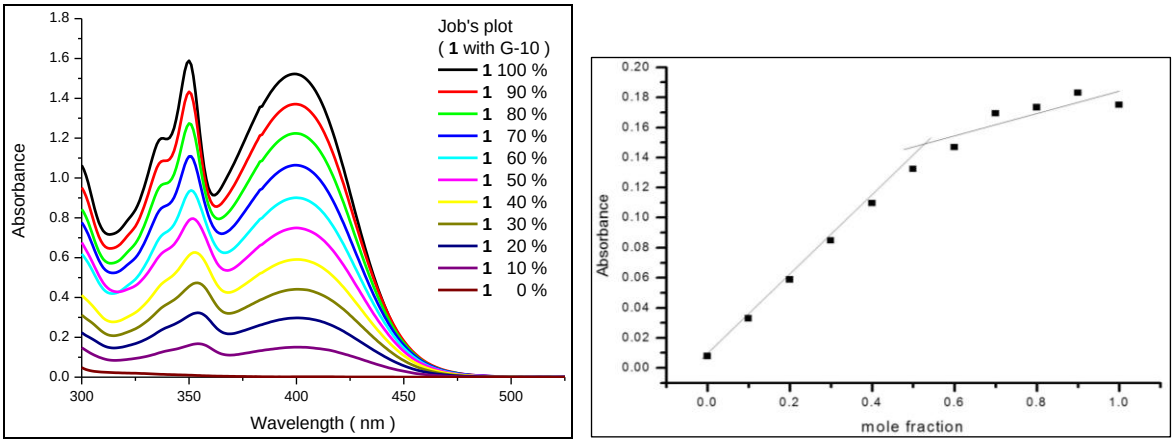


Figure S5. Job's plot for the 1:1 complex of **1**–G10 in CH_2Cl_2 solution. Stock solutions of receptor compound (**1**) and analyte (G10) were prepared in the same concentration (1×10^{-5} M). (A) Absorption spectra of eleven sample solutions containing **1** and G10 in total volume of 2 mL; (B) Changes of the 400-nm absorbance were monitored as a function of receptor–analyte molar ratios (0:10 to 10:0).

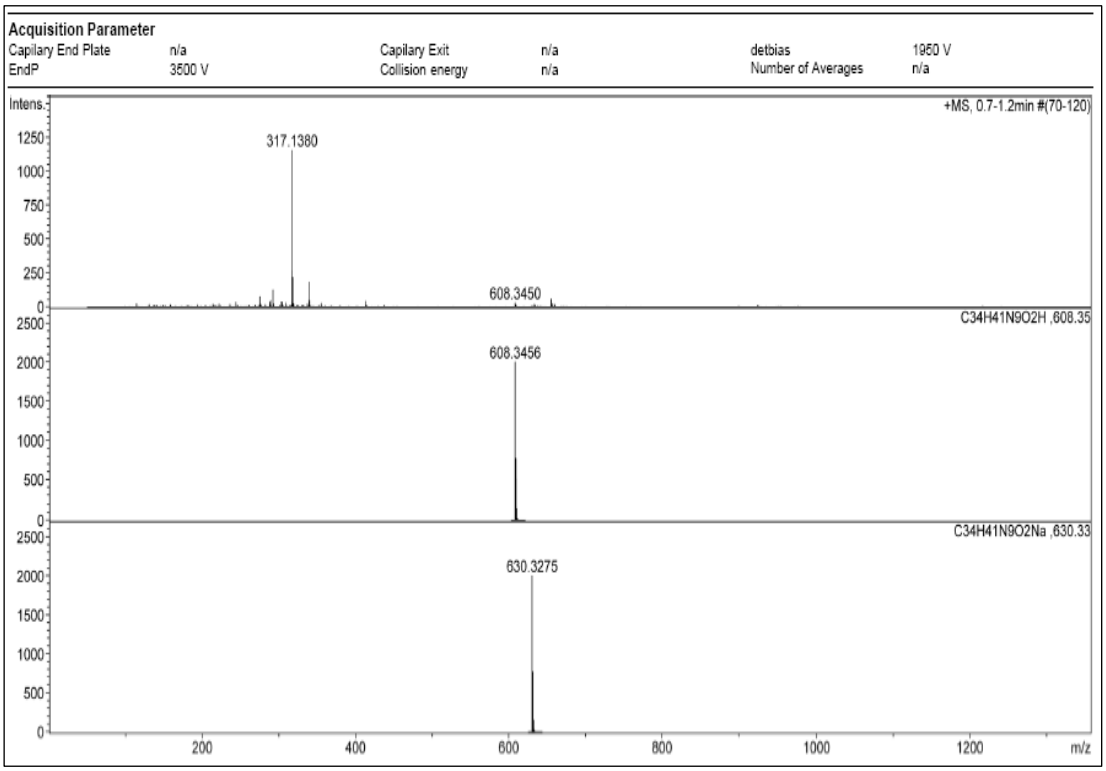


Figure S6. ESI–MS analysis for the 1:1 complex of **1**–G10. Calcd for $C_{34}H_{42}N_9O_2$: 608.3461; found: *m*/*z* 608.3450 $[M + H]^+$. Calcd for $C_{34}H_{41}N_9NaO_2$: 630.3281; found: *m*/*z* 608.3275 $[M + Na]^+$.

(A) (B)

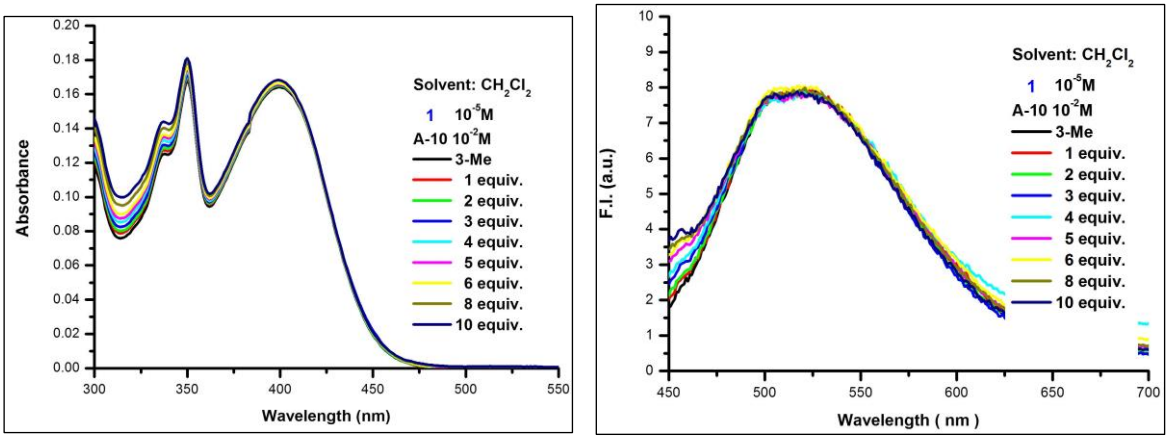


Figure S7. Titration of receptor **1** (1×10^{-5} M) upon incremental additions of 9-decyladenine (A10, 1×10^{-2} M) in CH_2Cl_2 solution. (A) UV-vis titration; (B) Fluorescence titration (λ_{ex} = 400 nm).

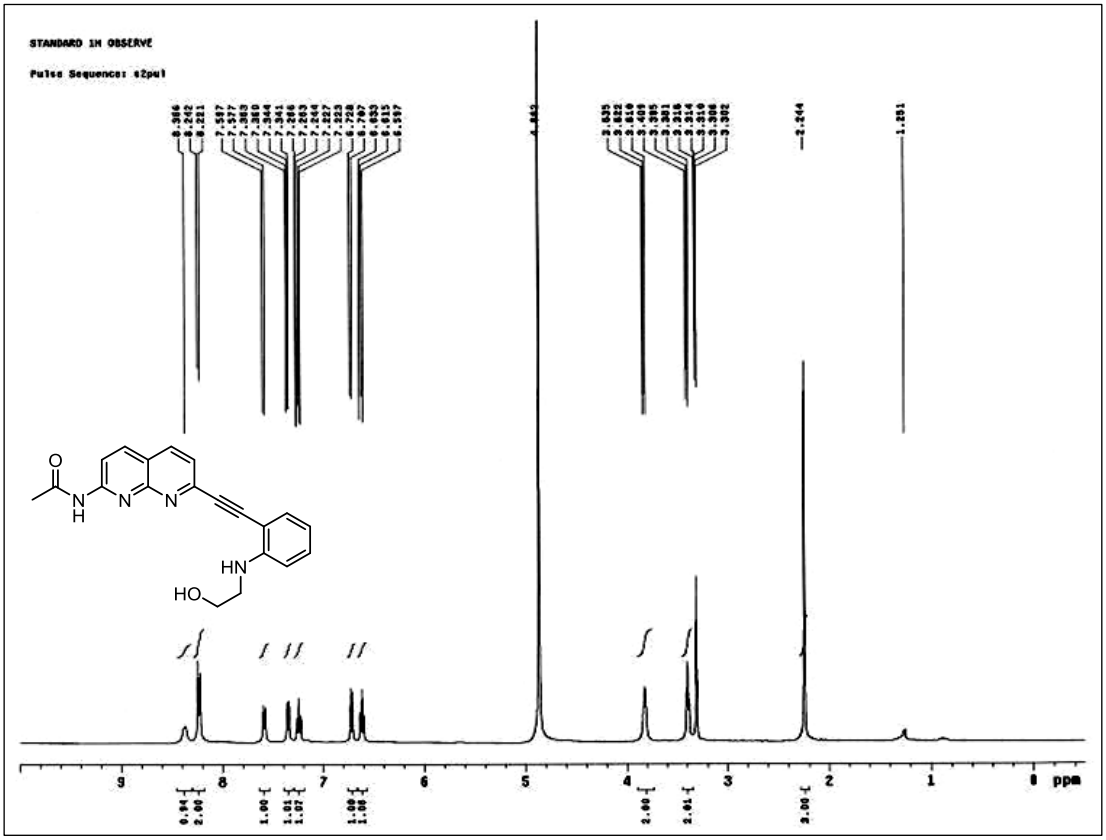


Figure S8. ^{1}H NMR spectrum of compound **2** (CD_3OD, 400 MHz)

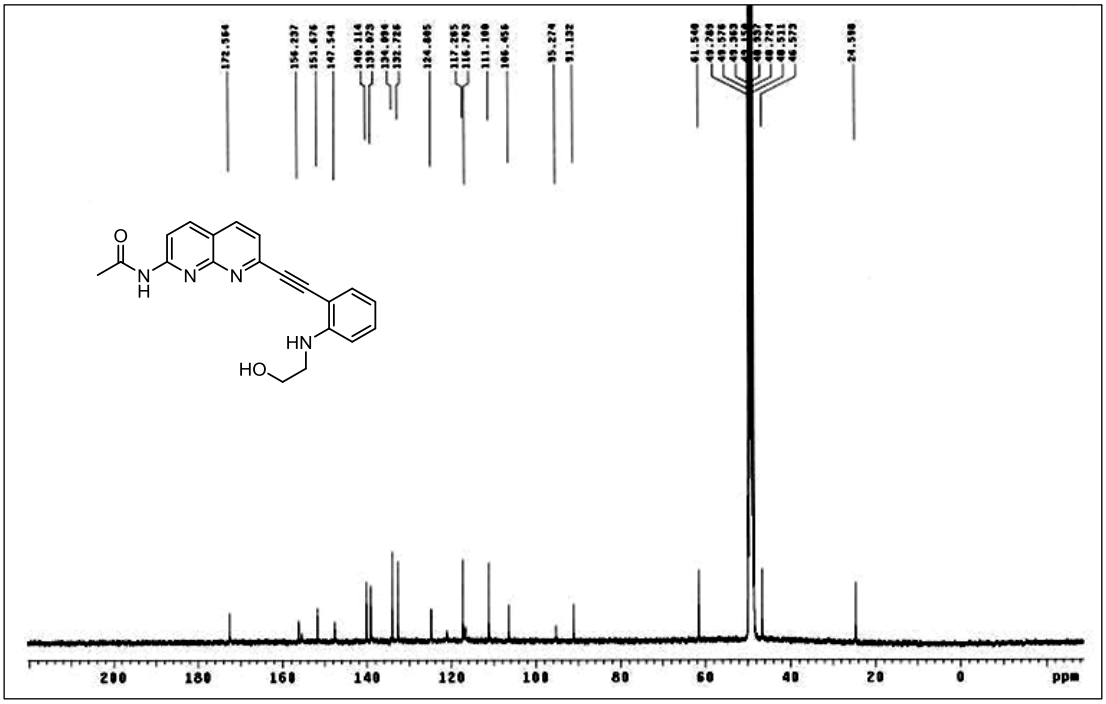


Figure S9. ^{13}C NMR spectrum of compound **2** (CD_3OD, 100 MHz)

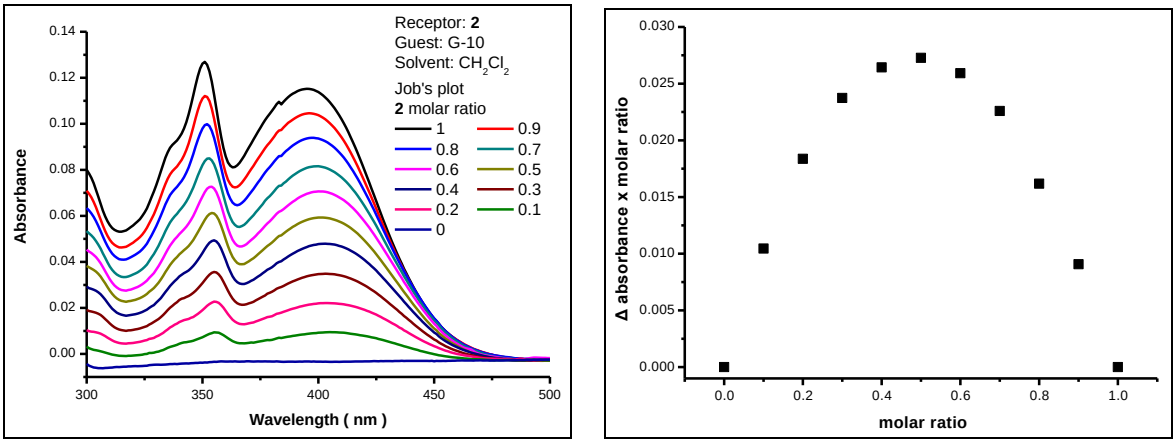


Figure S10. Job's plot for the 1:1 complex of **2**–G10 in CH_2Cl_2 solution. Stock solutions of receptor compound (**2**) and analyte (G10) were prepared in the same concentration (1×10^{-5} M). (A) Absorption spectra of eleven sample solutions containing **2** and G10 in total volume of 2 mL; (B) Changes of the 400-nm absorbance were monitored as a function of receptor–analyte molar ratios (0:10 to 10:0).

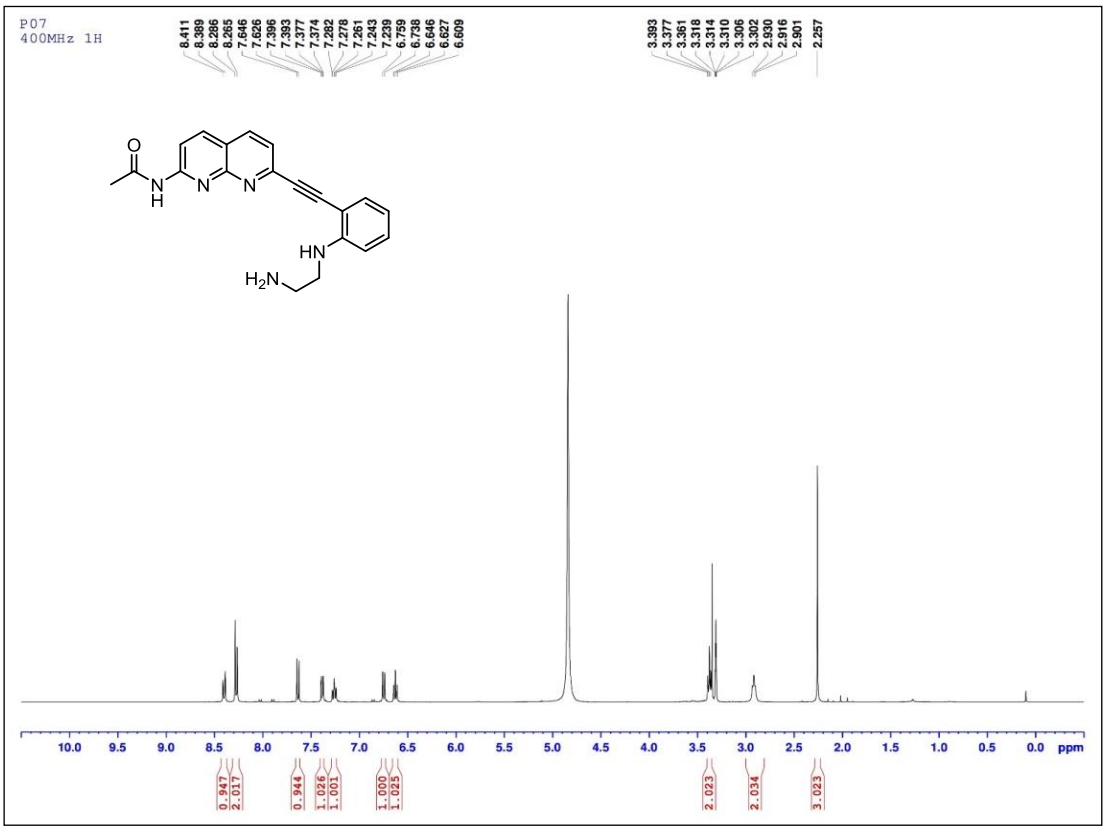


Figure S11. ^{1}H NMR spectrum of compound **3** (CD_3OD, 400 MHz)

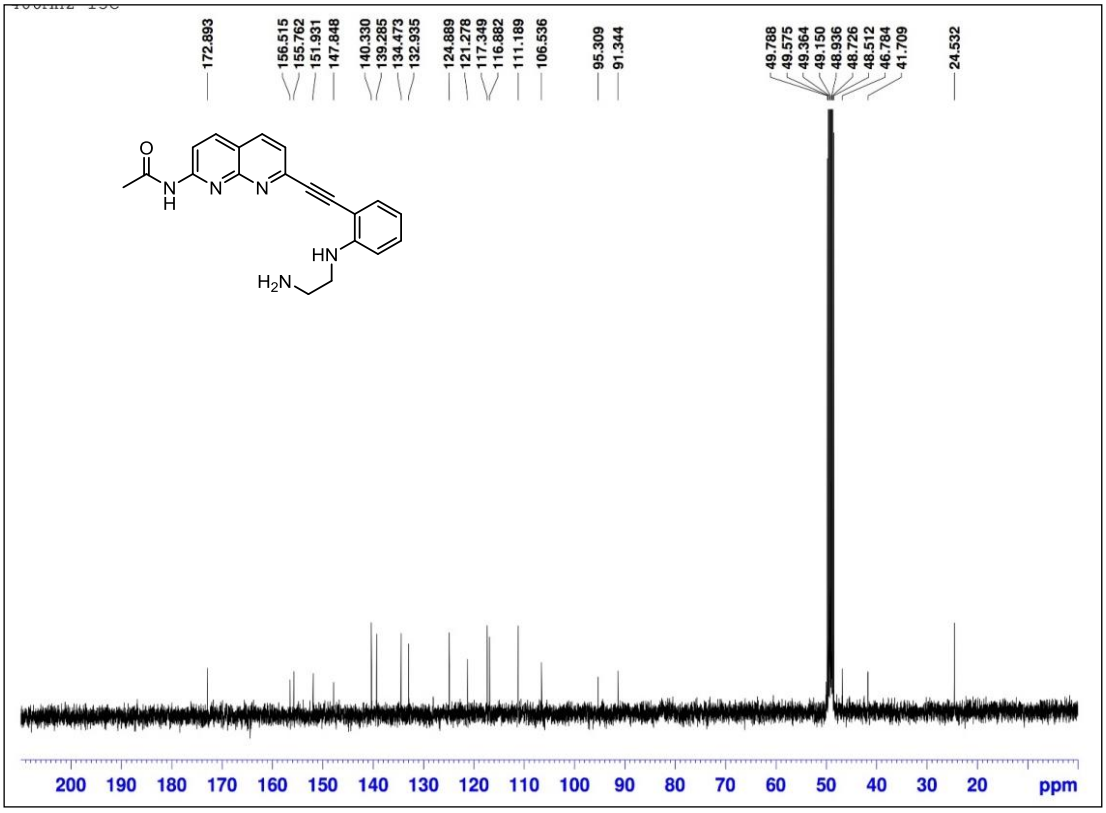


Figure S12. ^{13}C NMR spectrum of compound **3** (CD_3OD, 100 MHz)

(A) (B)

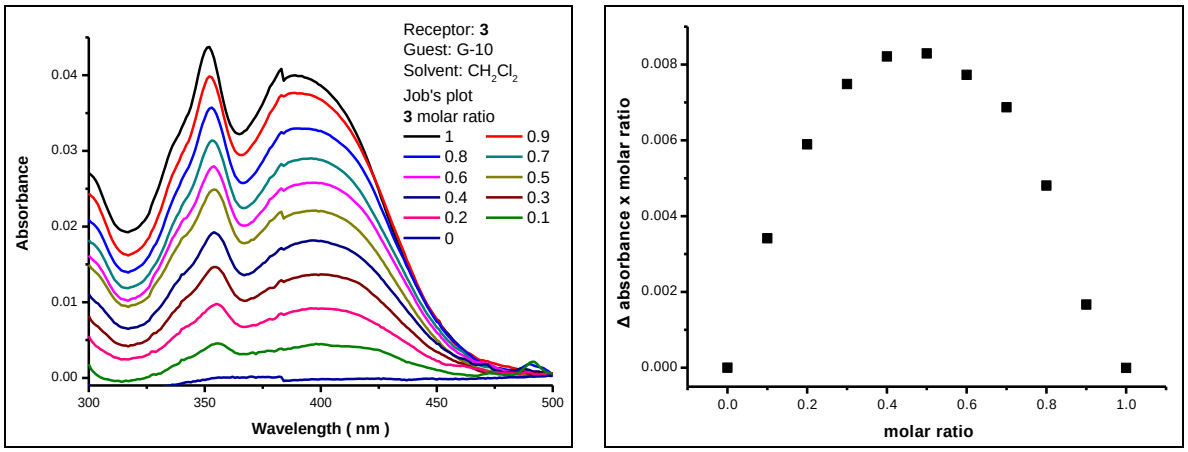


Figure S13. Job's plot for the 1:1 complex of **3**–G10 in CH_2Cl_2 solution. Stock solutions of receptor compound (**3**) and analyte (G10) were prepared in the same concentration (1×10^{-5} M). (A) Absorption spectra of eleven sample solutions containing **3** and G10 in total volume of 2 mL; (B) Changes of the 400-nm absorbance were monitored as a function of receptor–analyte molar ratios (0:10 to 10:0).

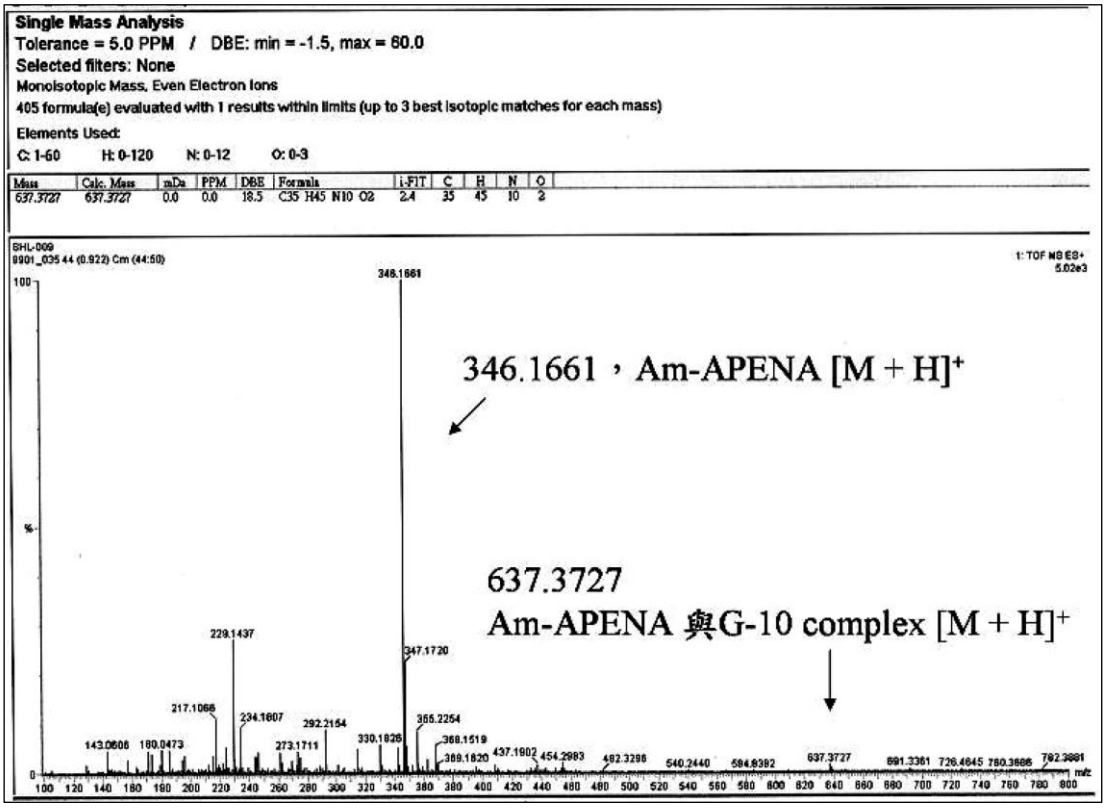


Figure S14. ESI–MS analysis for the 1:1 complex of **3**–G10. Calcd for $C_{35}H_{43}N_9O_3$: 637.3489; found: *m*/*z* 637.3727 $[M + H]^+$.

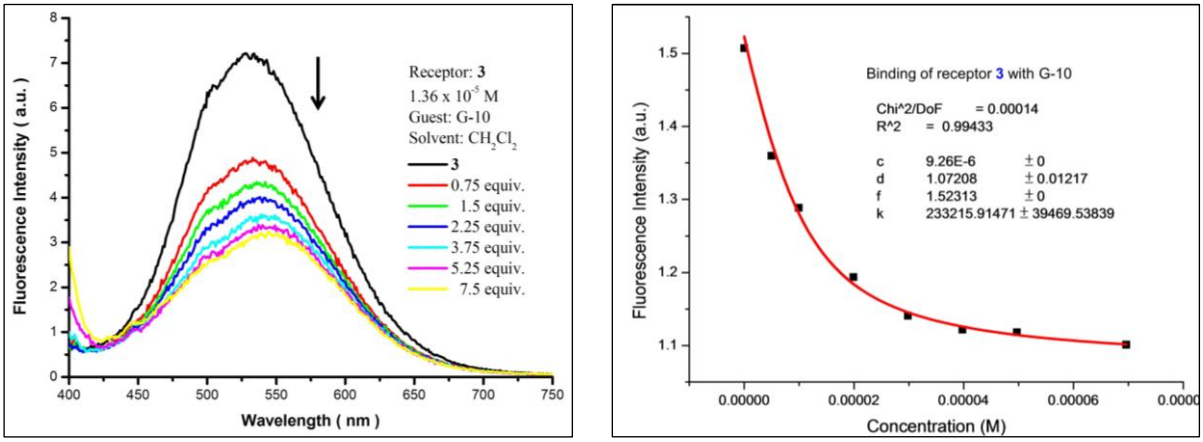


Figure S15. (A) Fluorescence titration of receptor **3** (1.36×10^{-5} M) upon incremental additions of 9-decylguanine (1×10^{-2} M) in CH_2Cl_2 solution. Excitation wavelength: 392 nm. (B) Binding isotherm of **3**–G10 obtained from the changes of intensity at the highest point of each curve (528–545 nm) in fluorescence titration; K_{ass} = 233200 ± 39500 M^{-1} in CH_2Cl_2 solution using non-linear least squares curve-fitting method.[19]

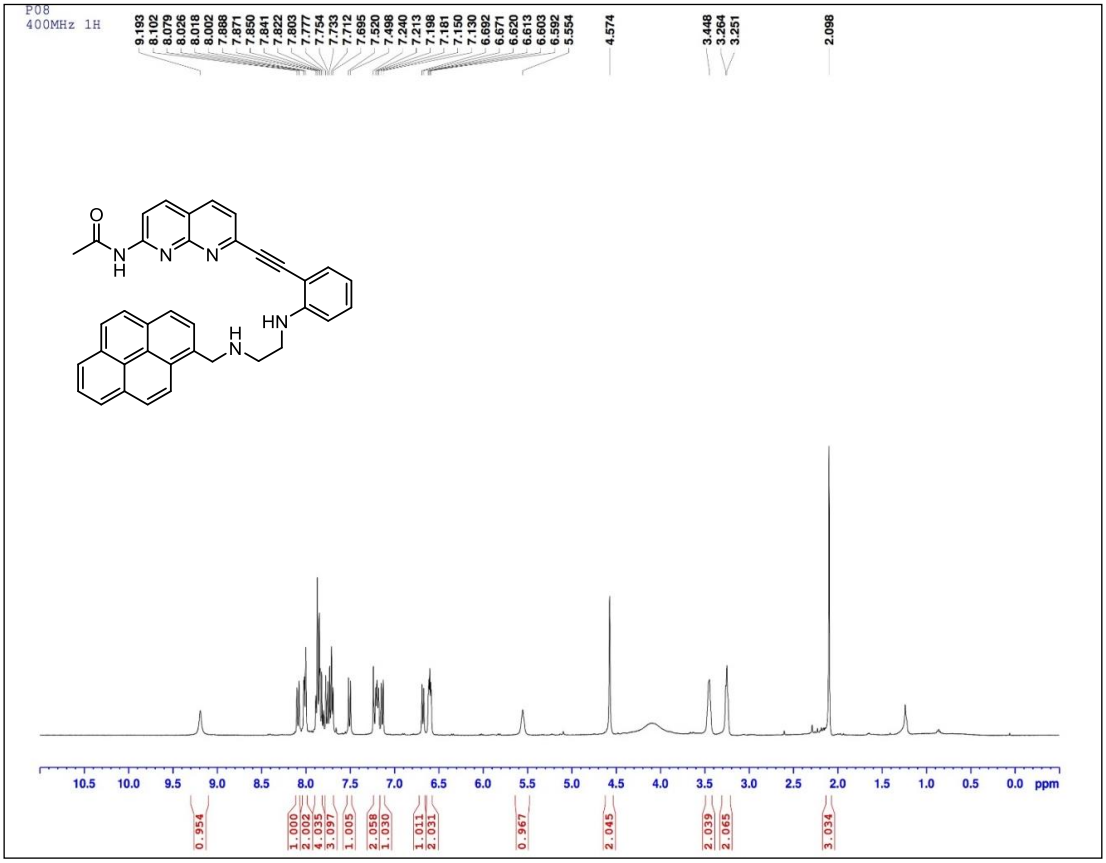


Figure S16. ^{1}H NMR spectrum of compound **4** ($CDCl_3$, 400 MHz)

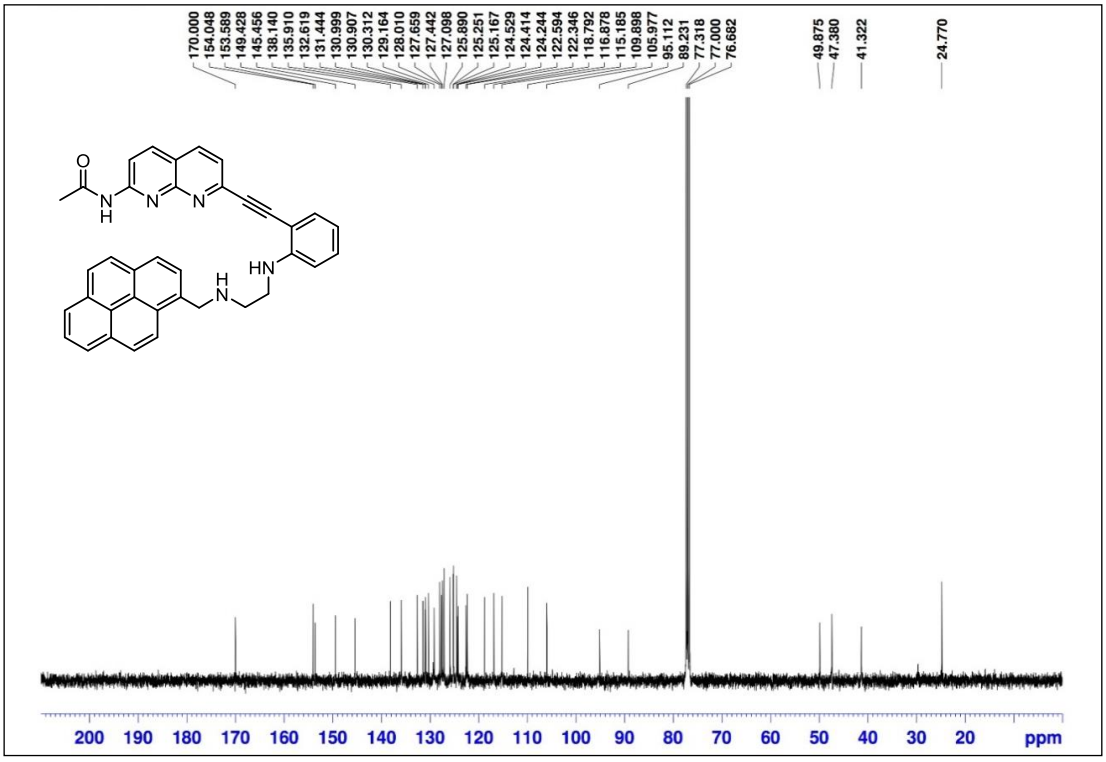


Figure S17. ^{13}C NMR spectrum of compound **4** ($CDCl_3$, 100 MHz)

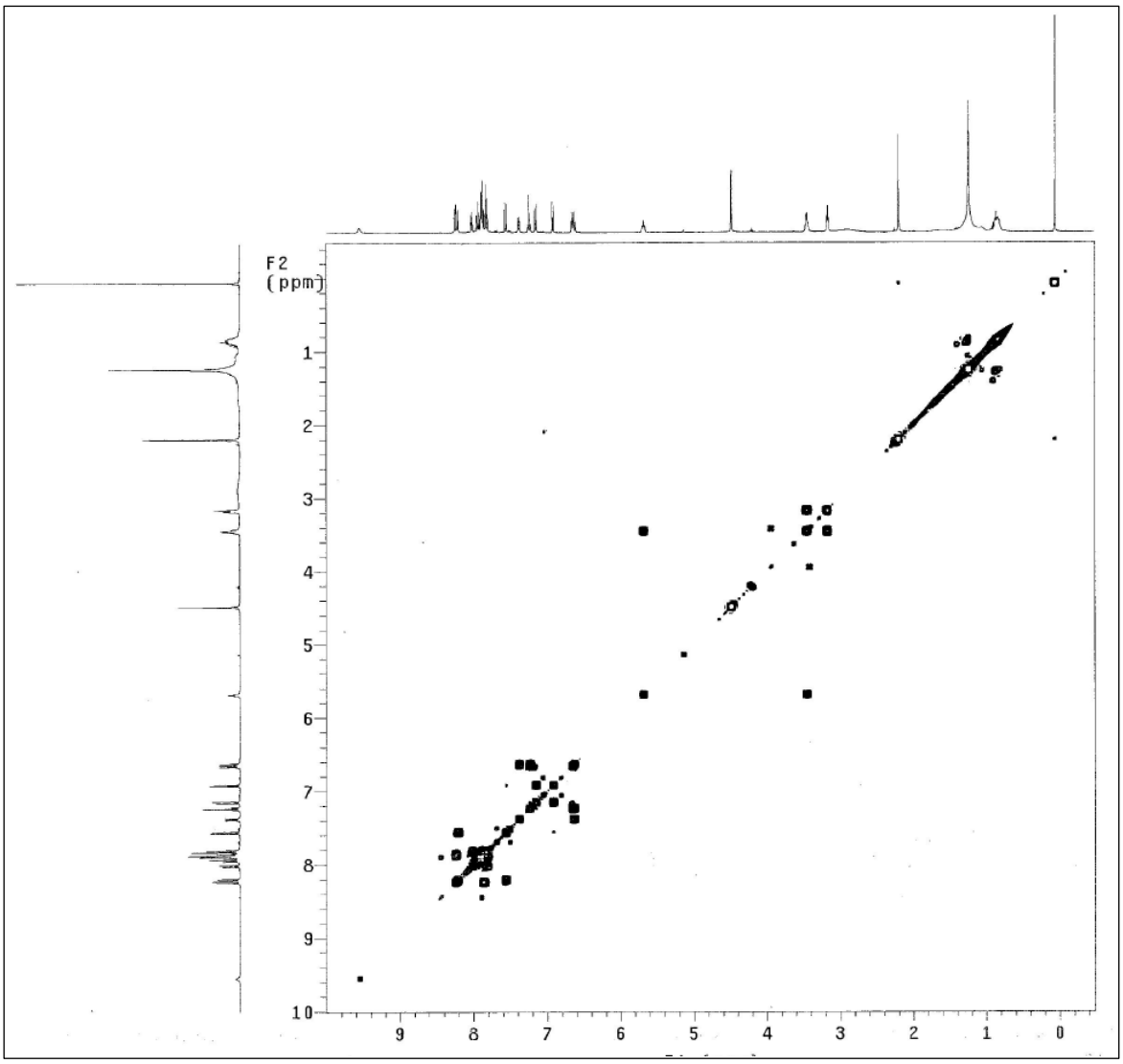


Figure S18. $^{1}H–^{1}H$ COSY spectrum of compound **4** ($CDCl_3$, 400 MHz).

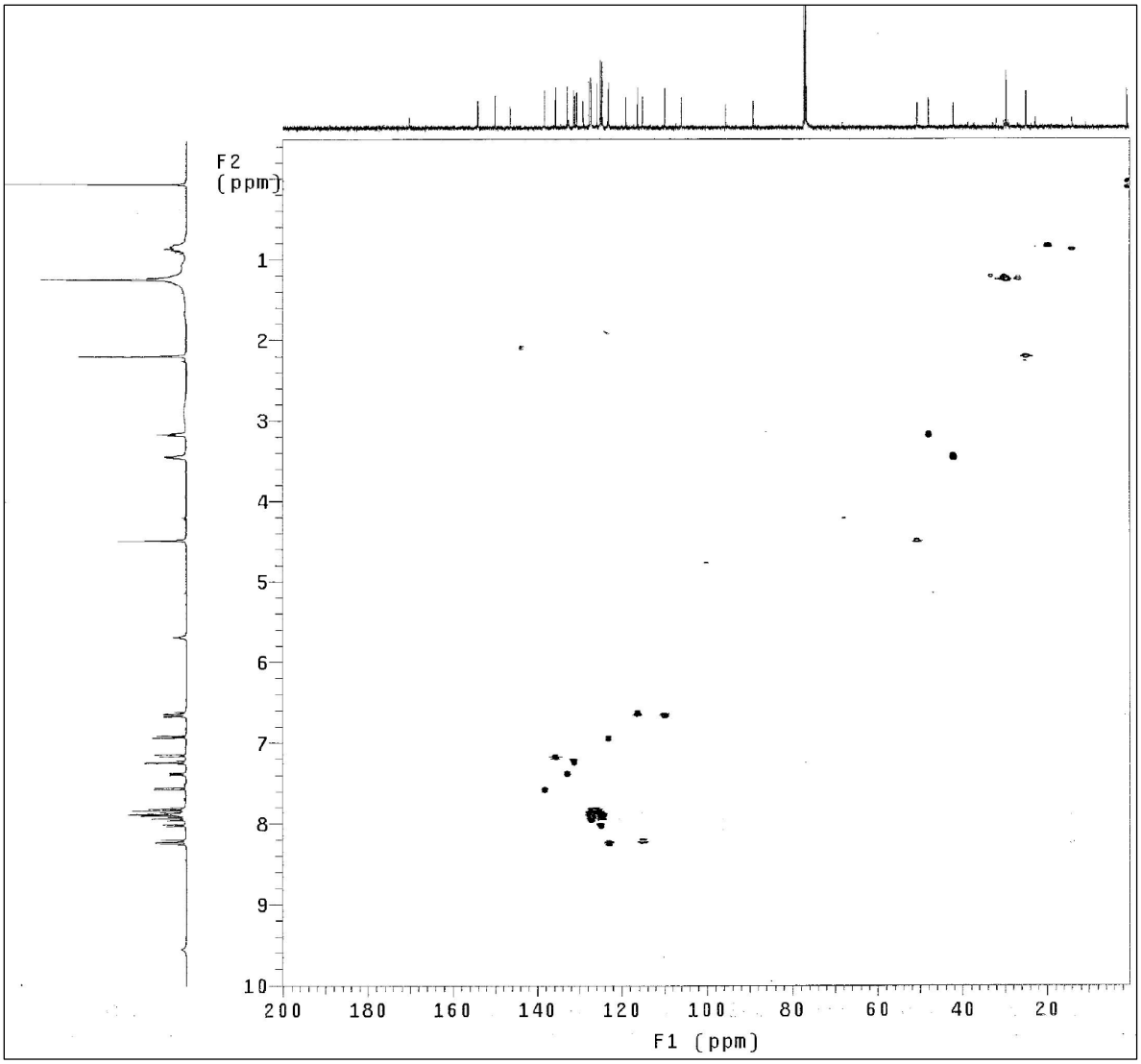


Figure S19. HMQC spectrum of compound **4** ($CDCl_3$, 400 MHz).

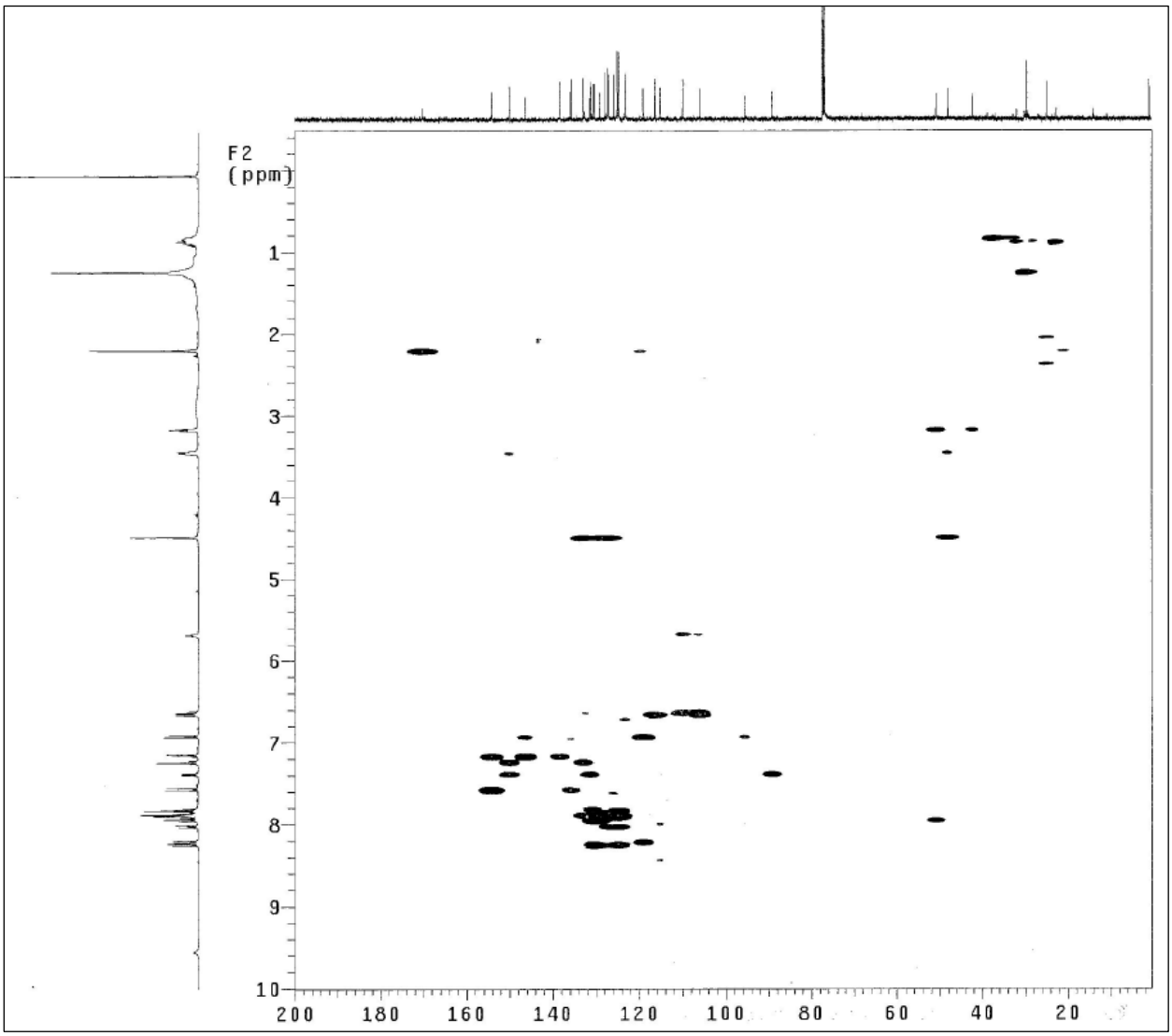


Figure S20. HMBC spectrum of compound **4** ($CDCl_3$, 400 MHz).

Table S1. Photophysical properties of pyrene-hinged molecule **4**.

solvent	dielectric constant	λ_{abs} (nm) (ε)[a]	λ_{em} (nm)[b]
EtOAc	6.0	327 (10800), 342 (15600), 395 (5100)	503
THF	7.5	328 (13100), 343 (18700), 394 (6700)	503
CH_2Cl_2	8.9	326 (20700), 344 (20700), 397 (8100)	523
MeOH	33	326 (24000), 341 (27900), 398 (9400)	none[c]
MeCN	36	326 (29300), 346 (32900), 391 (12800)	none[c]
DMSO	47	330 (23800), 346 (31400), 399 (10900)	542

[a] Extinction coefficient ε is shown in a unit of $M^{-1}\cdot cm^{-1}$.

[b] Excitation wavelength at 400 nm.

[c] No detectable fluorescence.

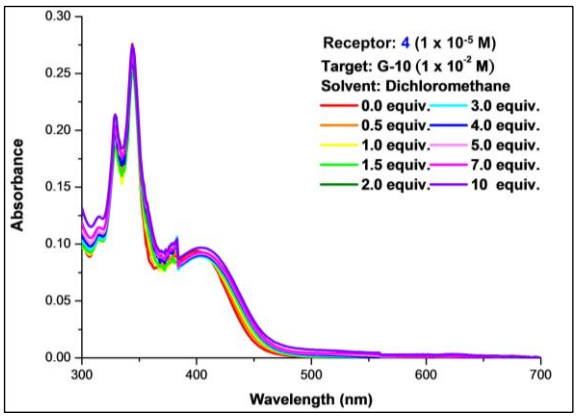


Figure S21. UV-vis titration of receptor **4** (1×10^{-5} M) upon incremental additions of 9-decylguanine (G10, 1×10^{-2} M) in CH_2Cl_2 solution.

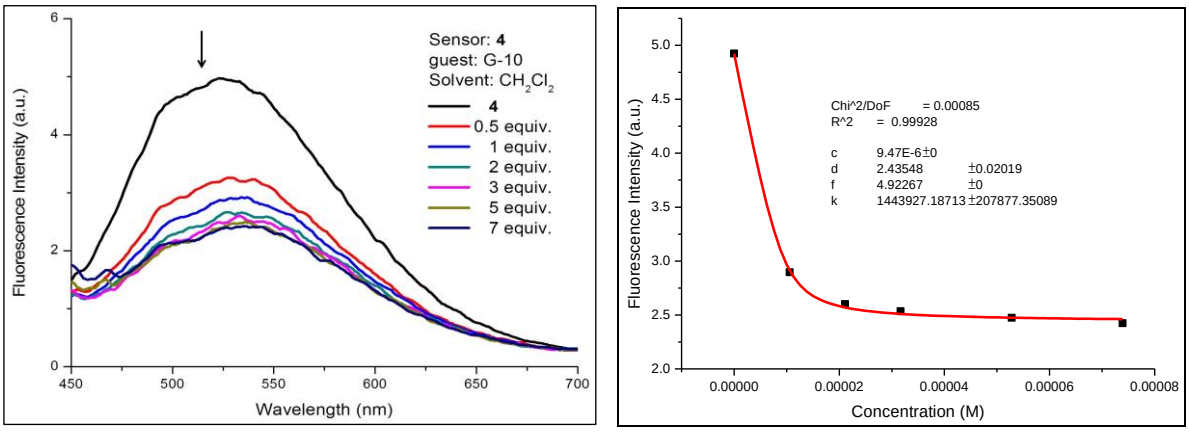


Figure S22. (A) Fluorescence titration of receptor **4** (1×10^{-5} M) upon incremental additions of 9-decylguanine (1×10^{-2} M) in CH_2Cl_2 solution. Excitation wavelength: 417 nm. (B) Binding isotherm of **4**–G10 obtained from the changes of intensity at the highest point of each curve (523–536 nm) in fluorescence titration; K_{ass} = 1443900 ± 207900 M^{-1} in CH_2Cl_2 solution using nonlinear least-squares curve-fitting method.[19]

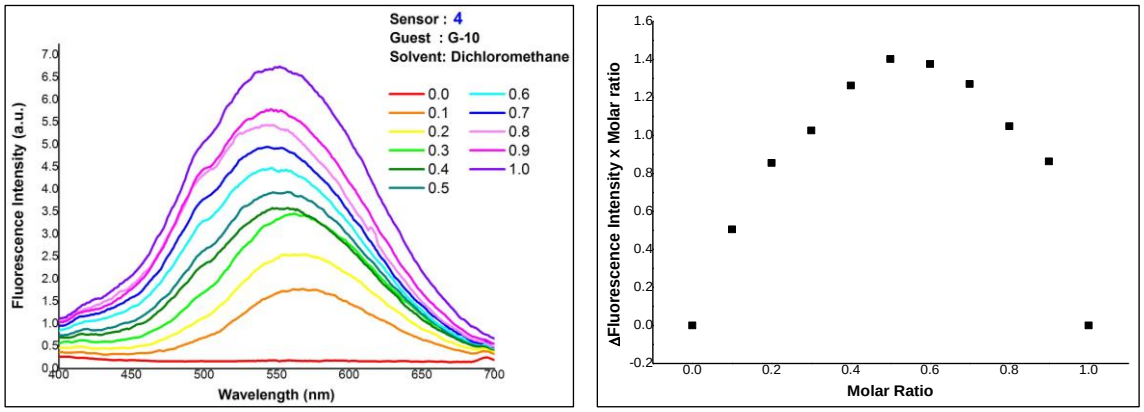


Figure S23. Job's plot for the 1:1 complex of **4**–G10 in CH_2Cl_2 solution. Stock solutions of receptor compound (**4**) and analyte (G10) were prepared in the same concentration (1×10^{-5} M). (A) Fluorescence spectra of eleven sample solutions containing **4** and G10 in total volume of 2 mL; (B) Changes of intensity at the 550-nm fluorescence were monitored as a function of receptor–analyte molar ratios (0:10 to 10:0).

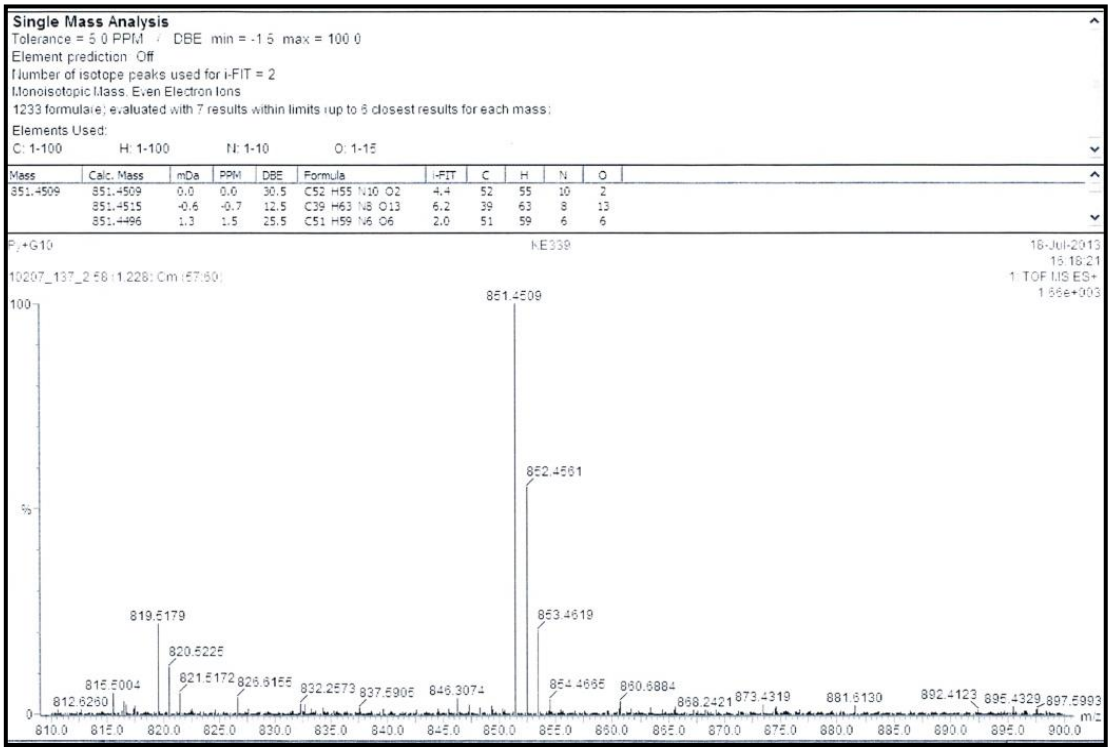


Figure S24. ESI–MS analysis for the 1:1 complex of **4**–G10. Calcd for $C_{34}H_{42}N_9O_2$: 851.4509; found: *m/z* 851.4509 $[M + H]^+$.

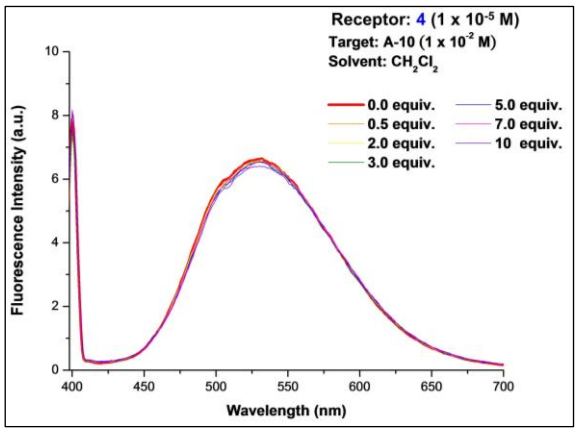


Figure S25. Fluorescence titration of receptor **4** (1×10^{-5} M) upon incremental additions of 9-decyladenine (A10, 1×10^{-2} M, 0.5–10 equiv) in CH_2Cl_2 solution. λ_{ex} = 400 nm; λ_{em} = 523 nm.

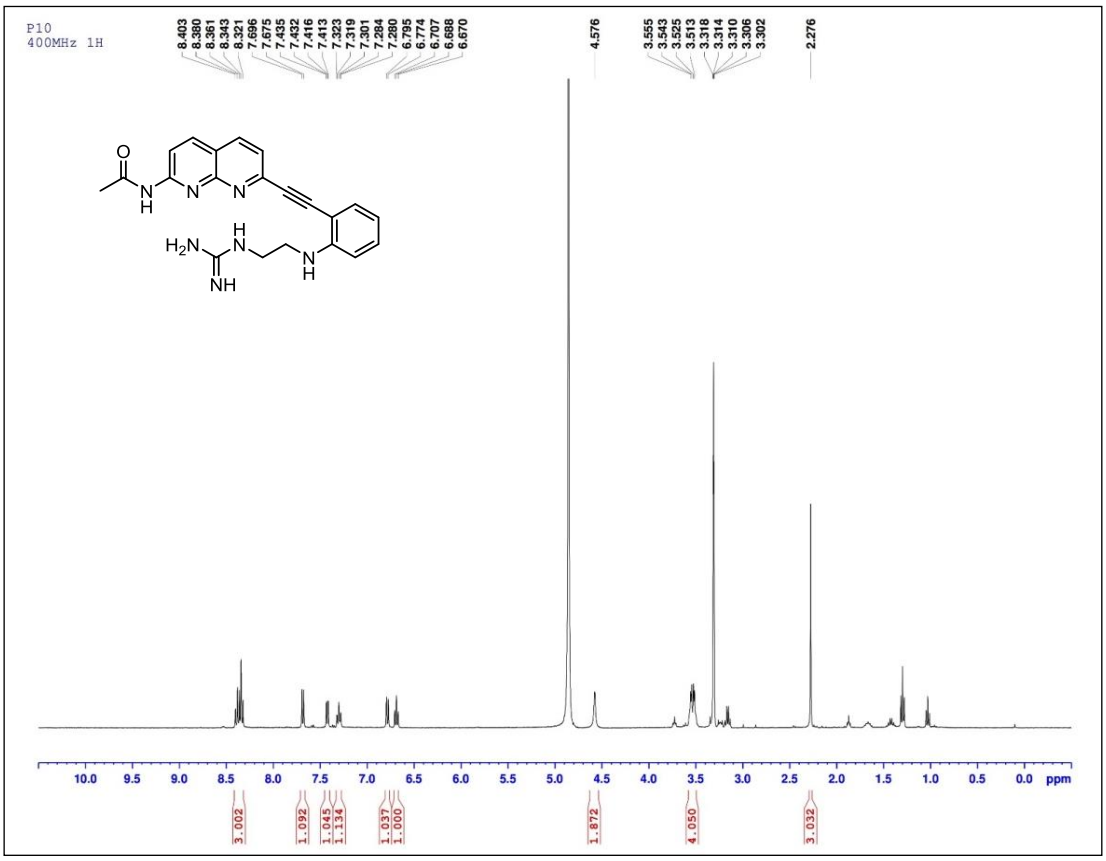


Figure S26. ^{1}H NMR spectrum of compound **5** (CD_3OD, 400 MHz)

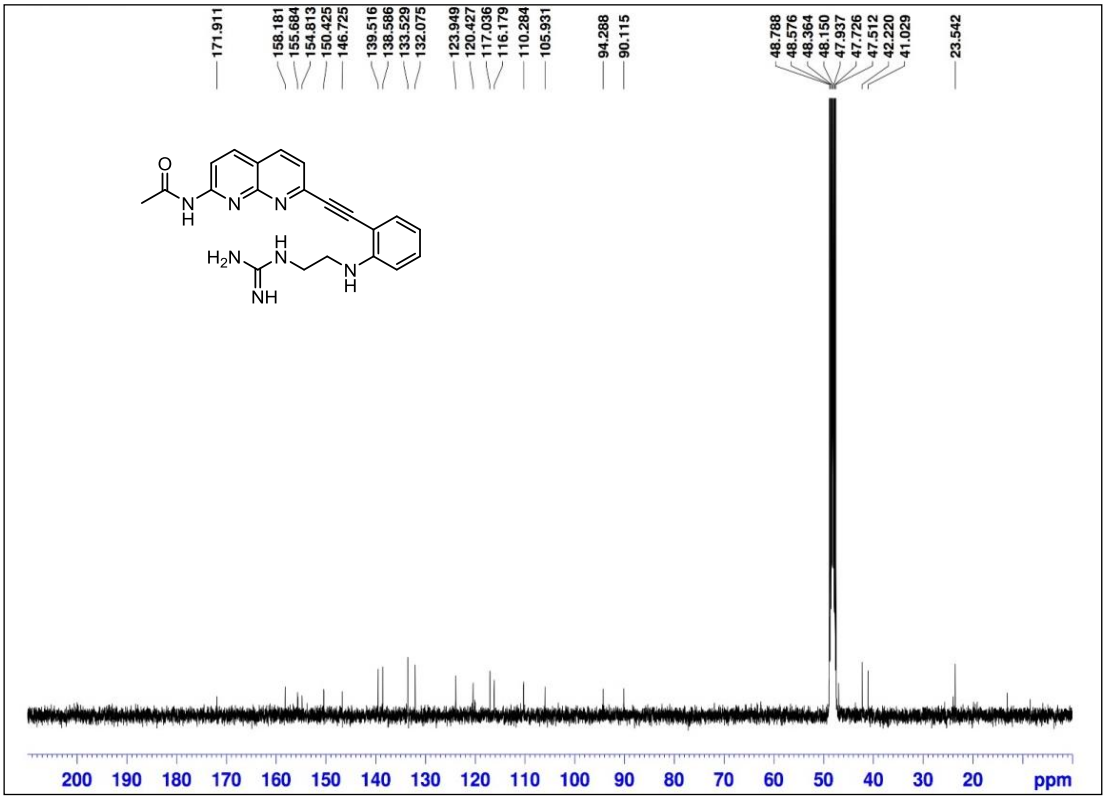


Figure S27. ^{13}C NMR spectrum of compound **5** (CD_3OD, 100 MHz)

Table S2. Photophysical properties of guanidine-hinged molecule **5**.

solvent	dielectric constant	λ_{abs} (nm) (ε)[a]	λ_{em} (nm)[b]
THF	7.5	399 (4030)	500
MeOH	33	396 (9830)	523
DMSO	47	353 (6200), 397 (6270)	548
H_2O	80	350 (11350), 381 (10190)	448

[a] Extinction coefficient ε is shown in a unit of $M^{-1}cm^{-1}$.

[b] Excitation wavelength at 400 nm.

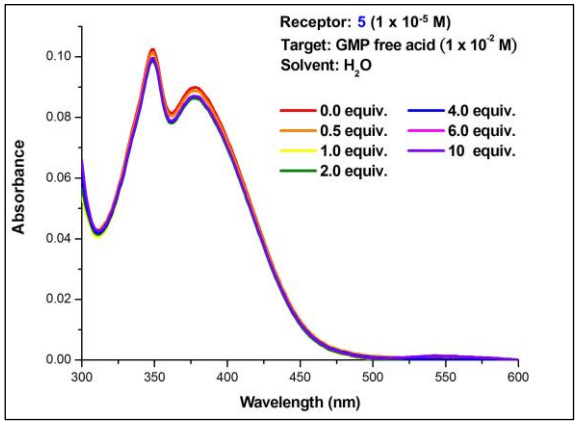


Figure S28. UV-vis titration of receptor **5** (1×10^{-5} M) upon incremental additions of guanosine 5′-monophosphate (GMP, 0.5–10 equiv, 1×10^{-2} M) in aqueous solution.

(A) (B)

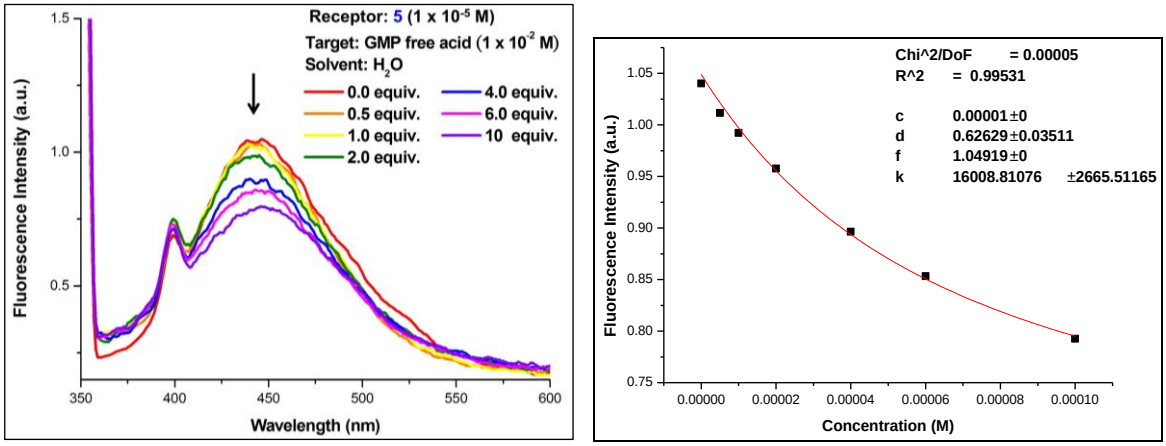


Figure S29. (A) Fluorescence titration of receptor **5** (1×10^{-5} M) upon incremental additions of GMP (1×10^{-2} M) in aqueous solution. Excitation wavelength: 350 nm. (B) Binding isotherm of **5**–GMP obtained from the changes of 445 nm emission in fluorescence titration; K_{ass} = 16,000 ± 2700 M^{-1} in water using nonlinear least-squares curve-fitting method.[19]

(A) (B)

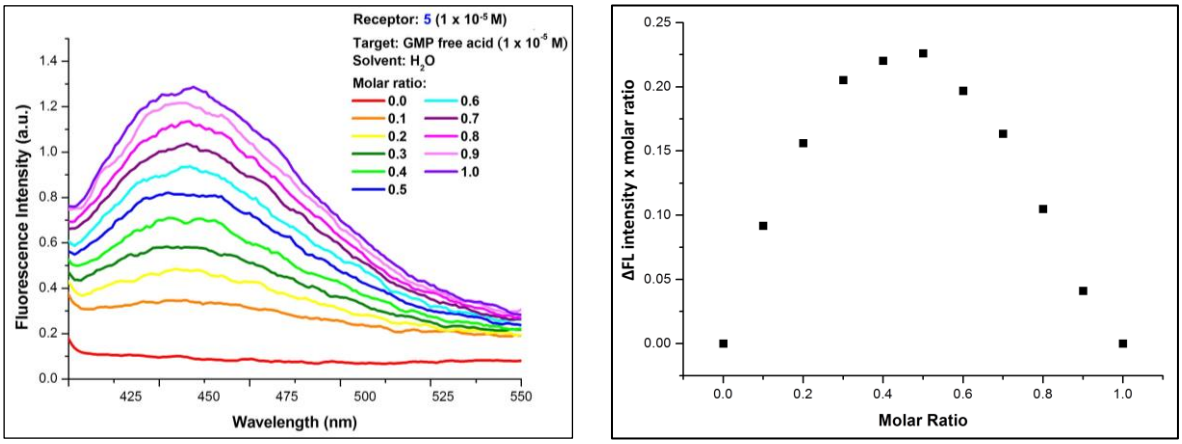


Figure S30. Job's plot for the 1:1 complex of **5**–GMP in water. Stock solutions of receptor compound (**5**) and analyte (GMP) were prepared in the same concentration (1×10^{-5} M). (A) Fluorescence spectra of eleven sample solutions containing **5** and GMP in total volume of 2 mL; (B) Changes of intensity at the 450-nm fluorescence were monitored as a function of receptor–analyte molar ratios (0:10 to 10:0).

(A) (B)

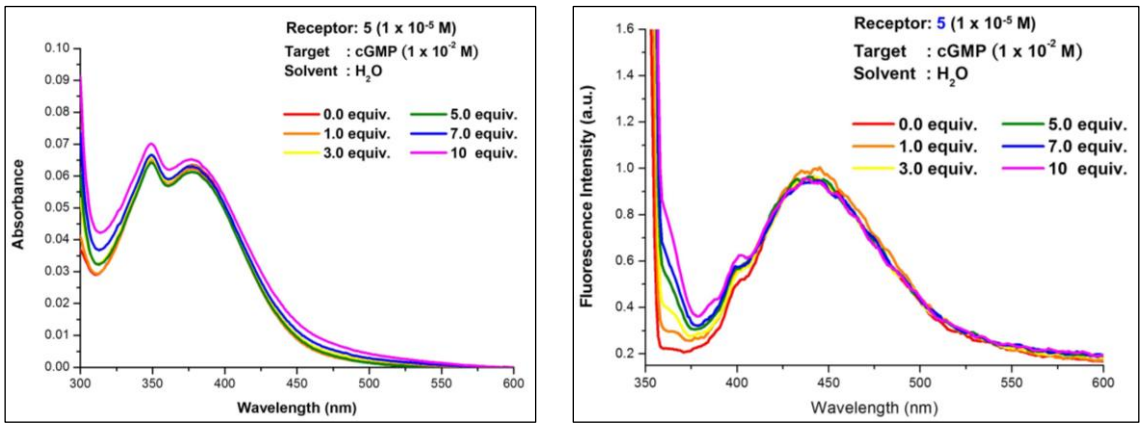


Figure S31. Titration of receptor **5** (1×10^{-5} M) upon incremental additions of 3′,5′-cyclic GMP (cGMP, 1×10^{-2} M) in aqueous solution. (A) UV-vis curves; (B) fluorescence curves (λ_{ex} = 350 nm).

(A) (B)

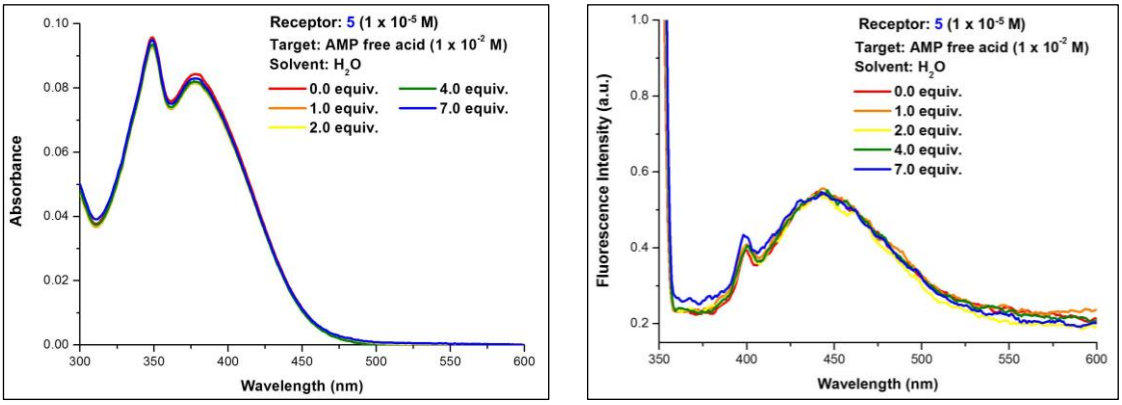


Figure S32. Titration of receptor **5** (1×10^{-5} M) upon incremental additions of adenosine 5′-monophosphate (AMP, 1×10^{-2} M) in aqueous solution. (A) UV-vis curves; (B) fluorescence curves (λ_{ex} = 350 nm).

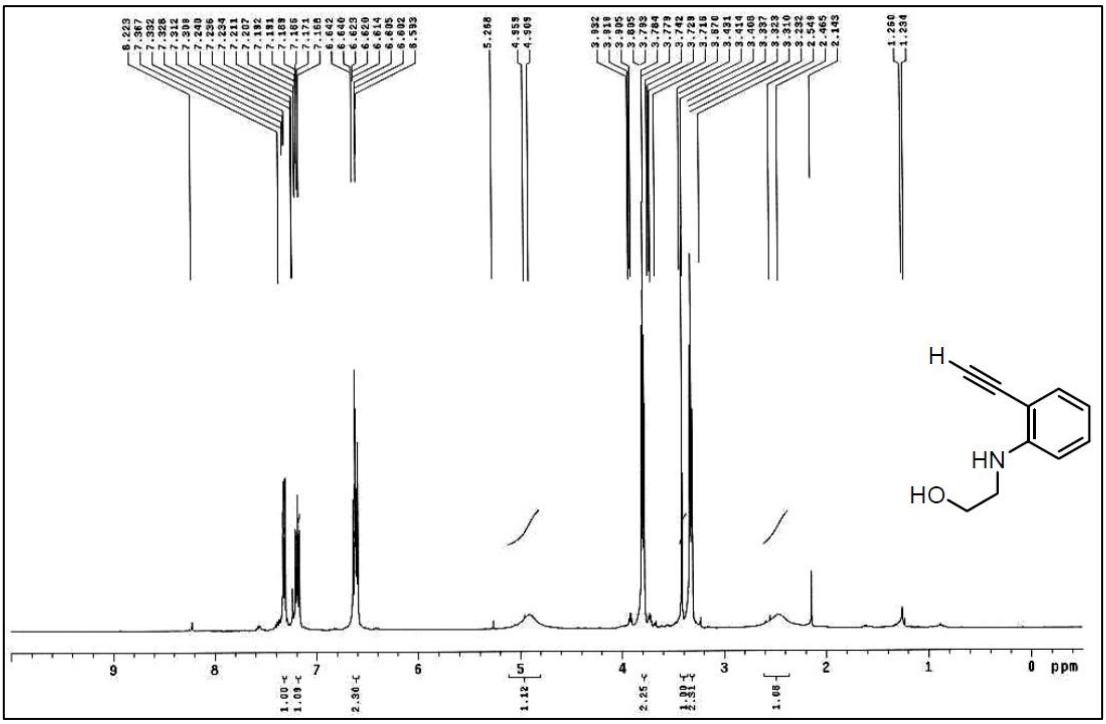


Figure S33. ^{1}H NMR spectrum of compound **8** (400 MHz, $CDCl_3$)

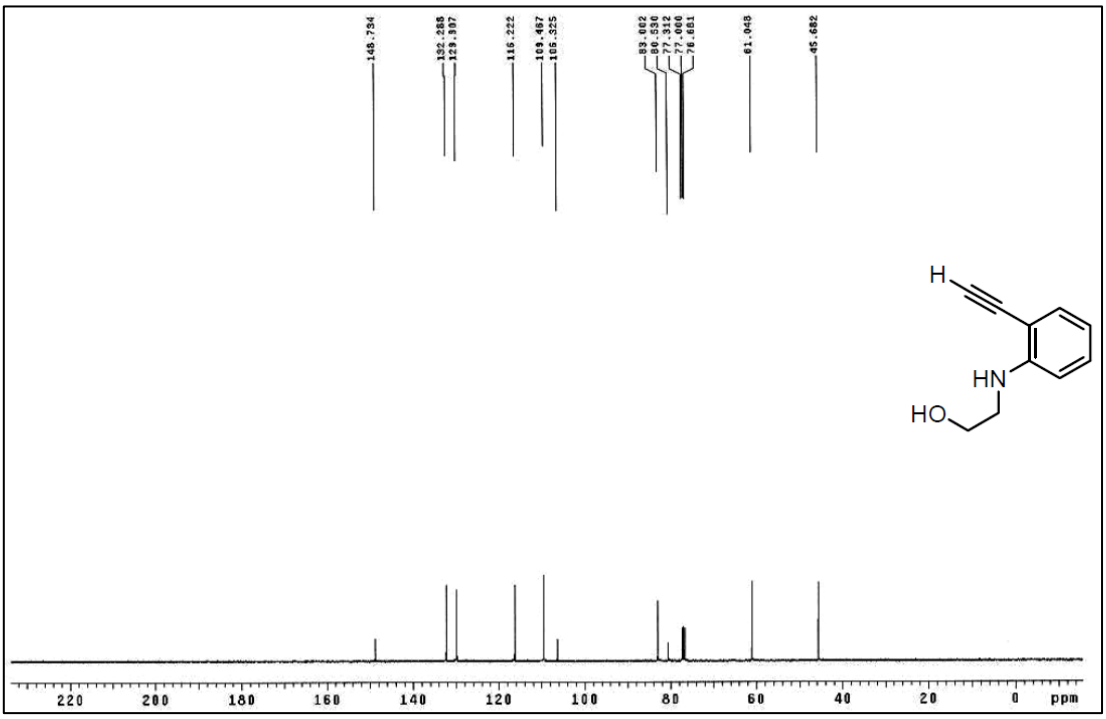


Figure S34. ^{13}C NMR spectrum of compound **8** (100 MHz, $CDCl_3$)

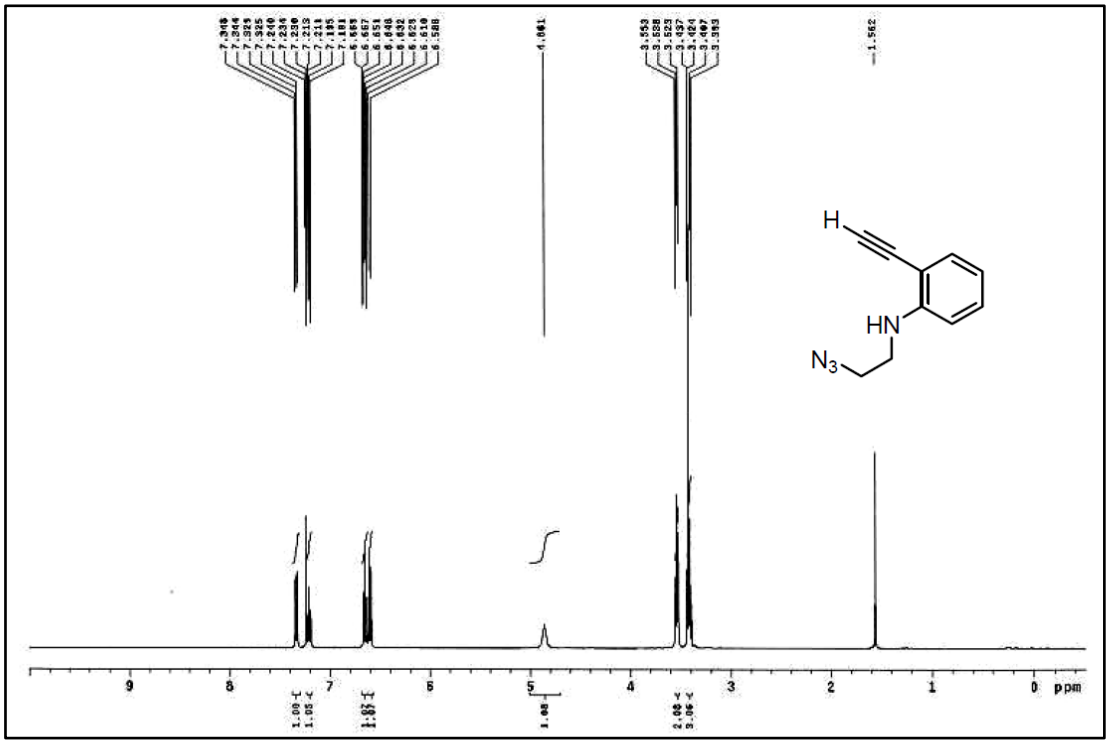


Figure S35. ^{1}H NMR spectrum of compound **9** (400 MHz, $CDCl_3$)

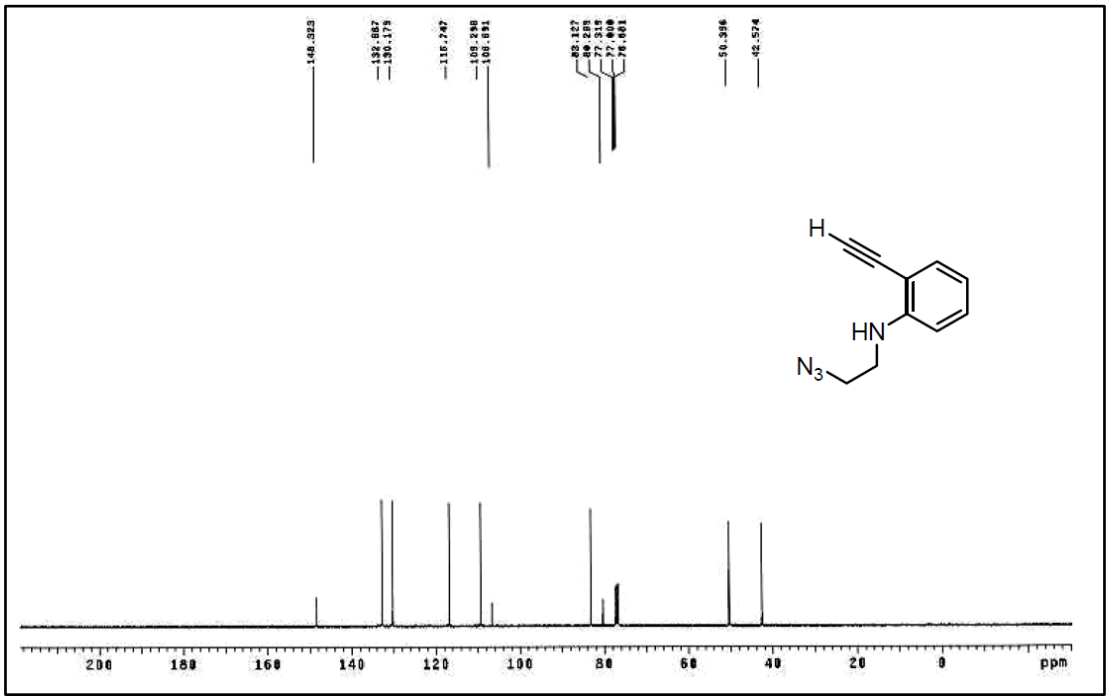


Figure S36. ^{13}C NMR spectrum of compound **9** (100 MHz, $CDCl_3$)

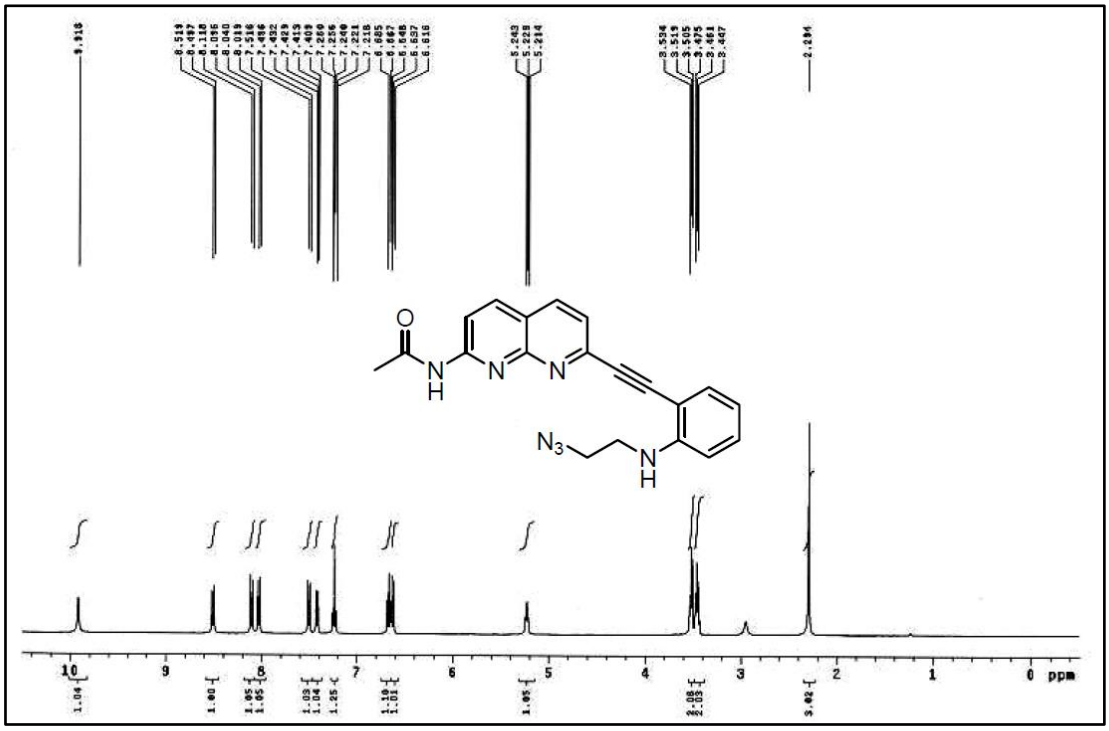


Figure S37. ^{1}H NMR spectrum of compound **10** (400 MHz, $CDCl_3$)

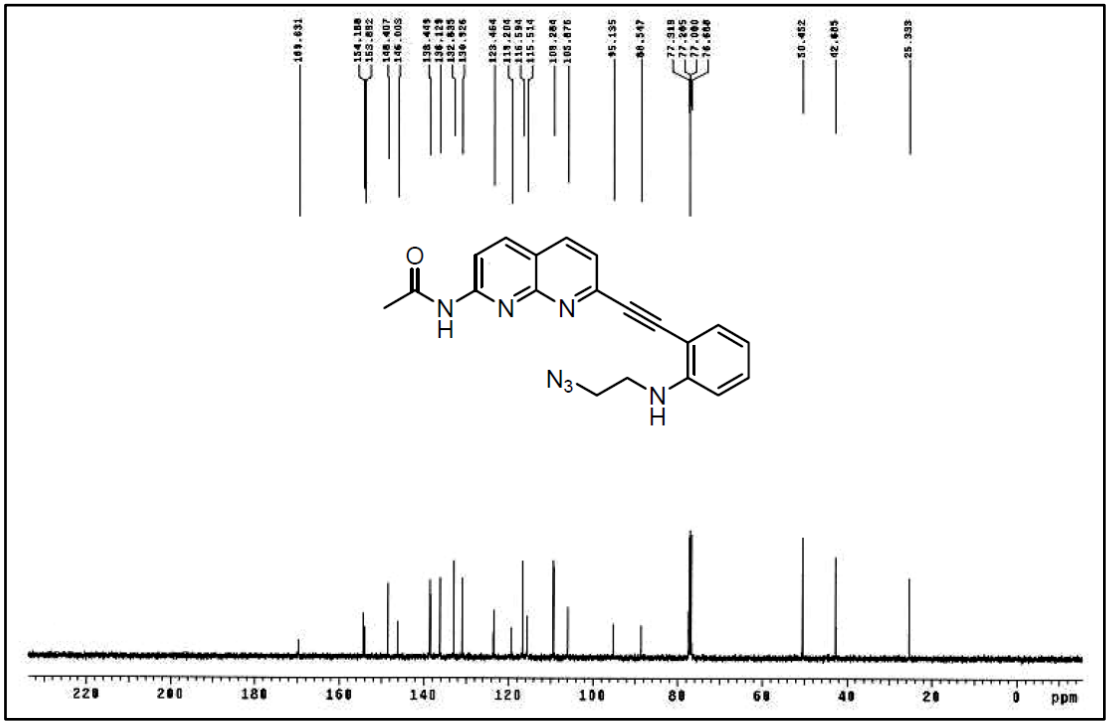


Figure S38. ^{13}C NMR spectrum of compound **10** (100 MHz, $CDCl_3$)

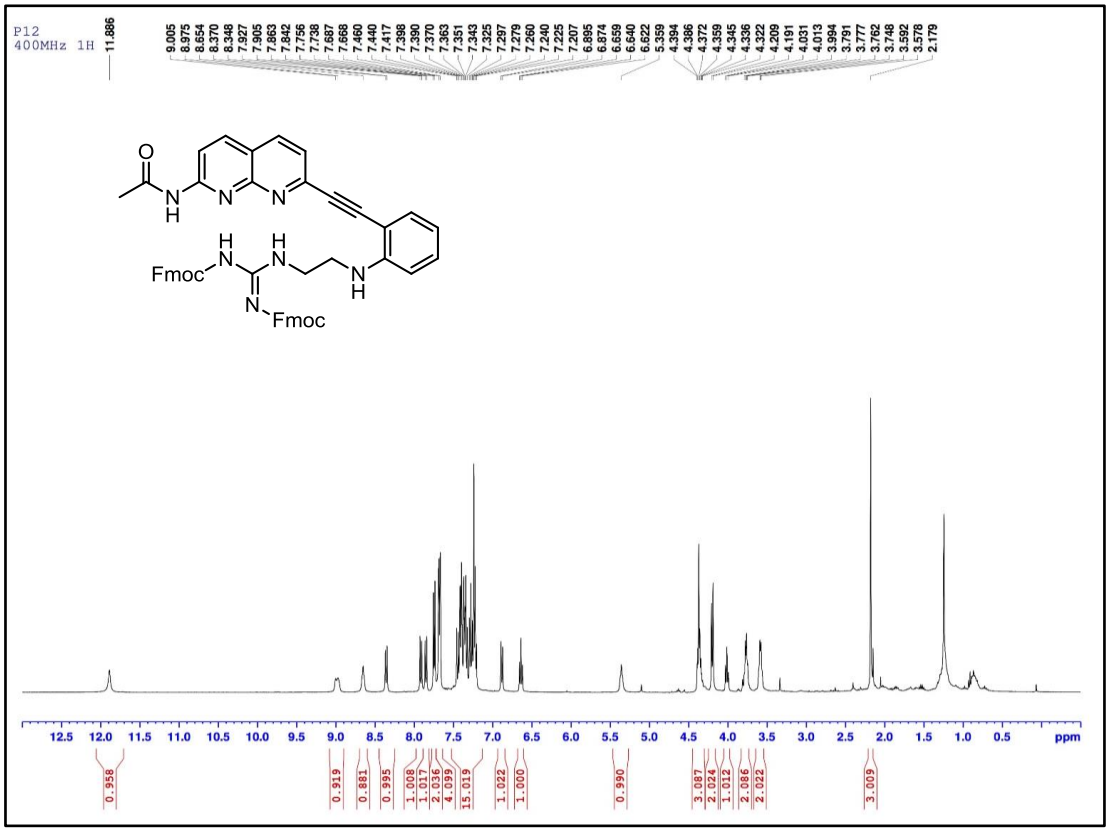


Figure S39. ^{1}H NMR spectrum of compound **13** (400 MHz, $CDCl_3$)

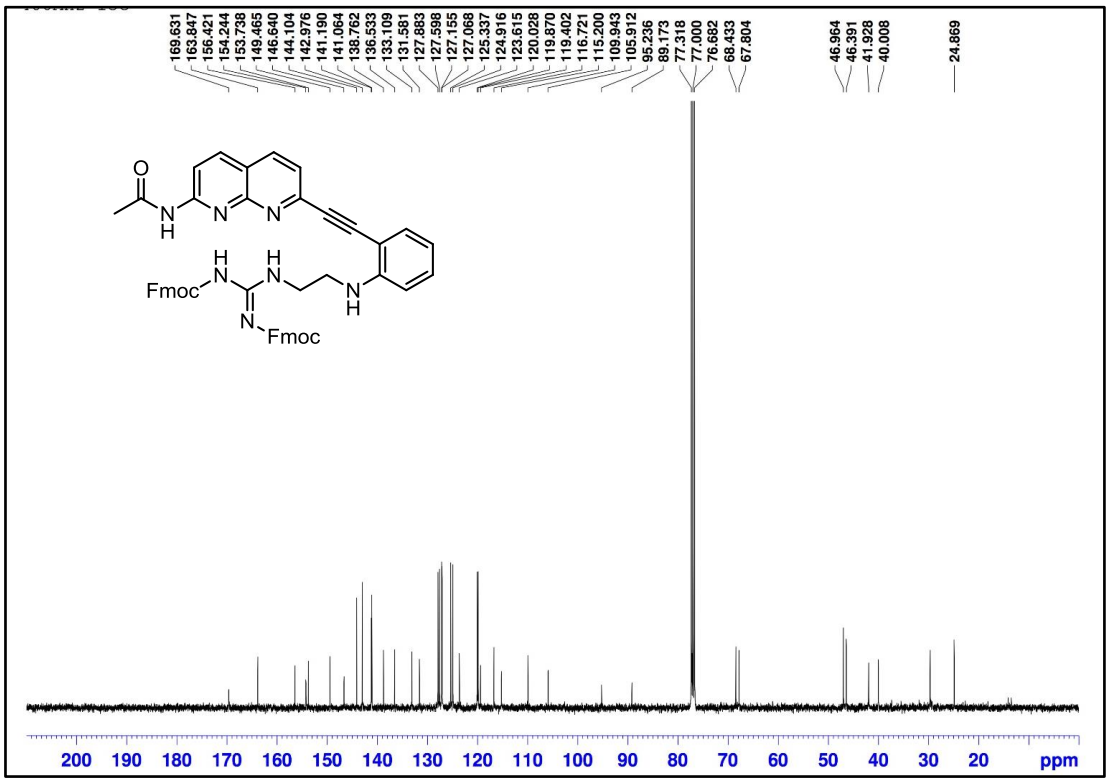


Figure S40. ^{13}C NMR spectrum of compound **13** (100 MHz, $CDCl_3$)