L-shaped benzimidazole fluorophores: synthesis, characterization and optical response to bases, acids and anions

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Supporting Information

General Methods

All reactions were performed under nitrogen atmosphere in oven-dried glassware. Reagents were purchased from commercial suppliers and used without further purification. Solvents were used as received, except *N*,*N*-dimethylformamide, which was dried over activated alumina in an mBraun Solvent Purification System. Compounds 4-bromo-2,1,3-benzothiadiazole and 3-bromo-1,2-diaminobenzene were synthesized according to literature procedures.[1,2] Diisopropylamine ((*i*-Pr)$_2$NH) was distilled over KOH pellets and degassed by a 15 min nitrogen purge prior to use. Microwave-assisted reactions were performed in a Biotage Initiator 2.0 microwave reactor, producing monochomatic microwave radiation with the frequency of 2.45 GHz.

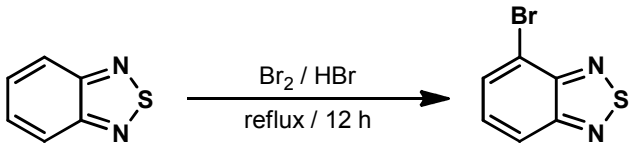
Mass spectral measurements were performed by the Mass Spectrometry Facility of the Department of Chemistry and Biochemistry at the University of Texas at Austin. NMR spectra were obtained on JEOL ECX-400, JEOL ECA-500 and Bruker Avance-800 MHz spectrometers, with working frequencies (for ^{1}H nuclei) of 400, 500 and 800 MHz, respectively. All ^{13}C-NMR spectra were recorded with simultaneous decoupling of ^{1}H nuclei. ^{1}H-NMR chemical shifts are reported in ppm units relative to the residual signal of the solvent ($CDCl_3$: 7.25 ppm, DMSO-d_6: 2.50 ppm, acetone-d_6: 2.05 ppm). NMR spectra were recorded at 25 ^{o}C for samples analyzed in $CDCl_3$ and $(CD_3)_2CO$-d_6, while samples in DMSO-d_6 were analyzed at 90 °C with 1–3 drops of D_2O added to eliminate asymmetry induced by N–H tautomerization. [5] Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer using Pike MIRacle Micrometer pressure clamp. Microanalyses were conducted by Intertek USA, Inc. Melting points were measured in open capillary tubes using Mel-Temp Thermo Scientific apparatus, and are uncorrected.

Column chromatography was carried out on silica gel 60, 32–63 mesh. Analytical TLC was performed on Merck aluminum-backed silica gel plates.

Experiments are presented in the order that follows the discussion of the manuscript.
Compound numbers are identical to those in the main text of the manuscript.

Syntheses

Synthesis of 4-bromo-2,1,3-benzothiadiazole[1]

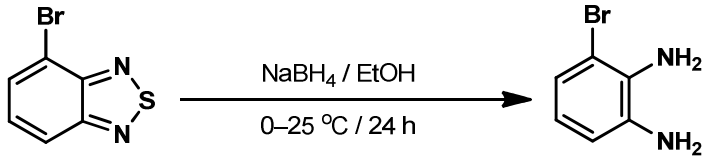


60%

In an oven-dried 250 mL 2-neck flask, compound 2,1,3-benzothiadiazole (13.6 g, 0.10 mol) was suspended in 47% aqueous solution of HBr (100 mL). The mixture was heated until boiling, and then Br_2 (4.70 mL, 0.09 mol) was added dropwise. The mixture was heated at reflux overnight. The product was purified by steam distillation, followed by recrystallization from EtOH, to ultimately yield white needle-like crystals in the yield of 13.0 g (60%).

4-Bromo-2,1,3-benzothiadiazole: white needle-like crystals: ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 7.97 (dd, $^3J_{H–H}$ = 7.8 Hz, $^4J_{H–H}$ = 1.2 Hz, 1H), 7.84 (dd, $^3J_{H–H}$ = 6.9 Hz, $^4J_{H–H}$ = 1.2 Hz, 1H), 7.48 (dd, $^3J_{H–H}$ = 6.9 Hz, $^3J_{H–H}$ = 7.5 Hz, 1H) ppm. This data agrees with a previous literature report.[3]

Synthesis of 3-bromo-1,2-diaminobenzene (**1**)

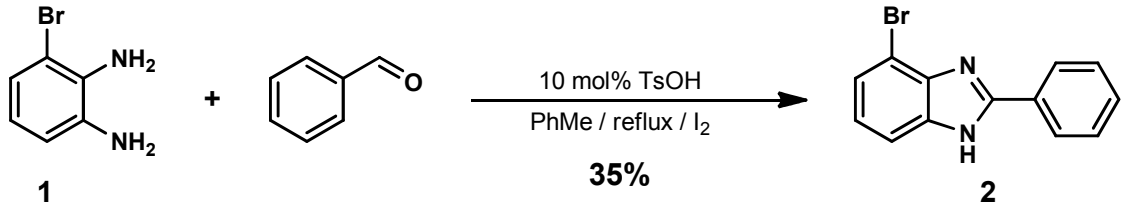


53% **1**

Compound **1** was synthesized using a modified method of Peng et al.[2] In an oven-dried 1 L Schlenk flask, 4-bromo-2,1,3-benzothiadiazole (6.63 g, 31.0 mmol) was suspended in 300 mL of absolute EtOH. Sodium borohydride (23.3 g, 61.6 mmol) was then added in several portions and the solution was kept at 0 °C until vigorous boiling of the solvent subsided, during which time the mixture gradually turned orange. Absolute EtOH was added occasionally to ensure that the mixture can be stirred. After 24 h, the orange solution was evaporated in vacuo, and the resulting solid was dissolved in deionized H_2O (300 mL) and then extracted with Et_2O. The Et_2O extract was washed with brine and dried over $MgSO_4$. Column chromatography on silica gel, using a mixture of hexanes and EtOAc (1:1) as the eluent, afforded pure compound **1** as orange oil (3.05 g, 53%).

1: orange oil. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ 6.61 (dd, $^3J_{H–H}$ = 7.8 Hz, $^4J_{H–H}$ = 1.4 Hz, 1H), 6.46 (dd, $^3J_{H–H}$ = 7.8 Hz, $^4J_{H–H}$ = 1.4 Hz, 1H), 6.29 (t, $^3J_{H–H}$ = 7.8 Hz, 1H), 4.80 (s, 2H), 4.56 (s, 2H) ppm. This data agrees with previous literature reports.[3,4]

Synthesis of 7-bromo-2-phenyl-1*H*-benzo[*d*]imidazole (**2**)

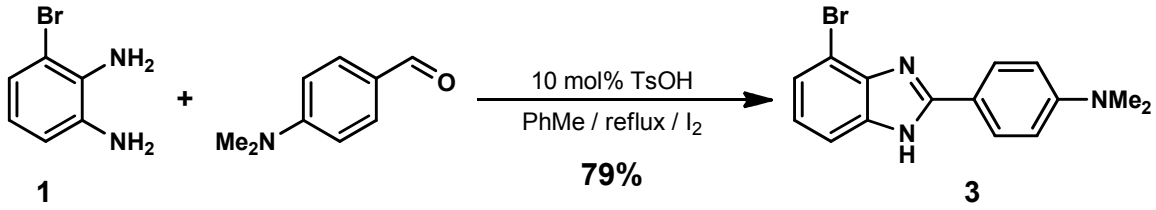


1 **2**

In a 250 mL round bottom flask, 3-bromo-1,2-phenylenediamine (**1**, 2.12 g, 11.4 mmol) and benzaldehyde (1.16 mL, 11.4 mmol) were dissolved in PhMe (150 mL). *para*-Toluenesulfonic acid (0.22 g, 1.17 mmol) was added and the solution was sonicated for 20 min. After sonication, the solution was heated at reflux with a Dean-Stark trap for 12 h. After that time, I_2 (2.90 g, 11.4 mmol) was added, and the solution was kept at reflux for 24 h. After cooling, the solvent was removed and the brown oily residue was sonicated with CH_2Cl_2 until it formed a solid precipitate. The solution was filtered and washed with hexane to give compound **2** as a yellow solid (1.11 g, 35%).

2: yellow powder, mp: 225–227 °C. IR (neat): 3061 (w, $\tilde{\nu}_{N-H}$), 1621 (s, $\tilde{\nu}_{C=N}$), 1457 (s), 1311 (s), 1029 (s), 931 (s), 750 (s), 690 (s, $\tilde{\nu}_{C-Br}$) cm^{-1}. UV-Vis (CH_3CN): λ_{max} (log ε) = 206 (4.71), 242 (4.36), 248 (4.30), 300 (4.46) nm. ^{1}H-NMR ($(CD_3)_2CO$-d_6, 500 MHz): δ 8.24 (dd, $^3J_{H-H}$ = 8.30 Hz, $^4J_{H-H}$ = 1.45 Hz, 2H), 7.55 (d, $^3J_{H-H}$ = 8.0 Hz, 1H), 7.50 (m, 3H), 7.39 (dd, $^3J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$ = 1.15 Hz, 1H), 7.12 (dd, $^3J_{H-H}$ = 8.0, $^3J_{H-H}$ = 7.45 Hz, 1H) ppm. ^{13}C-NMR ($(CD_3)_2CO$-d_6, 125 MHz): δ 152.7, 143.8, 136.3, 130.8, 130.4, 129.2, 125.5, 124.0, 113.2, 111.0 ppm. HRMS (ESI): Calcd for $C_{13}H_{10}BrN_2^+$: 273.0022. Found: 273.0020.

Synthesis of 4-(7-bromo-1*H*-benzo[*d*]imidazol-2-yl)-*N*,*N*-dimethylbenzenamine (**3**)

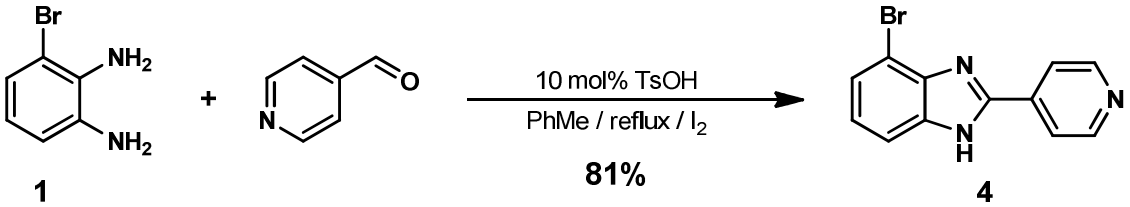


1 **3**

Compound **1** (1.12 g, 6.00 mmol) and 4-dimethylaminobenzaldehyde (895 mg, 6.00 mmol) were dissolved in PhMe (150 mL). *para*-Toluenesulfonic acid (196 mg, 1.03 mmol) was added, and the solution was sonicated for 20 min, during which time a precipitate formed. After sonication, the solution was heated at reflux with a Dean-Stark trap for 12 h. After that time, I_2 (1.52 g, 6mmol) was added and the solution was heated at reflux for 24 h. After cooling, the solution was filtered and the residue washed with hexane and Me_2CO to give a reddish brown solid that was identified as **3** (1.50 g, 79%). Further purification can be achieved by recrystallization in Me_2CO or EtOH.

3: red-brown powder, mp 161 °C (dec). IR (neat): 3432 (m, $\tilde{\nu}_{N-H}$), 1610 (s, $\tilde{\nu}_{C=N}$), 1524 (s), 1378 (s), 1216 (s), 816 (s), 776 (s), 641 (s, $\tilde{\nu}_{C-Br}$) cm^{-1}. UV-Vis (CH_3CN): λ_{max} (log ε) = 245 (4.46), 371 (4.64) nm. ^{1}H-NMR (DMSO-d_6, 500 MHz): δ 8.08 (d, $^3J_{H-H}$ = 9.2 Hz, 2H), 7.65 (d, $^3J_{H-H}$ = 8.0 Hz, 1H), 7.63 (d, $^3J_{H-H}$ = 8.0 Hz, 1H), 7.32 (t, $^3J_{H-H}$ = 8.0 Hz, 1H), 6.89 (d, $^3J_{H-H}$ = 9.2 Hz, 2H), 3.05 (s, 6H) ppm. ^{13}C-NMR (DMSO-d_6, 125 MHz): δ 153.8, 151.9, 133.4, 132.7, 130.4, 128.4, 126.9, 112.9, 112.2, 108.7, 105.7 ppm. HRMS (ESI): Calcd for $C_{15}H_{15}BrN_3^+$: 316.0444. Found: 316.0443.

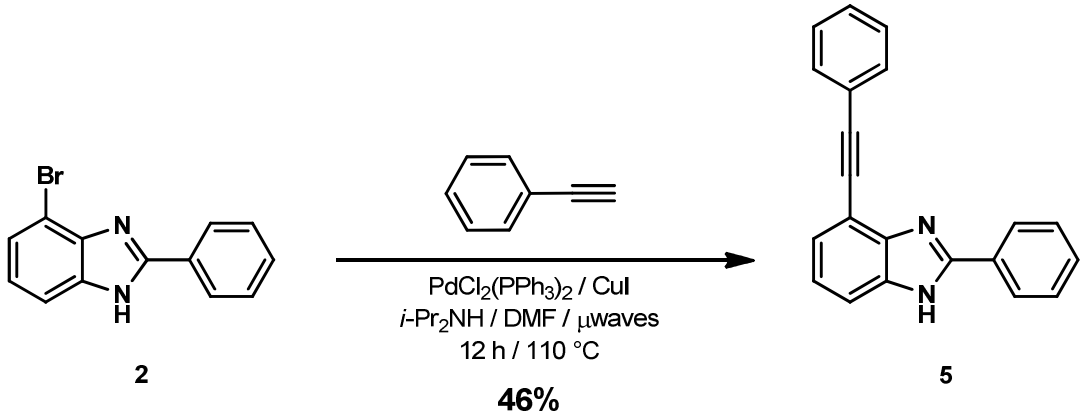
Synthesis of 7-bromo-2-(pyridine-4-yl)-1*H*-benzo[*d*]imidazole (**4**)



In a 250 mL round-bottom flask, 3-bromo-1,2-phenylenediamine (2.51 g, 13.4 mmol) and 4-pyridinecarboxaldehyde (1.26 mL, 13.4 mmol) were dissolved in PhMe (150 mL). *para*-Toluenesulfonic acid (255 mg, 1.34 mmol) was added and the solution was sonicated for 20 min. After sonication, the solution was heated at reflux with a Dean-Stark trap for 12 h. After that time, I_2 (3.40 g, 13.4 mmol) was added into the solution. Immediate formation of a yellow-brown precipitate was observed. The mixture was kept at reflux for additional 24 h. After cooling, the solution was filtered and the residue washed with hexane and Me_2CO and to give a pale yellow solid (2.98 g, 81%). Further purification can be achieved by recrystallization from Me_2CO or EtOH.

4: pale yellow powder, mp 243 °C (dec). IR (neat): 3071 (w, $\tilde{\nu}_{N-H}$), 1638 (s, $\tilde{\nu}_{C=N}$), 1503 (s), 1224 (s), 1151 (s), 1032 (s), 808 (s), 743 (s), 683 (s, $\tilde{\nu}_{C-Br}$) cm^{-1}. UV-Vis (CH_3CN): λ_{max} (log ε) = 202 (4.59), 245 (4.20), 313 (3.95), 350 (3.95) nm. ^{1}H-NMR (DMSO-d_6, 500 MHz): δ 8.96 (d, $^3J_{H-H}$ = 6.3 Hz, 2H), 8.50 (d, $^3J_{H-H}$ = 6.9 Hz, 2H), 7.68 (d, $^3J_{H-H}$ = 8.0 Hz, 1H), 7.54 (d, $^3J_{H-H}$ = 7.5 Hz, 1H), 7.26 (dd, $^3J_{H-H}$ = 8.0, 7.5 Hz, 1H) ppm. ^{13}C-NMR (DMSO-d_6, 125 MHz): δ 147.4, 144.2, 141.2, 138.3, 127.0, 126.4, 123.6, 114.4, 111.5 ppm. HRMS (ESI): Calcd for $C_{12}H_9BrN_3^+$: 273.9974. Found: 273.9974.

Synthesis of compound **5**

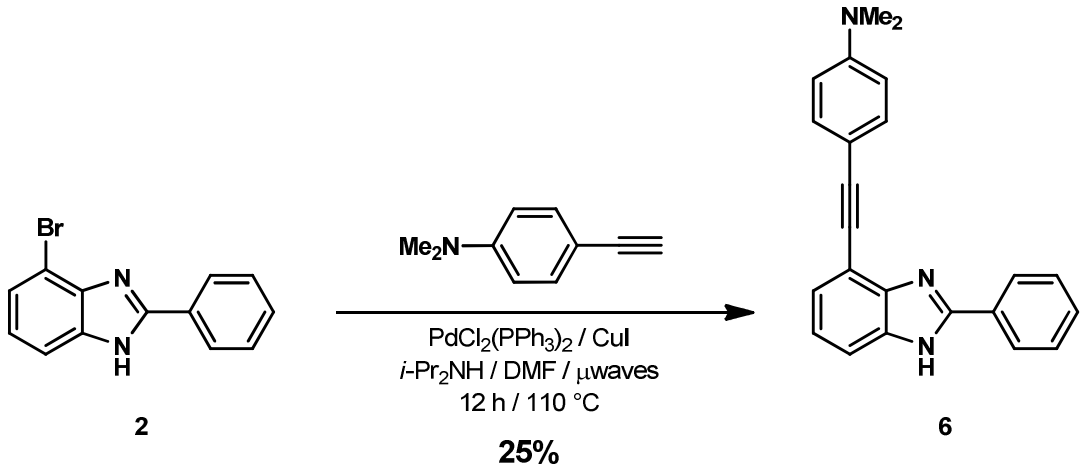


2 **5**

Phenylacetylene (450 mg, 4.40 mmol) was added to a thick-walled microwave pressure vial that contained a mixture of compound **2** (300 mg, 1.10 mmol), $PdCl_2$ $(PPh_3)_2$ (60.0 mg, 0.09 mmol), CuI (20.0 mg, 0.11 mmol), *i*-Pr_2NH (5 mL), and DMF (5 mL). The vial was sealed and exposed to microwave irradiation for 12 h at 110 °C. After cooling, the reaction mixture was extracted with EtOAc, washed with brine, and then dried over anhydrous $MgSO_4$. The product was isolated by column chromatography, eluting with a hexane/EtOAc (7:3) mixture. The solvent was removed under reduced pressure, and the solid recrystallized from a mixture of THF and hexane, to give compound **5** (150 mg, 46%) as a white powder (mp 280 °C).

5: UV-Vis (THF): λ_{max} (log ε) = 213 (4.67), 233 (4.51), 247 (4.47), 261 (4.43), 272 (4.43), 283 (4.41), 318 (4.60) nm. IR (neat): 3052 (w, $\tilde{\nu}_{N-H}$), 2324 (w, $\tilde{\nu}_{C\equiv C}$), 1473 (m, $\tilde{\nu}_{C=N}$), 1459 (m), 1418 (m), 1395 (m), 1253 (m), 965 (w), 973 (m), 753 (s), 707 (s), 691 (s) cm^{-1}. ^{1}H-NMR ($(CD_3)_2SO$ and 1 drop of D_2O, 500 MHz): δ 8.22 (br d, 2H), 7.64 (br d, 2H), 7.54 (m, 3H), 7.49 (m, 1H), 7.43 (m, 3H), 7.37 (d, $^3J_{H-H}$ = 7.5 Hz, 1H), 7.21 (dd, $^3J_{H-H}$ = 8.0 Hz; 7.5 Hz, 1H) ppm. ^{13}C-NMR ($(CD_3)_2SO$ and 1 drop of D_2O, 200 MHz): δ 152.0, 144.4, 135.1, 131.6, 130.4, 129.8, 129.1, 128.9, 127.4, 126.8, 125.8, 122.9, 122.7, 112.9, 112.4, 109.6, 92.7, 87.7 ppm. HRMS (ESI/$[M+H]^+$): calcd for $C_{21}H_{15}N_2^+$ 295.1230, found 295.1230. Anal. Calcd. for $C_{21}H_{14}N_2 \cdot ¼THF$: C, 84.59; H, 5.16; N, 8.97. Found: C, 84.84; H, 3.95; N, 9.29.

Synthesis of Compound **6**

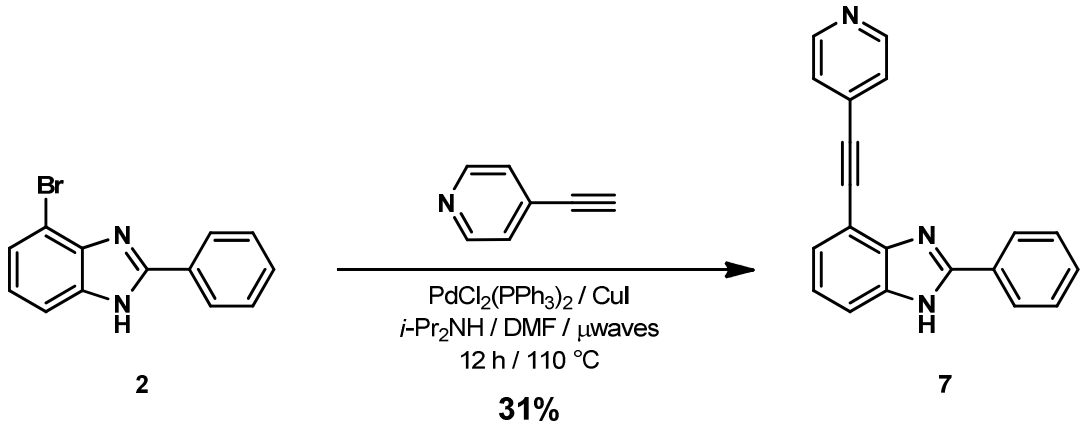


Anhydrous K_2CO_3 (831 mg, 6.01 mmol) was added to a solution of 2-(4-(*N*,*N*-dimethylamino) phenyl)trimethylsilylethyne (652 mg, 3.00 mmol) in a mixture of MeOH (5 mL) and THF (5 mL). After stirring for 30 min under nitrogen, the reaction mixture was filtered though Celite. The solvent was removed under reduced pressure to yield crude 4-ethynyl-*N*,*N*-dimethylaniline, which was used without purification in the next step. To minimize manipulations of this somewhat sensitive compound, we assumed a 95% yield for this reaction.[6]

The entire amount of 4-ethynyl-*N*,*N*-dimethylaniline (prepared as above-described) was added to a thick-walled microwave pressure vial that contained a mixture of compound **2** (300 mg, 1.10 mmol), $PdCl_2(PPh_3)_2$ (60.0 mg, 0.09 mmol), CuI (20.0 mg, 0.11 mmol), *i*-Pr_2NH (5 mL), and DMF (5 mL). The vial was sealed and exposed to microwave irradiation for 12 h at 110 °C. After cooling, the reaction mixture was extracted with EtOAc, washed with brine, and dried over anhydrous $MgSO_4$. The product was isolated by column chromatography, eluting with hexane/EtOAc mixtures (60:40, 50:50, 20:80 and 0:100, successively). The solvent was removed under reduced pressure, and the solid was washed with EtOAc (5 mL) and THF (3 mL) to give compound **6** (90.5 mg, 25%) as a light green powder (mp 284 °C, with decomposition).

6: UV-Vis (THF): λ_{max} (log ε) = 253 (4.45), 293 (4.59), 317 (4.65), 351 (4.53) nm. IR (neat): 3091 (w, $\tilde{\nu}_{N-H}$), 2206 (w, $\tilde{\nu}_{C\equiv C}$), 1607 (s, $\tilde{\nu}_{C=N}$), 1588 (m), 1524 (m), 1457 (m), 1386 (m), 1363 (m), 1186 (m), 819 (s), 747 (s), 707 (s) cm^{-1}. ^{1}H-NMR ($(CD_3)_2SO$ and 1 drop of D_2O, 500 MHz): δ 8.22 (br d, 2H), 7.51 (m, 5H), 7.41 (br s, 1H), 7.30 (d, $^3J_{H-H}$ = 7.5 Hz, 1H), 7.18 (dd, $^3J_{H-H}$ = 8.1 Hz, $^3J_{H-H}$ = 7.4 Hz, 1H), 6.73 (d, $^3J_{H-H}$ = 9.2 Hz, 2H), 2.94 (s, 6H) ppm. ^{13}C-NMR ($(CD_3)_2SO$ and 1 drop of D_2O, 200 MHz): δ 151.6, 150.1, 144.1, 135.1, 132.5, 130.1, 129.9, 128.9, 126.7, 125.2, 122.5, 113.9, 111.9, 111.4, 109.1, 94.2, 85.4, 39.5 ppm. HRMS (ESI/$[M+H]^+$): calcd for $C_{23}H_{20}N_3^+$ 338.1652, found 338.1650. Anal. Calcd. for $C_{23}H_{19}N_3 \cdot \frac{1}{3}$THF: C, 80.86; H, 6.04; N, 11.63. Found: C, 80.48; H, 5.46; N, 12.05.

Synthesis of compound **7**

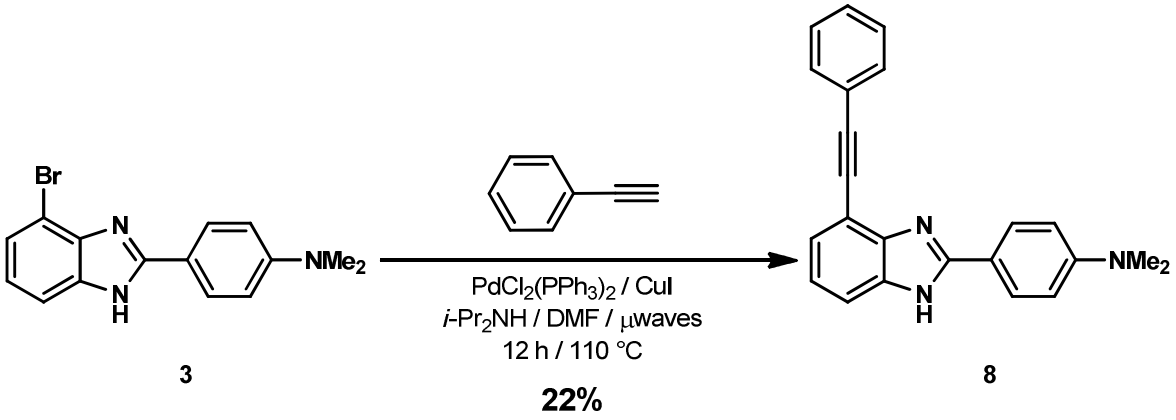


Anhydrous K_2CO_3 (1.00 g, 7.24 mmol) was added to a solution of 2-(4-(pyridyl)) trimethylsilylacetylene (630 mg, 3.59 mmol) in a mixture of MeOH (5 mL) and THF (5 mL). After being stirred for 30 min under nitrogen, the reaction mixture was filtered through Celite. The solvent was removed under reduced pressure to yield crude 4-ethynylpyridine, which was used without purification in the next step. To minimize manipulations of this somewhat sensitive compound, we assumed a 95% yield for this reaction.[6]

The entire amount of 4-ethynylpyridine (prepared as described above) was added to a thick-walled microwave pressure vial that contained a mixture of compound **2** (300 mg, 1.10 mmol), $PdCl_2(PPh_3)_2$ (60.0 mg, 0.09 mmol), CuI (20.0 mg, 0.11 mmol), *i*-Pr_2NH (5 mL), and DMF (5 mL). The vial was sealed and exposed to microwave irradiation for 12 h at 110 °C. After cooling, the reaction mixture was extracted with EtOAc, washed with brine, and dried over anhydrous $MgSO_4$. The product was isolated by column chromatography, eluting first with pure EtOAc, and then successively with EtOAc/MeOH mixtures in 95:5 and 90:10 ratios. The solvent was removed under reduced pressure, and the resulting solid was recrystallized from a mixture of THF and hexane to give 102 mg (31%) of compound **7** as a white powder (mp 251 °C, with decomposition).

7: UV-Vis (THF): λ_{max} (log ε) = 210 (4.66), 235 (4.48), 242 (4.48), 247 (4.46), 259 (4.34), 274 (4.30), 287 (4.36), 322 (4.57) nm. IR (neat): 3085 (w, $\tilde{\nu}_{N-H}$), 2224 (w, $\tilde{\nu}_{C\equiv C}$), 1598 (m, $\tilde{\nu}_{C=N}$), 1456 (m), 1415 (m), 1270 (w), 831 (m), 793 (w), 735 (s), 697 (s), 685 (s), 648 (m) cm^{-1}. ^{1}H-NMR ($(CD_3)_2SO$, 500 MHz): δ 12.86 (s, 1H), 8.63 (d, $^3J_{H-H}$ = 6.3 Hz, 2H), 8.22 (d, $^3J_{H-H}$ = 7.5 Hz, 2H), 7.65 (d, $^3J_{H-H}$ = 7.5 Hz, 1H), 7.53 (m, 5H), 7.43 (dd, $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-H}$ = 1.2 Hz, 1H), 7.24 (dd, $^3J_{H-H}$ = 8.1 Hz, $^3J_{H-H}$ = 7.5 Hz, 1H) ppm. ^{13}C-NMR ($(CD_3)_2SO$ and 1 drop of D_2O, 200 MHz): δ 152.5, 150.2, 144.5, 135.2, 131.0, 130.8, 129.7, 129.2, 127.1, 126.5, 125.7, 122.8, 113.4, 111.7, 109.6, 92.2, 90.2 ppm. HRMS (ESI/$[M+H]^+$): calcd for $C_{20}H_{14}N_3^+$ 296.1182, found 296.1183. Anal. Calcd for $C_{20}H_{13}N_3 \cdot {}^1/_6$THF: C, 80.76; H, 4.70; N, 13.67. Found: C, 80.76; H, 4.31; N, 13.88.

Synthesis of compound **8**

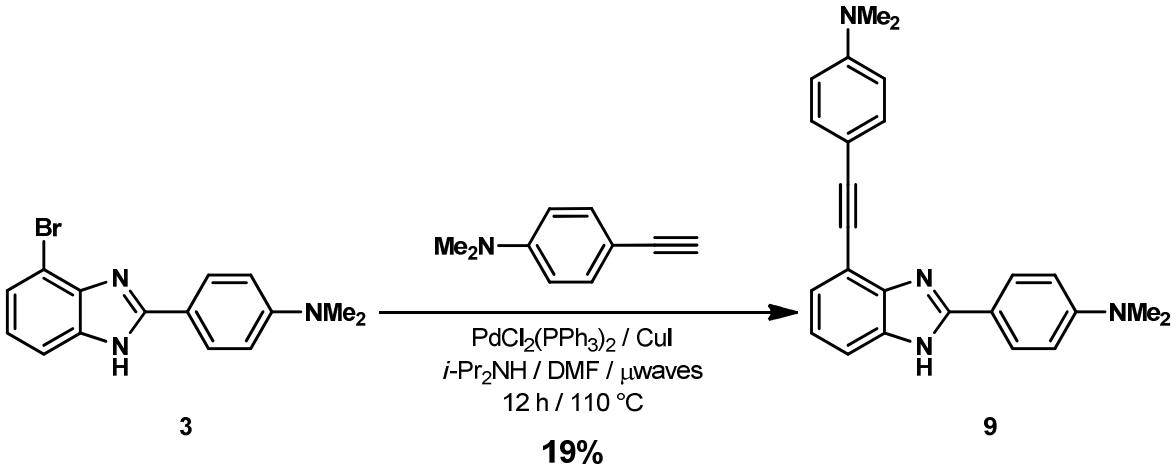


3 8

Phenylacetylene (387 mg, 3.79 mmol) was added to a thick-walled microwave pressure vial that contained a mixture of compound **3** (300 mg, 0.95 mmol), $PdCl_2(PPh_3)_2$ (60.0 mg, 0.09 mmol), CuI (20.0 mg, 0.11 mmol), *i*-Pr_2NH (5 mL), and DMF (5 mL). The vial was sealed and exposed to microwave irradiation for 12 h at 110 °C. After cooling, the reaction mixture was extracted with EtOAc, washed with brine, and dried over anhydrous $MgSO_4$. The product was isolated by column chomatography, eluting with a hexane/EtOAc (70:30) mixture. The solvent was removed under reduced pressure, and the solid was recrystallized from a mixture of Et_2O, CH_2Cl_2, and hexane to give 70 mg (22%) of compound **8** as a yellow powder (mp 247 °C).

8: UV-Vis (THF): λ_{max} (log ε) = 224 (4.59), 299 (4.48), 312 (4.45), 323 (4.46), 352 (4.57) nm. IR (neat): 3119 (w, $\tilde{\nu}_{N-H}$), 2320 (w, $\tilde{\nu}_{C\equiv C}$), 1612 (s, $\tilde{\nu}_{C=N}$), 1492 (m), 1416 (m), 1367 (m), 1202 (m), 956 (w), 820 (m), 753 (s), 689 (m), 668 (m), 636 (m), 601 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.96 (d, $^3J_{H-H}$ = 8.7 Hz, 2H), 7.68 (d, $^3J_{H-H}$ = 8.2 Hz, 1H), 7.58 (m, 2H), 7.40 (m, 4H), 7.20 (dd, $^3J_{H-H}$ = 8.2 Hz, $^3J_{H-H}$ = 7.8Hz, 1H), 6.74 (d, $^3J_{H-H}$ = 8.3 Hz, 2H), 3.03 (s, 6H) ppm. ^{13}C-NMR ($CDCl_3$, 200 MHz): δ 162.2, 153.0, 151.8, 143.5, 131.8, 131.7, 128.5, 128.3, 126.2, 123.1, 122.5, 121.6, 116.0, 112.0, 93.5, 85.6, 40.2 ppm. HRMS (ESI): calcd for $C_{23}H_{20}N_3^+$ 338.1652, found 338.1654. Anal. Calcd for $C_{23}H_{19}N_3 \cdot ¼Et_2O$: C, 80.98; H, 6.09; N, 11.81. Found: C, 80.93; H, 5.48; N, 12.23.

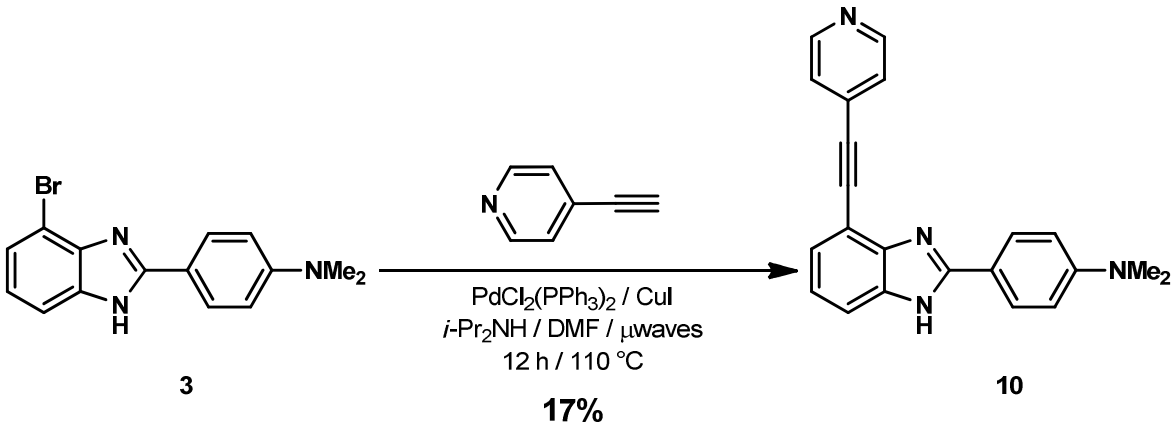
Synthesis of compound **9**



The entire amount of 4-ethynyl-*N*,*N*-dimethylaniline (prepared as in the synthesis compound **6** described above) was added to a thick-walled microwave pressure vial that contained a mixture of compound **3** (300 mg, 0.95 mmol), $PdCl_2(PPh_3)_2$ (60.0 mg, 0.09 mmol), CuI (20.0 mg, 0.11 mmol), *i*-Pr_2NH (5 mL), and DMF (5 mL). The vial was sealed and exposed to microwave irradiation for 12 h at 110 °C. After cooling, the reaction mixture was extracted with EtOAc, washed with brine, and dried over anhydrous $MgSO_4$. The product was isolated by column chromatography, eluting with pure EtOAc. The solvent was removed under reduced pressure, and the solid was recrystallized from a mixture of THF and hexane to give 67 mg (19%) of compound **9** as a yellow powder (mp 276 °C, with decomposition).

9: UV-Vis (THF): λ_{max} (log ε) = 220 (4.60), 292 (4.46), 339 (4.66), 353 (4.62) nm. IR (neat): 3046 (w, $\tilde{\nu}_{N-H}$), 2209 (w, $\tilde{\nu}_{C\equiv C}$), 1609 (s, $\tilde{\nu}_{C=N}$), 1517 (m), 1482 (m), 1443 (m), 1415 (m), 1366 (m), 1247 (m), 1183 (m), 920 (m), 821 (s), 755 (s) cm^{-1}. ^{1}H-NMR ($(CD_3)_2SO$ and 3 drops of D_2O, 500 MHz): δ 8.00 (d, $^3J_{H-H}$ = 8.1 Hz, 2H), 7.42 (m, 3H), 7.20 (d, $^3J_{H-H}$ = 7.5 Hz, 1H), 7.09 (dd, $^3J_{H-H}$ = 8.1 Hz; 7.5 Hz, 1H), 6.79 (d, $^3J_{H-H}$ = 9.2 Hz, 2H), 6.71 (d, $^3J_{H-H}$ = 8.6 Hz, 2H), 2.96 (s, 6H), 2.92 (s, 6H) ppm. ^{13}C-NMR ($(CD_3)_2SO$ and 1 drop of D_2O, 200 MHz): δ 152.6, 151.4, 150.1, 144.4, 135.0, 132.5, 127.9, 124.7, 121.5, 118.1, 117.0, 113.0, 111.8, 110.7, 109.4, 106.6, 93.8, 85.8, 39.5 ppm. HRMS (ESI/$[M+H]^+$): calcd for $C_{25}H_{25}N_4^+$ 381.2074, found 381.2073. Anal. Calcd for $C_{25}H_{24}N_4 \cdot ½THF$: C, 77.85; H, 6.78; N, 13.45. Found: C, 77.45; H, 6.00; N, 13.96.

Synthesis of compound **10**

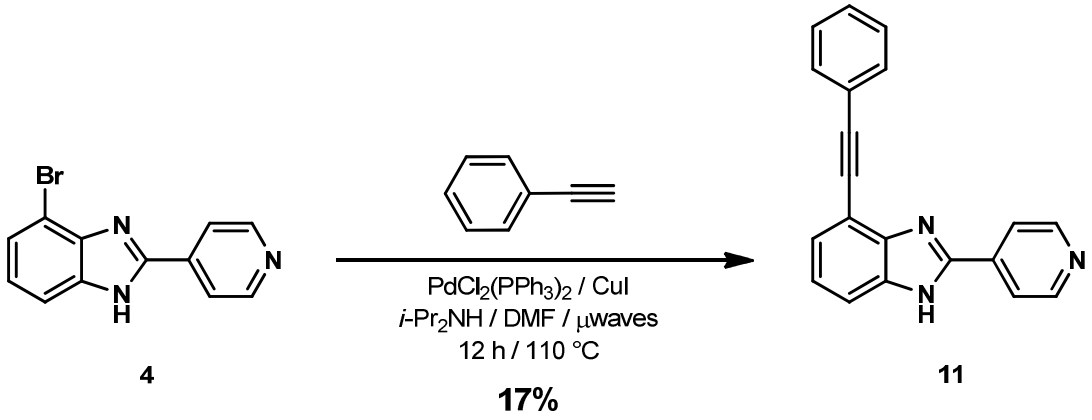


3 **10**

The entire amount of 4-ethynylpyridine (prepared as in the synthesis of compound **7** described above) was added to a thick-walled microwave pressure vial that contained a mixture of compound **3** (300 mg, 0.95 mmol), $PdCl_2(PPh_3)_2$ (60.0 mg, 0.09 mmol), CuI (20.0 mg, 0.11 mmol), *i*-Pr_2NH (5 mL), and DMF (5 mL). The vial was sealed and exposed to microwave irradiation for 12 h at 110 °C. After cooling, the reaction mixture was extracted with EtOAc, washed with brine, and dried over anhydrous $MgSO_4$. The product was isolated by column chromatography, eluting with pure EtOAc. The solvent was removed under reduced pressure, and the solid was recrystallized from a mixture of THF and hexane to give 55 mg (17%) of compound **10** as a yellow powder (mp 256 °C).

10: UV-Vis (THF): λ_{max} (log ε) = 222 (4.65), 306 (4.56), 314 (4.56), 326 (4.53), 359 (4.53) nm. IR (neat): 3419 (s, $\tilde{\nu}_{N-H}$), 2227 (w, $\tilde{\nu}_{C\equiv C}$), 1609 (s, $\tilde{\nu}_{C=N}$), 1500 (m), 1413 (m), 1365 (m), 1352 (m), 1205 (m), 790 (m), 739 (s), 688 (m), 608 (m) cm^{-1}. ^{1}H-NMR ($(CD_3)_2SO$ and 1 drop of D_2O, 500 MHz): δ 8.62 (d, $^3J_{H-H}$ = 5.2 Hz, 2H), 8.02 (br s, 2H), 7.58 (br s, 3H), 7.35 (dd, $^3J_{H-H}$ = 8.0 Hz; $^4J_{H-H}$ = 1.2 Hz, 1H), 7.16 (dd, $^3J_{H-H}$ = 8.1 Hz, $^3J_{H-H}$ = 7.5 Hz, 1H), 6.81 (d, $^3J_{H-H}$ = 9.2 Hz, 2H), 2.97 (s, 6H) ppm. ^{13}C-NMR ($(CD_3)_2SO$ and 1 drop of D_2O, 200 MHz): δ 153.5, 151.7, 150.0, 145.0, 135.1, 131.0, 128.2, 125.7, 125.5, 121.7, 116.6, 111.9, 111.5, 110.5, 92.5, 89.9, 39.5 ppm. HRMS (ESI/$[M+H]^+$): calcd for $C_{22}H_{19}N_4^+$ 339.1604, found 339.1606. Anal. Calcd. for $C_{22}H_{18}N_4 \cdot {}^1/_6$THF C, 77.69; H, 5.56; N, 15.99. Found: C, 77.24; H, 5.09; N, 13.34.

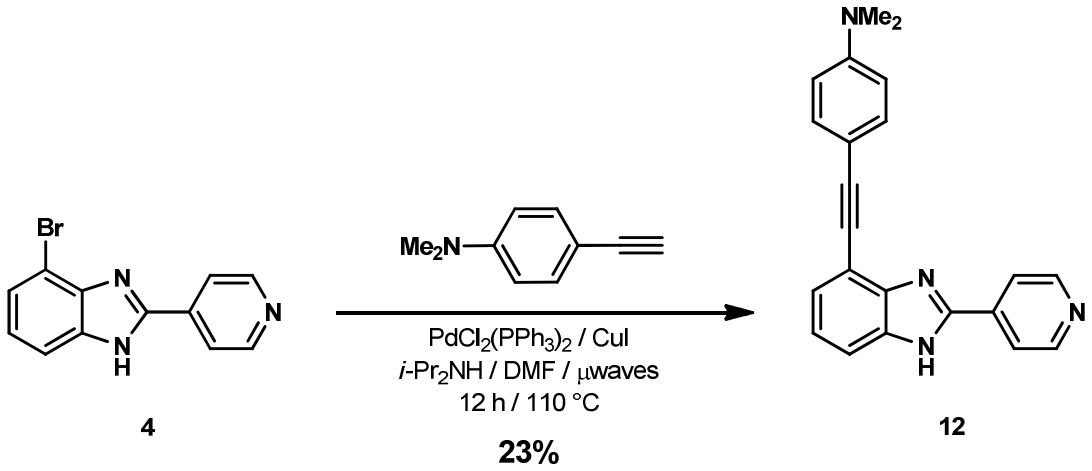
Synthesis of compound **11**



Phenylacetylene (418 mg, 4.09 mmol) was added to a thick-walled microwave pressure vial that contained a mixture of compound **4** (300 mg, 1.09 mmol), $PdCl_2(PPh_3)_2$ (60.0 mg, 0.09 mmol), CuI (20.0 mg, 0.11 mmol), *i*-Pr_2NH (5 mL), and DMF (5 mL). The vial was sealed and exposed to microwave irradiation for 12 h at 110 °C. After cooling, the reaction mixture was extracted with EtOAc, washed with brine, and dried over anhydrous $MgSO_4$. The product was isolated by column chromatography, eluting first with pure EtOAc, and then successively with EtOAc/MeOH mixtures in 95:5 and 90:10 ratios. The solvent was removed under reduced pressure, and the solid was recrystallized in the mixture of THF, CH_2Cl_2 and hexane to give 58 mg (17%) of compound **11** as a white powder (mp 226 °C).

11: UV-Vis (THF): λ_{max} (log ε) = 227 (4.45), 264 (4.46), 281 (4.36), 288 (4.34), 323 (4.46) nm. IR (neat): 3076 (w, $\tilde{\nu}_{C-H}$), 1609 (m, $\tilde{\nu}_{C=N}$), 1437 (m), 1250 (m), 999 (m), 829 (m), 756 (s), 736 (m), 696 (m), 630 (m) cm^{-1}. ^{1}H-NMR ($(CD_3)_2SO$, 500 MHz): δ 13.14 (br s, 1H), 8.74 (d, $^3J_{H-H}$ = 6.3 Hz, 2H), 8.13 (br s, 2H), 7.63 (br s, 3H), 7.43 (m, 4H), 7.28 (dd, $^3J_{H-H}$ = 8.0 Hz, $^3J_{H-H}$ = 7.5 Hz, 1H) ppm. ^{13}C-NMR ($(CD_3)_2SO$ and 1 drop of D_2O, 200 MHz): δ 150.5, 149.6, 144.1, 136.9, 135.1, 131.7, 128.9, 127.4, 126.4, 123.7, 122.7, 120.8, 113.6, 112.9, 93.2, 87.2 ppm. HRMS (ESI/$[M+H]^+$): calcd for $C_{20}H_{14}N_3^+$ 296.1182, found 296.1185. Anal. Calcd for $C_{20}H_{13}N_3 \cdot 1/5THF$: C, 80.65; H, 4.75; N, 13.57. Found: C, 80.41; H, 4.02; N, 13.97.

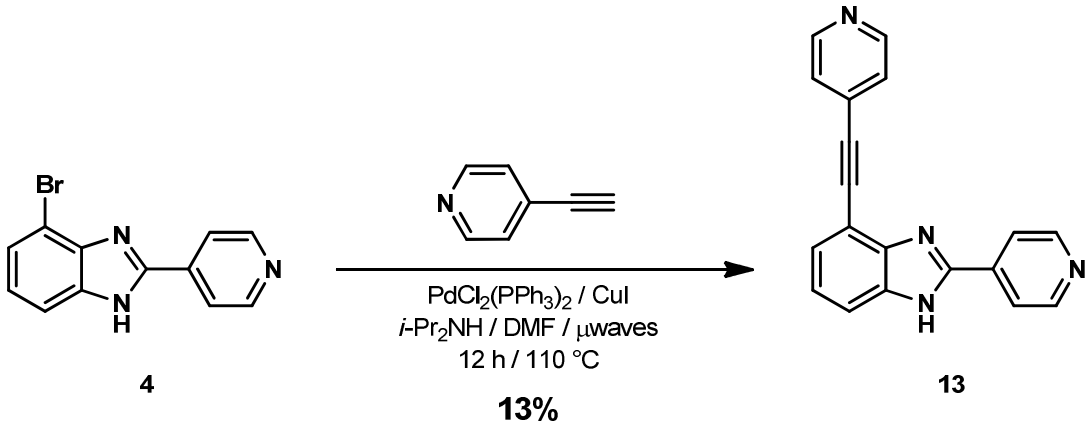
Synthesis of compound **12**



The entire amount of 4-ethynyl-*N*,*N*-dimethylaniline (prepared as in the synthesis of compound **6** described above) was added to a thick-walled microwave pressure vial that contained a mixture of compound **4** (300 mg, 1.09 mmol), $PdCl_2(PPh_3)_2$ (60.0 mg, 0.09 mmol), CuI (20.0 mg, 0.11 mmol), *i*-Pr_2NH (5 mL), and DMF (5 mL). The vial was sealed and exposed to microwave irradiation for 12 h at 110 °C. After cooling, the reaction mixture was extracted with EtOAc, washed with brine, and dried over anhydrous $MgSO_4$. The product was isolated by column chromatography, eluting first with pure EtOAc, and then successively with EtOAc/MeOH mixtures in 95:5 and 90:10 ratios. The solvent was removed under reduced pressure, and the solid was recrystallized from a mixture of THF, MeOH and hexane to give 85 mg (23%) of compound **12** as a yellow powder (mp 259 °C, with decomposition).

12: UV-Vis (THF): λ_{max} (log ε) = 265 (4.20), 294 (4.50), 315 (4.54), 357 (4.28) nm. IR (neat): 3098 (w, $\tilde{\nu}_{N-H}$), 2215 (w, $\tilde{\nu}_{C\equiv C}$), 1608 (s, $\tilde{\nu}_{C=N}$), 1524 (m), 1445 (m), 1363 (m), 1186 (m), 822 (m), 795 (m), 743 (s), 701 (m), 630 (m) cm^{-1}. ^{1}H-NMR ($(CD_3)_2SO$ and 1 drop of D_2O, 500 MHz): δ 8.73 (dd, $^3J_{H-H}$ = 6.3 Hz, 2H), 8.13 (br s, 2H), 7.60 (br s, 1H), 7.44 (d, $^3J_{H-H}$ = 8.6 Hz, 2H), 7.36 (d, $^3J_{H-H}$ = 8.0 Hz, 1H), 7.25 (dd, $^3J_{H-H}$ = 8.0 Hz, $^3J_{H-H}$ = 7.5 Hz, 1H), 6.72 (d, $^3J_{H-H}$ = 9.2 Hz, 2H), 2.93 (s, 6H) ppm. ^{13}C-NMR ($(CD_3)_2SO$ and 1 drop of D_2O, 200 MHz): δ 150.6, 150.4, 149.3, 143.9, 137.0, 135.2, 132.8, 125.9, 123.8, 120.8, 114.8, 112.1, 108.9, 95.1, 85.1, 39.5 ppm. HRMS (ESI/$[M+H]^+$): calcd for $C_{22}H_{19}N_4^+$ 339.1604, found 339.1605. Anal. Calcd for $C_{22}H_{18}N_4 \cdot ½THF$: C, 76.98; H, 5.92; N, 14.96. Found: C, 75.33; H, 5.35; N, 15.33.

Synthesis of compound **13**

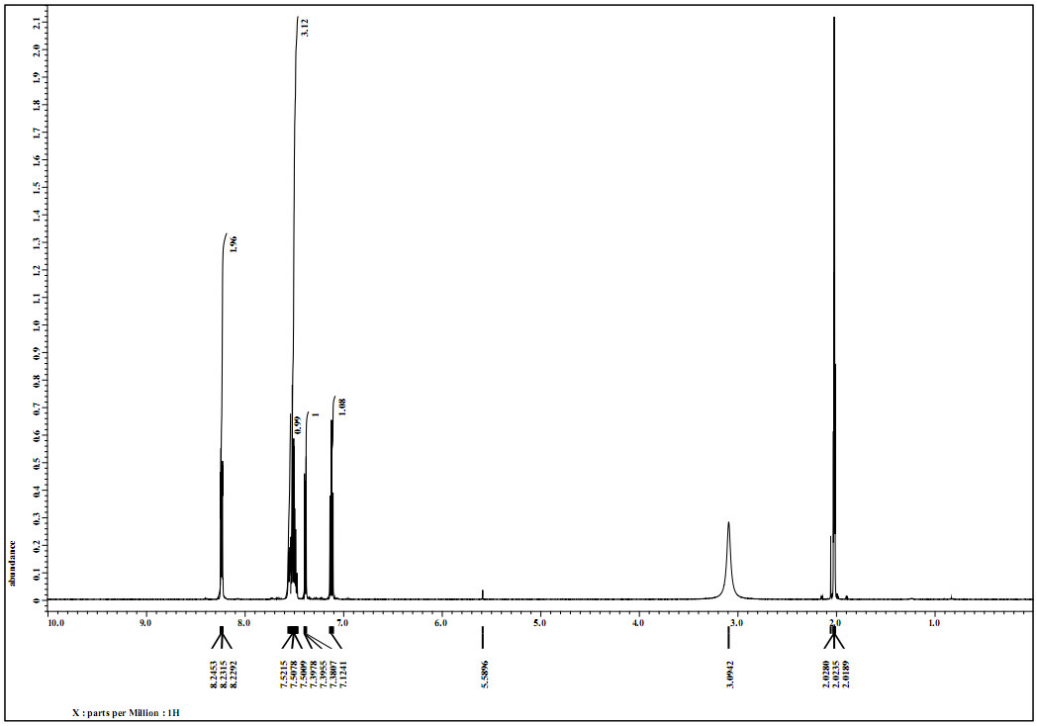


The entire amount of 4-ethynylpyridine (prepared as in the synthesis of compound **7** described above) was added to a thick-walled microwave pressure vial that contained a mixture of compound **4** (300 mg, 1.09 mmol), $PdCl_2(PPh_3)_2$ (60.0 mg, 0.09 mmol), CuI (20.0 mg, 0.11 mmol), *i*-Pr_2NH (5 mL), and DMF (5 mL). The vial was sealed and exposed to microwave irradiation for 12 h at 110 °C. After cooling, the reaction mixture was extracted with EtOAc, washed with brine, and dried over anhydrous $MgSO_4$. The product was isolated by column chromatography, eluting first with pure EtOAc, and then successively with EtOAc/MeOH mixtures in 95:5 and 90:10 ratios. The solvent was removed under reduced pressure, and the solid was recrystallized from a mixture of THF, MeOH and hexane to give 41 mg (13%) of compound **13** as an off-white powder (mp 252 °C, with decomposition).

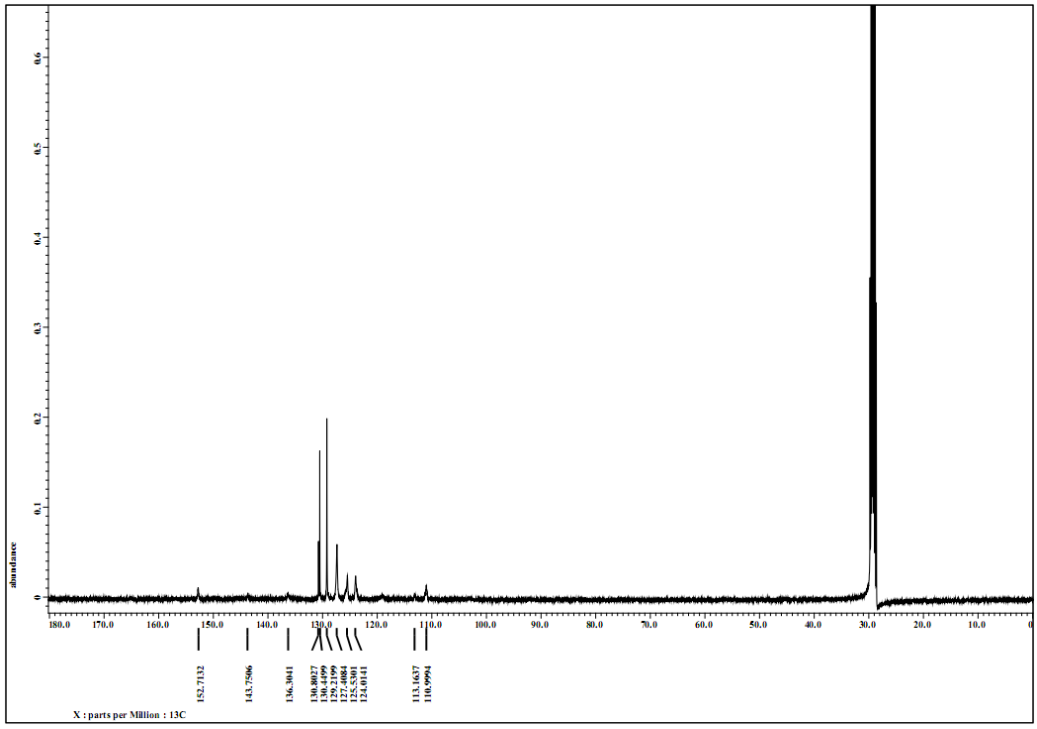
13: UV-Vis (THF): λ_{max} (log ε) = 262 (4.36), 277 (4.38), 289 (4.41), 327 (4.53) nm. IR (neat): 3067 (w, $\tilde{\nu}_{N-H}$), 2227 (w, $\tilde{\nu}_{C\equiv C}$), 1601 (s, $\tilde{\nu}_{C=N}$), 1438 (m), 829 (s), 792 (m), 738 (s), 698 (m), 613 (m) cm^{-1}. ^{1}H-NMR ($(CD_3)_2SO$, 500 MHz): δ 13.20 (br s, 1H), 8.75 (d, $^3J_{H-H}$ = 6.3 Hz, 2H), 8.64 (d, $^3J_{H-H}$ = 6.3 Hz, 2H), 8.13 (d, $^3J_{H-H}$ = 5.7 Hz, 2H), 7.72 (d, $^3J_{H-H}$ = 8.0 Hz, 1H), 7.56 (d, $^3J_{H-H}$ = 5.2 Hz, 2H), 7.49 (d, $^3J_{H-H}$ = 7.5 Hz, 1H), 7.31 (dd, $^3J_{H-H}$ = 8.0 Hz, $^3J_{H-H}$ = 7.5 Hz, 1H) ppm. ^{13}C-NMR ($(CD_3)_2SO$ and 1 drop of D_2O, 200 MHz): δ 150.7, 150.0, 149.8, 144.3, 136.8, 135.2, 130.7, 127.0, 125.7, 123.9, 120.8, 113.9, 112.3, 91.7, 90.4 ppm. HRMS (ESI/$[M+H]^+$): calcd for $C_{19}H_{13}N_4^+$ 297.1135, found 297.1136. Anal. Calcd for $C_{19}H_{12}N_4 \cdot \frac{1}{3}H_2O$: C, 75.48; H, 4.22; N, 18.53. Found: C, 75.19; H, 3.80; N, 18.22.

NMR Spectra of New Compounds

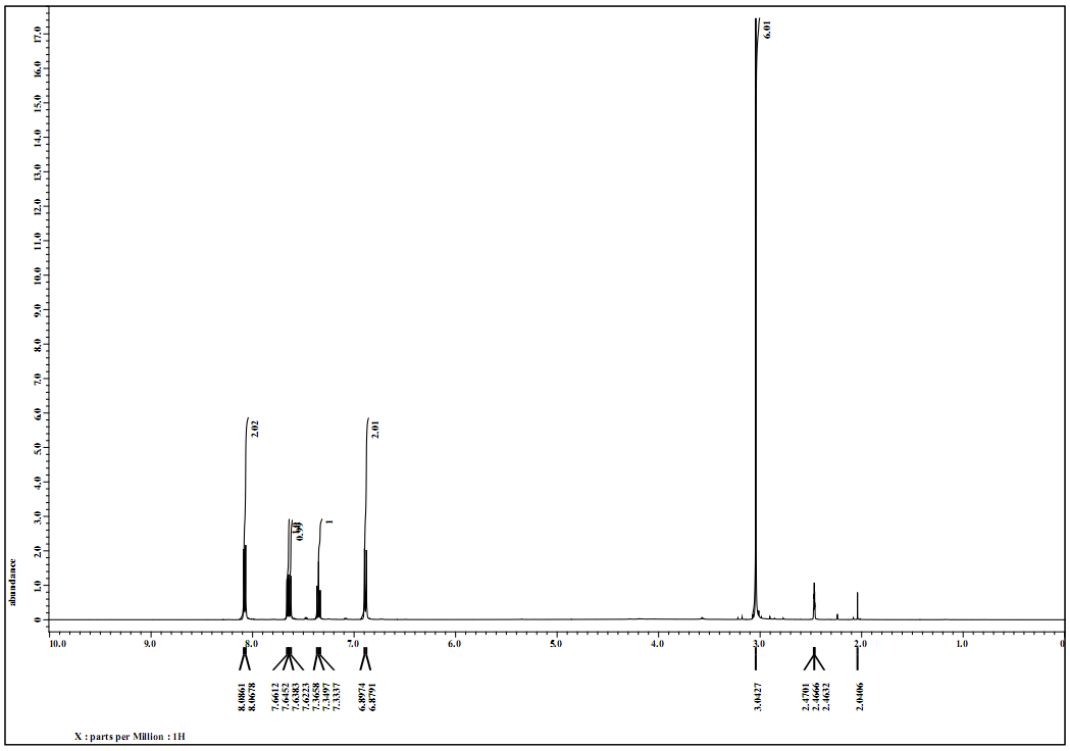
^{1}H-NMR spectrum of compound **2** (500 MHz, $(CD_3)_2CO$-d_6 and 1 drop D_2O)



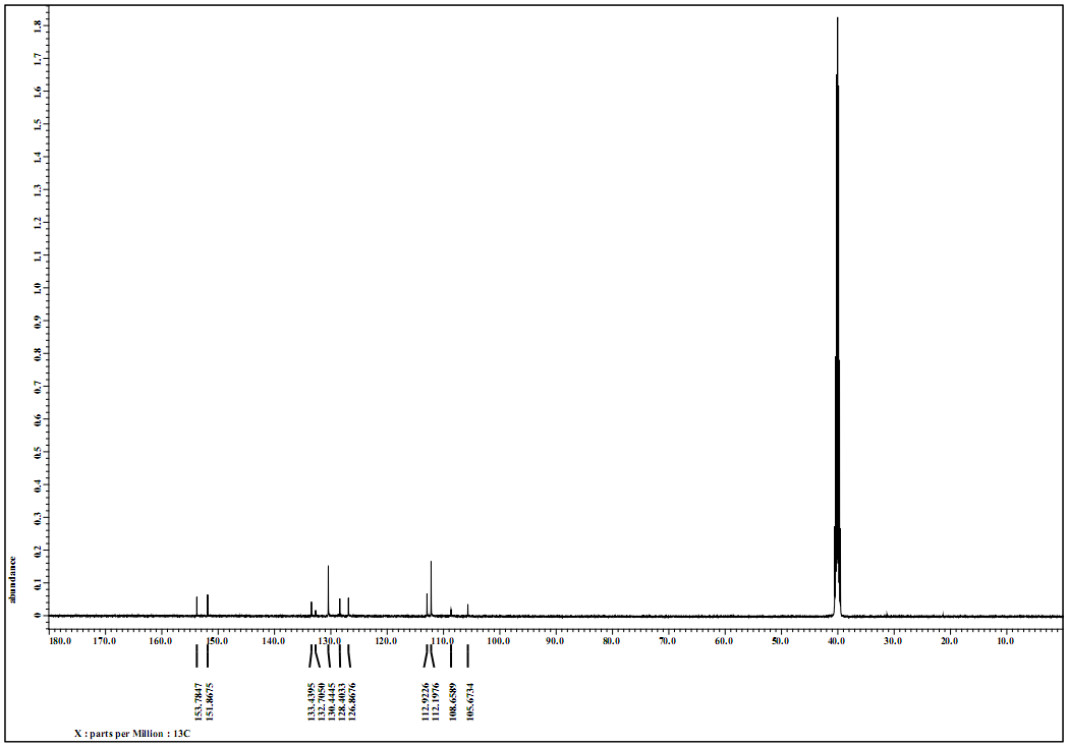
2: ^{13}C-NMR (400 MHz, $(CD_3)_2CO$-d_6 and 1 drop D_2O)



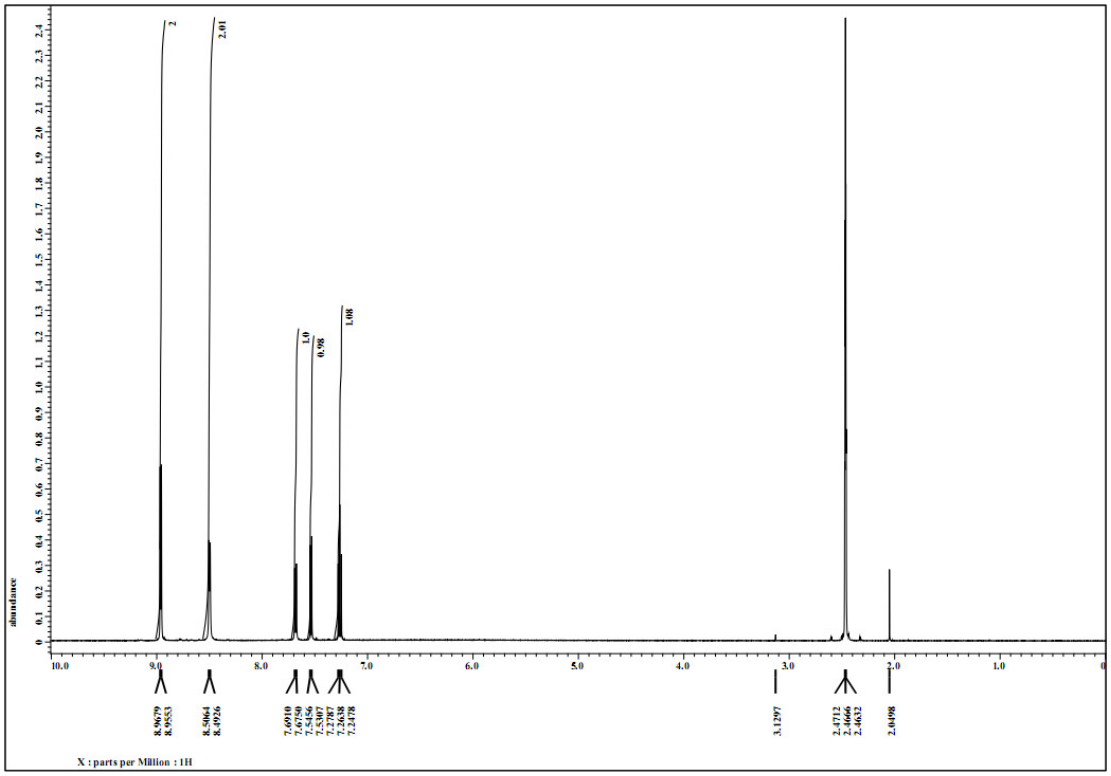
^{1}H-NMR spectrum of compound **3** (500 MHz, DMSO-d_6)



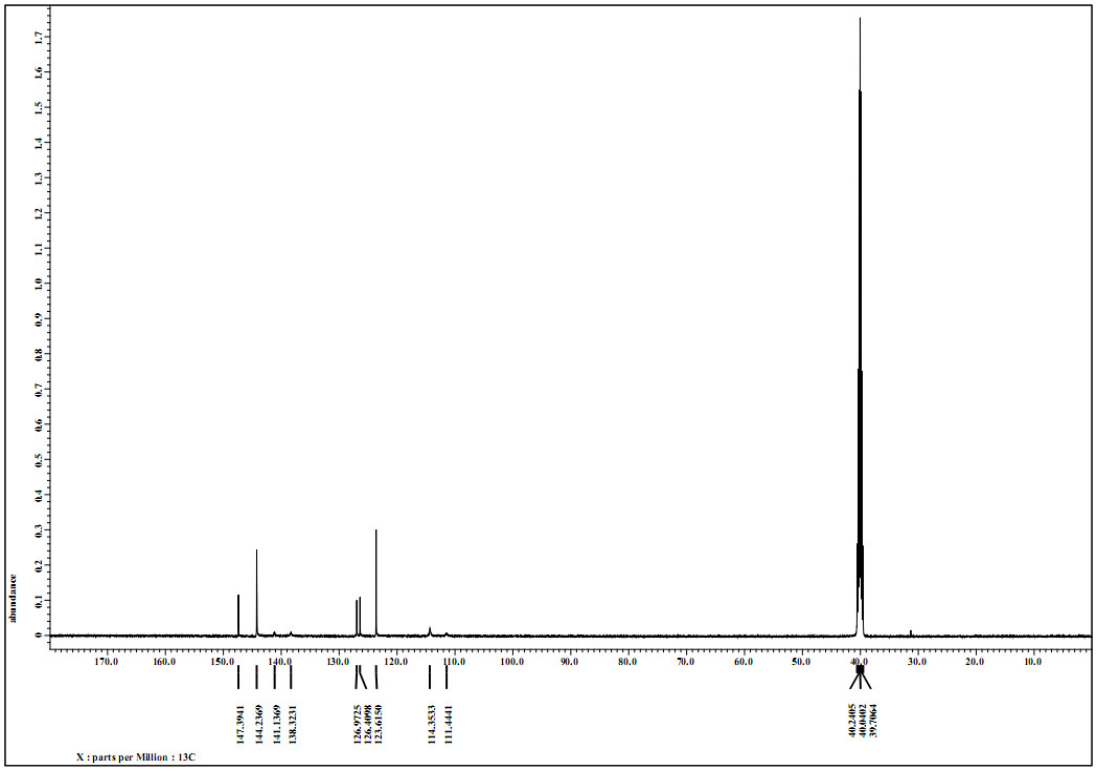
^{13}C-NMR spectrum of compound **3** (500 MHz, DMSO-d_6)



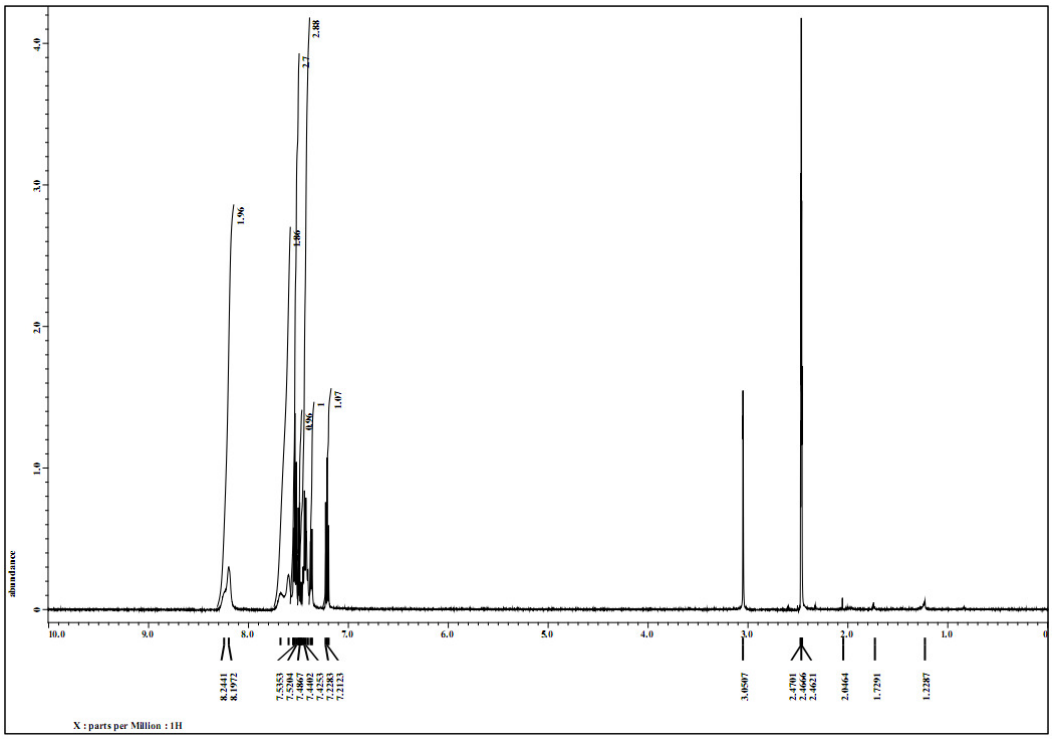
^{1}H-NMR spectrum of compound **4** (500 MHz, DMSO-d_6)



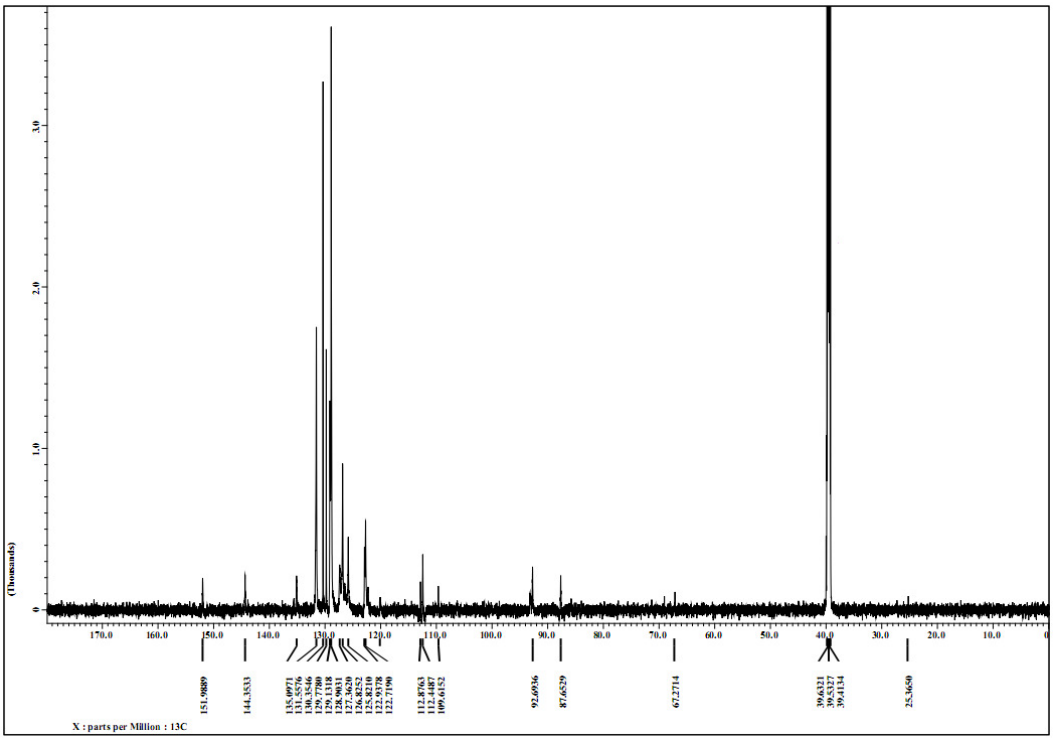
^{13}C-NMR spectrum of compound **4** (125 MHz, DMSO-d_6)



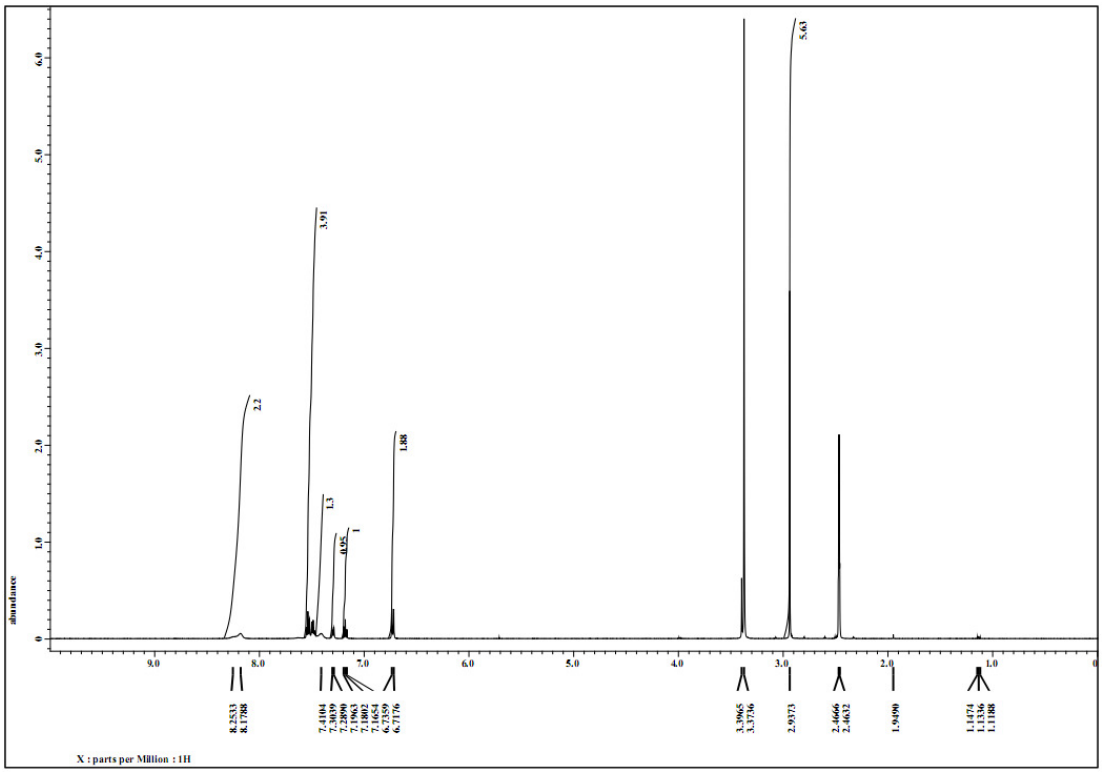
^{1}H-NMR spectrum of compound **5** (500 MHz, $((CD_3)_2SO$ and 1 drop of D_2O)



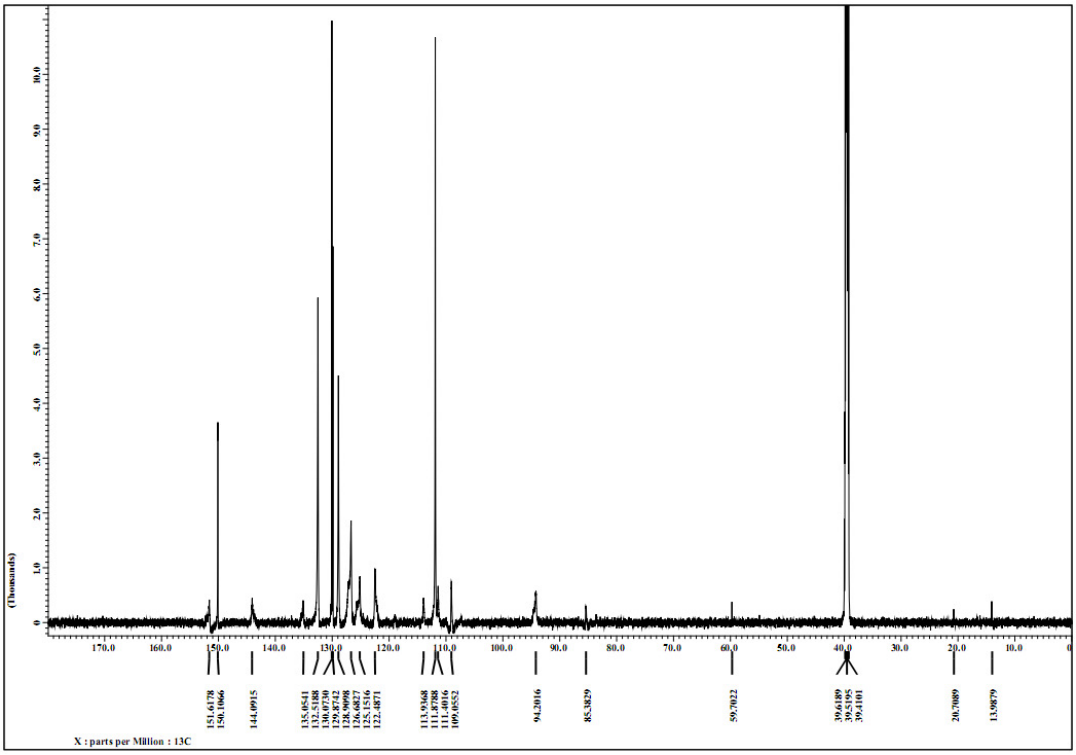
^{13}C-NMR spectrum of compound **5** (200 MHz, $(CD_3)_2SO$ and 1 drop of D_2O)



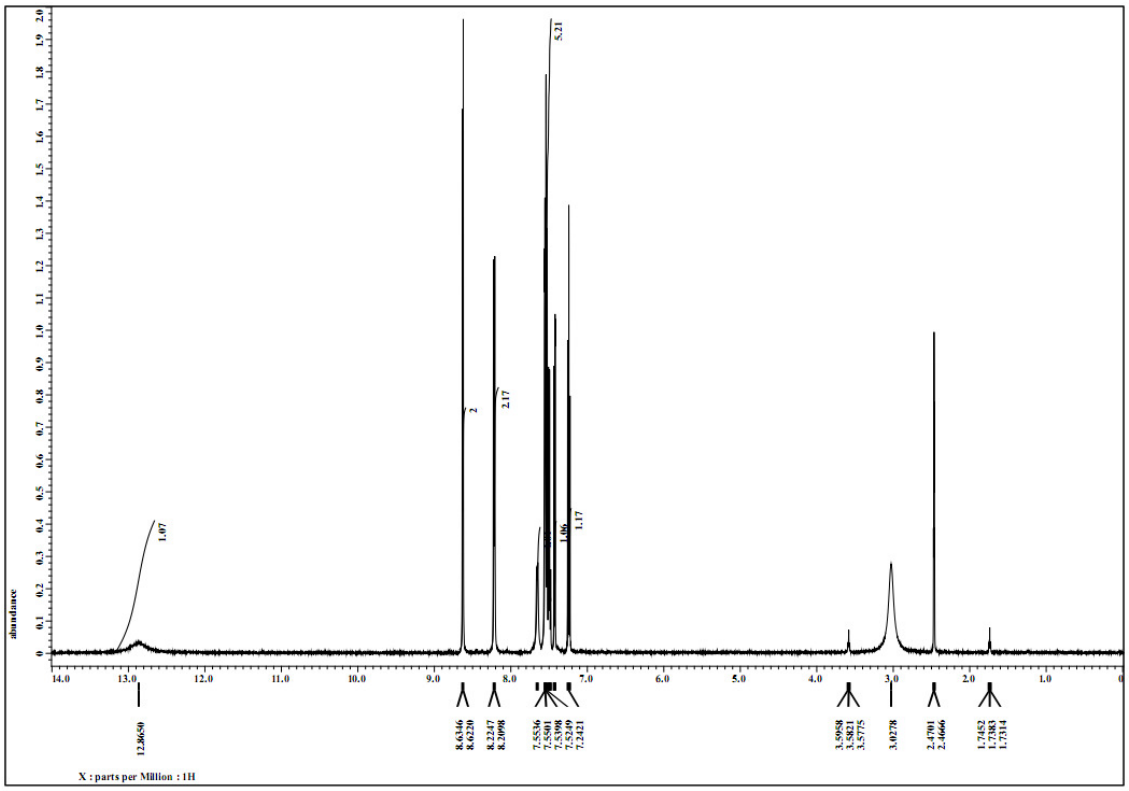
^{1}H-NMR spectrum of compound **6** (500 MHz, $(CD_3)_2SO$ and 1 drop of D_2O)



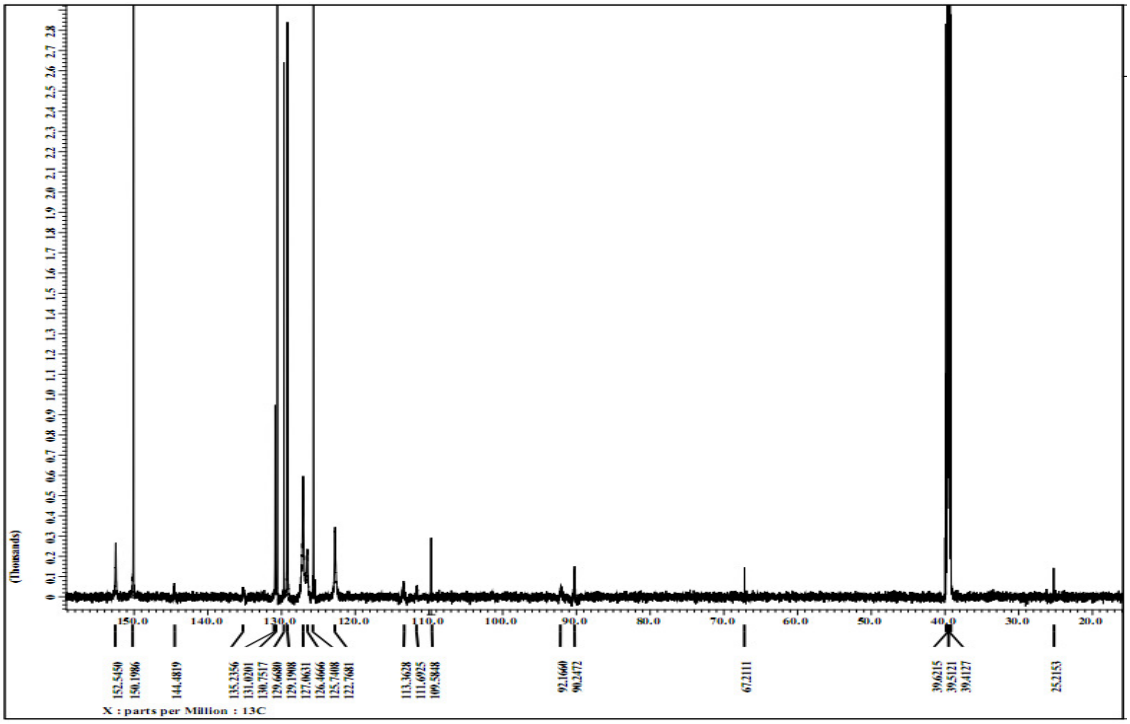
^{13}C-NMR spectrum of compound **6** (200 MHz, $(CD_3)_2SO$ and 1 drop of D_2O)



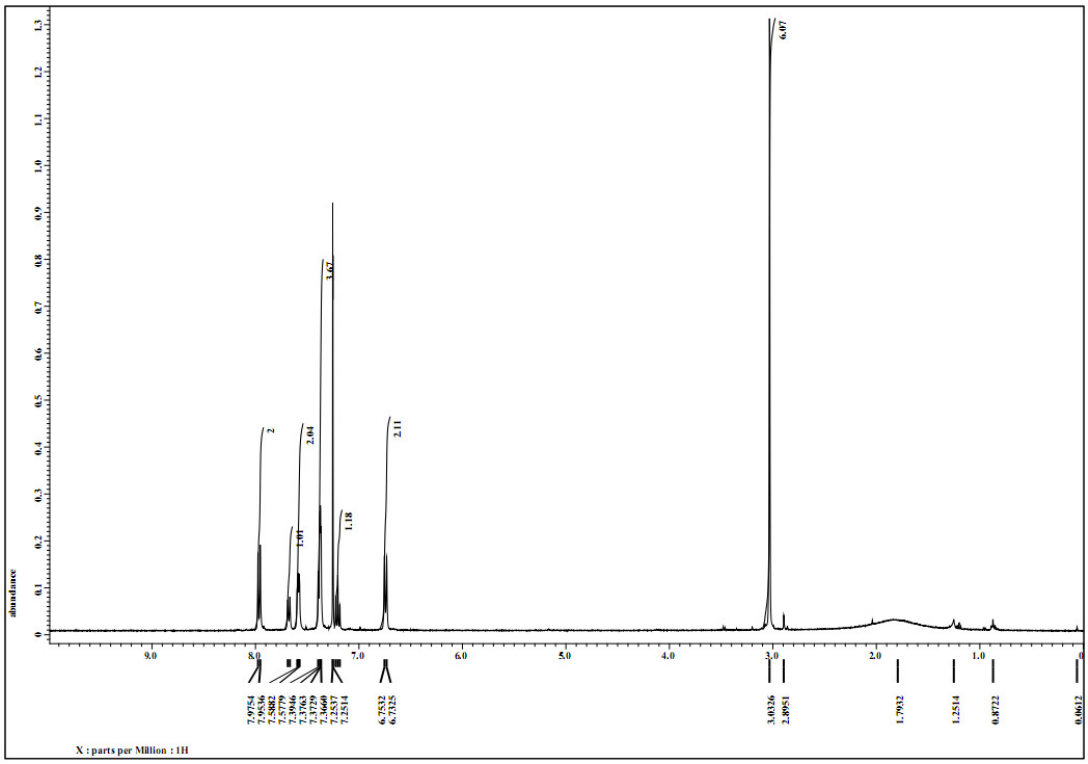
^{1}H-NMR spectrum of compound **7** (500 MHz, $(CD_3)_2SO$)



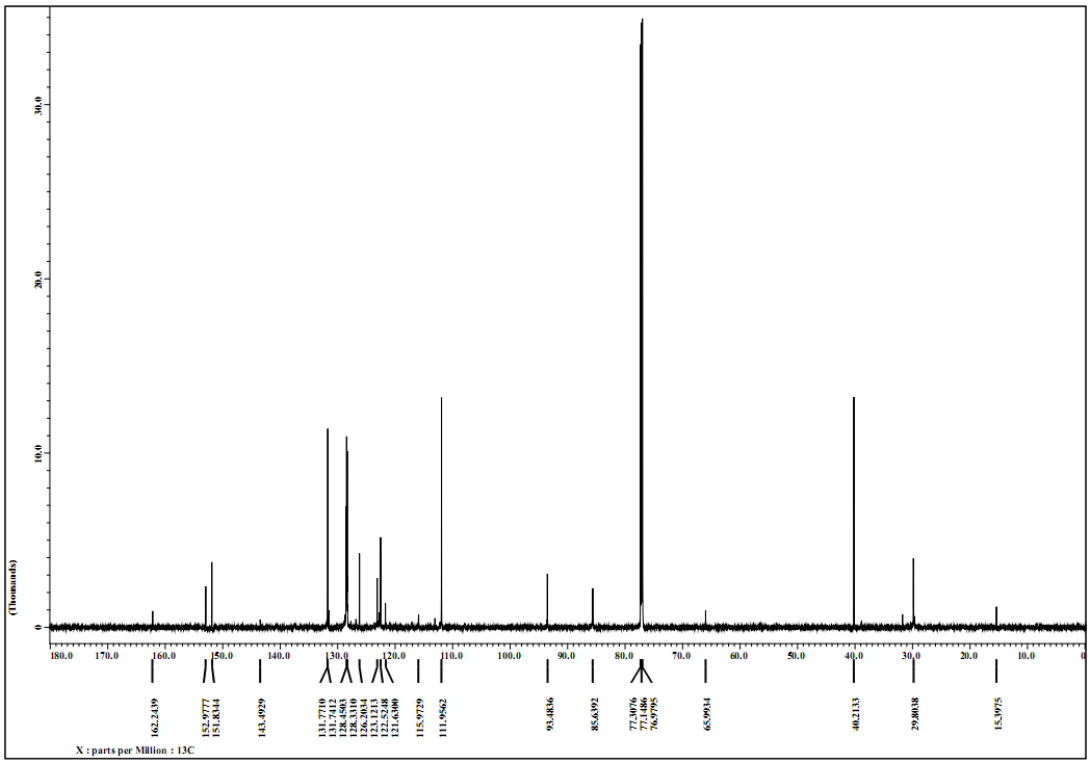
^{13}C-NMR spectrum of compound **7** (200 MHz, $(CD_3)_2SO$ and 1 drop of D_2O)



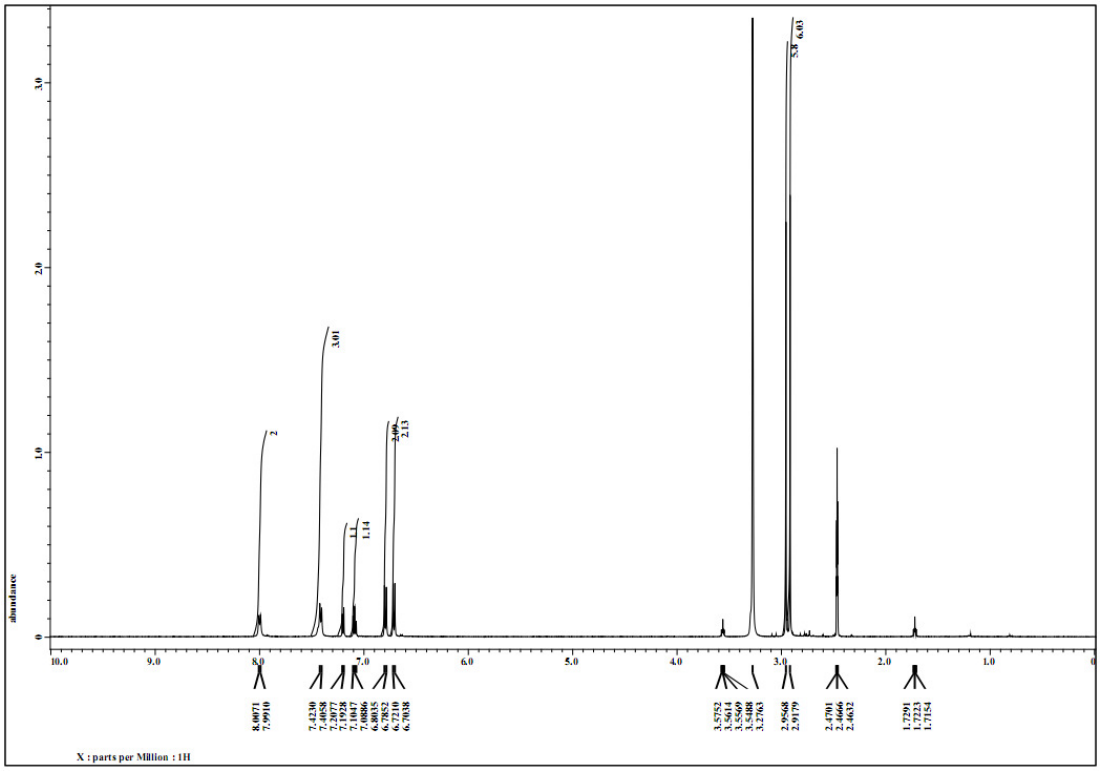
^{1}H-NMR spectrum of compound **8** (400 MHz, $CDCl_3$)



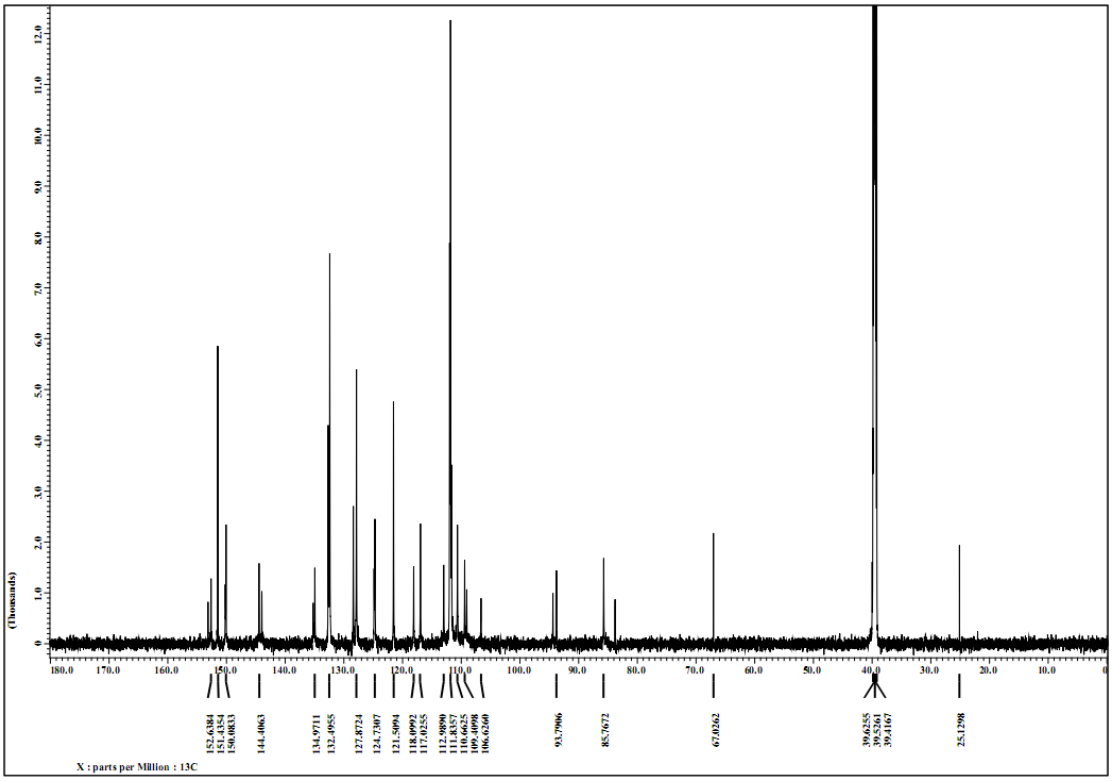
^{13}C-NMR spectrum of compound **8** (200 MHz, $CDCl_3$)



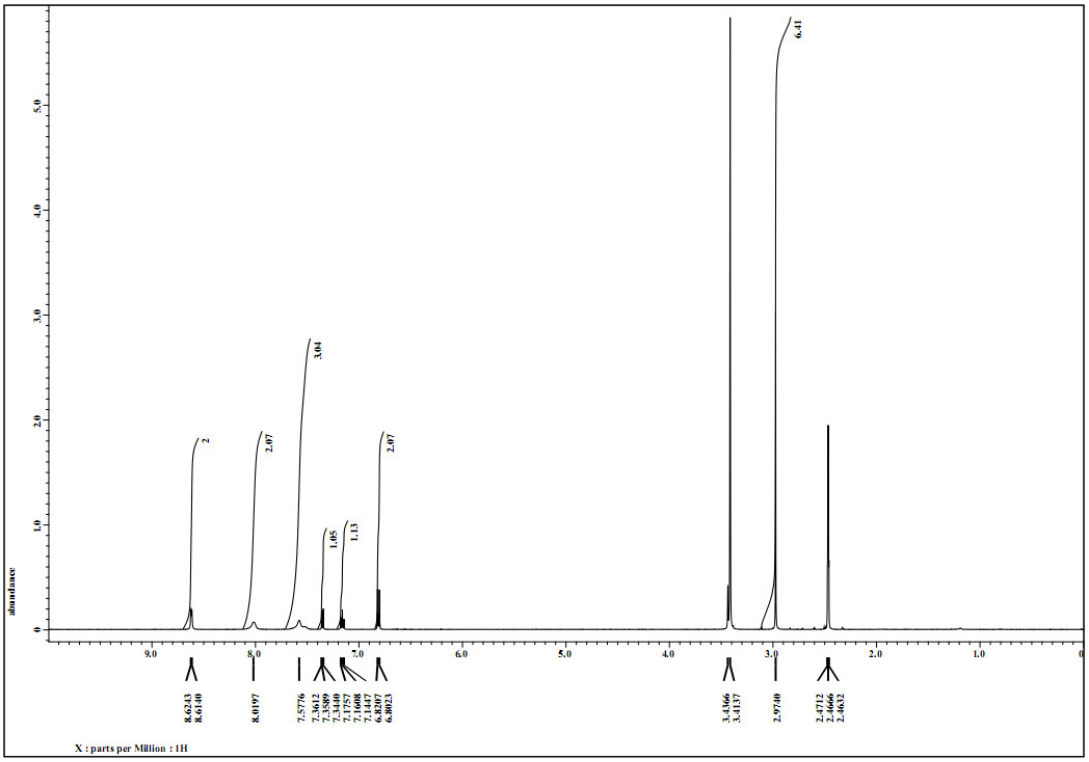
^{1}H-NMR spectrum of compound **9** (500 MHz, $(CD_3)_2SO$ and 3 drops of D_2O)



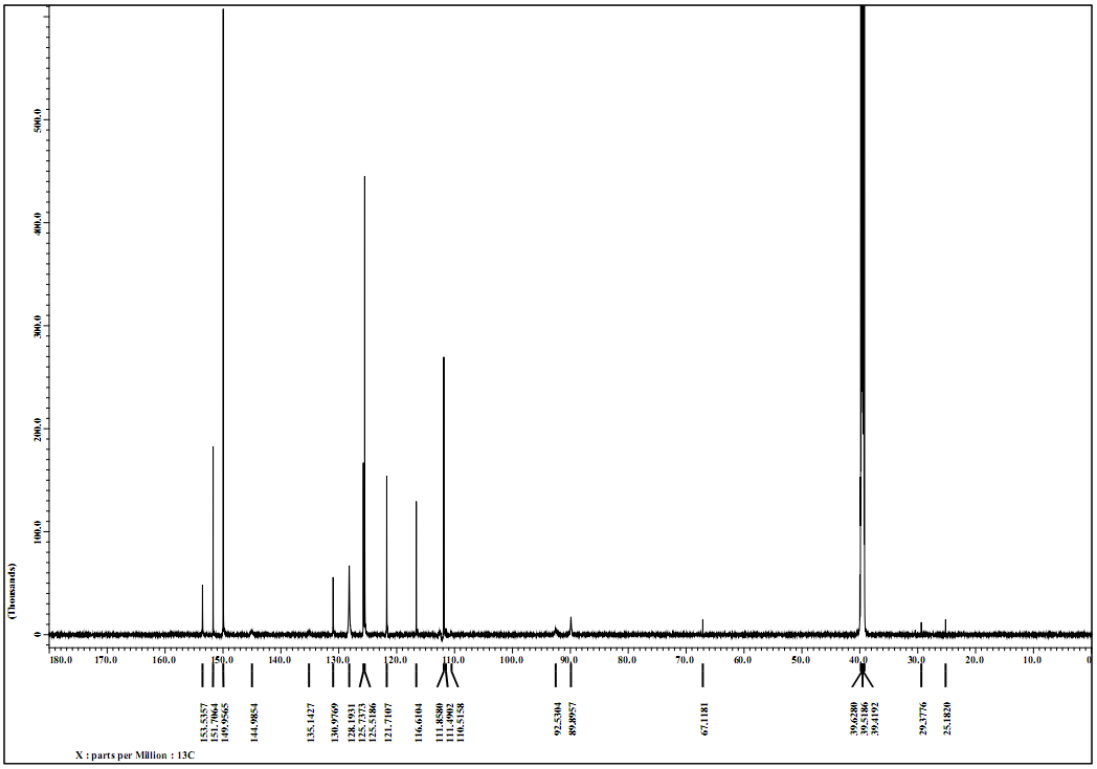
^{13}C-NMR spectrum of compound **9** (200 MHz, $(CD_3)_2SO$ and 1 drop of D_2O)



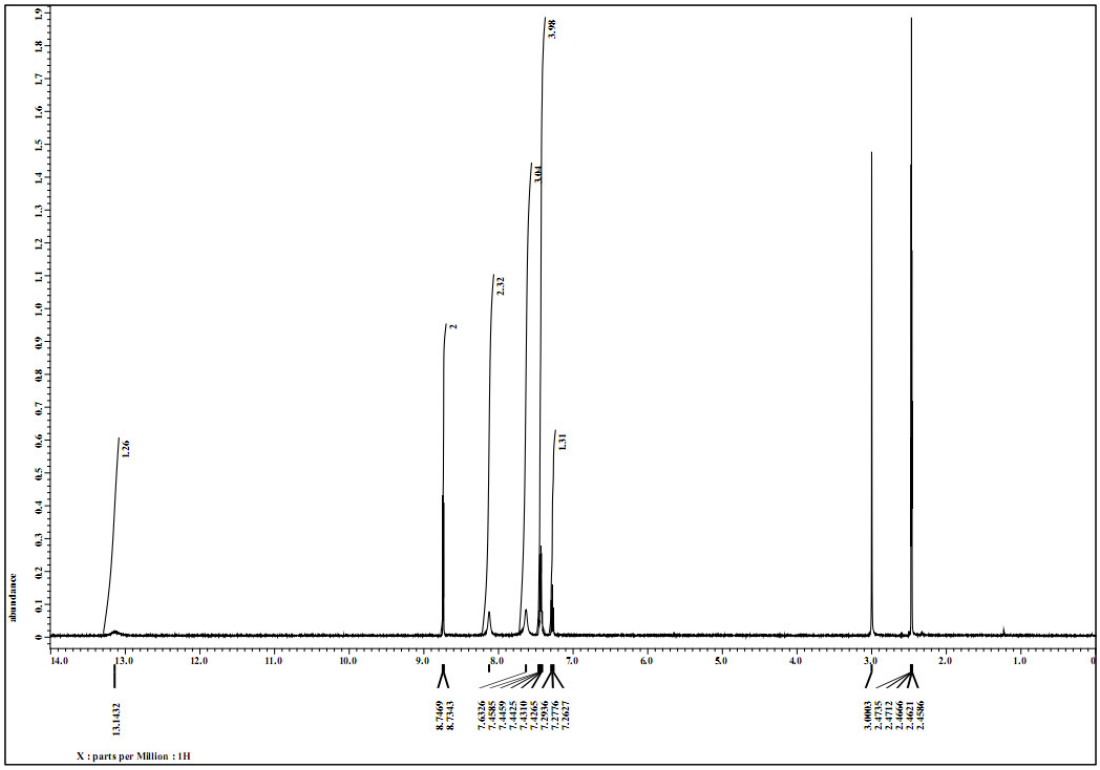
^{1}H-NMR spectrum of compound **10** (500 MHz, $(CD_3)_2SO$ and 1 drop of D_2O)



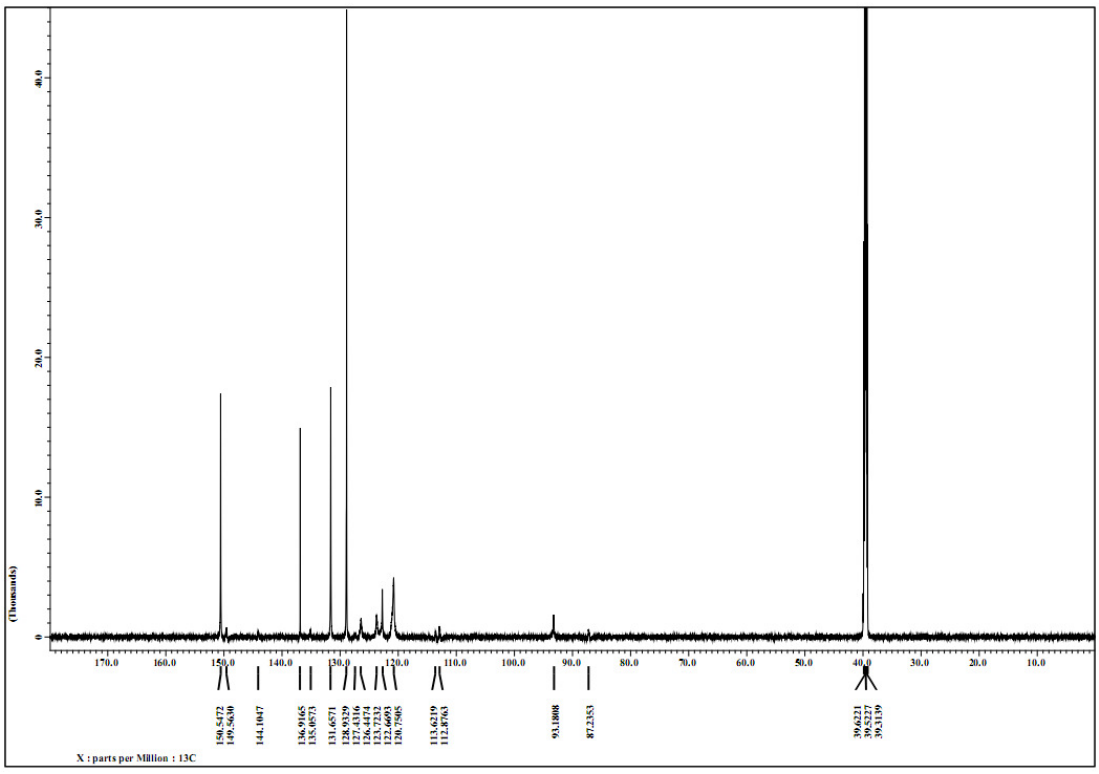
^{13}C-NMR spectrum of compound **10** (200 MHz, $(CD_3)_2SO$ and 1 drop of D_2O)



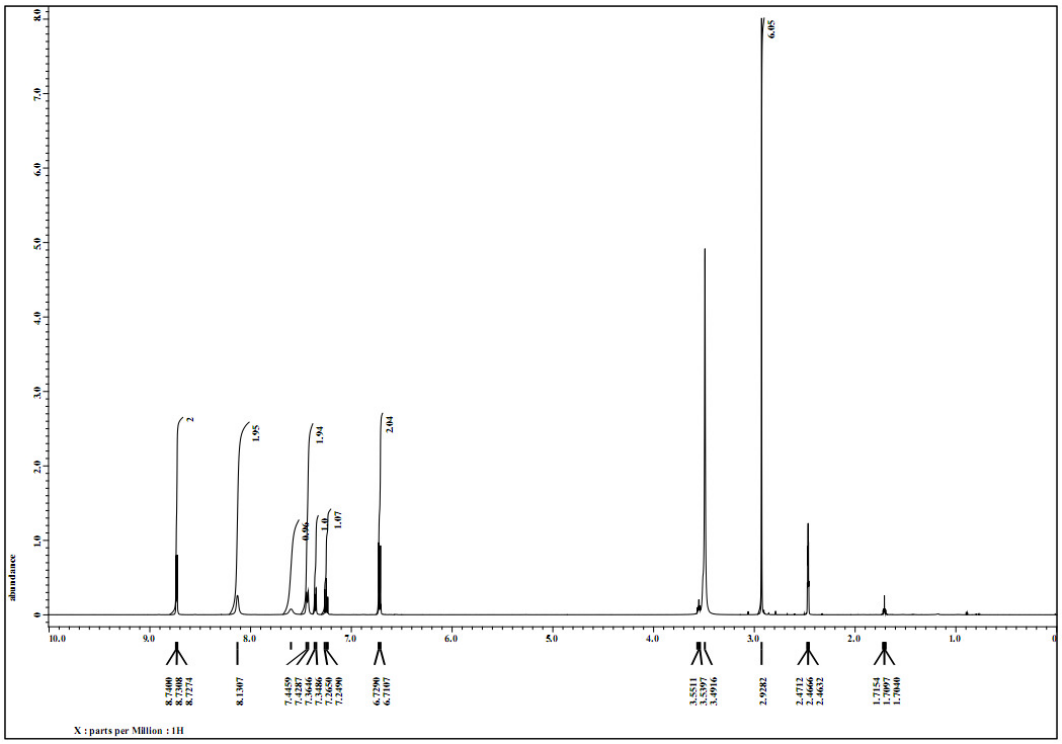
^{1}H-NMR spectrum of compound **11** (500 MHz, $(CD_3)_2SO$)



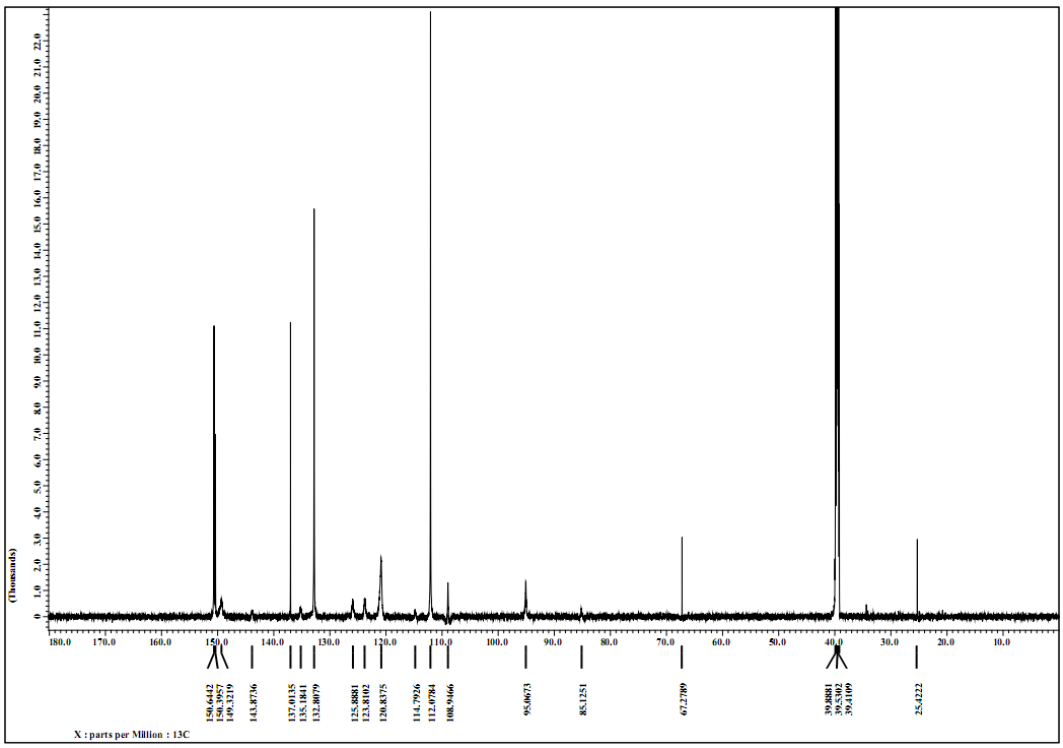
^{13}C-NMR spectrum of compound **11** (200 MHz, $(CD_3)_2SO$ and 1 drop of D_2O)



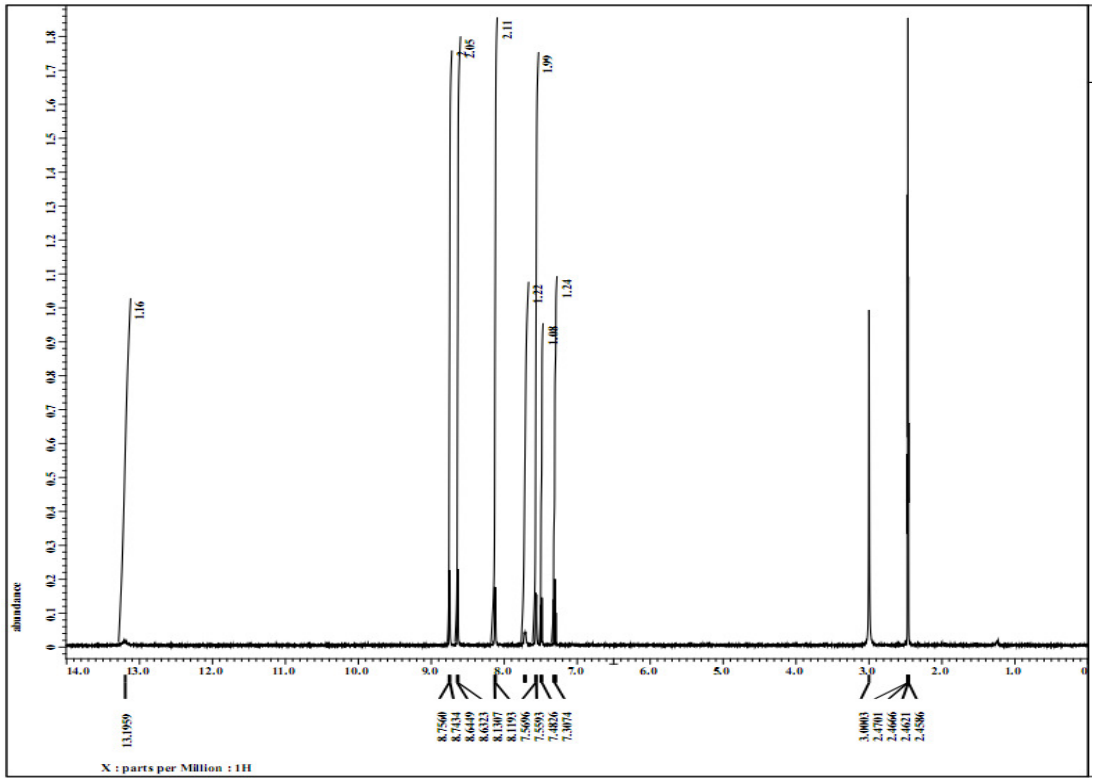
^{1}H-NMR spectrum of compound **11** (500 MHz, $(CD_3)_2SO$ and 1 drop of D_2O)



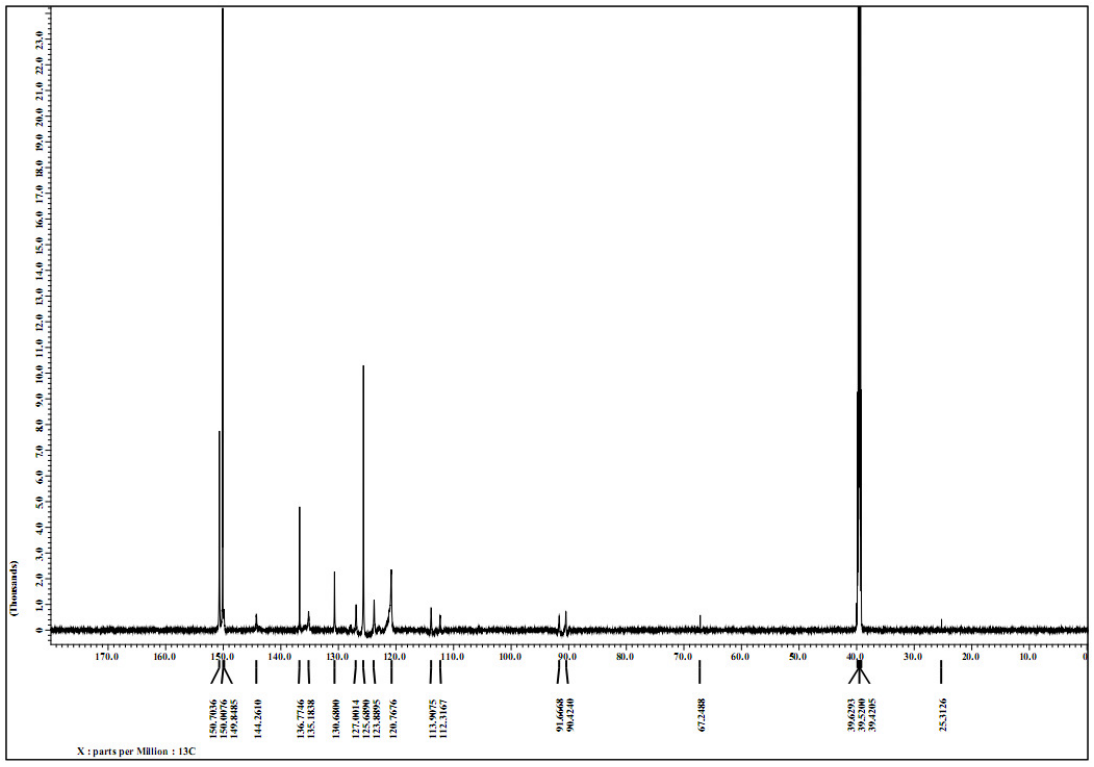
^{13}C-NMR spectrum of compound **12** (200 MHz, $(CD_3)_2SO$ and 1 drop of D_2O)



^{1}H-NMR spectrum of compound **13** (500 MHz, $(CD_3)_2SO$)

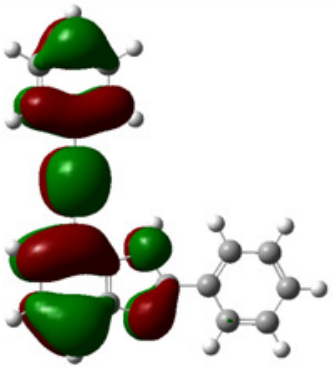
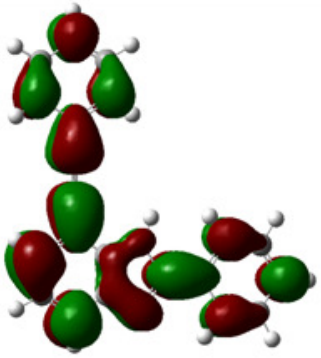
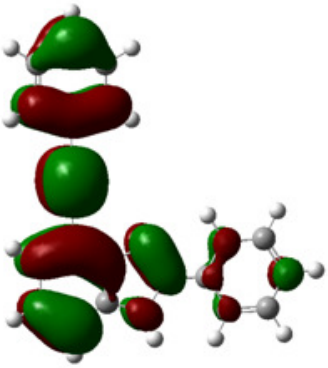
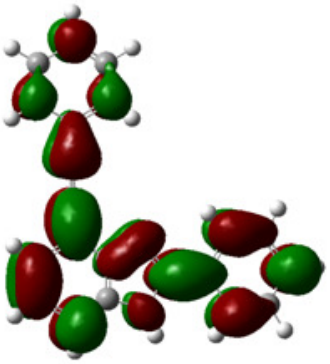


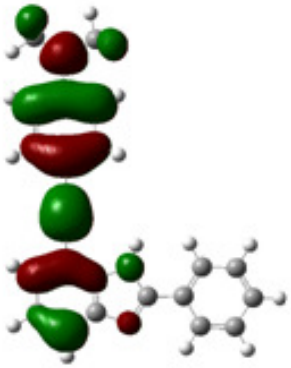
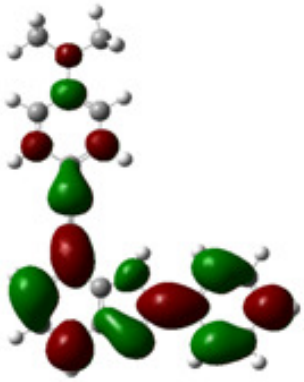
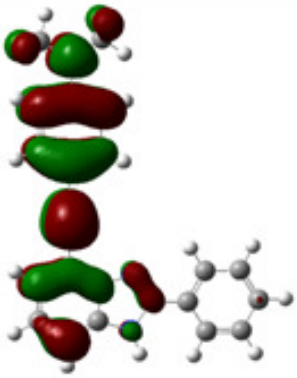
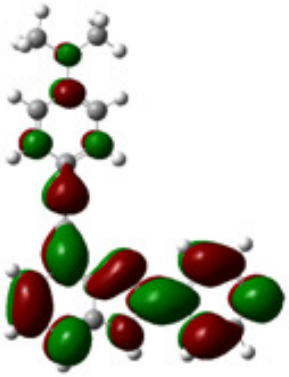
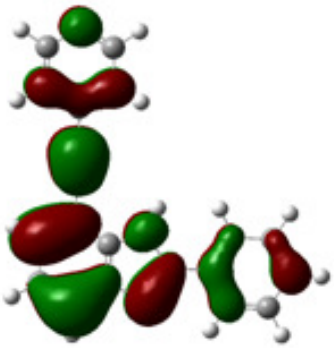
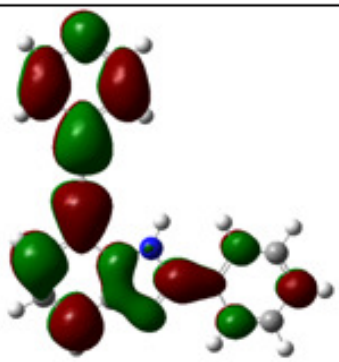
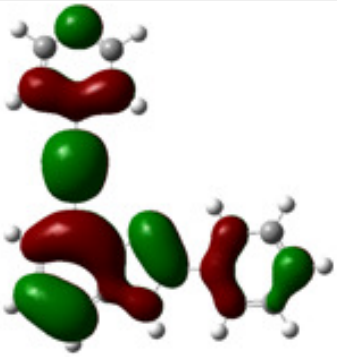
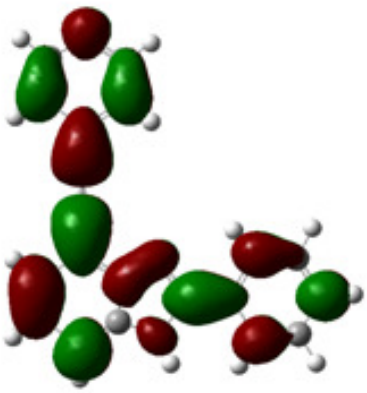
^{13}C-NMR spectrum of compound **13** (200 MHz, $(CD_3)_2SO$ and 1 drop of D_2O)

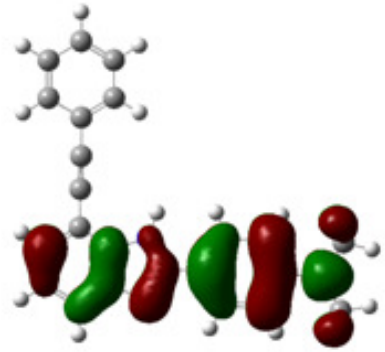
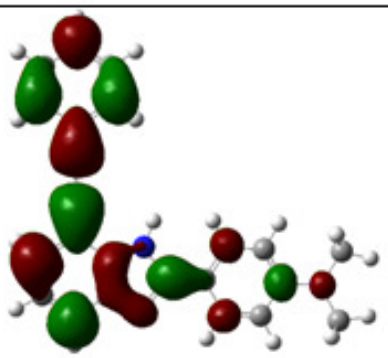
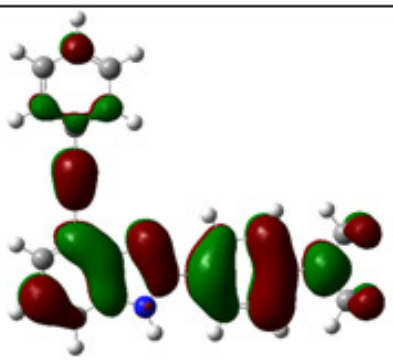
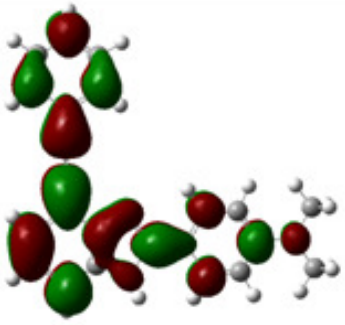
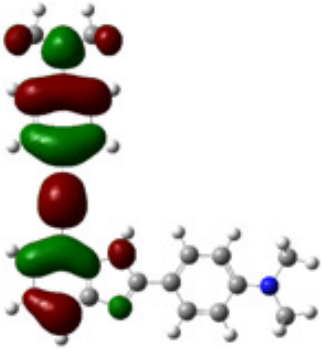
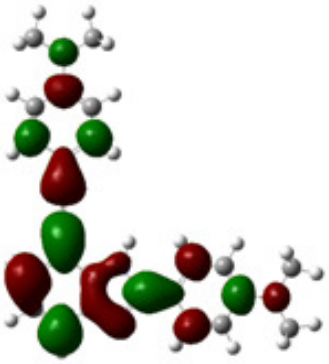
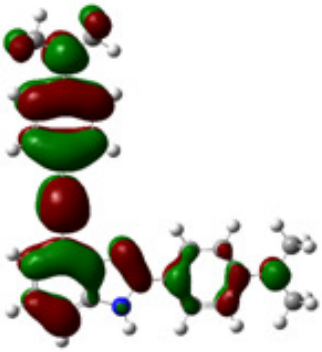
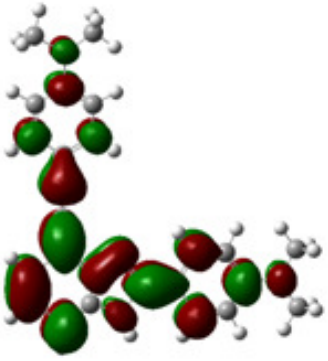


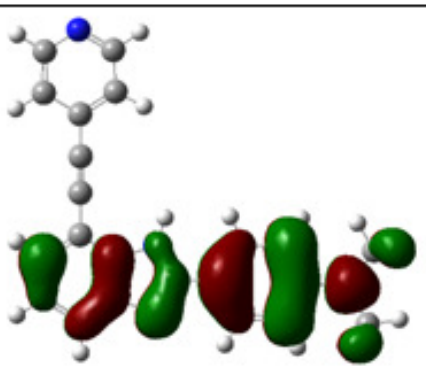
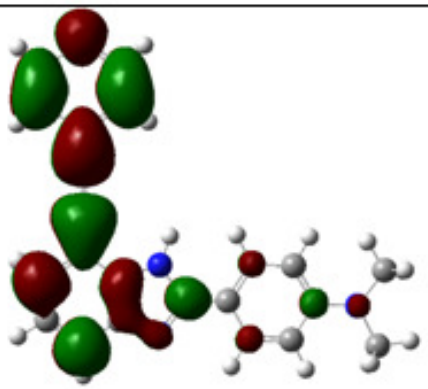
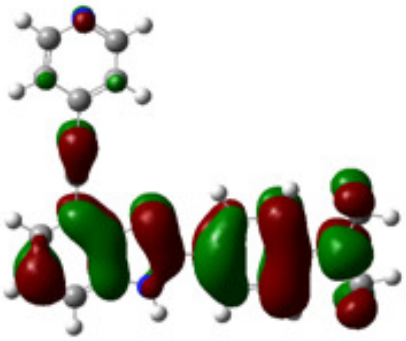
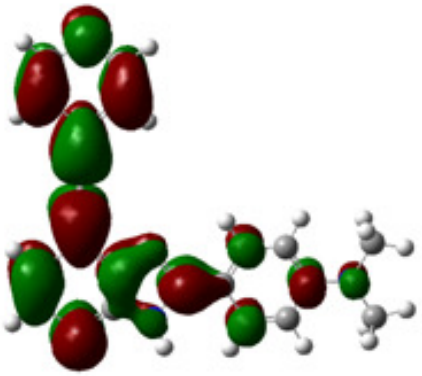
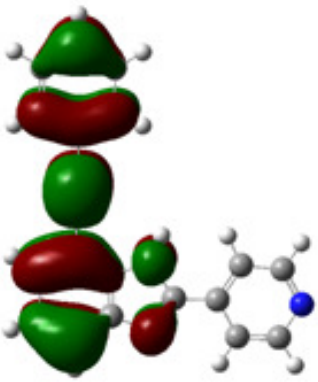
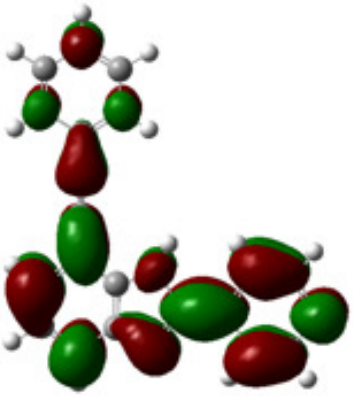
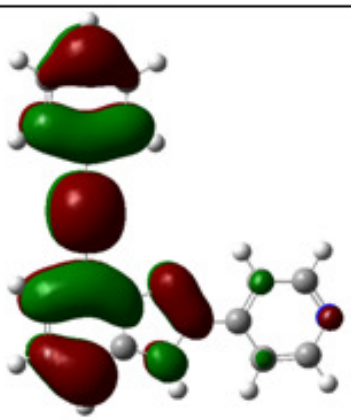
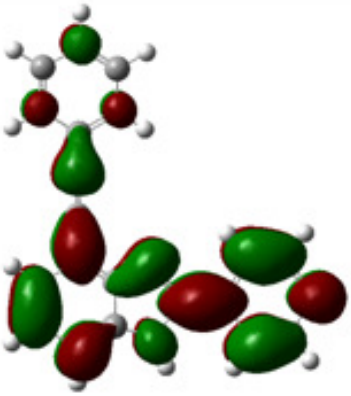
Computational Studies

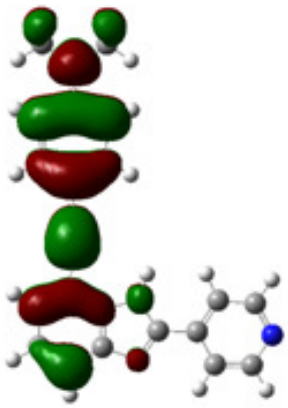
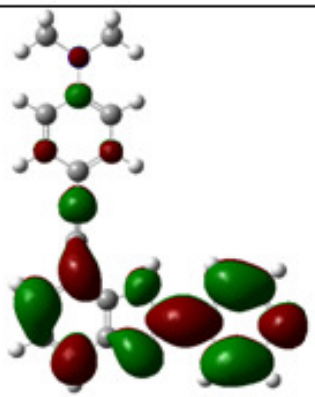
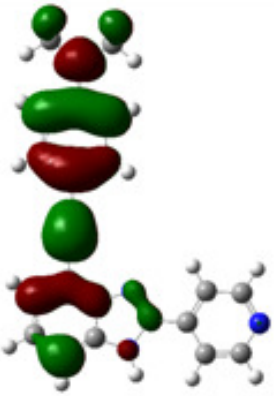
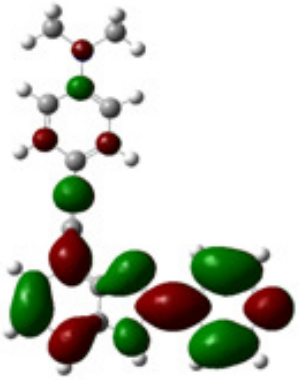
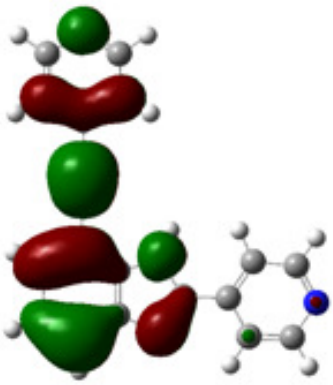
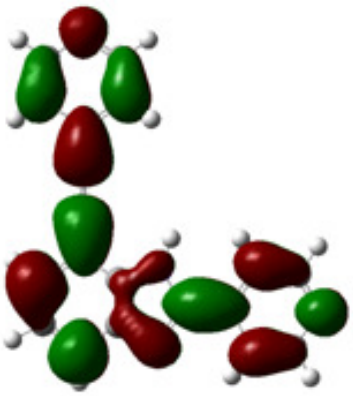
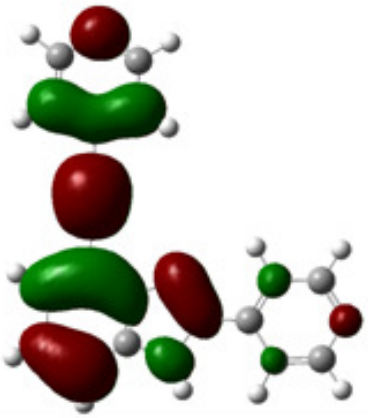
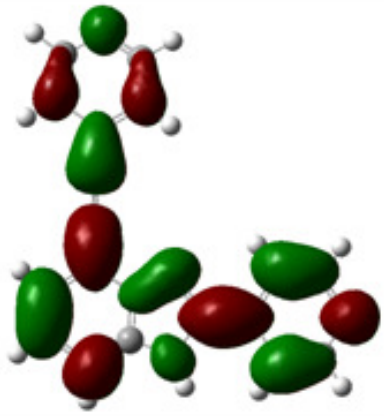
FMO calculations of compounds **5**–**13** were done using Gaussian 09W software package and its accompanying graphical interface program GaussView 5.0. The B3LYP hybrid density functional and a 6-31G^{++} basis set were used for the geometry optimizations. All structures were optimized within a C_s symmetry constraint. Calculations were done for both tautomeric forms of the benzimidazoles; for each compound, the tautomer with the proton on the "top" nitrogen of the imidazole ring is shown first.

Compound	HOMO	LUMO
5		
		

L-Form	HOMO	LUMO
6		
		
7		
		

L-form	HOMO	LUMO
8		
		
9		
		

L-form	HOMO	LUMO
10		
		
11		
		

L-form	HOMO	LUMO
12		
		
13		
		

UV/Vis absorption and fluorescence titrations of compounds 5–13 with acids and bases

UV-visible and fluorescence titrations were performed using Perkin-Elmer LAMBDA 25 UV/Vis Spectrometer and Perkin-Elmer Fluorescence Spectrometer LS-55, respectively. Five stock solutions of trifluoroacetic acid (TFA)—0.1 mM, 0.001 M, 0.01 M, 0.1 M, 1 M and 10 M and four stock solutions of 40% aqueous tetrabutylammonium hydroxide—0.1 mM, 0.001 M, 0.01 M and 0.1 M were prepared in THF. In a quartz cuvette, 3 mL of 1×10^{-5} M solution of a given fluorophore in THF were titrated using the stock solutions of (a) trifluoroacetic acid (TFA), or (b) 40% aqueous tetrabutylammonium hydroxide solution to give the indicated range of acid and base concentrations. The excitation wavelength used for fluorescence titration corresponds to the isosbestic point determined in the UV/Vis titration.

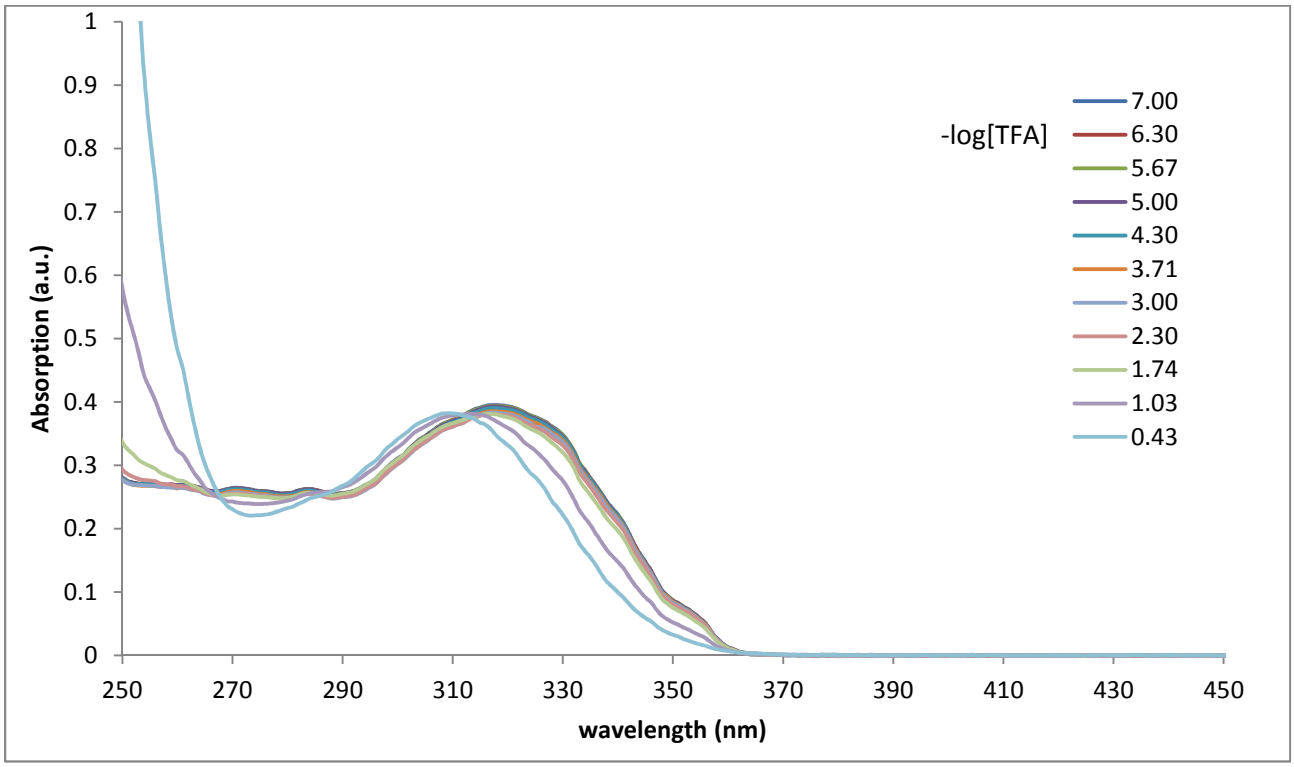


Figure S1. UV/Vis absorption titration of compound **5** with TFA.

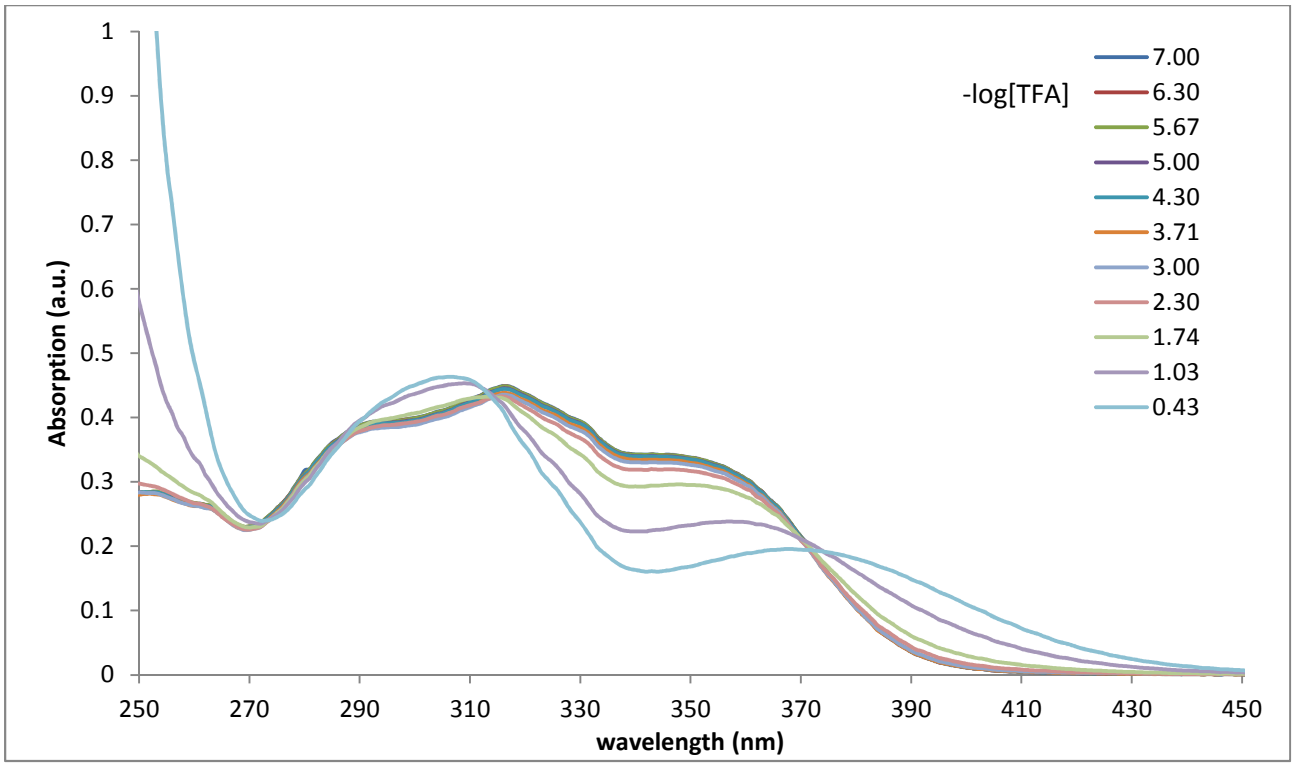


Figure S2. UV/Vis absorption titration of compound **6** with TFA.

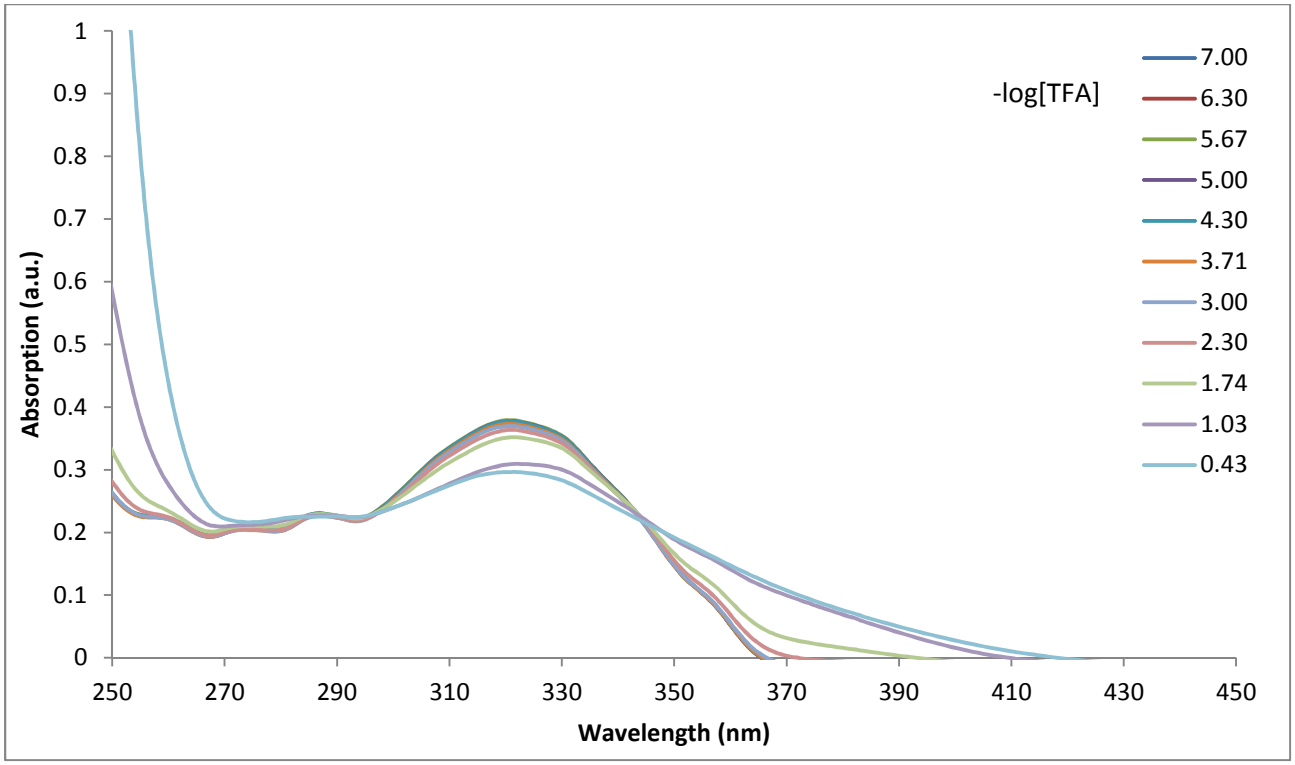


Figure S3. UV/Vis absorption titration of compound **7** with TFA.

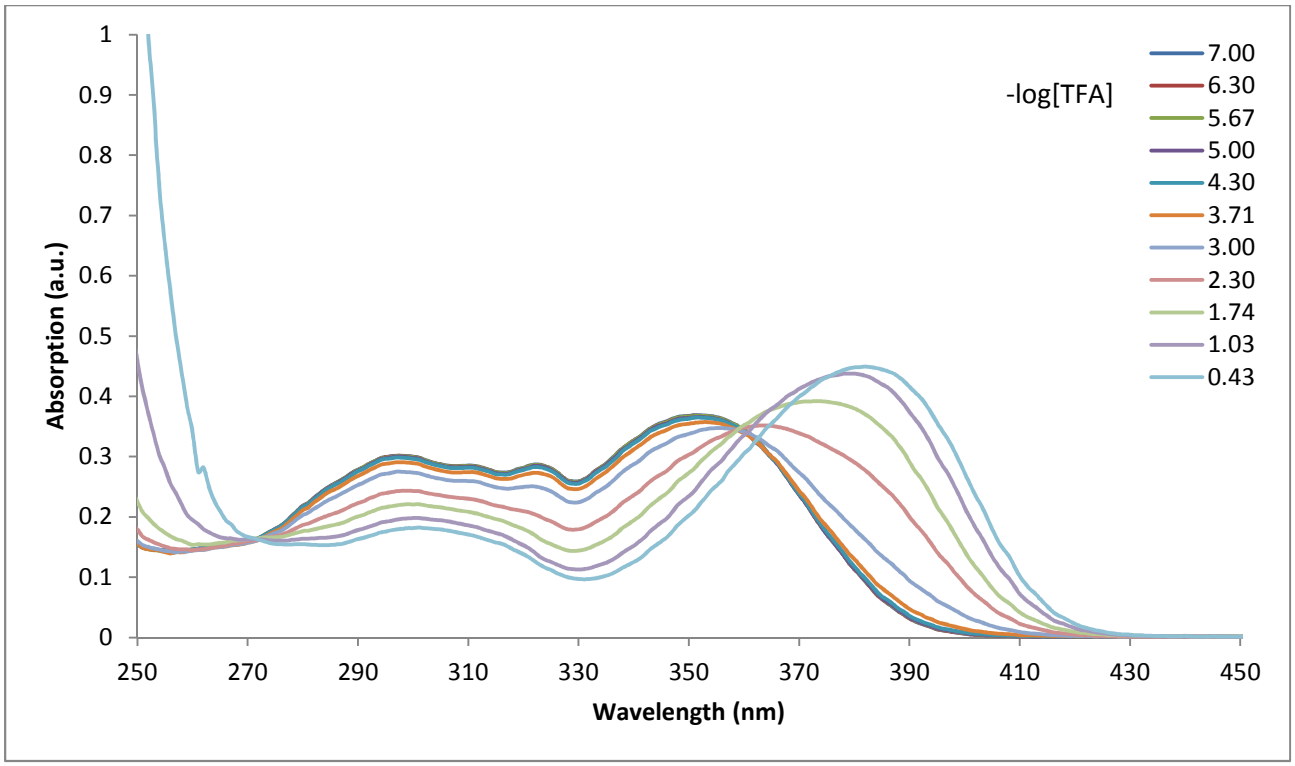


Figure S4. UV/Vis absorption titration of compound **8** with TFA.

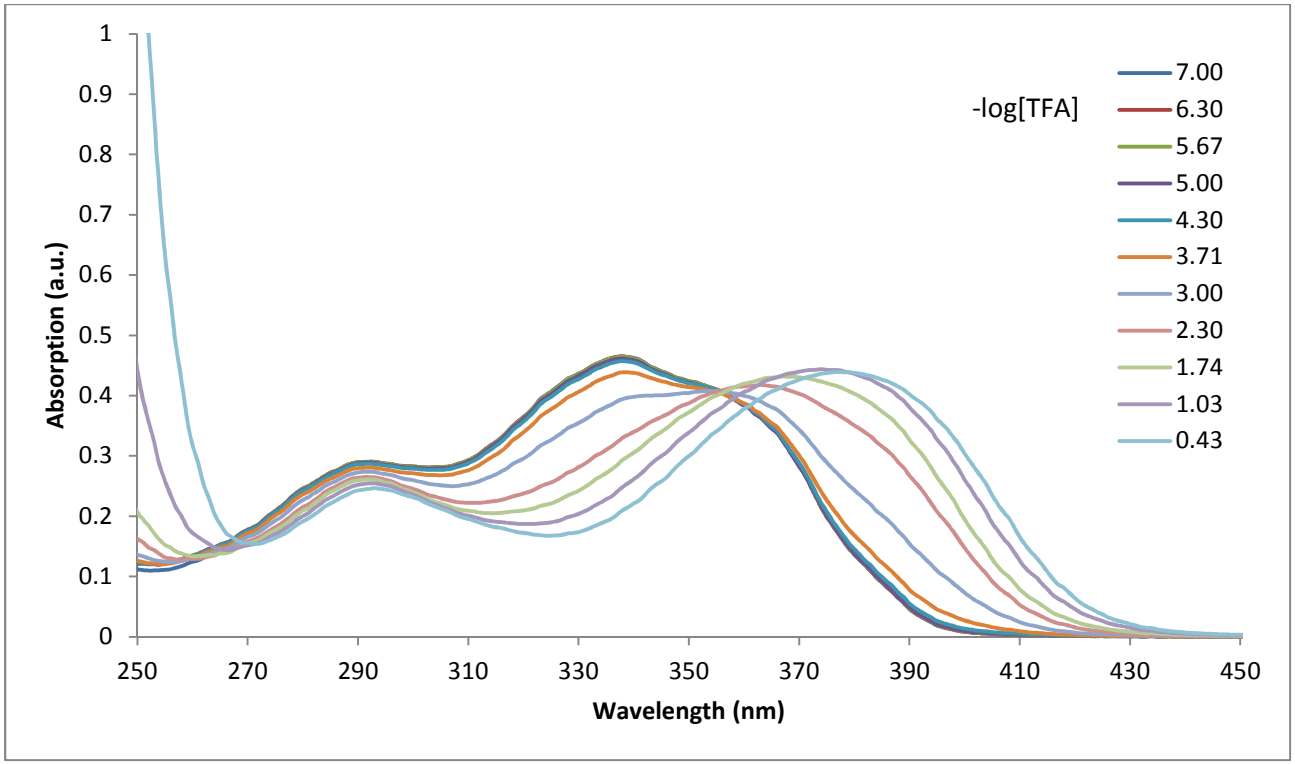


Figure S5. UV/Vis absorption titration of compound **9** with TFA.

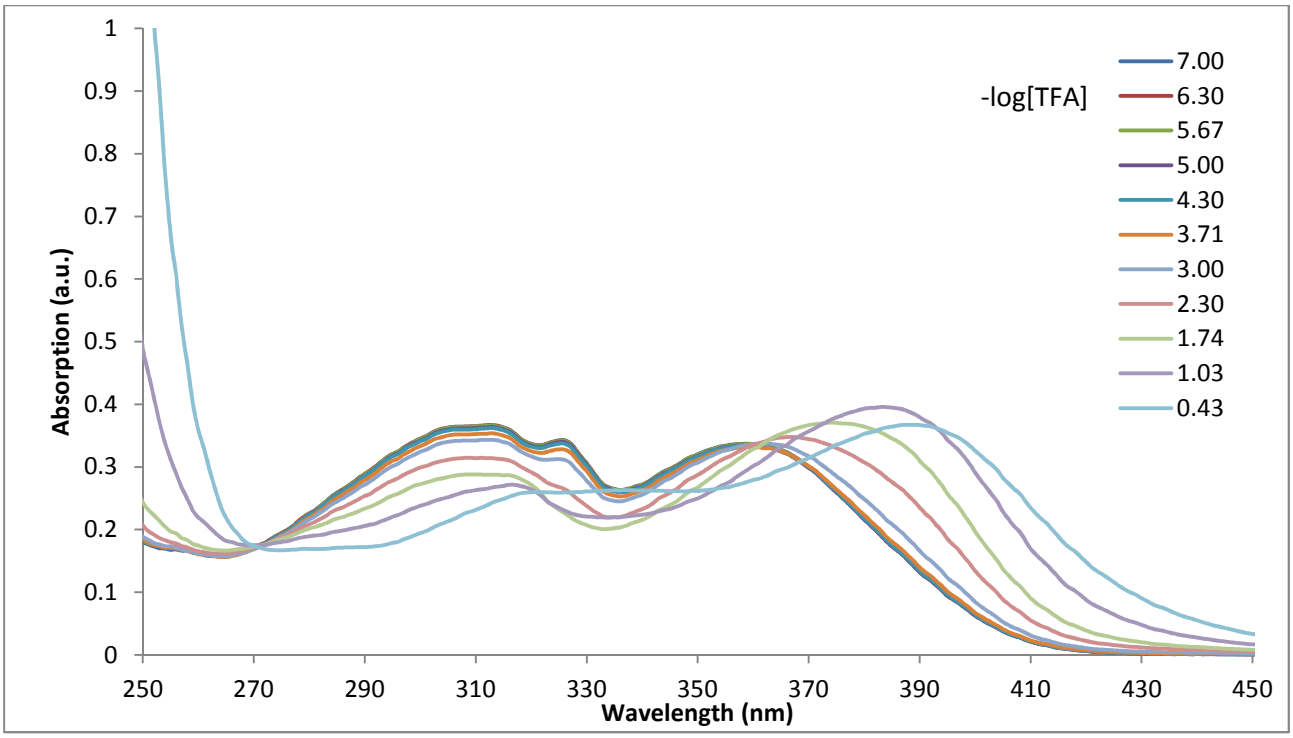


Figure S6. UV/Vis absorption titration of compound **10** with TFA.

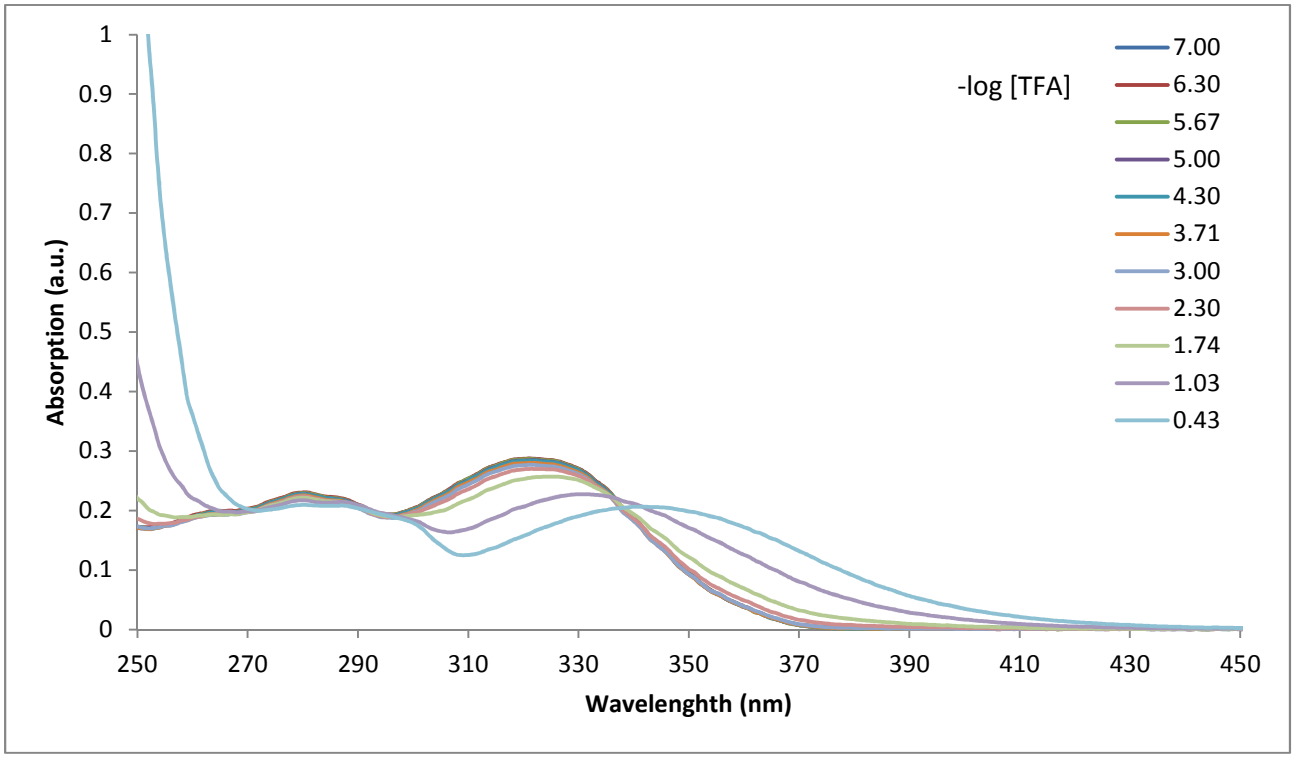


Figure S7. UV/Vis absorption titration of compound **11** with TFA.

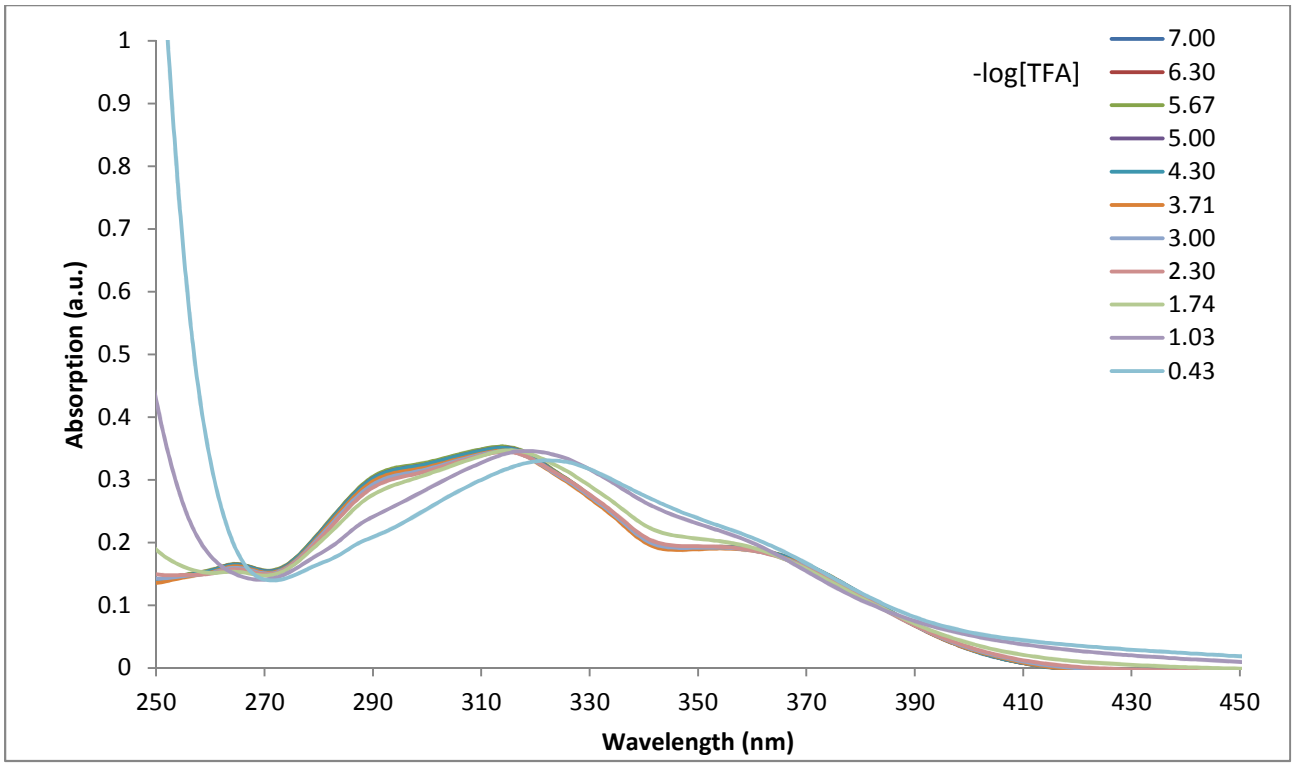


Figure S8. UV/Vis absorption titration of compound **12** with TFA.

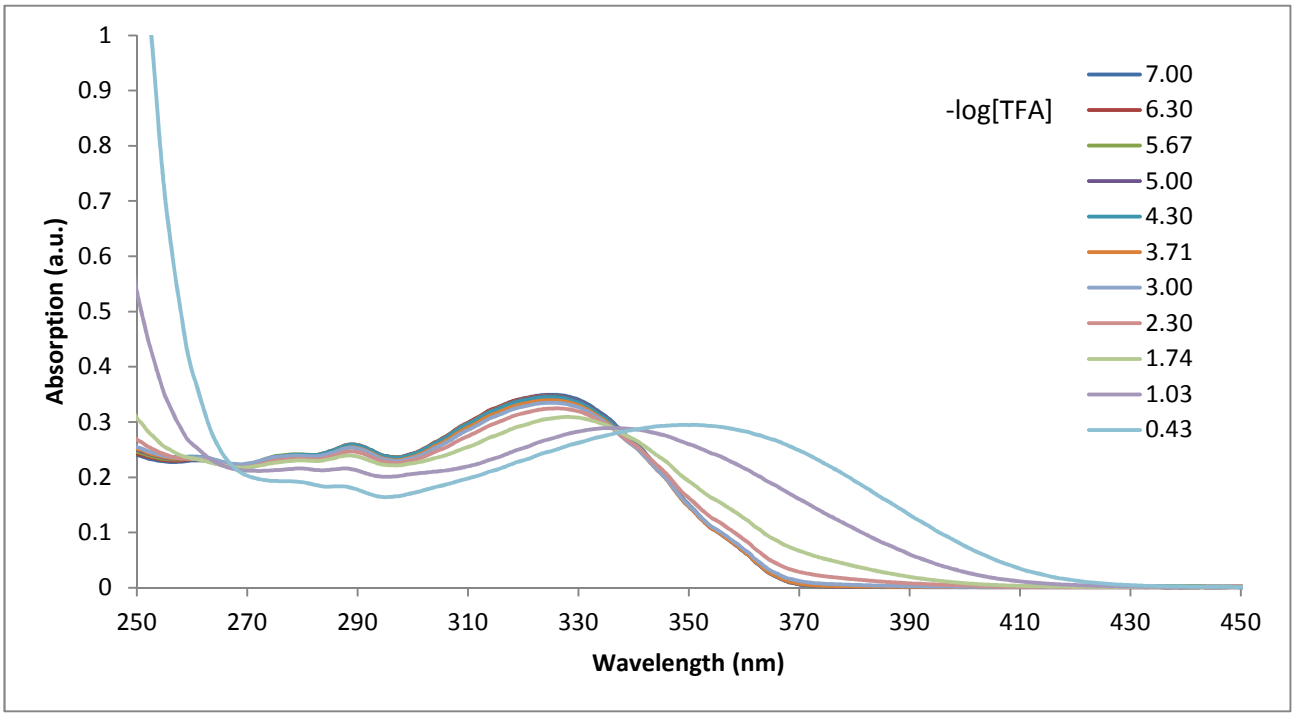


Figure S9. UV/Vis absorption titration of compound **13** with TFA.

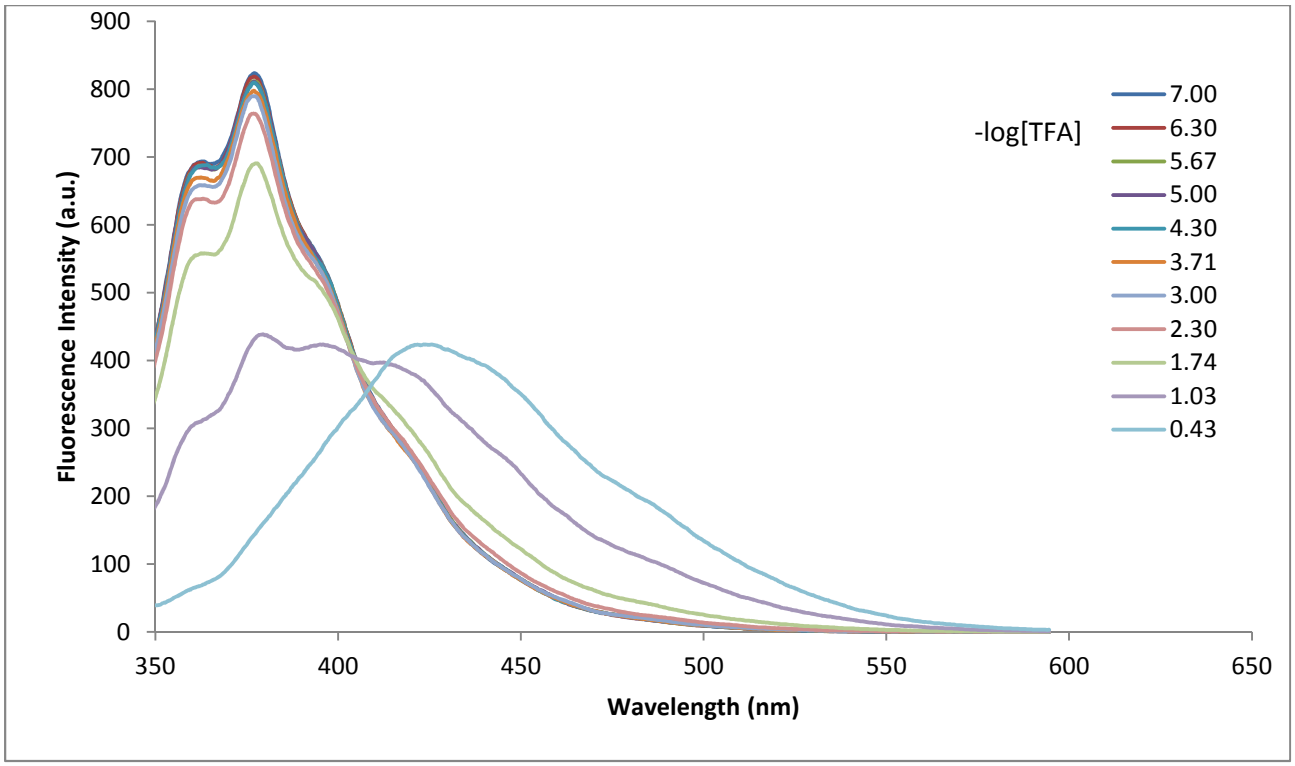


Figure S10. Fluorescence emission titration of compound **5** with TFA ($\lambda_{excitation}$ = 313 nm).

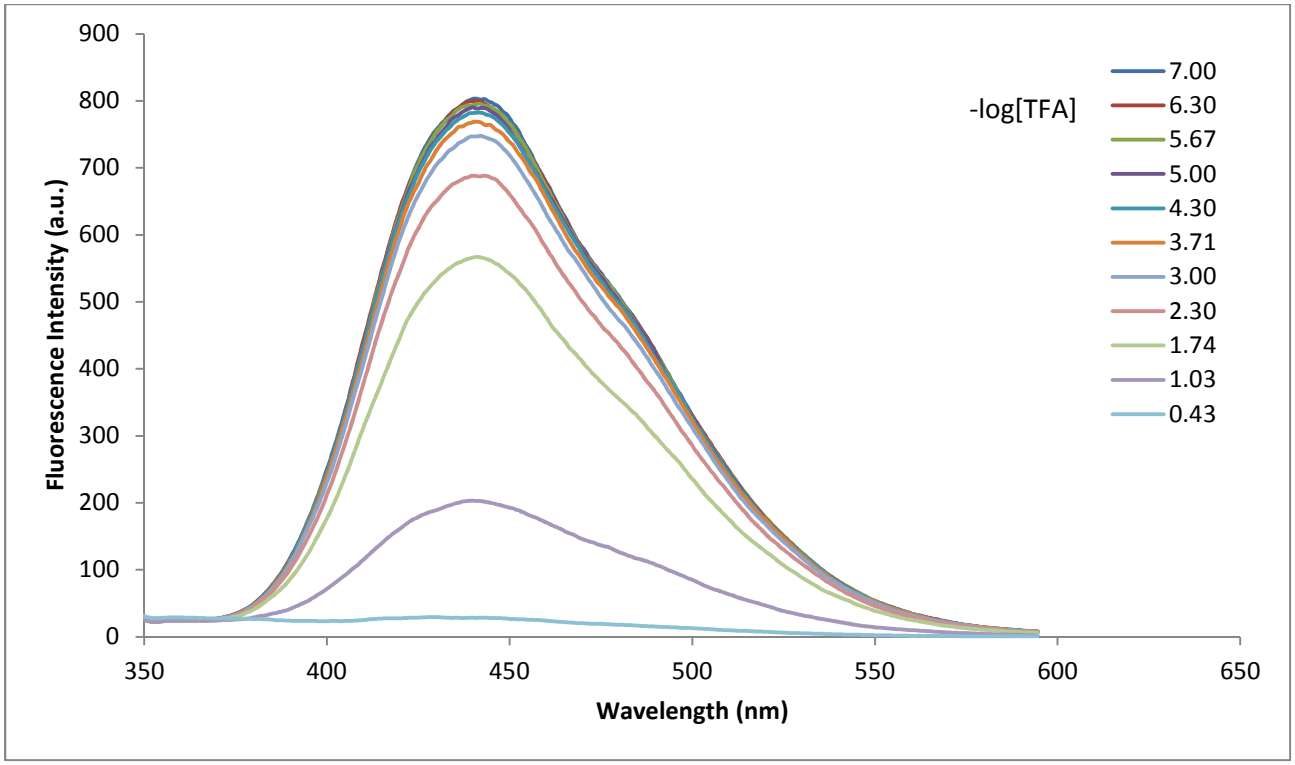


Figure S11. Fluorescence emission titration of compound **6** with TFA ($\lambda_{excitation}$ = 313 nm).

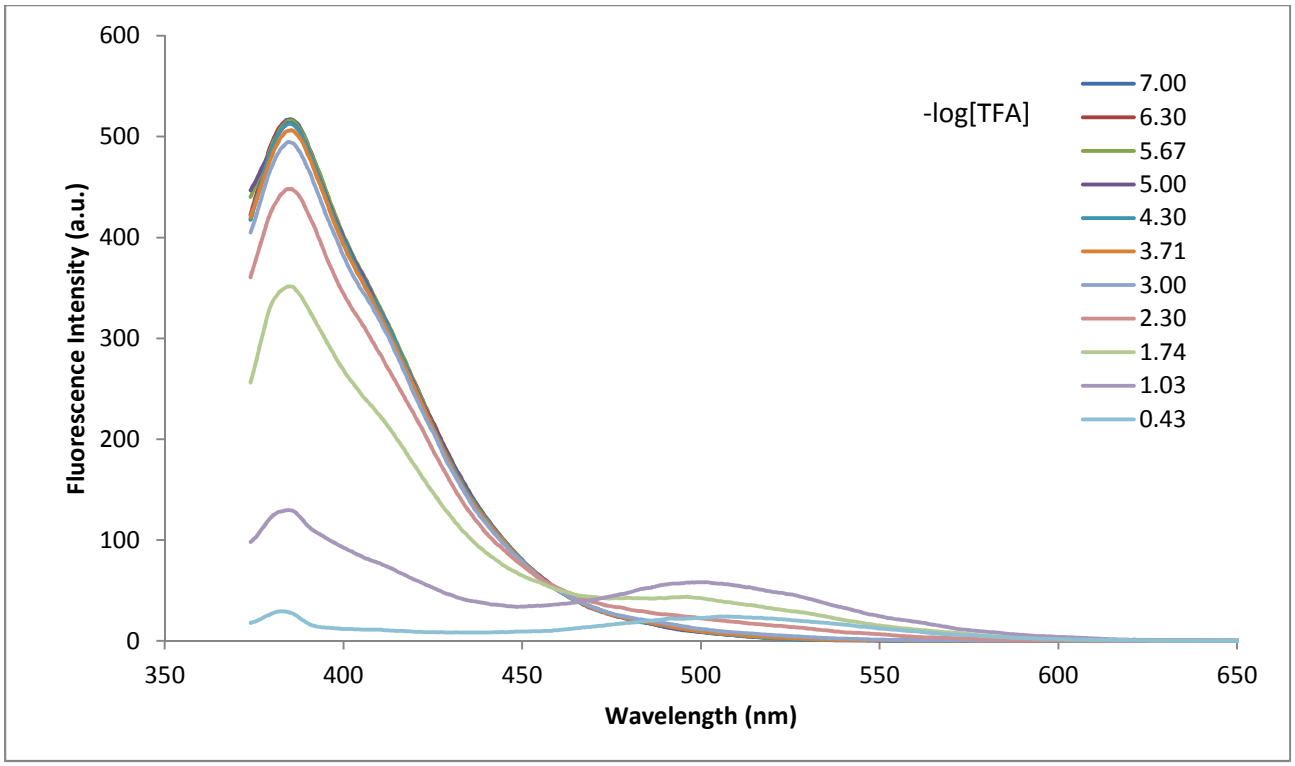


Figure S12. Fluorescence emission titration of compound **7** with TFA ($\lambda_{excitation}$ = 344 nm).

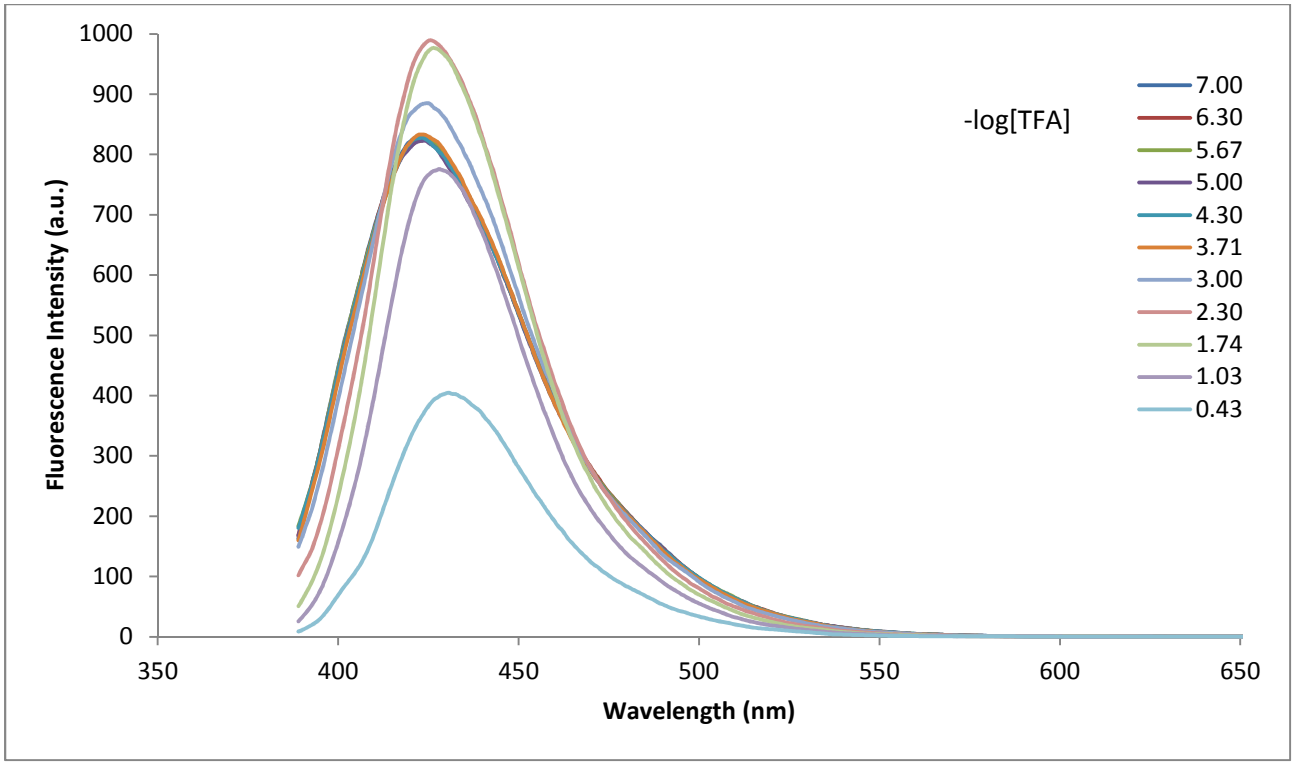


Figure S13. Fluorescence emission titration of compound **8** with TFA ($\lambda_{excitation}$ = 359 nm).

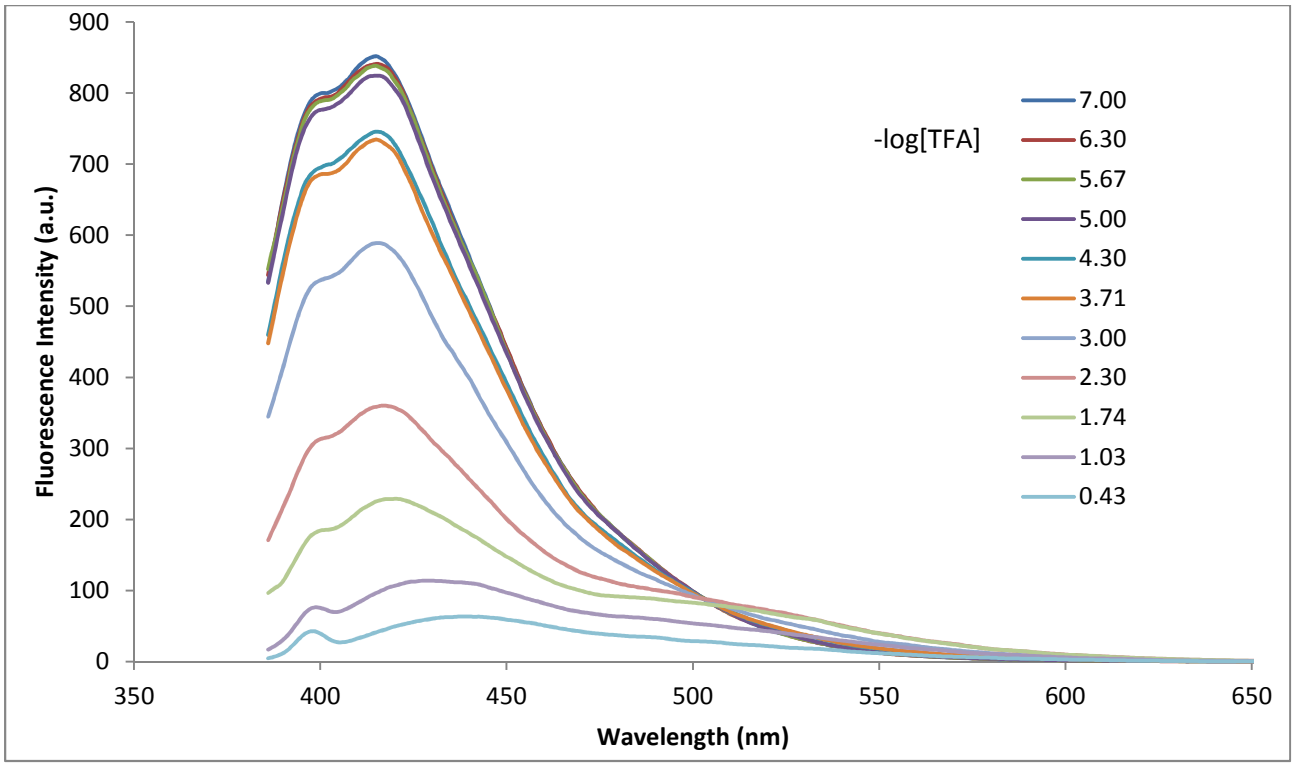


Figure S14. Fluorescence emission titration of compound **9** with TFA ($\lambda_{excitation}$ = 356 nm).

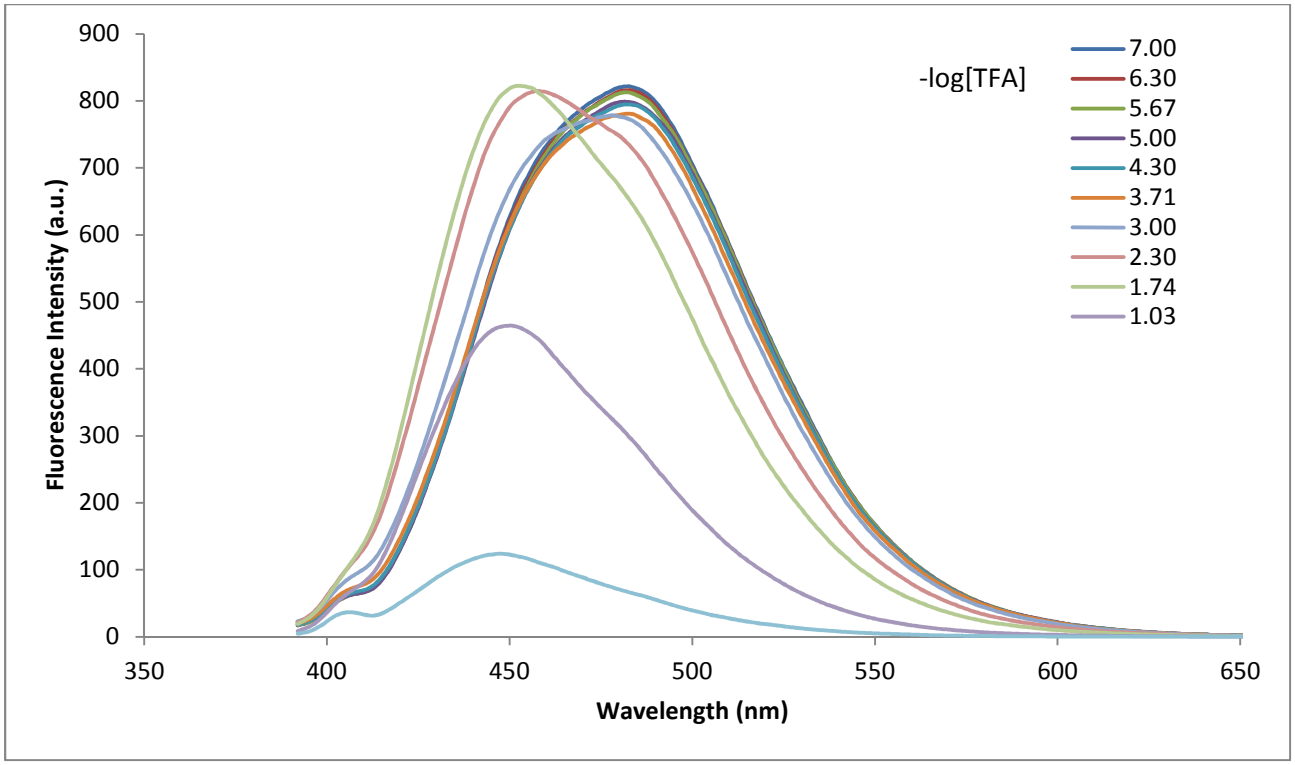


Figure S15. Fluorescence emission titration of compound **10** with TFA ($\lambda_{excitation}$ = 362 nm).

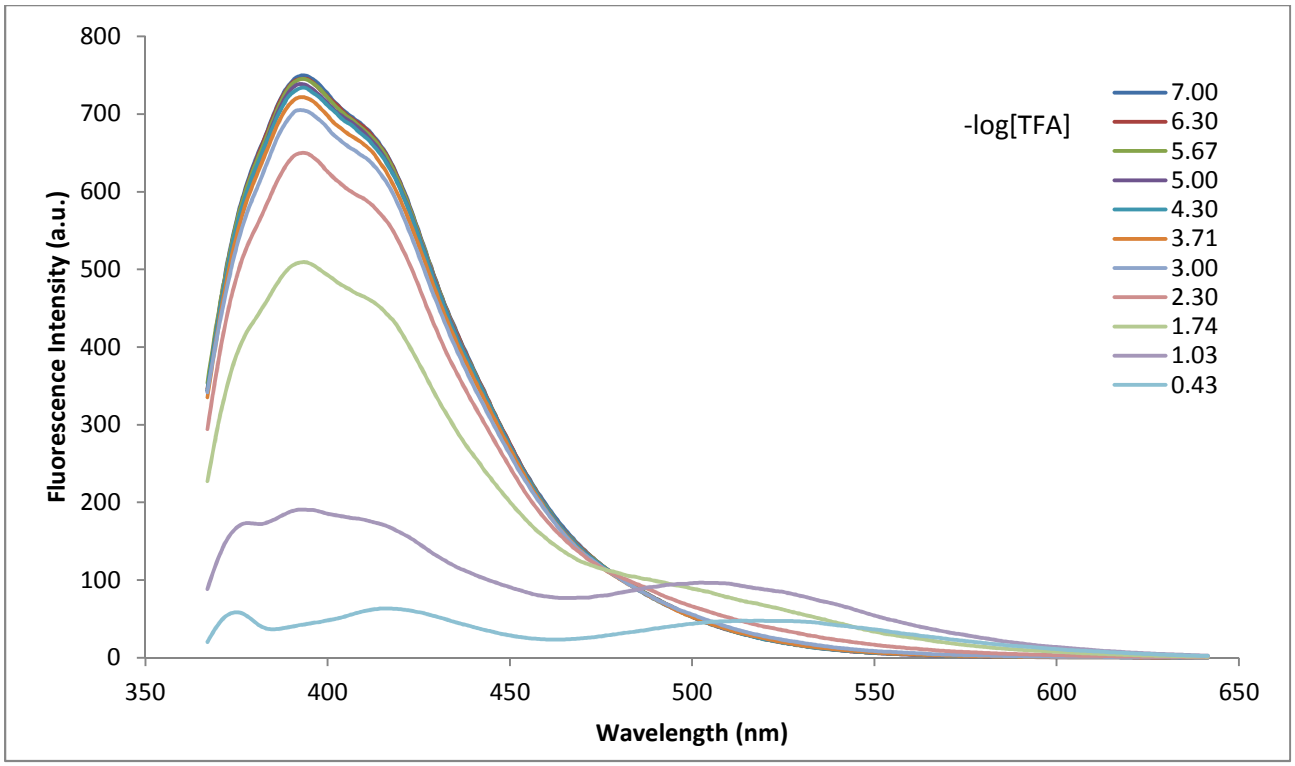


Figure S16. Fluorescence emission titration of compound **11** with TFA ($\lambda_{excitation}$ = 337 nm).

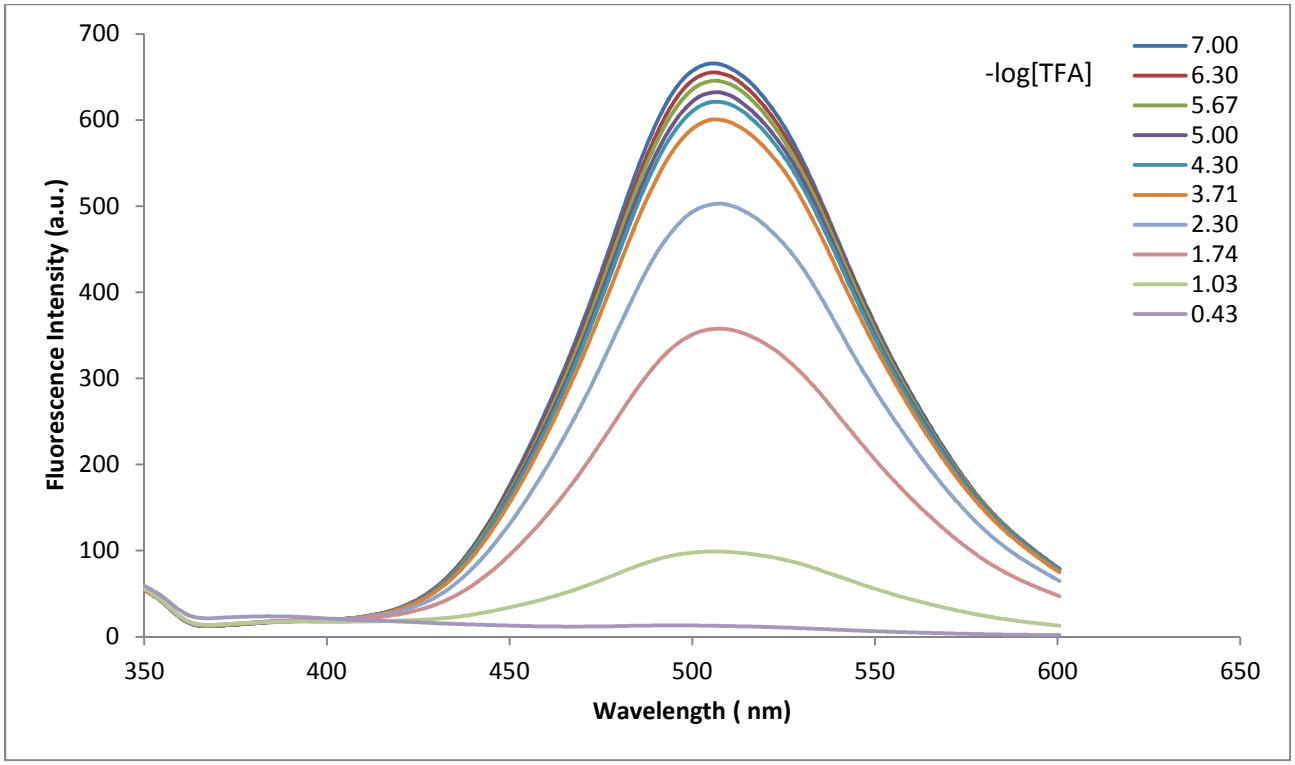


Figure S17. Fluorescence emission titration of compound **12** with TFA ($\lambda_{excitation}$ = 317 nm).

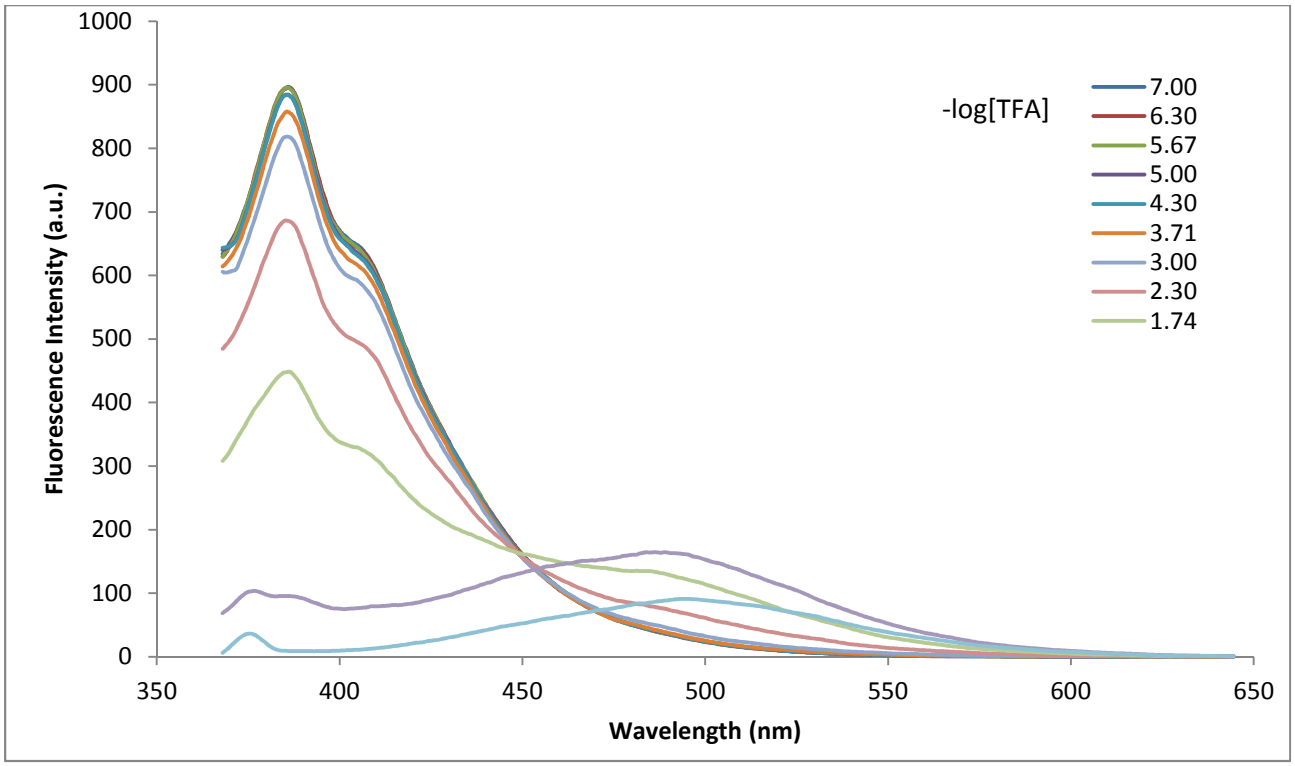


Figure S18. Fluorescence emission titration of compound **13** with TFA ($\lambda_{excitation}$ = 338 nm).

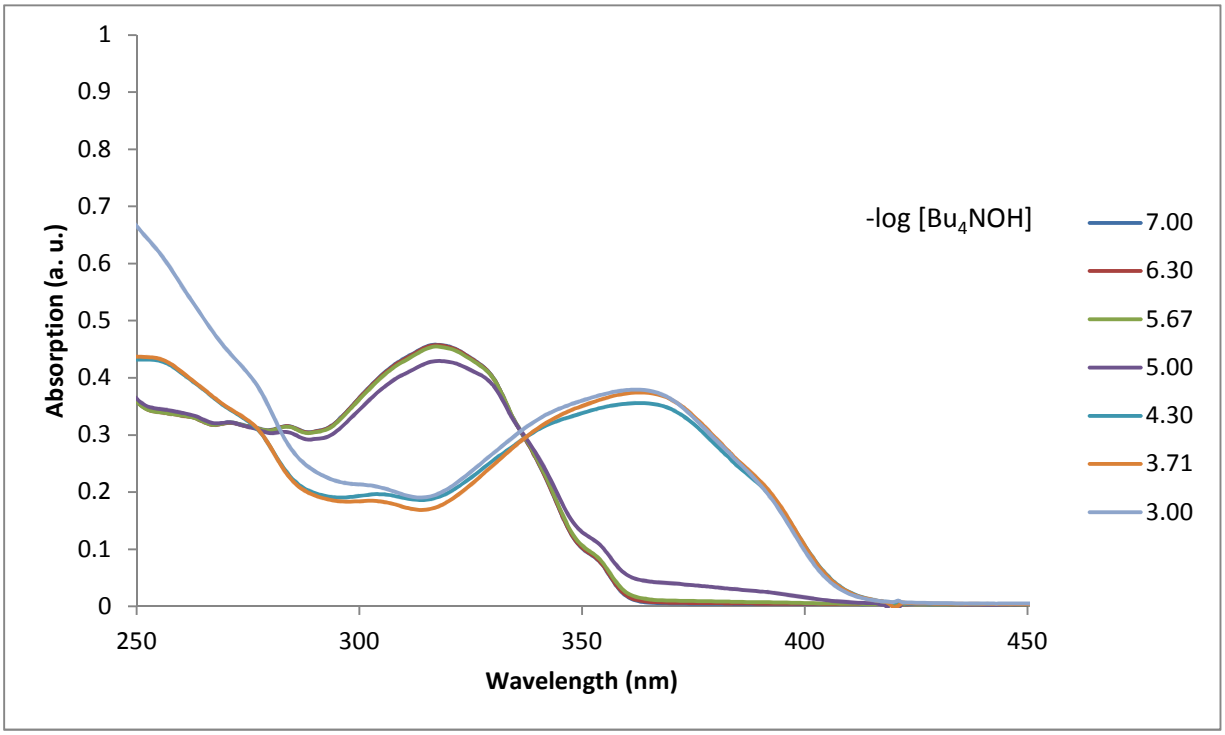


Figure S19. UV/Vis absorption titration of compound **5** with Bu_4NOH.

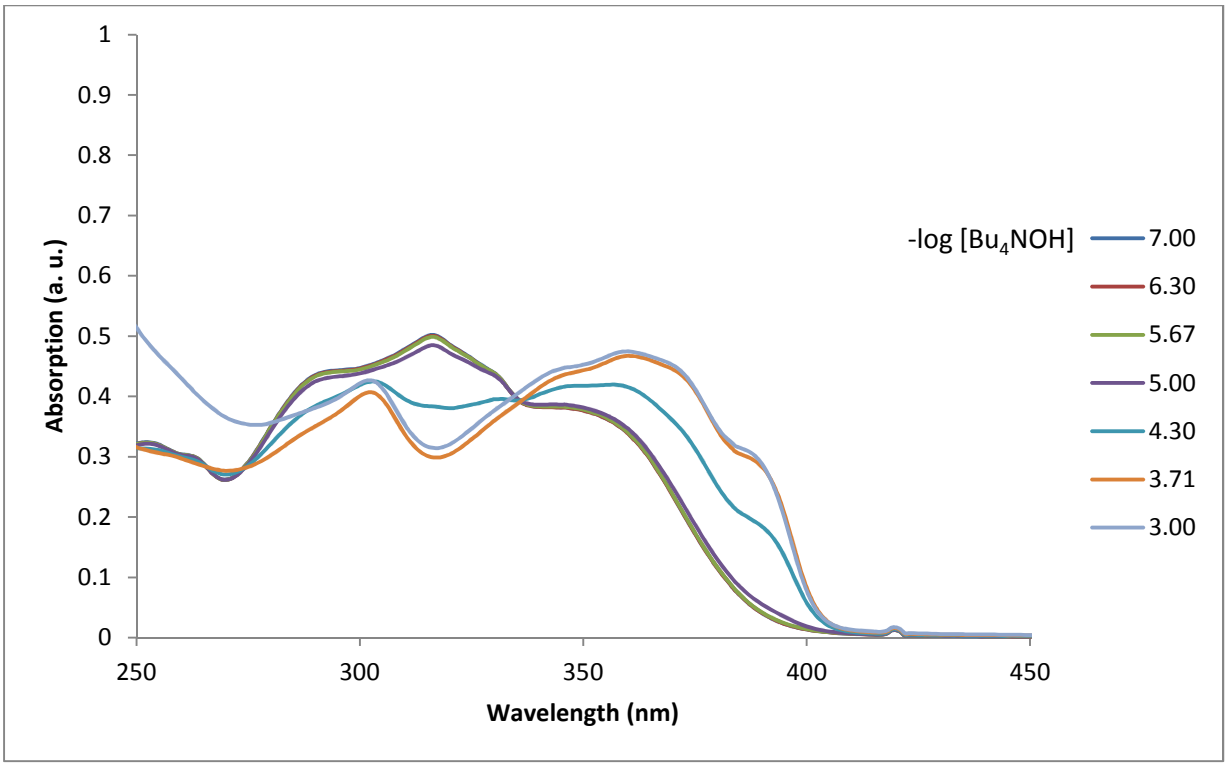


Figure S20. UV/Vis absorption titration of compound **6** with Bu_4NOH.

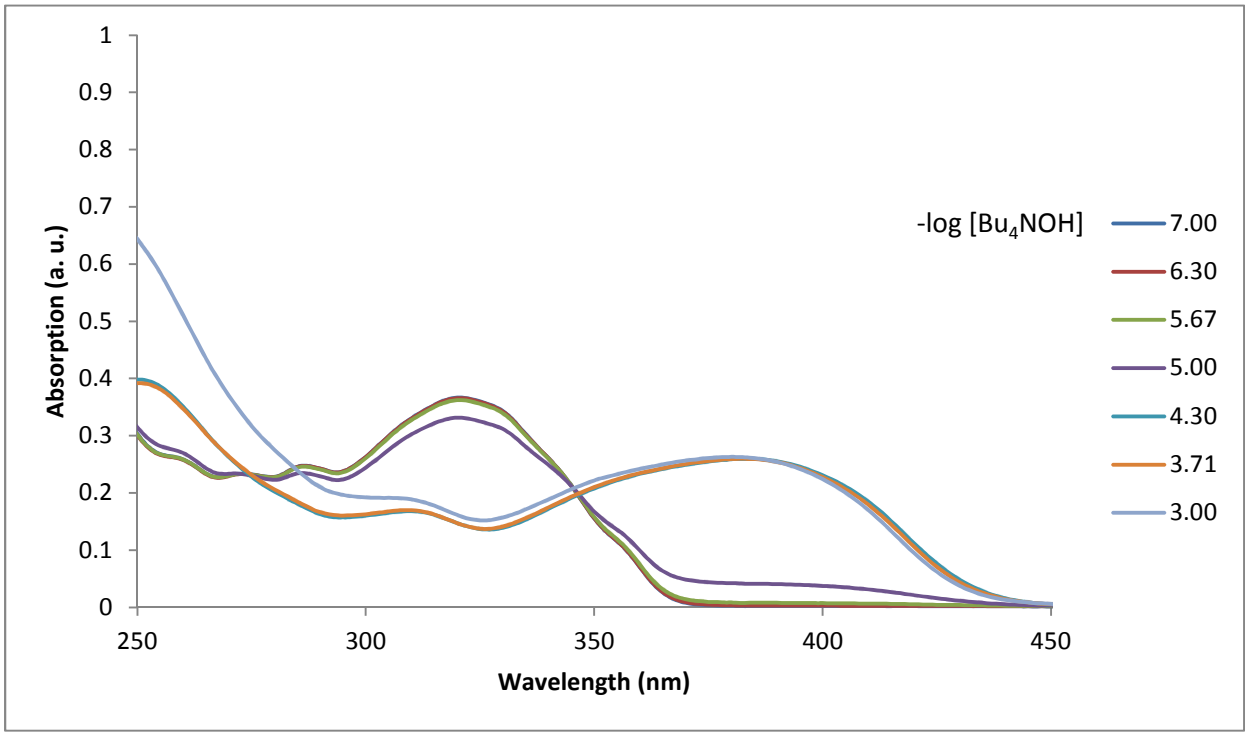


Figure S21. UV/Vis absorption titration of compound **7** with Bu_4NOH.

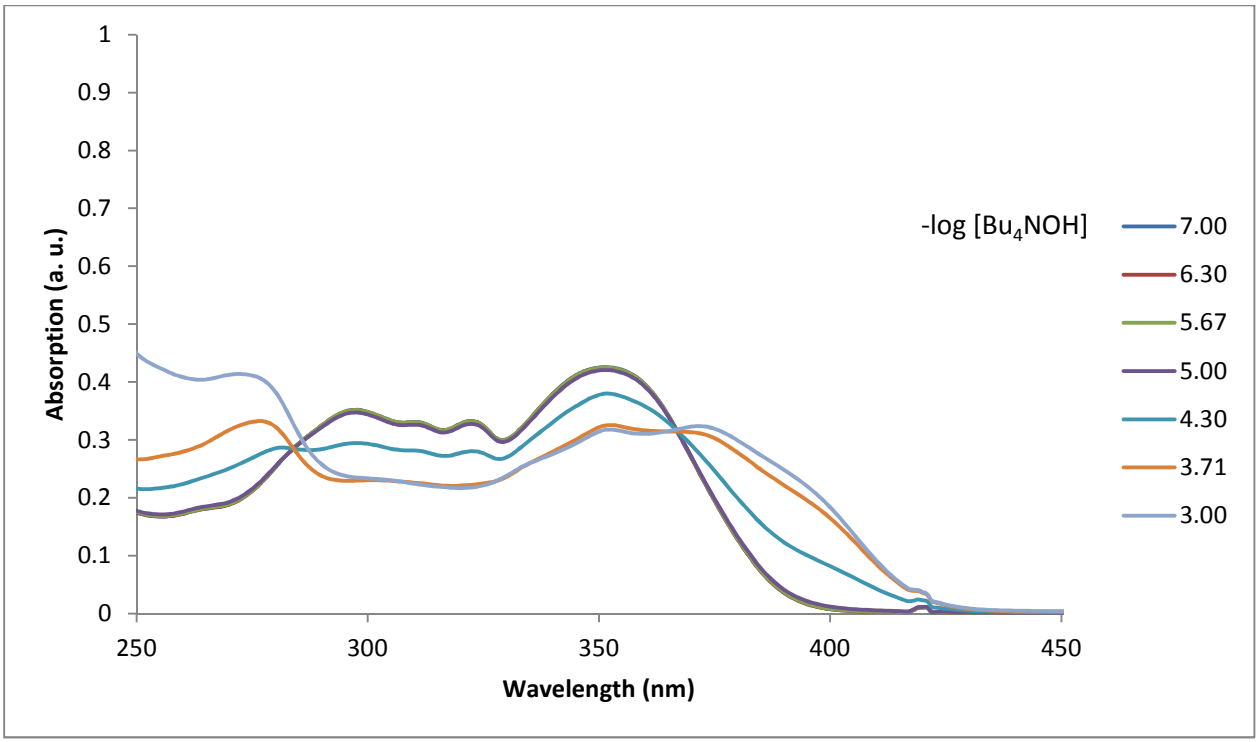


Figure S22. UV/Vis absorption titration of compound **8** with Bu_4NOH.

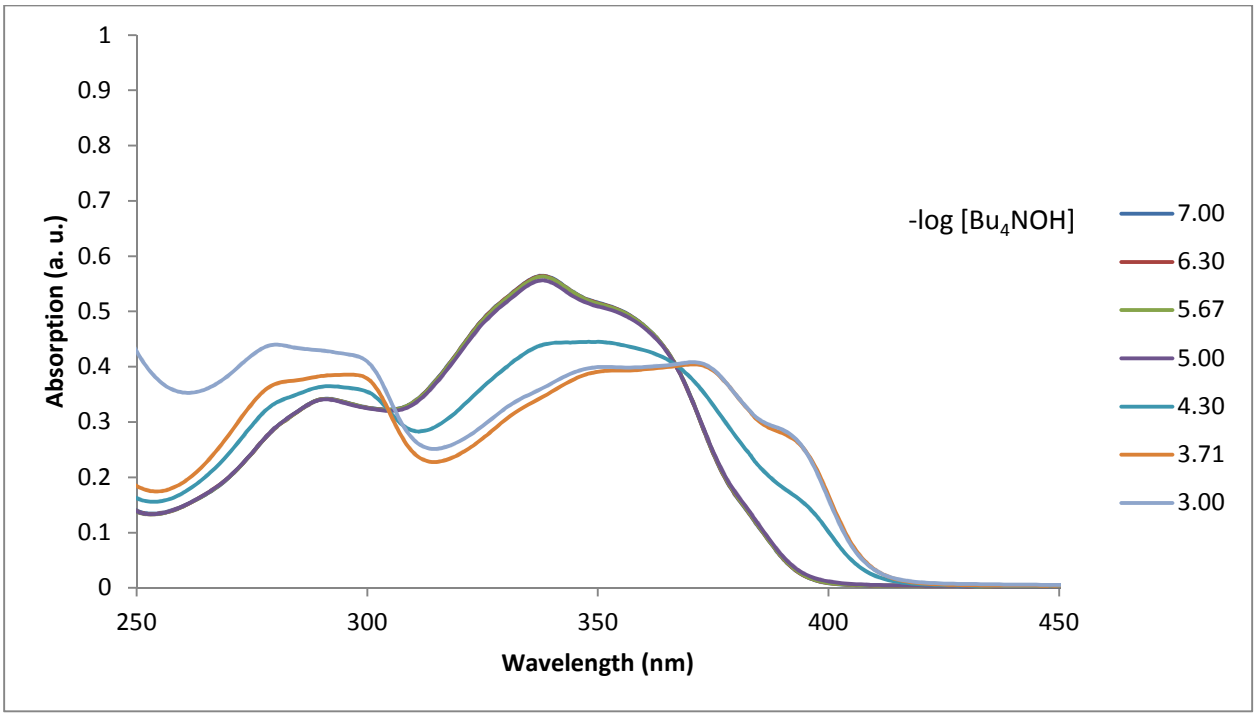


Figure S23. UV/Vis absorption titration of compound **9** with Bu_4NOH.

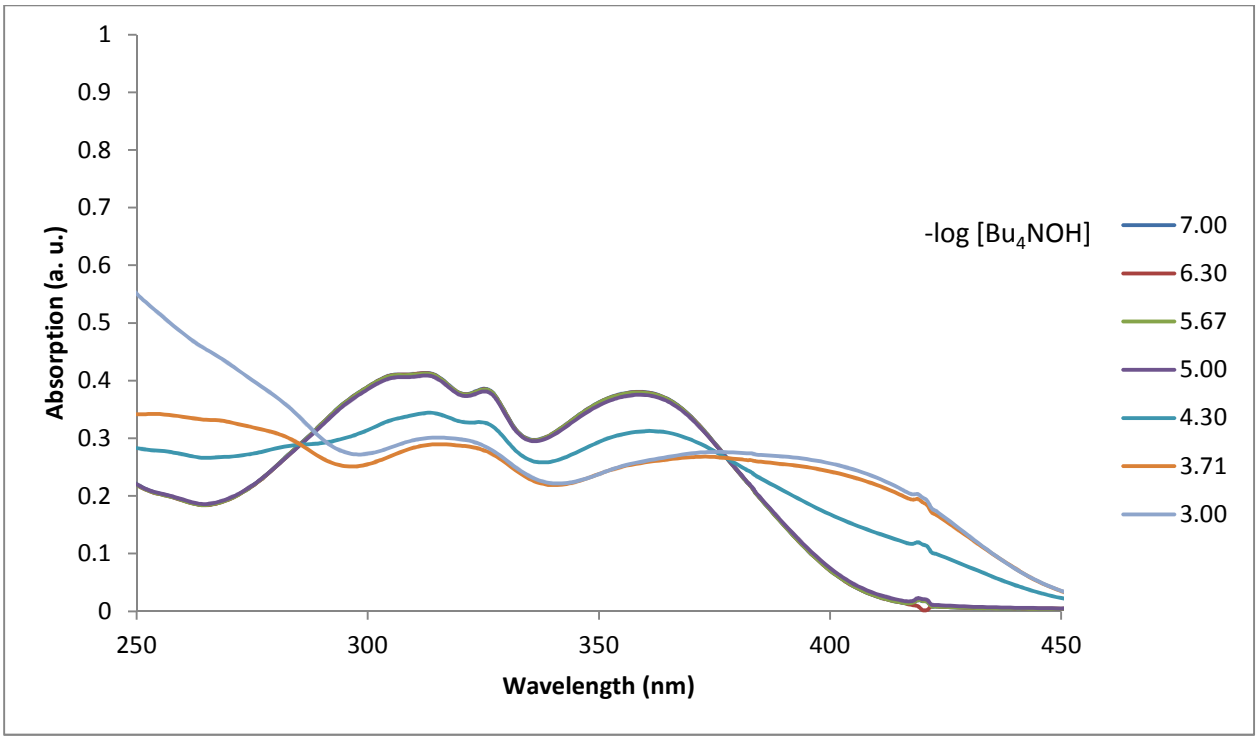


Figure S24. UV/Vis absorption titration of compound **10** with Bu_4NOH.

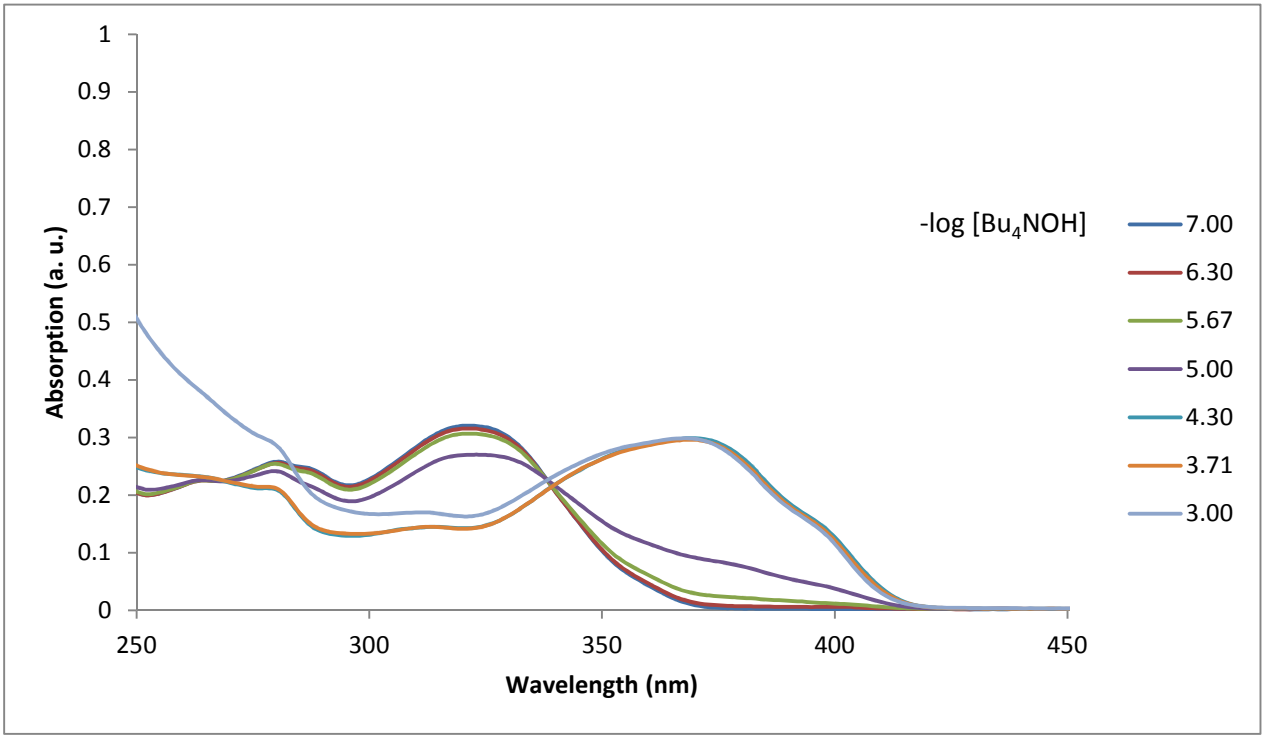


Figure S25. UV/Vis absorption titration of compound **11** with Bu_4NOH.

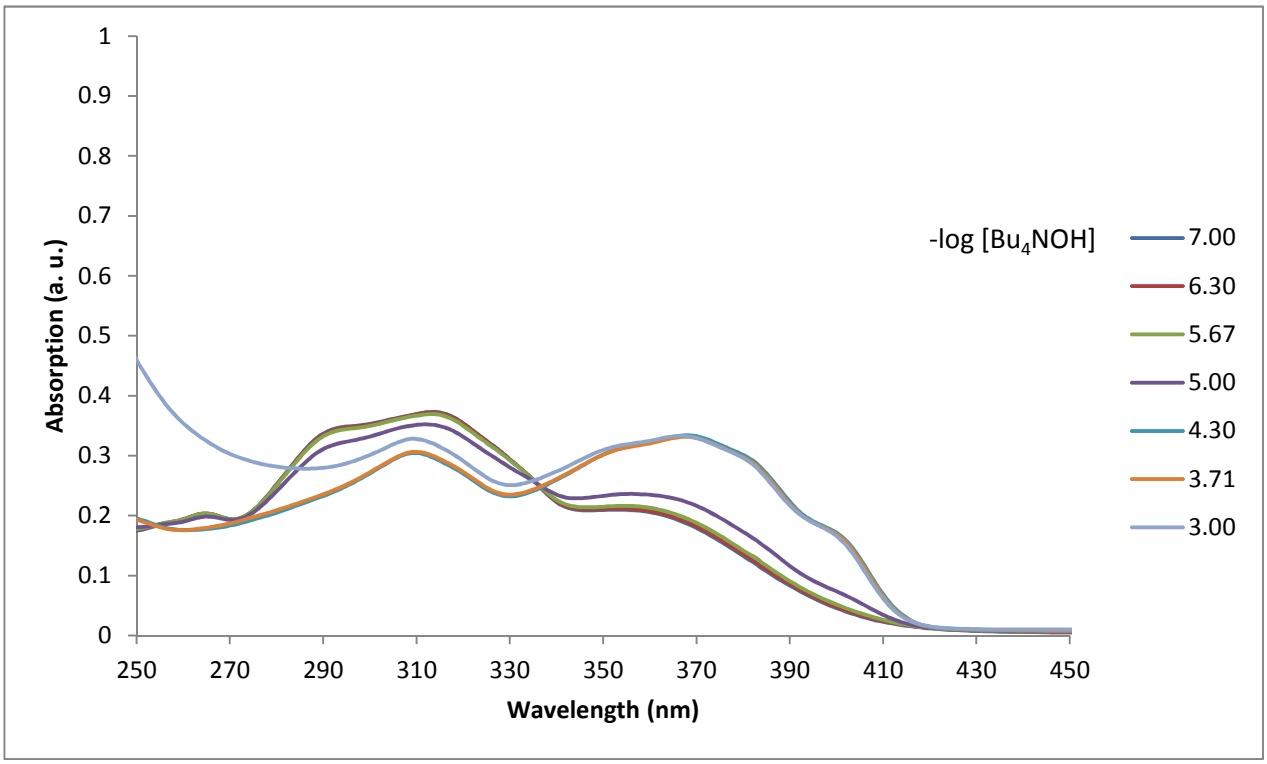


Figure S26. UV/Vis absorption titration of compound **12** with Bu_4NOH.

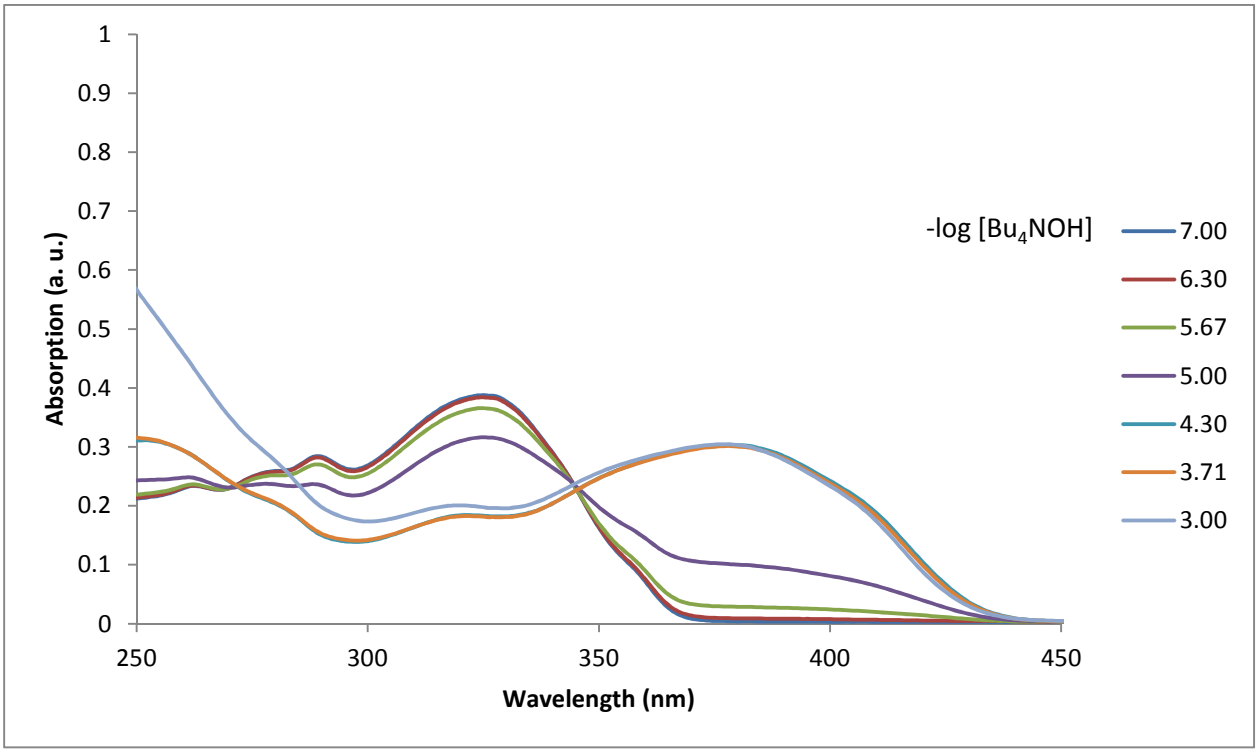


Figure S27. UV/Vis absorption titration of compound **13** with Bu_4NOH.

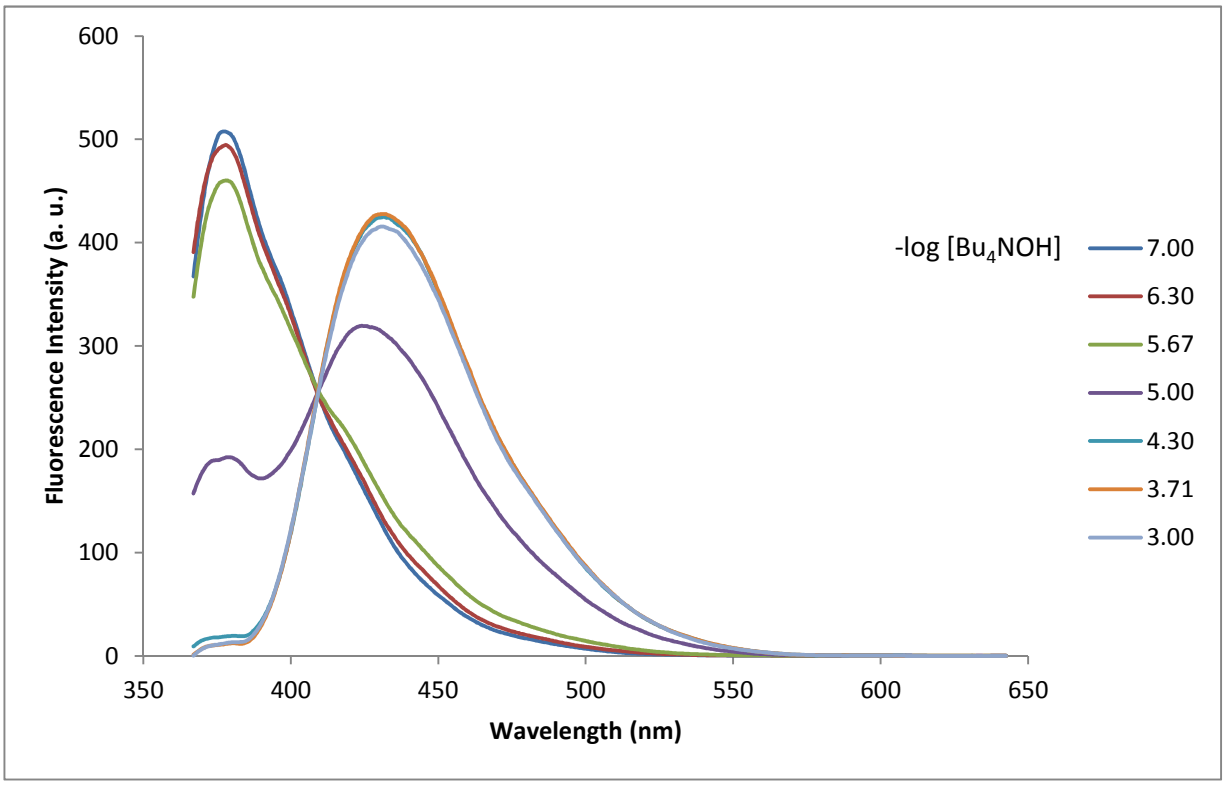


Figure S28. Fluorescence emission titration of compound **5** with Bu_4NOH ($\lambda_{excitation}$ = 337 nm).

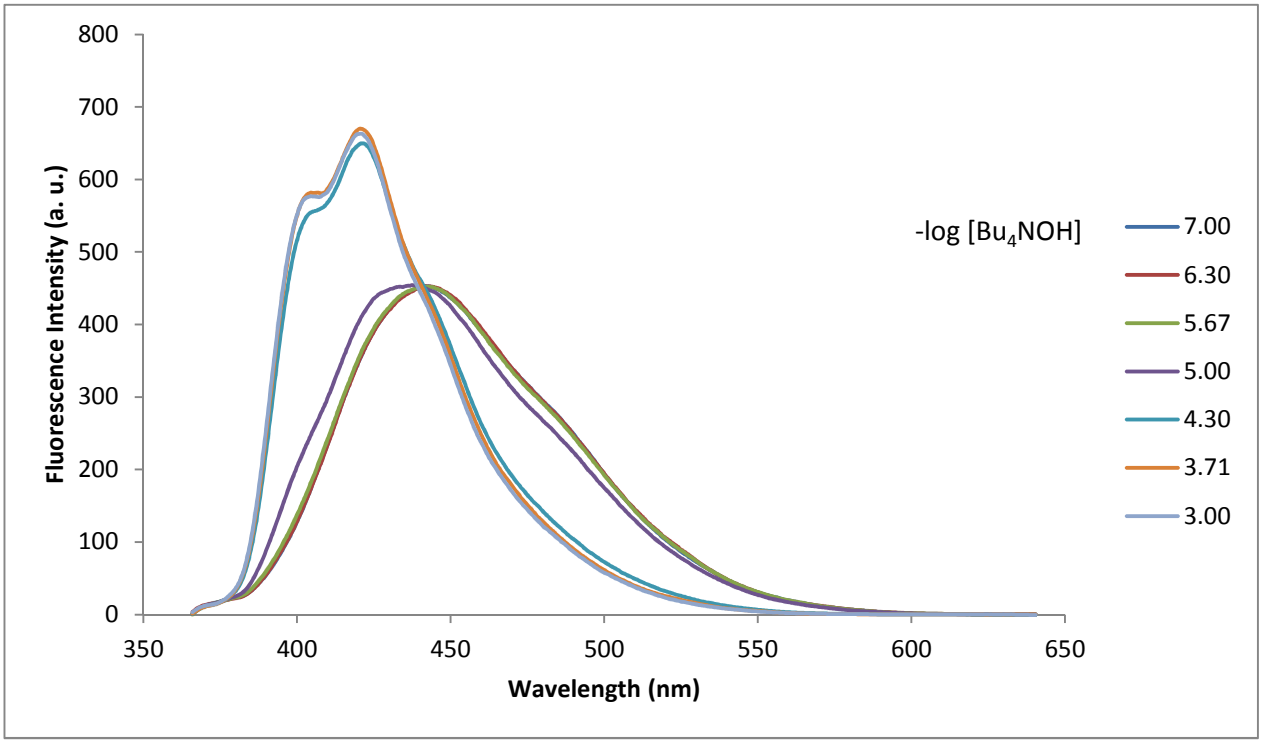


Figure S29. Fluorescence emission titration of compound **6** with Bu_4NOH ($\lambda_{excitation}$ = 336 nm).

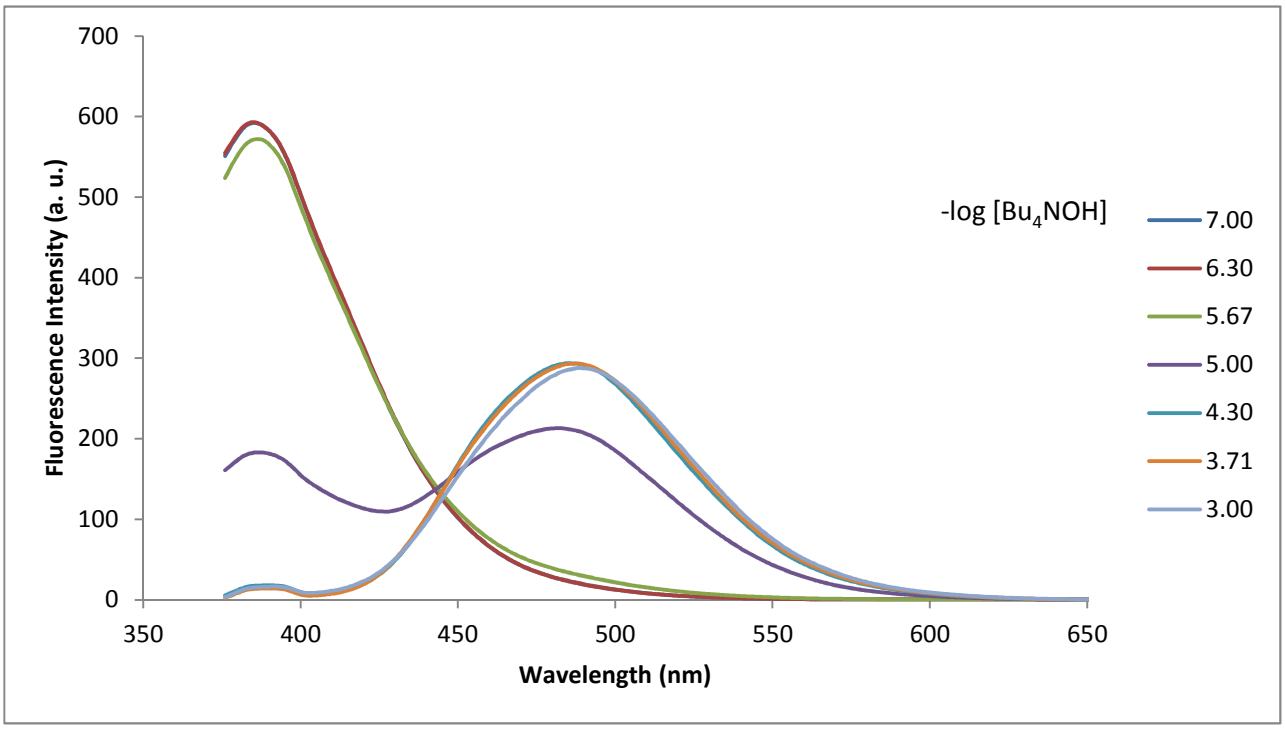


Figure S30. Fluorescence emission titration of compound **7** with Bu_4NOH ($\lambda_{excitation}$ = 346 nm).

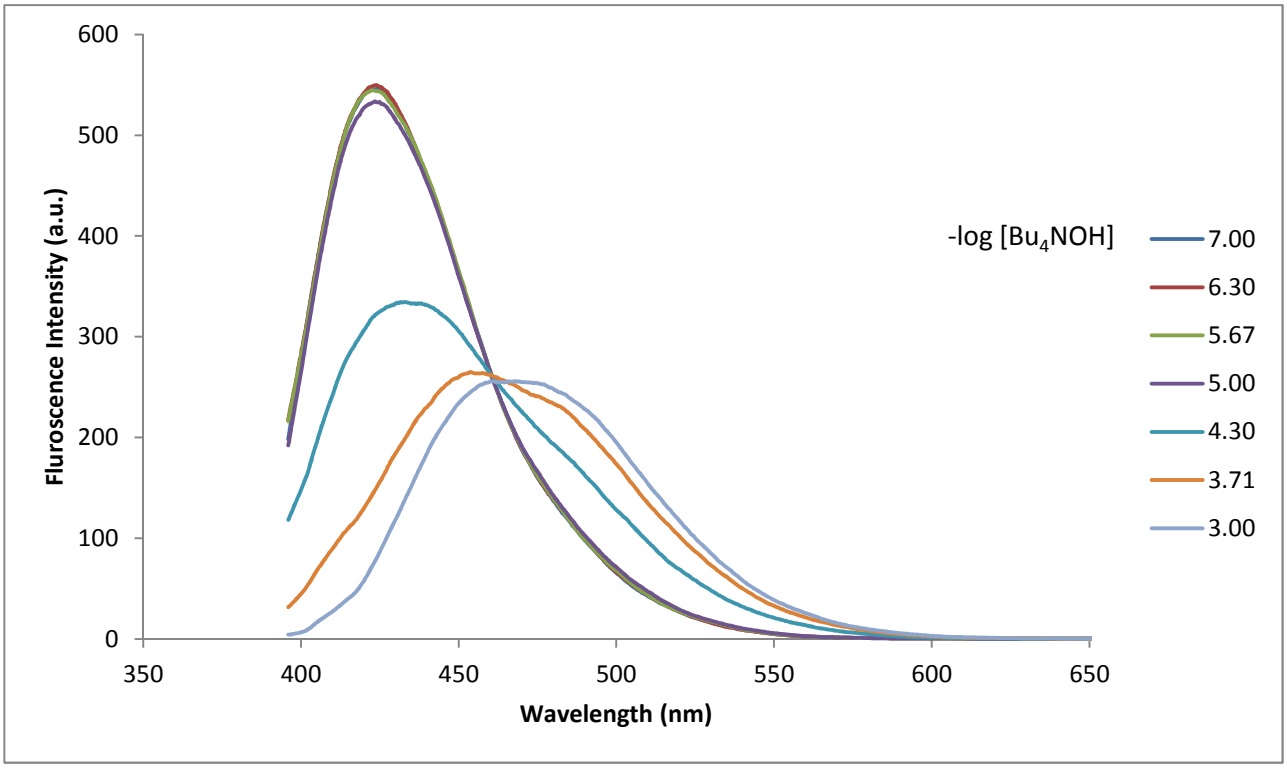


Figure S31. Fluorescence emission titration of compound **8** with Bu_4NOH ($\lambda_{excitation}$ = 366 nm).

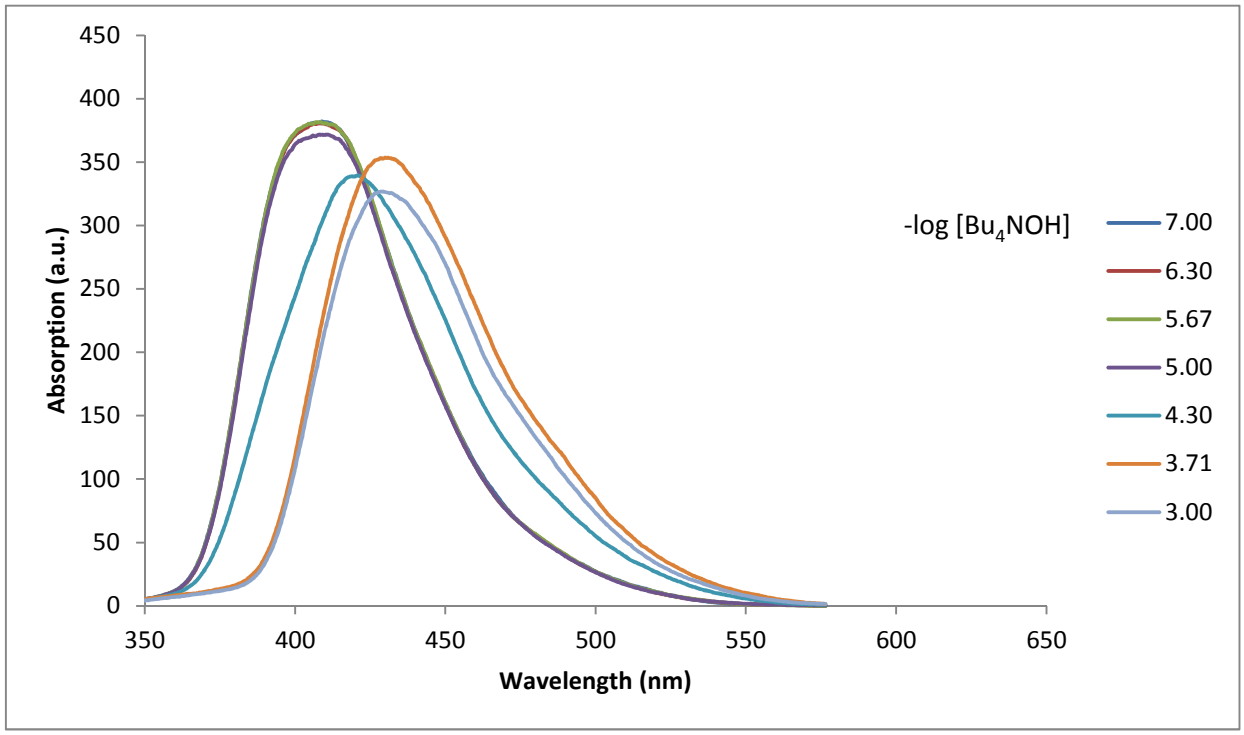


Figure S32. Fluorescence emission titration of compound **9** with Bu_4NOH ($\lambda_{excitation}$ = 304 nm).

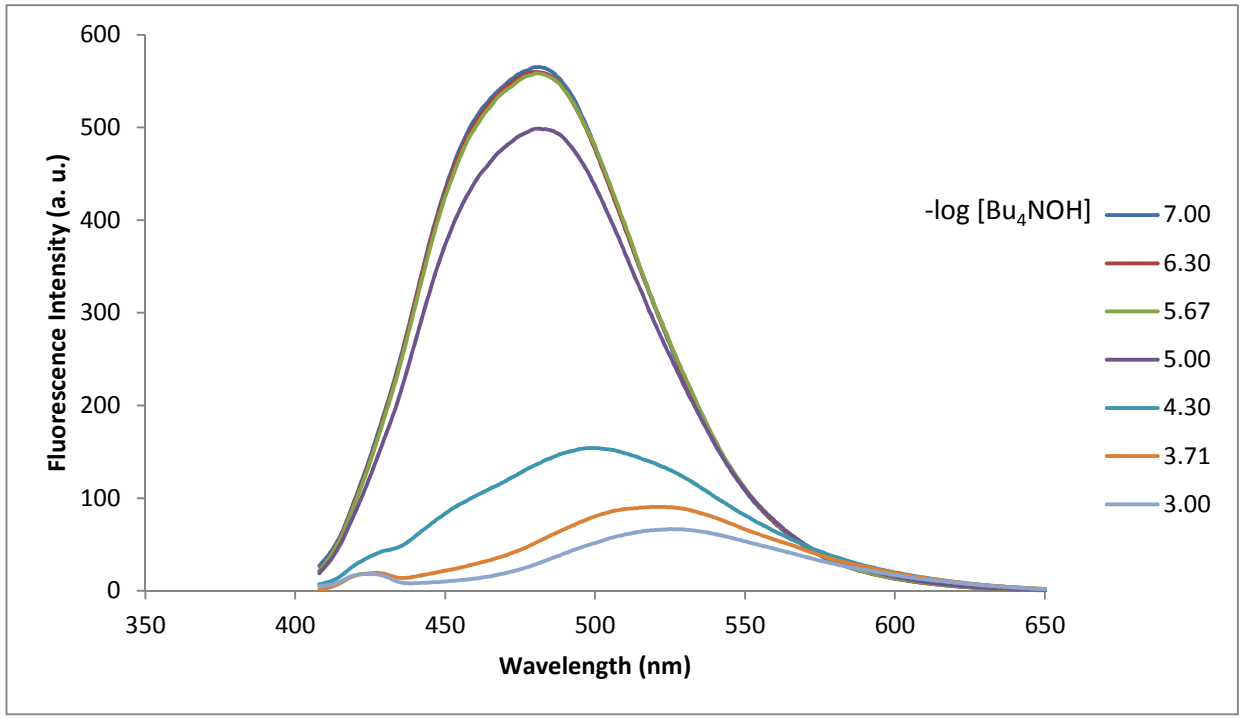


Figure S33. Fluorescence emission titration of compound **10** with Bu_4NOH ($\lambda_{excitation}$ = 378 nm).

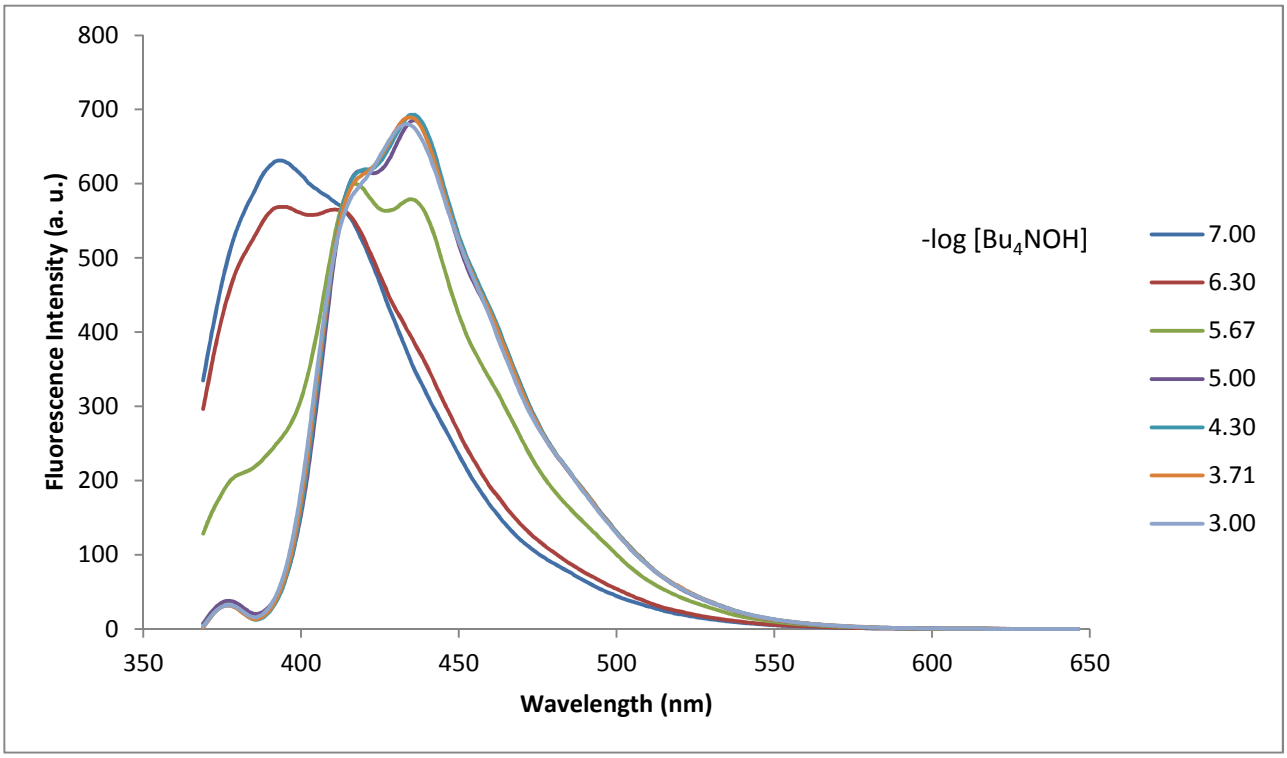


Figure S34. Fluorescence emission titration of compound **11** with Bu_4NOH ($\lambda_{excitation}$ = 339 nm).

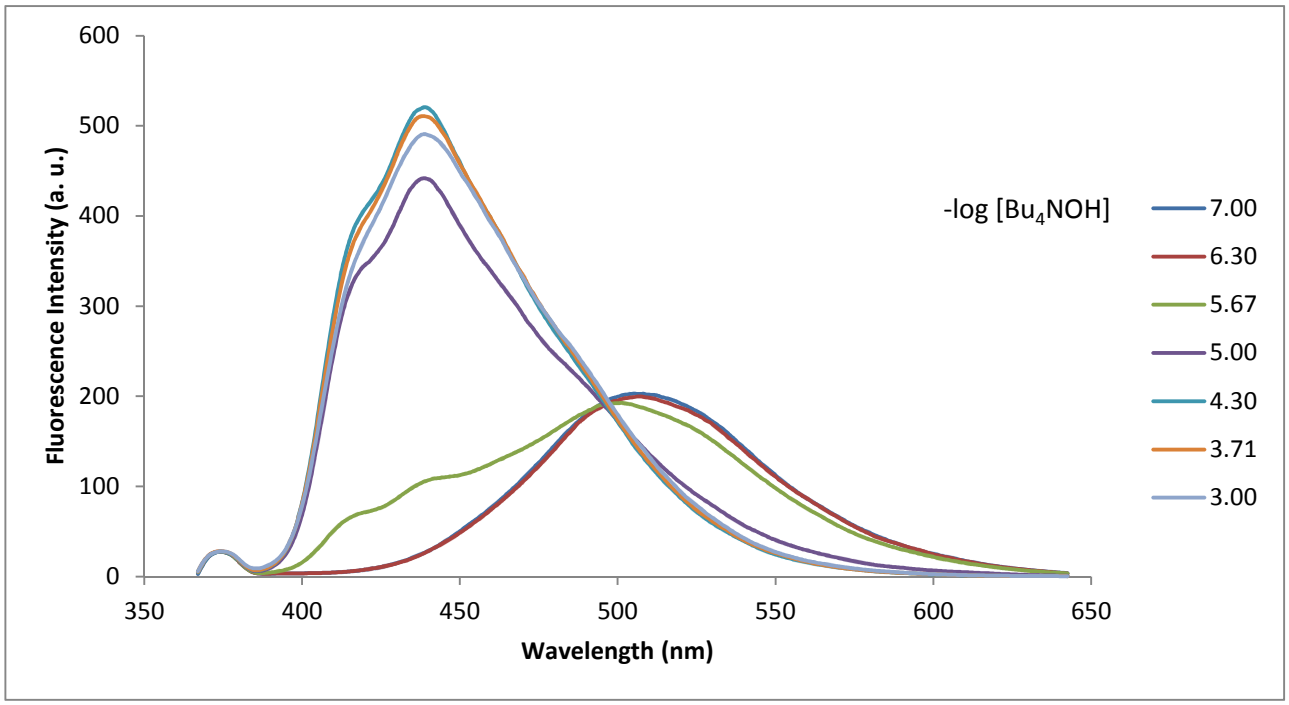


Figure S35. Fluorescence emission titration of compound **12** with Bu_4NOH ($\lambda_{excitation}$ = 337 nm).

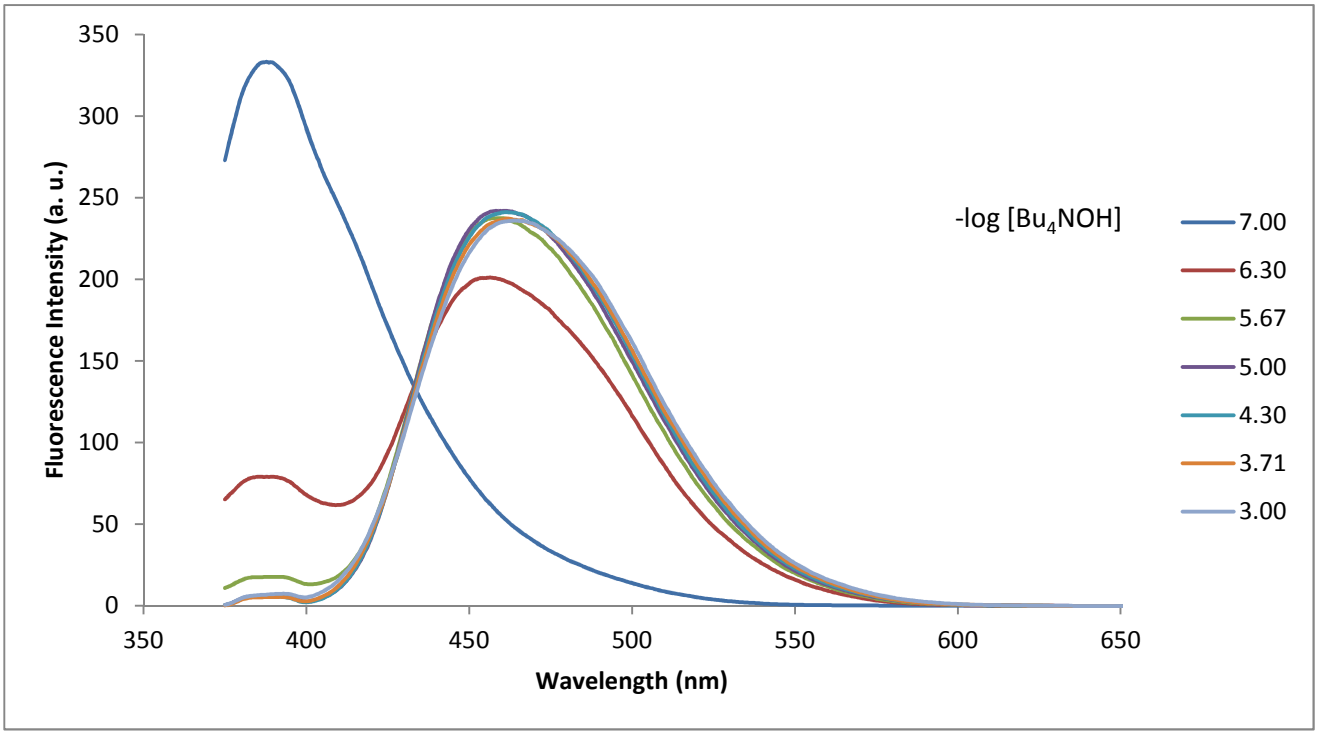


Figure S36. Fluorescence emission titration of compound **13** with Bu_4NOH ($\lambda_{excitation}$ = 345 nm).

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