Hydroxy-cruciforms,

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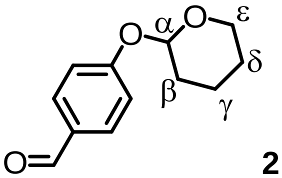
Supporting Information

Materials and Methods

All chemicals were purchased from Aldrich Chemical, Acros, TCI America, or Fisher Scientific and used without further purification unless otherwise specified. Column chromatography was performed using Standard Grade silica gel 60 Å, 32-63 μm (230 x 450 mesh) from Sorbent Technologies and the indicated eluent. Elution of cruciforms was readily monitored using a handheld UV lamp (365 nm). Melting points were obtained using a Mel-Temp apparatus fitted with a Fluke 51K/J digital thermometer. All IR spectra were obtained using a Simadzu FTIR-8400s spectrometer. Unless otherwise specified, NMR spectra were recorded at 298 K on a Bruker (500 MHz) or Varian Mercury spectrometer (300 MHz). Chemical shifts are reported in parts per million (ppm), using residual solvents (chloroform-*d*) or (THF-*d5*) as an internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant, and integration. Mass spectral analyses were provided by the Georgia Institute of Technology Mass Spectrometry Facility.

All absorption spectra were collected using a Shimadzu UV-2401PC spectrophotometer. All emission spectra were acquired using a Shimadzu RF-5301PC spectrofluorophotometer. Lifetime data were collected using a Lifespec-ps (Edinburgh Instruments), pulsed diode laser (PicoQuant, 372 nm excitation), and PMT detector (Hamamatsu). Data were fit to single exponential decay so as to optimize chi-squared values. Quantum yields for all cruciforms were measured using standard procedures[1]. In all cases, quinine sulfate was used as a standard.

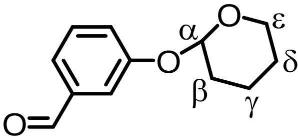
Synthesis of THP Aldehydes



2

Synthesis of 4-(tetrahydropyran-2-yloxy)-benzaldehyde 2: 4-Hydroxybenzaldehyde (5.80, 47.5 mmol) and 3,4-dihydro-2H-pyran (6.40 g, 76.1 mmol) were dissolved in dichloromethane (100 mL) in a 250 mL round bottom flask. Para-toluenesulfonic acid (0.430 g, 2.50 mmol) was added to the reaction mixture along with pyridine (1 mL). The pyridine was added drop wise over a 5 min period. The reaction solution was stirred for 24 h. The crude reaction mixture was washed three times with water, dried with magnesium sulfate and reduced until a dark brown oil was obtained. The product was washed with a solution of dilute NaOH and water to remove the starting material. The final product was obtained as a dark brown oil (8.23 g). Yield: 84%. ^{1}H

NMR (500 MHz, $CDCl_3$): δ = 9.90 (s, 1H, Ar-CHO), 7.84 (d, 2H, Ar-H, $J_{H,H}$ = 9 Hz), 7.17 (d, 2H, Ar-H, $J_{H,H}$ = 8.5 Hz), 5.55 (s, 1H, α-C-H), 3.85 (m, 1H, ε-CH), 3.64 (m, 1H, ε-C-H), 2.01 (m, 1H, β-C-H), 1.90 (m, 2H, γ-C-H) 1.71 (m, 2H, δ-C-H), 1.62 (m, 1H, β-C-H). *^{13}C NMR (500 MHz, $CDCl_3$):* δ = 191.19, 162.48, 132.11, 130.77, 116.82, 96.41, 62.34, 30.36, 25.35, 18.77.



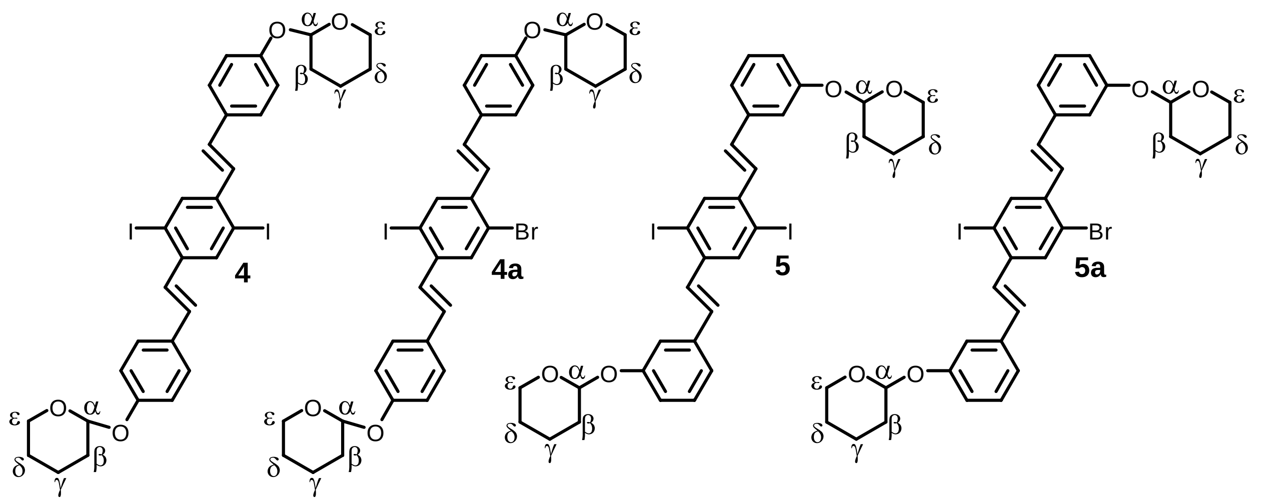
3

Synthesis of 3-(tetrahydropyran-2-yloxy)-benzaldehyde 3: 3-hydroxybenzaldehyde (5.80, 47.5 mmol) and 3,4-dihydro-2H-pyran (6.40 g, 76.1 mmol) were dissolved in dichloromethane (100 mL) in a 250 mL round bottom flask. Para-toluenesulfonic acid (0.430 g, 2.50 mmol) was added to the reaction mixture along with pyridine (1 mL). The pyridine was added drop wise over a 5 min period. The reaction mixture was stirred for 24 h. The crude reaction mixture was washed three times with water, dried with magnesium sulfate and reduced until a light brown oil was obtained. The product was washed with a solution of dilute NaOH and water to remove the starting material. The final product was obtained as a light brown oil (8.35 g). Yield: 85%. *^{1}H NMR (500 MHz, $CDCl_3$):* δ = 9.97 (s, 1H, Ar-CHO), 7.56 (s, 1H, Ar-H,), 7.50 (dt, 1H, Ar-H, $J_{H,H}$ = 7.5 Hz, *with long range coupling*), 7.44 (t, 1H, Ar-H, $J_{H,H}$ = 8 Hz), 7.31 (md, 1H, Ar-H, $J_{H,H}$ = 8 Hz, *with long range coupling*), 5.49 (s, 1H, α-C-H), 3.88 (m, 1H, ε-CH), 3.63 (m, 1H, ε-C-H), 2.01 (m, 1H, β-C-H), 1.90 (m, 2H, γ-C-H) 1.71 (m, 2H, δ-C-H), 1.62 (m, 1H, β-C-H). *^{13}C NMR (500 MHz, $CDCl_3$)*: δ = 192.19, 157.90, 138.10, 130.10, 123.63, 123.18, 116.59, 96.59, 62.21, 30.47, 25.40, 18.92.

Compounds 4 and 5:

General procedure for compounds 4 and 5: An oven dried Schlenk flask cooled under nitrogen was charged with **1**, NaH (2.5 eq), and dry THF. The flask was closed with a septum, a nitrogen-filled balloon was fitted to the arm and the stopcock was opened. With mild heating (40°C), the solution turned a vivid purple-red. The aldehyde **2** or **3** was introduced in small portions over 1 h with a syringe as a pure oil. The reaction was allowed to stir overnight before work-up. The small excess of NaH was quenched with water and the mixture was extracted three times with dichloromethane. The organic layer was washed three times with water, dried with magnesium sulfate, filtered and reduced until a precipitate was formed. The precipitate was recrystallized from chloroform and collected by suction filtration and dried under vacuum.

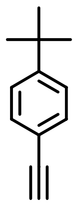
Note: Compounds **4** and **5** both contain ~ 10% of previously reported halogen exchange material (**4a** and **5a**) from the precursor **1,** which is inseparable but can be used for further reactions.[3]



4 **4a** **5** **5a**

Compound 4: Following the general procedure, **1** (0.500 g, 0.681 mmol), NaH (60 mg, 2.50 mmol), and THF (50 mL) were combined. 4-(Tetrahydropyran-2-yloxy)-benzaldehyde **2** (0.409 g, 1.98 mmol) was then added. Work up and recrystallization yielded (0.448 g, 77%) bright yellow crystals. *MP:* 268-270 ºC. *IR:* 2933, 2869, 1600, 1508, 1234, 1170, 1107, 1035, 970, 810 cm $^{-1}$. ^{1}*H NMR (500 MHz, CDCl$_3$):* δ = 8.07 (s, 2H, Ar-H), 7.58 (d, 4H, Ar-H, $J_{H,H}$ = 8.5 Hz), 7.10 (d, 4H, Ar-H, $J_{H,H}$ = 8.5 Hz), 7.09 (d, 2H, C=C-H, $J_{H,H}$ = 16.5 Hz), 6.95 (d, 2H, CH=CH, $J_{H,H}$ = 16.5 Hz), 5.49 (s, 2H, α-C-H), 3.95 (m, 2H, ε-CH), 3.65 (m, 2H, ε-C-H), 2.04 (m, 2H, β-C-H), 1.91 (m, 4H, γ-C-H) 1.71 (m, 4H, δ-C-H), 1.64 (m, 2H, β-C-H). ^{13}*C NMR (500 MHz, CDCl$_3$):* δ = 157.73, 141.10, 136.44, 132.17, 130.63, 129.05, 128.57, 117.14, 100.62, 96.69, 62.47, 30.70, 25.59, 19.13.

Compound 5: Following the general procedure, **1** (0.500 g, 0.681 mmol), NaH (60 mg, 2.50 mmol), and THF (50 mL) were combined. 3-(Tetrahydropyran-2-yloxy)-benzaldehyde **3** (0.409 g, 1.98 mmol) was then added. Work up and recrystallization yielded (0.399 g, 68%) pale yellow crystals. *MP:* 216-218 ºC. *IR:* 2947, 2873, 1581, 1488, 1251, 1120, 1037, 1014, 970, 904, 869, 777 cm $^{-1}$. ^{1}*H NMR (500 MHz, CDCl$_3$):* 8.09 (s, 2H, Ar-H), 7.33 (t, 2H, Ar-H, $J_{H,H}$ = 8 Hz), 7.27 (s, 2H, Ar-H), 7.22 (d, 2H, Ar-H, $J_{H,H}$= 5 Hz), 7.20 (d, 2H, C=C-H, $J_{H,H}$ =16 Hz), 7.05 (d, 2H, Ar-H, $J_{H,H}$ = 8.5 Hz), 6.97 (d, 2H, C=C-H, $J_{H,H}$ = 16 Hz), 5.49 (s, 2H, α-C-H), 3.95 (m, 2H, ε-C-H), 3.65 (m, 2H, ε-C-H), 2.04 (m, 2H, β-C-H), 1.91 (m, 4H, γ-C-H) 1.71 (m, 4H, δ-C-H), 1.64 (m, 2H, β-C-H). ^{13}*C NMR (500 MHz, CDCl$_3$):* δ = 157.86, 141.18, 138.36, 136.78, 132.70, 131.10, 130.13, 120.87, 116.94, 115.39, 100.69, 96.90, 62.59, 30.81, 25.62, 19.25.



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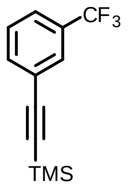


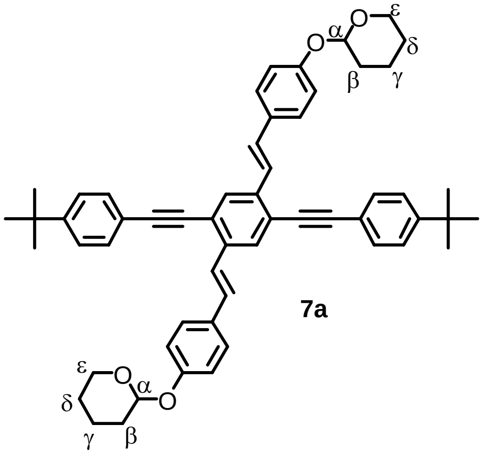
9

Compound **6** has been previously reported.[2]

Compound 9: In a nitrogen flushed Schlenk-flask, 3.50 g (12.9 mmol) of 1-iodo-3-(trifluoromethyl) benzene was dissolved in THF (2 mL) and piperidine (2 mL). Then $Pd(Ph_3)_2Cl_2$ (5 mg, 7.1 μmol) catalyst and CuI (5 mg, 33 μmol) were added and the mixture was stirred for 15 minutes before 1.6 g (16.3 mmol) of ethynyltrimethylsilane was added. The reaction was heated for 15 min and stirred at room temperature overnight. Afterwards, water (50 mL) was added until all the salts were dissolved. The mixture was then extracted three times with dichloromethane (75 mL), washed with water (75 mL) and dilute ammonia and brine. The organic layer was dried over $MgSO_4$, the solvent was removed, and the product was purified by filtration over a silica plug with dichloromethane. *^{1}H NMR (300 MHz, $CDCl_3$):* δ = 7.72 (s, 1H, Ar-H), 7.62 (d, 1H, Ar-H, $J_{H,H}$ = 7.7 Hz), 7.56 (d, 1H, Ar-H, $J_{H,H}$ = 8.4 Hz), 7.42 (t, 1H, Ar-H, $J_{H,H}$ = 7.3 Hz), 0.26 (s, 9H, -CH_3). *^{13}C NMR (300 MHz, $CDCl_3$):* δ = 134.98, 130.90(m), 128.73, 125.52, 124.93(m), 124.14, 121.91, 118.30, 103.28, 96.20. *MS (EI, 70-SE) ($C_{12}H_{13}F_3Si$):* m/z = 242

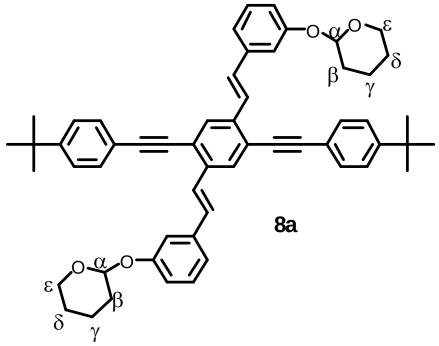
Compounds 7a,8a,10a:

Compounds **7a,8a** and **10a** were produced by the Sonogashira coupling of either the free alkyne **6** or by in-situ deprotection of the TMS group of **9** with potassium hydroxide and ethanol as a co-solvent. The reaction progress could be monitored by the development of the fluorescent products which were isolated by precipitating twice in non solvents.



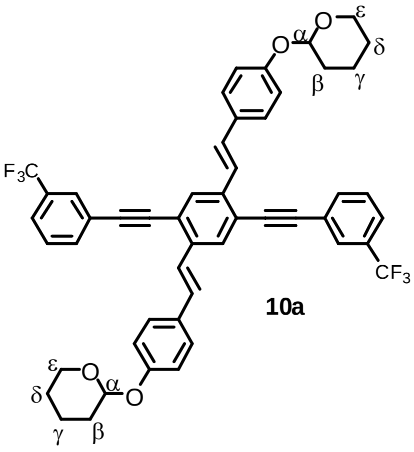
7a

Compound 7a: 4 (0.297 g, 0.404 mmol) was combined with **6** (0.192, g, 1.21 mmol), $(PPh_3)_2PdCl_2$ (5 mg, 7.1 μmol), CuI (5 mg, 33 μmol) and dissolved in THF (50 mL) and piperidine (5 mL) in a nitrogen purged Schlenk flask. The solution was degassed, capped with a septum and allowed to stir at room temperature for 24 h. The product was extracted with dichloromethane (100 mL), washed three times with water (100 mL), dried with magnesium sulfate and reduced until a yellow powder formed, which was purified by chromotagraphy eluting with 70:30 dichloromethane and hexanes, yielding 150 mg of yellow crystals. Yield: 47%. *MP:* 186-188 ºC. *IR:* 2939, 2866, 2250, 1602, 1508, 1236, 1170, 1035, 1018, 960, 919, 831, 813 cm $^{-1}$. *^{1}H NMR (500 MHz, $CDCl_3$):* δ = 7.90 (s, 2H, Ar-H), 7.59 (d, 2H, C=C-H, $J_{H,H}$ = 16.5 Hz), 7.57 (d, 4H, Ar-H, $J_{H,H}$ = 8 Hz), 7.54 (d, 4H, Ar-H, $J_{H,H}$ = 8 Hz), 7.45 (d, 4H, Ar-H, $J_{H,H}$ = 8.5 Hz), 7.25 (d, 2H, C=C-H, $J_{H,H}$ = 16.5 Hz), 7.10 (d, 4H, Ar-H, $J_{H,H}$ = 8.5 Hz), 5.49 (s, 2H, α-C-H), 3.95 (m, 2H, ε-C-H), 3.65 (m, 2H, ε-C-H), 2.04 (m, 2H, β-C-H), 1.91 (m, 4H, γ-C-H) 1.71 (m, 4H, δ-C-H), 1.64 (m, 2H, β-C-H), 1.37 (s, 18H, t-butyl). *^{13}C NMR (500 MHz, $CDCl_3$):* δ = 156.97, 151.80, 137.22, 131.29, 130.97, 129.91, 128.43, 127.90, 125.50, 123.89, 122.06, 120.18, 116.67, 96.24, 95.47, 87.38, 62.01, 34.85, 31.18, 30.29, 25.18, 18.70. *MS (FAB, 70-SE) ($C_{56}H_{58}O_4$):* m/z = 794.



8a

Compound 8a: 5 (0.399 g, 0.543 mmol) was combined with **6** (0.258 g, 1.63 mmol), $(PPh_3)_2PdCl_2$ (5 mg, 7.1 μmol), CuI (5 mg, 33 μmol) and dissolved in THF (50 mL) and piperidine (5 mL) in a nitrogen purged Schlenk flask. The solution was degassed, capped with a septum and allowed to stir at room temperature for 24 h. The product was extracted with dichloromethane (100 mL), washed three times with water (100 mL), dried with magnesium sulfate and reduced until a yellow powder formed, which was purified by chromotagraphy eluting with 70:30 dichloromethane and hexanes, yielding 190 mg of yellow crystals. Yield: 44%. *MP:* 266-268 ºC. *IR:* 2947, 2869, 2220, 1583, 1512, 1452, 1257, 1157, 1020, 956, 831, 775 cm $^{-1}$. *^{1}H NMR (500 MHz, CDCl$_3$):* δ = 7.93 (s, 2H, Ar-H), 7.72 (d, 2H, C=C-H, $J_{H,H}$ = 16.5 Hz), 7.60 (d, 4H, Ar-H, $J_{H,H}$ = 8.5), 7.45 (d, 4H, Ar-H, $J_{H,H}$ = 8.5), 7.36 (s, 2H, Ar-H), 7.32 (t, 2H, Ar-H, $J_{H,H}$ = 8 Hz), 7.27 (d,2H, $J_{H,H}$ = 16.5 Hz, CH=CH), 7.23 (d, 2H, $J_{H,H}$ = 8 Hz Ar-H), 7.02 (d, 2H, $J_{H,H}$ = 8 Hz, Ar-H), 5.49 (s, 2H, α-C-H), 3.95 (m, 2H, ε-C-H), 3.65 (m, 2H, ε-C-H), 2.04 (m, 2H, β-C-H), 1.91 (m, 4H, γ-C-H) 1.71 (m, 4H, δ-C-H), 1.64 (m, 2H, β-C-H), 1.37 (s, 18H, t-butyl). *^{13}C NMR (500 MHz, CDCl$_3$):* δ = 157.92, 152.27, 139.17, 137.68, 131.68, 130.82, 130.08, 129.06, 126.40, 125.93, 122.85, 120.99 120.62, 116.83, 114.74, 96.82, 96.82, 87.73, 62.41, 35.30, 31.65, 30.90, 25.73, 19.26. *MS (FAB, 70-SE) ($C_{56}H_{58}O_4$):* m/z = 794.

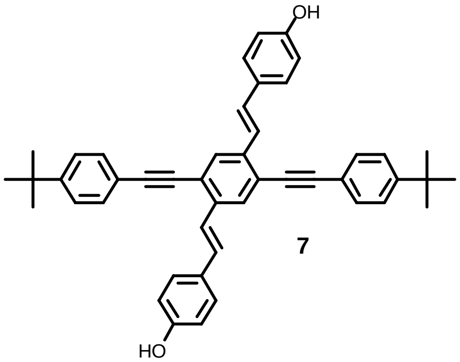


10a

Compound 10a: 4 (0.403 g, 0.549 mmol) was combined with **9** (0.399 g, 1.64 mmol), $(PPh_3)_2PdCl_2$ (5 mg, 7.1 μmol), CuI (5 mg, 33 μmol), KOH (0.500 g, 8.90 mmol) and dissolved in piperidine (5 mL), EtOH (10 mL) and THF (25 mL) in a nitrogen purged Schlenk flask. The solution was degassed, capped with a septum and allowed to stir at room temperature for 24 h. The product was extracted with dichloromethane (100 mL), washed three times with water (100 mL), dried with magnesium sulfate and reduced until a yellow powder formed, which was purified by chromotagraphy eluting with 60:40 dichloromethane and hexanes, yielding 280 mg of yellow crystals. Yield: 53%. *MP:* 246-248 ºC. *IR:* 3035, 2943, 2875, 2235, 1600, 1508, 1330, 1240, 1164, 1122, 958, 919, 800 cm $^{-1}$. *^{1}H NMR (500 MHz, CDCl$_3$):* δ = 7.92 (s, 2H, Ar-H), 7.90 (s, 2H, Ar-H), 7.79 (d, 2H, Ar-H, $J_{H,H}$ = 8 Hz), 7.66 (d, 2H, Ar-H, $J_{H,H}$ = 8 Hz), 7.56 (t, 2H, Ar-H, $J_{H,H}$ = 8 Hz), 7.54 (d, 2H, C=C-H, $J_{H,H}$ = 16.5 Hz), 7.54 (d, 4H, Ar-H, $J_{H,H}$ = 9 Hz), 7.26 (d, 2H, C=C-H, $J_{H,H}$ = 16.5 Hz), 7.11 (d, 4H, Ar-H, $J_{H,H}$ = 9 Hz), 5.49 (s, 2H, α-C-H), 3.95 (m, 2H, ε-C-H), 3.65 (m, 2H, ε-C-H), 2.04 (m, 2H, β-C-H), 1.91 (m, 4H, γ-C-H) 1.71 (m, 4H, δ-C-H), 1.64 (m, 2H, β-C-H). *^{13}C NMR (500 MHz, CDCl$_3$):* δ = 157.66, 138.01, 134.97, 131.70, 131.42, 131.09, 129.51, 129.14, 128.78 (m), 128.39, 125.49 (m), 125.21, 124.51, 123.76, 123.06, 122.13, 117.18, 96.75, 94.27, 89.88, 30.73, 25.61, 19.15. *MS (FAB, 70-SE) ($C_{50}H_{40}F_6O_4$):* m/z = 818.

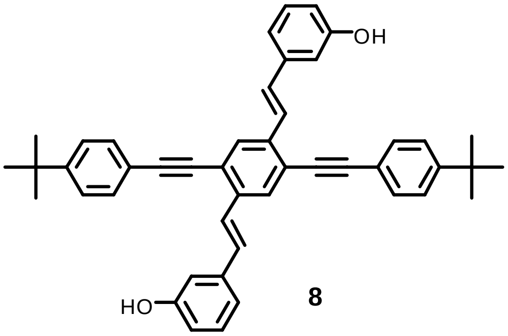
Compounds 7,8,10

Compounds **7a,8a,** and **10a** were deprotected by trifluoroacetic acid in a dry ice acetone bath. The products were obtained by extracting with dichloromethane or ethyl ether. The yields reported reflect the amount of pure material that was recovered after deprotection and recrystallization.



7

Compound 7: **7a** (0.080 g, 0.128 mmol) was dissolved in dichloromethane (30 mL) and trifluoroacetic acid (1 mL) was added into a 100-mL round bottom flask kept in a dry ice acetone bath. The solution was allowed to stir at -78 °C for 2h and then thawed to room temperature. The reaction mixture was washed three times with water (100 mL), dried with magnesium sulfate, filtered and reduced until a brown powder was formed. The powder was recrystallized by dissolving in hot chloroform and adding an excess amount of hexanes, yielding brown crystals (70.0 mg). Yield: 88%. *MP:* 236-238 ºC. *IR:* 3321, 2956, 2852, 2195, 1604, 1512, 1440 1168, 1016, 958, 833, 815 cm^{-1}. *^{1}H NMR (500 MHz, $CDCl_3$):* δ = 7.89 (s, 2H, Ar-H), 7.57 (d, 4H, Ar-H, $J_{H,H}$ = 8.5 Hz), 7.56 (d, 2H, C=C-H, $J_{H,H}$ = 16.5 Hz), 7.50 (d, 4H, Ar-H, $J_{H,H}$ = 9 Hz), 7.45 (d, 4H, Ar-H, $J_{H,H}$ = 8.5 Hz), 7.24 (d, 2H, C=C-H, $J_{H,H}$ = 16.5 Hz), 6.88 (d, 4H, Ar-H, $J_{H,H}$ = 9 Hz). *^{13}C NMR (500 MHz, $CDCl_3$):* δ = 155.97, 152.30, 137.64, 131.72, 130.82, 130.29, 128.93, 128.65, 125.93, 124.14, 122.50, 120.61, 116.15, 95.89, 87.80, 35.30, 31.30. *MS (FAB, 70-SE) ($C_{46}H_{42}O_2$):* m/z = 626.



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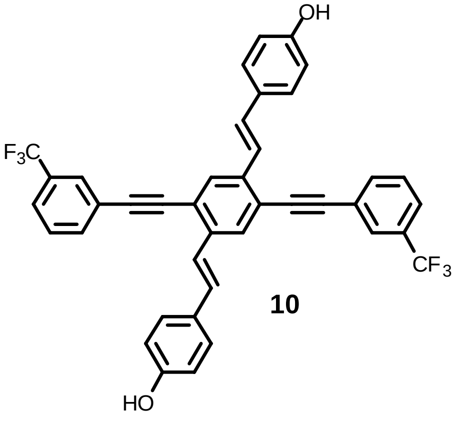
Compound 8: **8a** (0.102 g, 0.163 mmol) was dissolved in dichloromethane (30 mL) and trifluoroacetic acid (1 mL) was added into a 100-mL round bottom flask kept in a dry ice acetone bath. The solution was allowed to stir at -78 °C for 2 h and then thawed to room temperature. The reaction mixture was washed three times with water (100 mL), dried with magnesium sulfate and reduced until a green powder was formed. The powder was recrystallized by dissolving in hot chloroform and adding an excess amount of hexanes, yielding green crystals (91.8 mg). Yield: 90%. *MP:* 238-240 ºC. *IR:* 3319, 2954, 2862, 1784, 1683, 1591, 1506, 1450, 1265, 1151, 1016, 962, 833, 775 cm^{-1}. *^{1}H NMR (500 MHz, $CDCl_3$):* δ = 7.89 (s, 2H, Ar-H), 7.65 (d, 4H, C=C-H, $J_{H,H}$ = 16.5 Hz), 7.57 (d, 4H, Ar-H, $J_{H,H}$ = 8.5 Hz), 7.45 (d, 4H, Ar-H, $J_{H,H}$ = 8.5 Hz), 7.26 (t, 2H, Ar-H, $J_{H,H}$ = 8.5 Hz), 7.22 (d, 2H, C=C-H, $J_{H,H}$ = 16.5 Hz), 7.16 (d, 2H, Ar-H, $J_{H,H}$ = 7 Hz), 7.07 (s, 2H, Ar-H), 6.82 (d, 4H, Ar-H, $J_{H,H}$ = 7 Hz). *^{13}C NMR (500 MHz, $CDCl_3$):* δ = 156.41, 152.40, 139.40, 137.59, 131.78, 130.67, 130.37, 129.30, 126.56, 125.96, 122.81, 120.47, 119.97, 115.57, 113.77, 96.21, 87.57, 35.30, 31.61. *MS (FAB, 70-SE) ($C_{46}H_{42}O_2$):* m/z = 626.



10

Compound 10: **10a** (0.120 g, 0.184 mmol) was dissolved in dichloromethane (30 mL) and trifluoroacetic acid (1 mL) was added into a 100-mL round bottom flask kept in a dry ice acetone bath. The solution was allowed to stir at -78 °C for 2 h. The product was extracted with ethyl ether and washed three times with water, dried with magnesium sulfate and reduced until a yellow powder was formed. The resulting yellow powder was recrystallized from methanol yielding yellow crystals (102 mg). Yield: 85% *MP:* 236-238 ºC. *IR:* 3309, 2923, 2852, 1784, 1697, 1604, 1512, 1328, 1245, 1166, 1122, 962, 806 cm $^{-1}$. *^{1}H NMR (500 MHz, THF-d5)* δ = 8.57 (s, 2H, Ar-OH), 7.99 (s, 2H, Ar-H), 7.97 (s, 2H, Ar-H), 7.87 (d, 2H, Ar-H, $J_{H,H}$ = 8 Hz), 7.72 (d, 2H, Ar-H, $J_{H,H}$ = 8 Hz), 7.64 (t, 2H, Ar-H, $J_{H,H}$ = 8 Hz), 7.52 (d, 2H, C=C-H, $J_{H,H}$ = 16.5 Hz), 7.46 (d, 4H, Ar-H, $J_{H,H}$ = 8.5 Hz), 7.34 (d, 2H, C=C-H, $J_{H,H}$ = 16.5 Hz), 6.77 (d, 4H, Ar-H, $J_{H,H}$ = 8.5 Hz). *^{13}C NMR (500 MHz, THF-d5):* δ = 156.86, 136.23, 133.27, 129.77, 129.46, 129.21, 127.99, 127.09, 126.95, 126.61 (m), 123.55 (m), 122.83, 121.46, 120.05, 119.95, 114.05, 91.96, 87.94. *MS (FAB, 70-SE) ($C_{40}H_{24}F_6O_2$)*: m/z = 650.

Experiment 1. Influence of amines on the optical properties of 3d.

To investigate the sensory ability of hydroxy cruciforms towards amines, **3d** was tested. Approximately 0.1 mL of amine was added to each 20 mL vial and its optical properties were measured. The absorption and emission data are shown in **Figure 1.** and **Figure 2.** respectively. A picture of the fluorescent response of **3d** irradiated under a UV lamp is also shown below (see **Figure 6**). All amines showed bathochromic shifts except pyridine and quinoline, which showed quenching of fluorescence. Pyrrole is the only amine that did not show a change in fluorescence.

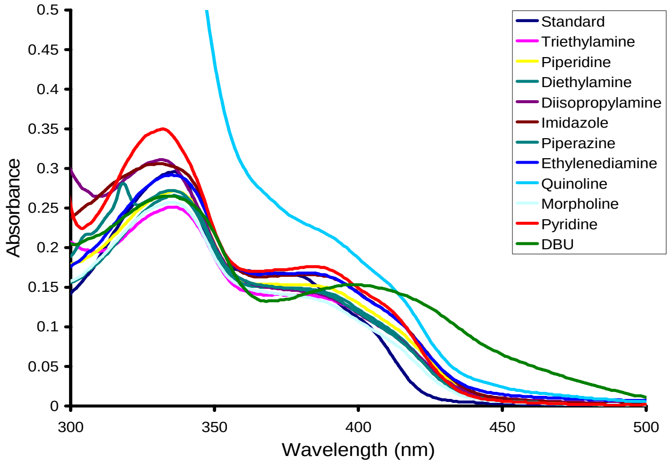


Figure 1. Absorption Spectrum of **7** with amines in dichloromethane.

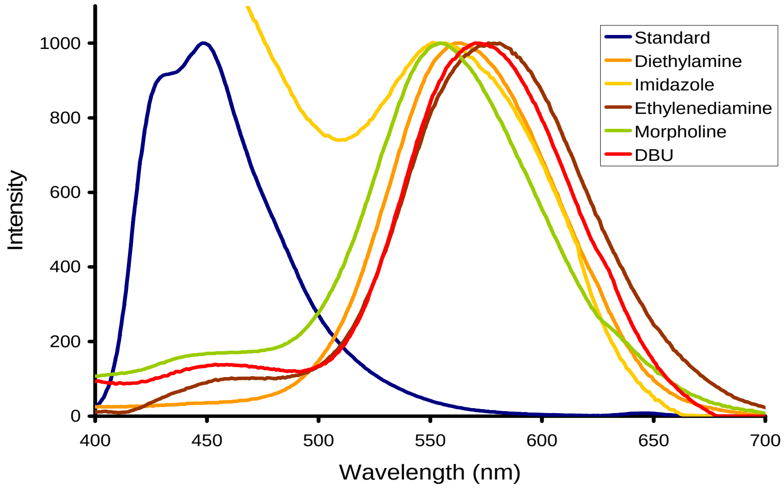


Figure 2. Emission spectrum of **7** with amines in dichloromethane.

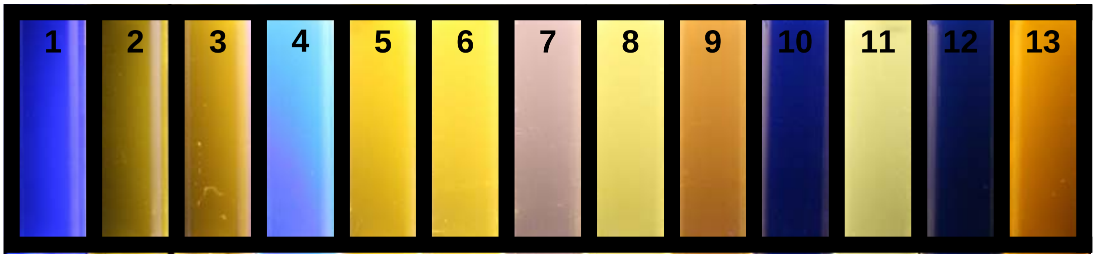


Figure 3. Emission of **7** in dichloromethane with the following amines: 1 only **7**, 2 triethylamine, 3 piperidine, 4 pyrrole, 5 diethylamine, 6 diisopropyl amine, 7 imidazole, 8 piperazine, 9 ethylenediamine, 10 quinoline, 11 morpholine, 12 pyridine, 13 1,8-diaza-bicyclo[5.4.0] undec-7-ene (DBU).

Experiment 2. Influence of amines on the optical properties of 8.

To investigate the sensory ability of hydroxy cruciforms towards amines, **8** was tested. Approximately 0.1 mL of amine was added to each 20 mL vial and its optical properties were measured. The absorption and emission data are shown in **Figure 4.** and **Figure 5.** respectively. A picture of the fluorescent response of **3e** irradiated under a UV lamp is also shown below (see **Figure 9**). **3e** shows quenching with all amines except pyrole.

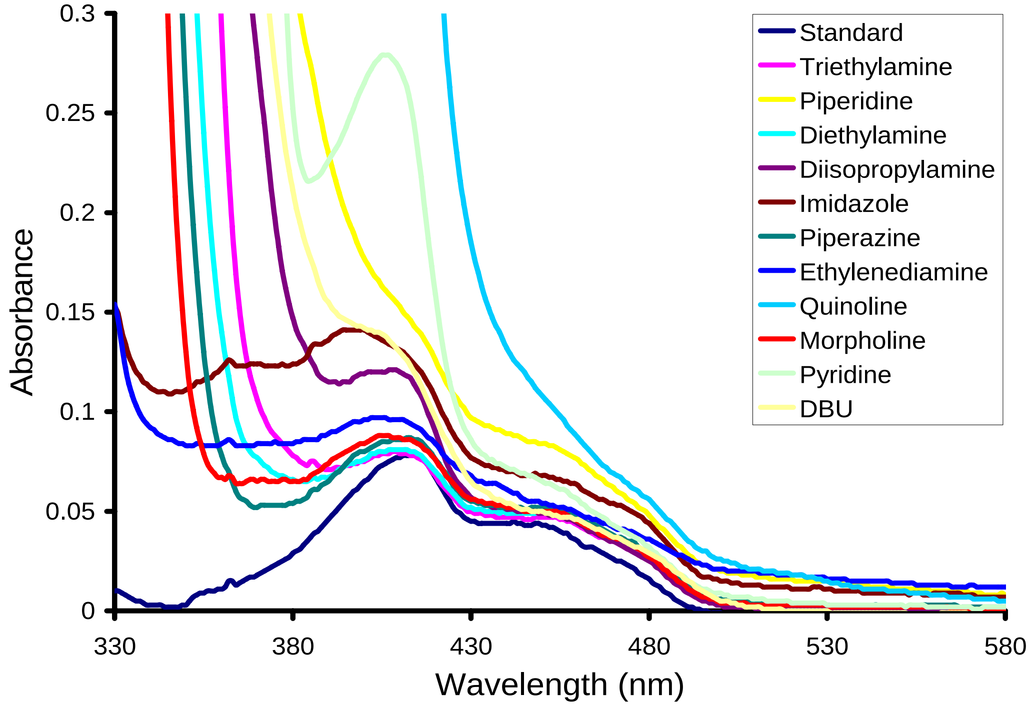


Figure 4. Absorption spectrum of **8** with amines in dichloromethane.

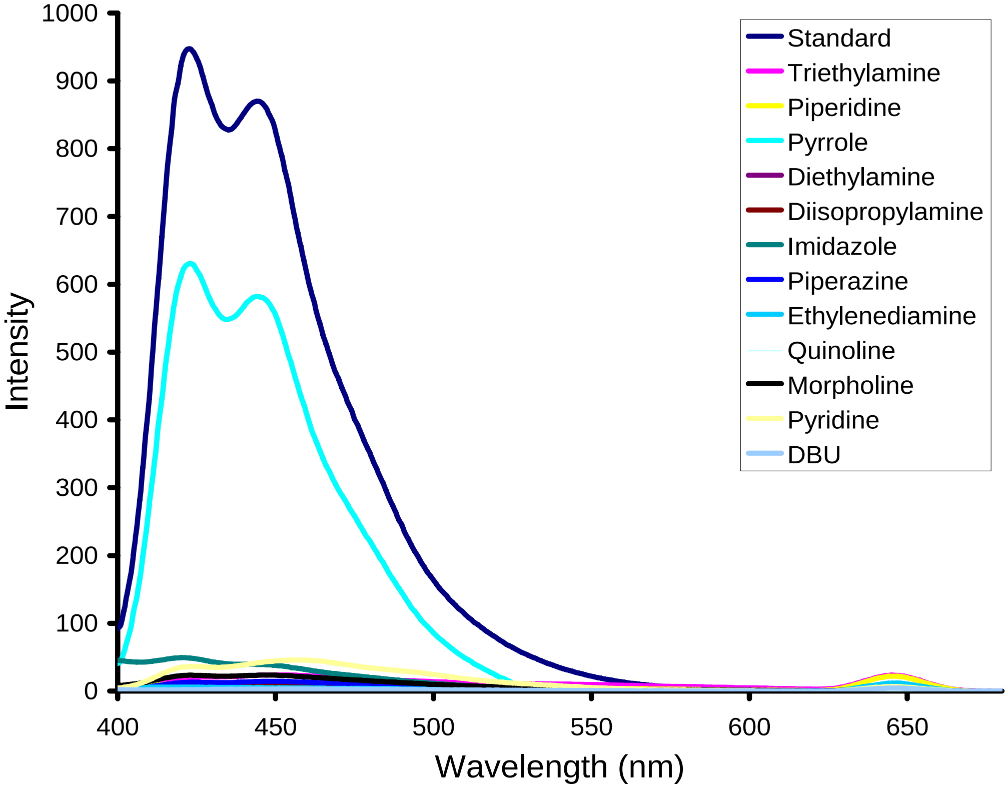


Figure 5. Emission spectrum of **8** with amines in dichloromethane**.**

Figure 6. Emission of **8** in dichloromethane with the following amines: 1 only **8**, 2 triethylamine, 3 piperidine, 4 pyrole, 5 diethylamine, 6 diisopropyl amine, 7 imidazole, 8 piperazine, 9 ethylenediamine, 10 quinoline, 11 morpholine, 12 pyridine, 13 1,8-diaza-bicyclo[5.4.0] undec-7-ene (DBU).

Experiment 3. Influence of amines on the optical properties of 10.

To investigate the sensory ability of hydroxy cruciforms towards amines, **10** was tested. Approximately 0.1 mL of amine was added to each 20 mL vial and its optical properties were measured. The absorption and emission data are shown in **Figure 7.** and **Figure 8.** respectively. A picture of the fluorescent response of **3f** irradiated under a UV lamp is also shown below (see **Figure 9**). **10** shows bathochromic shifts that are ~10 -15 nm larger than **7**, and **8**. Pyridine is the only amine that appears to show a quenching of fluorescence.

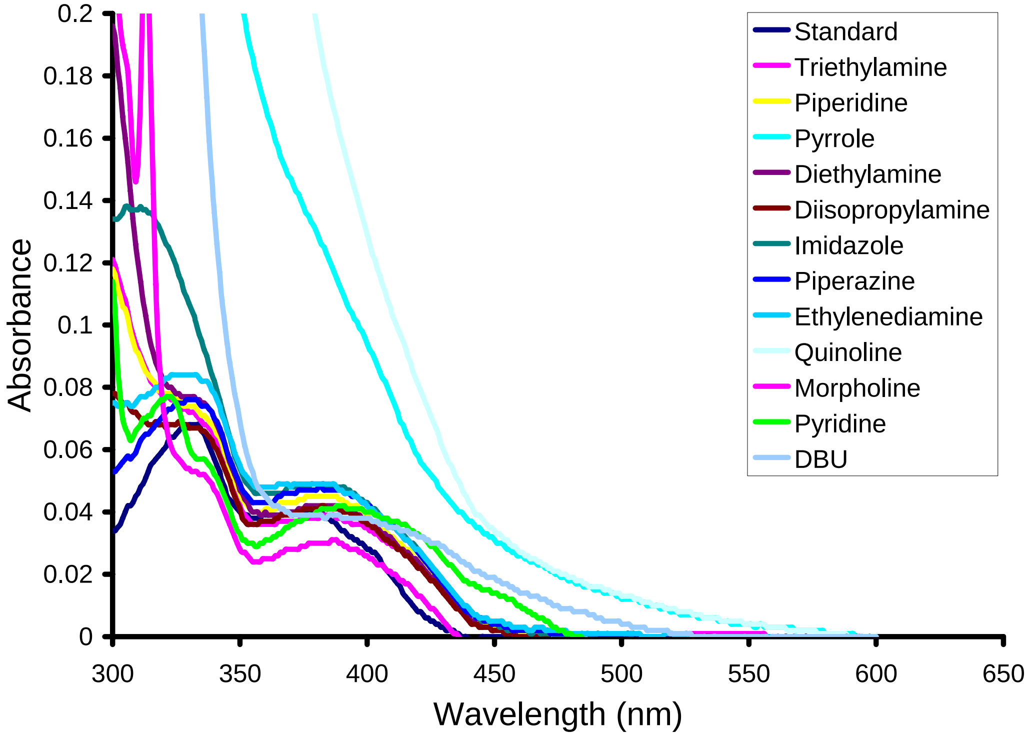


Figure 7. Absorption spectrum of **10** with amines in dichloromethane.

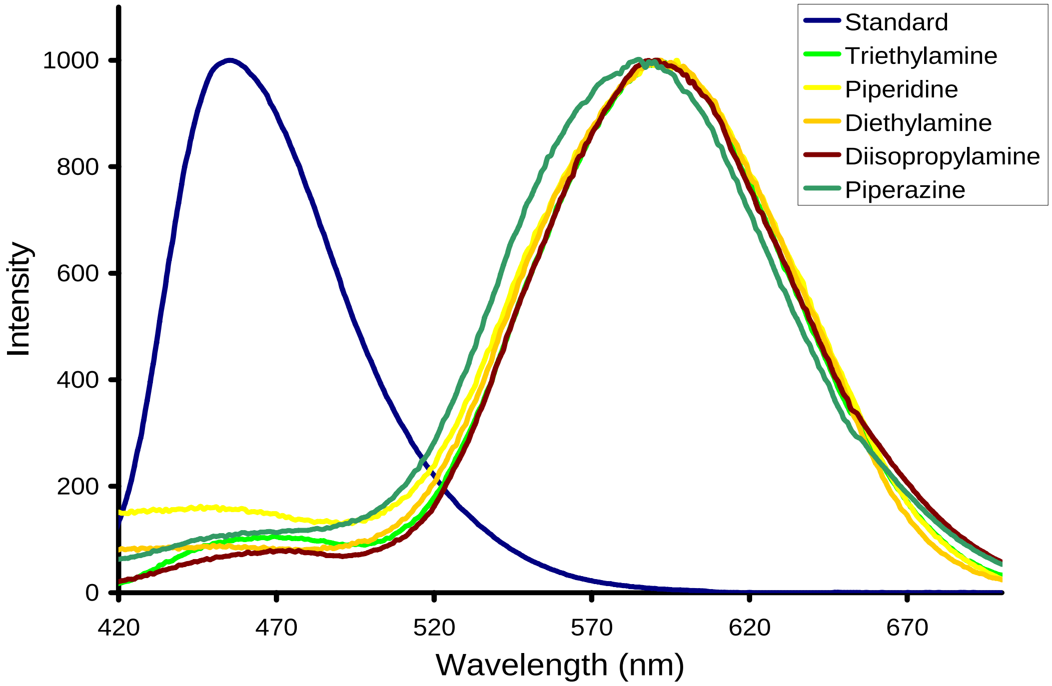


Figure 8. Emission spectrum of **10** with amines in dichloromethane.

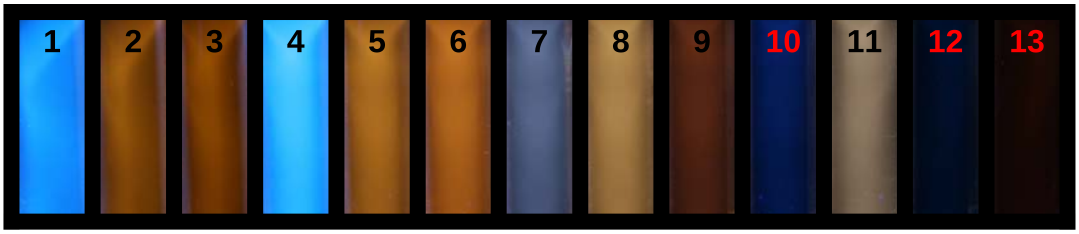


Figure 9. Emission of **10** in dichloromethane with the following amines: 1 only **10**, 2 triethylamine, 3 piperidine, 4 pyrole, 5 diethylamine, 6 diisopropyl amine, 7 imidazole, 8 piperazine, 9 ethylenediamine, 10 quinoline, 11 morpholine, 12 pyridine, 13 1,8-diaza-bicyclo[5.4.0] undec-7-ene (DBU).

Uv-vis/Fluorescence, Quantum Yields, and Lifetimes:

Dichloromethane	**7**	**8**	**10**
Ab	336, 380	413, 445	333, 376
Em	432, 450	423, 445	456
Φ	0.41	0.72	0.57
τ (ns)	1.42	2.99	-

Emission Spectra for **7** and **10** with all amines:

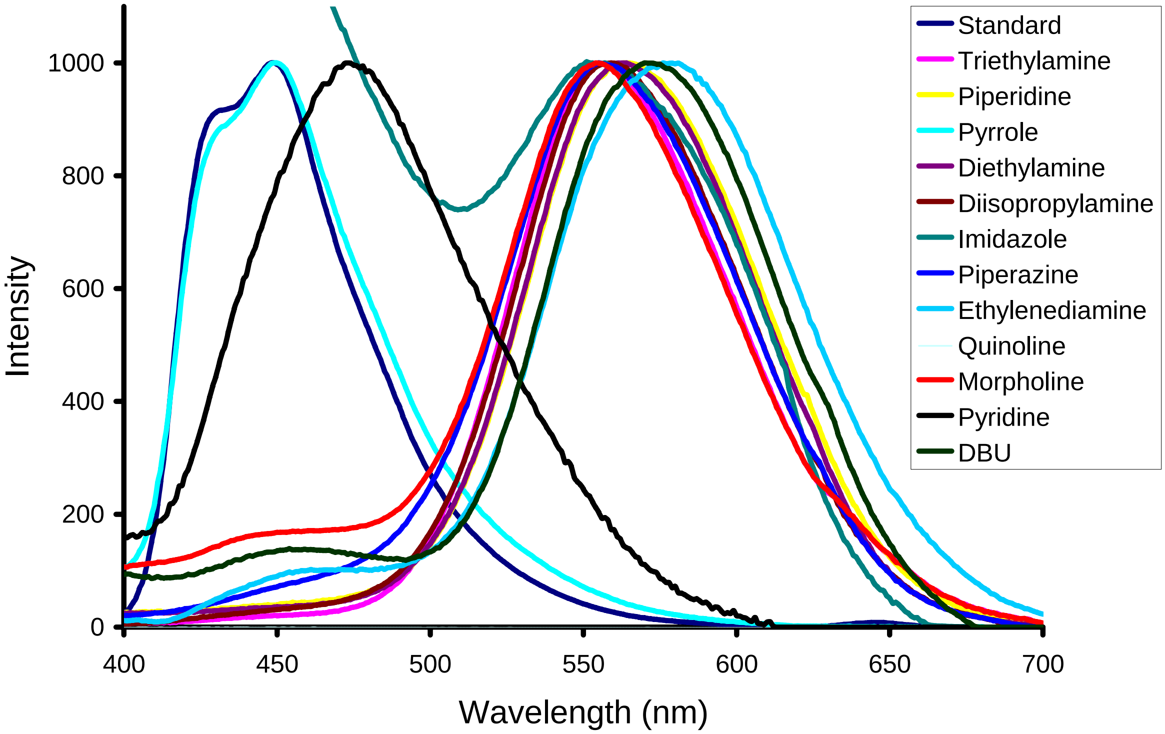


Figure 10. Normalized spectrum of **7** with all amines in dichloromethane**.**

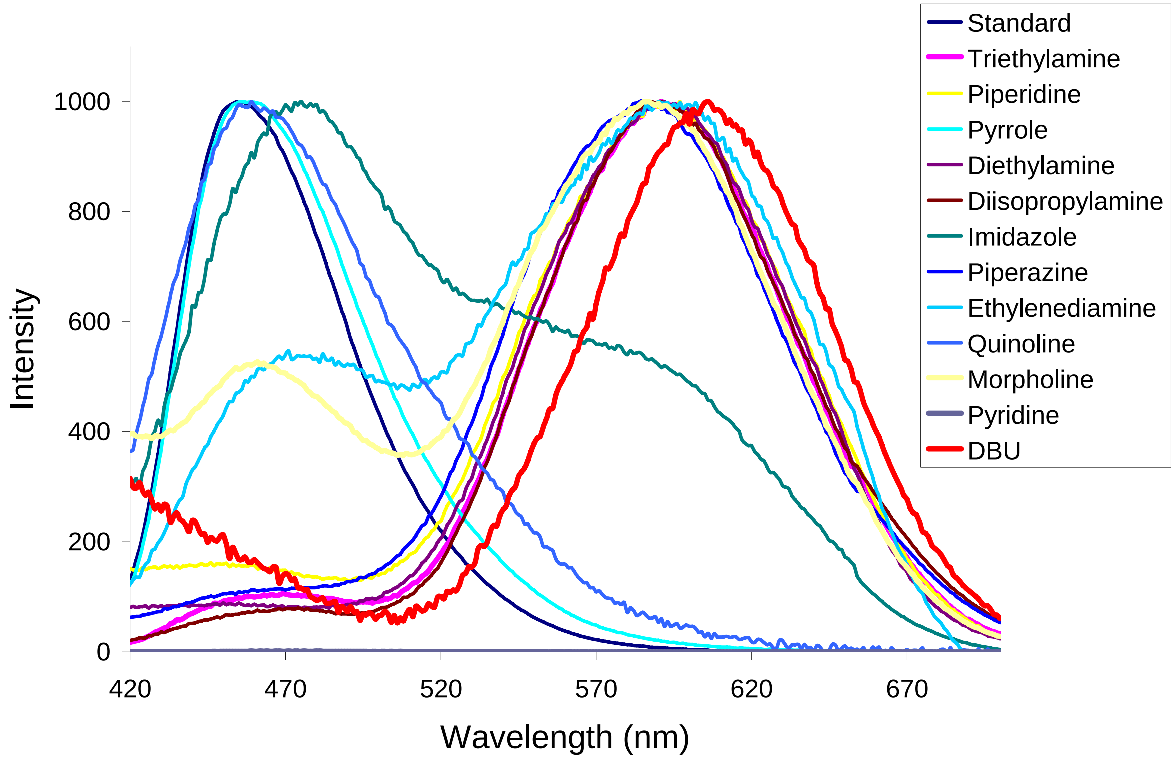


Figure 11. Normalized spectrum of**10** with all amines in dichloromethane**.**

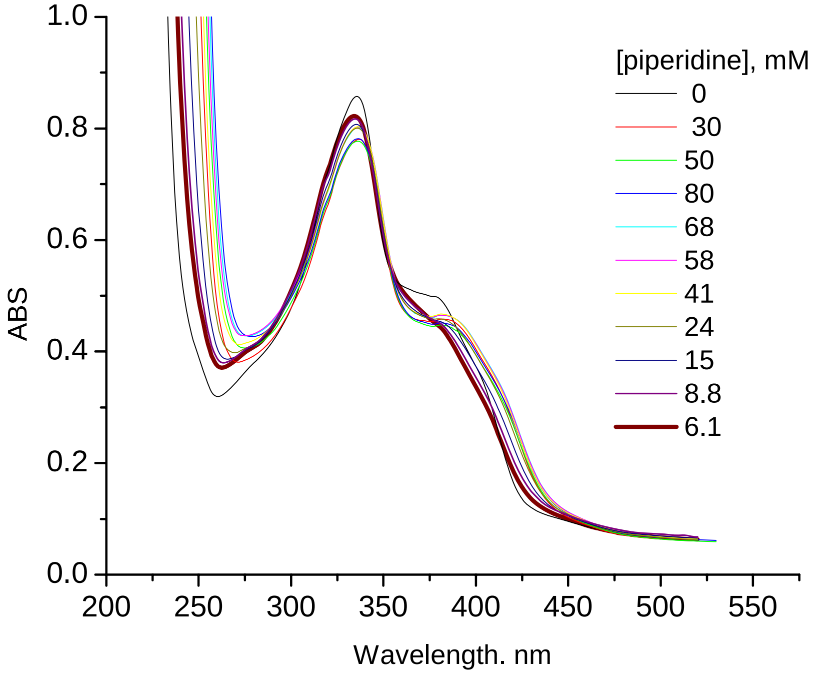


Figure 12. Titration of **7** with piperidine. Absorption spectra**.**

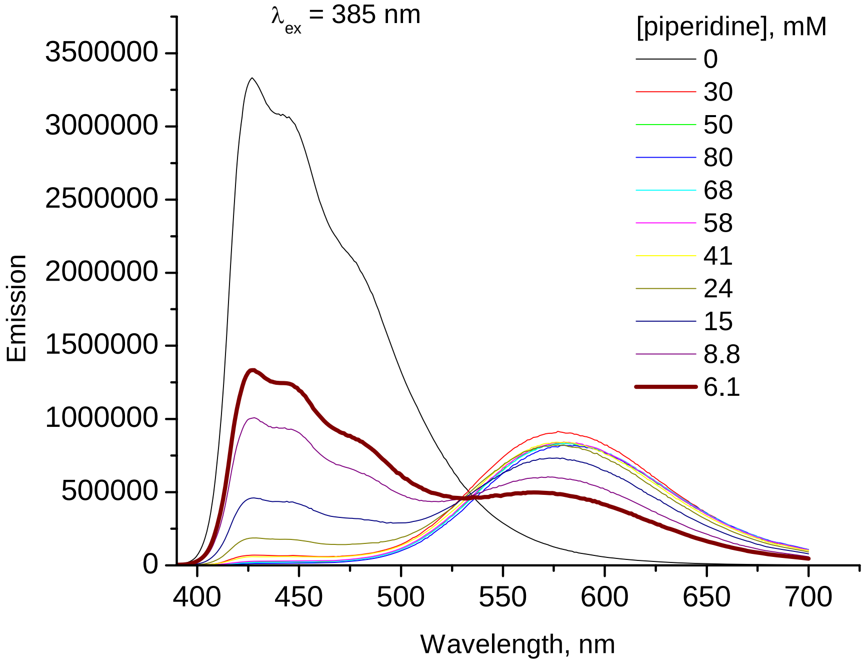


Figure 12. Titration of **7** with piperidine. Emission spectra**.**

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