Supporting Information

for

# $Cu^{2+}$-induced intermolecular *static* excimer formation of pyrenealkylamine

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## 1. Instruments and reagents

All fluorescence and UV-vis absorption spectra were recorded in RF-5301PC and S-3100 spectrophotometer, respectively. NMR and mass spectra were recorded at Varian instrument (200 MHz) and FAB MS mass spectra.

1-Pyrenemethylamine hydrochloride, *p*-toluenesulfonyl chloride, 1-iodopropane and all cationic compounds such as perchlorate of $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$, $Ag^+$, $Cd^{2+}$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$, $Zn^{2+}$, $Hg^{2+}$, $Pb^{2+}$, $Co^{2+}$, $Cu^{2+}$, $Al^{3+}$ were purchased from Aldrich and used as received. All solvents were analytical reagents and from Duksan Pure Chemical Co., ltd. $CH_3CN$ for spectra detection was HPLC reagent without fluorescent impurity and $H_2O$ was deionized water.

## 2. General Procedure for Fluorescence Studies

Fluorescence spectra were recorded with a RF-5301PC spectrofluorophotometer. Stock solutions (1.00 mM) of metal perchlorate salts were prepared in $H_2O/CH_3CN$ (1:1, v/v). Stock solutions of free **1** - **3** (0.060 mM) were prepared in $H_2O/CH_3CN$ (1:1, v/v). Excitations were carried out at 342 nm (for **1** - **3**) with all excitation slit widths is 1.5 nm, that of emission is 3 nm. Titration experiments were performed with 6.0 μM solutions of **1** in $H_2O/CH_3CN$ (1:1, v/v) and various concentrations of metal perchlorates in $H_2O/CH_3CN$ (1:1, v/v). For the Job Plot Experiment, **1** (20.0 μM) in $H_2O/CH_3CN$ (1:1, v/v) and $Cu(ClO_4)_2$ (20.0 μM) in $H_2O/CH_3CN$ (1:1, v/v) were prepared as stock solutions. The concentrations of each $CH_3CN$ solution were varied, but the total volume was fixed at 4.0 mL. After the mixture was shaken, the fluorescence emission at 340 nm was recorded.

## 3. Supplementary spectral data

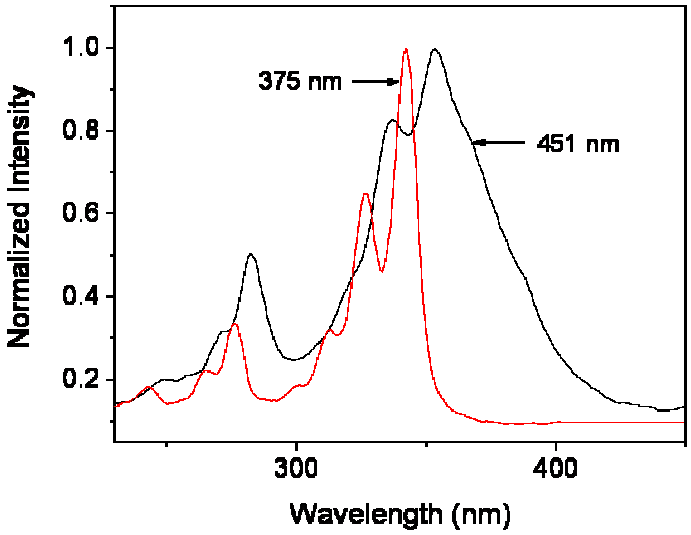



**Figure S1.** Excitation spectra (normalized) of **1** monitored at 375 (red line) and 451 (black line) in the presence of 50 equiv of $Cu(ClO_4)_2$.

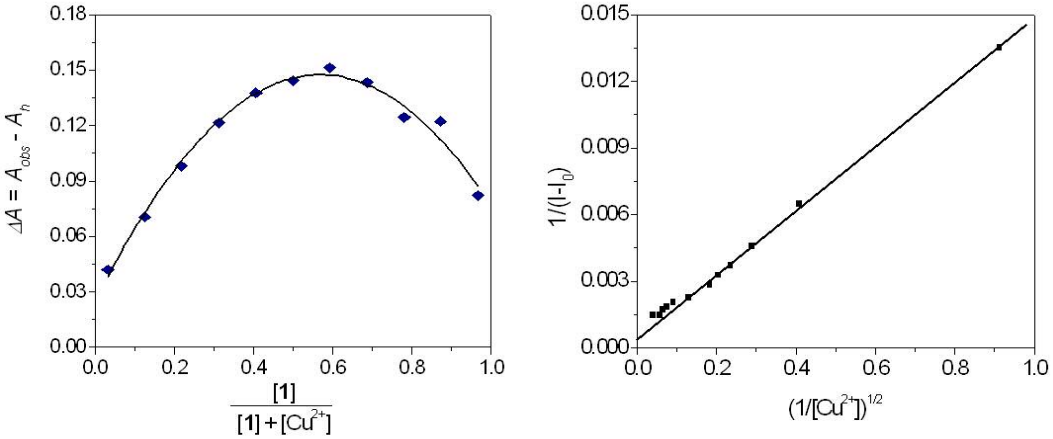



**Figure S2.** (Left) Job plot of a 2:1 complex of **1** and $Cu^{2+}$ion, where the difference in absorbance intensity at 340 nm was plotted against the mole fraction of **1** at an invariant total concentration of 20 μM in $H_2O/CH_3CN$ (1:1, v/v). (Right) Benesi-Hildebrand analysis of the emission changes for the complexation between **1** and $Cu^{2+}$.

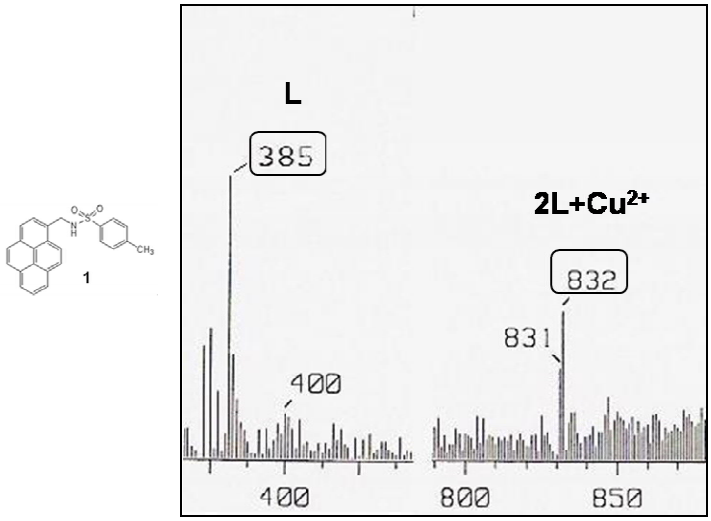



**Figure S3.** Mass spectra of compound **1** (left) and 2(**1**)+$Cu^{2+}$ (right).

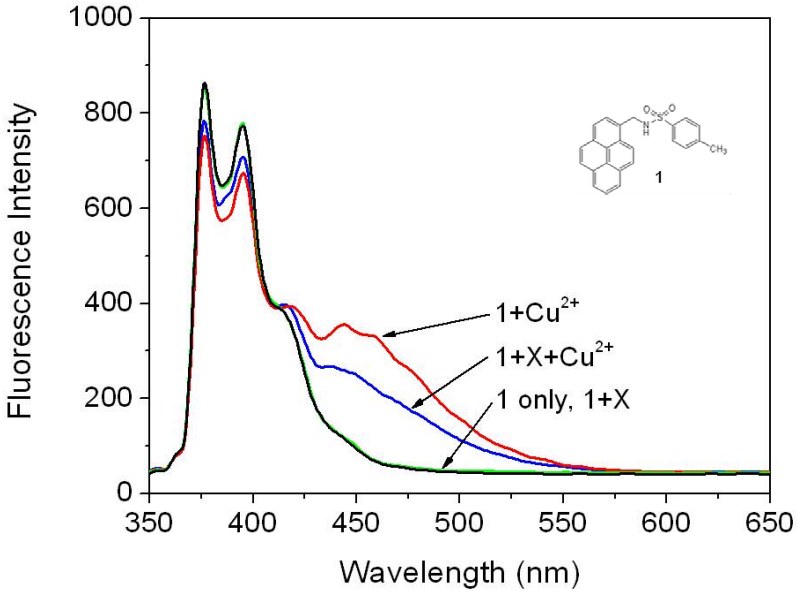



**Figure S4.** Fluorescence spectra of **1** (3.0 μM ) in 1:1 $CH_3OH/H_2O$ (v/v) at pH 7 in the presence of the $Cu^{2+}$ ion and miscellaneous cations including $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$, $Ag^+$, $Cd^{2+}$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$, $Zn^{2+}$, $Hg^{2+}$, $Pb^{2+}$, $Co^{2+}$, and $Al^{3+}$ (10 equiv, respectively, excitation wavelength at 341 nm).

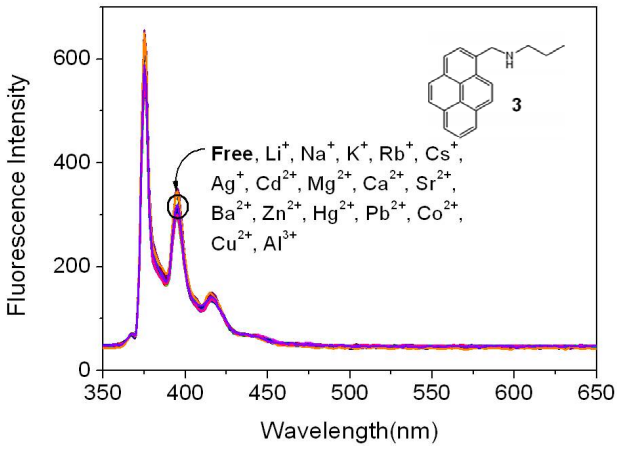



**Figure S5.** Fluorescence spectra of **3** (6.0 μM) with addition of $ClO_4^-$ salts of $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$, $Ag^+$, $Cd^{2+}$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$, $Zn^{2+}$, $Hg^{2+}$, $Pb^{2+}$, $Co^{2+}$, $Cu^{2+}$, and $Al^{3+}$ (100 equiv, respectively) in $H_2O/CH_3CN$ (1:1, v/v) with an excitation at 342 nm.

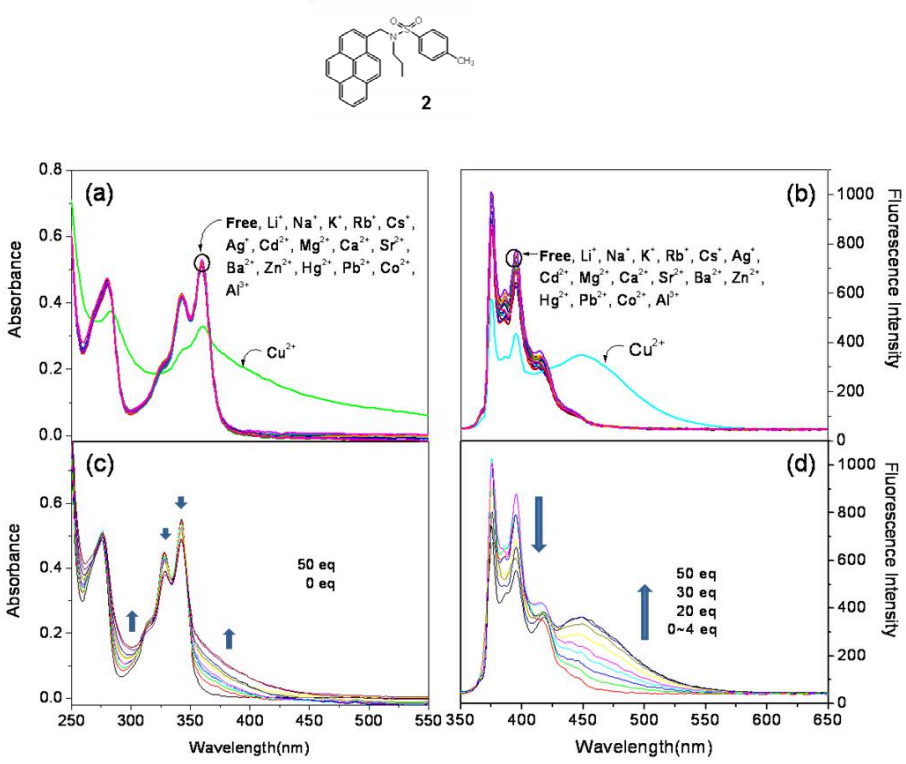



**Figure S6.** (a) Absorption spectra of **2** (20.0 μM) and (b) fluorescence spectra of **2** (6.0 μM) with addition of $ClO_4^-$ salts of $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$, $Ag^+$, $Cd^{2+}$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$, $Zn^{2+}$, $Hg^{2+}$, $Pb^{2+}$, $Co^{2+}$, $Cu^{2+}$, and $Al^{3+}$ (100 equiv, respectively) in $H_2O/CH_3CN$ (1:1, v/v) with an excitation at 342 nm. (c) Absorption titration spectra of **2** (20 μM) and (d) fluorescence titration spectra of **2** (6 μM) with addition of $Cu^{2+}$ in $H_2O/CH_3CN$ (1:1, v/v) with an excitation at 342 nm.

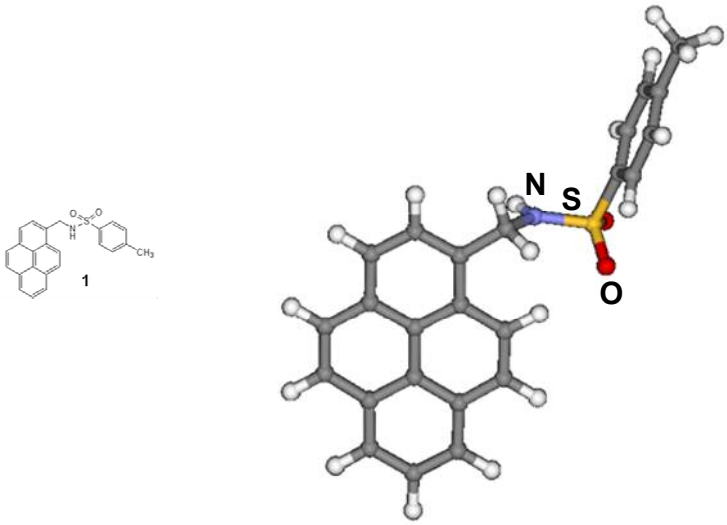



**Figure S7.** B3LYP/3-21G* optimized geometry for **1**.

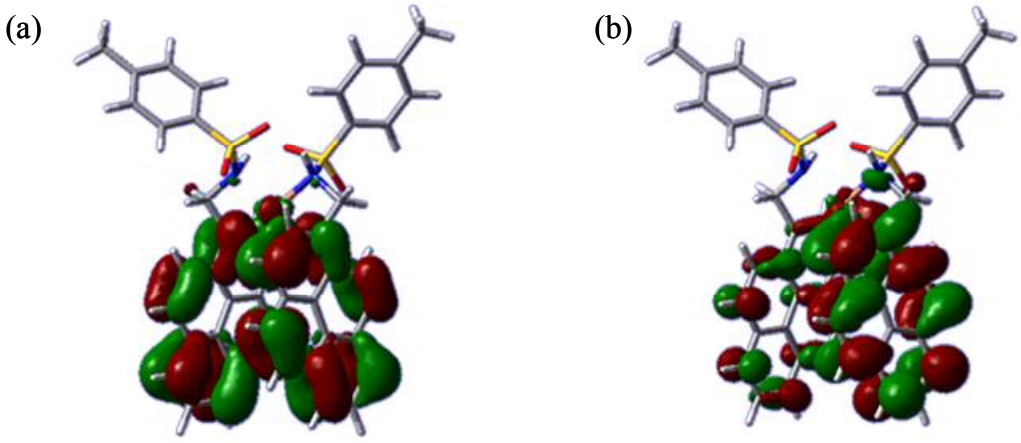



**Figure S8**. HOMO-1 and LUMO+1 for **1**-$Cu^{2+}$ complex.

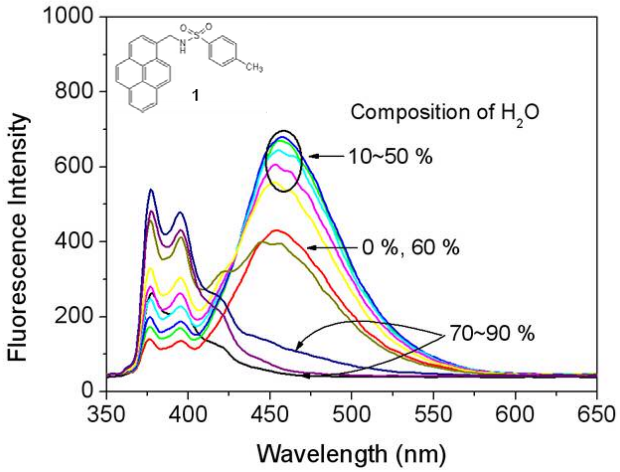



**Figure S9**. Changes in fluorescence intensity of **1**•$Cu^{2+}$ systems as a function of water composition in aqueous acetonitrile. [**1**] = $6.0\times10^{-6}$ M. [$Cu^{2+}$] = $6.0\times10^{-5}$ M as perchlorate salt. $\lambda_{ex}$ = 342 nm.

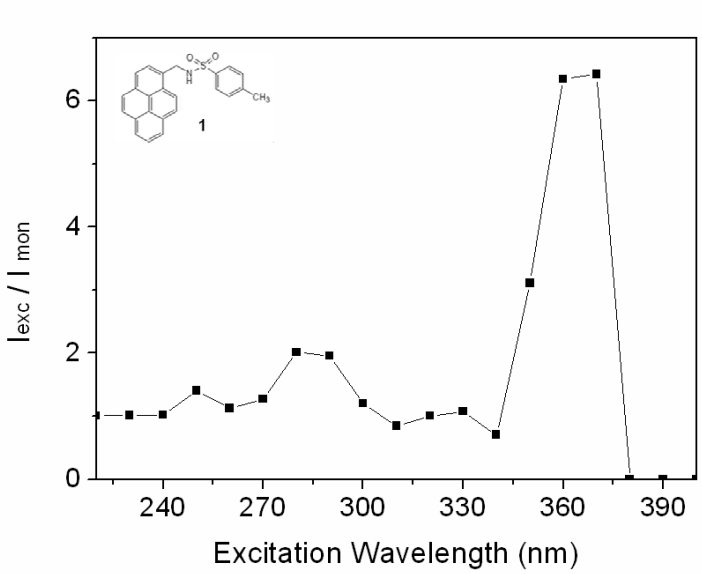



**Figure S10**. Relative intensity of the excimer and monomer emission bands of **1** ($I_{Exc=375\ nm}/I_{Mon=455\ nm}$) as a function of excitation wavelength.

## 4. Experimental Section

### 4-methyl-*N*-(pyren-1-ylmethyl)benzenesulfonamide (1).

A solution of 1-pyrenemethylamine hydrochloride (1.0 g, 3.6 mmol), *p*-toluenesulfonyl chloride (0.68 g, 3.6 mmol), and pyridine in dried $CH_2Cl_2$ (300 mL) was refluxed with stirring for 1 day and then evaporated in vacuo. The resulting solid was dissolved in $CH_2Cl_2$, and the organic layer was washed three times with water, dried over anhydrous $MgSO_4$, and evaporated in vacuo. Crude product was purified by recrystallization from MeOH to give 0.89 g of **1** (pale yellow solid) in 64 % yield. Mp: 175–180 $^oC$. $^1H$ NMR (200 MHz, $CDCl_3$): δ 8.22-7.98 (m, 5 H, Ar*H*, pyrene; 2 H, Ar*H*, tosyl), 7.36-7.32 (d, 1 H, Ar*H*, pyrene), 7.18-7.73 (t, 3 H, Ar*H*, pyrene), 4.82-4.76 (s, 4 H, ArC$H_2$NH), 2.44-2.34 (d, 3 H, benzene-C$H_3$, *J*= 7.26 Hz). $^{13}C$ NMR (50 MHz, $CDCl_3$): 143.4, 139.9, 136.4, 131.4, 130.5, 129.5, 128.5, 128.1, 127.7, 127.1, 126.1, 125.5, 124.5, 122.4, 45.6, 28.7, 21.4 ppm. FAB MS *m/z* ($M^+$): calcd, 385.48. Found, 386.28. Anal. Calcd for $C_{24}H_{19}NO_2S$: C, 74.78; H, 4.97. Found: C, 74.77; H, 4.99.

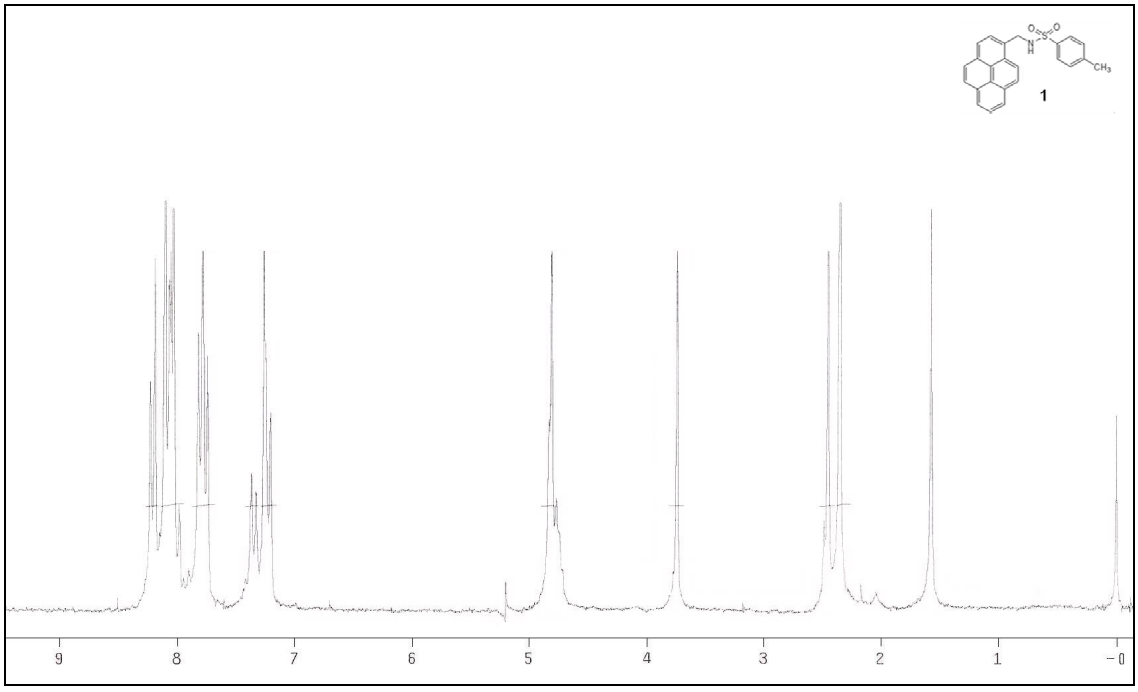
### 4-methyl-*N*-propyl-*N*-(pyren-1-ylmethyl)benzenesulfonamide (2).

Under nitrogen, a mixture of **1** (0.5 g, 1.29 mmol), 1-iodopropane (0.127 mL , 1.29 mmol), and $Cs_2CO_3$ (0.75 g, 1.29 mmol) in MeCN (100 mL) was refluxed for 24 h and the solvent was removed *in vacuo*. To the resulting white solid, 5% aqueous HCl solution (100 mL) and $CH_2Cl_2$ (50 mL) were added, and the organic layer was separated and washed with water (3 X 50 mL). The organic layer was dried over $MgSO_4$ and the solvent was evaporated *in vacuo* to give a white solid. Recrystallization from $CH_2Cl_2$–diethyl ether (1:9) gave 0.35 g (63%) of **2** as a yellow solid. Mp: 205–210 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.51-7.78 (m, 9 H, Ar*H*, pyrene; 2 H, Ar*H*, tosyl), 7.31-7.27 (d, 2 H, Ar*H*, tosyl), 4.92 (s, 2 H, ArC$H_2$NH), 3.04-2.96 (t, 2 H, NHC$H_2$CH$_2$, *J* = 7.60 Hz), 1.08-1.04 (m, 2 H, NHCH$_2$C$H_2$CH$_3$), 0.47-0.40 (t, 3 H, CH$_2$CH$_2$C$H_3$, *J* = 7.4 & 7.6 Hz). $^{13}C$ NMR (50 MHz, $CDCl_3$): 143.2, 136.1, 131.2, 131.0, 129.6, 128.8, 127.5, 127.2, 125.9, 125.2, 124.4, 123.0, 51.0, 50.0, 21.6, 21.4, 10.9 ppm. FAB MS *m/z* ($M^+$): Calcd, 427.56. Found, 428.12. Anal. Calcd for $C_{27}H_{25}NO_2S$: C, 75.85; H, 5.89. Found: C, 75.82; H, 5.88.

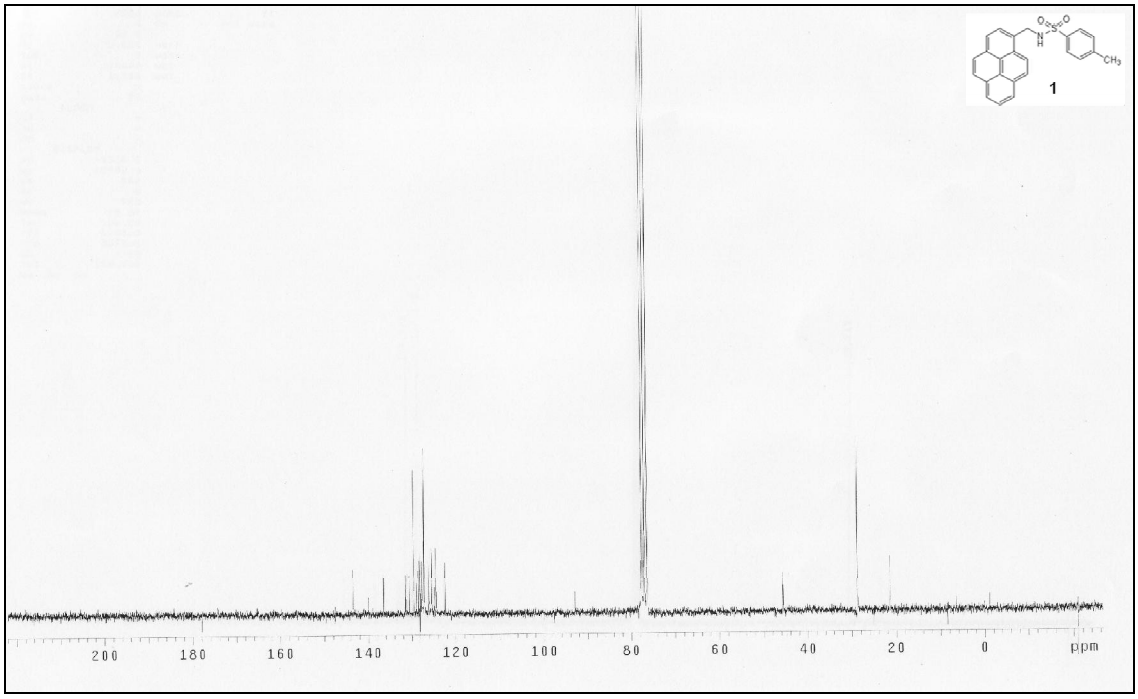
***N*-(pyren-1-ylmethyl)propan-1-amine (3).**

To a solution of 1-pyrenemethylamine hydrochloride (0.5 g, 0.17 mmol) in dried $CHCl_3$, 1-iodopropane (0.174 mL, 0.17 mmol) was added. The reaction mixture was stirred for 30 min, and then triethylamine (0.247 mL, 0.17 mmol) was added. The reaction mixture was stirred for an additional 12 h. The solution was washed with water, and the organic layer was dried over anhydrous $MgSO_4$. Removal of the organic solvent *in vacuo* afforded a reddish solid. Column chromatography on silica gel with EtOAc-hexane (1:3) as eluents gave 0.3 g (61 %) of **3**. Mp: 185–190 $^{o}$C. $^{1}$H NMR (200 MHz, $CDCl_3$): δ 8.31-7.92 (m, 9 H, Ar*H*, pyrene), 4.40 (s, 2 H, ArC$H_2$NH), 2.74-2.70 (t, 2 H, NHC$H_2$CH$_2$, $J$ = 7.60 Hz), 1.61-1.15 (m, 2 H, NHCH$_2$C$H_2$CH$_3$), 0.95-0.87 (t, 3 H, CH$_2$CH$_2$C$H_3$, $J$ = 7.4 & 7.6 Hz). $^{13}$C NMR (200 MHz, $CDCl_3$): 133.8, 131.1, 130.7, 127.4, 126.8, 125.7, 124.8, 124.7, 123.0, 51.7, 51.6, 23.1, 11.7 ppm. FAB MS *m/z* ($M^+$): calcd, 273.37. Found, 273.00. Anal. Calcd for $C_{20}H_{19}N$: C, 87.87; H, 7.01. Found: C, 87.80; H, 7.07.

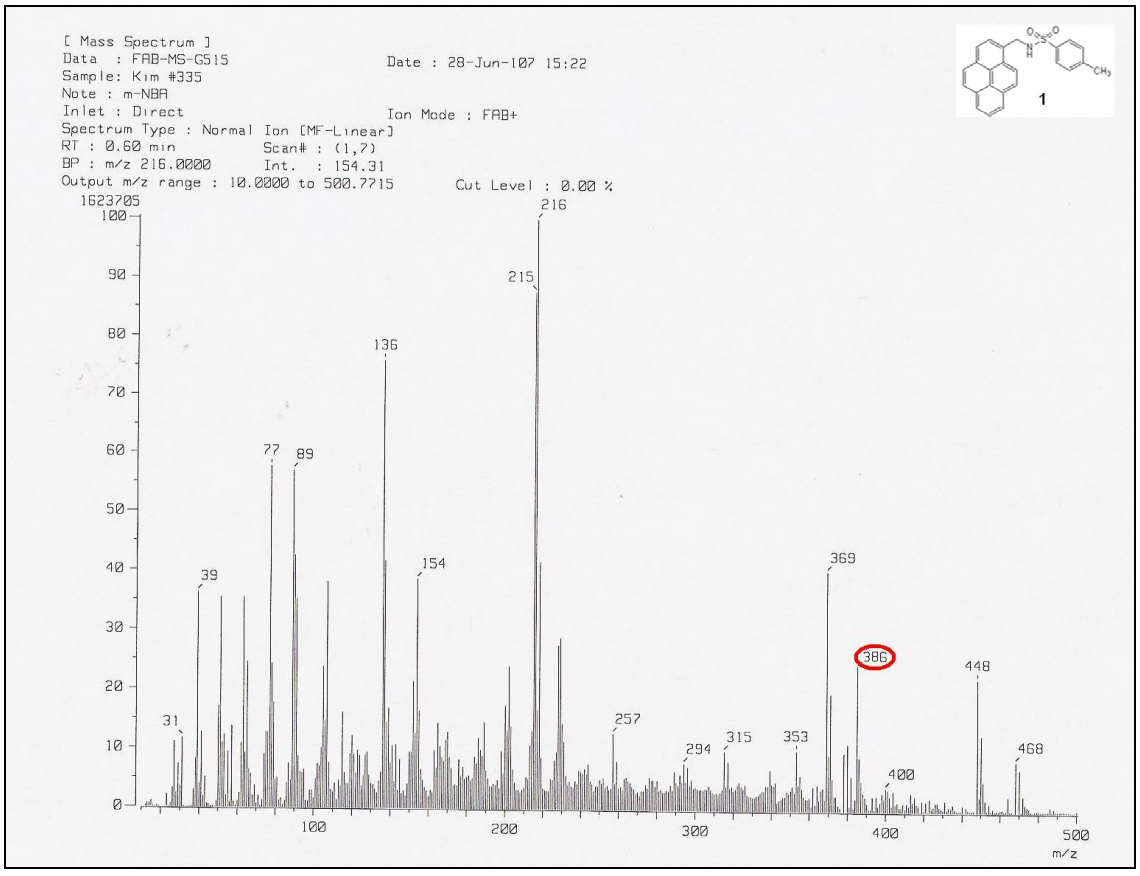
## 5. NMR copies of 1- 3



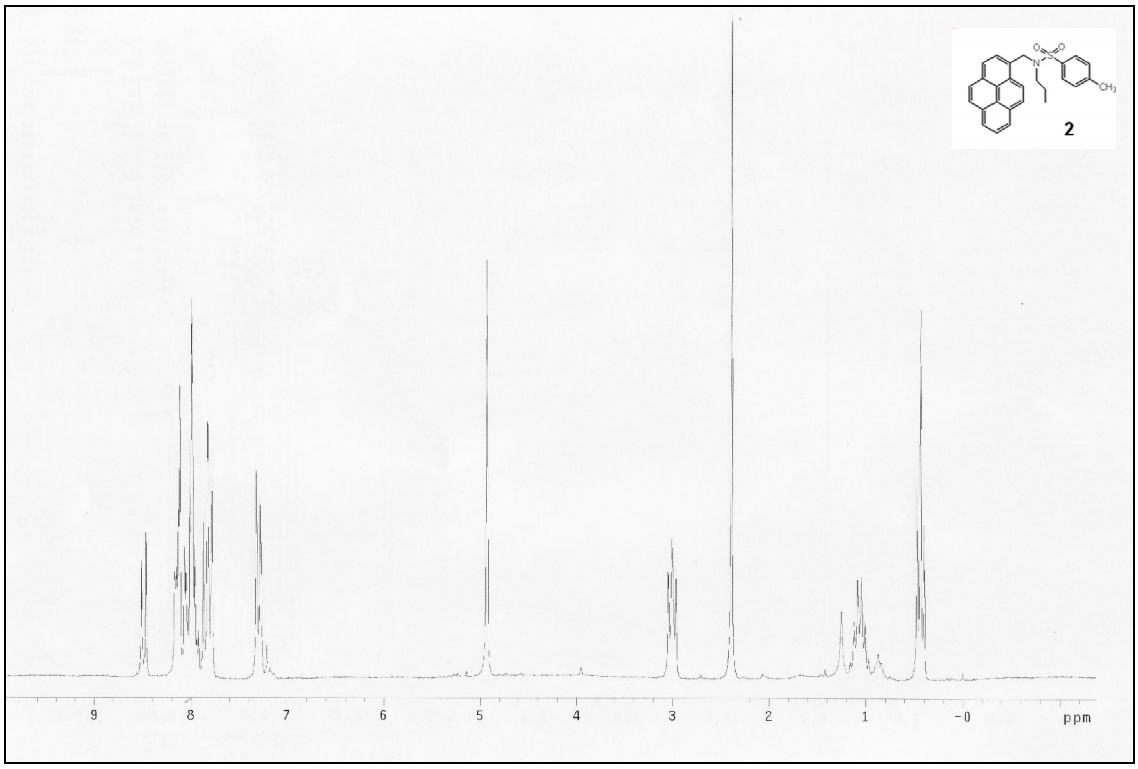

$^{1}$H NMR ($CDCl_3$, 200 MHz) spectrum of **1**.



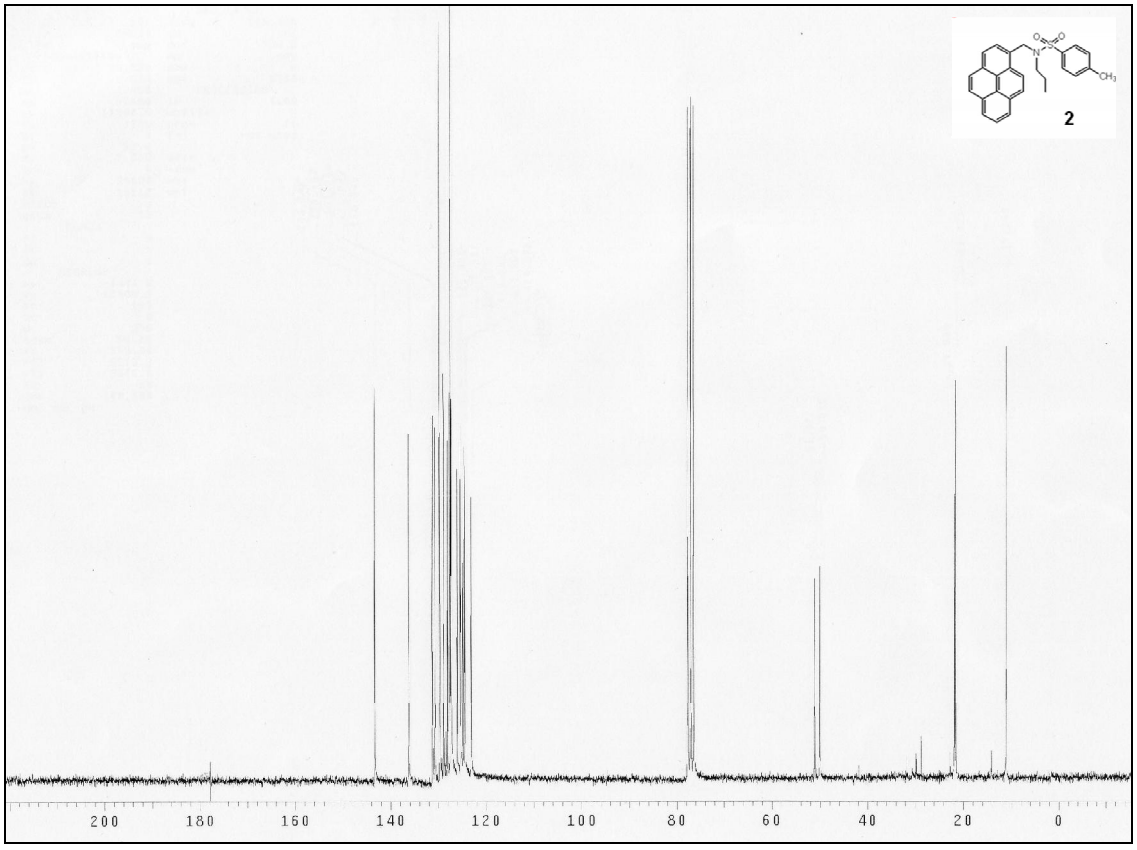

$^{13}C$ ($CDCl_3$, 50 MHz) spectrum of **1**.



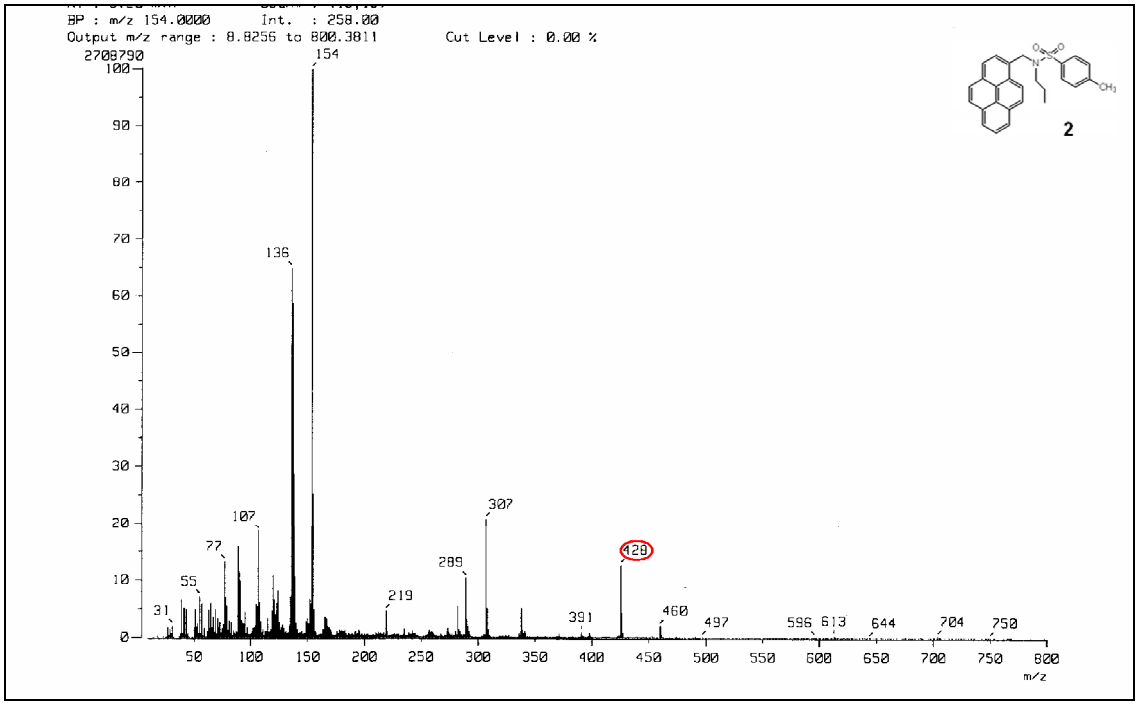

FAB-Mass spectrum of **1**.




$^{1}$H NMR ($CDCl_3$, 200 MHz) spectrum of **2**.




$^{13}$C NMR ($CDCl_3$, 50 MHz) spectrum of **2**.

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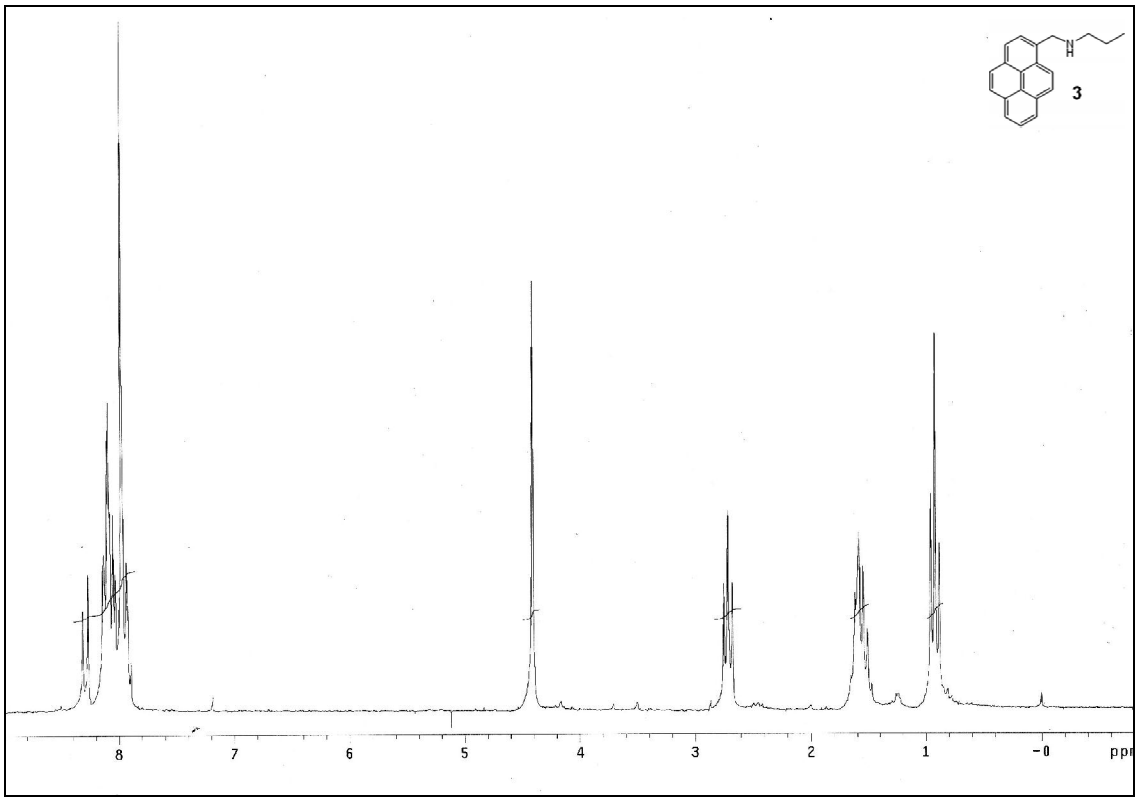
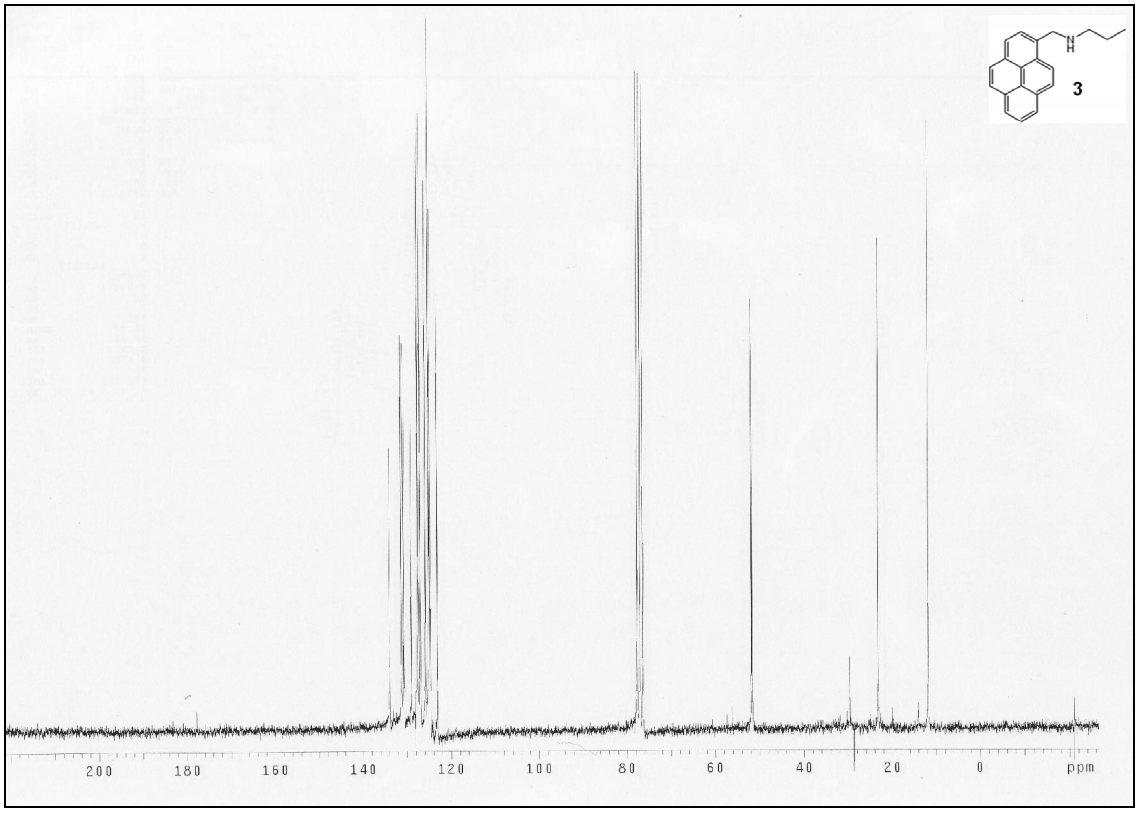
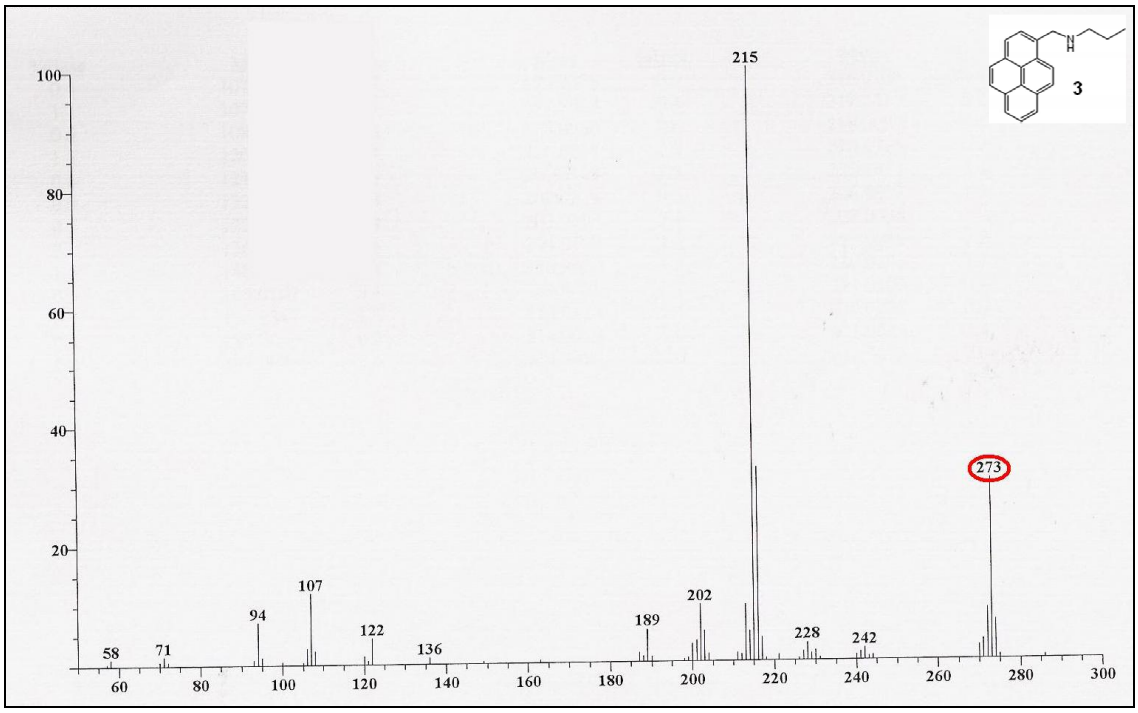



$^{1}$H NMR ($CDCl_3$, 200 MHz) spectrum of **3**.




$^{13}C$ NMR ($CDCl_3$, 50 MHz) spectrum of **3**.




FAB-Mass spectrum of **3**.

**Full author list of Ref. 17:**

Gaussian 03, revision C.02: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K.; Burant, J. C.; Millam, J. M.; Iyengay, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Comperts, R.; Startmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenbuerg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chem, W.; Wong, M. W., Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Wallingford CT, 2004.