Supporting Information

Cobalt-Catalyzed Intermolecular C-H Amination with Bromamine-T as Nitrene Source

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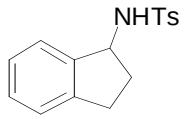
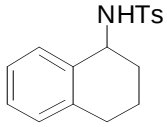
General Considerations. All reactions were carried out under nitrogen atmosphere in an oven dried Schlenk tube. All alkanes were purchased from Acros or Aldrich Chemicals and used without further purification. Acetonitrile and methylene chloride were dried by refluxing over calcium hydride. Toluene and tetrahydrofuran were dried by refluxing over sodium benzophenone. Metalloporphyrins were purchased from Strem or Midcentury Chemicals. Bromamine-T was prepared from Chloramine-T according to the literature procedure and dried at 80 $^{\circ}$C in vacuum overnight before use.[1] Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Varian Mercury 300 or Varian Inova400 spectrometer and referenced with respect to residual solvent. Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory. HRMS data was obtained on an Agilent 1100 LC/MS ESI/TOF mass spectrometer with electrospray ionization. Thin layer chromatography was carried out on E. Merck Silica Gel 60 F-254 TLC plates.

General Procedure for Amination. An oven dried Schlenk tube equipped with a stirring bar was degassed on vacuum line and purged with nitrogen. The tube was charged with metalloporphyrin (5 mol %), Bromamine-T (0.2 mmol) and activated 5 Å molecular sieves (200 mg). The tube was capped with a Teflon screw cap and evacuated on vacuum line for 30-45 min. The Teflon screw cap was replaced with a rubber septum and 0.5 mL of solvent and substrate (2 mmol) followed by the remaining solvent (total 2 mL) were then added successively. The tube was purged with nitrogen for 1-2 min and the contents were stirred overnight at ambient temperatures. After completion of the reaction, molecular sieves were removed by filtration and the filtrate was concentrated under vacuum. The residue was purified by flash chromatography, and the fractions containing product were collected and concentrated by rotary evaporation to afford the pure compound.

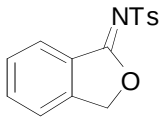


N-(p-Toluenesulfonyl)-1-aminoindan (Entry 1, Table 2)[1-5] was synthesized using indan as the substrate and the product was obtained as a tan-white solid (42.1 mg, 72.8%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.07-7.22 (m, 4H), 4.84 (dd, J_1 = 7.5 Hz, J_2 = 15.9 Hz, 1H), 4.71 (d, J = 8.7 Hz, 1H), 2.85-2.97 (m, 1H), 2.67-2.78 (m, 1H), 2.45 (s, 3H), 2.28-2.39 (m, 1H), 1.68-1.81

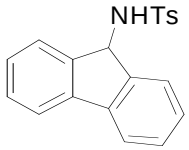
(m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.43, 142.79, 141.96, 138.16, 129.75, 128.24, 127.10, 126.81, 124.76, 124.06, 58.68, 34.66, 29.92, 21.53. IR (neat, cm^{-1}): 3257 (N-H), 1158 (S=O). HRMS (ESI): Calcd. for $C_{16}H_{21}N_2O_2S$ ($[M+NH_4]^+$) m/z 305.13183, Found 305.13292.



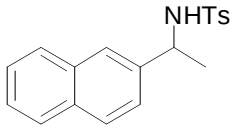
N-(p-Toluenesulfonyl)-1-amino-1,2,3,4-tetrahydronaphthalene (Entry 2, Table 2)[1,2,4-6] was synthesized using 1,2,3,4-tetrahydronaphthalene as the substrate and the product was obtained as a tan-white solid (40.1 mg, 66%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.12 (m, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 4.62 (d, *J* = 7.8 Hz, 1H), 4.44 (m, 1H), 2.71 (m, 2H), 2.46 (s, 3H), 1.72-1.86 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.40, 137.55, 135.57, 129.76, 129.21, 128.76, 127.64, 127.14, 126.30, 51.89, 30.75, 28.86, 21.56, 19.08. IR (neat, cm^{-1}) 3258 (N-H), 1153 (S=O). HRMS (ESI): Calcd. for $C_{17}H_{19}NO_2SNa$ ($[M+Na]^+$) m/z 324.10287, Found 324.10191.



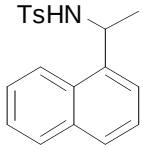
N-(isobenzofuran-1(3H)-ylidene)-4-methylbenzenesulfonamide (Entry 3, Table 2) was synthesized using phthalan as the substrate and the product was recovered as a dark tan solid (29.1 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 7.2 Hz, 1H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.53-7.46 (m, 2H), 7.31 (d, *J* = 7.6 Hz, 1H), 5.59 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.51, 129.39, 129.25, 127.52, 125.66, 121.42, 76.25, 29.68. IR (neat, cm^{-1}): 1634 (C=N), 1297 (C-O), 1152 (S=O). HRMS (ESI): Calcd. for $C_{15}H_{14}NO_3S$ ($[M+H]^+$) m/z 288.06889, Found 288.06848.



N-(p-Toluenesulfonyl)-1-aminofluorene.(Entry 4, Table 2)[7] was synthesized using fluorene as the substrate and the product was recovered as a dark tan solid (9.4 mg, 14%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.36 (m, 2H), 7.23 (m, 4H), 5.41 (d, *J* = 9.6 Hz, 1H), 4.75 (d, *J* = 9.3 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 144.06, 143.55, 138.60, 130.22, 129.24, 128.11, 127.58, 125.43, 120.19, 58.62, 21.89. IR (neat, cm^{-1}): 3303 (N-H), 1155 (S=O). HRMS (ESI): Calcd. for $C_{20}H_{21}N_2O_2S$ ($[M+NH_4]^+$) m/z 353.13183, Found 353.13296.



N-(p-Toluenesulfonyl)-1-amino-2-ethylnaphthalene (Entry 5, Table 2)[1,3,5,8,9] was synthesized using 2-ethylnaphthalene as the substrate and the product was recovered as a dark tan solid (22.1 mg, 34%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (t, J_1 = 6 Hz, J_2 = 3.3 Hz, 1H), 7.66 (d, J = 8.7 Hz, 2H), 7.57 (d, J = 10 Hz, 2H), 7.41-7.47 (m, 3H), 7.20 (d, J = 8.7 Hz, 1H), 7.03 (d, J = 8.4 Hz, 2H), 4.92 (d, J = 7.2 Hz, 1H), 4.64 (dt, J_1 = 13.5 Hz, J_2 = 6.6 Hz, 1H), 2.25 (s, 3H), 1.51 (d, J = 6.6 Hz, 3H). ^{13}NMR (75 MHz, $CDCl_3$): δ 143.11, 138.98, 137.50, 133.03, 132.67, 129.28, 128.44, 127.49, 127.06, 126.17, 125.96, 125.03, 124.03, 53.78, 23.44, 21.31. IR (neat, cm^{-1}): 3267 (N-H), 1155 (S=O). HRMS (ESI): Calcd. for $C_{19}H_{23}N_2O_2S$ ($[M+NH_4]^+$) m/z 343.14748, Found 343.14775.



N-(p-Toluenesulfonyl)-1-amino-1-ethylnaphthalene (Entry 6, Table 2)[5,10] was synthesized using 1-ethylnaphthalene as the substrate and the product was recovered as a dark tan solid (21.4 mg, 33%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, J = 7.2 Hz, 1H), 7.80 (d, J = 6 Hz, 1H), 7.60 (d, J = 8.1 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.44 (m, 2H), 7.35 (m, 2H), 7.07 (d, J =8.1 Hz, 2H), 5.28 (dt, J_1 = 13.5 Hz, J_2 = 6.6 Hz, 1H), 5.0 (d, J = 6.9 Hz, 1H), 2.33 (s, 3H), 1.59 (d, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.07, 137.56, 137.38, 133.77, 130.10, 129.26, 128.82, 128.14, 127.04, 126.27, 125.63, 125.21, 123.33, 122.59, 49.76, 23.20, 21.40. IR (neat, cm^{-1}): 3268 (N-H), 1155 (S=O). HRMS (ESI): Calcd. for $C_{19}H_{23}N_2O_2S$ ($[M+NH_4]^+$) m/z 343.14748, Found 343.14831.

References

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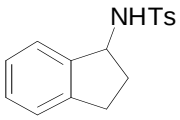
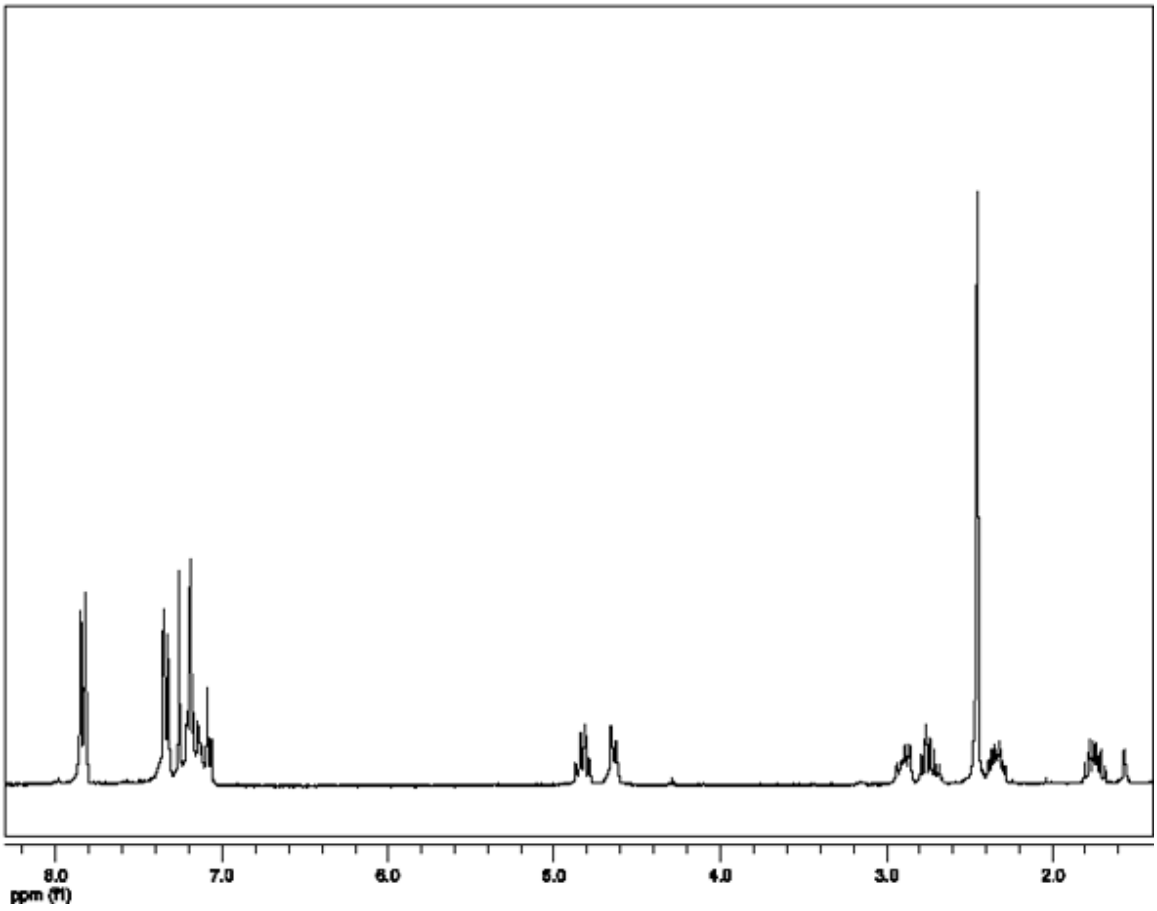
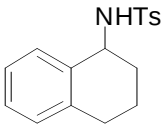
(10) Che, Chi-Ming; Huang, Jie-Sheng; Yu, Xiao-Qi; Zhou, Xiang-Ge. *Chem. Comm.* **1999**, 2377-2378.

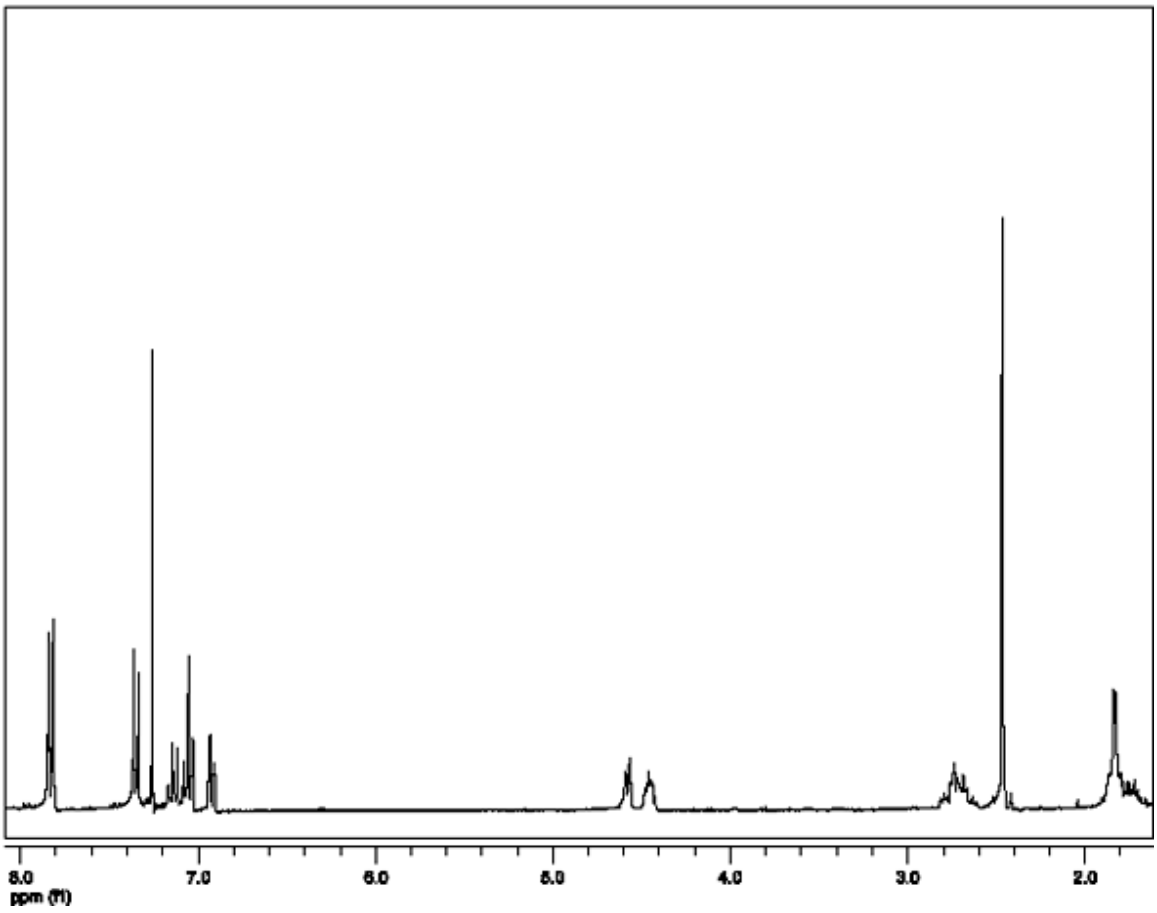


N-(p-Toluenesulfonyl)-1-aminoindan
Proton

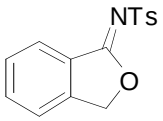


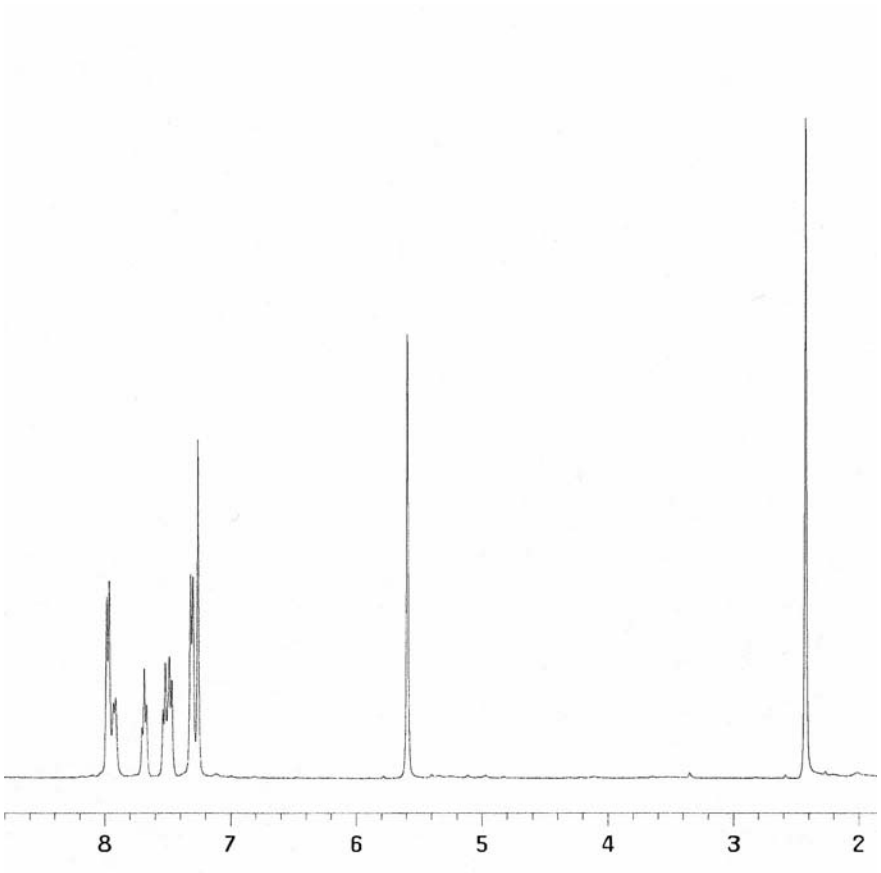


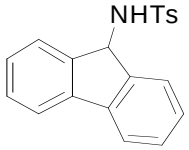
N-(p-Toluenesulfonyl)-1-amino-1,2,3,4 tetrahydronaphthalene



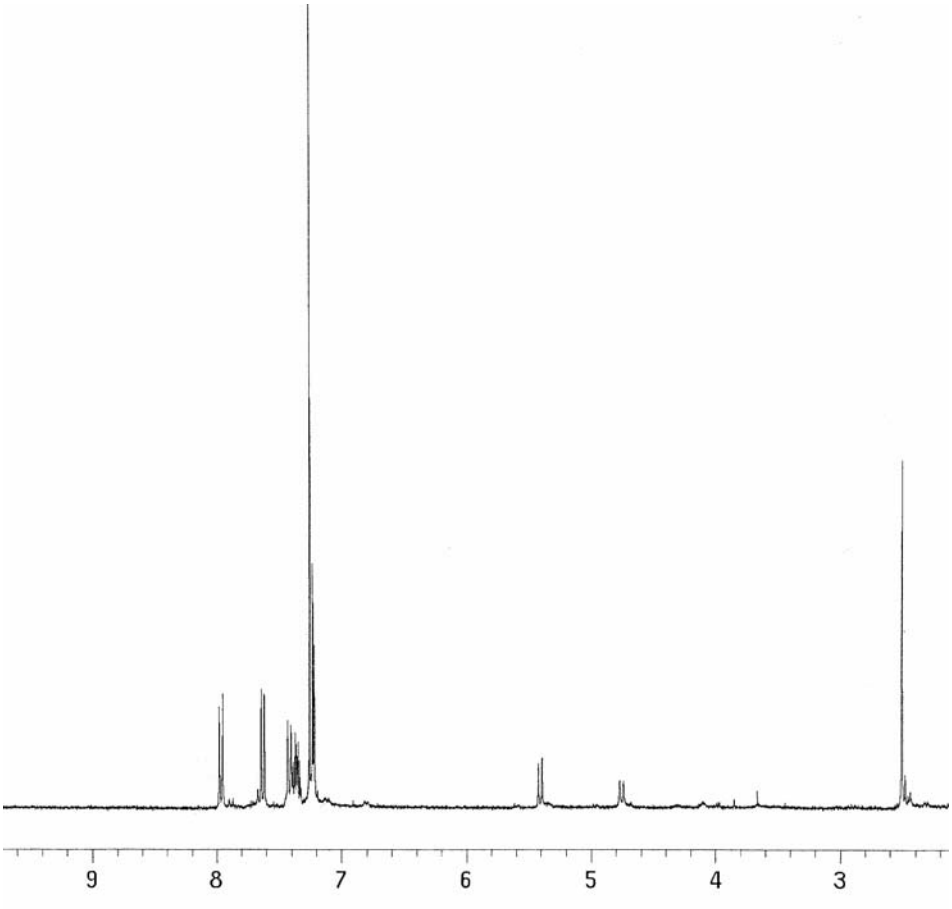
N-(isobenzofuran-1(3H)-ylidene)-4-methylbenzenesulfonamide



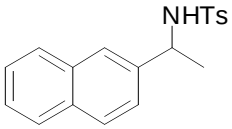


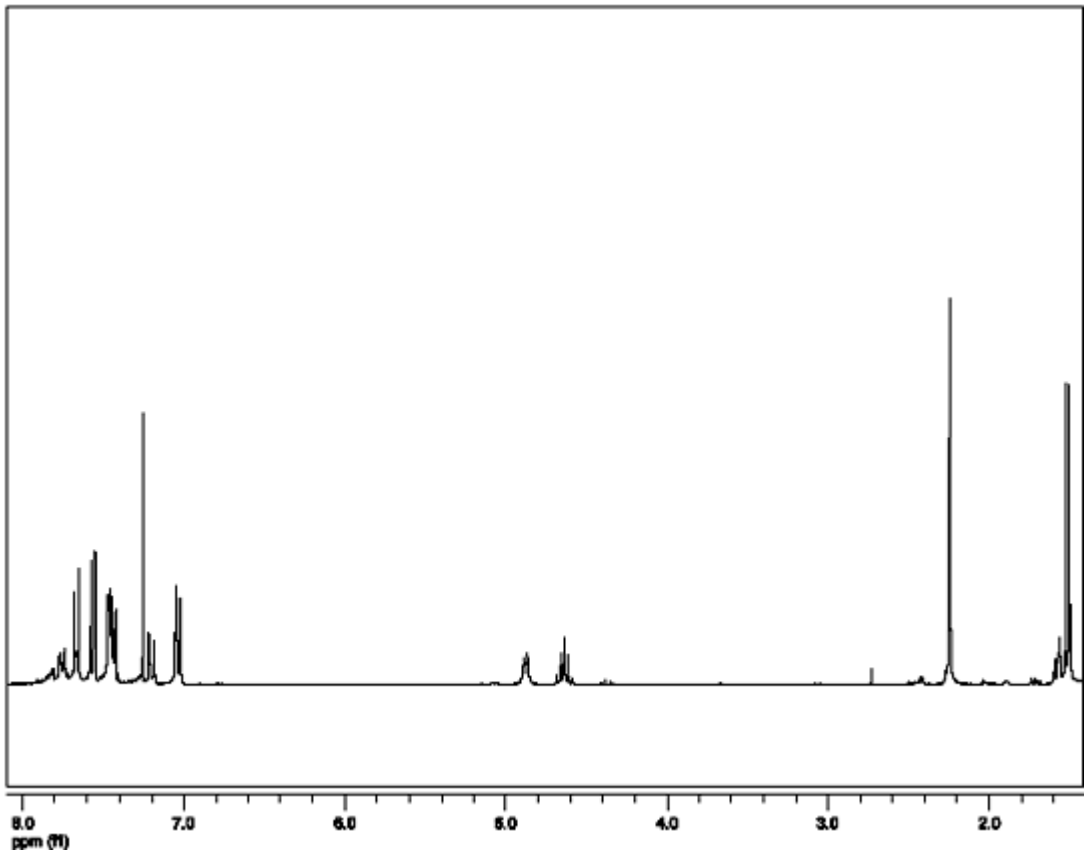


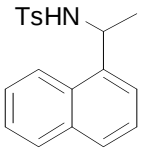
N-(p-Toluenesulfonyl)-1-aminofluorene



N-(p-Toluenesulfonyl)-1-amino-2-ethylnaphthalene







N-(p-Toluenesulfonyl)-1-amino-1-ethylnaphthalene