Aromatic Annulation Strategy for Naphthalenes Fused at 1,2- and 3,4-Positions with Two Heterocycles

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Supplementary Data

General experimental procedures

Melting points are uncorrected. ^{1}HNMR were recorded on a Bruker DPX 300 at 300MHZ with $CDCl_3$ as solvent. Chemical shifts are reported in δ (ppm). *J* values are given in Hz. Infrared spectra were taken with a Shimadzu IR 440 spectrometer in KBr pellets. Mass spectra were recorded with a VG ZAB-HS spectrometer. Elemental analyses were done on a Perkin-Elmer-240C analyzer. UV spectra were recorded with a Shimadzu UV-2401PC UV-VIS recording spectrophotometer. Fluorescence spectra were done on a SLM Aminco Bowman Series 2 Luminescence Spectrometer. Benzene (A R grade) was dried with sodium and distilled before use.

Preparative photolysis for *N*-methyl-3, 4-dichloromaleimide (1) and 3, 4-dichlorocoumarin (2)

The light source was a medium-pressure mercury lamp (500W) in a glass cooling water jacket. The solution of *N*-methyl-3, 4-dichloromaleimide (**1**) or 3, 4-dichlorocoumarin (**2**) (0.05M) and an excess amount of phenylbenzofuran and phenylbenzothiophene (**3a**-**3d**) in benzene was purged with dry nitrogen for 30 min and then irradiated with light of λ> 300nm under continuous nitrogen purging. The reaction course was monitored by TLC. After the photolysis, the solvent was removed *in vacuo* and the residue was separated by flash chromatography on a silica gel column with petroleum ether (b. p. 60-90°C)-ethyl acetate as eluents.

Photolysis of 1 with 2-phenylbenzofuran (**3a**): A solution of **1** (540 mg, 3.0 mmol) and **3a** (756 mg, 3.9 mmol) in benzene (60 ml) was photolyzed for 21h to reach a complete conversion of **1**. Work-up as described above gave **4a** (73.4%) and **5a** (24.2%).

Heating **4a** (200mg) on silica gel (2g) at 100℃ for 12h, a 98% conversion of **4a** was reached. Separation of the reaction mixture by flash chromatography on a silica gel gave **5a** (1.2%) and **6a** (93.9%). Irradiating a solution of **6a** (50mg) in acetone (20ml) with light of λ> 400nm under continuous nitrogen purging for 10h resulted in a complete conversion of **6a** and gave **5a** (96.1%).

If the mixture of **5a** and **6a** obtained by heating **4a** on silica was not separated but was dissolved in acetone and irradiated with light of λ> 400nm under continuous nitrogen purging for 10h to reach a complete conversion of **4a**, this gave **5a** (92.2%). The total yield of **5a** in photoreaction and in subsequent conversion of **4a** was 94.2%

4a

MP 160-161℃

^{1}H-NMR (300 MHz; $CDCl_3$) δ 2.83(3H, s, NCH_3), 4.97(1H, s), 7.05(1H, d, *J* = 8.2), 7.11(1H, dd, J_1=7.5, J_2= 0.8), 7.35(1H, d, *J*=7.9), 7.38-7.46(6H, m)

IR (KBr) ν 3066, 2963, 1795, 1726, 1594, 1479, 1457, 1427, 1370, 1279, 1237, 1007, 971, 779, 742, 699cm^{-1}

MS *m/z* (%) 337(M^+-HCl, 35.31), 302(M^+-2Cl, 9.08), 245(33.84), 217(20.82), 194(Base), 189(27.67), 165(16.12), 151(4.06), 44(5.41)

EA Found: C, 60.81; H, 3.34; N, 3.56. $C_{19}H_{13}Cl_2N_1O_3$ requires C, 60.98; H, 3.50; N 3.74.

5a

MP 244-245°C

^{1}H-NMR (300 MHz; $CDCl_3$) δ 3.31(3H, s, NCH_3), 7.53(1H, t, *J*=7.5), 7.62(1H, td, J_1=7.8, J_2=1.2), 7.73-8.82 (3H, m), 8.51(1H, m), 8.80(1H, d, *J*=8.1), 9.09(1H, m)

IR (KBr) ν 3071, 2924, 1756, 1699, 1600, 1572, 1458, 1373, 1350, 1286, 1191, 1102, 990, 753cm^{-1}

MS m/z (%) 301(M, base), 257(13.09), 216(37.48), 187(16.16), 151(4.16), 108(5.13)

EA Found: C, 75.84; H, 3.41; N, 4.68. $C_{19}H_{11}N_1O_3$ requires C, 75.74; H, 3.68; N, 4.65.

UV (nm) (log ε): 397(3.85), 292(4.50)

6a

MP 164-165℃

^{1}H-NMR (300 MHz; $CDCl_3$) δ 3.20(3H, s, NCH_3), 7.32(1H, d, *J*=7.3), 7.39(1H, d, *J*=7.7), 7.44-7.48(3H, m), 7.53(1H, d, *J*=7.7), 7.61(1H, d, *J*=7.8), 7.68-7.70(2H, m)

IR (KBr) ν 1781, 1720, 1650, 1442, 1386, 1224, 1141, 988, 830, 775, 688cm^{-1}

MS *m/z* (%) 339(M^++2, 26.46), 337(M^+, 77.23), 302(M^+-Cl, 14.71), 301(M^+-HCl, 11.26), 245(Base), 217(53.64), 189(47.52), 163 (7.62), 95(14.87), 77(7.55)

EA Found: C, 67.57; H, 3.41; N, 4.08. $C_{19}H_{12}N_1O_3Cl$ requires C, 67.66; H, 3.56; N, 4.15.

Photolysis of 1 with 3-phenylbenzofuran (**3b**): A solution of **1** (540 mg, 3 mmol) and **3b** (756 g, 3.9 mmol) in benzene (60 ml) was photolyzed for 48h to reach a 63.3% conversion of **1**. Work-up as described above gave **4b** (86.8%) and **5b** (5.84%).

Heating **4b** (200mg) on silica gel (2g) at 90℃ for 12h, a complete conversion was reached and this gave the only product **6b** (95.9%). Irradiating a solution of **6b** (100mg) in acetone (20ml) for 18h with light of λ> 400nm under continuous nitrogen purging resulted in a complete conversion of **6b** and gave **5b** (98.9%).

If **6b** obtained by heating **4b** on silica was not separated but was dissolved in acetone and irradiated with light of λ> 400nm under continuous nitrogen purging for 18h to reach a complete conversion of **4b**, this gave **5b** (97.2%). The total yield of **5b** in photoreaction and in subsequent conversion of **4b** was 90.0%.

4b

MP 193-194℃

^{1}H-NMR (300 MHz; $CDCl_3$) δ 3.01(3H, s, NCH_3), 5.58(1H, s), 7.00(1H, d, *J*=7.5), 7.04(1H, d, *J*=7.3), 7.28-7.34(3H, m), 7.37-7.39(1H, m), 7.42-7.46(3H, m)

IR (KBr) ν 3063, 2983, 3948, 2363, 1790, 1723, 1592, 1465, 1426, 1369, 1284, 1227, 1117, 1078, 1016, 939, 832, 790, 753, 698cm^{-1}

MS *m/z*(%) 337(M^+-HCl, 92.87), 302 (57.69), 257 (4.08), 252 (8.21), 245 (Base), 223 (4.51), 217 (60.61), 194 (73.99), 189 (58.78), 187 (24.59), 165 (34.26), 151 (6.76), 139 (3.97), 126 (6.97), 94 (15.62), 87 (8.04), 82 (2.41), 63 (2.55)

EA Found: C, 60.99; H, 3.56; N, 3.88. $C_{19}H_{13}Cl_2N_1O_3$ requires C, 60.98; H, 3.50; N, 3.74.

5b

MP 267-268℃

^{1}H-NMR (300 MHz; $CDCl_3$) δ 3.31(3H, s, NCH_3), 7.57(1H, t, *J*=7.5), 7.66(1H, t, *J*=7.6), 7.76(1H, t, *J*=7.6), 7.84-7.90(2H, m), 8.45(1H, d, *J*=7.7), 8.69(1H, *J*=8.3), 9.18(1H, d, *J*=8.3)

IR (KBr) ν 3081, 1767, 1701, 1621, 1573, 1459, 1433, 1375, 1341, 1210, 1066, 993, 864, 757, 691, 611cm^{-1}

MS *m/z*(%) 301(M^+, Base), 273(2.05), 257(33.25), 244(6.29), 216(83.61), 187(35.03), 161(1.65), 151(3.09), 136(2.78), 122(2.12), 108(9.36), 94(8.99)

EA Found: C, 75.82; H, 3.72; N, 4.57. $C_{19}H_{11}N_1O_3$ requires C, 75.74; H 3.68; N, 4.65.

UV (nm) (log ε): 403(4.06), 374(3.95), 279(4.22)

6b

MP 148-149℃

^{1}H-NMR (300 MHz; $CDCl_3$) δ 3.12(3H, s, NCH_3), 7.35(1H, t, *J*=7.5), 7.44-7.48(6H, m), 7.64(1H, d, *J*=8.3), 7.73(1H, d, *J*=7.8)

IR (KBr) ν 3040, 2940, 1785, 1720, 1628, 1567, 1437, 1379, 1250, 1163, 1111, 1004, 885, 858, 778, 745, 701 cm^{-1}

MS *m/z*(%) 337(M, 25.34), 302(39.51), 287(1.05), 257(4.07), 252(4.78), 245(Base), 223(3.01), 217(45.10), 189(41.41), 163(4.75), 151(4.22), 126(4.39), 94(11.29), 84(10.21), 63(1.29), 44(21.99)

EA Found: C, 67.48; H, 3.62; N, 4.11. $C_{19}H_{12}ClNO_3$ requires C, 67.56; H, 3.58; N, 4.15.

Photolysis of 1 with 2-phenylbenzothiophene (**3c**): A solution of **1** (540 mg, 3 mmol) and **3c** (819 g, 3.9 mmol) in benzene (60 ml) was photolyzed for 27h to reach a 79.3% conversion of **1**. Work-up as described above gave **4c** (84.0%) and **5c** (7.36%).

Heating **4c** (100mg) on silica gel (1g) to 100℃ for 16h, and then dissolving the products in benzene (20 ml) and irradiating the solution with light of λ> 400nm under continuous nitrogen purging for 6h to reach a complete conversion of **4c,** this gave **5c** (93.9%). The total yield of **5c** in photoreaction and in subsequent conversion of **4c** was 86.5%.

4c

MP 150-151℃

^{1}H-NMR (300 MHz; $CDCl_3$) δ2.82(3H, s), 5.08(1H, s), 7.20-7.29(4H, m), 7.31-7.42(5H, m)

IR (KBr) ν 3059, 1786, 1724, 1580, 1468, 1446, 1430, 1373, 1286, 1257, 1194, 1176, 1157, 1123, 1087, 1070, 1014, 940, 895, 737, 696cm^{-1}

MS *m/z*(%) 389(M^+, 0.47), 353(40.28), 318(43.69), 261(56.63), 233(45.22), 210(base), 165(25.44), 116(20.75), 87(13.51), 44(2.53)

EA Found: C, 58.54; H, 3.52; N, 3.46. $C_{19}H_{11}N_1O_2S_1Cl_2$ requires C, 58.46; H, 3.33; N, 3.59.

5c

MP 244-245℃

^{1}H-NMR (300 MHz; $CDCl_3$) δ 3.29(3H, s, NCH_3), 7.57-7.61(2H, m), 7.70-7.74(2H, m), 7.93(1H, dd, J_1=7.1, J_2=1.0), 8.14(1H, dd, J_1=7.1, J_2=1.2), 9.13(1H, dd, J_1=8.1, J_2=1.5), 9.70(1H, dd, J_1=8.1, J_2=1.3)

IR (KBr) ν 3058, 1758, 1702, 1545, 1450, 1441, 1381, 1327, 1258, 1243, 1075, 1003, 957, 752, 728, 650cm^{-1}

MS *m/z*(%) 317(M^+, base), 273(13.64), 232(40.36), 187(11.34), 158(3.23), 116(13.04), 57(3.37), 44(5.67)

EA Found: C, 71.94; H, 3.50; N, 4.20.$C_{19}H_{11}N_1O_2S_1$ requires C, 71.92; H, 3.47; N, 4.42.

UV (nm) (log ε): 405(3.74), 321(4.18), 302(4.42), 278(4.51)

Photolysis of 1 with 3-phenylbenzothiophene (**3d**): A solution of **1** (540 mg, 3 mmol) and **3d** (819 g, 3.9 mmol) in benzene (60 ml) was photolyzed for 44h to reach a 94.8% conversion of **1**. Work-up as described above gave **4d** (74.8%) and **5d** (8.33%).

Heating **4d** (100mg) absorbed on silica gel (1g) at 100℃ for 6h, and then dissolving the products in benzene (20 ml) and irradiating the solution with light of λ> 400nm under continuous nitrogen purging for 8h to reach a complete conversion of **4d**, this gave **5d** (85.5%). The total yield of **5d** in photoreaction and in subsequent conversion of **4d** was 72.3%.

4d

MP 215-216℃

^{1}H-NMR (300 MHz; $CDCl_3$) δ 3.05(3H, s), 4.89(1H, s), 7.09-7.14(1H, m), 7.24-7.27(2H, m), 7.29-7.39(4H, m), 7.55-7.58(2H, m)

IR (KBr) ν 3059, 2973, 1792, 1718, 1463, 1448, 1423, 1368, 1277, 1126, 1012, 941, 749, 727, 700, 631cm^{-1}

MS *m/z*(%) 354(M^+-Cl, 43.25), 318(27.74), 261(39.58), 210(base), 165(36.24), 116(16.83), 87(20.35), 45(10.39)

EA Found: C, 58.43; H, 3.24; N, 3.43.$C_{19}H_{11}N_1O_2S_1Cl_2$ requires C, 58.46; H, 3.33; N, 3.59.

5d

MP 251-252℃

^{1}H-NMR (300 MHz; $CDCl_3$) δ 3.30(3H, s), 7.62(1H, td, J_1=7.4, J_2=1.5), 7.68(1H, td, J_1=7.6, J_2=1.4), 7.77(1H, td, J_1=7.6, J_2=1.0), 7.87(1H, ddd, J_1=8.5, J_2=7.0, J_3=1.5), 8.10(1H, dd, J_1=8.1, J_2=1.5), 8.89(1H, dd, J_1=8.0, J_2=1.3), 9.08(1H, d, J=8.6), 9.17(1H, dd, J_1=8.7, J_2=1.1)

IR (KBr) ν 3059, 2939, 1764, 1695, 1551, 1450, 1421, 1386, 1371, 1361, 1327, 1256, 1185, 1059, 991, 780, 755, 732, 663cm^{-1}

MS m/z(%) 317(M^+, base), 273(5.54), 232(44.04), 187(13.05), 116(10.07), 43(18.14)

EA Found: C, 71.87; H, 3.36; N, 4.58. $C_{19}H_{11}N_1O_2S_1$ requires C, 71.92; H, 3.47; N, 4.42.

UV (nm) (log ε): 401(4.00), 279(4.40)

Photolysis of 2 with 2-phenylbenzofuran (**3a**): A solution of **2** (645 mg, 3 mmol) and **3a** (756 mg, 3.9 mmol) in benzene (60 ml) was photolyzed for 48h to reach a 42.6% conversion of **2**. After evaporation of the solvent, the reaction mixture was separated by flash column chromatography on silica gel with petroleum ether (b.p. 60-90℃) ethyl acetate as eluents to give **7a**(58.4%).

7a

MP 189-190℃

^{1}H-NMR (300 MHz; CDCl3) δ 7.36(1H, m), 7.44-7.57(4H, m), 7.66-7.70(2H, m), 7.80(1H, t, J=8.0), 8.33(1H, d, J=7.9), 8.52(1H, d, J=7.2), 8.81(1H, d, J=8.5), 9.18(1H, d, J=7.9)

IR (KBr) ν 3059, 2922, 1736, 1608, 1487, 1368, 1347, 1225, 1060, 976, 740cm^{-1}

MS *m/z*(%) 336(M^+, Base), 308(26.65), 279(19.32), 250(15.84), 154(5.61), 125(6.22)

EA Found: C, 82.35; H, 3.41. $C_{23}H_{12}O_3$ requires C, 82.13; H, 3.60.

UV (nm) (log ε): 403(4.36), 384(4.32), 342(4.21), 327(4.19), 291(4.59)

Photolysis of 2 with 3-phenylbenzofuran (**3b**): A solution of **2** (645 mg, 3 mmol) and **3b** (756 mg, 3.9 mmol) in benzene (60 ml) was photolyzed for 48h to reach a 35.7% conversion of **2**. Work-up as described above gave **7b** (70.8%).

7b

MP 204-5℃

^{1}H-NMR (300 MHz; $CDCl_3$) δ 7.45(1H, td, J_1=4.1, J_2=1.9), 7.51-7.62(3H, m), 7.70(1H, t, J=7.8), 7.90(2H, t, J=7.8), 8.39(1H, d, J=7.5), 8.47(1H, d, J=8.1), 8.73(1H, d, J=8.3), 8.93(1H, d, J=8.6)

IR (KBr) ν 3080, 1745, 1612, 1550, 1464, 1353, 1271, 1213, 1178, 1110, 1056, 1026, 759, 687cm^{-1}

MS *m/z*(%) 337(M^++1, 12.31), 336(M^+, Base), 308(60.63), 279(19.27), 250(11.08), 224(2.82), 168(2.52), 154(4.23), 140(4.39), 125(7.88), 112(3.63)

EA Found: C, 81.96; H, 3.55. $C_{23}H_{12}O_3$ requires C, 82.13; H, 3.60.

UV (nm) (log ε): 410(4.20), 391(4.20), 347(4.13), 331(3.96), 280(4.36)

Photolysis of 2 with 3-phenylbenzothiophene (**3d**): A solution of **2** (645 mg, 3 mmol) and **3d** (819 mg, 3.9 mmol) in benzene (60 ml) was photolyzed for 72h to reach a 36.1% conversion of **2**. Work-up as described above gave **7d** (66.6%).

7d

MP 219-221℃

^{1}H-NMR (300 MHz; $CDCl_3$) δ 7.45-7.49(1H, m), 7.57-7.67(4H, m), 7.75(1H,td, *J*=7.2), 7.93(1H, t, *J*=7.2), 8.14(1H, d, *J*=7.5), 8.50(1H, d, *J*=8.0), 8.85(1H, d, *J*=8.0), 8.98(1H, d, *J*=8.5), 9.18(1H, d, *J*=8.5)

IR (KBr) ν 3052, 1712, 1607, 1531, 1454, 1359, 1252, 1190, 1127, 1112, 1007, 764, 753, 727, 660cm^{-1}

MS *m/z*(%) 352(base), 324(13.95), 295(13.05), 44(15.22)

EA Found: C, 78.38; H, 3.49.$C_{23}H_{12}O_2S_1$ requires C, 78.40; H, 3.41.

UV (nm) (log ε): 418(3.96), 398(3.90), 366(4.19), 352(4.06), 323(4.01), 310(3.96), 280(4.52)

X-ray Crystallographic Study:

Crystal data for **4a** (Fig. 1): $C_{19}H_{13}Cl_2NO_3$, M = 374.20, colorless blocks, Enraf-Nonius CAD4 diffractometer, Mo-K_α radiation (λ= 0.71073 Å), 0.40 × 0.30 × 0.28mm, T = 293(2) K. Monoclinic, space group $P2_1/c$, a = 12.895(3) Å, b = 9.910(2) Å, c = 13.175(3) Å, α = 90.00º, β = 90.54(3)º, γ = 90.00º, V = 1683.6(6) Å^3, Z = 4, Dc = 1.476 g cm^{-3}, μ = 0.404mm^{-1}, F(000) = 768.00. The structure was solved by direct method (SHELXL) and refined on F^2 by full-matrix least-squares method. A total of 2971 independent reflections [R (int) = 0.0426] were used in the refinement, which converged with R = 0.0536 and wR = 0.1931 (GOF = 1.004).

Crystal data for **5b**(Fig. 2): $C_{19}H_{11}NO_3$, M = 301.29, yellow needles, Enraf-Nonius CAD4 diffractometer, Mo-K_α radiation (λ= 0.71073 Å), 0.42 × 0.30 × 0.24mm, T = 293(2) K. Monoclinic, space group $P2_1/c$, a = 9.5260(19) Å, b = 18.319(4) Å, c = 7.9420(16) Å, α = 90.00º, β = 96.25(3)º , γ = 90.00º, V = 1377.7(5) Å^3, Z = 4, Dc = 1.453 g cm^{-3}, μ = 0.099 mm^{-1}, F(000) = 624.00. The structure was solved by direct method (SHELXL) and refined on F^2 by full-matrix least-squares method. A total of 2439 independent reflections [R (int) = 0.0433] were used in the refinement, which converged with R = 0.0551 and wR = 0.1188 (GOF = 1.000).

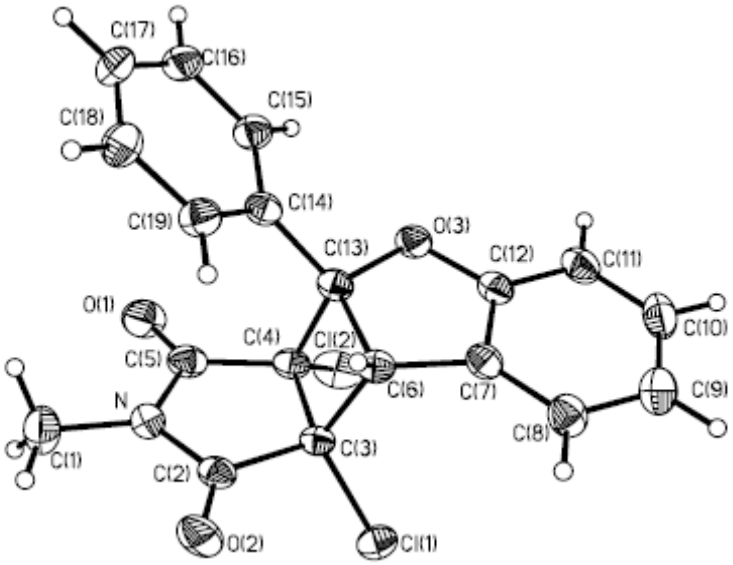


Fig. 1 ORTEP drawing of **4a**

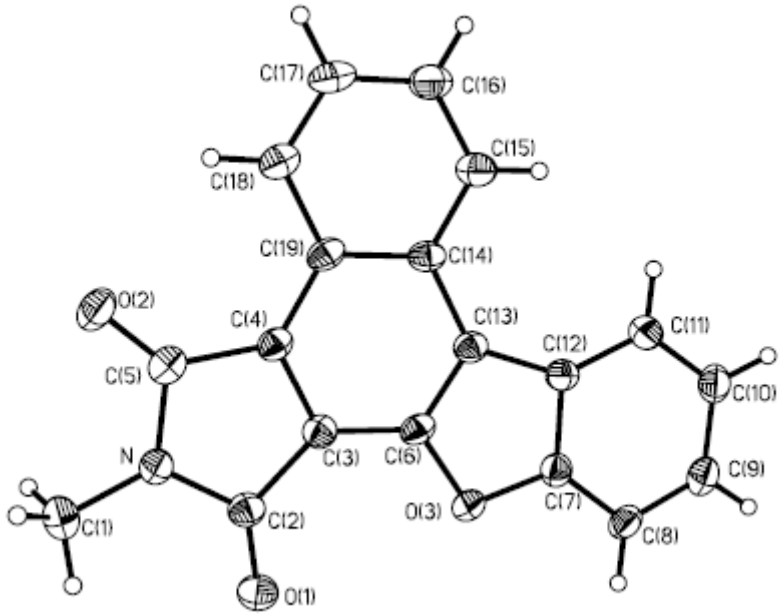


Fig. 2 ORTEP drawing of **5b**

Table Luminescence Quantum Yield

Compd[a]	$\lambda_{ex.}$[b](nm)	$\lambda_{em.}$[c](nm)	Φ_f[d]
5a	342	450	0.41
5b	372	453	0.63
5c	405	463	0.33
5d	402	461	0.38
7a	403	441	0.2
7b	347	449	0.73
7d	406	440	0.42

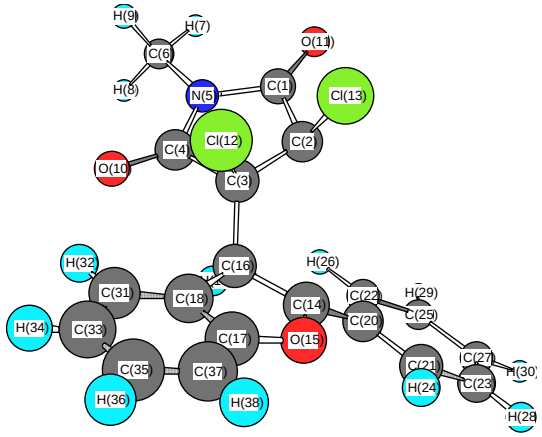
[a] Correct emission spectra were obtained in dilute benzene solution. [b] Only the absorption maxima appropriate to measure the quantum yield are shown. [c] Emission maximum wavelength excited at the absorption maximum. [d] Quantum efficiencies of **5a** and **7b** using quinine sulfate in 0.1N H_2SO_4 as a standard at the corresponding absorption maximum. The others were measured using **5a** in benzene as a standard at the corresponding absorption maximum.

DFT calculation results:

Optimized structures of triplet diradical intermediates **A(1, 3a)**, **A**(**1**, **3b**), **E**(**2**, **3a**) and **E**(**2**, **3b**)

Provided are the Cartesian coordinates for **A(1, 3a)**, **A**(**1**, **3b**), **E**(**2**, **3a**) and **E**(**2**, **3b**) along with the S^2 values. The structural optimizations were performed by standard procedures within Gaussian 03 package.

A(1, 3a)



SCF Done: E(UB+HF-LYP) = -1932.27632326

S**2 = 2.0328

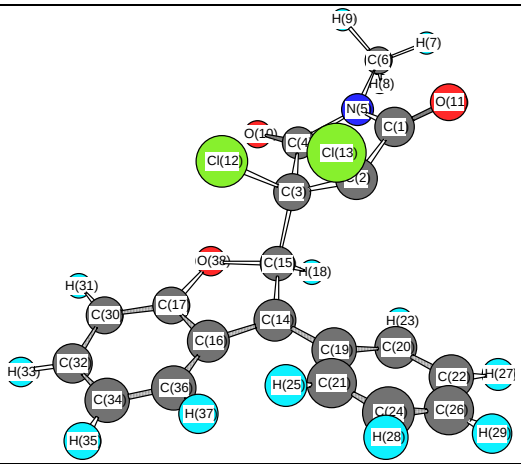
S**2 before annihilation 2.0328, after 2.0006

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.502419	2.682500	0.265718
2	6	1.009398	1.384016	0.713377
3	6	-0.331964	1.097725	0.156376
4	6	-0.553486	2.312712	-0.782348
5	7	0.521442	3.173703	-0.635875
6	6	0.642415	4.449540	-1.336838
7	1	1.663123	4.808251	-1.200739
8	1	0.425767	4.307659	-2.397943
9	1	-0.060822	5.179959	-0.926217
10	8	-1.497286	2.473336	-1.564003
11	8	2.550145	3.274299	0.560714
12	17	-1.568828	1.378529	1.639116
13	17	1.822191	0.513903	1.999944
14	6	0.093430	-1.494322	-0.090109
15	8	0.827614	-2.406269	0.473456
16	6	-0.633514	-0.259947	-0.590037
17	6	-2.121124	-1.950731	0.155382
18	6	-2.085841	-0.722156	-0.508824
19	1	-0.346220	-0.055413	-1.632692
20	6	1.408388	-1.955066	-0.353847
21	6	1.835884	-3.234088	0.108739
22	6	2.336385	-1.171241	-1.098417
23	6	3.122251	-3.689471	-0.158397
24	1	1.139174	-3.844159	0.670184
25	6	3.618627	-1.643124	-1.360512
26	1	2.042289	-0.196047	-1.473844
27	6	4.024828	-2.902421	-0.892323
28	1	3.428636	-4.665553	0.204656
29	1	4.307612	-1.029759	-1.932559
30	1	5.027084	-3.263929	-1.096217
31	6	-3.277746	-0.147875	-0.948026
32	1	-3.271423	0.809807	-1.453919
33	6	-4.479498	-0.829147	-0.697938
34	1	-5.416395	-0.397942	-1.033652
35	6	-4.485862	-2.054337	-0.013948
36	1	-5.426843	-2.561173	0.172850
37	6	-3.291413	-2.642230	0.428290
38	1	-3.272657	-3.591916	0.947968

Total atomic spin densities:

1	C	-0.101489
2	C	0.752716
3	C	-0.045619
4	C	0.000520
5	N	0.054859
6	C	-0.005172
7	H	-0.000116
8	H	0.003946
9	H	0.004746
10	O	-0.001496
11	O	0.152371
12	Cl	0.112893
13	Cl	0.093494
14	C	0.682369
15	O	0.066222
16	C	-0.043056
17	C	-0.009602
18	C	0.025332
19	H	0.027120
20	C	-0.225399
21	C	0.243823
22	C	0.241698
23	C	-0.137704
24	H	-0.009777
25	C	-0.136369
26	H	-0.009820
27	C	0.253438
28	H	0.004449
29	H	0.004487
30	H	-0.011084
31	C	-0.004579
32	H	0.000166
33	C	0.011984
34	H	-0.000474
35	C	-0.004878
36	H	0.000136
37	C	0.010211
38	H	-0.000346

A(1, 3b)



SCF Done: E(UB+HF-LYP) = -1932.27715920

S**2 = 2.0353

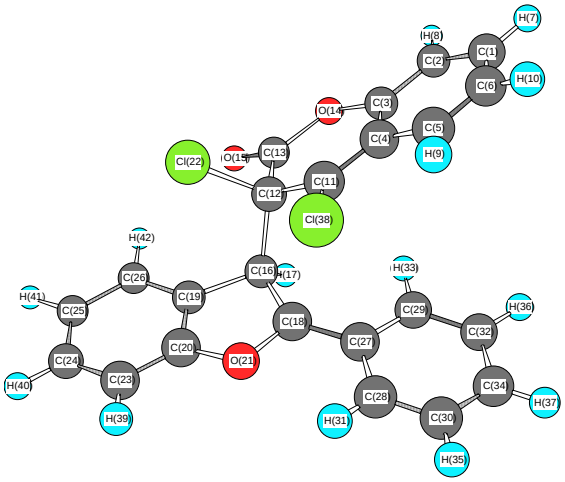
S**2 before annihilation 2.0353, after 2.0008

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.269743	0.371772	0.175277
2	6	-1.859839	0.455706	0.542806
3	6	-1.118100	-0.767154	0.143215
4	6	-2.243582	-1.618022	-0.525289
5	7	-3.421384	-0.875728	-0.471517
6	6	-4.696326	-1.360834	-0.993206
7	1	-5.444603	-0.590678	-0.804220
8	1	-4.616726	-1.552640	-2.066534
9	1	-4.978602	-2.289764	-0.490724
10	8	-2.139961	-2.730709	-1.038659
11	8	-4.180825	1.191037	0.367242
12	17	-0.600903	-1.697662	1.742041
13	17	-1.306466	1.723931	1.621257
14	6	1.286737	0.238938	-0.384141
15	6	0.119247	-0.640913	-0.810524
16	6	2.391456	-0.637978	-0.130580
17	6	1.993977	-1.955841	-0.481793
18	1	-0.289119	-0.360671	-1.790364
19	6	1.274691	1.685008	-0.459658
20	6	0.415797	2.367737	-1.361551
21	6	2.132306	2.476836	0.348060
22	6	0.430247	3.757544	-1.462394
23	1	-0.250177	1.803885	-2.006761
24	6	2.137874	3.867123	0.246436
25	1	2.754795	1.997306	1.093041
26	6	1.292596	4.518483	-0.661733
27	1	-0.230369	4.249773	-2.169044
28	1	2.795592	4.446856	0.886443
29	1	1.299763	5.600513	-0.739023
30	6	2.824296	-3.059172	-0.411572
31	1	2.464880	-4.040576	-0.693641
32	6	4.139605	-2.841078	0.030618
33	1	4.822269	-3.680505	0.107210
34	6	4.584659	-1.547058	0.361230
35	1	5.610948	-1.402429	0.681762
36	6	3.732692	-0.444244	0.277188
37	1	4.108325	0.543839	0.507743
38	8	0.685343	-1.990641	-0.959292

Total atomic spin densities:

1	C	-0.103470
2	C	0.772671
3	C	-0.049598
4	C	-0.000835
5	N	0.061464
6	C	-0.006069
7	H	-0.000068
8	H	0.005683
9	H	0.004218
10	O	0.003050
11	O	0.144277
12	Cl	0.087730
13	Cl	0.093286
14	C	0.653062
15	C	-0.036165
16	C	-0.200607
17	C	0.179416
18	H	0.027696
19	C	-0.161444
20	C	0.158049
21	C	0.158163
22	C	-0.088357
23	H	-0.006570
24	C	-0.088162
25	H	-0.006952
26	C	0.161019
27	H	0.003321
28	H	0.003090
29	H	-0.007026
30	C	-0.103612
31	H	0.003132
32	C	0.222918
33	H	-0.009942
34	C	-0.105828
35	H	0.003161
36	C	0.210280
37	H	-0.007476
38	O	0.026495

E(**2**, **3a**)



SCF Done: E(UB+HF-LYP) = -2020.35494883

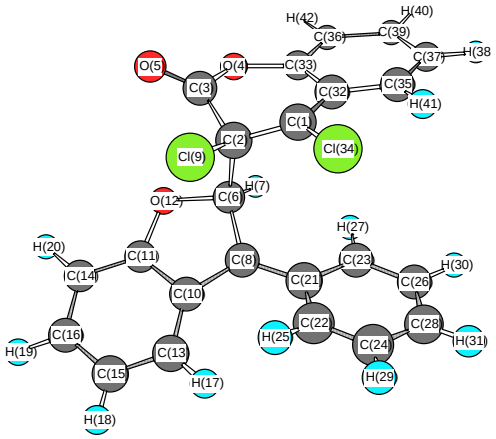
S**2 = 2.0431

S**2 before annihilation 2.0431, after 2.0012

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-4.982791	-1.559010	-0.178238
2	6	-3.916323	-2.180125	-0.826572
3	6	-2.617568	-1.843723	-0.494549
4	6	-2.328007	-0.876995	0.496436
5	6	-3.432443	-0.255921	1.144641
6	6	-4.730940	-0.592586	0.810545
7	1	-5.996234	-1.823292	-0.438387
8	1	-4.067596	-2.928423	-1.587059
9	1	-3.231396	0.487037	1.897751
10	1	-5.553766	-0.107828	1.313281
11	6	-0.980525	-0.580131	0.777230
12	6	0.167145	-1.193665	0.062440
13	6	-0.242487	-2.253268	-0.980650
14	8	-1.594819	-2.503659	-1.182201
15	8	0.564139	-2.828893	-1.685814
16	6	1.108943	-0.128075	-0.689642
17	1	0.798826	-0.156628	-1.736674
18	6	1.010556	1.297619	-0.177000
19	6	2.614144	-0.377564	-0.546365
20	6	3.181793	0.700112	0.131851
21	8	2.231087	1.699026	0.416386
22	17	1.168871	-2.172438	1.379723
23	6	4.526333	0.764706	0.445936
24	6	5.331312	-0.306311	0.037839
25	6	4.785303	-1.391247	-0.654573
26	6	3.415366	-1.437804	-0.946886
27	6	0.043601	2.296496	-0.438234
28	6	0.260144	3.623359	0.026685
29	6	-1.146947	2.027438	-1.166737
30	6	-0.670362	4.618887	-0.225043
31	1	1.165473	3.833358	0.572223
32	6	-2.065303	3.038206	-1.413743
33	1	-1.340829	1.030731	-1.533328
34	6	-1.840024	4.339281	-0.945499
35	1	-0.488093	5.621117	0.136406
36	1	-2.961706	2.815606	-1.974996
37	1	-2.560738	5.120155	-1.140371
38	17	-0.581963	0.522916	2.136500
39	1	4.929363	1.614156	0.972985
40	1	6.387858	-0.286612	0.261738
41	1	5.422267	-2.207950	-0.959541
42	1	2.970364	-2.279416	-1.446004

		Total atomic spin densities:
1	C	0.243765
2	C	-0.120745
3	C	0.200590
4	C	-0.194162
5	C	0.219995
6	C	-0.119289
7	H	-0.011116
8	H	0.004030
9	H	-0.009452
10	H	0.003981
11	C	0.645176
12	C	-0.011477
13	C	0.005355
14	O	0.004595
15	O	0.021227
16	C	-0.033583
17	H	0.024548
18	C	0.647605
19	C	0.027145
20	C	-0.009087
21	O	0.081872
22	Cl	0.110407
23	C	0.010126
24	C	-0.003476
25	C	0.012406
26	C	-0.003506
27	C	-0.198812
28	C	0.221626
29	C	0.218948
30	C	-0.119360
31	H	-0.009726
32	C	-0.118284
33	H	-0.009755
34	C	0.234709
35	H	0.004138
36	H	0.004103
37	H	-0.010939
38	Cl	0.037074
39	H	-0.000354
40	H	0.000093
41	H	-0.000458
42	H	0.000068

E(2, 3b)



SCF Done: E(UB+HF-LYP) = -2020.35512157

S**2 = 2.0480

S**2 before annihilation 2.0480, after 2.0015

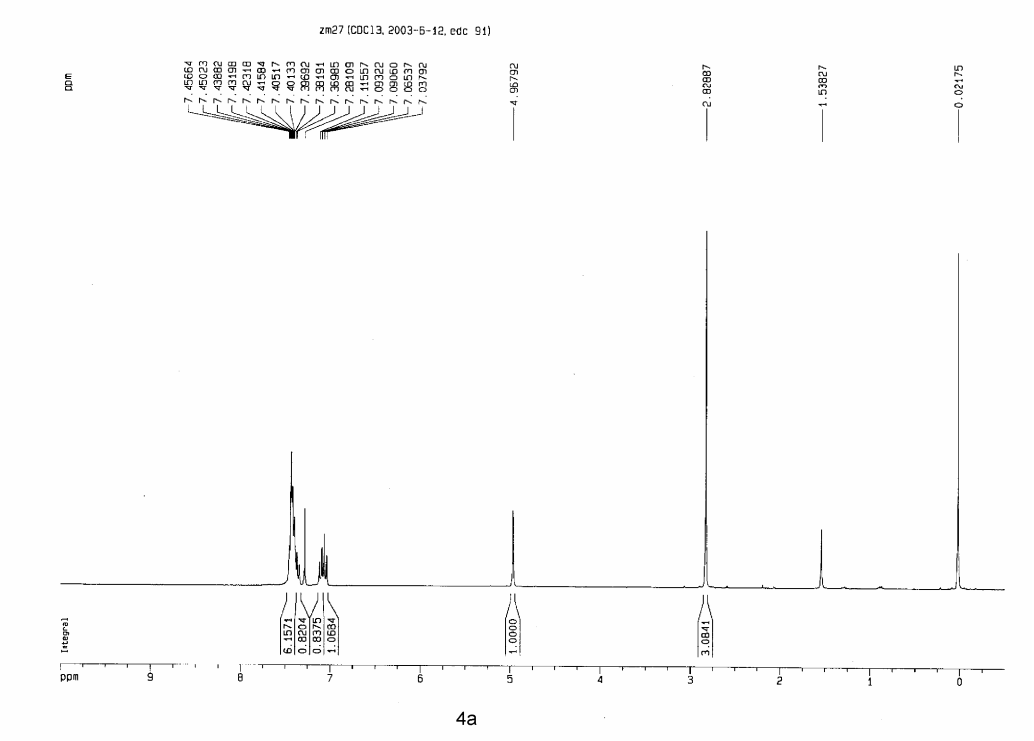
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.521046	-0.151112	0.944771
2	6	-0.365863	-1.073164	0.724098
3	6	-0.896523	-2.499933	0.485386
4	8	-1.919713	-2.525916	-0.489788
5	8	-0.509398	-3.532509	0.970076
6	6	0.448997	-0.695440	-0.561660
7	1	-0.267504	-0.630454	-1.387518
8	6	1.379392	0.500401	-0.445973
9	17	0.786028	-1.150208	2.181334
10	6	2.711813	-0.006107	-0.520502
11	6	2.642998	-1.409762	-0.736573
12	8	1.327791	-1.859718	-0.820189
13	6	3.983099	0.607129	-0.504477
14	6	3.761795	-2.201216	-0.891921
15	6	5.118467	-0.185413	-0.656402
16	6	5.015292	-1.574134	-0.838420
17	1	4.075444	1.678946	-0.396860
18	1	6.097737	0.277591	-0.640548
19	1	5.912632	-2.170263	-0.950359
20	1	3.661434	-3.265522	-1.051751
21	6	0.931208	1.874291	-0.402284
22	6	1.679104	2.867613	0.274967
23	6	-0.262117	2.275727	-1.051624
24	6	1.262671	4.195006	0.282545
25	1	2.556912	2.576212	0.836472
26	6	-0.667469	3.605555	-1.044517
27	1	-0.859503	1.542555	-1.579591
28	6	0.092437	4.575142	-0.381648
29	1	1.844699	4.935170	0.819584
30	1	-1.576568	3.890275	-1.561822
31	1	-0.227401	5.610278	-0.376315
32	6	-2.669350	-0.270907	0.140421
33	6	-2.813489	-1.460319	-0.629886
34	17	-1.365272	1.236311	2.077872
35	6	-3.682567	0.719316	0.016796
36	6	-3.873895	-1.629720	-1.504978
37	6	-4.743979	0.538924	-0.853632
38	1	-5.502179	1.307297	-0.941016
39	6	-4.841098	-0.630350	-1.626680
40	1	-5.671000	-0.766500	-2.308424
41	1	-3.589506	1.621101	0.606060
42	1	-3.936740	-2.554443	-2.062050

		Total atomic spin densities:
1	C	0.691913
2	C	-0.024610
3	C	0.008656
4	O	0.011878
5	O	0.038082
6	C	-0.013321
7	H	0.026607
8	C	0.635074
9	Cl	0.013254
10	C	-0.183338
11	C	0.164875
12	O	0.033645
13	C	0.207895
14	C	-0.093579
15	C	-0.099622
16	C	0.221121
17	H	-0.008553
18	H	0.003181
19	H	-0.010336
20	H	0.002986
21	C	-0.145385
22	C	0.142691
23	C	0.139823
24	C	-0.075496
25	H	-0.006617
26	C	-0.074909
27	H	-0.006425
28	C	0.144055
29	H	0.003052
30	H	0.003100
31	H	-0.006686
32	C	-0.203794
33	C	0.204974
34	Cl	0.036895
35	C	0.227627
36	C	-0.121338
37	C	-0.121720
38	H	0.004063
39	C	0.247418
40	H	-0.011327
41	H	-0.009838
42	H	0.004026

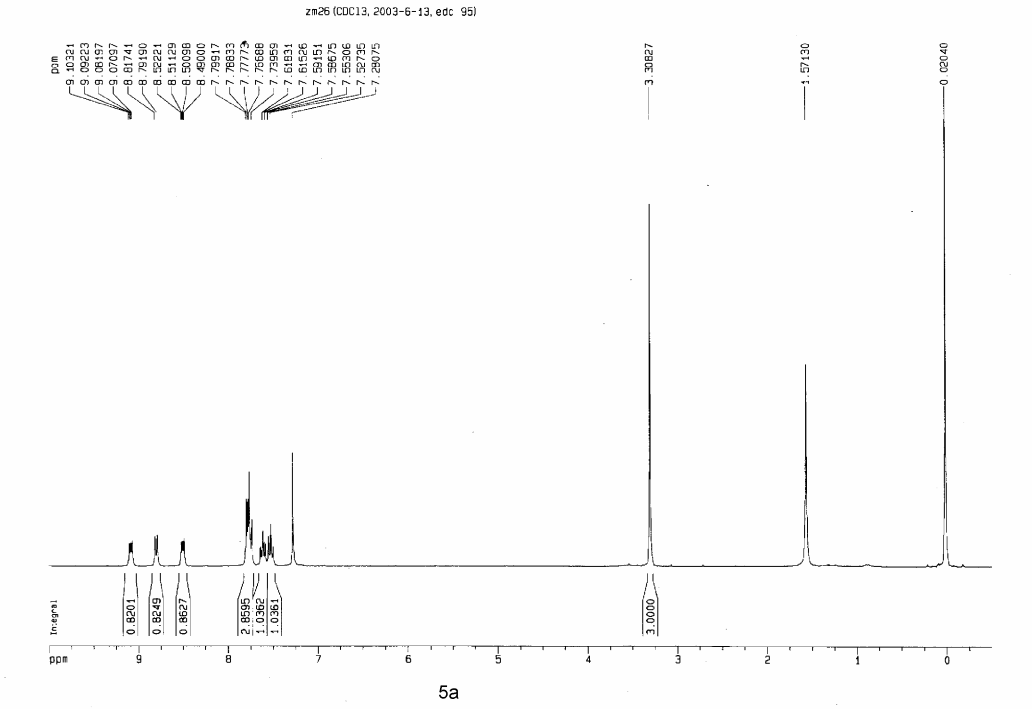
Title: **Aromatic Annulation Strategy for Naphthalenes Fused at 1,2- and 3,4- Positions with Two Heterocycles**

Author: Min Zhang, Hui-Ying An, Bao-Guo Zhao and Jian-Hua Xu*

[1]HNMR spectra of all the new compounds (4a, 5a, 6a, 4b, 5b, 6b, 4c, 5c, 4d, 5d, 7a, 7b, 7c):



4a



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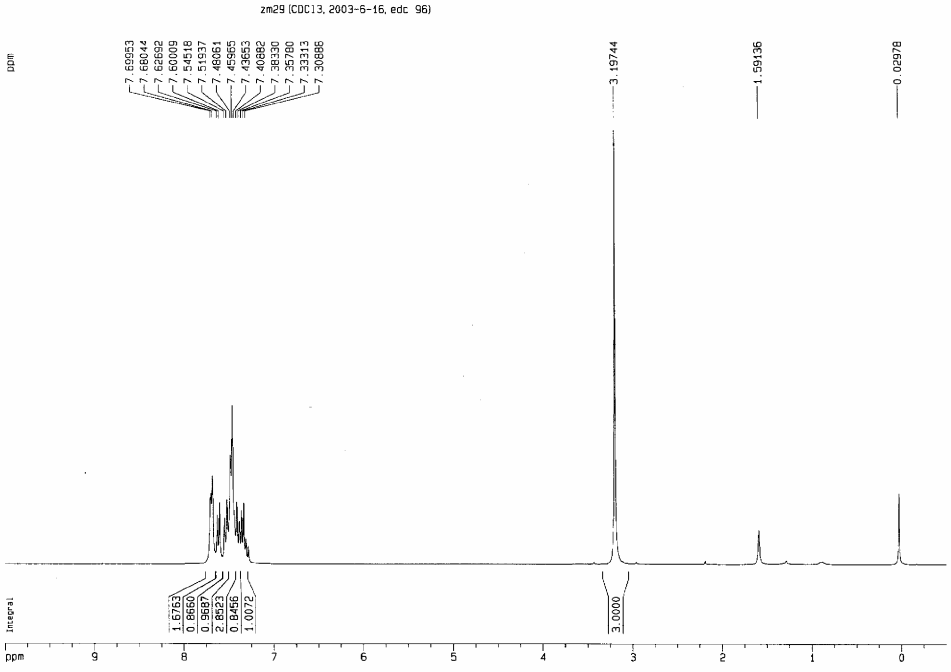
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7.45965
7.43653
7.40882
7.38330
7.35780
7.33313
7.30886
3.19744
1.59136
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Integral
1.6753
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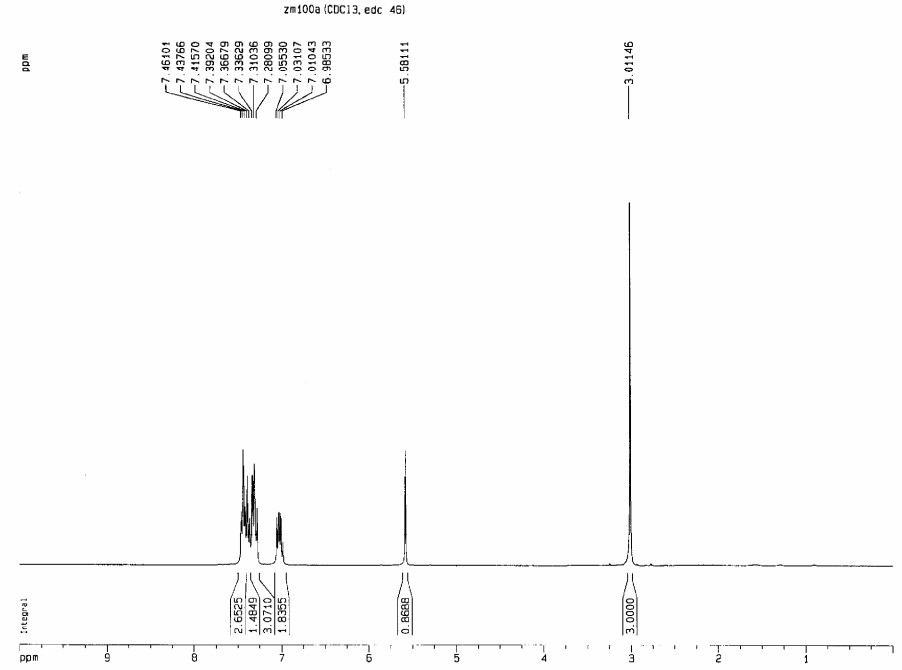
3.0000
ppm

6a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7.43766
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7.36679
7.33629
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7.28099
7.05530
7.03107
7.01043
6.98633
5.58111
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Integral
2.6525
1.4848
3.0710
1.8355
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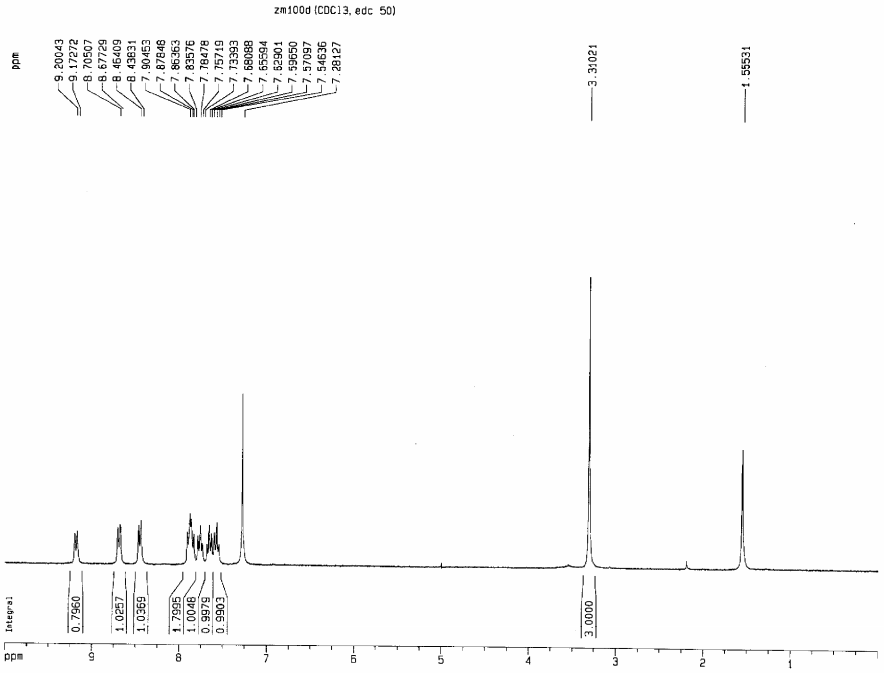
3.0000
ppm

4b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8.43831
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7.87846
7.86363
7.83576
7.78478
7.75719
7.73393
7.68088
7.65594
7.62901
7.59650
7.57097
7.54636
7.28127
3.31021
1.55531
Integral
0.7960
1.0257
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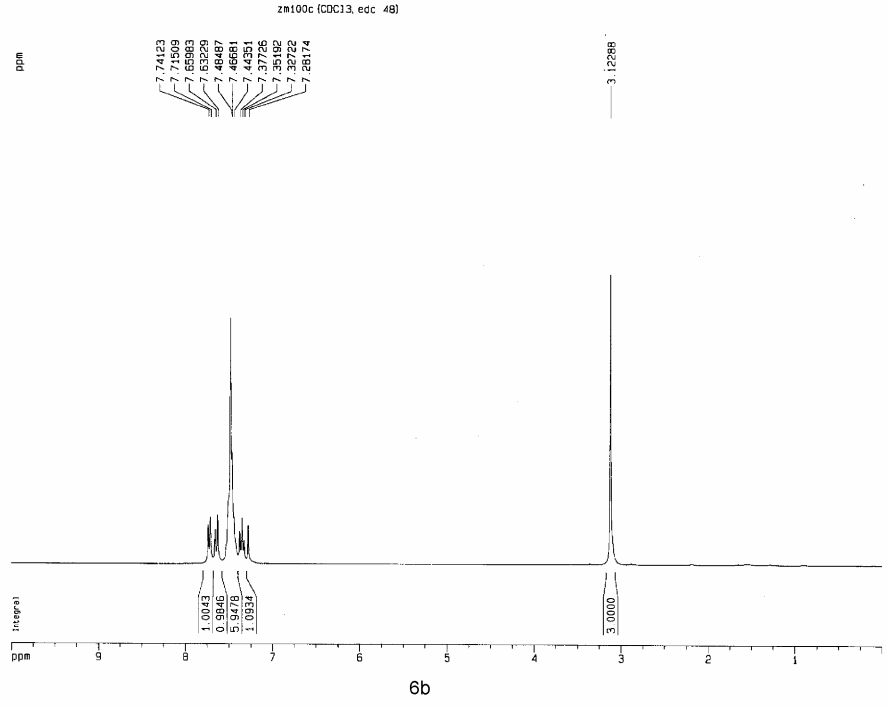
3.0000
ppm

5b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7.37726
7.35192
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Integral
1.0043
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5.9478
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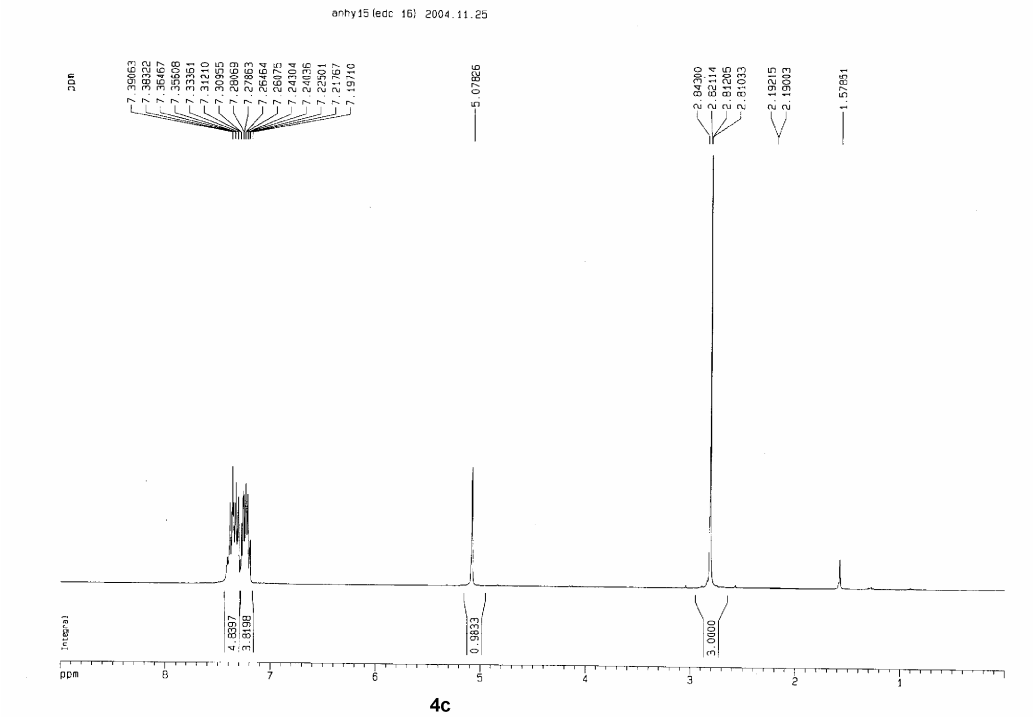
ppm

6b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7.24104
7.24036
7.22501
7.21767
7.19710
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2.84300
2.82114
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Integral
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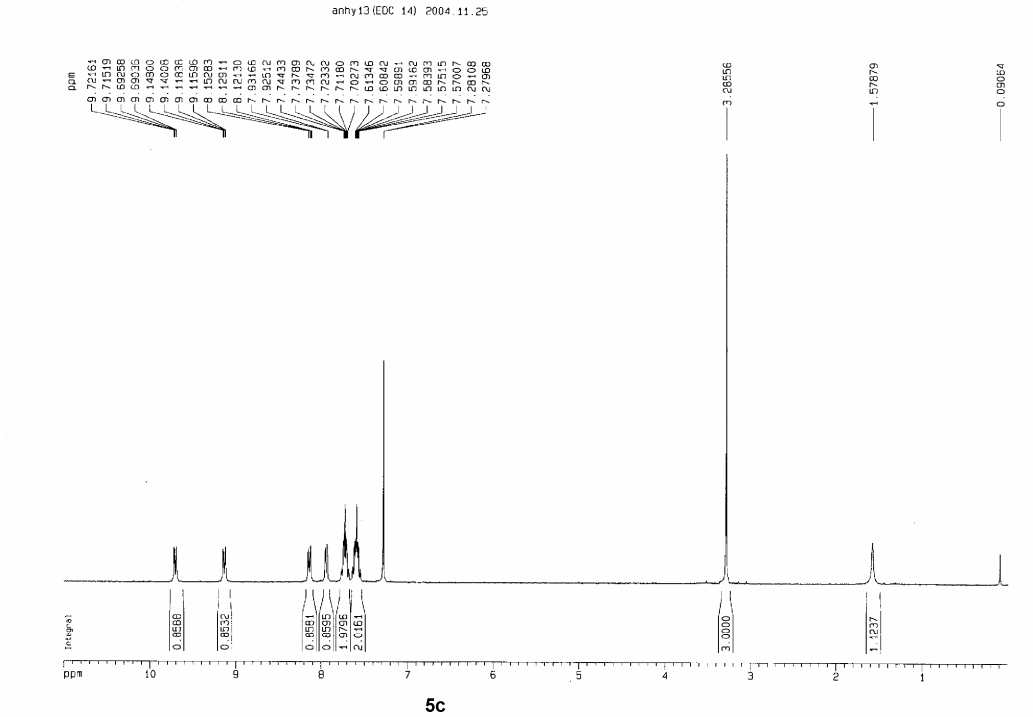
ppm

4c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9.14006
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8.12130
8.12911
8.03166
7.92512
7.74433
7.73789
7.73472
7.72332
7.71180
7.70273
7.61346
7.60842
7.59891
7.59162
7.58393
7.57515
7.57007
7.28108
7.27968
3.28556
1.57879
0.09064
Integral
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0.8532
0.8561
0.8595
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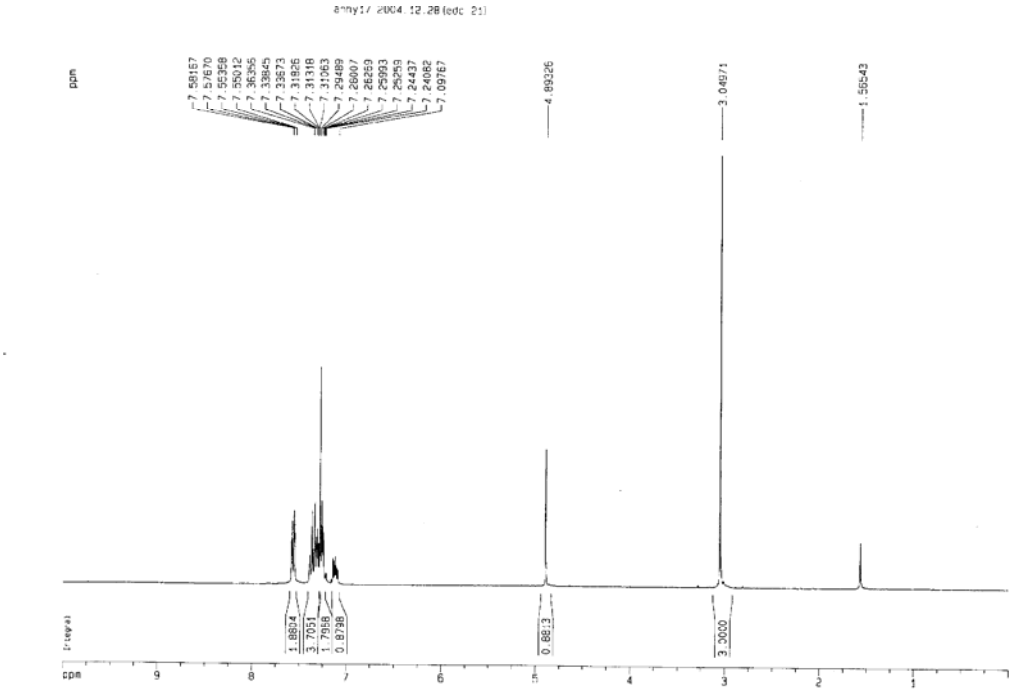
2.0161
3.0000
1.1237
ppm

5c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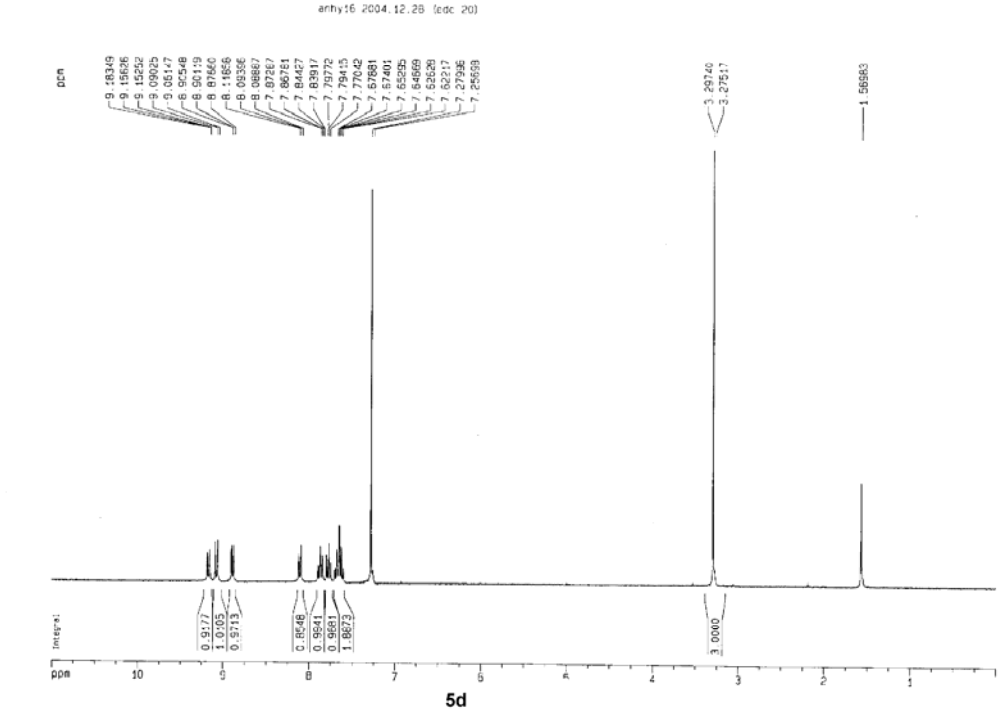
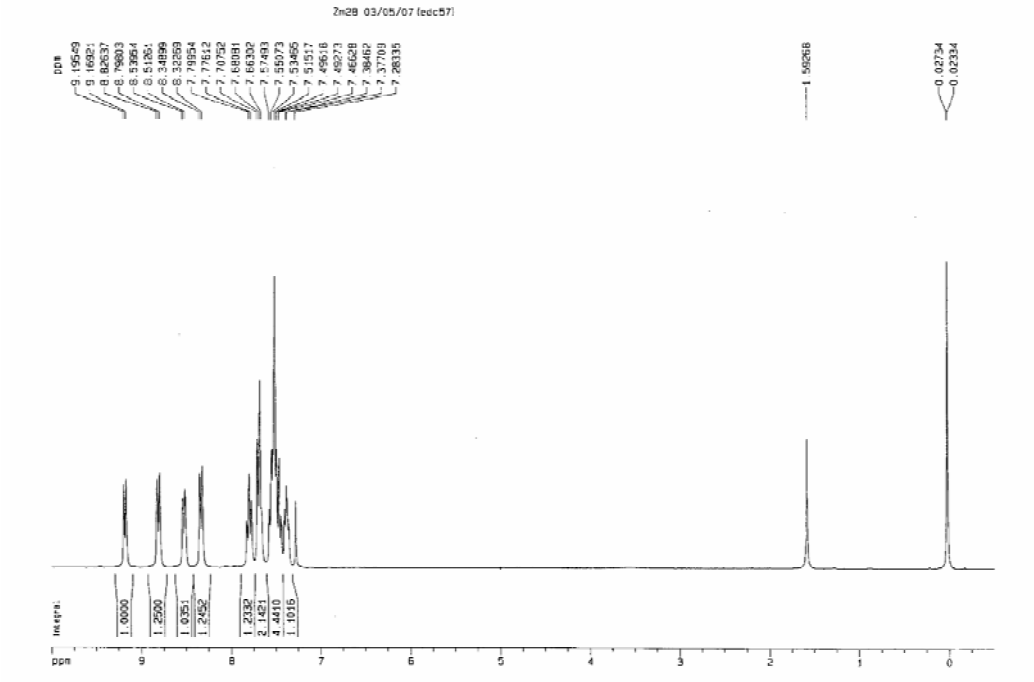
ppm
7.58167
7.57670
7.56358
7.55012
7.36355
7.33845
7.33673
7.31826
7.31318
7.31063
7.29489
7.26007
7.25259
7.25093
7.25053
7.24437
7.24062
7.09767
4.89326
3.04971
1.56543
Integral
1.8804
3.7051
1.7918
0.8798
0.8813
3.0000
ppm

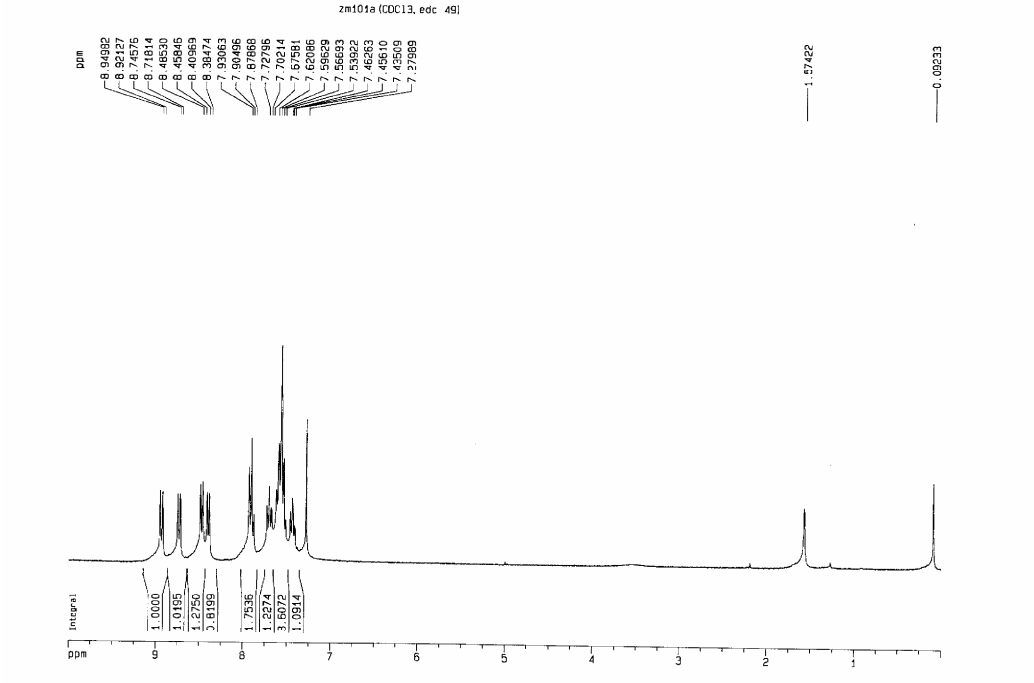
4d


anhy16 2004.12.28 (edc 20)
ppm
9.18349
9.15626
9.15252
9.09025
9.06147
8.90548
8.90119
8.87660
8.11856
8.09356
8.08867
7.87267
7.86761
7.84457
7.83917
7.79772
7.79415
7.77042
7.67681
7.67401
7.65295
7.64669
7.52628
7.52217
7.27998
7.25593
3.29746
3.27517
1.56983
Integral
0.9177
1.0105
0.5713
0.8548
0.9941
0.9661
1.8673
3.0000
ppm

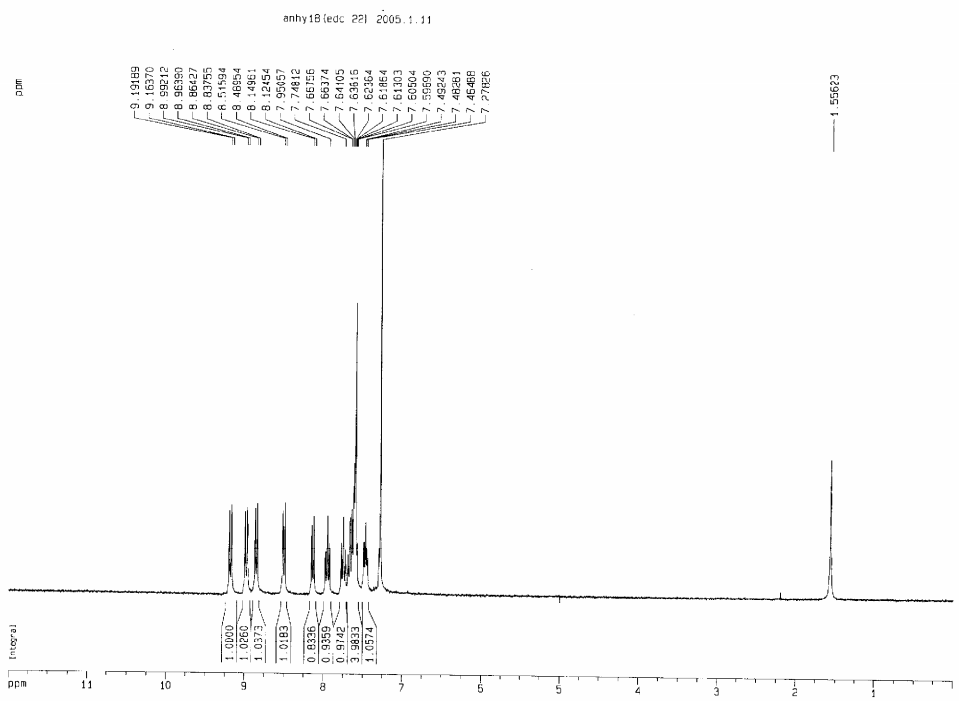
5d


Zm28 03/05/07 (edc57)
ppm
9.19549
9.16921
8.82637
8.79803
8.53954
8.51261
8.34899
8.32269
7.79954
7.77612
7.70752
7.68091
7.66330
7.57493
7.55073
7.53495
7.51517
7.49616
7.49273
7.46528
7.38462
7.37709
7.28335
1.59268
0.02734
0.02334
Integral
1.0000
1.2500
1.0351
1.2456
1.2339
2.1421
4.4410
1.1915
ppm

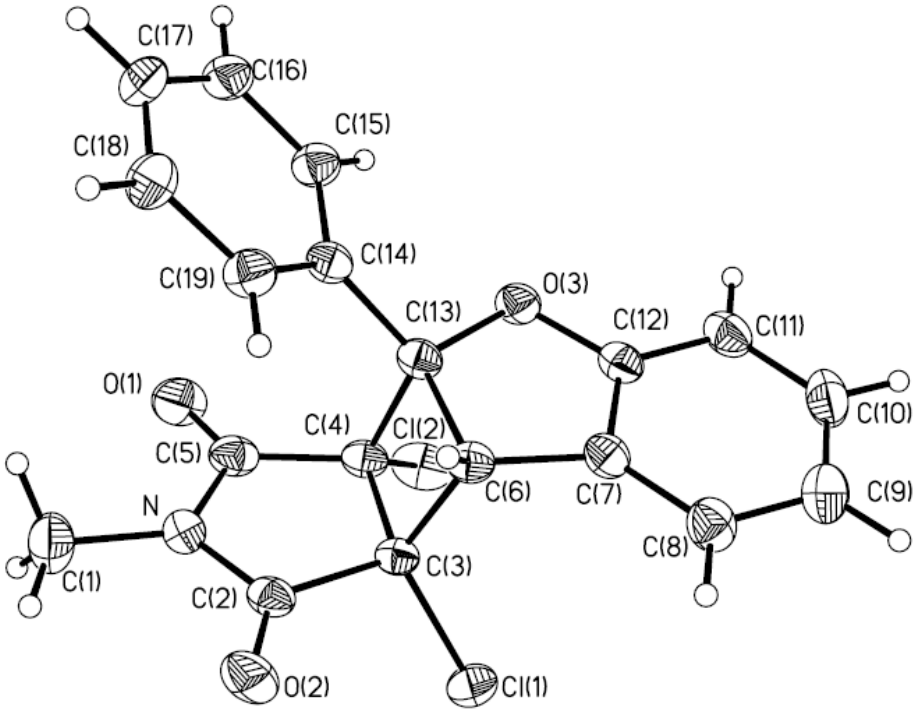
7a


zm101a (CDCl3, edc 49)
ppm
8.94982
8.92127
8.74576
8.71814
8.48530
8.45846
8.40969
8.38474
7.93063
7.90496
7.87868
7.72796
7.70214
7.67581
7.62086
7.59629
7.56693
7.53922
7.46263
7.45610
7.43569
7.27989
1.57422
0.09233
Integral
1.0000
1.0195
1.2750
3.8199
1.7536
1.2274
3.5072
1.0914
ppm

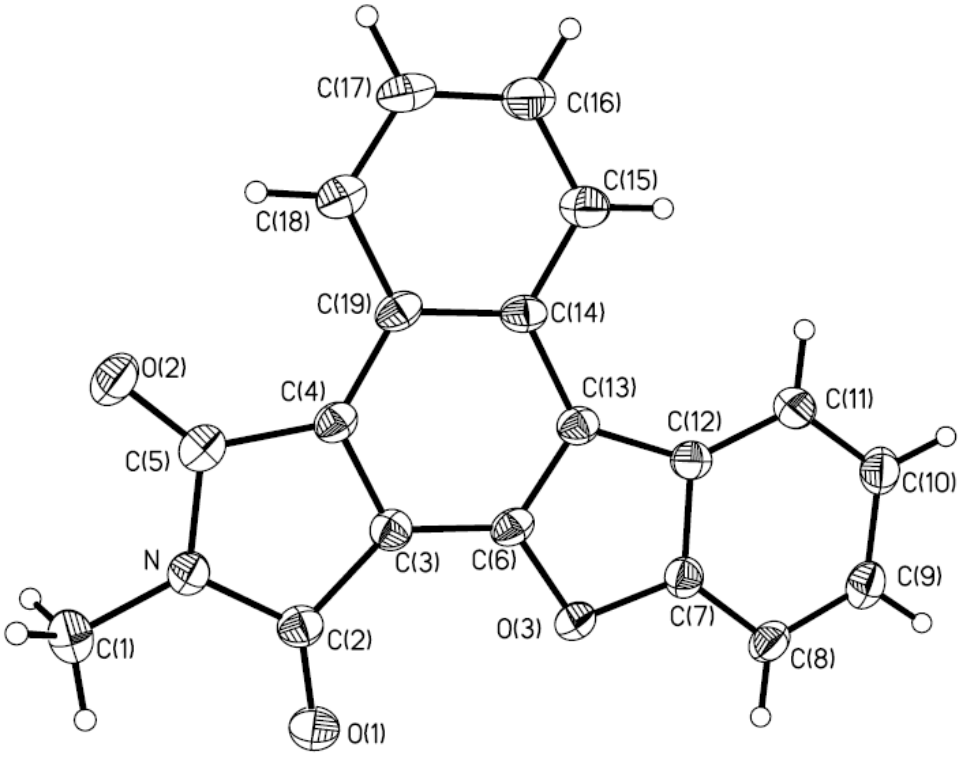
7b


anhy1B (edc 22) 2005.1.11
ppm
9.19189
9.16370
8.99212
8.96390
8.86427
8.83755
8.51594
8.48654
8.14961
8.12454
7.95057
7.74812
7.66756
7.66374
7.64105
7.63615
7.62364
7.61864
7.61103
7.60504
7.59690
7.49243
7.48281
7.46468
7.27826
1.55623
Integral
1.0000
1.0050
1.0373
1.0183
0.8336
0.9359
0.9742
3.0833
1.0574
ppm
11
10
9
8
7
6
5
4
3
2
1

7d



ORTEP drawing of **4a**



ORTEP drawing of **5b**