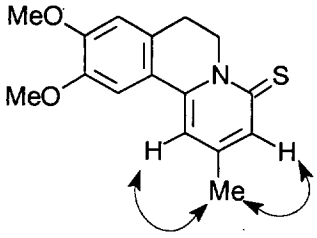
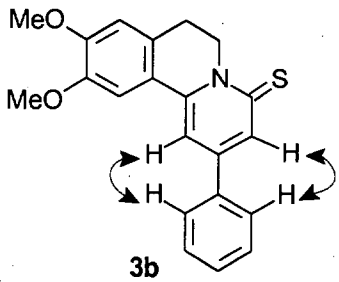
NOESY CORRELATIONS

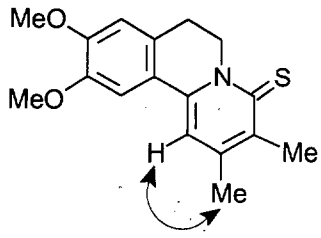
None of the newly synthesized compounds could be crystallized to give single crystal for X-ray crystallography. Therefore the regiochemistry for the products benzo[a]quinolizine-4-thiones was established on the basis of NOESY correlation spectra. Thus correlations were observed for H-1/ 2-Me and 2-Me/ H-3 in **3a**; H-1/ 2′-Ph and 2′-Ph/ H-3 in **3b**; H-1/ 2-Me in **3d**; H-13/ 12-CH_2 in **3f** and H-15/ H-14 in **3i.**



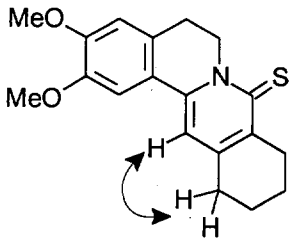
3a



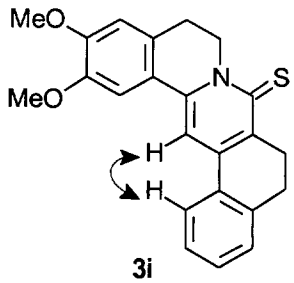
3b



3d



3f



3i

NOESY correlations ⟷

Characterization Data:

6,7-Dihydro-9,10-dimethoxy-2-(4-methoxy)-phenylbenzo[*a*]quinolizine-4-thione (3c): Yellow solid (chloroform-hexane): mp 186-187°C; Yield 1.35g (71%); IR (KBr): 2992, 1601, 1505, 1268, 1142 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.01 (t, J = 6.3 Hz, 2H, CH_2), 3.88 (s, 3H, OCH_3), 3.97 (s, 6H, OCH_3), 4.95 (t, J = 6.4 Hz, 2H, CH_2), 6.80 (s, 1H, ArH), 7.02 (d, J = 8.6 Hz, 2H, ArH); 7.18 (d, J = 2 Hz, 1H, H-1), 7.21 (s, 1H, ArH), 7.65 (d, J = 8.6 Hz, 2H, ArH), 7.93 (d, J = 2 Hz, 1H, H-3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.59, 47.04, 55.45, 56.14, 56.42, 108.37, 108.90, 110.26, 114.61, 127.01, 128.33, 129.53, 129.76, 130.52, 137.04, 145.19, 148.75, 151.86, 161.11, 179.53; MS m/e 379 (M^+, 100), 364 (41.6); Anal. Calcd for $C_{22}H_{21}NO_3S$ (379.49): C, 69.72; H, 5.58; N, 3.69%. Found: C, 70.01; H, 5.62; N, 3.99%.

6,7-Dihydro-9,10-dimethoxy-3-methyl-2-phenylbenzo[*a*]quinolizine-4-thione (3e): Yellow solid (chloroform-hexane); mp 253-254°C; Yield 1.3g (72%); IR (KBr): 2921, 1597, 1512, 1265, 1067 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.15 (s, 3H, CH_3), 2.83 (t, J = 6.1 Hz, 2H, CH_2), 3.72 (t, J = 6.1 Hz, 2H, NCH_2), 3.93 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 6.68 (s, 1H, ArH), 7.28 (s, 1H, H-1), 7.33 (s, 1H, ArH), 7.53-7.60 (m, 4H, ArH), 8.16 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.95, 27.82, 48.62, 56.13, 56.40, 108.25, 110.10, 120.54, 126.53, 127.85, 128.34, 128.38, 128.43, 129.62, 129.66, 129.72, 134.42, 135.97, 148.95, 151.37, 188.78; MS m/e 363 (M^+, 100), 348 (13.2); Anal. Calcd for $C_{22}H_{21}NO_2S$ (363.49): C, 72.69; H, 5.82; N,3.85%; Found: C, 72.36; H, 5.99; N, 3.91%.

5,6-Dihydro-2,3-dimethoxybenzo[*a*]cyclopentano[*g*]quinolizine-4-thione (3g): Light Yellow solid (chloroform-hexane); mp 129-130°C; Yield 0.70g (45%); IR (KBr): 2929, 1604, 1514, 1223, 1148 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.08-2.16 (m, 2H, CH_2), 2.94-3.03 (m, 4H, CH_2), 3.12 (t, J = 6.5 Hz, 2H, CH_2), 4.99 (t, J = 6.6 Hz, 2H, NCH_2), 6.78 (s, 1H, ArH), 7.00 (s, 1H, H-12), 7.15 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.97, 27.68, 34.66, 35.43, 46.98, 56.09, 56.23, 107.41, 107.97, 110.06, 121.90, 129.11,

145.12, 149.64, 179.01; MS m/e 313 (M^+, 100), 298 (40.1); Anal. Calcd for $C_{18}H_{19}NO_2S$ (313.43): C, 68.98; H, 6.11; N, 4.47%. Found: C, 68.97; H, 6.09; N, 4.45%.

***N*-benzyl-6,7-dimethoxy-5,6,9,11,12-pentahydrobenzo[*a*]pyrido[3,4-*g*]quinolizine-4-thione (3h):** Yellow solid (chloroform-hexane); mp 172-173°C; Yield 0.96g (46%); IR (KBr): 2929, 1607, 1513, 1263, 1177 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.68 (brs, 2H, CH_2), 2.84 (brs, 2H, CH_2), 2.95 (t, J = 6.1, 2H, CH_2), 3.83 (s, 2H, CH_2), 3.91 (s, 2H, CH_2), 3.95 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 5.00 (t, J = 6.1 Hz, 2H, NCH_2), 6.77 (s, 1H, ArH), 6.84 (s, 1H, H-13), 7.13 (s, 1H, ArH), 7.33-7.41 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.72, 29.08, 35.01, 46.09, 47.61, 56.10, 56.32, 61.28, 107.91, 110.21, 111.49, 121.56, 127.81, 128.44, 129.06, 129.28, 129.34, 138.03, 142.63, 144.61, 148.55, 151.12, 179.05; MS m/e 418 (M^+, 4.7), 136 (20.7); Anal. Calcd for $C_{25}H_{26}N_2O_2S$ (418.58): C, 71.74; H, 6.26; N, 6.69%. Found: C, 71.72; H, 6.24; N, 6.71%.

2,3-Dimethoxy-5,6,9,10-tetrahydrobenzo[*a*]naphtho[2,1-*g*]quinolizine-4-thione (3i): Yellow solid (chloroform-hexane); mp 160-161°C; Yield 1.23g (65%); IR (KBr): 2928, 1604, 1506, 1229, 1120 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.85 (t, J = 6.6 Hz, 2H, CH_2), 2.96 (t, J = 6.0 Hz, 2H, CH_2), 3.16 (t, J = 6.3 Hz, 2H, CH_2), 3.91 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 4.37 (t, J = 6.1 Hz, 2H, NCH_2), 6.63 (s, 1H, ArH), 6.71 (s, 1H, H-15), 7.01 (s, 1H, ArH), 7.13-7.16 (m, 1H, ArH), 7.29-7.35 (m, 2H, ArH), 8.02 (d, J = 9.0 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): 27.02, 29.08, 29.21, 47.37, 56.06, 56.17, 98.06, 102.39, 107.41, 110.21, 119.90, 125.04, 126.30, 126.74, 128.32, 130.11, 135.67, 136.55, 139.55, 148.65, 149.80, 179.11; MS m/e 375 (M^+, 13.8), 135 (36.6); Anal. Calcd for $C_{23}H_{21}NO_2S$ (375.50): C, 73.57; H, 5.64; N, 3.73%. Found: C, 73.51; H, 5.66; N, 3.71%.

5,6,9,10-Tetrahydro-2,3,12-trimethoxybenzo[*a*]-naphtho[2,1-*g*]quinolizine-4-thione (3j):

Yellow solid (chloroform-hexane); mp 168-169°C; Yield 1.09g (54%); IR (KBr): 2927, 1601, 1532, 1264, 1120 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.83 (t, J = 6.6 Hz, 2H, CH_2), 2.97 (t, J = 6.0 Hz, 2H, CH_2), 3.13 (t, J = 6.5 Hz, 2H, CH_2), 3.95 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 4.13 (t, J = 6.0 Hz, 2H, NCH_2), 6.77 (s, 1H, ArH), 7.02 (s, 1H, ArH), 7.07 (s, 1H, H-15), 7.48 (s, 1H, ArH), 7.80 (d, J = 8.7 Hz, 1H, ArH), 8.40 (d, J = 9.6 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.03, 29.08, 29.22,

47.37, 55.51, 56.06, 56.17, 98.01, 102.41, 108.01, 110.21, 121.23, 125.04, 126.30, 126.73, 127.12, 130.11, 135.66, 136.56, 139.55, 148.65, 149.80, 161.23, 179.12; MS m/e 405 (M^+, 3.1), 134 (61.8); Anal. Calcd for $C_{24}H_{23}NO_3S$ (405.52): C, 71.08; H, 5.71; N, 3.45%. Found: C, 70.10; H, 5.69; N, 3.39%.

6,7-Dihydro-9,10-dimethoxy-2-methyl-4-methylthiobenzo[*a*]quinolizinium iodide (4a): Yellow solid (chloroform-hexane); mp 218°C; Yield 2.10g (98%); IR (KBr): 2945, 1604, 1540, 1519, 1241 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.62 (s, 3H, CH_2), 2.86 (s, 3H, SCH_3), 3.15 (t, J = 6.3 Hz, 2H, CH_2); 3.87 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 4.52 (t, J = 6.5 Hz, 2H, NCH_2), 7.10 (s, 1H, ArH), 7.59 (s, 1H, H-1), 7.65 (s, 1H, ArH), 8.23 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.05, 21.35, 25.46, 48.04, 55.98, 55.24, 109.88, 110.76, 118.33, 119.56, 121.79, 148.58, 152.88, 155.48, 158.29; FABMS m/e 428 (M^+-127, 20); 302 (100); Anal. Calcd. for $C_{17}H_{20}NO_2SI$ (429.33): C, 47.56, H, 4.70, N, 3.26%. Found: C, 47.49, H, 4.66, N, 3.21%.

2,3-Dimethoxy-5,6,9,10,11,12-hexahydro-8-methylthiodibenzo[*a,g*]quinolizinium iodide (4f):

Yellow solid (chloroform-hexane); mp 191-192°C; Yield 2.30g (98%); IR (KBr): 2940, 1595, 1545, 1285 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 1.86-1.90 (m, 4H, CH_2), 2.57 (s, 3H, SCH_3), 3.12 (brs, 4H, CH_2), 3.20 (t, J = 5.6 Hz, 2H, CH_2), 3.92 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 4.85 (brs, 2H, NCH_2), 7.10 (s, 1H, ArH), 7.66 (s, 1H, H-13), 8.48 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.93, 20.45, 21.77, 26.21, 28.38, 29.91, 50.65, 56.01, 56.50, 109.95, 110.56, 119.00, 123.00, 130.22, 140.21, 147, 60, 148.66, 152.19, 152.86, 156.89; FABMS m/e 342 (M^+-127, 65); Anal. Calcd for $C_{20}H_{24}NO_2SI$ (469): C, 51.17; H, 5.12; N, 2.98%. Found: C, 50.91; H, 5.03; N, 2.54%.

6,7-Dihydro-9,10-dimethoxy-2-methylbenzo[*a*]quinolizine-4-one (5a): White crystals (chloroform-hexane); mp 79-80°C; Yield 1.11g (82%); IR (KBr): 2923, 1656, 1615, 1281cm^1; ^1H NMR (400 MHz, $CDCl_3$); δ 2.25 (s, 3H, CH_3), 2.89 (t, J = 6.5 Hz, 2H, CH_2), 3.94 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 4.24 (t, J = 6.5 Hz, 2H, NCH_2), 6.36 (s, 1H, ArH), 6.41 (s, 1H, H-1), 6.73 (s, 1H, ArH), 7.15 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.54, 27.67, 39.02, 56.06, 56.25, 104.35, 107.98, 110.43, 116.56, 121.54, 129.08, 142.32, 148.42, 150.07, 150.84, 162.66; MS m/e 271 (M^+, 100), 256 (69.8);

Anal. Calcd for $C_{16}H_{17}NO_3$ (271.32): C, 70.83; H, 6.31; N, 5.16%. Found: C, 71.00; H, 6.29; N, 5.14%.

6,7-Dihydro-9,10-dimethoxy-2-phenylbenzo[*a*]quinolizine-4-one (5b): White crystals (chloroform-hexane); mp 162-163°C, Yield 1.33g (80%); IR (KBr): 3059, 1652, 1510, 1212 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.95 (t, J = 6.5 Hz, 2H, CH_2), 3.95 (s, 6H, OCH_3), 4.31 (t, J = 6.5 Hz, 2H, NCH_2), 6.74 (s, 1H, ArH), 6.76 (s, 1H, H-1), 6.78 (s, 1H, ArH), 7.22 (s, 1H, ArH), 7.47-7.49 (m, 3H, ArH), 7.64 (d, J = 8 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.66, 39.30, 56.10, 56.35, 101.75, 108.20, 110.50, 114.44, 121.65, 126.85, 129.00, 129.20, 129.31, 138.39, 143.30, 148.56, 151.11, 151.23, 162.80; MS m/e 333 (M^+, 100), 318 (35.1); Anal. Calcd for $C_{21}H_{19}NO_3$ (333.39): C, 75.66; H, 5.74; N, 4.20%. Found: C, 75.76; H, 5.81; N, 3.99%.

2,3-Dimethoxy-5,6,9,10,11,12-hexahydrodibenzo[*a,g*]quinolizine-8-one (5f): White crystalline solid (chloroform-hexane); mp 131-132°C; Yield 1.26g (81%); IR (KBr): 2921, 1635, 1545, 1512, 1212 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.74-1.78 (m, 5H, CH_2), 2.58-2.61 (m, 3H, CH_2), 2.88 (t, J = 6 Hz, 2H, CH_2), 3.93 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 4.27 (t, J = 6 Hz, 2H, NCH_2), 6.32 (s, 1H, ArH), 6.72 (s, 1H, ArH), 7.13 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.19, 22.40, 23.92, 27.83, 29.51, 39.31, 56.04, 56.24, 103.78, 107.67, 110.47, 121.97, 124.95, 128.50, 138.80, 146.31, 148.40, 150.35, 162.26; MS m/e 311 (M^+, 100), 296 (61.0); Anal. Calcd for $C_{19}H_{21}NO_3$ (311): C, 73.27; H, 6.80; N, 4.52%. Found: C, 72. 99; H, 6.69; N, 4.49%.

2,3-Dimethoxy-5,6,9,10-tetrahydrobenzo[*a*]naphtho[2,1-*g*]quinolizine-4-one (5i): White crystalline solid; mp 120-121°C; Yield 1.40g (78%); IR (KBr): 2927, 1666, 1508, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.87 (t, J = 6.0 Hz, 2H, CH_2), 2.97 (t, J = 6.0 Hz, 2H, CH_2), 3.18 (t, J = 6.1 Hz, 2H, CH_2), 3.91 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 4.38 (t, J = 6.1 Hz, 2H, NCH_2), 6.72 (s, 1H, ArH), 6.98 (s, 1H, H-15), 7.11 (s, 1H, ArH), 7.31- 7.33 (m, 3H, ArH), 8.03 (d, J = 8.8 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.12, 29.15, 29.26, 47.42, 56.07, 56.22, 98.08, 102.43, 107.55, 110.32, 110.32, 110.91, 120.00, 125.10, 126.41, 126.79, 130.15, 135.71, 136.60, 139.58, 148.79, 149.93, 162.19; MS m/e 359 (M^+, 6), 134 (100); Anal. Calcd for $C_{23}H_{21}NO_3$ (359.43): C, 76.86; H, 5.89; N, 3.90%. Found: C, 76.99; H, 5.79; N, 4.01%.

9,10-Dimethoxy-2-phenyl-1,4,6,7-tetrahydro-11bH-benzo[*a*]quinolizine (6b): White solid; mp 139-140°C; Yield 1.30g (81%); IR (KBr): 3019, 1513, 1217 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.57-2.65 (m, 2H, CH_2), 2.98-3.24 (m, 4H, CH_2), 3.59 (d, J = 10.6 Hz, 1H, CH), 3.87 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.99 (t, J = 7.1 Hz, 2H, NCH_2), 6.14 (s, 1H, C=CH), 6.62 (s, 1H, ArH), 6.74 (s, 1H, ArH), 7.24- 7.28 (m, 1H, ArH), 7.32-7.36 (m, 2H, ArH), 7.42-7.44 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.07, 29.70, 35.70, 51.12, 55.76, 56.10, 58.84, 108.50, 111.43, 121.88, 125.14, 126.80, 127.13, 127.70, 128.37, 129.85, 135.55, 141.13, 147.50; MS m/e 321 (M^+, 45.3), 191 (100); Anal. Calcd for $C_{21}H_{23}NO_2$ (321.42): C, 78.47; H, 7.21; N, 4.36%. Found: C, 78.39; H, 7.19; N, 4.30%.

2,3-Dimethoxy-5,6,8,9,10,11,12,13-octahydro-13aH-dibenzo[*a,g*]quinolizine (6f): White solid; mp 101-102°C; Yield 1.40g (76%); IR (KBr): 2927, 1605, 1512 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.44-1.47 (m, 2H, CH_2), 1.65-1.68 (m, 2H, CH_2), 1.83-1.87 (m, 3H, CH_2), 2.02 (t, J = 13.0 Hz, 1H, CH_2), 2.36 (d, J = 19.5 Hz, 1H, CH_2), 2.43 (ddd, J = 3.2, 3.4, 4.2 Hz, 1H CH_2), 2.52 (d, J = 15.4 Hz, 1H, CH_2), 2.85 (t, J = 19.1 Hz, 1H, CH_2), 2.98 (ddd, J = 4.12, 5.6, 6.08 Hz, 1H, CH_2), 3.06 (d, J = 15.6 Hz, 1H, CH_2), 3.34 (dd, J = 3.9, 10.7 Hz, 1H, CH), 3.85 (s, 6H, OCH_3), 3.97 (t, J = 7.6 Hz, 2H, CH_2), 6.58 (s, 1H, ArH) 6.66 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.32, 22.81, 27.31, 29.04, 29.46, 38.27, 51.26, 55.82, 56.02, 59.28, 59.52, 108.44, 111.30, 126.64, 126.81, 126.99, 130.29, 147.31; MS m/e 299 (M^+, 100), 284 (19.0); Anal. Calcd for $C_{19}H_{25}NO_2$ (299.42): C, 76.22; H, 8.42; N, 4.68%. Found: C, 76.45; H, 8.61; N, 4.71%.