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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

J. Am. Chem. Soc., 1998, 120(12), 2817-2825, DOI:[10.1021/ja973846k](https://doi.org/10.1021/ja973846k)

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SUPPORTING INFORMATION

Total Synthesis of Roseophilin

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Instrumentation and Spectra Formats. NMR: Spectra were recorded on a Bruker AC 200, AMX 300, AMX 400 or DMX 600 spectrometer in the solvents indicated. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. IR: Nicolet FT-7199, wavenumbers in cm^{-1} . MS: Varian CH-5 (70 eV); HR-MS: Finnigan MAT SSQ 7000 (70 eV). Elemental analyses: Dornis & Kolbe, Mülheim.

tert-Butyl-(2-chloromethyl-allyloxy)-dimethylsilane (5). MS: m/z (rel. intensity) 165 (37), 164 (14), 163 (100), 127 (42), 125 (27), 123 (74), 95 (41), 93 (84), 75 (12), 73 (25), 57 (43), 41 (15). IR: 3084, 2956, 2930, 2886, 2858, 1656, 1258, 1115, 1089, 915, 846, 777 cm^{-1} .

1-[2-(tert-Butyldimethylsilyloxymethyl)-allyl]-tetrahydrothiophenium tetrafluoroborate (6). MS (ESI/pos): m/z (rel. intensity) 633 ($[2\text{M}^+-\text{BF}_4]$, 20), 273 ($[\text{M}^+-\text{BF}_4]$, 100). IR (KBr): 2956, 2931, 2887, 2859, 1652, 1474, 1462, 1431, 1255, 1112, 1059, 843, 777 cm^{-1} .

{2-[3-(8-Bromooctyl)-oxiranyl]-allyloxy}-tert-butyldimethylsilane (7). MS: m/z (rel. intensity) 350 (14), 349 (64), 348 (14), 347 (62), 157 (19), 144 (11), 143 (87), 127 (13), 113 (12), 109 (14), 107 (20), 105 (11), 95 (23), 93 (33), 81 (26), 79 (23), 75 (100), 73 (48), 69 (26), 67 (23), 59 (12), 57 (18), 55 (45), 43 (16), 41 (27), 29 (10). IR: 2929, 2856, 1656, 1471, 1463, 1389, 1255, 1107, 1085, 911, 838, 777 cm^{-1} .

Pyrone 17. MS: *m/z* (rel. intensity) 249 (17), 248 ($[M^+]$, 100), 163 (14), 151 (18), 150 (11), 149 (14), 138 (12), 137 (31), 136 (17), 135 (15), 124 (33), 123 (24), 122 (21), 121 (14), 108 (12), 107 (15), 95 (19), 94 (19), 91 (14), 81 (12), 79 (20), 77 (15), 67 (18), 66 (19), 65 (13), 55 (35), 43 (12), 41 (38), 39 (17), 29 (13), 27 (11). IR (KBr): 2925, 2849, 1707, 1695, 1647, 1565, 1256 cm^{-1} .

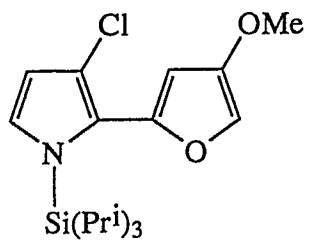
5-Bromo-4-chloro-1-(toluene-4-sulfonyl)-1H-pyrrole-2-carboxylic acid methyl ester (27). MS: *m/z* (rel. intensity) 241 (15), 239 (62), 237 ($[M^+]$, 47), 209 (25), 207 (100), 206 (18), 205 (76). IR (KBr): 3250, 1697, 1441, 1404, 1251, 1215, 759 cm^{-1} .

2-Bromo-3-chloro-1-(toluene-4-sulfonyl)-1H-pyrrole (28). MS: *m/z* (rel. intensity) 335 (19), 333 ($[M^+]$, 14), 155 (76), 91 (100), 65 (18). IR (KBr): 3148, 3123, 1595, 1533, 1450, 1374, 1207, 1185, 1134, 669 cm^{-1} .

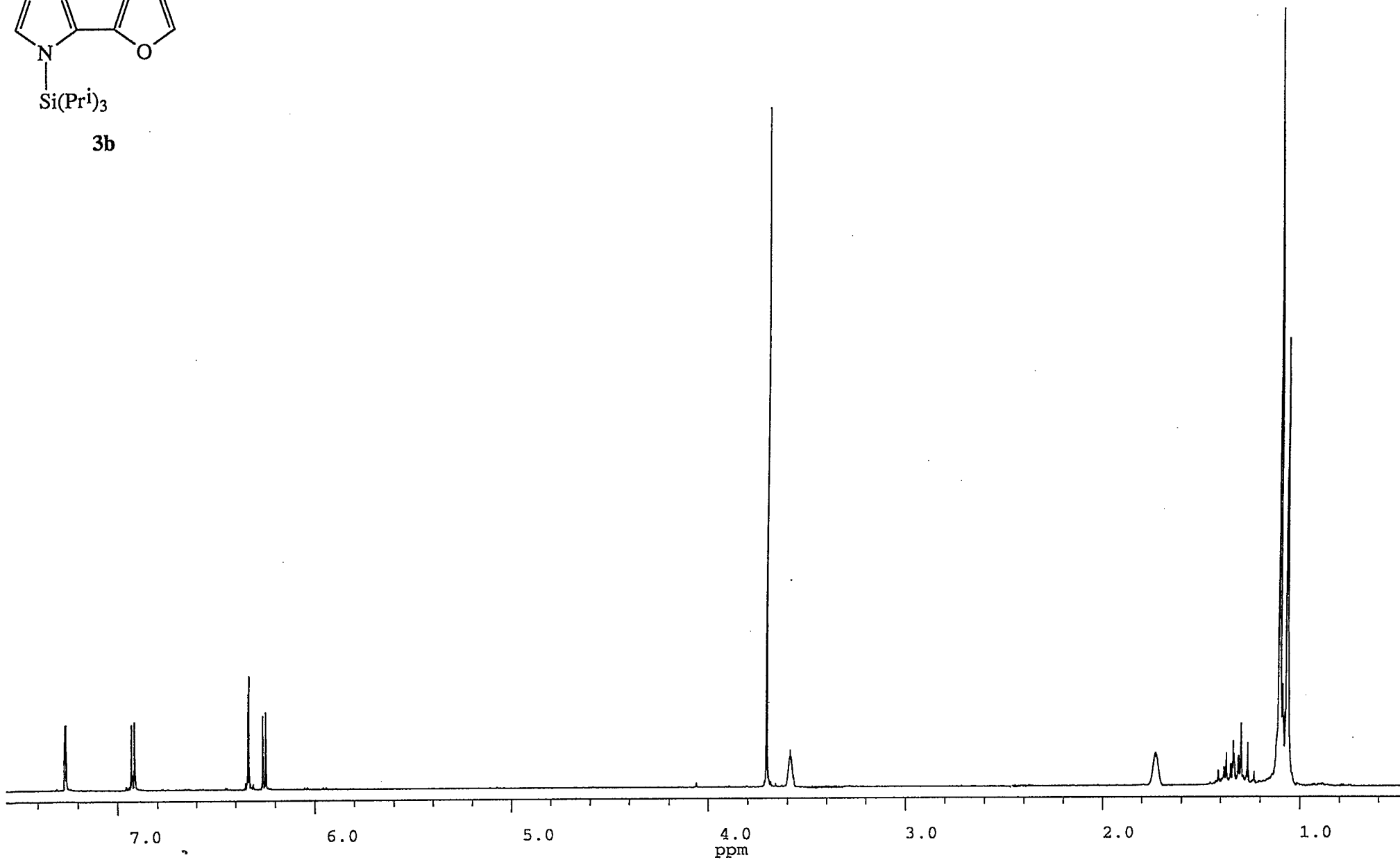
4-(tert-Butyldimethylsilyloxy)-3,3-dimethoxybutanoic acid (25a). MS: *m/z* (rel. intensity) 247 (11), 189 (66), 145 (66), 133 (100), 115 (12), 89 (85), 74 (25), 73 (26), 59 (16). IR: 3500-2500, 2955, 2931, 2858, 1715, 1258, 1130, 1073, 840, 778 cm^{-1} .

Ketopyrrole 29. MS: *m/z* (rel. intensity) 458 (19), 428 (13), 426 (30), 372 (30), 371 (15), 370 (78), 284 (38), 283 (15), 282 (100), 184 (14), 155 (54), 147 (32), 145 (24), 91 (54), 89 (37), 75 (10), 73 (29), 59 (10). IR 2954, 2930, 2857, 1683, 1402, 1379, 1176, 1128, 1113, 1044, 838, 671 cm^{-1} .

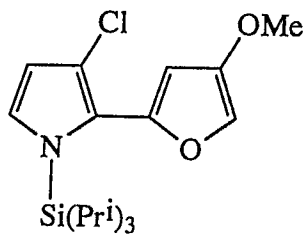
3-Chloro-2-(4-methoxyfuran-2-yl)-1-triisopropylsilyl-1H-pyrrole (3b). MS: *m/z* (rel. intensity) 355 (39), 354 (27), 353 ($[M^+]$, 100), 318 (31), 312 (16), 311 (10), 310 (43), 295 (14), 286 (17), 276 (11), 275 (32), 115 (20), 87 (14), 73 (19), 59 (28). IR: 2953, 2867, 1628, 1570, 1454, 1389, 1263, 1136, 1117, 1028, 979, 884, 801, 689, 652, 614 cm^{-1} .



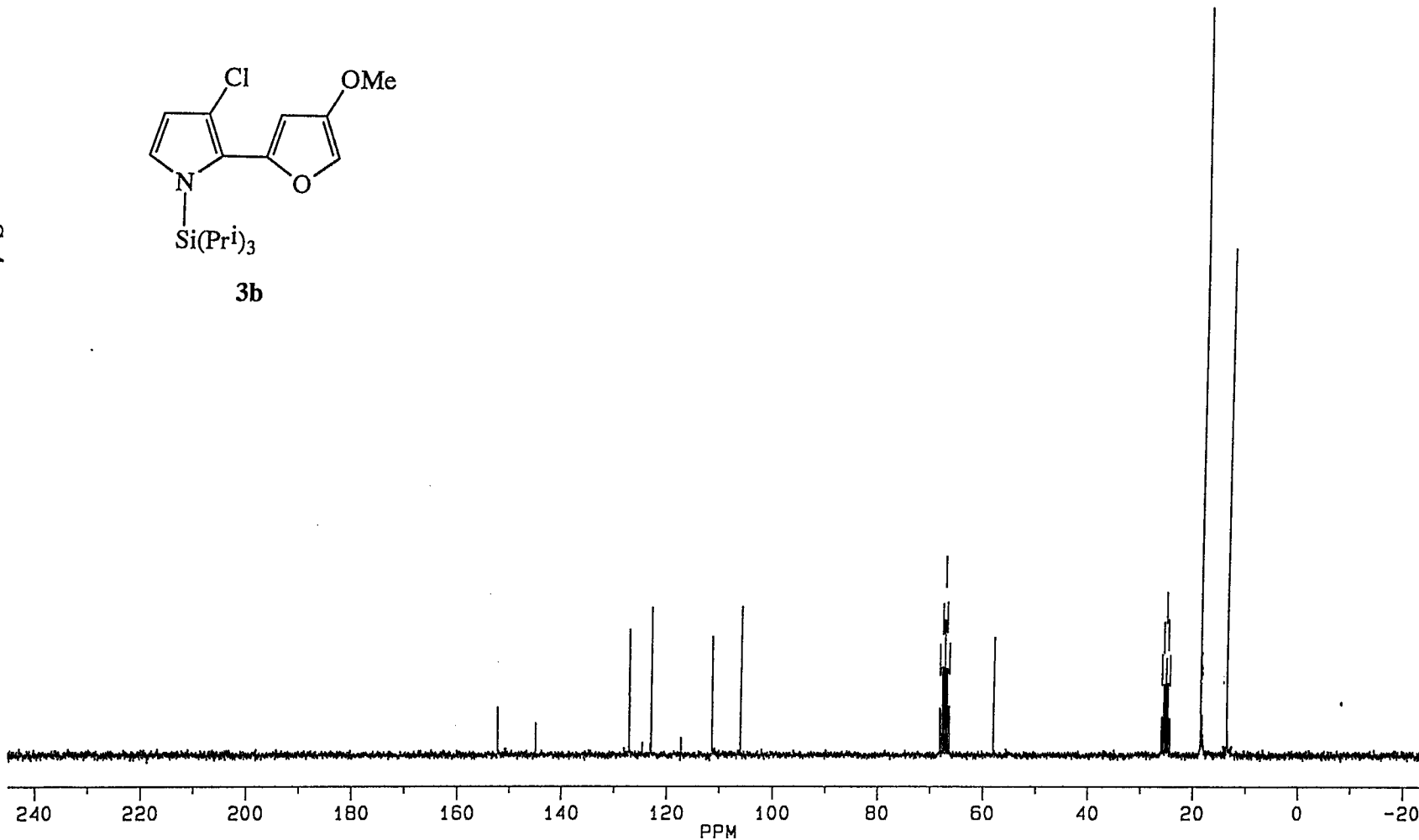
3b



S-4



3b



~~BRUKER~~

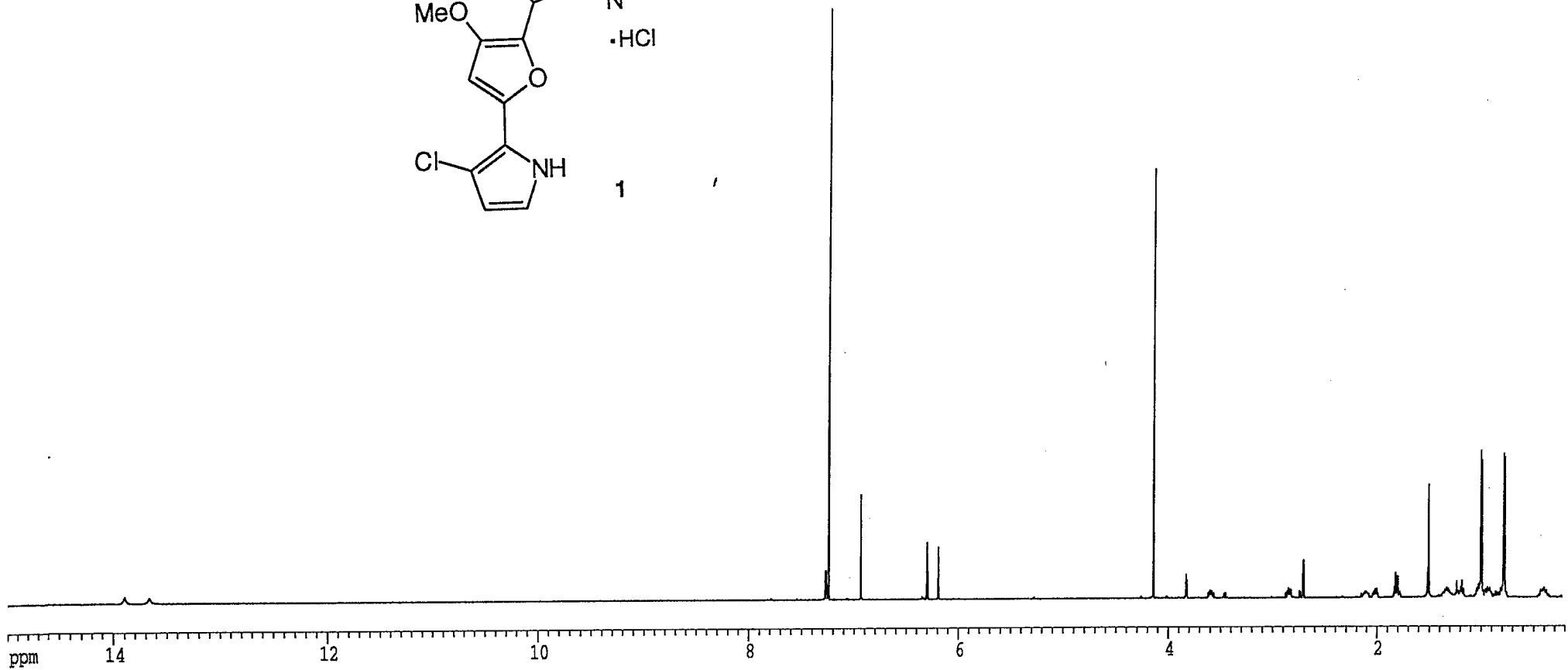
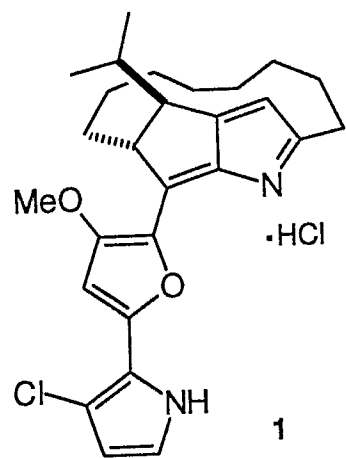
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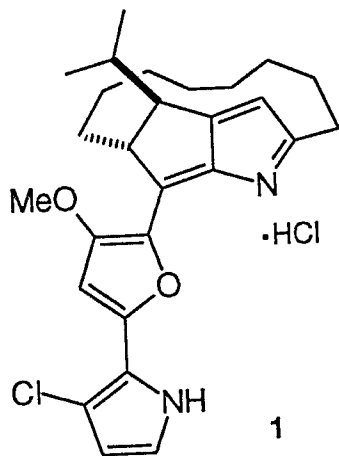
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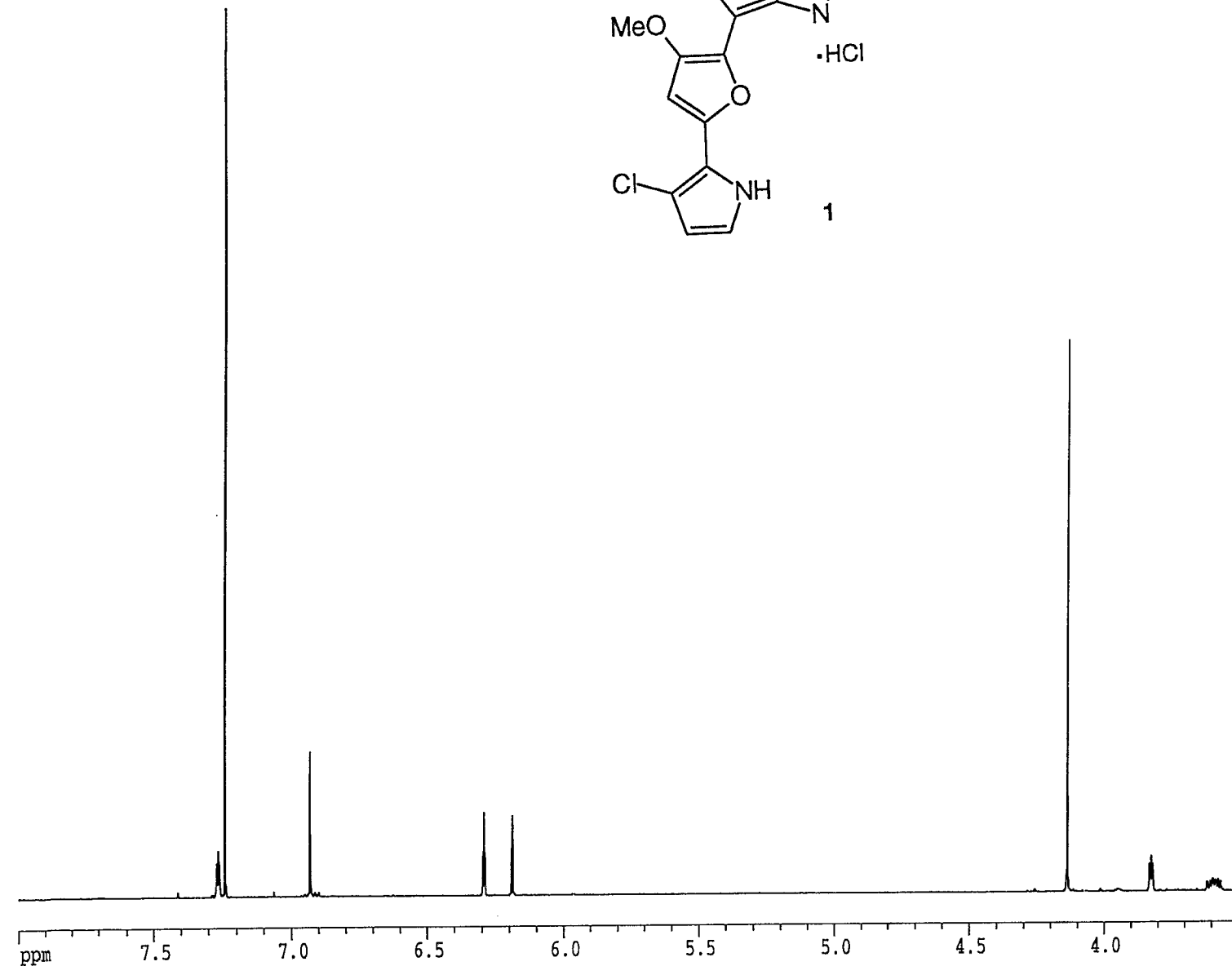


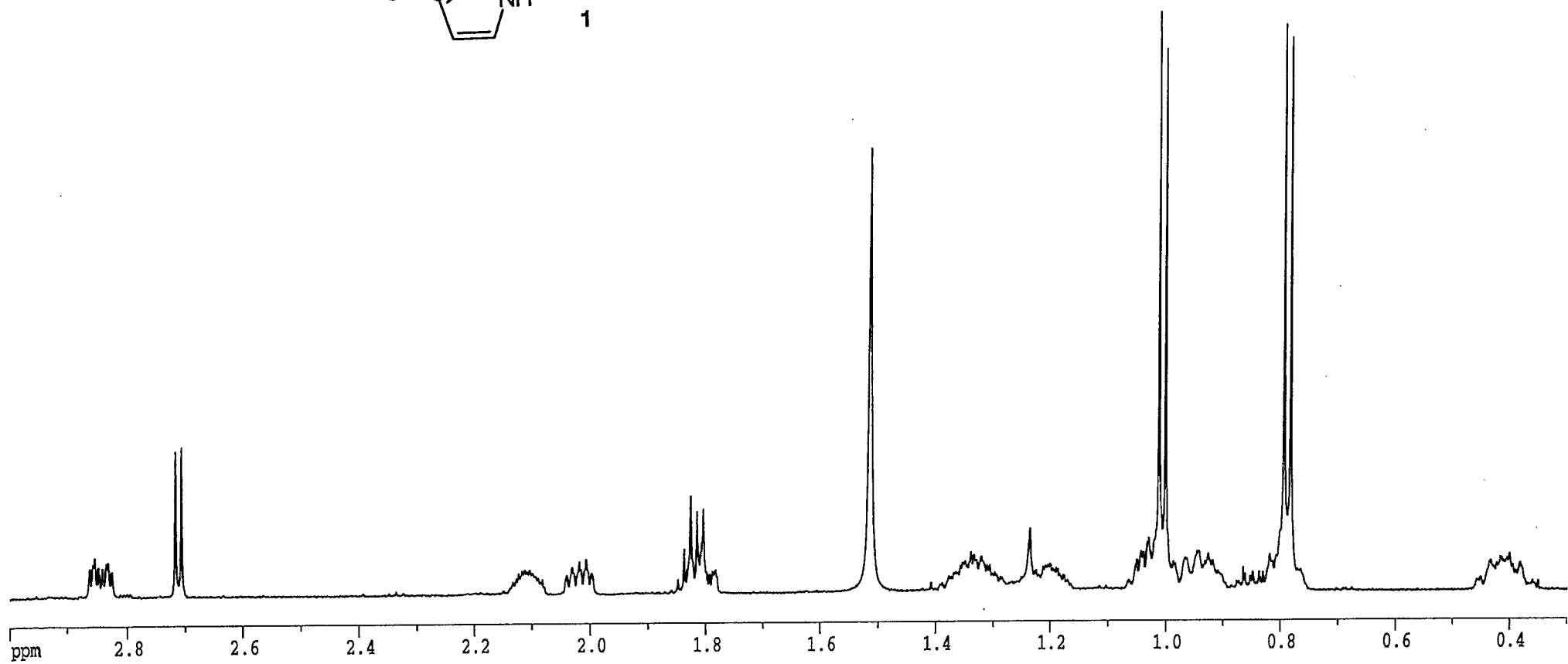
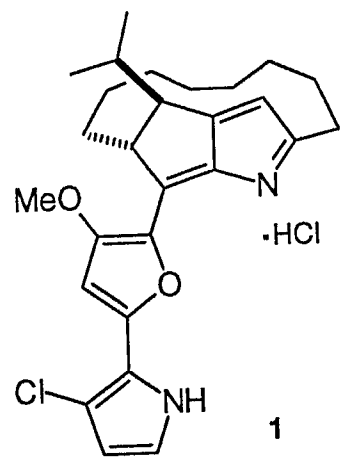
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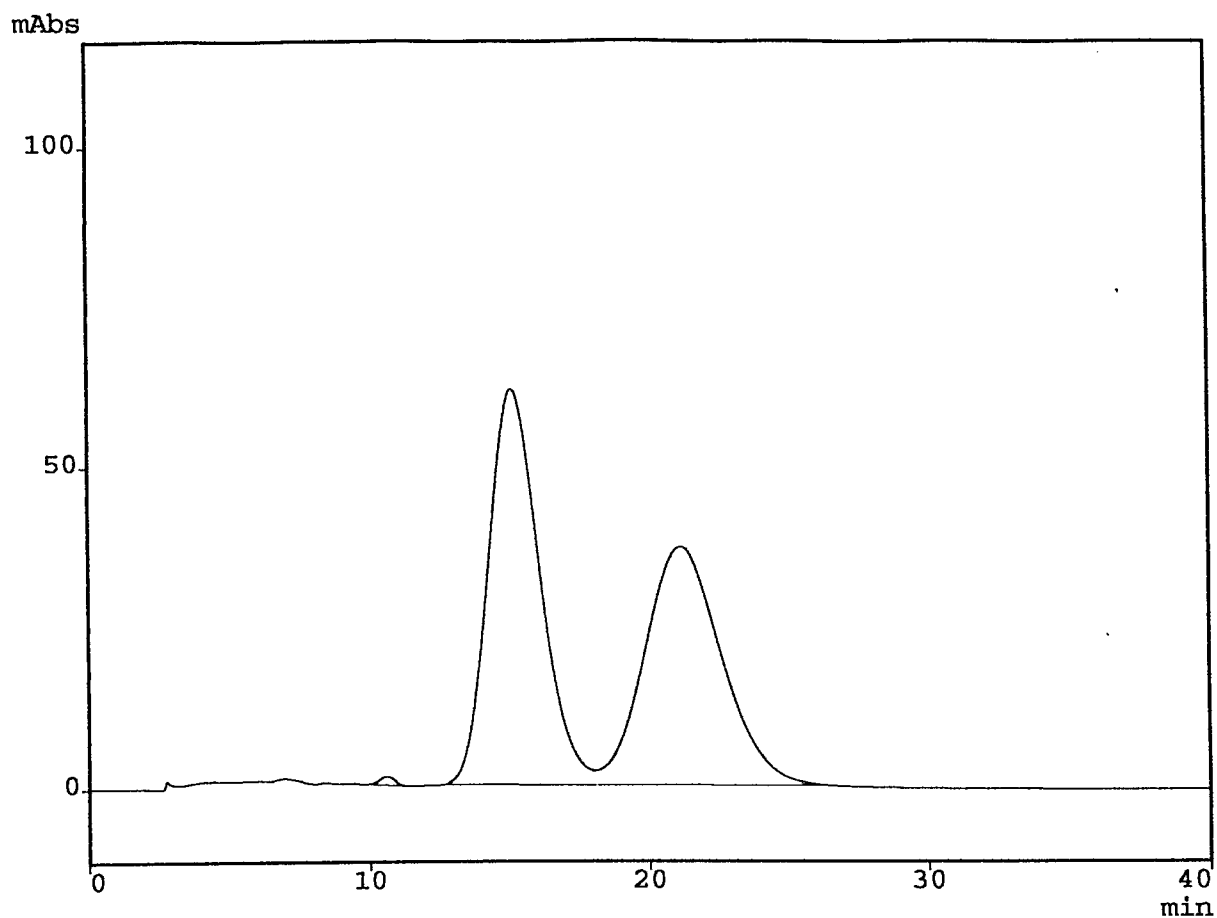
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 F2 2100.77 Hz
 PPMCM 0.22500 ppm/cm
 HZCM 135.04950 Hz/cm





HPLC Separation of Racemic Roseophilin (Shimadzu LC-10A; Chiraspher column: 250 mm, \varnothing 4.6 mm; eluent: n-heptane/*i*-propanol/triethylamine = 80/20/0.1; flow rate: 0.5 mL/min; T = 293K; pressure: 2.5 MPa; detection: DAD, 300 nm):



HPLC of Natural Roseophilin (conditions as above):

