Total synthesis of flustramine C via dimethylallyl rearrangement

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Supporting Information: experimental procedures and characterization

General. NMR spectra were recorded on a Varian VRX 400S (399.9 MHz *resp.* 100.6 MHz) spectrometer, with the solvent used as internal standard. Mass spectra were recorded on Finnigan MAT95Q and Varian MAT-311 spectrometers. IR and UV spectra were recorded on Perkin-Elmer PE 1600 FT-IR and Perkin-Elmer UV/Vis-spectrometer Lambda 16, respectively. HPLC isolations were performed using Varian Prep Star 218, equipped with a Varian Pro Star 320 UV/Vis detector. A Merck LiChroprep RP-18 (25–40 μm, 250 × 210) semipreparative HPLC column was used. Elemental analyses were obtained from the Microanalytical Laboratory of the Faculty of Chemistry and Pharmacy (LMU Munich).

***N*$_b$-Formyl-*N*$_b$-methyltryptamine.** A mixture of Ac_2O and HCO_2H (19.0 ml, 1:1) was stirred at 60 °C for 1 h. After cooling to rt a solution of *N*$_b$-methyltryptamine (**4**, 10.0 g, 57.4 mmol) in DCM (100 ml) was added dropwise. After 90 min the reaction mixture was added to conc. NaOH (150 ml) and ice (150 g). The alkaline mixture was diluted with DCM (300 ml) and the aqueous layer was extracted twice with DCM (100 ml). The combined organic layers were washed with 2 M HCl (100 ml) and 3x with water, dried over Na_2SO_4, filtered and concentrated in vacuo. The resulting viscous oil was dried further by stirring at 70 °C in high vacuum. Et_2O was added and concentrated in vacuo, affording the product (10.4 g, 51.7 mmol, 90%) as a brownish, semicrystalline oil. R_f (silica, EtOAc) = 0.3. Ratio of rotamers in

$CDCl_3$: 1.6:1. Major rotamer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (s, 1 H, 1-H), 7.73 (s, 1 H, C*H*O), 7.55 (d, ^3J = 7.8 Hz, 1 H, 7-H), 7.34 (d, ^3J = 8.0 Hz, 1 H, 4-H), 7.19 (dd, ^3J = 7.8, 7.0 Hz, 1 H, 6-H), 7.13 (dd, ^3J = 8.0, 7.0 Hz, 1 H, 5-H), 6.90 (s, 1 H, 2-H), 3.51 (m, 2 H, 2'-H), 2.98 (m, 2 H, 1'-H), 2.93 (s, 3 H, NCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.4 (*C*HO), 136.9 (C-7a), 127.7 (C-3a), 122.9 (C-2), 122.5 (C-6), 119.8 (C-5), 118.9 (C-7), 113.3 (C-3), 111.8 (C-4), 50.5 (C-2'), 30.1 (CH_3), 24.7 (C-1'). Minor rotamer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (s, 1 H, 1-H), 8.04 (s, 1 H, C*H*O), 7.64 (d, ^3J = 7.8 Hz, 1 H, 7-H), 7.34 (d, ^3J = 8.0 Hz, 1 H, 4-H), 7.16 (dd, ^3J = 7.7, 7.0 Hz, 1 H, 6-H), 7.10 (dd, ^3J = 7.7, 7.0 Hz, 1 H, 5-H), 6.98 (s, 1 H, 2-H), 3.66 (m, 2 H, 2'-H), 3.00 (m, 2 H, 1'-H), 2.87 (s, 3 H, NCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2 (*C*HO), 136.8 (C-7a), 127.2 (C-3a), 122.6 (C-2), 122.3 (C-6), 119.7 (C-5), 118.5 (C-7), 112.7 (C-3), 111.6 (C-4), 45.4 (C-2'), 35.4 (N*C*H$_3$), 23.2 (C-1'). MS (EI, 70 eV): *m/z* (%) = 202 (8) [M^+], 143 (78), 130 (100), 103 (5), 77 (5). HRMS (EI): calcd. 202.1106 ($C_{12}H_{14}N_2O$), found 202.1097. IR (KBr): $\tilde{\nu}$ = 3275 cm^{-1}, 3010, 2964, 2934, 2884, 1658, 1617, 1492, 1451, 1434, 1397, 1368, 1350, 1335, 1249, 1230, 1179, 1099, 1076, 1061, 1008, 932, 876, 810, 766, 756, 628, 427. UV/Vis (CH_3CN): λ_{max} (ε) = 289 nm (5257 mol^{-1}dm^{3}cm^{-1}), 280 (6165), 222 (36416). Calcd. for $C_{17}H_{22}N_2O$: C 71.26, H 6.98, N 13.85; found C 71.15, H 6.95, N 13.70.

***N*-{2'-[2-(1'',1''-Dimethyl-allyl)-1*H*-indol-3-yl]-ethyl}-*N*-methylformamide (5).** To a solution of N_b-Formyl-N_b-methyltryptamine (2.02 g, 10.0 mmol) in THF (36 ml) and Et_3N (1.66 ml, 12.0 mmol) was added *t*-BuOCl (1.36 ml, 12.0 mmol) at -78 °C. The colorless solution was stirred for 30 min at -78 °C, before a freshly prepared solution of prenyl-9-BBN (0.5 M, 40.0 ml, 20.0 mmol) in THF was added dropwise. It proved to be beneficial, if 1,1-dimethylallene and 9-BBN-H were allowed to react for 18 h at room temperature before use. After 30 min the yellow solution was allowed to warm to rt and was stirred for 1 h. Aqueous NaOH (3 M, 10 ml) and H_2O_2 (30%, 10 ml) were added dropwise. The mixture was stirred at

rt for 1 h and diluted in Et_2O (400 ml). The organic layer was washed three times with semisaturated solution of NaCl, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residual oil was washed twice with Et_2O (10 ml) affording **5** (2.16 g, 8.0 mmol, 80%) as colorless solid. Further purification was possible by recrystallisation in *n*-heptane/toluene (5:1). Mp.: 146-147 °C. R_f (silica, *iso*-hexane/EtOAc (1:1)) = 0.4. Ratio of rotamers in $CDCl_3$: 1.6:1. Major rotamer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (s, 1 H, 1-H), 8.05 (s, 1 H, C*H*O), 7.65 (d, ^3J = 7.2 Hz, 1 H, 7-H), 7.46 (d, ^3J = 7.3 Hz, 1 H, 4-H), 7.35-7.08 (m, 2 H, 6-H, 5-H), 6.13 (dd, ^3J = 17.4, 10.5 Hz, 1 H, 2"-H), 5.23-5.14 (m, 2 H, 3"-H), 3.49-3.42 (m, 2 H, 2'-H), 3.10-3.04 (m, 2 H, 1'-H), 2.99 (s, 3 H, NCH_3), 1.54 (s, 6 H, 4"-H, 5"-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6 (*C*HO), 145.8 (C-2"), 140.2 (C-2), 134.3 (C-3a), 129.1 (C-7a), 121.6 (C-6), 119.4 (C-7), 117.5 (C-4), 111.9 (C-3"), 110.5 (C-5), 106.7 (C-3), 50.2 (C-2'), 38.8 (C-1"), 35.0 (N*C*H$_3$), 27.7 (C-4", C-5") 25.0 (C-1'). Minor rotamer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (s, 1 H, C*H*O), 8.09 (s, 1 H, 1-H), 7.64 (d, ^3J = 6.8 Hz, 1 H, 7-H), 7.46 (d, ^3J = 6.9 Hz, 1 H, 4-H), 7.35-7.08 (m, 2 H, 6-H, 5-H), 6.14 (dd, ^3J = 17.4, 10.5 Hz, 1 H, 2"-H), 5.23-5.14 (m, 2 H, 3"-H), 3.58-3.52 (m, 2 H, 2'-H), 3.10-3.04 (m, 2 H, 1'-H), 2.96 (s, 3 H, NCH_3), 1.57 (s, 6 H, 4"-H, 5"-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.4 (*C*HO), 145.9 (C-2"), 139.9 (C-2), 134.2 (C-3a), 129.5 (C-7a), 119.9 (C-6), 119.4 (C-7), 117.5 (C-4), 112.0 (C-3"), 110.8 (C-5), 107.6 (C-3), 45.5 (C-2'), 38.9 (C-1"), 30.0 (N*C*H$_3$), 27.6 (C-4", C-5"), 22.7 (C-1'). MS (EI, 70 eV): *m/z* (%) = 270 (100) [M^+], 211 (79), 199 (43), 196 (53), 183 (95), 168 (78), 154 (10), 130 (7), 72 (4), 44 (8). HRMS (EI): calcd. 270.1732 ($C_{17}H_{22}N_2O$, [M^+]), found 270.1757. IR (KBr): $\tilde{\nu}$ = 3303 cm^{-1}, 3053, 2968, 2930, 2872, 1654, 1578, 1490, 1460, 1434, 1392, 1360, 1340, 1297, 1242, 1168, 1147, 1068, 1045, 1005, 914, 742, 724, 688, 583, 533, 423. UV/Vis (CH_3CN): λ_{max} (ε) = 283 nm (3670 mol^{-1}dm^{3}cm^{-1}), 226 (18949). Calcd. for $C_{17}H_{22}N_2O$: C 75.52, H 10.36, N 8.20; found C 75.12, H 10.20, N 8.20.

Flustrabromine (6). To a stirred solution of **5** (2.16 g, 8.0 mmol) in HOAc-HCO_2H (64 ml, 3:1) was added a solution of NBS (1.46 g, 8.2 mmol) in HOAc-HCO_2H (40 ml, 3:1). The solution was stirred at rt for 30 min, before the solution was added to a mixture of Et_2O (250 ml) and ice (250 g). It was diluted with Et_2O (300 ml). The organic layer was washed twice with H_2O (200 ml) and with aqueous NaOH (1 M, 150 ml). It was washed twice with H_2O (200 ml), dried over Na_2SO_4, filtered and concentrated in vacuo. The crude solid was washed 3 x with MeOH (10 ml). Remaining solvent was removed under reduced pressure, affording **6** (1.71 g, 4.9 mmol, 61%) and 4-brominated side product as a colorless solids which were separated by chromatography. R_f = (silica, *iso*-hexane/EtOAc (1:1)): 0.43. Ratio of rotamers in $CDCl_3$: 1:0.8. Mp.: 218-220 °C. Major rotamer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (s, 1 H, C*H*O), 7.91 (s, 1 H, 1-H), 7.49 (d, ^3J = 8.4 Hz, 1 H, 4-H), 7.46 (d, ^4J = 1.7 Hz, 1 H, 7-H), 7.20 (dd, ^3J = 8.4 Hz, ^{4}J = 1.7 Hz, 1 H, 5-H), 6.13-6.08 (dd, ^3J = 17.5, 10.4 Hz, 1 H, 2"-H), 5.21-5.15 (dd, ^3J = 17.5 Hz, ^2J = 1.2 Hz, 1 H, 3"-H_E), 5.21-5.15 (dd, ^3J = 10.4 Hz, ^2J = 1.2 Hz, 1 H, 3"-H_Z), 3.53-3.38 (m, 2H, 2'-H), 3.06-2.99 (m, 2H, 1'-H), 2.96 (s, 3H, NC*H*$_3$), 1.52 (s, 6H, 4"-H, 5"-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.5 (*C*HO), 145.5 (C-2"), 140.9 (C-2), 135.0 (C-7a), 128.1 (C-3a), 122.9 (C-5), 119.9 (C-4), 115.0 (C-6), 113.7 (C-7), 112.4 (C-3"), 107.1 (C-3), 50.2 (C-2'), 38.9 (C-1"), 30.1 (N*C*H$_3$), 27.6 (C-5", C-4"), 24.9 (C-1'). Minor rotamer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (s, 1 H, C*H*O), 8.00 (s, 1 H, 1-H), 7.43 (d, ^4J = 1.7 Hz, 1 H, 7-H), 7.29 (d, ^3J = 8.4 Hz, 1 H, 4-H), 7.19 (dd, ^3J = 8.4 Hz, ^{4}J = 1.7 Hz, 1 H, 5-H), 6.13-6.08 (dd, ^3J = 17.6, 10.4 Hz, 1 H, 2"-H), 5.21-5.15 (dd, ^3J = 17.6 Hz, ^2J = 1.2 Hz, 1 H, 3"-H_E), 5.21-5.15 (dd, ^3J = 10.4 Hz, ^2J = 1.2 Hz, 1 H, 3"-H_Z), 3.53-3.38 (m, 2H, 2'-H), 3.06-2.99 (m, 2H, 1'-H), 2.95 (s, 3H, NC*H*$_3$), 1.55 (s, 6H, 4"-H, 5"-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5 (*C*HO), 145.5 (C-2"), 140.5 (C-2), 134.9 (C-7a), 128.5 (C-3a), 122.7 (C-5), 119.5 (C-4), 114.9 (C-6), 113.4 (C-7), 112.3 (C-3"), 108.0 (C-3), 45.5 (C-2'), 39.0 (C-1"), 35.1 (N*C*H$_3$), 27.6 (C-5", C-4"), 22.6 (C-1'). MS (FAB+, NBA): *m/z* (%) = 371/373 (6/6) [M^+ + Na], 349/351 (36/33) [M^+ + 1], 276/278 (29/26) [$C_{14}H_{14}BrN^+$ + 1]. HRMS (EI): calcd.

348.0837 ($C_{17}H_{21}{}^{79}BrN_2O$, [$M^+$]), found 348.0838. IR (KBr): $\tilde{\nu}$ = 3435 cm^{-1}, 2970, 2930, 2872, 1657, 1571, 1463, 1394, 1335, 1285, 1225, 1193, 1165, 1070, 909, 861, 803, 725, 696, 591. UV/Vis (CH_3CN): λ_{max} (ε) = 289 nm (5756 $mol^{-1}dm^3cm^{-1}$), 232 (30906).

Deformylflustrabromine (1). To a solution of flustrabromine (**6**, 1.59 g, 5.0 mmol) in EtOH (400 ml) was added NaOH (32%, 15.3 ml). The reaction mixture was refluxed for 24 h, cooled to rt, and concentrated in vacuo to a volume of 50 ml. It was diluted with Et_2O (500 ml), washed four times with H_2O (100 ml), dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure affording **1** as a yellowish semi-crystalline oil (1.53 g, 4.8 mmol, 96%) which could be recrystallized from *iso*-hexane. R_f (silica, $CHCl_3$/MeOH (4:1)) = 0.4. ^{1}H NMR (400 MHz, CD_3OD): δ = 7.47 (d, ^4J = 1.6 Hz, 1 H, 7-H), 7.31 (d, ^3J = 8.4 Hz, 1 H, 4-H), 7.03 (dd, ^3J = 8.4 Hz, ^4J = 1.6 Hz, 1 H, 5-H), 6.06 (dd, ^3J = 17.3, 10.6 Hz, 1 H, 2"-H), 5.04 (dd, ^3J = 17.3 Hz, ^2J = 1.1 Hz, 1 H, 3"-H_E), 5.02 (dd, ^3J = 10.6 Hz, ^2J = 1.1 Hz, 1 H, 3"-H_Z), 4.88 (s, 1 H, N*H*), 2.90 (m, 2H, 1'-H), 2.65 (m, 2H, 2'-H), 2.31 (s, 3H, NC*H*$_3$), 1.46 (s, 6H, 4"-H, 5"-H). ^{13}C NMR (400 MHz, CD_3OD): δ = 146.8 (C-2"), 141.2 (C-2), 136.2 (C-7a), 128.7 (C-3a), 121.6 (C-5), 118.6 (C-4), 114.0 (C-6), 113.6 (C-7), 110.9 (C-3"), 108.2 (C-3), 52.5 (C-2'), 48.3 (*C*H_3), 39.1 (C-1"), 27.4 (C-4", C-5"), 24.8 (C-1'). ^{1}H,^{15}N-HMBC (600 MHz, $CDCl_3$): δ = 127 (indole-NH), 30 (side chain NH). MS (EI, 70 eV): *m/z* (%) = 320/322 (1/1) [M^+], 277/279 (26/26), 261/263 (13/8) [$C_{13}H_{14}BrN^+$], 194/196 (1/2) [$C_8H_6BrN^+$], 167 (16). HRMS (EI): calcd. 320.0888 ($C_{16}H_{21}{}^{79}BrN_2$, [M^+]); found 320.0881. IR (KBr): $\tilde{\nu}$ = 3447 cm^{-1}, 3247, 3082, 2969, 2929, 2873, 2800, 2447, 1634, 1612, 1566, 1463, 1413, 1382, 1363, 1336, 1306, 1286, 1217, 1182, 1142, 1100, 1051, 1008, 910, 852, 801, 756, 666, 592. UV/Vis (CH_3CN): λ_{max} (ε) = 297 nm (3989 $mol^{-1}dm^3cm^{-1}$), 289 (4240), 232 (21827).

Flustramine C (2). To a solution of **1** (100 mg, 0.31 mmol) in THF (5 ml) was added NBS (55 mg, 0.31 mmol). The reaction mixture was stirred at rt for 2 h and diluted in diethyl ether (50 ml). The organic layer was washed with 2 N NaOH (10 ml) and twice with water (10 ml),

dried over Na_2SO_4, filtered and concentrated in vacuo. The residual oil was purified by column chromatography (silica, EtOAc) affording **2** (90 mg, 0.28 mmol, 90%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19 (dd, ^3J = 1.1 Hz, ^4J =1.1 Hz, 1 H, 7-H), 6.89 (d, ^3J = 1.1 Hz, 2H, 5-H, 4-H), 5.99 (dd, ^3J = 17.3, 10.8 Hz , 1 H, 12-H), 5.05 (dd, ^3J = 10.8 Hz, ^2J = 1.2 Hz, 1 H, 13-H_Z), 5.03 (dd, ^3J = 17.3 Hz, ^2J = 1.2 Hz, 1 H, 13-H_E), 3.93 (ddd, ^2J = 10.1 Hz, ^3J = 8.8, 6.5 Hz, 1 H, 2-H_a), 3.38 (ddd, ^2J = 10.1 Hz, ^3J = 10.1, 0.9 Hz, 1 H, 2-H_b), 3.00 (s, 3H, NCH_3), 2.32 (ddd, ^2J = 13.0 Hz, ^3J = 6.5, 0.9 Hz, 1 H, 3-H_a), 2.05 (ddd, ^2J = 13.0, 10.1 Hz, ^3J = 8.8 Hz, 1 H, 3-H_b), 0.98 (s, 3H, 10-H), 0.87 (s, 3H, 11-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.1 (C-8a), 163.5 (C-7a), 143.4 (C-12), 137.6 (C-3b), 124.2 (C-4), 122.0 (C-6), 121.9 (C-5), 119.1 (C-7), 113.5 (C-13), 65.8 (C-3a), 59.7 (C-2), 42.9 (C-9), 33.1 (NCH_3), 27.9 (C-3), 22.8 (C-10), 21.6 (C-11). ^{1}H,^{15}N-HMBC (400 MHz, $CDCl_3$): δ = 217 (imine-N), 90 (NMe). MS (EI, 70 eV): *m/z* (%) = 320/318 (24/29) [M^+], 251/249 (100/97) [$C_{11}H_{10}N_2Br^+$], 170 (49) [$C_{11}H_{10}N_2^+$], 129 (21). FTHRMS (ESI+): calcd. 319.0810 ($C_{16}H_{20}N_2{}^{79}Br$, [M^++H]); found 319.0798. IR: $\tilde{\nu}$ = 2917 cm^{-1}, 1632 (s), 1582 (s), 1560 (s), 1452 (m), 1412 (m), 1394 (m), 1364 (w), 1300 (m), 1212 (w), 1153 (w), 1115 (w), 1056 (w), 1003 (w), 916 (w), 898 (w), 864 (m), 802 (w), 730 (w). UV/Vis (CH_3OH): λ_{max} (ε) = 290 nm (7208 $mol^{-1}dm^3cm^{-1}$), 232 (23412).

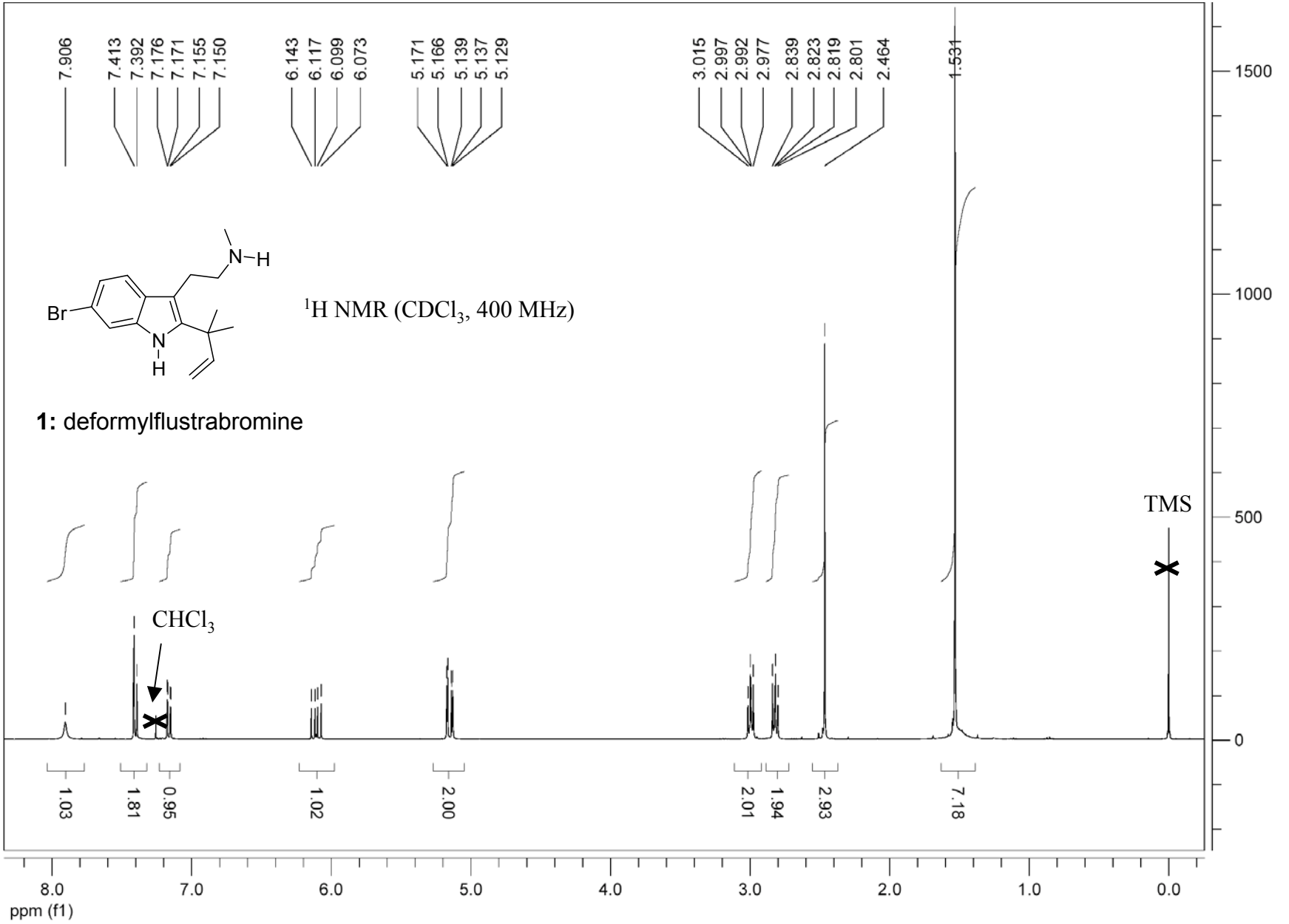
Reaction of deformylflustrabromine with 1 equiv. of *t*BuOCl. To a solution of **1** (100 mg, 0.31 mmol) in dry THF (2.5 ml) and triethylamine (52 µl, 0.37 mmol) was added *t*-BuOCl (35 µl, 0.31 mmol) at -78 °C. The reaction mixture was stirred at -78 °C for 30 min and was allowed to warm slowly to rt. It was diluted in Et_2O (50 ml). The organic layer was washed three times with water (10 ml), dried over Na_2SO_4, filtered and concentrated in vacuo, affording a 4:1 mixture of monochlorinated intermediate **7** and dichlorinated intermediate **11** as colorless oil. Data of *N*-chlorodeformylflustrabromine (**7**): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.92 (br. s, 1 H, NH), 7.43 (d, ^5J = 1.8 Hz, 1 H, 7-H), 7.40 (dd, ^3J = 8.4 Hz, ^5J = 1.8 Hz, 1

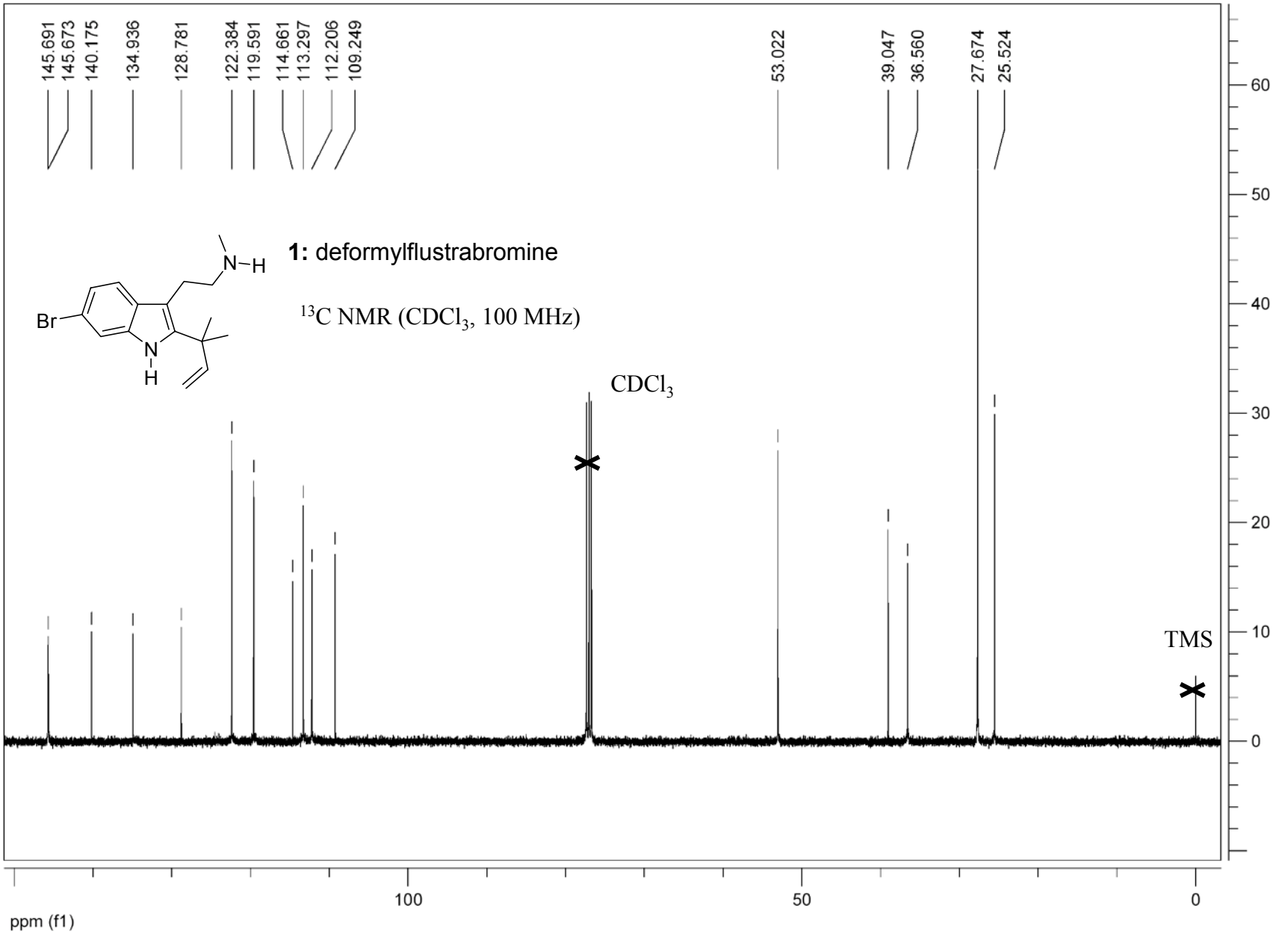
H, 4-H), 7.18 (d, ^3J = 8.4 Hz, 1 H, 5-H), 6.09 (dd, ^3J = 18.0, 10.4 Hz, 1 H, 2''-H), 5.17 (dd, ^3J = 10.4 Hz, ^2J = 1.2 Hz, 1 H, 3''-H_Z), 5.16 (dd, ^3J = 18.0 Hz, ^2J = 1.2 Hz, 1 H, 3''-H_E), 3.17 (m, 2H, 1'-H_2), 3.08 (m, 2H, 2'-H_2), 2.99 (s, 3H, NCH_3), 1.54 (s, 6H, 2 CCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.4 (C2''), 140.5 (C2), 134.9 (C7a), 128.5 (C3a), 122.5 (C5), 119.3 (C4), 114.8 (C6), 113.4 (C7), 112.4 (C3''), 107.8 (C3), 66.4 (C2'), 53.1 (NCH_3), 38.9 (C1''), 27.6 (2 CH_3), 23.8 (C1'). ^{1}H,^{15}N-HMBC (600 MHz, $CDCl_3$): δ = 127 (indole-NH), 105 (side chain N-Cl). FTHRMS (ESI–): calcd. 389.0187 ($C_{16}H_{20}{}^{79}Br^{35}Cl_2N_2$, [M+$Cl^-$]); found 389.0206. The mixture was stored in $CDCl_3$ (2.5 ml) at rt for 12 h. The solution was concentrated in vacuo and diluted with Et_2O (50 ml). The organic layer was washed with aqueous NaOH (2 M, 5 ml), three times with water (10 ml), dried over Na_2SO_4, filtered and concentrated in vacuo, affording flustramine C (**2**, 53 mg, 0.17 mmol, 60%) as a colorless oil. For data of **2** and **11**, see there.

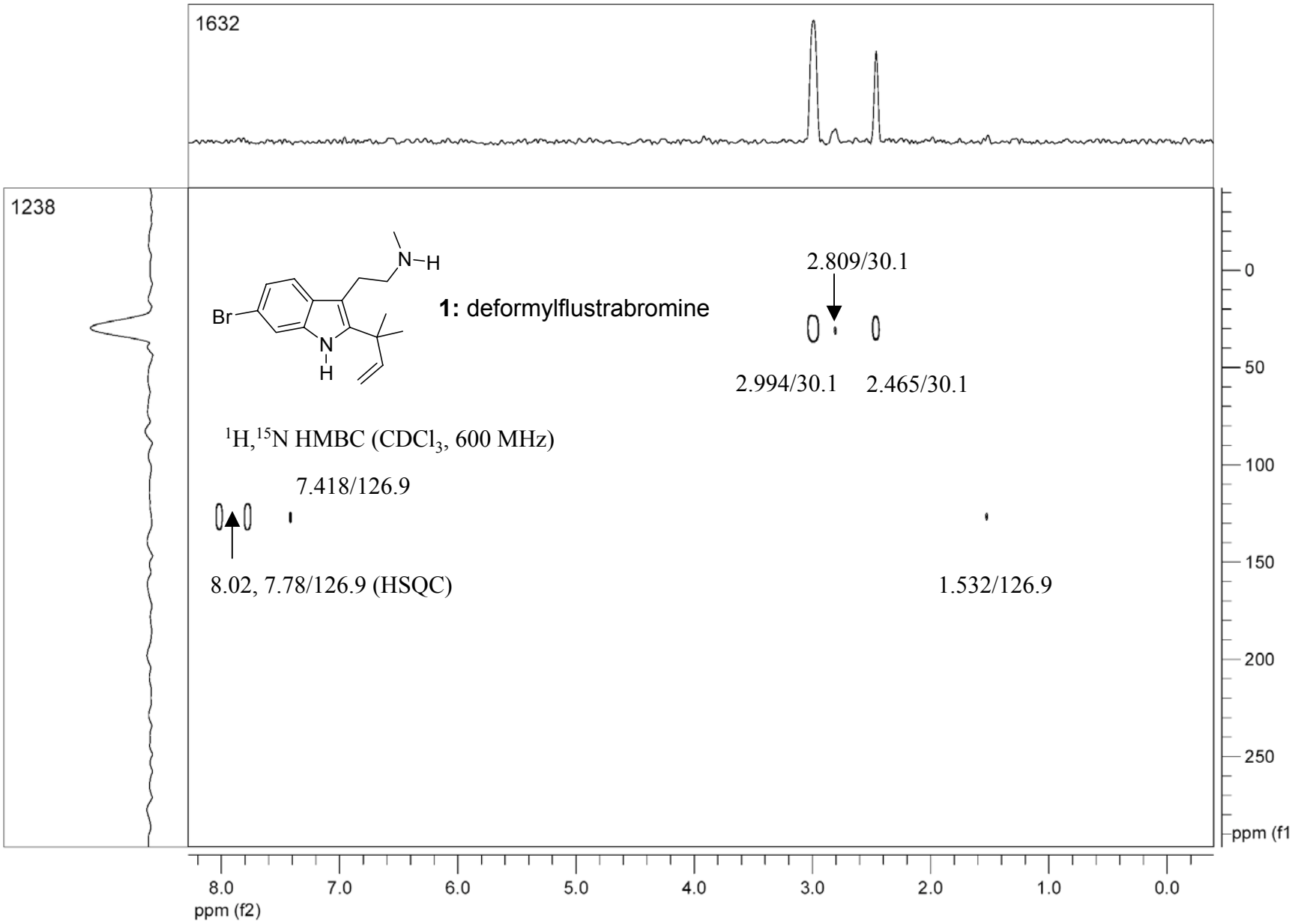
Reaction of deformylflustrabromine with 2 equiv. of *t*BuOCl. To a solution of **1** (550 mg, 1.71 mmol) in dry THF (14 ml) and triethylamine (0.52 ml, 3.77 mmol) was added *t*-BuOCl (0.38 ml, 3.42 mmol) at -78 °C. The reaction mixture was stirred at -78 °C for 30 min and was allowed to warm to rt. It was diluted in Et_2O (150 ml). The organic layer was washed three times with water (30 ml), dried over Na_2SO_4, filtered and concentrated in vacuo, affording chloroindolenine **11** as colorless oil (630 mg, 94 %) which was purified by chromatography (silica gel, petrol ether/EtOAc (15:1)). Data of chloroindolenine **11**: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.66 (d, ^4J = 1.7 Hz, 1 H, 7-H), 7.38 (dd, ^3J = 7.9 Hz, ^4J = 1.7 Hz, 1 H, 5-H), 7.21 (d, ^3J = 7.9 Hz, 1 H, 4-H), 6.37 (dd, ^3J = 17.4, 10.6 Hz, 1 H, 2''-H), 5.26 (dd, ^3J = 17.4 Hz, ^2J = 0.7 Hz, 1 H, 3''-H_E), 5.19 (dd, ^3J = 10.6 Hz, ^2J = 0.7 Hz, 1 H, 3''-H_Z), 2.83 (ddd, ^2J = 13.4 Hz, ^3J = 10.4, 5.1 Hz, 1 H, 1'-H_a), 2.74 (s, 3H, NCH_3), 2.67 (ddd, ^2J = 13.4 Hz, ^3J = 10.4, 4.5 Hz, 1 H, 1'-H_b), 2.30 (ddd, ^2J = 12.9 Hz, ^3J = 10.4, 5.1 Hz, 1 H, 2'-H_a), 2.24 (ddd, ^2J = 12.9 Hz, ^3J = 10.4, 4.5 Hz, 1 H, 2'-H_b), 1.62 (s, 3H, CH_3), 1.59 (s, 3H, CH_3). ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 188.2 (C2), 152.8 (C7a), 143.5 (C2''), 138.5 (C3a), 129.7 (C5), 124.3 (C7), 123.5 (C6), 123.2 (C4), 113.6 (C3''), 71.9 (C3), 60.5 (C2'), 53.1 (NCH_3), 43.7 (C1''), 37.7 (C1'), 28.1 (CCH_3), 27.2 (CCH_3). $^1H,^{15}N$-HMBC (600 MHz, $CDCl_3$): δ = 322 (indolenine-N), 101 (side chain N-Cl). FTHRMS (ESI+): calcd. 389.0187 ($C_{16}H_{20}{}^{79}Br^{35}Cl_2N_2$, [M+$H^+$]), found 389.0199. Chloroindolenine **11** (340 mg, 0.87 mmol) was heated in $CHCl_3$ (10 ml) at 55 °C for 17 h. The solution was concentrated in vacuo and diluted with Et_2O (50 ml). The organic layer was washed with aqueous NaOH (2 M, 25 ml), three times with water (10 ml), dried over Na_2SO_4, filtered and concentrated in vacuo. Column chromatography (silica gel, EtOAc) afforded flustramine C (**2**, 69 mg, 25%) and 5-chloroflustramine C (**13**, 92 mg, 30%) as colorless oils. Data of 5-chloroflustramine C (**13**): ^1H NMR (400 MHz, $CDCl_3$): δ = 7.27 (s, 1 H, 7-H), 7.10 (s, 1 H, 4-H), 5.96 (dd, ^3J = 17.4, 10.8 Hz , 1 H, 12-H), 5.08 (dd, ^3J = 10.8 Hz, ^2J = 1.1 Hz, 1 H, 13-H_Z), 5.04 (dd, ^3J = 17.4 Hz, ^2J = 1.1 Hz, 1 H, 13-H_E), 3.94 (ddd, ^2J = 10.1 Hz, ^3J = 8.8, 6.5 Hz, 1 H, 2-H_a), 3.39 (ddd, ^2J = 10.1 Hz, ^3J = 10.1, 0.9 Hz, 1 H, 2-H_b), 3.00 (s, 3H, NCH_3), 2.34 (ddd, ^2J = 13.1 Hz, ^3J = 6.5, 0.9 Hz, 1 H, 3-H_a), 2.06 (ddd, ^2J = 13.1 Hz, ^3J = 10.1, 8.8 Hz, 1 H, 3-H_b), 0.98 (s, 3H, 10-H), 0.89 (s, 3H, 11-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =187.9 (C8a), 161.8 (C7a), 142.9 (C12), 139.3 (C3b), 124.7 (C4), 124.1 (C5), 121.6 (C6), 120.2 (C7), 114.0 (C13), 66.2 (C3a), 59.7 (C2), 43.0 (C9), 33.1 (NCH_3), 27.8 (C3), 22.8 (C11), 21.6 (C10). MS (EI, 70 eV): *m/z* (%) = 356/354/352 (7/28/22) [M^+], 287/285/283 (27/50/100) [$C_{11}H_{10}N_2BrCl^+$], 204/206 (6/18) [$C_{11}H_9N_2Cl^+$], 169 (14) [$C_{11}H_9N_2^+$]. HRMS (EI): calcd. 352.0342 ($C_{16}H_{19}N_2{}^{79}Br^{35}Cl$), found 352.0320.

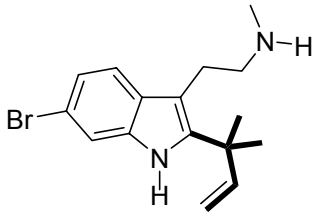
Following pages: NMR and MS spectra of compounds **1**, **2**, **5**, **6, 7, 11, 13**.


7.906
7.413
7.392
7.176
7.171
7.155
7.150
6.143
6.117
6.099
6.073
5.171
5.166
5.139
5.137
5.129
3.015
2.997
2.992
2.977
2.839
2.823
2.819
2.801
2.464
1.531
Br
N
H
N
H
^{1}H NMR ($CDCl_3$, 400 MHz)
1: deformylflustrabromine
TMS
$CHCl_3$
1.03
1.81
0.95
1.02
2.00
2.01
1.94
2.93
7.18
1500
1000
500
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

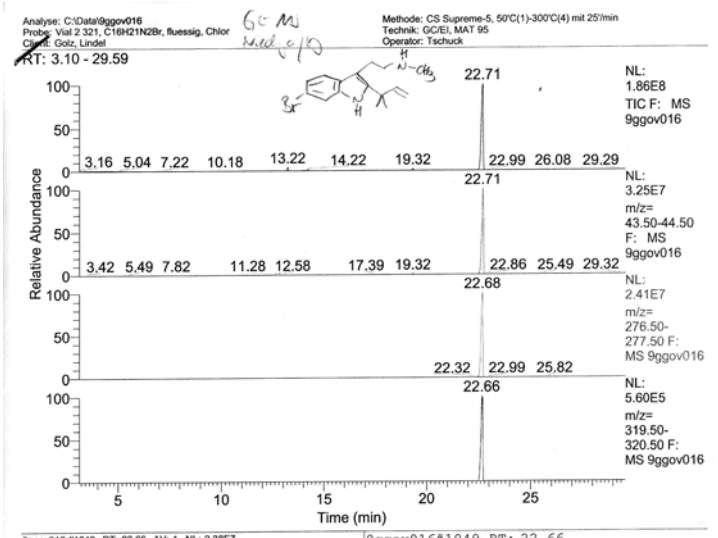

145.691
145.673
140.175
134.936
128.781
122.384
119.591
114.661
113.297
112.206
109.249
53.022
39.047
36.560
27.674
25.524
1: deformylflustrabromine
13C NMR (CDCl3, 100 MHz)
CDCl3
TMS
Br
N
H
N
H
60
50
40
30
20
10
0
100
50
0
ppm (f1)

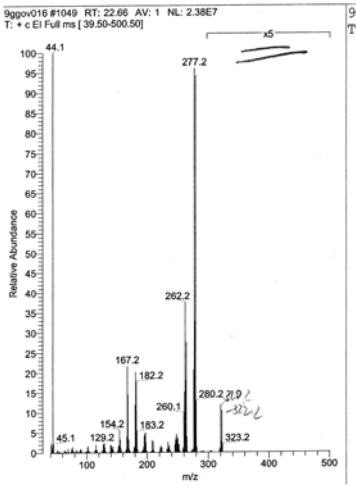

1632
1238
Br
N–H
N
H
1: deformylflustrabromine
2.809/30.1
2.994/30.1
2.465/30.1
$^{1}H,^{15}N$ HMBC ($CDCl_3$, 600 MHz)
7.418/126.9
8.02, 7.78/126.9 (HSQC)
1.532/126.9
0
50
100
150
200
250
ppm (f1
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f2)

HREIMS



1: deformylflustrabromine

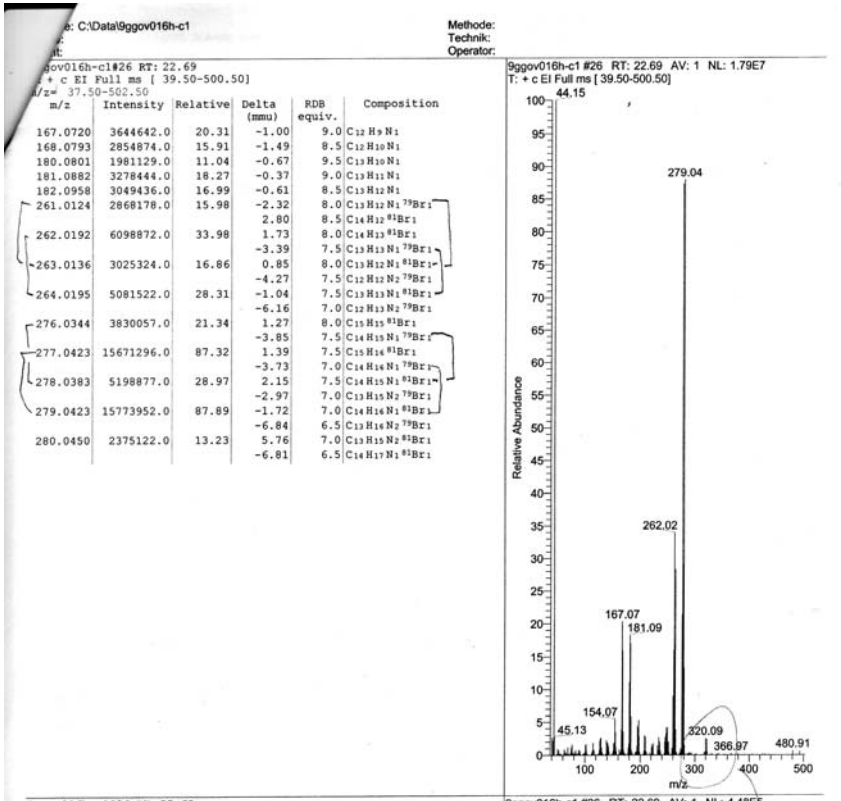




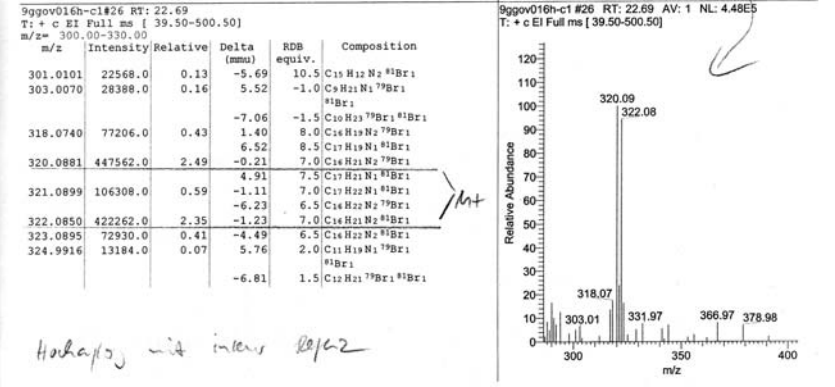
9ggov016#1049 RT: 22.66
T: + c EI Full ms [39.50-500.50]

m/z	Intensity	Relative
44.1	23792128.0	100.00
154.2	1335561.0	5.61
166.2	923632.0	3.88
167.2	5156710.0	21.67
168.2	3465878.0	14.57
180.2	2798573.0	11.76
181.2	4785285.0	20.11
182.2	4225594.0	17.76
183.2	1265599.0	5.32
195.2	947744.0	3.98
196.2	1098595.0	4.62
197.2	1185304.0	4.98
247.1	892987.0	3.75
248.1	1080659.0	4.54
260.1	2351248.0	9.88
261.2	3612928.0	15.19
262.2	8939520.0	37.57
263.2	4292586.0	18.04
264.2	6567934.0	27.61
265.2	911398.0	3.83
276.2	4935186.0	20.74
277.2	22867456.0	96.11
278.2	7815123.0	32.85
279.2	22433792.0	94.29
280.2	3086614.0	12.97

$C_{16}H_{21}BrN_2$ 320.0888

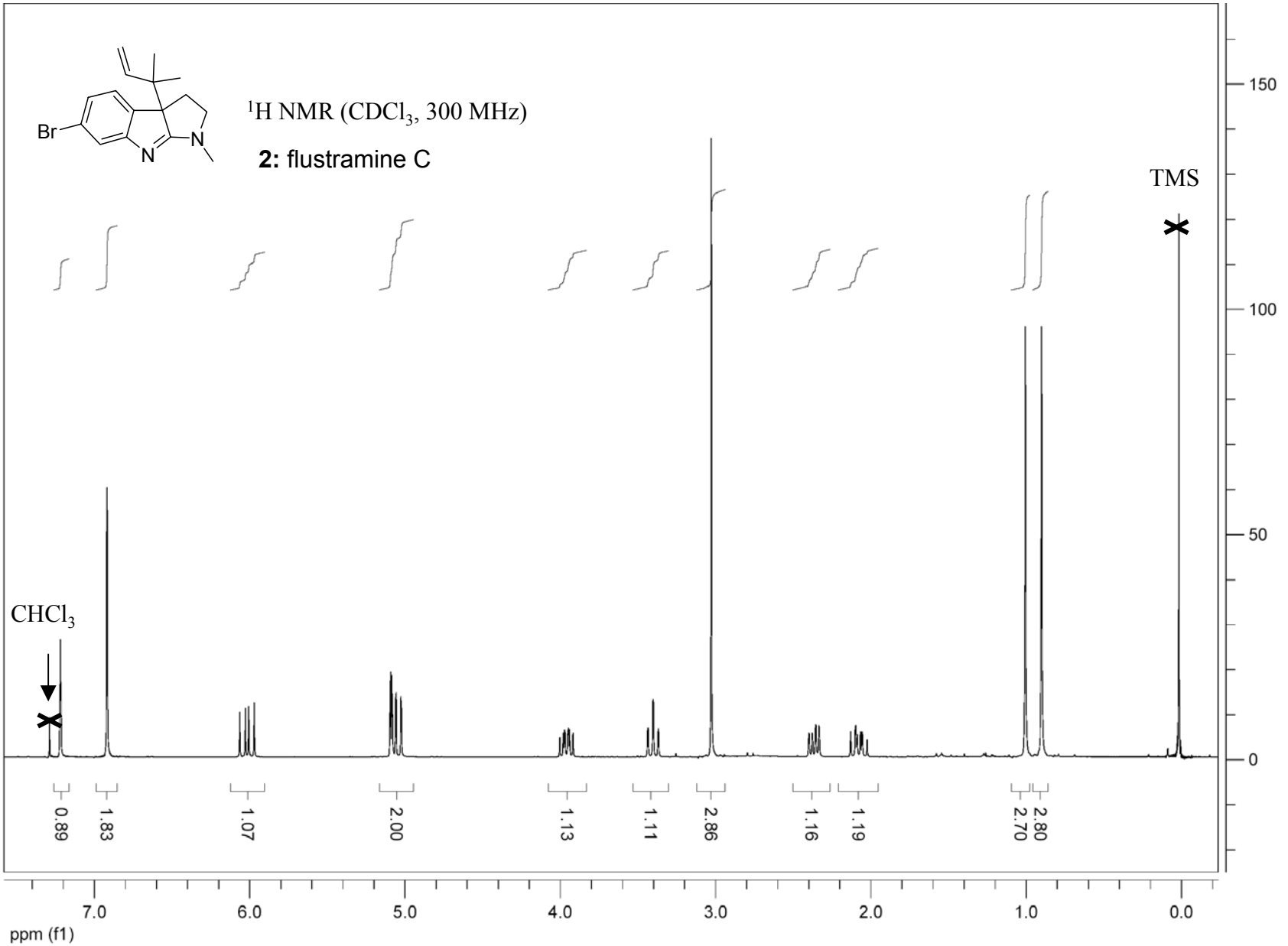


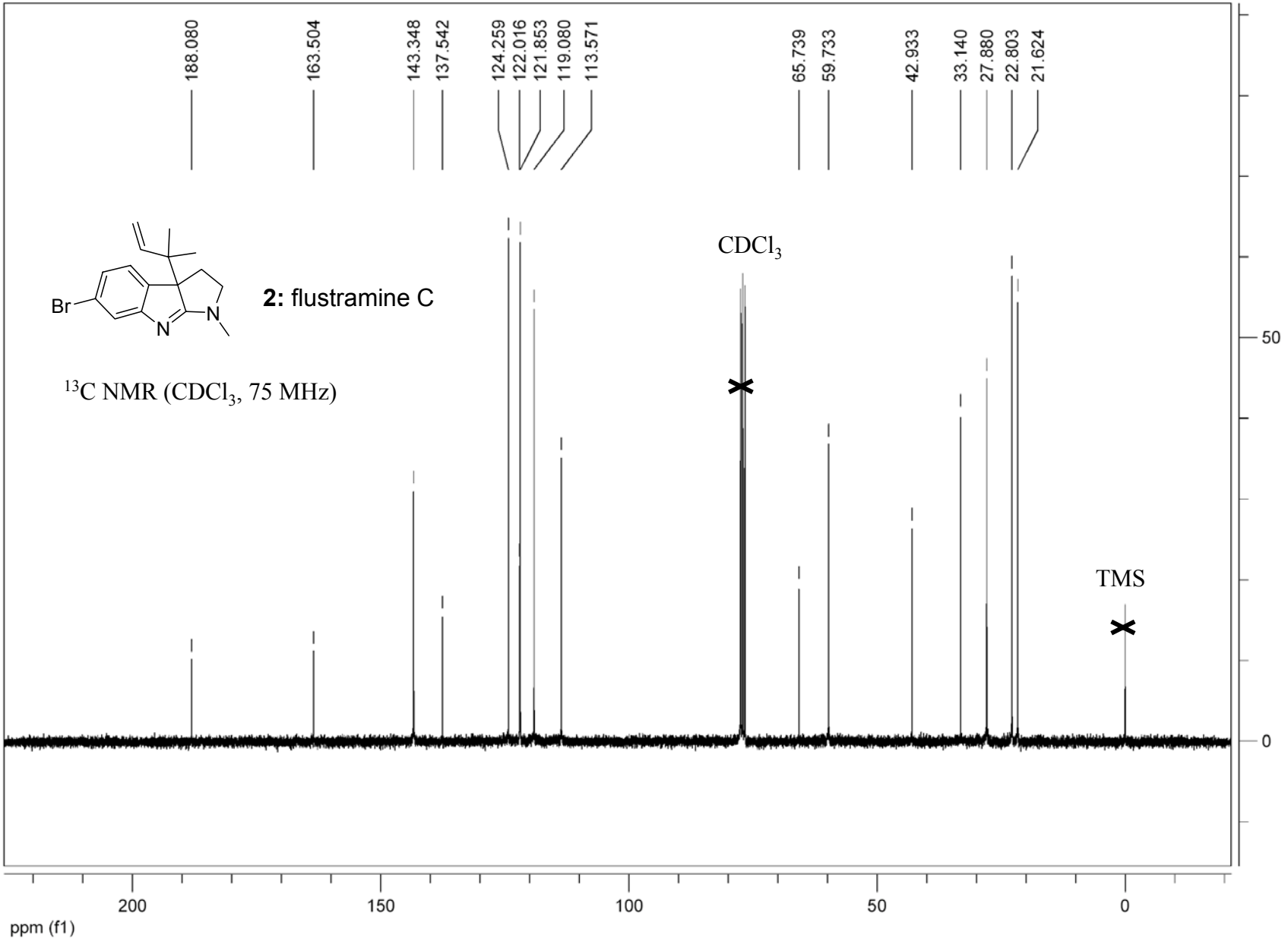
m/z	Intensity	Relative	Delta (mmu)	RDB equiv.	Composition
167.0720	3644642.0	20.31	-1.00	9.0	$C_{12}H_9N_1$
168.0793	2854874.0	15.91	-1.49	8.5	$C_{12}H_{10}N_1$
180.0801	1981129.0	11.04	-0.67	9.5	$C_{13}H_{10}N_1$
181.0882	3278444.0	18.27	-0.37	9.0	$C_{13}H_{11}N_1$
182.0958	3049436.0	16.99	-0.61	8.5	$C_{13}H_{12}N_1$
261.0124	2868178.0	15.98	-2.32	8.0	$C_{13}H_{12}N_1{}^{79}Br_1$
			2.80	8.5	$C_{14}H_{12}{}^{81}Br_1$
262.0192	6098872.0	33.98	1.73	8.0	$C_{14}H_{13}{}^{81}Br_1$
			-3.39	7.5	$C_{13}H_{13}N_1{}^{79}Br_1$
263.0136	3025324.0	16.86	0.85	8.0	$C_{13}H_{12}N_1{}^{81}Br_1$
			-4.27	7.5	$C_{12}H_{12}N_2{}^{79}Br_1$
264.0195	5081522.0	28.31	-1.04	7.5	$C_{13}H_{13}N_1{}^{81}Br_1$
			-6.16	7.0	$C_{12}H_{13}N_2{}^{79}Br_1$
276.0344	3830057.0	21.34	1.27	8.0	$C_{15}H_{15}{}^{81}Br_1$
			-3.85	7.5	$C_{14}H_{15}N_1{}^{79}Br_1$
277.0423	15671296.0	87.32	1.39	7.5	$C_{15}H_{16}{}^{81}Br_1$
			-3.73	7.0	$C_{14}H_{16}N_1{}^{79}Br_1$
278.0383	5198877.0	28.97	2.15	7.5	$C_{14}H_{15}N_1{}^{81}Br_1$
			-2.97	7.0	$C_{13}H_{15}N_2{}^{79}Br_1$
279.0423	15773952.0	87.89	-1.72	7.0	$C_{14}H_{16}N_1{}^{81}Br_1$
			-6.84	6.5	$C_{13}H_{16}N_2{}^{79}Br_1$
280.0450	2375122.0	13.23	5.76	7.0	$C_{13}H_{15}N_2{}^{81}Br_1$
			-6.81	6.5	$C_{14}H_{17}N_1{}^{81}Br_1$

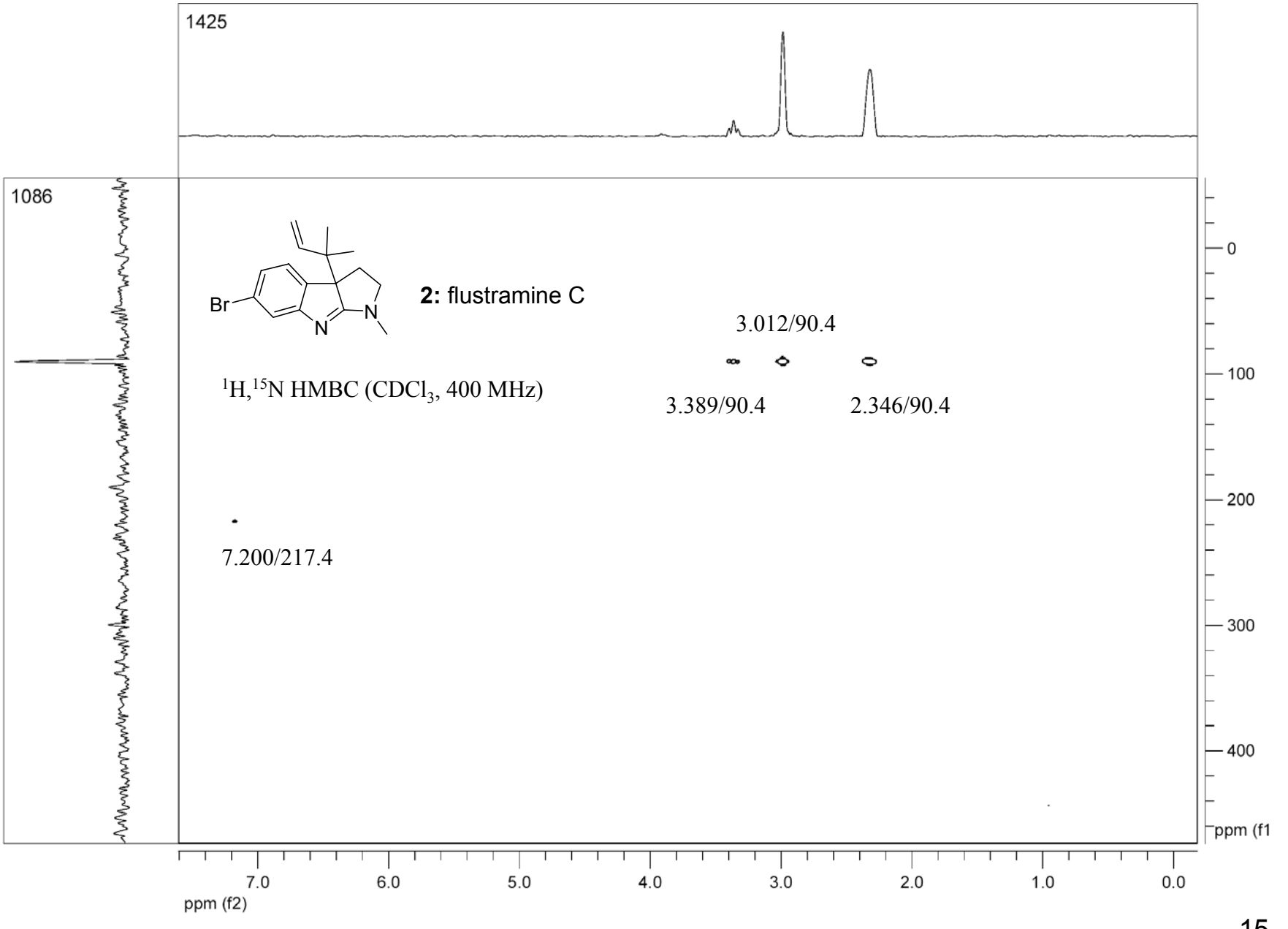


m/z	Intensity	Relative	Delta (mmu)	RDB equiv.	Composition
301.0101	22568.0	0.13	-5.69	10.5	$C_{15}H_{12}N_2{}^{81}Br_1$
303.0070	28388.0	0.16	5.52	-1.0	$C_9H_{21}N_1{}^{79}Br_1{}^{81}Br_1$
			-7.06	-1.5	$C_{10}H_{23}{}^{79}Br_1{}^{81}Br_1$
318.0740	77206.0	0.43	1.40	8.0	$C_{16}H_{19}N_2{}^{79}Br_1$
			6.52	8.5	$C_{17}H_{19}N_1{}^{81}Br_1$
320.0881	447562.0	2.49	-0.21	7.0	$C_{16}H_{21}N_2{}^{79}Br_1$
			4.91	7.5	$C_{17}H_{21}N_1{}^{81}Br_1$
321.0899	106308.0	0.59	-1.11	7.0	$C_{17}H_{22}N_1{}^{81}Br_1$
			-6.23	6.5	$C_{16}H_{22}N_2{}^{79}Br_1$
322.0850	422262.0	2.35	-1.23	7.0	$C_{16}H_{21}N_2{}^{81}Br_1$
323.0895	72930.0	0.41	-4.49	6.5	$C_{16}H_{22}N_2{}^{81}Br_1$
324.9916	13184.0	0.07	5.76	2.0	$C_{11}H_{19}N_1{}^{79}Br_1{}^{81}Br_1$
			-6.81	1.5	$C_{12}H_{21}{}^{79}Br_1{}^{81}Br_1$

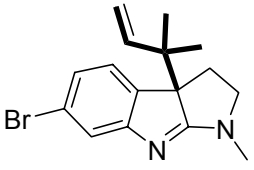
Hoher Anteil mit einem Br/Cl


Br
N
N
^{1}H NMR ($CDCl_3$, 300 MHz)
2: flustramine C
TMS
$CHCl_3$
150
100
50
0
0.89
1.83
1.07
2.00
1.13
1.11
2.86
1.16
1.19
2.70
2.80
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

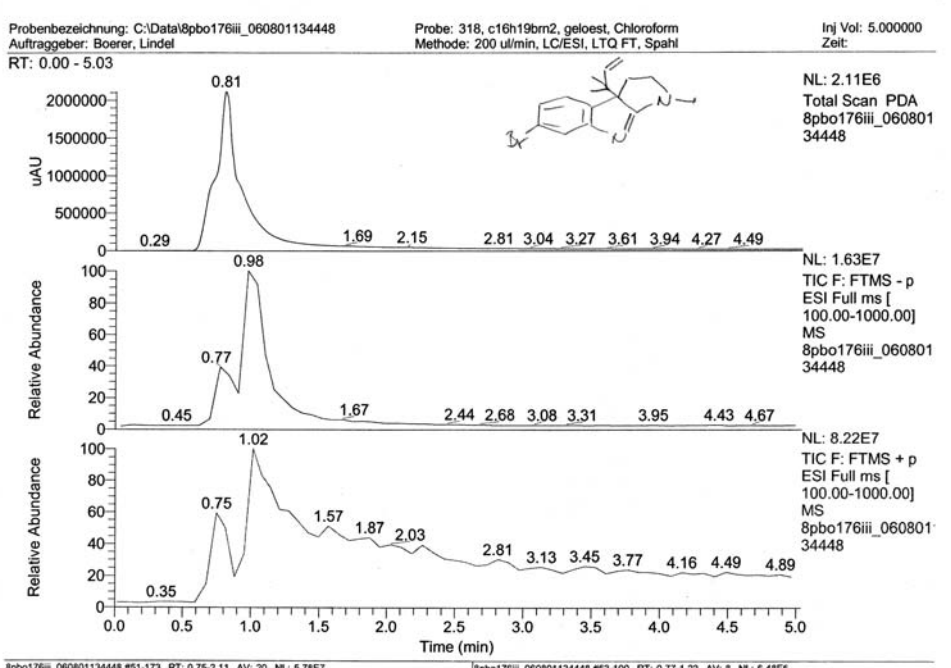

188.080
163.504
143.348
137.542
124.259
122.016
121.853
119.080
113.571
65.739
59.733
42.933
33.140
27.880
22.803
21.624
Br
N
N
2: flustramine C
^{13}C NMR ($CDCl_3$, 75 MHz)
$CDCl_3$
TMS
50
0
200
150
100
50
0
ppm (f1)

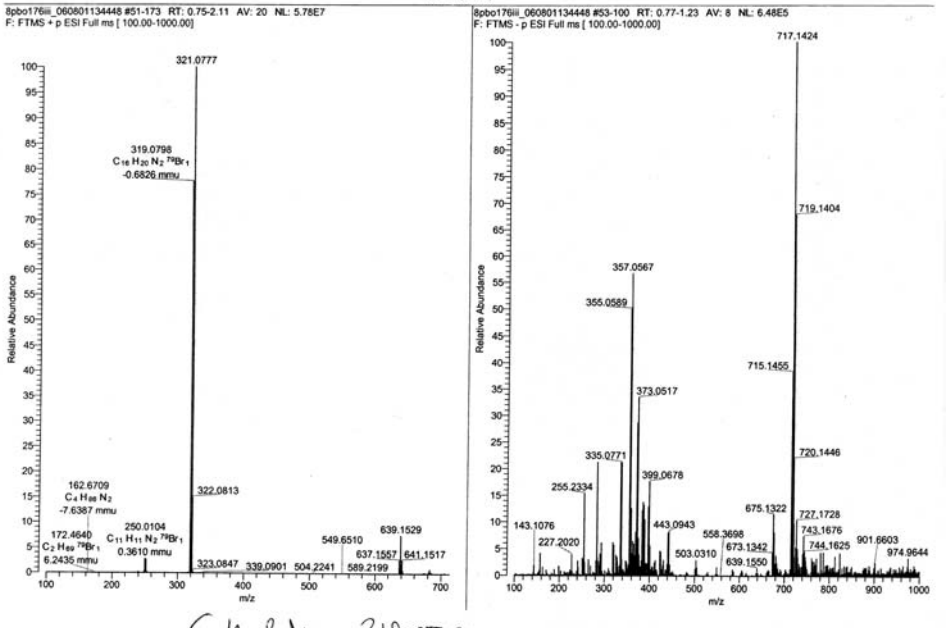

1425
1086
Br
N
N
2: flustramine C
3.012/90.4
3.389/90.4
2.346/90.4
1H,15N HMBC (CDCl3, 400 MHz)
7.200/217.4
0
100
200
300
400
ppm (f1
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f2)

HRESIMS

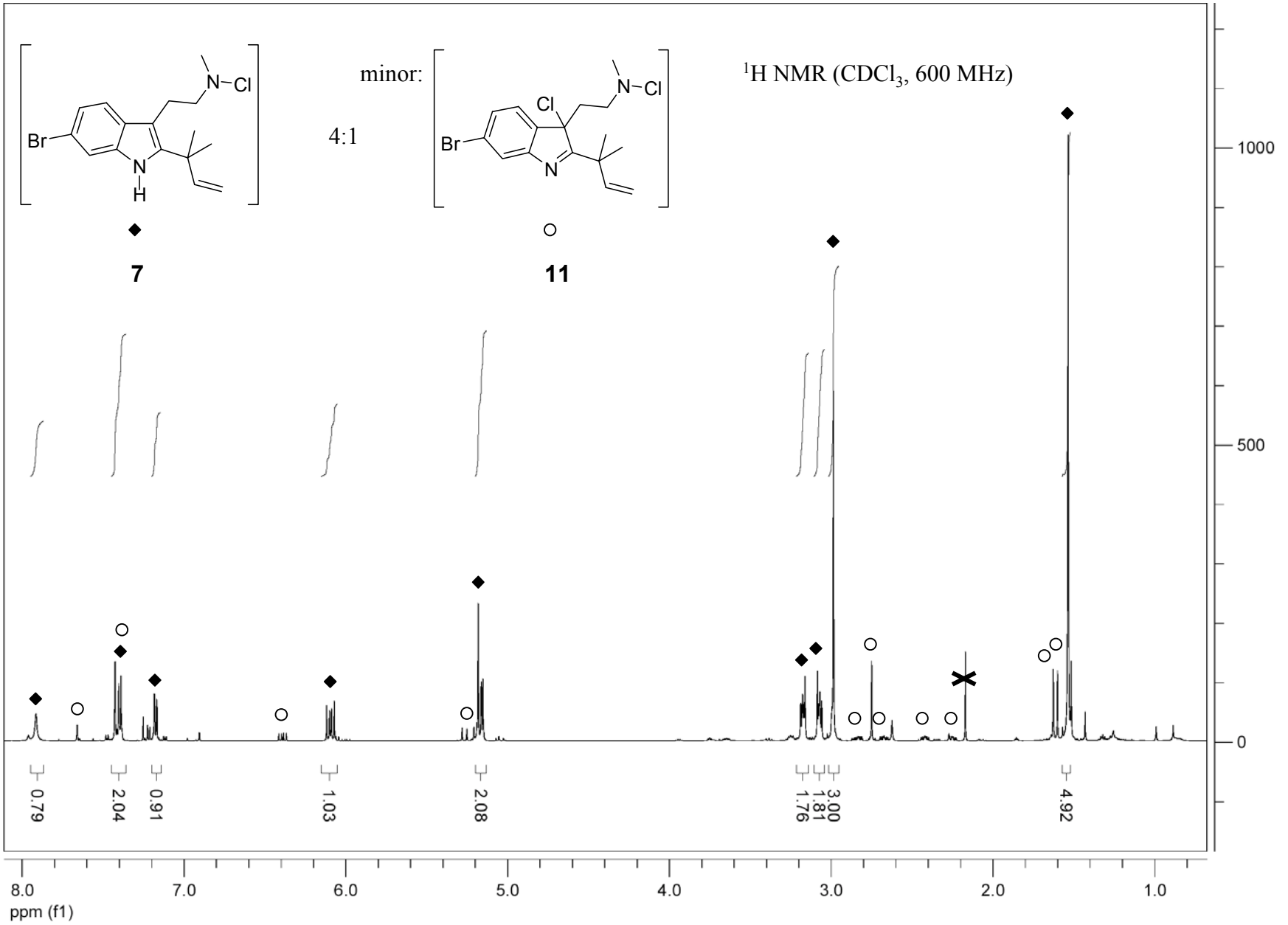


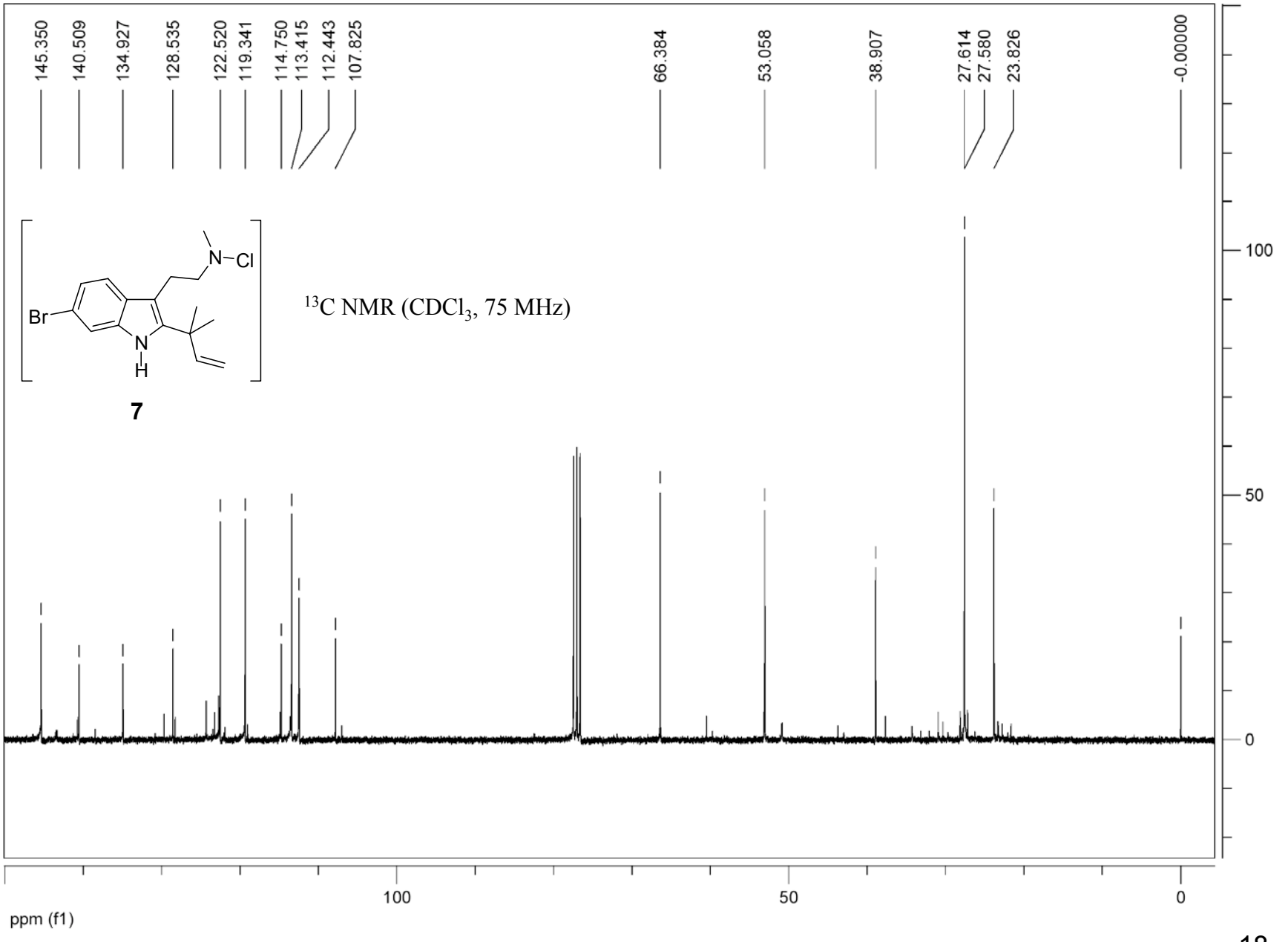
2: flustramine C





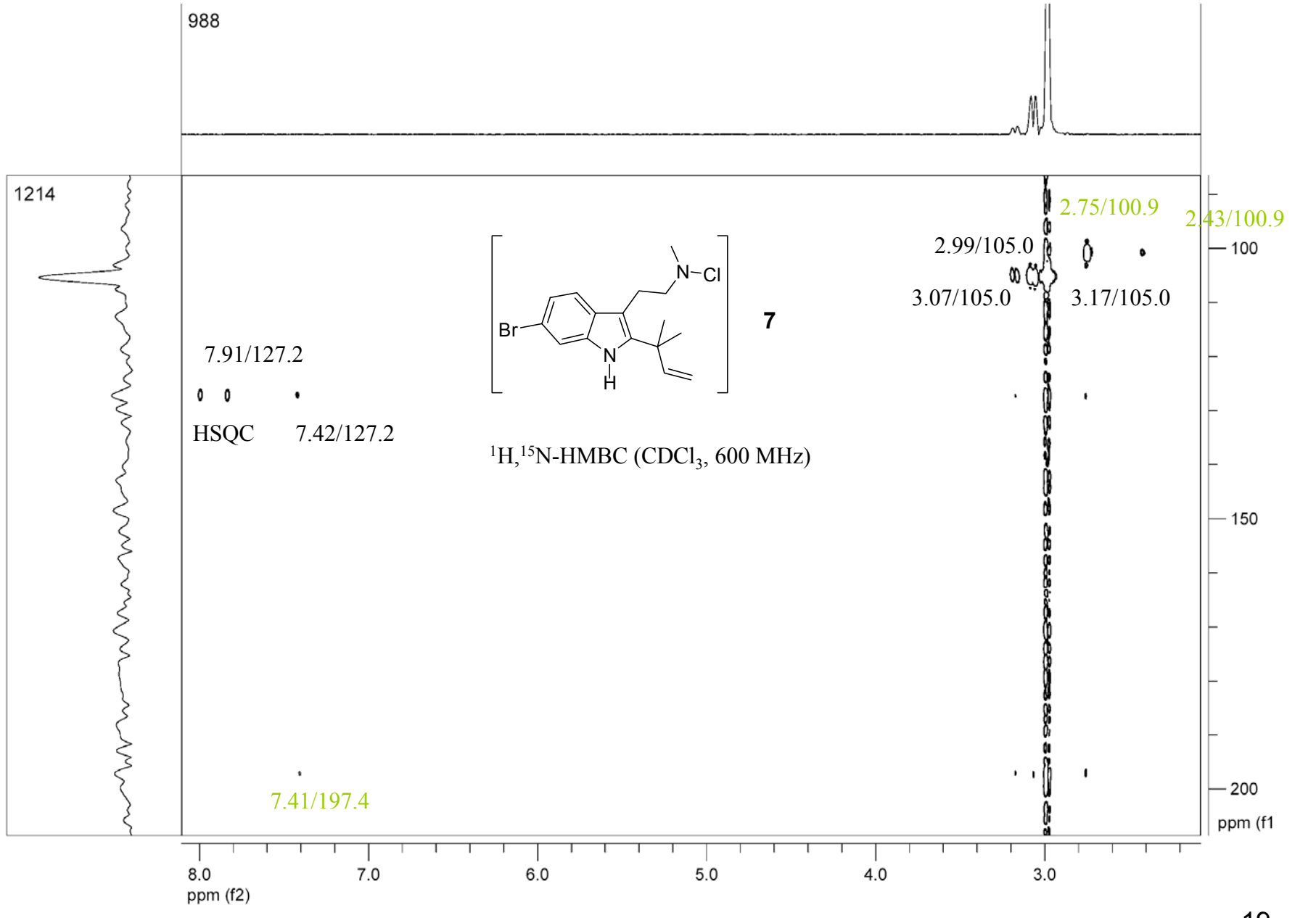
$C_{16}H_{19}BrN_2$, 318.0732


Br
N
H
N–Cl
◆
7
4:1
minor:
Br
Cl
N
N–Cl
○
11
^{1}H NMR ($CDCl_3$, 600 MHz)
1000
500
0
0.79
2.04
0.91
1.03
2.08
1.76
1.81
3.00
4.92
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

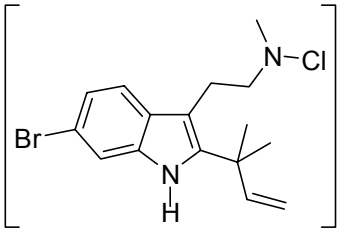


7

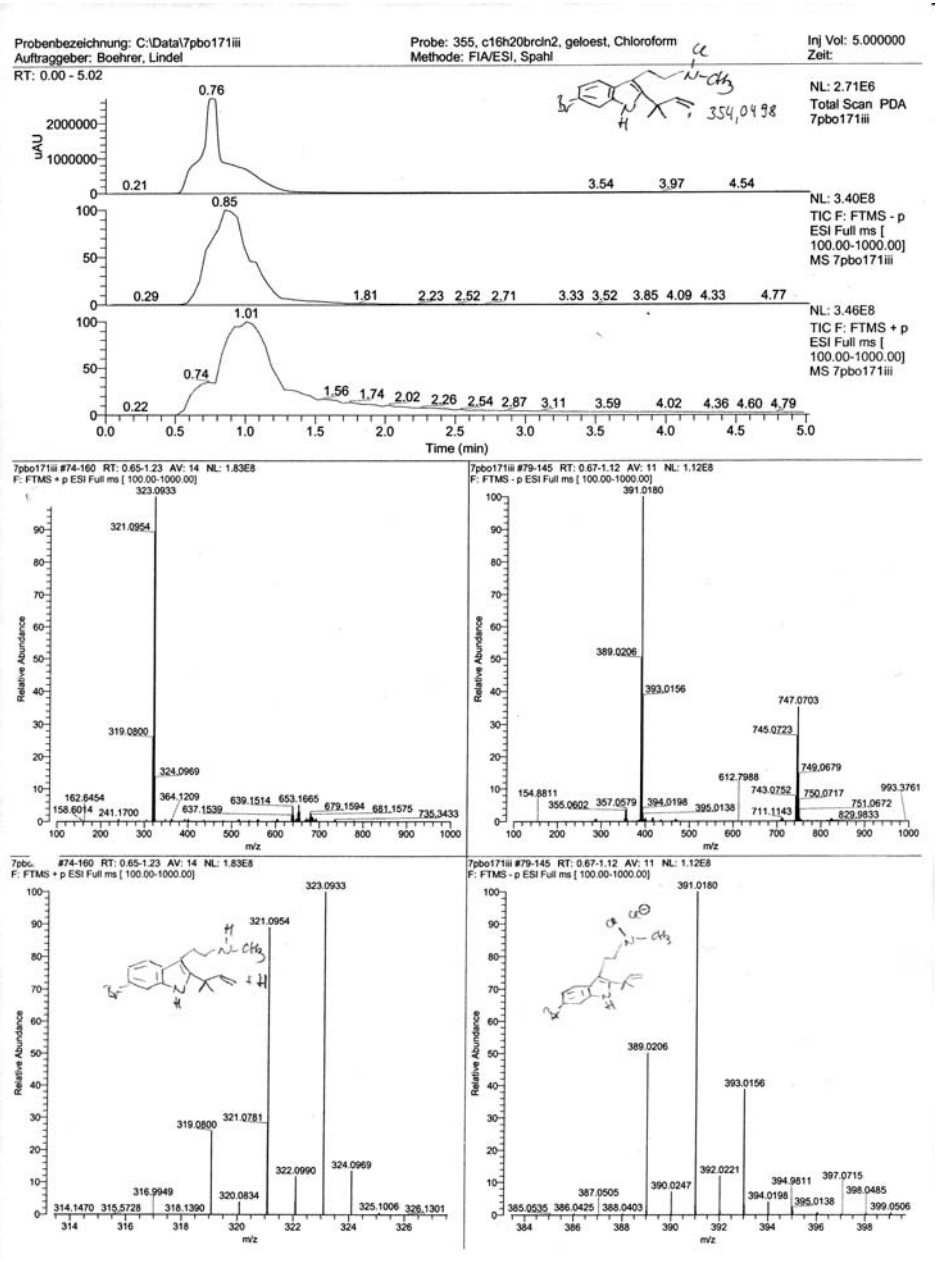
^{13}C NMR ($CDCl_3$, 75 MHz)


988
1214
2.75/100.9
2.43/100.9
2.99/105.0
3.07/105.0
3.17/105.0
7.91/127.2
HSQC
7.42/127.2
7.41/197.4
Br
N
Cl
N
H
7
$^{1}H,^{15}N$-HMBC ($CDCl_3$, 600 MHz)
100
150
200
ppm (f1
8.0
7.0
6.0
5.0
4.0
3.0
ppm (f2)

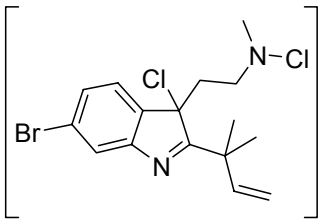
HRESIMS



7

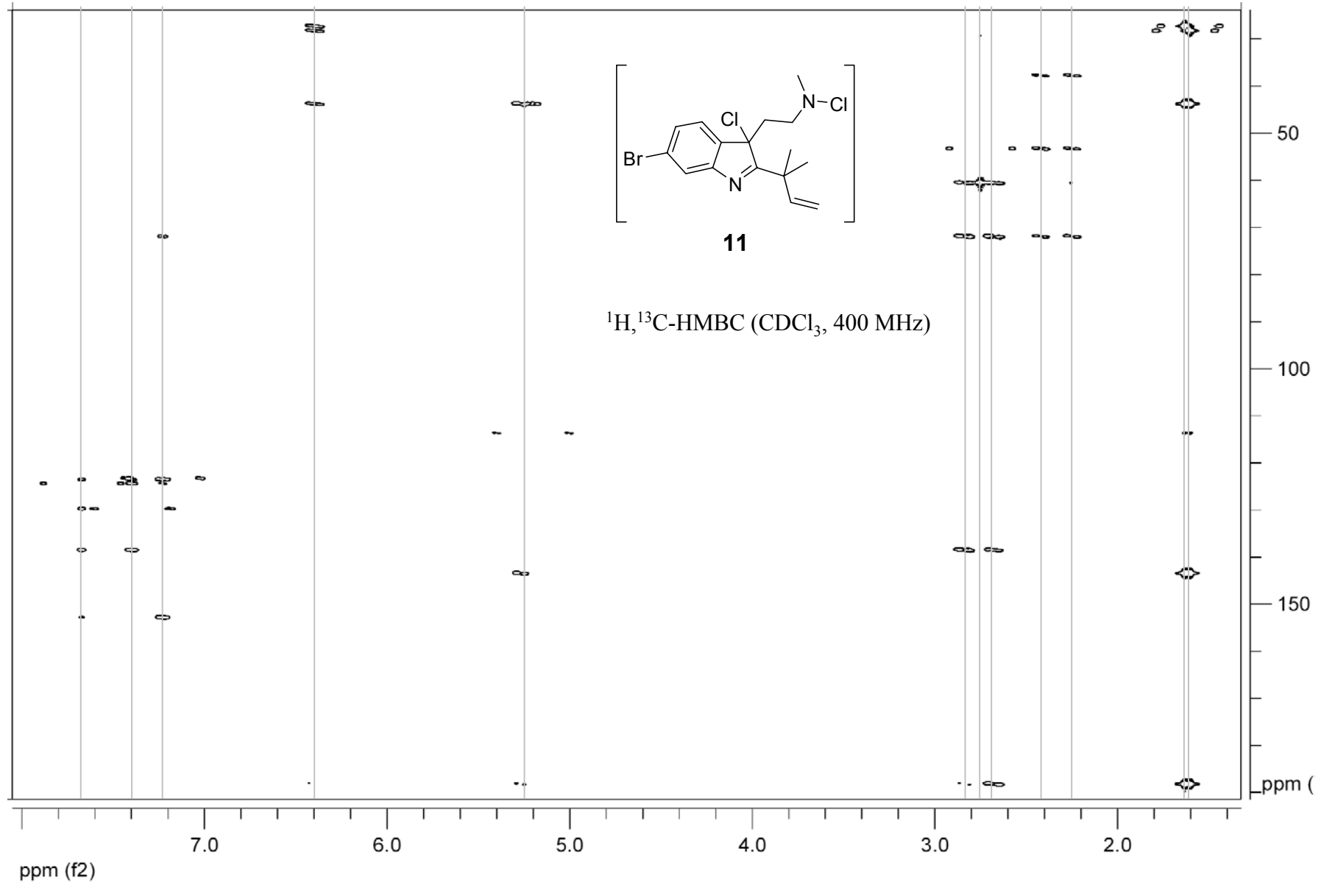


$C_{16}H_{20}BrClN_2$ 354.0498



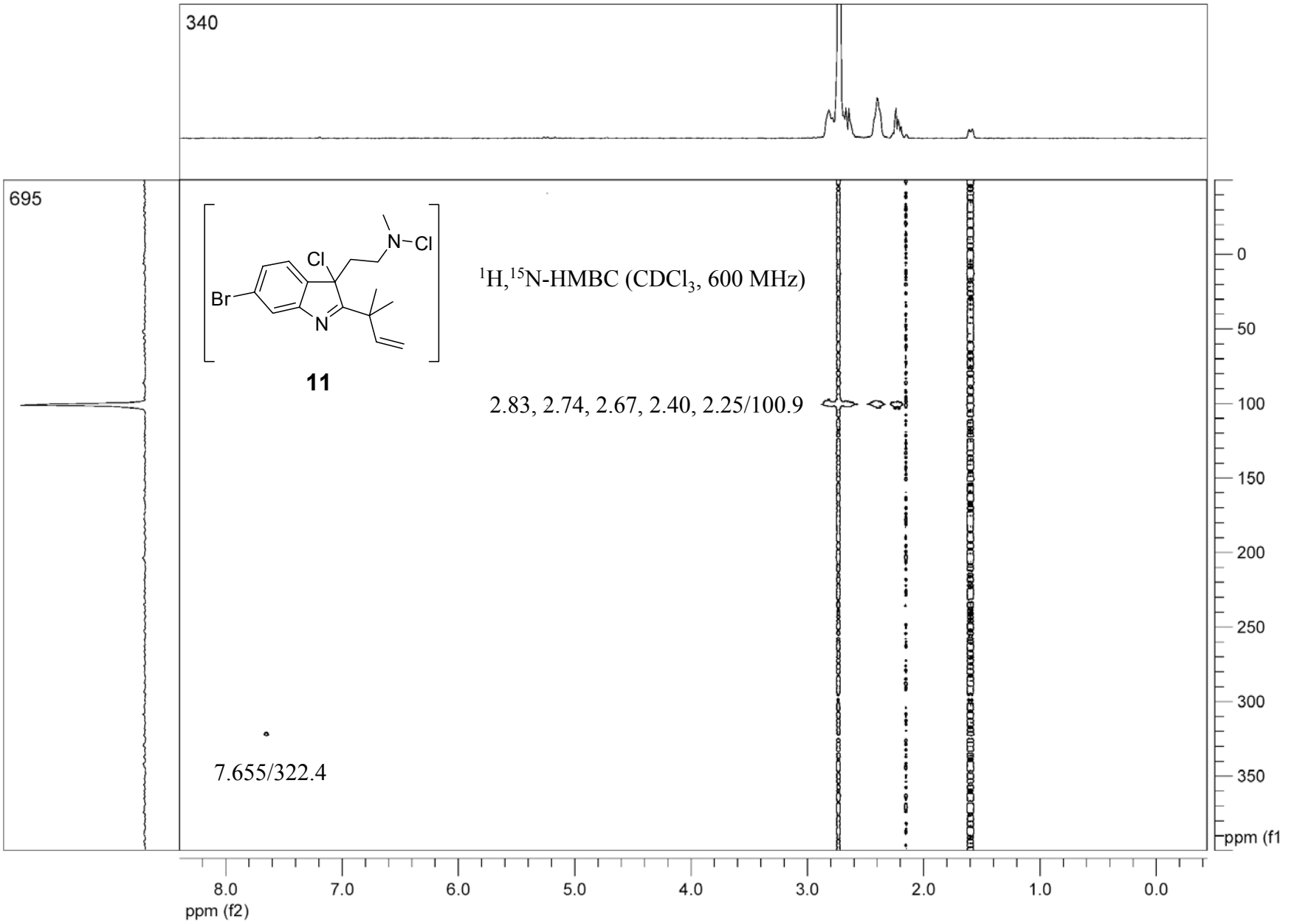
11

^{1}H NMR ($CDCl_3$, 600 MHz)

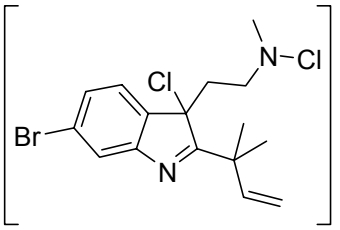


11

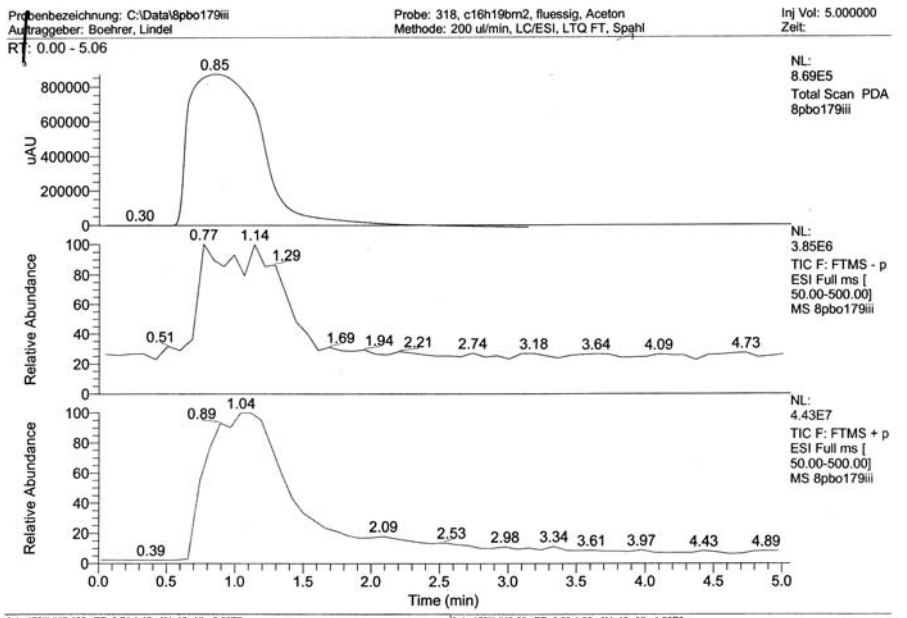
$^{1}H,^{13}C$-HMBC ($CDCl_3$, 400 MHz)

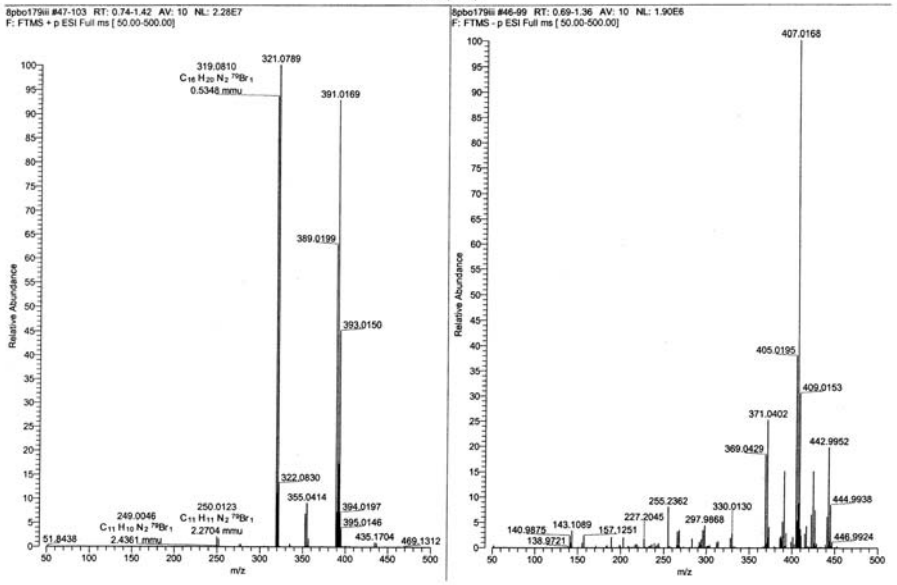

340
695
Cl
N–Cl
Br
N
11
$^{1}H,^{15}N$-HMBC ($CDCl_3$, 600 MHz)
2.83, 2.74, 2.67, 2.40, 2.25/100.9
7.655/322.4
0
50
100
150
200
250
300
350
ppm (f1
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f2)

HRESIMS

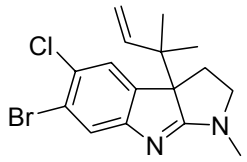


11



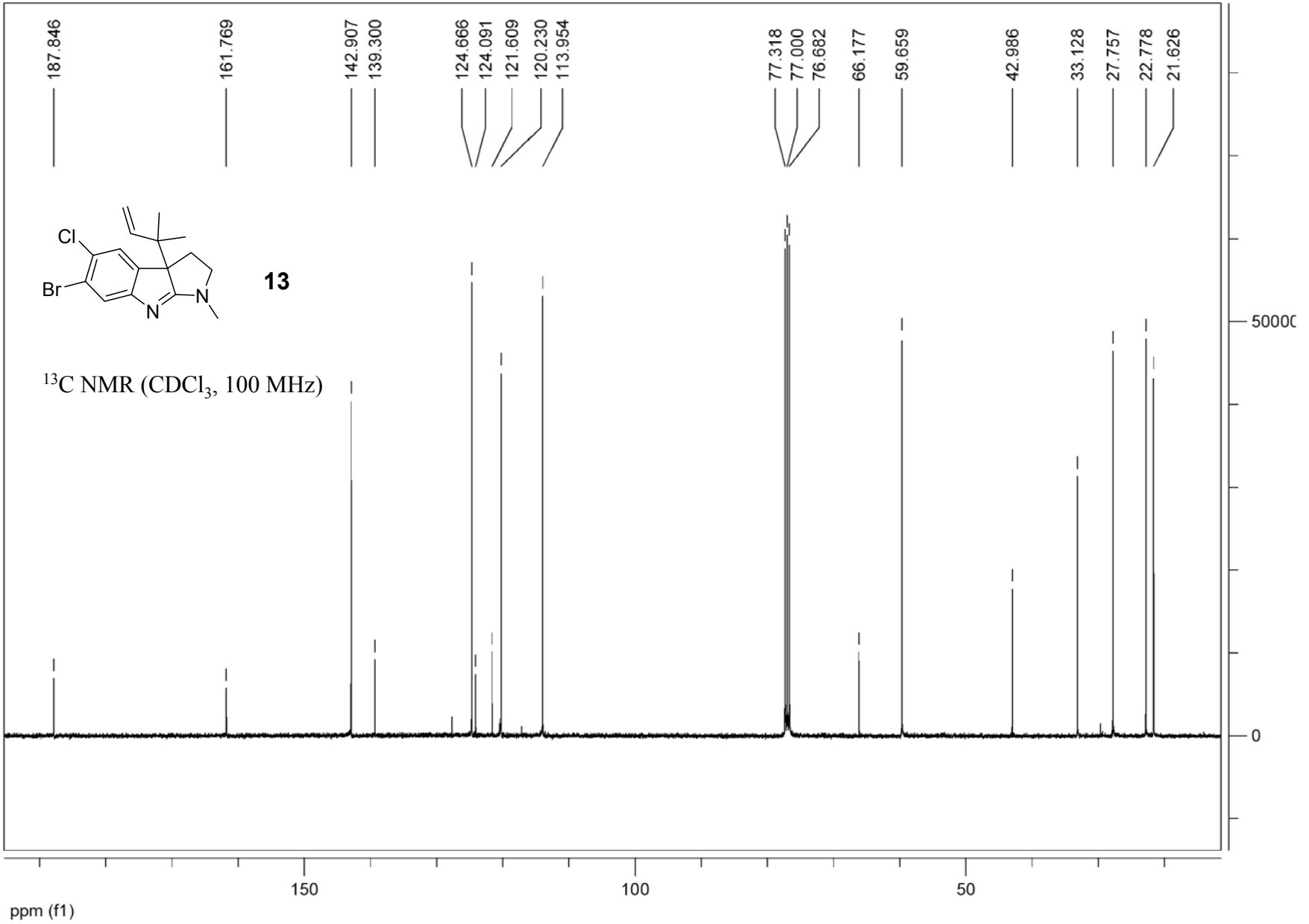


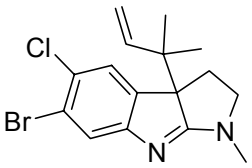
$C_{16}H_{19}BrN_2$ 318.0732 | $C_{16}H_{19}BrCl_2N_2$ 388.0109
$+H^{\oplus}$: 389.0187



13

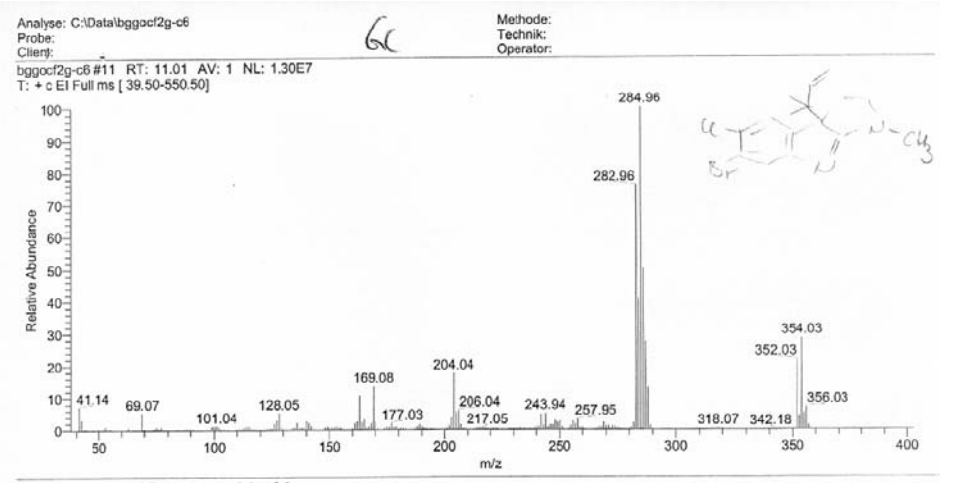
^{1}H NMR ($CDCl_3$, 400 MHz)


187.846
161.769
142.907
139.300
124.666
124.091
121.609
120.230
113.954
77.318
77.000
76.682
66.177
59.659
42.986
33.128
27.757
22.778
21.626
Cl
Br
N
N
13
^{13}C NMR ($CDCl_3$, 100 MHz)
50000
0
150
100
50
ppm (f1)



13

HREIMS

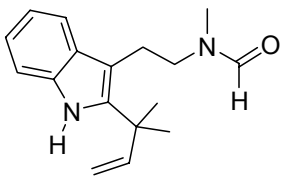


bggocf2g-c6#11 RT: 11.01
T: + c EI Full ms [39.50-550.50]
m/z= 37.5-552.5

m/z	Intensity	Relative	Delta (mmu)	RDB equiv.	Composition
163.0181	1390678.0	10.68	-0.20	7.0	$C_9H_6N_1{}^{35}Cl_1$
			5.83	7.5	$C_{10}H_6{}^{37}Cl_1$
169.0759	1768161.0	13.58	-0.11	8.5	$C_{11}H_9N_2$
			-1.94	3.5	$C_{10}H_{14}{}^{35}Cl_1$
204.0437	2300534.0	17.66	-1.16	8.0	$C_{11}H_9N_2{}^{35}Cl_1$
			4.87	8.5	$C_{12}H_9N_1{}^{37}Cl_1$
205.0469	714106.0	5.48	0.23	8.0	$C_{12}H_{10}N_1{}^{37}Cl_1$
			0.85	1.0	$C_8H_{16}N_1{}^{79}Br_1$
206.0434	787631.0	6.05	-0.32	3.0	$C_{10}H_{14}{}^{35}Cl_1{}^{37}Cl_1$
			1.51	8.0	$C_{11}H_9N_2{}^{37}Cl_1$
282.9630	9881088.0	75.87	-0.19	7.5	$C_{11}H_9N_2{}^{79}Br_1{}^{35}Cl_1$
			-0.81	14.5	$C_{15}H_3N_2{}^{35}Cl_1{}^{37}Cl_1$
283.9684	5300446.0	40.70	2.51	7.5	$C_{12}H_{10}N_1{}^{81}Br_1{}^{35}Cl_1$
			-2.61	7.0	$C_{11}H_{10}N_2{}^{79}Br_1{}^{35}Cl_1$
284.9608	13024512.0	100.00	-0.42	7.5	$C_{11}H_9N_2{}^{81}Br_1{}^{35}Cl_1$
			0.49	7.5	$C_{11}H_9N_2{}^{79}Br_1{}^{37}Cl_1$
285.9663	6532315.0	50.15	-1.80	7.0	$C_{11}H_{10}N_2{}^{79}Br_1{}^{37}Cl_1$
			-2.70	7.0	$C_{11}H_{10}N_2{}^{81}Br_1{}^{35}Cl_1$
286.9603	3550814.0	27.26	0.25	2.5	$C_{10}H_{14}{}^{81}Br_1{}^{35}Cl_1{}^{37}Cl_1$
			2.08	7.5	$C_{11}H_9N_2{}^{81}Br_1{}^{37}Cl_1$
287.9654	1710671.0	13.13	-0.04	0.0	$C_7H_{16}N_2{}^{79}Br_1{}^{81}Br_1$
			-0.66	7.0	$C_{11}H_{10}N_2{}^{81}Br_1{}^{37}Cl_1$
352.0320	2825067.0	21.69	-1.63	8.0	$C_{16}H_{18}N_2{}^{79}Br_1{}^{35}Cl_1$
354.0306	3685748.0	28.30	-0.09	8.0	$C_{16}H_{18}N_2{}^{79}Br_1{}^{37}Cl_1$
			-0.99	8.0	$C_{16}H_{18}N_2{}^{81}Br_1{}^{35}Cl_1$
356.0291	912112.0	7.00	0.43	8.0	$C_{16}H_{18}N_2{}^{81}Br_1{}^{37}Cl_1$

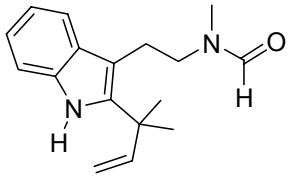
MF

^{1}H NMR, $CDCl_3$, 400 MHz



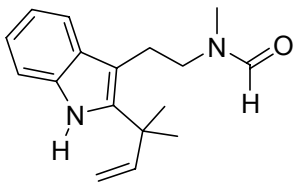
5 (two rotamers)

^{13}C NMR, $CDCl_3$, 100 MHz

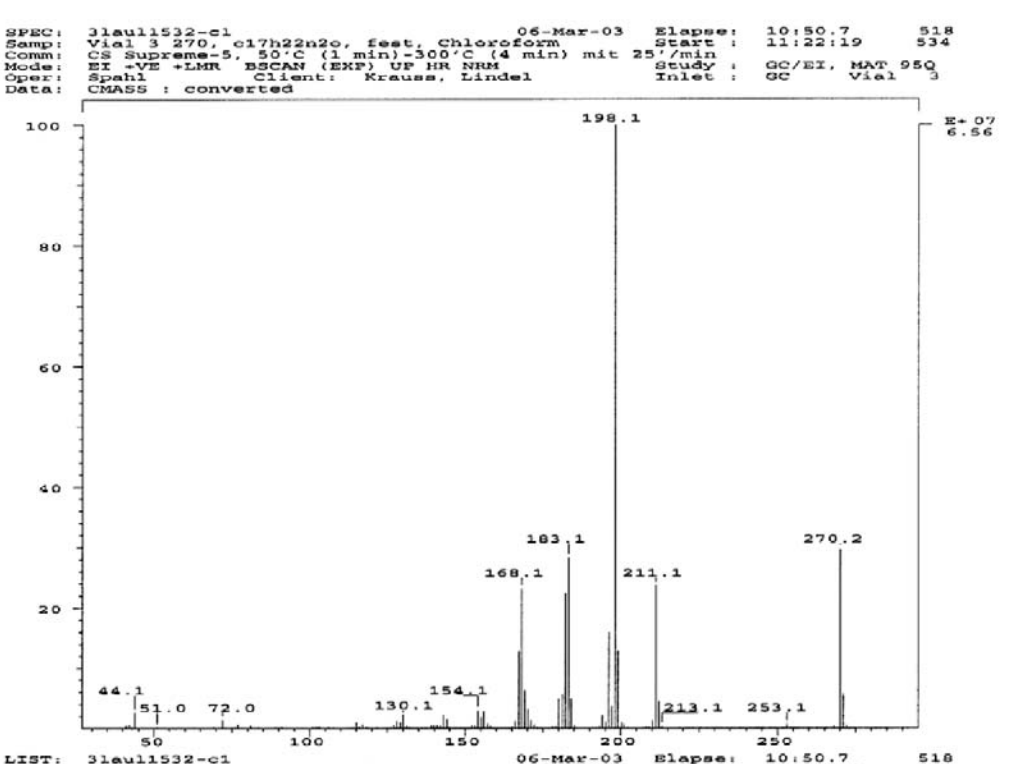


5 (two rotamers)

HREIMS



5 (two rotamers)

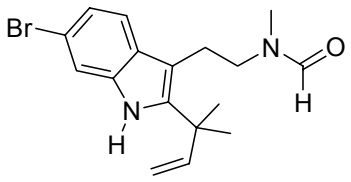


LIST: 31aul1532-c1 06-Mar-03 Elapse: 10:50.7 518
Samp: Vial 3 270, c17h22n2o, fest, Chloroform Start : 11:22:19 534
Comm: CS Supreme-5, 50°C (1 min)-300°C (4 min) mit 25°/min
Mode: EI +VE +LMR BSCAN (EXP) UP HR NRM Study : GC/EI, MAT 950
Oper: Spahl Client: Krauss, Lindel Inlet : GC Vial 3
Limt: (0) : :
: (1345) C100:H100:O:N2
Peak: 1000.00 mmu R+D: -1.0 > 50.0
Data: CMASS : converted

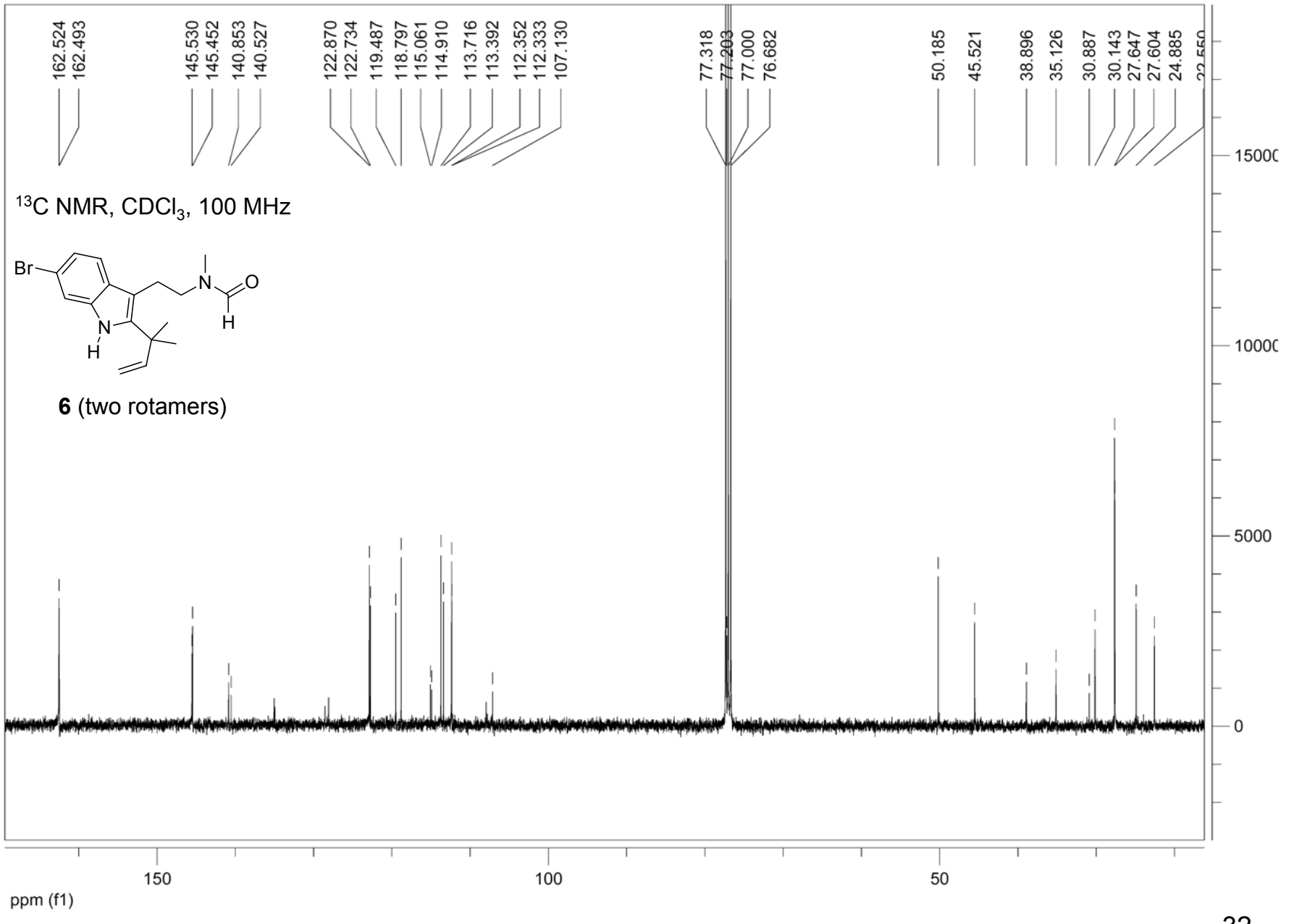
418835

Mass		Intensity	%RA	%RIC	(mmu) Delta	R+D	Composition
44.0963	*	1708795	8.78	0.72			
72.0449	*	951189	4.89	0.40	0.1	1.5	C3.H6.O.N
77.0396	*	426309	2.19	0.18	-0.4	4.5	C6.H5
115.0564	*	661170	3.40	0.28	-1.6	6.5	C9.H7
117.0602	*	460115	2.36	0.20	-2.3	6.0	C8.H7.N
127.0551	*	418836	2.15	0.18	-0.3	7.5	C10.H7
128.0576	*	854753	4.39	0.36			
129.0674	*	623806	3.20	0.26	3.0	6.5	C10.H9
130.0668	*	1539054	7.91	0.65	-1.1	6.5	C9.H8.N
143.0767	*	1463970	7.52	0.62	-3.2	7.0	C10.H9.N
144.0824	*	1019512	5.24	0.43	-1.1	6.5	C10.H10.N
154.0659	*	1969278	10.12	0.83	-0.3	8.5	C11.H8.N
155.0734	*	1193879	6.13	0.51	0.1	8.0	C11.H9.N
156.0819	*	1918747	9.86	0.81	-0.6	7.5	C11.H10.N
157.0899	*	502105	2.58	0.21	-0.7	7.0	C11.H11.N
166.0677	*	819524	4.21	0.35	-2.0	9.5	C12.H8.N
167.0737	*	8402176	43.16	3.56	-0.2	9.0	C12.H9.N
168.0815	*	15191040	78.03	6.44	-0.1	8.5	C12.H10.N
169.0886	*	4080185	20.96	1.73	0.6	8.0	C12.H11.N
170.0976	*	2076033	10.66	0.88	-0.7	7.5	C12.H12.N
171.1058	*	910978	4.68	0.39	-1.0	7.0	C12.H13.N
180.0833	*	3144297	16.15	1.33	-1.9	9.5	C13.H10.N
181.0906	*	3692307	18.97	1.56	-1.4	9.0	C13.H11.N
182.0984	*	14739200	75.71	6.25	-1.4	8.5	C13.H12.N
183.1063	*	18556160	95.32	7.86	-1.5	8.0	C13.H13.N
184.1109	*	3196607	16.42	1.35	-1.7	7.5	C13.H14.N
194.0980	*	1405610	7.22	0.60	-1.0	9.5	C14.H12.N
195.1059	*	768637	3.95	0.33	-1.1	9.0	C14.H13.N
196.1132	*	10426368	53.56	4.42	-0.5	8.5	C14.H14.N
197.1183	*	2407330	12.37	1.02	2.1	8.0	C14.H15.N
198.1301	*	65581056	336.87	27.80	-1.9	7.5	C14.H16.N
199.1326	*	8421888	43.26	3.57	3.5	7.0	C14.H17.N
200.1326	*	688571	3.54	0.29	-1.3	7.0	C13.H16.N2
201.1065	*	449795	2.31	0.19	-3.7	7.5	C12.H13.O.N2
210.1284	*	886780	4.56	0.38	-0.1	8.5	C15.H16.N
211.1371	*	15561216	79.93	6.60	-1.0	8.0	C15.H17.N
212.1399	*	2919755	15.00	1.24	4.1	7.5	C15.H18.N
253.1355	*	440899	2.26	0.19	-1.4	9.5	C16.H17.O.N2
270.1757	*	194675200	100.00	8.25	-2.4	8.0	C17.H22.O.N2
271.1786	*	3743550	19.23	1.59	2.5	7.5	C17.H23.O.N2

^{1}H NMR, $CDCl_3$, 400 MHz



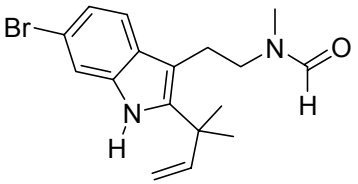
6 (two rotamers)



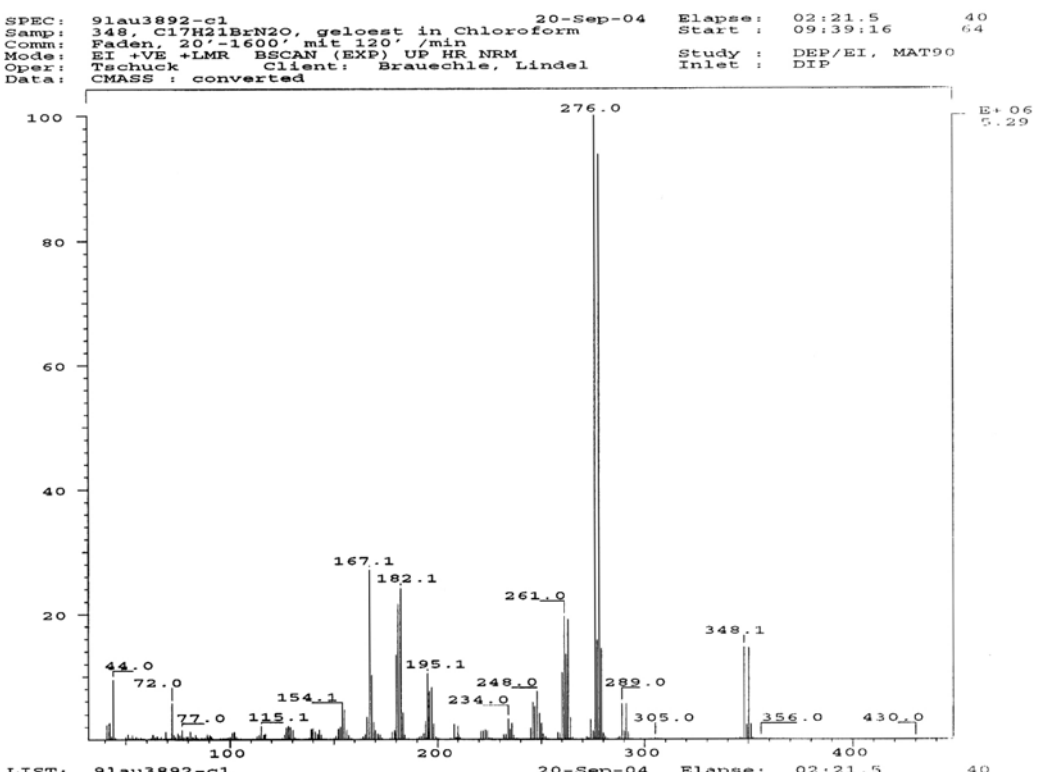
^{13}C NMR, $CDCl_3$, 100 MHz

6 (two rotamers)

HREIMS



6 (two rotamers)



LIST: 91au3892-c1 20-Sep-04 Elapse: 02:21.5 40
Samp: 348, C17H21BrN2O, geloest in Chloroform Start : 09:39:16 64
Comm: Faden, 20'-1600' mit 120' /min
Mode: EI +VE +LMR BSCAN (EXP) UP HR NRM Study : DEP/EI, MAT90
Oper: Tschuck Client: Braeuchle, Lindel Inlet : DIP
Limt: (0)
: (1424) C100.H100.O.Br.N2
Peak: 1000.00 mmu R+D: -1.0 > 50.0
Data: CMASS : converted

131399

Mass		Intensity	%RA	%RIC	(mmu) Delta	R+D	Composition
42.0261	*	140215	2.65	0.41	-4.3	2.0	C.H2.N2
44.0437	*	500811	9.47	1.46			
72.0435	*	298001	5.63	0.87	1.4	1.5	C3.H6.O.N
154.0637	*	276940	5.23	0.81	2.0	8.5	C11.H8.N
155.0718	*	244282	4.62	0.71	1.7	8.0	C11.H9.N
166.0657	*	188728	3.57	0.55	-1.1	9.5	C12.H8.N
167.0726	*	1431852	27.06	4.18	0.9	9.0	C12.H9.N
168.0777	*	540391	10.21	1.58	3.7	8.5	C12.H10.N
169.0842	*	145480	2.75	0.43	4.9	8.0	C12.H11.N
180.0805	*	711666	13.45	2.08	0.9	9.5	C13.H10.N
181.0884	*	1143376	21.61	3.34	0.8	9.0	C13.H11.N
182.0968	*	1275427	24.11	3.73	0.1	8.5	C13.H12.N
183.1012	*	224403	4.24	0.66	3.6	8.0	C13.H13.N
194.0959	*	154177	2.91	0.45	1.1	9.5	C14.H12.N
195.1054	*	558021	10.55	1.63	-0.6	9.0	C14.H13.N
196.1117	*	404080	7.64	1.18	1.0	8.5	C14.H14.N
197.1209	*	435436	8.23	1.27	-0.4	8.0	C14.H15.N
198.1236	*	131518	2.49	0.38	4.7	7.5	C14.H16.N
233.9878	*	173819	3.29	0.51	4.0	7.5	C11.H9.Br.N
235.9918	*	136724	2.58	0.40	3.1	7.0	C10.H9.Br.N2
245.9894	*	306343	5.79	0.90	2.4	8.5	C12.H9.Br.N
246.9898	*	272798	5.16	0.80	-2.7	8.5	C11.H8.Br.N2
247.9924	*	402838	7.61	1.18	2.5	8.0	C11.H9.Br.N2
248.9992	*	220794	4.17	0.65	3.6	7.5	C11.H10.Br.N2
250.0048	*	133825	2.53	0.39			
260.0070	*	563878	10.66	1.65	0.5	8.5	C13.H11.Br.N
261.0123	*	1034043	19.54	3.02	3.0	8.0	C13.H12.Br.N
262.0084	*	715512	13.52	2.09	2.2	8.0	C12.H11.Br.N2
263.0128	*	1012981	19.15	2.96			
264.0169	*	182516	3.45	0.53	-1.9	7.0	C13.H13.O.Br
274.0200	*	169737	3.21	0.50	3.1	8.5	C14.H13.Br.N
276.0394	*	5291028	100.00	15.46	-0.6	7.5	C14.H15.Br.N
277.0419	*	839872	15.87	2.45	-1.7	18.5	C19.H5.O.N2
278.0351	*	4961611	93.77	14.50	-4.5	7.0	C14.H15.O.Br
279.0363	*	765623	14.47	2.24	2.2	6.5	C14.H16.O.Br
289.0435	*	297765	5.63	0.87	3.1	8.0	C15.H16.Br.N
291.0411	*	296996	5.61	0.87	-2.6	7.5	C15.H16.O.Br
348.0838	*	778402	14.71	2.27	-0.1	8.0	C17.H21.O.Br.N2
350.0824	*	773728	14.62	2.26	2.0	23.0	C26.H10.N2
351.0846	*	131400	2.48	0.38	-3.6	22.5	C27.H11.O