Supporting Information to Accompany:

Resolution of 2,2-Disubstituted Epoxides via Biocatalytic Azidolysis

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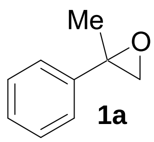
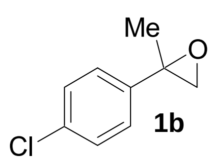
General Information. Unless otherwise noted, all reactions were performed under an oxygen-free atmosphere of nitrogen. All commercially available reagents were used without further purification. Liquid chromatography was performed using a forced flow (flash chromatography) of the indicated solvent system on silica gel (230-400 mesh). ^1H and ^{13}C NMR spectra were recorded in deuterochloroform ($CDCl_3$), unless otherwise noted, on a 400 or 500 MHz instrument. Chemical shifts of ^1H NMR spectra are reported in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.27 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet) and coupling constant in hertz (Hz). Chemical shifts of ^{13}C NMR spectra are reported in ppm from the central peak of $CDCl_3$ (77 ppm) on the δ scale. High Resolution mass spectra (HMRS) were performed on a high resolution magnetic sector mass spectrometer.

1- Preparation of Racemic Epoxides



1a

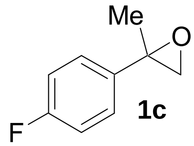
General procedure : 2-methyl-2-phenyloxirane (1a) : To a solution of potassium tertbutoxyde (14.24 g, 125 mmol) in dimethylsulfoxide (120 mL) at room temperature was added trimethylsulfoxonium iodide (30.63 g, 137.5 mmol) and stirred for 30 min. A solution of acetophenone (15.0 g, 125 mmol) in dimethylsulfoxide (30 mL) was added and stirred overnight. The reaction mixture was diluted with EtOAc and water and the layers were separated. The aqueous layer was back-extracted with EtOAc. The combined organic extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to provide 15.2 g (91 %) of **1a**. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.36 (m, 4H), 7.35-7.30 (m, 1H), 3.02 (d, J = 5.3 Hz, 1H), 2.84 (d, J = 5.5 Hz, 1H), 1.77 (s, 3H).[1]



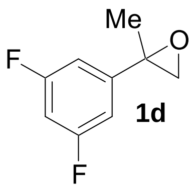
1b

2-(4-chlorophenyl)-2-methyloxirane (1b). The general procedure was followed. Isolated 15.4 g (94%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 4H), 2.98 (d, J = 5.2 Hz, 1H), 2.76 (d, J = 5.2 Hz, 1H), 1.70 (s, 3H)[1]

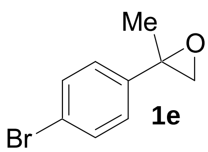
[1] Sone, T.; Yamaguchi, A.; Matsunaga, S.; Shibasaki, M.; *J. Am. Chem. Soc.* **2008**, *130*, 10078-10079.


1c

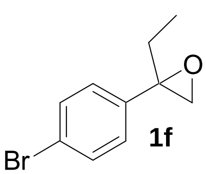
2-(4-fluorophenyl)-2-methyloxirane (1c). The general procedure was followed. Isolated 12.6 g (77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.29 (m, 2H), 7.05-6.97 (m, 2H), 2.96 (d, *J* = 5.4 Hz), 2.76 (d, *J* = 5.4 Hz), 1.70 (s, 3H).[1]


1d

2-(3,5-difluorophenyl)-2-methyloxirane (1d). The general procedure was followed. Isolated 15.6 g (95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90-6.83 (m, 2H), 6.73-6.66 (m, 1H), 2.96 (d, *J* = 5.44 Hz, 1H), 2.72 (d, *J* = 5.4 Hz, 1H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 (dd, *J* = 247, 13 Hz), 145.6 (t, *J* = 9.1 Hz), 108.4 (dd, *J* = 28, 11 Hz), 102.9 (t, *J* = 25 Hz), 57.1, 56.1, 21.2; IR (neat) 3089, 3054, 2988, 2933, 1623, 1600, 1433, 1351, 1117, 981; HRMS ESI (*m* / *z*): $[M + H]^+$ calcd for $C_9H_8F_2O$, 171.0616; found 171.0608.

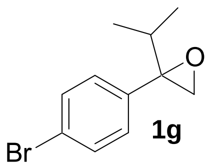

1e

2-(4-bromophenyl)-2-methyloxirane (1e). The general procedure was followed. Isolated 15.0 g (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 3.00 (d, *J* = 5.4 Hz, 1H), 2.78 (d, *J* = 5.5 Hz, 1H), 1.73 (s, 3H).[2]


1f

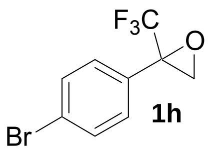
2-(4-bromophenyl)-2-ethyloxirane (1f). The general procedure was followed. Isolated 10.1 g (95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 3.00 (d, *J* = 5.2 Hz, 1H), 2.71 (d, *J* = 5.2 Hz, 1H), 2.20 (dq, *J* = 14.9, 7.2 Hz, 1H), 1.79 (dq, *J* = 14.7, 7.5 Hz, 1H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 131.4, 127.8, 121.3, 60.5, 55.4, 28.1, 8.9; IR (neat) 3039, 2969, 2937, 2880, 1591, 1487, 1458, 1069, 1009, 907, 819; HRMS ESI (*m* / *z*): $[M + H]^+$ calcd for $C_{10}H_{11}BrO$, 227.0066; found 227.0069.

[2] Cleij, M.; Archelas, A.; Furstoss, R.; *J. Org. Chem.* **1999**, *64*, 5029-5035.



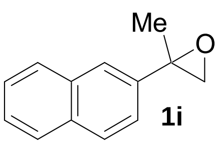
1g

2-(4-bromophenyl)-2-isopropyloxirane (1g). The general procedure was followed. Isolated 758 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 2.99 (d, *J* = 5.3 Hz, 1H), 2.66 (d, *J* = 5.3 Hz, 1H), 2.06 (sept, *J* = 6.9 Hz, 1H), 0.93 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 130.7, 128.5, 120.9, 63.6, 52.8, 32.4, 18.1, 17.2; IR (neat) 3054, 2964, 2929, 2880, 1486, 1466, 1383, 1069, 1008, 814; HRMS ESI (*m* / *z*): $[M + H]^+$ calcd for $C_{11}H_{13}BrO$, 241.0223; found 241.0199.



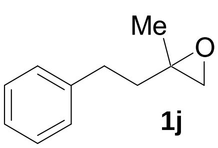
1h

2-(4-bromophenyl)-2-(trifluoromethyl)oxirane (1h). The general procedure was followed. Isolated 9.92 g (94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 3.4 (d, *J* = 5.3 Hz, 1H), 2.90 (dq, *J* = 5.2, 1.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.8, 130.1, 129.2, 124.0, 123.1 (q, *J* = 280 Hz), 57.4 (q, *J* = 37 Hz), 50.4 (q, *J* = 2 Hz); IR (neat) 2986, 1732, 1594, 1490, 1372, 1345, 1243, 1177, 1157, 1009, 817.



1i

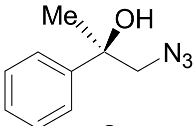
2-methyl-2-(naphthalen-2-yl)oxirane (1i). The general procedure was followed. Isolated 14.4 g (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.79-7.70 (m, 3H), 7.45-7.36 (m, 3H), 2.94 (d, *J* = 5.6 Hz, 1H), 2.80 (d, *J* = 5.3 Hz, 1H), 1.74 (s, 3H).[1]



1j

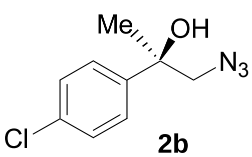
2-methyl-2-phenethyloxirane (1j). The general procedure was followed. Isolated 10.8 g (100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.24 (m, 2H), 7.22-7.15 (m, 3H), 2.72 (t, *J* = 8.1 Hz, 2H), 2.59 (d, *J* = 5.9 Hz, 2H), 1.98-1.77 (m, 2H), 1.38 (s, 3H).[1]

2- Enantiomerically Enriched 2,2-di-substituted Azidoalcohols



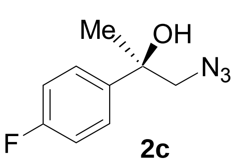
2a

(*R*)-1-azido-2-phenylpropan-2-ol (2a). To a solution of the enzyme (HHDH P2E2, 250 mg) in 0.1 M K_2HPO_4 [3] (70 mL) at room temperature was added a solution of sodium azide (133 mg, 2.05 mmol) in 0.1 M K_2HPO_4 (25 mL) followed by a solution of the epoxyde **1a** (500 mg, 3.73 mmol) in DMSO (5 mL) and stirred overnight. The reaction mixture was diluted with EtOAc and water and the layers were separated by centrifugation. The organic extracts were dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude mixture purified by column chromatography on silica gel with Hexane:EtOAc (gradient : 0 % to 100 % EtOAc) to provide 300 mg (45 %) of **2a**. $[\alpha]_D$ = - 27.50 (c 1.04, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.52-7.47 (m, 2H), 7.45-7.38 (m, 2H), 7.37-7.31 (m, 1H), 3.65 (d, *J* = 12.1 Hz, 1H), 3.49 (d, *J* = 12.3 Hz, 1H), 2.33 (s, 1H), 1.64 (s, 3H).[4] The enantiomeric excess was determined by SFC (chiralcel-OJ, 2 mL/min, 5-40% MeOH @4%MeOH/min, *T*r (major) 6.64min, *T*r(minor) 6.37 min (98%ee).



2b

(*R*)-1-azido-2-(4-chlorophenyl)propan-2-ol (2b). The general procedure was followed. Isolated 255 mg (41 %). $[\alpha]_D$ = - 36.83 (c 1.11, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 3.58 (d, *J* = 11.9 Hz, 1H), 3.45 (d, *J* = 11.9 Hz, 1H), 2.30 (s, 1H), 1.57 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 133.5, 128.6, 126.5, 74.3, 62.0, 27.2; IR (neat) 3572, 3432, 2977, 2929, 2880, 2099, 1720, 1591, 1489, 1274, 1093, 1011, 821; HRMS ESI (*m* / *z*): $[M + Na]^+$ calcd for $C_9H_{10}ClN_3O$, 234.0405; found 234.004. The enantiomeric excess was determined by SFC (chiralcel-AD-H, 2 mL/min, 5-40% MeOH @4%MeOH/min, *T*r (major) 8.95 min, *T*r(minor) 8.27 min (99%ee).

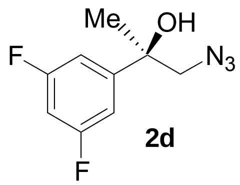


2c

(*R*)-1-azido-2-(4-fluorophenyl)propan-2-ol (2c). The general procedure was followed. Isolated 246 mg (38 %). $[\alpha]_D$ = - 26.98 (c 1.16, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46-7.39 (m, 2H), 7.05 (t, *J* = 8.5 Hz, 2H), 3.57 (d, *J* = 12.1 Hz, 1H), 3.43 (d, *J* = 12.1 Hz, 1H), 2.39 (s, 1H), 1.58

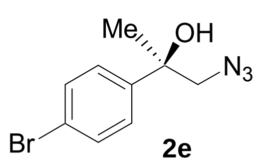
[3] Buffered at pH=7
[4] Lorenzin, M.; Guerriero, A.; Pietra, F. *J. Org. Chem.* **1980**, *45*, 1704-1705.

(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246 Hz), 140.5 (d, *J* = 18 Hz), 126.8 (d, *J* = 10 Hz), 115.3 (d, *J* = 26 Hz), 74.3, 62.2, 27.2; IR (neat) 3575, 3387, 2978, 2929, 2880, 2099, 1601, 1507, 1223, 1160, 1044, 833; HRMS ESI (*m* / *z*): $[M + Na]^+$ calcd for $C_9H_{10}FN_3O$, 218.0700; found 218. 0697. The enantiomeric excess was determined by HPLC (chiralcel-OJ-RH, 1 mL/min, 20-60% (0.1% H_3PO_4) over 40 min, *T*r (major) 15.31 min, *T*r(minor) 14.51 min (>97%ee).



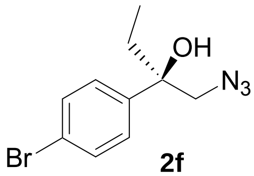
2d

(*R*)-1-azido-2-(3,5-difluorophenyl)propan-2-ol (2d). The general procedure was followed. Isolated 282 mg (45 %). $[\alpha]_D$ = - 10.95 (c 1.14, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02-6.93 (m, 2H), 6.78-6.78 (m, 1H), 3.57 (d, *J* = 12.2 Hz, 1H), 3.45 (d, *J* = 12.5 Hz, 1H), 2.34 (s, 1H), 1.56 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1 (dd, *J* = 247, 13 Hz), 148.9 (t, *J* = 8.2 Hz), 108.2 (dd, *J* = 20, 6.5 Hz), 108.2 (d, *J* = 14 Hz), 102.9 (t, *J* = 26 Hz), 74.3, 61.6, 27.0; IR (neat) 3579, 3434, 3096, 2986, 2929, 2857, 2100, 1622, 1593, 1434, 1289, 1115, 984, 855; HRMS ESI (*m* / *z*): $[M + Na]^+$ calcd for $C_9H_9F_2N_3O$, 236.0606; found 236.0613. The enantiomeric excess was determined by SFC (chiralcel-AD-H, 2 mL/min, 5-40% MeOH @4%MeOH/min, *T*r (major) 3.55 min, *T*r(minor) 3.12 min (99%ee).



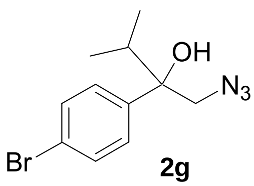
2e

(*R*)-1-azido-2-(4-bromophenyl)propan-2-ol (2e). The general procedure was followed. Isolated 258 mg (43 %). $[\alpha]_D$ = - 32.44 (c 1.05,$CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 3.59 (d, *J* = 12.4 Hz, 1H), 3.45 (d, *J* = 12.6 Hz, 1H), 2.30 (s, 1H), 1.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7 131.6, 126.8, 121.6, 74.4, 61.9, 27.1; IR (neat) 3579, 3400, 2976, 2930, 2864, 2099, 1486, 1395, 1271, 1075, 1007, 820; HRMS ESI (*m* / *z*): [M + H]+ calcd for $C_9H_{10}BrN_3O$, 256.0080; found 256.0149. The enantiomeric excess was determined by SFC (chiralcel-AD-H, 2 mL/min, 5-40% MeOH @4%MeOH/min, *T*r (major) 9.50 min, *T*r(minor) 8.49 min (99%ee).



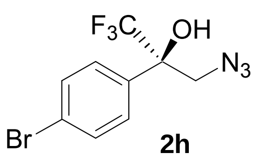
2f

(*R*)-1-azido-2-(4-bromophenyl)butan-2-ol (2f). The general procedure was followed. Isolated 157 mg (26 %). $[\alpha]_D$ = - 12.7 (c 1.44, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.7 Hz, 2H), 7.31 (d, J = 8.7 Hz, 2H), 3.65 (d, J = 13.0 Hz, 1H), 3.55 (d, J = 13.0 Hz, 1H), 2.36 (s, 1H), 1.98-1.80 (m, 2H), 0.79 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 131.5, 127.3, 121.4, 61.3, 32.2, 7.4; IR (neat) 3556, 3441, 2970, 2933, 2880, 2096, 1485, 1393, 1270, 1071, 1007, 82; HRMS ESI (*m* / *z*): $[M + Na]^+$ calcd for $C_{10}H_{12}BrN_3O$, 292.0056; found 292.0051. The enantiomeric excess was determined by SFC (chiralcel-AD-H, 2 mL/min, 5-40% MeOH @4%MeOH/min, *T*r (major) 9.46 min, *T*r(minor) 9.86 min (98%ee).



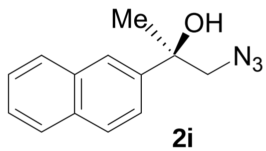
2g

(Racemic) 1-azido-2-(4-bromophenyl)-3-methylbutan-2-ol (2g). The general procedure was followed. Isolated 113 mg (90 %). ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 3.81 (d, J = 12.5 Hz, 1H), 3.72 (d, J = 12.4 Hz, 1H), 2.40 (s, 1H), 2.09 (sept, J = 6.9 Hz, 1H), 0.95 (d, J = 6.7 Hz, 3H), 0.80 (d, J = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7, 131.1, 127.7, 121.2, 78.5, 59.0, 35.8, 17.2, 16.5; IR (neat) 3556, 3473, 2967, 2937, 2880, 2098, 1487, 1283, 1073, 1007, 814; HRMS ESI (*m* / *z*): $[M + Na]^+$ calcd for $C_{11}H_{14}BrN_3O$, 306.0213; found 306.0213.



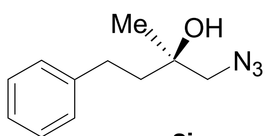
2h

(*R*)-3-azido-2-(4-bromophenyl)-1,1,1-trifluoropropan-2-ol (2h). The general procedure was followed. Isolated 70 mg (22 %). $[\alpha]_D$ = - 12.87 (c 1.01, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.9 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 4.04 (d, J = 13.1 Hz, 1H), 3.82 (d, J = 13.1 Hz, 1H), 3.26 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.8, 131.8, 127.8, 124.1 (q, J = 286 Hz), 123.7, 76.0 (q, J = 29 Hz), 55.2; IR (neat) 3529, 2978, 2105, 1592, 1489, 1401, 1267, 1158, 1075, 1009, 817; HRMS ESI (*m* / *z*): $[M - H]^-$ calcd for $C_9H_7BrF_3N_3O$, 307.9652; found 307.9782. The enantiomeric excess was determined by SFC (chiralcel-OJ, 2 mL/min, 1-10% MeOH @1%MeOH/min, *T*r (major) 8.51 min, *T*r(minor) 7.94 min (88%ee).



2i

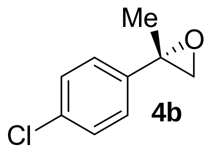
(*R*)-1-azido-2-(naphthalen-2-yl)propan-2-ol (2i). The general procedure was followed. Isolated 47 mg (19 %). $[\alpha]_D$ = -24.95 (c 0.940, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.83-7.76 (m, 3H), 7.50-7.41 (m, 3H), 3.62 (d, *J* = 14.1 Hz, 1H), 3.46 (d, *J* = 14.1 Hz, 1H), 2.58 (s, 1H), 1.61 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 133.0, 132.5, 128.1, 128.1, 127.5, 126.2, 126.0, 123.7, 123.0, 72.7, 61.8, 27.0; IR (neat) 3416, 3062, 2980, 2933, 2872, 2103, 1732, 1504, 1372, 1241, 1042, 856, 816, 747; HRMS ESI (*m* / *z*): $[M + Na]^+$ calcd for $C_{13}H_{13}N_3O$, 250.0951; found 250.0951. The enantiomeric excess was determined by SFC (chiralcel-AD-H, 2 mL/min, 5-40% MeOH @4%MeOH/min, *T*r (major) 9.80 min, *T*r(minor) 9.49 min (96%ee).



2j

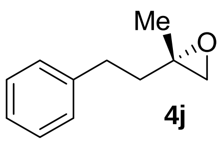
(*R*)-1-azido-2-methyl-4-phenylbutan-2-ol (2j). The general procedure was followed. Isolated 249 mg (39 %). $[\alpha]_D$ = - 10.95 (c 1.01, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 3H), 7.20 (d, *J* = 7.4 Hz, 3H), 3.35 (d, *J* = 12.1 Hz, 1H), 3.29 (d, *J* = 12.1 Hz, 1H), 2.77-2.62 (m, 2H), 1.82 (dt, *J* = 9.0 Hz, 2H), 176 (s, 1H), 1.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 128.6, 128.3, 126.0, 72.7, 60.9, 41.4, 30.1, 24.6; IR (neat) 3564, 3408, 3025, 2930, 2864, 2096, 1602, 1494, 1453, 1374, 1280; HRMS ESI (*m* / *z*): $[M + Na]^+$ calcd for $C_{11}H_{15}N_3O$, 228.1107; found 228.1108. The enantiomeric excess was determined by SFC (chiralcel-OD, 2 mL/min, 1-5% MeOH @0.25%MeOH/min, *T*r (major) 13.61 min, *T*r(minor) 12.96 min (98%ee).

3- Enantiomerically Enriched epoxides



4b

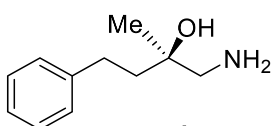
(2*S*)-2-(4-chlorophenyl)-2-methyloxirane (4b). Literature[1] 94% ee (*S*)-**4b**: $[\alpha]_D$ = + 19.9 (*c* 1.25, $CHCl_3$). Experimetal : $[\alpha]_D$ = + 18.7 (*c* 1.22, $CHCl_3$). The enantiomeric excess was determined by SFC (chiralcel-AD-H, 2 mL/min, 5-40% MeOH @4%MeOH/min, *T*r (major) 2.52 min, *T*r(minor) 2.75 min (99%ee).



4j

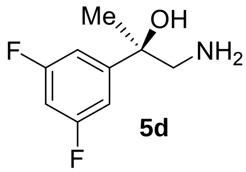
(2S)-2-methyl-2-(2-phenylethyl)oxirane (4j). Literature[1] 93% ee (*S*)-**4j**: $[\alpha]_D$ = + 2.9 (*c* 1.13, $CHCl_3$). Experimental : $[\alpha]_D$ = + 2.7 (*c* 1.03, $CHCl_3$). The enantiomeric excess was determined by SFC (chiralcel-OD, 2 mL/min, 1-5% MeOH @0.25%MeOH/min, *T*r (major) 5.33 min, *T*r(minor) 4.44 min (99%ee).

4- Enantiomerically Enriched 1,2-di-substituted amino alcohols and 2,2-di-substituted Aziridines



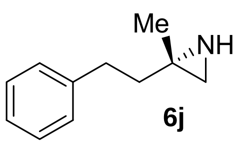
5j

(*R*)-1-amino-2-methyl-4-phenylbutan-2-ol (5j). To a stirred solution of azido-alcohol **2j** (104 mg, 0.51 mmol) in ethanol (2 mL) at r.t. was added 10% palladium on carbon (18 mg, 0.169 mmol). The solution was degassed and submitted to H_2 (45 psi) O/N. The reaction mixture was filtered and concentrated under reduced pressure to provide **5j** (90 mg, 99%). $[\alpha]_D$ = -7.08 (c 0.48, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.24-7.19 (m, 3H), 2.79-2.66 (m, 2H), 2.71 (d, *J* = 12.5 Hz, 1H), 2.64 (d, *J* = 12.5, 1H), 1.97 (s(br), 3H), 1.85-1.69 (m, 2H), 1.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 128..4, 128.3, 125.8, 71.3, 50.9, 41.6, 30.2, 24.2; HRMS ESI (*m* / *z*): [M + H]+ calcd for $C_{11}H_{17}NO$, 180.1383; found 180.1389. The enantiomeric excess was determined by HPLC (AD-RH, Isocratic 80% pH 9.2 $Na_2B_4O_7$ (aq)/ 20% ACN, 1.0mL/min for 18 min, *T*r (major) 11.88 min, *T*r(minor) 10.56 min (98%ee).



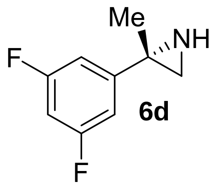
5d

(*R*)-1-amino-2-(3,5-difluorophenyl)propan-2-ol (5d). The general procedure was followed. Isolated 86 mg (98 %). $[\alpha]_D$ = -15.59 (c 0.63, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (d, *J* =7.5 Hz, 2H), 6.69 (t, *J* = 9.0 Hz, 1H), 3.02 (d, *J* = 12.5 Hz, 1H), 2.80 (d, *J* = 12.5 Hz, 1H), 2.33 (s(br), 3H), 1.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0 (dd, *J* = 246, 12 Hz), 151.3 (t, *J* = 8 Hz), 108.3 (dd, *J* = 20, 6 Hz), 101.9 (t, *J* = 25 Hz), 73.0, 51.4, 27.6; HRMS ESI (*m* / *z*): [M + H]+ calcd for $C_9H_{11}F_2NO$, 188.0881; found 188.0887. The enantiomeric excess was determined by HPLC (AD-RH, 20-36% pH 9.2 $Na_2B_4O_7$ (aq) in twelve minutes/ ACN, 1.0mL/min for 15 min, *T*r (major) 10.39 min, *T*r(minor) 6.69 min (97%ee).

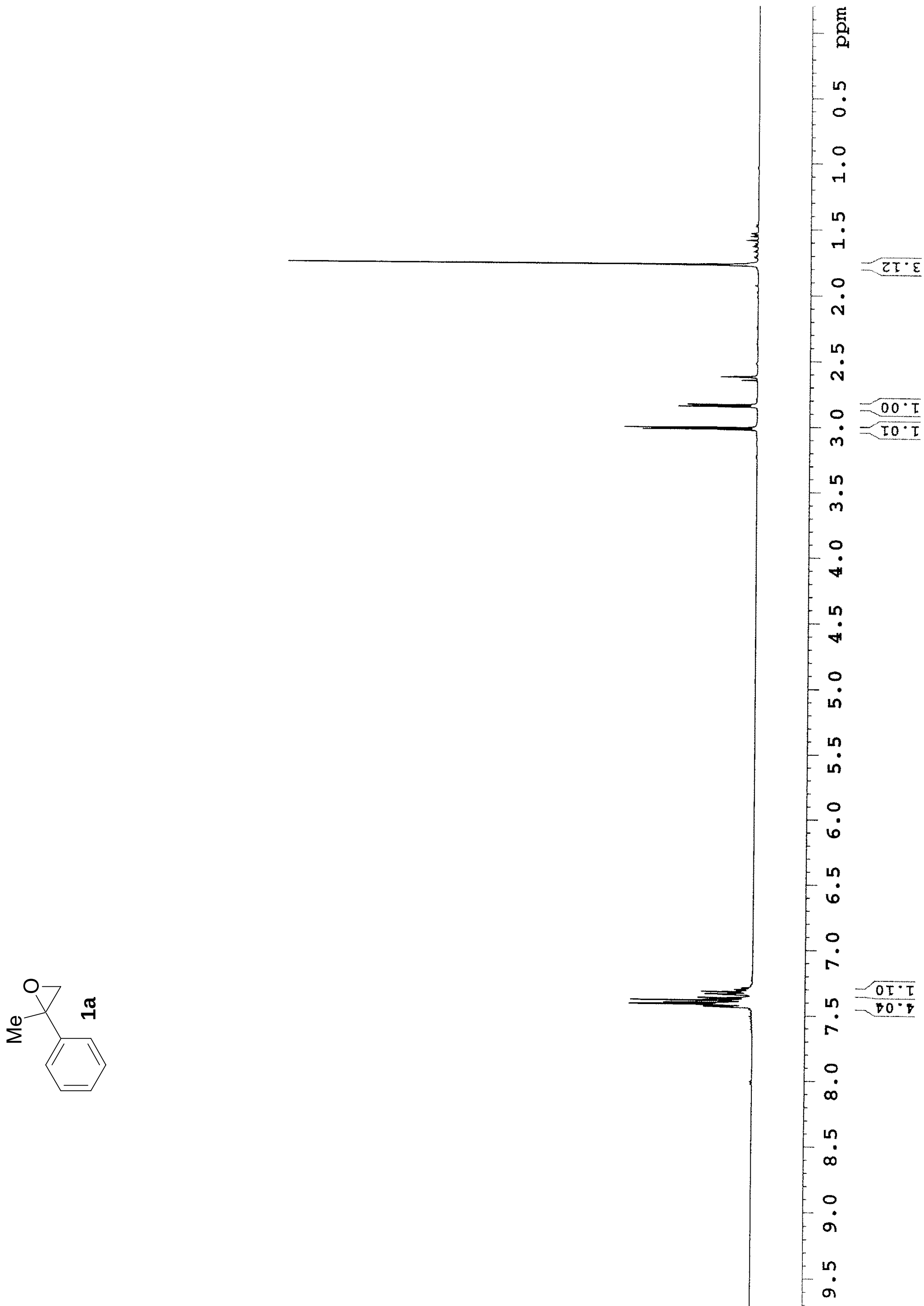


6j

(*S*)-2-methyl-2-phenethylaziridine (6j). To a stirred solution of azido-alcohol **2d** (400 mg, 1.93 mmol) in acetonitrile (3 mL) at 60°C was added portion wise triphenylphosphine (1.03 g, 3.91 mmol) and the reaction mixture was stirred at that temperature overnight The reaction mixture was diluted with MTBE and HCl 1N. The organic layer was wash with HCl 1N and the combined aqueous extracts were back extracted with MTBE. The aqueous layers were basify with K_2CO_3 6N until pH=12. The aqueous layer was extracted with MTBE. The combined organic extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to provide 188 mg (60%) of **6j**. $[\alpha]_D$ = + 10.52 (c 0.97, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.27 (m, 2H), 7.22 (d, *J* = 7.3 Hz, 3H), 2.84-2.70 (m, 2H), 1.87-1.68 (m, 2H), 1.58 (d, *J* = 6.8 Hz, 2H), 1.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 128.4, 128.3, 125.9, 40.9, 34.7, 33.0, 32 .5, 22.8; IR (neat) 3313, 3089, 3058, 3024, 2922, 2853, 1599, 1494, 1452, 1374, 1032, 743, 698; HRMS ESI (*m* / *z*): [M + H]+ calcd for $C_{11}H_{15}N$, 162.1277; found 162.1302. The enantiomeric excess was determined by SFC (chiralcel-OD, 2 mL/min, 5-40% MeOH @4%MeOH/min, *T*r (major) 6.82 min, *T*r(minor) 6.54 min (97%ee).


6d

(S)-2-(3,5-difluorophenyl)-2-methylaziridine (6d). The general procedure was followed. Isolated 130 mg (94 %). $[\alpha]_D$ = + 17.3 (c 0.60, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95-6.92 (m, 2H), 6.72-6.67 (m, 1H), 2.11 (d, J = 3.5 Hz, 1H), 1.93 (d, J = 4 Hz, 1H), 1.67 (s, 3H), 1.67 (s (br), 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0 (dd, J = 246, 13 Hz), 147.8 (t, J = 8.8 Hz), 109.1 (dd, 20, 6.1 Hz), 102.1 (t, J = 32 Hz), 36.1, 35.8, 24.5; HRMS ESI (*m* / *z*): [M + H]+ calcd for $C_9H_9NF_2$, 170.0776; found 170.0809. The enantiomeric excess was determined by GC (Restek Gamma dex SA, 30m x 0.32 mm x 0.25 um, 15 psi, split 20 : 1, 100 °C hold 2 min the ramp to 120 °C at 1 °C/min, hold 2 min, ramp to 200 °C at 20 °C/min hold 6 min), *T*r (major) 23.46 min, *T*r(minor) 22.45 min (94%ee).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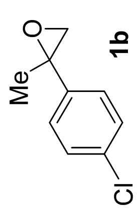
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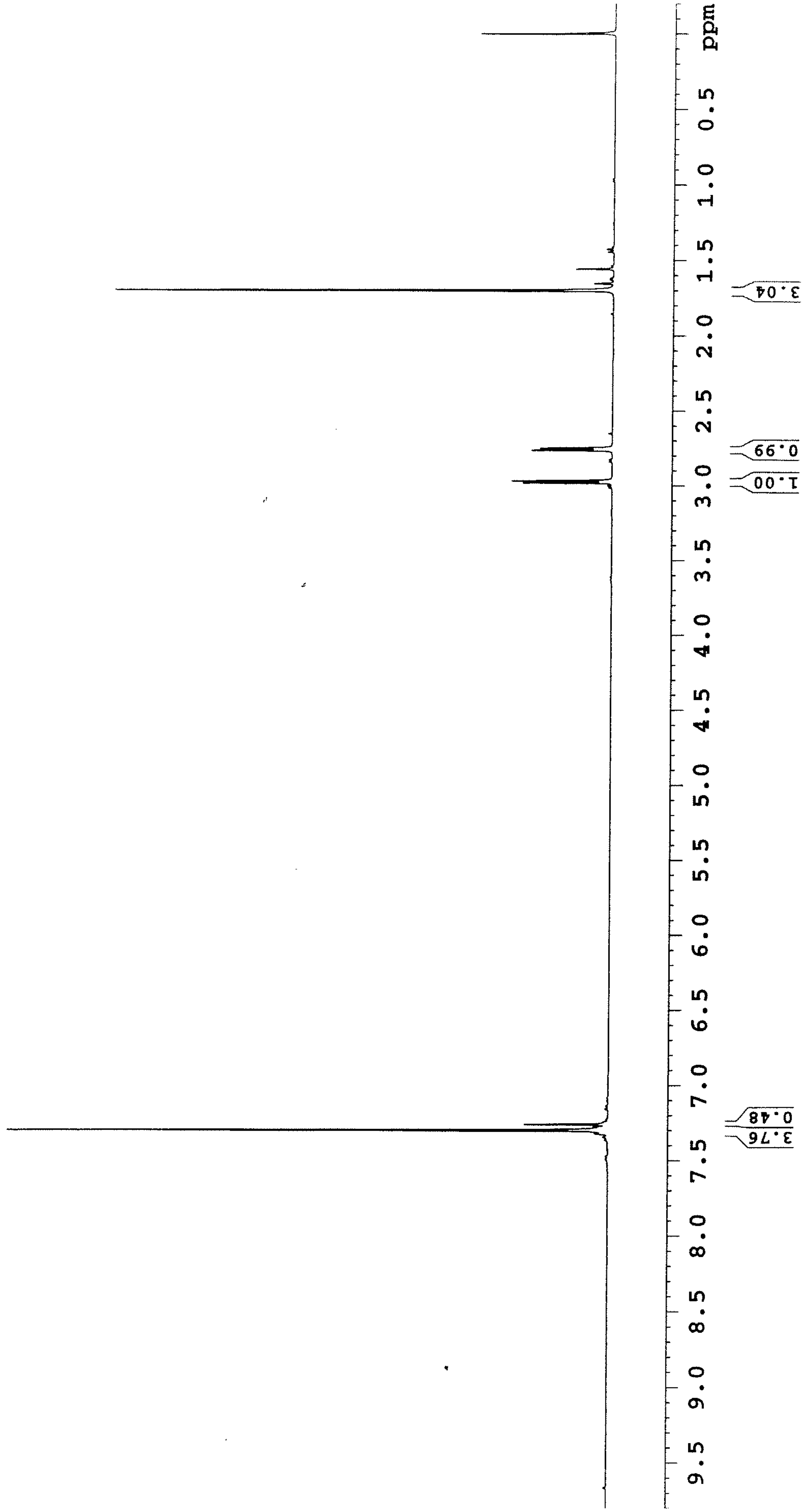
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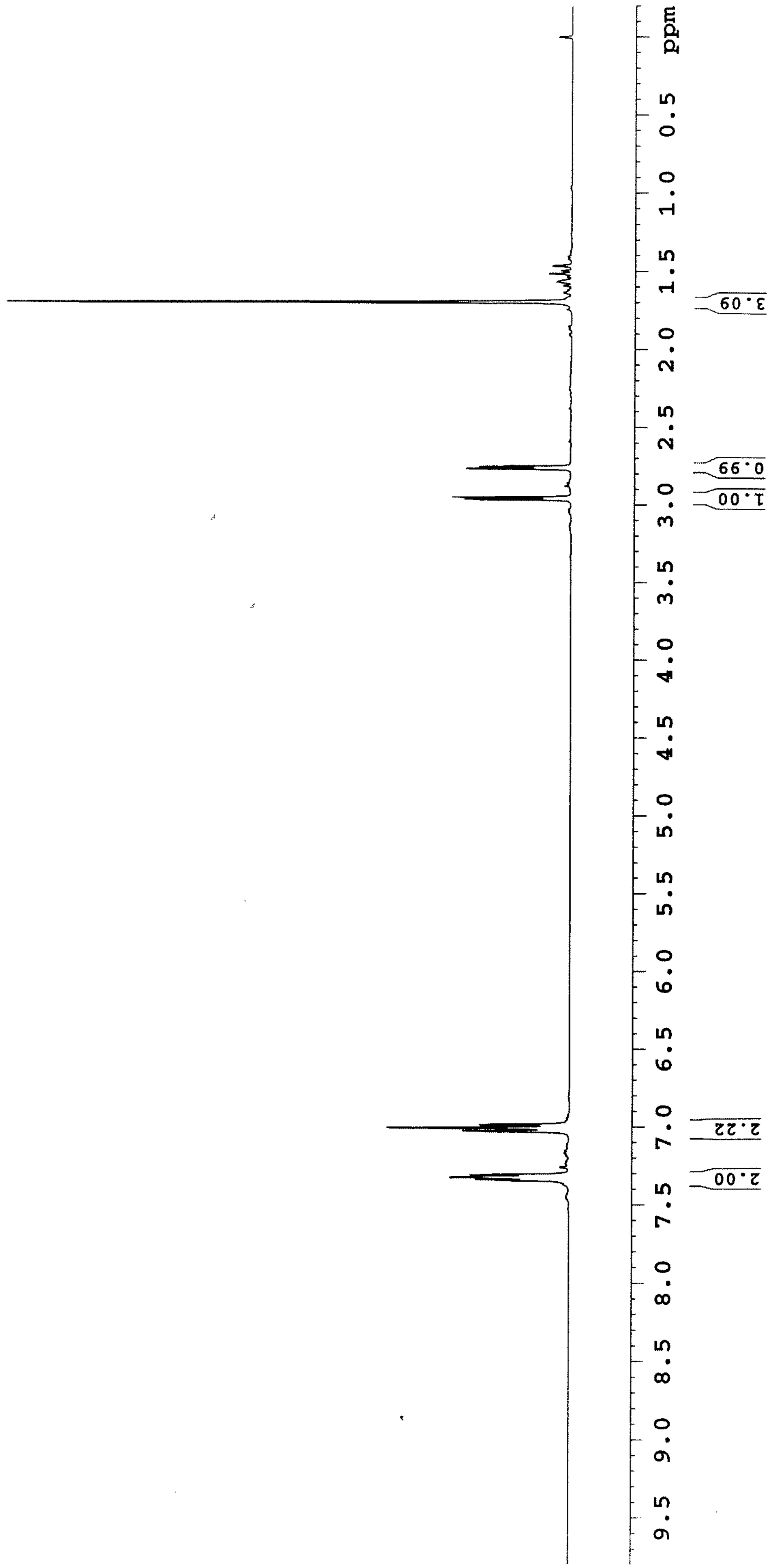
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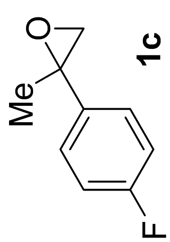
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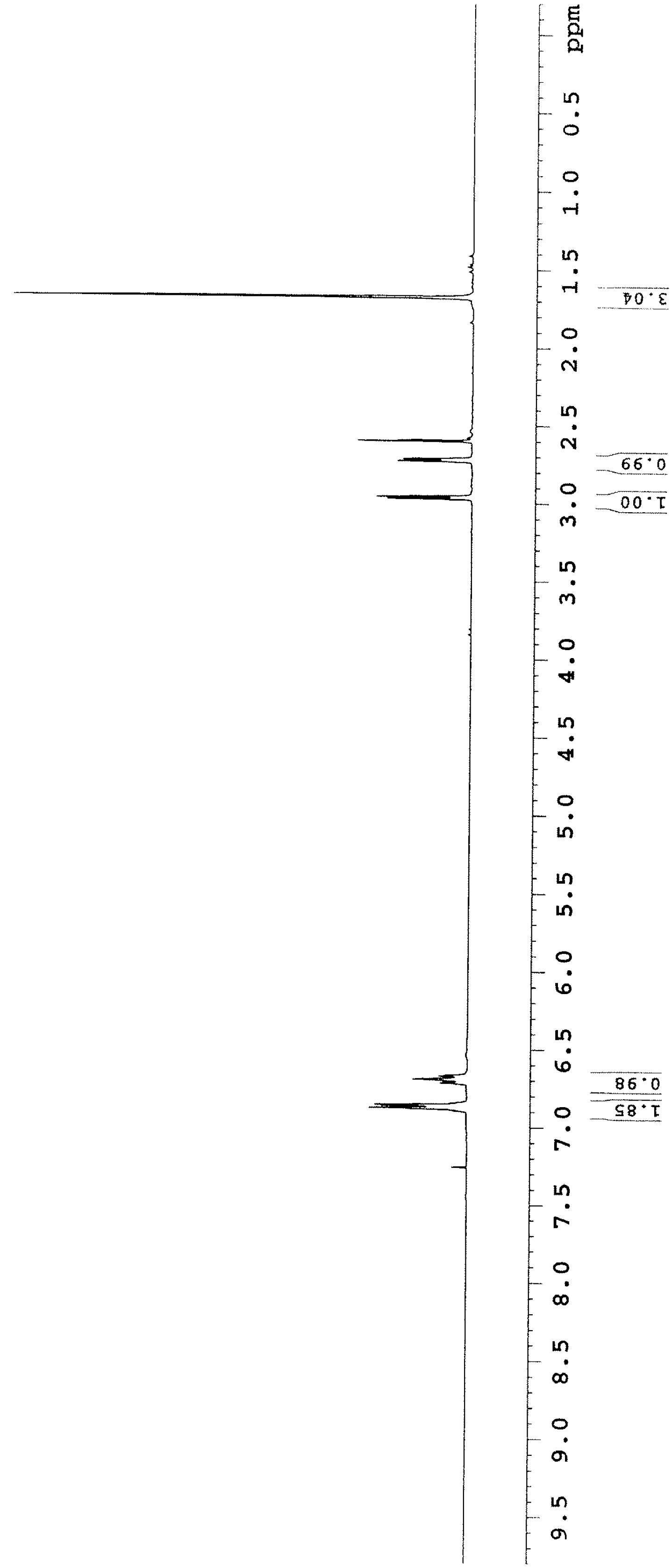
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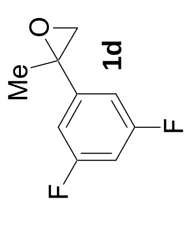
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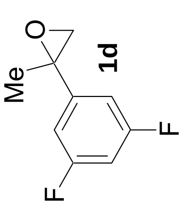

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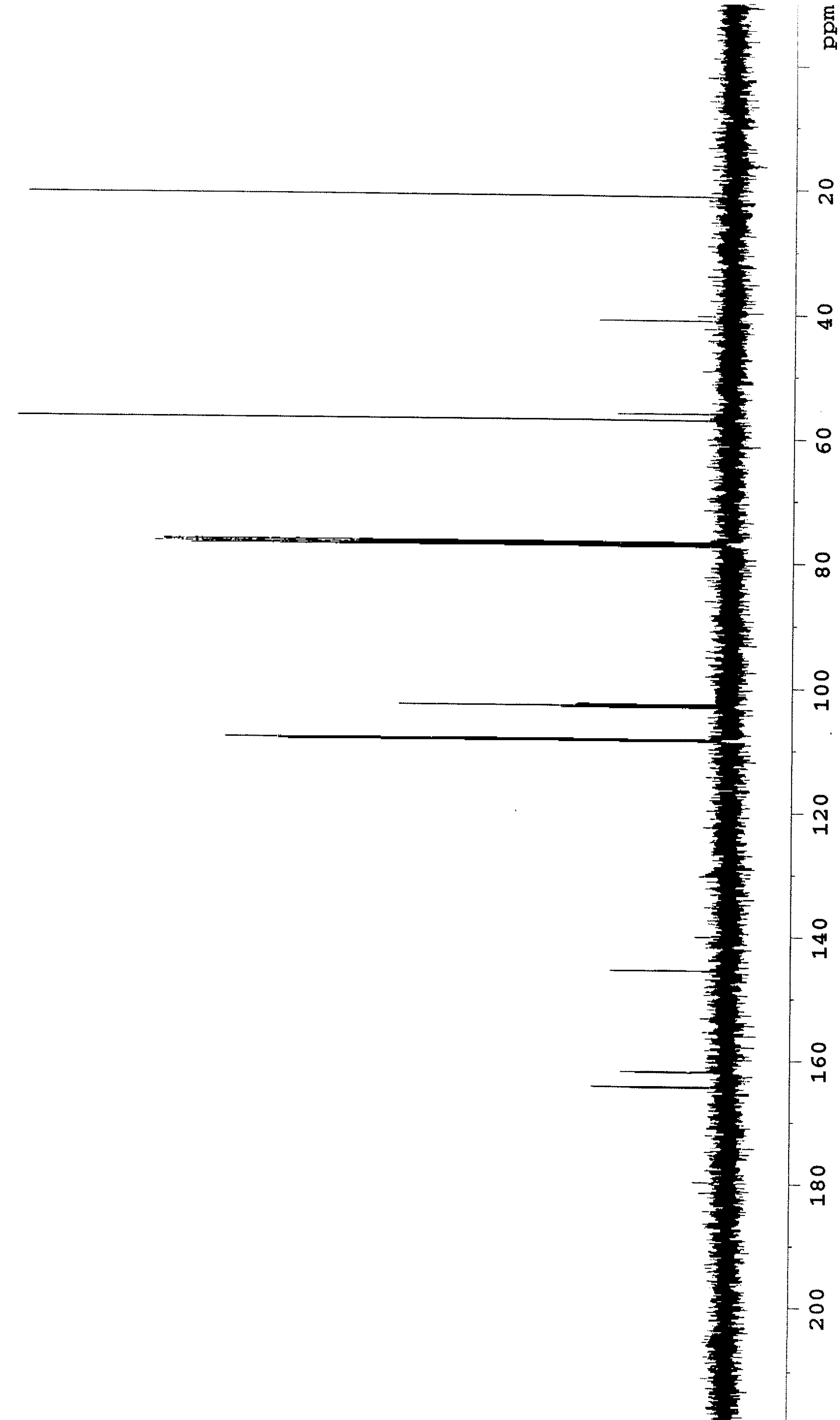

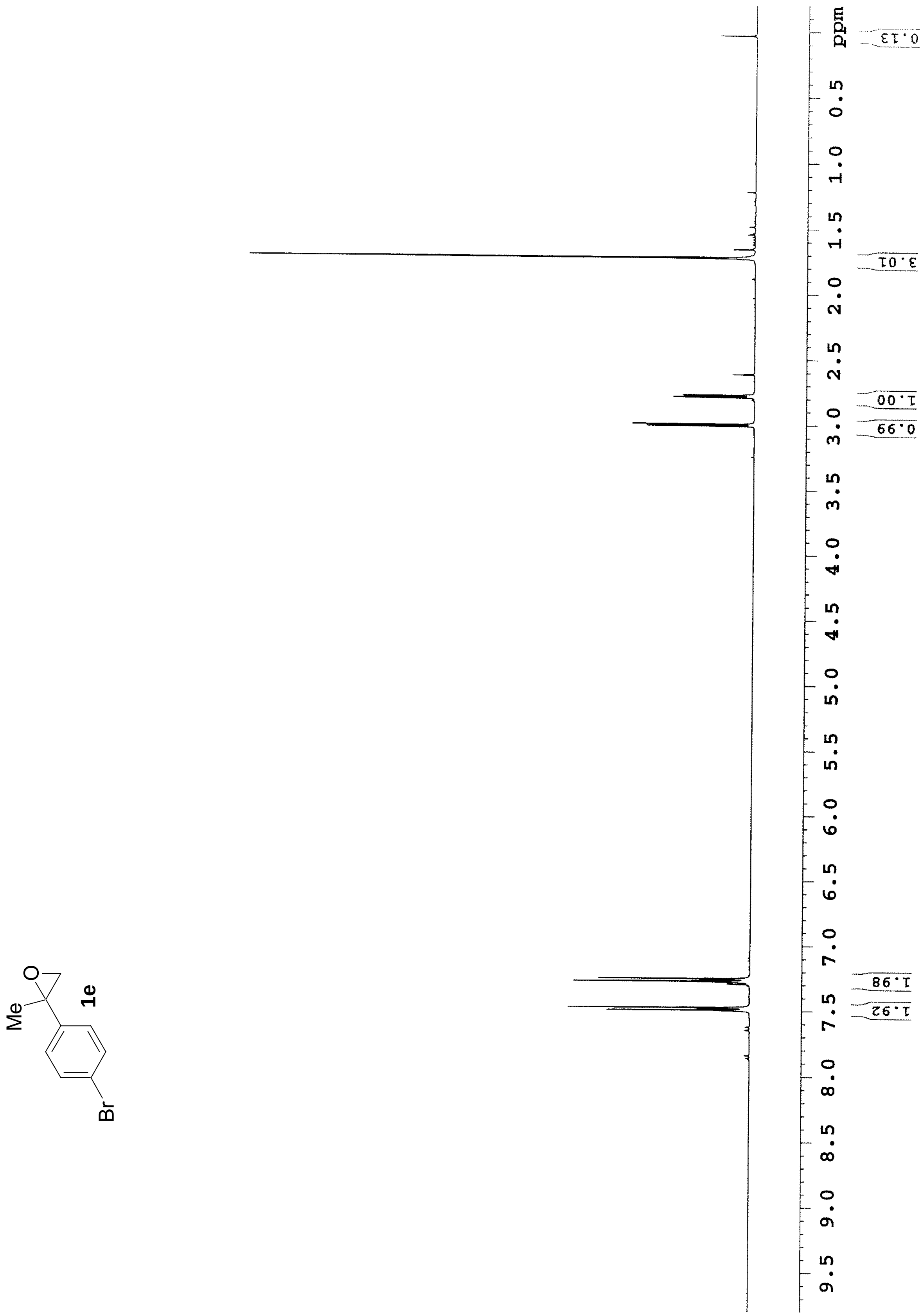
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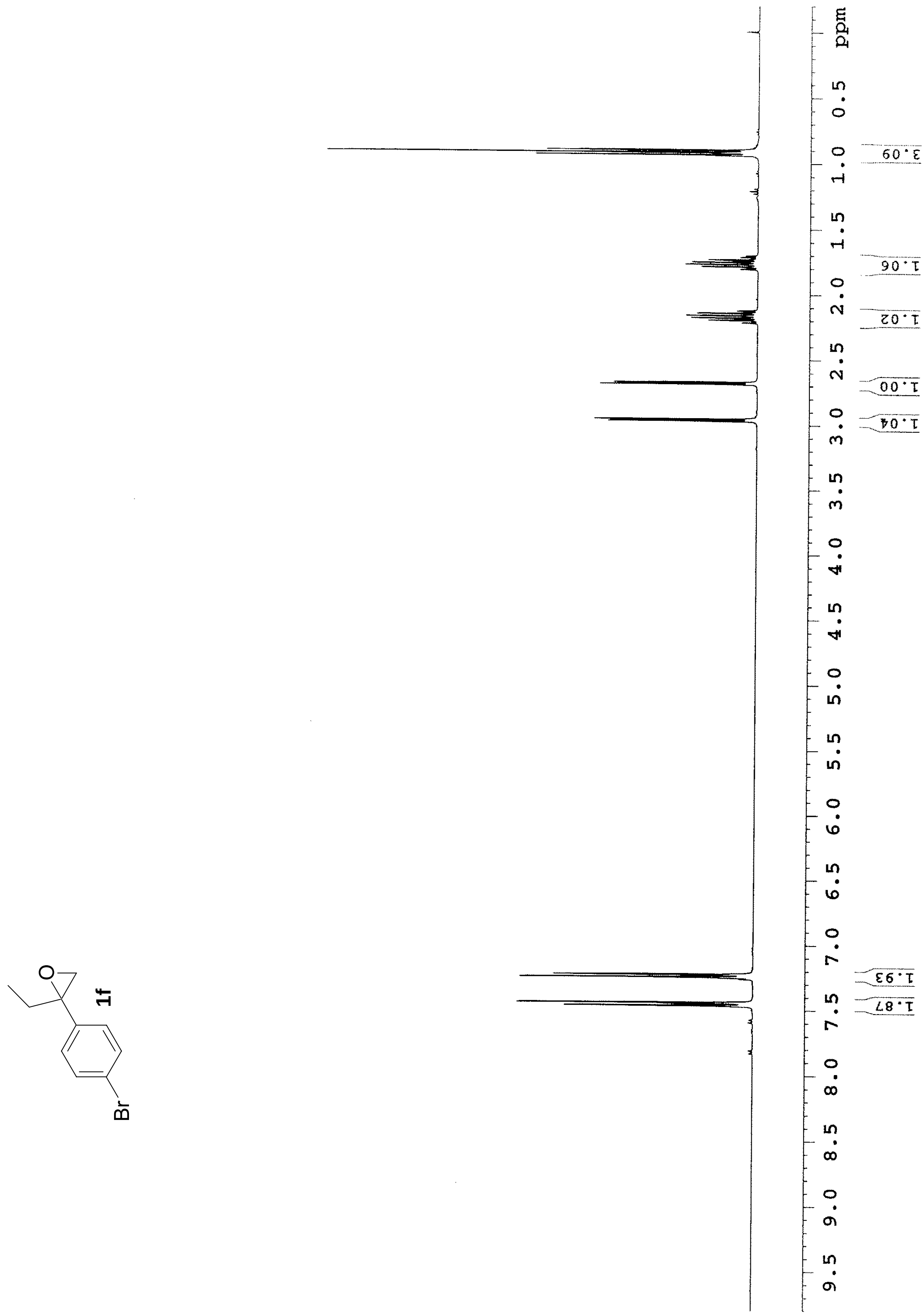
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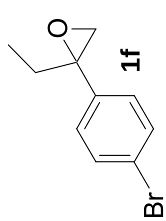

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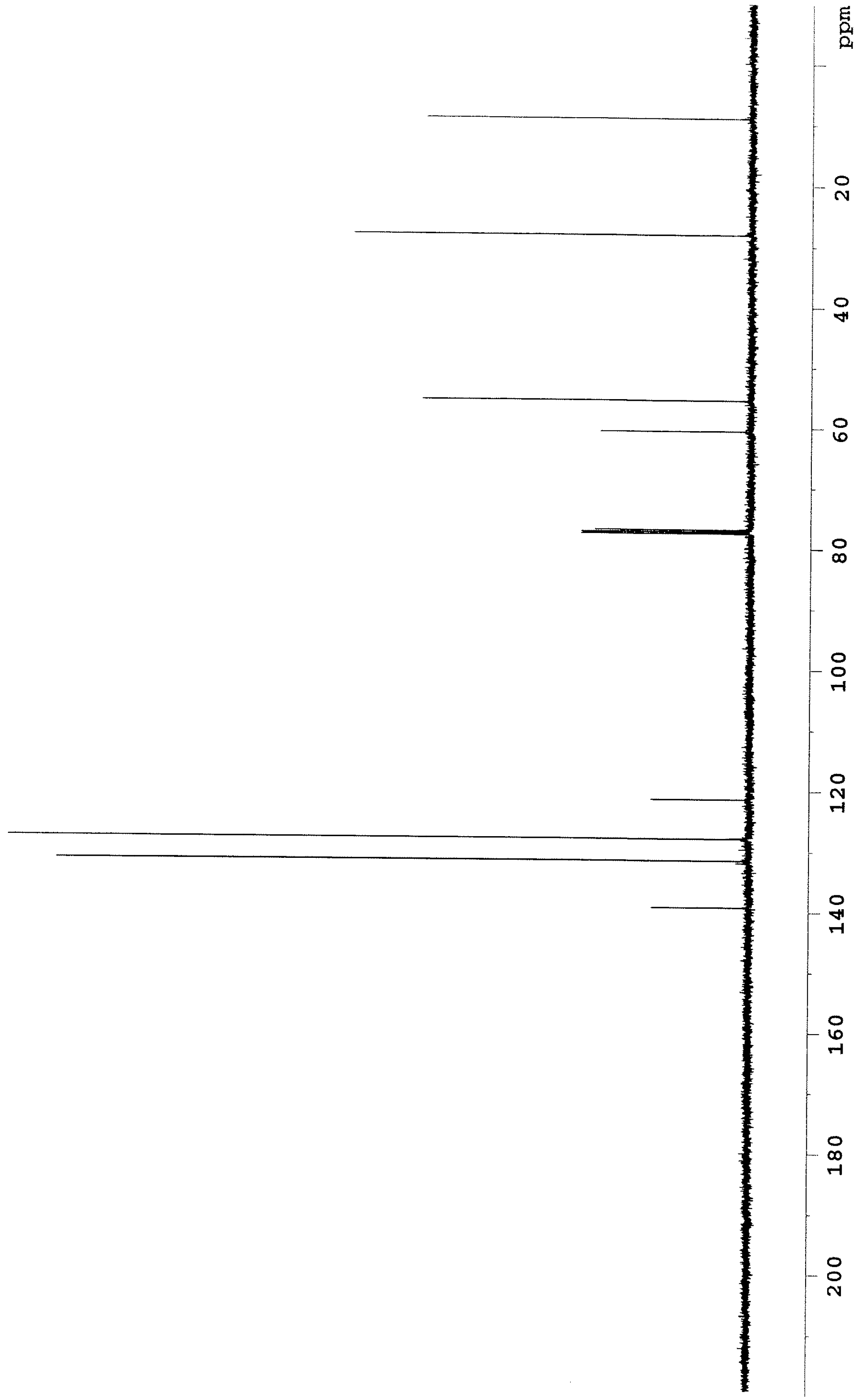

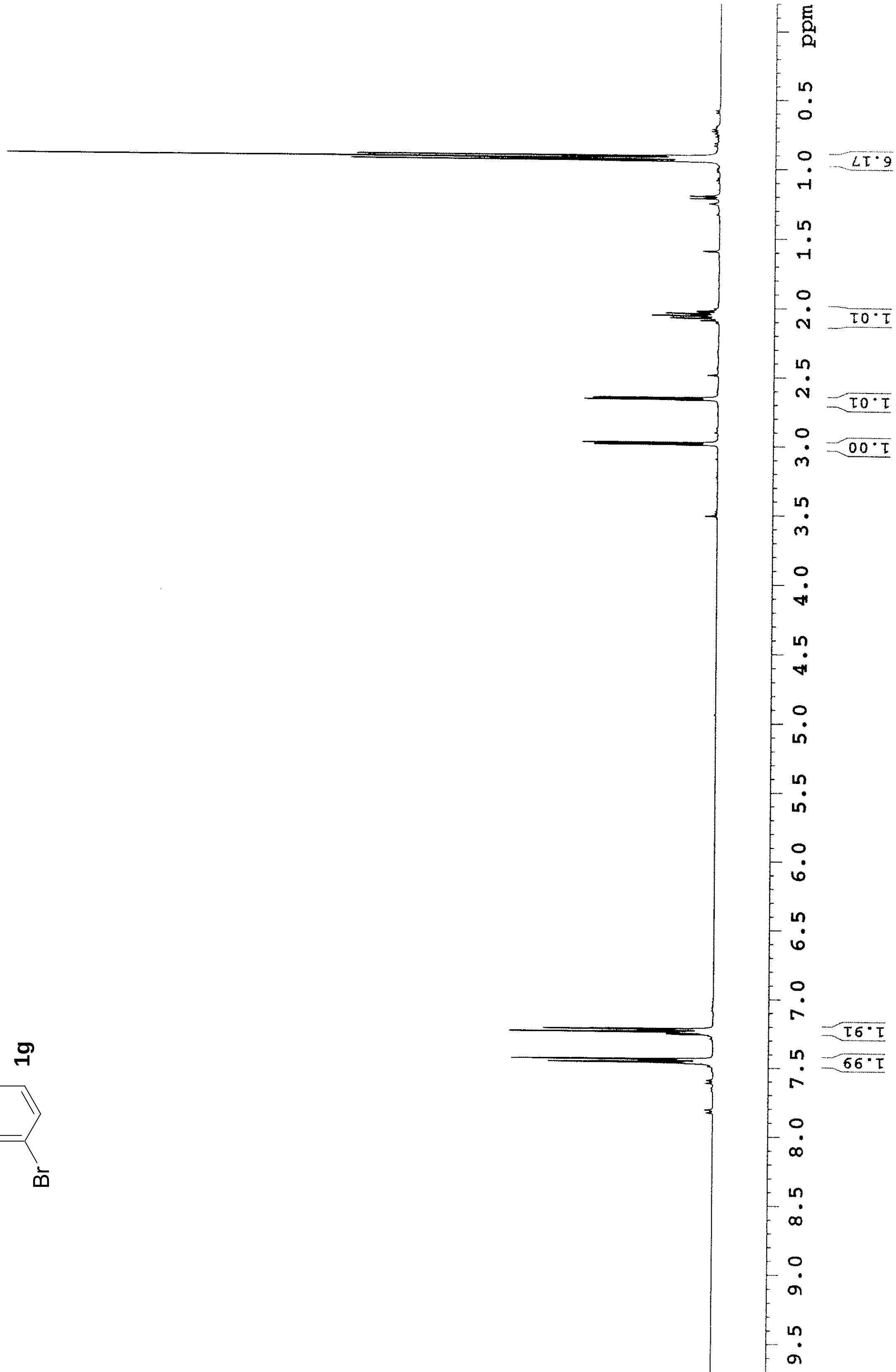
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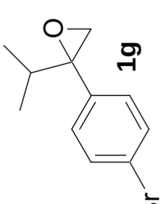
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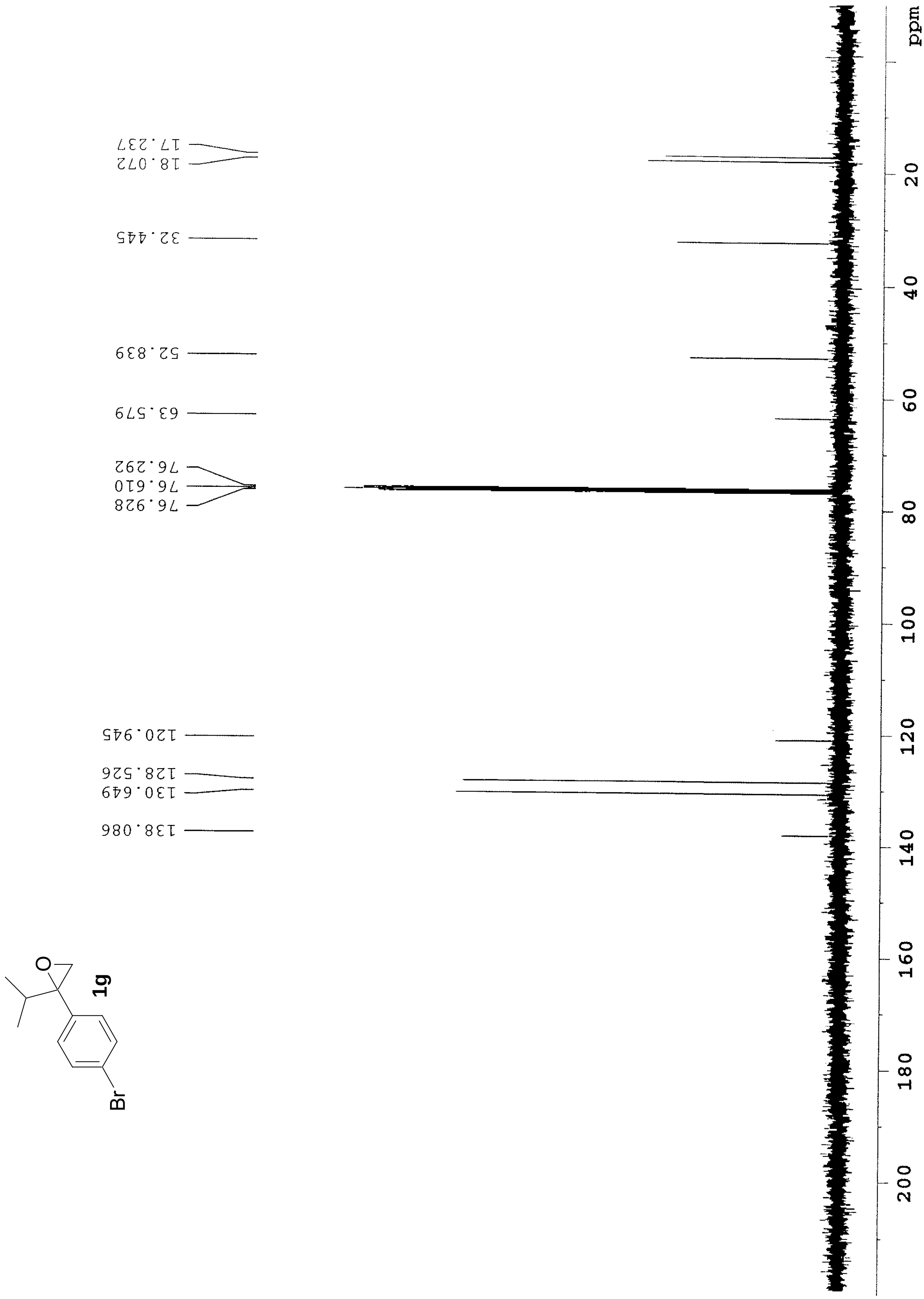
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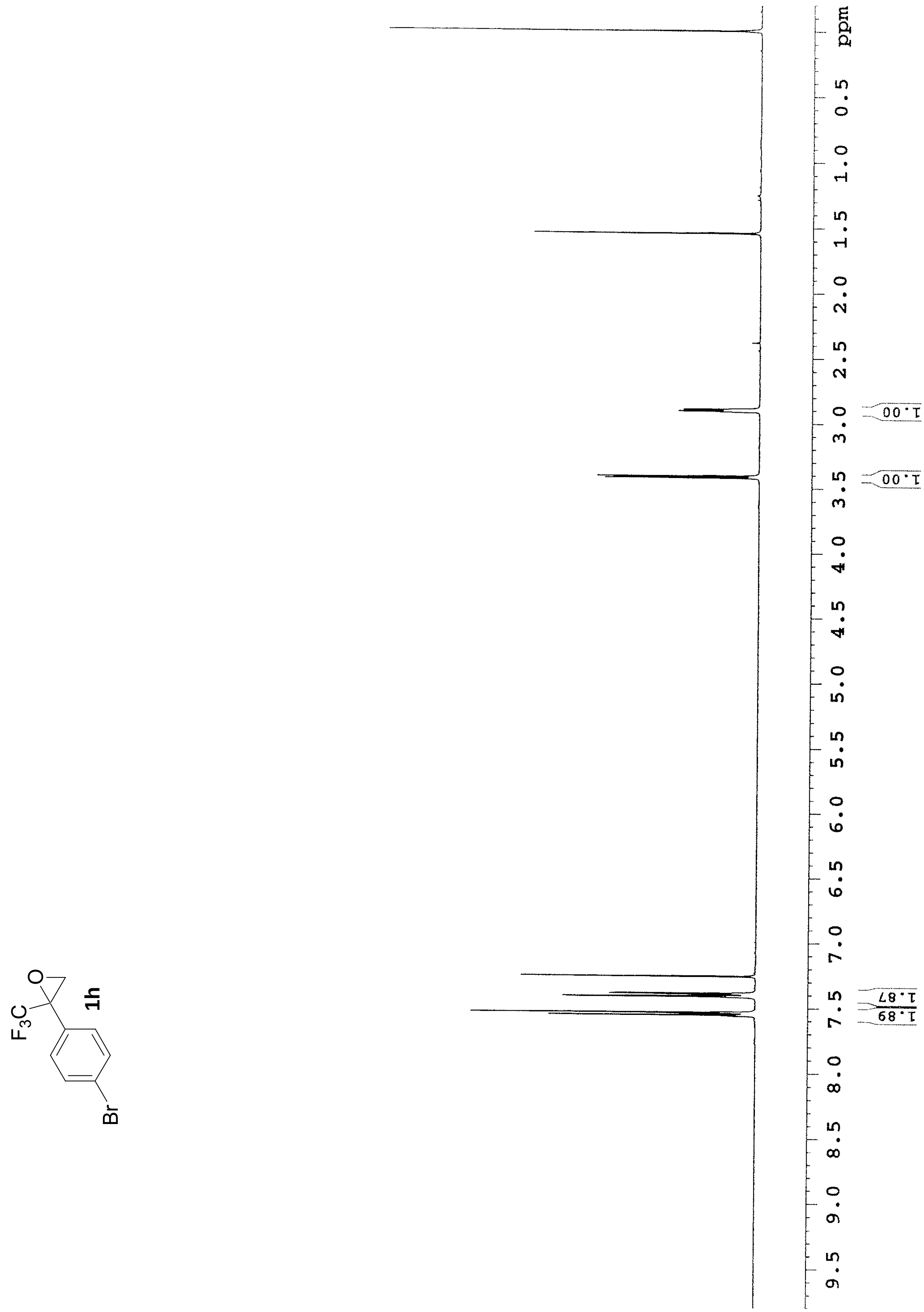

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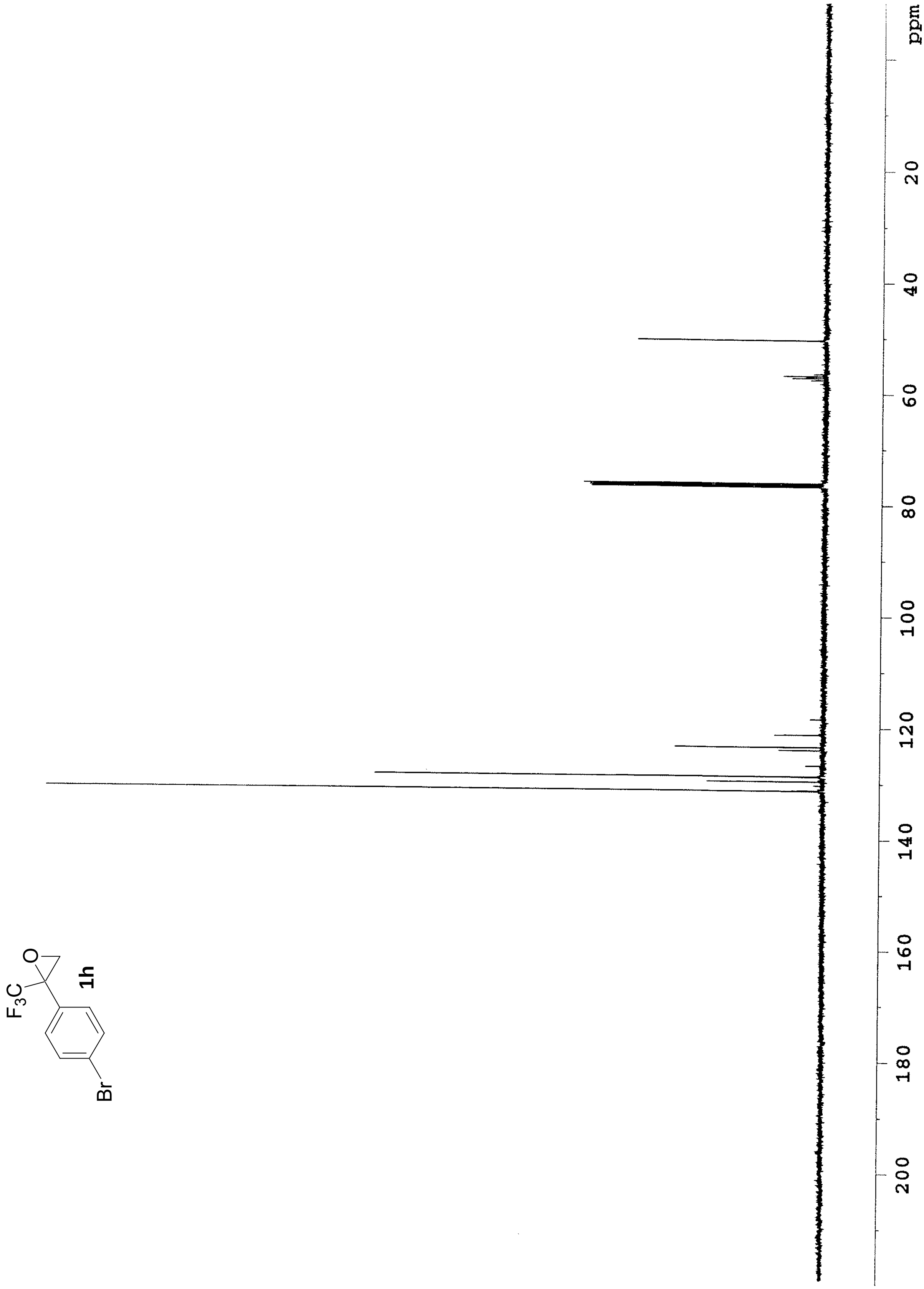
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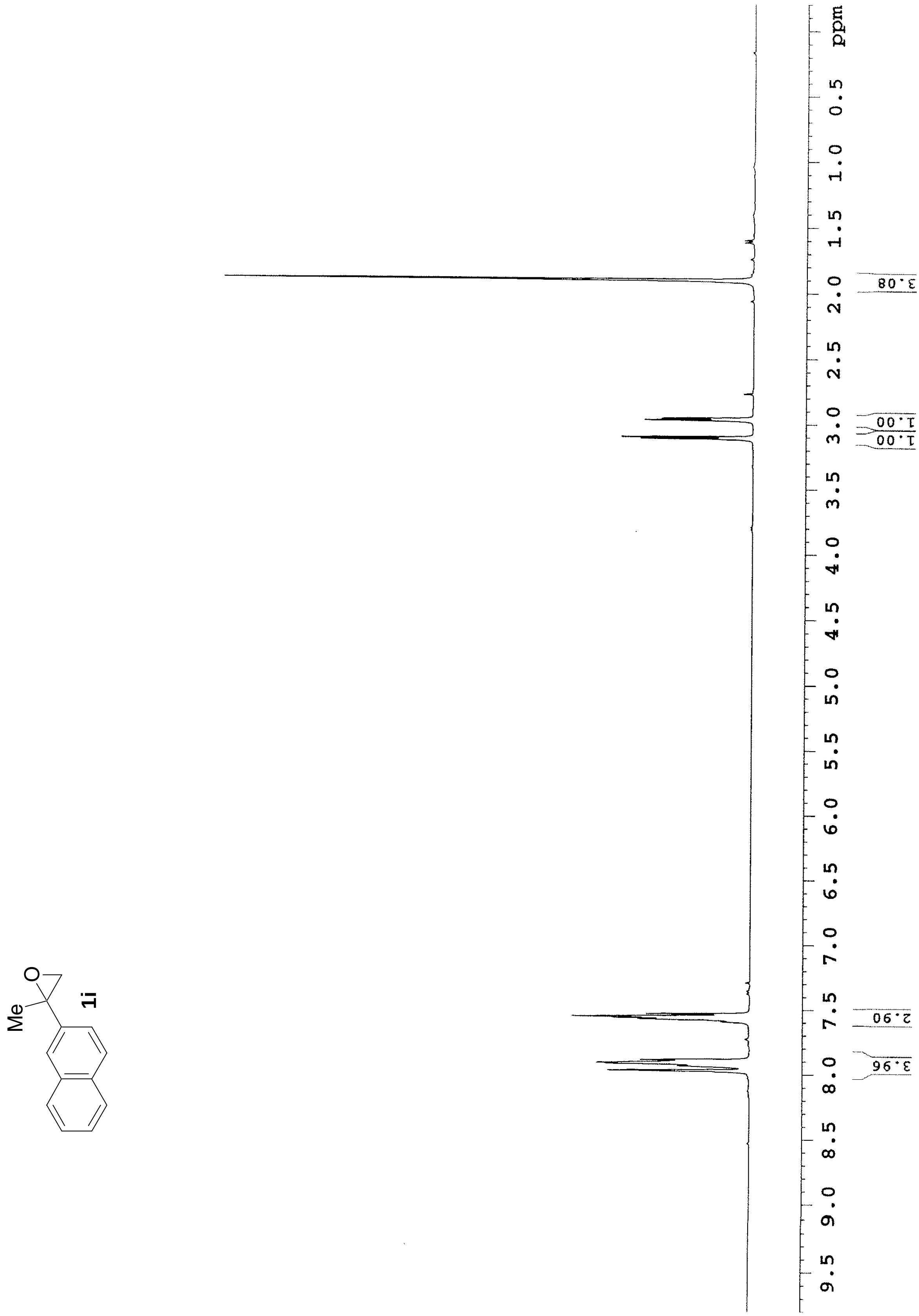
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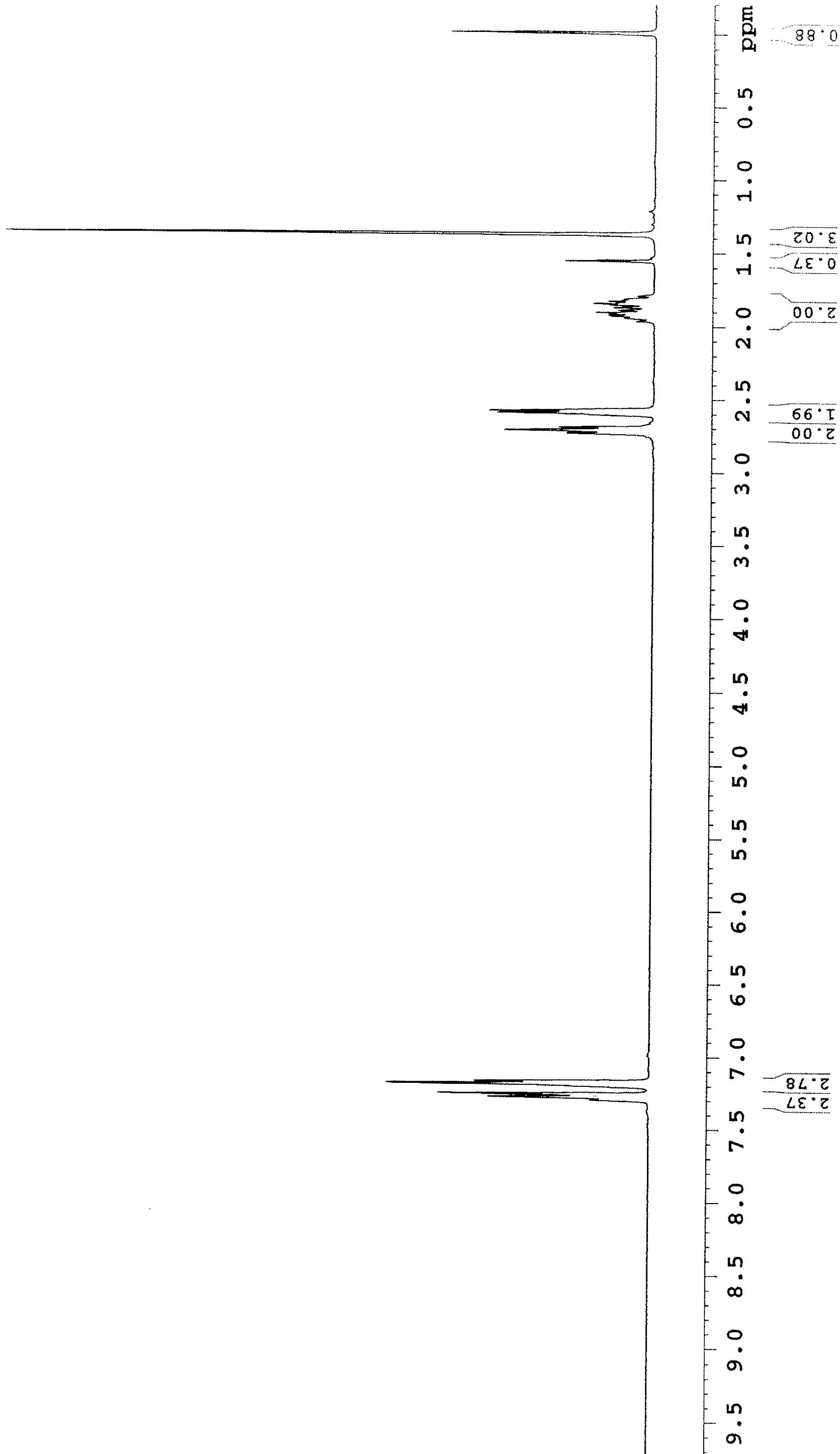
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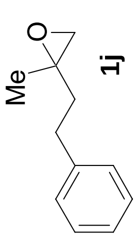
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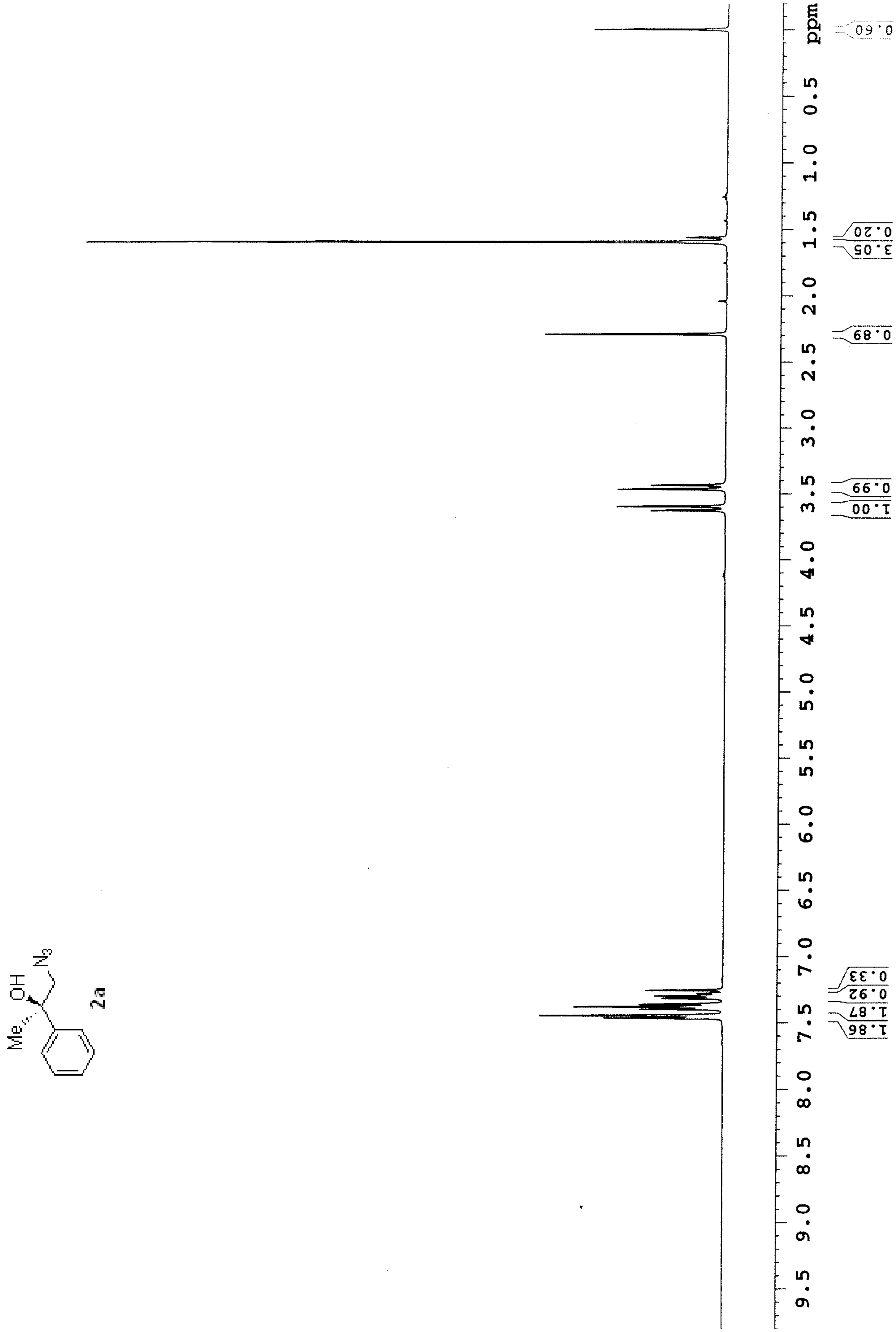

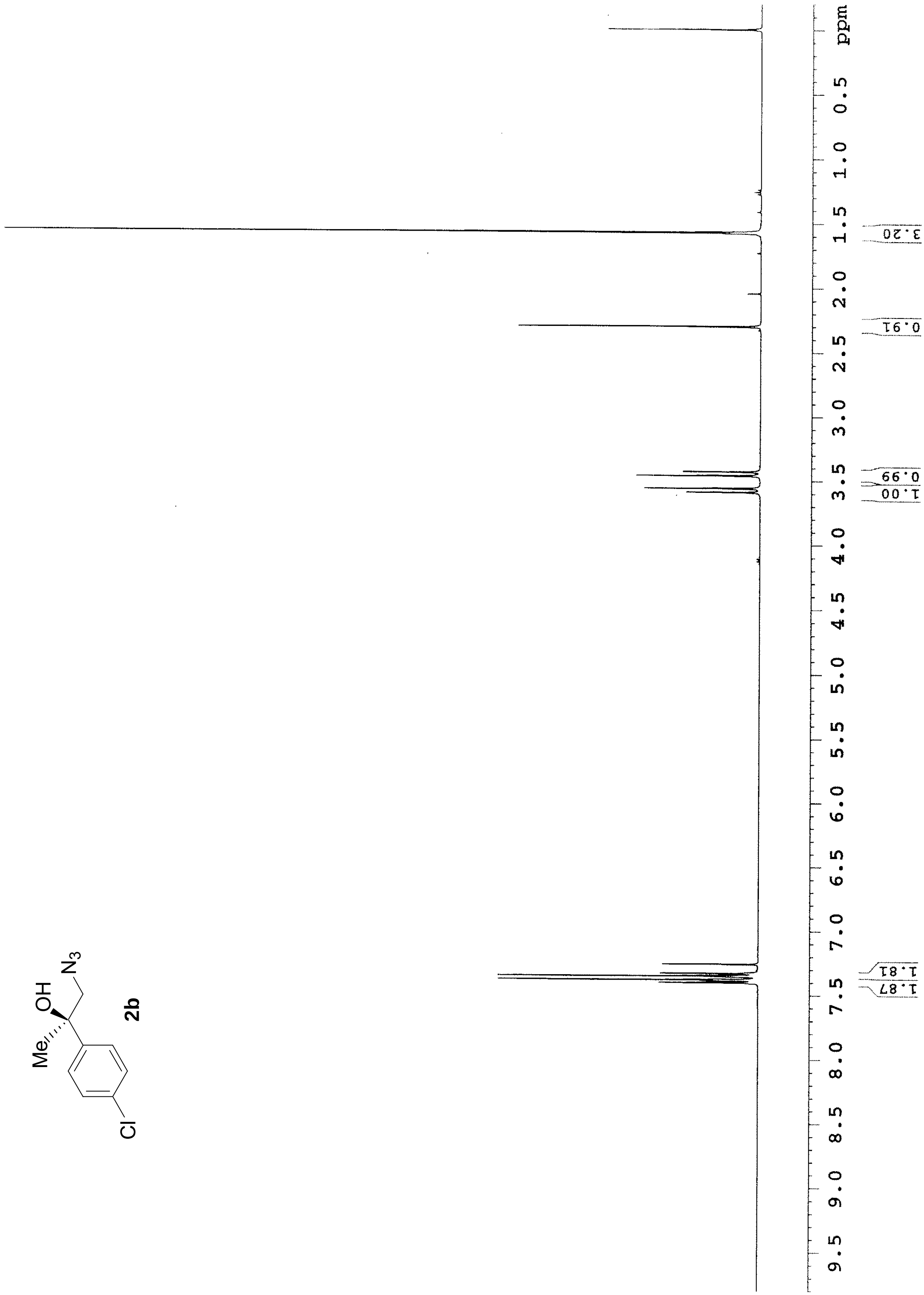
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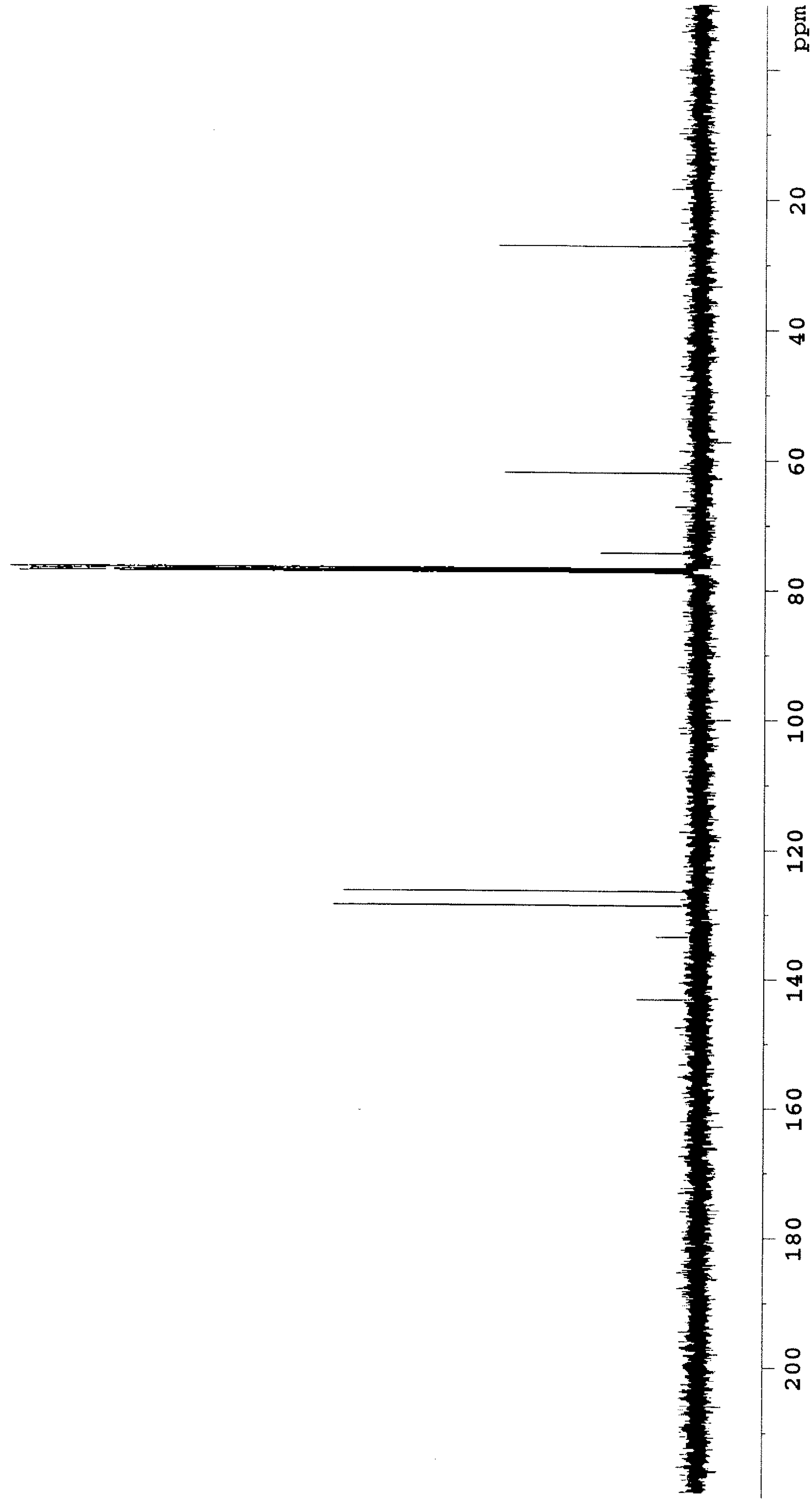
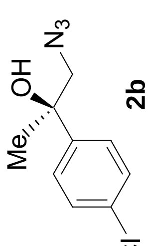
2b





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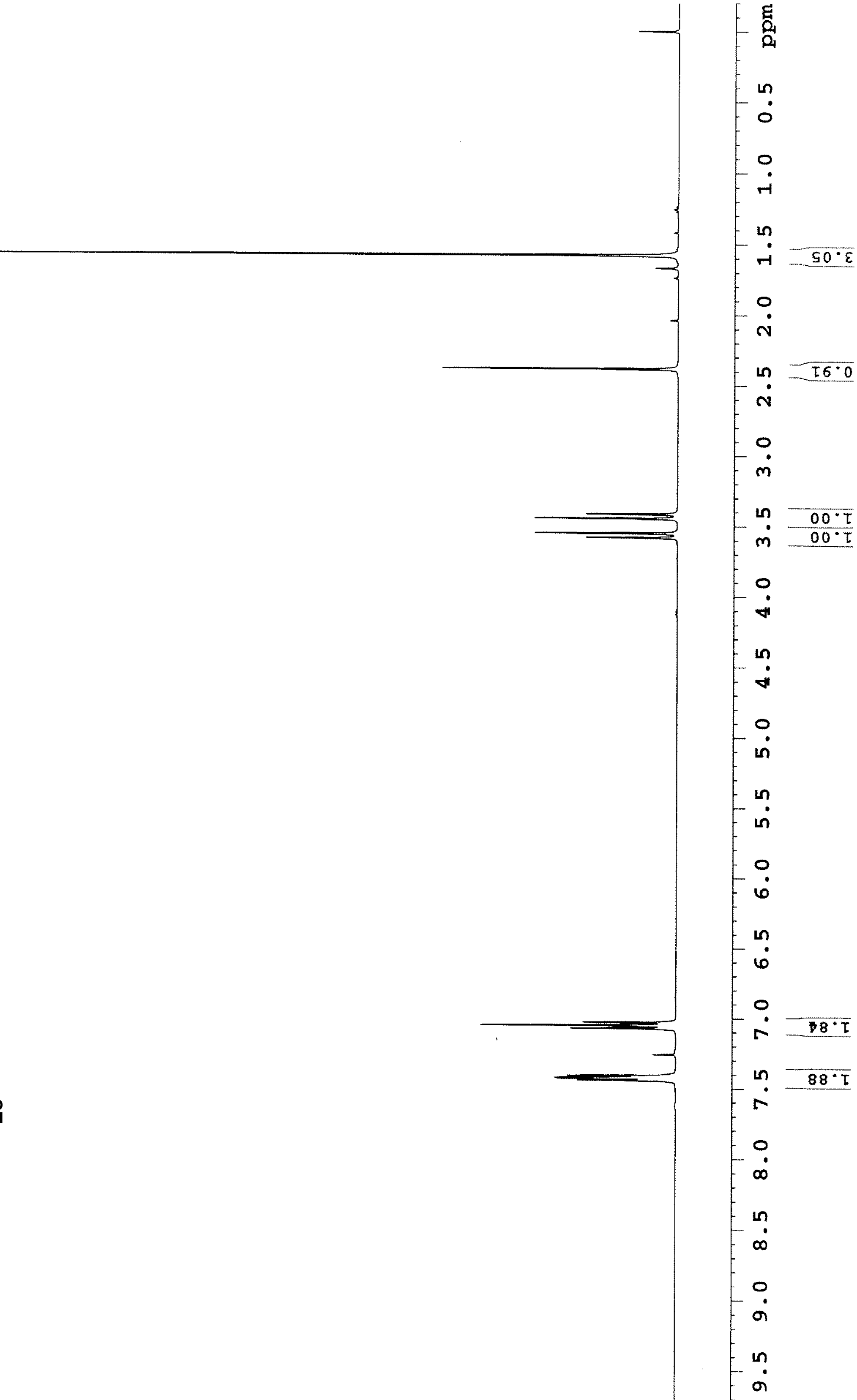
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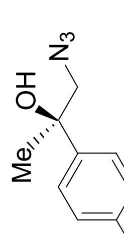
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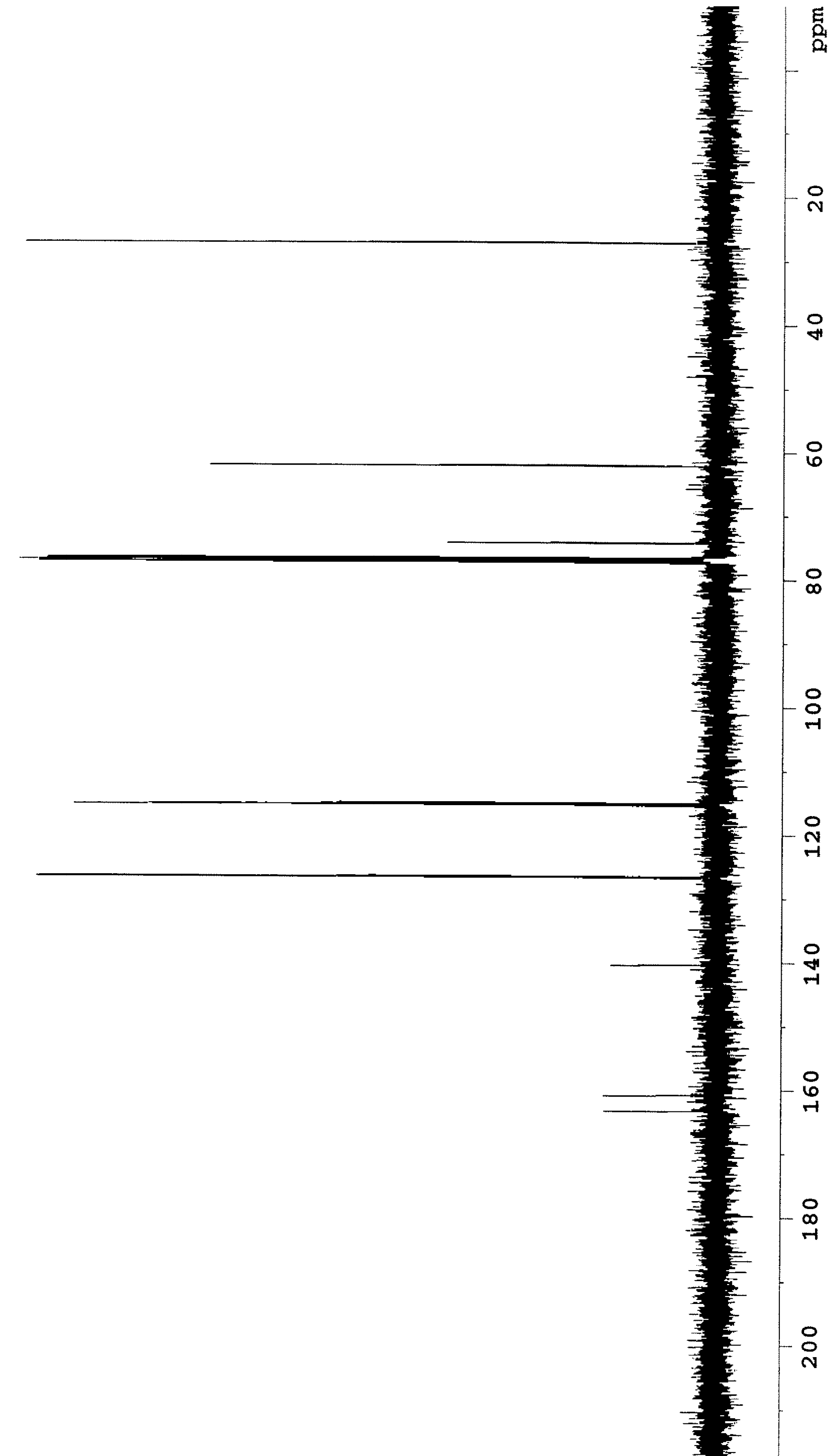

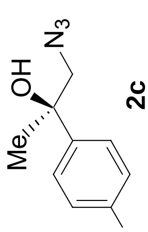

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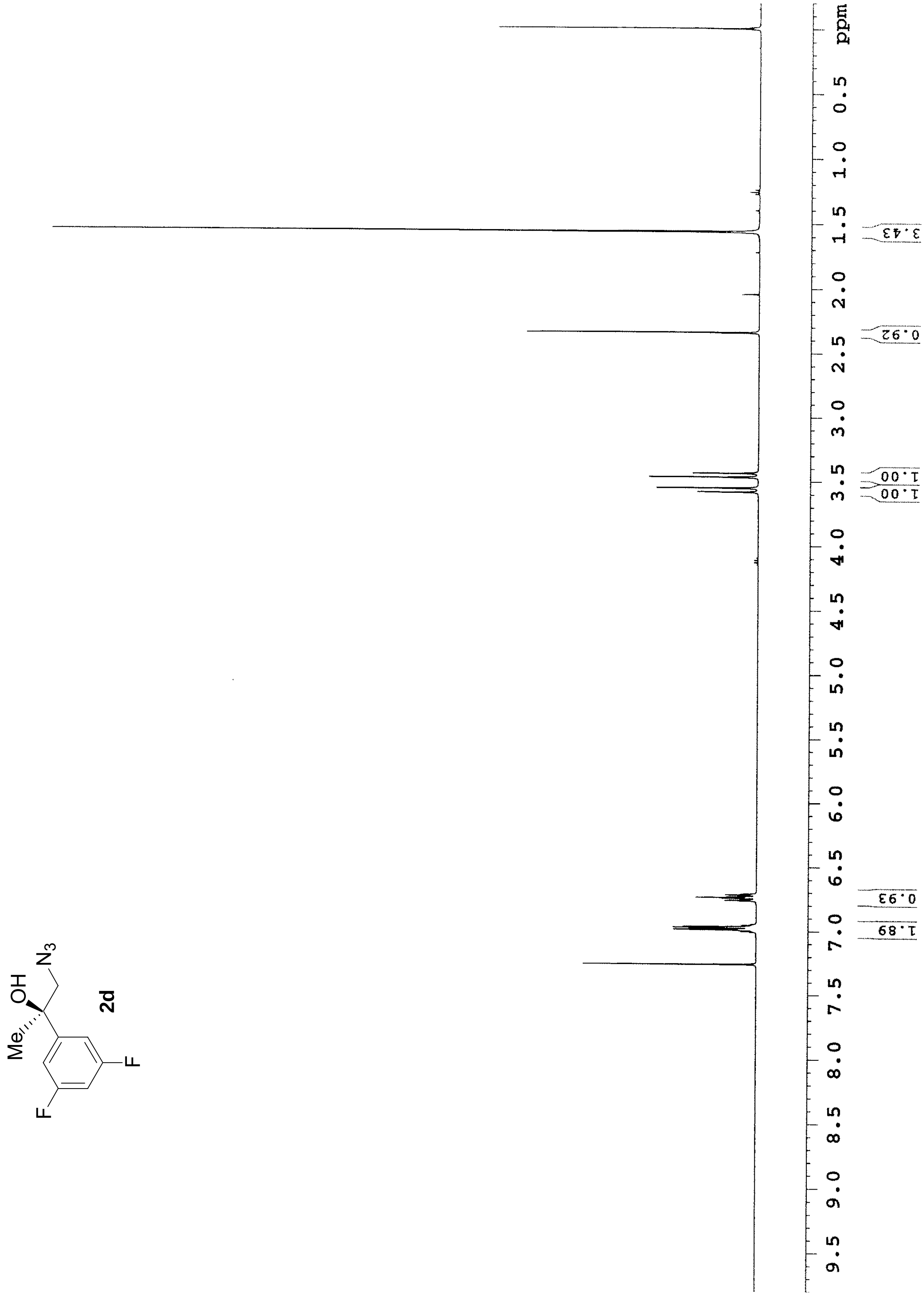

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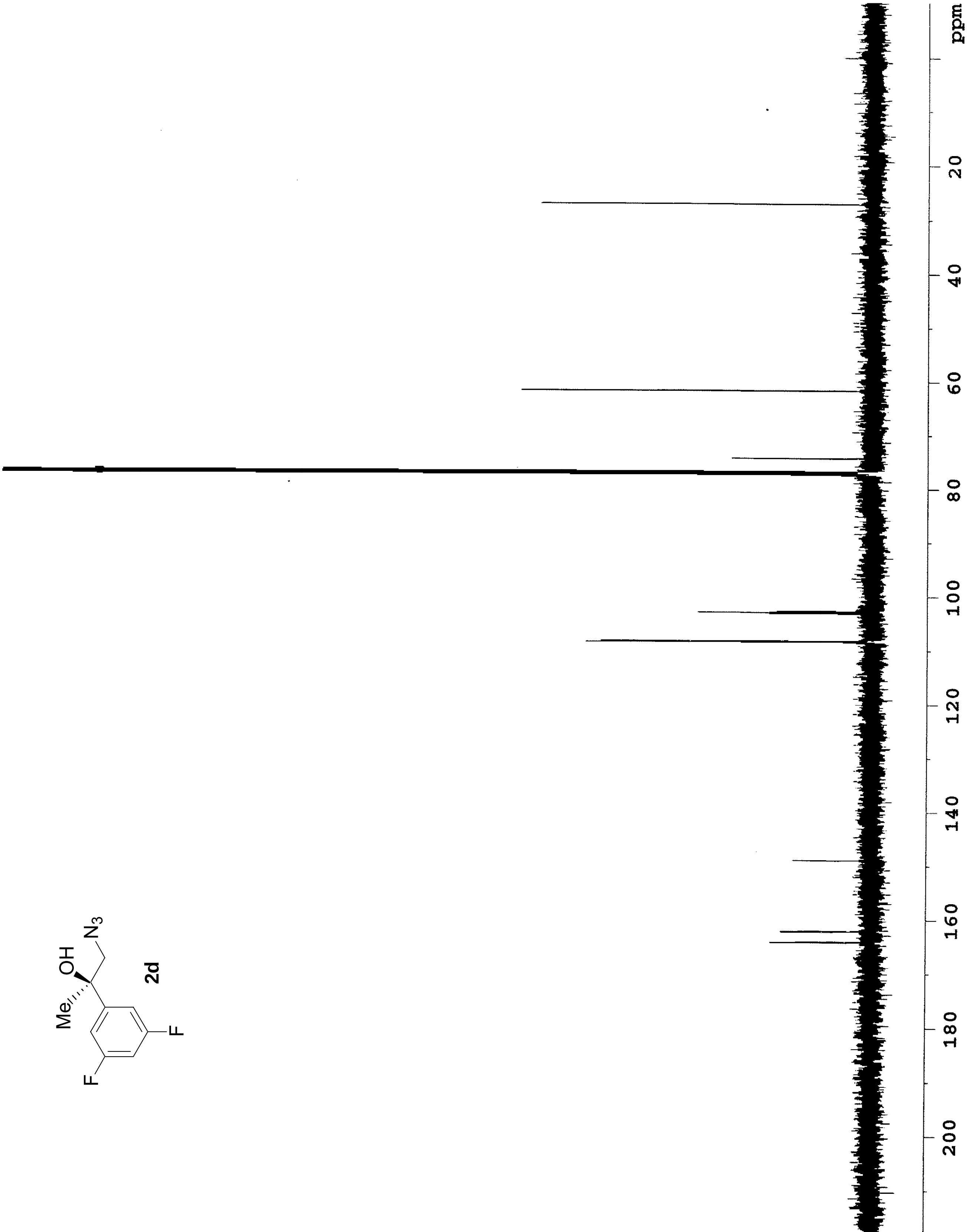

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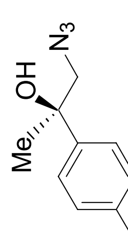
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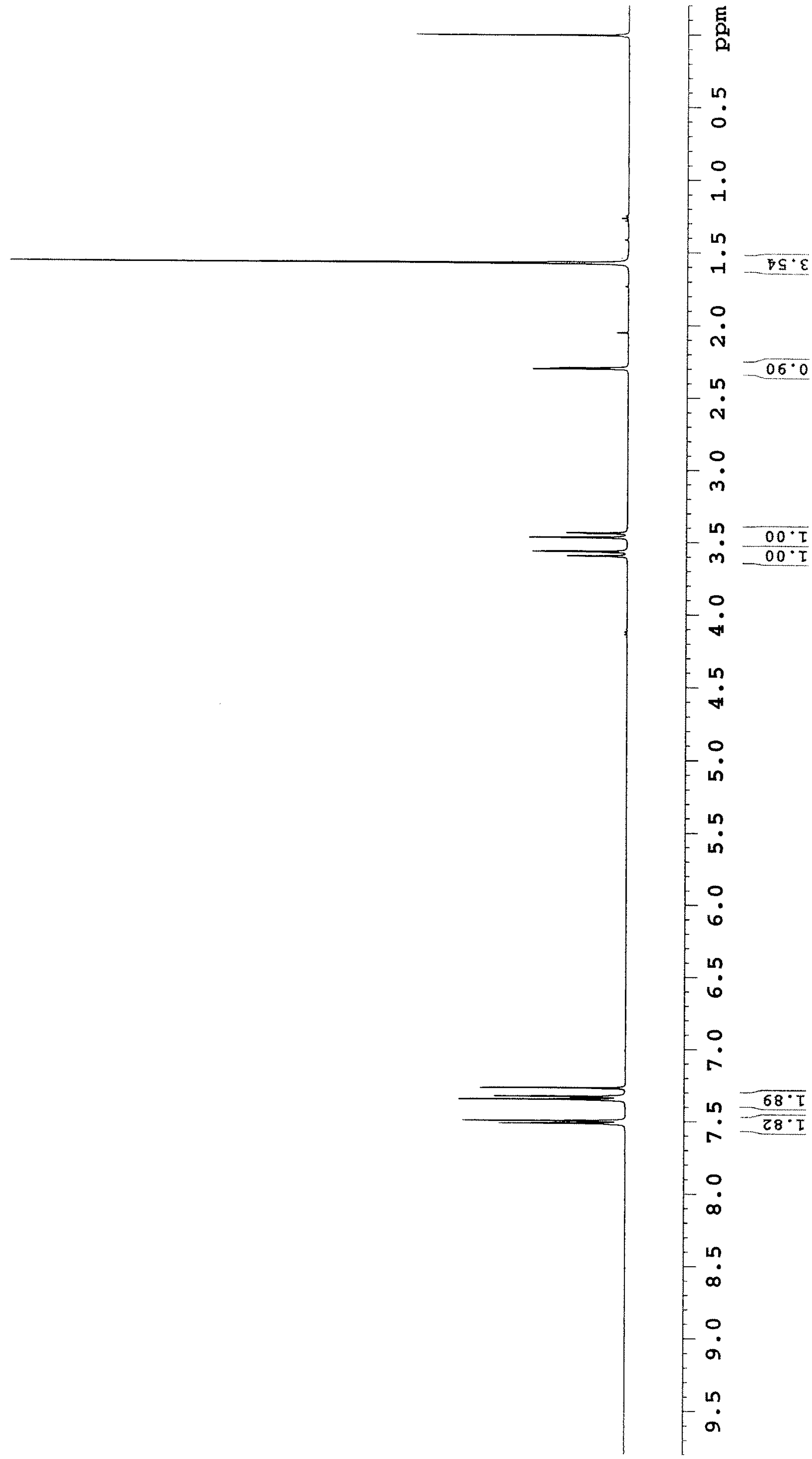
2e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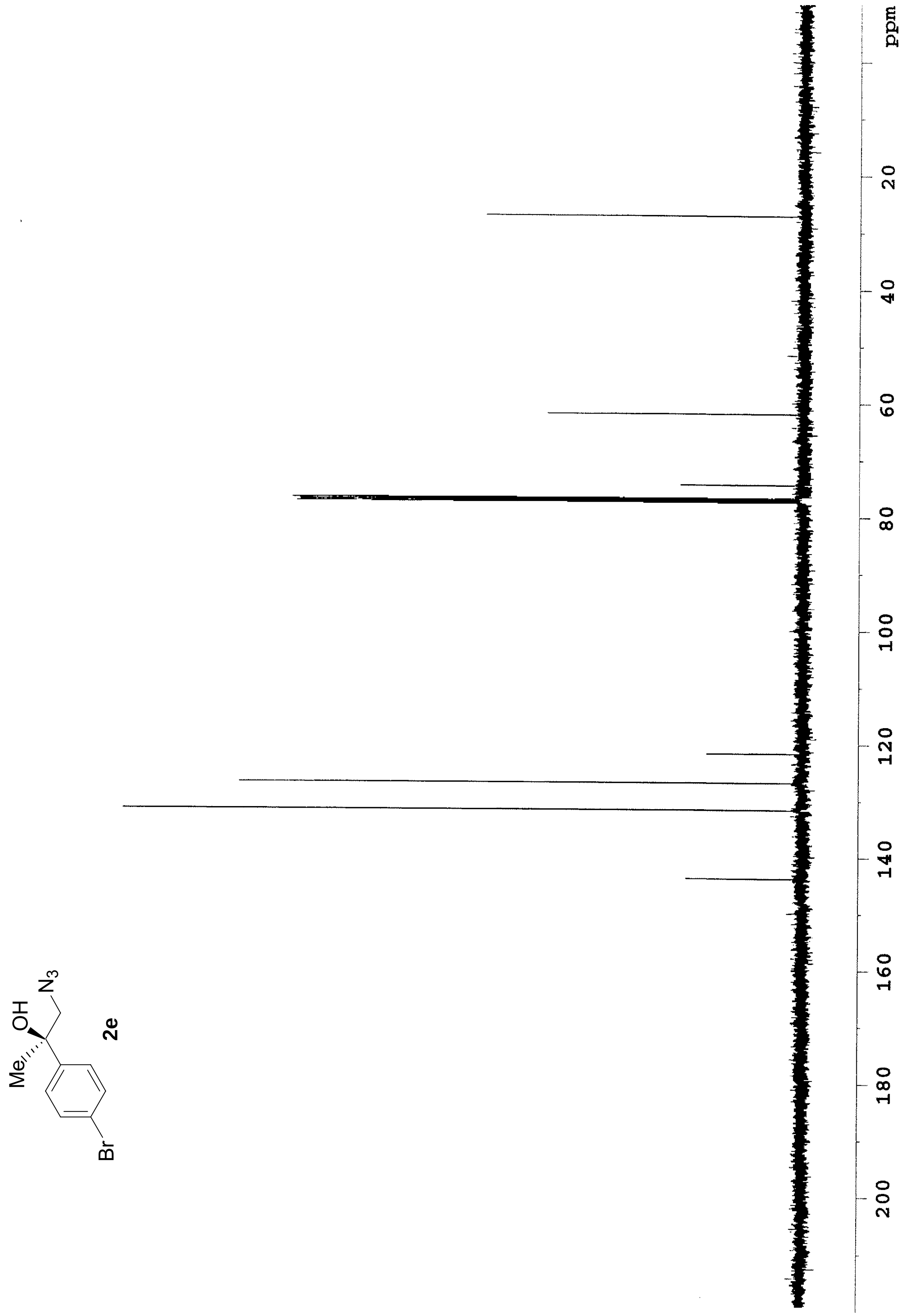
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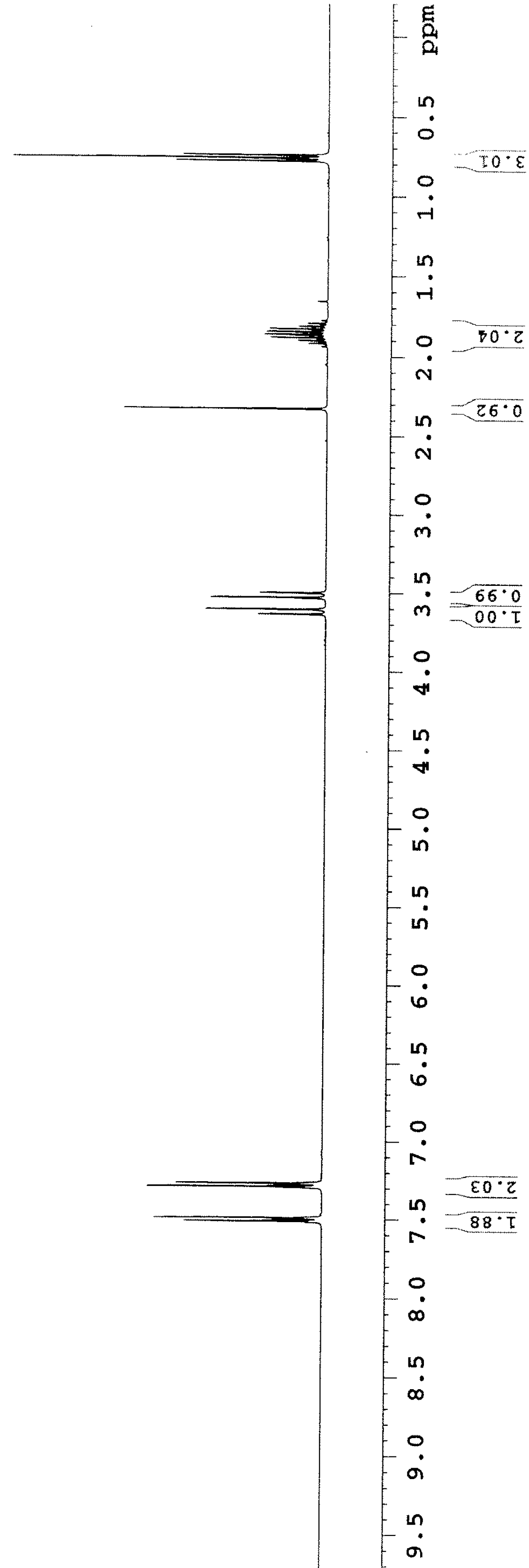
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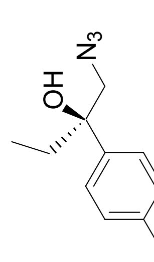
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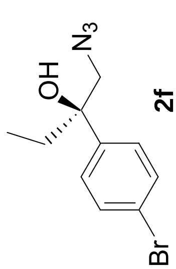

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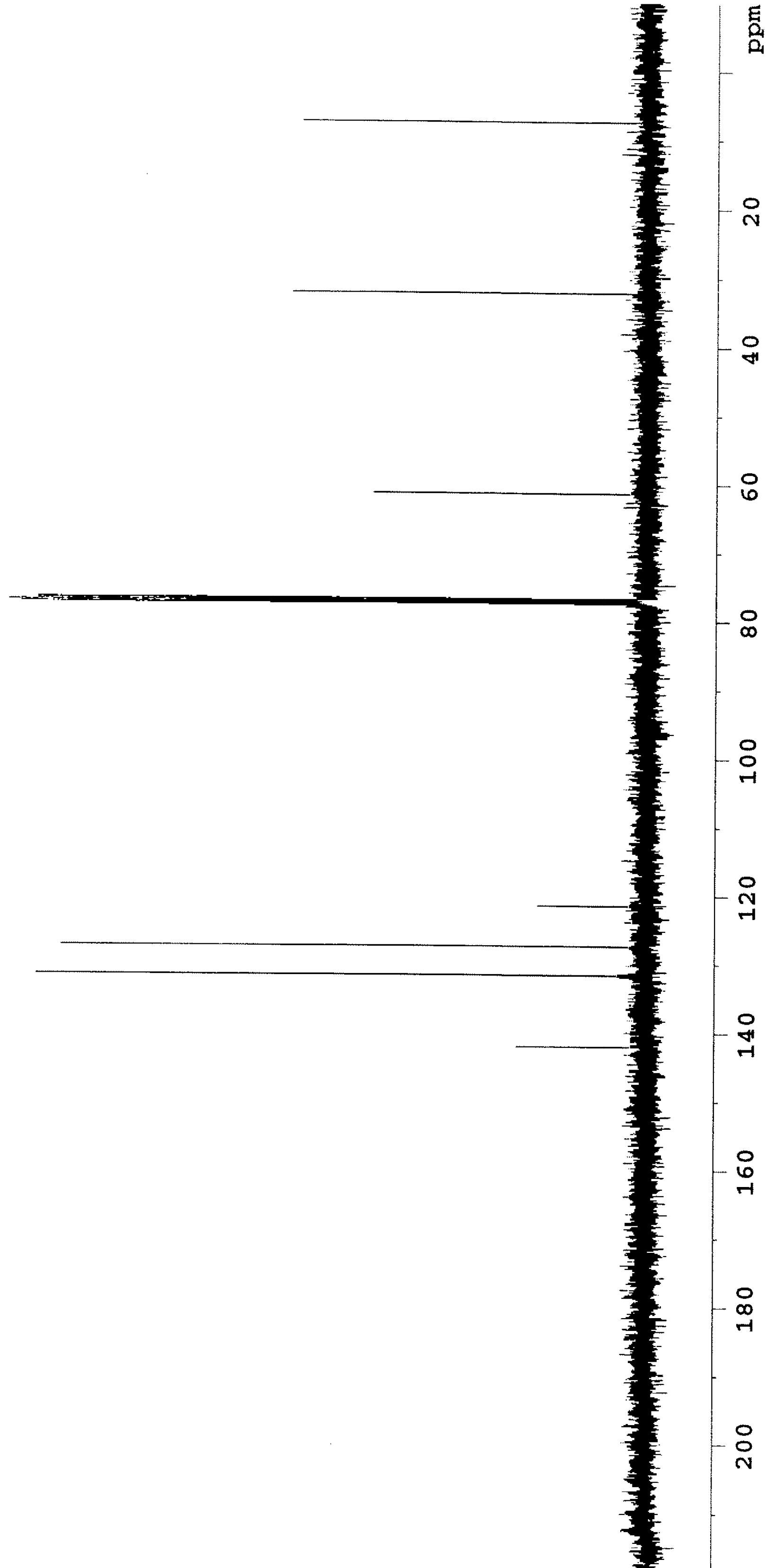

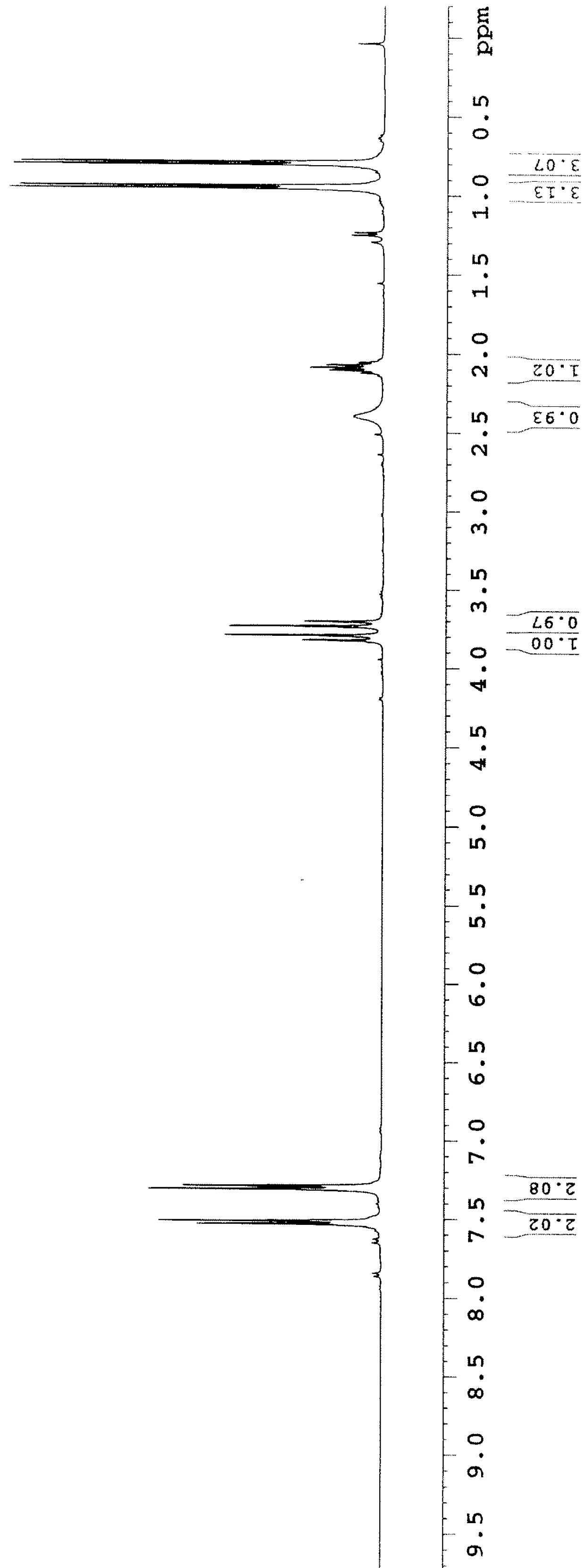
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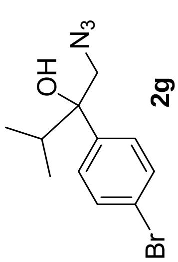
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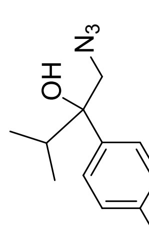

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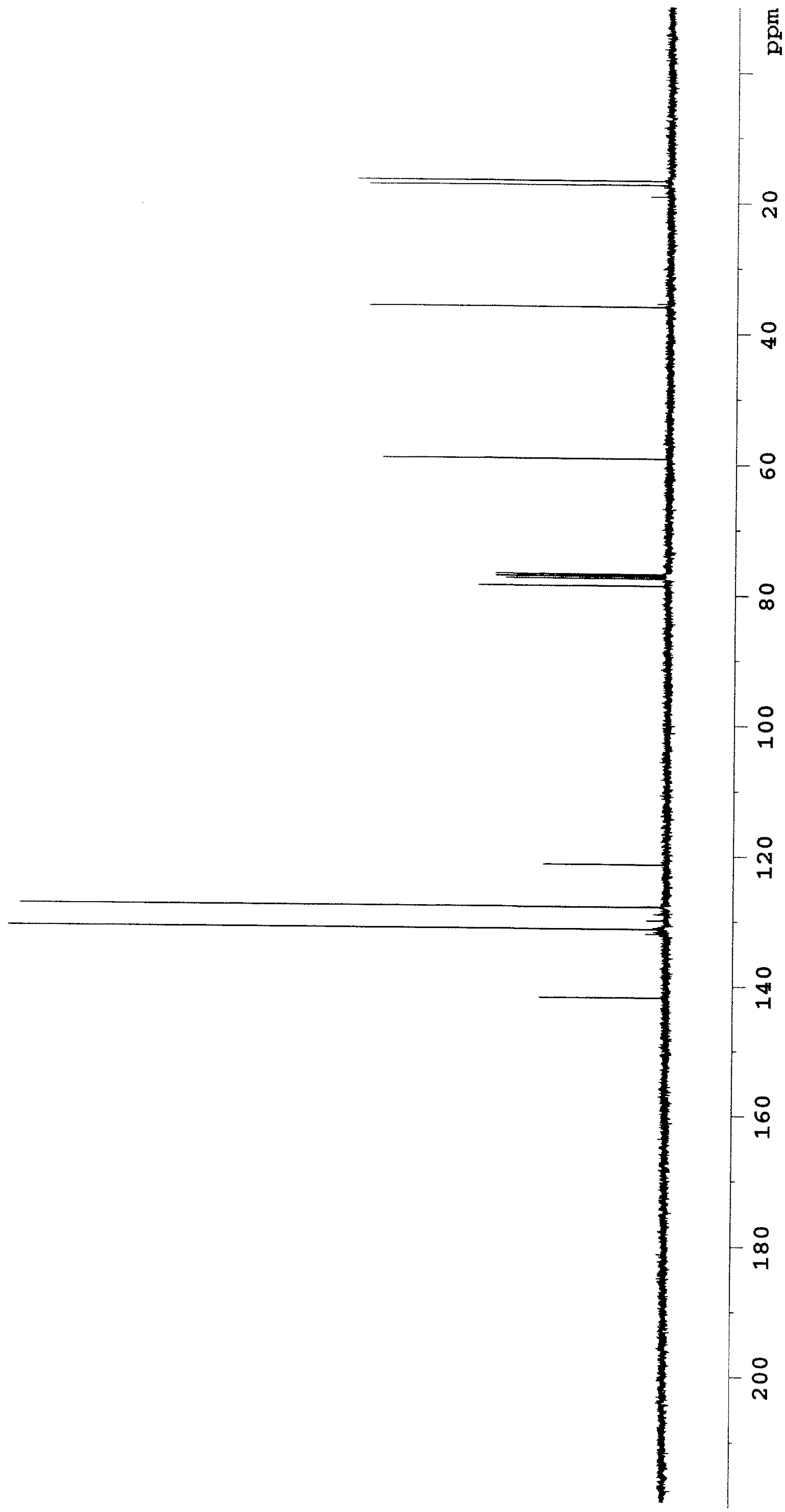

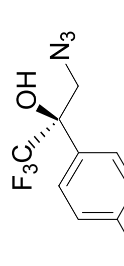

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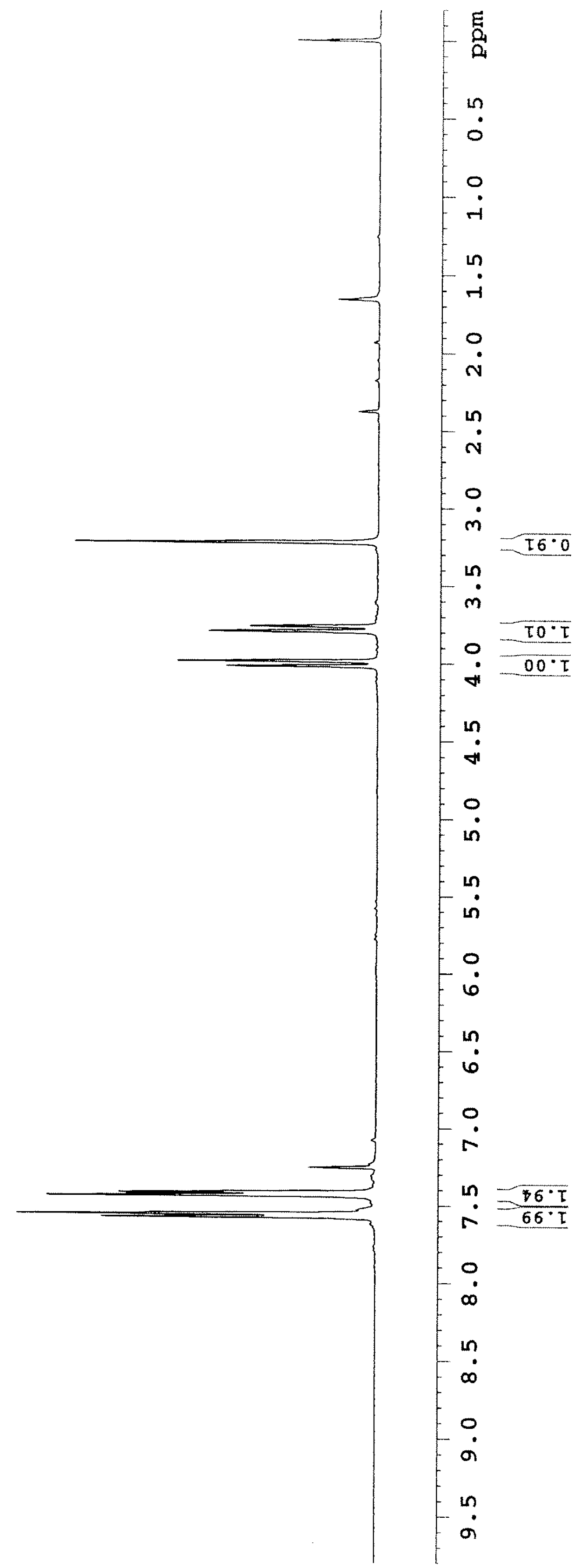
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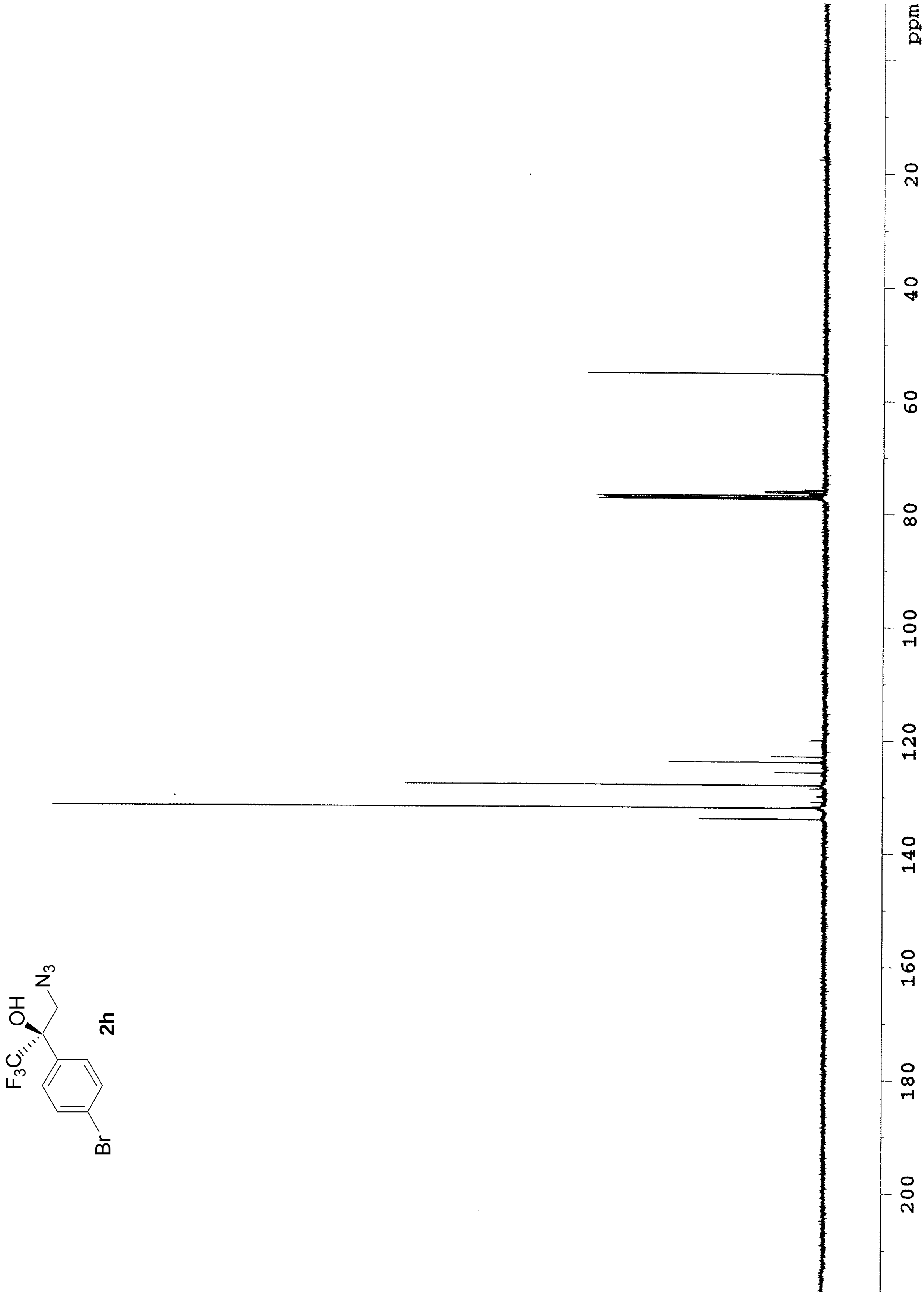

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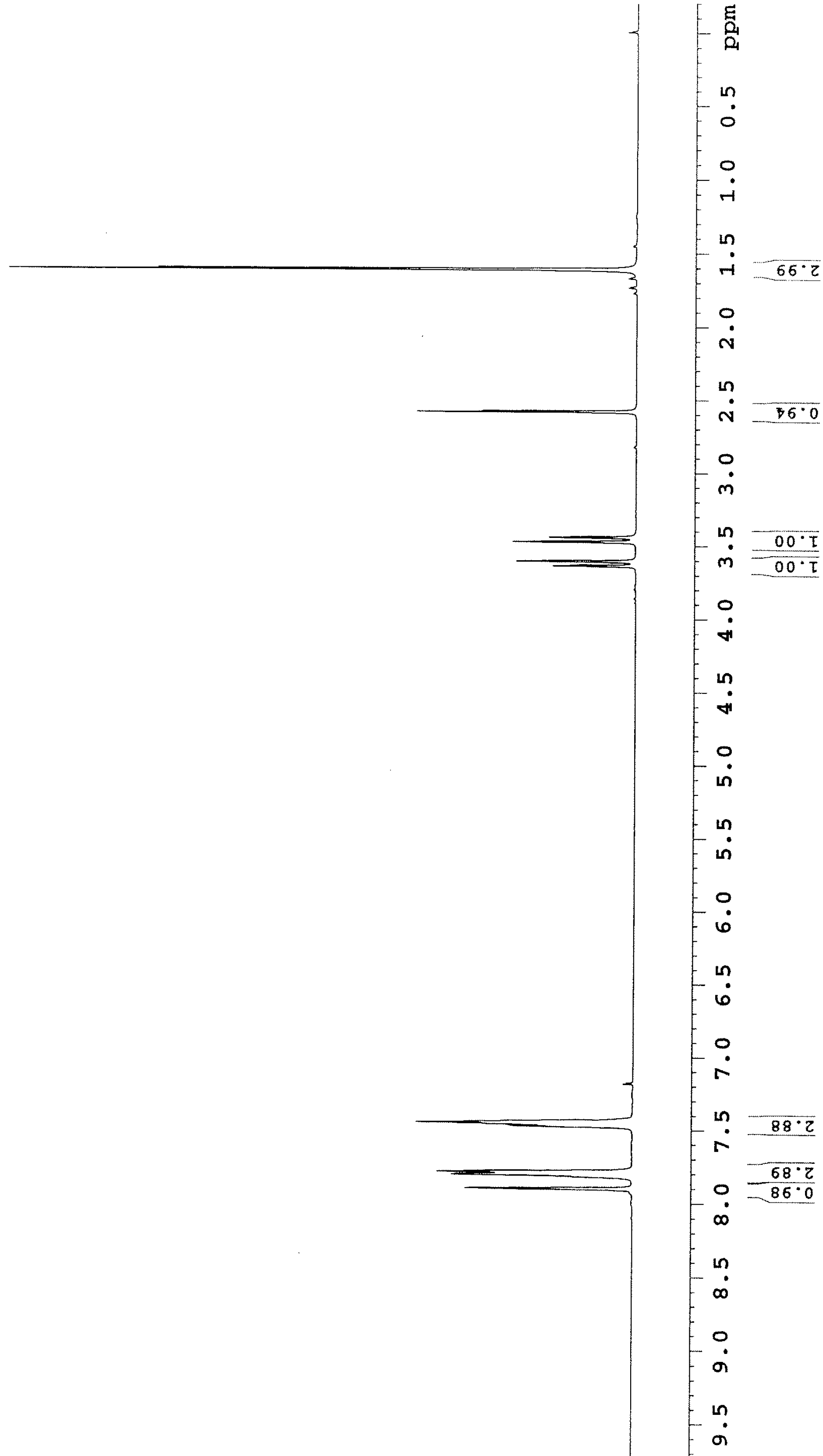
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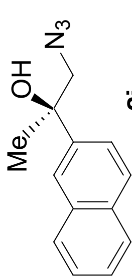
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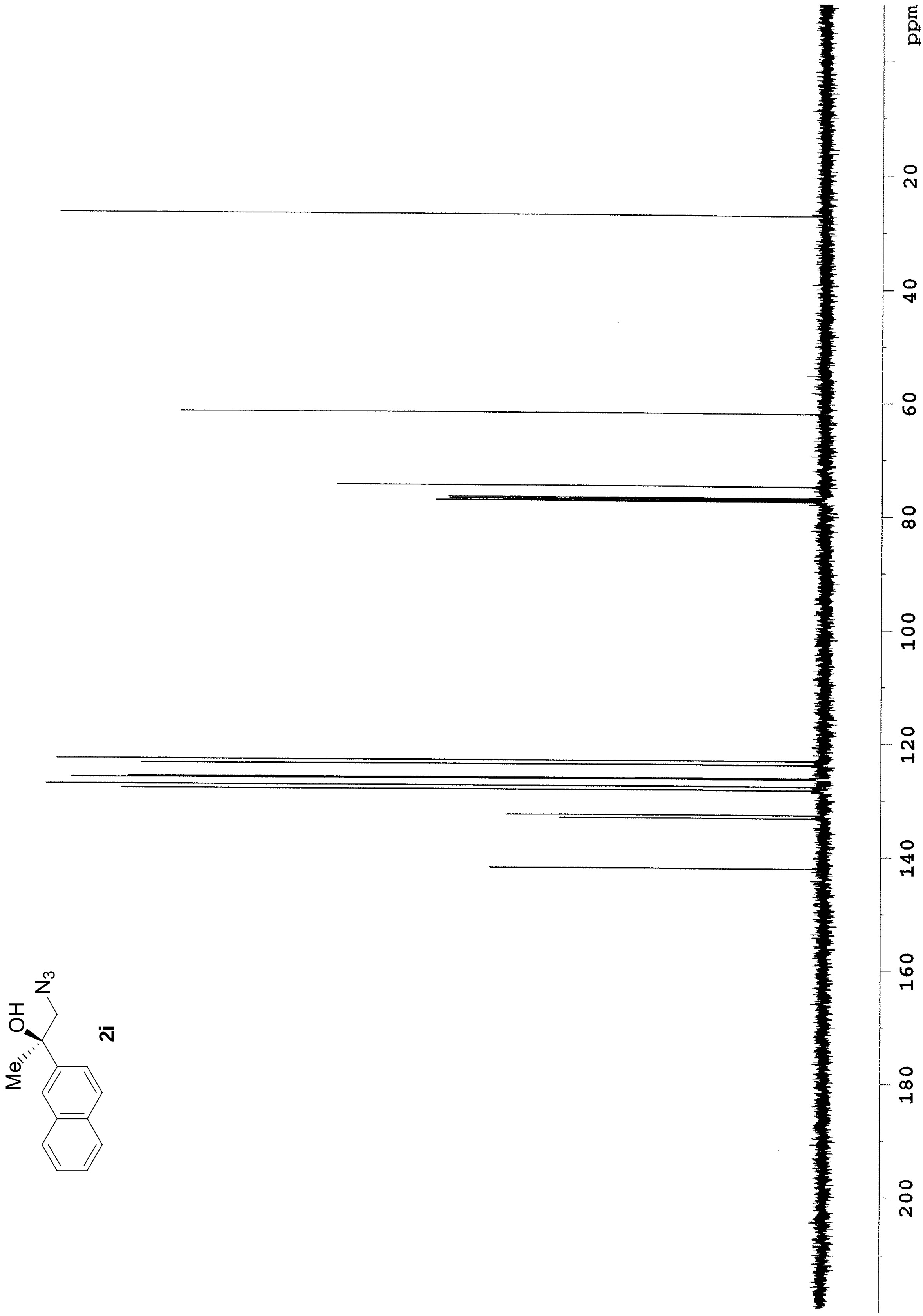

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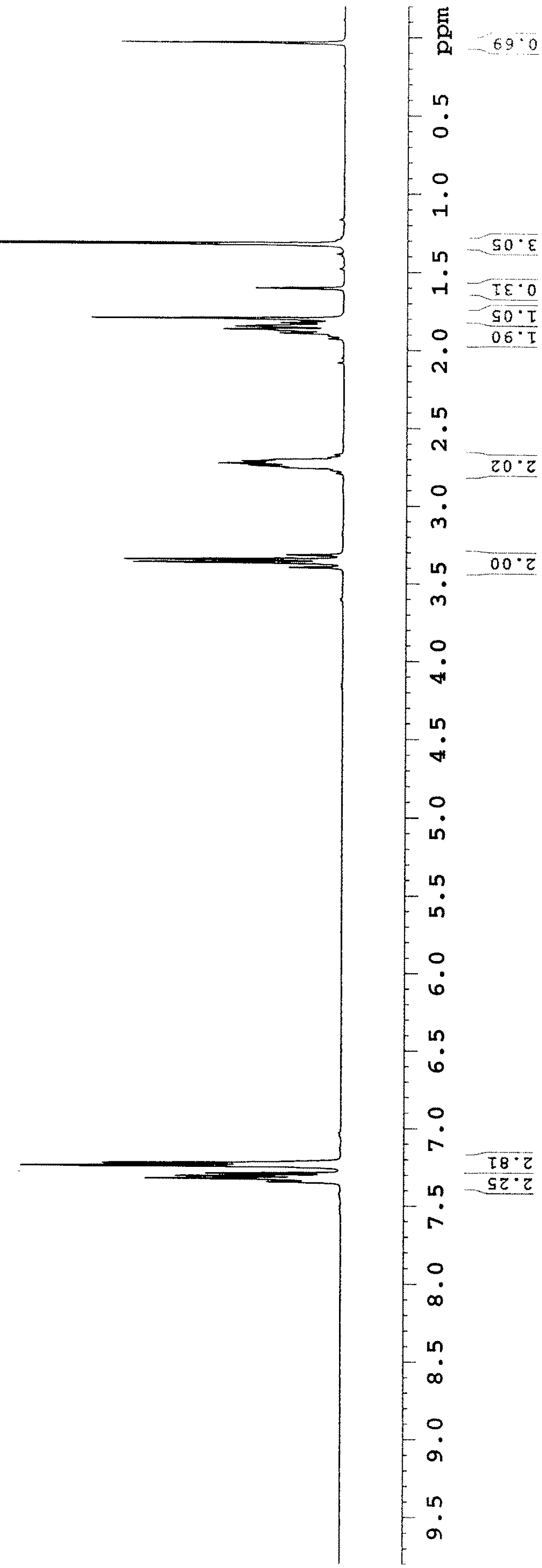
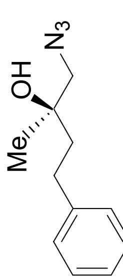
2i





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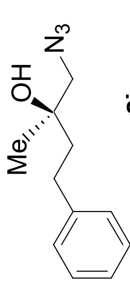

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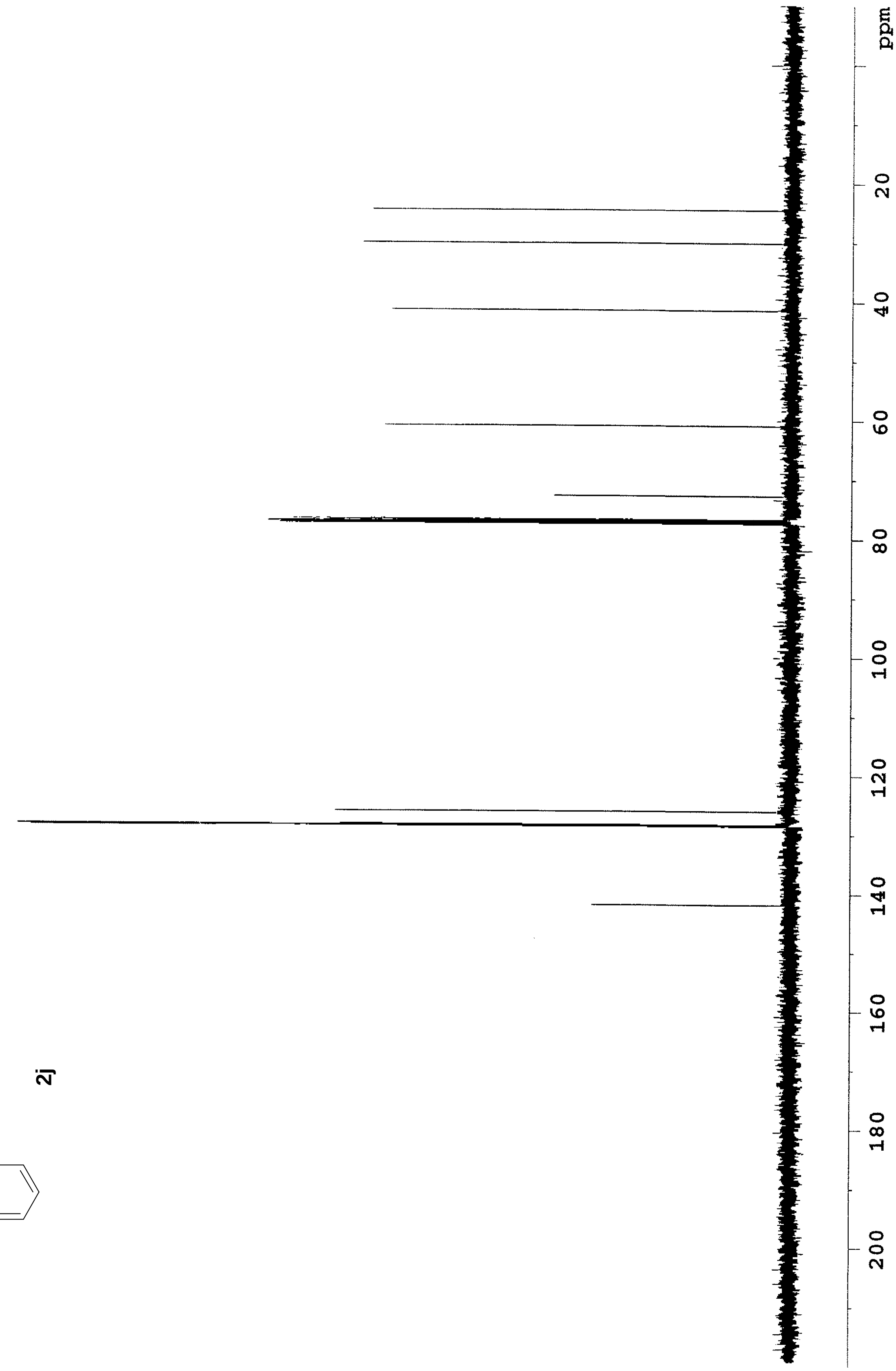

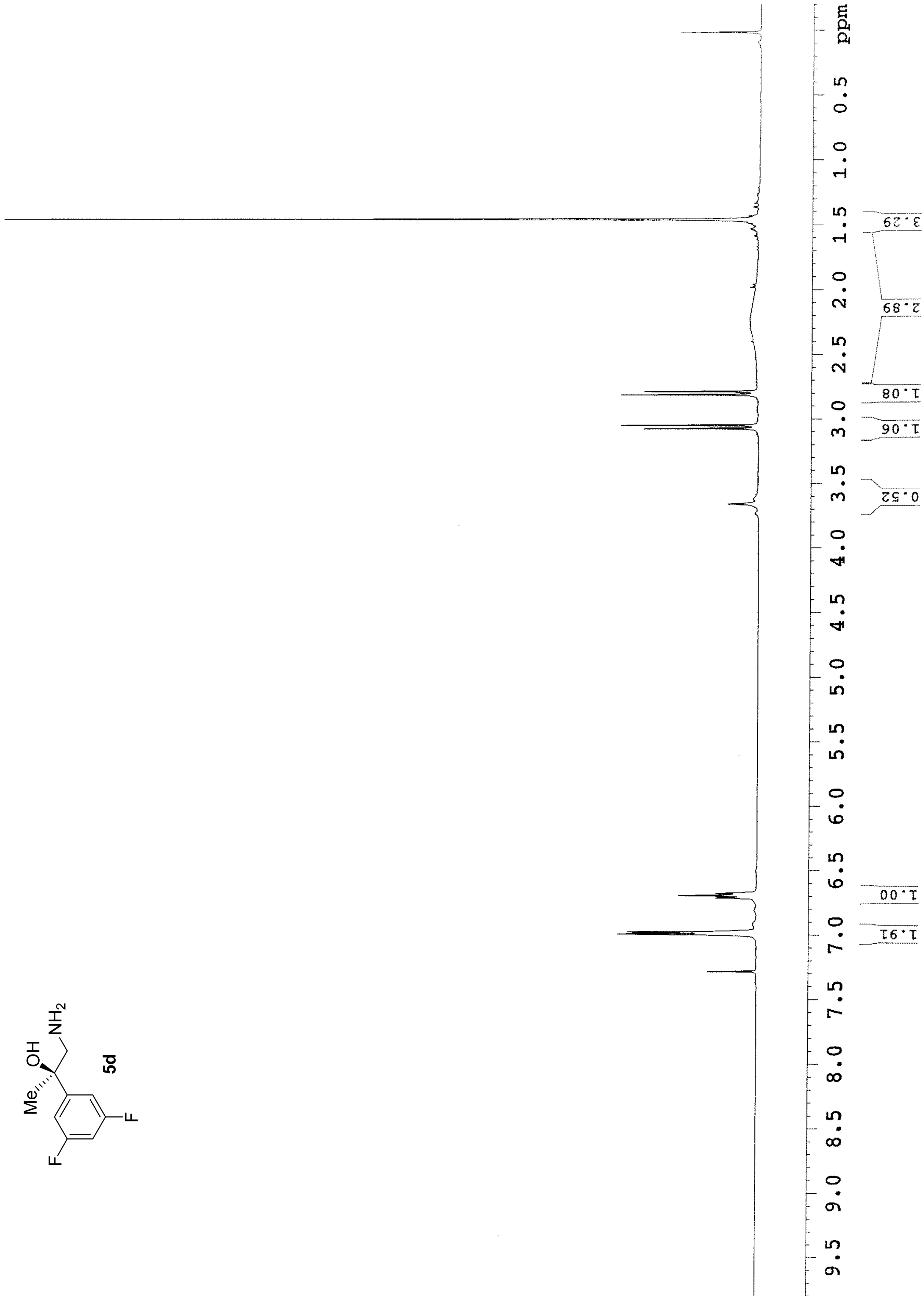
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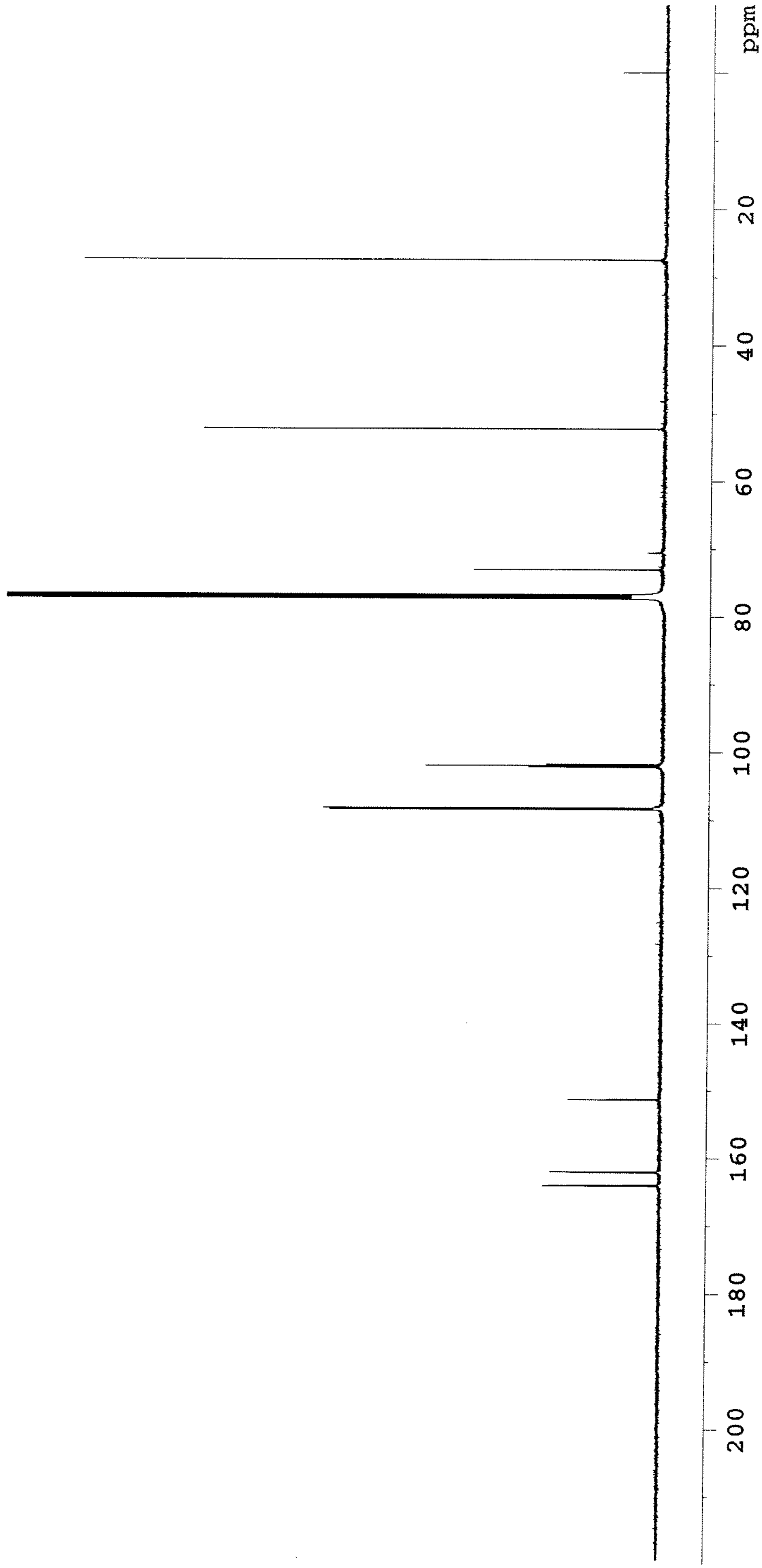

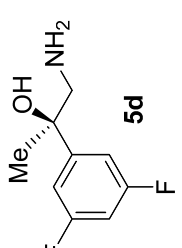

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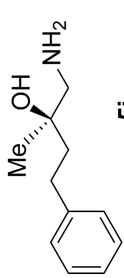

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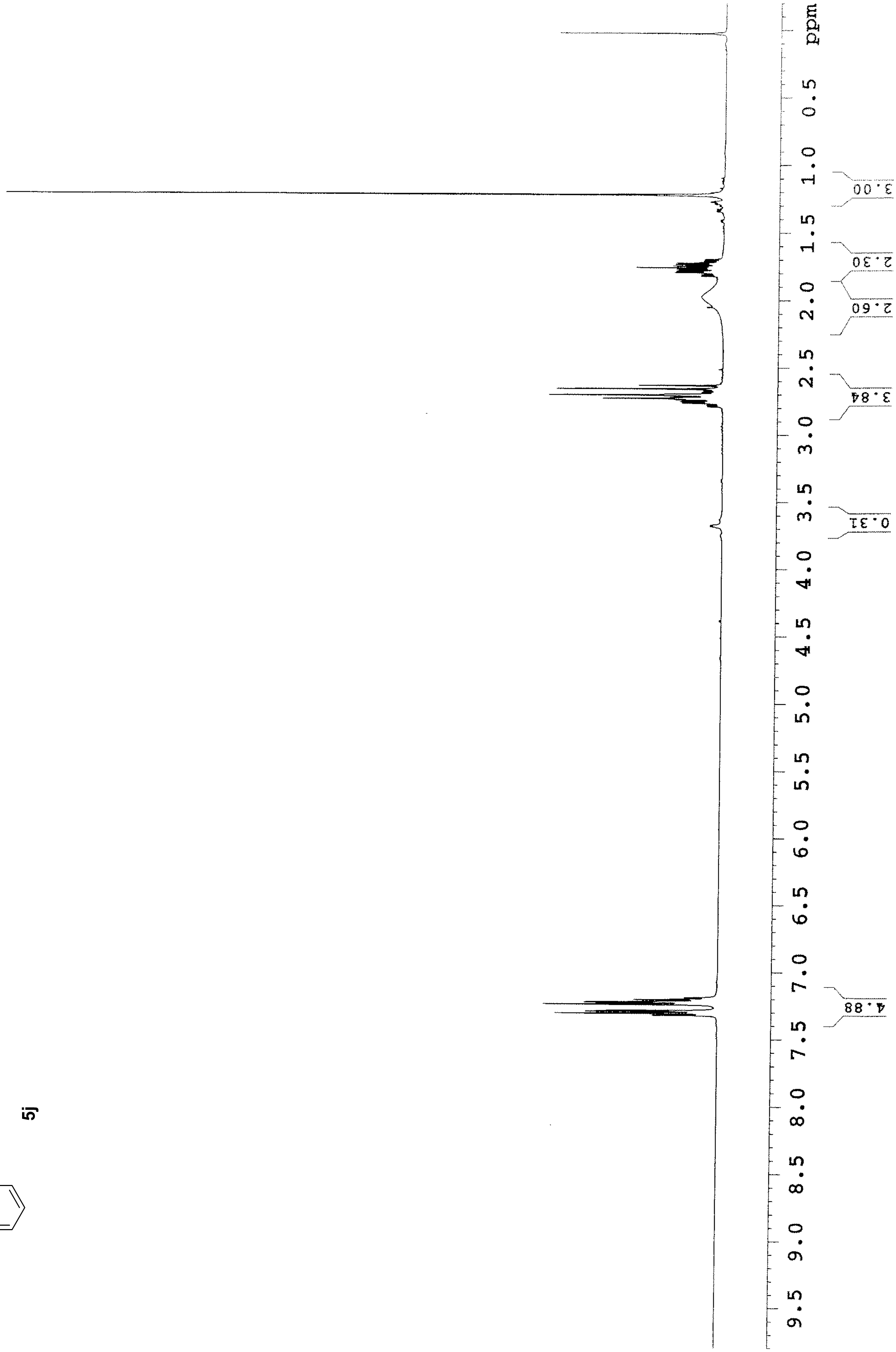
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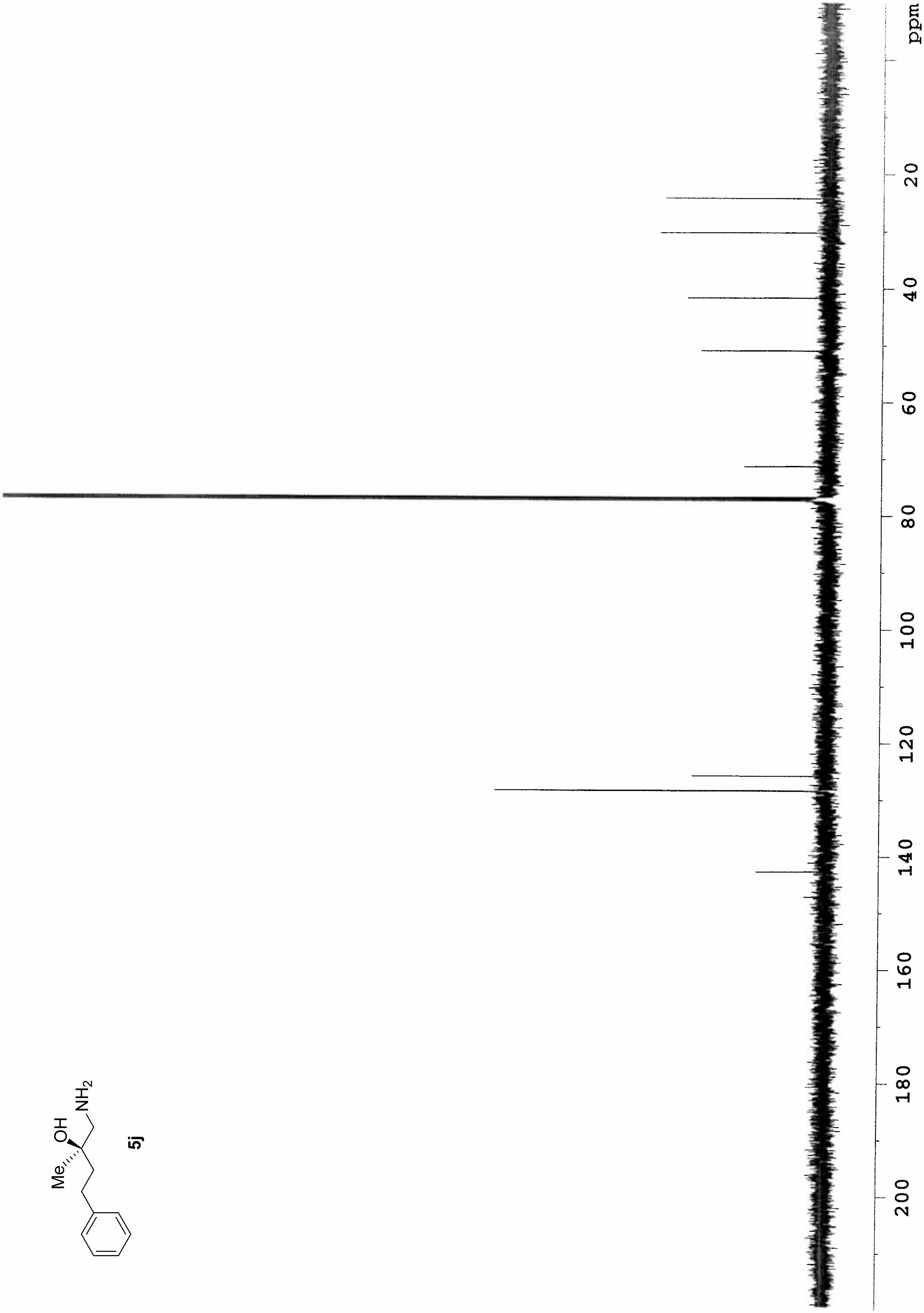

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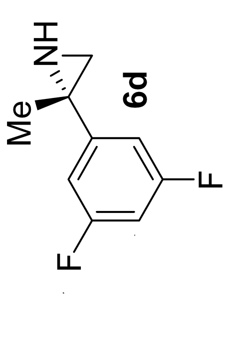
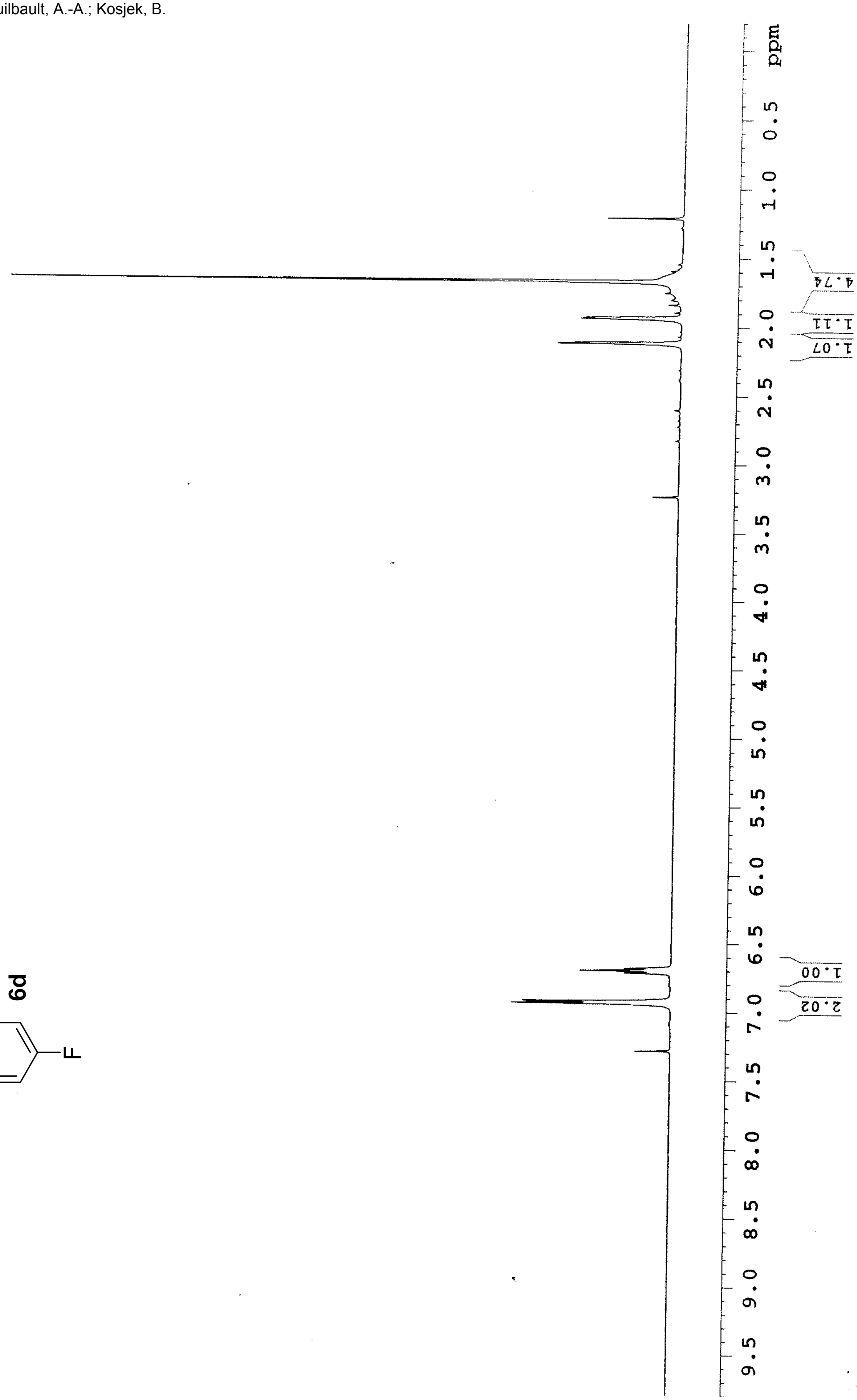

Me
NH
F
F

6d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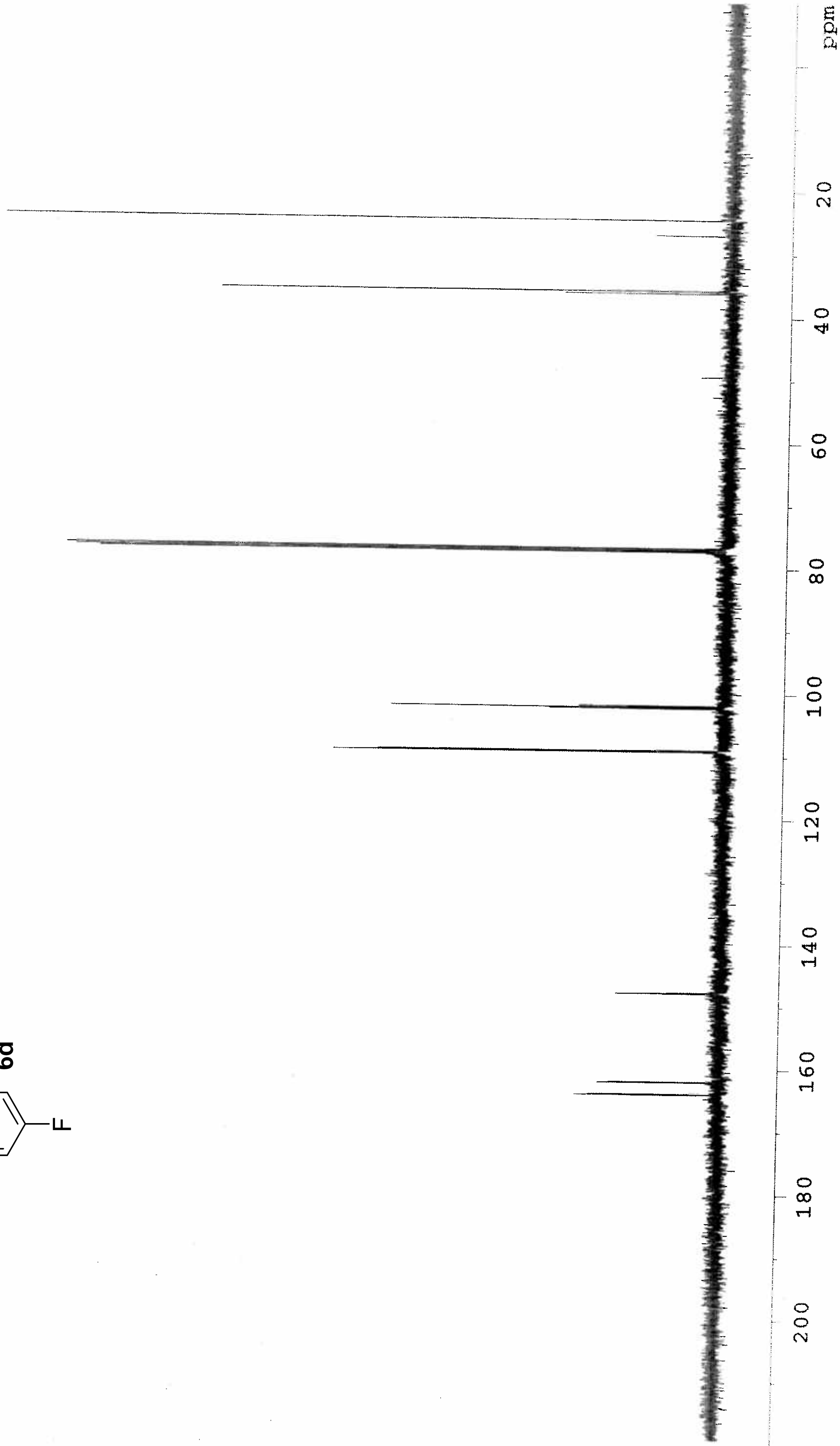

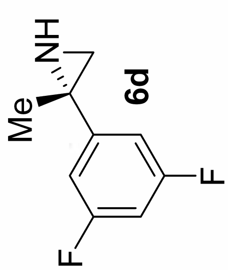

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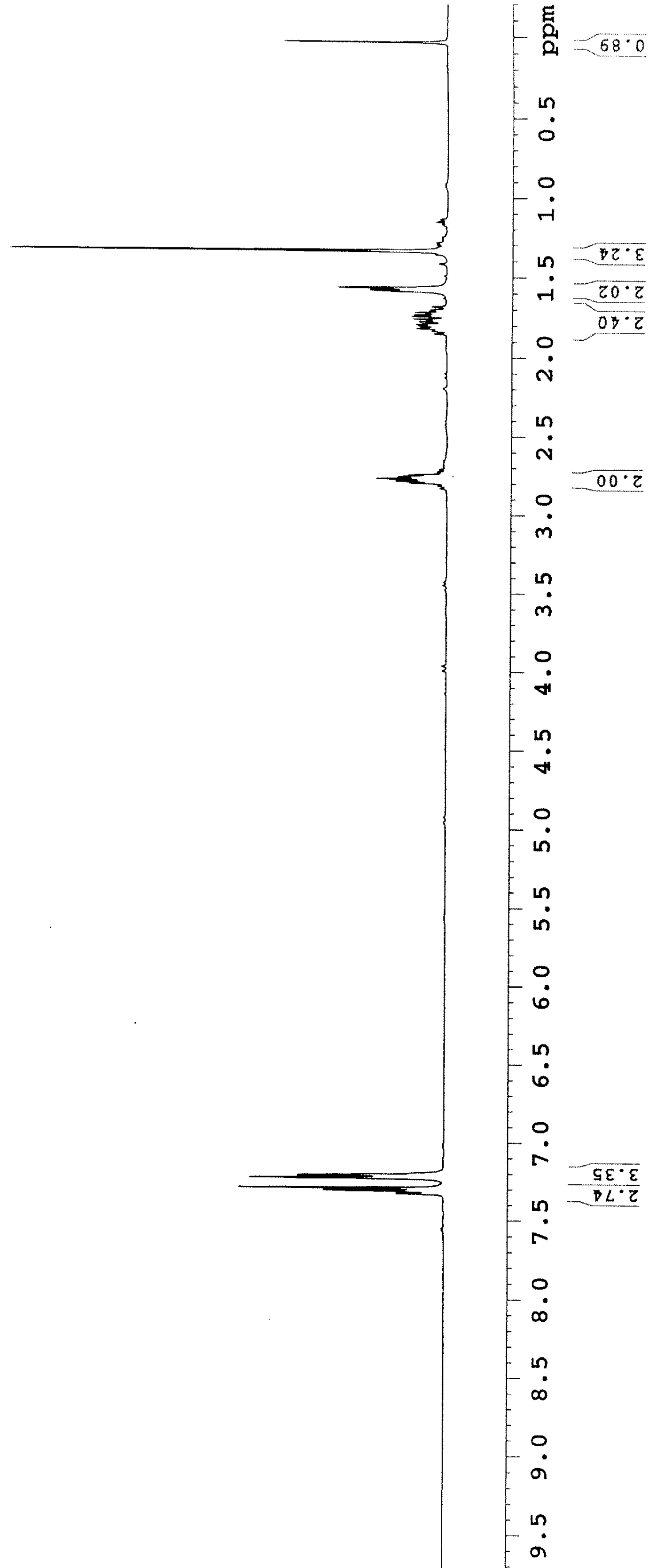
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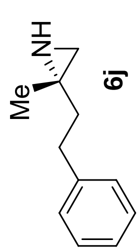
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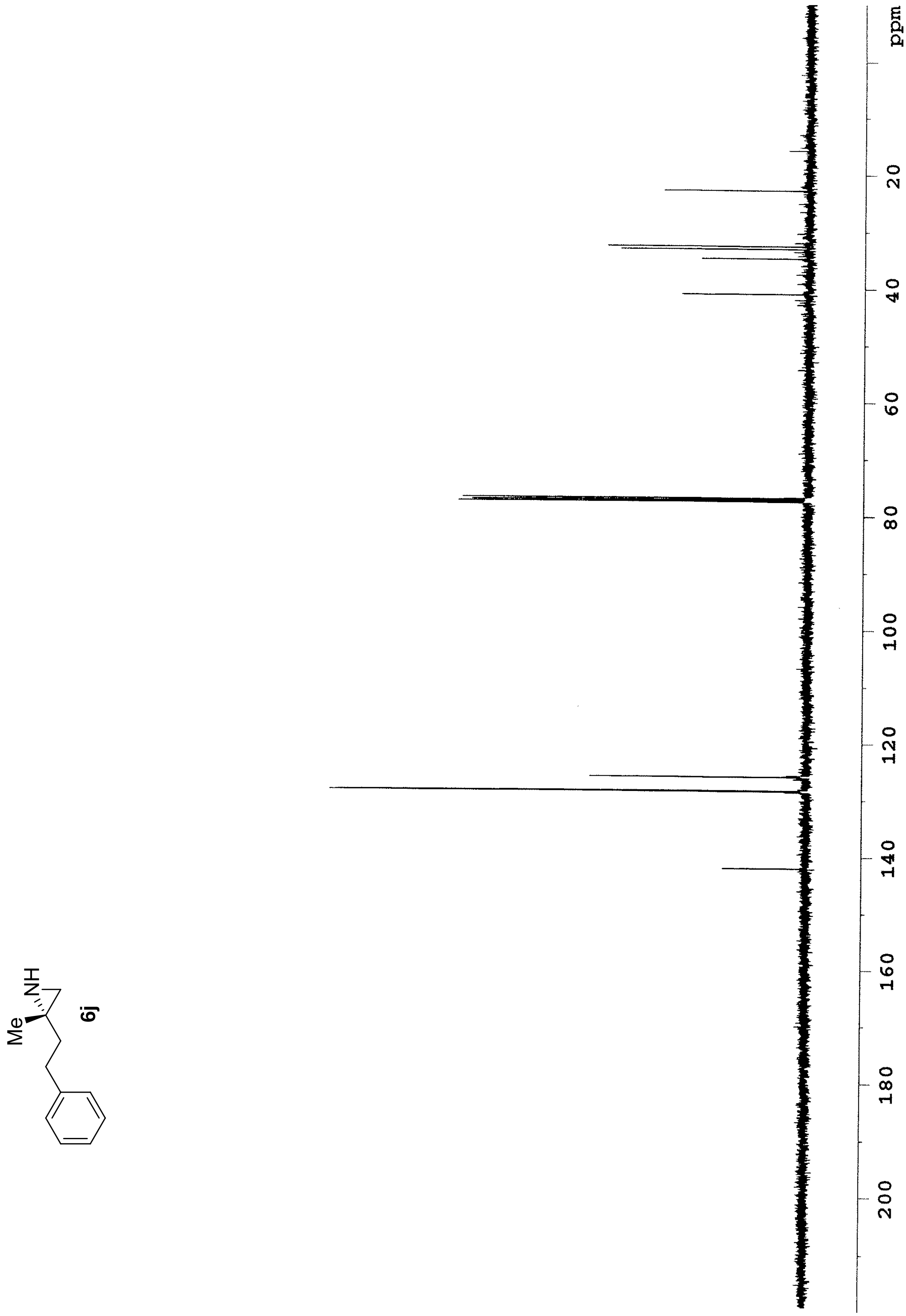
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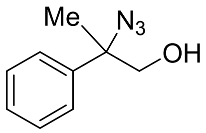
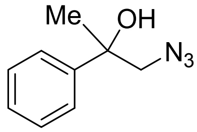
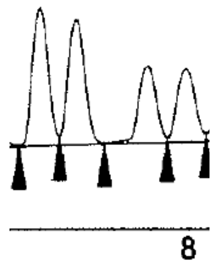
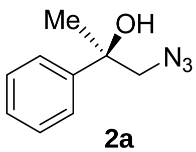






Start (min)	Time (min)	End (min)	Qty (%Area)
6.18	6.41	6.62	8.59
6.62	6.80	7.10	8.33
7.10	7.57	7.77	5.39
7.77	7.98	8.19	5.21



2a

Start (min)	Time (min)	End (min)	Qty (%Area)
6.14	6.37	6.47	0.88
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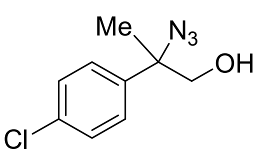
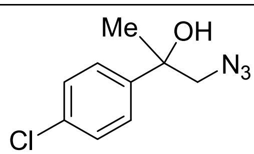
7.37	7.60	7.77	0.08
7.77	7.96	8.19	0.11





Start (min)	Time (min)	End (min)	Qty (%Area)
8.01	8.20	8.29	30.00
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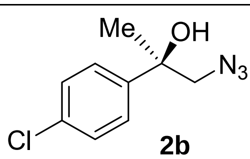
8.62	8.78	8.88	10.75
8.88	9.01	9.23	30.01



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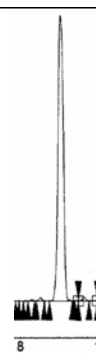

Start (min)	Time (min)	End (min)	Qty (%Area)
8.18	8.27	8.34	0.17
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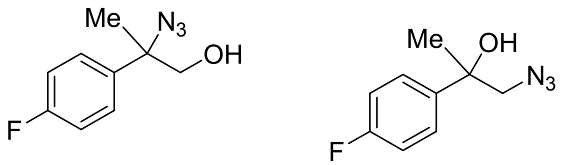
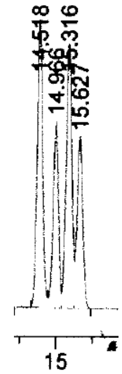
8.58	8.64	8.71	0.03
8.71	8.95	9.27	50.62





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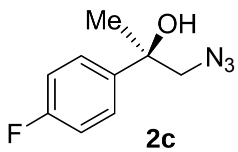

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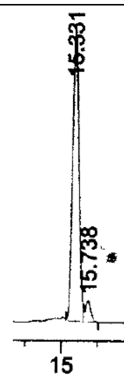

	Time (min)		Area (mAU*s)
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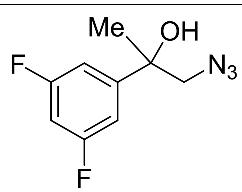

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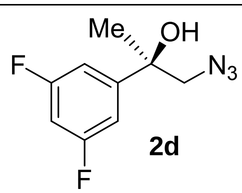
3.51	3.57	3.71	39.85



2d

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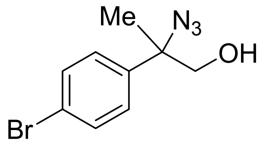
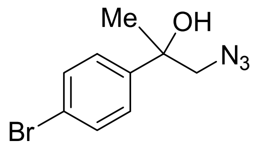
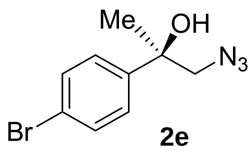




Start (min)	Time (min)	End (min)	Qty (%Area)
8.71	8.83	9.09	29.13
9.09	9.36	9.57	13.17
9.57	9.70	9.85	12.48
9.85	9.96	10.24	32.26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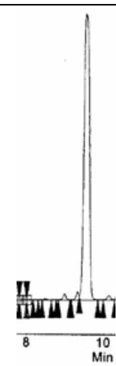

Start (min)	Time (min)	End (min)	Qty (%Area)
8.41	8.49	8.65	0.16
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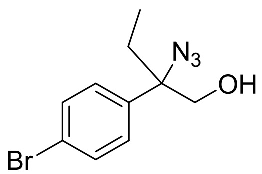
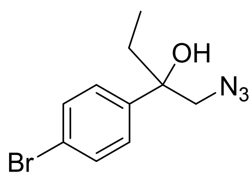
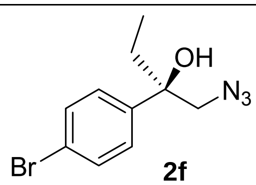
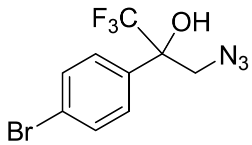
9.17	9.32	9.37	0.74
9.37	9.50	9.85	50.52

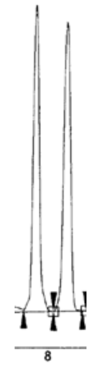




Start (min)	Time (min)	End (min)	Qty (%Area)
8.83	8.98	9.10	3.21
9.53	9.70	9.79	39.09
9.79	9.86	10.15	39.24
10.32	10.43	10.59	3.67

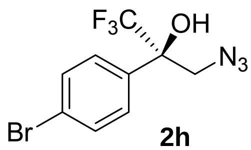

2f

Start (min)	Time (min)	End (min)	Qty (%Area)
8.78	8.96	9.05	0.39
9.17	9.46	9.74	91.96
9.74	9.86	10.11	1.11
10.38	10.42	10.48	0.04

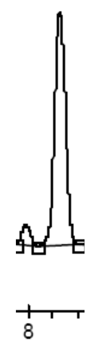




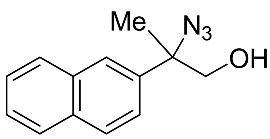
Start (min)	Time (min)	End (min)	Qty (%Area)
7.37	7.67	8.13	37.25
8.13	8.45	8.86	38.61

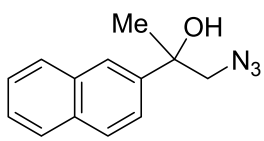


2h

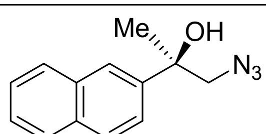


Start (min)	Time (min)	End (min)	Qty (%Area)
7.81	7.94	8.15	1.47
8.15	8.51	8.84	23.56



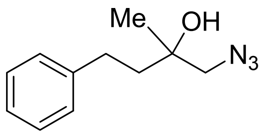


Start (min)	Time (min)	End (min)	Qty (%Area)
8.97	9.19	9.36	15.19
9.36	9.50	9.70	15.28
9.70	9.88	10.11	9.10
10.30	10.54	10.78	10.88

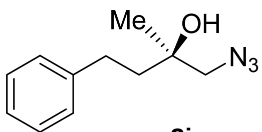


2i

Start (min)	Time (min)	End (min)	Qty (%Area)
9.39	9.49	9.60	0.58
9.60	9.80	10.03	28.02
10.03	10.14	10.19	0.20
10.66	10.82	11.00	7.32

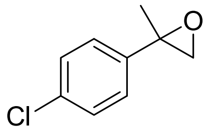


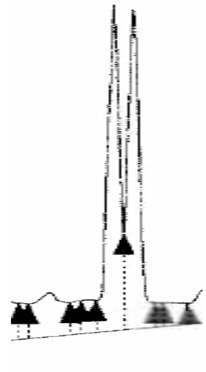
Start (min)	Time (min)	End (min)	Qty (%Area)
12.65	12.98	13.50	44.58
13.50	13.74	14.63	43.11



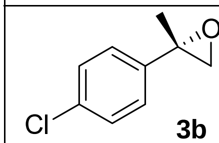
2j

Start (min)	Time (min)	End (min)	Qty (%Area)
12.64	12.96	13.22	0.41
13.31	13.61	14.56	43.52

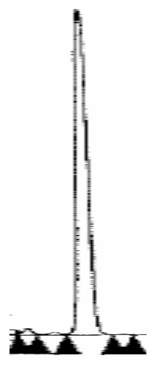




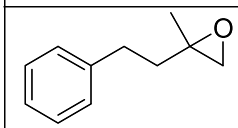
Start (min)	Time (min)	End (min)	Qty (%Area)
2.41	2.58	2.63	15.571
2.63	2.73	2.86	14.974



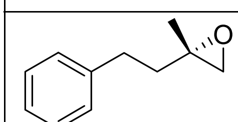
3b



Start (min)	Time (min)	End (min)	Qty (%Area)
2.42	2.52	2.69	28.427
2.69	2.75	2.81	0.077

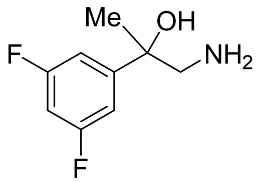
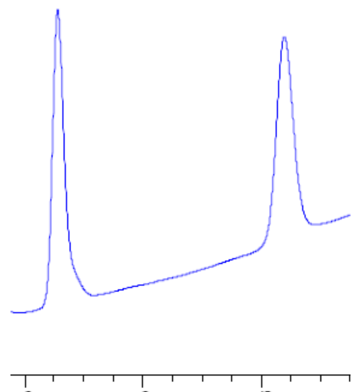
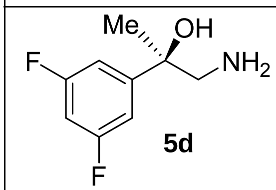
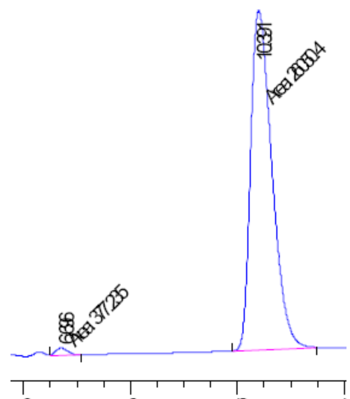
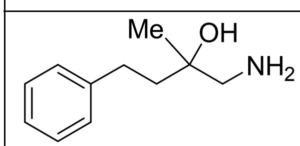
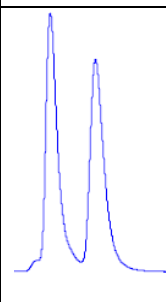
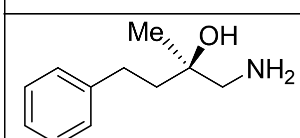
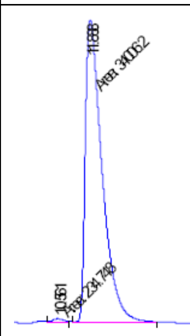


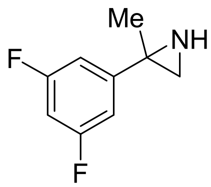
Start (min)	Time (min)	End (min)	Qty (%Area)
3.56	4.46	4.90	45.497
4.90	5.68	6.17	44.640

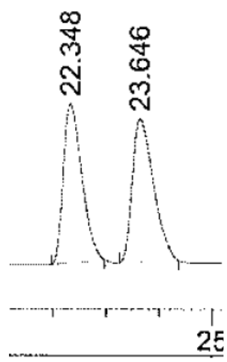


4j

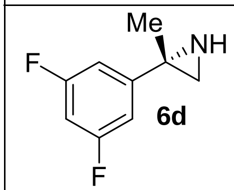
Start (min)	Time (min)	End (min)	Qty (%Area)
4.34	4.44	4.45	0.084
4.45	5.33	6.01	95.373

		
 **5d**		
		
 **5j**		

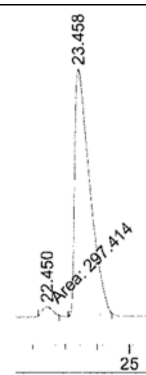




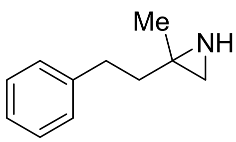
	Time (min)		Qty (%Area)
	22.348		
	23.646		

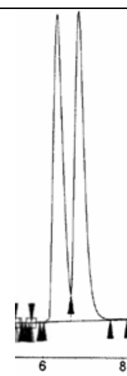


6d

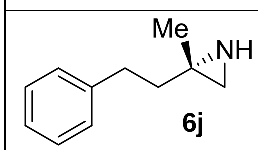


	Time (min)		Qty (%Area)
	22.450		1.56
	23.458		47.90

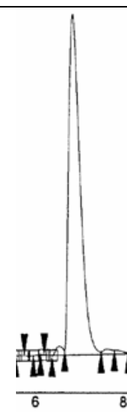




Start (min)	Time (min)	End (min)	Qty (%Area)
6.00	6.29	6.68	42.38
6.68	6.81	7.67	43.93



6j



Start (min)	Time (min)	End (min)	Qty (%Area)
6.37	6.54	6.66	1.30
6.66	6.82	7.48	78.18