SUPPORTING INFORMATION

Synthesis of Isoquinolines and Pyridines by the Palladium/ Copper-Catalyzed Coupling and Cyclization of Terminal Acetylenes and Unsaturated Imines: The Total Synthesis of Decumbenine B

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Aldehydes Prepared

2-(2-Cyclohex-1-enylethynyl)benzaldehyde (6). The aldehyde was prepared by the method used to prepare 2-(2-phenylethynyl)benzaldehyde, but employing 2-bromobenzaldehyde (1.85 g, 10.0 mmol) and 1-ethynylcyclohexene (1.27 g, 12.0 mmol) for 3 h. Column chromatography using 25:1 hexanes/EtOAc afforded 2.00 g (95%) of the compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.57-1.72 (m, 4H), 2.11-2.18 (m, 2H), 2.20-2.25 (m, 2H), 6.27 (dddd, J = 1.8, 1.8, 6.0, 6.0 Hz, 1H), 7.33-7.39 (m, 1H), 7.49-7.51 (m, 2H), 7.87 (dt, J = 1.2, 7.8 Hz, 1H), 10.52 (d, J = 0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.5, 22.3, 25.9, 29.0, 82.5, 98.6, 120.4, 127.1, 127.7, 128.1, 133.1, 133.8, 135.7, 136.9, 192.0.

2-(2-Cyclohexylethynyl)benzaldehyde (7). The aldehyde was prepared by the method used to prepare 2-(2-phenylethynyl)benzaldehyde, but employing 2-bromobenzaldehyde (1.85 g, 10.0 mmol) and cyclohexyl acetylene (1.29 g, 12.0 mmol) for 2 h. Column chromatography using 25:1 hexanes/EtOAc afforded 2.01 g (95%) of the compound as a yellow oil: ^{1}H NMR

($CDCl_3$) δ 1.34-1.45 (m, 3H), 1.52-1.63 (m, 3H), 1.71-1.78 (m, 2H), 1.87-1.92 (m, 2H), 2.68 (dddd, J = 3.6, 3.6, 12.6, 12.6 Hz, 1H), 7.34-7.39 (m, 1H), 7.48-7.54 (m, 2H), 7.88 (d, J = 8.1 Hz, 1H), 10.56 (d, J = 0.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 24.9, 25.9, 29.9, 32.5, 76.3, 102.2, 126.9, 127.9, 128.1, 133.3, 133.7, 136.0, 192.3.

2-[4-(Tetrahydropyran-2-yloxy)but-1-ynyl]benzaldehyde (8). The aldehyde was prepared by the method used to prepare 2-(2-phenylethynyl)benzaldehyde, but employing 2-bromobenzaldehyde (1.85 g, 10.0 mmol) and 2-(3-butynyloxy)tetrahydro-2*H*-pyran (1.85 g, 12.0 mmol) for 2 h. Column chromatography using 10:1 hexanes/EtOAc afforded 2.56 g (99%) of the compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.48-1.66 (m, 4H), 1.67-1.89 (m, 2H), 2.78 (t, J = 6.9 Hz, 2H), 3.49-3.56 (m, 1H), 3.57 (m, 1H), 3.57 (m, 1H), 3.85-3.98 (m, 2H), 3.45-3.41 (m, 1H), 7.49-7.51 (m, 2H), 7.87 (ddd, J = 0.6, 0.6, 7.2 Hz, 1H), 10.54 (d, J = 0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.5, 21.2, 25.5, 30.6, 62.3, 65.5, 77.2, 94.9, 98.9, 127.0, 127.6, 128.2, 133.3, 133.8, 136.2, 192.2.

2-(3-Hydroxyprop-1-ynyl)benzaldehyde (9). The aldehyde was prepared by the method used to prepare 2-(2-phenylethynyl)benzaldehyde, but employing 2-bromobenzaldehyde (1.85 g, 10.0 mmol) and propargyl alcohol (0.67 g, 12.0 mmol) for 6 h. Column chromatography using 1:1 hexanes/EtOAc afforded 1.43 g (89%) of the compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 3.68 (br s, 1H), 4.51 (s, 2H), 7.34 (dddd, J = 0.6, 3.9, 3.9, 8.7 Hz, 1H), 7.45 (ddd, J = 1.2, 1.2, 5.1 Hz, 2H), 7.80 (ddd, J = 0.9, 0.9, 7.8 Hz, 1H), 10.41 (d, J = 0.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 51.3, 81.0, 94.9, 126.2, 127.5, 128.8, 133.5, 133.9, 135.9, 192.1.

2-(3-Hydroxy-3-methylbut-1-ynyl)benzaldehyde (10). The aldehyde was prepared by the method used to prepare 2-(2-phenylethynyl)benzaldehyde, but employing 2-bromobenzaldehyde (1.85 g, 10.0 mmol) and 2-methyl-3-butyn-2-ol (1.01 g, 12.0 mmol) for 2

h. Column chromatography using 3:1 hexanes/EtOAc afforded 1.80 g (96%) of the compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.64 (s, 6H), 2.73 (br s, 1H), 7.36-7.42 (m, 1H), 7.48-7.51 (m, 2H), 7.86 (ddd, J = 0.9, 0.9, 6.9 Hz, 1H), 10.46 (d, J = 0.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 31.4, 65.7, 77.8, 101.2, 126.4, 127.4, 128.7, 133.4, 133.8, 135.9, 191.9.

2-(2-Triisopropylsilylethynyl)benzaldehyde (11). The aldehyde was prepared by the method used to prepare 2-(2-phenylethynyl)benzaldehyde, but employing 2-bromobenzaldehyde (1.85 g, 10.0 mmol) and (triisopropylsilyl)acetylene (2.19 g, 12.0 mmol) for 2 h. Column chromatography using 35:1 hexanes/EtOAc afforded 2.65 g (92%) of the compound as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 21H), 7.44 (dddd, J = 0.6, 0.6, 7.8, 7.8 Hz, 1H), 7.52-7.62 (m, 2H), 7.92 (ddd, J = 0.6, 0.6, 7.8 Hz, 1H), 10.62 (d, J = 0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.3, 18.7, 99.2, 102.1, 126.9, 127.2, 128.8, 133.7, 134.0, 136.3, 191.8.

Imines Prepared

***N*-(2-Phenylethynylbenzylidene)-*tert*-butylamine (3).** The imine was prepared by the method used to prepare imine **1**, but employing 2-(2-phenyl-ethynyl)benzaldehyde (0.80 g, 3.88 mmol). Removal of the solvent afforded 1.00 g (97%) of the imine **3** as a yellow oil, which solidified upon cooling: mp 52-53 °C; ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 9H), 7.28-7.35 (m, 5H), 7.49-7.54 (m, 3H), 8.07-8.10 (m, 1H), 8.94 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 30.0, 58.0, 86.9, 95.1, 123.3, 124.1, 126.2, 128.7, 128.7, 128.8, 129.9, 131.6, 132.4, 138.0, 154.2; IR ($CHCl_3$, cm^{-1}) 3060, 2214, 1637; HRMS Calcd for $C_{19}H_{19}N$: 261.1518. Found: 261.1518.

***N*-(2-Cyclohex-1-enylethynylbenzylidene)-*tert*-butylamine (12).** The imine was prepared by the method used to prepare imine **1**, but employing

2-(2-cyclohex-1-enylethynyl)benzaldehyde (1.05 g, 5 mmol). Removal of the solvent afforded 1.28 g (96%) of the imine **12** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 9H), 1.59-1.74 (m, 4H), 2.13-2.20 (m, 2H), 2.22-2.27 (m, 2H), 6.23 (dddd, J = 1.8, 1.8, 6.0, 6.0 Hz, 1H), 7.29-7.33 (m, 2H), 7.39-7.45 (m, 1H), 7.98-8.05 (m, 1H), 8.82 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.6, 22.4, 25.9, 29.3, 29.9, 57.8, 84.2, 97.0, 120.8, 124.5, 125.9, 128.2, 129.7, 132.1, 135.6, 137.6, 154.6; IR (neat, cm^{-1}) 3062, 2200, 1637; HRMS Calcd for $C_{19}H_{23}N$: 265.1830. Found: 265.1831.

***N*-(2-Cyclohexylethynylbenzylidene)-*tert*-butylamine (13).** The imine was prepared by the method used to prepare imine **1**, but employing 2-(2-cyclohexyl-ethynyl)benzaldehyde (0.85 g, 4 mmol). Removal of the solvent afforded 1.01 g (95%) of the imine **13** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 9H), 1.35-1.45 (m, 3H), 1.50-1.63 (m, 3H), 1.73-1.81 (m, 2H), 1.85-1.92 (m, 2H), 2.68 (dddd, J = 3.6, 3.6, 12.3, 12.3 Hz, 1H), 7.26-7.31 (m, 2H), 7.37-7.43 (m, 1H), 7.98-8.03 (m, 1H), 8.83 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 24.8, 26.0, 29.8, 29.9, 32.7, 57.8, 78.0, 100.2, 124.9, 125.8, 127.9, 129.7, 132.2, 137.8, 154.8; IR (neat, cm^{-1}) 3062, 2224, 1683; HRMS Calcd for $C_{19}H_{25}N$: 267.1987. Found: 267.1987.

***N*-[4-(Tetrahydropyran-2-yloxy)but-1-ynylbenzylidene]-*tert*-butylamine (14).** The imine was prepared by the method used to prepare imine **1**, but employing 2-[4-(tetrahydropyran-2-yloxy)but-1-ynyl]benzaldehyde (0.78 g, 3 mmol). Removal of the solvent afforded 0.88 g (94%) of the imine **14** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 9H), 1.48-1.65 (m, 4H), 1.68-1.89 (m, 2H), 2.78 (t, J = 7.2 Hz, 2H), 3.48-3.56 (m, 1H), 3.67 (m, 1H), 3.86-3.97 (m, 2H), 4.68 (t, J = 3.0 Hz, 1H), 7.26-7.31 (m, 2H), 7.37-7.42 (m, 1H), 7.97-8.03 (m, 1H), 8.78 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 19.5, 21.2, 25.5, 29.8, 30.7, 57.7, 62.3, 65.9, 78.8, 92.7, 98.9, 124.4, 125.9, 128.1, 129.7, 132.4, 137.8, 154.5; IR (neat, cm^{-1}) 3063, 2229, 1637; HRMS Calcd for $C_{20}H_{27}NO_2$: 313.2040. Found: 313.2042.

***N*-[2-(3-Hydroxyprop-1-ynyl)benzylidene]-*tert*-butylamine (15).** The imine was prepared by the method used to prepare imine **1**, but employing 2-(3-hydroxyprop-1-ynyl)benzaldehyde (1.00 g, 6.25 mmol). Removal of the solvent afforded 1.30 g (96%) of the imine **15** as a tan solid: mp 50-51 °C; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 9H), 4.04 (br s, 1H), 4.45 (s, 2H), 7.23-7.38 (m, 3H), 7.99 (dd, J = 1.8, 7.5 Hz, 1H), 8.01 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 29.8, 51.0, 58.1, 82.3, 93.6, 123.6, 126.1, 128.7, 129.9, 132.6, 137.6, 155.1; IR ($CHCl_3$, cm^{-1}) 3332, 3066, 2969, 1637; HRMS Calcd for $C_{14}H_{17}NO$: 215.1310. Found: 215.1310.

***N*-[2-(3-Hydroxy-3-methylbut-1-ynyl)benzylidene]-*tert*-butylamine (16).** The imine was prepared by the method used to prepare imine **1**, but employing 2-(3-hydroxy-3-methylbut-1-ynyl)benzaldehyde (0.75 g, 4 mmol). Removal of the solvent afforded 0.94 g (97%) of the imine **16** as a viscous yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 9H), 1.64 (s, 6H), 2.47 (br s, 1H), 7.27-7.36 (m, 2H), 7.38-7.43 (m, 1H), 8.01-8.04 (m, 1H), 8.77 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 29.8, 31.6, 58.0, 65.7, 79.5, 99.5, 123.4, 126.0, 128.7, 129.7, 132.3, 137.9, 154.3; IR (neat, cm^{-1}) 3359, 3063, 2222, 1637; HRMS Calcd for $C_{16}H_{21}NO$: 243.1619. Found: 243.1623.

***N*-[2-(Triisopropylsilylethynyl)benzylidene]-*tert*-butylamine (17).** The imine was prepared by the method used to prepare imine **1**, but employing 2-(tri-isopropylsilylethynyl)benzaldehyde (0.57 g, 2 mmol). Removal of the solvent afforded 0.66 g (97%) of the imine **17** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 21H), 1.31 (s, 9H), 7.29-7.38 (m, 2H), 7.49-7.52 (m, 1H), 8.02-8.08 (m, 1H), 8.88 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 11.37, 18.8, 29.9, 57.8, 96.5, 104.2, 124.2, 125.9, 128.7, 129.6, 133.1, 138.2, 154.3; IR (neat, cm^{-1}) 3064, 2153, 1702, 1637; HRMS Calcd for $C_{22}H_{35}NSi$: 341.2540. Found: 341.2539.

***N*-(6-Bromobenzo[1,3]dioxol-5-ylmethylene)-*tert*-butylamine (25).** The imine was prepared by the method used to prepare imine **1**, but employing 2-bromopiperonal (2.00 g, 8.73 mmol). Removal of the solvent afforded 2.27 g (92%) of the imine **25** as a white solid: mp 73-74 °C; ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 9H), 5.99 (s, 2H), 6.98 (s, 1H), 7.52 (s, 1H), 8.50 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 29.8, 57.8, 102.1, 107.8, 112.5, 117.2, 129.5, 147.9, 150.1, 154.2; IR ($CHCl_3$, cm^{-1}) 3077, 2963, 1627; HRMS Calcd for $C_{12}H_{14}BrNO_2$: 283.0208. Found: 283.0205.

***N*-(2-Bromopyridin-3-ylmethylene)-*tert*-butylamine (28).** The imine was prepared by the method used to prepare imine **1**, but employing 2-bromo-3-formylpyridine (0.51 g, 2.74 mmol). Removal of the solvent afforded 0.62 g (94%) of the imine **28** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 9H), 7.27 (dd, J = 4.8, 7.8 Hz, 1H), 8.25 (dd, J = 1.8, 7.5, Hz, 1H), 8.34 (dd, J = 0.9, 4.5 Hz, 1H), 8.48 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 29.6, 58.5, 123.2, 132.9, 136.9, 144.0, 151.1, 153.2; IR (neat, cm^{-1}) 3043, 2968, 1633, 1576; HRMS Calcd for $C_{10}H_{13}BrN_2$: 240.0262. Found: 240.0262.

***N*-(2-Bromocyclopent-1-enylmethylene)-*tert*-butylamine (31).** The imine was prepared by the method used to prepare imine **1**, but employing 2-bromocyclopentene-1-carboxaldehyde (0.75 g, 4.31 mmol). Removal of the solvent afforded 0.89 g (90%) of the imine **31** as a dark yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 9H), 1.97 (quintet, J = 7.5 Hz, 2H), 2.59 (tt, J = 2.1, 7.5 Hz, 2H), 2.79 (tt, J = 2.4, 7.5 Hz, 2H), 8.18 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.6, 29.8, 31.1, 41.6, 57.7, 127.9, 139.1, 151.8; IR (neat, cm^{-1}) 2965, 1630; HRMS Calcd for $C_{10}H_{16}BrN$: 229.0466. Found: 229.0460.

***N*-(1-Bromo-3,4-dihydronaphthalen-2-ylmethylene)-*tert*-butylamine (34).** The imine was prepared by the method used to prepare imine **1**, but employing 1-bromo-3,4-dihydronaphthalene-2-carboxaldehyde (0.77 g, 3.26 mmol). Removal of the solvent afforded

0.85 g (89%) of the imine **34** as a viscous yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 9H), 2.81-2.83 (m, 4H), 7.16 (dd, J = 1.8, 6.9 Hz, 1H), 7.22-7.31 (m, 2H), 7.79 (dd, J = 1.8, 7.2 Hz, 1H), 8.61 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 25.3, 27.7, 30.0, 58.1, 126.8, 127.3, 127.6, 128.6, 129.1, 134.2, 135.9, 138.3, 157.0; IR (neat, cm^{-1}) 3063, 2965, 1612; HRMS Calcd for $C_{15}H_{18}BrN$: 291.0623. Found: 290.0548 (M-H).

***N*-[(*Z*)-3-Iodo-3-phenylallylidene]-*tert*-butylamine (36).** The imine was prepared by the method used to prepare imine **1**, but employing *Z*-3-iodo-3-phenyl-2-propenal (0.60 g, 2.33 mmol). Removal of the solvent afforded 0.64 g (87%) of the imine **36** as a yellow solid: mp 81-83 °C; ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 9H), 6.77 (d, J = 7.8 Hz, 1H), 7.32-7.35 (m, 3H), 7.56-7.60 (m, 2H), 8.15 (d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 29.7, 58.4, 113.6, 128.5, 128.8, 129.6, 134.9, 142.0, 161.4; IR ($CHCl_3$, cm^{-1}) 3078, 2967, 1614; HRMS Calcd for $C_{13}H_{16}IN$: 313.0328. Found: 313.0332.

Isoquinolines Prepared by the Copper-Catalyzed Cyclization of Iminoalkynes

3-(Cyclohex-1-enyl)isoquinoline (4). The reaction mixture was chromatographed using 15:1 hexanes/EtOAc to afford 42 mg (81%) of the indicated compound as a yellow solid: mp 114-115 °C (hexanes/EtOAc); ^{1}H NMR ($CDCl_3$) δ 1.67-1.75 (m, 2H), 1.81-1.89 (m, 2H), 2.29-2.36 (m, 2H), 2.54-2.60 (m, 2H), 7.02 (tt, J = 2.4, 3.6 Hz, 1H), 7.48 (dt, J = 0.6, 14.4 Hz, 1H), 7.57 (s, 1H), 7.63 (dd, J = 1.2, 6.9 Hz, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 9.18 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.3, 23.1, 26.1, 26.2, 114.2, 126.4, 126.8, 127.6, 128.4, 130.3, 135.7, 136.7, 151.7, 152.5 (one sp^2 carbon missing due to overlap); IR ($CHCl_3$, cm^{-1}) 3060, 2919, 1621, 1574; MS *m/z* (rel intensity) 209 (100, M^+), 208 (89), 194 (42), 180 (51). Anal. Calcd for $C_{15}H_{15}N$: C, 86.09; H, 7.23; N, 6.69. Found: C, 86.03; H, 7.30; N, 6.73.

3-Cyclohexylisoquinoline (5). The reaction mixture was chromatographed using 15:1 hexanes/EtOAc to afford 49 mg (93%) of the indicated compound as a yellow oil, which solidified upon cooling: mp 40-41 °C (hexanes/EtOAc); ^{1}H NMR ($CDCl_3$) δ 1.25-1.67 (m, 6H), 1.89 (dt, *J* = 2.7, 12.6 Hz, 2H), 2.06 (dd, *J* = 1.5, 12.9 Hz, 2H), 2.84 (tt, *J* = 3.3, 11.7 Hz, 1H), 7.45 (s, 1H), 7.50 (ddd, *J* = 1.2, 6.9, 8.1 Hz, 1H), 7.62 (dt, *J* = 1.2, 6.9 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 9.19 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 26.3, 26.8, 33.2, 46.2, 116.2, 126.3, 126.4, 127.3, 127.5, 130.2, 136.7, 151.9, 160.2; IR ($CHCl_3$, cm^{-1}) 3055, 2926, 1628, 1585; HRMS Calcd for $C_{15}H_{17}N$: 211.1356. Found: 211.1361.

3-[2-(Tetrahydropyran-2-yloxy)ethyl]isoquinoline (18). The reaction mixture was chromatographed using 1:1 hexanes/EtOAc to afford 53 mg (83%) of the indicated compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.40-1.60 (m, 4H), 1.61-1.82 (m, 2H), 3.23 (t, *J* = 7.2 Hz, 2H), 3.42-3.48 (m, 1H), 3.76 (ddd, *J* = 3.3, 8.1, 11.7 Hz, 1H), 3.87 (ddd, *J* = 6.9, 9.6, 16.5 Hz, 1H), 4.18 (ddd, *J* = 6.9, 9.6, 16.8 Hz, 1H), 4.62 (m, 1H), 7.52 (ddd, *J* = 1.2, 6.9, 9.3 Hz, 1H), 7.55 (s, 1H), 7.63 (ddd, *J* = 1.2, 6.6, 9.3 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 9.19 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 19.6, 25.5, 30.7, 38.5, 62.3, 67.0, 98.9, 119.2, 126.2, 126.6, 127.3, 127.6, 130.3, 136.5, 152.1, 152.6; IR ($CHCl_3$, cm^{-1}) 3054, 2942, 1629, 1588; HRMS Calcd for $C_{16}H_{19}NO_2$: 257.1416. Found: 257.1415.

Isoquinolines and Pyridines Prepared by the Palladium/Copper-Catalyzed Coupling and Cyclization of Terminal Alkynes

3-(Cyclohex-1-enyl)isoquinoline (4). The reaction mixture was chromatographed using 15:1 hexanes/EtOAc to afford 85 mg (81%) of the indicated compound, whose spectral data were identical with that reported above.

3-Cyclohexylisoquinoline (5). The reaction mixture was chromatographed using 15:1 hexanes/EtOAc to afford 93 mg (88%) of the indicated compound, whose spectral data were identical with that reported above.

3-[2-(Tetrahydropyran-2-yloxy)ethyl]isoquinoline (18). The reaction mixture was chromatographed using 1:1 hexanes/EtOAc to afford 122 mg (95%) of the indicated compound, whose spectral data were identical with that reported above.

3-(Diethoxymethyl)isoquinoline (22). The reaction mixture was chromatographed using 4:1 hexanes/EtOAc to afford 97 mg (84%) of the indicated compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.25 (dt, J = 0.6, 13.5 Hz, 6H), 3.67 (dddd, J = 0.6, 7.2, 7.8, 16.5 Hz, 4H), 5.67 (s, 1H), 7.54 (dddd, J = 1.2, 1.2, 8.1, 8.1 Hz, 1H), 7.64 (dddd, J = 1.2, 1.2, 6.9, 6.9 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.90-7.93 (m, 2H), 9.23 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 15.3, 62.0, 102.4, 117.7, 127.2, 127.46, 127.51, 128.4, 130.5, 136.2, 151.5, 152.2; IR (neat, cm^{-1}) 3056, 2975, 1629, 1587; HRMS Calcd for $C_{14}H_{17}NO_2$: 231.1259. Found: 232.1338 (M+H).

4-(3-Isoquinolinyl)butanenitrile (23). The reaction mixture was chromatographed using 1:1 hexanes/EtOAc to afford 85 mg (87%) of the indicated compound as an off-white solid: mp 104-105 °C (hexanes/EtOAc); ^{1}H NMR ($CDCl_3$) δ 2.18 (pentet, J = 7.2 Hz, 2H), 2.36 (t, J = 7.8 Hz, 2H), 3.04 (t, J = 7.2 Hz, 2H), 7.48 (s, 1H), 7.53 (ddd, J = 1.2, 6.9, 9.3 Hz, 1H), 7.64 (ddd, J = 1.2, 6.9, 9.3 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 9.17 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 16.6, 25.3, 36.4, 118.9, 119.7, 126.2, 126.9, 127.4, 127.6, 130.7, 136.4, 152.6, 152.8; IR ($CHCl_3$, cm^{-1}) 3054, 2946, 1627, 1586; HRMS Calcd for $C_{13}H_{12}N_2$: 196.1000. Found: 196.1001.

3-[3-(3-Isoquinolinyl)propyl]isoquinoline (24). The reaction mixture was chromatographed using 1:1 hexanes/EtOAc to afford 42 mg (56%) of the indicated compound

as a yellow solid: mp 116-117 °C (hexanes/EtOAc); ^{1}H NMR ($CDCl_3$) δ 2.37 (pentet, J = 8.1 Hz, 2H), 3.05 (t, J = 8.4 Hz, 4H), 7.48 (s, 2H), 7.51 (ddd, J = 1.2, 6.9, 9.3 Hz, 2H), 7.62 (ddd, J = 1.2, 6.9, 9.6 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 9.19 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 30.1, 37.8, 118.3, 126.2, 126.4, 127.2, 127.5, 130.3, 136.6, 152.2, 155.3; IR ($CHCl_3$, cm^{-1}) 3054, 2946, 1627, 1586; HRMS Calcd for $C_{12}H_{18}N_2$: 298.1470. Found: 298.1469.

7-Cyclohexyl-1,3-dioxolo[4,5-*g*]isoquinoline (26). The reaction mixture was chromatographed using 2:1 hexanes/EtOAc to afford 97 mg (76%) of the indicated compound as a yellow solid: mp 93-94 °C (hexanes/EtOAc); ^{1}H NMR ($CDCl_3$) δ 1.20-1.61 (m, 5H), 1.71-1.77 (m, 1H), 1.85 (dt, J = 3.0, 12.3 Hz, 2H), 1.97-2.02 (m, 2H), 2.74 (tt, J = 3.3, 8.1 Hz, 1H), 6.01 (s, 2H), 6.95 (s, 1H), 7.09 (s, 1H), 7.25 (s, 1H), 8.89 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 26.3, 26.8, 33.3, 46.0, 101.4, 102.3, 103.0, 116.1, 124.3, 135.1, 147.7, 149.7, 150.8, 159.3; IR ($CHCl_3$, cm^{-1}) 3029, 2923, 1601, 1584, 1482, 1453; HRMS Calcd for $C_{16}H_{17}NO_2$: 255.1259. Found: 255.1254.

7-[2-(Tetrahydropyran-2-yloxy)ethyl]-1,3-dioxolo[4,5-*g*]isoquinoline (27). The reaction mixture was chromatographed using 1:2 hexanes/EtOAc to afford 122 mg (81%) of the indicated compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.38-1.79 (m, 6H), 3.12 (t, J = 6.9 Hz, 2H), 3.38-3.45 (m, 1H), 3.69-3.84 (m, 2H), 4.06-4.15 (m, 1H), 4.57-4.59 (m, 1H), 6.01 (s, 2H), 6.94 (s, 1H), 7.08 (s, 1H), 7.34 (s, 1H), 8.87 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 19.6, 25.5, 30.7, 38.3, 62.3, 67.1, 98.9, 101.5, 102.2, 103.0, 119.0, 124.4, 134.9, 147.9, 149.8, 150.9, 151.7; IR ($CHCl_3$, cm^{-1}) 3051, 2942, 1604, 1481, 1456; HRMS Calcd for $C_{17}H_{19}NO_4$: 301.1314. Found: 301.1313.

7-Phenyl-1,6-naphthyridine (29). The reaction mixture was chromatographed using 1:1 hexanes/EtOAc to afford 88 mg (85%) of the indicated compound as a yellow solid: mp 135-136 °C (hexanes/EtOAc); ^{1}H NMR ($CDCl_3$) δ 7.39-7.45 (m, 2H), 7.48-7.53 (m, 2H), 8.13-8.17 (m, 2H), 8.23 (d, J = 8.1 Hz, 1H), 8.31 (s, 1H), 9.04 (br s, 1H), 9.30 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 117.9, 122.3, 122.7, 127.3, 129.0, 129.2, 135.6, 138.9, 151.4, 152.7, 155.1, 155.2; IR ($CDCl_3$, cm^{-1}) 3048, 1618, 1594, 1558; HRMS Calcd for $C_{14}H_{10}N_2$: 206.0844. Found: 206.0840.

7-*n*-Butyl-1,6-naphthyridine (30). The reaction mixture was chromatographed using 1:1 hexanes/EtOAc to afford 67 mg (72%) of the indicated compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7.5 Hz, 3H), 1.38 (sextet, J = 7.5 Hz, 2H), 1.77 (quintet, J = 7.5 Hz, 2H), 2.95 (t, J = 7.5 Hz, 2H), 7.39 (dd, J = 4.2, 8.4 Hz, 1H), 7.69 (s, 1H), 8.19 (dd, J = 0.9, 8.4 Hz, 1H), 8.99 (d, J = 2.7 Hz, 1H), 9.16 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 31.9, 38.0, 119.6, 121.7, 121.9, 135.6, 151.1, 152.4, 154.8, 160.4; IR (neat, cm^{-1}) 3051, 2942, 1604, 1481, 1456; HRMS Calcd for $C_{12}H_{14}N_2$: 186.1157. Found: 186.1159.

6,7-Dihydro-5*H*[2]-3-phenylpyrindine (32). The reaction mixture was chromatographed using 7:1 hexanes/EtOAc to afford 68 mg (69%) of the indicated compound with ^{1}H spectral properties identical to those previously reported[1]: mp 49-50 °C (hexanes/EtOAc); ^{1}H NMR ($CDCl_3$) δ 2.13 (quintet, J = 7.5 Hz, 2H), 2.95 (t, J = 7.2 Hz, 4H), 7.35-7.41 (m, 1H), 7.42-7.48 (m, 2H), 7.59 (d, J = 0.3 Hz, 1H), 7.94-7.98 (m, 2H), 8.54 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 25.2, 30.1, 32.8, 116.9, 127.0, 128.5, 128.7, 138.8, 140.1, 145.5, 154.7, 155.5; IR ($CHCl_3$, cm^{-1}) 3067, 2950, 1611, 1556; HRMS Calcd for $C_{14}H_{13}N$: 195.1048. Found: 194.0965 (M-H).

6,7-Dihydro-5*H*[2]-3-(cyclohex-1-enyl)pyrindine (33). The reaction mixture was chromatographed using 7:1 hexanes/EtOAc to afford 55 mg (55%) of the indicated compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.62-1.69 (m, 2H), 1.74-1.81 (m, 2H), 2.07 (quintet, J = 7.5 Hz, 2H), 2.22-2.25 (m, 2H), 2.47-2.49 (m, 2H), 2.88 (q, J = 6.9 Hz, 4H), 6.56-6.59 (m, 1H), 7.24 (s, 1H), 8.38 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.3, 23.0, 25.2, 26.0, 26.4, 30.1, 32.8, 115.2, 127.5, 136.9, 137.9, 144.5, 154.1, 157.2; IR ($CHCl_3$, cm^{-1}) 3059, 2854, 1602, 1554, 1477; HRMS Calcd for $C_{14}H_{17}N$: 199.1361. Found: 199.1361.

2-*n*-Butyl-5,6-dihydrobenzo[*f*]isoquinoline (35). The reaction mixture was chromatographed using 4:1 hexanes/EtOAc to afford 55 mg (46%) of the indicated compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.96 (t, J = 7.5 Hz, 3H), 1.42 (sextet, J = 7.5 Hz, 2H), 1.75 (quintet, J = 7.8 Hz, 2H), 2.80-2.92 (m, 6H), 7.24-7.36 (m, 3H), 7.44 (s, 1H), 7.75-7.82 (m, 1H), 8.39 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 25.1, 28.7, 32.4, 38.2, 116.5, 124.2, 127.2, 128.6, 129.0, 129.3, 132.3, 138.4, 142.0, 148.5, 161.3; IR (neat, cm^{-1}) 3061, 2933, 1603, 1544, 1483; HRMS Calcd for $C_{17}H_{19}N$: 237.1517. Found: 237.1508.

2,4-Diphenylpyridine (37). The reaction mixture was chromatographed using 15:1 hexanes/EtOAc to afford 66 mg (57%) of the indicated compound as a yellow oil with spectral properties identical to those previously reported.[2]

^{1}H and ^{13}C Spectra for Compounds 3, 12-17, 18, 23-25, 27-29, 32 and 35 follow.

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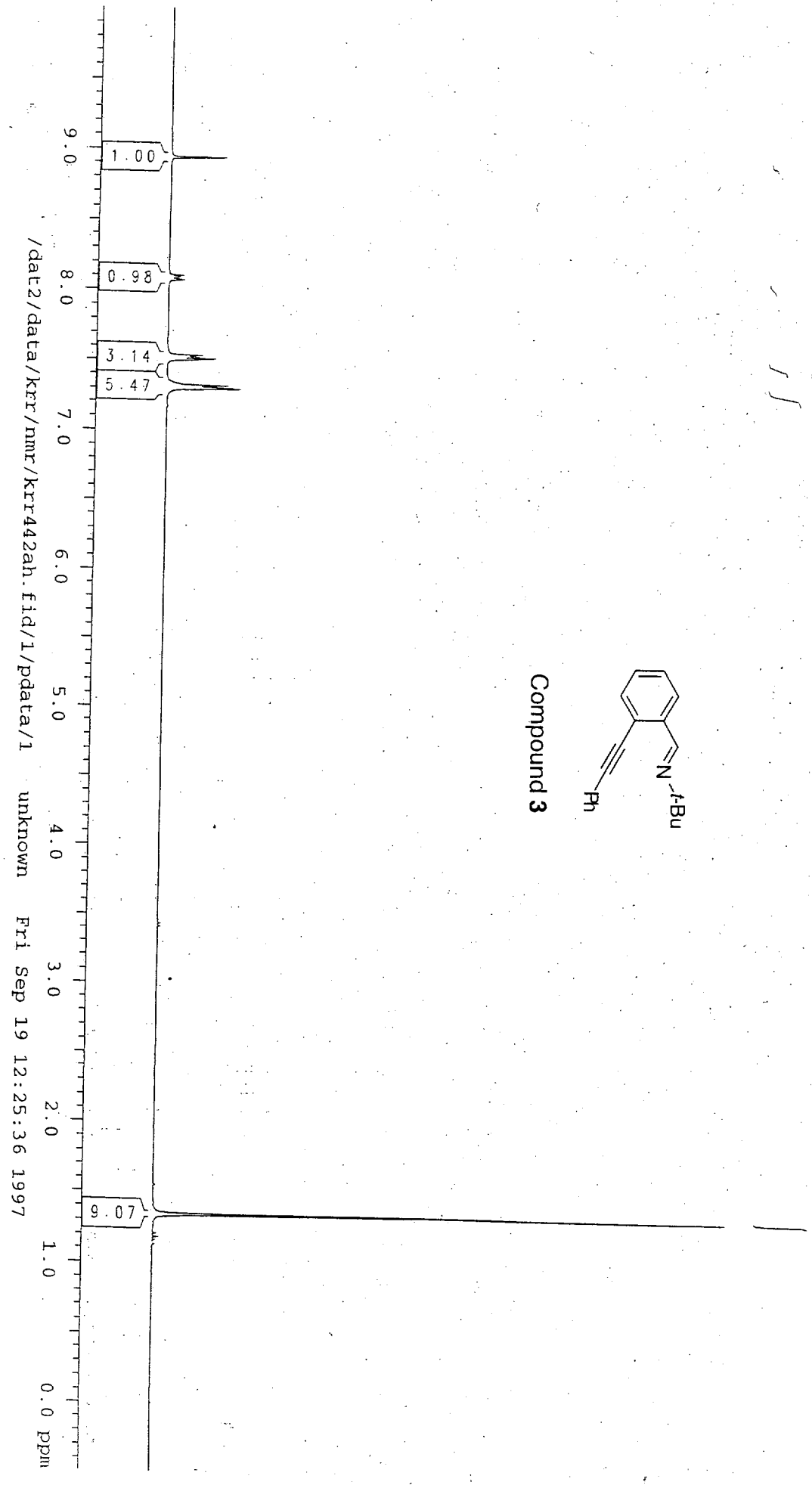
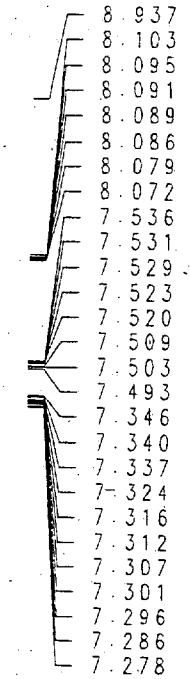


Compound **3**



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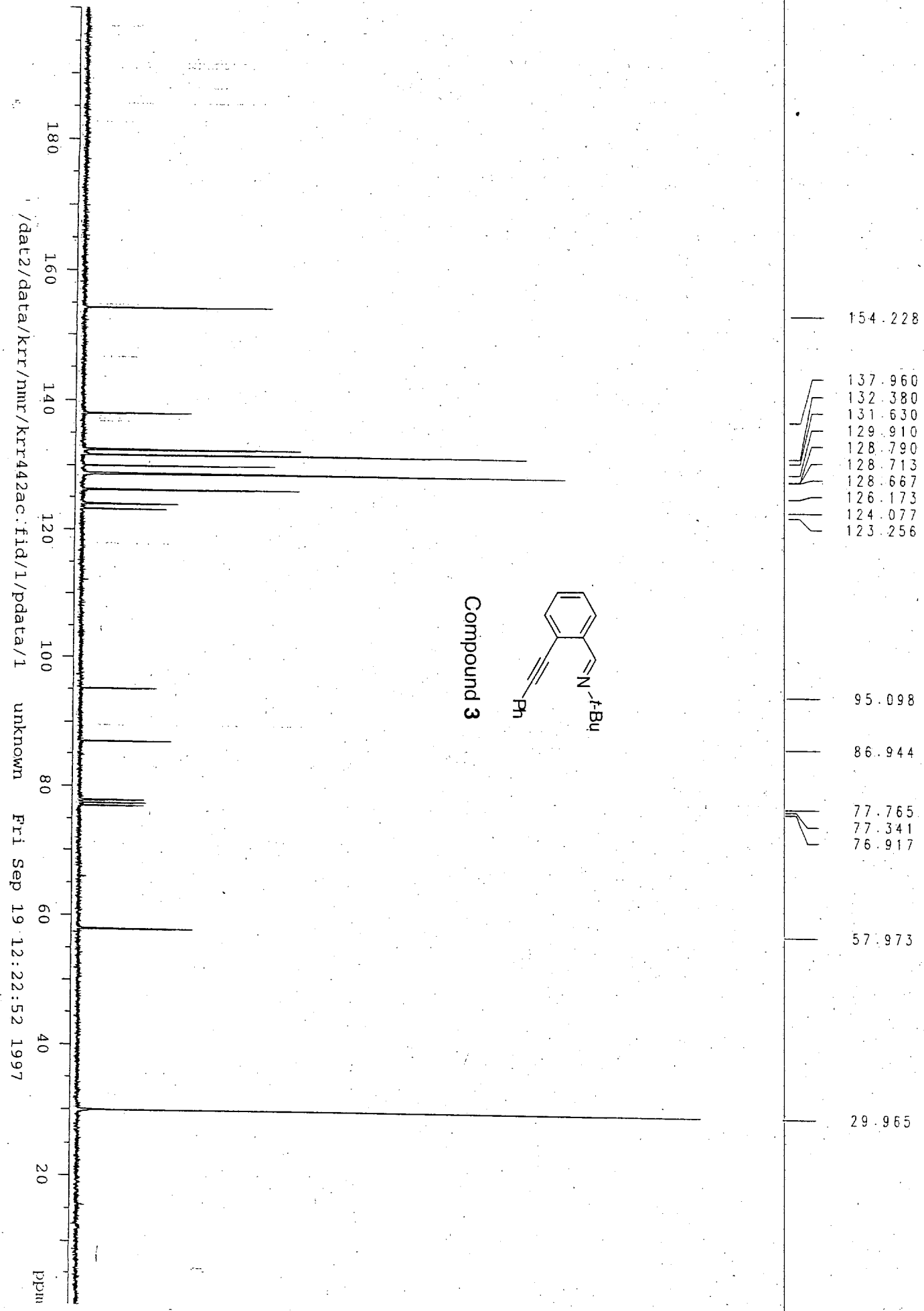
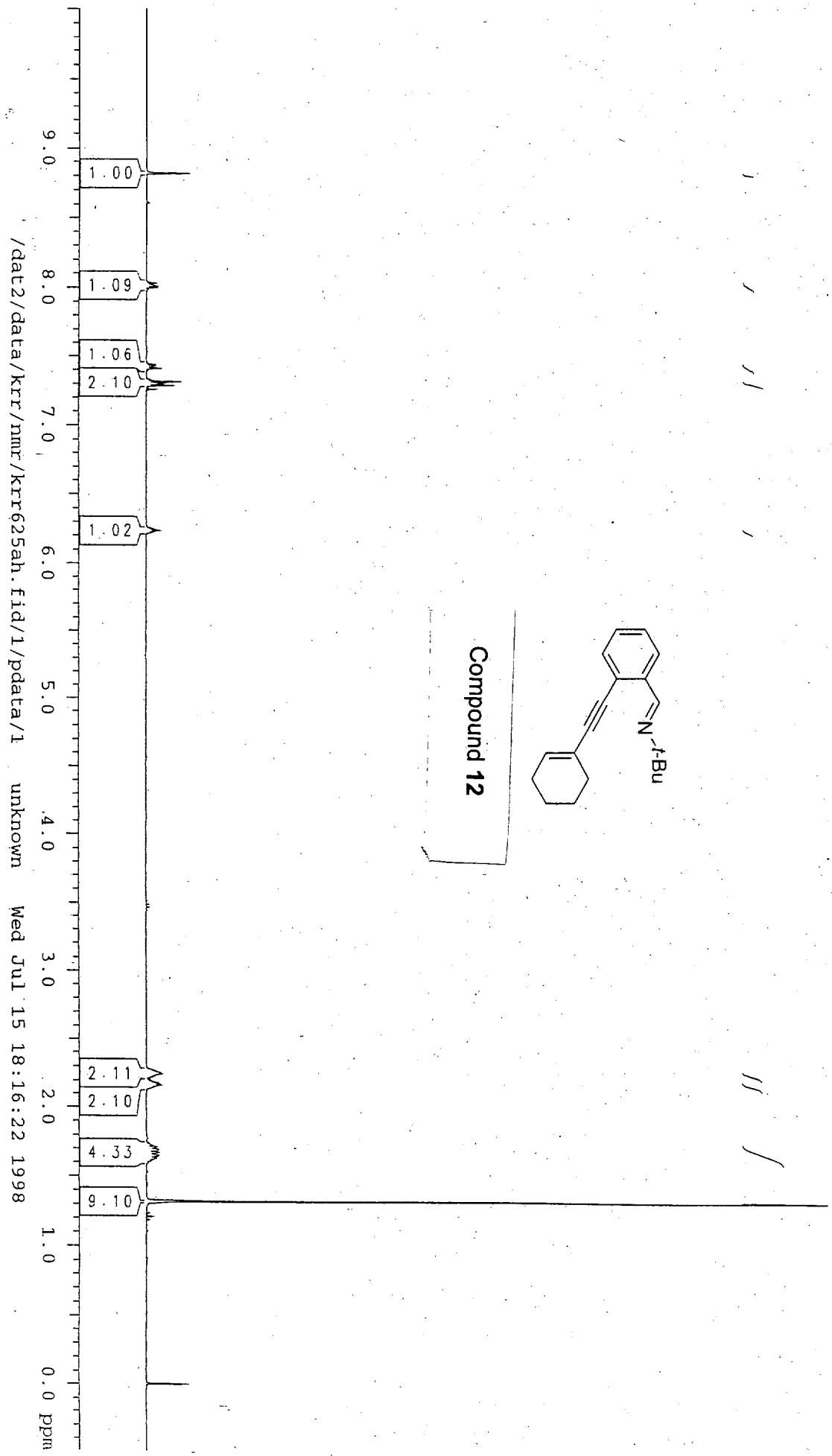
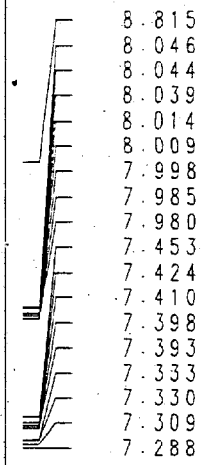
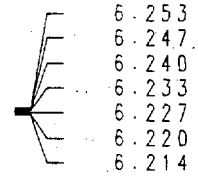
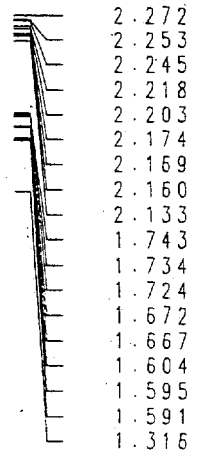
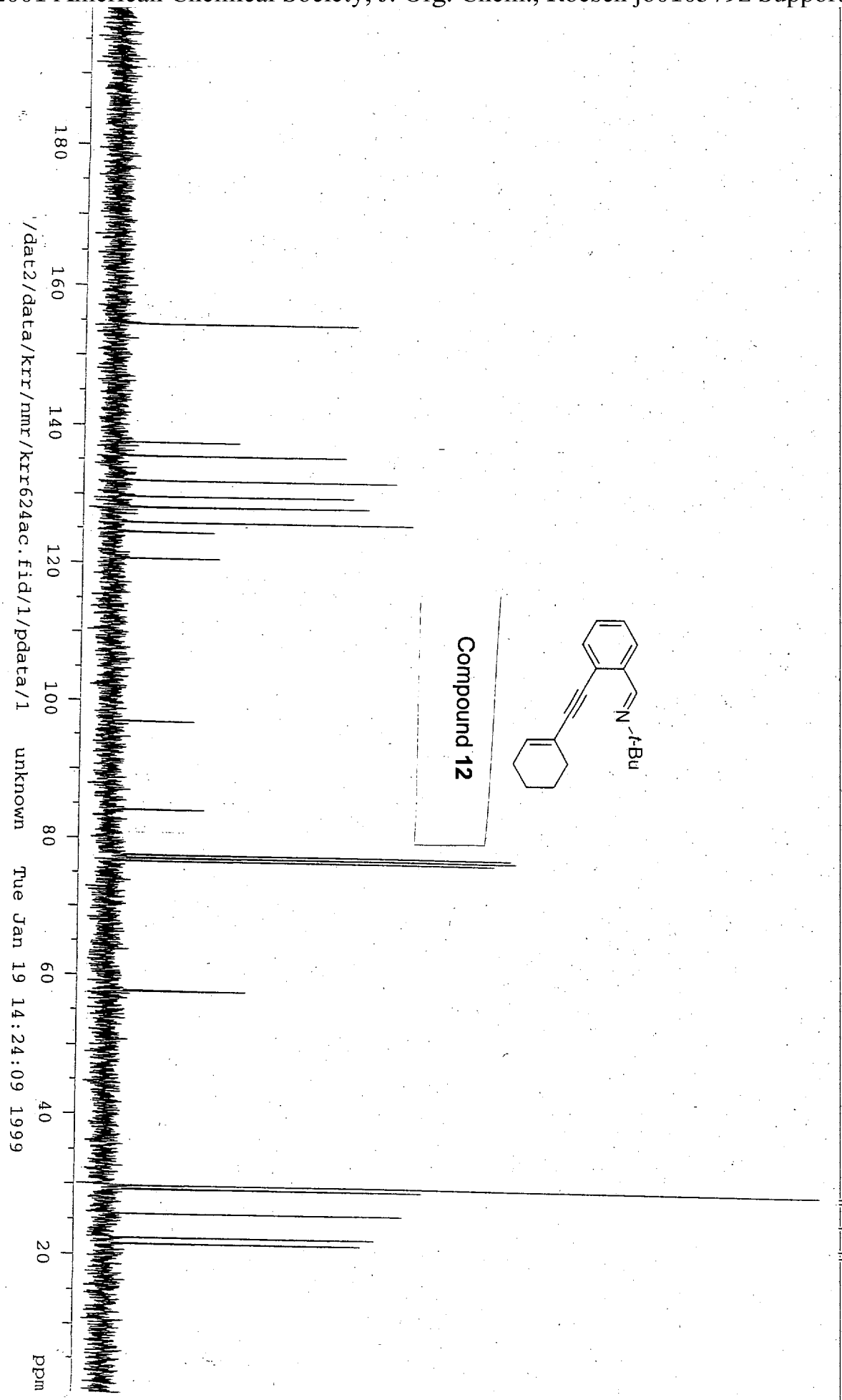


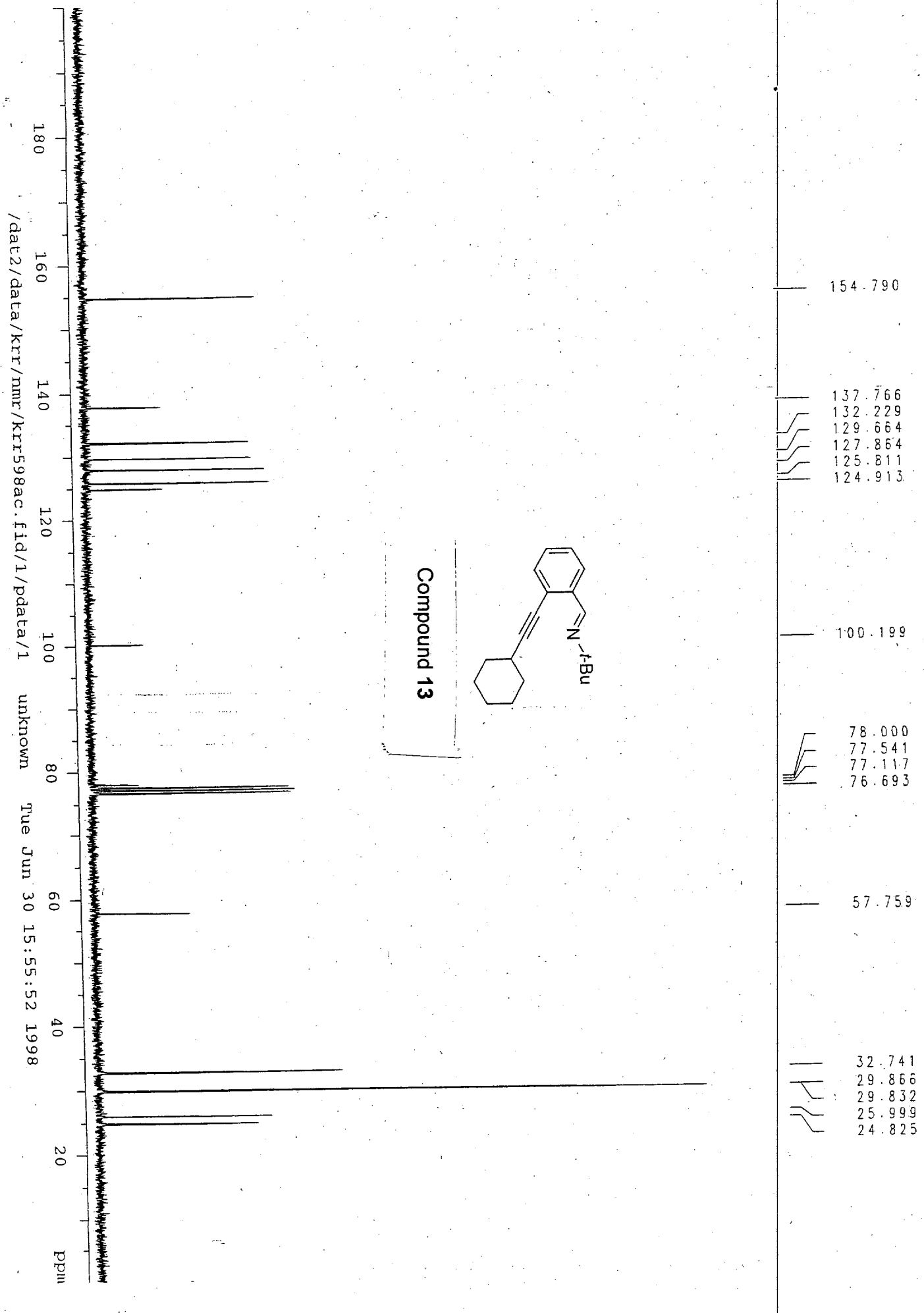


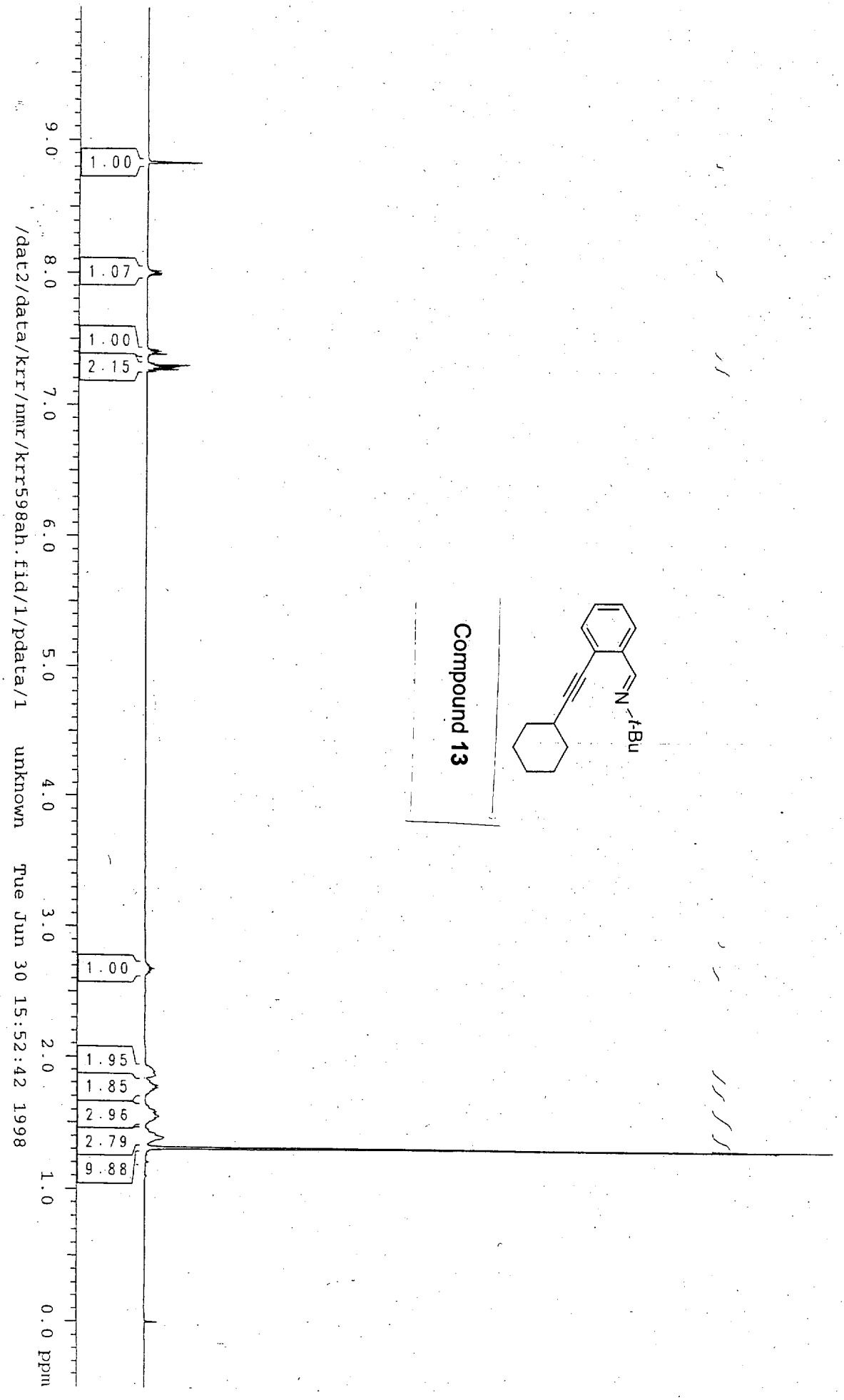


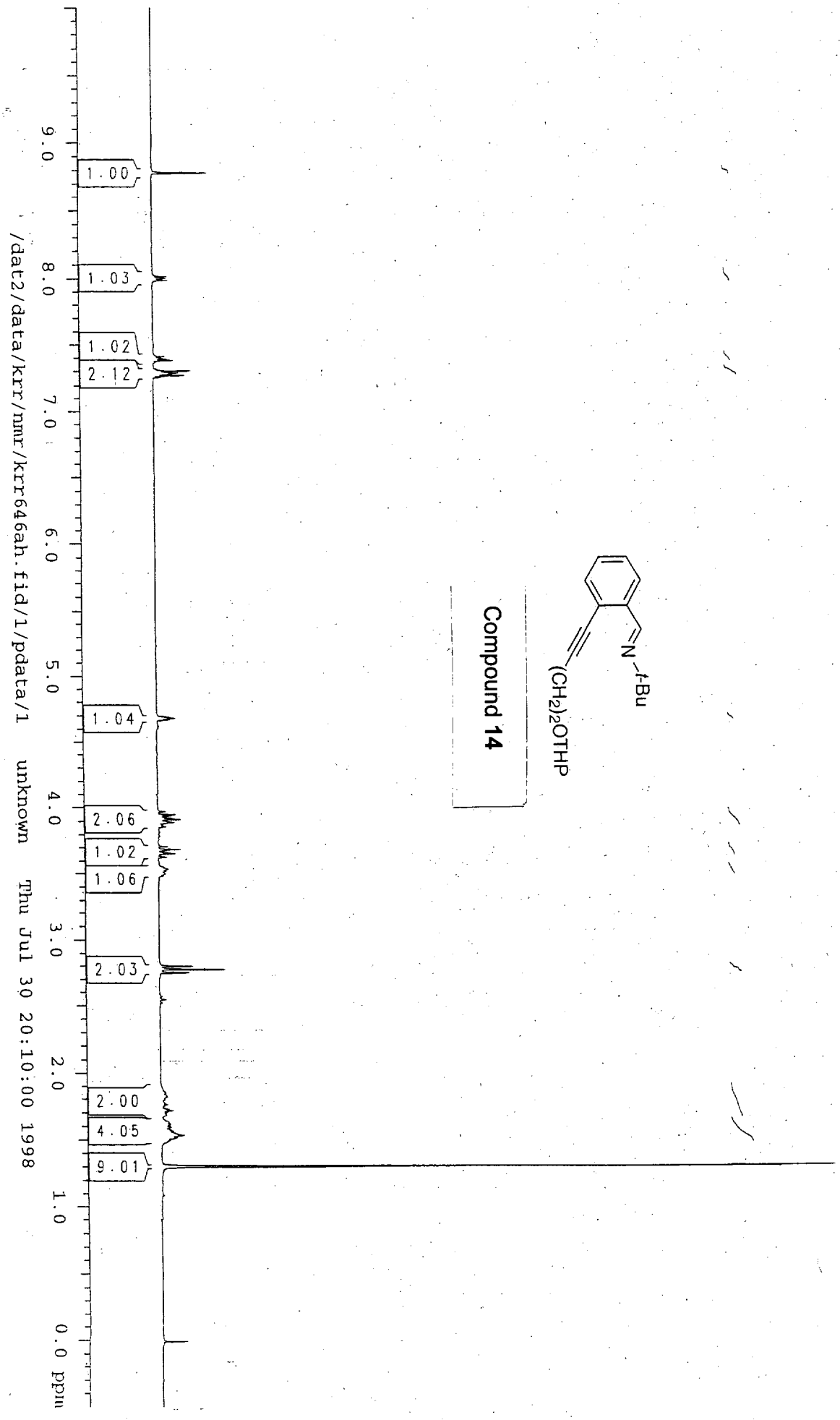


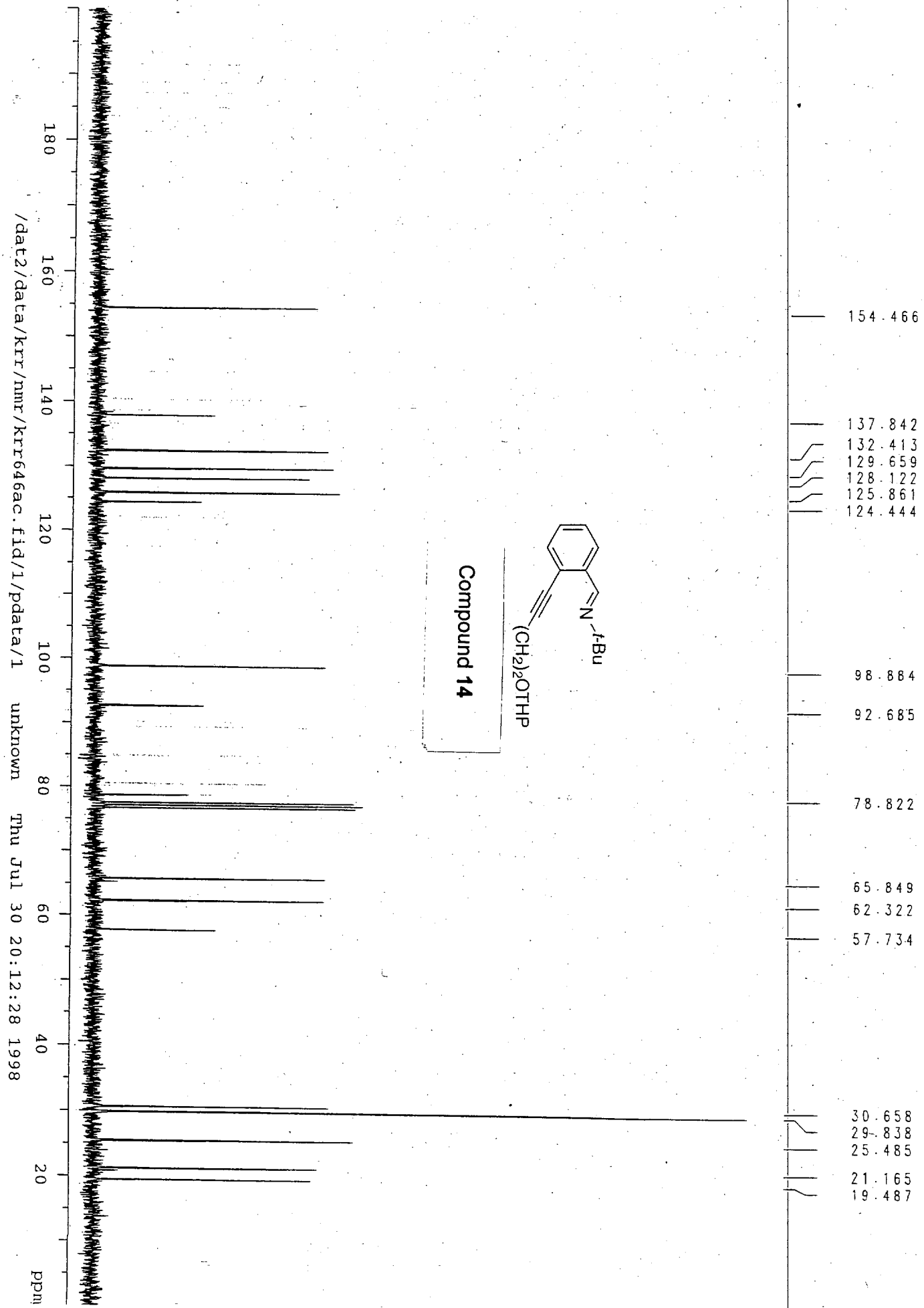


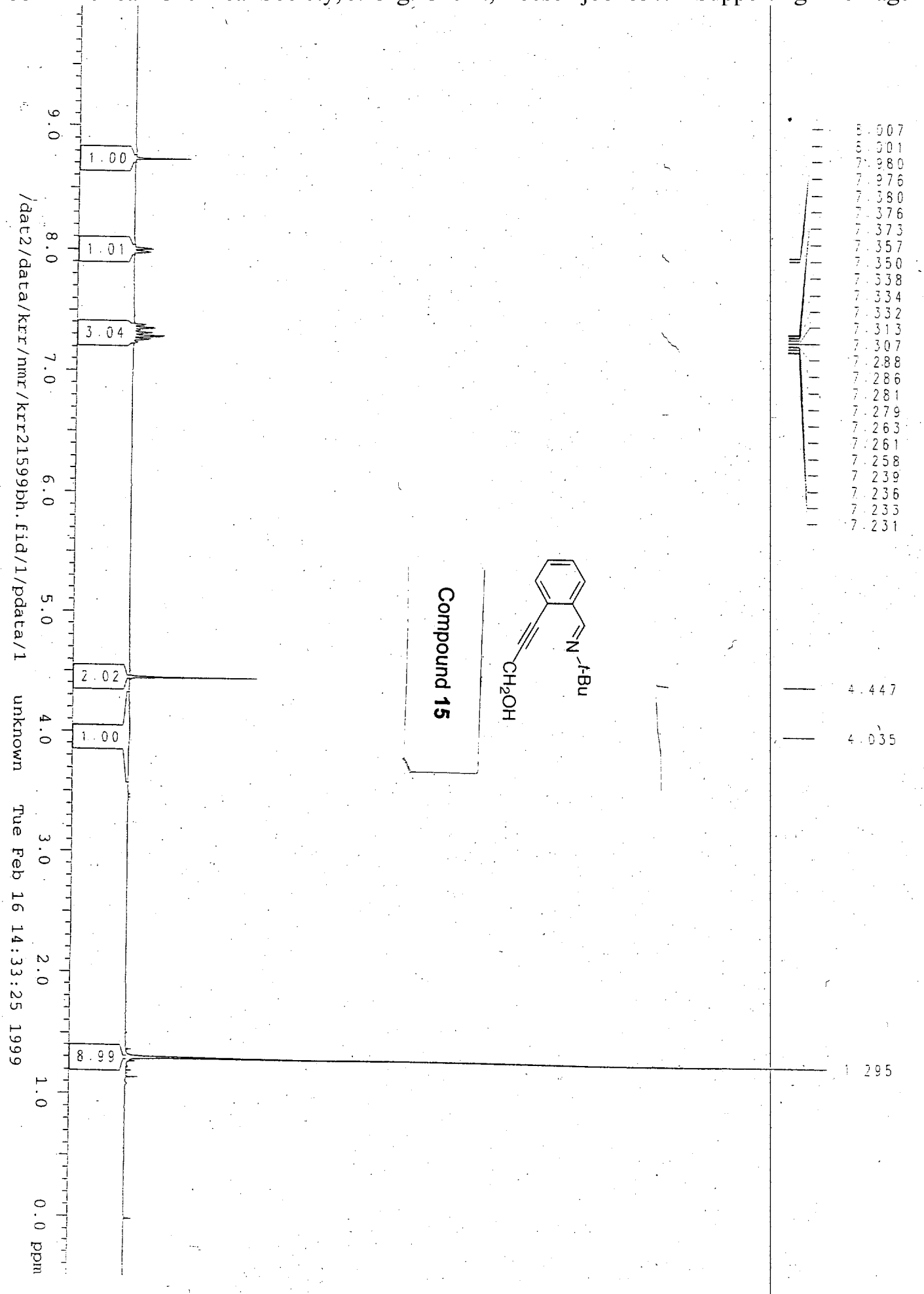


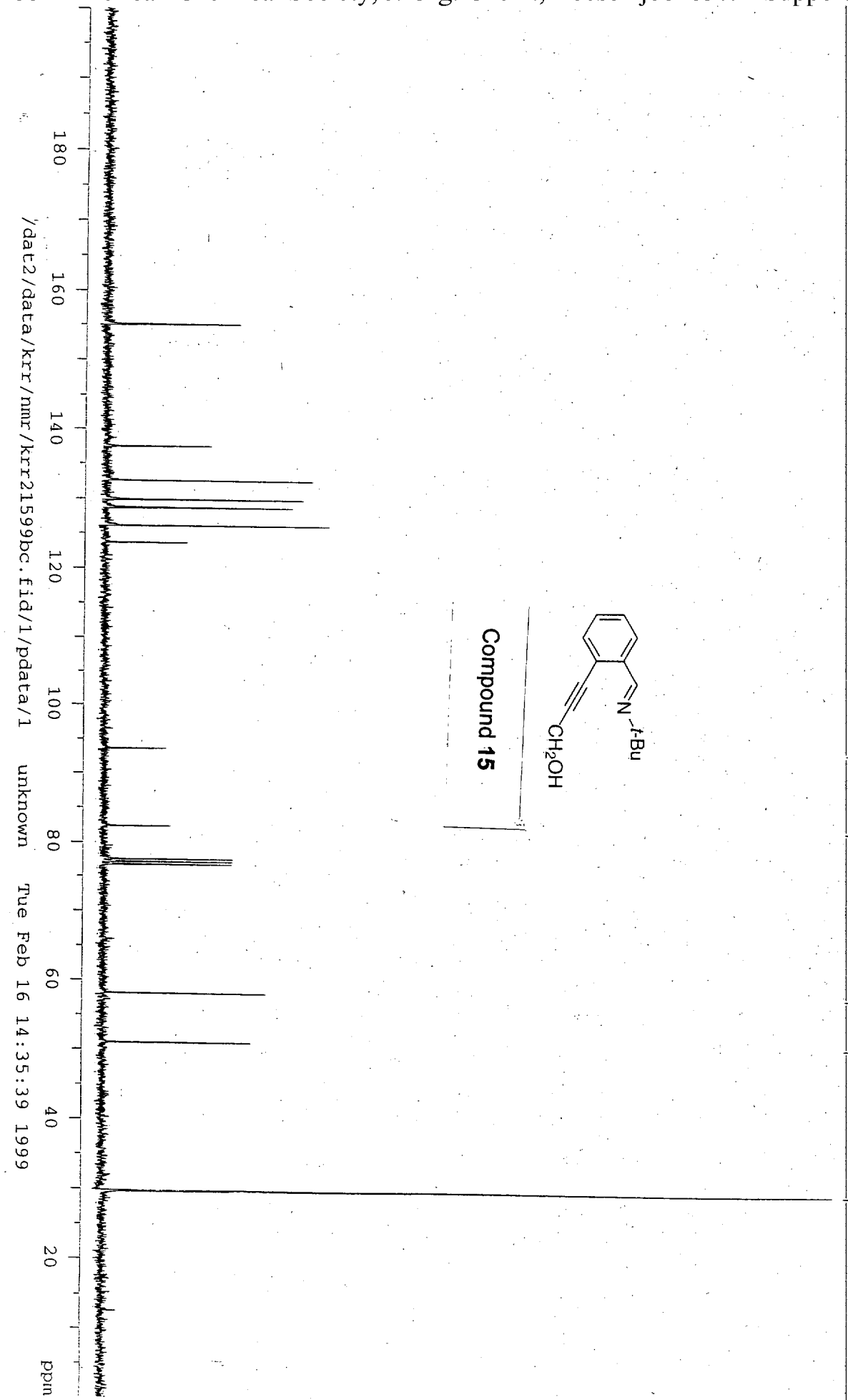


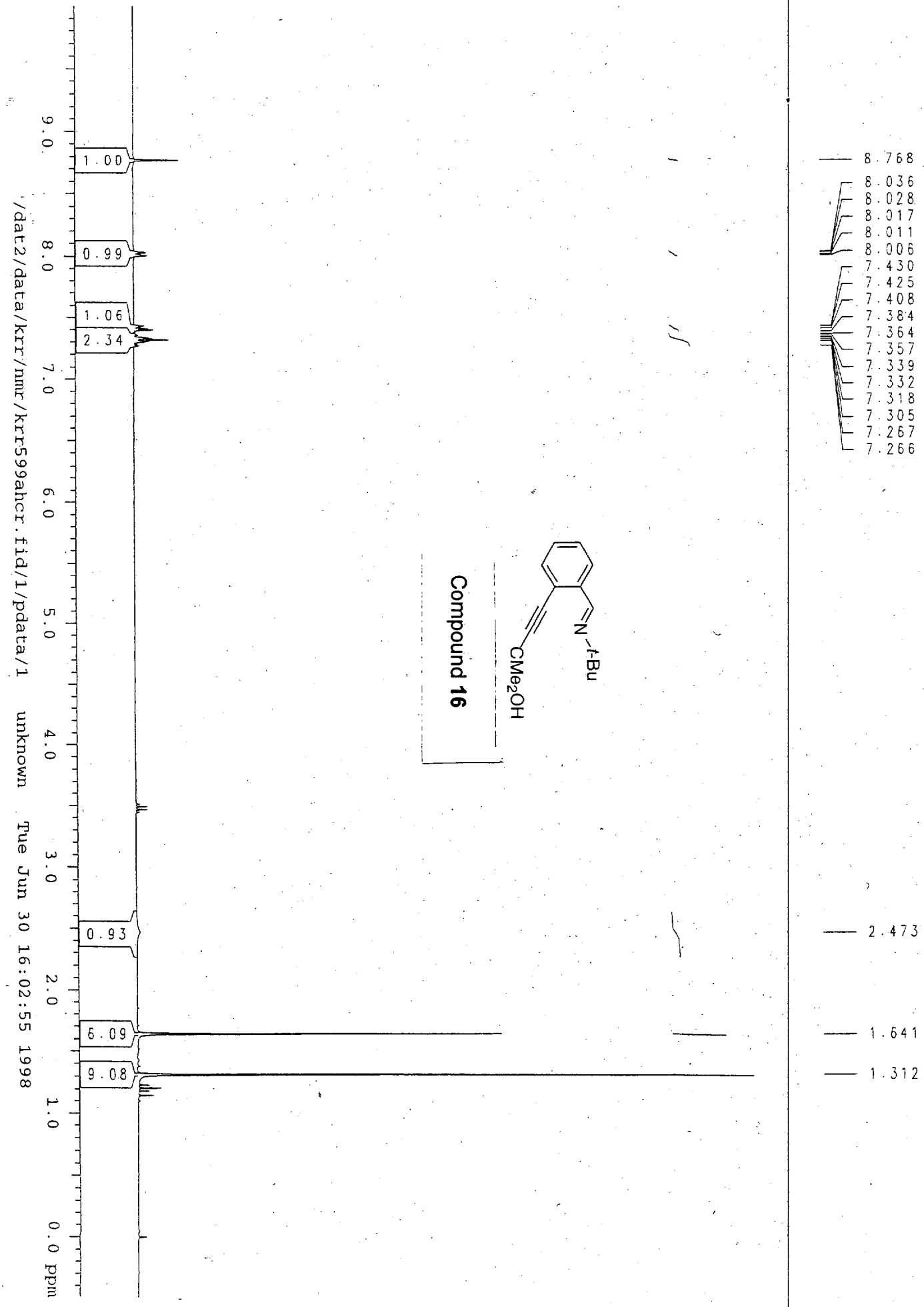


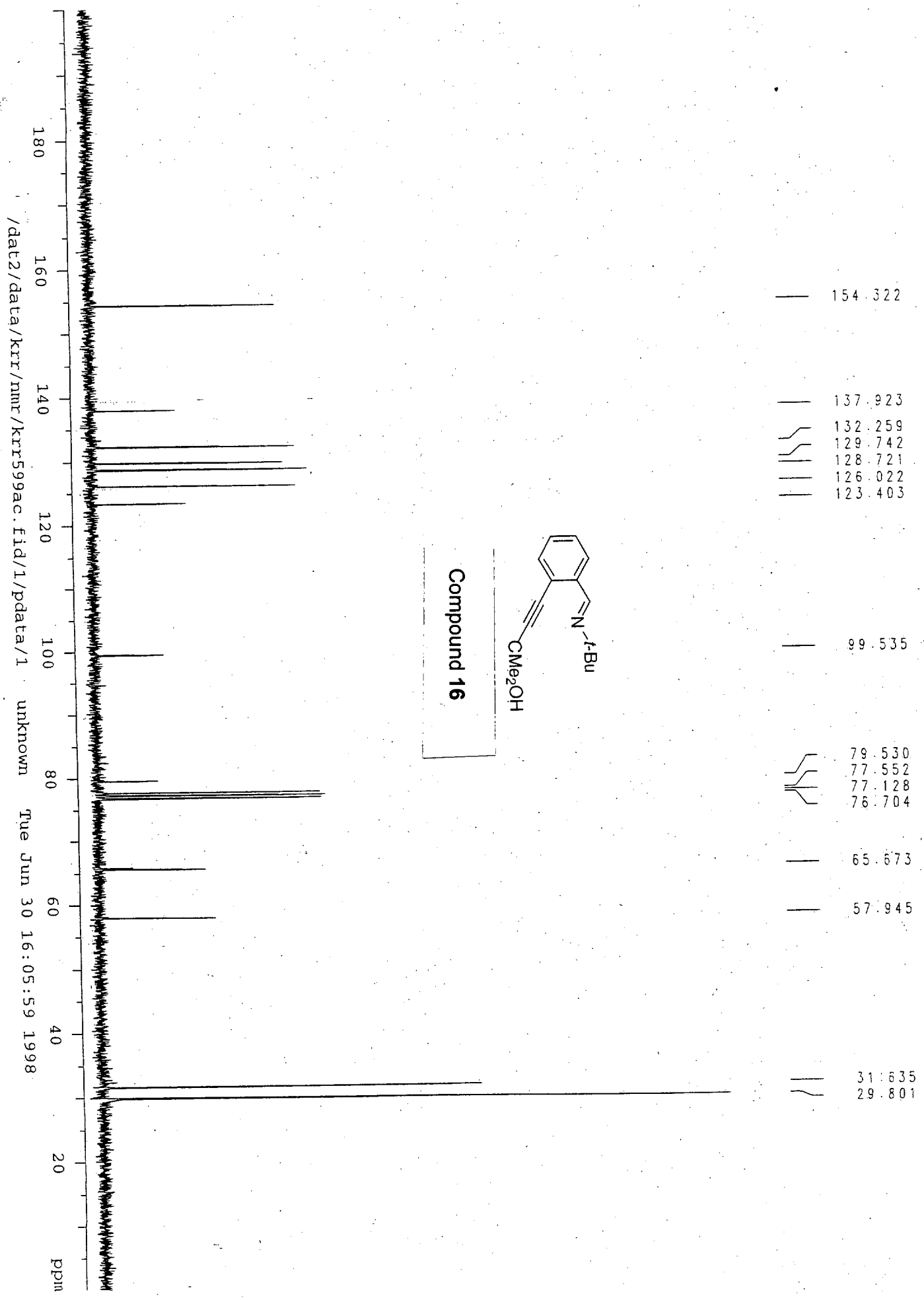


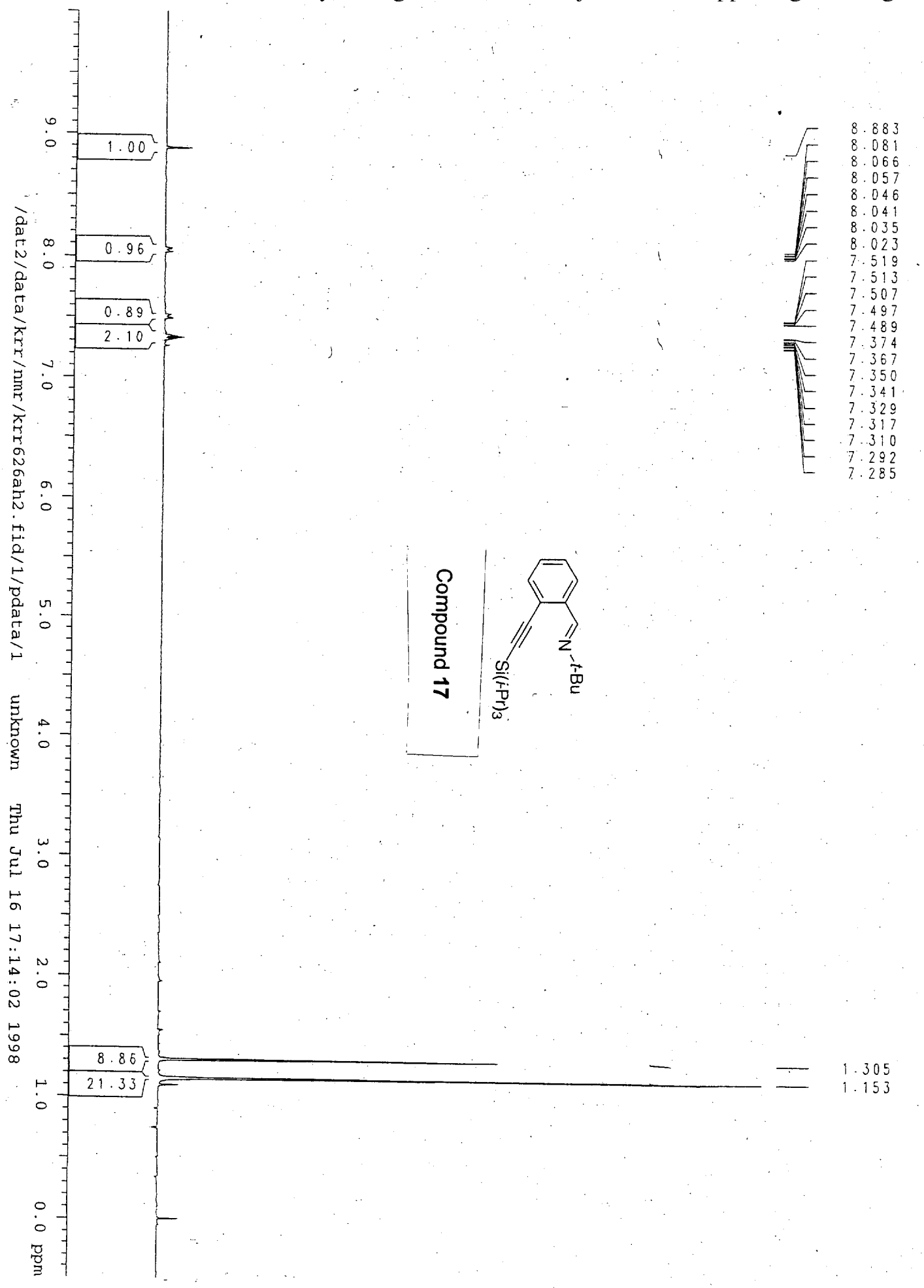


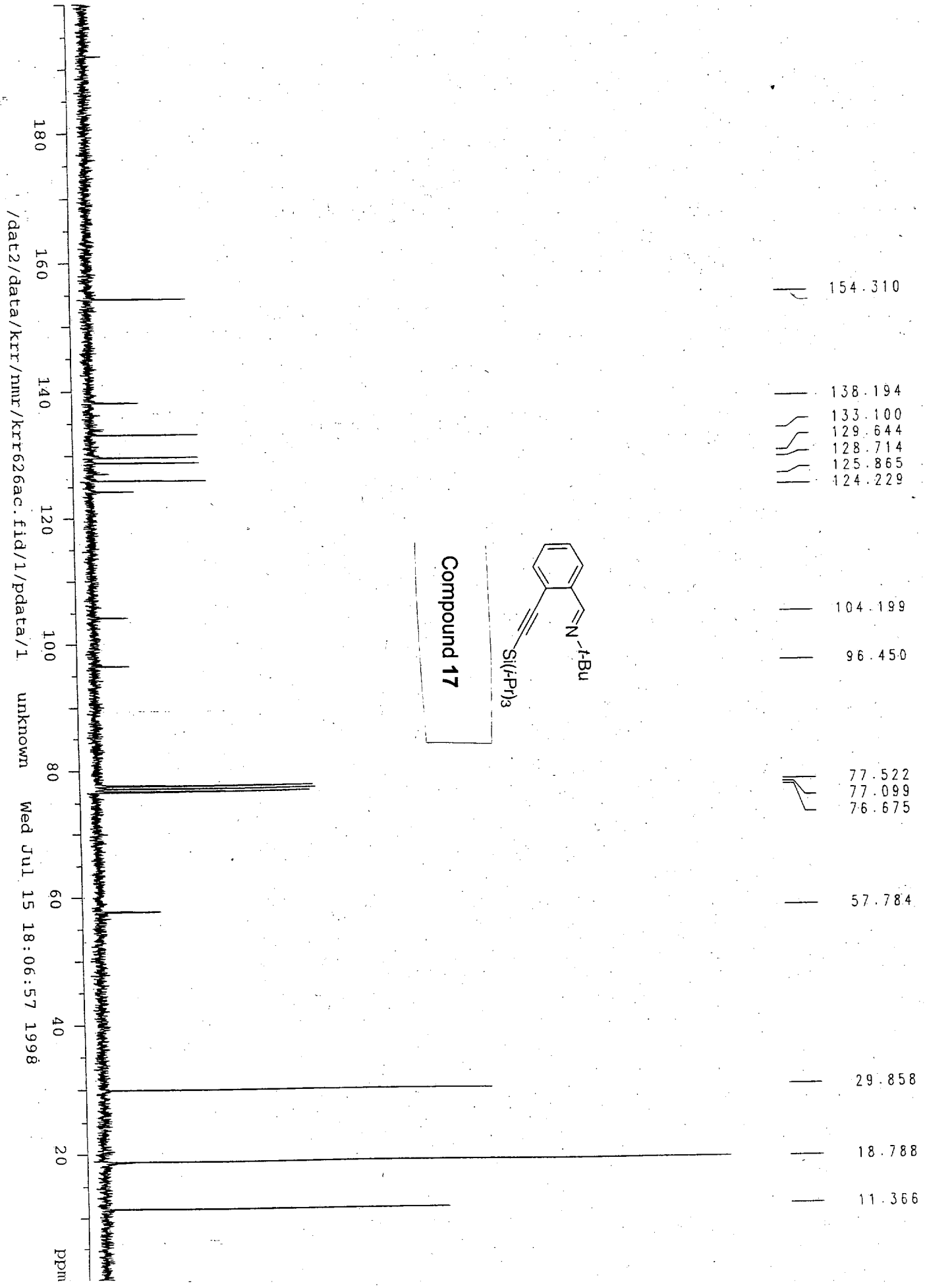


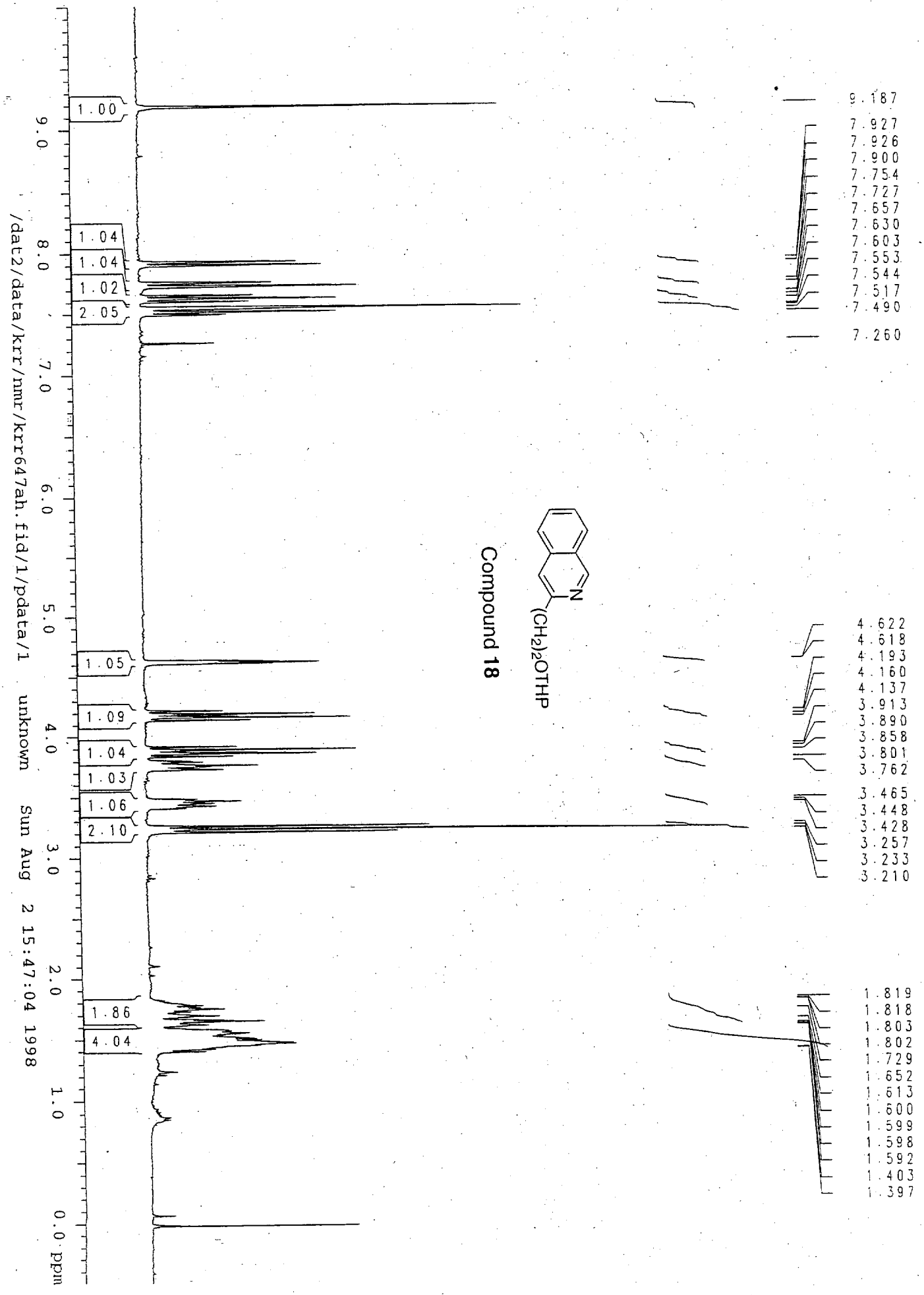


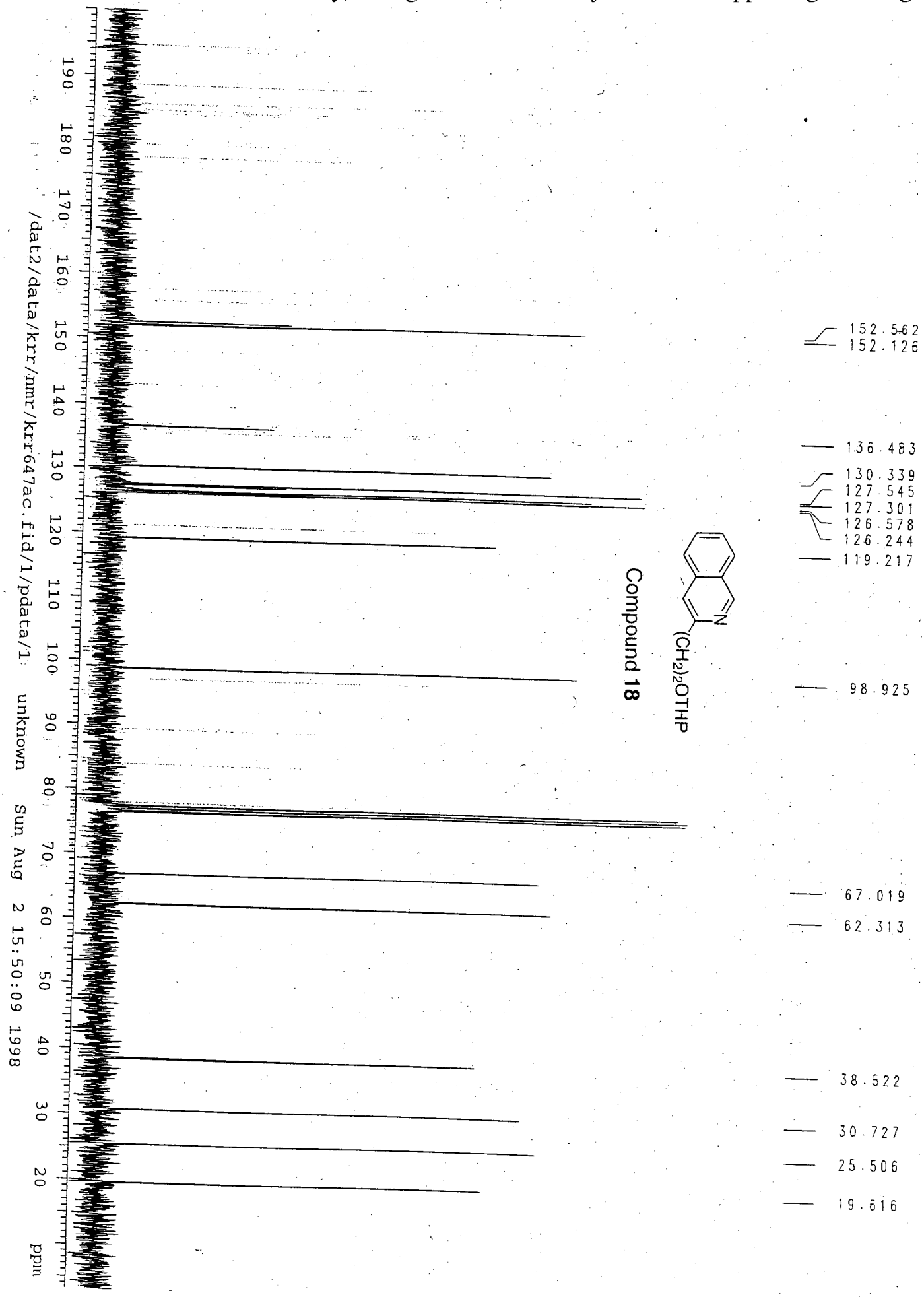


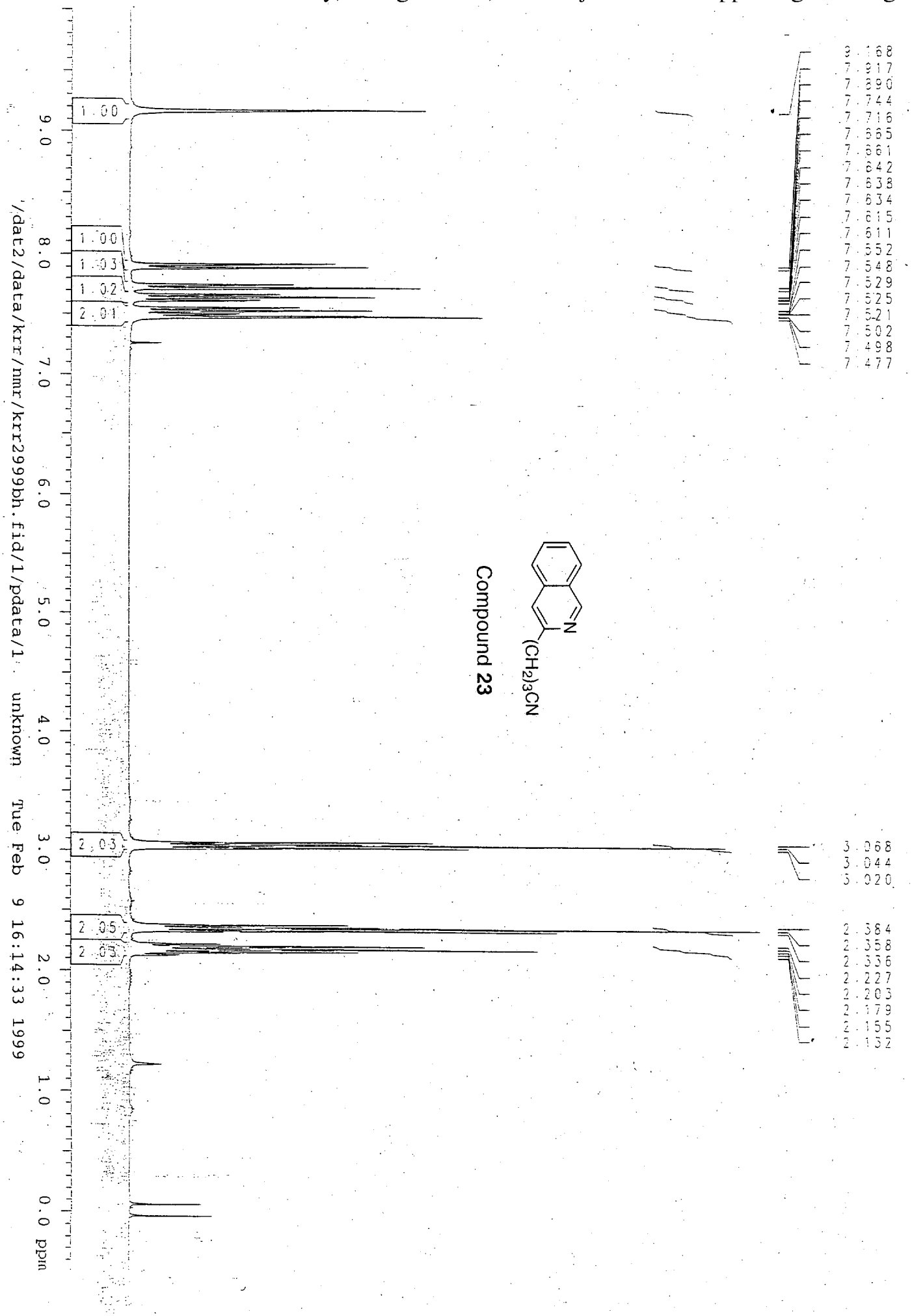




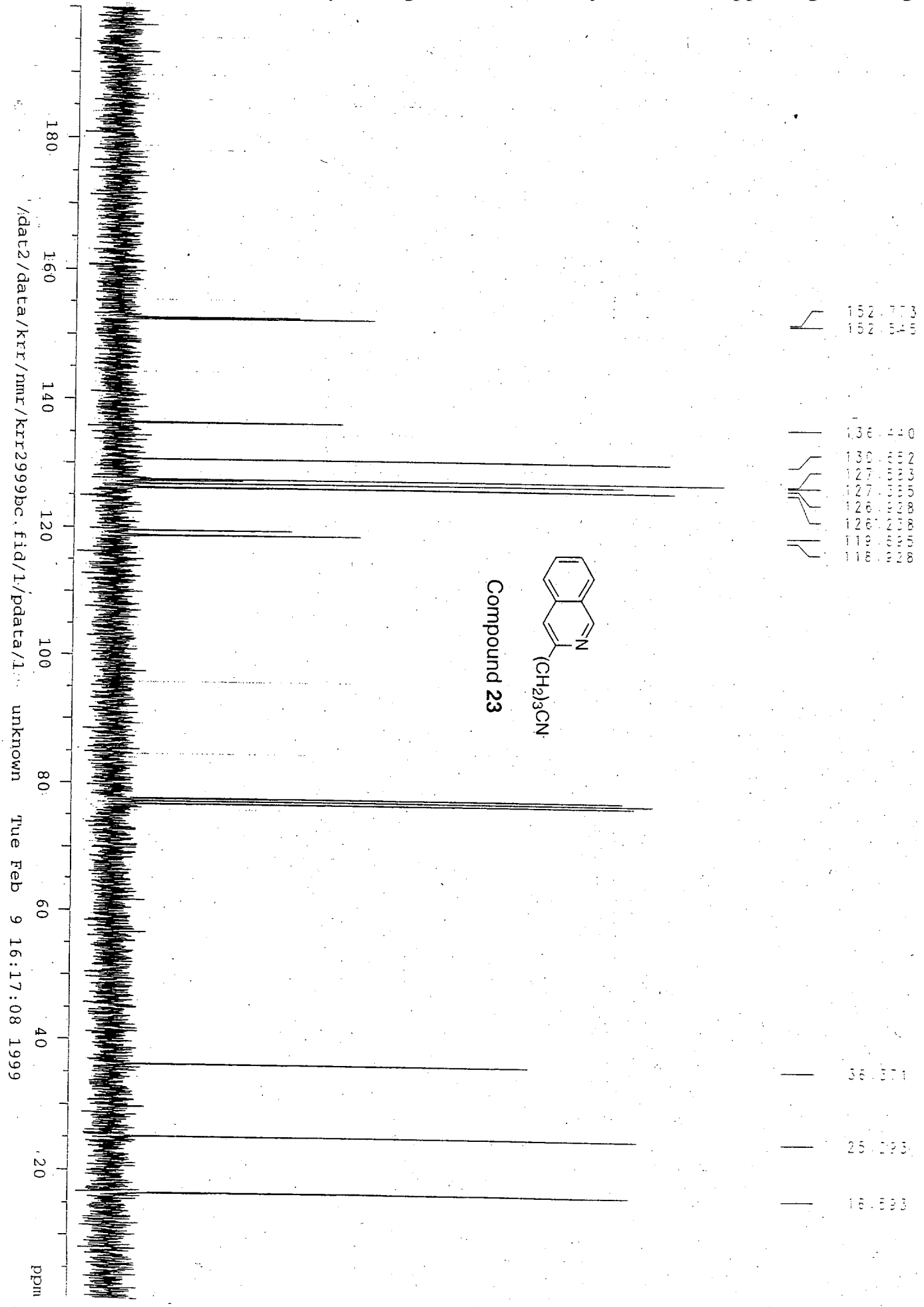


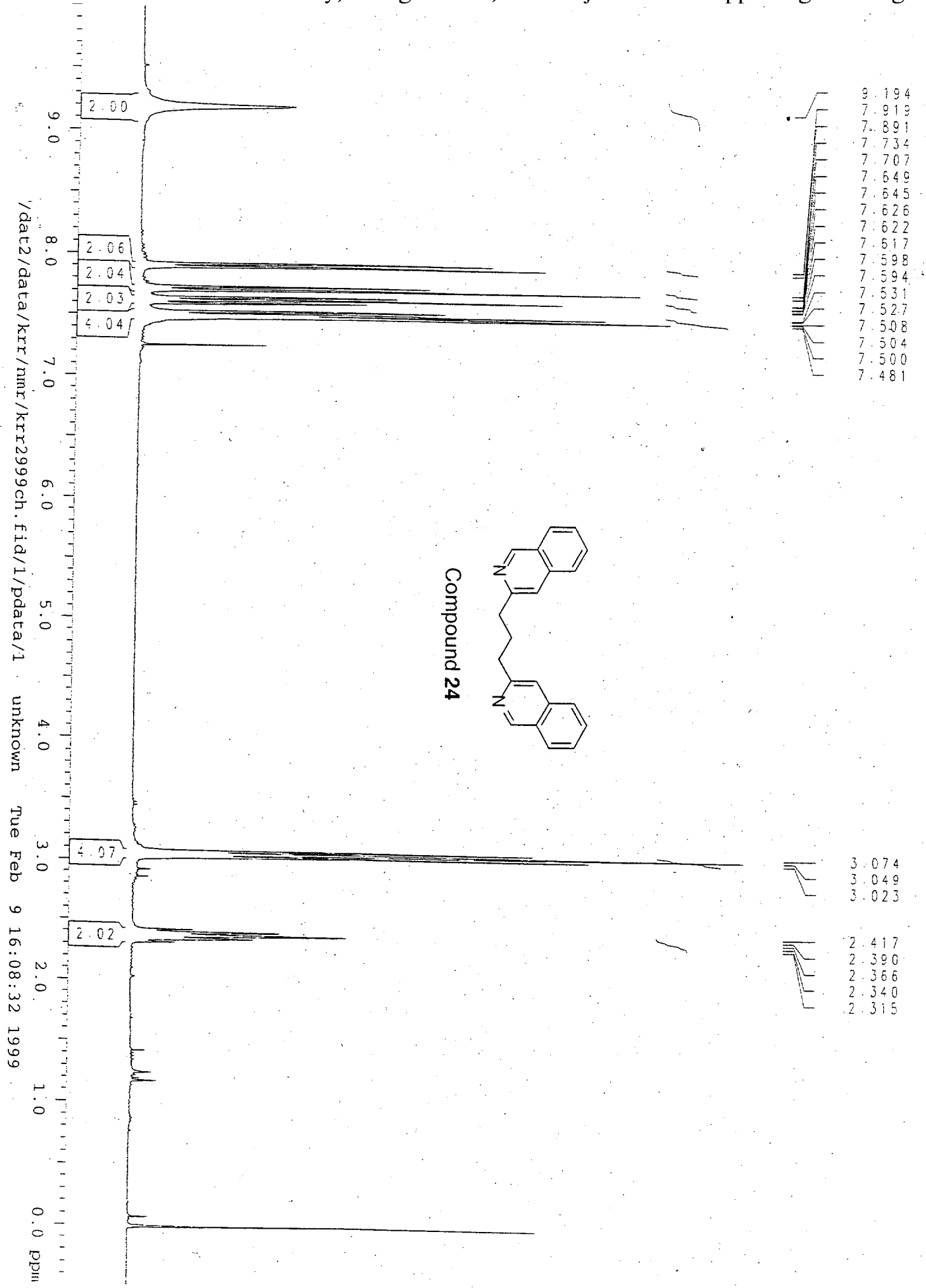






Compound **23**





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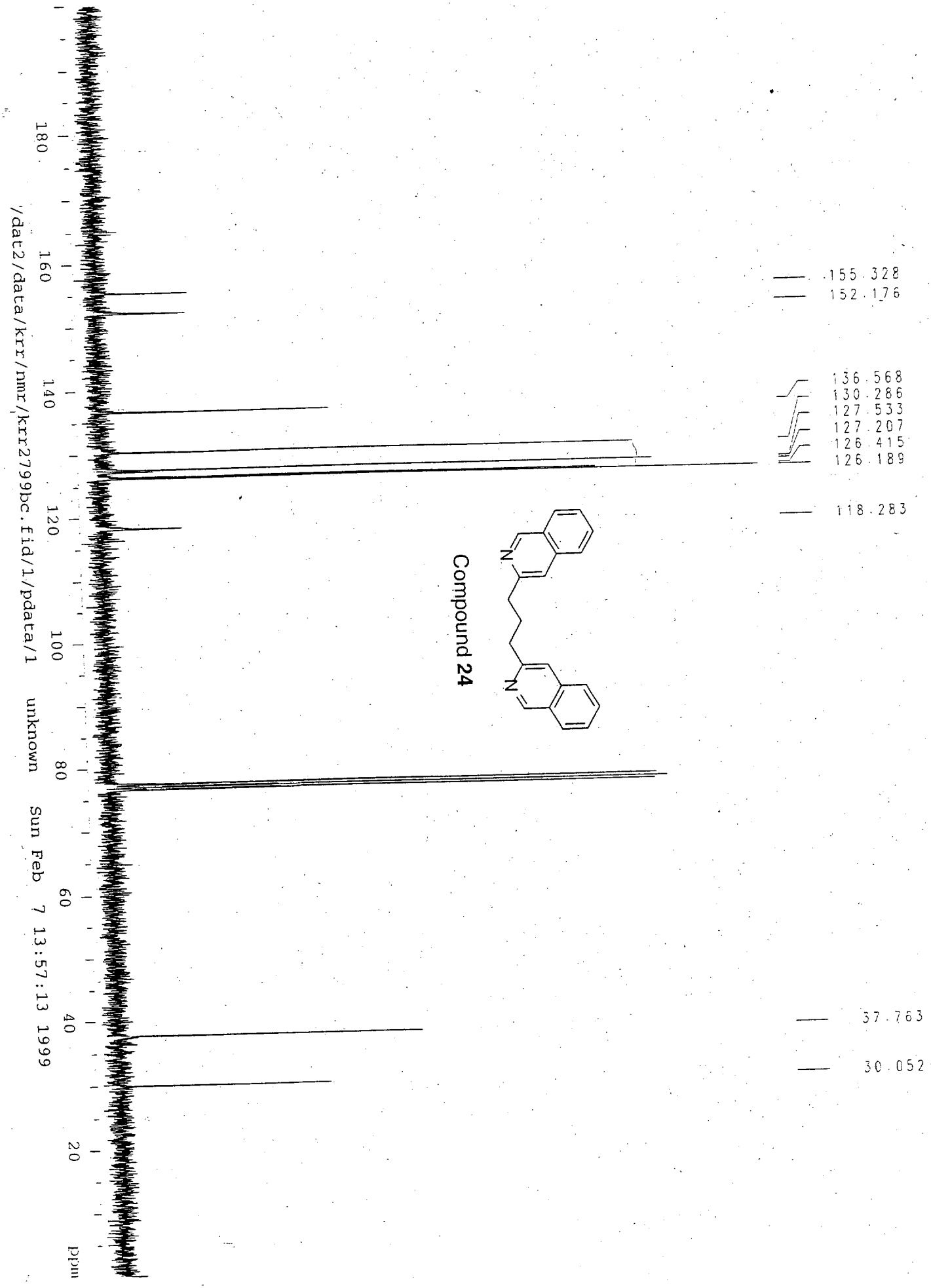
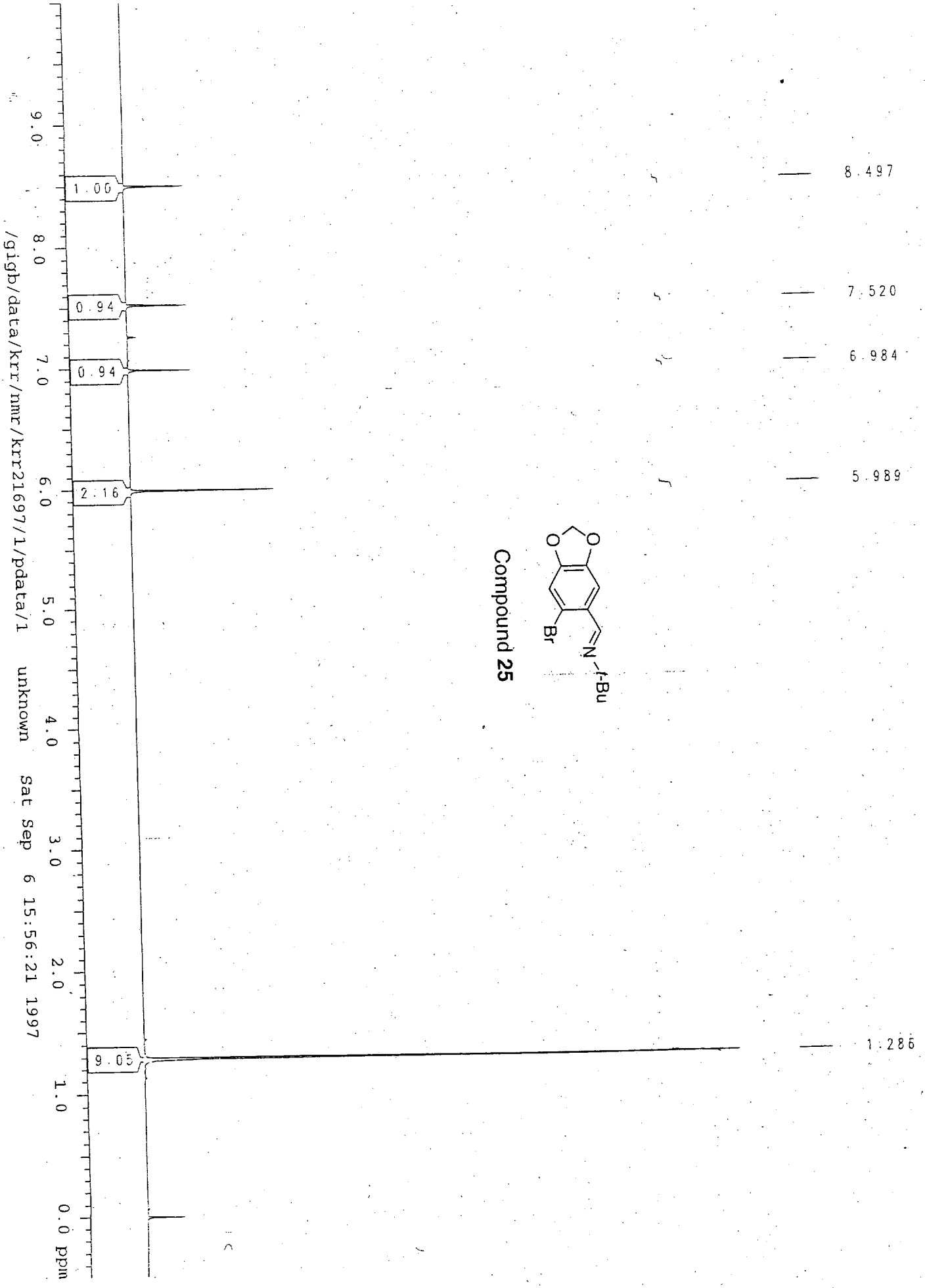
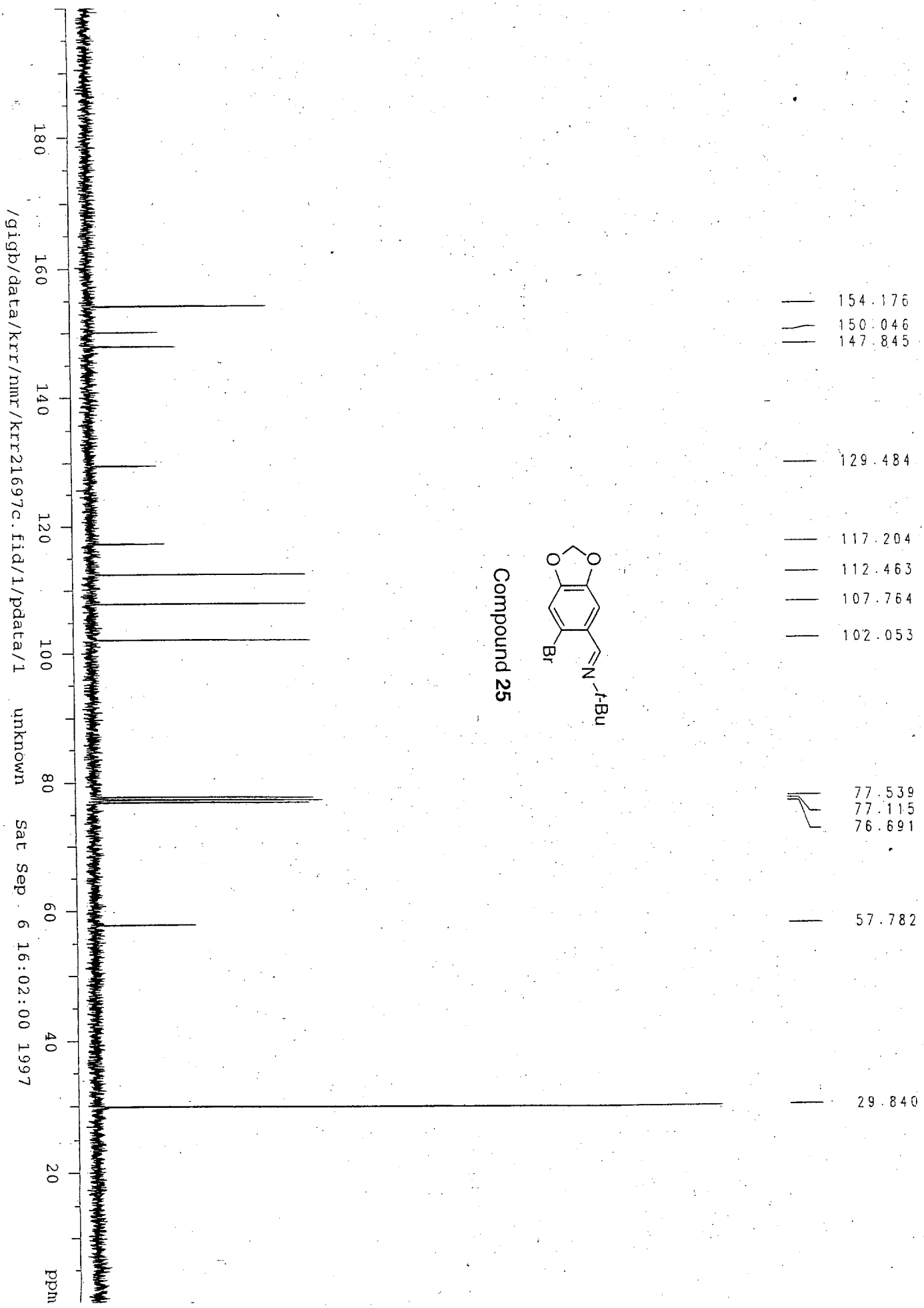
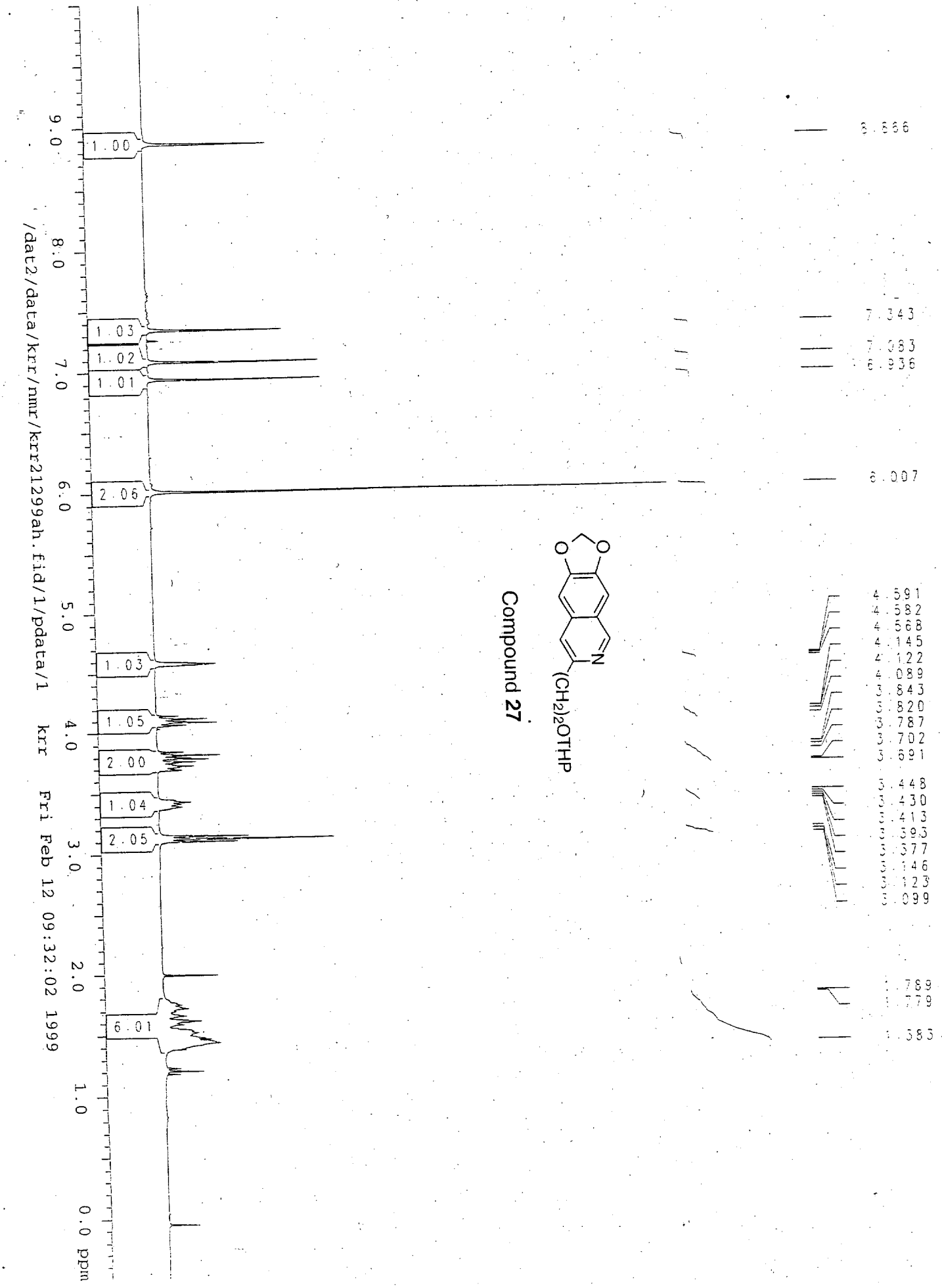
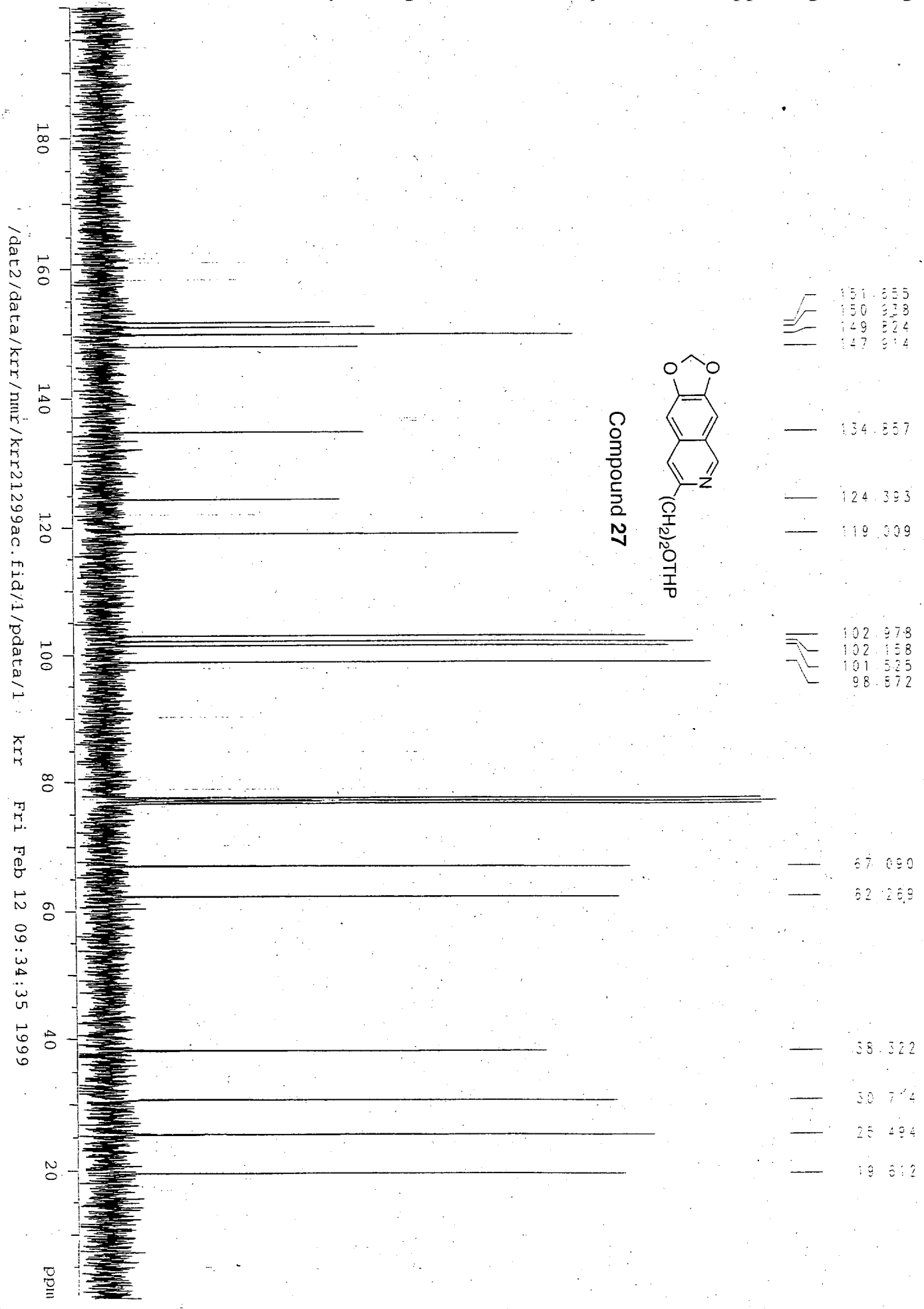
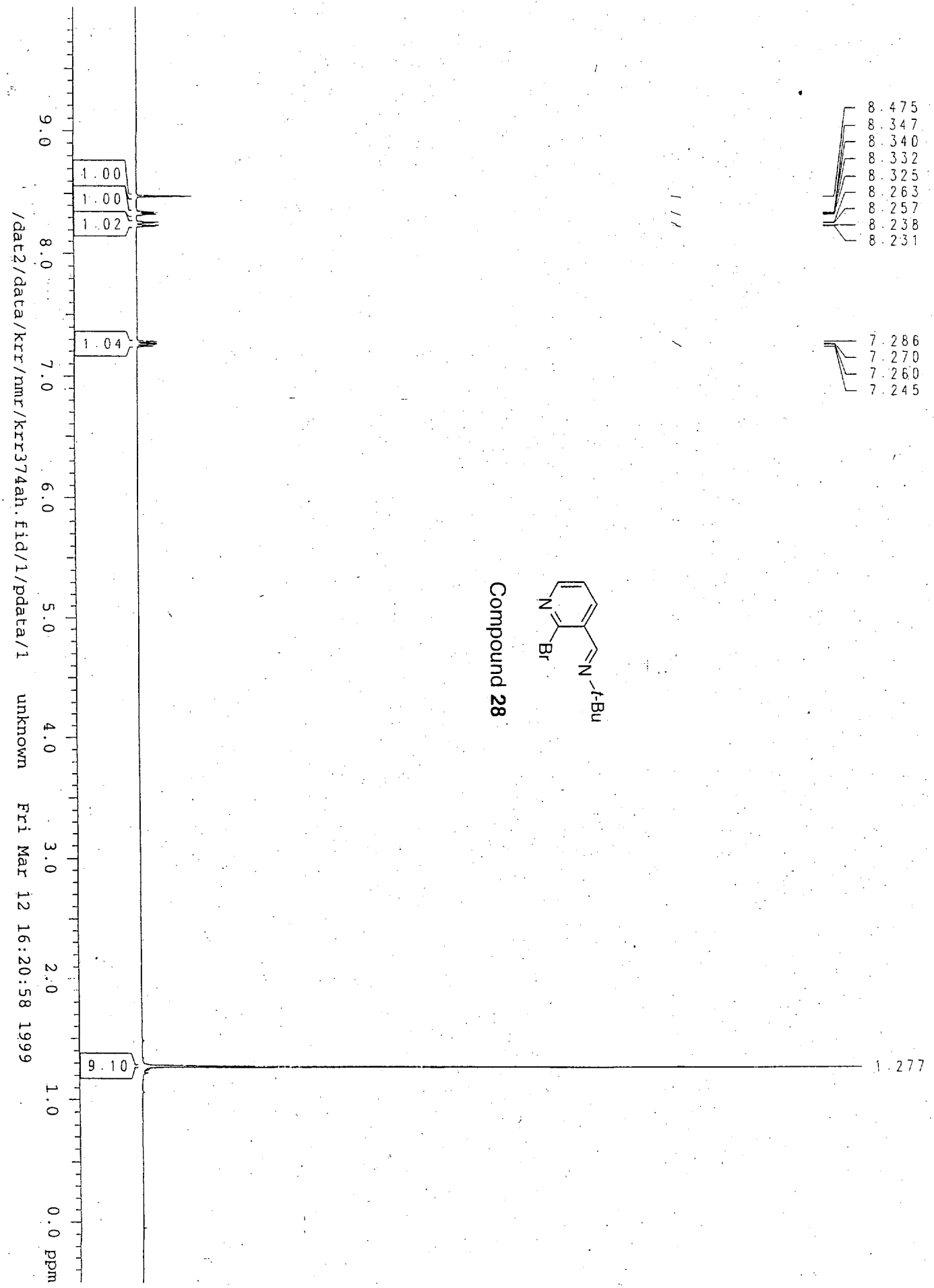




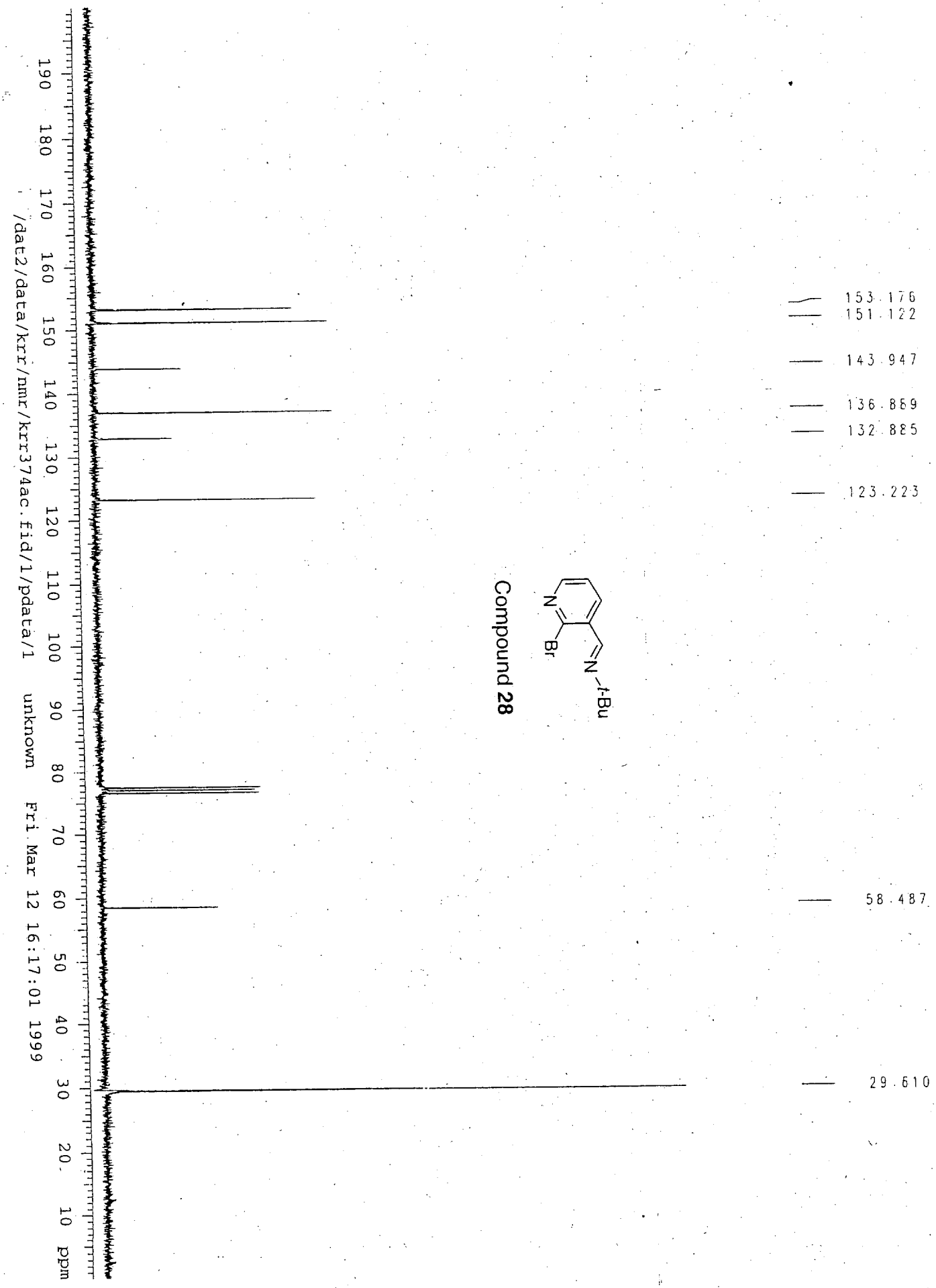








Compound **28**



Compound **28**