Supporting Information for Ytterbium(III) Triflate/TMSCl; Efficient Catalyst for Imino Ene Reaction

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General Experimental.

All reactions were carried out under argon atmosphere. Tetrahydrofuran was distilled from sodium/ benzophenone prior to use. Dichloromethane was distilled from P2O5 and redistilled from CaH2 prior to use. Analytical TLC was performed on Merck DC-Platten Kieselgel 60 GF254 plates. Silica gel column chromatgraphy was carried out with Merck Kieselgel (60 mesh). 1H-NMR spectra were recorded on JNM-GSX 400α (400 MHz). 13C-NMR spectra were recorded on JNM-GSX 400α (100 MHz). IR spectra were obtained with JASCO FT/ IR-230. Mass spectra (MS) were recorded on JEOL HX-100A (LR-FAB, HR-FAB) mass spectrometer. The imines **1a**,[1] **1b**,[2] **1c**,[1] **1d**,[3] and **1e**,[4] were prepared by known methods.

1 Jennings, W. B; Lovely, C. J. *Tetrahedron* **1991**, *47*, 5561-5568.
2 Kupfer, R.; Meier, S.; Wüthwein, E. U. *Synthesis* **1984**, 688-690.
3 Texier-Boullet, F. *Synthesis* **1985**, 679-681.
4 Bigelow, L. A.; Eatough, H. *Org. Synth.* **1941**, I, 80-81.

General Procedure of Imino Ene Reaction

Dichloromethane (4 mL) solution of imine (0.5 mmol) was added to the tetrahydrofuran (1 mL) solution of ytterbium(III) trifluoromethanesulfonate ($Yb(OTf)_3$). Then silyl reagent and a-methylstyrene (1.0 mmol) were added successively. Then the reaction mixture was stirred at room temperature. The reaction was monitored by TLC analysis. After usual work-up, obtained crude residure was purified by column chromatography.

General Procedure of Three-Component Coupling

Benzaldehyde (1.0 mmol) was added to the dichloromethane (8 mL) and tetrahydrofuran (2 mL) solution of ytterbium(III) trifluoromethanesulfonate ($Yb(OTf)_3$) and p-toluenesulfonamide (1.0 mmol). Then silyl reagent and a-methylstyrene (2.0 mmol) were added successively. Then the reaction mixture was stirred at room temperature. The reaction was monitored by TLC analysis. After usual work-up, obtained crude residure was purified by column chromatography.

Chemical yield of Figure 1

with TMSCl : $Sc(OTf)_3$: 88%, $Y(OTf)_3$: 67%, $La(OTf)_3$: 17%, $Ce(OTf)_3$: 21%, $Pr(OTf)_3$: 34%, $Nd(OTf)_3$: 25%, $Sm(OTf)_3$: 26%, $Eu(OTf)_3$: 42%, $Gd(OTf)_3$: 30%, $Tb(OTf)_3$: 34%, $Dy(OTf)_3$: 37%, $Ho(OTf)_3$: 47%, $Er(OTf)_3$: 53%, $Tm(OTf)_3$: 58%, $Yb(OTf)_3$: 93%, $Lu(OTf)_3$: 63%.

Spectral Data

2,4-Diphenyl-4-tosylamino-1-butene (**2a**)

pale yellow oil; IR (neat) 3278, 3031, 2925, 1599, 1495, 1443, 1323, 1158, 1093, 963, 904, 698, 663 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.33 (3H, s), 2.89 (2H, m), 4.23 (1H, dd, J = 7.2, 12.9 Hz), 4.94 (1H, d, J = 1.0 Hz), 5.17 (1H, brs), 5.22 (1H, d, J = 1.2 Hz), 7.02-7.05 (4H, m), 7.13-7.26 (8H, m), 7.44 (2H, d, J = 8.0 Hz); ^{13}C-NMR ($CDCl_3$) d 21.37, 44.05, 56.36, 111.34, 126.07, 126.60, 127.04, 127.35, 127.65, 128.25, 128.37, 129.18, 136.93, 139.26, 140.65, 142.86, 143.70; LRMS (FAB) m/z 376 [5, M^+-H], 260 [100]; HRMS ($C_{23}H_{22}NO_2S$) found 376.1371; calcd 376.1371.

2,4-Diphenyl-4-methoxycarbonylamino-1-butene (**2b**)

colorless oil; IR (neat) 3328, 3030, 1718, 1701, 1543, 1509, 1458, 1363, 1252, 1193, 904, 778, 699 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.95 (2H, d, J = 6.8 Hz), 3.57 (3H, s), 4.72 (1H, brs), 4.94 (1H, brs), 5.00 (1H, d, J = 1.2 Hz), 5.27 (1H, d, J = 1.2 Hz), 7.18-7.37 (10H, m); ^{13}C-NMR ($CDCl_3$) δ 43.23, 51.89, 54.20, 115.59, 126.30, 127.31, 127.69, 128.44, 128.50, 140.49, 142.35, 144.86, 156.24; LRMS (FAB) m/z 282 [7, M^++H], 164 [100]; HRMS ($C_{18}H_{20}NO_2$) found 282.1504; calcd 282.1494.

2,4-Diphenyl-4-diphenylphosphinoylamino-1-butene (**2c**)

white powder; IR (KBr) 3446, 3135, 2918, 1437, 1187, 1125, 1090, 900, 778, 749, 694 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.99 (1H, dd, *J* = 8.2, 14.0 Hz), 3.24 (1H, dd, *J* = 6.3, 13.8 Hz), 3.35 (1H, brs), 4.27 (1H, dd, *J* = 6.5, 8.4 Hz), 4.87 (1H, d, *J* = 0.9 Hz), 5.21 (1H, d, *J* = 1.2 Hz), 7.06 (2H, d, *J* = 6.4 Hz), 7.16-7.75 (18H, m); ^{13}C-NMR ($CDCl_3$) δ 45.51, 54.75, 115.96, 126.22, 126.61, 127.19, 127.51, 128.30, 128.35, 128.40, 128.47, 131.78, 131.86, 131.95, 132.22, 132.31, 140.00, 142.89, 144.37; LRMS (FAB) *m / z* 424 [20, M^++H], 306 [100]; HRMS ($C_{28}H_{27}NOP$) found 424.1817; calcd 424.1830.

2,4-Diphenyl-4-methyl-1,2,3,4-tetrahydroquinoline
(**3**, major diastereomer)

yellow solid; IR (KBr) 3383, 2966, 1602, 1495, 1474, 1345, 1311, 1256, 1113, 1028, 752, 702 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.82 (3H, s), 1.95 (1H, dd, *J* = 2.7, 13.4 Hz), 2.26 (1H, dd, *J* = 12.7, 12.7 Hz), 4.60 (1H, dd, *J* = 2.7, 12.0 Hz), 6.58 (1H, d, *J* = 8.5 Hz), 7.00 (1H, ddd, *J* = 1.6, 7.5, 7.6 hz), 7.14-7.37 (10H, m), 7.44 (2H, d, *J* = 7.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 29.73, 42.28, 48.30, 54.01, 114.50, 117.63, 125.82, 126.66, 126.86, 127.20, 127.32, 127.48, 127.63, 127.96, 128.58, 143.94, 144.73, 150.19; LRMS (FAB) *m / z* 299 [100, M^+]; HRMS ($C_{22}H_{21}N$) found 299.1659; calcd 299.1674.

2,4-Diphenyl-4-methyl-1,2,3,4-tetrahydroquinoline
(**3**, minor diastereomer)

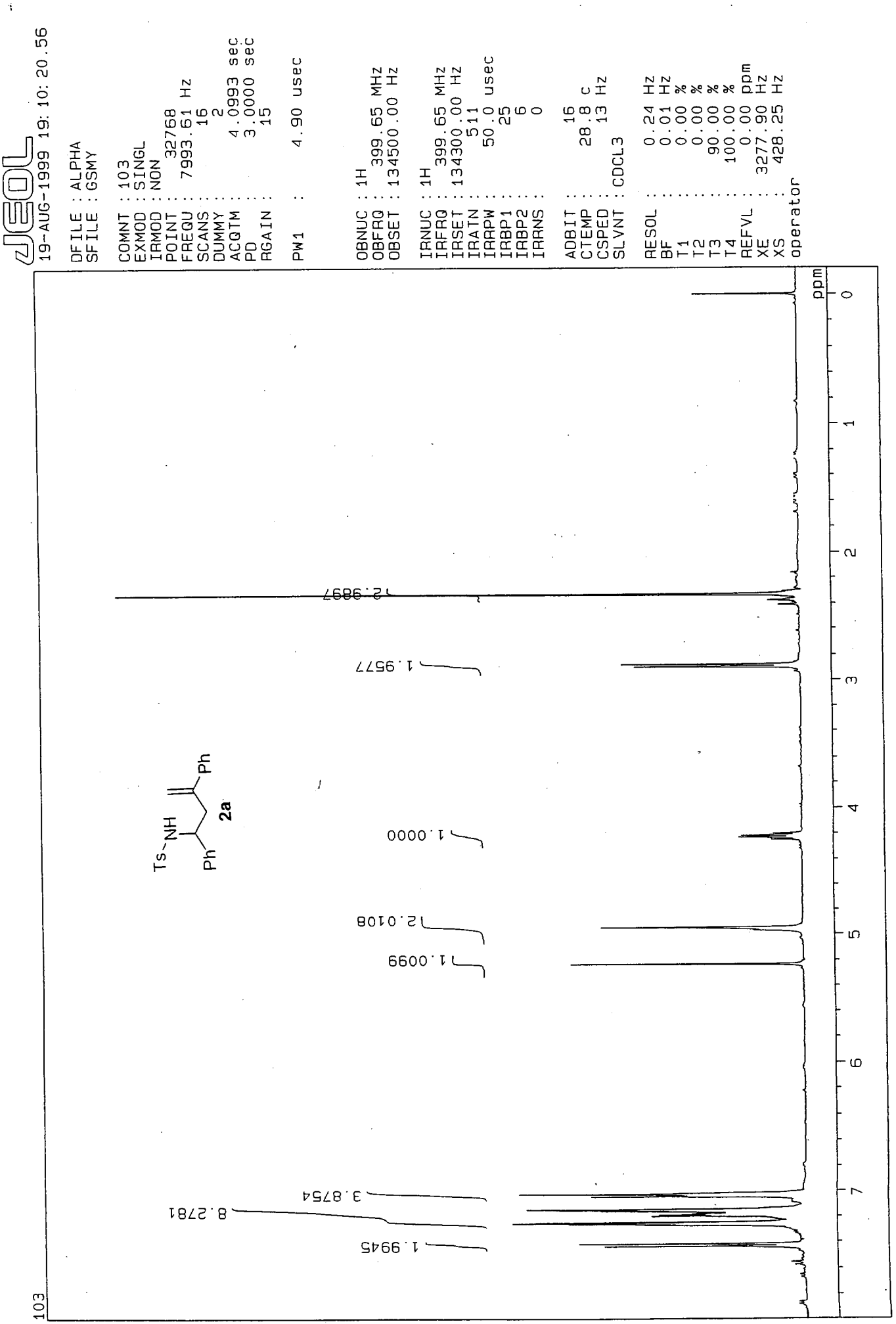
yellow solid; IR (KBr) 3385, 2958, 1602, 1482, 1444, 1338, 1312, 1259, 1119, 1030, 770, 751, 702 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.75 (3H, s), 2.14 (1H, dd, *J* = 11.7, 13.1 Hz), 2.26 (1H, dd, *J* = 3.1, 13.1 Hz), 4.01 (1H, dd, *J* = 2.9, 11.7 Hz), 6.60 (1H, dd, *J* = 1.2, 8.5 Hz), 6.75 (1H, ddd, *J* = 1.2, 7.6, 7.6 Hz), 7.09-7.13 (3H, m), 7.16-7.32 (9H, m); ^{13}C-NMR ($CDCl_3$) δ 29.62, 41.57, 47.93, 53.12, 114.19, 117.25, 125.77, 126.40, 126.63, 127.08, 127.53, 127.55, 128.16, 128.24, 128.53, 144.27, 144.56, 150.41; LRMS (FAB) *m / z* 299 [100, M^+]; HRMS ($C_{22}H_{21}N$) found 299.1672; calcd 299.1674.

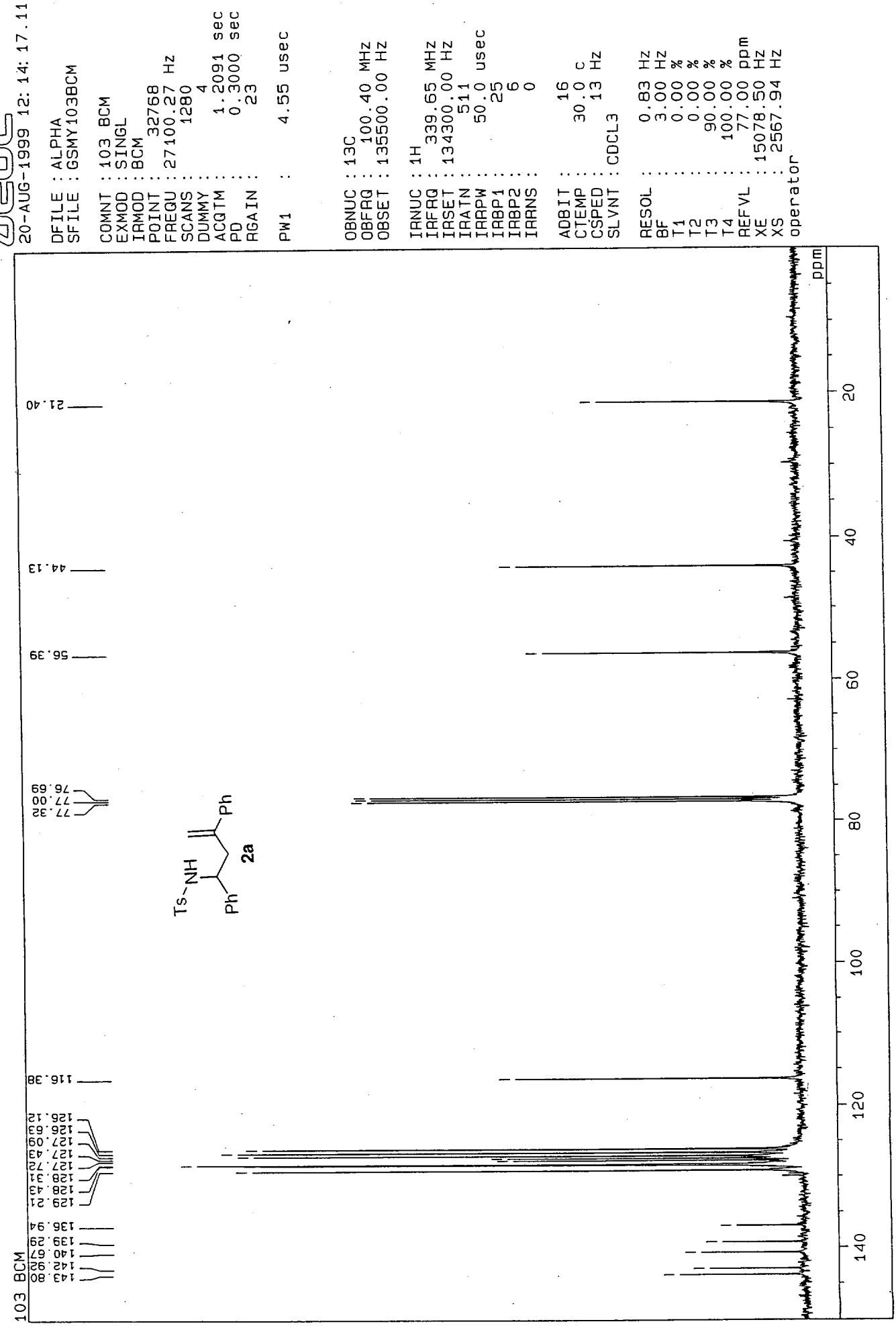
2-Phenyl-4-tosylamino-1-pentene (**4**)

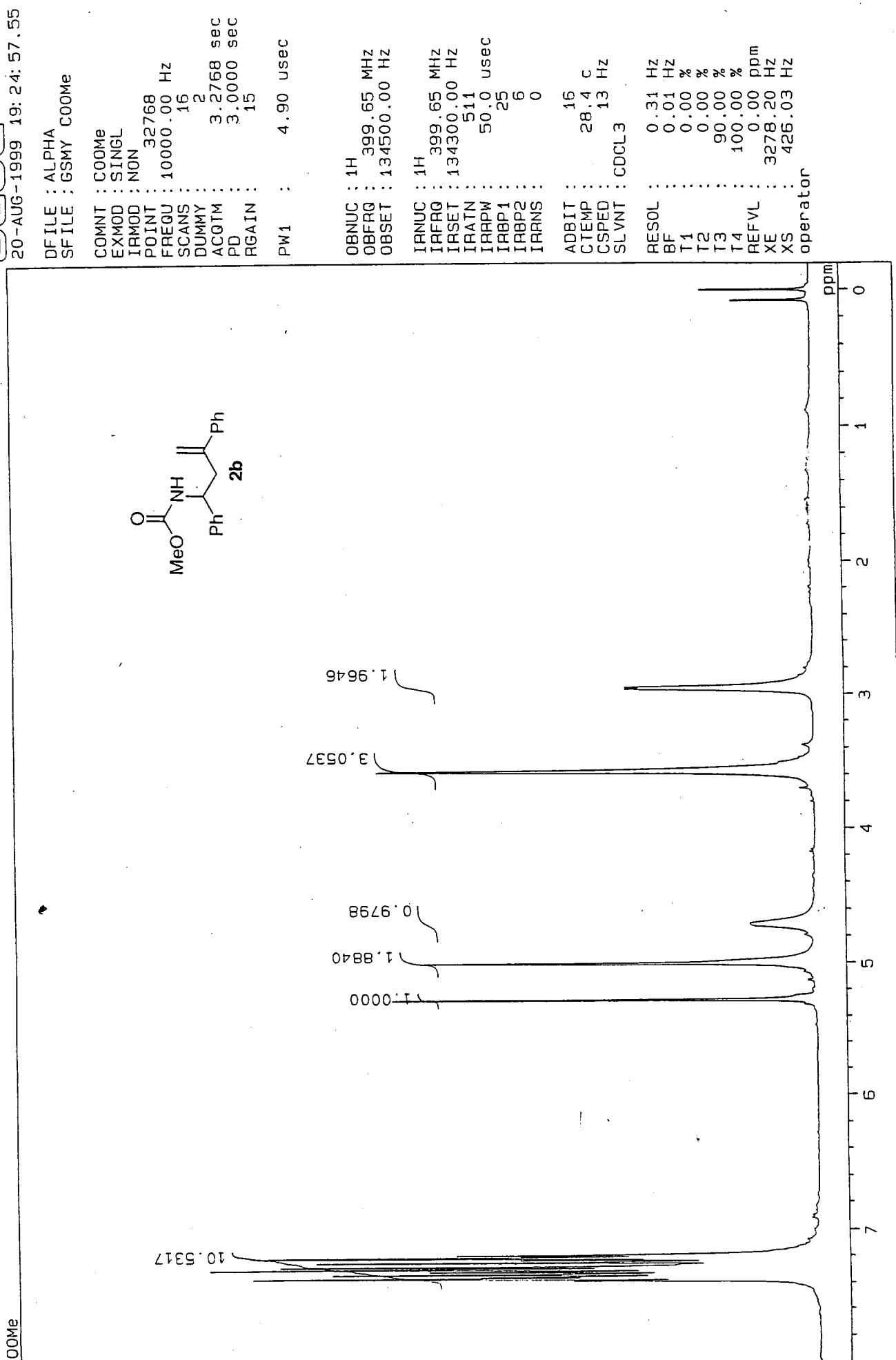
IR (neat) 3278, 2973, 2929, 1599, 1495, 1426, 1323, 1161, 1092, 991, 906, 815, 758, 706, 664 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98 (3H, d, J = 6.6 Hz), 2.31 (3H, s), 2.40 (1H, dd, J = 7.7, 14.1 Hz), 2.65 (1H, dd, J = 6.4, 13.4 Hz), 3.18 (1H, ddq, J = 6.6, 6.7, 7.0 Hz), 4.66 (1H, brs), 4.95 (1H, s), 5.20 (1H, s), 7.08-7.17 (7H, m), 7.56-7.58 (2H, m); ^{13}C NMR ($CDCl_3$) δ 21.21, 21.43, 43.44, 48.08, 115.73, 125.98, 127.03, 127.61, 128.33, 129.48, 137.47, 139.39, 143.06, 144.33; LRMS (FAB) m/z 315 [40, M^+], 198 [100]; HRMS ($C_{18}H_{21}NO_2S$) found 315.1301; calcd 315.1293.

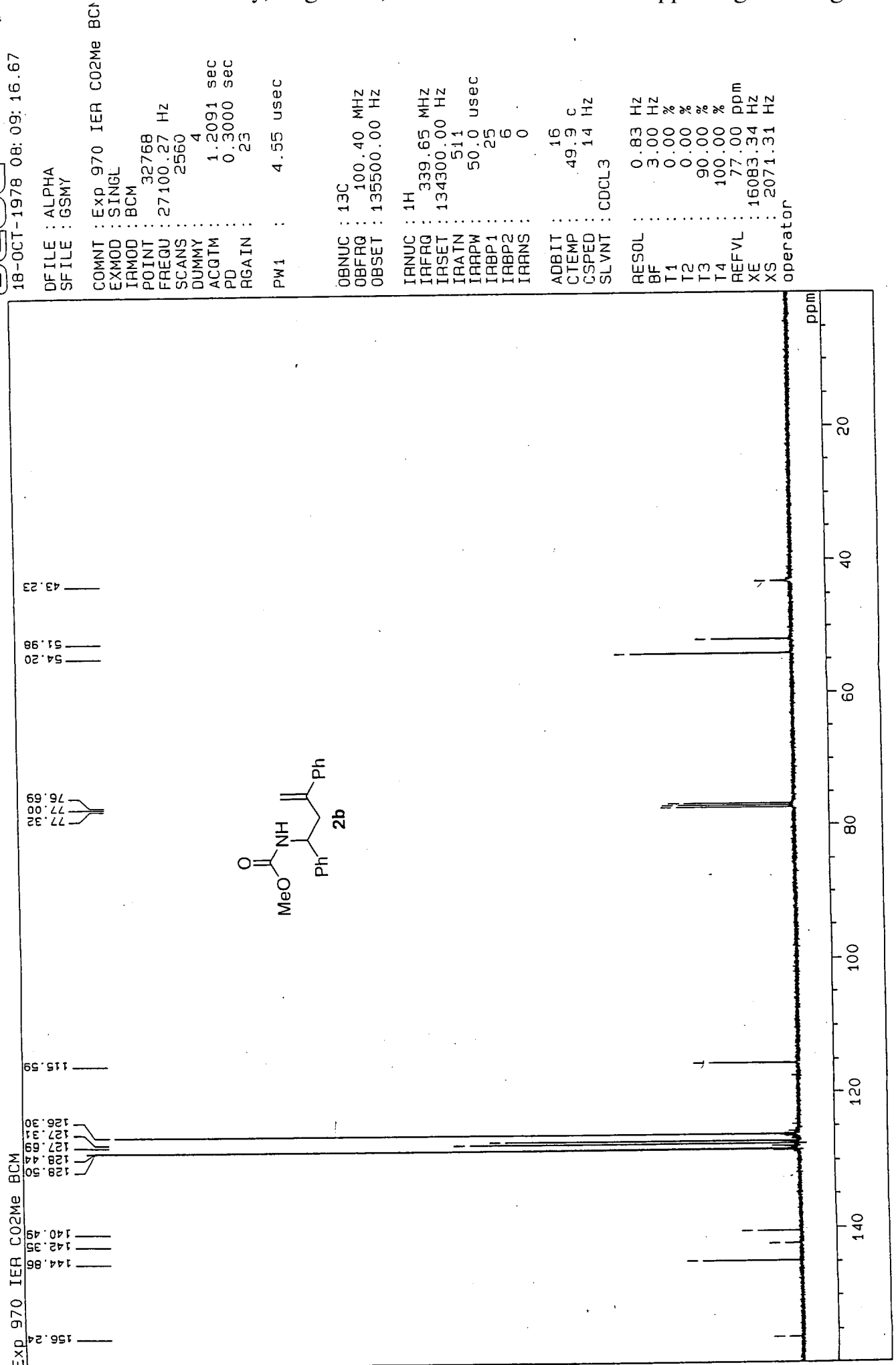
2-Phenyl-4-tosylamino-5-methyl-1-hexene (**5**)

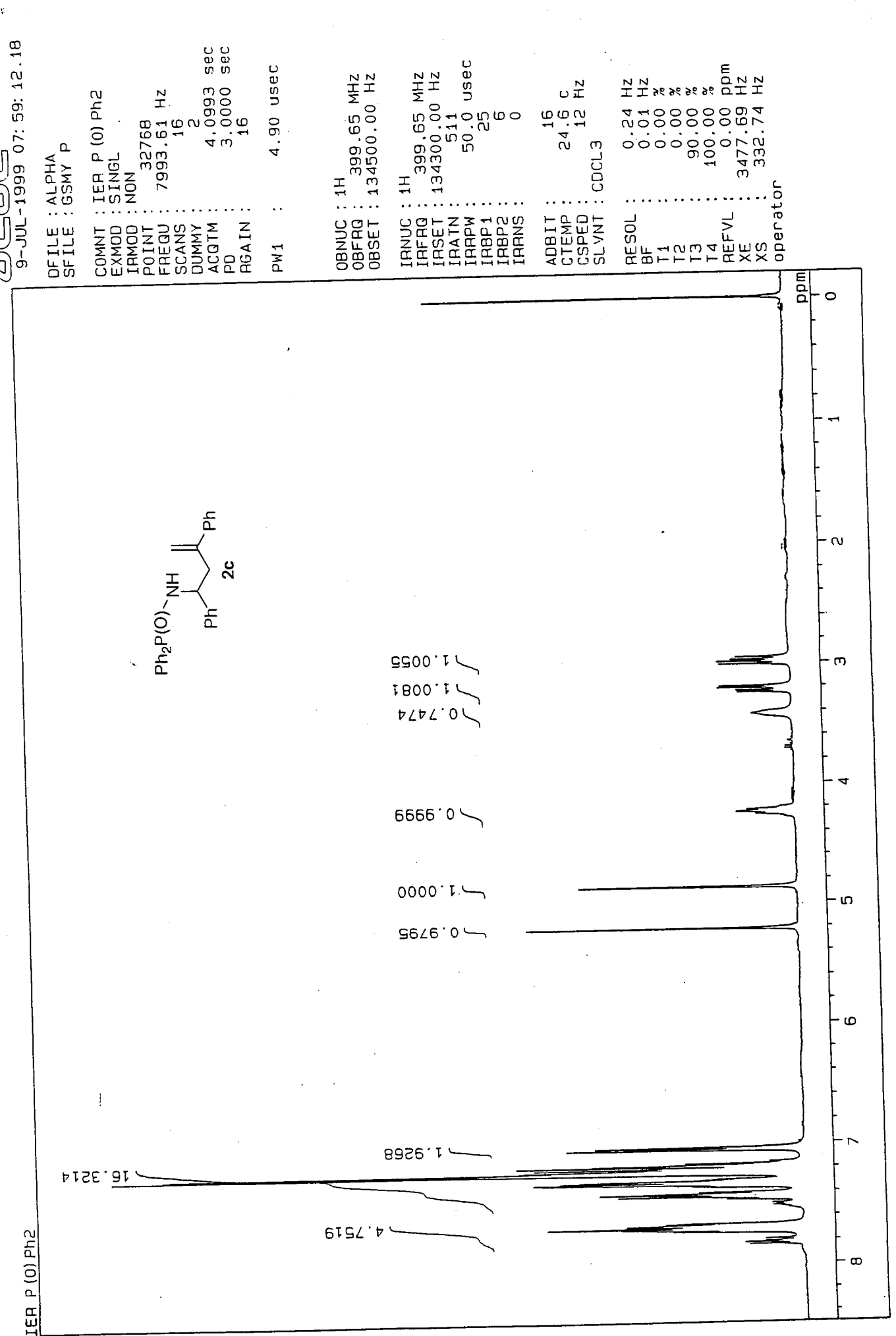
colorless solid, mp. 104-105 ℃ (acetone/*n*-hexane); IR (KBr) 3290, 2952, 1629, 1602, 1464, 1420, 1319, 1162, 1095, 1056, 956, 906, 812, 783, 715, 666 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.72 (3H, d, J = 6.8 Hz), 0.82 (3H, d, J = 6.8 Hz), 1.86 (1H, m), 2.40, (3H, s), 2.54 (1H, ddd, J = 1.0, 7.1, 14.4 Hz), 2.60 (1H, ddd, J = 1.0, 7.9, 14.4 Hz), 3.10 (1H, dddd, J = 3.4, 7.4, 7.4, 7.4 Hz), 4.57 (1H, d, J = 7.6 Hz), 5.01 (1H, d, J = 1.2 Hz), 5.22 (1H, d, J = 1.5 Hz), 7.11-7.27 (7H, m), 7.64 (2H, d, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 16.29, 18.30, 21.47, 29.53, 37.77, 56.76, 115.59, 126.07, 127.21, 127.61, 128.29, 129.41, 137.65, 139.44, 143.01, 144.64; LRMS (FAB) m/z 343 [35, M^+], 226 [100]; HRMS ($C_{20}H_{25}NO_2S$) found 343.1606; calcd 343.1606.

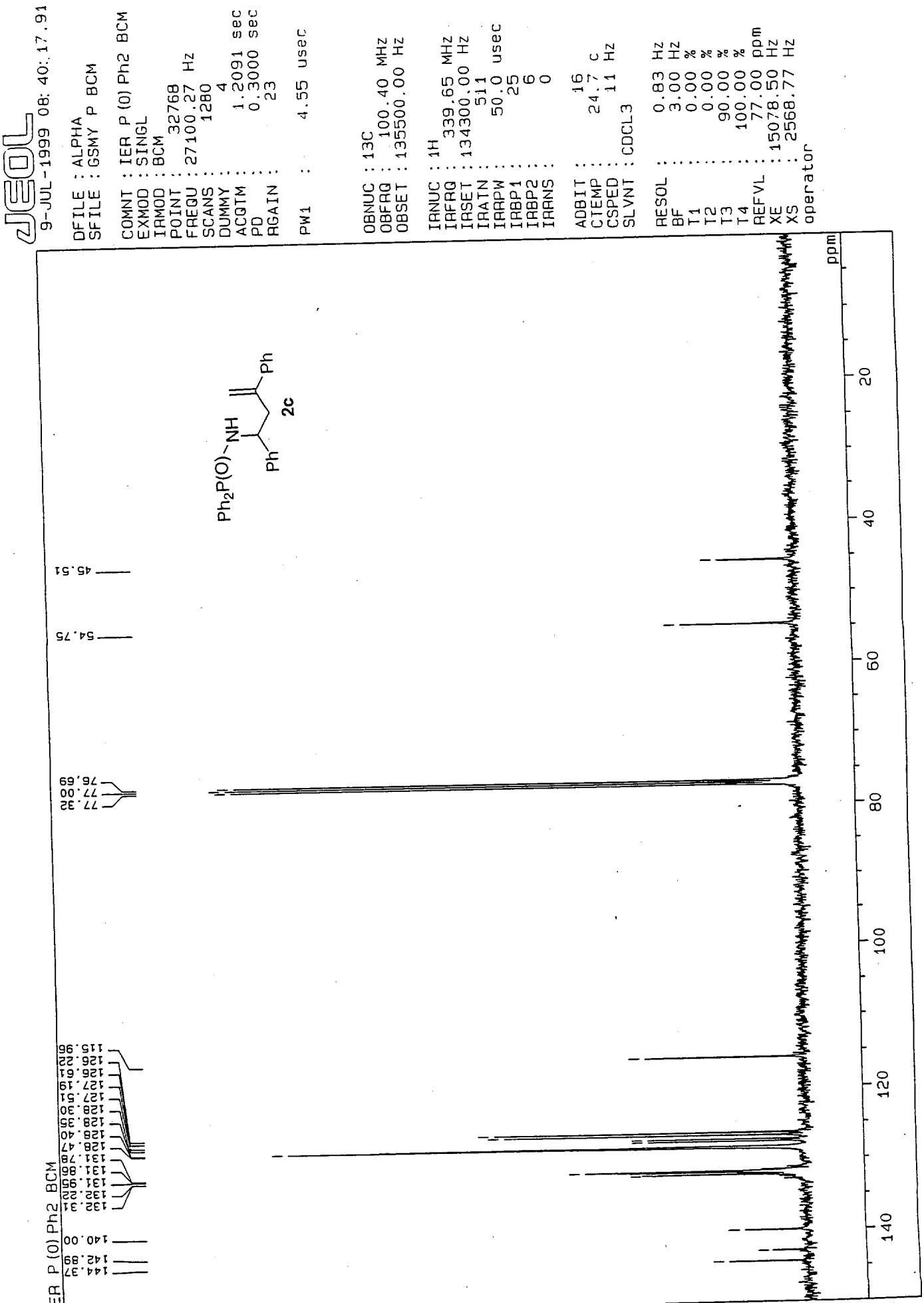


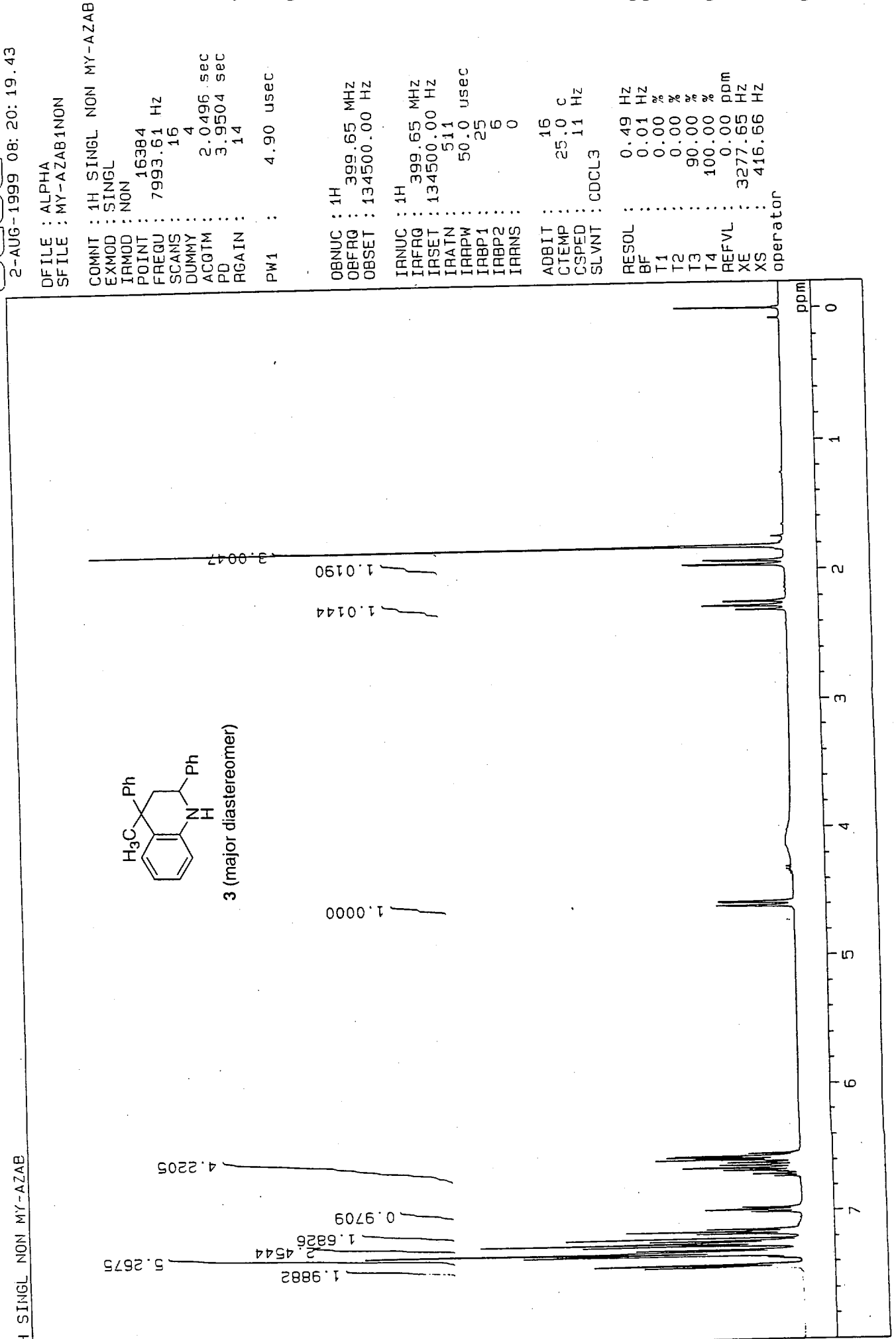


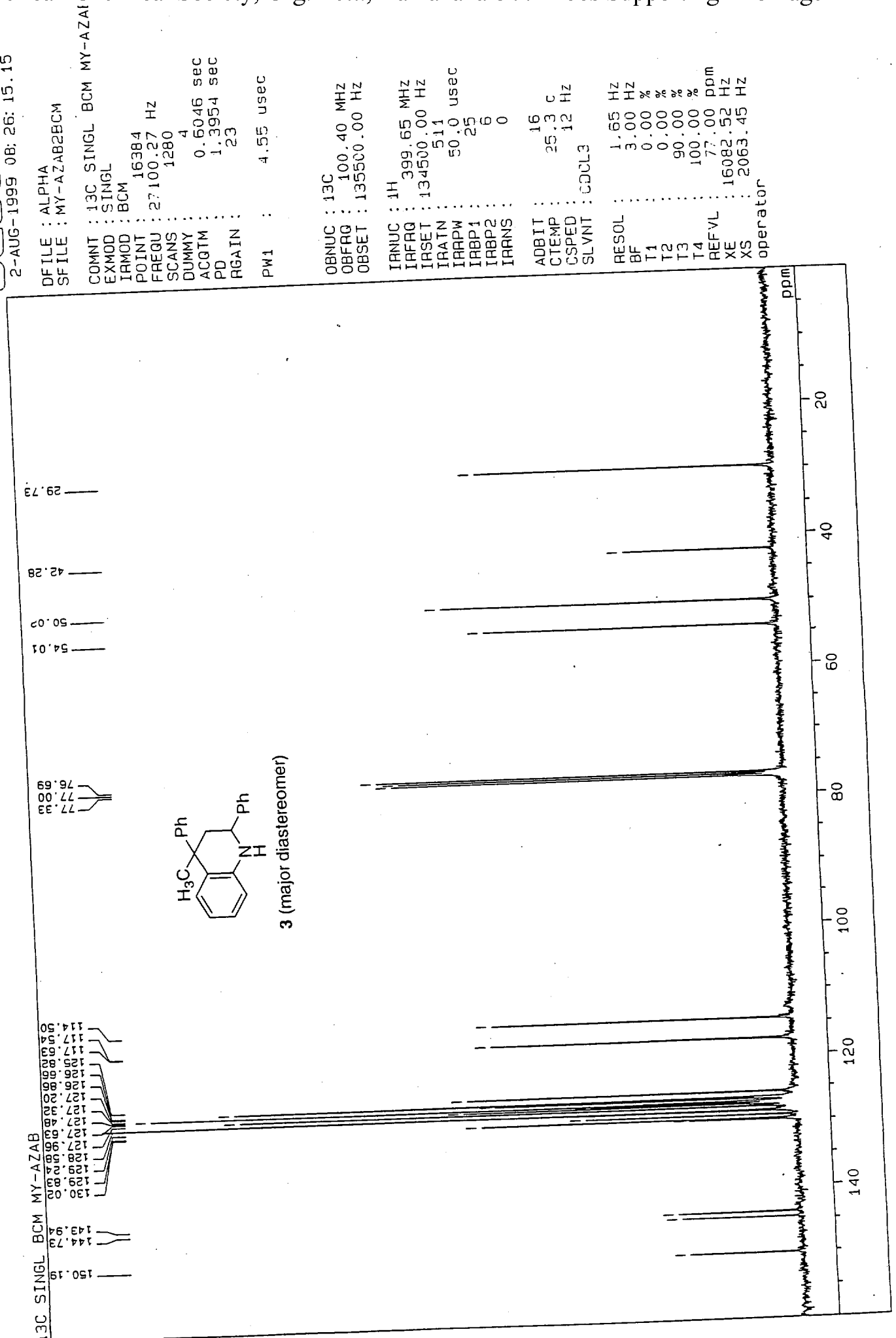


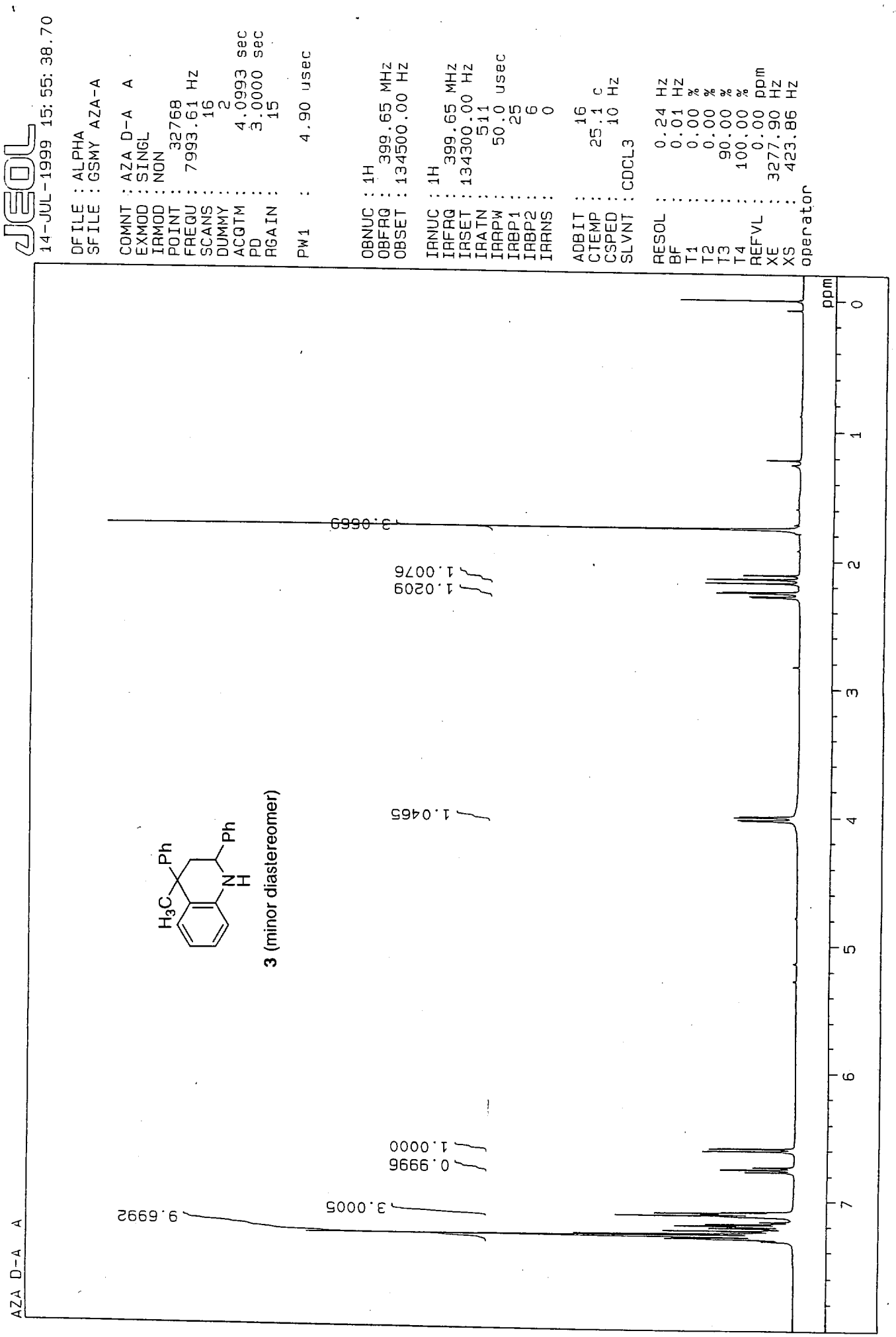


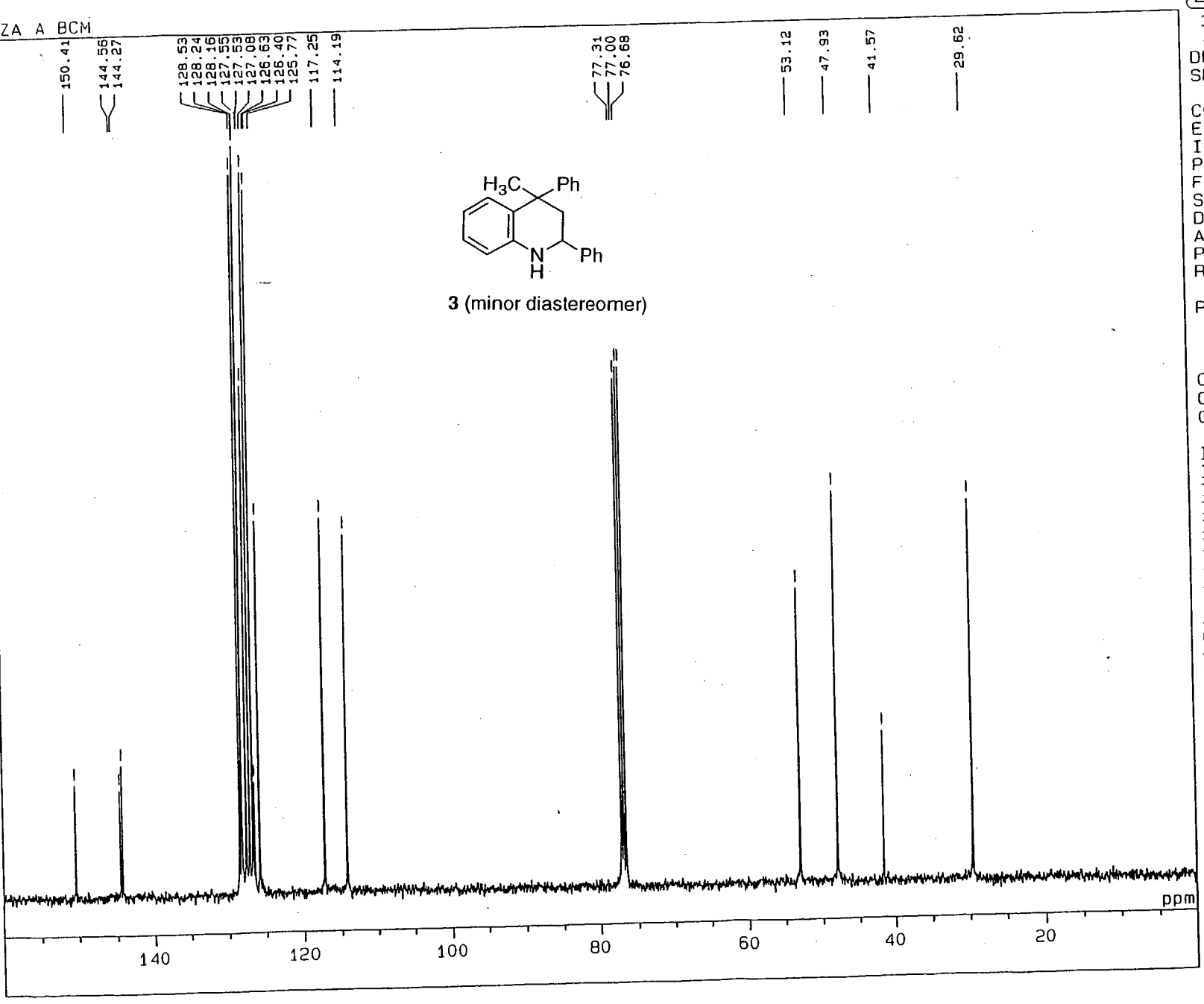












3 (minor diastereomer)

JEOL

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SLVNT : CDCL3

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operator
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