Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Palladium-catalyzed aerobic oxidative C–H amination: synthesis of 2-unsubstituted and 2-substituted *N*-aryl benzimidazoles

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General information: Anilines, $Pd(PPh_3)_2Cl_2$ (98%), $Pd(PPh_3)_2(OAc)_2$ (98%), $Pd(CH_3CN)_2Cl_2$ (98%), $Pd(PhCN)_2Cl_2$ (98%), Cs_2CO_3 (99%), Ag_2CO_3 (99%), KO^tBu (95%) and K_3PO_4 (98%) were purchased from Aldrich and were used as received. Triethylorthoformate (98%) and triethylorthoacetate (97%) were purchased from Avra synthesis. K_2CO_3 (99.9%) was procured from Central Drug House (P) LTD. Purification of the reaction products was carried out by column chromatography using Rankem silica gel (60-120/230-400 mesh). Analytical TLC was performed on Merck silica gel G/GF 254 plate. NMR spectra were recorded on DRX-400 Varian spectrometer using $CDCl_3$ as solvent and Me_4Si as internal standard. Chemical shifts (δ) are reported in ppm and spin-spin coupling constants (J) are given in Hz. Melting points were determined using Buchi B-540 melting point apparatus and are uncorrected. FT-IR spectra were recorded using Perkin Elmer IR spectrometer. Elemental analysis were recorded using Perkin Elmer CHNS analyzer. Mass spectra were recorded on a Waters Q-Tof Premier mass spectrometer. X-Ray data were collected on a Bruker SMART APEX equipped with a CCD area detector using Mo/Kα radiation. The structures were solved by direct method using *SHELLX-97* (Göttingen, Germany).

General procedure for synthesis of symmetrical *N,N′*-bis(aryl)formamidines 1a-g.[1] An oven dried round bottom flask (50 mL) was charged with triethylorthoformate (2.22 g, 15.0 mmol, 1.0 equiv), corresponding aniline (30.0 mmol, 2.0 equiv) and glacial acetic acid (45.0 mg, 0.75 mmol, 0.05 equiv). The resulting mixture was stirred for 10 h at 140 °C and allowed to cool to rt. The resulting white solid was triturated with cold hexane (30 mL), collected by vaccum filteration and dried *in vacuo* to give the symmetrical *N,N′*-bis(aryl)formamidines **1a-g** (80-90%) as a white solid.

General procedure for synthesis of unsymmetrical *N,N′*-bis(aryl)formamidine 1h.[1] An oven dried round bottom flask (50 mL) was charged with 3,5-dimethylaniline (913.5 mg, 7.5 mmol, 1 equiv), triethylorthoformate (1.11 g, 7.5 mmol, 1 equiv) and glacial acetic acid (22.5 mg, 0.375 mmol, 0.05 equiv). The resulting mixture was stirred for 5 h at 140 °C, then cooled to rt. 4-Methylaniline (803.7 mg, 7.5 mmol, 1.0 equiv) was then added to the reaction mixture and the resulting mixture was stirred for 10 h at 140 °C and allowed to cool to rt. The resulting white solid was triturated with cold hexane (30 mL), collected by vaccum filteration and dried *in vacuo* to provide unsymmetrical *N,N′*-bis(aryl)formamidine **1h** (700 mg, 39.2%) as a white solid.

General procedure for synthesis of symmetrical *N,N′*-bis(aryl)acetamidines 1i-n.[2] An oven dried round bottom flask (50 mL) was charged with triethylorthoacetate (2.43 g, 15.0 mmol, 1.0 equiv), corresponding aniline (30.0 mmol, 2.0 equiv) and glacial acetic acid (45.0 mg, 0.75 mmol, 0.05 equiv). The resulting mixture was stirred for 10 h at 140 °C and allowed to cool to rt. The resulting brown viscous oil was scratched in ice cold hexane and the resulting white solid was triturated with cold hexane (30 mL), collected by vaccum filteration and dried *in vacuo* to give the symmetrical *N,N′*-bis(aryl)acetamidines **1i-n** (70-80%) as a white solid.

General procedure for synthesis of *N,N′*-bis(aryl)benzamidines 1o-p.[4] An oven dried two neck round bottom flask (25 mL) was charged with 4-nitroaniline (345.0 mg, 2.49 mmol, 1.0 equiv) and corresponding benzamide (2.74 mmol, 1.1 equiv) under nitrogen atmosphere. Toluene (5 mL), triethylamine (381.0 µl, 2.74 mmol, 1.1 equiv) and $POCl_3$ (342.9 µl, 3.67 mmol, 1.5 equiv) were added and the resulting mixture was stirred for 5 h at 120 °C and allowed to cool to rt. Toluene was evaporaped *in vacuo* and saturated $NaHCO_3$ (10 mL) was added. The resulting yellow viscous oil was extraced with ethyl acetate (3 x 20 mL), dried over Na_2SO_4 and evaporated *in vacuo*. The residue was purified by silica gel column chromatography (60-120 mesh) using n-hexane and ethyl acetate (1:9) as eluent to afford *N,N′*-bis(aryl)benzamidines **1o-p** (50-60%) as a yellow solid.

General procedure for Pd-catalyzed synthesis of *N*-aryl benzimidazoles. Bis(aryl)amidines **1a-p** (0.5 mmol), $Pd(PPh_3)_2Cl_2$ (35.0 mg, 0.05 mmol), Cs_2CO_3 (325.8 mg, 1.0 mmol) and freshly activated 4Å molecular sieves (50 mg) were stirred at 120 ^oC in DMSO (1 mL) under oxygen balloon. The progress of the reaction was monitored by TLC using ethyl acetate and hexane as eluent. After the appropriate time, the reaction mixture was cooled to room temperature and water (5 mL) was added. The resulting solution was extracted with ethyl acetate (3 x 10 mL) and washed sucessively with brine (2 x 5 mL) and water (2 x 5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and ethyl acetate as eluent to afford analytically pure *N*-aryl benzimidazoles.

Single crystal X-ray structure of 2n

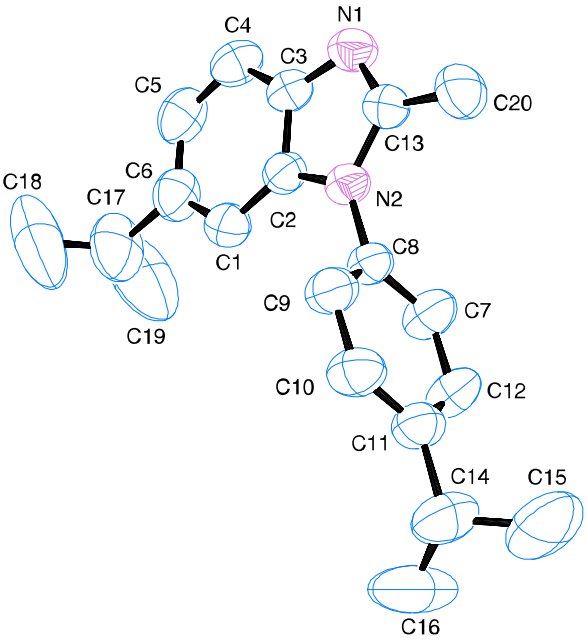


Figure 1. ORTEP diagram of the single-crystal X-ray structure of 6-Isopropyl-1-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole **2n.** H-Atoms are omitted for clarity (CCDC 863007).

Crystal data and structure refinement for 2n at 296(2) K

Identification code	2n
Empirical formula	$C_{20}H_{24}N_2$
Formula weight	292.41
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic

Space group	*P-1* Loop xyz 'x, y, z' '-x, -y, -z'
Unit cell dimensions	*a* = 8.8353(18) Å α(°)=106.121(18) *b* = 10.145(2) Å β(°)=109.391(19) *c* = 11.616(4) Å γ(°)=101.989(13)
Volume	890.3(5) $Å^3$
Z	2
Density (calculated)	1.091Mg/m^3
Absorption coefficient	0.064mm^{-1}
F(000)	316
Crystal size	0.46x 0.34 x 0.22 mm
Theta range for data collection	2.01 to 24.31 °
Index ranges	-10<=h<=10, -11<=k<=11, -13<=l<=13
Reflections collected	2900
Independent reflections	2049
Completeness to theta = 24.31°	100.0 %
Absorption correction	Multi-scan
Max. and min. transmission	0.986 and 0.974
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2900 / 0 /204
Goodness-of-fit on F^2	1.076
Final R indices [I>2sigma (I)]	*R1* = 0.0576, *wR2* = 0.1729
R indices (all data)	*R1* = 0.0767, *wR2* = 0.1902

Single crystal X-ray structure of 2p

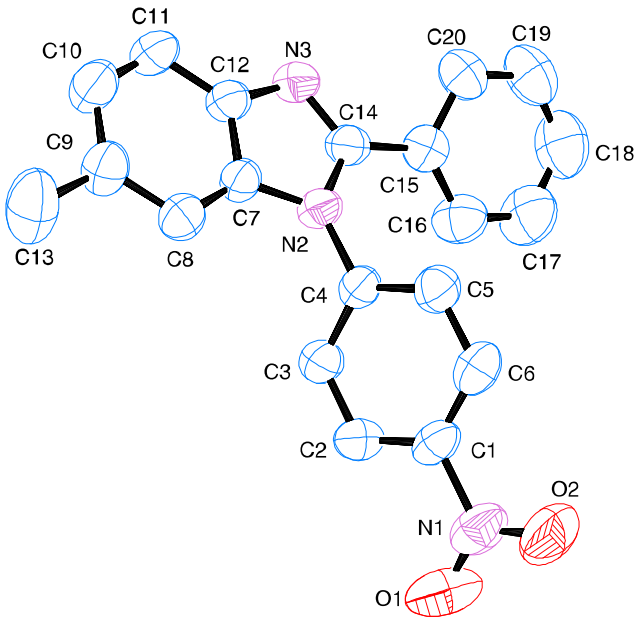
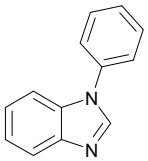


Figure 2. ORTEP diagram of the single-crystal X-ray structure of 6-Methyl-1-(4-nitrophenyl)-2-phenyl-1*H*-benzo[*d*]imidazole **2p.** H-Atoms are omitted for clarity (CCDC 863008).

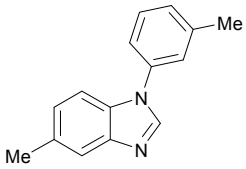
Crystal data and structure refinement for 2p at 296(2) K

Identification code	2p
Empirical formula	$C_{20}H_{15}N_3O_2$
Formula weight	329.35
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	*P-1*
	Loop xyz
	'x, y, z' '-x, -y, -z'
Unit cell dimensions	*a* = 8.2036(6) Å α(°)= 76.796(5)
	b = 10.3079(8) Å β(°)= 78.813(5)
	c = 10.9919(9) Å γ(°)= 70.229(5)
Volume	844.64(12) $Å^3$
Z	2
Density (calculated)	1.295 Mg/m^3
Absorption coefficient	0.086 mm^{-1}
F(000)	344.0
Crystal size	0.36x 0.24 x 0.18 mm
Theta range for data collection	1.92 to 25.25 °
Index ranges	-9<=h<=9, -12<=k<=12, -13<=l<=13
Reflections collected	3053
Independent reflections	1869
Completeness to theta = 25.25°	100.0 %
Absorption correction	Multi-scan
Max. and min. transmission	0.976 and 0.985
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3053 / 0 /227
Goodness-of-fit on F^2	1.066
Final R indices [I>2sigma (I)]	*R1* = 0.0502, *wR2* = 0.1387
R indices (all data)	*R1* = 0.0873, *wR2* = 0.1784

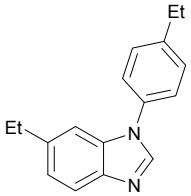
Characterization data of *N*-aryl benzimidazoles 2a-p



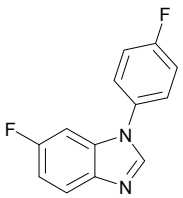
1-Phenyl-1*H*-benzo[*d*]imidazole 2a.[4] Analytical TLC on silica gel, R_f = 0.20 (3:7 ethyl acetate/hexane); yellow liquid; yield: 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11(s, 1H), 7.87-7.85 (m, 1H), 7.58-7.43 (m, 6H), 7.36-7.29 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.7, 142.3, 136.2, 133.7, 130.1, 128.2, 124.6, 124.1, 123.0, 120.3, 110.6 ppm; FT-IR (neat) v = 3065, 2927, 2846, 1599, 1503, 1454, 1382, 1319, 1286, 1248, 1231, 1201, 1028 cm^{-1}; Elemental analysis calcd (%) for $C_{13}H_{10}N_2$: C 80.39, H 5.19, N 14.42, found: C 80.29, H 5.21, N 14.50.



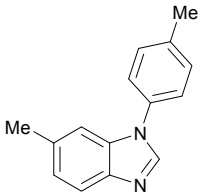
5-Methyl-1-(3-methylphenyl)-1*H*-benzo[*d*]imidazole 2c. Analytical TLC on silica gel, R_f = 0.30 (3:7 ethyl acetate/hexane) brown liquid; yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (s, 1H), 7.63 (s, 1H), 7.41(d, J = 8.4 Hz, 1H), 7.29-7.23 (m, 4H), 7.14 (d, J = 8.0 Hz, 1H), 2.48 (s, 3H), 2.44 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.5, 142.4, 140.4, 136.6, 132.6, 131.9, 129.9, 128.8, 125.3, 124.6, 121.0, 120.4, 110.2, 21.6 ppm; FT-IR (neat) ν = 2967, 2922, 2857, 1610, 1497, 1264, 1218, 1196, 1091, 850, 786, 739, 697 cm^{-1}; Elemental analysis calcd (%) for $C_{15}H_{14}N_2$: C 81.05, H 6.35, N 12.60, found: C 80.93, H 6.37, N 12.70.



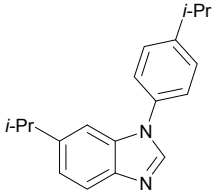
6-Ethyl-1-(4-ethylphenyl)-1*H*-benzo[*d*]imidazole 2d. Analytical TLC on silica gel, R_f = 0.30 (3:7 ethyl acetate/hexane); yellow liquid; yield: 66%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (s, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.39 (s, 4H), 7.30 (s, 1H), 7.18 (d, J = 8.4 Hz, 1H), 2.78-2.71 (m, 4H), 1.32-1.23 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.5, 142.4, 142.2, 140.5, 134.3, 129.5, 124.3, 123.4, 120.3, 109.3, 29.5, 28.7, 16.4, 15.6 ppm; FT-IR (neat) ν = 2964, 2928, 2862, 1615, 1518, 1283, 1264, 1229, 1015, 836, 738 cm^{-1}; Elemental analysis calcd (%) for $C_{17}H_{18}N_2$: C 81.56, H 7.25, N 11.19, found: C 81.45, H 7.26, N 11.29.



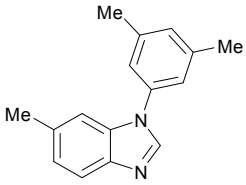
6-Fluoro-1-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole 2e. Analytical TLC on silica gel, R_f = 0.40 (3:7 ethyl acetate/hexane); yellow solid; yield: 74%; mp 109-111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (s, 1H), 7.79 (dd, J = 8.8, 5.2 Hz, 1H), 7.46-7.42 (m, 2H), 7.28 (d, J = 8.4, Hz, 1H), 7.12-7.03 (m, 2H), 6.83 ppm (dd, J = 10.4, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.5, 161.6, 161.0, 159.2, 143.0, 140.3, 134.2, 132.1, 126.1, 126.1, 121.6, 121.5, 117.4, 117.2, 111.7, 111.4, 97.2, 97.0 ppm; FT-IR (KBr) ν = 2917, 2846, 1625, 1516, 1259, 1208, 1152, 1094, 832, 803, 738 cm^{-1}; Elemental analysis calcd (%) for $C_{13}H_8F_2N_2$: C 67.82, H 3.50, N 12.17, found: C 67.69, H 3.52, N 12.18.



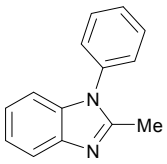
6-Methyl-1-(4-methylphenyl)-1*H*-benzo[*d*]imidazole 2f. Analytical TLC on silica gel, R_f = 0.30 (3:7 ethyl acetate/hexane); yellow liquid; yield: 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.35 (s, 4H), 7.27 (s, 1H), 7.14 (d, J = 8.0 Hz, 1H), 2.45 (s, 3H), 2.44 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.1, 138.1, 134.3, 134.0, 133.8, 130.7, 124.4, 124.2, 120.1, 110.4, 21.9, 21.3 ppm; FT-IR (neat) ν = 2967, 2924, 2851, 1633, 1518, 1500, 1292, 1265, 1235, 1017, 809, 739 cm^{-1}; Elemental analysis calcd (%) for $C_{15}H_{14}N_2$: C 81.05, H 6.35, N 12.60, found: C 80.95, H 6.36, N 12.69.



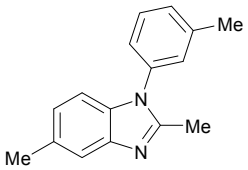
6-Isopropyl-1-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole 2g. Analytical TLC on silica gel, R_f = 0.30 (3:7 ethyl acetate/hexane); yellow liquid; yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (s, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.41 (s, 4H), 7.33 (s, 1H), 7.22 (dd, J = 8.4, 1.2 Hz, 1H), 3.05-2.97 (m, 2H), 1.32 (s, 3H), 1.30 (s, 3H), 1.28 (s, 3H), 1.26 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.0, 145.2, 142.4, 142.3, 134.3, 128.1, 124.2, 121.9, 120.2, 107.8, 34.7, 34.0, 24.6, 24.1 ppm; FT-IR (neat) ν = 2960, 2928, 2862, 1639, 1517, 1489, 1289, 1265, 1229, 1053, 812, 740 cm^{-1}; Elemental analysis calcd (%) for $C_{19}H_{22}N_2$: C 81.97, H 7.97, N 10.06, found: C 81.85, H 7.99, N 10.16.



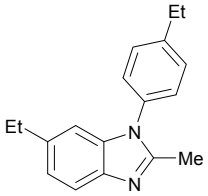
6-Methy-1-(3,5-dimethylphenyl)-1*H*-benzo[*d*]imidazole 2h. Analytical TLC on silica gel, R_f = 0.30 (3:7 ethyl acetate/hexane); yellow solid; yield: 76%; mp 130-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.29 (s, 1H), 7.14 (d, J = 8.4 Hz, 1H), 7.08 (s, 3H); 2.46 (s, 3H), 2.40 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.1, 140.0, 136.4, 133.7, 129.7, 124.4, 121.9, 120.1, 110.5, 22.0, 21.4 ppm; FT-IR (KBr) ν = 2956, 2921, 2857, 1623, 1497, 1294, 1268, 1215, 1037, 845, 808, 699 cm^{-1}; Elemental analysis calcd (%) for $C_{16}H_{16}N_2$: C 81.32, H 6.82, N 11.85, found: C 81.20, H 6.83, N 11.96.



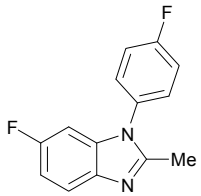
2-Methyl-1-phenyl-1*H*-benzo[*d*]imidazole 2i. Analytical TLC on silica gel, R_f = 0.18 (3:7 ethyl acetate/hexane); yellow liquid; yield: 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, J = 7.6 Hz, 1H), 7.59 (t, J = 7.2Hz, 2H), 7.53 (d, J = 6.8 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 8.0 Hz, 1H), 7.13 Hz (d, J = 8.0 Hz, 1H), 2.51 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.5, 142.4, 136.4, 135.9, 129.9, 128.8, 127.0, 122.6, 122.4, 119.9, 118.8, 110.0, 14.3 ppm; FT-IR (neat) ν = 3056, 2956, 2923, 1672, 1597, 1499, 1457, 1395, 1324, 1287, 1248, 1181, 1016, 797, 760, 744, 698 cm^{-1}; Elemental analysis calcd (%) for $C_{14}H_{12}N_2$: C 80.74, H 5.81, N 13.45, found: C 80.63, H 5.82, N 13.55.



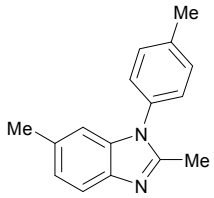
2,5-Dimethyl-1-(3-methylphenyl)-1*H*-benzo[*d*]imidazole 2j. Analytical TLC on silica gel, R_f = 0.23 (3:7 ethyl acetate/hexane); yellow liquid; yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (s, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.13 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 0.8 Hz, 2H), 2.46 (s, 3H), 2.45 (s, 3H), 2.42 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.3, 142.7, 139.9, 136.0, 134.5, 131.8, 129.5, 127.4, 123.8, 118.6, 109.5, 21.4, 21.2, 14.3 ppm; FT-IR (neat) ν = 3054, 2956, 2922, 2857, 1607, 1520, 1493, 1262, 1085, 1017, 793, 745, 703 cm^{-1}; Elemental analysis calcd (%) for $C_{16}H_{16}N_2$: C 81.32, H 6.82, N 11.85, found: C 81.21, H 6.83, N 11.95.



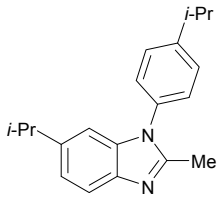
6-Ethyl-1-(4-ethylphenyl)-2-methyl-1*H*-benzo[*d*]imidazole 2k. Analytical TLC on silica gel, R_f = 0.30 (3:7 ethyl acetate/hexane); yellow liquid; yield: 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.12 (dd, J = 8.4, 1.6 Hz, 1H), 6.92 (s, 1H), 2.80 (q, J = 8.0 Hz, 3H), 2.72 (q, J = 7.6 Hz, 3H), 2.47 (s, 3H), 1.35 (t, J = 7.6 Hz, 3H), 1.24 ppm (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.1, 144.8, 140.7, 139.0, 136.7, 133.6, 129.2, 126.8, 122.5, 118.4, 108.6, 29.1, 28.5, 16.2, 15.3, 14.2 ppm; FT-IR (neat) ν = 3033, 2965, 2931, 2872, 1619, 1515, 1450, 1394, 1320, 1254, 1210, 1055, 1009, 818 cm^{-1}; Elemental analysis calcd (%) for $C_{18}H_{20}N_2$: C 81.78, H 7.63, N 10.60, found: C 81.65, H 7.65, N 10.70.



6-Fluoro-1-(4-fluorophenyl)-2-methyl-1*H*-benzo[*d*]imidazole 2l. Analytical TLC on silica gel, R_f = 0.35 (3:7 ethyl acetate/hexane); yellow liquid; yield: 75%; ; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (dd, J = 8.8, 5.2 Hz, 1H), 7.34 (m, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.75 (dt, J = 9.2, 2.4 Hz, 1H), 6.75 (dd, J = 8.4, 2.4 Hz, 1H), 2.44 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.7, 161.2, 160.8, 158.4, 152.1, 138.7, 136.5, 136.4, 131.6, 128.8, 128.7, 119.6, 119.5, 117.1, 116.9, 110.6, 110.3, 96.7, 96.4, 14.1 ppm; FT-IR (neat) ν = 3074, 2961, 2930, 1620, 1513, 1480, 1396, 1311, 1261, 1228, 1145, 1105, 1010, 969, 836, 796, 619 cm^{-1}; Elemental analysis calcd (%) for $C_{14}H_{10}F_2N_2$: C 68.85, H 4.13, N 11.47, found: C 68.73, H 4.14, N 11.58.

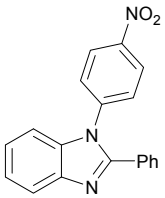


2,6-Dimethyl-1-(4-methylphenyl)-1*H*-benzo[*d*]imidazole 2m. Analytical TLC on silica gel, R_f = 0.40 (3:7 ethyl acetate/hexane); yellow liquid; yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 (d, J = 8.4 Hz, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 1H), 6.87 (s, 1H), 2.44 (s, 3H,) 2.44 (s, 3H), 2.37 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.0, 140.5, 138.7, 136.7, 133.4, 132.3, 130.4, 126.8, 123.6, 118.3, 109.8, 21.5, 21.1, 14.2 ppm; FT-IR (neat) ν = 3035, 2967, 2922, 2862, 1626, 1515, 1484, 1448, 1396, 1318, 1257, 1212, 1108, 1010, 808, 715 cm^{-1}; Elemental analysis calcd (%) for $C_{16}H_{16}N_2$: C 81.32, H 6.82, N 11.85, found: C 81.22, H 6.81, N 11.97.

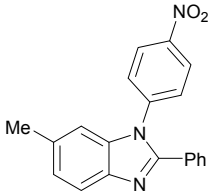


6-Isopropyl-1-(4-isopropylphenyl)-2-methyl-1*H*-benzo[*d*]imidazole 2n. Analytical TLC on silica gel, R_f = 0.30 (3:7 ethyl acetate/hexane); yellow solid; yield: 78%; mp 126-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.16 (dd, J = 8.4, 1.6 Hz, 1H), 6.96 (s, 1H), 3.06-2.92 (m, 2H), 2.46 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H), 1.25 (s, 3H), 1.23 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.2, 149.4, 143.8, 140.9, 136.6, 133.7, 127.8, 126.8,

121.0, 118.5, 107.3, 34.4, 33.8, 24.5, 23.9, 14.3 ppm; FT-IR (KBr) ν = 3035, 2960, 2923, 2870, 1621, 1515, 1480, 1448, 1394, 1324, 1298, 1263, 1210, 1100, 1056, 1008, 817 cm^{-1}; Elemental analysis calcd (%) for $C_{20}H_{24}N_2$: C 82.15, H 8.27, N 9.58, found: C 82.05, H 8.28, N 9.67.



1-(4-Nitrophenyl)-2-phenyl-1*H*-benzo[*d*]imidazole 2o. Analytical TLC on silica gel, R_f = 0.50 (3:7 ethyl acetate/hexane); yellow solid; yield: 80%; mp 174-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 (d, J = 8.8 Hz, 1H), 8.25 (d, J = 9.2 Hz, 1H), 7.89-7.82 (m, 3H), 7.52-7.46 (m, 4H), 7.39-7.29 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.4, 143.4, 142.7, 136.3, 130.2, 129.7, 128.9, 128.1, 127.4, 125.3, 120.5, 110.1 ppm; FT-IR (KBr) ν = 2923, 2862, 1638, 1500, 1329, 1300, 1282, 1176, 1111, 790, 743, 695 cm^{-1}; Elemental analysis calcd (%) for $C_{19}H_{13}N_3O_2$: C 72.37, H 4.16, N 13.33, found: C 72.25, H 4.17, N 13.44.



6-Methyl-1-(4-nitrophenyl)-2-phenyl-1*H*-benzo[*d*]imidazole 2p. Analytical TLC on silica gel, R_f = 0.50(3:7 ethyl acetate/hexane) ; yellow solid; yield: 82%; mp 167-169 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.34 (d, J = 9.2 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.46-7.45 (m, 4H), 7.37-7.30 (m, 4H), 7.19 (d, J = 8.4 Hz, 1H), 7.06 (s, 1H), 2.45 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.8, 147.0, 142.8, 141.4, 136.5, 134.4, 129.9, 129.5, 129.4, 128.7, 128.0, 125.4, 119.9, 109.9, 21.9 ppm; FT-IR (KBr) ν = 3076, 2923, 2851, 1594, 1520, 1350, 1214, 1109, 1028, 855, 810, 771, 735, 698 cm^{-1}; Elemental analysis calcd (%) for $C_{20}H_{15}N_3O_2$: C 72.94, H 4.59, N 12.76, found: C 72.83, H 4.60, N 12.86.

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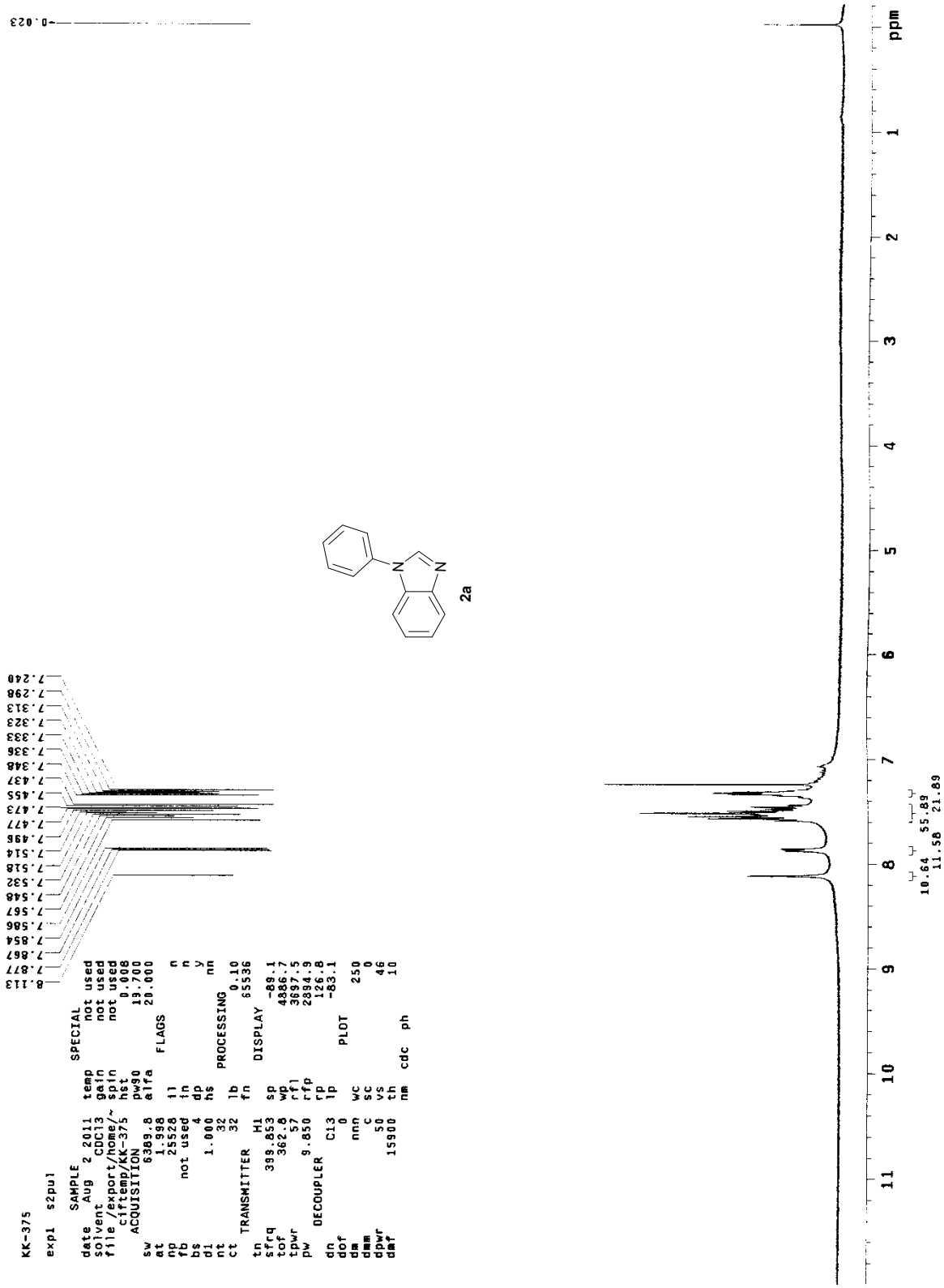
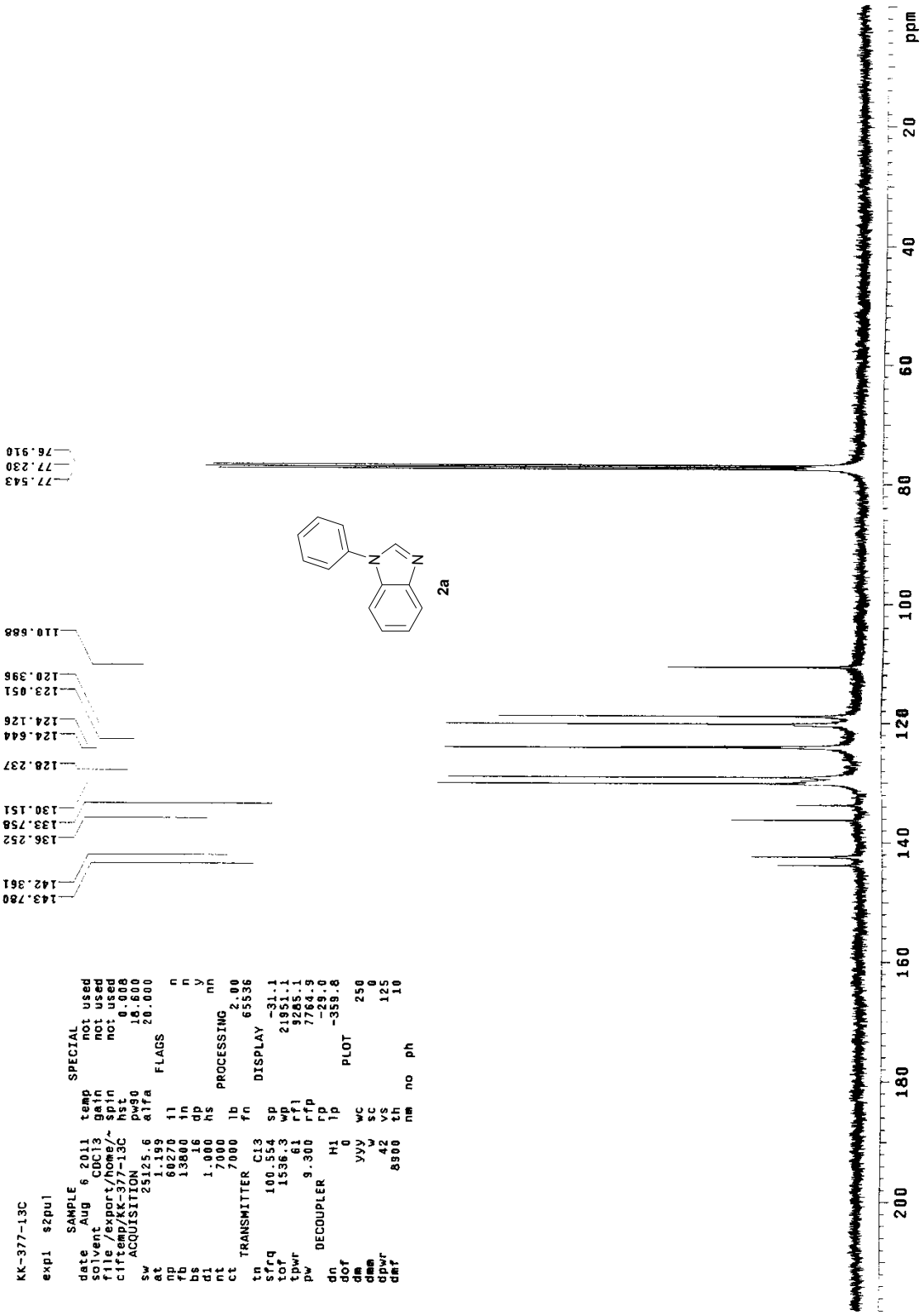
2. P. Harding, D. J. Harding, H. Adams and S. Youngme, *Synth. Commun.* 2007, **37**, 2655.
3. C. T. Brain and S. A. Brunton, *Tetrahedron Lett.* 2002, **4**3, 1893.
4. S. Jammi, S. Krishnamoorthy, P. Saha, D. S. Kundu, S. Sakthivel, Md. A. Ali, R. Paul and T. Punniyamurthy, *Synlett* 2009, 3323.

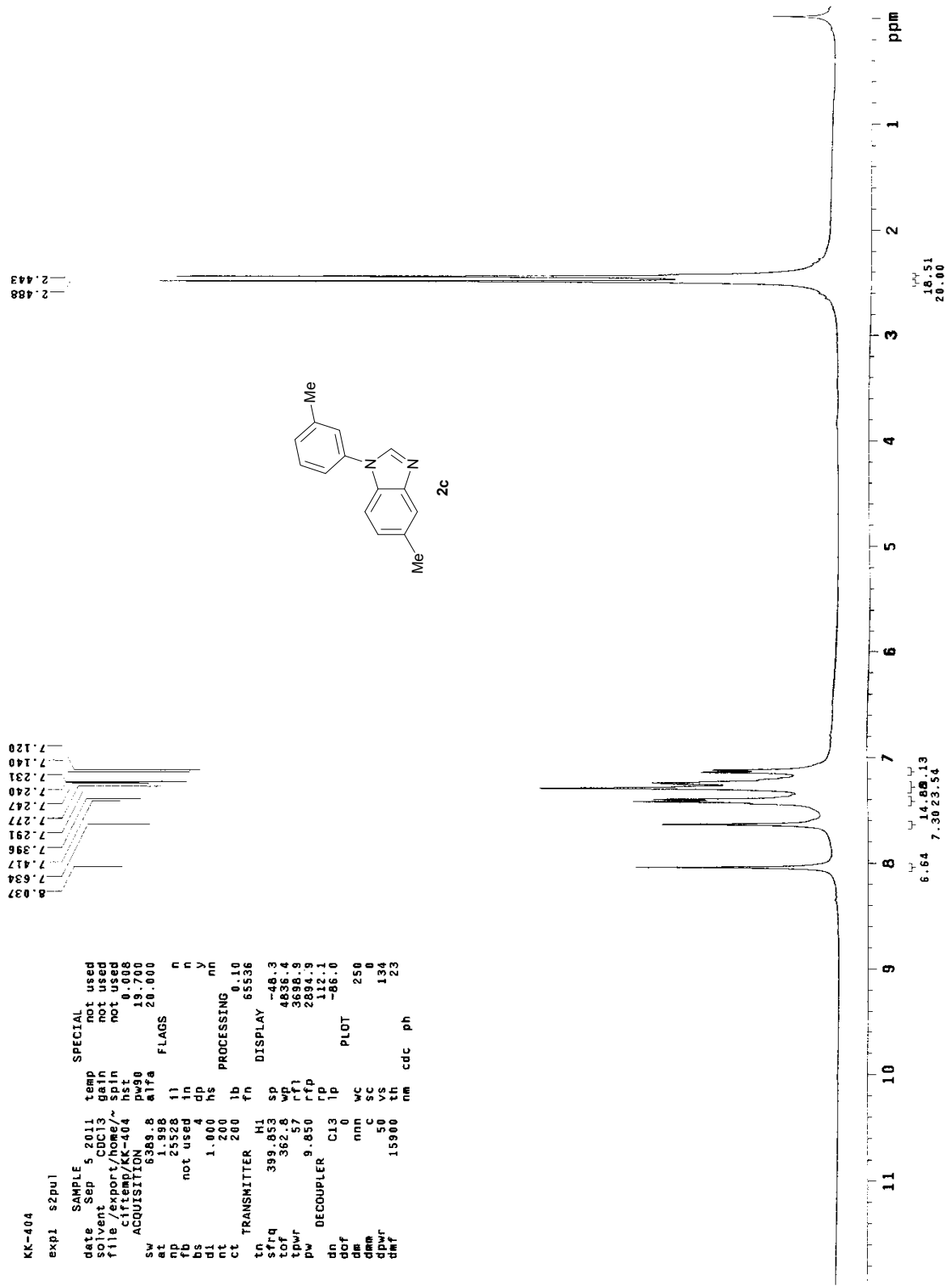
^{1}H NMR ($CDCl_3$) spectra of 1-phenyl-1*H*-benzo[*d*]imidazole 2a.



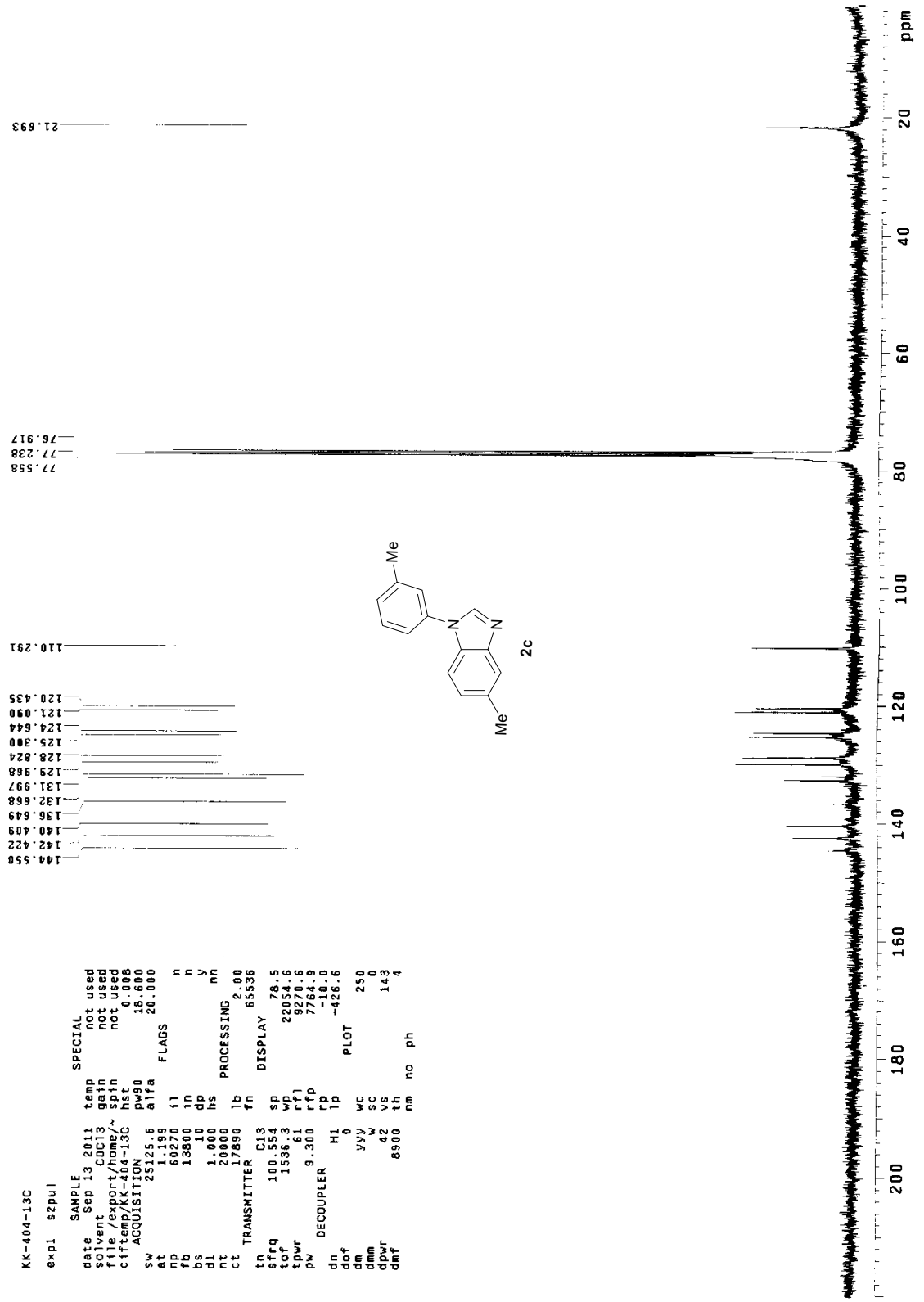
^{13}C NMR ($CDCl_3$) spectra of 1-phenyl-1*H*-benzo[*d*]imidazole 2a.



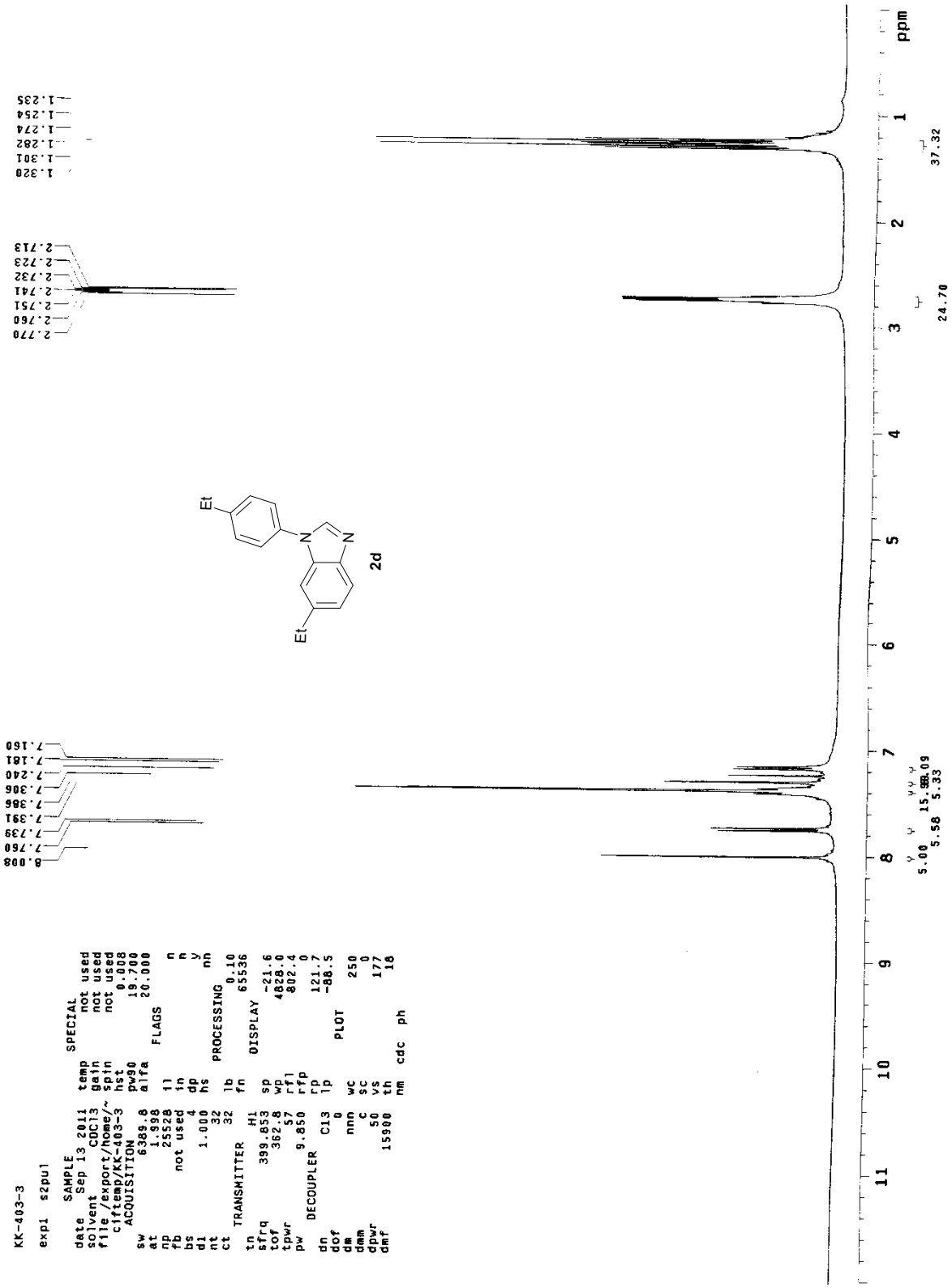
^{1}H NMR ($CDCl_3$) spectra of 5-methyl-1-(3-methylphenyl)-1*H*-benzo[*d*]imidazole 2c.



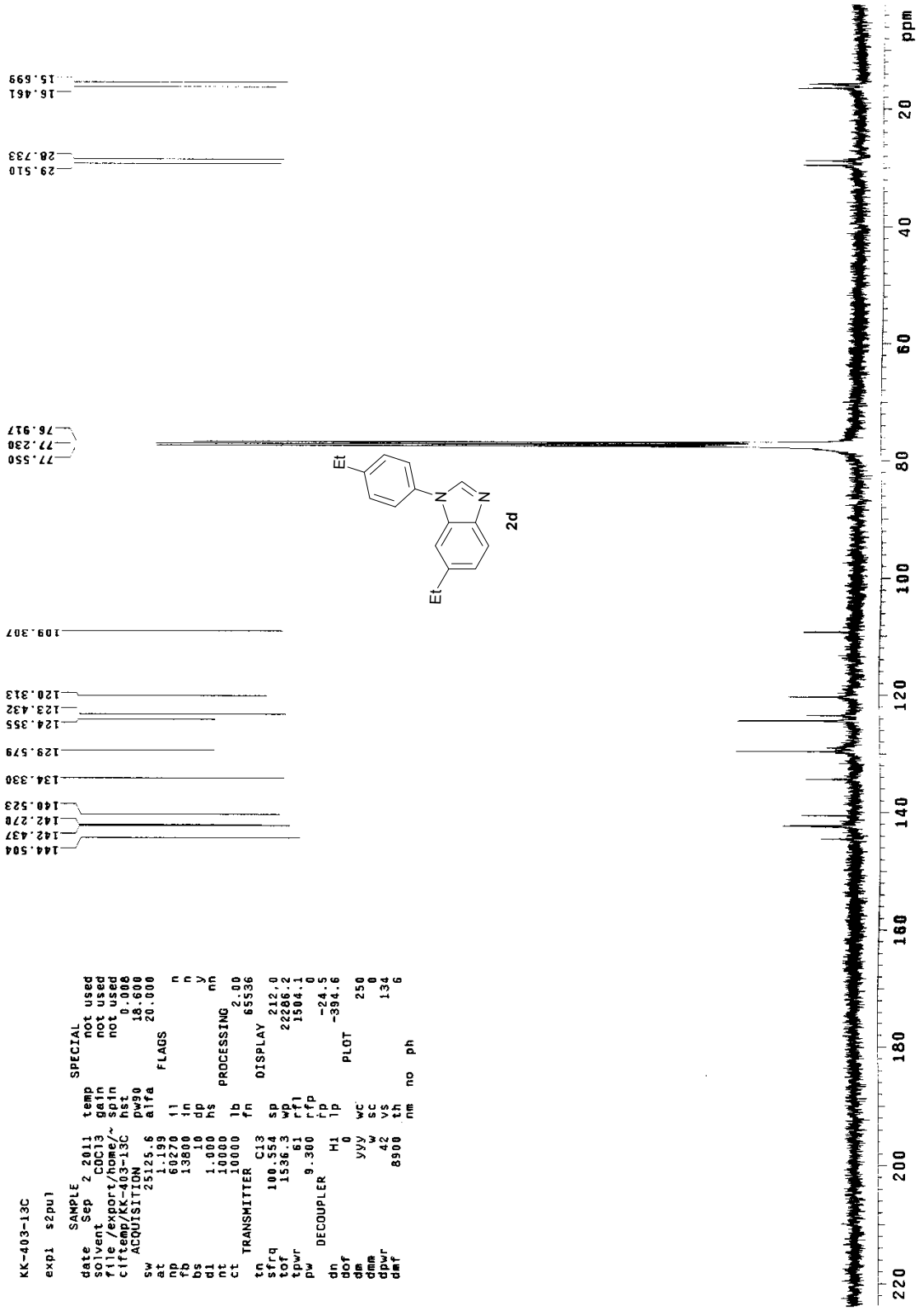
^{13}C NMR ($CDCl_3$) spectra of 5-methyl-1-(3-methylphenyl)-1*H*-benzo[*d*]imidazole 2c.



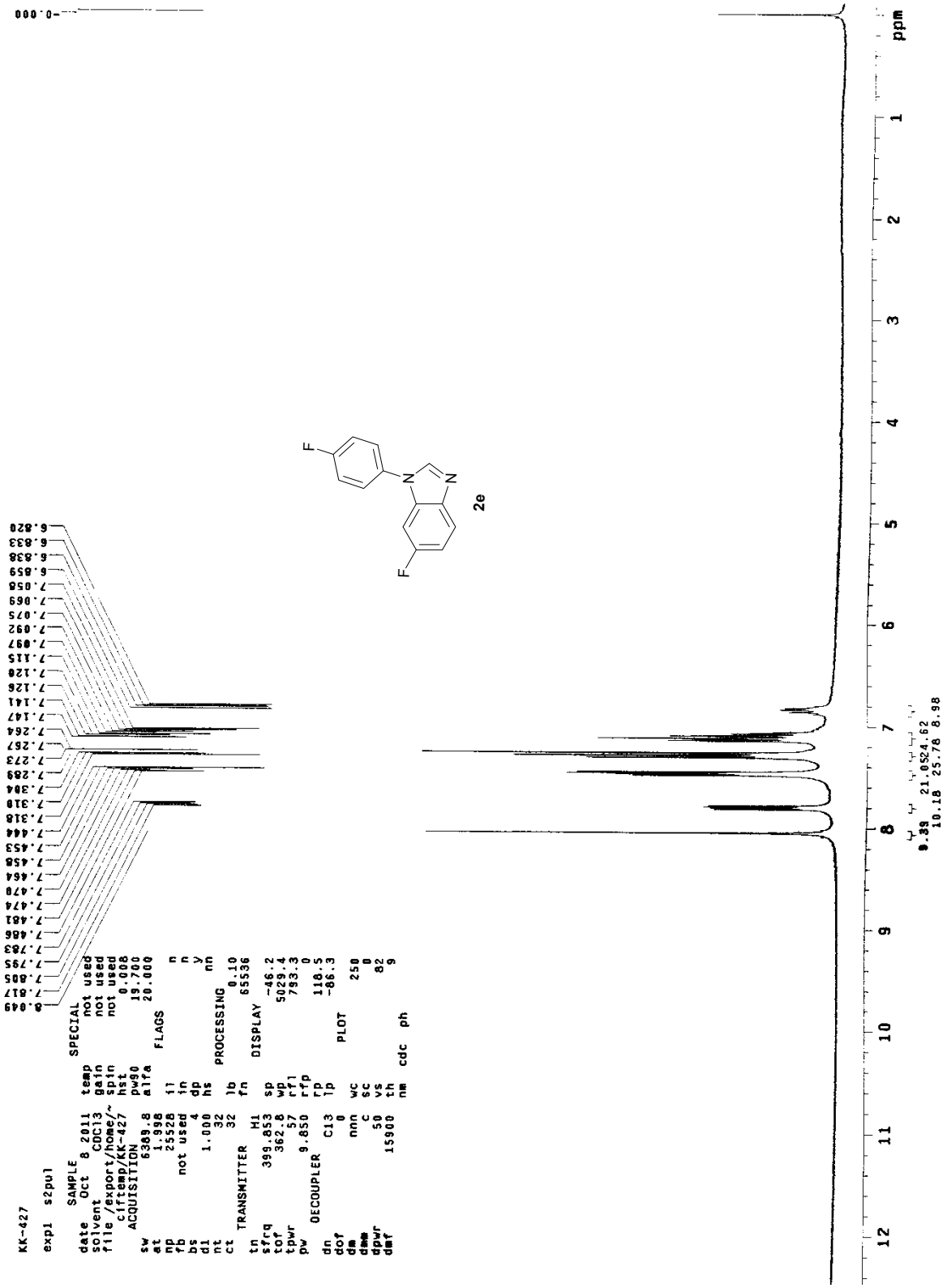
^{1}H NMR ($CDCl_3$) spectra of 6-ethyl-1-(4-ethylphenyl)-1*H*-benzo[*d*]imidazole 2d.



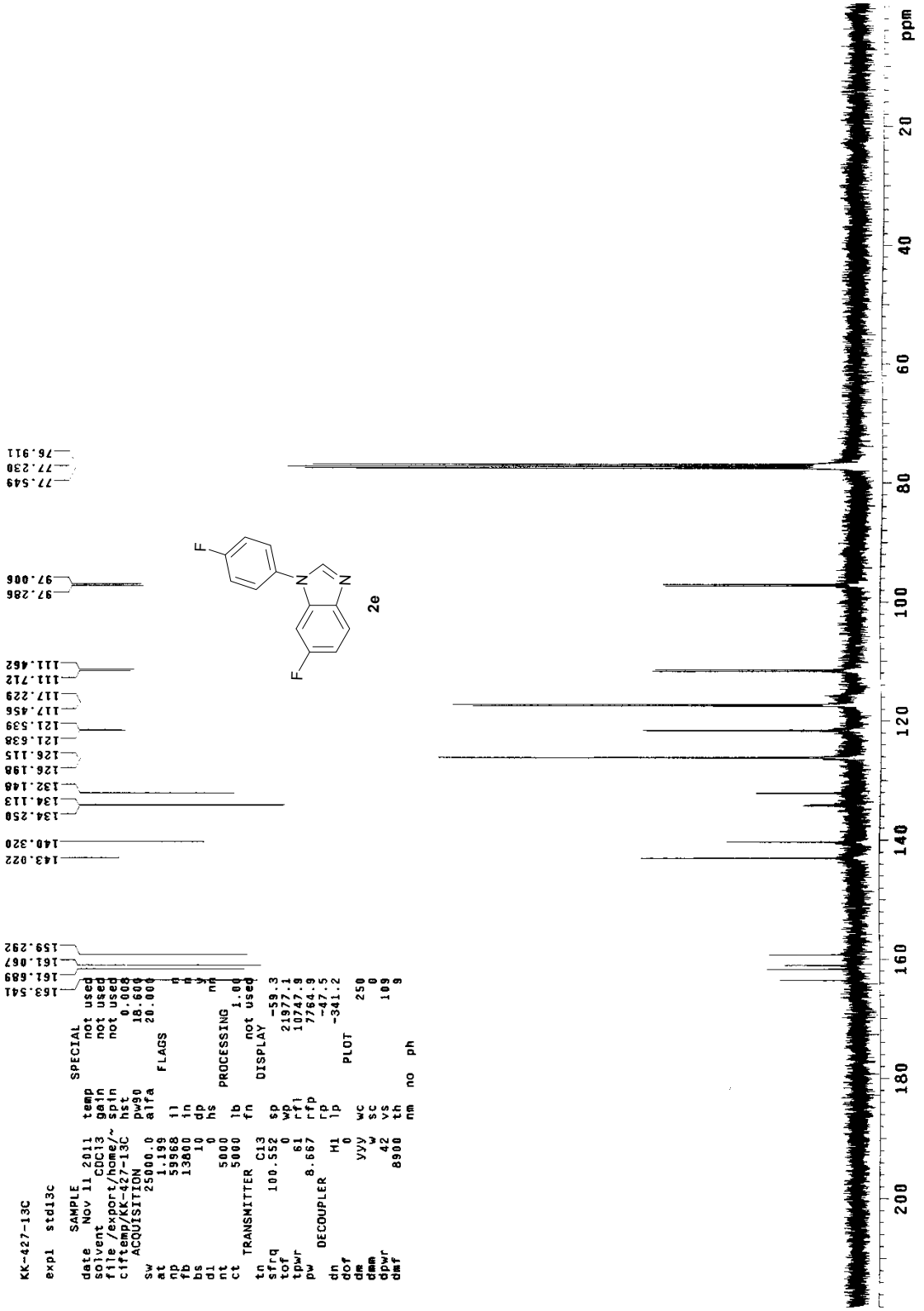
^{13}C NMR ($CDCl_3$) spectra of 6-ethyl-1-(4-ethylphenyl)-1*H*-benzo[*d*]imidazole 2d.



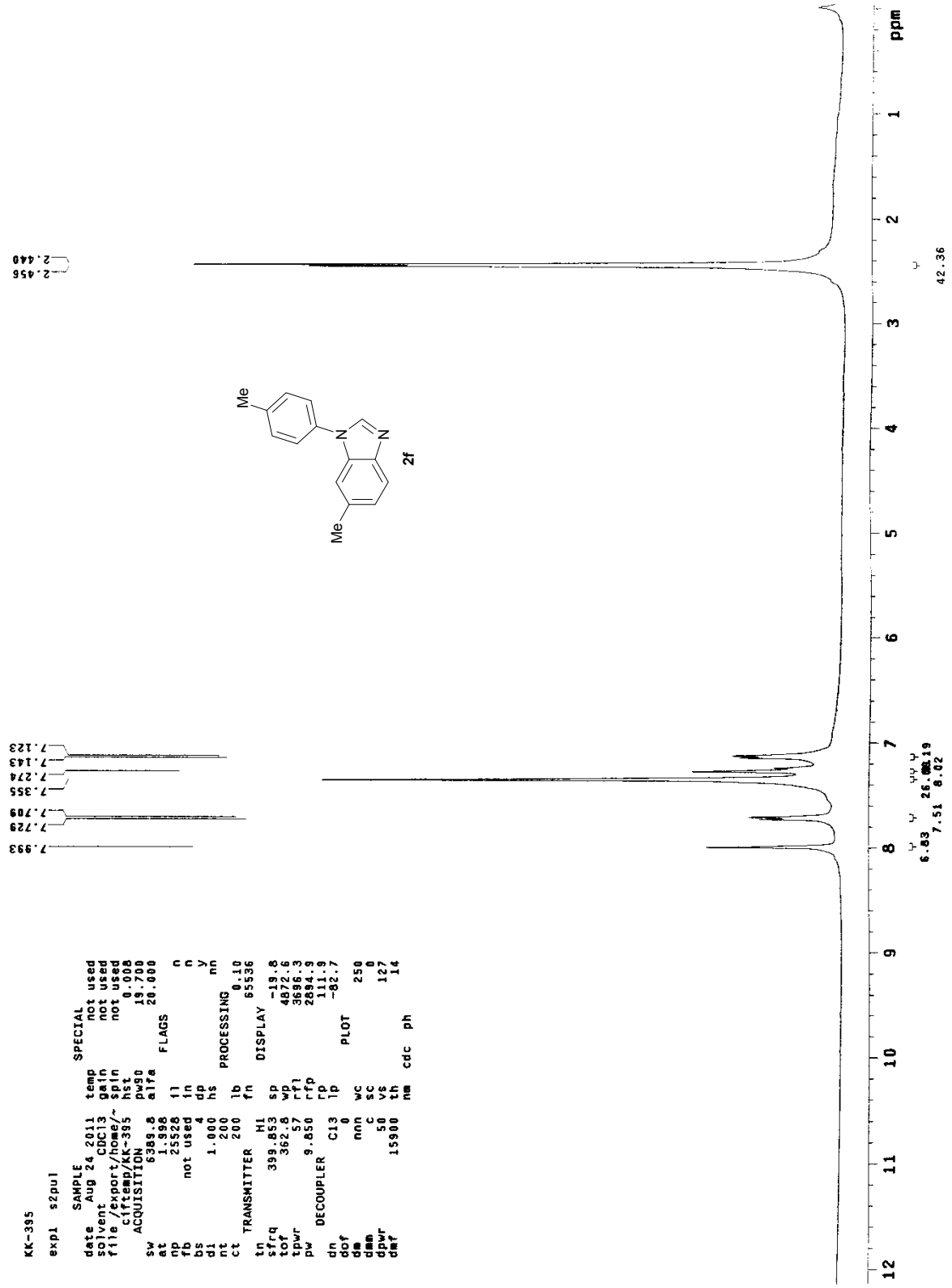
^{1}H NMR ($CDCl_3$) spectra of 6-fluoro-1-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole 2e.



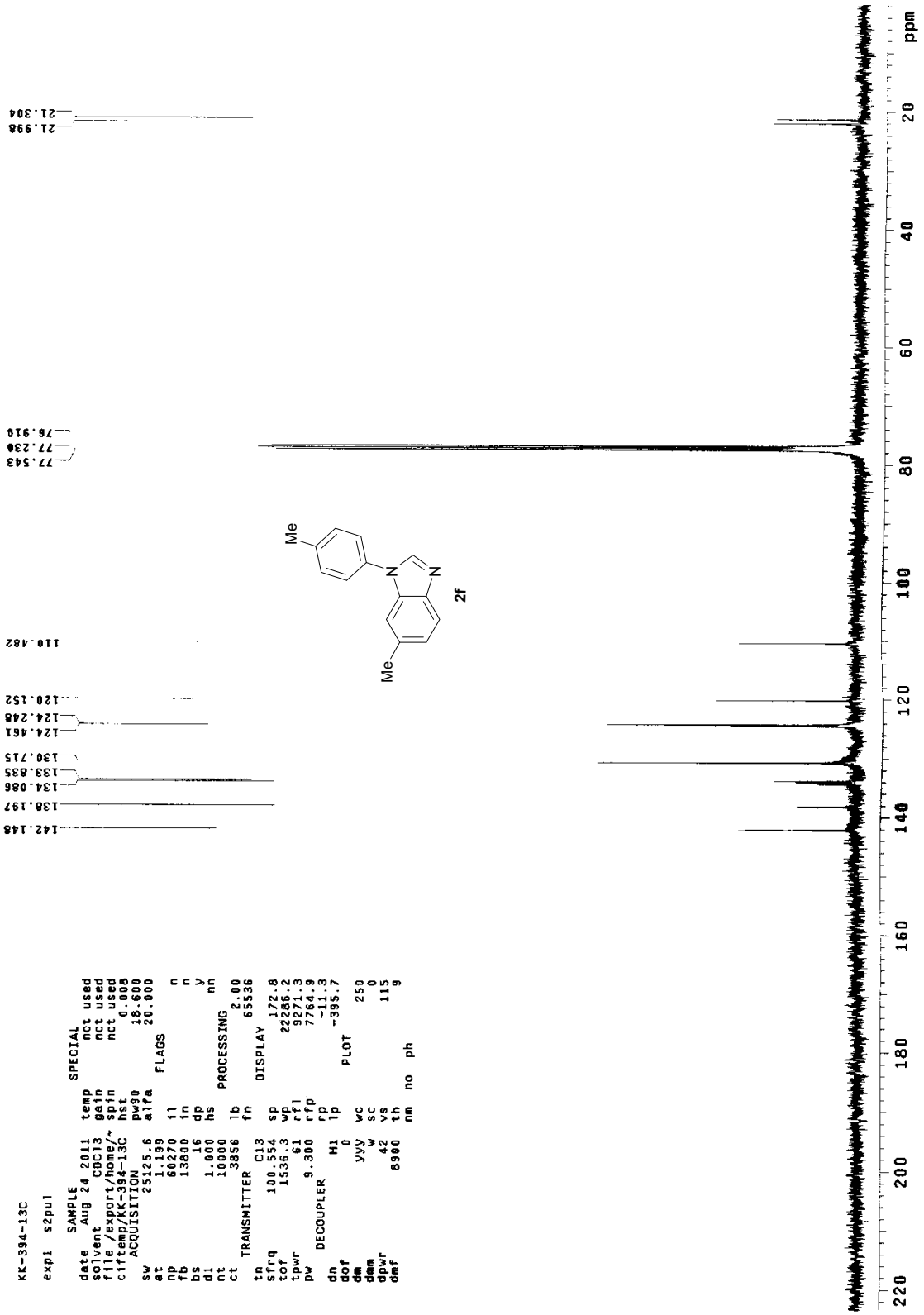
^{13}C NMR ($CDCl_3$) spectra of 6-fluoro-1-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole 2e.



^{1}H NMR ($CDCl_3$) spectra of 6-methyl-1-(4-methylphenyl)-1*H*-benzo[*d*]imidazole 2f.

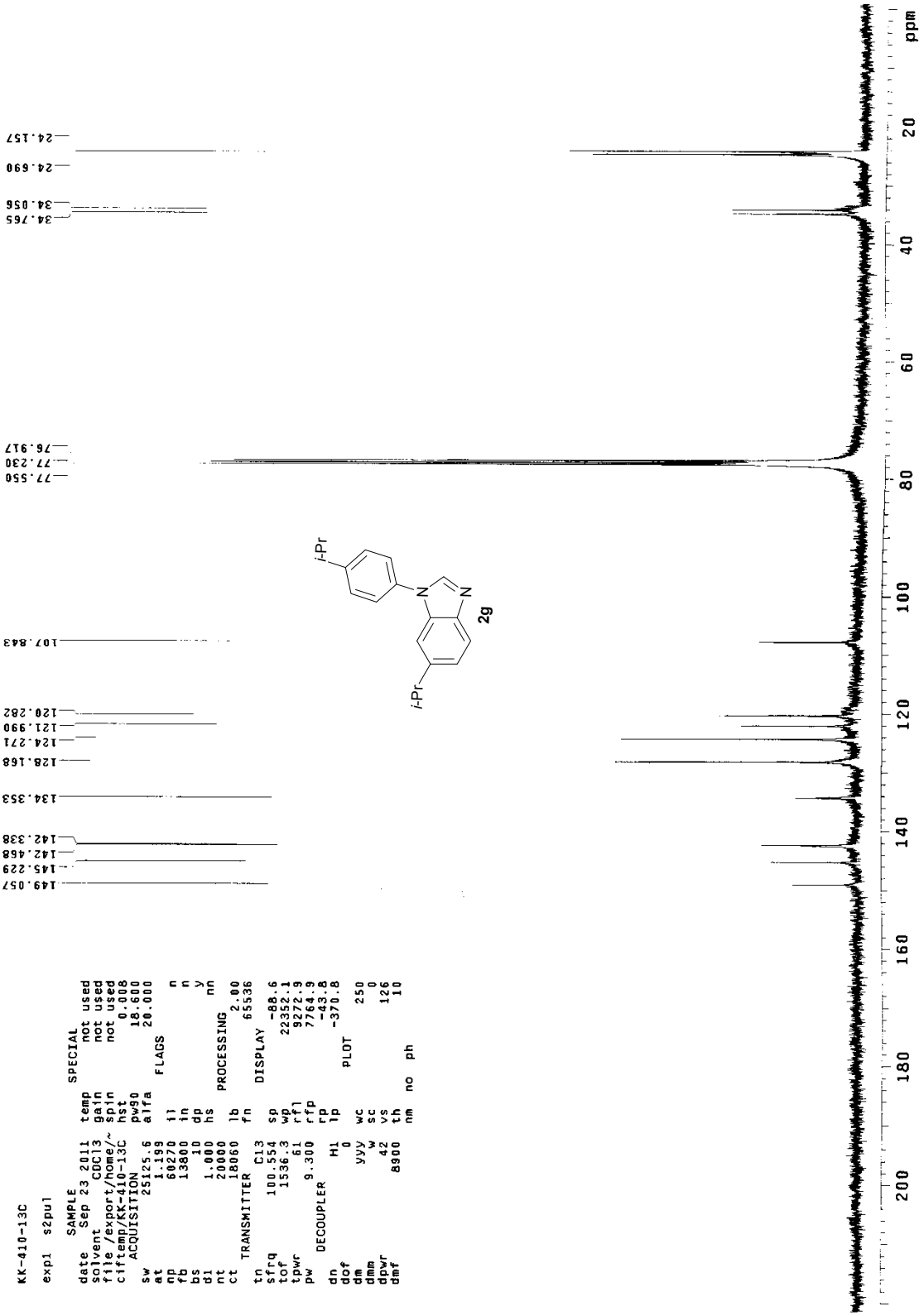


^{13}C NMR ($CDCl_3$) spectra of 6-methyl-1-(4-methylphenyl)-1*H*-benzo[*d*]imidazole 2f.

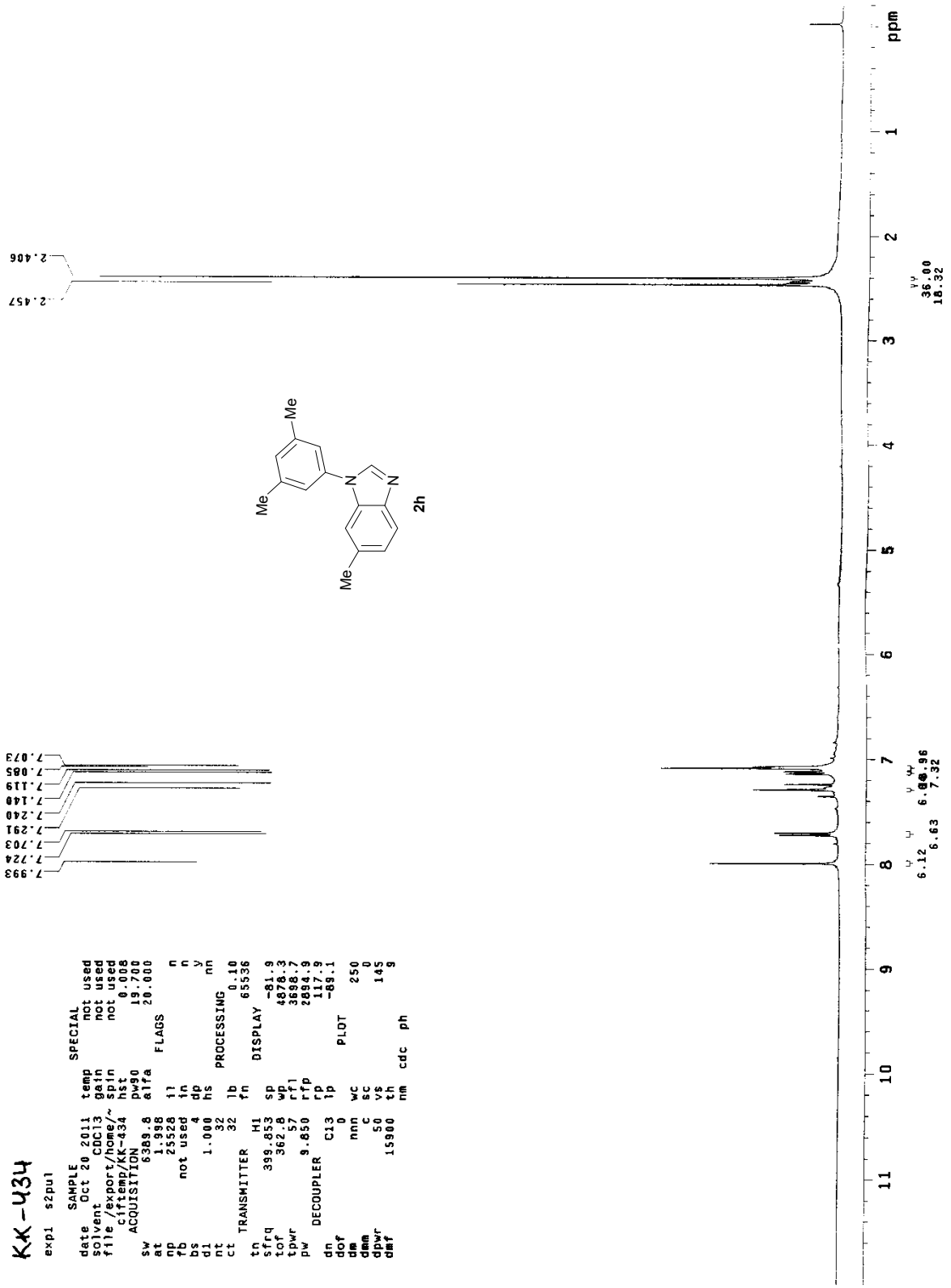


^{1}H NMR ($CDCl_3$) spectra of 6-isopropyl-1-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole 2g.

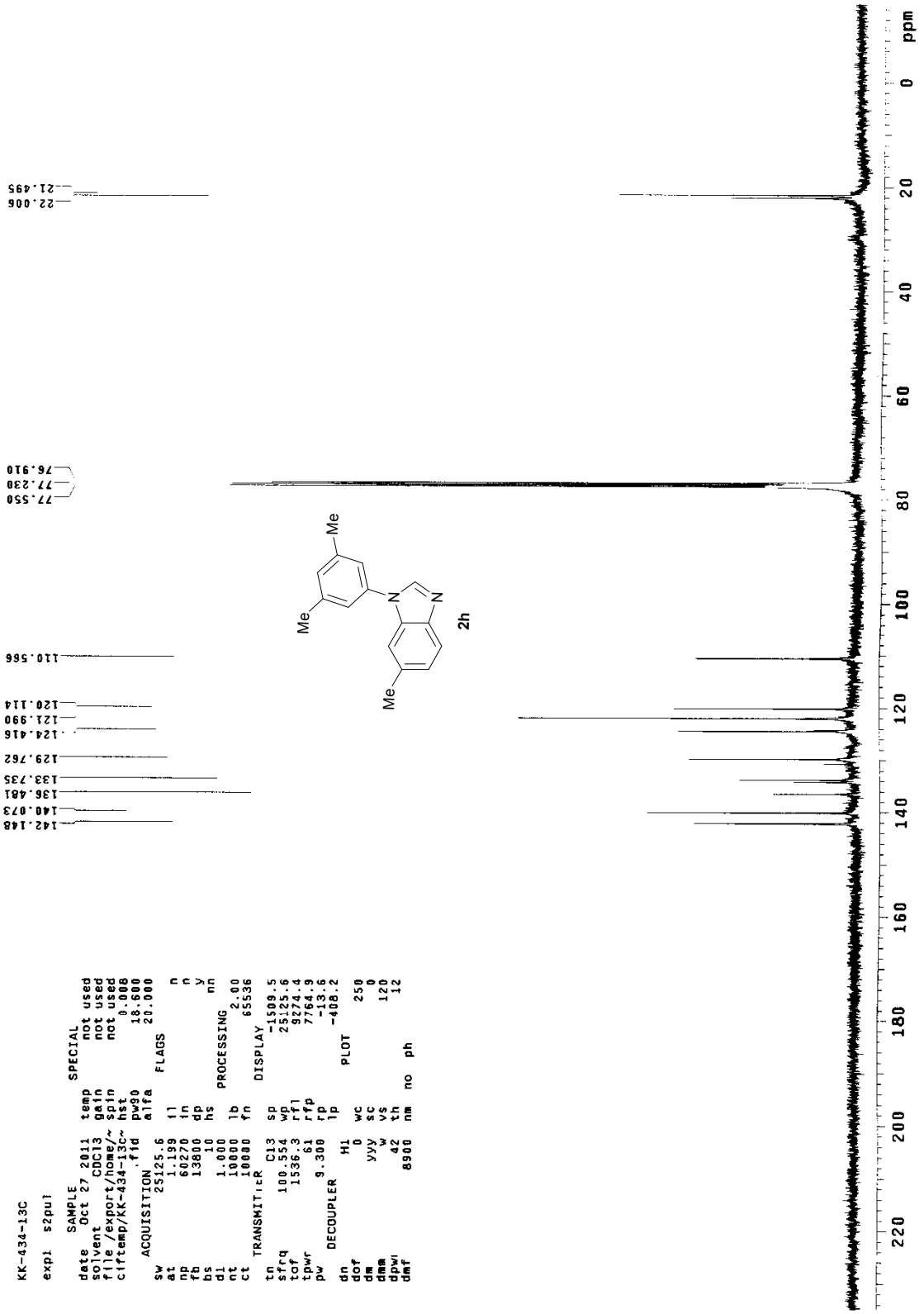
^{13}C NMR ($CDCl_3$) spectra of 6-isopropyl-1-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole 2g.



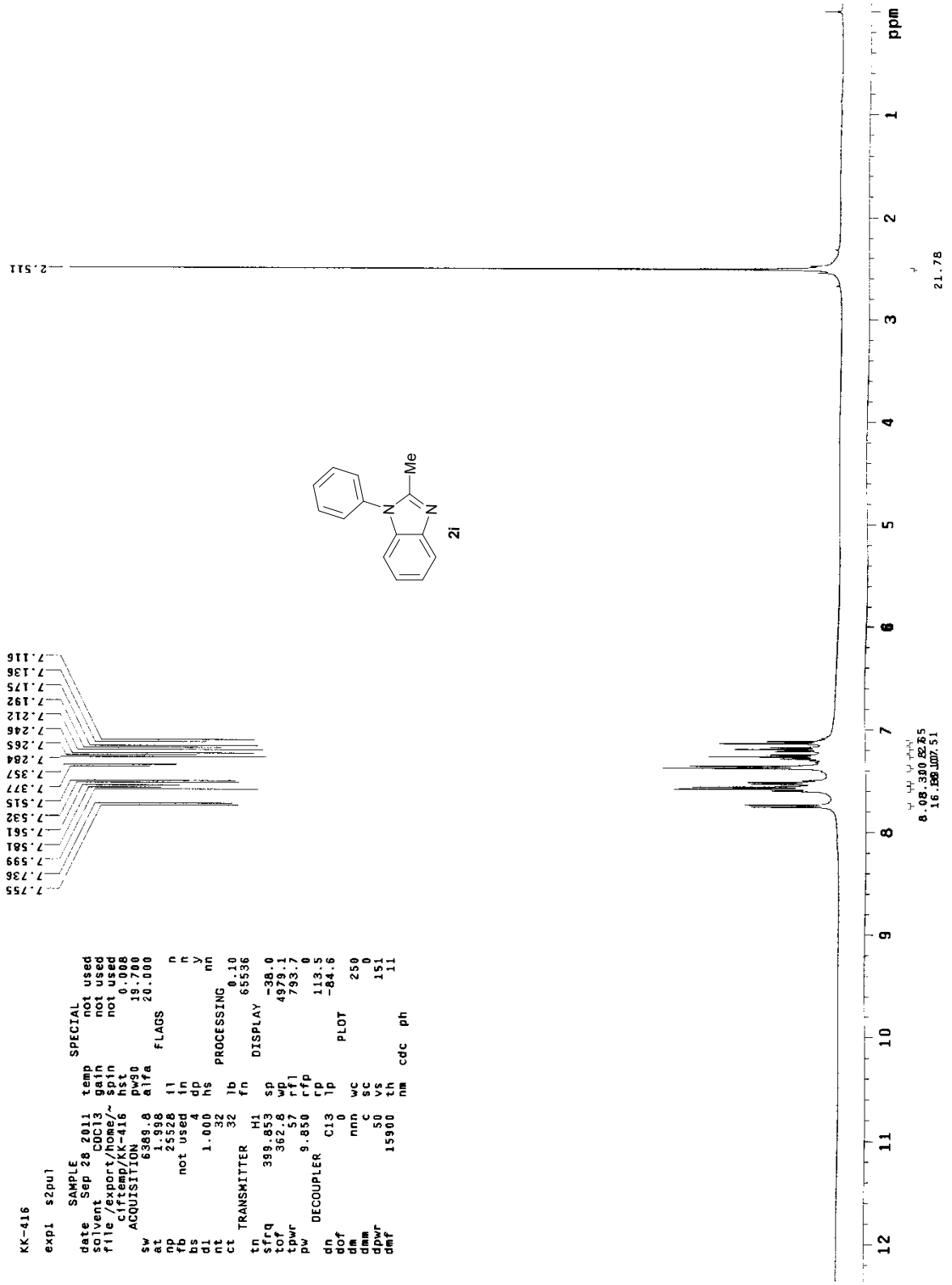
^{1}H NMR ($CDCl_3$) spectra of 6-methy-1-(3,5-dimethylphenyl)-1*H*-benzo[*d*]imidazole 2h.



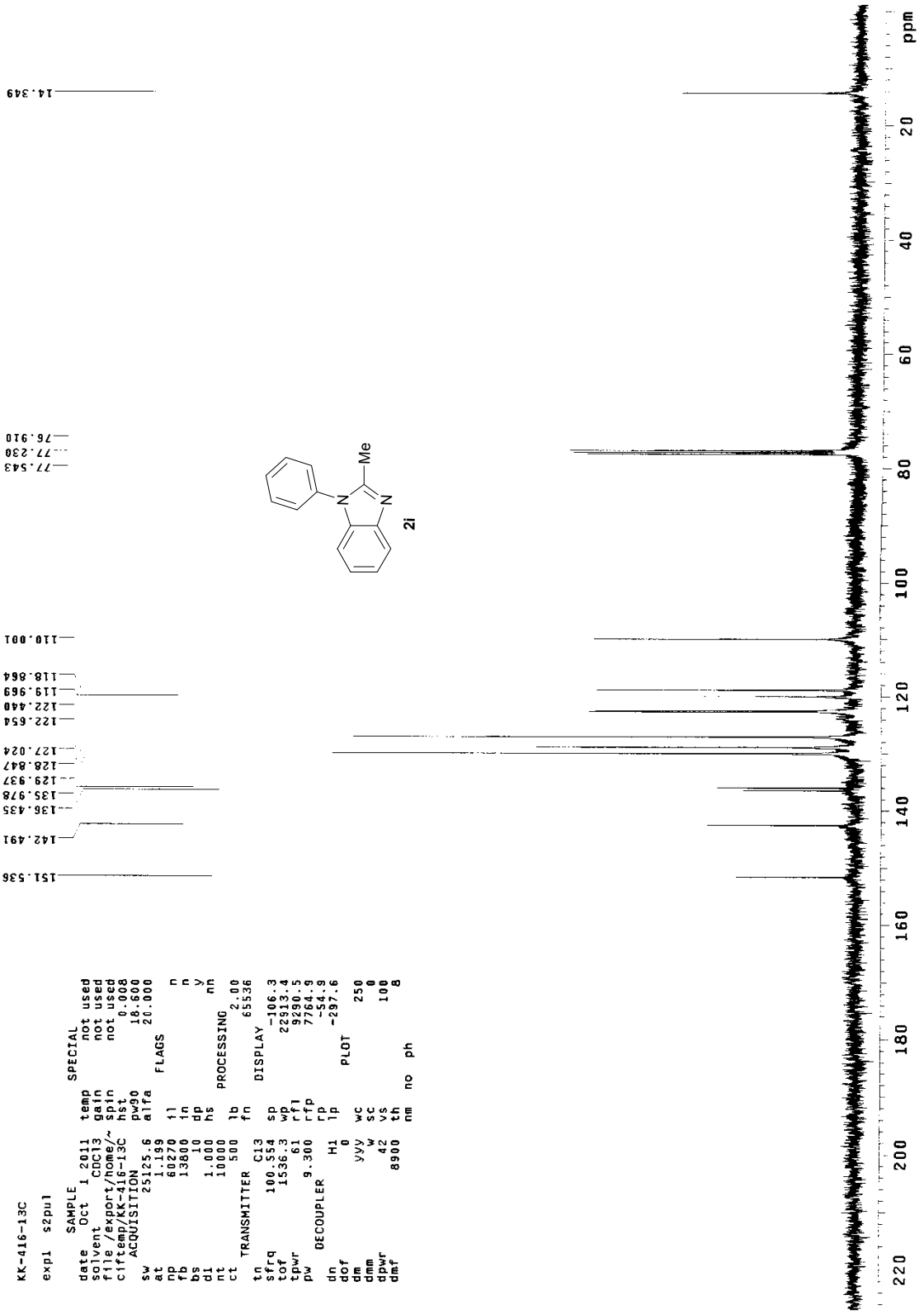
^{13}C NMR ($CDCl_3$) spectra of 6-methy-1-(3,5-dimethylphenyl)-1*H*-benzo[*d*]imidazole 2h.



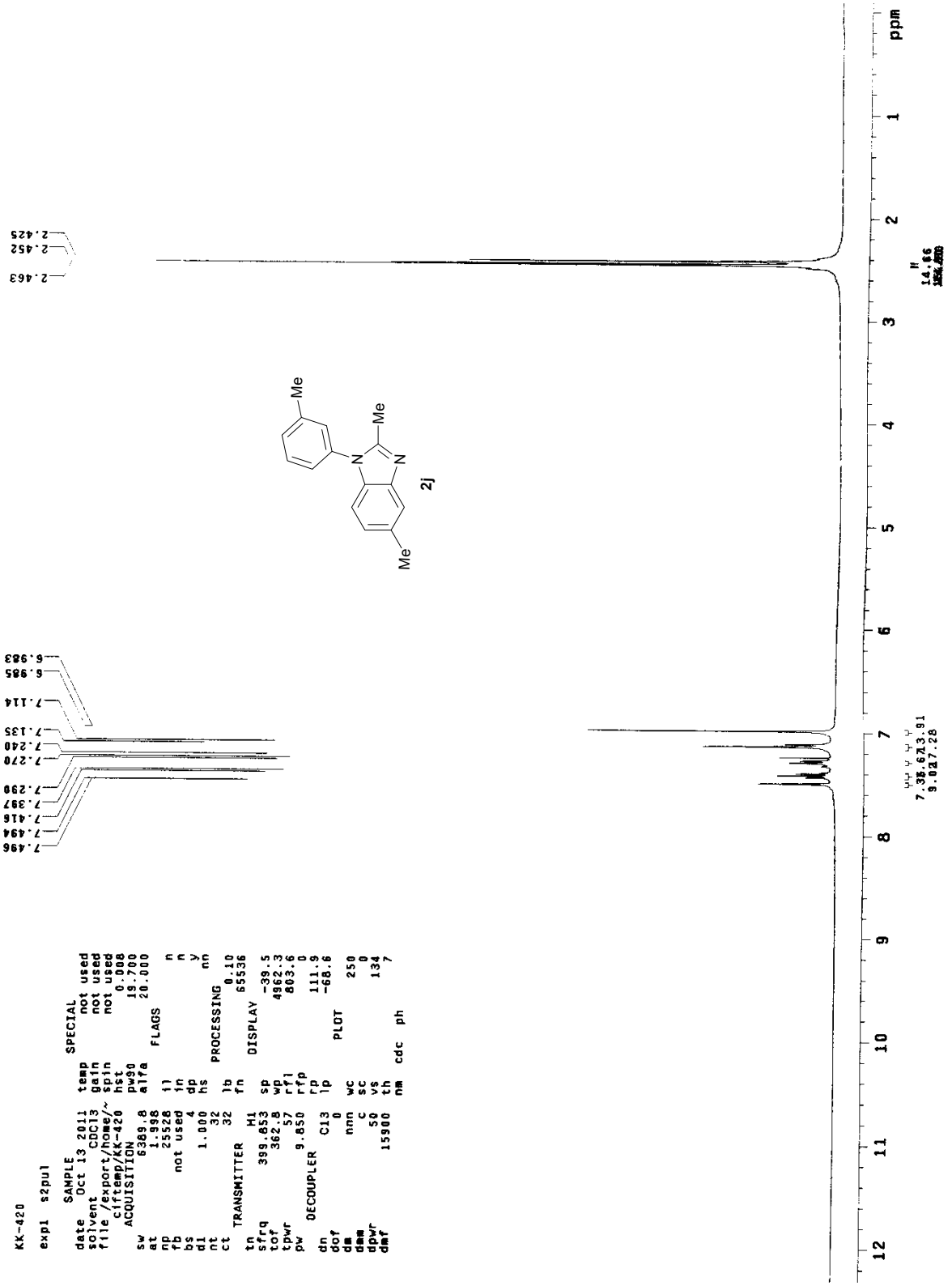
^{1}H NMR ($CDCl_3$) spectra of 2-methyl-1-phenyl-1*H*-benzo[*d*]imidazole 2i.



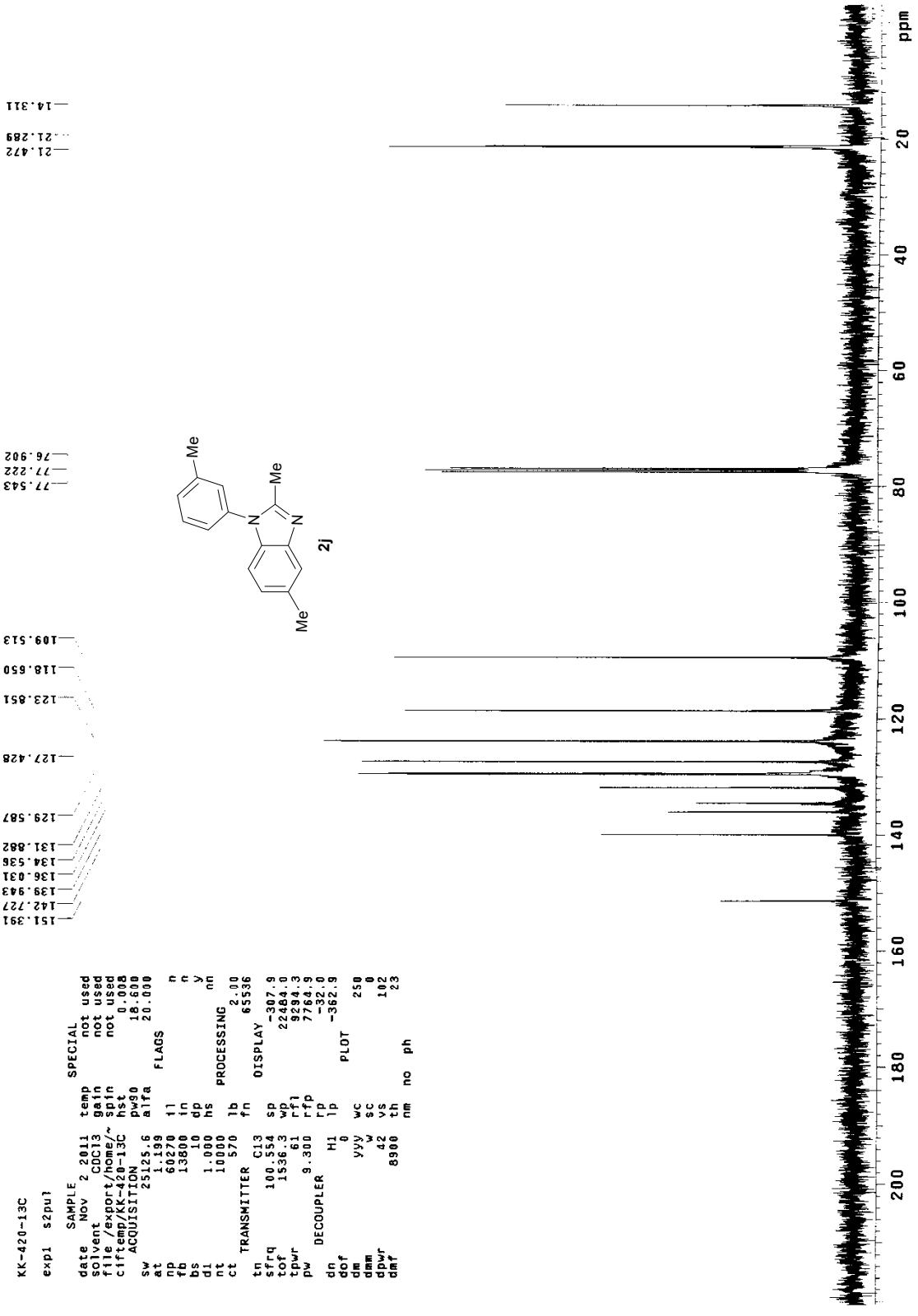
^{13}C NMR ($CDCl_3$) spectra of 2-methyl-1-phenyl-1*H*-benzo[*d*]imidazole 2i.



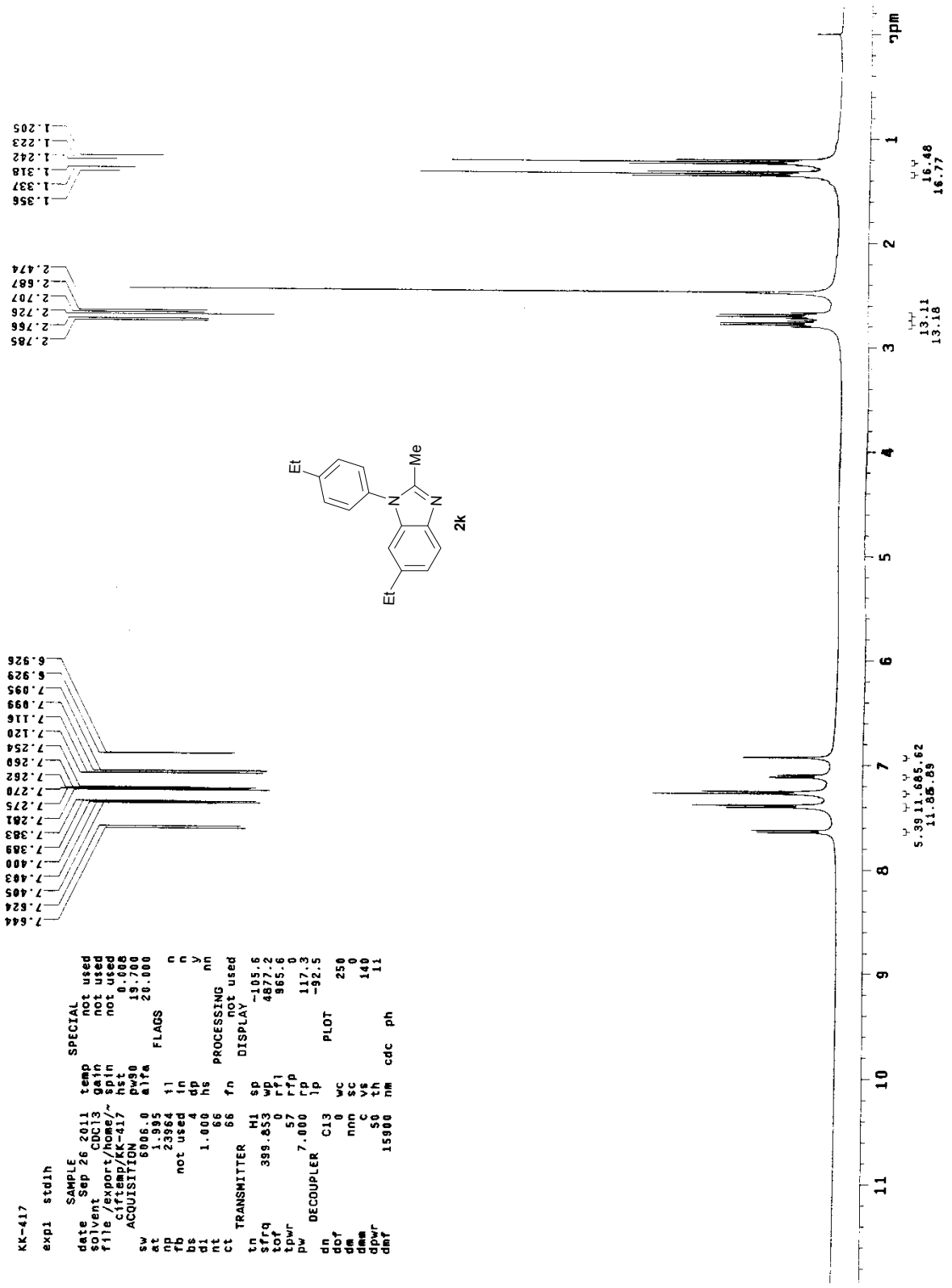
^{1}H NMR ($CDCl_3$) spectra of 2,5-dimethyl-1-(3-methylphenyl)-1*H*-benzo[*d*]imidazole 2j.



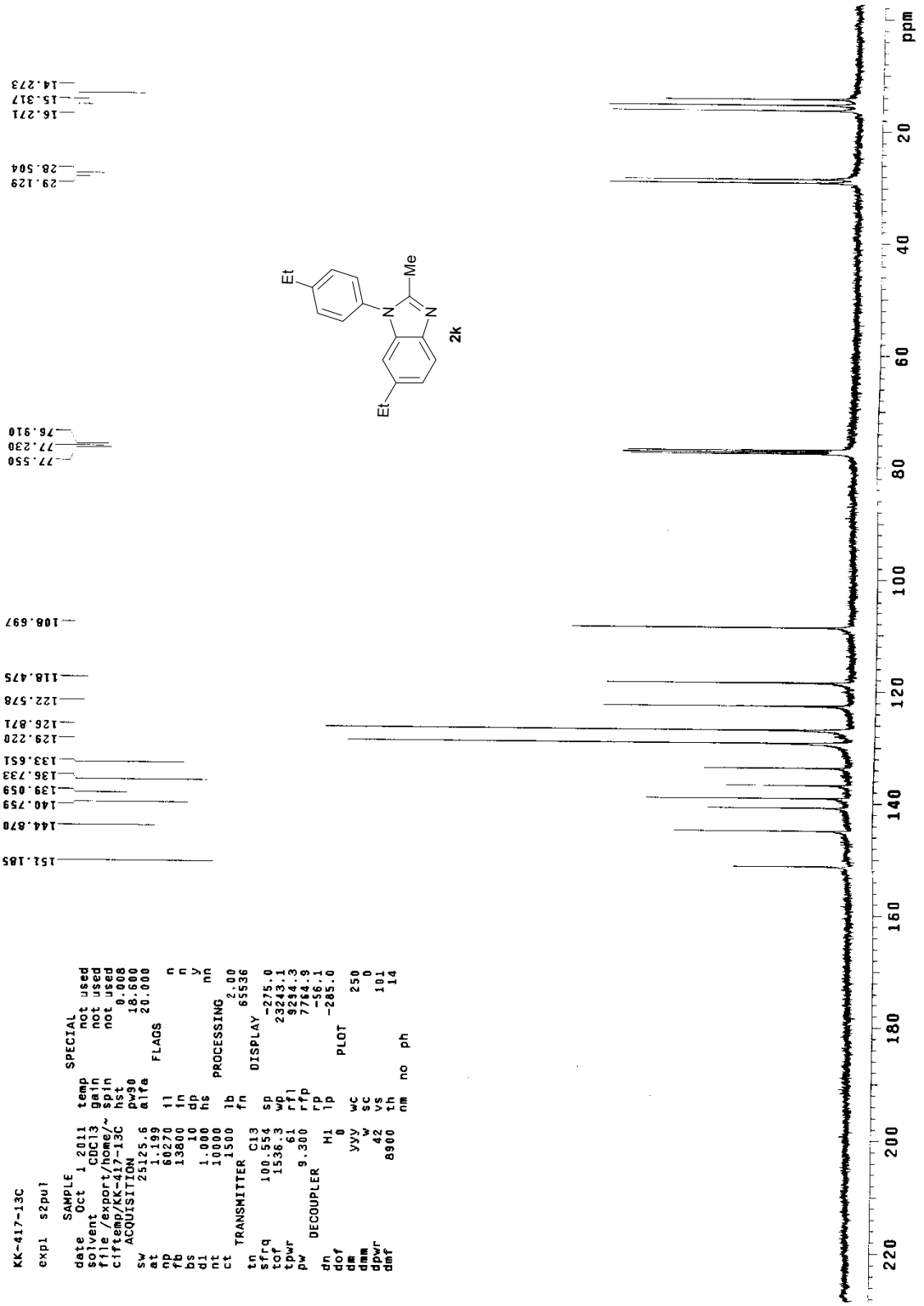
^{13}C NMR ($CDCl_3$) spectra of 2,5-dimethyl-1-(3-methylphenyl)-1*H*-benzo[*d*]imidazole 2j.



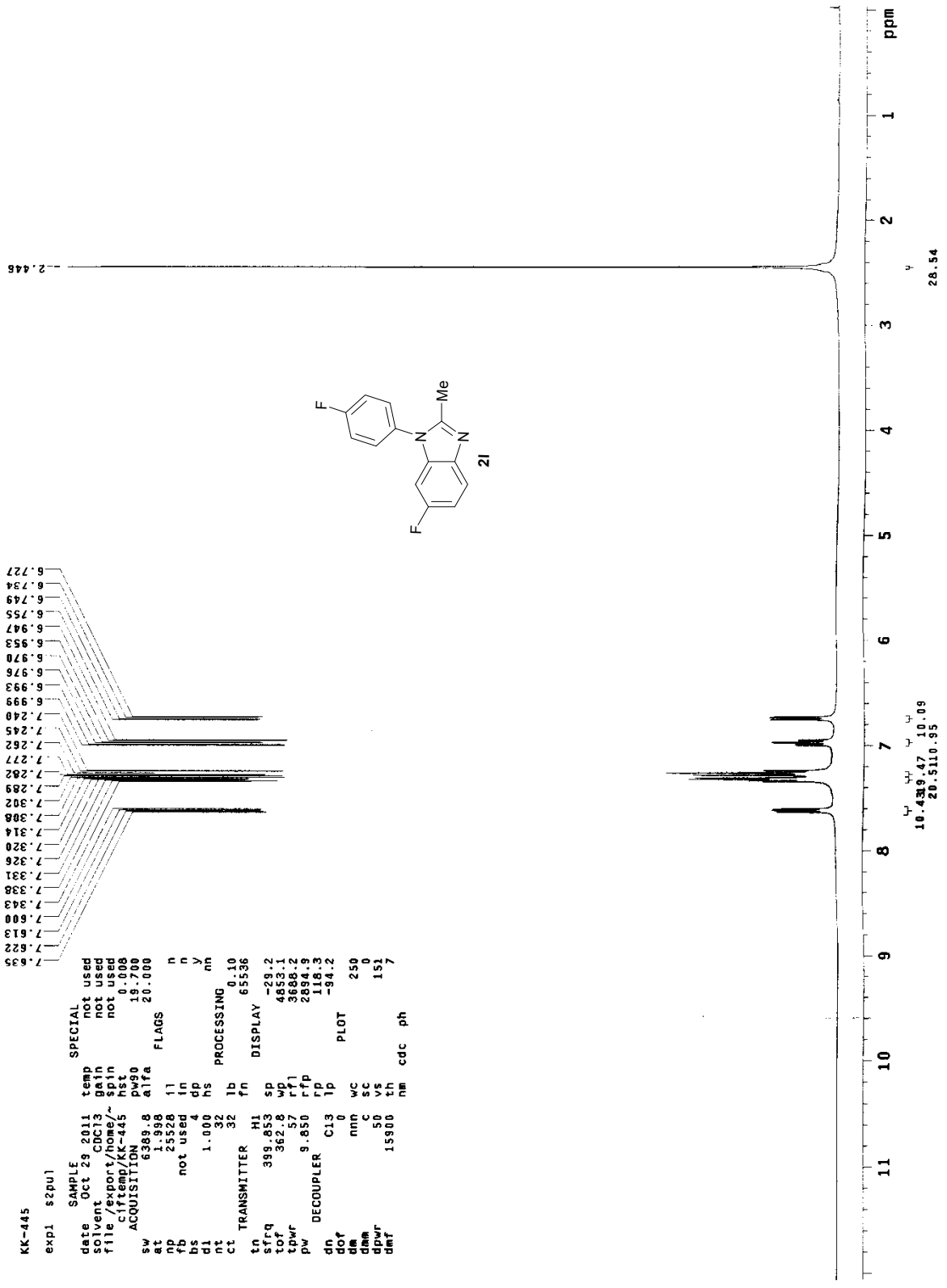
^{1}H NMR ($CDCl_3$) spectra of 6-ethyl-1-(4-ethylphenyl)-2-methyl-1*H*-benzo[*d*]imidazole 2k.



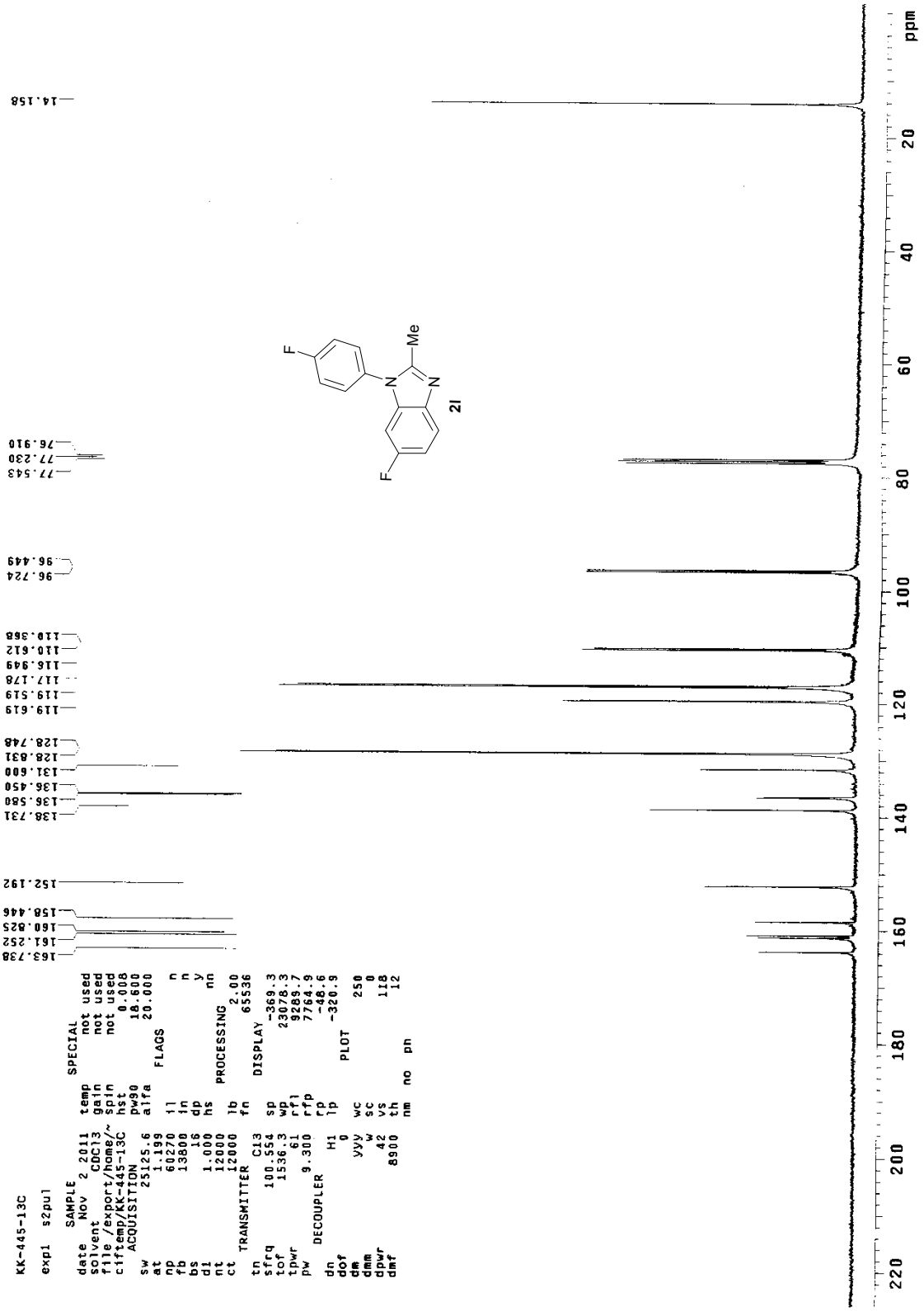
^{13}C NMR ($CDCl_3$) spectra of 6-ethyl-1-(4-ethylphenyl)-2-methyl-1*H*-benzo[*d*]imidazole 2k.



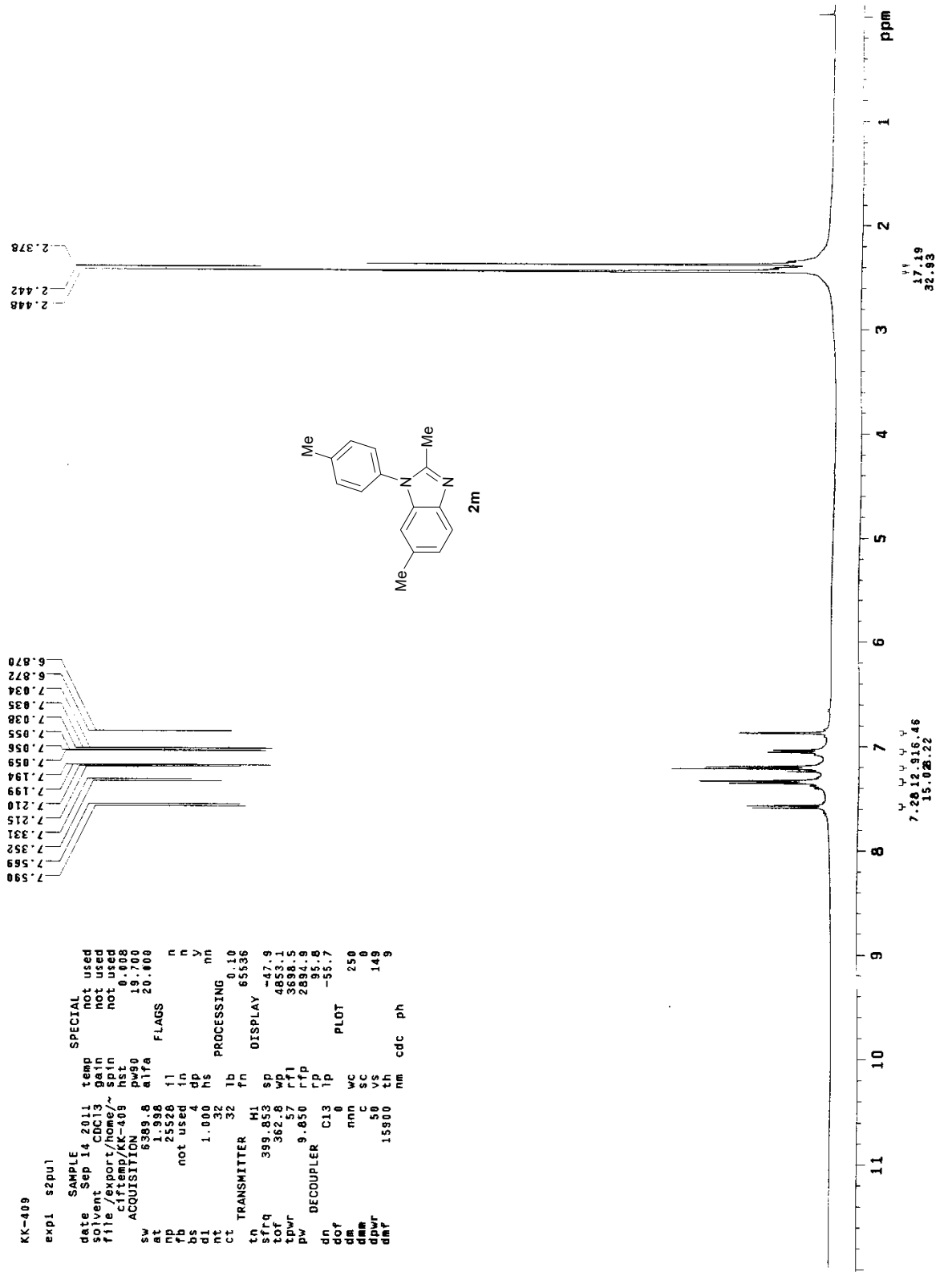
^{1}H NMR ($CDCl_3$) spectra of 6-fluoro-1-(4-fluorophenyl)-2-methyl-1*H*-benzo[*d*]imidazole 2l.



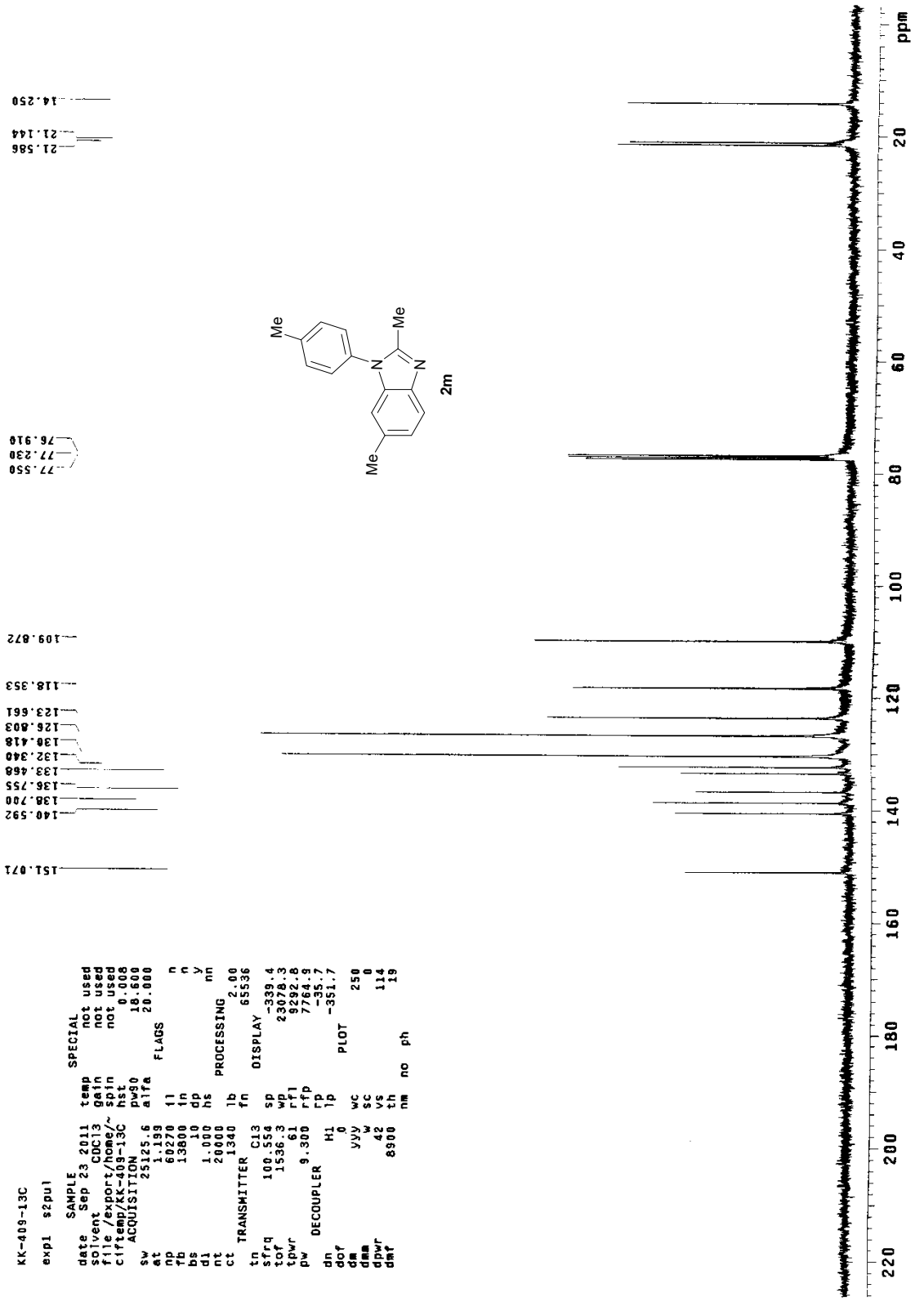
^{13}C NMR ($CDCl_3$) spectra of 6-fluoro-1-(4-fluorophenyl)-2-methyl-1*H*-benzo[*d*]imidazole 2l.



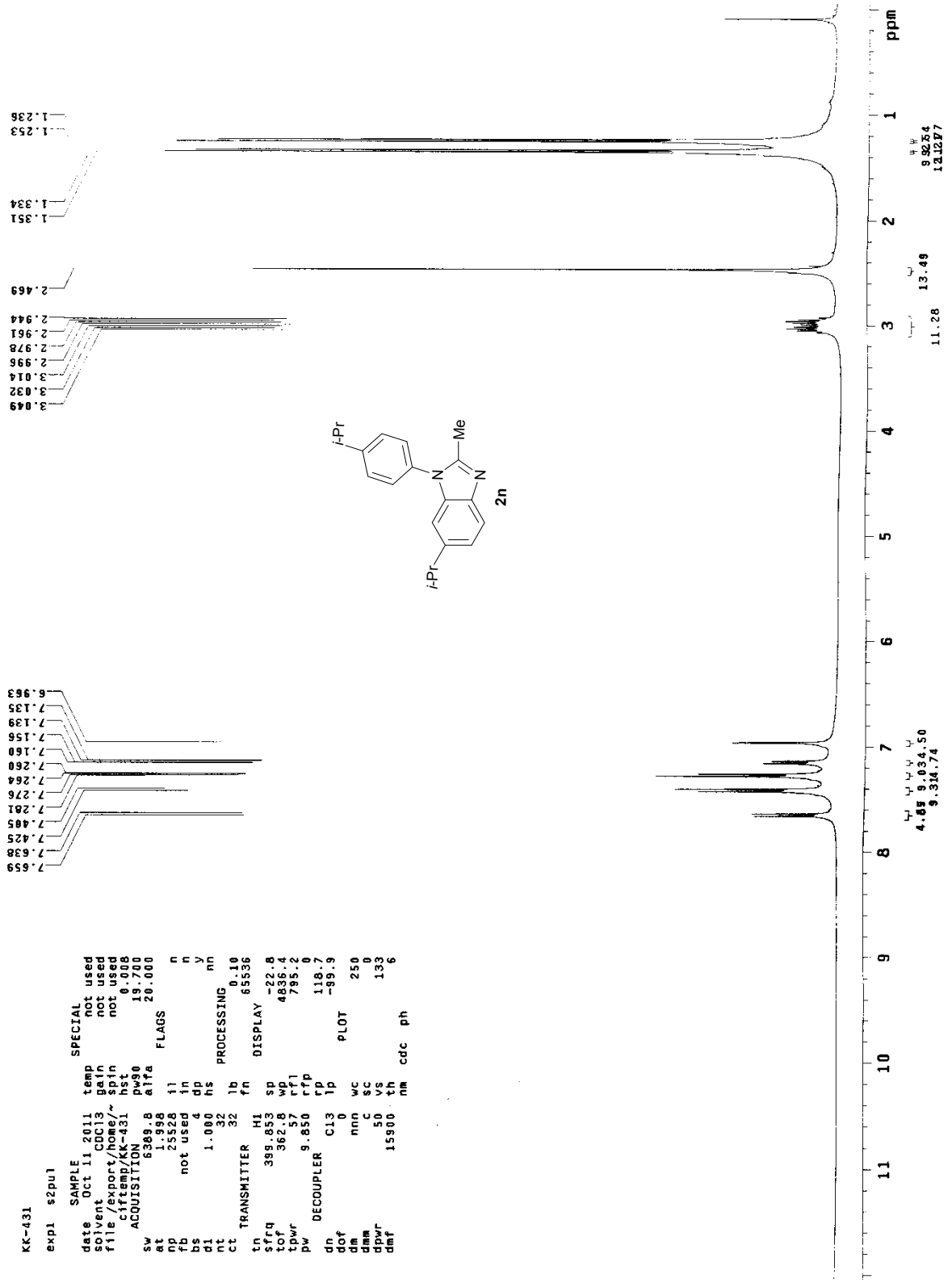
^{1}H NMR ($CDCl_3$) spectra of 2,6-dimethyl-1-(4-methylphenyl)-1*H*-benzo[*d*]imidazole 2m.



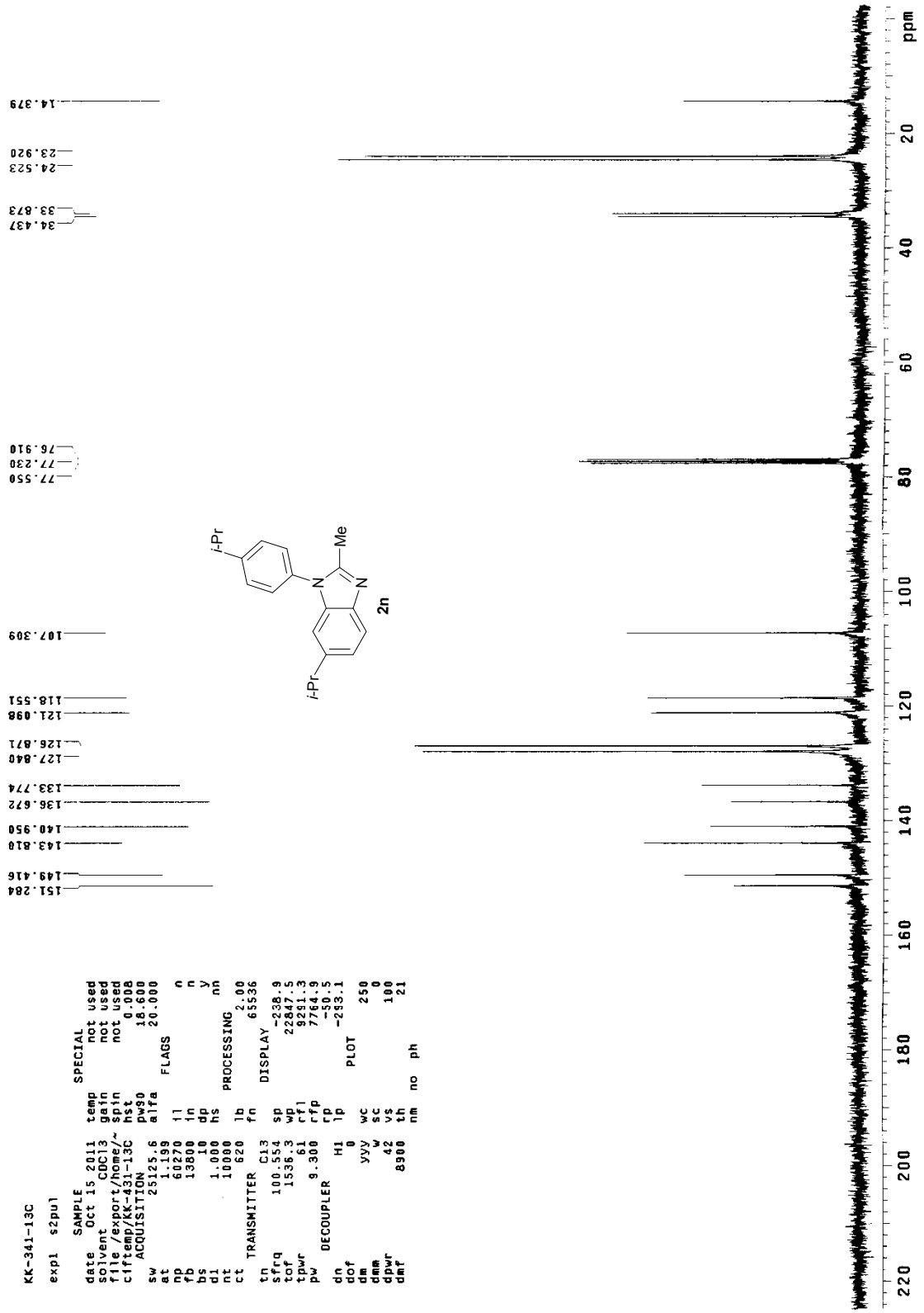
^{13}C NMR ($CDCl_3$) spectra of 2,6-dimethyl-1-(4-methylphenyl)-1*H*-benzo[*d*]imidazole 2m.



^{1}H NMR ($CDCl_3$) spectra of 6-isopropyl-1-(4-isopropylphenyl)-2-methyl-1*H*-benzo[*d*]imidazole 2n.



^{13}C NMR ($CDCl_3$) spectra of 6-isopropyl-1-(4-isopropylphenyl)-2-methyl-1*H*-benzo[*d*]imidazole 2n.



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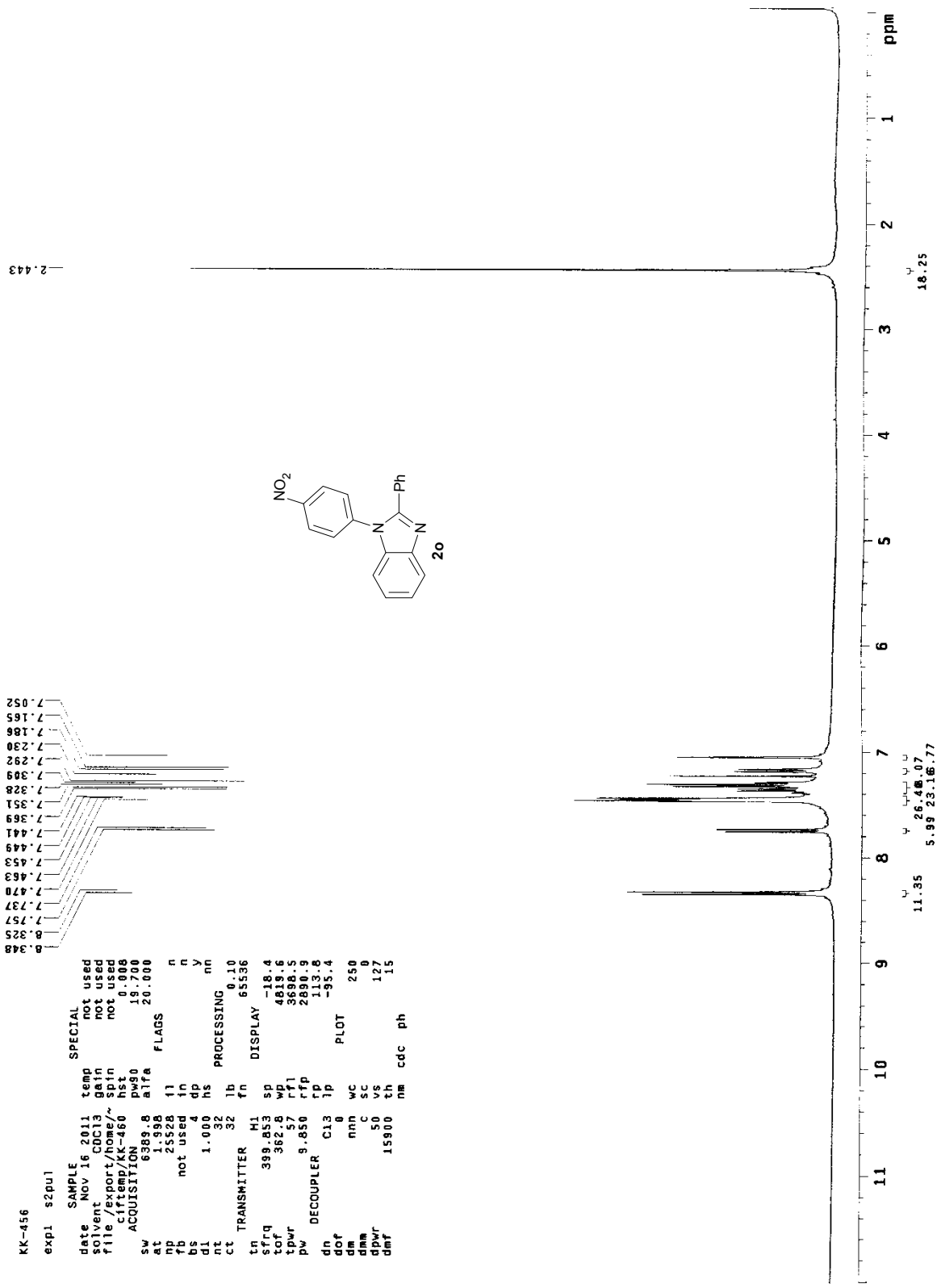
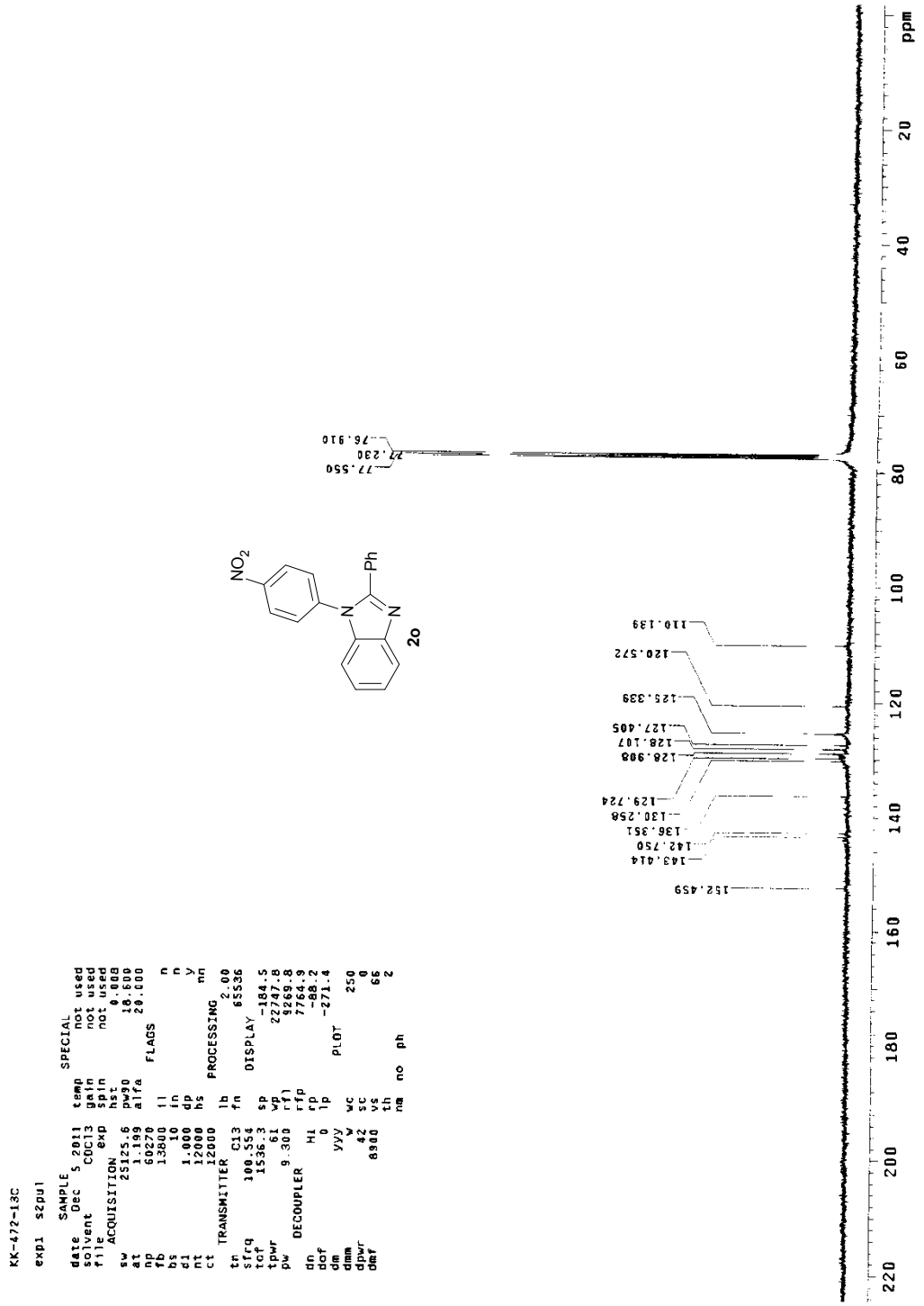
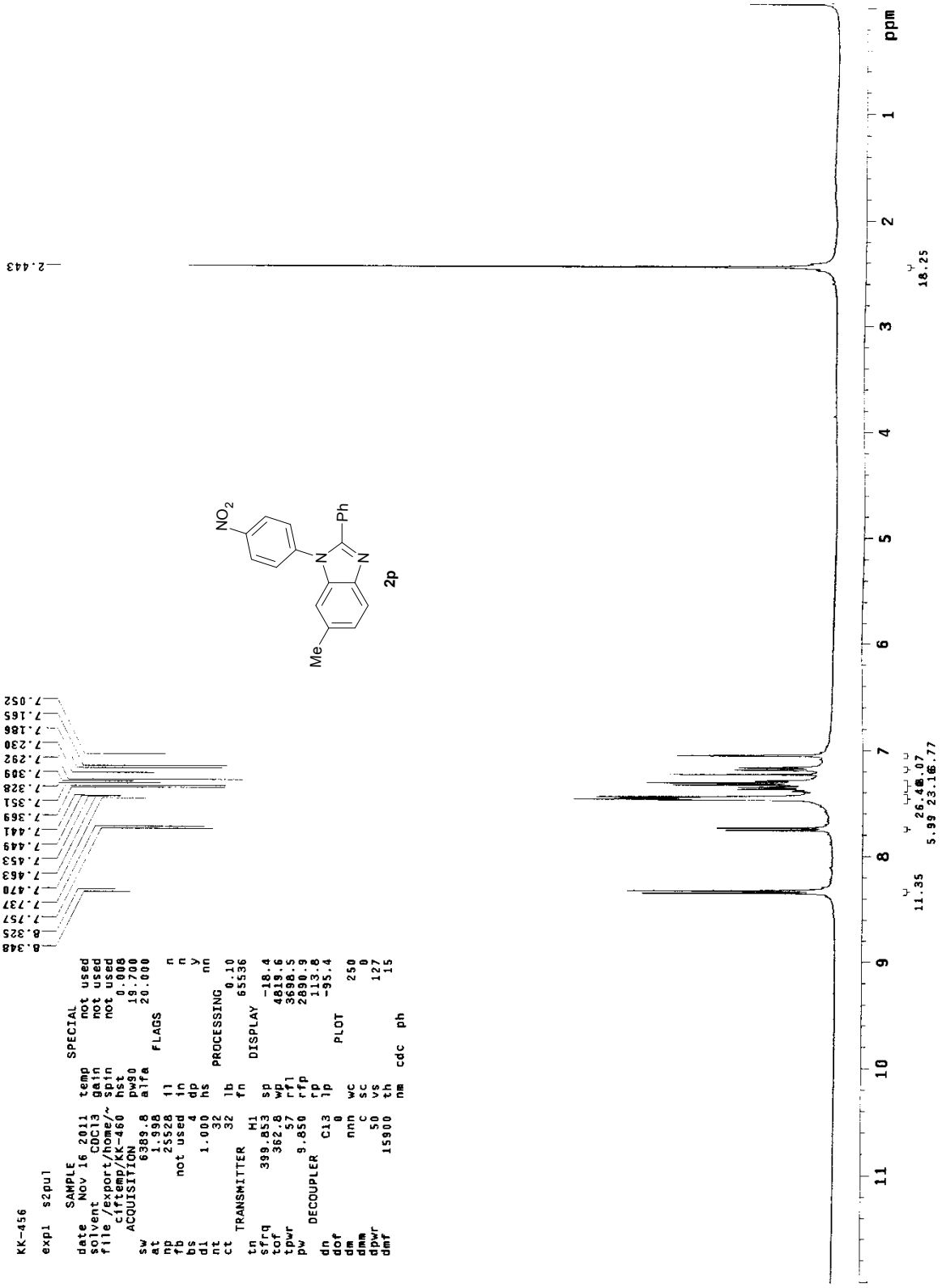


^{13}C NMR ($CDCl_3$) spectra of 1-(4-nitrophenyl)-2-phenyl-1*H*-benzo[*d*]imidazole 2o.



^{1}H NMR ($CDCl_3$) spectra of 6-methyl-1-(4-nitrophenyl)-2-phenyl-1*H*-benzo[*d*]imidazole 2p.



^{13}C NMR ($CDCl_3$) spectra of 6-methyl-1-(4-nitrophenyl)-2-phenyl-1*H*-benzo[*d*]imidazole 2p.