Supporting Information for

Silver-catalyzed intramolecular hydroamination of alkynes in aqueous media: efficient and regioselective synthesis for fused benzimidazoles

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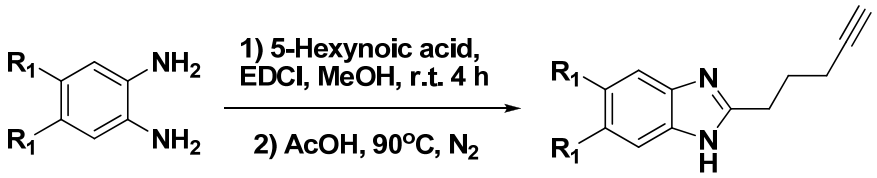
General Information

Commercially available reagents and solvents were used without further purification. Column chromatography was carried out on silica gel. ^{1}H and ^{13}C NMR spectra were obtained on Varian Mercury-300 and/or Varian Mercury-400 spectrometers (TMS as IS). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multipet (m) and broad (br). Low- and high-resolution mass spectra (LRMS and HRMS) were measured on Finnigan MAT 95 spectrometer.

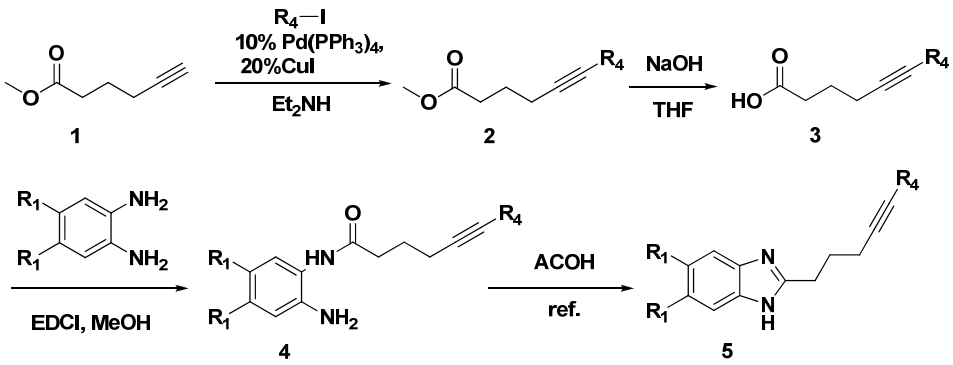
General Procedure for Synthesis of A1-A27

General Procedure for Synthesis of 2-(Pent-4-ynyl)-1*H*-benzo[*d*]imidazoles (A1-A3, A13, A15)



To a solution of substituted or unsubstituted 1, 2-phenylenediamine (2.0 mmol) in methanol (20 ml) was added 5-Hexynoic acid (1.0 equiv.) and EDCI (1.1 equiv.). The reaction mixture was stirred at room temperature for 4-5 h with being monitored by TLC. The solvent was concentrated in vacuums and the amidic intermediate derivatives were precipitated by the addition of water. After filtration, the solid was dried. Then the solid was dissolved in neat acetic acid, and stirred at 90 °C under N_2 for 5 h. The acetic acid was distilled off; the residue was dissolved in EtOAc, and washed by saturated $NaHCO_3$, brine, dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by chromatography on a silica gel column with Petro Ether (PE) / EtOAc (4 / 1, v / v) as eluent afforded products.

General Procedure for Synthesis of 2-(5-Phenylpent-4-ynyl)-1*H*-benzo[*d*]imidazoles (A4-A12, A14)

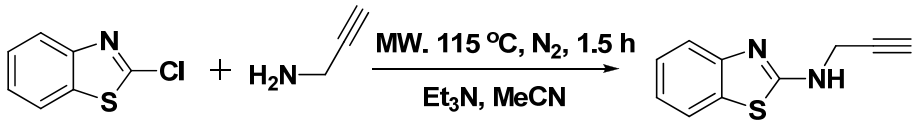


A solution of iodobenzenes (7.83 mmol), Pd $(PPh_3)_4$ (0.1eq.) and CuI (0.2eq) in Et_2NH (20 ml) was stirred at room temperature for 5 minutes. To the resulting mixture, a solution of 1 (0.9eq) in Et_2NH (10 ml) was added. The reaction mixture was stirred at room temperature until completion (TLC, 2 hours). Then, the reaction was diluted with EtOAc, an aqueous saturated solution of NH_4Cl (30 ml) was added, and the mixture extracted with EtOAc (3 x 30ml). The combined organic layers were dried with Na_2SO_4, filtered, and the solvent evaporated under reduced pressure. The crude ester was filtered through a short pad of SiO_2 Petro Ether (PE) / EtOAc (9 / 1, v / v), dissolved in THF (25 ml), 25 ml of aqueous KOH 1M were added and the mixture was vigorously stirred at room temperature until completion (TLC, 3 hours). The reaction mixture was washed with Et_2O and this organic layer was discharged. To the aqueous phase was added aqueous HCl 5% until PH = 2 and was extracted with Et_2O (3 x 50 ml). The combined organic layers were dried over Na_2SO_4, filtered and the solvent evaporated under reduced pressure and get crude acids.

To a solution of substituted or unsubstituted 1, 2-phenylenediamine (2.0 mmol) in methanol (20 ml) was added crude acid (1.0 equiv.) and EDCI (1.1 equiv.). The reaction mixture was stirred at room temperature for 4-5 h with being monitored by TLC. The solvent was concentrated in vacuo and the amidic intermediate derivatives were precipitated by the addition of water. After filtration, the solid was dried. Then the solid was dissolved in neat acetic acid, and stirred at 90 °C under N_2 for 5 h. The acetic acid was distilled off; the residue was dissolved in EtOAc, and washed by saturated $NaHCO_3$, brine, dried over anhydrous Na_2SO_4. Evaporation of the solvent

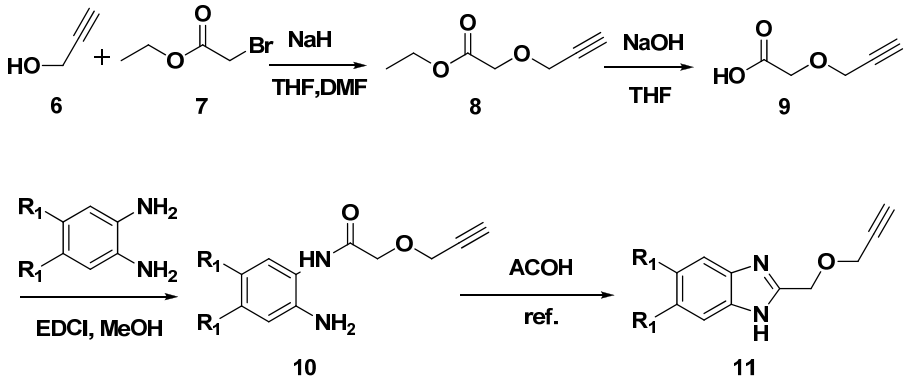
followed by recrystallization from Petro Ether (PE) / EtOAc (2 / 1, v / v), and get pure products.

General Procedure for Synthesis of *N*-(Prop-2-ynyl)benzo[*d*]thiazol-2-amine (A16)



A mixture of 2-chlorobenzo[*d*]thiazole (0.6mmol), prop-2-yn-1-amine (1.5eq.) and Et_3N (1.5eq.) was stirred in CH_3CN (5ml) under N_2. The vial was sealed and the mixture was then irradiated for 1.5 h at 115 °C. After the reaction was cooled to ambient temperature, and evaporation of the solvent followed by chromatography on a silica gel column with Petro Ether (PE) / EtOAc (4 / 1, v / v) as eluent afforded pure product.

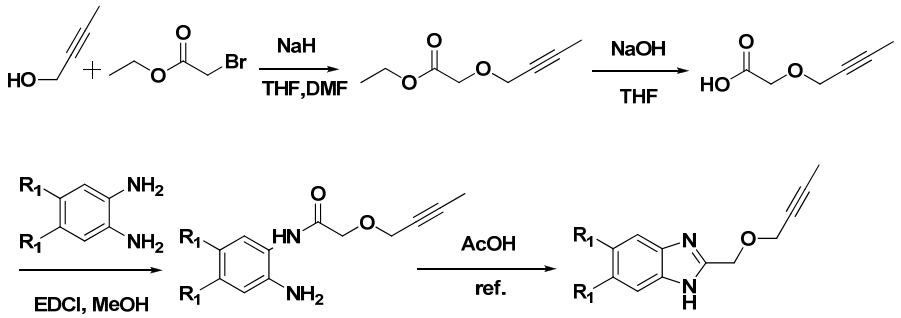
General Procedure for Synthesis of 2-((Prop-2-ynyloxy) methyl)-1*H*-benzo[*d*]imidazoles (A17-A19, A27)



To a solution of propargyl alcohol (6) 1g (17.86 mmol) in THF/DMF (5:1, 20 ml) was added NaH (1.0 equiv.) at 0℃, and the reaction mixture was stirred for 30min. To the resulting mixture, a solution of 7 (2.668g, 16.1 mmol) in THF/DMF (5:1, 10 ml) was added. The reaction mixture was stirred at room temperature until completion (TLC, 4 hours). The solvent was concentrated in vacuums and diluted with EtOAc (50 ml), washed by water, brine, and the solvent evaporated under reduced pressure and get crude product. The residue was dissolved in THF (15 ml), 20 ml of aqueous NaOH 1M were added and the mixture was vigorously stirred at room temperature until completion (TLC, 3 hours). The solvent was concentrated in vacuums and the reaction mixture was washed with Et_2O and this organic layer was discharged. To the aqueous

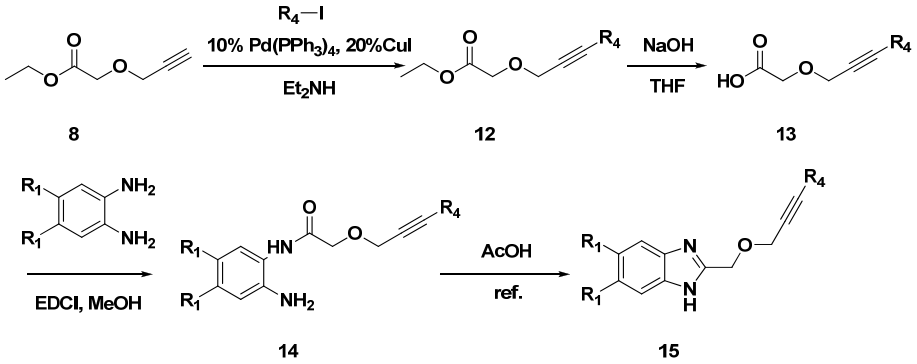
phase was added aqueous HCl 5% until PH = 2 and was extracted with Et_2O (3 x 50 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvent evaporated under reduced pressure and get crude product. The next steps followed by the general procedure (**A1-A3**) using substituted or unsubstituted 1, 2-phenylenediamine and crude acid provided **A17-A19, A27**.

General Procedure for Synthesis of 2-((But-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazole (A20-A22)



Following the general procedure (**A17-A19**) using substituted or unsubstituted 1, 2-phenylenediamine and crude acid provided **A20-A22**.

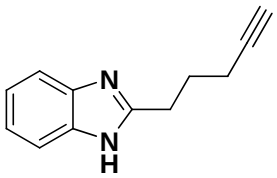
General Procedure for Synthesis of 2-((3-Phenylprop-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazoles (A23-A26)



Following the general procedure (**A17-A19, A4-A12**) using substituted or unsubstituted 1, 2-phenylenediamine and crude acid provided **A23-A26**.

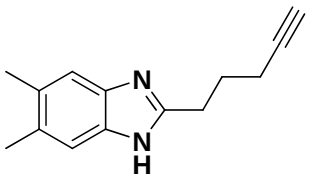
Characterization Data for A1-A27

2-(Pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A1)



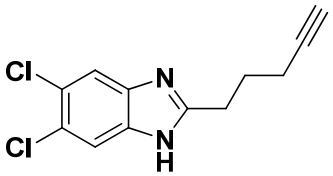
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.91 (t, 1H, CH), 2.07-2.17 (m, 2H, CH_2), 2.26-2.32 (m, 2H, CH_2), 3.14 (t, 2H, CH_2), 7.21-7.25 (m, 2H, ArH), 7.55-7.61 (m, 2H, ArH), 11.06 (brs, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.9, 26.8, 28.0, 69.4, 83.1, 114.6, 122.2, 138.5, 154.6; ESI-MS m/z 185 $[M + H]^+$; HRMS (ESI) calcd. for $C_{12}H_{13}N_2$ $[M + H]^+$ 185.1079, found 185.1085.

5,6-Dimethyl-2-(pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A2)



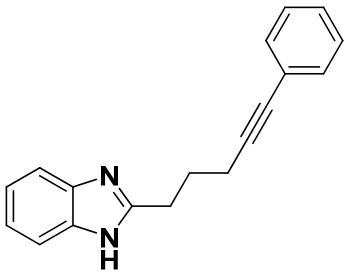
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.94 (t, 1H, CH), 2.03-2.13 (m, 2H, CH_2), 2.24-2.30 (m, 2H, CH_2), 2.35 (s, 6H, CH_3), 3.05 (t, 2H, CH_2), 7.33 (s, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.9, 20.3, 26.8, 27.9, 69.4, 83.3, 114.8, 131.0, 137.0, 153.4; ESI-MS m/z 213 $[M + H]^+$; HRMS (ESI) calcd. for $C_{14}H_{17}N_2$ $[M + H]^+$ 213.1392, found 213.1389.

5, 6-Dichloro-2-(pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A3)



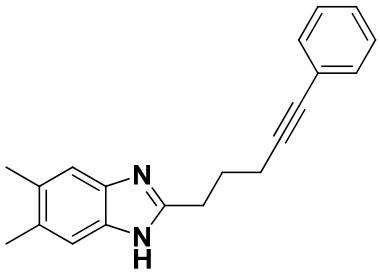
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.02 (m, 3H, CH, CH_2), 2.30-2.35 (m, 2H, CH_2), 3.06 (t, 2H, CH_2), 7.65 (s, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.8, 26.3, 27.8, 69.9, 82.9, 126.4, 156.2; ESI-MS m/z 253 $[M + H]^+$; HRMS (ESI) calcd. for $C_{12}H_{11}N_2Cl_2$ $[M + H]^+$ 253.0299, found 253.0306.

2-(5-Phenylpent-4-ynyl)-1*H*-benzo[*d*]imidazole (A4)



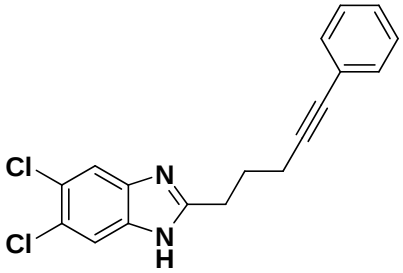
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.11-2.21 (m, 2H, CH_2), 2.49 (t, 2H, CH_2), 3.13 (t, 2H, CH_2), 7.18-7.29 (m, 7H, ArH), 7.53-7.58 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9, 27.0, 28.2, 81.7, 88.8, 114.6, 122.2, 123.5, 127.7, 128.2, 131.5, 154.4; EI-MS m/z 260 $[M]^+$; HRMS (EI) calcd. for $C_{18}H_{16}N_2$ $[M]^+$ 260.1313, found 260.1303.

5,6-Dimethyl-2-(5-phenylpent-4-ynyl)-1*H*-benzo[*d*]imidazole (A5)



^{1}H NMR (300 MHz, DMSO-d_6,): δ 2.02-2.07 (m, 2H, CH_2), 2.28 (s, 6H, CH_3), 2.54 (t, 2H, CH_2), 2.94 (t, 2H, CH_2), 7.18-7.40 (m, 7H, ArH), 12.08 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.3, 19.9, 26.6, 27.6, 81.0, 90.0, 110.9, 118.3, 123.2, 127.9, 128.5, 128.7, 131.2, 153.3; EI-MS m/z 288 $[M]^+$; HRMS (EI) calcd. for $C_{20}H_{20}N_2$ $[M]^+$ 288.1626, found 288.1627.

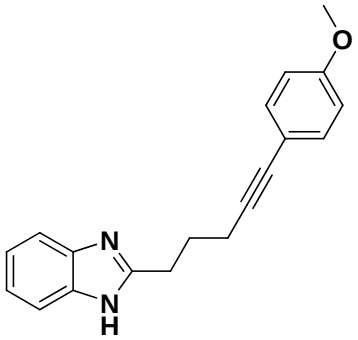
5, 6-Dichloro-2-(5-phenylpent-4-ynyl)-1*H*-benzo[*d*]imidazole (A6)



^{1}H NMR (300 MHz, $CDCl_3$): δ 2.10-2.17 (m, 2H, CH_2), 2.48-2.52 (m, 2H, CH_2), 3.11 (t, 2H, CH_2), 7.18-7.26 (m, 5H, ArH), 7.59 (s, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9, 26.8, 28.1, 82.0, 88.2, 115.9, 123.2, 126.3, 127.8, 128.2, 131.3, 137.9, 156.6; EI-MS m/z 328 $[M]^+$; HRMS (EI) calcd. for $C_{18}H_{14}N_2Cl_2$ $[M]^+$ 328.0534, found

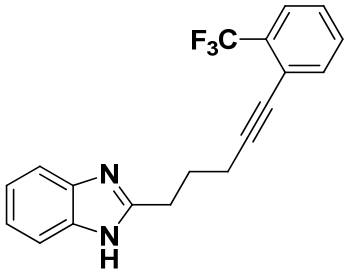
328.0532.

2-(5-(4-Methoxyphenyl)pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A7)



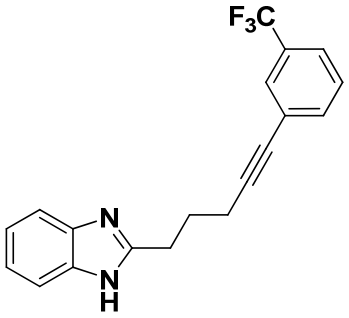
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.12-2.19 (m, 2H, CH_2), 2.47 (t, 2H, CH_2), 3.14 (t, 2H, CH_2), 3.76 (s, 3H, CH_3), 6.73-6.75 (m, 2H, ArH), 7.18-7.23 (m, 4H, ArH), 7.54-7.57 (m, 2H, ArH); ^{13}C NMR δ (100 MHz, $CDCl_3$): 19.0, 27.1, 28.2, 55.2, 81.5, 87.1, 113.7, 114.6, 115.6, 122.2, 132.8, 138.5, 154.5, 159.0; EI-MS m/z 290 $[M]^+$; HRMS (EI) calcd. for $C_{19}H_{18}N_2O$ $[M]^+$ 290.1419, found 290.1421.

2-(5-(2-(Trifluoromethyl)phenyl)pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A8)



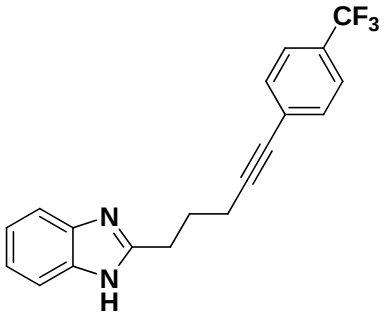
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.14-2.24 (m, 2H, CH_2), 2.56 (t, 2H, CH_2), 3.16 (t, 2H, CH_2), 7.20-7.30 (m, 2H, ArH), 7.35-7.66 (m, 6H, ArH); ^{13}C NMR δ (100 MHz, $CDCl_3$): 18.9, 26.6, 27.7, 77.9, 95.0, 121.9, 122.2, 125.7 (d, J = 5.1 Hz), 127.5, 131.4, 134.0, 154.1; EI-MS m/z 328 $[M]^+$; HRMS (EI) calcd. for $C_{19}H_{15}N_2F_3$ $[M]^+$ 328.1187, found 328.1193.

2-(5-(3-(Trifluoromethyl)phenyl)pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A9)



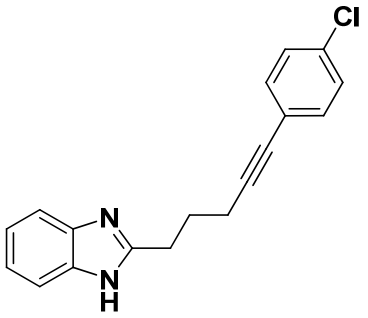
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.16-2.25 (m, 2H, CH_2), 2.52 (t, 2H, CH_2), 3.16 (t, 2H, CH_2), 7.18-7.24 (m, 2H, ArH), 7.30-7.35 (m, 2H, ArH), 7.46-7.49 (d, *J* = 7.5 Hz, 1H, ArH), 7.52-7.58 (m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9, 27.0, 28.3, 80.2, 90.5, 114.6, 122.3, 124.2 (d, *J* = 3.2 Hz), 124.4, 125.0, 128.1 (d, *J* = 3.8 Hz), 128,6, 130.6 (d, *J* = 32.2 Hz) 134.6, 138.5, 154.4; EI-MS m/z 328 $[M]^+$; HRMS (EI) calcd. for $C_{19}H_{15}N_2F_3$ $[M]^+$ 328.1187, found 328.1184.

2-(5-(4-(Trifluoromethyl)phenyl)pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A10)



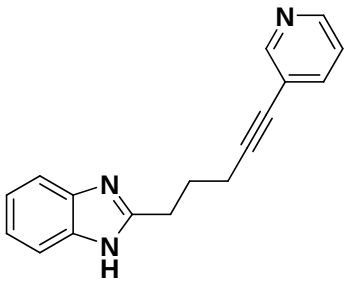
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.16-2.26 (m, 2H, CH_2), 2.51 (t, 2H, CH_2), 3.18 (t, 2H, CH_2), 7.19-7.23 (m, 4H, ArH), 7.41-7.43 (d, *J* = 8.1 Hz, 2H, ArH), 7.56-7.59 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0, 27.0, 28.3, 80.5, 91.4, 114.5, 122.3, 123.9 (d, *J* = 270.8 Hz), 125.0 (d, *J* = 3.6 Hz), 127.2, 129.3 (d, *J* = 32.6 Hz), 131.6, 138.5, 154.4; EI-MS m/z 328 $[M]^+$; HRMS (EI) calcd. for $C_{19}H_{15}N_2F_3$ $[M]^+$ 328.1187, found 328.1186.

2-(5-(4-Chlorophenyl)pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A11)



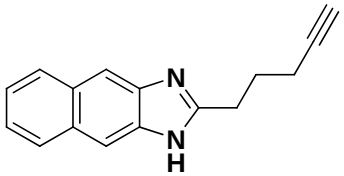
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.14-2.18 (m, 2H, CH_2), 2.45-2.48 (m, 2H, CH_2), 3.17 (m, 2H, CH_2), 7.08-7.15 (m, 4H, ArH), 7.21 (br, 2H, ArH), 7.56 (br, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9, 26.9, 27.7, 80.7, 89.5, 114.4, 121.8, 123.1, 128.4, 132.6, 133.6, 136.8, 154.0; EI-MS m/z 294 $[M]^+$; HRMS (EI) calcd. for $C_{18}H_{15}N_2Cl$ $[M]^+$ 294.0924, found 294.0890.

2-(5-(Pyridin-3-yl)pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A12)



^{1}H NMR (300 MHz, $CDCl_3$): δ 2.15-2.24 (m, 2H, CH_2), 2.52 (t, 2H, CH_2), 3.13 (t, 2H, CH_2), 7.01-7.03 (m, 2H, ArH), 7.17-7.23 (m, 2H, ArH), 7.52-7.57 (m, 2H, ArH), 8.44-8.46 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9, 26.7, 28.1, 79.027, 95.0, 114.6, 122.0, 125.9, 132.3, 148.9, 154.3; EI-MS m/z 261 $[M]^+$; HRMS (EI) calcd. for $C_{17}H_{15}N_3$ $[M]^+$ 261.1266, found 261.1257.

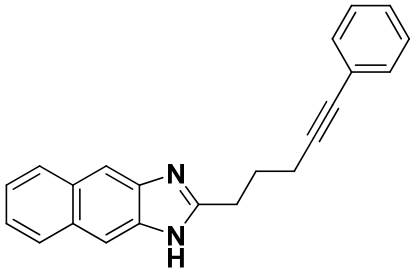
2-(Pent-4-ynyl)-1*H*-naphtho[2,3-*d*]imidazole (A13)



^{1}H NMR (300 MHz, $CDCl_3$): δ 2.04 (m, 1H, CH), 2.14-2.19 (m, 2H, CH_2), 2.35-2.39 (m, 2H, CH_2), 3.15 (t, 2H, CH_2), 7.39-7.42 (m, 2H, ArH), 7.92-7.96 (m, 2H, ArH),

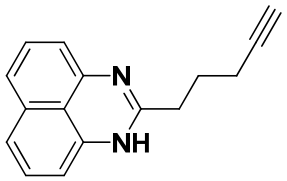
7.99 (s, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.9, 26.3, 28.1, 69.8, 83.2, 110.9, 123.9, 127.9, 130.4, 158.0; ESI-MS m/z 235 $[M + H]^+$; HRMS (ESI) calcd. for $C_{16}H_{15}N_2$ $[M + H]^+$ 235.1235, found 235.1232.

2-(5-Phenylpent-4-ynyl)-1*H*-naphtho[2,3-*d*]imidazole (A14)



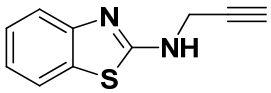
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.26-2.31 (m, 2H, CH_2), 2.66 (t, 2H, CH_2), 3.41 (t, 2H, CH_2), 7.19-7.25 (m, 5H, ArH), 7.55-7.58 (m, 2H, ArH), 8.15-8.18 (m, 2H, ArH), 8.32 (s, 2H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.3, 25.3, 26.0, 81.5, 89.0, 110.4, 122.7, 125.5, 127.9, 128.1, 128.3, 130.6, 130.7, 131.1, 158.3; EI-MS m/z 310 $[M]^+$; HRMS (EI) calcd. for $C_{22}H_{18}N_2$ $[M]^+$ 310.1470, found 310.1468.

2-(Pent-4-ynyl)-1*H*-perimidine (A15)



^{1}H NMR (300 MHz, $CDCl_3$): δ 1.92-2.00 (m, 3H, CH, CH_2), 2.26-2.31 (m, 2H, CH_2), 2.47 (t, 2H, CH_2), 6.52-6.54 (m, 2H, ArH), 7.07-7.16 (m, 4H, ArH); ^{13}C NMR δ (100 MHz, $CDCl_3$): 17.9, 25.8, 34.2, 69.6, 83.0, 107.7, 119.4, 121.8, 128.2, 135.3, 140.6, 156.9; EI-MS m/z 234 $[M]^+$; HRMS (EI) calcd. for $C_{16}H_{14}N_2$ $[M]^+$ 234.1157, found 234.1149.

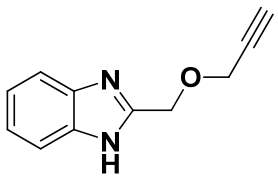
***N*-(Prop-2-ynyl)benzo[*d*]thiazol-2-amine (A16)**



^{1}H NMR (300 MHz, $CDCl_3$): δ 2.33 (t, 1H, CH), 4.29 (d, J = 2.7 Hz, 2H, CH_2), 7.11-7.16 (t, 1H, ArH), 7.27-7.35 (t, 1H, ArH), 7.60-7.63 (d, J = 8.1 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.5, 72.5, 79.1, 119.4, 120.9, 122.1, 126.0, 130.8,

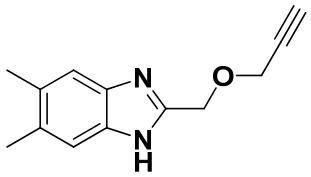
152.0, 166.2; EI-MS m/z 188 $[M]^+$; HRMS (EI) calcd. for $C_{10}H_8N_2S$ $[M]^+$ 188.0408, found 188.0406.

2-((Prop-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazole (A17)



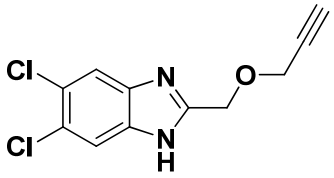
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.39 (t, 1H, CH), 4.24 (d, J = 2.1 Hz, 2H, CH_2), 4.97 (s, 2H, CH_2), 7.27-7.29 (m, 2H, ArH), 7.64-7.68 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 58.0, 65.0, 75.5, 78.5, 115.1, 122.5, 138.2, 151.0; EI-MS m/z 186 $[M]^+$; HRMS (EI) calcd. for $C_{11}H_{10}N_2O$ $[M]^+$ 186.0793, found 186.0787.

5,6-Dimethyl-2-((prop-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazole (A18)



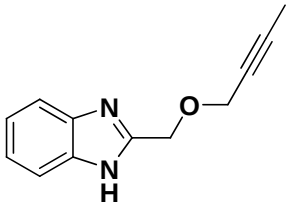
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 6H, CH_3), 2.49 (t, 1H, CH), 4.28 (d, J = 2.1 Hz, 2H, CH_2), 4.88 (s, 2H, CH_2), 7.35 (s, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.3, 58.2, 65.5, 75.5, 78.7, 115.2, 131.6, 136.8, 149.8; EI-MS m/z 214 $[M]^+$; HRMS (EI) calcd. for $C_{13}H_{14}N_2O$ $[M]^+$ 214.1106, found 214.1099.

5,6-Dichloro-2-((prop-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazole (A19)



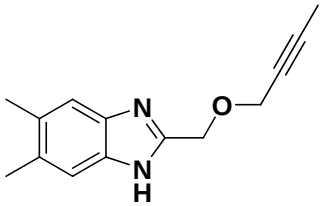
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.49 (t, 1H, CH), 4.30 (d, J = 2.7 Hz, 2H, CH_2), 4.89 (s, 2H, CH_2), 7.68 (s, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 58.7, 65.3, 76.1, 78.2, 126.8, 153.1; EI-MS m/z 254 $[M]^+$; HRMS (EI) calcd. for $C_{11}H_8Cl_2N_2O$ $[M]^+$ 254.0014, found 254.0012.

2-((But-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazole (A20)



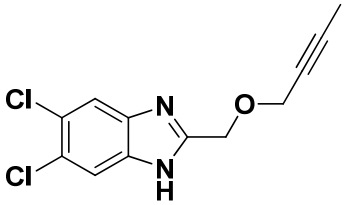
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.76 (m, 3H, CH_3), 4.23 (m, 2H, CH_2), 4.91 (s, 2H, CH_2), 7.23-7.26 (m, 2H, ArH), 7.59-7.62 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.3, 58.8, 65.0, 74.0, 83.7, 115.1, 122.4, 138.3, 151.4; EI-MS m/z 200 $[M]^+$; HRMS (EI) calcd. for $C_{12}H_{12}N_2O$ $[M]^+$ 200.0950, found 200.0950.

2-((But-2-ynyloxy)methyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (A21)



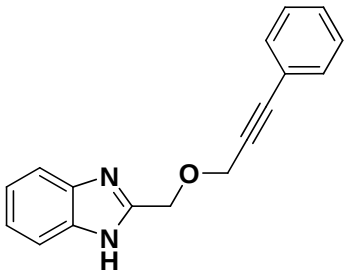
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.79 (t, 3H, CH_3), 2.36 (s, 6H, CH_3), 4.22 (m, 2H, CH_2), 4.88 (s, 2H, CH_2), 7.37 (s, 2H, ArH); ^{13}C NMR δ (100 MHz, $CDCl_3$): 3.4, 20.3, 58.7, 65.2, 74.2, 83.7, 131.4, 150.3; EI-MS m/z 228 $[M]^+$; HRMS (EI) calcd. for $C_{14}H_{16}N_2O$ $[M]^+$ 228.1263, found 228.1270.

2-((But-2-ynyloxy)methyl)-5,6-dichloro-1*H*-benzo[*d*]imidazole (A22)



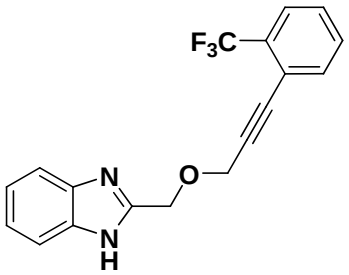
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.83 (s, 3H, CH_3), 4.28 (s, 2H, CH_2), 4.88 (s, 2H, CH_2), 7.68 (s, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.6, 59.3, 65.1, 73.7, 84.4, 126.6, 153.5; EI-MS m/z 268 [M]; HRMS (EI) calcd. for $C_{12}H_{10}Cl_2N_2O$ $[M]^+$ 268.0170, found 268.0177.

2-((3-Phenylprop-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazole (A23)



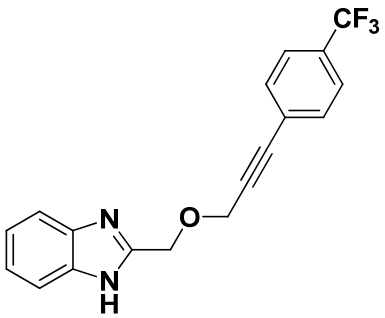
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.50 (s, 2H, CH_2), 5.01 (s, 2H, CH_2), 7.24-7.30 (m, 5H, ArH), 7.31-7.35 (m, 2H, ArH), 7.60-7.61 (br, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 59.2, 65.6, 83.9, 87.3, 122.0, 122.6, 128.2, 128.6, 131.7, 151.1; EI-MS m/z 262 $[M]^+$; HRMS (EI) calcd. for $C_{17}H_{14}N_2O$ $[M]^+$ 262.1106, found 262.1098.

2-((3-(2-(Trifluoromethyl)phenyl)prop-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazole (A24)



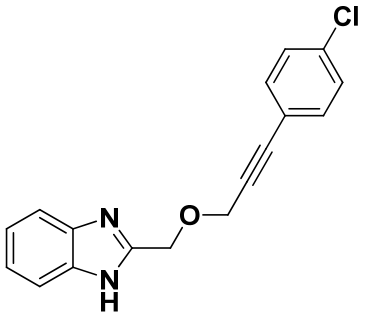
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.52 (s, 2H, CH_2), 5.02 (s, 2H, CH_2), 7.22-7.27 (m, 2H, ArH), 7.37-7.41 (m, 3H, ArH), 7.59-7.63 (m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 59.0, 65.5, 83.1, 89.6, 113.0, 120.2, 122.6, 123.4 (d, J = 271.4 Hz), 125.7 (d, J = 5.0 Hz), 127.4, 128.3, 131.35, 131.4 (d, J = 30.0 Hz), 134.0, 151.0; EI-MS m/z 330 $[M]^+$; HRMS (EI) calcd. for $C_{18}H_{13}F_3N_2O$ $[M]^+$ 330.0980, found 330.0973.

2-((3-(4-(Trifluoromethyl)phenyl)prop-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazole (A25)



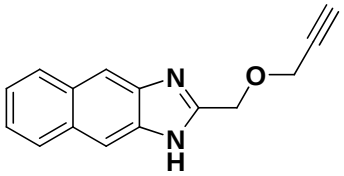
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.53 (s, 2H, CH_2), 5.00 (s, 2H, CH_2), 7.25-7.28 (m, 2H, ArH), 7.39-7.42 (d, J = 7.8 Hz, 2H, ArH), 7.51-7.53 (d, J = 8.4 Hz, 2H, ArH), 7.60-7.62 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 59.1, 65.8, 86.0, 86.3, 122.8, 125.2 (d, J = 3.6 Hz), 125.8, 131.9, 150.8; EI-MS m/z 330 $[M]^+$; HRMS (EI) calcd. for $C_{18}H_{13}F_3N_2O$ $[M]^+$ 330.0980, found 330.0985.

2-((3-(4-Chlorophenyl)prop-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazole (A26)



^{1}H NMR (300 MHz, $CDCl_3$): δ 4.50 (s, 2H, CH_2), 4.98 (s, 2H, CH_2), 7.24-7.28 (m, 6H, ArH), 7.59-7.62 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 59.2, 65.7, 84.8, 86.3, 115.2, 120.5, 122.7, 128.6, 132.9, 134.7, 150.9; EI-MS m/z 296 $[M]^+$; HRMS (EI) calcd. for $C_{17}H_{13}ClN_2O$ $[M]^+$ 296.0716, found 296.0710.

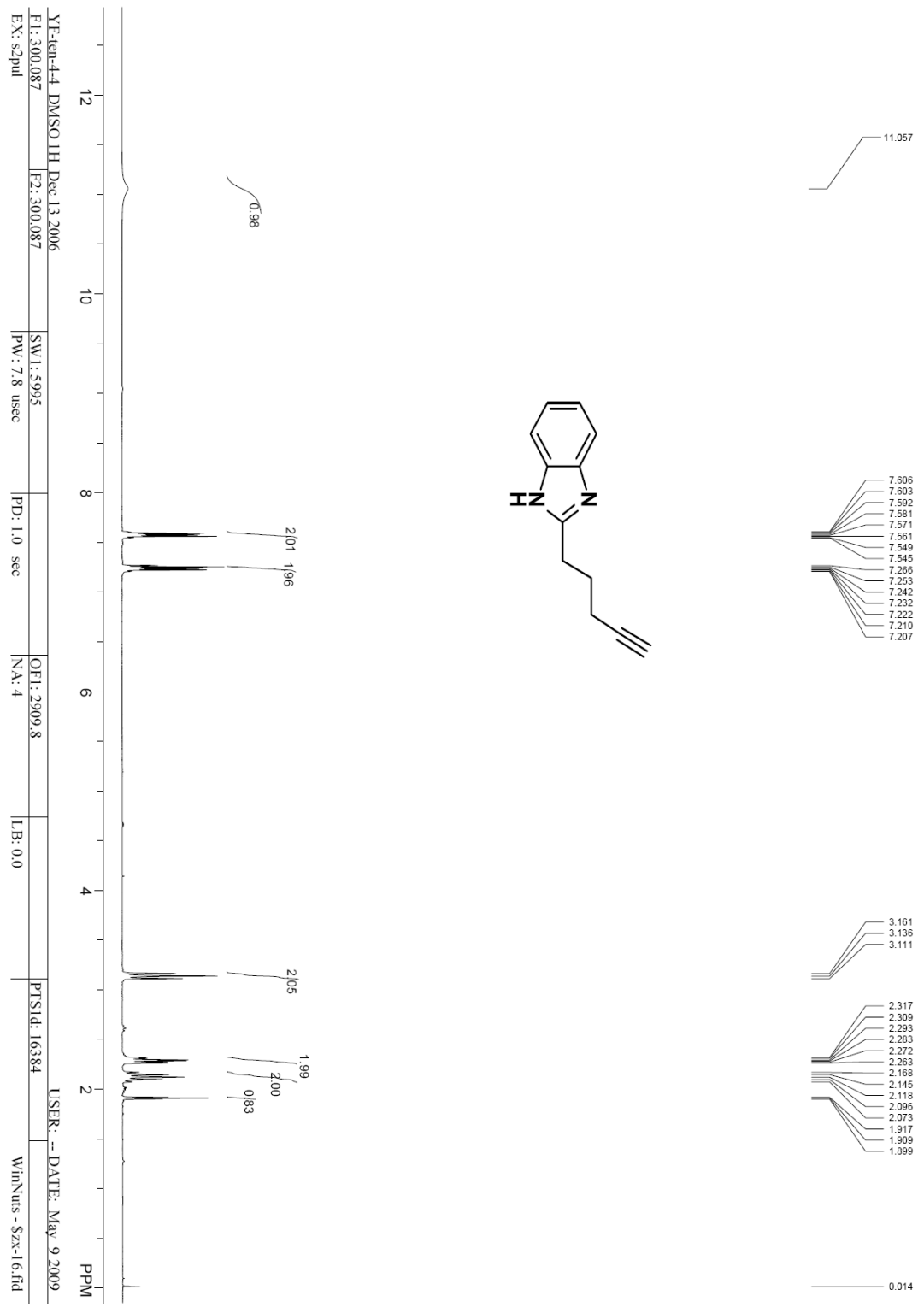
2-((Prop-2-ynyloxy)methyl)-1*H*-naphtho[2,3-*d*]imidazole (A27)

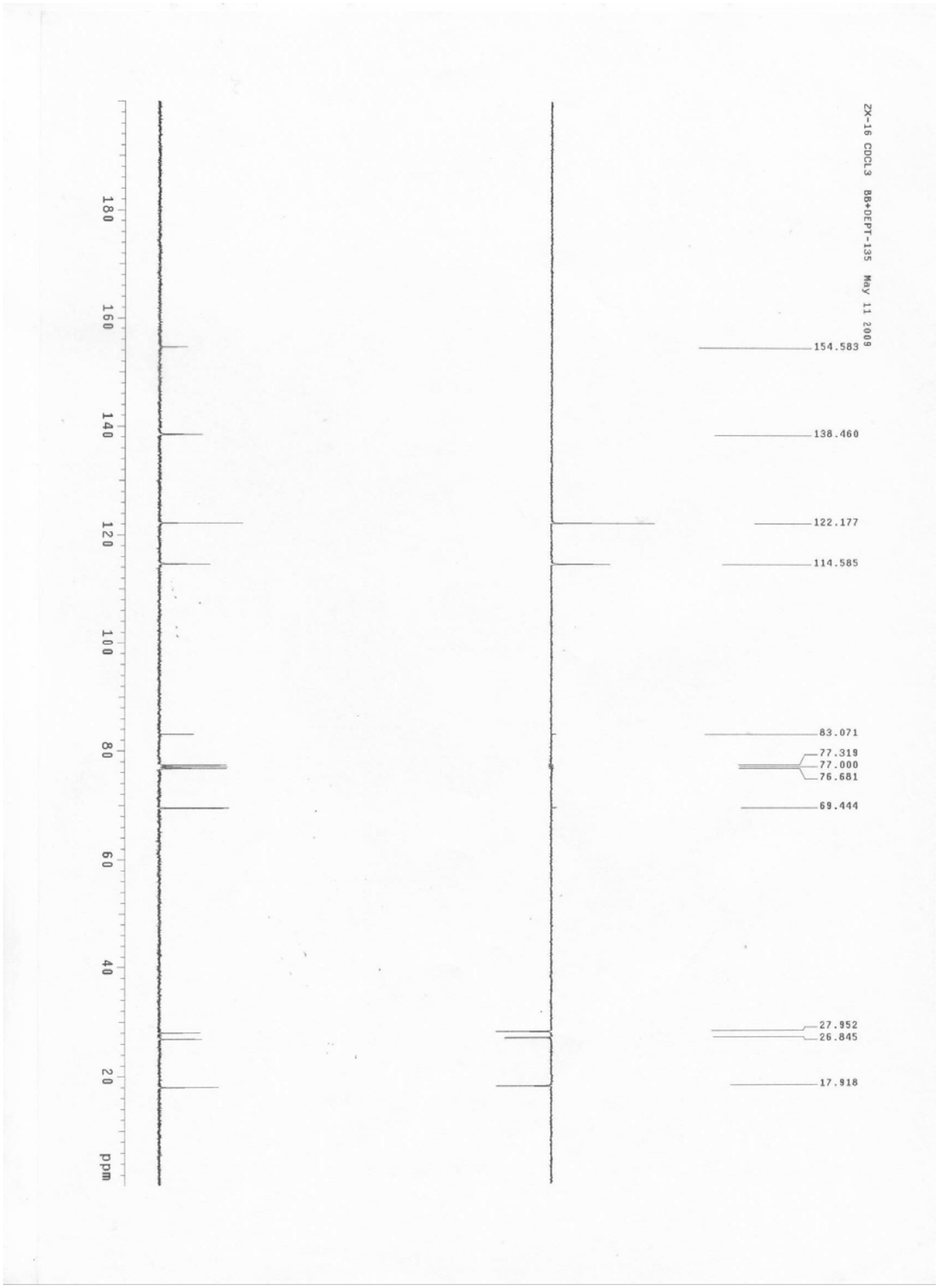


^{1}H NMR (300 MHz, $CDCl_3$): δ 2.49 (s, 1H, CH), 4.34 (s, 2H, CH_2), 4.99 (s, 2H, CH_2), 7.39-7.43 (m, 2H, ArH), 7.93-7.96 (m, 2H, ArH), 8.04 (s, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 58.7, 65.7, 75.9, 78.4, 124.0, 127.9, 130.5, 155.2; EI-MS m/z 236 $[M]^+$; HRMS (EI) calcd. for $C_{15}H_{12}N_2O$ $[M]^+$ 236.0950, found 236.0944.

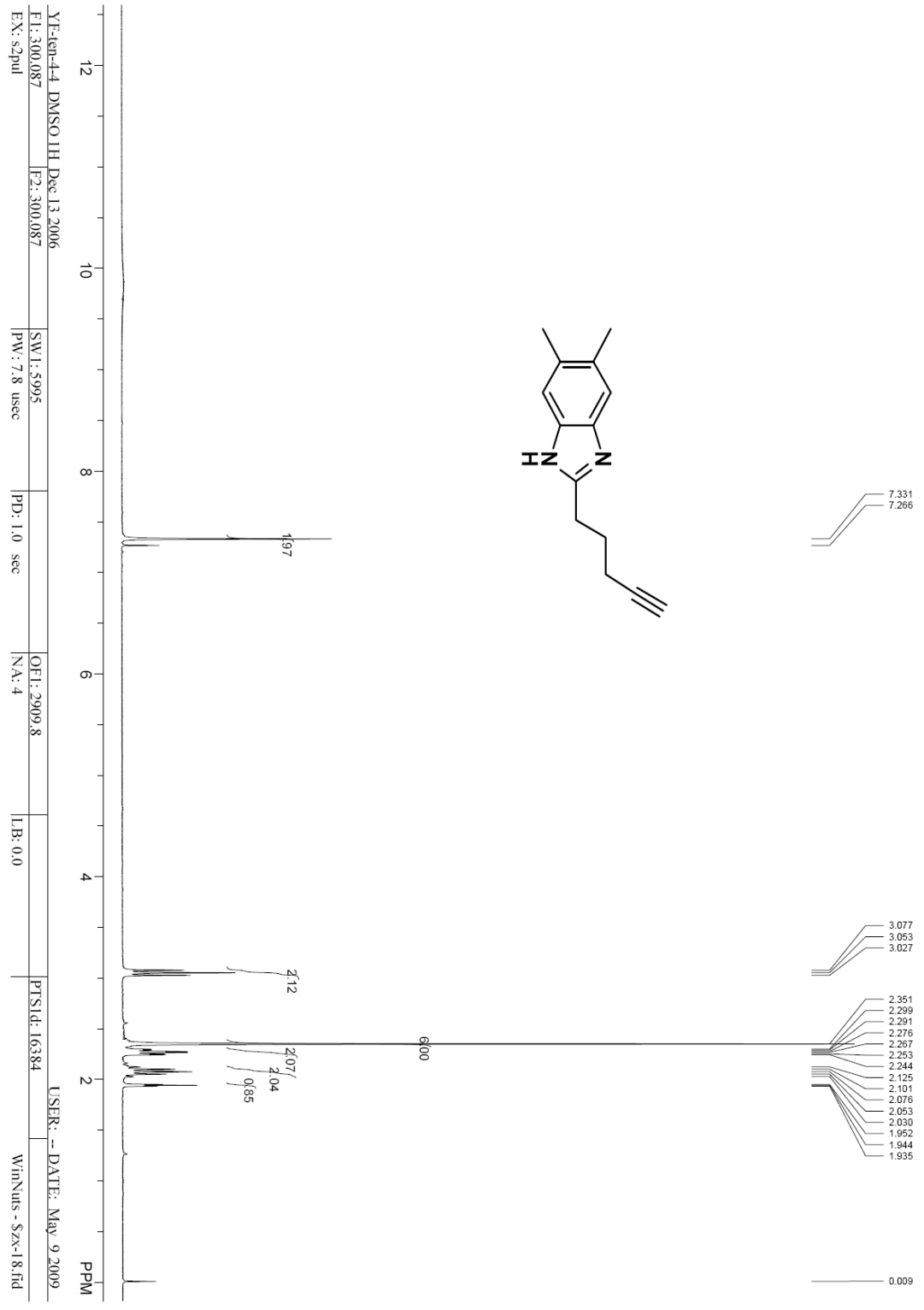
Copies of ^{1}H NMR and ^{13}C NMR of A1-A27

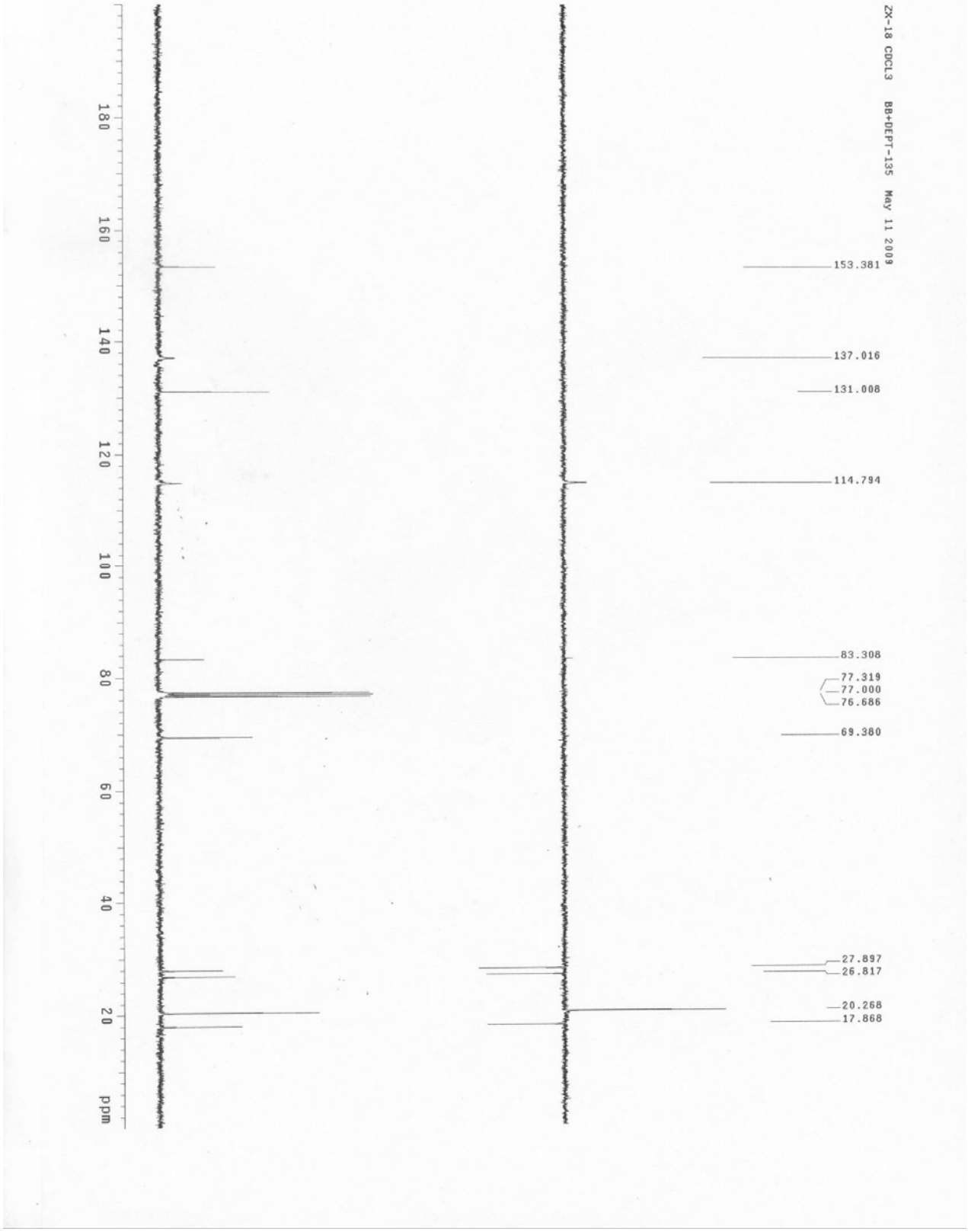
2-(Pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A1)



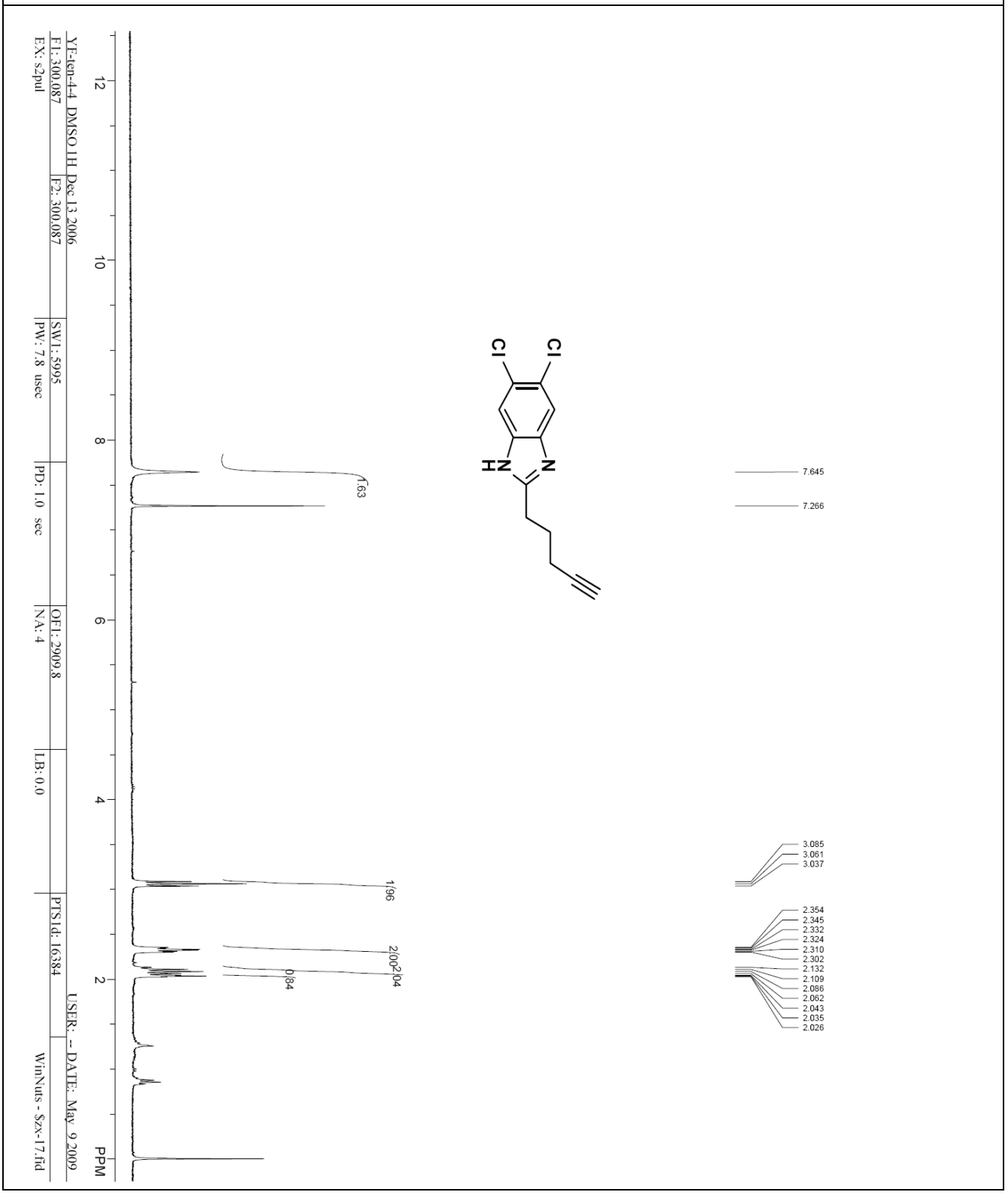

ZX-16 CDCL3 BB+DEPT-135 May 11 2009
154.583
138.460
122.177
114.585
83.071
77.319
77.000
76.681
69.444
27.952
26.845
17.918
180
160
140
120
100
80
60
40
20
ppm

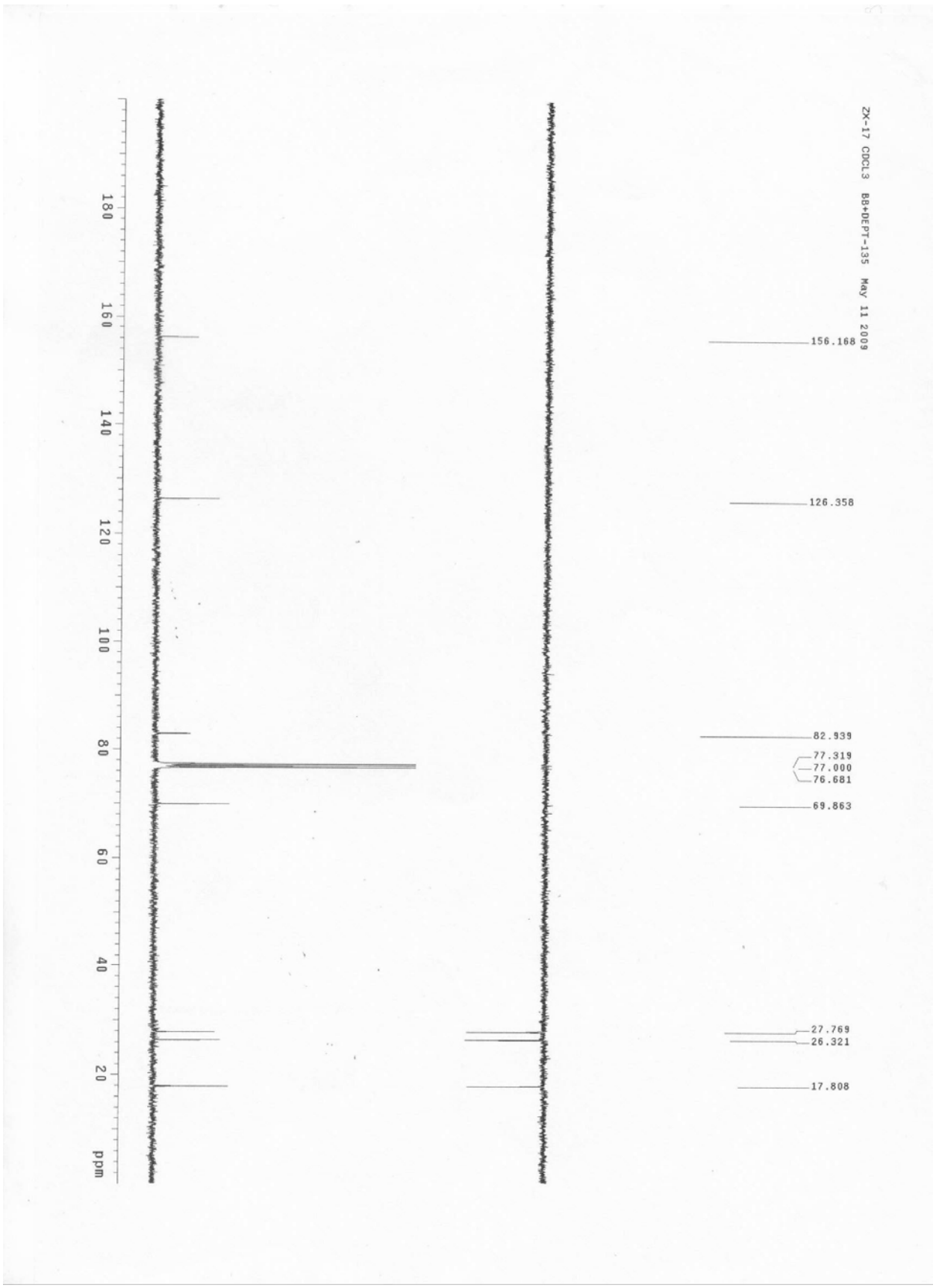
5,6-Dimethyl-2-(pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A2)



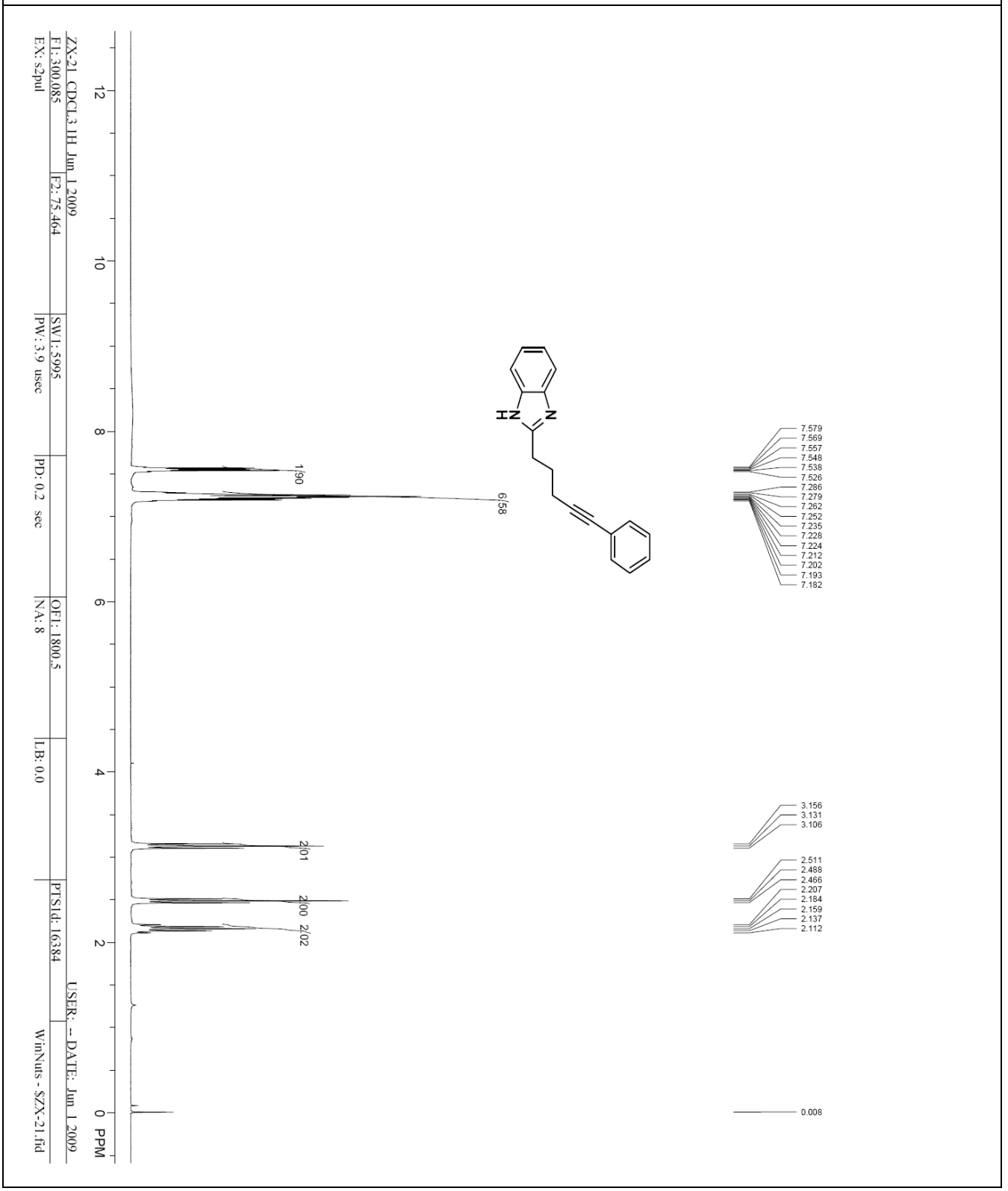

ZX-18 CDCL3 BB+DEPT-135 May 11 2009
153.381
137.016
131.008
114.794
83.308
77.319
77.000
76.686
69.380
27.897
26.817
20.268
17.868
180
160
140
120
100
80
60
40
20
ppm

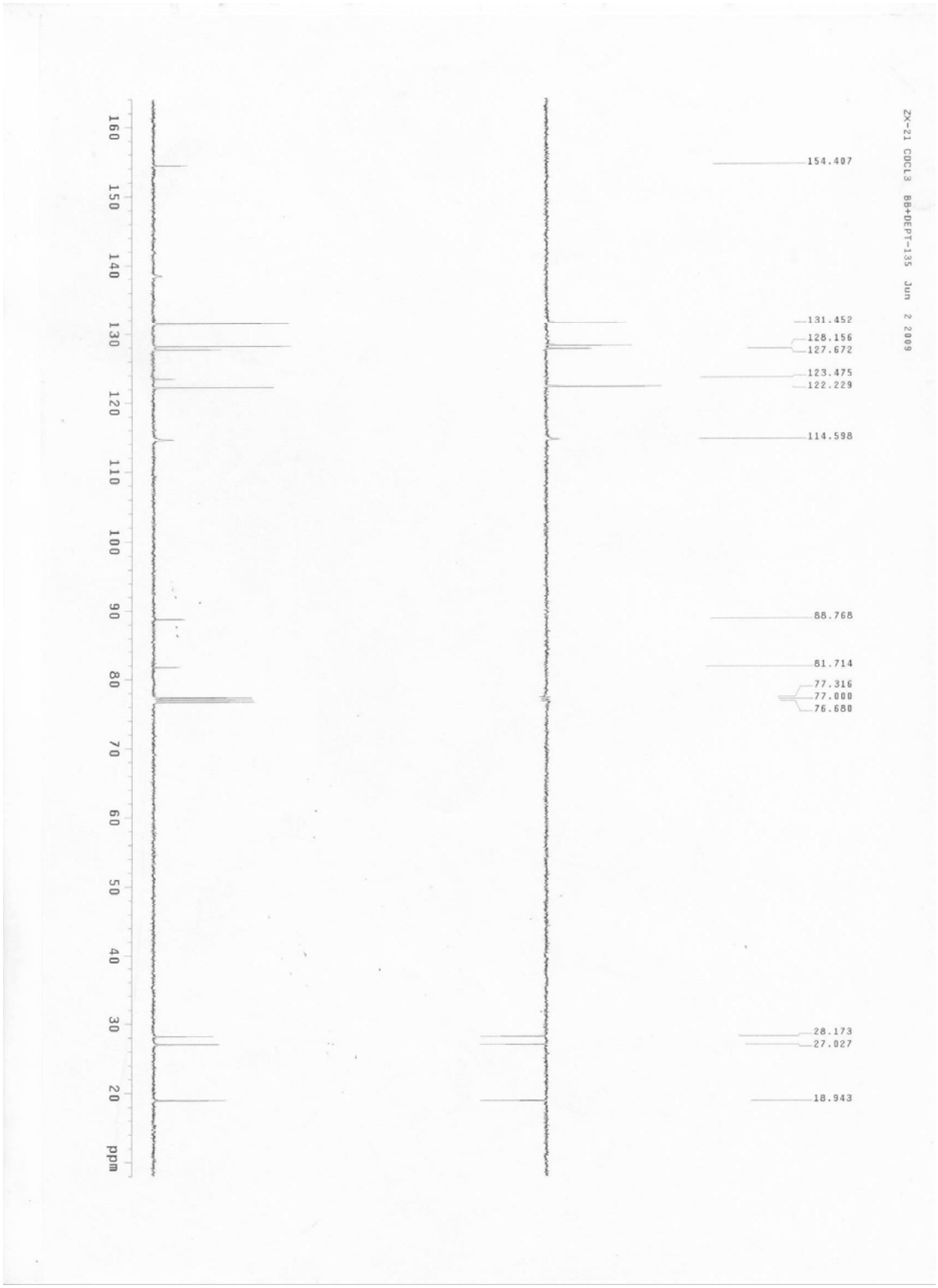
5, 6-Dichloro-2-(pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A3)



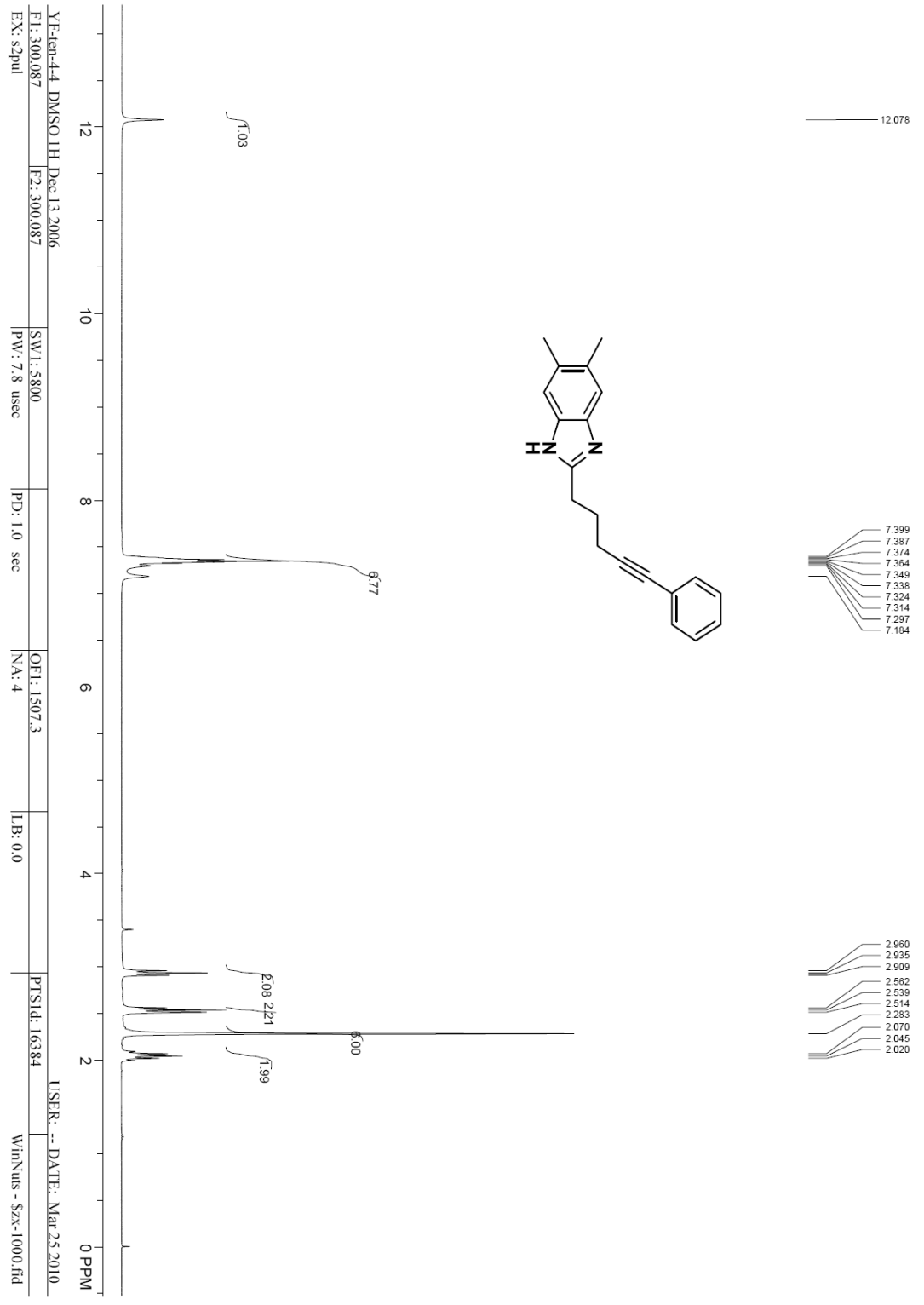

ZX-17 CDCL3 BB+DEPT-135 May 11 2009
156.168
126.358
82.939
77.319
77.000
76.681
69.863
27.769
26.321
17.808
180
160
140
120
100
80
60
40
20
ppm

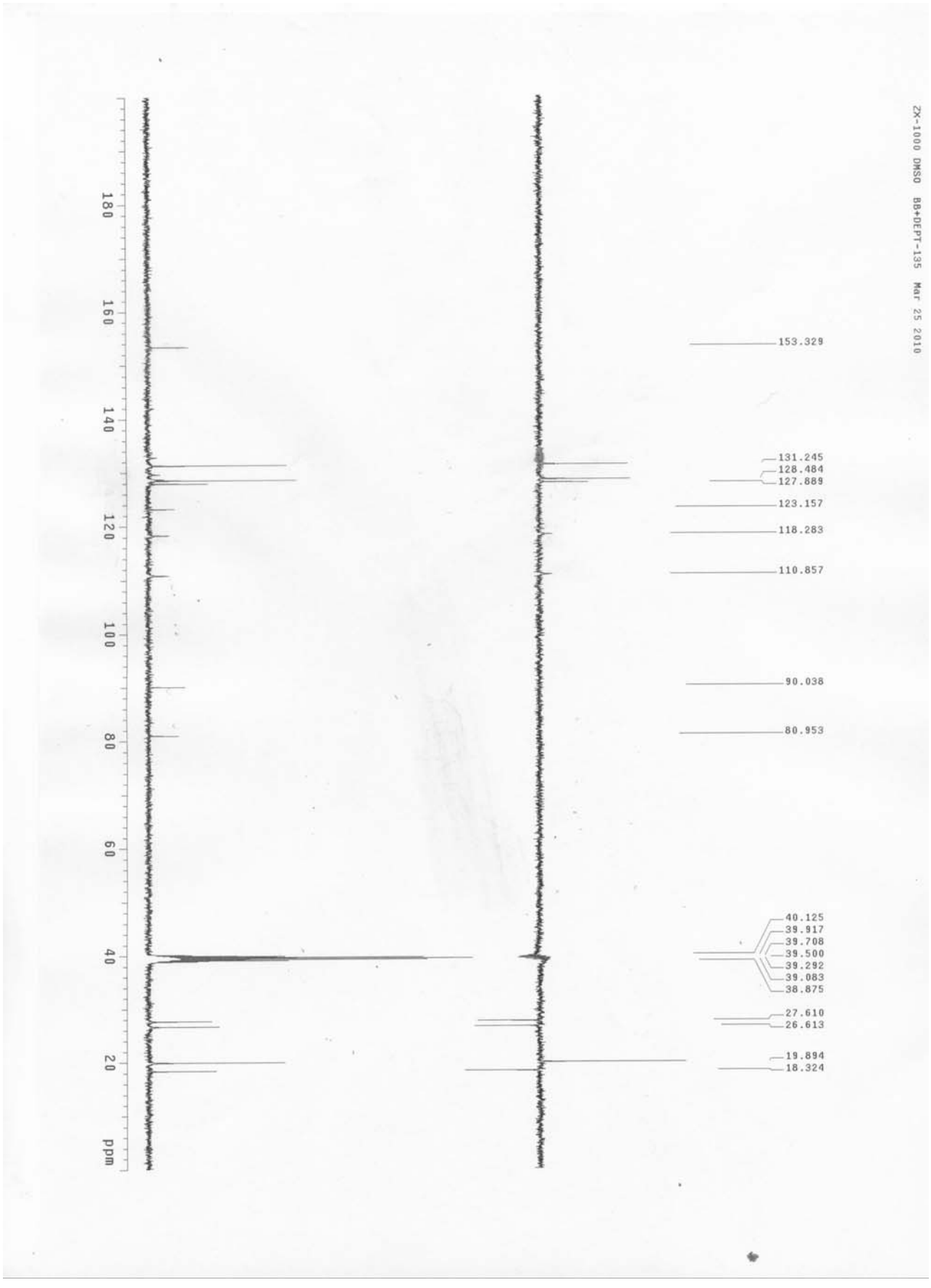
2-(5-Phenylpent-4-ynyl)-1*H*-benzo[*d*]imidazole (A4)



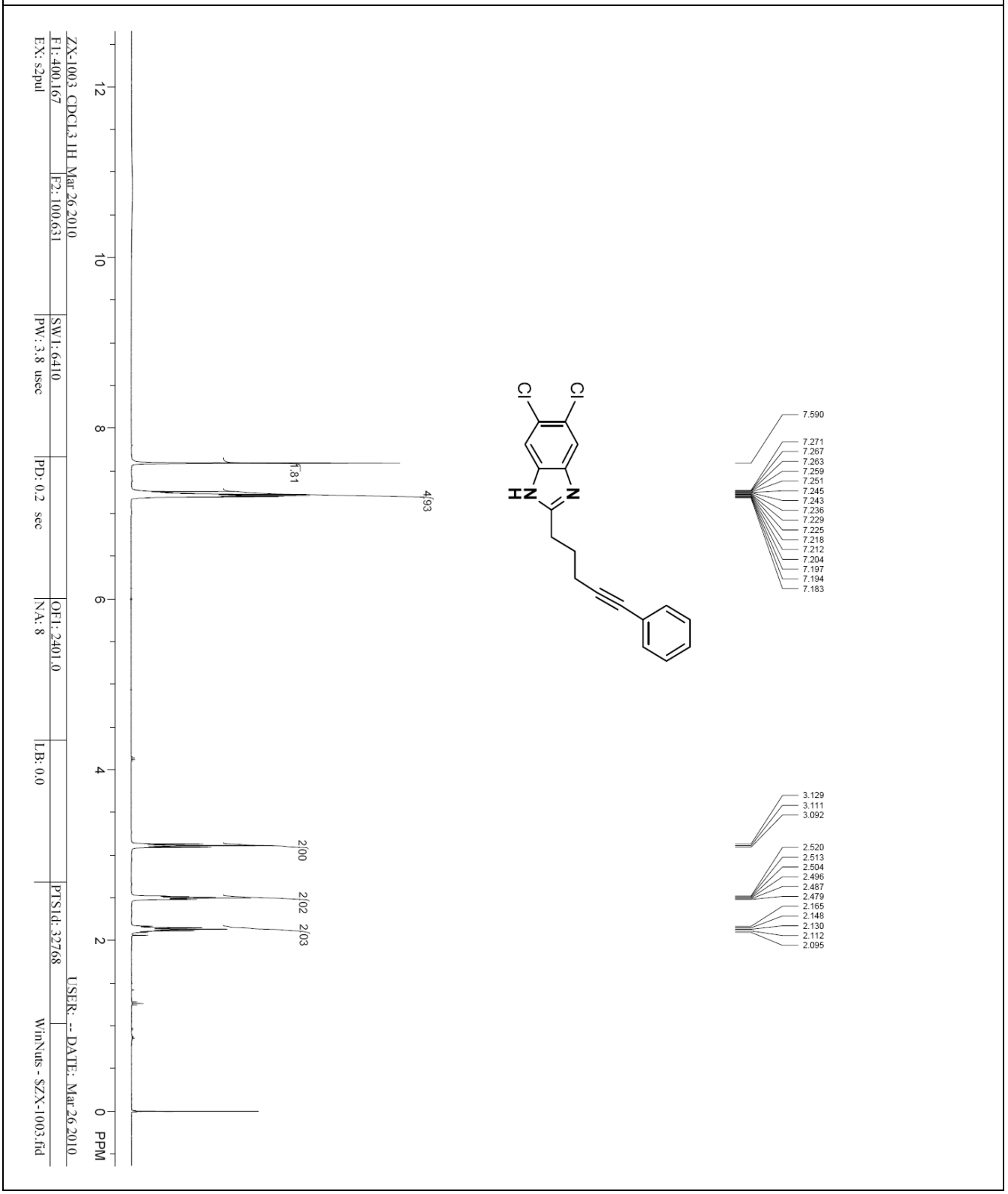

ZX-21 CDCl3 BB+DEPT-135 Jun 2 2009
154.407
131.452
128.156
127.672
123.475
122.229
114.598
88.768
81.714
77.316
77.000
76.680
28.173
27.027
18.943
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

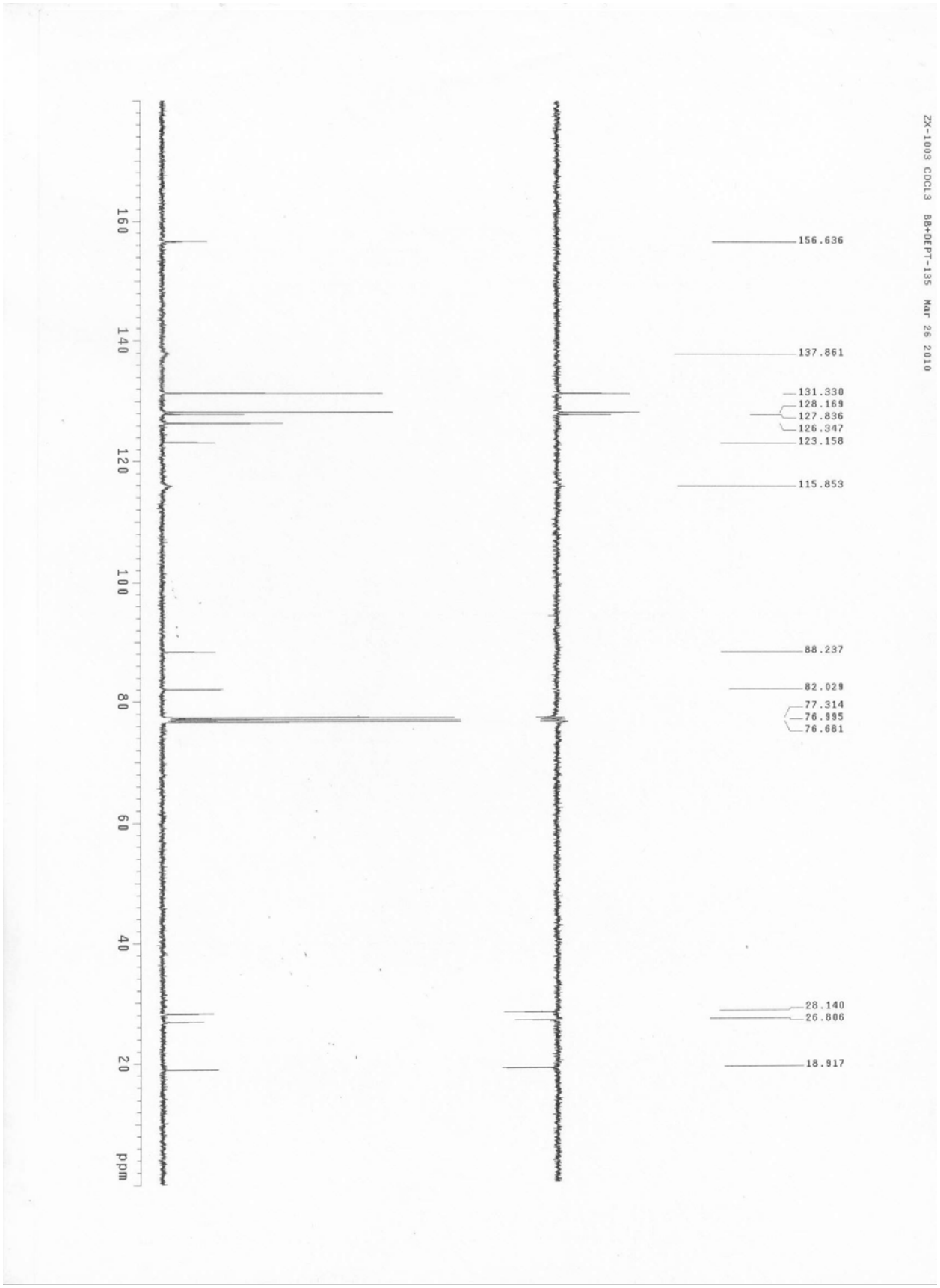
5,6-Dimethyl-2-(5-phenylpent-4-ynyl)-1*H*-benzo[*d*]imidazole (A5)



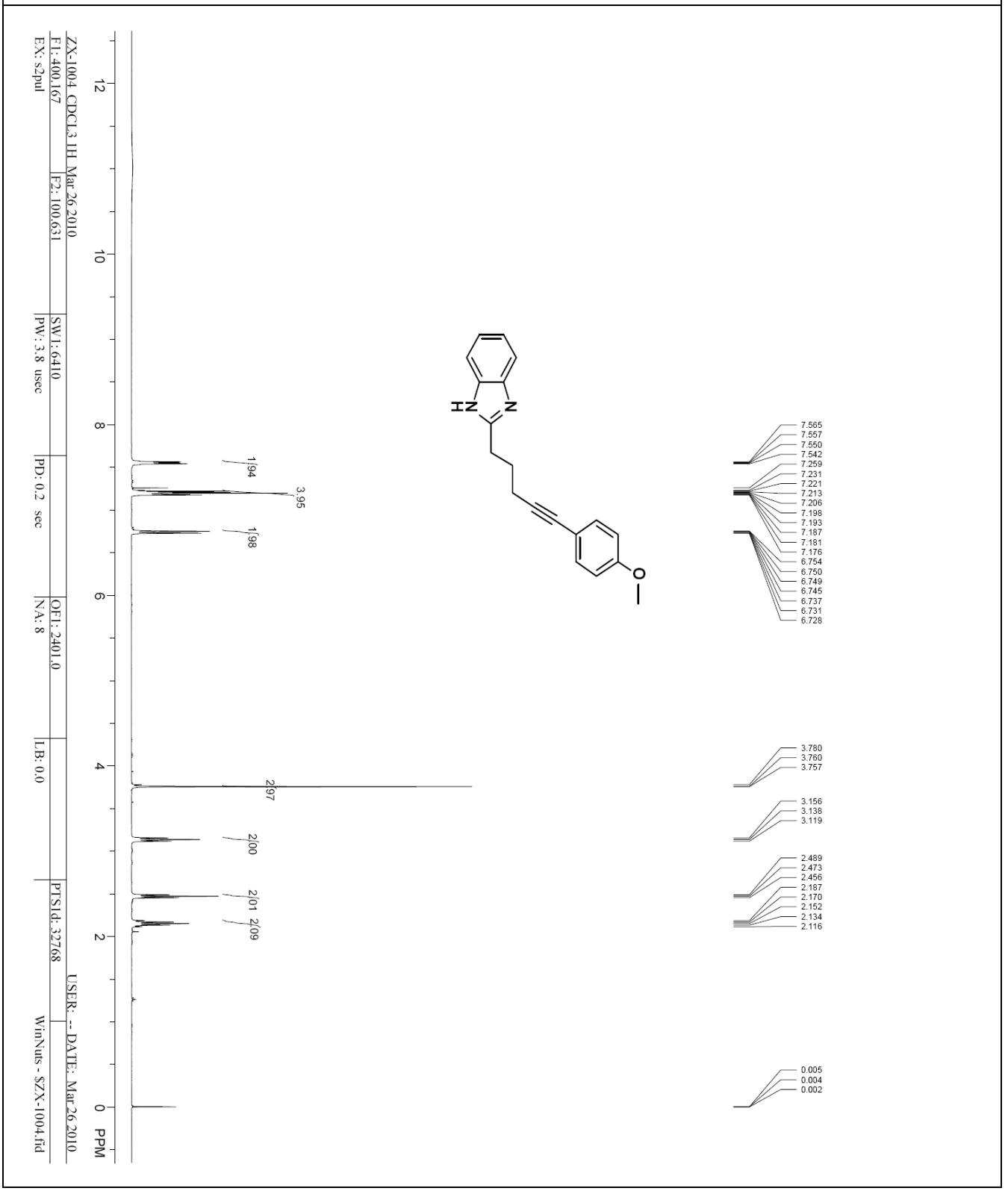

ZX-1000 DMSO BB+DEPT-135 Mar 25 2010
153.329
131.245
128.484
127.889
123.157
118.283
110.857
90.038
80.953
40.125
39.917
39.708
39.500
39.292
39.083
38.875
27.610
26.613
19.894
18.324
180
160
140
120
100
80
60
40
20
ppm

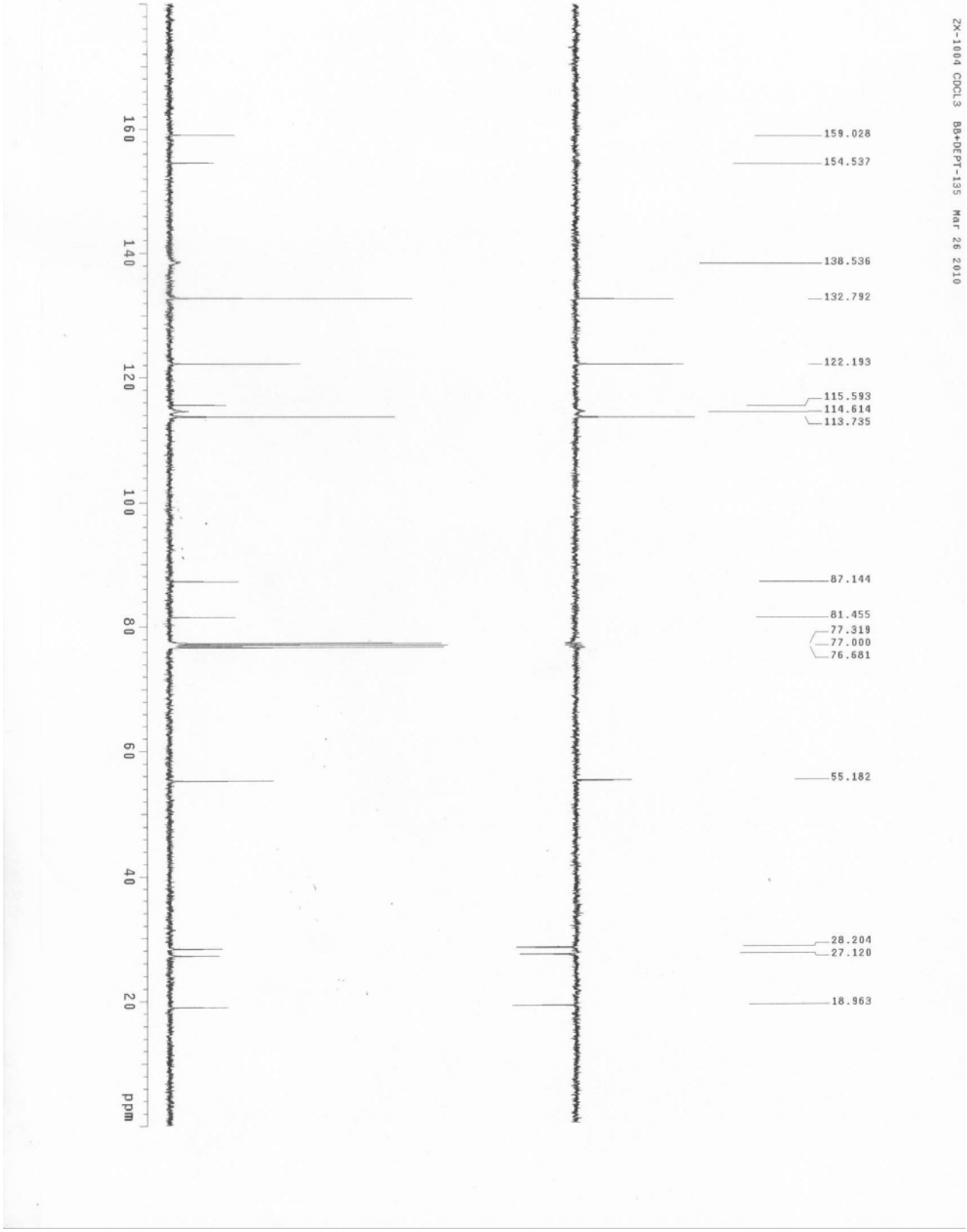
5, 6-Dichloro-2-(5-phenylpent-4-ynyl)-1*H*-benzo[*d*]imidazole (A6)



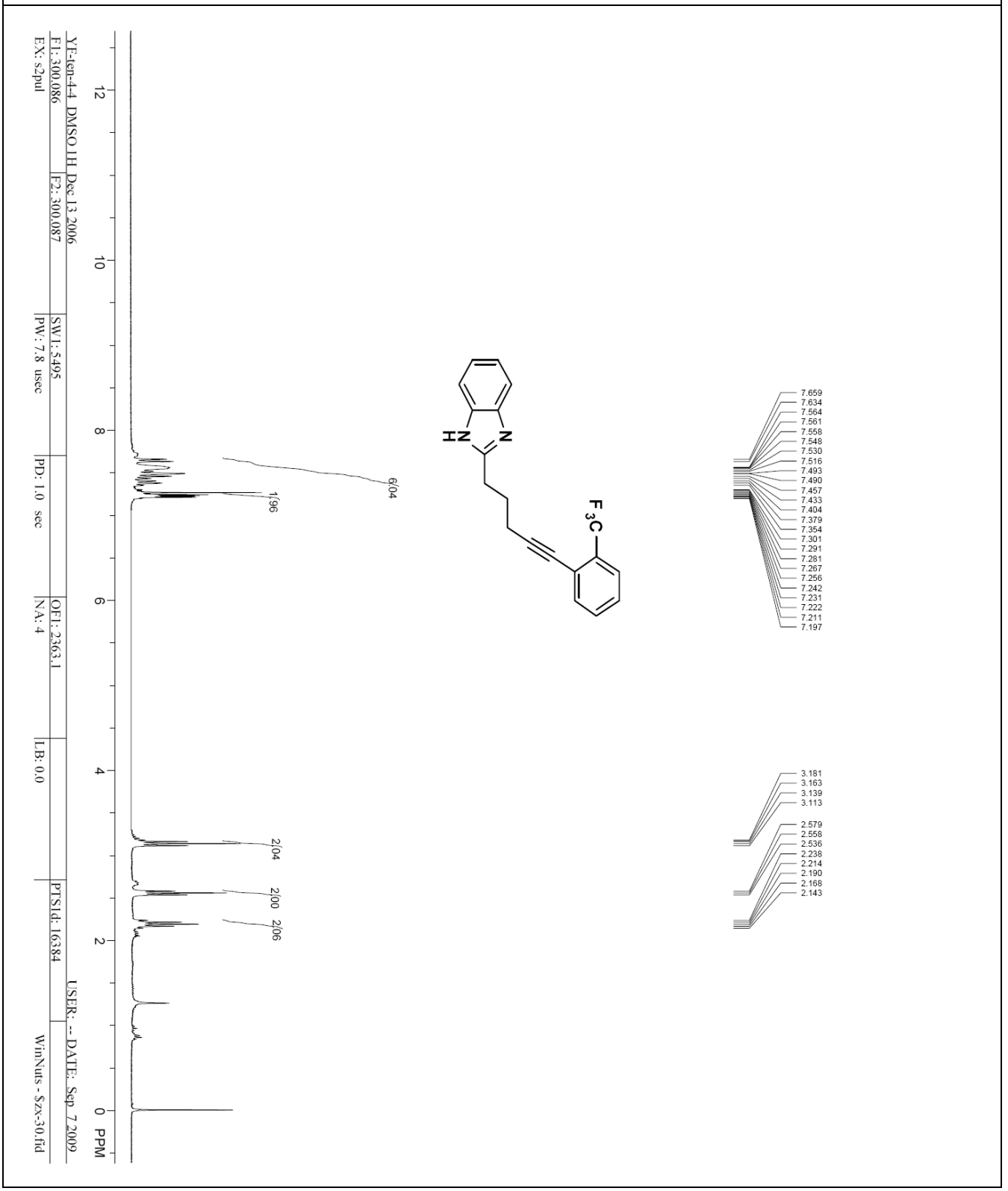

ZX-1003 CDCL3 BB+DEPT-135 Mar 26 2010
156.636
137.861
131.330
128.169
127.836
126.347
123.158
115.853
88.237
82.029
77.314
76.995
76.681
28.140
26.806
18.917
160
140
120
100
80
60
40
20
ppm

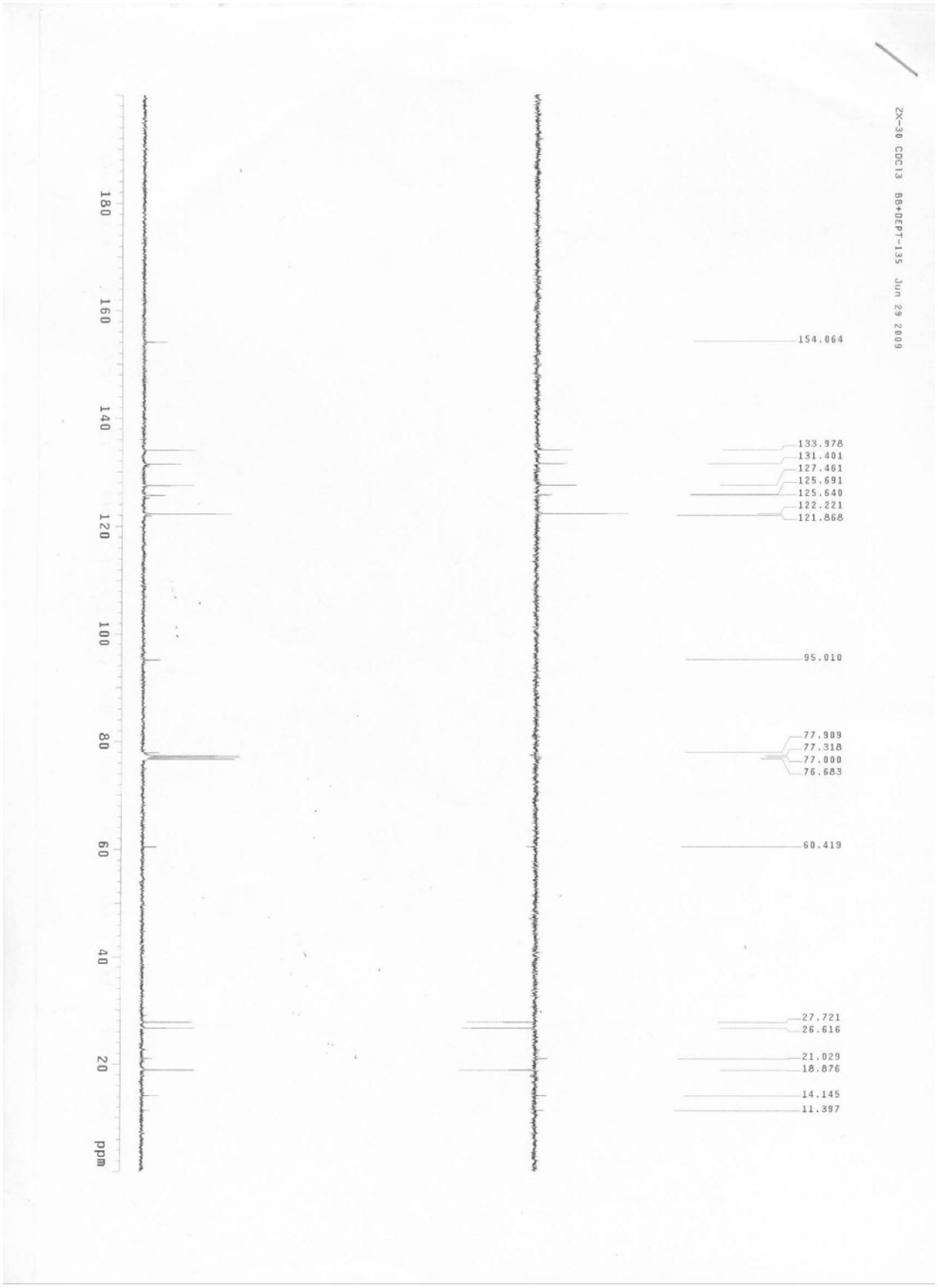
2-(5-(4-Methoxyphenyl)pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A7)



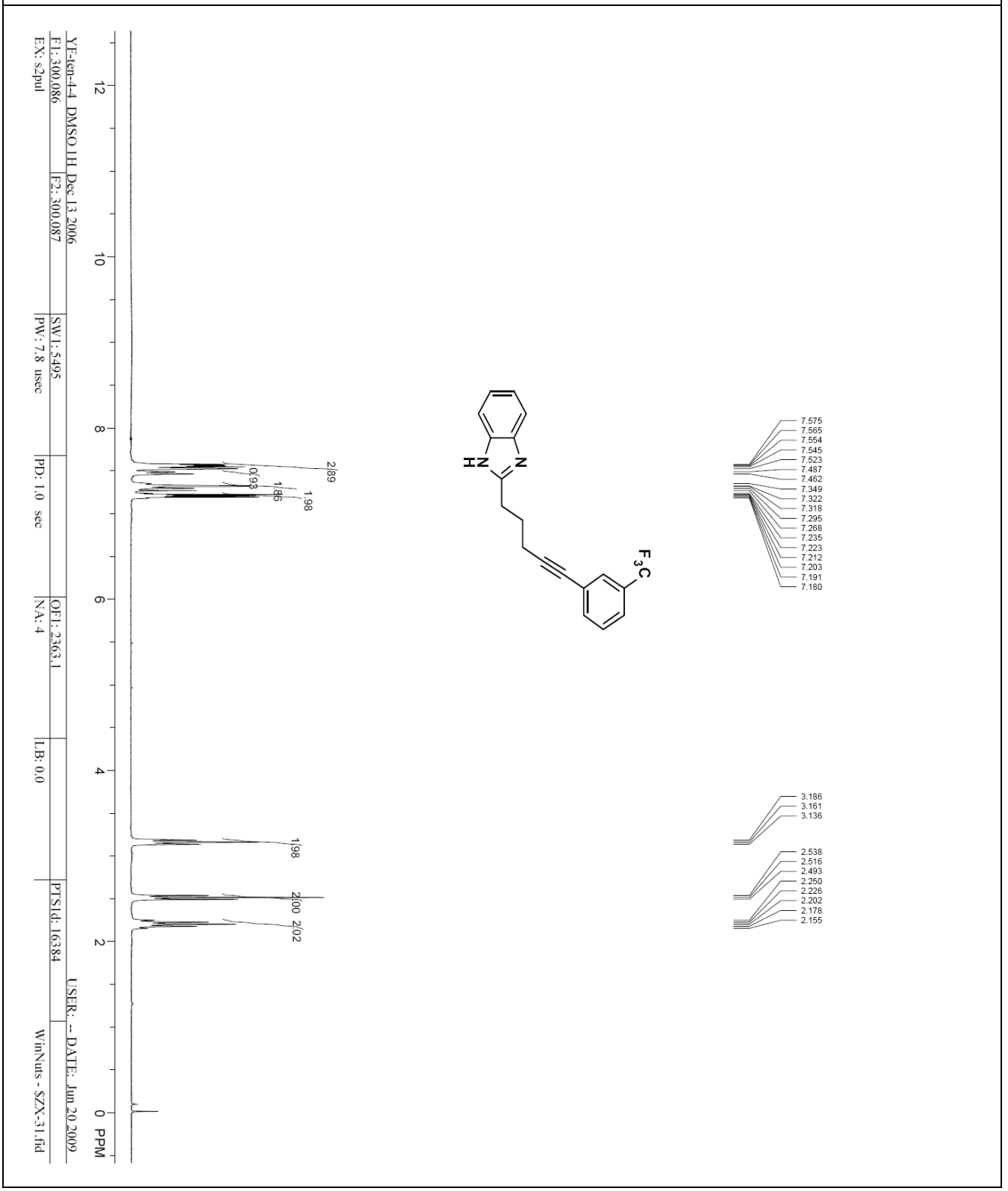

ZX-1004 CDCL3 BB+DEPT-135 Mar 26 2010
159.028
154.537
138.536
132.792
122.193
115.593
114.614
113.735
87.144
81.455
77.319
77.000
76.681
55.182
28.204
27.120
18.963
160
140
120
100
80
60
40
20
ppm

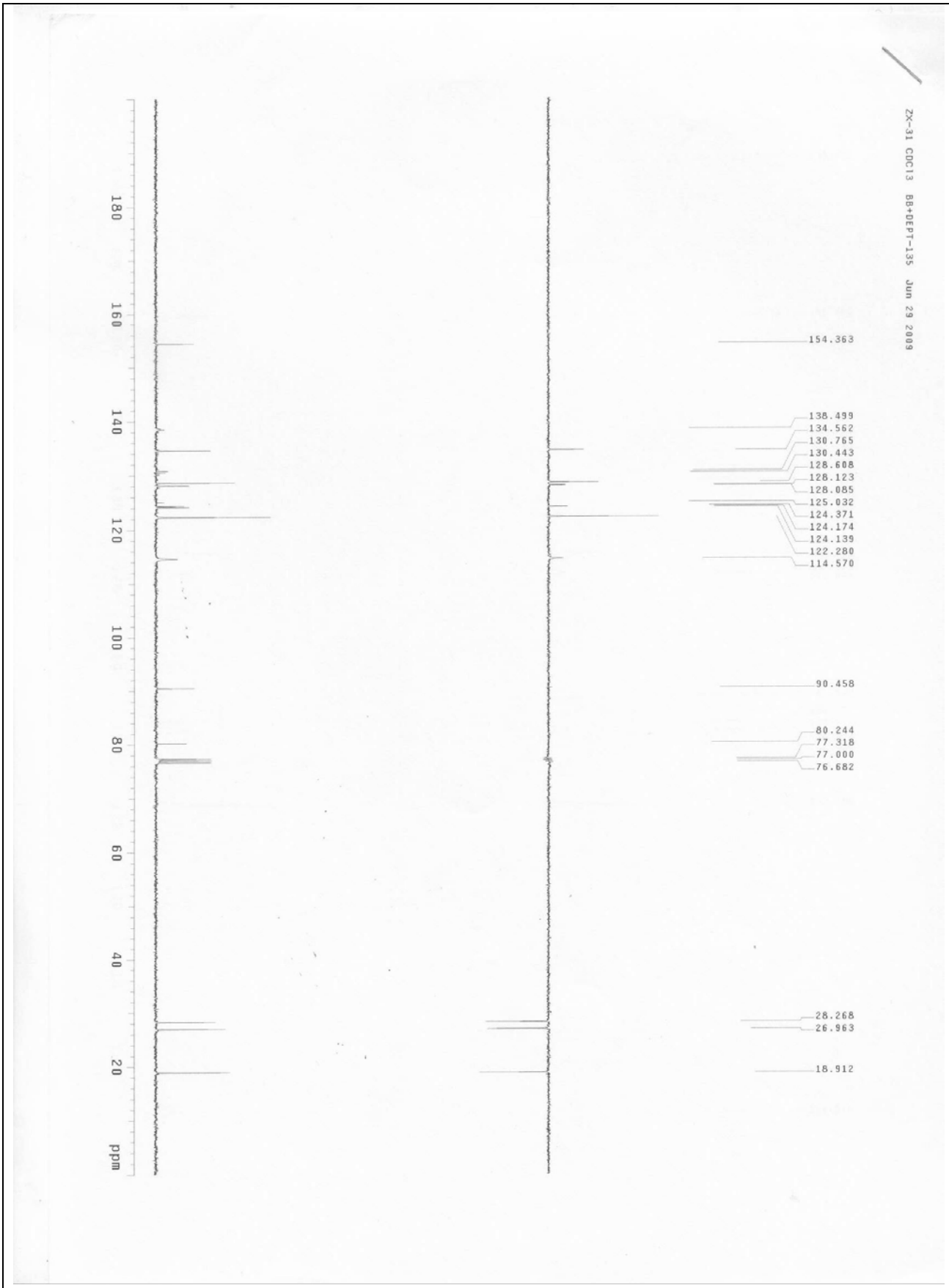
2-(5-(2-(Trifluoromethyl)phenyl)pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A8)



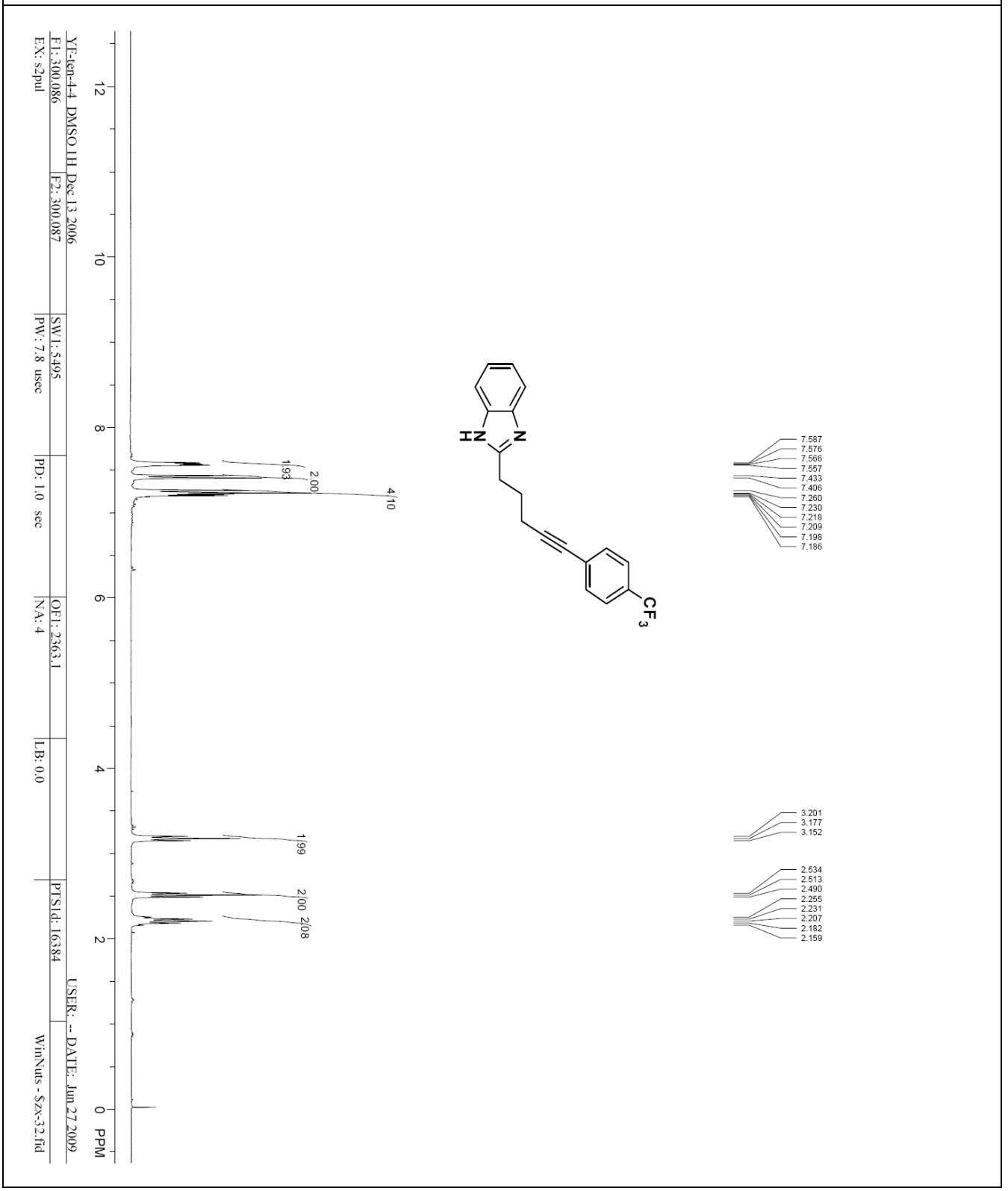

2X-30 CDCl3 BB+DEPT-135 Jun 29 2009
154.064
133.978
131.401
127.461
125.691
125.640
122.221
121.868
95.010
77.909
77.318
77.000
76.683
60.419
27.721
26.616
21.029
18.876
14.145
11.397
180
160
140
120
100
80
60
40
20
ppm

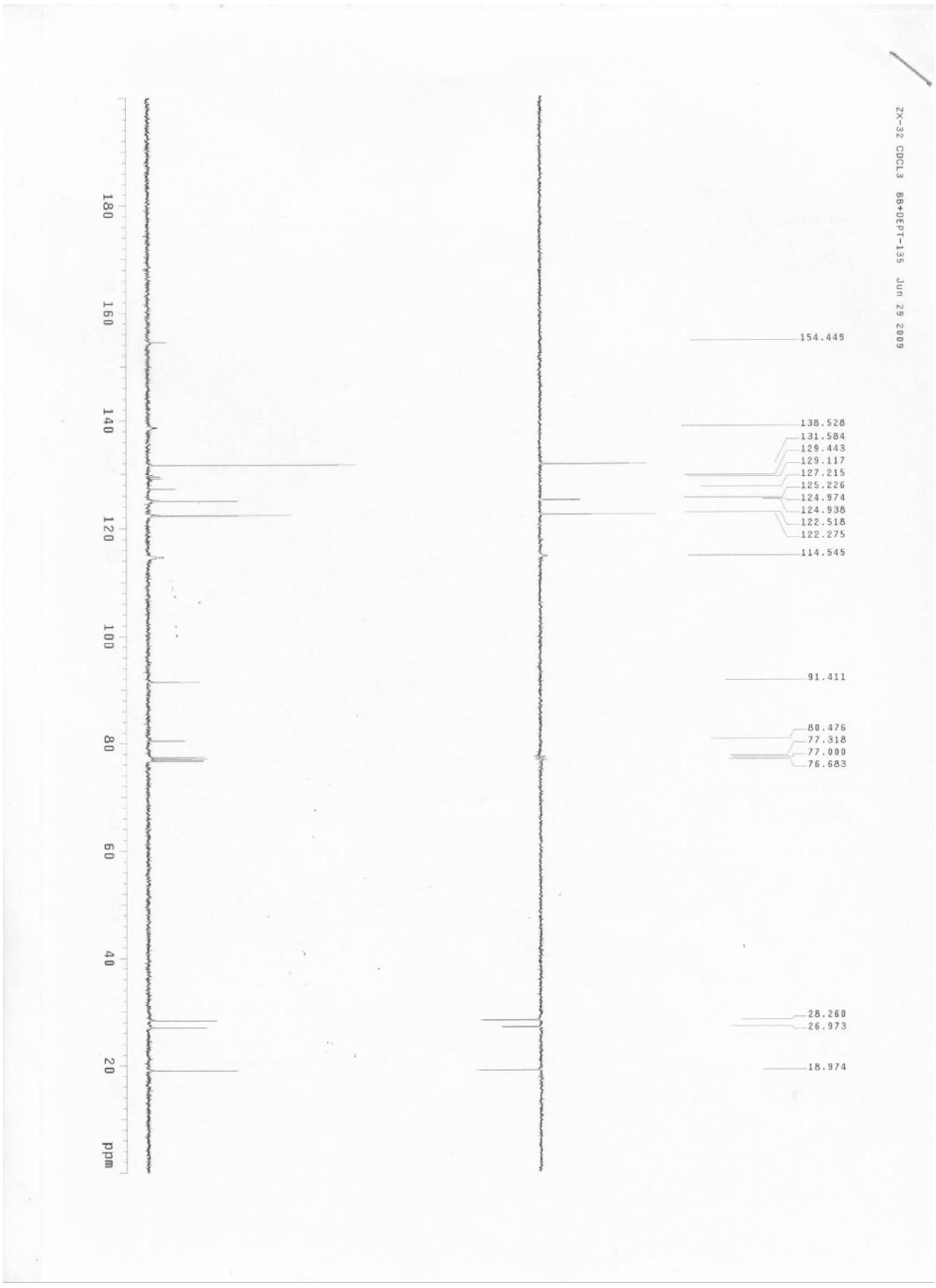
2-(5-(3-(Trifluoromethyl)phenyl)pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A9)



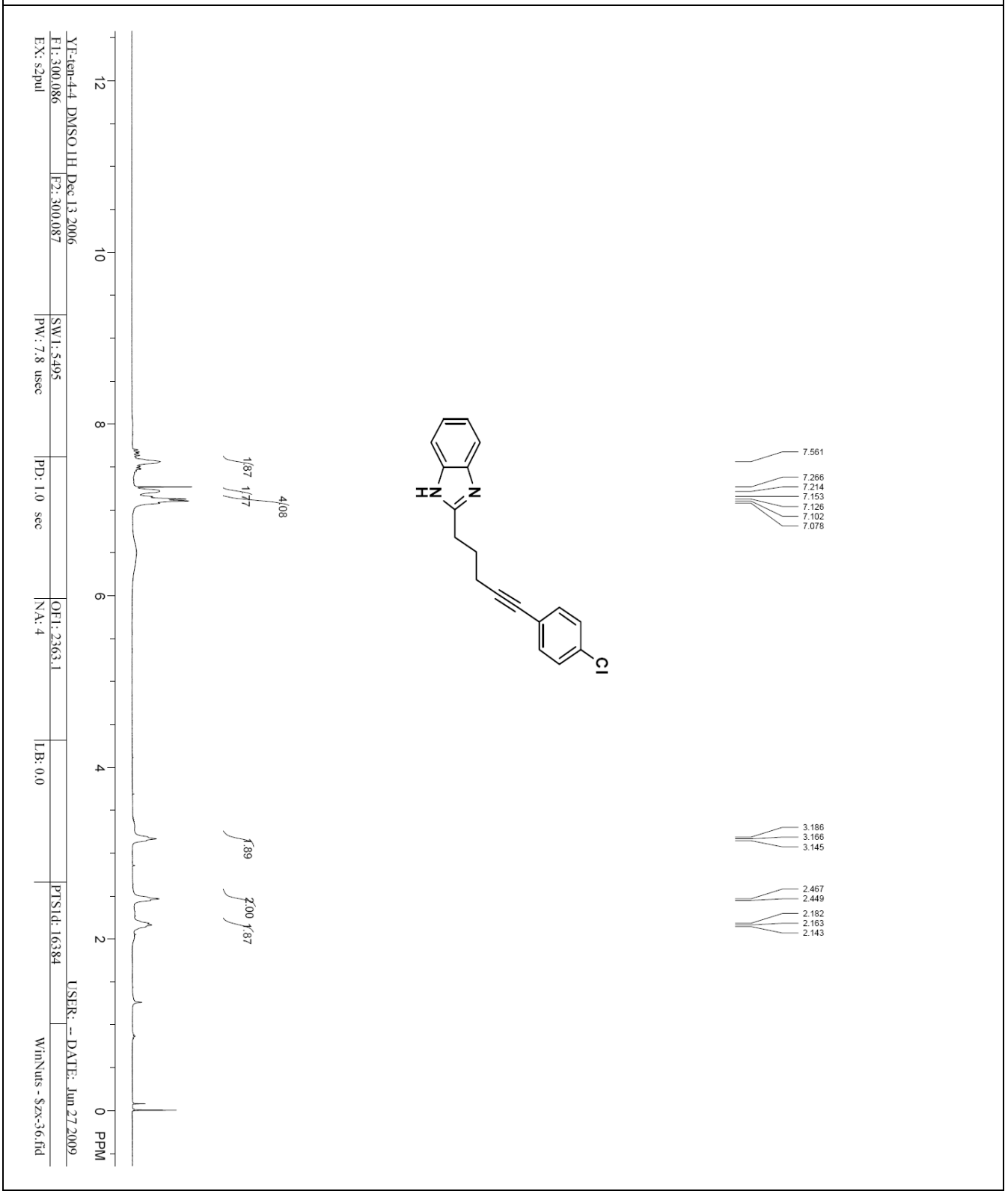

ZX-31 CDCl3 BB+DEPT-135 Jun 29 2009
154.363
138.499
134.562
130.765
130.443
128.608
128.123
128.085
125.032
124.371
124.174
124.139
122.280
114.570
90.458
80.244
77.318
77.000
76.682
28.268
26.963
18.912
180
160
140
120
100
80
60
40
20
ppm

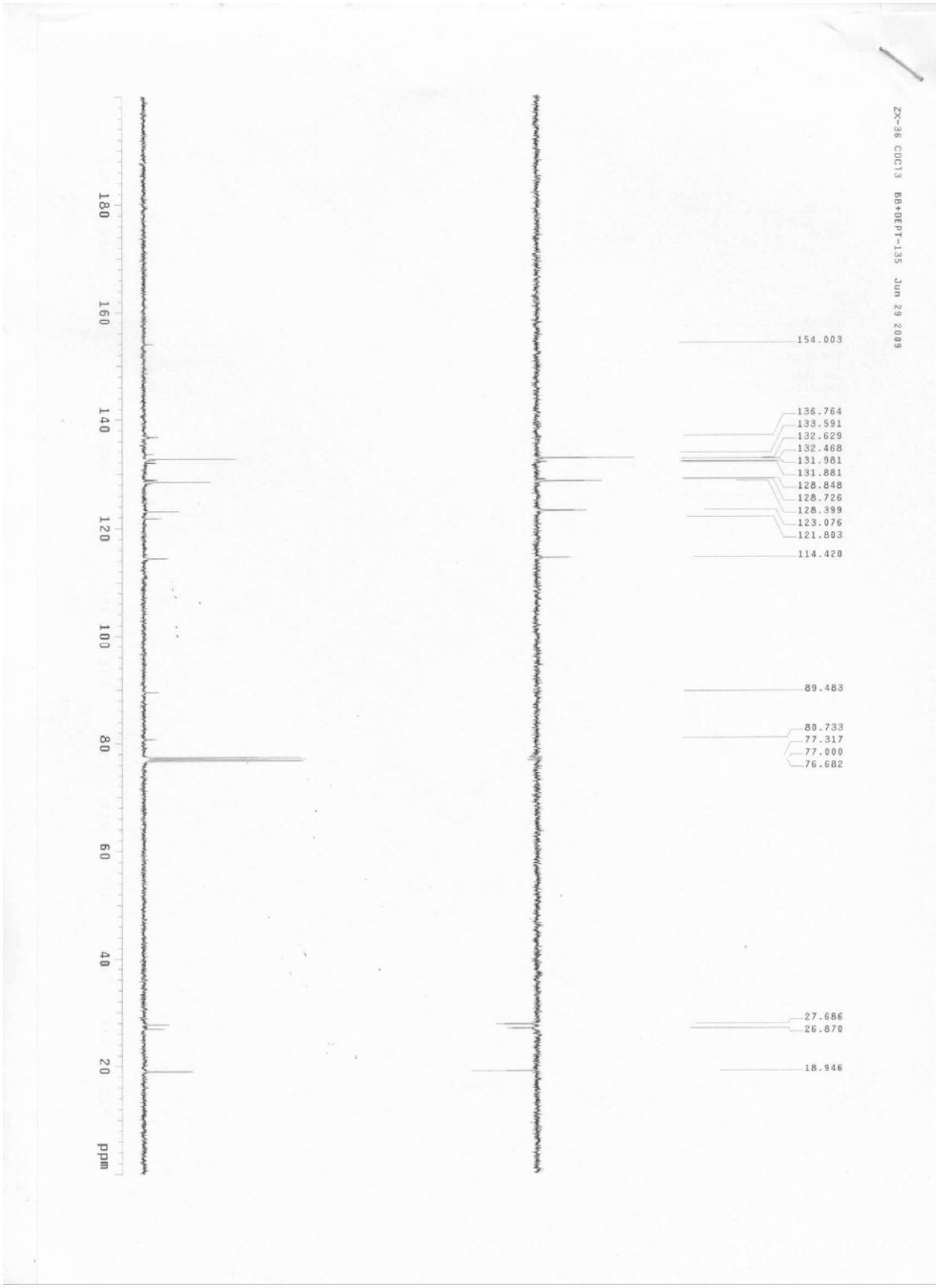
2-(5-(4-(Trifluoromethyl)phenyl)pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A10)



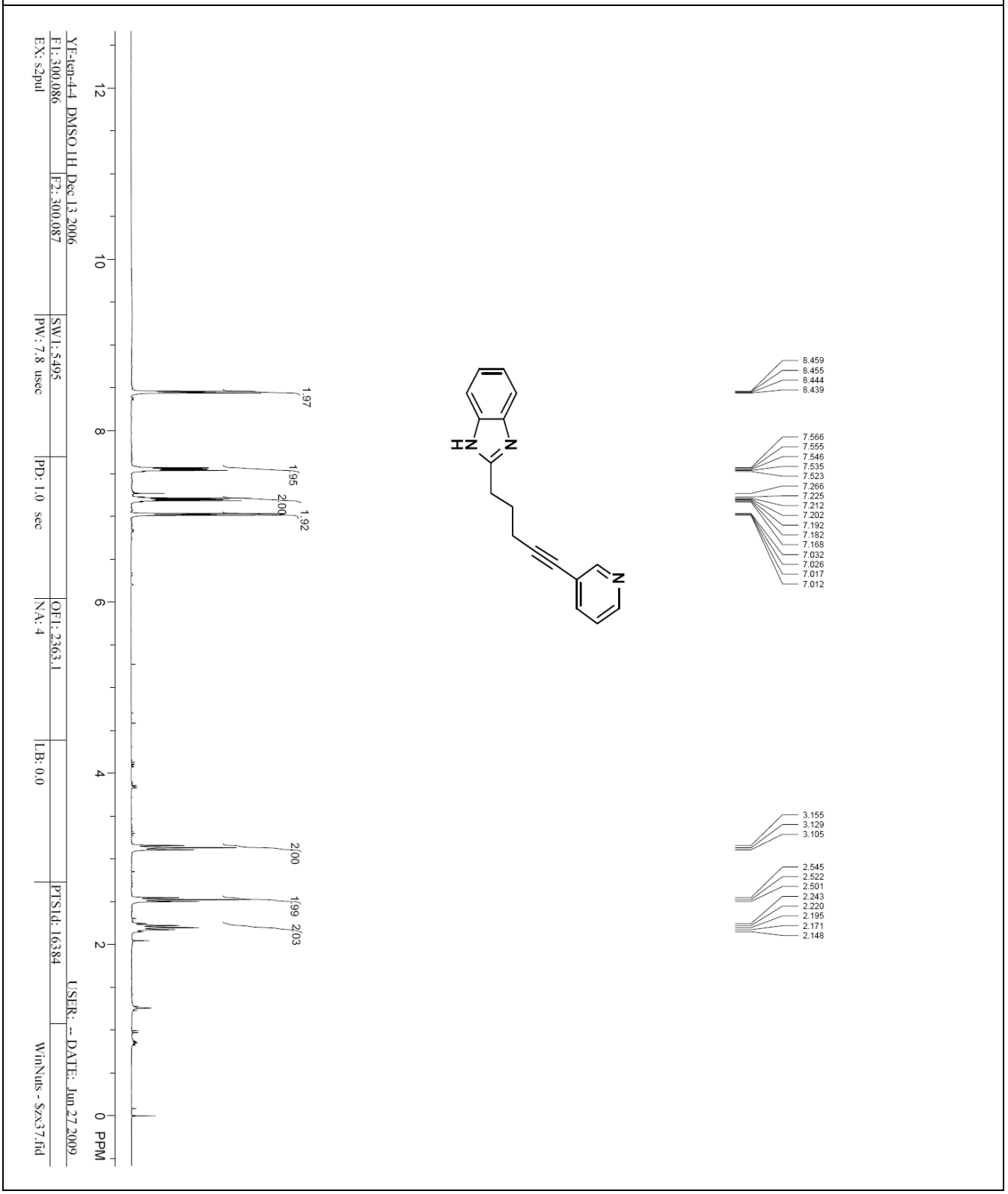

ZX-32 CDCL3 88+DEPT-135 Jun 29 2009
154.449
138.528
131.584
129.443
129.117
127.215
125.226
124.974
124.938
122.518
122.275
114.545
91.411
80.476
77.318
77.000
76.683
28.260
26.973
18.974
180
160
140
120
100
80
60
40
20
ppm

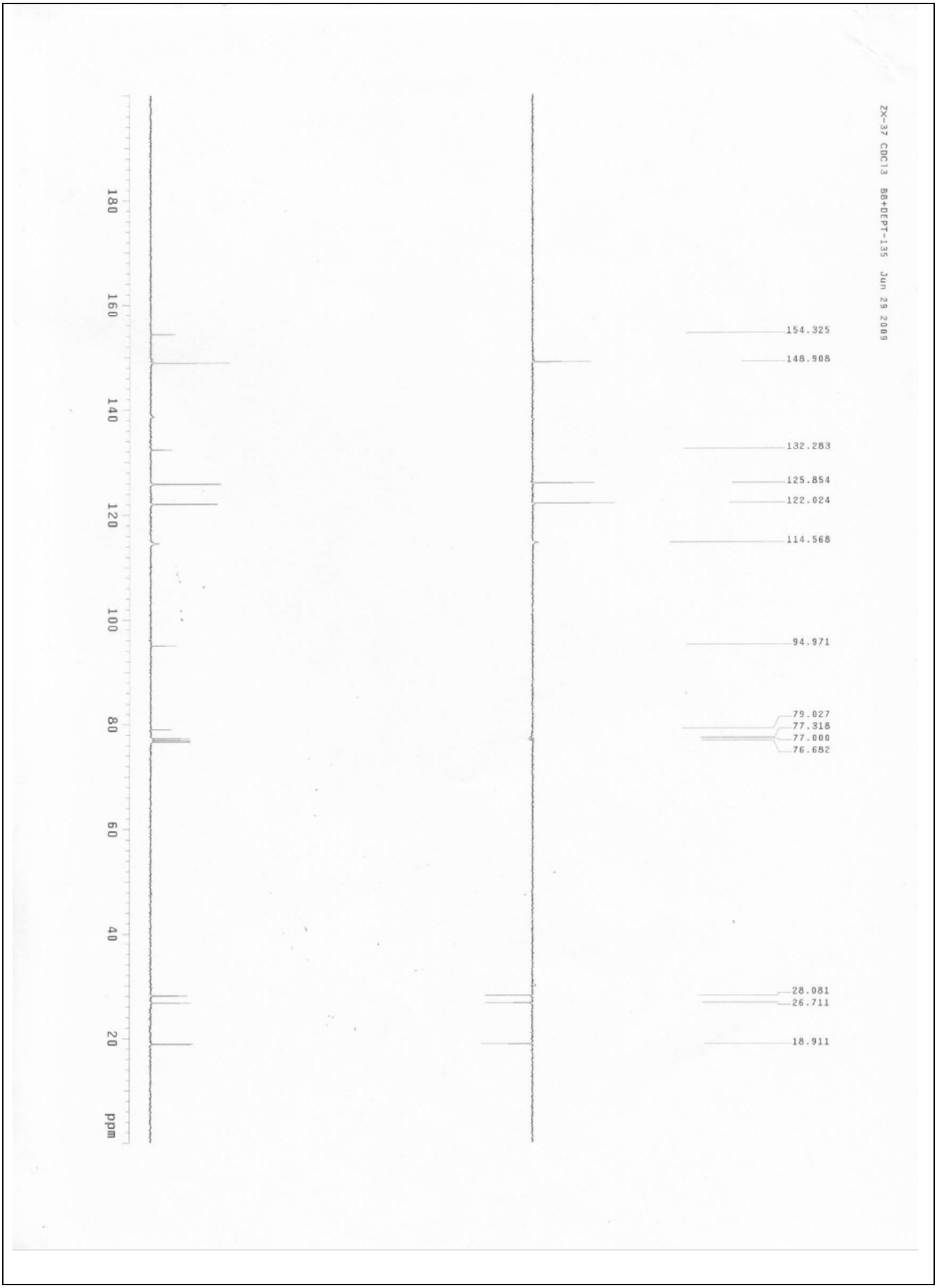
2-(5-(4-Chlorophenyl)pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A11)



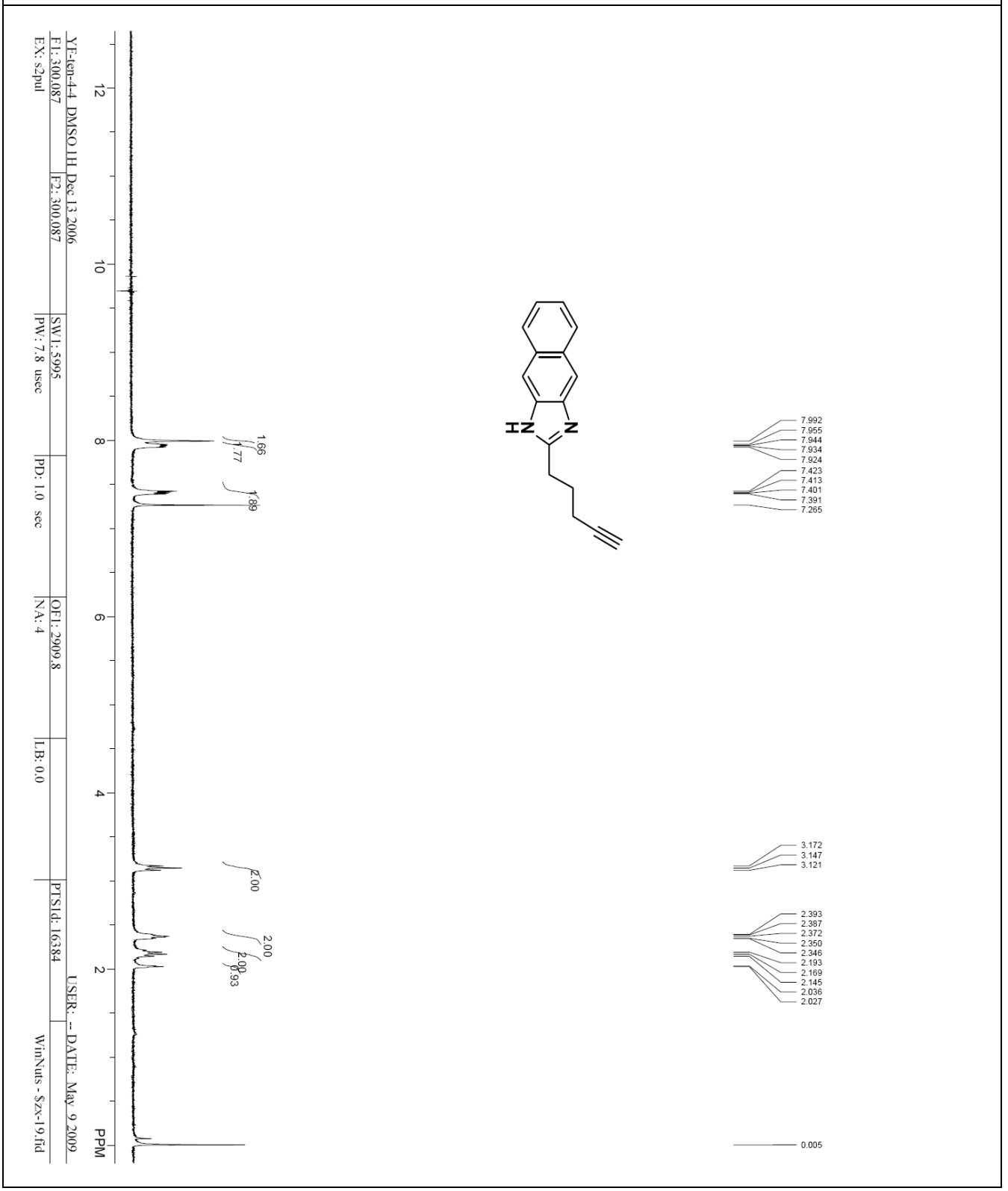

ZX-36 CDCl3 BB+DEPT-135 Jun 29 2009
154.003
136.764
133.591
132.629
132.468
131.981
131.881
128.848
128.726
128.399
123.076
121.803
114.420
89.483
80.733
77.317
77.000
76.682
27.686
26.870
18.946
180
160
140
120
100
80
60
40
20
ppm

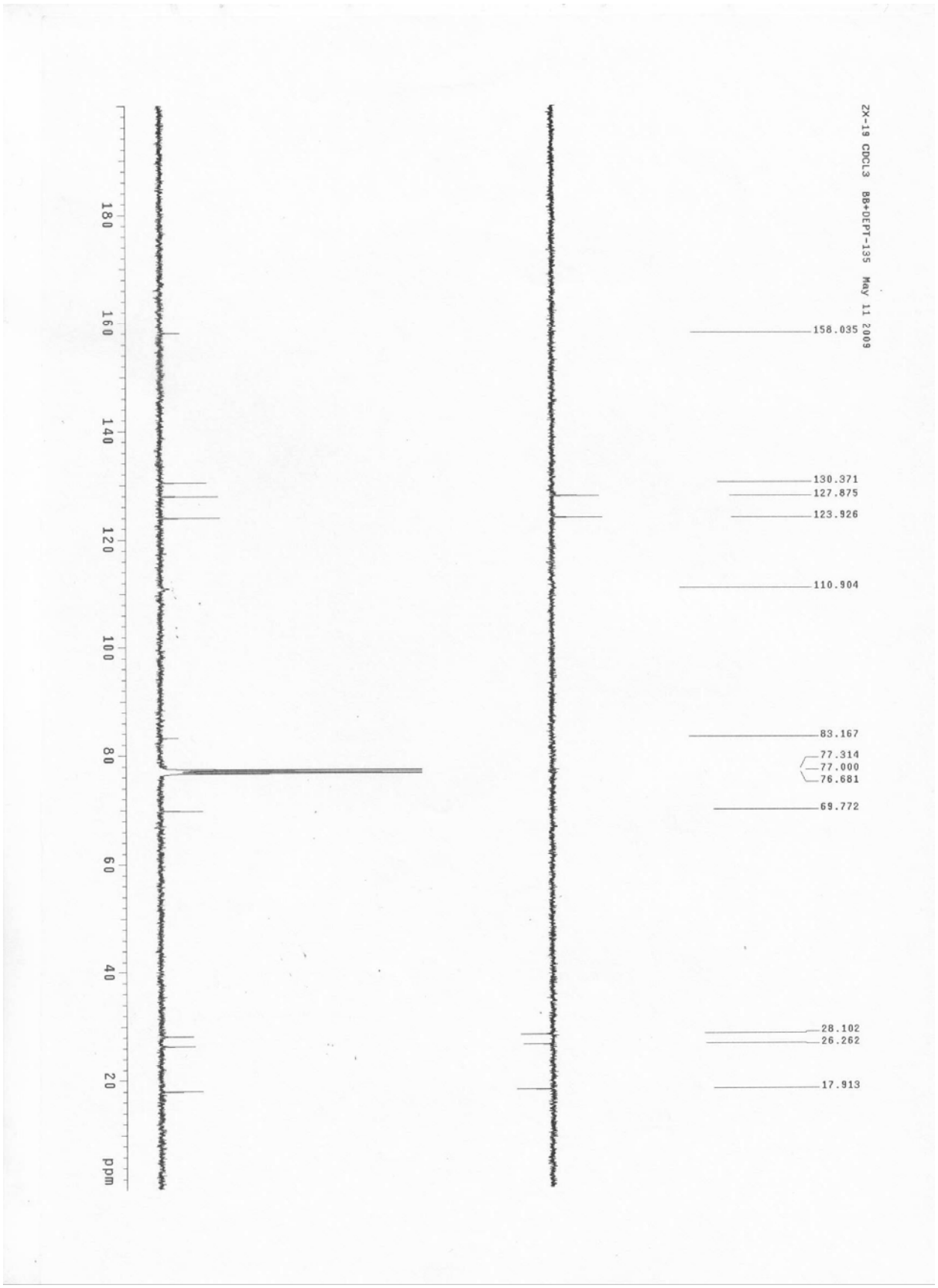
2-(5-(Pyridin-3-yl)pent-4-ynyl)-1*H*-benzo[*d*]imidazole (A12)



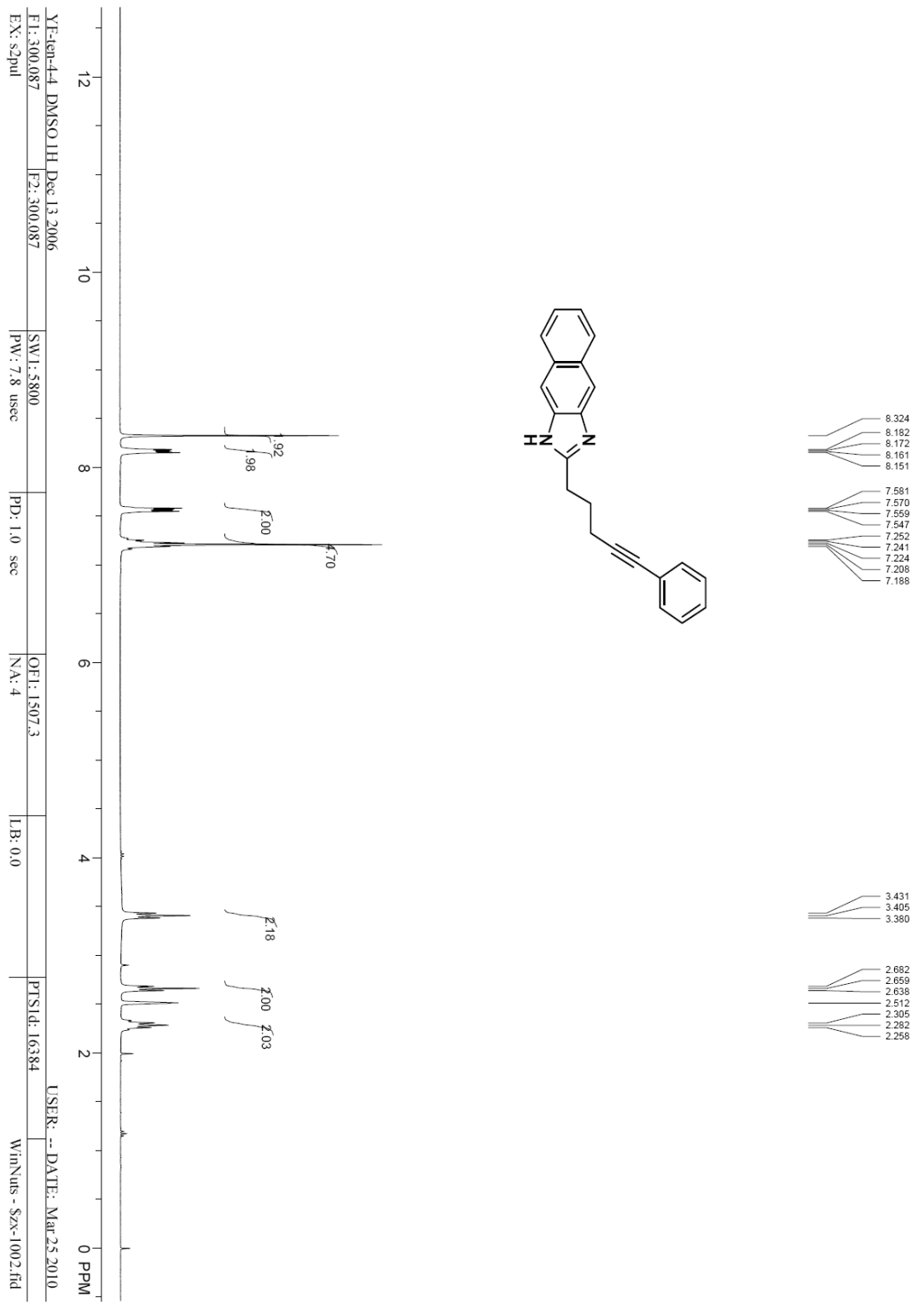

ZX-37 CDCl3 BB+DEPT-135 Jun 29 2009
154.325
148.908
132.283
125.854
122.024
114.568
94.971
79.027
77.318
77.000
76.682
28.081
26.711
18.911
180
160
140
120
100
80
60
40
20
ppm

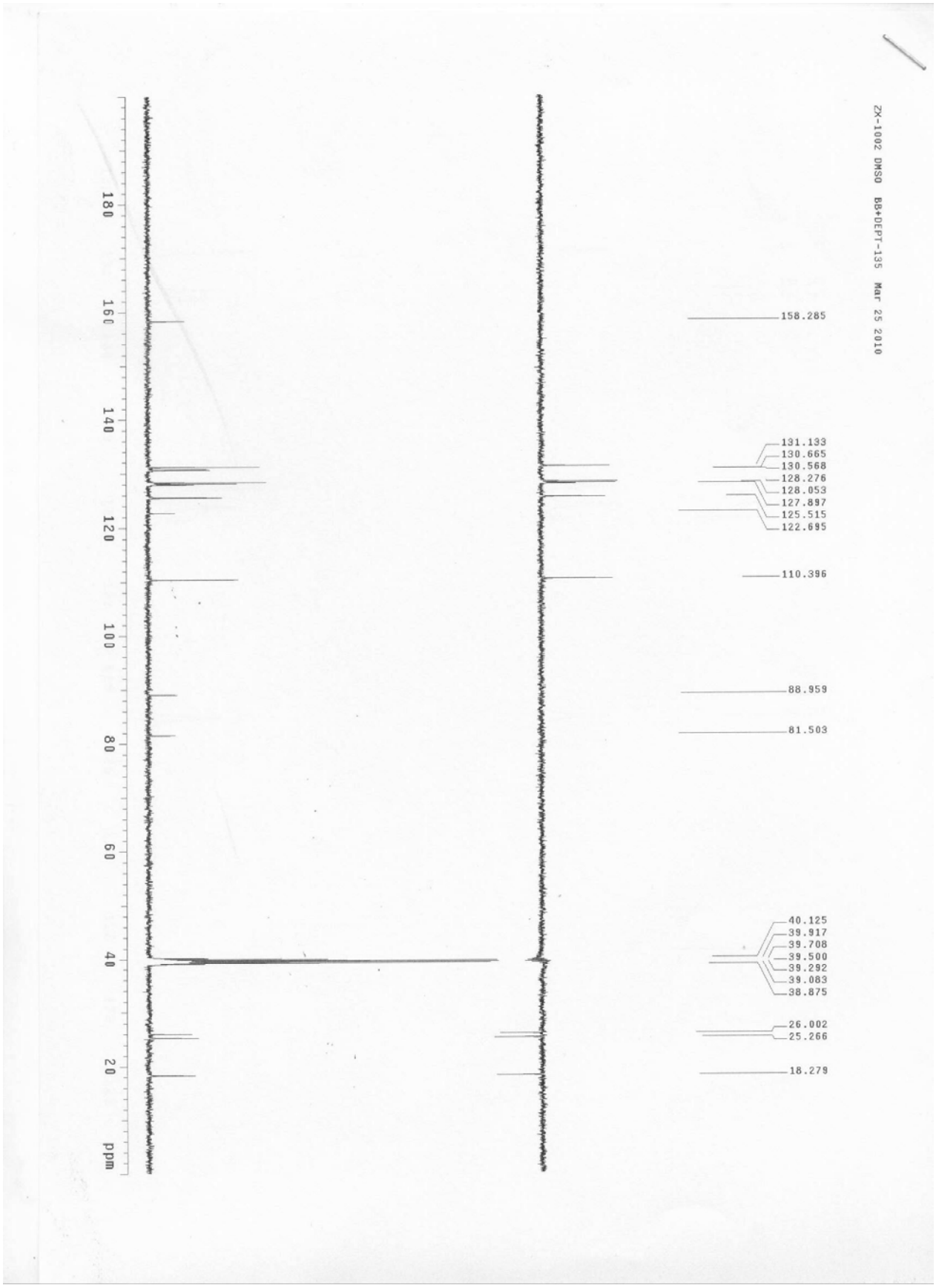
2-(Pent-4-ynyl)-1*H*-naphtho[2,3-*d*]imidazole (A13)



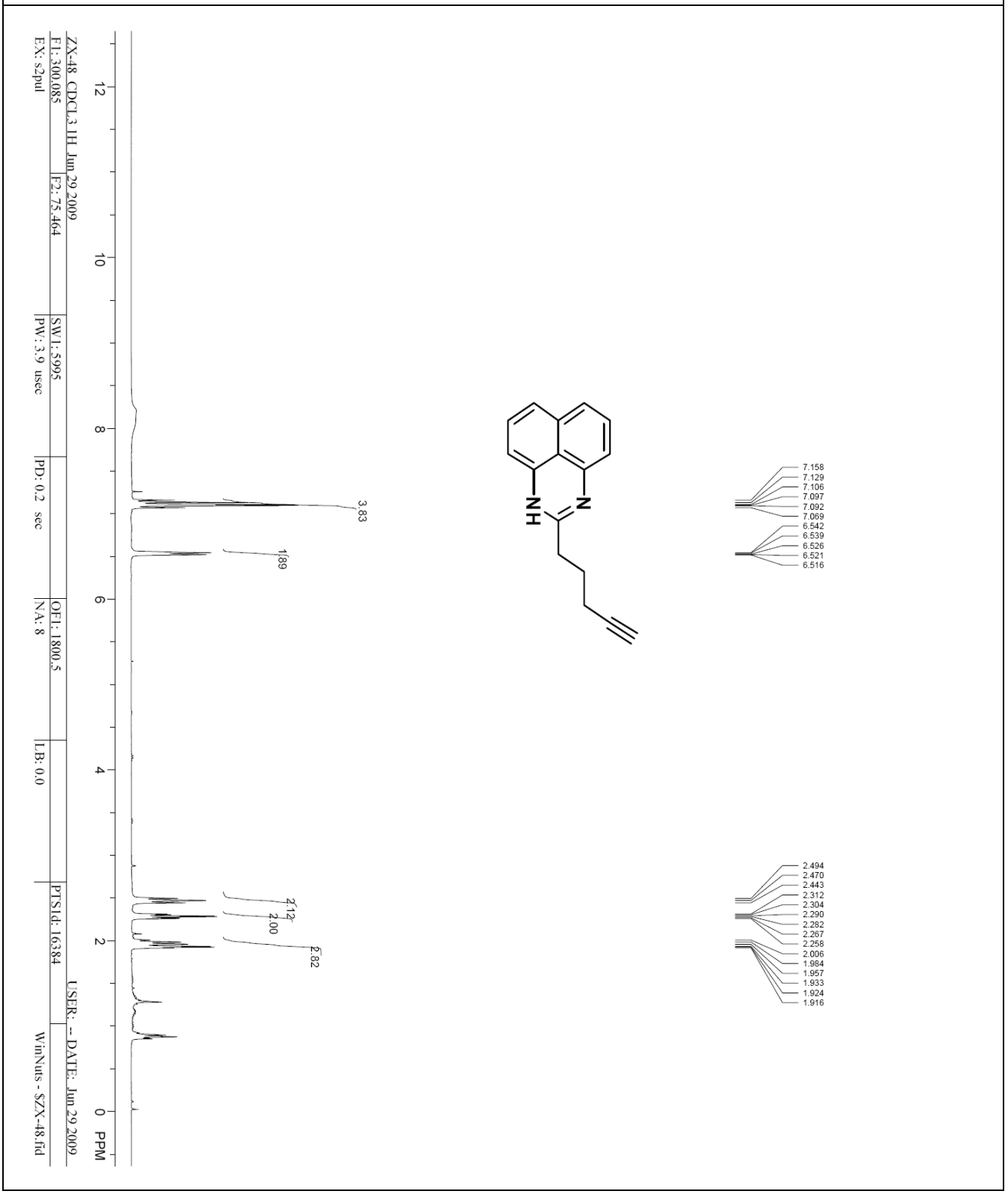

ZX-19 CDCL3 BB+DEPT-135 May 11 2009
158.035
130.371
127.875
123.926
110.904
83.167
77.314
77.000
76.681
69.772
28.102
26.262
17.913
180
160
140
120
100
80
60
40
20
ppm

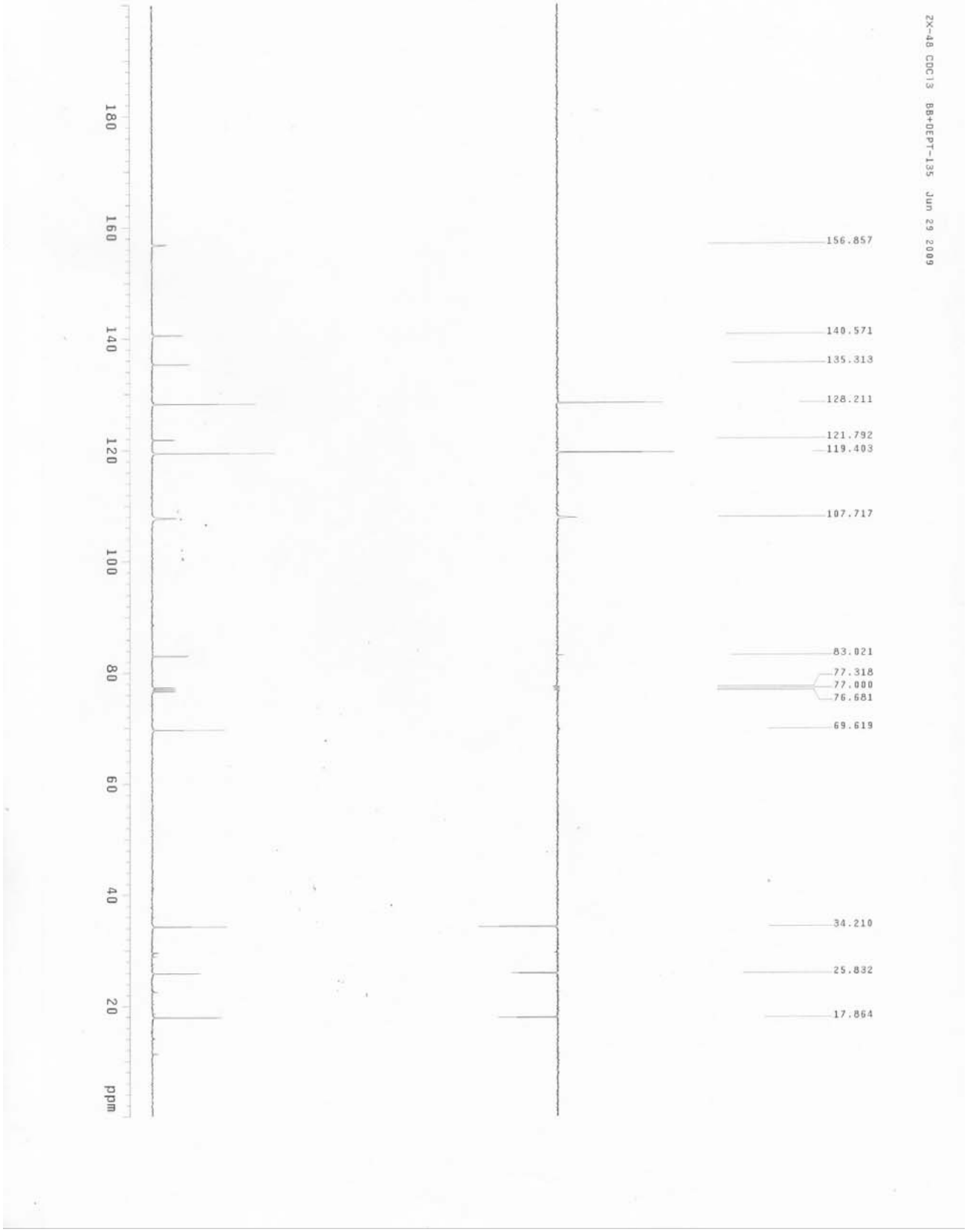
2-(5-Phenylpent-4-ynyl)-1*H*-naphtho[2,3-*d*]imidazole (A14)



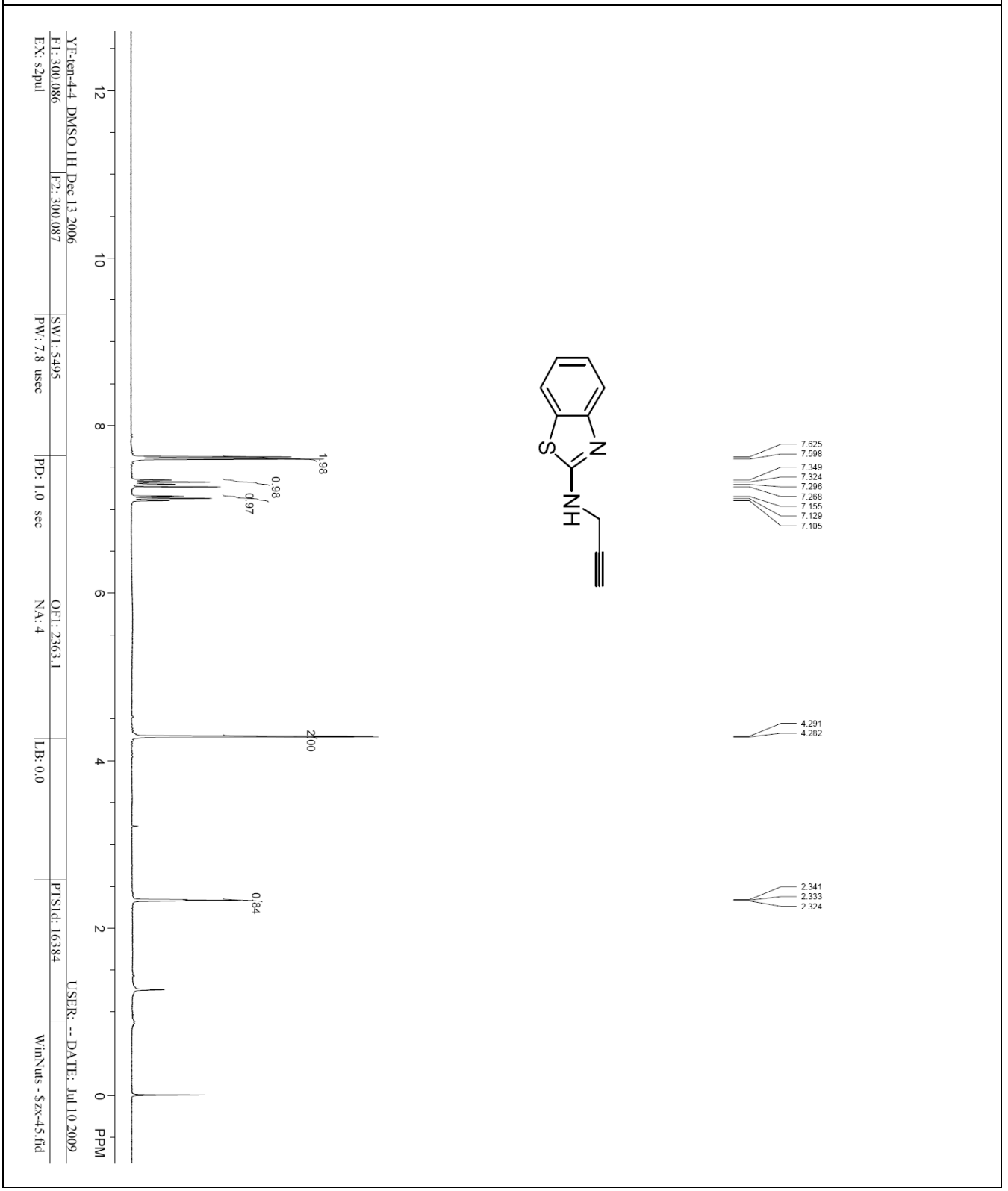

ZX-1002 DMSO BB+DEPT-135 Mar 25 2010
158.285
131.133
130.665
130.568
128.276
128.053
127.897
125.515
122.695
110.396
88.959
81.503
40.125
39.917
39.708
39.500
39.292
39.083
38.875
26.002
25.266
18.279
180
160
140
120
100
80
60
40
20
ppm

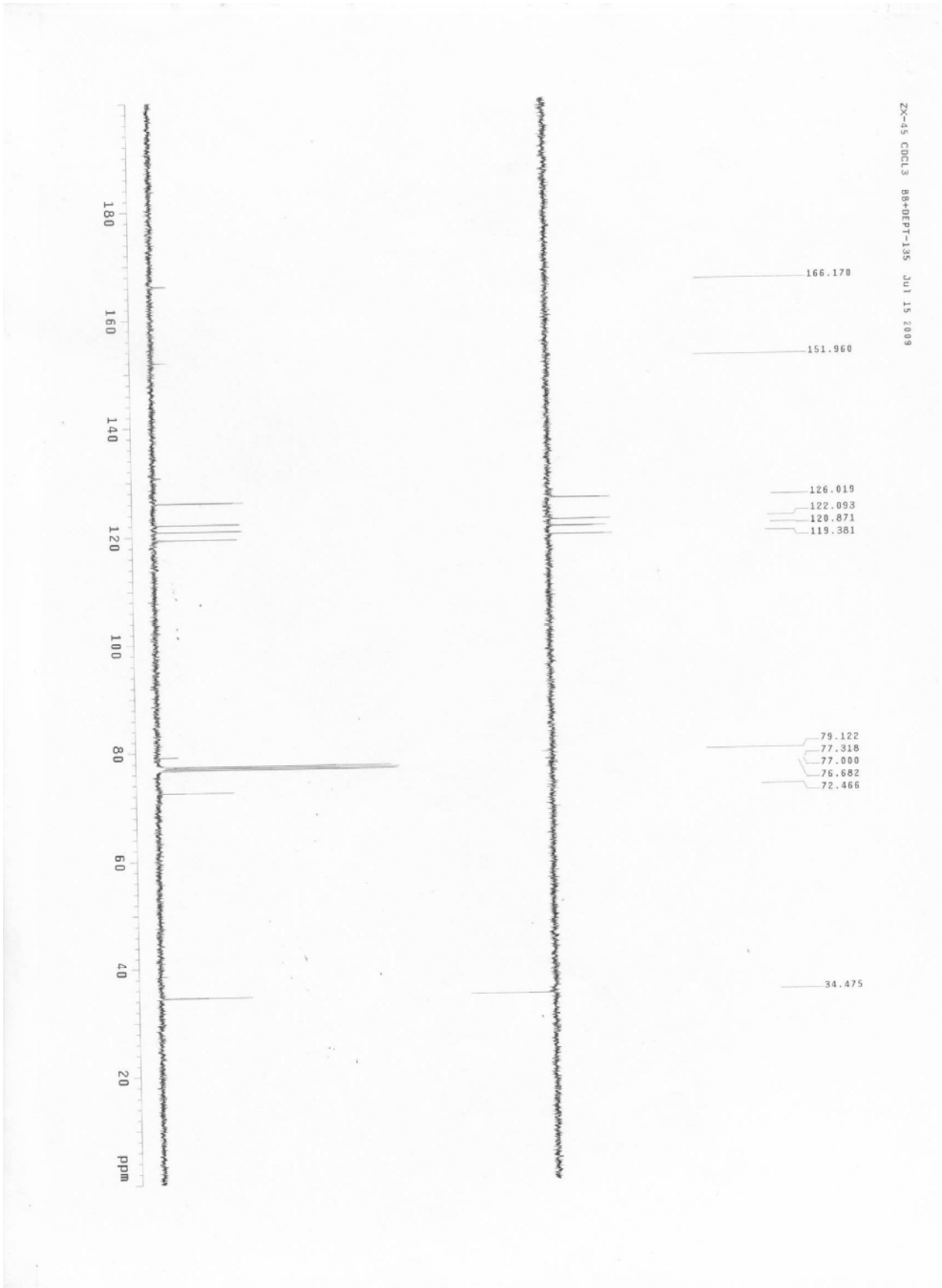
2-(Pent-4-ynyl)-1*H*-perimidine (A15)



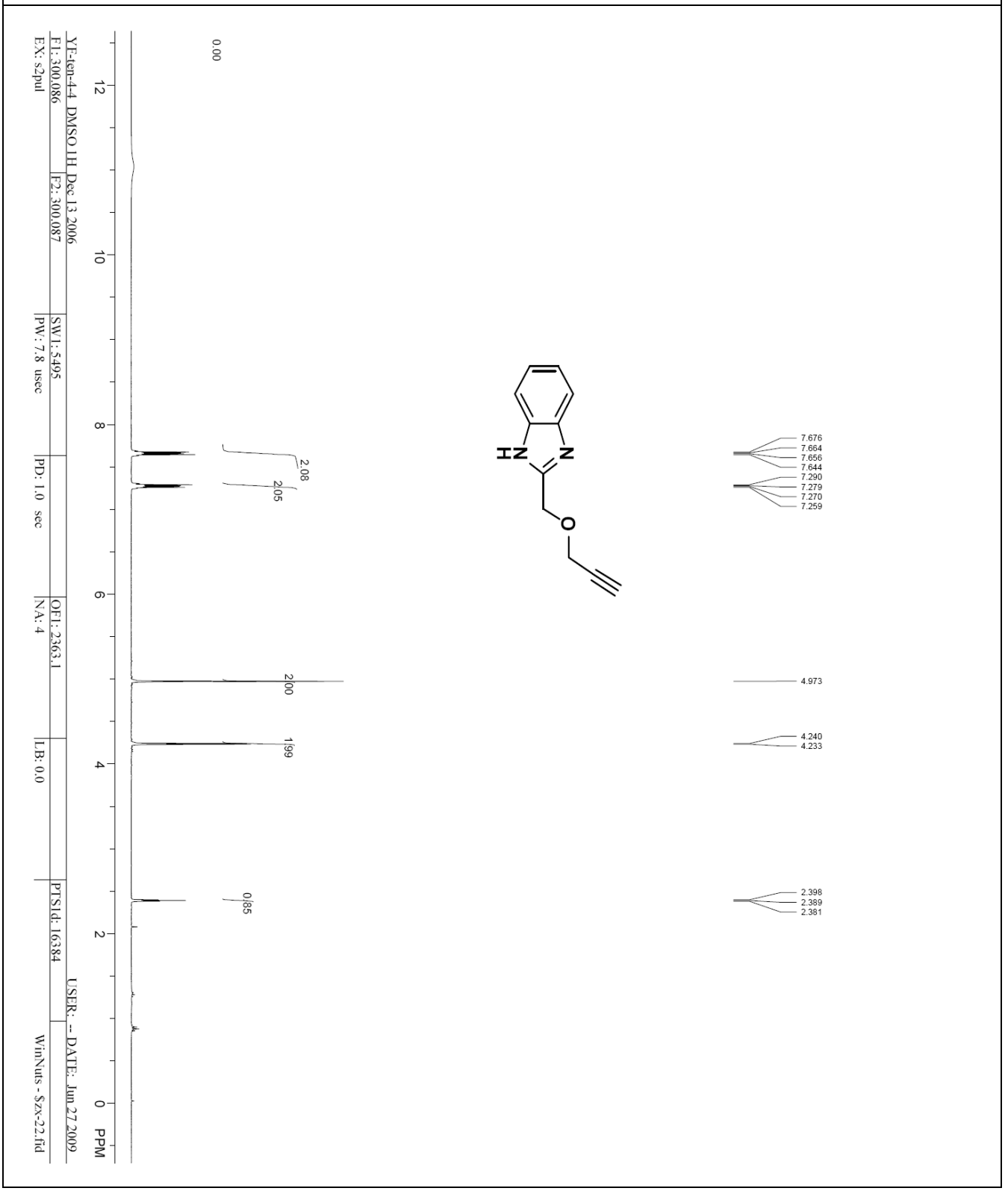

2X-48 CDCl3 BB+DEPT-135 Jun 29 2009
156.857
140.571
135.313
128.211
121.792
119.403
107.717
83.021
77.318
77.000
76.681
69.619
34.210
25.832
17.864
180
160
140
120
100
80
60
40
20
ppm

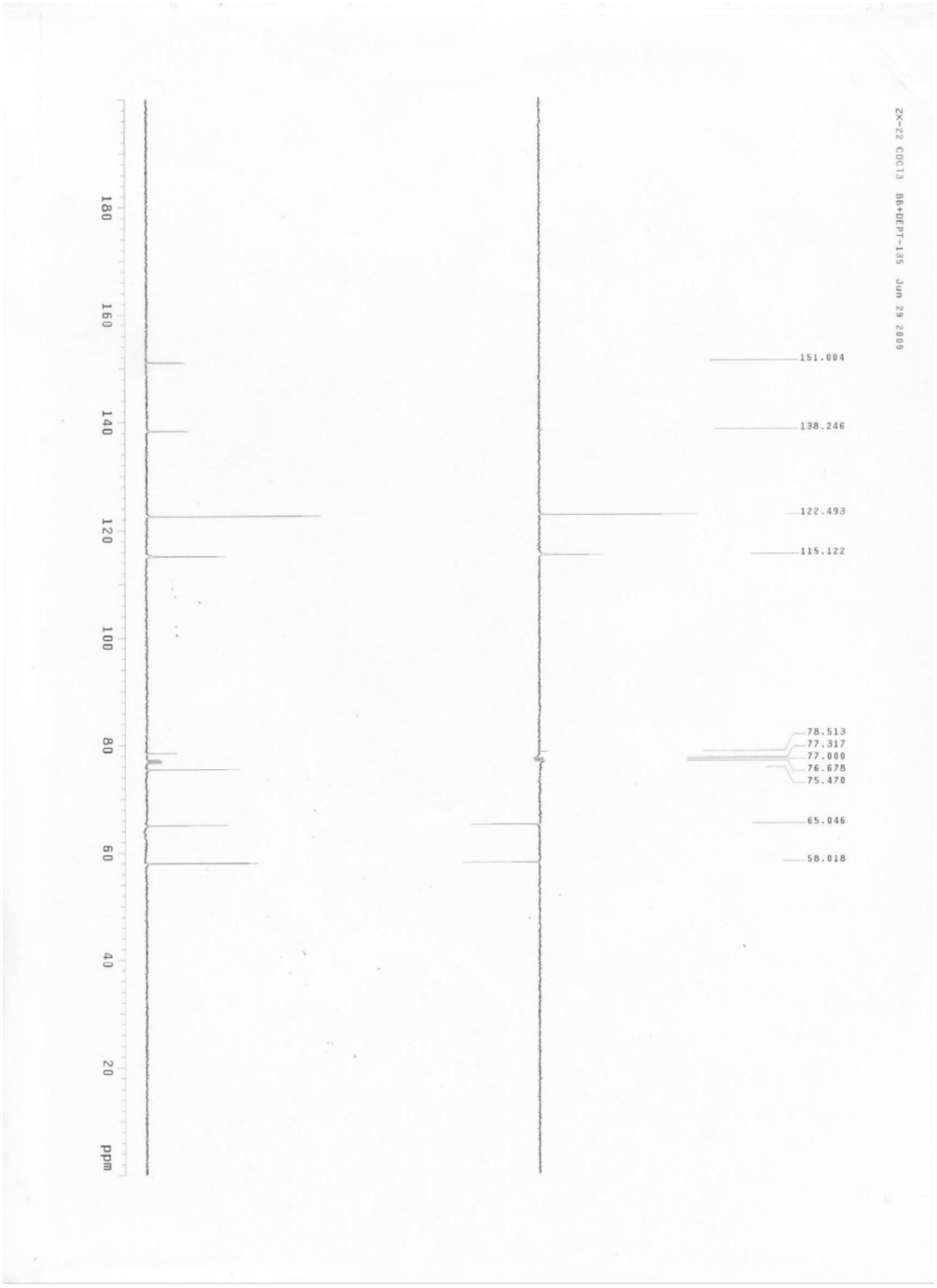
N-(Prop-2-ynyl)benzo[*d*]thiazol-2-amine (A16)



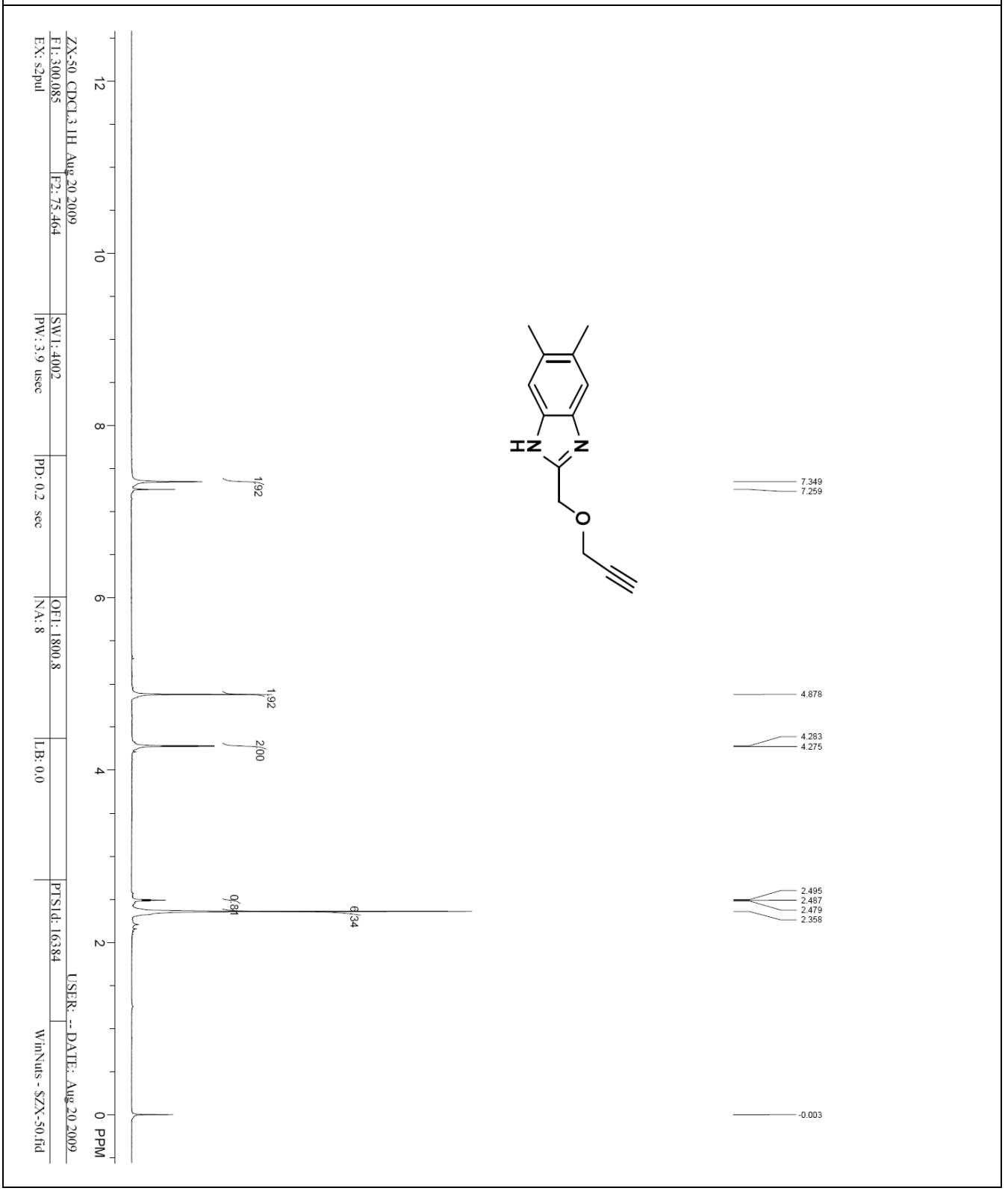

ZX-45 CDCL3 BB+DEPT-135 Jul 15 2009
166.170
151.960
126.019
122.093
120.871
119.381
79.122
77.318
77.000
76.682
72.466
34.475
180
160
140
120
100
80
60
40
20
ppm

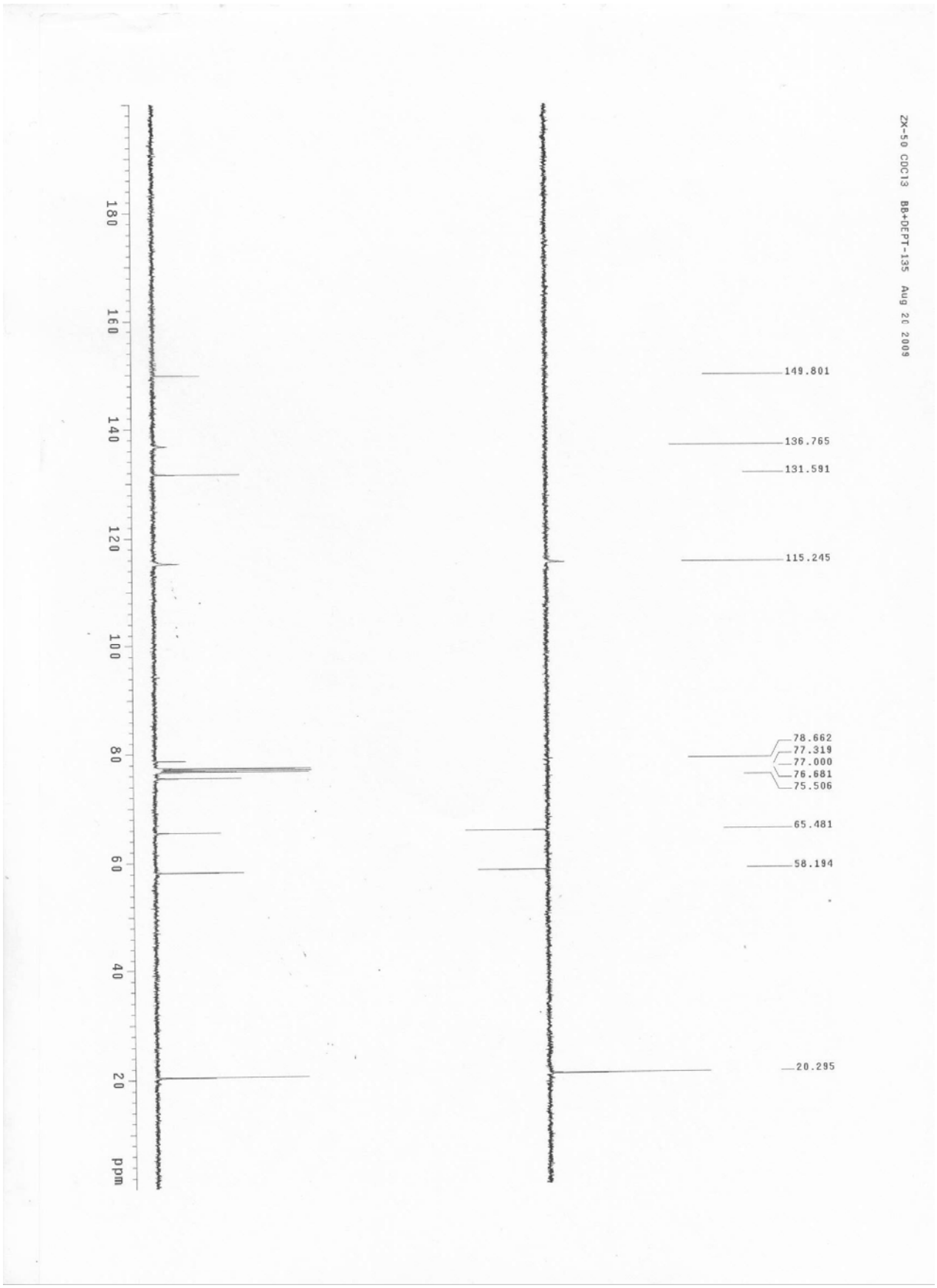
2-((Prop-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazole (A17)



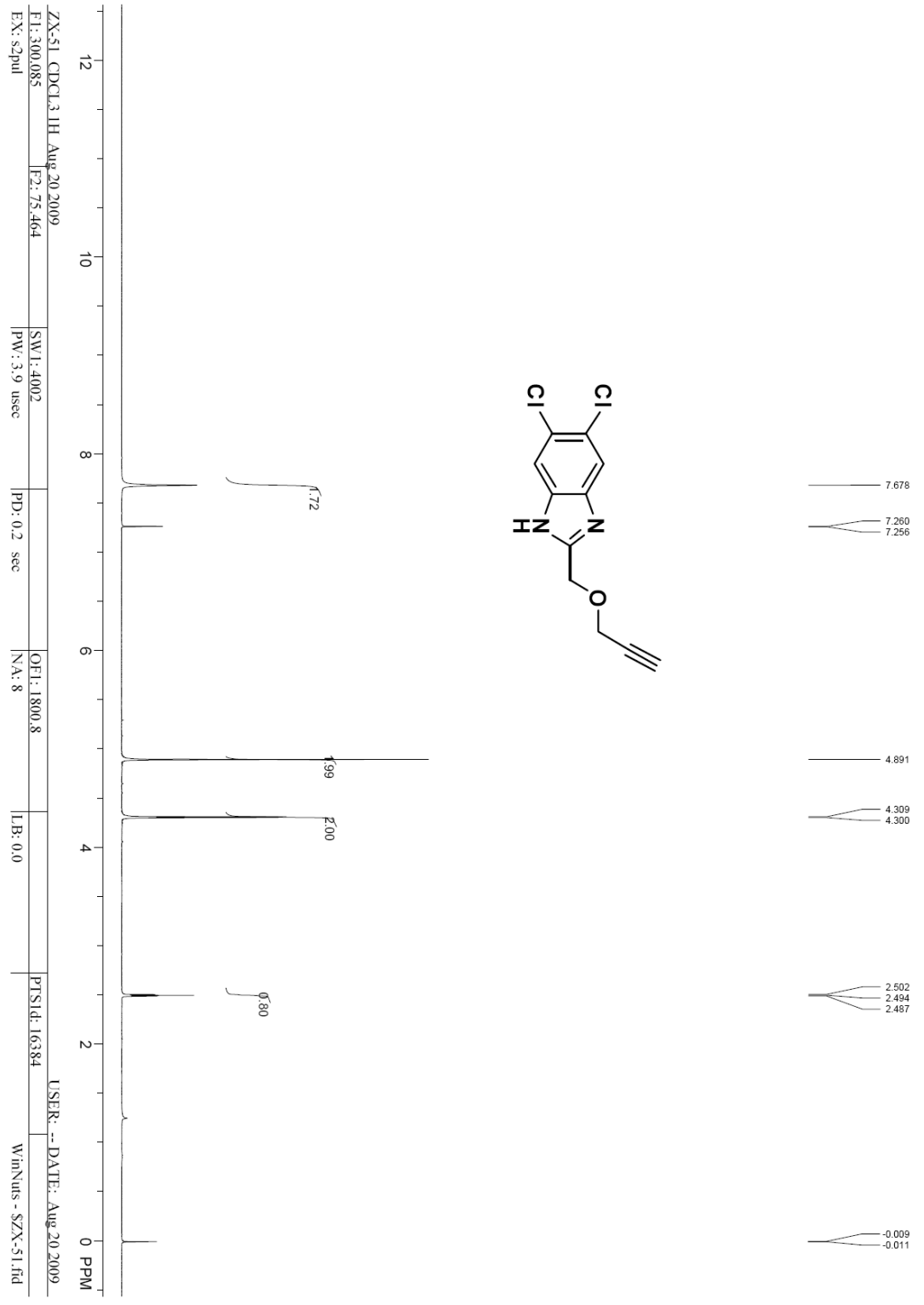

ZX-22 CDCl3 BB+DEPT-135 Jun 29 2009
151.004
138.246
122.493
115.122
78.513
77.317
77.000
76.678
75.470
65.046
58.018
180
160
140
120
100
80
60
40
20
ppm

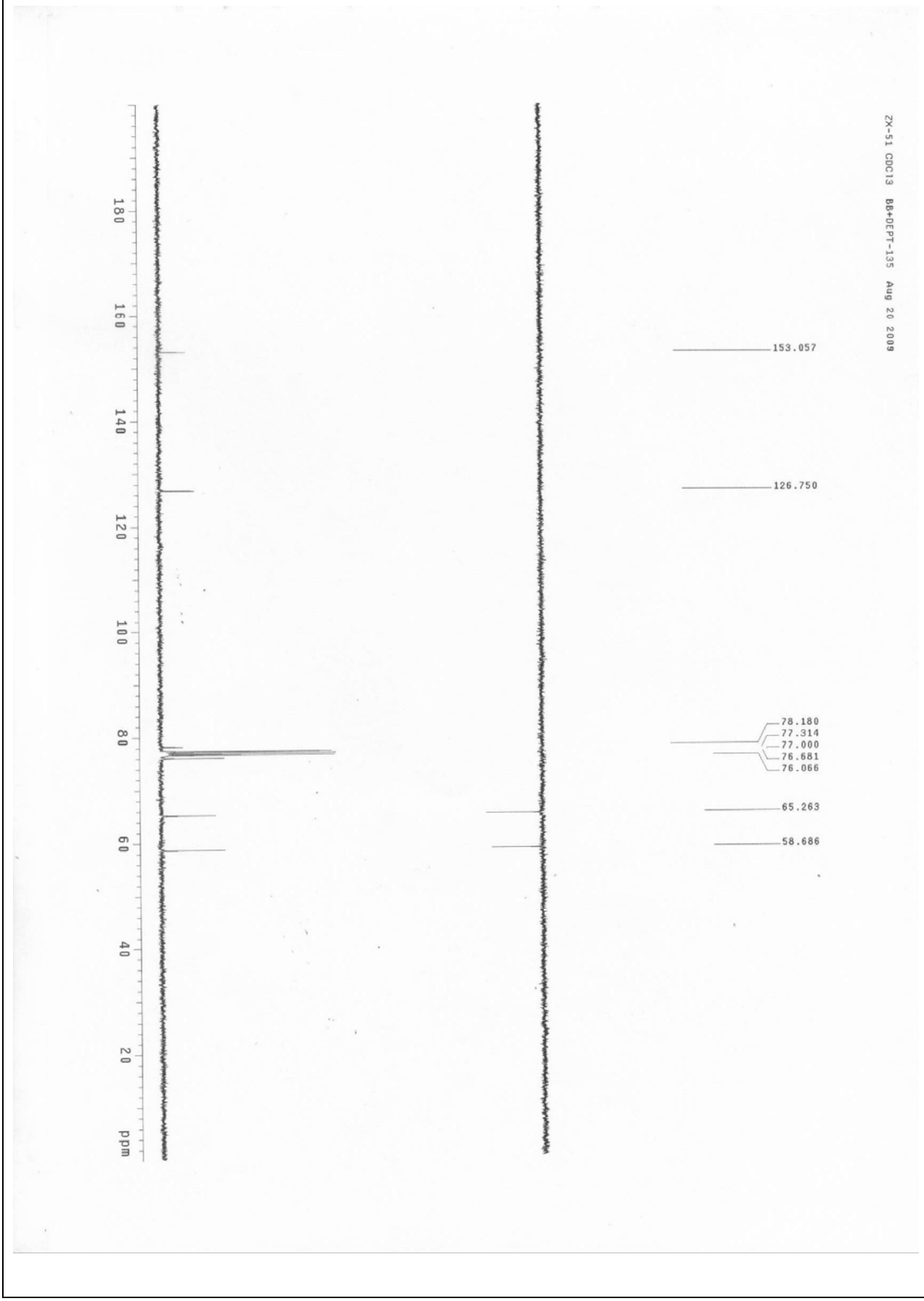
5,6-Dimethyl-2-((prop-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazole (A18)



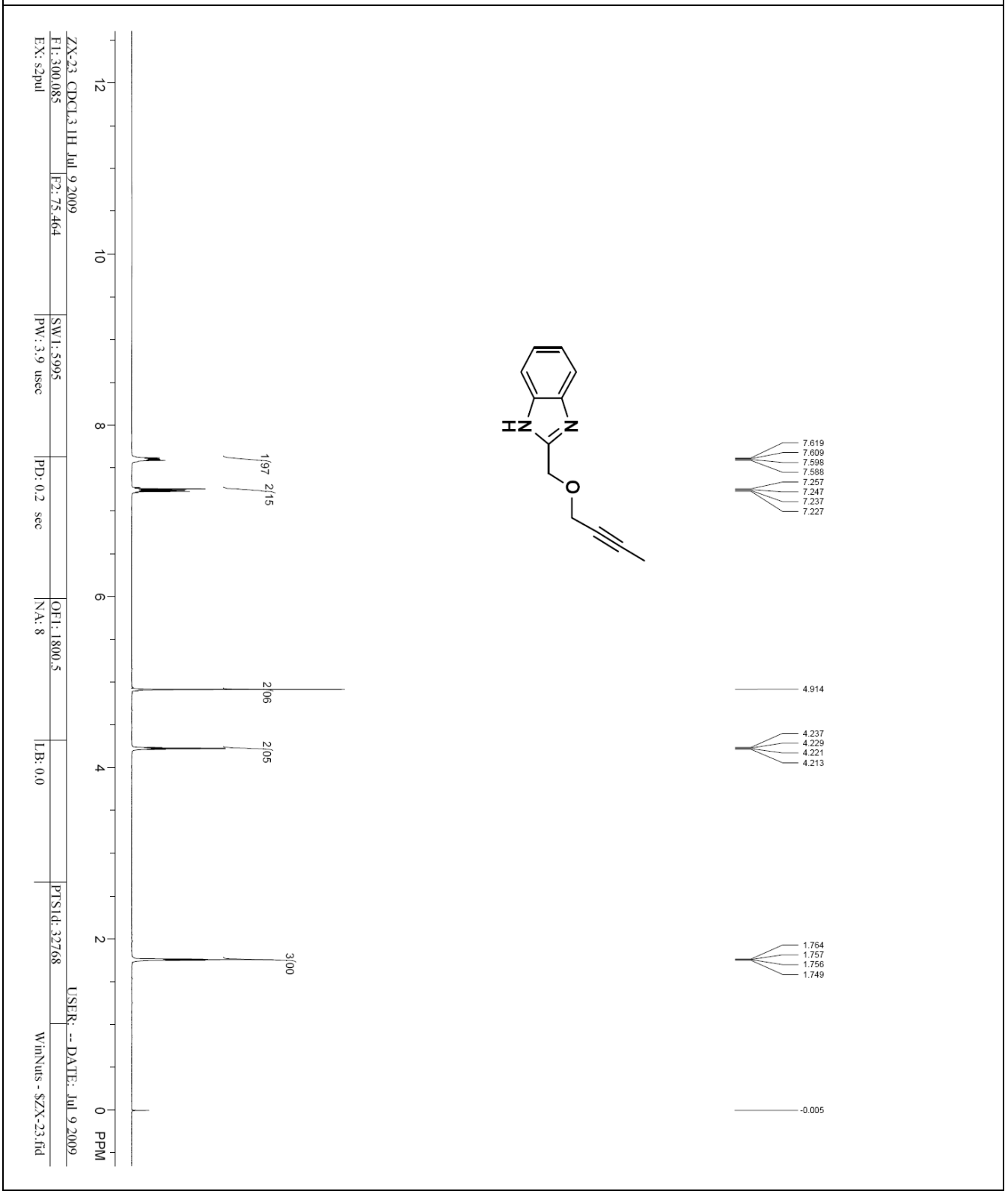

ZX-50 CDCl3 BB+DEPT-135 Aug 20 2009
149.801
136.765
131.591
115.245
78.662
77.319
77.000
76.681
75.506
65.481
58.194
20.295
180
160
140
120
100
80
60
40
20
ppm

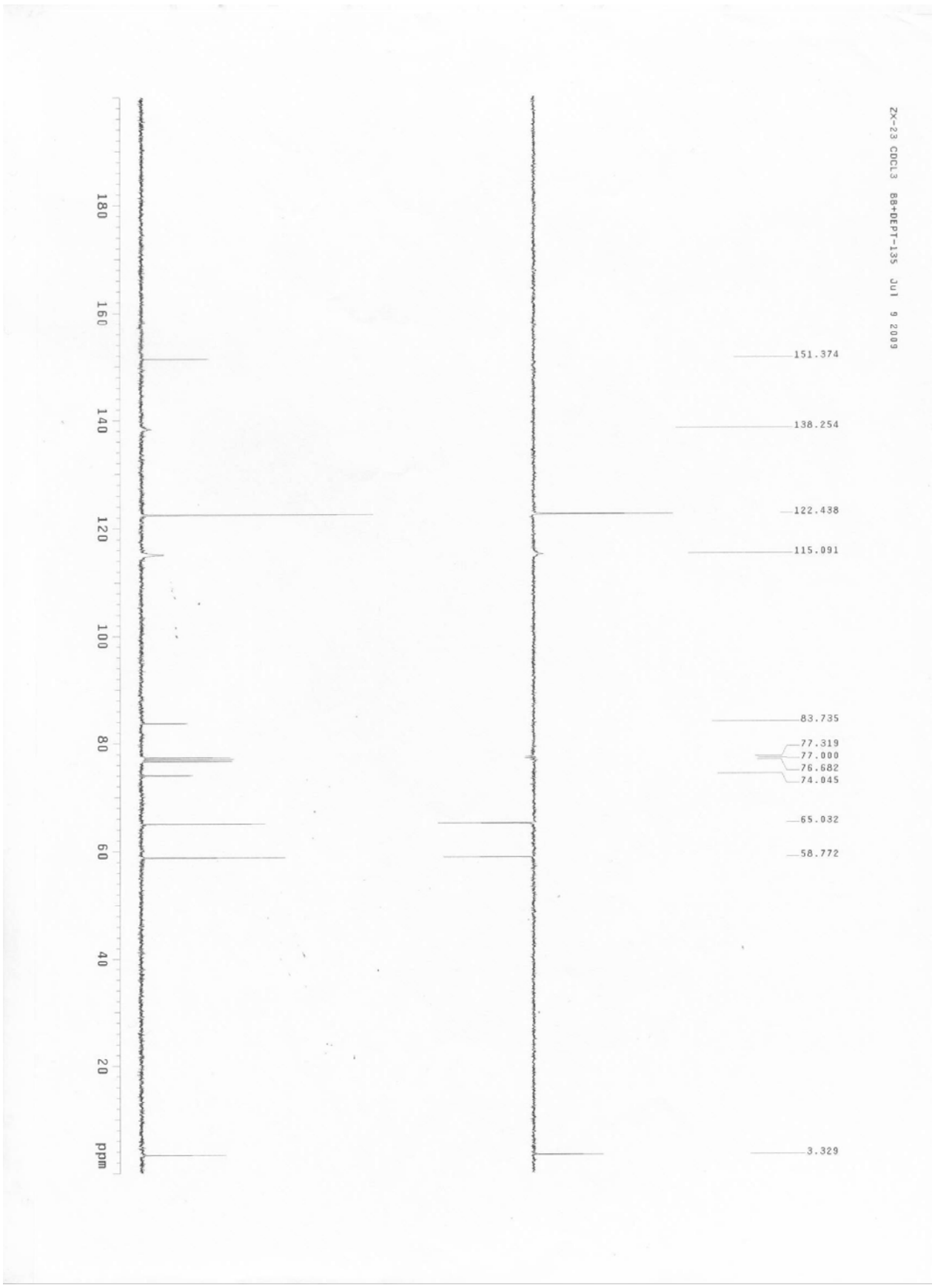
5,6-Dichloro-2-((prop-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazole (A19)



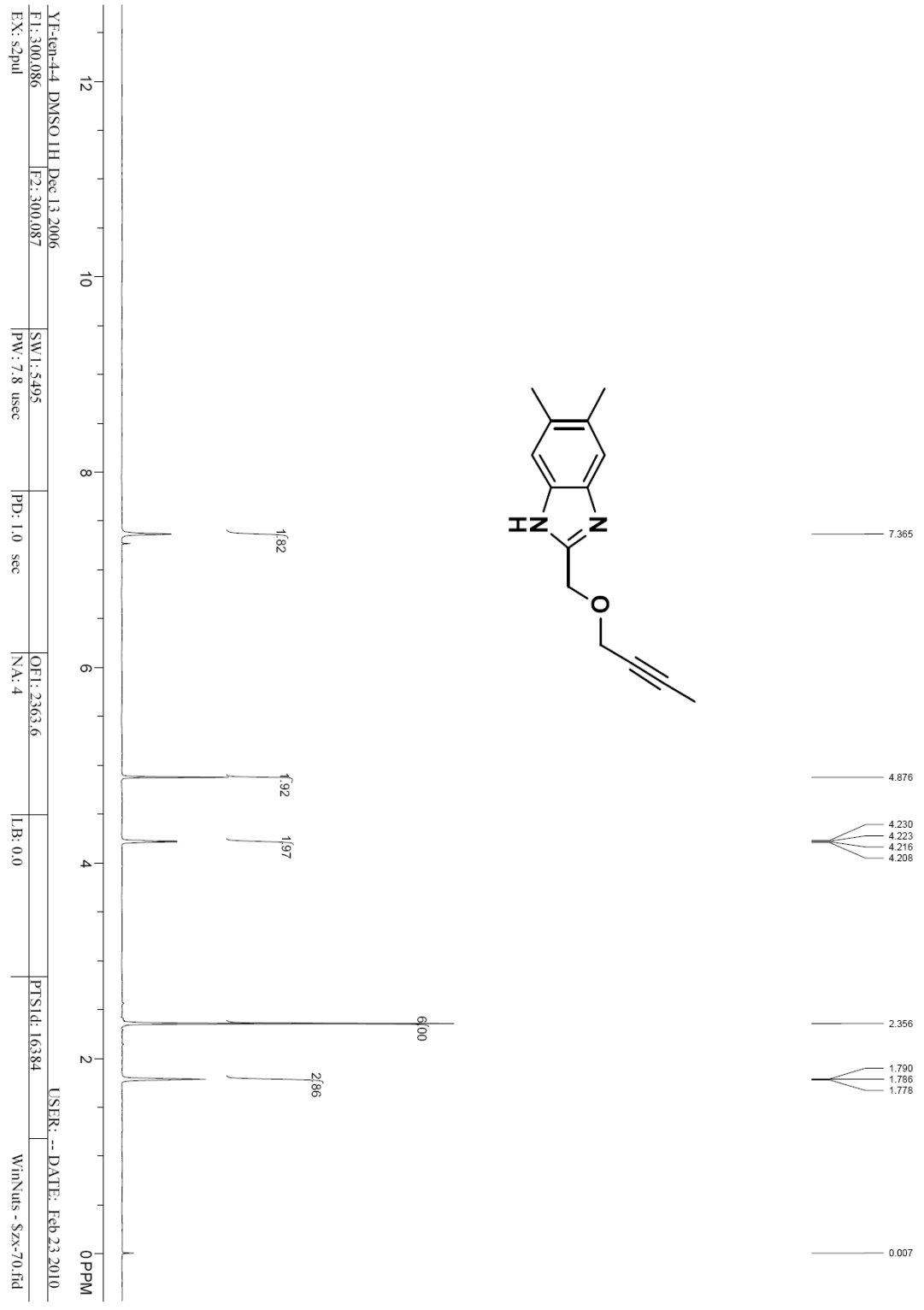

ZX-51 CDCl3 BB+DEPT-135 Aug 20 2009
153.057
126.750
78.180
77.314
77.000
76.681
76.066
65.263
58.686
180
160
140
120
100
80
60
40
20
ppm

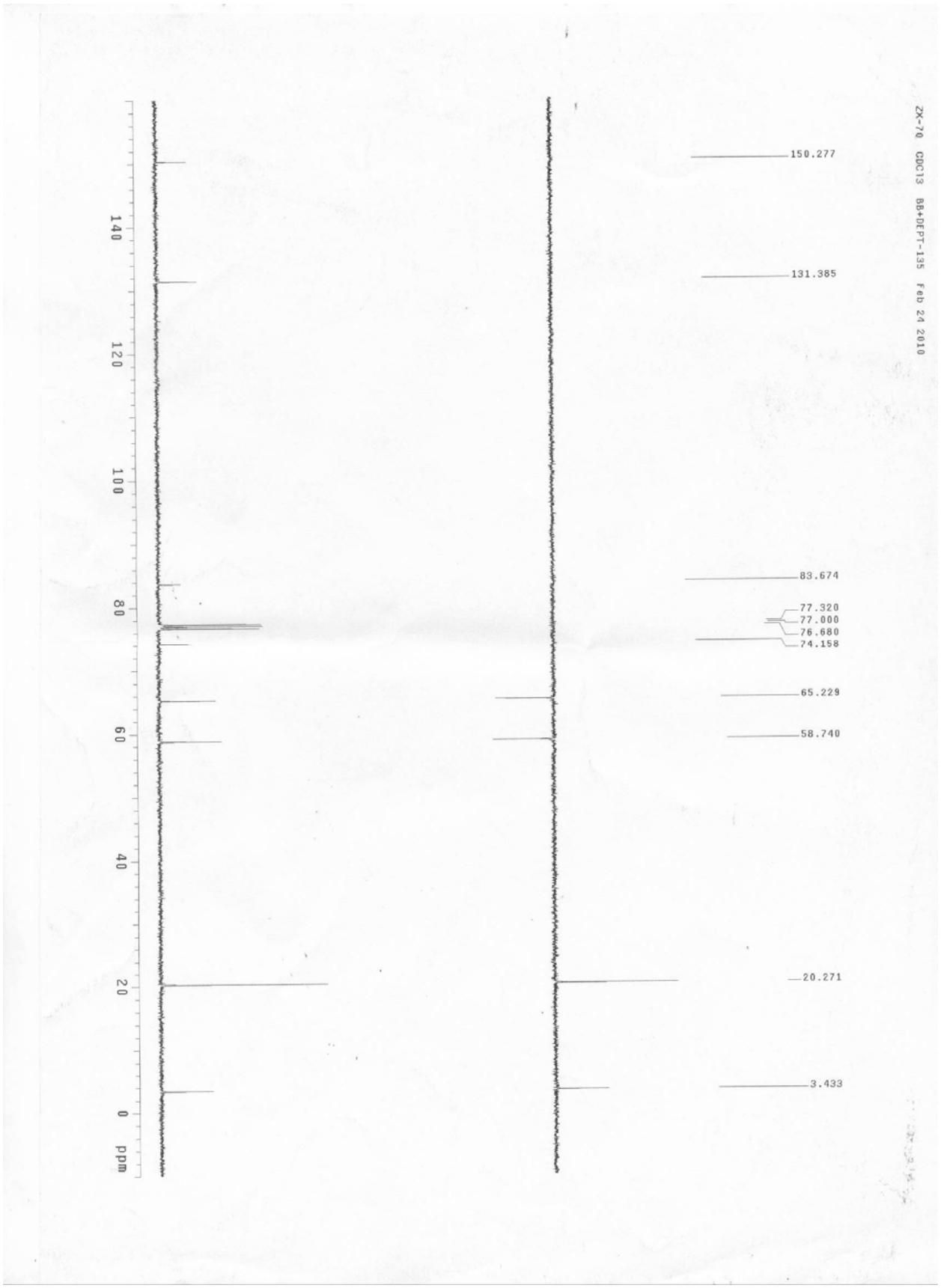
2-((But-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazole (A20)



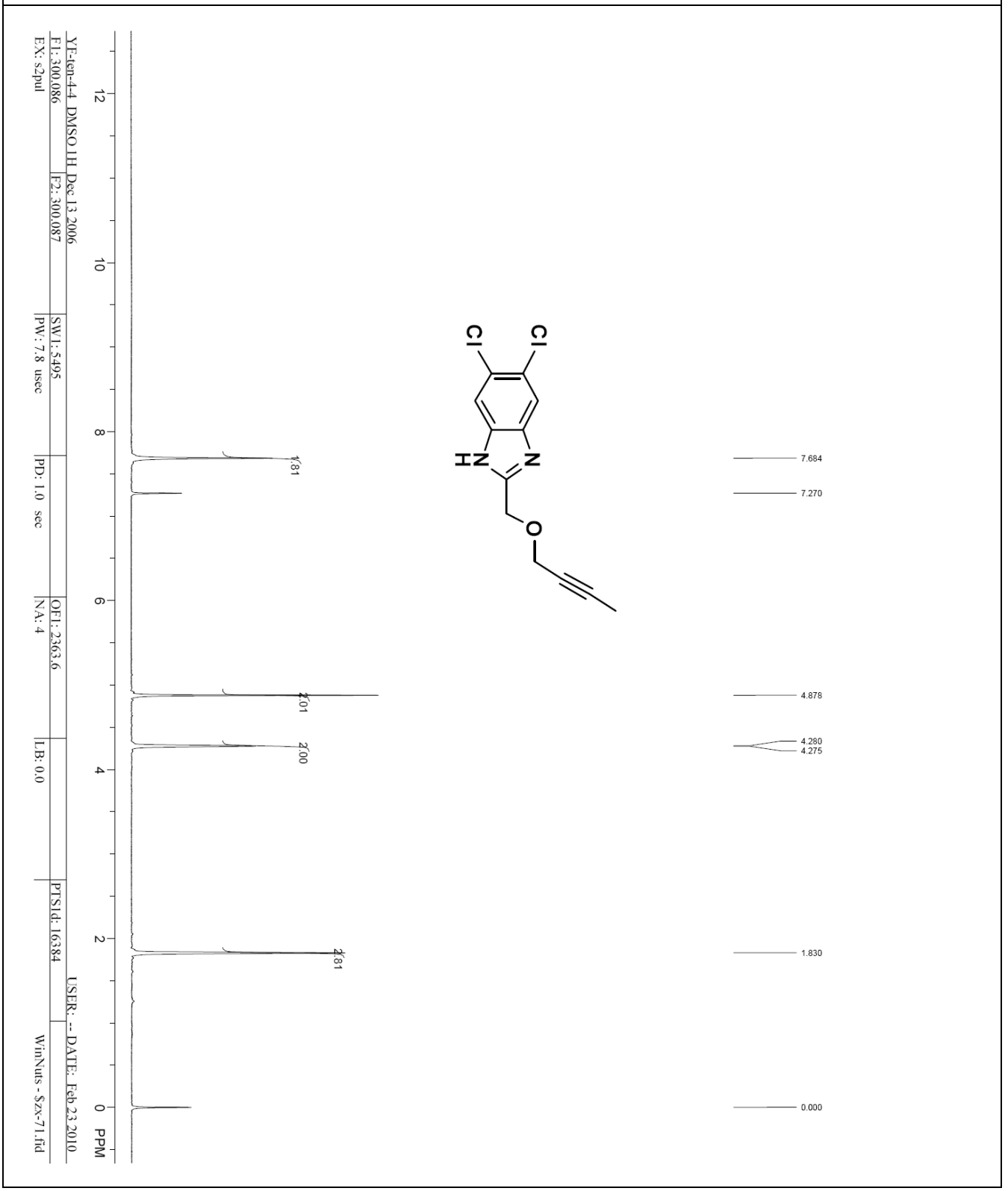

ZX-23 CDCL3 BB+DEPT-135 Jul 9 2009
151.374
138.254
122.438
115.091
83.735
77.319
77.000
76.682
74.045
65.032
58.772
3.329
180
160
140
120
100
80
60
40
20
ppm

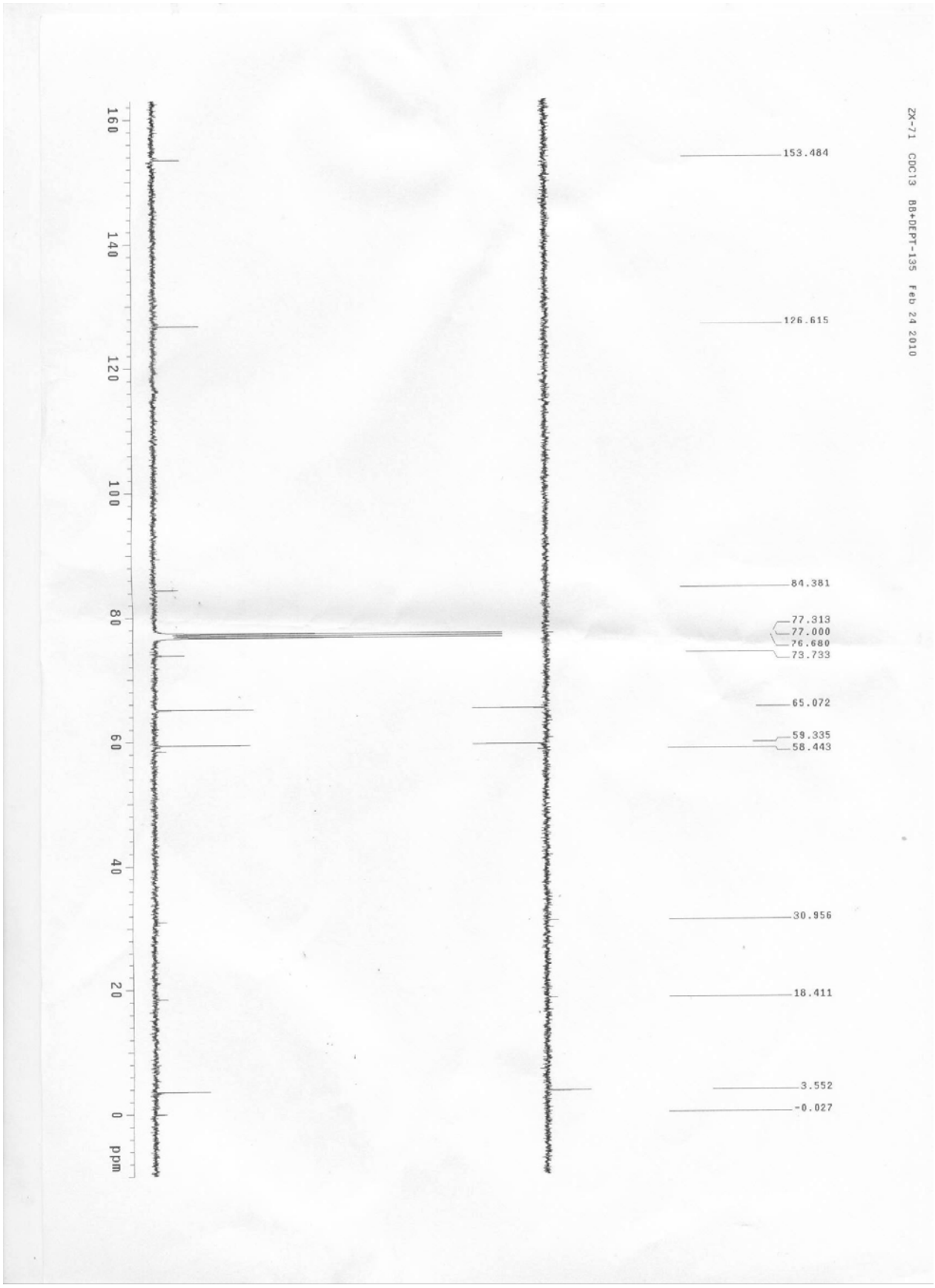
2-((But-2-ynyloxy)methyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (A21)



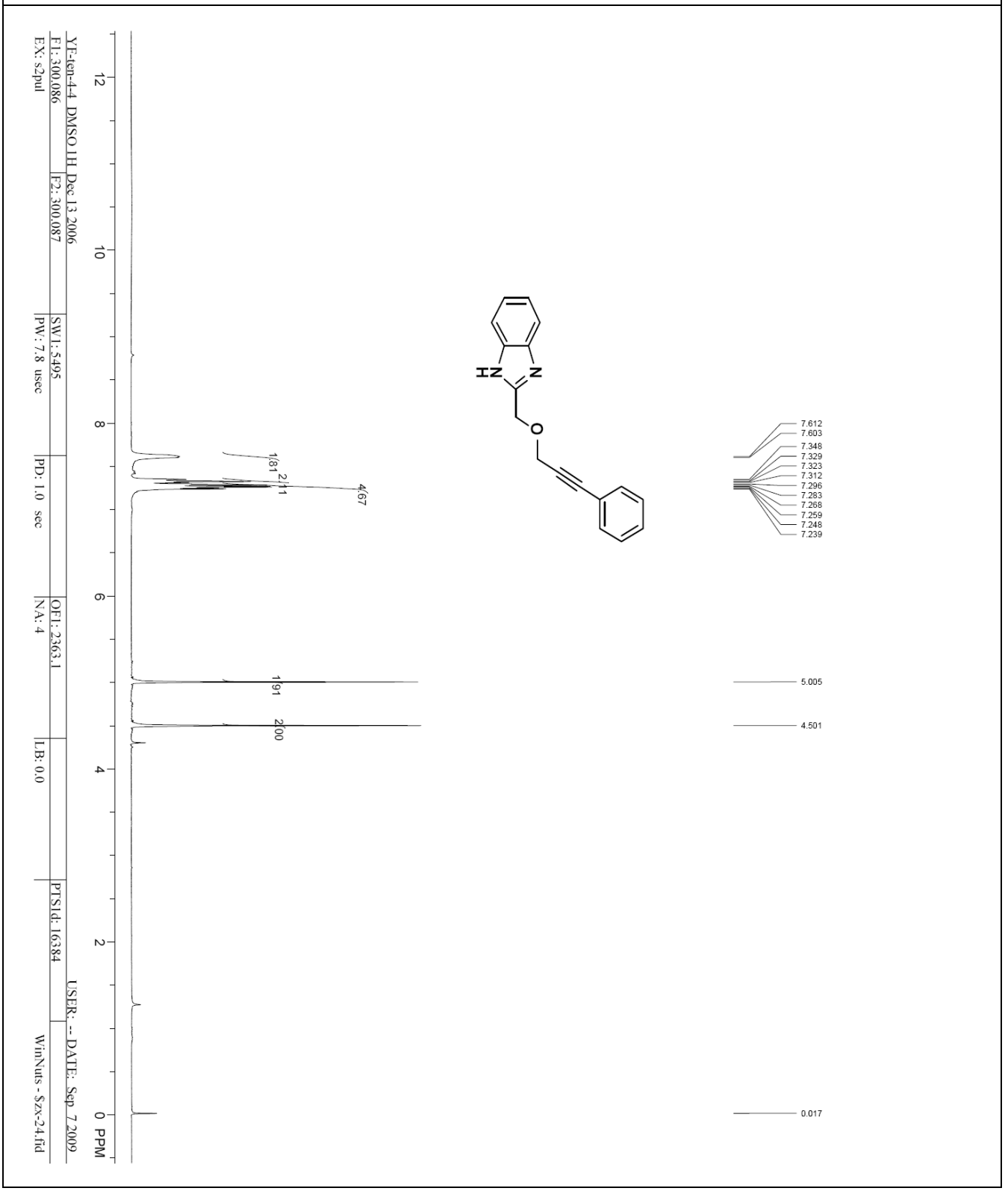

ZX-70 CDCl3 BB+DEPT-135 Feb 24 2010
150.277
131.385
83.674
77.320
77.000
76.680
74.158
65.229
58.740
20.271
3.433
140
120
100
80
60
40
20
0
ppm

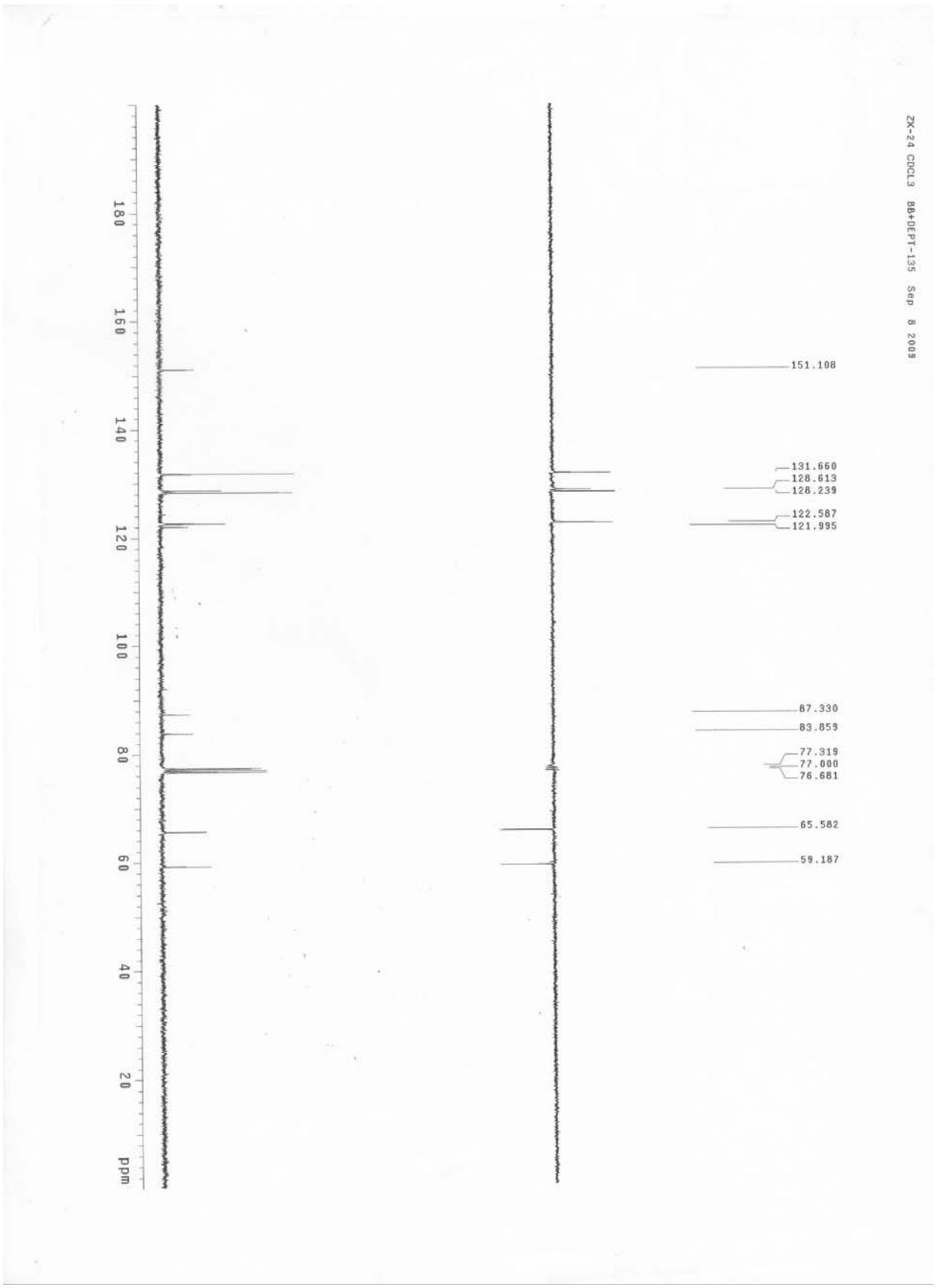
2-((But-2-ynyloxy)methyl)-5,6-dichloro-1*H*-benzo[*d*]imidazole (A22)



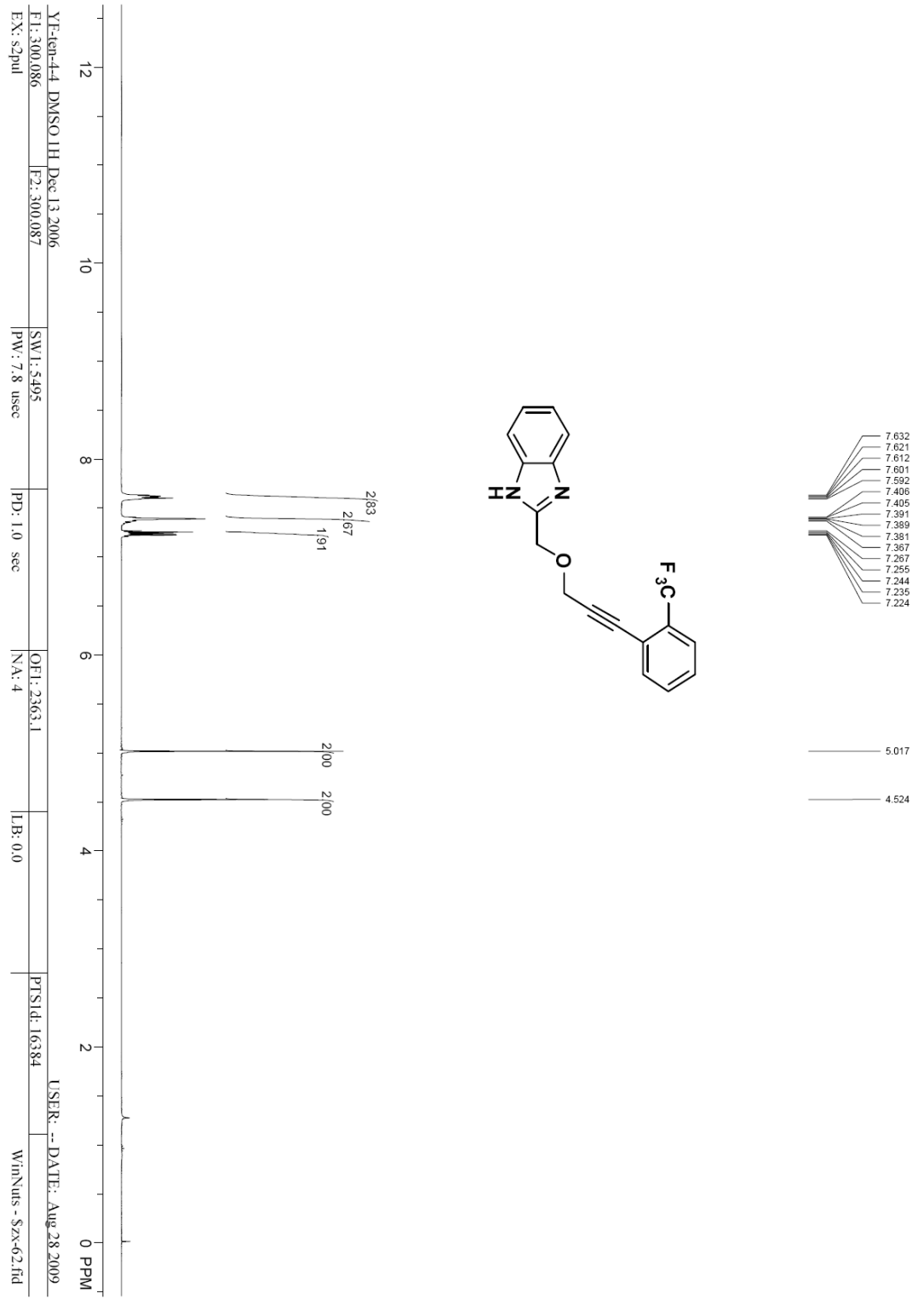

ZX-71 CDCl3 BB+DEPT-135 Feb 24 2010
153.484
126.615
84.381
77.313
77.000
76.680
73.733
65.072
59.335
58.443
30.956
18.411
3.552
-0.027
160
140
120
100
80
60
40
20
0
ppm

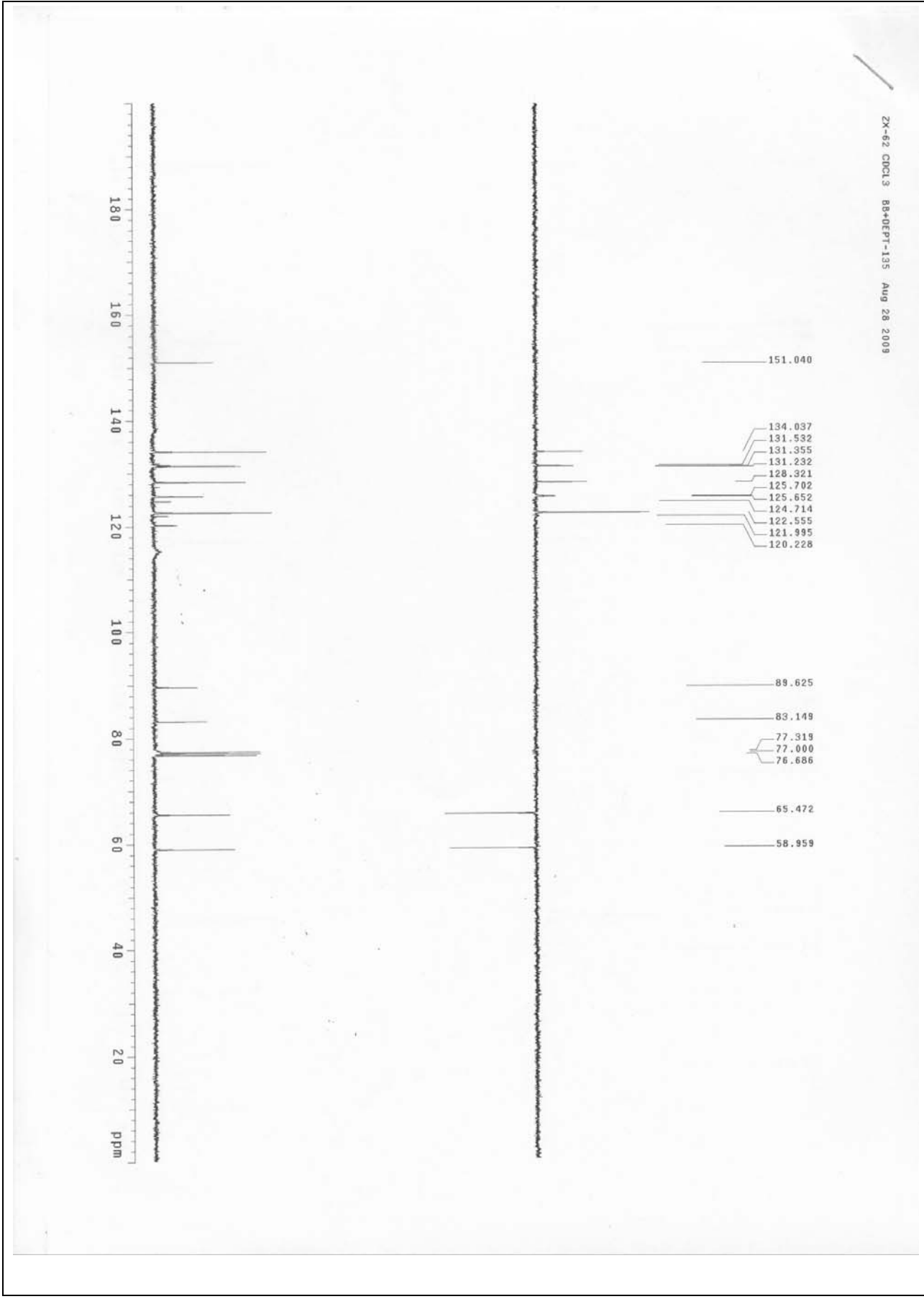
2-((3-Phenylprop-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazole (A23)



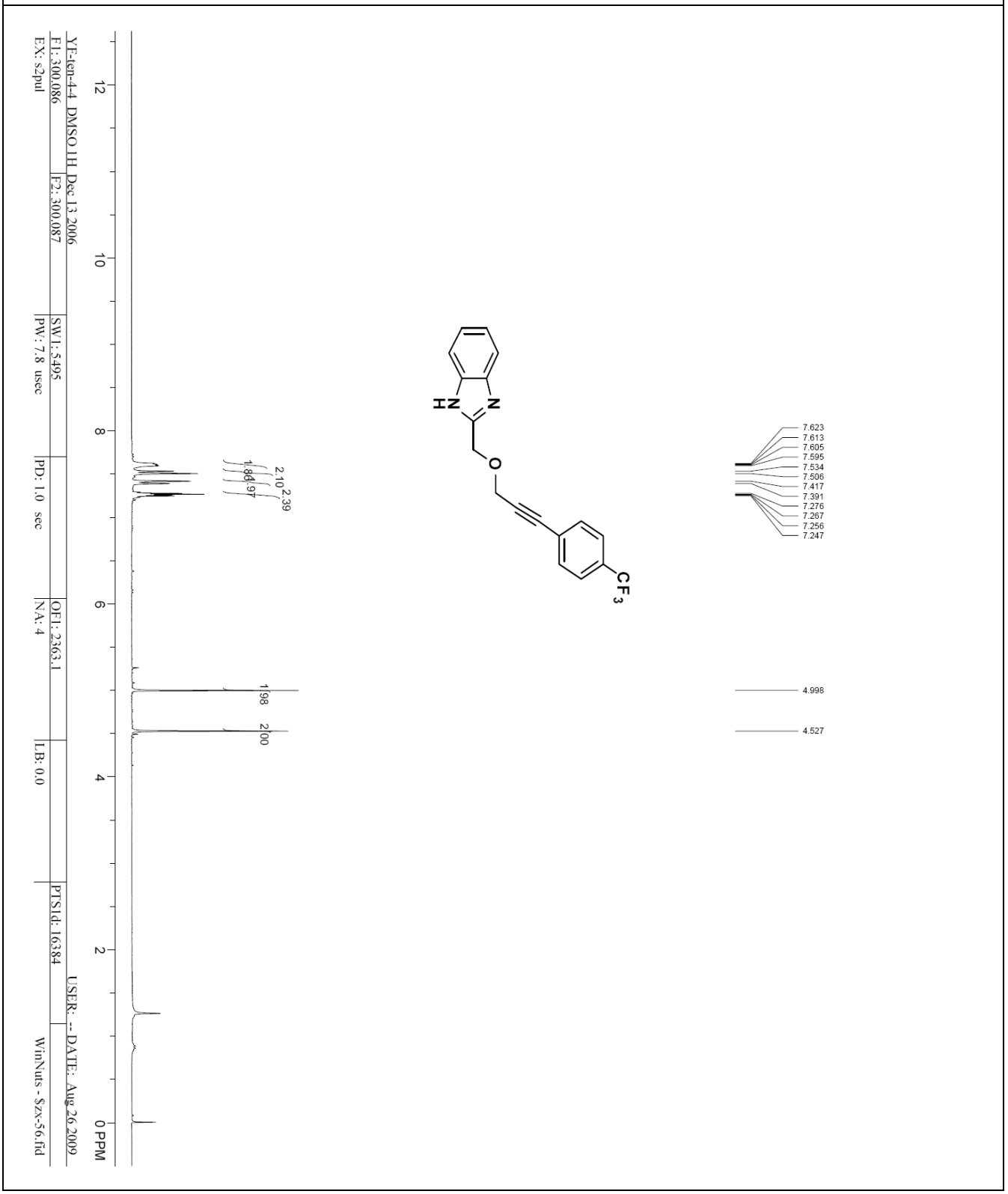

ZX-24 CDCL3 BB+DEPT-135 Sep 8 2009
151.108
131.660
128.613
128.239
122.587
121.995
87.330
83.859
77.319
77.000
76.681
65.582
59.187
180
160
140
120
100
80
60
40
20
ppm

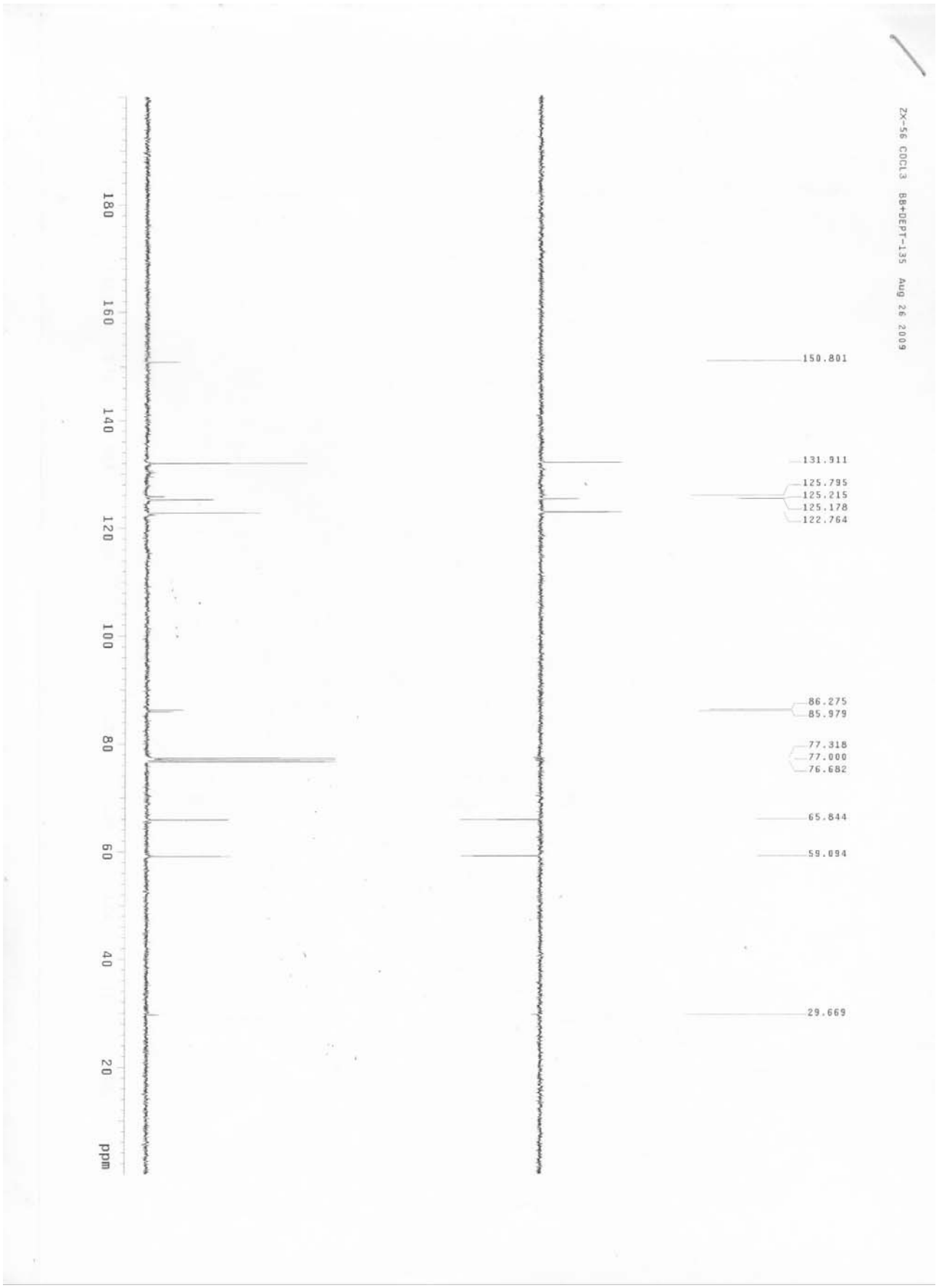
2-((3-(2-(Trifluoromethyl)phenyl)prop-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazole (A24)



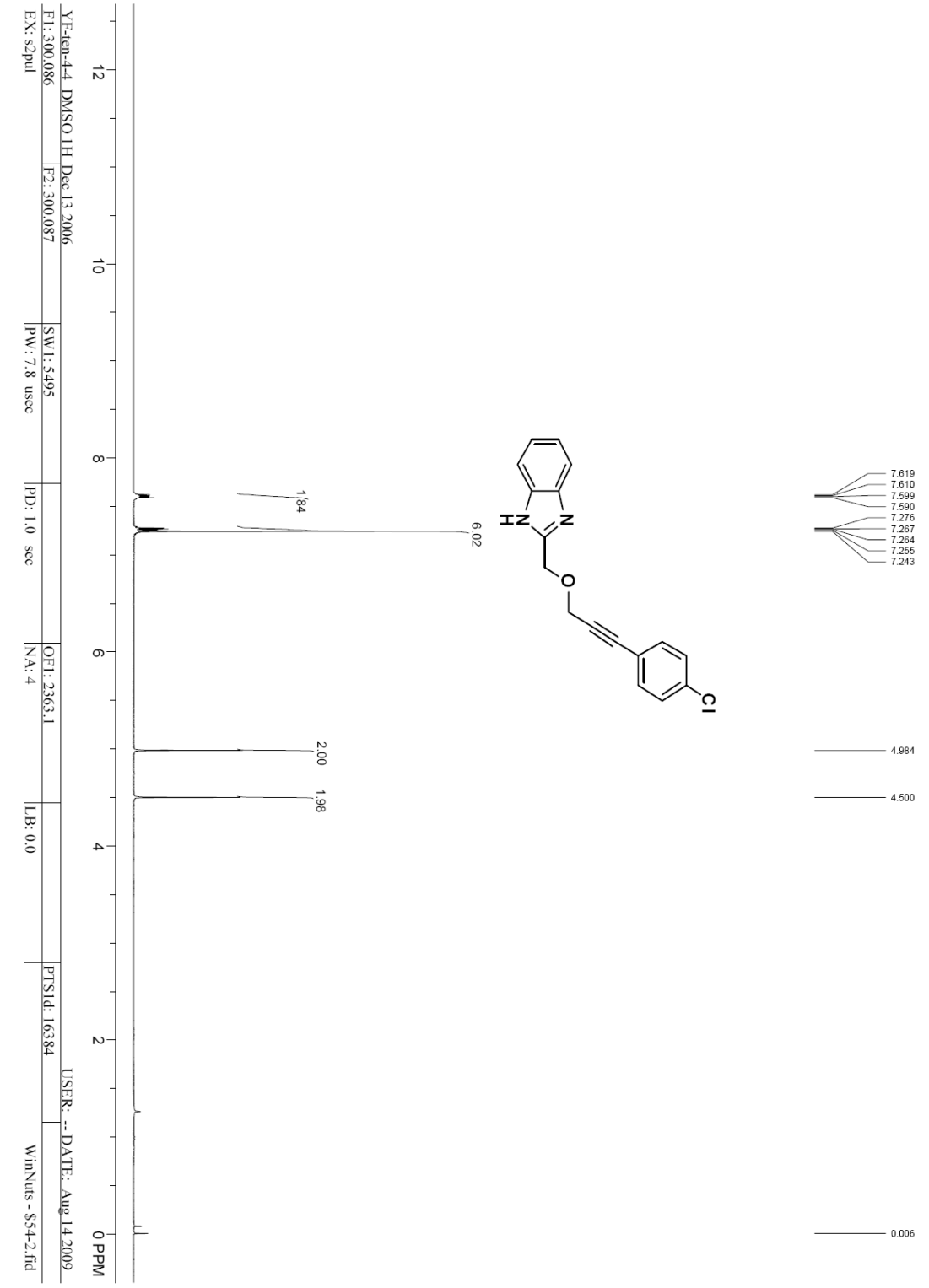

ZX-62 CDCL3 88+DEPT-135 Aug 28 2009
151.040
134.037
131.532
131.355
131.232
128.321
125.702
125.652
124.714
122.555
121.995
120.228
89.625
83.149
77.319
77.000
76.686
65.472
58.959
180
160
140
120
100
80
60
40
20
ppm

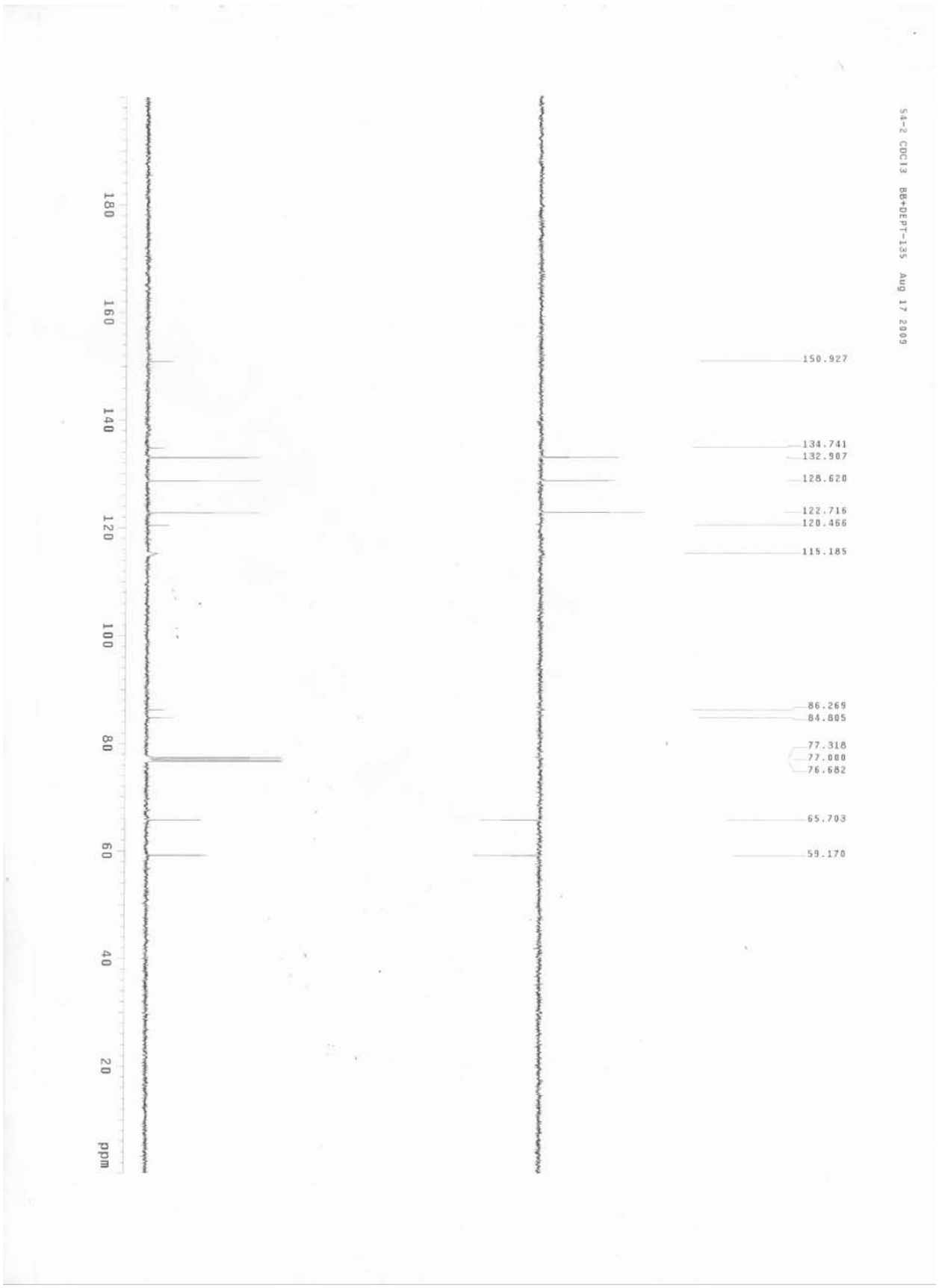
2-((3-(4-(Trifluoromethyl)phenyl)prop-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazole (A25)



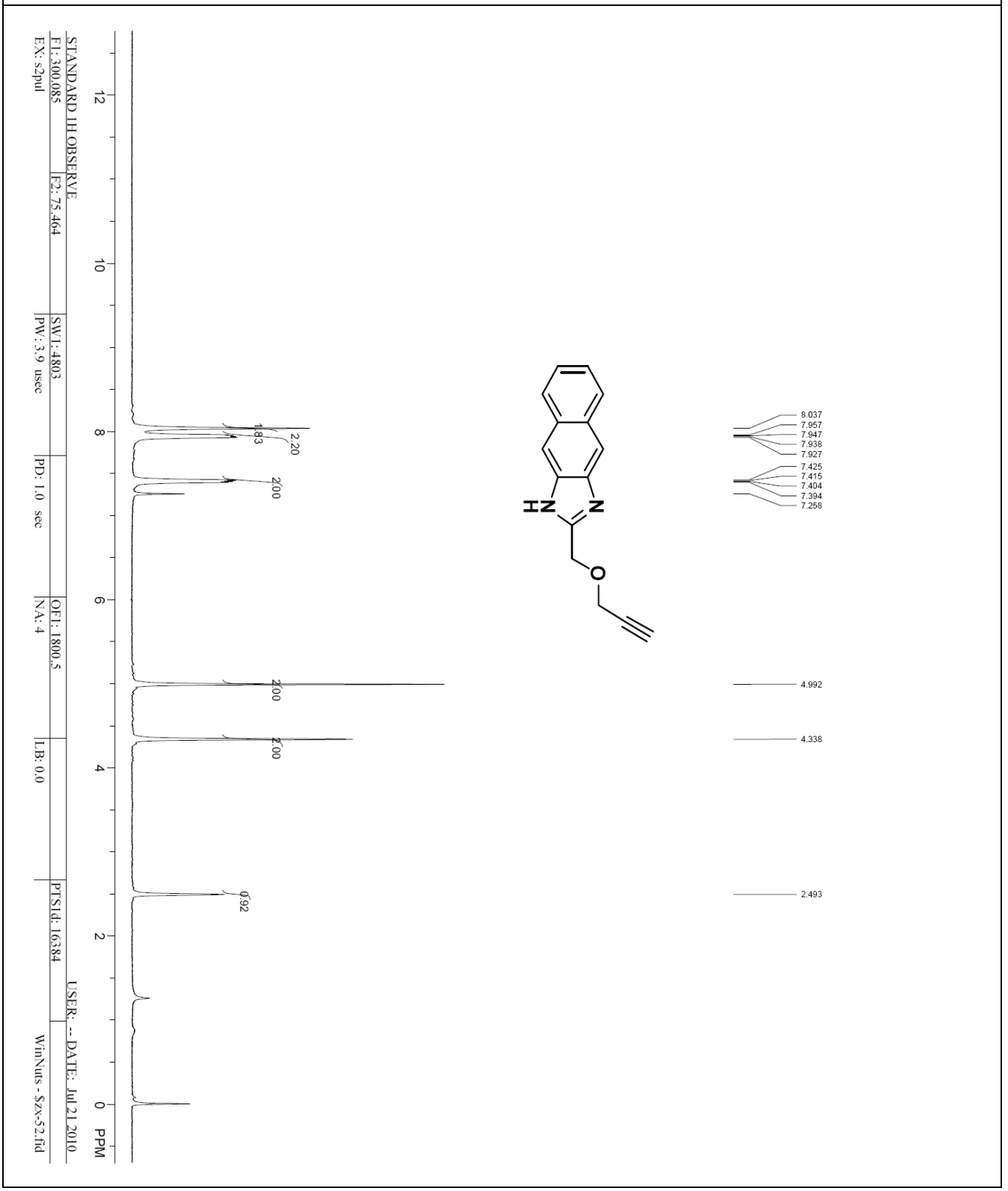

ZX-56 CDCl3 BB+DEPT-135 Aug 26 2009
150.801
131.911
125.795
125.215
125.178
122.764
86.275
85.979
77.318
77.000
76.682
65.844
59.094
29.669
180
160
140
120
100
80
60
40
20
ppm

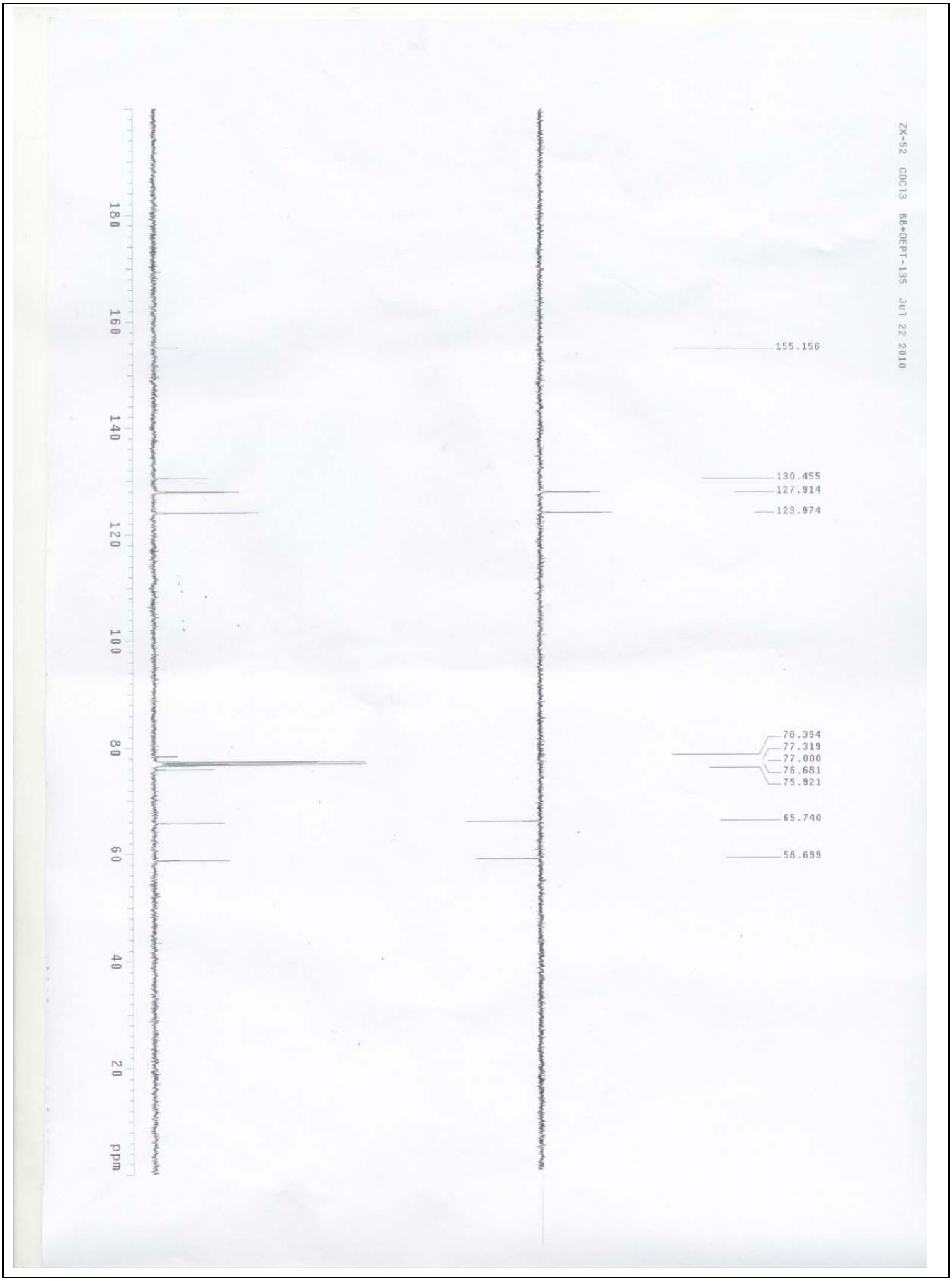
2-((3-(4-Chlorophenyl)prop-2-ynyloxy)methyl)-1*H*-benzo[*d*]imidazole (A26)




S4-2 CDCl3 BB+DEPT-135 Aug 17 2009
150.927
134.741
132.907
128.620
122.716
120.466
115.185
86.269
84.805
77.318
77.000
76.682
65.703
59.170
180
160
140
120
100
80
60
40
20
ppm

2-((Prop-2-ynyloxy)methyl)-1*H*-naphtho[2,3-*d*]imidazole (A27)




ZX-52 CDCl3 BB+DEPT-135 Jul 22 2010
155.156
130.455
127.914
123.974
78.394
77.319
77.000
76.681
75.921
65.740
58.699
180
160
140
120
100
80
60
40
20
ppm