Novel Oxa-di-π-methane and Norrish Type I Reactions in the S_2 (π,π*) Excited State of a Series of β,γ-Unsaturated Ketones

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Supporting Information

Experimental Section

General Procedures. Starting materials and reagents are commercially available unless synthesis is described. Spectral data of the known compounds were in accordance with the literature data. Flash chromatography was performed using silica gel 60 (40-63 mm). NMR spectra were recorded in $CDCl_3$ solution. Chemical shifts (δ) are expressed in parts per million (ppm), and coupling constants *J* are given in hertz (Hz). UV-vis spectra were recorded in CH_2Cl_2 solution. Melting points were determined in open capillaries and are uncorrected.

Ketone **20** was synthesized by the method previously described.[1]

General Procedure for the Synthesis of Ketones 7b, 7c, 24 and 25. To a solution of lithium diisopropylamide (LDA) in dry THF (prepared from diisopropylamine and BuLi at 0 ºC for 30 min) at –78 ºC under an atmosphere of argon, was added dropwise the phosphonate in dry THF. The mixture was stirred for 1 h and then a solution of the aldehyde in dry THF was added dropwise. The LDA/phosphonate/aldehyde ratio was 1:1:1 for all the experiments. The reaction was kept at –78 ºC for 2 h, allowed to warm at rt and stirred for 24 h before being quenched with saturated NH_4Cl solution and extracted with Et_2O. The combined organic phases were dried, filtered and concentrated to dryness. The ketones were purified by flash chromatography on silica gel.

5,5-Dicyano-3,3-dimethyl-4-penten-2-one (7a). A solution of 2,2-dimethyl-3-oxobutanal[2] (1.5 g, 13.2 mmol), malononitrile (1 g, 14.5 mmol), β-alanine (287 mg, 3.2 mmol) and acetic acid (4 mL) in toluene (40 mL) was refluxed for 24 h. The water generated during the condensation was azeotropically removed by using a Dean Stark trap. The mixture was then cooled, diluted with Et_2O and washed with water. The organic layers were dried ($MgSO_4$), filtered and concentrated to dryness. Flash chromatography using hexane/EtAcO (9:1) afforded enone **7a** (850 mg, 44%) as a yellow oil; ^{1}H NMR (200 MHz) δ 7.55 (s, 1H), 2.21 (s, 3H), 1.51 (s, 6H); ^{13}C NMR (50 MHz) δ 206.1, 171.0, 112.6, 110.8, 90.0, 52.5, 25.4, 24.0; IR (neat) ν 2255, 1713 cm^{-1};

[1] van der Weerdt, A. J. A.; Cerfontain, H. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 247-248.
[2] Redlich, H.; Bruns, W.; Francke, W.; Schuring, V.; Payne, T. L.; Vité, J.-P. *Tetrahedron* **1987**, *43*, 2029-2034.

UV (CH_2Cl_2) λ_{max} 226 nm (ε 12544), 254 nm (ε 1980), 313 nm (ε 449); MS *m/e* (%) 43 (M^+-119, 100).

5-Cyano-3,3-dimethyl-4-hexen-2-one (7b). Diisopropylamine (1.9 mL, 13.6 mmol), BuLi (8.5 mL, 1.6 M in hexane), diethyl 1-cyanoethylphosphonate (2.58 g, 13.6 mmol) and 2,2-dimethyl-3-oxobutanal[2] (1.56 g, 13.6 mmol) were reacted. Flash chromatography using hexane/EtAcO (95:5) afforded (*E*)-**7b** (1.05 g, 53%) as a colorless oil and (*Z*)-**7b** (187 mg, 9%) as a colorless oil.

Compound (*E*)-**7b**: ^{1}H NMR (200 MHz) δ 6.36 (q, *J* = 1.6, 1H), 2.09 (s, 3H), 1.70 (d, *J* = 1.6, 3H), 1.24 (s, 6H); ^{13}C NMR (50 MHz) δ 208.6, 151.3, 120.1, 112.5, 50.2, 26.0, 25.1, 15.9; IR (neat) ν 2220, 1711 cm^{-1}; UV (CH_2Cl_2) λ_{max} 227 nm (ε 5945), 254 nm (ε 1980), 313 nm (ε 125); MS *m/e* (%) 151 (M^+, 28), 123 (26), 109 (80), 108 (78), 85 (52), 81 (45), 71 (100), 67 (33), 57 (96), 43 (21).

Compound (*Z*)-**7b**: ^{1}H NMR (200 MHz) δ 6.09 (q, *J* = 1.6, 1H), 2.01 (s, 3H), 1.81 (d, *J* = 1.6, 3H), 1.23 (s, 6H); ^{13}C NMR (50 MHz) δ 208.5, 150.4, 120.1, 109.4, 50.6, 25.7, 24.7, 22.2.

5-Cyano-3,3-dimethyl-4-penten-2-one (7c). Diisopropylamine (1.9 mL, 13.6 mmol), BuLi (8.5 mL, 1.6 M in hexane), diethyl cyanomethylphosphonate (2.63 g, 13.6 mmol) and 2,2-dimethyl-3-oxobutanal[2] (1.56 g, 13.6 mmol) were reacted. Flash chromatography using hexane/EtAcO (9:1) afforded enone **7c** (880 mg, 47%) as a 2:1 mixture of *E*/*Z* isomers and as a colorless oil; ^{1}H NMR (200 MHz) δ 6.81 (d, *J* = 16.6, 0.66H, *E*-isomer), 6.54 (d, *J* = 12.2, 0.33H, *Z*-isomer), 5.42 (d, *J* = 12.2, 0.33H, *Z*-isomer), 5.35 (d, *J* = 16.6, 0.66H, *E*-isomer), 2.16 (s, 1H, *Z*-isomer), 2.10 (s, 2H, *E*-isomer), 1.41 (s, 2H, *Z*-isomer), 1.24 (s, 4H, *E*-isomer); ^{13}C NMR (50 MHz) δ 207.9 (*Z*-isomer), 207.6 (*E*-isomer), 157.9 (*E*-isomer), 156.4 (*Z*-isomer), 112.6 (*E*-isomer), 110.8 (*Z*-isomer), 99.5 (*E*-isomer), 99.1 (*Z*-isomer), 51.5 (*E*-isomer), 51.4 (*Z*-isomer), 25.7 (*Z*-isomer), 24.7 (*E*-isomer), 24.1 (*Z*-isomer), 23.0 (*E*-isomer); IR (neat) ν 2224, 1715 cm^{-1}; UV (CH_2Cl_2) λ_{max} 230 nm (ε = 2642), 254 nm (ε = 1300), 313 nm (ε = 94); MS *m/e* (%) 137 (M^+, 6), 122 (2), 95 (36), 43 (100).

5,5-Dimethoxycarbonyl-3,3-dimethyl-4-penten-2-one (16). A suspension of $TiCl_4$ (28 mL, 1 M in CH_2Cl_2) was added to dry THF (20 mL) at 0 ºC under an atmosphere of argon. Then, a solution of 2,2-dimethyl-3-oxobutanal[2] (1.27 g, 11.1 mmol) and dimethyl

malonate (1.63 g, 12.3 mmol) in dry THF (30 mL) were added dropwise. The mixture was stirred at 0 ºC for 20 min followed by addition of dry pyridine (6.5 mL, 84 mmol) in dry THF (10 mL). The mixture was allowed to warm to rt and stirred for an additional 24 h. Then, water was added and the reaction was extracted with Et_2O. The combined organic layers were washed with brine, saturated $NaHCO_3$ solution and water, dried, filtered and concentrated to dryness. Flash chromatography using hexane/EtAcO (95:5) afforded enone **16** (1.5 g, 59%) as a colorless oil; ^{1}H NMR (200 MHz) δ 7.00 (s, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 2.10 (s, 3H), 1.25 (s, 6H); ^{13}C NMR (50 MHz) δ 207.8, 165.6, 164.2, 150.9, 128.1, 52.7, 52.2, 50.1, 26.3, 24.7; IR (neat) ν 1725, 1719, 1637 cm^{-1}; UV (CH_2Cl_2) λ_{max} 227 nm (ε 2014), 254 nm (ε 1980), 313 nm (ε 449); MS *m/e* (%) 213 (M^+-15, 3), 186 (72), 154 (25), 122 (100), 101 (37), 96 (40), 71 (24), 59 (62), 43 (90).

(*E*)-5-(4-Cyanophenyl)-3,3-dimethyl-4-penten-2-one (*E*-24). Diisopropylamine (1.5 mL, 10.6 mmol), BuLi (6.6 mL, 1.6 M in hexane), diethyl 4-cyanophenylmethylphosphonate* (2.69 g, 10.6 mmol) and 2,2-dimethyl-3-oxobutanal[2] (1.2 g, 10.6 mmol) were reacted. Flash chromatography using hexane/EtAcO (95:5) afforded (*E*)-**24** (820 mg, 40%) as a white solid (m.p.: 87.1-87.8 ºC, hexane); ^{1}H NMR (200 MHz) δ 7.46 (AA´XX´system, *J* = 8.4, 4H), 6.38 (AB system, *J* = 16.5, 2H), 2.10 (s, 3H), 1.29 (s, 6H); ^{13}C NMR (50 MHz) δ 210.1, 141.3, 138.0, 132.3, 127.7, 126.7, 118.7, 110.6, 50.6, 25.6, 23.8; IR (KBr) ν 2228, 1709 cm^{-1}; UV (CH_2Cl_2) λ_{max} 272 nm (ε 24803), 254 nm (ε 10400), 313 nm (ε 1871); MS *m/e* (%) 213 (M^+, 1), 170 (100), 142 (28), 128 (11), 116 (15), 43 (41); Anal. Calcd for $C_{14}H_{15}NO$: C, 78.87; H, 7.04; N, 6.57. Found: C, 78.76; H, 7.15; N, 6.55.

* This compound was synthesized by refluxing triethyl phosphite (6.6 mL, 38.3 mmol) and 4-bromobenzonitrile (5 g, 25.5 mmol) for 2 h. The reaction mixture was distilled under reduced pressure (125 ºC, 0.2 mbar) to afford diethyl 4-cyanophenylmethylphosphonate (6.02 g, 93%) as a white solid (m.p.: 47.2-48.0 ºC, hexane); ^{1}H NMR (200 MHz) δ 7.54 (d, *J* = 8.3, 2H), 7.34 (dd, *J* = 8.3, 2.3, 2H), 3.99 (q, *J* = 7.1, 2H), 3.95 (q, *J* = 7.1, 2H), 3.10 (d, *J* = 22.3, 2H), 1.18 (t, *J* = 7.1, 6H); ^{13}C NMR (50 MHz) δ 137.6, 132.2-130.4, 118.6, 110.7, 62.3, 34.1, 16.3.

(*E*)-5-(3-Cyanophenyl)-3,3-dimethyl-4-penten-2-one (*E*-25). Diisopropylamine

(2.5 mL, 19.3 mmol), BuLi (12.1 mL, 1.6 M in hexane), diethyl 3-cyanophenylmethylphosphonate* (4.88 g, 19.3 mmol) and 2,2-dimethyl-3-oxobutanal[2] (2.2 g, 19.3 mmol) were reacted to form the ketone. Flash chromatography using hexane/EtAcO (95:5) afforded enone (*E*)-**25** (650 mg, 16%) as a yellow oil; ^{1}H NMR (200 MHz) δ 7.59-7.32 (m, 4H), 6.34 (AB system, *J* = 16.3, 2H), 2.11 (s, 3H), 1.30 (s, 6H); ^{13}C NMR (50 MHz) δ 210.1, 138.1, 137.0, 130.7-127.2, 118.5, 112.8, 50.5, 25.6, 23.9; IR (neat) ν 2232, 1707, 1597 cm^{-1}; UV (CH_2Cl_2) λ_{max} 227 nm (ε 21025), 254 nm (ε 9089), 313 nm (ε 120); MS *m/e* (%) 213 (M^+, 5), 170 (100), 143 (22), 128 (10), 116 (17), 85 (12), 43 (55).

* This compound was synthesized by refluxing triethyl phosphite (6.6 mL, 38.3 mmol) and 3-bromobenzonitrile (5 g, 25.5 mmol) for 2 h. The excess of triethyl phosphite was removed under reduced pressure to afford diethyl 3-cyanophenylmethylphosphonate (5.94 g, 92%) as a colorless oil; ^{1}H NMR (200 MHz) δ 7.51-7.32 (m, 4H), 4.02 (q, *J* = 7.1, 2H), 3.94 (q, *J* = 7.1, 2H), 3.10 (d, *J* = 21.8, 2H), 1.19 (t, *J* = 7.1, 6H); ^{13}C NMR (50 MHz) δ 134.3-129.2, 118.5, 112.6, 62.2, 33.4, 16.3.

General Procedure for Preparative Photolyses. Sensitized and direct irradiations were carried out in a quartz immersion well apparatus with a Pyrex filter and a 400 W medium pressure Hg arc lamp. The direct irradiations at 254 nm were performed through quartz in a multilamp photoreactor, equipped with six 9 W low pressure Hg arc lamps with a maximum emission at 254 nm. Solutions of the compounds, the sensitizer (in the sensitized runs) and the solvent (CH_2Cl_2) were purged for 1 h with argon and irradiated under a positive pressure of argon. After completion of the irradiation, the solvent and the sensitizer were removed under reduced pressure. The products were separated by flash chromatography on silica gel.

Acetophenone-Sensitized Irradiation of 7a. Compound **7a** (195 mg, 1.2 mmol) and acetophenone (5.5 mL, 46 mmol) in CH_2Cl_2 (160 mL) were irradiated for 14 h. Chromatography using hexane/EtAcO (95:5) as eluent gave starting ketone **7a** (117 mg, 60%). Further elution with EtAcO afforded 28 mg of highly polar material.

Pyrex-Filtered Direct Irradiation of 7a. Compound **7a** (252 mg, 1.6 mmol) in CH_2Cl_2 (160 mL) was irradiated for 24 h. Chromatography using hexane/EtAcO (95:5)

as eluent gave starting ketone **7a** (224 mg, 89%). Further elution with EtAcO afforded 19 mg of highly polar material.

Direct Irradiation of 7a at 254 nm. Compound **7a** (128 mg, 0.79 mmol) in CH_2Cl_2 (270 mL) was irradiated for 12 h. Chromatography using hexane/EtAcO (95:5) as eluent gave diene **11** (22 mg, 12%) as a colorless oil, starting ketone **7a** (39 mg, 31%) and cyclopropylketone **10a** (20 mg, 16%) as a colorless oil. Further elution with EtAcO afforded 29 mg of highly polar material.

Compound **10a**: ^{1}H NMR (200 MHz) δ 2.63 (s, 1H), 2.34 (s, 3H), 1.53 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (50 MHz) δ 197.4, 113.4, 110.9, 45.0, 36.7, 32.0, 24.0, 17.2, 16.1; IR (neat) ν 2247, 1720 cm^{-1}; MS *m/e* (%) 119 (M^+-43, 1), 43 (100).

Compound **11**: ^{1}H NMR (200 MHz) δ 5.19-5.18 (m, 2H), 1.99 (d, *J* = 1.3, 6H), 1.85 (d, *J* = 1.4, 6H); ^{13}C NMR (50 MHz) δ 134.5-127.0, 112.1, 112.0, 36.4, 26.7, 20.7; IR (neat) ν 2240 cm^{-1}.

Acetone-Sensitized Irradiation of (*E*)-7b. Compound (*E*)-**7b** (144 mg, 1.1 mmol) in acetone (160 mL) was irradiated for 7 h. Chromatography using hexane/EtAcO (95:5) as eluent gave starting ketone **7b** (129 mg, 90%) as a 2:3 mixture of *E*/*Z* isomers. Further elution with EtAcO afforded 12 mg of highly polar material.

Pyrex-Filtered Direct Irradiation of (*E*)-7b. Compound (*E*)-**7b** (110 mg, 0.79 mmol) in CH_2Cl_2 (160 mL) was irradiated for 6 h. Chromatography using hexane/EtAcO (95:5) as eluent gave diene **13** (8.5 mg, 5%) as a white solid (m.p.: 118.0-118.6 ºC, hexane), diene (*E*)-**14** (8.5 mg, 5%) as a colorless oil, ketone **12** (6 mg, 5%) as a colorless oil and starting ketone **7b** (85 mg, 77%) as a 2:1 mixture of *E*/*Z* isomers. Further elution with EtAcO afforded 7 mg of highly polar material.

Compound **12**: ^{1}H NMR (200 MHz) δ 5.07-5.04 (m, 1H), 2.21 (s, 3H), 1.73 (d, *J* = 1.4, 3H), 1.71 (d, *J* = 1.3, 3H), 1.58 (s, 3H); ^{13}C NMR (50 MHz) δ 200.5, 141.8, 119.9, 119.7, 48.9, 26.3, 25.0, 23.9, 18.7; IR (neat) ν 2241, 1719 cm^{-1}; MS *m/e* (%) 151 (M^+, 3), 149 (28), 136 (6), 108 (58), 57 (48), 43 (100).

Compound **13**: ^{1}H NMR (200 MHz) δ 5.12 (sept, *J* = 1.5, 2H), 1.90 (d, *J* = 1.5, 3H), 1.88 (d, *J* = 1.5, 3H), 1.75 (d, *J* = 1.5, 6H), 1.58 (s, 6H); ^{13}C NMR (50 MHz) δ 139.7, 120.7, 120.0, 44.1, 27.7, 24.0, 18.8; IR (KBr) ν 2220, 1597 cm^{-1}; MS *m/e* (%) 180 (M^+-

108, 30), 105 (100), 91 (16), 77 (41), 57 (26), 43 (44). Anal. Calcd for $C_{14}H_{20}N_2$: C, 77.77; H, 9.26; N, 12.96. Found: C, 77.42; H, 9.03; N, 12.70.

Compound (*E*)-**14**: ^{1}H NMR (200 MHz) δ 6.15-6.14 (m, 1H), 4.89-4.88 (m, 1H), 1.97 (d, *J* = 1.6, 3H), 1.86 (d, *J* = 1.3, 3H), 1.72 (d, *J* = 1.3, 3H), 1.37 (s, 3H), 1.18 (s, 6H); ^{13}C NMR (50 MHz) δ 153.0, 138.4, 120.7, 120.5, 109.1, 44.0, 43.9, 29.3, 27.5, 23.4, 23.0; IR (neat) ν 2222, 1628 cm^{-1}.

Direct Irradiation of (*E*)-7b at 254 nm. Compound (*E*)-**7b** (167 mg, 1.2 mmol) in CH_2Cl_2 (220 mL) was irradiated for 1 h. Chromatography using hexane/EtAcO (95:5) as eluent gave diene **13** (16 mg, 8%), diene (*E*)-**14** (8 mg, 4%), ketone **12** (38 mg, 23%), starting ketone **7b** (49 mg, 29%) as a 2:3 mixture of *E*/*Z* isomers and cyclopropylketone **10b** (10 mg, 6%) as a colorless oil. Further elution with EtAcO afforded 17 mg of highly polar material.

Compound **10b**: ^{1}H NMR (200 MHz) δ 2.23 (s, 3H), 1.80 (s, 1H), 1.43 (s, 3H), 1.32 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (50 MHz) δ 201.9, 119.8, 45.0, 32.9, 32.8, 29.5, 21.9, 18.5, 18.1; IR (neat) ν 2235, 1718 cm^{-1}; MS *m/e* (%) 136 (M^+-15, 5), 108 (12), 43 (100).

Acetone-Sensitized Irradiation of 7c. Compound **7c** (188 mg, 1.4 mmol) as a 2:1 mixture of *E*/*Z* isomers in acetone (160 mL) was irradiated for 8 h. Chromatography using hexane/EtAcO (95:5) as eluent gave starting ketone **7c** (80 mg, 44%) as a 2:1 mixture of *E*/*Z* isomers. Further elution with EtAcO afforded 80 mg of highly polar material.

Pyrex-Filtered Direct Irradiation of 7c. Compound **7c** (178 mg, 1.3 mmol) as a 2:1 mixture of *E*/*Z* isomers in CH_2Cl_2 (160 mL) was irradiated for 6 h. Chromatography using hexane/EtAcO (95:5) as eluent gave diene **15** (7 mg, 4%) as a colorless oil, starting ketone **7c** (130 mg, 73%) as a 1:1 mixture of *E*/*Z* isomers and cyclopropylketone (*Z*)-**10c** (5 mg, 8%) as a colorless oil. Further elution with EtAcO afforded 15 mg of highly polar material.

Compound (*Z*)-**10c**: ^{1}H NMR (200 MHz) δ 2.26 (s, 3H), 2.16 (d, *J* = 8.0, 1H), 1.68 (d, *J* = 8.0, 1H), 1.29 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (50 MHz) δ 201.4, 116.6, 37.6, 32.5, 29.2, 26.9, 18.9, 15.5; IR (neat) ν 2243, 1708 cm^{-1}; MS *m/e* (%) 137 (M^+, 4), 122 (3), 94 (14), 43 (100).

Compound **15**: ^{1}H NMR (200 MHz) δ 5.19-5.07 (m, 2H), 3.63-3.53 (m, 2H), 1.76 (br s, 6H), 1.69 (d, *J* = 1.7, 3H), 1.67 (d, *J* = 1.5, 3H); ^{13}C NMR (50 MHz) δ 141.9, 141.6, 117.8, 114.8, 114.6, 34.1, 34.0, 25.8, 18.7; IR (neat) ν 2230 cm^{-1}.

Direct Irradiation of 7c at 254 nm. Compound **7c** (138 mg, 1 mmol) as a 2:1 mixture of *E*/*Z* isomers in CH_2Cl_2 (220 mL) was irradiated for 9 h. Chromatography using hexane/EtAcO (95:5) as eluent gave diene **15** (8 mg, 4%), starting ketone **7c** (99 mg, 73%) as a 3:2 mixture of *E*/*Z* isomers and cyclopropylketone (*Z*)-**10c** (10 mg, 7%). Further elution with EtAcO afforded 10 mg of highly polar material.

Acetophenone-Sensitized Irradiation of 16. Compound **16** (192 mg, 0.84 mmol) and acetophenone (3.8 mL, 32 mmol) in CH_2Cl_2 (260 mL) were irradiated for 14 h. Chromatography using hexane/EtAcO (98:2) as eluent gave cyclopropylketone **17** (30 mg, 15%) as a colorless oil and starting ketone **16** (160 mg, 83%). Further elution with EtAcO afforded 12 mg of highly polar material.

Compound **17**: ^{1}H NMR (200 MHz) δ 3.68 (s, 3H), 3.65 (s, 3H), 2.77 (s, 1H), 2.22 (s, 3H), 1.31 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (50 MHz) δ 202.6, 167.9, 166.4, 53.0, 52.6, 46.1, 42.7, 34.5, 32.4, 22.3, 17.0; IR (neat) ν 1738, 1713 cm^{-1}; MS *m/e* (%) 228 (M^+, 4), 213 (4), 185 (13), 153 (21), 125 (14), 111 (17), 97 (21), 82 (28), 69 (28), 55 (28), 43 (100).

Pyrex-Filtered Direct Irradiation of 16. Compound **16** (199 mg, 0.87 mmol) in CH_2Cl_2 (160 mL) was irradiated for 14 h. Chromatography using hexane/EtAcO (9:1) as eluent gave ketone **18** (5 mg, 3%) as a colorless oil, cyclopropylketone **17** (17 mg, 8%), starting ketone **16** (170 mg, 85%) and diene **19** (7 mg, 2%) as a colorless oil. Further elution with EtAcO afforded 5 mg of highly polar material.

Compound **18**: ^{1}H NMR (200 MHz) δ 5.66-5.64 (m, 1H), 3.73 (s, 6H), 2.21 (s, 3H), 1.78 (d, *J* = 1.4, 3H), 1.57 (d, *J* = 1.2, 3H); ^{13}C NMR (50 MHz) δ 199.5, 168.0, 141.5, 117.0, 73.4, 53.4, 27.3, 23.3, 19.9; IR (neat) ν 1736 cm^{-1}; MS *m/e* (%) 228 (M^+, 1), 213 (3), 186 (11), 169 (7), 153 (22), 97 (32), 83 (34), 69 (27), 57 (51), 55 (48), 43 (100).

Compound **19**: ^{1}H NMR (200 MHz) δ 6.94 (s, 2H), 3.73 (s, 6H), 3.72 (s, 6H), 1.06 (s, 12H); ^{13}C NMR (50 MHz) δ 167.1, 164.4, 151.1, 126.5, 52.5, 52.2, 43.7, 21.9; IR

(neat) ν 1736, 1601 cm^{-1}; MS *m/e* (%) 185 (M^+-185, 61), 153 (100), 122 (28), 105 (30), 43 (14), 41 (10).

Direct Irradiation of 16 at 254 nm. Compound **16** (219 mg, 0.9 mmol) in CH_2Cl_2 (220 mL) was irradiated for 8 h. Chromatography using hexane/EtAcO (95:5) as eluent gave ketone **18** (37 mg, 17%), cyclopropylketone **17** (27 mg, 12%), starting ketone **16** (74 mg, 34%) and diene **19** (45 mg, 14%). Further elution with EtAcO afforded 33 mg of highly polar material.

Acetophenone-Sensitized Irradiation of (*E*)-20. Compound (*E*)-**20** (205 mg, 1.1 mmol) and acetophenone (5 mL, 40.5 mmol) in CH_2Cl_2 (260 mL) were irradiated for 5 h. Chromatography using hexane/Et_2O (97:3) as eluent gave starting ketone **20** (187 mg, 91%) as a 1:1 mixture of *E*/*Z* isomers. Further elution with Et_2O afforded 12 mg of highly polar material.

Pyrex-Filtered Direct Irradiation of (*E*)-20. Compound (*E*)-**20** (156 mg, 0.84 mmol) in CH_2Cl_2 (160 mL) was irradiated for 1 h. Chromatography using hexane/Et_2O (99:1) as eluent gave diene **22** (24 mg, 10%) as a 1:3 mixture of A/B diastereoisomers and as a colorless oil, ketone **21** (42 mg, 27%) as a colorless oil and starting ketone **20** (84 mg, 54%) as a 1:6 mixture of *E*/*Z* isomers. Further elution with Et_2O afforded 20 mg of highly polar material.

Compound **21**: ^{1}H NMR (200 MHz) δ 7.33-7.01 (m, 5H), 5.57 (dq, *J* = 9.4, 1.4, 1H), 4.46 (d, *J* = 9.4, 1H), 2.02 (s, 3H), 1.70 (d, *J* = 1.3, 3H), 1.60 (d, *J* = 1.3, 3H); ^{13}C NMR (50 MHz) δ 207.3, 136.9-126.4, 121.7, 59.0, 28.4, 24.2, 18.4; IR (neat) ν 1704 cm^{-1}.

Compound **22**: ^{1}H NMR (200 MHz) δ 7.35-7.02 (m, 10H), 5.43 (m, 0.5H, A-diastereoisomer), 5.32-5.29 (m, 1.5H, B-diastereoisomer), 3.75-3.70 (m, 2H), 1.71 (d, *J* = 1.2, 1.5H, A-diastereoisomer), 1.59 (br s, 1.5H, A-diastereoisomer), 1.55 (d, *J* = 1.4, 4.5H, B-diastereoisomer), 1.40 (d, *J* = 1.3, 4.5H, B-diastereoisomer); ^{13}C NMR (50 MHz) δ 145.0, 144.3, 132.1, 131.7, 128.3-125.5, 52.3, 50.8, 26.0, 25.7, 17.9.

Direct Irradiation of (*E*)-20 at 254 nm. Compound (*E*)-**20** (158 mg, 0.84 mmol) in CH_2Cl_2 (220 mL) was irradiated for 3 h. Chromatography using hexane/Et_2O (98:2) as eluent gave diene **22** (21 mg, 9%) as a 1:3 mixture of A/B diastereoisomers, ketone **21** (65 mg, 41%), starting ketone (*E*)-**20** (45 mg, 28%) and cyclopropylketone (*E*)-**23** (2

mg, 1%) as a colorless oil. Further elution with Et_2O afforded 8 mg of highly polar material.

Compound (*E*)-**23**: ^{1}H NMR (200 MHz) δ 7.29-7.15 (m, 5H), 2.78 (d, *J* = 5.9, 1H), 2.27 (s, 3H), 2.23 (d, *J* = 5.9, 1H), 1.20 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (50 MHz) δ 204.6, 139.0-123.7, 118.7, 40.3, 37.8, 32.4, 31.8, 22.3, 19.5; IR (neat) ν 1700 cm^{-1}.

3-Methoxyacetophenone-Sensitized Irradiation of (*E*)-24. Compound (*E*)-**24** (180 mg, 0.84 mmol) and 3-methoxyacetophenone (1.6 mL, 9.3 mmol) in CH_2Cl_2 (260 mL) were irradiated for 8 h. Chromatography using hexane/EtAcO (95:5) as eluent gave starting ketone (*Z*)-**24** (66 mg, 37%) as a colorless oil and (*E*)-**24** (93 mg, 52%). Further elution with EtAcO afforded 10 mg of highly polar material.

Compound (*Z*)-**24**: ^{1}H NMR (200 MHz) δ 7.42-6.98 (m, 4H), 6.31 (d, *J* = 12.6, 1H), 5.65 (d, *J* = 12.6, 1H), 1.73 (s, 3H), 1.04 (s, 6H); ^{13}C NMR (50 MHz) δ 210.7, 141.6-127.9, 118.7, 111.0, 50.4, 26.8, 25.9.

Pyrex-Filtered Direct Irradiation of (*E*)-24. Compound (*E*)-**24** (60 mg, 0.28 mmol) in CH_2Cl_2 (160 mL) was irradiated for 1 h. Chromatography using hexane/EtAcO (95:5) as eluent gave diene **28** (9 mg, 9%), as a 1:1 mixture of A/B diastereoisomers and as a colorless oil, ketone **27** (24 mg, 40%) as a colorless oil, starting ketone (*Z*)-**24** (9 mg, 15%), (*E*)-**24** (3 mg, 5%) and cyclopropylketone (*E*)-**26** (4 mg, 7%) as a colorless oil. Further elution with EtAcO afforded 13 mg of highly polar material.

Compound (*E*)-**26**: ^{1}H NMR (200 MHz) δ 7.57-7.16 (m, 4H), 2.80 (d, *J* = 6.1, 1H), 2.29 (d, *J* = 6.1, 1H), 2.28 (s, 3H), 1.29 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (50 MHz) δ 204.8, 143.3, 138.0-126.7, 118.7, 110.1, 40.1, 37.6, 32.8, 32.1, 22.0, 19.7; IR (neat) ν 2255, 1697 cm^{-1}; MS *m/e* (%) 213 (M^+, 4), 198 (3), 170 (89), 154 (24), 142 (22), 43 (100).

Compound **27**: ^{1}H NMR (200 MHz) δ 7.41 (AA´XX´system, *J* = 8.3, 4H), 5.47 (br d, *J* = 9.5, 1H), 4.54 (d, *J* = 9.5, 1H), 2.08 (s, 3H), 1.72 (br s, 3H), 1.62 (d, *J* = 0.9, 3H); ^{13}C NMR (50 MHz) δ 205.8, 144.6, 137.4-128.9, 118.8, 111.1, 58.7, 28.8, 26.1, 18.5; IR (neat) ν 2245, 1699, 1599 cm^{-1}.

Compound **28**: ^{1}H NMR (200 MHz) δ 7.50-7.00 (m, 8H), 5.28 (br d, *J* = 6.3, 1H, A-diastereoisomer), 5.10 (br d, *J* = 6.6, 1H, B-diastereoisomer), 3.73-3.62 (m, 2H), 1.64 (d, *J* = 1.1, 3H, A-diastereoisomer), 1.46 (d, *J* = 1.2, 3H, B-diastereoisomer), 1.42 (d, *J*

= 1.2, 3H, A-diastereoisomer), 1.28 (d, *J* = 1.2, 3H, B-diastereoisomer); ^{13}C NMR (50 MHz) δ 149.5, 149.4, 135.1-124.9, 119.1, 119.0, 110.1, 110.0, 51.3, 50.8, 26.1, 25.8, 18.4, 18.2; IR (neat) ν 1736, 1601 cm^{-1}; MS *m/e* (%) 170 (M^+-170, 100), 154 (9), 142 (15), 105 (20), 77 (9).

Pyrex-Filtered Direct Irradiation of (*E*)-24 at 254 nm. Compound (*E*)-**24** (130 mg, 0.61 mmol) in CH_2Cl_2 (220 mL) was irradiated for 8 h. Chromatography using hexane/EtAcO (98:2) as eluent gave diene **28** (17 mg, 9%), ketone **27** (44 mg, 34%), starting ketone (*Z*)-**24** (7 mg, 5%) and (*E*)-**24** (17 mg, 13%) and cyclopropylketone (*E*)-**26** (5 mg, 4%). Further elution with EtAcO afforded 20 mg of highly polar material.

3-Methoxyacetophenone-Sensitized Irradiation of (*E*)-25. Compound (*E*)-**25** (188 mg, 0.88 mmol) and 3-methoxyacetophenone (1 mL, 6.4 mmol) in CH_2Cl_2 (260 mL) were irradiated for 8 h. Chromatography using hexane/EtAcO (95:5) as eluent gave starting ketone **25** (147 mg, 78%) as a 1:2 mixture of *E*/*Z* isomers. Further elution with EtAcO afforded 13 mg of highly polar material.

Compound **25**: ^{1}H NMR (200 MHz) δ 7.58-7.23 (m, 4H), 6.43 (d, *J* = 12.5, 0.66H, *Z*-isomer), 6.34 (AB system, *J* = 16.3, 0.66H, *E*-isomer), 5.77 (d, *J* = 12.5, 0.66H, *Z*-isomer), 2.10 (s, 1H, *E*-isomer), 1.87 (s, 2H, *Z*-isomer), 1.28 (s, 2H, *E*-isomer), 1.17 (s, 4H, *Z*-isomer); ^{13}C NMR (125 MHz) δ 210.9 (*Z*-isomer), 210.1 (*E*-isomer), 138.8-128.3, 118.5, 112.8 (*E*-isomer), 112.2 (*Z*-isomer), 50.5 (*E*-isomer), 50.3 (*Z*-isomer), 26.2 (*Z*-isomer), 25.8 (*Z*-isomer), 25.6 (*E*-isomer), 23.9 (*E*-isomer).

Pyrex-Filtered Direct Irradiation of (*E*)-25. Compound (*E*)-**25** (178 mg, 0.84 mmol) in CH_2Cl_2 (260 mL) was irradiated for 1 h. Chromatography using hexane/EtAcO (97:3) as eluent gave diene **30** (38 mg, 13%) as a 3:2 mixture of A/B diastereoisomers and as a white solid, ketone **29** (55 mg, 31%) as a colorless oil and starting ketone **25** (41 mg, 23%) as a 1:5 mixture of *E*/*Z* isomers. Further elution with EtAcO afforded 35 mg of highly polar material. The mixture of A/B diastereoisomers **30** was separated by recrystallization to yield diastereoisomer **30A** as a white solid (m.p.: 153.0-153.8 ºC, hexane) and diastereoisomer **30B** as a white solid (m.p.: 206.8-207.1 ºC, EtOH)

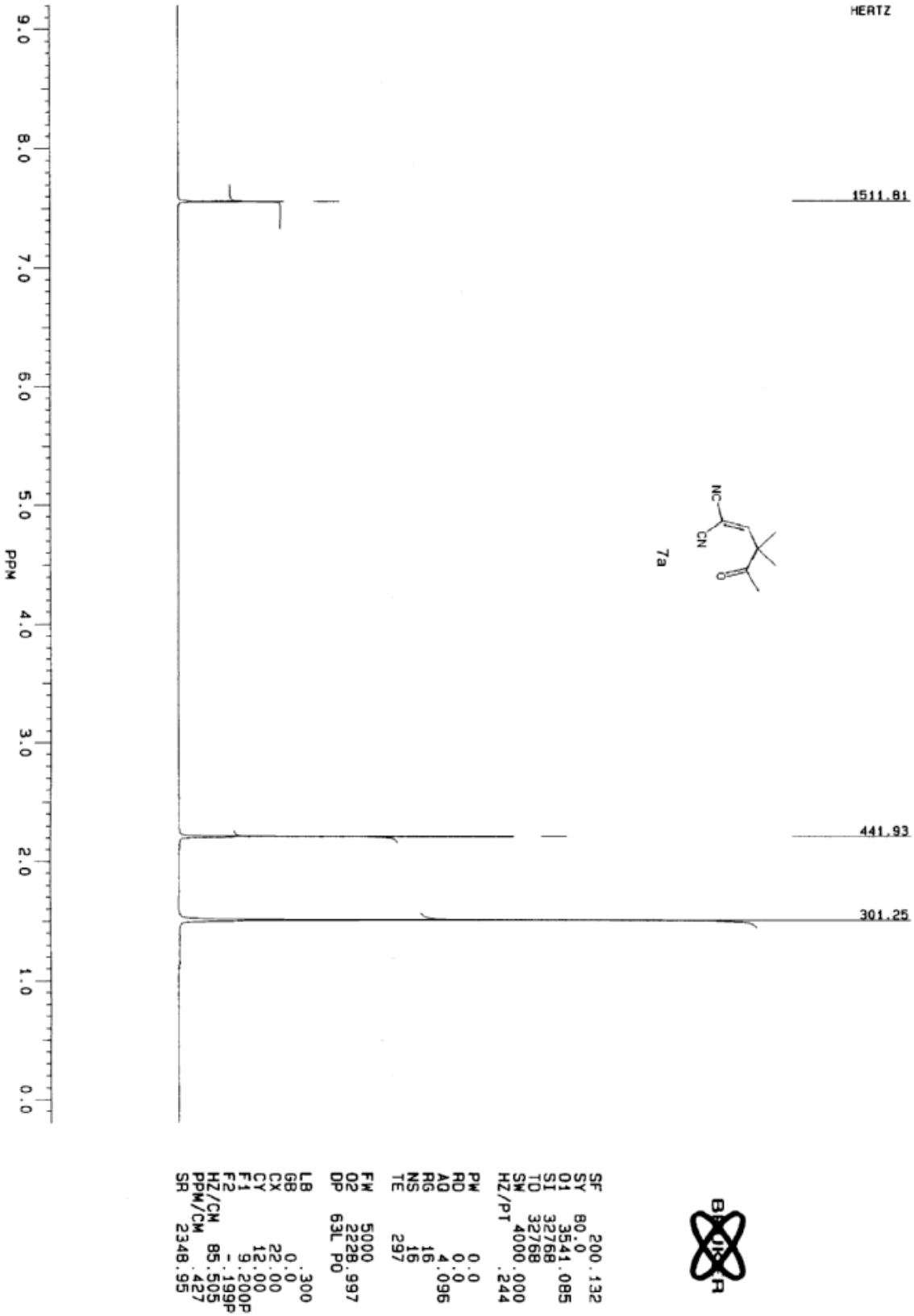
Compound **29**: ^{1}H NMR (200 MHz) δ 7.50-7.32 (m, 4H), 5.40 (dsept, *J* = 9.6, 1.4, 1H), 4.52 (d, *J* = 9.6, 1H), 2.09 (s, 3H), 1.74 (d, *J* = 1.4, 3H), 1.63 (d, *J* = 1.4, 3H); ^{13}C NMR (50 MHz) δ 145.3, 140.4, 135.2-119.0, 112.3, 50.4, 25.8, 18.2.

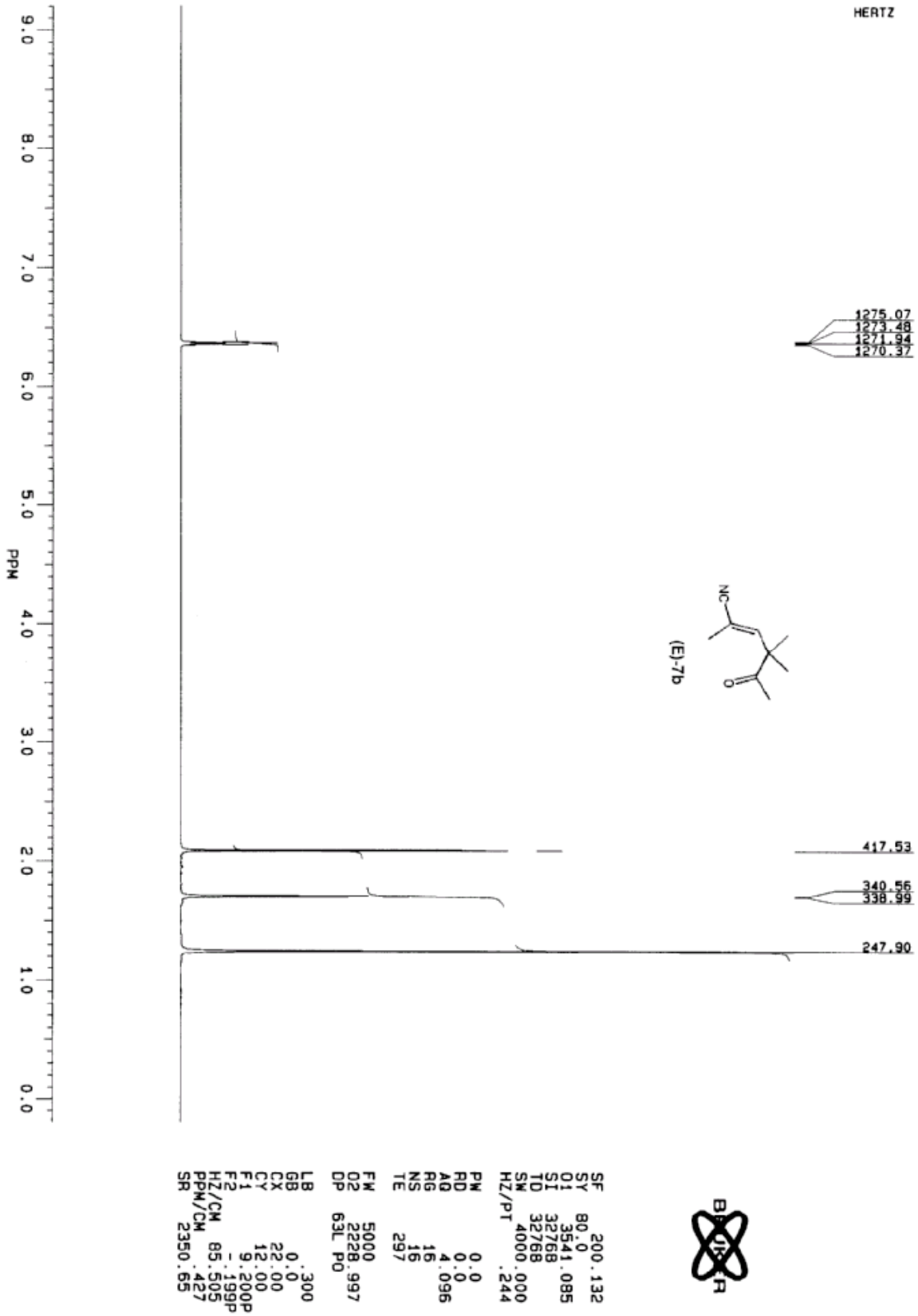
Compound **30A**: ^{1}H NMR (200 MHz) δ 7.40-7.11 (m, 8H), 5.33-5.27 (m, 1H), 5.10 (d, *J* = 6.6, 1H), 3.69-3.62 (m, 2H), 1.66 (d, *J* = 0.9, 6H), 1.41 (d, *J* = 1.1, 6H); ^{13}C NMR (125 MHz) δ 145.4, 140.6, 135.1-119.1, 112.4, 50.7, 26.1, 18.4; IR (KBr) ν 2232, 1601 cm^{-1}; MS *m/e* (%) 170 (M^{+}-170, 100), 142 (14), 116 (9), 89 (3), 41 (9). Anal. Calcd for $C_{24}H_{24}N_2$: C, 84.70; H, 7.06; N, 8.23. Found: C, 84.46; H, 7.07; N, 8.02.

Compound **30B**: ^{1}H NMR (200 MHz) δ 7.43-7.23 (m, 8H), 5.14-5.08 (m, 1H), 5.07 (d, *J* = 6.6, 1H), 3.64 (t, *J* = 6.7, 1H), 3.60 (t, *J* = 6.7, 1H), 1.48 (br s, 6H), 1.28 (d, *J* = 1.2, 6H); ^{13}C NMR (125 MHz) δ 145.3, 140.4, 135.2-119.0, 112.3, 50.4, 25.8, 18.2; Anal. Calcd for $C_{24}H_{24}N_2$: C, 84.70; H, 7.06; N, 8.23. Found: C, 84.50; H, 7.05; N, 8.09.

Direct Irradiation of (*E*)-25 at 254 nm. Compound (*E*)-**25** (199 mg, 0.93 mmol) in CH_2Cl_2 (220 mL) was irradiated for 8 h. Chromatography using hexane/EtAcO (95:5) as eluent gave diene **30** (50 mg, 25%) as a 1:1 mixture of A/B diastereoisomers, ketone **29** (56 mg, 28%) and starting ketone **25** (7 mg, 5%) as a 1:7 mixture of *E*/*Z* isomers. Further elution with EtAcO afforded 65 mg of highly polar material.

[1]HRMN-Spectra

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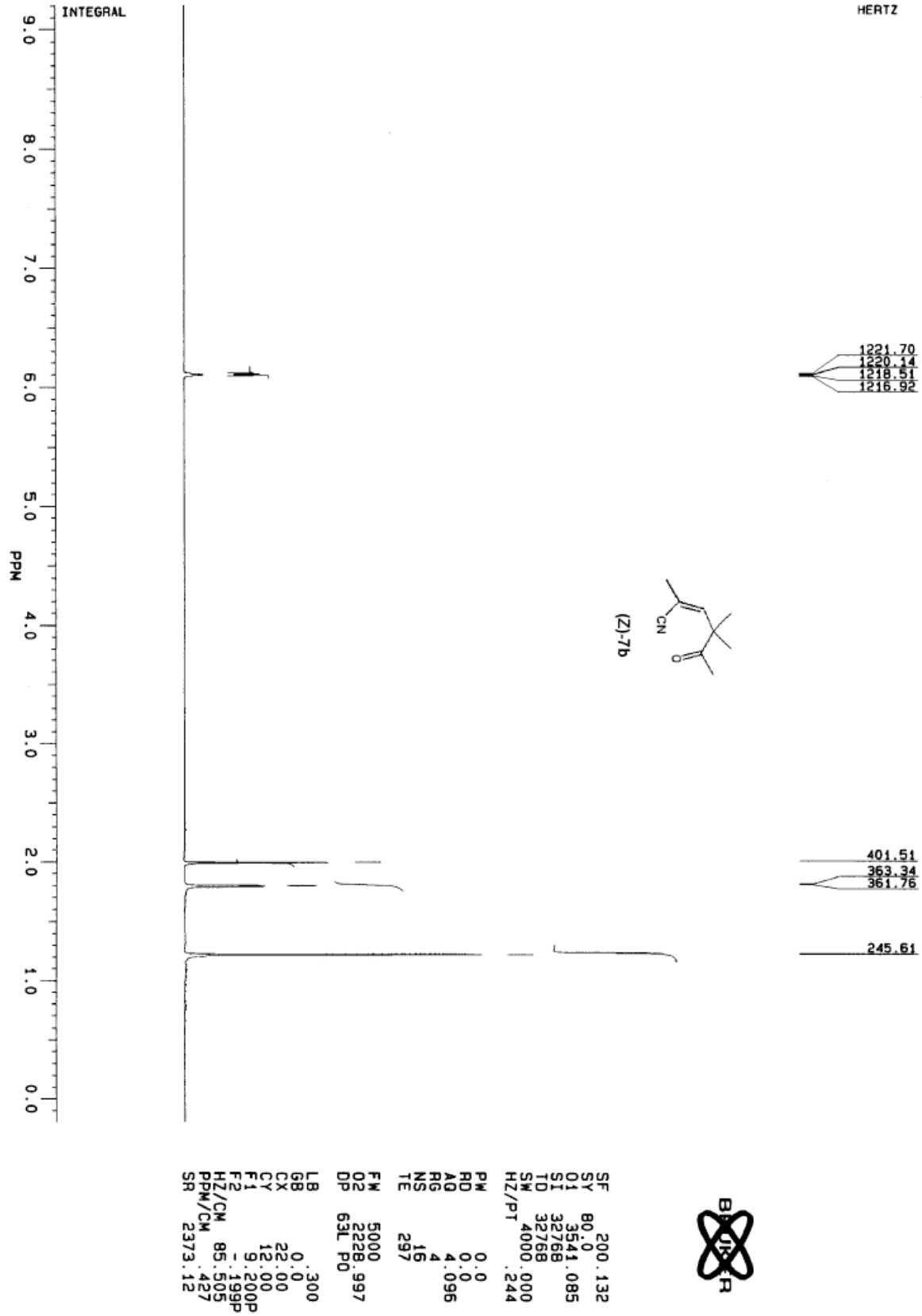
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O
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PW 0.0
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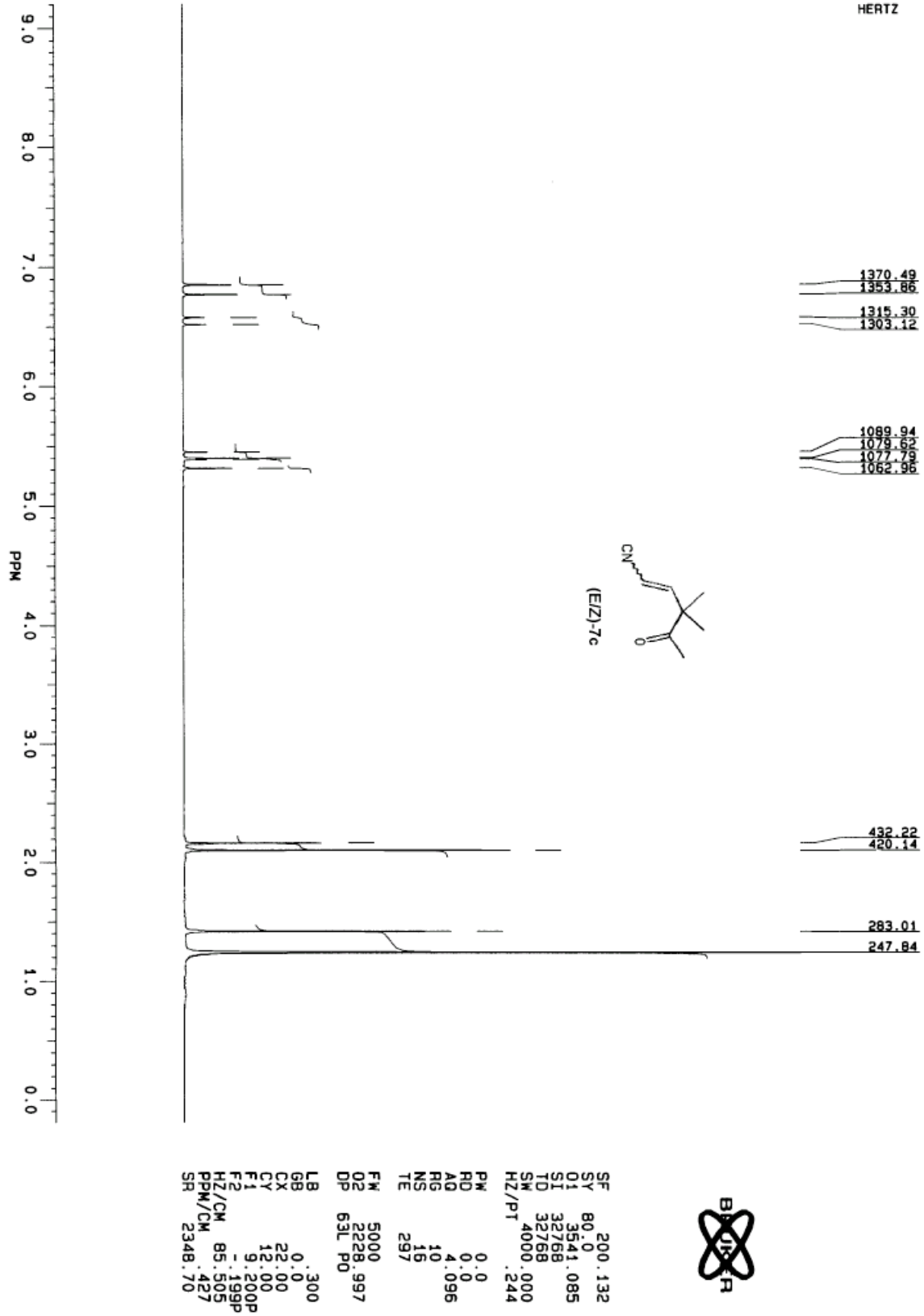
BRUKER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CN
O
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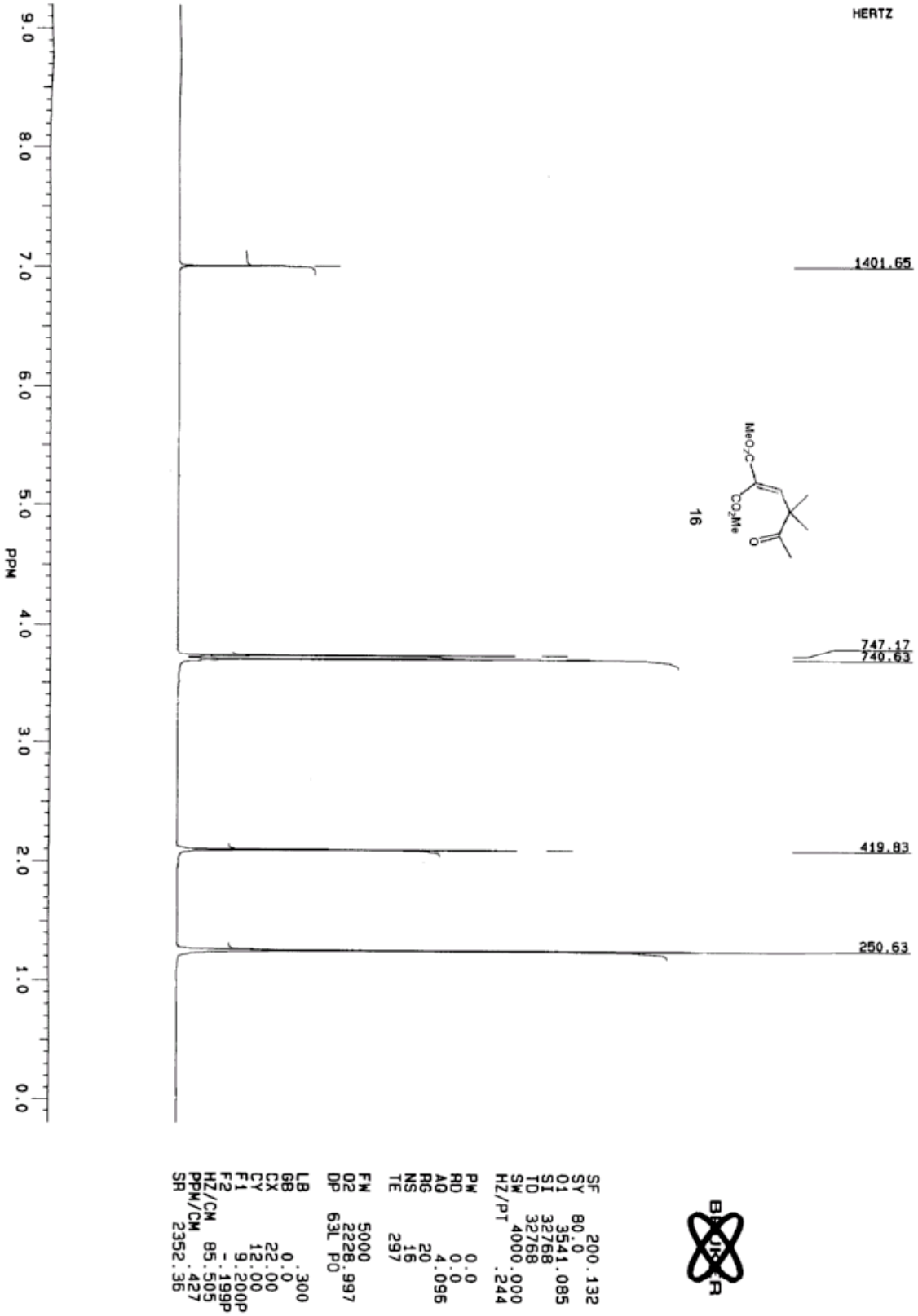
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16
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O
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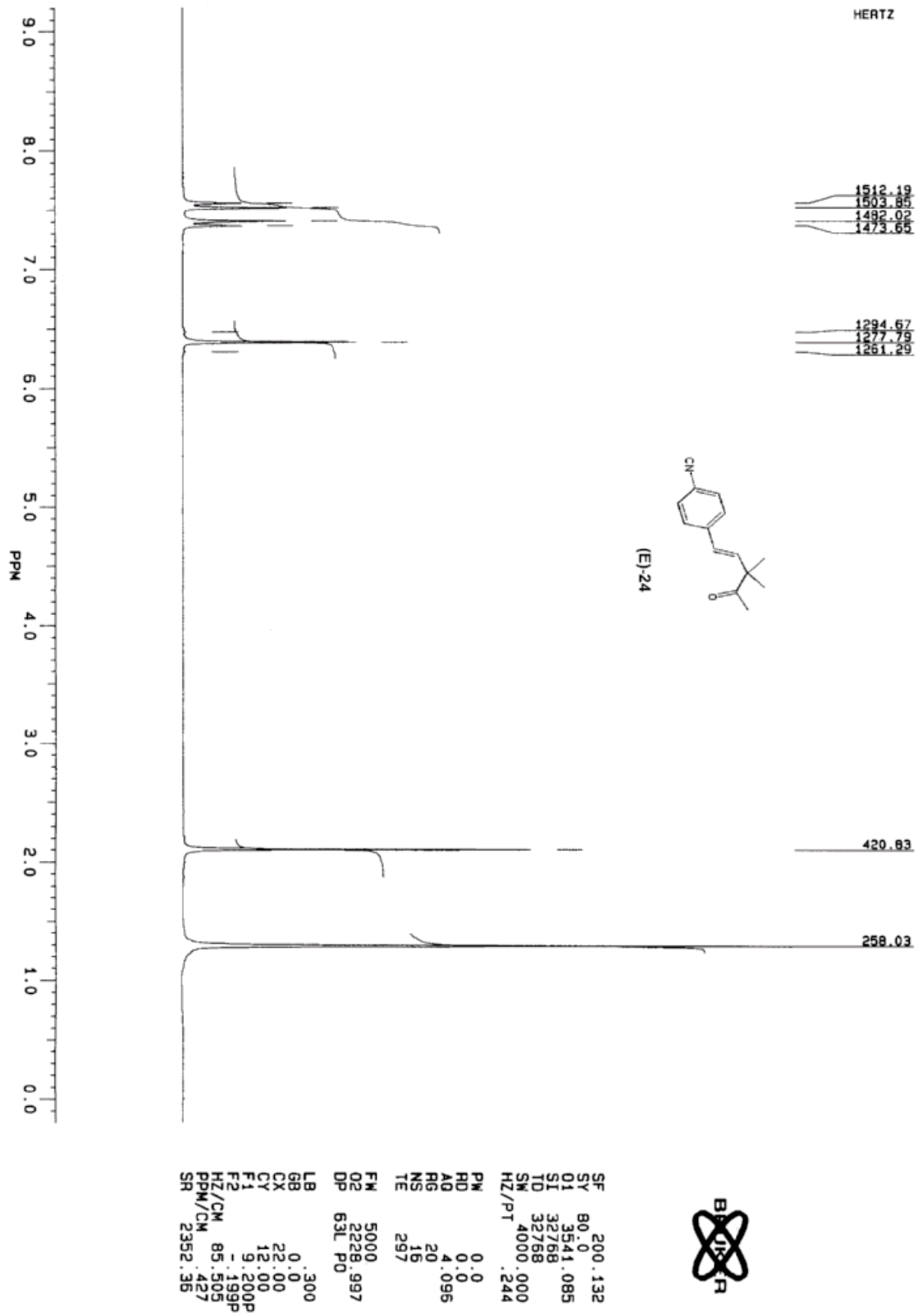
BRUKER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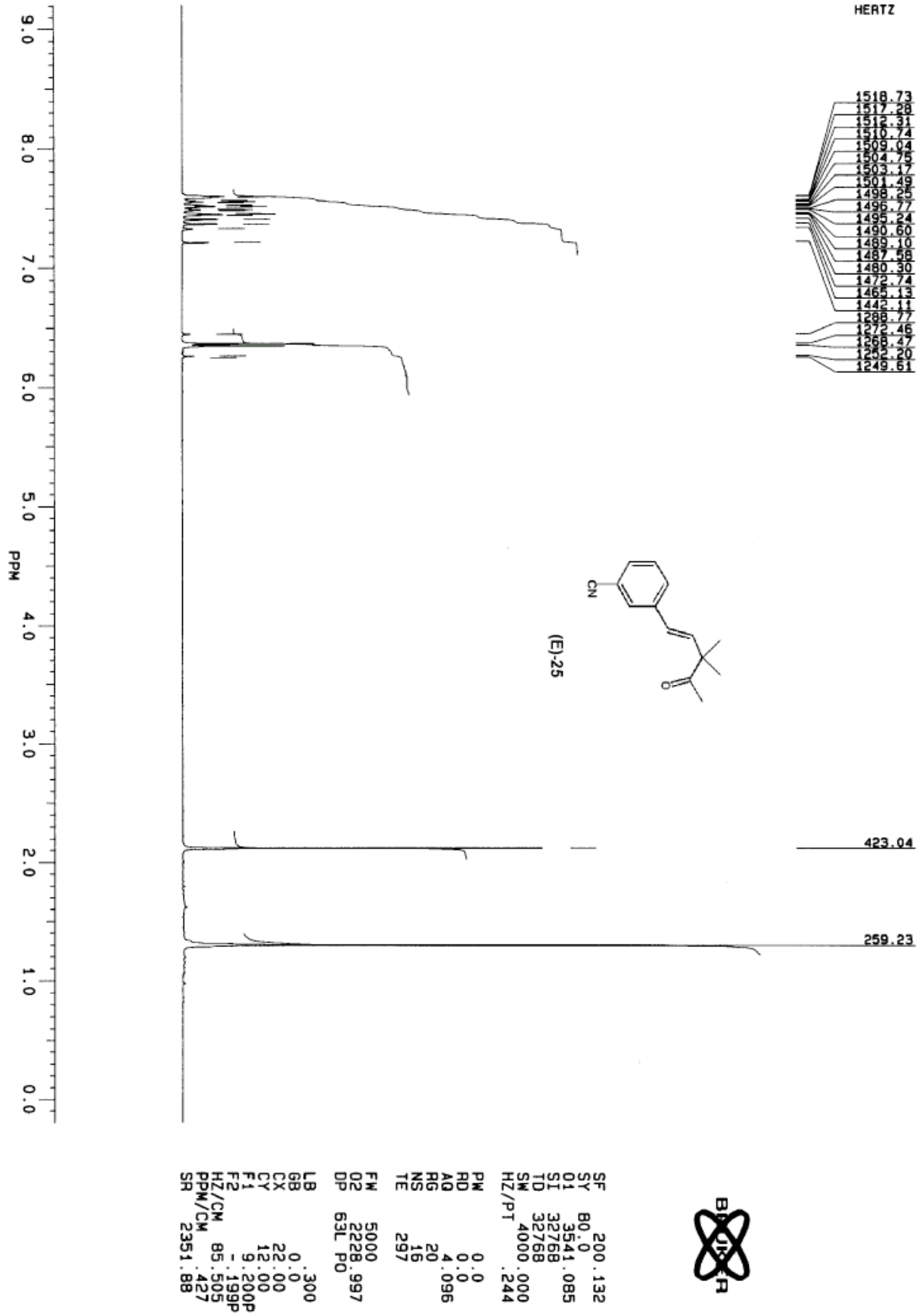
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2.0
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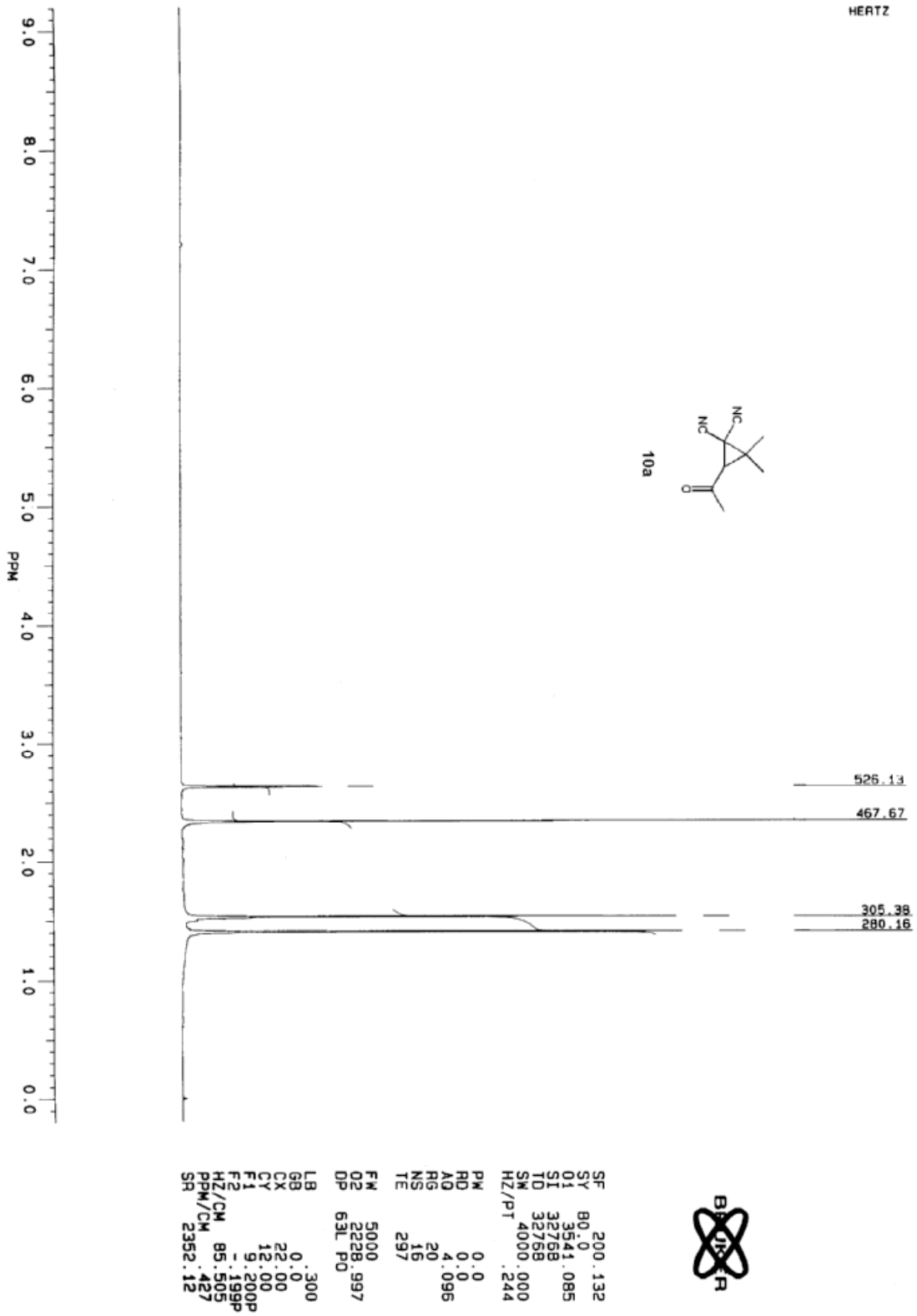
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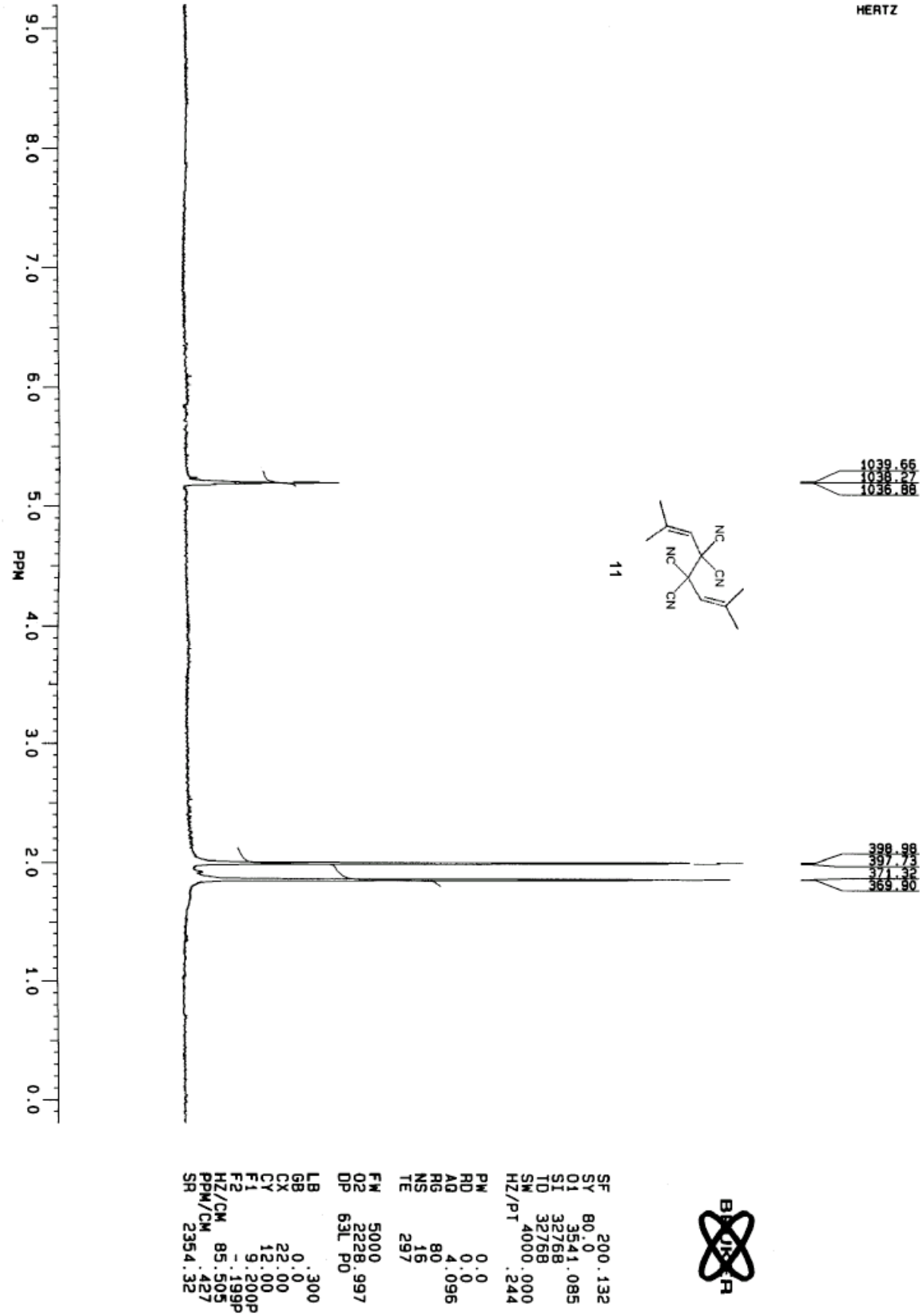
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6.0
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4.0
3.0
2.0
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0.0
SF 200.132
SY 80.0
O1 3541.085
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TD 32768
SW 4000.000
HZ/PT .244
PW 0.0
RD 0.0
AQ 4.096
RG 80
NS 16
TE 297
FW 5000
O2 2228.997
DP 63L PO
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CY 12.00
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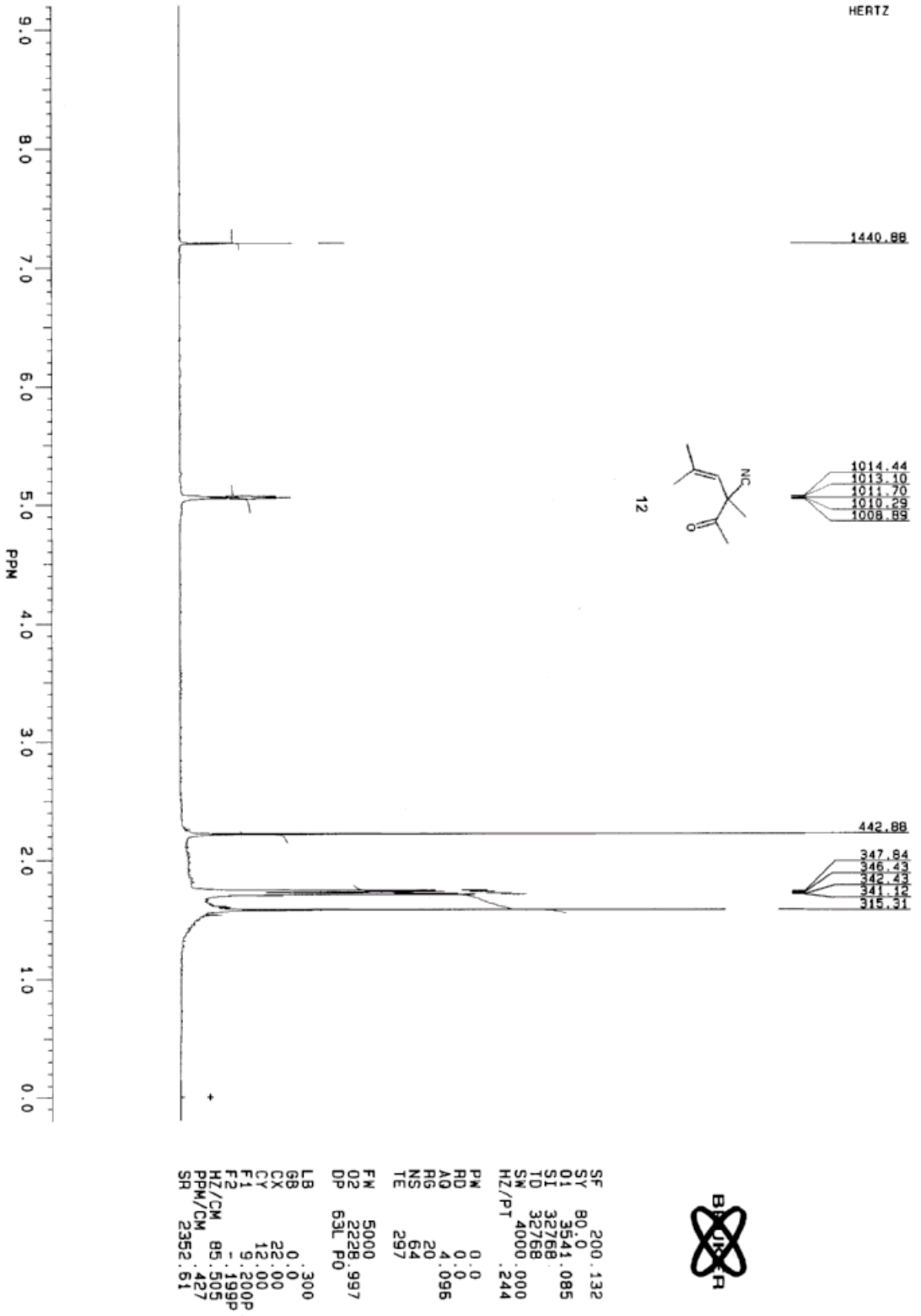
SR 2354.32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AQ 4.096
RG 20
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02 2228.997
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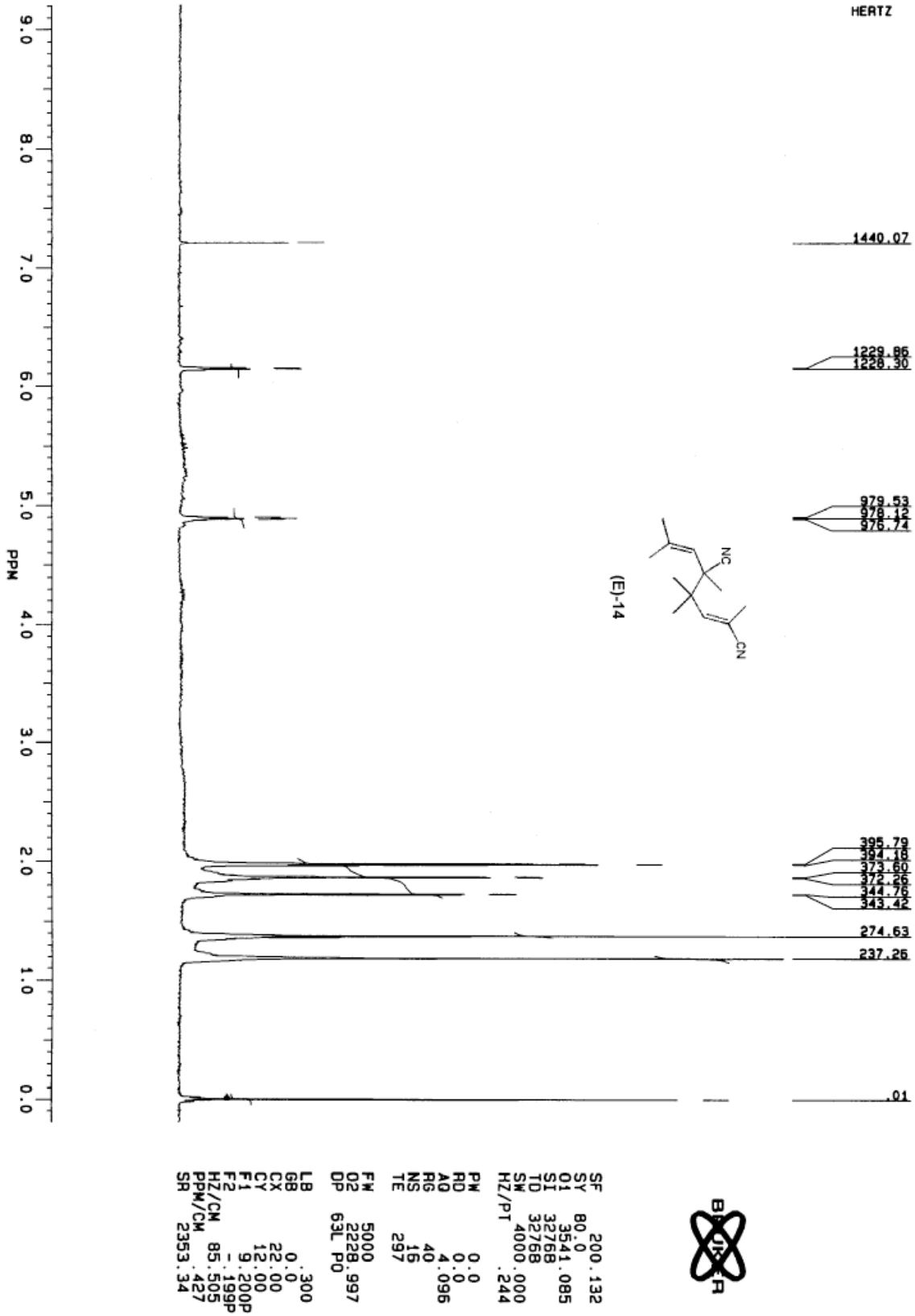
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TD 32768
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HZ/PT .244
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RD 0.0
AQ 4.096
RG 40
NS 16
TE 297
FW 5000
O2 2228.997
OP 63L PO
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CY 12.00
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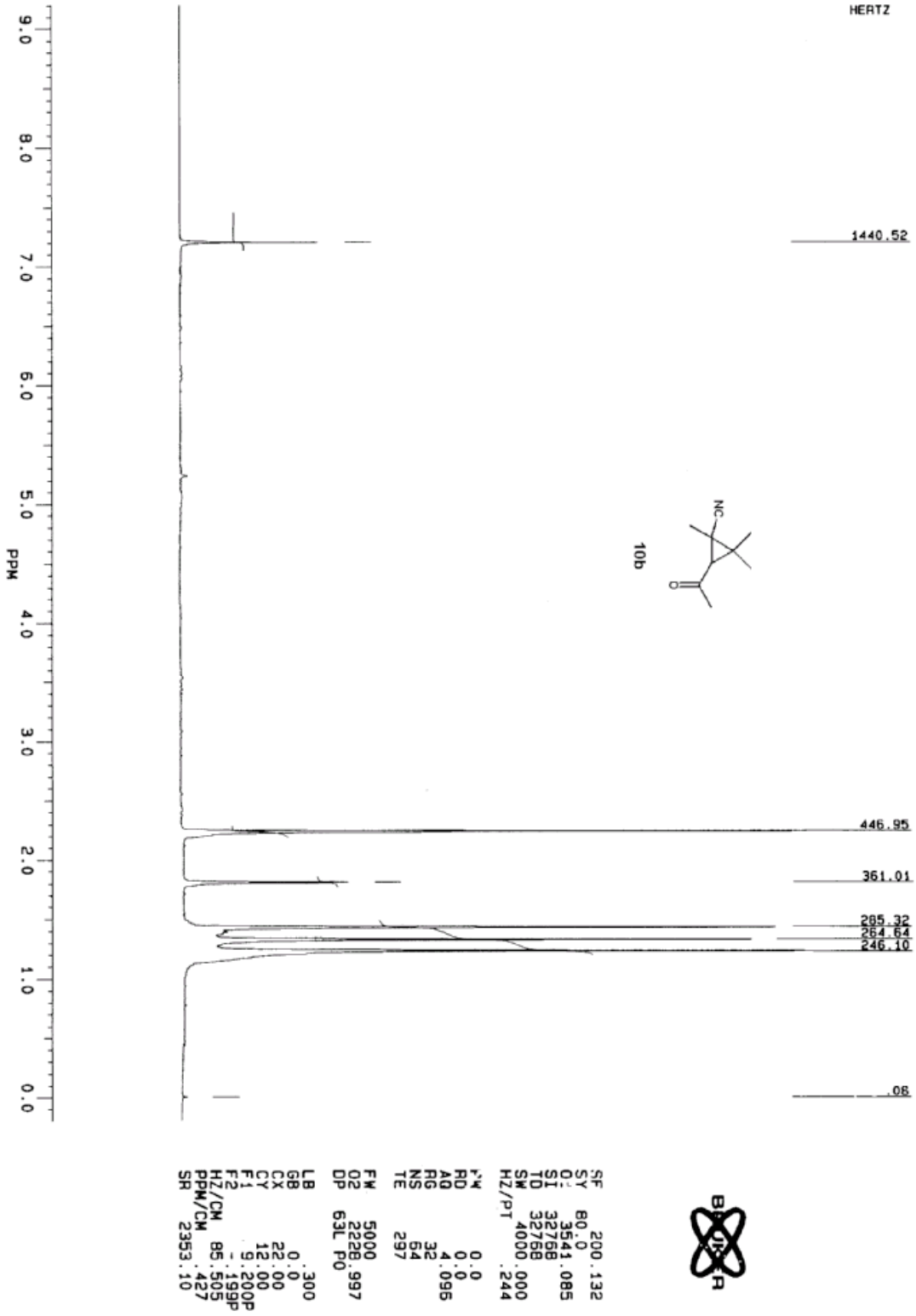
PPM/CM .427
SR 2353.34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3.0
2.0
1.0
0.0
10b
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O
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OF 3541.085
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TD 32768
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HZ/PT .244
PW 0.0
RD 0.0
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RG 32
NS 64
TE 297
FW 5000
O2 2228.997
DP 63L PO
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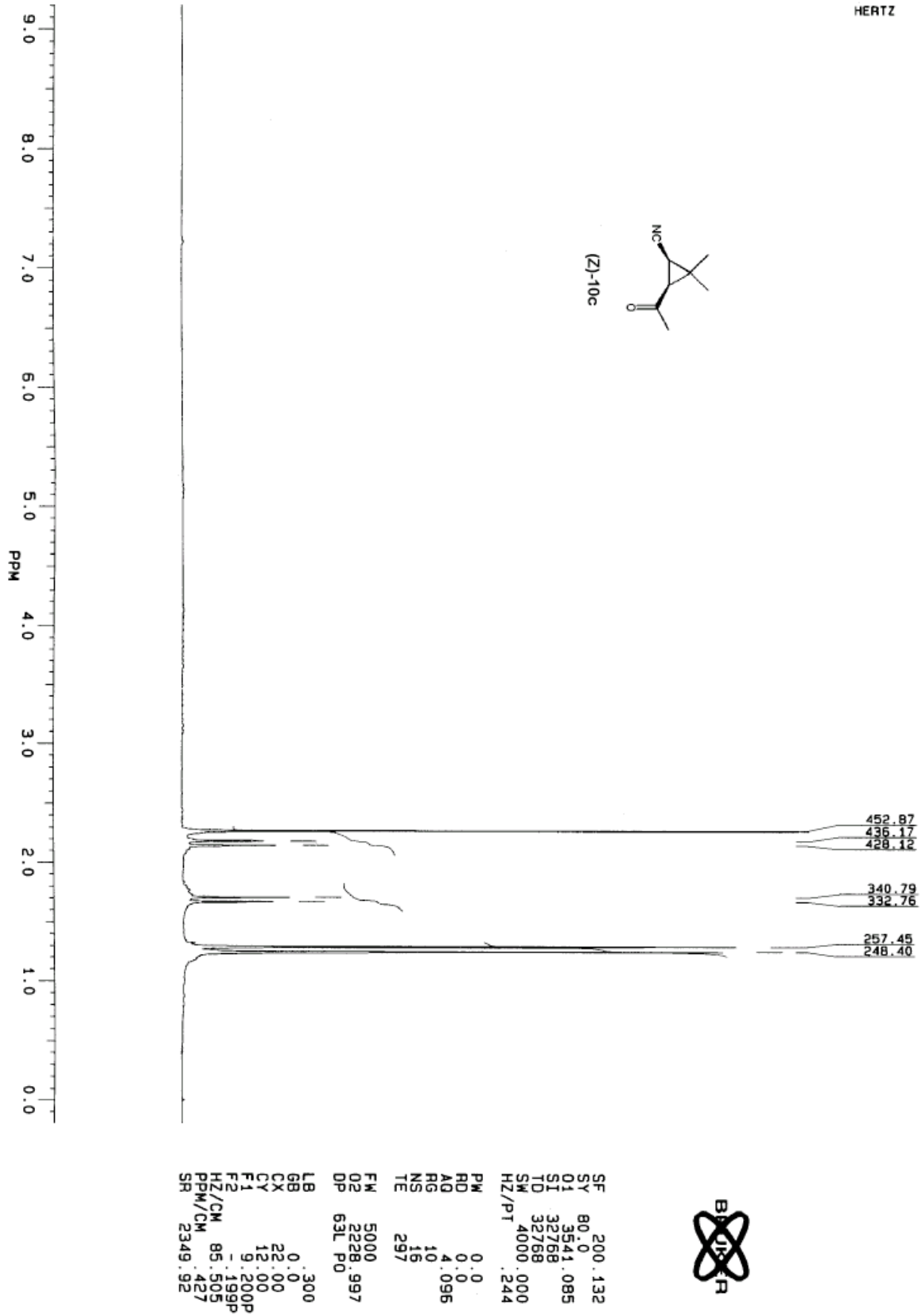
SR 2353.10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7.0
6.0
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4.0
3.0
2.0
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SY 80.0
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TD 32768
SW 4000.000
HZ/PT .244
PW 0.0
RD 0.0
AQ 4.096
RG 10
NS 16
TE 297
FW 5000
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DP 63L PO
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GB 0.0
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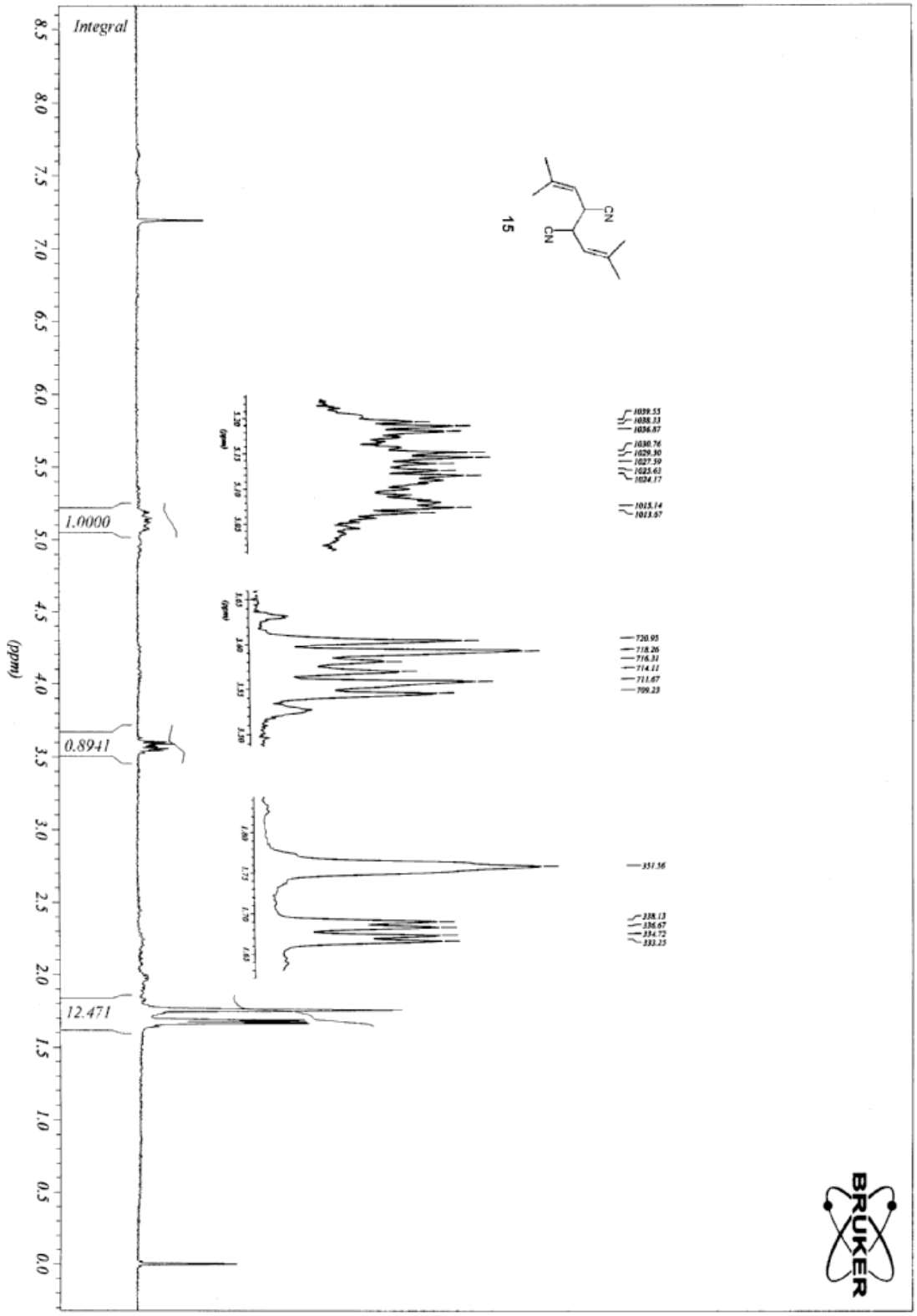
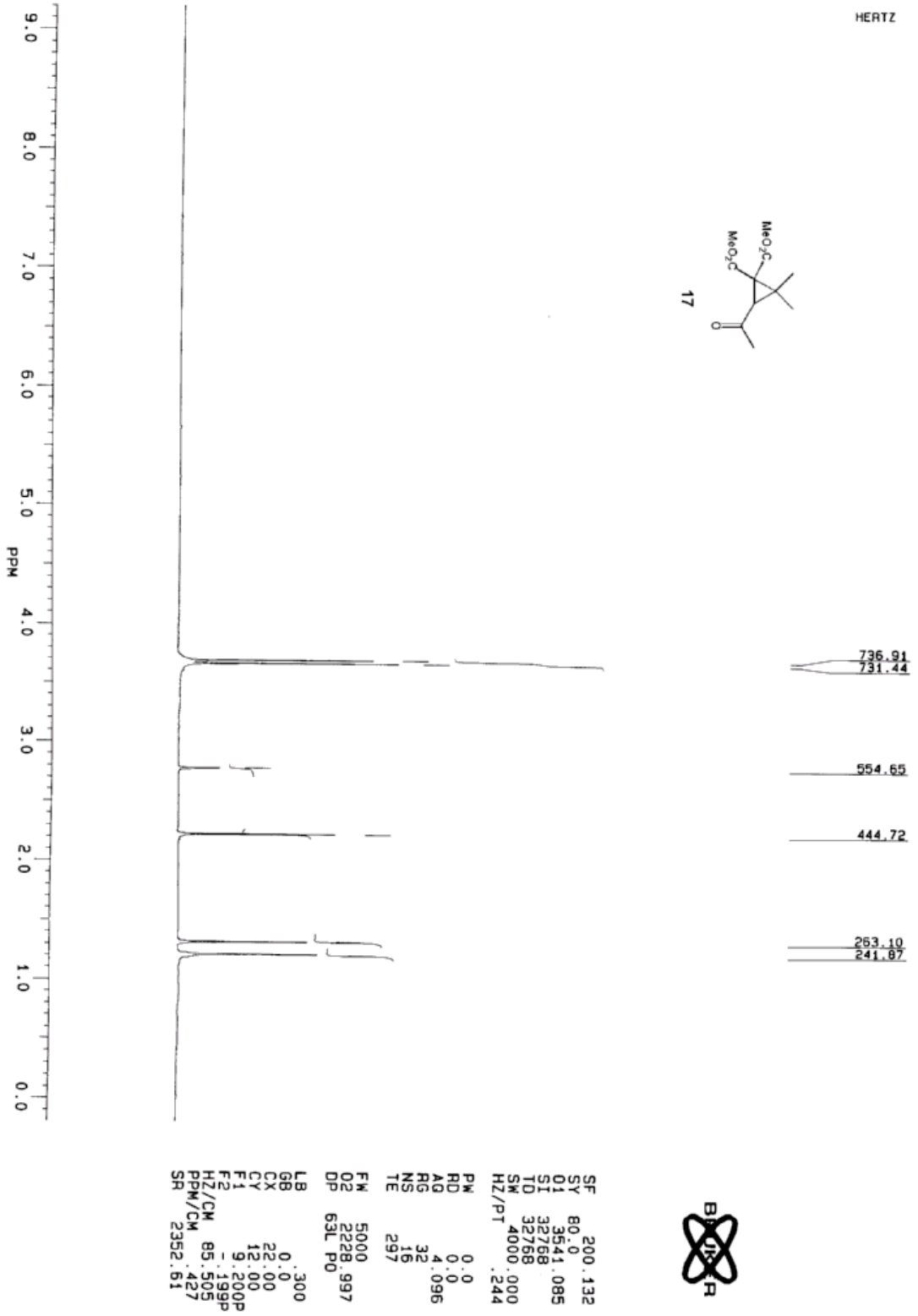
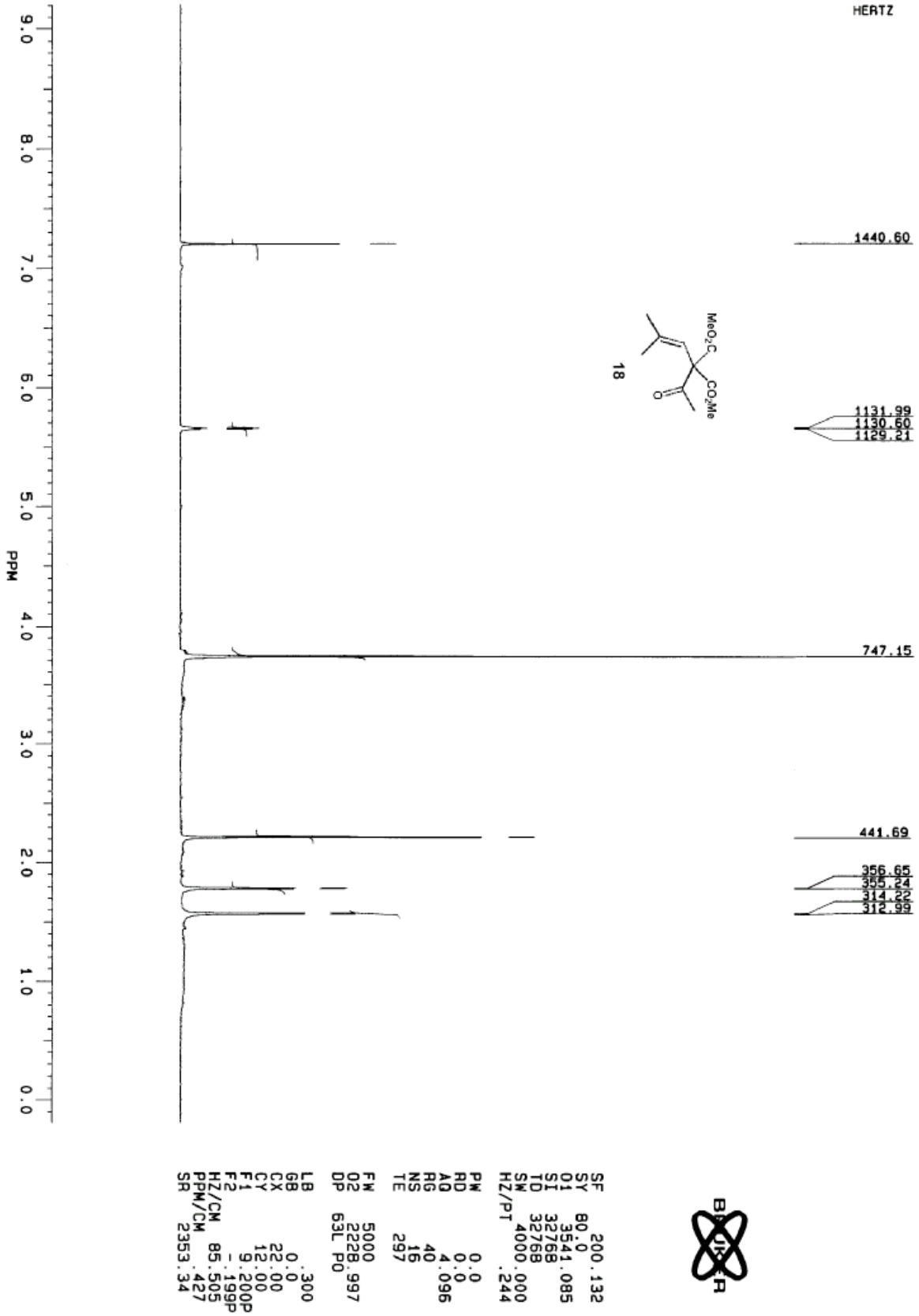
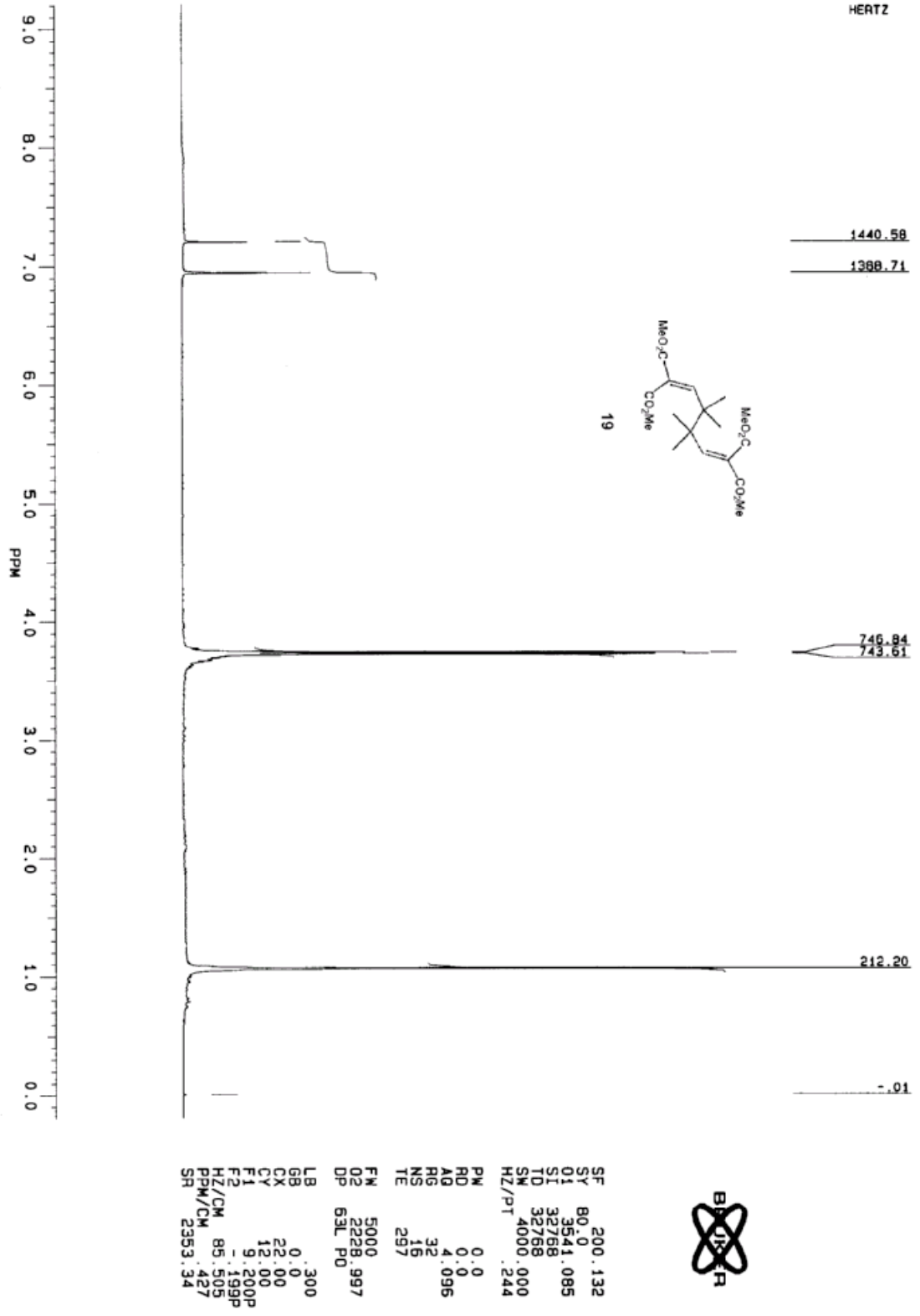
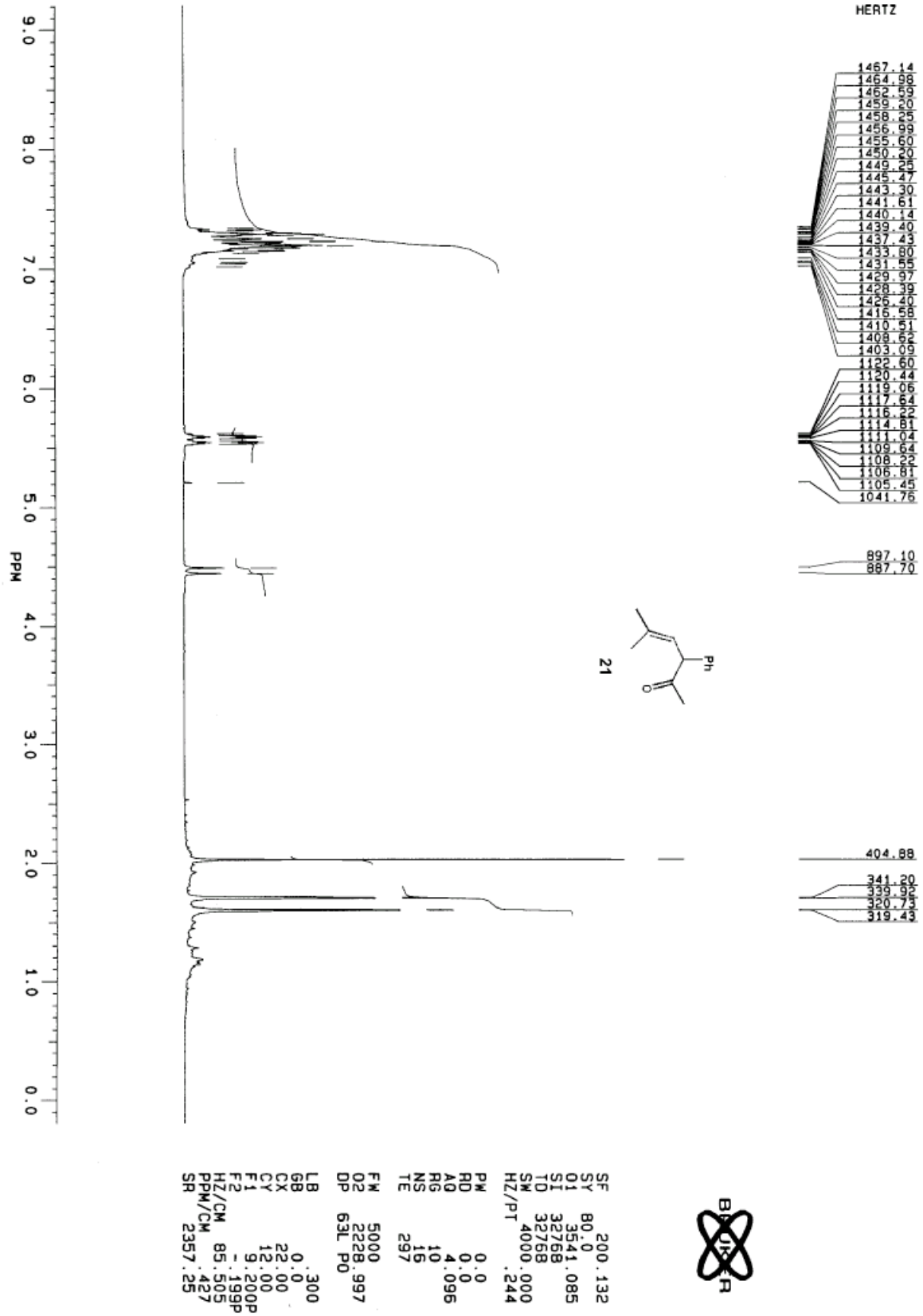
CY 12.00
F1 9.200P
F2 -.199P
HZ/CM 85.505
PPM/CM .427
SR 2349.92

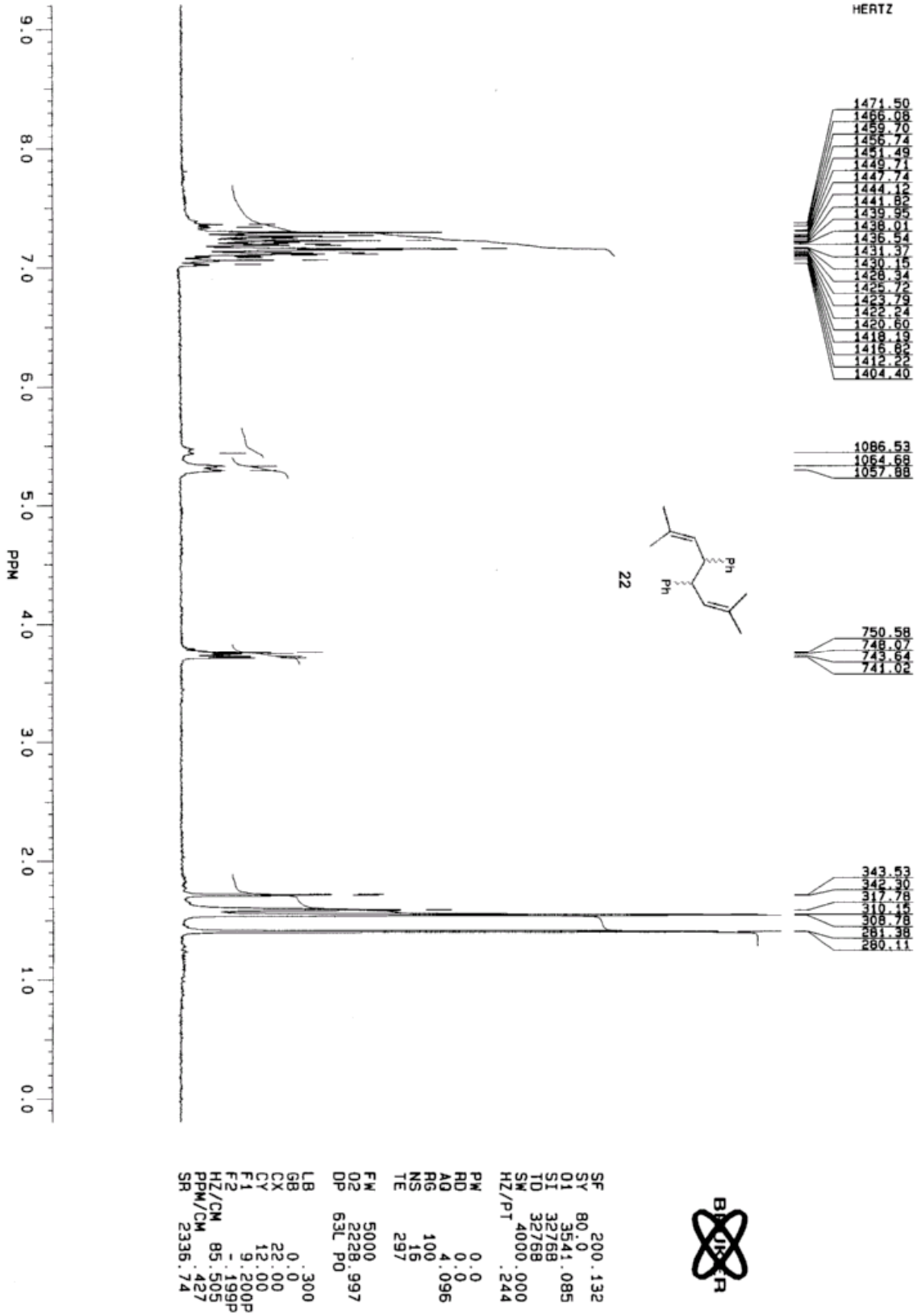

Integral
1.0000
0.8941
12.471
(ppm)
15
CN
CN
BRUKER

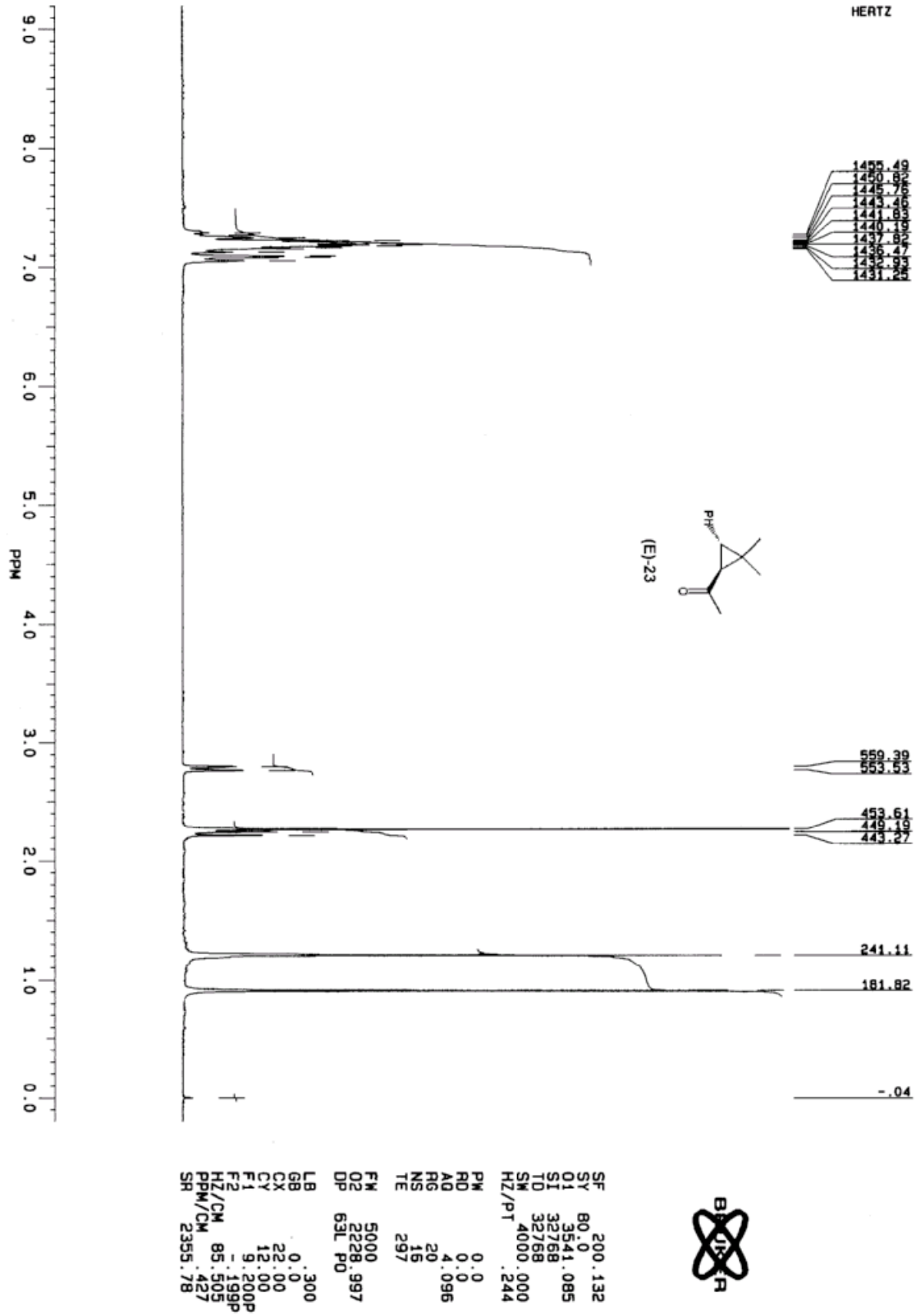

HERTZ
17
MeO2C
MeO2C
O
736.91
731.44
554.65
444.72
263.10
241.87
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
SF 200.132
SY 60.0
O1 3541.085
SI 32768
TD 32768
SW 4000.000
HZ/PT .244
PW 0.0
RD 0.0
AQ 4.096
RG 32
NS 16
TE 297
FW 5000
O2 2228.997
DP 63L PO
LB .300
GB 0.0
CX 22.00
CY 12.00
F1 9.200P
F2 -.199P
HZ/CM 85.505
PPM/CM .427
SR 2352.61

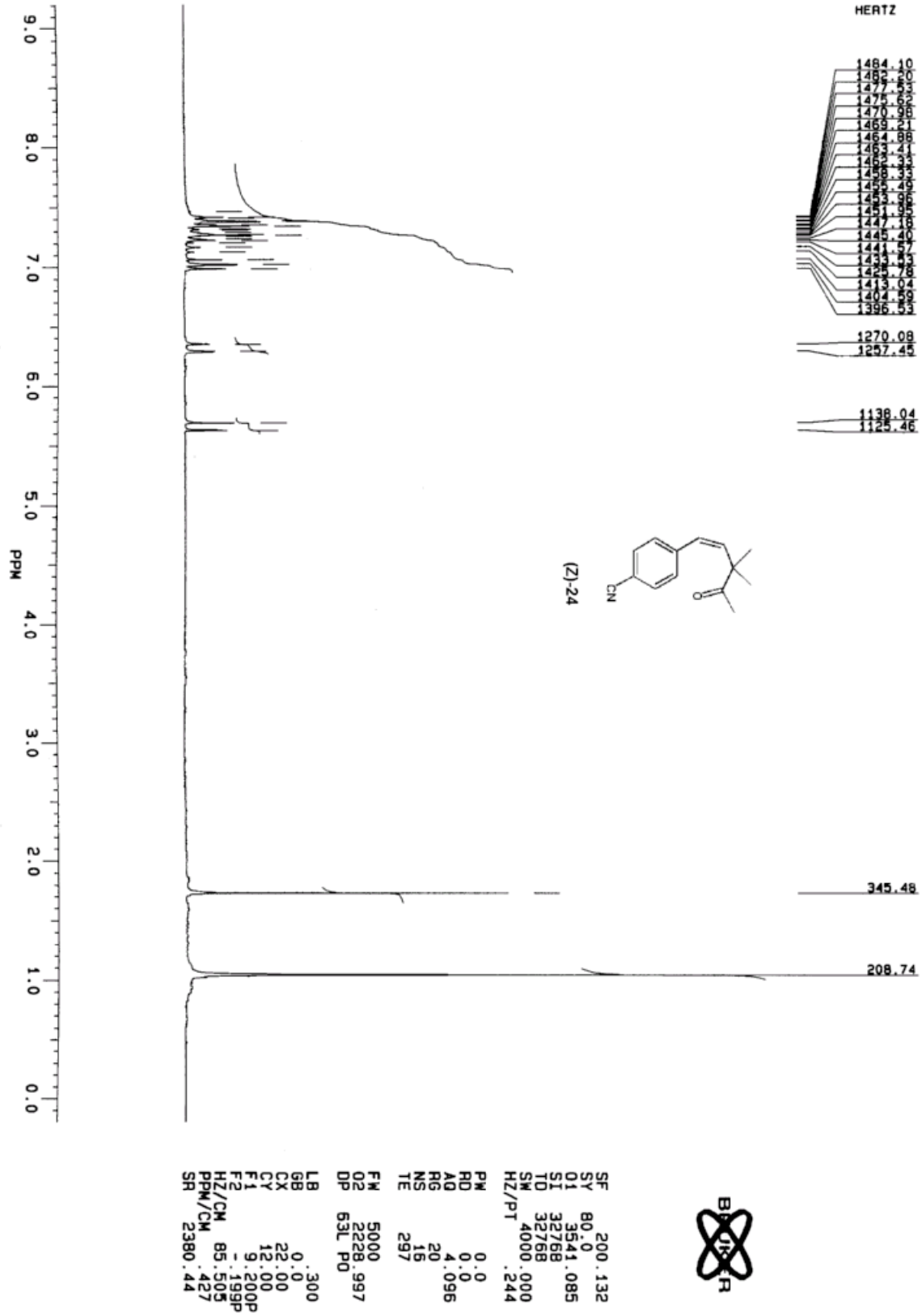

HERTZ
1440.60
1131.99
1130.60
1129.21
747.15
441.69
356.65
355.24
314.22
312.99
18
MeO2C
CO2Me
O
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
SF 200.132
SY 80.0
01 3541.085
SI 32768
TD 32768
SW 4000.000
HZ/PT .244
PW 0.0
RD 0.0
AQ 4.096
RG 40
NS 16
TE 297
FW 5000
02 22228.997
DP 63L PO
LB .300
GB 0.0
CX 22.00
CY 12.00
F1 9.200P
F2 -.199P
HZ/CM 85.505
PPM/CM .427
SR 2353.34

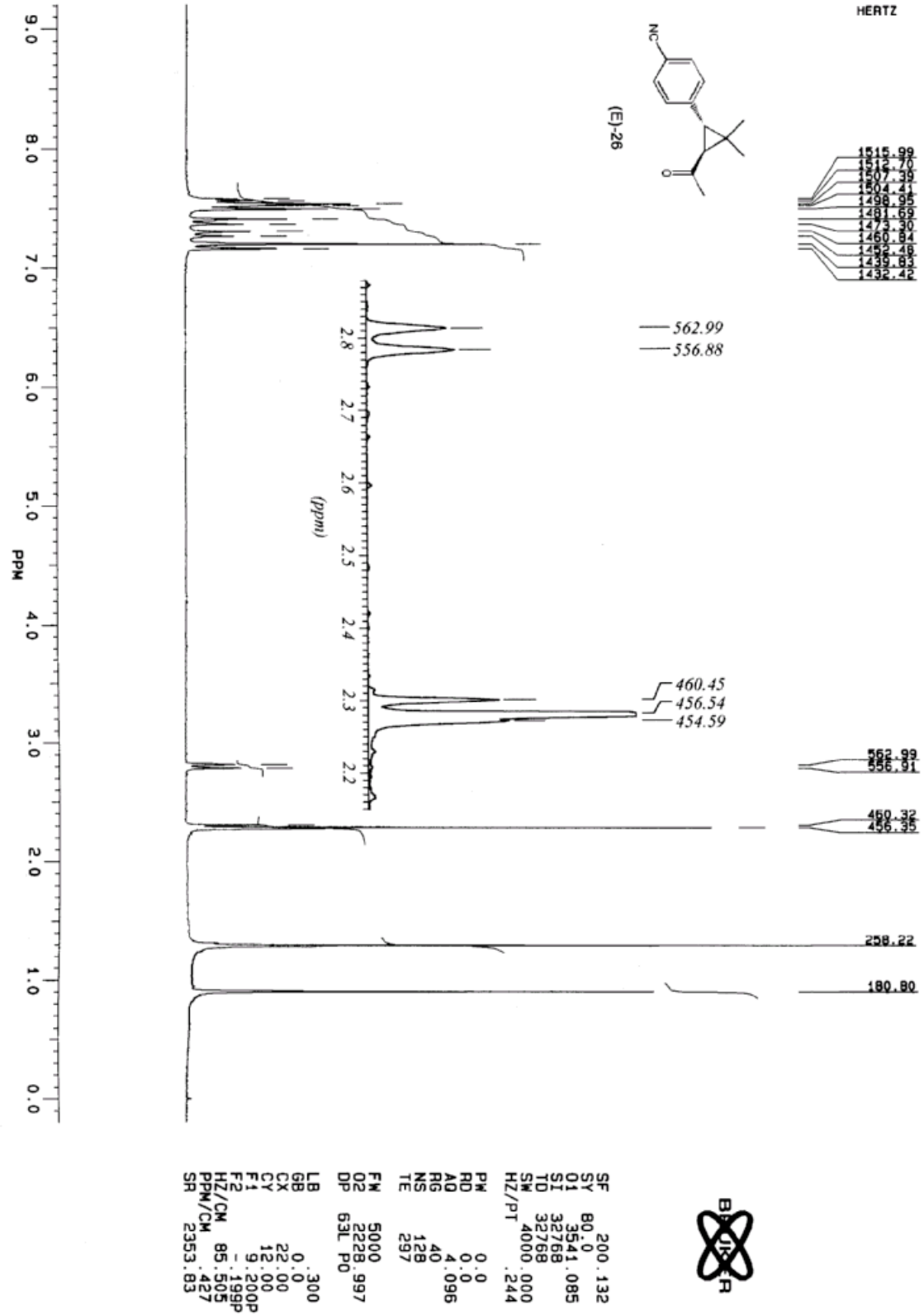

HERTZ
1440.58
1388.71
746.84
743.61
212.20
-.01
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
MeO2C
CO2Me
MeO2C
CO2Me
19
SF 200.132
SY 80.0
O1 3541.085
SI 32768
TD 32768
SW 4000.000
HZ/PT .244
PW 0.0
RD 0.0
AQ 4.096
RG 32
NS 16
TE 297
FW 5000
O2 2228.997
DP 53L PO
LB .300
GB 0.0
CX 22.00
CY 12.00
F1 9.200P
F2 -.199P
HZ/CM 85.505
PPM/CM .427
SR 2353.34
BRUKER

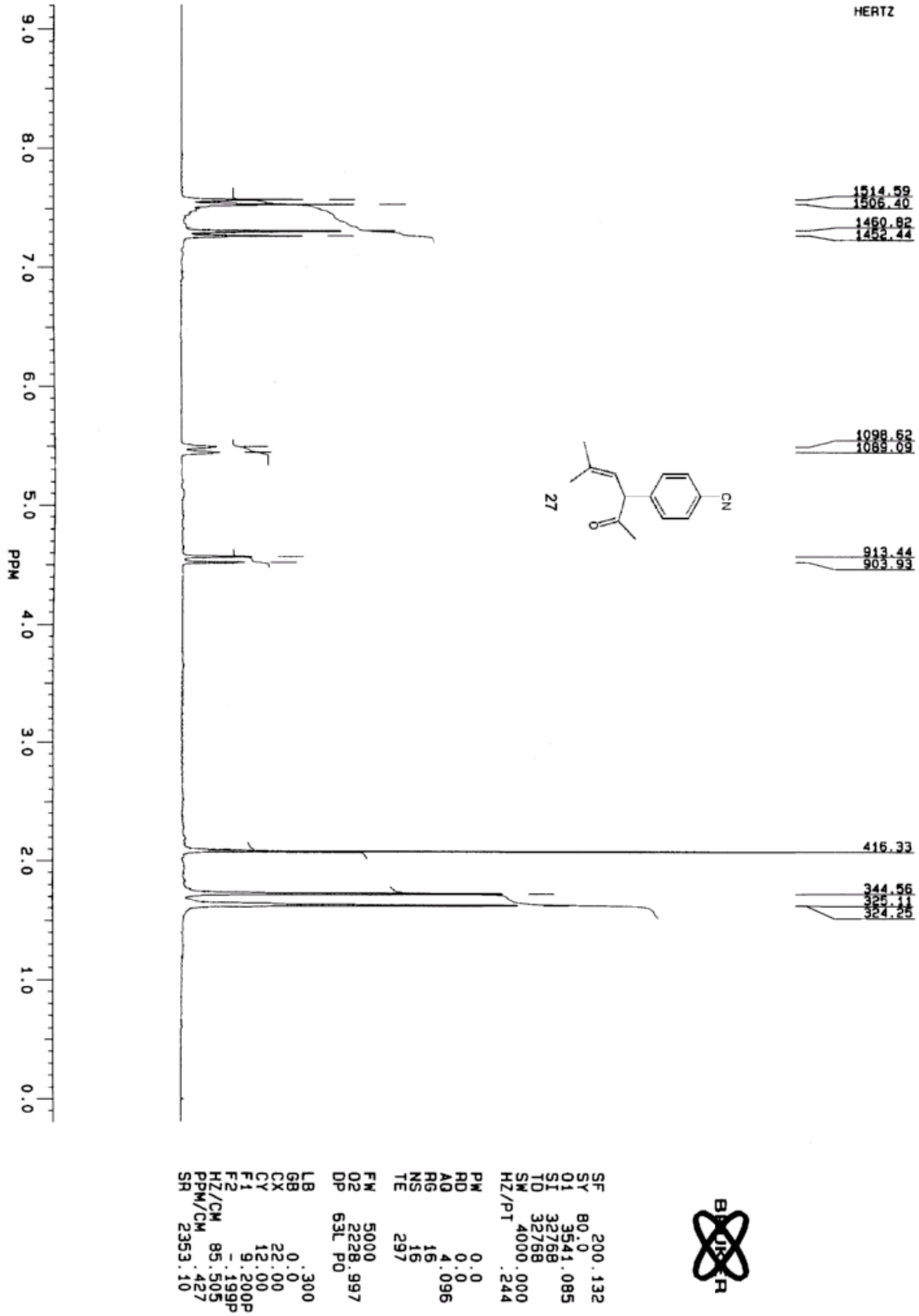

HERTZ
1467.14
1464.98
1462.59
1459.20
1458.25
1456.99
1455.60
1450.20
1449.25
1445.47
1443.30
1441.61
1440.14
1439.40
1437.43
1433.80
1431.55
1429.97
1428.39
1426.40
1416.58
1410.51
1409.62
1403.09
1122.60
1120.44
1119.06
1117.64
1116.22
1114.81
1111.04
1109.64
1108.22
1106.81
1105.45
1041.76
897.10
887.70
404.88
341.20
339.96
320.73
319.43
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Ph
O
21
SF 200.132
SY 80.0
01 3541.085
SI 32768
TD 32768
SW 4000.000
HZ/PT .244
PW 0.0
RD 0.0
AQ 4.096
RG 10
NS 16
TE 297
FW 5000
O2 2228.997
DP 63L PO
LB .300
GB 0.0
CX 22.00
CY 12.00
F1 9.200P
F2 -.199P
HZ/CM 85.505
PPM/CM .427
SR 2357.25

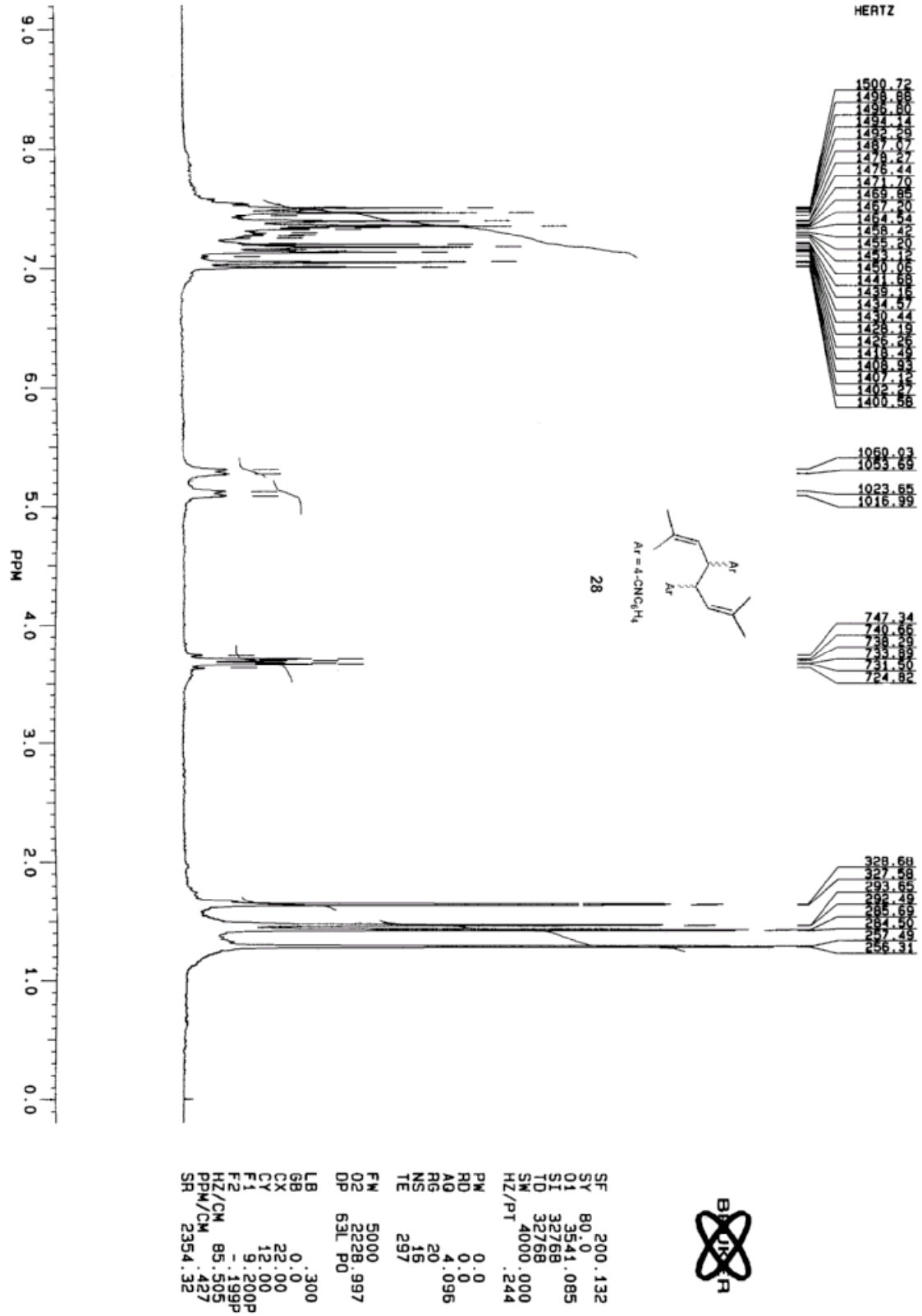

HERTZ
1471.50
1466.08
1459.70
1456.74
1451.49
1449.71
1447.74
1444.12
1441.82
1439.95
1438.01
1436.54
1431.37
1430.15
1428.34
1425.72
1423.79
1422.24
1420.60
1418.19
1416.62
1412.22
1404.40
1086.53
1064.68
1057.88
750.58
748.07
743.64
741.02
343.53
342.30
317.78
310.15
308.78
281.38
280.11
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Ph
Ph
22
SF 200.132
SY 80.0
01 3541.085
SI 32768
TD 32768
SW 4000.000
HZ/PT .244
PW 0.0
RD 0.0
AQ 4.096
RG 100
NS 16
TE 297
FW 5000
02 2228.997
DP 63L PO
LB .300
GB 0.0
CX 22.00
CY 12.00
F1 9.200P
F2 -.199P
HZ/CM 85.505
PPM/CM .427
SR 2336.74

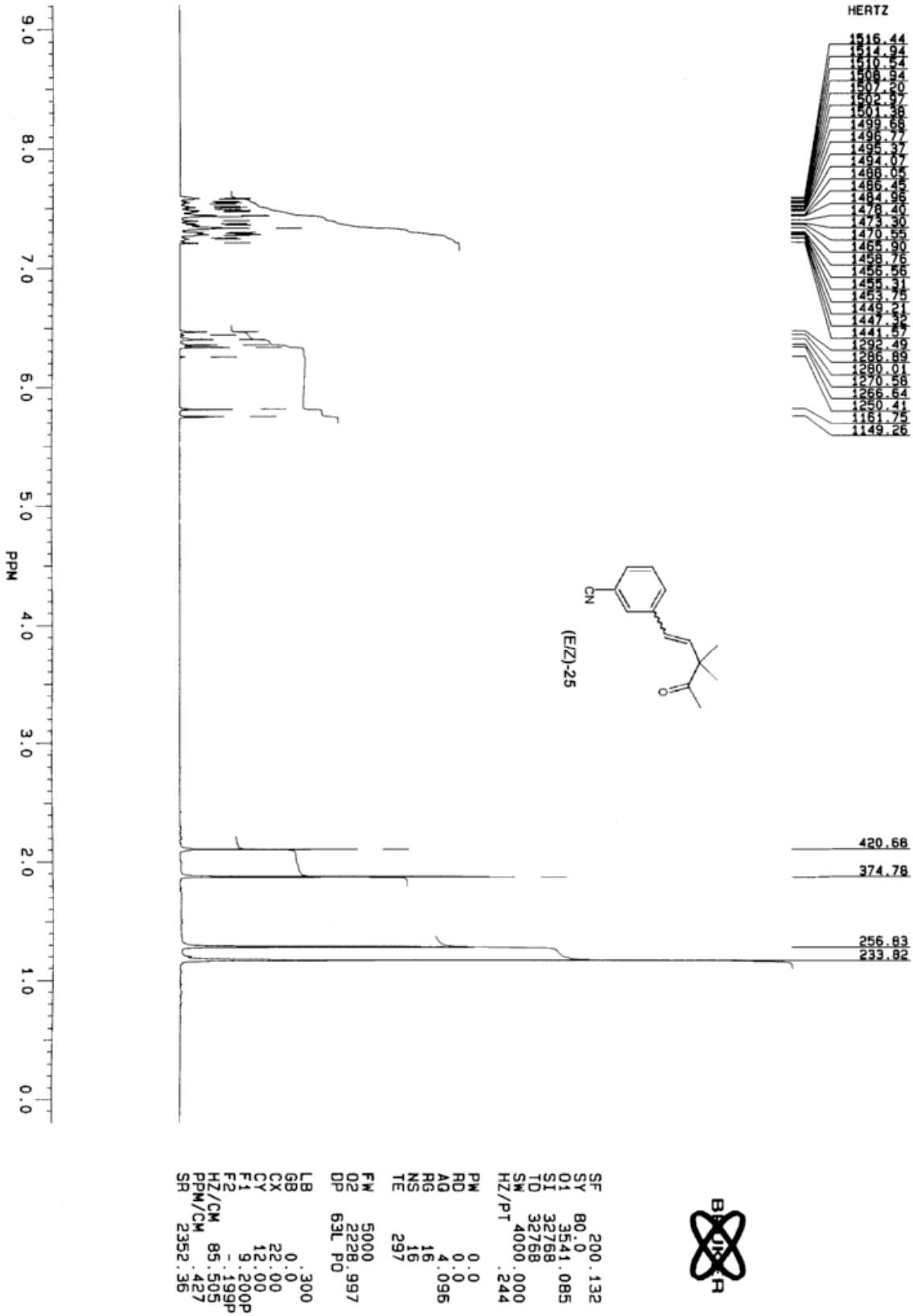

HERTZ
1455.49
1450.85
1445.76
1443.46
1441.83
1440.19
1437.82
1436.47
1432.93
1431.25
(E)-23
559.39
553.53
453.61
449.19
443.27
241.11
181.82
-.04
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
SF 200.132
SY 80.0
O1 3541.085
SI 32768
TD 32768
SW 4000.000
HZ/PT .244
PW 0.0
RD 0.0
AQ 4.096
RG 20
NS 16
TE 297
FW 5000
O2 2228.997
DP 63L PO
LB .300
GB 0.0
CX 22.00
CY 12.00
F1 9.200P
F2 -.199P
HZ/CM 85.505
PPM/CM .427
SR 2355.78

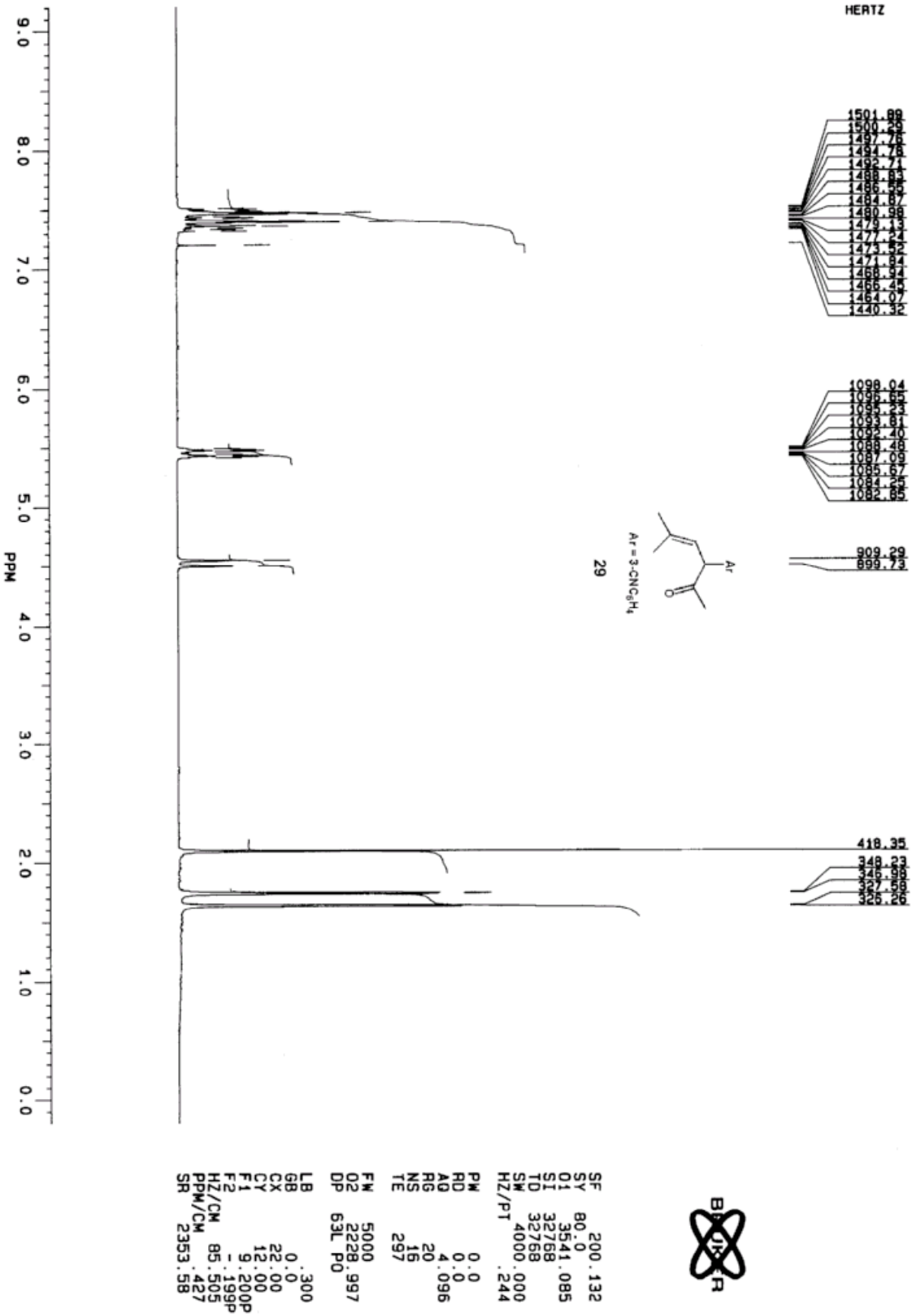

HERTZ
1484.10
1462.20
1477.53
1475.62
1470.98
1469.21
1464.86
1463.41
1458.33
1453.96
1451.95
1447.18
1445.40
1441.57
1433.83
1425.78
1413.04
1404.59
1396.53
1270.08
1257.45
1138.04
1125.46
345.48
208.74
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(Z)-24
CN
O
SF 200.132
SY 80.0
O1 3541.085
SI 32768
TD 32768
SW 4000.000
HZ/PT .244
PW 0.0
RD 0.0
AQ 4.096
RG 20
NS 16
TE 297
FW 5000
O2 2228.997
DP 63L PO
LB .300
GB 0.0
CX 22.00
CY 12.00
F1 9.200P
F2 -.199P
HZ/CM 85.505
PPM/CM .427
SR 2380.44


HERTZ
(E)-26
562.99
556.88
460.45
456.54
454.59
562.99
556.91
460.32
456.35
258.22
180.80
(ppm)
PPM


HERTZ
1514.59
1506.40
1460.82
1452.44
1098.62
1089.09
913.44
903.93
416.33
344.56
335.11
324.25
27
CN
O
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
SF 200.132
SY 80.0
O1 3541.085
SI 32768
TD 32768
SW 4000.000
HZ/PT .244
PW
RD 0.0
AQ 0.0
RG 4.096
NS 16
TE 16
297
FW 5000
O2 2228.997
DP 63L PO
LB .300
GB 0.0
CX 22.00
CY 12.00
F1 9.200P
F2 -.199P
HZ/CM 85.505
PPM/CM .427
SR 2353.10


HERTZ
1500.72
1060.03
1023.65
1016.99
747.34
328.68
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Ar = 4-CNC6H4
Ar
Ar
28
SF 200.132
SY 80.0
O1 3541.085
SI 32768
TD 32768
SW 4000.000
HZ/PT .244
PW 0.0
RD 0.0
AQ 4.096
RG 20
NS 16
TE 297
FW 5000
O2 2228.997
DP 63L PD
LB .300
GB 0.0
CX 22.00
CY 12.00
F1 9.200P
F2 -.199P
HZ/CM 85.505
PPM/CM .427
SR 2354.32


HERTZ
1516.44
1514.94
1510.54
1508.94
1507.20
1505.57
1504.97
1501.38
1499.66
1496.77
1495.37
1494.07
1488.05
1486.45
1484.96
1478.40
1473.30
1470.55
1465.90
1459.76
1456.56
1455.31
1453.75
1449.21
1447.32
1441.57
1292.49
1286.89
1280.01
1270.58
1266.64
1250.41
1161.75
1149.26
420.68
374.78
256.83
233.82
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CN
O
(E/Z)-25
BRUKER
SF 200.132
SY 80.0
O1 3541.085
SI 32768
TD 32768
SW 4000.000
HZ/PT .244
PW 0.0
RD 0.0
AQ 4.096
RG 16
NS 16
TE 297
FW 5000
O2 2228.997
DP 63L PO
LB .300
GB 0.0
CX 22.00
CY 12.00
F1 9.200P
F2 -.199P
HZ/CM 85.505
PPM/CM .427
SR 2352.36


HERTZ
1501.89
1500.29
1497.76
1494.78
1492.71
1488.93
1486.99
1484.87
1480.98
1479.13
1477.24
1473.52
1471.84
1468.94
1466.45
1464.07
1440.32
1099.04
1095.65
1095.23
1093.81
1092.40
1088.46
1087.09
1085.67
1084.25
1082.85
909.29
899.73
418.35
348.23
346.98
327.58
326.26
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Ar = 3-CNC6H4
29
Ar
O
BRUKER
SF 200.132
SY 80.0
01 3541.085
SI 32768
TD 32768
SW 4000.000
HZ/PT .244
PW 0.0
RD 0.0
AQ 4.096
RG 20
NS 16
TE 297
FW 5000
O2 2228.997
DP 63L PO
LB .300
GB 0.0
CX 22.00
CY 12.00
F1 9.200P
F2 -.199P
HZ/CM 85.505
PPM/CM .427
SR 2353.58