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Nitro-Substituted Hoveyda-Grubbs Ruthenium Carbenes: Enhancement of Catalysts Activity through Electronic Activation

Supplementary Information

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1. General

Unless otherwise noted, all reactions were carried out under Ar in pre-dried glassware using Schlenk techniques. The solvents were dried by distillation over the following drying agents and were transferred under argon: THF (K/benzophenone), toluene (Na), *n*-pentane, *n*-hexane, CH₂Cl₂ (CaH₂), Et₂O (LiAlH₄), MeOH (Mg). Flash column chromatography: Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on Bruker AVANCE 500, Varian Gemini 200 and 400 spectrometers in CDCl₃; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. IR: Perkin-Elmer Spectrum 2000 FT-IR, wavenumbers in cm⁻¹. MS (EI, LSIMS): AMD 604 Intectra GmbH. MS (ESI): Mariner Perseptive Biosystems, Inc. GC: HP 6890 with HP 5 column. GC/MS: HP 5890 with HP 5 column. Micro-analyses were provided by Institute of Organic Chemistry, PAS, Warsaw. The following catalysts

and substrates were prepared according to the literature procedures: **4b**,¹ **22**,², **29**,³ substrates for **36** and **42–44**,⁴ **45**,⁵ **50**, **51** and **53**,⁶ **55**,⁷ **56–57**,⁸ **71**.⁹ All commercially available chemicals were used as received.

2. Synthesis of catalysts 6–10 and 70

Alkylation of nitrosalicylaldehydes 11–13.
General Procedure: To a suspension of K₂CO₃ (1.11 g, 8.0 mmol) and Cs₂CO₃ (0.52 g, 40 mmol) in DMF (20 mL) a corresponding nitrosalicylaldehyde (4.0 mmol) was added. After stirring for 10 min at room temperature, 2-iodopropane (0.8 mL, 1.36 g, 8.0 mmol) was added and the reaction mixture was stirred for 1–2 days at 40 °C. Then the reaction mixture was poured into 20 mL water and extracted three times with EtOAc. The combined extracts were washed with brine, water

¹ Wakamatsu, H.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 2403–2405.

² Henley, R. V.; Turner, E. E. *J. Chem. Soc.* **1930**, 928–940

³ Mąkosza, M.; Stalewski, J.; Wojciechowski, K.; Danikiewicz, W. *Tetrahedron* **1997**, *53*, 193–214.

⁴ Moskalev, N.; Mąkosza, M. *Tetrahedron Lett.* **1999**, *40*, 5935; (b) Moskalev, N.; Barbasiewicz, M.; Mąkosza, M. *Tetrahedron* **2004**, *60*, 347–358.

⁵ (a) Pietrusiewicz, K. M.; Zablocka, M.; Monkiewicz, J. *J. Org. Chem.*, **1984**, *49*, 152; (b) Pietrusiewicz, K. M.; Zablocka, M. *Tetrahedron Lett.*, **1988**, *29*, 199.

⁶ Mąkosza, M.; Nieczydor, P.; Grela, K. *Tetrahedron* **1998**, *54*, 10827–10836.

⁷ Prowotorow, I.; Wicha, J.; Mikami, K. *Synthesis* **2001**, 145–149.

⁸ Furman, B.; Dziedzic, M. *Tetrahedron Lett.* **2003**, *44*, 8249–8252.

⁹ Grela, K.; Michrowska, A.; Bieniek, M.; Kim, M.; Klajn, R. *Tetrahedron*, **2003**, *59*, 4525–4531.

and dried. The solvent was evaporated. The products **11a–13a** were used without further purification.

2-isopropoxy-5-nitrobenzaldehyde (11a):

Yellow low melting solid (86%). IR (KBr): ν 3115, 2991, 2942, 1679, 1609, 1526, 1348, 1284, 1111, 950, 832, 748, 667 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.48 (d, 6H, $J = 6.1$ Hz), 4.85 (q, 1H, $J = 6.1$ Hz), 7.10 (d, 1H, $J = 9.2$ Hz), 8.39 (dd, 1H, $J = 2.9, 9.2$ Hz), 8.69 (d, 1H, $J = 2.9$ Hz), 10.41 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 21.8, 72.6, 113.6, 124.7, 125.1, 130.4, 141.1, 164.3, 187.8; MS (EI) m/z (rel intensity) 209 (10, $[\text{M}]^+$), 167 (100), 137 (18), 120 (11), 93 (7), 75 (3), 65 (10), 53 (4); HRMS (EI) calcd for $[\text{M}]^+$ ($\text{C}_{10}\text{H}_{11}\text{O}_4\text{N}$): 209.0688. found 209.0686.

2-isopropoxy-3-nitrobenzaldehyde (12a):

Brown oil (56%). ^1H NMR (400 MHz, CDCl_3) δ 1.88 (d, 6H, $J = 6.3$ Hz), 4.34 (heptet, 1H, $J = 6.2$ Hz), 7.31–7.36 (m, 1H), 8.07–8.12 (m, 2H), 10.42 (d, 1H, $J = 0.9$ Hz); MS (ESI) m/z (rel intensity) 264.1 ($[\text{M}+\text{H}+2\text{MeOH}]^+$), 232.1 ($[\text{M}+\text{H}+\text{MeOH}]^+$).

2-isopropoxy-3-methoxy-5-nitrobenzaldehyde (13a): yellow-brown crystals (71%). MS (LSIMS) m/z (rel intensity) 240 ($[\text{M}+\text{H}]^+$); HRMS (LSIMS) calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{11}\text{H}_{14}\text{O}_5\text{N}$): 240.08720; found: 240.08661.

General procedure for Wittig olefination: In a three-necked flame-dried flask solid methyltriphenylphosphonium bromide (0.384 g, 1.1 mmol, Aldrich) and THF (3.5 mL) were placed under argon. Then a solution of *n*-BuLi (1 mL, 1.5 mmol, 1.5M) was added dropwise at -78 °C. After stirring 15 min at -78 °C, a solution of corresponding 2-isopropoxybenzaldehyde **11a–13a** (0.75 mmol) in THF (1 mL) was added and the reaction mixture was stirred at the same temperature for 30 min. After warming to RT the reaction mixture was stirred for 48 h. The reaction mixture was treated with saturated solution of NH_4Cl , extracted with EtOAc and dried. The solvent was evaporated and the product was purified by column chromatography (*c*-hexane-ethyl acetate 2:8).

2-isopropoxy-5-nitrostyrene (14): Pale yellow oil (57%). IR (film): ν 3088, 2982, 2967, 1627, 1607, 1583, 1516, 1341, 1271, 1107, 950, 742 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.41 (d, 6H, $J = 6.0$ Hz), 4.71 (q, 1H, $J = 6.0$ Hz),

5.40 (dd, 1H, $J = 0.5, 11.2$ Hz), 5.87 (dd, 1H, $J = 0.5, 17.7$ Hz), 6.91 (d, 1H, $J = 9.1$ Hz), 7.00 (dd, 1H, $J = 11.2, 17.7$ Hz), 8.12 (dd, 1H, $J = 2.8, 9.1$ Hz), 8.36 (d, 1H, $J = 2.8$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 21.9, 71.5, 112.2, 116.8, 122.4, 124.5, 128.1, 130.1, 141.0, 159.9; MS (EI) m/z (rel intensity) 207 (4, $[\text{M}]^+$), 165 (59), 148 (100), 135 (4), 118 (96), 104 (2), 90 (15), 65 (8), 63 (7), 51 (4); MS (ESI): m/z 230 ($[\text{M}+\text{Na}]^+$); HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ ($\text{C}_{11}\text{H}_{13}\text{O}_3\text{NNa}$): 230.0788. found 230.0776.

2-isopropoxy-3-nitrostyrene (15):

Brown oil (67%). ^1H NMR (200 MHz, CDCl_3) δ 1.28 (d, 6H, $J = 6.0$ Hz), 4.23 (heptet, 1H, $J = 6.2$ Hz), 5.43 (dd, 1H, $J = 11.0, 1.0$ Hz), 5.80 (dd, 1H, $J = 17.8, 1.0$ Hz), 6.95–7.28 (m, 2H), 7.65–7.74 (m, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 148.2, 134.8, 130.7, 130.4, 124.1, 123.4, 117.0, 78.9, 22.1; MS (EI) m/z (rel intensity) 207 (4, $[\text{M}]^+$), 165 (59), 149 (10), 148 (100), 90 (15), 89 (14); HRMS (EI) calcd for $[\text{M}]^+$ ($\text{C}_{11}\text{H}_{13}\text{O}_3\text{N}$): 207.08954; found: 207.09005

2-isopropoxy-3-methoxy-5-nitrostyrene (16):

Brown oil (63%). IR (film): ν 3095, 2978, 2937, 2872, 2664, 1694, 1612, 1580, 1524, 1465, 1430, 1373, 1340, 1300, 1282, 1226, 1185, 1141, 1099, 1073, 1048, 996, 928, 885, 852, 802, 776, 747, 576, 463 cm^{-1} ; ^1H NMR (500 MHz, acetone- d_6) δ 1.30 (d, 6H, $J = 6.1$ Hz), 3.93 (s, 3H), 4.63 (heptet, 1H, $J = 6.1$ Hz), 5.41 (dd, 1H, $J = 11.1, 1.0$ Hz), 5.84 (dd, 1H, $J = 17.7, 1.0$ Hz) 7.03–7.09 (m, 1H) 7.67 (d, 1H, $J = 2.6$ Hz), 8.07 (d, 1H, $J = 2.6$ Hz); ^{13}C NMR (125 MHz, acetone- d_6) δ 153.2, 150.0, 143.5, 132.8, 130.5, 117.0, 113.8, 106.1, 76.4, 56.2, 22.5; MS (EI) m/z (rel intensity) 238 (2), 237 (11, M^+), 196 (10), 195 (100), 134 (9), 43 (9); HRMS (EI) calcd for $[\text{M}]^+$ ($\text{C}_{12}\text{H}_{15}\text{O}_4\text{N}$): 237.10011; found: 237.09979.

3,5-dibromobiphenyl-2-ol (18): To a solution of **7** (4.25 g, 25 mmole) in AcOH (5 mL), Br_2 (3 mL, 9.33 g, 58 mmole) was added at RT in portions—the reaction is exothermic in initial stage and the flask was cooled in cold water when necessary. The mixture was stirred at RT for 2 h, then poured into water (80 mL) and solid K_2CO_3 was added in portions to pH 5. The mixture was extracted with MTBE (3 x 50 mL), the combined extracts were washed with aqueous Na_2SO_3 , dried and evaporated. The product (7.56 g, 92%) was used without further purification.

Yellowish solid, mp = 52–55 °C; lit.:¹⁰ 56–57 °C.

3-bromo-5-nitrobiphenyl-2-ol (19): To a suspension of **18** (0.64 g, 1.9 mmol) in AcOH (0.8 mL) concentrated HNO₃ (0.15 mL, 2.1 mmol) was added slowly (3 minutes) at 5 °C and the mixture was stirred for additional 5 min. Water (25 mL) was then added and the resulted mixture was extracted with CH₂Cl₂ (3 x 25 mL). The combined extracts were washed with water (3 x 25 mL), dried and evaporated to dryness to give 0.216 g (39%) of the product as an orange-brown solid. mp = 111–113 °C, lit.:¹¹ 113.5–114 °C.

2-isopropoxy-3-bromo-5-nitrobiphenyl

(19a): The compound was obtained according to procedure used for alkylation of the nitrosalicylaldehydes **11–13**. Yellow oil (70%). IR (film): ν 3081, 2979, 2932, 2871, 1602, 1581, 1567, 1523, 1497, 1464, 1452, 1429, 1384, 1373, 1337, 1288, 1237, 1175, 1141, 1099, 1054, 924, 904, 850, 809, 782, 768, 743, 701, 634, 566, 510, 437 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.06 (d, 6H, *J* = 6.2 Hz), 4.06 (heptet, 1H, *J* = 6.1 Hz), 7.42–7.50 (m, 3H), 7.54–7.57 (m, 2H), 8.18 (d, 1H, *J* = 2.7 Hz) 8.44 (d, 1H, *J* = 2.9 Hz); MS (EI) *m/z* (rel intensity) 337 (4), 335 (4, [M]⁺), 296 (13), 295 (99), 293 (100), 168 (31) 140 (9), 139 (24), 43 (10).

2-Isopropoxy-5-nitro-3-vinylbiphenyl

(20): In a Schlenk flask was placed solid Pd[Ph₃P]₄ (0.015 g, 5 mol%) and a solution of **19a** (0.088 g, 0.26 mmol) in toluene (1.0 mL) was added under argon. Neat Bu₃SnCH=CH₂ (0.093 g, 0.29 mmol) was added via syringe and the resulting solution was heated at 115 °C for 6 h. After cooling to RT the mixture was evaporated and a solution of KF (0.58 g) in methanol (5 mL) were added to the residue. The mixture was stirred at RT for 2 h and evaporated again. To the resulting residue MTBE (15 mL) and water (10 mL) were added. Organic phase was removed, inorganic phase was extracted with MTBE (4x15 mL). The combined extracts were dried and evaporated. The product was purified by column chromatography (*c*-hexane-ethyl acetate 1.5:8) to give 0.059 g (78%) of **20** as a yellow oil. IR (film): ν 3085, 3030, 2976, 2929, 2871, 2854, 1734, 1628, 1603, 1584, 1525, 1497, 1464, 1453, 1430, 1408, 1384, 1341, 1302, 1282, 1229, 1219, 1176, 1140,

1102, 1083, 1029, 996, 939, 922, 858, 816, 775, 762, 747, 721, 699, 653, 622, 551, 511, 462, 435 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.00 (d, 6H, *J* = 6.2 Hz), 3.86 (heptet, 1H, *J* = 6.2 Hz), 5.47 (dd, 1H, *J* = 11.1, 0.8 Hz), 5.90 (dd, 1H, *J* = 17.7, 0.8 Hz) 7.12 (dd, 1H, *J* = 17.8, 11.1 Hz) 7.38–7.48 (m, 3H), 7.55–7.58 (m, 2H), 8.13 (d, 1H, *J* = 2.9 Hz) 8.39 (d, 1H, *J* = 2.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 158.0, 143.7, 137.3, 136.8, 134.0, 131.0, 128.9, 128.5, 128.1, 125.4, 120.4, 117.2, 76.8, 22.0; MS (EI) *m/z* (rel intensity) 284 (3), 283 (15, [M]⁺), 242 (16), 241 (100), 224 (37), 195 (9), 194 (29), 165 (19), 152 (11), 43 (9); HRMS (EI) calcd for [M]⁺ (C₁₇H₁₇O₃N): 283.12084; found: 283.12106.

1-Bromo-2-isopropoxy-4-nitrobenzene

(22a): The compound was obtained according to procedure used for alkylation of the nitrosalicylaldehydes **11–13**. Yellowish solid, mp = 38–40 °C. IR (film): ν 3104, 2983, 2938, 1897, 1755, 1566, 1531, 1467, 1410, 1351, 1310, 1262, 1179, 1139, 1124, 1106, 1035, 979, 878, 848, 821, 799, 740, 701, 607, 502, 470, 441 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.44 (d, 6H, *J* = 6.0 Hz), 4.70 (heptet, 1H, *J* = 6.0 Hz), 7.69–7.70 (m, 2H), 7.72–7.73 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 155.0, 147.9, 133.6, 121.1, 116.2, 108.4, 72.8, 21.7; MS (EI) *m/z* (rel intensity) 261 (11), 259 (11, [M]⁺), 219 (97), 217 (100), 189 (13), 187 (14), 173 (16), 171 (16), 161 (19), 159 (20), 145 (13), 143 (14), 92 (18), 79 (13), 75 (12), 63 (54), 62 (13), 43 (77), 41 (39), 39 (15).

2-Isopropoxy-4-nitrostyrene (23) In a Schlenk flask was placed solid Pd[Ph₃P]₄ (0.069 g, 3 mol %) and a solution of **22a** (0.517 g, 2.0 mmol) in toluene (8 mL) was added under argon. Neat Bu₃SnCH=CH₂ (0.692 g, 2.2 mmol) was added via syringe and the resulting solution was refluxed for 6 h. After cooling to RT the mixture was evaporated and to the residue a solution of KF (0.7 g) in methanol (10 mL) were added. The mixture was stirred at RT for 2 h and evaporated again. To the residue MTBE (30 mL) and water (15 mL) were added. Organic phase was removed, inorganic phase (containing insoluble material) was extracted with MTBE (3 x 25 mL) and combined extracts were dried and evaporated. The product was purified by column chromatography (*c*-hexane-ethyl acetate 2:18) to give 0.343 g (83%) of **23** as a yellow oil. IR (film): ν 3091, 2980, 2933,

¹⁰ Auwers, V.; Wittig, G. J. *Prakt. Chem.* **1924**, 108, 103.

¹¹ Hartshorn, M. P.; Robinson, W. T.; Vaughan, J.; White, J. M. *Austr. J. Chem.* **1985**, 38, 575.

1694, 1626, 1584, 1520, 1486, 1417, 1345, 1293, 1248, 1179, 1111, 981, 916, 870, 846, 831, 801, 737 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.41 (d, 6H, $J = 6.1$ Hz), 4.68 (heptet, 1H, $J = 6.0$ Hz), 5.46 (dd, 1H, $J = 11.3, 1.2$ Hz), 5.90 (dd, 1H, $J = 17.8, 1.1$ Hz) 7.02–7.10 (m, 1H), 7.58 (d, 1H, $J = 8.6$ Hz), 7.72 (d, 1H, $J = 3.2$ Hz), 7.77–7.80 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.1, 147.8, 134.1, 130.5, 126.6, 118.2, 115.6, 108.2, 71.4, 21.8; MS (EI) m/z (rel intensity) 208 (4), 207 (22, $[\text{M}]^+$), 165 (100), 135 (20), 119 (10), 118 (13), 107 (16), 91 (38), 89 (18), 79 (14), 65 (19), 63 (10), 43 (32), 41 (19), 39 (13); HRMS (EI) calcd for $[\text{M}]^+$ ($\text{C}_{11}\text{H}_{13}\text{O}_3\text{N}$): 207.08954; found: 207.08872; Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{O}_3\text{N}$: C, 63.76; H, 6.32; N, 6.76. found: C, 63.54; H, 6.49; N, 6.61.

2-methoxy-5-nitrostyrene (70a): Solid $\text{Ph}_3\text{P}=\text{CH}_2$ (0.693 g, 2.5 mmol, Aldrich) and THF (20 mL) were placed under argon in a Schlenk tube. A solution of 2-methoxy-5-nitrobenzaldehyde (0.202 g, 1.1 mmol, Aldrich) in THF (5 mL) was added at -78 °C. The reaction mixture was stirred at the same temperature for 1 h. Then the reaction mixture was warmed to RT and treated with saturated solution of NH_4Cl , extracted with MTBE (4 x 20 mL) and dried. The solvent was evaporated and the product was purified by column chromatography to give 0.115 g (58%) of the product as a yellow oil. IR (KBr): ν 3115, 3090, 3023, 2962, 2924, 2851, 2655, 2513, 2247, 2018, 1902, 1847, 1805, 1779, 1731, 1624, 1610, 1583, 1515, 1467, 1458, 1445, 1421, 1339, 1257, 1186, 1141, 1085, 1018, 992, 918, 903, 827, 802, 759, 743, 637, 597, 520, 504, 433 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 3.96 (s, 3H), 5.41 (dd, 1H, $J = 11.2, 0.9$ Hz), 5.86 (dd, 1H, $J = 17.7, 1.0$ Hz), 6.91–7.02 (m, 2H), 8.14 (dd, 1H, $J = 9.1, 2.8$ Hz), 8.34 (d, 1H, $J = 2.8$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 161.3, 141.5, 129.8, 127.6, 124.7, 122.1, 117.2, 110.4, 56.1; MS (EI) m/z (rel intensity) 180 (8), 179 (68, $[\text{M}]^+$), 164 (46), 149 (9), 118 (100), 103 (14), 90 (33), 89 (35), 79 (11), 77 (30), 63 (17), 51 (11); HRMS (EI) calcd for $[\text{M}]^+$ ($\text{C}_{19}\text{H}_9\text{O}_3\text{N}$): 179.05824; found: 179.05780.

2.1. General procedure for preparation of catalysts 6a and 7a

Catalyst 6a: Under an argon atmosphere Grubbs' catalyst **1a** (164.6 mg, 0.20 mmol) was placed in a Schlenk tube. Then CH_2Cl_2 (15 mL) was added followed by a solution

of styrene **14** in CH_2Cl_2 (5 mL). The resulted suspension was stirred at 40 °C for 1 h. After this point forth all manipulations can be done without a protective atmosphere of argon. The resulting mixture was concentrated in vacuo, and purified by silica-gel column chromatography, using *c*-hexane-EtOAc (5:2) as eluent and collecting a product as a brown band. After removal of solvents and washing with small amount of dry *n*-pentane **6a** was obtained as brown, microcrystalline solid (95 mg, 83%). IR (solid film): ν 2930, 2852, 1604, 1575, 1521, 1476, 1447, 1379, 1342, 1275, 1241, 1205, 1181, 1136, 1095, 1049, 1005, 951, 918, 851, 830, 789, 745, 656, 606, 518 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.26–2.35 (m, 39 H), 5.33–5.40 (m, 1H), 7.18 (d, 1H, $J = 5$ Hz), 8.54 (d, 1H, $J = 5$ Hz), 8.60 (s, 1H), 17.38 (d, 1H, $J = 5.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 273.2, 157.0, 143.3, 124.2, 117.6, 113.2, 78.2, 35.8 (d, $J = 10$ Hz), 30.1, 27.7 (d, $J = 24$ Hz), 26.2, 22.1; MS (EI) m/z (rel intensity) 645 (9, $[\text{M}]^+$), 569 (4), 567 (6), 566 (4), 419 (4), 418 (3), 417 (8), 416 (10), 415 (10), 414 (14), 413 (10), 412 (10), 411 (7), 410 (6), 409 (4), 408 (5), 379 (7), 378 (5), 377 (13), 376 (11), 375 (11), 374 (10), 373 (6), 372 (4), 371 (4), 285 (14), 281 (13), 280 (10), 279 (10), 215 (15), 214 (69), 213 (10), 199 (24), 198 (43), 167 (12), 159 (10), 153 (18), 133 (69), 132 (57), 123 (10), 117 (100), 116 (27), 115 (23), 113 (11), 83 (50), 82 (18), 81 (37), 79 (18), 78 (16), 77 (15), 67 (18), 55 (74), 54 (11), 43 (70), 42 (16), 41 (77); HRMS (EI): calcd. for $[\text{M}]^+$ ($\text{C}_{28}\text{H}_{44}\text{O}_3\text{N}^{35}\text{Cl}_2\text{P}^{102}\text{Ru}$): 645.14794. found: 645.14706.

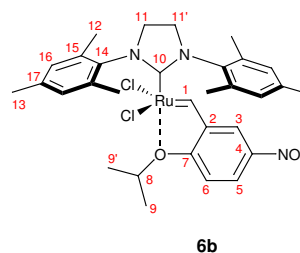
Catalyst 7a: brown solid (70%) IR (solid film): ν 2930, 2853, 1605, 1575, 1521, 1447, 1342, 1275, 1242, 1205, 1181, 1135, 1095, 1049, 1005, 951, 918, 851, 830, 789, 745, 656, 606, 518 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.27–2.34 (m, 39H), 5.35–5.40 (m, 1H), 7.84 (s, 1H), 7.92–7.99 (m, 2H), 17.42 (d, 1H, $J = 4.2$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 271.1, 152.2, 146.7, 145.7, 121.9, 119.1, 108.6, 77.5, 35.9, 35.7 (d, $J = 10$ Hz), 30.1 27.7 (d, $J = 24$ Hz), 26.9, 26.2, 22.1; MS (ESI) m/z (rel intensity) 675.4 ($[\text{M}+\text{MeOH}]^+$). MS (EI) m/z (rel intensity) 645 (3, $[\text{M}]^+$), 296 (10), 280 (10), 241 (12), 215 (24), 214 (100), 213 (17), 207 (24), 199 (29), 198 (39), 180 (13), 179 (29), 178 (11), 177 (12), 167 (23), 166 (15), 165 (82), 162 (15), 159 (16), 153 (20), 149 (11), 135 (18), 133 (88), 132 (63), 131 (13), 118 (10), 117 (67), 116 (16), 115 (18), 113 (11), 107 (11), 105 (11), 97 (10), 95 (11), 91 (29), 89 (10), 83 (44), 82 (18), 81 (36), 79 (21), 78 (18), 77 (20), 71 (13), 69 (17), 67

(17), 65 (14), 57 (19), 55 (57), 43 (65), 42 (11), 41 (63), 39 (21), 36 (10); HRMS (EI): calcd. for $[M]^+$ ($C_{28}H_{44}O_3^{35}Cl_2N^{102}Ru$): 645.14794. found 645.14957.

2.2. General procedure for preparation of catalysts **6b**, **7b**, **10** and **70** from **1b**

Catalyst 6b: Carbene complex **1b** (153 mg, 0.18 mmol), CuCl (18 mg, 0.18 mmol) and CH_2Cl_2 (10 mL) were placed in a Schlenk flask. A solution of styrene **14** (38 mg, 0.18 mmol) in CH_2Cl_2 (4 mL) was then added and the resulted solution was stirred under argon at 30 °C for 1 h. From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated in vacuo and the resulted material was purified by column chromatography on silica. Elution with *c*-hexane-EtOAc (5:2) removes **6b** as a green band. Removal of solvent, washing with cold *n*-pentane and drying under vacuum afforded **6b** as a green microcrystalline solid (100 mg, 83%). IR (KBr): ν 2924, 2850, 1606, 1521, 1480, 1262, 1093, 918, 745 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 16.47 (s, 1H, H-1), 8.42 (dd, 1H, $J = 9.1, 2.5$ Hz), 7.80 (d, 1H, $J = 2.5$ Hz), 7.09 (s, 4H), 6.88 (d, 1H, $J = 9.1$ Hz), 4.97 (sept, 1H, $J = 6.1$ Hz), 4.20 (s, 4H, H-11, 11'), 2.44 (2s, 18H, H-12, 13), 1.30 (d, 6H, $J = 6.1$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 291.1, 208.4, 156.4, 150.3, 144.7, 143.1, 139.3, 139.1, 129.5, 124.1, 117.4, 112.7, 77.6, 51.5, 21.1, 21.0, 19.4; 1H NMR (500 MHz, CD_2Cl_2) δ 16.42 (s, 1H, H-1), 8.46 (dd, 1H, $J = 9.1, 2.5$ Hz, H-5), 7.80 (d, 1H, $J = 2.5$ Hz, H-3), 7.10 (s, 4H, H-16), 6.94 (d, 1H, $J = 9.1$ Hz, H-6), 5.01 (sept, 1H, $J = 6.1$ Hz, H-8), 4.22 (s, 4H, H-11, 11'), 2.47 (2s, 18H, H-12, 13), 1.30 (d, $J = 6.1$ Hz, 6H, H-9, 9'); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 289.1 (C-1), 208.2 (C-10), 156.8 (C-7), 150.3, 145.0 (C-2), 143.5 (C-4), 139.6 (C-15), 139.3, 129.8 (C-16), 124.5 (C-5), 117.2 (C-3), 113.3 (C-6), 78.2 (C-8), 52.0 (C-11, 11'), 21.3 (C-9, 9'), 21.2 (C-12), 19.4 (C-13) (where assignments of the NMR signals (based on 2D $^1H,^{13}C$ -chemical shift correlated spectra: GHSQC, GHMBC) are given, they are unambiguous and refer to the arbitrary numbering shown on Scheme 1); MS (ESI) m/z (rel intensity) 636 $[M-Cl]^+$; HRMS (IE): m/z calcd for $[M]^+$ ($C_{31}H_{37}N_3O_3^{35}Cl_2^{102}Ru$): 671.1255. found 671.1229; Anal. Calcd. for $C_{31}H_{37}Cl_2N_3O_3Ru$: C, 55.44; H, 5.55; N, 6.26. found: C, 55.35; H,

5.70; N, 6.09.



Scheme 1

Catalyst 7b: green microcrystalline solid (83%). IR (KBr): ν 2922, 2853, 1740, 1666, 1607, 1520, 1484, 1448, 1423, 1401, 1378, 1337, 1262, 1200, 1158, 1114, 1097, 1034, 968, 902, 853, 801, 736, 579, 453, 427 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 1.29 (d, 6H, $J = 6.1$ Hz), 2.40–2.47 (m, 18H), 4.18 (s, 4H), 4.94–5.02 (heptet, 1H, $J = 6.1$ Hz), 7.06 (s, 1H), 7.08 (bs, 4H), 7.65 (bs, 1H), 7.77 (dd, 1H, $J = 8.4, 1.9$ Hz), 16.73 (s 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 51.5, 76.7, 108.2, 119.2, 121.4, 129.4, 139.1, 145.3, 147.8, 151.5, 207.6, 288.7; MS (EI) m/z (rel intensity) 671 (5, $[M]^+$), 670 (3), 442 (12), 406 (18), 405 (11), 404 (13), 403 (10), 338 (21), 337 (14), 323 (28), 305 (33), 304 (94), 303 (92), 301 (14), 289 (21), 167 (63), 166 (22), 165 (39), 161 (11), 159 (10), 158 (21), 155 (11), 153 (31), 152 (10), 148 (10), 146 (33), 145 (17), 144 (15), 139 (37), 137 (10), 136 (13), 135 (11), 131 (11), 130 (11), 123 (12), 122 (14), 121 (25), 120 (10), 119 (12), 107 (17), 93 (16), 91 (25), 79 (12), 78 (15), 77 (29), 65 (30), 63 (15), 44 (10), 43 (100), 42 (31), 41 (76), 40 (12), 39 (48), 38 (10), 36 (42); HRMS (EI): calcd. for $[M]^+$ ($C_{31}H_{37}N_3O_3^{35}Cl_2^{102}Ru$): 671.12555. found: 671.12151.

Catalyst 10: Second generation Grubbs' catalyst **1b** (0.089 g, 0.10 mmol) and CuCl (0.013, 0.13 mmol) were placed in a Schlenk flask. Methylene chloride (3 mL) was added under argon and then a solution of 2-isopropoxy-3-methoxy-5-nitrostyrene **16** (0.031 g, 0.13 mmol) in methylene chloride (2 mL) was added. The solution was stirred at room temperature for 15 min. The solvent was evaporated and the product was purified by column chromatography (*c*-hexane-AcOEt 4:1). The product (0.034 g, 46%) was obtained as a green microcrystalline solid. IR (film): ν 3531, 2974, 2927, 2855, 1937, 1694, 1631, 1607, 1572, 1523, 1481, 1464, 1446, 1400, 1381, 1338, 1267, 1235, 1217, 1183, 1163, 1147,

1097, 1037, 978, 909, 889, 853, 818, 776, 742, 695, 646, 621, 579, 404 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.35 (d, 6H, $J = 6.1$ Hz), 2.43 (bs, 18H), 3.85 (s, 3H), 4.19 (s, 4H), 5.84 (heptet, 1H, $J = 6.1$ Hz), 7.10 (s, 4H), 7.43 (d, 1H, $J = 2.5$ Hz), 7.94 (d, 1H, $J = 2.5$ Hz), 16.38 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 293.8, 208.6, 153.2, 150.5, 149.1, 146.4, 145.2, 143.6, 143.3, 139.2, 132.0, 129.4, 125.3, 124.0, 115.2, 114.0, 111.3, 107.9, 106.3, 83.1, 56.7, 56.5, 56.2, 38.2, 29.6, 26.9, 22.4, 21.9, 21.0; MS (LSIMS) m/z (rel intensity) 701.1 ($[\text{M}]^+$) 666.2 ($[\text{M}-\text{Cl}]^+$); HRMS (LSIMS) calcd for $[\text{M}-\text{Cl}]^+$ ($\text{C}_{32}\text{H}_{39}\text{O}_4\text{N}_3\text{ClRu}$): 667.1679; found: 667.1664.

Catalyst 70: green solid (39%). IR (KBr): ν 3461, 2924, 2853, 1934, 1678, 1608, 1576, 1523, 1483, 1447, 1380, 1343, 1267, 1133, 1085, 1010, 942, 905, 853, 826, 746, 636, 613, 579 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.45 (s, 18H), 3.95 (s, 3H), 4.17 (s, 4H), 6.93 (d, 1H, $J = 9.3$ Hz), 7.10 (s, 4H), 7.78 (d, 1H, $J = 2.4$ Hz), 8.43 (dd, 1H, $J = 9.0, 2.5$ Hz), 16.39 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 285.5, 207.5, 157.5, 143.9, 143.5, 139.2, 138.6, 135.8, 129.7, 129.6, 124.2, 124.0, 116.6, 111.5, 59.5, 51.7, 20.9, 19.1; MS (ESI) m/z (rel intensity) 675.4 ($[\text{M}+\text{MeOH}]^+$).

2.3. A one-pot tree-step preparation of **6b** from **1a**

To a suspension of salt **24** (152 mg, 0.388 mmol, Strem) in *n*-hexane (7 mL) a solution potassium tert-amylate, $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{OK}$, (0.22 mL, 0.372 mmol, 1.7 M in toluene, Fluka) was added under argon and the resulted slightly turbid, yellow solution was stirred at room temperature for 30 min. Grubbs' catalyst **1a** (255 mg, 0.310 mmol) was then added to the flask as a solid and the reaction mixture was heated to reflux for 30 min. To the resulted brown-pink suspension a solution of **14** (83.5 mg, 0.403 mmol) in CH_2Cl_2 (7 mL) and solid CuCl (33.8 mg, 0.341 mmol) were added at RT. After 1 h at 40 $^\circ\text{C}$ the resulted product was purified as described above to afford catalyst **6b** as green crystals (149 mg, 72%). Analytical data were identical with these reported above.

3. General procedures for metathesis reactions

3.1. Cross-metathesis

To a mixture of an alkene (1.0 mmol) and a cross-metathesis partner (2.0–4.0 mmol) in CH_2Cl_2 (5 mL) was added a solution of a Ru-catalyst (0.01–0.05 mmol, 1–5 mol%) in CH_2Cl_2 (1 mL). The resulting mixture was stirred at 25–45 $^\circ\text{C}$ for 0.5–16 h. The solvent was removed under reduced pressure. The crude product was purified by flash chromatography (*c*-hexane-ethyl acetate).

3.2. RCM and enyne metathesis

To a mixture of an alkene (1.0 mmol) in CH_2Cl_2 (50 mL, $c=0.02\text{M}$) was added a solution of a Ru-catalyst (0.01–0.05 mmol, 1–5 mol%) in CH_2Cl_2 (1 mL). The resulting mixture was stirred at 0–45 $^\circ\text{C}$ for 0.5–16 h. The solvent was removed under reduced pressure. The crude product was purified by flash chromatography (*c*-hexane-ethyl acetate).

(Z)-5-Methoxy-1-(methoxymethyl)-3-[(4-methylphenyl)sulfonyl]-1H-indol-4-yl-1-propenyl phenyl sulfone (30):⁹ Colourless crystals, mp = 140–141 $^\circ\text{C}$ (54%). IR (KBr): ν 3532, 3119, 2926, 2852, 1627, 1514, 1286, 1143, 1085, 1027, 798, 676, 593 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 3.32 (s, 3H), 3.58 (s, 3H), 3.96 (dd, 2H, $J = 5.8, 1.5$ Hz), 5.46 (s, 2H), 5.74 (dt, 1H, $J = 15.0, 1.5$ Hz), 6.54 (dt, 1H, $J = 15.0, 5.8$ Hz), 6.92 (d, 1H, $J = 9.0$ Hz), 7.25–7.32 (m, 2H), 7.39–7.56 (m, 4H), 7.66–7.77 (AA'XX', 4H), 8.08 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 21.6, 29.7, 56.2, 56.4, 78.6, 109.6, 110.6, 115.4, 116.6, 124.4, 126.5, 127.2, 128.9, 129.1, 130.1, 132.7, 137.4, 139.5, 141.3, 144.3, 145.8, 154.2; MS (LSIMS) m/z (rel intensity) 548 $[\text{M}+\text{Na}]^+$; MS (EI) m/z (rel intensity) 525 (5, $[\text{M}]^+$), 494 (6), 384 (52), 370 (37), 366 (10), 349 (12), 306 (16), 229 (47), 214 (20), 198 (31), 184 (16), 169 (17), 105 (38), 77 (19); Anal. Calcd. for $\text{C}_{17}\text{H}_{27}\text{NO}_6\text{S}_2$: C, 61.70; H, 5.18; N, 2.66. found: C, 61.46; H, 5.35; N, 2.76.

Methyl-7-[1-(tert-butyl)-1,1-dimethylsilyloxy-2-heptenoate (31):¹² Colorless oil, (E):(Z) = 95:5 (95%). IR (film): ν 2952, 2933, 2859, 1729, 1659, 1472, 1437, 1389, 1317, 1258,

¹² Nicolaou, K. C.; Hwang, C.-K.; Marron, B. E.; DeFrees, S. A.; Couladouros, E. A. *J. Am. Chem. Soc.* **1990**, *112*, 3040–3054.

1201, 1165, 1102, 1040, 983, 838, 777 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 0.03 (s, 6H), 0.88 (s, 9H), 1.46–1.57 (m, 4H), 2.17–2.25 (m, 2H), 3.61 (t, 2H, $J = 5.9$ Hz), 3.71 (s, 3H), 5.81 (dt, 1H, $J = 15.7, 1.6$ Hz), 6.96 (dt, 1H, $J = 15.7, 7.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 167.1, 149.4, 121.0, 62.7, 51.3, 32.2, 31.9, 25.9, 24.4, 18.3, –5.3; MS (EI) m/z (rel intensity) 257 (1, $[\text{M}-15]^+$), 241 (3), 217 (4), 215 (23), 183 (15), 171 (0.5), 155 (1), 139 (3), 119 (3), 101 (3), 89 (100), 81 (53), 79 (13), 75 (32), 73 (25), 59 (24), 47 (11), 41 (21), 39 (10); HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ ($\text{C}_{14}\text{H}_{28}\text{O}_3\text{SiNa}$): 295.1700. found: 295.1691.

7-[1-(*tert*-butyl)-1,1-dimethylsilyloxy-2-heptenenitrile (32):¹³ Yellow oil, (Z):(E) = 2.7:1 (90%). IR (film): ν 2953, 2931, 2858, 2222, 1633, 1523, 1472, 1388, 1344, 1255, 1179, 1101, 1006, 978, 836, 776 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 0.07 (s, 6H), 0.89 (s, 9H), 1.49–1.54 and 1.54–1.58 (2m, 4H), 2.42–2.48 (m, 2H), 3.60–3.64 (m, 2H), 5.29–5.35 (m, 1H), 6.45–6.51 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.0, 118.2, 99.6, 62.5, 32.0, 31.6, 25.9, 24.6, 21.9, –5.3; MS (EI) m/z (rel intensity) 238 (0.5), 224 (3), 183 (15), 182 (100), 166 (1), 152 (9), 138 (1), 126 (22), 108 (10), 101 (6), 81 (7), 75 (74), 73 (21), 59 (22), 57 (11), 49 (17), 47 (19), 41 (25), 39 (16) (GC/MS for (Z)-isomer); MS (EI) m/z (rel intensity) 238 (0.5), 224 (3), 183 (14), 182 (73), 166 (1), 155 (9), 140 (2), 126 (15), 115 (7), 108 (8), 101 (11), 81 (15), 75 (100), 73 (26), 59 (25), 57 (11), 56 (11), 47 (17), 45 (18), 41 (24), 39 (16) (GC/MS for (E)-isomer); HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ ($\text{C}_{13}\text{H}_{25}\text{NOSiNa}$): 262.1598. found: 262.1610.

Diethyl 2-[3-cyano-2-propenyl]malonate (33):¹⁴ Colorless oil, (E):(Z) = 1:2 (87%). IR (film): ν 2986, 2941, 2223, 1749, 1732, 1467, 1447, 1371, 1339, 1228, 1177, 1097, 1032, 859 cm^{-1} ; (E)-isomer: ^1H NMR (500 MHz, CDCl_3) δ 1.28 (t, 6H, $J = 3.6$ Hz), 2.77–2.81 (m, 2H), 3.46 (t, 1H, $J = 3.6$ Hz), 4.19–4.25 (m, 4H), 5.42–5.44 (m, 1H), 6.66–6.78 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.9, 150.7, 116.8, 102.6, 61.8, 50.2, 32.0, 14.0; (Z)-isomer: ^1H NMR (500 MHz, CDCl_3) δ 1.28 (t, 6H, $J = 3.6$ Hz), 2.97–3.00 (m, 2H), 3.51 (t, 1H, $J = 3.6$ Hz), 4.19–4.25 (m, 4H), 5.42–5.44 (m, 1H), 6.51–6.60 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.8, 149.8, 115.2, 102.1, 61.8, 50.3, 30.4, 14.0; MS (EI) m/z (rel intensity) 225 (7),

197 (12), 180 (38), 179 (27), 169 (12), 152 (24), 151 (68), 134 (20), 124 (21), 123 (82), 107 (55), 106 (63), 93 (24), 80 (100), 79 (80), 78 (25), 69 (18), 55 (24), 53 (48), 52 (52), 39 (25).

Phenyl [(E)-3-phenyl-1-propenyl] sulfone (34):⁹ Colourless oil (84%). IR (film): ν 3057, 2921, 1630, 1496, 1384, 1315, 1127, 976, 792 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.59 (dd, 2H, $J = 6.4, 1.7$ Hz), 6.05 (d, 1H, $J = 9.9$ Hz), 6.16 (dt, 1H, $J = 15.1, 1.7$ Hz), 6.37 (d, 1H, $J = 16.5$ Hz), 6.56 (dd, 1H, $J = 16.5, 9.9$ Hz), 7.11 (dt, 1H, $J = 15.1, 6.4$ Hz), 7.14–7.18, 7.24–7.37 (2m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 37.7, 127.1, 128.7, 128.8, 128.8, 128.9, 129.7, 136.0, 137.4, 147.7; MS (EI) m/z (rel intensity) 208 (11, $[\text{M}]^+$), 163 (3), 142 (5), 128 (2), 117 (100), 103 (2), 91 (34), 89 (7), 77 (6), 65 (13); HRMS (EI) calcd for $[\text{M}]^+$ ($\text{C}_{11}\text{H}_{12}\text{O}_2\text{S}$): 208.0558. found 208.0556.

(E)-6-[1-(*tert*-butyl)-1,1-dimethylsilyloxy-1-hexenyl(diphenyl)phosphine oxide (35):¹⁵ Colourless oil (82%). IR (KBr): ν 3059, 2948, 2959, 1617, 1438, 1252, 1189, 1097, 839, 701, 528 cm^{-1} ; ^{31}P NMR (CDCl_3 , 202 MHz): δ 24.8; ^1H NMR (CDCl_3 , 500 MHz): δ 7.71–7.64 (m, 4H), 7.52–7.40 (m, 6H), 6.71 (ddt, 1H, $J = 19.5, 17.0, 6.5$ Hz), 6.22 (ddt, 1H, $J = 24.5, 17.0, 1.5$ Hz), 3.61–3.57 (m, 2H), 2.34–2.26 (m, 2H), 1.57–1.49 (m, 4H), 0.86 (s, 9H), 0.01 (s, 6H); ^{13}C NMR (CDCl_3 , 126 MHz): δ 152.5 (d, $J = 1.9$ Hz), 133.0 (d, $J = 105.0$ Hz), 131.5 (d, $J = 2.6$ Hz), 131.2 (d, $J = 9.8$ Hz), 128.4 (d, $J = 12.1$ Hz), 122.3 (d, $J = 103.3$), 62.7 (s), 34.1 (d, $J = 16.9$ Hz), 32.28 (s), 25.88 (s), 24.26 (s), 18.25 (s), –5.37 (s); MS (EI) m/z (rel intensity) 414 (1, $[\text{M}]^+$), 399 (3), 357 (100), 202 (10), 135 (5), 115 (3), 81 (4), 75 (8), 59 (4); HRMS (EI) calcd for $[\text{M}]^+$ ($\text{C}_{24}\text{H}_{35}\text{SiO}_2\text{P}$): 414.2144. found 414.2162; Anal. calcd for $\text{C}_{24}\text{H}_{35}\text{SiO}_2\text{P}$: C, 69.53; H, 8.51. found: C, 68.99; H, 8.79.

4-(2-Methyl-4-nitro-1H-indol-3-yl)-2-butenenitrile (36): Orange crystals, (E):(Z) = 1:2.4 (69%). IR (KBr): ν 3313, 3056, 2928, 2218, 1609, 1568, 1512, 1432, 1338, 1304, 1253, 1191, 1116, 993, 787, 724 cm^{-1} ; (Z)-isomer: ^1H NMR (500 MHz, CDCl_3) δ 2.47 (s, 3H), 3.88 (dd, 2H, $J = 6.9, 1.6$ Hz), 5.41 (dt, 1H, $J = 10.9, 1.6$ Hz), 6.61–6.68 (m, 1H), 7.13 (t, 1H, $J = 7.9$ Hz), 7.61 (dd, 1H, $J = 7.9, 1.0$ Hz), 7.77 (dd, 1H, $J = 7.9, 1.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 156.1, 155.2, 153.2, 141.3,

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¹⁴ Randl, S.; Gessler, S.; Wakamatsu, H.; Blechert, S. *Synlett* **2001**, 430–432.

¹⁵ Demchuk, O. M.; Pietrusiewicz, K. M.; Michrowska, A.; Grela, K. *Org. Lett.* **2003**, *5*, 3217–3220.

138.8, 138.0, 119.1, 117.5, 116.9, 104.4, 98.6, 29.4, 11.3; MS (EI) m/z (rel intensity) 241 (58), 225 (12), 224 (78), 207 (11), 194 (31), 193 (100), 192 (19), 181 (12), 180 (13), 179 (73), 169 (23), 168 (21), 167 (12), 152 (12), 127 (7), 115 (4), 77 (3); HRMS (EI) calcd for $[M]^+$ ($C_{13}H_{11}N_3O_2$): 241.0851. found: 241.0854.

8-[1-(*tert*-Butyl)-1,1-dimethylsilyloxy-3-octen-2-one (37):¹⁶ Yellow oil, (*E*):(*Z*) = 99:1 (95%). ¹H NMR (500 MHz, $CDCl_3$) δ 0.04 (s, 6H), 0.88 (s, 9H), 1.50–1.56 (m, 4H), 2.22 (s, 3H), 2.21–2.27 (m, 2H), 3.58–2.63 (m, 2H), 6.07 (dt, 1H, $J = 15.9, 1.4$ Hz), 6.79 (dt, 1H, $J = 15.9, 6.9$ Hz); ¹³C NMR (125 MHz, $CDCl_3$) δ 198.6, 148.2, 131.4, 62.7, 32.2, 32.1, 26.8, 25.9, 24.5, 18.3, –5.3; MS (EI) m/z (rel intensity) 256 (0.1), 241 (2), 200 (15), 199 (96), 157 (10), 156 (20), 155 (100), 131 (7), 115 (5), 101 (5), 75 (36), 73 (5), 59 (3), 43 (6), 39 (2); HRMS (ESI) $[M+Na]^+$ ($C_{14}H_{28}O_2SiNa$): calcd. 279.1751. found: 279.1749.

7-[1-(*tert*-butyl)-1,1-dimethylsilyloxy-2-methyl-2-heptenenitrile (38):¹⁶ Colorless oil, (*E*):(*Z*) = 1:2 (58%). ¹H NMR (500 MHz, $CDCl_3$) δ 0.08 (s, 6H), 0.93 (s, 9H), 1.25–1.46 (m, 2H), 1.48–1.64 (m, 2H), 1.87–2.08 (m, 3H), 2.18–2.42 (m, 2H), 3.60–3.69 (m, 2H), 6.16 (t, 1H, $J = 7.6$ Hz) ppm; ¹³C NMR (125 MHz, $CDCl_3$) δ 148.3, 118.1, 109.3, 62.6, 32.2, 31.3, 25.9, 24.9, 24.7, 21.9, –5.3; (*Z*)-isomer: MS (EI) m/z (rel intensity) 252 (0.5, $[M-H]^+$) 238 (2), 197 (13), 196 (100), 166 (3), 140 (9), 128 (3), 122 (3), 101 (3), 75 (56), 73 (20), 59 (12), 51 (7), 45 (11), 41 (19), 39 (10); (*E*)-isomer: MS (EI) m/z (rel intensity) 253 (1, $[M]^+$), 238 (3), 197 (12), 196 (100), 169 (1), 140 (7), 115 (7), 101 (8), 75 (91), 73 (18), 59 (12), 51 (7), 45 (11), 41 (19), 39 (10); HRMS (ESI) calcd for $[M+Na]^+$ ($C_{14}H_{27}NOSiNa$): 276.1754. found: 276.1773.

(*E*)-6-[1-(*tert*-butyl)-1,1-dimethylsilyloxy-1-hexenyl phenyl sulfone (39):⁹ Colourless oil (90%). IR (film): ν 2952, 2931, 2858, 1321, 1148, 1088, 836, 777, 753, 688, 596, 553 cm^{-1} ; ¹H NMR (200 MHz, $CDCl_3$) δ 0.03 (s, 6H), 0.88 (s, 9H), 1.46–1.60 (m, 4H), 2.20–2.35 (m, 2H), 3.53–3.62 (m, 2H), 6.32 (dt, 1H, $J = 15.1, 1.5$ Hz), 7.00 (dt, 1H, $J = 15.1, 6.8$ Hz), 7.47–7.93 (m, 5H); ¹³C NMR (50 MHz, $CDCl_3$) δ –5.37, 18.26, 24.04, 25.90, 31.22, 32.00, 62.50, 127.50, 127.65, 129.18, 130.43, 133.16, 140.72, 147.00; MS (EI) m/z (rel intensity) 299 (16), 298 (22), 297 (100), 199 (10), 135 (50), 125 (5), 81 (5), 79 (5), 77 (4), 75 (13),

73 (8); HRMS (LSIMS): calcd for $[M+H]^+$ ($C_{18}H_{31}O_3SSi$): 355.1763. found 335.1768.

(*E*)-11-(Phenylsulfonyl)-10-undecen-1-ol (40):⁹ Colourless oil (81%). IR (film): ν 3370, 2928, 2855, 1447, 1318, 1306, 1289, 1147, 1086, 753, 688, 595 cm^{-1} ; ¹H NMR (500 MHz, $CDCl_3$) δ 1.24–1.35, 1.41–1.49, 1.51–1.58 (3m, 15H), 2.23 (m, 2H), 3.62 (t, 2H, $J = 6.6$ Hz), 6.32 (dt, 1H, $J = 15.1, 1.5$ Hz), 6.98 (dt, 1H, $J = 15.1, 6.9$ Hz), 7.51–7.92 (m, 5H); ¹³C NMR (125 MHz, $CDCl_3$) δ 25.6, 27.4, 28.8, 29.0, 29.2, 29.2, 31.3, 32.6, 62.8, 127.4, 129.1, 130.2, 133.1, 140.7, 147.2; MS (ESI) m/z (rel intensity) 333 ($[M+Na]^+$); HRMS (ESI) calcd for $[M+Na]^+$ ($C_{17}H_{26}O_3SNa$): 333.1495. found 333.1515; Anal. Calcd for $C_{17}H_{22}NO_3S$: C, 65.77; H, 8.44; S, 10.33. found: C, 65.35; H, 8.20; S, 10.27.

(*S*_P)-(–)-[(1*E*)-6-bromohex-1-enyl](methyl)phenylphosphine oxide (41):¹⁵ Pale brown oil (86%). $[\alpha]_D^{20}$ –28.9 deg (c 1.32, CH_2Cl_2); IR (film): ν 2936, 1629, 1437, 1294, 1181, 1115, 980, 896, 742, 696, 502 cm^{-1} ; ³¹P NMR (202 MHz, $CDCl_3$): δ 27.4; ¹H NMR (500 MHz, $CDCl_3$): δ 7.81–7.69 (m, 2 H), 7.54–7.44 (m, 3 H), 6.66 (ddt, 1H, $J = 19.4, 17.0, 6.5$ Hz), 6.02 (ddt, 1H, $J = 24.9, 17.0, 1.6$ Hz), 3.39 (t, 2H, $J = 6.7$), 2.31–2.24 (m, 2H), 1.92–1.83 (m, 2H), 1.75 (d, 3H, $J = 13.2$ Hz), 1.65–1.58 (m, 2H); ¹³C NMR (126 MHz, $CDCl_3$): δ 149.8 (d, $J = 1.7$ Hz), 134 (d, $J = 90.6$ Hz), 131.6 (d, $J = 2.7$ Hz), 130.0 (d, 9.7 Hz), 128.6 (d, $J = 11.8$ Hz), 124.0 (d, $J = 99.6$ Hz), 33.3 (d, $J = 16.8$ Hz), 33.2 (s), 32.0 (s), 26.4 (d, $J = 1.1$ Hz), 17.0 (d, $J = 74.5$ Hz); MS (ESI) m/z (rel intensity) 301 (12) $[M+H]^+$; 323 (100) $[M+Na]^+$; HRMS (ESI) calcd for $[M+Na]^+$ ($C_{13}H_{18}BrOPNa$): 323.0171. found 323.0168.

Methyl (*E*)-4-(2-methyl-6-nitro-1*H*-indol-3-yl)-2-butenolate (42): Yellow crystalline solid (91%). IR (KBr): ν 3364, 2953, 2904, 1707, 1655, 1504, 1324, 1215, 750 cm^{-1} ; ¹H NMR (500 MHz, $CDCl_3$): δ 2.42 (s, 3H), 3.61 (dd, 2H, $J = 1.7, 6.0$ Hz), 3.70 (s, 3H), 5.74 (dt, 1H, $J = 1.7, 15.7$ Hz), 7.09 (dt, 1H, $J = 6.0, 15.7$ Hz), 7.42 (d, 1H, $J = 8.8$ Hz), 7.98 (dd, 1H, $J = 2.0, 8.8$ Hz), 8.24 (d, 1H, $J = 2.0$ Hz), 8.51 (br. s, 1H); ¹³C NMR (125 MHz, $CDCl_3$): 12.0, 26.7, 51.5, 107.2, 108.8, 115.4, 117.5, 121.4, 133.2, 133.6, 138.9, 142.6, 146.7, 167.0; MS (EI) m/z (rel intensity) 274 (100, $[M]^+$), 259 (75), 242 (63), 215 (38), 199 (11), 189 (15), 175 (15), 168 (53), 154 (18),

¹⁶ Grela, K.; Harutyunyan, S.; Michrowska, A. *Angew. Chem. Int. Ed.* **2002**, *41*, 4038–4040.

143 (31), 127 (12), 115 (12), 84 (17); HRMS (EI) calcd for $[M]^{+}$ ($C_{14}H_{14}O_4N_2$): 247.0954. found 274.0959; Anal. calcd for $C_{14}H_{14}O_4N_2$: C, 61.31; H, 5.14; N, 10.21. found: C, 61.05; H, 5.22; N, 10.09.

4-(2-methyl-6-nitro-1*H*-indol-3-yl)-2-butenenitrile (43): Yellow crystals, (*E*):(*Z*) = 1:2.4 (76%). IR (KBr): ν 3306, 2229, 1609, 1592, 1556, 1505, 1471, 1391, 1324, 1114, 1067, 940, 871, 792 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 2.49 (s, 3H), 3.62 (dd, 2H, $J = 5.5, 1.6$ Hz), 5.18 (dt, 1H, $J = 16.2, 1.6$ Hz), 6.50–6.58 (m, 1H), 7.15 (t, 1H, $J = 7.9$ Hz), 7.55 (d, 1H, $J = 7.9$ Hz), 7.86 (d, 1H, $J = 7.9$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1, 152.1, 142.7, 139.1, 133.6, 132.9, 117.2, 115.9, 115.6, 107.4, 99.5, 26.7, 12.1; MS (EI) m/z (rel intensity) 241 (100, $[M]^{+}$), 226 (17), 224 (27), 211 (11), 194 (38), 193 (18), 192 (7), 189 (45), 180 (16), 179 (19), 169 (6), 168 (12), 167 (13), 155 (13), 154 (12), 143 (32), 142 (7), 127 (9), 115 (9), 77 (6); HRMS (EI) calcd for $[M]^{+}$ ($C_{13}H_{11}N_3O_2$): 241.0851. found: 241.0853.

(*E*)-3-(2-methyl-6-nitro-1*H*-indol-3-yl)-1-propenyl(diphenyl)phosphine oxide (44):¹⁵ Yellow crystals, mp = 193–194 °C (76%). IR (KBr): ν 3368, 2961, 2854, 1587, 1505, 1468, 1261, 1104, 1065, 820, 732 cm^{-1} ; ^{31}P NMR (202 MHz, $CD_3S(O)CD_3$): δ 21.4 ppm; 1H NMR (500 MHz, $CD_3S(O)CD_3$): δ 11.70 (s, 1H), 8.16 (d, 1H, $J = 2.0$ Hz), 7.80 (dd, 1H, $J = 2.1, 8.8$ Hz), 7.64–7.45 (m, 11H), 6.74–6.51 (m, 2H), 3.77–3.70 (m, 2H), 3.29 (s, 3H); ^{13}C NMR (125 MHz, $CD_3S(O)CD_3$): δ 149.3 (s), 140.9 (d, $J = 18.3$ Hz), 134.0 (d, $J = 112.1$ Hz), 133.5 (s), 132.8 (s), 132.5 (s), 131.5 (s), 130.5 (d, $J = 9.7$ Hz), 128.5 (d, $J = 11.7$ Hz), 122.0 (d, $J = 100.5$ Hz), 117.3 (s), 113.8 (s), 108.1 (s), 107.1 (s), 28.2 (d, $J = 18$ Hz), 11.6 (s); MS (EI) m/z (rel intensity) 416 (14, $[M]^{+}$), 386 (6), 215 (100), 201 (13), 198 (17), 185 (8), 168 (15), 154 (6), 127 (2), 77 (4); HRMS (EI) calcd for $[M]^{+}$ ($C_{24}H_{21}O_3N_2P$): 416.1289. found 416.1281; Anal. calcd for $C_{24}H_{21}O_3N_2P$: C, 69.23; H, 5.08; N, 6.73. found: C, 69.04; H, 5.09; N, 6.76.

(*S_P*, *S_P*)-(–)-(*E*)-ethene-1,2-diylbis[methyl(phenyl)phosphine] dioxide (46):^{15,17} To a mixed solution of **45** (0.5 mmol) in CH_2Cl_2 (4 mL) was added solution **6b**

(0.025 mmol) in CH_2Cl_2 (1 mL). The resulting solution was refluxed for 16 h. Solvent was evaporated and the crude residue was purified using flash chromatography (*n*-hexane-ethyl acetate-methanol 5:2:0.5 then CH_2Cl_2 -methanol 10:1) to afford the title compound as a white crystalline powder, 95% yield. $[\alpha]_D^{20} -255.0$ deg (c 1, CH_2Cl_2); mp = 238–239 °C; IR (KBr): ν 3054, 2989, 2904, 1838, 1590, 1482, 1437, 1301, 1177, 1113, 1025, 894, 882, 754, 740, 692, 484 cm^{-1} ; ^{31}P NMR (200 MHz, $CDCl_3$): δ 26.4; 1H NMR (500 MHz, $CDCl_3$), (*second order spectrum*): δ 7.68–7.62 (m, 4H), 7.53–7.42 (m, 6H), 7.33 (t, 2H, $J_{AX} + J_{BX} = 50$ Hz), 1.83 (filled-in doublet, 6H, *line separation* = 13.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$), (*second order spectrum, only the central of multiplet signals are listed*): δ 141.8 (6 lines), 132.2 (s), 132 (6 lines), 130.0 (3 lines), 128.9 (3 lines), 16.7 (6 lines); MS (ESI) m/z (rel intensity) 305 (25, $[M+H]^+$), 327 (100, $[M+Na]^+$); HRMS (ESI) calcd for $[M+Na]^+$ ($C_{16}H_{18}O_2P_2Na$): 327.0674. found 327.0690.

2,2-Diphenyl-3-vinyl-2,5-dihydrofuran (47):¹⁸

Brown oil (98%). IR (film): ν 3427, 3059, 3026, 2925, 1765, 1682, 1598, 1490, 1447, 1226, 1179, 1064, 758, 700 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 4.11 (q, 1H, $J = 7.1$ Hz), 5.10 (dd, 1H, $J = 11.2, 0.8$ Hz), 5.31 (dd, 1H, $J = 17.7, 0.8$ Hz), 6.16–6.18 (m, 1H), 6.20–6.27 (m, 1H), 7.10–7.40 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 143.6, 143.3, 129.7, 127.9, 127.8, 124.8, 117.5, 94.5, 60.3; MS (EI) m/z (rel intensity) 248 (15, $[M]^{+}$), 229 (8), 215 (9), 205 (18), 204 (12), 203 (19), 191 (13), 189 (10), 183 (15), 182 (22), 172 (11), 171 (77), 165 (17), 157 (18), 143 (15), 141 (10), 129 (10), 128 (22), 115 (23), 105 (100), 97 (14), 95 (9), 91 (34), 83 (11), 77 (43), 71 (16), 69 (15), 57 (20), 55 (14), 51 (14), 43 (41), 41 (12), 39 (9); HRMS (I) calcd for E (I): ; found: calcd for $[M]^{+}$ ($C_{18}H_{16}O$): 248.1201. found: 248.1196.

1-[(4-methylphenyl)sulfonyl]-2,3,6,7-tetrahydro-1*H*-azepine (48):¹⁹ Colorless solid (99%). IR (KBr): ν 3030, 2942, 2899, 2855, 1657, 1596, 1450, 1332, 1286, 1162, 910, 816, 712 cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$) δ 2.28 (m, 4H), 2.39 (s, 3H), 3.25 (m, 4H), 5.72 (m, 2H), 7.25 (d, 2H, $J = 8.2$ Hz), 7.64

¹⁷ K. M. Pietrusiewicz, W. Wiśniewski, M. Zabłocka, *Tetrahedron* **1989**, 45, 337.

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¹⁹ Grela, K.; Kim, M. *Eur. J. Org. Chem.* **2003**, 963–966.

(d, 2H, $J = 8.2$ Hz); ^{13}C NMR (500 MHz, CDCl_3) δ 21.5, 29.948.2, 126.9, 129.5, 130.1, 136.2, 142.9; MS (EI) m/z (rel intensity) 251 (5, $[\text{M}]^+$), 223 (2), 184 (6), 155 (4), 105 (2), 91 (19), 96 (16), 77 (1), 65 (13), 42 (100); HRMS (EI) calcd for $[\text{M}]^+$ ($\text{C}_{13}\text{H}_{17}\text{O}_2\text{NS}$): 251.0980. found 2251.0979.

6-Hexyl-3,6-dimethyl-5,6-dihydro-2H-pyran-2-one (50):²⁰ Colourless oil (99%). IR (film): ν 2932, 2858, 1721, 1454, 1436, 1380, 1360, 1177, 1116, 986 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.43–6.47 (m, 1H), 2.47 (ddd, 1H, $J = 2.1, 14.2, 18.19$ Hz), 2.27 (ddd, 1H, $J = 1.7, 13.24, 19.19$ Hz), 1.91 (d, 3H, $J = 1.8$ Hz), 1.60–1.75 (m, 2H), 1.38 (s, 3H), 1.25–1.32 (m, 8H), 0.88 (t, 3H, $J = 6.8$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 13.9, 16.9, 22.5, 23.7, 25.1, 29.5, 31.6, 34.1, 40.8, 76.7, 77.0, 77.2, 82.3, 127.7, 137.3, 165.3; MS (EI) m/z (rel intensity) 195 (2), 145 (1), 125 (100), 113 (3), 108 (2), 97 (9), 82 (29), 69 (7), 57 (15), 43 (22).

3-Methyl-5-propyl-2(5H)-furanone (51):^{20,21} Colourless oil (76%). IR (film): ν 3080, 2962, 2933, 2876, 1755, 1660, 1455, 1341, 1093, 989 cm^{-1} ; MS (EI) m/z (rel intensity) 140 (14, $[\text{M}]^+$), 127 (3), 111 (29), 98 (35), 97 (50), 83 (4), 69 (49), 55 (57), 53 (5), 43 (43), 41 (100); ^1H NMR (500 MHz, CDCl_3) δ 7.03 (s, 1H), 4.87–4.89 (m, 1H), 1.91 (s, 3H), 1.39–1.72 (m, 4H), 0.96 (t, 3H, $J = 7.3$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 10.6, 13.8, 18.4, 35.5, 76.7, 77.0, 77.2, 80.8, 129.8, 148.7, 147.3; HRMS (ESI) calc for $[\text{M}]^+$ ($\text{C}_8\text{H}_{12}\text{O}_2$): 140.08378. found 140.08373.

11-Methyldodec-10-en-1-ol (52): Colorless oil (99%). IR (film): ν 3338, 2964, 2927, 2855, 1452, 1377, 1262, 1057, 801, 701 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.25–1.38 (m, 14H), 1.46 (s, 1H), 1.59 (s, 3H), 1.69 (s, 3H), 1.92–1.99 (m, 2H), 3.63 (t, 6.6, $J = 2\text{H}$ Hz), 5.09–5.14 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 131.1, 124.9, 63.0, 32.8, 29.9, 29.8, 29.6, 29.5, 29.4, 29.3, 28.0, 25.7, 17.6; MS (EI) m/z (rel intensity) 198 (10, $[\text{M}]^+$), 180 (7), 124 (10), 123 (7), 109 (14), 96 (26), 95 (38), 83 (14), 82 (51), 81 (30), 70 (14), 69 (100), 68 (22), 67 (27), 57 (12), 56 (27), 55 (29), 41 (31), 39 (4); HRMS (EI) calcd for $[\text{M}]^+$ ($\text{C}_{13}\text{H}_{26}\text{O}$): 198.1984. found: 198.1986; Anal. calcd for $\text{C}_{13}\text{H}_{26}\text{O}$: C 78.72, H 13.21. found: C 78.76, H 13.34.

1-(6-Methylhept-5-enyl)cyclohexanol

(53): Colorless oil (99%): IR (film): ν 3392, 2932, 2857, 1449, 1378, 1262, 1169, 966, 835 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.23–1.58 (m, 17H), 1.60 (s, 3H), 1.68 (s, 3H), 1.99 (q, 2H, $J = 6.5$ Hz), 5.09–5.14 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 131.2, 124.7, 71.4, 42.4, 37.4, 30.5, 28.0, 25.8, 25.7, 22.5, 22.2, 17.6; MS (EI) m/z (rel intensity) 192 (26, $[\text{M}-18]^+$), 149 (32), 136 (30), 135 (20), 122 (16), 121 (18), 111 (10), 110 (15), 109 (40), 108 (19), 107 (19), 99 (68), 97 (13), 96 (48), 95 (38), 93 (17), 82 (91), 81 (100), 79 (21), 69 (40), 67 (40), 56 (7), 55 (41), 53 (7), 43 (8), 41 (25); HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ ($\text{C}_{14}\text{H}_{26}\text{ONa}$): 233.1876. found: 233.1887.

7-[1-(tert-Butyl)-1,1-dimethylsilyloxy-2-heptenyl acetate (54): Colorless oil, (E):(Z) = 7.9:1 (67%). IR (film): ν 3474, 2931, 2858, 2256, 1743, 1673, 1520, 1472, 1463, 1384, 1362, 1255, 1102, 1025, 970, 911, 836, 776, 734 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 0.05 (s, 6H), 0.89 (s, 9H), 1.35–1.47 (m, 2H), 1.49–1.54 (m, 2H), 2.06 (s, 3H), 2.07–2.10 (m, 2H), 3.60 (t, 2H, $J = 6.4$ Hz), 4.51 (d, 2H, $J = 6.5$ Hz), 5.52–5.60 (m, 1H), 5.73–5.80 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.8, 136.3, 123.9, 65.2, 62.9, 32.2, 31.9, 25.9, 25.1, 21.0, 18.3, –5.3; MS (EI) m/z (rel intensity) 229 (1, $[\text{M}-57]^+$), 207 (1), 170 (2), 169 (15), 159 (7), 141 (6), 118 (10), 117 (100), 101 (4), 95 (59), 93 (4), 89 (3), 75 (18), 67 (9), 43 (6), 41 (2); HRMS (ESI) calcd for $[\text{M}+\text{Na}]^+$ ($\text{C}_{15}\text{H}_{30}\text{O}_3\text{SiNa}$): 309.1856. found: 309.1859

Isopropyl 8-(acetyloxy)-6-methyl-6-oxoenoate (55): Colorless oil (E):(Z) = 2.3:1 (37%). IR (film): ν 3454, 2981, 2939, 2870, 1732, 1454, 1375, 1235, 1181, 1146, 1109, 1026, 959, 824 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.23 (d, 6H, $J = 6.2$ Hz), 1.37–1.51 (m, 2H), 1.57–1.65 (m, 2H), 1.69 (d, 3H, isomer (E), $J = 0.3$ Hz), 1.74 (d, 3H, isomer (Z), $J = 0.9$ Hz), 2.04 (s, 3H, isomer (E)), 2.10 (s, 3H, isomer (Z)), 2.27 (t, 2H, $J = 7.4$ Hz), 4.55 (d, 2H, isomer (Z), $J = 7.3$ Hz), 4.58 (d, 2H, isomer (E), $J = 7.1$ Hz), 5.01 (hept, 1H, $J = 6.2$ Hz), 5.30–5.37 (m, 1H), ^{13}C NMR (125 MHz, CDCl_3) δ 173.1, 171.1, 141.9, 118.5, 67.4, 61.3, 39.1, 34.5, 26.9, 24.6, 21.8, 21.0, 16.2; MS (EI) m/z (rel intensity) 213 (1, $[\text{M}-43]^+$), 197 (7), 196 (37), 179 (4), 171 (4), 155 (19), 154 (100), 153 (40), 139 (4), 137 (48), 136 (10), 135 (22), 127 (7), 125 (10), 111 (8), 110 (11),

²⁰ Grela, K.; Trynowski, M.; Bieniek, M. *Tetrahedron Lett.* **2002**, *43*, 9055–9059.

²¹ Ma, S.; Yu, Z.; Wu, S. *Tetrahedron* **2001**, *57*, 1585–1588.

109 (33), 108 (13), 97 (10), 95 (39), 94 (80), 93 (41), 81 (28), 79 (31), 71 (9.5), 68 (18), 67 (18), 55 (13), 43 (43), 41 (13), 39 (4); HRMS (ESI) calcd for $[M+Na]^+$ ($C_{14}H_{24}O_4Na$): 279.1567. found: 279.1580.

2-[1-[(4-Methylphenyl)sulfonyl]tetrahydro-4(1*H*)-pyridinylidene]ethyl acetate (56): Colorless oil (47%). IR (film): ν 2910, 2846, 1737, 1598, 1466, 1338, 1234, 1166, 1096, 1025, 931, 817, 728 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 2.01 (s, 3H), 2.28–2.33 (m, 3H), 2.38–2.43 (m, 4H), 3.02–3.09 (m, 4H), 4.51 (d, 2H, $J = 7.2$ Hz), 5.35 (t, 1H, $J = 7.2$ Hz), 7.29–7.33 (m, 2H), 7.62–7.65 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 143.5, 139.8, 133.4, 129.6, 127.6, 118.7, 59.9, 47.4, 46.9, 35.0, 27.9, 21.4, 20.9; MS (EI) m/z (rel intensity) 323 (0.2), 279 (0.5), 263 (13), 184 (6), 168 (6), 155 (18), 109 (11), 108 (100), 107 (12), 91 (49), 81 (41), 79 (9), 77 (7), 65 (13), 43 (26), 42 (25), 41 (11), 39 (8); HRMS (ESI) calcd for $[M+Na]^+$ ($C_{16}H_{21}NO_4SNa$): 346.1084. found: 346.1097; Anal. calcd for $C_{16}H_{21}NO_4S$: C 59.42, H 6.54, N 4.33, S 9.91. found: C 59.40, H 6.57, N 4.17, S 9.98.

1-[(4-Methylphenyl)sulfonyl]-4-[2-(1,1,1-trimethylsilyl)ethylidene]piperidine (57):²² Colorless oil (5%). IR (film): ν 3087, 2957, 2852, 1727, 1673, 1627, 1598, 1582, 1516, 1484, 1340, 1271, 1258, 1165, 1105, 1040, 995, 950, 847, 799, 728 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 0.10 (2, 9H), 1.45 (d, 2H, $J = 6.0$ Hz), 1.56 (s, 3H), 2.30–2.43 (m, 4H), 3.05–3.12 (m, 4H), 5.18–5.26 (m, 1H), 7.31–7.37 (m, 2H), 7.64–7.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 143.4, 130.2, 129.6, 127.6, 112.2, 47.8, 47.5, 38.6, 32.9, 21.9, 0.2; MS (EI) m/z (rel intensity) 337 (17, $[M]^+$), 323 (16), 308 (15), 257 (17), 256 (100), 228 (9), 180 (28), 168 (14), 155 (8), 149 (21), 109 (5), 91 (13), 73 (39), 59 (5), 45 (2). HRMS (EI) calcd for $[M]^+$ ($C_{17}H_{27}NO_2Si$): 337.1532. found: 337.1536.

3,4-dimethyl-1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole (59):²³ MS (EI) m/z (rel intensity) 251 (3), 250 (4), 236 (18), 186 (1), 170 (1), 155 (23), 139 (3), 96 (100), 94 (22), 91 (69), 81 (14), 80 (15), 67 (9), 65 (32), 63 (7), 55 (9), 53 (10), 41 (40), 39 (29).

4-Methyl-2,2-diphenyl-3-vinyl-2,5-

-dihydrofuran (62):¹⁸ MS (EI) m/z (rel intensity) 262 (6), 247 (4), 229 (9), 215 (6), 205 (14), 202 (7), 186 (12), 185 (100), 171 (11), 165 (11), 157 (6), 141 (10), 129 (18), 115 (21), 105 (55), 91 (38), 79 (29), 77 (68), 65 (6), 51 (34), 43 (39), 41 (5), 39 (21).

1,3,4-trimethyl-cyclohex-3-en-1-ol (63):²⁴ MS (EI) m/z (rel intensity) 140 (2), 125 (10), 122 (31), 106 (5), 107 (66), 105 (6), 97 (10), 91 (17), 83 (19), 82 (39), 79 (15), 69 (6), 67 (98), 65 (8), 58 (29), 55 (40), 53 (18), 51 (10), 43 (100), 41 (43), 39 (40), 38 (3).

2-Phenyl-3,6-dihydro-2*H*-pyran (64):²⁵ Colourless oil (90%). IR (thin film): ν 3339, 3034, 2926, 2895, 2830, 1723, 1452, 1388, 1179, 1090, 762, 699, 657 cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$) δ 7.45–7.25 (m, 5H), 6.00–5.88 (m, 1H), 5.87–5.77 (m, 1H), 4.57 (dd, 1H, $J = 12.2, 4$ Hz), 4.43–4.33 (m, 2H), 2.41–2.18 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.5, 128.3, 127.4, 126.4, 125.8, 124.4, 75.6, 66.5, 32.8; HRMS (EI) calcd for $[M]^+$ ($C_{11}H_{12}O$): 160.0888. found 160.0893.

1-[(4-Methylphenyl)sulphonyl]-3-(2-methyl-1-propenyl)-2,5-dihydro-1*H*-pyrrole (65):¹⁸ White solid (99%). 1H NMR (200 MHz, $CDCl_3$) δ 7.71 (d, 2H, $J = 8.2$ Hz), 7.31 (d, 2H, $J = 7.9$ Hz), 5.60 (bs, 1H), 5.37 (bs, 1H), 4.22 (d, 2H, $J = 3.3$ Hz), 4.12 (bs, 2H), 2.41 (s, 3H), 1.74 (d, 6H, $J = 6.4$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.3, 137.8, 136.2, 129.7, 127.4, 120.8, 117.9, 56.3, 54.5, 27.3, 21.6, 19.9; HRMS (EI) calcd for $[M]^+$ ($C_{15}H_{19}O_2NS$): 277.1136. found: 277.1132.

2,5,2',5'-tetrahydro-[3,3']bifuranyl (67): White solid (55%). 1H NMR (500 MHz, $CDCl_3$) δ 5.67 (bs, 2H), 4.80–4.73 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.8, 122.9, 76.3, 75.1; HRMS (EI) calcd for $[M]^+$ ($C_8H_{10}O_2$): 138.0681. found: 138.0683.

4-[(Allyloxy)methyl]-3-methylene-3,6-dihydro-2*H*-pyran (68): Yellow oil (24%). 1H NMR (200 MHz, $CDCl_3$) δ 6.05–5.85 (m, 2H), 5.36 (q, 1H, $J = 1.7$ Hz), 5.28–5.22 (m, 1H), 5.20 (q, 1H, $J = 1.3$ Hz), 5.08 (s, 1H), 4.88 (s, 1H), 4.34–4.28 (m, 2H), 4.26 (t, 2H, $J = 1.2$ Hz), 4.18 (q, 2H, $J = 1.6$ Hz), 4.03 (dt, 2H, $J = 5.7, 1.4$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$)

²² Ciufolini, M. A.; Rivera-Fortin, M. A.; Byrne, N. E. *Tetrahedron Lett.* **1993**, 34, 3505–3508.

²³ Krafft, M. E.; Bonaga, L. V. R.; Wright, J. A.; Hirosawa, C. *J. Org. Chem.* **2002**, 67, 1233–1246.

²⁴ Singleton, D. A.; Leung, S.-W. *J. Organomet. Chem.* **1997**, 544, 157–162.

²⁵ Larock, R. C.; Gong, W. H.; Baker, B. E. *Tetrahedron Lett.* **1989**, 30, 2603–2606.

δ 138.0, 134.7, 131.5, 126.9, 117.2, 107.7, 71.3, 69.6, 69.4, 66.0; IR (thin film): ν 3345, 3084, 2855, 1727, 1647, 1614, 1451, 1342, 1270, 1126, 1081, 931 cm^{-1} ; HRMS (LSIMS) calcd for $[\text{M}+\text{Na}]^+$ ($\text{C}_{10}\text{H}_{14}\text{O}_2\text{Na}$): 189.0886. found: 189.0900.

4. Procedures for recycling of the catalyst

RCM formation of 47: In a Schlenk flask the catalyst **6b** (0.025 g, 0.037 mmol) was placed. The flask was filled with argon and methylene chloride (65 mL) was added. The solution was cooled to 0 °C and then a solution of the substrate (0.374 g, 1.5 mmol) in methylene chloride (10 mL) was added. The resulting solution was stirred at 0 °C for 55 minutes. The solvent was evaporated and the residue was dissolved in minimal amount of methylene chloride. The catalyst was precipitated with *n*-pentane. The crude **6b** was purified by column chromatography (0–20% ethyl acetate/cyclohexane). The catalyst (0.018 g, 72%) was obtained as a green solid. The product **47** was formed in quantitative yield (purity \geq 98% by GC).

RCM formation of 49: In a Schlenk flask the catalyst **6b** (0.025 g, 0.037 mmol) was placed. The flask was filled with argon and methylene chloride (65 mL) was added. Then a solution of the substrate (0.362 g, 1.5 mmol) in methylene chloride (10 mL) was added and the resulting solution was stirred at room temperature for 45 minutes. The solvent was evaporated and the residue was dissolved in minimal amount of methylene chloride. The catalyst was precipitated with *n*-pentane. The crude **6b** was purified by column chromatography (0–20% ethyl acetate/cyclohexane). The catalyst (0.010 g, 40%) was obtained as a green solid. The product **49** was formed in quantitative yield (purity \geq 98% by GC).

RCM formation of 28a: In a Schlenk flask the catalyst **6b** (0.025 g, 0.037 mmol) was placed. The flask was filled with argon and methylene chloride (65 mL) was added.

Then a solution of **27a** (0.208 g, 1.5 mmol) in methylene chloride (10 mL) was added under an argon atmosphere and the resulting solution was stirred at room temperatures for 1 h. The solvent was evaporated and the residue was subject to column chromatography (50% ethyl acetate/cyclohexane). The crude catalyst was dissolved in minimal amount of methylene chloride and it was precipitated with *n*-pentane. The catalyst 0.013 g, (52%) was obtained as a green solid. The product **28a** was formed in quantitative yield (purity \geq 98% by GC).

5. *Ab initio* studies

All the calculations were performed using Gaussian 98 (Gaussian 98, Revision A.11.4, Gaussian, Inc., Pittsburgh PA, 2002)²⁶ on a IRIX64/Linux workstation. The structures of 2-isopropoxy styrenes were optimized using B3LYP with 6-31G** basis set. Only real values of the analytical harmonic vibrational frequencies confirmed that geometries under study correspond to the minimum-energy structures.

5.1. Electron density distribution surface maps

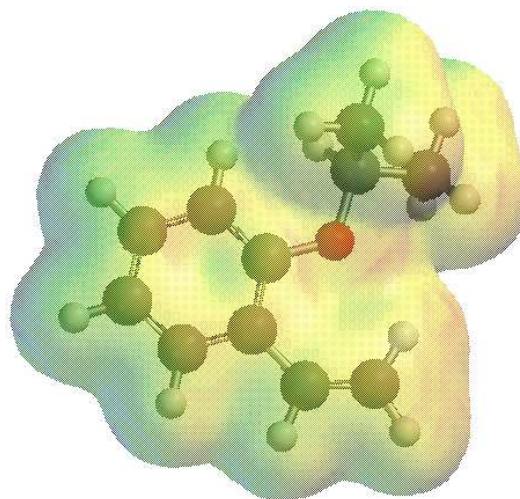


Figure 1a. 2-Isopropoxystyrene **72**

²⁶ M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc.

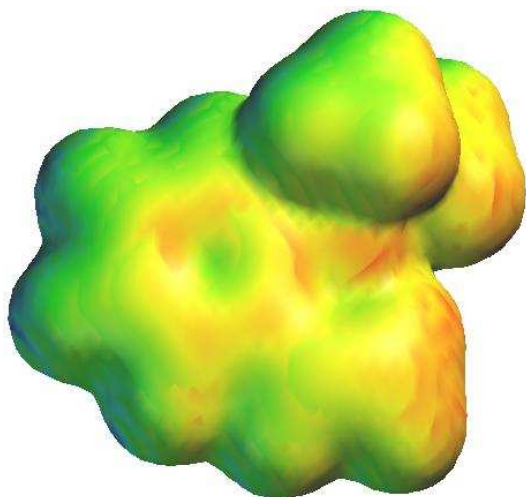


Figure 1b. 2-Isopropoxystyrene 72

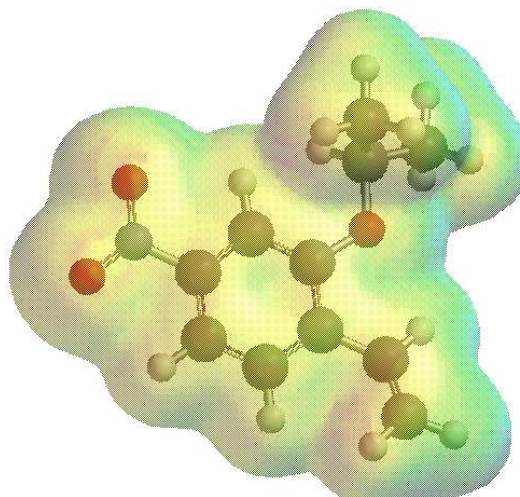


Figure 3a. 2-Isopropoxy-4-nitrostyrene 15

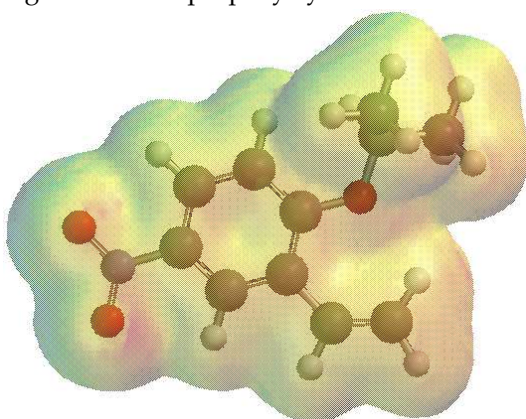


Figure 2a. 2-Isopropoxy-5-nitrostyrene 14

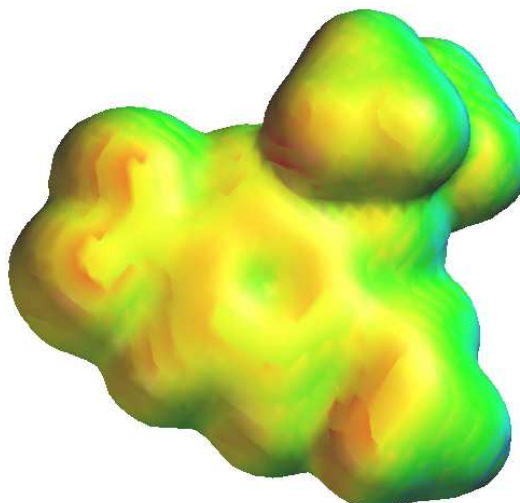


Figure 3b. 2-Isopropoxy-4-nitrostyrene 15

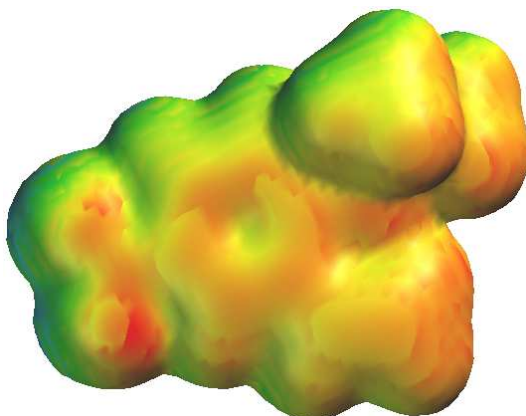


Figure 2b. 2-Isopropoxy-5-nitrostyrene 14

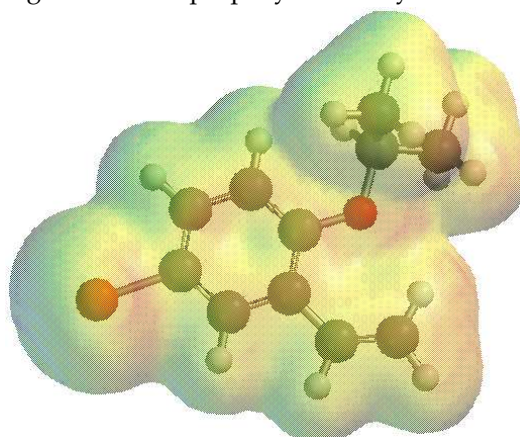


Figure 4a. 2-Isopropoxy-5-bromostyrene

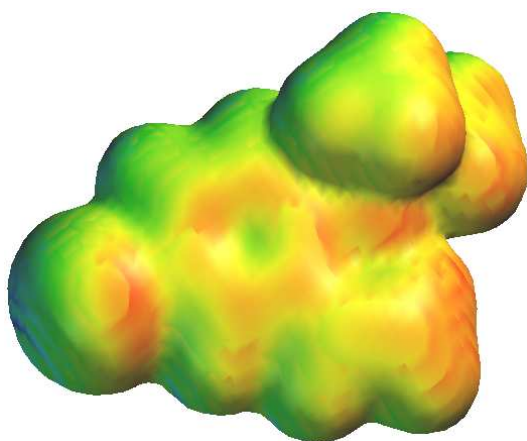


Figure 4b. 2-Isopropoxy-5-bromostyrene

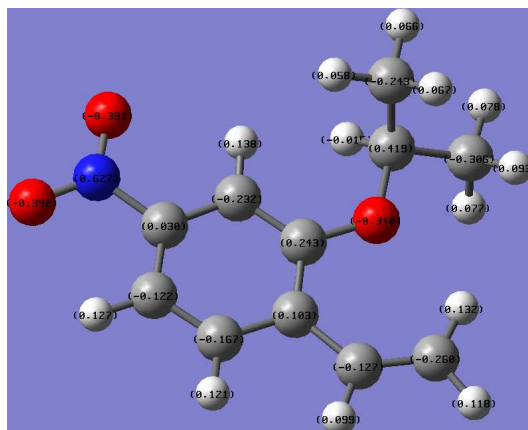


Figure 3. 2-Isopropoxy-4-nitrostyrene 15

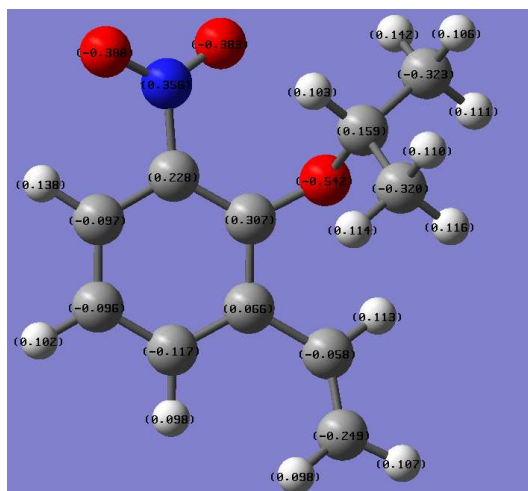


Figure 7. 2-Isopropoxy-3-nitrostyrene

5.2. ESP charges

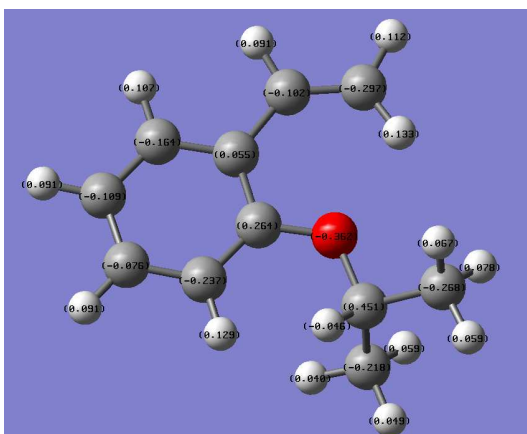


Figure 5. 2-Isopropoxystyrene 72

5.3. Mulliken charges

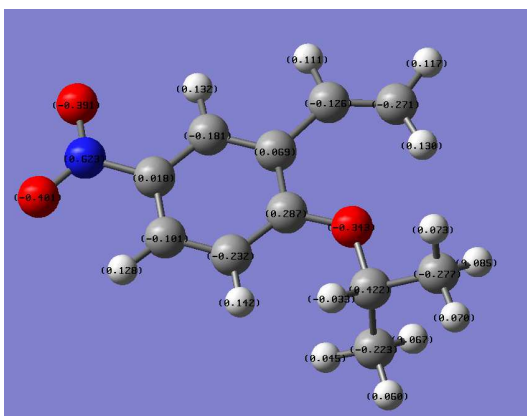


Figure 6. 2-Isopropoxy-5-nitrostyrene 14

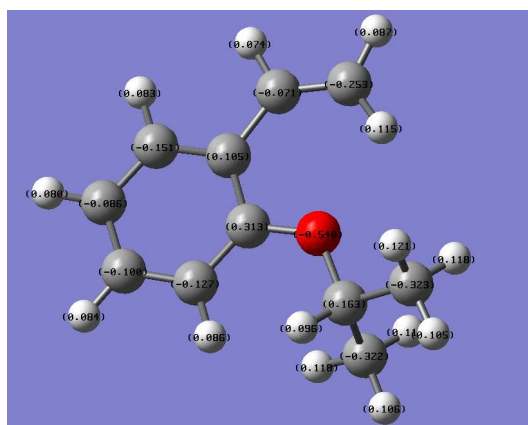
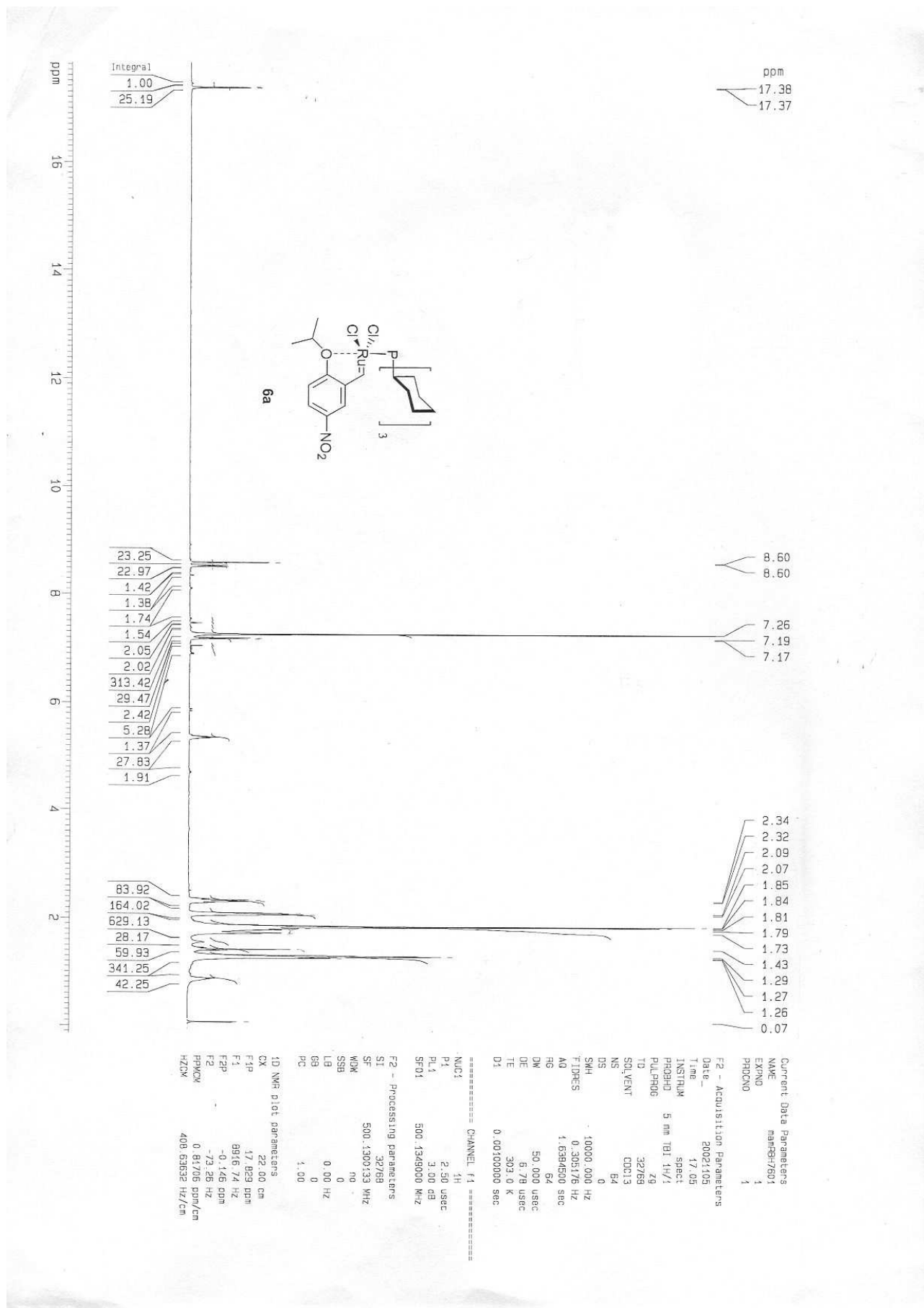
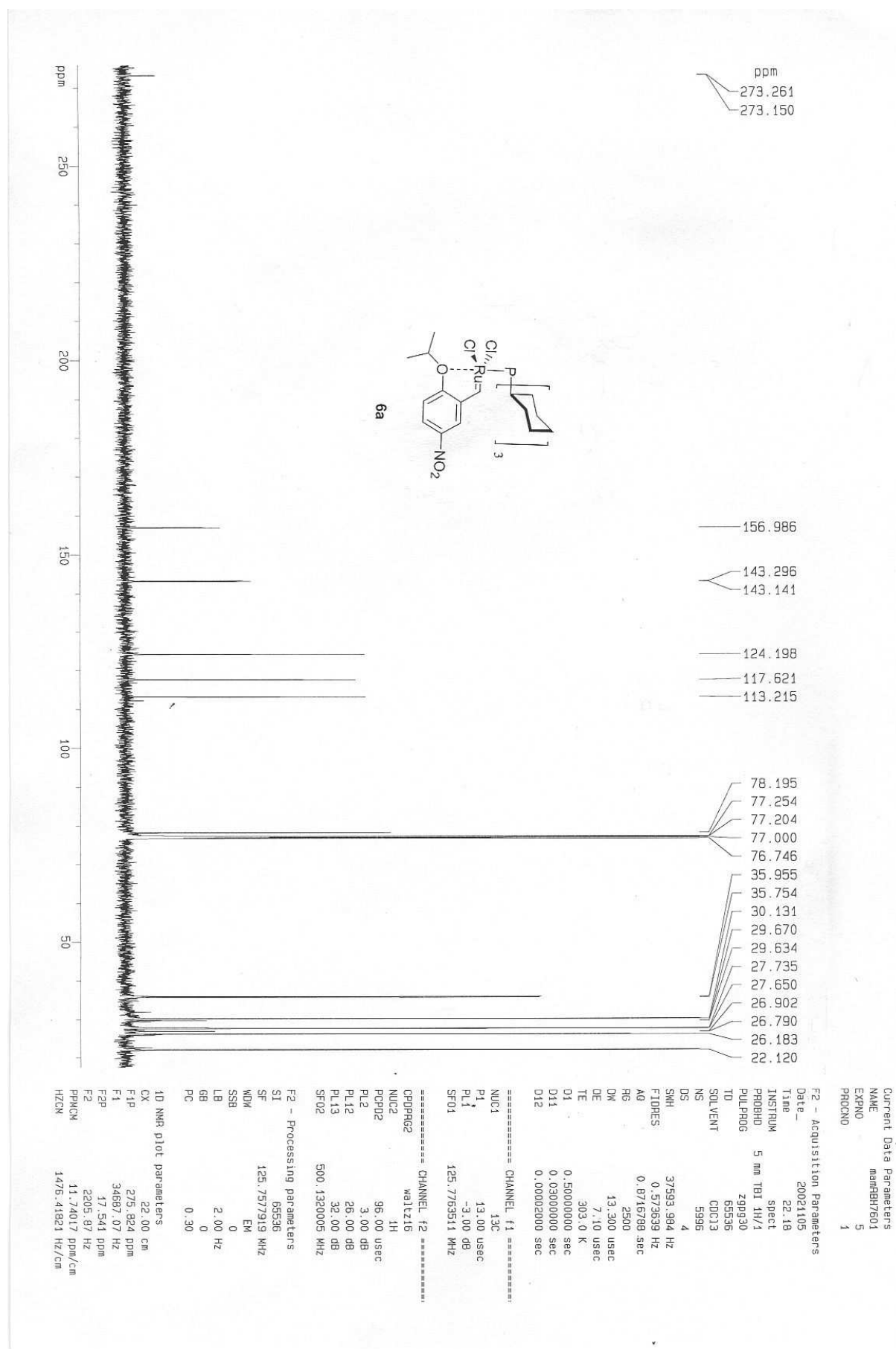
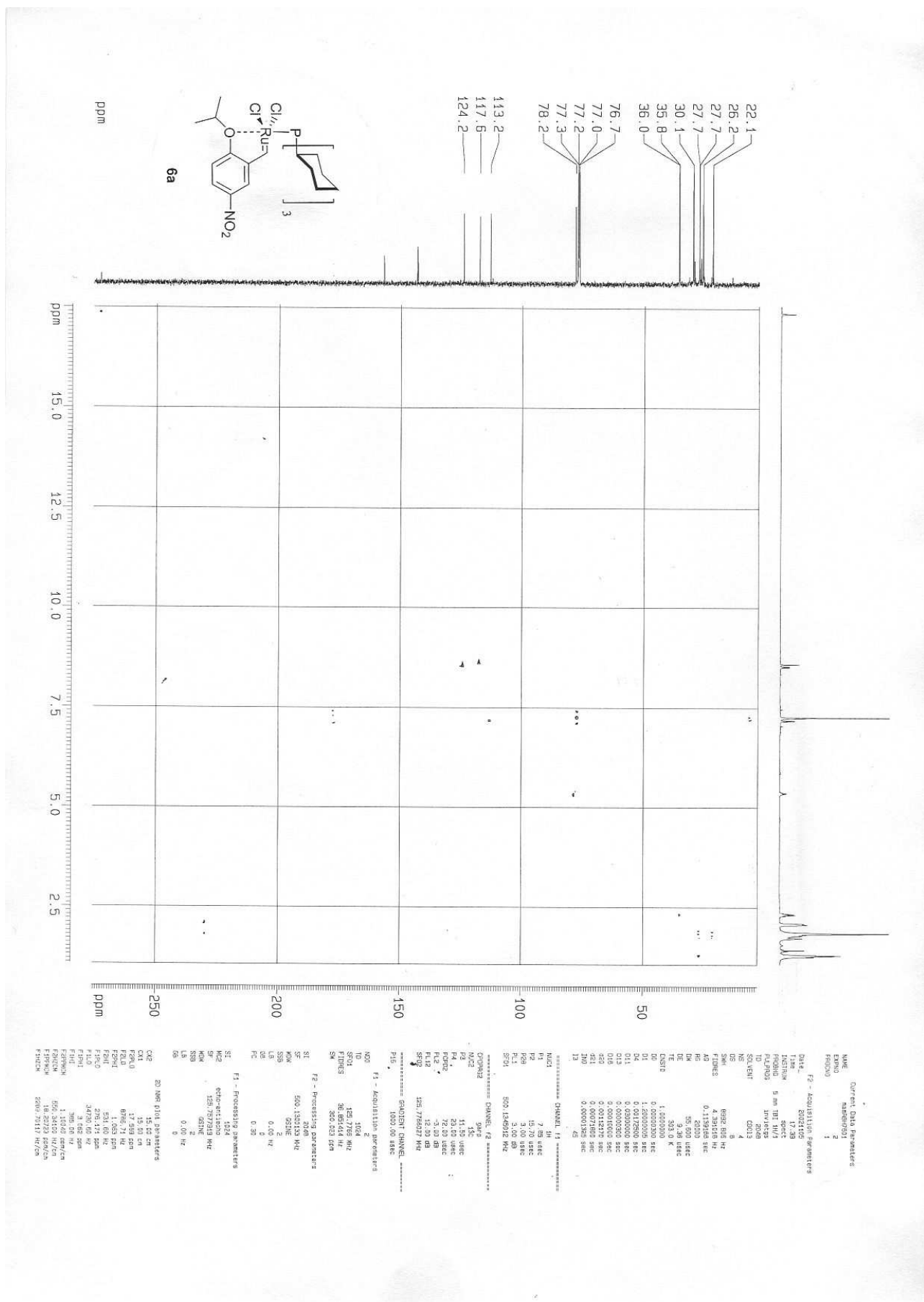


Figure 8. 2-Isopropoxystyrene 72

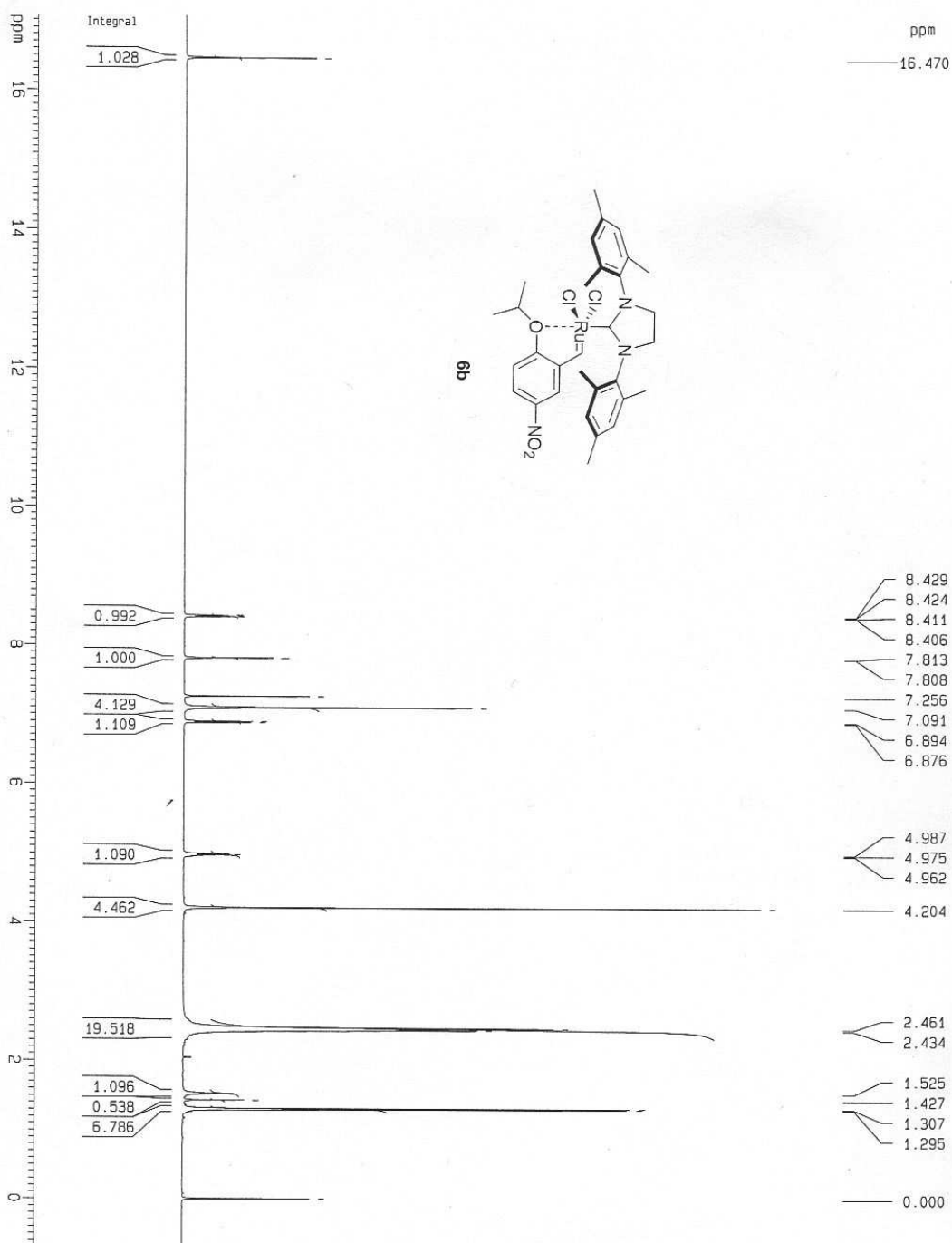
7. Compound 6a







8. Compound 6b



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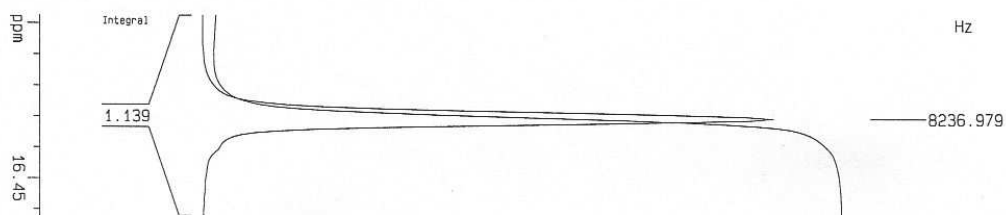
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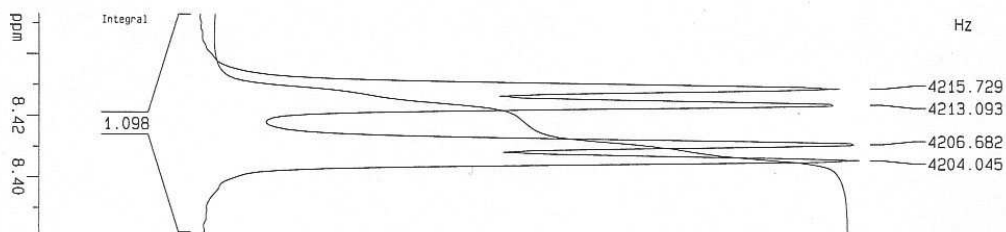
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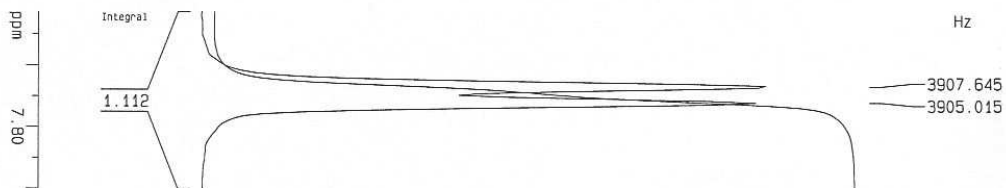
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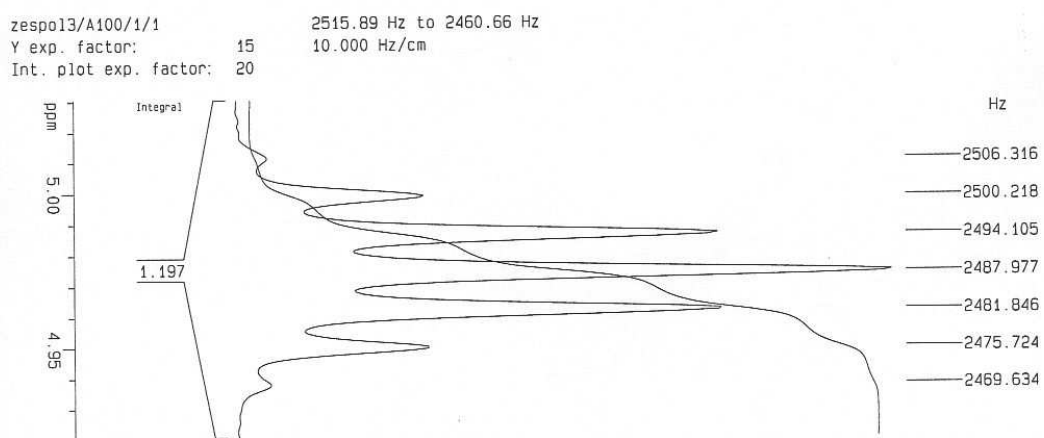
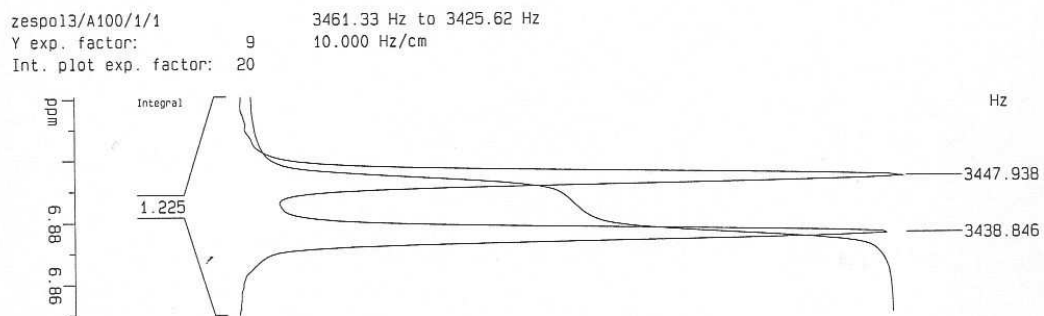
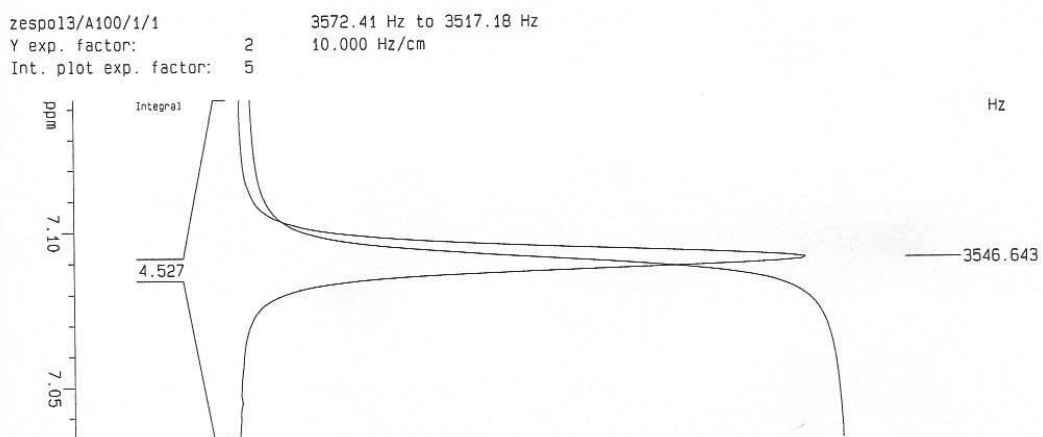


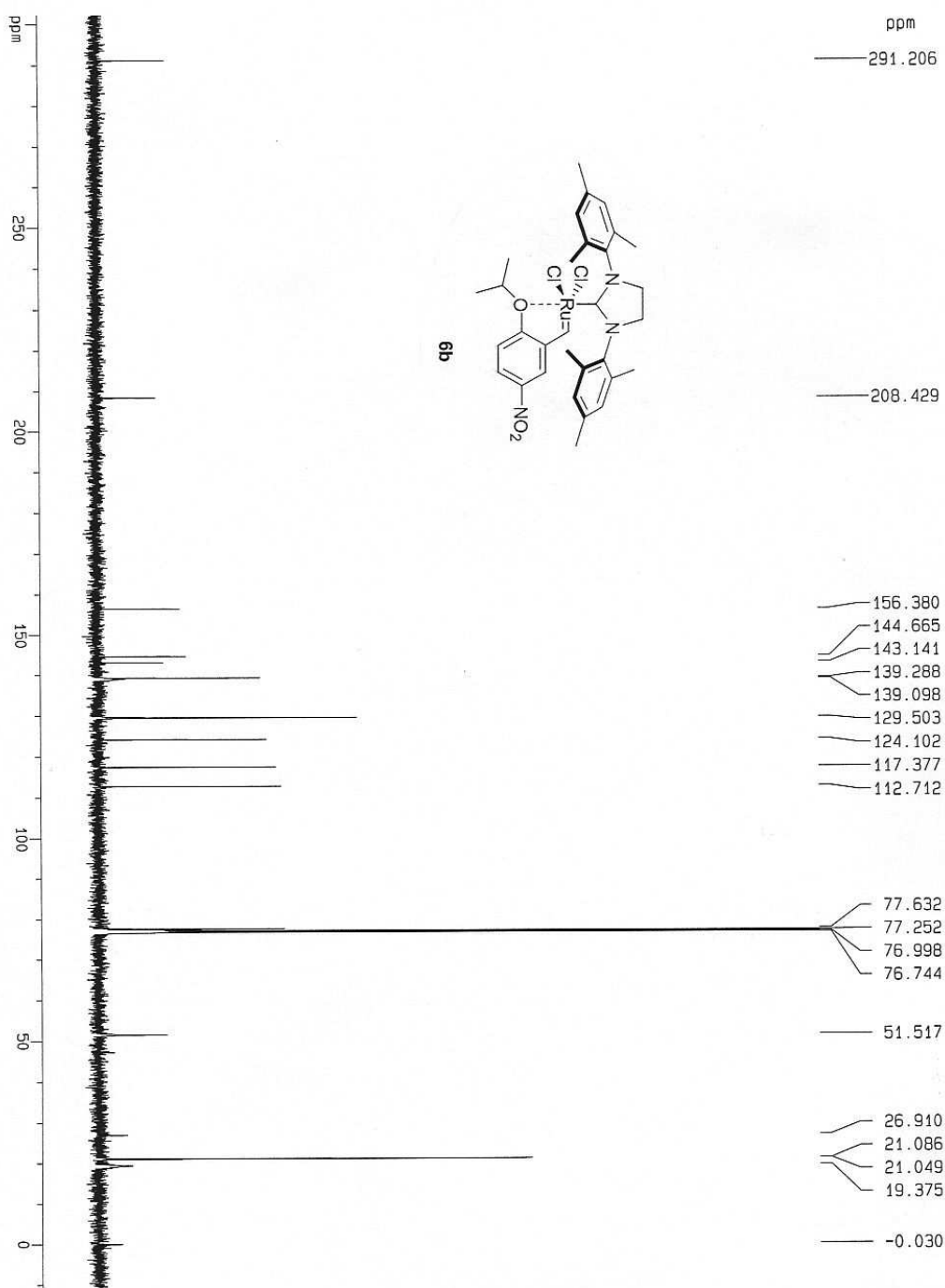
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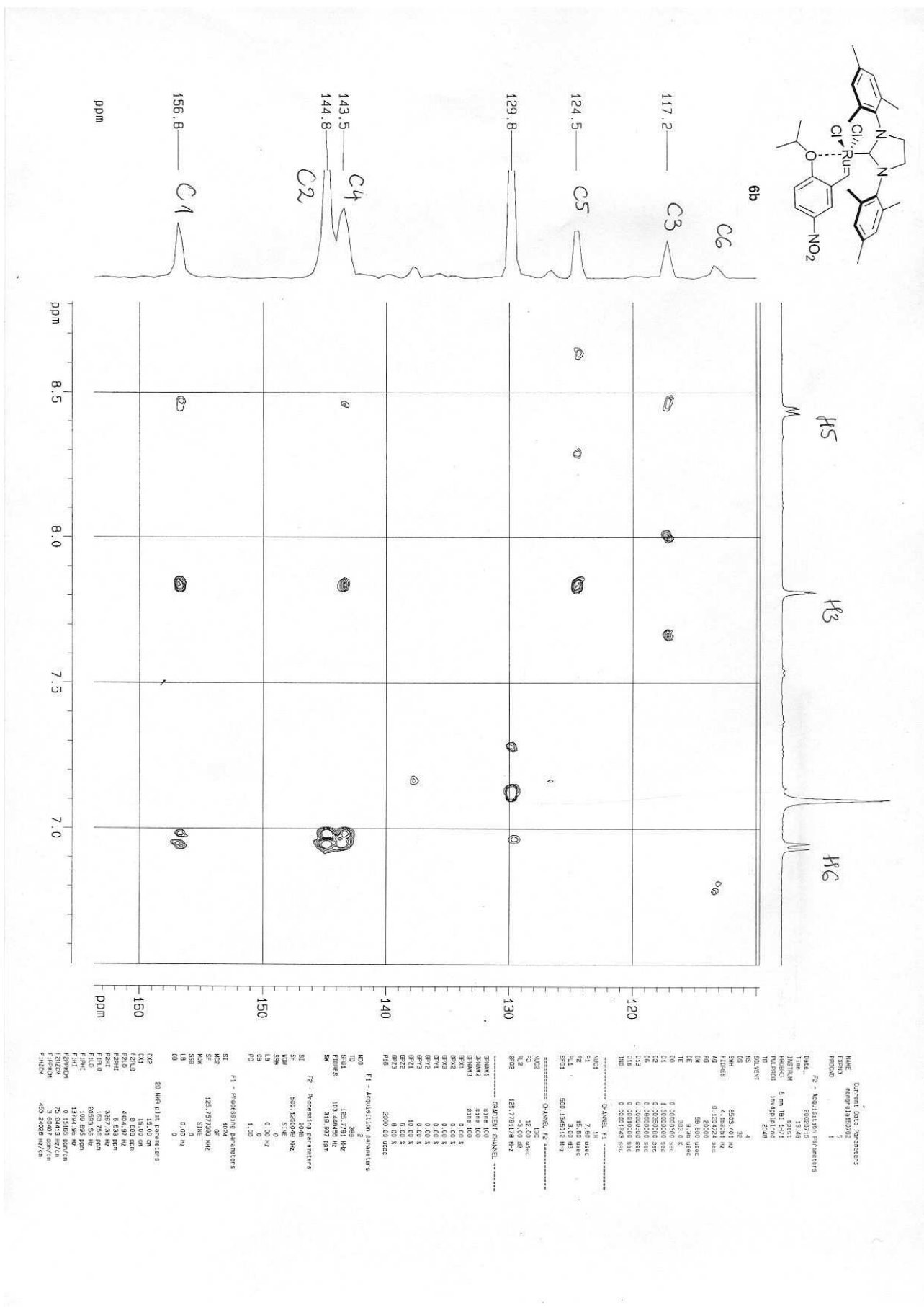
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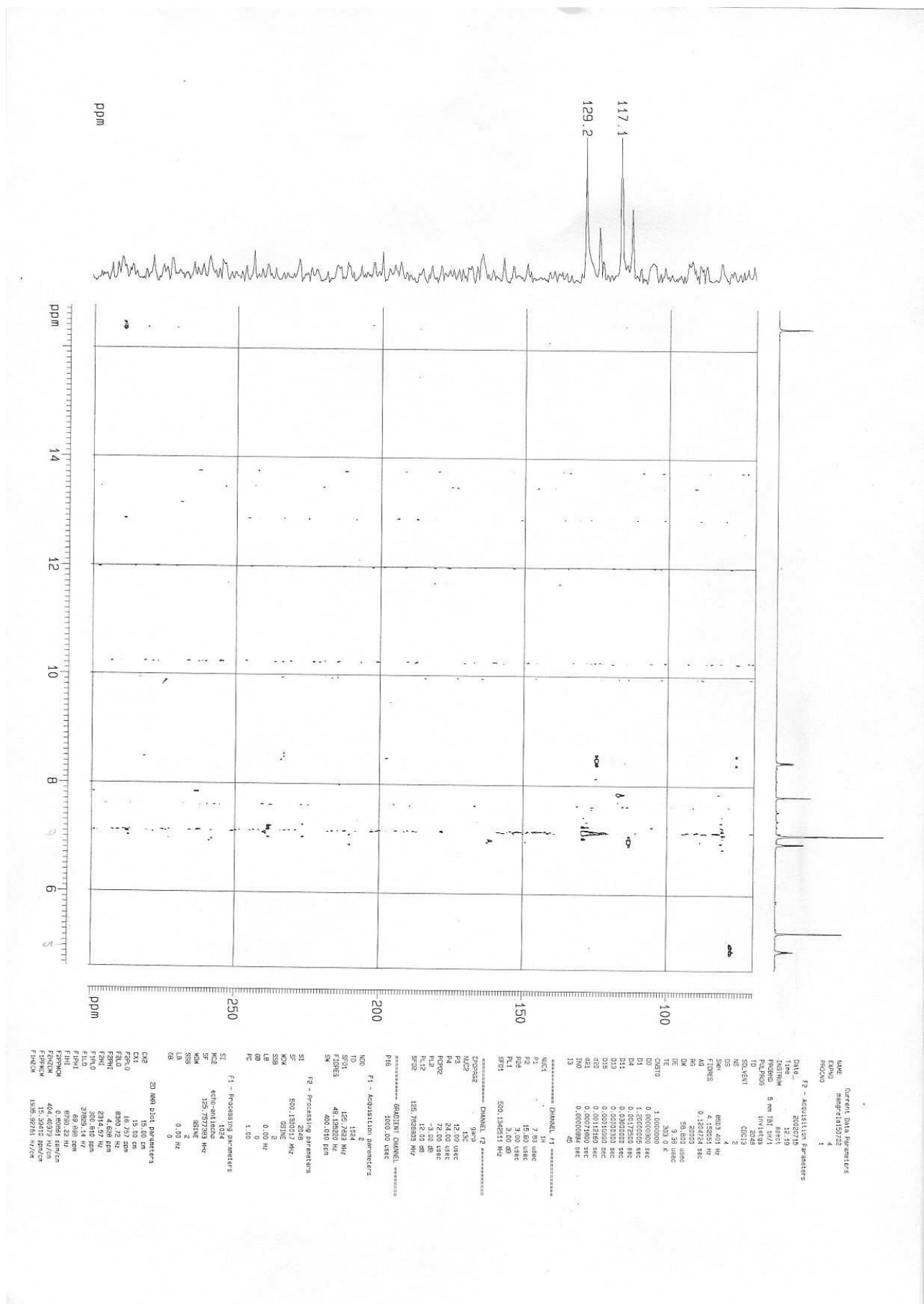
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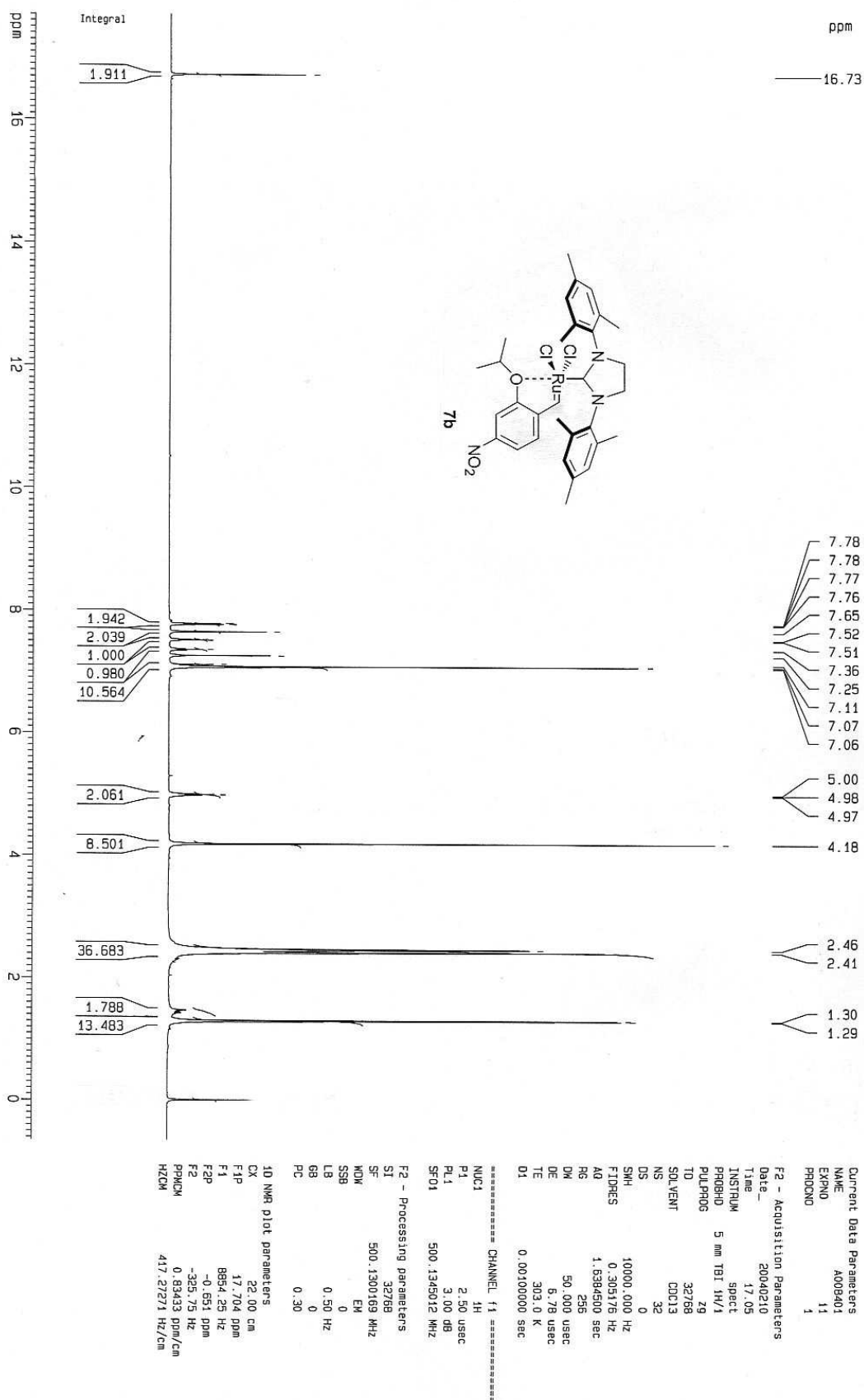
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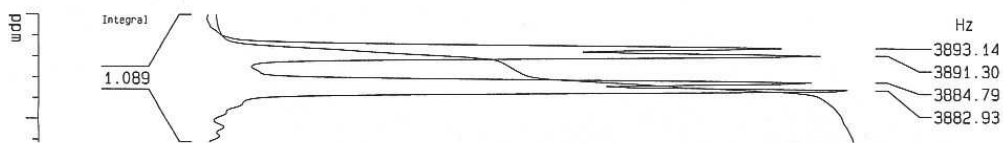




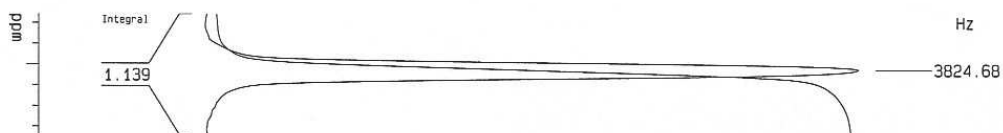
9. Compound 7b



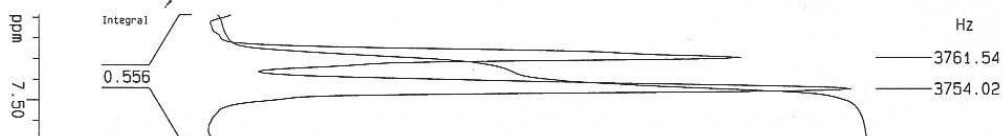
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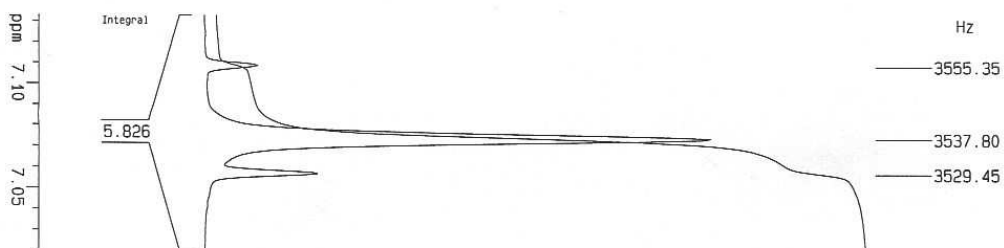
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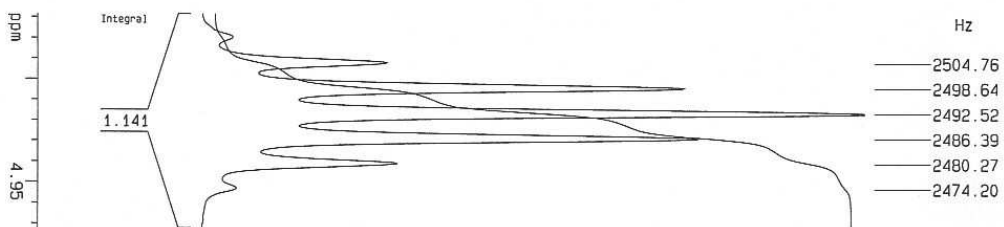
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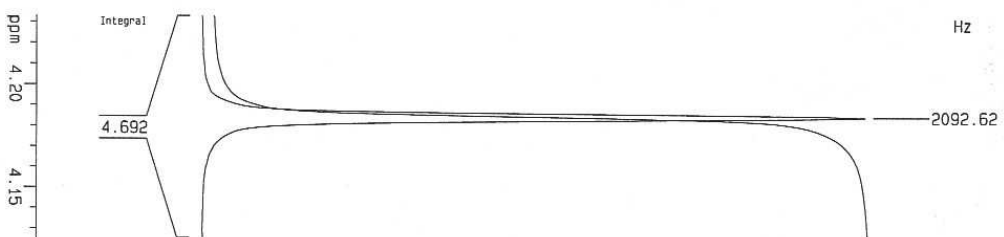
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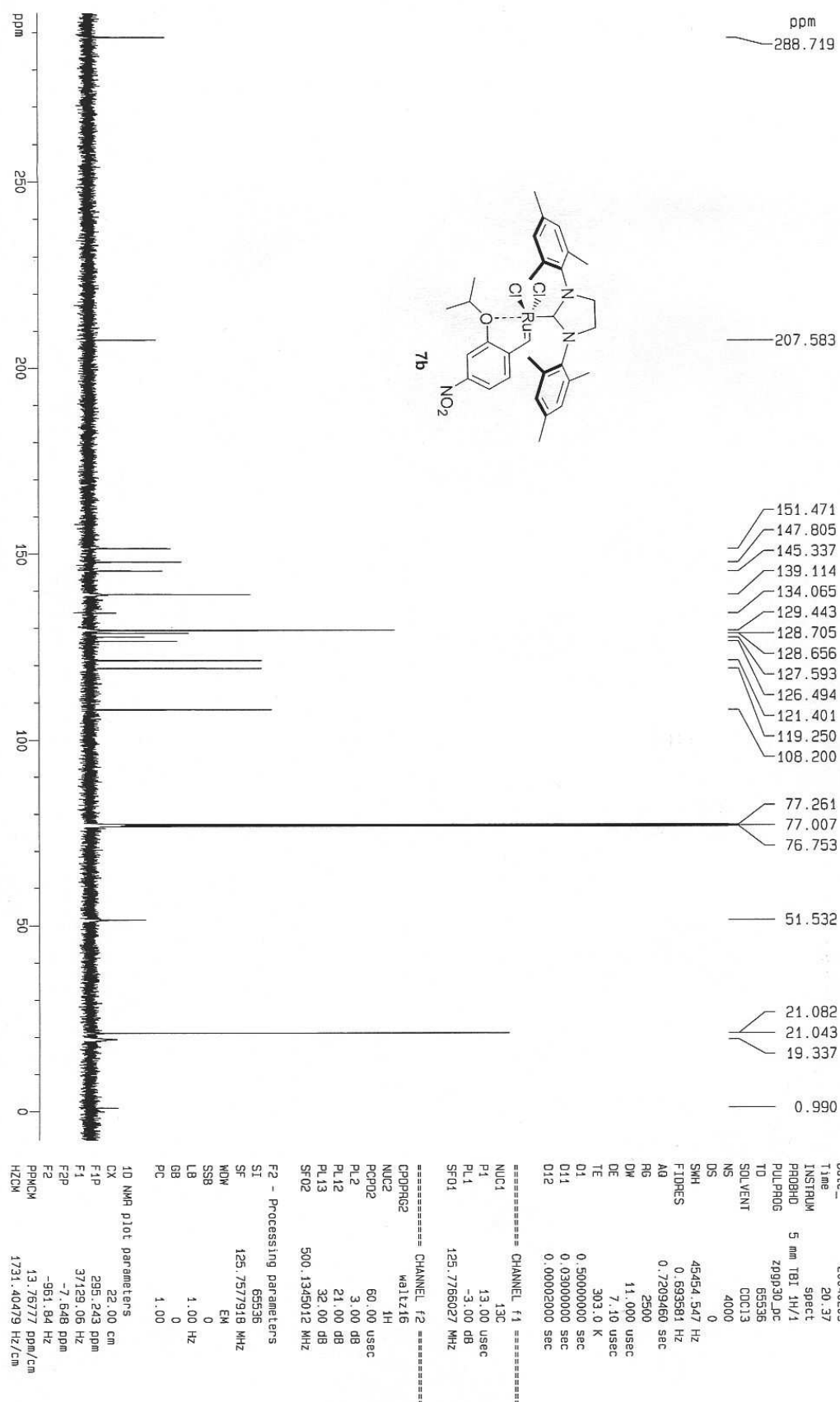


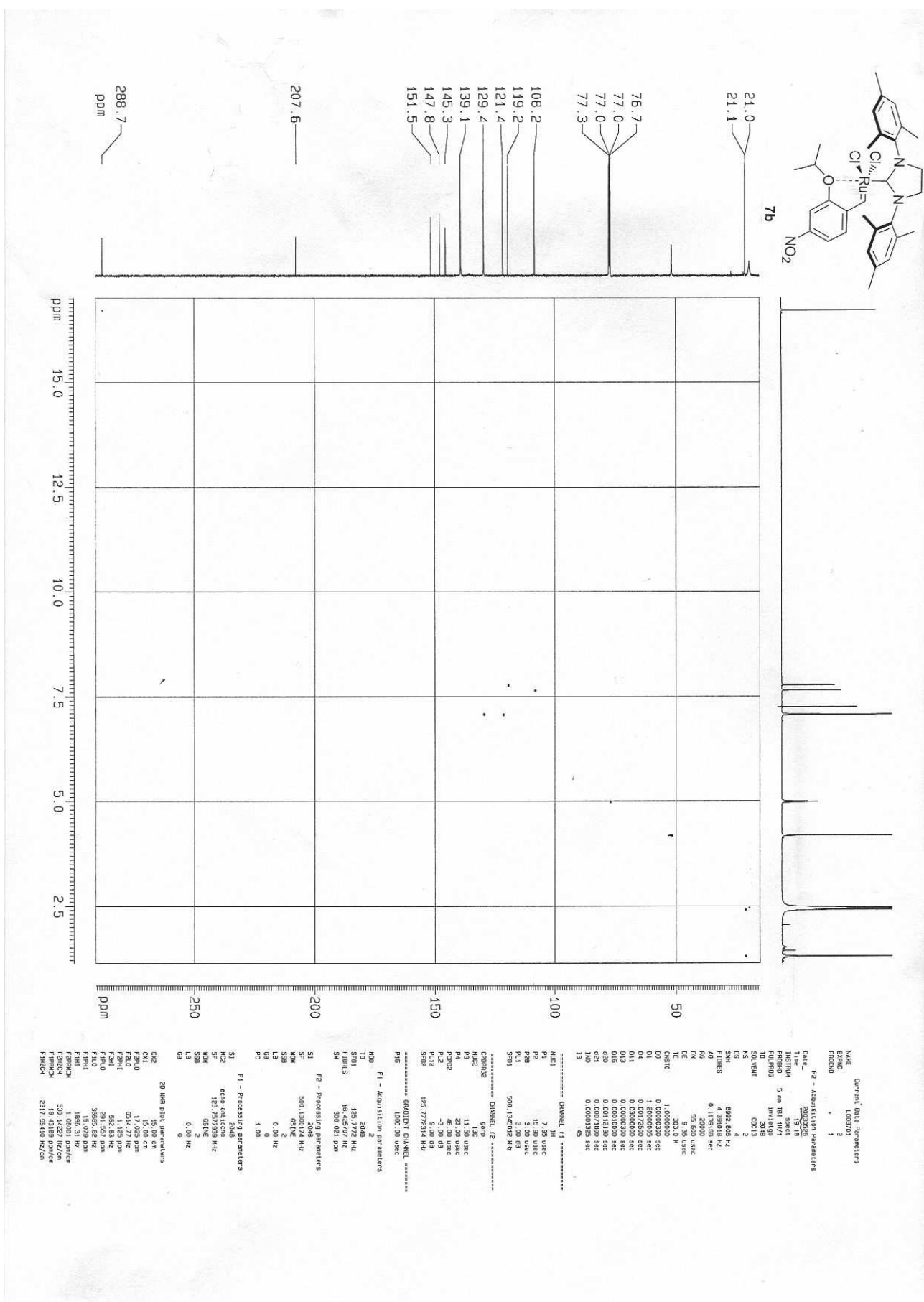
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 Y exp. factor: 14 15.004 Hz/cm
 Int. plot exp. factor: 20

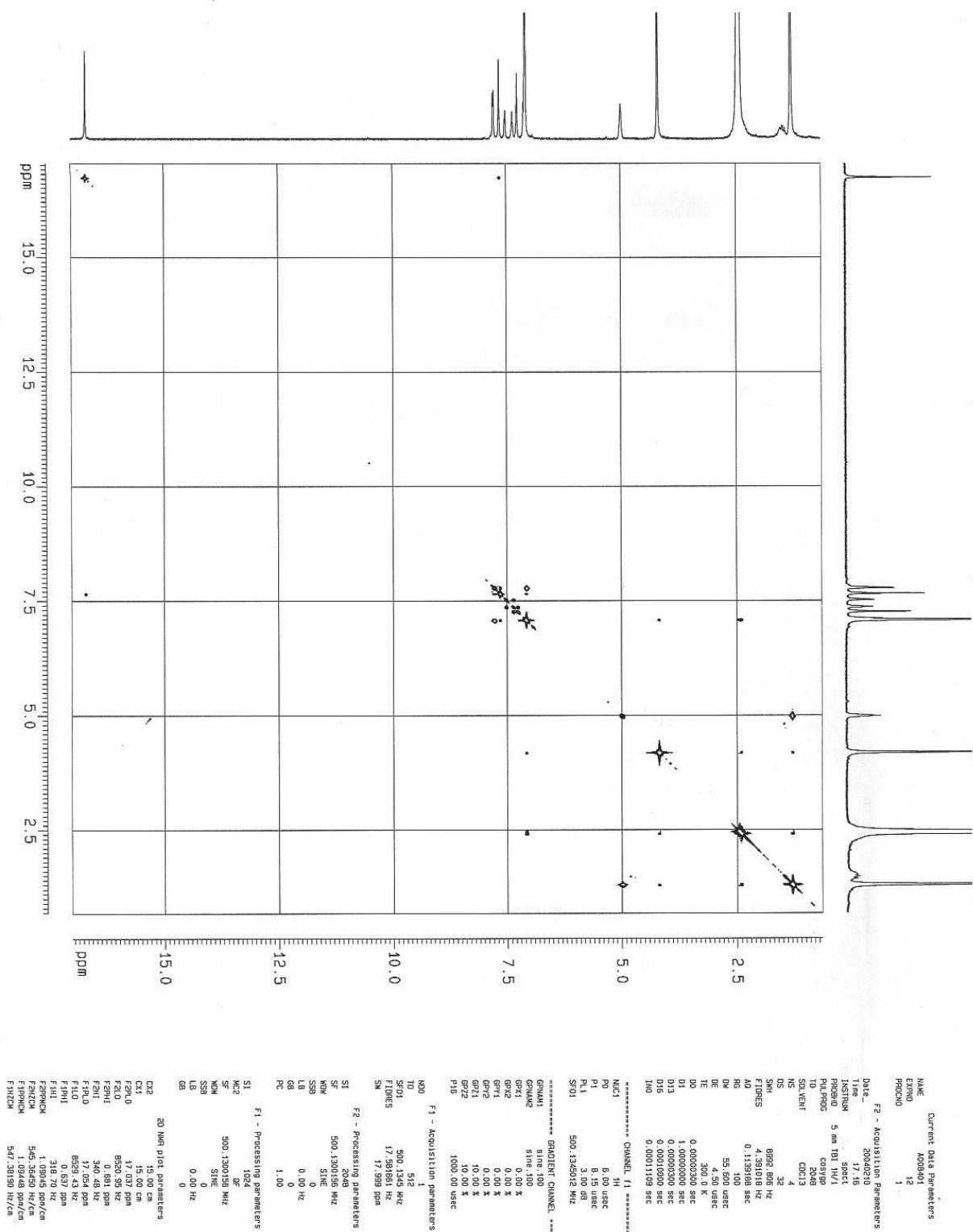


zesp013/A008401/11/1 2117.04 Hz to 2063.02 Hz
 Y exp. factor: 1 15.004 Hz/cm
 Int. plot exp. factor: 5

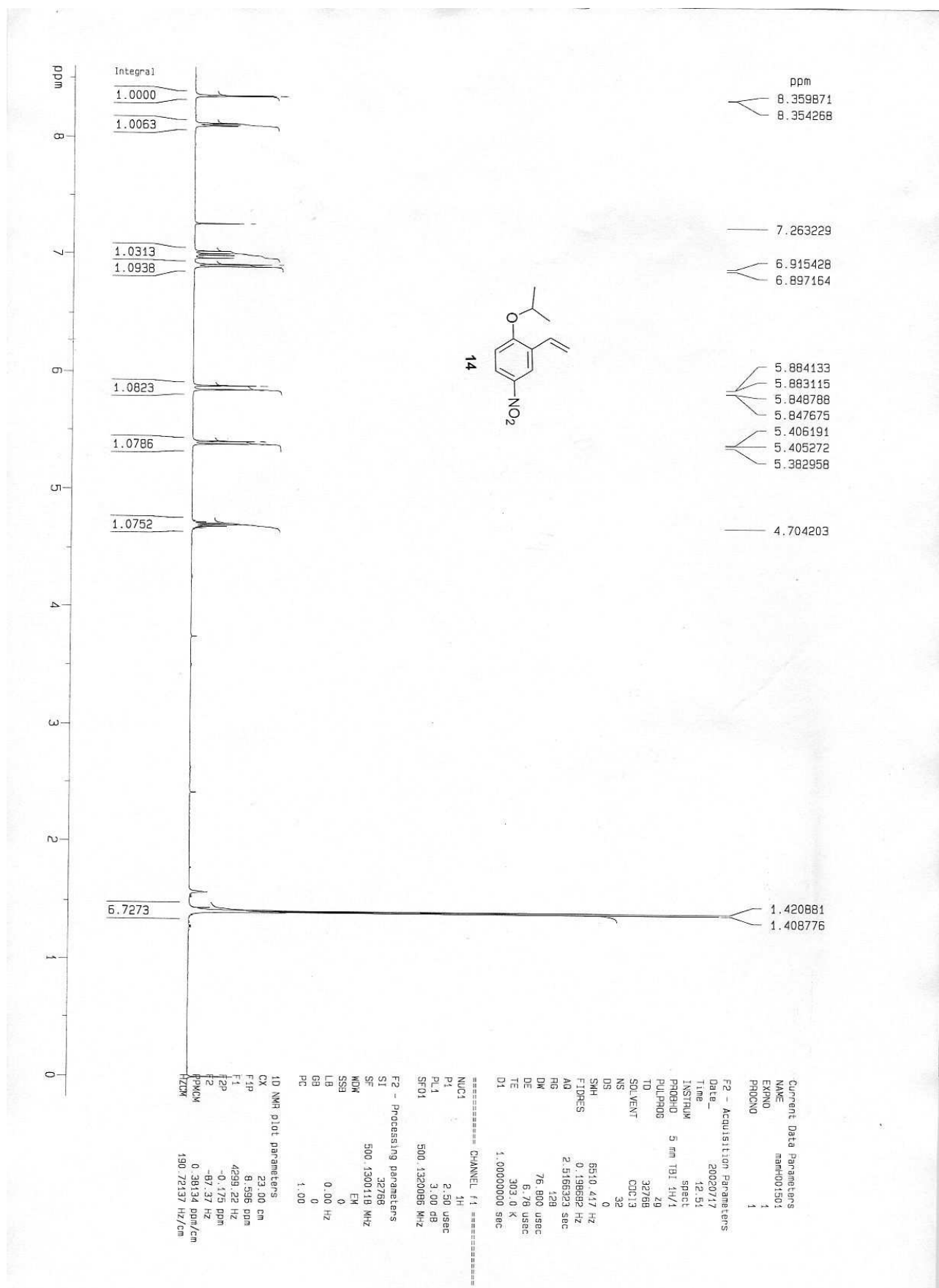


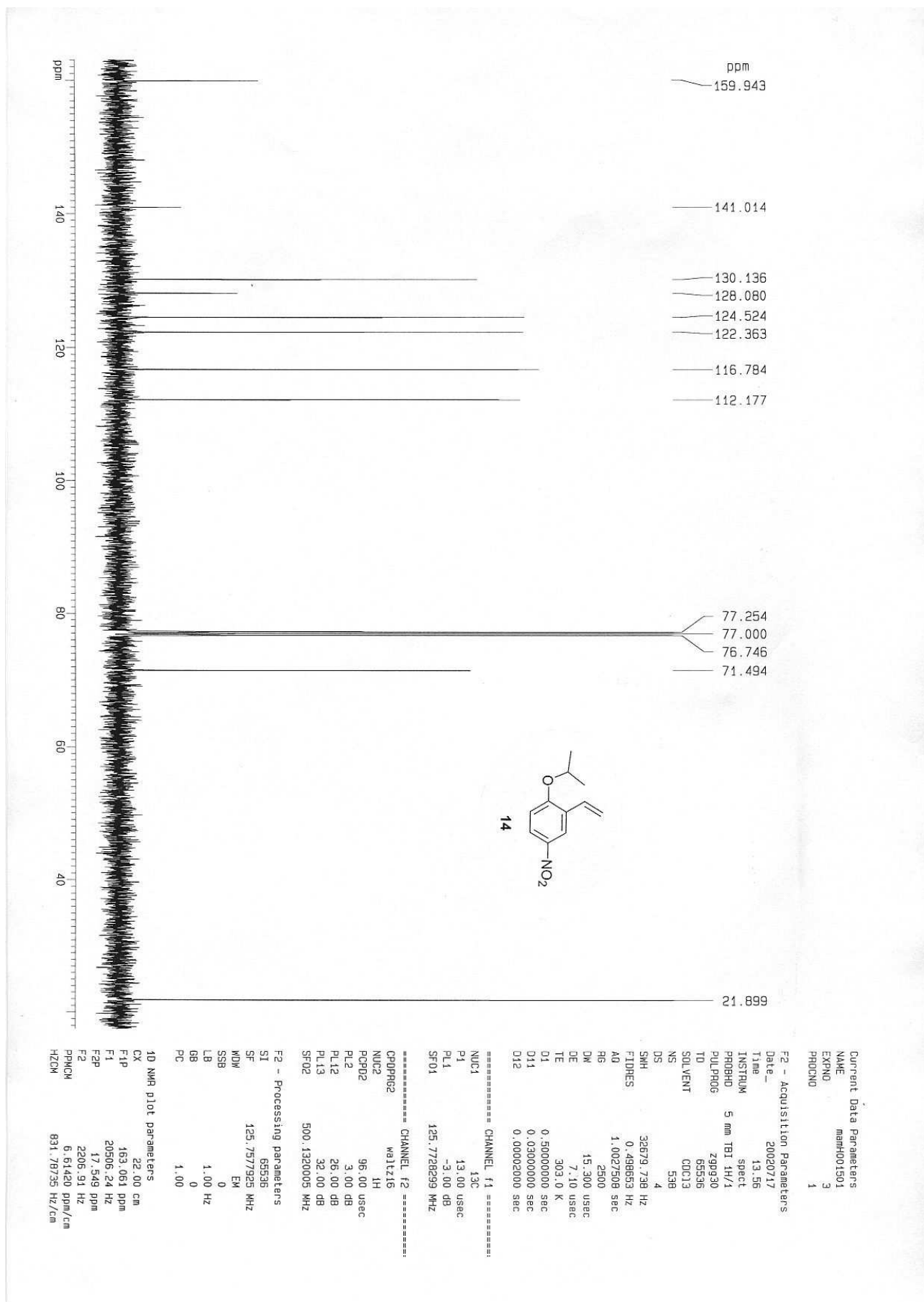




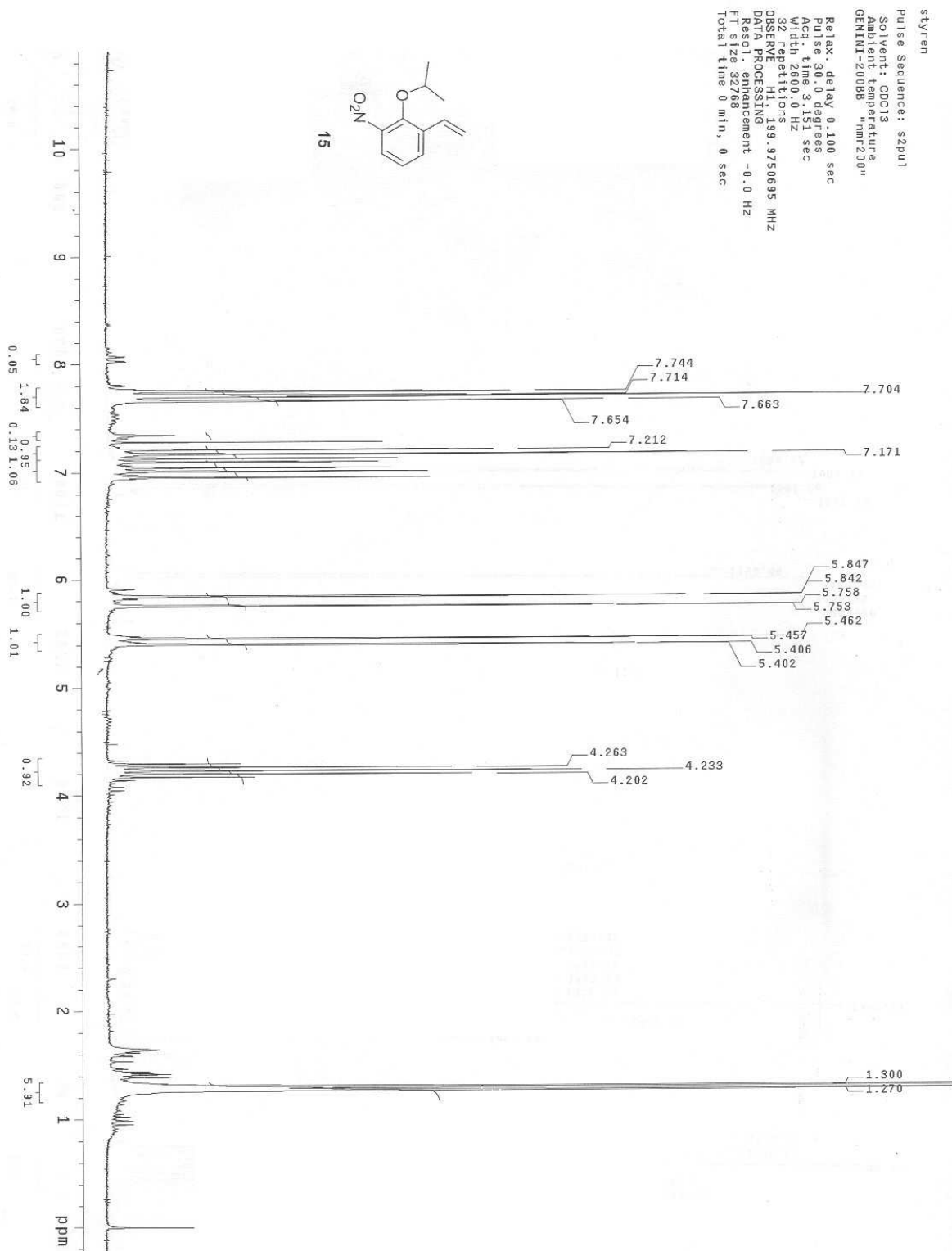


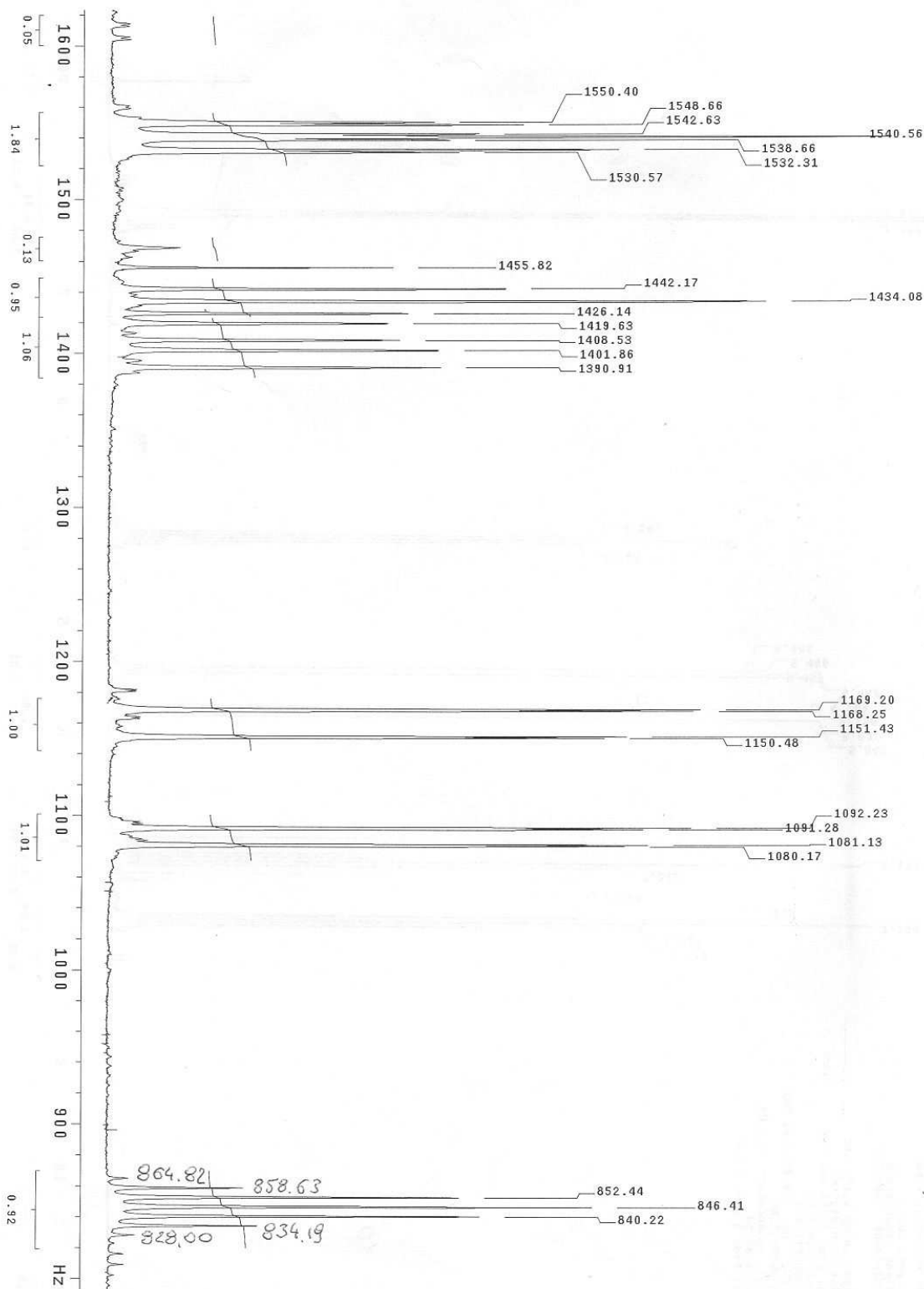
10. Compound 14

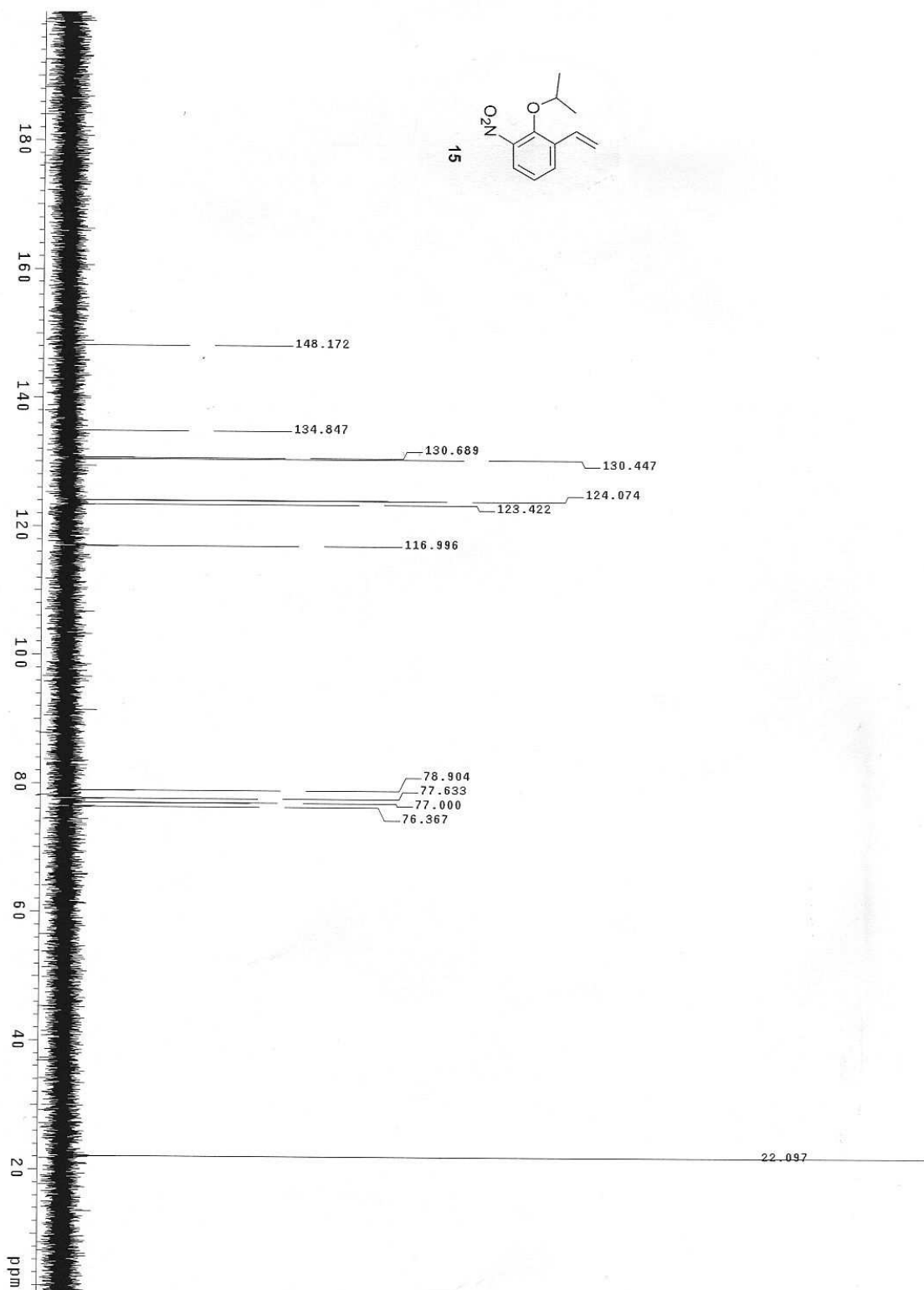




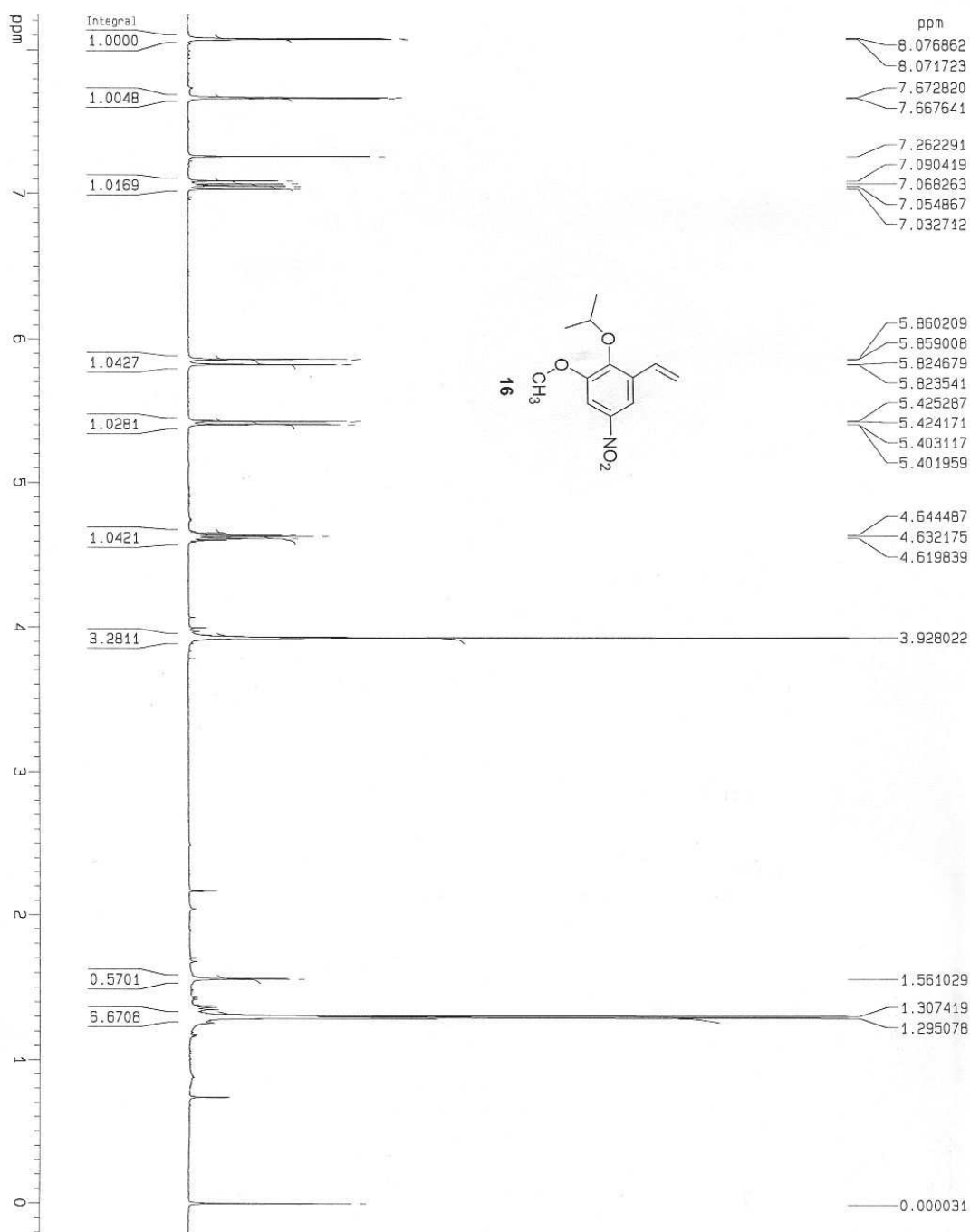
11. Compound 15







12. Compound 16



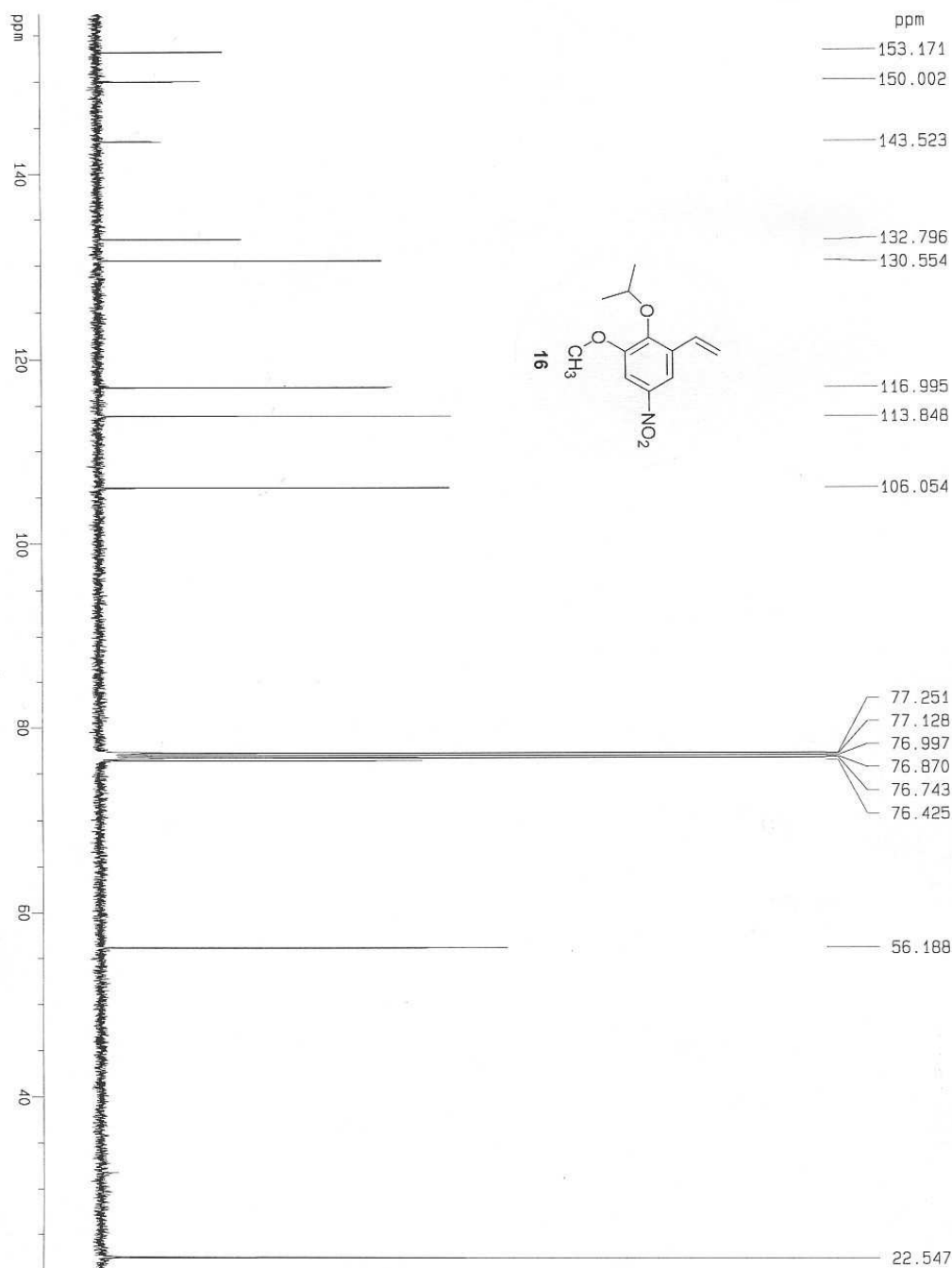
Current Date Parameters
 NAME mhm0051000
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020930
 Time 11:46
 INSTRUM spect
 PROBHD 5 mm Dui1 13
 PULPROG zg
 TD 32768
 SOLVENT Acetone
 NS 32
 DS 0
 SMH 5681.818 Hz
 FIDRES 0.173395 Hz
 AQ 2.883241 sec
 RG 512
 DM 88.000 us/cf
 DE 6.78 us/cf
 TE 303.0 K
 D1 0.00100000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 2.50 us/cf
 PL1 3.00 dB
 SFO1 500.1322178 MHz

F2 - Processing parameters
 SI 32768
 SF 500.1300125 MHz
 WDK EM
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.00 cm
 F1P 8.238 ppm
 F1 4120.01 Hz
 F2p -0.203 ppm
 F2 -101.58 Hz
 PPMCK 0.38368 ppm/cm
 HZCM 191.89050 Hz/cm



Current Data Parameters
 NAME manH0051000
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20020930
 Time 12.01
 INSTRUM spect
 PROBHD 5 mm Dui1 13
 PULPROG zgpg30
 TD 65536
 SOLVENT Aceton
 NS 809
 DS 0
 SMH 30303.031 Hz
 FTIDRES 0.462398 Hz
 AQ 1.0813940 sec
 RG 3200
 DW 16.500 usec
 DE 7.10 usec
 TE 303.0 K
 D1 0.50000000 sec
 D11 0.03000000 sec
 D12 0.00002000 sec

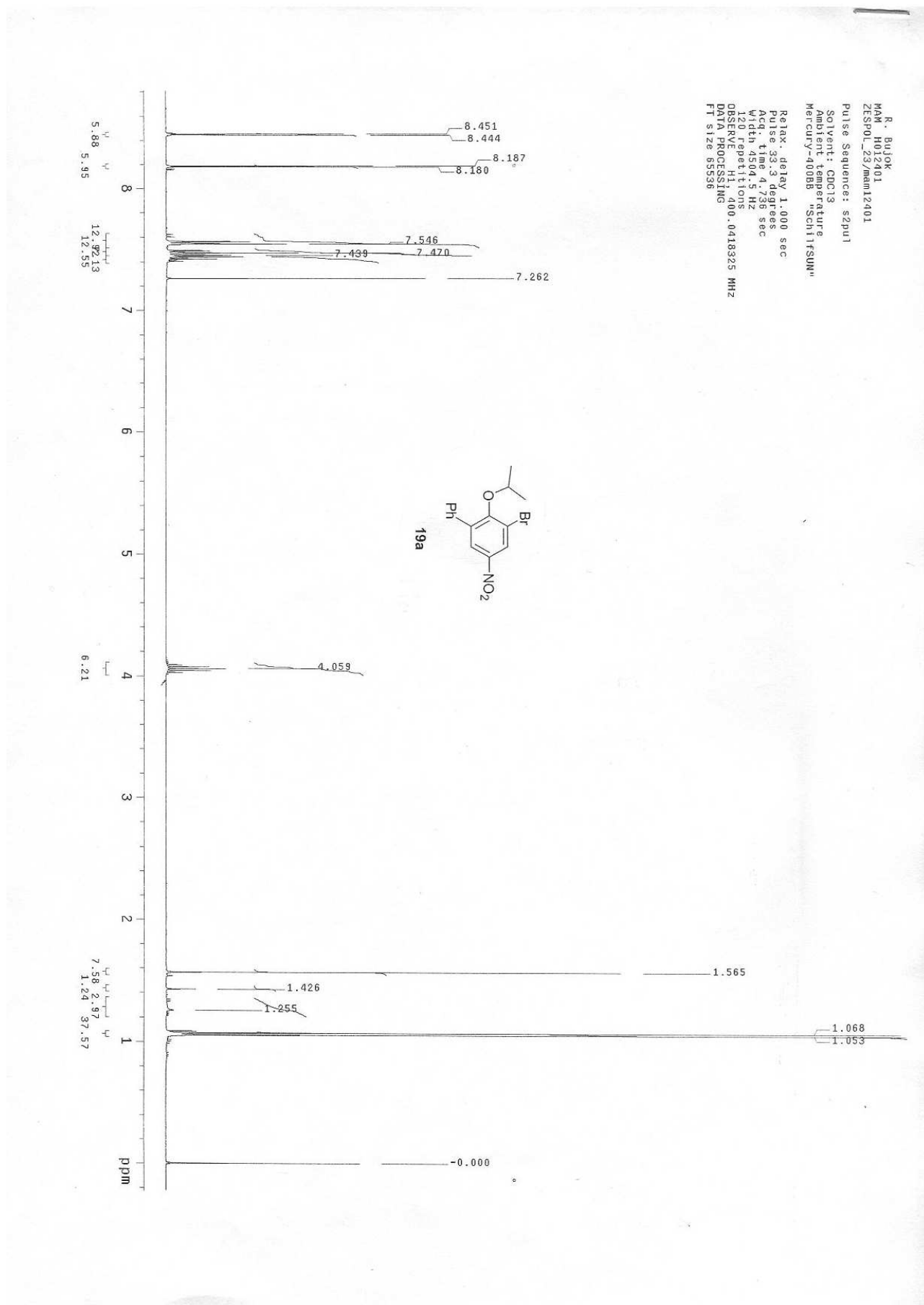
===== CHANNEL f1 =====
 NUC1 13C
 P1 7.50 usec
 PL1 3.00 dB
 SF01 125.7690572 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 3.00 dB
 PL12 21.00 dB
 PL13 32.00 dB
 SF02 500.1320005 MHz

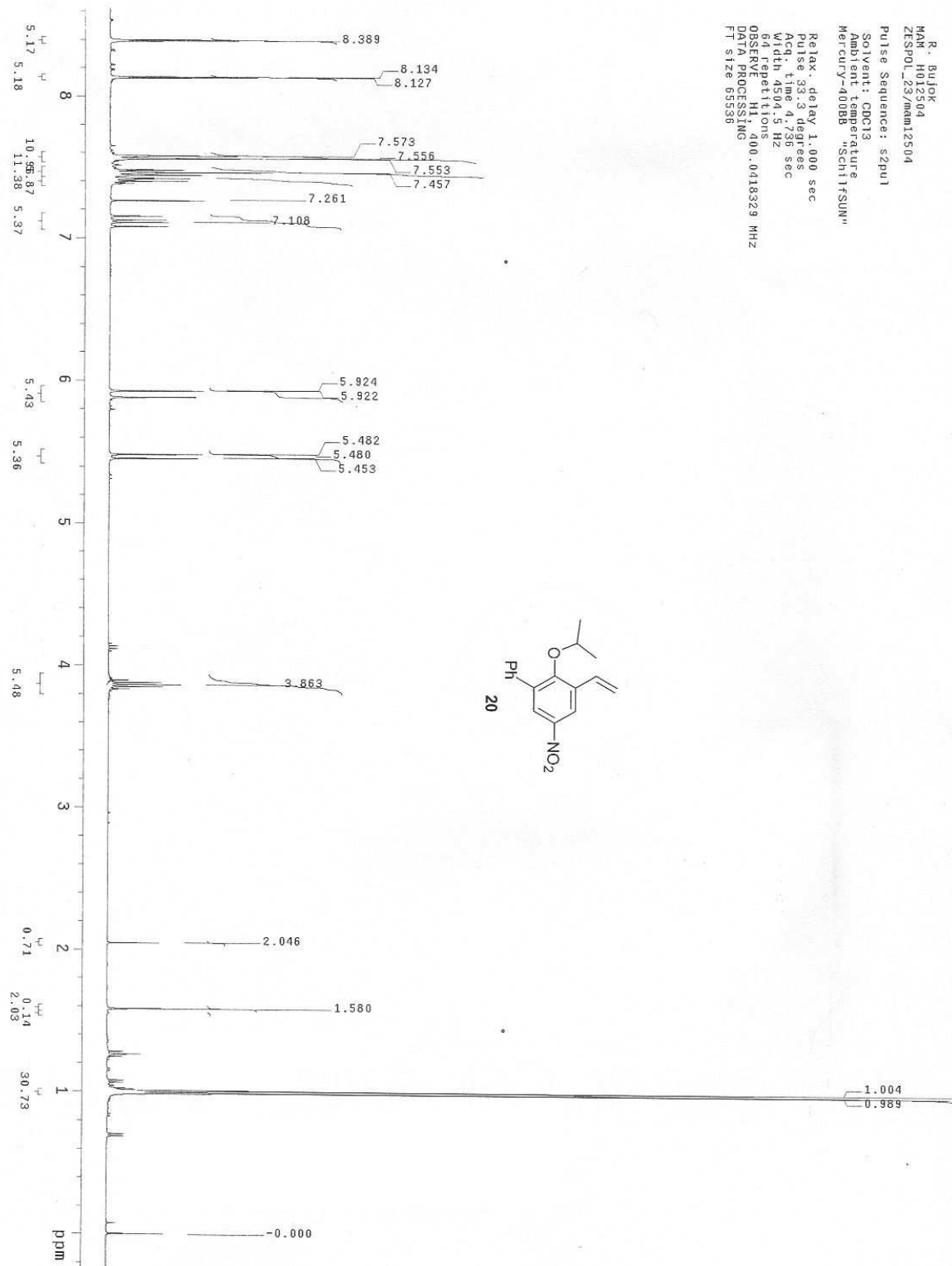
F2 - Processing parameters
 SI 65536
 SF 125.7577911 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 0.25

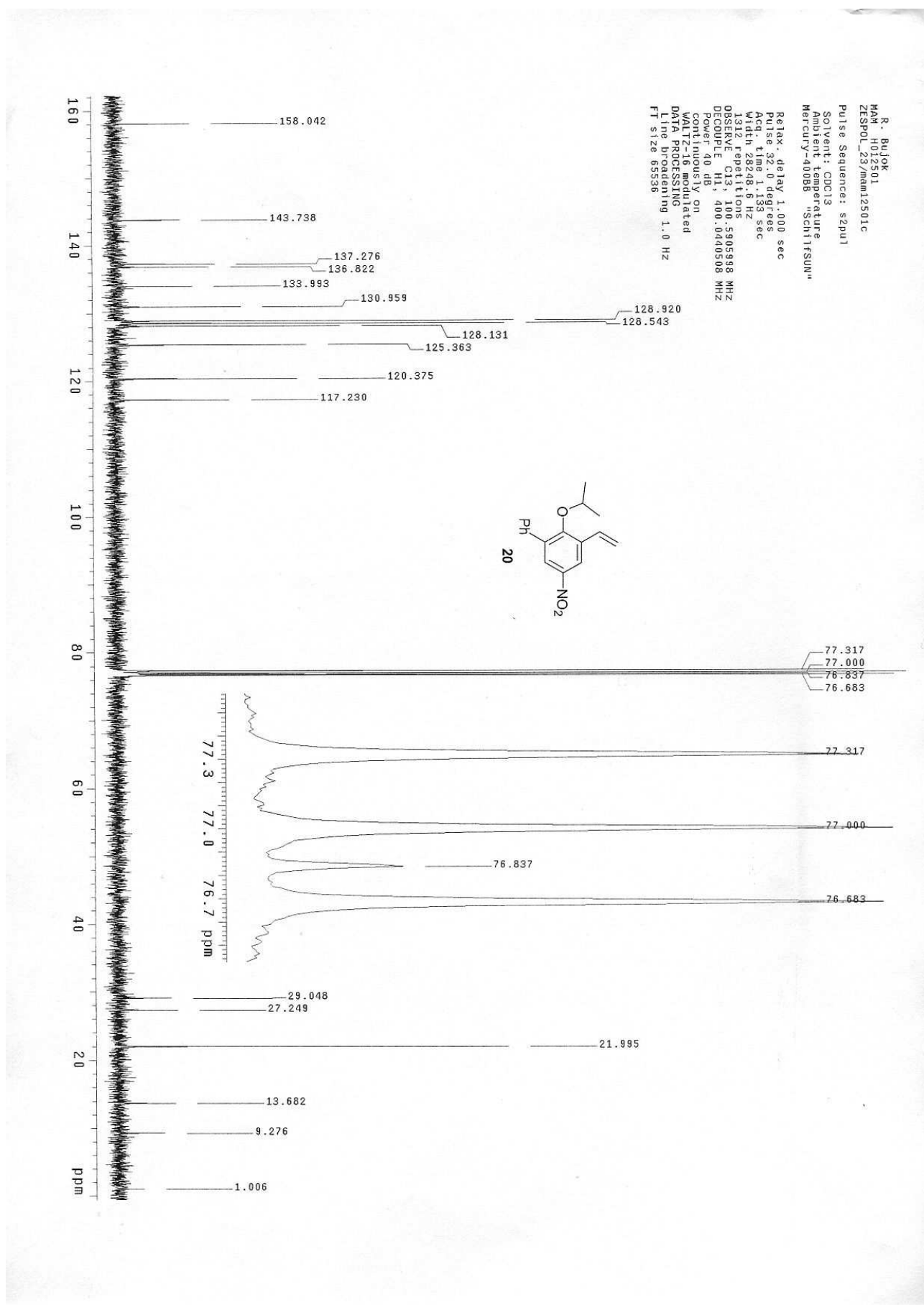
1D NMR plot parameters
 CX 22.00 cm
 F1P 157.295 ppm
 F1 19781.25 Hz
 F2P 19.947 ppm
 F2 2508.52 Hz
 PPMCM 6.24314 ppm/cm
 HZCM 785.12396 Hz/cm

13. Compound 19a

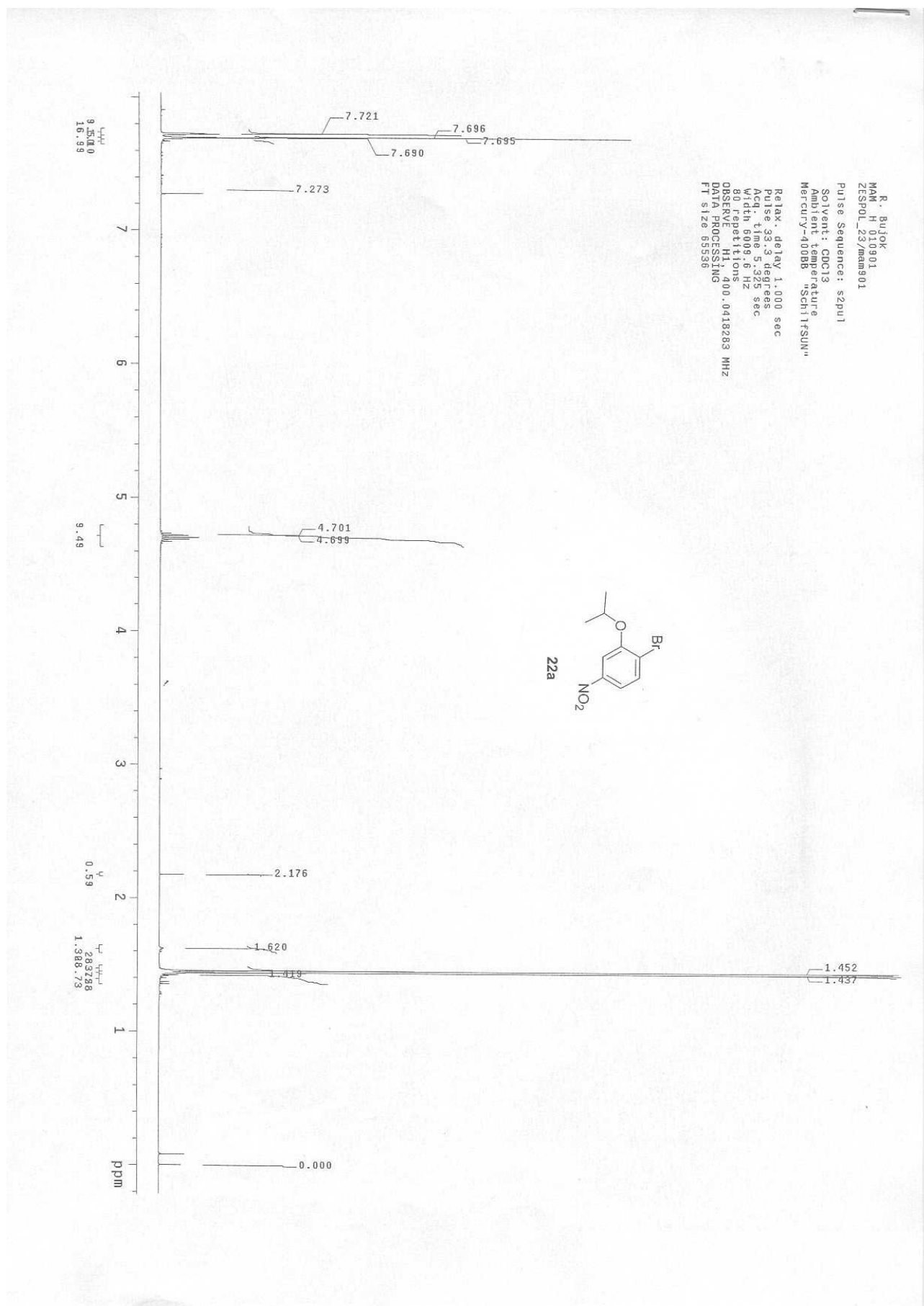


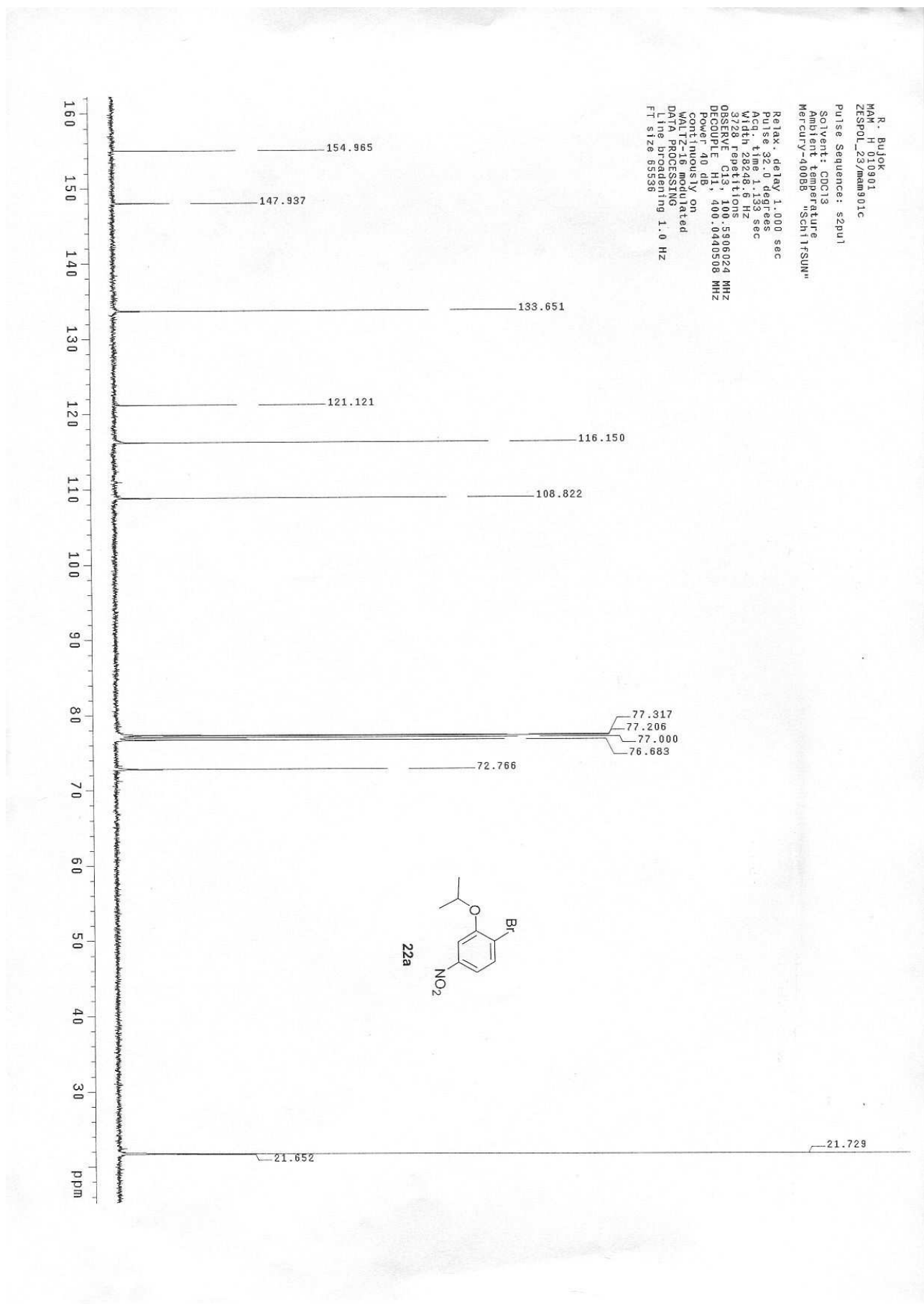
14. Compound 20



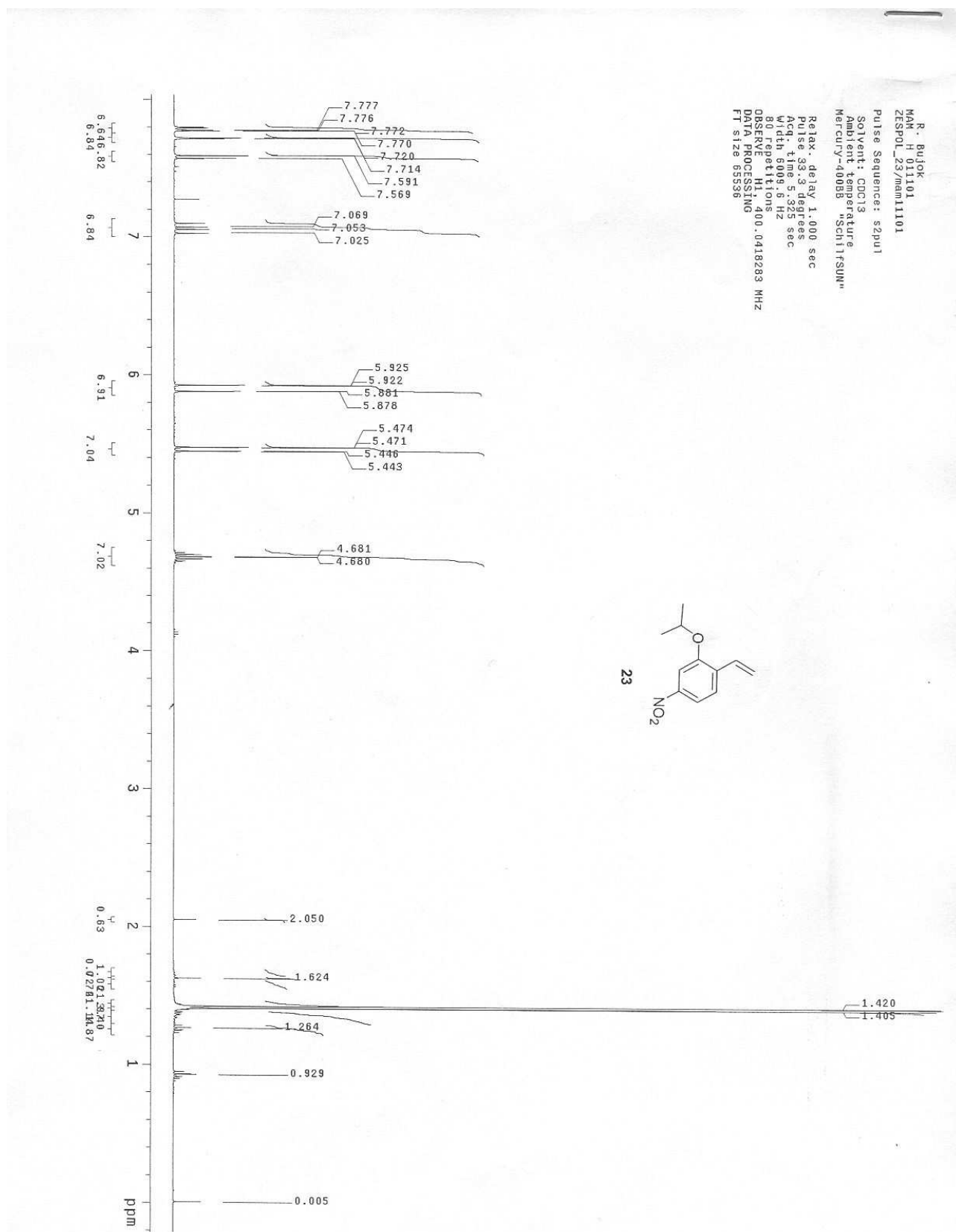


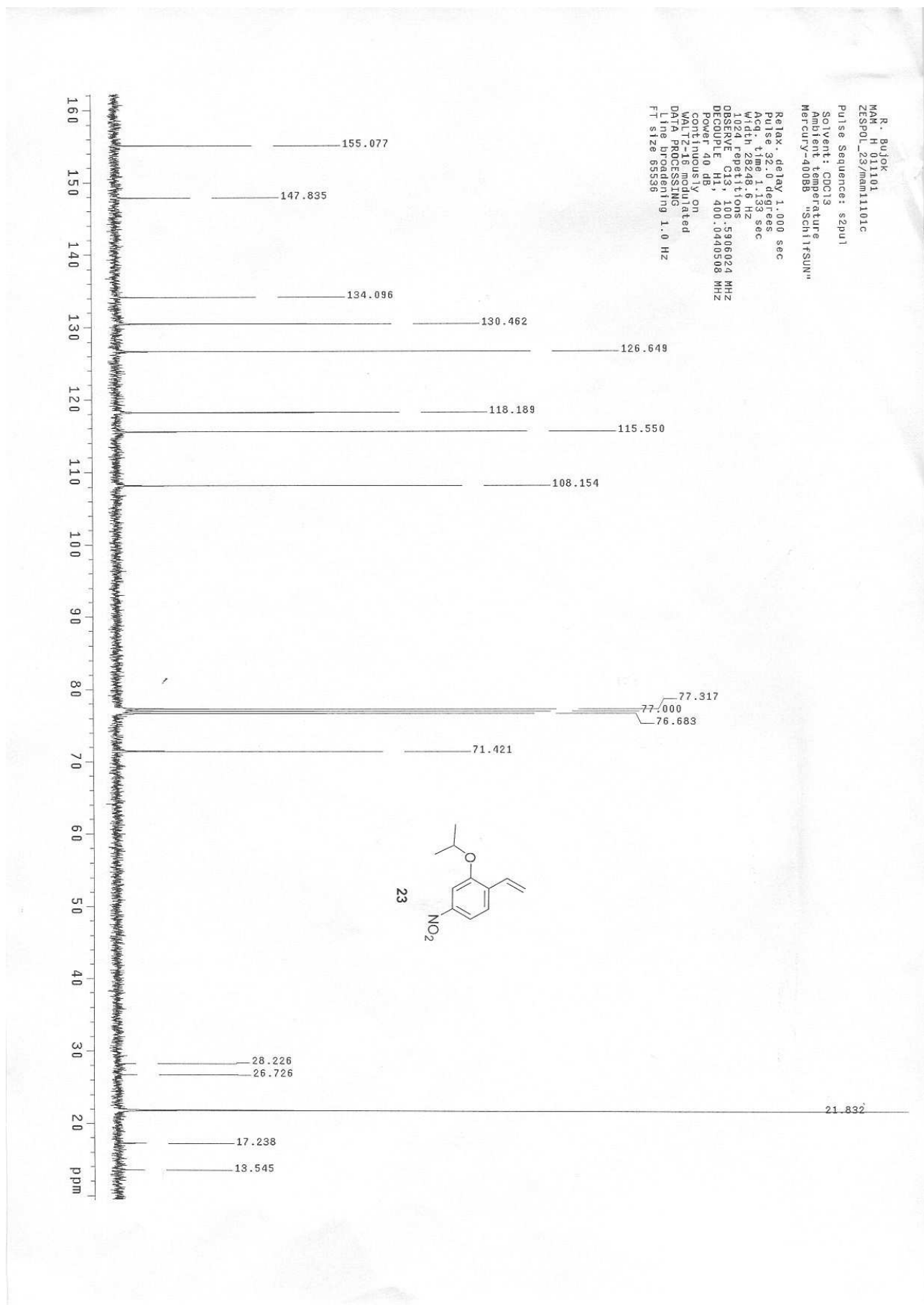
15. Compound 22a



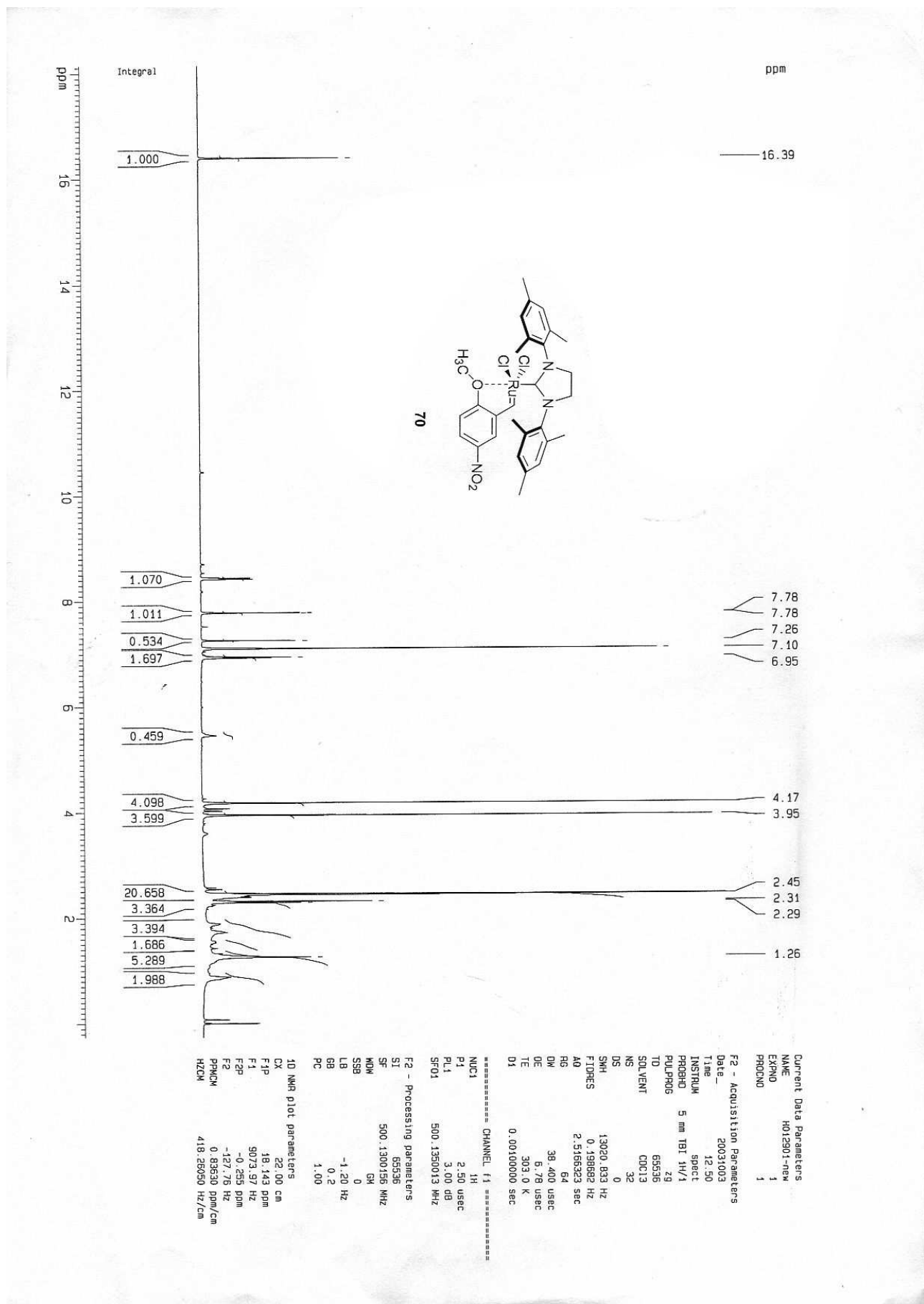


16. Compound 23





17. Compound 70



18. Compound 70a

