

Supplementary Information

**Ultra-Fast Suzuki and Heck Reactions for the Synthesis of Styrenes and
Stilbenes Using Arenediazonium Salts as Super-Electrophiles**

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General experimental remarks

¹H NMR spectra were recorded on BRUKER AM 400 (400 MHz) and BRUKER AM 300 (300 MHz) spectrometer. Chemical shifts are given in parts per million (δ /ppm), referenced to dimethylsulfoxide (2.51) as internal standards. All coupling constants are absolute values and are expressed in Hertz (Hz). The description of signals include: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt doublet of triplets, m = multiplet. ¹³C NMR spectra were recorded on Bruker AM 400 (100 MHz) and BRUKER AM 300 (300 MHz) spectrometers. High Resolution mass-spectra were recorded on XEVO G2-XS OTOF from WATERS with ESI ionization (column Zorbax Eclipse Plus C18 Rapid Resolution HD 2.1x50mm 1.8-Micron). Routine monitoring of reactions were performed using silica gel coated aluminium plates (Merck, silica gel 60, F254) which were analyzed under UV-light at 254 nm and dipped into a solution of 2-naphthol (5 % naphthol in 10 % NaOH aqueous, dipping solution). Solvent mixtures are understood as volume/volume. Solvents, reagents and chemicals were purchased from Sigma/Aldrich. Solvents, reagents and chemicals were used as purchased unless stated otherwise.

1. General Procedure for Preparation of styrenes from vinyl-BF₃K and ADT. To a mixture of ADT (**2a-m**) (0.2 mmol) and potassium vinyltrifluoroborate (0.3 mmol, 0.0402 g) in 5 ml water/acetonitrile (1/1) was added 1 mol % Pd(OAc)₂ (0.002 mmol, 0.0005 g). The end of the nitrogen evolution and the formation of Pd(0) indicated the reaction completion. Brine (10 ml) was added to the reaction mixture and the organic layer was extracted with pentane (3×50 mL). The organic layers were dried over anhydrous MgSO₄. The solvent was removed in *vacuo* to give the corresponding styrene without further purification (**3a-m**).

1-nitro-4-vinylbenzene (3a). According to the general procedure, the reaction of 4-nitrobenzenediazonium tosylate **2a** (0.2 mmol, 0.064 g) with potassium vinyltrifluoroborate (0.3 mmol, 0.040 g) for 25 sec afforded compound **3a** (0.03 g, 97 % yield) as a yellow oil.¹ ¹H NMR (400 MHz, CDCl₃): δ 8.18 (d, *J* = 10.8 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 6.81-6.74 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.93 (d, *J* = 17.6 Hz, 1H), 5.49 (d, *J* = 10.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 147.1; 143.8; 135.0; 126.8; 124.0; 118.7.

4-vinylbenzonitrile (3b). According to the general procedure, the reaction of 4-cyanobenzenediazonium tosylate **2b** (0.2 mmol, 0.060 g) with potassium vinyltrifluoroborate (0.3 mmol, 0.040 g) for 20 sec afforded compound **3b** (0.023 g, 90% yield) as a yellow oil.¹ ¹H NMR (300 MHz, CDCl₃): δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 6.77-6.68 (dd, *J* = 17.7, 11.1, 10.8 Hz, 1H), 5.87 (d, *J* = 17.4 Hz, 1H), 5.45 (d, *J* = 10.8 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 142.0; 135.5; 132.5; 126.9; 119.0; 117.9; 111.2.

4-vinylbenzoic acid (3c). According to the general procedure, the reaction of 4-carboxybenzenediazonium tosylate **2c** (0.2 mmol, 0.064 g) with potassium vinyltrifluoroborate (0.3 mmol, 0.040 g) for 35 sec afforded compound **3c** (0.028 g, 94% yield) as a brown solid. mp = 141-142 °C [lit. 143-144 °C].² ¹H NMR (400 MHz, CDCl₃): δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 6.81-6.74 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.91 (d, *J* = 17.6 Hz, 1H), 5.43 (d, *J* = 10.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 172.3; 142.9; 136.1; 130.7; 128.5; 126.4; 117.2.

1-bromo-4-vinylbenzene (3d). According to the general procedure, the reaction of 4-bromobenzenediazonium tosylate **2d** (0.2 mmol, 0.071 g) with potassium vinyltrifluoroborate (0.3 mmol, 0.040 g) for 30 sec afforded compound **3d** (0.030 g, 83 % yield) as a yellow oil.³ ¹H NMR (400 MHz, CDCl₃): δ 7.45 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 6.69-6.62 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.75 (d, *J* = 17.6 Hz, 1H), 5.29 (d, *J* = 10.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 136.7; 135.8; 131.7; 128.0; 121.9; 114.6.

4-vinylaniline (3e). According to the general procedure, the reaction of 4-aminobenzenediazonium tosylate **2e** (0.2 mmol, 0.058 g), potassium vinyltrifluoroborate (0.3 mmol, 0.040 g) and AcONa (0.2 mmol, 0.027 g) for 20 sec afforded compound **3e** (0.012 g, 52% yield) as a yellow oil.⁴ ¹H NMR (300 MHz, CDCl₃): δ 7.25 (d, *J* = 8.7 Hz, 2H), 6.71-6.57

(m, 3H), 5.56 (d, J = 17.7 Hz, 1H), 5.06 (d, J = 10.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 146.3; 136.7; 127.5; 115.4; 113.3; 110.4.

4-vinyl-1,1'-biphenyl (3f). According to the general procedure, the reaction of 4-phenylbenzenediazonium tosylate **2f** (0.2 mmol, 0.070 g) with potassium vinyltrifluoroborate (0.3 mmol, 0.040 g) for 40 sec afforded compound **3f** (0.026 g, 72 % yield) as a white solid. mp = 114-116 °C [lit. 115-117 °C.⁵]. ^1H NMR (400 MHz, CDCl_3): δ 7.61-7.56 (m, 4H), 7.50-7.42 (m, 4H), 7.37-7.33 (m, 1H), 6.80-6.73 (dd, J = 17.6, 10.8 Hz, 1H), 5.80 (d, J = 17.6 Hz, 1H), 5.28 (d, J = 10.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 140.8; 140.7; 136.7; 136.5; 128.9; 127.4; 127.3; 127.1; 126.7; 114.0.

2-(4-vinylphenyl)benzo[d]thiazole (3g). According to the general procedure, the reaction of 4-(benzo[d]thiazol-2-yl)benzenediazonium tosylate **2g** (0.2 mmol, 0.085 g) with potassium vinyltrifluoroborate (0.3 mmol, 0.040 g) for 50 sec afforded compound **3g** (0.037 g, 78% yield) as a white solid.⁶ mp = 107-109 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.09-8.05 (m, 3H), 7.90 (d, J = 8.4 Hz, 1H), 7.54-7.48 (m, 3H), 7.40-7.37 (m, 1H), 6.80-6.73 (dd, J = 17.6, 11.2, 10.8 Hz, 1H), 5.87 (d, J = 17.6 Hz, 1H), 5.37 (d, J = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.8; 154.3; 140.2; 136.2; 135.1; 133.0; 127.9; 126.9; 126.5; 123.3; 121.7; 115.8.

(E)-1-phenyl-2-(4-vinylphenyl)diazene (3h). According to the general procedure, the reaction of (E)-4-(phenyldiazenyl)benzenediazonium tosylate **2h** (0.2 mmol, 0.062 g) with potassium vinyltrifluoroborate (0.3 mmol, 0.040 g) for 25 sec afforded compound **3h** (0.038 g, 91 % yield) as an orange solid. mp = 72-74 °C [lit. 74-75 °C.⁷]. ^1H NMR (400 MHz, CDCl_3): δ 7.93-7.89 (m, 4H), 7.57-7.47 (m, 5H), 6.83-6.76 (dd, J = 17.6, 10.8 Hz, 1H), 5.87 (d, J = 17.6 Hz, 1H), 5.37 (d, J = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 152.9; 152.2; 140.3; 136.3; 131.1; 129.2; 127.1; 123.4; 123.0; 115.8.

5-vinyluracil (3i). According to the general procedure, the reaction of 5-uracildiazonium tosylate **2i** (0.2 mmol, 0.062 g) with potassium vinyltrifluoroborate (0.3 mmol, 0.040 g) for 340 sec afforded compound **3i** (0.017 g, 62 % yield) as a white solid m.p. = 234-236 °C [lit. 230-270 °C.⁸]. ^1H NMR (400 MHz, DMSO-d_6): δ 11.15-11.06 (m, 2H), 7.58 (s, 1H); 6.39-6.32 (dd, J = 17.6, 11.6 Hz, 1H), 5.94 (d, J = 17.6 Hz, 1H), 5.04 (d, J = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 136.2; 150.6; 139.9; 129.0; 113.4; 109.6.

1-nitro-2-vinylbenzene (3j). According to the general procedure, the reaction of 2-nitrobenzenediazonium tosylate **2j** (0.2 mmol, 0.064 g) with potassium vinyltrifluoroborate (0.3 mmol, 0.040 g) for 62 sec afforded compound **3j** (0.025 g, 83 % yield) as a yellow oil.⁹ ^1H NMR (400 MHz, CDCl_3): δ 7.93 (d, J = 8.0 Hz, 1H), 7.64-7.56 (m, 2H), 7.43-7.39 (m, 1H), 7.21-7.14 (dd, J = 17.6, 11.2, 10.8 Hz, 1H), 5.75 (d, J = 17.2 Hz, 1H), 5.49 (d, J = 10.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.9; 133.5; 133.3; 132.6; 128.6; 128.5; 124.6; 119.1.

2-vinylbenzoic acid (3k). According to the general procedure, the reaction of 2-carboxybenzenediazonium tosylate **2k** (0.2 mmol, 0.064 g) with potassium vinyltrifluoroborate (0.3 mmol, 0.040 g) for 450 sec afforded compound **3k** (0.022 g, 75 % yield) as a white solid. mp = 93-95 °C [lit. 93-95 °C.¹⁰]. ^1H NMR (400 MHz, CDCl_3): δ 8.06 (d, J = 7.6 Hz, 1H), 7.63-7.54 (m, 3H), 7.39-7.36 (m, 1H), 5.68 (d, J = 17.2 Hz, 1H), 5.40 (d, J = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.1; 140.8; 136.2; 133.3; 131.5; 127.8; 127.7; 127.2; 117.0.

2-chloro-4-nitro-1-vinylbenzene (3l). According to the general procedure, the reaction of 2-chloro-4-nitrobenzenediazonium tosylate **2l** (0.2 mmol, 0.071 g) with potassium vinyltrifluoroborate (0.3 mmol, 0.040 g) for 35 sec afforded compound **3l** (0.034 g, 91 % yield) as a white solid mp 111-112 °C [lit. 110-112 °C.¹]. ^1H NMR (400 MHz, CDCl_3): δ 7.93 (s, 1H), 7.59-7.53 (m, 2H), 7.15-7.08 (dd, J = 17.6, 11.2, 10.8 Hz, 1H), 5.75 (d, J = 17.2 Hz, 1H), 5.52 (d, J = 10.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.6; 133.8; 133.1; 131.6; 131.3; 129.4; 124.3; 119.5.

2,4,6-tribromo-1-vinylbenzene (3m). According to the general procedure, the reaction of 2,4,6-tribromobzenediazonium tosylate **2m** (0.2 mmol, 0.103 g) with potassium vinyltrifluoroborate (0.3 mmol, 0.040 g) for 3.5 h afforded compound **3m** (0.037 g, 54 % yield) as a white solid mp 124-127 °C [lit. 123-125 °C.¹¹]. ^1H NMR (400 MHz, CDCl_3): δ 7.72 (s, 2H),

6.57-6.50 (dd, J = 17.6, 11.6 Hz, 1H), 5.68-5.60 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 138.2; 135.1; 134.9; 124.3; 123.7; 121.5.

2. General Procedure for preparation of symmetric stilbenes from vinyl-BF₃K and ADT. To a mixture of ADT (0.4 mmol) and potassium vinyltrifluoroborate (0.2 mmol, 0.027 g) in water/acetonitrile (5 mL, 1/1) was added Pd(OAc)₂ (1 mol %). The reaction vessel was immediately placed into a microwave reactor (70 °C, 30 bars). After completion, brine was added, the reaction mixture was extracted with CHCl_3 (3×50 mL) and dried over anhydrous MgSO₄. The solvent was removed in *vacuo* to give the corresponding stilbenes without further purification.

(E)-4,4'-dinitrostilbene 4a. According to the general procedure, the reaction of 4-nitrobenzenediazonium tosylate **2a** (0.4 mmol, 0.128 g) with potassium vinyltrifluoroborate (0.2 mmol, 0.027 g) for 56 min afforded compound **4a** (0.048 g, 86% yield) as a white solid mp 290 °C (decomp.) [lit. 292-295 °C.¹²]. ^1H NMR (400 MHz, DMSO-d₆): δ 8.28 (d, J = 8.8 Hz, 4H), 7.95 (d, J = 8.8 Hz, 4H), 7.70 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d₆): δ 147.0; 143.2; 131.1; 128.2; 124.3.

(E)-4,4'-dicyanoestilbene 4b. According to the general procedure, the reaction of 4-cyanobenzenediazonium tosylate **2b** (0.4 mmol, 0.12 g) with potassium vinyltrifluoroborate (0.2 mmol, 0.027 g) for 1 min afforded compound **4b** (0.024 g, 51% yield) as a white solid mp 291- 293 °C (decomp.) [lit. 294- 296 °C.¹³]. ^1H NMR (400 MHz, CDCl_3): δ 7.74 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8 Hz, 2H), 7.32 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 140.8; 132.8; 130.4; 127.4; 118.9; 111.8.

(E)-4,4'-dibromostilbene 4c. According to the general procedure, the reaction of 4-bromobenzenediazonium tosylate **2d** (0.4 mmol, 0.142 g) with potassium vinyltrifluoroborate (0.2 mmol, 0.027 g) for 9 min afforded compound **4c** (0.058 g, 86 % yield) as a white solid mp 216- 218 °C [lit. mp. 216- 219 °C.¹⁴]. ^1H NMR (400 MHz, CDCl_3): δ 7.48 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.02 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 135.7; 131.7; 128.0; 127.8; 121.5.

(E)-1,2-bis(4-((E)-phenyldiazenyl)phenyl)ethene 4d. The reaction of (E)-4-(phenyldiazenyl)benzenediazonium tosylate **2h** (0.4 mmol, 0.124 g) and potassium vinyltrifluoroborate (0.2 mmol, 0.027 g) according to the general procedure during 5 min afforded compound **4d** (0.067 g, 86 % yield) as an red solid mp = 199-201 °C. ^1H NMR (400 MHz, DMSO-d₆ 70 degrees): δ 7.94-7.86 (m, 5 H), 7.62-7.56 (m, 4H), 7.52 (s, 1H); HRMS (TOF MS ES+): calcd for C₂₂H₂₁N₄ (M+H⁺) 389.1766; found 389.1764.

(E)-2,2'-dinitrostilbene 4e. According to the general procedure, the reaction of 2-nitrobenzenediazonium tosylate **2j** (0.4 mmol, 0.128 g) with potassium vinyltrifluoroborate (0.2 mmol, 0.027 g) for 132 min afforded compound **4e** (0.045 g, 83 % yield) as a white solid mp 199-201 °C [lit. 204 °C.¹⁵]. ^1H NMR (400 MHz, CDCl_3): δ 8.05 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.69-7.66 (t, J = 7.6 MHz, 1H), 7.57 (s, 1H), 7.51-7.47 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 133.8; 132.7; 129.2; 129.1; 129.0; 125.0.

(E)-1,2-di-p-tolyethene 4f. According to the general procedure, the reaction of 4-methylbenzenediazonium tosylate **2n** (0.4 mmol, 0.116 g) with potassium vinyltrifluoroborate (0.2 mmol, 0.027 g) for 1 min afforded compound **4f** (0.013 g, 31 % yield) as a white solid mp 178- 180 °C [lit. 177- 179 °C¹⁶]. ^1H NMR (300 MHz, CDCl_3): δ 7.40 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 7.04 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 137.8; 135.3; 129.9; 128.2; 126.9; 21.9.

3. General Procedure for preparation of unsymmetrical stilbenes from vinyl-BF₃K and ADT. To a solution of ADT (0.2 mmol) and potassium vinyltrifluoroborate (0.3 mmol, 0.040 g) water/acetonitrile (5 mL, 1/1) was added Pd(OAc)₂ (1 mol%). The reaction mixture was stirred until the cessation of the nitrogen evolution, then the second (0.2 mmol) was added to

reaction mixture. The reaction vessel was placed into a microwave reactor (70 °C, 30 bars). After completion, brine was added, the reaction mixture was extracted with CHCl₃ (3×50 mL) and dried over anhydrous MgSO₄. The organic extracts were filtered through short silica pad. The solvent was removed in *vacuo* to give the corresponding stilbenes without further purification.

(E)-1-methyl-4-(4-nitrostyryl)benzene 4g. The reaction of 4-nitrobenzenediazonium tosylate **2a** (0.2 mmol, 0.064 g), 4-methylbenzenediazonium tosylate **2n** (0.2 mmol, 0.058 g) and potassium vinyltrifluoroborate (0.2 mmol, 0.027 g) afforded compound **4g** (0.039 g, 82 % yield) as a white solid mp 148- 150 °C [lit. 150 °C.¹⁷]. ¹H NMR (400 MHz, DMSO-d₆): δ 8.22 (d, *J* = 9.2 Hz, 2H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 16.4 Hz, 1H), 7.36 (d, *J* = 16.8 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆): δ 146.0; 144.3; 138.4; 133.6; 133.3; 129.5; 127.2; 127.2; 125.4; 124.1; 21.0.

(E)-4-(4-bromostyryl)-1,1'-biphenyl 4h. The reaction of 4-bromobenzenediazonium tosylate **2d** (0.2 mmol, 0.071 g), 4-phenylbenzenediazonium tosylate **2f** (0.2 mmol, 0.070 g) and potassium vinyltrifluoroborate (0.2 mmol, 0.027 g) afforded compound **4h** (0.064 g, 96 % yield) as a grey solid mp 232- 234 °C [lit. 229-231 °C.¹⁸]. ¹H NMR (400 MHz, CDCl₃): δ 7.63-7.57 (m, 7H), 7.50-7.43 (m, 4H), 7.41-7.34 (m, 3H), 7.14 (d, *J* = 16.4 Hz, 1H), 7.08 (d, *J* = 16.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 140.8; 140.7; 136.4; 136.1; 132.0; 129.0; 129.0; 128.1; 127.6; 127.1; 127.1; 121.5.

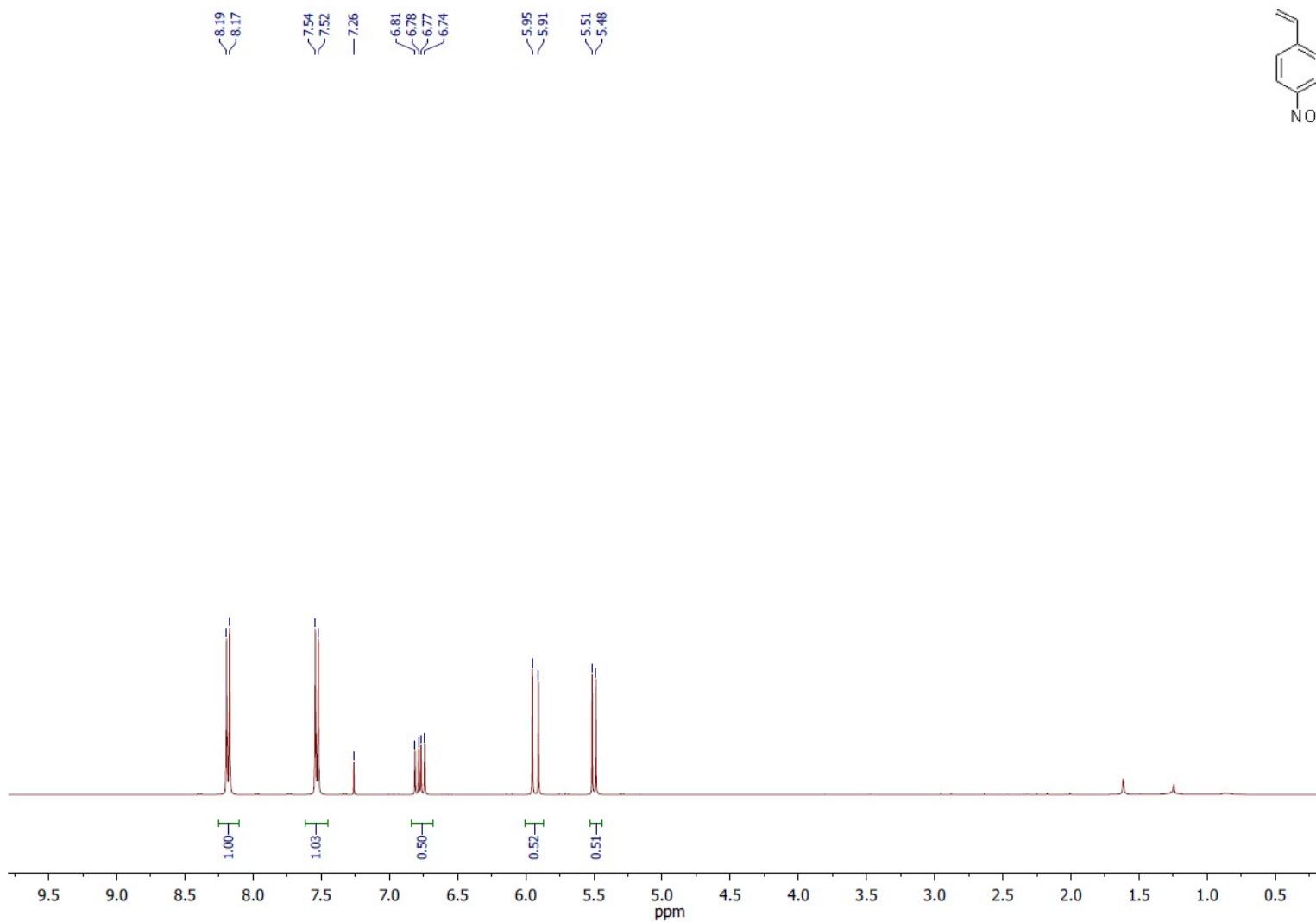
(E)-1-(4-((E)-4-nitrostyryl)phenyl)-2-phenyldiazene 4i. The reaction of 4-nitrobenzenediazonium tosylate **2a** (0.2 mmol, 0.064 g), (E)-4-(phenyldiazenyl)benzenediazonium tosylate **2h** (0.2 mmol, 0.076 g) and potassium vinyltrifluoroborate (0.2 mmol, 0.027 g) afforded compound **4i** (0.057 g, 87 % yield) as a white solid mp 238 °C (decomp.). ¹H NMR (400 MHz, CDCl₃): δ 8.25 (d, *J* = 8.4 Hz, 2H), 7.98-7.93 (m, 4H), 7.72-7.67 (m, 4H), 7.56-7.49 (m, 3H), 7.34 (d, *J* = 16.4 Hz, 1H), 7.25 (d, *J* = 16.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 152.8; 152.6; 147.1; 143.6; 138.9; 132.5; 131.4; 129.3; 127.9; 127.2; 124.4; 123.7; 123.1. HRMS (TOF MS ESI⁺): calcd for C₂₀H₁₆N₃O₂ (M+H⁺) 330.1243; found 330.1246.

(E)-2-(4-(4-nitrostyryl)phenyl)benzothiazole 4j. The reaction of 4-nitrobenzenediazonium tosylate **2a** (0.2 mmol, 0.064 g), 4-(benzo[d]thiazol-2-yl)benzenediazonium tosylate **2g** (0.2 mmol, 0.085 g) and potassium vinyltrifluoroborate (0.2 mmol, 0.027 g) afforded compound **4j** (0.056 g, 78 % yield) as a white solid mp 249 °C (decomp.). ¹H NMR (400 MHz, CDCl₃): δ 8.25 (d, *J* = 8.8 Hz, 2H), 8.14 (d, *J* = 8.4 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 3H), 7.54-7.50 (t, *J* = 7.2 Hz, 1H), 7.43-7.40 (t, *J* = 7.2, 6.8 Hz, 1H), 7.32 (d, *J* = 16.0 Hz, 1H), 7.26 (d, *J* = 16.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 143.5; 138.9; 132.3; 128.2; 128.0; 127.7; 127.3; 126.7; 125.6; 124.4; 123.4; 121.8. HRMS (TOF MS ESI⁺): calcd for C₂₁H₁₅N₂O₂S (M+H⁺) 359.0854; found 359.0852.

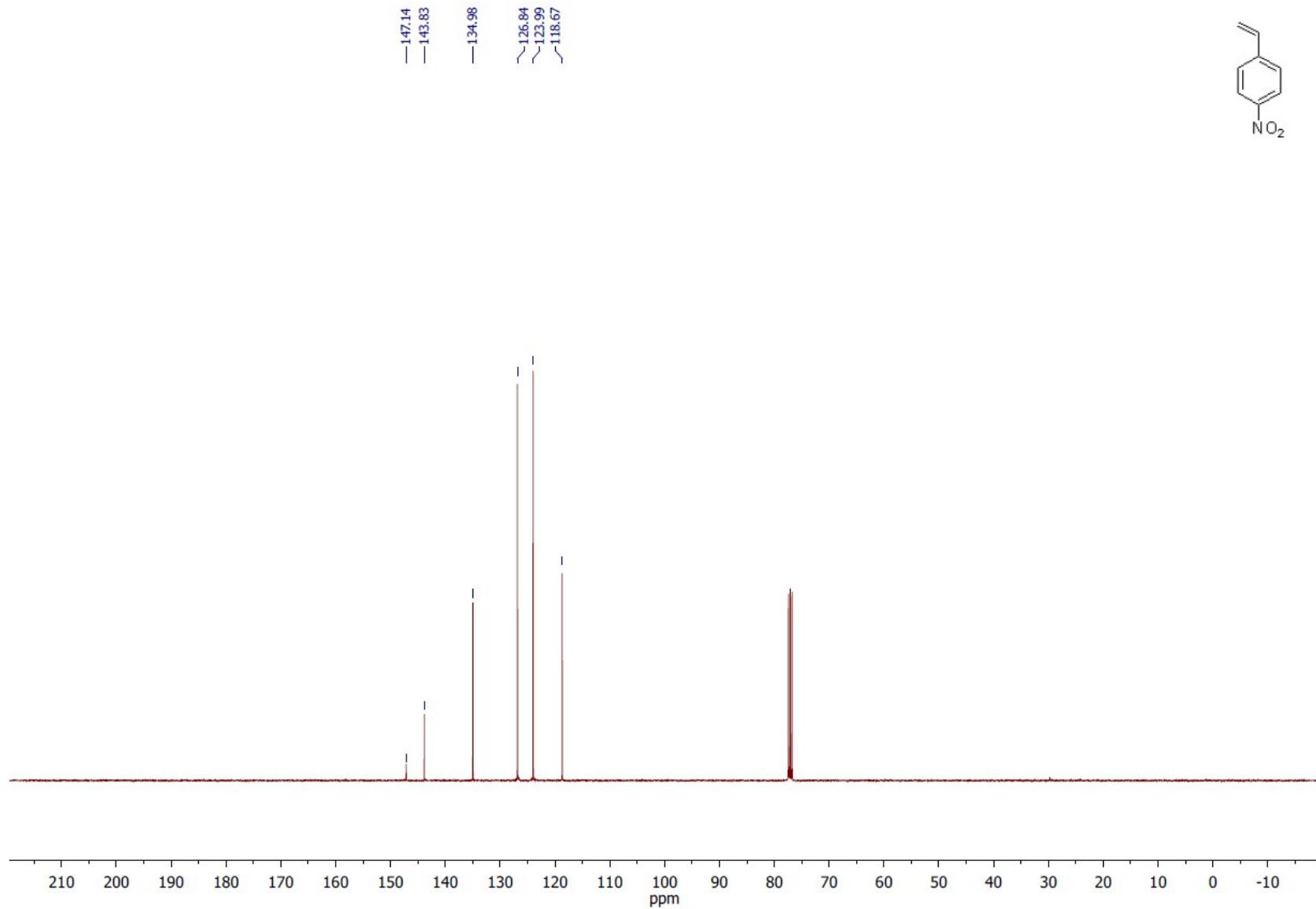
(E)-1-(4-methylstyryl)-2-nitrobenzene 4k. The reaction of 2-nitrobenzenediazonium tosylate **2j** (0.2 mmol, 0.064 g), 4-methylbenzenediazonium tosylate **2n** (0.2 mmol, 0.058 g), and potassium vinyltrifluoroborate (0.2 mmol, 0.027 g) afforded compound **4k** (0.023 g, 48 % yield) as an orange oil.¹⁹ ¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.61-7.57 (m, 1H), 7.53 (s, 1H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.40-7.37 (m, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.12-7.05 (m, 2H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 138.7; 133.8; 133.7; 133.5; 133.0; 129.5; 128.0; 127.7; 127.0; 124.8; 122.3; 120.0; 21.3.

4. Spectra of products

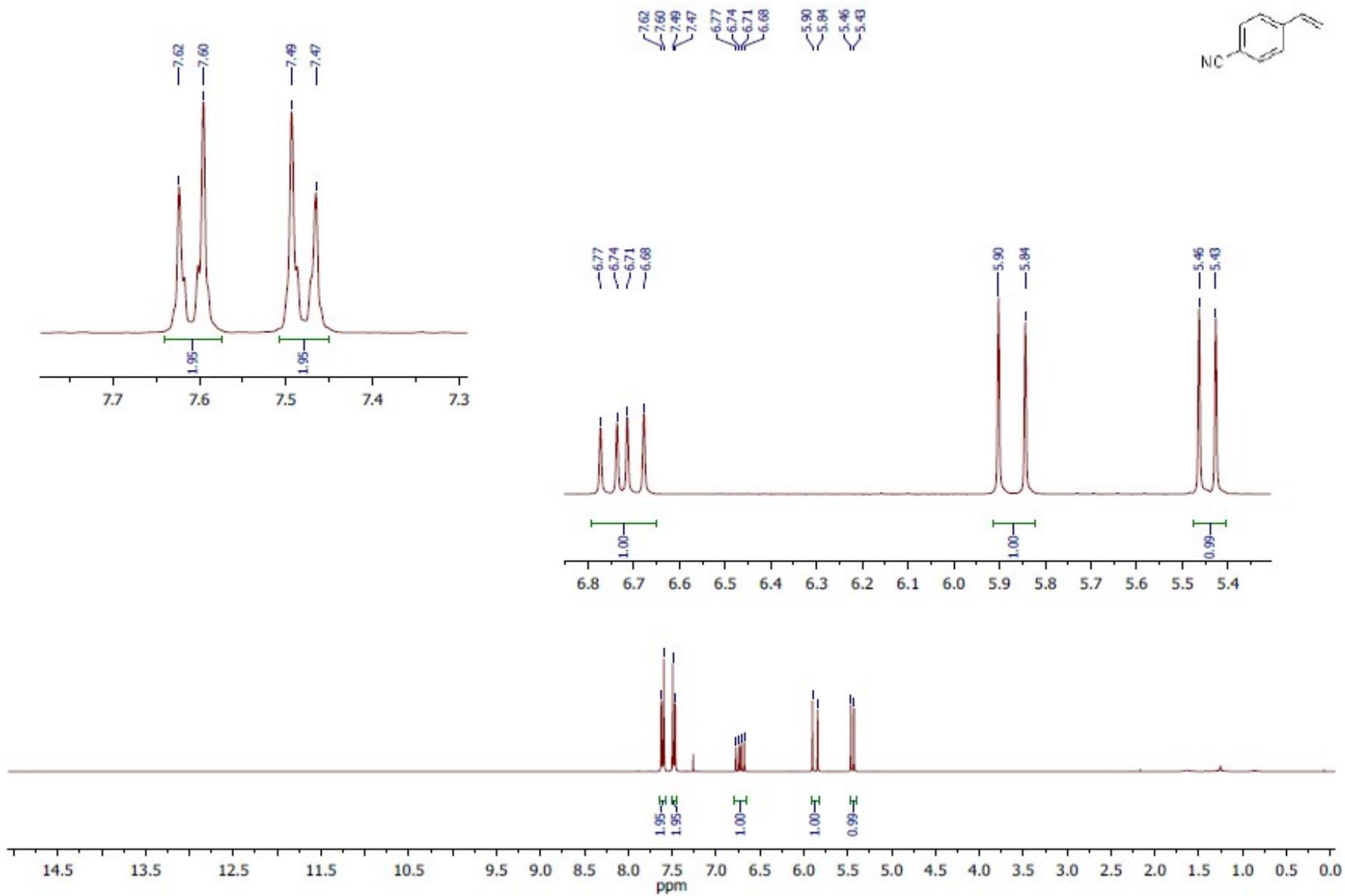
NMR ^1H spectrum of **1-nitro-4-vinylbenzene (3a)**



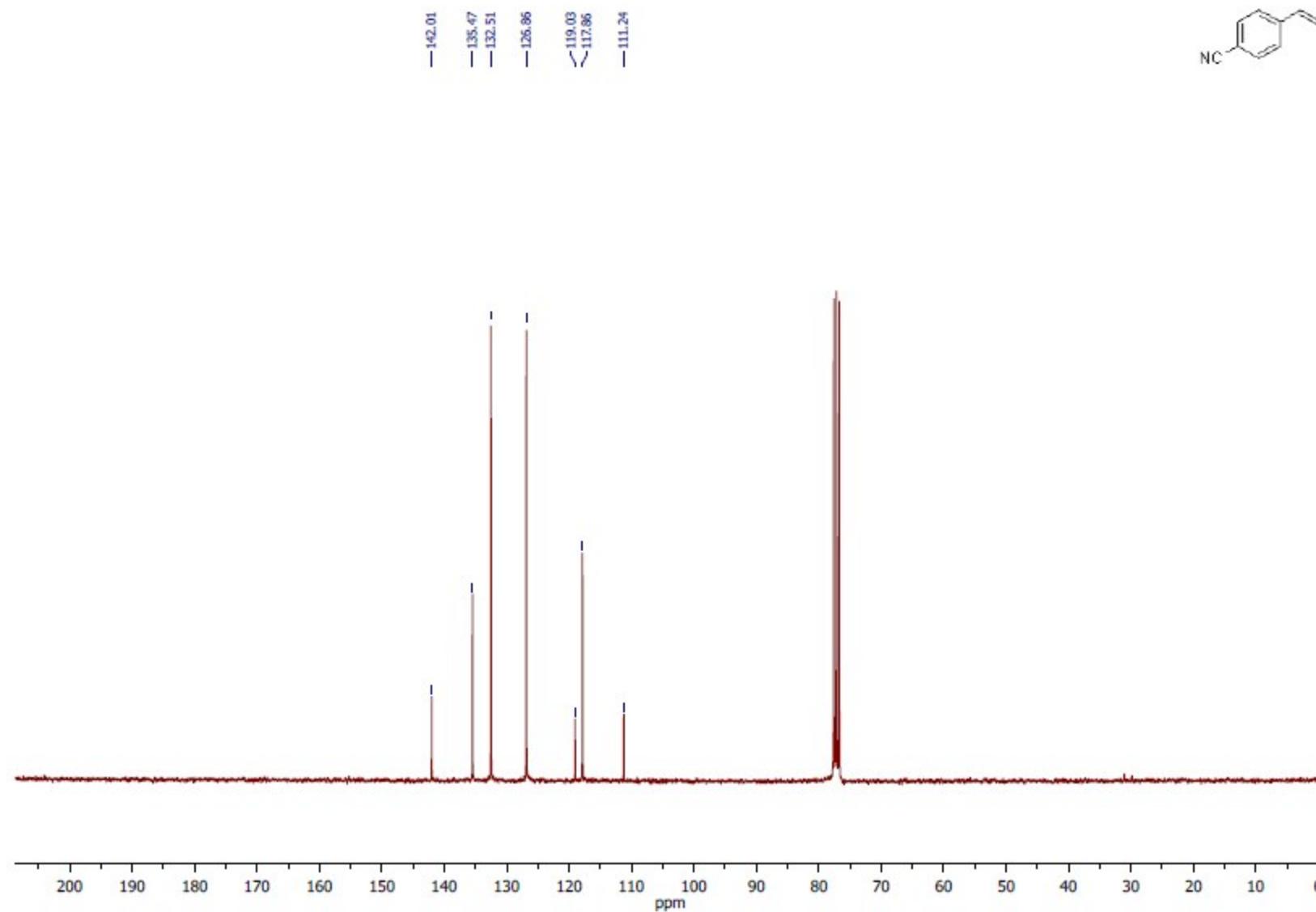
NMR ^{13}C spectrum of **1-nitro-4-vinylbenzene (3a)**



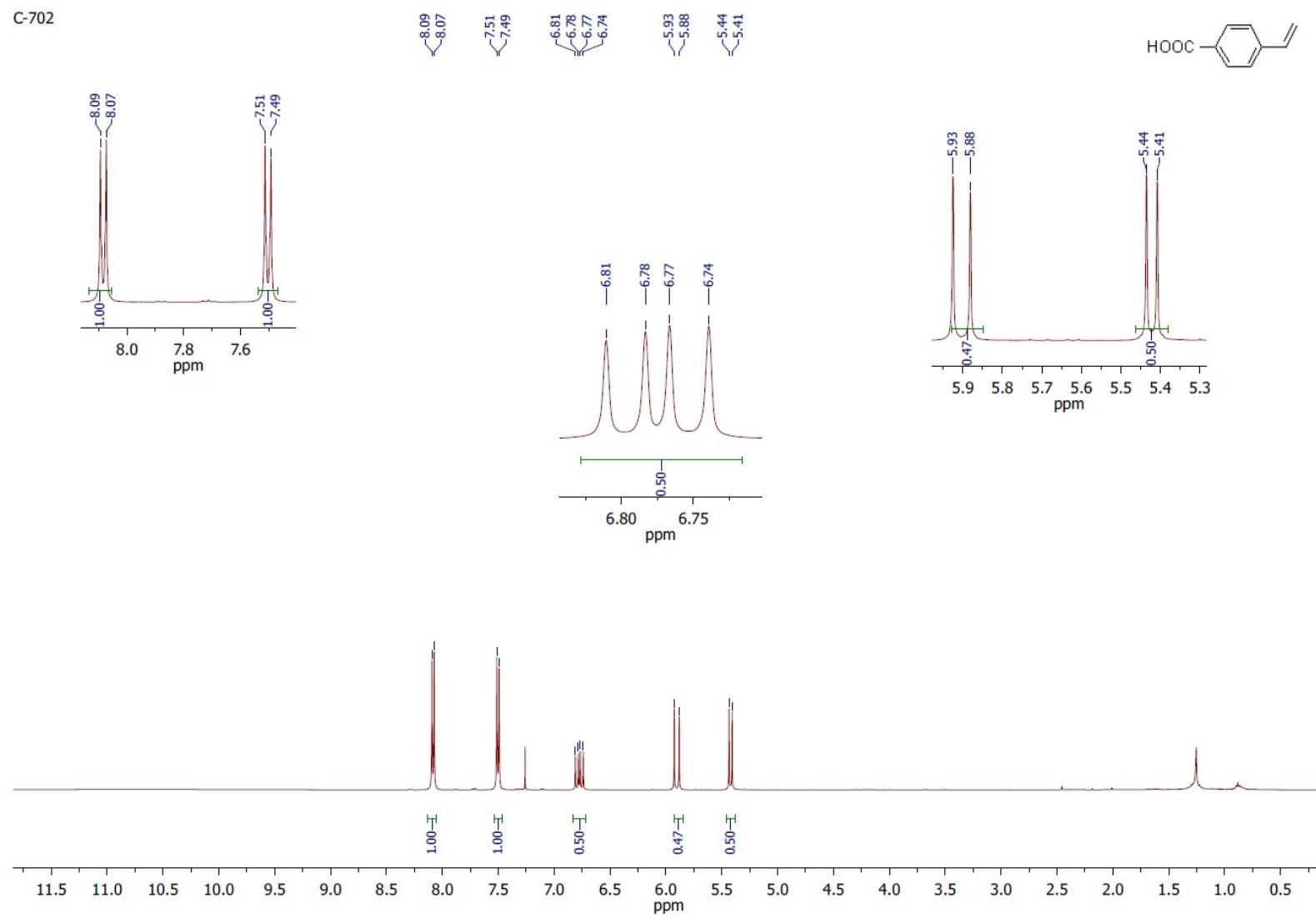
NMR ^1H spectrum of 4-vinylbenzonitrile (**3b**).



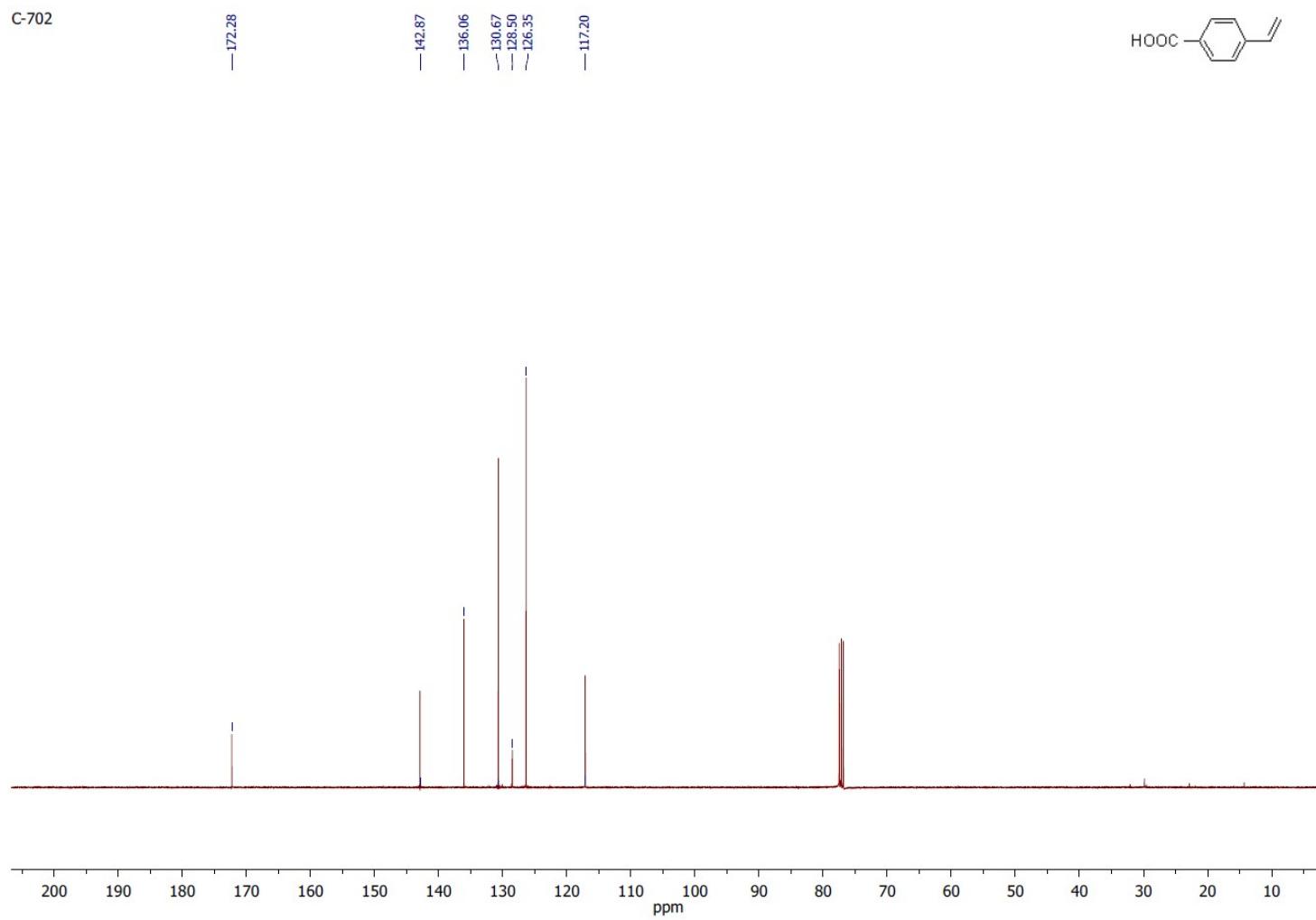
NMR ^{13}C spectrum of **4-vinylbenzonitrile (3b)**.



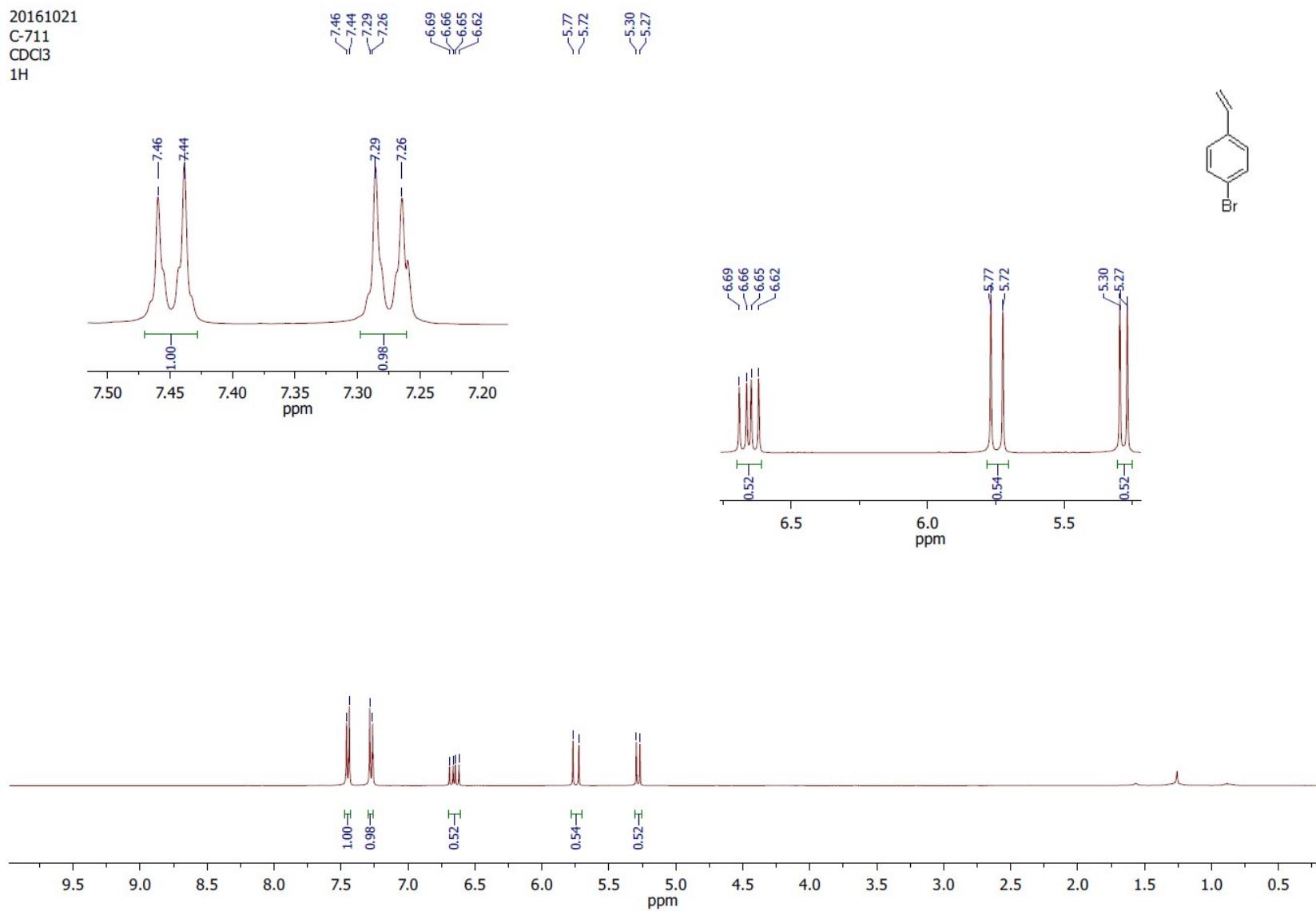
NMR ^1H spectrum of **4-vinylbenzoic acid (3c)**.



NMR ^{13}C spectrum of **4-vinylbenzoic acid (3c)**.

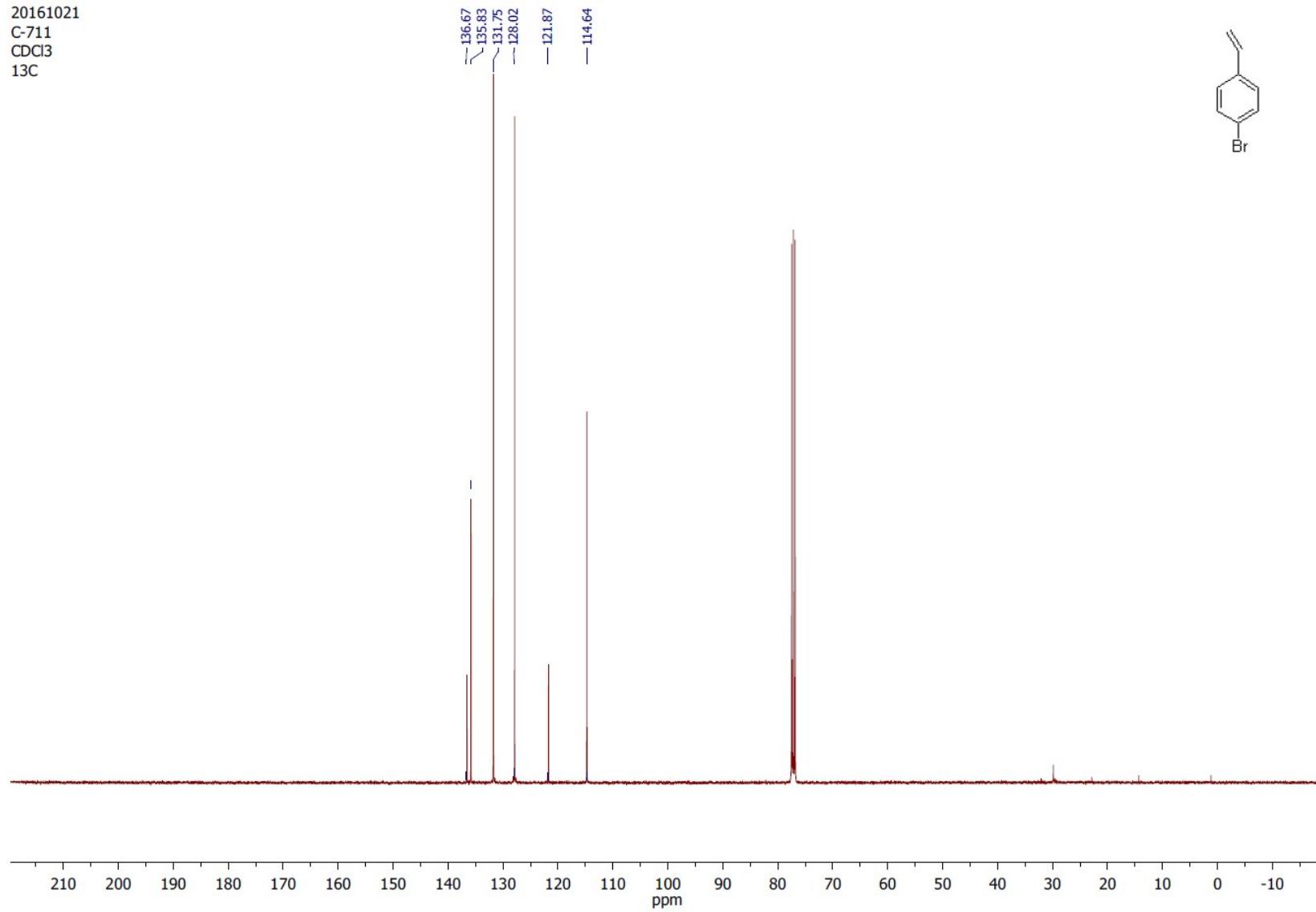


NMR ^1H spectrum of **1-bromo-4-vinylbenzene (3d)**.

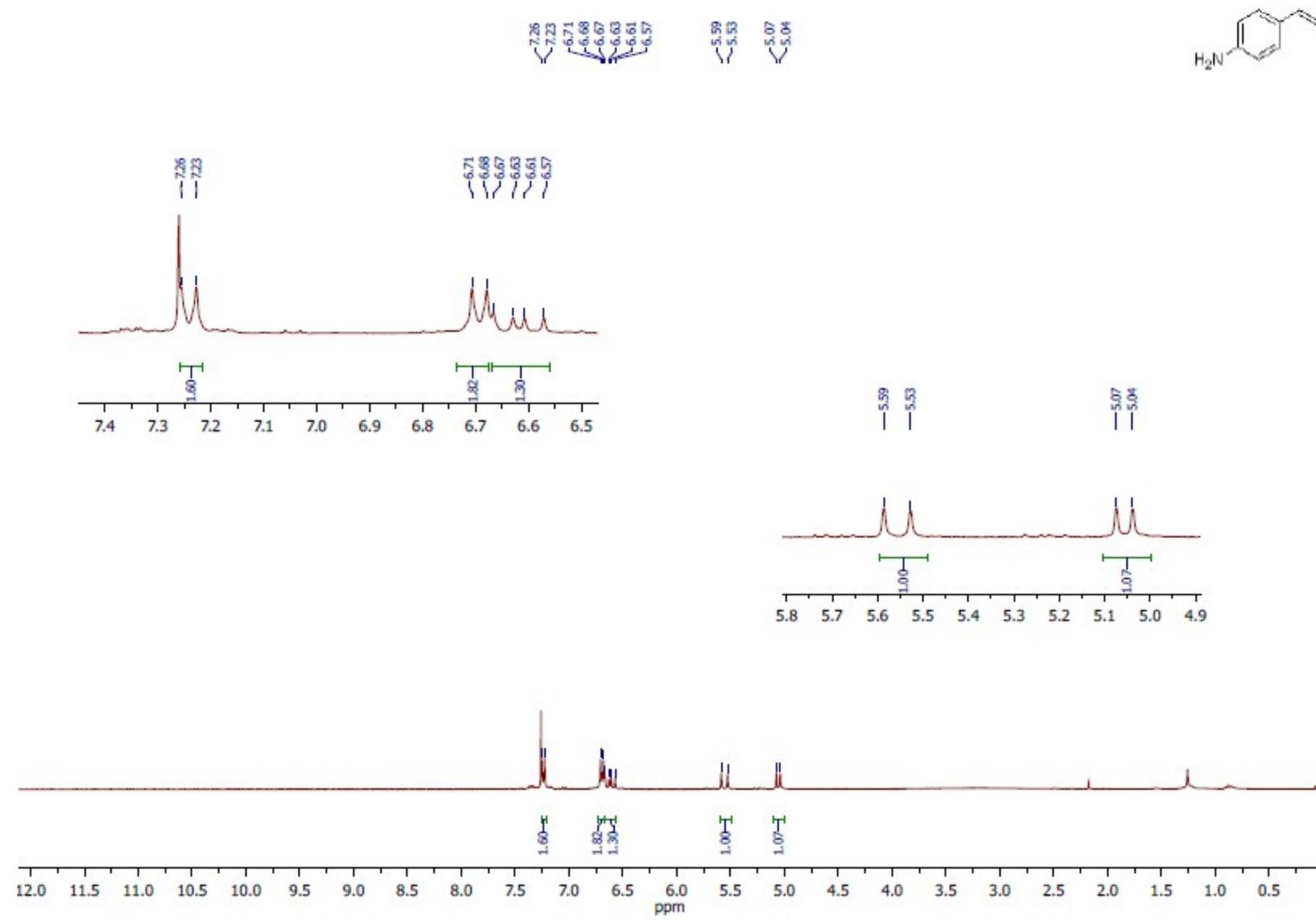


NMR ^{13}C spectrum of **1-bromo-4-vinylbenzene (3d)**.

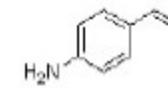
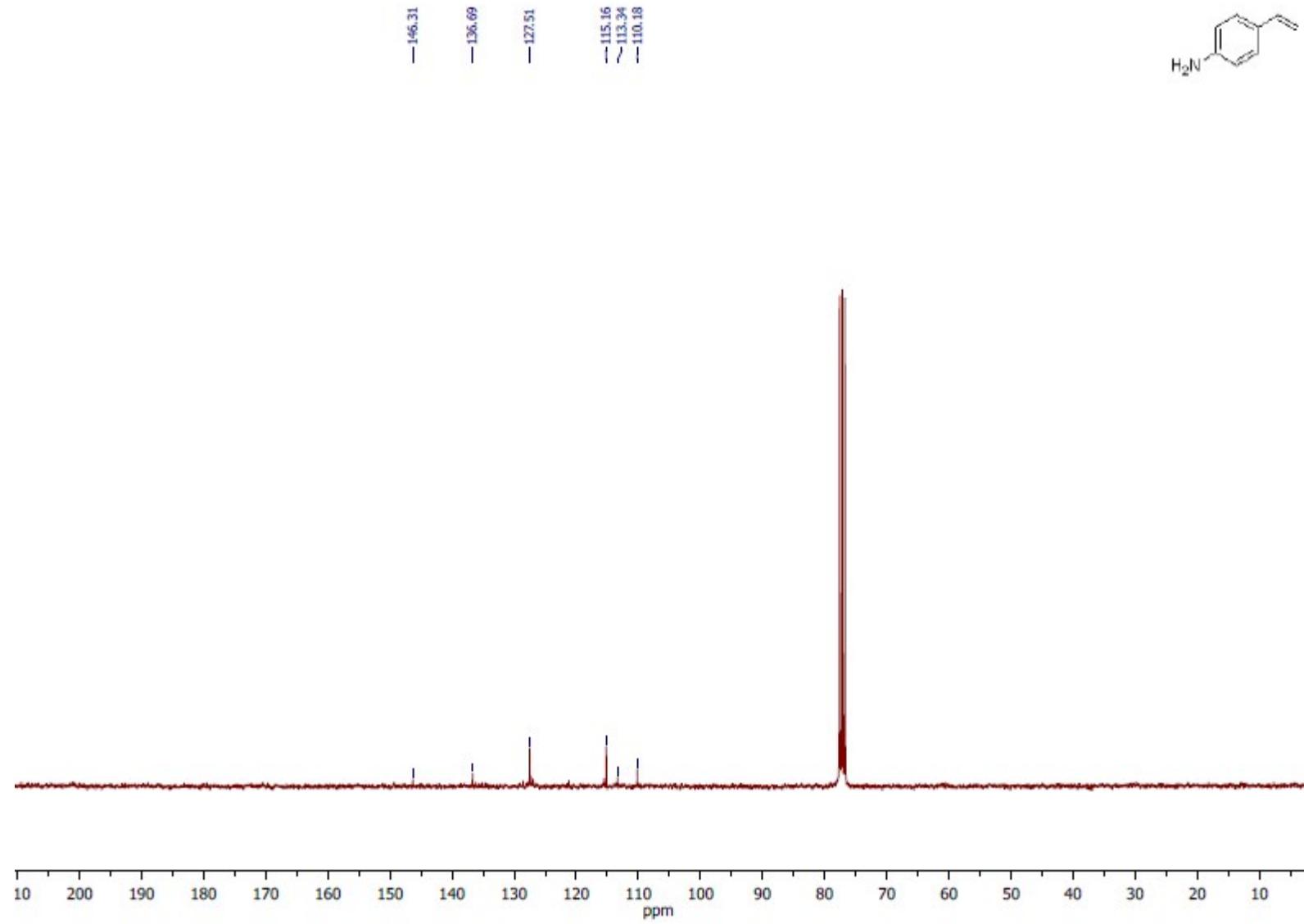
20161021
C-711
 CDCl_3
 ^{13}C



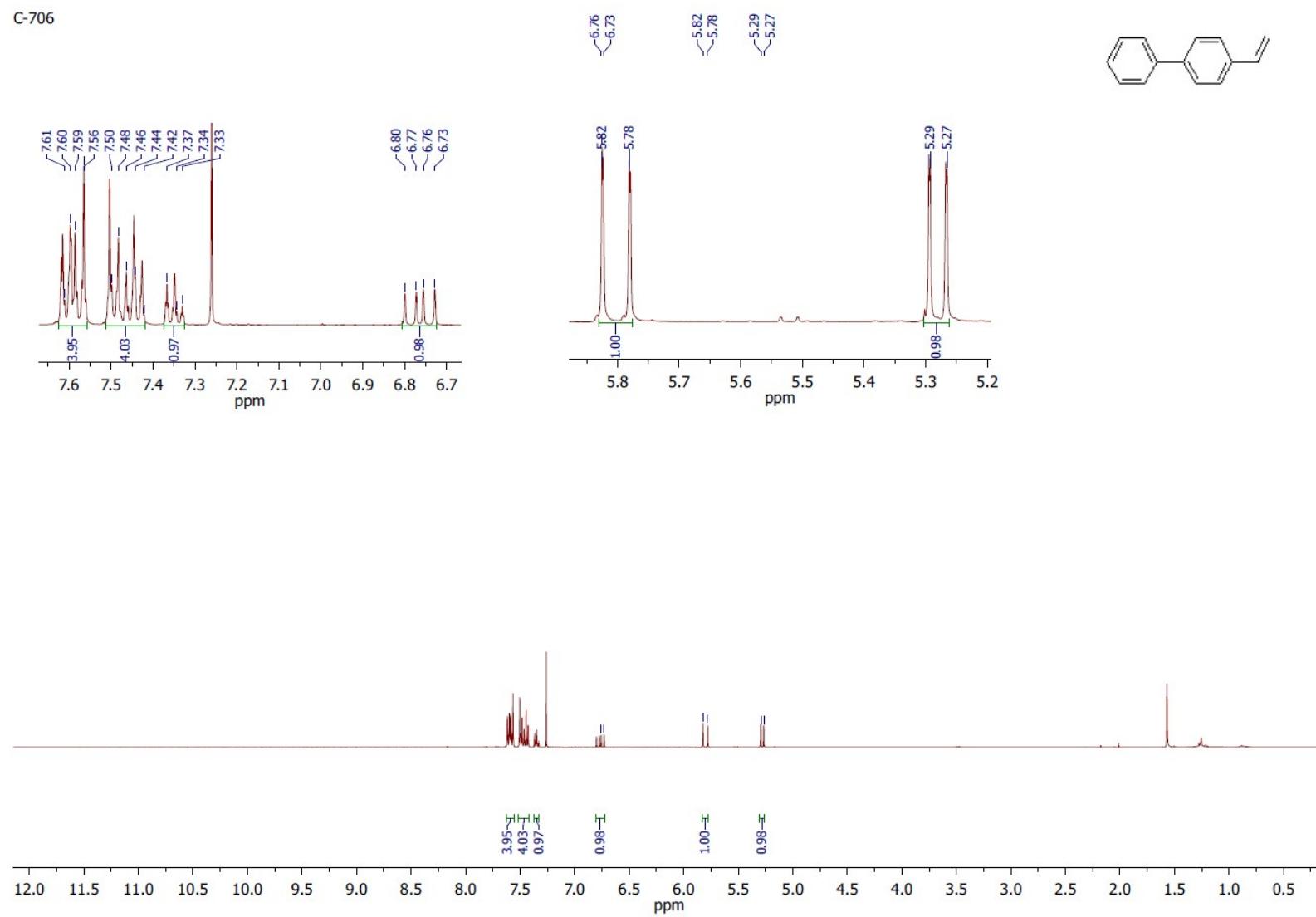
NMR ^1H spectrum of **4-vinylaniline (3e)**.



NMR ^{13}C spectrum of **4-vinylaniline (3e)**.

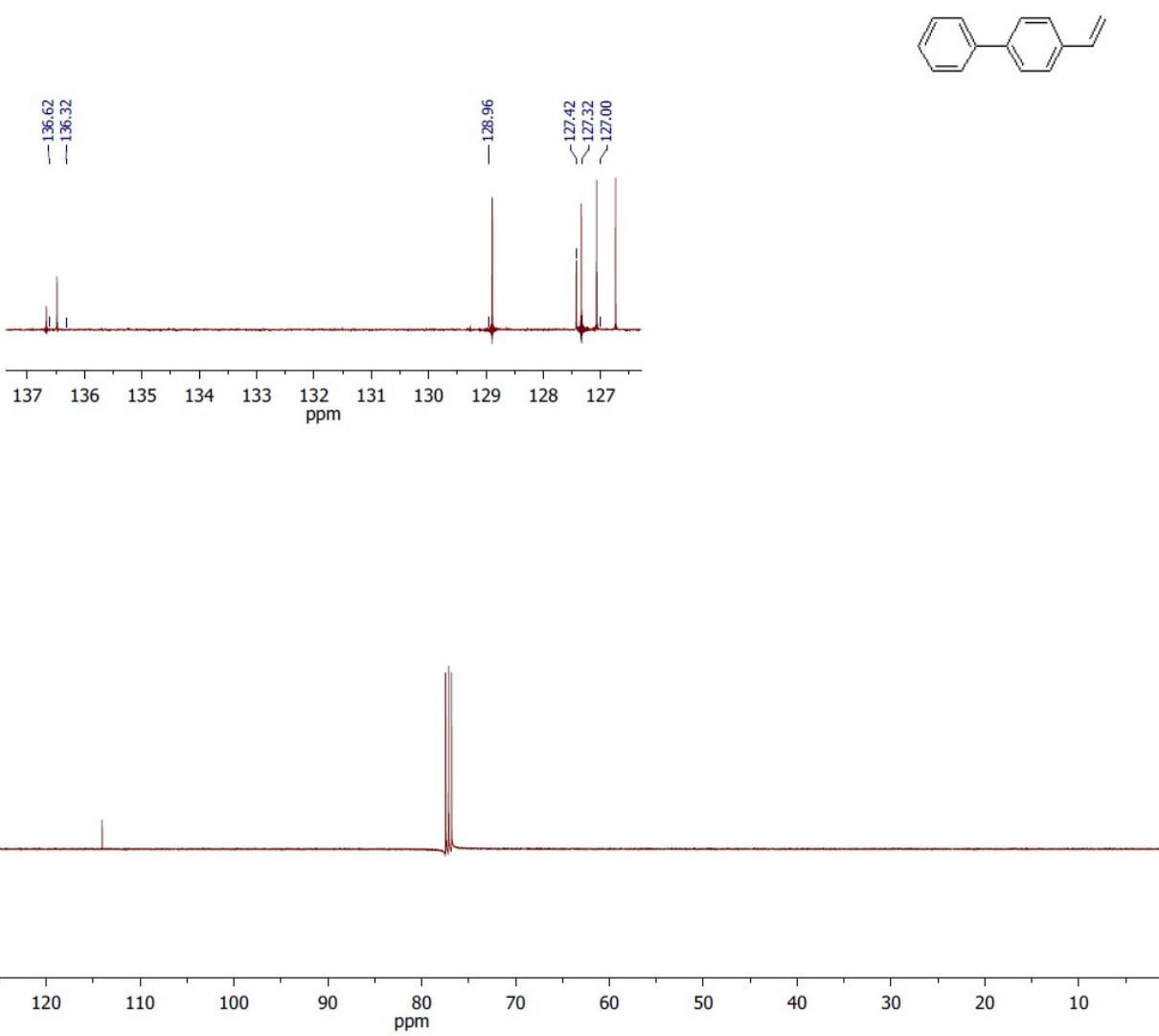


NMR ^1H spectrum of **4-vinyl-1,1'-biphenyl (3f)**

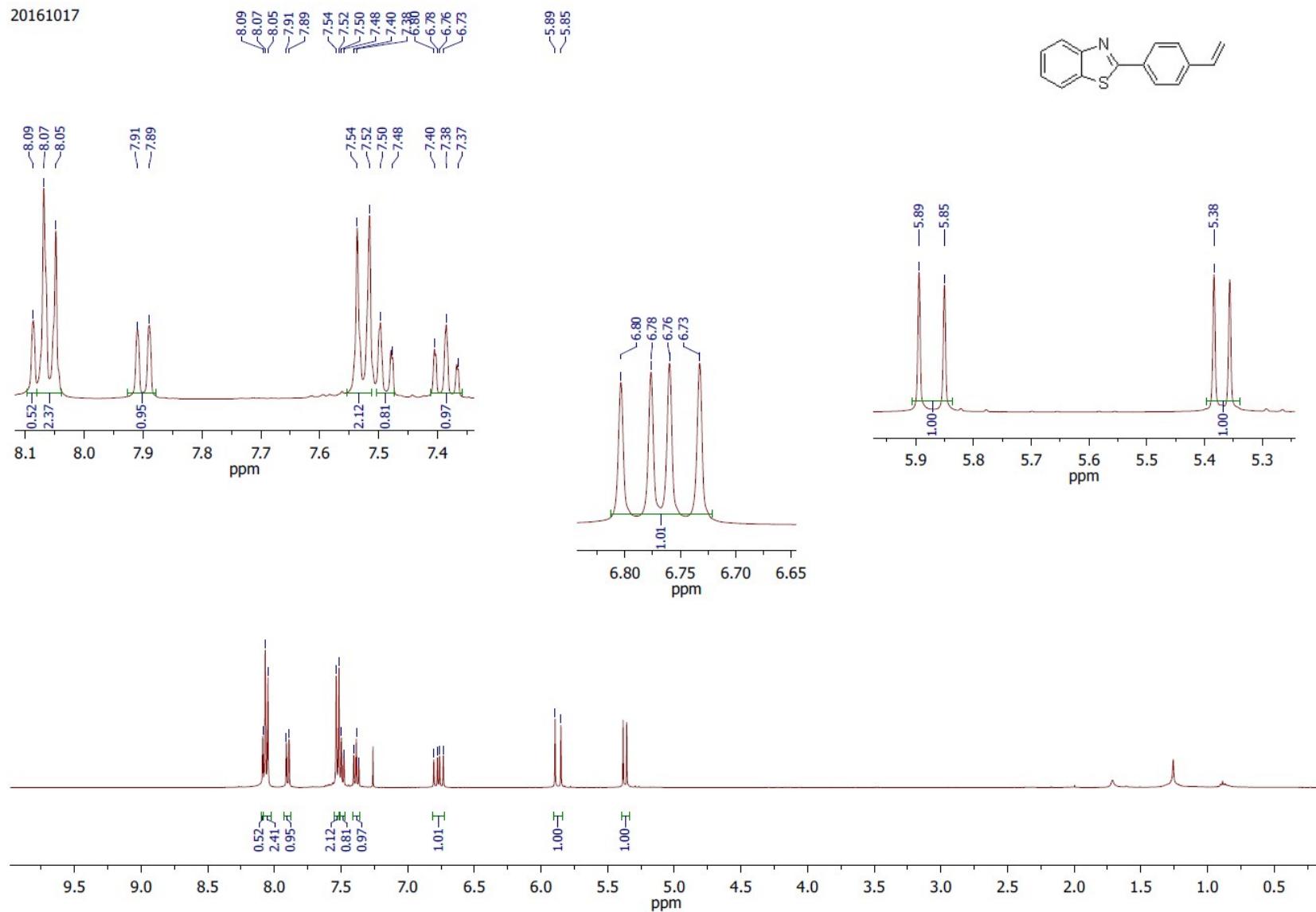


NMR ^{13}C spectrum of **4-vinyl-1,1'-biphenyl (3f)**

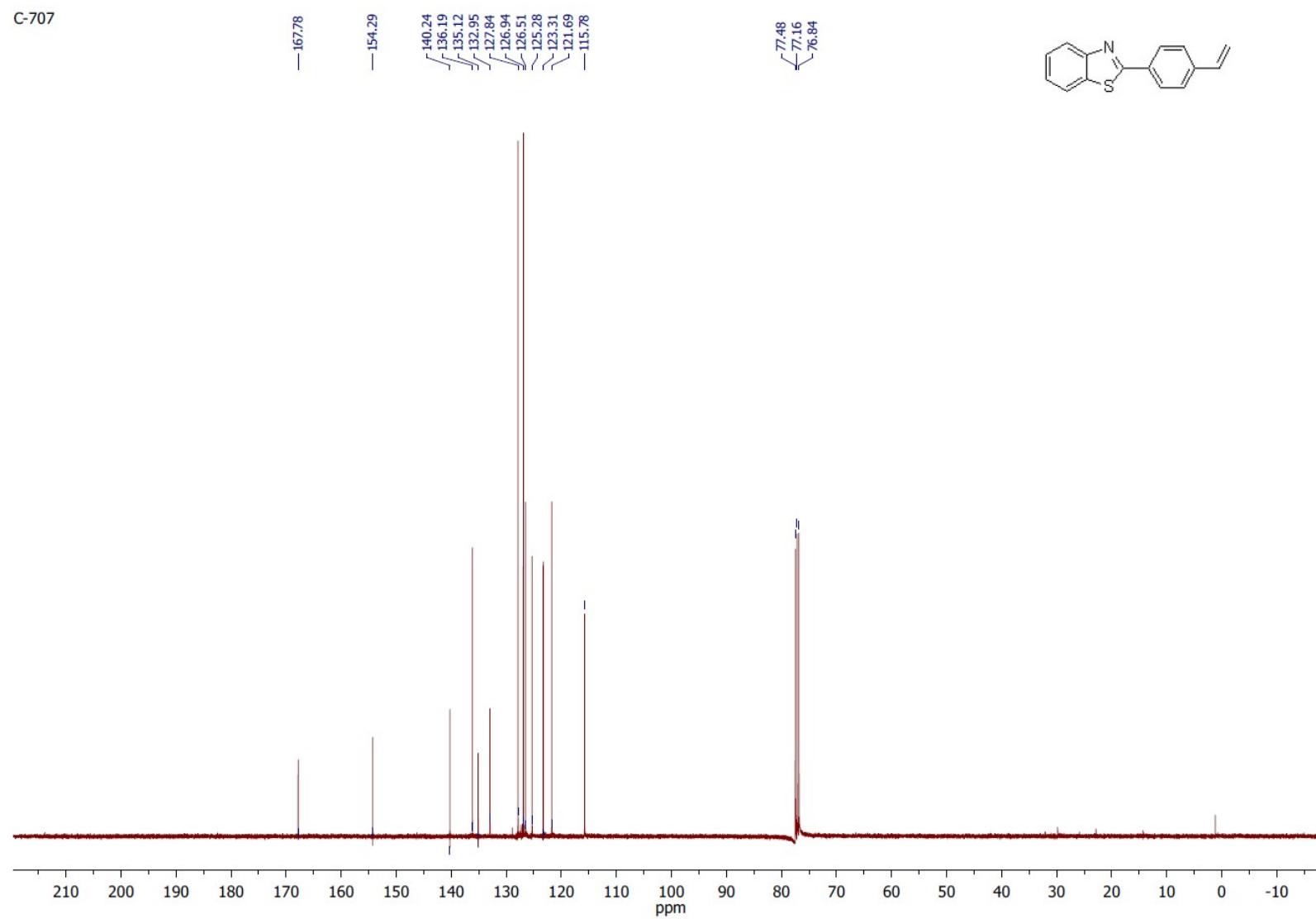
C-706



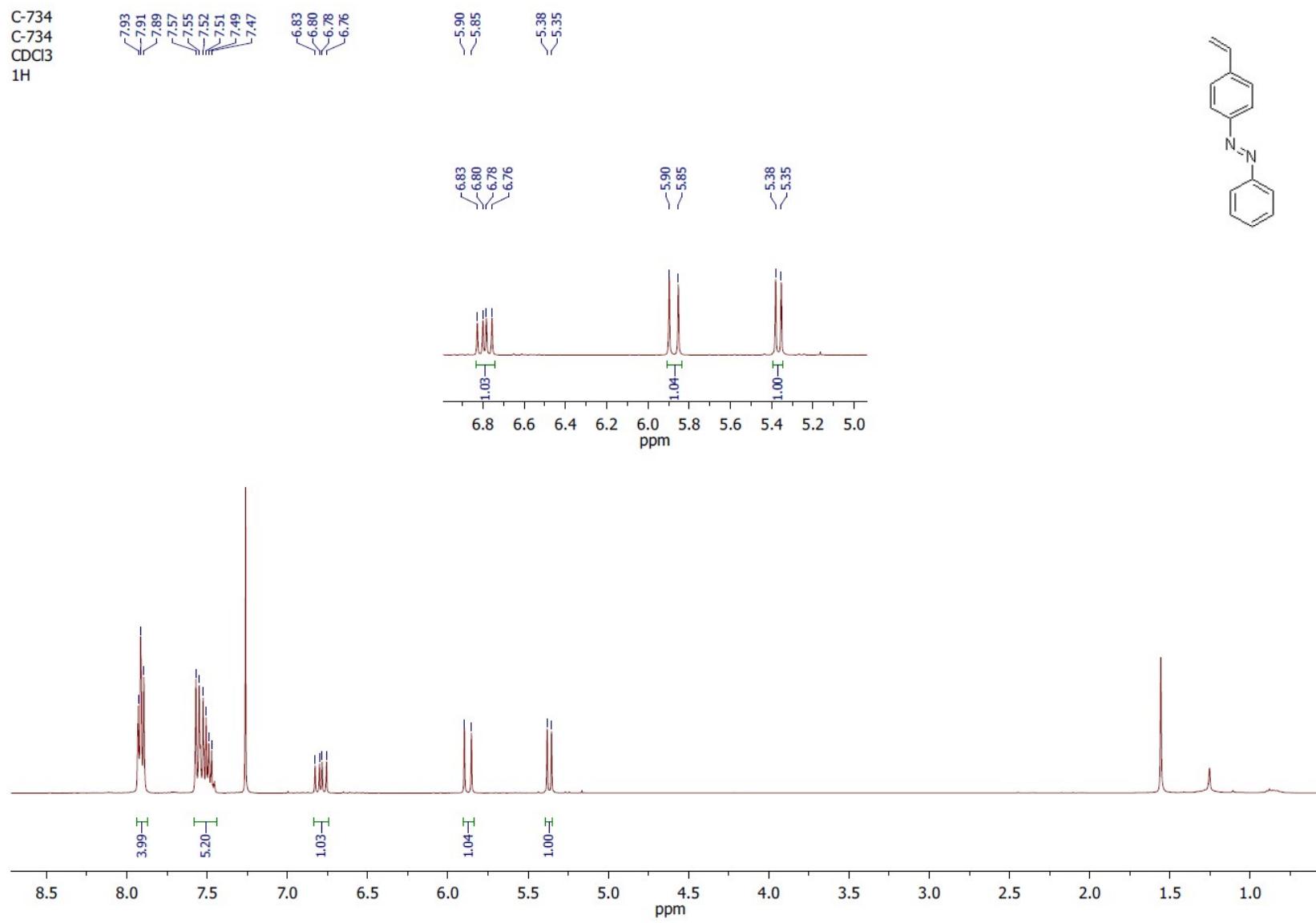
NMR ^1H spectrum of **2-(4-vinylphenyl)benzo[d]thiazole (3g)**.



NMR ^{13}C spectrum of **2-(4-vinylphenyl)benzo[d]thiazole (3g)**.

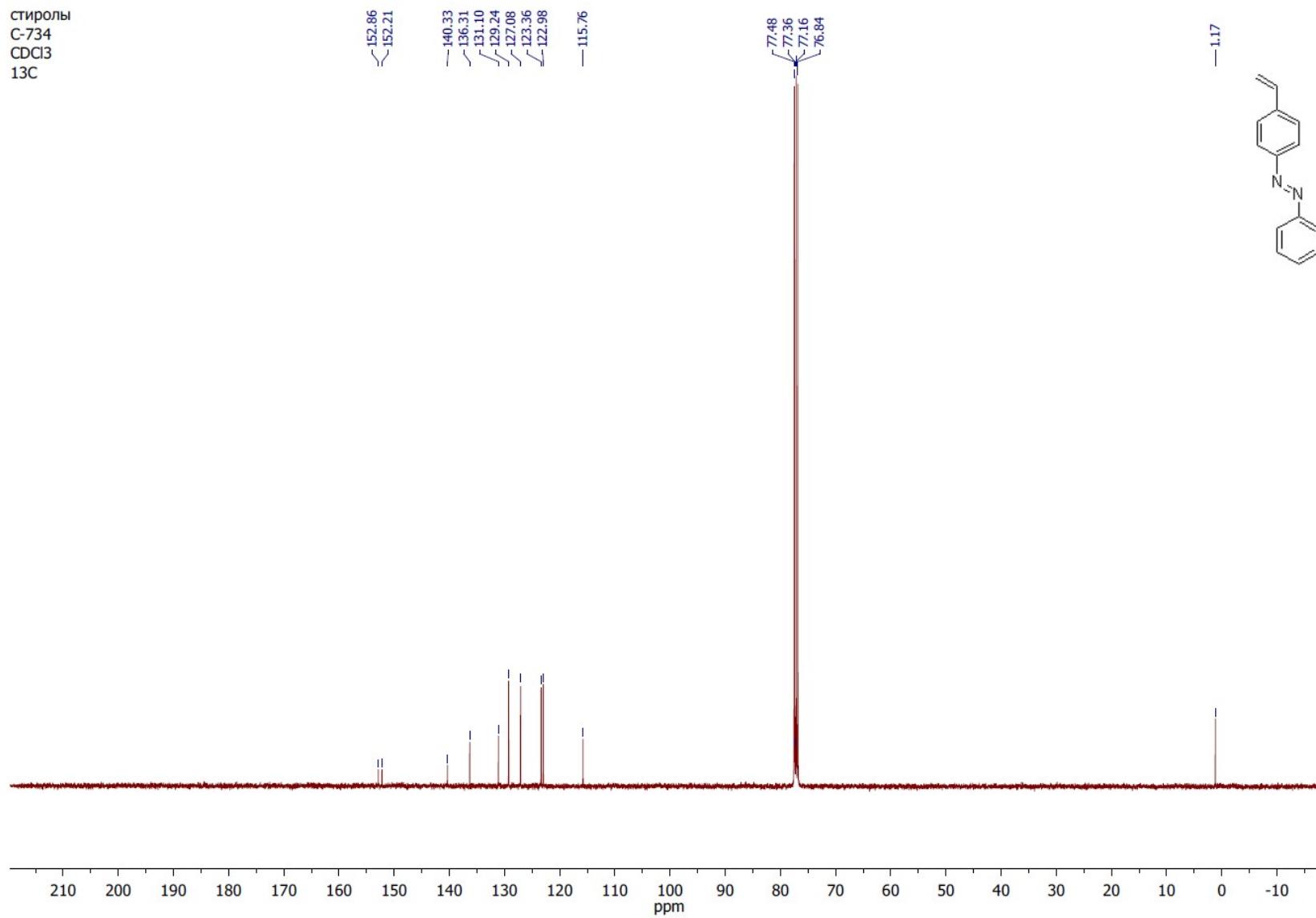


NMR ^1H spectrum of **(E)-1-phenyl-2-(4-vinylphenyl)diazene (3h)**.

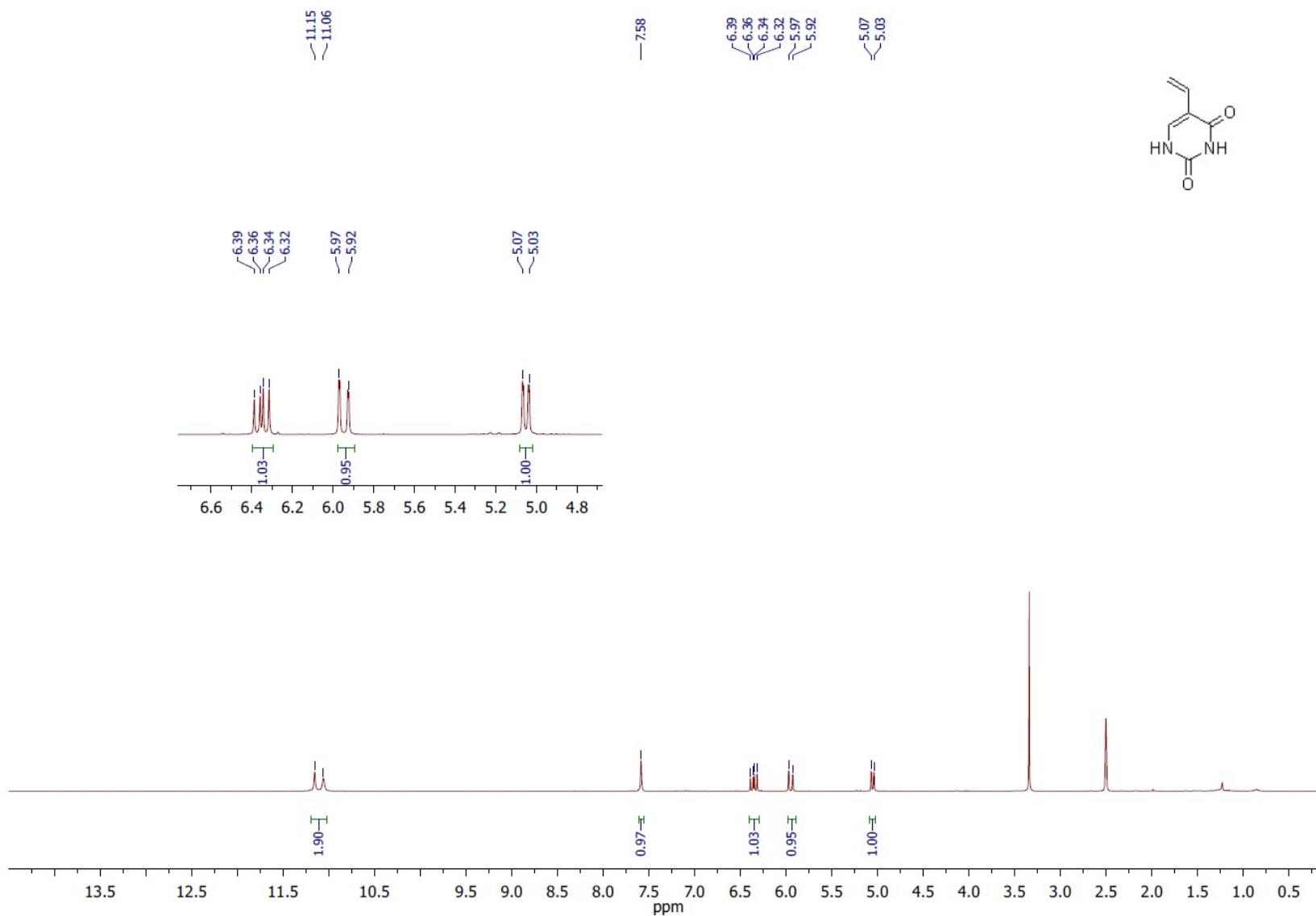


NMR ^{13}C spectrum of **(E)-1-phenyl-2-(4-vinylphenyl)diazene (3h)**.

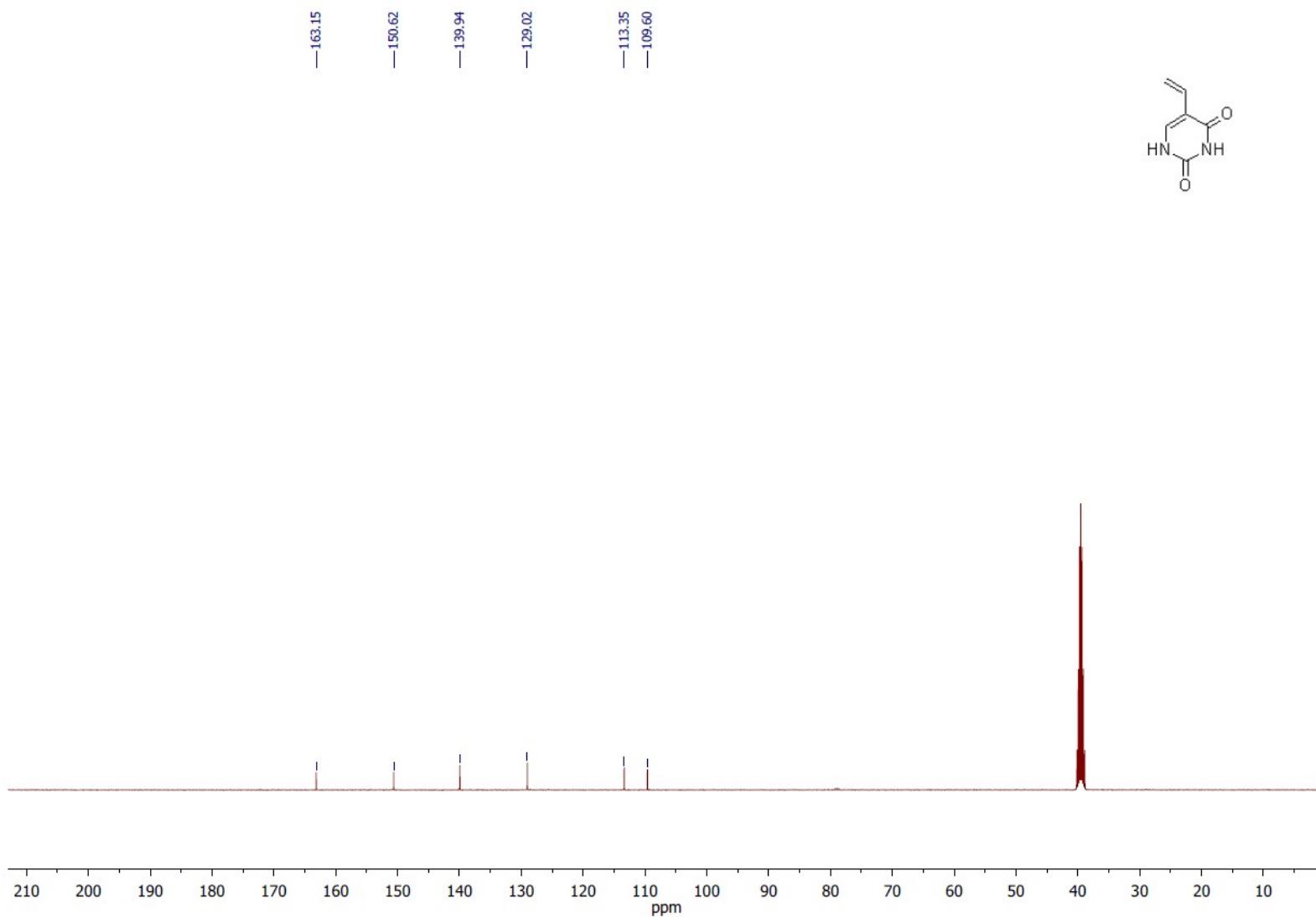
стиролы
C-734
 CDCl_3
 ^{13}C



NMR ^1H spectrum of **5-vinyluracil (3i)**

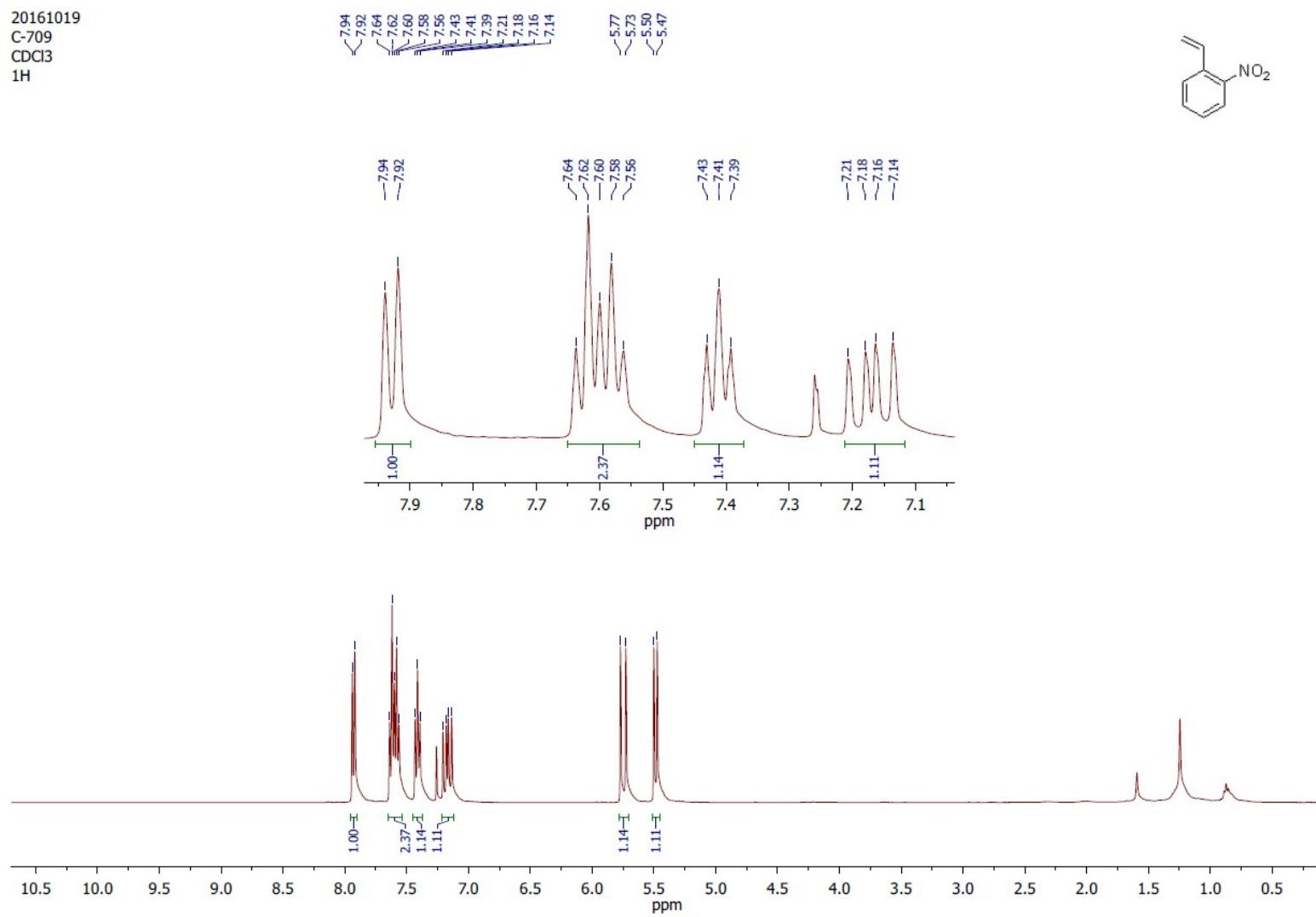


NMR ^{13}C spectrum of **5-vinyluracil (3i)**

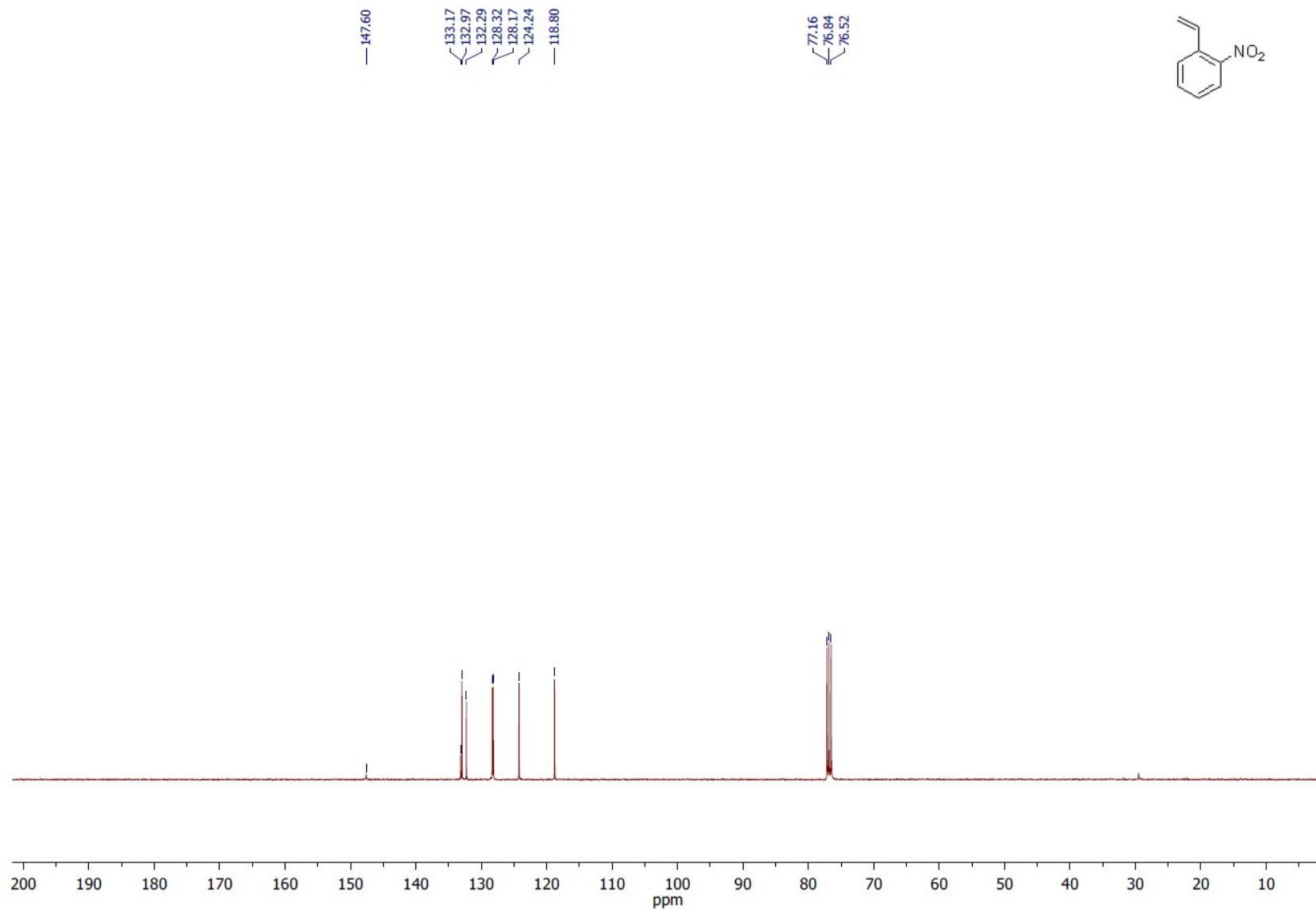


NMR ^1H spectrum of **1-nitro-2-vinylbenzene (3j)**.

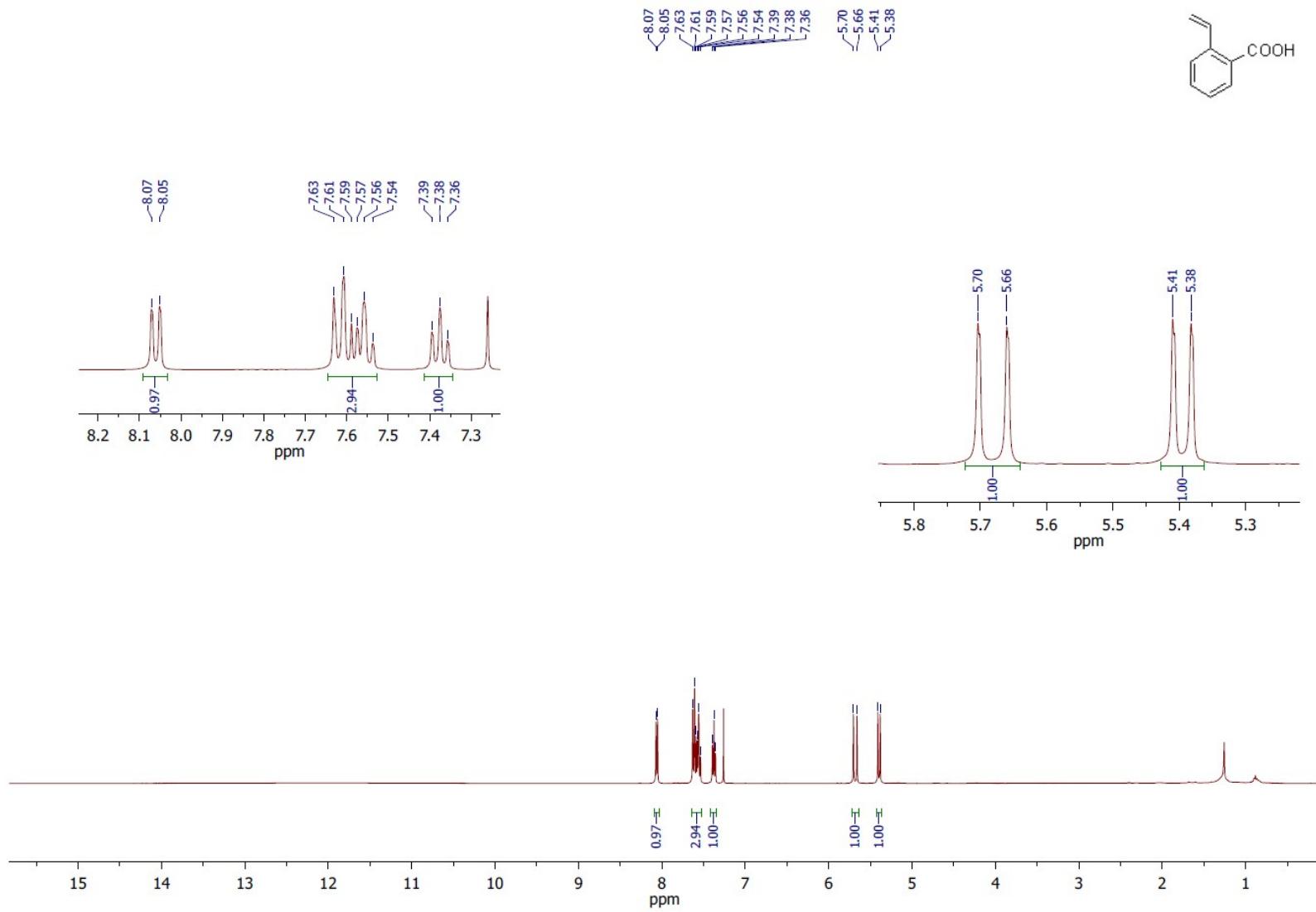
20161019
C-709
 CDCl_3
 ^1H



NMR ^{13}C spectrum of **1-nitro-2-vinylbenzene (3j)**.



NMR ^1H spectrum of **2-vinylbenzoic acid (3k)**.



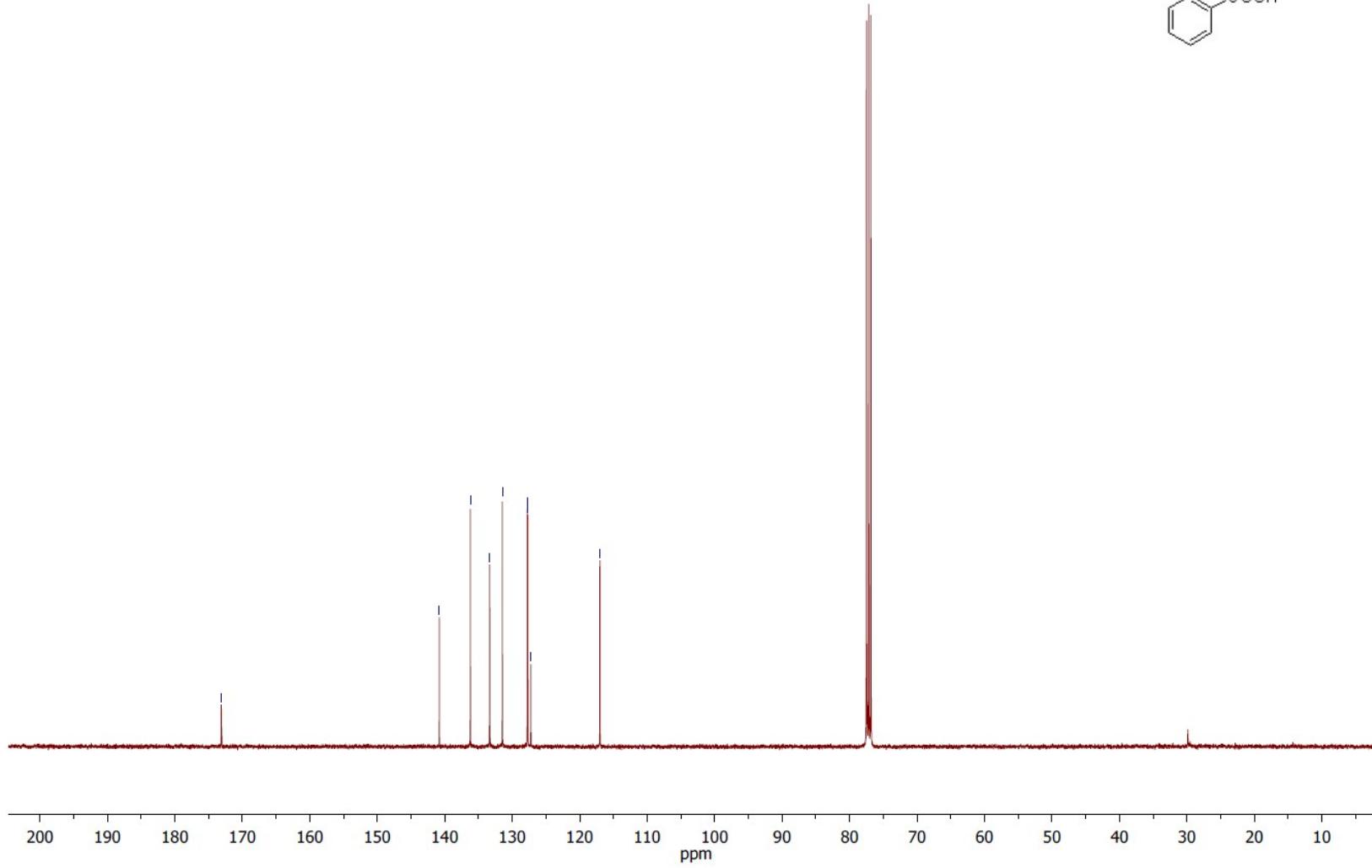
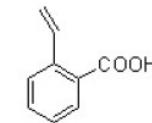
NMR ^{13}C spectrum of **2-vinylbenzoic acid (3k)**.

20161021
C-710
 CDCl_3
 ^{13}C

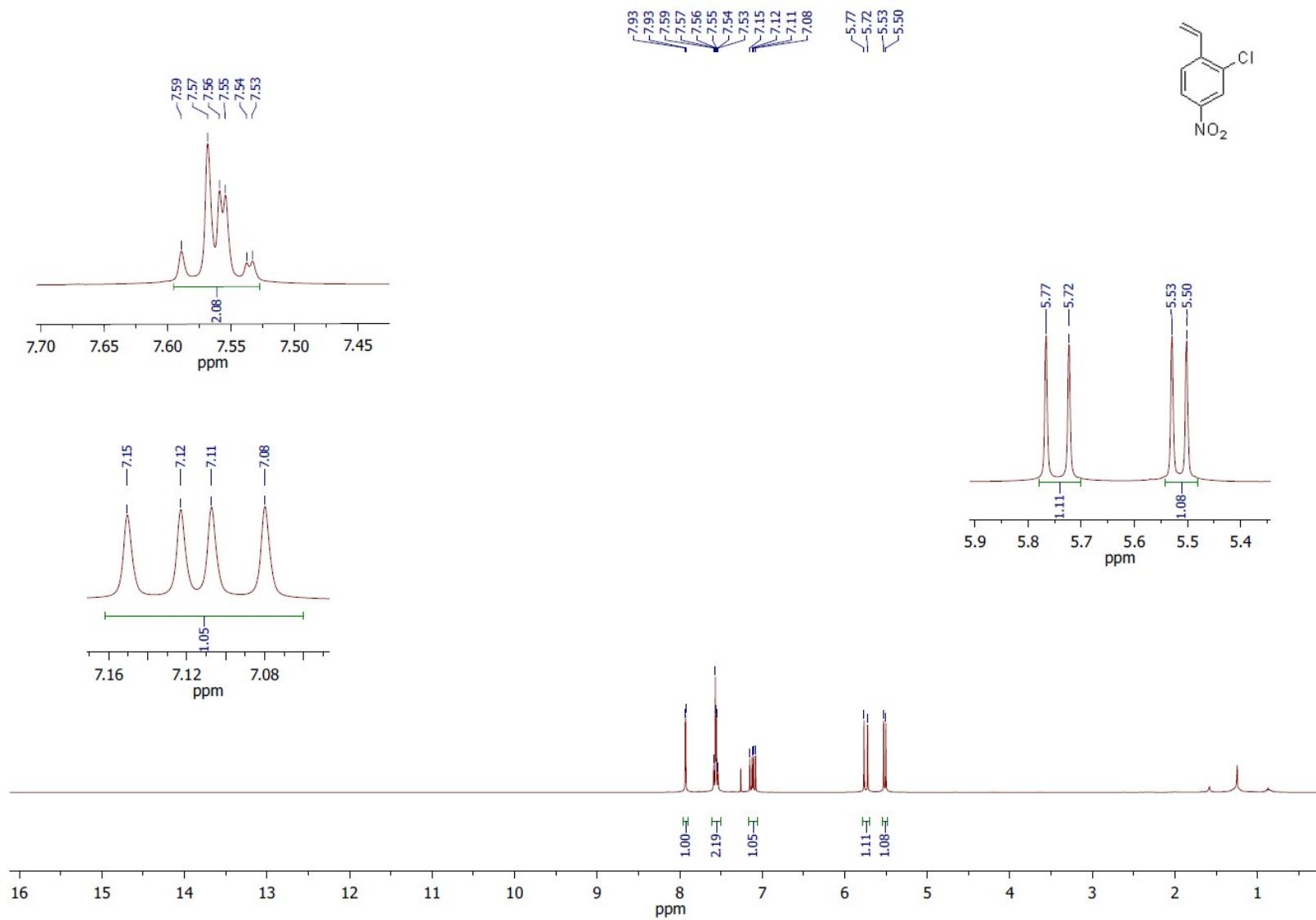
— 173.11

— 140.79
— 136.20
— 133.33
— 131.46
— 127.75
— 127.68
— 127.22

— 117.00



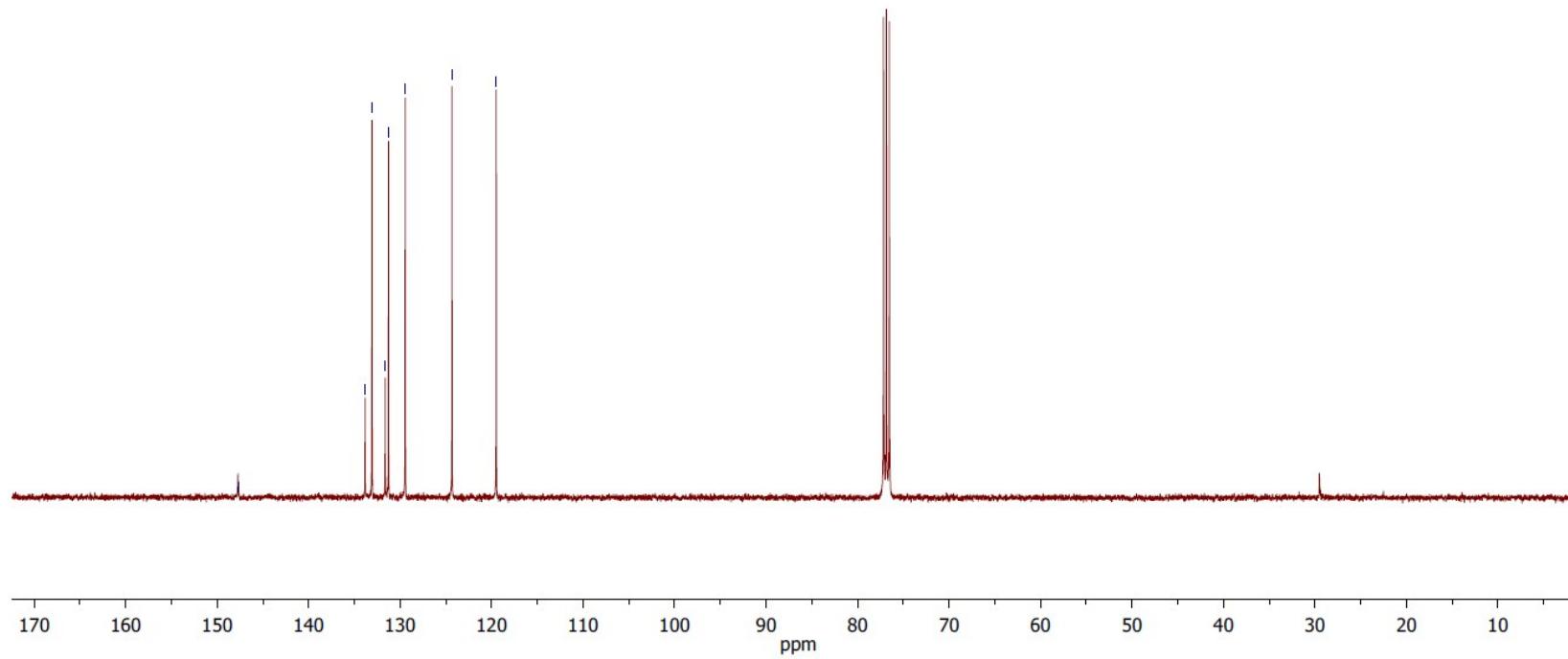
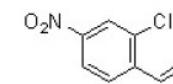
NMR ^1H spectrum of **2-chloro-4-nitro-1-vinylbenzene (3l)**.



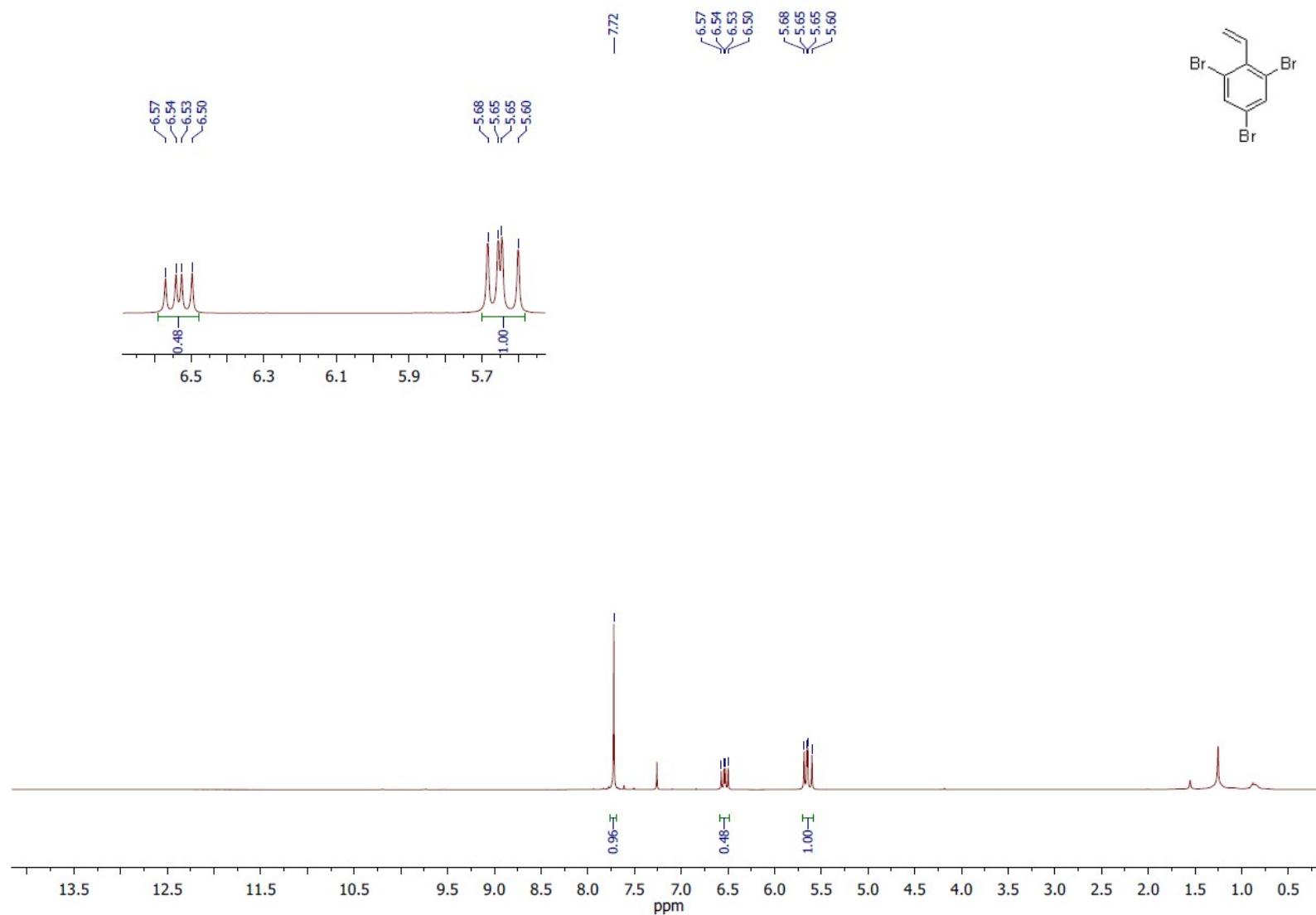
NMR ^{13}C spectrum of **2-chloro-4-nitro-1-vinylbenzene (3l)**.

20161028
C-713
 CDCl_3
 ^{13}C

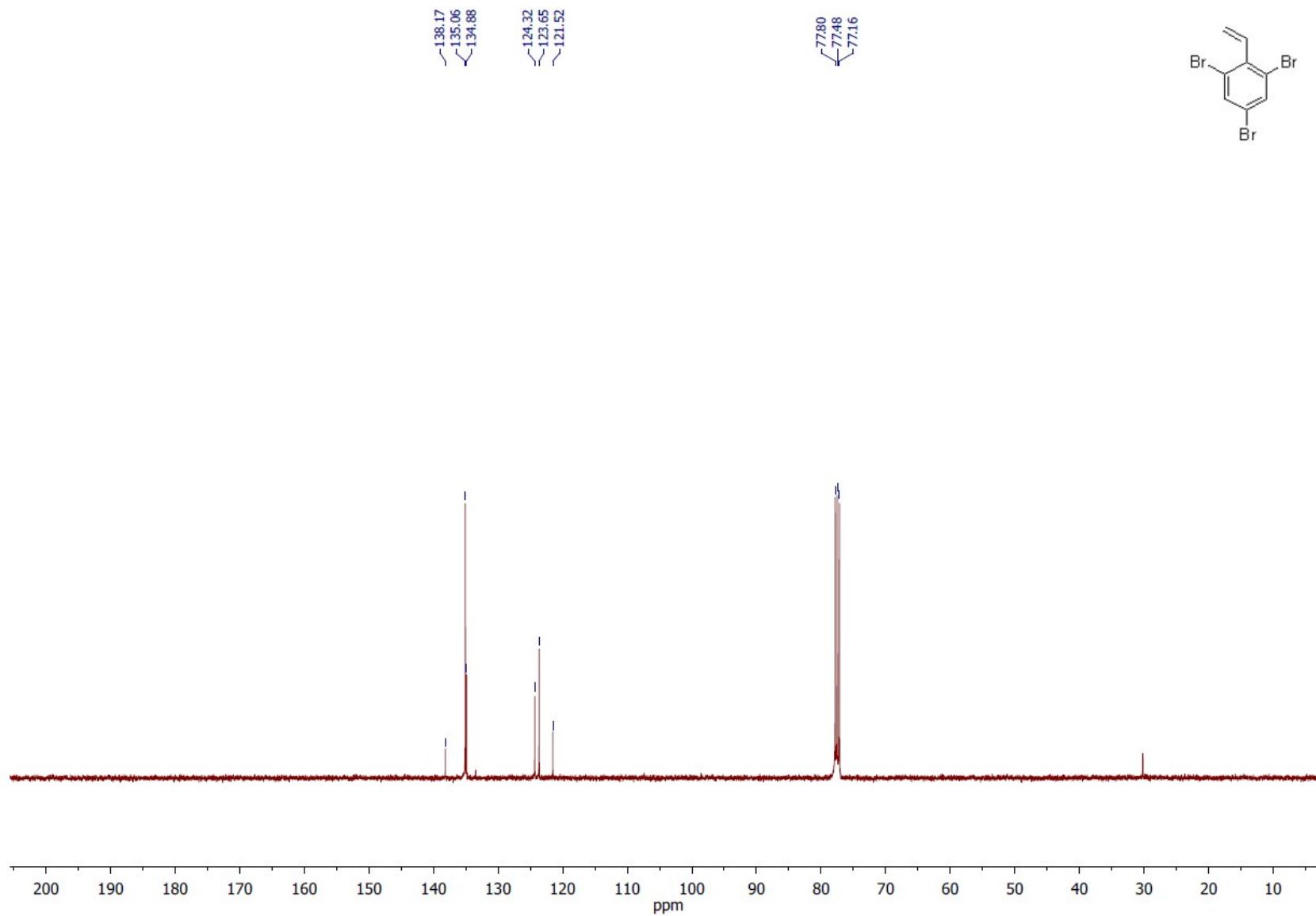
— 147.62
— 133.82
— 133.07
— 131.63
— 131.27
— 129.44
— 124.33
— 119.49



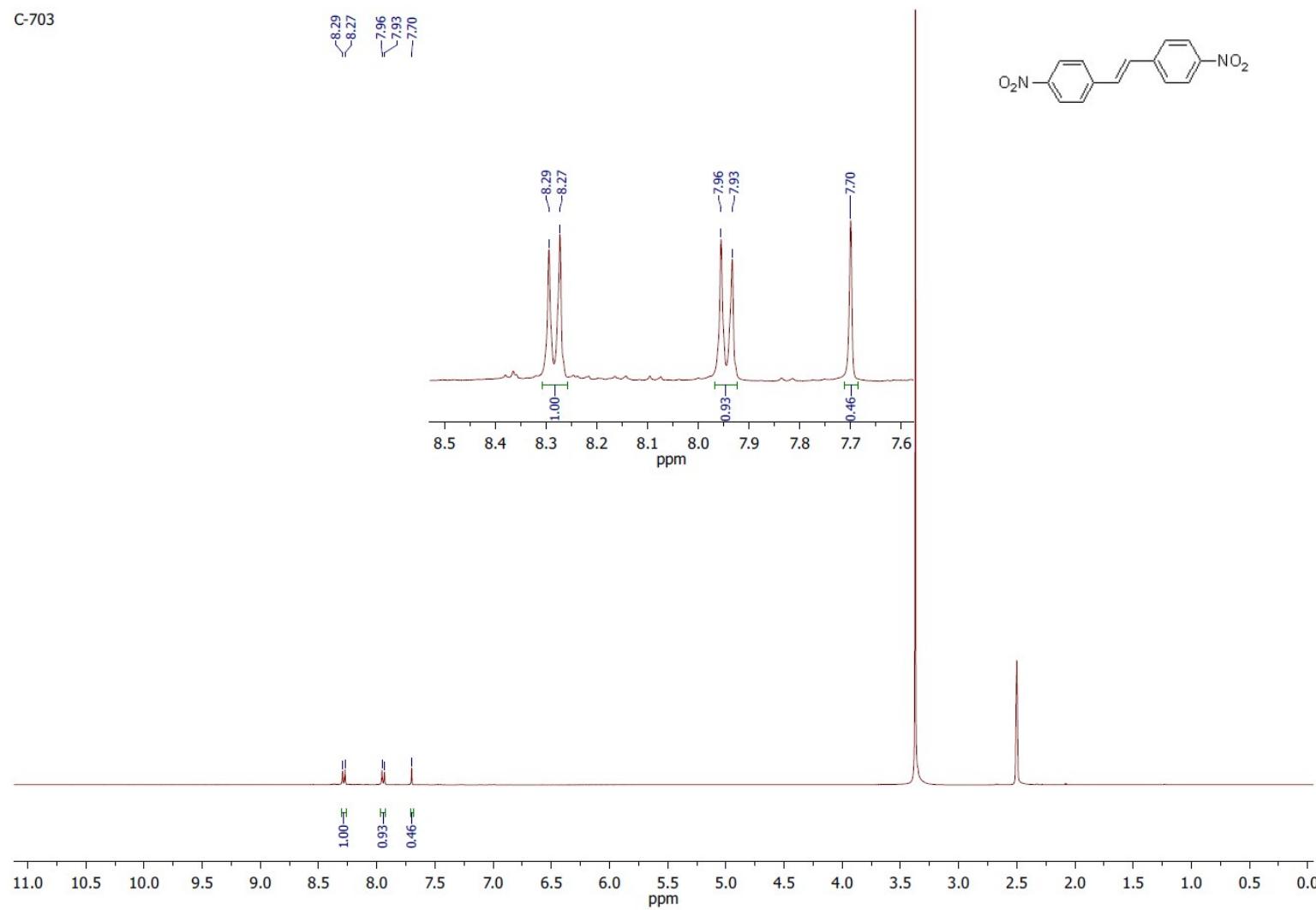
NMR ^1H spectrum of **2,4,6-tribromo-1-vinylbenzene (3m)**.



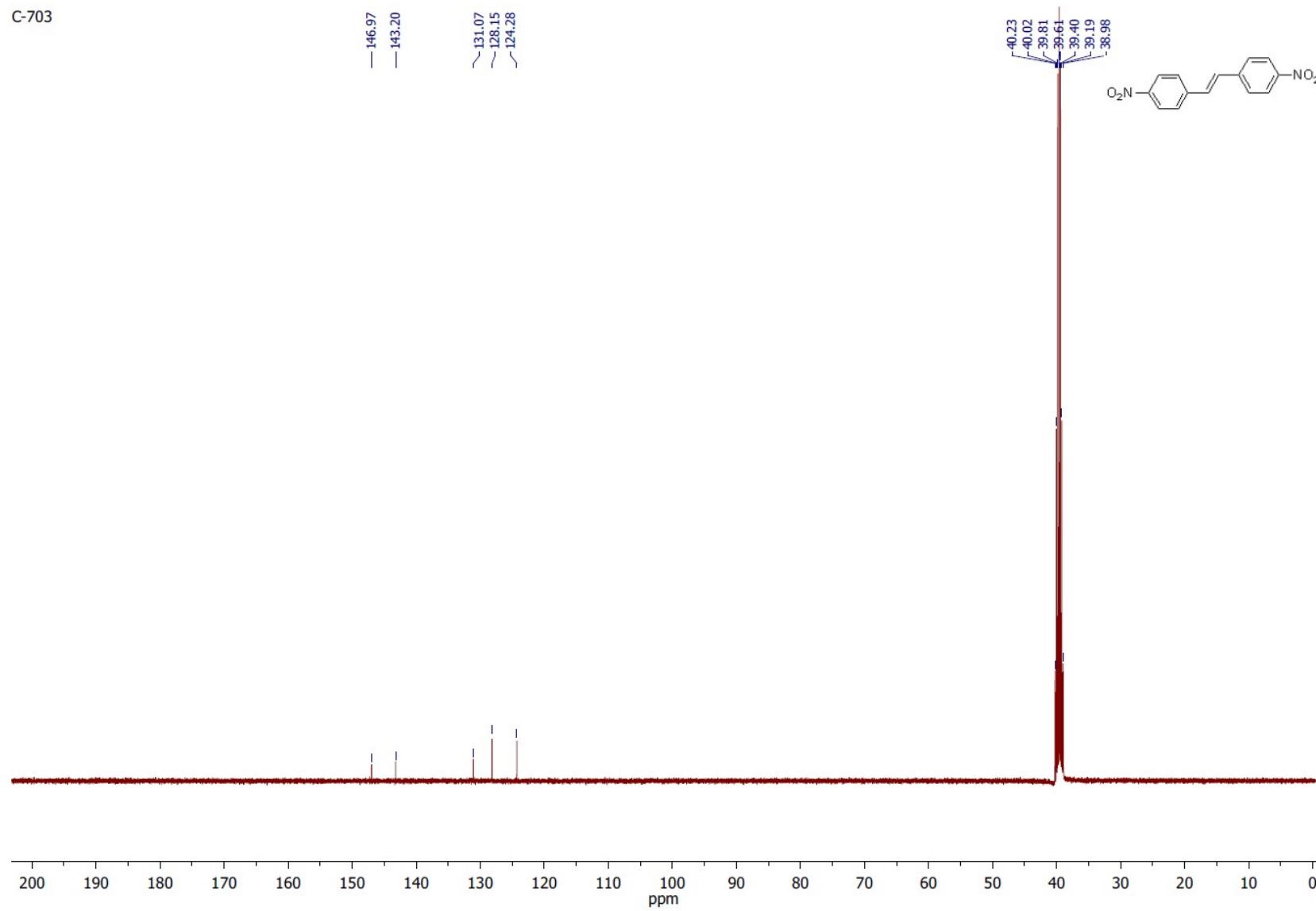
NMR ^{13}C spectrum of **2,4,6-tribromo-1-vinylbenzene (3m)**



NMR ^1H spectrum of (**E**)-4,4'-dinitrostilbene (**4a**).



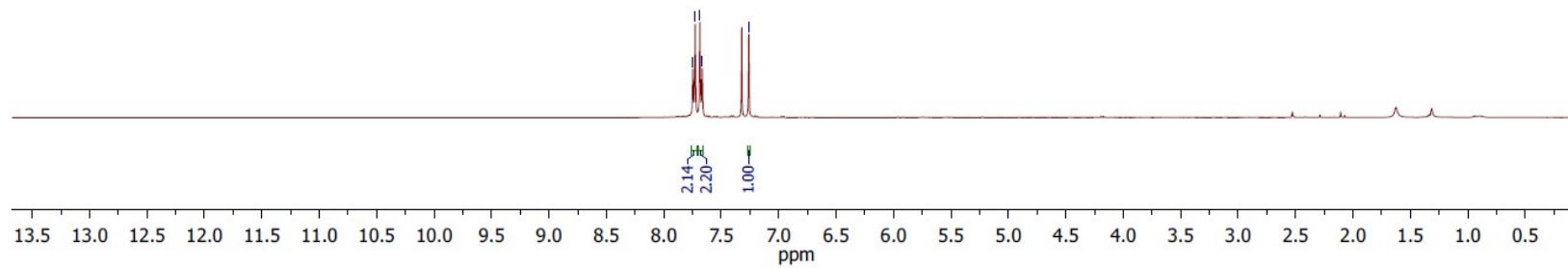
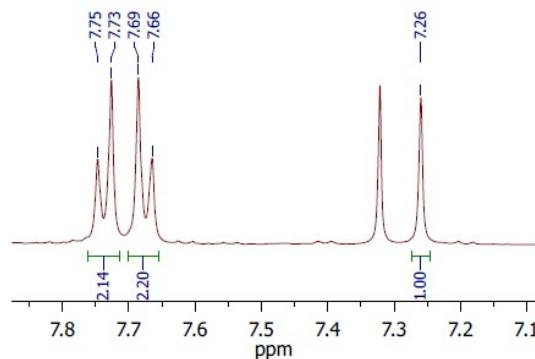
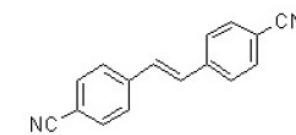
NMR ^{13}C spectrum of **(E)-4,4'-dinitrostilbene (4a)**.



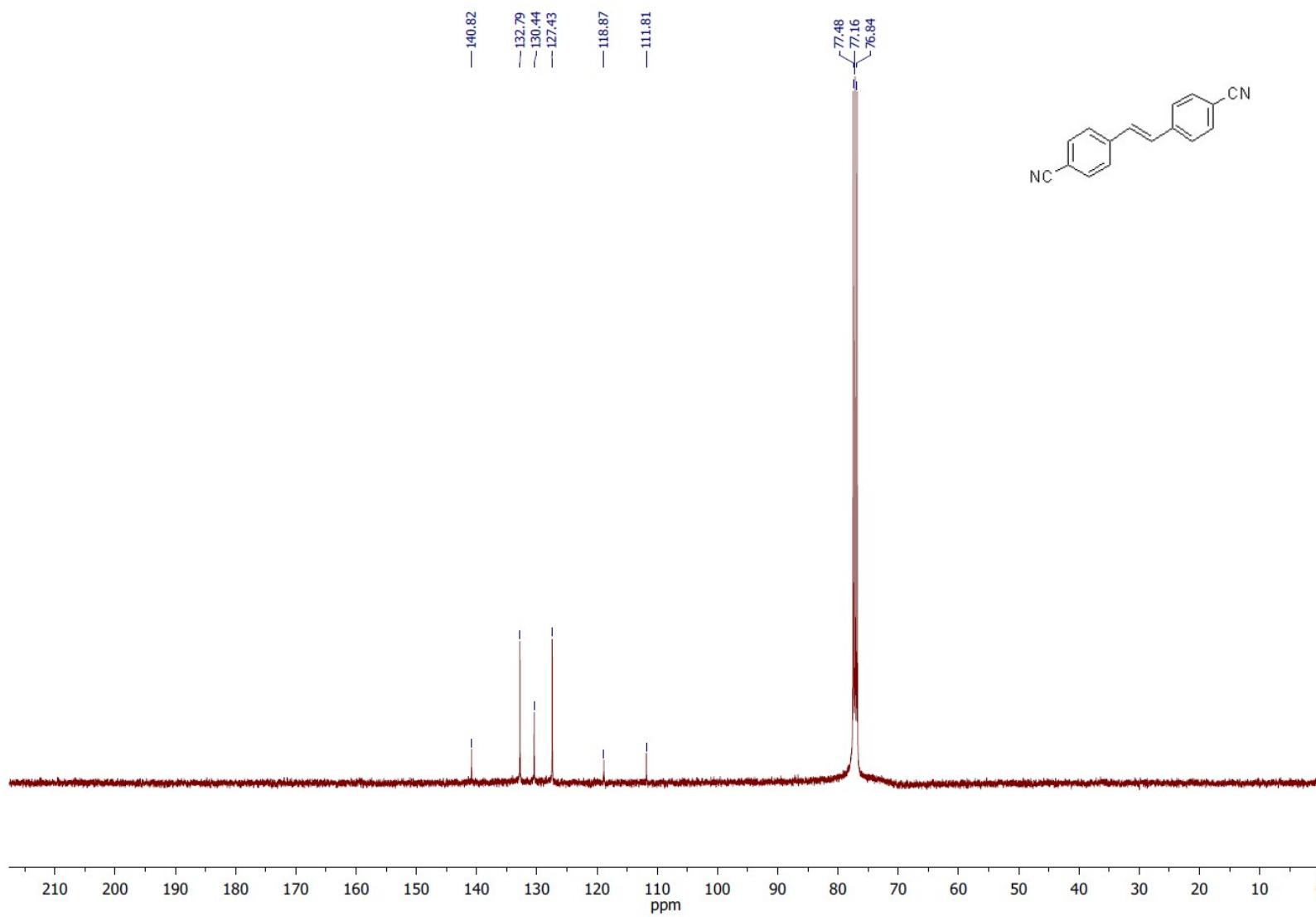
NMR ^1H spectrum of (**E**)-4,4'-dicyanostilbene (**4b**).

C-739
C-739
CDCl₃
 ^1H

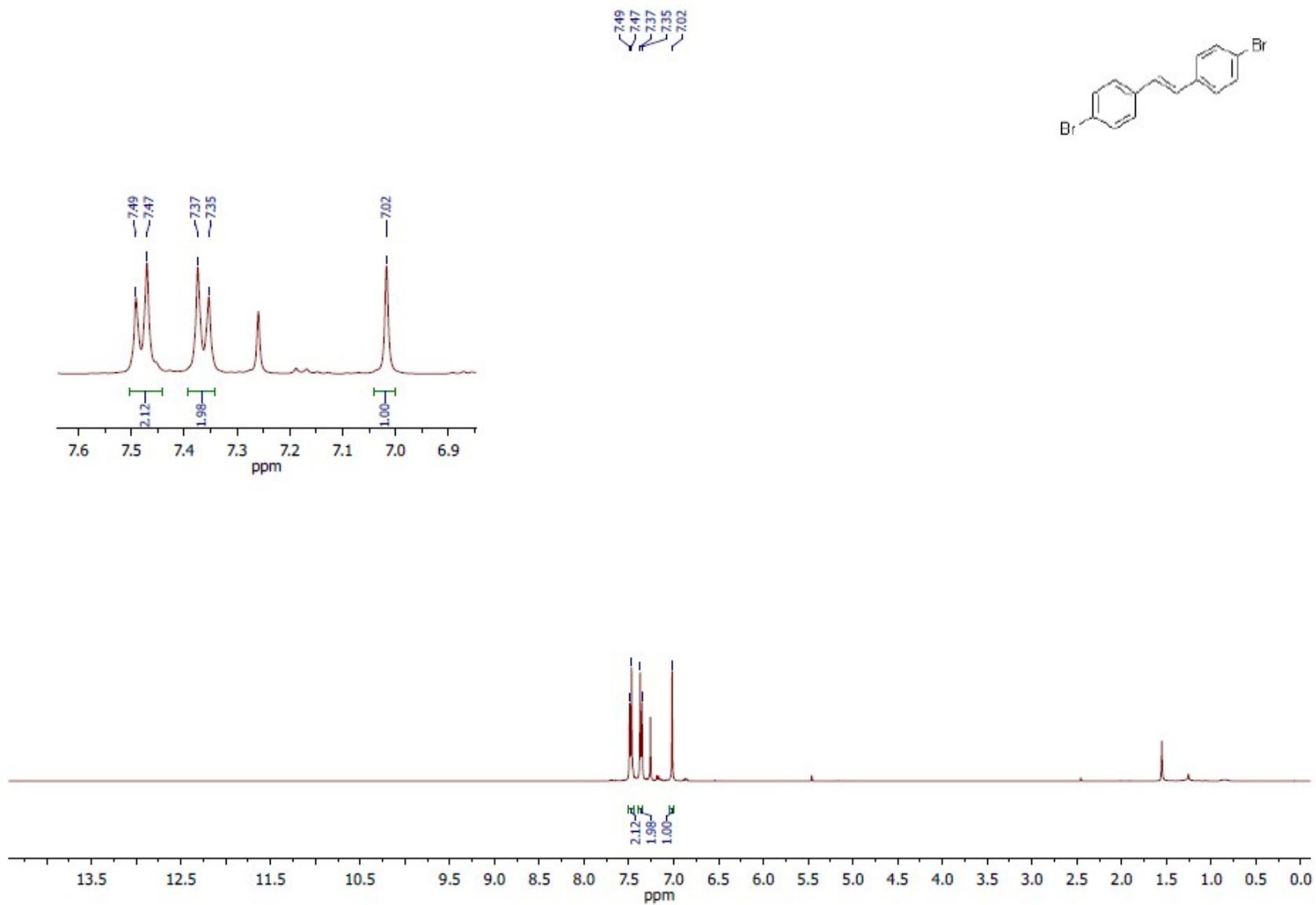
7.75
7.73
7.69
7.66
— 7.26



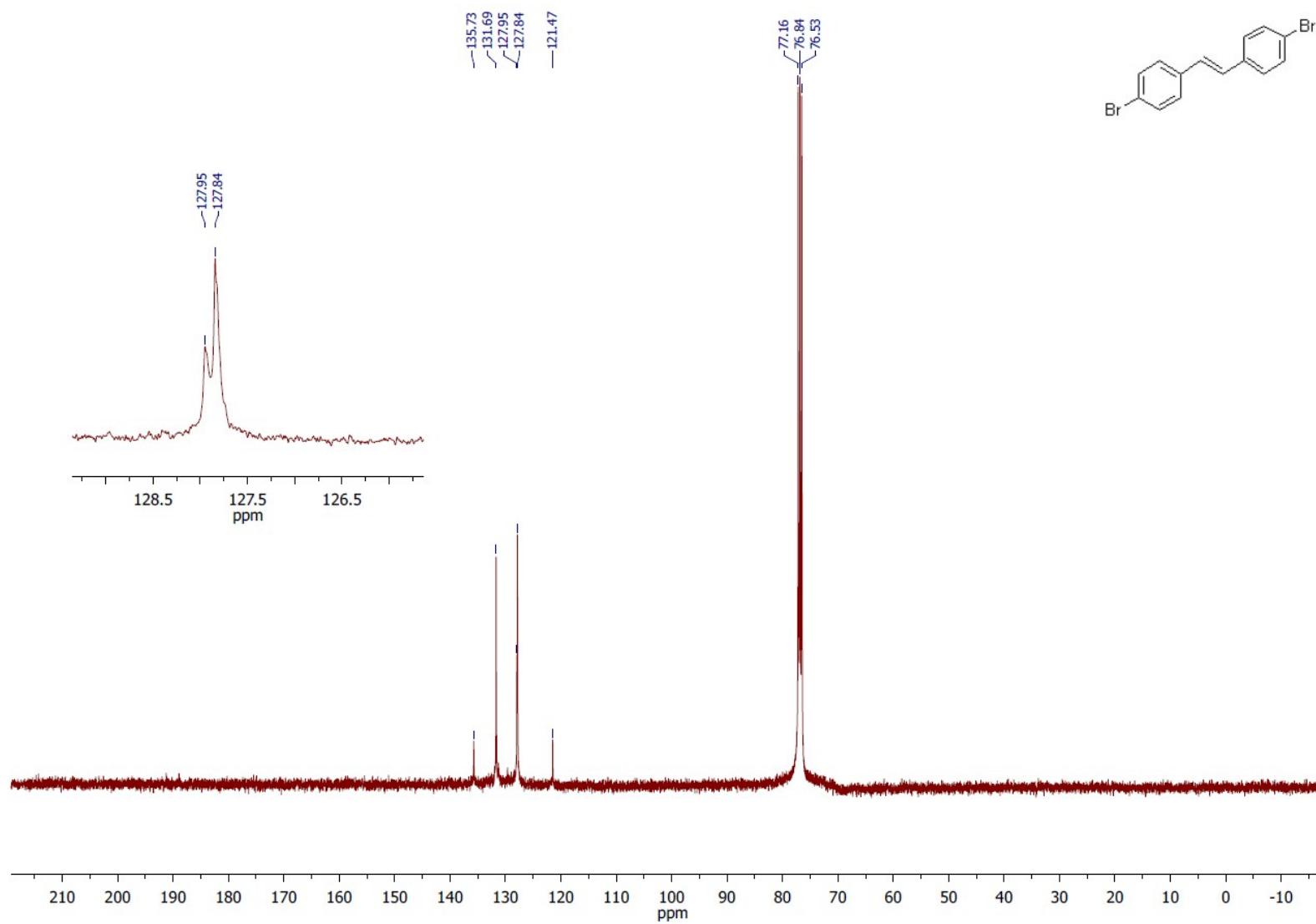
NMR ^{13}C spectrum of (*E*)-4,4'-dicyanostilbene (**4b**).



NMR ^1H spectrum of (**E**)-4,4'-dibromostilbene (**4c**).



NMR ^{13}C spectrum of (**E**)-4,4'-dibromostilbene (**4c**).



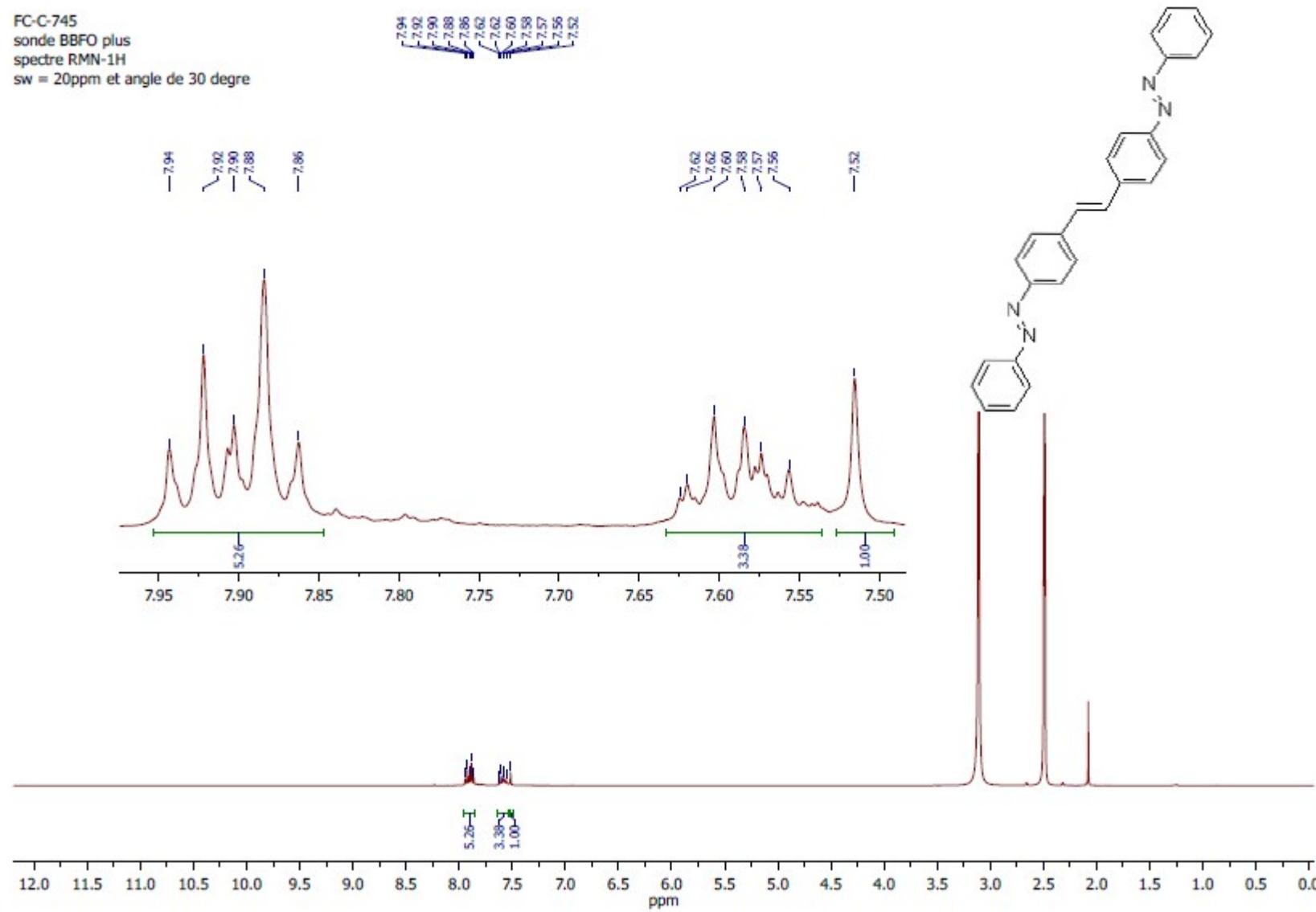
NMR ^1H spectrum of **(E)-1,2-bis(4-((E)-phenyldiazenyl)phenyl)ethane (4d)**.

FC-C-745

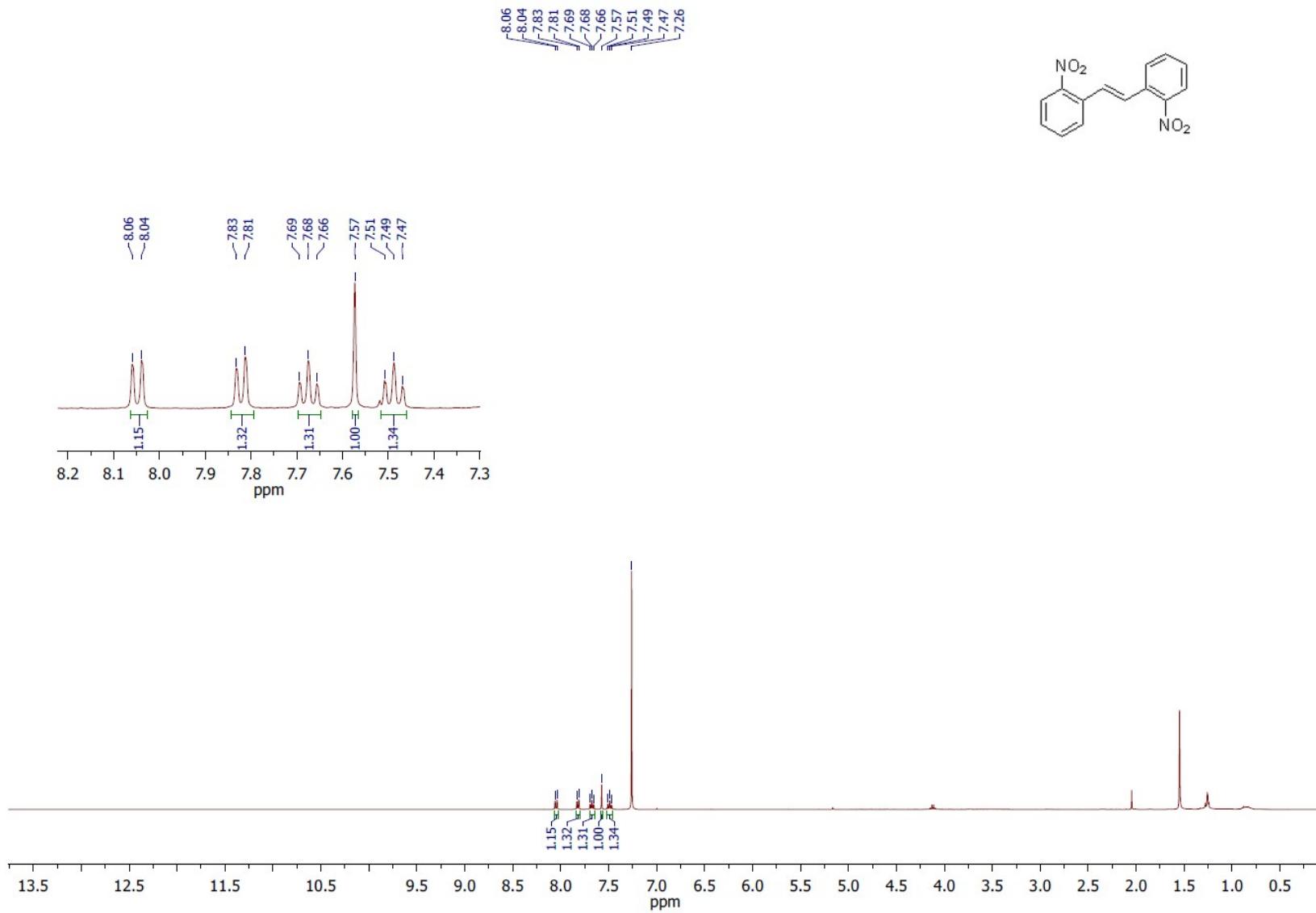
sonde BBFO plus

spectre RMN- ^1H

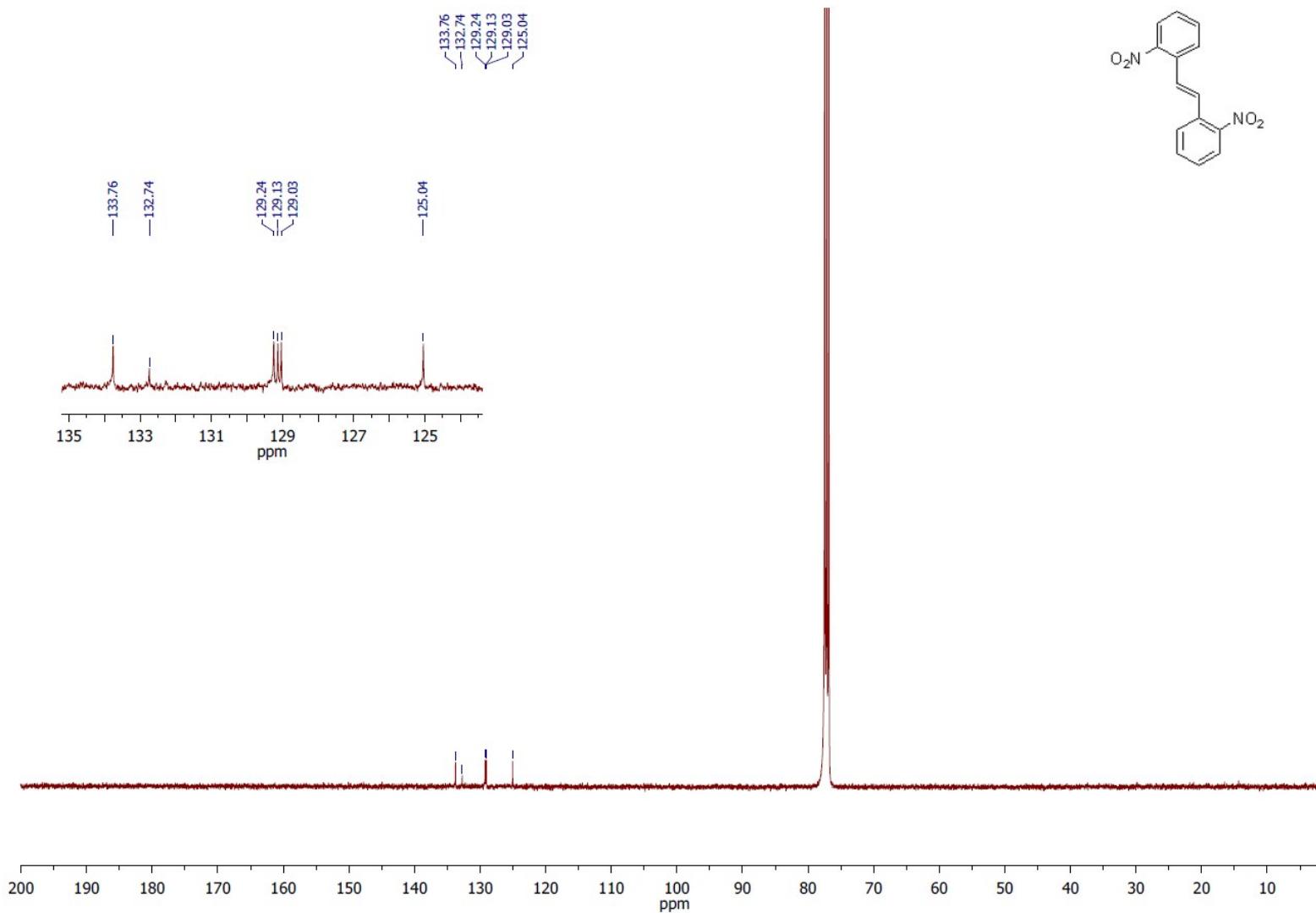
sw = 20ppm et angle de 30 degré



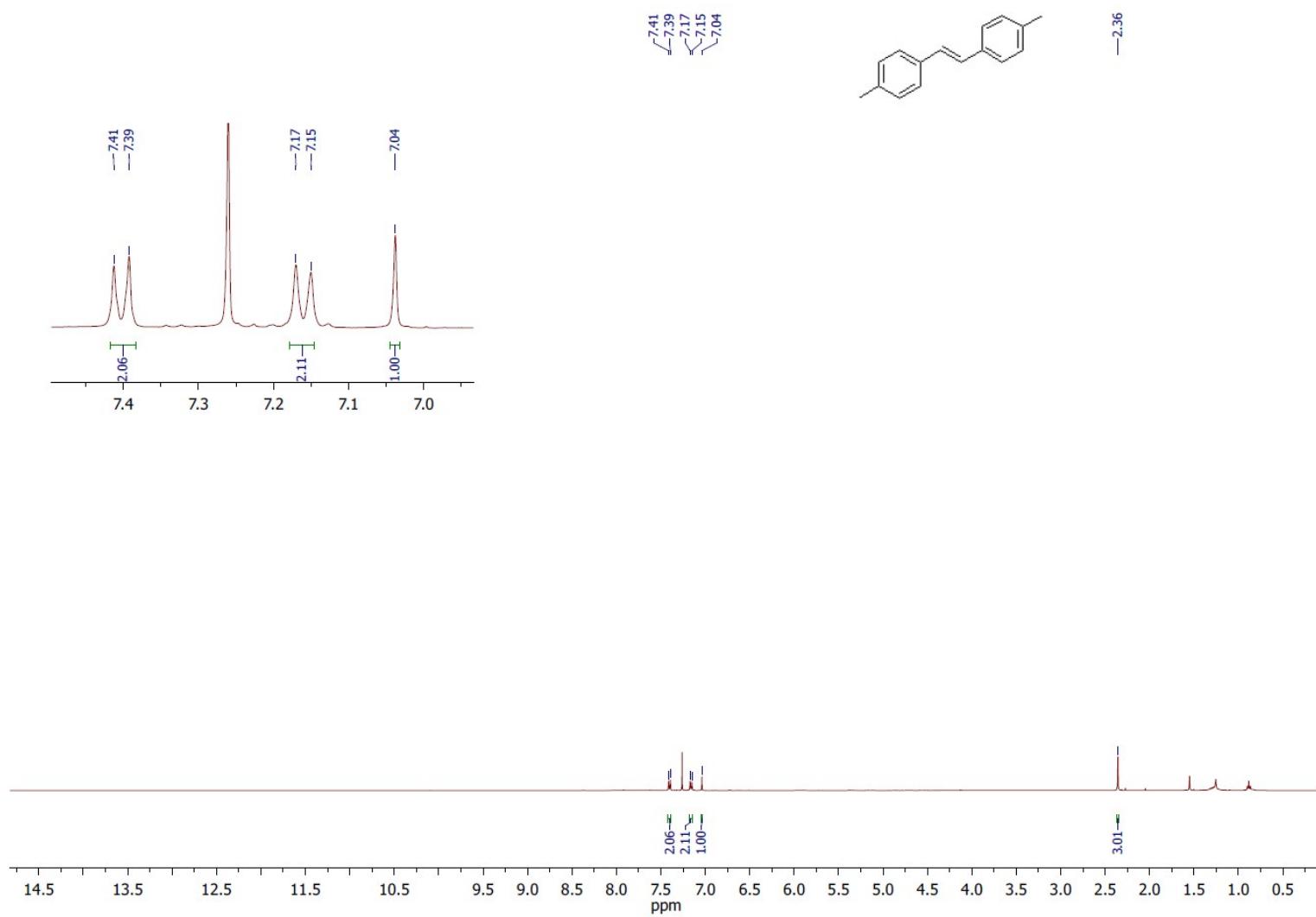
NMR ^1H spectrum of (**E**)-2,2'-dinitrostilbene (**4e**).



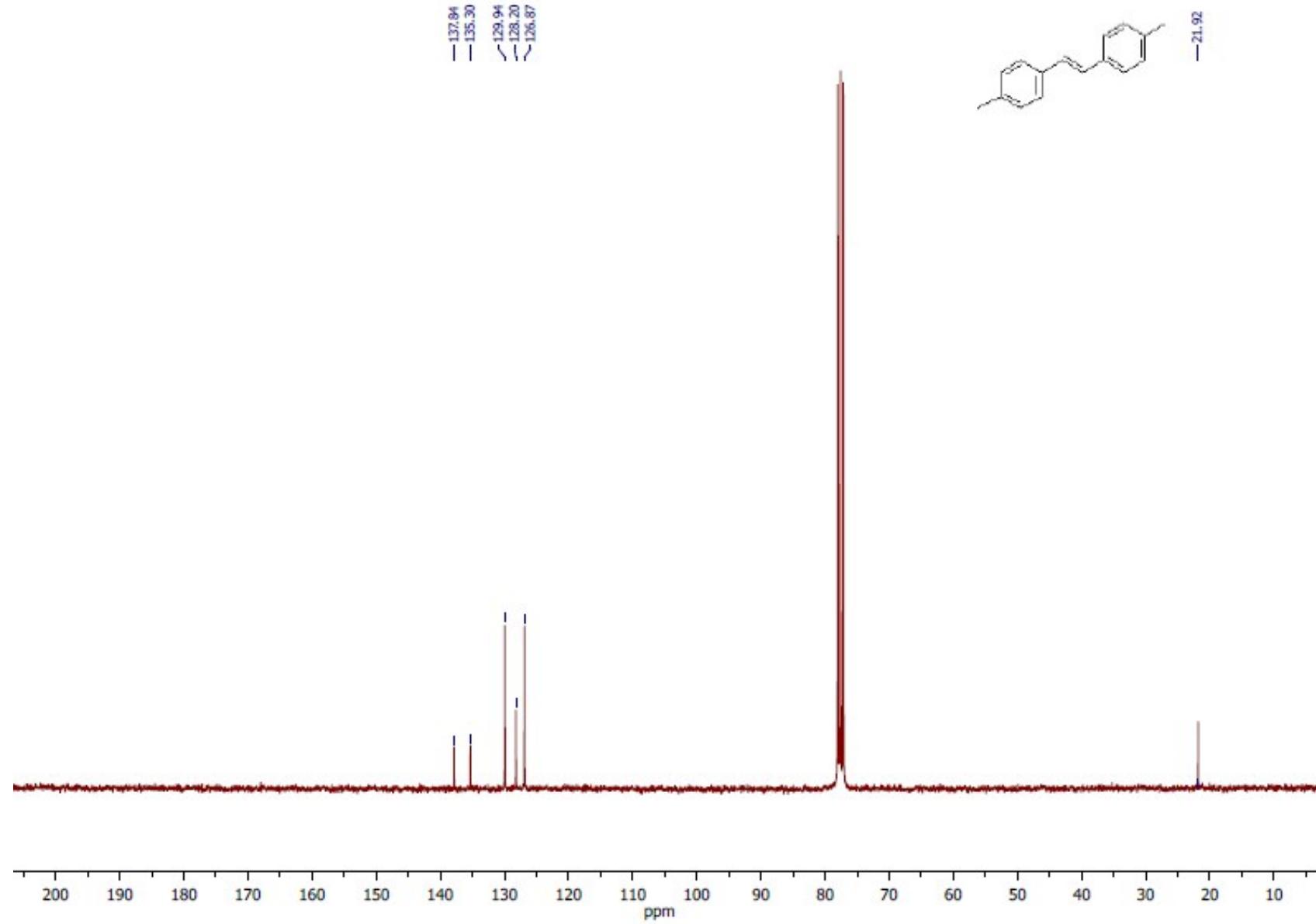
NMR ^{13}C spectrum of **(E)-2,2'-dinitrostilbene (4e)**.



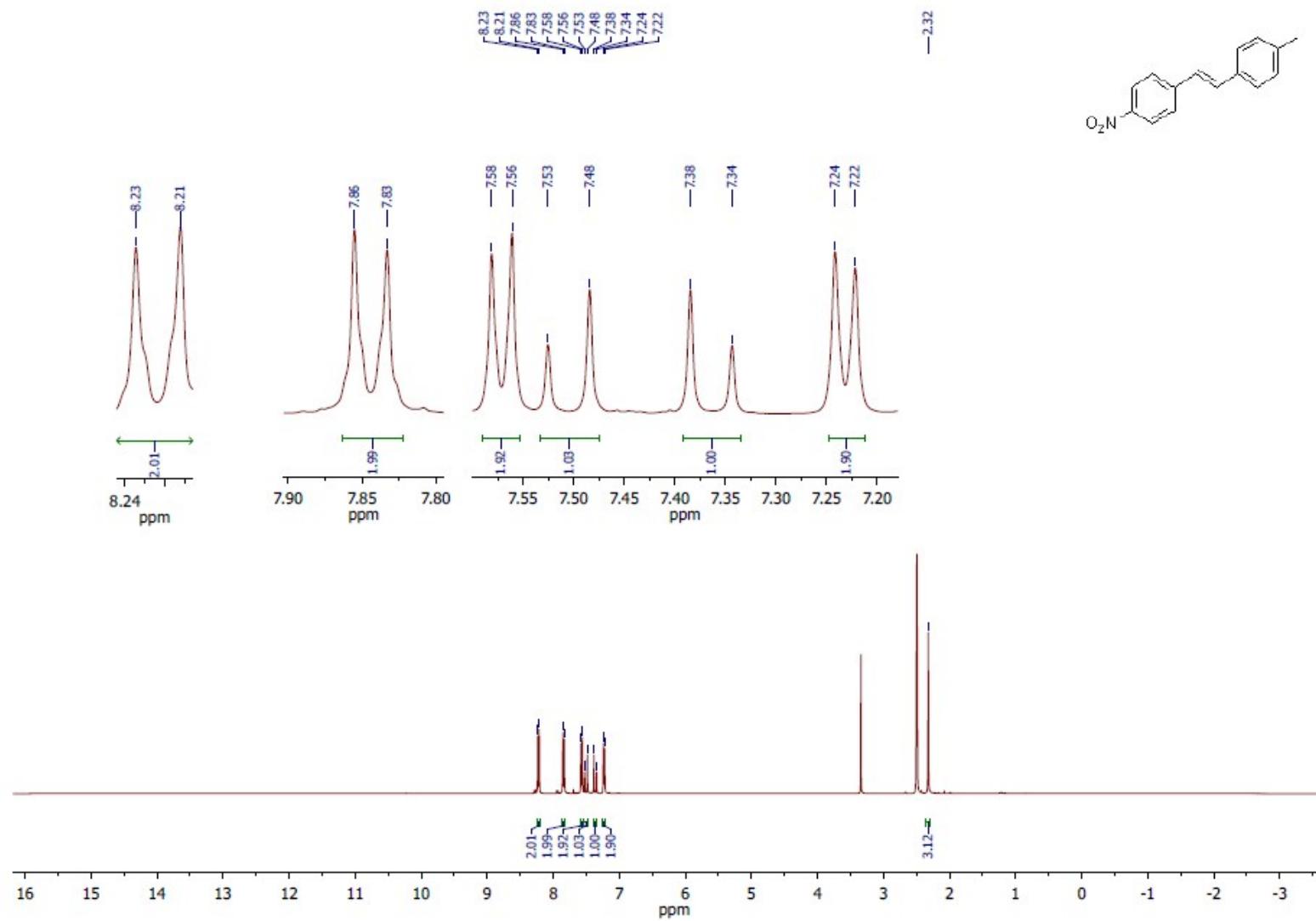
NMR ^1H spectrum of (**E**)-1,2-di-p-tolylethene (**4f**)



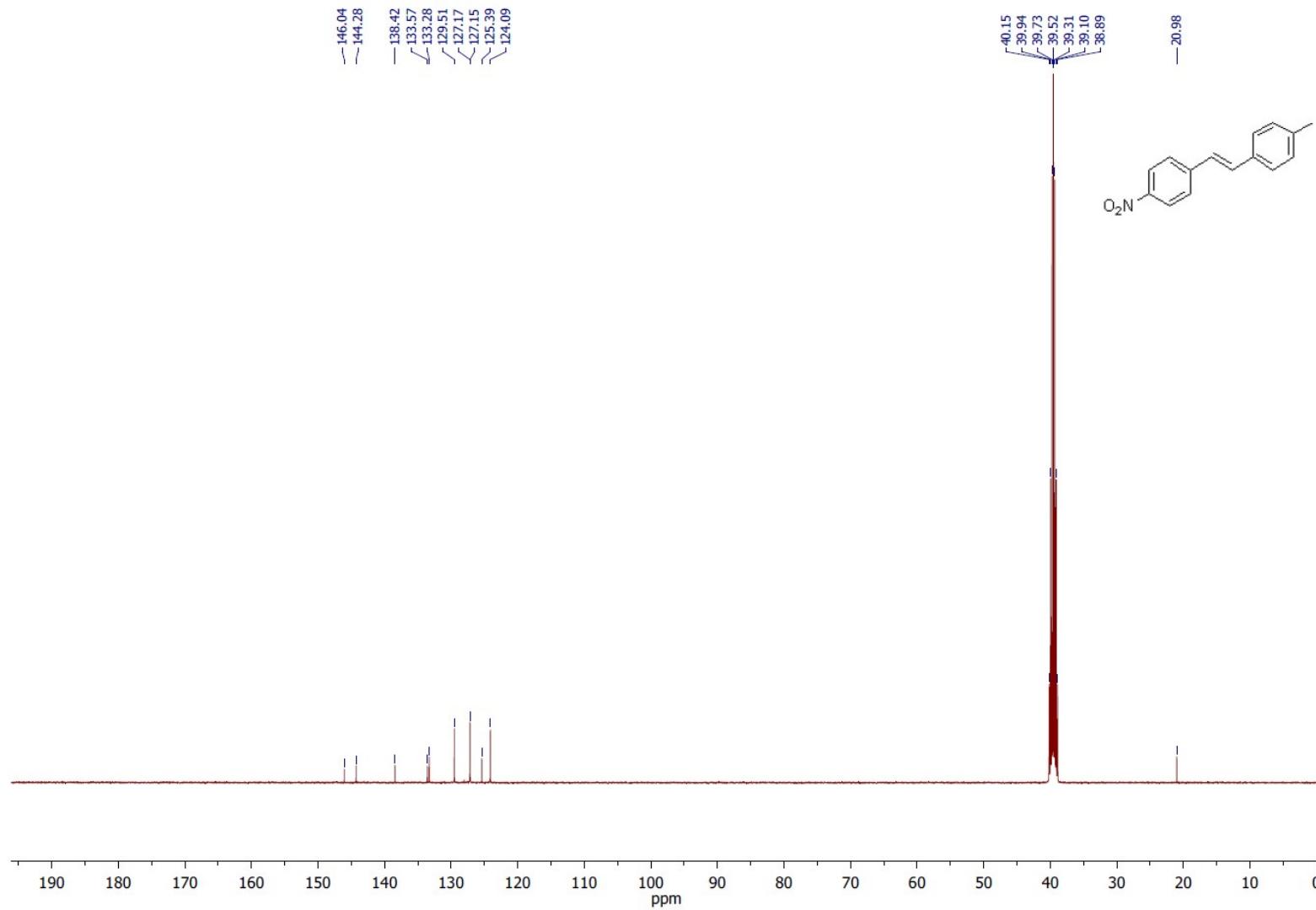
NMR ^{13}C spectrum of **(E)-1,2-di-p-tolylethene (4f)**



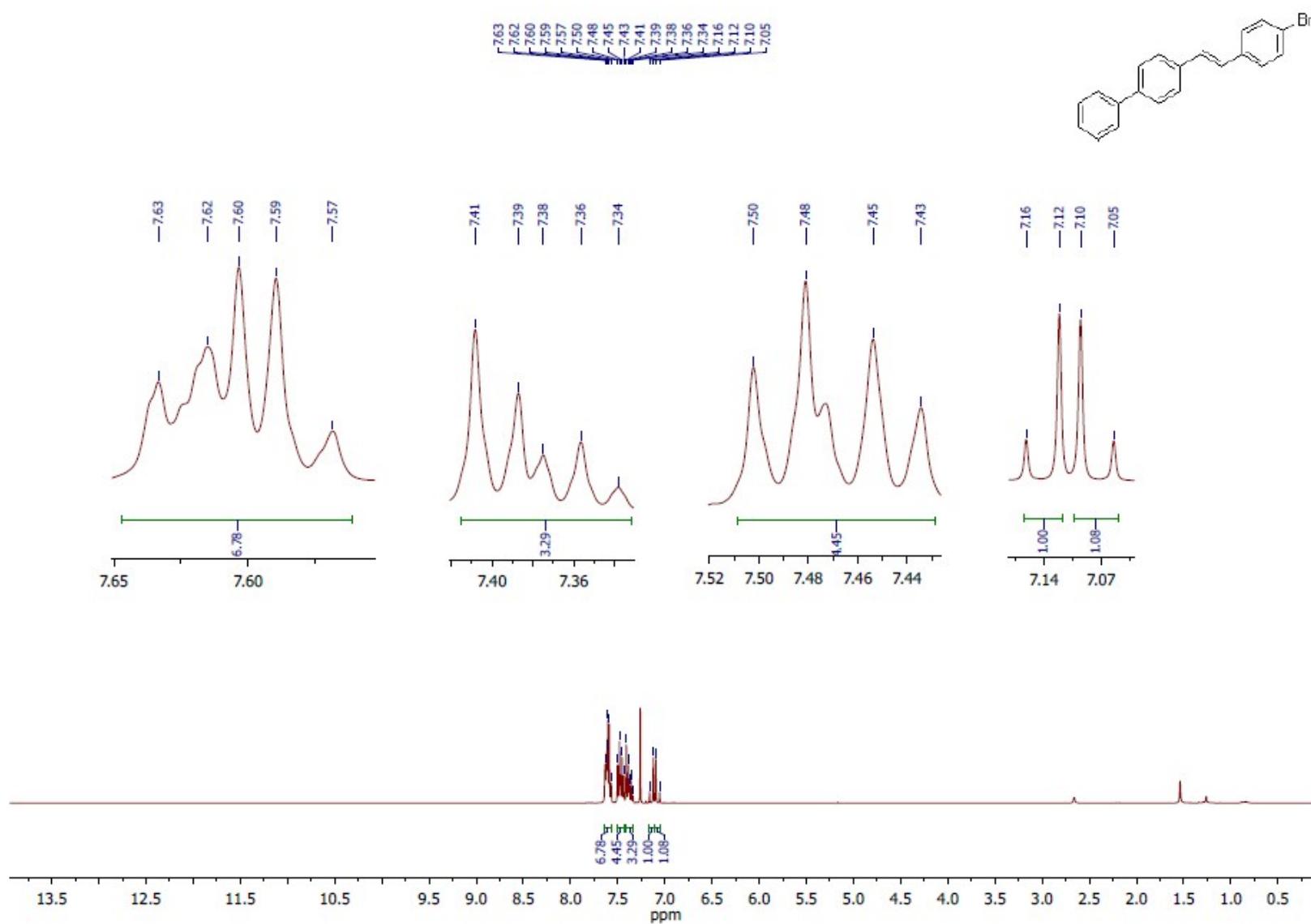
NMR ^1H spectrum of **(E)-1-methyl-4-(4-nitrostyryl)benzene (4g)**.



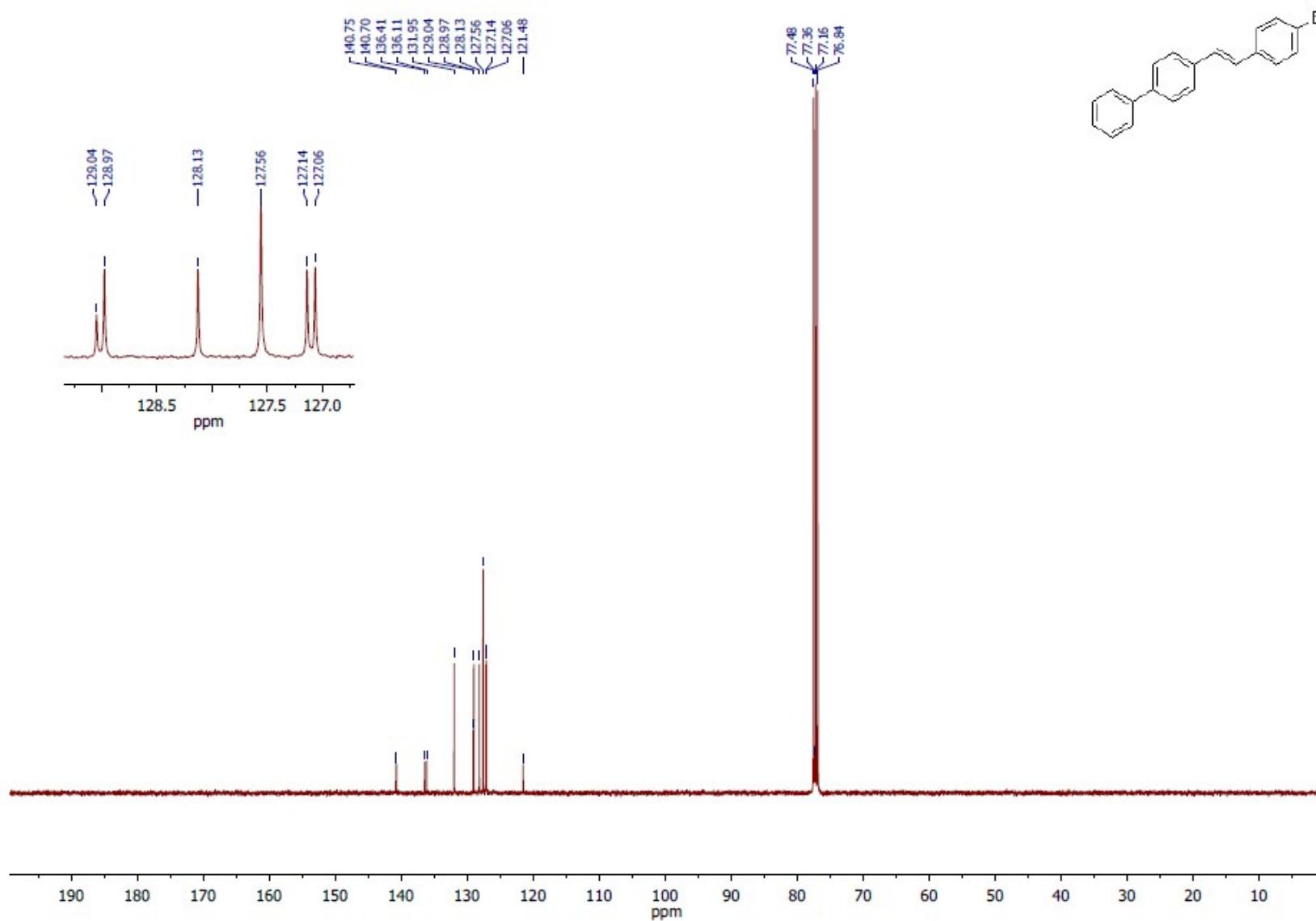
NMR ^{13}C spectrum of **(E)-1-methyl-4-(4-nitrostyryl)benzene (4g)**.



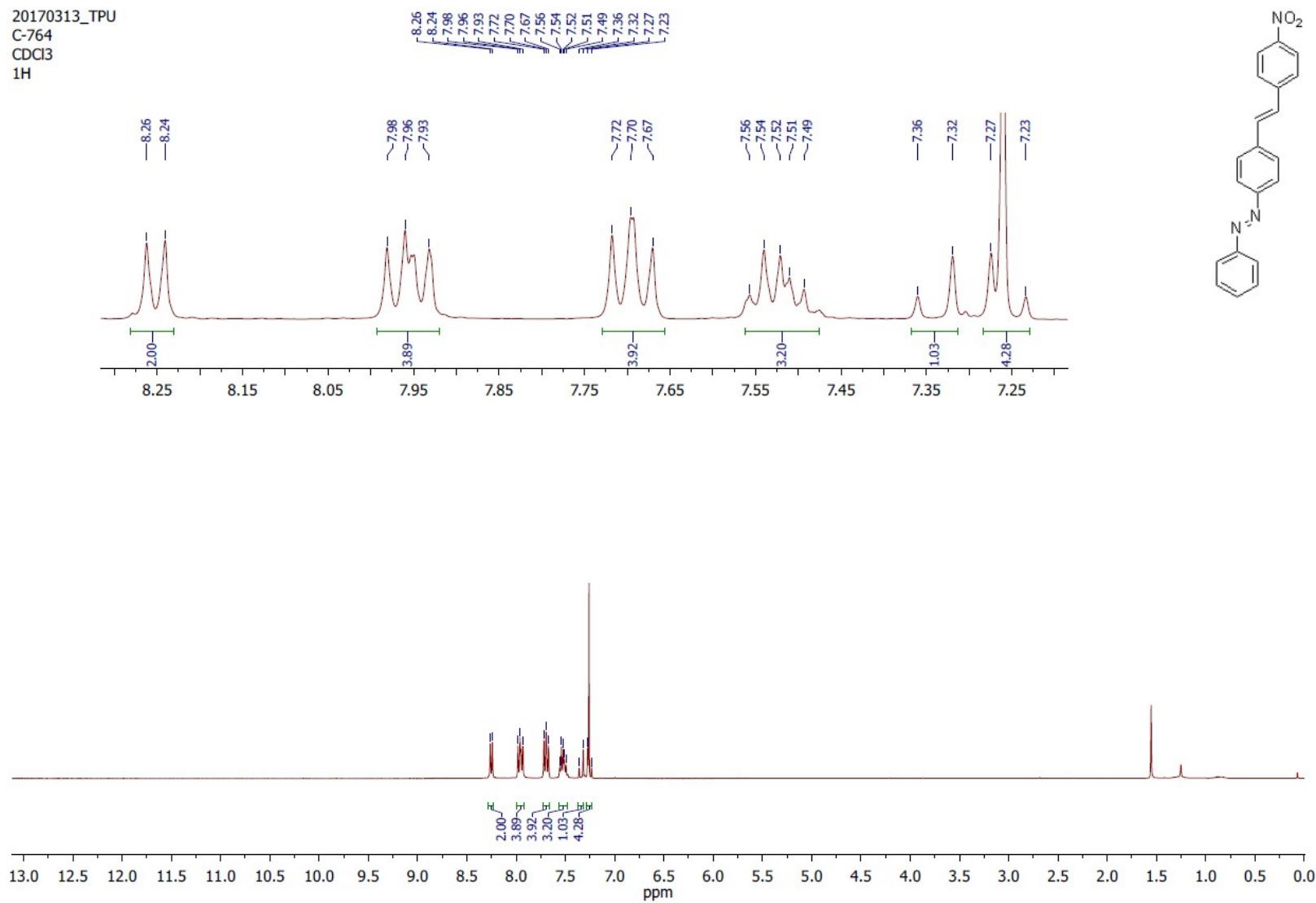
NMR ^1H spectrum of (E)-4-(4-bromostyryl)-1,1'-biphenyl (4h).



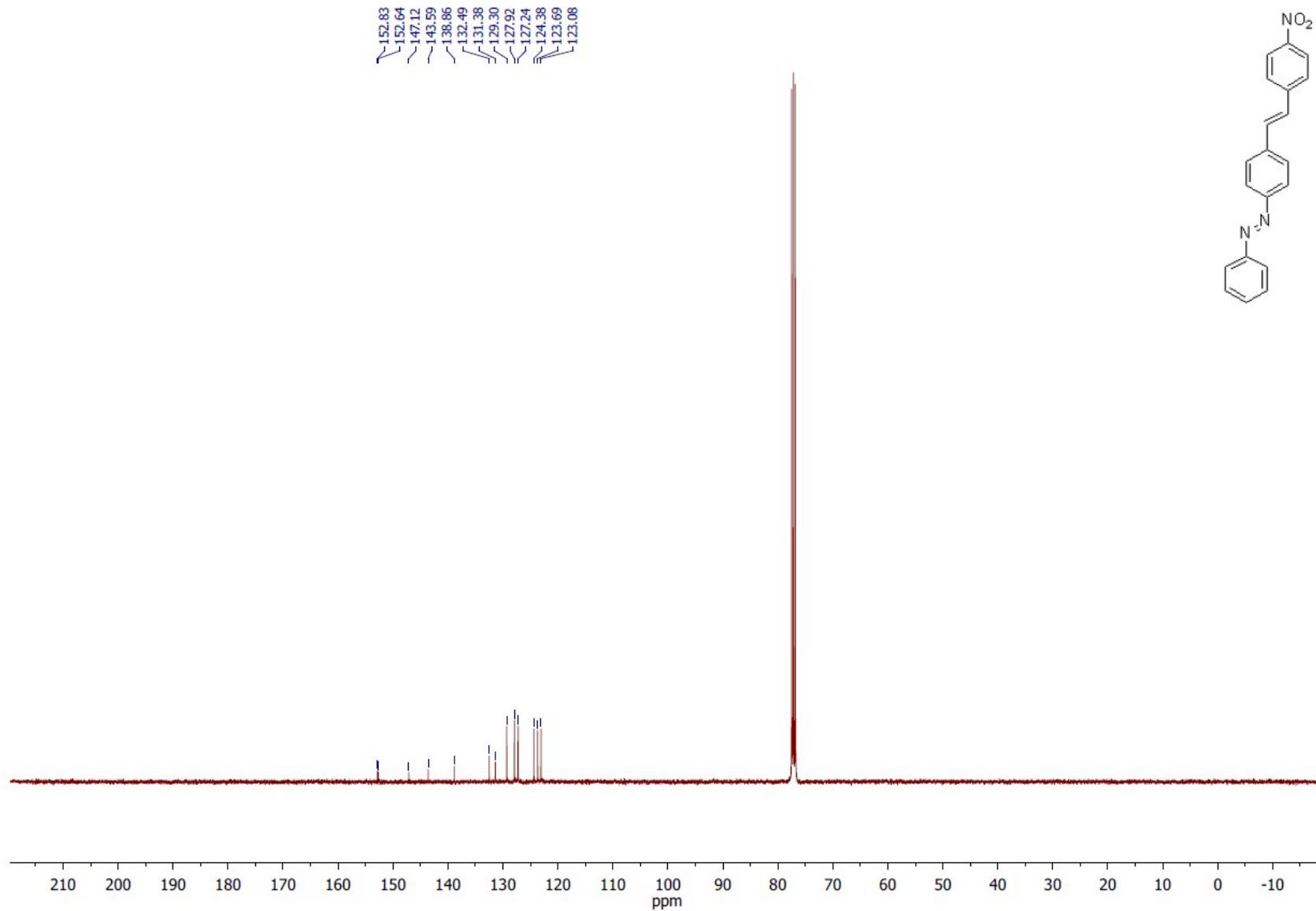
NMR ^{13}C spectrum of **(E)-4-(4-bromostyryl)-1,1'-biphenyl (4h).**



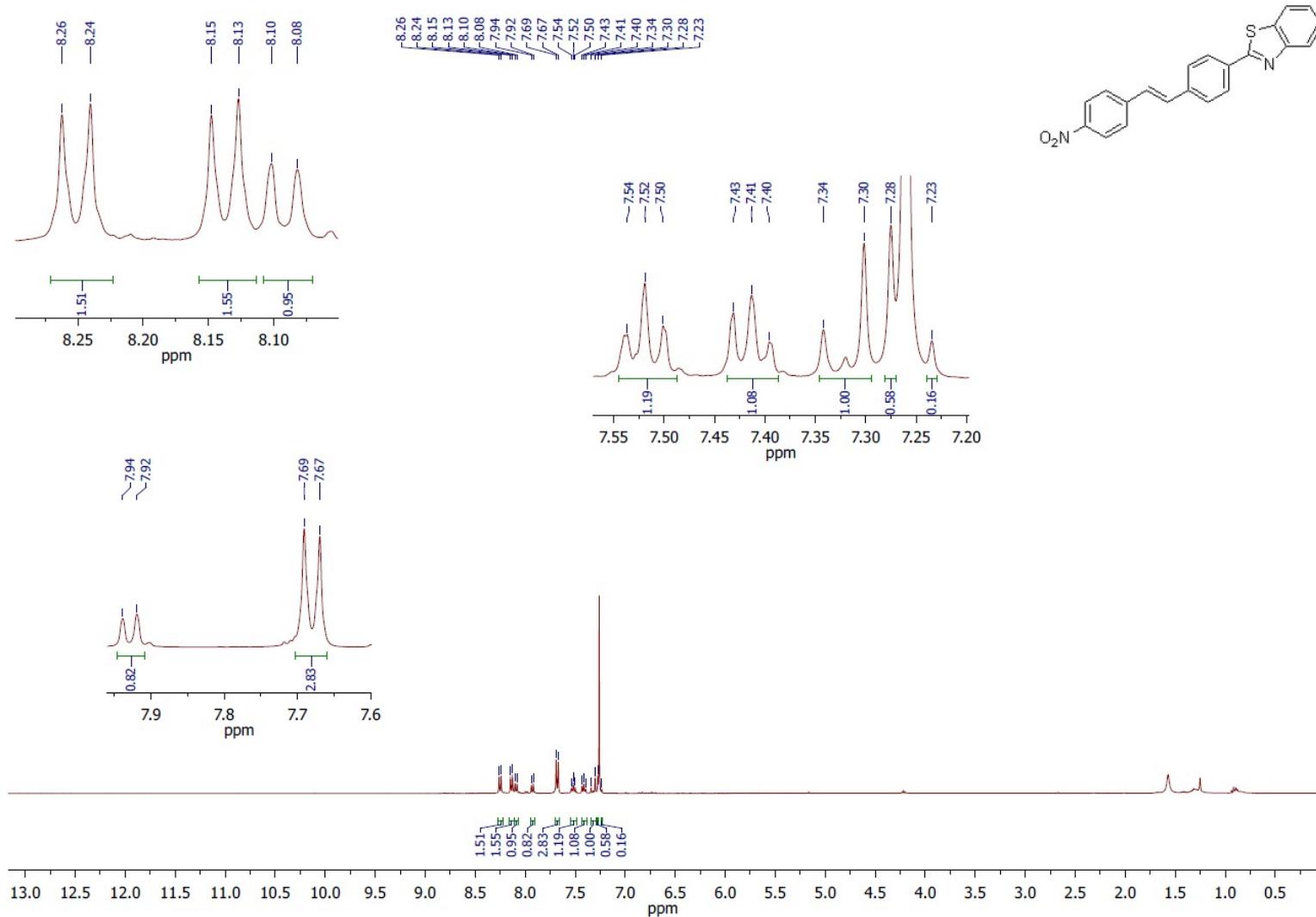
NMR ^1H spectrum of **(E)-1-((E)-4-nitrostyryl)phenyl-2-phenyldiazene (4i)**



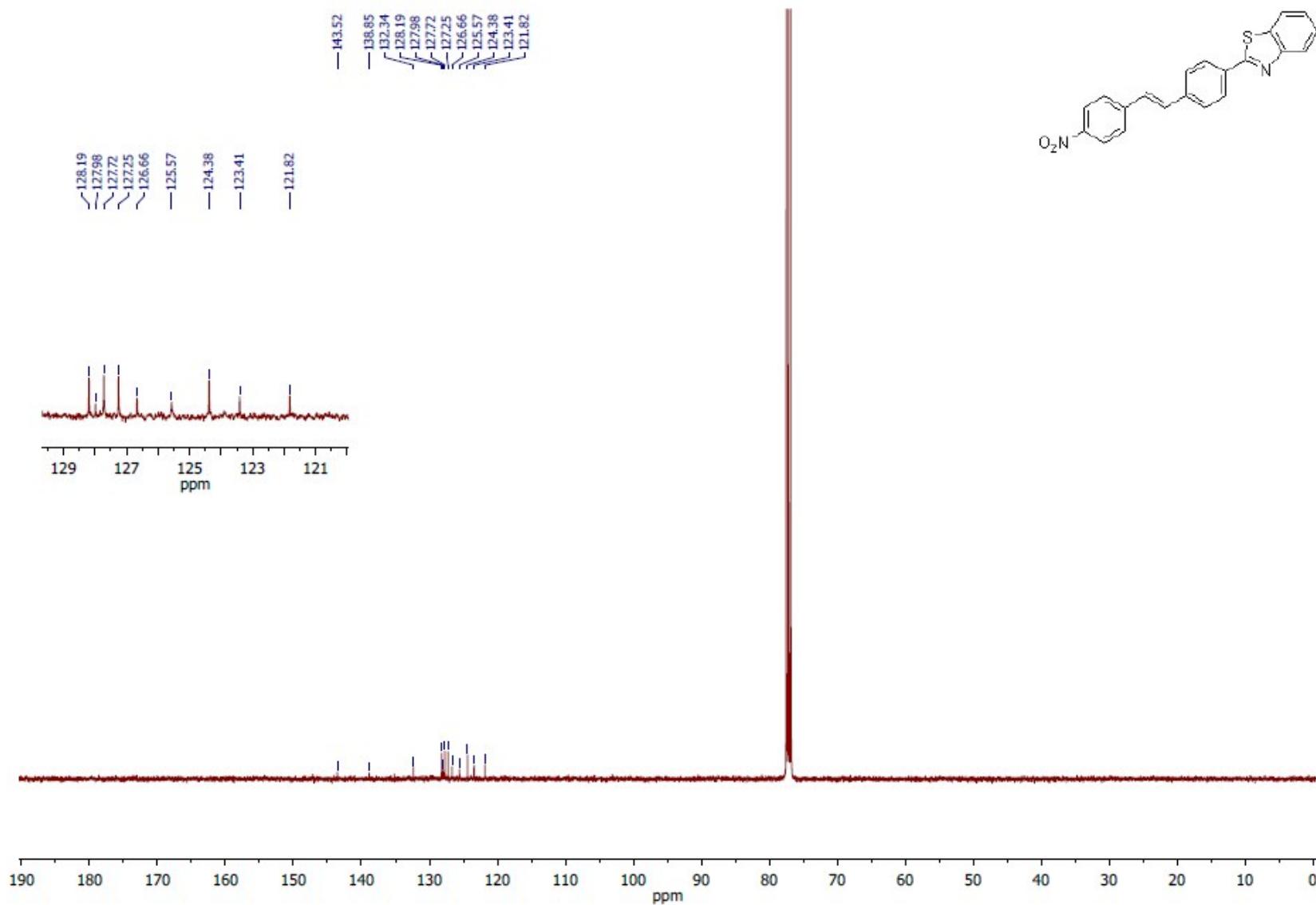
NMR ^{13}C spectrum of **(E)-1-((E)-4-nitrostyryl)phenyl-2-phenyldiazene (4i)**



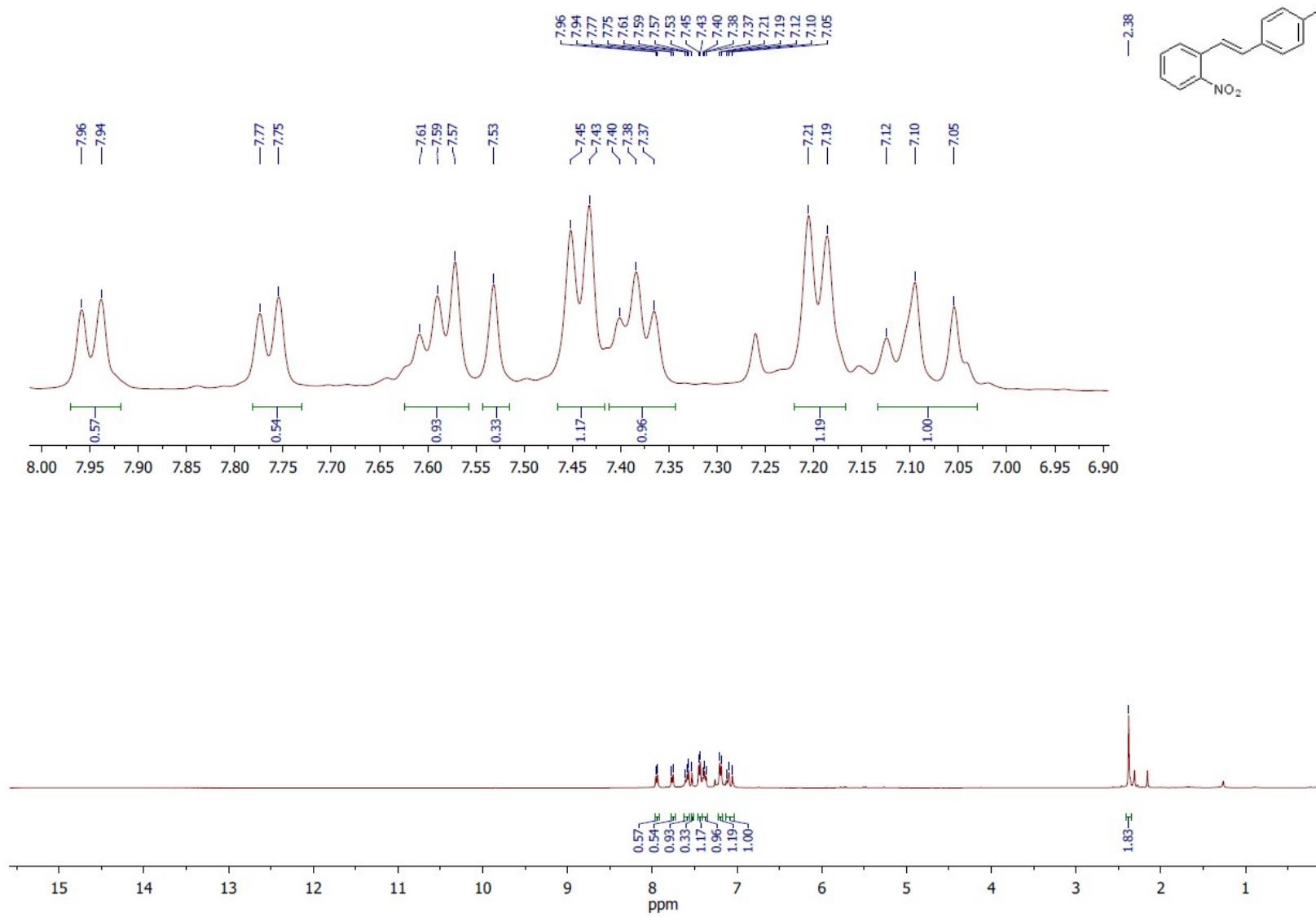
NMR ^1H spectrum of **(E)-2-(4-(4-nitrostyryl)phenyl)benzothiazole (4j)**.



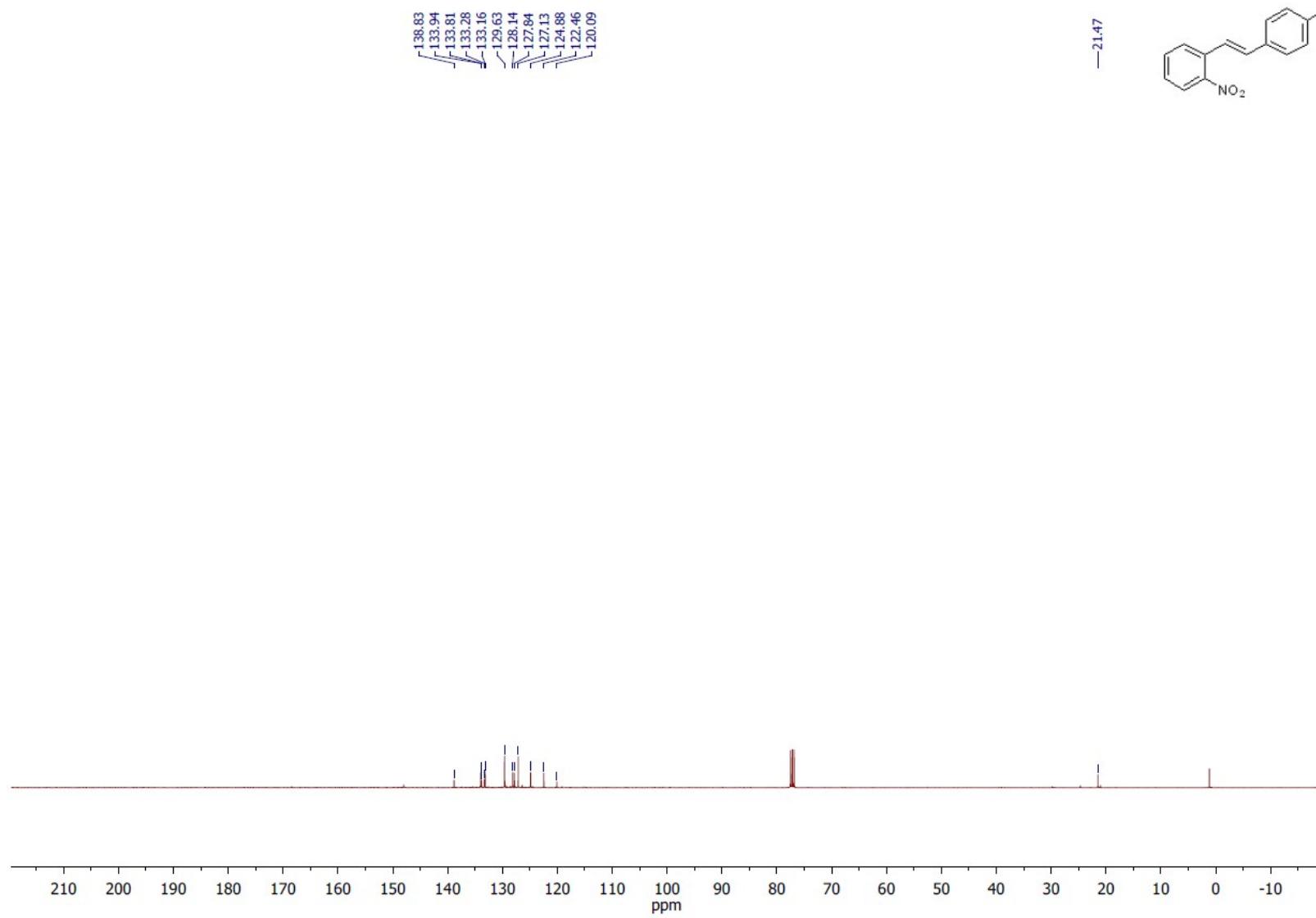
NMR ^{13}C spectrum of (**E**)-2-(4-(4-nitrostyryl)phenyl)benzothiazole (**4j**).



NMR ^1H spectrum of **(E)-1-(4-methylstyryl)-2-nitrobenzene (4k)**



NMR ^{13}C spectrum of **(E)-1-(4-methylstyryl)-2-nitrobenzene (4k)**



References

1. S.E. Estrada, C. Ochoa-Puentes, C.A. Sierra. *Journal of Molecular Structure*, 2017, **1133**, 448;
2. T. Ohishi, M. Nishiura, Z. Hou. *Angew. Chem.*, 2008, **120**, 5876;
3. N.S.Y. Loy, S. Kim. *Org. Lett.* 2015, **17**, 3, 395;
4. Ma Yu, Z. Jin. *Synth. Commun.*, 2014, **44**, 5, 707;
5. Ch.H Kee, A.A. Ariffin, T.K. Khalijah, H. Morita, S.I. Hussain, K.M. Chan, P.J. Wood, M.D. Threadgill, Ch.G. Lim, J.F.F. Weber, N.F. Thomas. *Org. Biomol. Chem.* 2010, **8**, 24, 5646;
6. D. Kevin, A.R.M. Belfield, K. Bong-Soo, M.H. Joel, J.H. David, E.W. Van Stryland, V.M. Chapela, J.Percino. *Chem. Mater.* 2004, **16**, 4634;
7. M.E. Bouillon, H.H. Meyer. *Tetrahedron*, 2016, **72**, 23, 3151;
8. S. Fissekis. *J. Org. Chem.* 1973, **38**, 264;
9. S. Llona-Minguez, M. Desroses, A.J. Ghassemanian, A. Sylvain, L. Eriksson, R. Isacksson, T. Koolmeister, P.S. Stenmark, H.T. Martin. *Chem. Eur. J.* 2015, **21**, 20, 7394;
10. B. Batanero, F. Barba, E. Isidoro, N. Michail. *Tetrahedron Lett.* 2014, **55**, 1, 82;
11. G. Kiang, B. Geoffrey, St. Lee, Zh. Xu, E.B. Lobkovsky. *J. Am. Chem. Soc.*, 1999, **121**, 36, 8204;
12. A. Shuzo, T. Kunihiko, N. Shin'ichi, N. Kenichiro, A. Kazuko; W. Miwa. *Bull. Chem. Soc. Jpn.*, 1995, **68**, 7, 2043;
13. G. He, H.-Ya. Mei, Th. C. Bruic. *J. Am. Chem. Soc.*, 1991, **113**, 15, 5644;
14. Sk. Aymen, S. Ridha, S. Jean-Francois, D. Henri. *Synthesis (Germany)*, 2016, **48**, 18, 3097;
15. A. Blanc, Ch.G. Bochet. *J. Org. Chem.*, 2003, **68**, 3, 1138;
16. S.K. Sahoo. *Tetrahedron Lett.*, 2016, **57**, 31, 3476;
17. H.F. Sore, Ch.M. Boehner, L. Laraia, P.P. Logoteta, S.M. Cora, K. Williams, W.R.J.D. Galloway, D.R. Spring. *Org. Biomol. Chem.*, 2011, **9**, 2, 504;
18. M. Das, A.J.M. Manvar, M. Blangetti, R.C. Jones, D.F. O'Shea. *Chem. Eur. J.*, 2015, **21**, 24, 8737;
19. J.G. Lukas, Z. Bettina, K. Thomas. *Beilstein J. Org. Chem.*, 2010, **6**, 43.