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Novel capto-dative (*Z,E*)-2-(alkylthio)alk-2-en-4-ynals: synthesis and heterocyclization

Victoria G. Fedoseeva, Ekaterina A. Verochkina, Ludmila I. Larina, Evgeniy V. Kondrashov, Igor B. Rozentsveig and Nadezhda V. Vchislo

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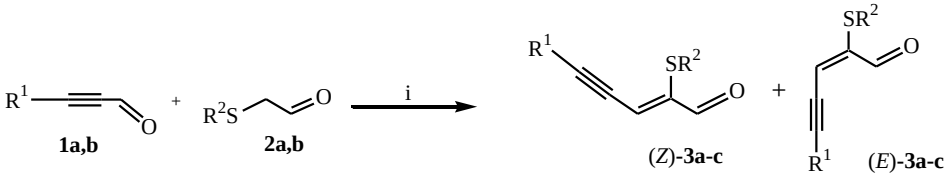
1. Experimental Details

General. The ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded in $CDCl_3$ solutions at room temperature on Bruker DPX-400 and AV-400 spectrometers (400.13, 100.61 and 40.56 MHz, respectively). ^{1}H, ^{13}C and ^{15}N Chemical shifts (δ in ppm) were measured with accuracy of 0.01, 0.02 and 0.1 ppm, respectively, and referred to TMS (^{1}H, ^{13}C) and nitromethane (^{15}N). Chromato-mass spectrometry analysis was performed on a Shimadzu GCMS-QP5050A mass spectrometer (EI ionization, 70 eV). The IR spectra of the compounds were recorded on a Varian 3100 FT-IR spectrometer with the sample in thin film. Elemental analysis was performed on a Thermo Finnigan Flash series 1112 Elemental analyzer. Column chromatography was carried out on silica gel 60 (70–200 mesh; Merk).

General procedure for the synthesis of alk-2-en-4-ynals (3a-c):



a R^1 = Ph **b** R^1 = Et_3Ge

a R^2 = Bu **b** R^2 = *n*-C_7H_{15}

a R^1 = Ph, R^2 = Bu
b R^1 = Ph, R^2 = *n*-C_7H_{15}
c R^1 = Et_3Ge, R^2 = Bu

Ynal **1** (1 mmol) was added in one portion to a stirred mixture of solid NaOH (0.5 mmol) in abs. DMF (10 ml) at room temperature. A solution of 2-(alkylthio)acetaldehyde **2** (1 mmol) in DMF (1 ml) was slowly added dropwise and the stirring was continued for 2-24 h at room temperature until the reaction was completed (^{1}H NMR monitoring). The reaction mixture was diluted with water and extracted with benzene. The organic extract was washed with water 5 times (to remove DMF) and dried over Na_2SO_4 or $MgSO_4$. The solvent was evaporated and product was isolated by column chromatography [Silica gel, hexane/ether, (7:1 for **3a**, 3:1 for **3b, 3c**)].

The initial reaction mixture contained **(*Z*)-3a:(*E*)-3a** isomers in a ratio of 3:1 (^{1}H NMR). The purification by column chromatography gave 0.19 g of yellow oil, 78%.

(2*Z*)-2-Butylthio-5-phenylpent-2-en-4-ynal (*Z*)-3a: NMR ^{1}H ($CDCl_3$): δ=0.93 (t, 3H, CH_3, J = 7.2 Hz), 1.46 (m, 2H, $SCH_2CH_2\underline{CH_2}$), 1.58 (m, 2H, $SCH_2\underline{CH_2}$), 3.16 (t, 2H, SCH_2, J = 7.4 Hz), 6.77 (s, 1H, CH=), 7.38 (m, 3H, *m*-H, *p*-H), 7.52 (d, 2H, *o*-

H, *J* = 7.7 Hz), 9.48 (s, 1H, CHO). NMR ^{13}C ($CDCl_3$): *δ*=13.73 (CH_3), 21.85 ($SCH_2CH_2\underline{C}H_2$), 31.35 ($SCH_2\underline{C}H_2$), 32.32 ($SCH_2$), 86.25 (C-4), 109.90 (C-5), 119.08 (C-2), 122.43 (C-3), 128.73 (*m*-C), 129.89 (*p*-C), 131.99 (*o*-C), 146.33 (C_i), 190.49 (C=O).

(2*E*)-2-Butylthio-5-phenylpent-2-en-4-ynal (*E*)-3a: NMR ^{1}H ($CDCl_3$): *δ*=0.95 (t, 3H, CH_3, *J* = 7.3 Hz), 1.47 (m, 2H, $SCH_2CH_2\underline{CH_2}$), 1.66 (m, 2H, $SCH_2\underline{CH_2}$), 2.78 (t, 2H, SCH_2, *J* = 7.5 Hz), 6.50 (s, 1H, CH=), 7.36 (m, 3H, *m*-H, *p*-H), 7.44 (d, 2H, *o*-H, *J* = 7.7 Hz), 10.31 (s, 1H, CHO). NMR ^{13}C ($CDCl_3$): *δ*=13.77 (CH_3), 22.25 ($SCH_2CH_2\underline{C}H_2$), 30.26 ($SCH_2\underline{C}H_2$), 30.48 ($SCH_2$), 84.57 (C-4), 100.32 (C-5), 119.08 (C-2), 122.43 (C-3), 128.38 (*m*-C), 129.40 (*p*-C), 131.74 (*o*-C), 148.16 (C_i), 188.51 (C=O).

GC-MS, m/z (%): 244 $[M]^+$ (26), 215 (9), 187 (37), 126 (87), 115 (100), 41 (40). Elemental analysis calcd for $C_{15}H_{16}SO$: C, 73.82; H, 6.48; S, 13.16; found: C, 73.77; H, 6.56; S, 13.11.

The initial reaction mixture contained **(*Z*)-3b:(*E*)-3b** isomers in a ratio of 4:1 (^{1}H NMR). The purification by column chromatography gave 0.23 g of yellow oil, 81%.

(2*Z*)-2-Heptylthio-5-phenylpent-2-en-4-ynal (*Z*)-3b: NMR ^{1}H ($CDCl_3$ + CCl_4): *δ*=0.87 (t, 3H, CH_3 in SHept, *J* = 6.8 Hz), 1.27-1.301 (m, 6H, $(\underline{CH_2})_3CH_3$ in SHept), 1.42 (m, 2H, $SCH_2CH_2\underline{CH_2}$), 1.61 (m, 2H, $SCH_2\underline{CH_2}$), 3.16 (t, 2H, SCH_2, *J* = 7.5 Hz), 6.78 (s, 1H, CH=), 7.38 (m, 3H, *m*-H, *p*-H), 7.51 (d, 2H, *o*-H, *J* = 7.7 Hz), 9.49 (s, 1H, CHO). NMR ^{13}C ($CDCl_3$ + CCl_4): *δ*=14.31 (CH_3), 22.80 ($SCH_2CH_2CH_2CH_2CH_2\underline{C}H_2$), 28.73 ($SCH_2CH_2CH_2CH_2\underline{C}H_2$), 29.04 ($SCH_2CH_2CH_2\underline{C}H_2$), 30.77 ($SCH_2CH_2\underline{C}H_2$), 31.87 ($SCH_2$), 31.91 ($SCH_2\underline{C}H_2$), 86.35 (C-4), 109.77 (C-5), 122.57 (C-2), 127.90 (C-3), 128.70 (*m*-C), 129.80 (*p*-C), 132.03 (*o*-C), 146.48 (C_i), 189.96 (C=O).

(2*E*)-2-Heptylthio-5-phenylpent-2-en-4-ynal (*E*)-3b: NMR ^{1}H ($CDCl_3$ + CCl_4): *δ*=0.89 (t, 3H, CH_3 in SHept, *J* = 6.8 Hz), 1.27-1.301 (m, 6H, $(\underline{CH_2})_3CH_3$ in SHept), 1.42 (m, 2H, $SCH_2CH_2\underline{CH_2}$), 1.68 (m, 2H, $SCH_2\underline{CH_2}$), 2.78 (t, 2H, SCH_2, *J* = 7.3 Hz), 6.50 (s, 1H, CH=), 7.36 (m, 3H, *m*-H, *p*-H), 7.44 (d, 2H, *o*-H, *J* = 7.7 Hz), 10.32 (s, 1H, CHO). NMR ^{13}C ($CDCl_3$ + CCl_4): *δ*=14.31 (CH_3), 22.78 ($SCH_2CH_2CH_2CH_2CH_2\underline{C}H_2$), 28.28 ($SCH_2CH_2CH_2CH_2\underline{C}H_2$), 29.15 ($SCH_2CH_2CH_2\underline{C}H_2$), 30.35 ($SCH_2CH_2\underline{C}H_2$), 31.53 ($SCH_2$), 31.91 ($SCH_2\underline{C}H_2$), 84.68 (C-4), 100.22 (C-5), 118.72 (C-2), 127.90 (*m*-C), 128.70 (C-3), 129.34 (*p*-C), 131.75 (*o*-C), 148.34 (C_i), 187.94 (C=O).

GC-MS, m/z (%): 286 $[M]^+$ (28), 187 (38), 126 (100), 115 (67), 41 (29). Elemental analysis calcd for $C_{18}H_{22}SO$: C, 75.52; H, 7.69; S, 11.19; found: C, 75.61; H, 7.67; S, 11.21.

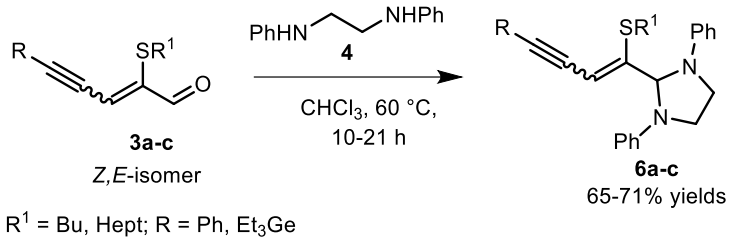
The initial reaction mixture contained **(*Z*)-3c:(*E*)-3c** isomers in a ratio of 5:1 (^{1}H NMR). The purification by column chromatography gave 0.25 g of light-yellow oil, 76%.

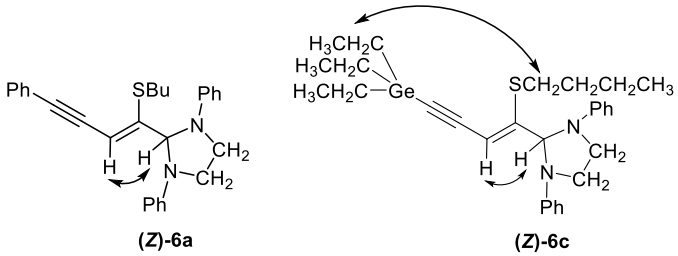
(2*Z*)-2-Butylthio-5-(triethylgermyl)pent-2-en-4-ynal (*Z*)-3c: NMR ^{1}H ($CDCl_3$ + CCl_4): *δ*=0.91 (q, 6H, CH_2 in Et_3Ge, *J* = 8.0 Hz), 1.11 (t, 3H, CH_3 in SBu, *J* = 7.5 Hz), 1.14 (t, 3H, CH_3 in Et_3Ge, *J* = 8.0 Hz), 1.43 (m, 2H, $C\underline{H_2}CH_3$ in SBu), 1.55 (m, 2H, $C\underline{H_2}CH_2CH_3$ in SBu), 3.11 (t, 2H, SCH_2, *J* = 7.4 Hz), 6.56 (s, 1H, =CH), 9.41 (s, 1H, CHO). NMR ^{13}C ($CDCl_3$ + CCl_4): *δ*=5.97 (CH_3 (Ge)), 9.23 (CH_2 (Ge)), 13.86 (CH_3 in SBu), 21.77 ($SCH_2CH_2\underline{C}H_2$), 30.94 ($SCH_2$), 32.37 ($SCH_2\underline{C}H_2$), 101.89 (C-4), 116.89 (C-5), 128.12 (C-3), 146.79 (C-2), 190.19 (CHO).

(2*E*)-2-Butylthio-5-(triethylgermyl)pent-2-en-4-ynal (*E*)-3c: NMR ^{1}H ($CDCl_3$ + CCl_4): *δ*=0.95 (q, 6H, CH_2 in Et_3Ge, *J* = 8.0 Hz), 1.11 (t, 3H, CH_3 in SBu, *J* = 7.5 Hz), 1.14 (t, 3H, CH_3 in Et_3Ge, *J* = 8.0 Hz), 1.47 (m, 2H, $C\underline{H_2}CH_3$ in SBu), 1.64 (m, 2H, $C\underline{H_2}CH_2CH_3$ in SBu), 2.72 (t, 2H, SCH_2, *J* = 7.3 Hz), 6.30 (s, 1H, =CH), 10.23 (s, 1H, CHO). NMR ^{13}C ($CDCl_3$ + CCl_4): *δ*=6.05 (CH_3 (Ge)), 9.27 (CH_2 (Ge)), 13.81 (CH_3 in Bu), 22.29 ($SCH_2CH_2\underline{C}H_2$), 30.34 ($SCH_2$), 32.37 ($SCH_2\underline{C}H_2$), 100.32 (C-4), 105.66 (C-5), 119.26 (C-3), 149.02 (C-2), 187.94 (CHO).

GC-MS, m/z (%): 326 (3) $[M]^+$, 299 (100), 271 (31), 215 (25), 167 (26), 153 (27), 133 (32), 105 (38), 91 (22), 79 (21), 57 (46), 41 (48). Elemental analysis calcd for $C_{15}H_{26}GeSO$: C, 55.20; H, 7.95; Ge, 22.08; S, 9.81; found: C, 55.19; H, 7.99; Ge, 22.06; S, 9.80.

General procedure for the synthesis of imidazolidines 6a-c. To a mixture of aldehydes **(*Z*,*E*)-3** (0.5 mmol) in $CHCl_3$ (2 ml) was added *N,N'*-diphenylethylendiamine **4** (0.5 mmol), and the mixture was stirred at 60 °C for 10-21 h. The reaction mixture was dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the solid residue was analyzed by ^{1}H NMR spectroscopy.





Reaction of 2-(butylthio)-5-phenylpent-2-en-4-ynal ***(3a)*** *with N,N-diphenylethylendiamine* ***(4)****.* The reaction time was 11 h. Analysis of the reaction mixture (^{1}H NMR) showed that the ratio of **(*Z*)-6a:(*E*)-6a** isomers was 3:1, as well as in the mixture of starting aldehydes. In order to isolate individual isomers, the solid residue was dissolved in $CHCl_3$ (1 ml), and MeOH (1 ml) was added. The formed after some hours precipitate was found to be pure ***(Z)*-6a** (0.073 g, 33%). Further precipitate formed was the mixture of **(*Z*)-6a:(*E*)-6a** isomers in the ratio 1:0.7 (0.052 g, 24%), and the last collected precipitate was ***(E)*-6a** (0.03 g, 14%). The total yield was (0.155 g, 71%).

***2-[(1Z)-1-Butylthio-4-phenylbut-1-en-3-yn-1-yl]*-1,3-diphenylimidazolidine (*Z*)-6a:** Light yellow solid, mp. 108 °C. NMR ^{1}H ($CDCl_3$+CCl_4): δ=0.75 (t, 3H, CH_3 in SBu, J = 7.3 Hz), 1.20 (m, 2H, $SCH_2CH_2\underline{CH_2}CH_3$), 1.31 (m, 2H, $SCH_2\underline{CH_2}$), 2.53 (t, 2H, SCH_2, J = 7.2 Hz), 3.71 (m, 2H, CH_2), 3.99 (m, 2H, CH_2), 5.76 (s, 1H, CH), 6.45 (s, 1H, CH=), 6.75 (t, 2H, *p*-H in NPh), 6.91 (d, 4H, *o*-H in NPh, J = 8.2 Hz), 7.26 (dd, 4H, *m*-H in NPh, J = 7.8, 8.2 Hz), 7.35 (m, 3H, *p,m*-H in ΞC-Ph), 7.55 (m, 2H, *o*-H in ΞC-Ph). NMR ^{13}C ($CDCl_3$+CCl_4): δ=13.85 (CH_3 in SBu), 22.23 ($SCH_2CH_2\underline{C}H_2$), 30.30 ($SCH_2\underline{C}H_2$), 31.83 ($SCH_2$), 46.61 ($NCH_2$), 74.46 (CH), 86.53 (≡C), 97.91 (C≡), 107.77 (CH=), 113.93 *(o*-C in PhN), 118.11 *(p*-C in PhN), 123.59 (C_i in PhC), 128.61 (*p*-C in PhC), 128.74 (*m*-C in PhC), 129.24 (*m*-C in PhN), 131.43 (*o*-C in PhC), 145.02 (C_i in PhN), 153.45 (=C-S). NMR ^{15}N ($CDCl_3$): -301.7.

***2-[(1E)-1-Butylthio-4-phenylbut-1-en-3-yn-1-yl]*-1,3-diphenylimidazolidine (*E*)-6a:** Light yellow solid, mp. 92 °C. NMR ^{1}H ($CDCl_3$): δ=0.66 (t, 3H, CH_3 in SBu, J = 6.9 Hz), 1.20 (m, 2H, $SCH_2\underline{CH_2}CH_2$), 2.85 (t, 2H, SCH_2, J = 7.3 Hz), 3.69 (m, 2H, CH_2), 4.00 (m, 2H, CH_2), 5.64 (s, 1H, CH), 6.53 (s, 1H, CH=), 6.76 (m, 6H, *o,p*-H in NPh), 7.27 (m, 7H, *m,p*-H in ΞC-Ph, *m*-H in NPh), 7.39 (m, 2H, *o*-H in ΞC-Ph). NMR ^{13}C ($CDCl_3$): δ=13.68 (CH_3 in SBu), 21.92 ($SCH_2CH_2\underline{C}H_2$), 32.04 ($SCH_2\underline{C}H_2$), 33.09 ($SCH_2$), 46.57 ($NCH_2$), 79.99 (CH), 85.43 (≡C), 95.87 (C≡), 113.13 *(o*-C in PhN), 114.99 (C_i in PhC), 118.11 *(p*-C in PhN), 128.51 (*m*-C in PhC), 128.58 (*p*-C in PhC), 129.24 (*m*-C in PhN), 129.63 (CH=), 131.37 (*o*-C in PhC), 145.22 (C_i in PhN), 148.47 (=C-S). NMR ^{15}N ($CDCl_3$): -302.6.

GC-MS, *m/z* (%): 438 (4) [M]+, 381 (5) [M-Bu]+, 349 (3) [M-SBu]+, 224 (31), 223 (100), 77 (14). Elemental analysis calcd for $C_{29}H_{30}N_2S_1$: C, 79.41; H, 6.89; S, 7.31; N, 6.39; found: C, 79.45; H, 6.76; S, 7.19; N, 6.38.

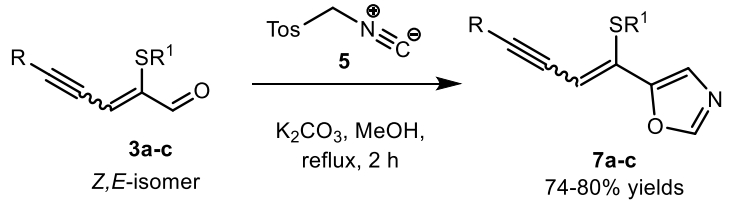
Reaction of 2-heptylthio-5-phenylpent-2-en-4-ynal ***(3b)*** *with N,N-diphenylethylendiamine* ***(4)****.* The reaction time was 21 h. Analysis of the reaction mixture (^{1}H NMR) showed that the ratio of **(*Z*)-6b:(*E*)-6b** isomers was 4:1, as in the mixture of the starting aldehydes. In order to isolate individual isomers, the solid residue was dissolved in 1 mL of $CHCl_3$ and 1 mL of MeOH was added. The formed after 24 hours precipitate was found to be pure ***(Z)*-6b** (0.17 g, 70%).

***2-[(1Z)-1-Heptylthio-4-phenylbut-1-en-3-yn-1-yl]*-1,3-diphenylimidazolidine (*Z*)-6b:** Light yellow solid, mp. 218 °C. NMR ^{1}H ($CDCl_3$): δ=0.84 (t, 3H, CH_3 in SHept, J = 7.3 Hz), 1.08-1.21 (m, 6H, $(\underline{CH_2})_3CH_3$ in SHept), 1.27 (m, 4H, $SCH_2\underline{CH_2}\underline{CH_2}$), 2.86 (t, 2H, SCH_2, J = 7.1 Hz), 3.71 (m, 2H, CH_2), 4.02 (m, 2H, CH_2), 5.66 (s, 1H, CH), 6.55 (s, 1H, CH=), 6.76 (m, 6H, *o,p*-H in NPh), 7.27 (m, 7H, *m,p*-H in ΞC-Ph, *m*-H in NPh), 7.41 (m, 2H, *o*-H in ΞC-Ph). NMR ^{13}C ($CDCl_3$): δ=14.18 (CH_3), 22.70 ($\underline{C}H_2CH_3$), 28.82 ($\underline{C}H_2CH_2CH_3$), 28.90 ($\underline{C}H_2CH_2CH_2CH_3$), 30.00 ($SCH_2\underline{C}H_2$), 31.79 ($SCH_2CH_2\underline{CH_2}$), 33.39 ($SCH_2$), 46.57 ($NCH_2$), 80.01 (CH), 86.50

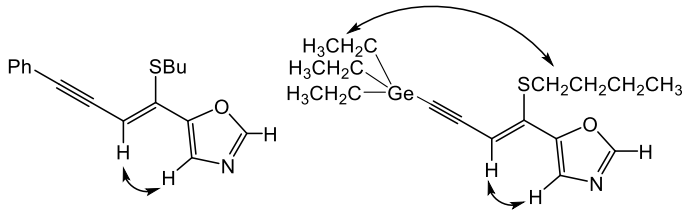
(≡C), 98.52 (C≡), 113.80 (*o*-C in PhN), 114.94 (CH=), 118.13 (*p*-C in PhN), 123.41 (C_i in PhC), 128.50 (*m*-C in PhC), 128.58 (*p*-C in PhC), 129.24 (*m*-C in PhN), 131.39 (*o*-C in PhC), 145.24 (C_i in PhN), 149.07 (=C-S). NMR ^{15}N ($CDCl_3$): -302.3.
GC-MS, *m*/*z* (%): 480 (<1) [M]+, 349 (1) [M-SBu]+, 224 (21), 223 (100), 77 (9). Elemental analysis calcd for $C_{32}H_{36}N_2S_1$: C, 79.95; H, 7.55; S, 6.67; N, 5.83; found: C, 79.98; H, 7.61; S, 6.81; N, 8.86.

*Reaction of 2-butylthio-5-(triethylgermyl)pent-2-en-4-ynal **(3c)** with N,N-diphenylethylendiamine **(4)**.* The reaction time was 10 h. Analysis of the reaction mixture (^1H NMR) showed that the ratio of **(*Z*)-6c:(*E*)-6c** isomers was 5:1, as well as in the mixture of the starting aldehydes. After recrystallization of the residue from ethanol pure ***(Z)-6c*** isomer was isolated (0.17 g, 65%).
***2-[(1Z)-1-Butylthio-4-(triethylgermyl)but-1-en-3-yn-1-yl]*-1,3-diphenylimidazolidine (*Z*)-6c:** Light yellow solid, mp. 73 °C. NMR ^1H ($CDCl_3$): *δ*=0.69 (t, 3H, CH_3 in SBu, *J* = 7.3 Hz), 0.88 (q, 6H, CH_2 in Et_3Ge, *J* = 7.8 Hz), 1.08 (t, 9H, CH_3 in Et_3Ge, *J* = 7.8 Hz), 1.18 (m, 2H, $SCH_2\underline{CH_2}\underline{CH_2}CH_3$), 2.82 (t, 2H, SCH_2, *J* = 7.2 Hz), 3.68 (m, 2H, CH_2), 3.99 (m, 2H, CH_2), 5.57 (s, 1H, CH), 6.36 (s, 1H, CH=), 6.72 (d, 2H, *o*-H, *J* = 7.9 Hz), 6.79 (t, 4H, *p*-H, *J* = 7.2 Hz), 7.26 (dd, 4H, *m*-H, *J* = 7.2, 7.9 Hz). NMR ^{13}C ($CDCl_3$): *δ*=5.84 (CH_3 in Et_3Ge), 9.10 (CH_2 in Et_3Ge), 13.73 (CH_3 in SBu), 21.87 ($SCH_2CH_2\underline{CH_2}$), 32.05 ($SCH_2\underline{CH_2}$), 32.54 ($SCH_2$), 46.54 ($NCH_2$), 79.90 (≡C), 102.14 (C≡), 113.71 (*o*-C), 115.56 (CH=), 117.96 (*p*-C), 129.21 (*m*-C), 145.29 (C_i), 148.54 (=C-S). NMR ^{15}N ($CDCl_3$): -302.2.
GC-MS, *m*/*z* (%): 520 (<1) [M]+, 431 (3) [M-SBu]+, 224 (16), 223 (100), 77 (7). Elemental analysis calcd for $C_{29}H_{40}N_2S_1Ge_1$: C, 66.92; H, 7.69; S, 6.15; N, 5.38; found: C, 66.87; H, 7.65; S, 6.17; N, 5.40.

Synthesis of 1,3-oxazoles 7a-c was carried out according to the published procedure [N. V. Vchislo *et al*, *Mendeleev Commun,* **2020**, 30, 350]. To a solution of aldehydes **(*Z*,*E*)-3** (1 mmol) in MeOH (6 ml), was added TosMIC **5** (1.1 mmol) and K_2CO_3 (1.4 mmol). The mixture was stirred for 2 h at 50-60 °C. Then methanol was removed in vacuum, the residue was dissolved in ether and the precipitate was filtered off. Then the ether was removed and the residue was purified by column chromatography (SiO_2, eluent-chloroform).



R^1 = Bu, Hept; R = Ph, Et_3Ge



(*Z*)-7a **(*Z*)-7c**

*Reaction of 2-butylthio-5-phenylpent-2-en-4-ynal **(3a)** with TosMIC **(5)**.* After completion of the reaction, the mixture contained **(*Z*)-7a:(*E*)-7a** isomers in a 3:1 ratio (^1H NMR) along with the starting aldehydes. After purification by column chromatography, the target oxazoles were isolated as a mixture of isomers (0.167 g, 59%), and additionally ***(Z)-7a*** (0.043 g, 15%) isomer was also isolated individually. Total yield was (0.21 g, 74%).
5-[(1Z)-1-Butylthio-4-phenylbut-1-en-3-yn-1-yl]-1,3-oxazole (Z)-7a: IR (n/cm^{-1}): 2958, 2871, 2192, 1598, 1105. NMR ^1H ($CDCl_3$): *δ*=0.89 (t, 3H, CH_3 in SBu, J =7.3 Hz), 1.45 (m, 2H, $SCH_2CH_2\underline{CH_2}CH_3$), 1.59 (m, 2H, $SCH_2\underline{CH_2}$), 2.99 (t, 2H, SCH_2, J = 7.2 Hz), 6.63 (s, 1H, CH=), 7.35 (m, 4H, *m*-H, *p*-H, H-4 in cycle), 7.51 (m, 2H, *o*-H), 7.86 (s, 1H, H-2). NMR ^{13}C ($CDCl_3$): *δ*=13.72 (CH_3), 21.80 ($SCH_2CH_2\underline{CH_2}$), 31.91 ($SCH_2\underline{CH_2}$), 34.04 ($SCH_2$), 87.23 (≡C), 100.80 (C≡), 113.11 (=CH), 123.26 (=C-S), 126.41 (C-4), 128.56 (*m*-C), 128.86 (*p*-C), 131.67 (*o*-C), 132.06 (C_i), 151.20 (C-5), 151.46 (C-2). NMR ^{15}N ($CDCl_3$): -121.

5-[(1E)-1-Butylthio-4-phenylbut-1-en-3-yn-1-yl]-1,3-oxazole (E)-7a: NMR ^{1}H ($CDCl_3$): *δ*=0.93 (t, 3H, CH_3 in SBu, *J* = 7.3 Hz), 1.45 (m, 2H, $SCH_2CH_2\underline{CH_2}CH_3$), 1.63 (m, 2H, $SCH_2\underline{CH_2}$), 2.83 (t, 2H, SCH_2, *J* = 7.3 Hz), 5.93 (s, 1H, CH=), 7.35 (m, 3H, *m*-H, *p*-H), 7.45 (m, 2H), 7.79 (s, 1H, H-4), 7.94 (s, 1H, H-2). NMR ^{13}C ($CDCl_3$): *δ*=13.70 (CH_3), 22.06 ($SCH_2CH_2\underline{C}H_2$), 30.74 ($SCH_2\underline{C}H_2$), 32.82 ($SCH_2$), 87.53 (≡C), 97.49 (C≡), 106.34 (=CH), 123.26 (=C-S), 127.56 (C-4), 128.60 (*m*-C), 128.73 (p-C), 131.52 (*o*-C), 134.05 (C_i), 150.58 (C-5), 151.47 (C-2).

GC-MS, *m*/*z* (%): 283 (100) $[M]^+$, 240 (57), 227 (17), 171 (26), 112 (15), 41 (13). Elemental analysis calcd for $C_{17}H_{17}SON$: C, 72.08; H, 6.00; S, 11.31; N, 4.95; found: C, 72.00; H, 5.96; S, 11.34; N, 4.95.

Reaction of 2-heptylthio-5-phenylpent-2-en-4-ynal ***(3b)*** *with TosMIC* ***(5)****.* After completion of the reaction, the mixture contained **(*Z*)-7b:(*E*)-7b** isomers in a 5:1 ratio (^{1}H NMR) along with the starting aldehydes. After purification by column chromatography, the target oxazoles were isolated as a mixture of isomers (0.18 g, 55%), and additionally ***(Z)-7b*** (0.08 g, 25%) isomer was also isolated individually. Total yield was (0.26 g, 80%).

5-[(1Z)-1-Heptylthio-4-phenylbut-1-en-3-yn-1-yl]-1,3-oxazole (Z)-7b: IR (n/cm^{-1}): 2926, 2855, 2194, 1598, 1489, 1109. NMR ^{1}H ($CDCl_3$): *δ*=0.84 (t, 3H, CH_3 in SHept, *J* = 7.2 Hz), 1.23-1.30 (m, 6H, $(\underline{CH_2})_3CH_3$ in SHept), 1.42 (m, 2H, $SCH_2CH_2\underline{CH_2}$), 1.62 (m, 2H, $SCH_2\underline{CH_2}$), 2.98 (t, 2H, SCH_2, *J* = 7.3 Hz), 6.63 (s, 1H, CH=), 7.34 (m, 4H, *m*-H, *p*-H, H-4 in cycle), 7.51 (m, 2H, *o*-H), 7.86 (s, 1H, H-2). NMR ^{13}C ($CDCl_3$): *δ*=14.16 (CH_3), 22.70 ($\underline{C}H_2CH_3$), 28.64 ($\underline{C}H_2CH_2CH_3$), 28.95 ($\underline{C}H_2CH_2CH_2CH_3$), 29.86 ($SCH_2\underline{C}H_2$), 31.83 ($SCH_2CH_2\underline{CH_2}$), 34.38 ($SCH_2$), 87.26 (≡C), 100.81 (C≡), 113.13 ($\underline{C}H$=C-S), 123.29 (=C-S), 126.43 (C-4), 128.56 (*m*-C), 128.87 (*p*-C), 131.70 (*o*-C), 132.10 (C_i), 151.16 (C-5), 151.47 (C-2). NMR ^{15}N ($CDCl_3$): -120.6 ($^{2}J_{NH}$ = 13.6 cross peak with H-2).

5-[(1E)-1-Heptylthio-4-phenylbut-1-en-3-yn-1-yl]-1,3-oxazole (E)-7b: NMR ^{1}H ($CDCl_3$): *δ*=0.88 (t, 3H, CH_3 in SBu, *J* = 7.3 Hz), 1.22-1.26 (m, 6H, $(\underline{CH_2})_3CH_3$ in SHept), 1.41 (m, 2H, $SCH_2CH_2\underline{CH_2}$), 1.61 (m, 2H, $SCH_2\underline{CH_2}$), 2.80 (t, 2H, SCH_2, *J* = 7.3 Hz), 5.93 (s, 1H, CH=), 7.35 (m, 3H, *m*-H, *p*-H), 7.45 (m, 2H, *o*-H), 7.79 (s, 1H, H-4), 7.92 (s, 1H, H-2). NMR ^{13}C ($CDCl_3$): *δ*=14.07 (CH_3), 22.60 ($\underline{C}H_2CH_3$), 28.60 ($\underline{C}H_2CH_2CH_3$), 28.80 ($\underline{C}H_2CH_2CH_2CH_3$), 28.82 ($SCH_2\underline{C}H_2$), 31.70 ($SCH_2CH_2\underline{CH_2}$), 33.05 ($SCH_2$), 87.21 (≡C), 97.42 (C≡), 106.14 (=C-S), 123.13 ($\underline{C}H$=C-S), 127.47 (C-4), 128.52 (*m*-C), 128.63 (*p*-C), 131.44 (*o*-C), 134.03 (C_i), 148.95 (C-5), 150.50 (C-2).

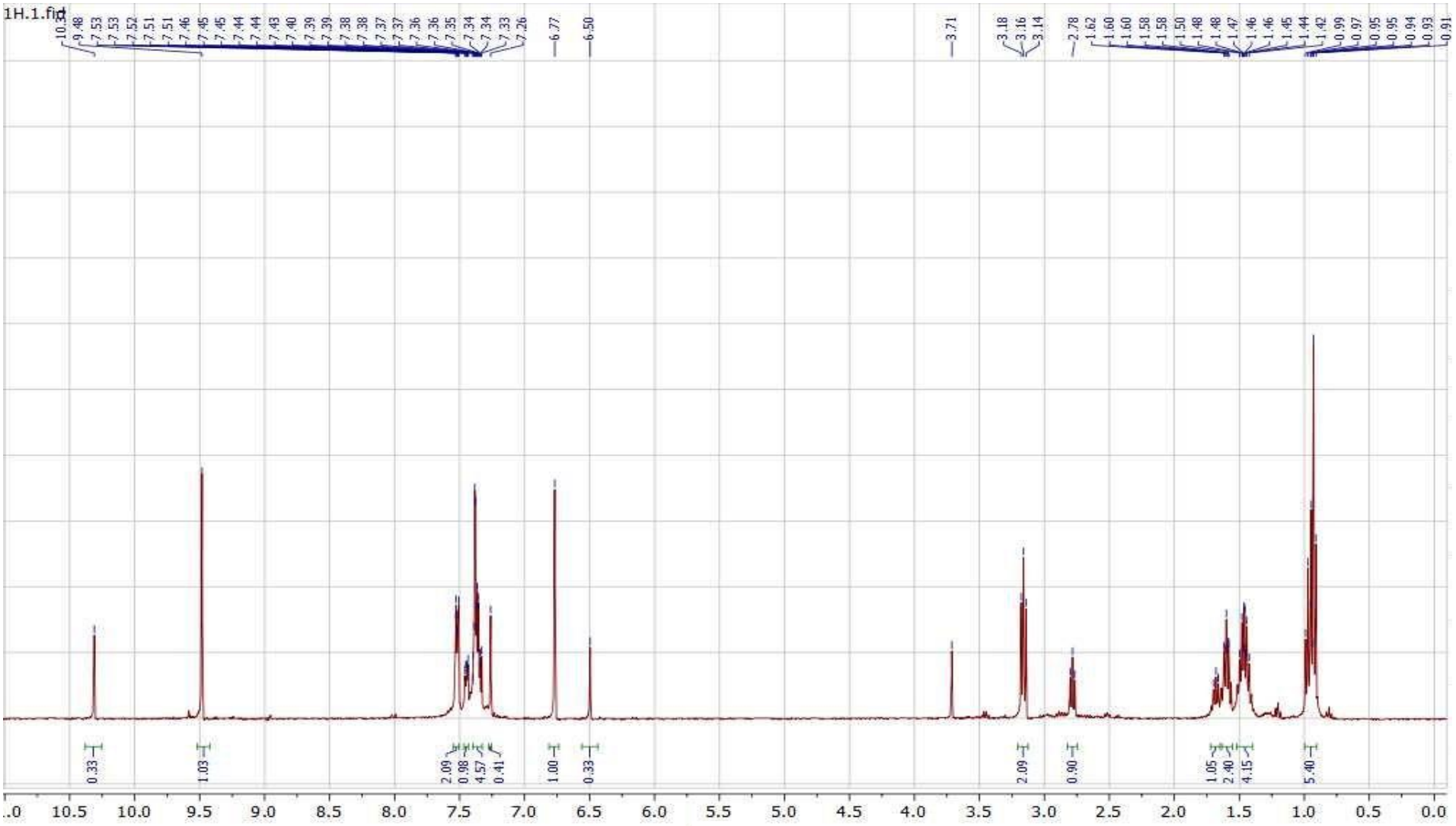
GC-MS, *m*/*z* (%): 325 (100) $[M]^+$, 240 (94), 227 (44), 172 (49), 112 (29), 57 (60), 41 (59). Elemental analysis calcd for $C_{20}H_{23}SON$: C, 73.81; H, 7.09; S, 9.81; N, 4.32; found: C, 73.80; H, 7.12; S, 9.85; N, 4.30.

Reaction of 2-butylthio-5-(triethylgermyl)pent-2-en-4-ynal ***(3c)*** *with TosMIC* ***(5)****.* After completion of the reaction, the mixture contained **(*Z*)-7c:(*E*)-7c** isomers in a 5:1 ratio (^{1}H NMR) along with the starting aldehydes. After purification by column chromatography, ***(Z)-7c*** (0.29 g, 80%) isomer was isolated individually.

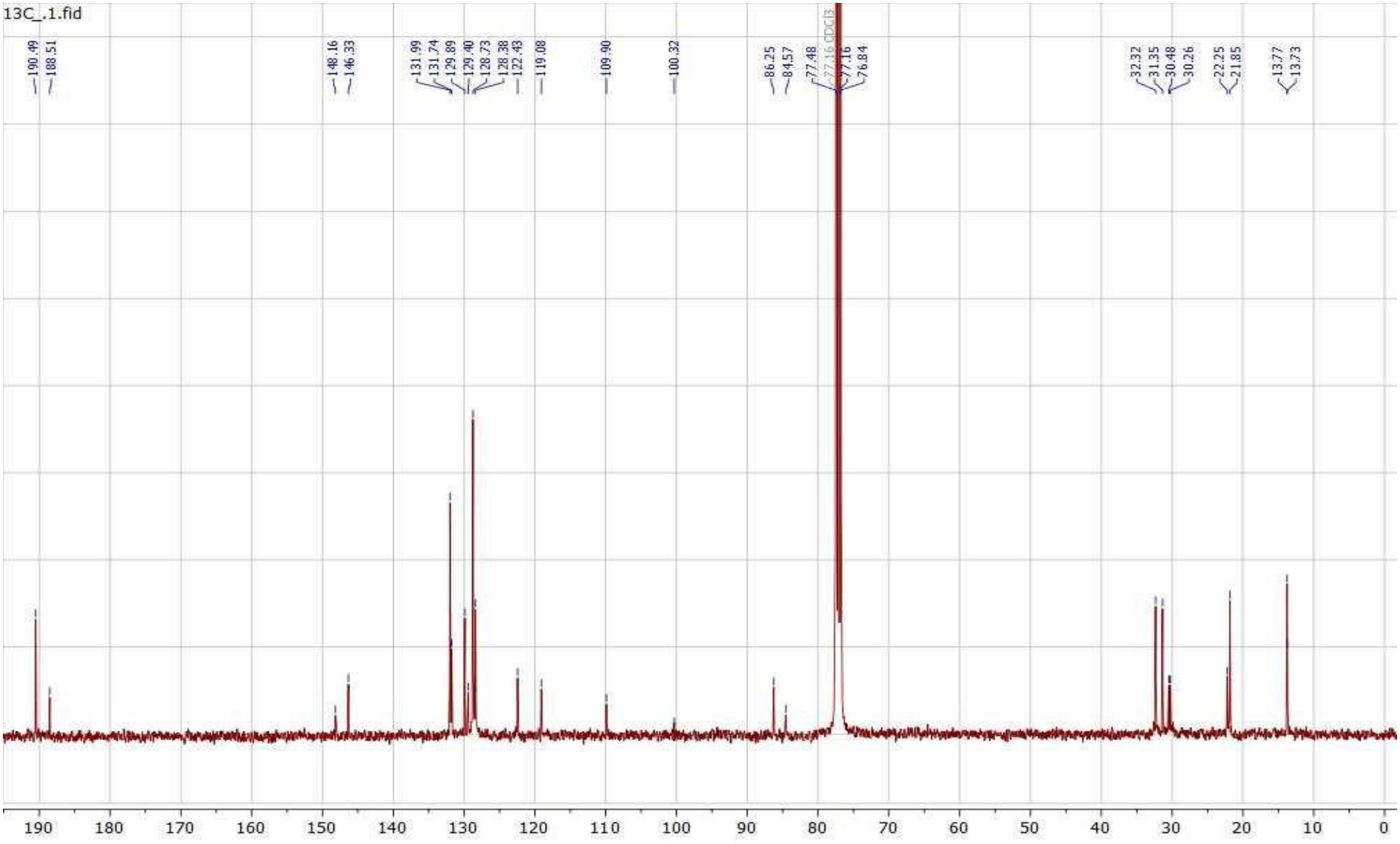
***5-[(1Z)-1-Butylthio-4-(triethylgermyl)but-1-en-3-yn-1-yl]-1,3-oxazole* (*Z*)-7c:** IR (n/cm^{-1}): 2955, 2925, 1723, 1458, 1103. NMR ^{1}H ($CDCl_3$): *δ*=0.89 (t, 3H, CH_3 in SBu, *J* = 7.3 Hz), 0.91 (q, 6H, CH_2 in Et_3Ge, *J* = 7.8 Hz), 1.13 (t, 9H, CH_3 in Et_3Ge, *J* = 7.8 Hz), 1.42 (m, 2H, $SCH_2CH_2\underline{CH_2}CH_3$), 1.54 (m, 2H, $SCH_2\underline{CH_2}$), 2.95 (t, 2H, SCH_2, *J* = 7.3 Hz), 6.44 (s, 1H, CH=), 7.30 (s, H-4), 7.82 (s, 1H, H-2). NMR ^{13}C ($CDCl_3$): *δ*=5.92 (CH_2 in Et_3Ge), 9.18 (CH_3 in Et_3Ge), 13.77 (CH_3 in SBu), 21.79 ($SCH_2CH_2\underline{C}H_2$), 31.86 ($SCH_2\underline{C}H_2$), 33.56 ($SCH_2$), 102.81 (≡C), 106.25 (C≡), 113.40 ($\underline{C}H$=C-S), 126.29 (C-4), 132.07 (=C-S), 151.27 (C-2), 151.41 (C-5). NMR ^{15}N ($CDCl_3$): -121.4 ($^{2}J_{NH}$ = 11.9 Hz cross peak with H-2).

GC-MS, *m*/*z* (%): 366 (10) [M]+, 338 (100), 206 (38), 281 (15), 57 (38). Elemental analysis calcd for $C_{17}H_{27}SONGe$: C, 55.77; H, 7.43; S, 8.76; N, 3.83; found: C, 55.89; H, 7.38; S, 8.81; N, 3.85.

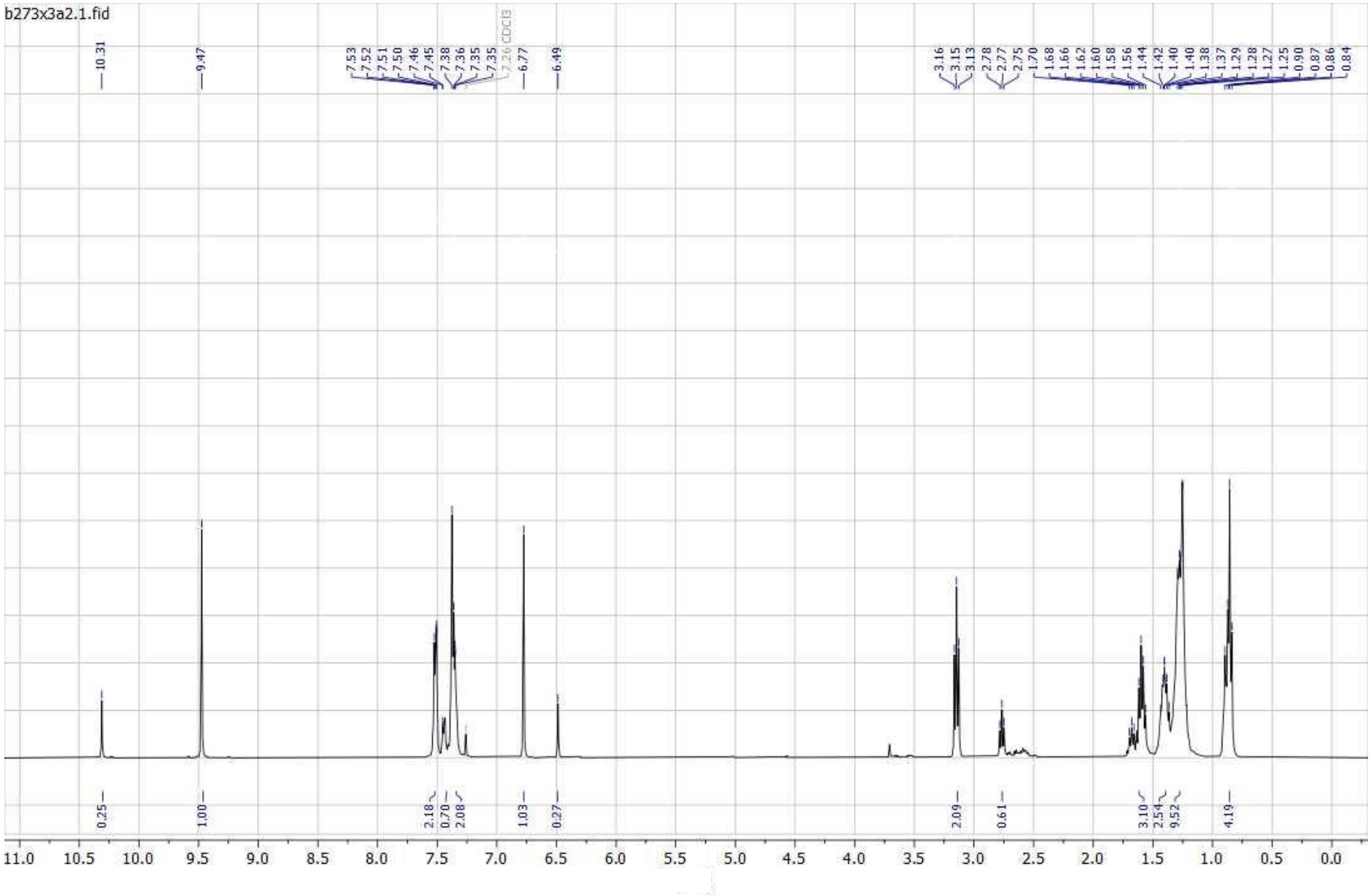
2. Spectral Data



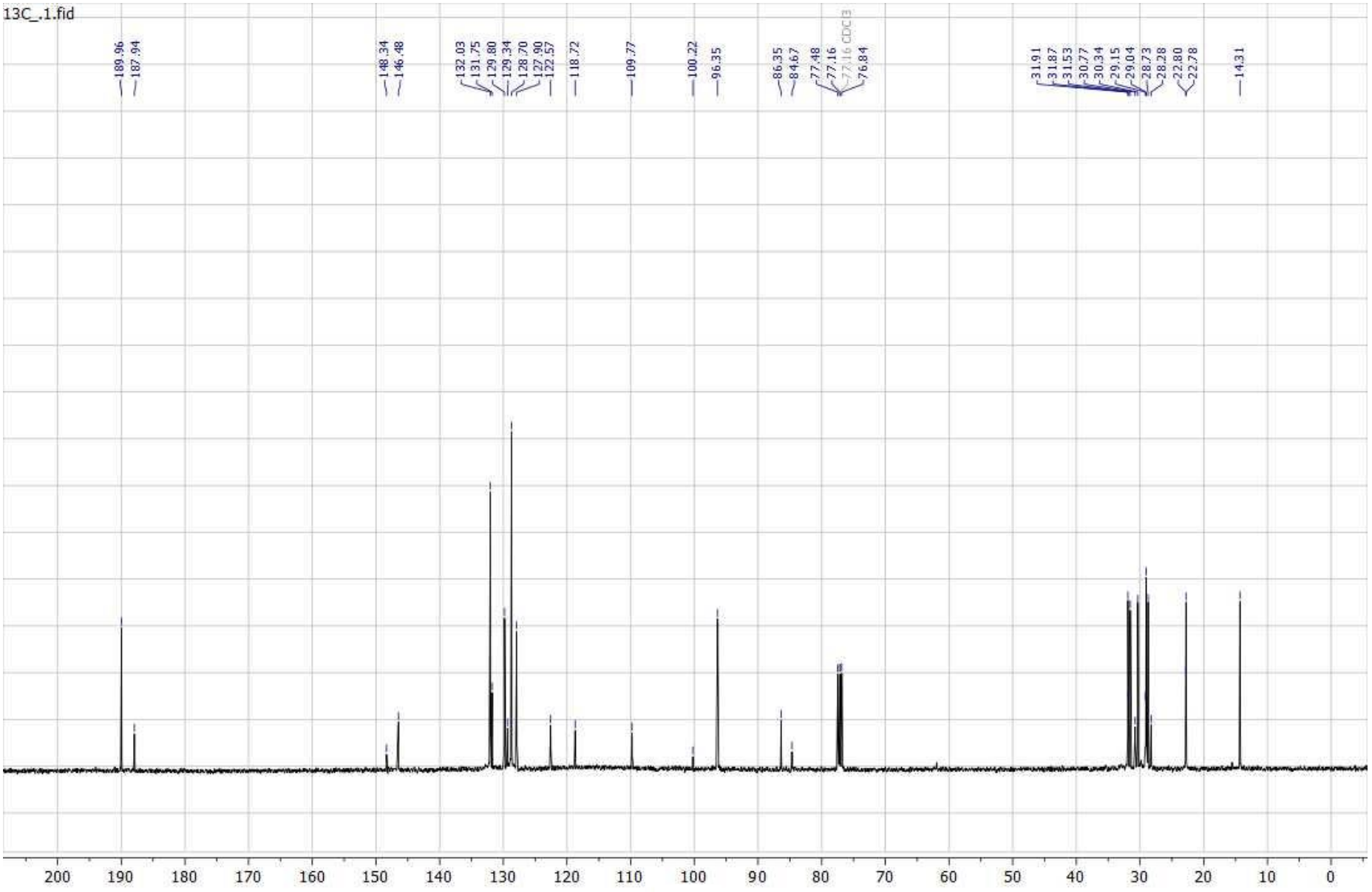
^{1}H NMR spectrum of mixture (*Z*)-**3a** and (*E*)-3**a** (3:1)



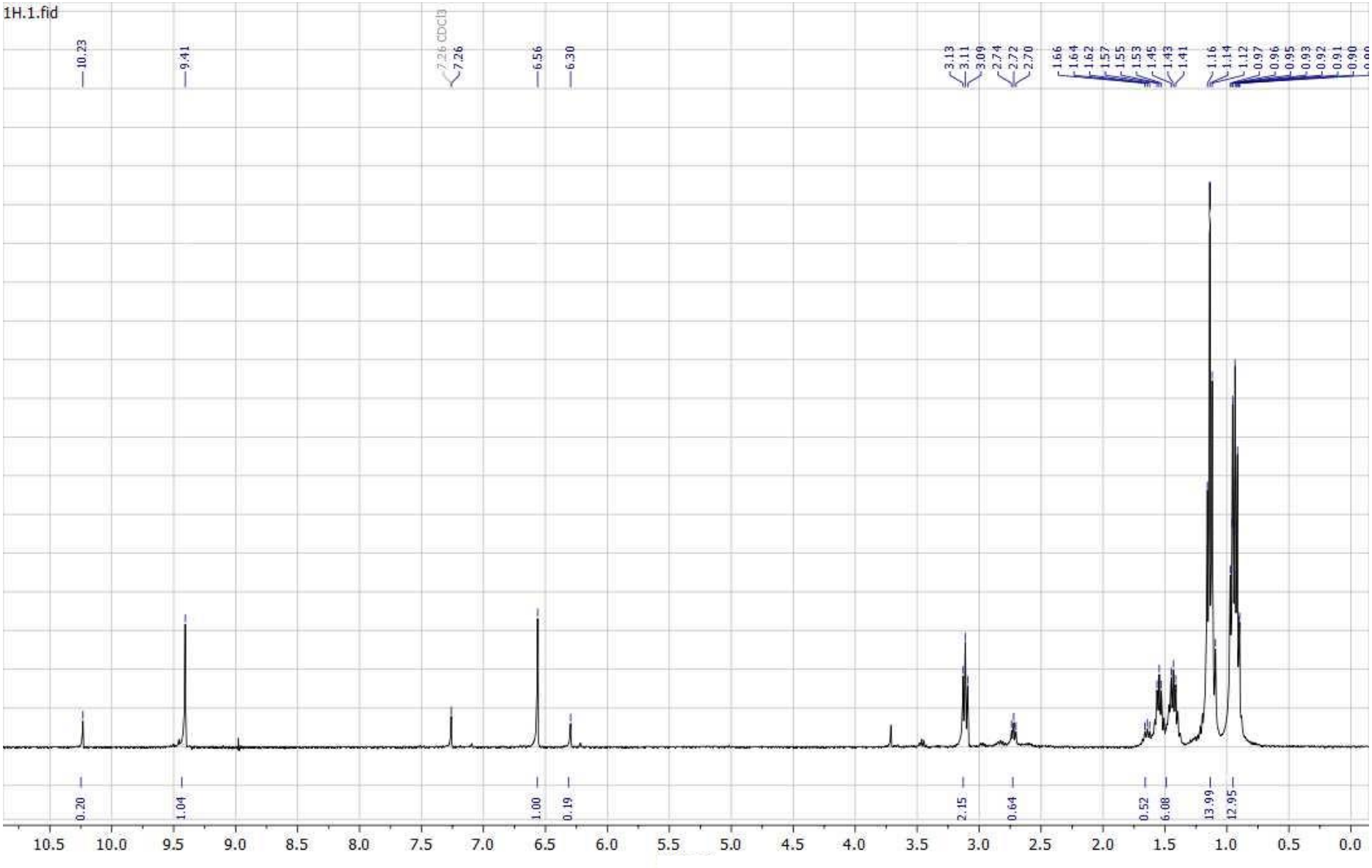
^{13}C NMR spectrum of mixture (*Z*)-**3a** and (*E*)-3**a** (3:1)



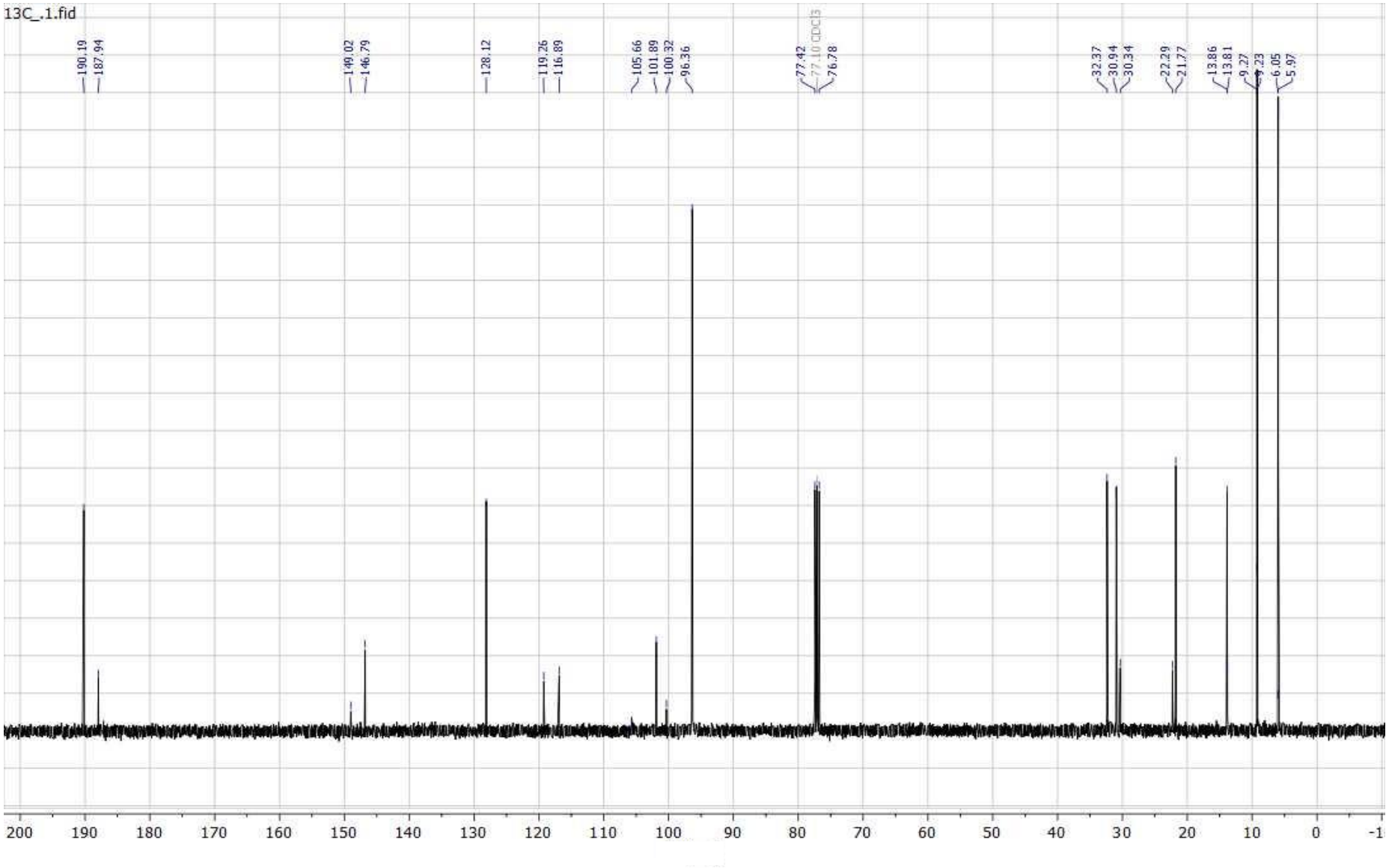
^{1}H NMR spectrum of mixture **(*Z*)-b**:**(*E*)-3b** (4:1)



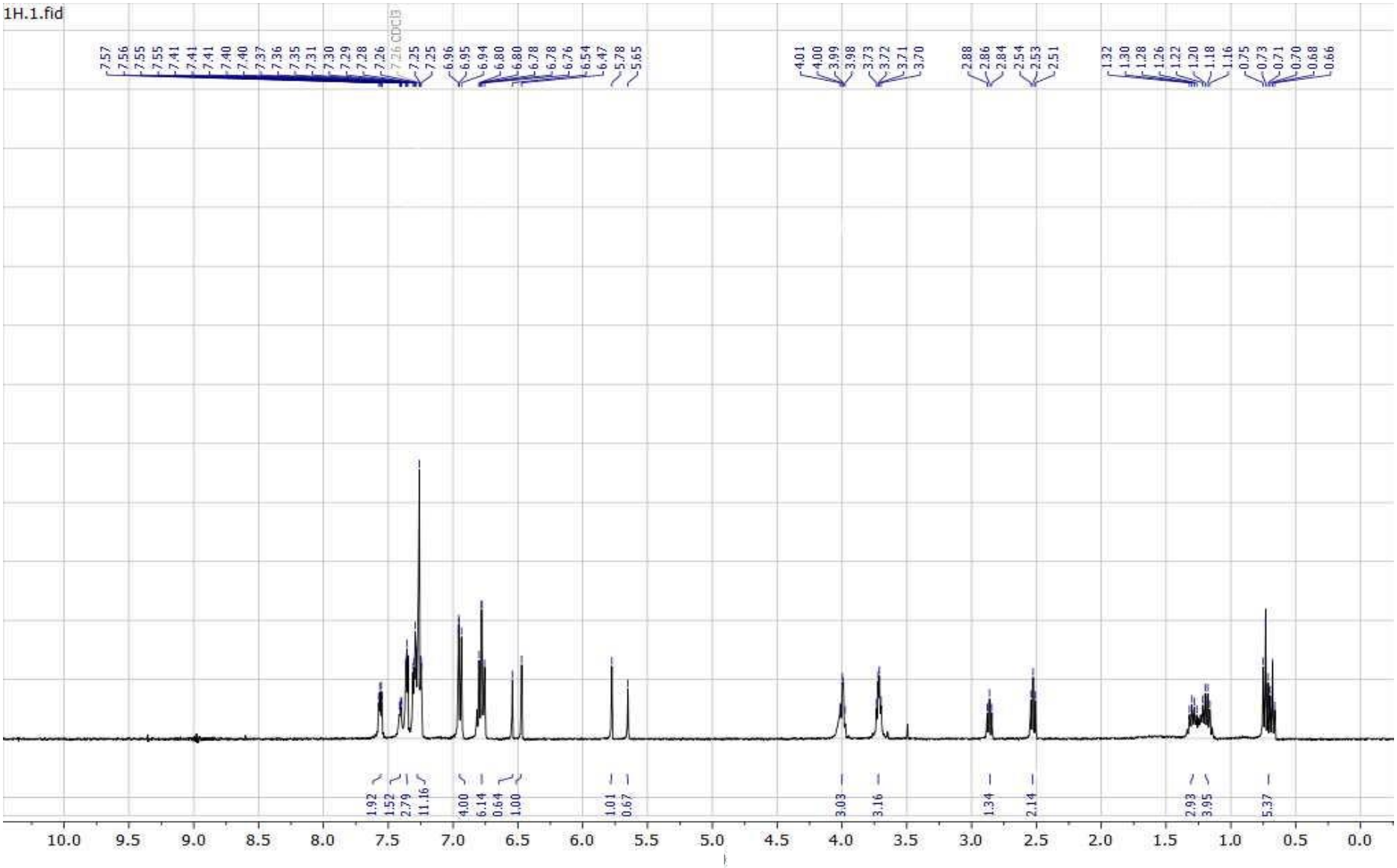
^{13}C NMR spectrum of mixture **(*Z*)-b:(*E*)-3b** (4:1)



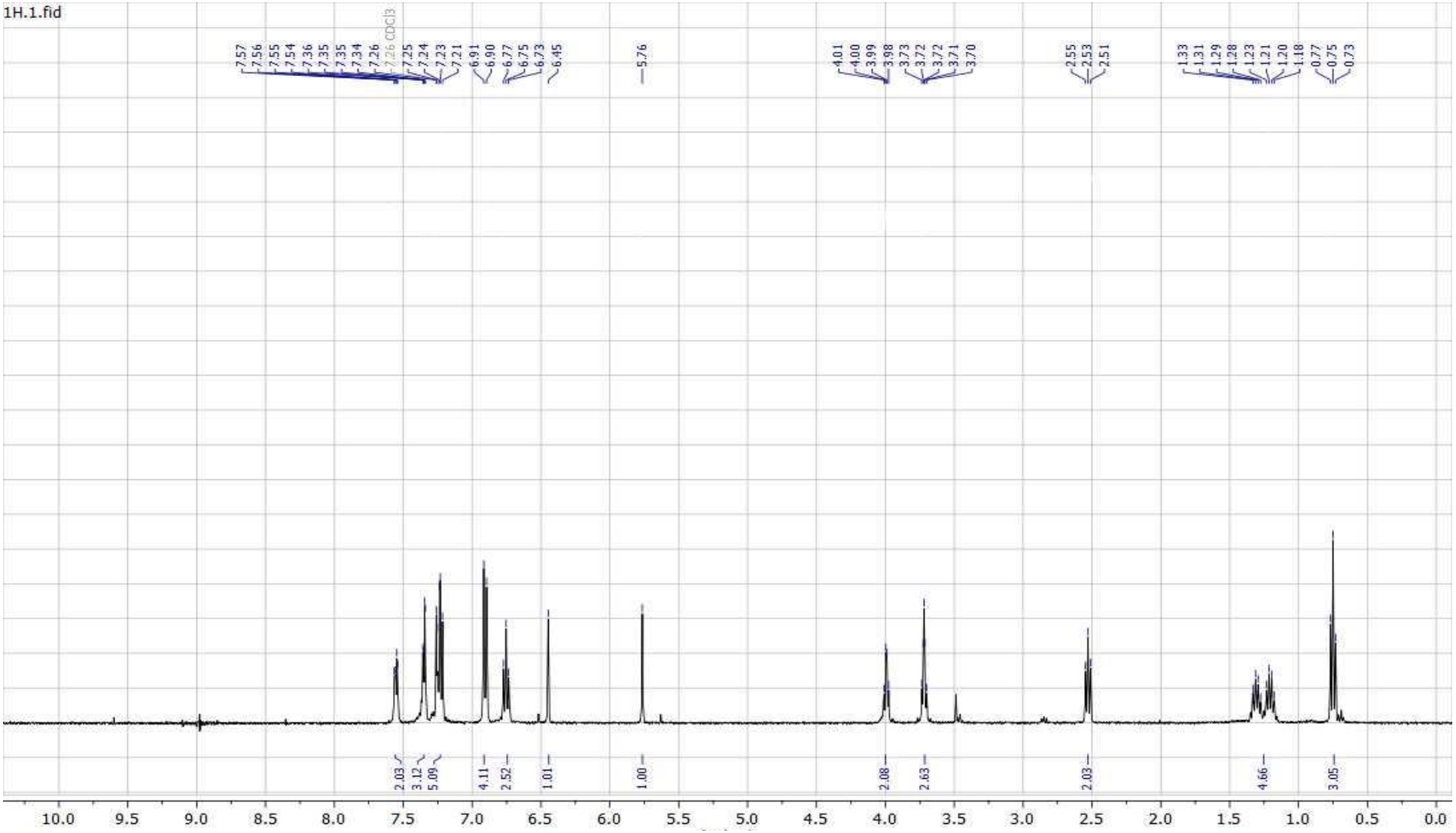
^{1}H NMR spectrum of mixture **(*Z*)-3c**:**(*E*)-3c** (5:1)



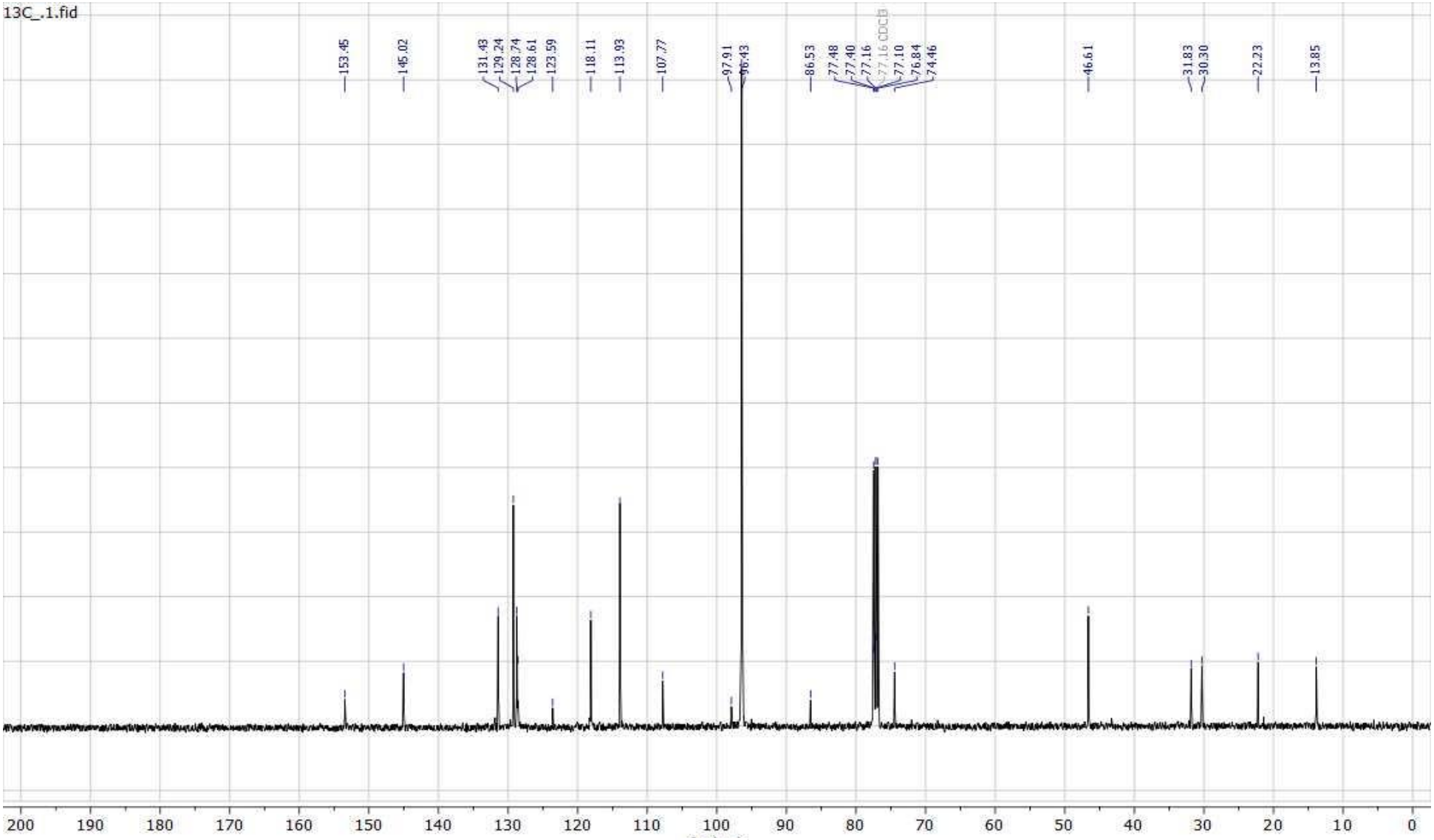
^{13}C NMR spectrum of mixture **(*Z*)-3c**:**(*E*)-3c** (5:1)



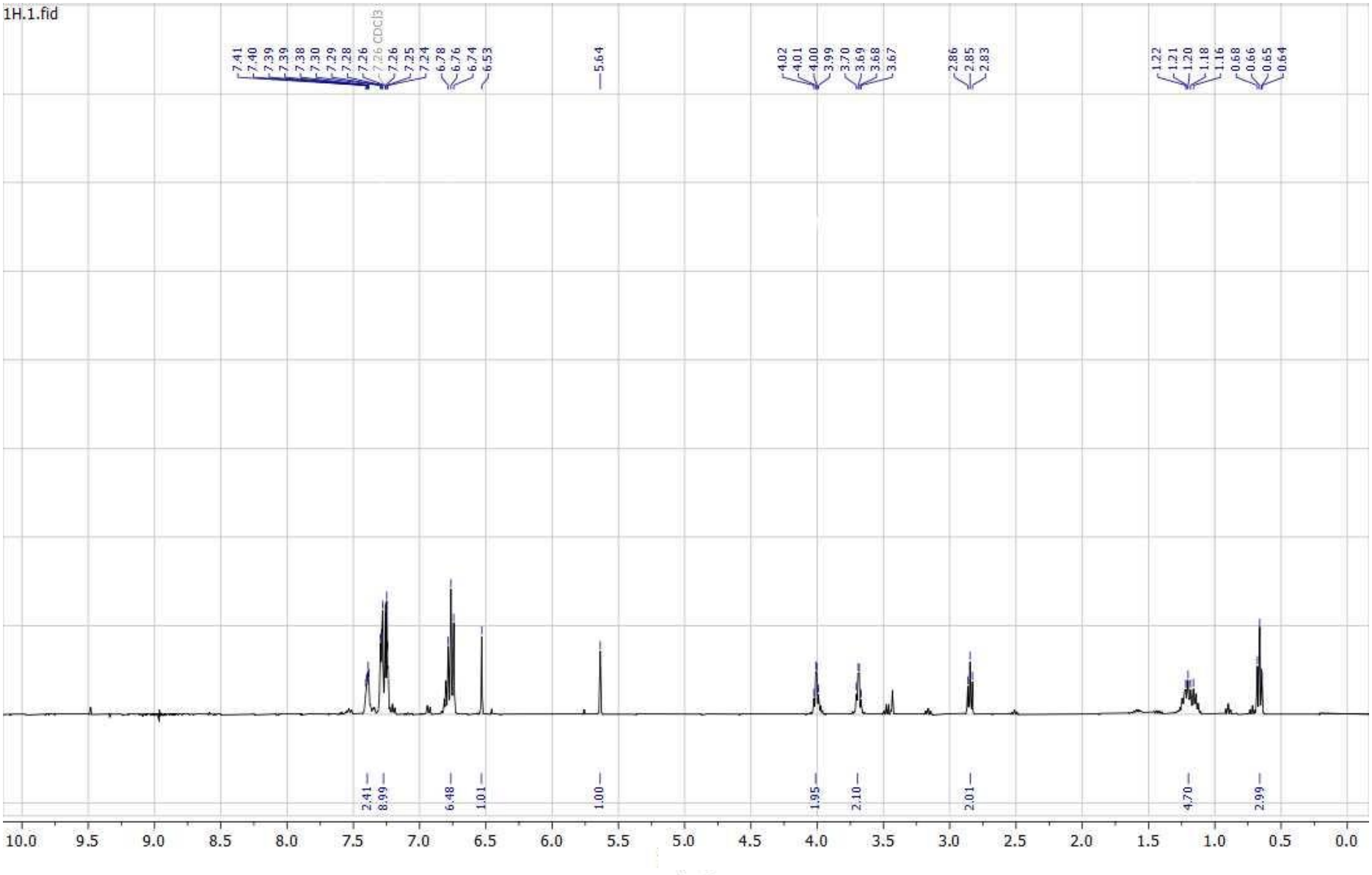
^{1}H NMR spectrum of mixture ***(Z,E)*-6a** (1:0.7)



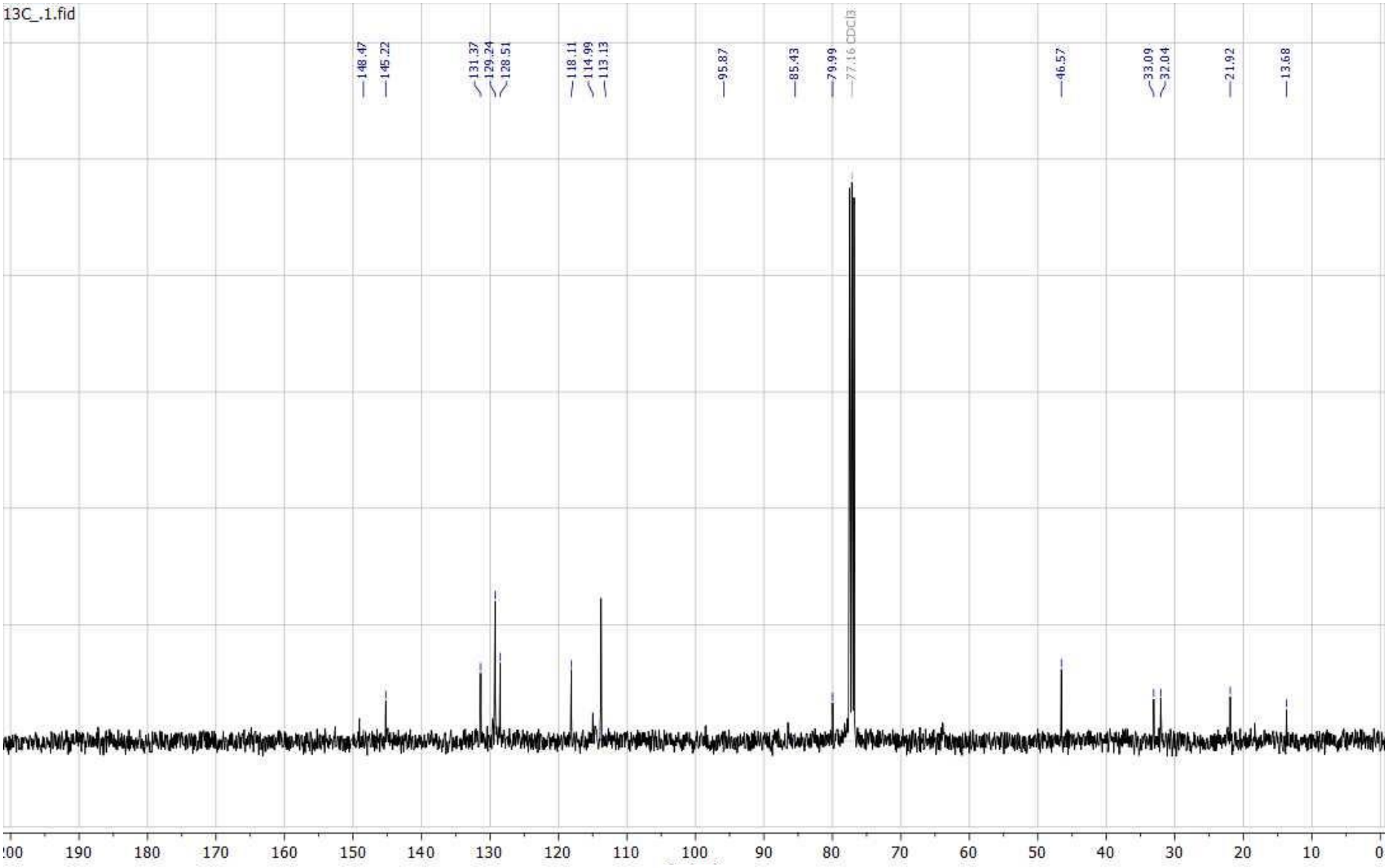
^{1}H NMR spectrum of **(*Z*)-6a**



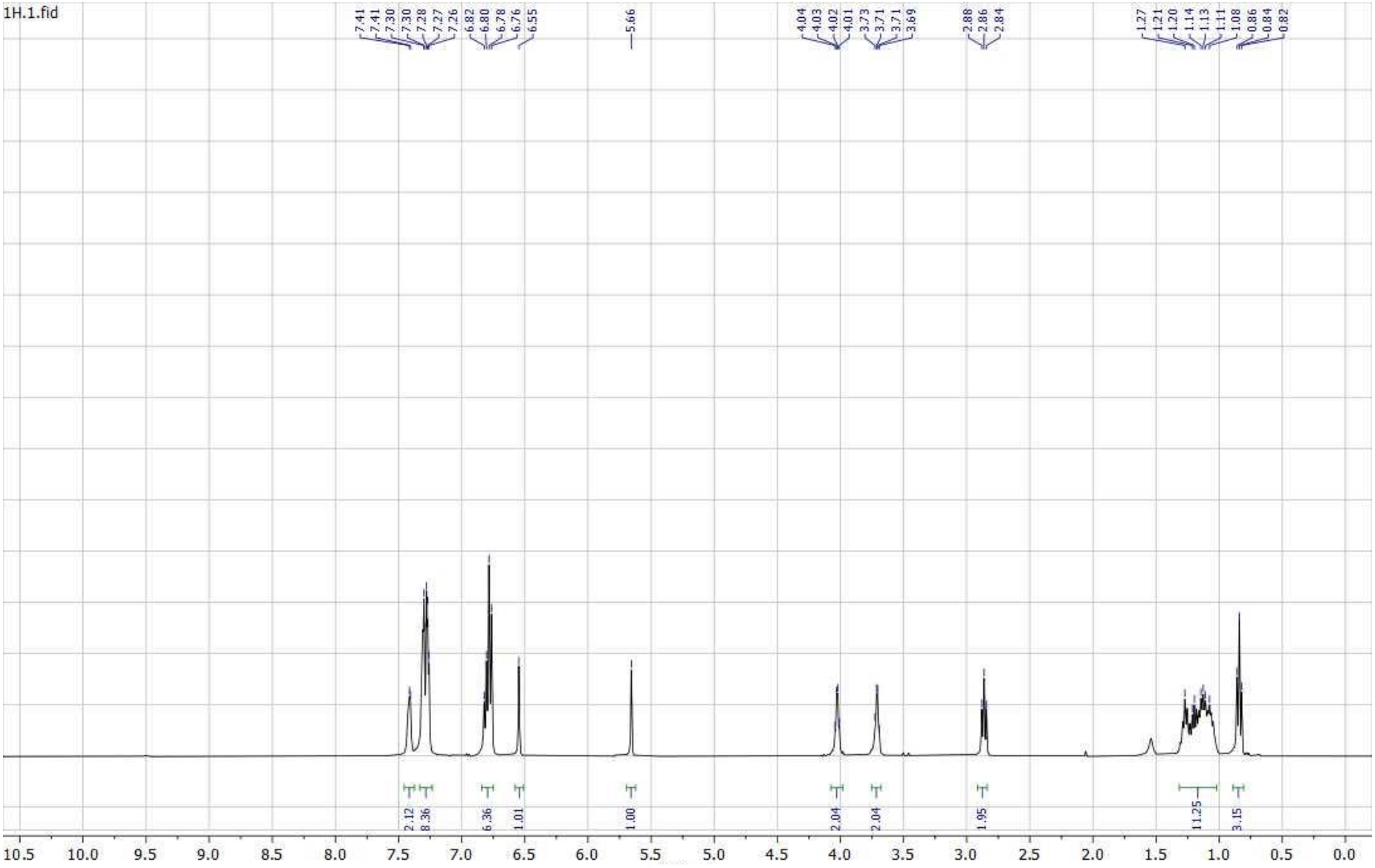
^{13}C NMR spectrum of **(*Z*)-6a**



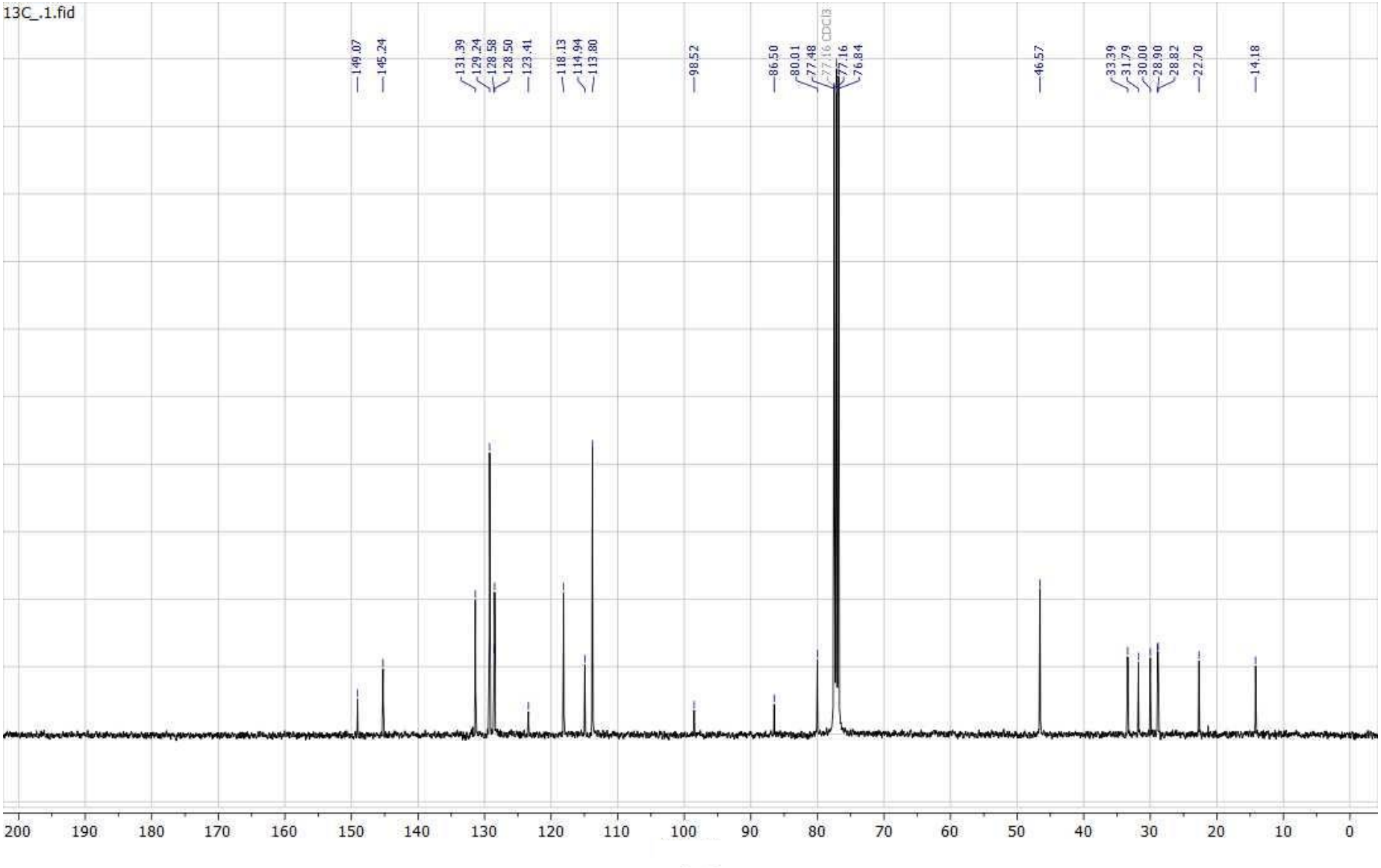
^{1}H NMR spectrum of ***(E)*-6a**



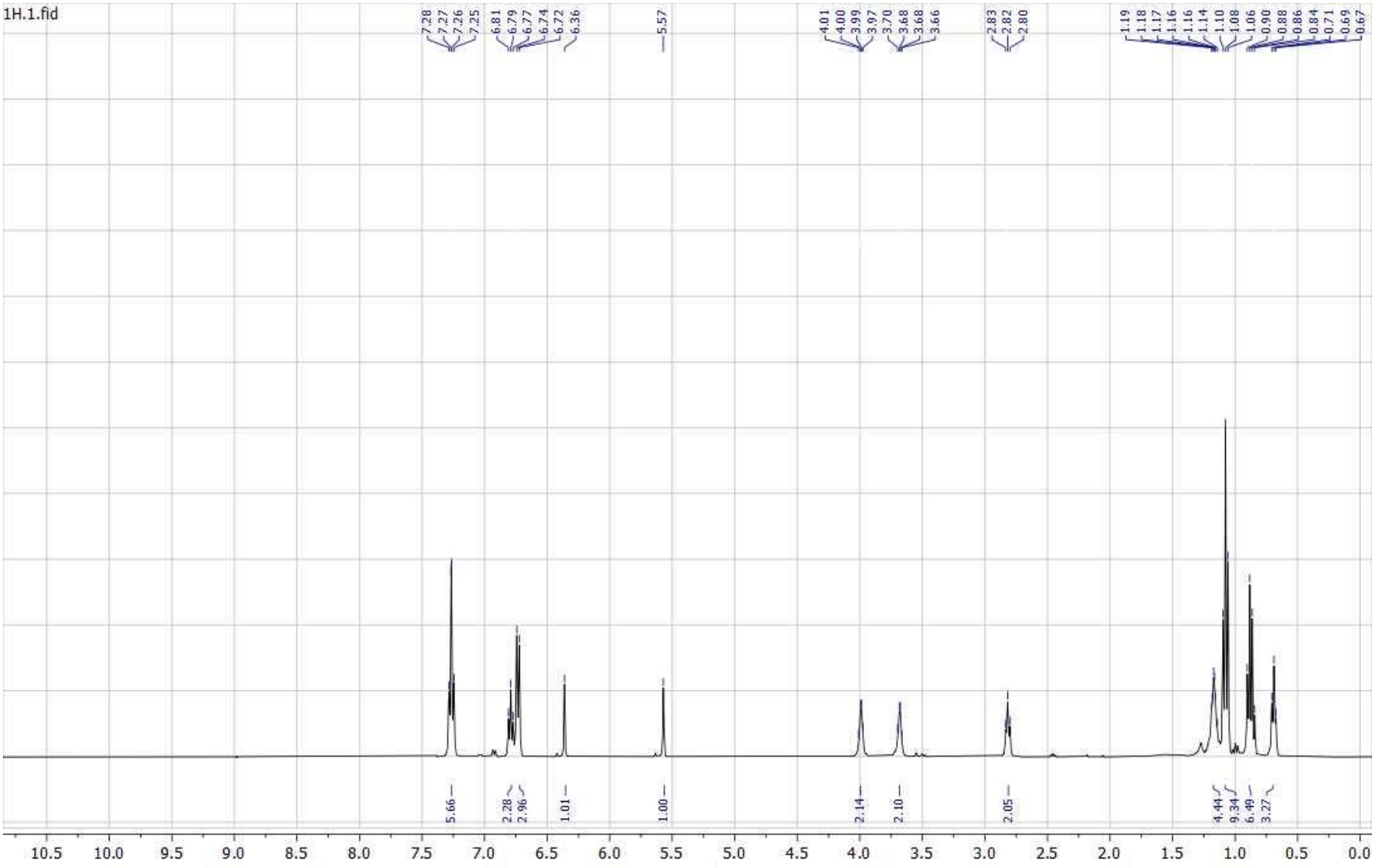
^{13}C NMR spectrum of ***(E)*-6a**



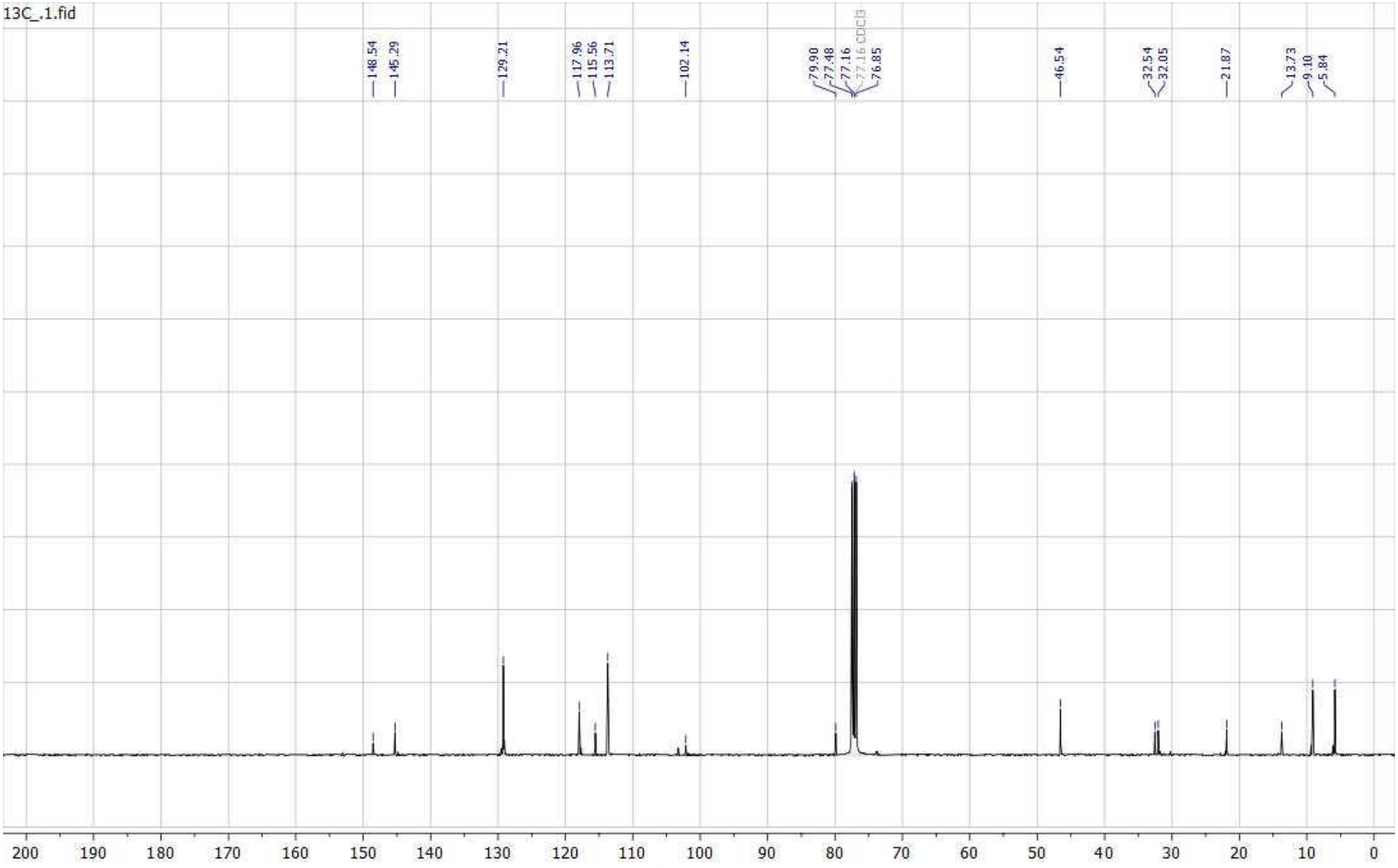
^{1}H NMR spectrum of **(*Z*)-6b**



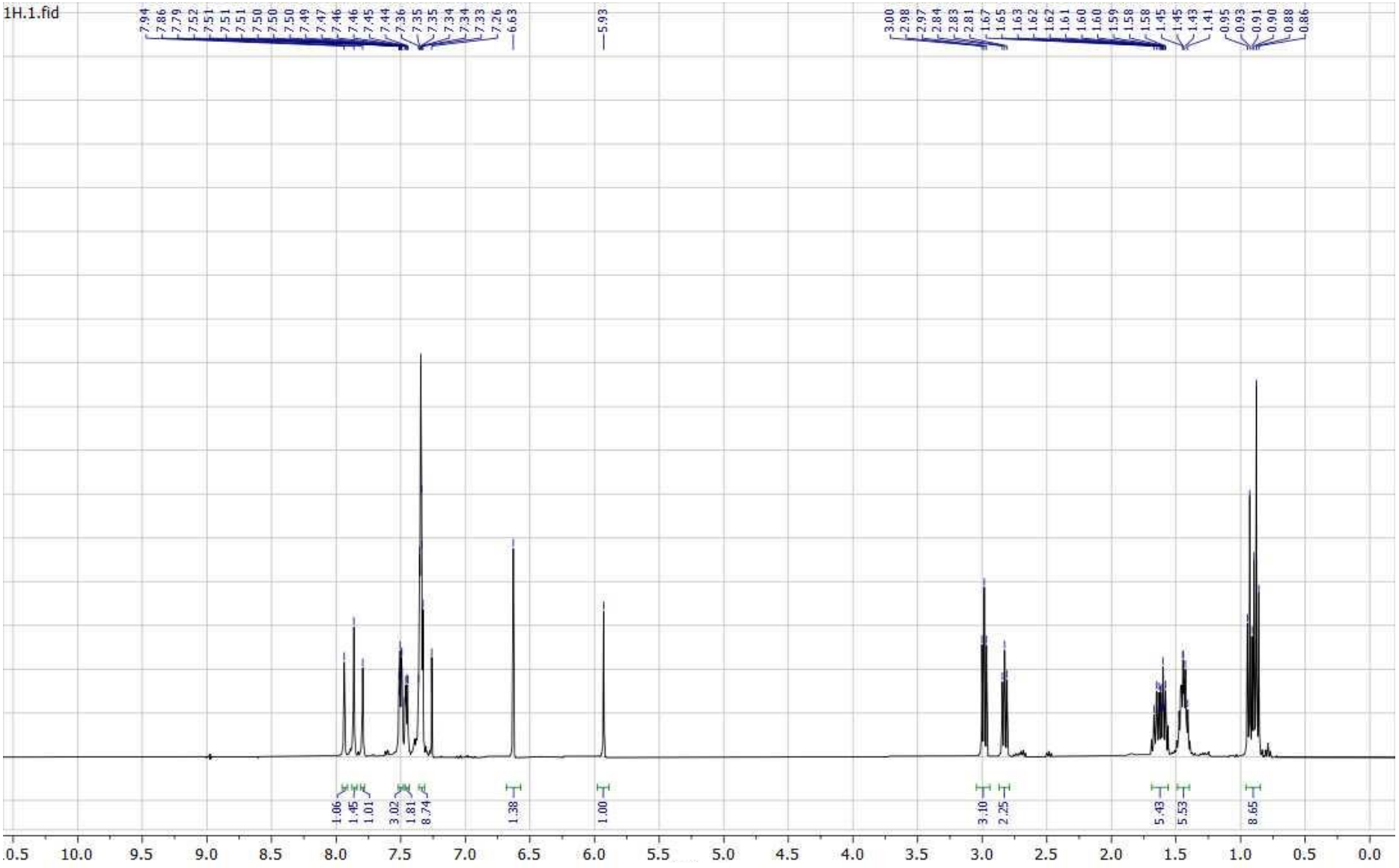
^{13}C NMR spectrum of **(*Z*)-6b**



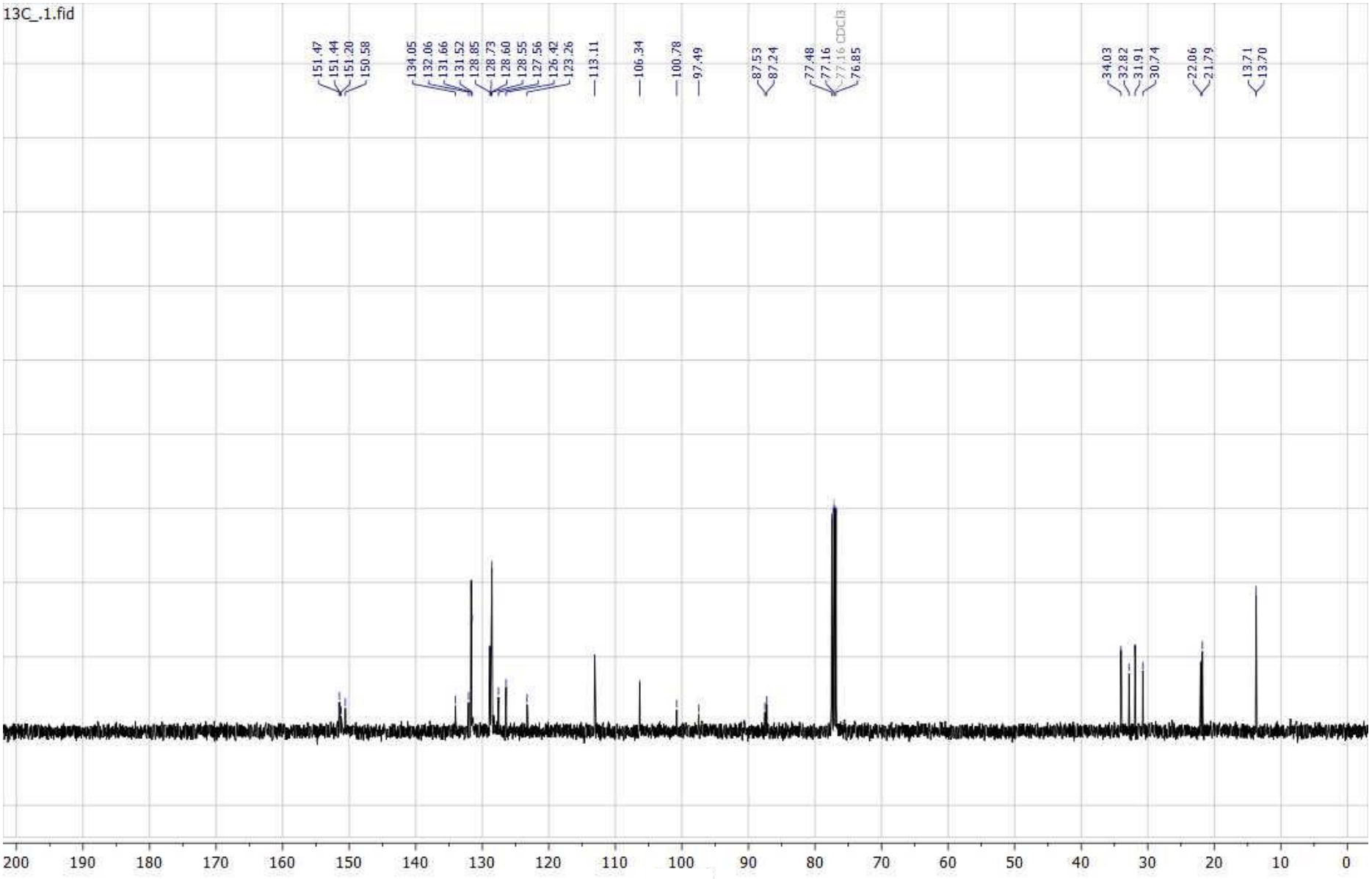
^{1}H NMR spectrum of **(*Z*)-6c**



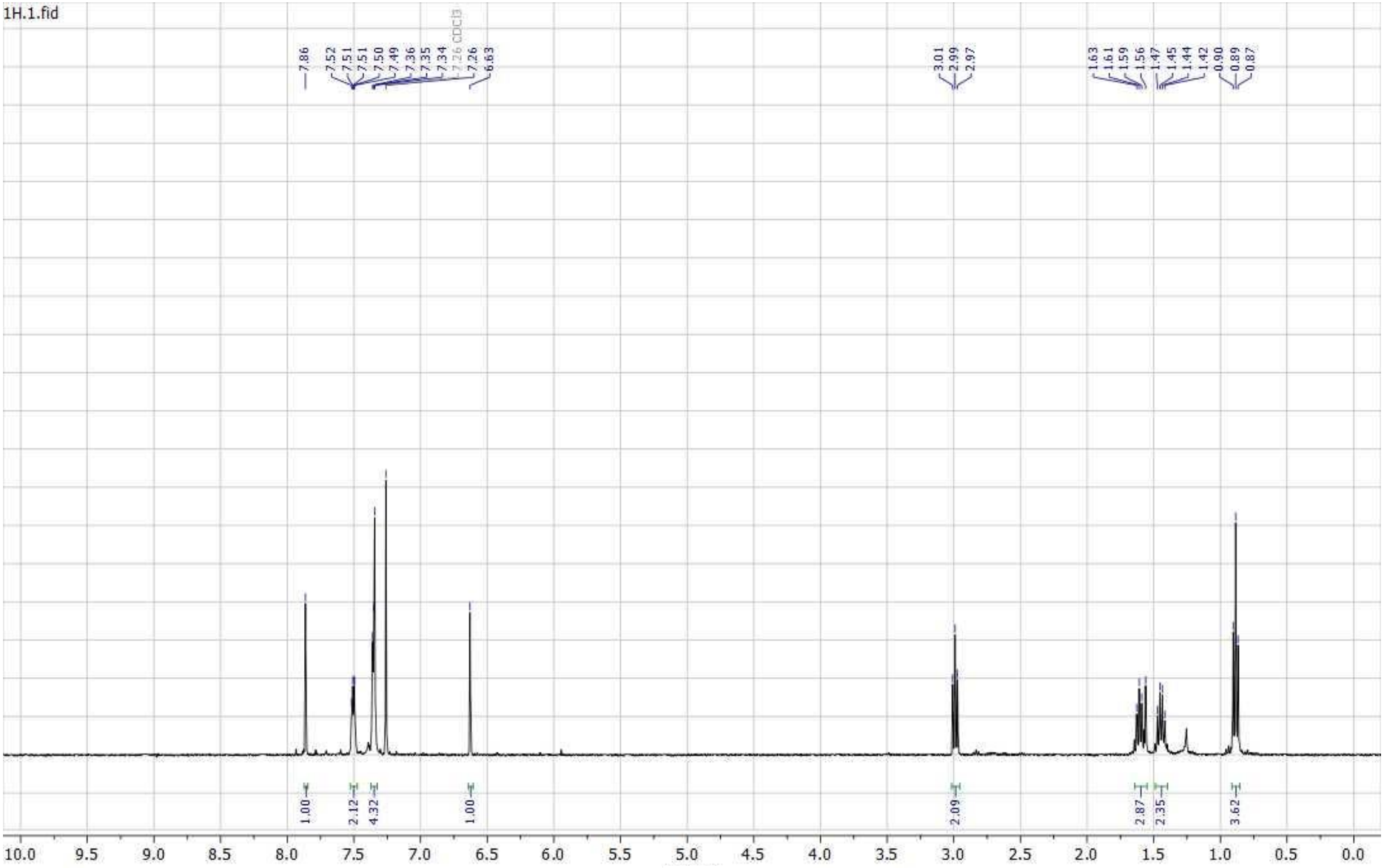
^{13}C NMR spectrum of **(*Z*)-6c**



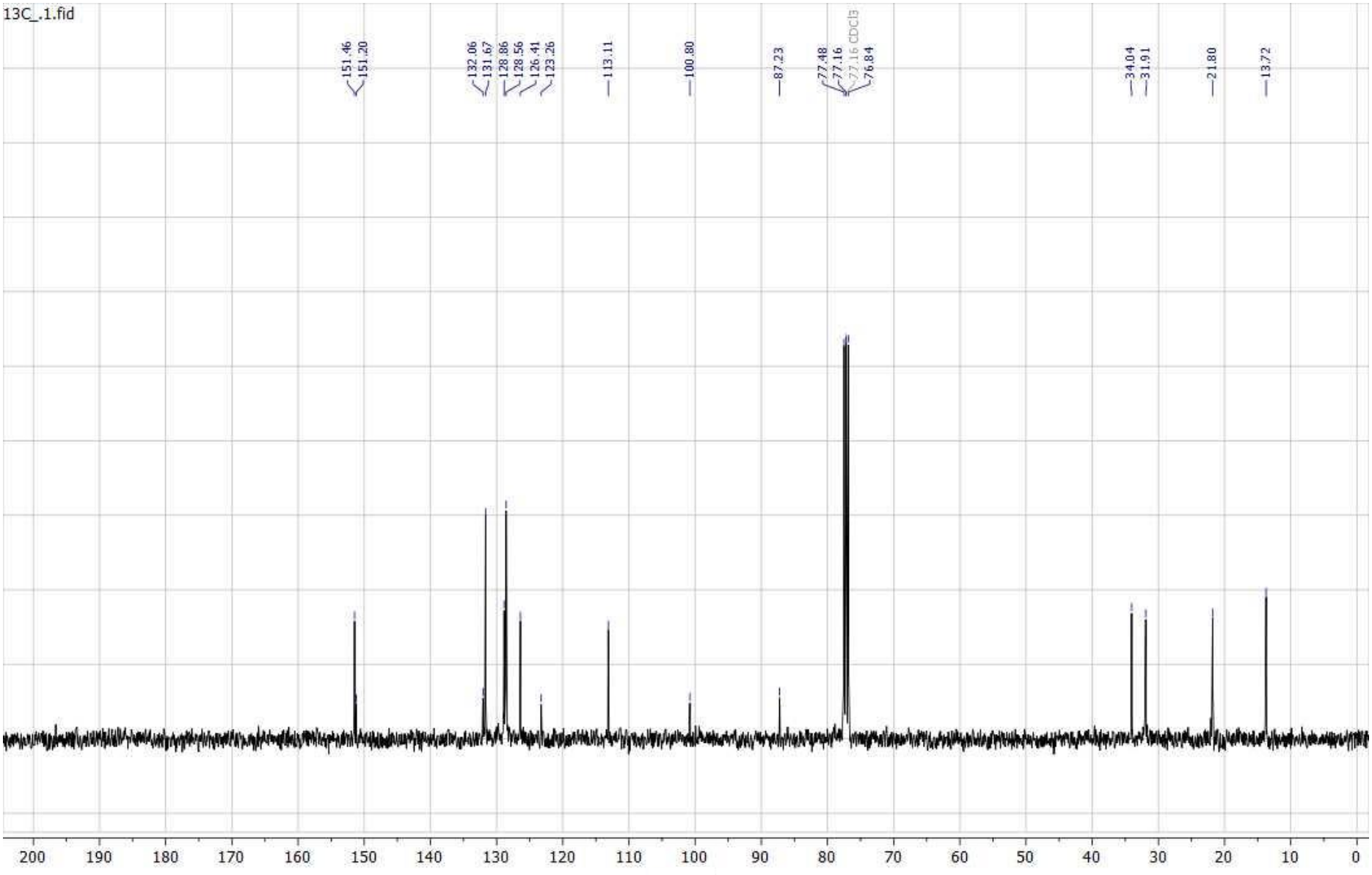
^{1}H NMR spectrum of mixture ***(Z,E)*-7a**



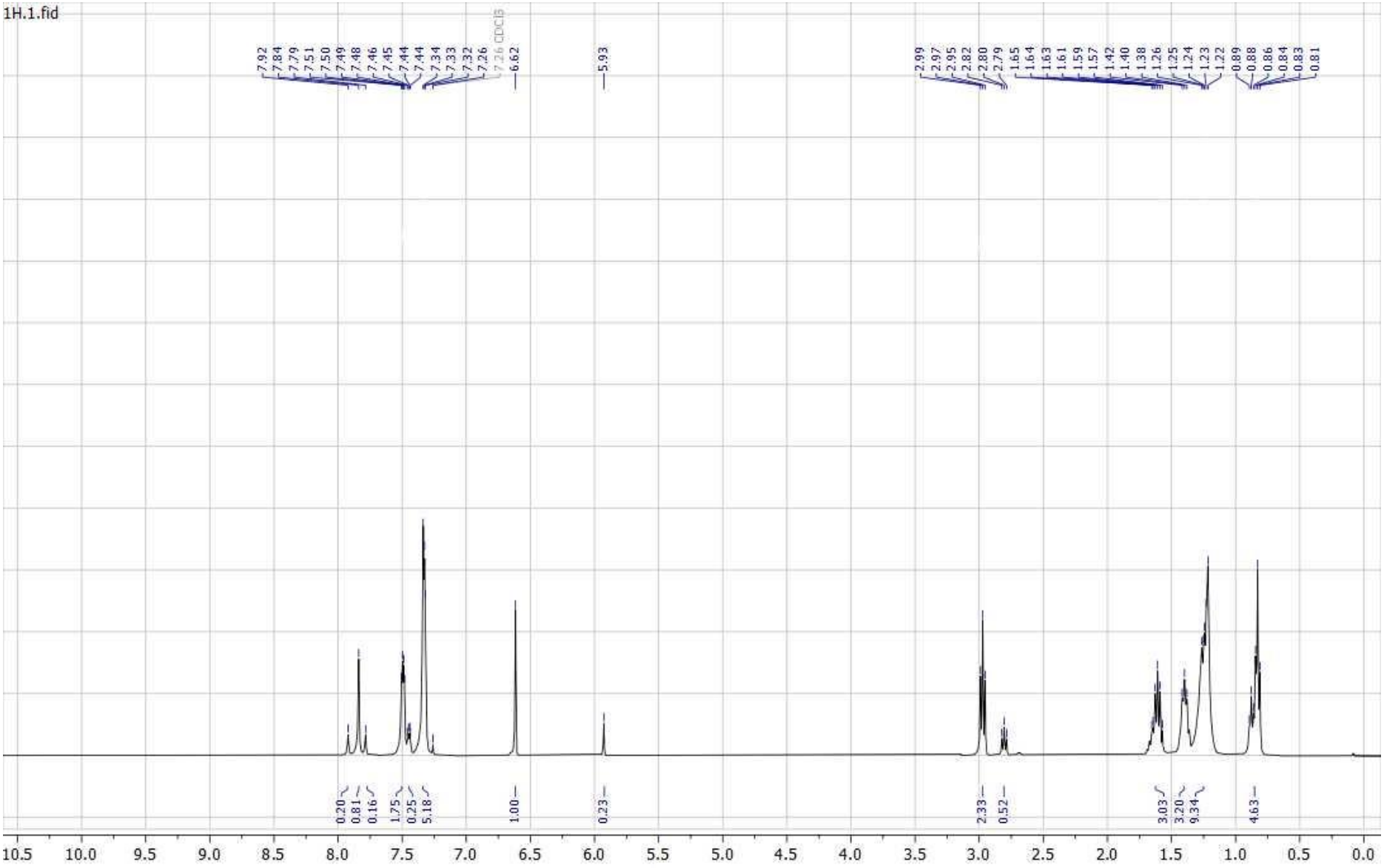
^{13}C NMR spectrum of mixture (***Z,E***)-7**a**



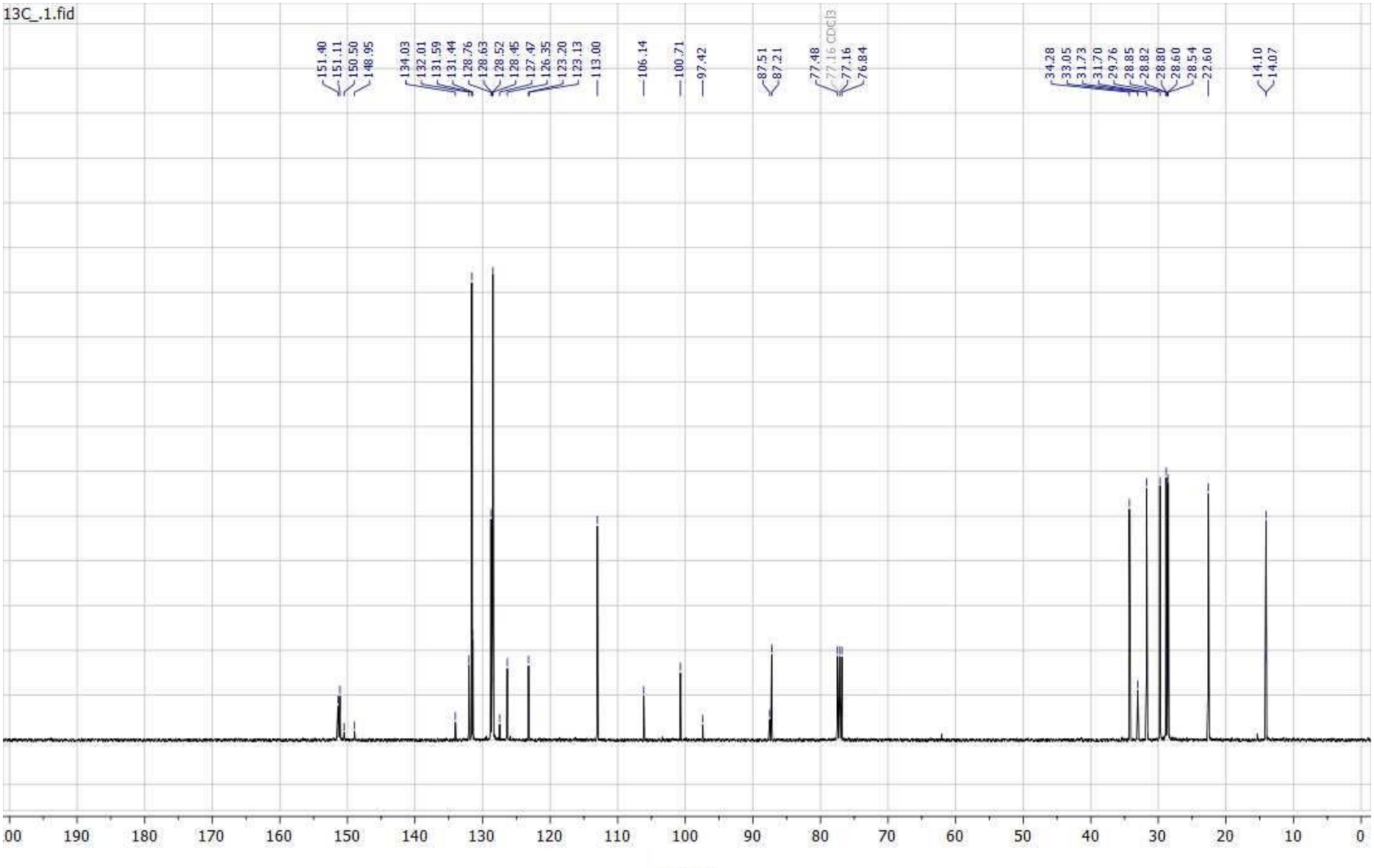
^{1}H NMR spectrum of mixture **(*Z*)-7a**



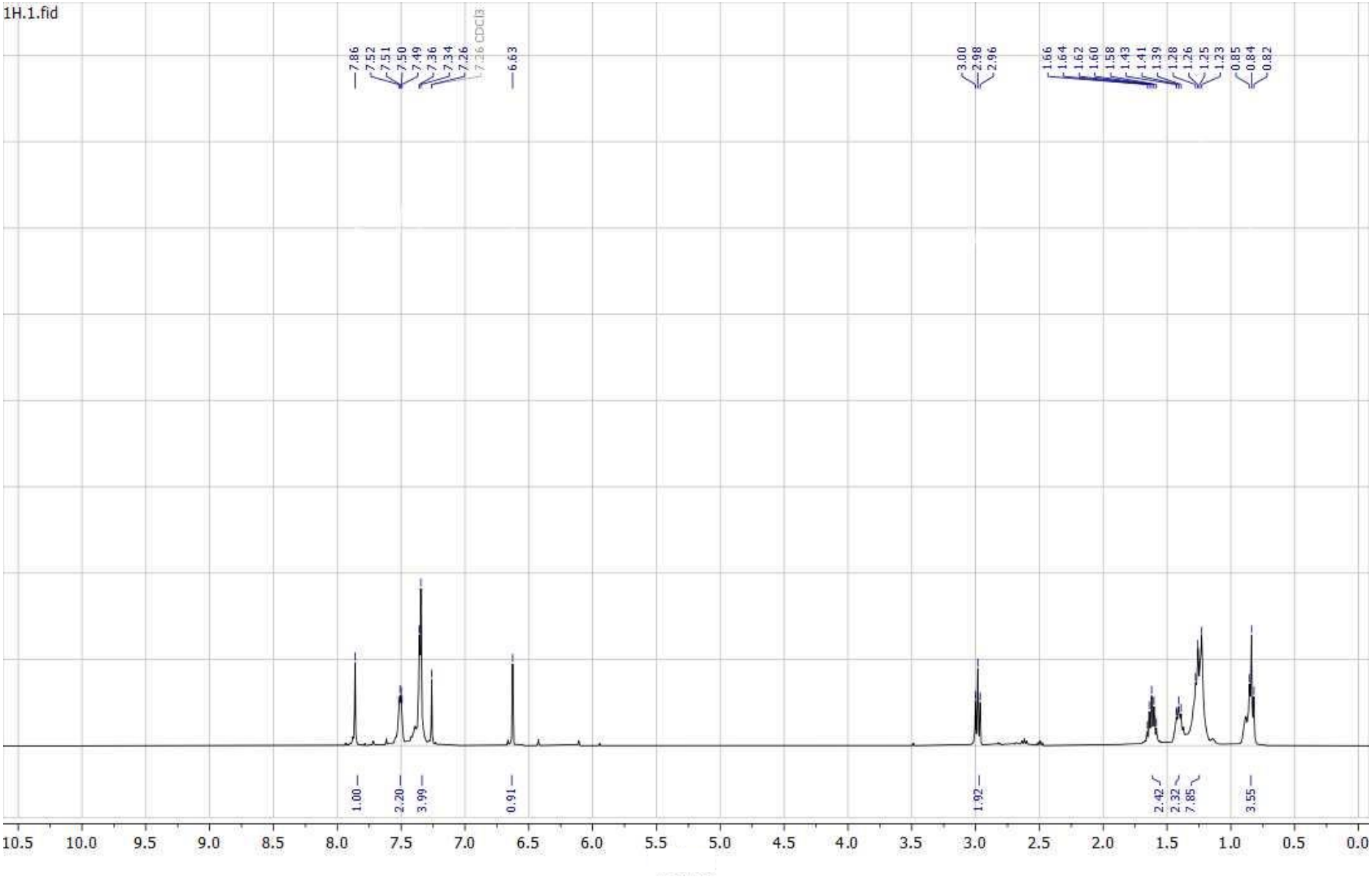
^{13}C NMR spectrum of **(*Z*)-7a**



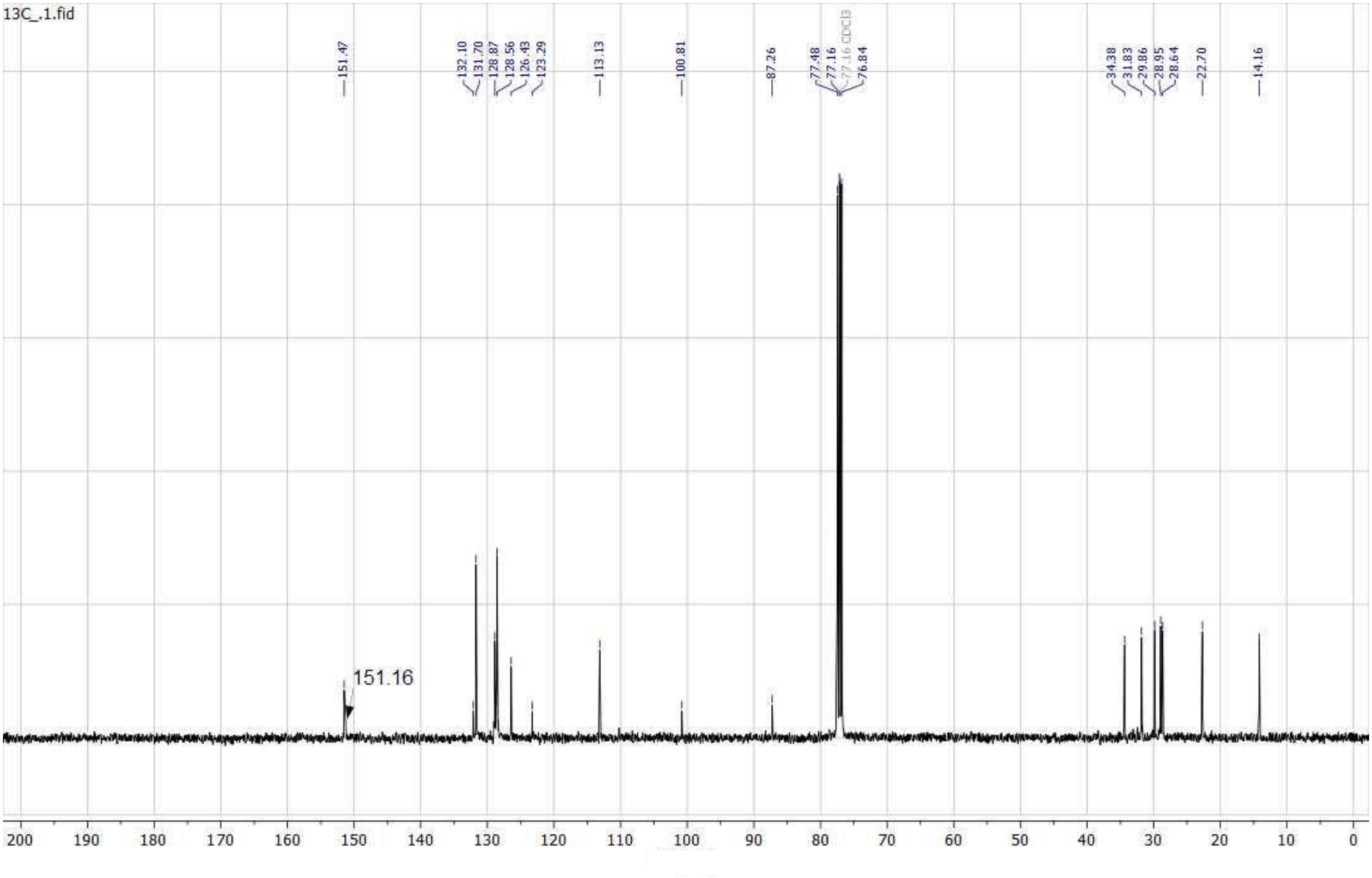
^{1}H NMR spectrum of mixture **(*Z*)-7b**:**(*E*)-7b** (4:1)



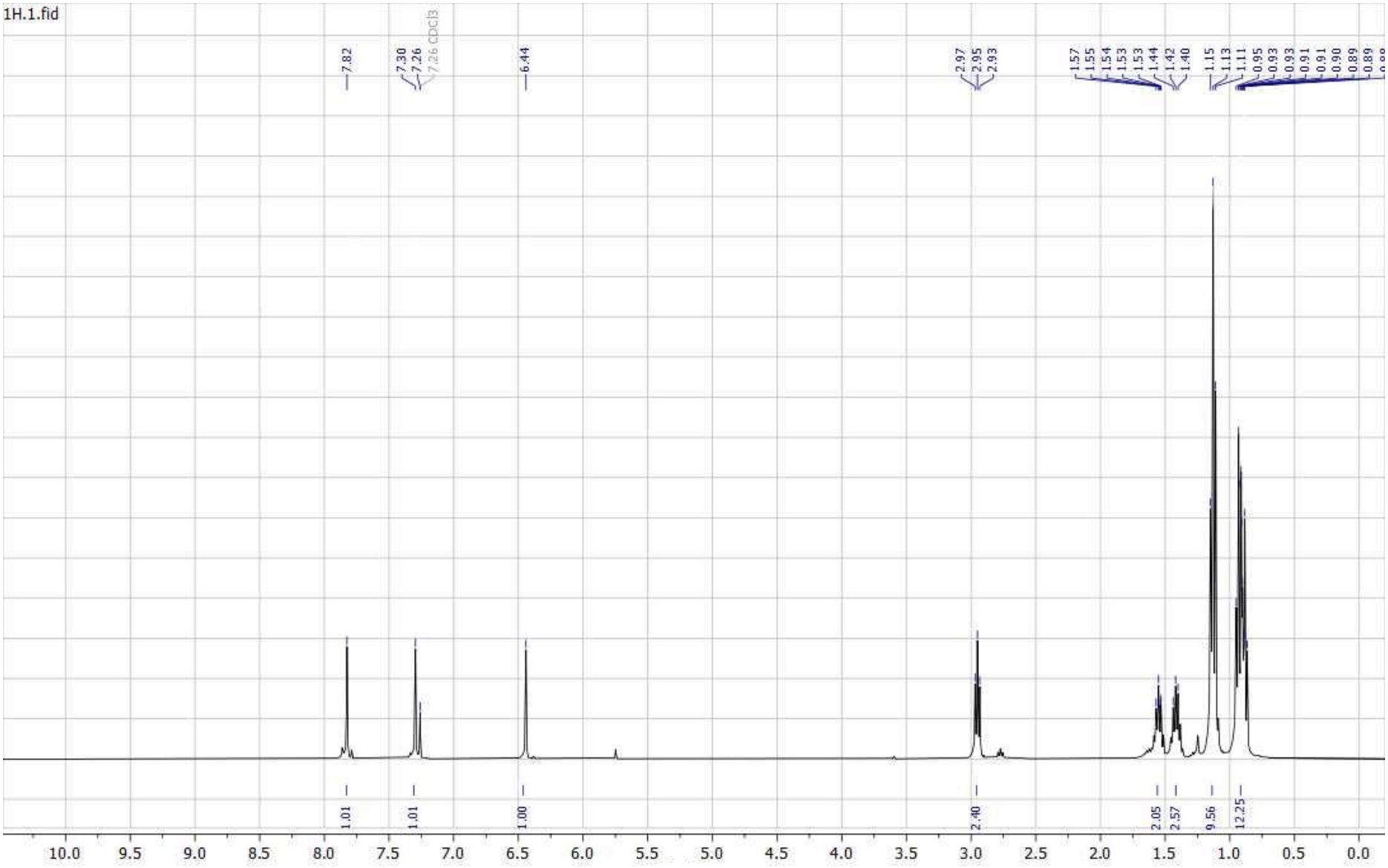
^{13}C NMR spectrum of mixture **(*Z*)-7b**:**(*E*)-7b** (4:1)



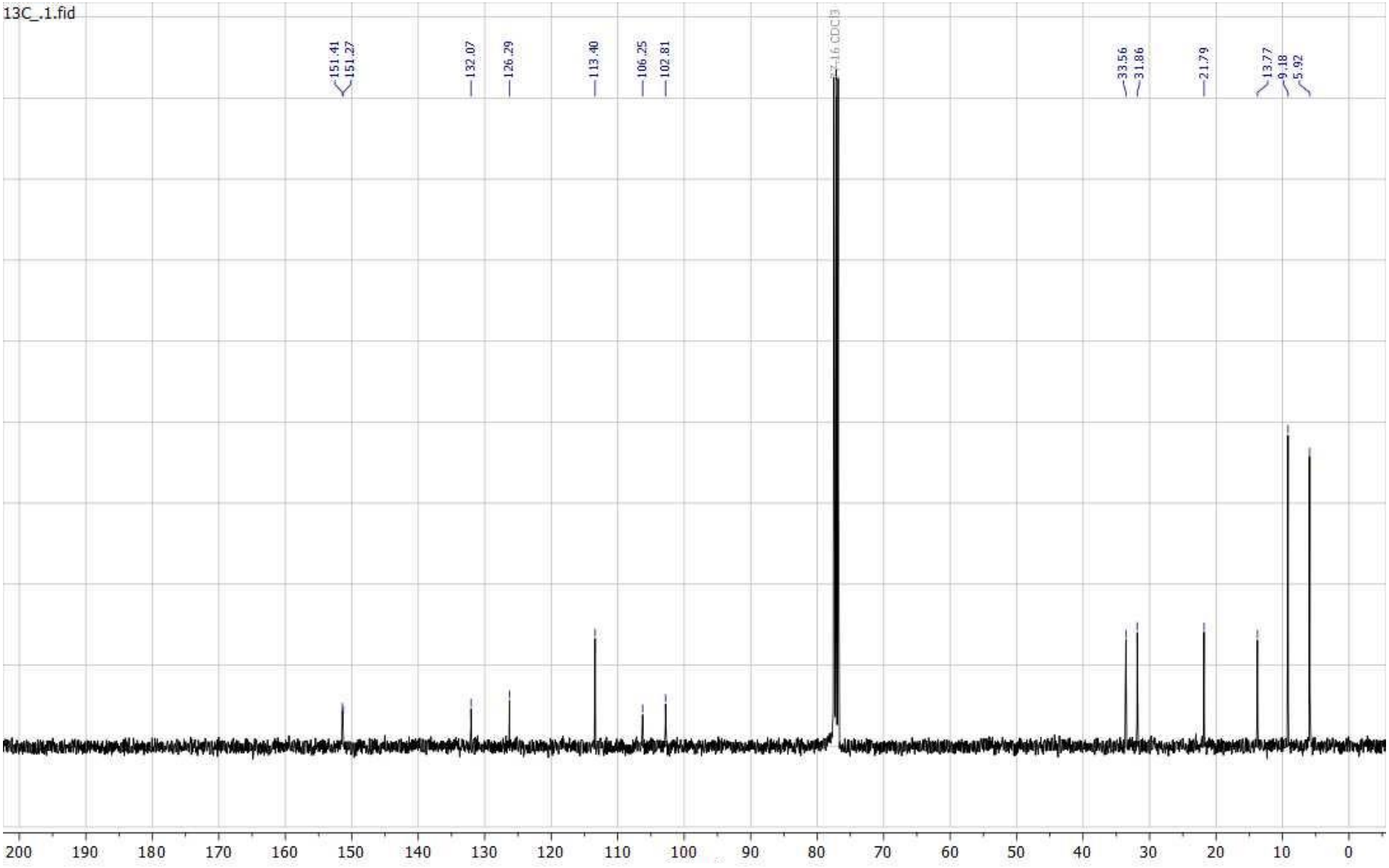
^{1}H NMR spectrum of **(*Z*)-7b**



^{13}C NMR spectrum of **(*Z*)-7b**



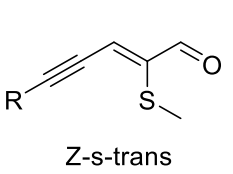
^{1}H NMR spectrum of **(*Z*)-7c**



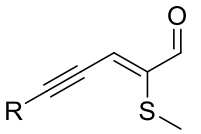
^{13}C NMR spectrum of **(*Z*)-7c**

3. Computation details

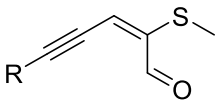
All geometry optimization and thermodynamic functions calculations for model enynals were performed at B3LYP 6-311++G** level of theory using Gaussian 09 suite of programs. Relative Gibbs free energies are summarized in the table below.



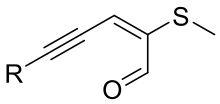
Z-s-trans



Z-s-cis

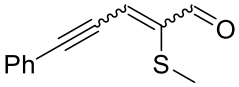
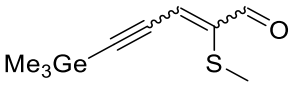


E-s-trans

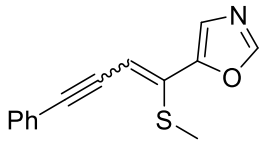
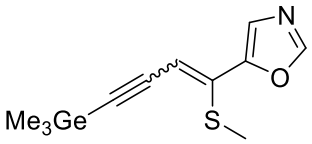


E-s-cis

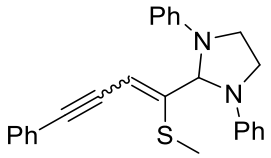
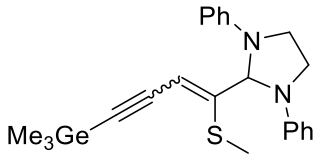
Relative Gibbs free energies at B3LYP 6-311++G** (kcal mol^{-1})

		
E-s-cis	3.53	4.27
E-s-trans	**1.20**	**0.92**
Z-s-cis	1.57	1.67
Z-s-trans	**0**	**0**

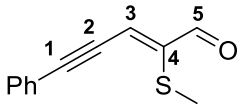
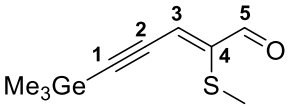
Relative Gibbs free energies of isomers of oxazoles at B3LYP 6-311++G** (kcal mol^{-1})

		
E	1.11	0.66
Z	0	0

Relative Gibbs free energies of isomers of imidazolidines at B3LYP 6-311++G** (kcal mol^{-1})

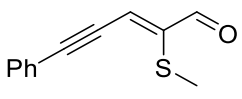
		
E	0	0
Z	0.41	2.25

Electrophilic Parr functions $(P^{+})^{1}$ for carbon atoms of Z-s-trans isomers of model enynals were calculated at UB3LYP 6-311++G** level of theory

	
C-1 0.206	C-1 0.307
C-2 0.002	C-2 -0.041
C-3 0.184	C-3 0.270
C-4 0.102	C-4 0.090
C-5 0.144	C-5 0.196

Electrophilic Parr functions were calculated for most preferable *Z-s-trans* isomers as Mulliken atomic spin densities obtained for corresponding anion-radicals at optimized geometries after single point calculation (according to the online tutorial http://www.luisrdomingo.com/p/tutot.html written by Luis R. Domingo, see also R. Domingo, P. Pérez, J. A. Sáez, *RSC Adv*. **2013**, 3, 1486).

Cartesian coordinates and Energies for studied model structures of enynals



Z-s-trans

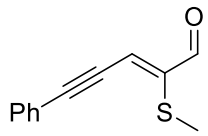
E = -936.804342818

E(ZPE) = -936.623065

G = -936.666501

6	-1.424926000	-1.397712000	0.095319000
6	-2.526213000	-0.598589000	-0.016736000
6	-3.831190000	-1.292953000	0.007082000
8	-4.914825000	-0.798964000	-0.212538000
1	-3.741423000	-2.372289000	0.253468000
1	-1.600003000	-2.468056000	0.190925000
16	-2.370193000	1.130810000	-0.344105000
6	-3.789247000	1.884070000	0.540548000
1	-4.734388000	1.564891000	0.112703000
1	-3.746703000	1.647559000	1.603257000
1	-3.654155000	2.958163000	0.408175000
6	-0.086045000	-0.988545000	0.069300000

6	1.086486000	-0.674457000	0.051459000
6	2.449264000	-0.279908000	0.028527000
6	3.475769000	-1.242523000	0.077776000
6	2.794125000	1.083607000	-0.045002000
6	4.807868000	-0.848371000	0.053256000
6	4.129225000	1.467399000	-0.067229000
6	5.138972000	0.505327000	-0.018520000
1	3.214036000	-2.292185000	0.134175000
1	2.005841000	1.825433000	-0.082334000
1	5.590402000	-1.597572000	0.090735000
1	4.384191000	2.519512000	-0.123303000
1	6.179362000	0.809227000	-0.036495000



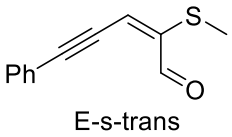
Z-s-cis

E = -936.801164697

E(ZPE) = -936.620194

G = -936.664000

6	-1.557877000	-1.210481000	-0.005438000
6	-2.620927000	-0.375264000	-0.148365000
6	-3.987868000	-0.958180000	-0.155547000
8	-4.250047000	-2.098462000	0.161371000
1	-4.784208000	-0.267800000	-0.494649000
1	-1.795503000	-2.267590000	0.102087000
16	-2.440578000	1.355613000	-0.514306000
6	-3.450846000	2.110259000	0.819443000
1	-4.485959000	1.770465000	0.784412000
1	-3.015668000	1.896331000	1.795112000
1	-3.427697000	3.185658000	0.639990000
6	-0.202903000	-0.856547000	-0.002081000
6	0.985225000	-0.607986000	0.008780000
6	2.366842000	-0.284781000	0.017238000
6	3.339943000	-1.296487000	0.128327000
6	2.784353000	1.056245000	-0.086689000
6	4.690903000	-0.971722000	0.134463000
6	4.137638000	1.370728000	-0.078800000
6	5.093882000	0.360299000	0.031521000
1	3.021914000	-2.328898000	0.208473000
1	2.037038000	1.835590000	-0.172266000
1	5.431950000	-1.758231000	0.219945000
1	4.448784000	2.406005000	-0.159396000
1	6.148782000	0.609855000	0.037104000



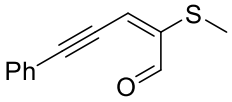
E-s-trans

E = -936.802912296

E(ZPE) = -936.621445

G = -936.664584

6	1.489400000	-0.749229000	-0.000012000
6	2.468837000	0.199851000	-0.000002000
6	2.122554000	1.639548000	-0.000009000
8	2.940985000	2.532640000	-0.000012000
1	1.038377000	1.850338000	-0.000033000
1	1.766505000	-1.798469000	-0.000010000
16	4.207598000	-0.095293000	0.000018000
6	4.295136000	-1.913569000	0.000021000
1	3.839026000	-2.337007000	0.896428000
1	3.839054000	-2.337009000	-0.896400000
1	5.359028000	-2.151469000	0.000037000
6	0.102866000	-0.505148000	-0.000033000
6	-1.104737000	-0.380306000	-0.000042000
6	-2.515213000	-0.213294000	-0.000016000
6	-3.368210000	-1.333741000	-0.000016000
6	-3.085097000	1.074469000	0.000005000
6	-4.747620000	-1.166215000	0.000005000
6	-4.465784000	1.231605000	0.000027000
6	-5.301614000	0.114454000	0.000027000
1	-2.936162000	-2.327148000	-0.000034000
1	-2.435255000	1.941194000	0.000005000
1	-5.393456000	-2.036965000	0.000005000
1	-4.891531000	2.228552000	0.000043000
1	-6.378144000	0.240987000	0.000044000



E-s-cis

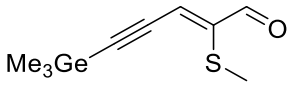
E = -936.798488705

E(ZPE) = -936.617485

G = -936.660883

6	-1.626248000	-0.671288000	0.000092000
6	-2.561413000	0.318694000	0.000051000
6	-2.230742000	1.765687000	-0.000004000
8	-1.112512000	2.227119000	-0.000021000

1	-3.116375000	2.434639000	-0.000029000
1	-1.960771000	-1.704127000	0.000161000
16	-4.320284000	0.069375000	0.000074000
6	-4.490403000	-1.739548000	-0.000244000
1	-4.049393000	-2.177114000	-0.897147000
1	-4.048073000	-2.177553000	0.895795000
1	-5.562963000	-1.933482000	0.000488000
6	-0.233761000	-0.504566000	0.000090000
6	0.979084000	-0.458299000	0.000086000
6	2.389881000	-0.308014000	0.000033000
6	3.240969000	-1.429462000	0.000068000
6	2.958864000	0.980986000	-0.000051000
6	4.620792000	-1.263231000	0.000019000
6	4.339544000	1.136119000	-0.000098000
6	5.174552000	0.017607000	-0.000064000
1	2.807455000	-2.422367000	0.000133000
1	2.302898000	1.842966000	-0.000078000
1	5.266859000	-2.133909000	0.000047000
1	4.766949000	2.132465000	-0.000163000
1	6.251334000	0.143428000	-0.000101000



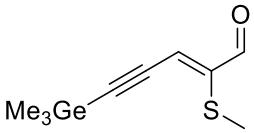
Z-s-trans

E = -2901.90989079

E(ZPE) = -2901.709427

G = -2901.758460

6	1.635247000	-1.397433000	-0.143345000
6	2.758152000	-0.636547000	-0.010949000
6	4.041440000	-1.374167000	-0.052395000
8	5.138910000	-0.925075000	0.189606000
1	3.916162000	-2.441031000	-0.334605000
1	1.776197000	-2.469332000	-0.272359000
16	2.655971000	1.088497000	0.357814000
6	4.127401000	1.812781000	-0.463035000
1	5.048044000	1.456198000	-0.012208000
1	4.113975000	1.599999000	-1.531506000
1	4.020007000	2.887636000	-0.312495000
6	0.305247000	-0.944273000	-0.097367000
6	-0.858864000	-0.588484000	-0.061634000
32	-2.685416000	0.036699000	-0.003734000
6	-3.133641000	0.698617000	-1.802671000
1	-2.462561000	1.511780000	-2.084894000
1	-3.038326000	-0.102730000	-2.537643000
1	-4.161214000	1.069592000	-1.819945000
6	-3.824574000	-1.486161000	0.501585000
1	-3.532787000	-1.871705000	1.480273000
1	-4.870501000	-1.173604000	0.547457000
1	-3.732413000	-2.290337000	-0.230830000
6	-2.777499000	1.477413000	1.332838000
1	-2.099534000	2.288646000	1.061913000
1	-3.794461000	1.873001000	1.388782000
1	-2.493543000	1.101677000	2.317498000



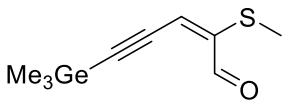
Z-s-cis

E = -2901.90653715

E(ZPE) = -2901.706358

G = -2901.755802

6	-2.207267000	-1.079105000	-0.096171000
6	-3.369921000	-0.416829000	-0.319788000
6	-3.343392000	1.070893000	-0.367265000
8	-2.411041000	1.752088000	-0.001353000
1	-4.254874000	1.537607000	-0.788000000
1	-1.324493000	-0.457458000	0.045095000
16	-4.883789000	-1.245834000	-0.747861000
6	-6.040905000	-0.534254000	0.486197000
1	-5.741525000	-0.814265000	1.495645000
1	-6.111306000	0.550066000	0.399547000
1	-7.016517000	-0.968182000	0.264707000
6	-2.022337000	-2.472489000	-0.050360000
6	-1.796320000	-3.667992000	-0.000068000
32	-1.482017000	-5.572331000	0.059888000
6	-3.225132000	-6.463325000	0.253269000
1	-3.711475000	-6.149916000	1.178856000
1	-3.876318000	-6.207774000	-0.584540000
1	-3.092450000	-7.547592000	0.277169000
6	-0.603269000	-6.072590000	-1.629184000
1	0.339865000	-5.534492000	-1.740180000
1	-0.397675000	-7.145640000	-1.640722000
1	-1.244762000	-5.830051000	-2.478293000
6	-0.315578000	-5.935310000	1.603103000
1	-0.795059000	-5.609628000	2.528065000
1	-0.110064000	-7.006076000	1.674322000
1	0.631789000	-5.403661000	1.496610000



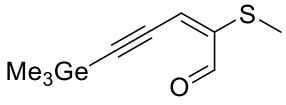
E-s-trans

E = -2901.90916228

E(ZPE) = -2901.708555

G = -2901.757000

6	-1.744576000	-0.743102000	0.000507000
6	-2.735887000	0.189664000	0.000099000
6	-2.407796000	1.635880000	0.000011000
8	-3.239118000	2.516427000	0.000491000
1	-1.326696000	1.860423000	-0.000570000
1	-2.003245000	-1.797094000	0.000785000
16	-4.471302000	-0.127968000	0.000018000
6	-4.532992000	-1.947192000	-0.000643000
1	-4.070192000	-2.363567000	-0.896922000
1	-4.070844000	-2.364278000	0.895640000
1	-5.593269000	-2.200721000	-0.001121000
6	-0.357317000	-0.472466000	0.000470000
6	0.851100000	-0.319926000	0.000307000
32	2.762998000	-0.059770000	-0.000213000
6	3.112729000	1.840361000	-0.373695000
1	2.706517000	2.118402000	-1.348021000
1	2.650906000	2.470719000	0.388552000
1	4.188741000	2.029913000	-0.377431000
6	3.435916000	-0.571974000	1.777815000
1	3.189928000	-1.613864000	1.991331000
1	4.521427000	-0.453608000	1.817640000
1	2.987376000	0.056327000	2.549551000
6	3.521054000	-1.212992000	-1.404046000
1	3.110472000	-0.944482000	-2.379179000
1	4.607168000	-1.098812000	-1.438510000
1	3.286180000	-2.260153000	-1.204117000



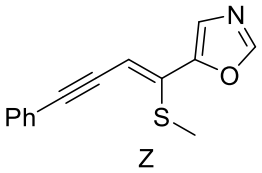
E-s-cis

E = -2901.90355855

E(ZPE) = -2901.703294

G = -2901.751650

6	-1.859487000	-0.649285000	-0.001648000
6	-2.816539000	0.315236000	-0.000644000
6	-2.524582000	1.773524000	-0.000155000
8	-1.420561000	2.264529000	0.000195000
1	-3.429088000	2.417121000	-0.000136000
1	-2.168986000	-1.690108000	-0.002167000
16	-4.569404000	0.024397000	-0.000032000
6	-4.695958000	-1.788065000	0.000767000
1	-4.244319000	-2.215173000	-0.895883000
1	-4.242525000	-2.214421000	0.896874000
1	-5.763471000	-2.008075000	0.001902000
6	-0.464717000	-0.454351000	-0.002040000
6	0.751917000	-0.401914000	-0.001992000
32	2.659768000	-0.136444000	-0.000078000
6	3.100765000	1.009796000	-1.538168000
1	2.815330000	0.520695000	-2.471433000
1	2.564261000	1.957274000	-1.464324000
1	4.174385000	1.211874000	-1.562336000
6	3.133872000	0.738861000	1.698456000
1	2.860500000	0.104096000	2.543446000
1	4.209048000	0.930133000	1.737200000
1	2.603438000	1.688224000	1.790537000
6	3.525495000	-1.898495000	-0.156507000
1	3.223145000	-2.389614000	-1.083561000
1	4.612486000	-1.786869000	-0.159861000
1	3.243574000	-2.537382000	0.682791000



Z

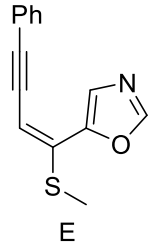
E = -1068.39344771

E(ZPE) = -1068.182576

G = -1068.228771

6	-0.900725000	-0.869782000	0.140901000
6	-1.857218000	0.078314000	-0.054173000
1	-1.235739000	-1.882799000	0.348177000
16	-1.498516000	1.807886000	-0.345345000
6	-0.609311000	2.275417000	1.188798000
1	-1.235262000	2.091157000	2.061190000
1	0.336297000	1.744464000	1.275039000
1	-0.420297000	3.346025000	1.099120000
6	0.488252000	-0.672987000	0.090868000
6	1.696436000	-0.565532000	0.040818000
7	-5.508016000	-0.392724000	-0.142648000
6	-4.422122000	0.466761000	-0.128398000

6	-4.985628000	-1.573268000	-0.105764000
8	-3.631104000	-1.588912000	-0.069802000
6	-3.262859000	-0.258096000	-0.081952000
1	-5.483565000	-2.529765000	-0.099485000
1	-4.536835000	1.536835000	-0.148576000
6	3.107811000	-0.420435000	-0.026792000
6	3.956870000	-1.474354000	0.362221000
6	3.683050000	0.780163000	-0.486328000
6	5.337066000	-1.326585000	0.294753000
6	5.064454000	0.918362000	-0.550013000
6	5.896240000	-0.131795000	-0.159996000
1	3.520607000	-2.401125000	0.714852000
1	3.035154000	1.591393000	-0.795692000
1	5.979398000	-2.145901000	0.597266000
1	5.494287000	1.847347000	-0.907274000
1	6.973254000	-0.020546000	-0.211801000



E = -1068.39192794

E(ZPE) = -1068.180787

G = -1068.227008

6	1.047860000	-1.383660000	-0.007915000
6	2.120508000	-0.541943000	-0.013635000
1	1.225661000	-2.452021000	-0.000644000
16	3.809573000	-1.100516000	0.042398000
6	3.646231000	-2.908622000	0.146085000
1	3.108344000	-3.210838000	1.045620000
1	3.169970000	-3.322380000	-0.743711000
1	4.670027000	-3.279775000	0.203642000
6	-0.306347000	-1.006659000	-0.002015000
6	-1.493474000	-0.751629000	0.018019000
7	1.505490000	3.082838000	-0.323560000
6	1.011876000	1.792461000	-0.401151000
6	2.742465000	2.937490000	0.021192000
8	3.129590000	1.652856000	0.184242000
6	2.002857000	0.903280000	-0.086688000
1	3.488296000	3.696791000	0.192748000
1	-0.004066000	1.585805000	-0.685852000
6	-2.878905000	-0.435311000	0.035534000
6	-3.840126000	-1.407644000	-0.302024000
6	-3.317640000	0.855379000	0.389363000
6	-5.193933000	-1.094033000	-0.287473000
6	-4.673785000	1.159865000	0.399218000
6	-5.616986000	0.188991000	0.061568000
1	-3.510795000	-2.402934000	-0.575156000
1	-2.587155000	1.608218000	0.660292000
1	-5.922357000	-1.852949000	-0.550164000
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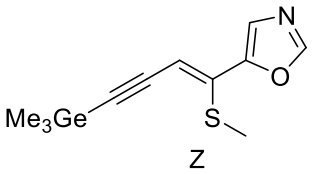

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G = -3033.320706

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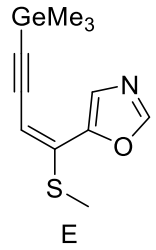
1	1.496234000	-1.768707000	-0.599511000
16	1.875107000	1.799496000	0.544930000
6	0.912146000	2.468790000	-0.862569000
1	1.475321000	2.365167000	-1.789357000
1	-0.057866000	1.983439000	-0.944229000
1	0.774842000	3.527590000	-0.638922000
6	-0.201495000	-0.558840000	-0.192495000
6	-1.411916000	-0.434923000	-0.132434000
7	5.803581000	-0.485846000	0.068658000
6	4.745513000	0.405151000	0.142956000
6	5.243195000	-1.639282000	-0.084250000
8	3.889170000	-1.607798000	-0.116929000
6	3.564191000	-0.273816000	0.028264000
1	5.710024000	-2.605891000	-0.187430000
1	4.895019000	1.463875000	0.267149000
32	-3.322864000	-0.252520000	0.035087000
6	-3.753223000	1.669067000	0.031846000
1	-4.830242000	1.813583000	0.146296000
1	-3.244569000	2.173801000	0.855407000
1	-3.439563000	2.129934000	-0.906915000
6	-3.857879000	-1.091792000	1.733819000
1	-3.362439000	-0.598890000	2.572241000
1	-4.939317000	-1.012122000	1.868771000
1	-3.581257000	-2.147724000	1.738882000
6	-4.155313000	-1.164828000	-1.498248000
1	-3.873603000	-2.219414000	-1.511331000

1	-5.243755000	-1.094654000	-1.432910000
1	-3.831550000	-0.707396000	-2.435105000



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G = -3033.319659

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1	-1.388207000	-2.435898000	-0.001900000
16	-4.031854000	-1.210121000	-0.000096000
6	-3.782162000	-3.011128000	-0.000270000
1	-3.259306000	-3.345128000	-0.897441000
1	-3.258115000	-3.345043000	0.896239000
1	-4.787974000	-3.432603000	0.000421000
6	0.078697000	-0.921962000	-0.001215000
6	1.256084000	-0.606599000	-0.000824000
7	-1.924423000	3.095534000	-0.003318000
6	-1.343716000	1.839235000	-0.006290000
6	-3.196152000	2.866595000	0.003536000
8	-3.527361000	1.556666000	0.005458000
6	-2.322682000	0.882551000	-0.000833000
1	-4.008937000	3.574838000	0.007787000
1	-0.278112000	1.700656000	-0.012469000
32	3.117500000	-0.112270000	0.000554000
6	3.227875000	1.847674000	-0.151935000
1	4.273502000	2.164909000	-0.152128000
1	2.762810000	2.187083000	-1.079517000
1	2.721168000	2.327761000	0.687584000
6	3.977622000	-0.988251000	-1.539397000
1	3.509385000	-0.664222000	-2.470721000
1	5.039540000	-0.732899000	-1.573939000
1	3.881425000	-2.072911000	-1.461488000
6	3.909135000	-0.733953000	1.693413000
1	3.806723000	-1.817012000	1.784509000
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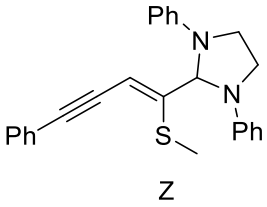
1	3.407373000	-0.265453000	2.542135000



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E = -1513.13627691

E(ZPE) = -1512.705955

G = -1512.767044

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1	-0.347913000	0.082748000	-1.812040000
16	0.119631000	-0.008469000	1.916875000
6	-1.072472000	1.358083000	2.200942000
1	-0.707443000	2.274359000	1.738661000
1	-2.064109000	1.113247000	1.828528000
1	-1.107016000	1.486138000	3.283754000
6	-2.028677000	-0.064881000	-0.535301000
6	-3.228610000	-0.178668000	-0.401203000
6	1.814711000	-0.009062000	-0.304589000
7	2.573298000	-1.074560000	0.349462000
7	2.567897000	1.192946000	0.055950000
6	3.709057000	-0.544502000	1.100502000
6	3.403242000	0.944807000	1.221491000
1	4.648934000	-0.710513000	0.556465000
1	3.789876000	-1.019539000	2.081987000
1	4.315184000	1.544235000	1.169992000
1	2.884403000	1.169873000	2.161663000
1	1.824472000	-0.144275000	-1.395167000
6	2.586868000	-2.383186000	-0.132100000
6	3.555645000	-3.298287000	0.327115000
6	1.639814000	-2.843678000	-1.067775000
6	3.575491000	-4.608690000	-0.140164000
6	1.675836000	-4.156327000	-1.526721000
6	2.641285000	-5.052662000	-1.072836000
1	4.295172000	-2.991900000	1.054443000
1	0.856924000	-2.188397000	-1.420699000
1	4.335378000	-5.286930000	0.232944000
1	0.930681000	-4.479516000	-2.245647000
1	2.661302000	-6.074059000	-1.433365000
6	2.212646000	2.477898000	-0.344855000
6	1.497937000	2.705114000	-1.537609000
6	2.602551000	3.600178000	0.411654000
6	1.193343000	3.997285000	-1.948554000
6	2.296964000	4.889240000	-0.017081000
6	1.588560000	5.103332000	-1.196431000
1	1.191832000	1.872264000	-2.155461000

1	3.141487000	3.469180000	1.340745000
1	0.644546000	4.138879000	-2.873394000
1	2.613547000	5.732586000	0.587257000
1	1.348914000	6.107900000	-1.523602000
6	-4.632553000	-0.314371000	-0.219250000
6	-5.155558000	-0.755106000	1.011334000
6	-5.524231000	-0.012496000	-1.265762000
6	-6.528503000	-0.884671000	1.186043000
6	-6.895611000	-0.145388000	-1.081862000
6	-7.403260000	-0.580475000	0.142684000
1	-4.474527000	-0.998438000	1.818015000
1	-5.128354000	0.325912000	-2.215719000
1	-6.917588000	-1.226497000	2.138530000
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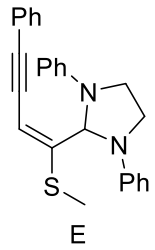

E

E = -1513.13889829

E(ZPE) = -1512.708082

G = -1512.767700

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1	0.089568000	-0.496476000	3.003006000
16	-2.663677000	-0.131956000	2.085749000
6	-2.298675000	-0.762123000	3.754618000
1	-1.815910000	-1.739007000	3.709533000
1	-1.688695000	-0.058466000	4.322514000
1	-3.267796000	-0.861918000	4.244065000
6	1.373446000	-0.250413000	1.345325000
6	2.503013000	-0.189601000	0.905163000
6	-1.175265000	0.115892000	-0.226654000
7	-1.982173000	1.291660000	-0.555414000
7	-1.861027000	-0.956439000	-0.952900000
6	-3.112674000	0.949782000	-1.413946000
6	-3.224026000	-0.564593000	-1.275833000
1	-2.916587000	1.239321000	-2.455626000
1	-4.027070000	1.451290000	-1.084887000
1	-3.540551000	-1.029242000	-2.212227000
1	-3.939854000	-0.845001000	-0.490650000
1	-0.151843000	0.227421000	-0.601396000
6	-1.456672000	2.582177000	-0.543705000
6	-2.184693000	3.648885000	-1.108654000
6	-0.204745000	2.871642000	0.033457000
6	-1.675431000	4.943637000	-1.096056000
6	0.290530000	4.171707000	0.033993000
6	-0.434319000	5.220947000	-0.527789000
1	-3.153496000	3.472168000	-1.556390000
1	0.386083000	2.090860000	0.490612000
1	-2.260881000	5.741978000	-1.539484000
1	1.259234000	4.360666000	0.483965000
1	-0.041749000	6.230708000	-0.521260000
6	-1.459794000	-2.291928000	-0.936674000
6	-0.115114000	-2.651295000	-0.724961000
6	-2.387738000	-3.321315000	-1.184851000
6	0.276462000	-3.984006000	-0.769628000
6	-1.978070000	-4.651387000	-1.234960000
6	-0.645865000	-4.998133000	-1.027889000
1	0.631064000	-1.893273000	-0.531520000
1	-3.434005000	-3.089129000	-1.333205000
1	1.320421000	-4.228297000	-0.605280000
1	-2.716375000	-5.421560000	-1.431208000
1	-0.331942000	-6.034534000	-1.063875000
6	3.820927000	-0.117913000	0.375542000
6	4.935221000	-0.406010000	1.186559000
6	4.036942000	0.243291000	-0.968042000
6	6.222041000	-0.334803000	0.665909000
6	5.327535000	0.310853000	-1.479887000
6	6.424415000	0.022919000	-0.667398000
1	4.777232000	-0.684673000	2.221524000
1	3.186084000	0.470439000	-1.599022000
1	7.070504000	-0.559589000	1.302447000
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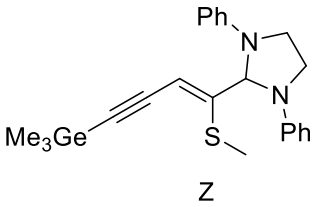

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E(ZPE) = -3477.793010

G = -3477.858219

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16	0.511490000	0.016394000	1.964006000

6	-0.758861000	1.295446000	2.299449000
1	-0.496449000	2.224541000	1.794922000
1	-1.750515000	0.967332000	1.998906000
1	-0.729329000	1.447604000	3.379313000
6	-1.729947000	-0.036243000	-0.443479000
6	-2.934105000	-0.137325000	-0.296518000
6	2.122789000	0.009313000	-0.307949000
7	2.906294000	-1.041246000	0.341235000
7	2.882253000	1.220384000	0.006551000
6	4.065200000	-0.493062000	1.042145000
6	3.753306000	0.995747000	1.150569000
1	4.985923000	-0.661400000	0.466925000
1	4.184094000	-0.952624000	2.027098000
1	4.658963000	1.600414000	1.062997000
1	3.260960000	1.231310000	2.102459000
1	2.097974000	-0.146071000	-1.395512000
6	2.910058000	-2.357668000	-0.118995000
6	3.901170000	-3.259791000	0.317454000
6	1.930465000	-2.838072000	-1.010061000
6	3.910879000	-4.577510000	-0.129204000
6	1.956949000	-4.157654000	-1.449206000
6	2.944497000	-5.041325000	-1.018424000
1	4.666117000	-2.937547000	1.010876000
1	1.130533000	-2.192347000	-1.341924000
1	4.688491000	-5.245618000	0.225191000
1	1.186921000	-4.496469000	-2.133946000
1	2.957053000	-6.068208000	-1.363426000
6	2.508798000	2.497576000	-0.403780000
6	1.764879000	2.703185000	-1.582318000
6	2.909758000	3.632835000	0.326945000
6	1.442838000	3.987431000	-2.004567000
6	2.586525000	4.913811000	-0.112906000
6	1.849220000	5.106569000	-1.278122000
1	1.449644000	1.859647000	-2.180746000
1	3.470873000	3.518382000	1.244996000
1	0.871482000	4.112357000	-2.918076000
1	2.912216000	5.767649000	0.471553000
1	1.596044000	6.104910000	-1.614128000
32	-4.835606000	-0.337199000	-0.066182000
6	-5.323983000	0.424256000	1.683742000
1	-4.799238000	-0.097314000	2.486627000
1	-5.062956000	1.483500000	1.726465000
1	-6.399440000	0.324449000	1.849489000
6	-5.727232000	0.634835000	-1.528028000
1	-6.812178000	0.544537000	-1.434773000
1	-5.460861000	1.693098000	-1.499063000
1	-5.424802000	0.227169000	-2.494527000
6	-5.256715000	-2.259311000	-0.135869000
1	-4.727397000	-2.792572000	0.655937000
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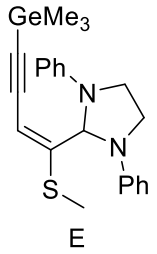

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G = -3477.861805

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16	-2.830163000	-0.051940000	2.148026000
6	-2.414146000	-0.652412000	3.815813000
1	-1.946423000	-1.636763000	3.773883000
1	-1.774130000	0.054038000	4.345919000
1	-3.366010000	-0.728406000	4.341983000
6	1.176429000	-0.249232000	1.257842000
6	2.284775000	-0.212228000	0.753356000
6	-1.417867000	0.134102000	-0.217561000
7	-2.210126000	1.322808000	-0.537393000
7	-2.155435000	-0.934343000	-0.898235000
6	-3.373123000	0.994250000	-1.356506000
6	-3.517650000	-0.513528000	-1.185522000
1	-3.200736000	1.259345000	-2.408908000
1	-4.264942000	1.524217000	-1.010799000
1	-3.876496000	-0.987169000	-2.101909000
1	-4.214146000	-0.760390000	-0.372019000
1	-0.406094000	0.213777000	-0.630173000
6	-1.661957000	2.603634000	-0.553504000
6	-2.389397000	3.678727000	-1.103553000
6	-0.387784000	2.875964000	-0.018461000
6	-1.860051000	4.965341000	-1.114558000
6	0.126469000	4.168462000	-0.039954000
6	-0.598466000	5.226420000	-0.585111000
1	-3.373958000	3.515115000	-1.520723000
1	0.206287000	2.087553000	0.420820000
1	-2.446066000	5.770114000	-1.545415000
1	1.110889000	4.345242000	0.380169000
1	-0.190470000	6.230034000	-0.595801000
6	-1.789539000	-2.279229000	-0.866864000
6	-0.450376000	-2.671415000	-0.678287000
6	-2.750641000	-3.287422000	-1.073669000

6	-0.097279000	-4.015322000	-0.705897000
6	-2.378824000	-4.629004000	-1.107333000
6	-1.052149000	-5.008562000	-0.923917000
1	0.319948000	-1.930685000	-0.514308000
1	-3.793503000	-3.029586000	-1.201979000
1	0.942561000	-4.286487000	-0.557755000
1	-3.142353000	-5.381935000	-1.271310000
1	-0.767488000	-6.053783000	-0.946110000
32	4.028659000	-0.120502000	-0.059518000
6	3.823683000	0.682580000	-1.845419000
1	3.170578000	0.067009000	-2.467095000
1	3.388642000	1.680711000	-1.768235000
1	4.796881000	0.762158000	-2.336033000
6	5.172755000	0.994183000	1.092586000
1	6.177809000	1.066381000	0.669901000
1	4.757945000	2.000085000	1.180615000
1	5.244154000	0.559311000	2.091419000
6	4.745701000	-1.950019000	-0.192403000
1	4.097850000	-2.569141000	-0.815884000
1	5.743277000	-1.930342000	-0.637985000
1	4.814383000	-2.405049000	0.797539000