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Supporting Information for:

New polymers based on thieno[3,2-b]pyrrole derivatives and their electrochemical properties

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Experimental section

Bromination reactions

a) Bromination of ester 3a with NBS. NBS (0.15 g, 0.82 mmol) was added in small portions to a chloroform solution of **3a** (0.16 g, 0.82 mmol in 6 mL), then AcOH (2 mL) was added dropwise. The reaction mixture was stirred at room temperature until the initial compound disappeared (TLC control, ~5 days). Then $NaHCO_3$ was added, the reaction products were extracted with $CHCl_3$ (3×6 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution, dried over $MgSO_4$, then the solvent was evaporated. The products were isolated by column chromatography on a SiO_2 column (eluent - petroleum ether : ethyl acetate, 7:1). We obtained 0.16 g (73%) of bromide **4** and 40 mg (18%) of bromide **5**. Similar amounts were yielded upon bromination by Br_2-dioxane complex (71% and 18% for **4** and **5**, respectively).

Methyl 2-bromo-4-methyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (4). Light yellow crystals, m.p. 109-111ºC. IR (film) ν, cm^{-1}: 3121, 2949, 1705, 1539, 1462, 1398, 1389, 1364, 1236, 1165, 1092, 968, 922, 822, 795, 758, 480. ^{1}HNMR ($CDCl_3$, δ, ppm, *J*Hz): 3.92 s (3H, NCH_3), 4.02 s (3H, OCH_3), 7.00 s (1H, H-3), 7.06 s (1H, H-2). ^{13}CNMR ($CDCl_3$, δ, ppm): 34.62 (NCH_3), 51.37 (OCH_3), 108.58 (C-6), 113.51 (C-3), 116.05 (C-2), 121.95 (C-6a), 125.73 (C-5), 143.39 (C-3a), 162.07 ($\underline{C}O_2Me$).*m/z* (EI, %): 274 $[M\text{H}]^+$ (50).

Methyl 6-bromo-4-methyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (5). Light yellow crystals, m.p. 89-91ºC. IR (film) ν, cm^{-1}: 3104, 2949, 1701, 1541, 1489, 1454, 1391, 1366, 1252, 1167, 1113, 1053, 968, 789, 766, 723, 694. ^{1}HNMR ($CDCl_3$, δ, ppm, *J*Hz): 3.92 s (3H, NCH_3), 4.02 s (3H, OCH_3), 6.95 d (1H, J = 5.4, H-3), 7.35 d (1H, J = 5.3, H-2). ^{13}CNMR ($CDCl_3$, δ, ppm): 36.04 (NCH_3), 51.46 (OCH_3), 96.21 (C-6), 110.60 (C-3), 123.94 (C-6a), 125.09 (C-5), 129.42 (C-2), 143.66 (C-3a), 161.50 ($\underline{C}O_2Me$). *m/z* (EI, %):274 (275) $[M\text{H}]^+$ (100), 195 $[M\text{H-Br}]^+$ (26).

b) Bromination of ester 3b by the action of a bromo–dioxane complex. Br_2-dioxane complex (0.19 g, 0.775 mmol) was added to a dioxane solution of compound **3b** (0.21 g, 0.775 mmol in 10 mL).The reaction mixture was stirred at room temperature until the starting ester was disappeared (TLC monitoring, ~24 h). The reaction products were extracted with $CHCl_3$ (3×10 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution, dried over $MgSO_4$, then the solvent was evaporated. The products were isolated by chromatography on a SiO_2column (eluent - petroleum ether:ethyl acetate, 5:1).We have received 0.22 g (73%) of bromide **6** and 16 mg (6%) of bromide **7**.

Methyl-4-benzyl-2-bromo-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (6). Light yellow crystals, m.p. 105-107ºC. IR (film) ν, cm^{-1}: 3122, 3109, 3088, 2924, 1604, 1676, 1533, 1454, 1430, 1416, 1355, 1322, 1289, 1177, 1159, 1045, 958, 843, 826, 784, 757, 717, 691, 670. ^{1}HNMR ($CDCl_3$, δ, ppm, *J*Hz):

3.83 s (3H, CH_3), 5.71 s (2H, $C\underline{H}_2Ph$), 6.91 s (1H, H-3), 7.11 d (2H, *J* = 7.0, Ph), 7.15 s (1H, H-6), 7.24-7.28 m (3H, Ph). ^{13}CNMR ($CDCl_3$, δ, ppm): 50.46 (NCH_2), 51.45 (OCH_3), 109.56 (C-6), 113.97 (C-3), 116.45 (C-2), 122.65 (C-6a), 125.40 (C-5), 126.66 (C-Ar), 127.58 (C-Ar), 128.73 (C-Ar), 137.52 (C-Ar), 143.19 (C-3a), 161.85 ($\underline{C}O_2Me$). *m/z* (EI, %): 350 [*M*H]$^+$ (45), 155 (100%).

Methyl-4-benzyl-6-bromo-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (7). Yellow oily substance. IR (film) ν, cm^{-1}: 3122, 3109, 3088, 2924, 1604, 1676, 1533, 1454, 1430, 1416, 1355, 1322, 1289, 1177, 1159, 1045, 958, 843, 826, 784, 757, 717, 691, 670. ^{1}HNMR ($CDCl_3$, δ, ppm, *J*Hz): 3.87 s (3H, OCH_3), 5.72 s (2H, $C\underline{H}_2Ph$), 6.89 d (1H, *J* = 5.3, H-3), 7.09 d (2H, *J* = 7.7, Ph), 7.26-7.33 m (4H, Ph, H-2). ^{13}CNMR ($CDCl_3$, δ, ppm): 51.44 (NCH_2), 51.21 (OCH_3), 97.21 (C-6), 113.13 (C-3), 121.50 (C-6a), 123.91 (C-5), 126.69 (C-Ar), 127.43 (C-Ar), 128.65 (C-Ar), 129.80 (C-2), 137.94 (C-Ar), 142.11 (C-3a), 161.27 ($\underline{C}O_2Me$). *m/z* (EI, %): 350 [*M*H]$^+$ (45), 155 (100%).

c) Bromination of 3a with bromine. Bromine (0.65 g, 4.1 mmol) in 20 mL of CH_2Cl_2 was added dropwise to a CH_2Cl_2solution of ester **3a** (0.16 g, 0.82 mmol in 30 mL). The reaction mixture was stirred until the starting compound disappeared (TLC control), then the solvent was evaporated. The mixture of di- and tribromides **8, 9** was separated by column chromatography on a SiO_2 column (eluent - petroleum ether:ethyl acetate, 5:1).

Methyl-2,6-dibromo-4-methyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (8). Yield 0.26 g (90%). Colorless crystals, m.p. 146-148 ºC.IR (film) ν, cm^{-1}: 1692, 1450, 1391, 1364, 1246, 1157, 1115, 1053, 935, 826, 766, 721. ^{1}HNMR ($CDCl_3$, δ, ppm, *J*Hz): 3.92 s (3H, NCH_3), 3.97 s (3H, OCH_3), 7.01 s (1H, H-3). ^{13}CNMR ($CDCl_3$, δ, ppm): 36.15 (NCH_3), 51.57 (OCH_3), 95.79 (C-6), 114.08 (C-3), 116.81 (C-2), 123.33 (C-6a), 125.17 (C-5), 141.69 (C-3a), 161.48 ($\underline{C}O_2Me$). *m/z* (EI, %): 354 [*M*H]$^+$ (100).

Methyl-2,3,6-tribromo-4-methyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (9). Yield 20 mg (7%). Colorless crystals, m.p. 139-141ºC. IR (film)ν, cm^{-1}: 1703, 1533, 1441, 1402, 1377, 1358, 1229, 1186, 1119, 1109, 1063, 978, 964, 803, 841, 768, 733. ^{1}HNMR ($CDCl_3$, δ, ppm, *J*Hz): 3.92 s (3H, NCH_3), 4.25 s (3H, OCH_3). ^{13}CNMR ($CDCl_3$, δ, ppm): 34.04 (NCH_3), 51.76 (OCH_3), 95.05 (C-3), 95.85 (C-6), 115.59 (C-2), 124.90 (C-6a, C-5), 136.52 (C-3a), 161.11 ($\underline{C}O_2Me$). *m/z* (EI, %): 432 (434) [*M*H]$^+$ (100).

d) Bromination of bis-thieno[3,2-b]pyrroles and thieno[3,2-b]pyrrolopyrroles with bromo-dioxane complex

Bromination of 1b with bromo-dioxane complex. Br_2-dioxane complex (0.23 g, 0.92 mmol) was added to a solution of **1b** (0.27 g, 0.92 mmol) in 50 mL of anhydrous CH_2Cl_2. The reaction mixture was stirred at room temperature until the starting compound was consumed (TLC monitoring, ~24 h).

The resulting dark blue precipitate was filtered off, washed with solvents (petroleum ether, EtOAc, $CHCl_3$, CH_2Cl_2), the precipitate was dried in air, and 0.250 g of insoluble polymer was obtained. IR (oil) ν, cm^{-1}: 3600-3800 (unpermitted), 1701 w, 1995 w, 1458 s, 1377 m, 1074 w, 968 w, 720 w. Found, %: C 58.34, H 3.77, Br 19.82, N 7.35, S 8.07. Calculated, %: C 58.23, H 4.07, Br 21.52, N 7.54, S 8.64.

Bromination of 2b with bromo-dioxane complex. The reaction proceeds similarly to **1b** bromination with the formation of a dark blue polymer precipitate. IR (oil) ν, cm^{-1}: 3600-3800 (unpermitted), 2800 s, 1600 s, 1458 s, 1377 m, 1147-1124 m, 721 w. Found, %: C 62.17, H 3.91, Br 13.23, N 5.70, S 10.80. Calculated, %: C 62.66, H 4.09, Br 15.44, N 5.41, S 12.39.

Bromination of 1a by the action of a bromo-dioxane complex. The reaction proceeds similarly to **1b** bromination with the formation of a dark blue polymer precipitate. IR (oil) ν, cm^{-1}: 3600-3800 (unpermitted), 2800-3000 s, 1714 w, 1581 m, 1456 s, 1377 m, 1298 m, 1215 m, 1074 m, 960 w, 783 w, 721 w. Found, %: C 47.33, H 3.13, Br 25.93, N 8.99, S 9.97. Calculated, %: C 48.82, H 3.76, Br 27.07, N 9.49, S 10.86.

Bromination of 2a with bromo-dioxane complex. The reaction proceeds similarly to **1b** bromination with the formation of a dark blue polymer precipitate. IR (oil) ν, cm^{-1}: 3600-3800 (unpermitted), 2800-3000 s, 1655 w, 1604 m, 1522 m, 1456 s, 1377 s, 1289 m, 1261 m, 1152 m, 1084 w, 1020 w, 797 w, 721 m. Found, %: C 49.25, H 3.08, Br 16.81, N 7.45, S 16.06. Calculated, %: C 49.32, H 3.59, Br 21.87, N 7.67, S 17.56.

Bromination of 2c with bromo-dioxane complex. The reaction proceeds similarly to **1b** bromination with the formation of a dark blue polymer precipitate. IR (oil) ν, cm^{-1}: 3389-3330 (unpermitted), 2951 s, 2853 s, 1701 w, 1587 m, 1530 m, 1462 s, 1456 s, 1377 s, 1165 w, 1119 w, 989 w, 932 w, 806 w, 721 m. Found, %: C 54.30, H 4.41, Br 19.45, N 5.61, S 16.79. Calculated, %: C 54.41, H 4.57, Br 19.05, N 6.68, S 15.29.

e) Synthesis of 4-benzyl-N,N-diethyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxamide (11). Diethylamine (45 mg, 0.618 mmol) was added to a solution of acid chloride **10** (0.17 g, 0.618 mmol). The latter compound was obtained according to [S1]. The mixture was boiled until the reaction was completed (TLC control), then cooled, washed with a cold 5% HCl solution. The organic layer was dried over $MgSO_4$, and the solvent was evaporated. The reaction product was isolated by column chromatography on SiO_2.Yield 0.10 g (53%). Dark yellow oil. IR (film) ν, cm^{-1}: 2970, 2934, 2874, 1616, 1528, 1497, 1475, 1458, 1420, 1341, 1267, 1217, 1155, 1084, 1028, 943, 841, 785, 748, 716, 700, 656. ^{1}HNMR ($CDCl_3$, δ, ppm, JHz): 1.08 t (6H, J= 7.1, CH_3), 3.39 q (4H, J= 7.1, CH_2), 5.46 s (2H, C$\underline{H}_2$Ph), 6.57 s (1H, H-6), 6.88 d (1H, J = 5.2, H-3), 7.13 d (2H, J = 6.7, Ph), 7.15 d (1H, J = 5.3, H-2), 7.20-7.26 m

(3H, Ph). ^{13}CNMR ($CDCl_3$, δ, ppm): 13.36 (CH_3), 41.50 (NCH_2), 50.20 (NCH_2), 102.74 (C-6), 110.56 (C-3), 121.87 (C-6a), 125.85 (C-2), 127.26 (C-Ph), 127.50 (C-Ph), 128.51 (C-Ph), 130.69 (C-5), 138.14 (C-Ph), 142.58 (C-3a), 163.70 ($\underline{C}O_2Me$). *m/z* (EI, %): 313 $[M H]^+$ (100%), 354 $[M H + MeCN]^+$ (19).

f) Synthesis of N-[(4-benzyl-4H-thieno[3,2-b]pyrrol-5-yl)methyl]-N,N-diethylamine (12). A THF solution of amide **11** (0.12 g, 0.384 mmol in 5 mL) was added to a suspension of $LiAlH_4$ (30 mg, 0.77 mmol) in 5 mL of THF, the reaction mixture was stirred on heating until the starting amide was disappeared (TLC control). The excess hydride was decomposed by adding a saturated solution of NH_4Cl with followed evaporation of the solvent. The residue was dissolved in CH_2Cl_2, washed with a saturated solution of NaCl, dried over $MgSO_4$, then the solvent was evaporated. The product was isolated by column chromatography on a SiO_2 column (eluent–chloroform : methanol, 30:1). The amount of 0.03 g (27%) of amine **12** was obtained as a dark yellow oil. IR (film) ν, cm^{-1}: 2966, 2928, 2806, 1653, 1518, 1454, 1400, 1358, 1335, 1294, 1196, 1165, 1115, 1084, 1053, 970, 781, 731, 710, 648. ^{1}H NMR ($CDCl_3$, δ, ppm, *J* Hz): 1.40 t (6H, *J* = 7.1, CH_3), 2.96 q (4H, *J* = 7.2, CH_2), 4.02 s (2H, NCH_2), 5.97 s (2H, $C\underline{H}_2Ph$), 6.79 s (1H, H-6), 7.30 d (1H, *J* = 5.3, H-3), 7.49 d (1H, *J* = 5.2, H-2), 7.52 d (2H, *J* = 7.4, Ph), 7.68 t (1H, *J* = 7.3, Ph), 7.73-7.75 m (2H, Ph). ^{13}CNMR ($CDCl_3$, δ, ppm): 11.36 (CH_3), 46.49 (NCH_2), 49.00 (NCH_2), 51.01 ($N\underline{C}H_2Ph$), 101.90 (C-6), 111.27 (C-3), 122.13 (C-6a), 122.36 (C-2), 126.99 (C-Ph), 127.43 (C-Ph), 128.88 (C-Ph), 136.22 (C-5), 139.44 (C-Ph), 141.66 (C-3a). *m/z* (EI, %): 226 $[M H\text{-}CH_2Ph+H_2O]^+$ (100%).

g) Dedoping of polymers with hydrazine hydrate

Dedoping of polymer P-1b. To 0.21 g of polymer **P-1b** was added 7 mL of hydrazine hydrate and stirred for 4 days at room temperature, then another 3 mL of hydrazine hydrate was added. After 3 days of stirring, the solvent was decanted, the precipitate was washed with solvents (water, acetonitrile, acetone, chloroform, petroleum ether), the precipitate was dried in air, and 0.195 g of an insoluble brown polymer was obtained.

Dedoping of polymer P-2b. The reaction proceeds similarly to the dedoping of **P-1b**. Prepared from 0.21 g of **P-2b** and 10 mL of hydrazine hydrate 0.19 g of brown insoluble polymer.

References

S1) S. A. Torosyan, Z. F. Nuriakhmetova, F. A. Gimalova, M. S. Miftakhov, *Russ. J. Org. Chem*., 2019, **55**, 1907–1911.

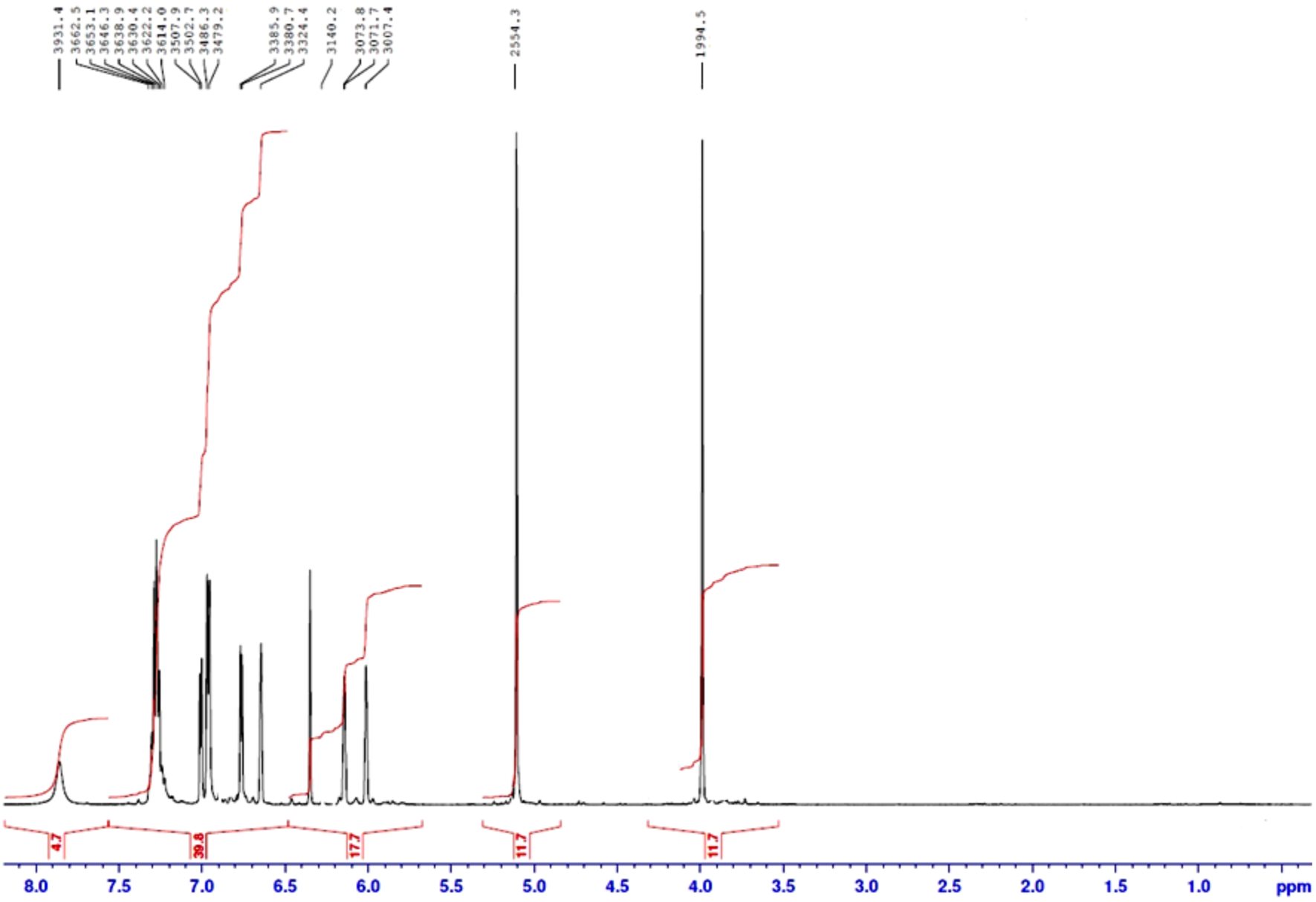

Fig. S1. Complete ^{1}H NMR spectrum of compound **1b** in $CDCl_3$, 500MHz

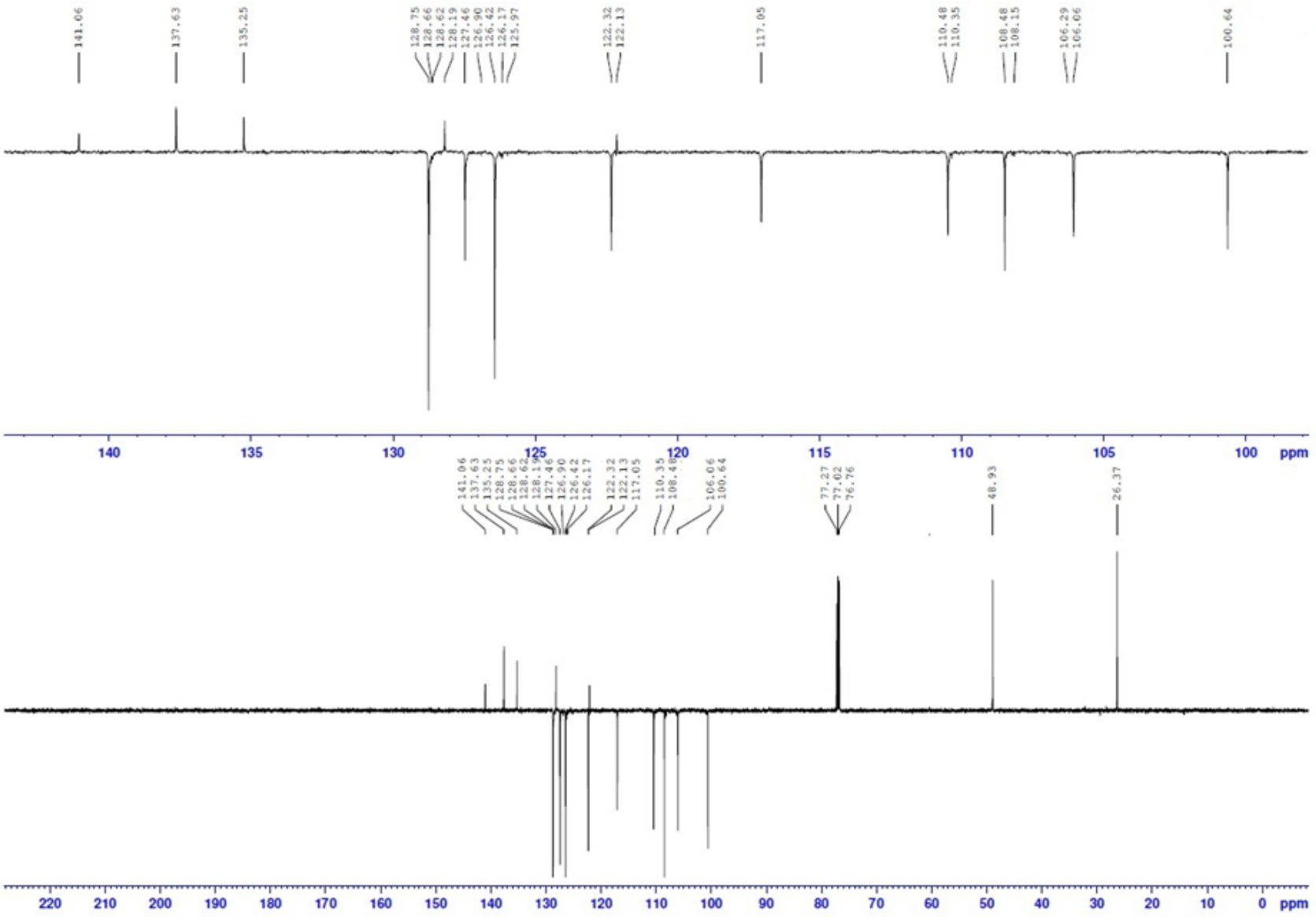

Fig. S2. Complete $^{13}C\{^{1}H\}$ NMR spectrum of compound **1b** in $CDCl_3$, 125MHz

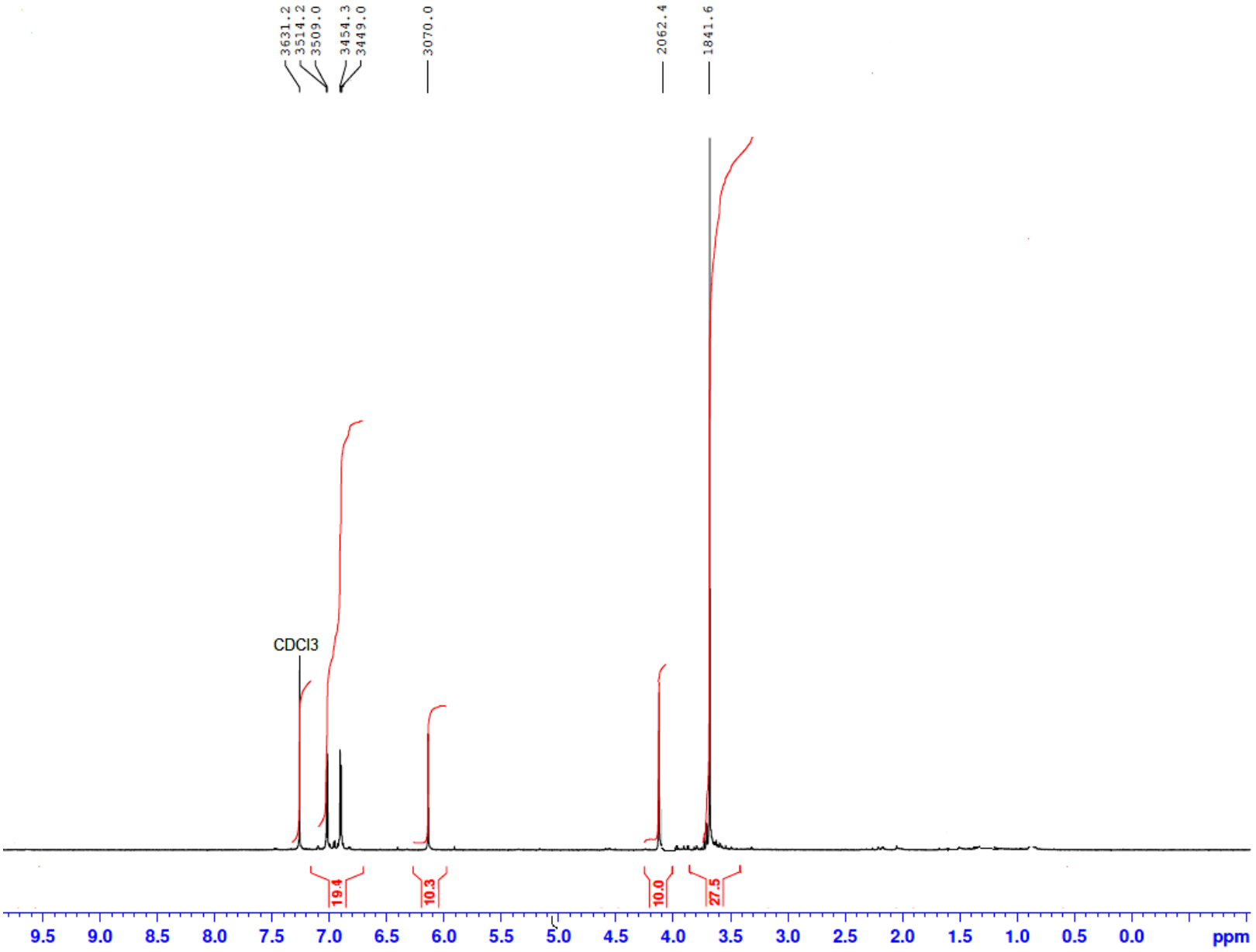

Fig. S3. Complete ^{1}H NMR spectrum of compound **2a** in $CDCl_3$, 500MHz

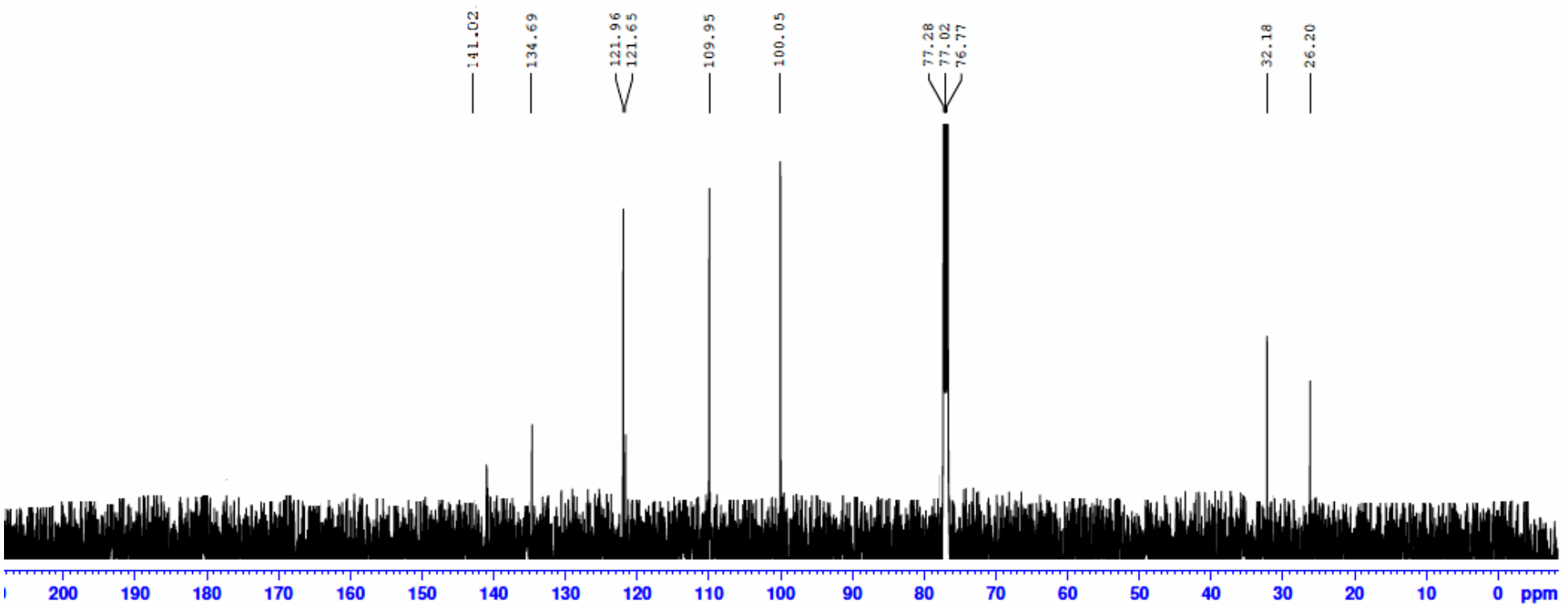

Fig. S4. Complete $^{13}C\{^{1}H\}$ com NMR spectrum of compound **2a** in $CDCl_3$, 125MHz

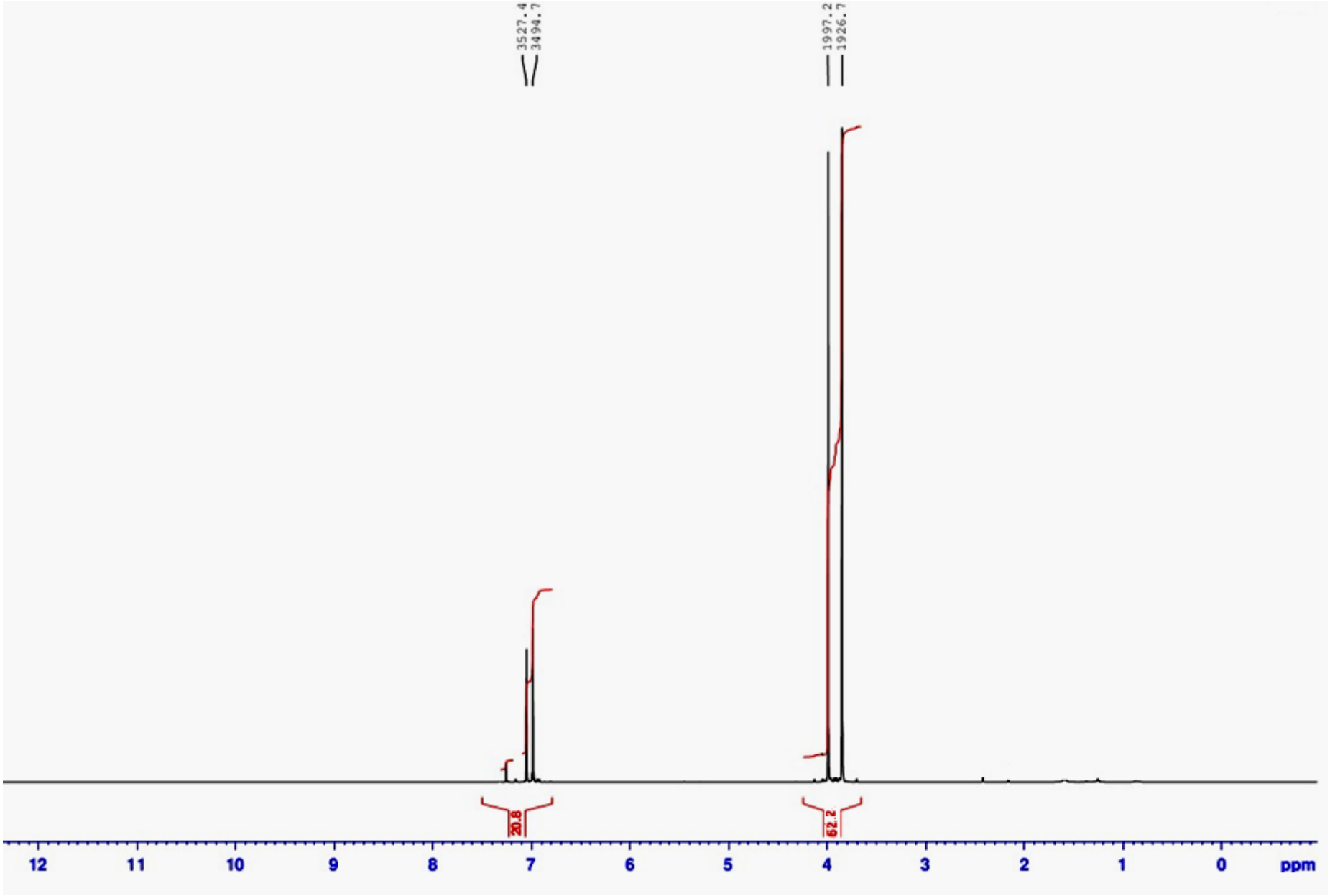

Fig. S5. Complete ^{1}H NMR spectrum of compound **4** in $CDCl_3$, 500MHz

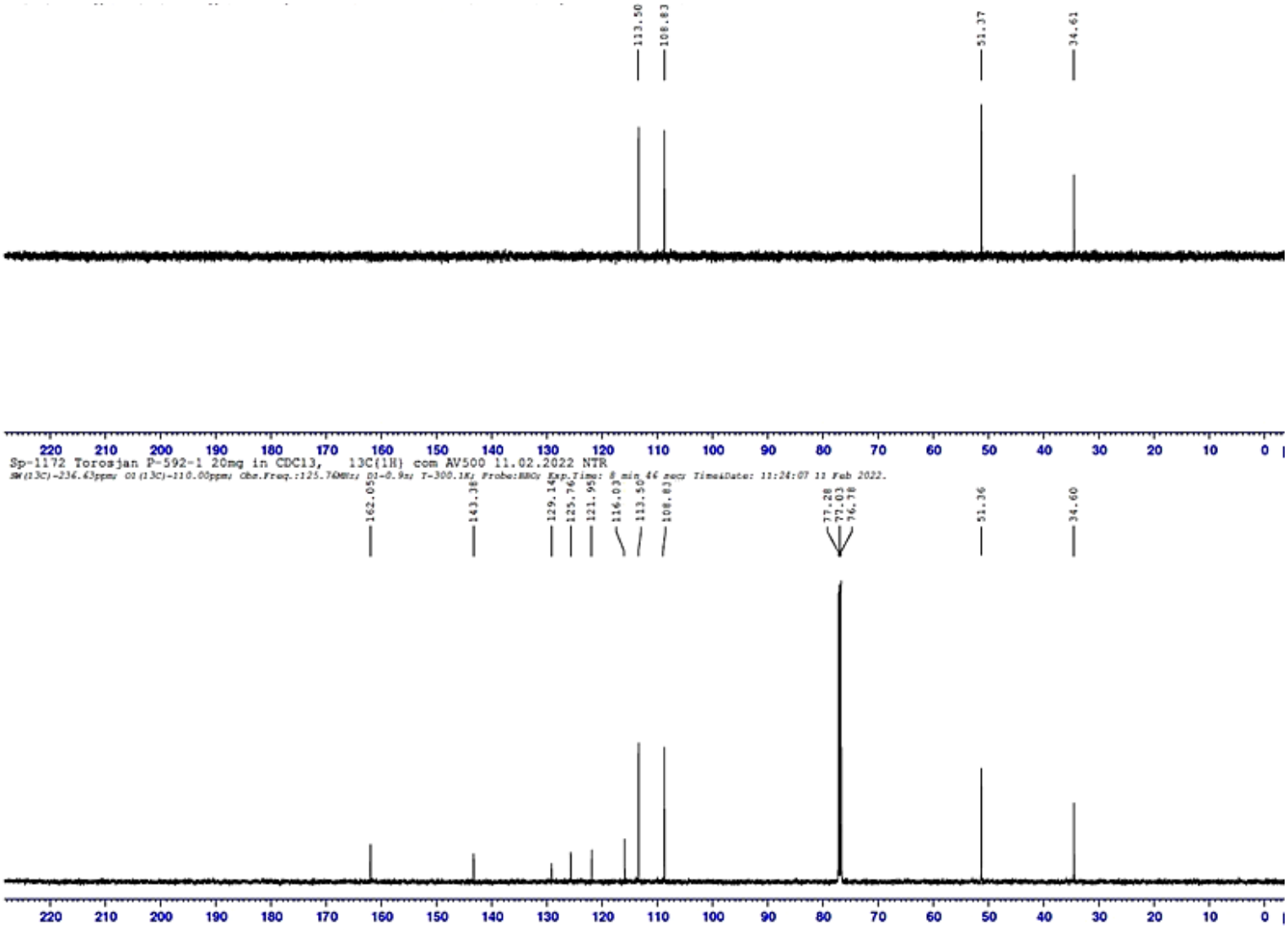

Fig. S6. Complete $^{13}C\{^{1}H\}$ NMR spectrum of compound **4** in $CDCl_3$, 125MHz

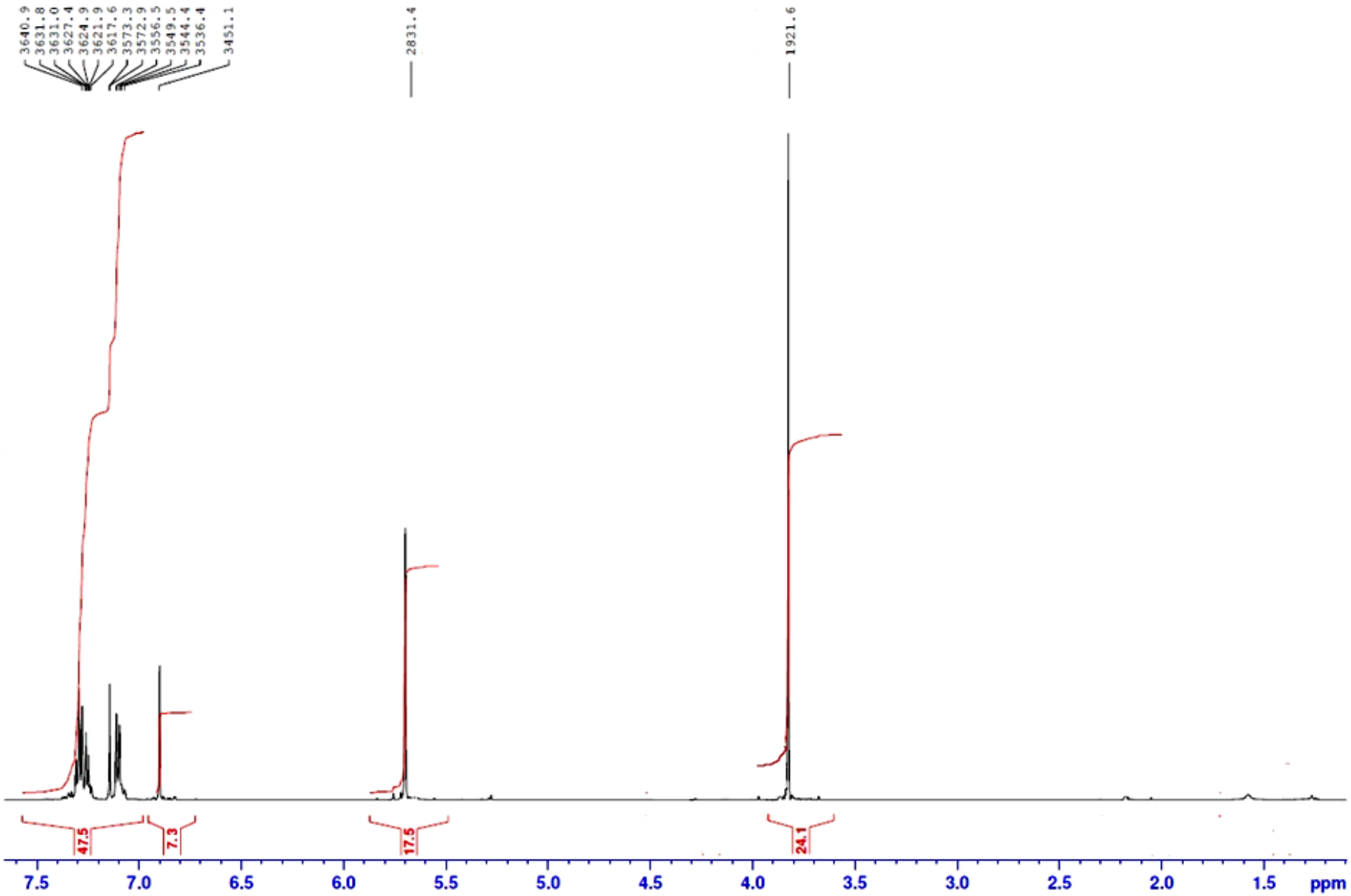

Fig. S7. Complete ^{1}H NMR spectrum of compound **6** in $CDCl_3$, 500MHz

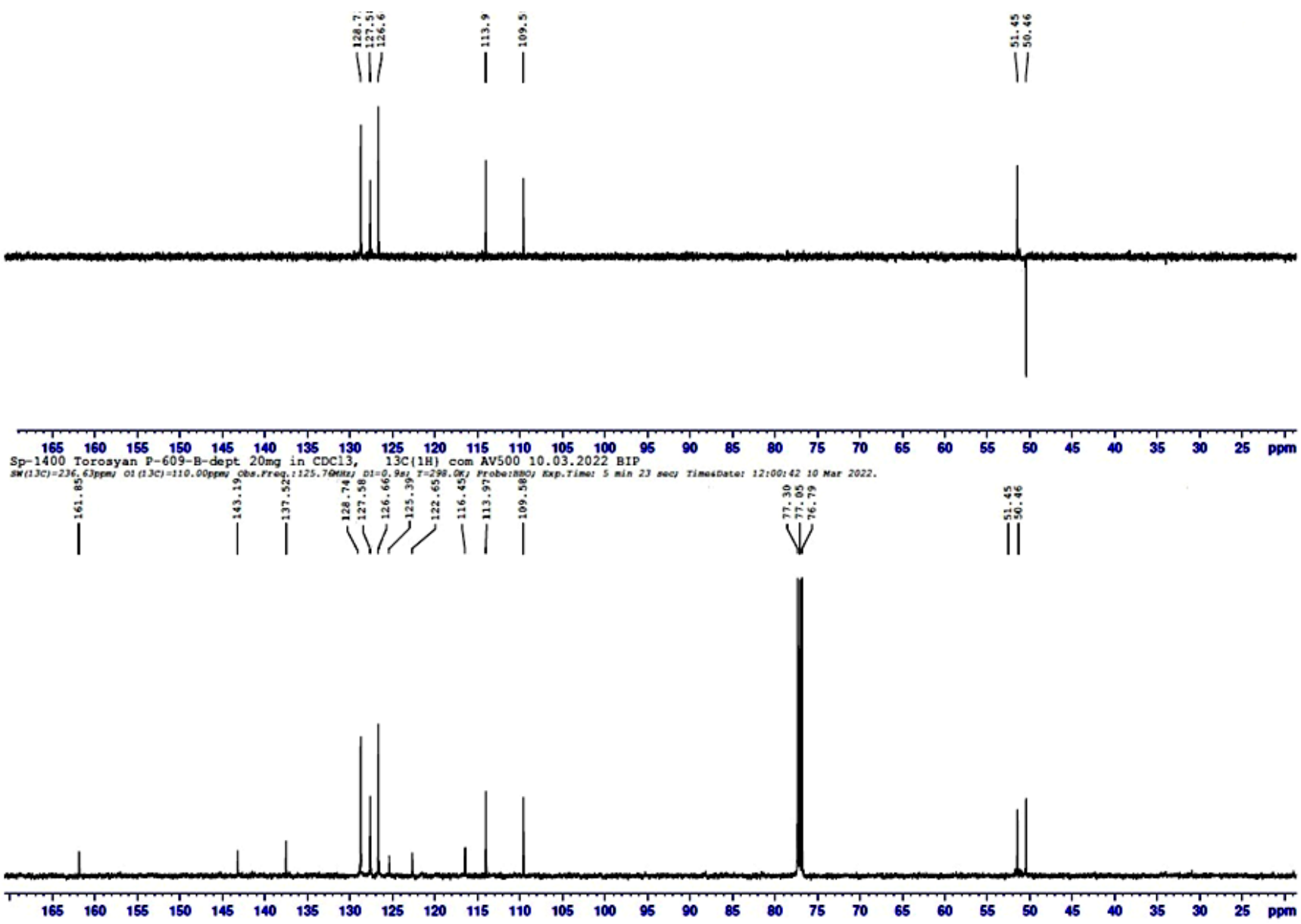

Fig. S8. Complete $^{13}C\{^{1}H\}$ NMR spectrum of compound **6** in $CDCl_3$, 125MHz

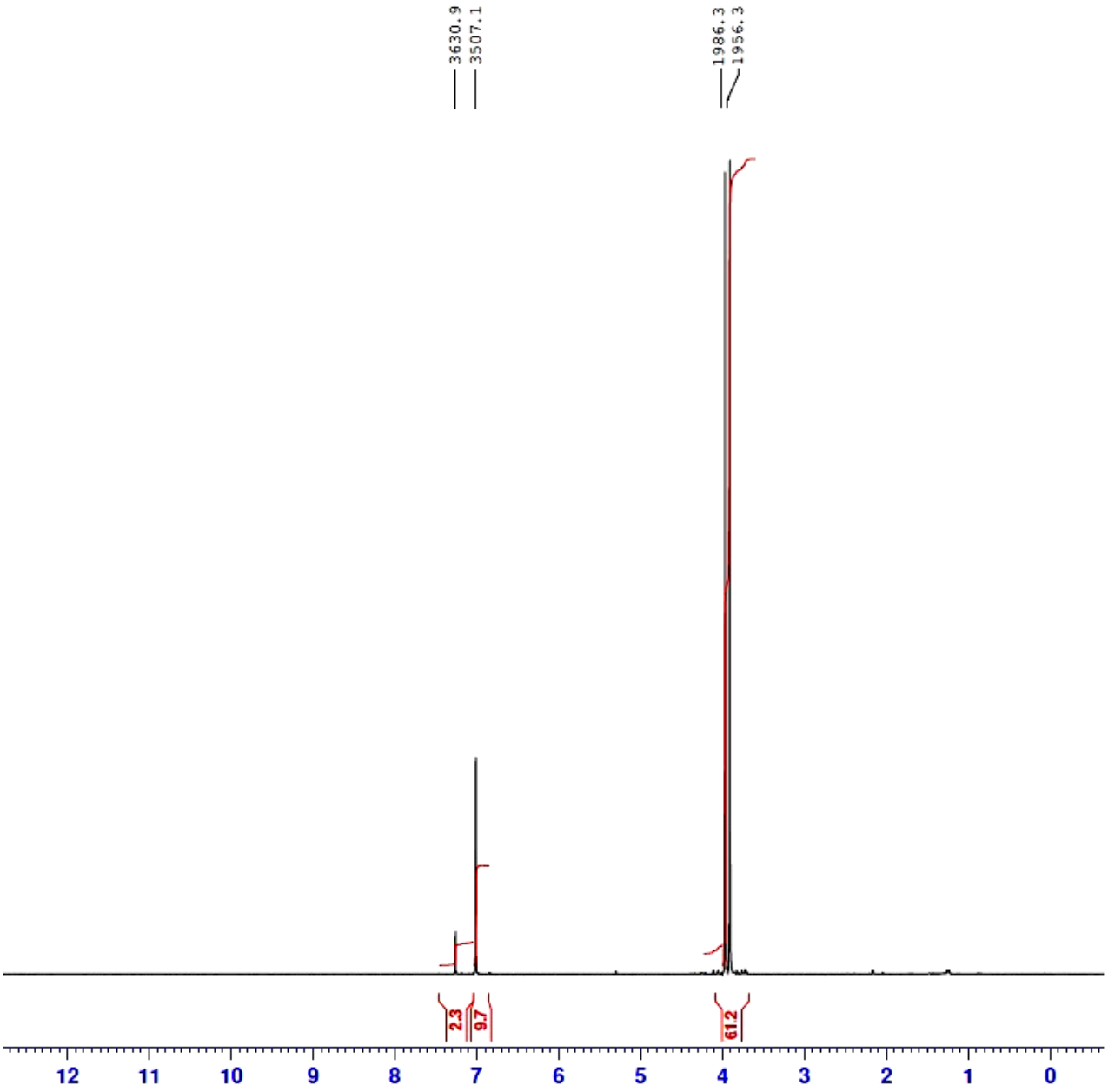

Fig. S9. Complete ^{1}H NMR spectrum of compound **8** in $CDCl_3$, 500MHz

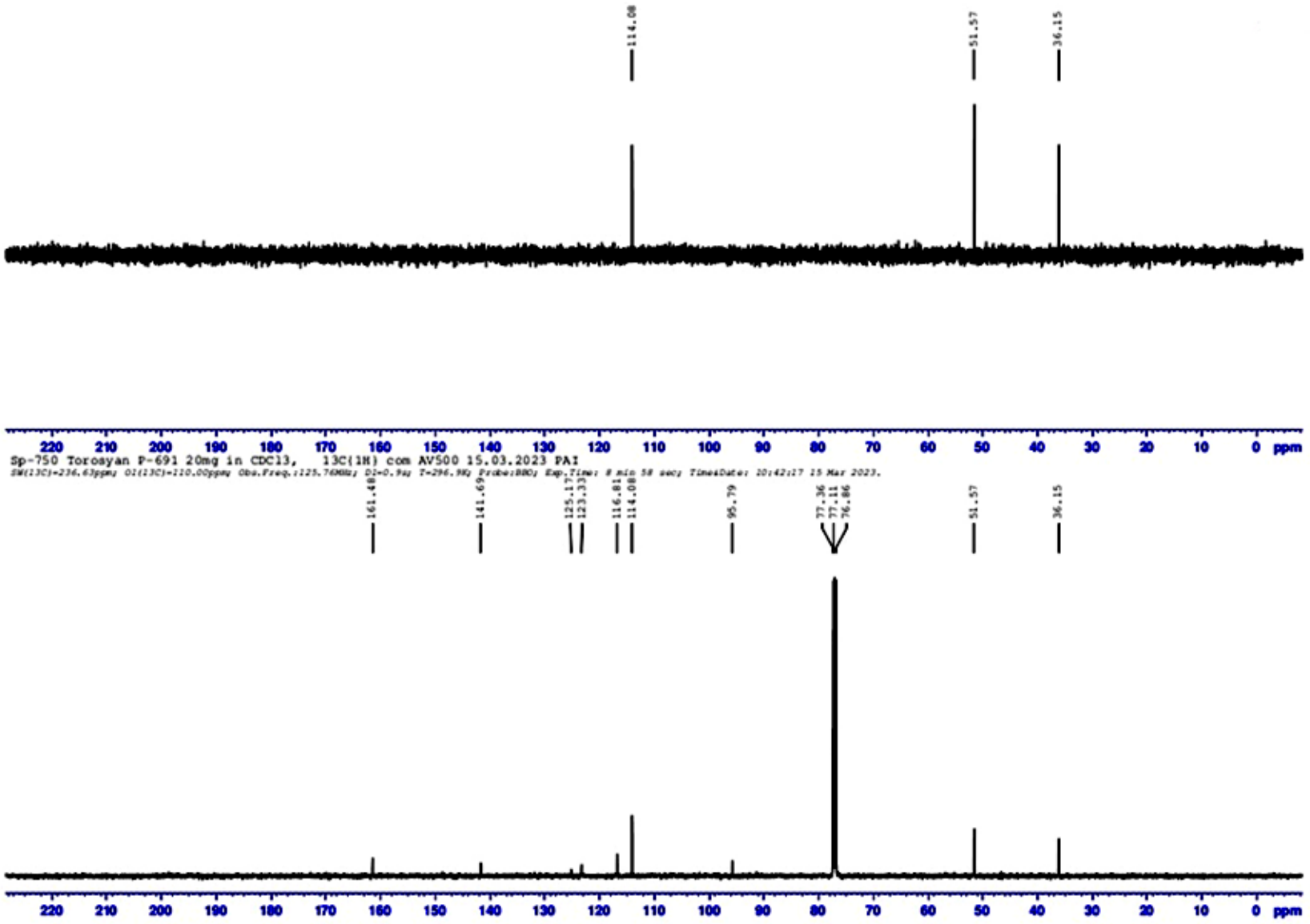

Fig. S10. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8** in $CDCl_3$, 125MHz

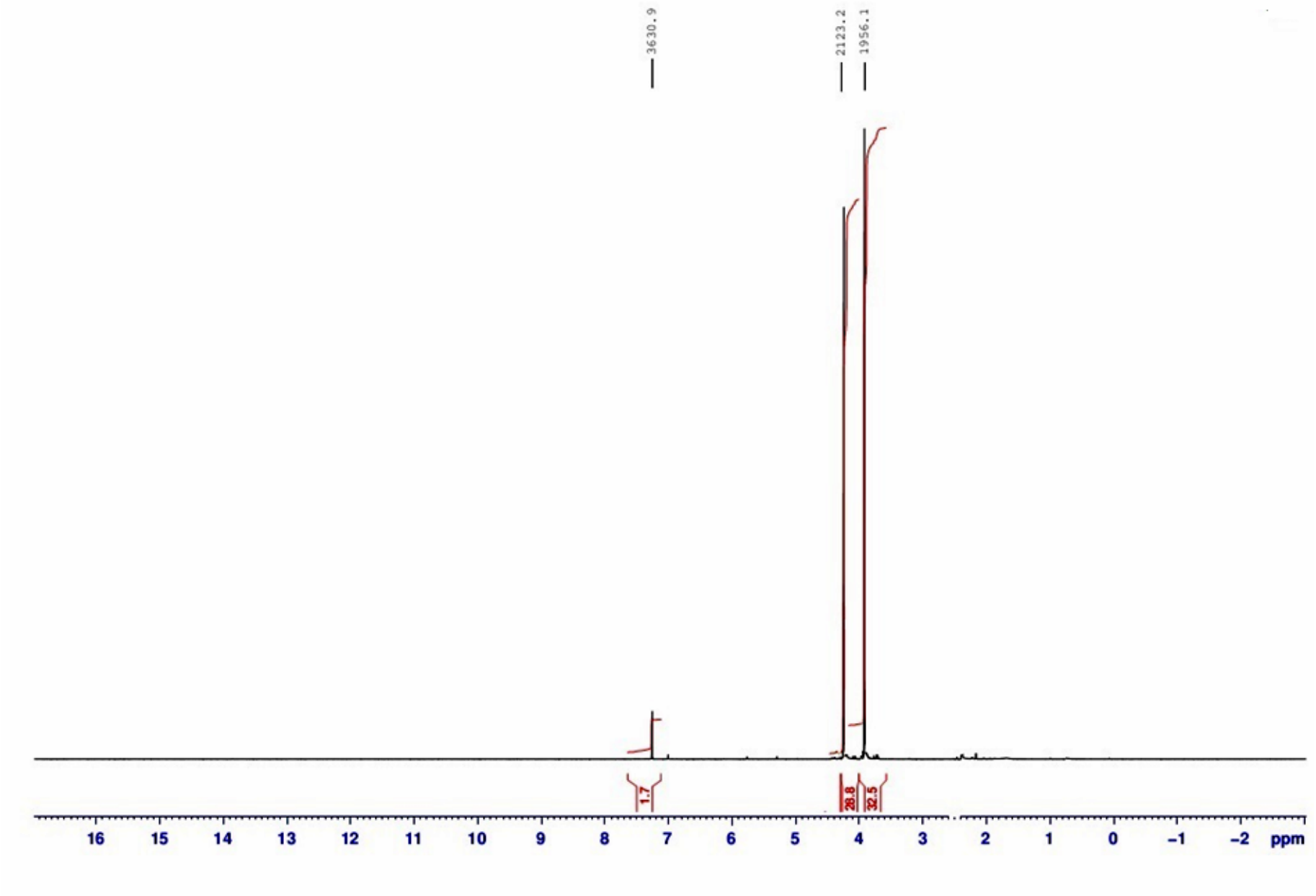

Fig. S11. Complete ^{1}H NMR spectrum of compound **9** in $CDCl_3$, 500MHz

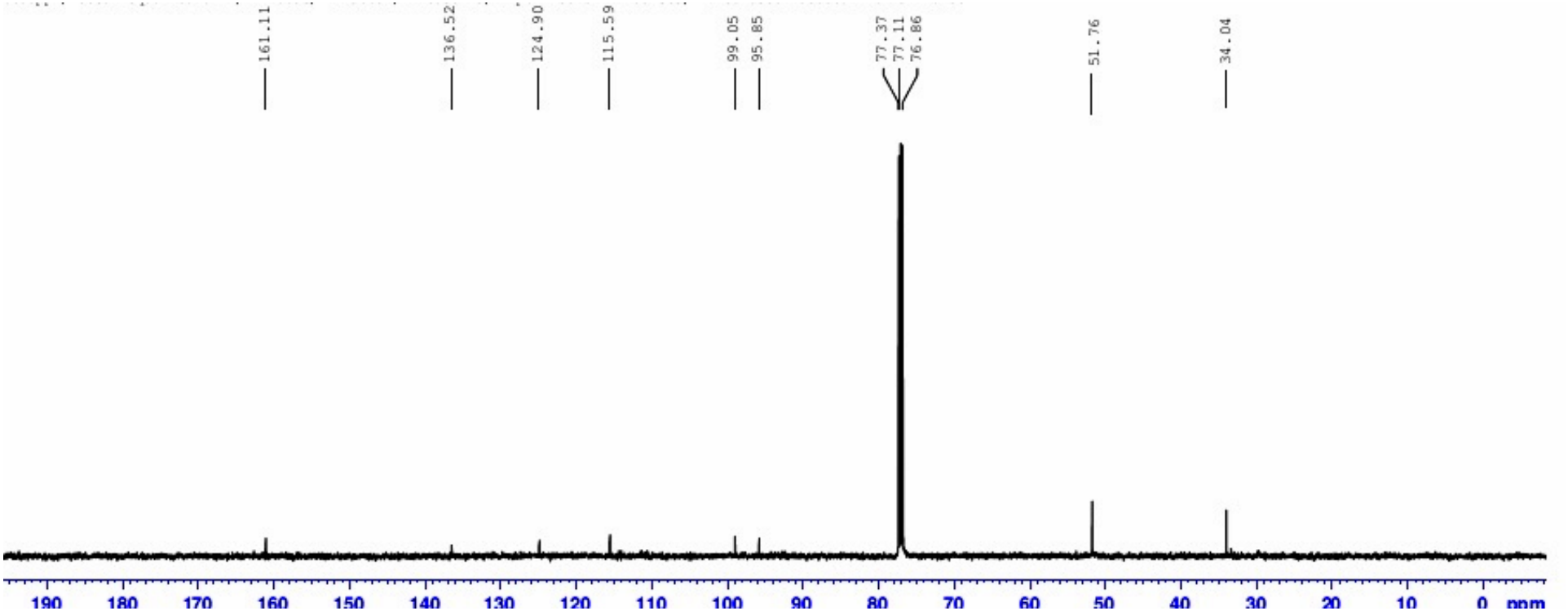

Fig. S12. $^{13}C\{^{1}H\}$ com NMR spectrum of compound **9** in $CDCl_3$, 125MHz

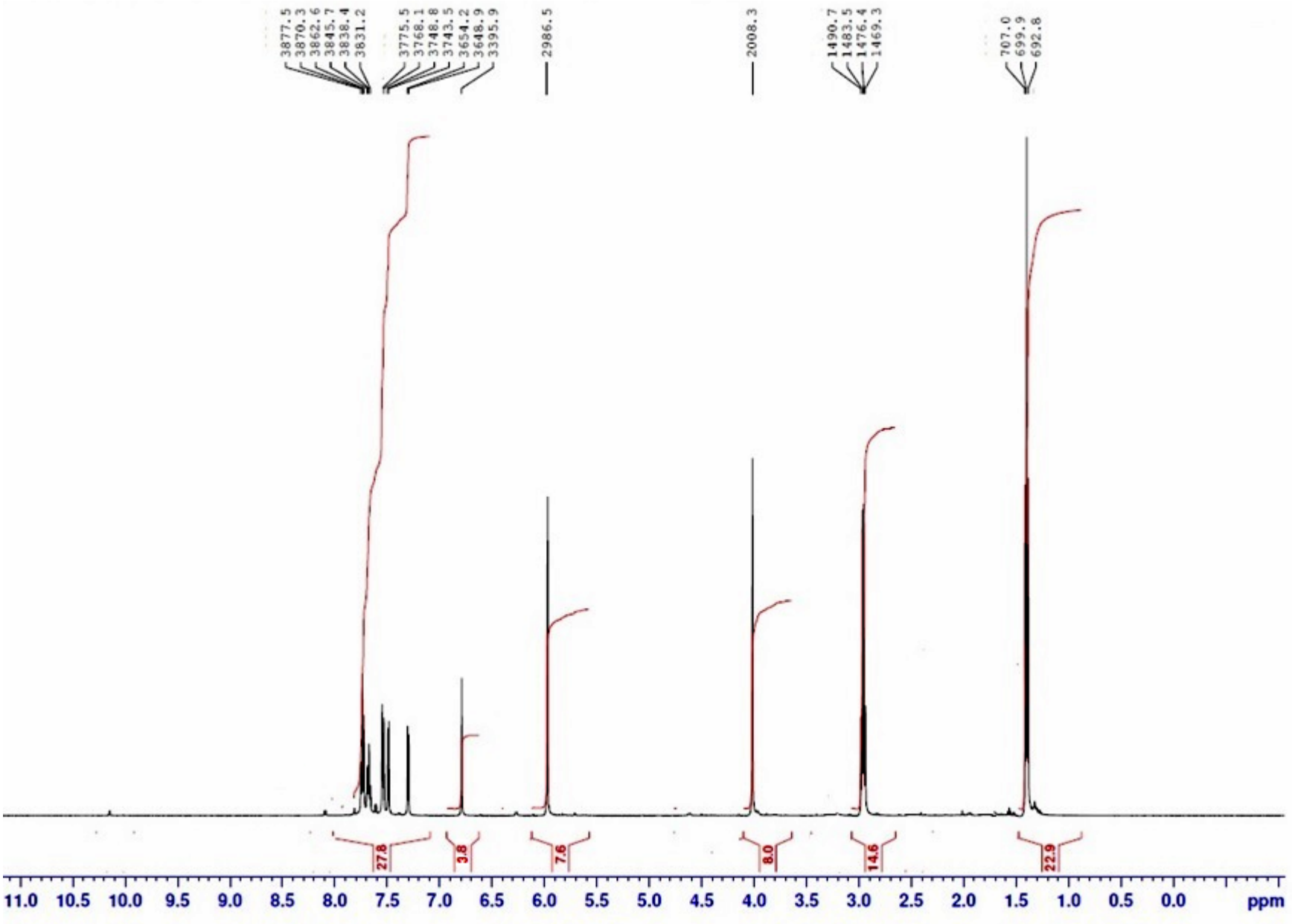

Fig. S13. Complete ^{1}H NMR spectrum of compound **12** in in acetone-d_6, 500MHz

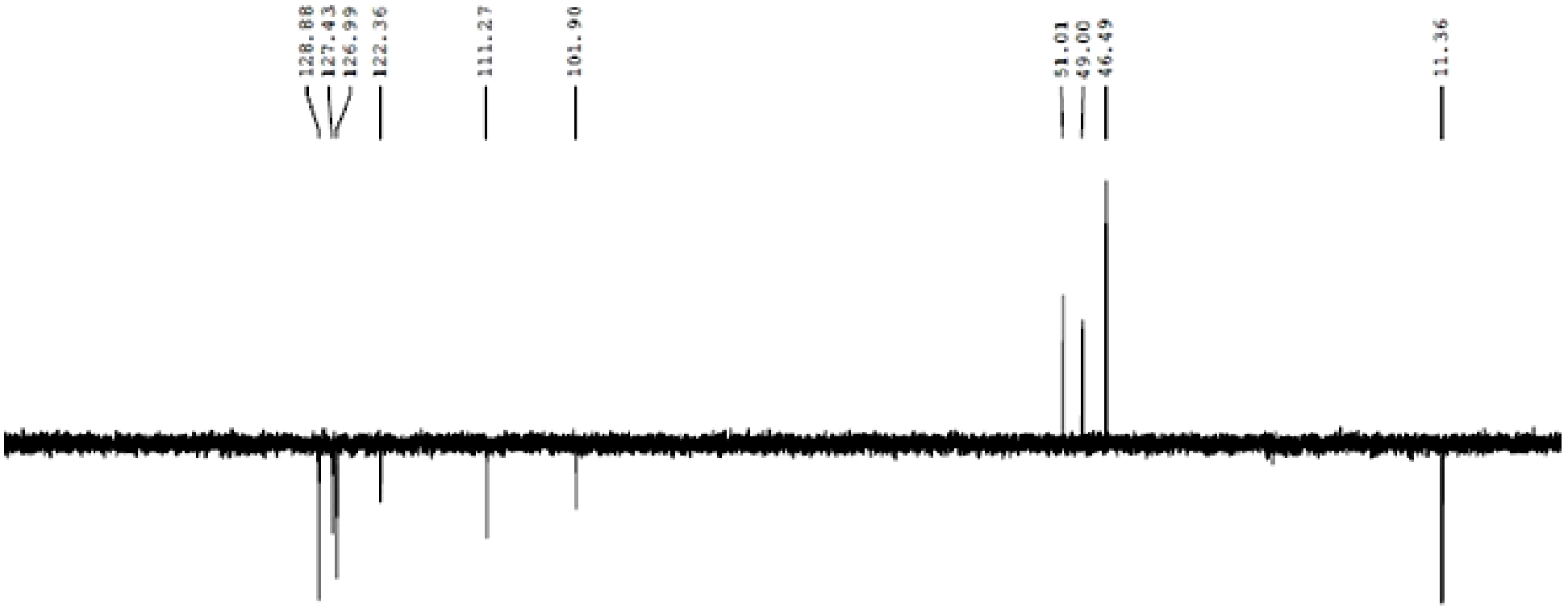

Fig. S14. Complete $^{13}C\{^{1}H\}$ NMR spectrum of compound **12** in in acetone-d_6, 125MHz

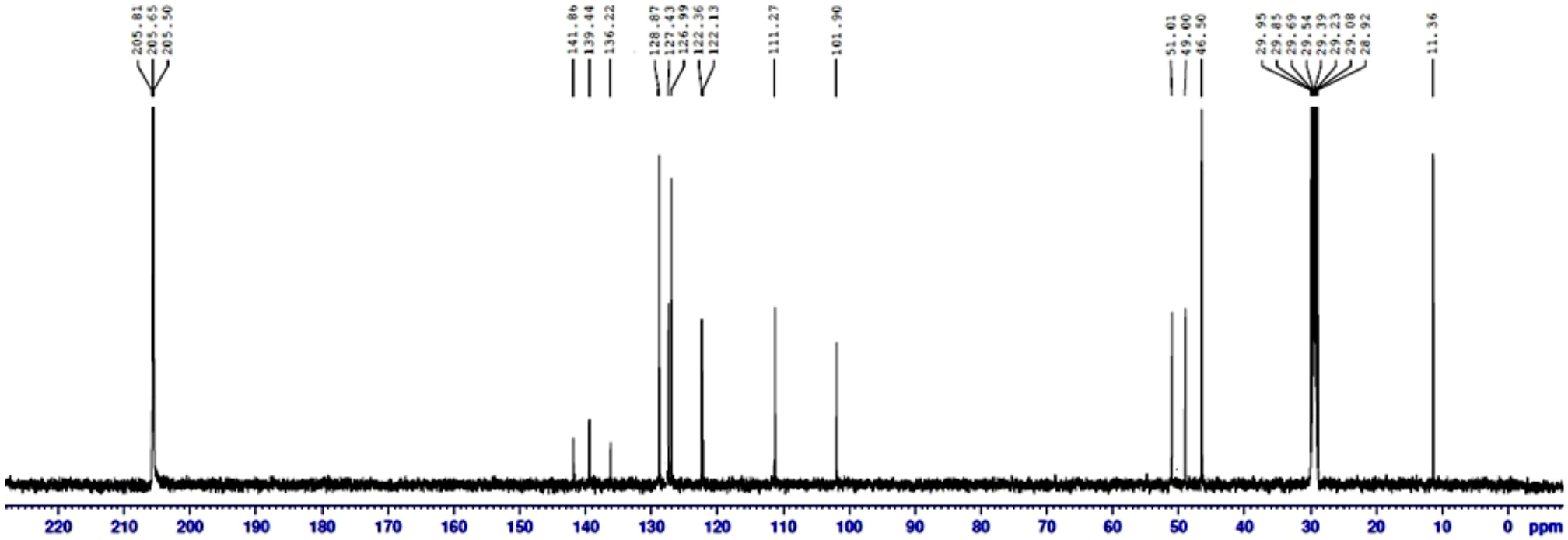

Fig. S15. $^{13}C\{^{1}H\}$ com NMR spectrum of compound **12** in acetone-d_6, 125MHz

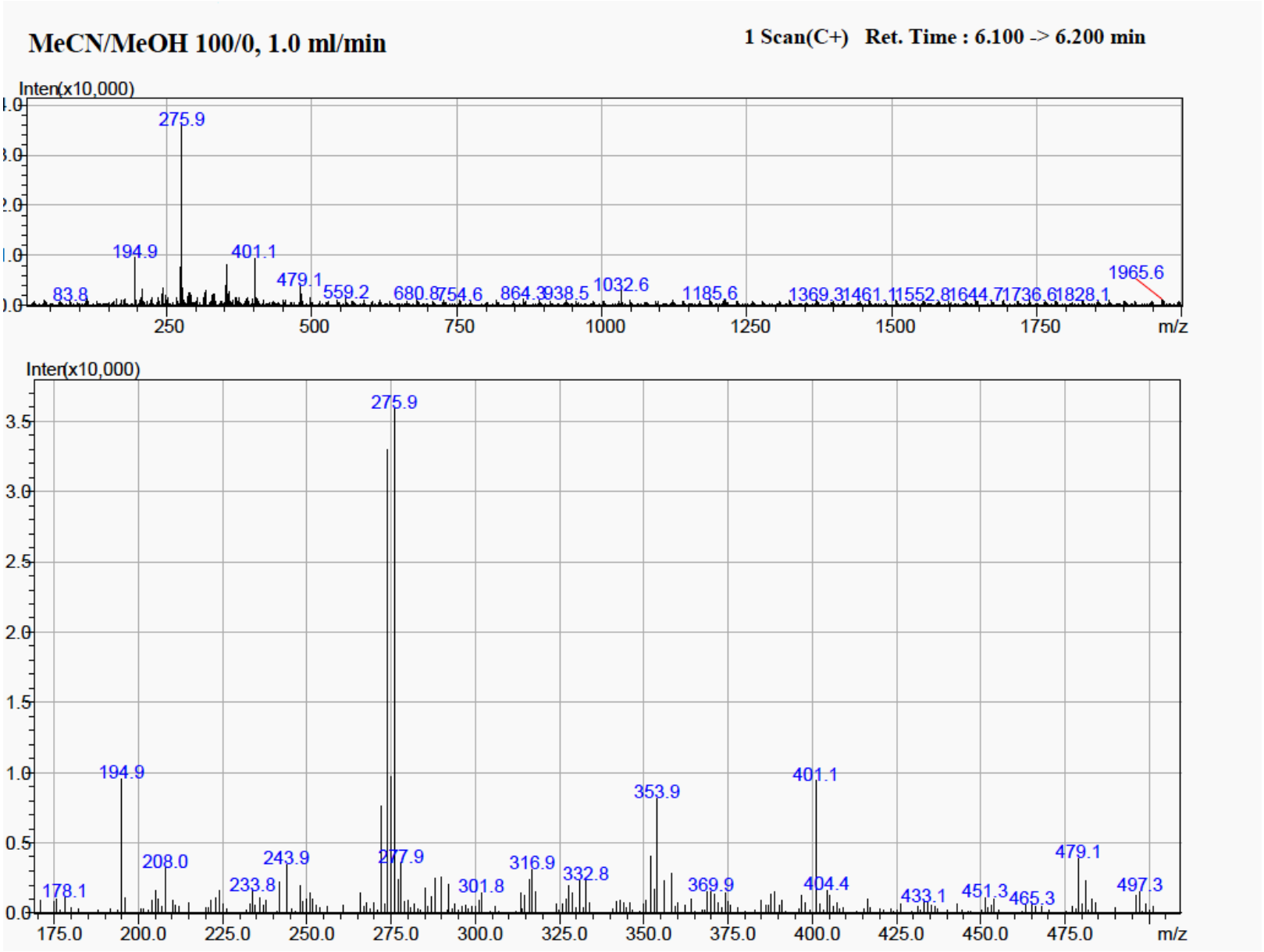

Fig. S16. Mass-spectrum of compound **5**

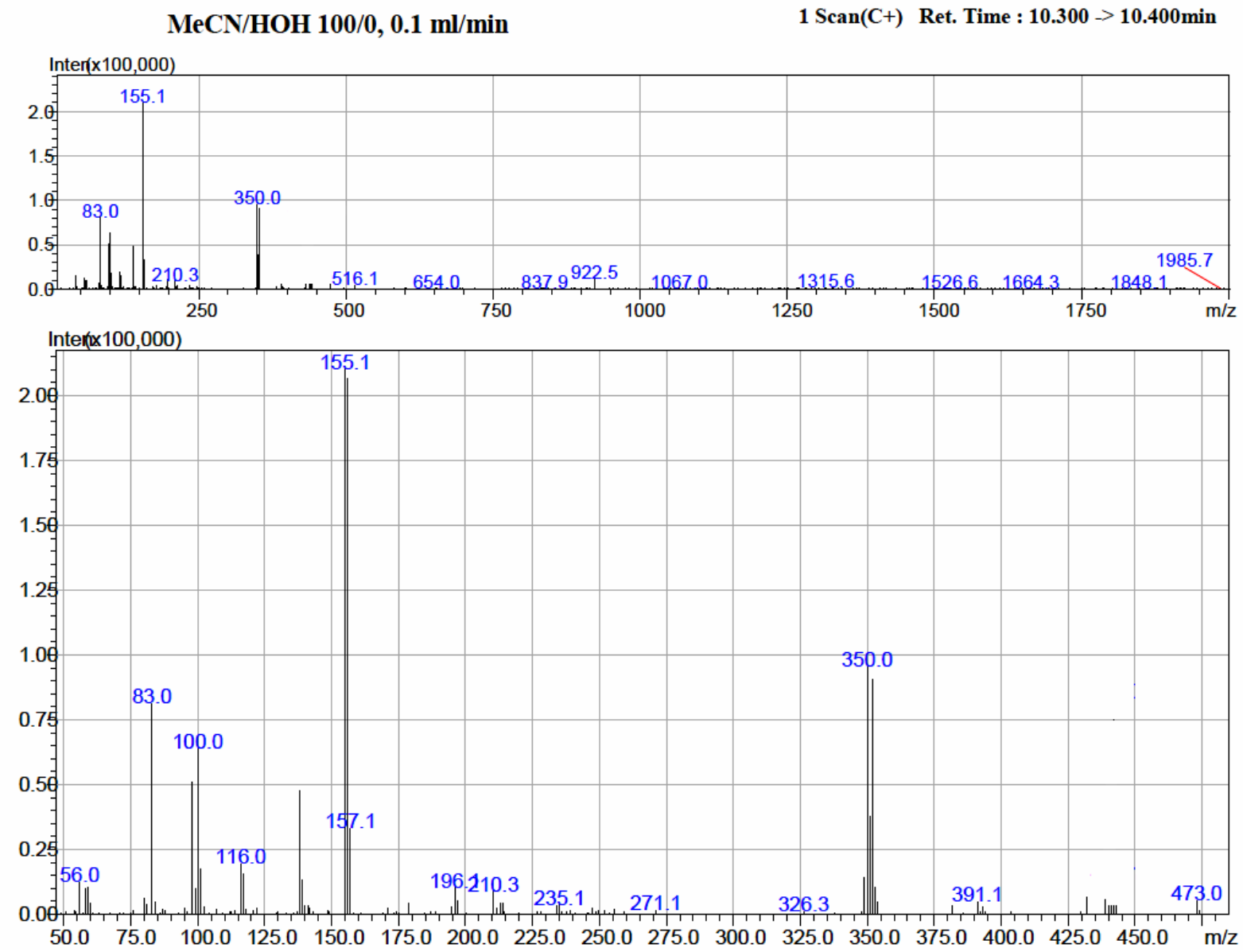

Fig. S17. Mass-spectrum of compound **6**

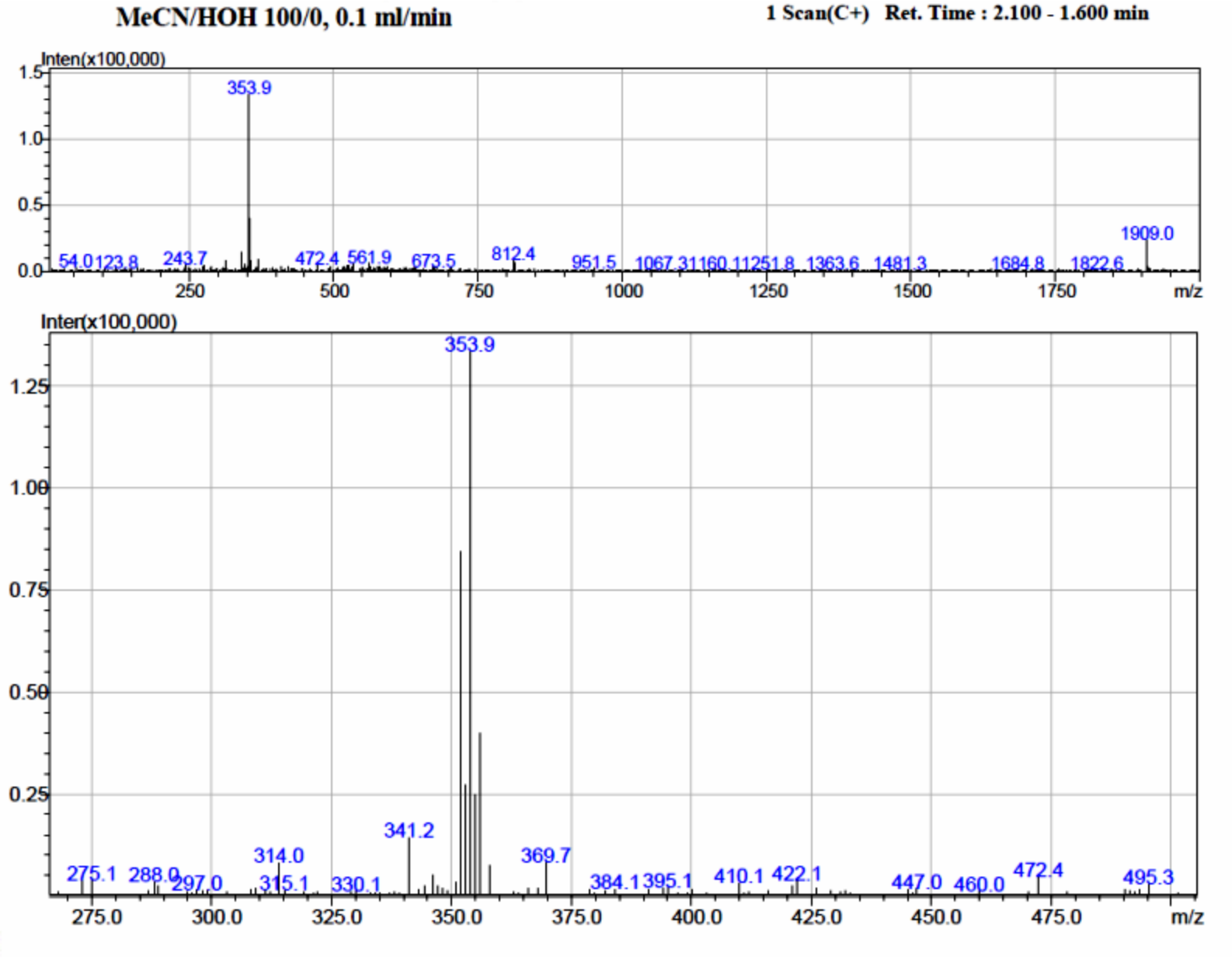

Fig. S18. Mass-spectrum of compound **8**

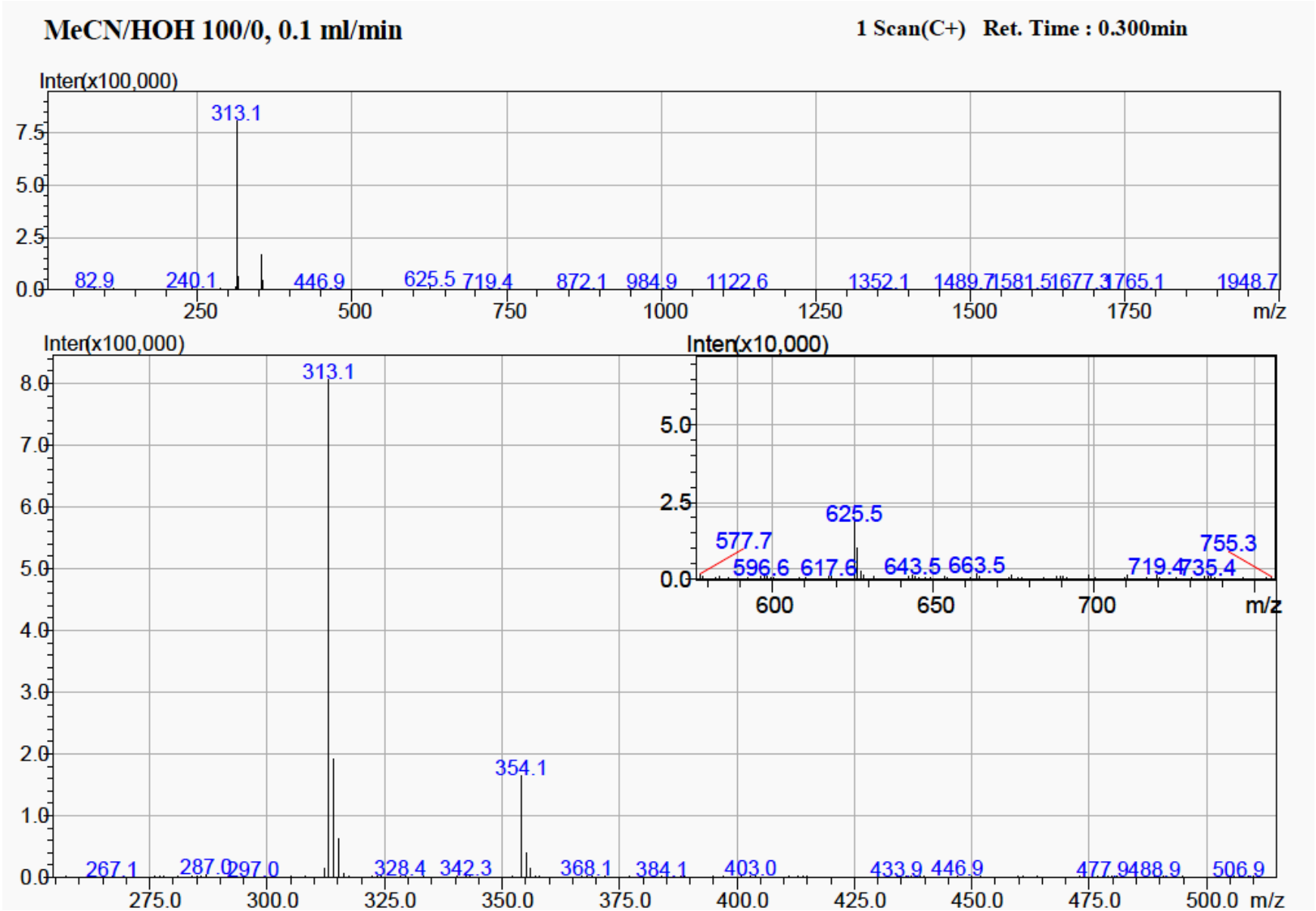

Fig. S19. Mass-spectrum of compound **11**

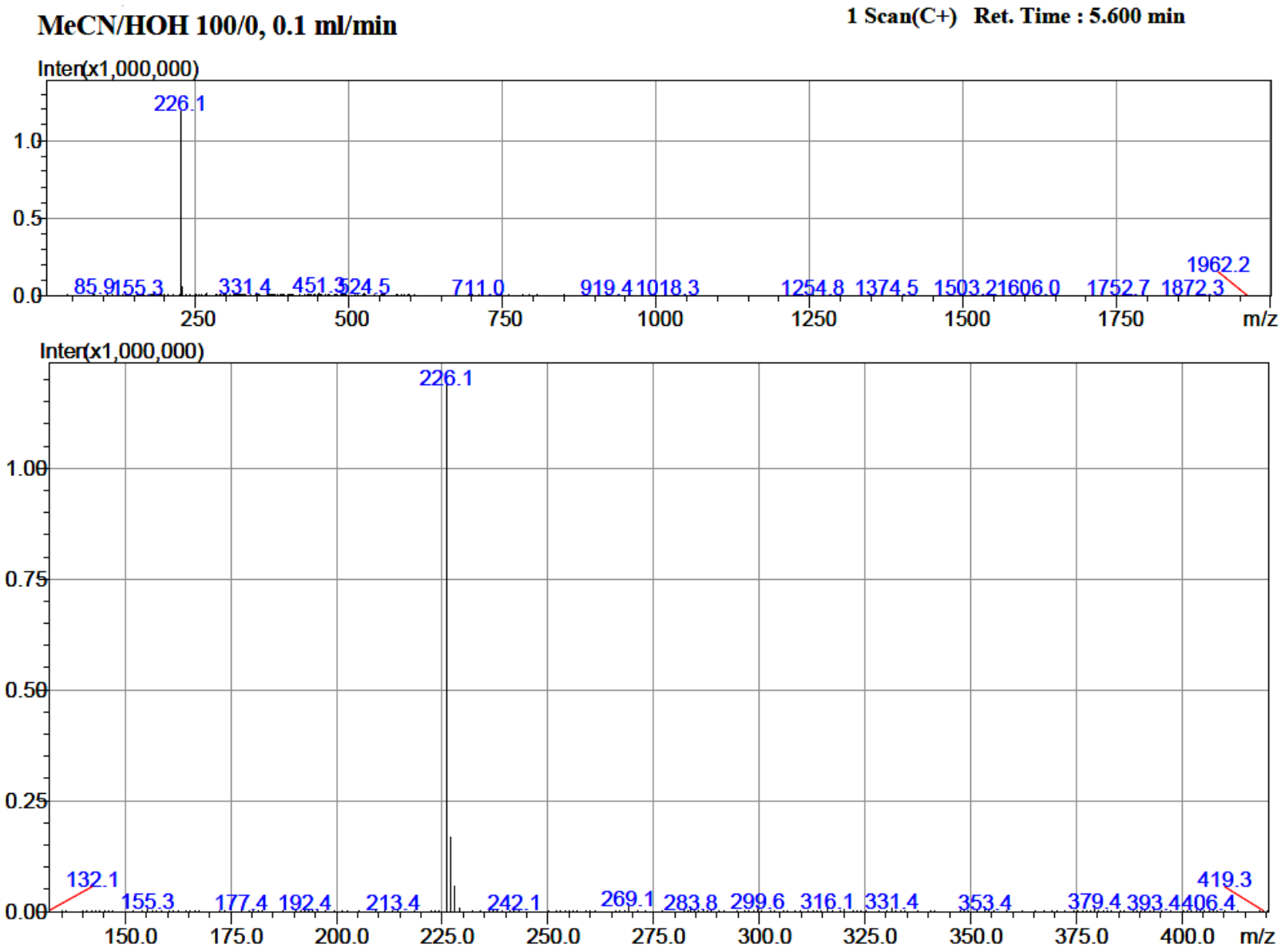

Fig. S20. Mass-spectrum of compound **12**