SUPPLEMENTARY MATERIAL TO

**Determination of enol form of asymmetric 1,3-dicarbonyl compounds: 2D HMBC NMR data and DFT calculations**

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**Experimental Section**

**General Methods:** NMR spectra were recorded on a 400 MHz spectrometer. Infrared (IR) spectra were recorded in the range 4000-600 cm-1 via ATR diamond. Melting points were determined using a melting point apparatus and were uncorrected. Mass spectra were recorded by LC-MS TOF electrospray ionization technique. Column chromatography was performed on silica gel (60-mesh), TLC was carried out on 0.2 mm silica gel 60 F254 analytical aluminium plates. Evaporation of solvents was performed at reduced pressure, using a rotary vacuum evaporator.

**Syntheses:**

**General procedure for synthesis of the compounds 1-10:**

Acetyl ketone (1 equiv) was added to dry 1,4-dioxane and NaH(60% oil suspension, 5 equiv) was added by pieces to the mixture at ice-bath. It was stirred at room temperature for 1 h. Related ester (5 equiv) was added to the mixture and refluxed for 1 h. After cooling 10% HCl solution was added to the reaction mixture and extracted with CH2Cl2 (3×20 mL). Crude product dried on MgSO4. Recrystallization or column chromatography gave the product, which was dried *in* *vacuo* (25°C, 0.5 mbar), affording spectroscopically pure product.1

**Synthesis of 1-(2,6-dimethoxyphenyl)-3-phenylpropane-1,3-dione (1)**

1-(2,6- dimethoxphenyl)ethanone (0.72 g, 4 mmol) and ethyl benzoate (2,8 mL, 20 mmol) reacted according to general procedure. Column chromatography heksan/ethyl acetate (5:1) gave the product as a white crystals in 95% yield (1,113 g). Mp: 85-88 oC.2

1H-NMR (400 MHz, CDCl3) δ 16.13 (bs, 1H, OH), 7.92-7.90 (m, 2H, Ar-H), 7.53-7.49 (m, 1H, Ar-H), 7.47-7.42 (m, 2H, Ar-H), 7.33 (t, J5,4=8.4 Hz, 1H, H-5), 6.61 (d, J4,5=8.4 Hz, 2H, H-4 and H-6), 6.4 (s, 1H, H-13), 3.83 (s, 6H, H-8 and H-12); 13C-NMR (100 MHz, CDCl3) δ 189.4, 181.5, 157.7, 135.0, 132.1, 131.2, 128.5, 127.1, 117.2, 104.2, 100.6, 56.1; IR (ATR, cm-1) 2921, 2989, 1681, 1598, 1582, 1495, 1469, 1453, 1424, 1323, 1287, 1247, 1176, 1111, 1071; HR-MS m/z (M+H)+ (C17H17O4) theoretical: 285.1121; experimental: 285.1119.

**Synthesis of 1-phenyl-3-(2,4,6-trimethoxyphenyl)propane-1,3-dione (2)**

1-(2,4,6-trimethoxyphenyl)ethanone (0.84 g, 4 mmol) and ethyl benzoate (2,8 mL, 20 mmol) reacted according to general procedure. Column chromatography heksan/ethyl acetate (5:1) gave the product as a honey yellow crystals in 87% yield (1,09 g). Mp: 95-98 oC.3

1H-NMR (400 MHz, CDCl3) δ 16.23 (bs, 1H, OH), 7.91-7.89 (m, 2H, Ar-H), 7.52-7.48 (m, 1H, Ar-H), 7.46-7.42 (m, 2H, Ar-H), 6.41 (s, 1H, H-15), 6.16 (s, 2H, H-4 and H-6), 3.85 (s, 3H, H-14), 3.82 (s, 6H, H-8 and H-12); 13C-NMR (100 MHz, CDCl3) δ 188.7, 181.3, 162.8, 159.1, 135.3, 131.9, 128.5, 127.0, 110.3, 101.0, 90.8, 56.1, 55.5; IR (ATR, cm-1) 2969, 2940, 2838, 1698, 1682, 1585, 1490, 1452, 1411, 1331, 1274, 1226, 1203, 1185, 1154, 1123; HR-MS m/z (M+H)+ (C18H19O5) theoretical: 315.1227; experimental: 315.1224.

**Synthesis of 1-(2,6-dimethoxyphenyl)butane-1,3-dione (3)**

1-(2,6-dimethoxyphenyl)ethanone (0.54 g, 3 mmol) and ethyl acetate (1,47 mL, 15 mmol) reacted according to general procedure. Column chromatography heksan/ethyl acetate (5:1) gave the product as a bright gel-like in 54% yield (0,852 g).4

1H-NMR (400 MHz, CDCl3) δ 15.54 (bs, 0.8 H, OH), 7.32-7.27 (m, 1.75 H, keto and enol H-5), 6.59-6.55 (m, 3H, keto and enol H-4 ve H-6), 5.71 (s, 0.8 H, enol H-13), 3.88 (s, 0.8 H, keto H-13), 3.81 (s, 8.5 H, keto and enol H-8 and H-12), 2.29 (s, 1H, keto H-16), 2.12 (s, 3H, H-16); 13C-NMR (100 MHz, CDCl3) δ 189.5, 186.8, 157.6, 131.1, 116.4, 104.1, 104.0, 56.0, 24.6 (enol form), 201.8, 197.3, 157.0, 131.7, 119.2, 104.1, 60.1, 55.8, 30.2 (keto form); HR-MS m/z (M+H)+  (C12H15O4) theoretical: 223.0965; experimental: 223.0964.

**Synthesis of 1-(2,4,6-trimethoxyphenyl)butane-1,3-dione (4)**

1-(2,4,6-trimethoxyphenyl)ethanone (0.63 g, 3 mmol) and ethyl acetate (1,47 mL, 15 mmol) reacted according to general procedure. Column chromatography heksan/ethyl acetate (5:1) gave the product as a light yellow solid in 86% yield (0,653 g). Mp: 99-102 oC.5

1H-NMR (400 MHz, CDCl3) δ 15.65 (bs, 1H, OH), 6.12 (s, 2H,enol H-4 ve H-6), 6.09 (s, 1H, keto H-4 and H-6), 5.71 (s, 1H, enol H-15), 3.85 (s, 1H, keto H-15), 3.83 (s, 5 H, keto and enol H-14), 3.80 (s, 10H, keto and enol H-8 ve H-12), 2.26 (s, 1.5H, keto H-18), 2.10 (s, 3H, enol H-18); 13C-NMR (100 MHz, CDCl3) δ 189.5, 186.0, 162.6, 159.0, 104.3, 90.8, 90.6, 56.0, 55.8, 24.8 (enol form), 202.4, 195.9, 163.3, 159.1, 112.4, 109.6, 60.5, 55.5, 55.4, 30.1 (keto form); HRMS m/z (M+H)+ (C13H17O5) theoretical: 253.1071; experimental: 253.1064.

**Synthesis of 1,3-di(naphthalen-1-yl)propane-1,3-dione (5)**

1-acetyl naphthalene (0.3 mL, 2 mmol) and ethyl-1-naftoat (1,8 mL, 10 mmol) reacted according to general procedure. Column chromatography heksan/ethyl acetate (8:1) gave the product as a light yellow crystal in 89% yield (0,58 g). Mp: 104-108 oC.6

1H-NMR (400 MHz, CDCl3 ) δ 8.61 (d, 2H, Ar-H), 8.00 (d, 2H, Ar-H), 7.92 (d, 2H, Ar-H), 7.84 (dd, 2H, Ar-H), 7.64-7.58 (m, 3H, Ar-H), 7.56-7.53 (m, 3H, Ar-H), 6.60 (s, 1H, H-13); 13C-NMR (100 MHz, CDCl3 ) δ 188.2, 133.4, 132.9, 130.9, 129.2, 127.6, 126.4, 126.3, 125.4, 124.6, 123.8, 102.1; IR (ATR, cm-1) 3041, 1708, 1673, 1593, 1574, 1527, 1506, 1459, 1423, 1384, 1364, 1338, 1290, 1278, 1243, 1194, 1123, 1065; HRMS m/z (M+H)+ (C23H17O2) theoretical: 325.1223; experimental: 325.1219.

**Synthesis of 1-(naphthalen-1-yl)butane-1,3-dione (6)**

1-acetyl naphthalene (0.75 mL, 5 mmol) and ethyl acetate (2.45 mL, 25 mmol) reacted according to general procedure. Column chromatography heksan/ethyl acetate (5:1) gave the product in 81% yield (0,766 g).7

1H-NMR (400 MHz, CDCl3) δ 16.12 (bs, 1H, OH), 8.46 (m, 1H, Ar-H), 7.96 (m, 1H, Ar-H), 7.89 (m, 1H, Ar-H), 7.72 (m, 1H, Ar-H), 7.59-7.48 (m, 3H, Ar-H), 6.04 (s, 1H, H-13), 2.22 (s, 3H, H-16); 13C-NMR (100 MHz, CDCl3) δ 191.4, 187.3, 133.3, 132.8, 130.6, 129.1, 127.5, 126.2, 125,9, 125.3, 124.5, 123.7, 100.7, 24.4; IR (ATR, cm-1) 3048, 1717, 1575, 1508, 1418, 1392, 1363, 1339, 1280, 1244, 1210, 1173, 1123, 1068; HRMS m/z (M+H)+ (C14H13O2) theoretical: 213.0910; experimental: 213.0905.

**Synthesis of 1-(naphthalen-1-yl)-3-phenylpropane-1,3-dione (7)**

Acetophenone (0.58 mL, 5 mmol) and ethyl-1-naftoate (4.5 mL, 25 mmol) reacted according to general procedure. Column chromatography heksan/ethyl acetate (8:1) gave the product as a yellow crystal in 80% yield (1 g). Mp: 60-63 oC.8

1H-NMR (400 MHz, CDCl3) δ 8.53 (m, 1H, Naf-H), 8.01-7.98 (m, 3H, Ar-H, Naf-H), 7.92 (m, 1H, Naf-H), 7.83 (m, 1H, Naf-H), 7.62-7.54 (m, 4H, Ar-H, Naf-H), 7.52-7.48 (m, 2H, Ar-H), 6.73 (s, 1H, H-13); 13C-NMR (100 MHz, CDCl3) δ 188.5, 182.4, 133.1, 133.0, 131.8, 130.5, 129.7, 128.1, 126.7, 126.5, 125.3, 125.2, 125.0, 124.4, 123.6, 122.8, 96.2; IR (ATR, cm-1) 3045, 2952, 2922, 2853, 1722, 1603, 1590, 1542, 1508, 1462, 1420, 1388, 1287, 1256, 1229, 1210, 1178, 1157, 1123, 1086, 1066; HRMS m/z (M+H)+ (C19H15O2) for theoretical: 275.1067; experimental: 275. 1064.

**Synthesis of 1-(3-bromothiophene-2-yl)butane-1,3-dione (8)**

3-bromo-2-acetyl thiophene (1.025 g, 5 mmol) and ethyl acetate (2.45 mL, 25 mmol) reacted according to general procedure. Column chromatography heksan/ethyl acetate (4:1) gave the product as a yellow solid in 53% yield (0.65 g). Mp: 55-58 oC.

1H-NMR (400 MHz, CDCl3) δ 15.88 (bs, 1H, OH), 7.51 (d, *J*2,3=5.2 Hz, 1H, H-2), 7.10 (d, *J*3,2=5.2 Hz, 1H, H-3), 6.56 (s, 1H, H-9), 2.19 (s, 3H, H-12); 13C-NMR (100 MHz, CDCl3) δ 190.9, 178.8, 135.4, 133.5, 130.8, 112.6, 97.9, 24.9; IR (ATR, cm-1) 3101, 2915, 1716, 1698, 1559, 1540, 1499, 1458, 1398, 1363, 1350, 1255, 1179, 1151; HRMS m/z (M+Na)+ (C8H7BrNaO2S) theoretical: 268.9242; experimental: 268.9242.

**Synthesis of 1,3-di(thiophen-2-yl)propane-1,3-dione (9)**

1-(thiophen-2-yl)ethanone (0.43 mL, 4 mmol) and ethyl thiophene-2-carboxylate (2.7 mL, 20 mmol) reacted according to general procedure. Column chromatography heksan/ethyl acetate (5:1) gave the product as a lemon yellow solid in 78% yield (0.736 g). Mp: 99-101 oC.9

1H-NMR (400 MHz, CDCl3) δ 16.18 (bs, 1H, OH), 7.78 (dd, *J*4,2=1.2 Hz, *J*4,3=3.8 Hz, 2H, H-4), 7.62 (dd, *J*2,3=4.9 Hz, *J*2,4=1.2 Hz, 2H, H-2), 7.17 (t, *J*3,2=4.9 Hz, *J*3,4=3.8 Hz, 2H, H-3), 6.54 (s, 1H, H-8); 13C-NMR (100 MHz) δ 176.3, 138.2, 129.5, 127.5, 125.8, 90.2; IR (ATR, cm-1) 3102, 3080, 1526, 1406, 1336, 1276, 1228; HR-MS m/z (M+H)+ (C11H9O2S2) theoretical: 237.0038; experimental: 237.0037.

**Synthesis of 1-(thiophen-2-yl)butane-1,3-dione (10)**

2-acetyl thiophene (0.54 mL, 5 mmol) and ethyl acetate (2.45 mL, 25 mmol) reacted according to general procedure. Column chromatography heksan/ethyl acetate (5:1) gave the product as a brick red solid in 90% yield (0.80 g). Mp: 44-48 oC.10

1H-NMR (400 MHz, CDCl3) δ 15.65 (bs, 1H, OH) 7.69 (dd, *J*4,2=1.2 Hz, *J*4,3=3.8 Hz, 1H, H-4), 7.60 (dd, *J*2,3=4.9 Hz, *J*2,4=1.2 Hz, 1H, H-2), 7.13 (t, *J*3,2=4.9 Hz, *J*3,4=3.8 Hz, 1H, H-3), 6.03 (s, 1H, H-8), 2.14 (s, 3H, H-11); 13C-NMR (100 MHz, CDCl3 ) δ 187.3, 181.7, 141.7, 132.3, 130.2, 128.2, 96.5, 23.9; IR (ATR, cm-1) 3105, 1698, 1558, 1515, 1425, 1404, 1368, 1354, 1268, 1236; HRMS m/z (M+Na)+ (C8H8NaO2S) theoretical: 191.0137; experimental: 191.0137.

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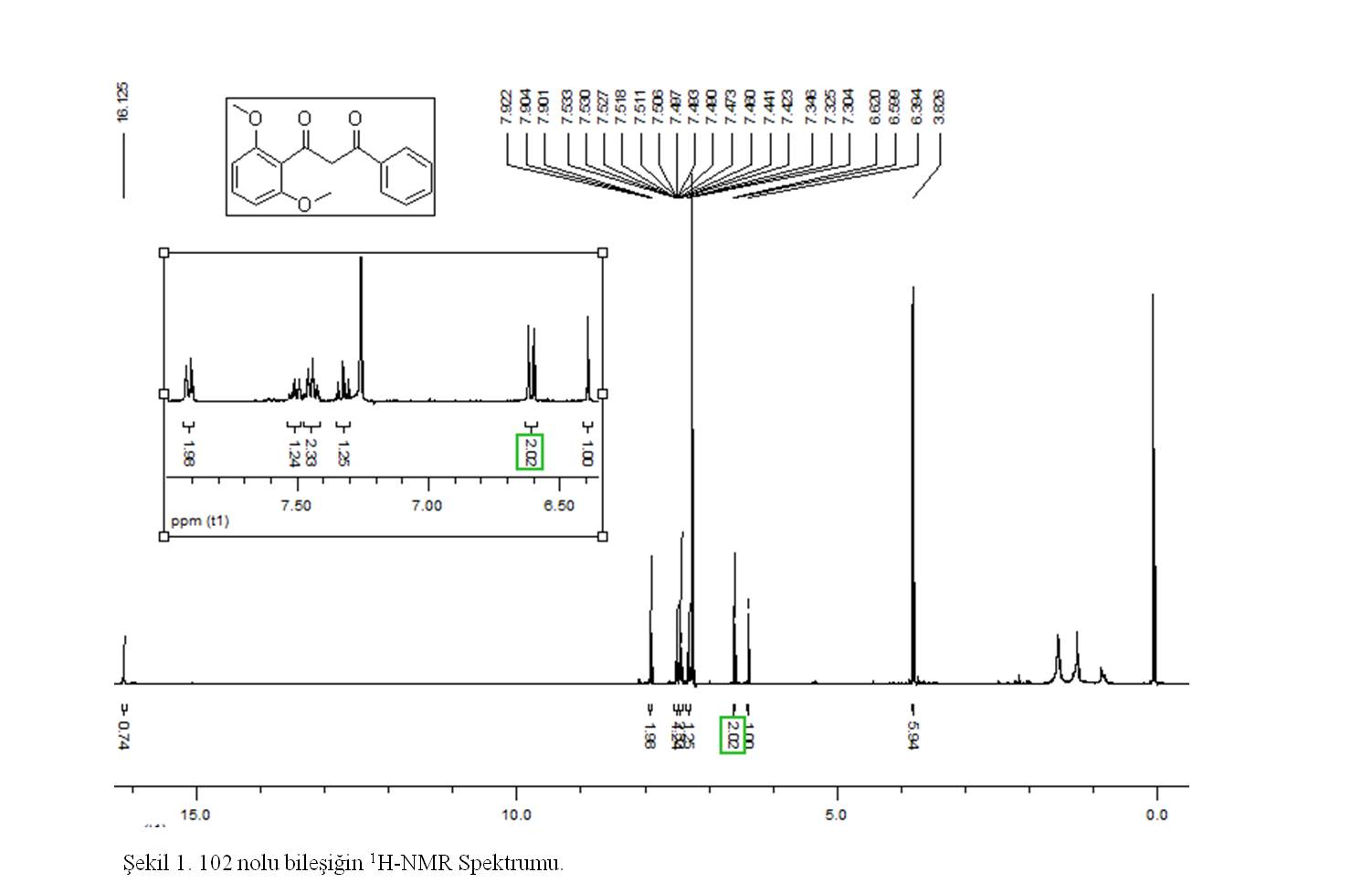
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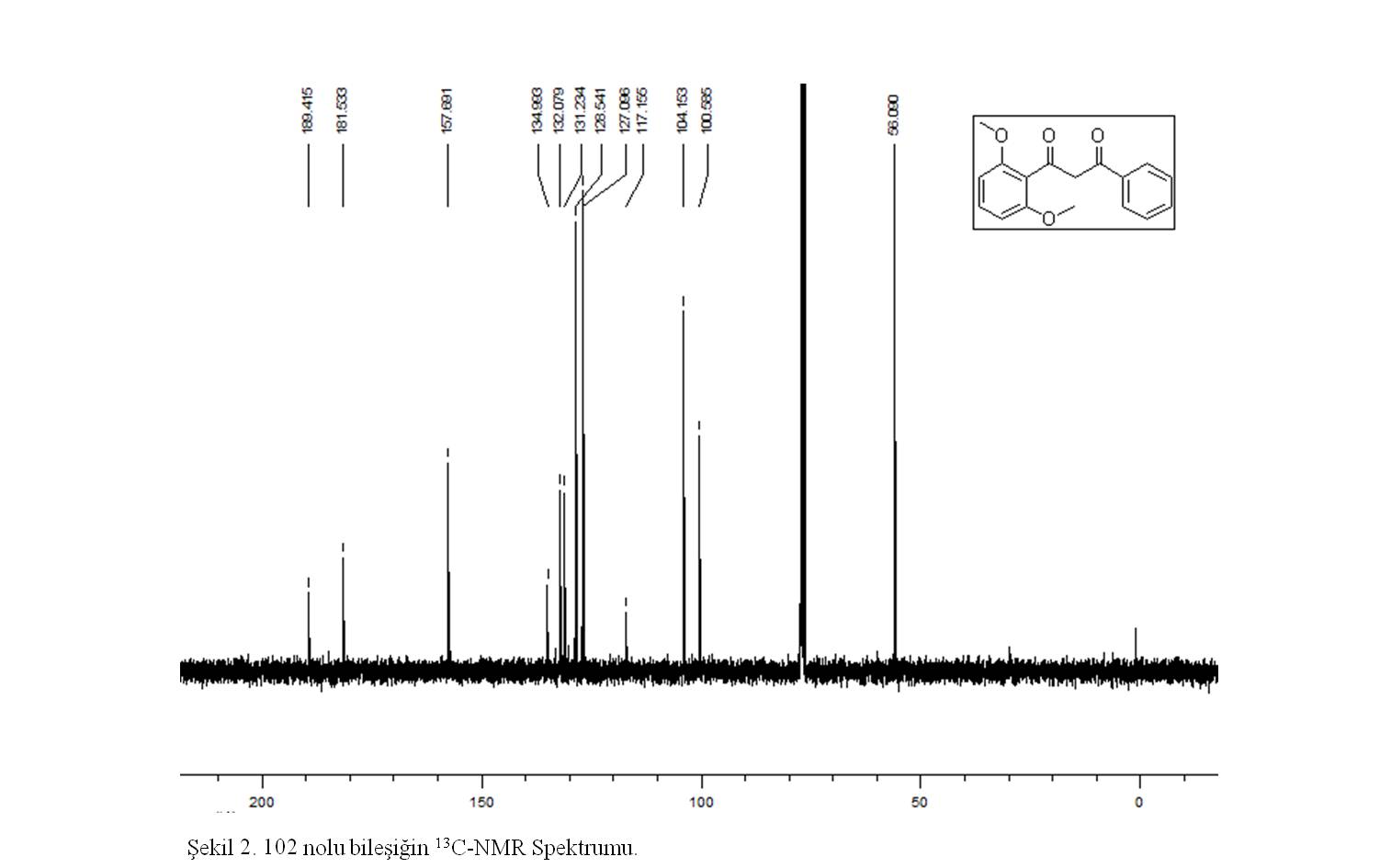
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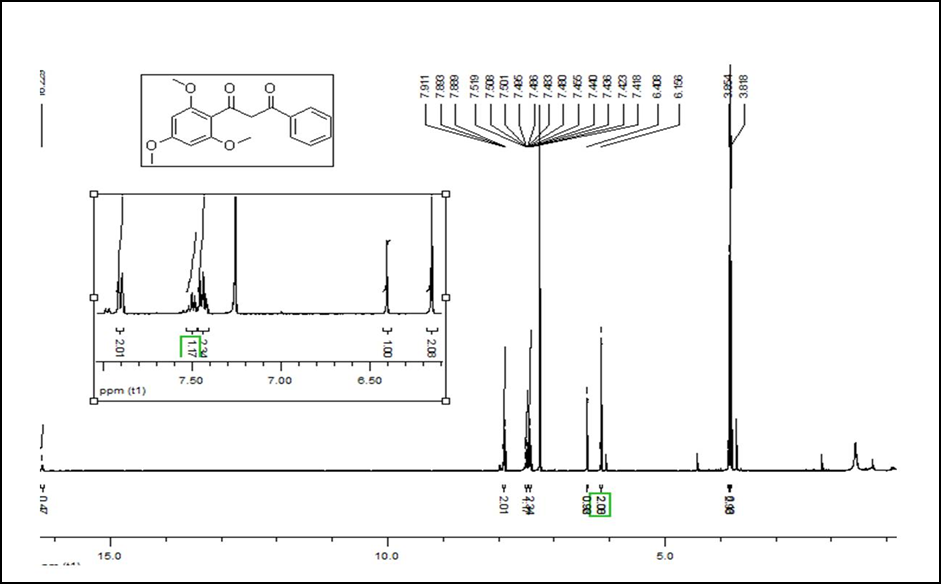
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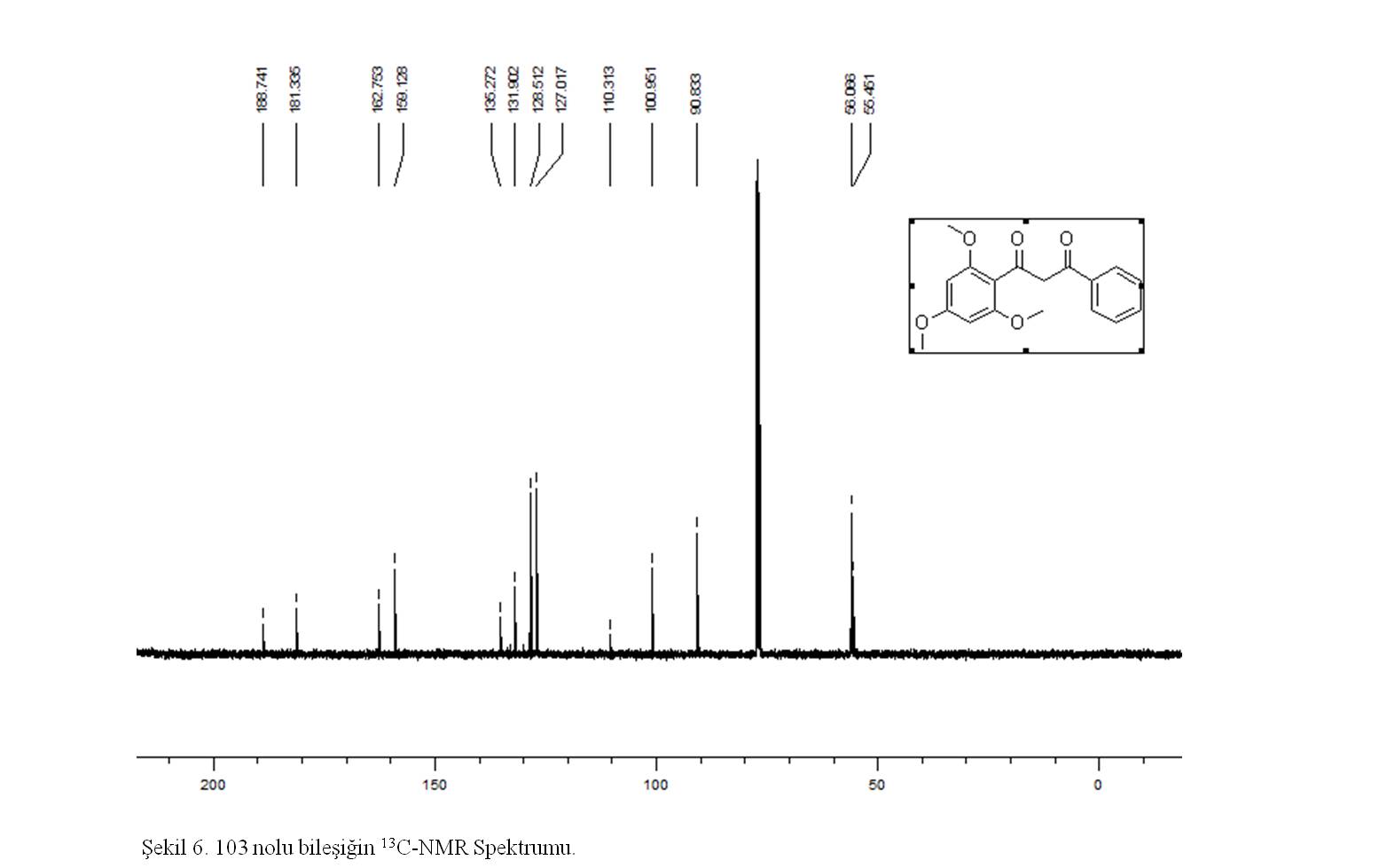
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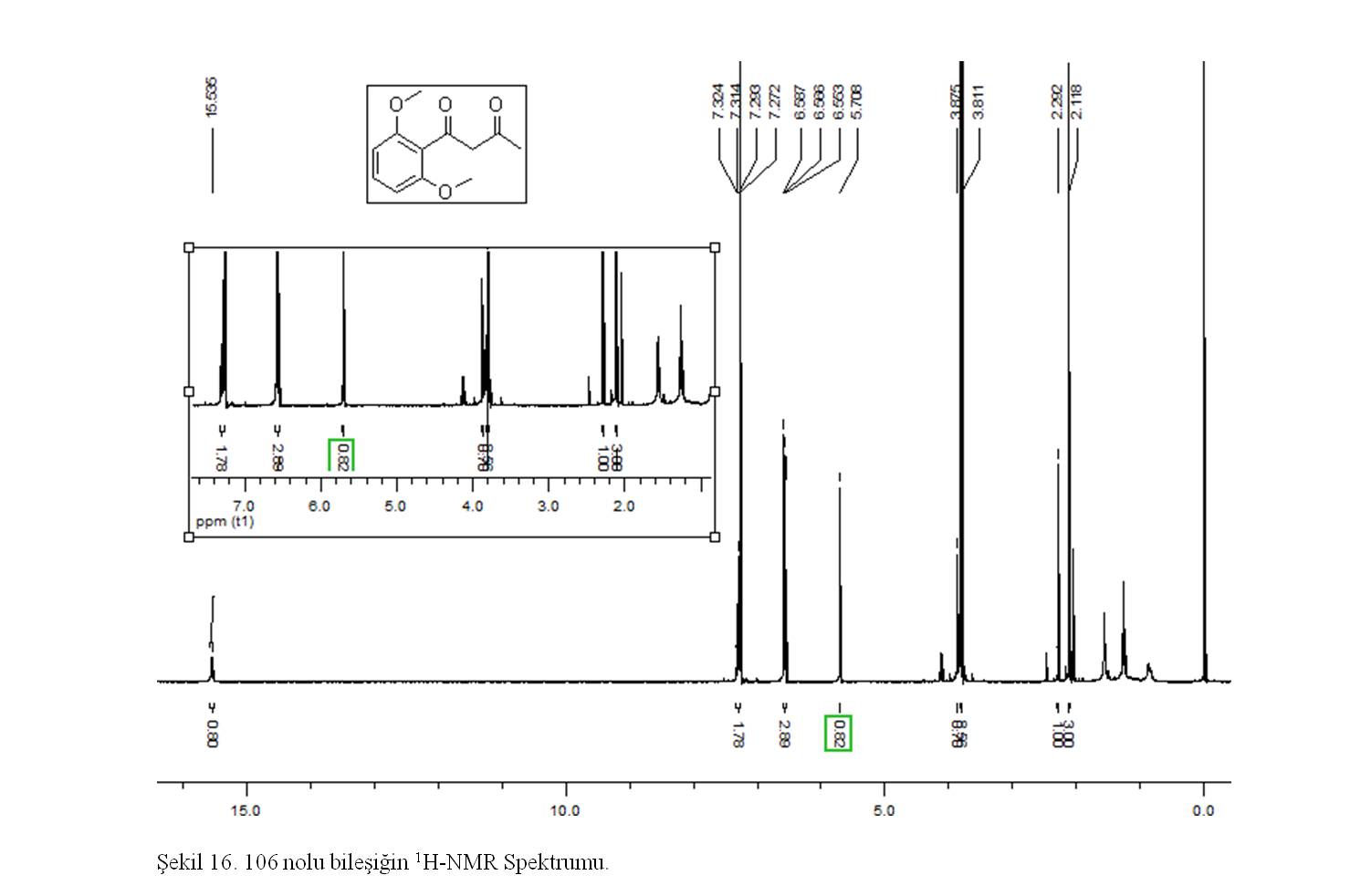
**Fig. S1.** 1H NMR (400 MHz, CDCl3) spectrum of **1.**

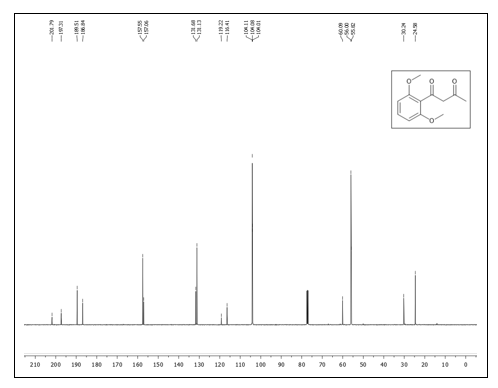


**Fig. S2**. 13C NMR (100 MHz, CDCl3) spectrum of **1.**

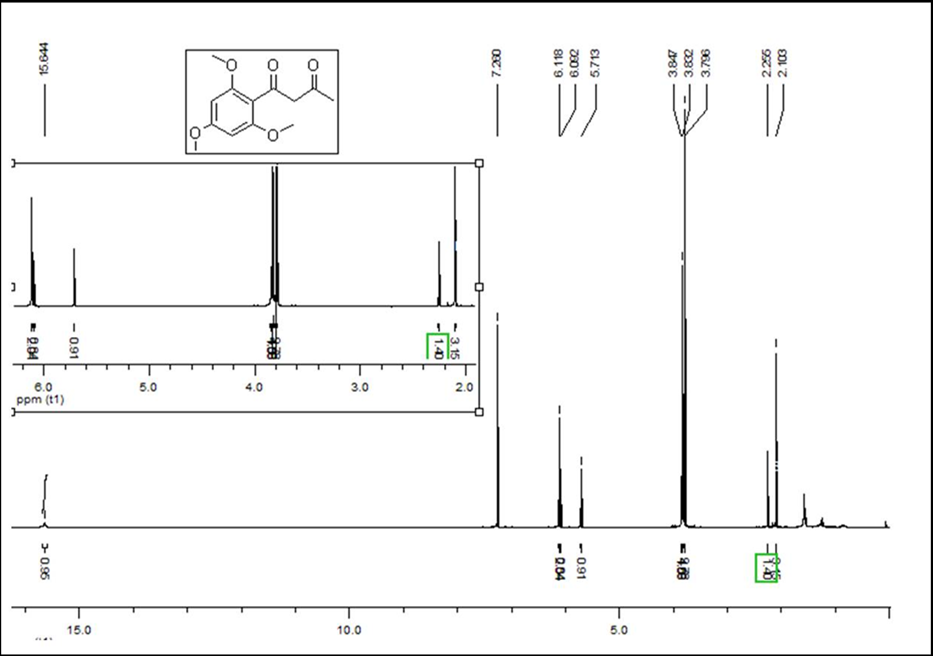
 **Fig. S3.** 1H NMR (400 MHz, CDCl3) spectrum of **2.**

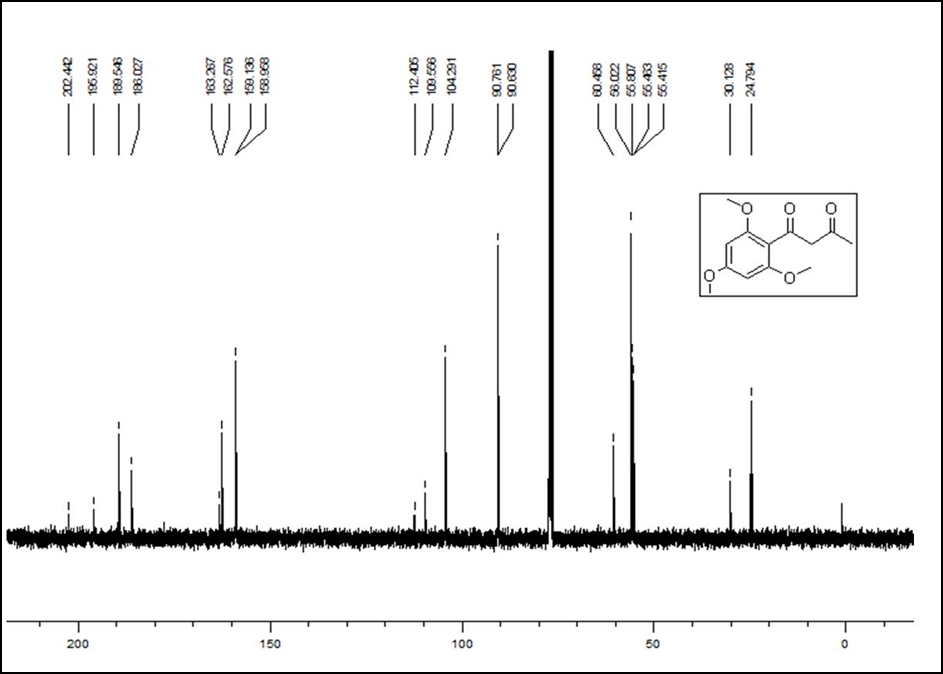
**Fig. S4**. 13C NMR (400 MHz, CDCl3) spectrum of **2**

**Fig. S5.** 1H NMR (400 MHz, CDCl3) spectrum of **3.**

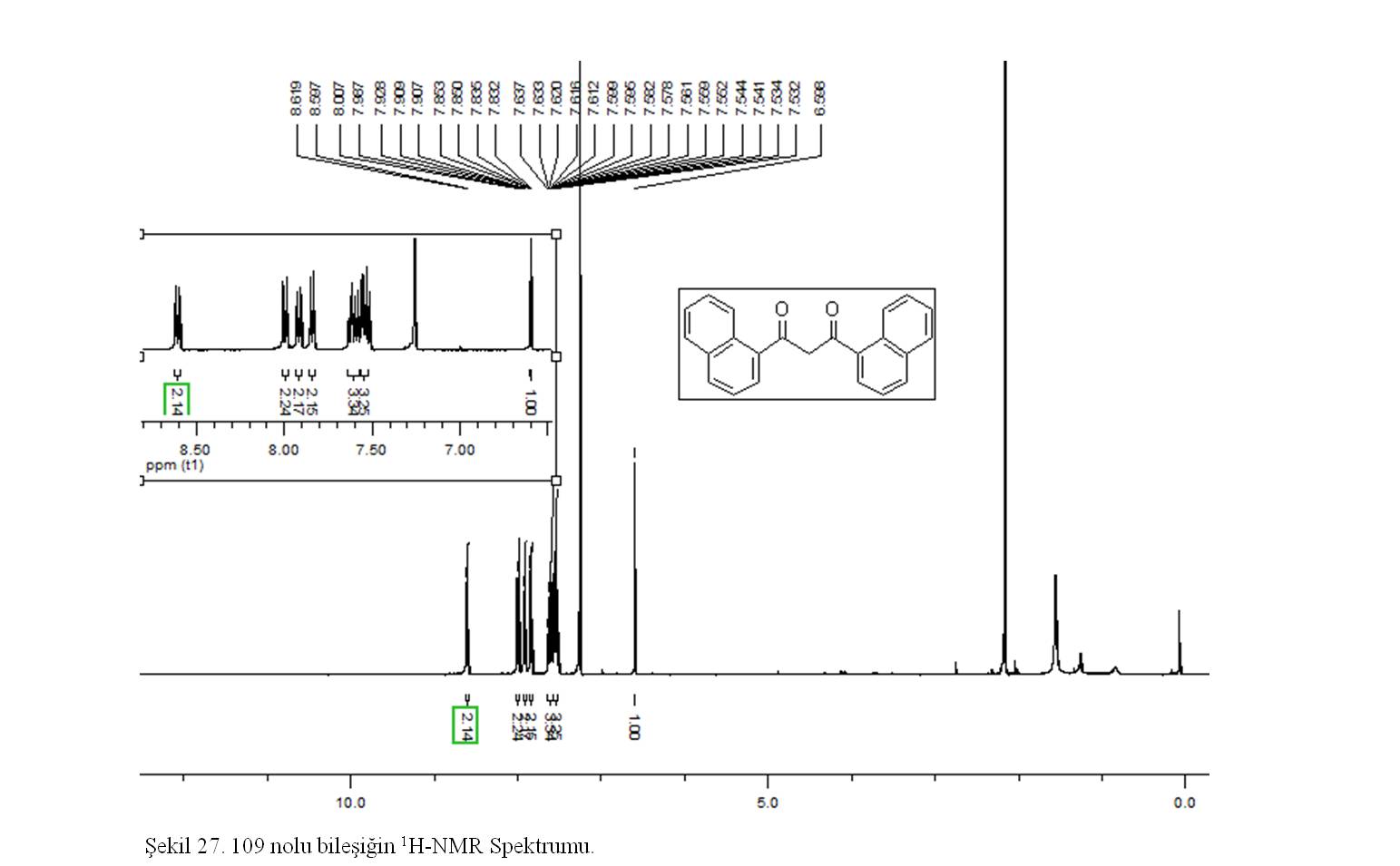


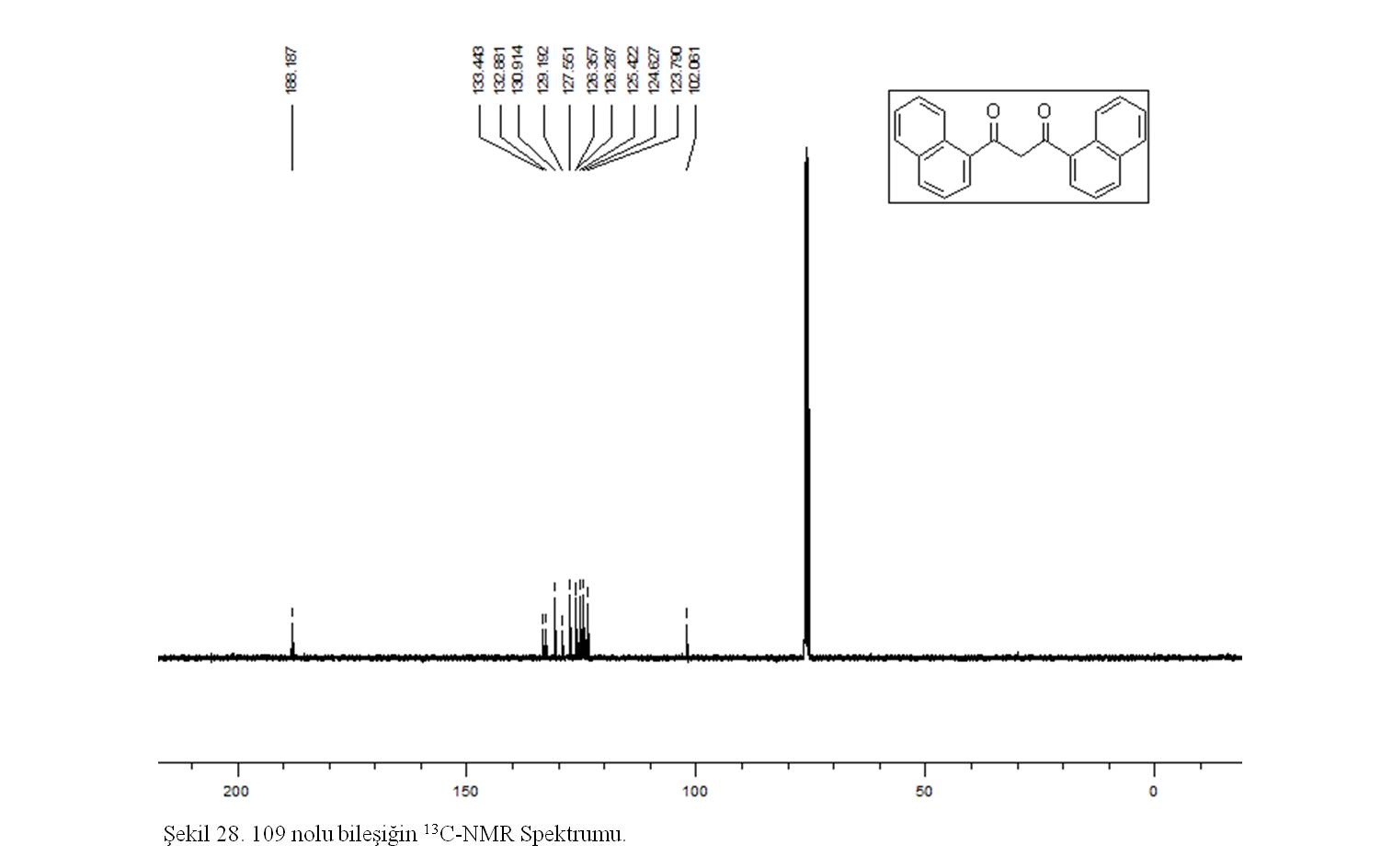
**Fig. S6**. 13C NMR (100 MHz, CDCl3) spectrum of **3.**

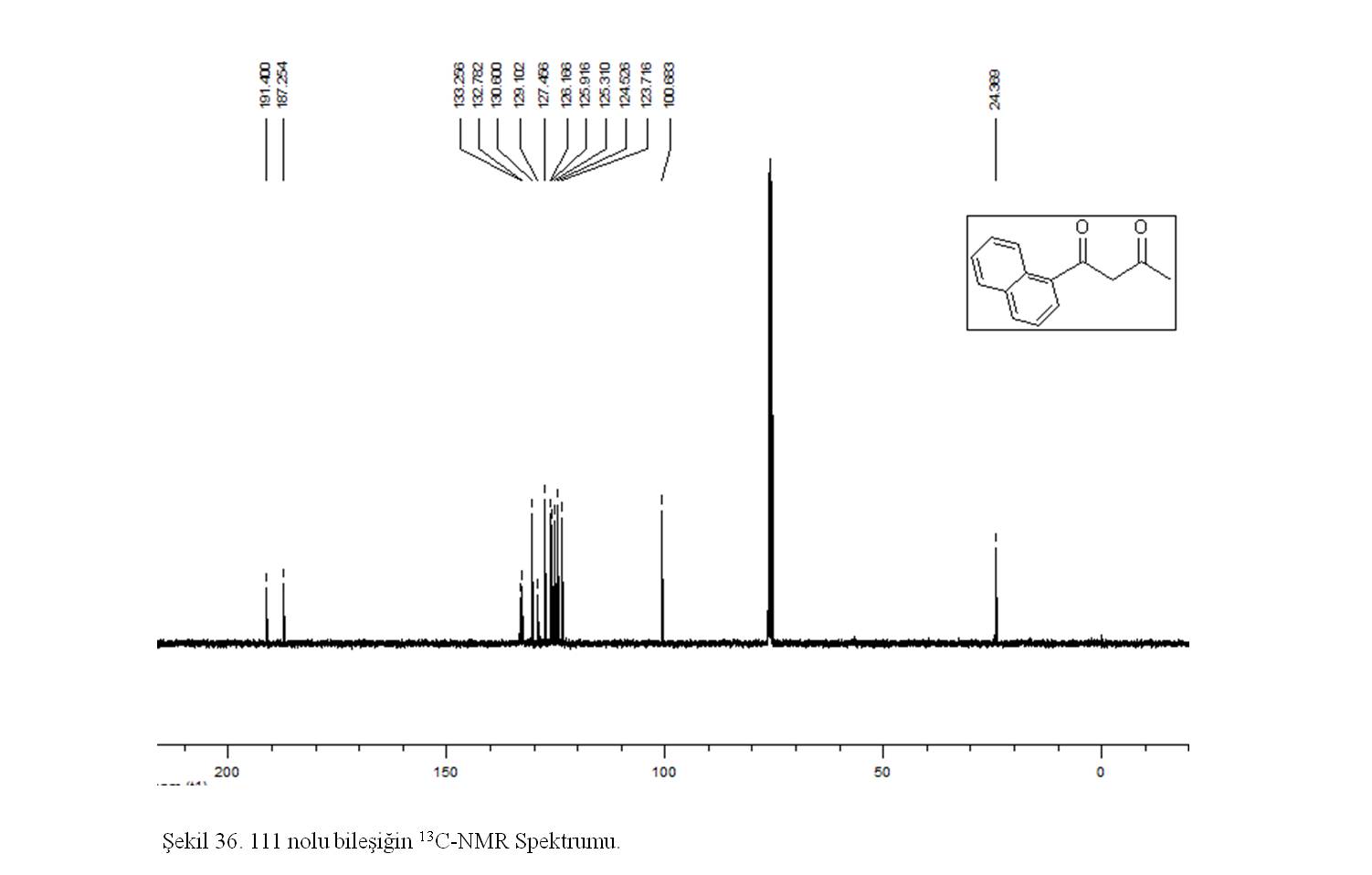
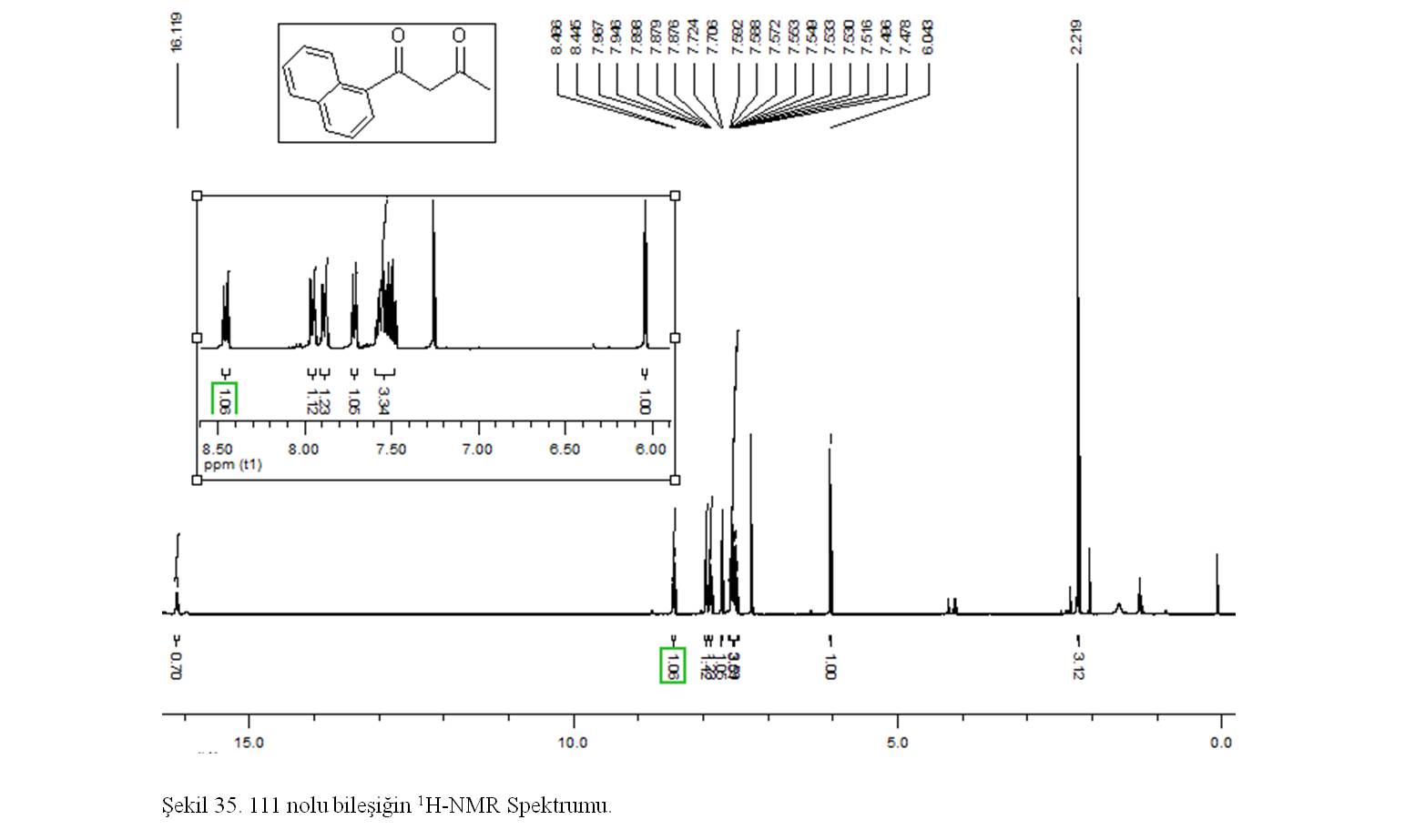
**Fig. S7.** 1H NMR (400 MHz, CDCl3) spectrum of **4.**



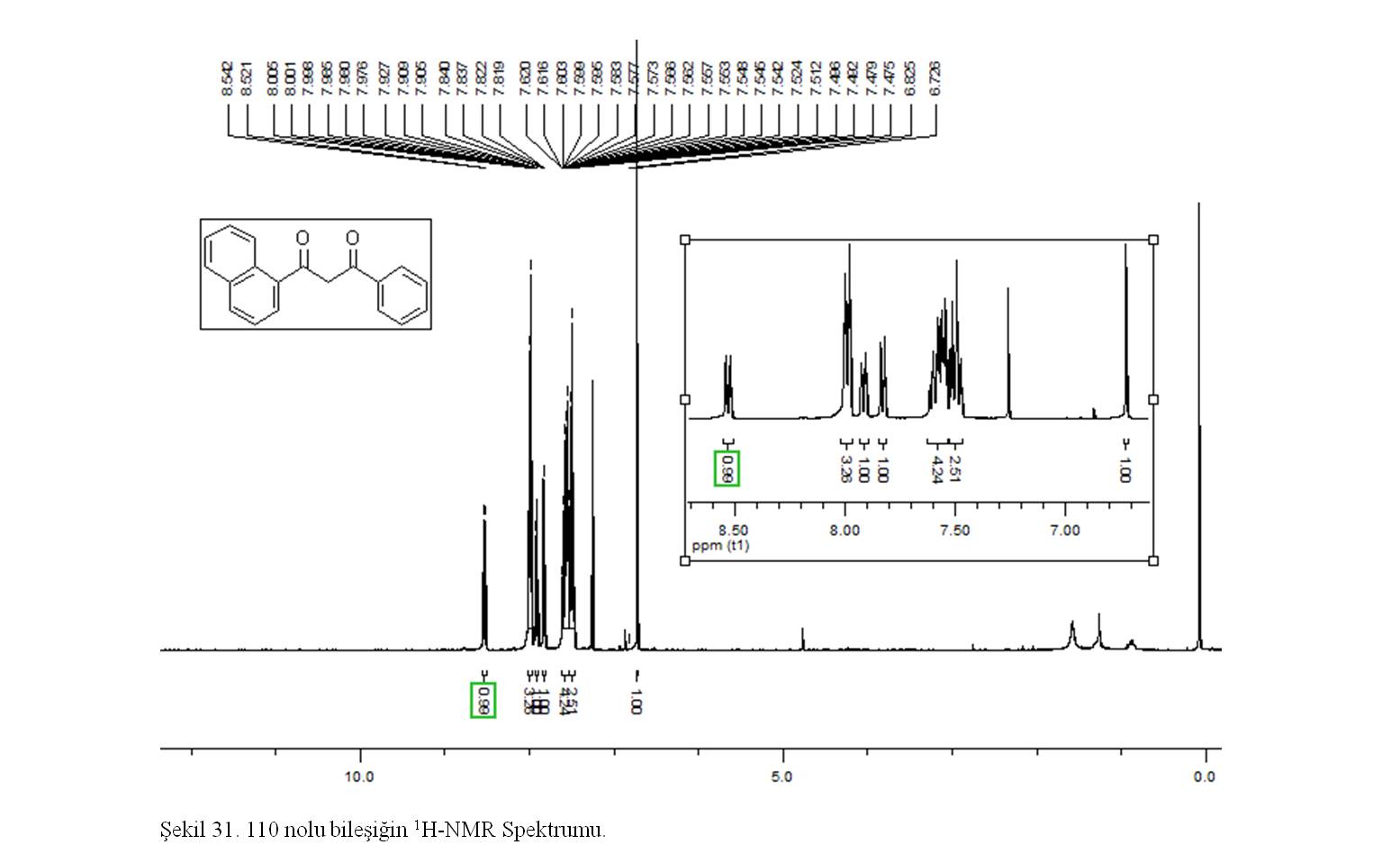
**Fig. S8**. 13C NMR (100 MHz, CDCl3) spectrum of **4.**

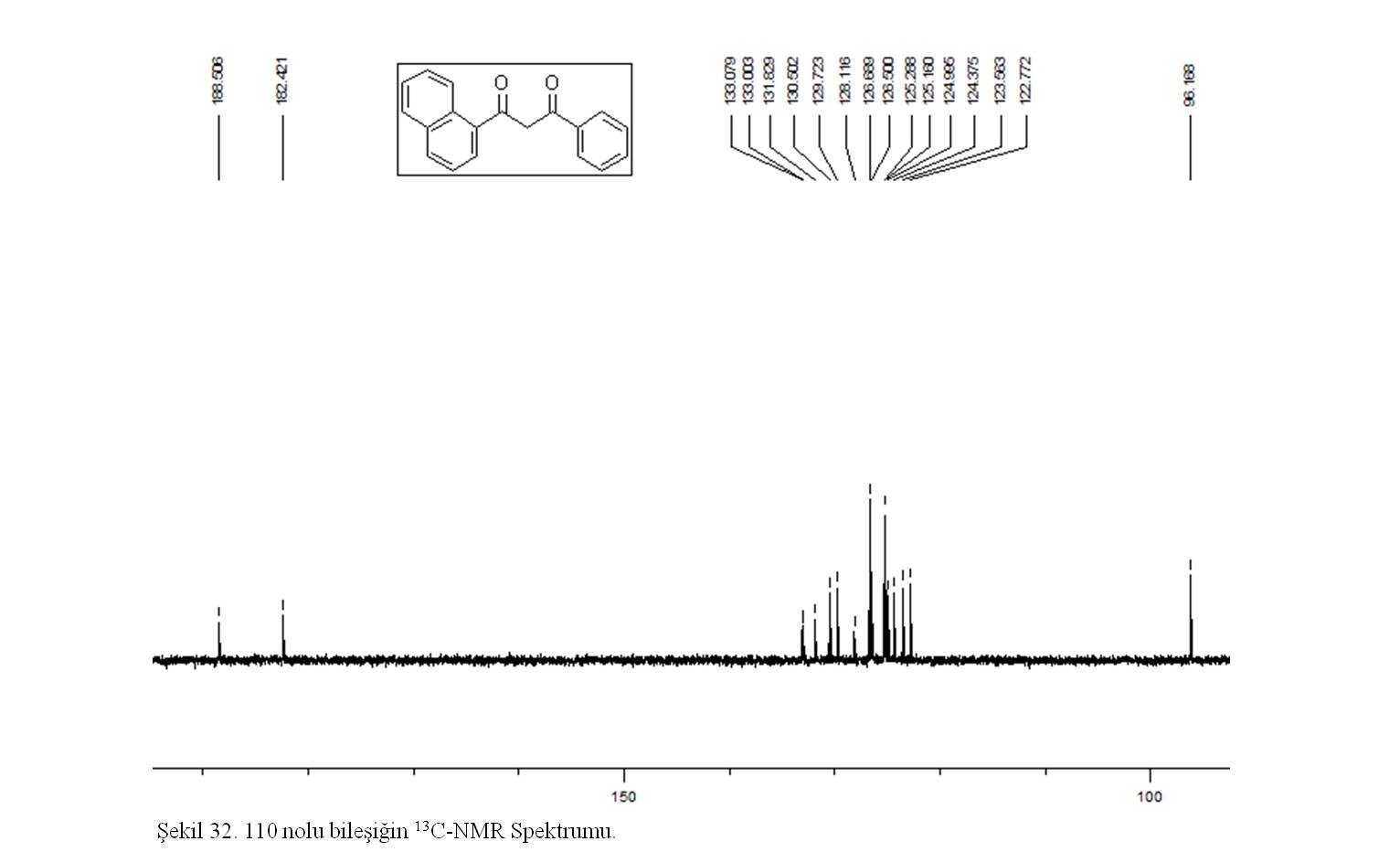
**Fig. S9.** 1H NMR (400 MHz, CDCl3) spectrum of **5.**

**Fig. S10**. 13C NMR (100 MHz, CDCl3) spectrum of **5.**

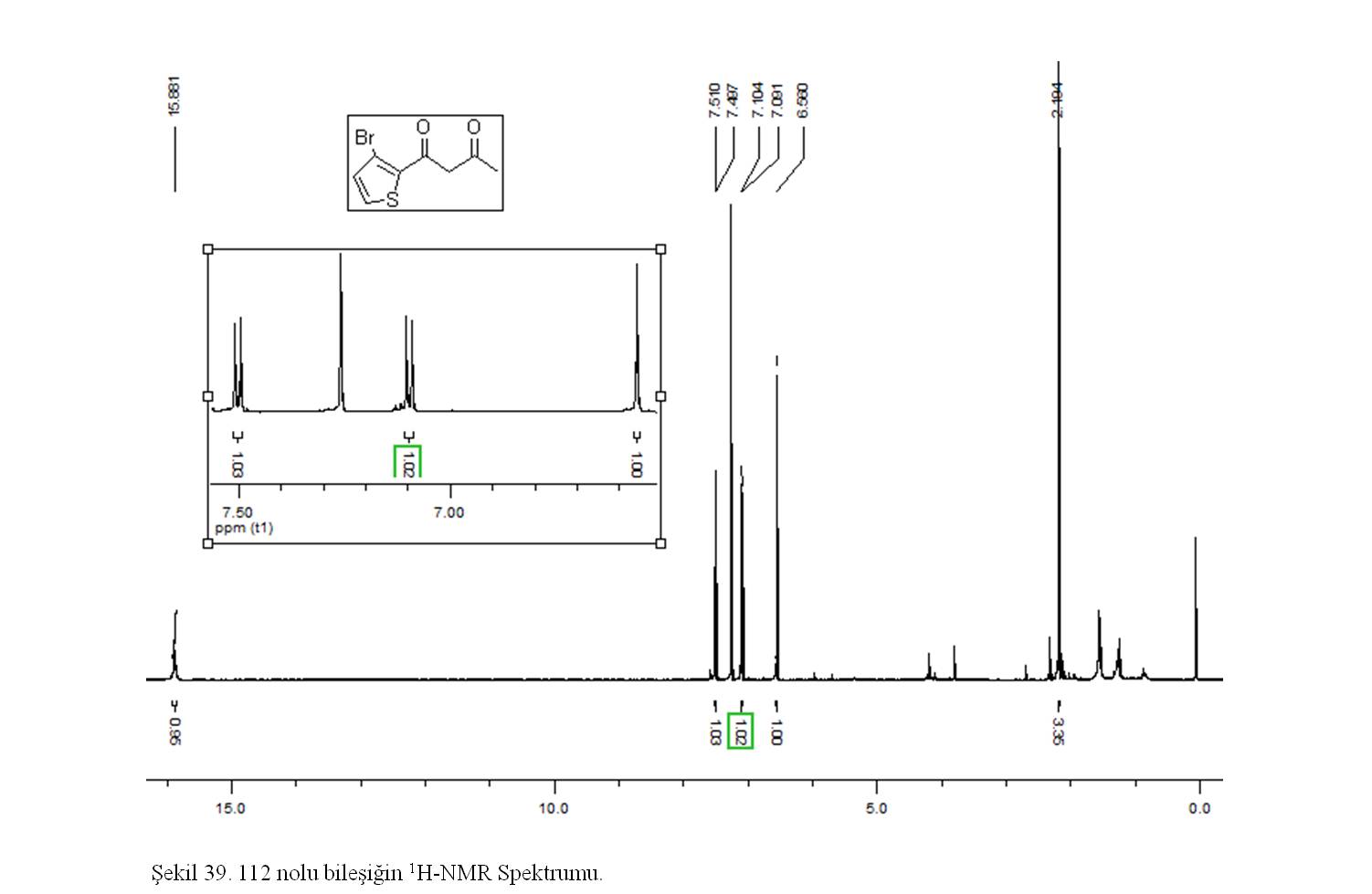
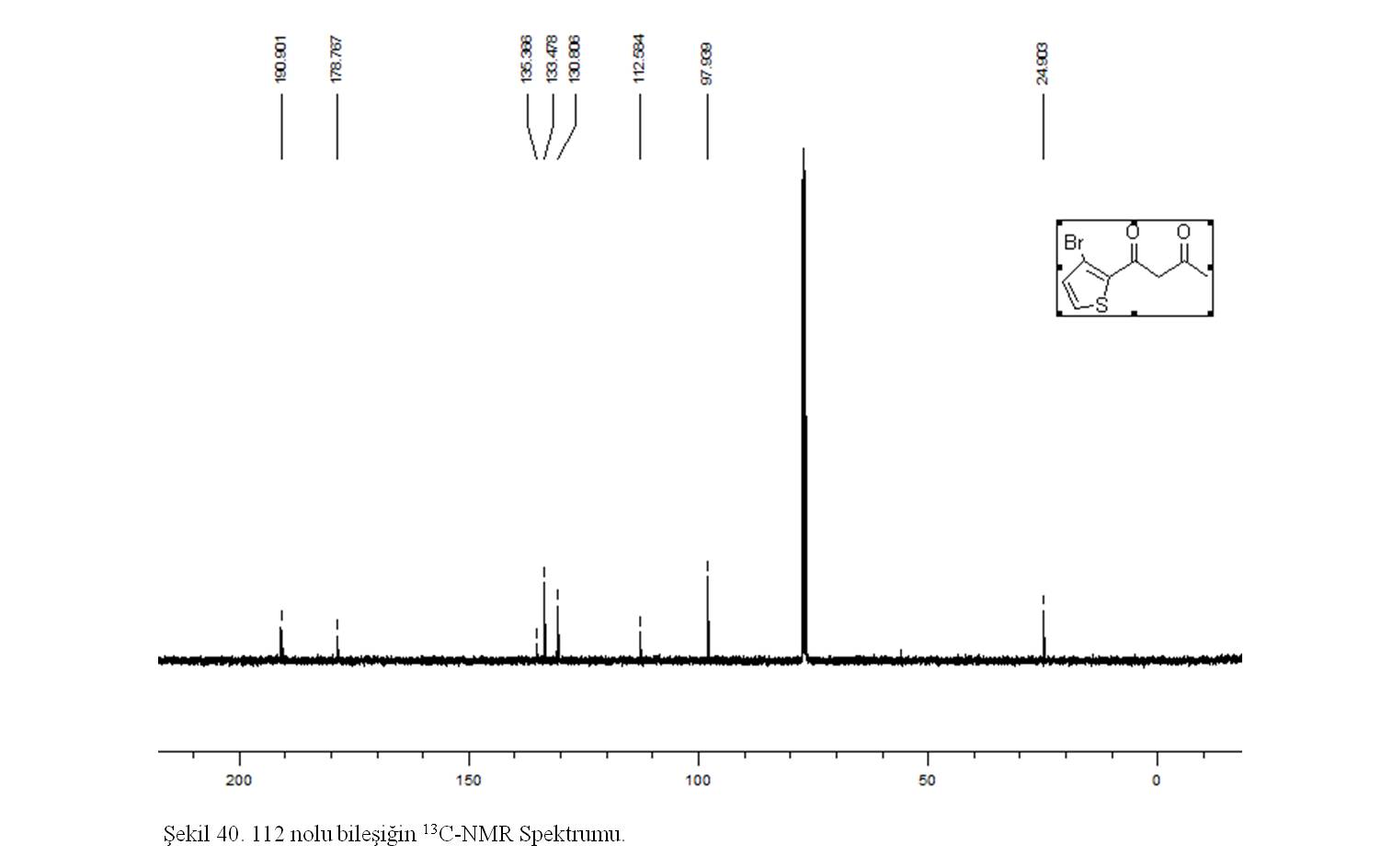
**Fig. S11.** 1H NMR (400 MHz, CDCl3) spectrum of **6.**

**Fig. S12**. 13C NMR (100 MHz, CDCl3) spectrum of **6.**

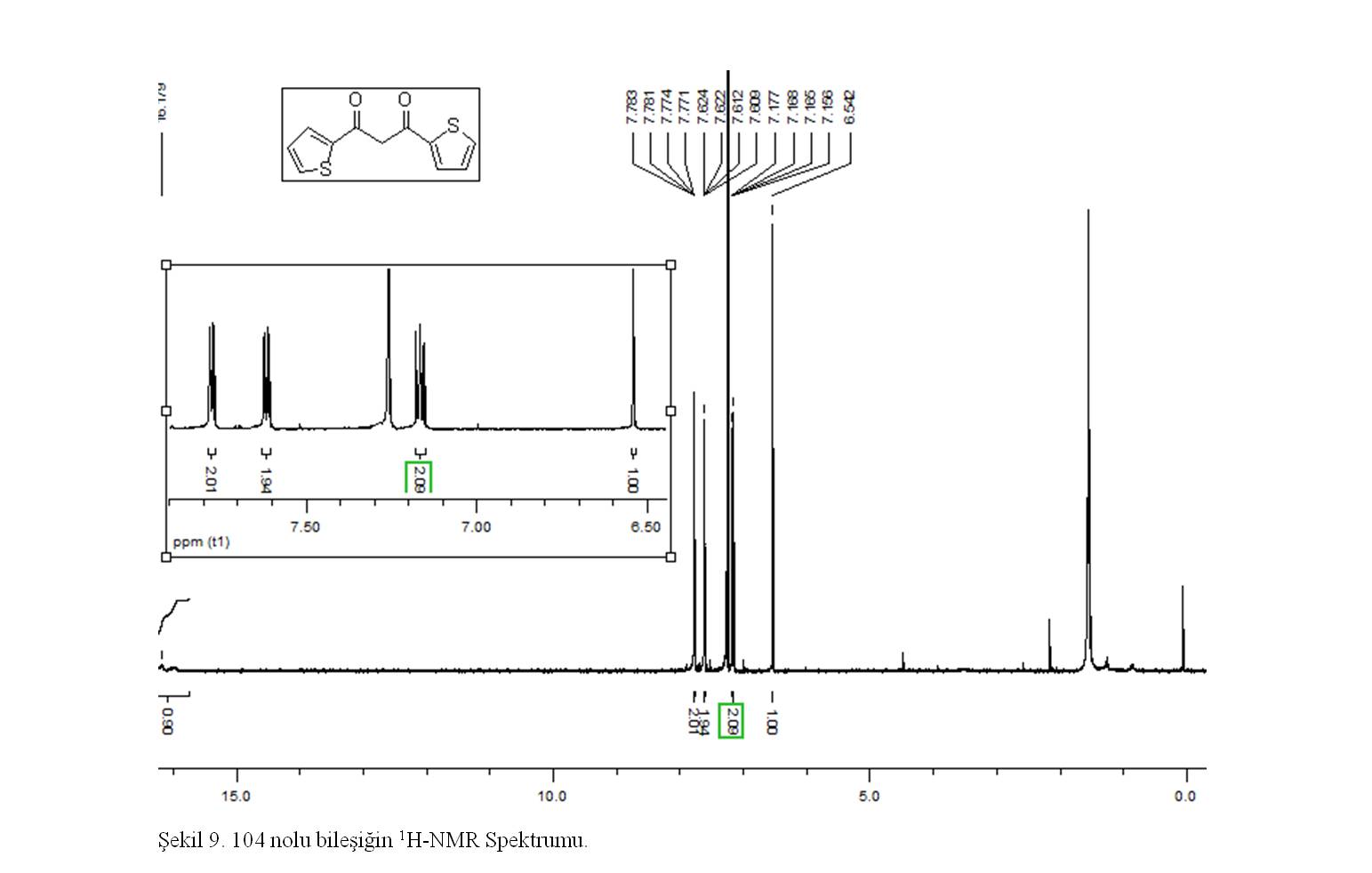
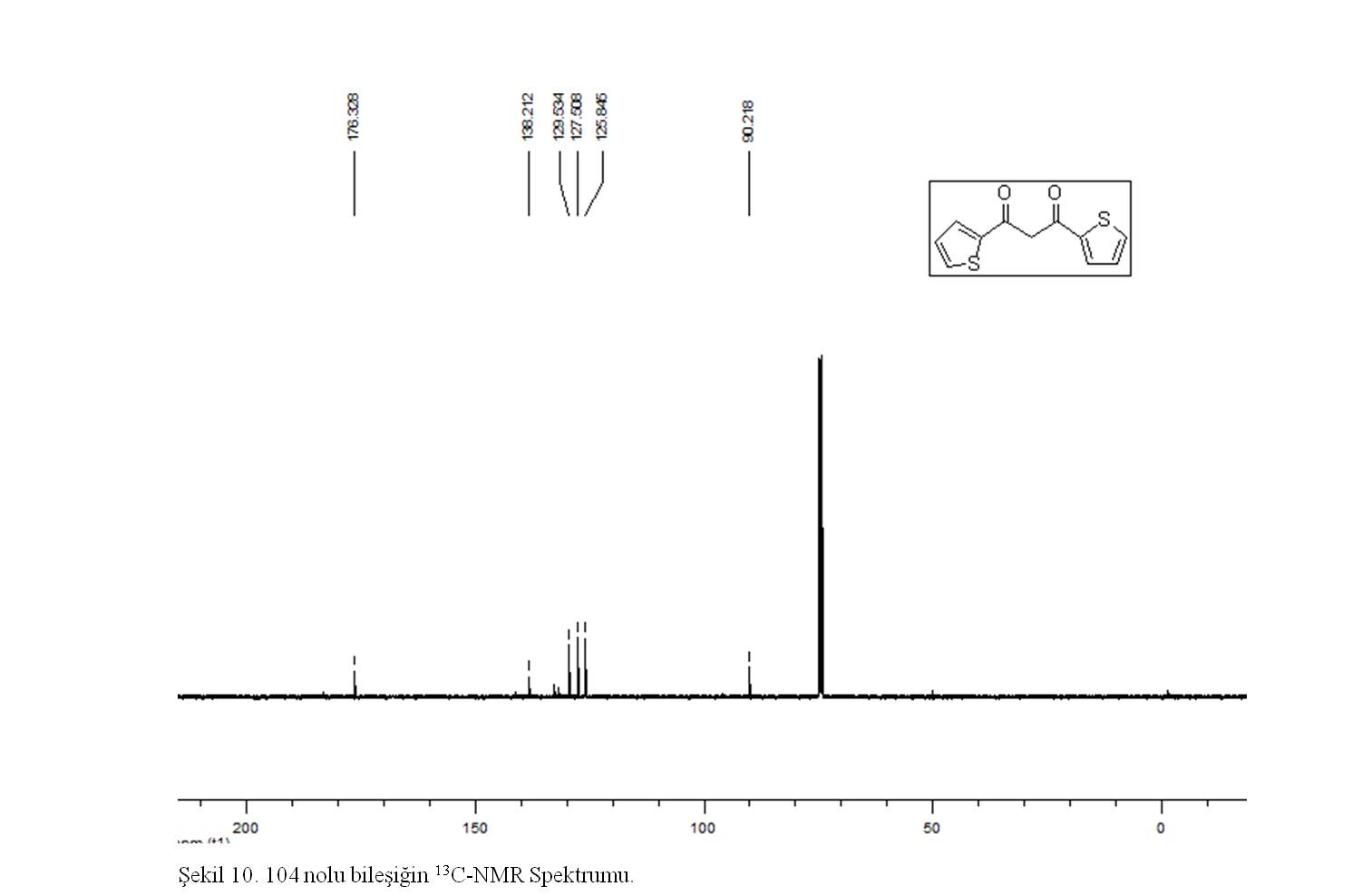
**Fig. S13.** 1H NMR (400 MHz, CDCl3) spectrum of **7.**



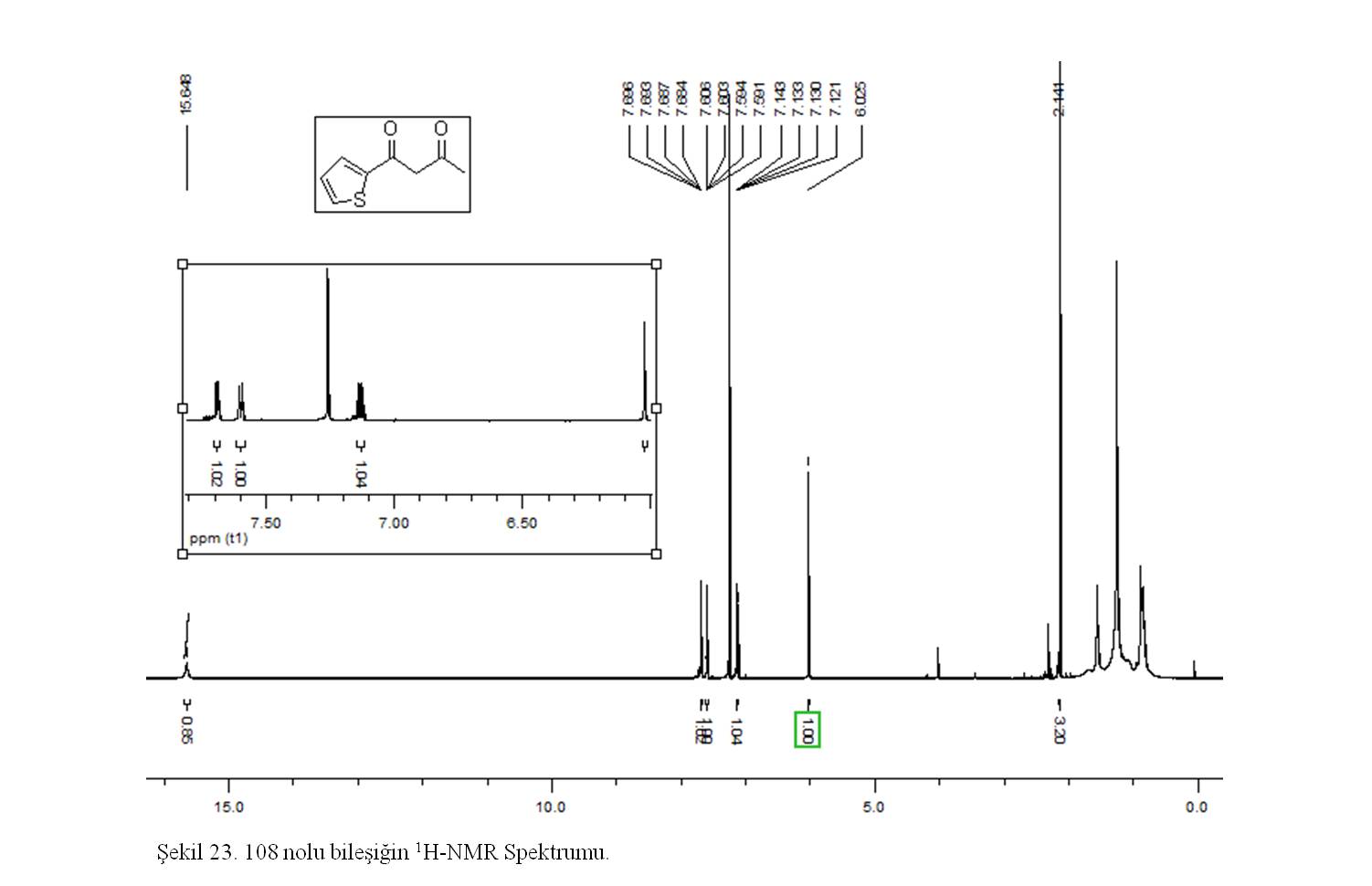
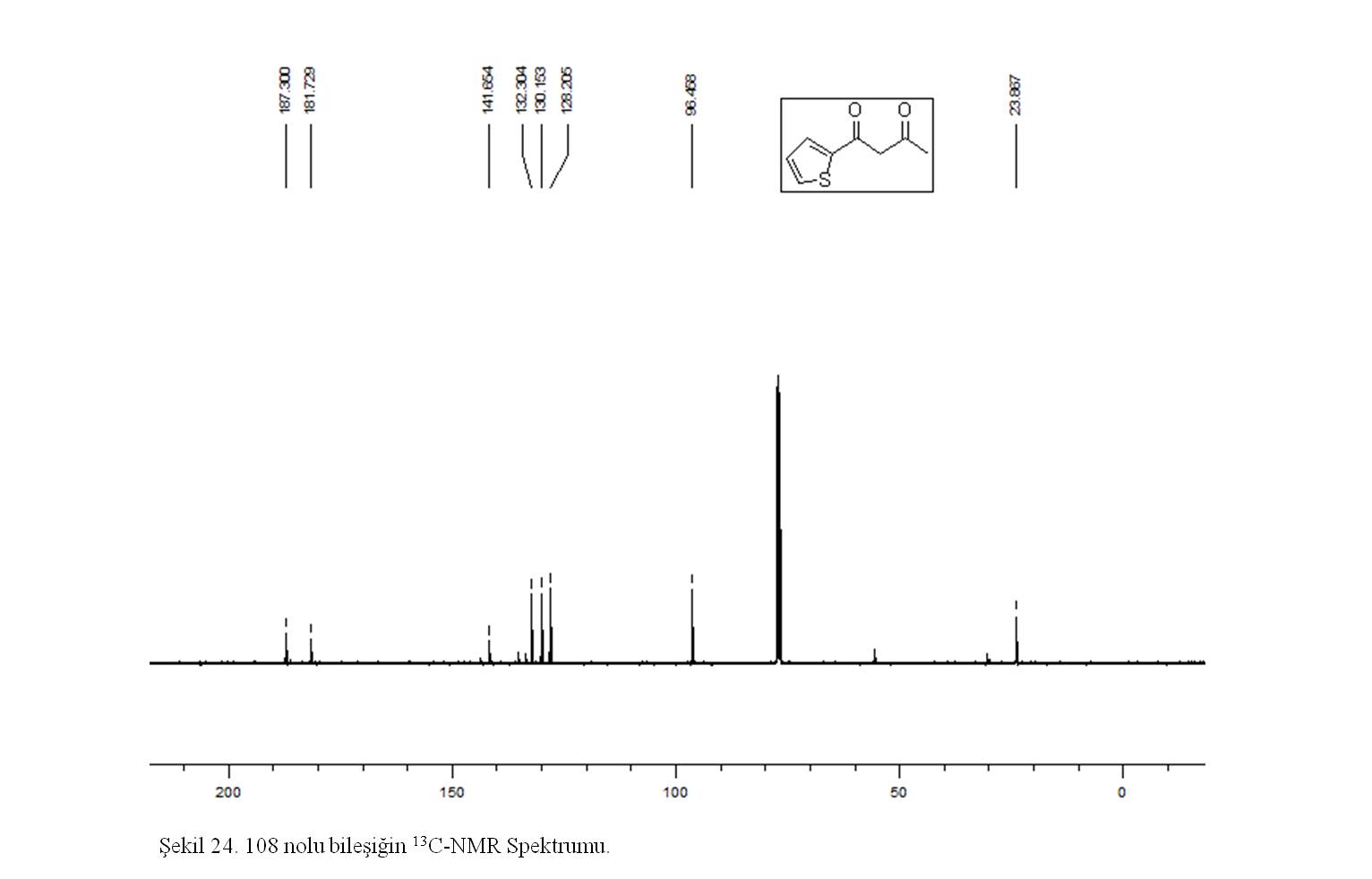
**Fig. S14**. 13C NMR (100 MHz, CDCl3) spectrum of **7.**

**Fig. S15.** 1H NMR (400 MHz, CDCl3) spectrum of **8.**

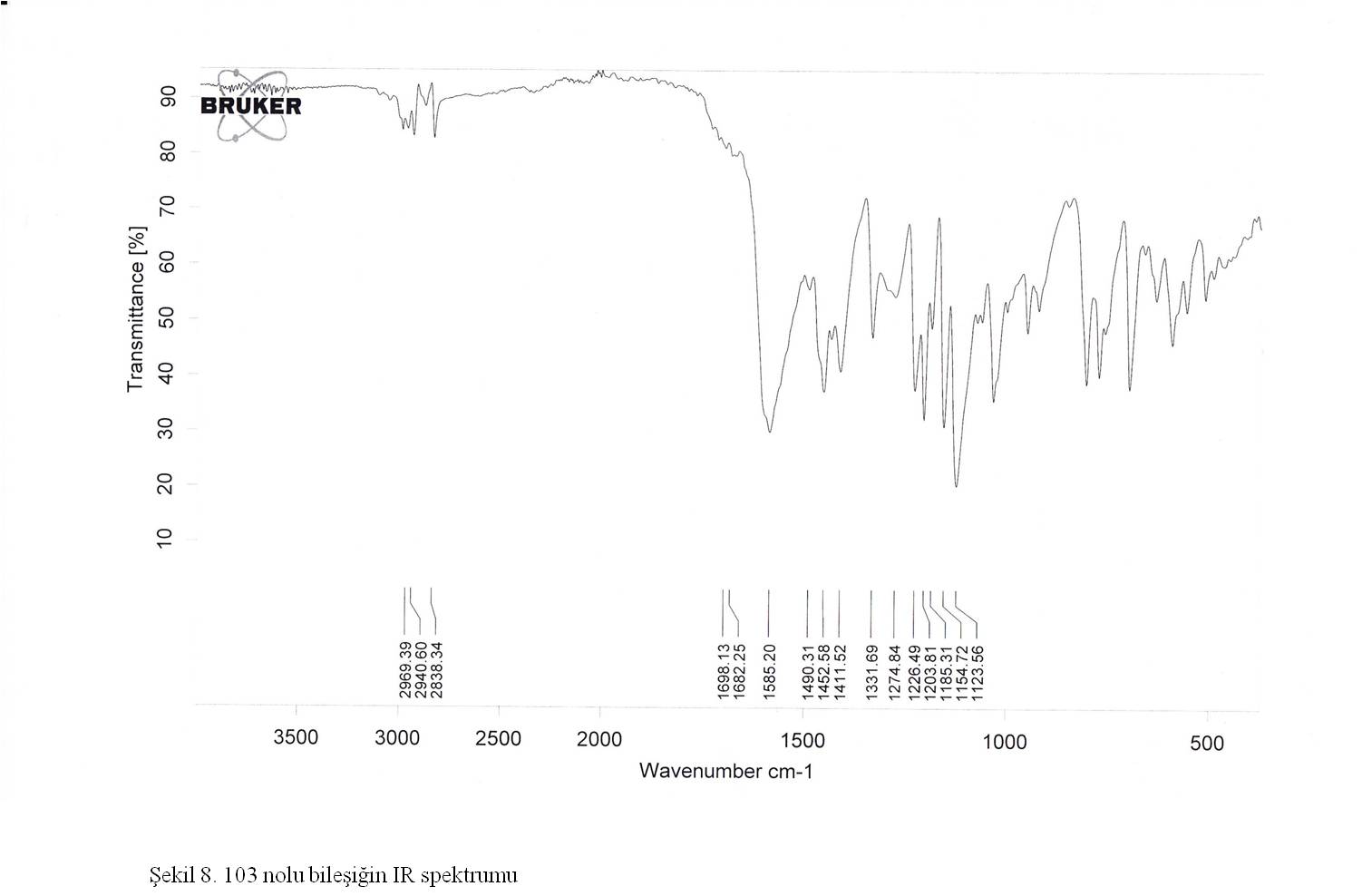
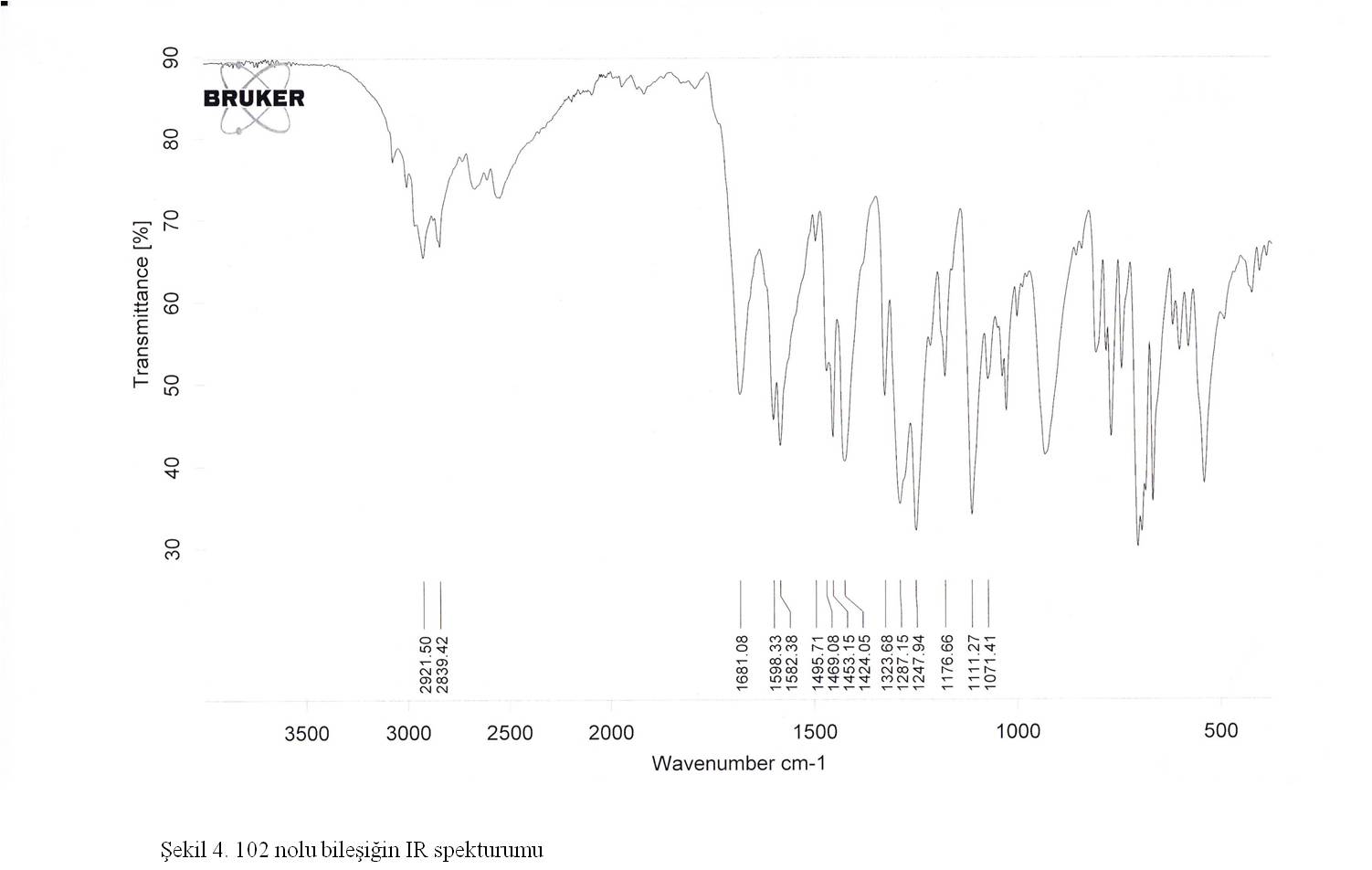
**Fig. S16**. 13C NMR (100 MHz, CDCl3) spectrum of **8**

**Fig. S17.** 1H NMR (400 MHz, CDCl3) spectrum of **9.**

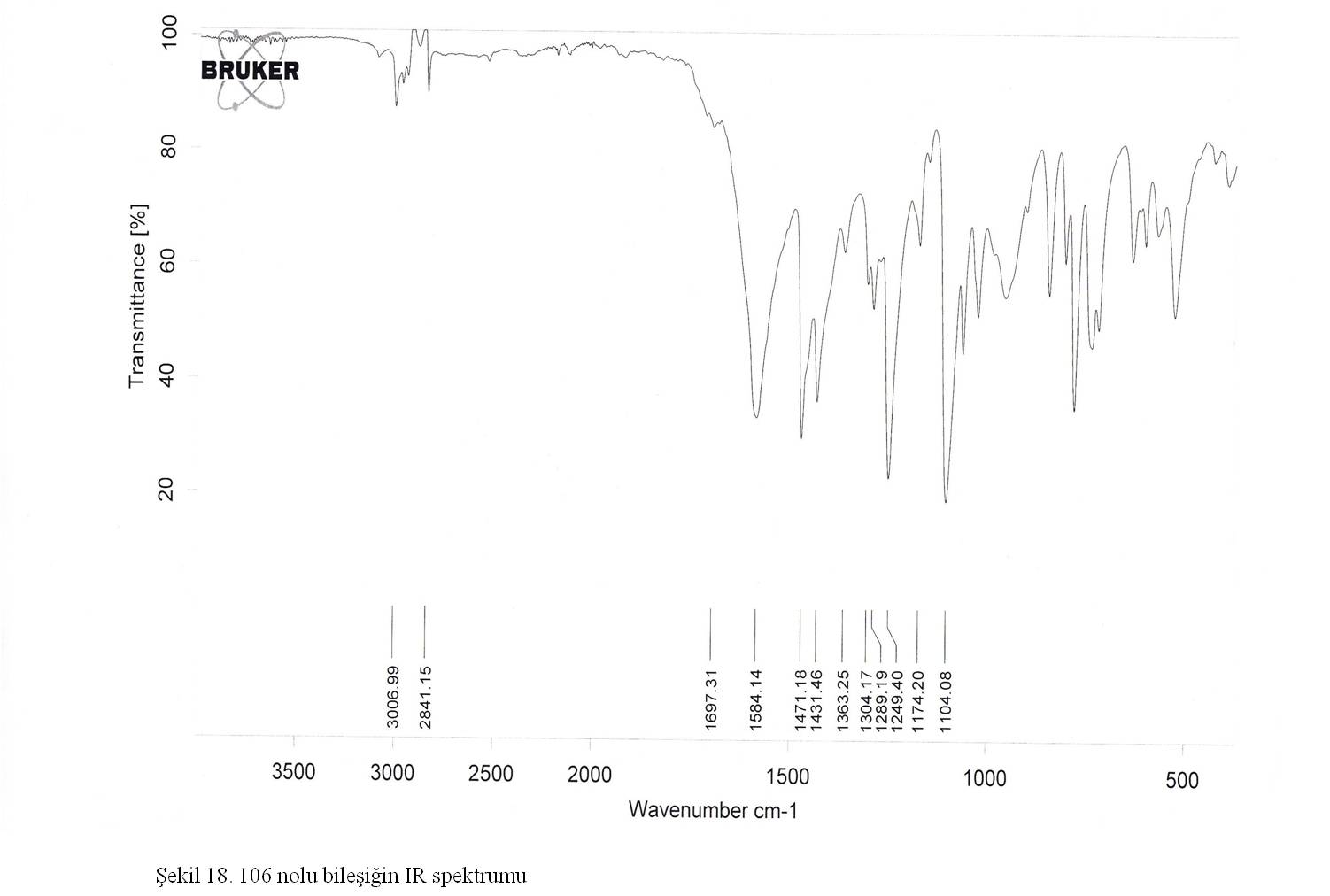
**Fig. S18**. 13C NMR (100 MHz, CDCl3) spectrum of **9.**

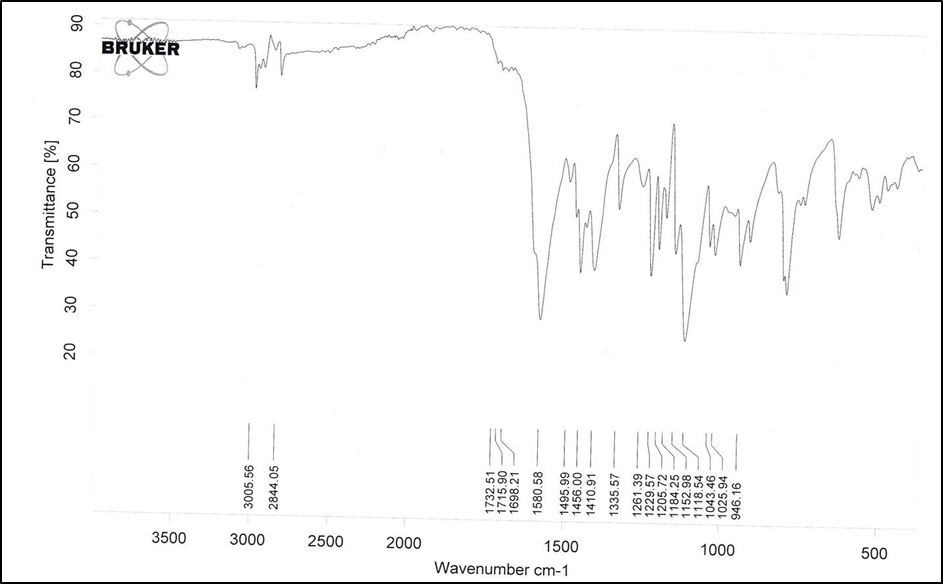
**Fig. S19.** 1H NMR (400 MHz, CDCl3) spectrum of **10.**

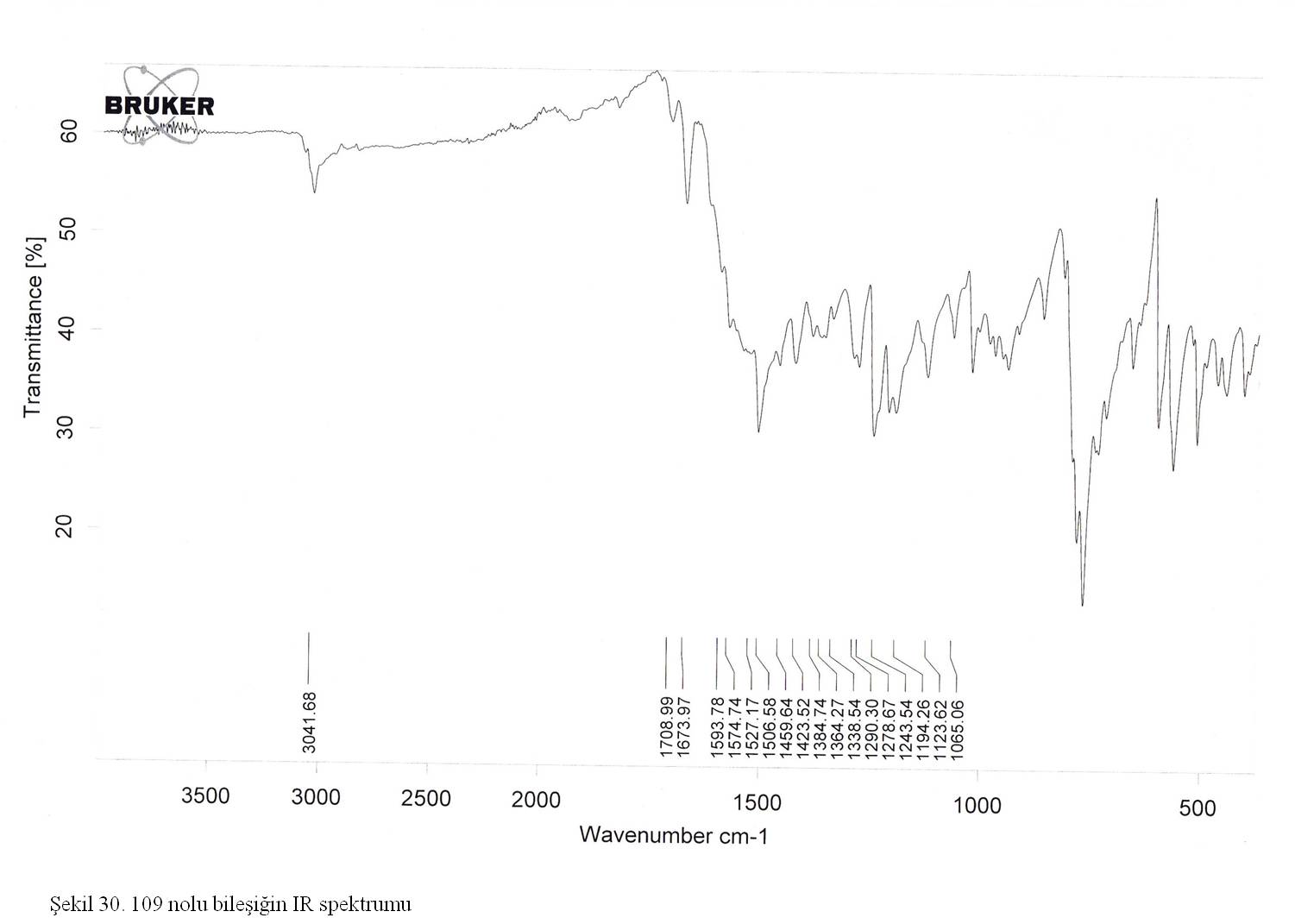
**Fig. S20**. 13C NMR (100 MHz, CDCl3) spectrum of **10**

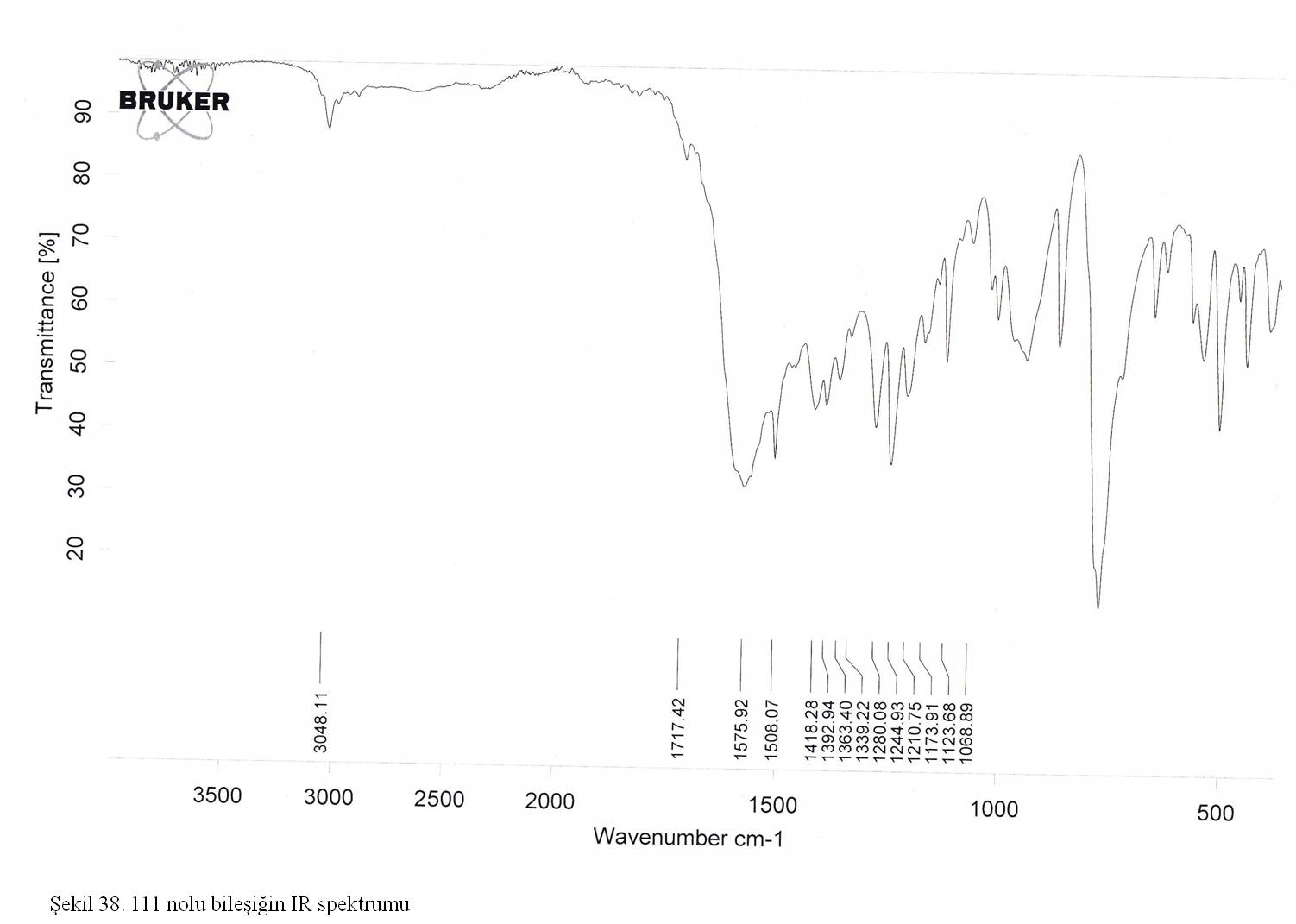
**Fig. S21.** IR (ATR, cm-1) spectrum of **1.**

**Fig. S22.** IR (ATR, cm-1) spectrum of **2.**

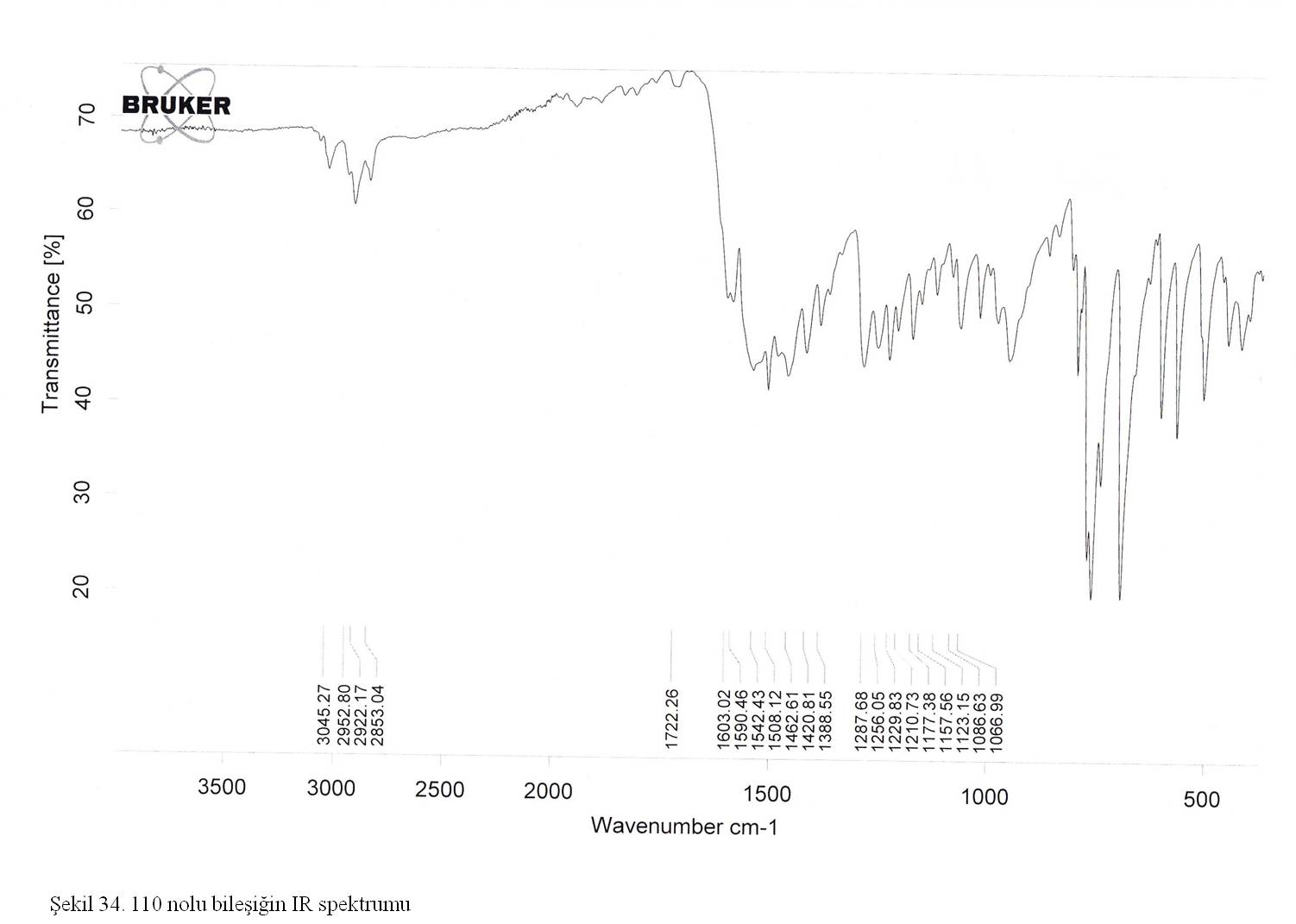
**Fig. S23.** IR (ATR, cm-1) spectrum of **3.**

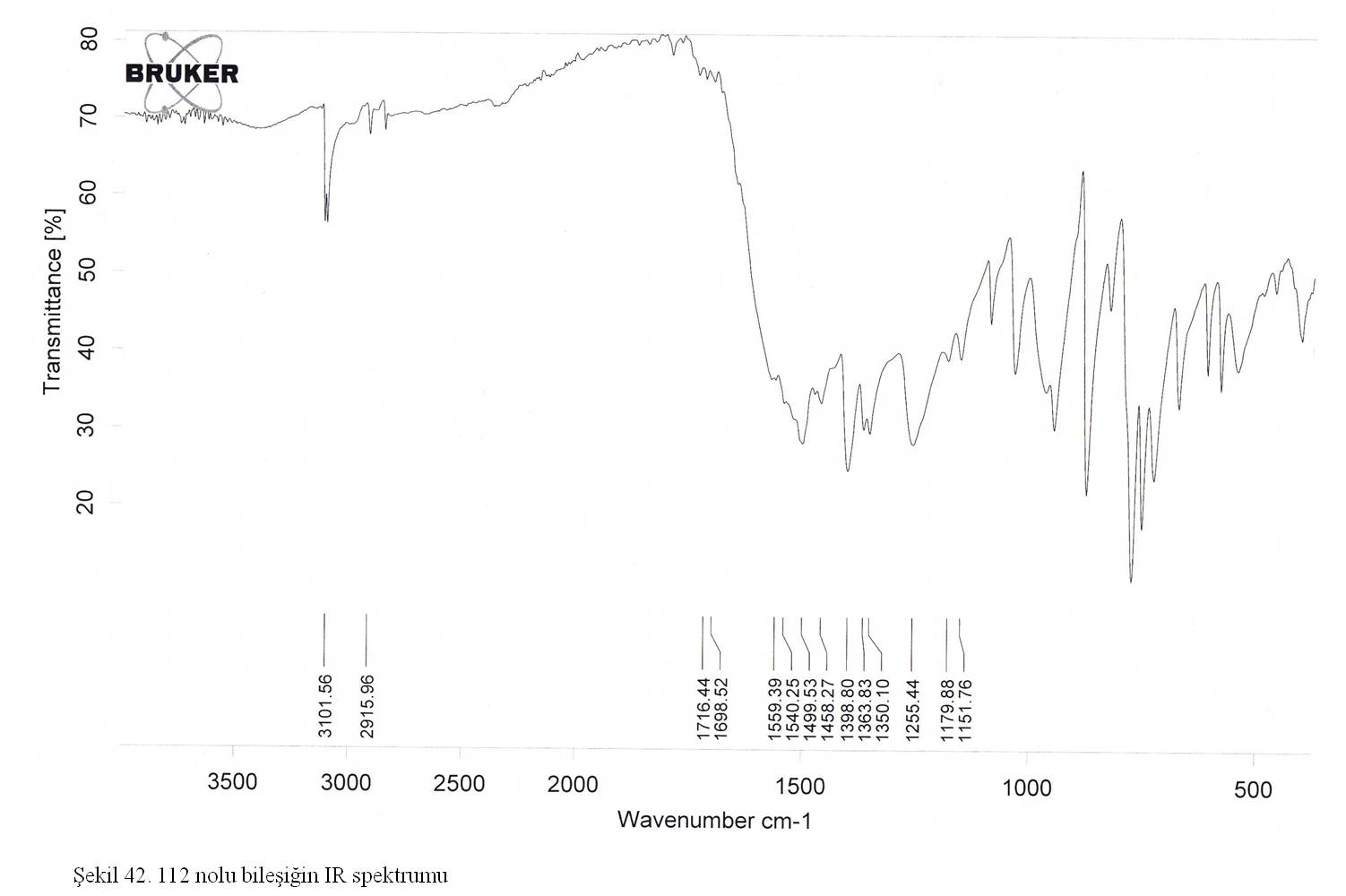
**Fig. S24.** IR (ATR, cm-1) spectrum of **4.**



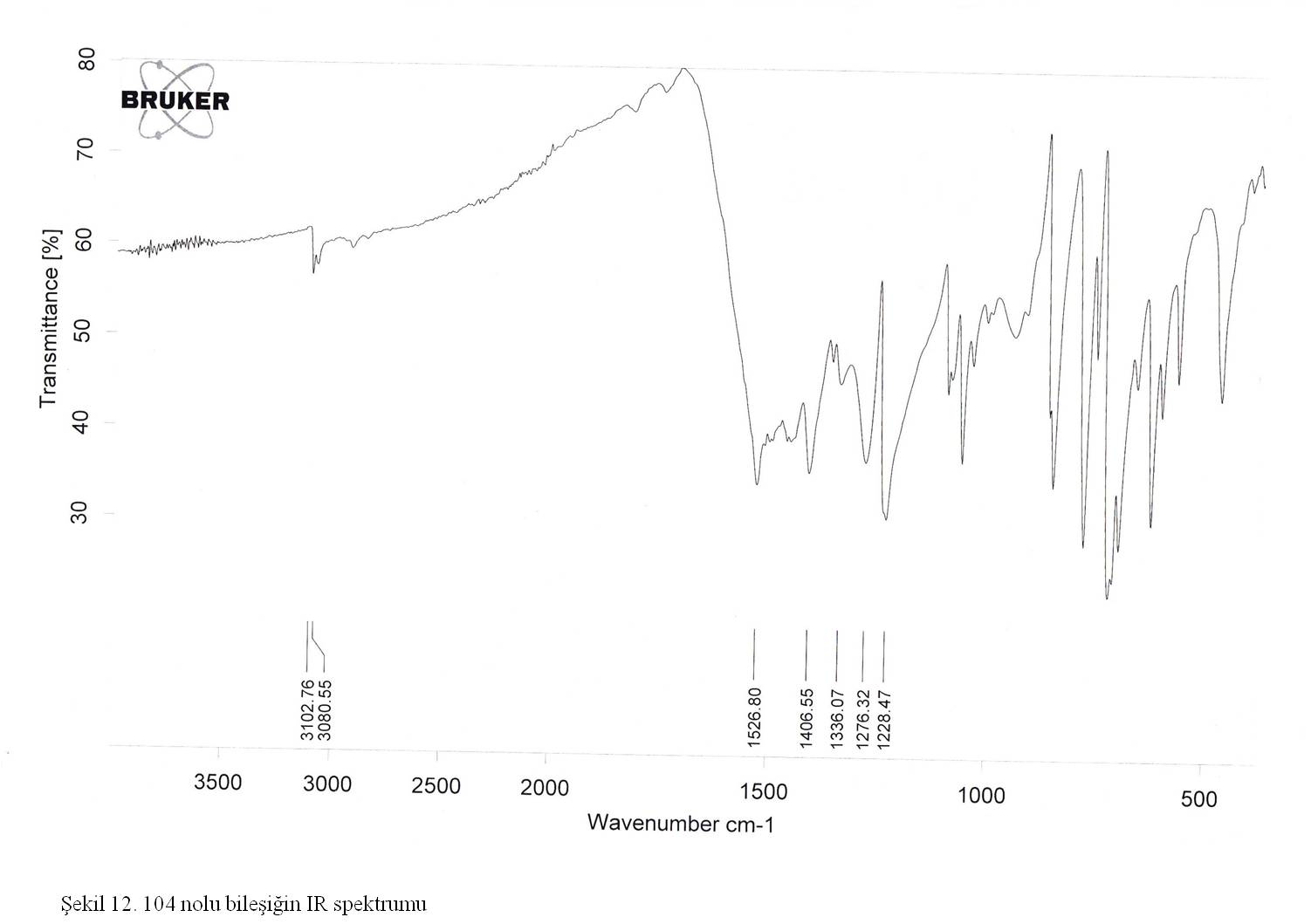
**Fig. S25.** IR (ATR, cm-1) spectrum of **5.**

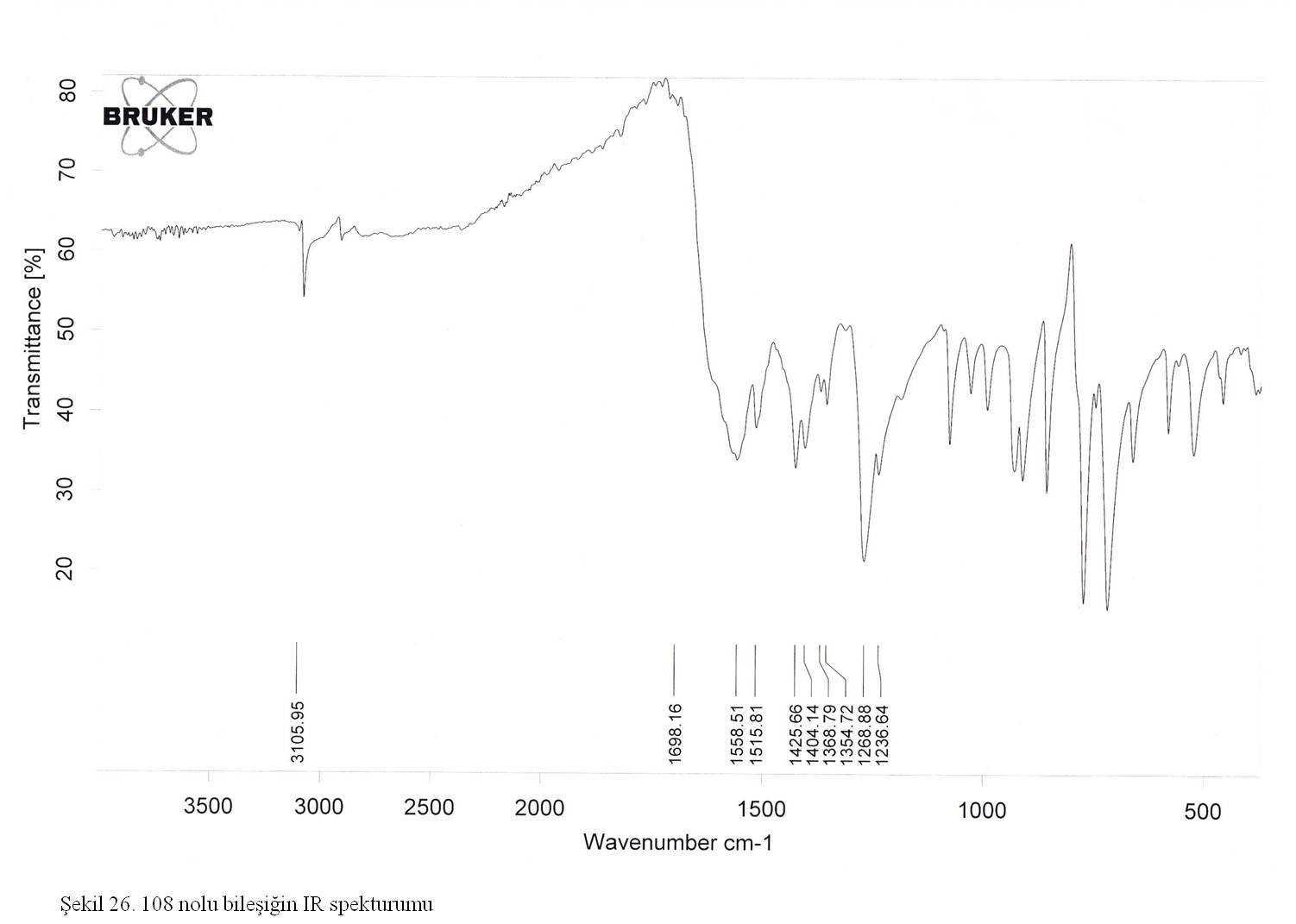
**Fig. S26.** IR (ATR, cm-1) spectrum of **6.**

**Fig. S27.** IR (ATR, cm-1) spectrum of **7.**

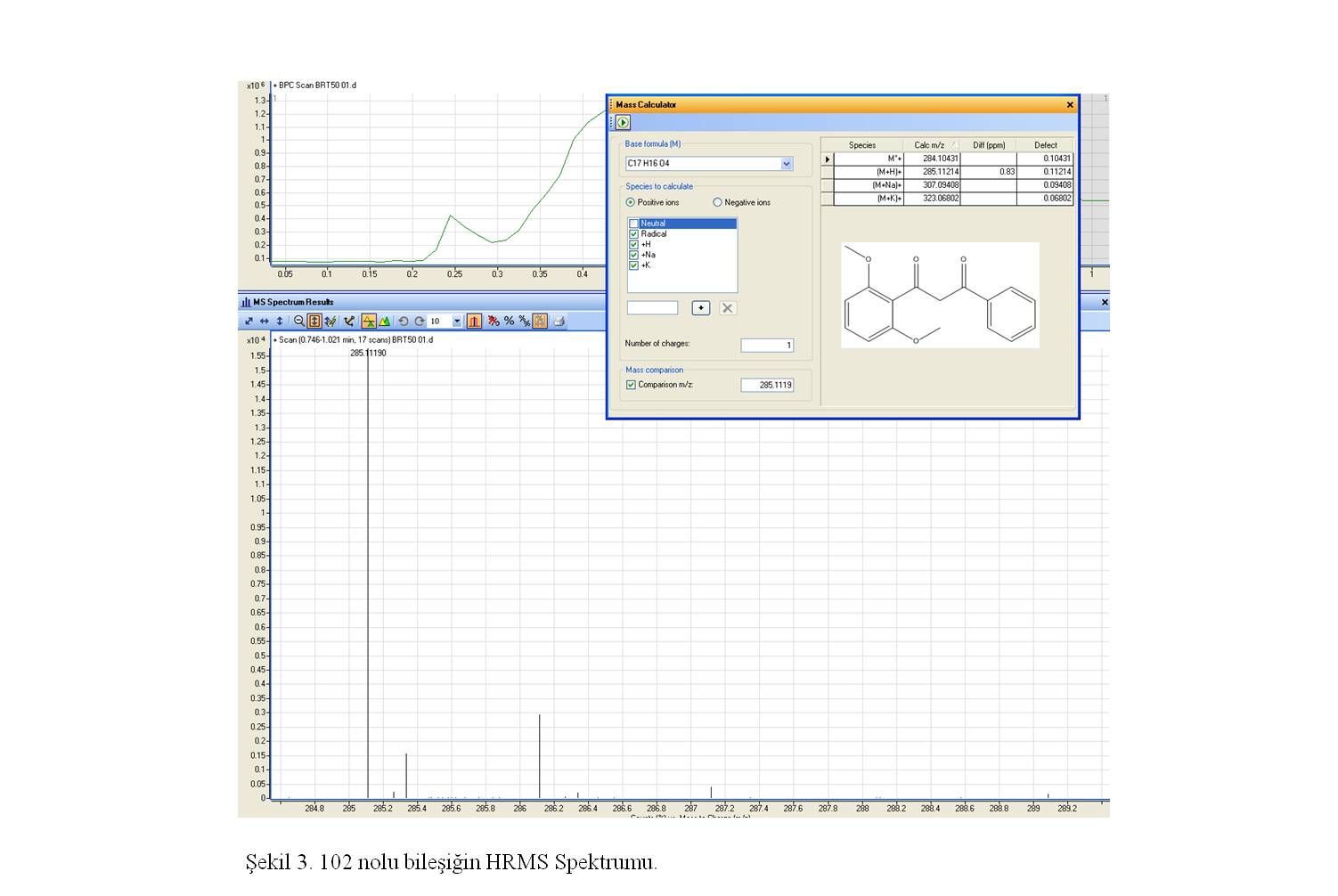


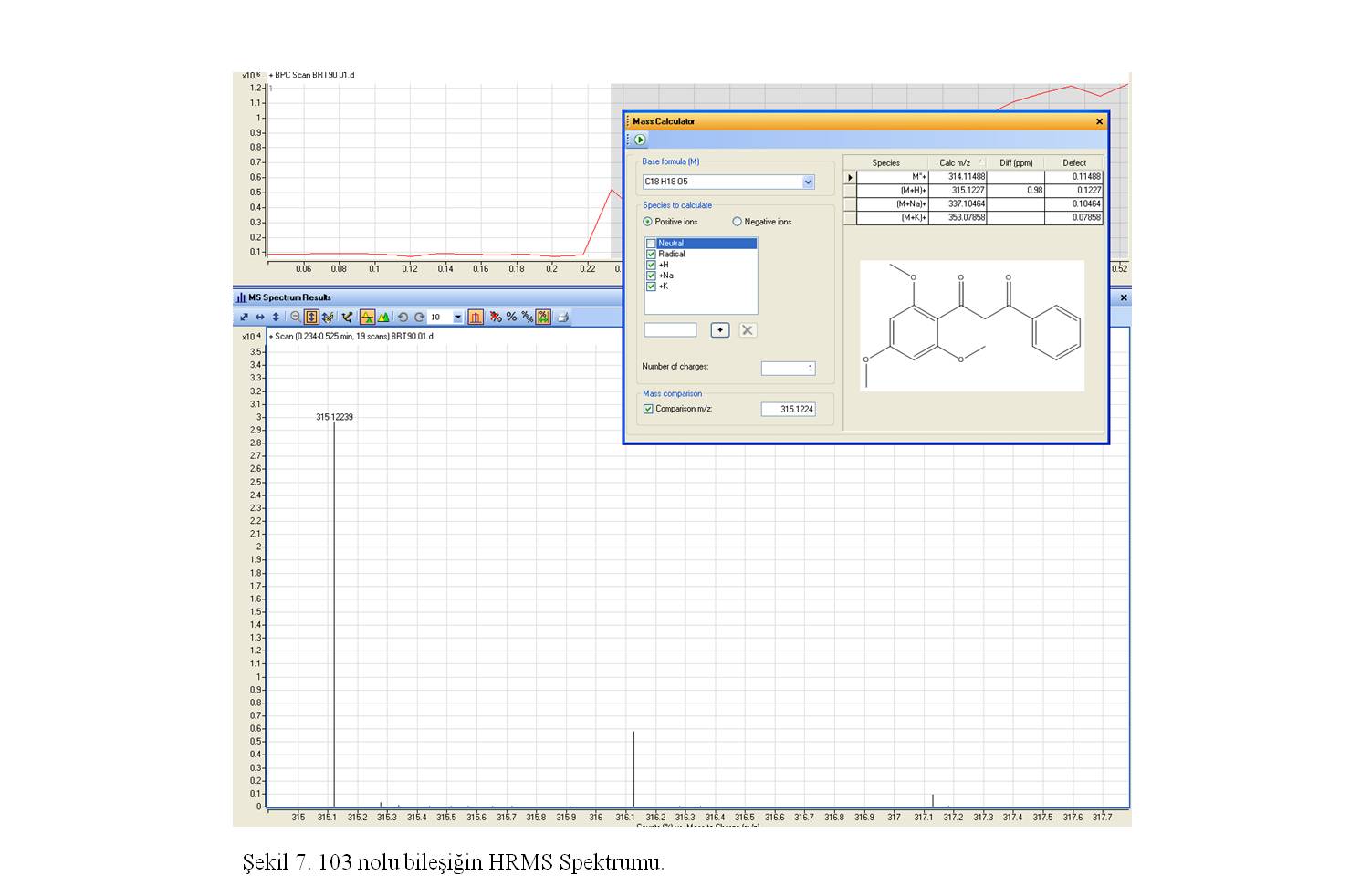
**Fig. S28.** IR (ATR, cm-1) spectrum of **8.**

**Fig. S29.** IR (ATR, cm-1) spectrum of **9.**

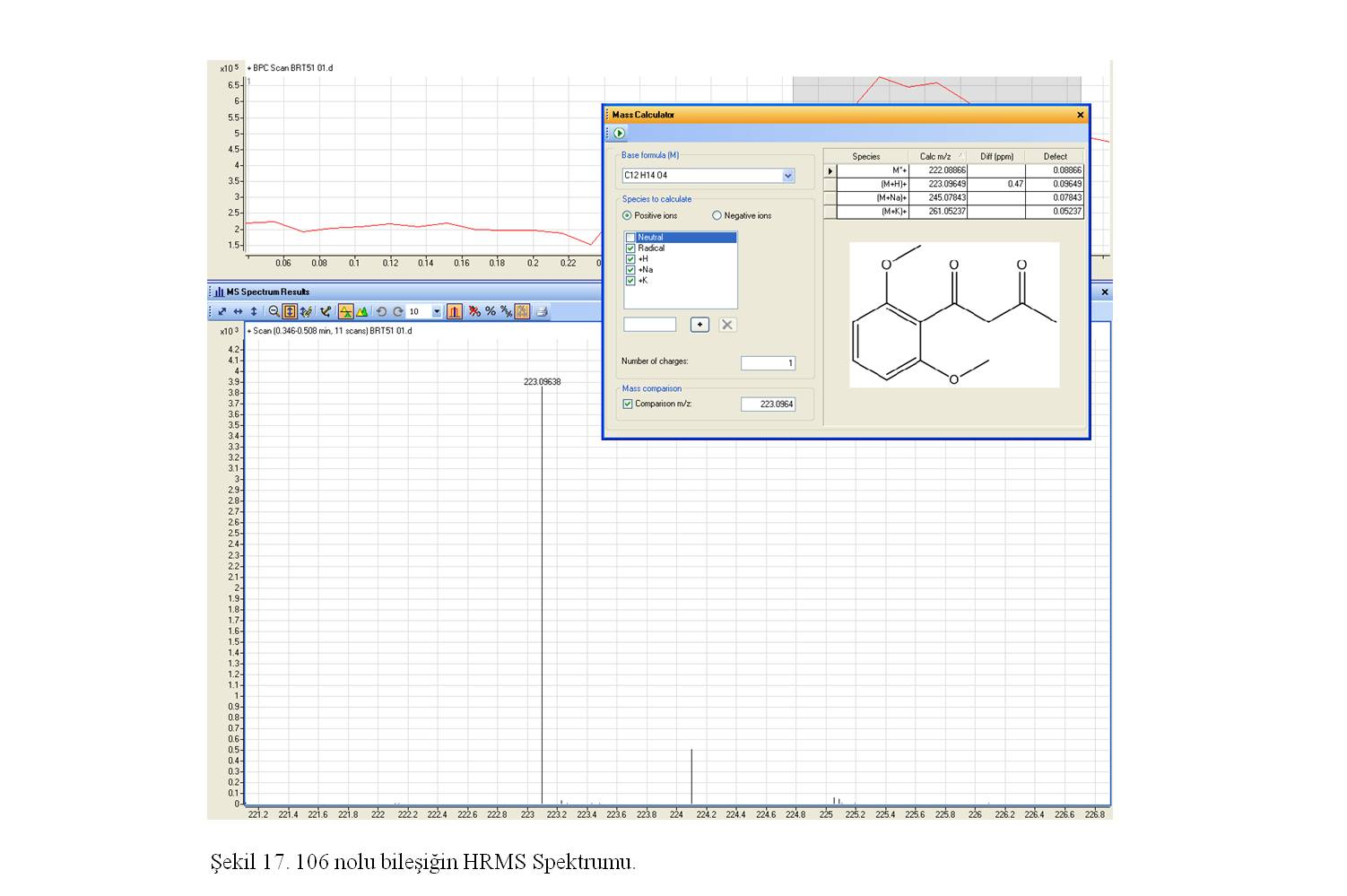


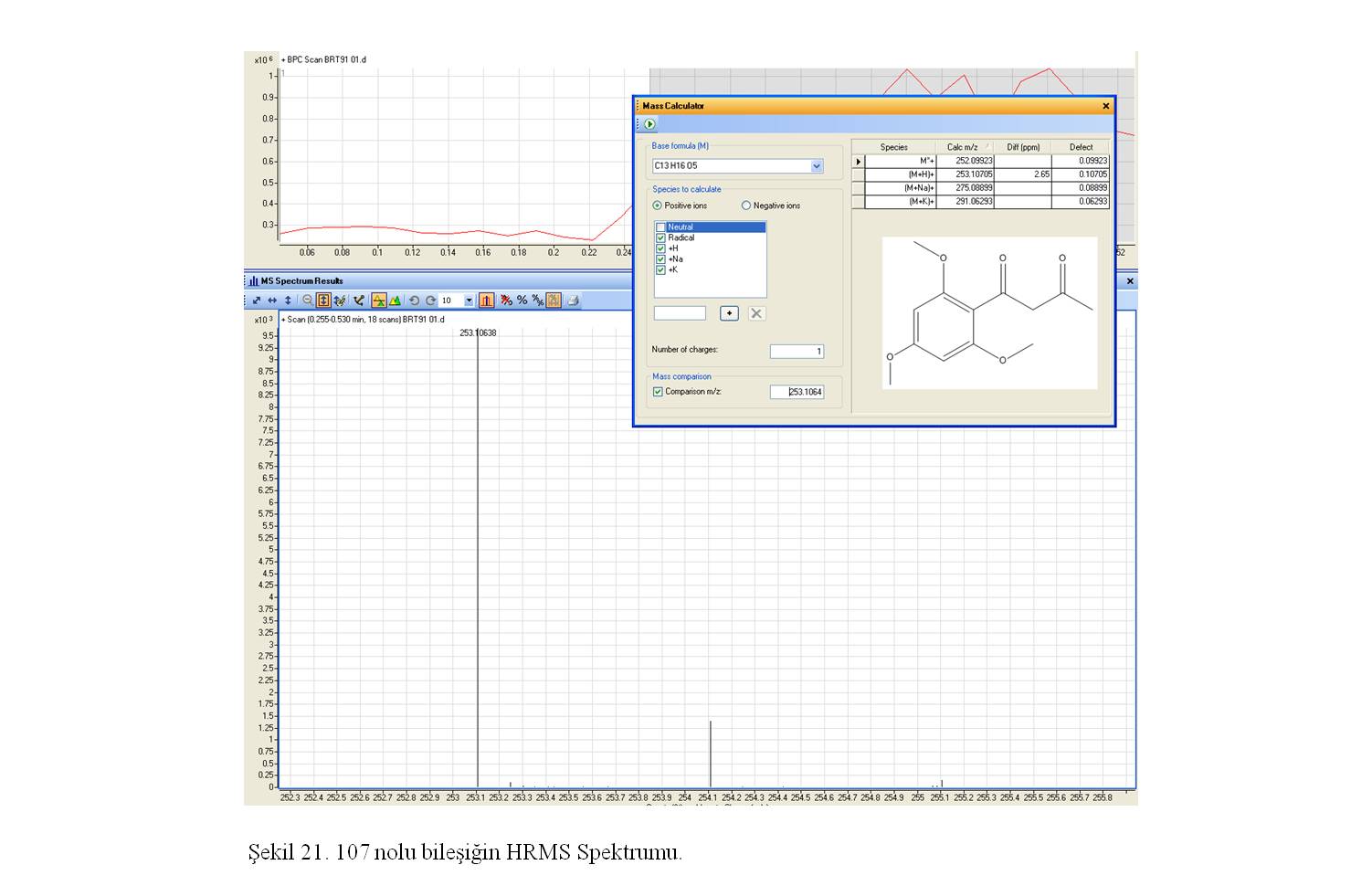
**Fig. S30.** IR (ATR, cm-1) spectrum of **10.**

**Fig. S31.** HR-MS (m/z (M+H)+) spectrum of **1**.

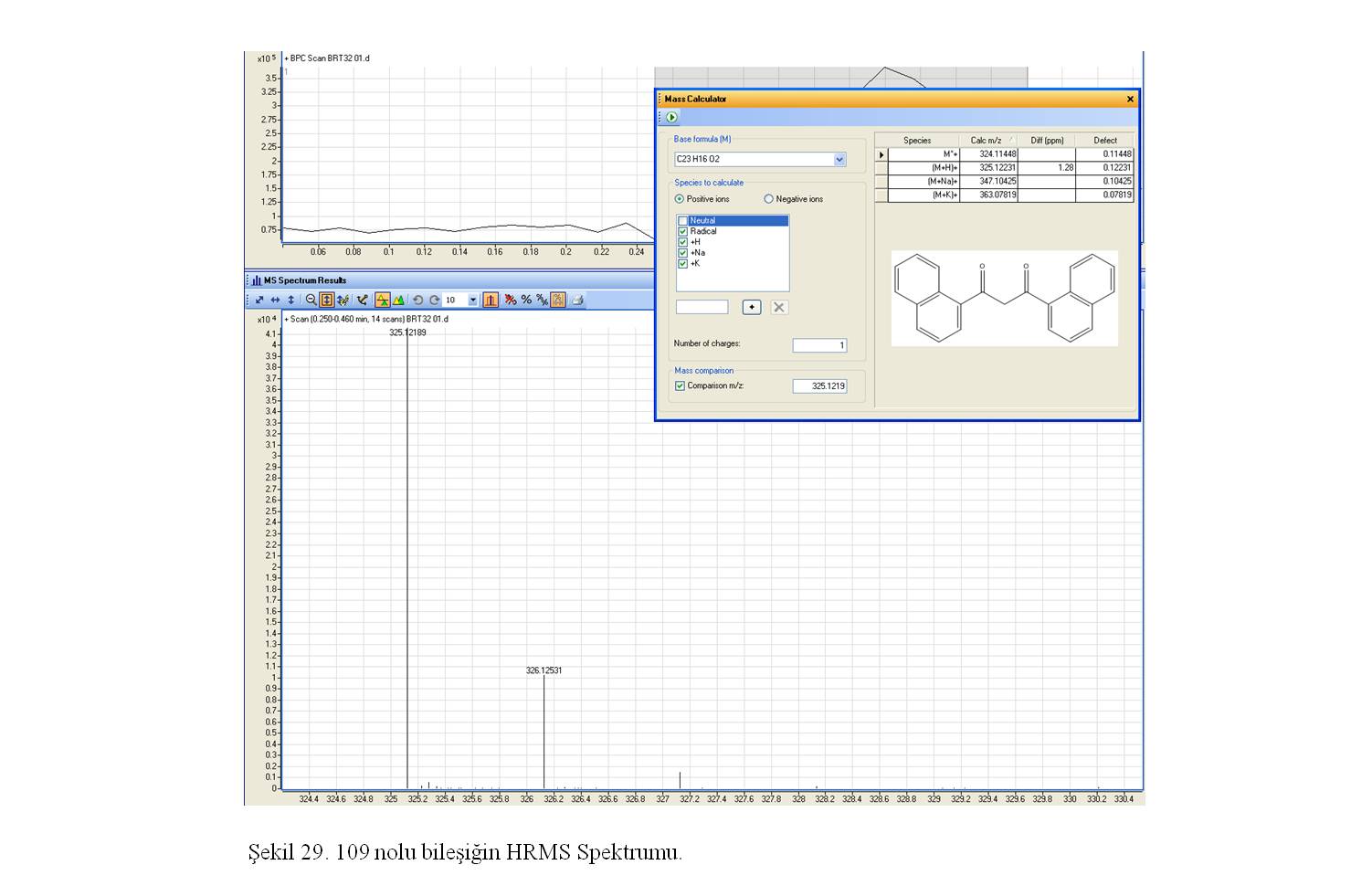


**Fig. S32.** HR-MS (m/z (M+H)+) spectrum of **2**.

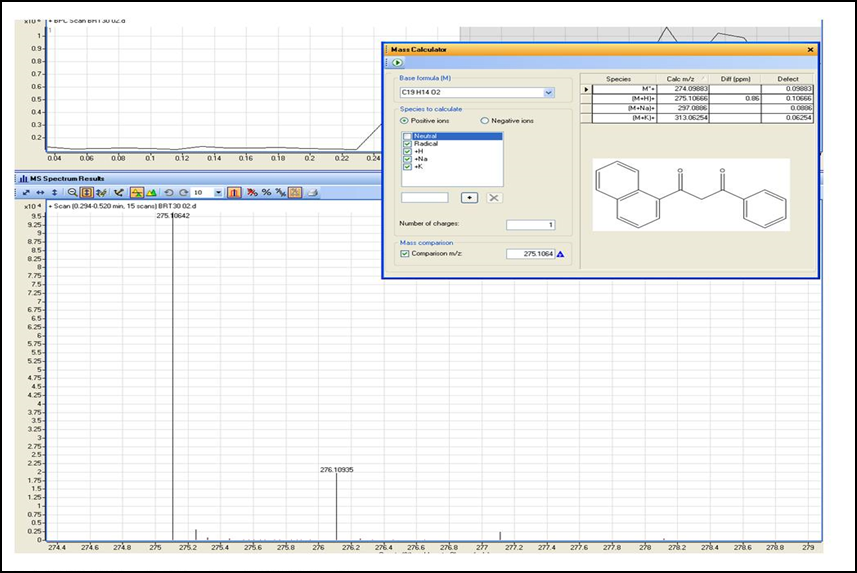
**Fig. S33.** HR-MS (m/z (M+H)+) spectrum of **3**.



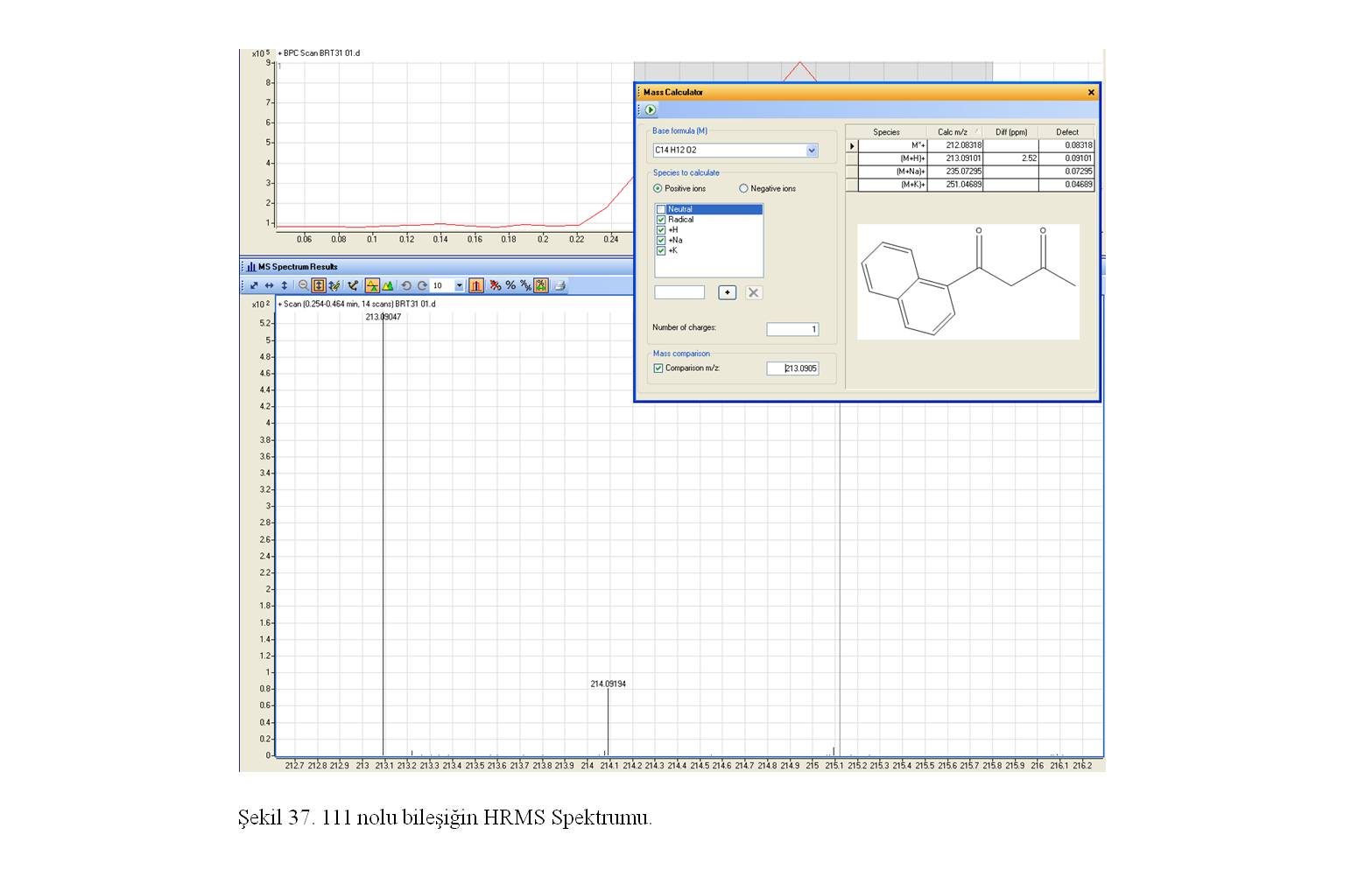
**Fig. S34.** HR-MS (m/z (M+H)+) spectrum of **4**.



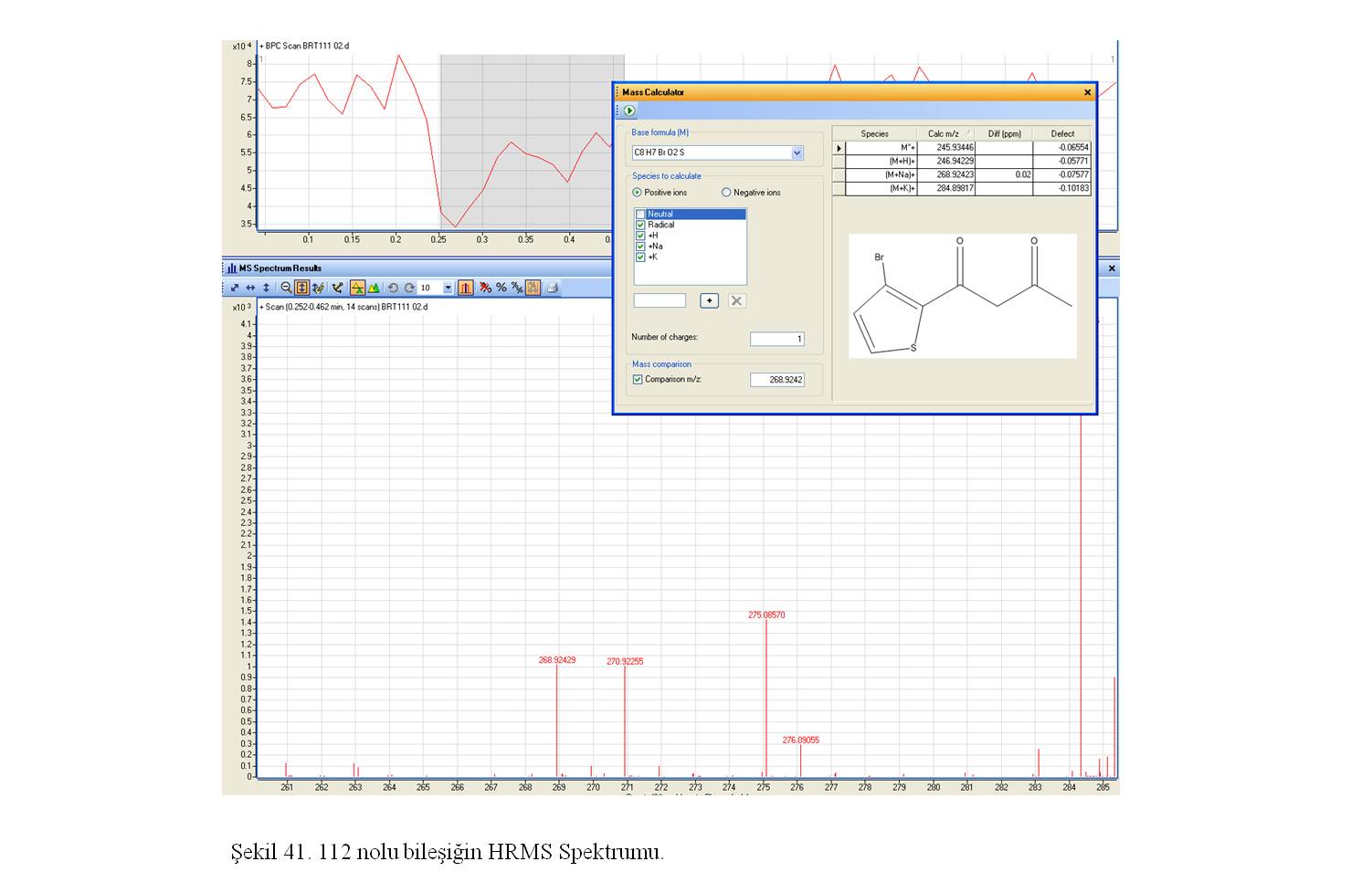
**Fig. S35.** HR-MS (m/z (M+H)+) spectrum of **5**.



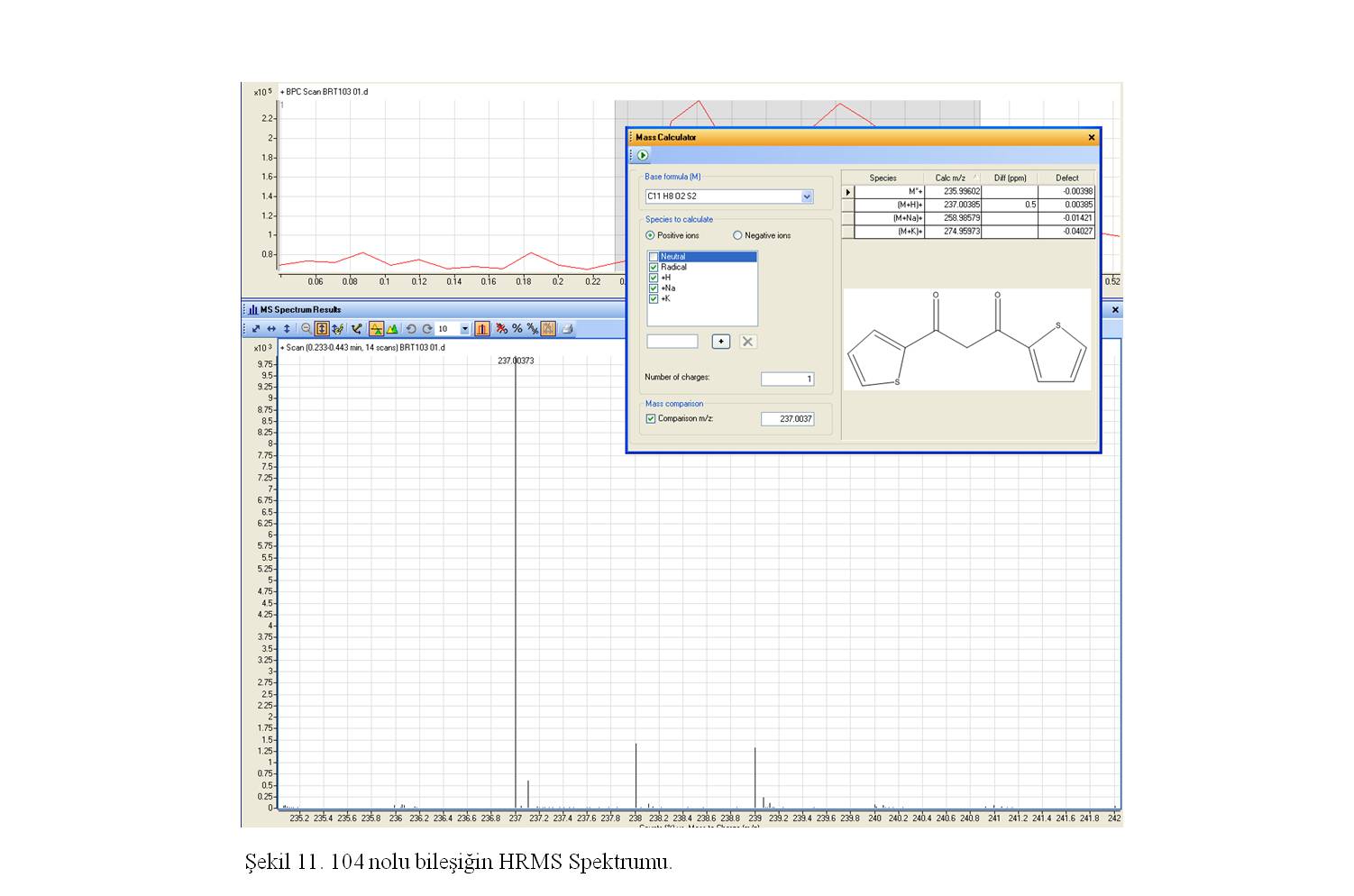
**Fig. S36.** HR-MS (m/z (M+H)+) spectrum of **6**.



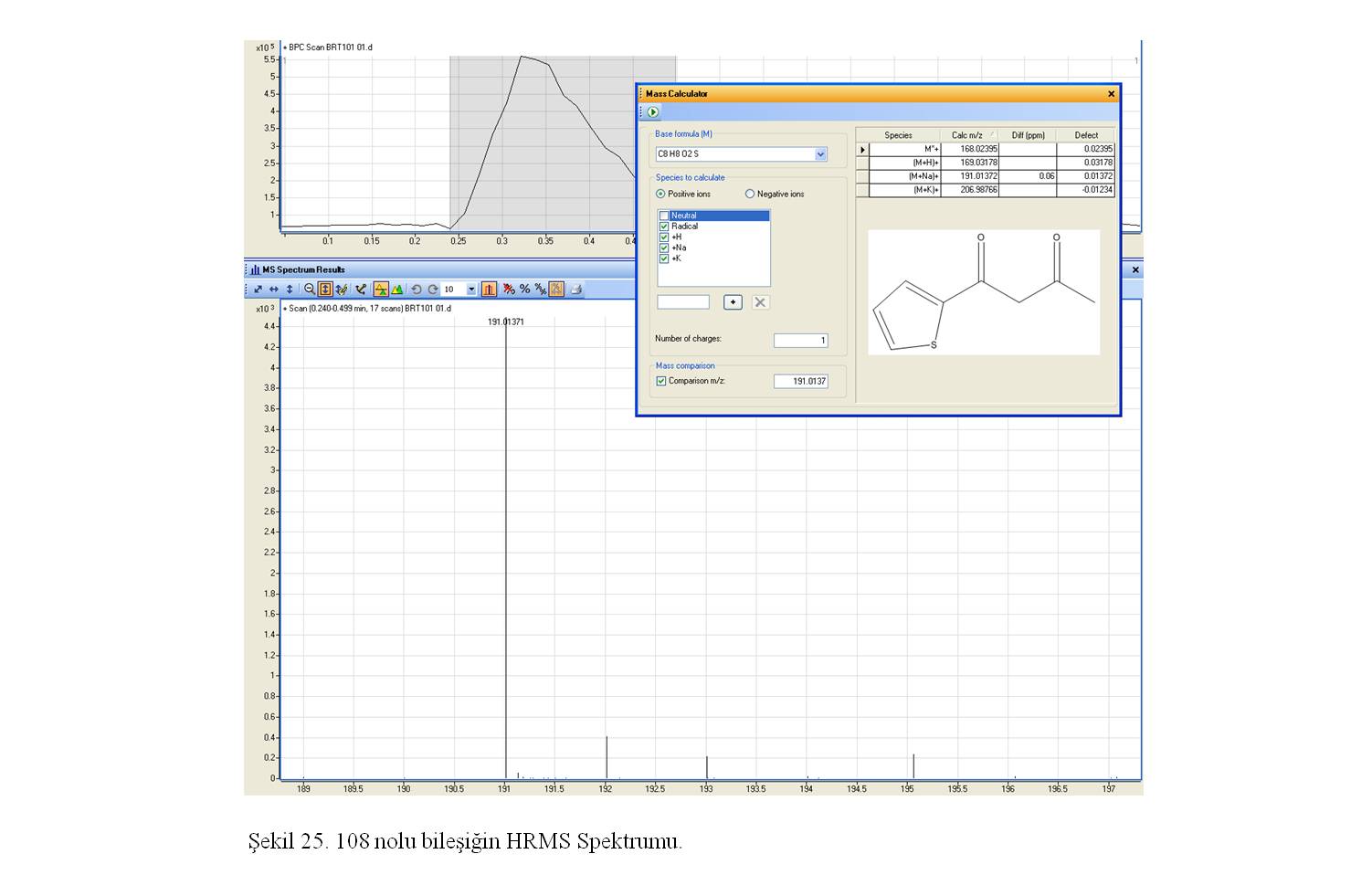
**Fig. S37.** HR-MS (m/z (M+H)+) spectrum of **7**.



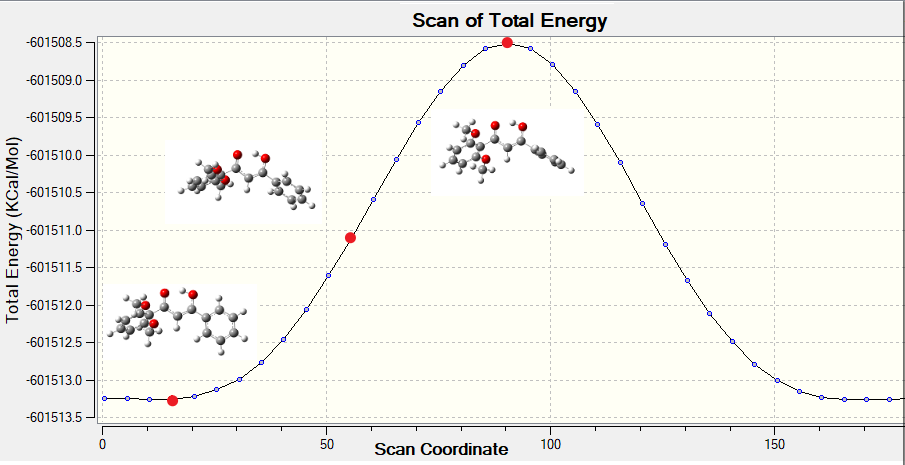
**Fig. S38.** HR-MS (m/z (M+Na)+) spectrum of **8**.

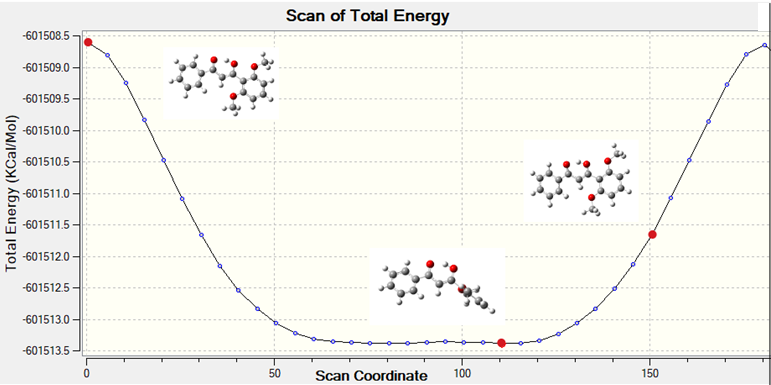


**Fig. S39.** HR-MS (m/z (M+H)+) spectrum of **9**.



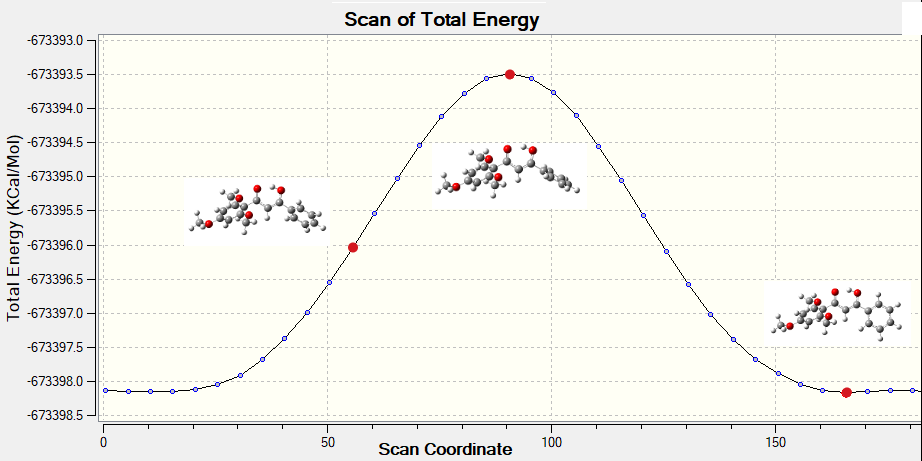
**Fig. S40.** HR-MS (m/z (M+Na)+) spectrum of **10**.

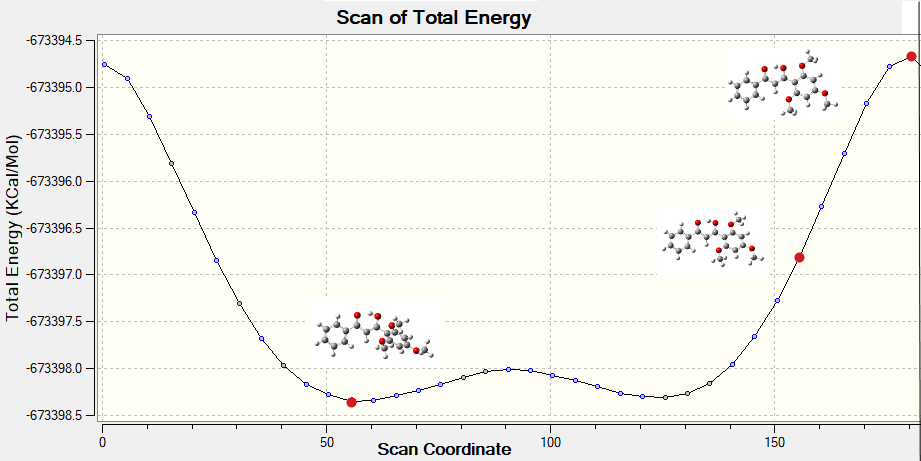
**a.**

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**b.**

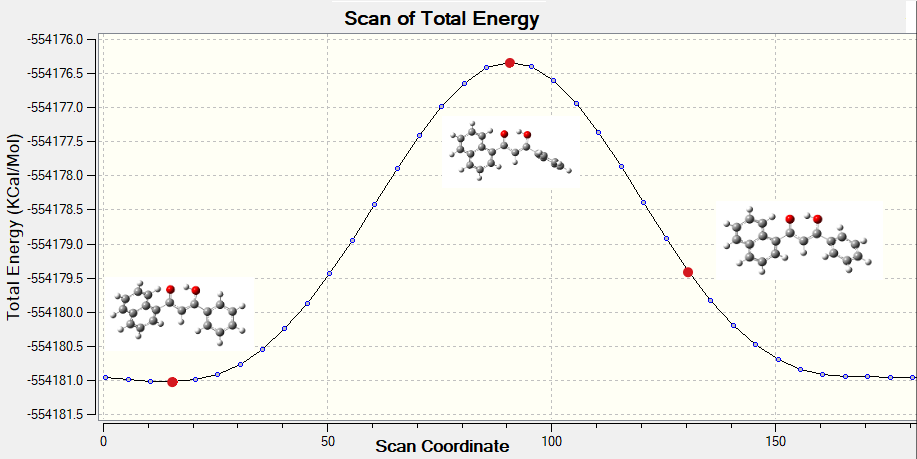
**Fig. S41. a**. Dihedral angle scanning of the enol form **1a** (most and least stable conformers)**; b.** Dihedral angle scanning of the enol form **1b** (most and least stable conformers).

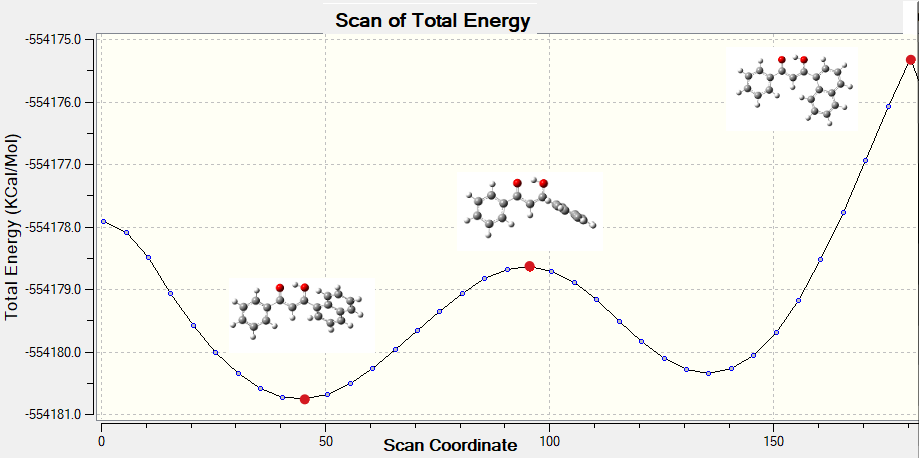
**a.**

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**b.**

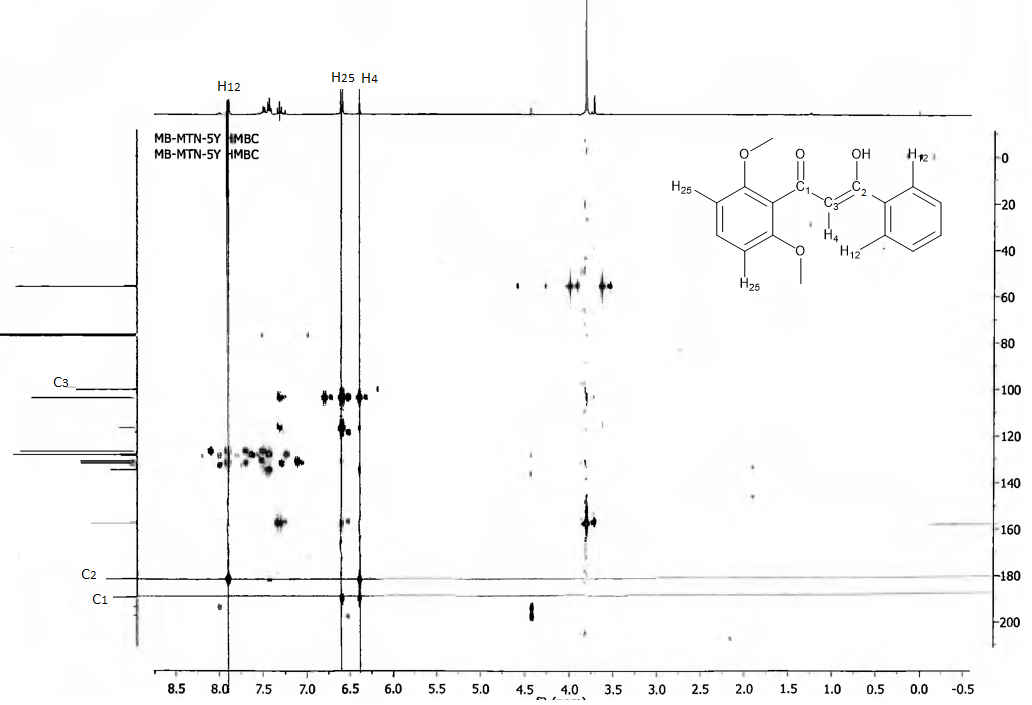
**Fig. S42. a**. Dihedral angle scanning of the enol form **2a** (most and least stable conformers)**; b.** Dihedral angle scanning of the enol form **2b** (most and least stable conformers).

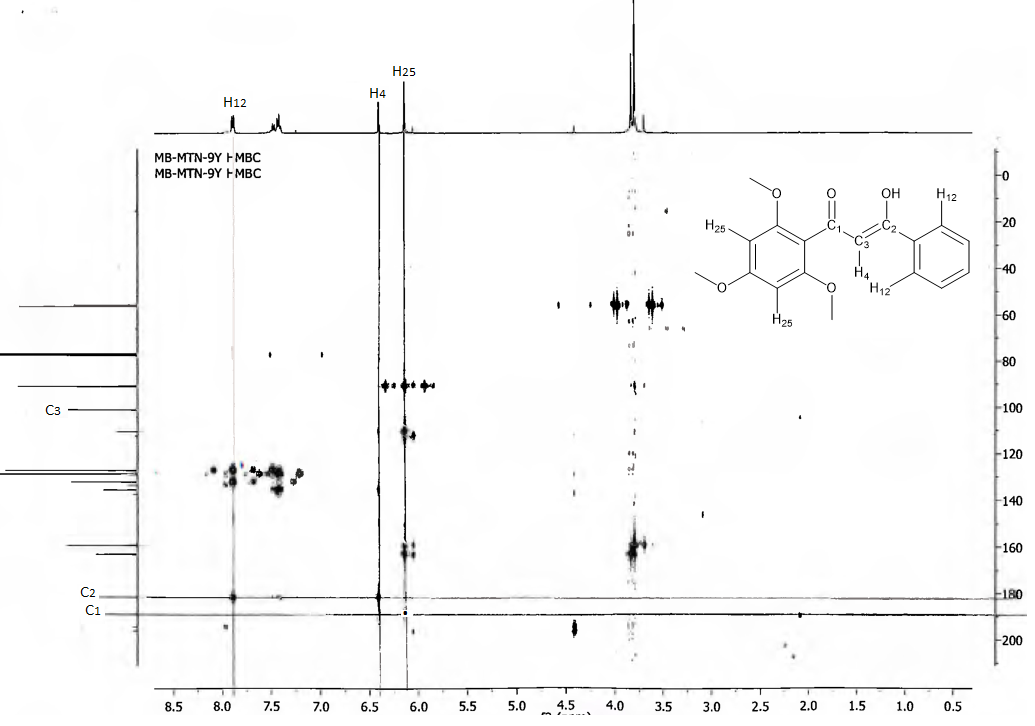
**a.**

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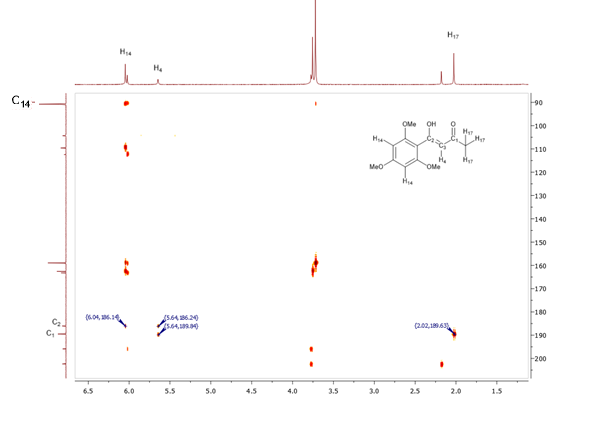
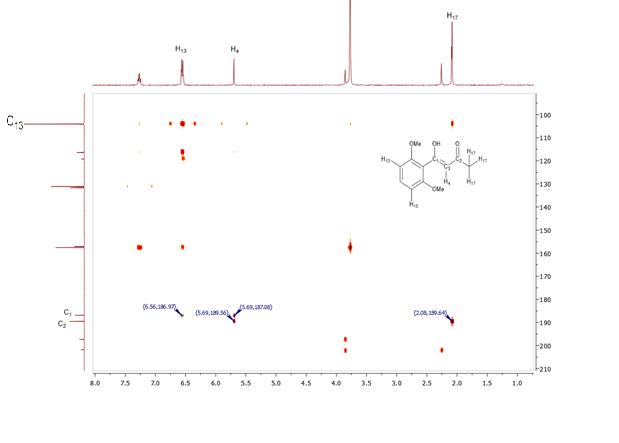
**b.**

**Fig. S43. a**. Dihedral angle scanning of the enol form **7a** (most and least stable conformers)**; b.** Dihedral angle scanning of the enol form **7b** (most and least stable conformers).

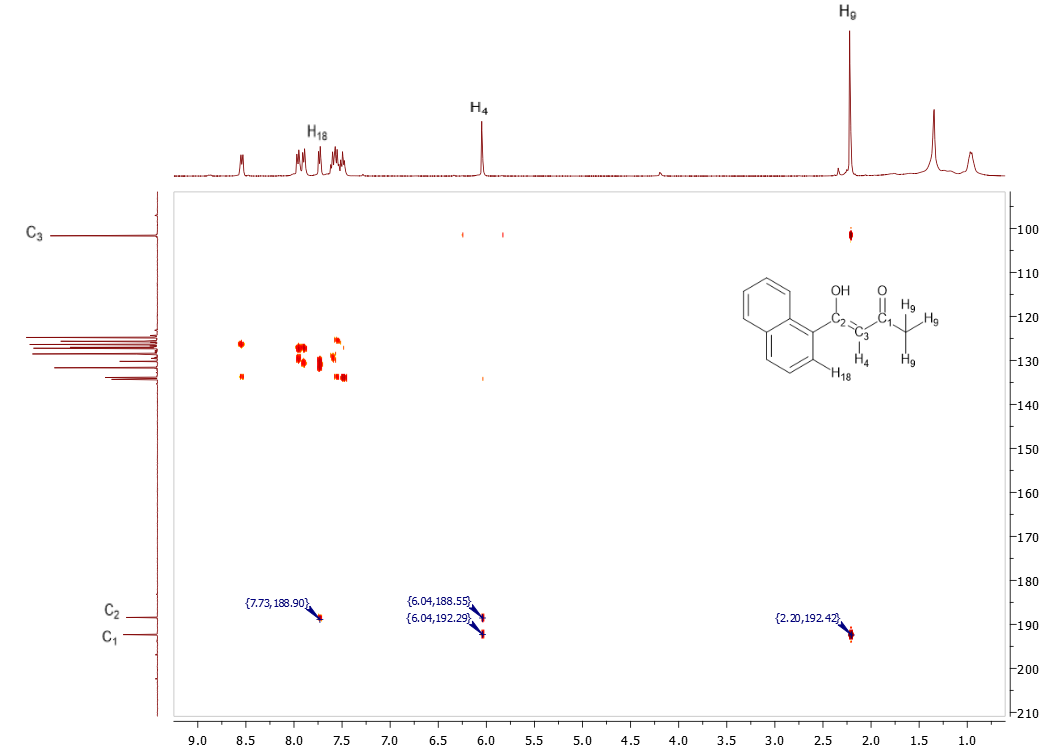
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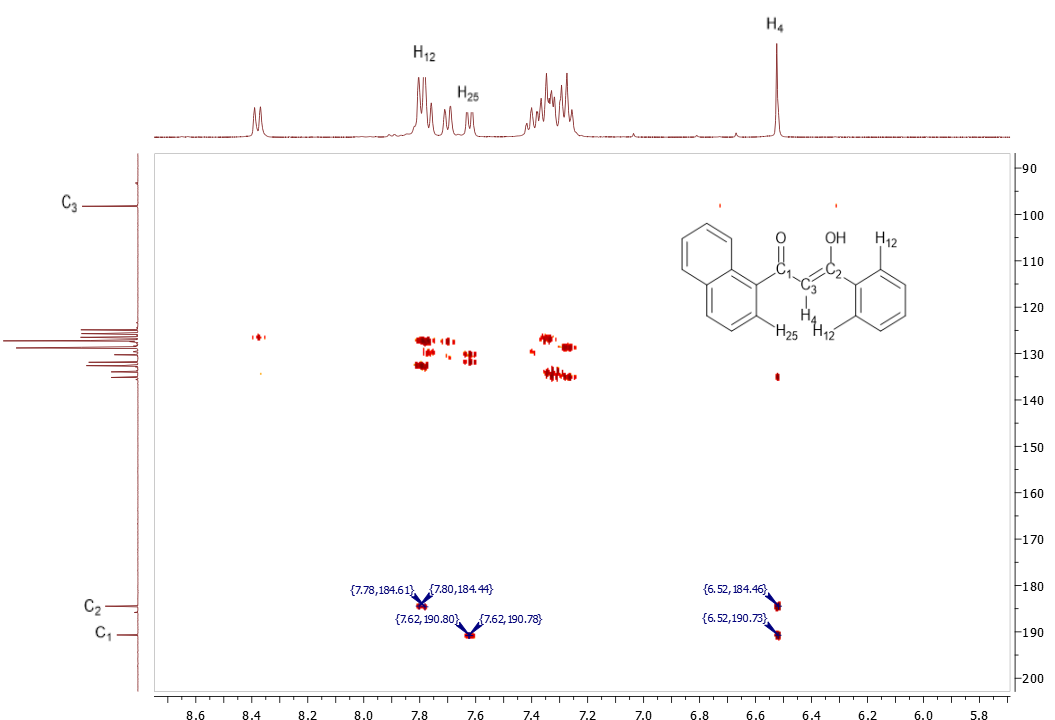
**Fig. S44.** HMBC spectrum of the compound **1.**

**Fig. S45.** HMBC spectrum of the compound **2.**

******Fig. S46.** HMBC spectrum of the compound **3.**

**Fig. S47.** HMBC spectrum of the compound **4.**



**Fig. S48.** HMBC spectrum of the compound **6.**

**Fig. S49.** HMBC spectrum of the compound **7.**