Theophylline as the catalyst for the diastereoselective synthesis of *trans*-1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazines in water

Afshin Yazdani-Elah-Abadi,[a] Razieh Mohebat[b,*] and Malek-Taher Maghsoodlou[c]

[a] *Young Researchers and Elite Club, Yazd Branch, Islamic Azad University, Yazd, Iran*

[b] *Department of Chemistry, Yazd Branch, Islamic Azad University, Yazd, Iran*

[c] *Department of Chemistry, Faculty of Science, University of Sistan and Baluchestan, P. O. Box: 98135-674, Zahedan, Iran*

Corresponding author: E-mail: mohebat@iauyazd.ac.ir

Table of contents

Experimental

General

All melting points were determined on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a shimadzu IR-470 spectrometer. Elemental analyses for C, H, and N were performed using a Costech ECS 4010 CHNS-O analyser at the analytical laboratory of Islamic Azad University Yazd branch. Mass spectra were recorded on an Agilent Technology (HP) spectrometer operating at an ionization potential of 70 eV. The ^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-300 spectrometer operating at 300 MHz for ^{1}H analysis and 75 MHz for ^{13}C analysis. Thin-layer chromatography (TLC) was performed on silica-gel Polygram SILG/UV 254 plates. All reagents and solvent were purchased from Merck and Aldrich and used without further purification.

General procedure for the synthesis of novel 1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazine derivatives (6a-p)

Initially, a mixture of 2-hydroxynaphthalene-1,4-dione **1** (1 mmol), benzene-1,2-diamine **2** (1 mmol), theophylline (20 mol%) and water (10 mL) was placed in a 50 mL round-bottomed flask mounted over a magnetic stirrer. The contents were stirred magnetically in an oil-bath maintained at 70°C until in less than 10 minutes benzo[*a*]phenazin-5-ol **3** was formed. Then, aryl aldehyde **4** (1 mmol) and 1-(2-(4-bromophenyl)-2-oxoethyl)pyridinium bromide **5** (1 mmol) were added to the above reaction mixture which was heated further at same temperature for an appropriate time as shown in Table 2. Upon completion of the reaction, monitored by TLC, the reaction mixture was allowed to cool to room temperature. Then, 5 mL of water was added to the mixture and filtered for separation of the crude product. The separated product was washed twice with water (2×5 mL). The solid crude product subsequently recrystallized from hot ethanol to give the pure product **6**.

Spectral data

(4-Bromophenyl)(1-(4-chlorophenyl)-1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazin-2-yl)methanone (6a)

Yellow powder; yield 0.502 g (89%), mp 279-281 °C; IR (KBr): ν_{max} = 3045, 2900, 1691, 1627, 1591, 1535, 1499, 1415, 1386, 1332, 1224, 1131, 1045, 978, 800, 759 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 5.46 (d, 1H, J = 4.2 Hz, CH), 6.10 (d, 1H, J = 4.2 Hz, CH), 7.22 (d, 2H, J = 8.4 Hz, Ar-H), 7.32 (d, 2H, J = 8.4 Hz, Ar-H), 7.59-7.67 (m, 4H, Ar-H), 7.78-7.83 (m, 4H, Ar-H), 7.89-7.92 (m, 1H, Ar-H), 8.15-8.20 (m, 2H, Ar-H), 9.32-9.35 (m, 1H, Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 50.1 and 91.9 (2CH), 115.4, 122.6, 123.9, 126.1, 128.6, 128.8, 128.9, 129.0, 129.2, 129.5, 129.7, 129.9, 130.0, 130.6, 132.3, 132.5, 133.2, 140.2, 140.4, 141.3, 141.5, 142.5 and 157.9 ($C_{olefinic}$ and C_{arom}), 192.7 (C=O) ppm; MS (*m/z*, %): 565 (M^+, 1), 448 (1), 381 (100), 246 (91), 185 (15), 43 (76); Anal. Calcd for $C_{31}H_{18}BrClN_2O_2$: C, 65.80; H, 3.21; N, 4.95 %. Found: C, 66.03; H, 3.46; N, 4.87 %.

(4-Bromophenyl)(1-(2-chlorophenyl)-1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazin-2-yl)methanone (6b)

Orange powder; yield 0.492 g (87%), mp 243-245 °C; IR (KBr): ν_{max} = 3035, 2895, 1692, 1626, 1594, 1534, 1498, 1414, 1386, 1332, 1223, 1129, 1045, 978, 800, 759 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.11 (s, 2H, 2CH), 6.99-7.14 (m, 3H, Ar-H), 7.39 (d, 1H, J = 7.8 Hz, Ar-H), 7.60 (d, 2H, J = 8.7 Hz, Ar-H), 7.64-7.67 (m, 2H, Ar-H), 7.73-7.82 (m, 2H, Ar-H), 7.88 (d, 2H, J = 8.4 Hz, Ar-H), 7.93-7.96 (m, 1H, Ar-H), 8.08-8.11 (m, 1H, Ar-H), 8.17-8.21 (m, 1H, Ar-H), 9.33-9.36 (m, 1H, Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 46.6 and 90.9 (2CH), 115.3, 122.5, 124.0, 125.7, 126.1, 127.3, 128.5, 128.6, 128.8, 129.1, 129.3, 129.6, 129.7, 129.8, 129.9, 130.8, 131.4, 131.9, 132.2, 132.5, 132.9, 133.5, 139.3, 140.3, 141.2, 141.7, 142.7 and 158.1 ($C_{olefinic}$ and C_{arom}), 191.9 (C=O) ppm; MS (*m/z*, %): 565 (M^+, 1), 529 (1), 381 (100), 246 (9), 183 (11), 76 (4); Anal. Calcd for $C_{31}H_{18}BrClN_2O_2$: C, 65.80; H, 3.21; N, 4.95 %. Found: C, 65.93; H, 3.51; N, 5.10 %.

(4-Bromophenyl)(1-(2,4-dichlorophenyl)-1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazin-2-yl)methanone (6c)

Yellow powder; yield 0.534 g (89%), mp 256-257 °C; IR (KBr): ν_{max} = 3110, 2905, 1683, 1626, 1591, 1534, 1500, 1412, 1380, 1351, 1221, 1134, 1065, 978, 800, 761 cm^{-1}; ^1H NMR

(300 MHz, DMSO-d_6): δ 5.92 (d, 1H, J = 3.9 Hz, CH), 6.74 (d, 1H, J = 3.9 Hz, CH), 7.16 (d, 1H, J = 8.4 Hz, Ar-H), 7.25 (dd, 1H, J_1 = 8.7 Hz, J_2 = 2.1 Hz, Ar-H), 7.73 (d, 1H, J = 2.1 Hz, Ar-H), 7.84-7.89 (m, 4H, Ar-H), 7.94-8.02 (m, 3H, Ar-H), 8.05 (d, 2H, J = 8.7 Hz, Ar-H), 8.13-8.16 (m, 1H, Ar-H), 8.28-8.32 (m, 1H, Ar-H), 9.31-9.34 (m, 1H, Ar-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 49.3 and 90.4 (2CH), 114.9, 122.9, 123.7, 126.1, 128.3, 128.8, 129.0, 129.3, 129.8, 131.1, 131.2, 131.7, 132.1, 132.6, 133.0, 133.2, 134.0, 138.2, 140.0, 140.9, 141.5, 142.3 and 158.5 ($C_{olefinic}$ and C_{arom}), 193.2 (C=O) ppm; MS (*m/z*, %): 600 (M^+, 1), 523 (1), 415 (100), 352 (16), 182 (20), 57 (14); Anal. Calcd for $C_{31}H_{17}BrCl_2N_2O_2$: C, 62.03; H, 2.85; N, 4.67 %. Found: C, 62.27; H, 2.64; N, 4.76 %.

(4-Bromophenyl)(1-(4-nitrophenyl)-1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazin-2-yl)methanone (6d)

Yellow powder; yield 0.516 g (90%), mp 283-285 °C; IR (KBr): ν_{max} = 3025, 2905, 1689, 1624, 1593, 1532, 1507, 1447, 1393, 1336, 1223, 1132, 1046, 941, 803, 754 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.72 (d, 1H, J = 4.8 Hz, CH), 6.10 (d, 1H, J = 4.8 Hz, CH), 7.56-7.70 (m, 7H, Ar-H), 7.78-7.83 (m, 2H, Ar-H), 7.86-7.89 (m, 3H, Ar-H), 8.11-8.14 (m, 3H, Ar-H), 9.34-9.37 (m, 1H, Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 50.5 and 90.6 (2CH), 115.3, 122.3, 124.0, 125.5, 127.3, 128.0, 128.5, 128.7, 129.1, 129.5, 129.7, 130.0, 130.1, 130.2, 130.3, 131.6, 132.5, 132.9, 133.5, 139.3, 140.3, 141.4, 141.5, 142.5, and 157.5 ($C_{olefinic}$ and C_{arom}), 192.6 (C=O) ppm; MS (*m/z*, %): 576 (M^+, 1), 530 (1), 384 (2), 344 (48), 271 (68), 57 (100); Anal. Calcd for $C_{31}H_{18}BrN_3O_4$: C, 64.60; H, 3.15; N, 7.29 %. Found: C, 64.48; H, 3.37; N, 7.53 %.

(4-bromophenyl)(1-(2-hydroxy-5-nitrophenyl)-1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazin-2-yl)methanone (6e)

Green powder; yield 0.503 g (85%), mp 156-157 °C; IR (KBr): ν_{max} = 3050, 2910, 1688, 1632, 1591, 1527, 1500, 1415, 1386, 1336, 1224, 1152, 1063, 948, 811, 754 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.74 (d, 1H, J = 4.8 Hz, CH), 6.13 (d, 1H, J = 4.5 Hz, CH), 7.43 (t, 1H, J = 7.8 Hz, Ar-H), 7.60-7.67 (m, 3H, Ar-H), 7.75-7.84 (m, 3H, Ar-H), 7.86-7.90 (m, 3H, Ar-H), 8.03-8.06 (m, 1H, Ar-H), 8.12-8.19 (m, 2H, Ar-H), 8.30 (t, 1H, J = 2.1 Hz, Ar-H), 9.32-9.35 (m, 1H, Ar-H), 10.80 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 49.7 and 91.6 (2CH), 114.8, 122.5, 122.7, 123.1, 126.1, 128.7, 129.1, 129.7, 129.8, 130.0, 130.7, 130.9, 131.2, 131.5, 131.6, 132.3, 132.6, 134.2, 137.2, 138.5, 140.2, 141.4, 141.9, 143.9 and 157.8

($C_{olefinic}$ and C_{arom}), 192.4 (C=O) ppm; MS (*m/z*, %): 592 (M^+, 1), 575 (2), 415 (100), 345 (22), 182 (49), 57 (92); Anal. Calcd for $C_{31}H_{18}BrN_3O_5$: C, 62.85; H, 3.06; N, 7.09 %. Found: C, 62.63; H, 3.15; N, 7.26 %.

(4-Bromophenyl)(1-(thiophen-2-yl)-1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazin-2-yl)methanone (6f)

Brown powder; yield 0.431 g (80%), mp 160 °C; IR (KBr): ν_{max} = 3050, 2895, 1687, 1629, 1579, 1524, 1489, 1412, 1386, 1330, 1219, 1133, 1063, 973, 834, 750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 5.79 (d, 1H, *J* = 3.9 Hz, CH), 6.21 (d, 1H, *J* = 3.9 Hz, CH), 7.87-8.89 (m, 1H, Ar-H), 7.05 (d, 1H, *J* = 3.3 Hz, Ar-H), 7.11 (d, 1H, *J* = 4.8 Hz, Ar-H), 7.60-7.68 (m, 5H, Ar-H), 7.76-8.79 (m, 2H, Ar-H), 7.89 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.95-7.98 (m, 1H, Ar-H), 8.14-8.19 (m, 2H, Ar-H), 9.30-9.34 (m, 1H, Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 45.6 and 91.8 (2CH), 115.0, 122.7, 123.9, 124.7, 125.4, 126.0, 127.1, 128.5, 128.8, 128.9, 129.5, 129.6, 129.7, 129.8, 129.9, 130.7, 132.0, 132.3, 132.5, 132.6, 140.2, 141.3, 141.6, 142.5, 145.0, and 157.8 ($C_{olefinic}$ and C_{arom}), 192.5 (C=O) ppm; MS (*m/z*, %): 537 (M^+, 1), 426 (2), 353 (100), 246 (18), 183 (14), 76 (5); Anal. Calcd for $C_{29}H_{17}BrN_2O_2S$: C, 64.81; H, 3.19; N, 5.21; S, 5.97 %. Found: C, 65.06; H, 3.26; N, 5.30; S, 5.82 %.

(4-bromophenyl)(1-(*p*-tolyl)-1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazin-2-yl)methanone (6g)

Green powder; yield 0.441 g (81%), mp 260-263 °C; IR (KBr): ν_{max} = 3045, 2900, 1684, 1633, 1594, 1533, 1500, 1416, 1382, 1331, 1222, 1130, 1063, 978, 828, 749 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.27 (s, 3H, CH_3), 5.37 (d, 1H, *J* = 3.9 Hz, CH), 6.15 (d, 1H, *J* = 4.2 Hz, CH), 7.06 (d, 2H, *J* = 7.8 Hz, Ar-H), 7.29 (d, 2H, *J* = 7.8 Hz, Ar-H), 7.58-7.66 (m, 4H, Ar-H), 7.77-7.82 (m, 4H, Ar-H), 7.89-7.94 (m, 1H, Ar-H), 8.15-8.22 (m, 2H, Ar-H), 9.32-9.35 (m, 1H, Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1 (CH_3), 50.6 and 92.2 (2CH), 116.0, 122.6, 124.1, 126.0, 127.7, 128.4, 128.7, 128.8, 129.3, 129.6, 129.7, 129.8, 129.9, 130.6, 132.2, 132.5, 132.6, 137.1, 138.9, 140.2, 141.3, 141.8, 142.5 and 157.9 ($C_{olefinic}$ and C_{arom}), 192.9 (C=O) ppm; MS (*m/z*, %): 545 (M^+, 1), 466 (2), 361 (100), 270 (5), 183 (9), 57 (3); Anal. Calcd for $C_{32}H_{21}BrN_2O_2$: C, 70.47; H, 3.88; N, 5.14 %. Found: C, 70.71; H, 3.69; N, 5.22 %.

(4-Bromophenyl)(1-(4-methoxyphenyl)-1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazin-2-yl)methanone (6h)

Brown powder; yield 0.566 g (83%), mp 180-181 °C; IR (KBr): ν_{max} = 3025, 2895, 1688, 1628, 1583, 1531, 1507, 1410, 1390, 1330, 1223, 1133, 1061, 948, 820, 750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.68 (s, 3H, OCH_3), 5.35 (d, 1H, J = 3.9 Hz, CH), 6.12 (d, 1H, J = 4.2 Hz, CH), 6.77 (d, 2H, J = 8.4 Hz, Ar-H), 7.30 (d, 2H, J = 8.7 Hz, Ar-H), 7.53-7.62 (m, 4H, Ar-H), 7.67-7.80 (m, 5H, Ar-H), 8.12-8.19 (m, 2H, Ar-H), 9.29-9.32 (m, 1H, Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 50.3 (CH), 55.2 (OCH_3), 92.2 (CH), 114.2, 116.0, 122.6, 124.0, 126.0, 128.4, 128.7, 128.8, 128.9, 129.3, 129.6, 129.7, 129.9, 130.6, 132.2, 132.4, 132.5, 134.0, 140.1, 141.3, 141.8, 142.5 and 158.8 ($C_{olefinic}$ and C_{arom}), 193.0 (C=O) ppm; MS (*m/z*, %): 561 (M^+, 1), 425 (1), 377 (100), 246 (20), 183 (12), 76 (4); Anal. Calcd for $C_{32}H_{21}BrN_2O_3$: C, 68.46; H, 3.77; N, 4.99 %. Found: C, 68.57; H, 3.96; N, 5.18 %.

(4-Bromophenyl)(1-(3,4-dimethoxyphenyl)-1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazin-2-yl)methanone (6i)

Brown powder; yield 0.460 g (78%), mp 162-164 °C; IR (KBr): ν_{max} = 3040, 2910, 1688, 1629, 1594, 1551, 1512, 1415, 1386, 1331, 1223, 1137, 1048, 948, 800, 752 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.76 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 5.37 (d, 1H, J = 4.2 Hz, CH), 6.18 (d, 1H, J = 4.2 Hz, CH), 6.73 (d, 1H, J = 8.4 Hz, Ar-H), 6.91 (dd, 1H, J_1 = 8.1 Hz, J_2 = 1.8 Hz, Ar-H), 6.99 (d, 1H, J = 1.8 Hz, Ar-H), 7.58-7.67 (m, 4H, Ar-H), 7.77-8.84 (m, 4H, Ar-H), 7.89-7.93 (m, 1H, Ar-H), 8.16-8.21 (m, 2H, Ar-H), 9.32-9.35 (m, 1H, Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 50.6 (CH), 55.8 and 56.0 ($2OCH_3$), 92.1 (CH), 111.4, 111.5, 115.8, 119.7, 122.6, 124.0, 126.0, 128.4, 128.7, 129.4, 129.7, 129.8, 129.9, 130.6, 131.7, 131.9, 132.2, 132.4, 132.5, 134.4, 140.1, 141.3, 141.8, 142.5, 148.3, 149.0 and 157.8 ($C_{olefinic}$ and C_{arom}), 193.0 (C=O) ppm; MS (*m/z*, %): 591 (M^+, 1), 454 (1), 407 (100), 345 (13), 182 (23), 57 (11); Anal. Calcd for $C_{33}H_{23}BrN_2O_4$: C, 67.01; H, 3.92; N, 4.74 %. Found: C, 67.19; H, 3.85; N, 4.90 %.

(4-Bromophenyl)(1-(2-hydroxy-3-methoxyphenyl)-1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazin-2-yl)methanone (6j)

Orange powder; yield 0.458 g (79%), mp 251-252 °C; IR (KBr): ν_{max} = 3025, 2900, 1674, 1620, 1581, 1524, 1468, 1416, 1392, 1337, 1220, 1133, 1063, 979, 809, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.82 (s, 3H, OCH_3), 5.67 (d, 1H, J = 3.0 Hz, CH), 6.55 (d, 1H, J = 3.0

Hz, CH), 6.74-6.77 (m, 1H, Ar-H), 6.85 (t, 1H, J = 7.8 Hz, Ar-H), 7.07 (d, 1H, J = 6.9 Hz, Ar-H), 7.55 (d, 2H, J = 8.4 Hz, Ar-H), 7.66-7.82 (m, 6H, Ar-H), 8.15-8.21 (m, 3H, Ar-H), 9.25-9.28 (m, 1H, Ar-H), 10.12 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 44.0 (CH), 56.0 (OCH_3), 90.3 (CH), 111.0, 116.1, 118.1, 121.5, 122.7, 124.1, 126.0, 127.5, 128.7, 129.0, 129.4, 129.8, 129.9, 130.2, 130.3, 130.7, 131.8, 132.1, 132.4, 140.3, 140.6, 141.9, 143.8, 150.5 and 158.5 ($C_{olefinic}$ and C_{arom}), 192.4 (C=O) ppm; MS (*m/z*, %): 577 (M^+, 1), 407 (1), 358 (96), 285 (100), 142 (6), 89 (4); Anal. Calcd for $C_{32}H_{21}BrN_2O_4$: C, 66.56; H, 3.67; N, 4.85 %. Found: C, 66.78; H, 3.90; N, 4.89 %.

(4-bromophenyl)(1-(4-chlorophenyl)-11-methyl-1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazin-2-yl)methanone (6k)

Yellow powder; yield 0.504 g (87%), mp 307-309 °C; IR (KBr): ν_{max} = 3025, 2910, 1690, 1624, 1593, 1530, 1501, 1405, 1352, 1315, 1225, 1132, 1047, 1003, 817, 761 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.54 (s, 3H, CH_3), 5.45 (d, 1H, J = 4.2 Hz, CH), 6.08 (d, 1H, J = 4.2 Hz, CH), 7.22 (d, 2H, J = 8.4 Hz, Ar-H), 7.32 (d, 2H, J = 8.4 Hz, Ar-H), 7.49 (dd, 1H, J_1 = 8.7 Hz, J_2 = 1.8 Hz, Ar-H), 7.61 (d, 2H, J = 8.4 Hz, Ar-H), 7.76-7.83 (m, 5H, Ar-H), 7.95 (s, 1H, Ar-H), 8.14-8.17 (m, 1H, Ar-H), 9.29-9.33 (m, 1H, Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9 (CH_3), 50.1 and 91.9 (2CH), 115.4, 122.6, 126.0, 128.2, 128.3, 128.4, 128.7, 129.0, 129.2, 129.4, 129.8, 130.6, 131.1, 132.3, 132.5, 132.6, 133.2, 135.0, 137.1, 137.2, 139.2, 140.5, 141.0, 157.4 and 157.7 ($C_{olefinic}$ and C_{arom}), 192.8 (C=O) ppm; MS (*m/z*, %): 579 (M^+, 1), 439 (1), 395 (27), 260 (100), 130 (12), 57 (14); Anal. Calcd for $C_{32}H_{20}BrClN_2O_2$: C, 66.28; H, 3.48; N, 4.83 %. Found: C, 66.45; H, 3.51; N, 4.98 %.

(4-bromophenyl)(11-methyl-1-(4-nitrophenyl)-1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazin-2-yl)methanone (6l)

Yellow powder; yield 0.511 g (87%), mp 296-297 °C; IR (KBr): ν_{max} = 3045, 2900, 1690, 1629, 1594, 1563, 1508, 1480, 1391, 1330, 1226, 1144, 1062, 943, 820, 761 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.51 (s, 3H, CH_3), 5.72 (d, 1H, J = 4.5 Hz, CH), 6.07 (d, 1H, J = 4.5 Hz, CH), 7.49-7.64 (m, 6H, Ar-H), 7.76-7.88 (m, 5H, Ar-H), 8.09-8.13 (m, 3H, Ar-H), 9.32-9.35 (m, 1H, Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7 (CH_3), 51.2 and 90.4 (2CH), 110.9, 115.9, 118.1, 121.5, 122.8, 124.1, 126.1, 127.4, 128.8, 129.0, 129.4, 129.7, 129.9, 130.2, 130.4, 130.6, 131.8, 132.0, 132.4, 140.2, 140.6, 141.8, 143.9, 150.6 and 158.4 ($C_{olefinic}$ and C_{arom}), 192.3 (C=O) ppm; MS (*m/z*, %): 590 (M^+, 1), 406 (100), 360 (20), 284 (7), 184

(16), 57 (20); Anal. Calcd for $C_{32}H_{20}BrN_3O_4$: C, 65.10; H, 3.41; N, 7.12 %. Found: C, 65.33; H, 3.52; N, 7.01 %.

(4-Bromophenyl)(11-methyl-1-(*p*-tolyl)-1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazin-2-yl)methanone (6m)

Brown powder; yield 0.449 g (80%), mp 205-207 °C; IR (KBr): ν_{max} = 2995, 2910, 1692, 1631, 1595, 1532, 1502, 1479, 1396, 1331, 1223, 1147, 1049, 950, 820, 758 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.33 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 5.48 (d, 1H, J = 4.2 Hz, CH), 6.23 (d, 1H, J = 3.9 Hz, CH), 7.16 (d, 2H, J = 7.2 Hz, Ar-H), 7.38 (d, 2H, J = 7.8 Hz, Ar-H), 7.53-7.58 (m, 2H, Ar-H), 7.68 (d, 2H, J = 8.4 Hz, Ar-H), 7.82-8.82 (m, 5H, Ar-H), 8.27-8.30 (m, 1H, Ar-H), 9.37-9.41 (m, 1H, Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1 and 21.9 ($2CH_3$), 50.6 and 92.1 (2CH), 116.0, 122.5, 123.8, 125.8, 125.9, 127.4, 127.7, 128.1, 128.3, 128.5, 128.6, 129.1, 129.3, 129.6, 129.7, 130.6, 131.0, 132.2, 132.3, 132.5, 137.0, 138.8, 139.0, 140.3, 141.1, 142.6, 157.4 and 157.7 ($C_{olefinic}$ and C_{arom}), 193.0 (C=O) ppm; MS (*m/z*, %): 559 (M^+, 1), 440 (2), 375 (100), 260 (20), 183 (10), 57 (3); Anal. Calcd for $C_{33}H_{23}BrN_2O_2$: C, 70.85; H, 4.14; N, 5.01 %. Found: C, 70.77; H, 3.37; N, 5.25 %.

(4-Bromophenyl)(1-(4-chlorophenyl)-10-nitro-1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazin-2-yl)methanone (6n)

Yellow powder; yield 0.518 g (85%), mp 275-277 °C; IR (KBr): ν_{max} = 3055, 2900, 1684, 1625, 1590, 1551, 1514, 1415, 1388, 1332, 1220, 1125, 1046, 1005, 818, 761 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 5.43 (d, 1H, J = 4.5 Hz, CH), 6.16 (d, 1H, J = 4.5 Hz, CH), 7.23-7.35 (m, 4H, Ar-H), 7.63 (d, 2H, J = 8.7 Hz, Ar-H), 7.80-7.88 (m, 4H, Ar-H), 8.00 (d, 1H, J = 9.3 Hz, Ar-H), 8.19-8.22 (m, 1H, Ar-H), 8.40 (dd, 1H, J_1 = 8.7 Hz, J_2 = 2.4 Hz, Ar-H), 9.11 (d, 1H, J = 2.4 Hz, Ar-H), 9.31-9.35 (m, 1H, Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 49.8 and 92.2 (2CH), 115.6, 122.9, 123.1, 126.4, 126.5, 128.6, 128.8, 128.9, 129.0, 129.1, 129.2, 129.8, 130.2, 130.6, 131.0, 132.4, 132.5, 139.8, 140.4, 141.3, 141.5, 142.5 and 157.9 ($C_{olefinic}$ and C_{arom}), 192.2 (C=O) ppm; MS (*m/z*, %): 610 (M^+, 1), 551 (1), 426 (53), 291 (100), 182 (23), 43 (44); Anal. Calcd for $C_{31}H_{17}BrClN_3O_4$: C, 60.95; H, 2.81; N, 6.88 %. Found: C, 70.19; H, 2.88; N, 6.98 %.

(4-bromophenyl)(10-nitro-1-(4-nitrophenyl)-1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazin-2-yl)methanone (6o)

Yellow powder; yield 0.544 g (88%), mp 312-314 °C; IR (KBr): ν_{max} = 3070, 2910, 1688, 1629, 1589, 1552, 1510, 1412, 1386, 1337, 1225, 1141, 1046, 979, 822, 762 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 5.69 (d, 1H, J = 4.5 Hz, CH), 6.16 (d, 1H, J = 4.5 Hz, CH), 7.53-7.59 (m, 2H, Ar-H), 7.65 (d, 2H, J = 8.7 Hz, Ar-H), 7.88-7.89 (m, 4H, Ar-H), 8.13-8.20 (m, 3H, Ar-H), 8.33 (d, 1H, J = 9.3 Hz, Ar-H), 8.42 (dd, 1H, J_1 = 9.3 Hz, J_2 = 2.4 Hz, Ar-H), 8.80 (d, 1H, J = 2.4 Hz, Ar-H), 9.34-9.37 (m, 1H, Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.1 and 90.5 (2CH), 113.8, 115.8, 122.2, 123.4, 125.3, 125.5, 127.1, 128.1, 129.2, 130.3, 130.4, 130.9, 131.0, 132.2, 133.0, 133.5, 137.3, 139.9, 140.2, 141.1, 141.7, 143.0 and 157.3 ($C_{olefinic}$ and C_{arom}), 191.7 (C=O) ppm; MS (*m/z*, %): 621 (M^+, 1), 577 (2), 437 (17), 375 (65), 184 (33), 43 (100); Anal. Calcd for $C_{31}H_{17}BrN_4O_6$: C, 59.92; H, 2.76; N, 9.02 %. Found: C, 60.11; H, 2.59; N, 8.90 %.

(4-bromophenyl)(1-(2-chlorophenyl)-10-nitro-1,2-dihydrobenzo[*a*]furo[2,3-*c*]phenazin-2-yl)methanone (6p)

Yellow powder; yield 0.521 g (85%), mp 300 °C; IR (KBr): ν_{max} = 3030, 2900, 1686, 1627, 1583, 1526, 1493, 1409, 1386, 1333, 1223, 1145, 1048, 1004, 808, 757 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.07 (d, 1H, J = 4.2 Hz, CH), 6.18 (d, 1H, J = 4.2 Hz, CH), 7.06-7.14 (m, 3H, Ar-H), 7.34 (d, 1H, J = 7.8 Hz, Ar-H), 7.62 (d, 2H, J = 8.4 Hz, Ar-H), 7.83-7.88 (m, 4H, Ar-H), 8.14-8.17 (m, 1H, Ar-H), 8.32 (d, 1H, J = 9.3 Hz, Ar-H), 8.40 (dd, 1H, J_1 = 9.3 Hz, J_2 = 2.4 Hz, Ar-H), 8.83 (d, 1H, J = 2.4 Hz, Ar-H), 9.34-9.37 (m, 1H, Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 50.3 and 91.3 (2CH), 113.9, 122.9, 125.2, 125.3, 127.1, 127.2, 128.1, 128.2, 128.9, 129.0, 129.1, 129.6, 129.7, 129.9, 131.6, 132.2, 132.8, 132.9, 140.1, 140.5, 141.4, 141.5, 142.8 and 156.9 ($C_{olefinic}$ and C_{arom}), 192.5 (C=O) ppm; MS (*m/z*, %): 610 (M^+, 1), 572 (1), 426 (100), 316 (20), 182 (20), 76 (6); Anal. Calcd for $C_{31}H_{17}BrClN_3O_4$: C, 60.95; H, 2.81; N, 6.88 %. Found: C, 61.12; H, 2.94; N, 6.71 %.

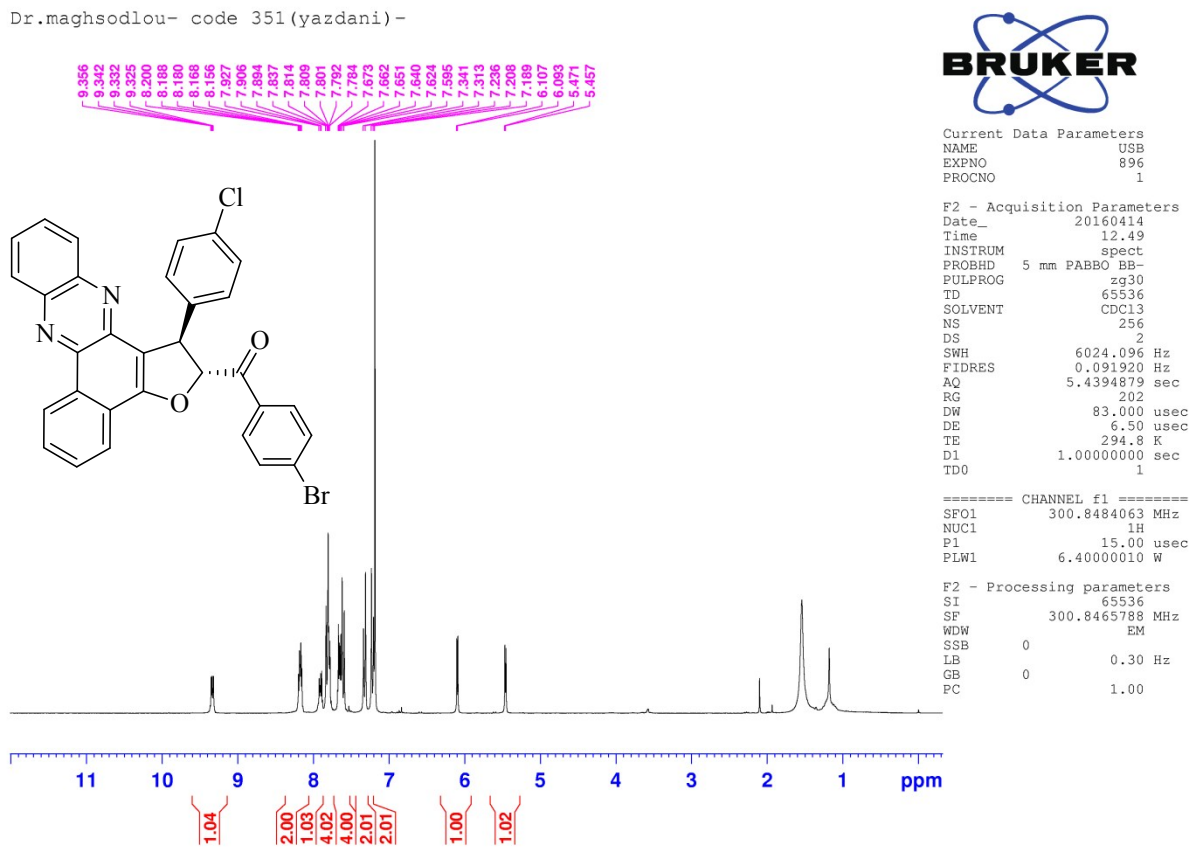

Figure 1: ^{1}H NMR spectrum of compound **6a** (300 MHz, $CDCl_3$).

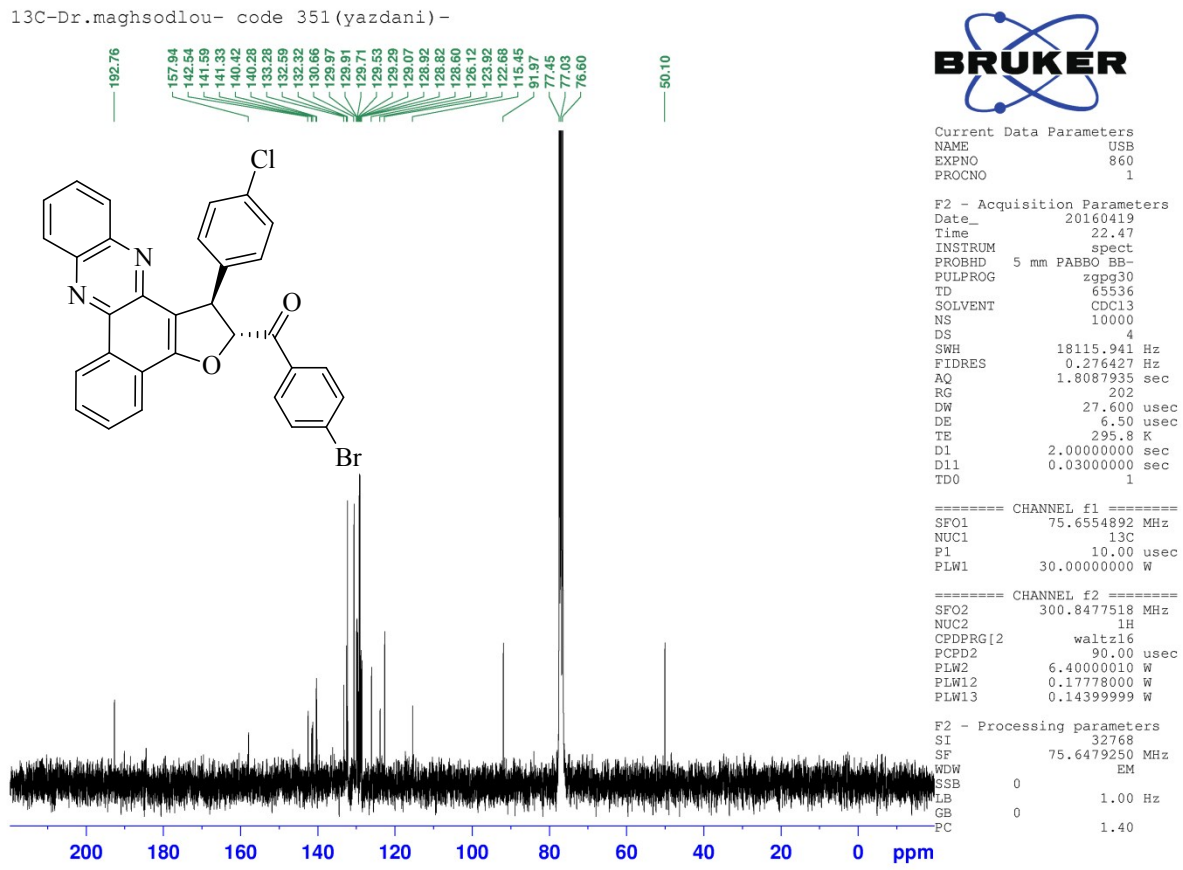

Figure 2: ^{13}C NMR spectrum of compound **6a** (75 MHz, $CDCl_3$).

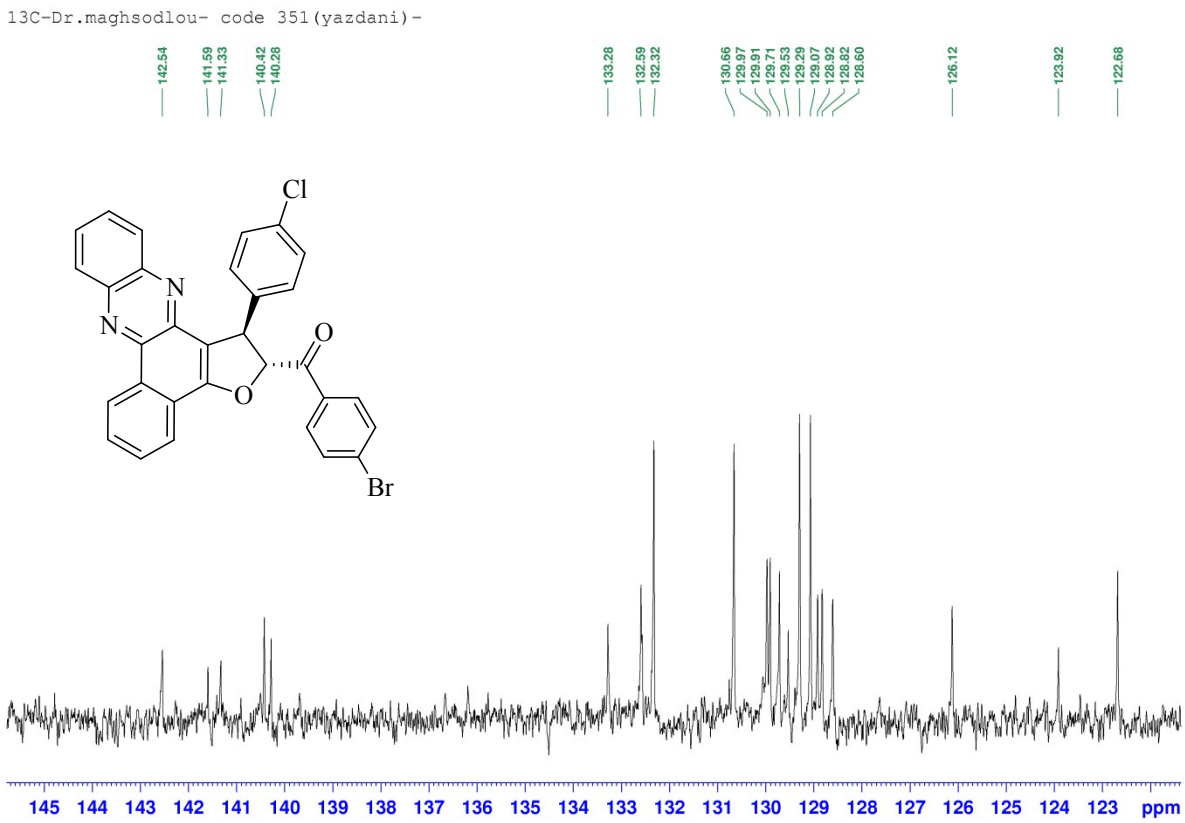

Figure 3: Expanded ^{13}C NMR spectrum of compound **6a** (75 MHz, $CDCl_3$).

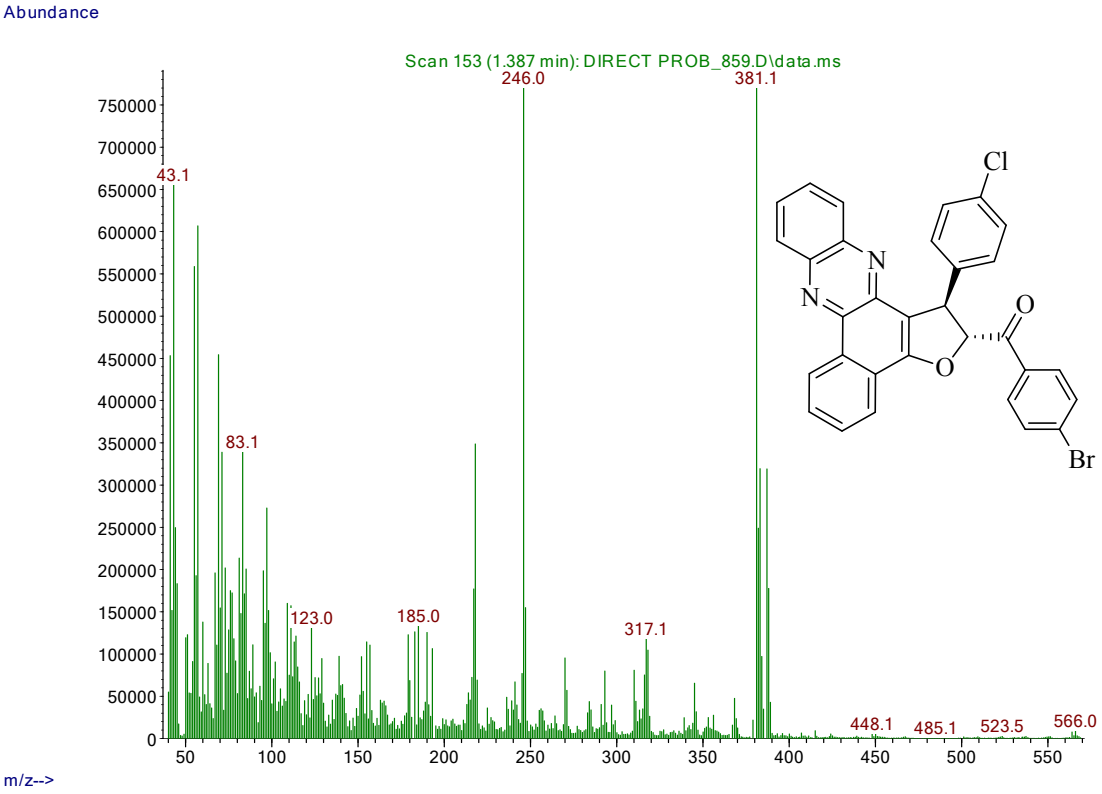

Figure 4: Mass spectrum of compound **6a**.

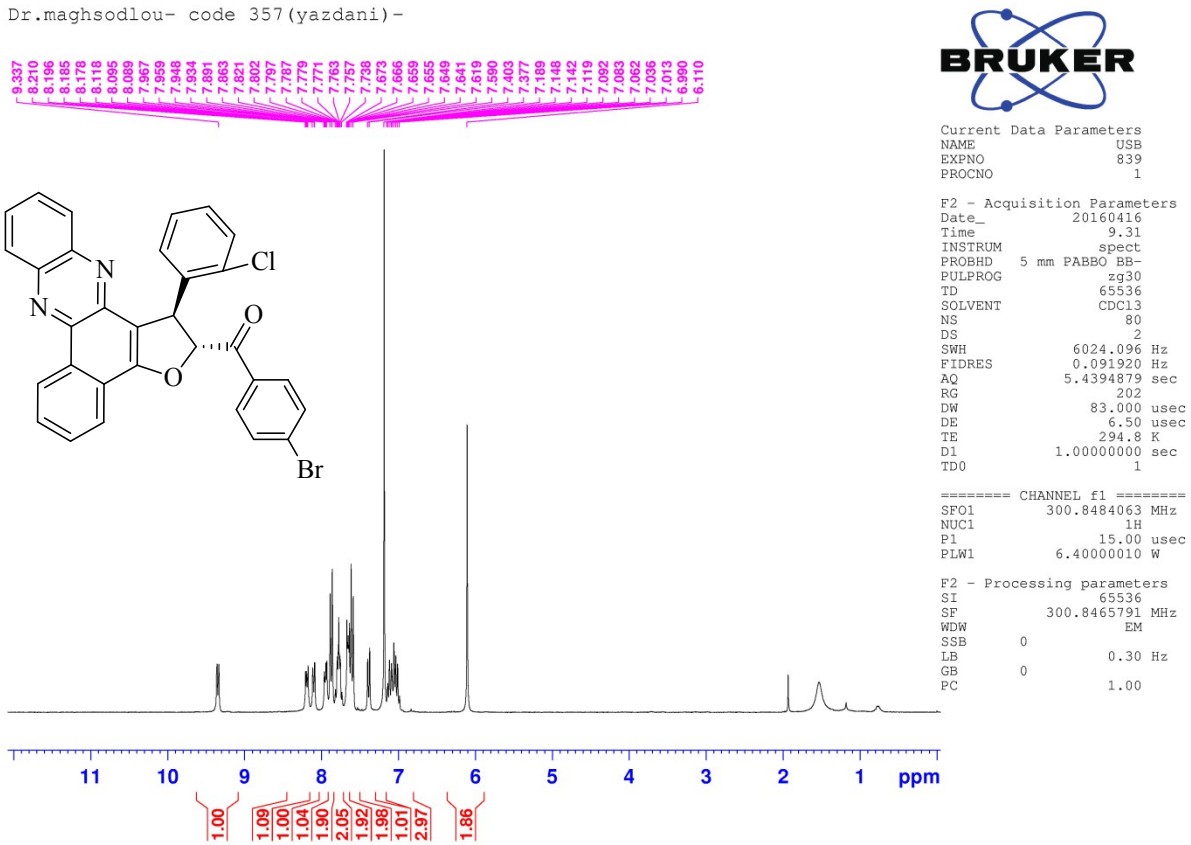

Figure 5: ^{1}H NMR spectrum of compound **6b** (300 MHz, $CDCl_3$).

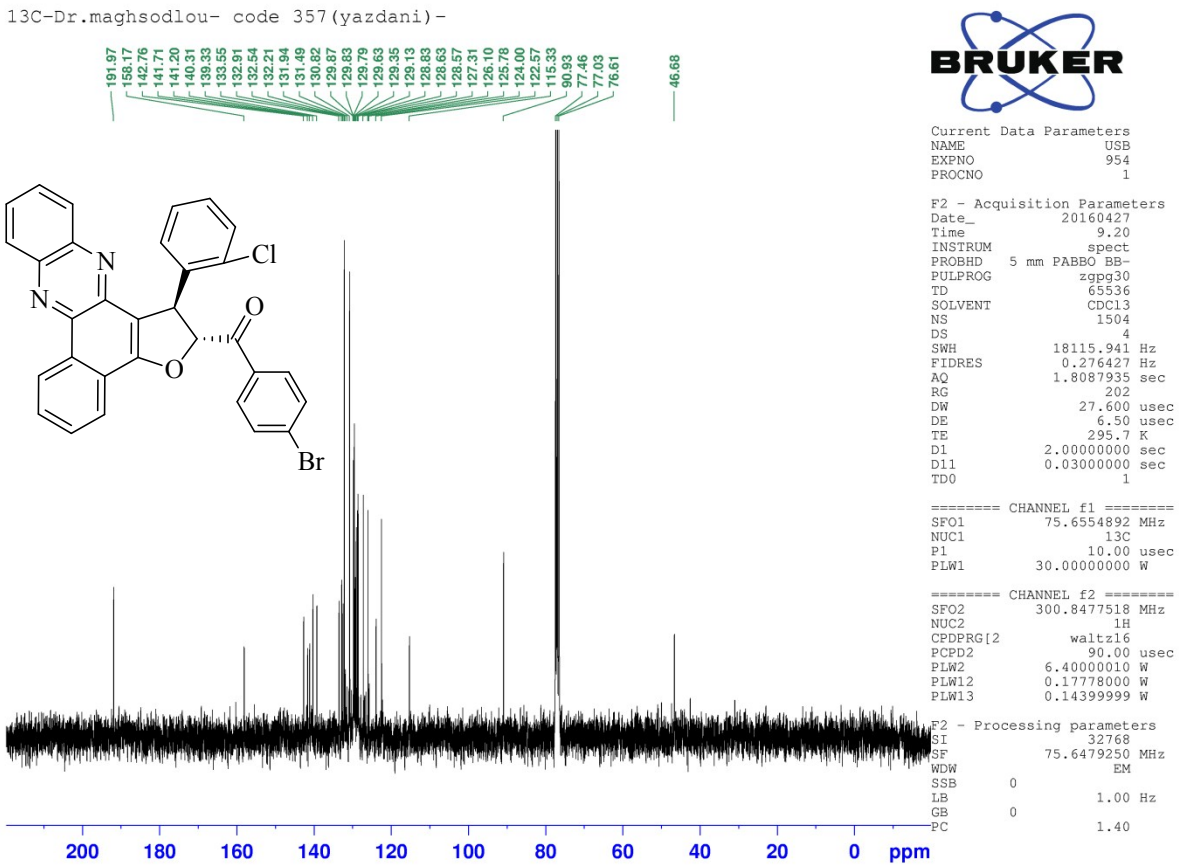

Figure 6: ^{13}C NMR spectrum of compound **6b** (75 MHz, $CDCl_3$).

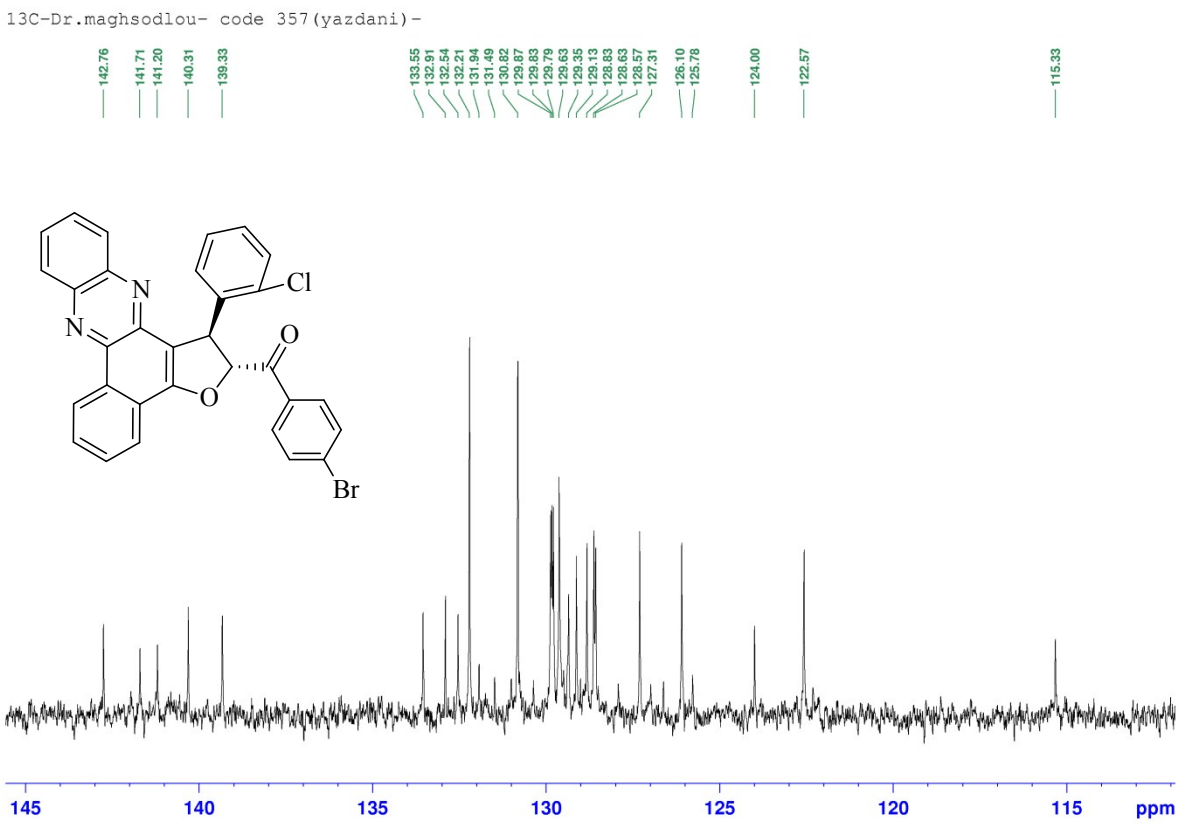

Figure 7: Expanded ^{13}C NMR spectrum of compound **6b** (75 MHz, $CDCl_3$).

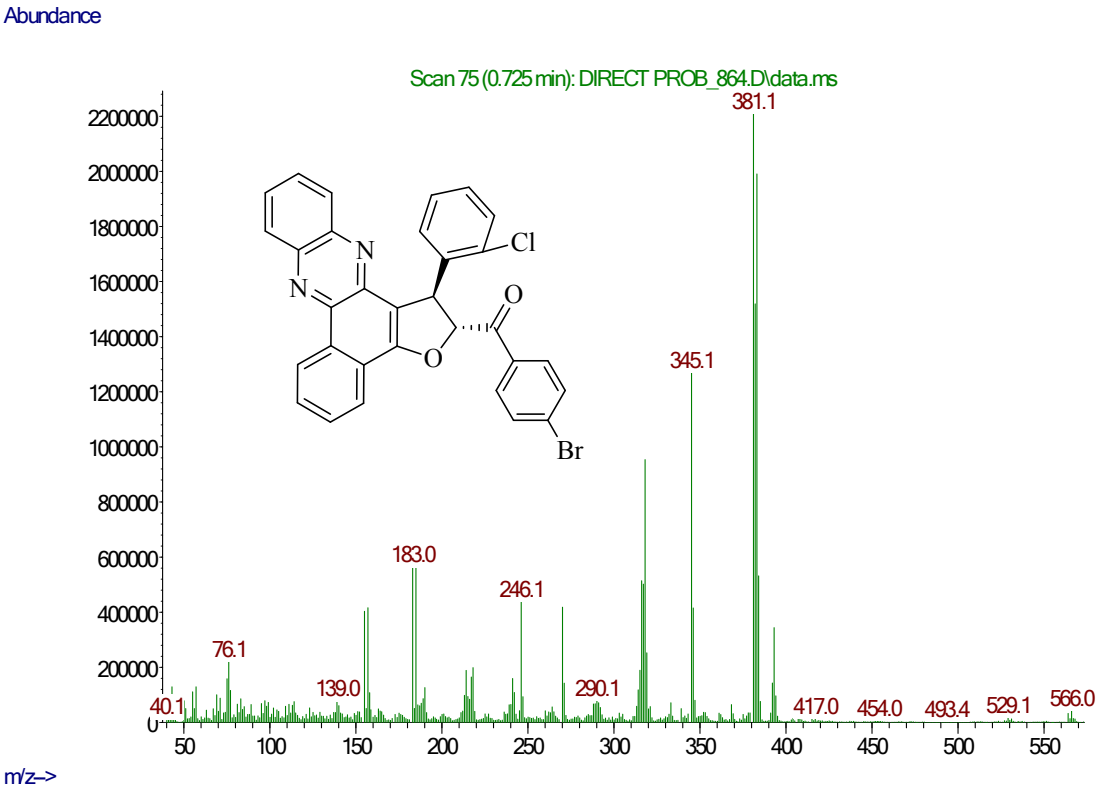

Figure 8: Mass spectrum of compound **6b**.

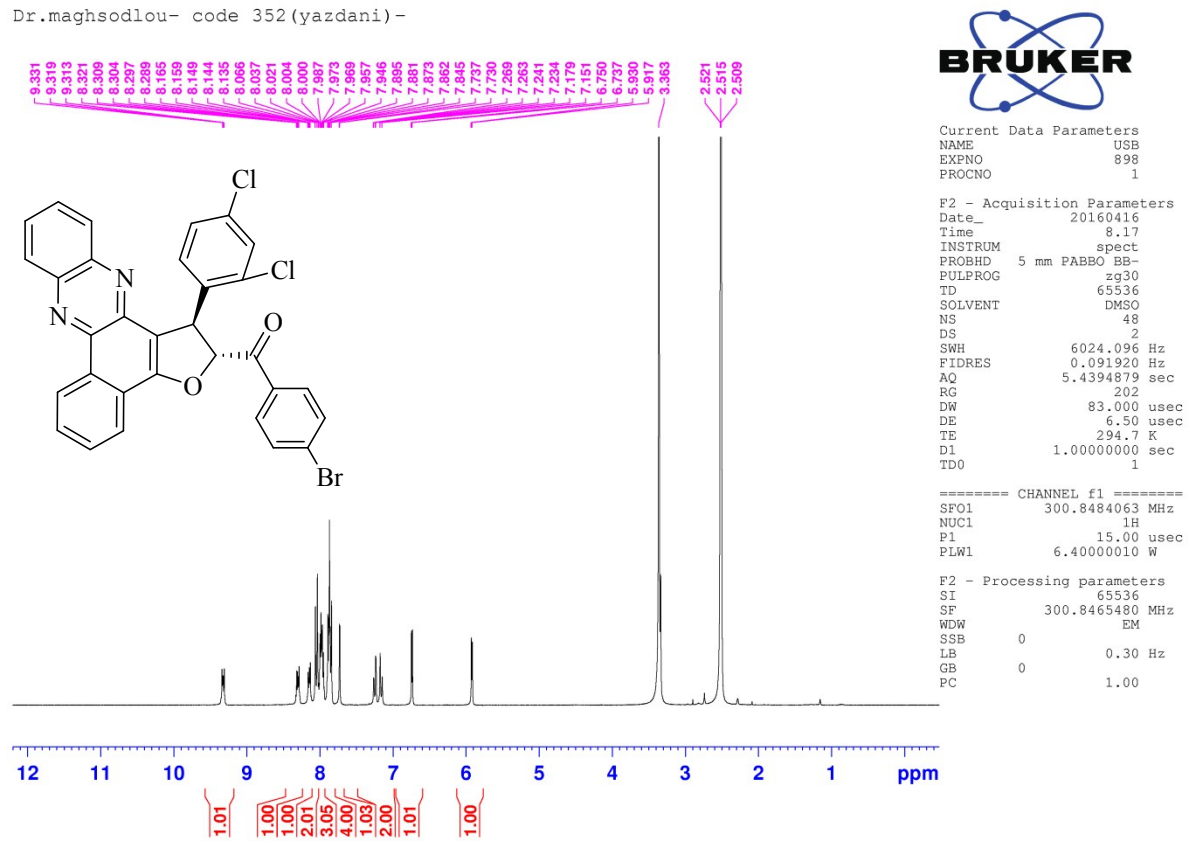

Figure 9: ^{1}H NMR spectrum of compound **6c** (300 MHz, DMSO).

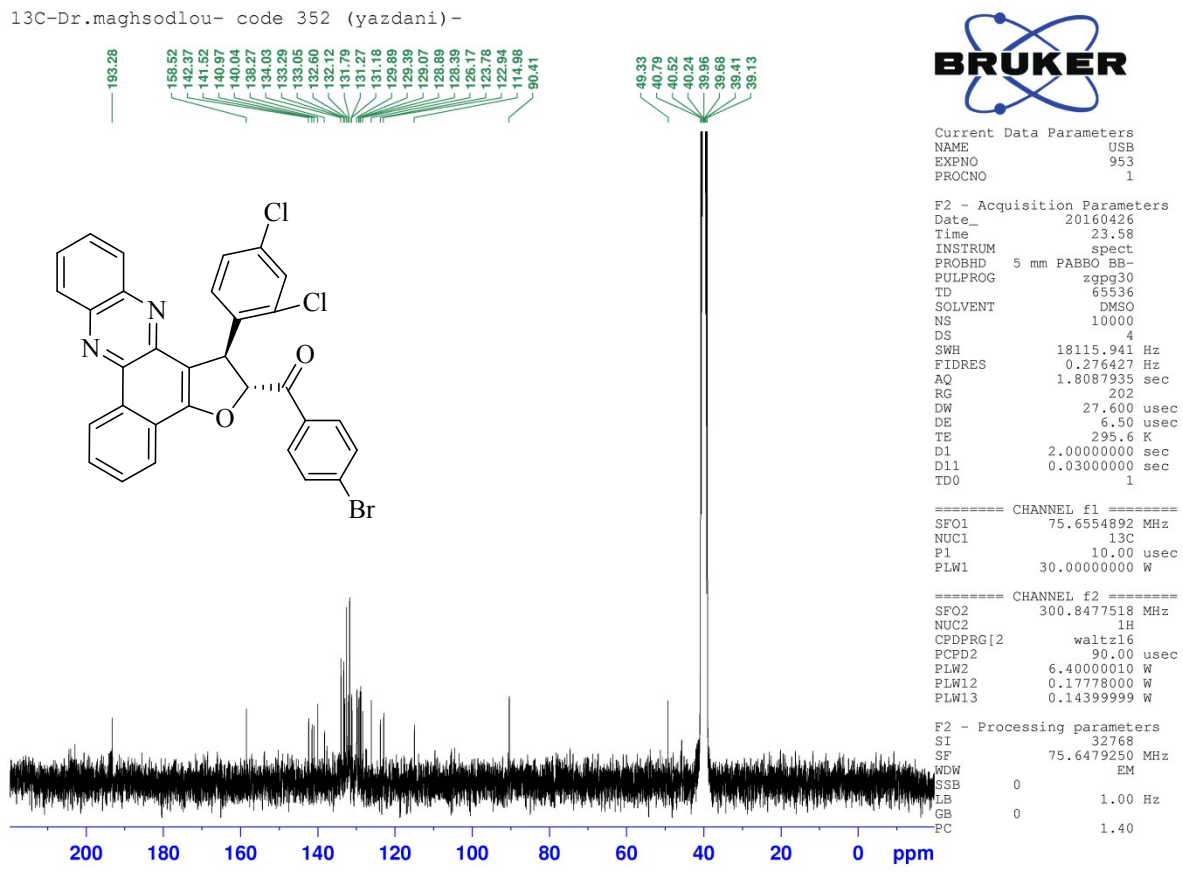

Figure 10: ^{13}C NMR spectrum of compound **6c** (75 MHz, DMSO).

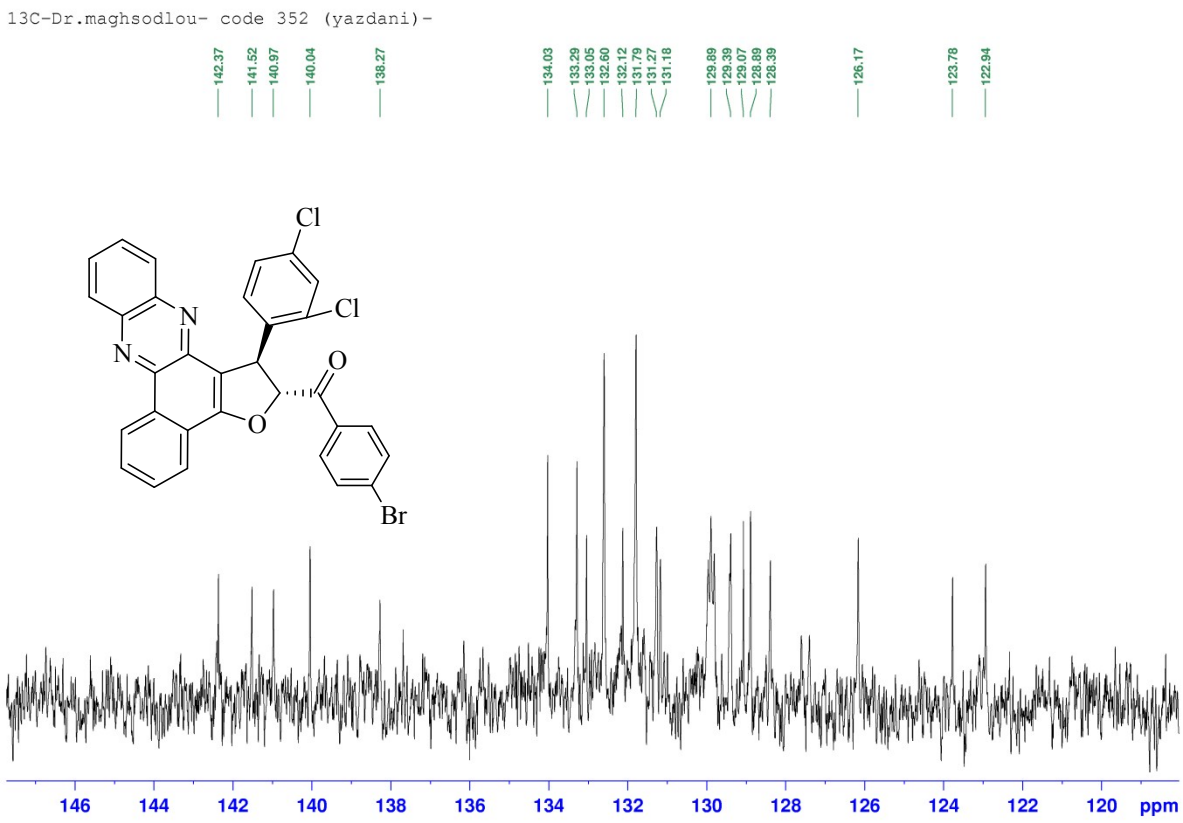

Figure 11: Expanded ^{13}C NMR spectrum of compound **6c** (75 MHz, $CDCl_3$).

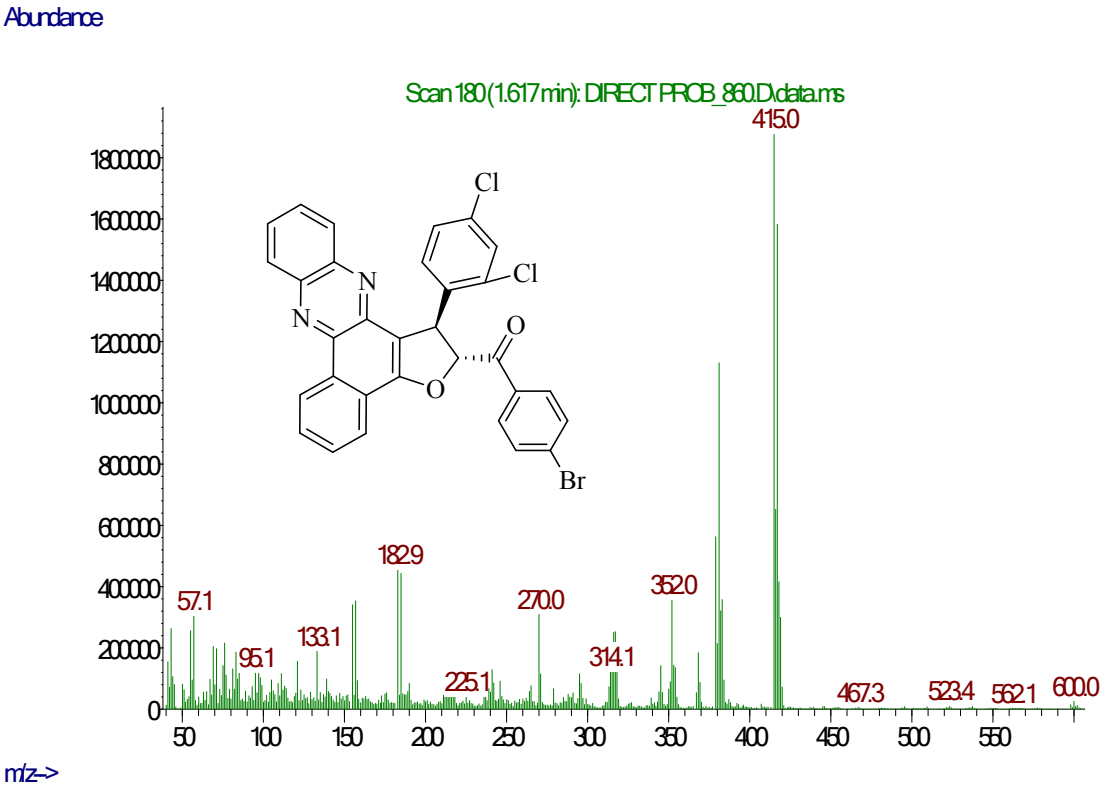

Figure 12: Mass spectrum of compound **6c**.

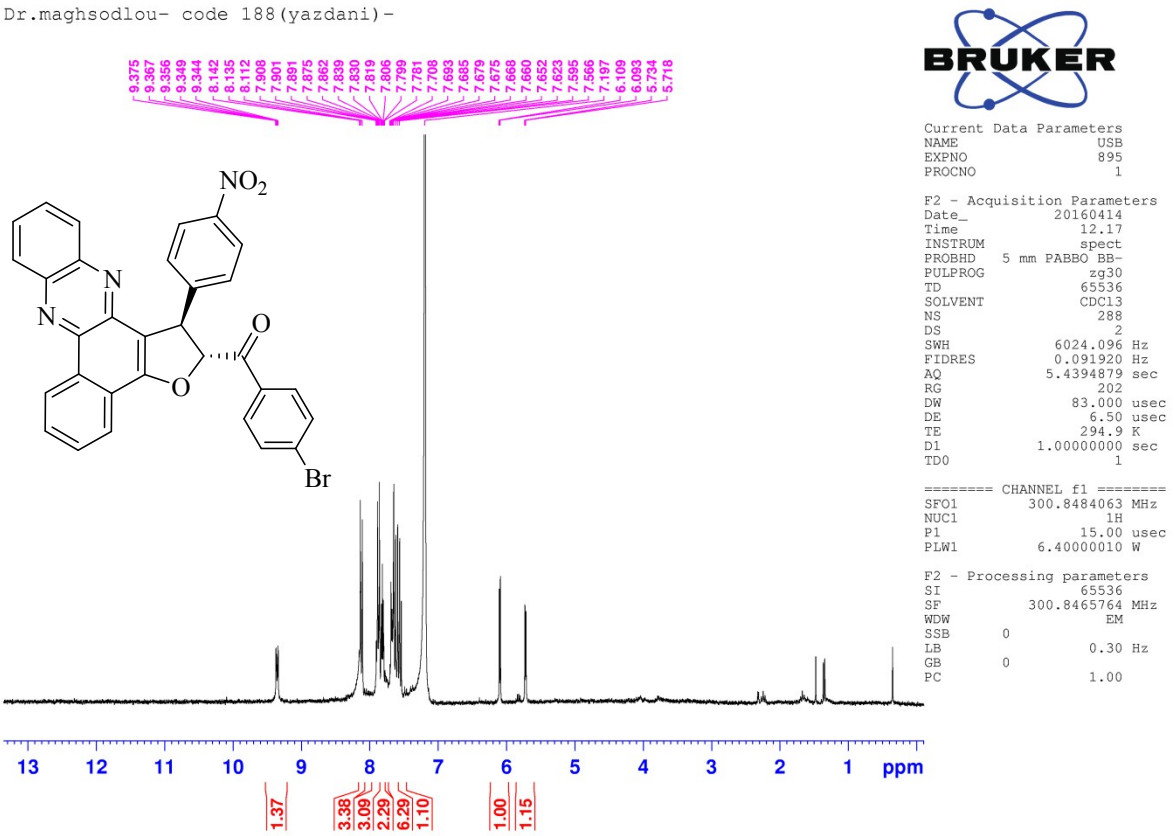

Figure 12: ^{1}H NMR spectrum of compound **6d** (300 MHz, $CDCl_3$).

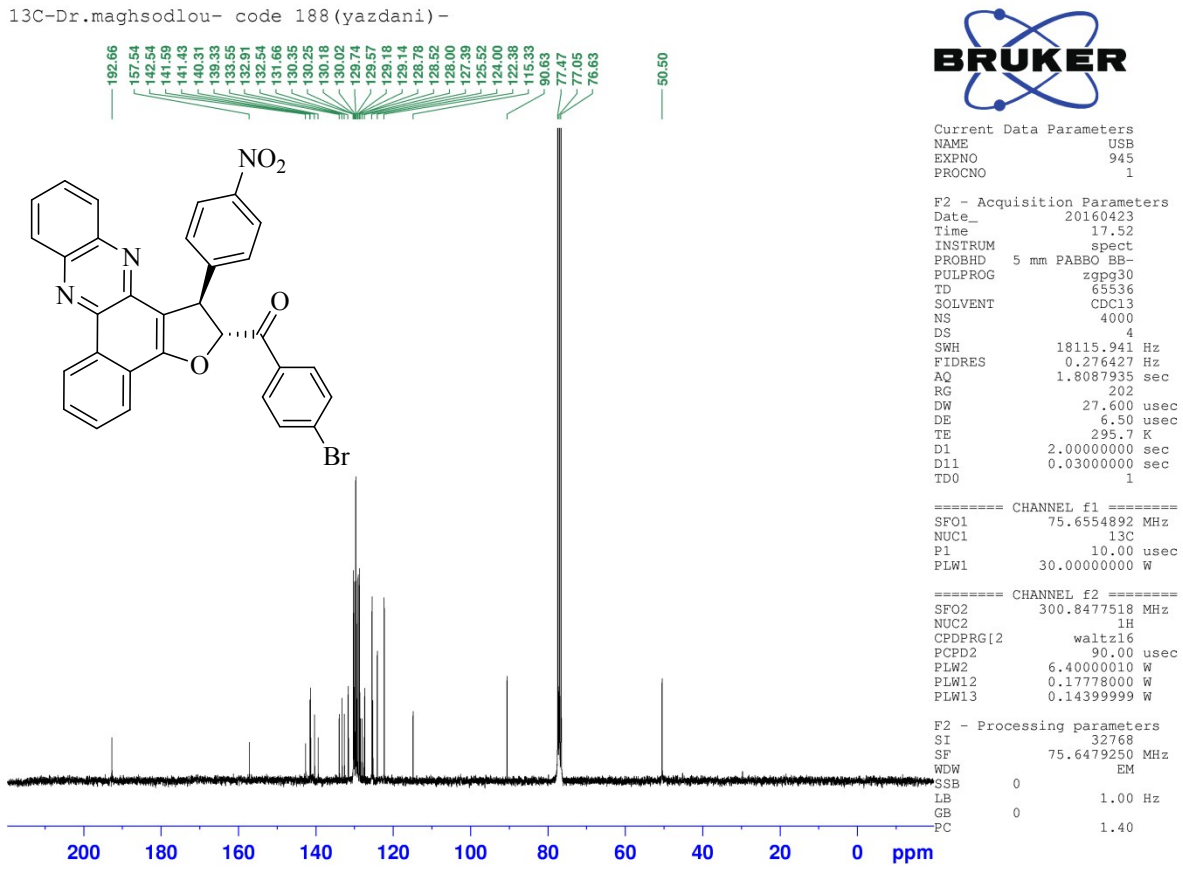

Figure 14: ^{13}C NMR spectrum of compound **6d** (75 MHz, $CDCl_3$).

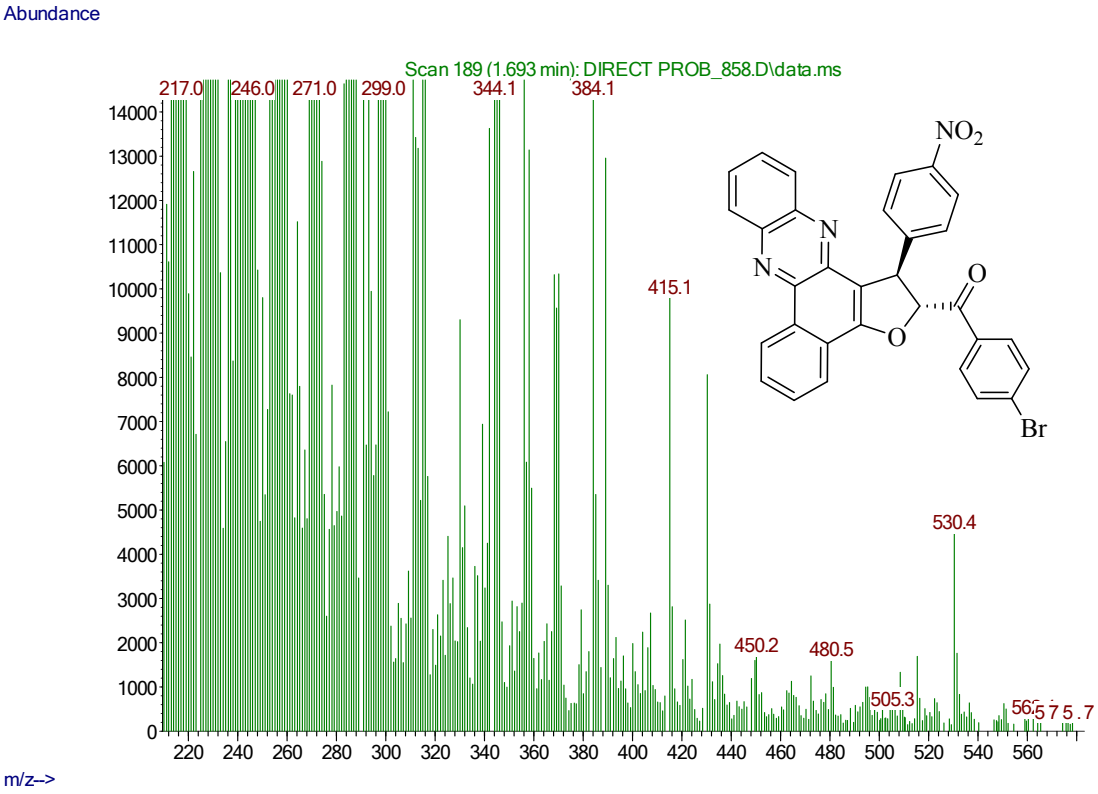

Figure 15: Mass spectrum of compound **6d**.

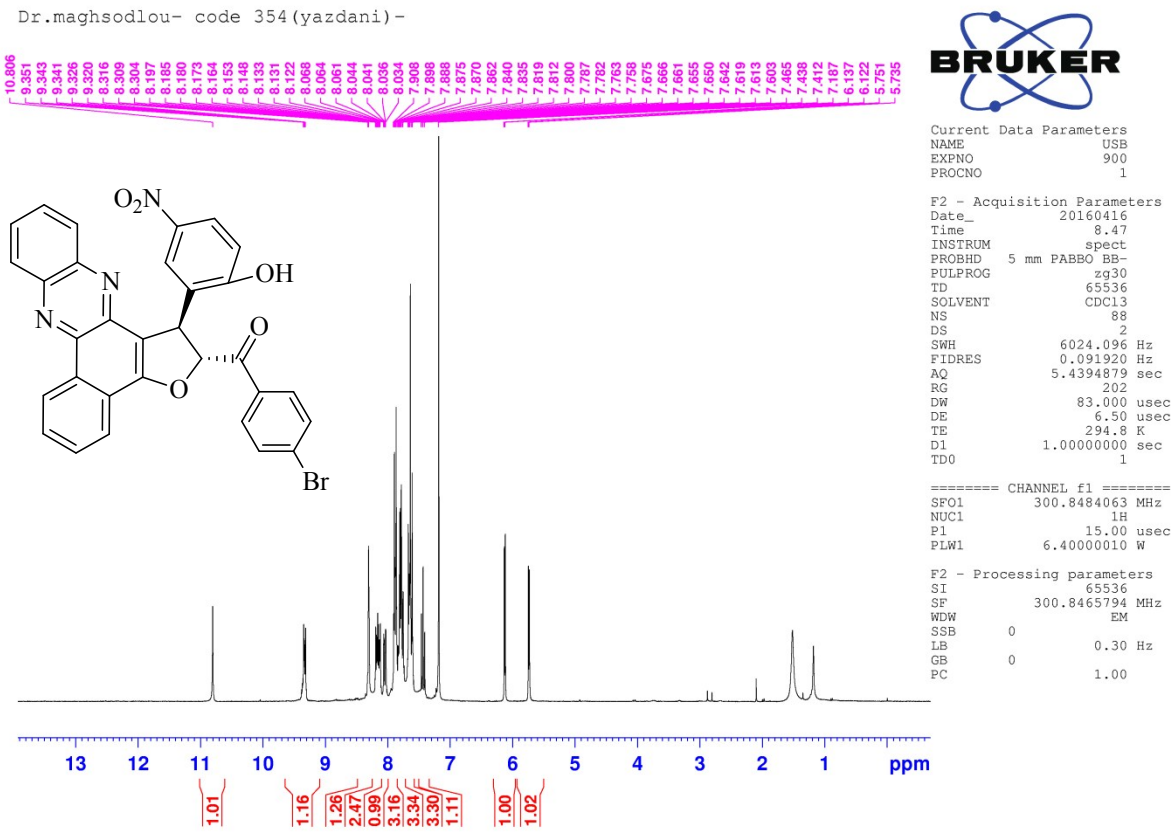

Figure 16: ^{1}H NMR spectrum of compound **6e** (300 MHz, $CDCl_3$).

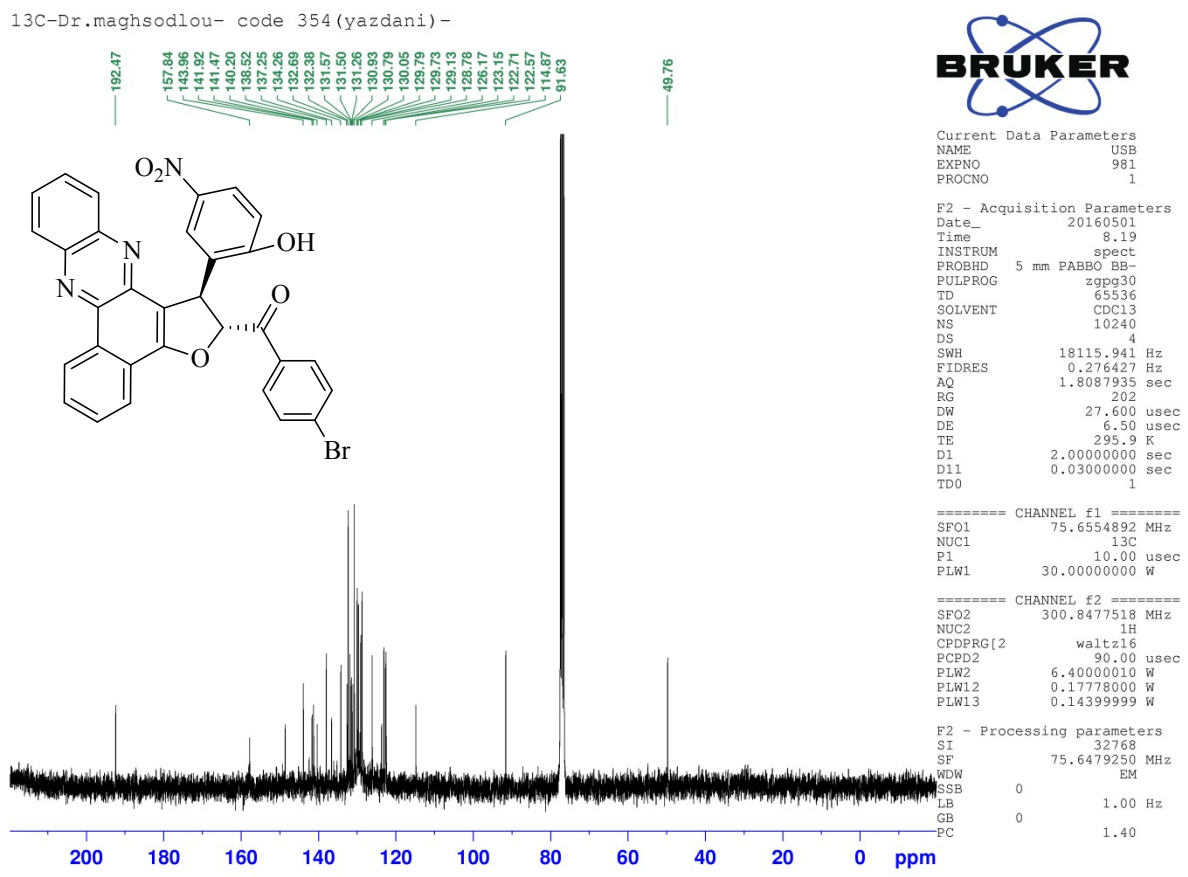

Figure 17: ^{13}C NMR spectrum of compound **6e** (75 MHz, $CDCl_3$).

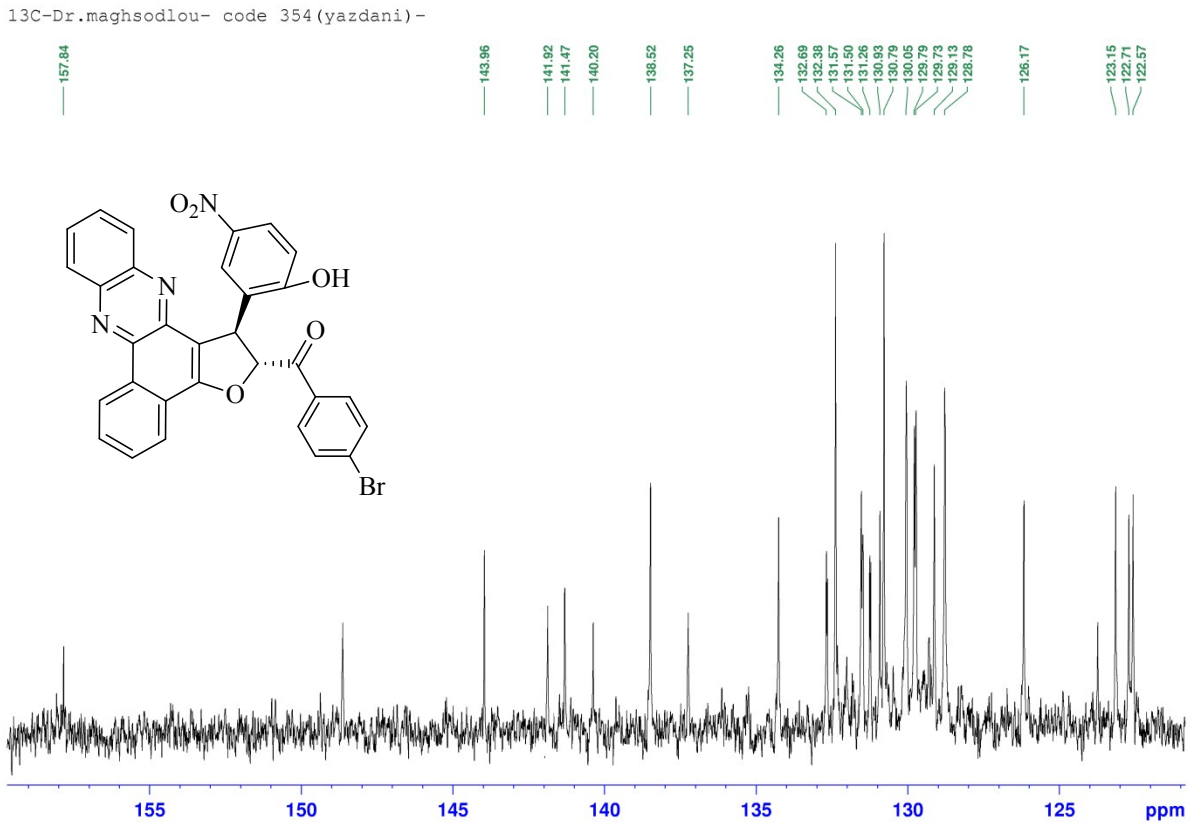

Figure 18: Expanded ^{13}C NMR spectrum of compound **6e** (75 MHz, $CDCl_3$).

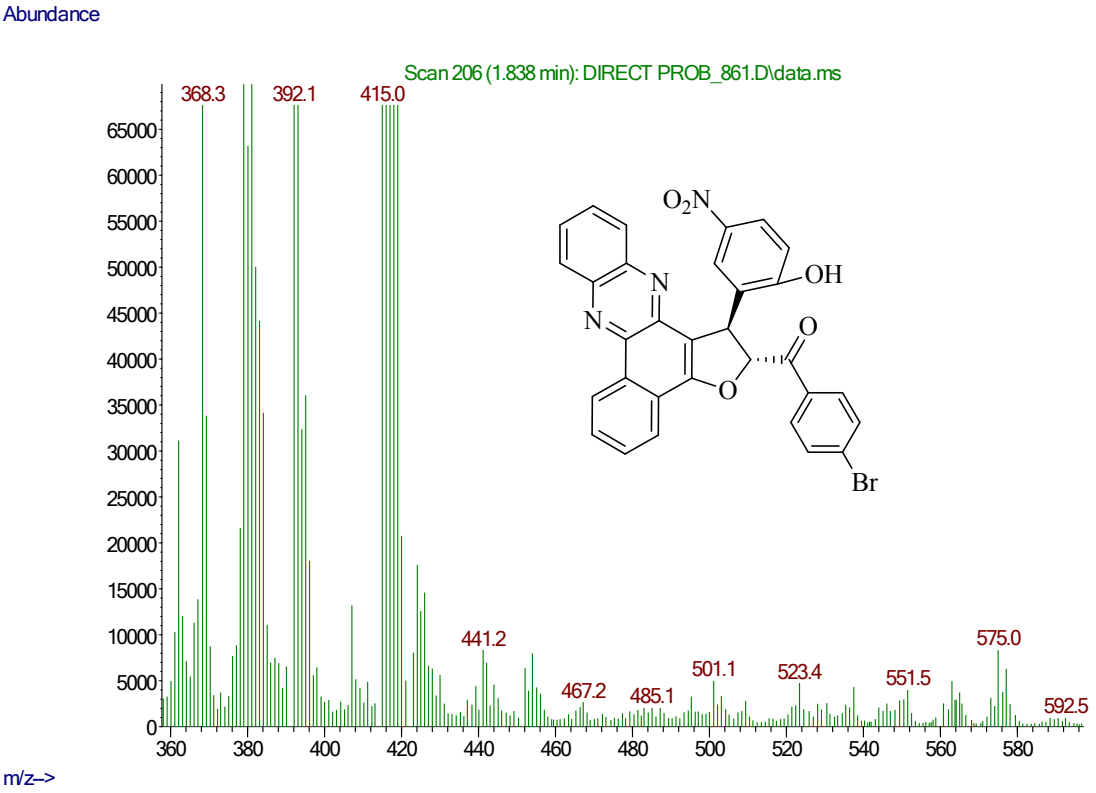

Figure 19: Mass spectrum of compound **6e**.

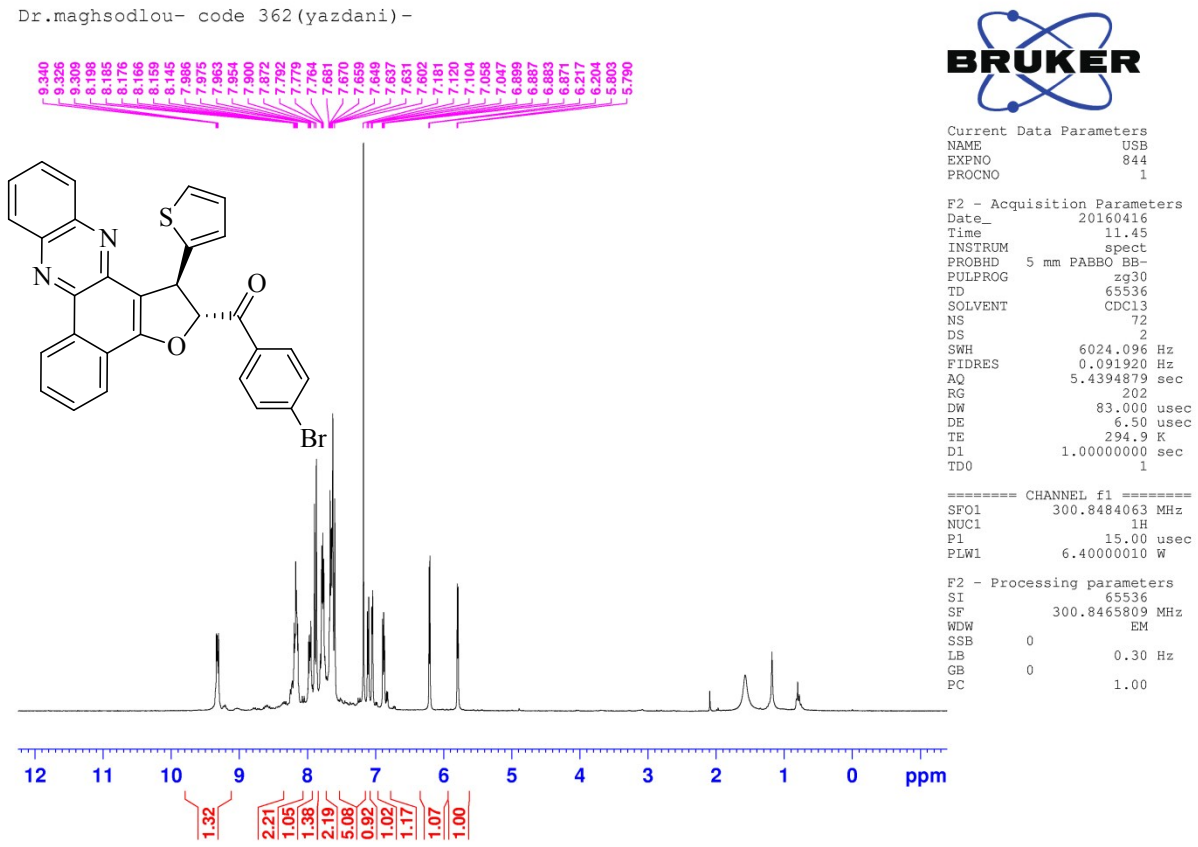

Figure 20: ^{1}H NMR spectrum of compound **6f** (300 MHz, $CDCl_3$).

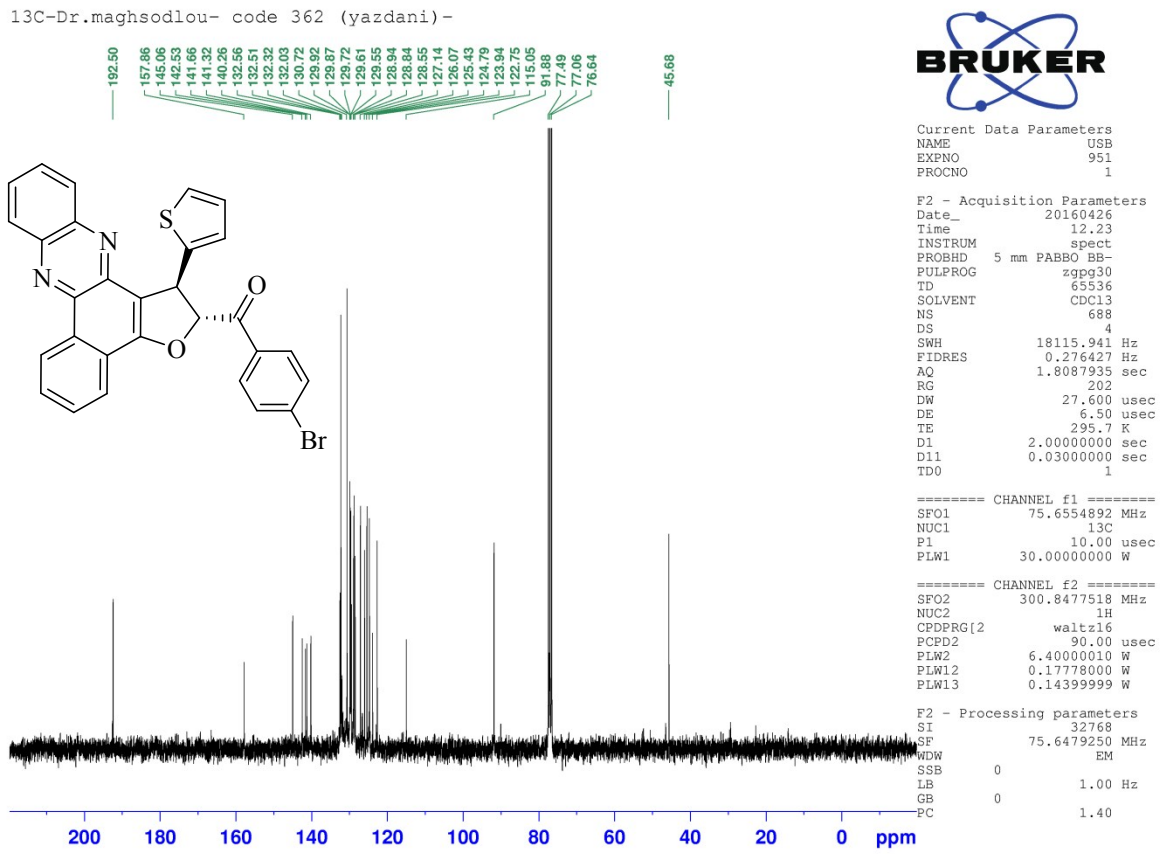

Figure 21: ^{13}C NMR spectrum of compound **6f** (75 MHz, $CDCl_3$).

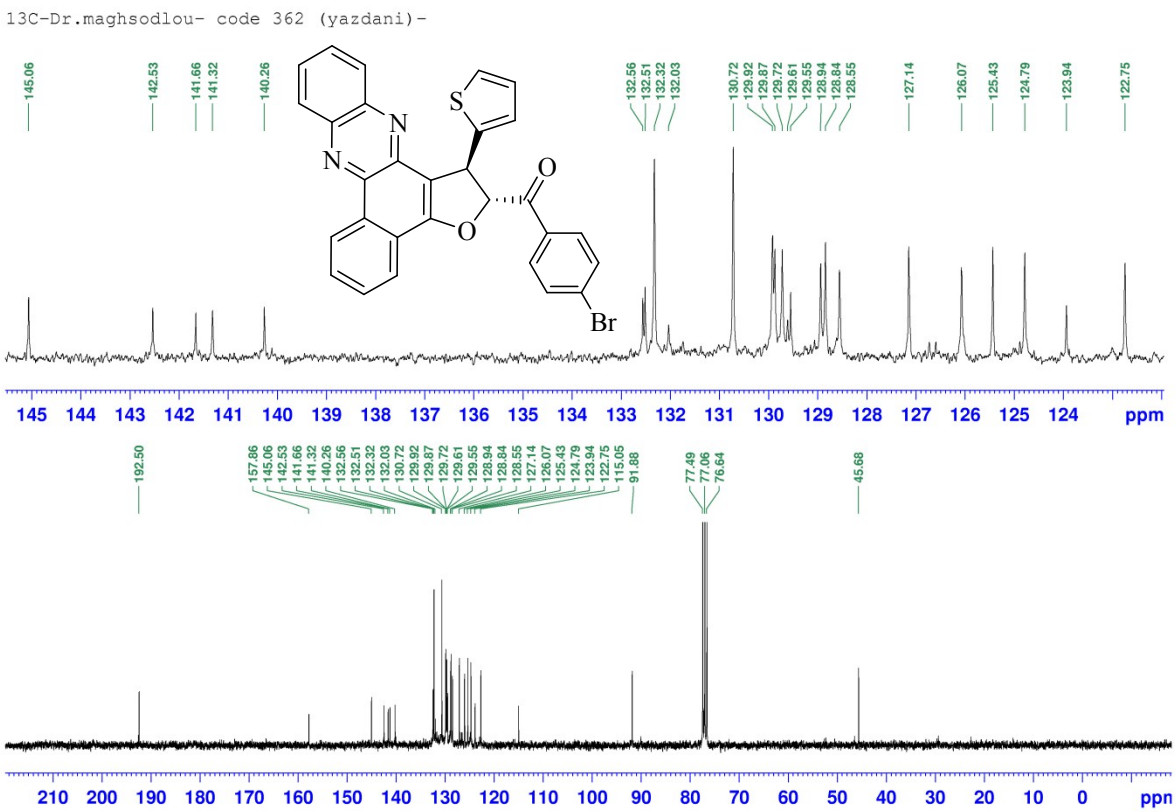

Figure 22: Expanded ^{13}C NMR spectrum of compound **6f** (75 MHz, $CDCl_3$).

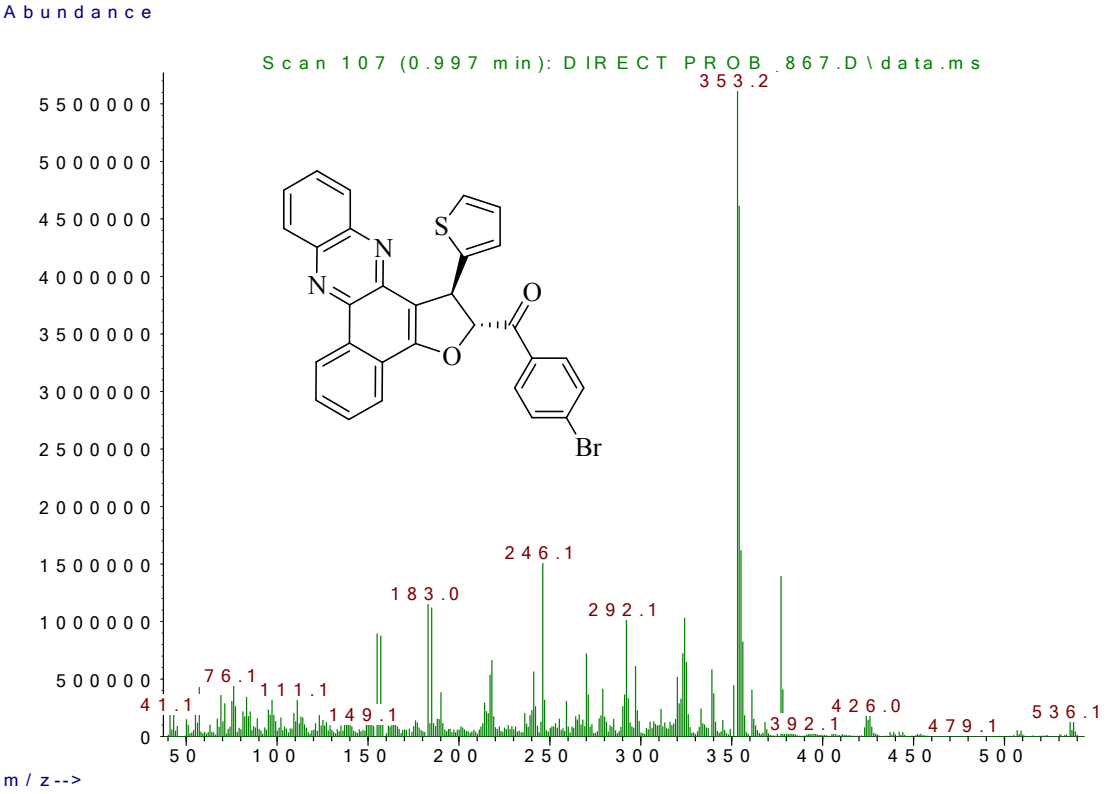

Figure 23: Mass spectrum of compound **6f**.

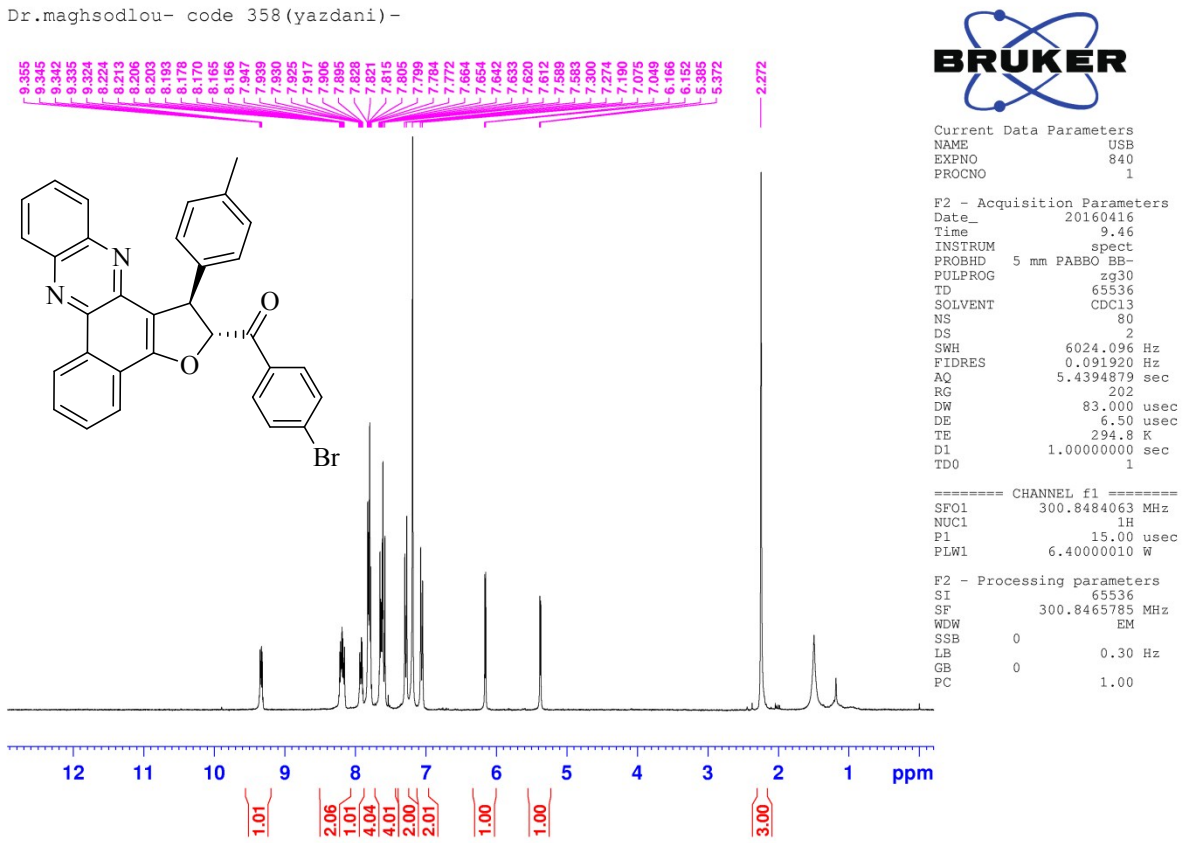

Figure 24: ^{1}H NMR spectrum of compound **6g** (300 MHz, $CDCl_3$).

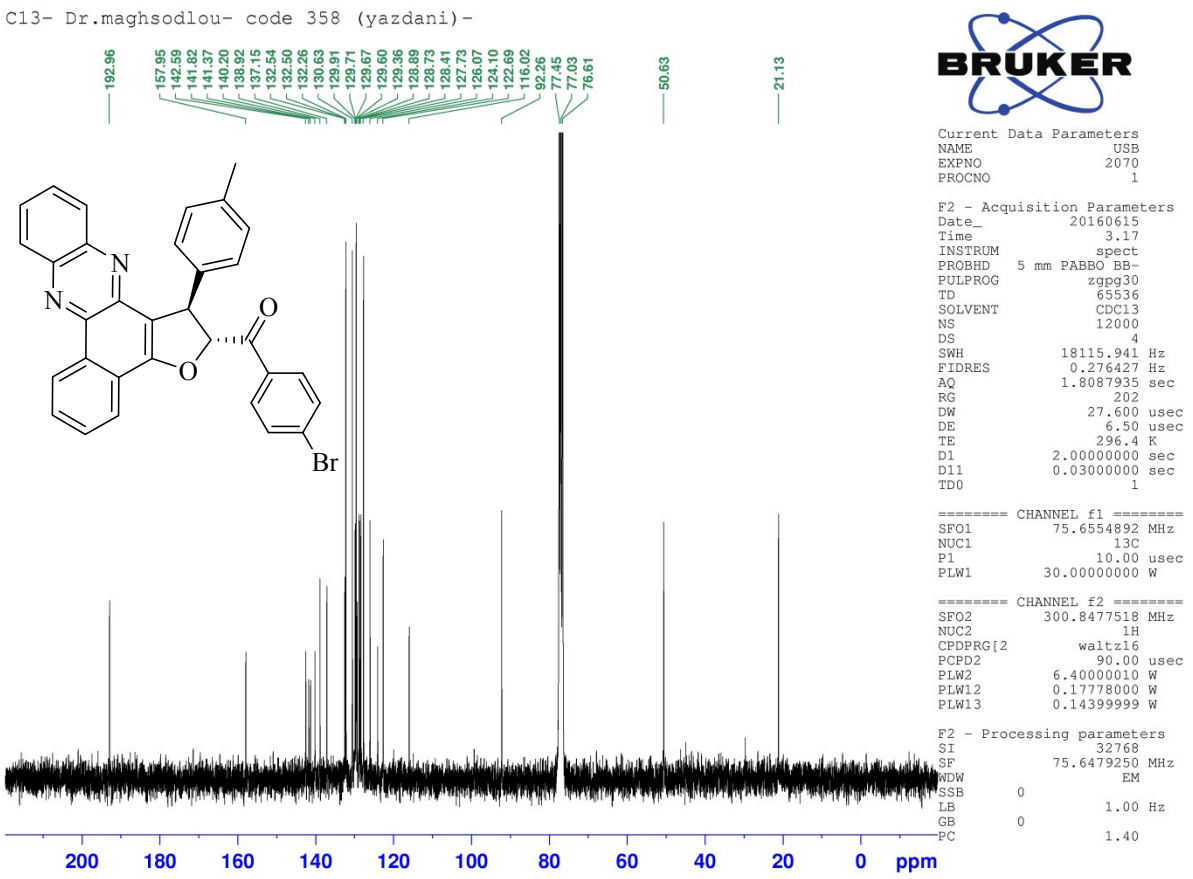

Figure 25: ^{13}C NMR spectrum of compound **6g** (75 MHz, $CDCl_3$).

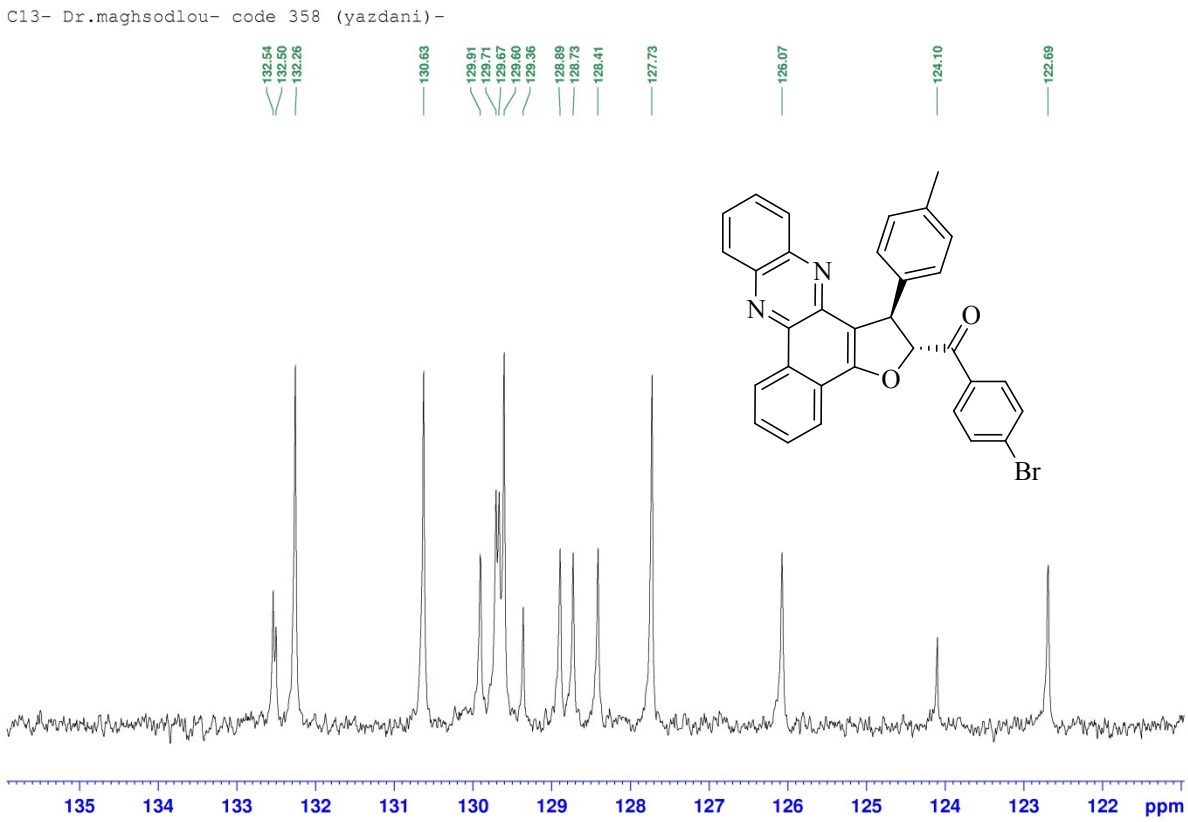

Figure 26: Expanded ^{13}C NMR spectrum of compound **6g** (75 MHz, $CDCl_3$).

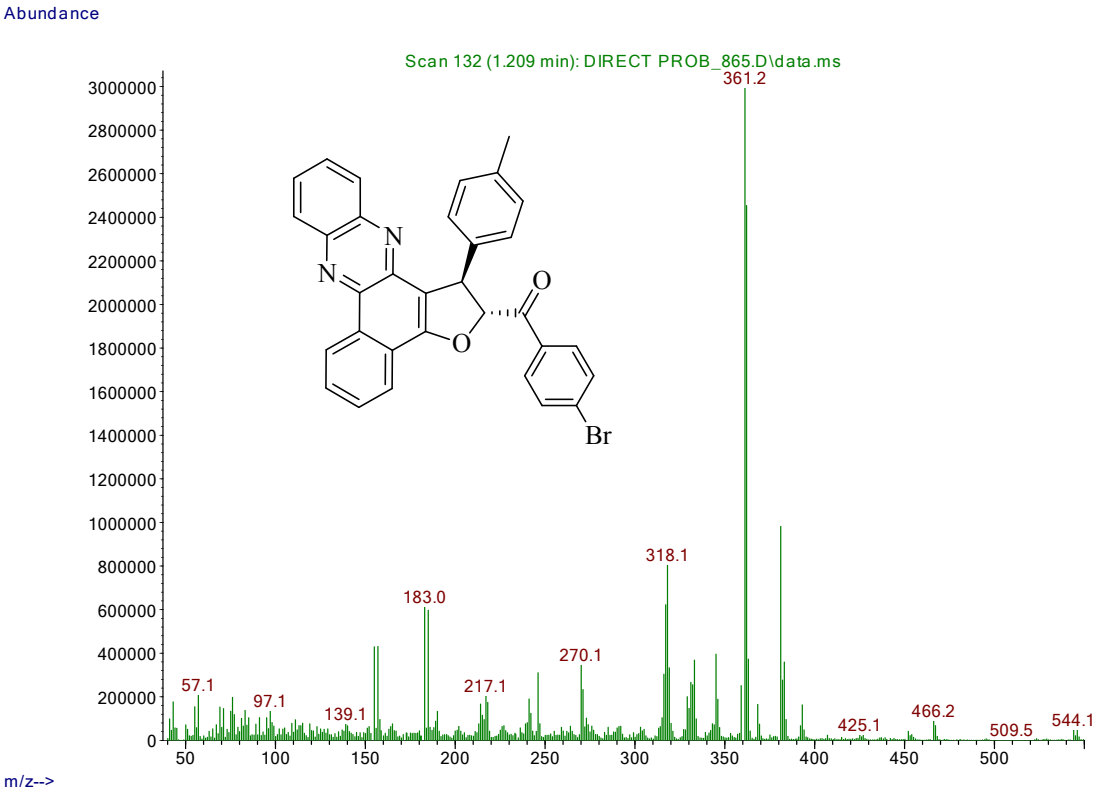

Figure 27: Mass spectrum of compound **6g**.

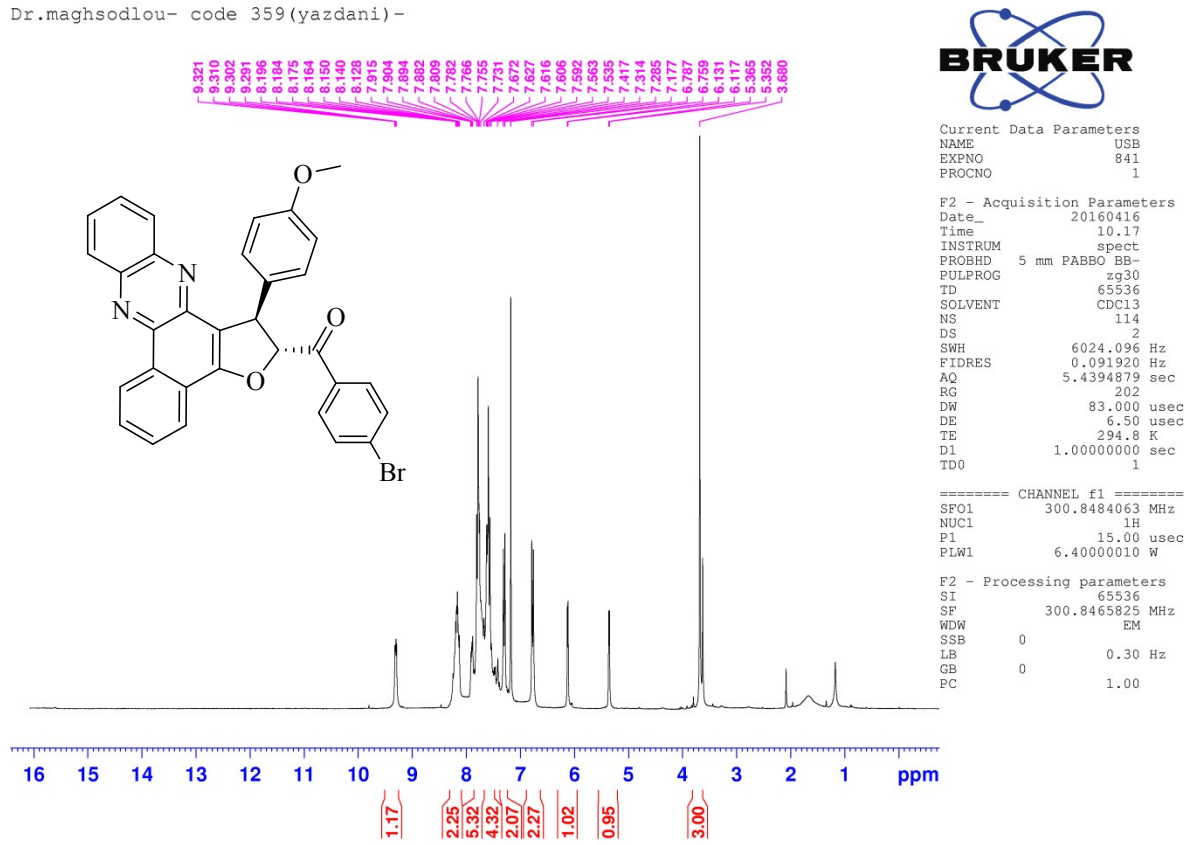

Figure 28: ^{1}H NMR spectrum of compound **6h** (300 MHz, $CDCl_3$).

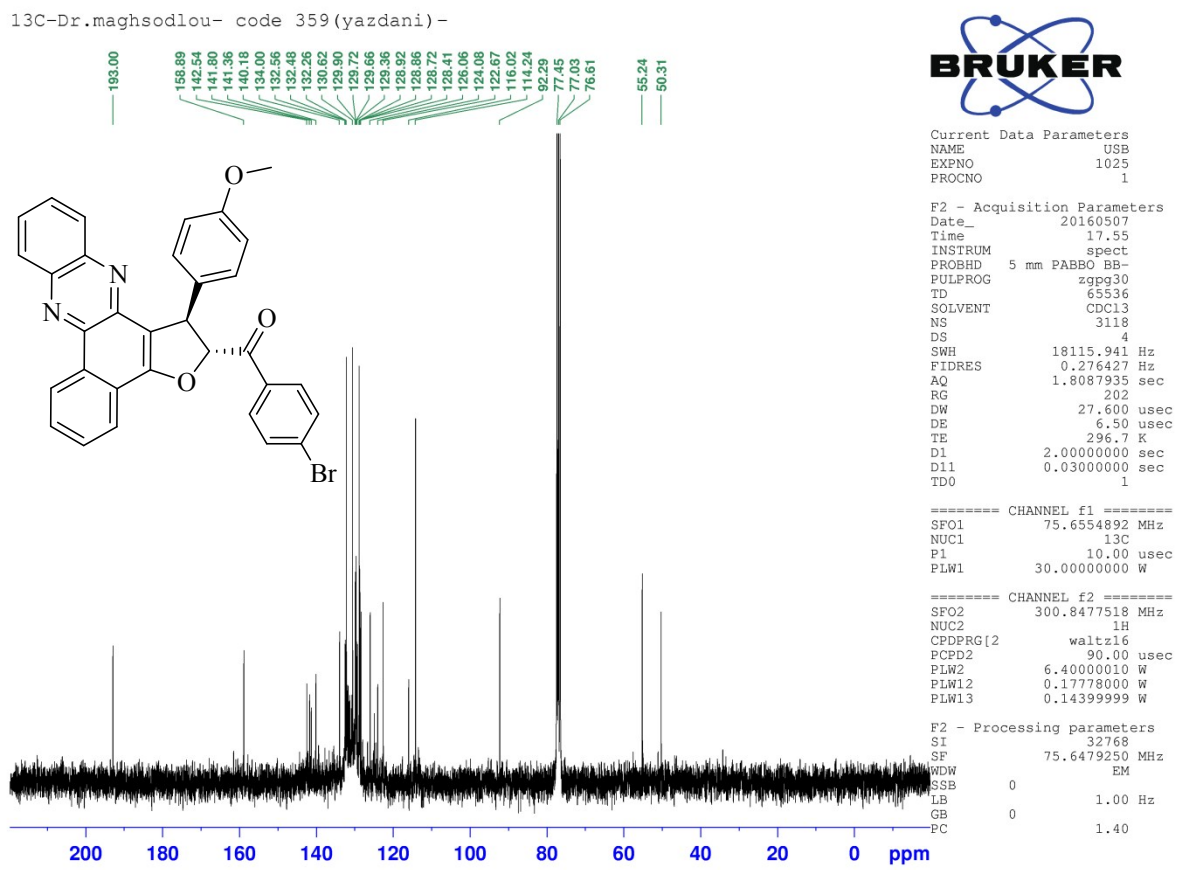

Figure 29: ^{13}C NMR spectrum of compound **6h** (75 MHz, $CDCl_3$).

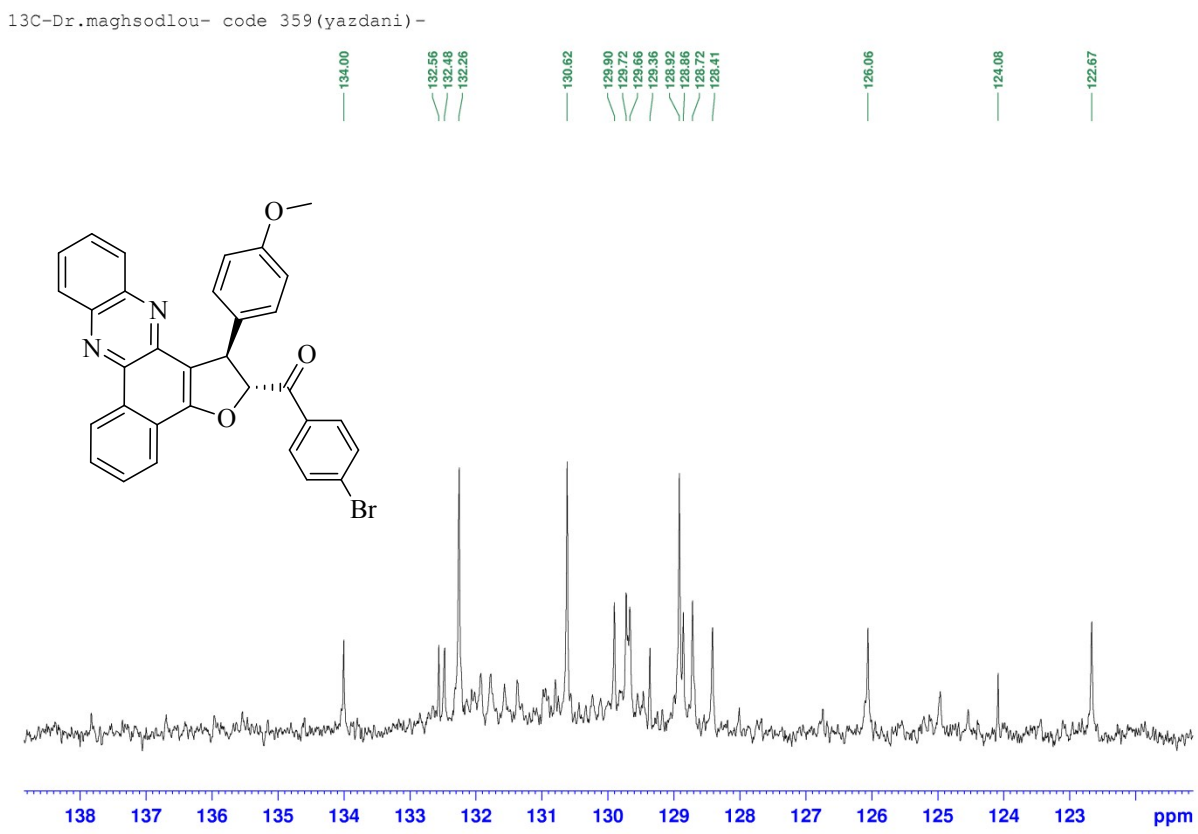

Figure 30: Expanded ^{13}C NMR spectrum of compound **6h** (75 MHz, $CDCl_3$).

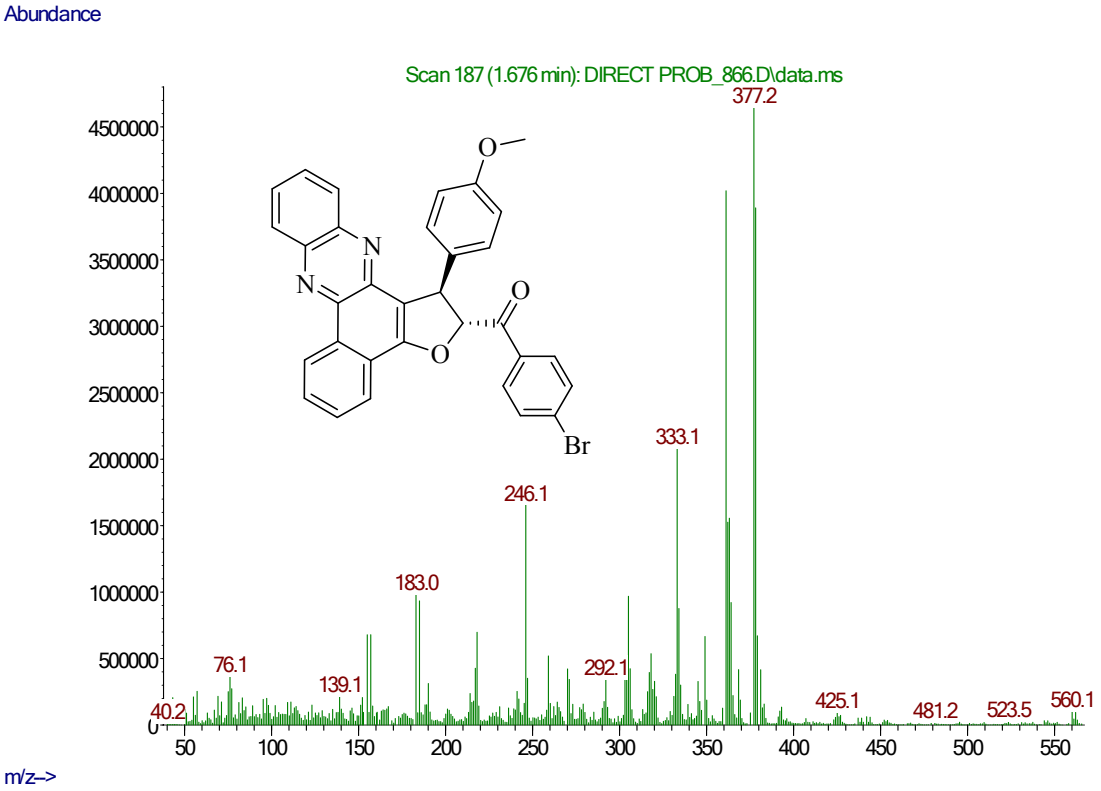

Figure 31: Mass spectrum of compound **6h**.

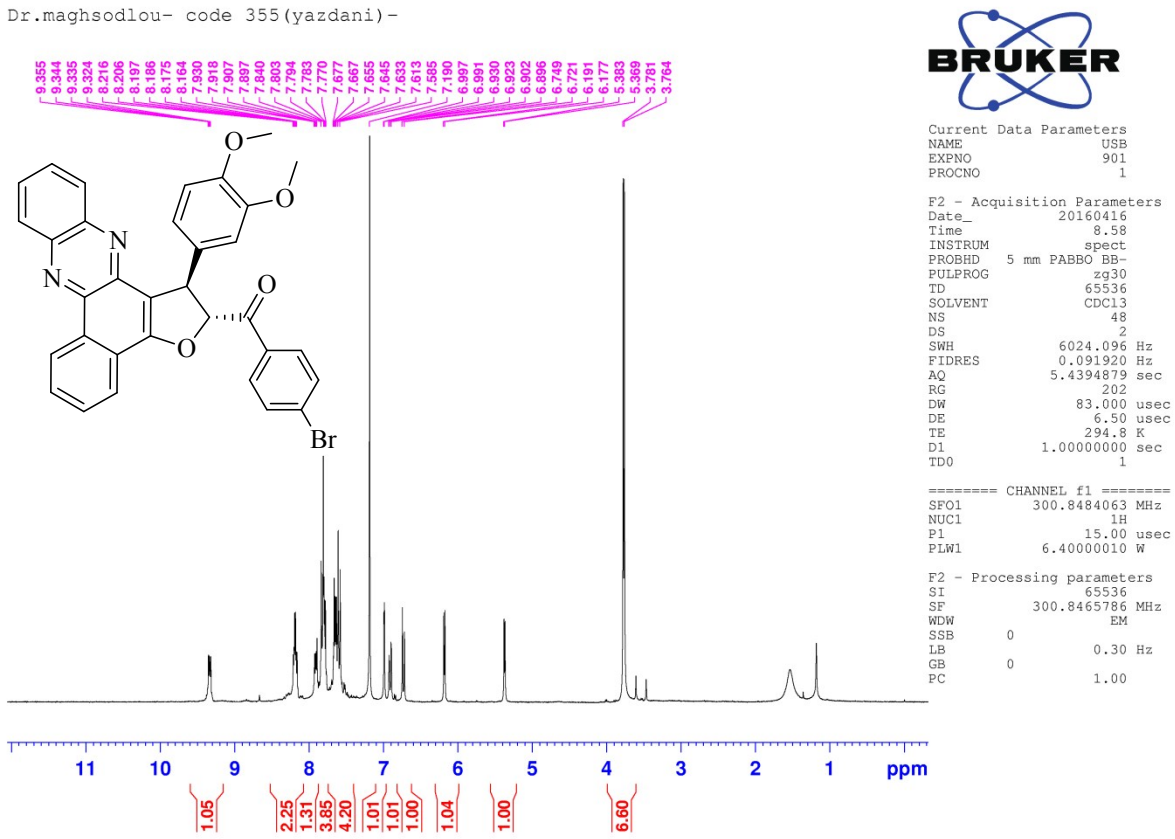

Figure 32: ^{1}H NMR spectrum of compound **6i** (300 MHz, $CDCl_3$).

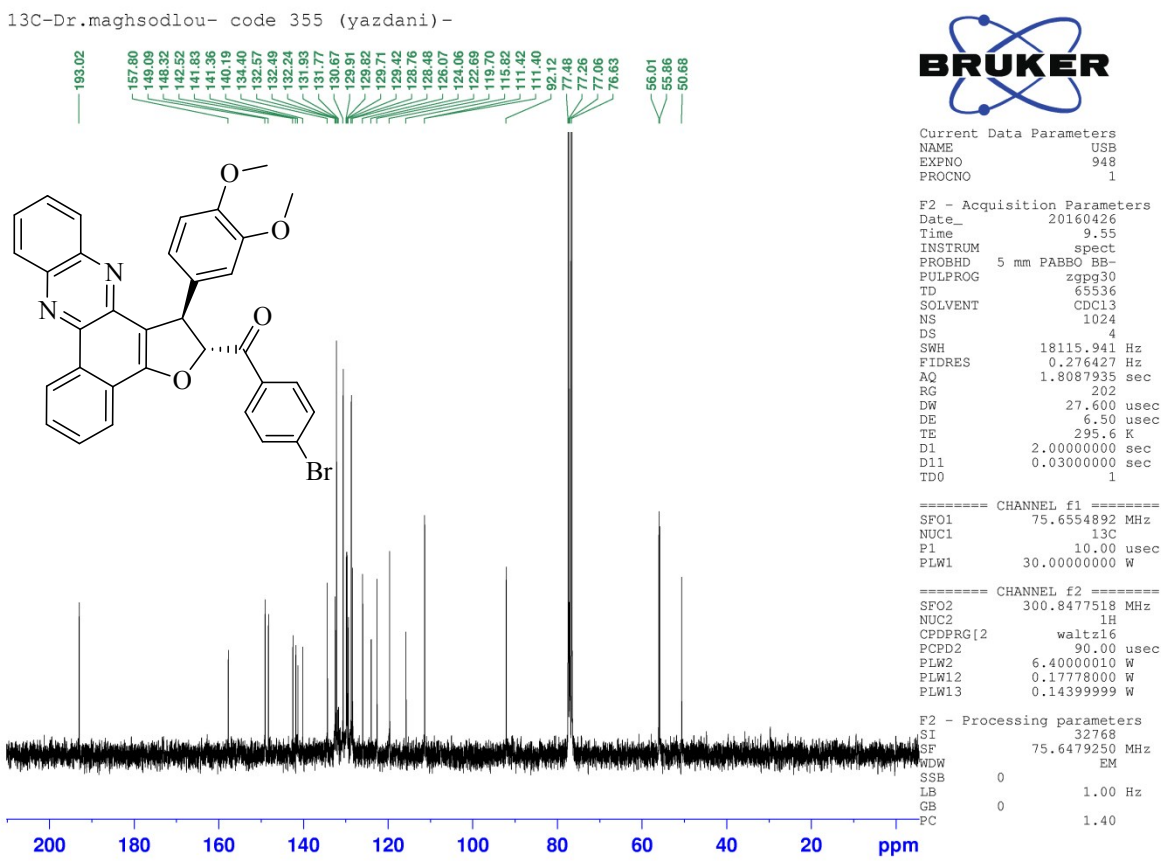

Figure 33: ^{13}C NMR spectrum of compound **6i** (75 MHz, $CDCl_3$).

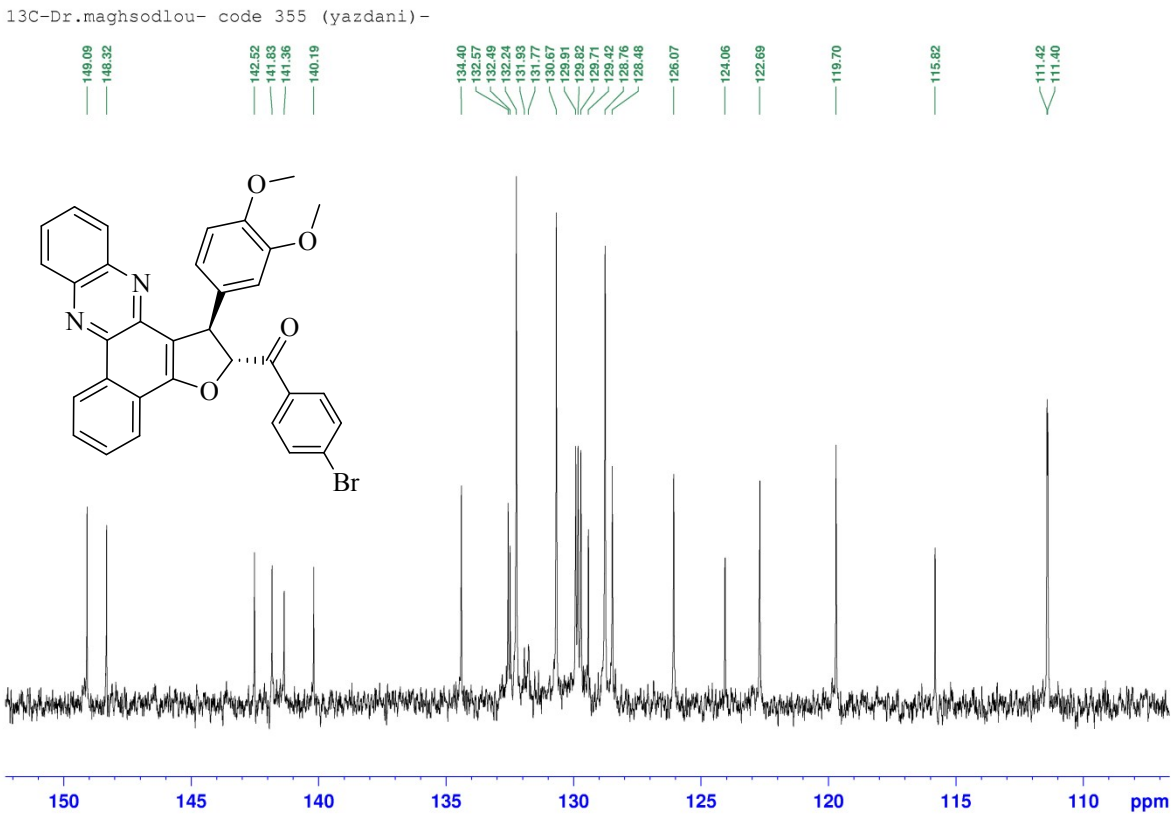

Figure 34: Expanded ^{13}C NMR spectrum of compound **6i** (75 MHz, $CDCl_3$).

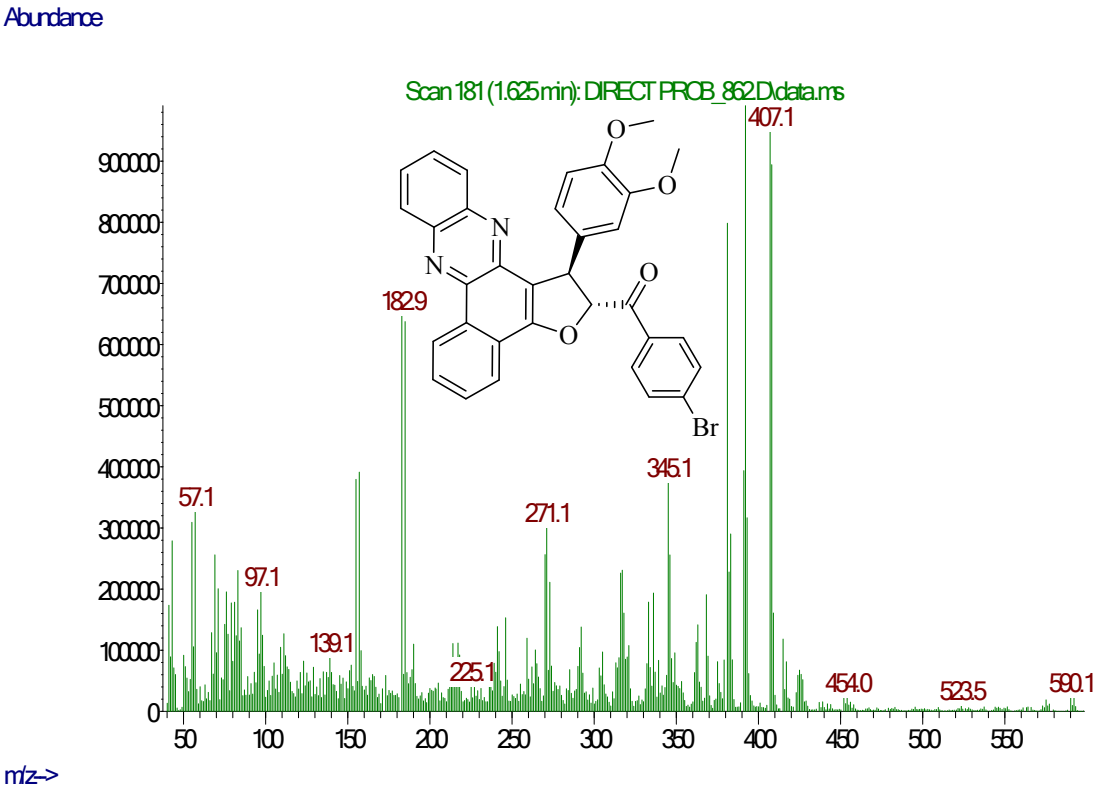

Figure 35: Mass spectrum of compound **6i**.

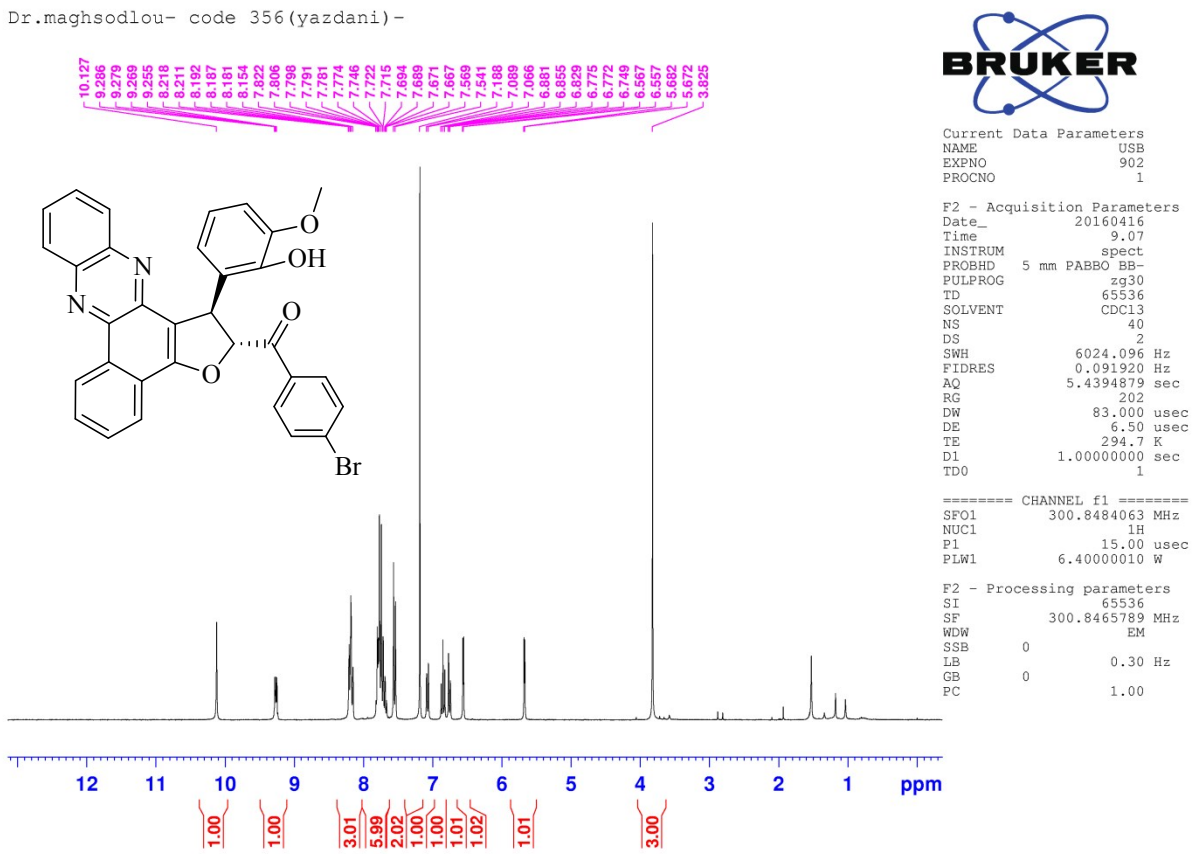

Figure 36: ^{1}H NMR spectrum of compound **6j** (300 MHz, $CDCl_3$).

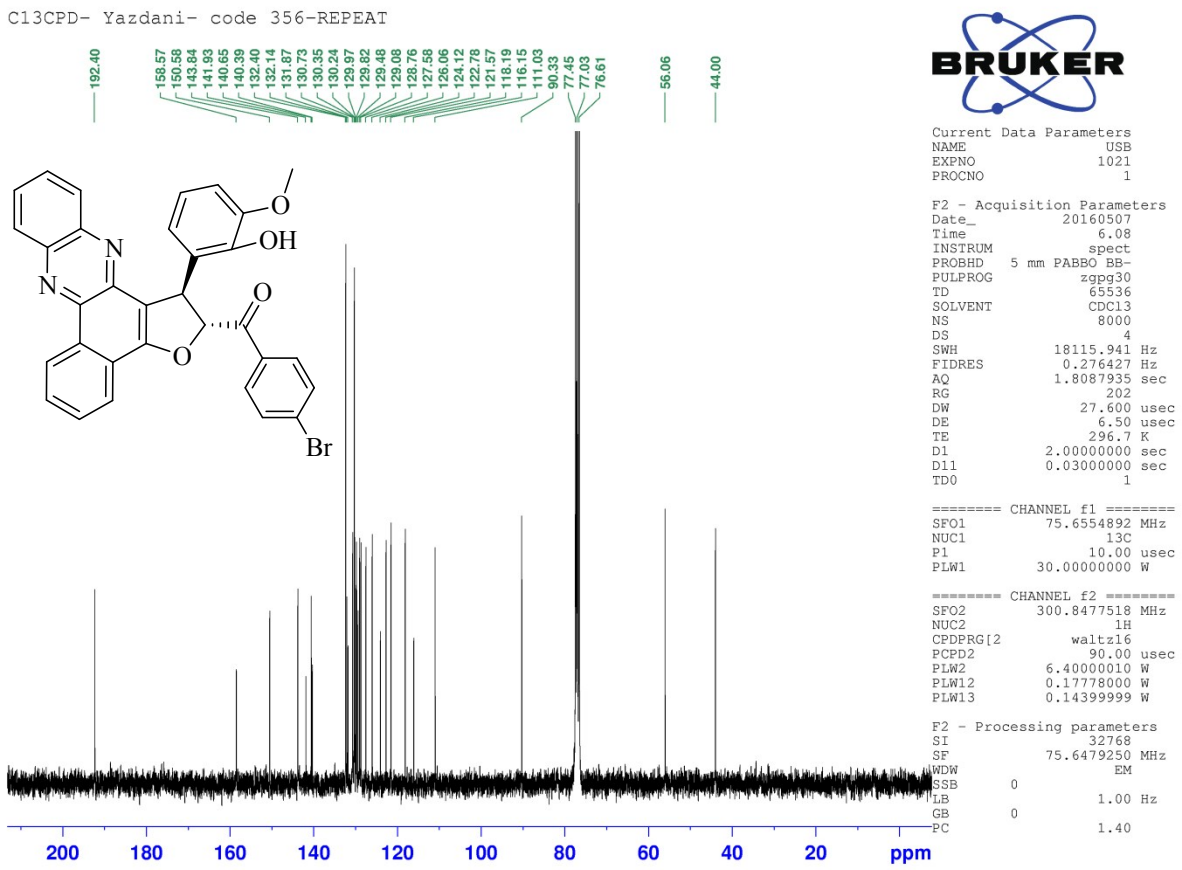

Figure 37: ^{13}C NMR spectrum of compound **6j** (75 MHz, $CDCl_3$).

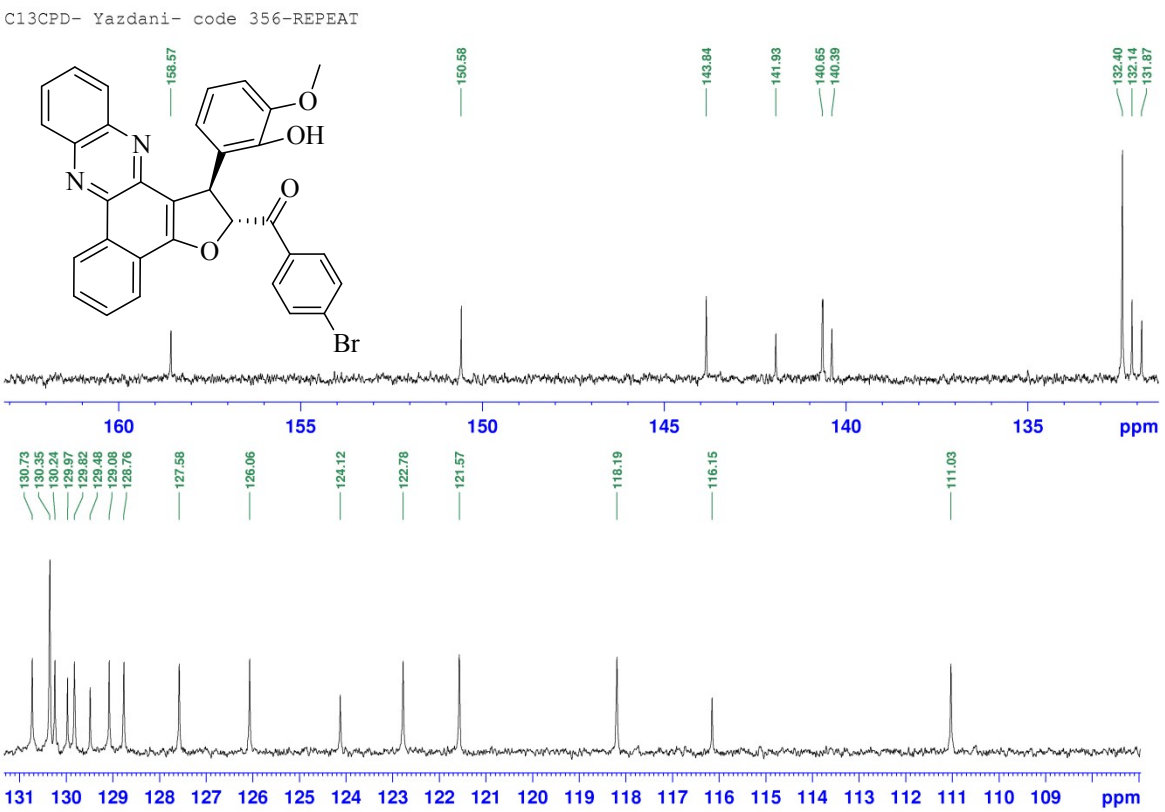

Figure 38: Expanded ^{13}C NMR spectrum of compound **6j** (75 MHz, $CDCl_3$).

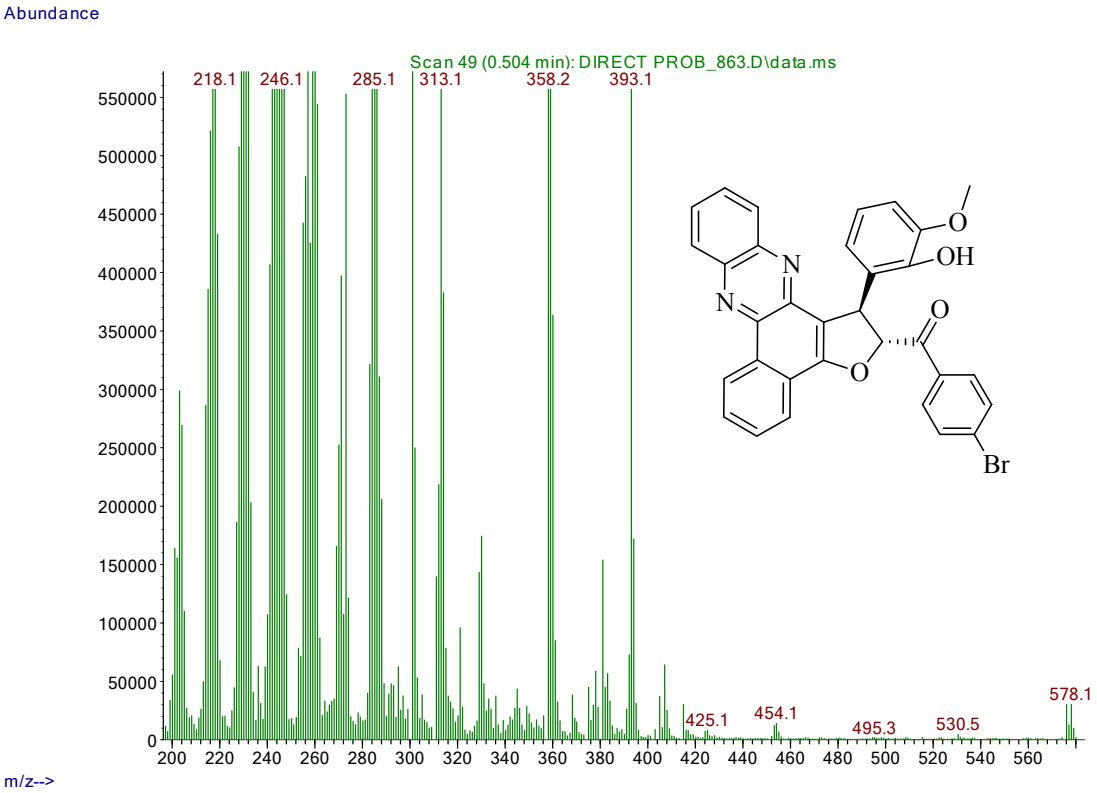

Figure 39: Mass spectrum of compound **6j**.

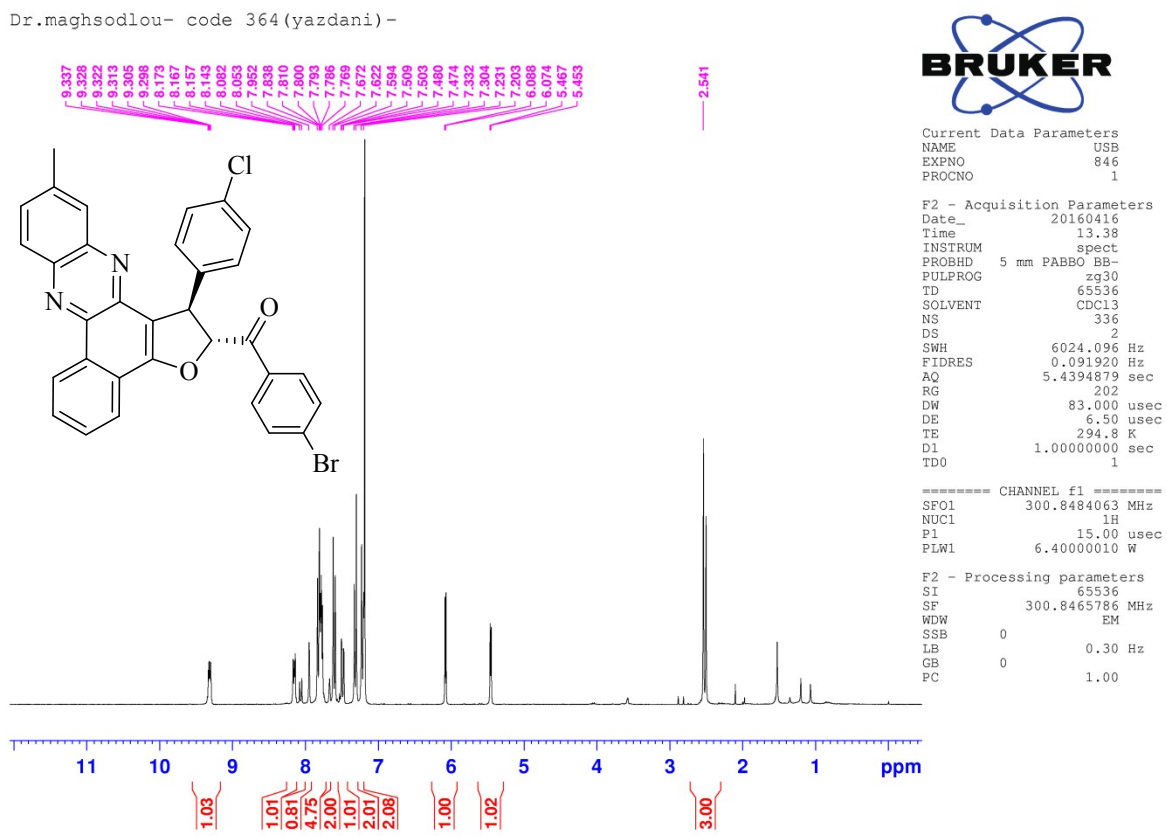

Figure 40: ^{1}H NMR spectrum of compound **6k** (300 MHz, $CDCl_3$).

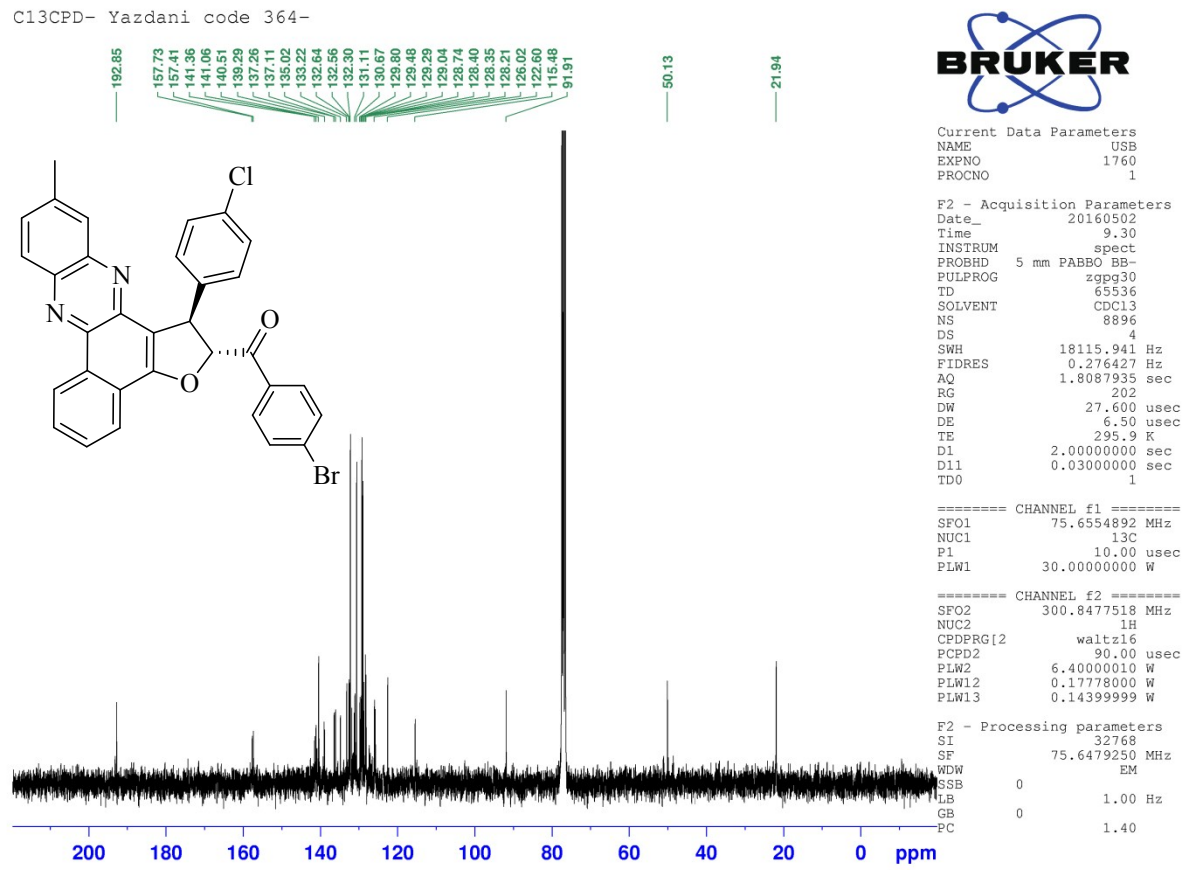

Figure 41: ^{13}C NMR spectrum of compound **6k** (75 MHz, $CDCl_3$).

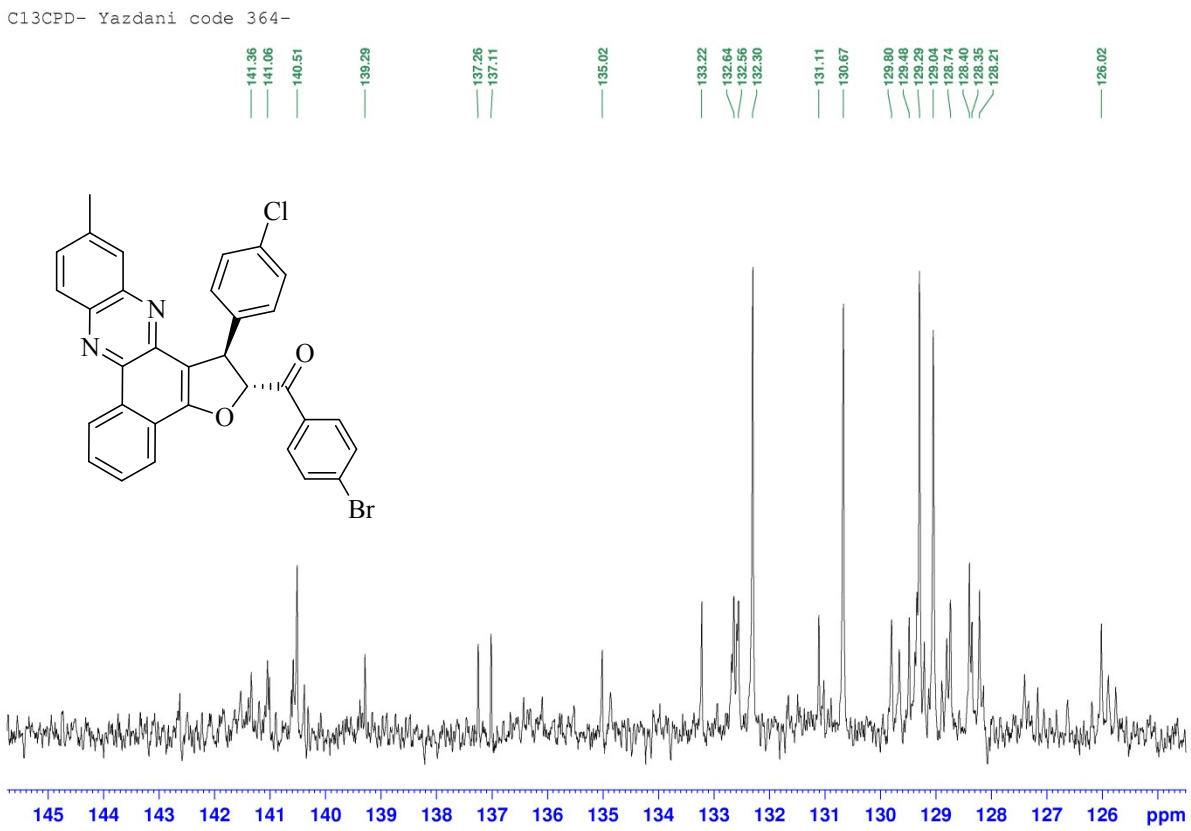

Figure 42: Expanded ^{13}C NMR spectrum of compound **6k** (75 MHz, $CDCl_3$).

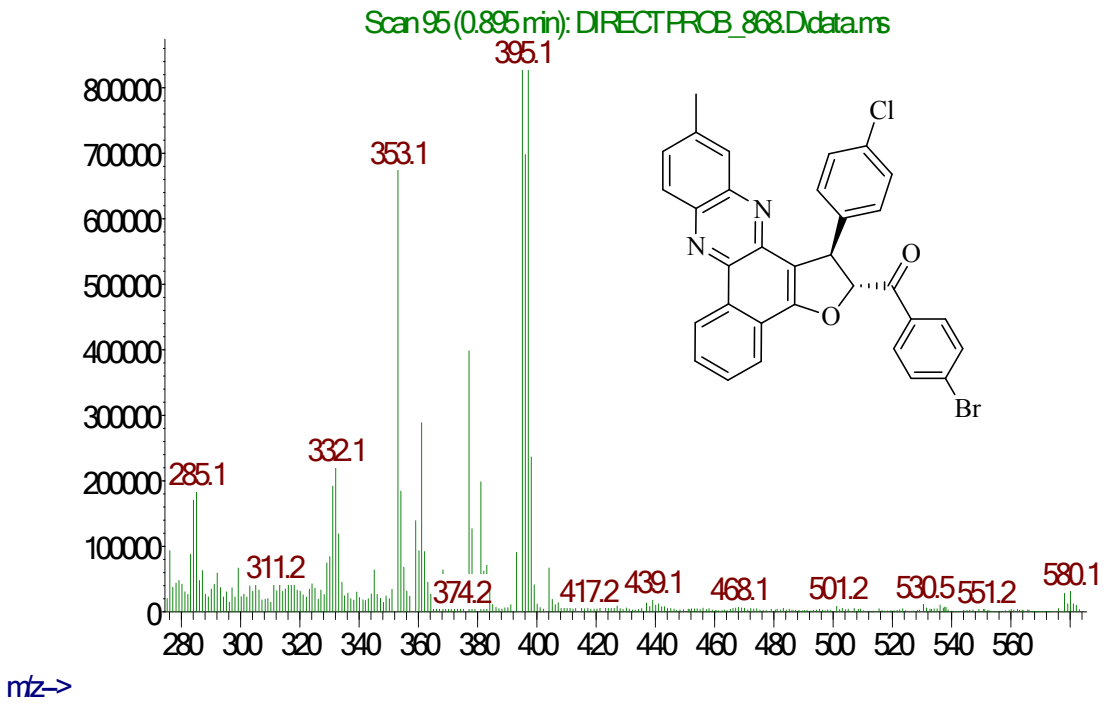

Figure 43: Mass spectrum of compound **6k**.

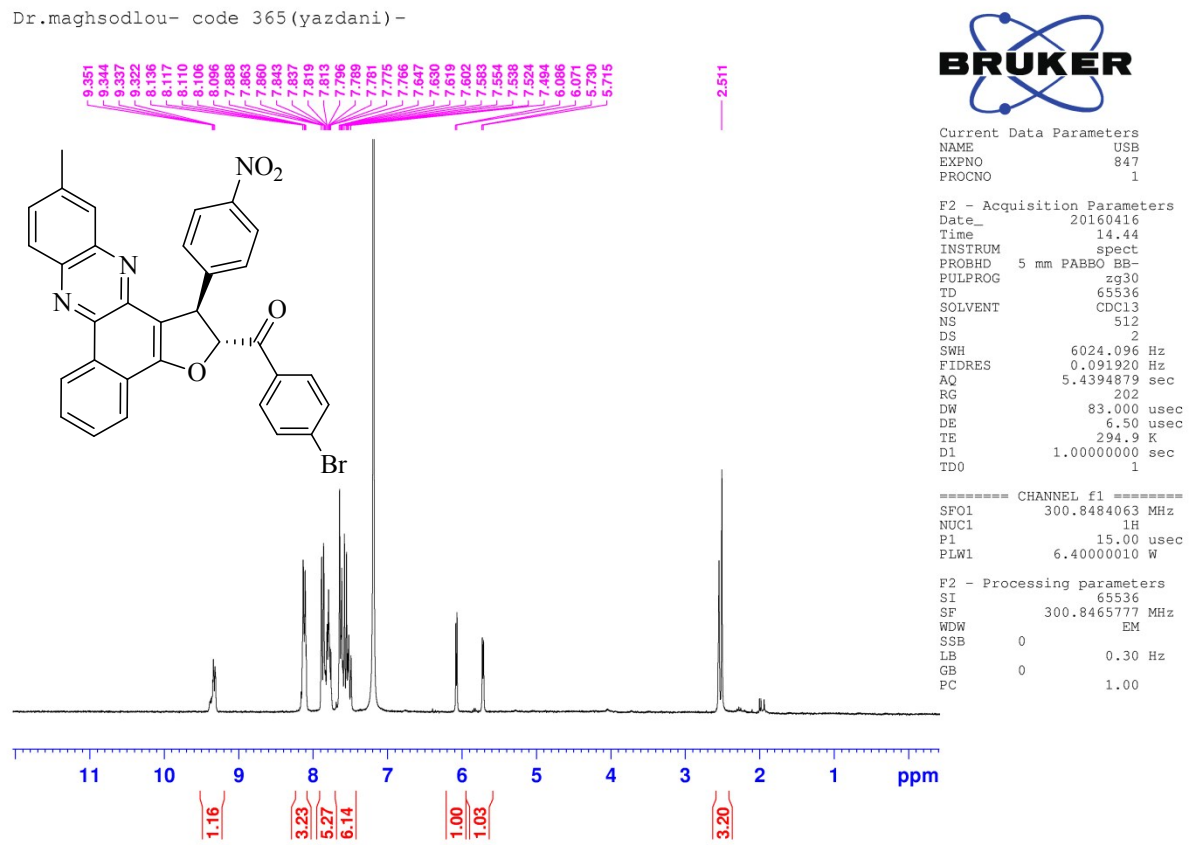

Figure 44: ^{1}H NMR spectrum of compound **6l** (300 MHz, $CDCl_3$).

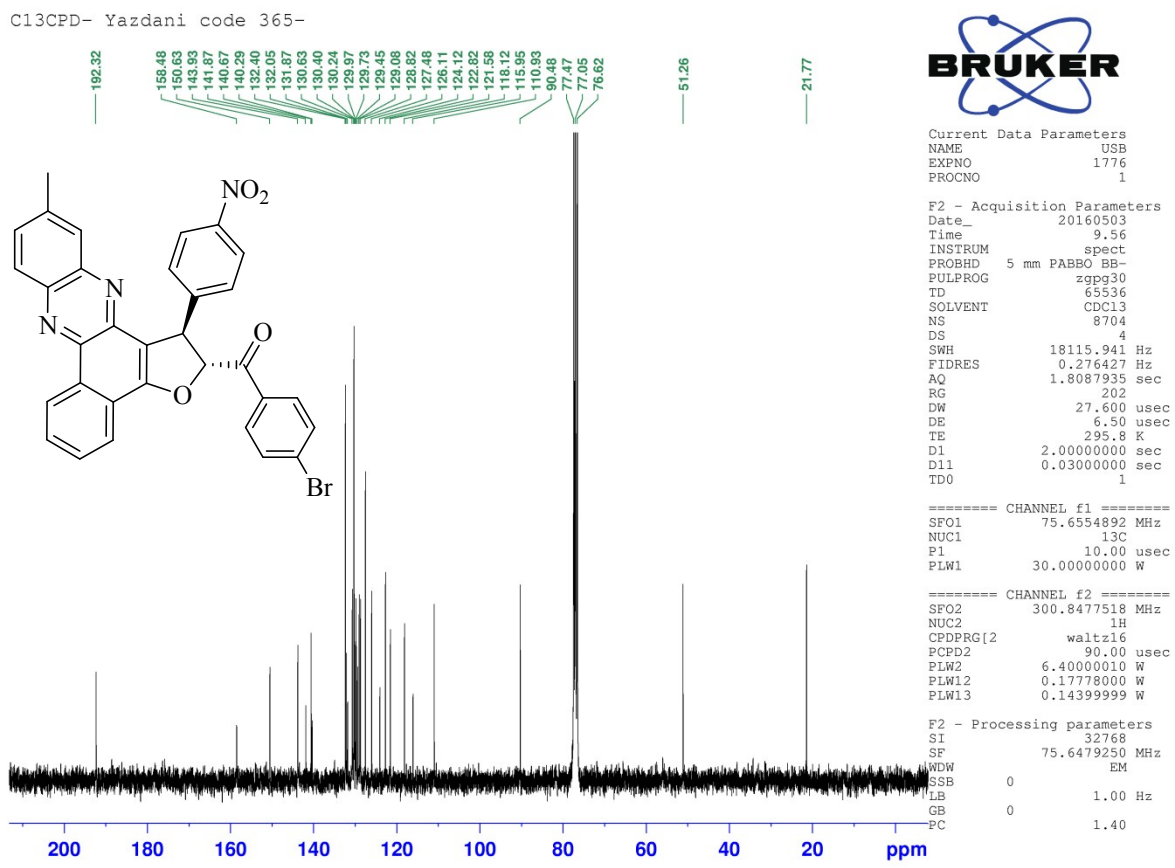

Figure 45: ^{13}C NMR spectrum of compound **6l** (75 MHz, $CDCl_3$).

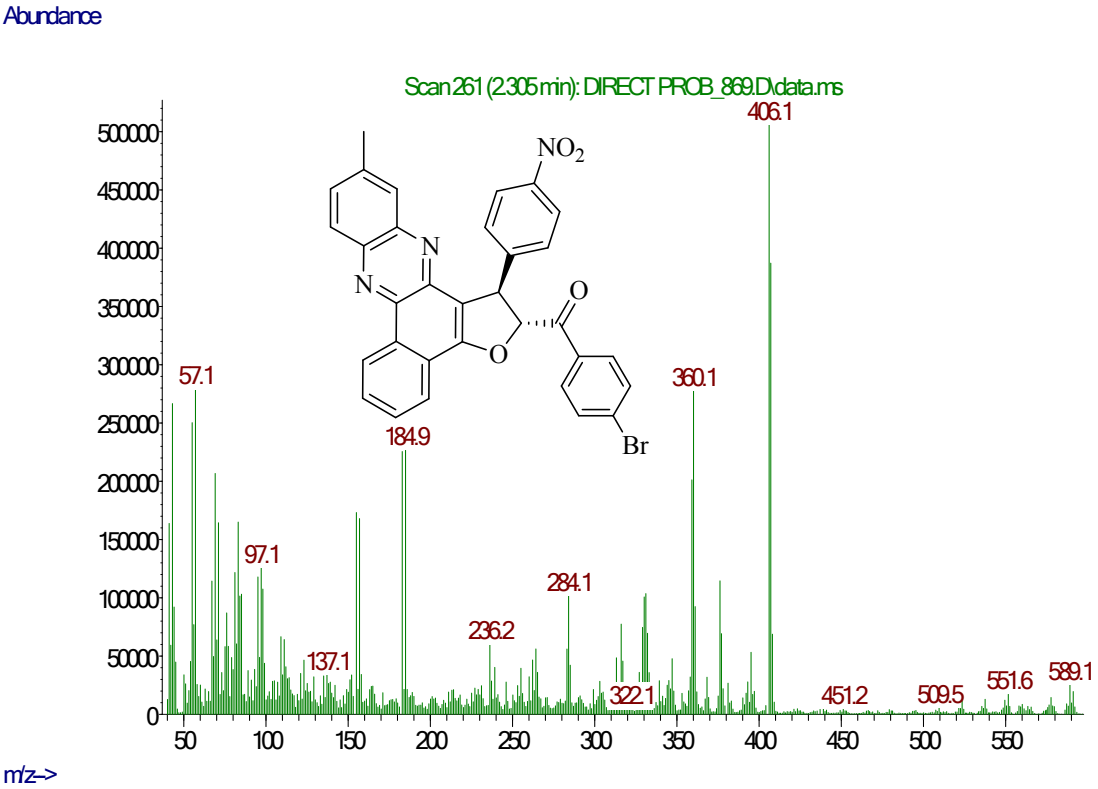

Figure 46: Mass spectrum of compound **6l**.

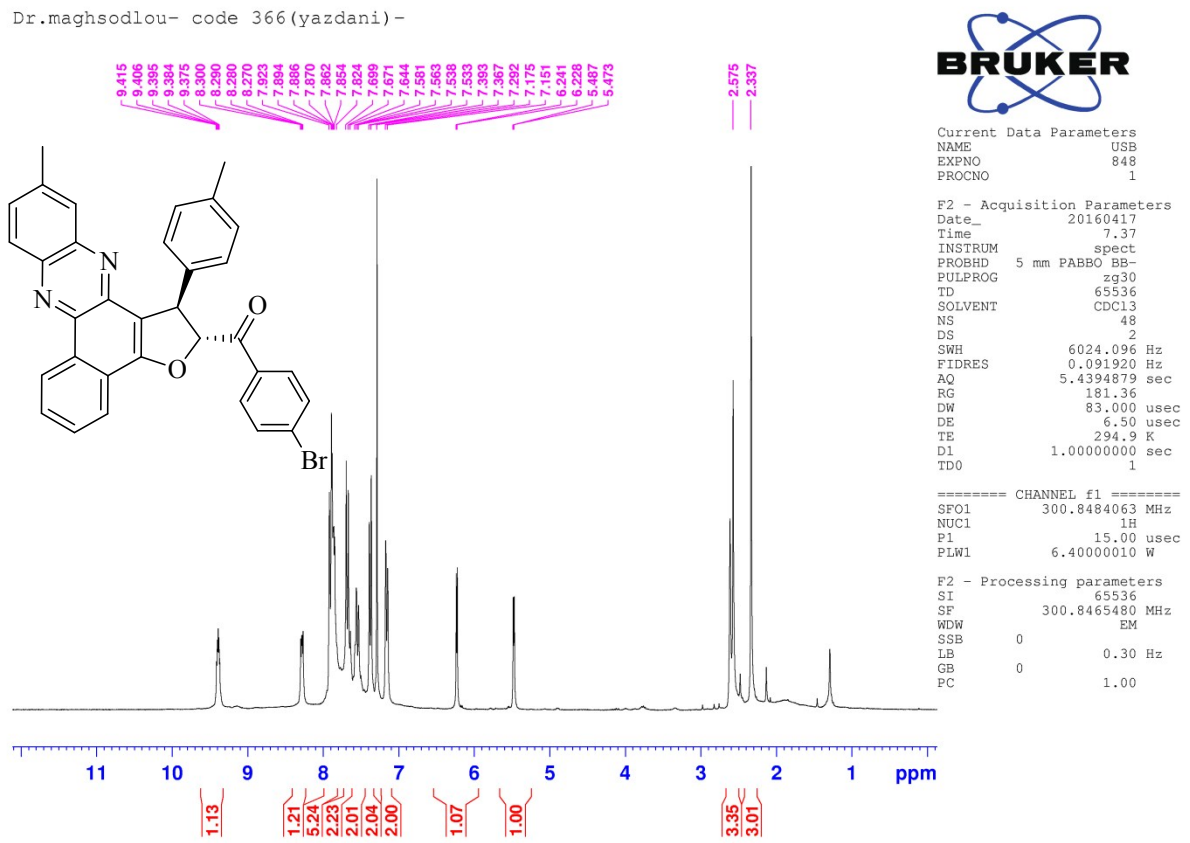

Figure 47: ^{1}H NMR spectrum of compound **6m** (300 MHz, $CDCl_3$).

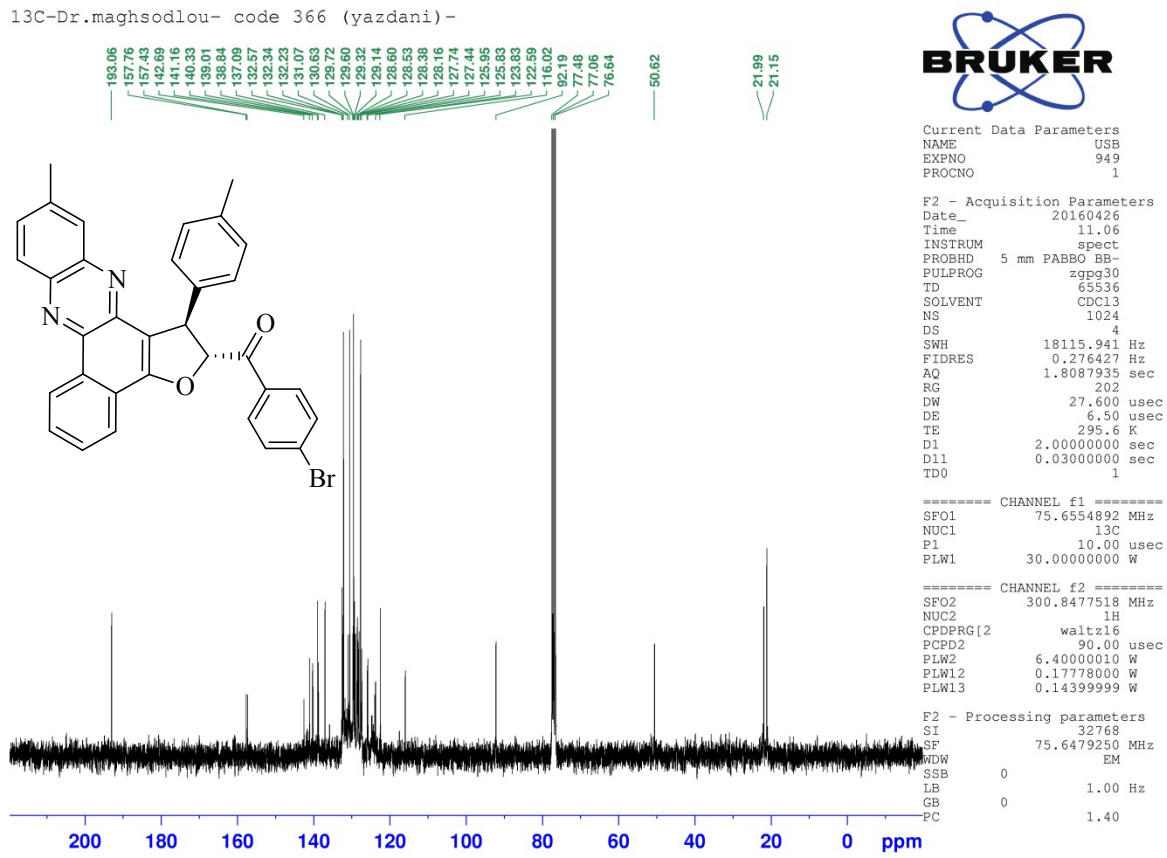

Figure 48: ^{13}C NMR spectrum of compound **6m** (75 MHz, $CDCl_3$).

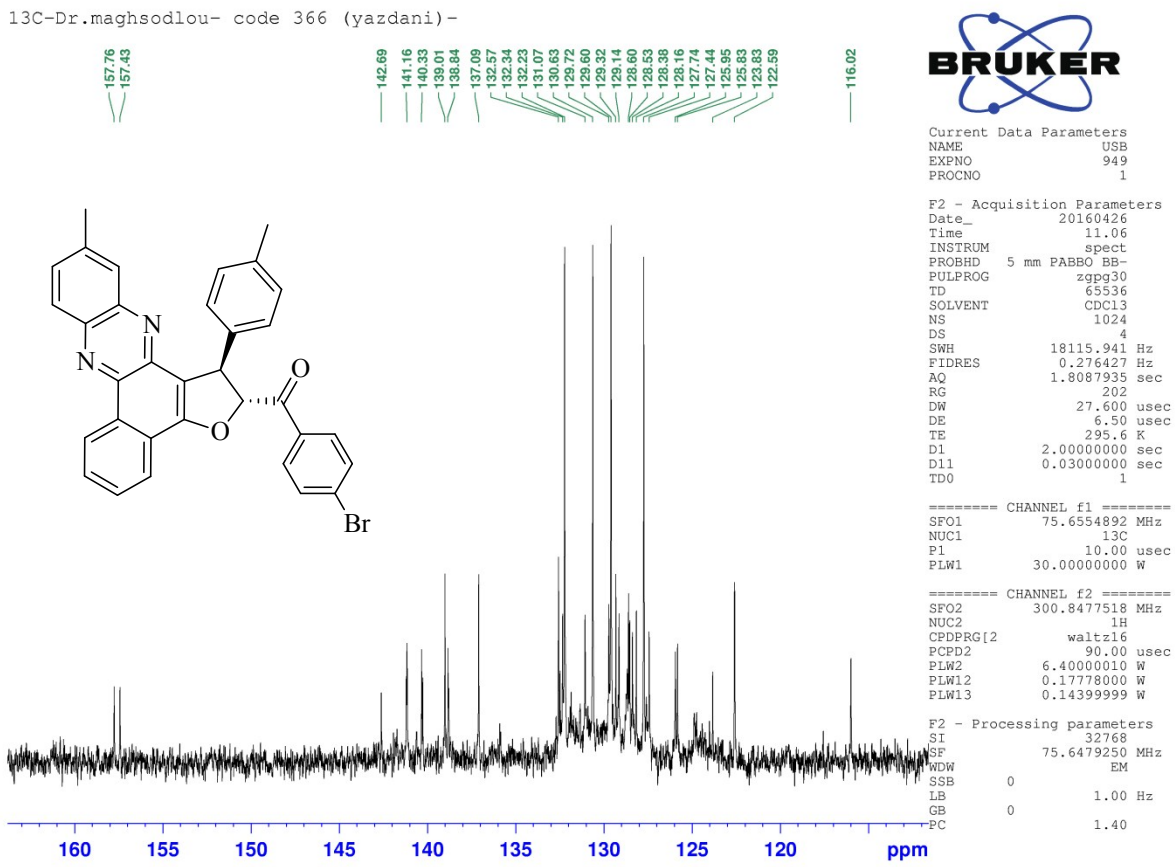

Figure 49: Expanded ^{13}C NMR spectrum of compound **6m** (75 MHz, $CDCl_3$).

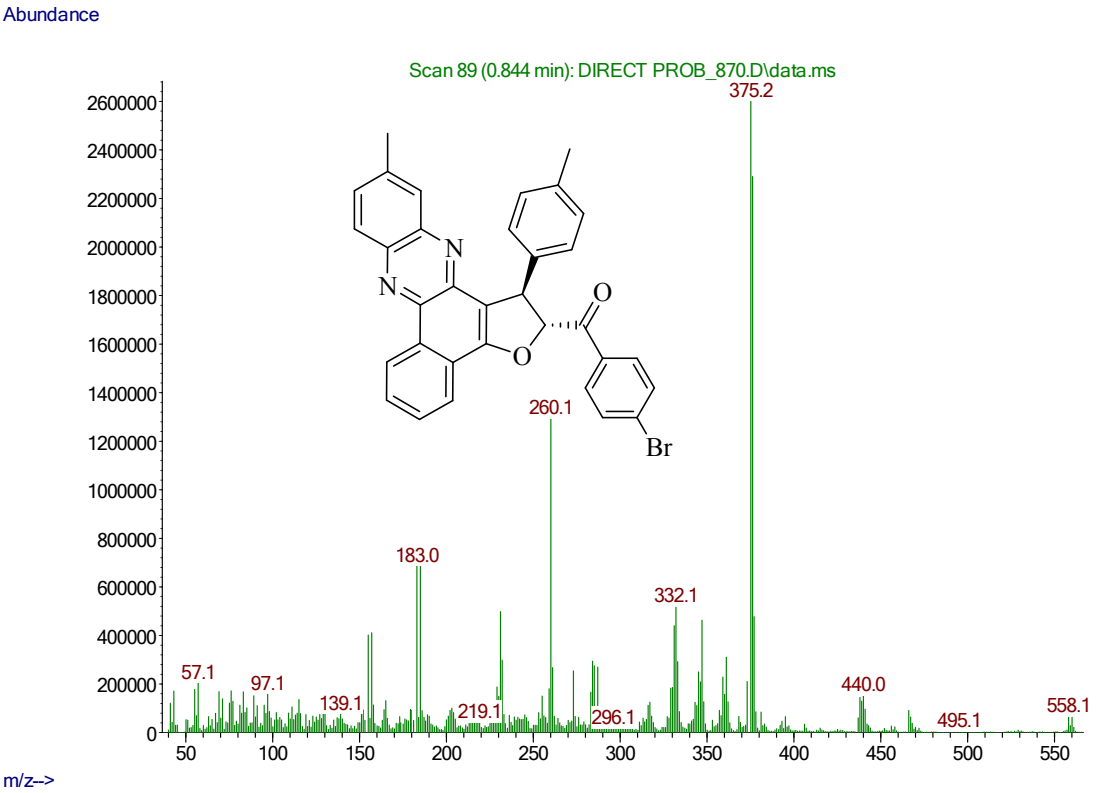

Figure 50: Mass spectrum of compound **6m**.

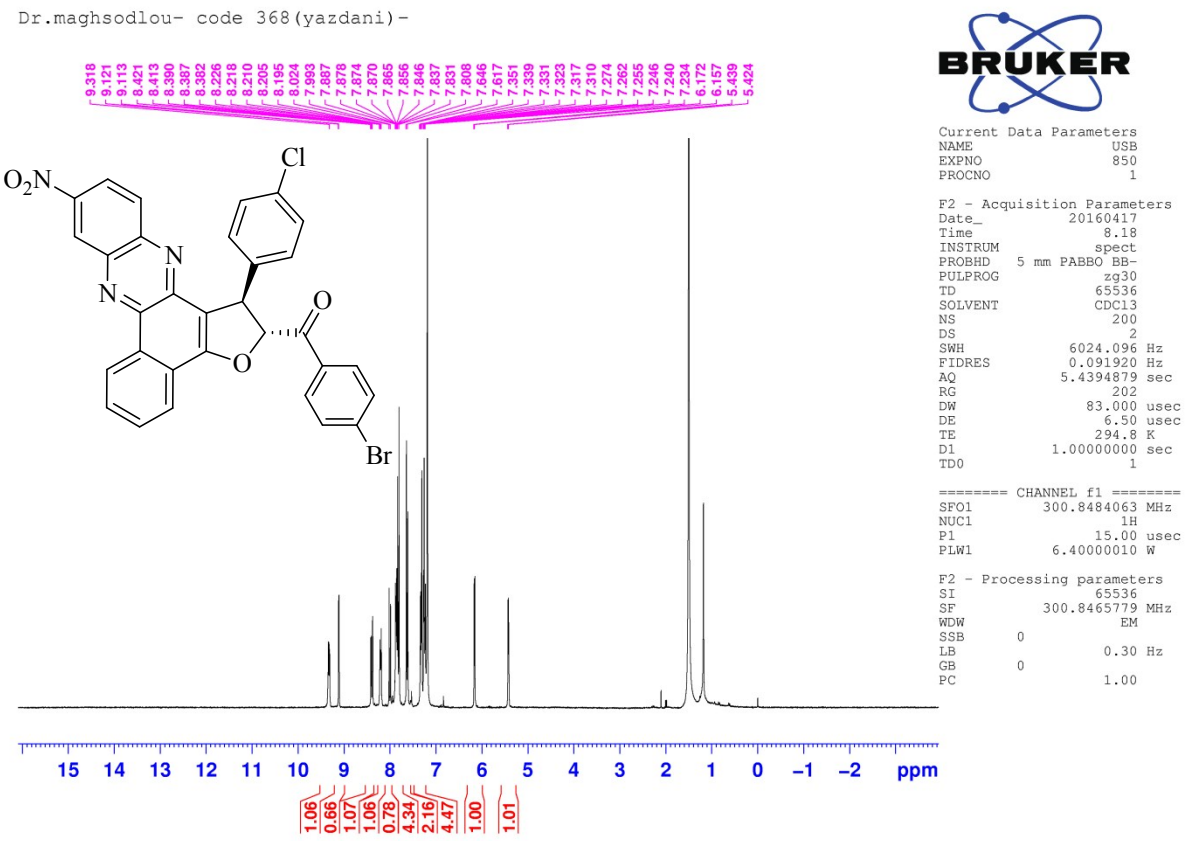

Figure 51: ^{1}H NMR spectrum of compound **6n** (300 MHz, $CDCl_3$).

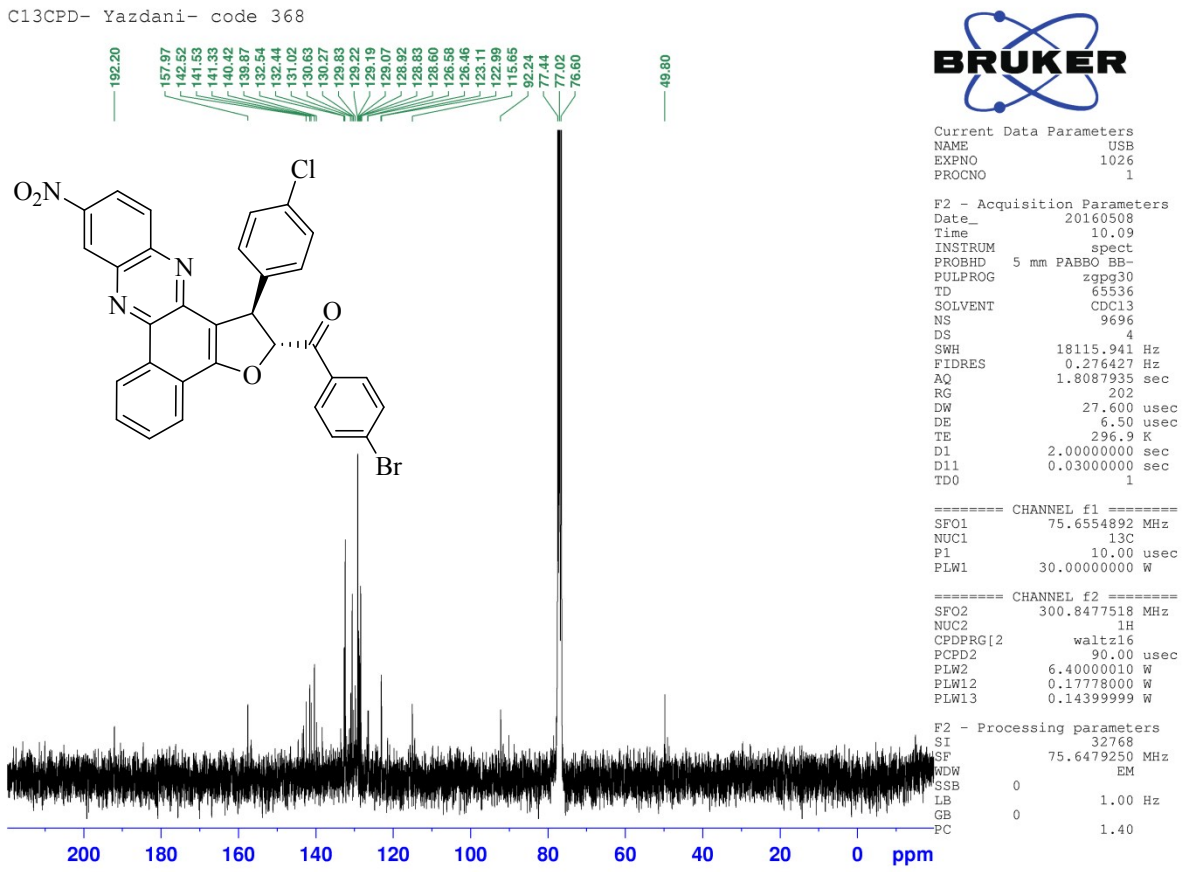

Figure 52: ^{13}C NMR spectrum of compound **6n** (75 MHz, $CDCl_3$).

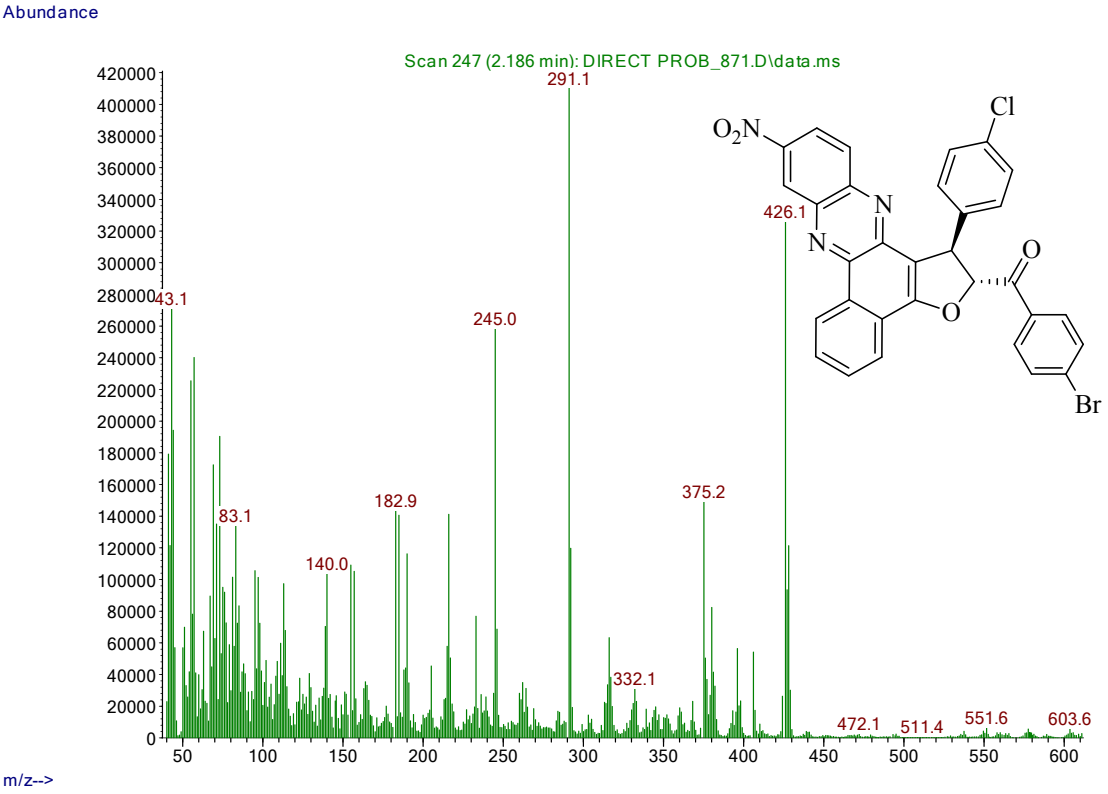

Figure 53: Mass spectrum of compound **6n**.

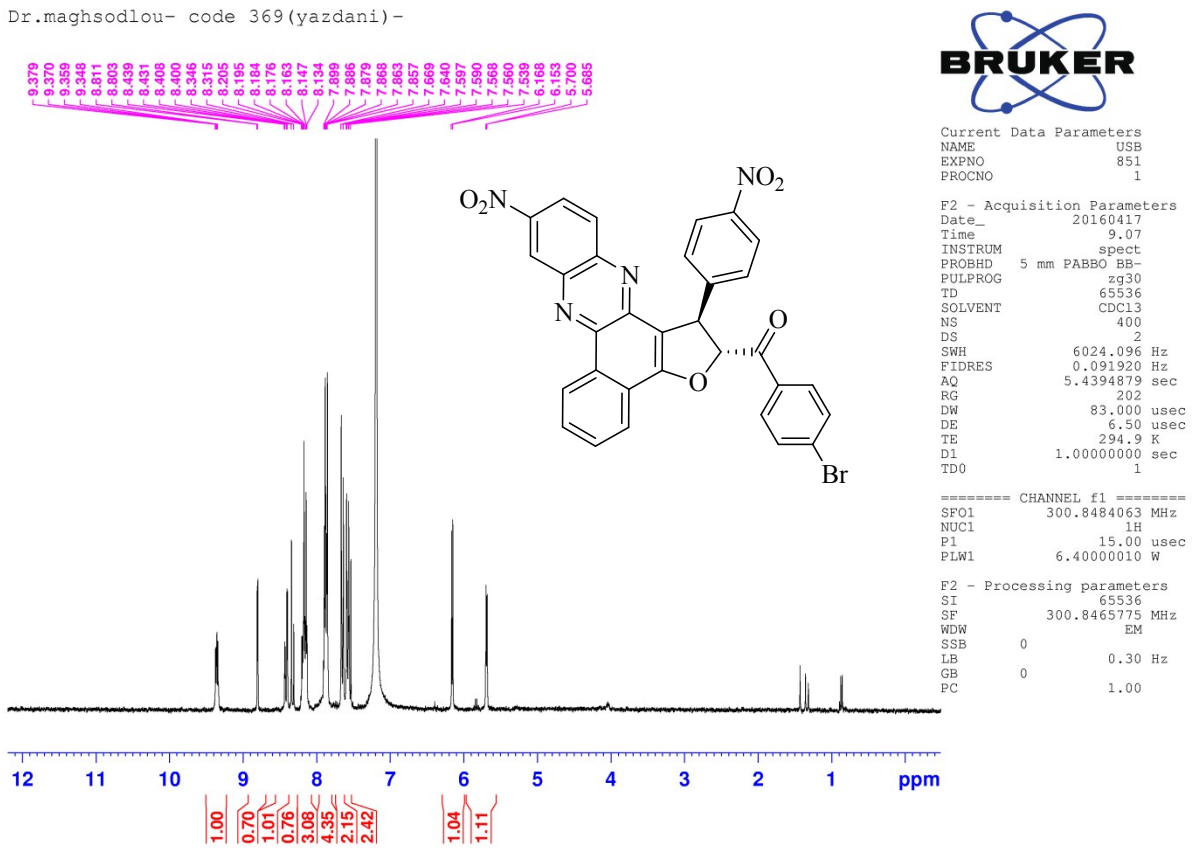

Figure 54: ^{1}H NMR spectrum of compound **6o** (300 MHz, $CDCl_3$).

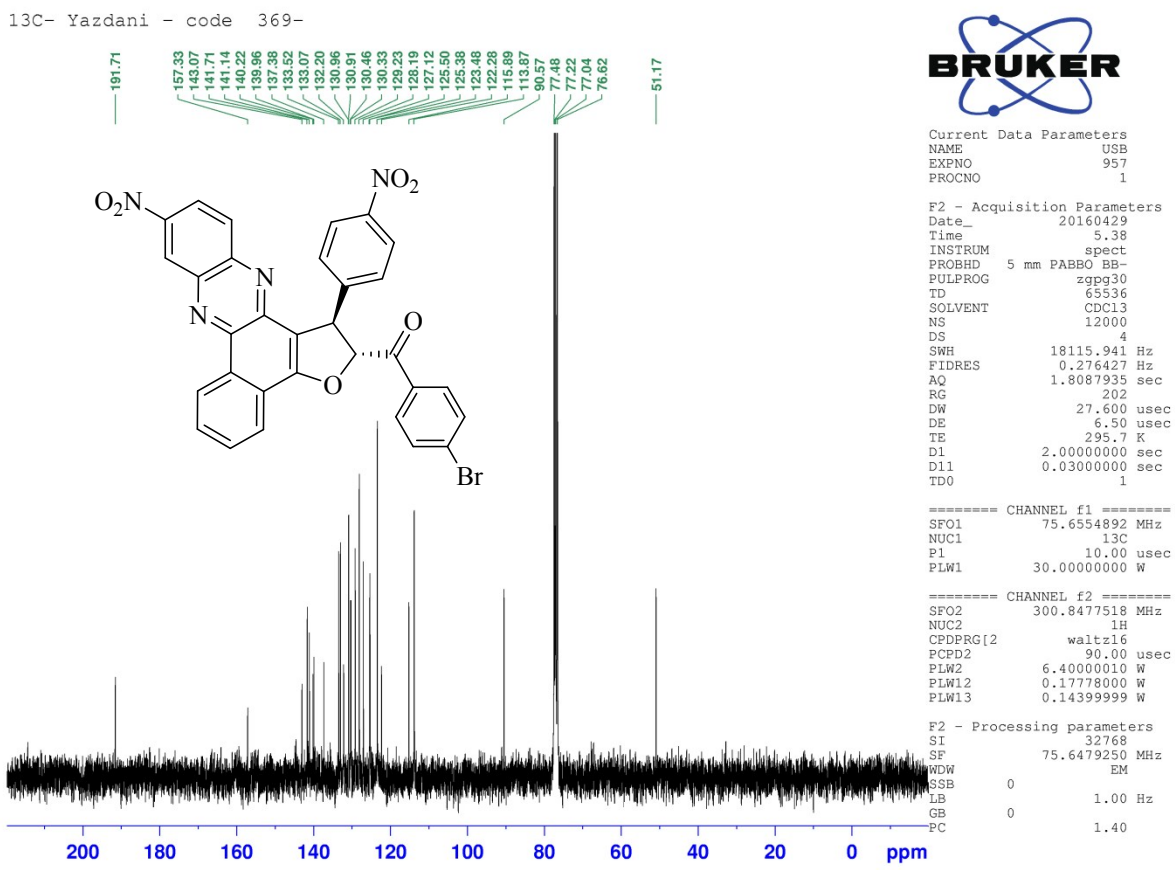

Figure 55: ^{13}C NMR spectrum of compound **6o** (75 MHz, $CDCl_3$).

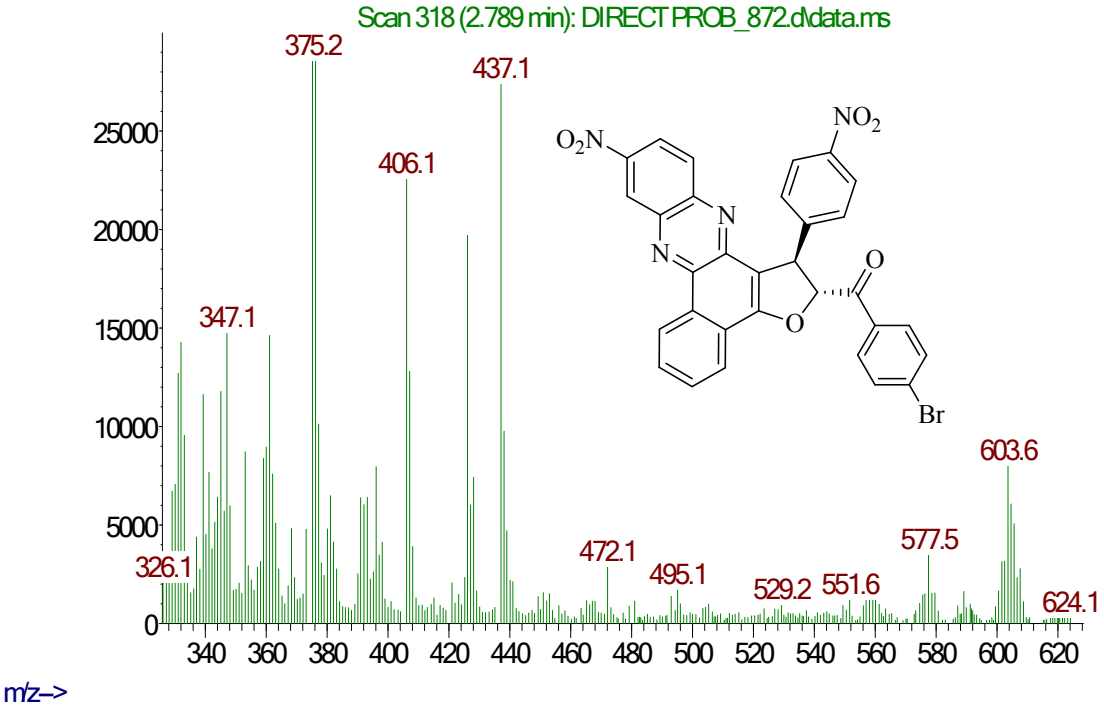

Figure 56: Mass spectrum of compound **6o**.

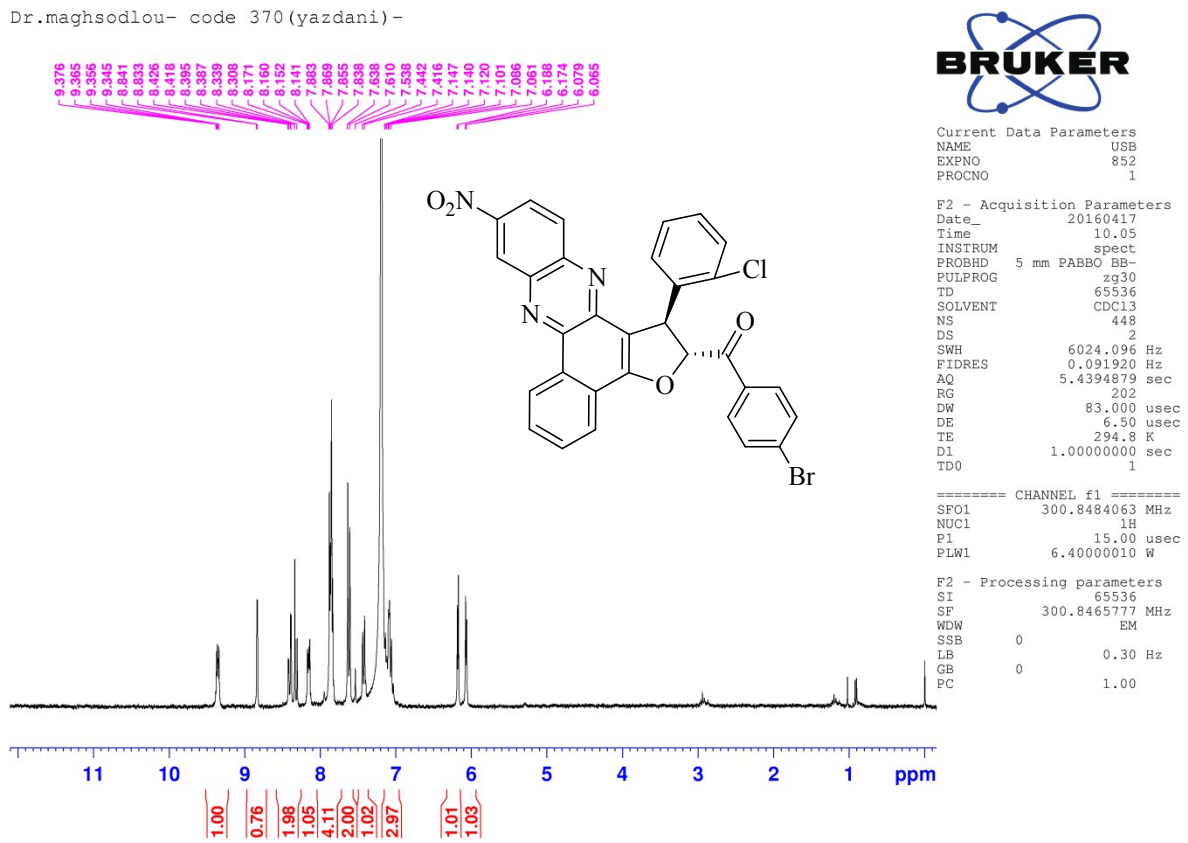

Figure 57: ^{1}H NMR spectrum of compound **6p** (300 MHz, $CDCl_3$).

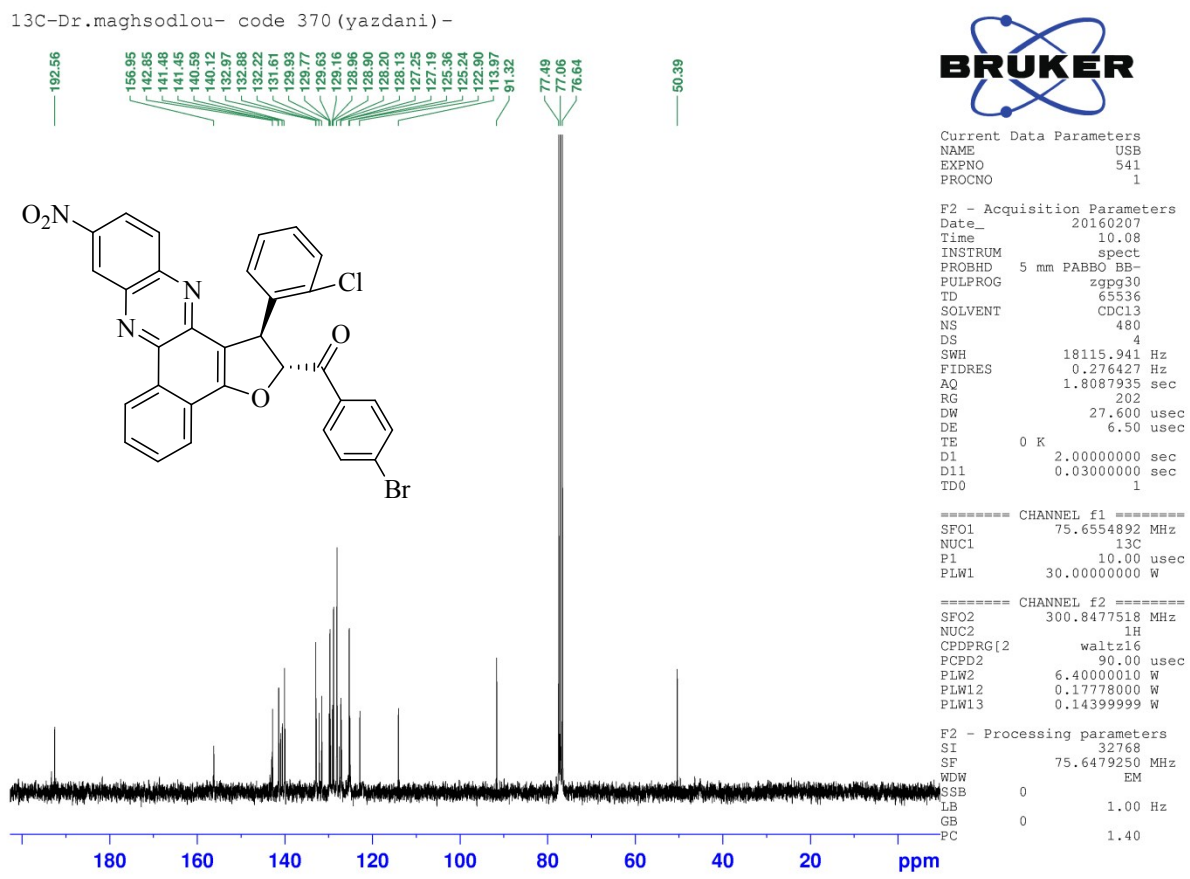

Figure 58: ^{13}C NMR spectrum of compound **6p** (75 MHz, $CDCl_3$).

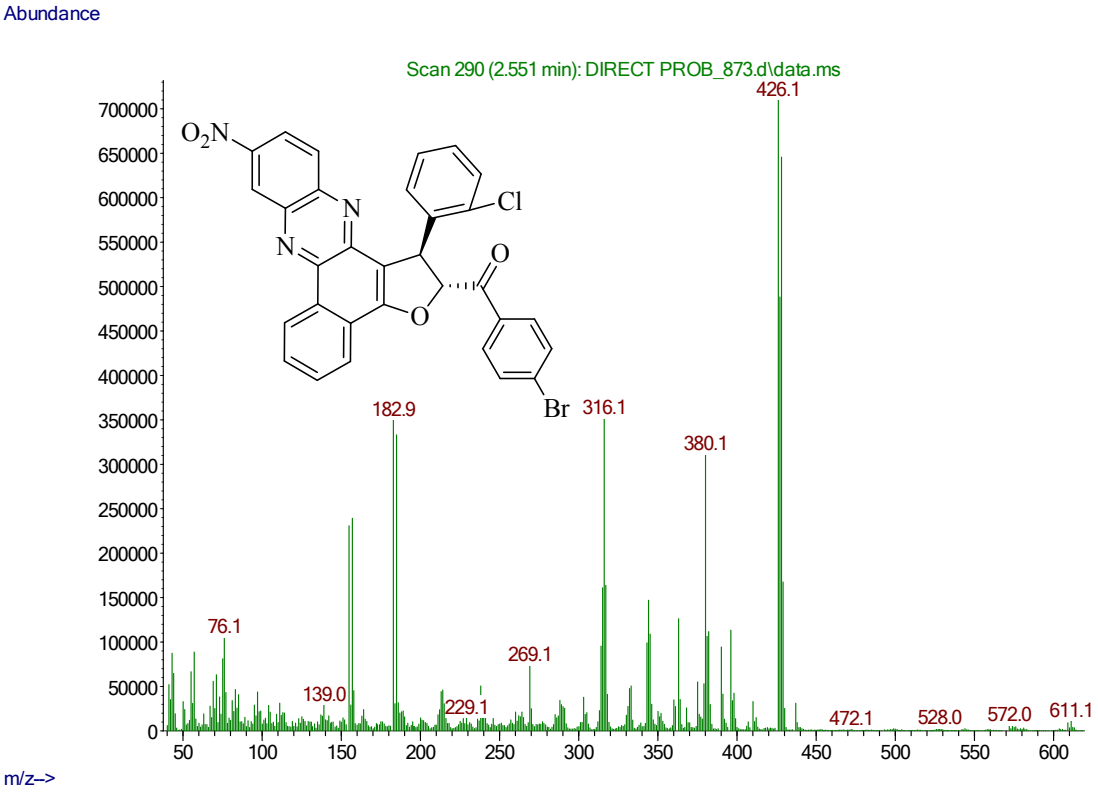

Figure 59: Mass spectrum of compound **6p**.