Electronic supplementary materials *Mendeleev Commun.*, 2024, **34**, 828–830

Synthesis, structure and properties of spin-labeled photosensitive chromone derivative

Kirill V. Agliulin, Andrey V. Stepanov, Vladimir N. Yarovenko, Mikhail M. Krayushkin, Evgeny V. Tretyakov, Darina I. Nasyrova, Valentina V. Ilyushenkova, Anton O. Ait and Tatyana M. Valova

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General Procedures and Syntheses

4-(1,3-Dioxolan-2-yl)benzoyl chloride was synthesized according to known procedures.[S1,S2]

^{1}H and ^{13}C NMR spectra (200 and 50 MHz, respectively) were recorded on a Bruker AC 200 spectrometer. Chemical shifts (δ, ppm) are given relative to the residual signal of chloroform-d proton (7.26 ppm for ^{1}H NMR) or carbon signal in chloroform-d (77.16 ppm for ^{13}C NMR). High-resolution mass spectra (HRMS) were recorded on a Bruker maXis Q-TOF instrument (Bruker Daltonik GmbH, Bremen, Germany) equipped with an electrospray ionization (ESI) ion source. Measurements were performed in a positive (+) MS ion mode (HV capillary: 4500 V; spray shield: –500 V) with a scan range of m/z 50–1500. Direct syringe injection was applied for the analyzed solutions at a flow rate 3 μL min^{-1}. Nitrogen was used as nebulizer gas (0.4 bar) and dry gas (4.0 L min^{-1}). The dry temperature was established at 250 °C. Melting points were determined in open capillary tubes using a «Boetius» apparatus and are uncorrected. TLC analysis performed on Merck silica gel 60 F_{254} on aluminum plates. All R_f data were given for 40% ethylacetate in petroleum ether solvent mixture. IR spectra were measured on FTIR Spectrometer Infralum FT-08. EPR spectrum of 10^{-4} M toluene solution degassed and stored under Argon was measured using JEOL JES-FA200 spectrometer at room temperature. UV spectra were registered on «Cary 60 bio» (Agilent Technologies) with 1 nm resolution. Fluorescence measurements were carried on «Cary Eclipse» (Varian) using 1 cm cuvette.

(2*Z*)-3-[4-(1,3-Dioxolan-2-yl)phenyl]-3-hydroxy-1-(2-hydroxyphenyl)prop-2-en-1-one (3). A solution of 7.2 g (33.8 mmol) 4-(1,3-dioxolan-2-yl)benzoyl chloride **2**, 5.07 g (37.2 mmol) 2-hydroxyacetophenone **1** in 7 ml dry pyridine was stirred for 30 min. The precipitate formed was filtered off, washed with 20 ml ethanol and air dried. The resulting substance (7.8 g, 25 mmol) was dissolved in 25 ml pyridine and heated to 50 °C. To that solution 2.1 g KOH, thoroughly grinded in preheated to 100°C mortar, was added by portions under hand stirring. After additional 15 minutes of stirring, the orange solution was cooled to room temperature and poured into 30 ml 10% acetic acid. Pale yellow precipitate was filtered off, washed with 2 × 20 ml water and air dried to give the title product. Yield 6.5 g (83%), yellow solid, mp 114–115 °C, R_f 0.66. IR spectrum, ν_{max}, cm^{-1}: 1917, 1678, 1636, 1619, 1597, 1573, 1517, 1435, 1383, 1370, 1348, 1271, 1203, 1176, 1122, 1016, 892, 853. ^{1}H NMR (200 MHz, $CDCl_3$) δ 15.52 (s, 1H), 12.09 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.80 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.49 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.02 (dd, *J* = 8.4, 1.3 Hz, 1H), 6.94 (dt, *J* = 7.3, 1.5 Hz, 1H), 6.86 (s, 1H), 5.90 (s, 1H), 4.21 – 3.96 (m, 4H). ^{13}C NMR (50

MHz, $CDCl_3$) δ 195.87, 177.00, 162.63, 142.44, 136.01, 134.40, 130.52, 128.64, 126.95, 119.21, 118.94, 103.05, 92.62, 65.51. ESI-MS m/z: $[M+H]^+$: calculated for $C_{18}H_{17}O_5^+$ 313.1071, found m/z 313.1072. Found (%): C, 69.19; H, 5.07. Calc. for $C_{18}H_{16}O_5$ (%): C, 69.22; H, 5.16.

(3*Z*)-2-(5-Bromo-2-furyl)-3-{[4-(1,3-dioxolan-2-yl)phenyl](hydroxy)methylene}-2,3-dihydro-4*H*-chromen-4-one (5b). To a 4 g (12.8 mmol) (2*Z*)-3-[4-(1,3-dioxolan-2-yl)phenyl]-3-hydroxy-1-(2-hydroxyphenyl)prop-2-en-1-one **3**, 2.7 g (15.4 mmol) 5-bromo-2-furaldehyde was added 50 ml ethanol and 0.1 ml piperidine. The resulting suspension was stirred for 12 h, then the precipitate was filtered and recrystallized from ethanol. The title product was obtained as a colorless solid. Yield 4.74 g (78%), mp 136–137 °C, R_f 0.71. IR spectrum, ν_{max}, cm^{-1}: 2876, 1603, 1544, 1489, 1418, 1380, 1341, 1292, 1262, 1209, 1169, 1148, 1119, 1076, 1008, 742. ^{1}H NMR (200 MHz, $CDCl_3$) δ 16.63 (s, 1H), 7.93 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.44 (dt, *J* = 7.9, 1.7 Hz, 1H), 7.06 (dt, *J* = 7.9, 1.1 Hz, 1H), 6.92 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.29 (dd, *J* = 3.5, 1.1 Hz, 1H), 6.18 (d, *J* = 3.5, 1H), 6.17 (s, 1H), 5.87 (s, 1H), 4.26 – 3.98 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$) 182.98, 181.07, 156.90, 154.78, 141.41, 135.77, 135.19, 129.95, 128.28, 127.78, 126.88, 126.36, 123.61, 122.25, 120.52, 118.09, 114.12, 112.23, 103.04, 102.33, 70.42, 65.50. ESI-MS m/z: $[M+H]^+$: calculated for $C_{23}H_{18}BrO_6^+$ 469.0281, found m/z 469.0282. Found (%): C, 58.91; H, 3.42. Calc. for $C_{23}H_{17}BrO_6$ (%): C, 58.87; H, 3.65.

2-(5-Bromo-2-furyl)-3-[4-(1,3-dioxolan-2-yl)benzoyl]-4*H*-chromen-4-one (6). To a solution of compound **5b** (0.5 g, 1.1 mmol) in 20 ml dioxane, SeO_2 (0.24 g, 2.2 mmol) was added. The resulting mixture was heated to 60 °C under vigorous stirring for 8 hours. The solvent was evaporated under vacuum, the residue was dissolved in 100 ml CH_2Cl_2 and filtered through a short pad of silica to remove excess of SeO_2. The residue formed after removal of the solvent was subjected to column chromatography on 30 g SiO_2. The desired 2*H*-chromene was eluted by 50% ethylacetate-hexane mixture. The crude product obtained as an oil was solidified by slow evaporation of CH_2Cl_2 from its solution in CH_2Cl_2-hexane mixture. Yield 0.21 g (42%), mp 142–143 °C, R_f 0.45. IR spectrum, ν_{max}, cm^{-1}: 3136, 2881, 1672, 1614, 1576, 1535, 1457, 1391, 1335, 1302, 1266, 1221, 1090, 1011, 756. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 2H), 7.75 (ddd, *J* = 1.8, 7.1, 8.7 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 3H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 3.6 Hz, 1H), 6.43 (d, *J* = 3.6 Hz, 1H), 5.88 (s, 1H), 4.14 – 3.99 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 192.18, 176.03, 155.54, 150.18, 146.57, 143.75, 137.53, 134.52, 129.99, 129.47, 127.83, 126.86, 126.11, 125.76,

123.52, 119.40, 118.03, 114.56, 102.99, 65.39. ESI-MS m/z: $[M+H]^+$: calculated for $C_{23}H_{16}BrO_6^+$ 467.0130, found m/z 467.0125. Found (%): C, 59.34; H, 3.25. Calc. for $C_{23}H_{15}BrO_6$ (%): C, 59.12; H, 3.24.

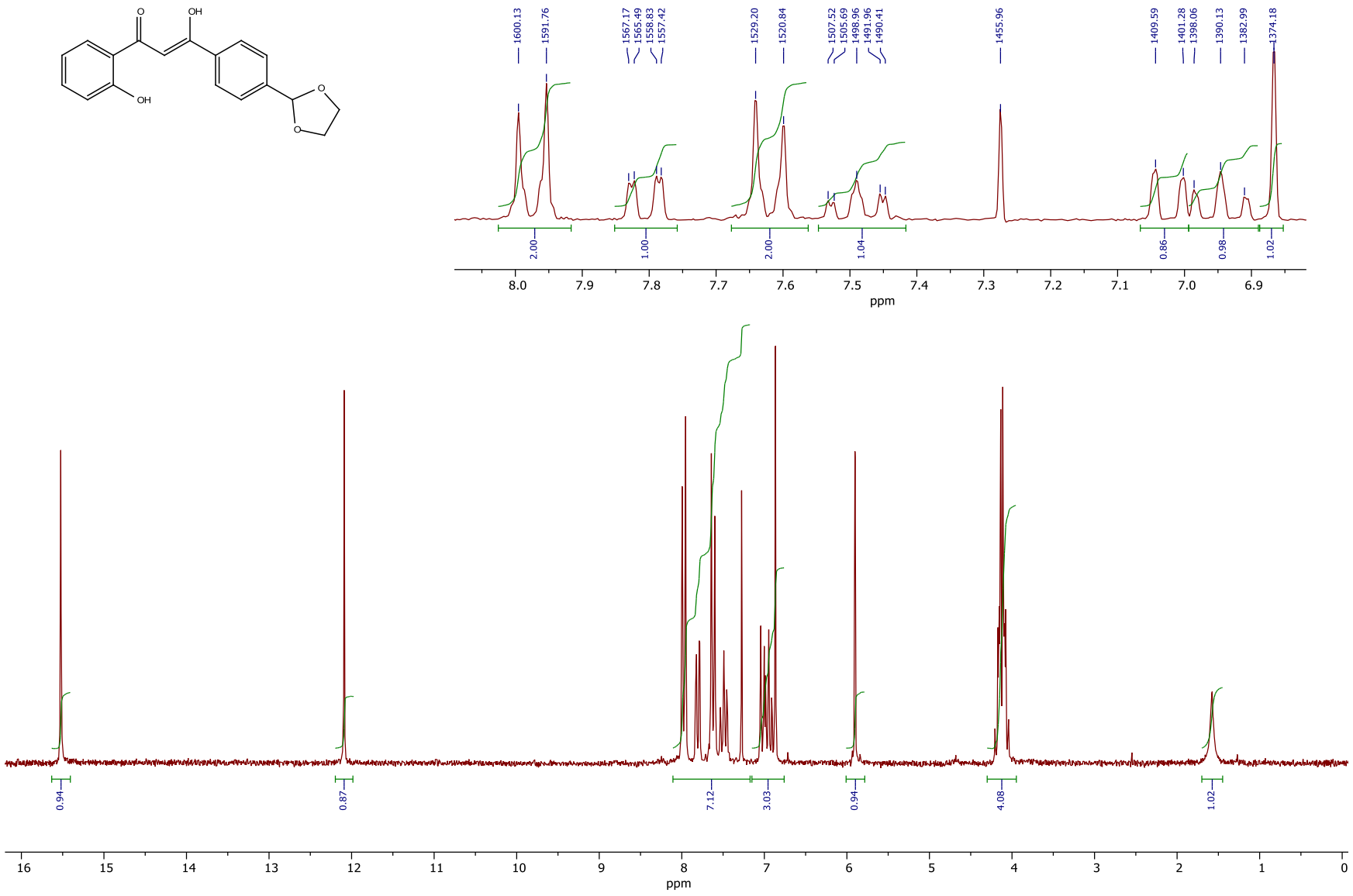
4-{[2-(5-Bromo-2-furyl)-4-oxo-4*H*-chromen-3-yl]carbonyl}benzaldehyde (7). A solution of compound **5b** (4.23 g, 9.27 mmol) and SeO_2 (2.05, 18.54 mmol) in 60 ml dioxane was refluxed with vigorous stirring for 12 h. Dioxane was evaporated under reduced pressure, the residue was dissolved in 200 ml CH_2Cl_2 and filtered through a short pad of silica to remove excess of SeO_2. The resulting solid was dissolved 50 ml CH_2Cl_2, 20 ml ethanol and 20 ml methyl *tert*-butyl ether. This solution was slowly evaporated on a rotary evaporator without heating until white precipitate forms. Yield 1.85 g (43%), mp 220–221 °C, R_f 0.5. Dioxolan **6** (360 mg, 77 mmol) was added to a stirred solution of 20 mg (10 mmol) p-toluenesulfonic acid monohydrate in 30 ml acetone. Resulting slurry was stirred 12 h at room temperature and filtered, precipitate washed by acetone and air dried. Aldehyde **7** (300 mg, 92%) was obtained with the same properties as described in previous method. IR spectrum, ν_{max}, cm^{-1}: 2866, 1602, 1565, 1508, 1487, 1392, 1331, 1267, 1242, 1217, 1191, 1156, 1086, 1033, 834, 801, 762, 718. ^1H NMR (200 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.23 (d, *J* = 7.0 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 2H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.78 (t, *J* = 7.0 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 3.6 Hz, 1H), 6.47 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 192.00, 191.76, 176.12, 155.59, 150.54, 146.61, 141.41, 139.52, 134.82, 130.06, 129.87, 128.12, 126.21, 126.03, 123.54, 118.60, 118.17, 118.11, 114.75. ESI-MS m/z: $[M+H]^+$: calculated for $C_{21}H_{12}BrO_5^+$ 422.9863, found m/z 422.9851. Found (%): C, 59.67; H, 2.61. Calc. for $C_{21}H_{11}BrO_5$ (%): C, 59.60; H, 2.62.

2-(5-Bromo-2-furyl)-3-(4-{(*E*)-[(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)imino]methyl}-benzoyl)-4*H*-chromen-4-one (8). To a solution of aldehyde **7** (0.1 g, 0.24 mmol) in 5 ml toluene, 81 mg (0.47 mmol) of 4-amino-TEMPO was added followed by one drop of acetic acid. The solution was heated at 70 °C for 6 hours. The reaction progress was monitored by NMR of an aliquot of the reaction mixture. After evaporation to dryness, the residue was washed with 10% solution of CH_2Cl_2 in methyl *tert*-butyl ether to remove excess of 4-amino-TEMPO. The resulting oily substrance was triturated with 5% solution of ethyl acetate in light petroleum. This forms pale orange solid which was dried in vacuum to constant weight. Yield 90 mg (66%), mp. 165–170 °C. Crystals for XRD were grown by slow evaporation of a CH_2Cl_2-hexane solution. EPR spectrum (toluene): g = 2.0061, a_N = 1.54 mT, line withdraw 0.283 mT. IR spectrum, ν_{max}, cm^{-1}: 2975, 2931, 1688, 1625, 1605, 1576, 1538,

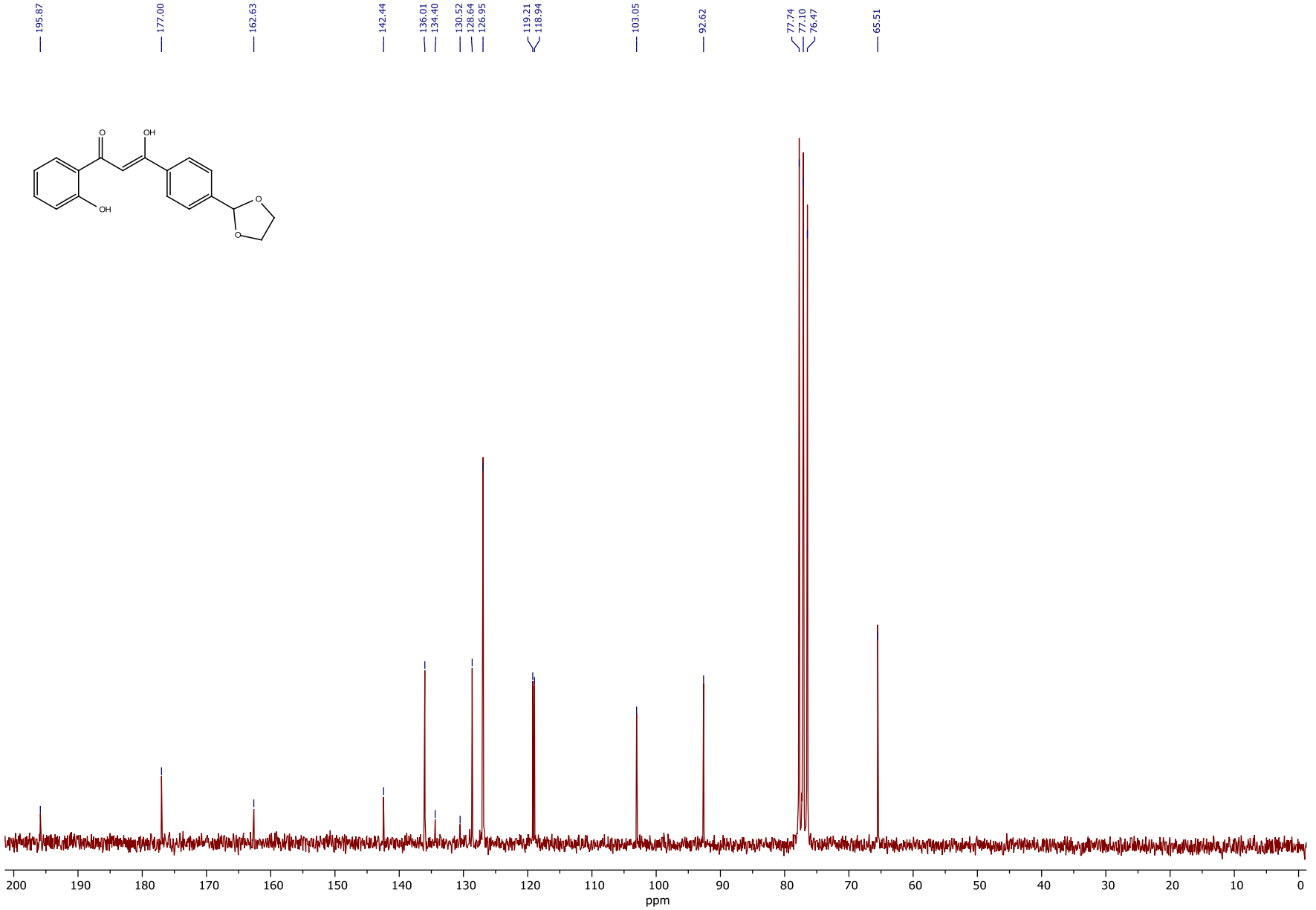
1457, 1391, 1127, 842, 767. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.28 (s, *J* = 8.0 Hz, 1H), 8.09 (s, 2H), 7.91 (s, 2H), 7.82 (t, *J* = 7 Hz, 1H), *7*.63 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7 Hz, 1H), 7.12 (s, 1H), 6.49 (s, 1H). ^{1}H NMR after addition of triple molar excess of $PhNHNH_2$ (500 MHz, DMSO-d_6) δ 8.41 (s, 1H), 8.23 (d, *J* = 6.8 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.77 (t, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 3.3 Hz, 1H), 6.44 (d, *J* = 3.3 Hz, 1H), 3.75 – 3.66 (m, 1H), 1.97 (t, *J* = 11.4 Hz, 2H), 1.74 (d, *J* = 13.7 Hz, 21H), 1.30 (s, 12H). ESI-MS m/z: $[M]^+$: calculated for $C_{30}H_{28}BrN_2O_5^+$ 575.1176, found m/z 575.1172.

Spectra Data

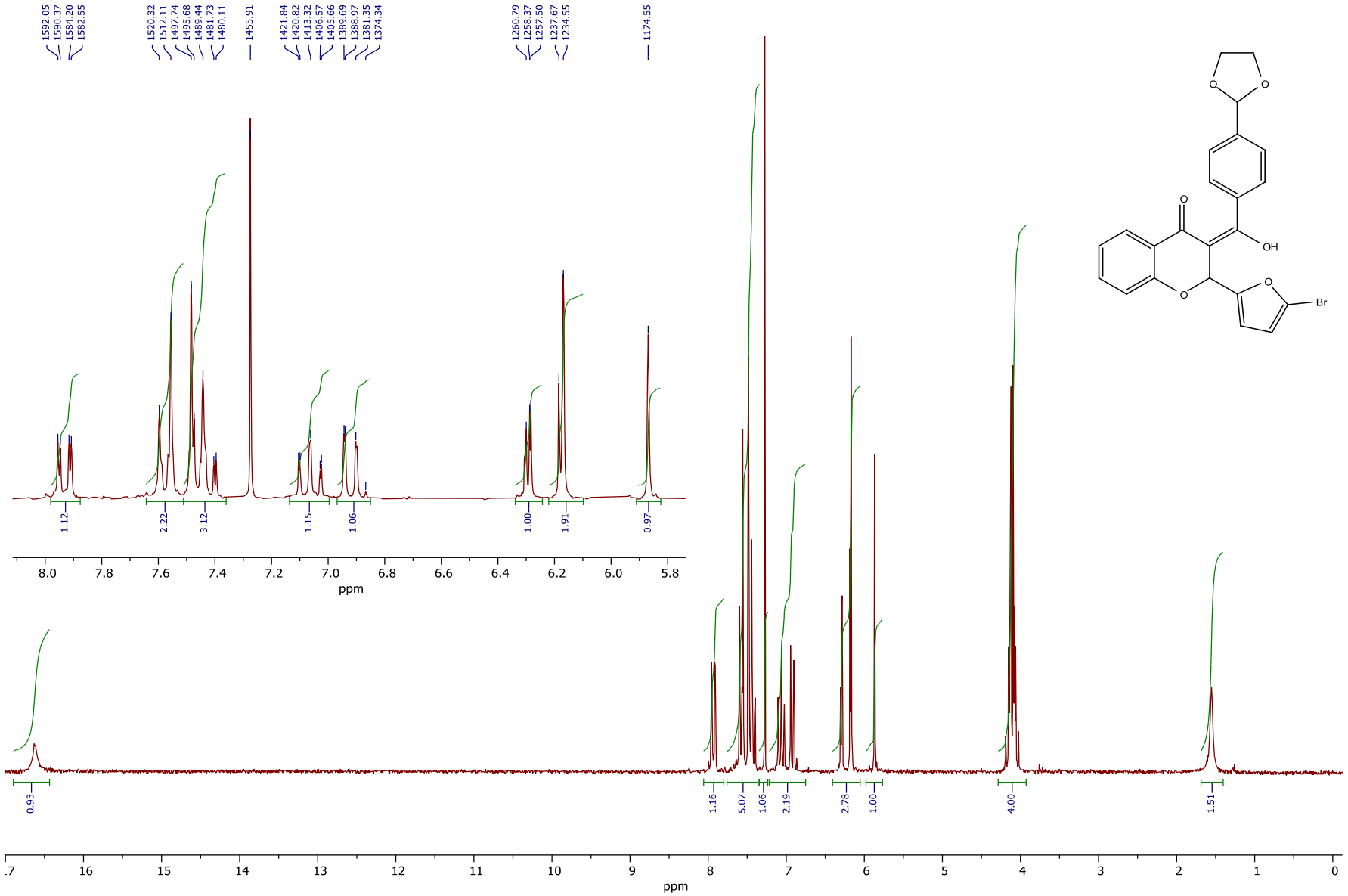
^{1}H NMR spectrum of (2*Z*)-3-[4-(1,3-dioxolan-2-yl)phenyl]-3-hydroxy-1-(2-hydroxyphenyl)prop-2-en-1-one (**3**)



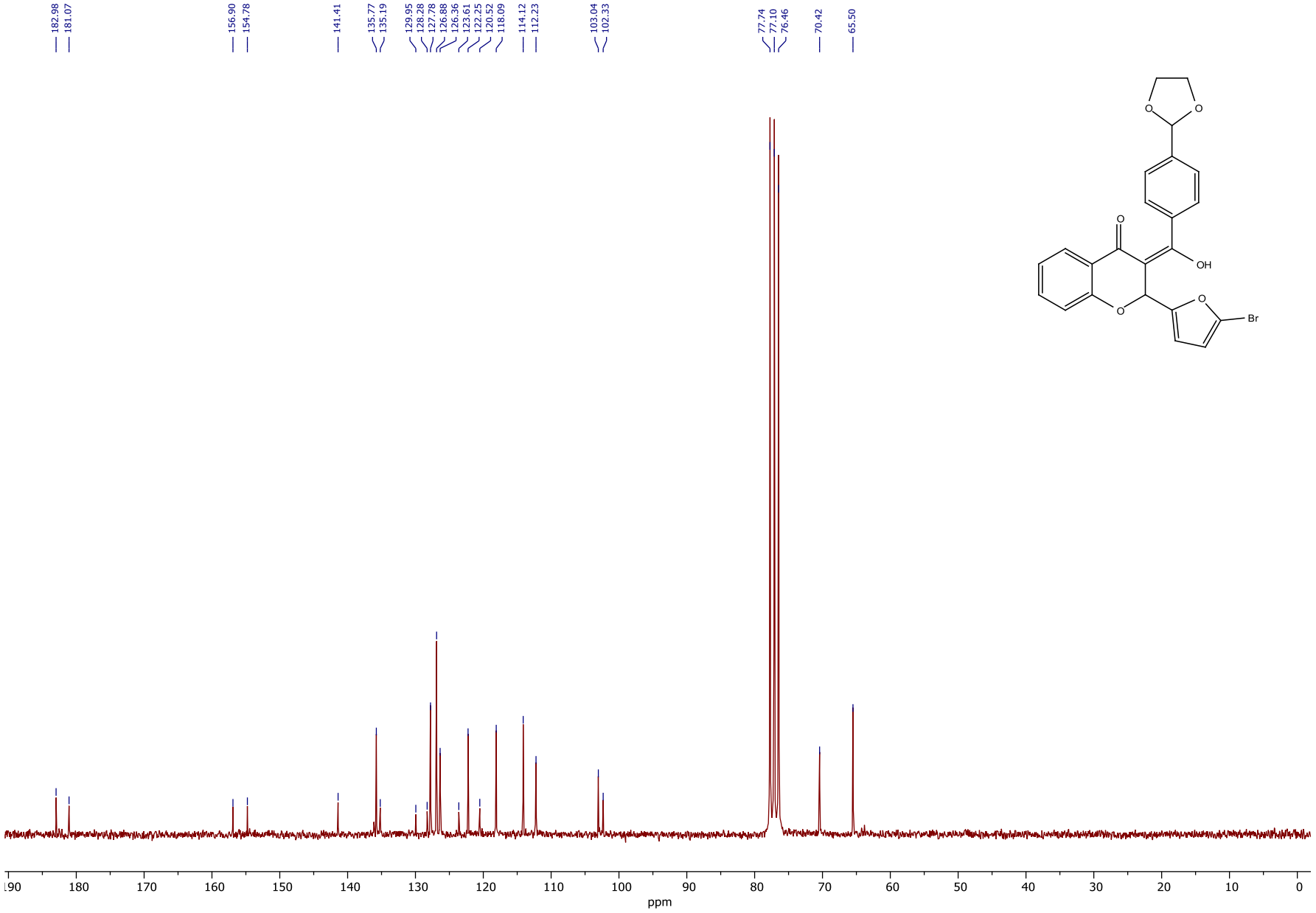
^{13}C NMR spectrum of (2*Z*)-3-[4-(1,3-dioxolan-2-yl)phenyl]-3-hydroxy-1-(2-hydroxyphenyl)prop-2-en-1-one (**3**)



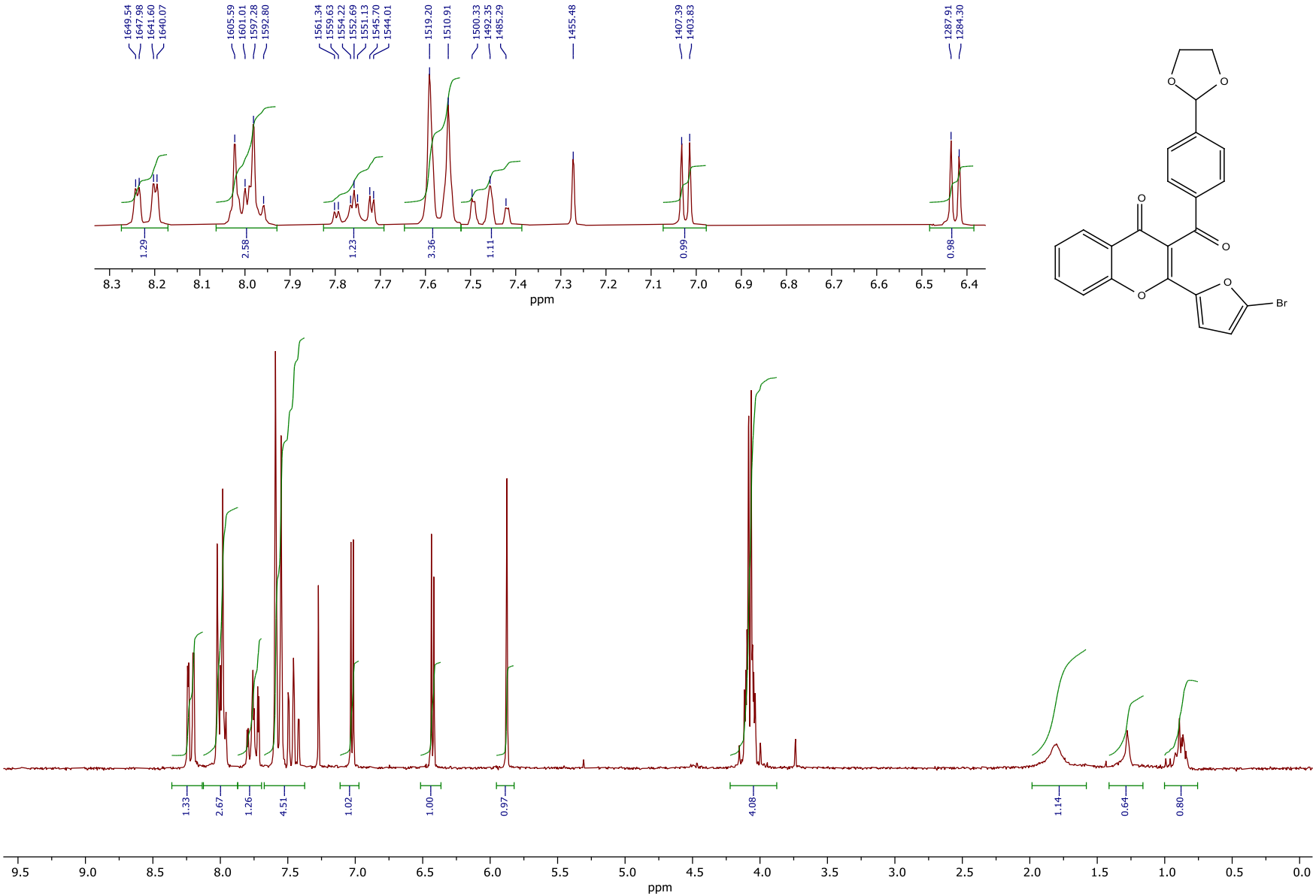
^{1}H NMR spectrum of 2-(5-bromo-2-furyl)-3-[[4-(1,3-dioxolan-2-yl)phenyl](hydroxy)methylene]-2,3-dihydro-4*H*-chromen-4-one (**5b**)



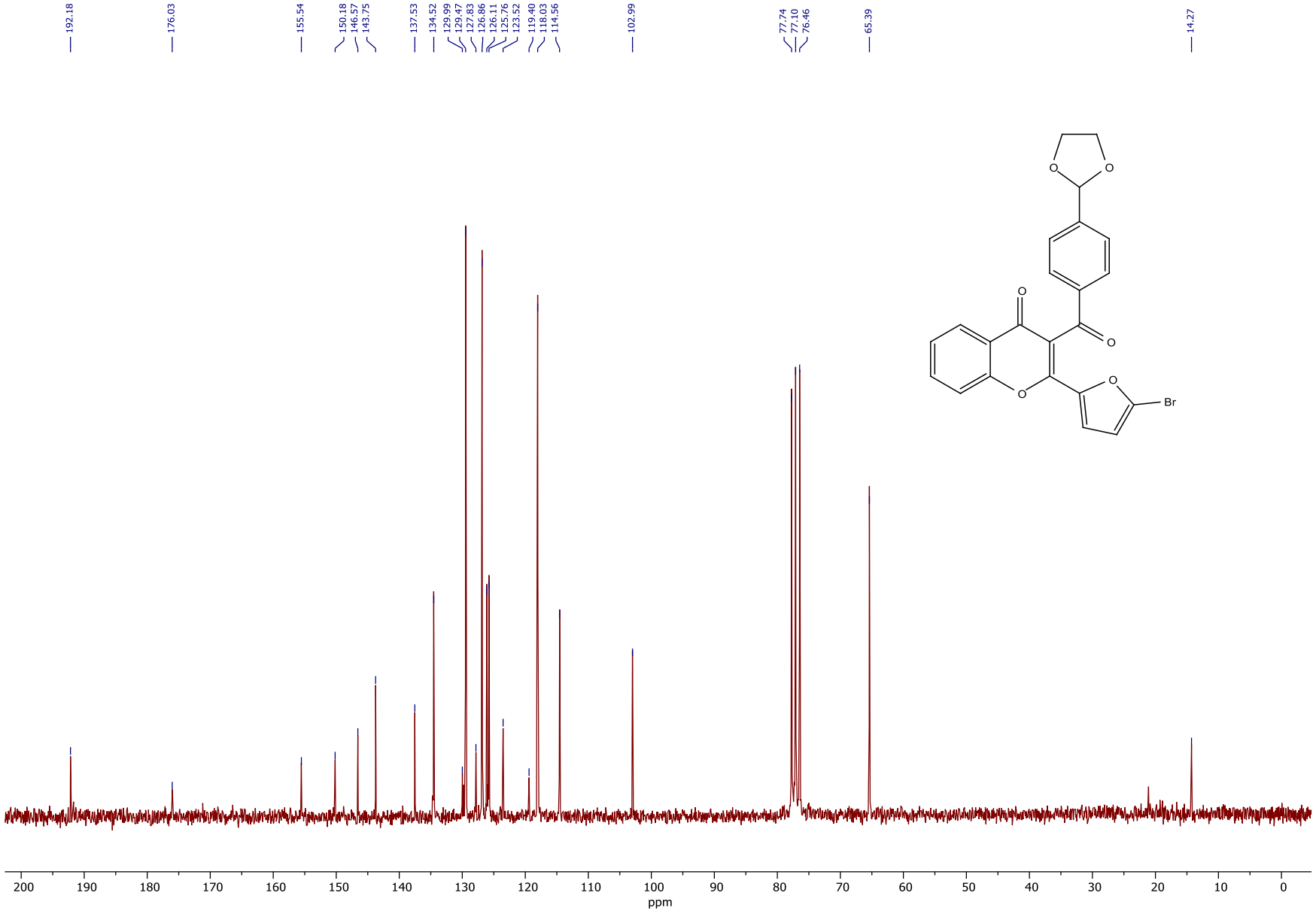
^{13}C NMR spectrum of 2-(5-bromo-2-furyl)-3-[[4-(1,3-dioxolan-2-yl)phenyl](hydroxy)methylene]-2,3-dihydro-4*H*-chromen-4-one (**5b**)



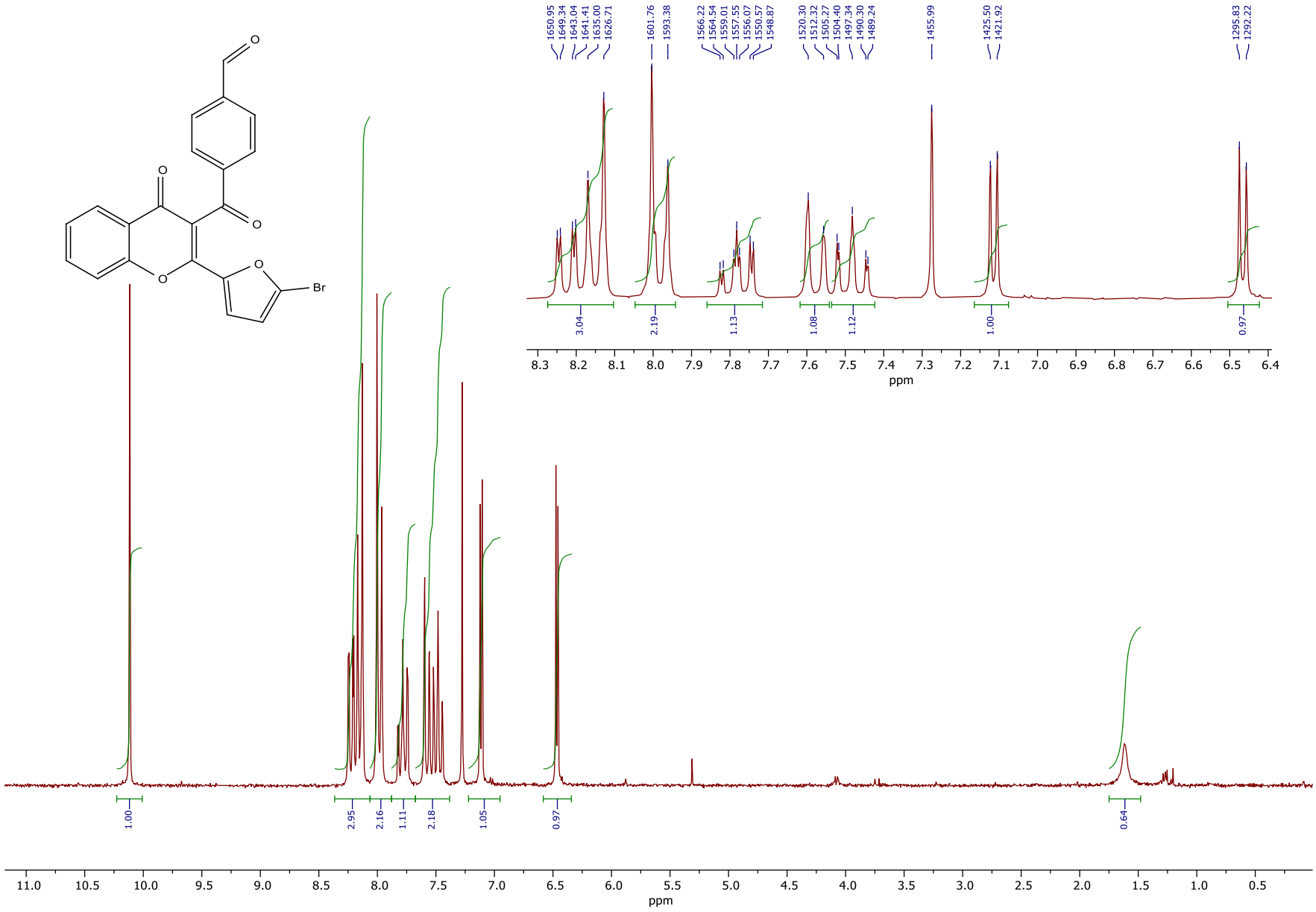
^{1}H NMR spectrum of 2-(5-bromo-2-furyl)-3-[4-(1,3-dioxolan-2-yl)benzoyl]-4*H*-chromen-4-one (**6**)



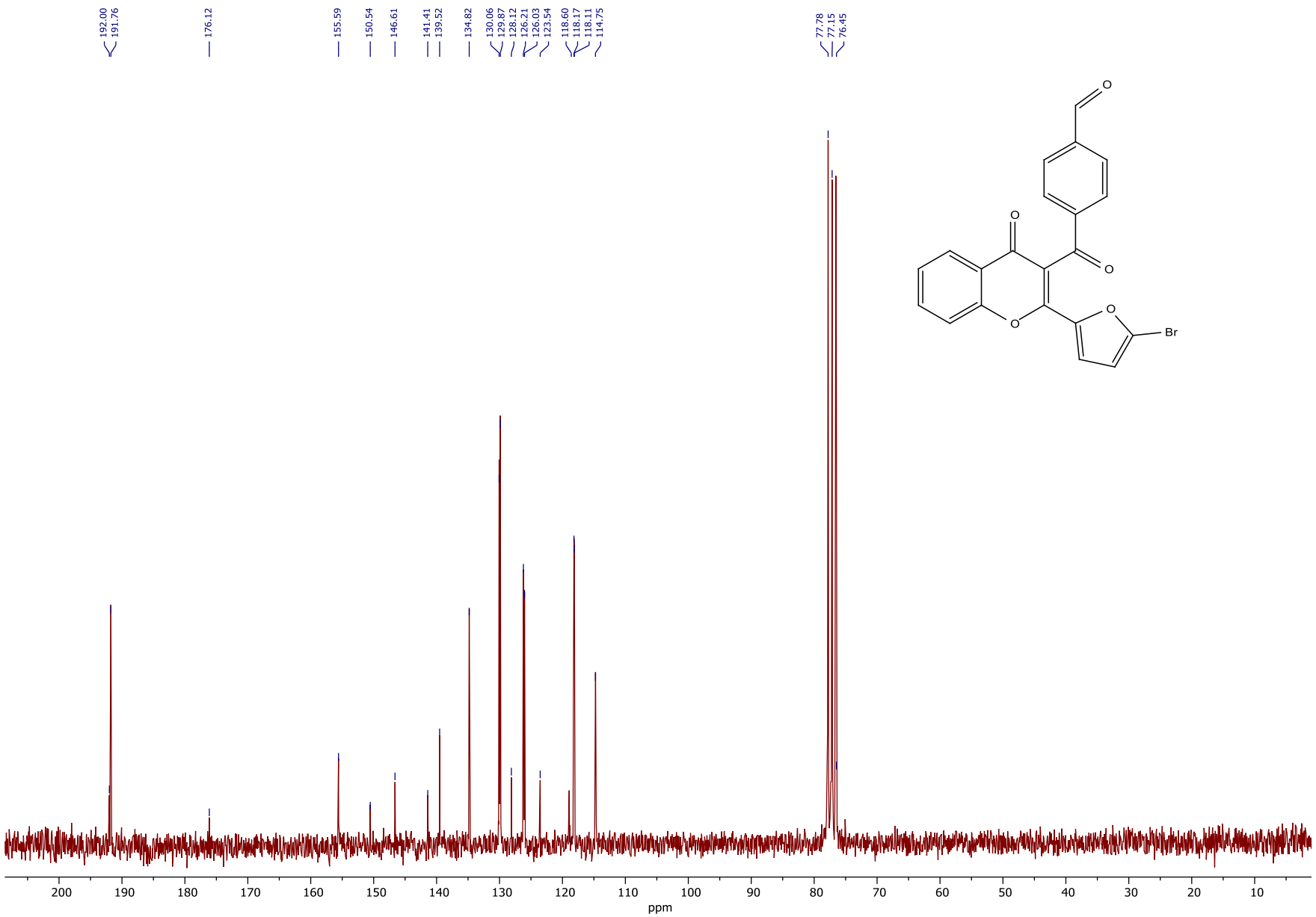
^{13}C NMR spectrum of 2-(5-bromo-2-furyl)-3-[4-(1,3-dioxolan-2-yl)benzoyl]-4*H*-chromen-4-one (**6**)



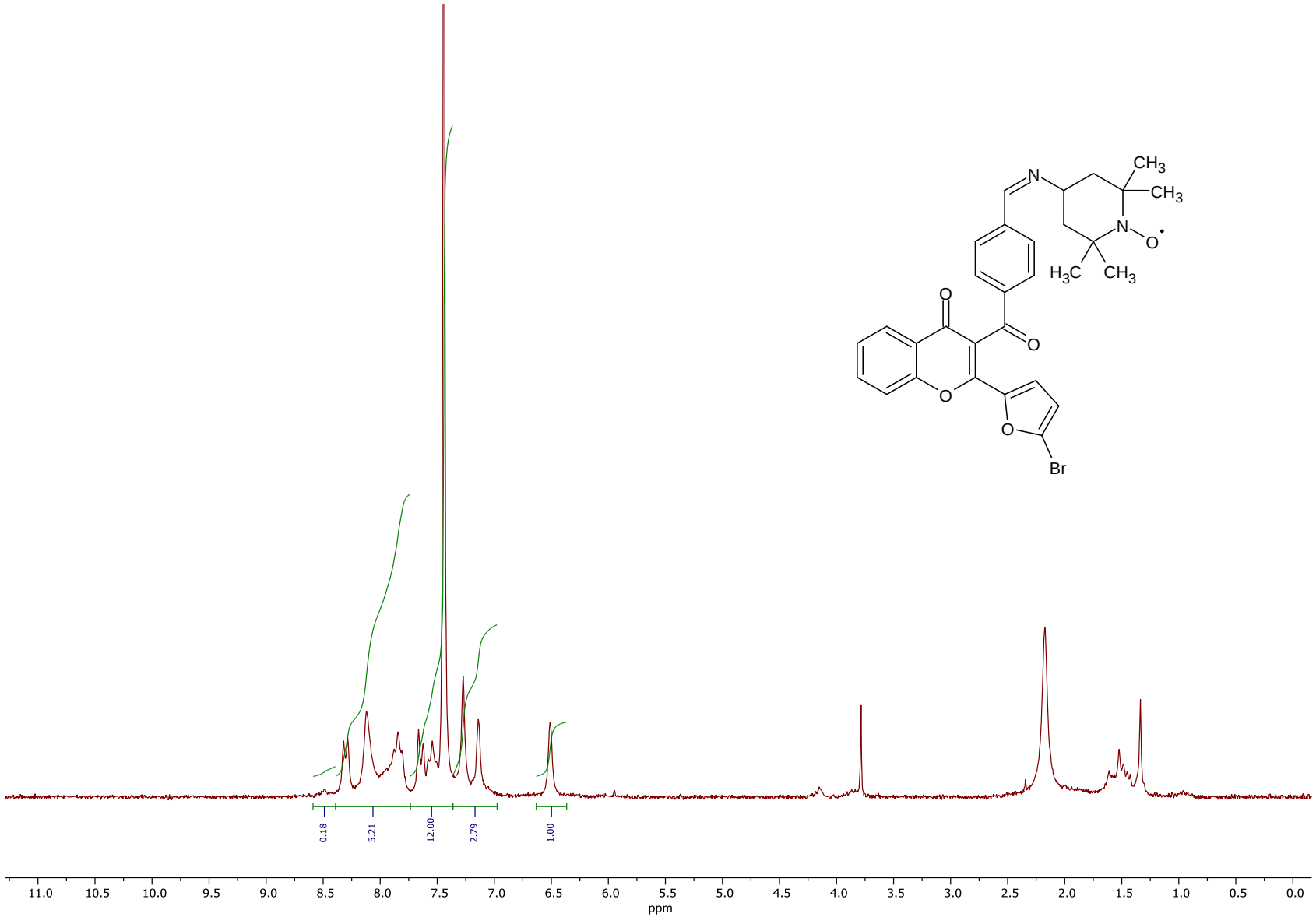
^{1}H NMR spectrum of 4-{[2-(5-bromo-2-furyl)-4-oxo-4*H*-chromen-3-yl]carbonyl}benzaldehyde (**7**)



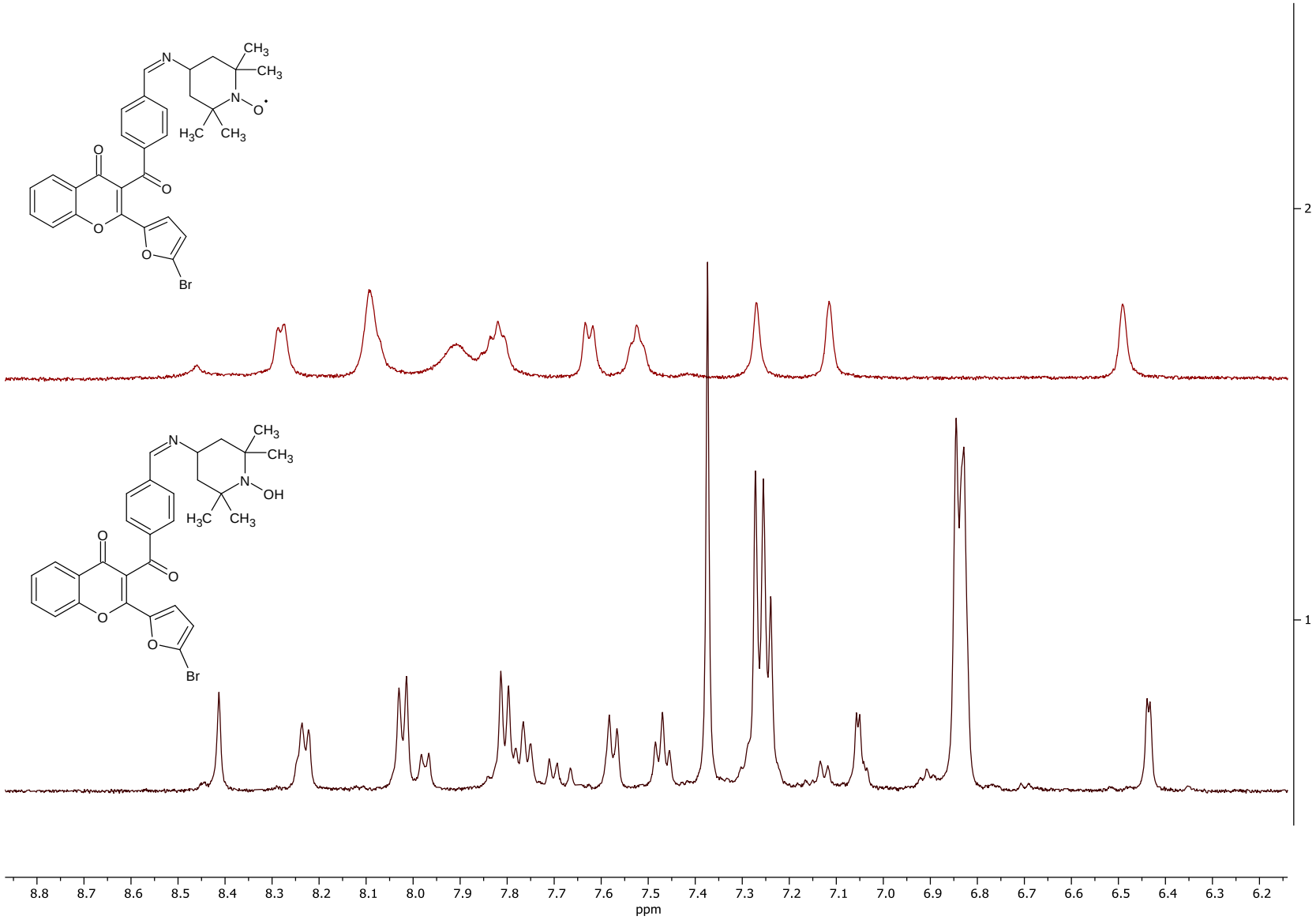
^{13}C NMR spectrum of 4-{[2-(5-bromo-2-furyl)-4-oxo-4*H*-chromen-3-yl]carbonyl}benzaldehyde (**7**)



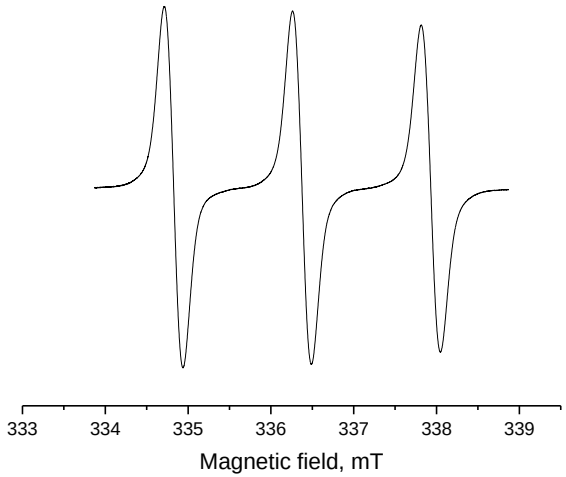
^{1}H NMR spectrum of 2-(5-bromo-2-furyl)-3-(4-{(*E*)-[(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)imino]methyl}benzoyl)-4*H*-chromen-4-one (**8**)



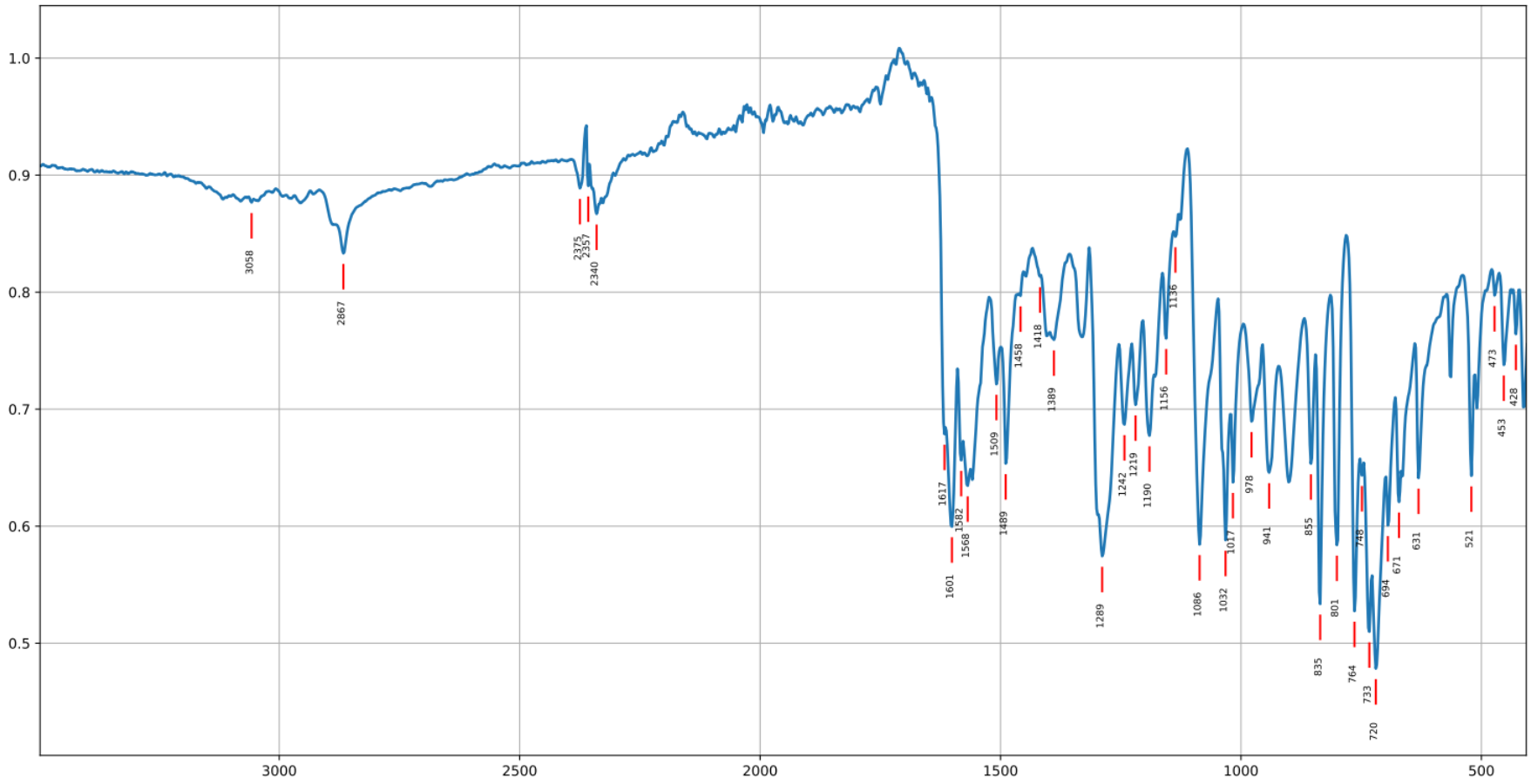
500 MHz ^{1}H NMR spectra of radical **8** before and after phenylhydrazine addition (aromatic region)



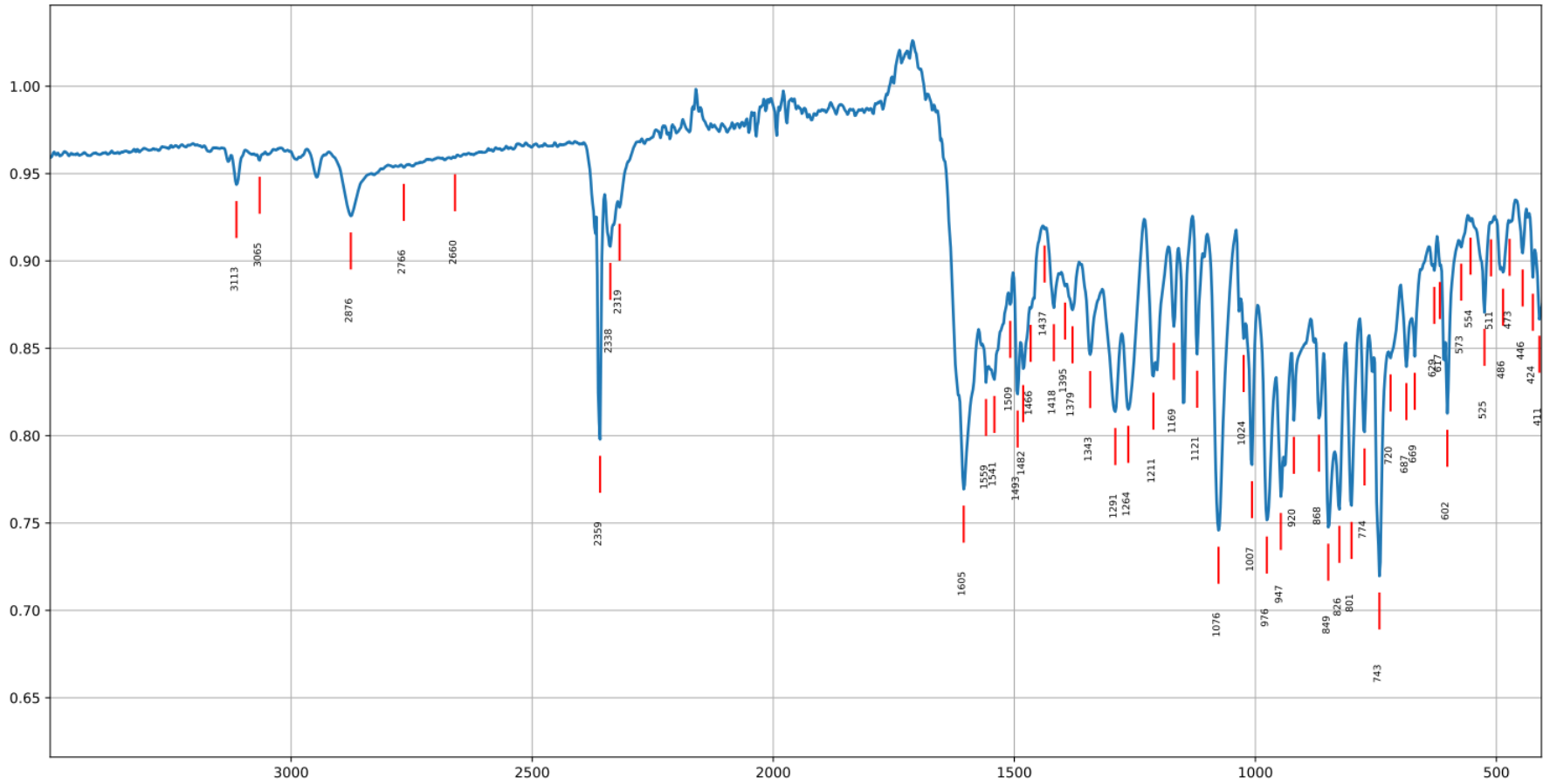
EPR spectrum of radical **8**



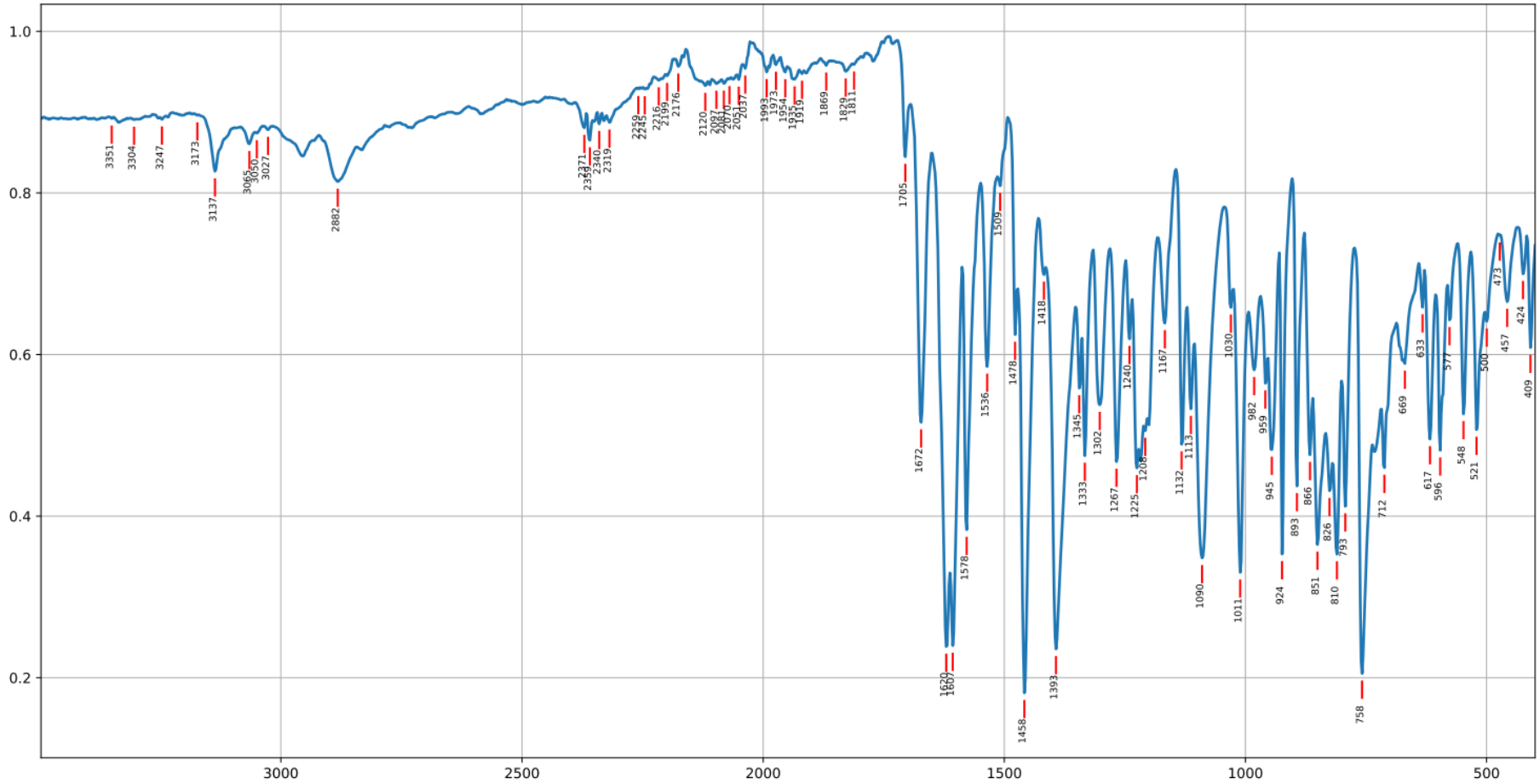
IR spectrum of (2*Z*)-3-[4-(1,3-dioxolan-2-yl)phenyl]-3-hydroxy-1-(2-hydroxyphenyl)prop-2-en-1-one (**3**)



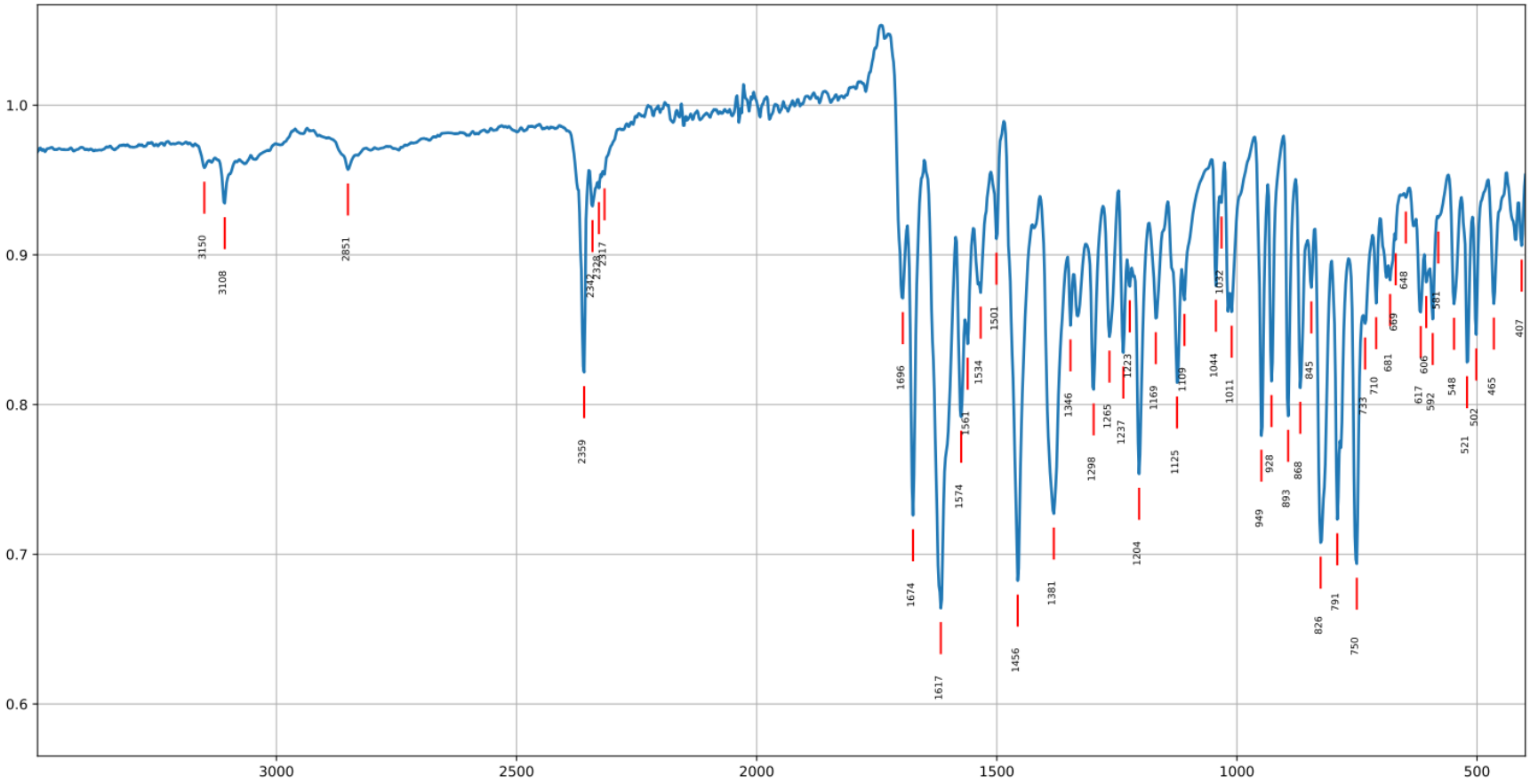
IR spectrum of 2-(5-bromo-2-furyl)-3-[[4-(1,3-dioxolan-2-yl)phenyl](hydroxy)methylene]-2,3-dihydro-4*H*-chromen-4-one (**5b**)



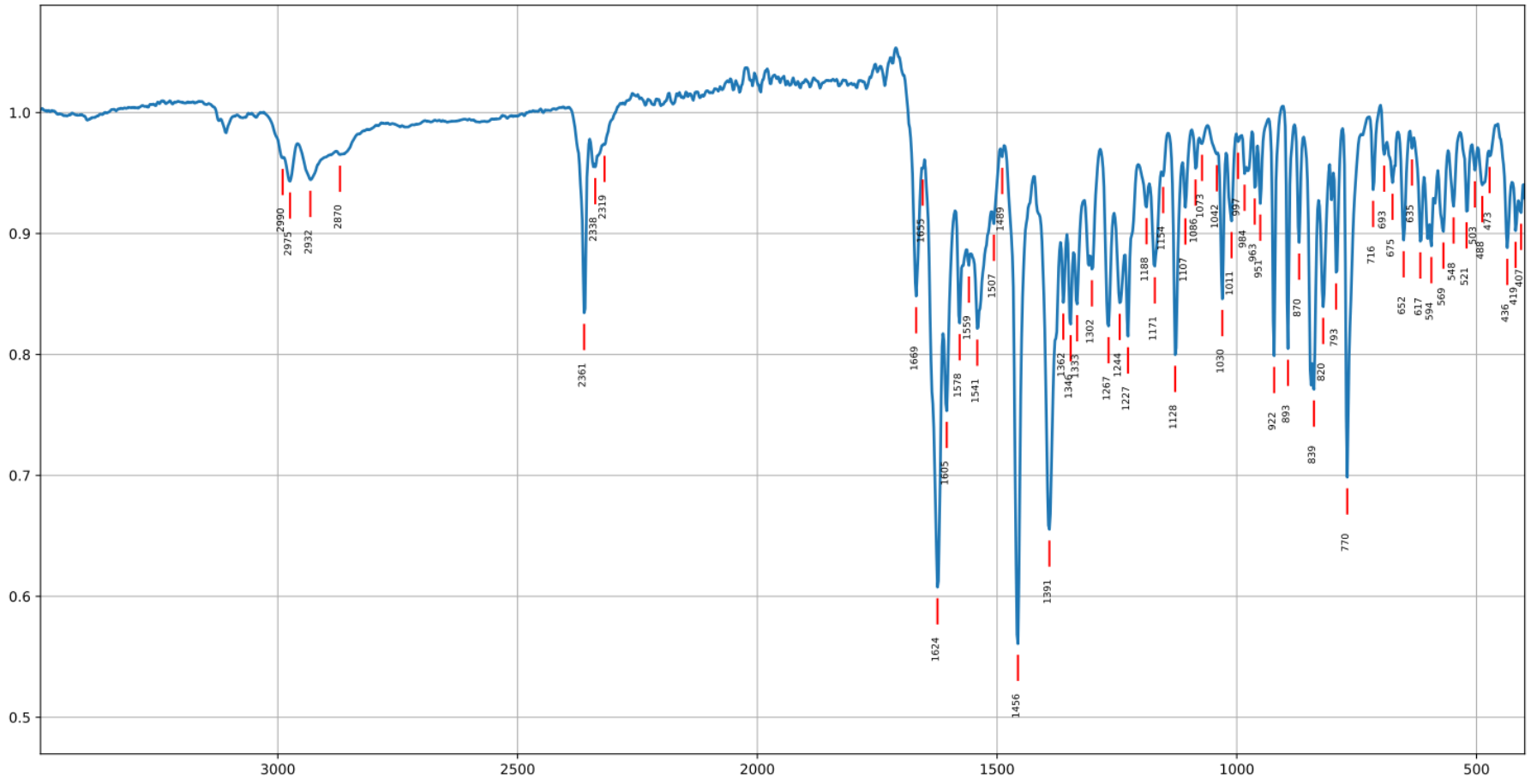
IR spectrum of 2-(5-bromo-2-furyl)-3-[4-(1,3-dioxolan-2-yl)benzoyl]-4*H*-chromen-4-one (**6**)



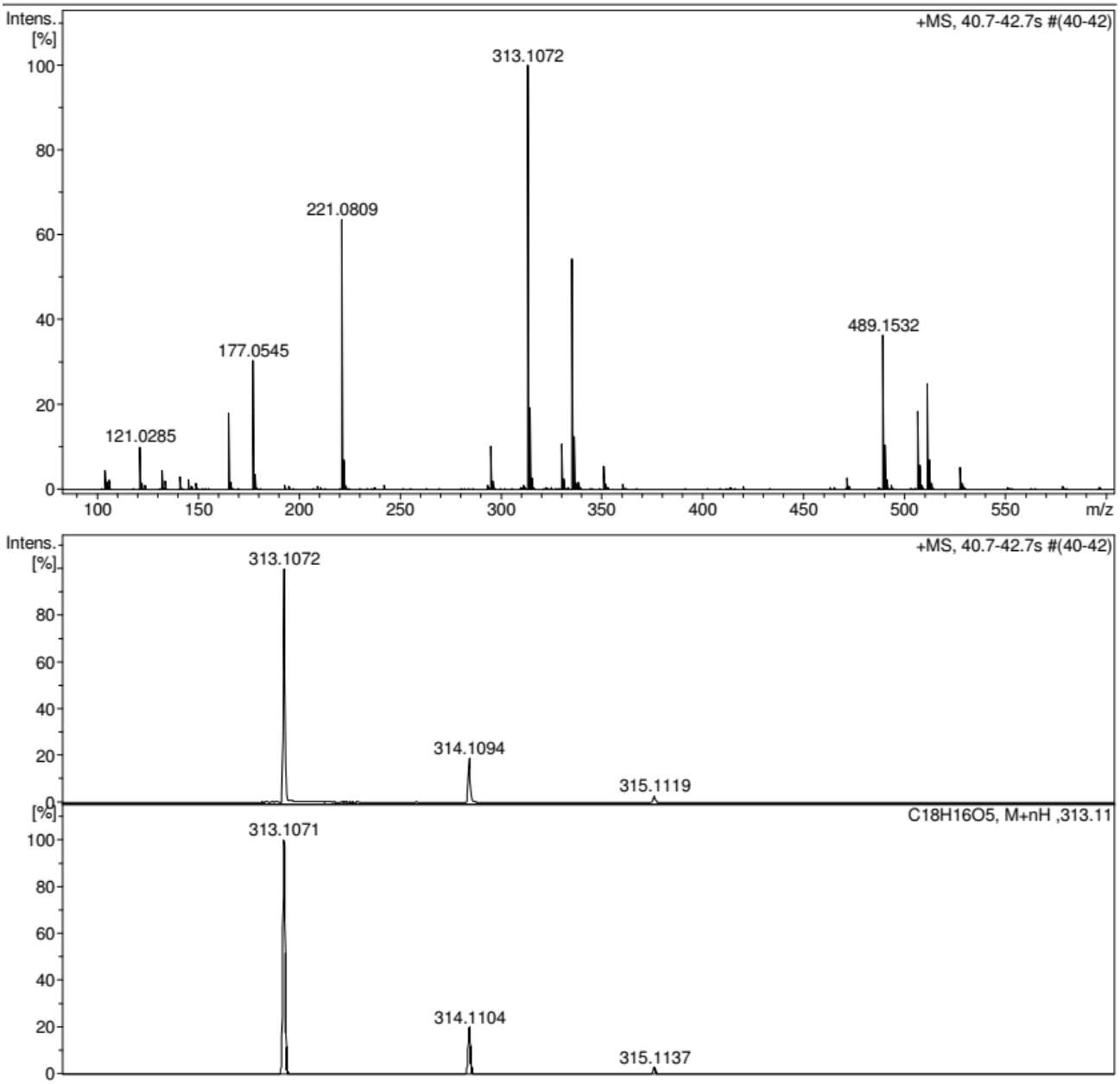
IR spectrum of 4-{[2-(5-bromo-2-furyl)-4-oxo-4*H*-chromen-3-yl]carbonyl}benzaldehyde (**7**)



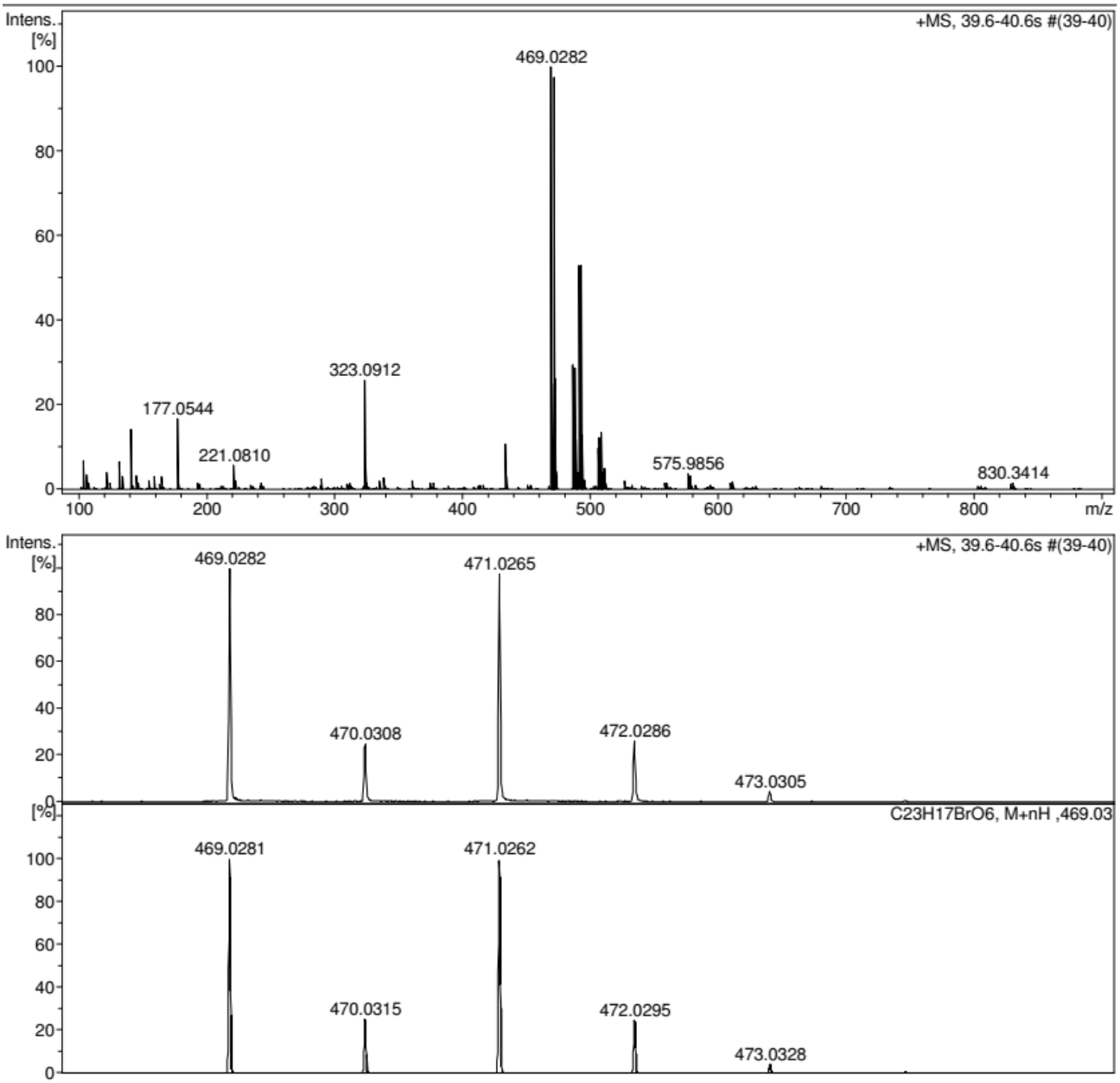
IR spectrum of 2-(5-bromo-2-furyl)-3-(4-{(*E*)-[(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)imino]methyl}benzoyl)-4*H*-chromen-4-one (**8**)



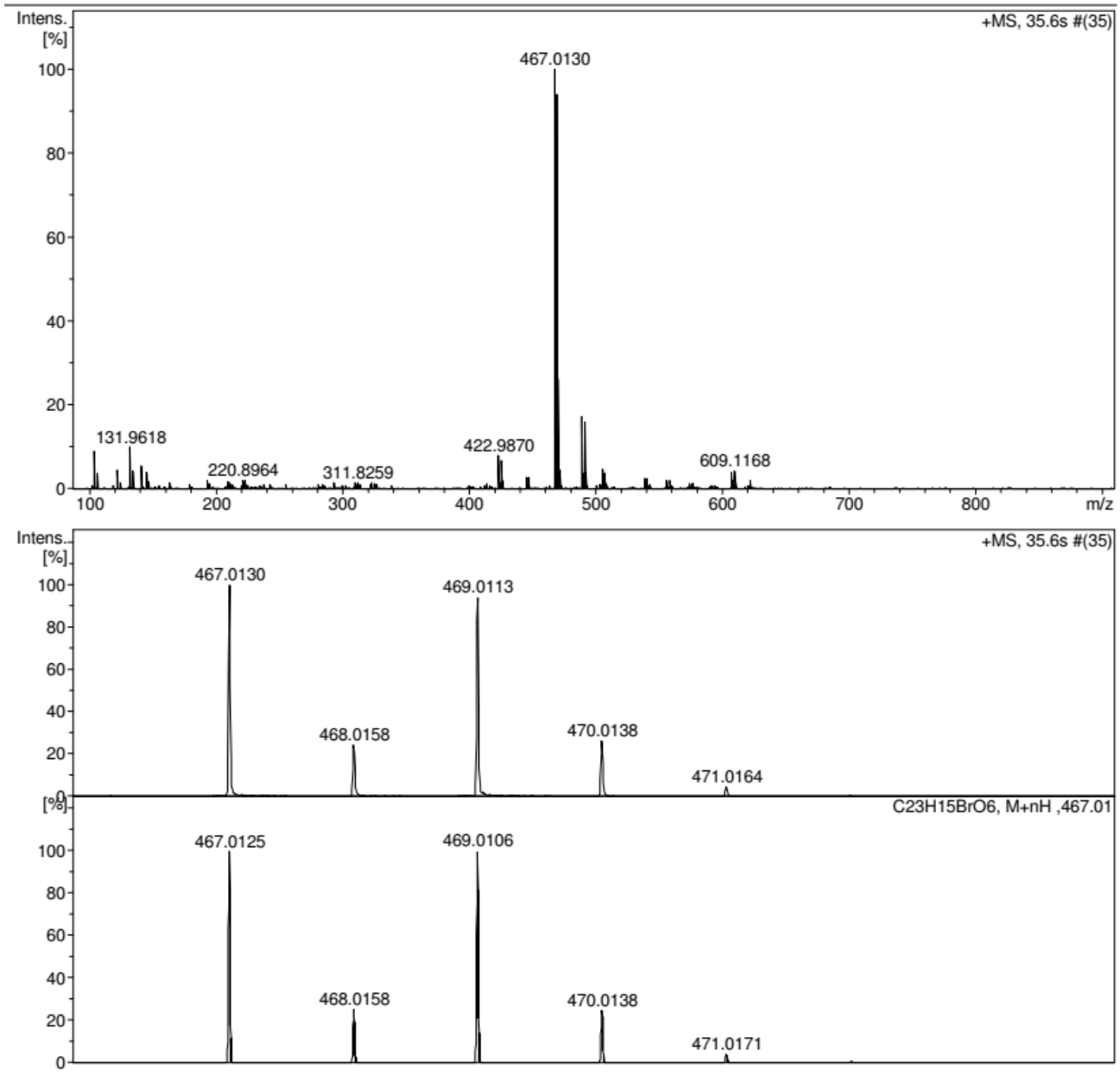
HRMS spectrum of 3-[4-(1,3-dioxolan-2-yl)phenyl]-3-hydroxy-1-(2-hydroxyphenyl)prop-2-en-1-one (**3**)



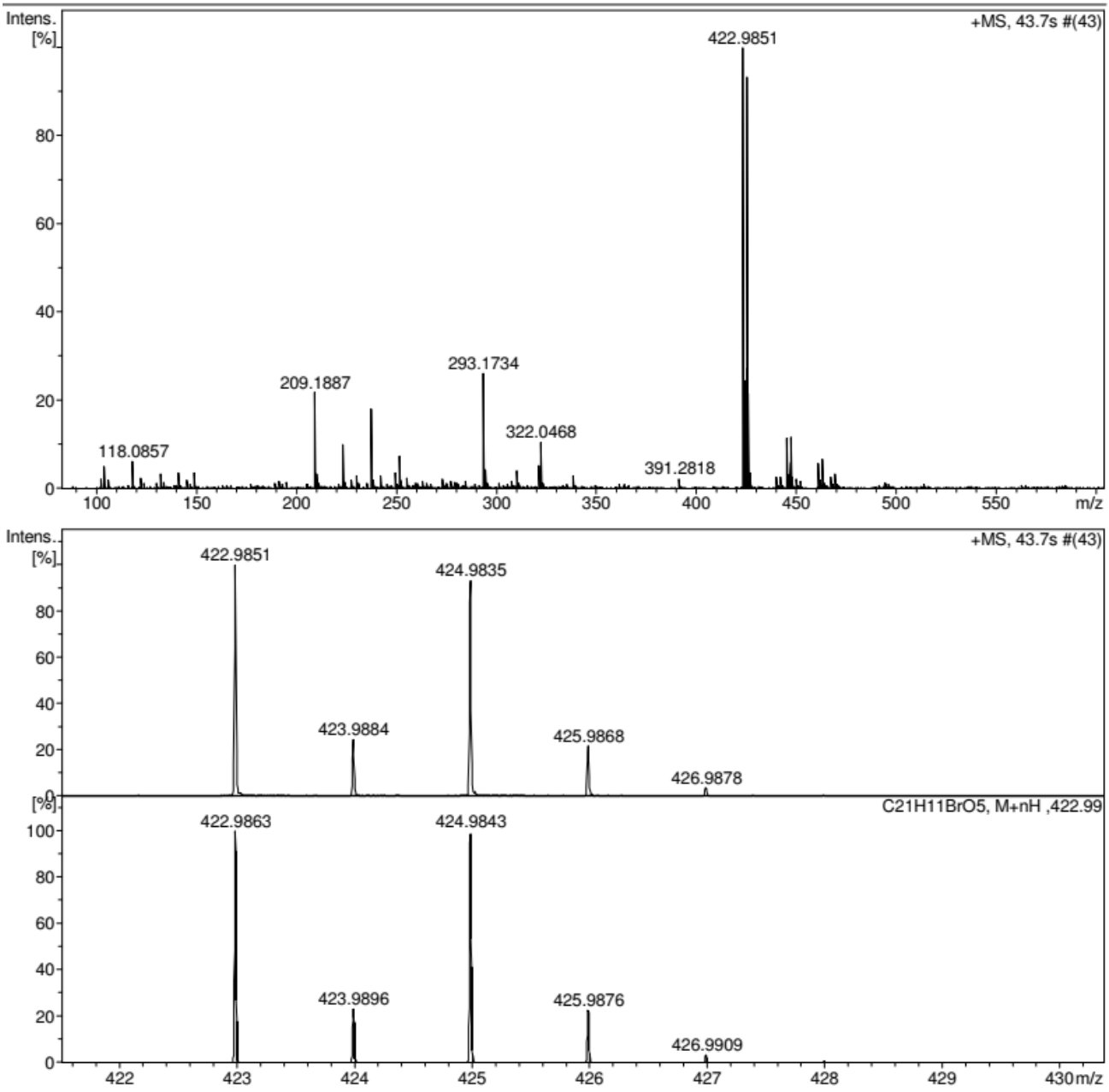
HRMS spectrum of 2-(5-bromo-2-furyl)-3-[[4-(1,3-dioxolan-2-yl)phenyl](hydroxy)methylene]-2,3-dihydro-4*H*-chromen-4-one (**5b**)



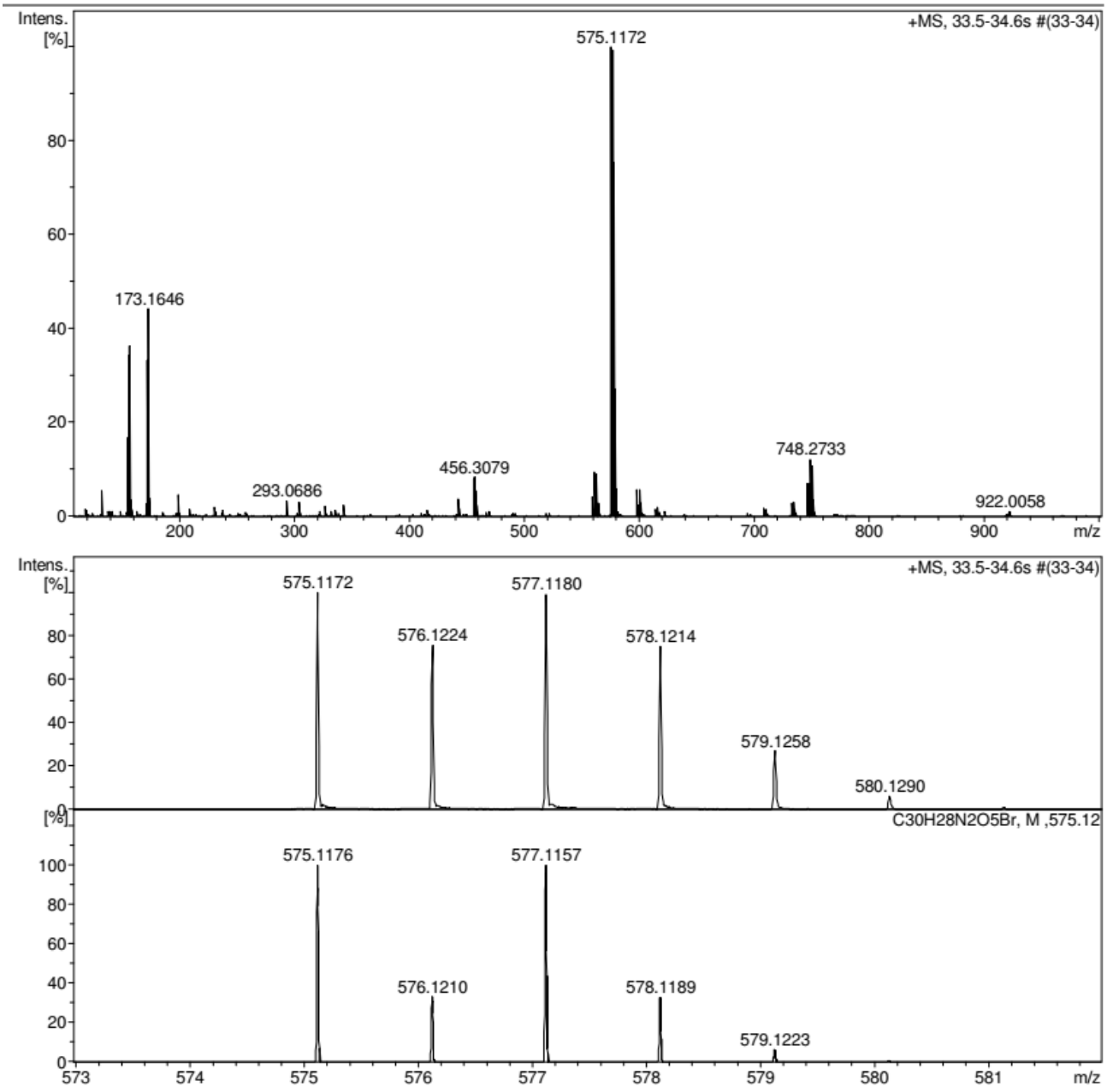
HRMS spectrum of 2-(5-bromo-2-furyl)-3-[4-(1,3-dioxolan-2-yl)benzoyl]-4*H*-chromen-4-one (**6**)



HRMS spectrum of 4-{[2-(5-bromo-2-furyl)-4-oxo-4*H*-chromen-3-yl]carbonyl}benzaldehyde (**7**)



HRMS spectrum of 2-(5-bromo-2-furyl)-3-(4-{(*E*)-[(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)imino]methyl}benzoyl)-4*H*-chromen-4-one (**8**)



X-ray Crystallography Data

Table S1. Crystal data and structure refinement for **8**.

Empirical formula	$C_{30}H_{28}BrN_2O_5$	
Formula weight	576.45	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	*Pbca*	
Unit cell dimensions	*a* = 10.12010(10) Å	α = 90°.
	b = 20.61980(10) Å	β = 90°.
	c = 25.3495(2) Å	γ = 90°.
Volume	5289.79(7) $Å^3$	
Z	8	
Density (calculated)	1.448 mg/m^3	
Absorption coefficient	2.477 mm^{-1}	
F(000)	2376	
Crystal size	0.48 x 0.37 x 0.15 mm^3	
Theta range for data collection	3.487 to 80.060°.	
Index ranges	$-12 \le h \le 12$, $-26 \le k \le 26$, $-26 \le l \le 32$	
Reflections collected	58954	
Independent reflections	5737 [R(int) = 0.0489]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.233	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5737 / 0 / 347	
Goodness-of-fit on F^2	1.137	
Final R indices [I>2sigma(I)]	R1 = 0.0708, wR2 = 0.1858	
R indices (all data)	R1 = 0.0718, wR2 = 0.1868	
Largest diff. peak and hole	3.186 and -0.893 e.$Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for **8**.

Br(1)-C(30)	1.861(3)	C(1)-C(7)-H(7)	118.0
O(1)-N(1)	1.299(3)	N(2)-C(8)-H(8)	110.3
O(2)-C(17)	1.218(4)	N(2)-C(8)-C(9)	107.3(2)
O(3)-C(19)	1.359(4)	N(2)-C(8)-C(12)	110.6(2)
O(3)-C(20)	1.373(4)	C(9)-C(8)-H(8)	110.3
O(4)-C(26)	1.232(4)	C(9)-C(8)-C(12)	108.0(2)
O(5)-C(27)	1.376(4)	C(12)-C(8)-H(8)	110.3
O(5)-C(30)	1.363(3)	C(8)-C(9)-H(9A)	108.5
N(1)-C(10)	1.487(4)	C(8)-C(9)-H(9B)	108.5
N(1)-C(11)	1.502(4)	C(8)-C(9)-C(10)	115.2(2)
N(2)-C(7)	1.262(4)	H(9A)-C(9)-H(9B)	107.5
N(2)-C(8)	1.468(3)	C(10)-C(9)-H(9A)	108.5
C(1)-C(2)	1.396(4)	C(10)-C(9)-H(9B)	108.5
C(1)-C(6)	1.404(4)	N(1)-C(10)-C(9)	109.4(2)
C(1)-C(7)	1.471(4)	N(1)-C(10)-C(13)	108.3(2)
C(2)-H(2)	0.9500	N(1)-C(10)-C(14)	110.1(3)
C(2)-C(3)	1.386(4)	C(13)-C(10)-C(9)	108.7(2)
C(3)-H(3)	0.9500	C(13)-C(10)-C(14)	109.4(3)
C(3)-C(4)	1.395(4)	C(14)-C(10)-C(9)	110.9(3)
C(4)-C(5)	1.392(4)	N(1)-C(11)-C(12)	110.0(2)
C(4)-C(17)	1.485(4)	N(1)-C(11)-C(15)	108.3(2)
C(5)-H(5)	0.9500	N(1)-C(11)-C(16)	108.3(3)
C(5)-C(6)	1.378(4)	C(12)-C(11)-C(16)	112.1(3)
C(6)-H(6)	0.9500	C(15)-C(11)-C(12)	109.3(3)
C(7)-H(7)	0.9500	C(15)-C(11)-C(16)	108.7(3)
C(8)-H(8)	1.0000	C(8)-C(12)-C(11)	112.9(2)
C(8)-C(9)	1.517(4)	C(8)-C(12)-H(12A)	109.0
C(8)-C(12)	1.526(4)	C(8)-C(12)-H(12B)	109.0
C(9)-H(9A)	0.9900	C(11)-C(12)-H(12A)	109.0
C(9)-H(9B)	0.9900	C(11)-C(12)-H(12B)	109.0
C(9)-C(10)	1.536(4)	H(12A)-C(12)-H(12B)	107.8
C(10)-C(13)	1.520(4)	C(10)-C(13)-H(13A)	109.5
C(10)-C(14)	1.530(5)	C(10)-C(13)-H(13B)	109.5
C(11)-C(12)	1.534(4)	C(10)-C(13)-H(13C)	109.5
C(11)-C(15)	1.528(5)	H(13A)-C(13)-H(13B)	109.5
C(11)-C(16)	1.535(4)	H(13A)-C(13)-H(13C)	109.5

C(12)-H(12A)	0.9900	H(13B)-C(13)-H(13C)	109.5
C(12)-H(12B)	0.9900	C(10)-C(14)-H(14A)	109.5
C(13)-H(13A)	0.9800	C(10)-C(14)-H(14B)	109.5
C(13)-H(13B)	0.9800	C(10)-C(14)-H(14C)	109.5
C(13)-H(13C)	0.9800	H(14A)-C(14)-H(14B)	109.5
C(14)-H(14A)	0.9800	H(14A)-C(14)-H(14C)	109.5
C(14)-H(14B)	0.9800	H(14B)-C(14)-H(14C)	109.5
C(14)-H(14C)	0.9800	C(11)-C(15)-H(15A)	109.5
C(15)-H(15A)	0.9800	C(11)-C(15)-H(15B)	109.5
C(15)-H(15B)	0.9800	C(11)-C(15)-H(15C)	109.5
C(15)-H(15C)	0.9800	H(15A)-C(15)-H(15B)	109.5
C(16)-H(16A)	0.9800	H(15A)-C(15)-H(15C)	109.5
C(16)-H(16B)	0.9800	H(15B)-C(15)-H(15C)	109.5
C(16)-H(16C)	0.9800	C(11)-C(16)-H(16A)	109.5
C(17)-C(18)	1.516(4)	C(11)-C(16)-H(16B)	109.5
C(18)-C(19)	1.358(4)	C(11)-C(16)-H(16C)	109.5
C(18)-C(26)	1.456(4)	H(16A)-C(16)-H(16B)	109.5
C(19)-C(27)	1.450(4)	H(16A)-C(16)-H(16C)	109.5
C(20)-C(21)	1.386(4)	H(16B)-C(16)-H(16C)	109.5
C(20)-C(25)	1.388(4)	O(2)-C(17)-C(4)	121.6(3)
C(21)-H(21)	0.9500	O(2)-C(17)-C(18)	117.4(2)
C(21)-C(22)	1.380(5)	C(4)-C(17)-C(18)	120.9(2)
C(22)-H(22)	0.9500	C(19)-C(18)-C(17)	124.5(3)
C(22)-C(23)	1.396(4)	C(19)-C(18)-C(26)	120.3(3)
C(23)-H(23)	0.9500	C(26)-C(18)-C(17)	114.4(2)
C(23)-C(24)	1.380(4)	O(3)-C(19)-C(27)	109.0(2)
C(24)-H(24)	0.9500	C(18)-C(19)-O(3)	123.1(3)
C(24)-C(25)	1.409(4)	C(18)-C(19)-C(27)	127.9(3)
C(25)-C(26)	1.471(4)	O(3)-C(20)-C(21)	116.0(3)
C(27)-C(28)	1.364(4)	O(3)-C(20)-C(25)	121.9(3)
C(28)-H(28)	0.9500	C(21)-C(20)-C(25)	122.1(3)
C(28)-C(29)	1.423(5)	C(20)-C(21)-H(21)	120.6
C(29)-H(29)	0.9500	C(22)-C(21)-C(20)	118.8(3)
C(29)-C(30)	1.346(5)	C(22)-C(21)-H(21)	120.6
		C(21)-C(22)-H(22)	119.7
C(19)-O(3)-C(20)	119.5(2)	C(21)-C(22)-C(23)	120.7(3)
C(30)-O(5)-C(27)	104.6(2)	C(23)-C(22)-H(22)	119.7

O(1)-N(1)-C(10)	115.1(2)	C(22)-C(23)-H(23)	120.0
O(1)-N(1)-C(11)	115.5(2)	C(24)-C(23)-C(22)	120.0(3)
C(10)-N(1)-C(11)	124.4(2)	C(24)-C(23)-H(23)	120.0
C(7)-N(2)-C(8)	116.4(3)	C(23)-C(24)-H(24)	119.9
C(2)-C(1)-C(6)	118.8(3)	C(23)-C(24)-C(25)	120.3(3)
C(2)-C(1)-C(7)	124.1(3)	C(25)-C(24)-H(24)	119.9
C(6)-C(1)-C(7)	116.9(3)	C(20)-C(25)-C(24)	118.2(3)
C(1)-C(2)-H(2)	119.8	C(20)-C(25)-C(26)	119.3(3)
C(3)-C(2)-C(1)	120.3(3)	C(24)-C(25)-C(26)	122.5(3)
C(3)-C(2)-H(2)	119.8	O(4)-C(26)-C(18)	121.1(3)
C(2)-C(3)-H(3)	119.9	O(4)-C(26)-C(25)	123.4(3)
C(2)-C(3)-C(4)	120.2(3)	C(18)-C(26)-C(25)	115.4(2)
C(4)-C(3)-H(3)	119.9	O(5)-C(27)-C(19)	117.5(2)
C(3)-C(4)-C(17)	123.4(3)	C(28)-C(27)-O(5)	111.2(3)
C(5)-C(4)-C(3)	119.8(3)	C(28)-C(27)-C(19)	131.3(3)
C(5)-C(4)-C(17)	116.9(3)	C(27)-C(28)-H(28)	127.1
C(4)-C(5)-H(5)	120.0	C(27)-C(28)-C(29)	105.8(3)
C(6)-C(5)-C(4)	120.0(3)	C(29)-C(28)-H(28)	127.1
C(6)-C(5)-H(5)	120.0	C(28)-C(29)-H(29)	127.0
C(1)-C(6)-H(6)	119.6	C(30)-C(29)-C(28)	106.0(3)
C(5)-C(6)-C(1)	120.8(3)	C(30)-C(29)-H(29)	127.0
C(5)-C(6)-H(6)	119.6	O(5)-C(30)-Br(1)	115.8(2)
N(2)-C(7)-C(1)	124.1(3)	C(29)-C(30)-Br(1)	131.8(2)
N(2)-C(7)-H(7)	118.0	C(29)-C(30)-O(5)	112.4(3)

Table S3. Torsion angles [°] for **8**.

O(1)-N(1)-C(10)-C(9)	172.1(3)	C(7)-C(1)-C(2)-C(3)	-175.4(3)
O(1)-N(1)-C(10)-C(13)	53.8(3)	C(7)-C(1)-C(6)-C(5)	174.0(3)
O(1)-N(1)-C(10)-C(14)	-65.8(3)	C(8)-N(2)-C(7)-C(1)	173.8(3)
O(1)-N(1)-C(11)-C(12)	-170.1(3)	C(8)-C(9)-C(10)-N(1)	44.8(4)
O(1)-N(1)-C(11)-C(15)	-50.6(4)	C(8)-C(9)-C(10)-C(13)	162.8(3)
O(1)-N(1)-C(11)-C(16)	67.1(3)	C(8)-C(9)-C(10)-C(14)	-76.9(3)
O(2)-C(17)-C(18)-C(19)	87.8(4)	C(9)-C(8)-C(12)-C(11)	60.2(3)
O(2)-C(17)-C(18)-C(26)	-82.4(3)	C(10)-N(1)-C(11)-C(12)	36.2(4)
O(3)-C(19)-C(27)-O(5)	-177.0(3)	C(10)-N(1)-C(11)-C(15)	155.7(3)
O(3)-C(19)-C(27)-C(28)	2.2(5)	C(10)-N(1)-C(11)-C(16)	-86.6(3)
O(3)-C(20)-C(21)-C(22)	-179.3(3)	C(11)-N(1)-C(10)-C(9)	-34.1(4)
O(3)-C(20)-C(25)-C(24)	178.7(3)	C(11)-N(1)-C(10)-C(13)	-152.4(3)
O(3)-C(20)-C(25)-C(26)	-0.2(4)	C(11)-N(1)-C(10)-C(14)	88.0(3)
O(5)-C(27)-C(28)-C(29)	0.4(4)	C(12)-C(8)-C(9)-C(10)	-59.3(3)
N(1)-C(11)-C(12)-C(8)	-47.6(3)	C(15)-C(11)-C(12)-C(8)	-166.5(2)
N(2)-C(8)-C(9)-C(10)	-178.5(3)	C(16)-C(11)-C(12)-C(8)	73.0(3)
N(2)-C(8)-C(12)-C(11)	177.3(2)	C(17)-C(4)-C(5)-C(6)	-178.3(3)
C(1)-C(2)-C(3)-C(4)	1.6(4)	C(17)-C(18)-C(19)-O(3)	-170.2(3)
C(2)-C(1)-C(6)-C(5)	-2.5(5)	C(17)-C(18)-C(19)-C(27)	9.2(5)
C(2)-C(1)-C(7)-N(2)	2.1(5)	C(17)-C(18)-C(26)-O(4)	-11.0(4)
C(2)-C(3)-C(4)-C(5)	-2.3(4)	C(17)-C(18)-C(26)-C(25)	166.1(2)
C(2)-C(3)-C(4)-C(17)	176.5(3)	C(18)-C(19)-C(27)-O(5)	3.6(5)
C(3)-C(4)-C(5)-C(6)	0.6(5)	C(18)-C(19)-C(27)-C(28)	-177.2(4)
C(3)-C(4)-C(17)-O(2)	-171.0(3)	C(19)-O(3)-C(20)-C(21)	173.9(3)
C(3)-C(4)-C(17)-C(18)	13.1(4)	C(19)-O(3)-C(20)-C(25)	-5.1(4)
C(4)-C(5)-C(6)-C(1)	1.9(5)	C(19)-C(18)-C(26)-O(4)	178.3(3)
C(4)-C(17)-C(18)-C(19)	-96.2(3)	C(19)-C(18)-C(26)-C(25)	-4.6(4)
C(4)-C(17)-C(18)-C(26)	93.6(3)	C(19)-C(27)-C(28)-C(29)	-178.8(3)
C(5)-C(4)-C(17)-O(2)	7.8(4)	C(20)-O(3)-C(19)-C(18)	5.5(4)
C(5)-C(4)-C(17)-C(18)	-168.0(3)	C(20)-O(3)-C(19)-C(27)	-174.0(3)
C(6)-C(1)-C(2)-C(3)	0.8(4)	C(20)-C(21)-C(22)-C(23)	0.8(6)
C(6)-C(1)-C(7)-N(2)	-174.2(3)	C(20)-C(25)-C(26)-O(4)	-178.1(3)
C(7)-N(2)-C(8)-C(9)	-130.0(3)	C(20)-C(25)-C(26)-C(18)	4.9(4)
C(7)-N(2)-C(8)-C(12)	112.4(3)	C(21)-C(20)-C(25)-C(24)	-0.2(5)
C(23)-C(24)-C(25)-C(20)	0.3(5)	C(21)-C(20)-C(25)-C(26)	-179.1(3)
C(23)-C(24)-C(25)-C(26)	179.2(3)	C(21)-C(22)-C(23)-C(24)	-0.7(5)

C(24)-C(25)-C(26)-O(4)	3.1(5)	C(22)-C(23)-C(24)-C(25)	0.1(5)
C(24)-C(25)-C(26)-C(18)	-173.9(3)	C(27)-C(28)-C(29)-C(30)	-0.2(4)
C(25)-C(20)-C(21)-C(22)	-0.3(5)	C(28)-C(29)-C(30)-Br(1)	-179.8(3)
C(26)-C(18)-C(19)-O(3)	-0.5(5)	C(28)-C(29)-C(30)-O(5)	-0.1(4)
C(26)-C(18)-C(19)-C(27)	178.9(3)	C(30)-O(5)-C(27)-C(19)	178.9(3)
C(27)-O(5)-C(30)-Br(1)	-179.9(2)	C(30)-O(5)-C(27)-C(28)	-0.4(4)
C(27)-O(5)-C(30)-C(29)	0.3(4)		

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