Supporting information

Novel functionalized benzimidazole-salicylic acid derivatives: synthesis, photophysical characteristics and biological applications

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Materials and methods

1.1 Chemistry

All chemical reagents are reagent grade and used as purchased. ^{1}H NMR (600 MHz) spectra were recorded on a Bruker A VIII 600 MHz spectrometer (Bruker, Billerica, MA, USA). The chemical shifts were reported in parts per million (ppm) using the 2.50 signal of DMSO (^{1}H NMR) and the 39.52 signal of DMSO (^{13}C NMR) as internal standards. ESI Mass spectra (MS) were obtained on a SHIMADZU 2020 Liquid Chromatograph Mass Spectrometer (SHIMADZU, Kyoto, Japan).

1.2 UV-vis and fluorescence measurements

The electronic absorption spectra and absorbances were measured on a SHIMADZU 2550 UV–vis spectrophotometer (SHIMADZU, Kyoto, Japan). Corrected steady-state emission spectra were recorded on a SHIMADZU RF-6000 Fluorolog instrument (SHIMADZU, Kyoto, Japan). Freshly prepared samples in 1 cm quartz cells were used to perform all UV–vis absorption and fluorescence measurements. These experiments as a function of solvent allowed us to determine the spectral maxima ($\lambda_{abs,\ max}$ and $\lambda_{em,\ max}$), and the Stokes shifts.

1.3 Quantum yield Measurements and determination of the limit of detection (LOD)/ Limit of Quantification (LOQ)

Relative fluorescence quantum yields(QY) were calculated using diluted solutions, with an absorbance between 0.01 and 0.05 at the used excitation wavelength, and a fluorescein standard (quinine sulfate in water，QY =0.54). The following equation (1) was used to determine the QY [1].

$$QY_X = \frac{A_s \times F_X \times n_X^2 \times QY_S}{A_X \times F_S \times n_S^2} \#（1）$$

According to the equation, x is the symbol of the samples and s is the symbol of the standard, where QY is the fluorescence quantum yield, F is the area under the fluorescence emission curves and A shows the absorbance at the excitation wavelength (360 nm), and n_x and n_s are the refractive indexes of DMSO and water (1.479 and 1.333, respectively).

The LOD was determined from the fluorescence titration curves. The emission intensity of the probe was measured 10 times to determine the standard deviation (SD) of the blank. The emission intensity in the presence of each analyte was measured three times. The relationship of average value of the fluorescence intensity with concentration of the analyte was built and plotted. From the slope of the linearity plot, the LOD was calculated using equation (2) [2].

$$LOD = 3SD_0/K \#（2）$$

the LOQ was calculated using equation (3).

$$LOQ = 10SD_0/K \#（3）$$

where SD_0 is the standard deviation of the blank experiments, and k is the slope value of the linearity plot.

1.4 Cytotoxicity investigation

The PBMC cell line was maintained in growth 1640 medium supplemented with 20% fetal bovine serum and 1% penicillin/streptomycin at 37 ^{o}C, 5% CO_2. For cell viability assay, PBMC cells (10000 cells per well) were plated onto 96-well plates in 80 μL of medium (1640 containing 20% FBS, Gibico), compound **5q** with gradient concentrations were added 1 h after cell plating. At day 3, 30 μL of CTG solution (Promega) was added. After 10min at 37^{o}C in a humidified, 5% CO_2 atmosphere, the absorbance was recorded using a 96-well plate reader (Wallac EnVision Manager, Molecular Devices).

1.5 Subcellular localization fluorescence microscopy imaging

The subcellular localization of compound **5q** was investigated using following protocol: Hela cells were cultured onto glass-bottom petri dishes for 12 h before treatment. Live cells were treated with compound **5q** at 20 μM for 16 h, washed with PBS for 3 times, fixed in 4% paraformaldehyde solution for 15 min, then cells were stained with propidium iodide at 20 μg/ml for 15 min, washed with PBS for 2 times. Cell images were obtained using Olympus FV3000 confocal microscope.

1.6 The influence of compound 5q and Fe^{3+} on the PTPs (SHP1, SHP2, PTP1B and TCPTP) enzyme activity

We took DiFUMP as a substrate to detect the activity of SHP1, SHP2, PTP1B and TCPTP. They can hydrolyze DiFUMP to DiFUM which was a fluorescent product. The assay system contained 60 mM HEPES, pH 7.2, 75 mM NaCl, 75 mM KCl, 1 mM EDTA, 0.05% Tween-20, 5 mM DTT, 2 nM enzyme, and 20 μM substrate (DiFMUP) was 50 μL. 10 μL compound and Fe^{3+} was added into 20 μL enzyme, incubated for 20

min, and then added with 20 μL substrate (DiFMUP).The reaction was carried out on 384-well plates and detected the fluorescence at Ex/Em= 355/460 nm by a microplate reader (Envision). The reaction rate was determined by the production of DiFUMP fluorescence signal per unit time.

[1] B. Verbelen, W. Dehaen, Org. Lett. 18 (2016) 6412-6415..

[2] Y. Geng, L. Chen, Q. Wan, Anal. Chim. Acta. 1187 (2021) 339168.

Table S1 Photophysical characteristics of compounds **4a-4r** and **5a-5r** in DMSO.

Compound	R	$\lambda_{max,abs}$ [nm]	$\lambda_{max,em}$ [nm]	Stokes shift [nm] (cm^{-1})
4a	2-MeC_6H_5	320	405	85
4b	2-$OMeC_6H_5$	320	405	85
4c	3-MeC_6H_5	320	405	85
4d	3-$OMeC_6H_5$	320	405	85
4e	3-OHC_6H_5	320	395	75
4f	4-MeC_6H_5	320	410	90
4g	4-$OMeC_6H_5$	320	430	110
4h	4-OHC_6H_5	320	432	112
4i	4-$(Me)_2NC_6H_5$	340	400	60
4j	4-$(Et)_2NC_6H_5$	360	435	75
4k	2,4-MeC_6H_5	320	408	88
4l	3,4-MeC_6H_5	320	410	90
4m	3,4-$OMeC_6H_5$	320	425	105
4n	3-OMe, 4-MeC_6H_5	320	405	85
4o	3-Me, 4-$OMeC_6H_5$	320	430	110
4p		340	418	78
4q		370	432	62
4r		330	395	65
5a	2-MeC_6H_5	320	475	155
5b	2-$OMeC_6H_5$	320	465	145
5c	3-MeC_6H_5	320	465	145
5d	3-$OMeC_6H_5$	320	465	145
5e	3-OHC_6H_5	320	465	145
5f	4-MeC_6H_5	320	468	148
5g	4-$OMeC_6H_5$	320	443	123
5h	4-OHC_6H_5	320	430	110
5i	4-$(Me)_2NC_6H_5$	360	428	68
5j	4-$(Et)_2NC_6H_5$	350	420	70
5k	2,4-MeC_6H_5	320	460	140
5l	3,4-MeC_6H_5	320	455	135
5m	3,4-$OMeC_6H_5$	320	442	122
5n	3-OMe, 4-MeC_6H_5	320	455	135
5o	3-Me, 4-$OMeC_6H_5$	320	440	120
5p		340	545	205
5q		370	440	70
5r		330	432	102

Table S2 The calculated charge transfer quantity (q_{EMI}^{CT}) and charge transfer distance (d_{EMI}^{CT}) of compounds 5**a, 5b, 5c, 5d, 5e, 5n, 5p** using TD-DFT method.

Compound	$q_{EMI/e}^{CT}$	$d_{EMI/Å}^{CT}$
5a	0.803	4.708

5b	0.845	5.009
5c	0.809	4.845
5d	0.783	4.520
5e	0.788	4.755
5n	0.849	5.142
5p	0.496	4.318

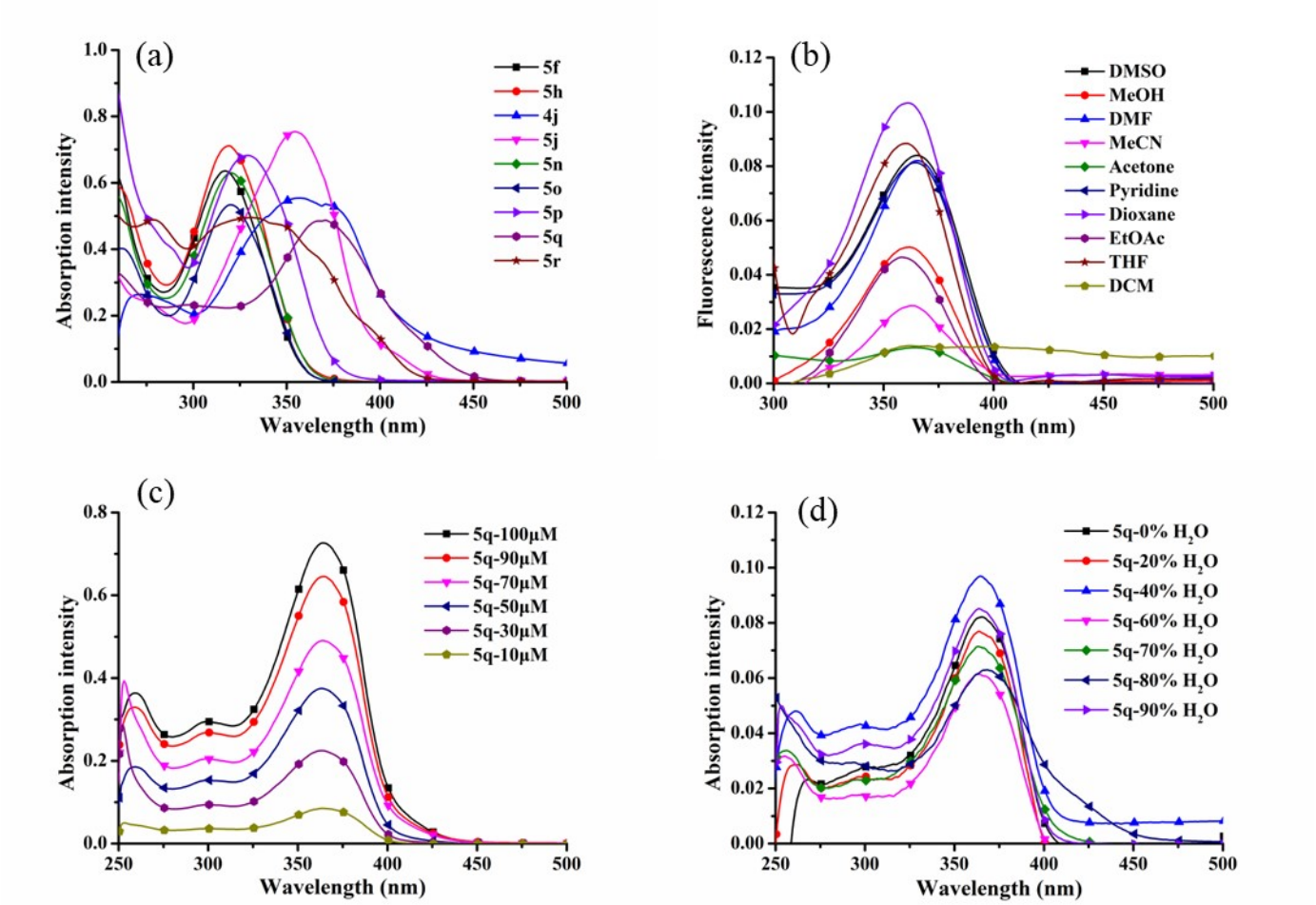


Figure S1 (a) Absorption spectra of compounds **5f, 5h, 4j, 5j, 5n, 5o, 5p, 5q, 5r** in 90% PBS at room temperature (c = 100 μM). **(b)** Absorption spectra of compounds and **5q** in different solvents (c = 10 μM, λ_{ex}: 370 nm, slit: 5 nm) and **(c)** different concentration. **(d)** Absorption spectra of compound **5q** in DMSO (c = 10 μM, λ_{ex}: 370 nm, slit: 5 nm) with varying amounts of water.

Table S3 Photophysical characteristics of compounds **5f, 5h, 4j, 5j, 5n, 5o, 5p, 5q, 5r** in PBS.

Compound	$\lambda_{max,abs}$ [nm]	$\lambda_{max,em}$ [nm]	Stokes shift [nm] (cm^{-1})	QY[a]
5f	320	450	130	0.10
5h	320	437	117	0.19
4j	350	472	112	0.02
5j	350	420	70	0.02
5n	320	480	160	0.07
5o	320	440	120	0.12
5p	320	545	225	0.04
5q	370	490	120	0.07
5r	330	460	130	0.03

a: Quantum yield (QY) was calculated by using the standard solution of quinine sulfate dissolved in 1N H_2SO_4.

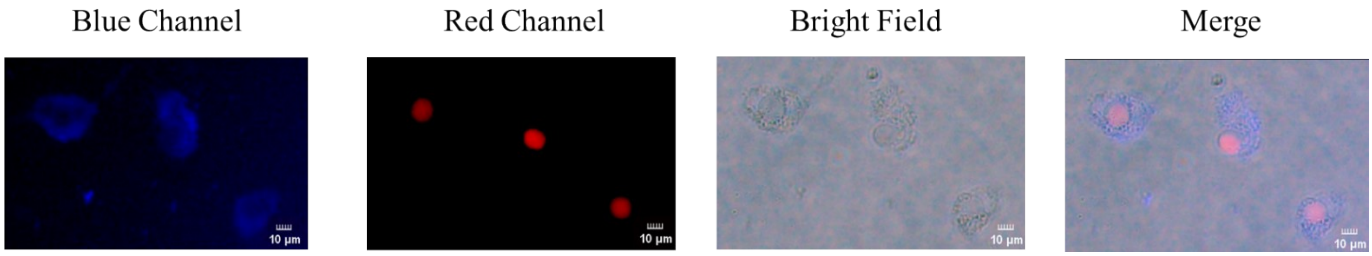


Figure S2 Fluorescence images of Hela cells incubated with compound **5q**. The cells were co-stained with propidium iodide to visualize the nuclei (red).

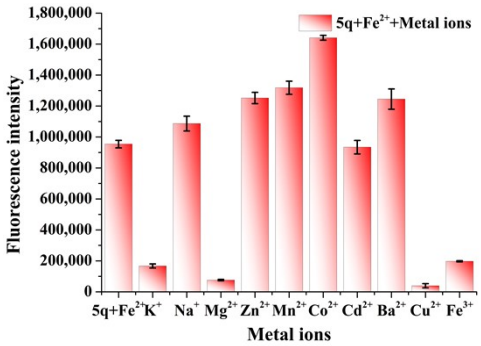


Figure S3 Fluorescence responses of compound **5q** (10 μM, λ_{ex}: 370 nm, slit: 5 nm) upon addition of Fe^{2+} (50 μM) in the presence of various metal ions (50 μM).

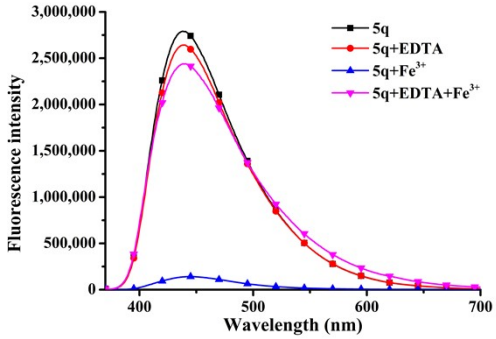


Figure S4 Competitive binding Fe^{3+} of compound **5q** with EDTA (1.0 eq, a strong chelating agent of Fe^{3+}), λ_{ex}: 370 nm, slit: 5 nm

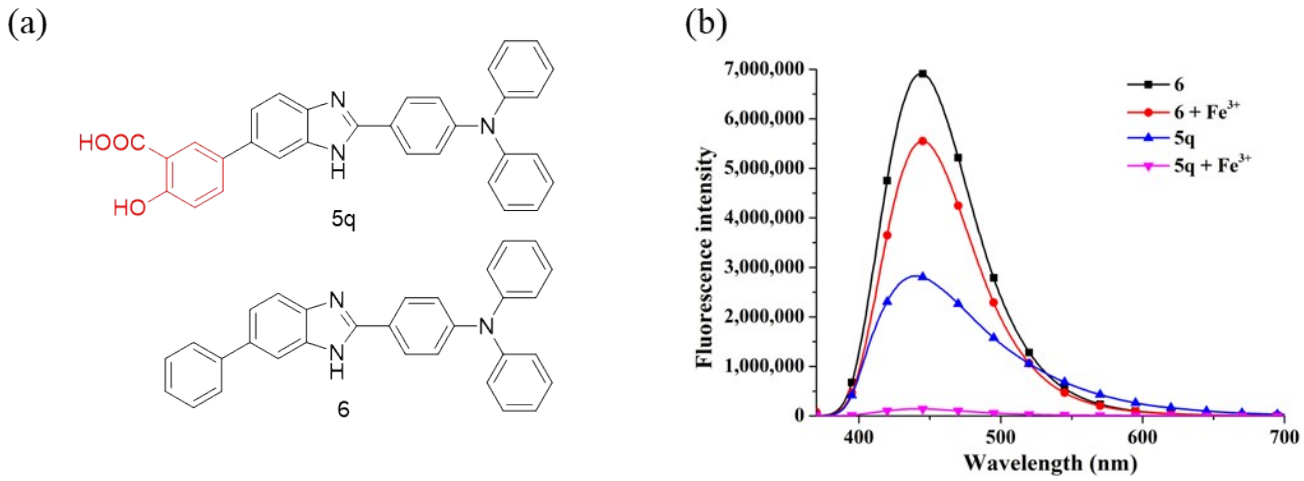


Figure S5 (a) The molecular structure of **5q** and **6**. **(b)** Fluorescence responses of compound **5q** and **6** (10 μM, λ_{ex}: 370 nm, slit: 5 nm) in DMSO:H_2O (9:1) solution with Fe^{3+} (100 μM) .

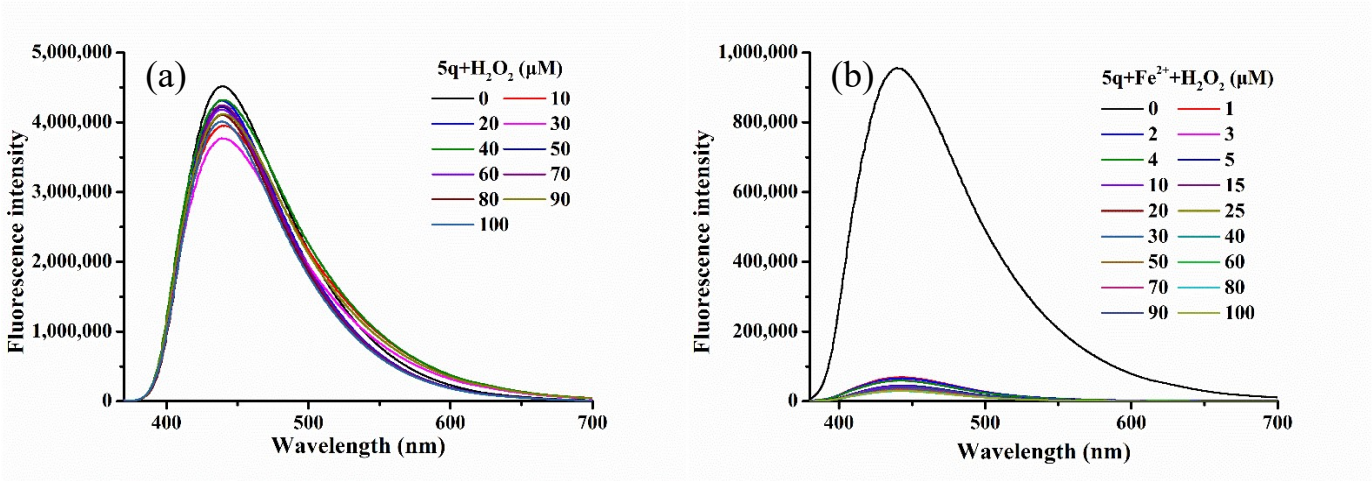


Figure S6 (a) The emission spectra of compound **5q** in the presence of H_2O_2 at different concentration, **(b)** those of **5q**-Fe^{2+} ([Fe^{2+}] at 100 μM, λ_{ex}: 370 nm, slit: 5 nm) in the presence of H_2O_2 at different concentration.

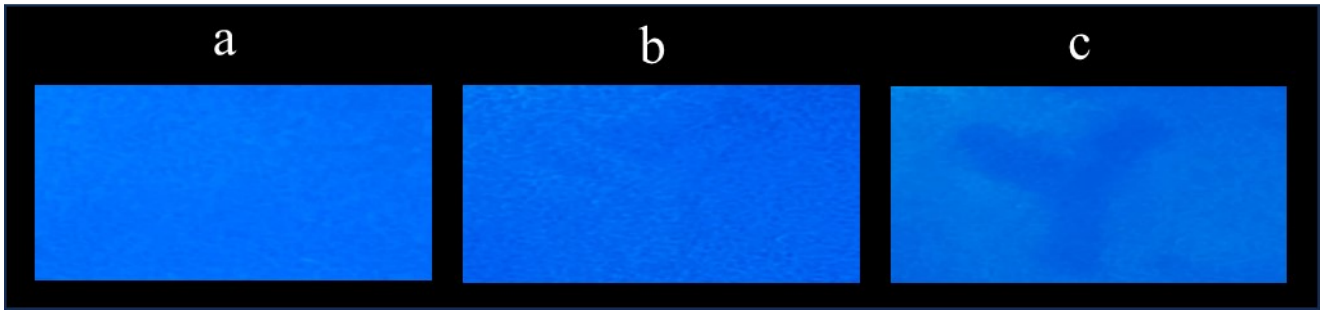


Figure S7 (a) Under UV lamp (365 nm), photo of a non-fluorescent paper piece after dipping in compound **5q** solution (10 μM), **(b)** and that of the same paper after writing letter "Y" using $FeCl_2$ (1.0 mM), **(c)** that paper b after brushing H_2O_2 solution (2.0 mM) and drying up.

Methyl 2-hydroxy-5-(2-(o-tolyl)-1H-benzo[d]imidazol-6-yl)benzoate (4a)

White solid. Yield 70%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.68 (s, 1H), 10.49 (s, 1H), 8.06 (d, J = 2.4 Hz, 1H), 7.93 – 7.86 (m, 1H), 7.76 (dd, J = 7.2, 1.8 Hz, 1H), 7.73 – 7.35 (m, 6H), 7.10 (d, J = 8.4 Hz, 1H), 3.94 (s, 3H), 2.63 (s, 3H). MS (ESI$^+$) m/z calcd. for $C_{22}H_{19}N_2O_3$ $[M+H]^+$ 359.1, found 359.0. m.p: 120.5-121.5°C.

2-hydroxy-5-(2-(o-tolyl)-1H-benzo[d]imidazol-6-yl)benzoic acid (5a)

White solid. Yield 85%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.12 (d, J = 2.4 Hz, 1H), 7.98 (d, J = 1.8 Hz, 1H), 7.94 (dd, J = 9.0, 2.4 Hz, 1H), 7.90 (d, J = 9 Hz, 1H), 7.85 – 7.80 (m, 2H), 7.63 (td, J = 7.5, 1.4 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.13 (d, J = 8.4 Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.65, 160.82, 149.83, 137.89, 136.99, 134.36, 133.21, 132.33, 131.74, 131.50, 130.91, 130.74, 128.54, 126.48, 124.53, 124.11, 118.12, 114.83, 113.64, 111.33, 20.04. HRMS (ESI): m/z calcd for $C_{21}H_{16}N_2O_3Na$ $[M+Na]^+$ 367.1053, found 367.1054. MS (ESI$^+$) m/z calcd. for $C_{21}H_{17}N_2O_3$ $[M+H]^+$ 345.1, found 345.0. m.p: 269.8-270.8°C

Methyl 2-hydroxy-5-(2-(2-methoxyphenyl)-1H-benzo[d]imidazol-6-yl)benzoate (4b)

White solid. Yield 76%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.16 (d, J = 12.0 Hz, 1H), 10.49 (s, 1H), 8.35 (ddd, J = 7.8, 4.4, 1.8 Hz, 1H), 8.07 (dd, J = 6.4, 2.5 Hz, 1H), 7.89 (td, J = 9.1, 2.5 Hz, 1H), 7.84 (dd, J = 14.4, 1.8 Hz, 1H), 7.69 (dd, J = 17.5, 8.3 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.26 (d, J = 8.3 Hz, 1H), 7.16 – 7.08 (m, 2H), 4.05 (d, J = 4.2 Hz, 3H), 3.94 (d, J = 1.2 Hz, 3H). MS (ESI$^+$) m/z calcd. for $C_{22}H_{19}N_2O_4$ $[M+H]^+$ 375.1, found 375.0. m.p: 123.5-124.5°C

2-hydroxy-5-(2-(2-methoxyphenyl)-1H-benzo[d]imidazol-6-yl)benzoic acid (5b)

White solid. Yield 83%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.32 (dd, J = 7.8, 1.2 Hz, 1H), 8.10 (d, J = 2.4 Hz, 1H), 7.92 (d, J = 1.8 Hz, 1H), 7.90 (dd, J = 8.4, 2.4 Hz, 1H), 7.81 (d, J = 9.0 Hz, 1H), 7.69 – 7.61 (m, 2H), 7.35 (d, J = 8.4 Hz, 1H), 7.22 (td, J = 7.8, 1.0 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 4.08 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.75, 160.57, 157.37, 147.93, 135.38, 134.35, 134.02, 133.68, 133.51, 131.35, 129.97, 128.25, 122.94, 121.17, 117.96, 115.23, 114.24, 113.67, 112.62, 111.56, 56.16. HRMS (ESI): m/z calcd for $C_{21}H_{16}N_2O_4Na$ $[M+Na]^+$ 383.1002, found 383.1004. MS (ESI^+) m/z calcd. for $C_{21}H_{17}N_2O_4$ $[M+H]^+$ 361.1, found 361.0. m.p: 224.1-225.1°C

Methyl 2-hydroxy-5-(2-(m-tolyl)-1H-benzo[d]imidazol-6-yl)benzoate (4c)

White solid. Yield 84%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.92 (s, 1H), 10.49 (s, 1H), 8.05 (d, J = 2.4 Hz, 1H), 8.03 (d, J = 1.8 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.89 (dd, J = 8.6, 2.5 Hz, 1H), 7.88 – 7.42 (m, 4H), 7.32 (d, J = 7.5 Hz, 1H), 7.11 (d, J = 8.6 Hz, 1H), 3.94 (s, 3H), 2.43 (s, 3H). MS (ESI^+) m/z calcd. for $C_{22}H_{19}N_2O_3$ $[M+H]^+$ 359.1, found 359.0. m.p: 114.5-115.5°C

2-hydroxy-5-(2-(m-tolyl)-1H-benzo[d]imidazol-6-yl)benzoic acid (5c)

White solid. Yield 86%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.09 (d, J = 1.8 Hz, 1H), 8.08 (d, J = 3.0 Hz, 1H), 8.05 (d, J = 7.8 Hz, 1H), 7.90 (dd, J = 9.0, 2.4 Hz, 1H), 7.83 (d, J = 1.7 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.62 (dd, J = 8.4, 1.8 Hz, 1H), 7.53 (t, J = 7.7 Hz, 1H), 7.44 (d, J = 7.2 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.80, 160.54, 150.79, 138.72, 136.54, 135.42, 135.36, 134.24, 132.23, 131.48, 129.26, 128.31, 127.71, 126.78, 124.45, 122.93, 117.94, 115.11, 113.55, 111.64, 21.04. HRMS (ESI): m/z calcd for $C_{21}H_{16}N_2O_3Na$ $[M+Na]^+$ 367.1053, found 367.1050. MS (ESI^+) m/z calcd. for $C_{21}H_{17}N_2O_3$ $[M+H]^+$ 345.1, found 345.0. m.p: 272.3-273.3°C

Methyl 2-hydroxy-5-(2-(3-methoxyphenyl)-1H-benzo[d]imidazol-6-yl)benzoate (4d)

White solid. Yield 76%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.97 (s, 1H), 10.50 (s, 1H), 8.06 (d, J = 2.4 Hz, 1H), 7.89 (dd, J = 8.4, 2.4 Hz, 1H), 7.80 – 7.76 (m, 2H), 7.74 – 7.56 (m, 2H), 7.51 – 7.43 (m, 2H), 7.11 (d, J = 8.4 Hz, 1H), 7.09 – 7.05 (m, 1H), 3.94 (s, 3H), 3.87 (s, 3H). MS (ESI^+) m/z calcd. for $C_{22}H_{19}N_2O_4$ $[M+H]^+$ 375.1, found 375.1. m.p: 120.5-121.5°C

2-hydroxy-5-(2-(3-methoxyphenyl)-1H-benzo[d]imidazol-6-yl)benzoic acid (5d)

White solid. Yield 90%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.09 (d, J = 2.4 Hz, 1H), 7.94 (t, J = 1.8 Hz, 1H), 7.92 – 7.87 (m, 3H), 7.82 (d, J = 8.4 Hz, 1H), 7.70 (dd, J = 8.4, 1.8 Hz, 1H), 7.59 (t, J = 8.4 Hz, 1H), 7.24 (ddd, J = 8.4, 2.4, 0.6 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.72, 160.68, 159.81, 149.84, 136.26, 134.87, 134.26, 133.51, 131.03, 130.69, 128.40, 126.45, 123.84, 119.82, 118.48, 118.00, 114.86, 113.54, 112.56, 111.32, 55.72. HRMS (ESI): m/z calcd for $C_{21}H_{16}N_2O_4Na$ $[M+Na]^+$ 383.1002, found 383.0993. MS (ESI^+) m/z calcd. for $C_{21}H_{17}N_2O_4$ $[M+H]^+$ 361.1, found 361.0. m.p: 216.3-217.3°C

Methyl 2-hydroxy-5-(2-(3-hydroxyphenyl)-1H-benzo[d]imidazol-6-yl)benzoate (4e)

White solid. Yield 79%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.88 (s, 1H), 10.49 (s, 1H), 9.74 (s, 1H), 8.05 (d, J = 2.4 Hz, 1H), 7.89 (dd, J = 8.4, 2.4 Hz, 1H), 7.73 – 7.57 (m, 4H), 7.45 (d, J = 8.4 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 6.91 (dd, J = 7.8, 1.8 Hz, 1H), 3.94 (s, 3H). MS (ESI^+) m/z calcd. for $C_{21}H_{17}N_2O_4$ $[M+H]^+$ 361.1, found 361.2. m.p: 220.5-221.5°C

2-hydroxy-5-(2-(3-hydroxyphenyl)-1H-benzo[d]imidazol-6-yl)benzoic acid (5e)

White solid. Yield 83%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.07 (s, 1H), 8.09 (d, J = 2.4 Hz, 1H), 7.91 (dd, J = 8.4, 2.4 Hz, 1H), 7.85 (s, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.71 – 7.63 (m, 3H), 7.46 (t, J = 7.8 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 7.06 (dd, J = 8.4, 2.4 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.78, 160.55, 158.05, 150.79, 135.51, 134.27, 131.46, 130.51, 128.33, 123.06, 118.81, 118.04, 117.97, 115.07, 114.01, 111.63. HRMS (ESI): m/z calcd for $C_{20}H_{14}N_2O_4Na$ $[M+Na]^+$ 369.0846, found 369.0835. MS (ESI^+) m/z calcd. for $C_{20}H_{15}N_2O_4$ $[M+H]^+$ 347.1, found 347.0. m.p: 252.6-253.6°C

Methyl 2-hydroxy-5-(2-(p-tolyl)-1H-benzo[d]imidazol-6-yl)benzoate (4f)

White solid. Yield 70%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.88 (s, 1H), 10.49 (s, 1H), 8.10 – 8.07 (m, 2H), 8.05 (d, J = 2.4 Hz, 1H), 7.88 (dd, J = 8.4, 2.4 Hz, 1H), 7.86 – 7.41 (m, 3H), 7.37 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 1H), 3.94 (s, 3H), 2.39 (s, 3H). MS (ESI$^+$) m/z calcd. for $C_{22}H_{19}N_2O_3$ $[M+H]^+$ 359.1, found 359.2. m.p: 210.5-211.5^{o}C

2-hydroxy-5-(2-(p-tolyl)-1H-benzo[d]imidazol-6-yl)benzoic acid (5f)

White solid. Yield 84%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.15 (d, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 2.4 Hz, 1H), 7.89 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.82 (d, *J* = 1.8 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.60 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.81, 160.49, 151.01, 141.52, 136.93, 135.76, 135.11, 134.19, 131.59, 129.85, 128.26, 127.11, 124.48, 122.60, 117.91, 115.06, 113.55, 111.64, 21.13. HRMS (ESI): m/z calcd for $C_{21}H_{16}N_2O_3Na$ $[M+Na]^+$ 367.1053, found 367.1046. MS (ESI$^+$) m/z calcd. for $C_{21}H_{17}N_2O_3$ $[M+H]^+$ 345.1, found 345.2. m.p: 252.1-253.1^{o}C

Methyl 2-hydroxy-5-(2-(4-methoxyphenyl)-1H-benzo[d]imidazol-6-yl)benzoate (4g)

White solid. Yield 81%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.81 (s, 1H), 10.49 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 2H), 8.05 (s, 1H), 7.91 – 7.85 (m, 1H), 7.84 – 7.52 (m, 2H), 7.46 – 7.39 (m, 1H), 7.15 – 7.06 (m, 3H), 3.94 (s, 3H), 3.85 (s, 3H). MS (ESI$^+$) m/z calcd. for $C_{22}H_{19}N_2O_4$ $[M+H]^+$ 374.1, found 375.0. m.p: 216.5-217.5^{o}C

2-hydroxy-5-(2-(4-methoxyphenyl)-1H-benzo[d]imidazol-6-yl)benzoic acid (5g)

White solid. Yield 87%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.25 – 8.19 (m, 2H), 8.08 (d, *J* = 2.4 Hz, 1H), 7.89 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.81 (d, *J* = 1.8 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.60 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.78, 162.00, 160.52, 150.69, 136.30, 135.25, 134.97, 134.16, 131.44, 129.11, 128.27, 122.72, 118.86, 117.91, 114.83, 114.73, 113.59, 111.35, 55.62. HRMS (ESI): m/z calcd for $C_{21}H_{16}N_2O_4Na$ $[M+Na]^+$ 383.1002, found 383.1001. MS (ESI$^+$) m/z calcd. for $C_{21}H_{17}N_2O_4$ $[M+H]^+$ 361.1, found 361.0. m.p: 219.3-220.3^{o}C

Methyl 2-hydroxy-5-(2-(4-hydroxyphenyl)-1H-benzo[d]imidazol-6-yl)benzoate (4h)

White solid. Yield 73%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.70 (s, 1H), 10.48 (s, 1H), 9.98 (s, 1H), 8.04 (d, *J* = 2.4 Hz, 1H), 8.03 – 7.99 (m, 2H), 7.87 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.83 – 7.23 (m, 3H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.95 – 6.90 (m, 2H), 3.94 (s, 3H). MS (ESI$^+$) m/z calcd. for $C_{21}H_{17}N_2O_4$ $[M+H]^+$ 361.1, found 361.0. m.p: 260.5-261.5^{o}C

2-hydroxy-5-(2-(4-hydroxyphenyl)-1H-benzo[d]imidazol-6-yl)benzoic acid (5h)

White solid. Yield 89%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.71 (s, 1H), 8.23 – 8.15 (m, 2H), 8.08 (d, *J* = 2.4 Hz, 1H), 7.89 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.85 (d, *J* = 1.8 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.70 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.09 – 7.04 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.71, 161.99, 160.74, 150.08, 136.40, 134.22, 133.68, 132.24, 130.87, 130.00, 128.42, 123.89, 118.02, 116.46, 114.54, 114.24, 113.67, 110.78. HRMS (ESI): m/z calcd for $C_{20}H_{14}N_2O_4Na$ $[M+Na]^+$ 369.0846, found 369.0847. MS (ESI$^+$) m/z calcd. for $C_{20}H_{15}N_2O_4$ $[M+H]^+$ 347.1, found 347.1. m.p: 260.5-261.5^{o}C

Methyl 5-(2-(4-(dimethylamino)phenyl)-1H-benzo[d]imidazol-6-yl)-2-hydroxybenzoate (4i)

White solid. Yield 75%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.59 (s, 1H), 10.48 (s, 1H), 8.05 (d, *J* = 2.4 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.88 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.72 – 7.52 (m, 3H), 7.39 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 3.95 (s, 3H), 3.01 (s, 6H). MS (ESI$^+$) m/z calcd. for $C_{23}H_{22}N_3O_3$ $[M+H]^+$ 388.2, found 388.0. m.p: 125.3-126.3^{o}C

5-(2-(4-(dimethylamino)phenyl)-1H-benzo[d]imidazol-6-yl)-2-hydroxybenzoic acid (5i)

White solid. Yield 90%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.11 – 8.06 (m, 3H), 7.85 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.75 (d, *J* = 1.8 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.57 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.94 – 6.88 (m, 2H), 3.05 (s, 6H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 172.29, 161.24, 153.04, 151.44, 136.02, 135.44, 134.06, 132.53, 131.98, 131.35, 129.26, 128.71, 123.22, 118.21, 114.93, 114.43, 112.27, 111.54, 111.01. HRMS (ESI): m/z calcd for $C_{22}H_{19}N_3O_3Na$ $[M+Na]^+$ 396.1319, found 396.1313. MS (ESI$^+$) m/z calcd. for $C_{22}H_{20}N_3O_3$ $[M+H]^+$ 374.1, found 374.0. m.p: 190.3-191.3^{o}C

Methyl 5-(2-(4-(diethylamino)phenyl)-1H-benzo[d]imidazol-6-yl)-2-hydroxybenzoate (4j)

Yellow solid. Yield 90%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.52 (s, 1H), 8.05 (d, J = 2.4 Hz, 1H), 8.00 (d, J = 8.4 Hz, 2H), 7.89 (dd, J = 8.4, 2.4 Hz, 1H), 7.75 (s, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 6.87 (d, J = 8.4 Hz, 2H), 3.94 (s, 3H), 3.46 (q, J = 7.2 Hz, 4H), 1.15 (t, J = 7.2 Hz, 6H). MS (ESI$^+$) m/z calcd. for $C_{25}H_{26}N_3O_3$ $[M+H]^+$ 416.2, found 416.2. m.p: 240.1-241.1^{o}C

5-(2-(4-(diethylamino)phenyl)-1H-benzo[d]imidazol-6-yl)-2-hydroxybenzoic acid (5j)

Yellow solid. Yield 91%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.05 (d, J = 2.4 Hz, 1H), 8.00 (d, J = 8.4 Hz, 2H), 7.81 (dd, J = 8.4, 2.4 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.02 (d, J = 8.4 Hz, 1H), 6.84 (d, J = 8.4 Hz, 2H), 3.45 (q, J = 7.2 Hz, 4H), 1.15 (t, J = 7.2 Hz, 6H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.82, 160.94, 151.84, 149.52, 134.79, 133.01, 131.52, 130.96, 128.65, 128.13, 121.68, 117.48, 114.23, 112.77, 111.22, 110.77, 43.81, 12.44. HRMS (ESI): m/z calcd for $C_{24}H_{23}N_3O_3Na$ $[M+Na]^+$ 424.1632, found 424.1634. MS (ESI$^+$) m/z calcd. for $C_{20}H_{14}N_2O_4$ $[M+H]^+$ 346.0954, found . MS (ESI$^+$) m/z calcd. for $C_{24}H_{24}N_3O_3$ $[M+H]^+$ 402.2, found 402.2. m.p: 240.6-241.6^{o}C

Methyl 5-(2-(2,4-dimethylphenyl)-1H-benzo[d]imidazol-6-yl)-2-hydroxybenzoate (4k)

White solid. Yield 75%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.60 (s, 1H), 10.49 (s, 1H), 8.06 (d, J = 2.4 Hz, 1H), 7.89 (dd, J = 8.4, 2.4 Hz, 1H), 7.67 (m, 3H), 7.45 (d, J = 8.4 Hz, 1H), 7.21 (s, 1H), 7.19 (dd, J = 7.8, 1.8 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 3.94 (s, 3H), 2.61 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 169.56, 159.40, 153.31, 139.43, 137.36, 134.52, 133.83, 132.48, 129.79, 128.25, 127.75, 127.53, 127.09, 118.57, 116.06, 114.00, 53.02, 21.54, 21.28. MS (ESI$^+$) m/z calcd. for $C_{23}H_{21}N_2O_3$ $[M+H]^+$ 373.2, found 373.0. m.p: 181.6-182.6^{o}C

5-(2-(2,4-dimethylphenyl)-1H-benzo[d]imidazol-6-yl)-2-hydroxybenzoic acid (5k)

White solid. Yield 84%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.07 (d, J = 2.4 Hz, 1H), 7.88 (dd, J = 8.4, 2.4 Hz, 1H), 7.79 (d, J = 1.8 Hz, 1H), 7.68 (dd, J = 8.0, 6.8 Hz, 2H), 7.52 (dd, J = 8.4, 1.8 Hz, 1H), 7.24 (d, J = 1.8 Hz, 1H), 7.21 (dd, J = 7.8, 1.8 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H), 2.60 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.86, 160.41, 152.20, 139.88, 137.09, 134.34, 134.10, 132.07, 131.92, 129.74, 128.18, 126.78, 125.69, 121.73, 117.85, 115.40, 113.68, 111.98, 20.90, 20.81. HRMS (ESI): m/z calcd for $C_{22}H_{18}N_2O_3Na$ $[M+Na]^+$ 381.1210, found 381.1200. MS (ESI$^+$) m/z calcd. for $C_{22}H_{19}N_2O_3$ $[M+H]^+$ 359.1, found 359.0. m.p: 245.4-246.4^{o}C

Methyl 5-(2-(3,4-dimethylphenyl)-1H-benzo[d]imidazol-6-yl)-2-hydroxybenzoate (4l)

White solid. Yield 87%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.84 (s, 1H), 10.49 (s, 1H), 8.05 (d, J = 2.4 Hz, 1H), 8.01 – 7.97 (m, 1H), 7.92 – 7.86 (m, 2H), 7.85 – 7.40 (m, 3H), 7.32 (d, J = 7.8 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 3.94 (s, 3H), 2.34 (s, 3H), 2.30 (s, 3H). MS (ESI$^+$) m/z calcd. for $C_{23}H_{21}N_2O_3$ $[M+H]^+$ 373.2, found 373.0. m.p: 123.5-124.5^{o}C

5-(2-(3,4-dimethylphenyl)-1H-benzo[d]imidazol-6-yl)-2-hydroxybenzoic acid (5l)

White solid. Yield 86%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.07 (d, J = 2.4 Hz, 1H), 8.02 (d, J = 1.8 Hz, 1H), 7.94 (dd, J = 7.8, 1.8 Hz, 1H), 7.88 (dd, J = 8.4, 2.4 Hz, 1H), 7.78 (d, J = 1.8 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.55 (dd, J = 8.4, 1.8 Hz, 1H), 7.38 (d, J = 7.8 Hz, 1H), 7.09 (d, J = 8.4 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.84, 160.50, 151.19, 140.27, 137.34, 136.00, 135.01, 134.15, 131.62, 130.32, 128.24, 127.99, 124.89, 124.60, 122.47, 117.90, 115.05, 113.63, 111.61, 19.53, 19.51. HRMS (ESI): m/z calcd for $C_{22}H_{18}N_2O_3Na$ $[M+Na]^+$ 381.1210, found 381.1204. MS (ESI$^+$) m/z calcd. for $C_{22}H_{19}N_2O_3$ $[M+H]^+$ 359.1, found 359.0. m.p: 251.8-252.8^{o}C

Methyl 5-(2-(3,4-dimethoxyphenyl)-1H-benzo[d]imidazol-6-yl)-2-hydroxybenzoate (4m)

White solid. Yield 86%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.80 (s, 1H), 10.48 (s, 1H), 8.05 (s, 1H), 7.88 (dd, J = 8.4, 2.4 Hz, 1H), 7.85 – 7.53 (m, 4H), 7.46 – 7.40 (m, 1H), 7.14 (d, J = 8.4 Hz, 1H), 7.13 – 7.09 (m, 1H), 3.94 (s, 3H), 3.89 (s, 3H), 3.85 (s, 3H). MS (ESI$^+$) m/z calcd. for $C_{23}H_{21}N_2O_5$ $[M+H]^+$ 405.1, found 405.1. m.p: 160.1-161.1^{o}C

5-(2-(3,4-dimethoxyphenyl)-1H-benzo[d]imidazol-6-yl)-2-hydroxybenzoic acid (5m)

White solid. Yield 90%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.09 (d, J = 2.4 Hz, 1H), 8.06 (d, J = 1.8 Hz, 1H), 7.98 (dd, J = 8.4, 1.8 Hz, 1H), 7.91 (dd, J = 8.4, 2.4 Hz, 1H), 7.88 (d, J = 1.8 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.76 (dd, J = 8.4, 1.8 Hz, 1H), 7.30 (d, J = 8.4 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 3.94 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.65, 160.78, 152.89, 149.47, 149.20, 136.81, 134.25, 132.92, 131.43,

130.64, 128.44, 124.38, 121.87, 118.05, 115.31, 114.16, 113.56, 112.19, 110.95, 110.61, 56.19, 55.96. HRMS (ESI): m/z calcd for $C_{22}H_{18}N_2O_5Na$ $[M+Na]^+$ 413.1108, found 413.1103. MS (ESI^+) m/z calcd. for $C_{22}H_{19}N_2O_5$ $[M+H]^+$ 391.1, found 391.0. m.p: 260.4-261.4°C

Methyl 2-hydroxy-5-(2-(3-methoxy-4-methylphenyl)-1H-benzo[d]imidazol-6-yl)benzoate (4n)

White solid. Yield 71%. ^1H NMR (600 MHz, DMSO-d_6) δ 12.90 (s, 1H), 10.49 (s, 1H), 8.05 (d, J = 2.4 Hz, 1H), 7.92 – 7.56 (m, 5H), 7.45 (dd, J = 15.7, 8.4 Hz, 1H), 7.32 (d, J = 7.8 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 2.22 (s, 3H). MS (ESI^+) m/z calcd. for $C_{23}H_{21}N_2O_4$ $[M+H]^+$ 389.1, found 389.0. m.p: 150.6-151.6°C

2-hydroxy-5-(2-(3-methoxy-4-methylphenyl)-1H-benzo[d]imidazol-6-yl)benzoic acid (5n)

White solid. Yield 89%. ^1H NMR (600 MHz, DMSO-d_6) δ 8.08 (d, J = 2.4 Hz, 1H), 7.98 (d, J = 1.8 Hz, 1H), 7.90 (dd, J = 8.4, 2.4 Hz, 1H), 7.87 (d, J = 1.8 Hz, 1H), 7.84 – 7.80 (m, 2H), 7.72 (dd, J = 8.4, 1.8 Hz, 1H), 7.45 (dd, J = 7.8, 0.6 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 3.97 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.69, 160.74, 157.84, 149.73, 136.49, 134.19, 133.83, 132.43, 131.40, 131.26, 130.77, 128.38, 124.08, 122.95, 119.81, 117.99, 114.50, 113.53, 110.91, 109.42, 56.00, 16.26. HRMS (ESI): m/z calcd for $C_{22}H_{18}N_2O_4Na$ $[M+Na]^+$ 397.1159, found 397.1149. MS (ESI^+) m/z calcd. for $C_{22}H_{19}N_2O_4$ $[M+H]^+$ 375.1, found 375.2. m.p: 290.0-291.0°C

Methyl 2-hydroxy-5-(2-(4-methoxy-3-methylphenyl)-1H-benzo[d]imidazol-6-yl)benzoate (4o)

White solid. Yield 90%. ^1H NMR (600 MHz, DMSO-d_6) δ 12.77 (s, 1H), 10.49 (s, 1H), 8.04 (d, J = 2.4 Hz, 1H), 8.02 – 7.98 (m, 2H), 7.88 (dd, J = 8.4, 2.4 Hz, 1H), 7.80 – 7.55 (m, 2H), 7.42 (dd, J = 8.4, 1.8 Hz, 1H), 7.14 – 7.08 (m, 2H), 3.94 (s, 3H), 3.88 (s, 3H), 2.25 (s, 3H). MS (ESI^+) m/z calcd. for $C_{23}H_{21}N_2O_4$ $[M+H]^+$ 389.1, found 389.2. m.p: 135.8-136.8°C

2-hydroxy-5-(2-(4-methoxy-3-methylphenyl)-1H-benzo[d]imidazol-6-yl)benzoic acid (5o)

White solid. Yield 90%. ^1H NMR (600 MHz, DMSO-d_6) δ 8.18 (dd, J = 8.4, 2.4 Hz, 1H), 8.14 (d, J = 2.4 Hz, 1H), 8.07 (d, J = 2.4 Hz, 1H), 7.88 (dd, J = 8.4, 2.4 Hz, 1H), 7.82 (d, J = 1.2 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.66 (dd, J = 8.4, 1.8 Hz, 1H), 7.24 (d, J = 8.4 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 3.92 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.72, 160.75, 160.66, 150.08, 135.98, 134.58, 134.15, 133.12, 130.99, 129.60, 128.32, 127.50, 126.88, 123.47, 117.94, 116.55, 114.39, 113.60, 111.12, 110.90, 55.86, 16.11. HRMS (ESI): m/z calcd for $C_{22}H_{18}N_2O_4Na$ $[M+Na]^+$ 397.1159, found 397.1153. MS (ESI^+) m/z calcd. for $C_{22}H_{19}N_2O_4$ $[M+H]^+$ 375.1, found 375.1. m.p: 285.6-286.6°C

Methyl 2-hydroxy-5-(2-(naphthalen-2-yl)-1H-benzo[d]imidazol-6-yl)benzoate (4p)

Yellow solid. Yield 82%. ^1H NMR (600 MHz, DMSO-d_6) δ 10.51 (s, 1H), 8.78 – 8.75 (m, 1H), 8.33 (dd, J = 8.4, 1.8 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 8.09 – 8.05 (m, 2H), 8.03 – 7.99 (m, 1H), 7.91 (dd, J = 8.4, 2.4 Hz, 1H), 7.81 (s, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.49 (dd, J = 8.4, 1.8 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 3.95 (s, 3H). MS (ESI^+) m/z calcd. for $C_{25}H_{19}N_2O_3$ $[M+H]^+$ 395.1, found 395.2. m.p: 203.5-204.5°C

2-hydroxy-5-(2-(naphthalen-2-yl)-1H-benzo[d]imidazol-6-yl)benzoic acid (5p)

Yellow solid. Yield 89%. ^1H NMR (600 MHz, DMSO-d_6) δ 16.44 (s, 1H), 8.74 (s, 1H), 8.41 (dd, J = 8.4, 1.8 Hz, 1H), 8.03 (d, J = 2.4 Hz, 1H), 7.98 (dd, J = 10.7, 8.4 Hz, 2H), 7.93 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 1.8 Hz, 1H), 7.58 – 7.47 (m, 4H), 7.24 (dd, J = 8.4, 1.8 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.65, 161.90, 154.29, 134.05, 133.12, 133.07, 130.09, 129.87, 128.77, 128.34, 128.20, 128.07, 127.73, 126.57, 126.44, 125.32, 124.61, 120.57, 119.75, 116.31, 115.91, 111.87. HRMS (ESI): m/z calcd for $C_{24}H_{16}N_2O_3Na$ $[M+Na]^+$ 403.1053, found 403.1049. MS (ESI^+) m/z calcd. for $C_{24}H_{17}N_2O_3$ $[M+H]^+$ 381.1, found 381.1. m.p: >300°C

Methyl 5-(2-(4-(diphenylamino)phenyl)-1H-benzo[d]imidazol-6-yl)-2-hydroxybenzoate (4q)

Yellow solid. Yield 86%. ^1H NMR (600 MHz, DMSO-d_6) δ 12.79 (s, 1H), 10.48 (s, 1H), 8.09 – 8.02 (m, 3H), 7.87 (dd, J = 8.4, 2.4 Hz, 1H), 7.84 – 7.35 (m, 7H), 7.16 – 7.03 (m, 9H), 3.94 (s, 3H). MS (ESI^+) m/z calcd. for $C_{33}H_{26}N_3O_3$ $[M+H]^+$ 512.2, found 512.1. m.p: 190.5-191.5°C

5-(2-(4-(diphenylamino)phenyl)-1H-benzo[d]imidazol-6-yl)-2-hydroxybenzoic acid (5q)

Yellow solid. Yield 87%. ^1H NMR (600 MHz, DMSO-d_6) δ 8.15 – 8.11 (m, 2H), 8.08 (d, J = 2.4 Hz, 1H), 7.90 (dd, J = 8.4, 2.4 Hz, 1H), 7.83 (d, J = 1.8 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.68 (dd, J = 8.4, 1.8 Hz, 1H), 7.43 (t, J = 7.8 Hz, 4H), 7.25 – 7.19 (m, 6H), 7.11 (d, J = 8.4 Hz, 1H), 7.07 – 7.03 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.70 , 160.69 , 150.46 (d, J = 209.9 Hz), 145.68, 136.22, 134.24, 130.99, 130.09, 129.12, 128.38, 126.07, 125.30, 123.73, 119.40, 118.02, 114.31, 113.58, 110.86. HRMS (ESI): m/z calcd for $C_{32}H_{23}N_3O_3Na$ $[M+Na]^+$ 520.1632, found

520.1628. MS (ESI$^+$) m/z calcd. for $C_{32}H_{24}N_3O_3$ $[M+H]^+$ 498.2, found 498.2. m.p: 254.3-255.3^{o}C

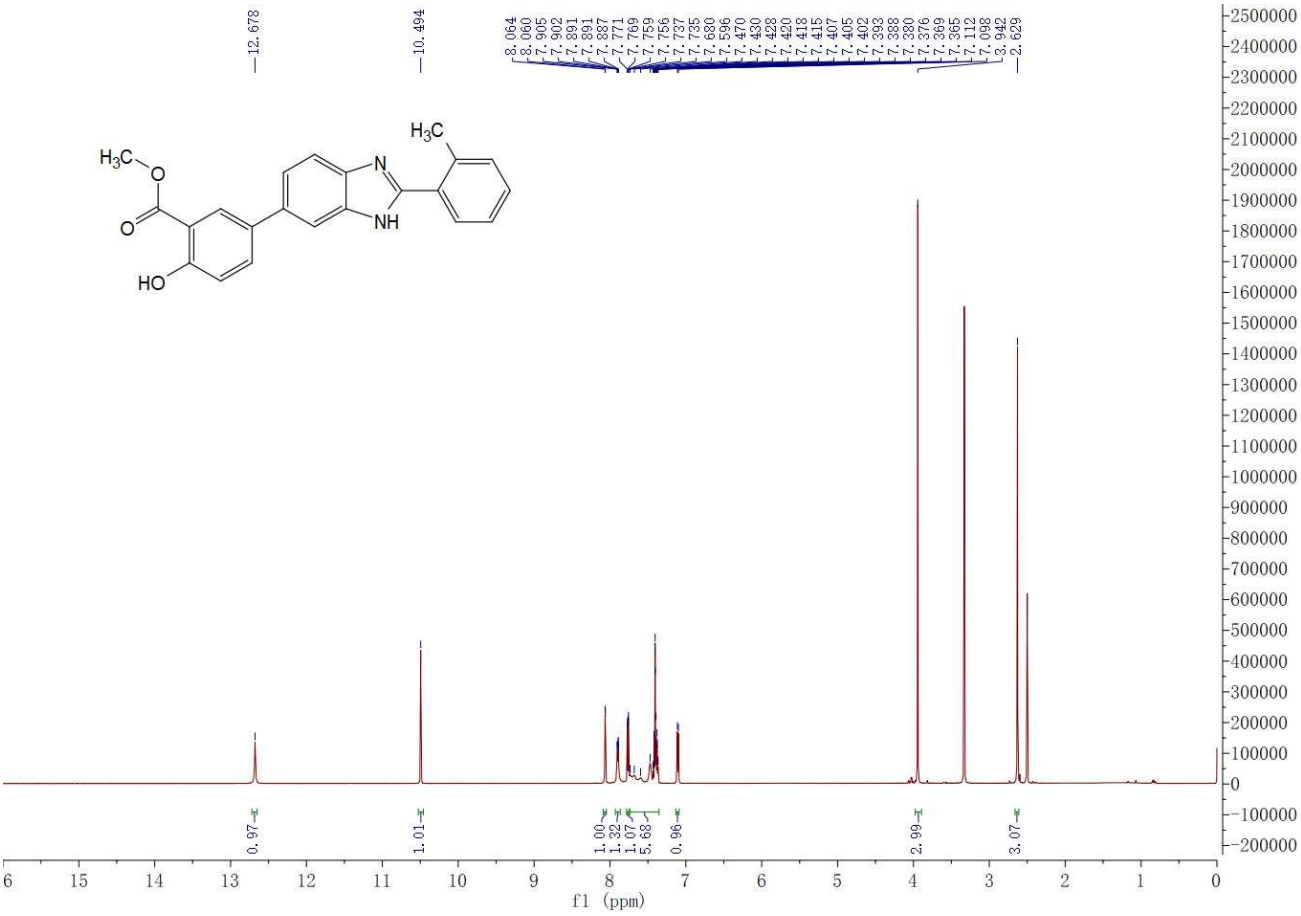
Methyl 5-(2-(9-ethyl-9H-carbazol-3-yl)-1H-benzo[d]imidazol-6-yl)-2-hydroxybenzoate (4r)

White solid. Yield 86%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.91 (d, J = 3.5 Hz, 1H), 10.49 (d, J = 3.8 Hz, 1H), 9.00 (d, J = 2.2 Hz, 1H), 8.32 (dt, J = 8.5, 2.3 Hz, 1H), 8.25 (dd, J = 7.7, 5.1 Hz, 1H), 8.07 (t, J = 2.7 Hz, 1H), 7.93 – 7.89 (m, 1H), 7.86 (d, J = 1.6 Hz, 1H), 7.80 (d, J = 8.7 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.59 (d, J = 8.2 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.44 (ddd, J = 10.2, 8.2, 1.7 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.12 (dd, J = 8.6, 6.1 Hz, 1H), 4.52 (q, J = 7.1 Hz, 2H), 3.95 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). MS (ESI$^+$) m/z calcd. for $C_{29}H_{24}N_3O_3$ $[M+H]^+$ 462.2, found 462.1. m.p: 181.6-18.6^{o}C

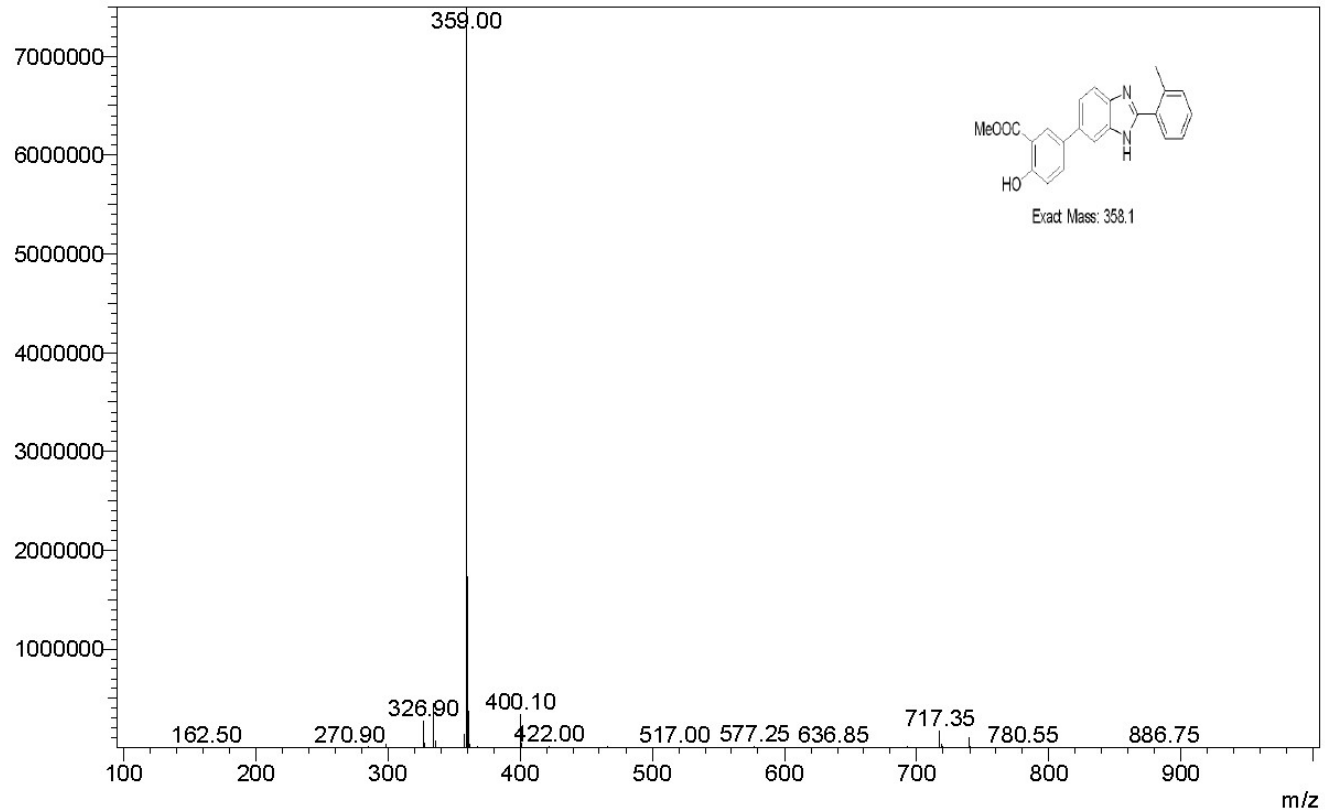
5-(2-(9-ethyl-9H-carbazol-3-yl)-1H-benzo[d]imidazol-6-yl)-2-hydroxybenzoic acid (5r)

White solid. Yield 84%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.03 (d, J = 1.8 Hz, 1H), 8.33 (dd, J = 8.4, 1.8 Hz, 1H), 8.24 (d, J = 7.8 Hz, 1H), 8.09 (d, J = 2.4 Hz, 1H), 7.89 (dd, J = 8.4, 2.4 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 1.8 Hz, 1H), 7.70 (dd, J = 8.4, 2.4 Hz, 2H), 7.58 – 7.49 (m, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 8.4 Hz, 1H), 4.53 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.89, 160.42, 152.82, 140.76, 140.21, 134.15, 133.92, 131.91, 128.13, 126.51, 124.65, 122.48, 122.15, 121.48, 120.48, 119.65, 119.31, 117.74, 114.96, 113.89, 109.71, 37.25, 13.78. HRMS (ESI): m/z calcd for $C_{28}H_{21}N_3O_3Na$ $[M+Na]^+$ 470.1475, found 470.1468. MS (ESI$^+$) m/z calcd. for $C_{28}H_{22}N_3O_3$ $[M+H]^+$ 448.2, found 448.1. m.p: 257.6-258.6^{o}C

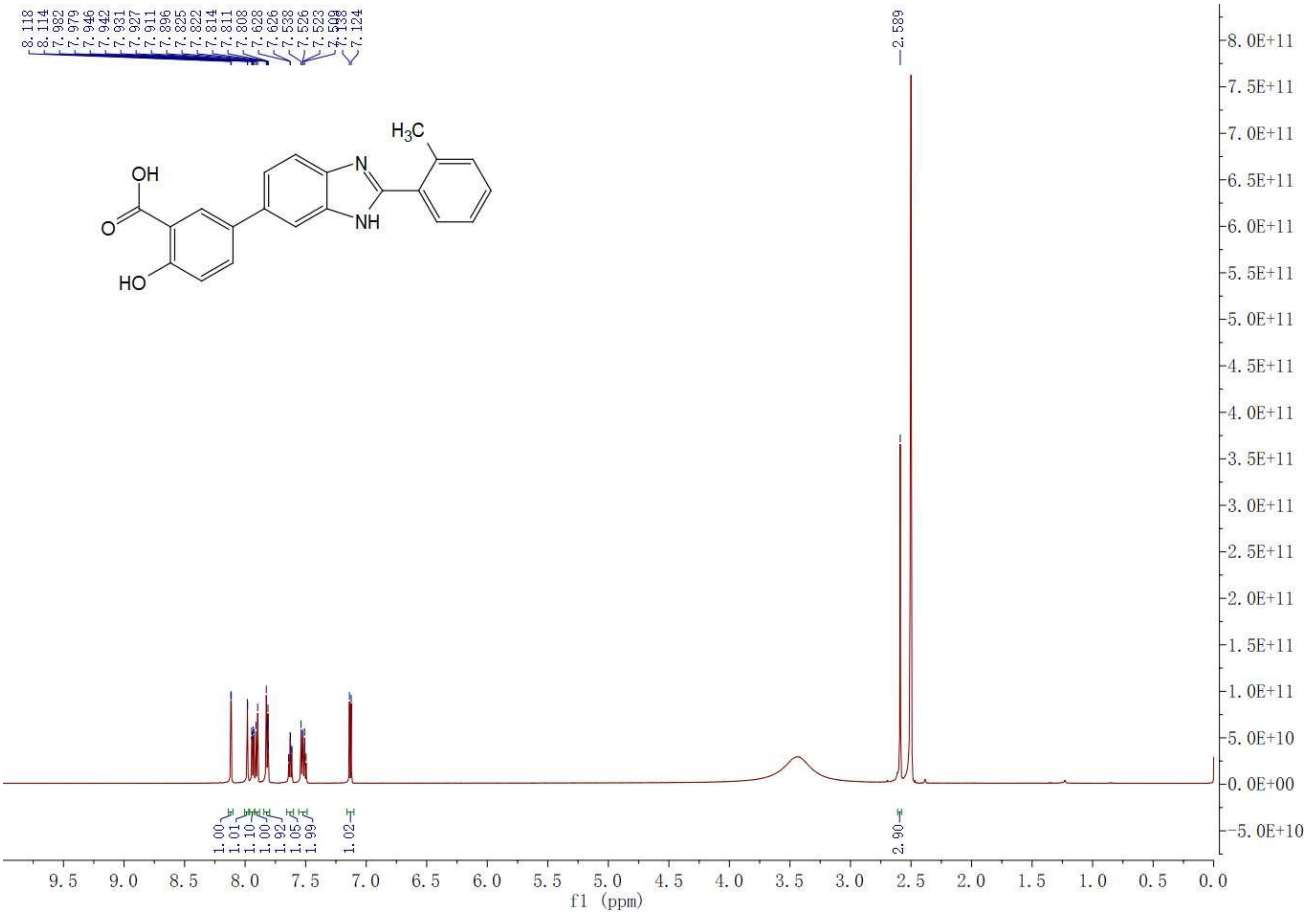
[1]H-NMR spectrum for compound **4a**.



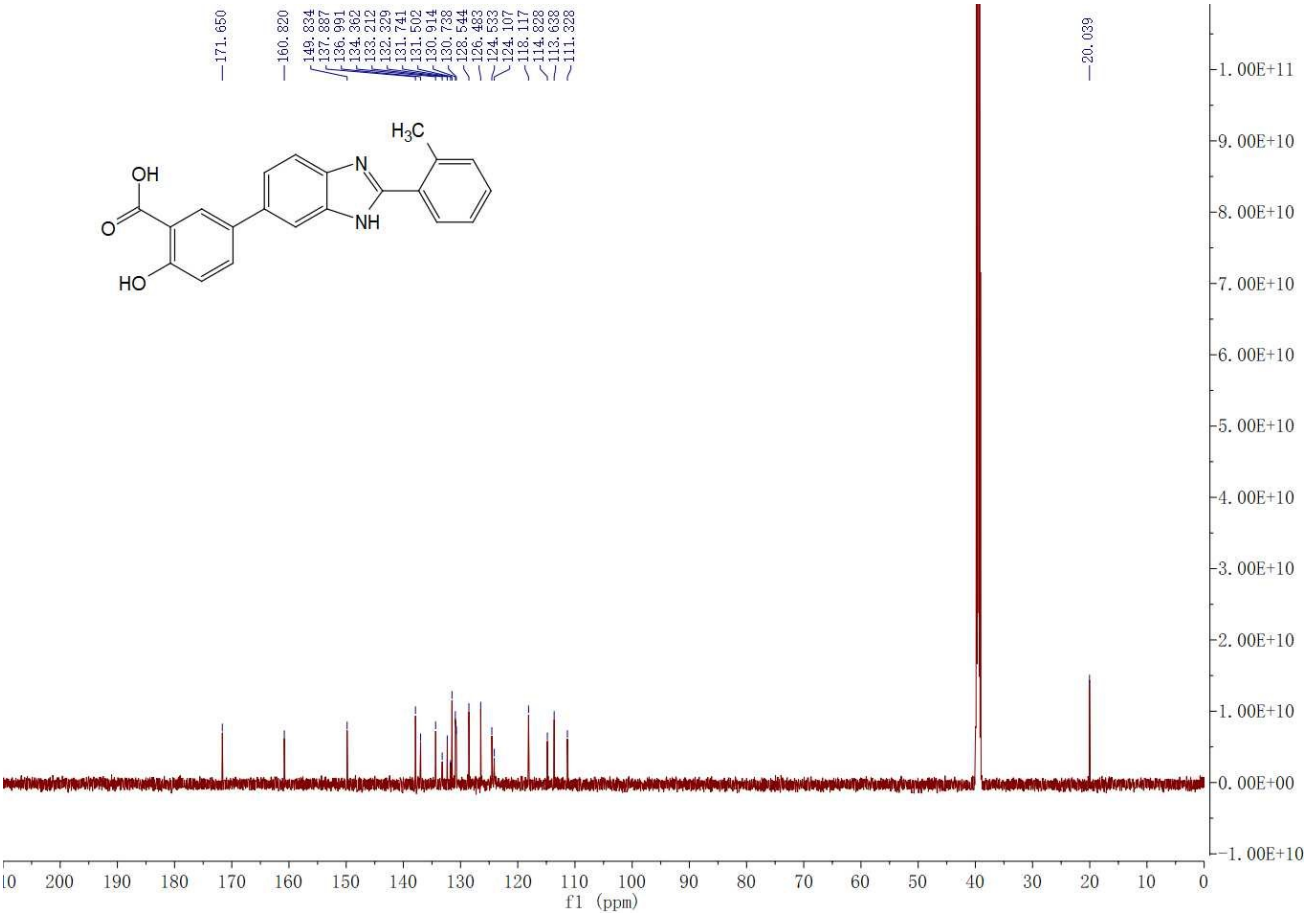
MS (ESI) for compound **4a**.



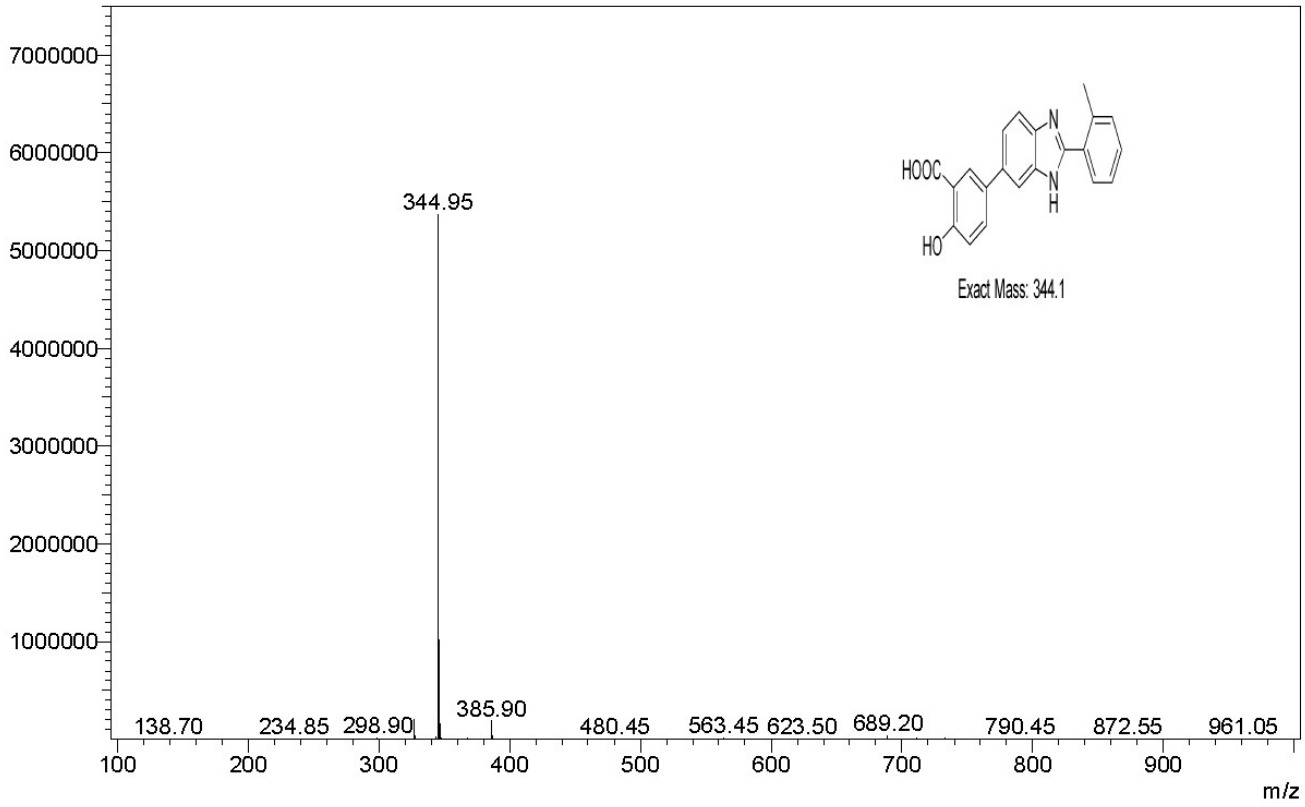
[1]H-NMR spectrum for compound **5a**.



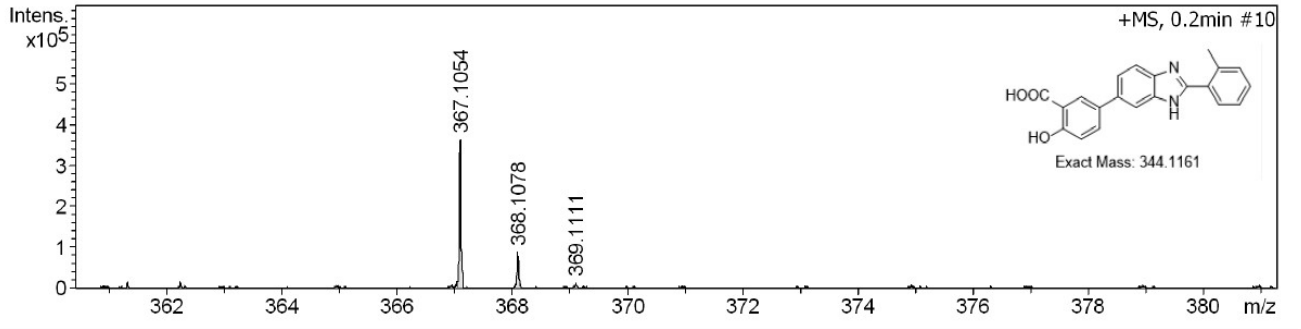
^{13}C-NMR spectrum for compound **5a**.



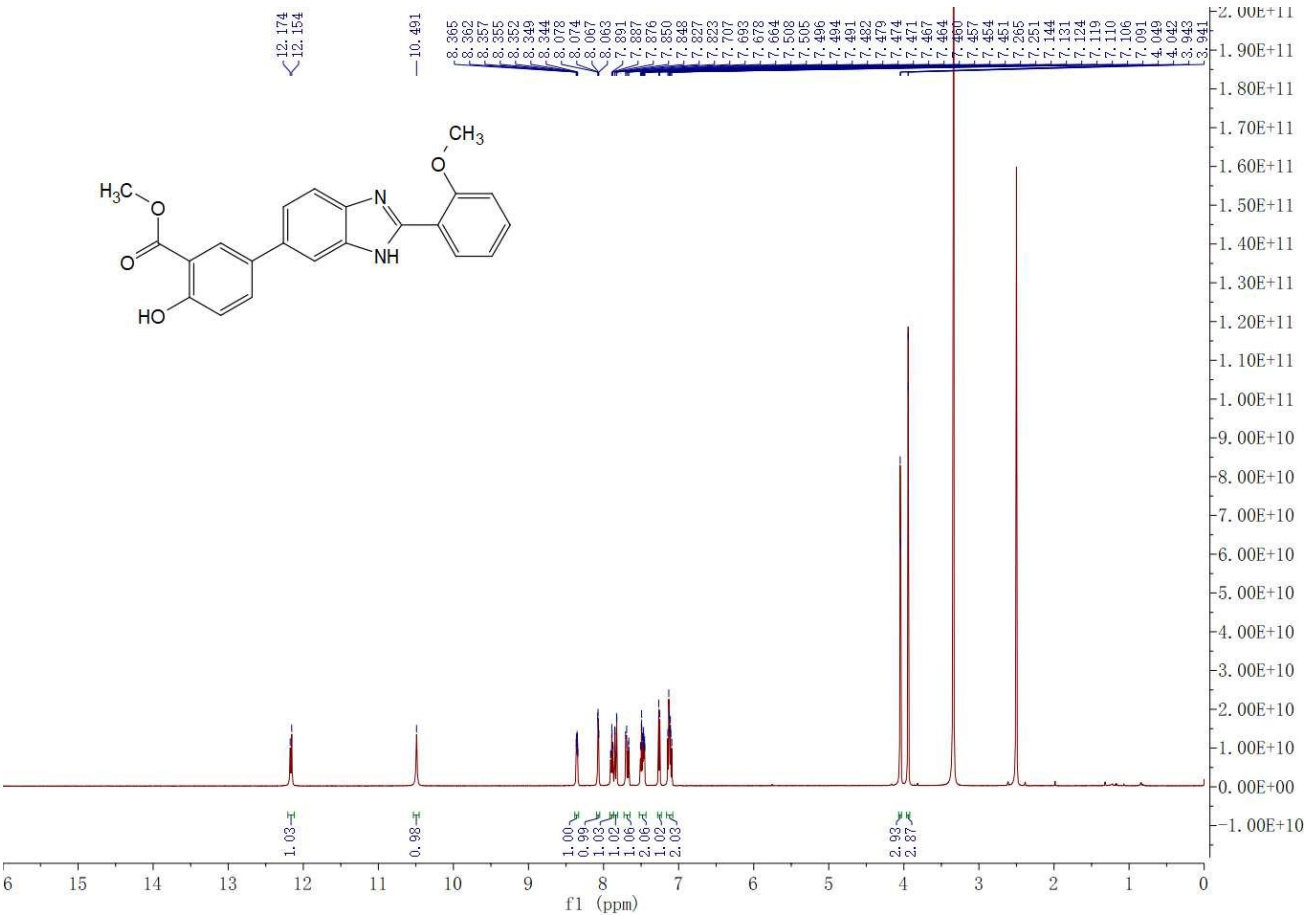
MS (ESI) for compound **5a**.



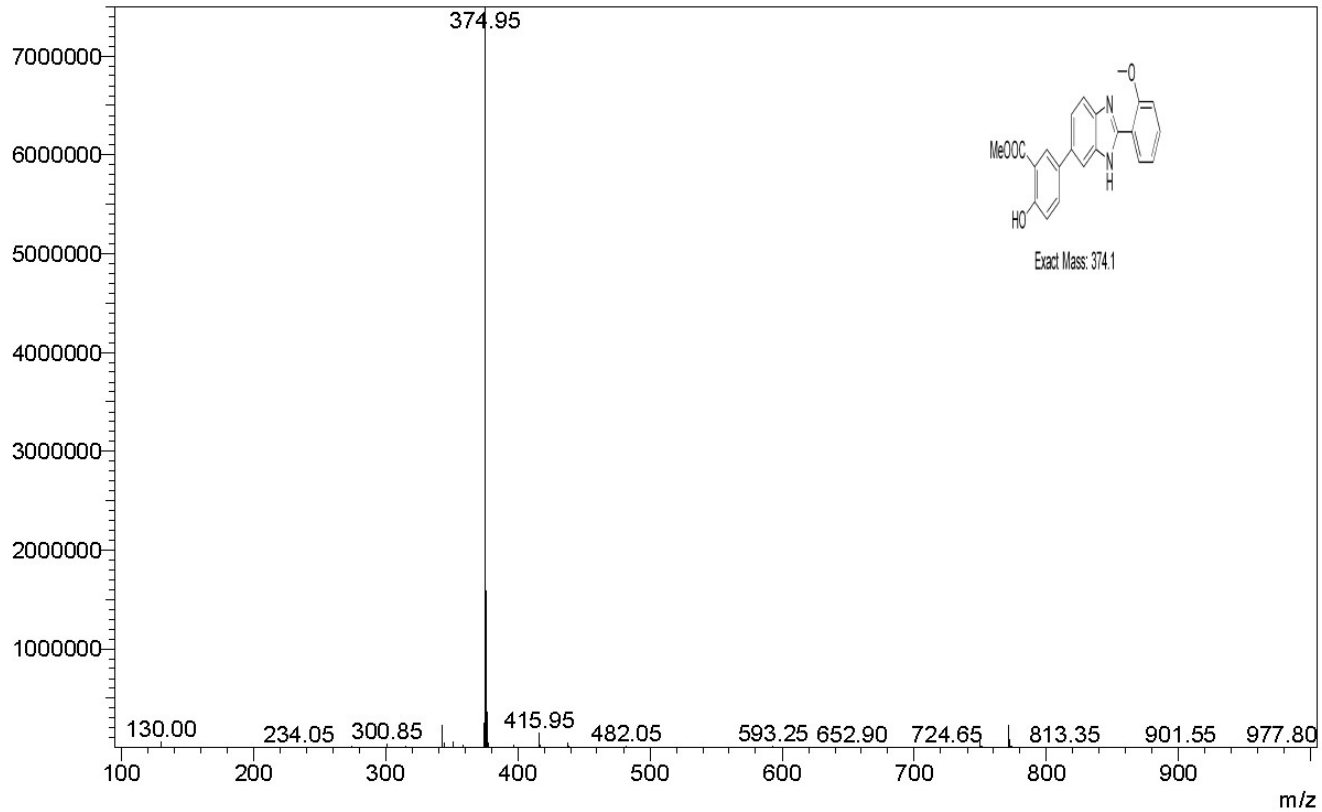
HRMS (ESI) for compound **5a**.



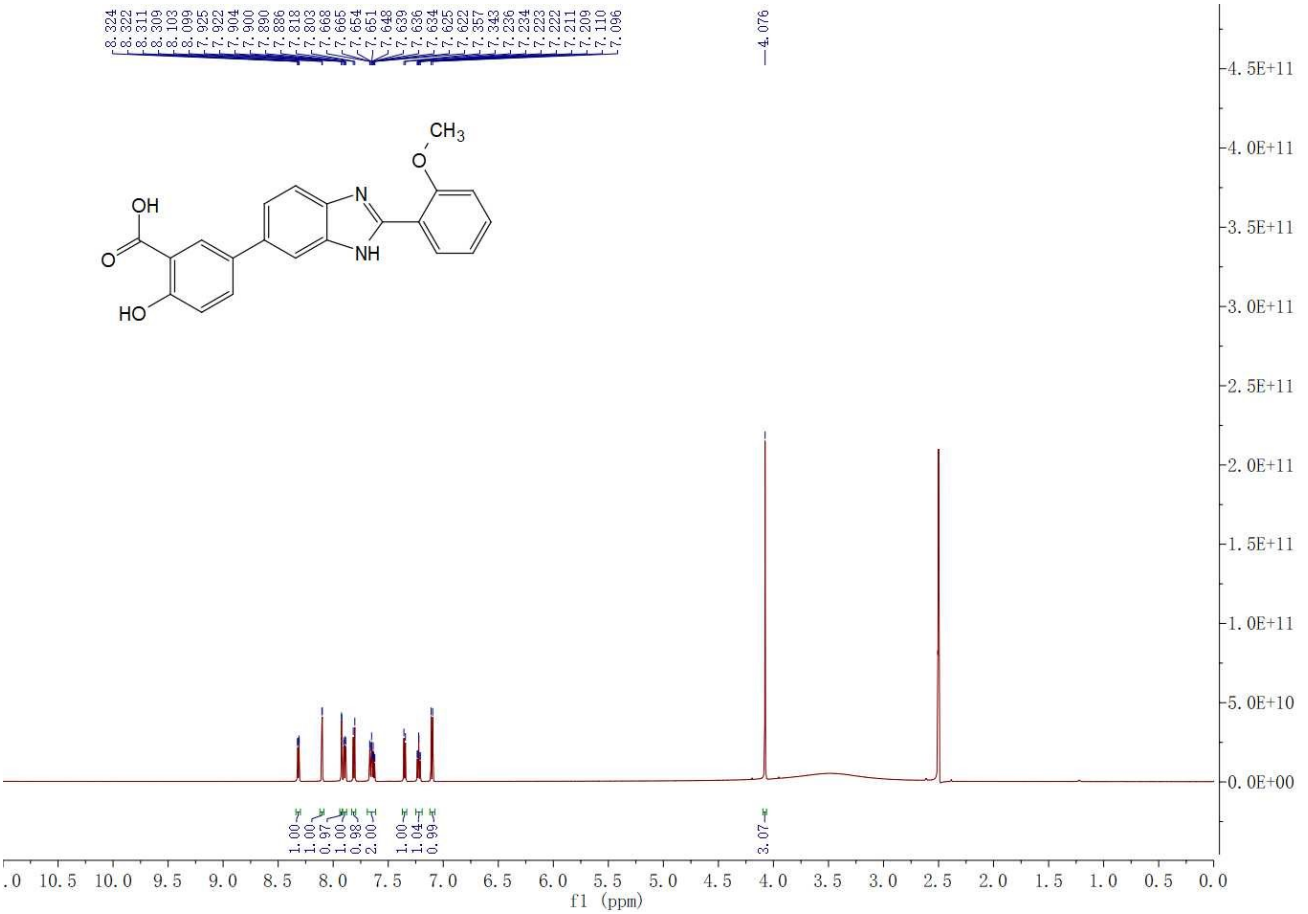
[1]H-NMR spectrum for compound **4b**.



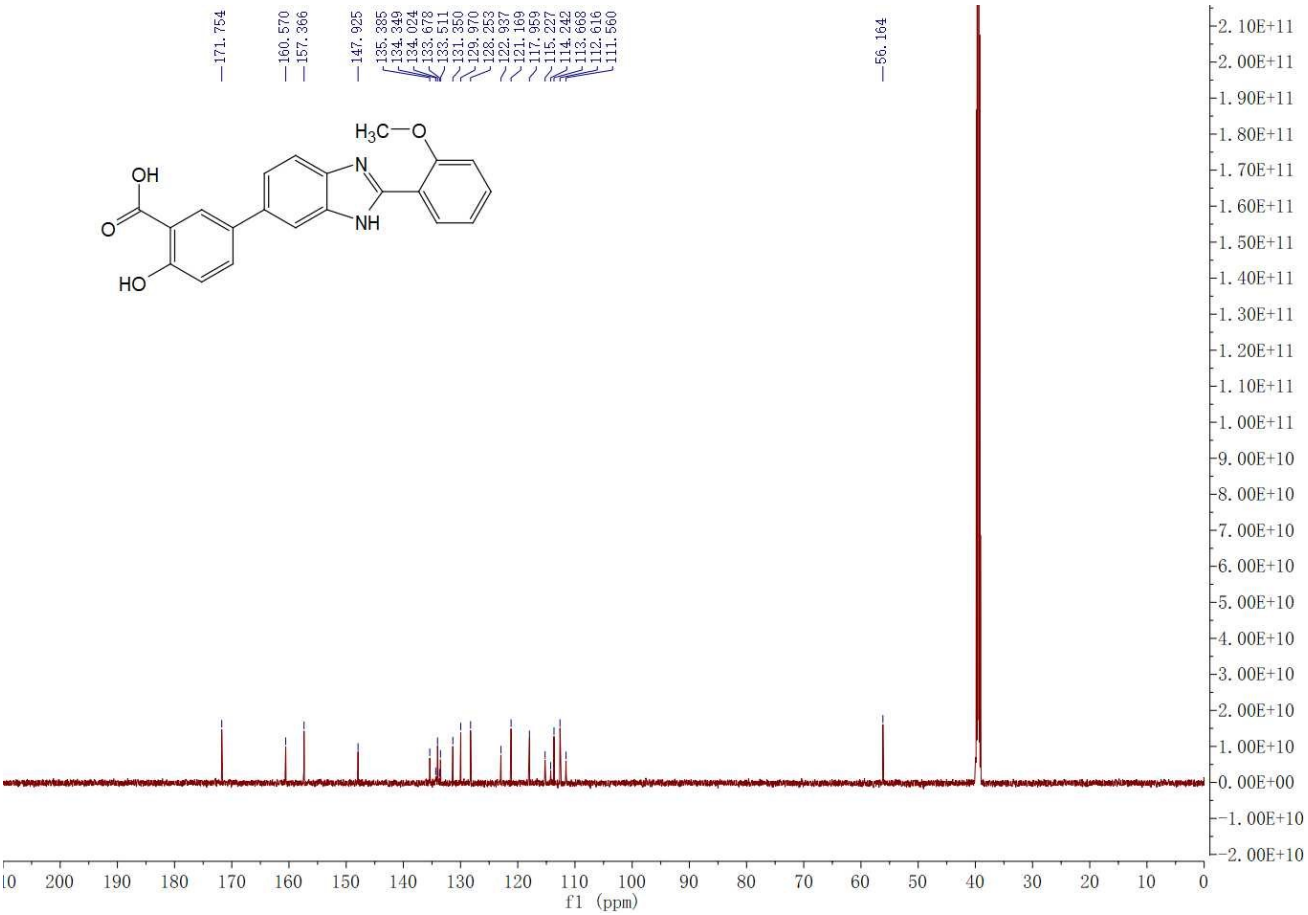
MS (ESI) for compound **4b**.



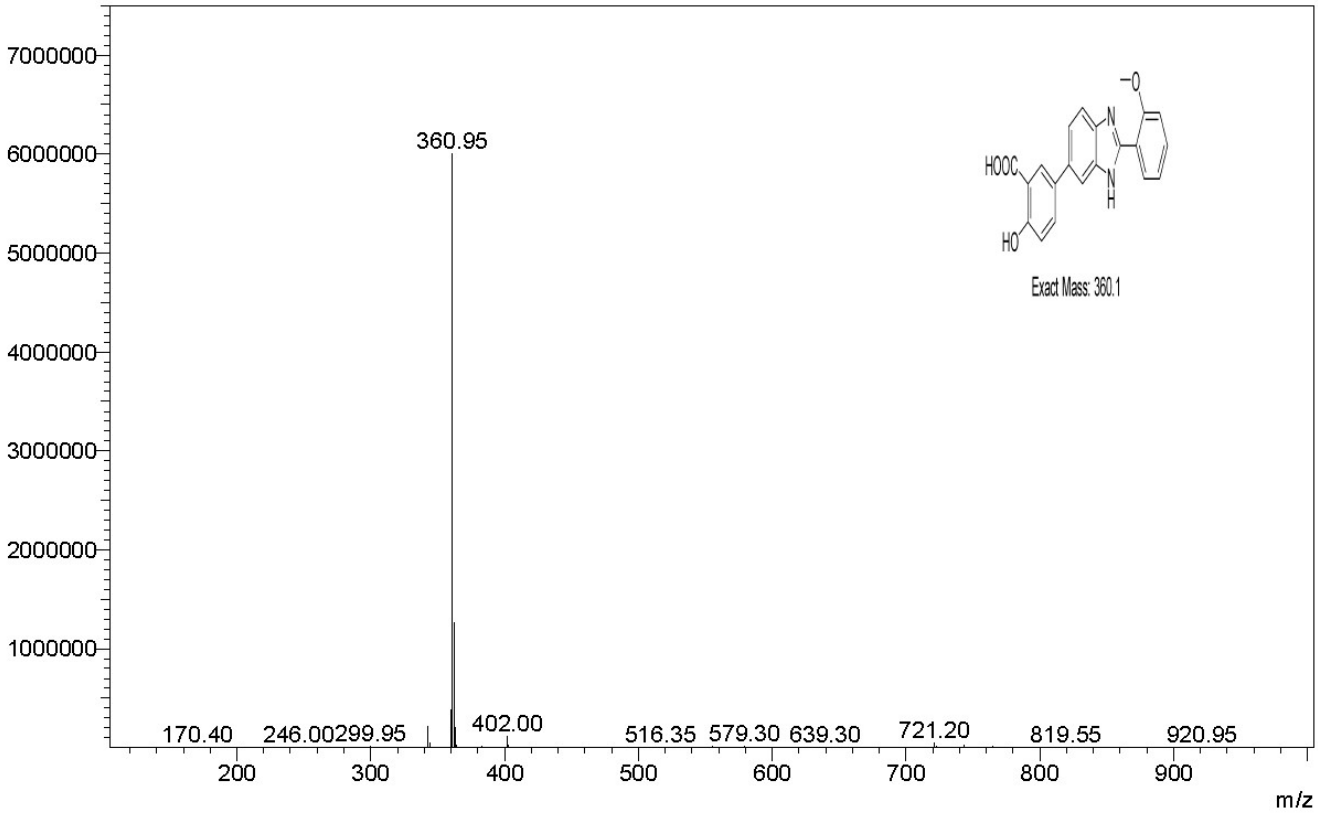
[1]H-NMR spectrum for compound **5b**.



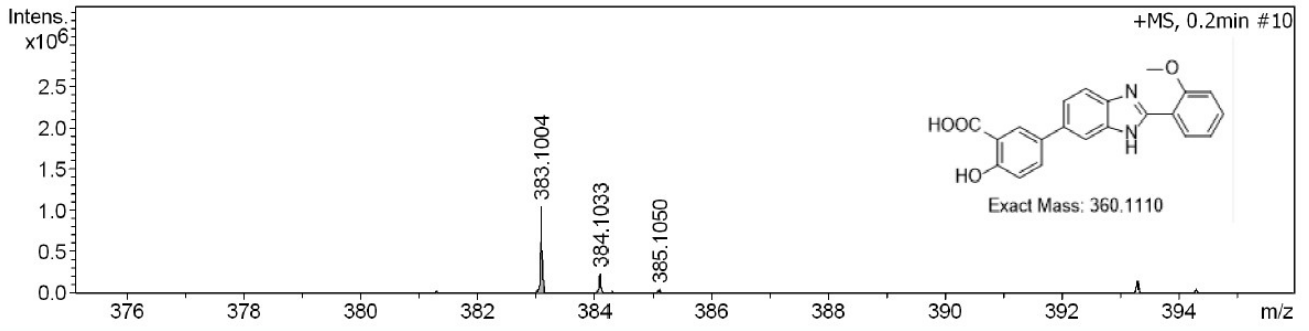
^{13}C-NMR spectrum for compound **5b**.



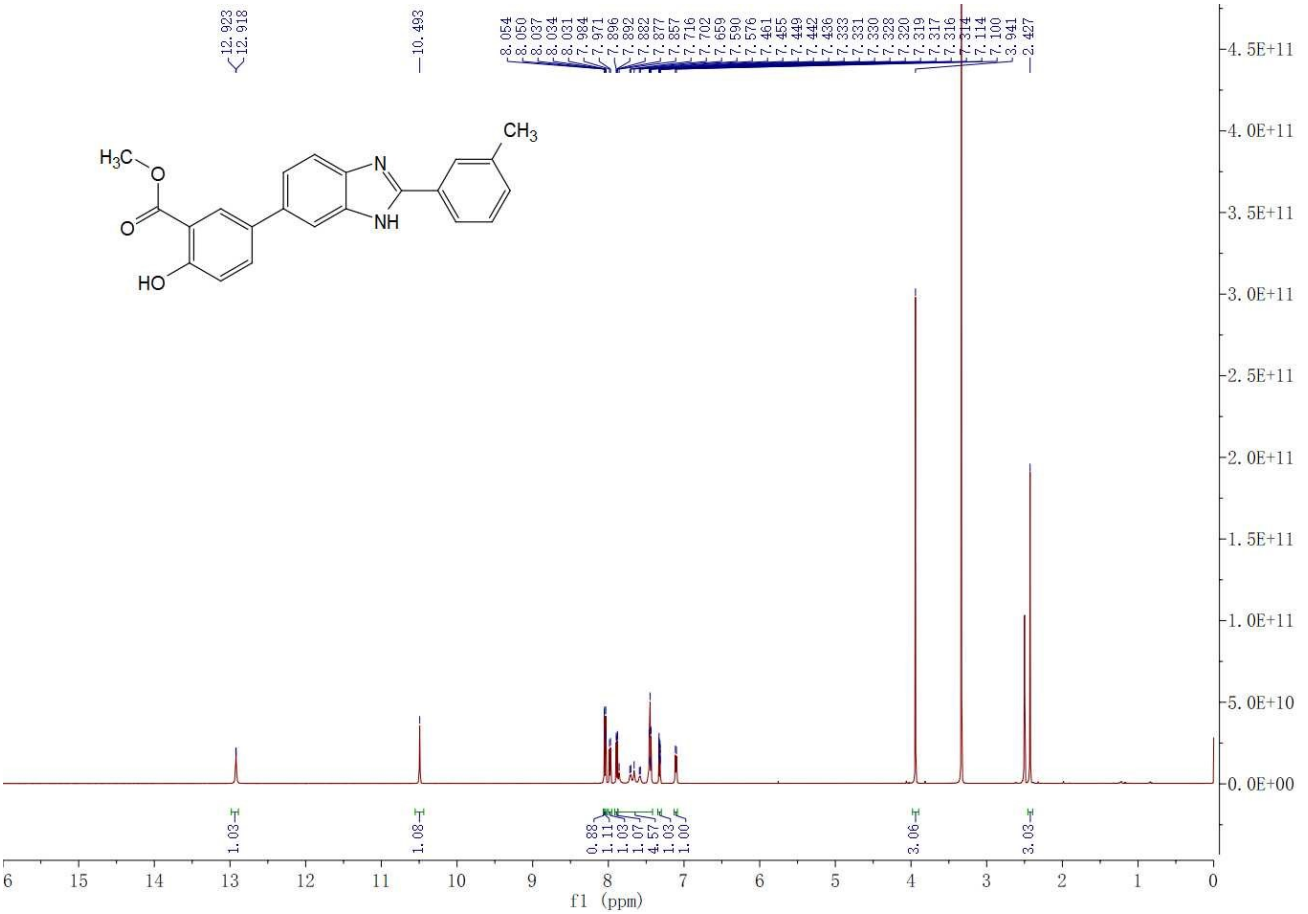
MS (ESI) for compound **5b**.



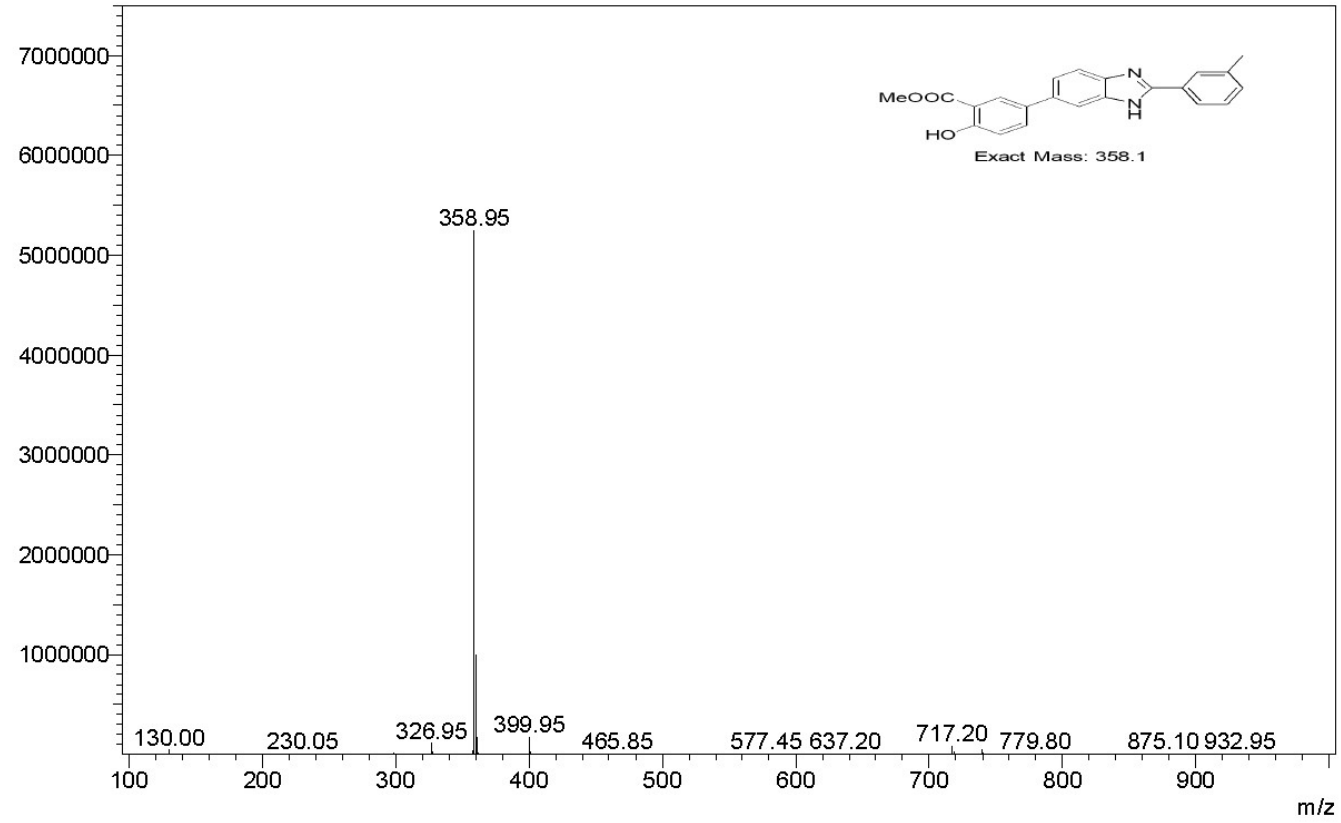
HRMS (ESI) for compound **5b**.



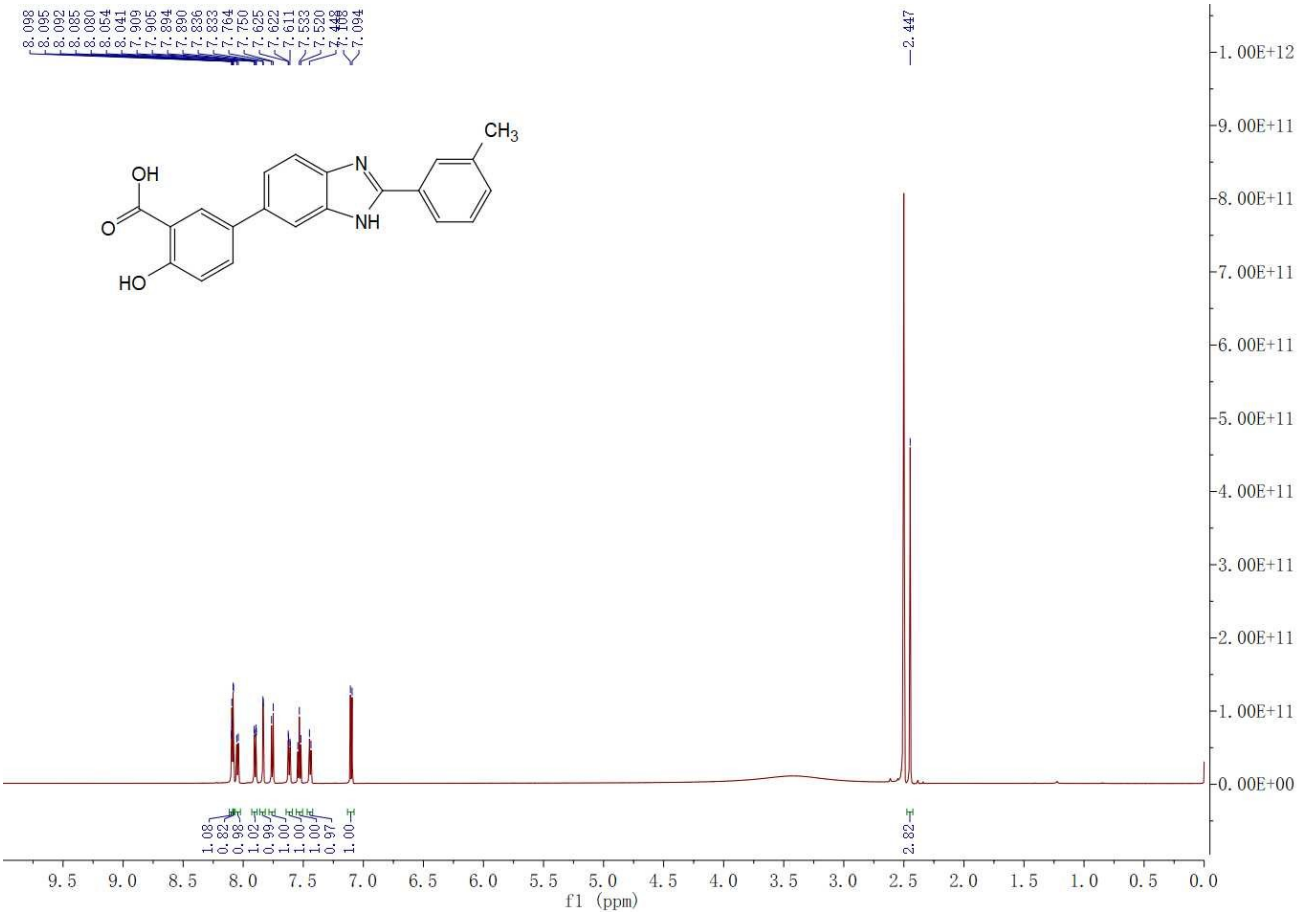
[1]H-NMR spectrum for compound **4c**.



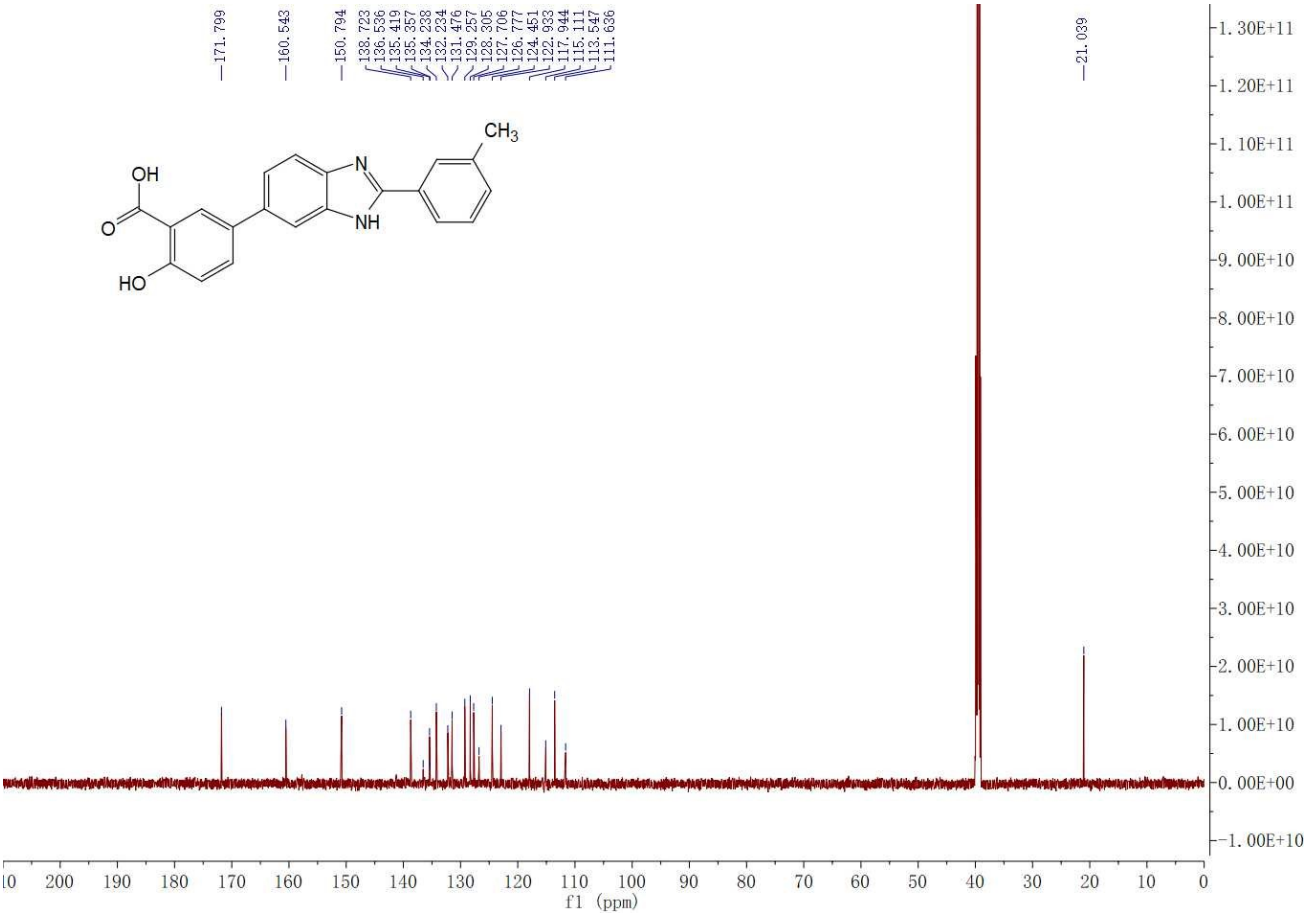
MS (ESI) for compound **4c**.



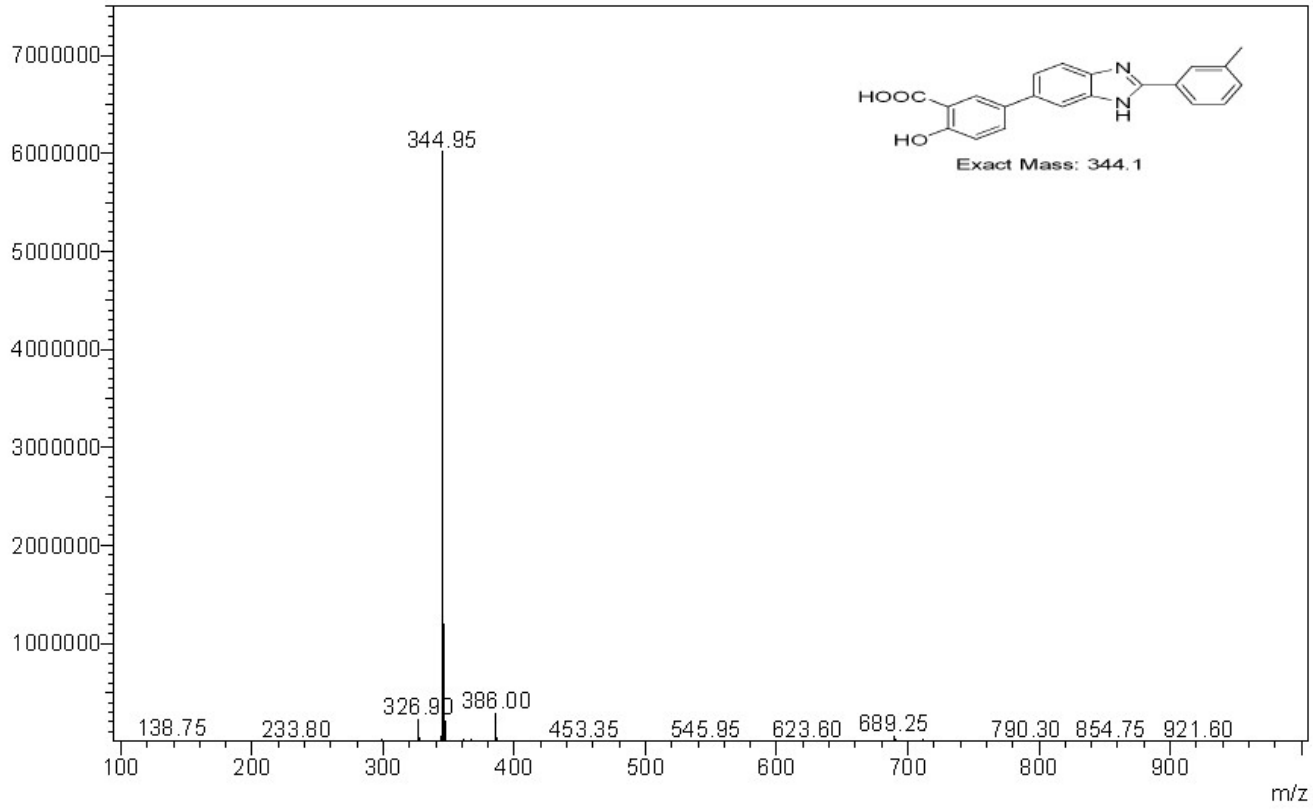
[1]H-NMR spectrum for compound **5c**.



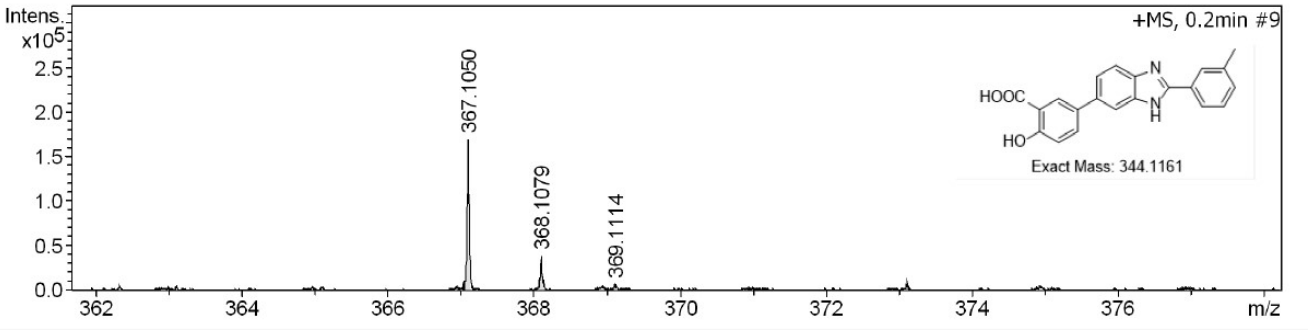
^{13}C-NMR spectrum for compound **5c**.



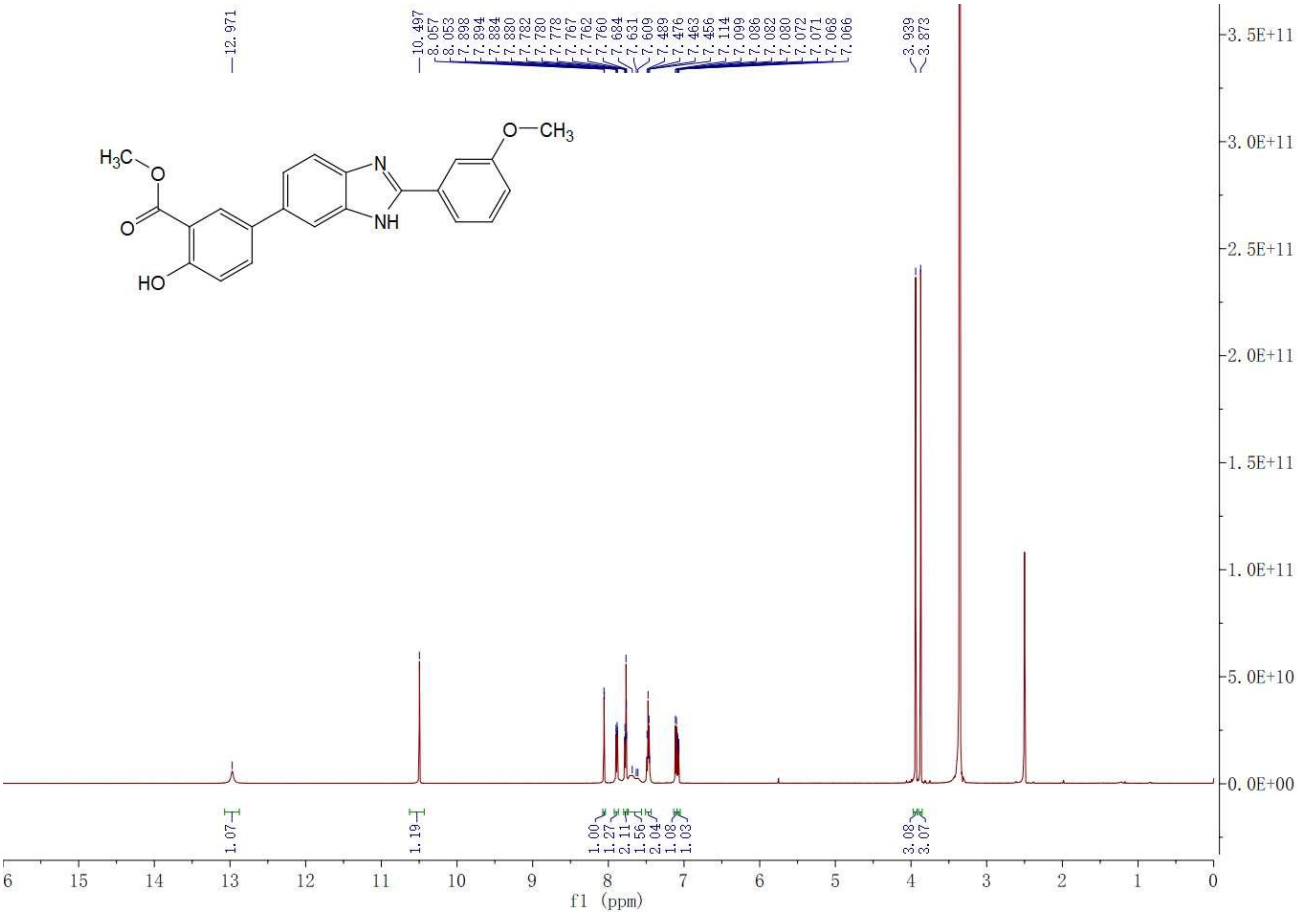
MS (ESI) for compound **5c**.



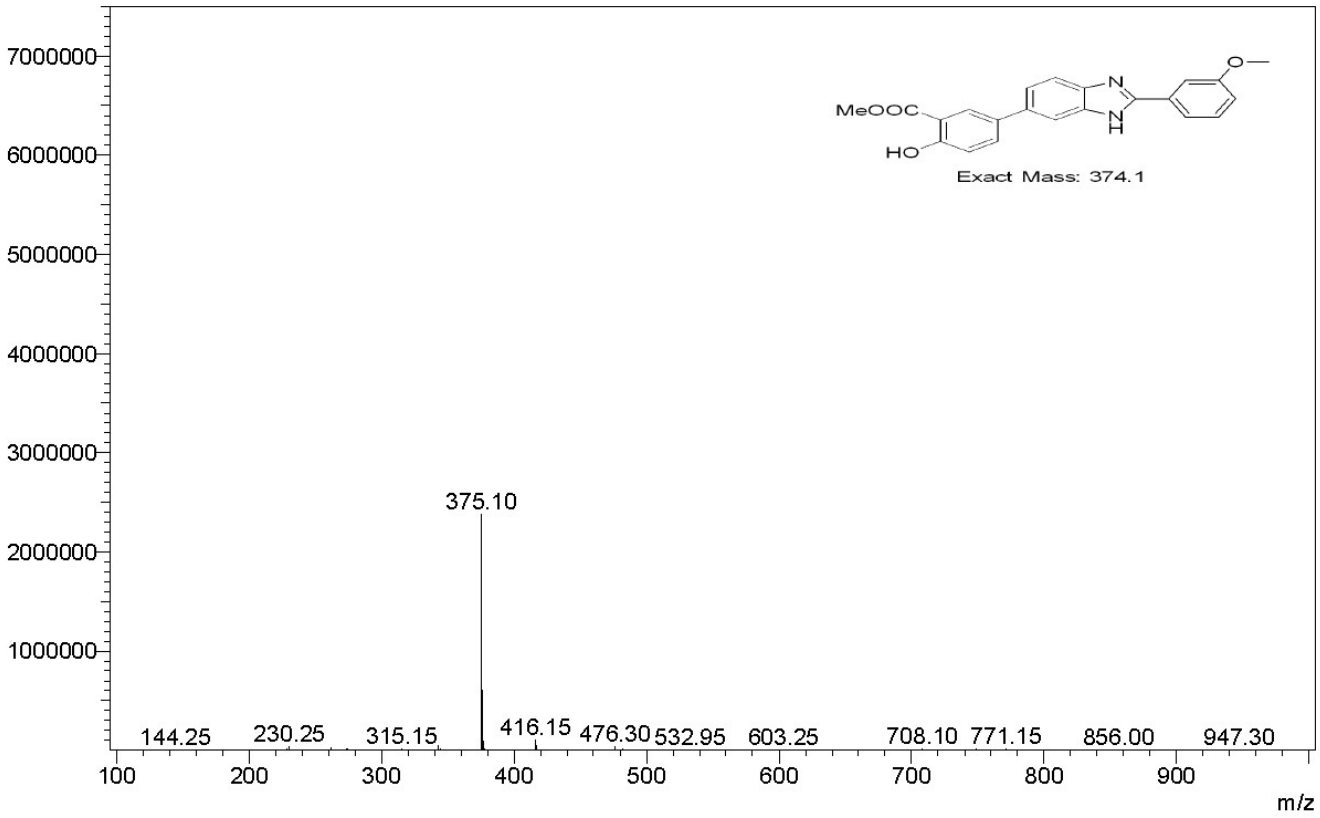
HRMS (ESI) for compound **5c**.



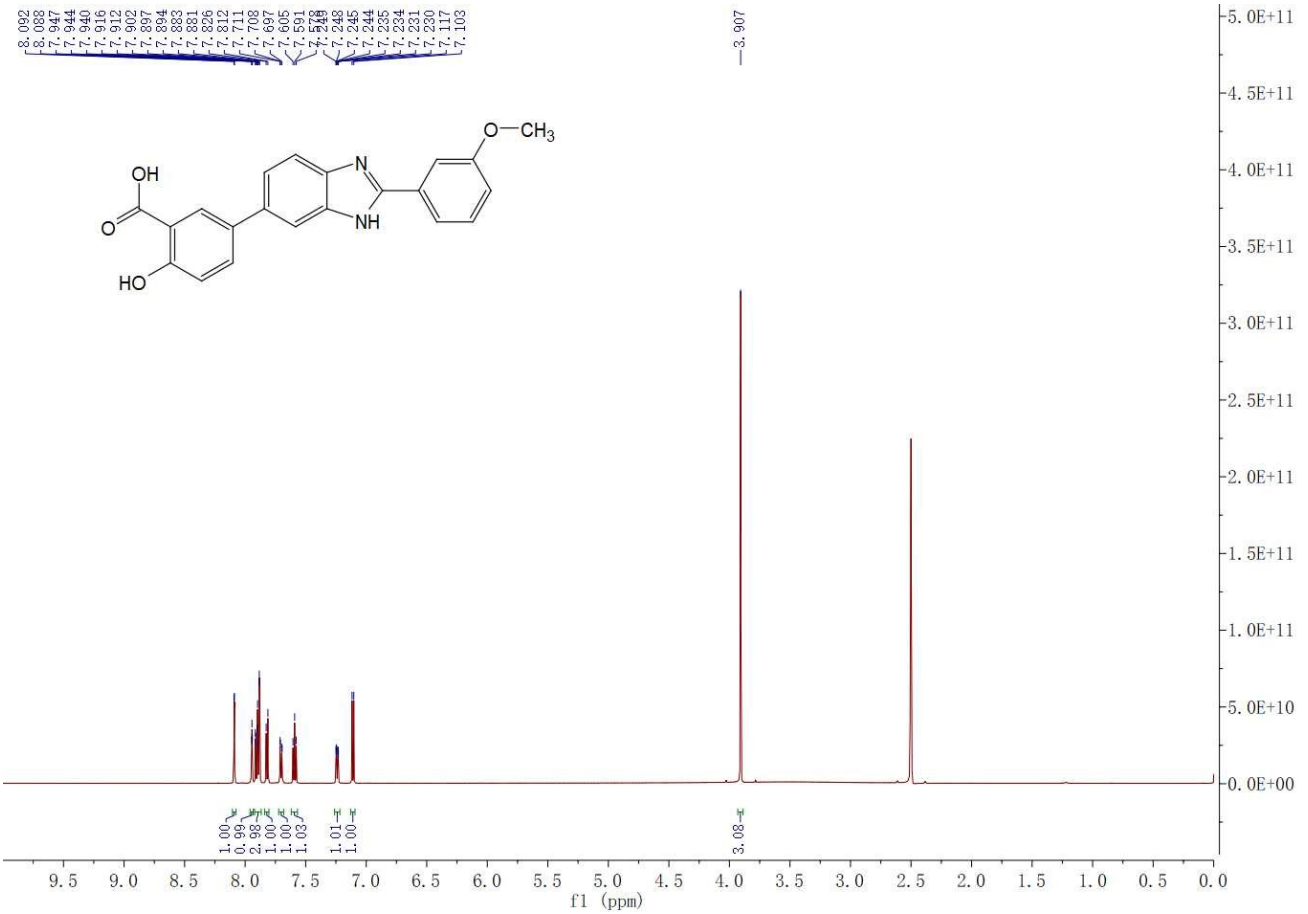
[1]H-NMR spectrum for compound **4d**.



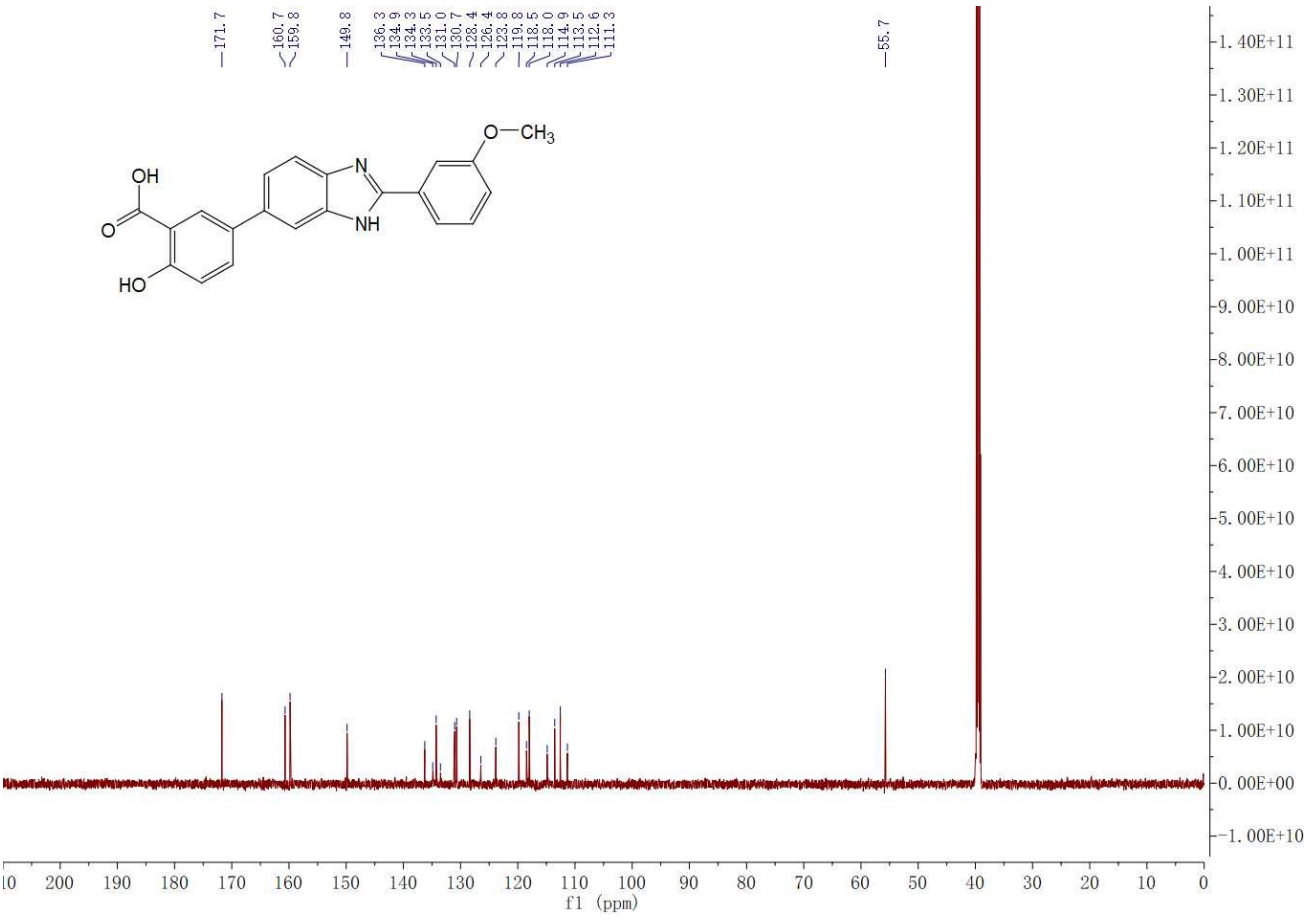
MS (ESI) for compound **4d**.



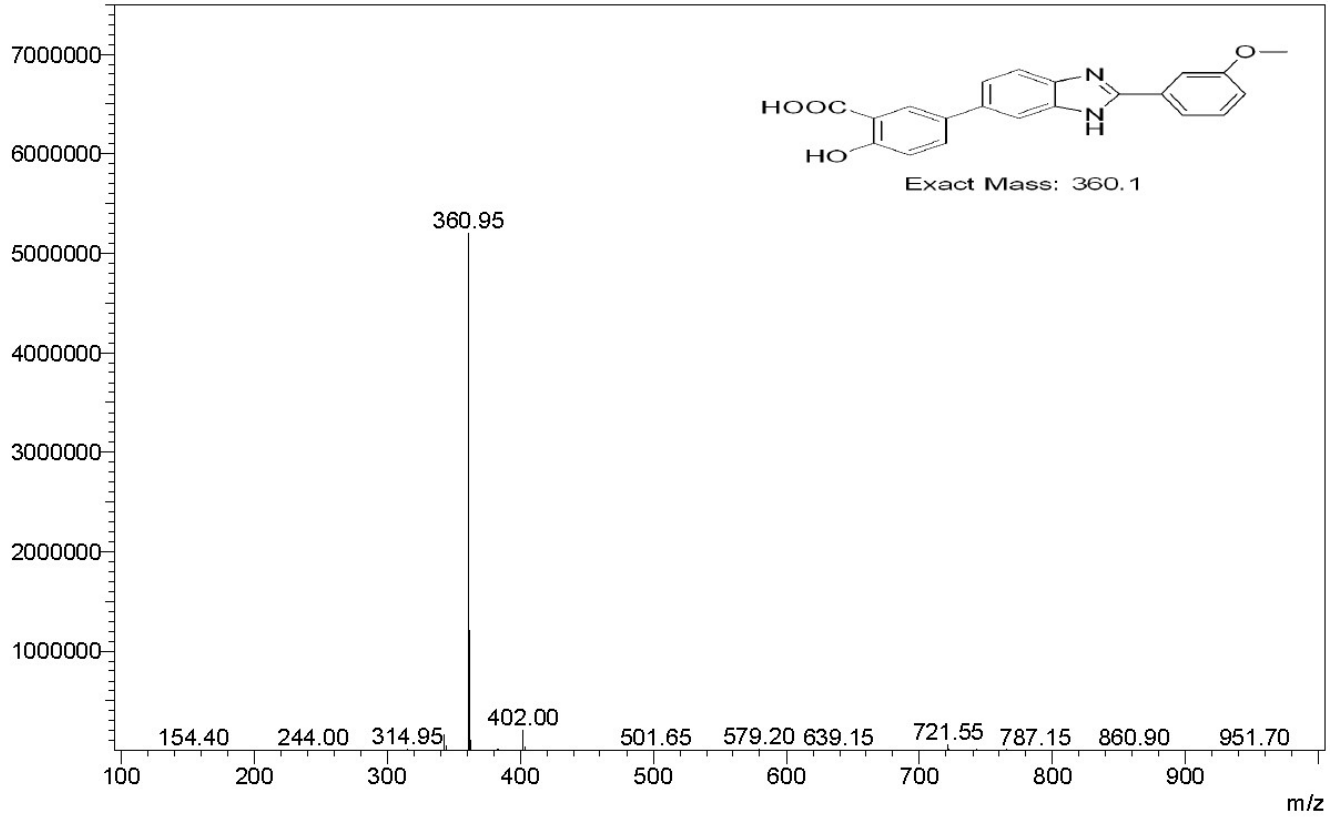
[1]H-NMR spectrum for compound **5d**.



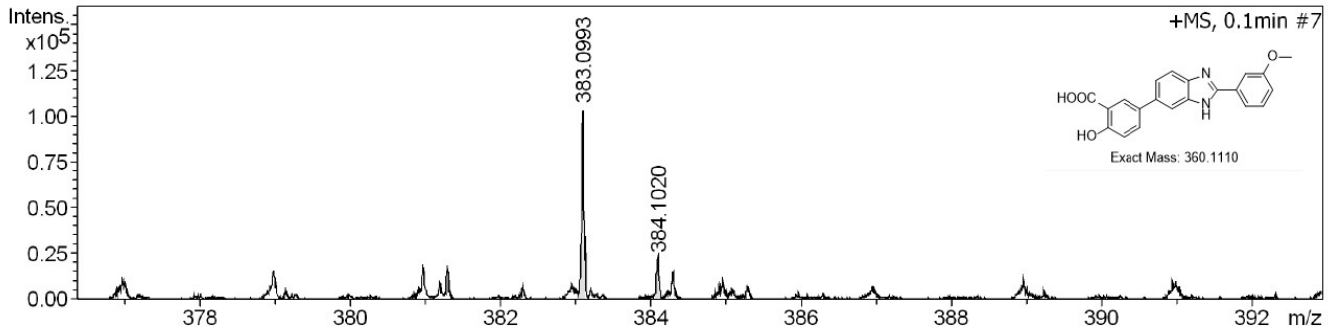
^{13}C-NMR spectrum for compound **5d**.



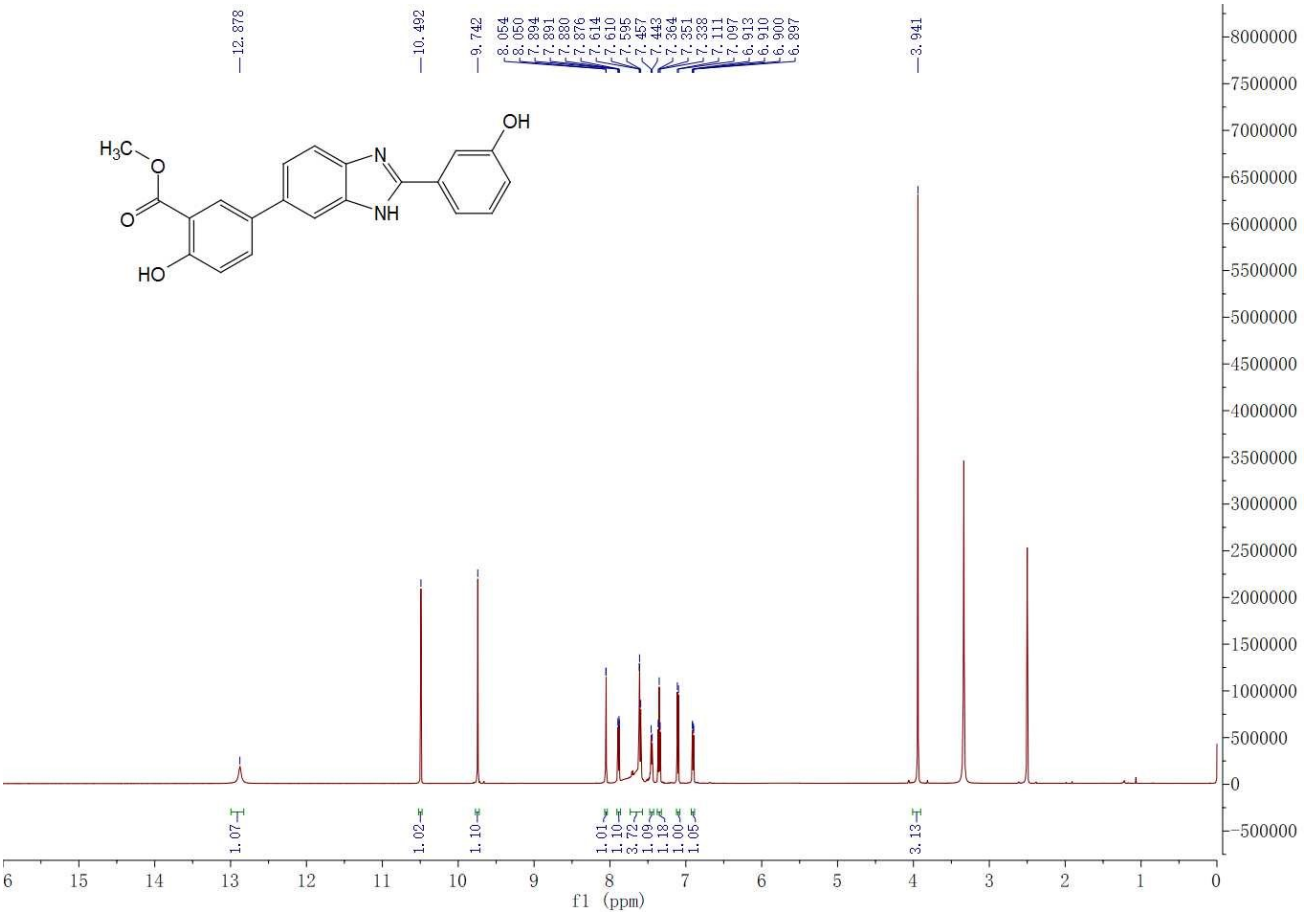
MS (ESI) for compound **5d**.



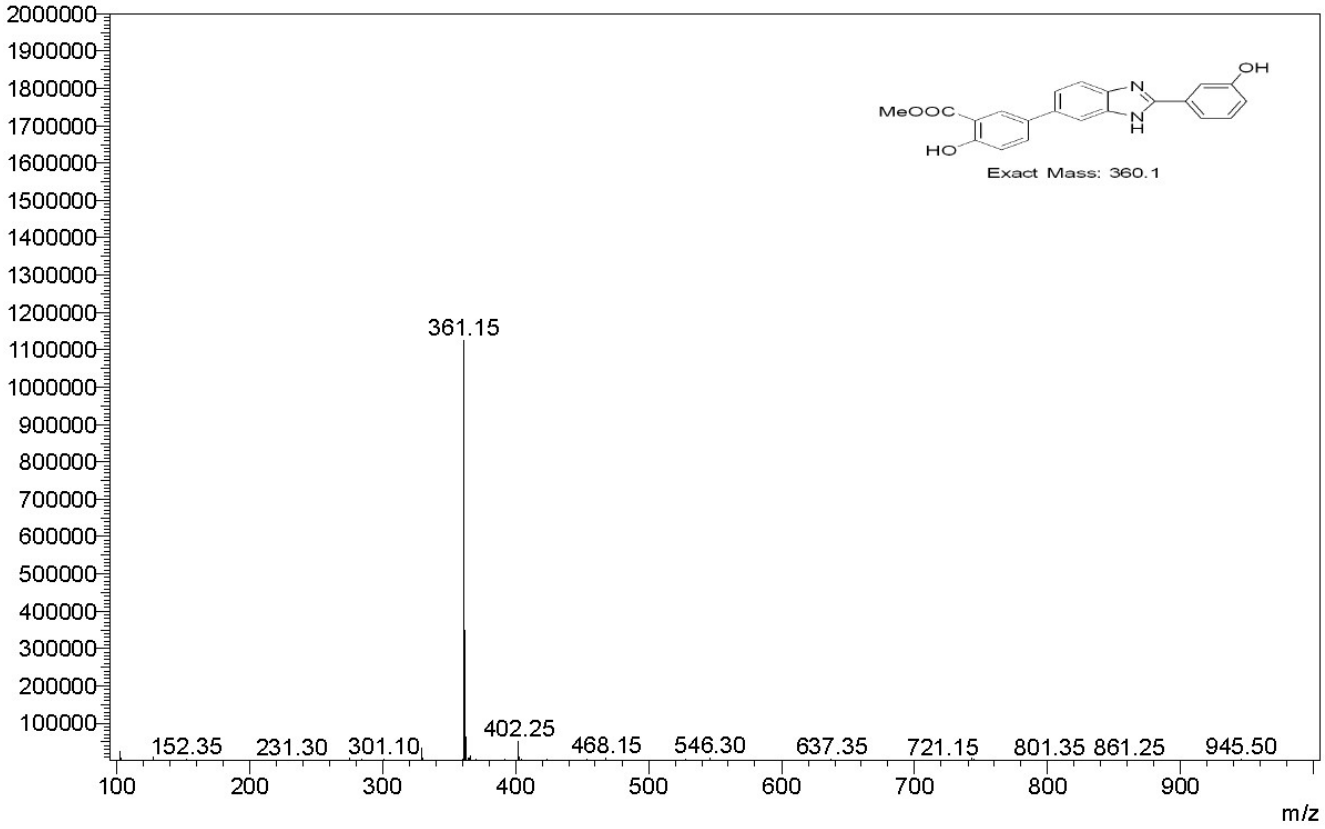
HRMS (ESI) for compound **5d**.



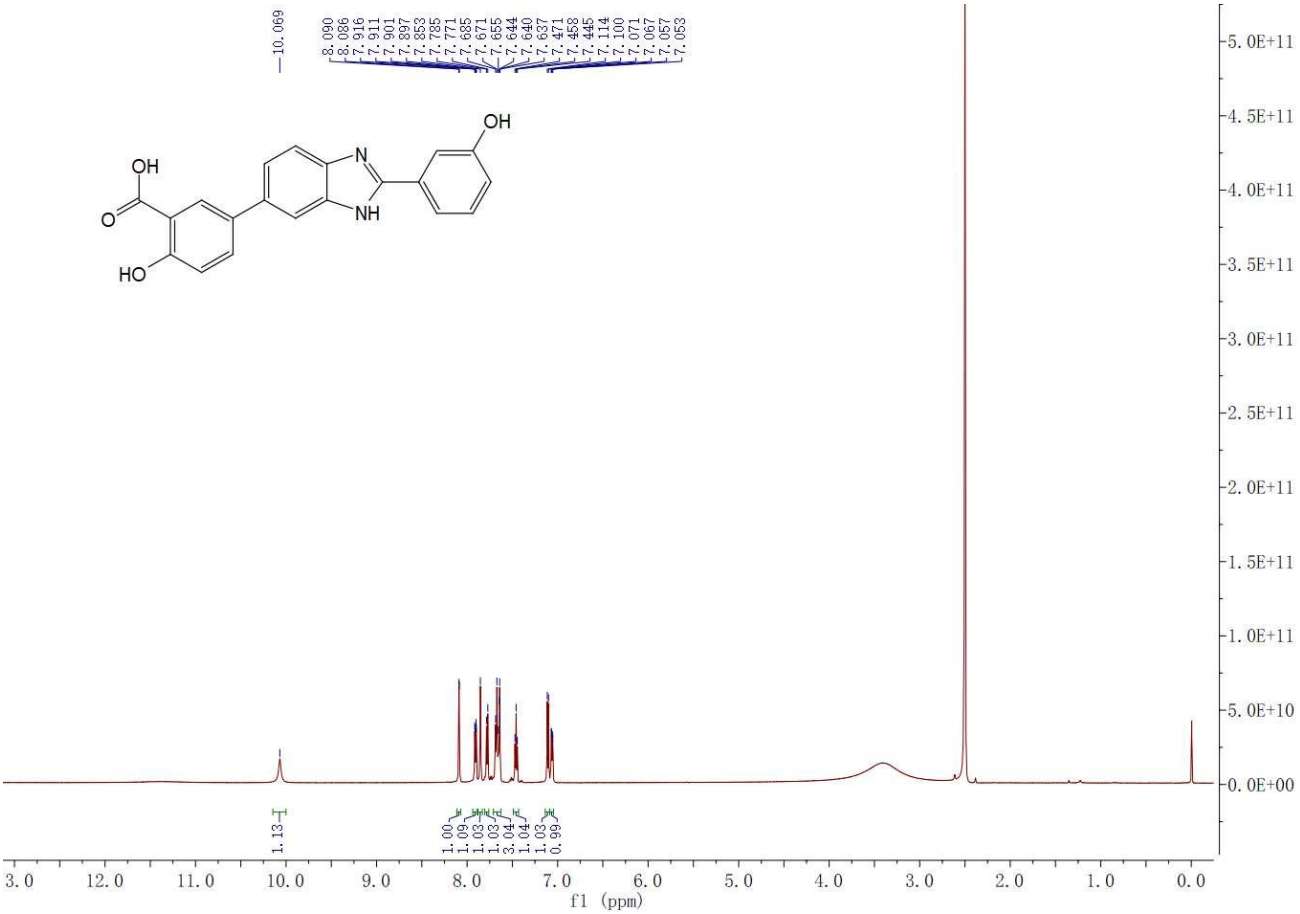
^{1}H-NMR spectrum for compound **4e**.



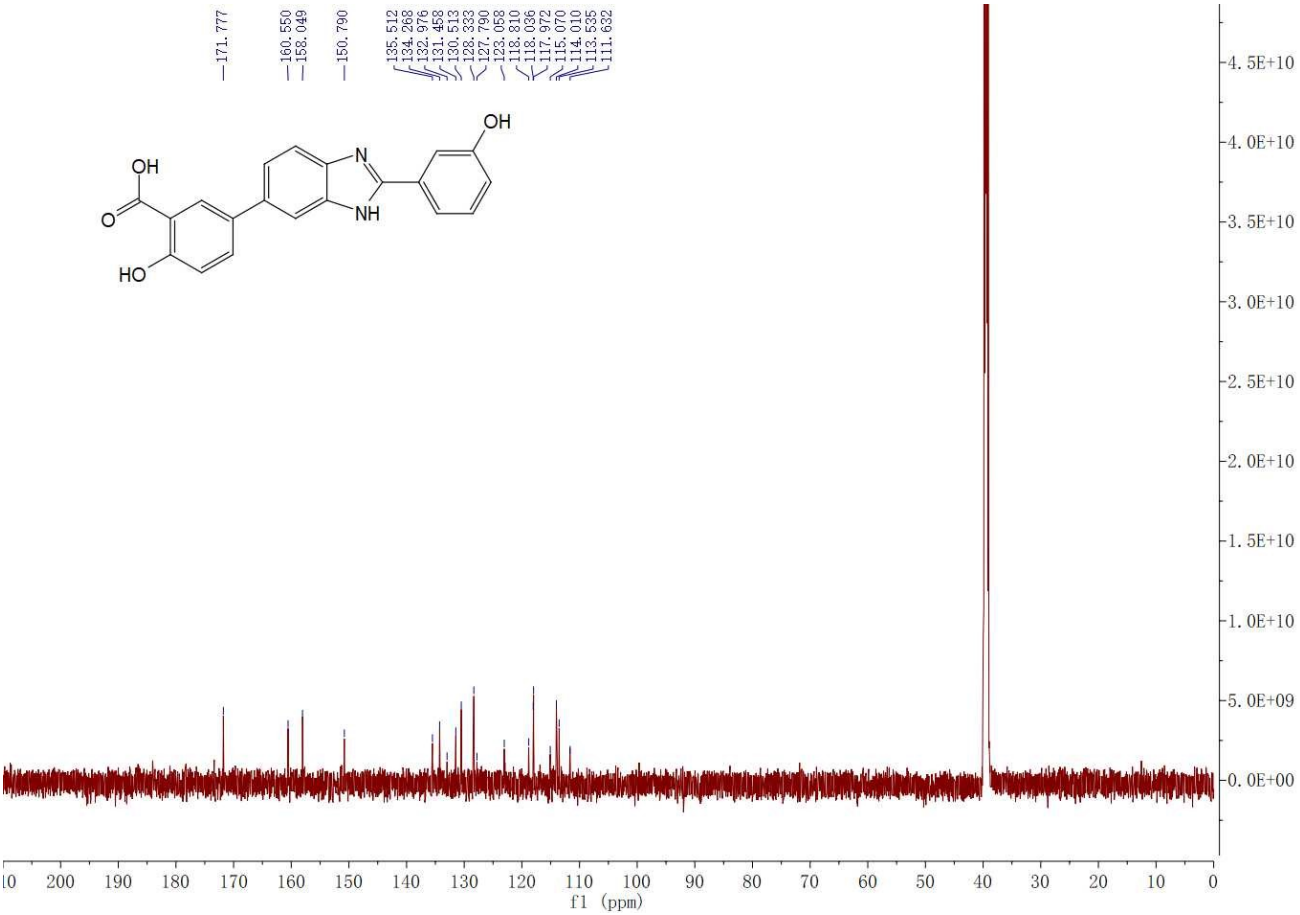
MS (ESI) for compound **4e**.



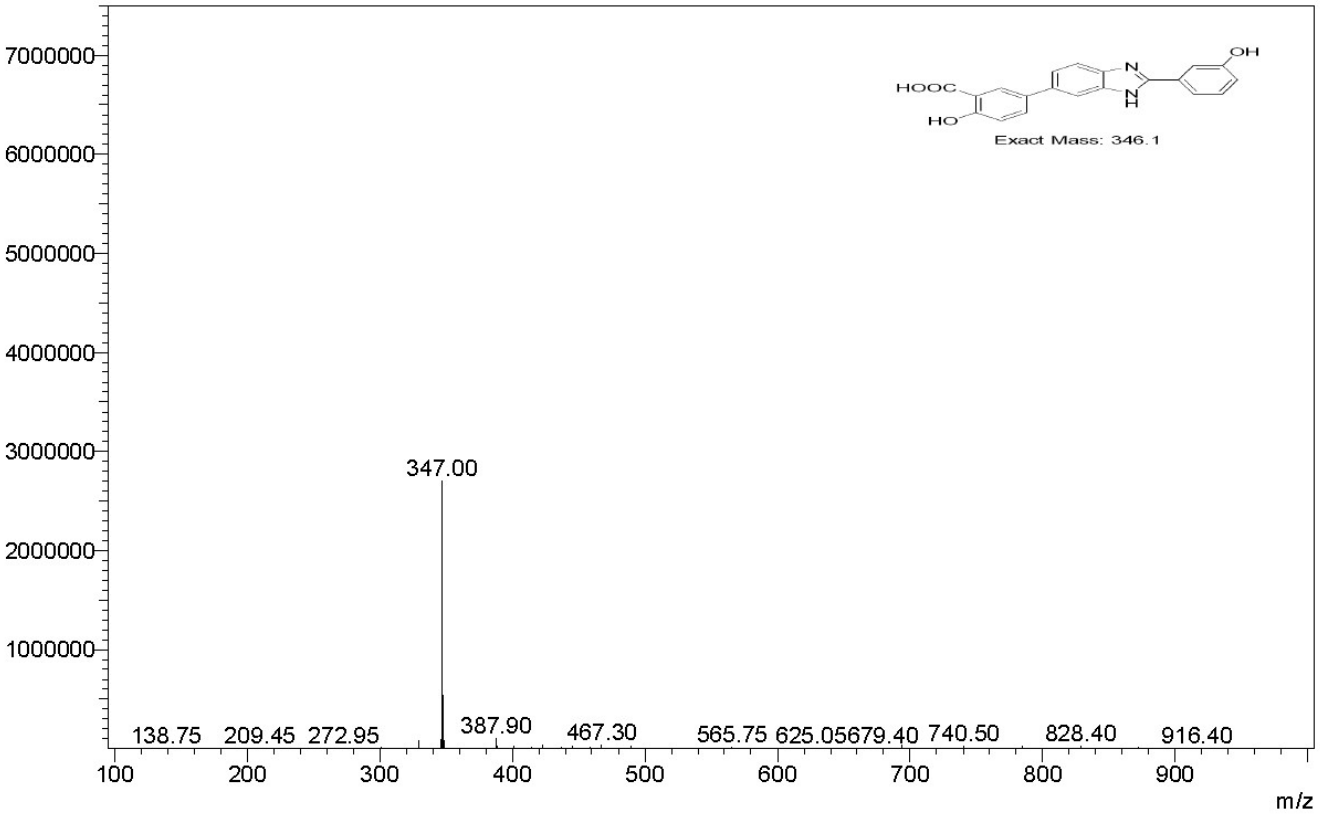
[1]H-NMR spectrum for compound **5e**.



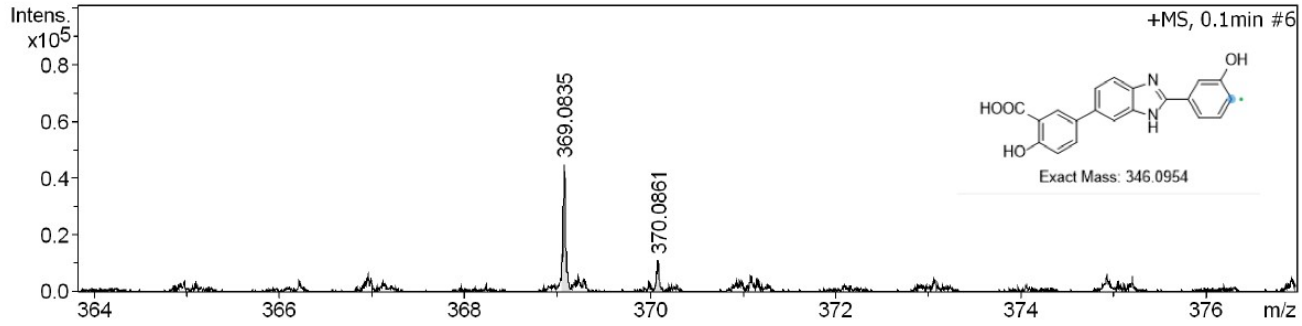
^{13}C-NMR spectrum for compound **5e**.



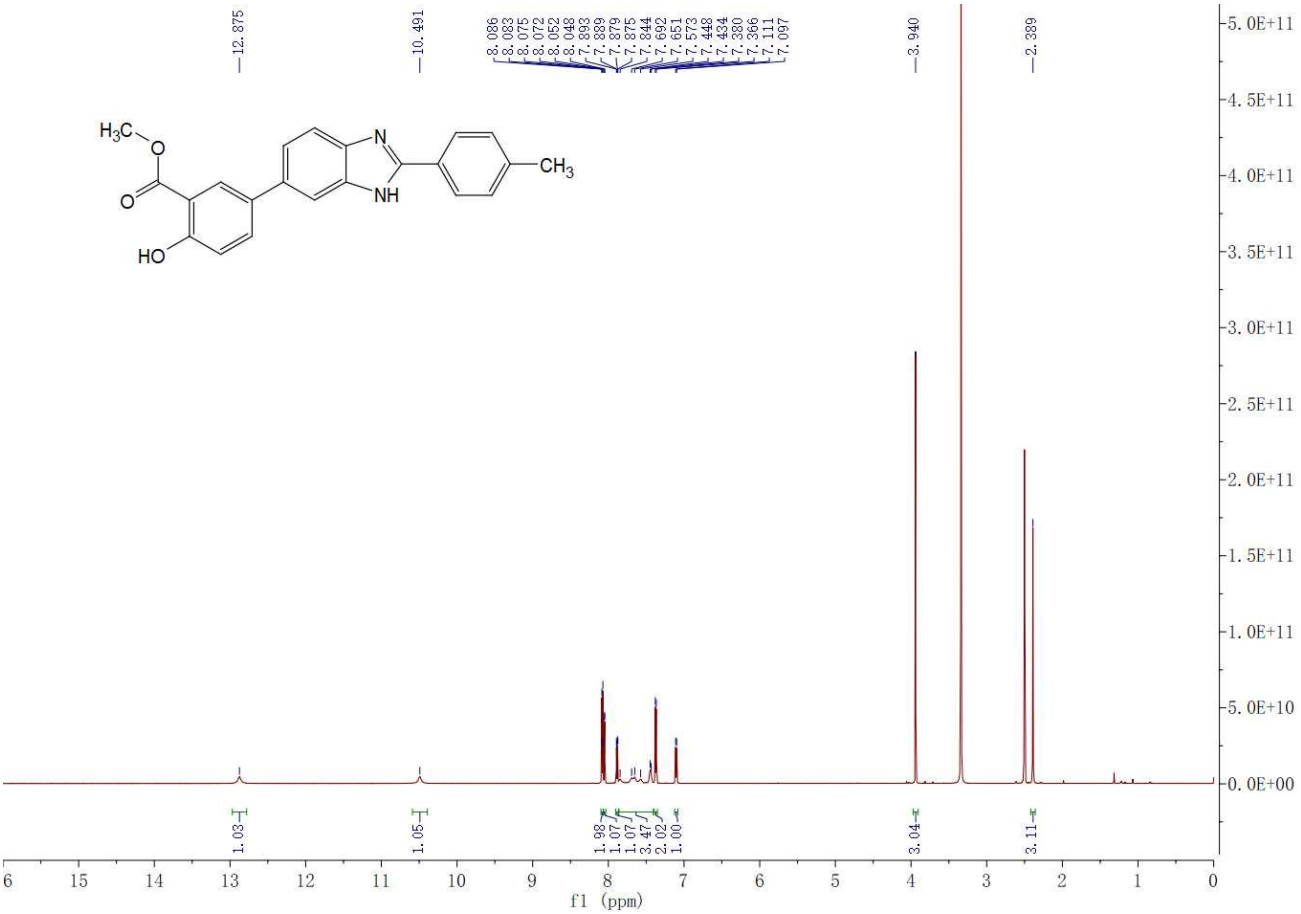
MS (ESI) for compound **5e**.



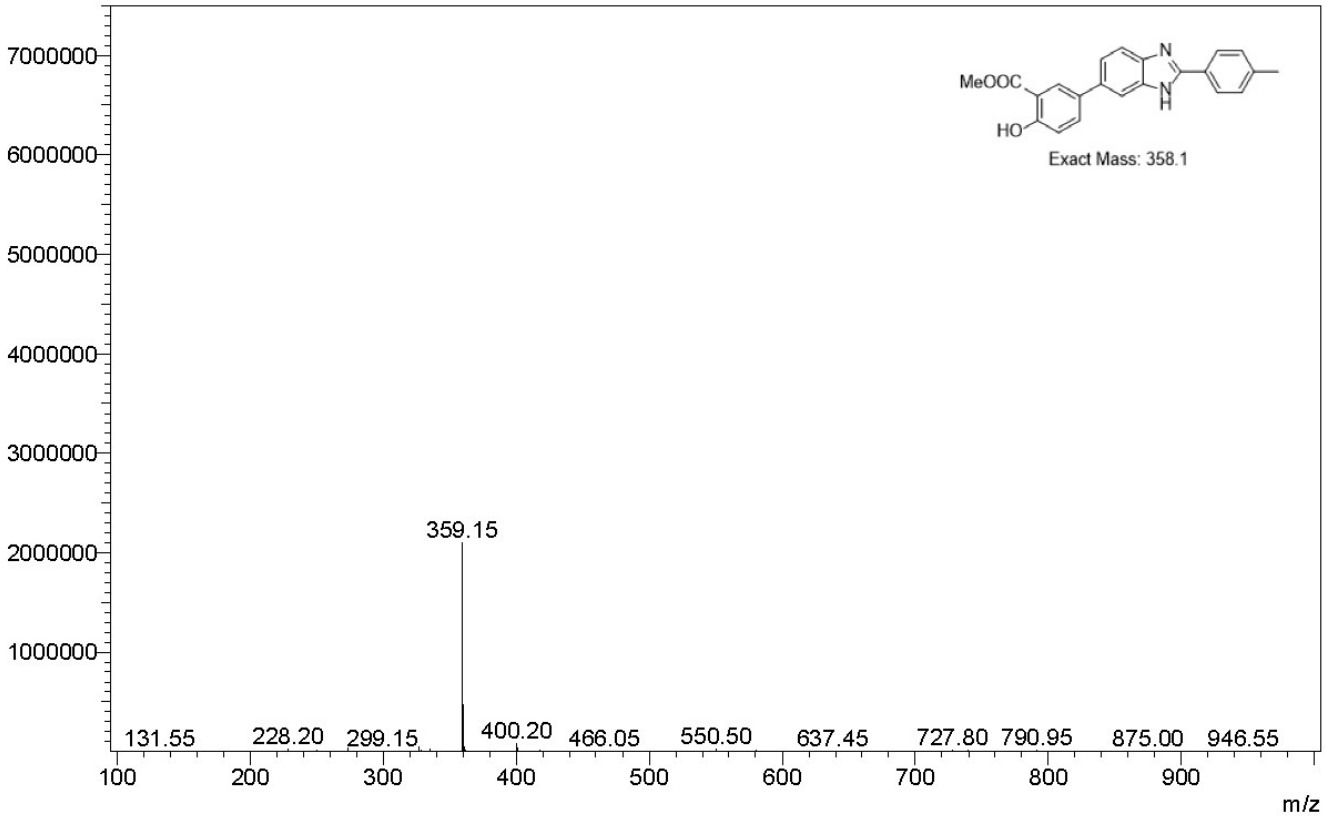
HRMS (ESI) for compound **5e**.



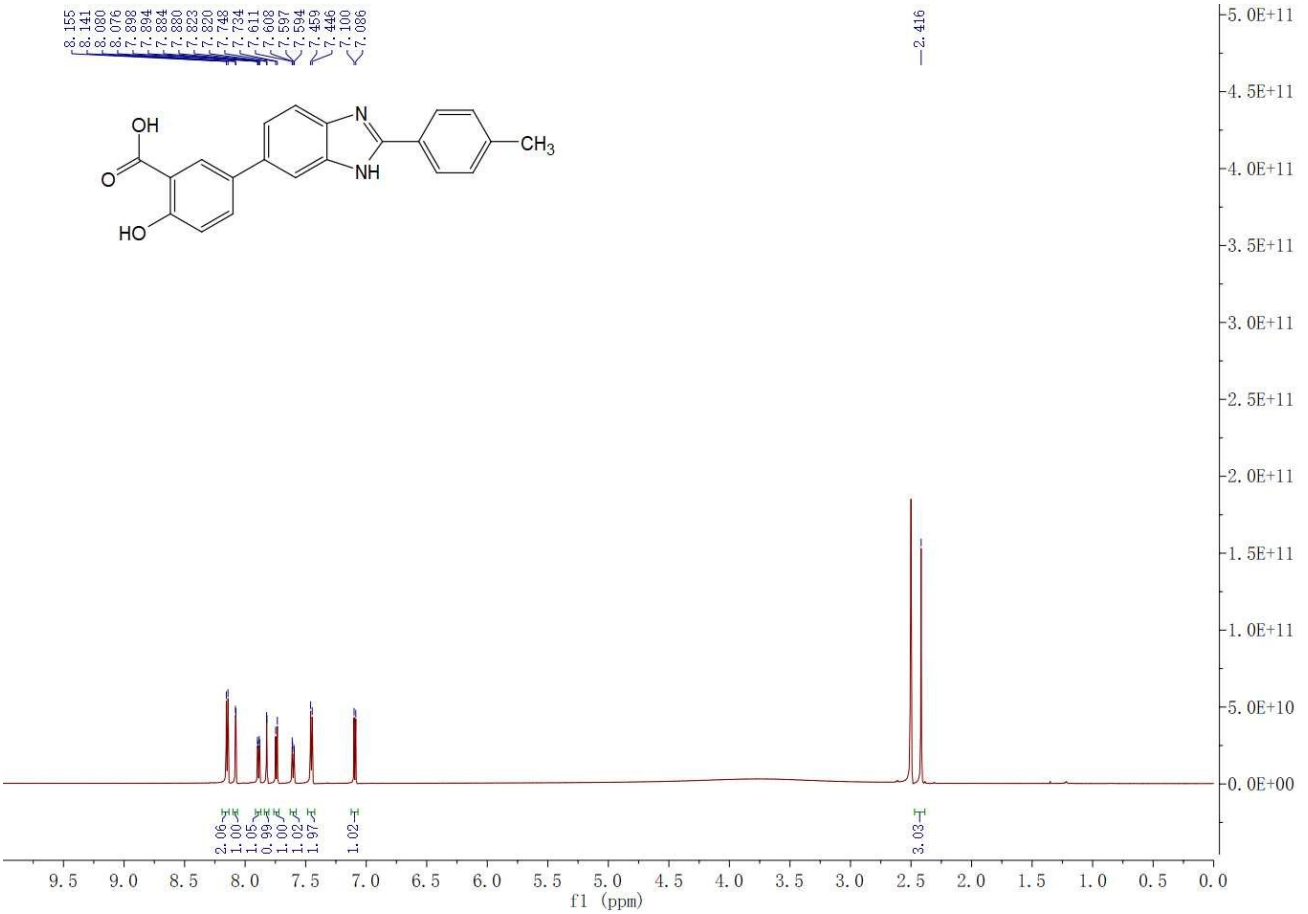
^{1}H-NMR spectrum for compound **4f**.



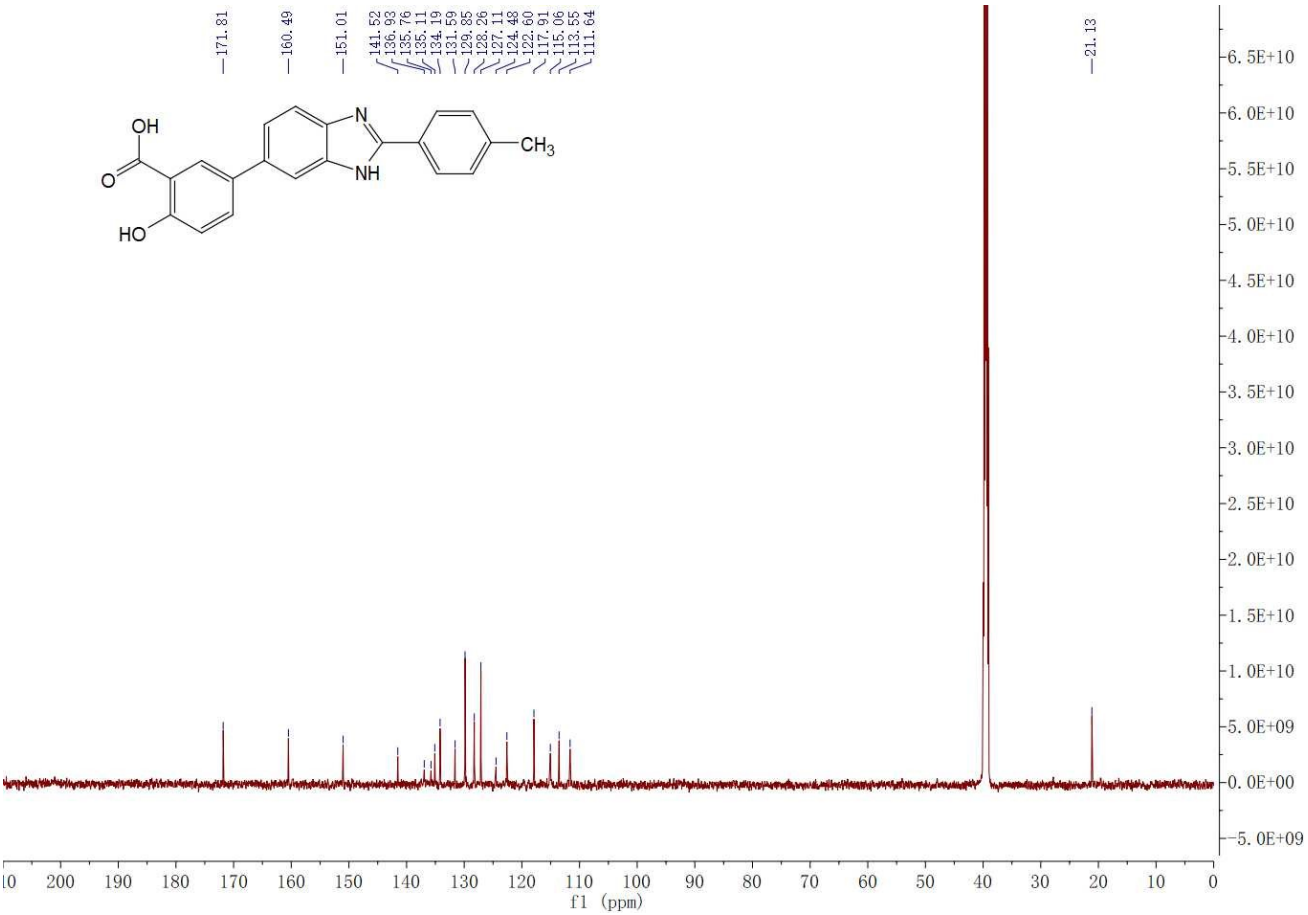
MS (ESI) for compound **4f**.



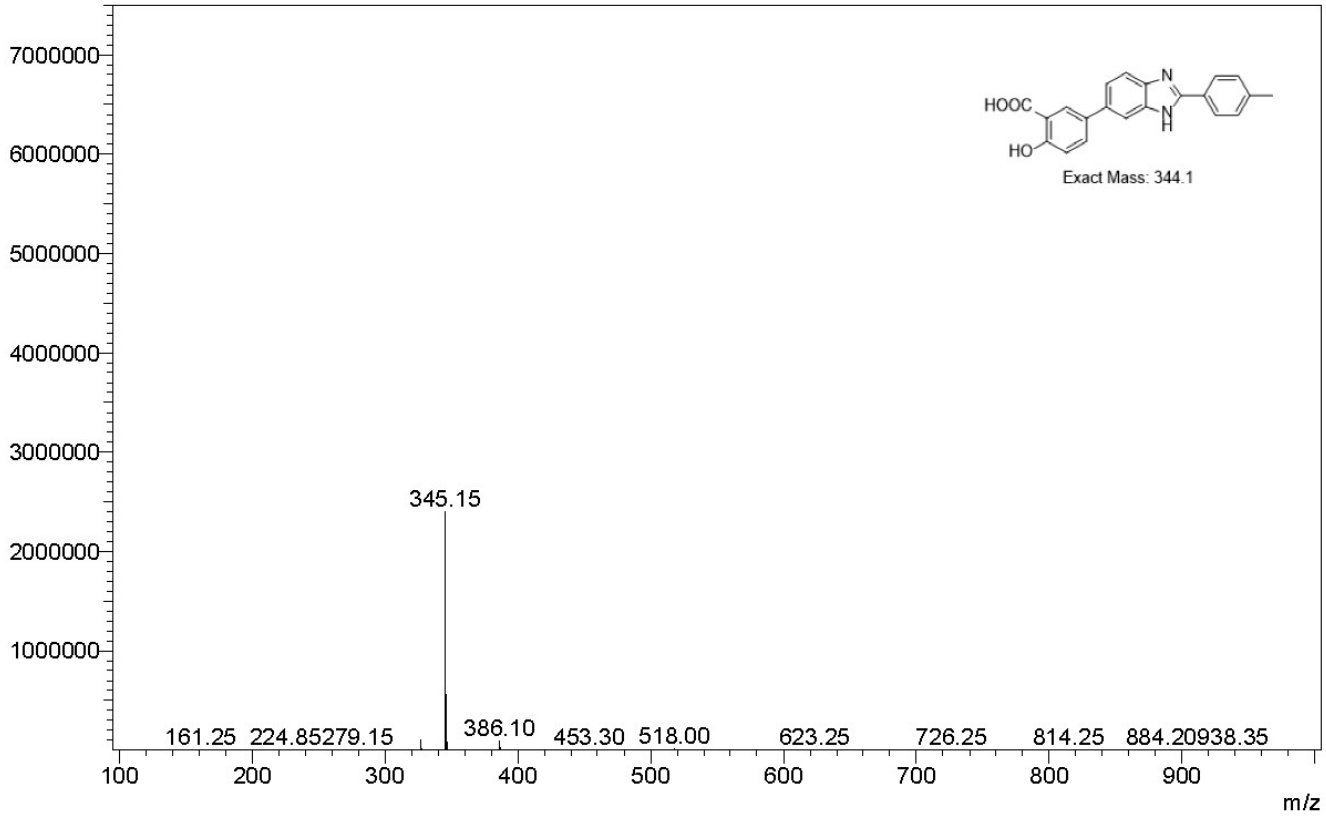
[1]H-NMR spectrum for compound **5f**.



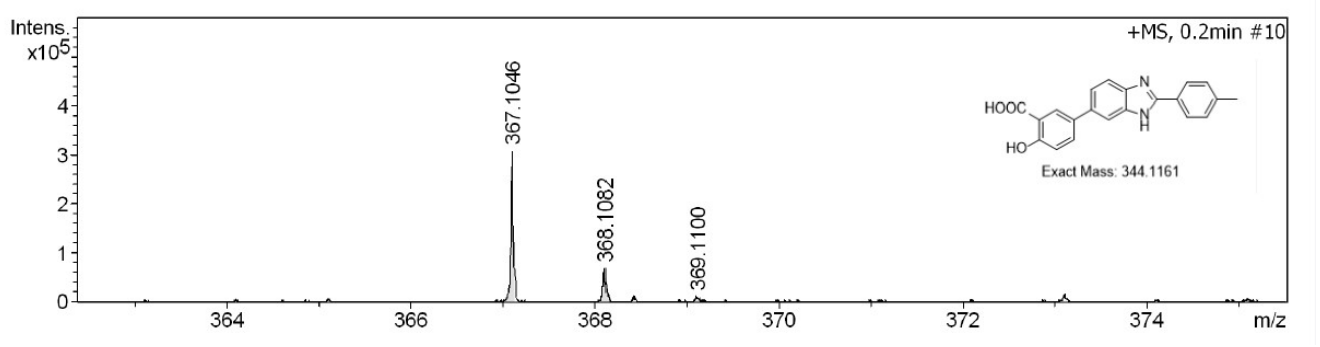
^{13}C-NMR spectrum for compound **5f**.



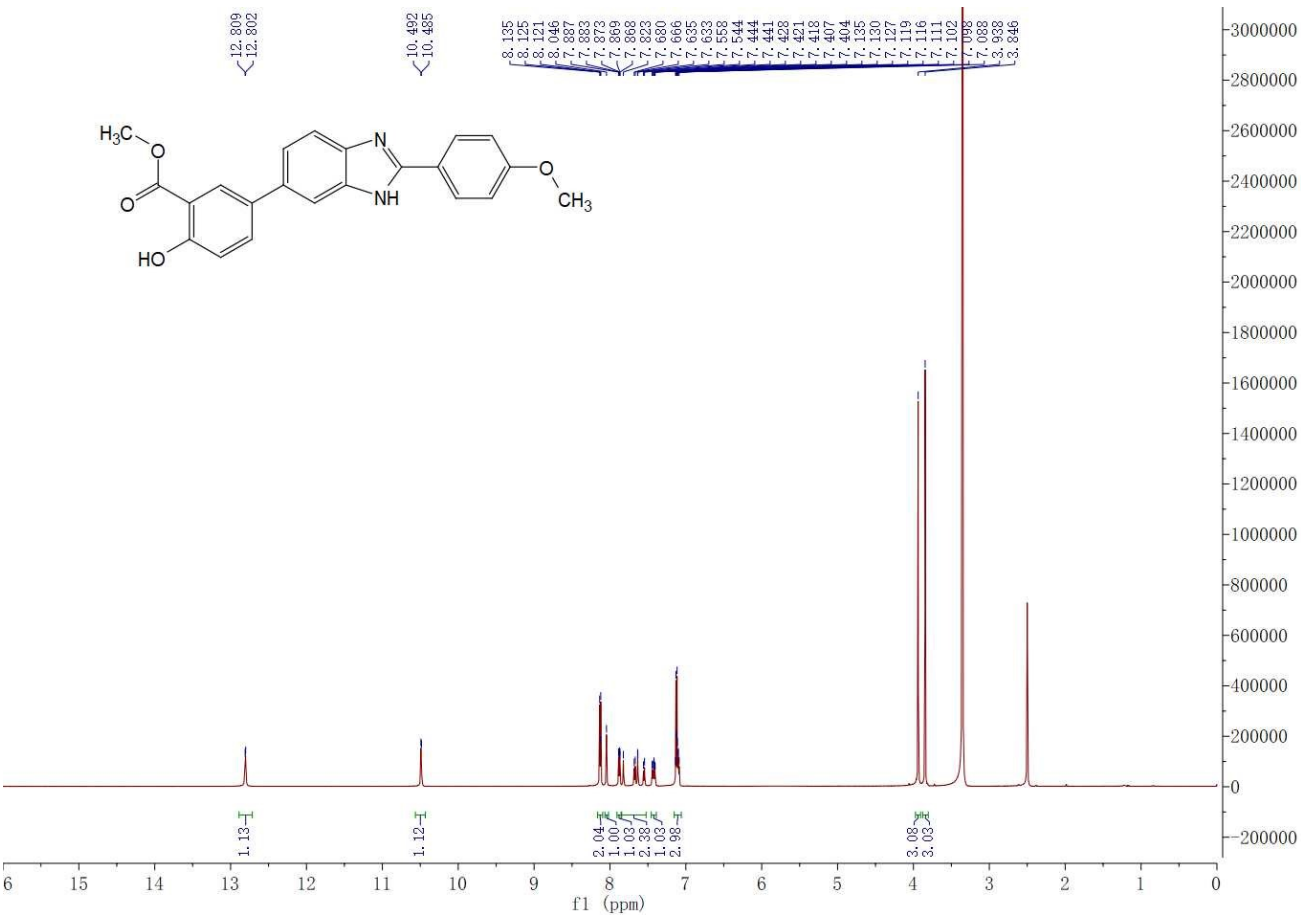
MS (ESI) for compound **5f**.



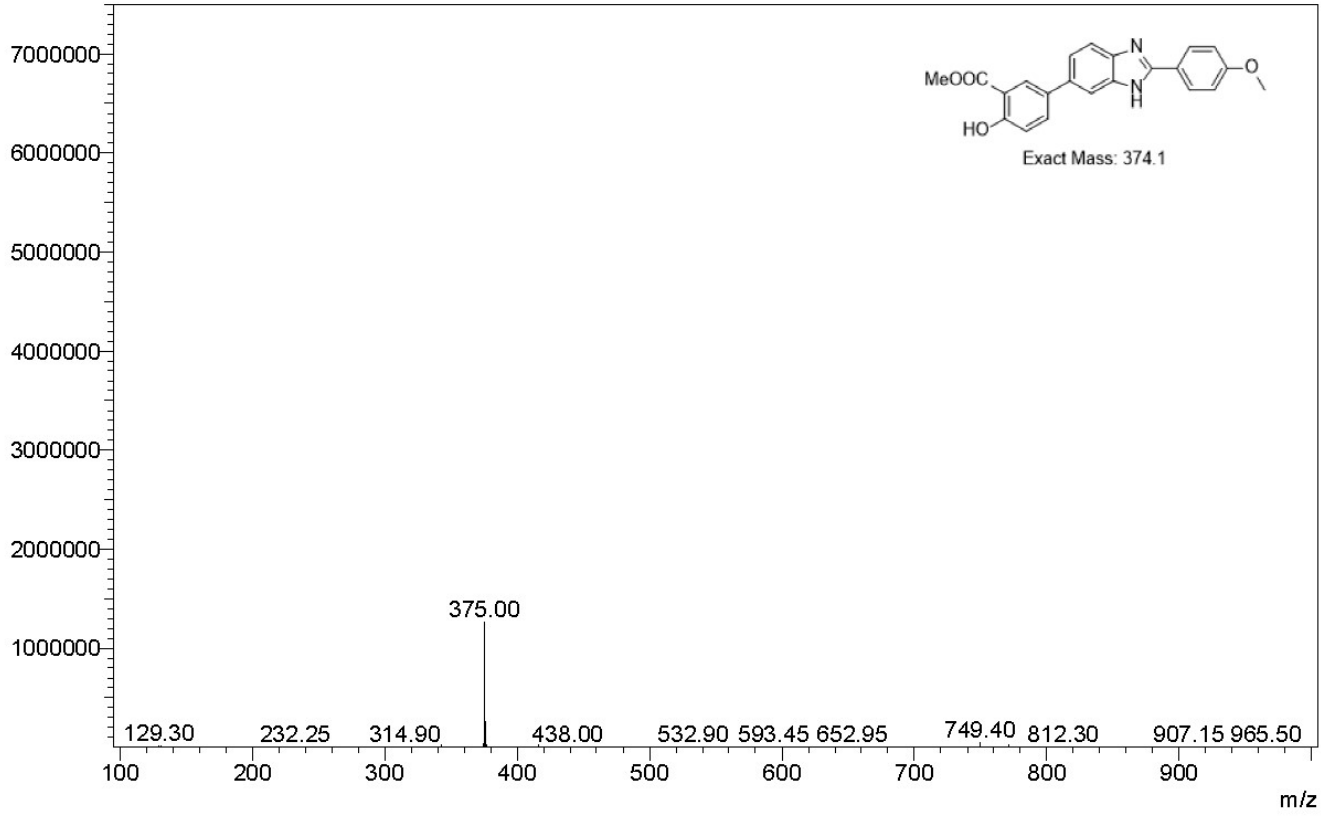
HRMS (ESI) for compound **5f**.



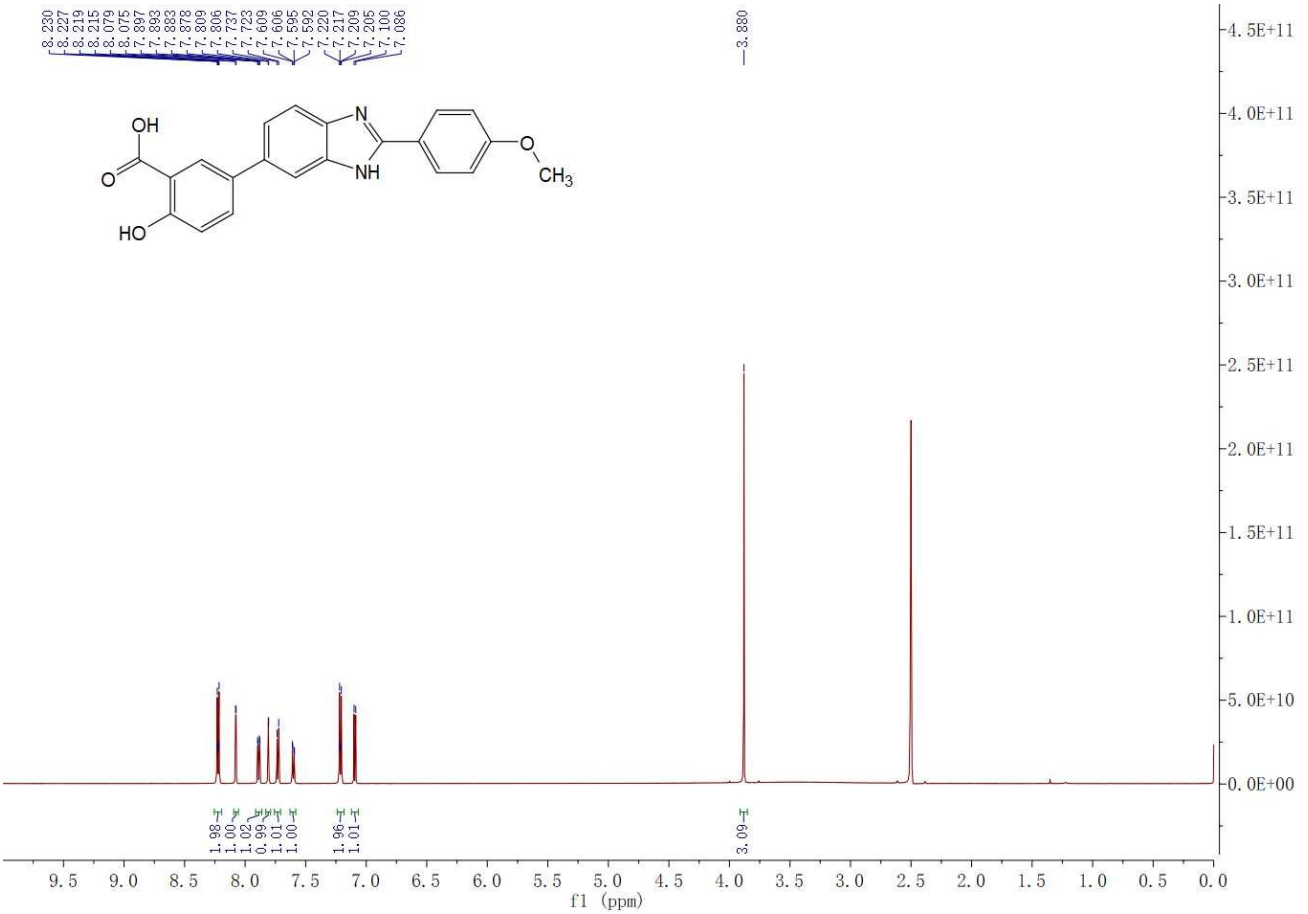
^{1}H-NMR spectrum for compound **4g**.



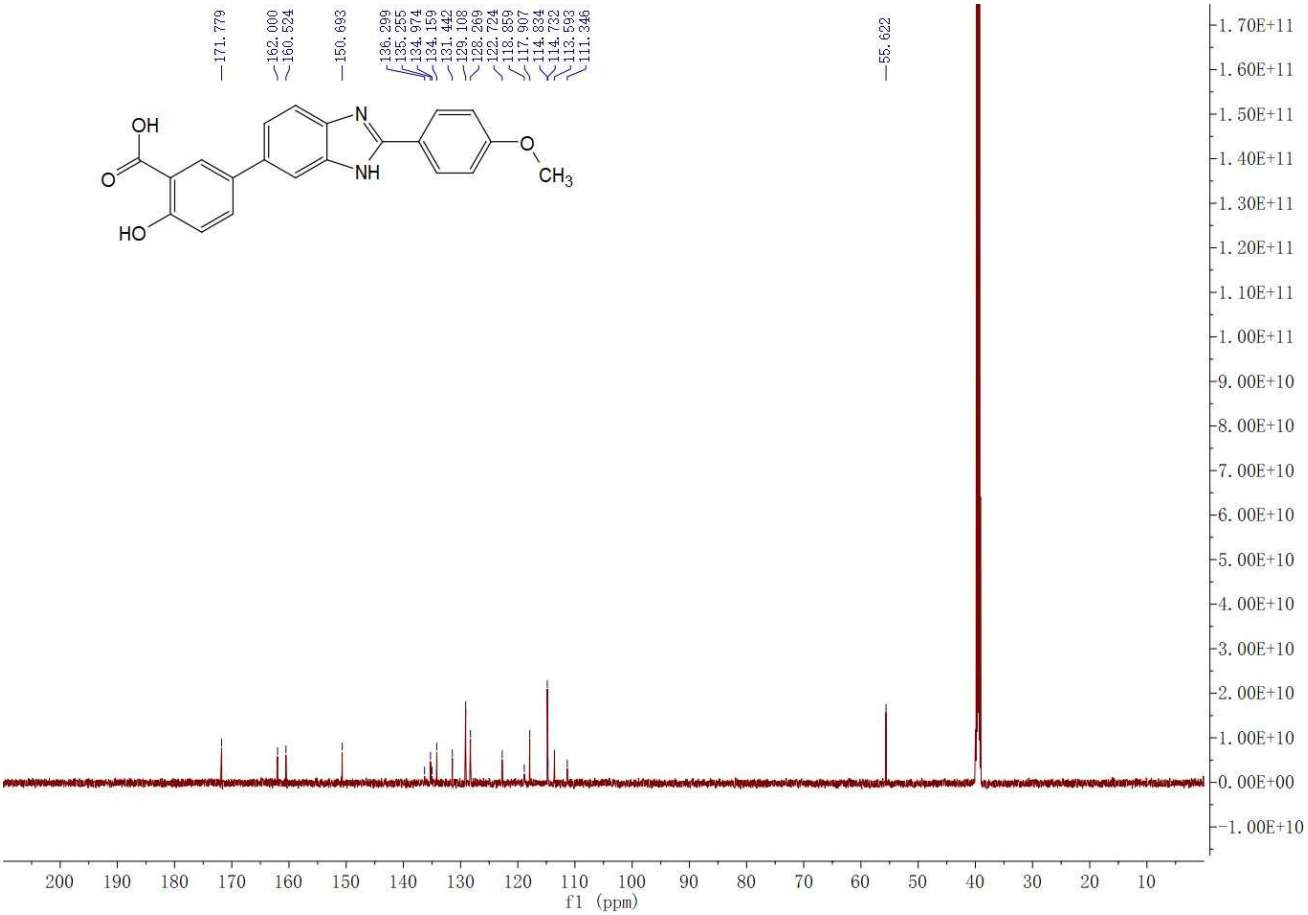
MS (ESI) for compound **4g**.



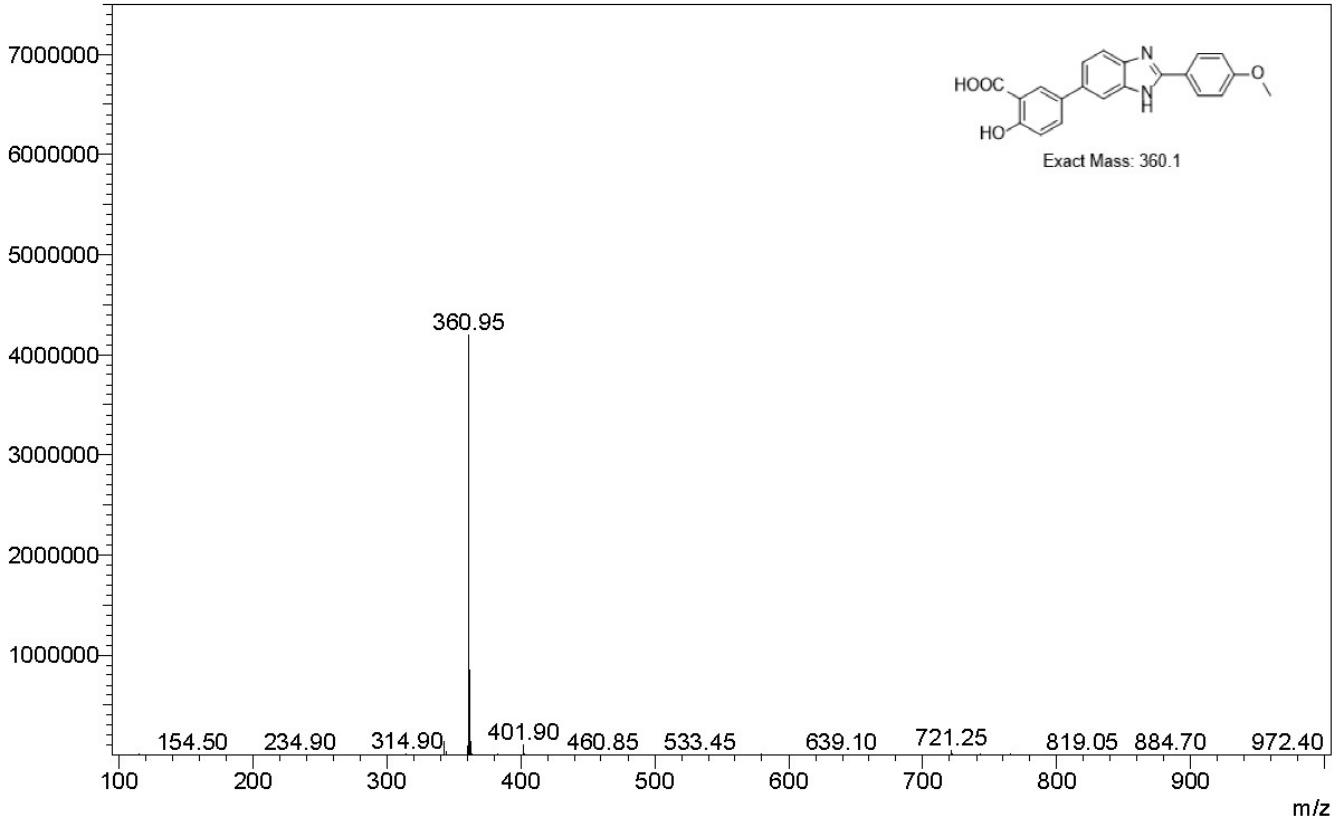
[1]H-NMR spectrum for compound **5g**.



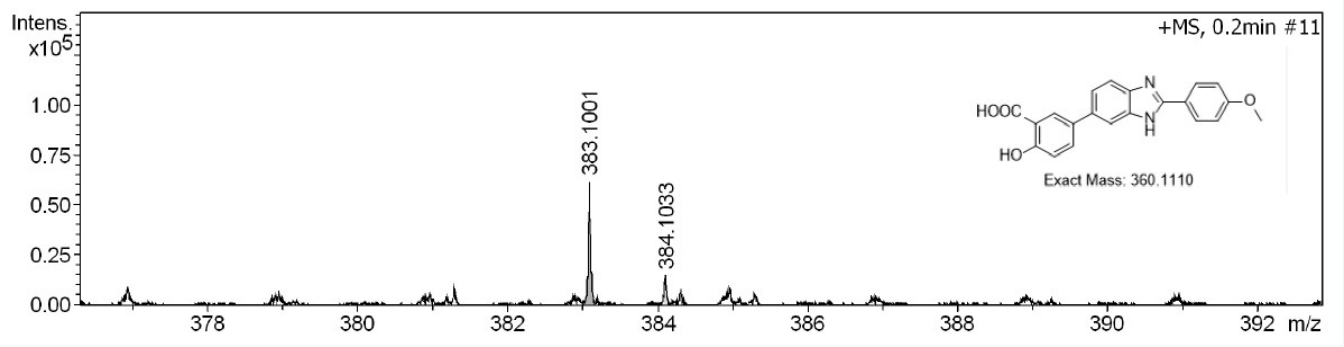
^{13}C-NMR spectrum for compound **5g**.



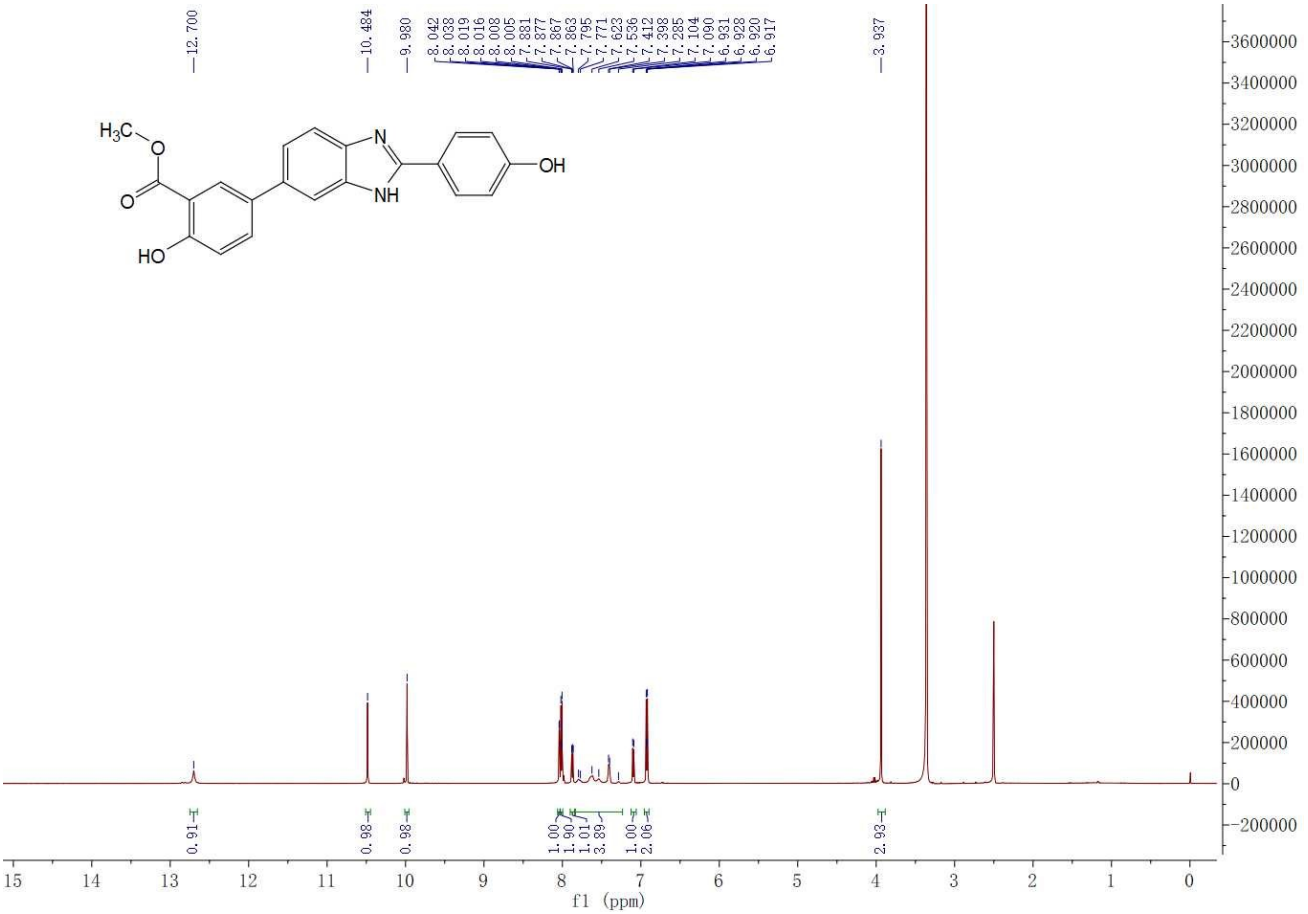
MS (ESI) for compound **5g**.



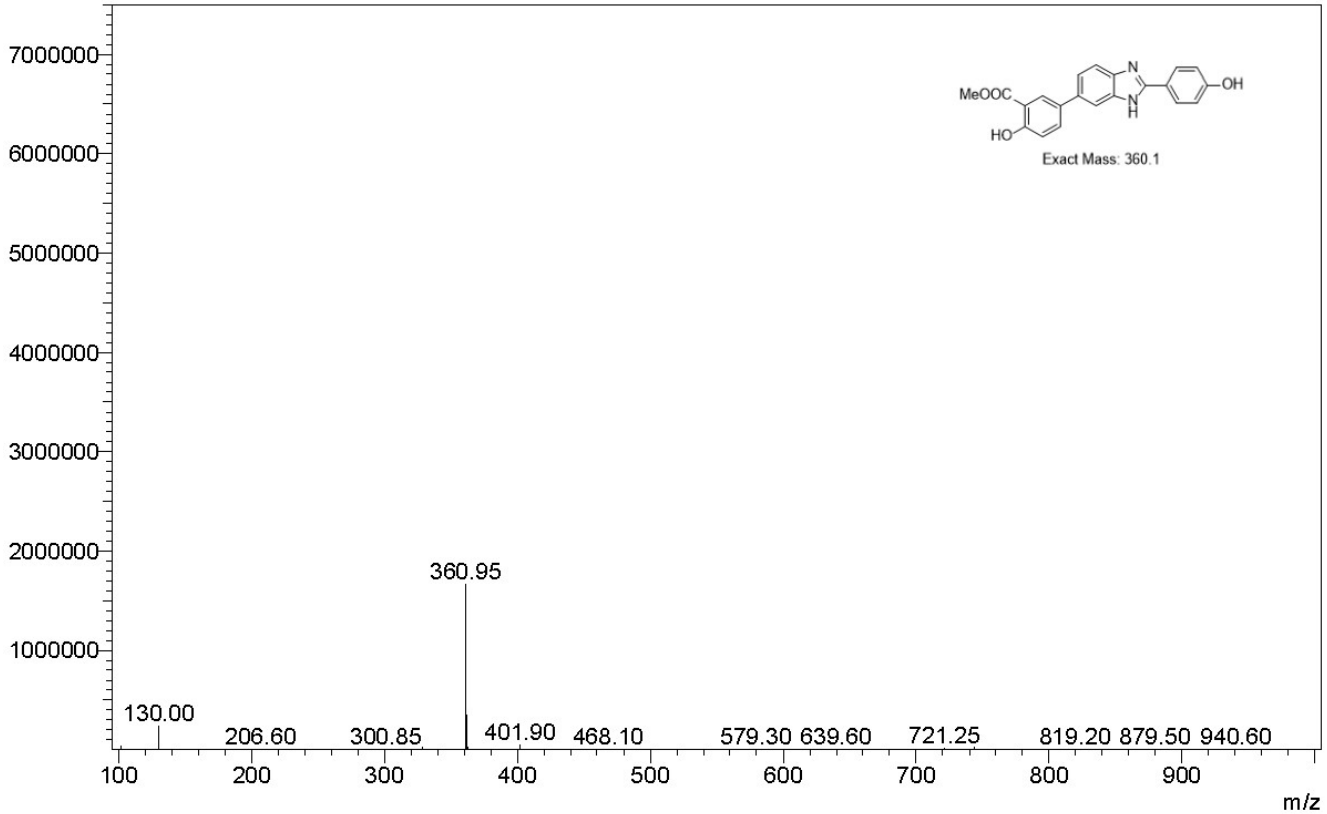
HRMS (ESI) for compound **5g**.



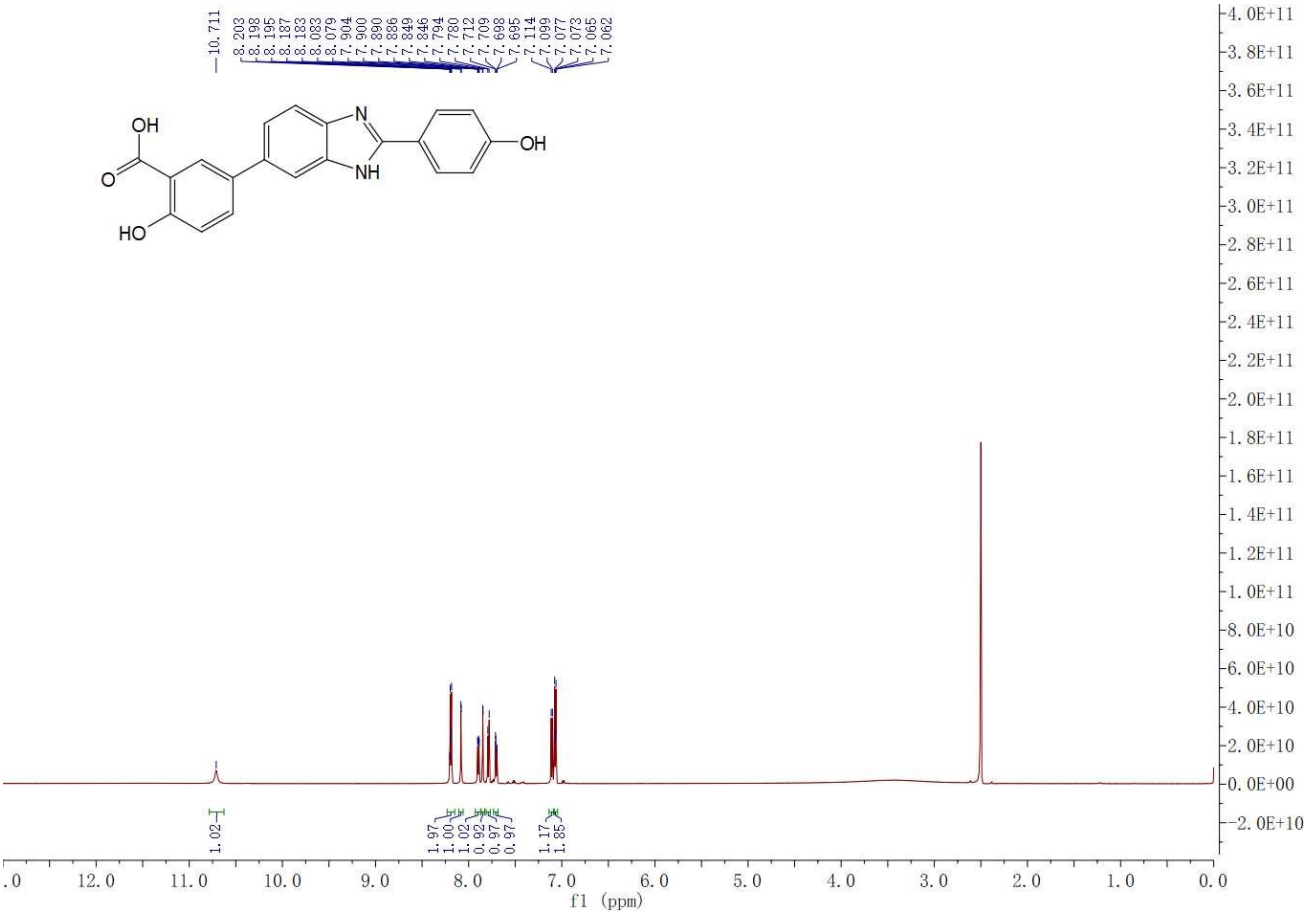
^{1}H-NMR spectrum for compound **4h**.



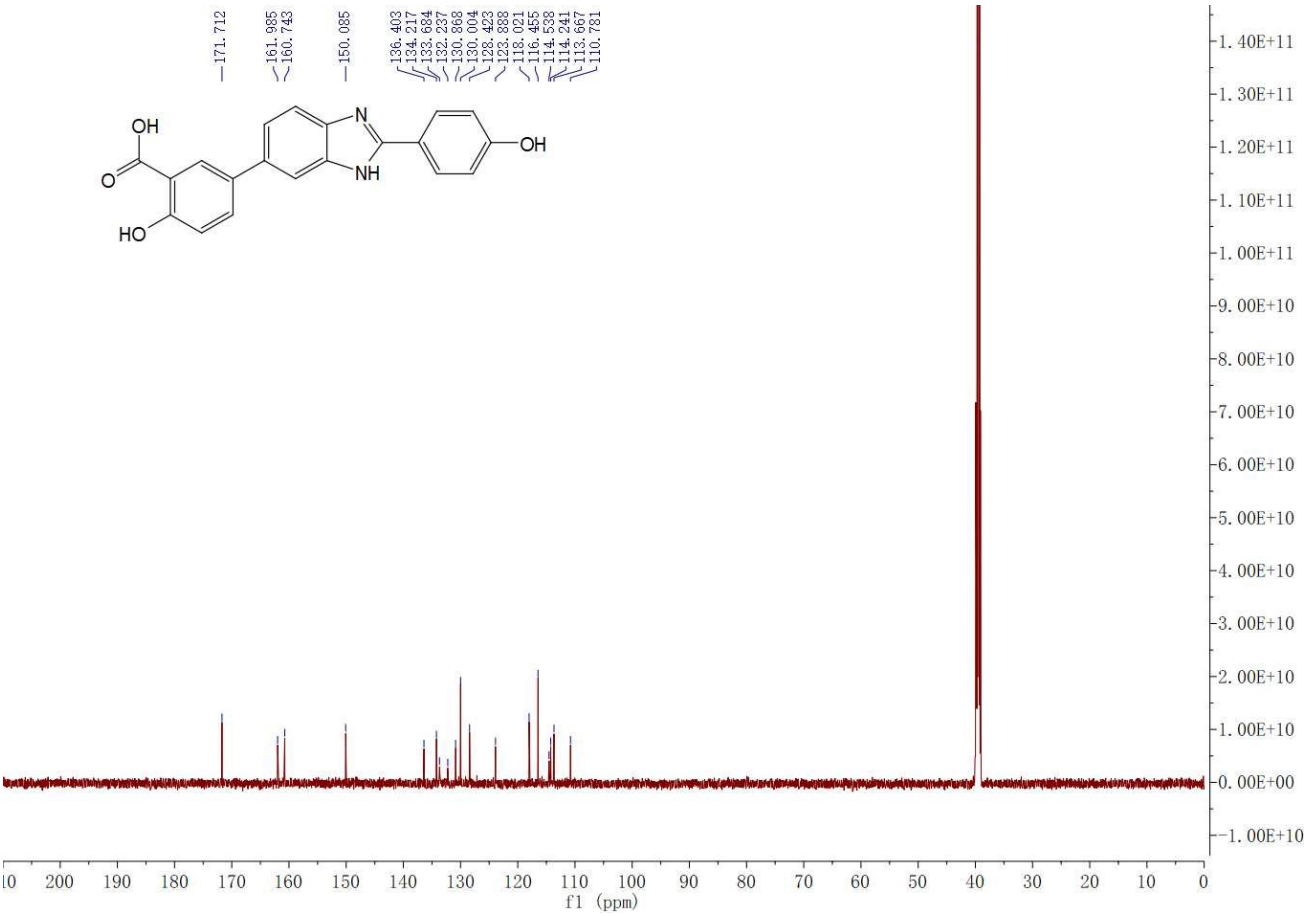
MS (ESI) for compound **4h**.



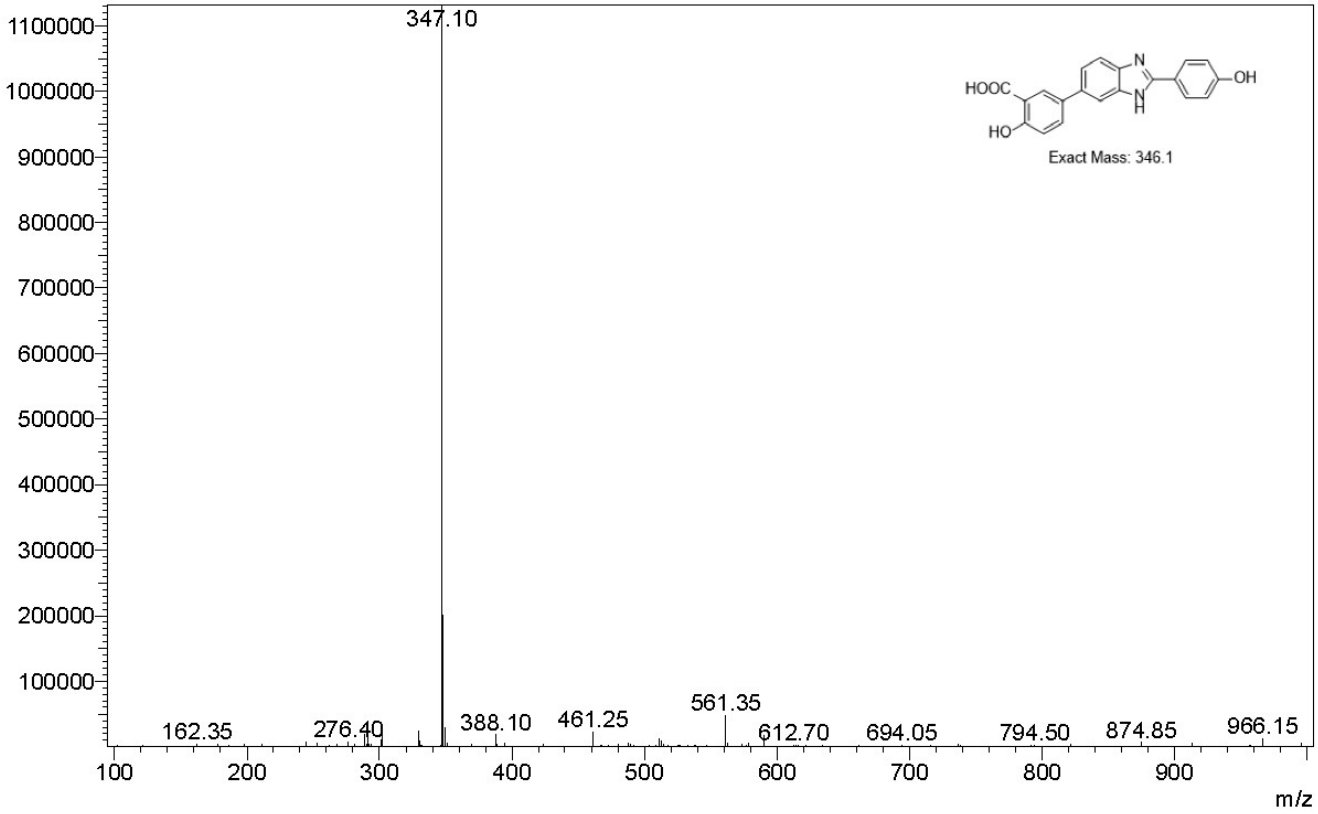
^{1}H-NMR spectrum for compound **5h**.



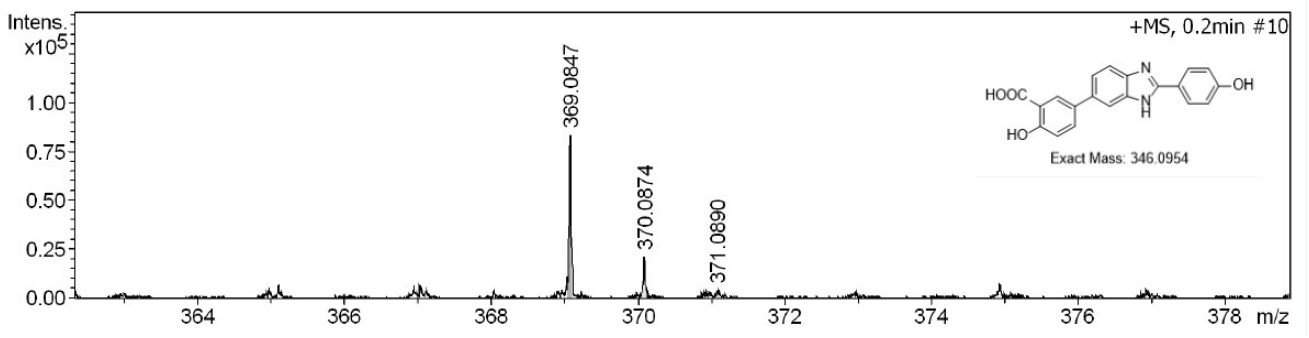
^{13}C-NMR spectrum for compound **5h**.



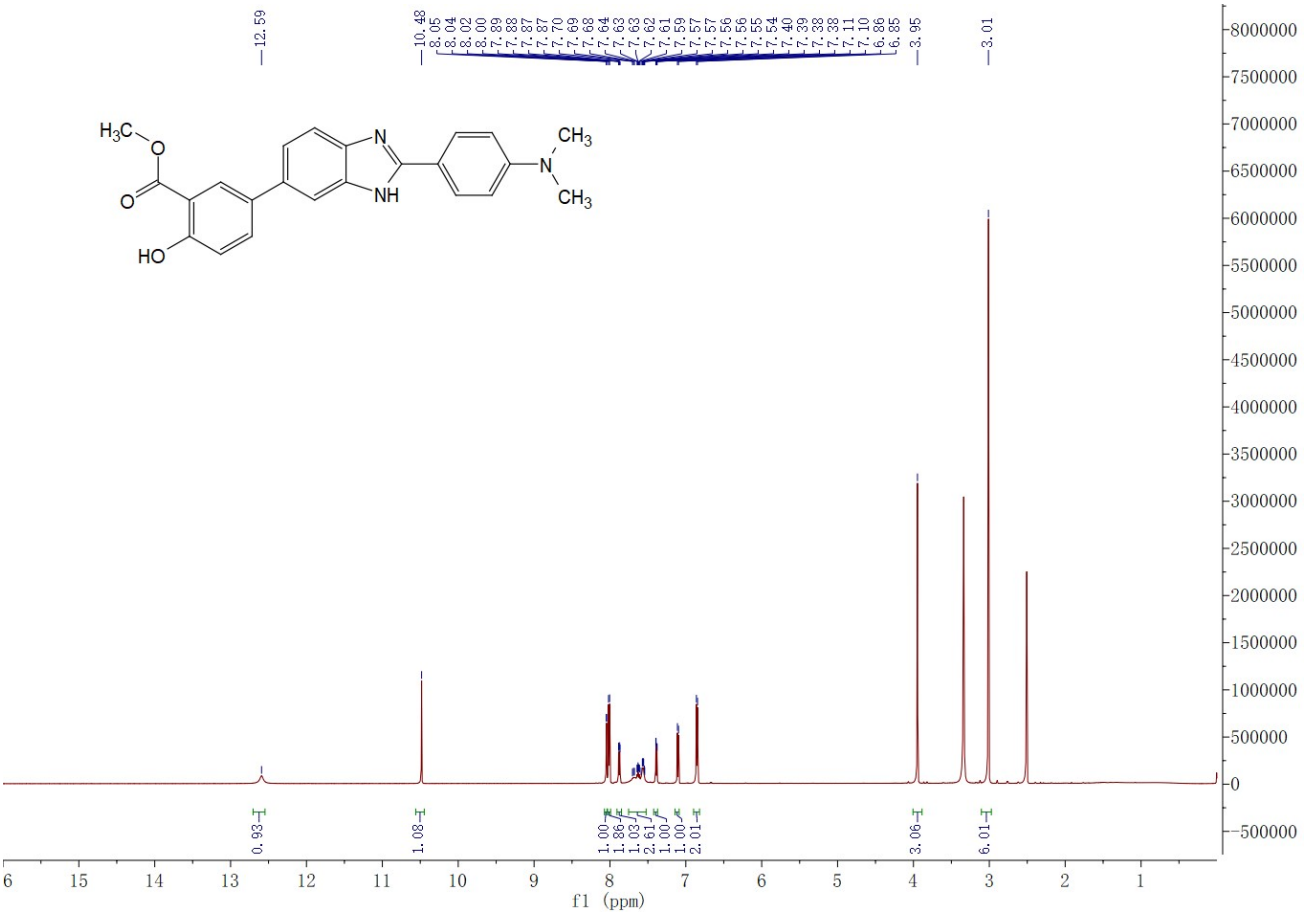
MS (ESI) for compound **5h**.



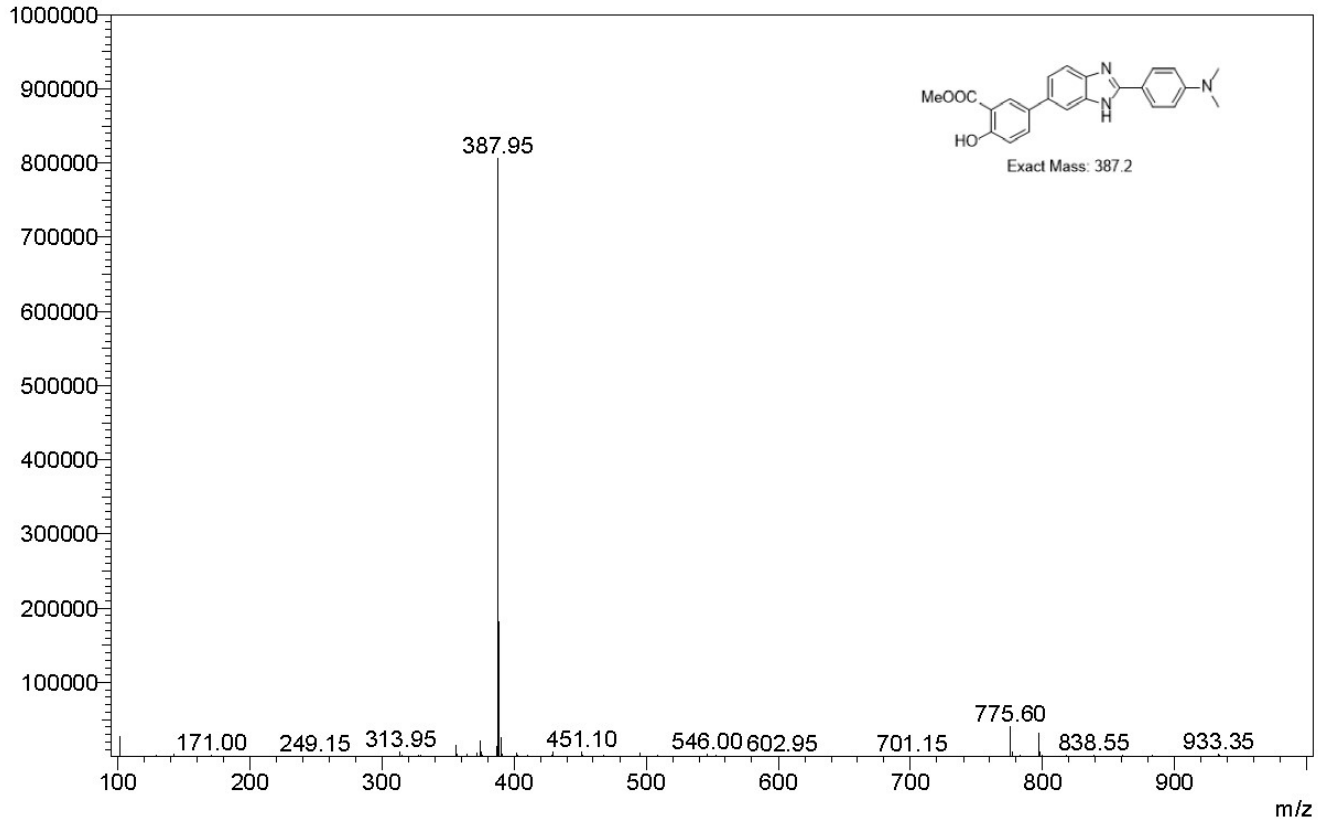
HRMS (ESI) for compound **5h**.



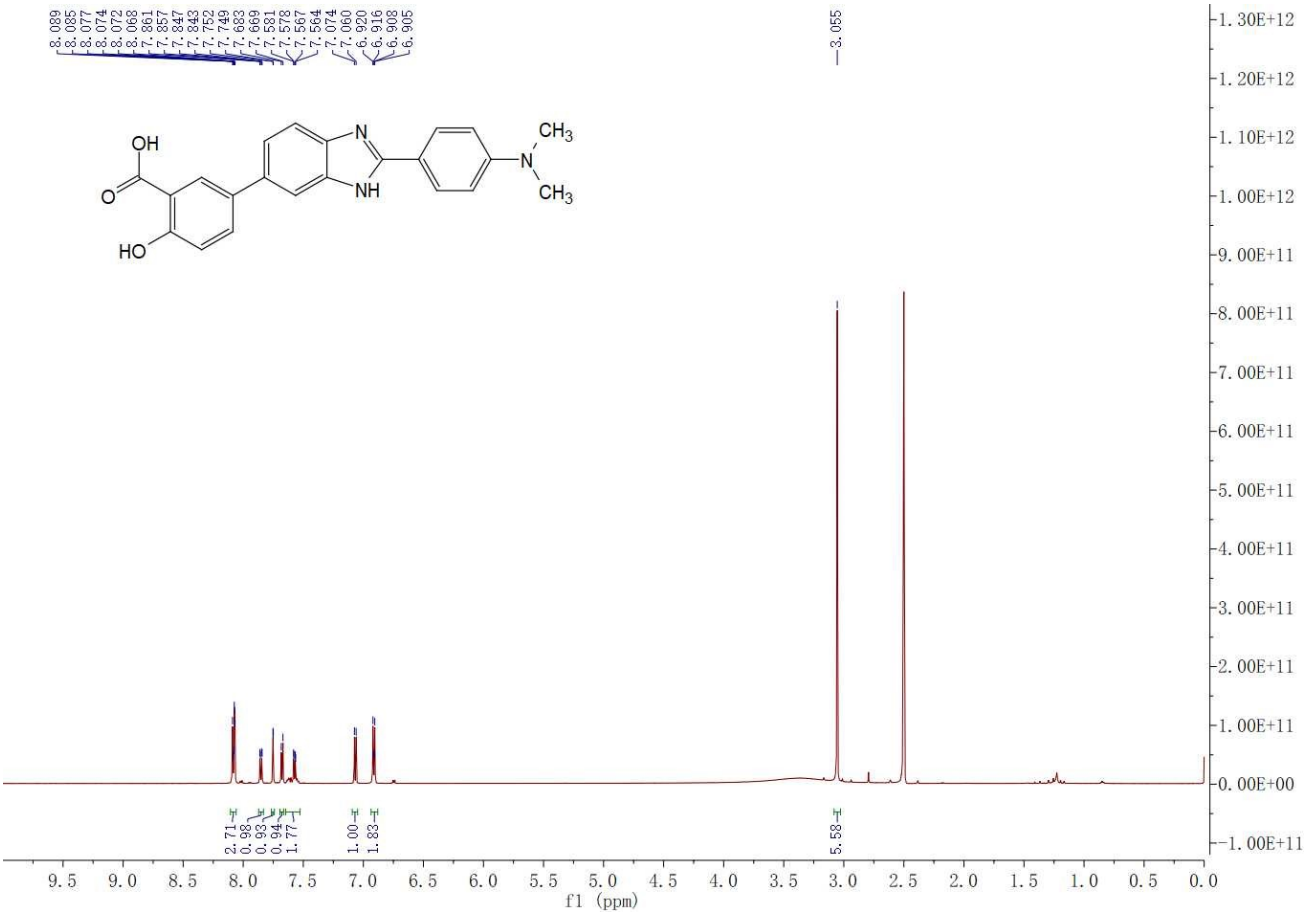
^{1}H-NMR spectrum for compound **4i**.



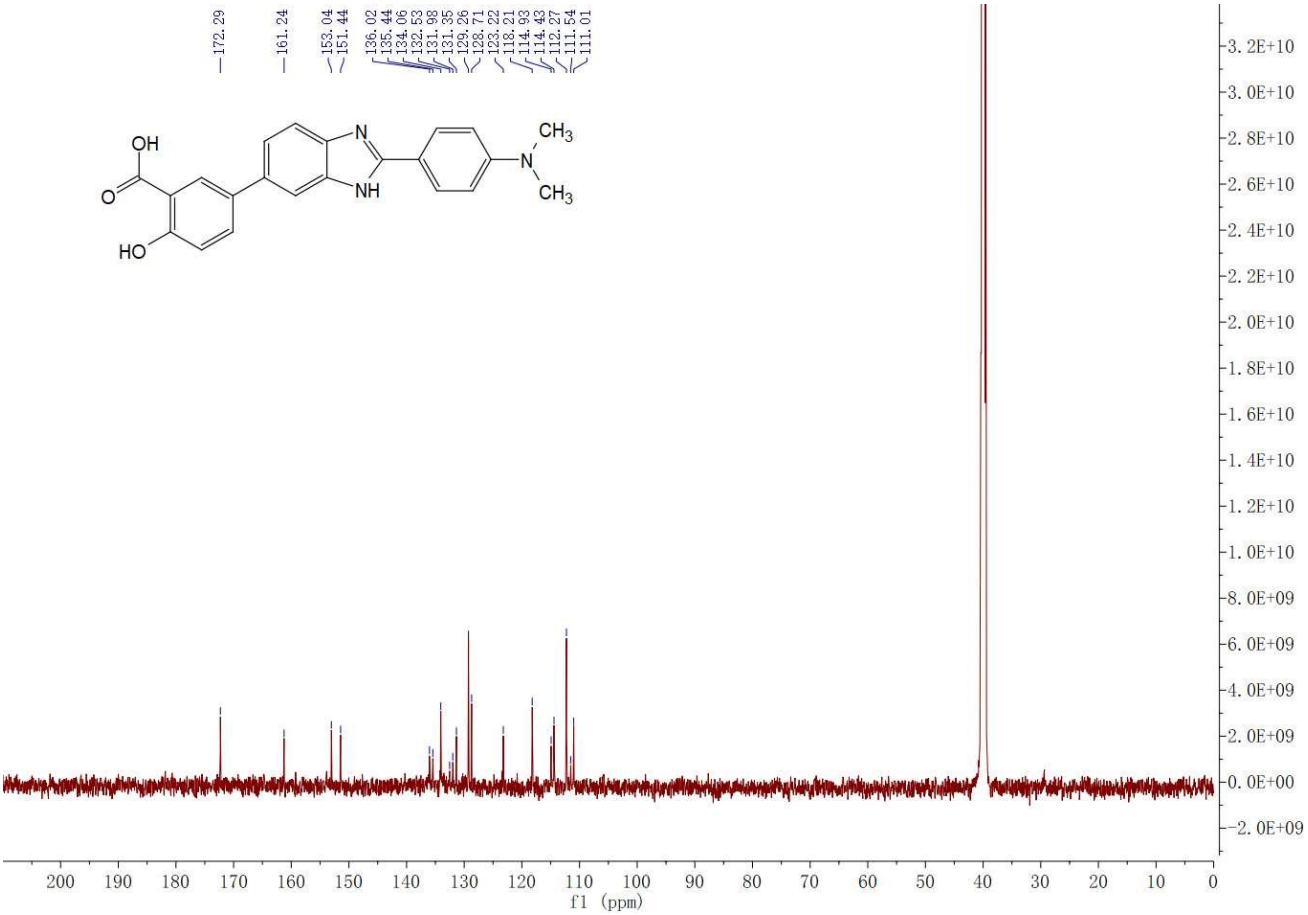
MS (ESI) for compound **4i**.



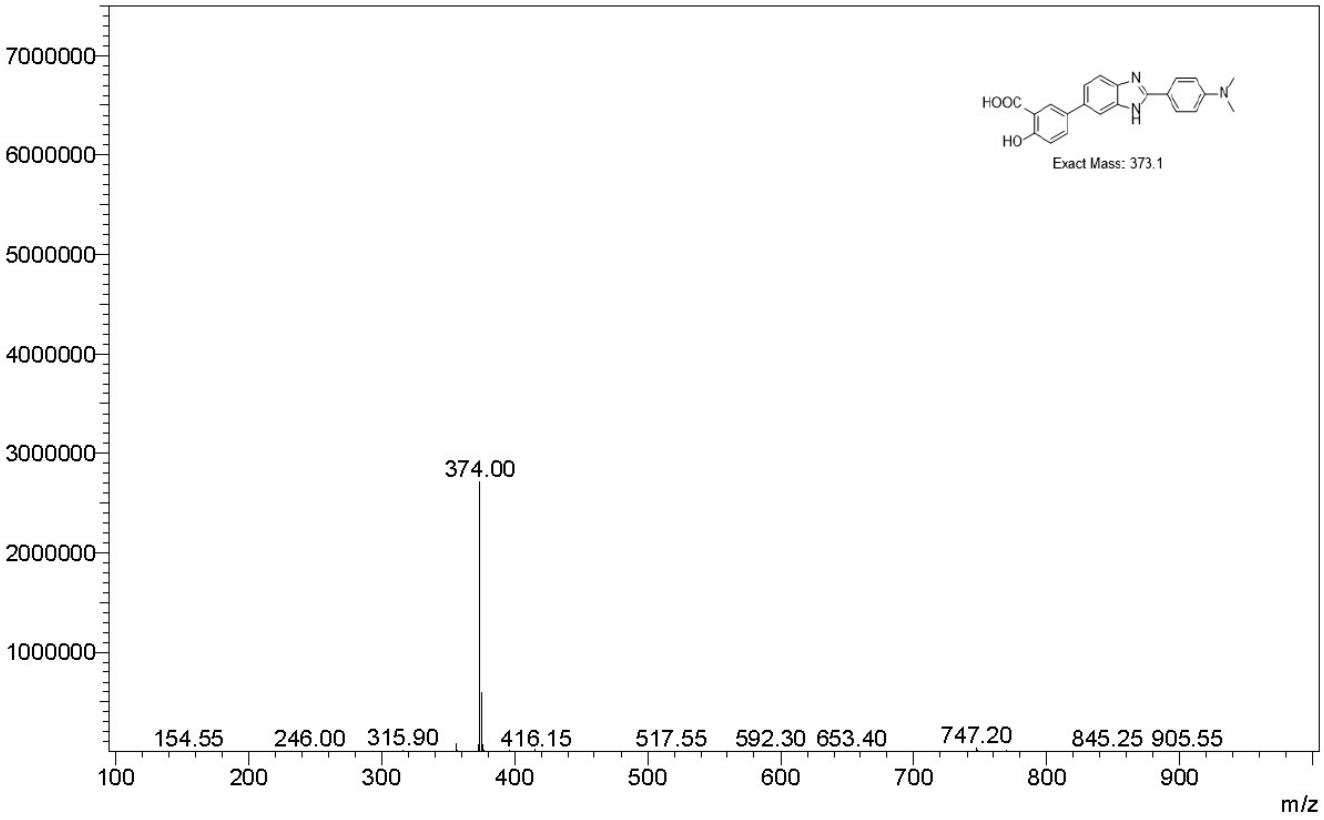
[1]H-NMR spectrum for compound **5i**.



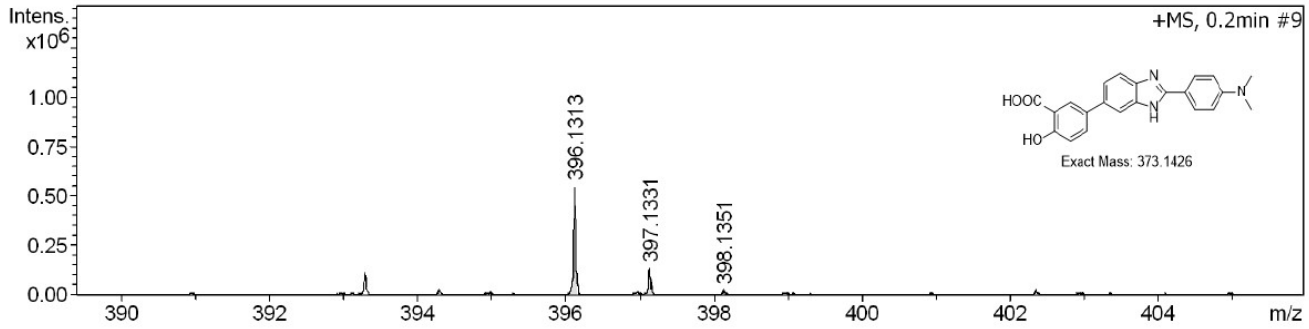
^{13}C-NMR spectrum for compound **5i**.



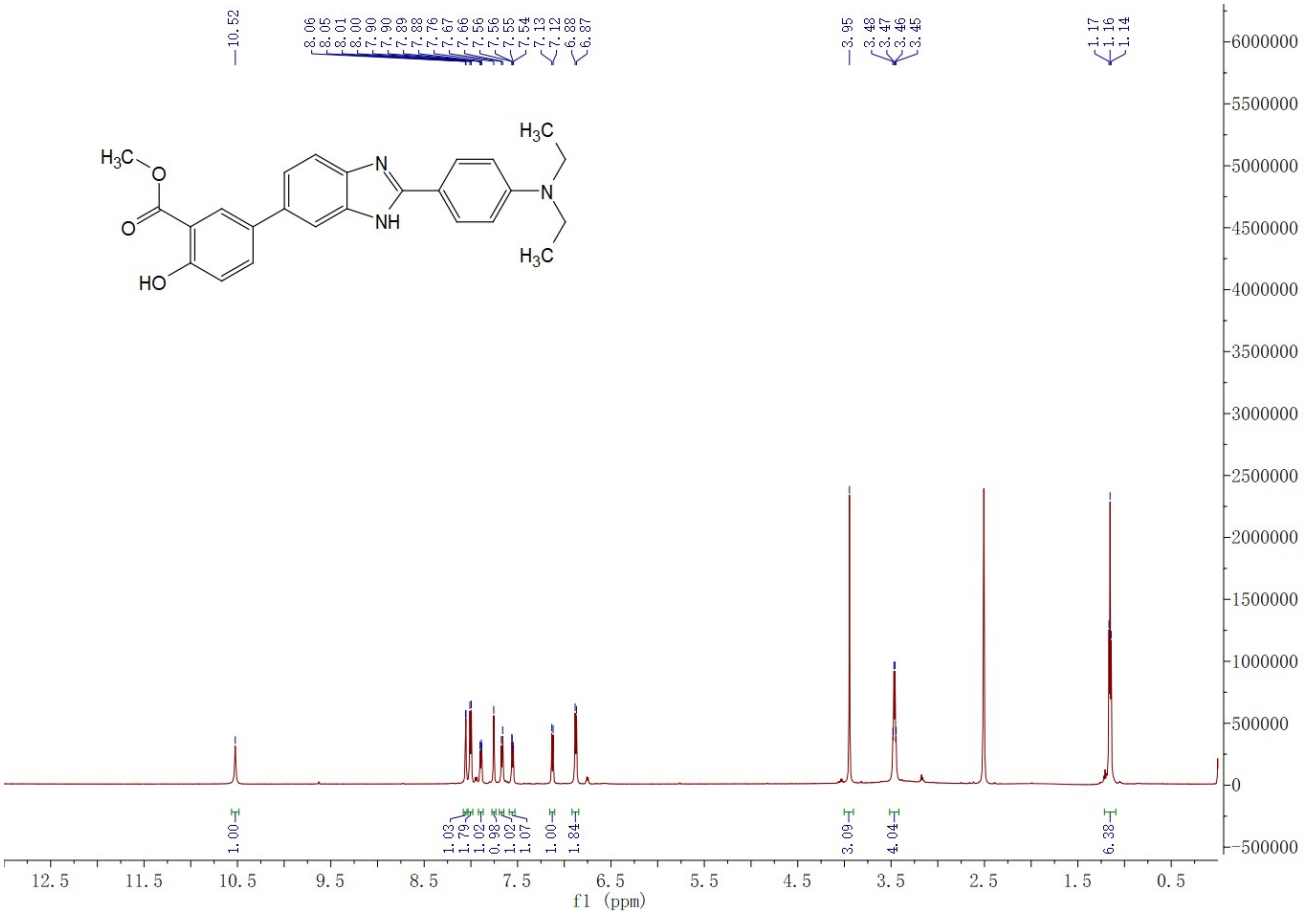
MS (ESI) for compound **5i**.



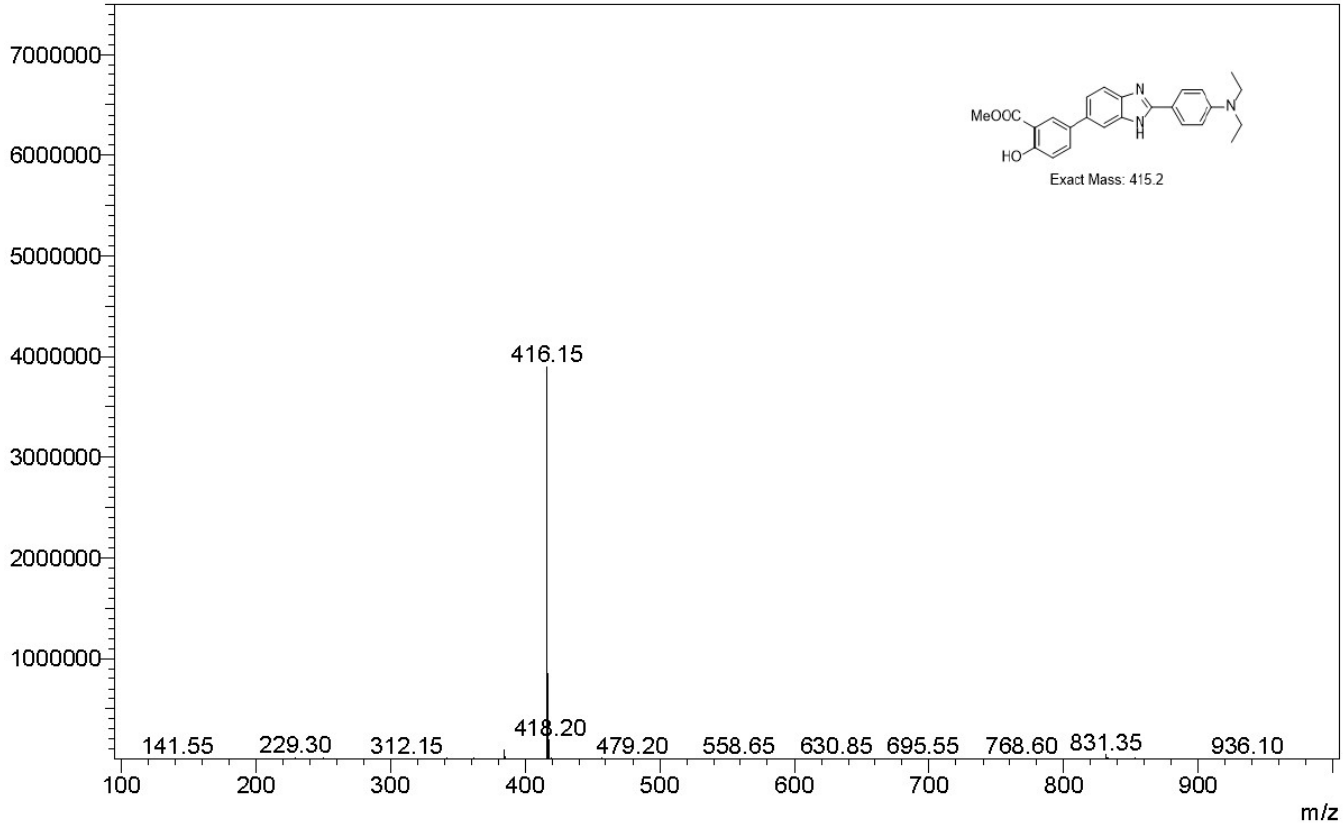
HRMS (ESI) for compound **5i**.



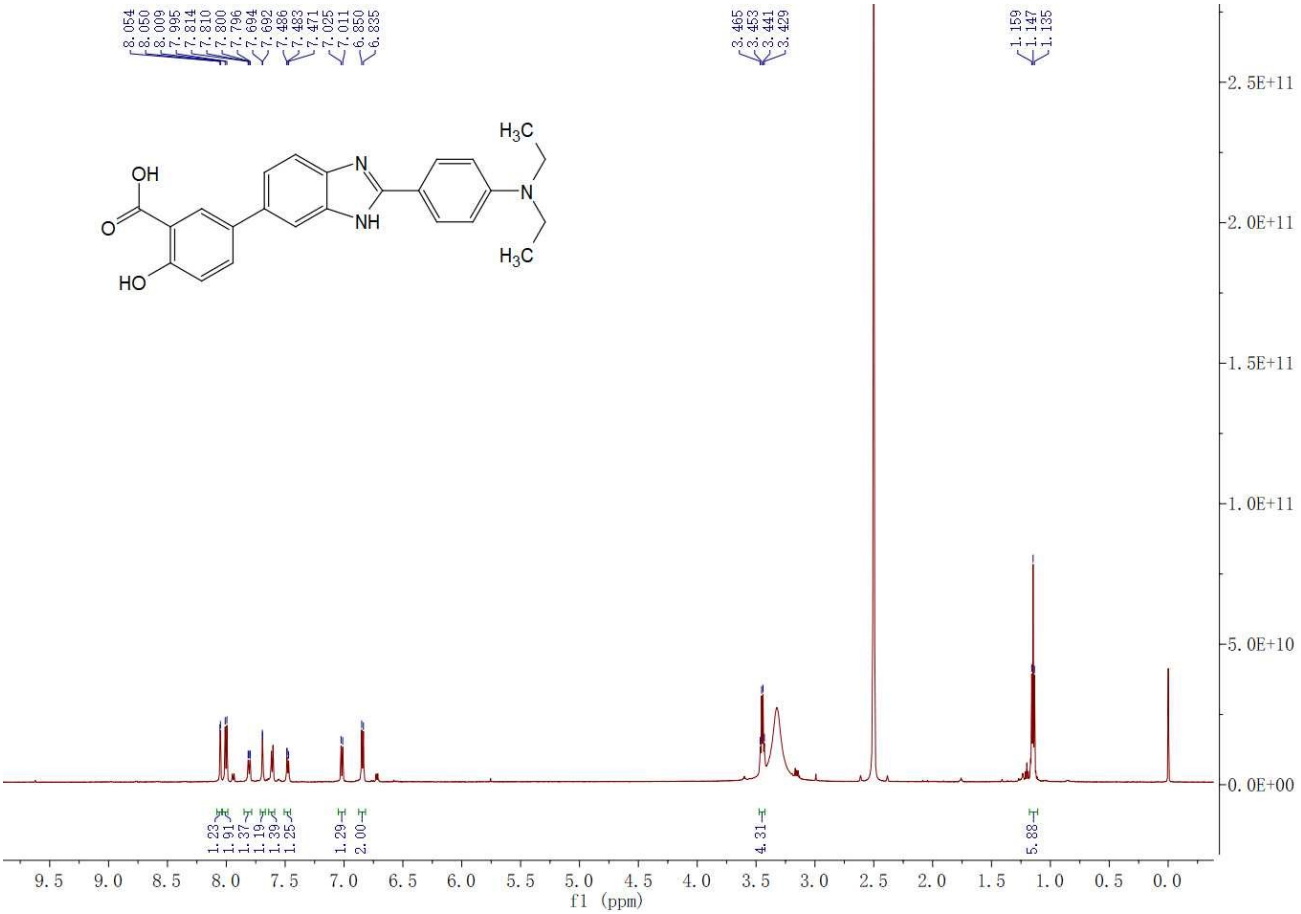
[1]H-NMR spectrum for compound **4j**.



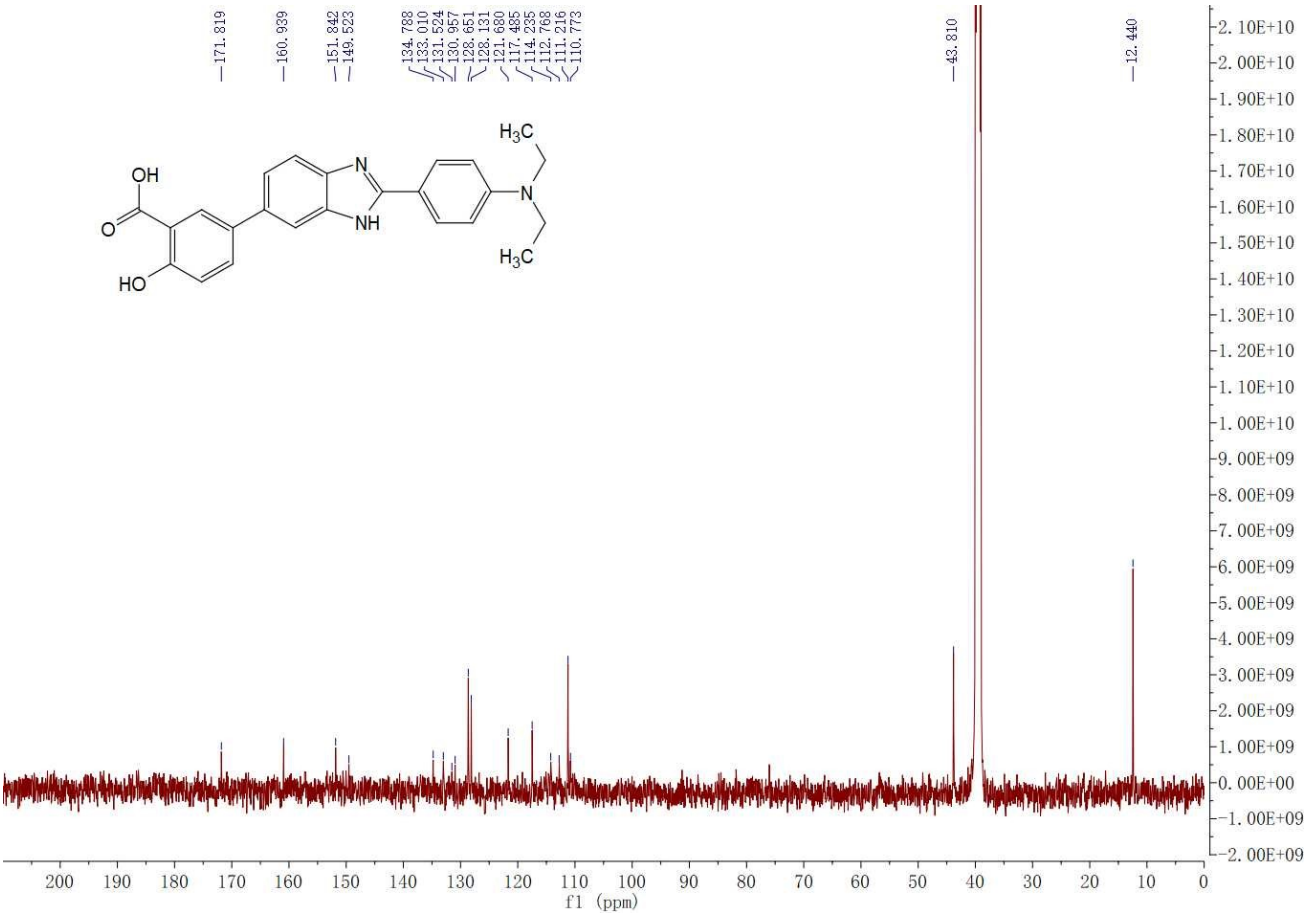
MS (ESI) for compound **4j**.



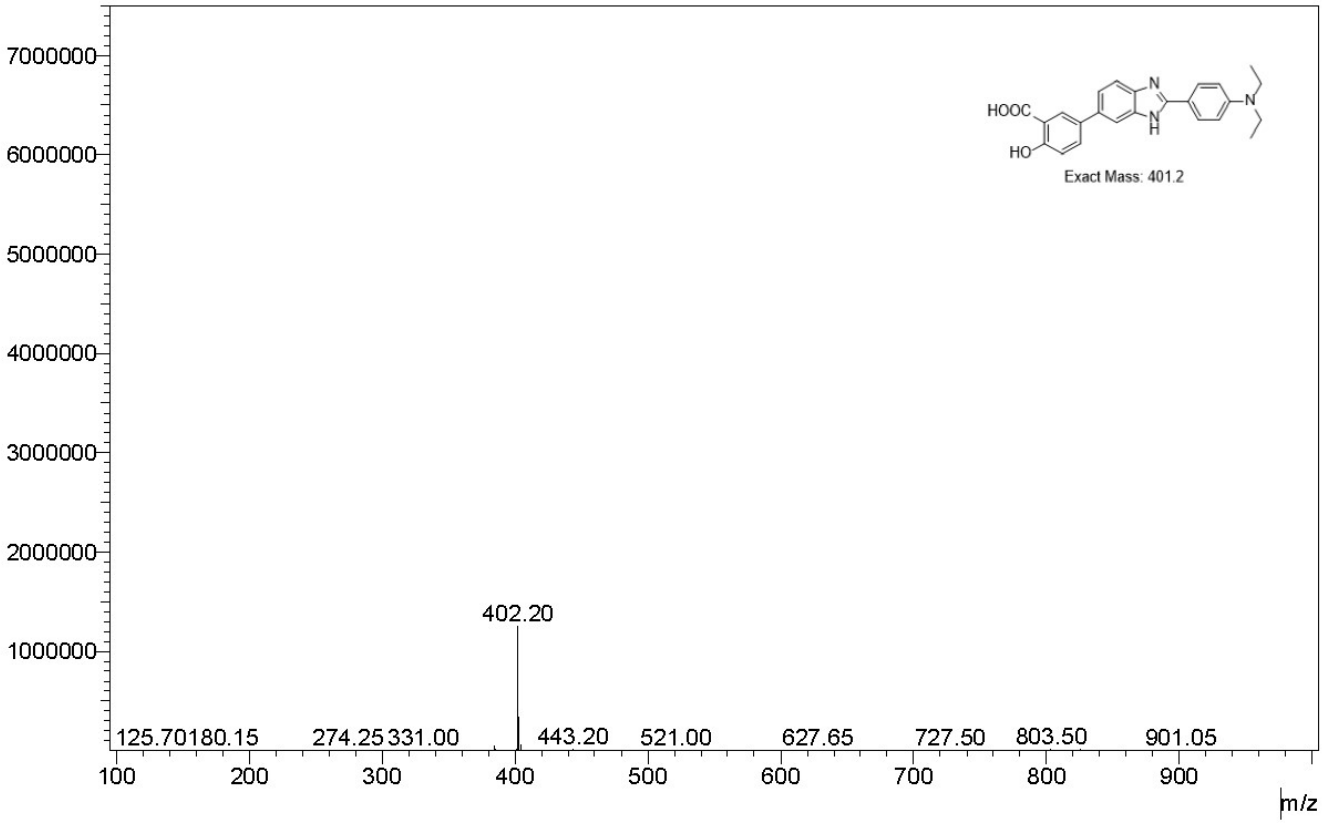
[1]H-NMR spectrum for compound **5j**.



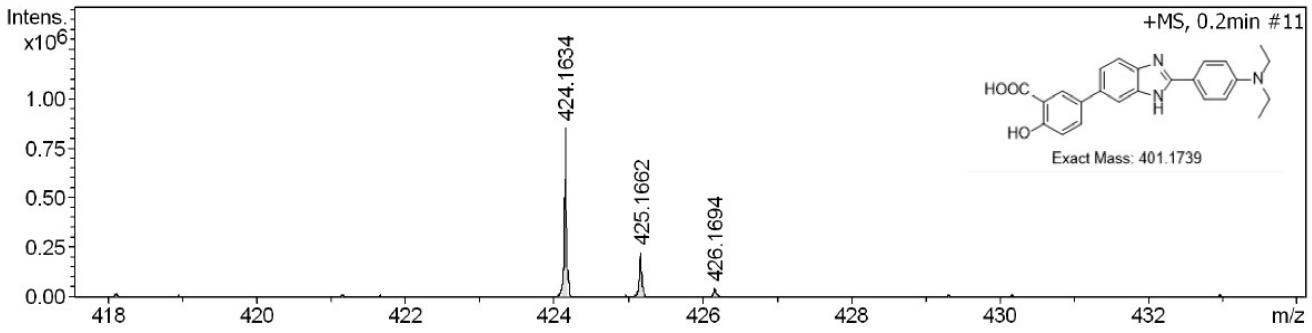
^{13}C-NMR spectrum for compound **5j**.



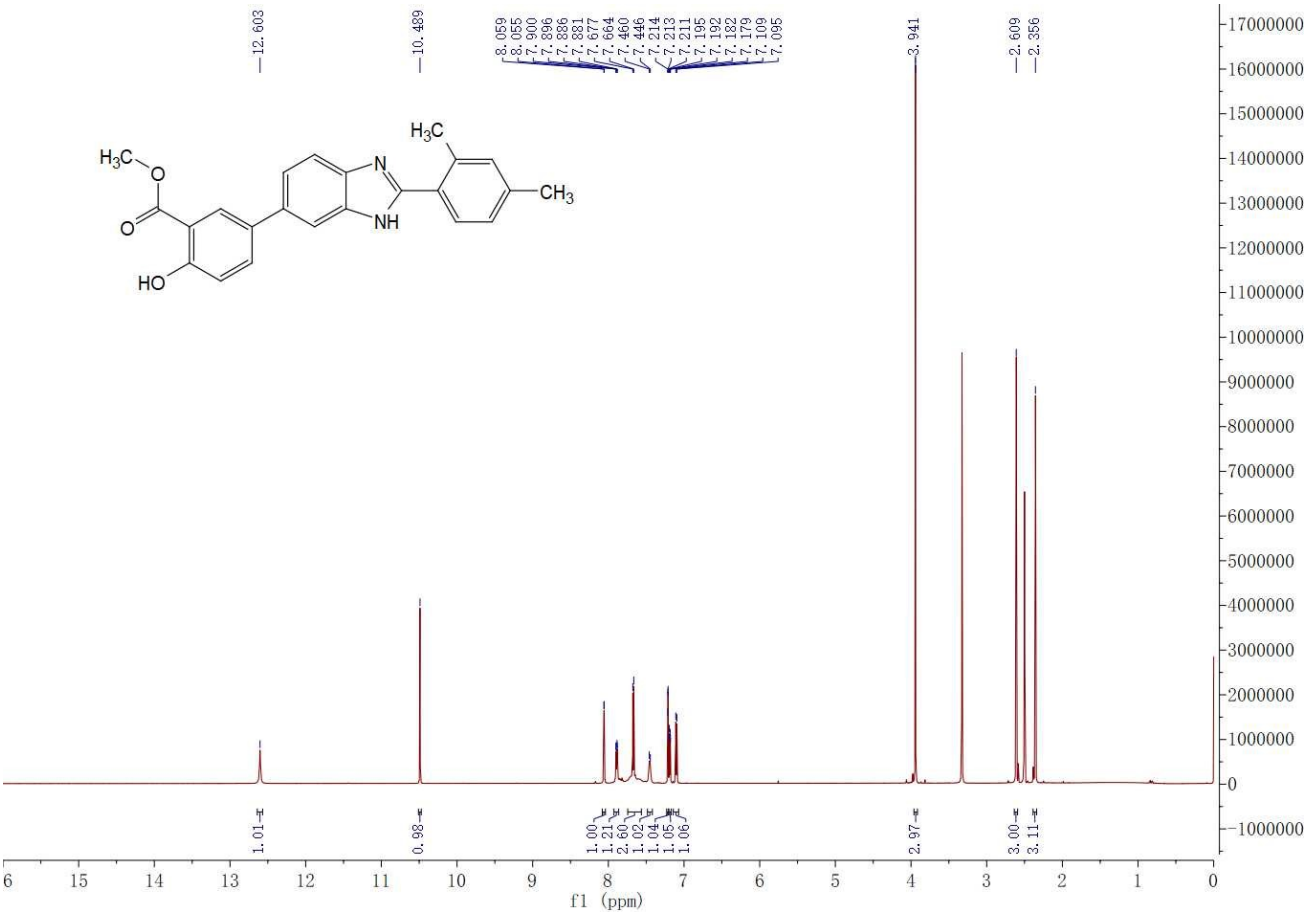
MS (ESI) for compound **5j**.



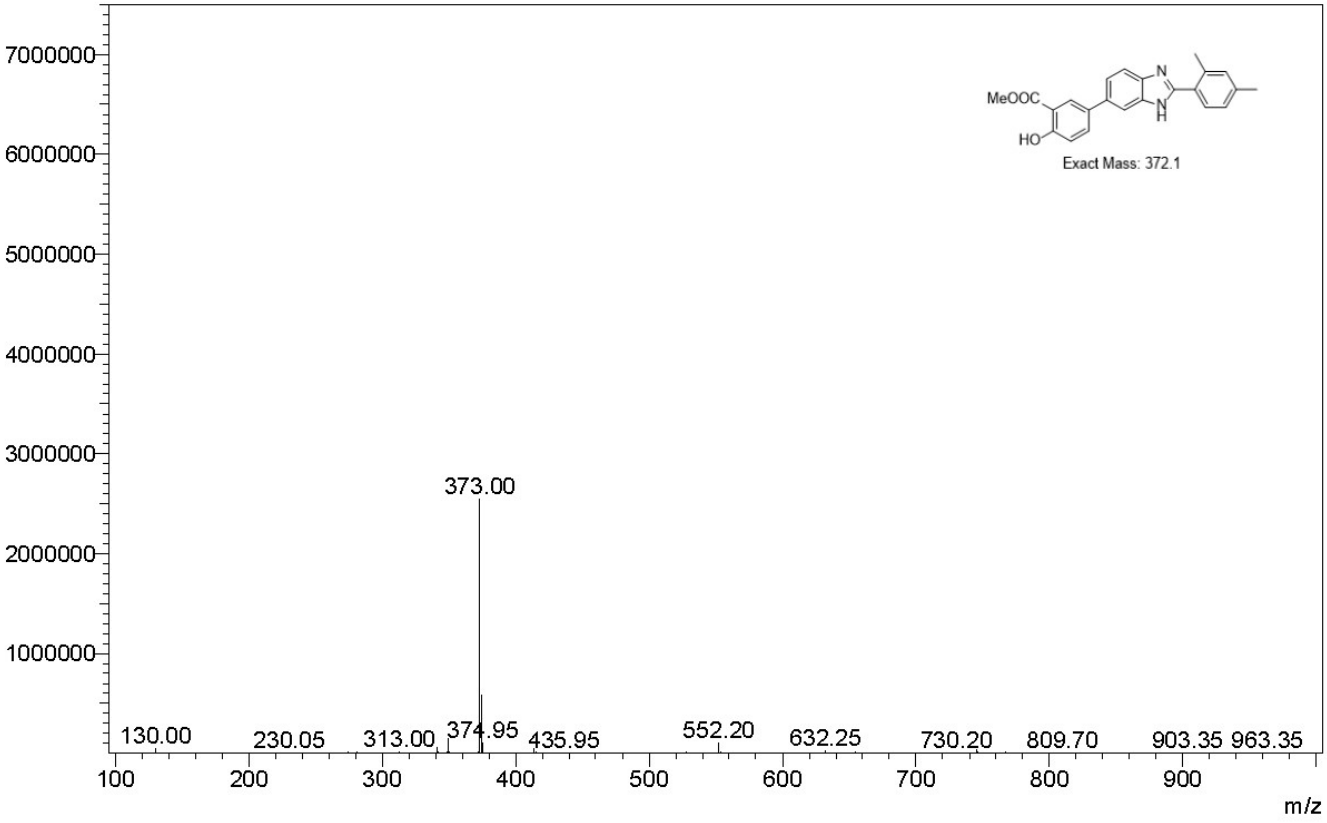
HRMS (ESI) for compound **5j**.



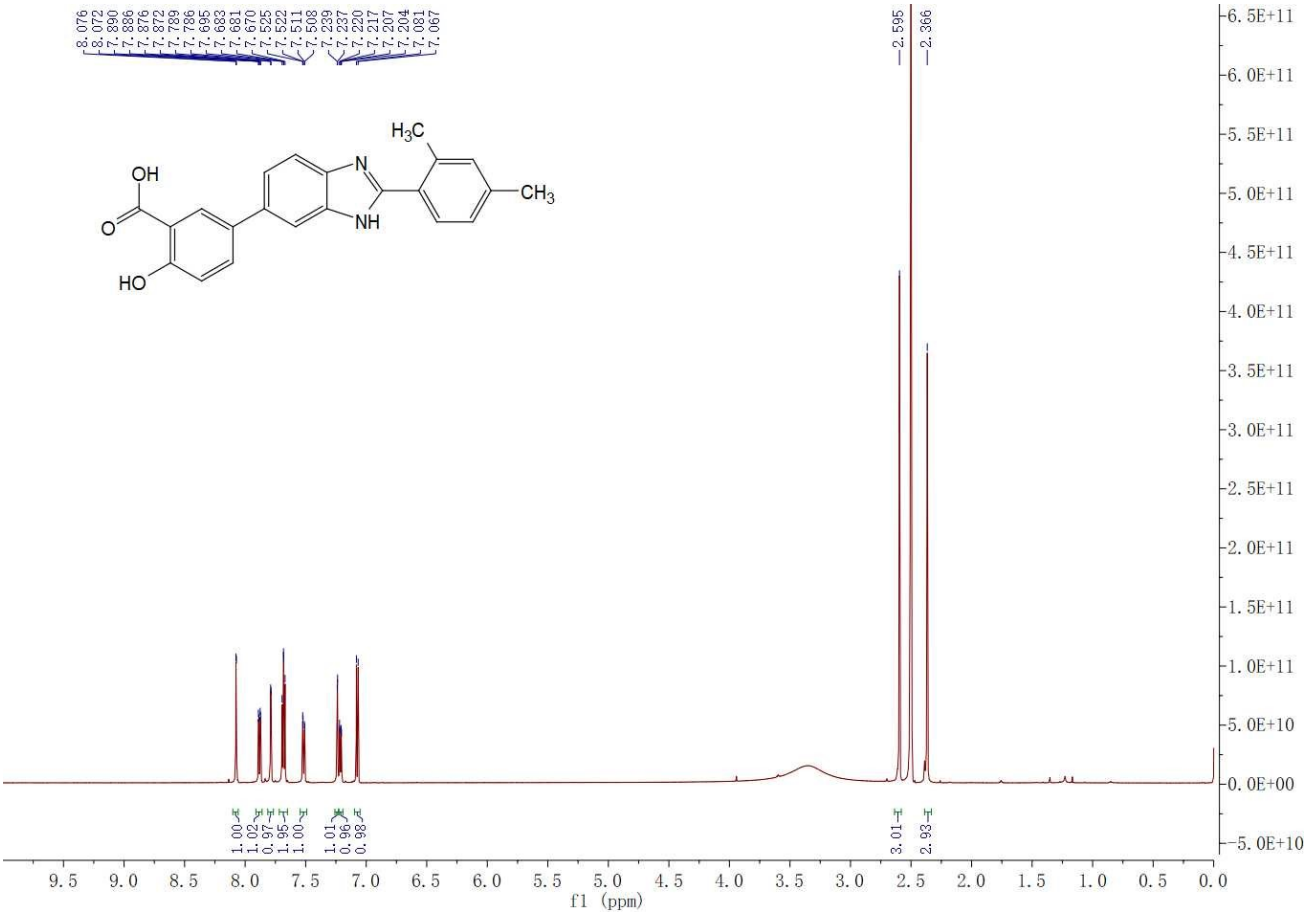
^{1}H-NMR spectrum for compound **4k**.



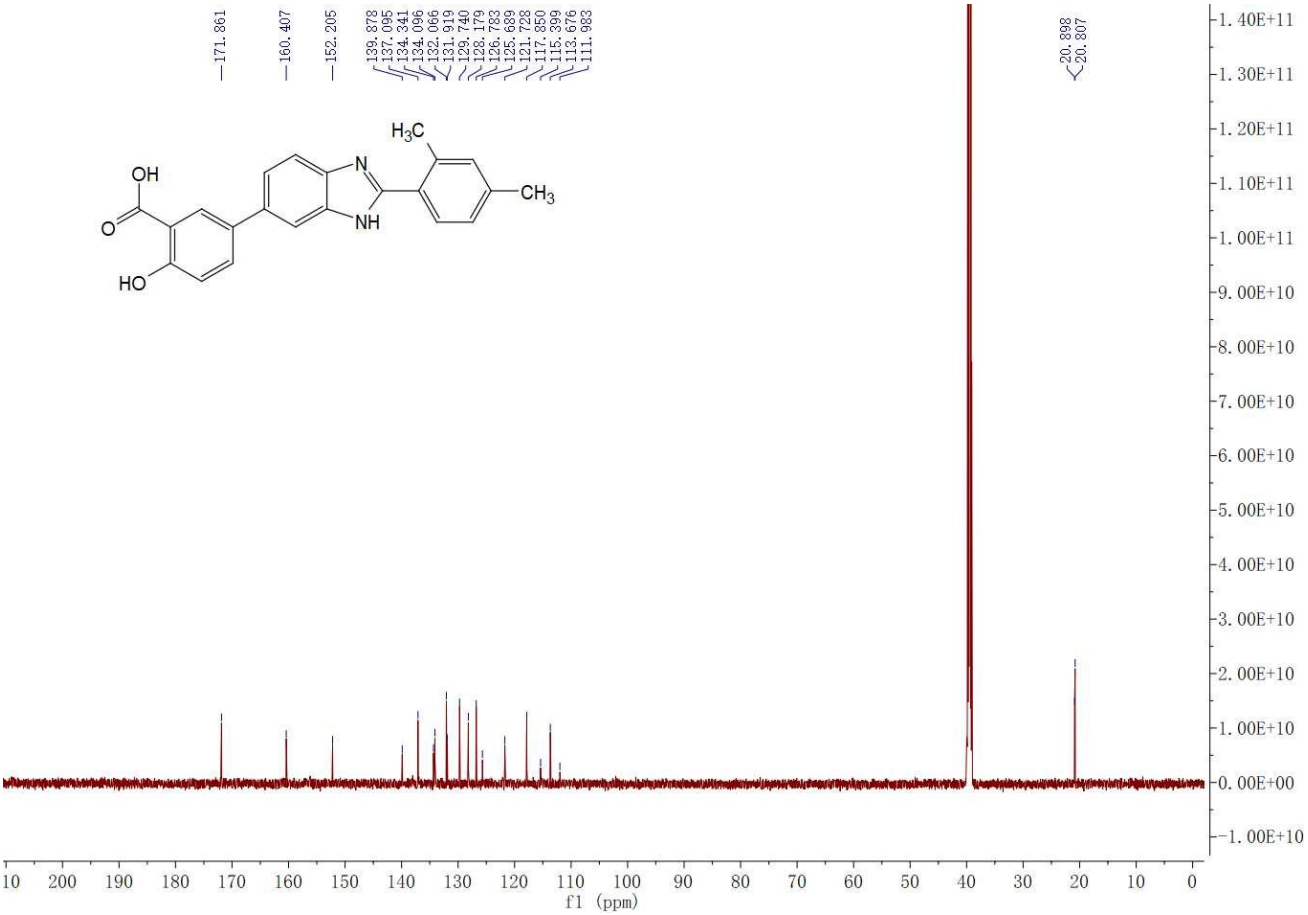
MS (ESI) for compound **4k**.



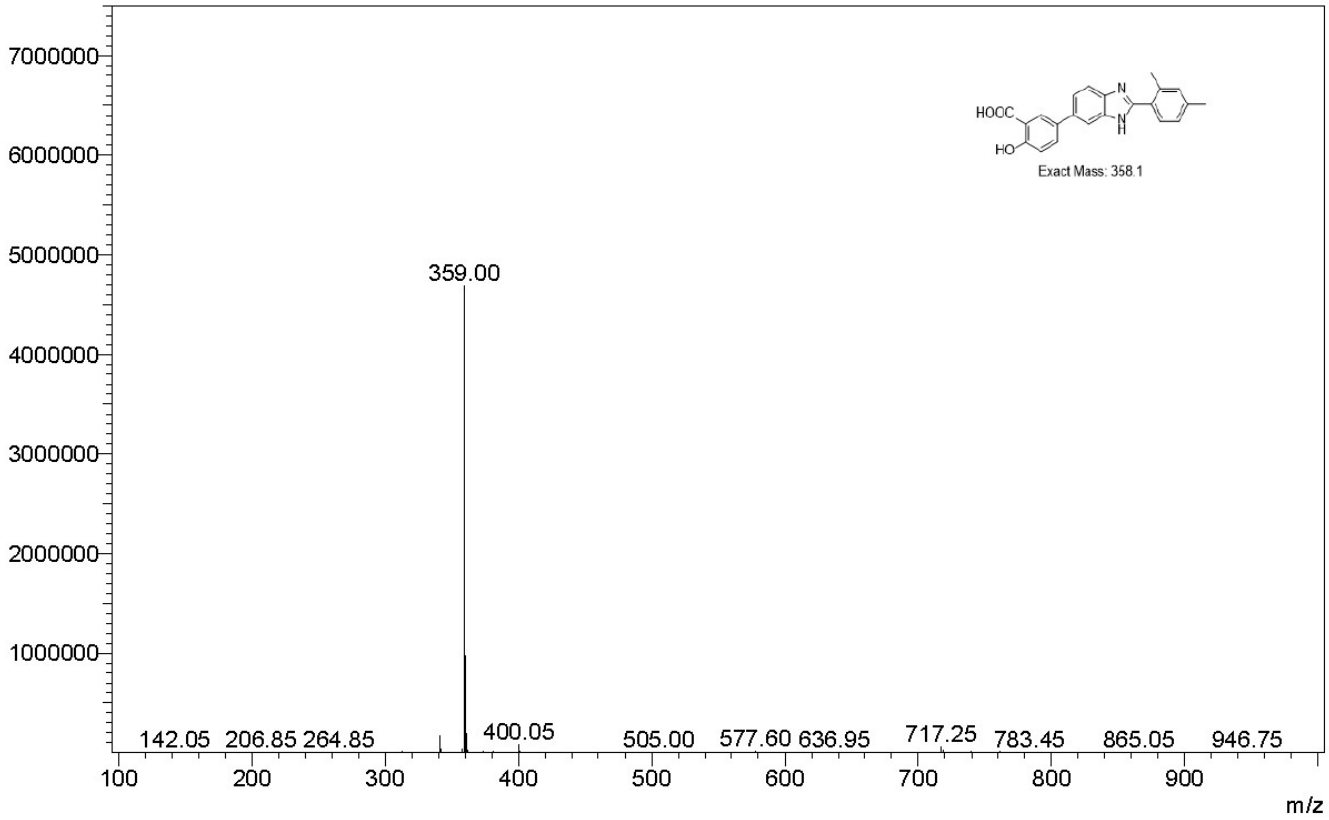
[1]H-NMR spectrum for compound **5k**.



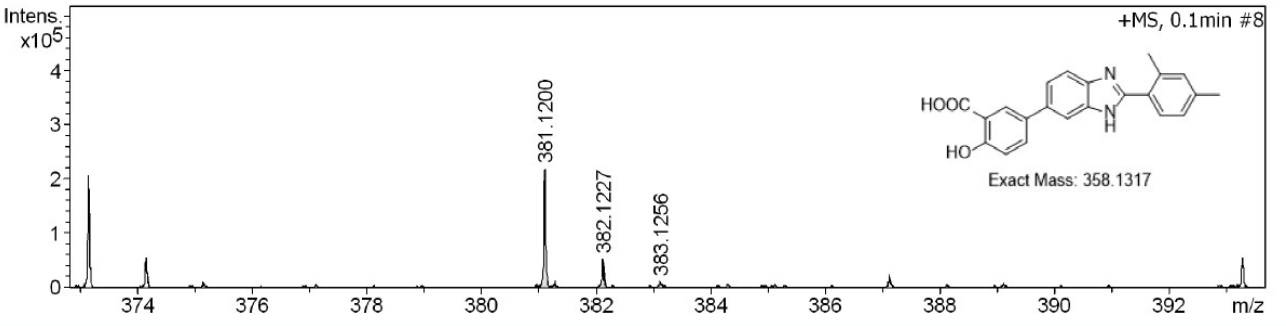
^{13}C-NMR spectrum for compound **5k**.



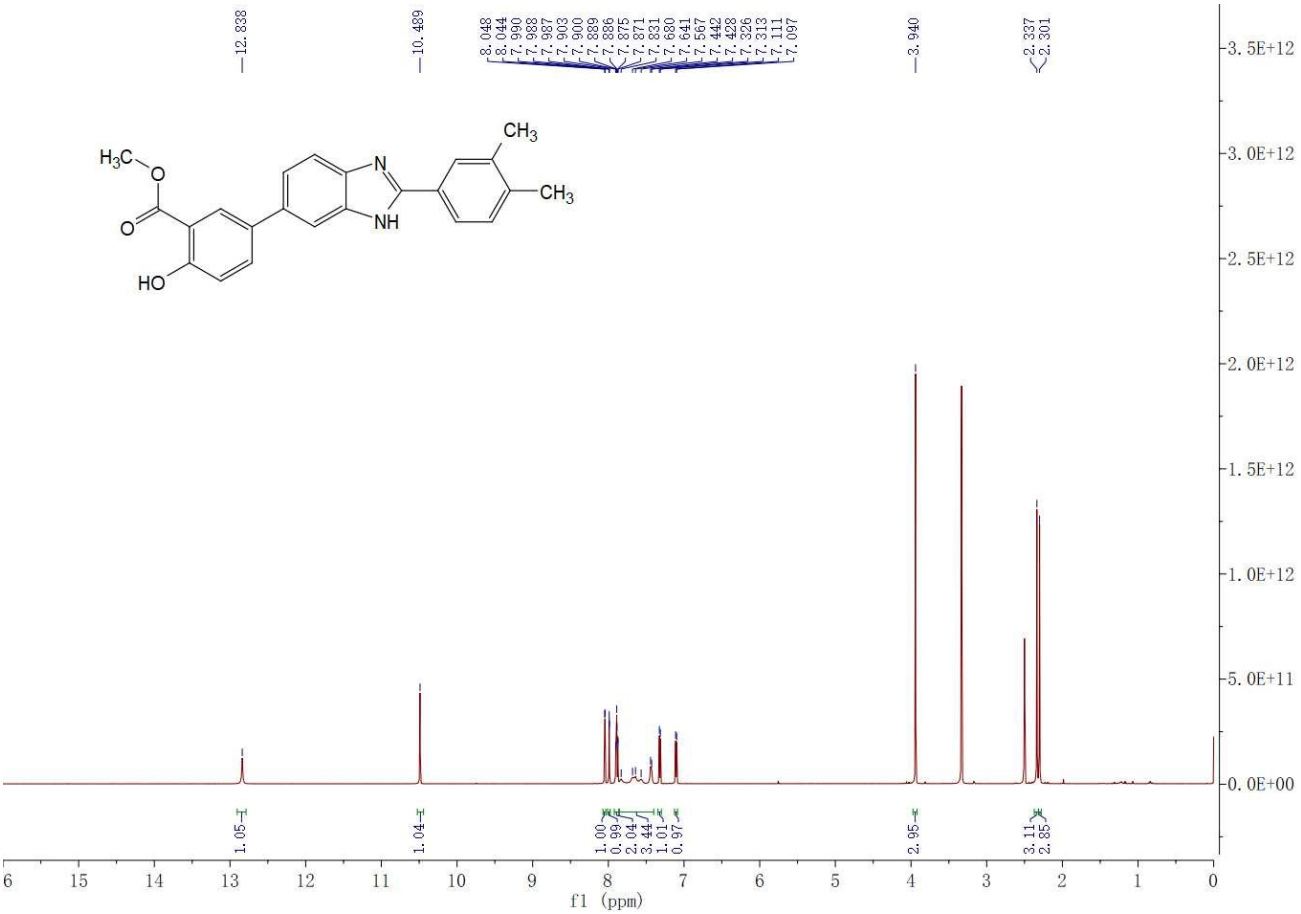
MS (ESI) for compound **5k**.



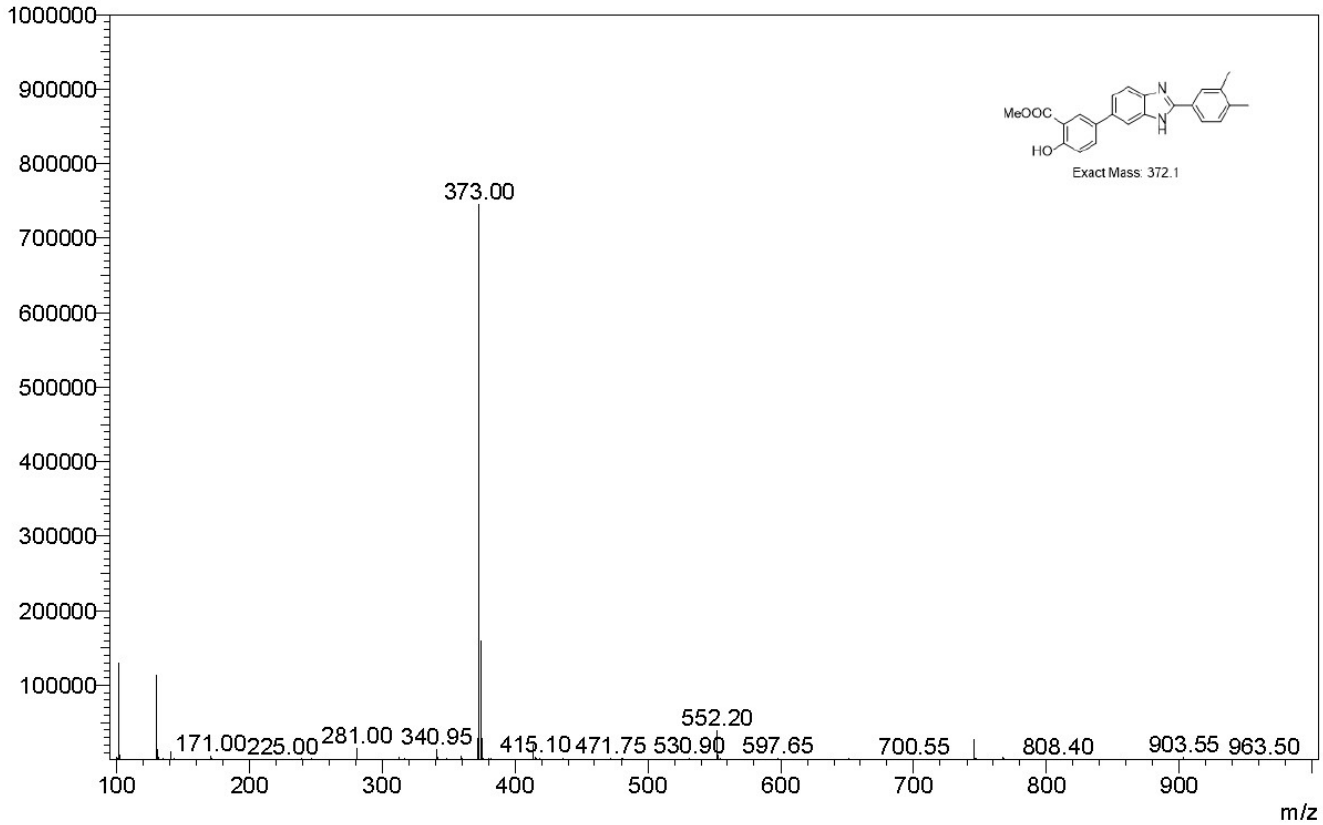
HRMS (ESI) for compound **5k**.



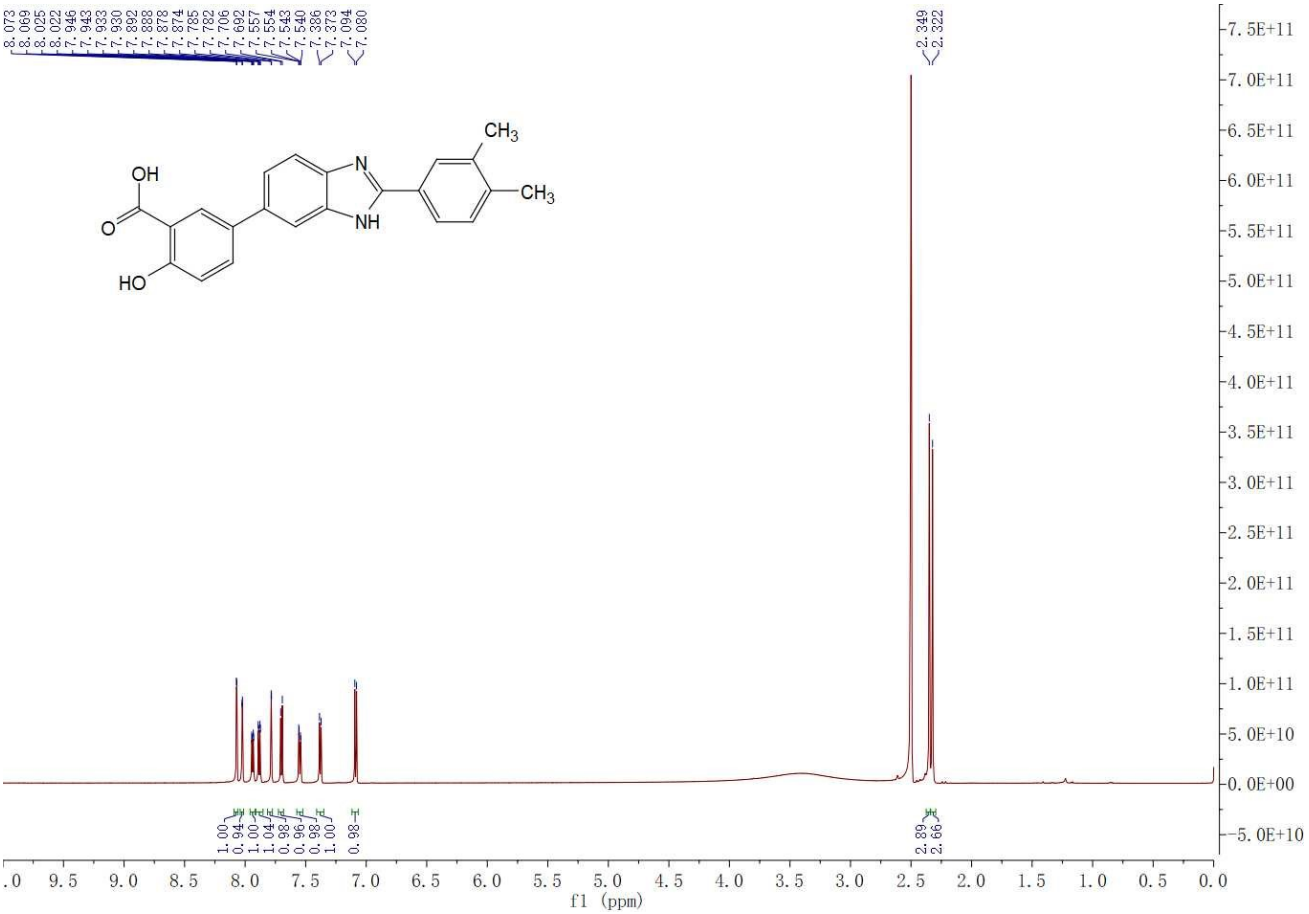
^{1}H-NMR spectrum for compound **4l**.



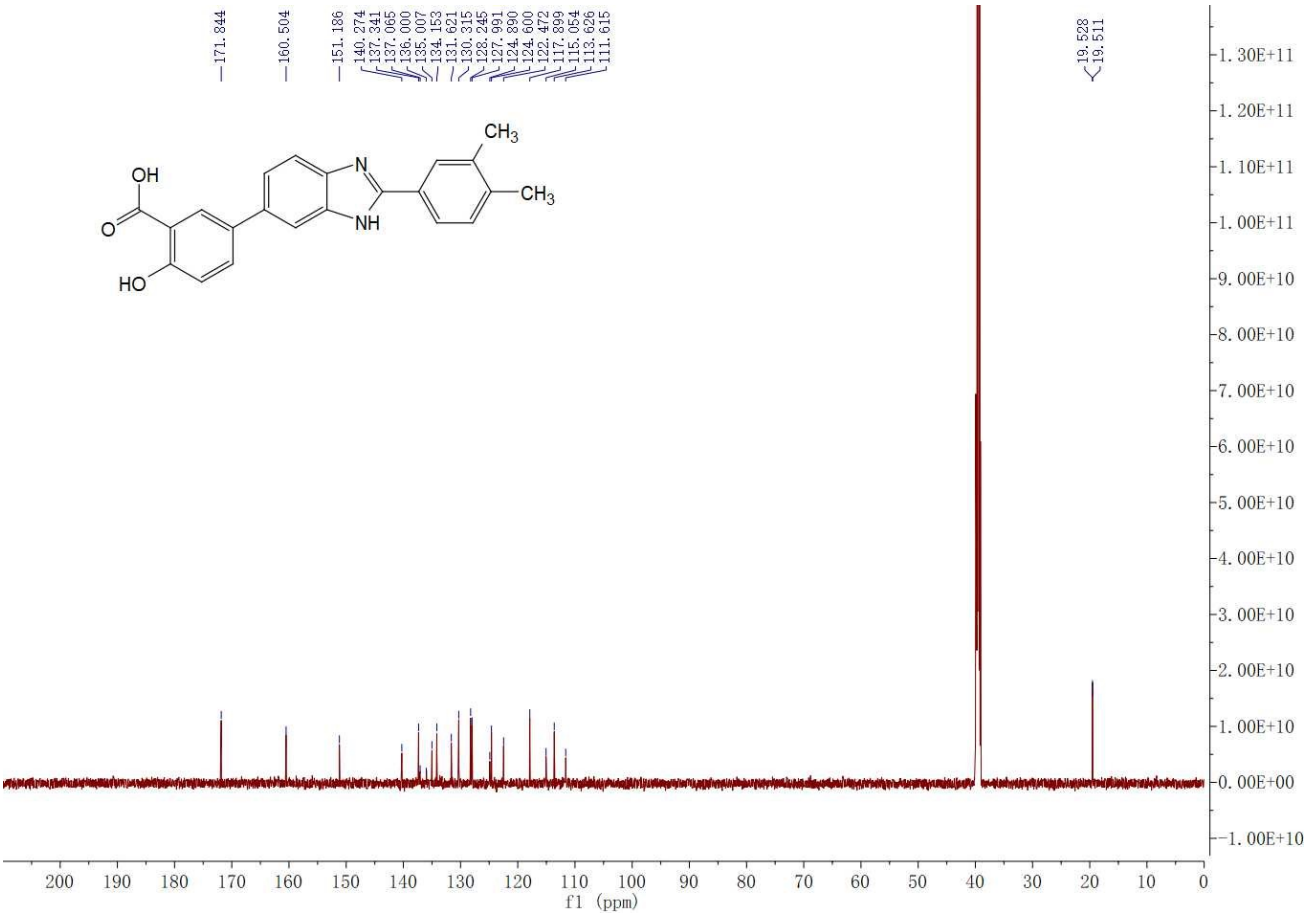
MS (ESI) for compound **4l**.



[1]H-NMR spectrum for compound **5l**.



^{13}C-NMR spectrum for compound **5l**.



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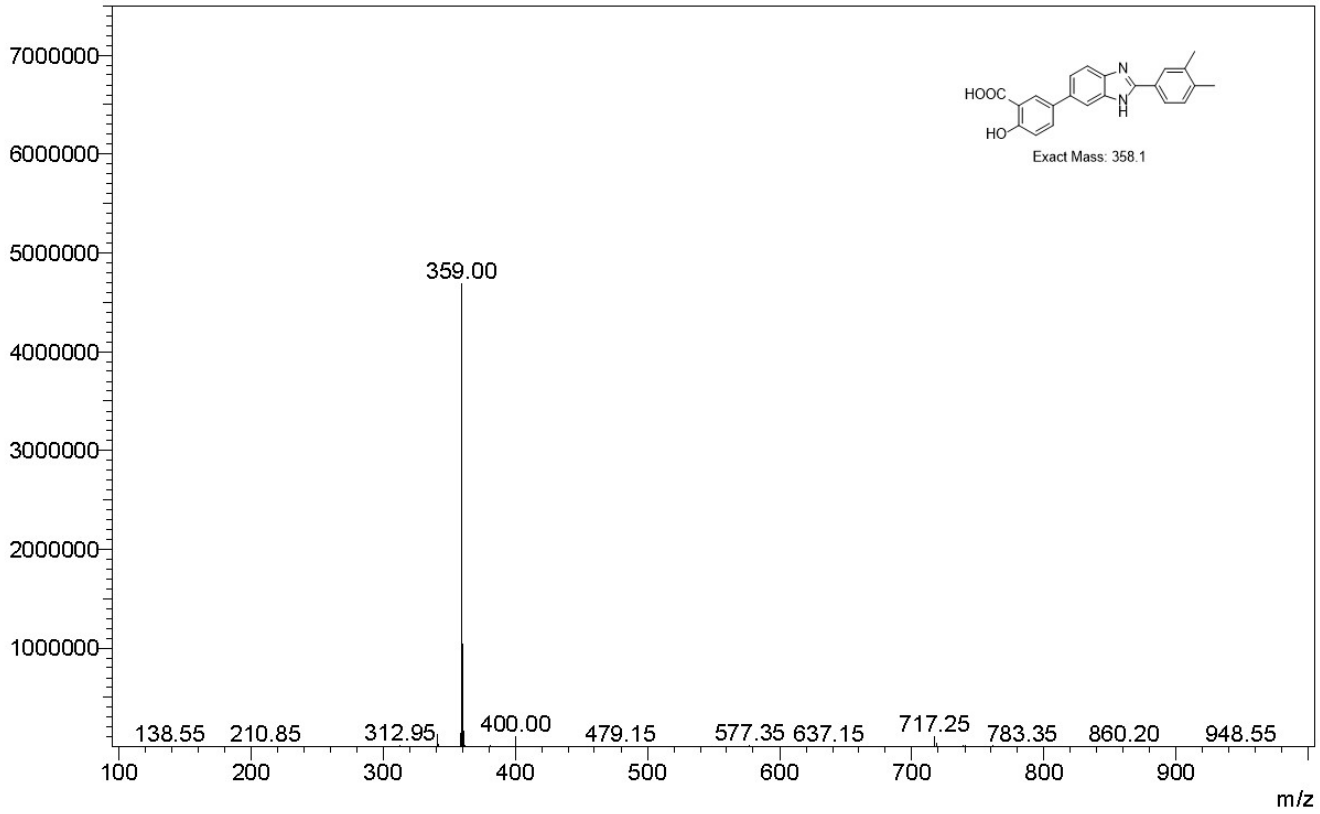
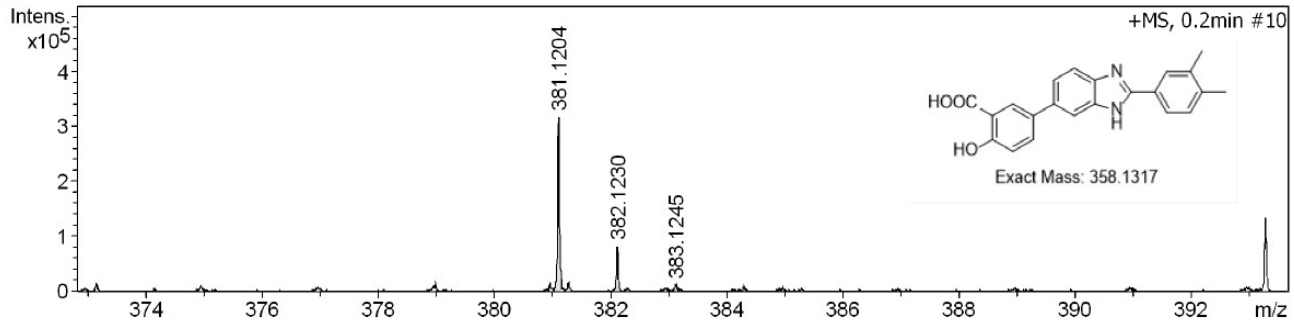
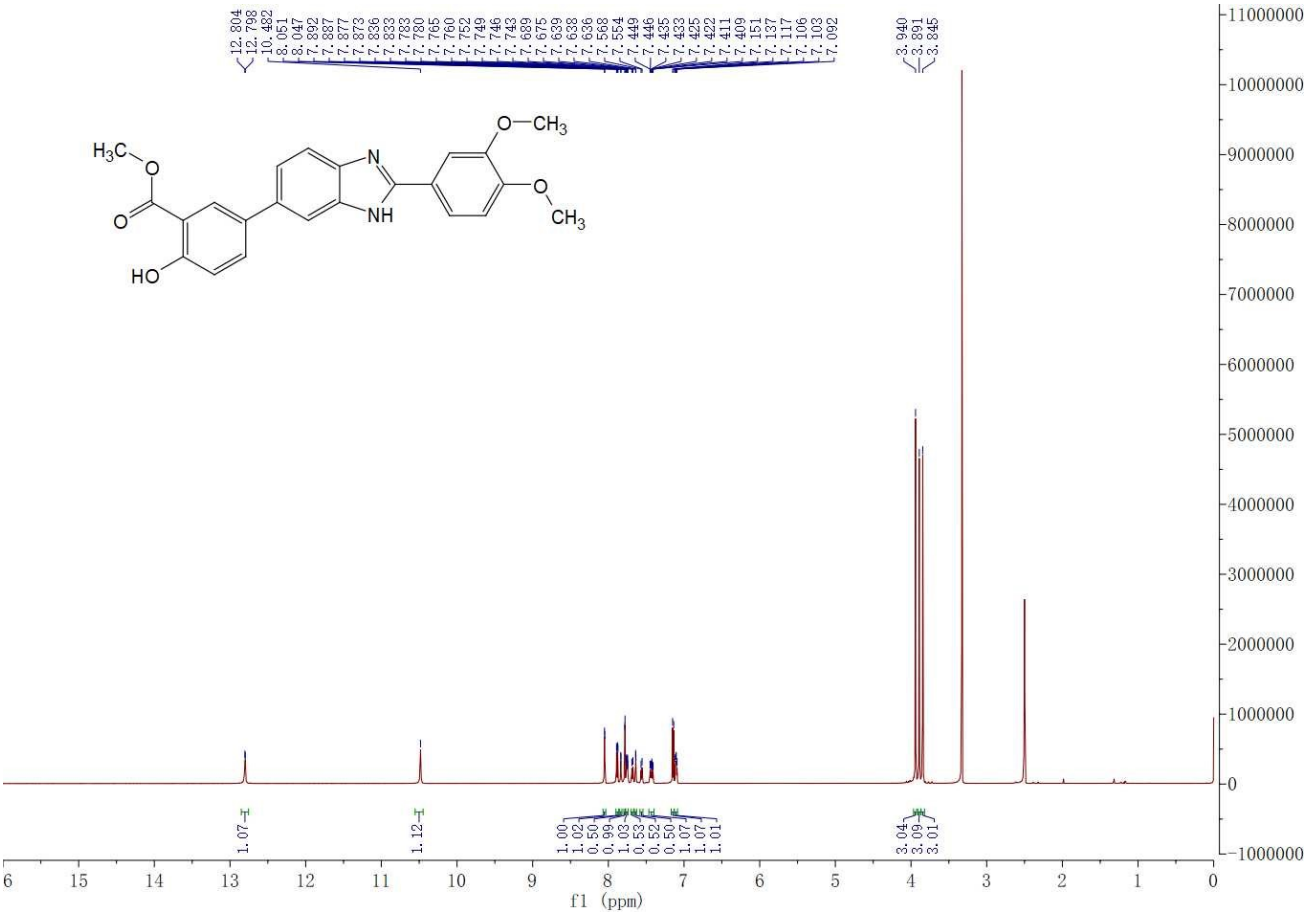


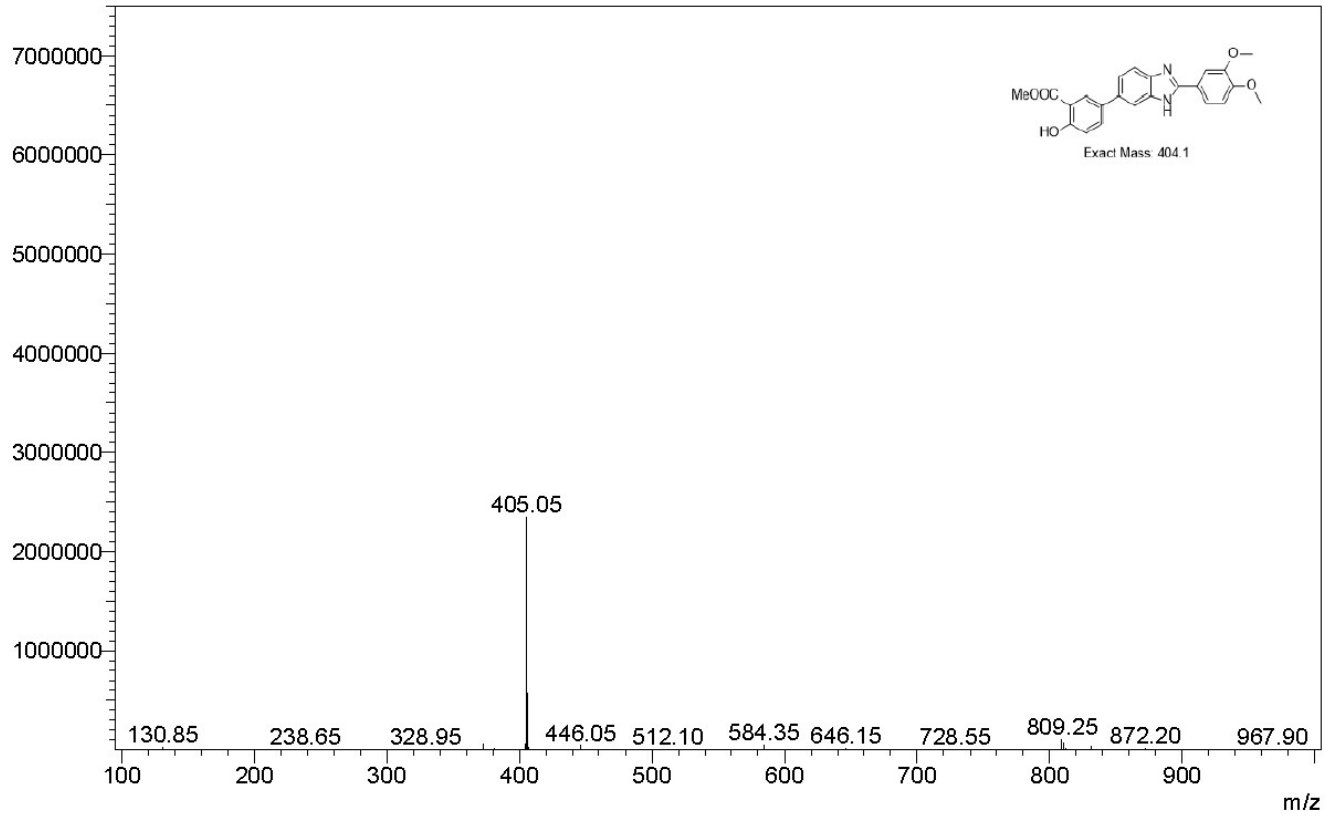
HRMS (ESI) for compound **5l**.



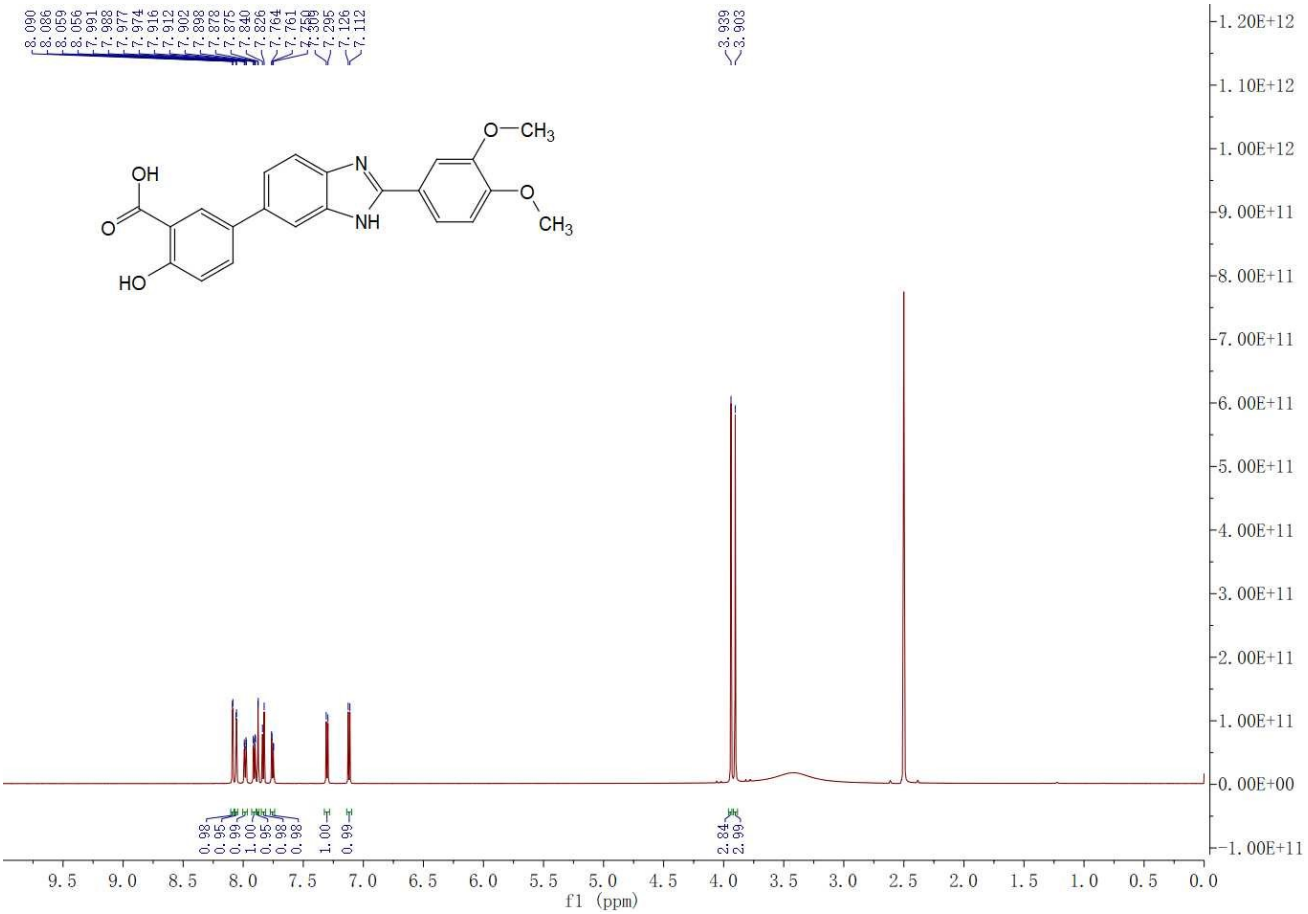
[1]H-NMR spectrum for compound **4m**.



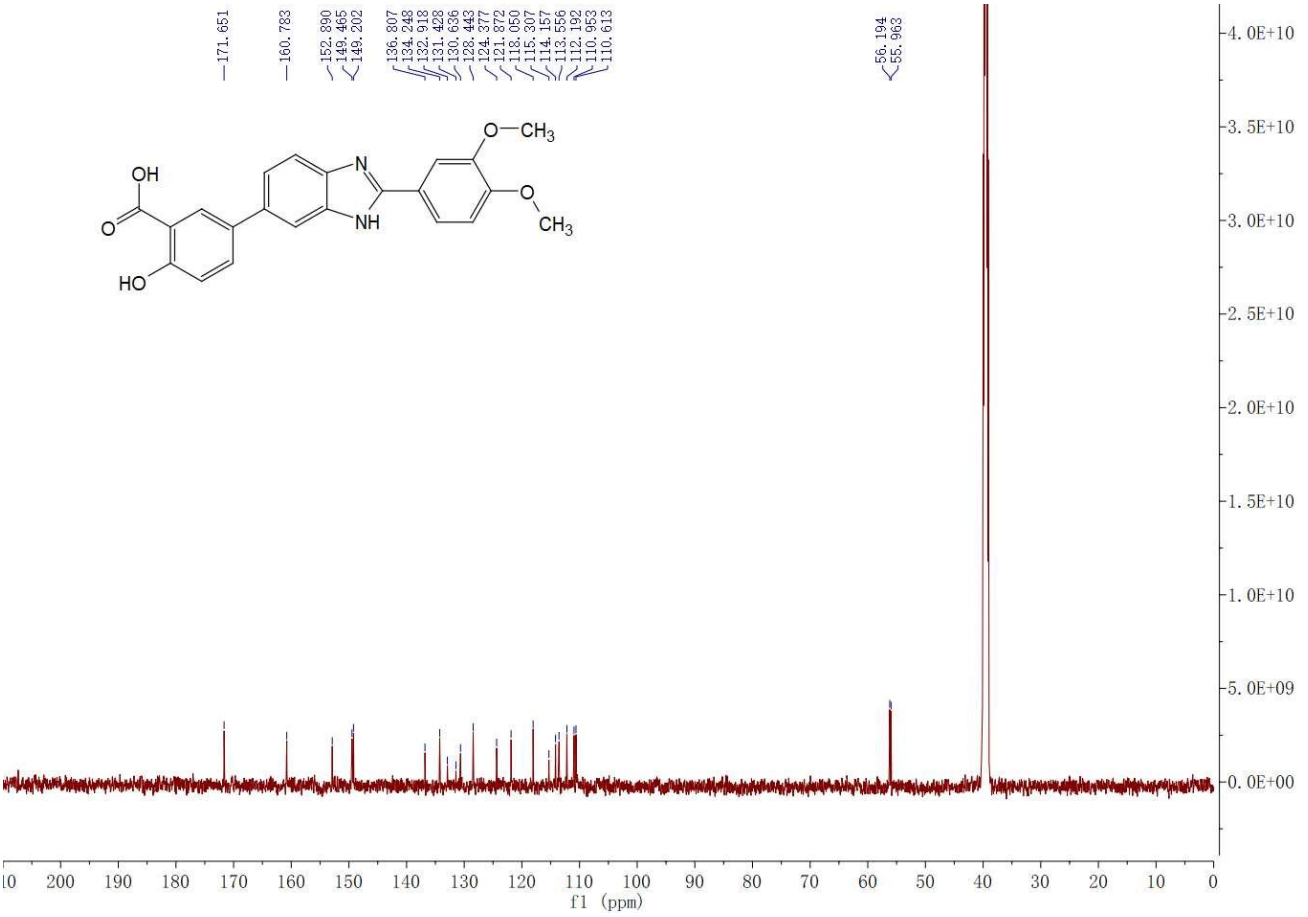
MS (ESI) for compound **4m**.



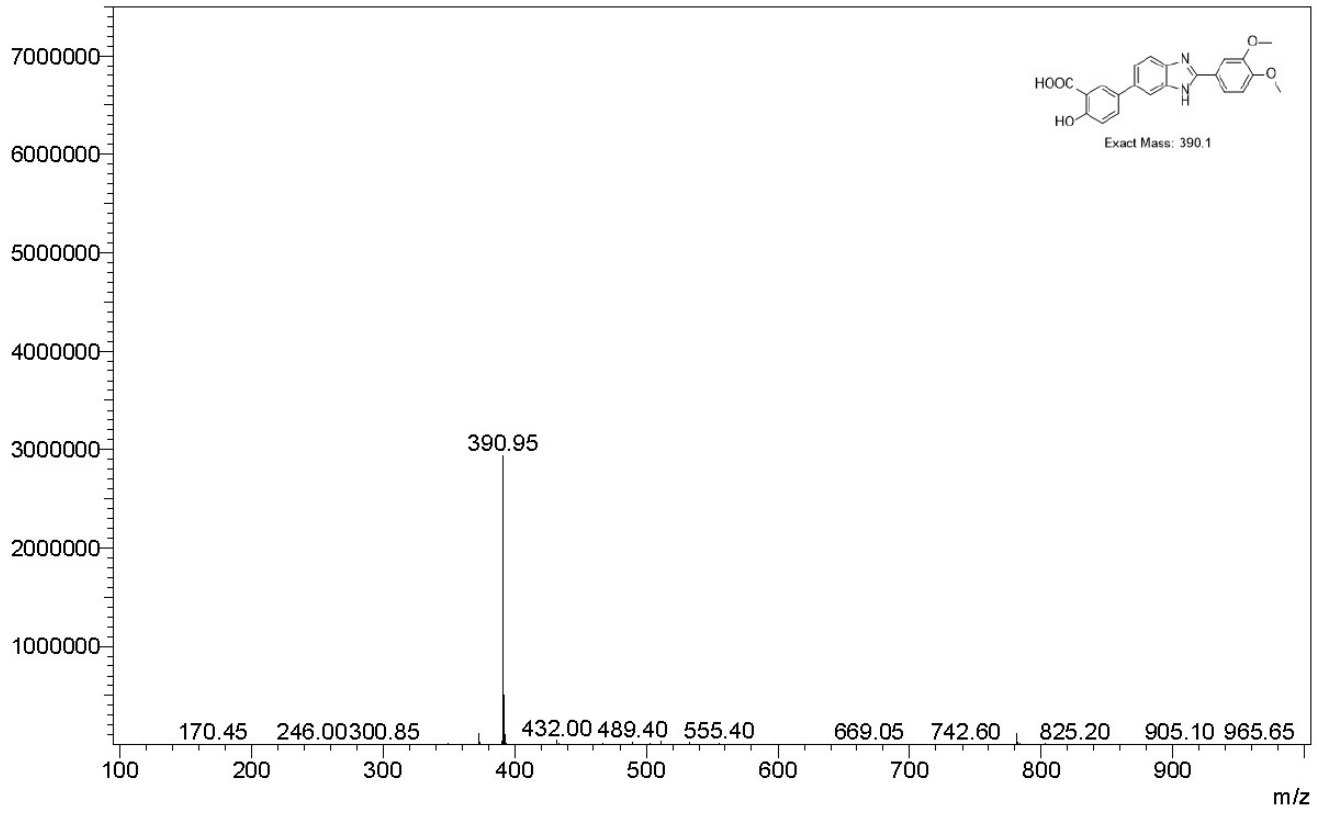
[1]H-NMR spectrum for compound **5m**.



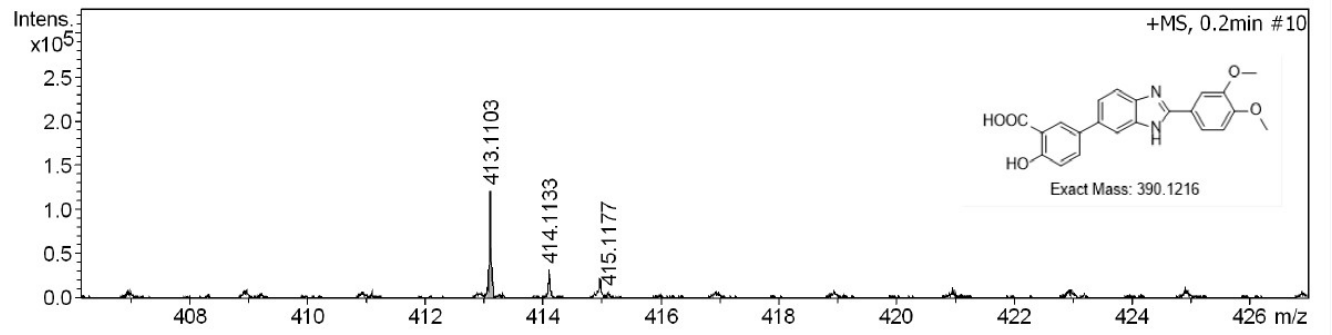
^{13}C-NMR spectrum for compound **5m**.



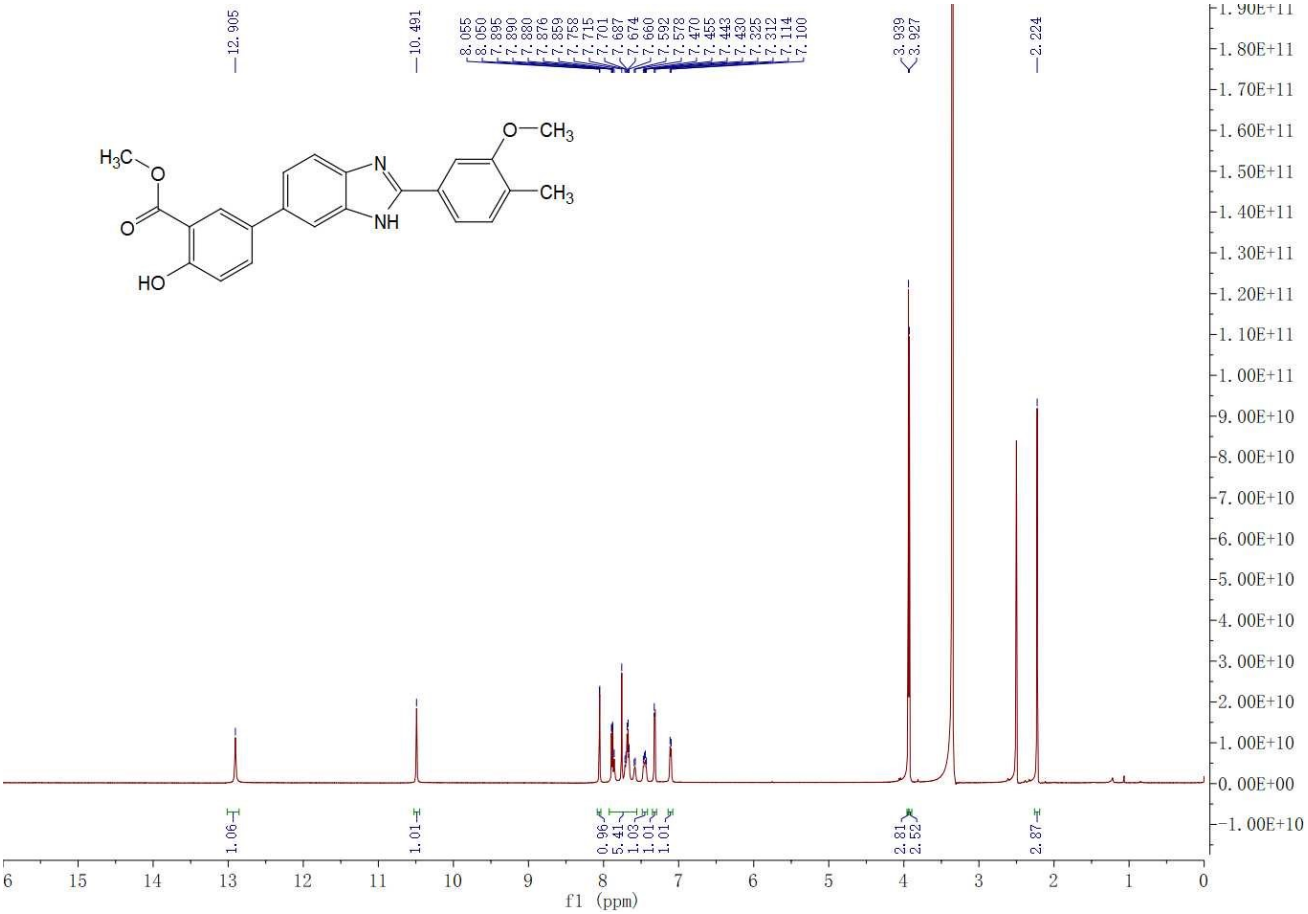
MS (ESI) for compound **5m**.



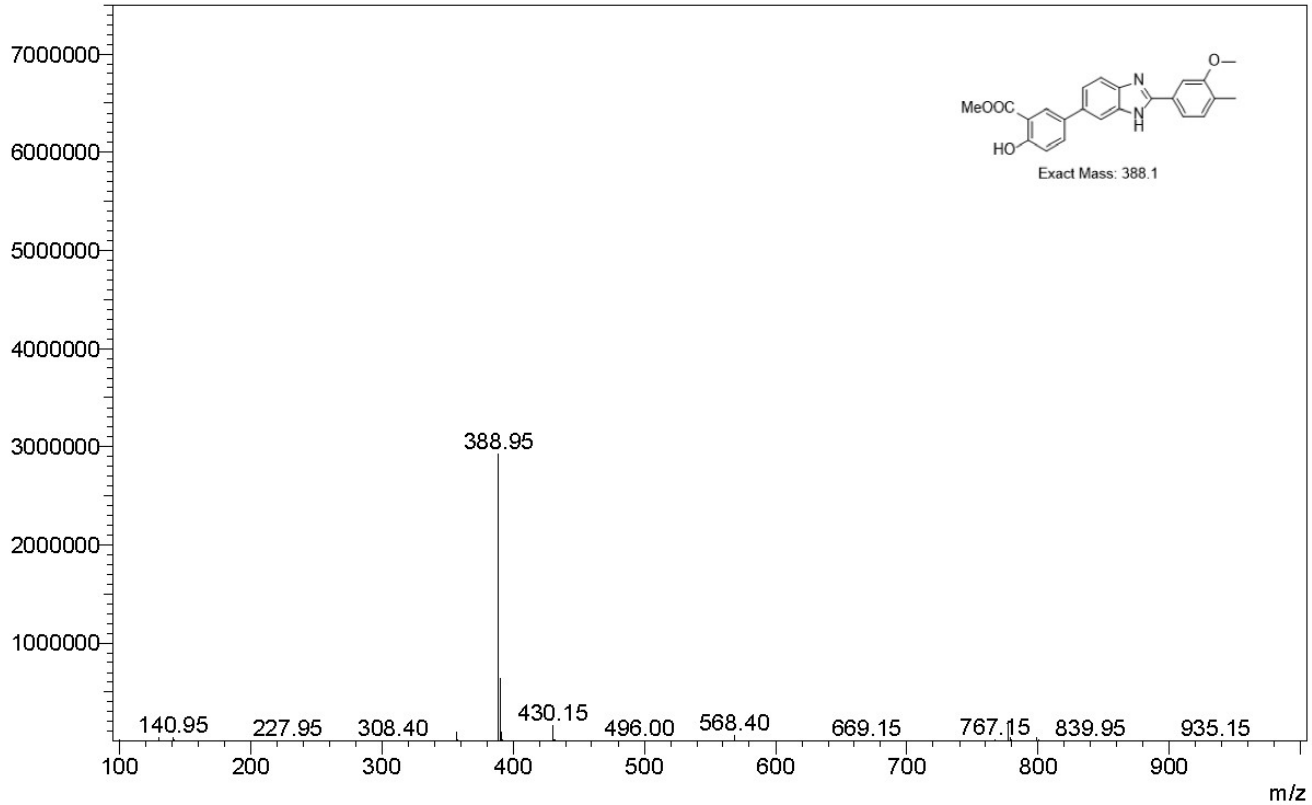
HRMS (ESI) for compound **5m**.



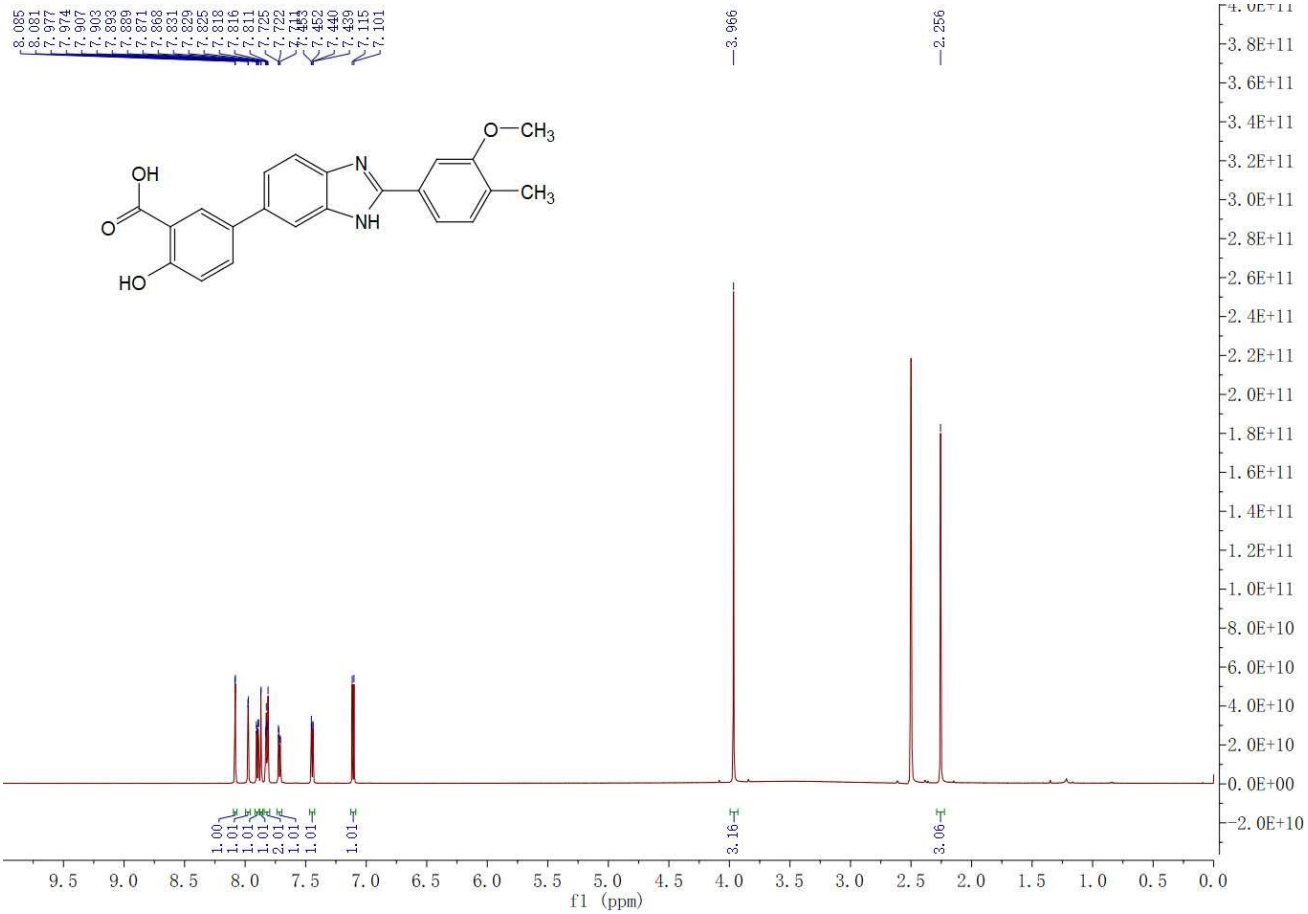
^{1}H-NMR spectrum for compound **4n**.



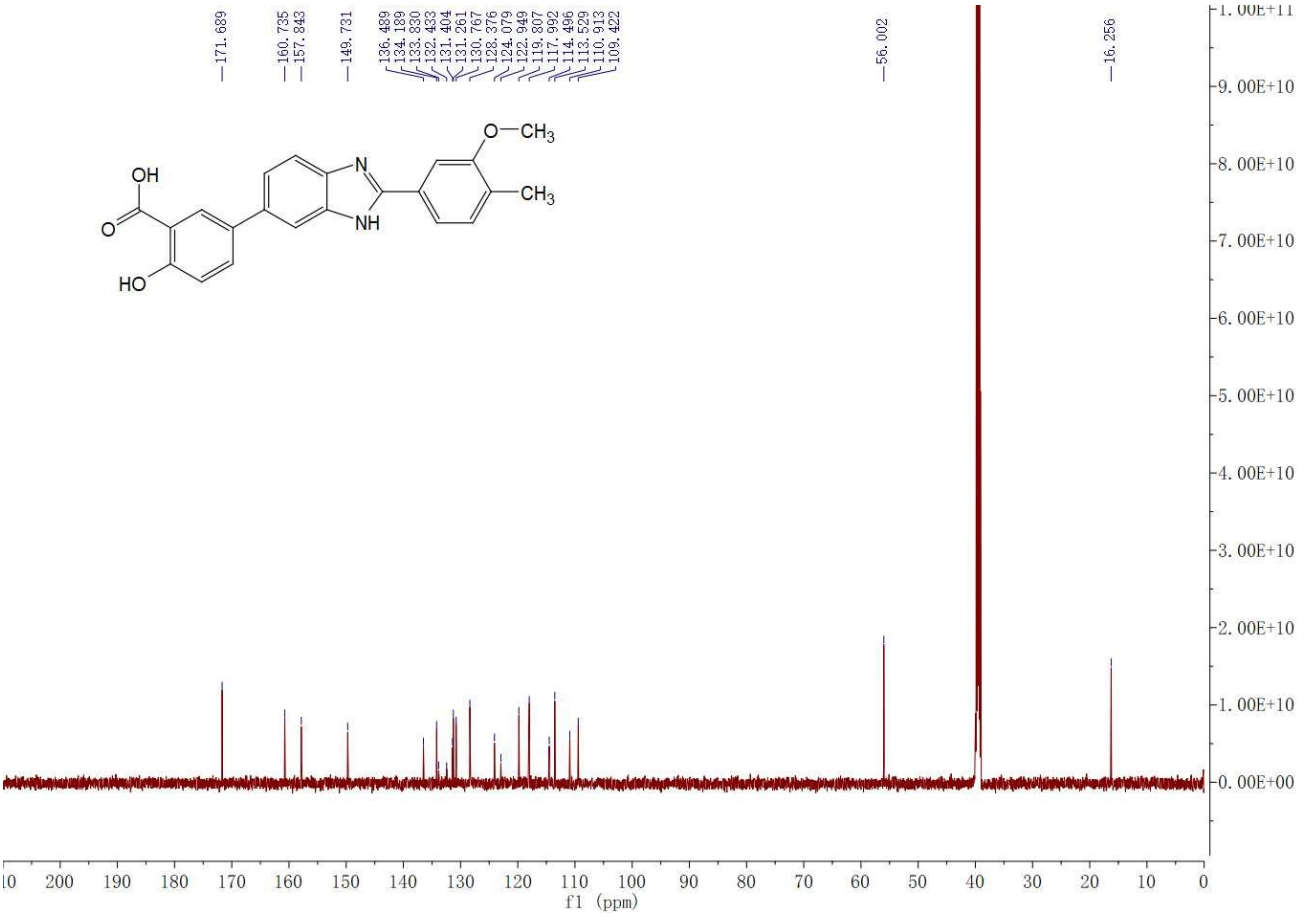
MS (ESI) for compound **4n**.



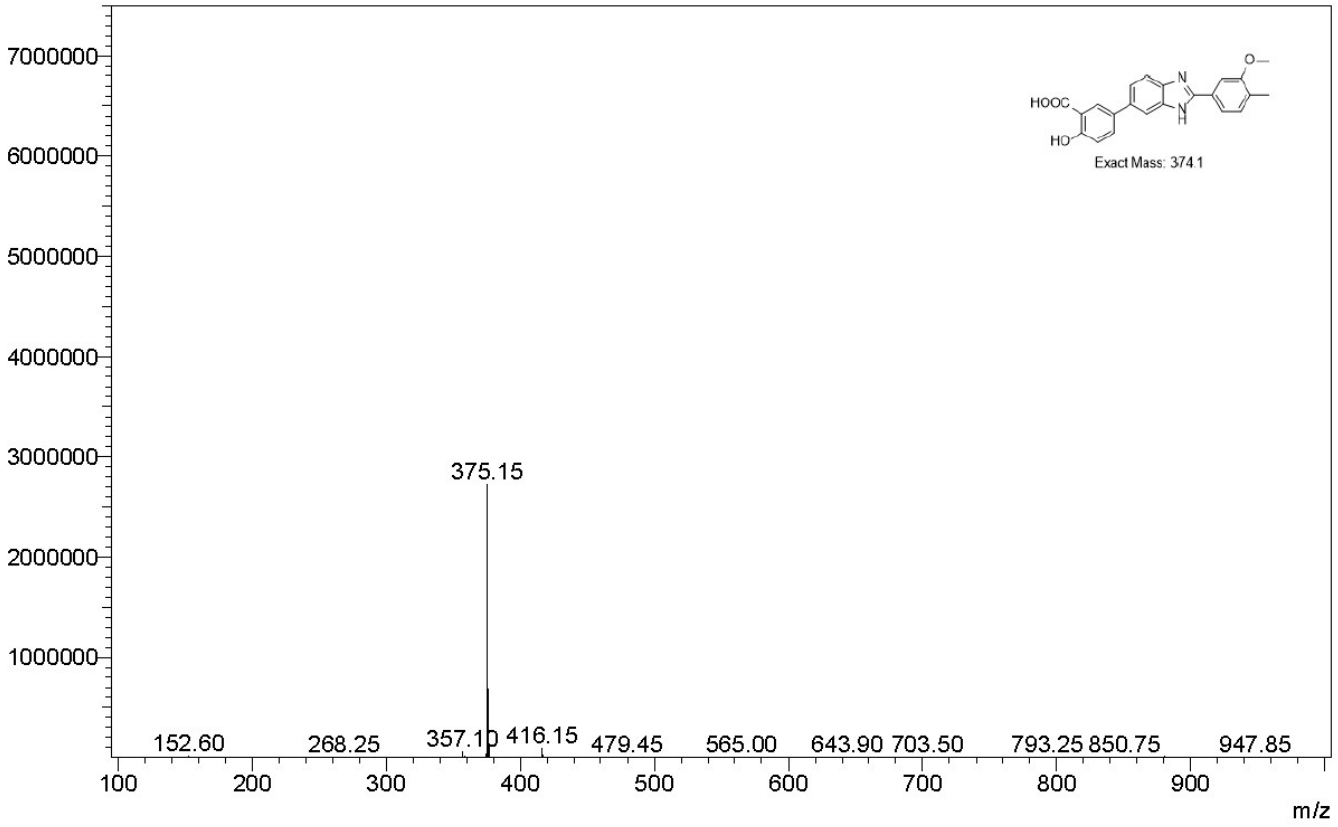
[1]H-NMR spectrum for compound **5n**.



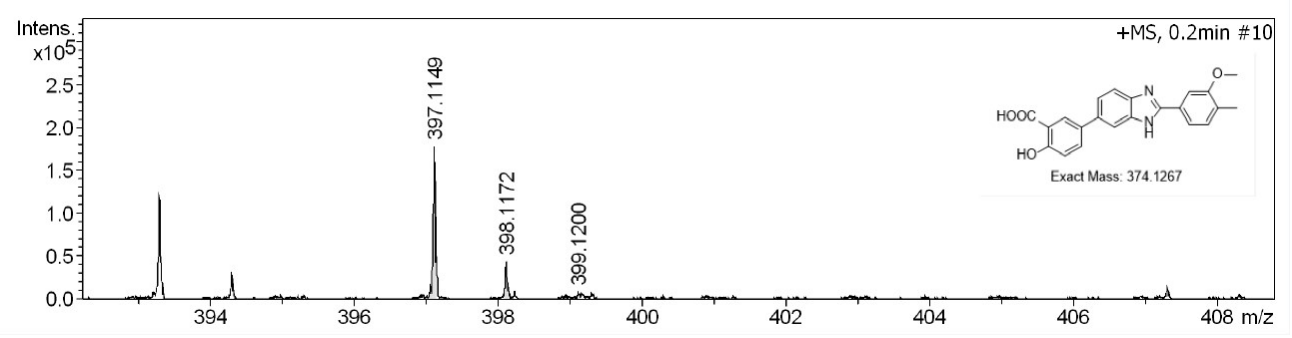
^{13}C-NMR spectrum for compound **5n**.



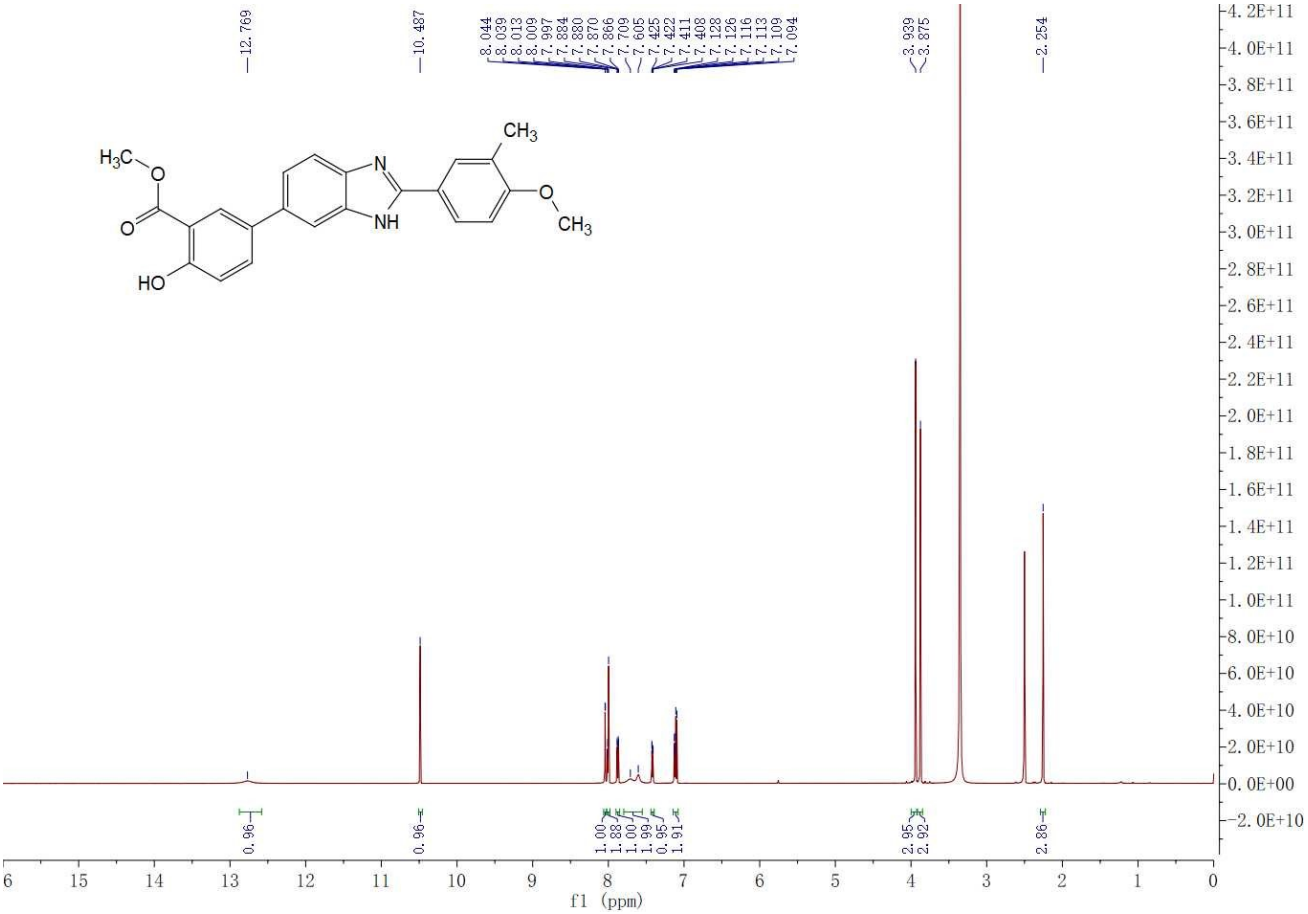
MS (ESI) for compound **5n**.



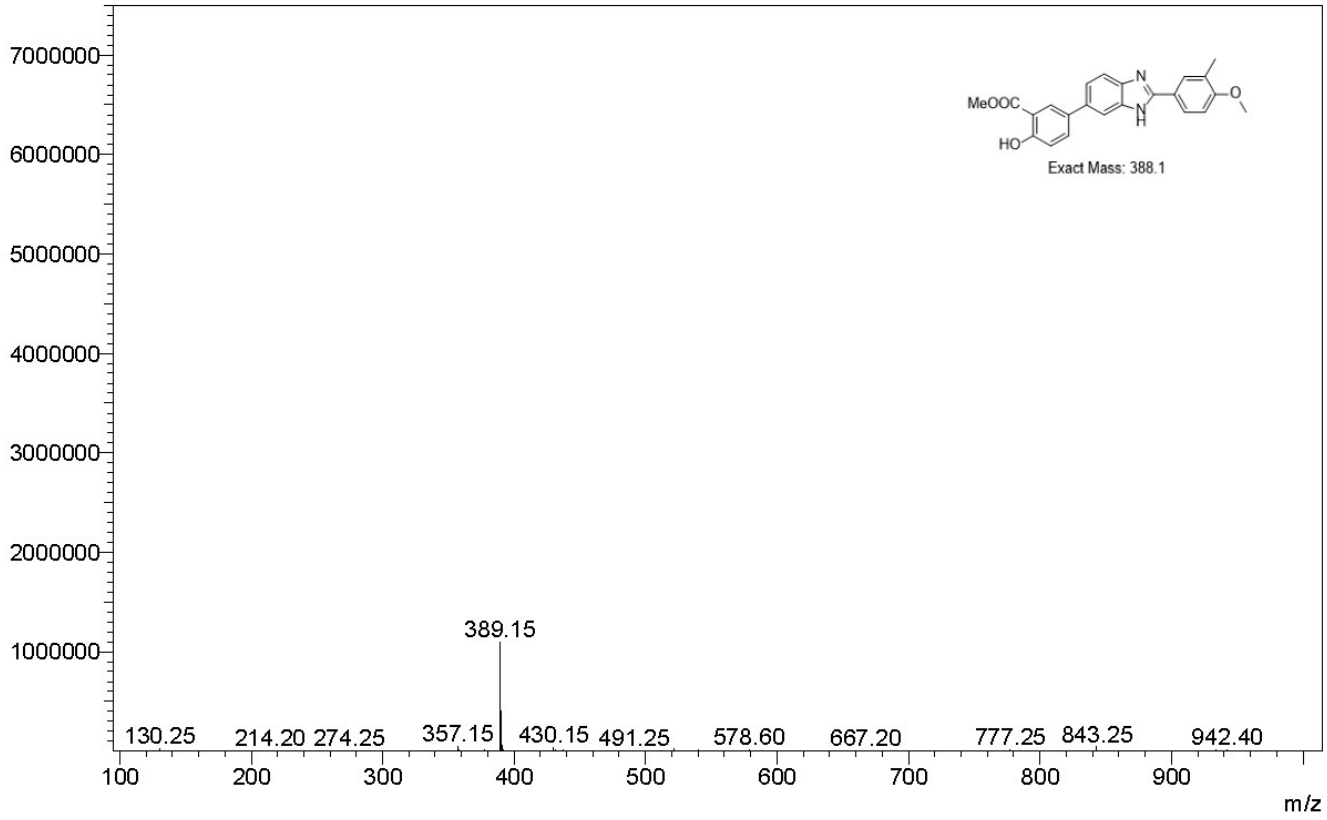
HRMS (ESI) for compound **5n**.



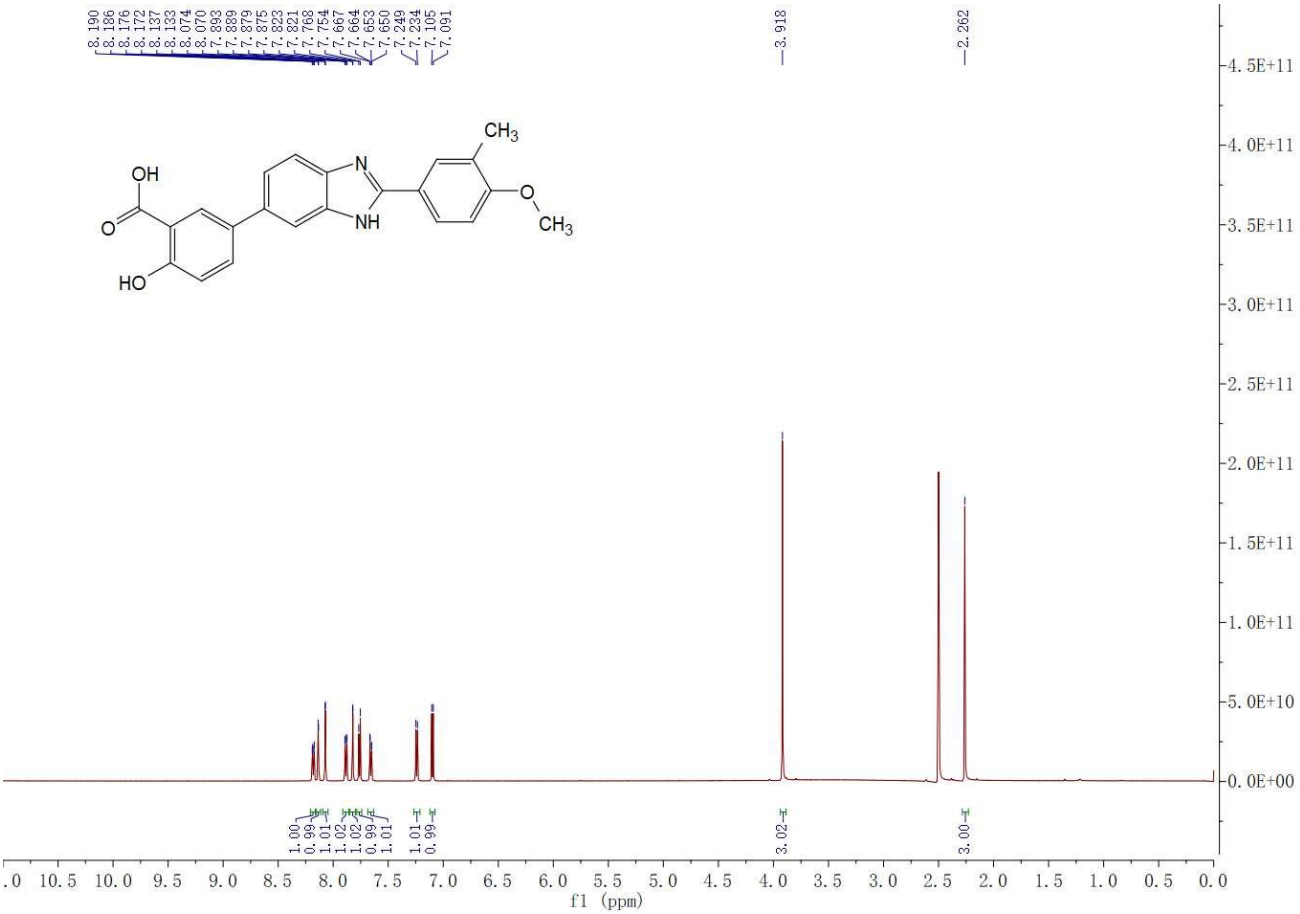
^{1}H-NMR spectrum for compound **4o**.



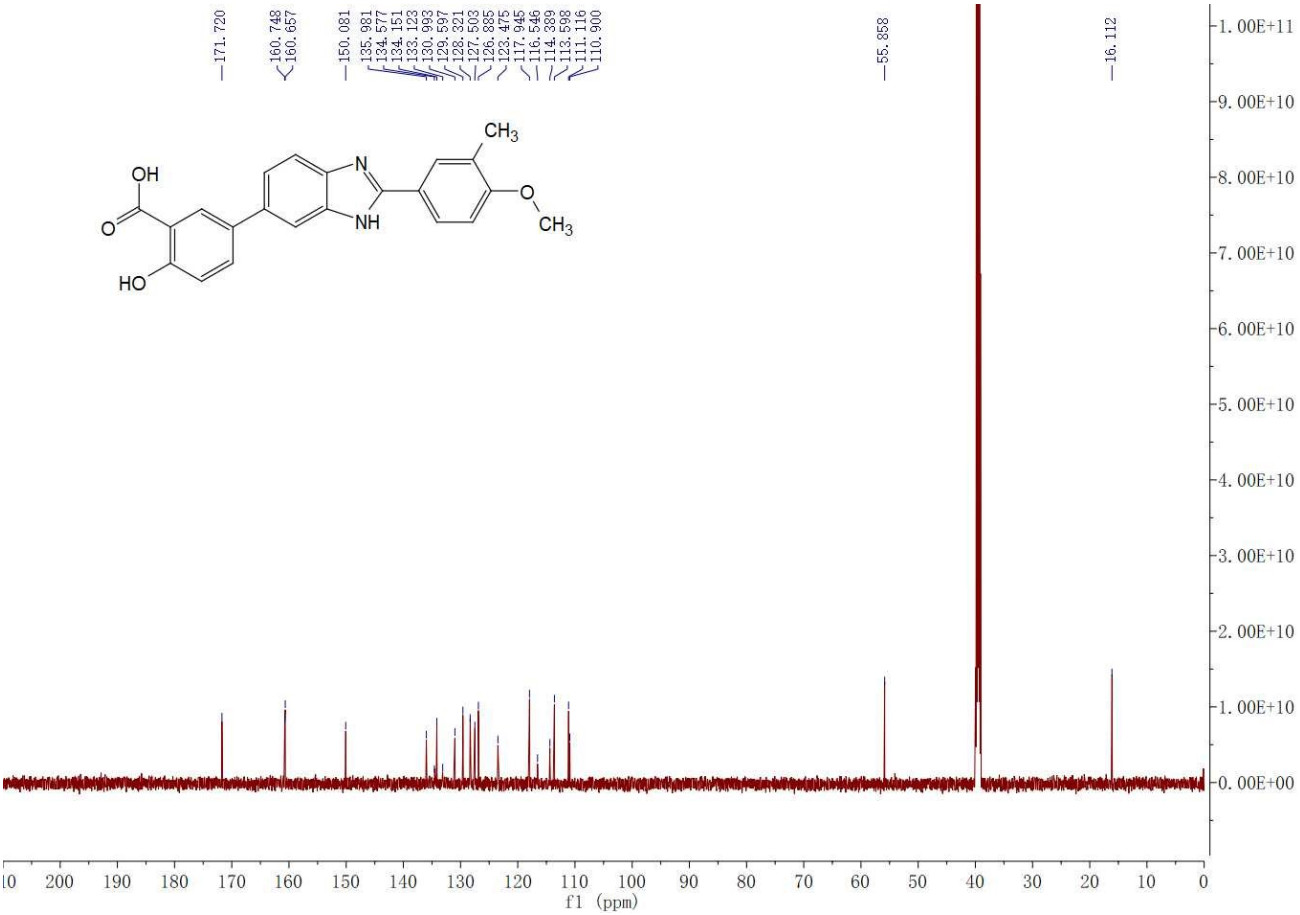
MS (ESI) for compound **4o**.



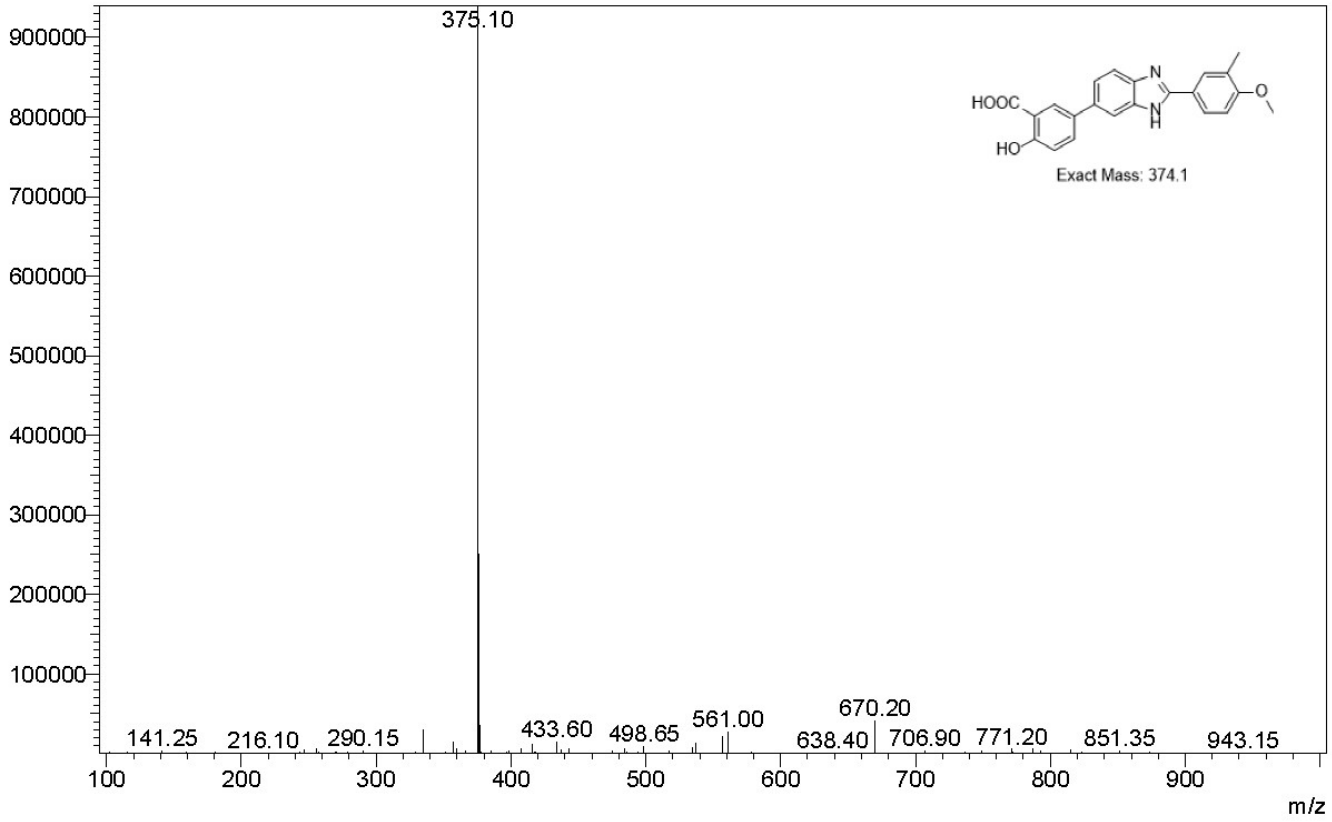
[1]H-NMR spectrum for compound **5o**.



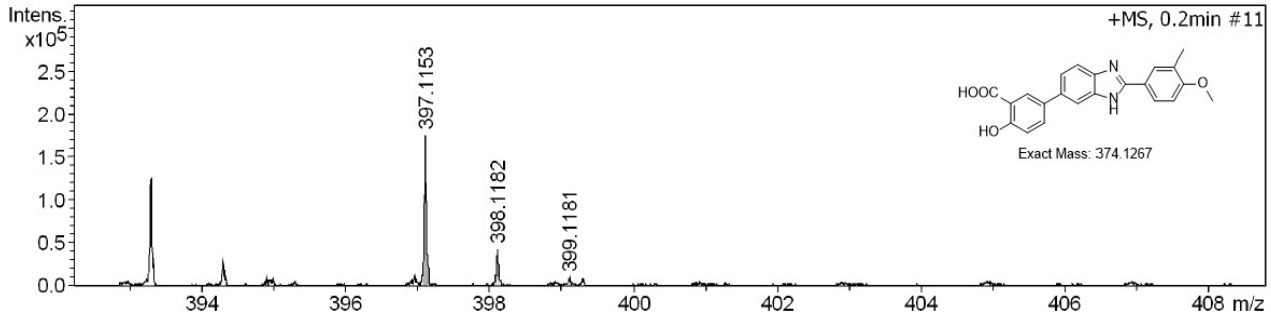
^{13}C-NMR spectrum for compound **5o**.



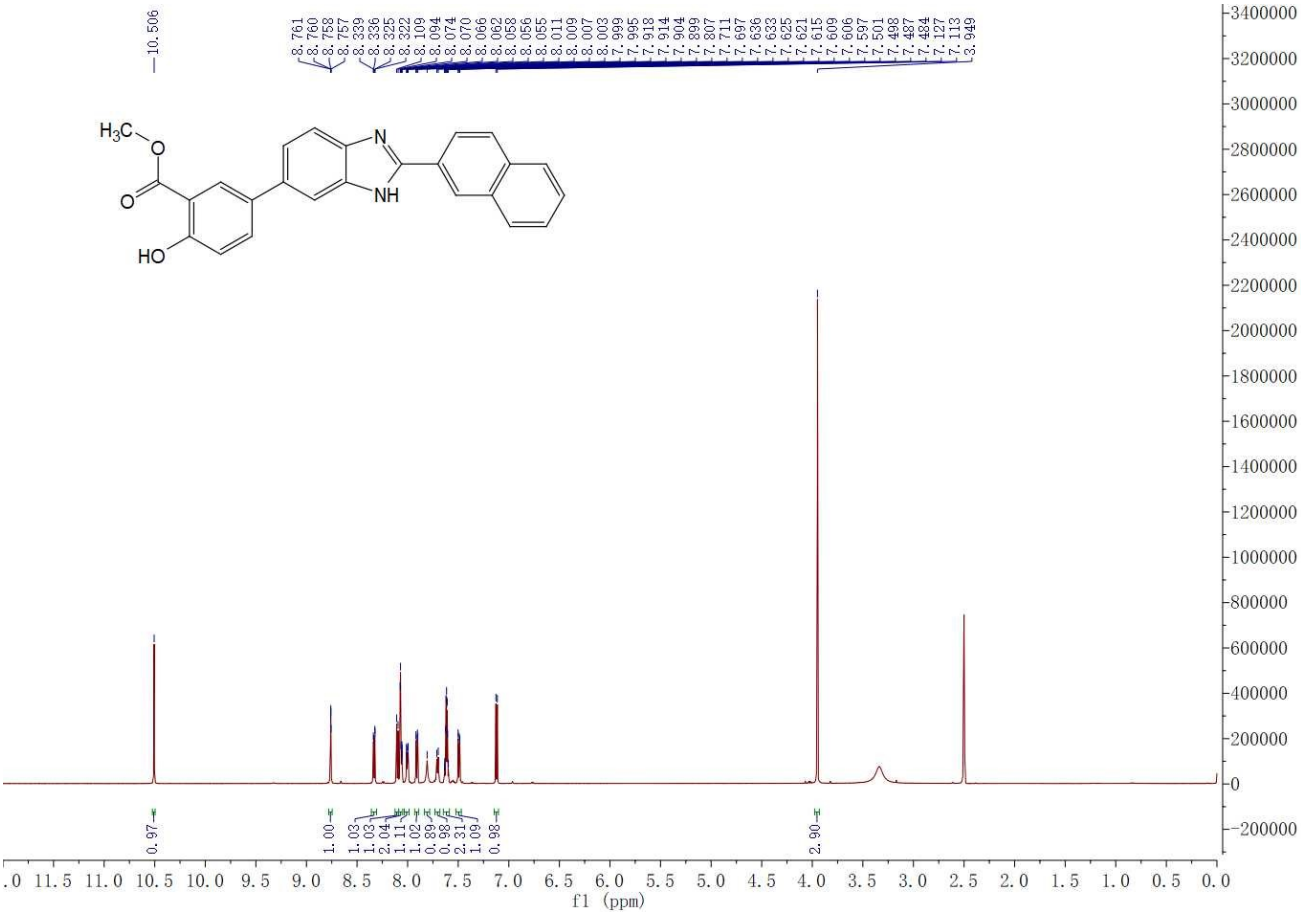
MS (ESI) for compound **5o**.



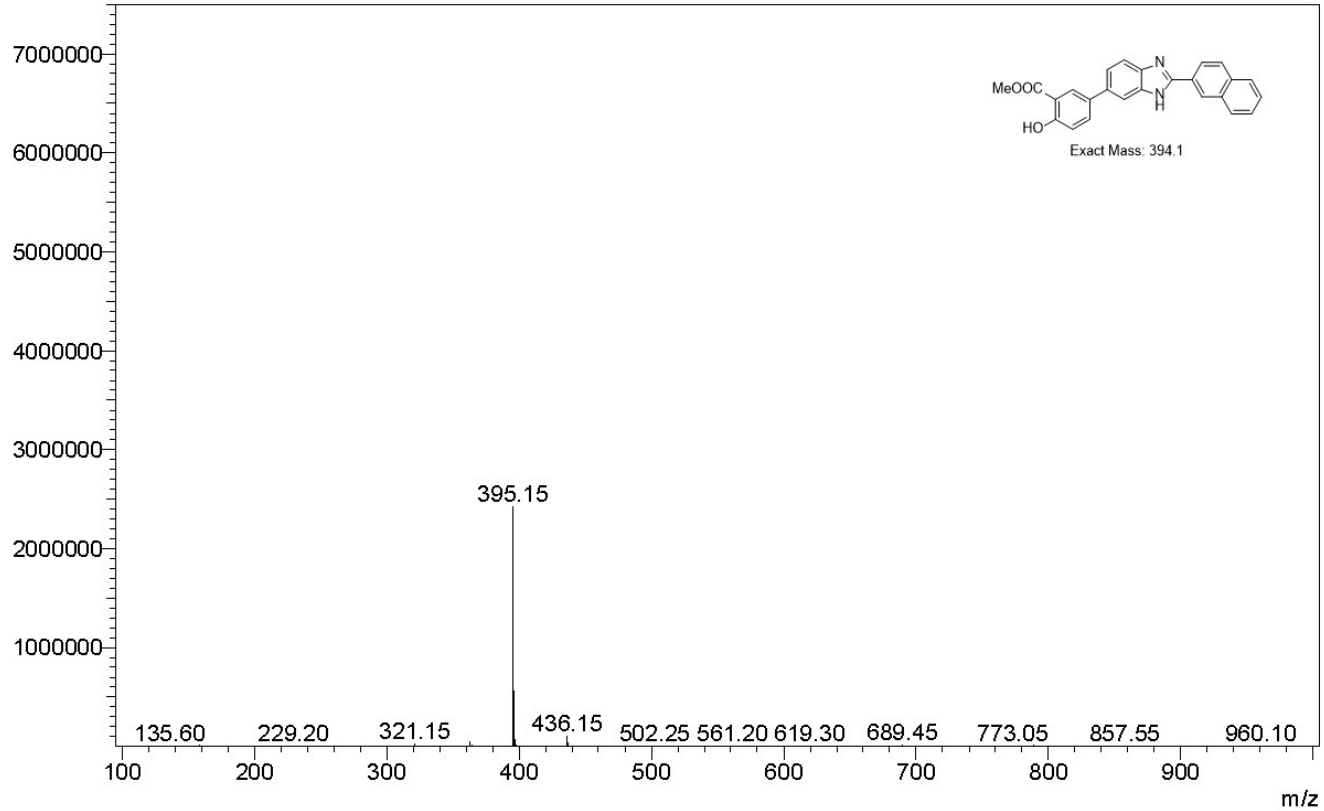
HRMS (ESI) for compound **5o**.



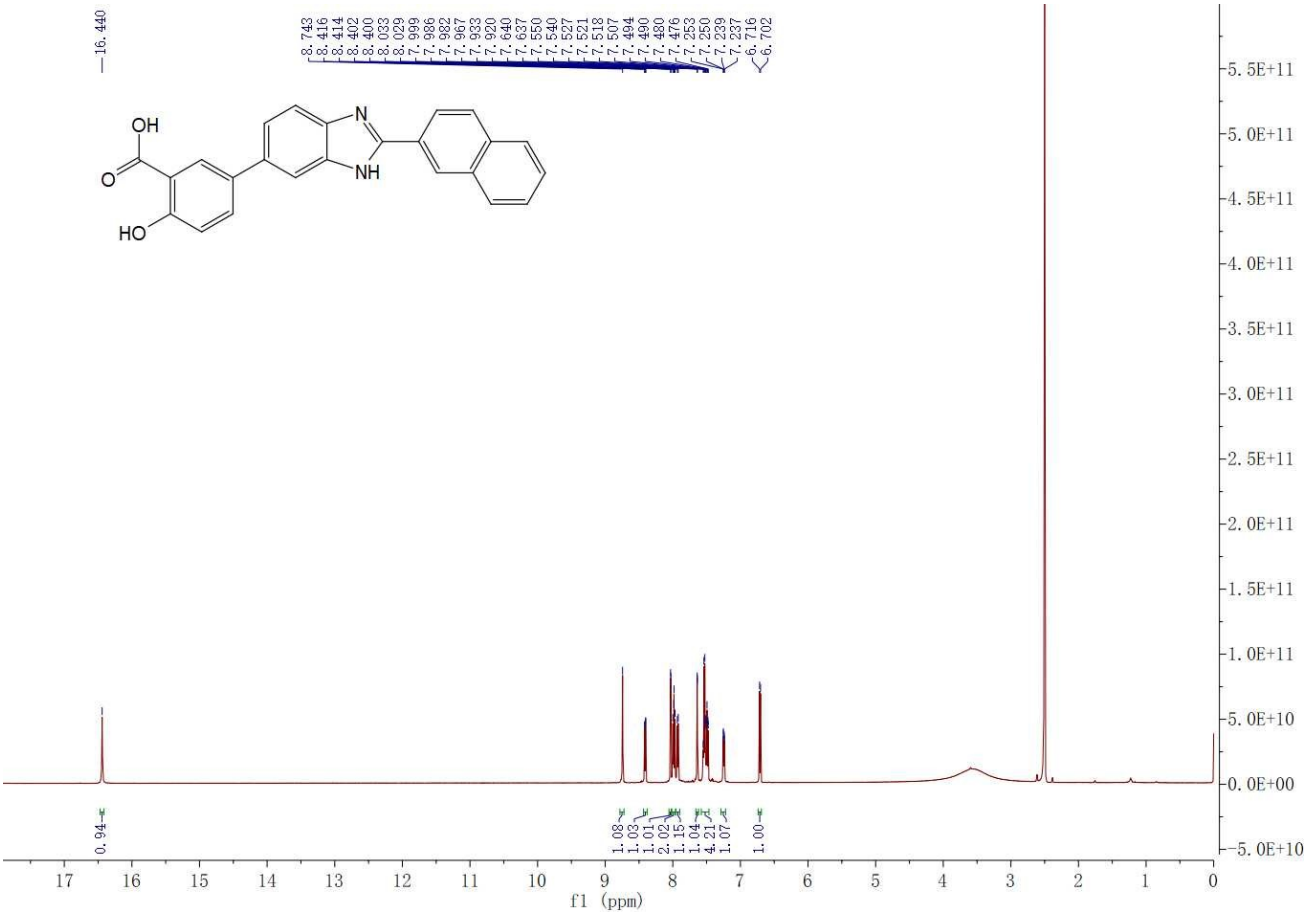
[1]H-NMR spectrum for compound **4p**.



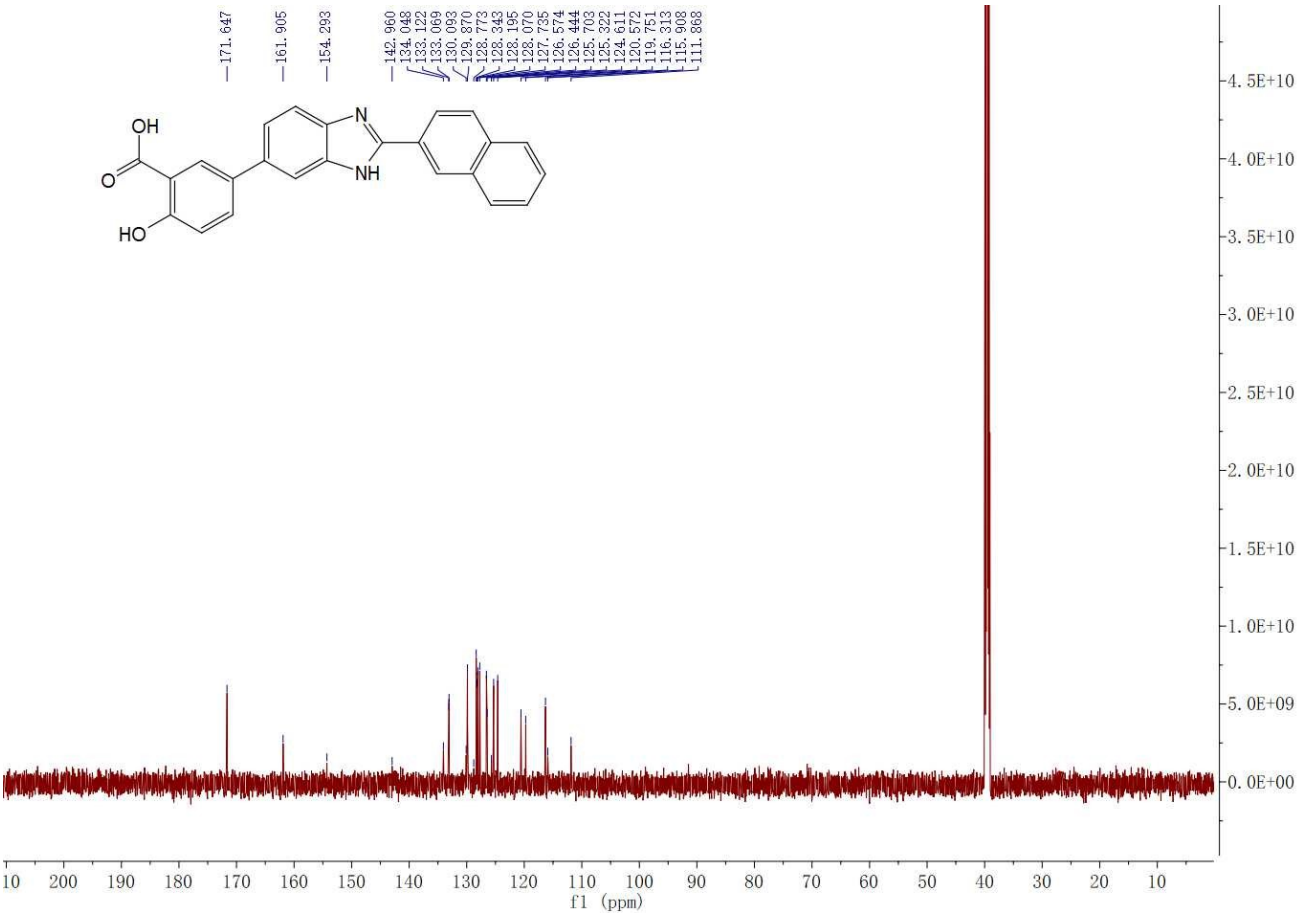
MS (ESI) for compound **4p**.



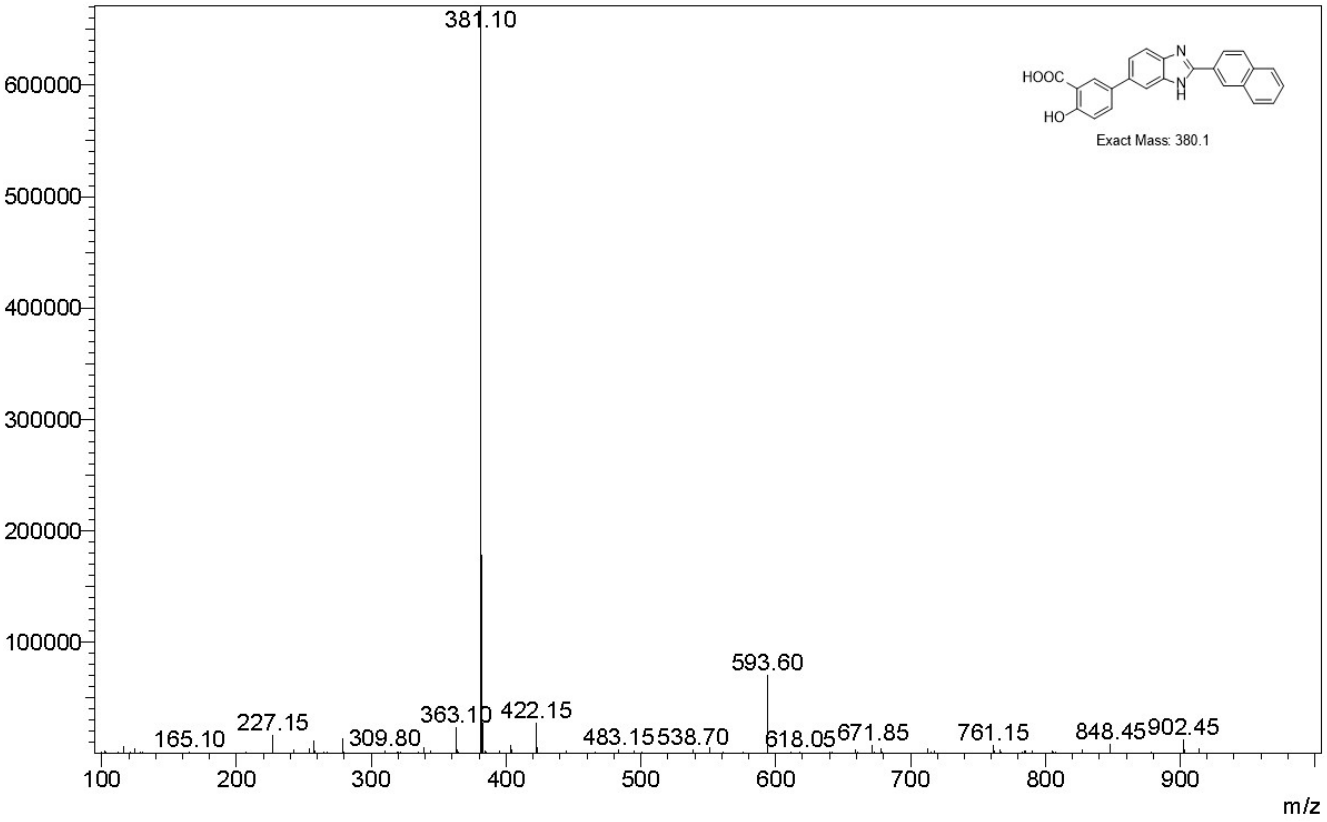
[1]H-NMR spectrum for compound **5p**.



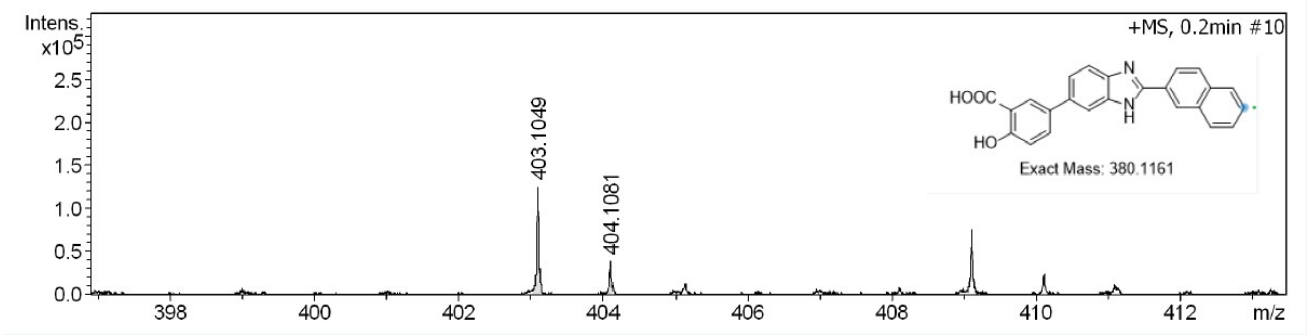
^{13}C-NMR spectrum for compound **5p**.



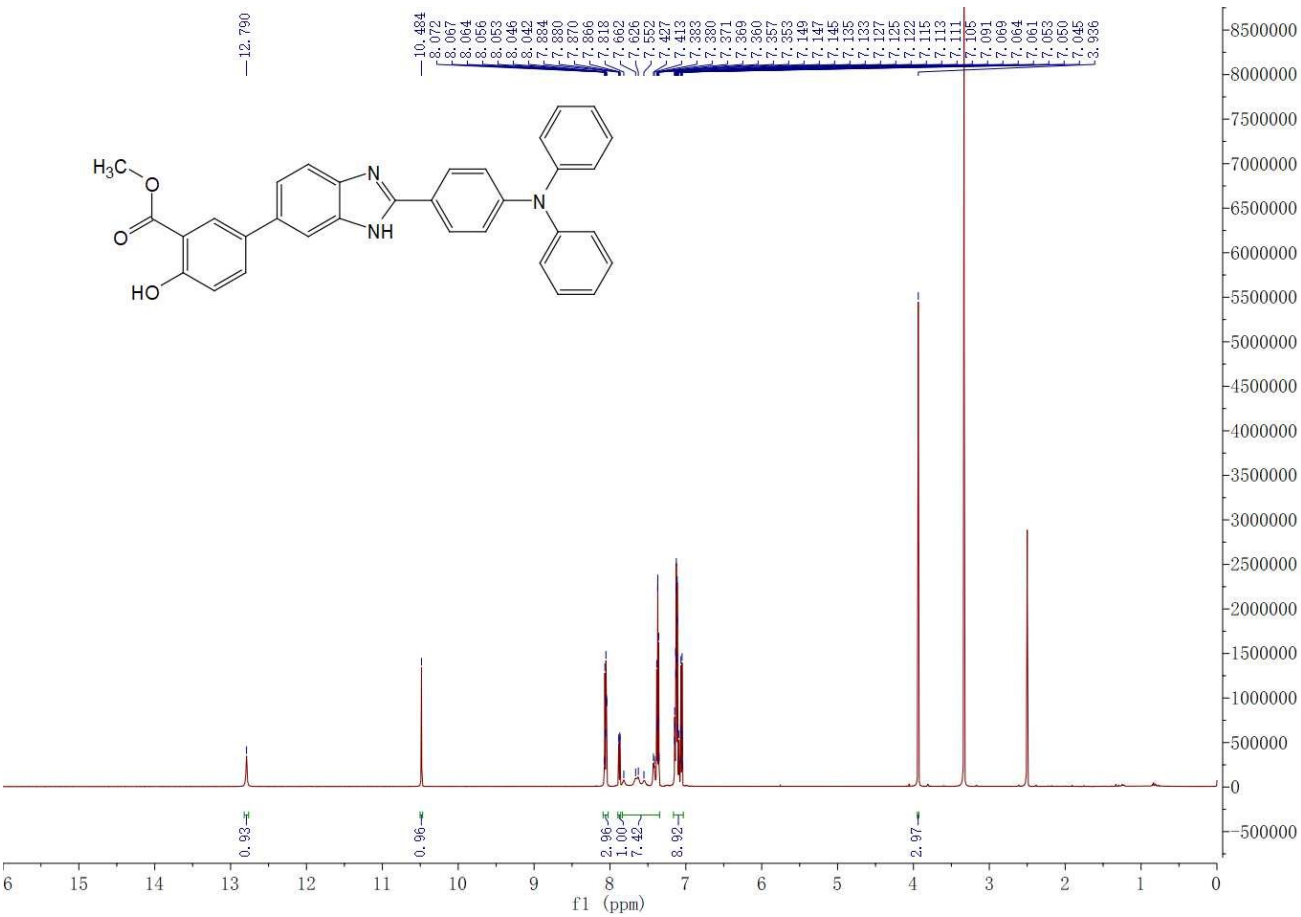
MS (ESI) for compound **5p**.



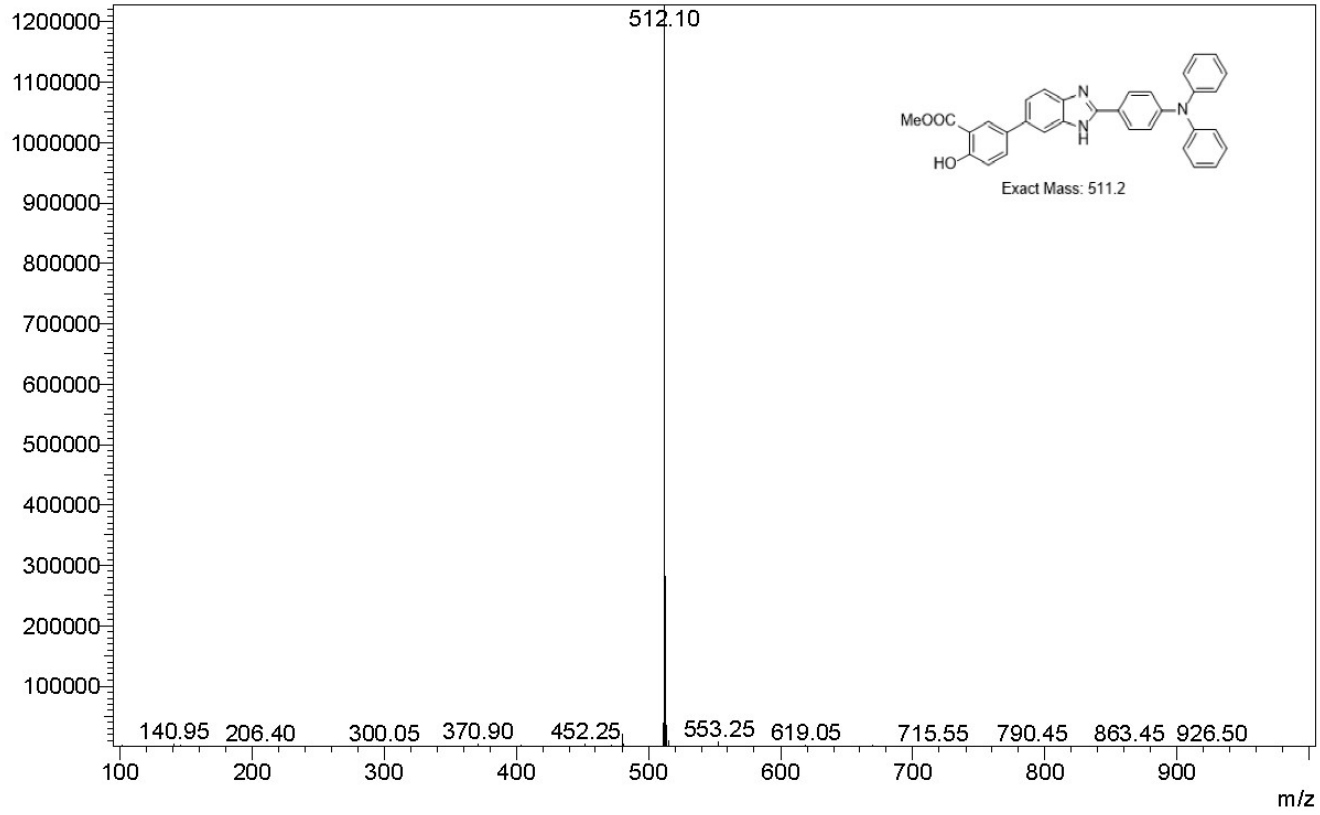
HRMS (ESI) for compound **5p**.



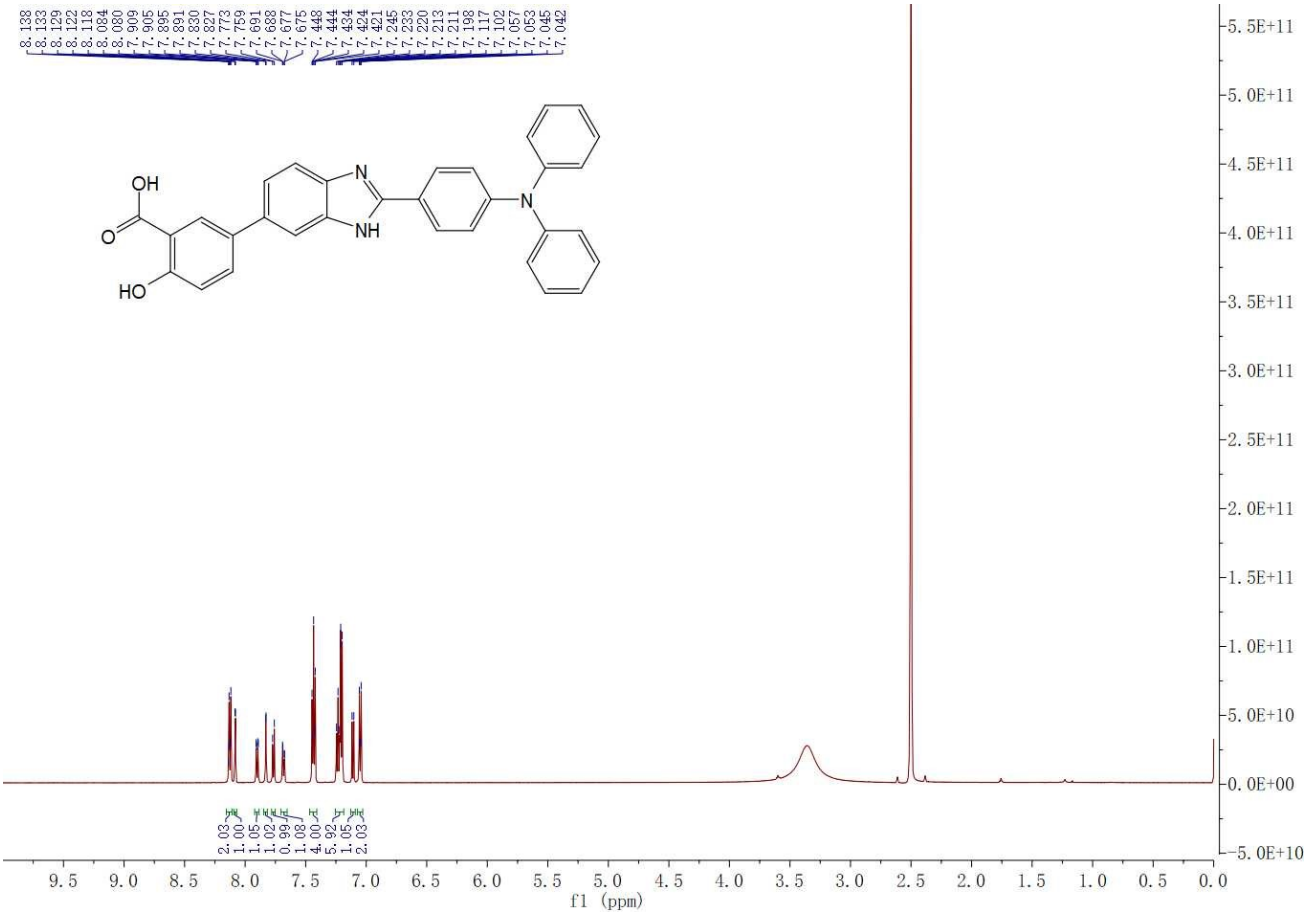
^{1}H-NMR spectrum for compound **4q**.



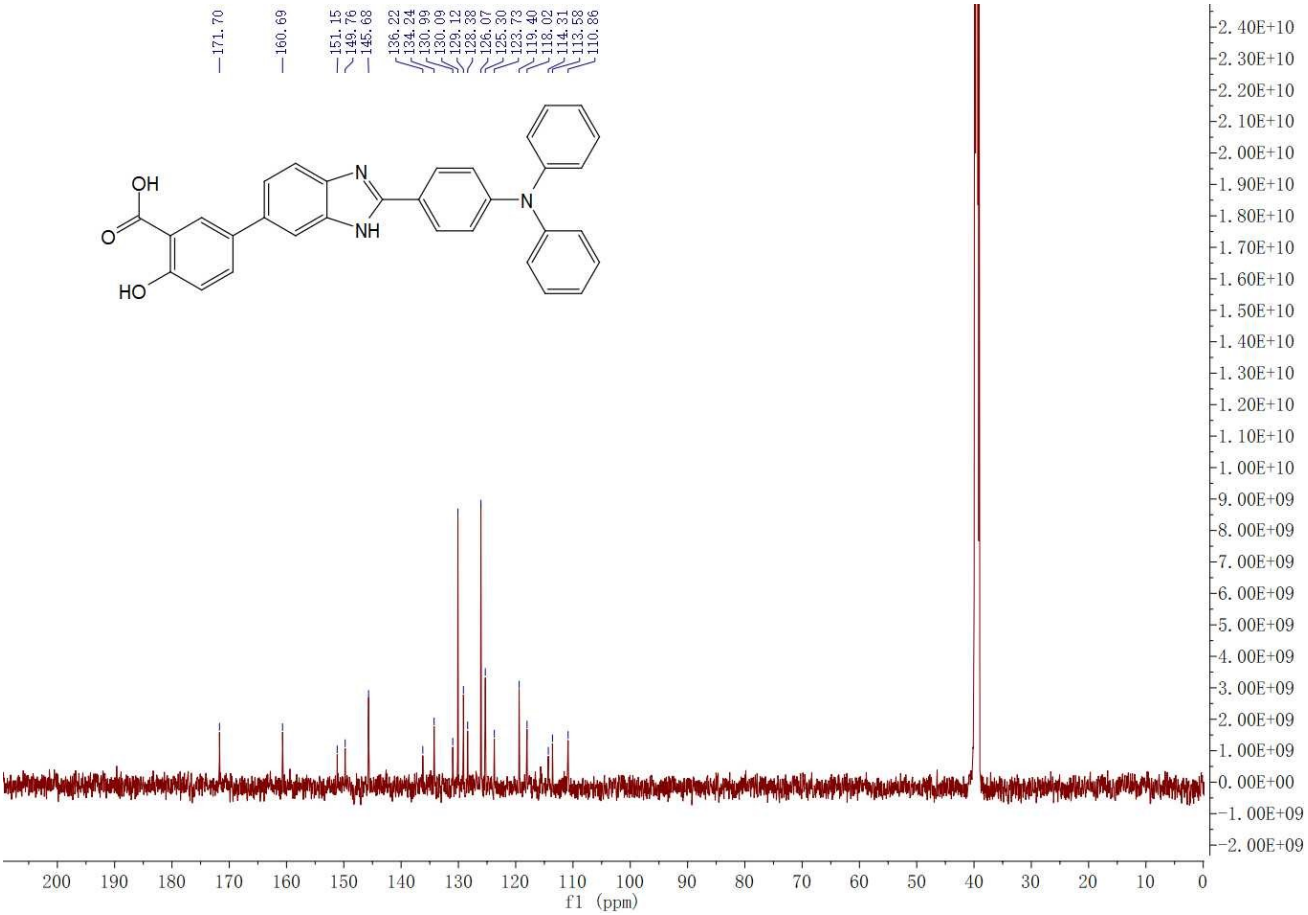
MS (ESI) for compound **4q**.



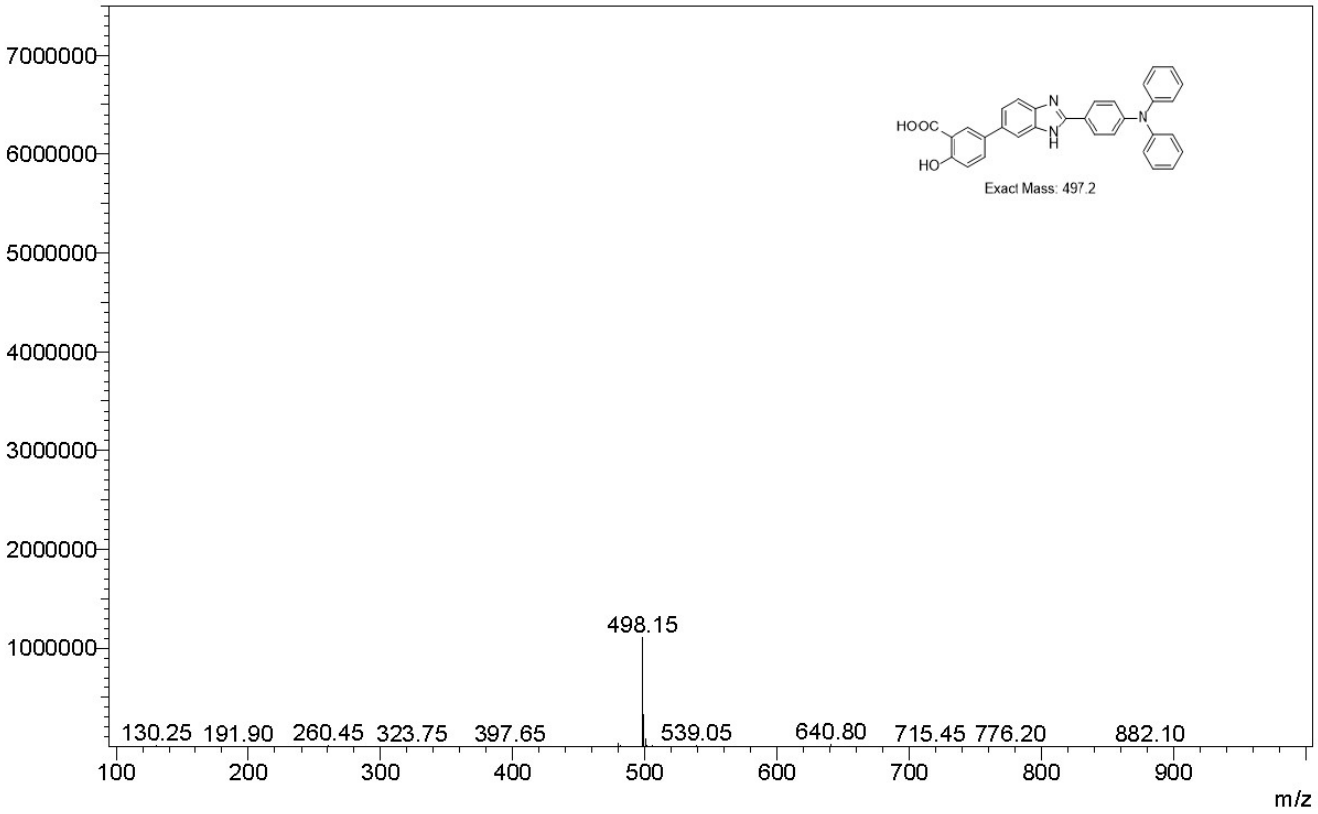
[1]H-NMR spectrum for compound **5q**.



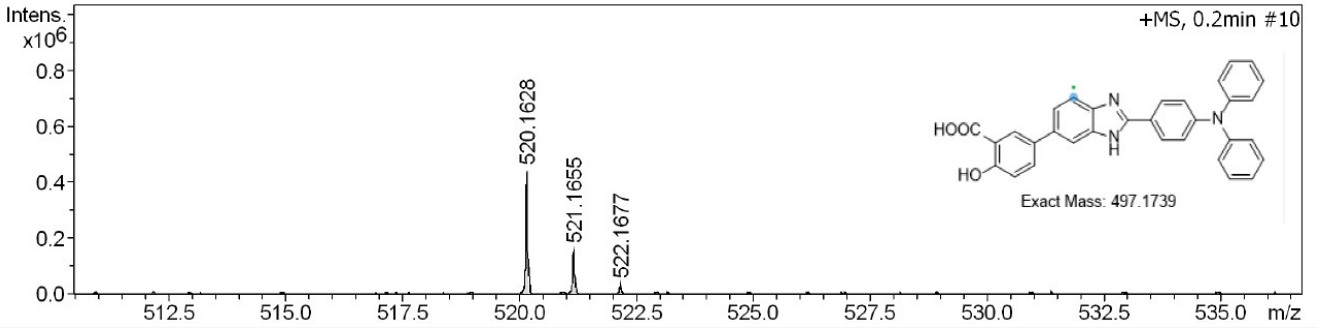
^{13}C-NMR spectrum for compound **5q**.



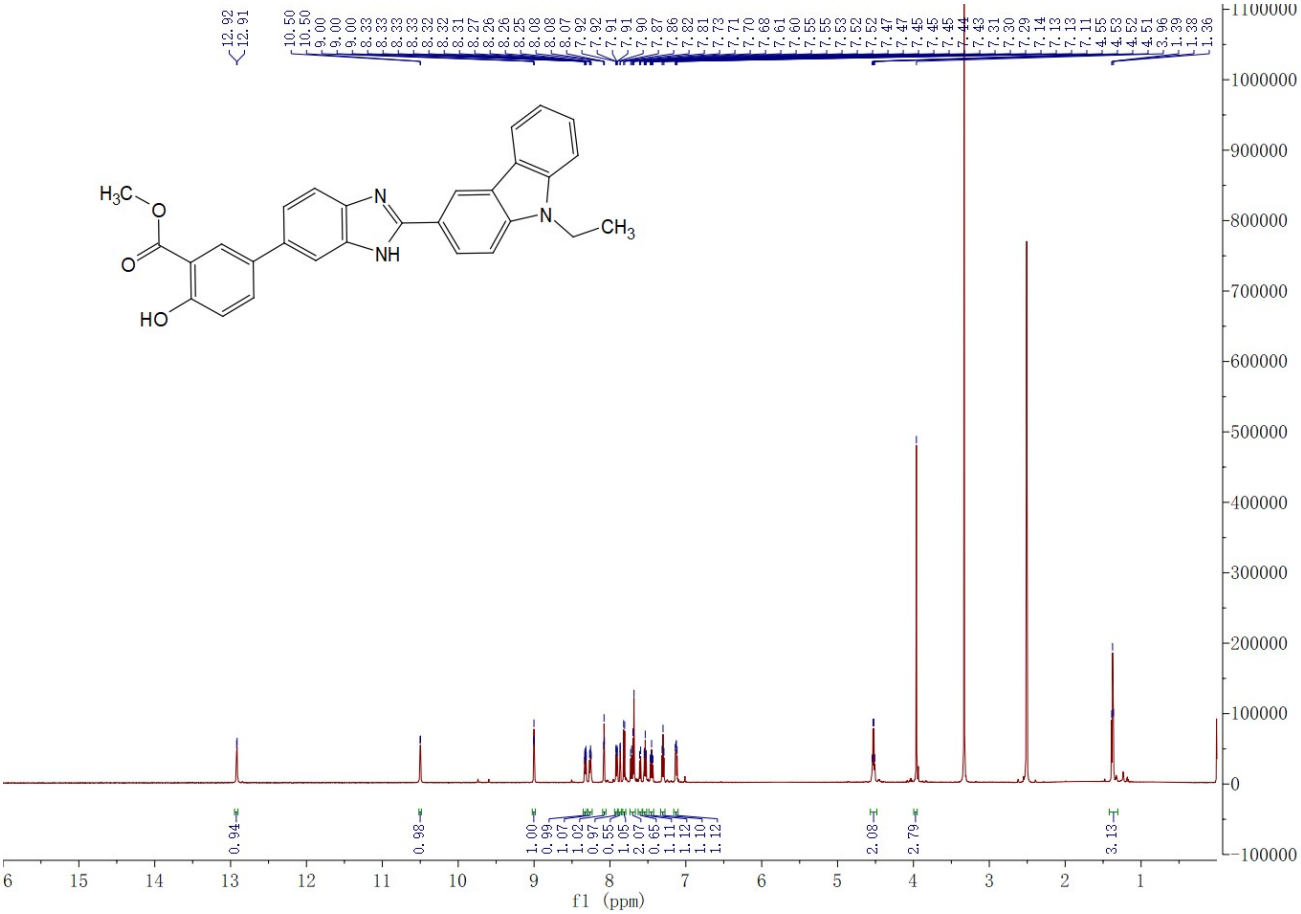
MS (ESI) for compound **5q**.



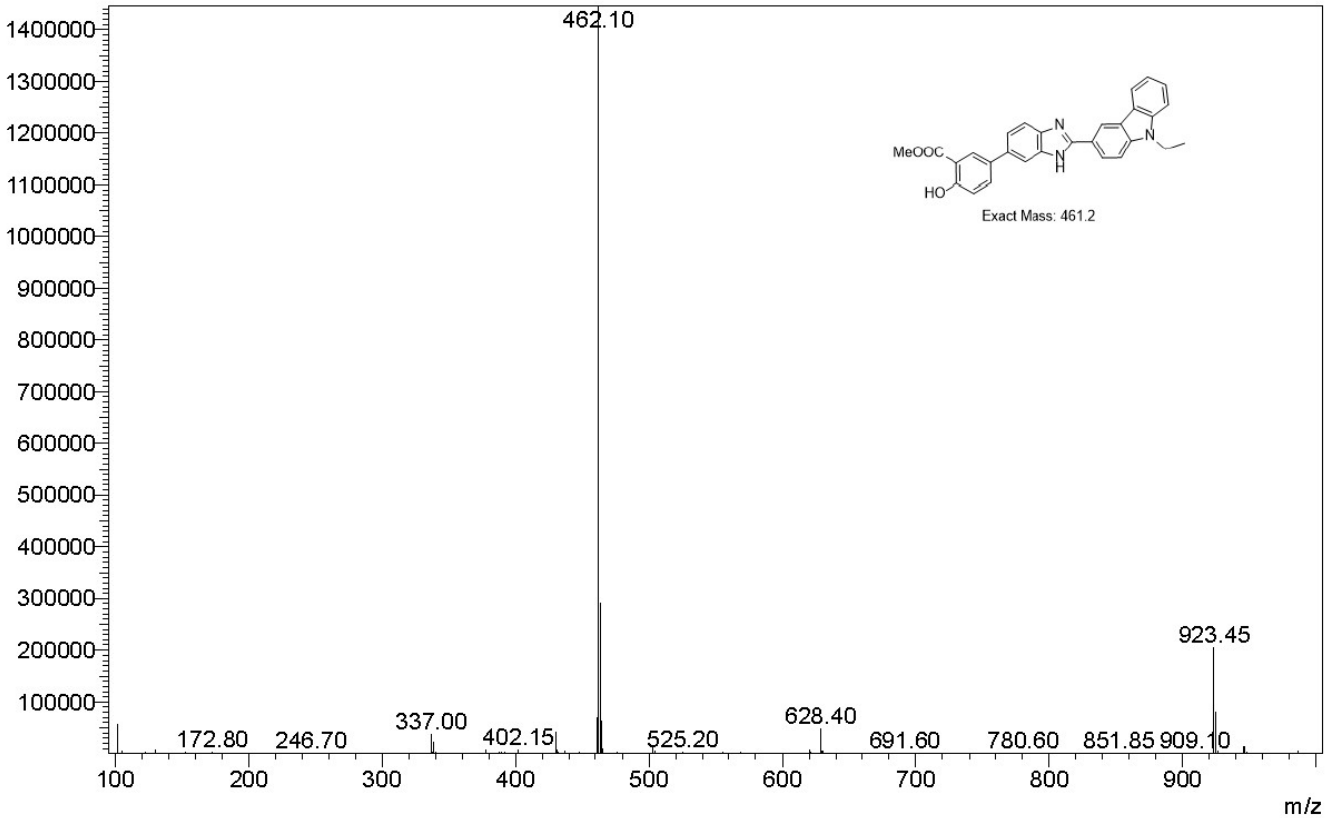
HRMS (ESI) for compound **5q**.



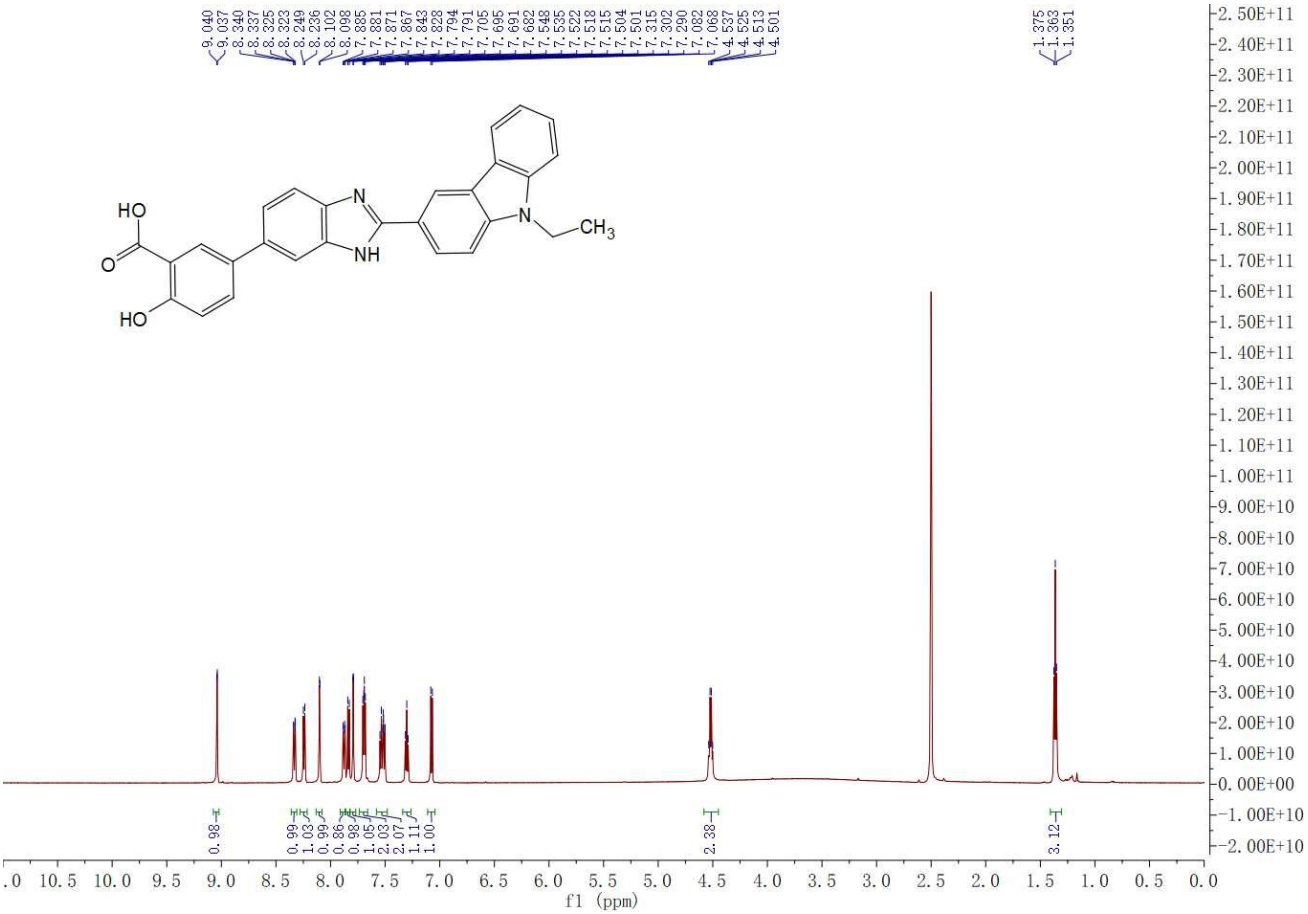
^{1}H-NMR spectrum for compound **4r**.



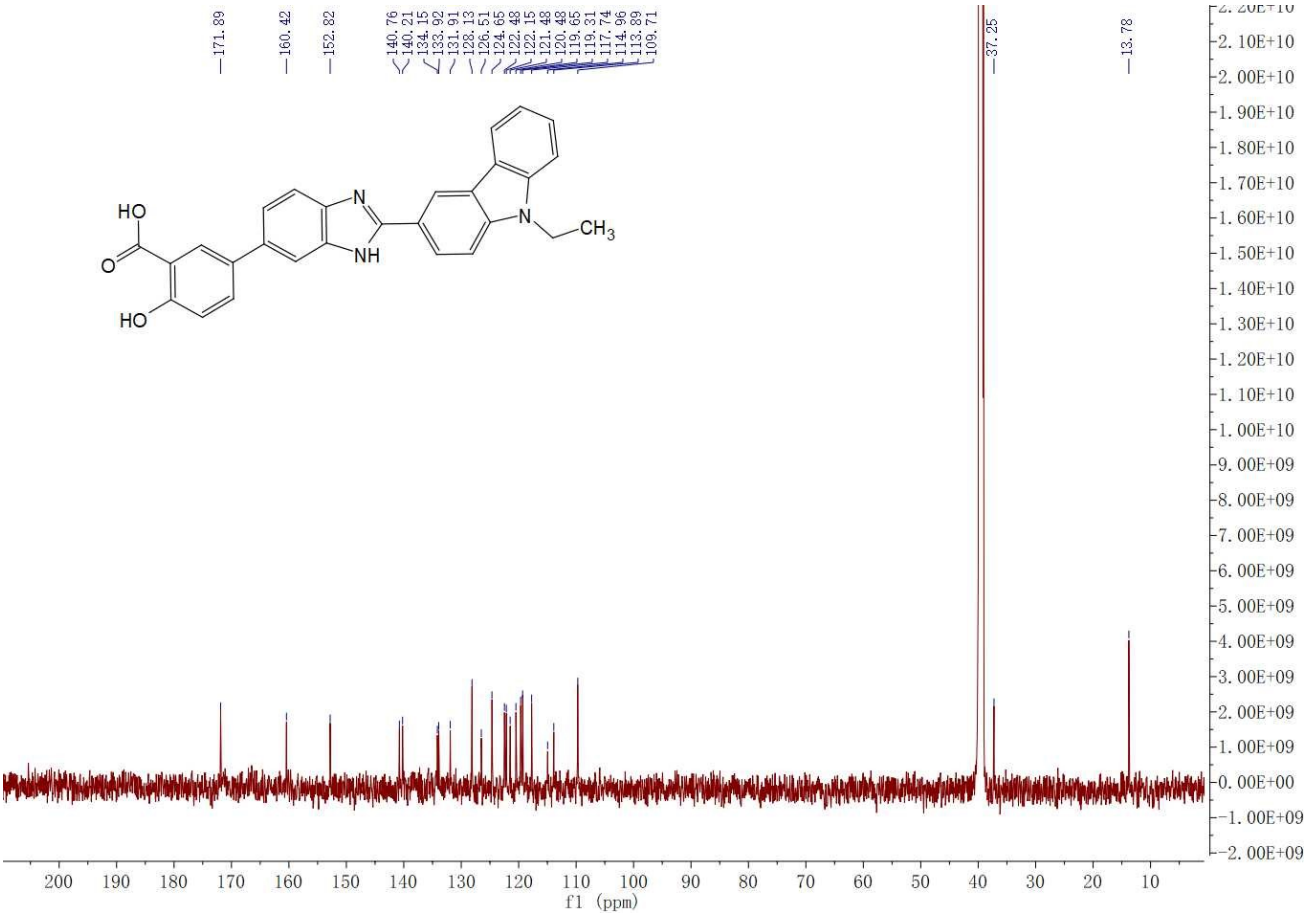
MS (ESI) for compound **4r**.



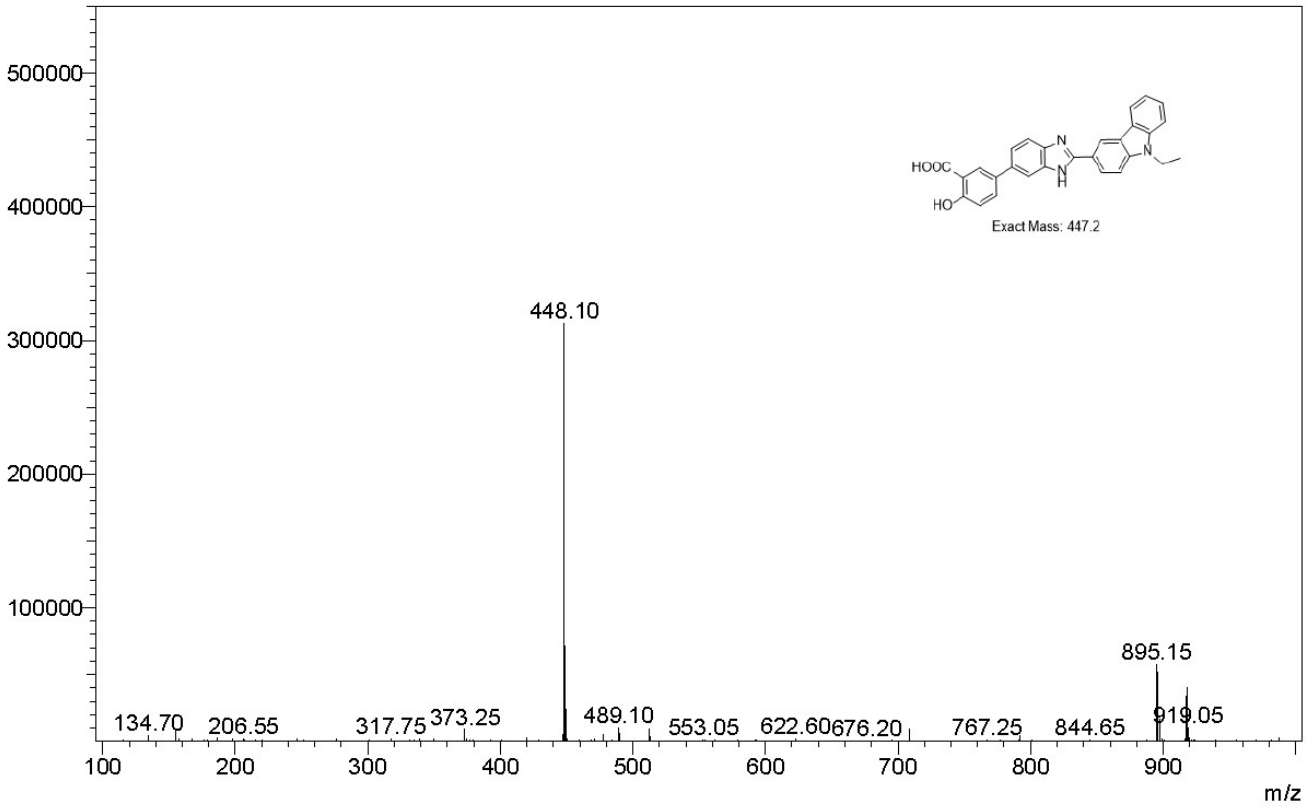
[1]H-NMR spectrum for compound **5r**.



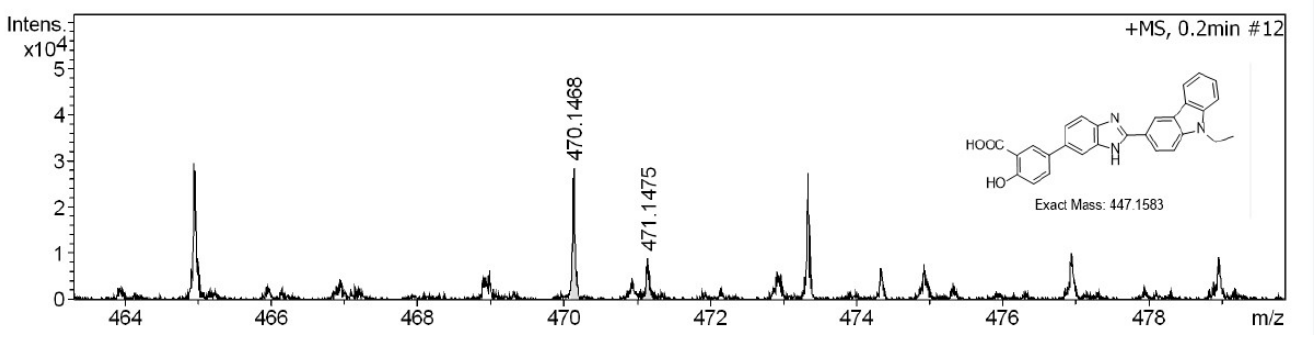
^{13}C-NMR spectrum for compound **5r**.



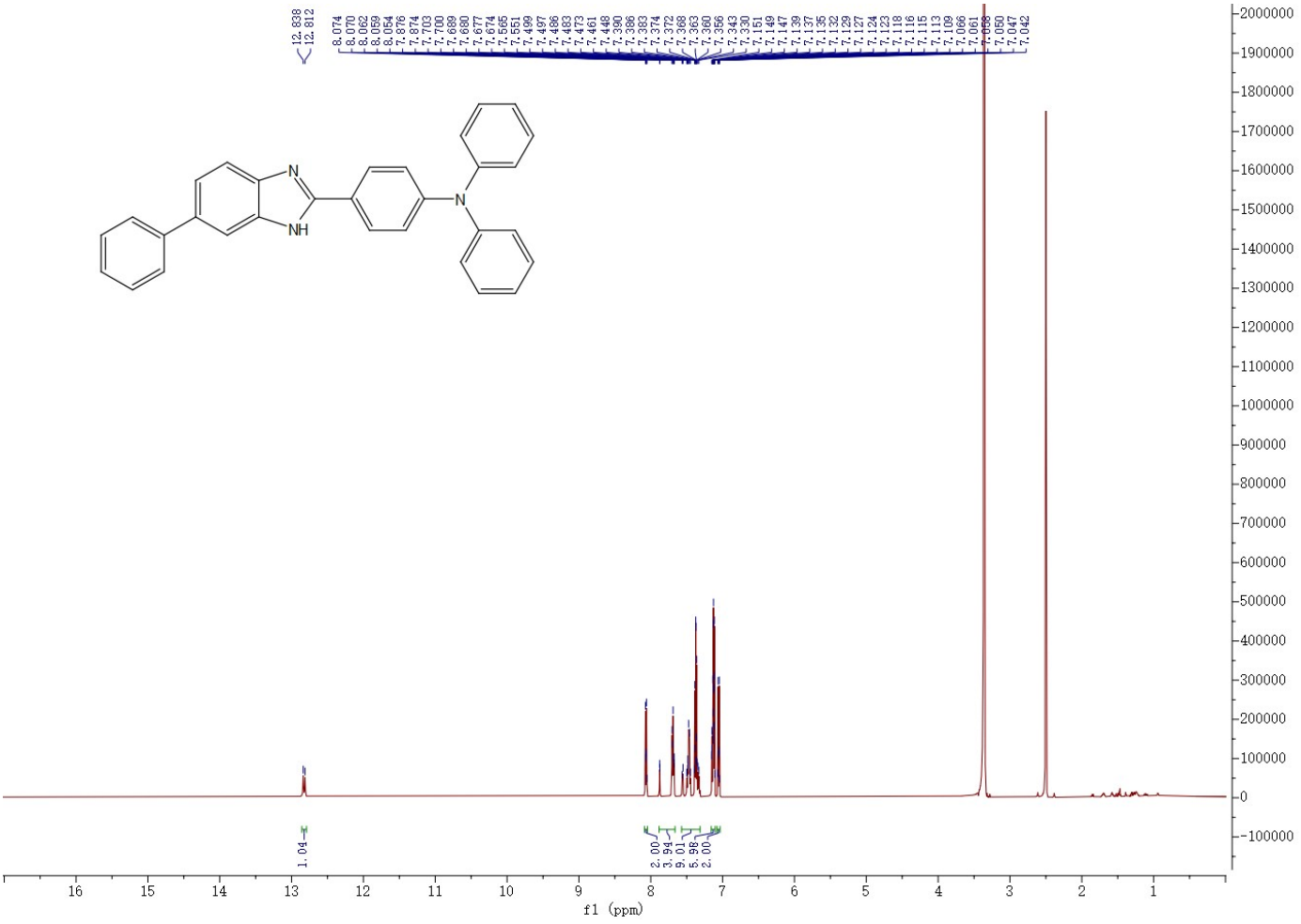
MS (ESI) for compound **5r**.



HRMS (ESI) for compound **5r**.



^{1}H-NMR spectrum for compound **6**.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8.070
8.062
8.059
8.054
7.876
7.874
7.703
7.700
7.689
7.680
7.677
7.674
7.565
7.551
7.499
7.497
7.486
7.483
7.473
7.461
7.448
7.390
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7.383
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7.139
7.137
7.135
7.132
7.129
7.127
7.124
7.123
7.118
7.116
7.115
7.113
7.109
7.066
7.061
7.058
7.050
7.047
7.042
N
NH
N
1.04
2.00
3.94
9.01
5.98
2.00
f1 (ppm)