Fluorescent Boron (III) Iminocoumarins (Borico)

Denis Frath, Arnaud Poirel, Gilles Ulrich, Antoinette De Nicola and Raymond Ziessel*

Supporting Information (27 pages)

Table of contents

1) General Methods

All chemicals were used as received from commercial sources without further purification. Dichloroethane was distilled according common procedure and other reaction solvents were used as received from commercial sources. Thin layer chromatography (TLC) was performed on silica gel or aluminium oxide plates coated with fluorescent indicator. Chromatographic purifications were conducted using 40-63 µm silica gel. All mixtures of solvents are given in *v*/*v* ratio.

The 300 (^{1}H), 400 (^{1}H), 75 (^{13}C), 100 (^{13}C) 128 (^{11}B) MHz NMR spectra were recorded at room temperature with perdeuterated solvents with residual protonated solvent signals as internal references. The 128 (^{11}B) MHz NMR spectra were recorded at room temperature with borosilicate glass as reference. UV-vis spectra were recorded using a dual-beam grating spectrophotometer with a 1 cm quartz cell. All fluorescence spectra were corrected. The fluorescence quantum yield (Φ_{cmp}) was calculated from equation:

$$\Phi_{\mathrm{cmp}} = \Phi_{\mathrm{ref}} \frac{\mathrm{I}}{\mathrm{I}_{\mathrm{ref}}} \frac{OD_{ref}}{OD} \frac{n^2}{n_{ref}^2}$$

Here, *I* denotes the integral of the corrected emission spectrum, *OD* is the optical density at the excitation wavelength and η is the refractive index of the medium. Quinine sulfate cresyl violet as reference ($\Phi = 0.55$ $\lambda_{ex} = 546$ nm in ethanol) for dyes **2a**, **2b**, **2c**, **3** and tetramethoxy diisoindolomethene-difluoroborate ($\Phi = 0.51$, λ_{ex}=650 nm in CH_2Cl_2) for dye **4**.

Luminescence lifetimes were measured on a spectrofluorimeter, using software with Time-Correlated Single Photon Mode coupled to a Stroboscopic system. The excitation source was a laser diode (λ 310 nm). No filter was used for the excitation. The instrument response function was determined by using a light-scattering solution (LUDOX).

Electrochemical studies employed cyclic voltammetry with a conventional 3-electrode system using a BAS CV-50W voltammetric analyser equipped with a Pt microdisk (2 mm^2) working electrode and a silver wire counter-electrode. Ferrocene was used as an internal standard and was calibrated against a saturated calomel reference electrode (SCE) separated from the electrolysis cell by a glass frit presoaked with electrolyte solution. Solutions contained the electro-active substrate in deoxygenated and anhydrous dichloromethane containing tetra-n-butylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The quoted half-wave potentials were reproducible within ≈ 15 mV.

2) Experimental Part

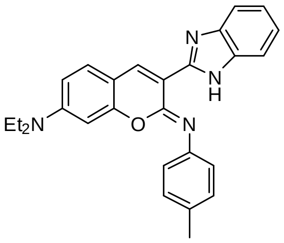
General procedure for preparation of iminocoumarins

A solution of 4-dimethylaminosalicylaldehyde (1 equiv), 2-cyanomethylbenzimidazole (1.1 equiv) and a catalytic amount of piperidine was refluxed in ethanol (0.1 M) until a precipitate appears in about 1h. The solution was diluted with ethanol (0.015M). A catalytic amount of pTsOH and the corresponding aniline (2.2 equiv) were added and the resulting mixture was refluxed overnight (disappearance of the precipitate). The solvent was then removed by vacuum and the residue was purified by column chromatography (SiO_2, CH_2Cl_2 with various percentage of EtOH).

General procedure for preparation of Boricos

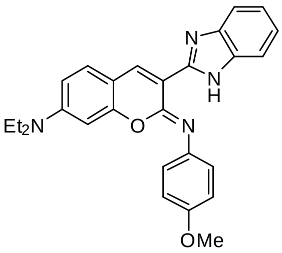
A solution of iminocoumarin (1 equiv), diisopropylamine (2.5 equiv) and $BF_3.OEt_2$ (2.5 equiv) was stirred at 85°C for 1h and the cooled down. The resulting mixture was washed with a saturated solution of $NaHCO_3$ in water and extracted with CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$ and the solvent was removed by vacuum. The residue was purified by column chromatography (SiO_2, CH_2Cl_2 with various percentage of EtOH).

Iminocoumarin 1a



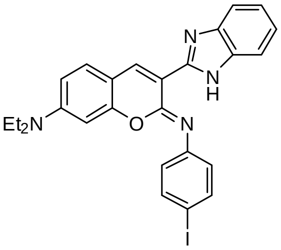
SiO_2, CH_2Cl_2/EtOH 95:5. Yellow powder. Yield: 75%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 12.68 (1H, br s, NH), 8.74 (1H, s, CH 4), 7.62 (2H, br m, CH Arom), 7.35 (1H, d, ^3J = 8.7 Hz CH Arom), 7.24 (6H, m, CH Arom), 6.53 (1H, dd, ^3J = 8.7 Hz, ^4J = 2.1 Hz), 6.28 (1H, d, ^4J = 2.1 Hz), 3.40 (4H, q, ^3J = 7.2 Hz, CH_2 NEt_2), 2.43 (3H, s, Me), 1.20 (6H, t, ^3J = 7.2 Hz, CH_3 NEt_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 155.5, 151.2, 149.7, 149.0, 142.8, 136.9, 133.5, 130.0, 129.5, 123.0, 122.5, 111.0, 108.7, 96.7, 44.7, 21.1, 12.6;

Iminocoumarin 1b



SiO_2, CH_2Cl_2. Yellow powder. Yield: 86%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 12.67 (1H, br s, NH), 8.69 (1H, s, CH 4), 7.78 (1H, br m, CH Arom), 7.51 (1H, br m, CH Arom), 7.33 (3H, m, CH Arom), 7.25 (2H, m, CH Arom), 7.00 (2H, d, ^3J = 8.7 Hz, CH Arom), 6.53 (1H, dd, ^3J = 8.7 Hz, ^4J = 2.4 Hz), 6.28 (1H, d, ^4J = 2.4 Hz), 3.88 (3H, s, OMe), 3.41 (4H, q, ^3J = 7.2 Hz, CH_2 NEt_2), 1.20 (6H, t, ^3J = 7.2 Hz, CH_3 NEt_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 156.5, 155.6, 151.3, 149.7, 149.3, 138.8, 136.7, 130.1, 124.6, 122.6, 114.4, 108.9, 96.9, 55.8, 44.9, 12.8;

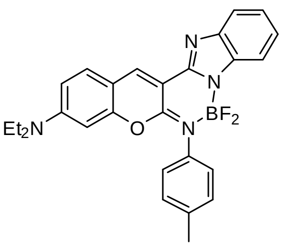
Iminocoumarin 1c



SiO_2, CH_2Cl_2.Yellow powder. Yield: 54%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 12.40 (1H, br s, NH), 8.74 (1H, s, CH 4), 7.62 (2H, br m, CH Arom), 7.73 (2H, d, ^3J = 8.4 Hz, CH Arom), 7.34 (1H, d, ^3J = 8.7 Hz, CH Arom), 7.26 (2H, m, CH Arom), 7.06 (2H, ^3J = 8.4 Hz, CH Arom), 6.54 (1H, dd, ^3J = 8.7 Hz, ^4J = 2.1 Hz), 6.24 (1H, d, ^4J = 2.1 Hz), 3.40 (4H, q, ^3J = 7.2 Hz, CH_2 NEt_2), 1.20 (6H, t, ^3J = 7.2 Hz,

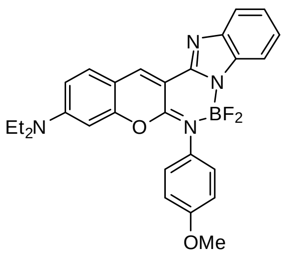
CH_3 NEt_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 155.5, 151.5, 150.6, 148.9, 145.8, 138.1, 137.6, 130.2, 125.5, 122.7, 110.9, 109.2, 108.7, 96.7, 87.5, 45.0, 12.8;

Borico 2a



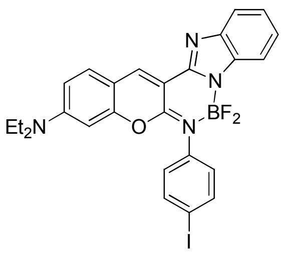
SiO_2, CH_2Cl_2/EtOH 99:1.Orange powder. Yield: 95%. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 9.07 (1H, s, CH 4), 7.77 (2H, m, CH Arom), 7.55 (1H, d, ^3J = 9.0 Hz, CH Arom), 7.38 (4H, s, CH Arom), 7.29 (2H, m CH Arom), 6.76 (1H, dd, ^3J = 9.0 Hz, ^4J = 2.4 Hz), 6.27 (1H, d, ^4J = 2.4 Hz), 3.42 (4H, q, ^3J = 7.2 Hz, CH_2 NEt_2), 2.49 (3H, s, Me), 1.21 (6H, t, ^3J = 7.2 Hz, CH_3 NEt_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 154.7, 152.8, 145.8, 144.7, 139.7, 138.3, 136.6, 134.3, 131.2, 130.2, 126.7, 122.9, 122.8, 118.1, 114.2, 112.2, 109.5, 105.9, 96.9, 45.3, 21.5, 12.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm): 1.50 (t, J_{BF} = 24.8 Hz);

Borico 2b



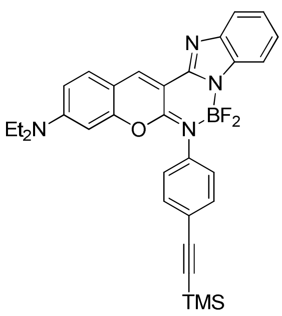
SiO_2, CH_2Cl_2/EtOH 99:1.Orange powder. Yield: 94%. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 9.03 (1H, s, CH 4), 7.76 (2H, m, CH Arom), 7.54 (1H, d, ^3J = 9.3 Hz, CH Arom), 7.42 (2H, d, ^3J = 9.0 Hz, CH Arom), 7.26 (2H, m, CH Arom), 7.09 (2H, d, ^3J = 9.0 Hz, CH Arom), 6.75 (1H, dd, ^3J = 9.3 Hz, ^4J = 2.1 Hz), 6.26 (1H, d, ^4J = 2.1 Hz), 3.92 (3H, s, Me), 3.43 (4H, q, ^3J = 7.2 Hz, CH_2 NEt_2), 1.22 (6H, t, ^3J = 7.2 Hz, CH_3 NEt_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 159.6, 154.8, 153.2, 145.3, 142.7, 140.7, 131.6, 129.4, 128.1, 123.5, 123.3, 117.5, 114.9, 114.4, 112.3, 109.5, 96.8, 55.8, 45.4, 12.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm): 1.48 (t, J_{BF} = 24.1 Hz);

Borico 2c



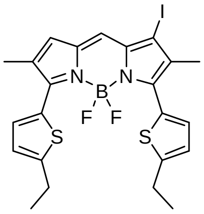
SiO_2, CH_2Cl_2/EtOH 98:2.Orange powder. Yield: 73%. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 9.09 (1H, s, CH 4), 7.92 (2H, d, ^3J = 9.0 Hz, CH Arom), 7.69 (2H, m, CH Arom), 7.51 (1H, d, ^3J = 9.0 Hz, CH Arom), 7.33 (2H, d, ^3J = 9.0 Hz, CH Arom), 7.22 (2H, m, CH Arom), 6.71 (1H, dd, ^3J = 9.0 Hz, ^4J = 1.8 Hz), 6.19 (1H, d, ^4J = 1.8 Hz), 3.43 (4H, q, J = 7.2 Hz, CH_2 NEt_2), 1.23 (6H, t, J = 7.2 Hz, CH_3 NEt_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 154.7, 153.1, 145.5, 140.7, 138.8, 136.8, 131.6, 129.3, 123.1, 123.0, 117.9, 114.2, 112.4, 109.6, 104.8, 96.7, 94.1, 45.4, 12.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm): 0.82 (t, J_{BF} = 24.1 Hz);

Borico-TMS



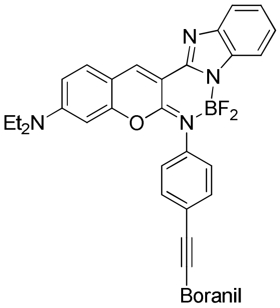
A solution of Borico **2c** (62 mg, 0.11 mmol, 1 equiv) was solubilised with $PdCl_2(PPh_3)_2$ (7.7 mg, 0.011 mmol, 0.1 equiv) and triethylamine (0.5 mL) in THF/toluene (10 mL, 1:1). The solution was then degassed with argon, TMS-Acetylene (0.13ml, 0.88 mmol, 8 equiv) and CuI (2.5 mg, 0.013 mmol, 0.12 equiv) were added. The solution was stirred at rt. for 2h. The resulting solution was washed with water and extracted with CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$ and the solvent was removed by vacuum. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/EtOH 99:1). Orange powder. Yield: 75%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 9.08 (1H, s, CH 4), 7.68 (4H, br m, CH Arom), 7.51 (3H, br m, CH Arom), 7.23 (2H, br m CH Arom), 6.70 (1H, dd, ^3J = 9.0 Hz, ^4J = 2.1 Hz), 6.15 (1H, d, ^4J = 2.1 Hz), 3.41 (4H, q, ^3J = 7.2 Hz, CH_2 NEt_2), 1.22 (6H, t, ^3J = 7.2 Hz, CH_3 NEt_2), 0,31 (9H, s, CH_3 TMS); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 154.7, 153.1, 140.5, 137.1, 133.3, 131.5, 127.3, 123.0, 118.0, 114.2, 112.3, 109.5, 104.6, 96.6, 45.4, 12.7, 0.2;

Bodipy



To a solution of 3,5-di-(5-ethylthien-2-yl)-4,4'-difluoro-2,6-dimethyl-4-bora-3a,4a-diaza-s-indacene (100 mg, 0.23 mmol, 1 equiv) in MeOH/DMF (20 mL, 1:1) was added dropwise a solution of ICl (41 mg, 0.25 mmol, 1.1 equiv) in MeOH (2 mL) at rt. The reaction was followed by TLC. After 1 h a solution of ICl (41 mg, 0.25 mmol, 1.1 equiv) in MeOH (2 mL) was added. After 1.5 h the reaction mixture was diluted with CH_2Cl_2, washed with a saturated solution of $Na_2S_2O_3$, abundantly with water and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$. The solvent was removed under vacuum. The residue was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 60:40) and recrystallized from CH_2Cl_2/EtOH. Blue metallic crystals. Yield: 63%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.74 (1H, d, ^3J = 4.0 Hz), 7.50 (1H, d, ^3J = 3.6 Hz), 7.01 (1H, s), 6.91 (1H, s), 6.86 (2H, m), 2.90 (4H, q, ^3J = 7.6 Hz), 2.26 (3H, s), 2.22 (3H, s), 1.36 (3H, t, ^3J = 7.6 Hz), 1.35 (3H, t, ^3J = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 152.7, 152.0, 151.4, 147.5, 135.8, 135.7, 132.9 (t, $J_{C\text{-}F}$ = 6.6 Hz), 131.9 (t, $J_{C\text{-}F}$ = 4.9 Hz), 131.3, 130.6, 129.5, 124.8, 124.2, 123.7, 93.4, 23.6, 23.5, 15.4, 15.3, 14.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm): 1.28 (t, ^1J = 31.8 Hz);

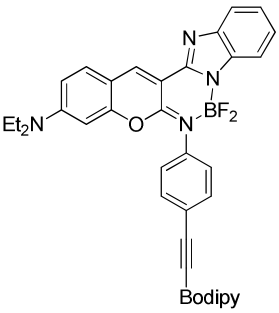
Dyad Borico-Boranils 3



A solution of Borico-TMS (29 mg, 0.05 mmol, 1 equiv) and potassium fluoride (24 mg, 0.42 mmol, 8 equiv) in THF/MeOH (6 mL, 1:1) was stirred at rt. overnight. Then the mixture was washed with water, extracted with CH_2Cl_2 and dried over $MgSO_4$. The residual solvent was removed. The deprotected product was solubilised with $PdCl_2(PPh_3)_2$ (3.5 mg, 0.005 mmol, 0.1 equiv) triethylamine (0.5 mL) and Boranil (23 mg, 0.05 mmol, 1 equiv) in THF/toluene (10 mL, 1:1). The solution was then degassed with argon and CuI (1.1 mg, 0.006 mmol, 0.12 equiv) was added. The solution was stirred at 40 °C for 4h. Then the residue was washed with water, extracted with CH_2Cl_2 and dried over $MgSO_4$. The residual solvent was removed. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/EtOH 99:1). Orange powder. Yield: 53%. Poor solubility in

NMR solvents. ^{1}H NMR (300 MHz, CD_2Cl_2) δ (ppm): 9.00 (1H, s, CH 4), 8.08 (1H, br m, CH Imine), 7.74 (2H, d, ^3J = 8.4 Hz, CH Arom), 7.62 (5H, br m, CH Arom), 7.49 (4H, m, CH Arom), 7.24 (3H, m CH Arom), 6.80 (1H, dd, ^3J = 9.3 Hz, ^4J = 2.1 Hz), 6.41 (1H, dd, ^3J = 9.3 Hz, ^4J = 2.1 Hz), 6.31 (1H, d, ^4J = 2.1 Hz), 6.20 (1H, d, ^4J = 2.1 Hz), 3.44 (8H, m, CH_2 NEt_2), 1.20 (12H, m, CH_3 NEt_2); ^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm): 161.9, 157.8, 156.7, 154.7, 153.0, 143.2, 137.0, 134.1, 132.7, 132.6, 132.0, 131.9, 131.1, 128.5, 128.4, 127.2, 123.1, 123.0, 122.4, 122.3, 122.1, 118.1, 113.5, 112.3, 109.4, 107.1, 97.6, 96.5, 89.9, 89.6, 45.3, 45.2, 12.4, 12.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm): 1.58 (br m, Borico), 0.86 (t, J_{BF} = 17.2 Hz, Boranil);

Dyad Borico-Bodipy 4



A solution of Borico-TMS (36 mg, 0.07 mmol, 1 equiv) and potassium fluoride (30 mg, 0.52 mmol, 8 equiv) in THF/MeOH (6 mL, 1:1) was stirred at rt overnight. Then the mixture was washed with water, extracted with CH_2Cl_2 and dried over $MgSO_4$. The residual solvent was removed. The deprotected product was solubilised with $PdCl_2(PPh_3)_2$ (5 mg, 0.007 mmol, 0.1 equiv) triethylamine (0.5 mL) and Bodipy (37 mg, 0.07 mmol, 1 equiv) in THF/toluene (10 mL, 1:1). The solution was then degassed with argon and CuI (2 mg, 0.008 mmol, 0.12 equiv) was added. The solution was stirred at 40 °C for 4 days. Then the residue was washed with water, extracted with CH_2Cl_2 and dried over $MgSO_4$. The residual solvent was removed. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/EtOH 98:2) and recrystallized from THF/pentane. Dark green powder. Yield: 35%. Poor solubility in NMR solvents. ^{1}H NMR (400 MHz, CD_2Cl_2) δ (ppm): 9.20 (1H, brs), 7.77 (2H, m), 7.66 (2H, m), 7.54 (4H, m), 7.30 (4H, m), 6.99 (1H, s), 6.90 (2H, m), 6.78 (1H, s), 6.29 (1H, s), 3.41 (4H, m), 2.92 (4H, q, ^3J = 7.4 Hz), 2.33 (3H, s), 2.23 (3H, s), 1.36 (3H, t, ^3J = 7.4 Hz), 1.35 (3H, t, ^3J = 7.4 Hz), 1.18(6H, t, ^3J = 6.0 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm): 154.7, 153.5, 151.6, 147.2, 137.2, 135.8, 132.9, 132.7, 132.3, 131.9, 131.6, 131.4, 130.7, 129.9, 129.5, 129.4, 128.4, 128.2, 127.4, 126.4, 124.6, 124.1, 122.9, 122.7, 122.3, 112.4, 99.0, 96.3, 82.8, 45.2, 23.53, 23.46, 15.41, 15.37, 13.7, 12.2; ^{11}B NMR (128 MHz, CD_2Cl_2) δ (ppm): ~ 1.4 (br m, Borico) 1.16 (t, ^1J = 32.7 Hz).

3) Spectroscopic data

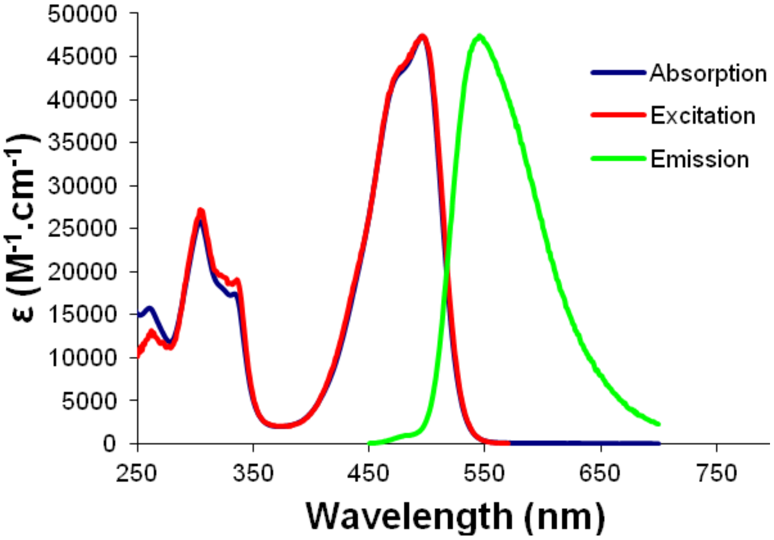
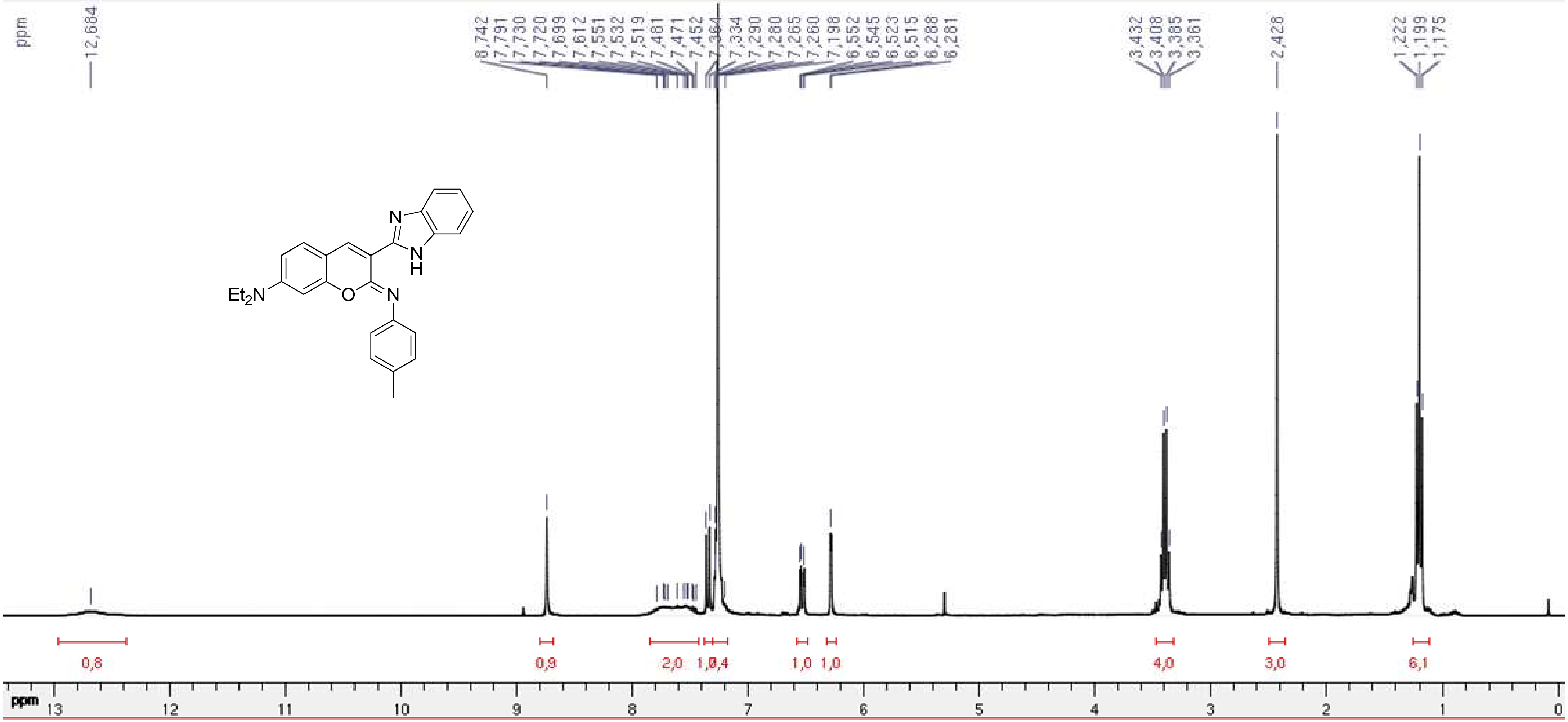
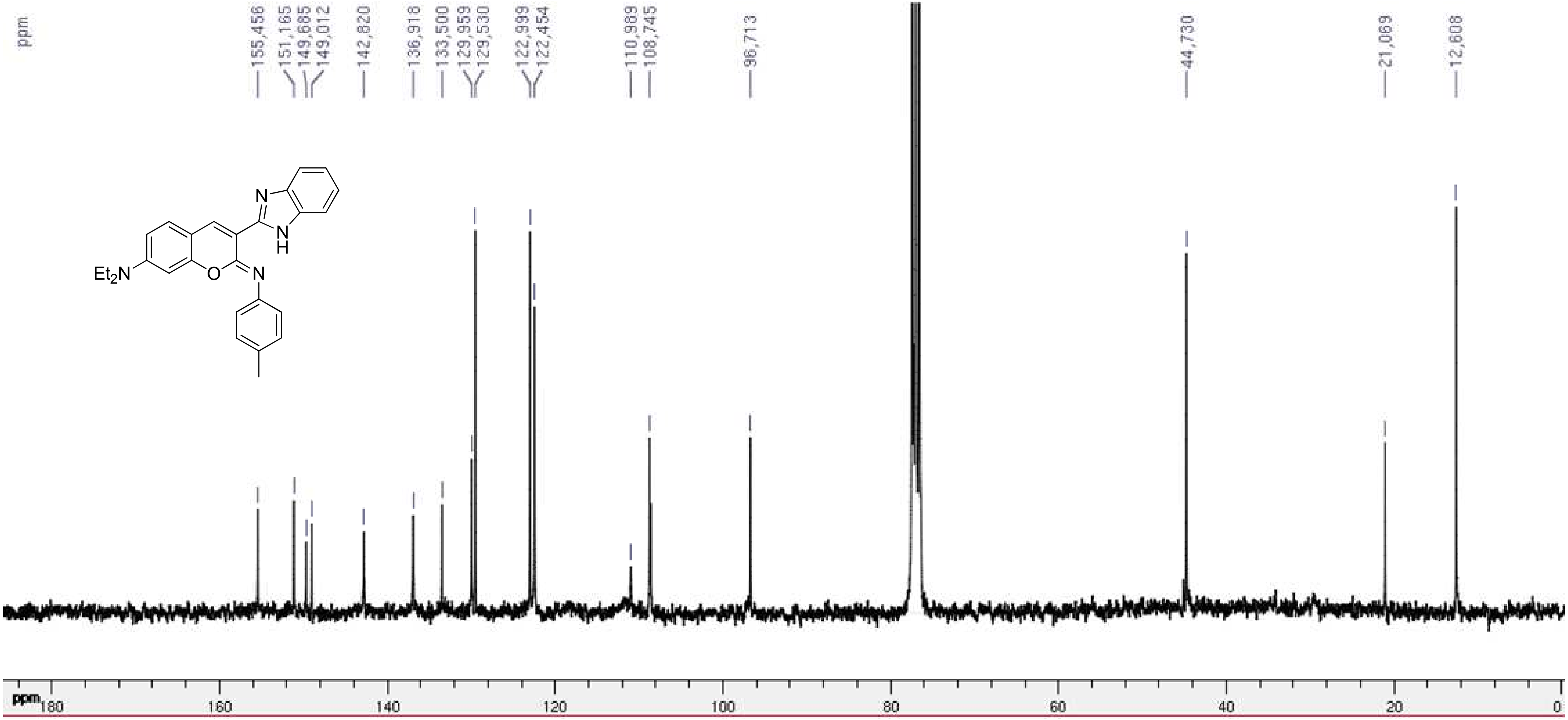
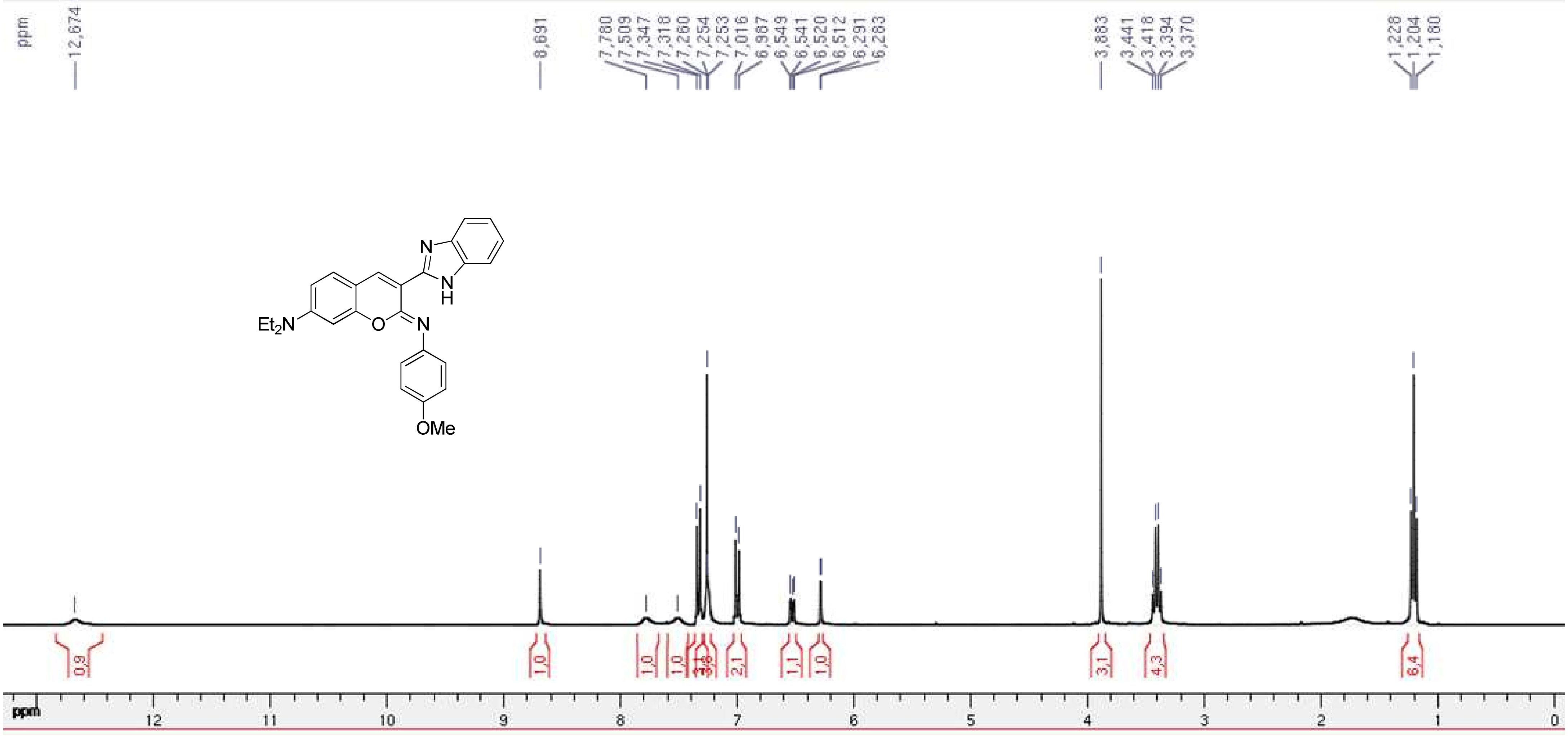


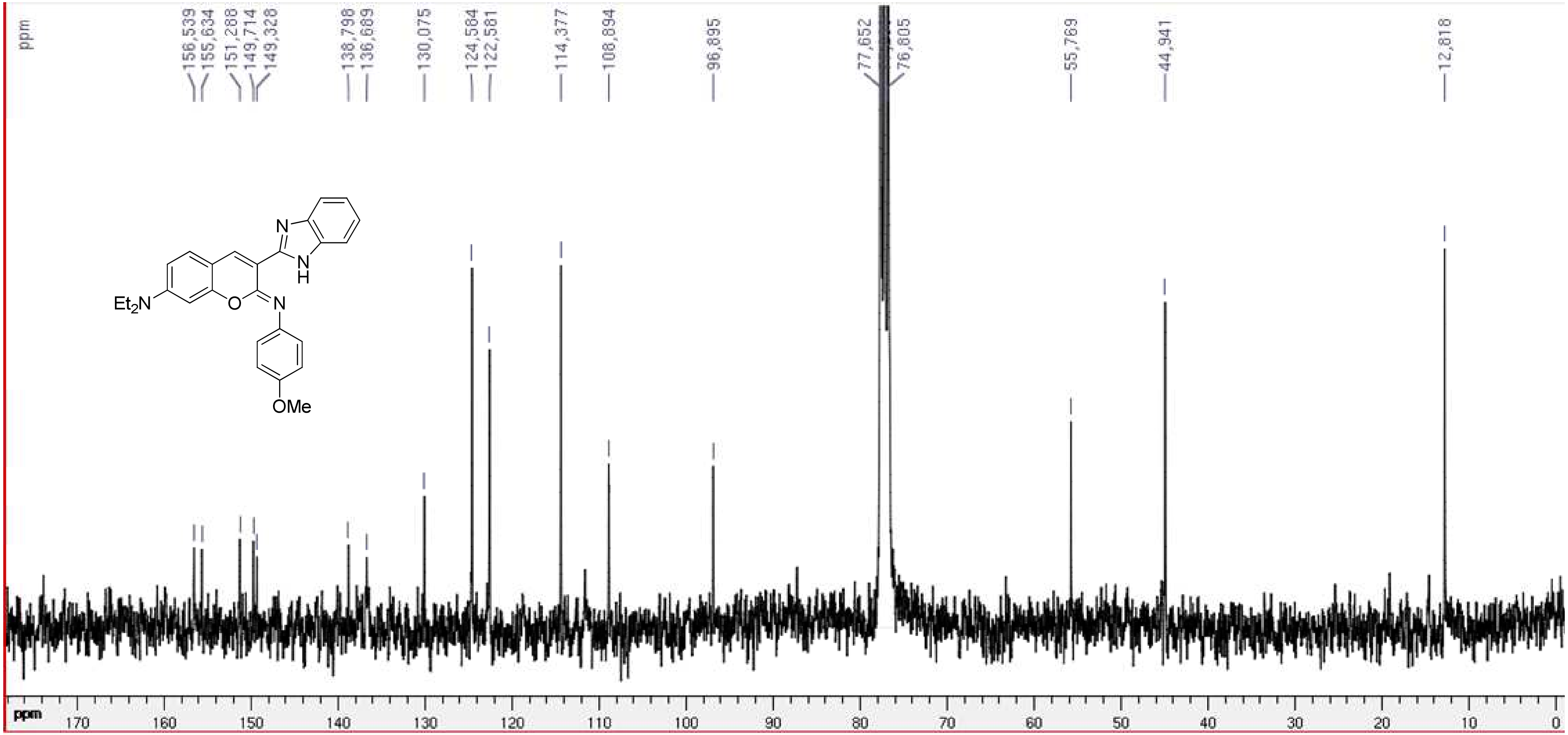
Figure S1. Spectroscopic spectra for **2c** in DCM.

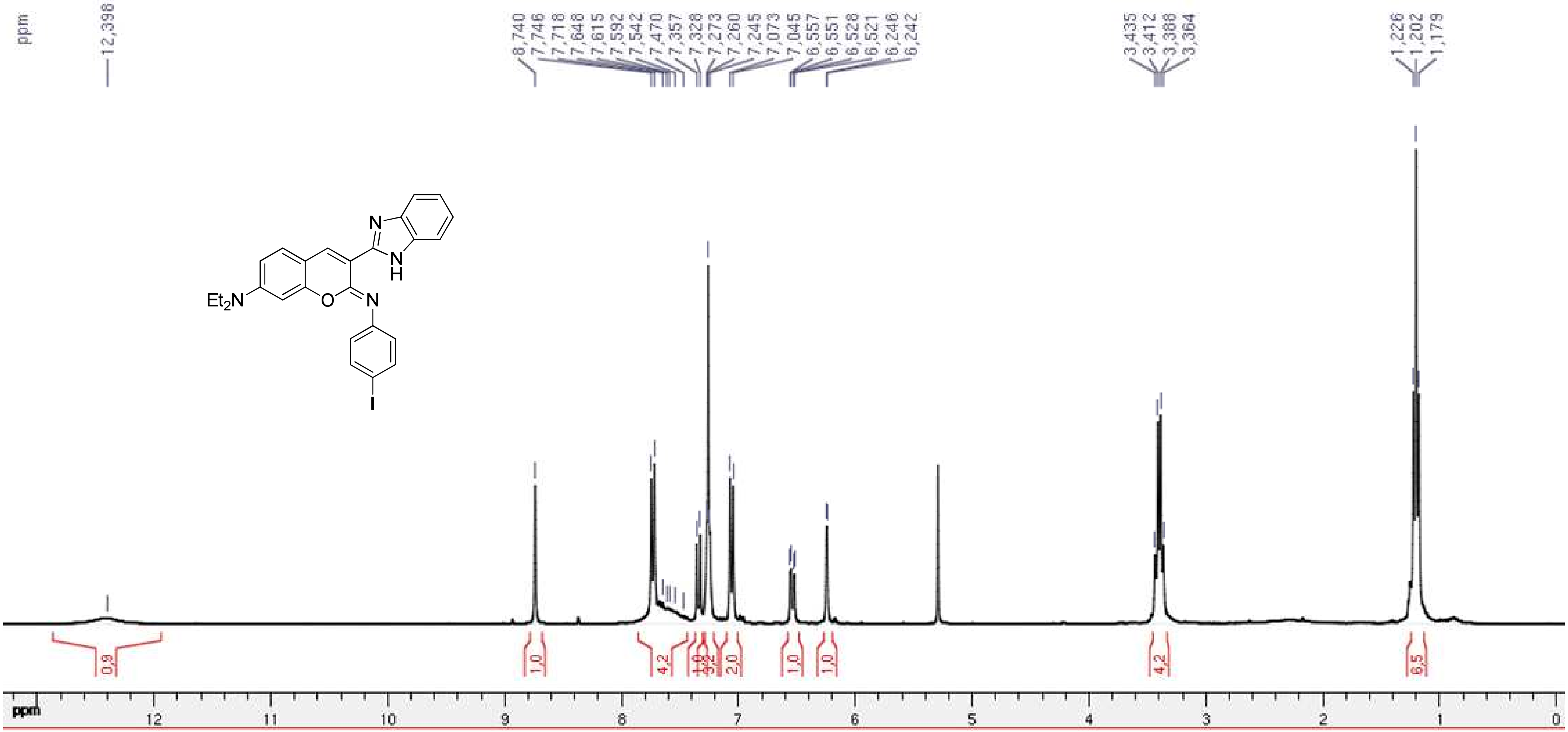
4) ^{1}H and ^{13}C NMR Spectra

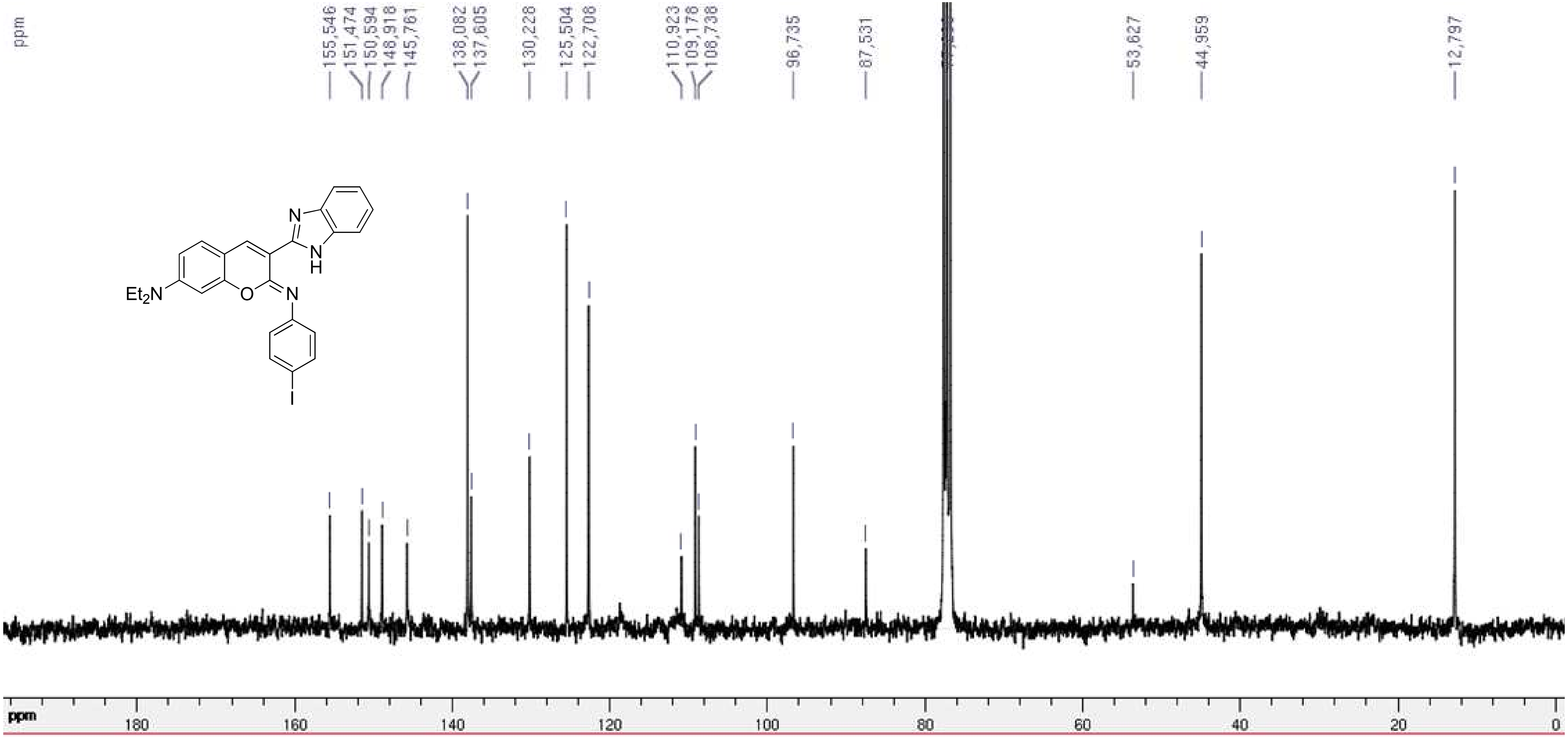

ppm
12,684
8,742
7,791
7,730
7,720
7,699
7,612
7,551
7,532
7,519
7,481
7,471
7,452
7,364
7,334
7,290
7,280
7,265
7,260
7,198
6,552
6,545
6,523
6,515
6,288
6,281
3,432
3,408
3,385
3,361
2,428
1,222
1,199
1,175
N
N
H
Et$_2$N
O
N
0,8
0,9
2,0
1,0
0,4
1,0
1,0
4,0
3,0
6,1
ppm
13
12
11
10
9
8
7
6
5
4
3
2
1
0

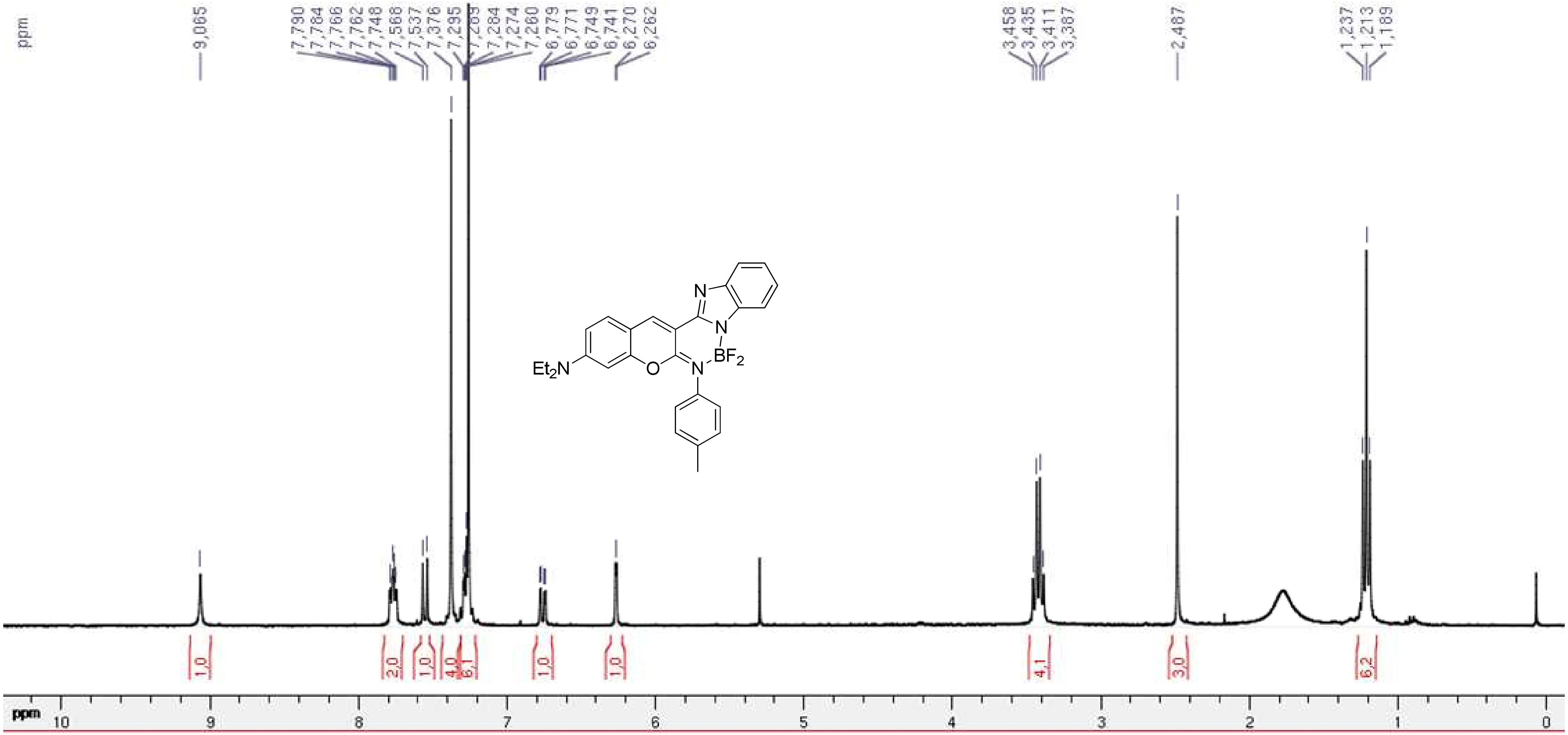

ppm
155,456
151,165
149,685
149,012
142,820
136,918
133,500
129,959
129,530
122,999
122,454
110,989
108,745
96,713
44,730
21,069
12,608
Et2N
O
N
N
N
H
ppm
180
160
140
120
100
80
60
40
20
0

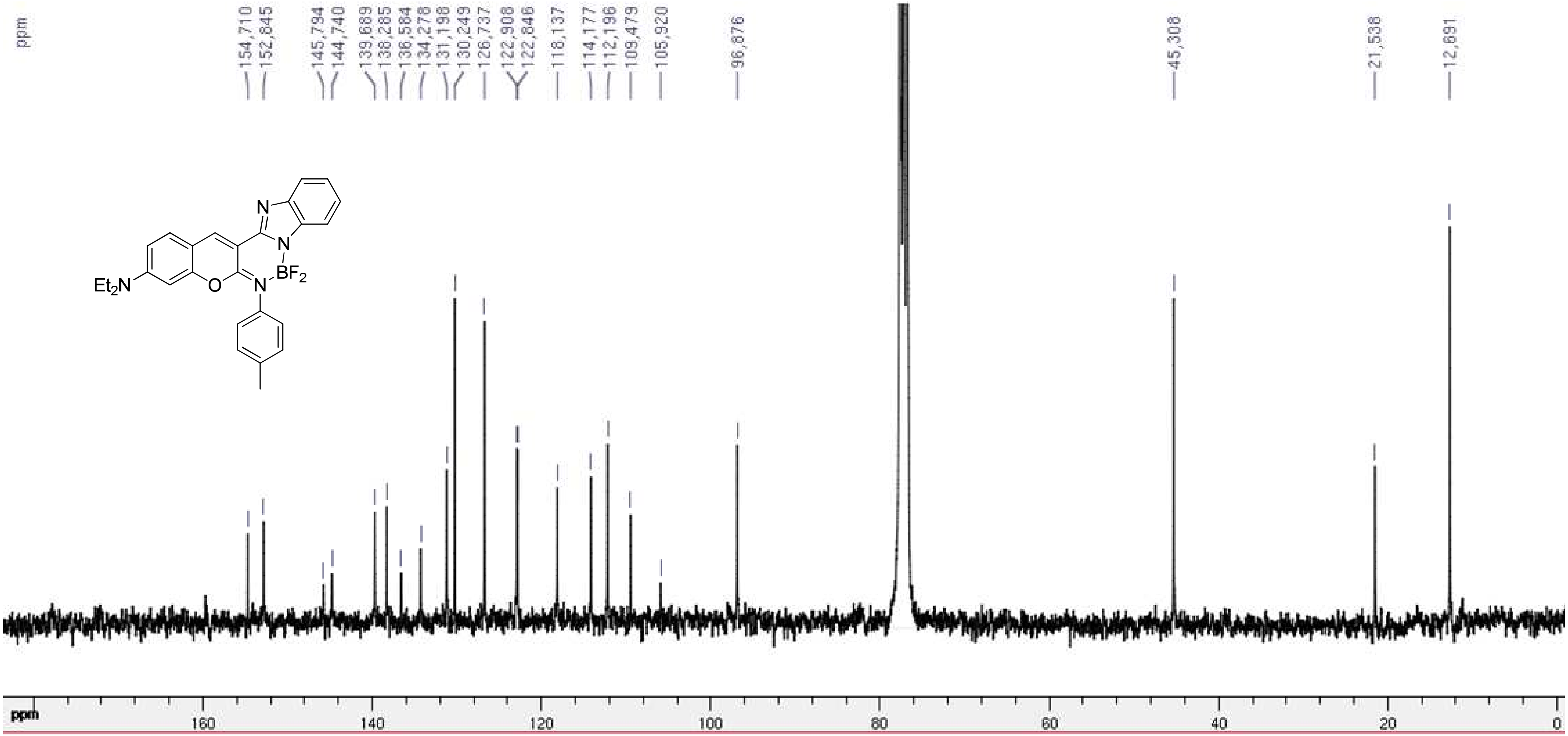

ppm
12,674
8,691
7,780
7,509
7,347
7,318
7,260
7,254
7,253
7,016
6,987
6,549
6,541
6,520
6,512
6,291
6,283
3,883
3,441
3,418
3,394
3,370
1,228
1,204
1,180
N
N
H
Et2N
O
N
OMe
0,9
1,0
1,0
1,0
2,1
1,1
1,0
3,1
4,3
6,4
ppm
12
11
10
9
8
7
6
5
4
3
2
1
0

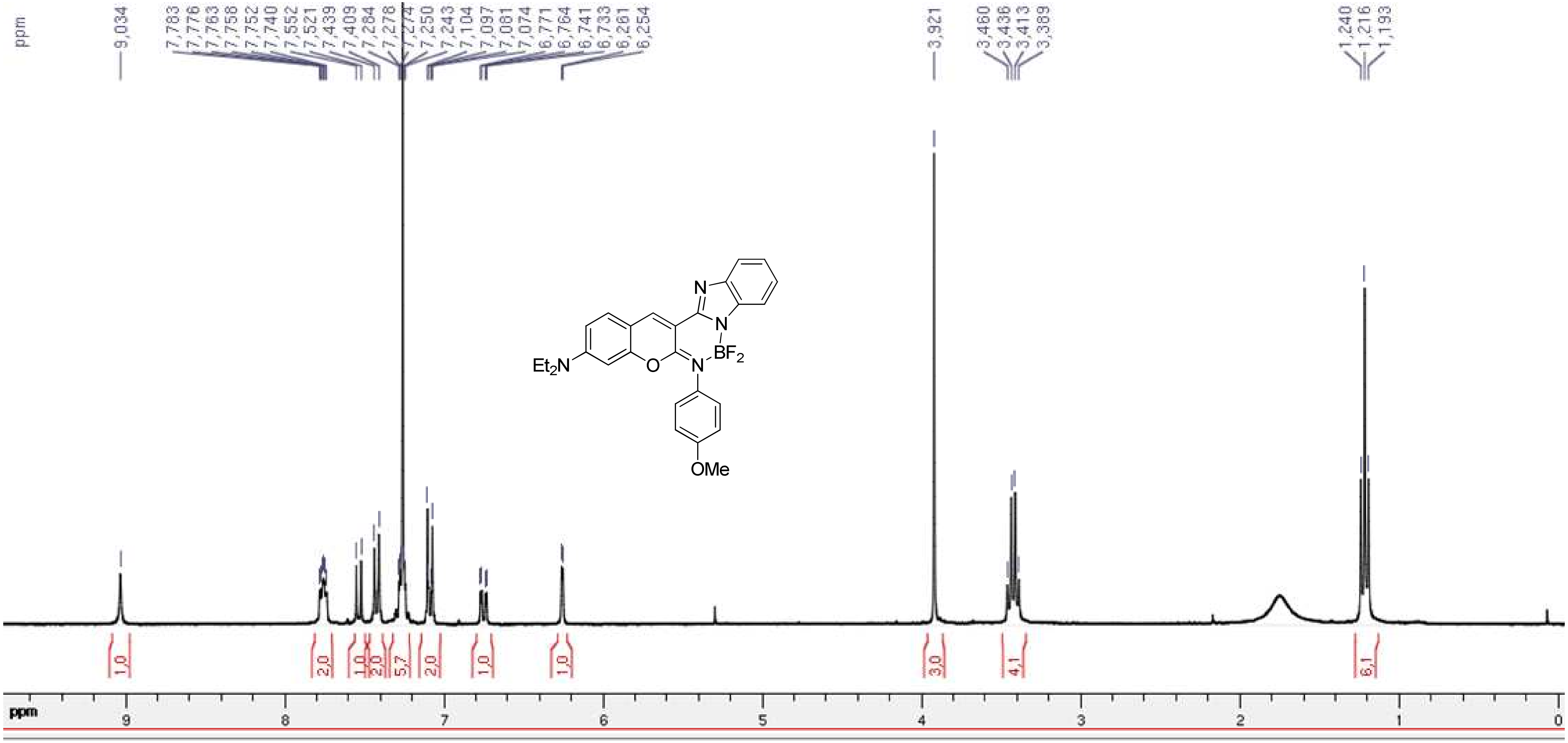

ppm
156,539
155,634
151,288
149,714
149,328
138,798
136,689
130,075
124,584
122,581
114,377
108,894
96,895
77,652
76,805
55,769
44,941
12,818
N
N
H
Et2N
O
N
OMe
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

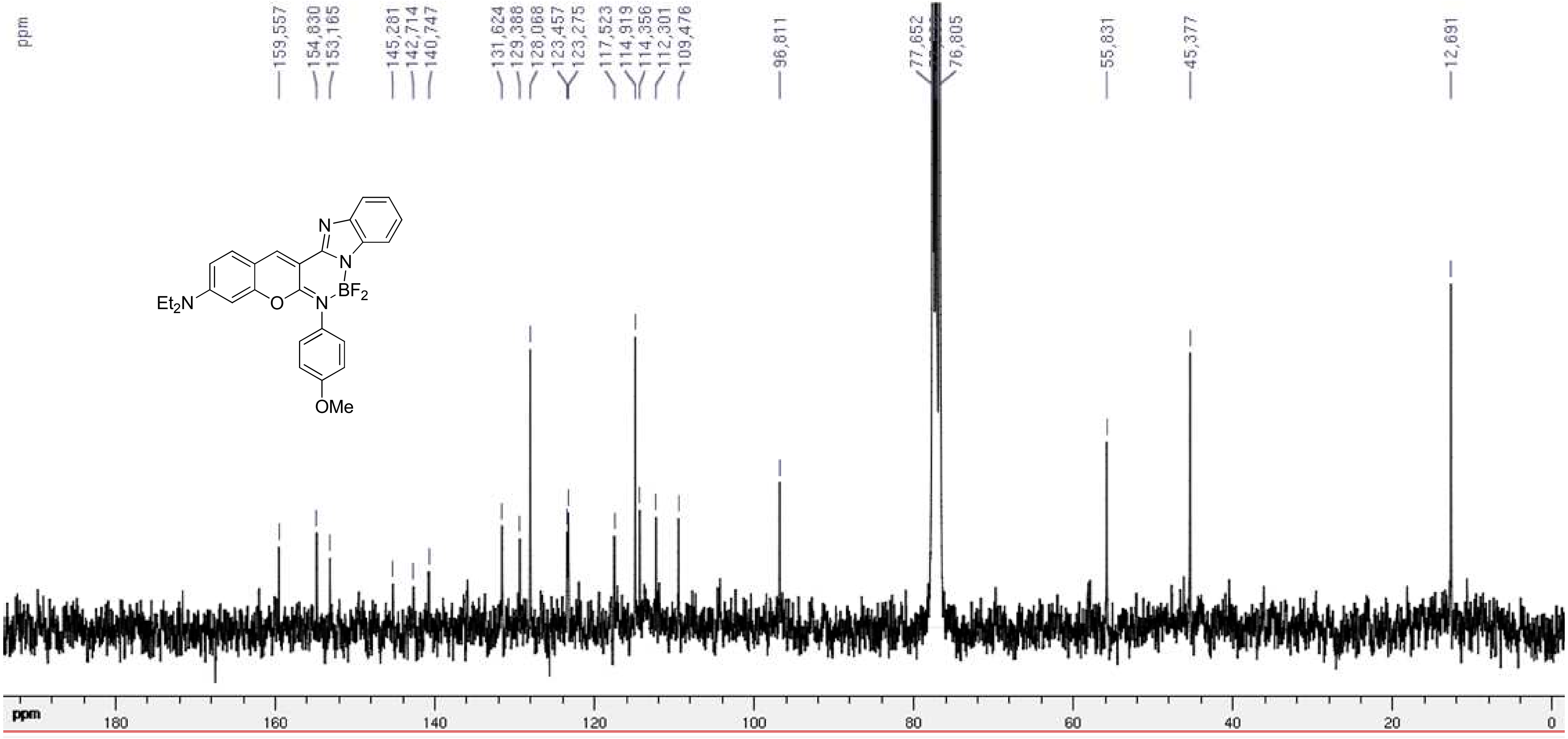

ppm
12,398
8,740
7,746
7,718
7,648
7,615
7,592
7,542
7,470
7,357
7,328
7,273
7,260
7,245
7,073
7,045
6,557
6,551
6,528
6,521
6,246
6,242
3,435
3,412
3,388
3,364
1,226
1,202
1,179
N
N
H
Et$_2$N
O
N
I
0,9
1,0
4,2
1,0
3,2
2,0
1,0
1,0
4,2
6,5
ppm
12
11
10
9
8
7
6
5
4
3
2
1
0

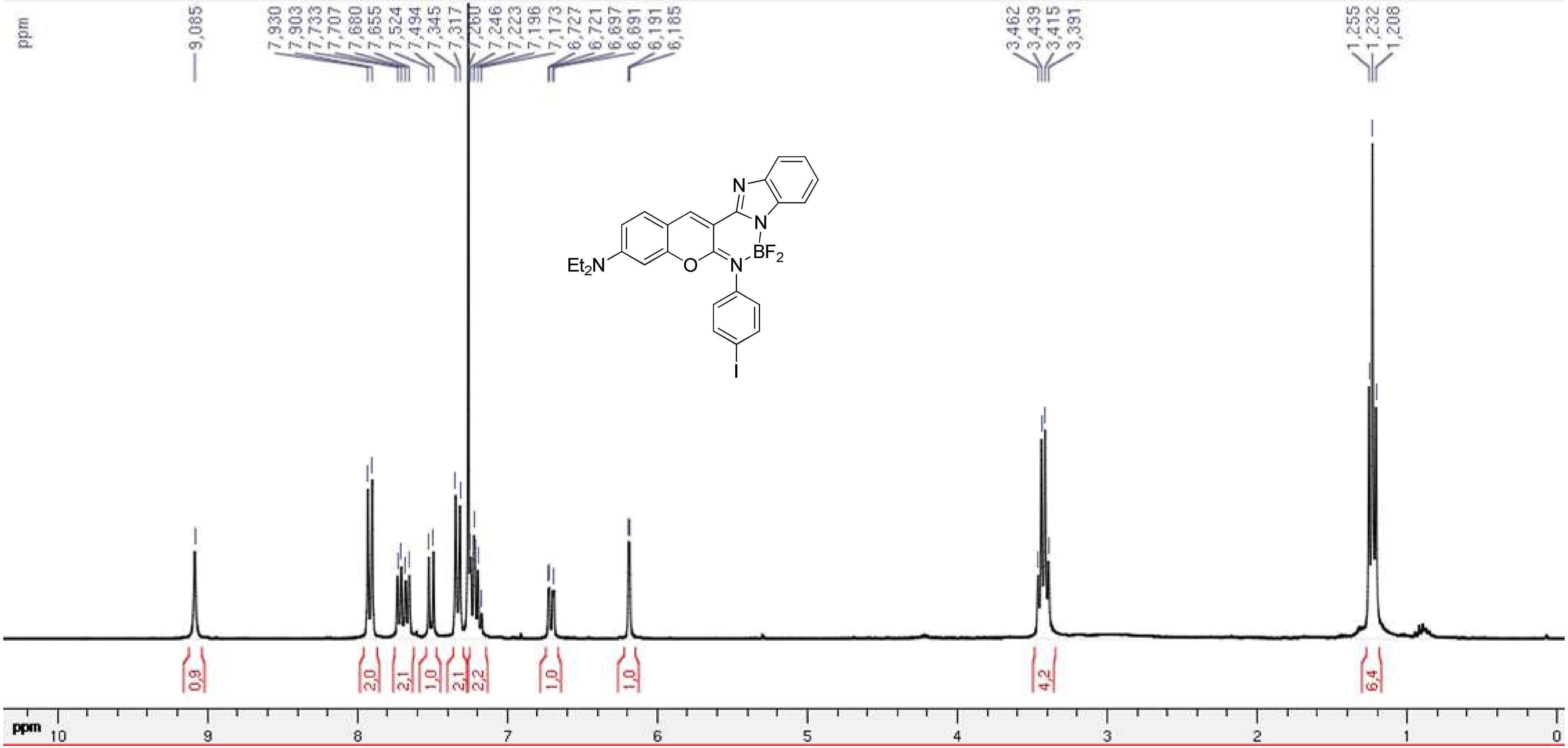

ppm
155,546
151,474
150,594
148,918
145,761
138,082
137,605
130,228
125,504
122,708
110,923
109,178
108,738
96,735
87,531
53,627
44,959
12,797
Et2N
O
N
N
N
H
I
ppm
180
160
140
120
100
80
60
40
20
0

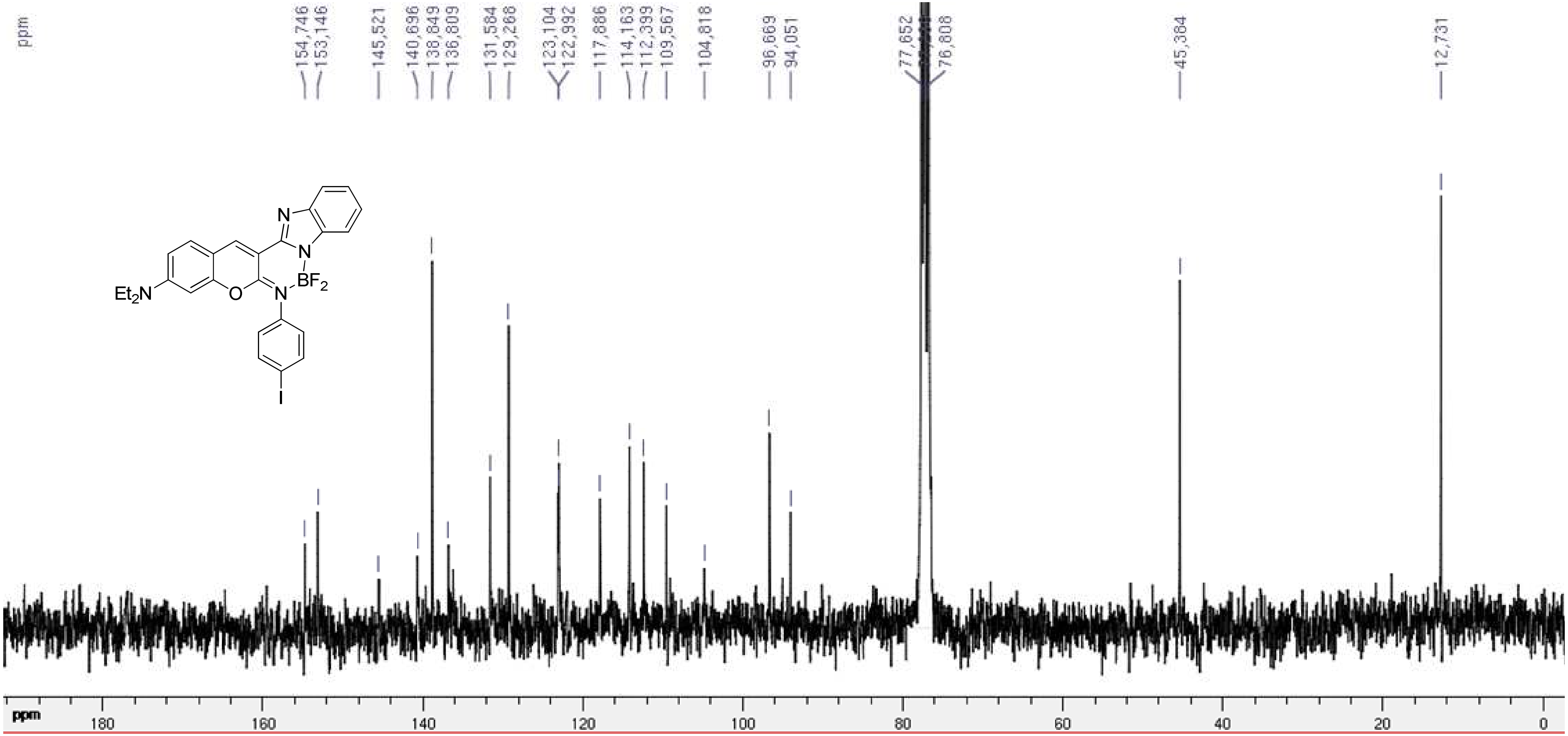

ppm
9,065
7,790
7,784
7,766
7,762
7,748
7,568
7,537
7,376
7,295
7,289
7,284
7,274
7,260
6,779
6,771
6,749
6,741
6,270
6,262
3,458
3,435
3,411
3,387
2,487
1,237
1,213
1,189
N
N
BF2
Et2N
O
N
1,0
2,0
1,0
4,0
6,1
1,0
1,0
4,1
3,0
6,2
ppm
10
9
8
7
6
5
4
3
2
1
0

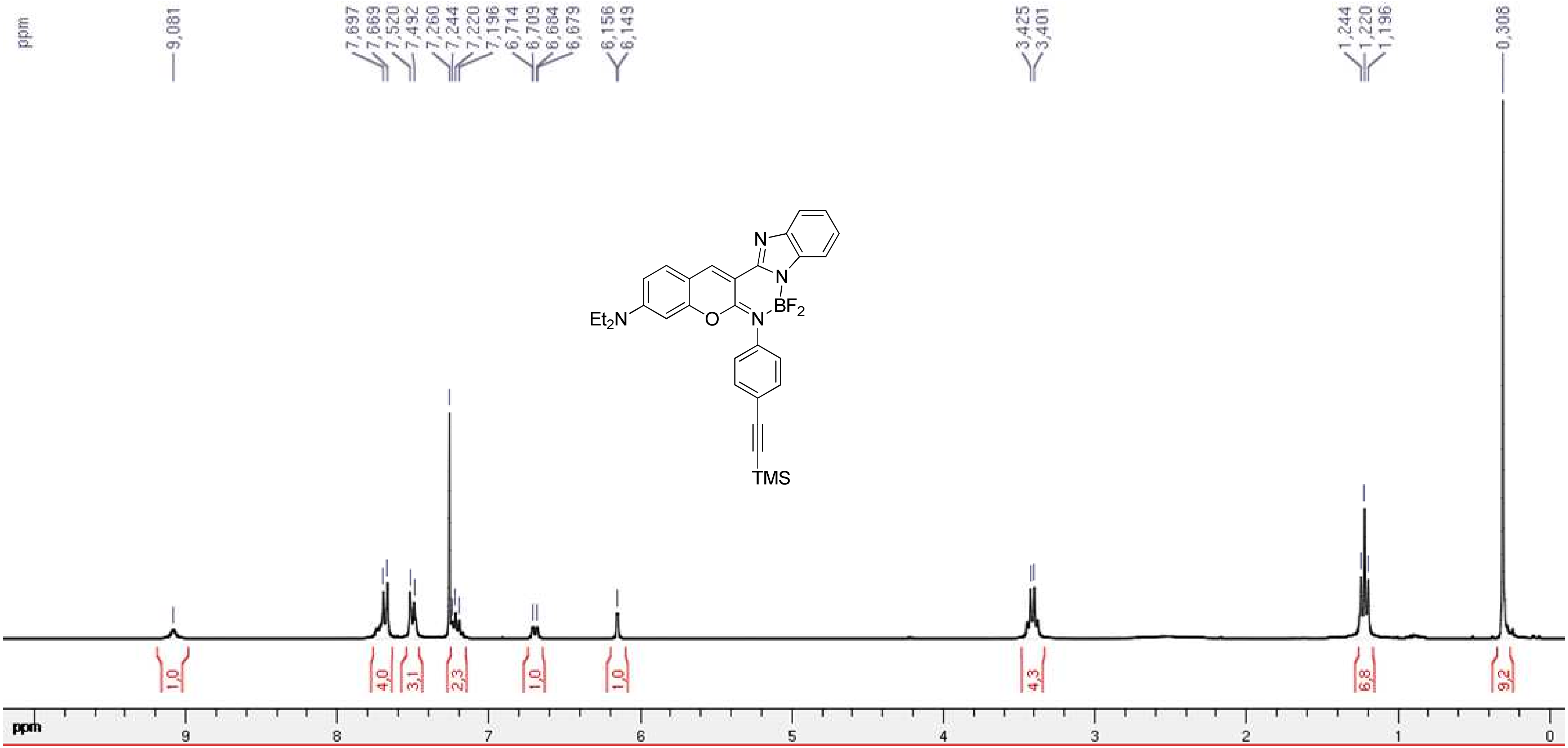

ppm
154,710
152,845
145,794
144,740
139,689
138,285
136,584
134,278
131,198
130,249
126,737
122,908
122,846
118,137
114,177
112,196
109,479
105,920
96,876
45,308
21,538
12,691
N
N
BF2
Et2N
O
N
ppm
160
140
120
100
80
60
40
20
0

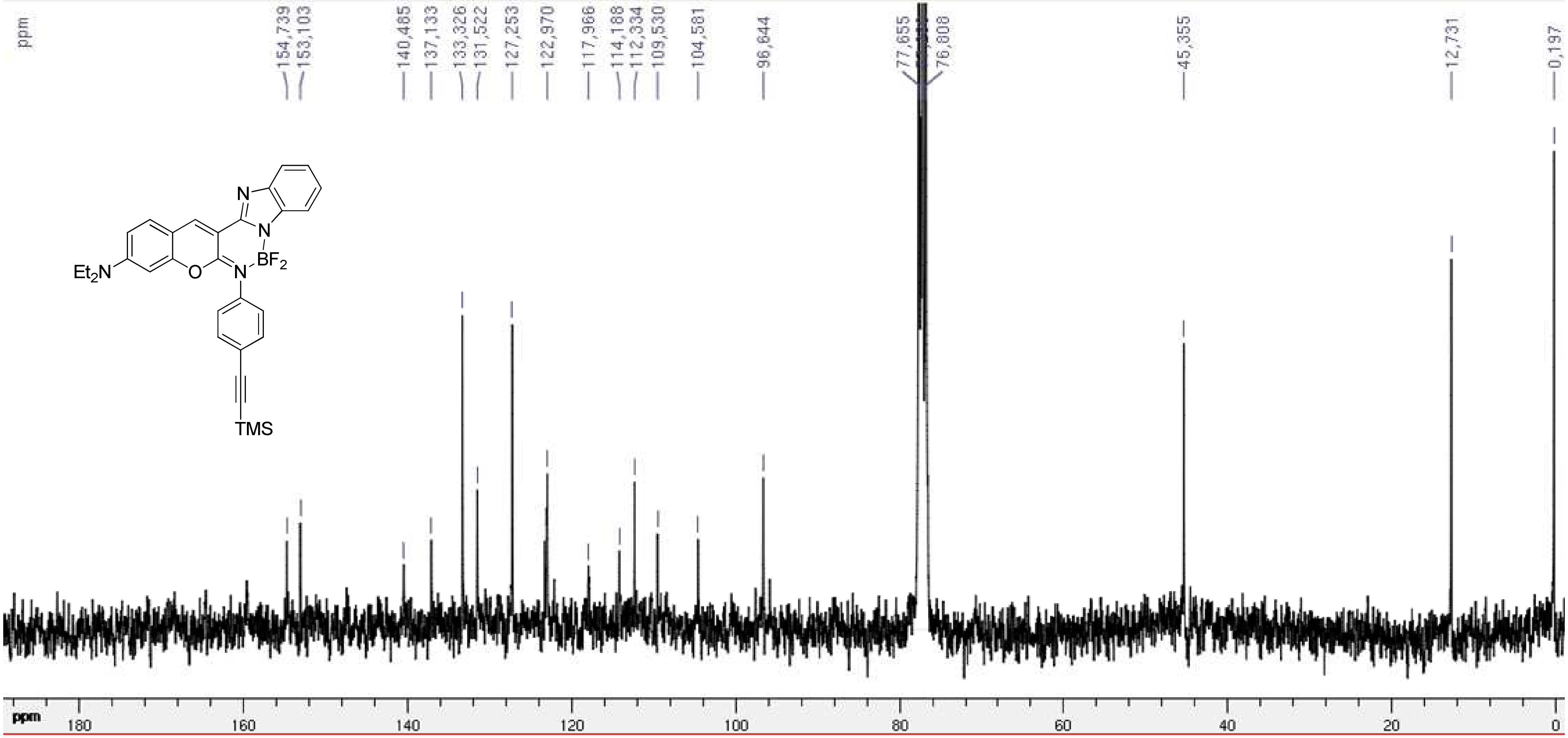

ppm
9,034
7,783
7,776
7,763
7,758
7,752
7,740
7,552
7,521
7,439
7,409
7,284
7,278
7,274
7,250
7,243
7,104
7,097
7,081
7,074
6,771
6,764
6,741
6,733
6,261
6,254
3,921
3,460
3,436
3,413
3,389
1,240
1,216
1,193
N
N
BF2
Et2N
O
N
OMe
1,0
2,0
1,0
2,0
5,7
2,0
1,0
1,0
3,0
4,1
6,1
ppm
9
8
7
6
5
4
3
2
1
0

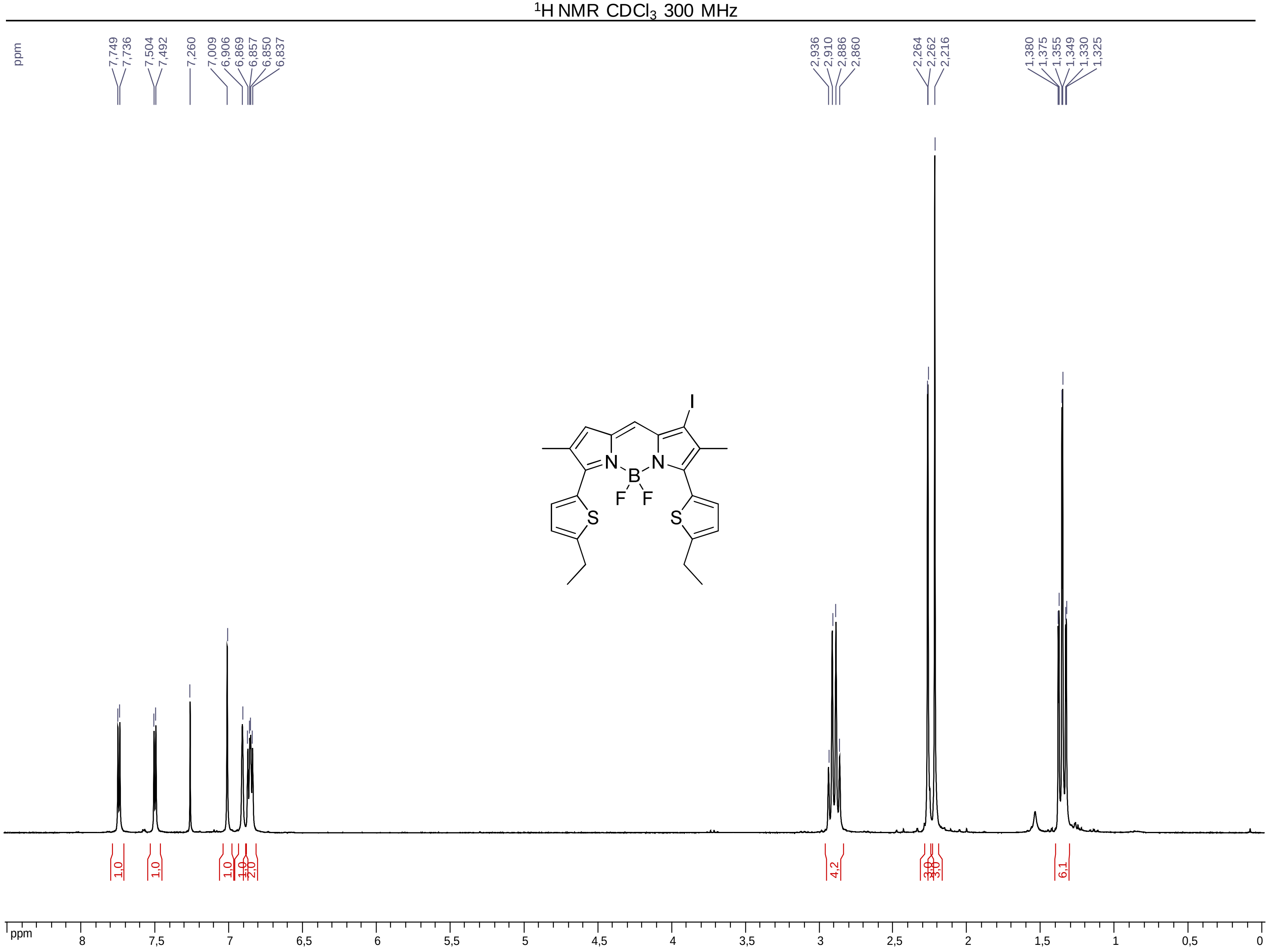

ppm
159,557
154,830
153,165
145,281
142,714
140,747
131,624
129,388
128,068
123,457
123,275
117,523
114,919
114,356
112,301
109,476
96,811
77,652
76,805
55,831
45,377
12,691
N
N
BF$_2$
Et$_2$N
O
N
OMe
ppm
180
160
140
120
100
80
60
40
20
0

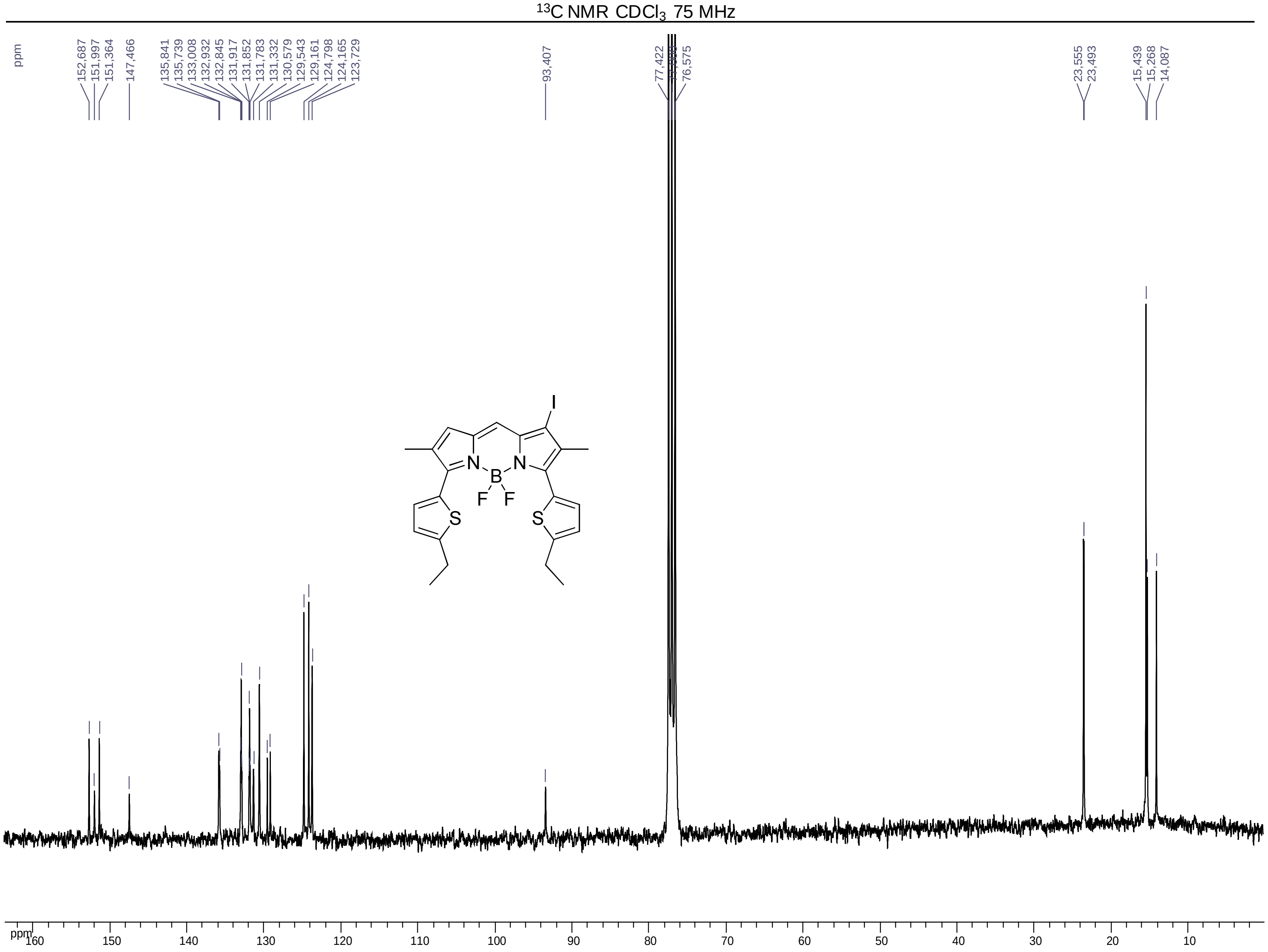

ppm
9,085
7,930
7,903
7,733
7,707
7,680
7,655
7,524
7,494
7,345
7,317
7,260
7,246
7,223
7,196
7,173
6,727
6,721
6,697
6,691
6,191
6,185
3,462
3,439
3,415
3,391
1,255
1,232
1,208
N
N
BF2
Et2N
O
N
I
0,9
2,0
2,1
1,0
2,1
2,2
1,0
1,0
4,2
6,4
ppm
10
9
8
7
6
5
4
3
2
1
0

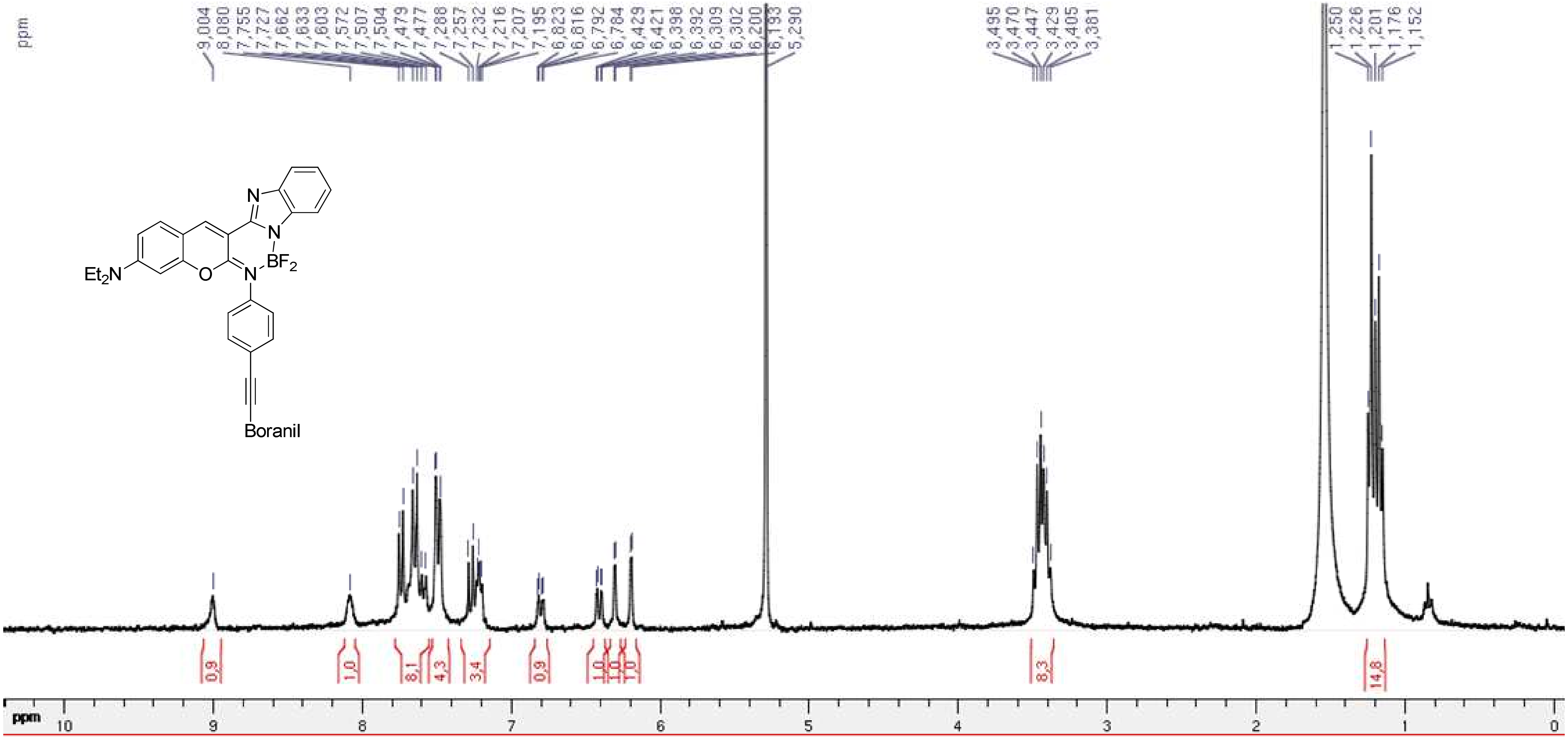

ppm
154,746
153,146
145,521
140,696
138,849
136,809
131,584
129,288
123,104
122,992
117,886
114,163
112,399
109,567
104,818
96,669
94,051
77,652
76,808
45,384
12,731
N
N
BF$_2$
Et$_2$N
O
N
I
ppm
180
160
140
120
100
80
60
40
20
0

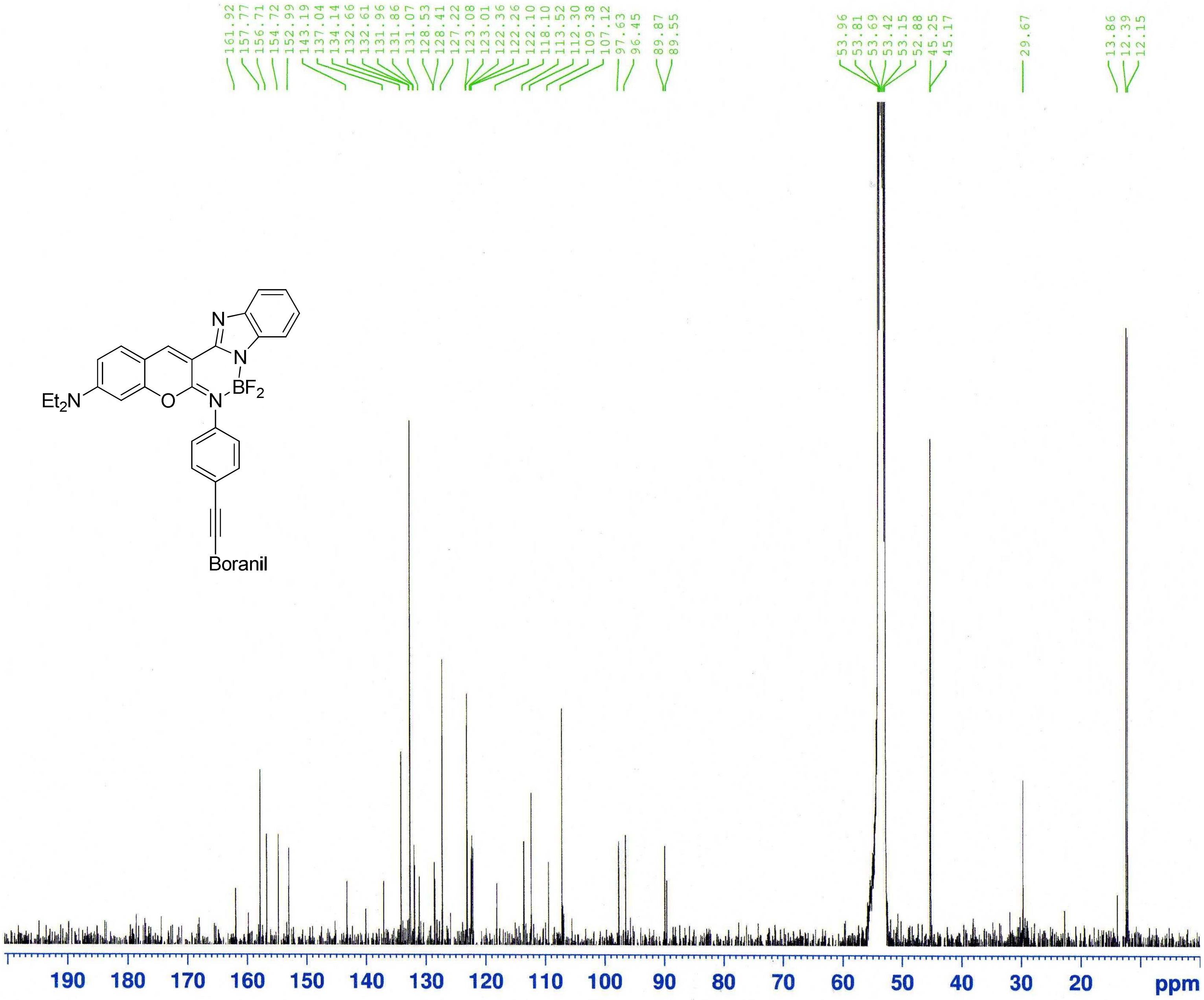

ppm
9,081
7,697
7,669
7,520
7,492
7,260
7,244
7,220
7,196
6,714
6,709
6,684
6,679
6,156
6,149
3,425
3,401
1,244
1,220
1,196
0,308
N
N
BF2
Et2N
O
N
TMS
1,0
4,0
3,1
2,3
1,0
1,0
4,3
6,8
9,2
ppm
9
8
7
6
5
4
3
2
1
0

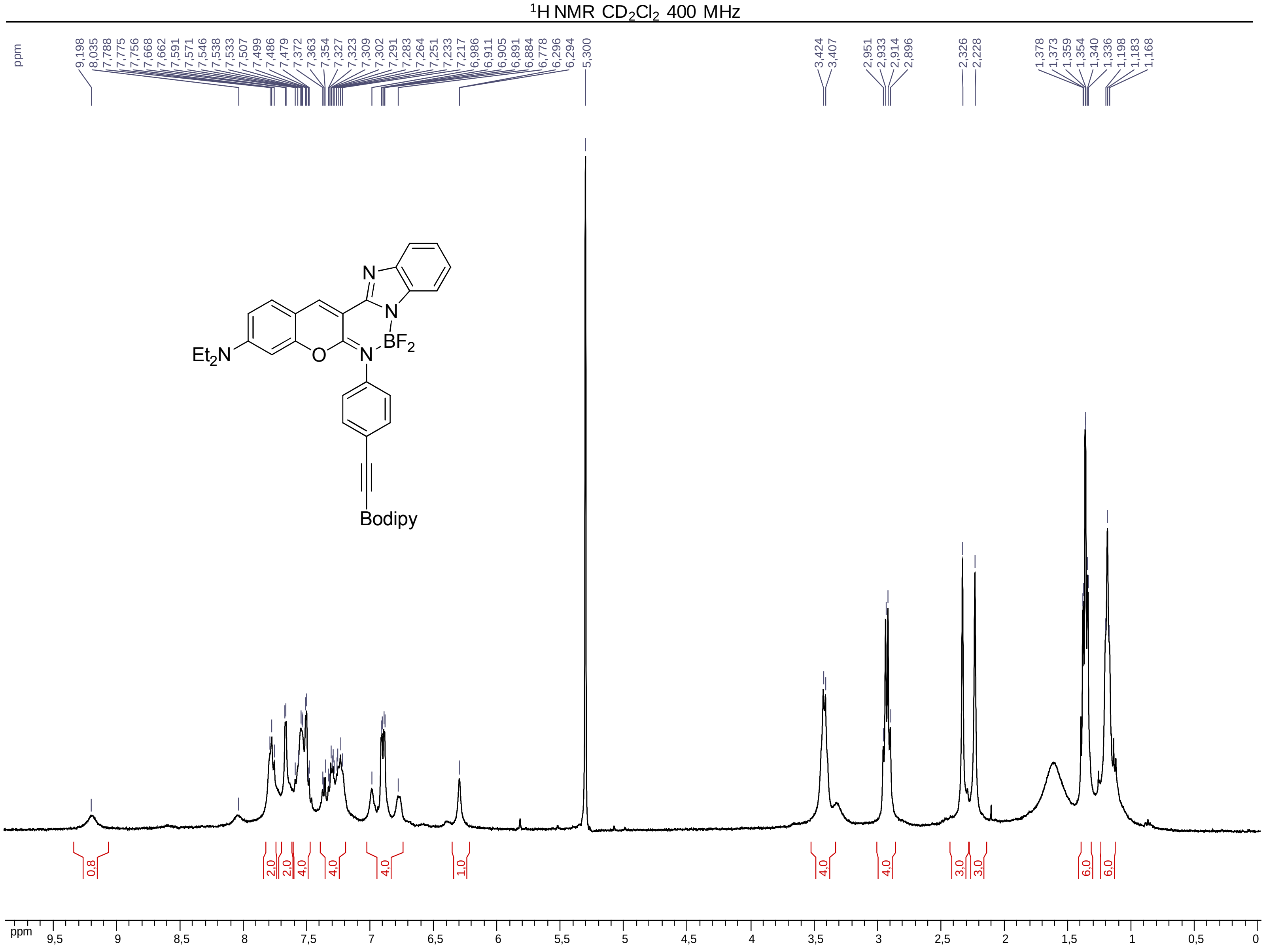

ppm
154,739
153,103
140,465
137,133
133,326
131,522
127,253
122,970
117,966
114,188
112,334
109,530
104,581
96,644
77,655
76,808
45,355
12,731
0,197
N
N
BF2
Et2N
O
N
TMS
ppm
180
160
140
120
100
80
60
40
20
0

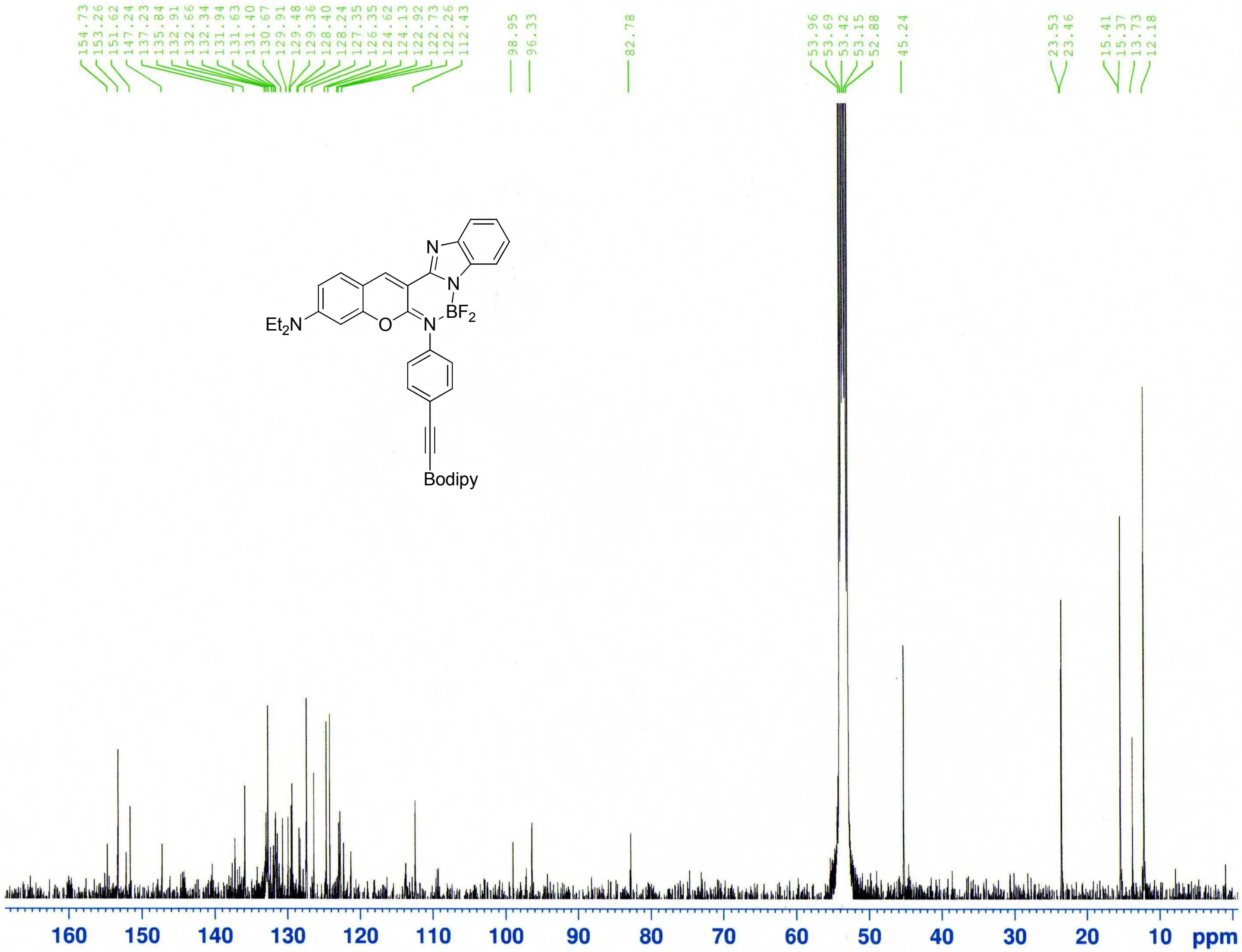

^{1}H NMR CDCl$_3$ 300 MHz
ppm
7,749
7,736
7,504
7,492
7,260
7,009
6,906
6,869
6,857
6,850
6,837
2,936
2,910
2,886
2,860
2,264
2,262
2,216
1,380
1,375
1,355
1,349
1,330
1,325
I
N
B
N
F
F
S
S
1,0
1,0
1,0
1,0
2,0
4,2
3,0
3,0
6,1
ppm
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0


^{13}C NMR CDCl$_3$ 75 MHz
ppm
152,687
151,997
151,364
147,466
135,841
135,739
133,008
132,932
132,845
131,917
131,852
131,783
131,332
130,579
129,543
129,161
124,798
124,165
123,729
93,407
77,422
76,575
23,555
23,493
15,439
15,268
14,087
I
N
B
N
F
F
S
S
ppm
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


ppm
9,004
8,080
7,755
7,727
7,662
7,633
7,603
7,572
7,507
7,504
7,479
7,477
7,288
7,257
7,232
7,216
7,207
7,195
6,823
6,816
6,792
6,784
6,429
6,421
6,398
6,392
6,309
6,302
6,200
6,193
5,290
3,495
3,470
3,447
3,429
3,405
3,381
1,250
1,226
1,201
1,176
1,152
N
N
BF2
Et2N
O
N
Boranil
0,9
1,0
8,1
4,3
3,4
0,9
1,0
1,0
1,0
8,3
14,8
ppm
10
9
8
7
6
5
4
3
2
1
0


161.92
157.77
156.71
154.72
152.99
143.19
137.04
134.14
132.66
132.61
131.96
131.86
131.07
128.53
128.41
127.22
123.08
123.01
122.36
122.26
122.10
118.10
113.52
112.30
109.38
107.12
97.63
96.45
89.87
89.55
53.96
53.81
53.69
53.42
53.15
52.88
45.25
45.17
29.67
13.86
12.39
12.15
N
N
BF2
Et2N
O
N
Boranil
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


^{1}H NMR CD_2Cl_2 400 MHz
ppm
9,198
8,035
7,788
7,775
7,756
7,668
7,662
7,591
7,571
7,546
7,538
7,533
7,507
7,499
7,486
7,479
7,372
7,363
7,354
7,327
7,323
7,309
7,302
7,291
7,283
7,264
7,251
7,233
7,217
6,986
6,911
6,905
6,891
6,884
6,778
6,296
6,294
5,300
3,424
3,407
2,951
2,933
2,914
2,896
2,326
2,228
1,378
1,373
1,359
1,354
1,340
1,336
1,198
1,183
1,168
N
N
BF$_2$
Et$_2$N
O
N
Bodipy
0,8
2,0
2,0
4,0
4,0
4,0
1,0
4,0
4,0
3,0
3,0
6,0
6,0
ppm
9,5
9
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0


154.73
153.26
151.62
147.24
137.23
135.84
132.91
132.66
132.34
131.94
131.63
131.40
130.67
129.91
129.48
129.36
128.40
128.24
127.35
126.35
124.62
124.13
122.92
122.73
122.26
112.43
98.95
96.33
82.78
53.96
53.69
53.42
53.15
52.88
45.24
23.53
23.46
15.41
15.37
13.73
12.18
N
N
BF2
Et2N
O
N
Bodipy
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm