Electronic Supporting Information (ESI)

Tunable solid state emission of novel V-shaped fluorophores by subtle structure modification: polymorphism, mechanofluorochromism and micro-fabrication

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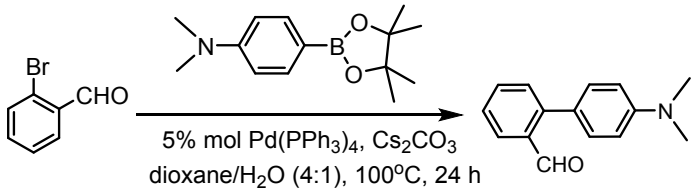
Materials and instruments

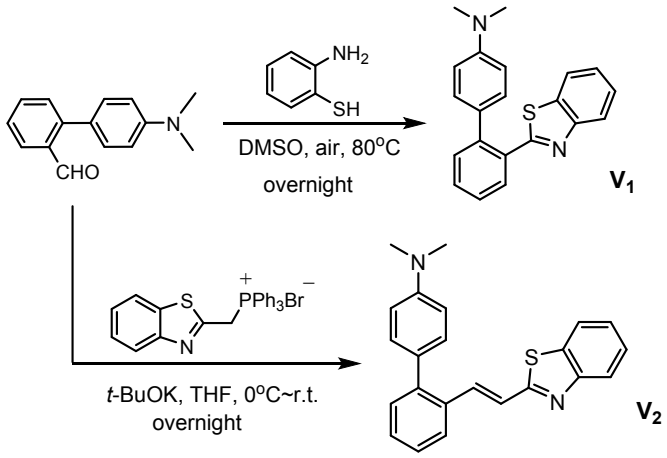
All the reagents were analytically pure and some chemicals were further purified by recrystallization or distillation. Melting points were determined by an OptiMelt automated melting point system. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a Bruker Avance II DMX 400 spectrometer with $CDCl_3$or DMSO-d_6 as the solvent. The absorption spectra were measured on a Shimadzu UV 2501(PC)S UV–Vis spectrometer, and the fluorescence spectra were acquired on a Perkin-Elmer LS55 spectrophotometer. The quantum yields were measured with quinine sulfate in 0.1 M sulfuric acid solution (Φ_f =0.55) as the reference and the solid-state quantum yields were gained by an integral sphere. The mass spectrum was recorded on a HP 1110 mass spectrometer. The crystallographic data were determined on a Bruker Gemini Ultra diffractometer with a CCD counter. The powder X-ray diffraction patterns were recorded on DX2700 with Cu-K_α radiation operating at 40 kV and 40 mA by a 0.3°/min scanning rate. Dynamic light scattering is carried out on a Beckman Coulter particle analyzer with 50 μM aggregate in MeCN/H_2O mixture (5 : 95, v/v) at 25 °C.

Synthetic procedures



At room temperature and N_2 flux, the solution of *N, N*-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (12 mmol, 2.95 g) in dioxane/H_2O (4:1, v/v, 20 mL) was injected into the mixture of 2-bromobenzaldehyde (10 mmol, 1.83 g), $Pd(PPh_3)_4$ (0.5 mmol, 0.577 g) and $CsCO_3$(15 mmol, 2.89 g) in dioxane/H_2O (4:1, v/v, 30 mL). The resulted mixture was heated at 100°C for 24 h and then cooled to room temperature. After filtration, the filtrate was diluted with water and extracted by CH_2Cl_2 (2×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the removal of solvent, the residue was purified on a silica gel column chromatography.

4'-(dimethylamino)-[1,1'-biphenyl]-2-carbaldehyde: 88% yield; m.p. 77.4-79.3°C; ^{1}H NMR(400MHz, $CDCl_3$) δ 2.93(s, 6H), 6.71(d, *J*=7.6 Hz, 2H), 7.17(d, *J*=8.0Hz, 2H), 7.31-7.37(m, 2H), 7.50(t, *J*=7.6Hz, 1H), 7.79(d, *J*=8.0Hz, 1H), 9.94(s, 1H); ^{13}C NMR(100MHz, $CDCl_3$) δ 40.58, 112.05, 126.63, 127.54, 130.63, 131.10, 133.42, 133.61, 146.30, 150.26, 193.54; EI-MS (70eV) *m/z* (%) 225(M^+, 100), 196(45), 182(29), 167(12), 152(49), 141(13), 128(17), 115(17), 69(23), 51 (25), 42(47).

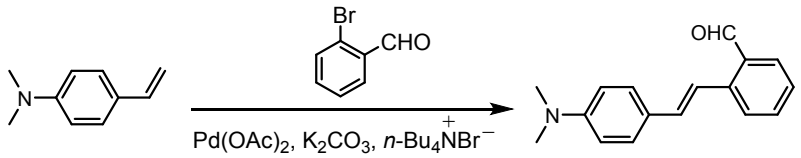


At room temperature, the solution of 2-aminothiophenol (12 mmol, 1.5 g) in DMSO (10 mL) was added into the solution of 4'-(dimethylamino)-[1,1'-biphenyl]-2-carbaldehyde (10 mmol, 2.25 g) in DMSO (10 ML) and the resulted solution was heated at 80 ^{0}C open to the air overnight and then cooled to room temperature. The solution was diluted with water and extracted by CH_2Cl_2 (2×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the removal of solvent, the residue was purified on a silica gel column chromatography to produce **V_1**.

2'-(benzo[*d*]thiazol-2-yl)-N,N-dimethyl-[1,1'-biphenyl]-4-amine (V_1): 64% yield; m.p. 125.1-126.3°C; ^{1}H NMR(400MHz, $CDCl_3$) δ 2.97(s, 6H), 6.69(d, *J*=8 Hz, 2H), 7.18(d, *J*=8 Hz, 2H), 7.29(t, *J*=8 Hz, 1H), 7.39-7.50(m, 4H), 7.71(d, *J*=8 Hz, 1H), 8.05-8.08(m, 2H); ^{13}C NMR(100MHz, $CDCl_3$) δ40.39, 112.09, 121.38, 123.08, 124.67, 125.68, 126.92, 127.66, 129.97, 130.33, 130.85, 130.98, 132.53, 136.85, 142.01, 150.05, 152.74, 168.54; EI-MS (70eV) *m/z* (%) 330(M^+,100), 313(22), 286(13).

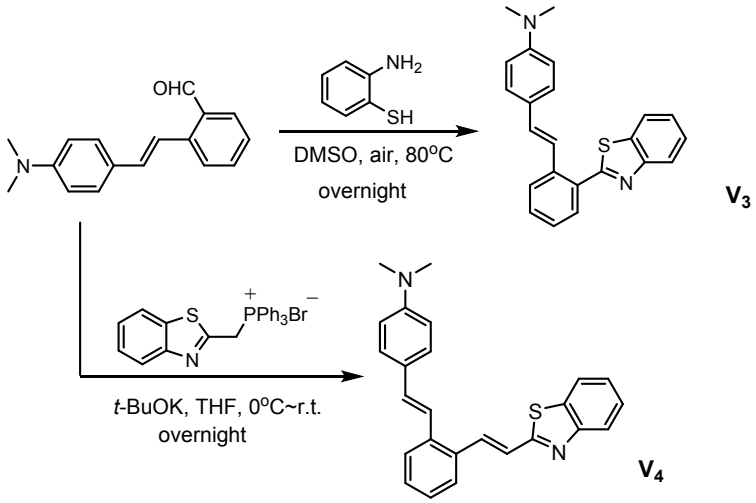
At 0°C and N_2 flux, *t*-BuOK (10mmol, 1.12 g) was added into 2-methylbenzo[d]thiazolyltriphenyl-phosphonium bromide (10 mmol, 4.90 g) in dried THF (20 mL), the mixture was stirred for 30 min. The solution of compound 4'-(dimethylamino)-[1,1'-biphenyl]-2-carbaldehyde (10 mmol, 2.25 g)in dried THF (15 mL) was injected into the above mixture. The resulted mixture was kept at the same temperature for 1 h and stirred at room temperature overnight. After poured into water, the mixture was extracted with ethyl acetate (2×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the removal of solvent, the residue was purified on a silica gel column chromatography to produce **V_2**.

(*E*)-2'-(2-(benzo[*d*]thiazol-2-yl)vinyl)-N,N-dimethyl-[1,1'-biphenyl]-4-amine(V_2):73% yield; m.p. 114.9-116.3°C; ^{1}H NMR(400MHz, $CDCl_3$) δ 3.03(s, 6H), 6.83(d, *J*=8.8Hz, 2H), 7.29-7.47(m, 8H), 7.62(d, *J*=16Hz, 1H), 7.78(m, 2H), 7.98(d, *J*=8.0Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 40.51, 112.13, 121.38, 121.70, 122.57, 122.86, 123.61, 125.19, 126.15, 126.45, 126.85, 129.16, 130.34, 130.83, 133.34, 134.30, 138.21, 142.32, 153.88, 167.89; EI-MS (70eV) *m/z* (%) 356(M^+, 57), 310(11), 236(22), 221(100), 178(24), 108(12), 69(21), 42(12).



At room temperature and N_2 flux, the solution of 2-bromobenzaldehyde (10 mmol, 1.83 g) in acetonitrile (10 mL) was injected into the mixture of $Pd(OAc)_2$ (0.5 mmol, 0.112 g), K_2CO_3 (12 mmol, 1.66 g), 4-dimethylaminostyrene (12 mmol, 1.76 g) and *n*-tetrabutylammonium bromide (30 mmol, 9.63 g) in acetonitrile (15 mL). The resulted mixture was stirred and refluxed for overnight. After cooled to the room temperature, the mixture was filtrated and the filtrate was diluted with water. The extracted EtOAc layers (2×15 mL) were combined and dried over anhydrous Na_2SO_4. After the removal of solvent, the residue was purified on a silica gel column chromatography.

(*E*)-2-(4-(dimethylamino)styryl)benzaldehyde: 81% yield;m.p. 115.5-117^oC;^1H NMR(400MHz, $CDCl_3$) δ2.99(s, 6H), 6.72(d, *J*=8 Hz, 2H), 7.00(d, *J*=16 Hz, 1H), 7.35(t, *J*=7.6 Hz, 1H), 7.46(d, *J*=8 Hz, 2H), 7.53(t, *J*=7.6 Hz, 1H), 7.69(d, *J*=7.6 Hz, 1H), 7.80 (s, 1H), 7.83(d, *J*=8 Hz, 1H), 10.34(s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ40.45, 112.38, 119.72, 126.66, 126.76, 128.20, 131.74, 132.48, 133.61, 134.48, 141.06, 150.49, 192.73; EI-MS (70eV) *m/z* (%)251(M^+, 100), 222(78), 207(33), 178(46), 165(12).



At room temperature, the solution of 2-aminothiophenol (12 mmol, 1.5 g) in DMSO (10 mL) was added into the solution of (*E*)-2-[4-(dimethylamino)styryl]benzaldehyde (10 mmol, 2.51 g) in DMSO (10 ML) and the resulted solution was heated at 80 ^0C open to the air overnight and then cooled to room temperature. The solution was diluted with water and extracted by CH_2Cl_2 (2×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the removal of solvent, the residue was purified on a silica gel column chromatography to produce **V_3**.

(*E*)-4-(2-(benzo[*d*]thiazol-2-yl)styryl)-N,N-dimethylaniline (V_3): 56% yield; m.p. 104.5-106.1^oC; ^1H NMR(400MHz, $CDCl_3$) δ2.95(s, 6H), 6.68(d, *J*=8 Hz, 2H), 7.04(d, *J*=16 Hz, 1H), 7.32(t, *J*=8 Hz, 1H), 7.39(m, 3H), 7.45(t, *J*=8 Hz, 1H), 7.50(t, *J*=8 Hz, 1H), 7.59(d, *J*=16 Hz, 1H), 7.45(d, *J*=8 Hz, 1H), 7.84(d, *J*=8 Hz, 1H), 7.90(d, *J*=8 Hz, 1H), 8.14(d, *J*= 8Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 40.40, 112.34, 121.39, 122.46, 122.50, 123.43, 125.03, 125.80, 126.12, 126.63, 126.79, 128.00, 130.22, 130.64, 131.64, 131.95, 137.86, 150.23, 153.68, 167.58; EI-MS (70eV) *m/z* (%) 356(M^+, 100), 339(16), 236(100),178(11).

At 0°C and N_2 flux, *t*-BuOK (10mmol, 1.12 g) was added into 2-methylbenzo[d]thiazolyltriphenyl-phosphonium bromide (10 mmol, 4.90 g) in dried THF (20 mL), the mixture was stirred for 30 min. The solution of compound (*E*)-2-[4-(dimethylamino)styryl]benzaldehyde (10 mmol, 2.51 g) in dried THF (15 mL) was injected into the above mixture. The resulted mixture was kept at the same temperature for 1 h and stirred at room temperature overnight. After poured into water, the mixture was extracted with ethyl acetate (2×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the removal of solvent, the residue was purified on a silica gel column chromatography to produce **V_4**.

4-{(*E*)-2-[(*E*)-2-(benzo[*d*]thiazol-2-yl)vinyl]styryl}-N,N-dimethylaniline (V_4): 42% yield; m. p. 123.5-124.8°C; ^{1}H NMR(400MHz, $CDCl_3$) δ 2.99(s, 6H), 6.73(d, *J*= 8Hz, 2H), 6.94(d, *J*=16 Hz, 1H), 7.24-7.38(m, 5H), 7.46(m, 3H), 7.58(d, *J*= 8Hz, 1H), 7.63(d, *J*= 8 Hz, 1H), 7.84(d, *J*= 8 Hz, 1H), 7.94(d, *J*=16 Hz, 1H), 8.00(d, *J*=8 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 40.45, 112.43, 121.29, 121.50, 123.00, 123.71, 123.75, 125.32, 126.28, 126.85, 127.05, 127.89, 129.30, 132.92, 133.32, 134.39, 136.15, 136.20, 137.88, 150.90, 153.97, 167.37; EI-MS (70eV) *m/z* (%) 382（M^+, 100）, 370(11), 262(12), 247(82), 234(12), 202(10), 191(11), 134(36), 121(10).

X-ray structure analysis

Single crystals of the title compounds grown in MeCN/EtOH were selected for the X-ray analysis. The diffraction data were collected on a Bruker CCD area-detector diffractometer equipped with a graphite-monochromated Mo*Ka* radiation (λ=0.71073 Å). The unit cell parameters were determined from a least-squares refinement of the setting angles. The structure was solved by direct methods and refined on F^2 by the full-matrix least-squares methods with SHELXS-97. The refinement was carried out by full-matrix least squares method on the positional and anisotropic temperature parameters of the non-hydrogen atoms using SHELXL-97. All H atoms were placed in the idealized positions and constrained to ride on their parent atoms. Compound **V_1**: $C_{21}H_{18}N_2S$, M_w= 330.43, monoclinic, P 2_1/C space group, a = 6.1982(5) Å, b = 24.956(2) Å, c = 10.8550(9)Å, α = 90 °, β = 97.234(8) °, γ = 90°, D_{calcud} = 1.318 g cm^{-3}, Z = 4, $F(000)$ = 696, μ = 0.198 mm^{-1}, 3767 reflections were corrected, 3648 unique, R_1 = 0.0456, wR_2 = 0.1268; Compound **V_2**: $C_{23}H_{20}N_2S$, M_w= 356.47, monoclinic, P 2_1/C space group, a= 12.5537(8) Å, b = 6.3103(4) Å, c = 23.6534(17) Å, α = 90 °, β = 99.738(6)°, γ = 90°, D_{calcud} = 1.282 g cm^{-3}, Z = 4, $F(000)$ = 752, μ = 0.184 mm^{-1}, 3389 reflections were corrected, 3377 unique, R_1 = 0.0437, wR_2 = 0.1125; Compound **V_3**: $C_{23}H_{20}N_2S$, M_w= 356.47, monoclinic, P 2_1/C space group , a = 12.0528(7) Å, b = 7.5440(3) Å, c = 40.438(2) Å, α = 90 °, β = 90.907(5) °, γ = 90 °, D_{calcud} = 1.288 g cm^{-3}, Z = 8, $F(000)$ = 1504, μ = 0.185 mm^{-1}, 6724 reflections were corrected, 6696 unique, R_1 = 0.0549, wR_2 = 0.1334.Crystallographic data for compound **V_1** (CCDC1551667),**V_2** (CCDC1521255),**V_3** (CCDC1551666) were deposited at CCDC center and can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

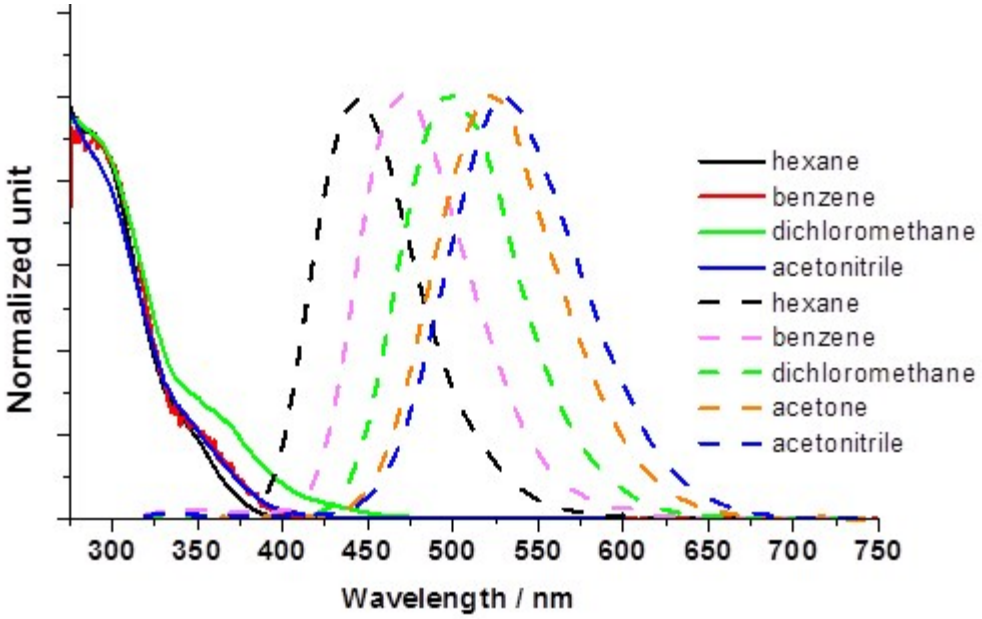


Fig.S1 Absorption (solid lines) and emission spectra (dash lines, λ_{ex} = 300 nm) of **V_1** (20 μM) in different solvents

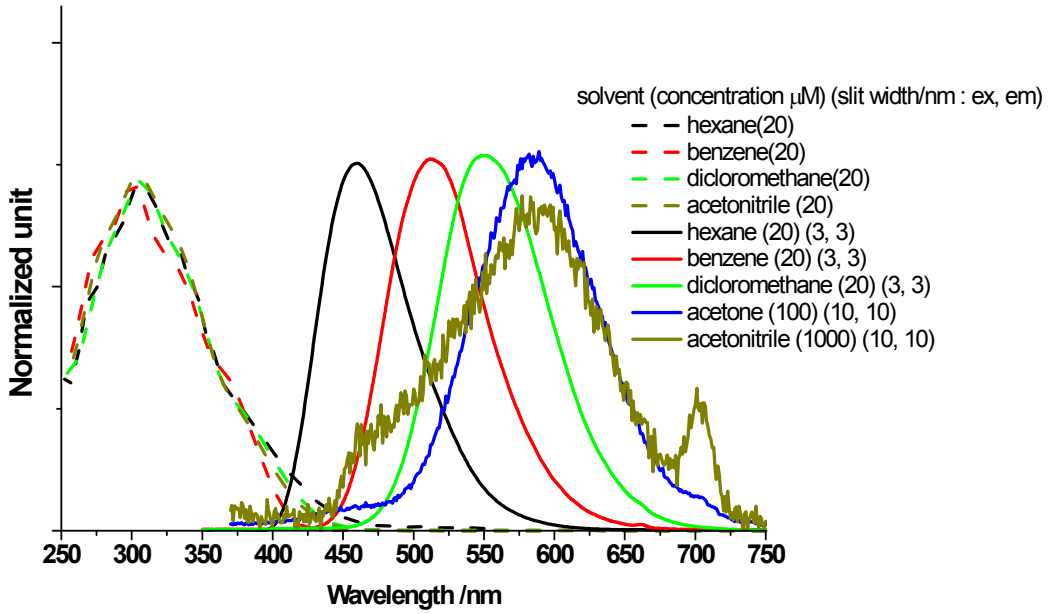


Fig. S2 Absorption (dash line) and emission spectra (solid line, λ_{ex} = 350 nm) of **V_2** in different solvents

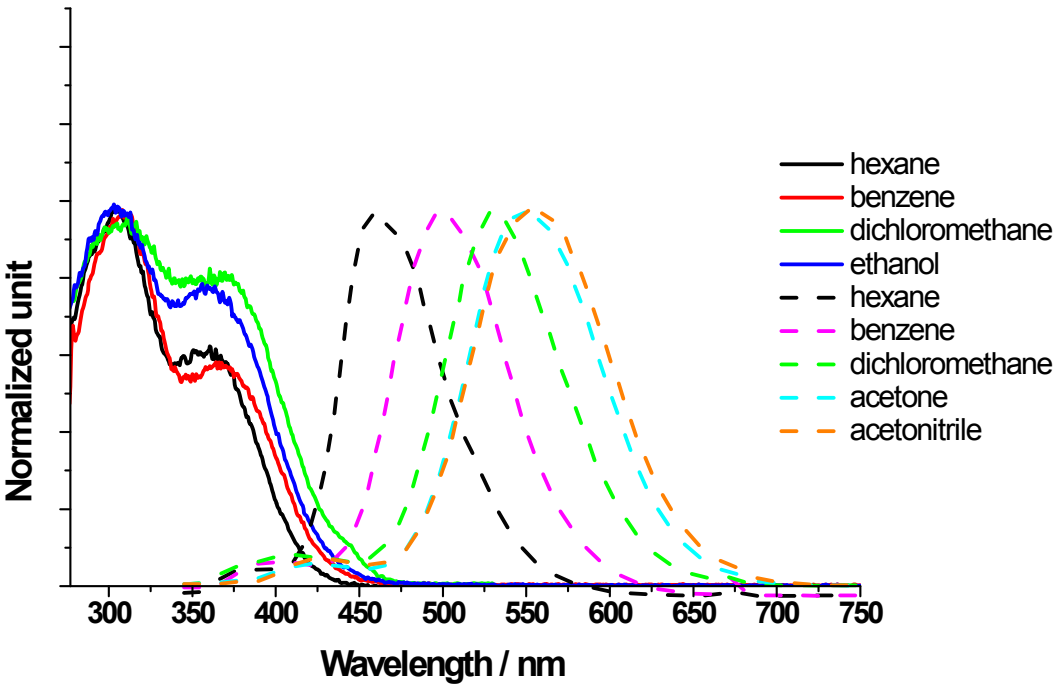


Fig.S3 Absorption (solid lines) and emission spectra (dash lines, λ_{ex} = 335 nm) of **V_3** (20 μM) in different solvents

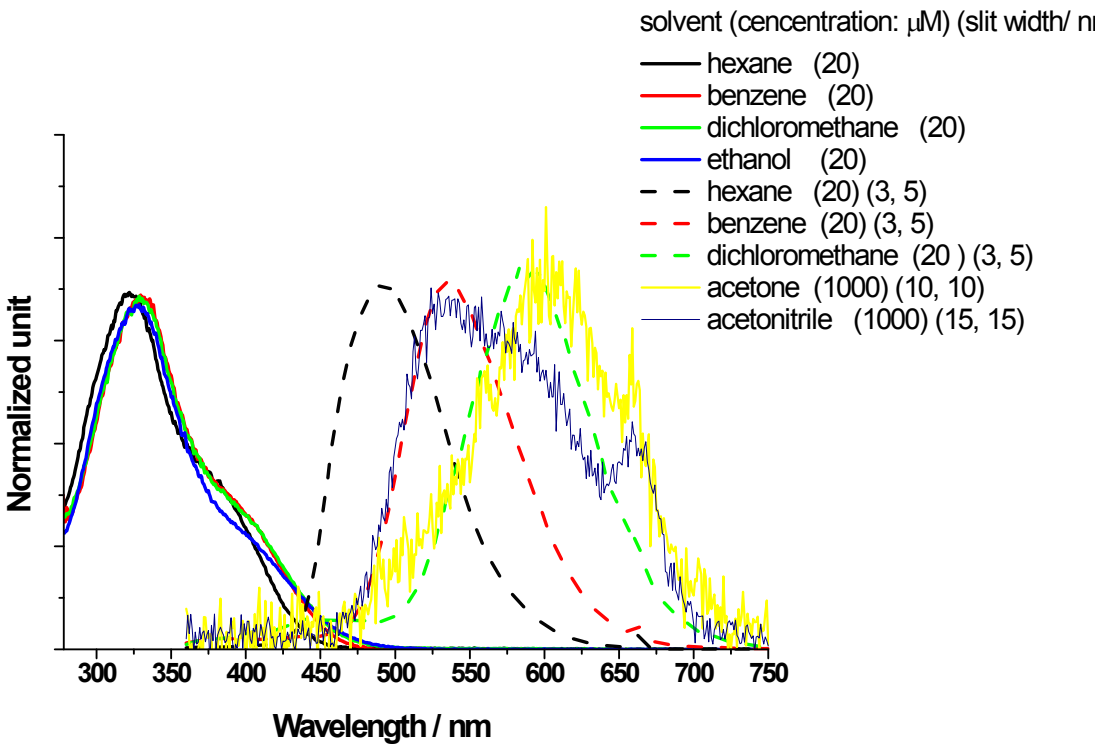


Fig. S4 Absorption (solid lines) and emission spectra (dash lines, λ_{ex} = 330 nm) of **V_4** in different solvents

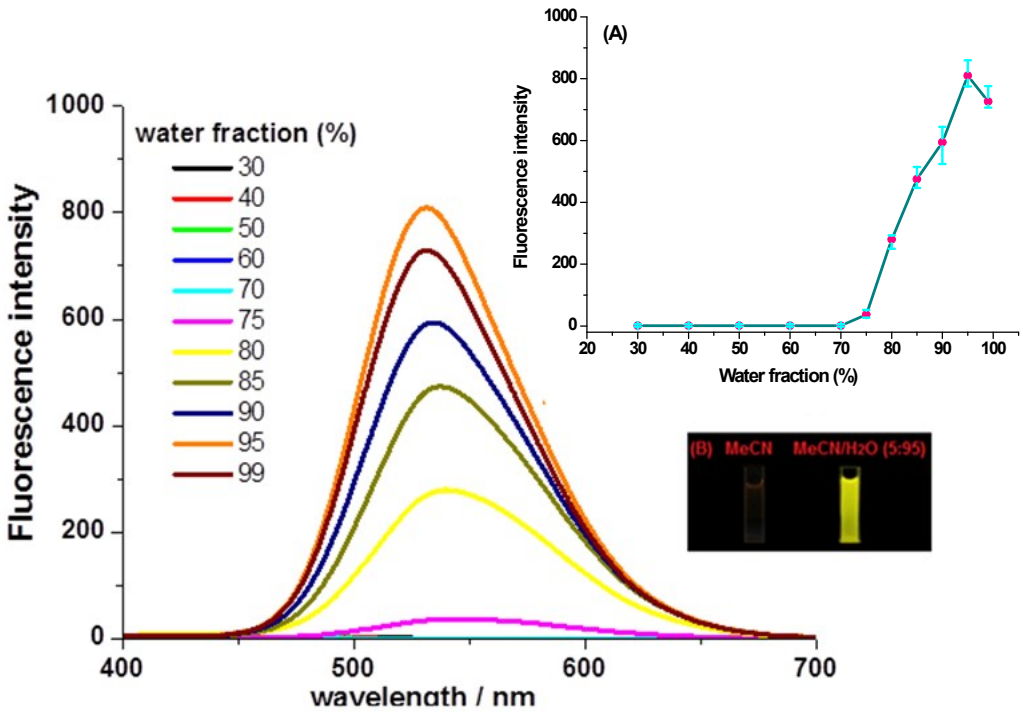


Fig. S5 Emission spectra of $\mathbf{V_2}$ (50 μM) in MeCN with varied water fraction [*inserted*: (A) the fluorescence intensity of $\mathbf{V_2}$ in MeCN with varied water fraction; (B) photos of $\mathbf{V_2}$ in MeCNand MeCN/H_2O (v/v, 5:95) mixture]

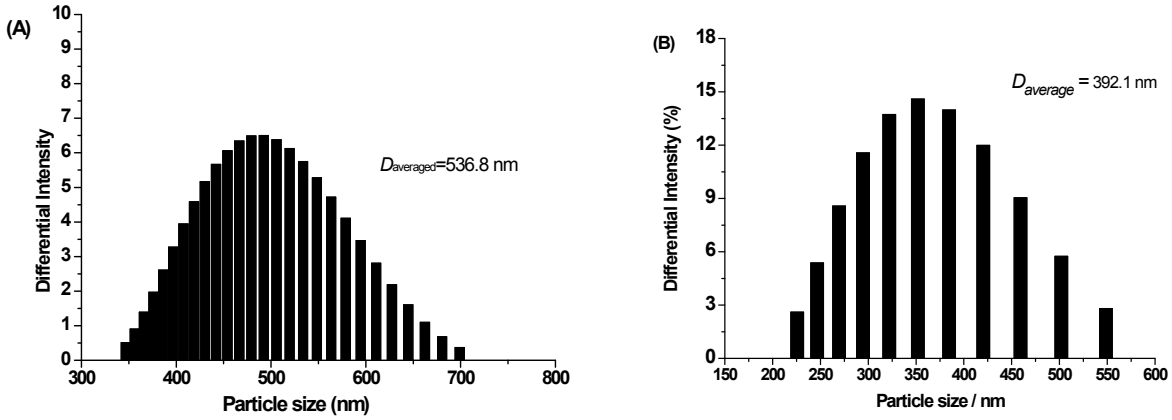


Fig.S6 Dynamical light scattering measurement of $\mathbf{V_4}$ **(A)** and $\mathbf{V_2}$**(B)** (50 μM) in MeCN/H_2O (5:95, v/v) mixture

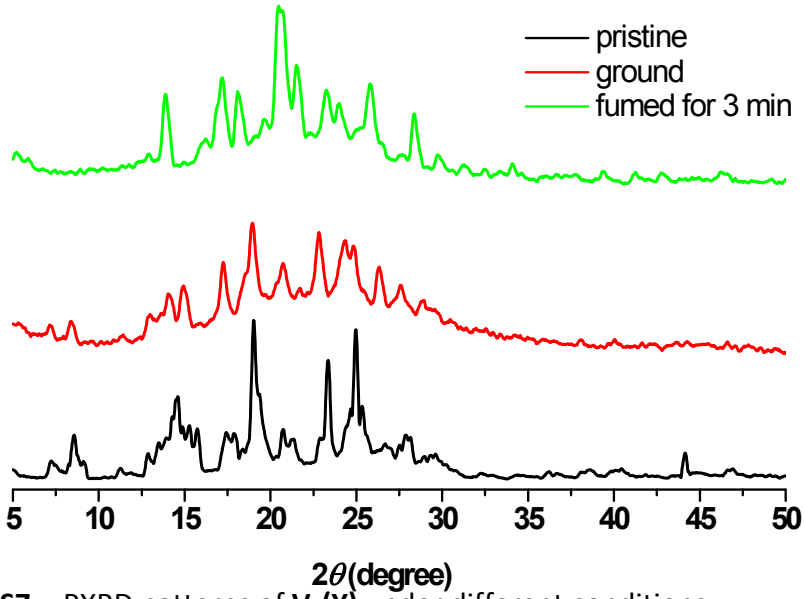


Fig. S7 PXRD patterns of **V_3(Y)** under different conditions

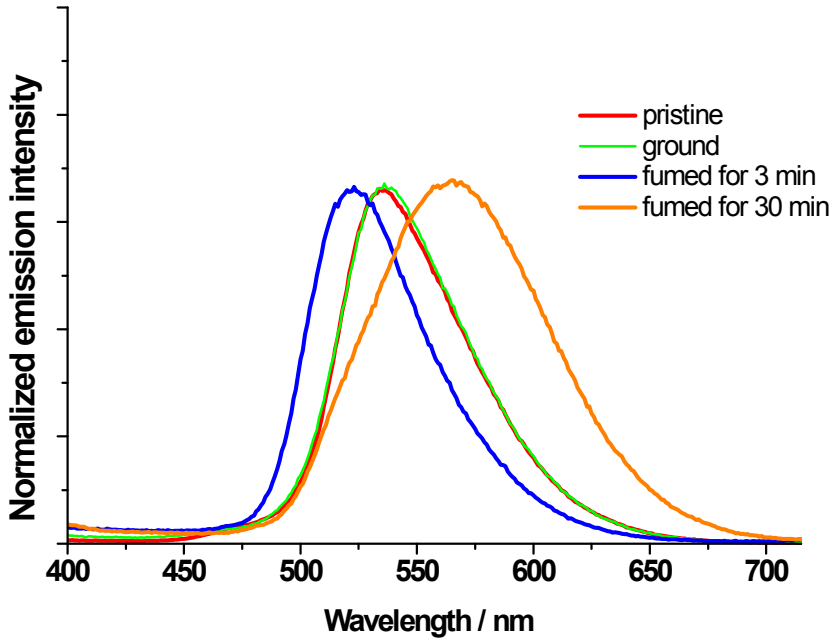


Fig. S8 Solid-state emission spectra of **V_3(Y)** under different conditions

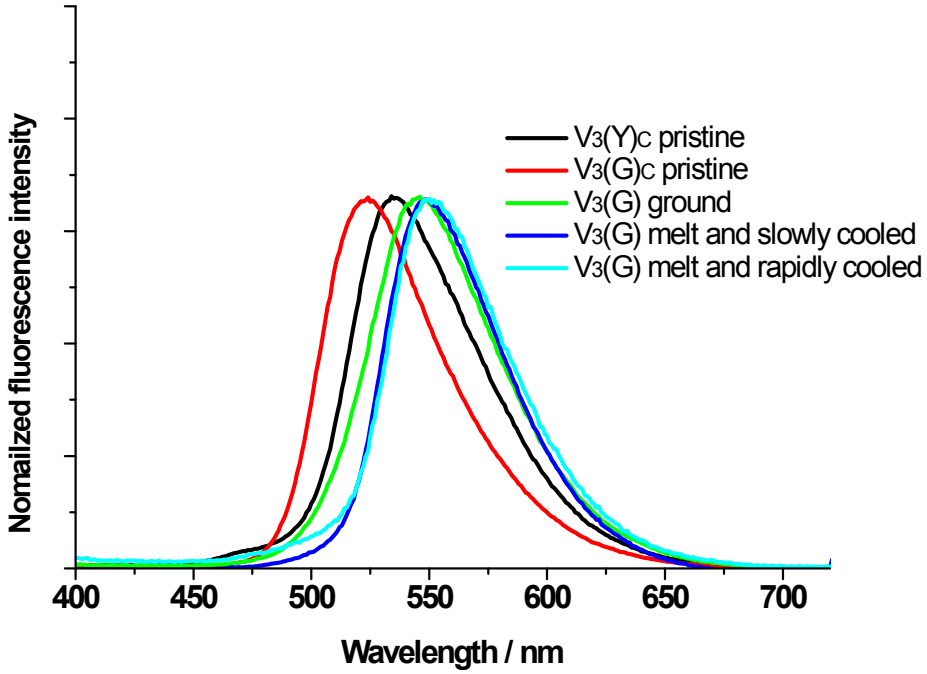


Fig. S9 Solid-state emission spectra of $\mathbf{V_3(Y)_C}$ and $\mathbf{V_3(G)}$ under different conditions

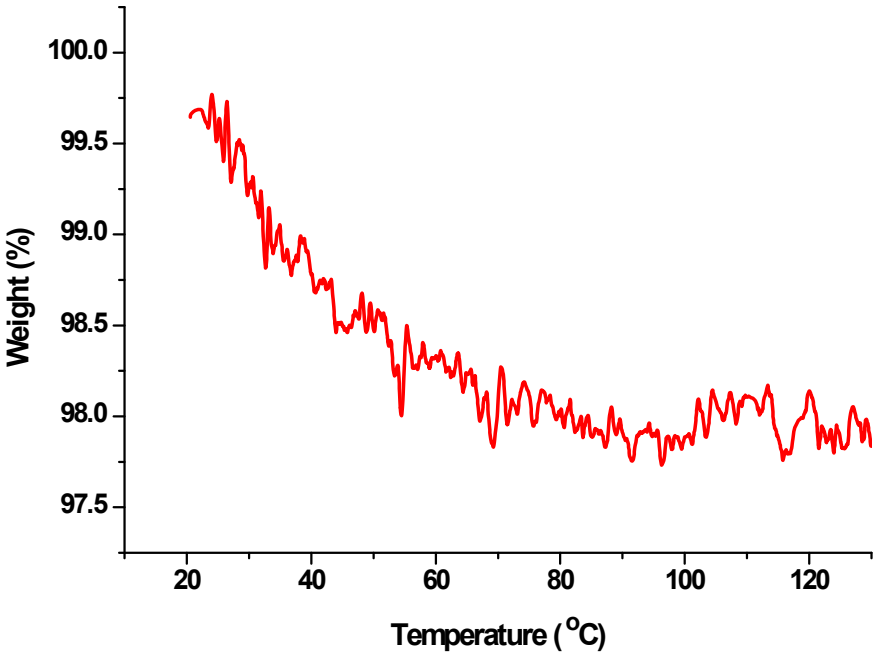


Fig. S10 Thermal gravimetric curve of $\mathbf{V_3(G)_c}$ sample

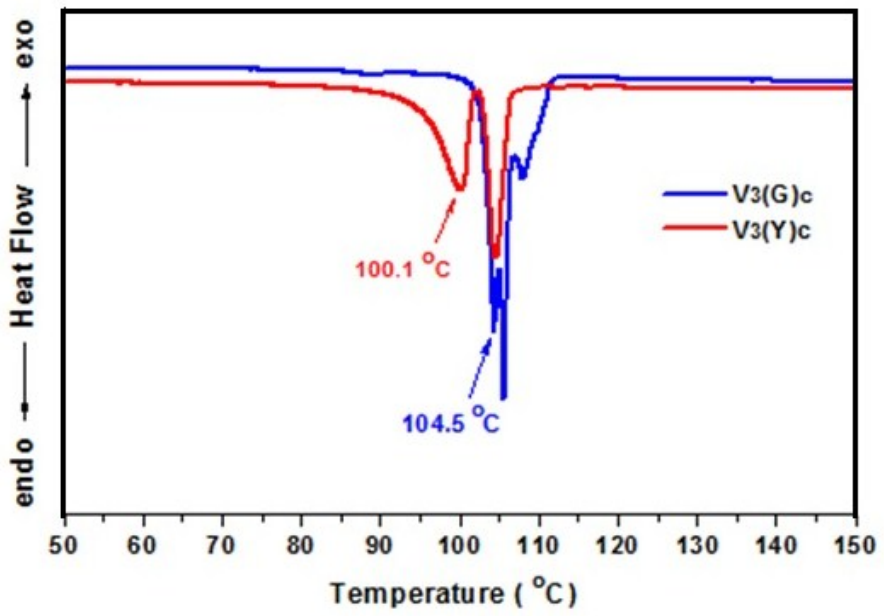


Fig. S11 Differential scanning calorimetry curves of $\mathbf{V_3(G)_C}$ and $\mathbf{V_3(Y)_C}$

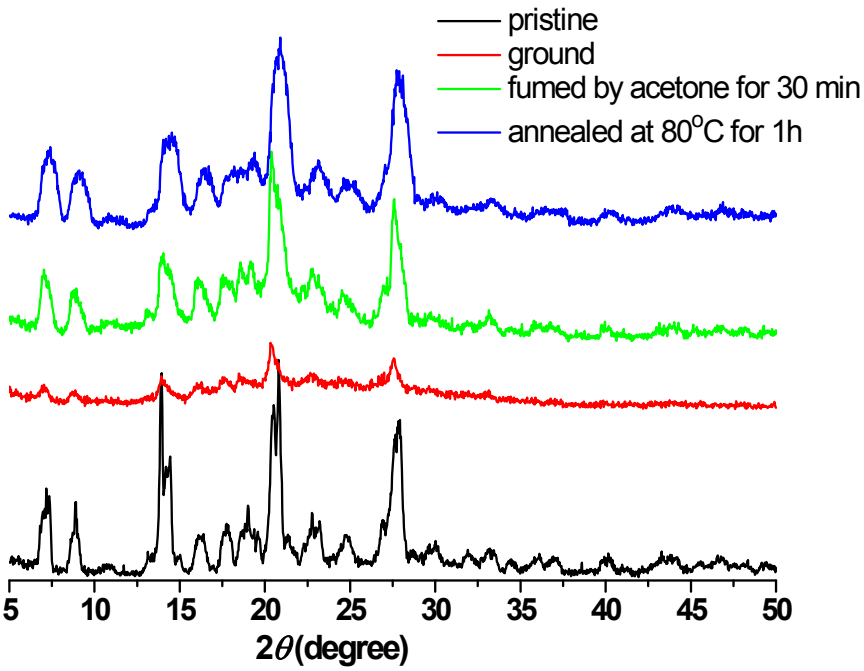


Fig. S12 PXRD patterns of $\mathbf{V_1}$ under different conditions

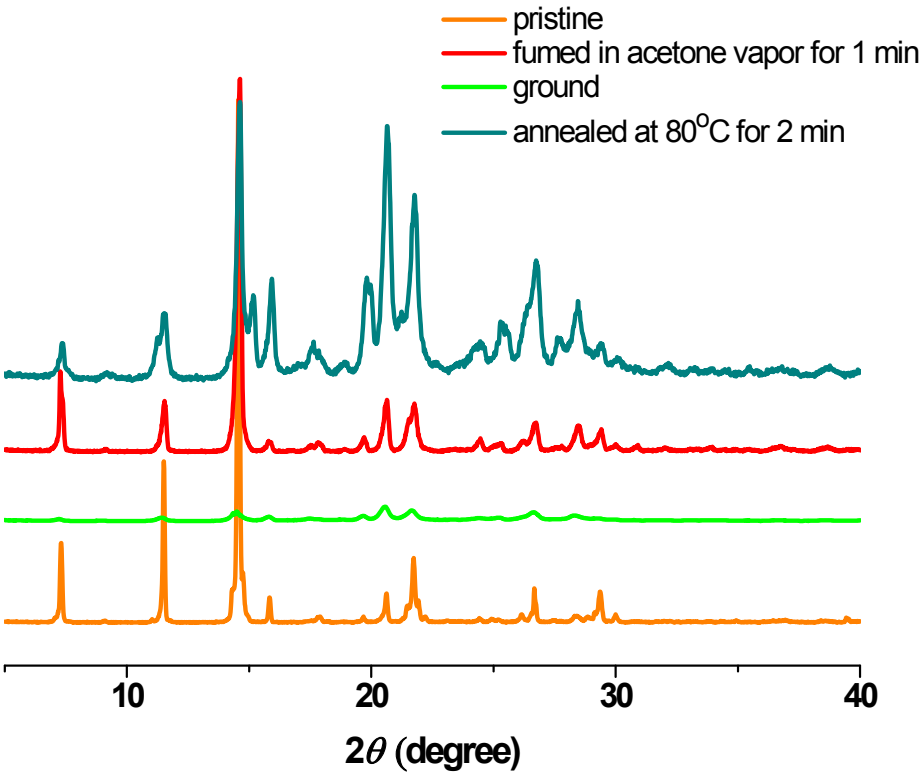


Fig.S13 PXRD patterns of $\mathbf{V_2}$ under different conditions

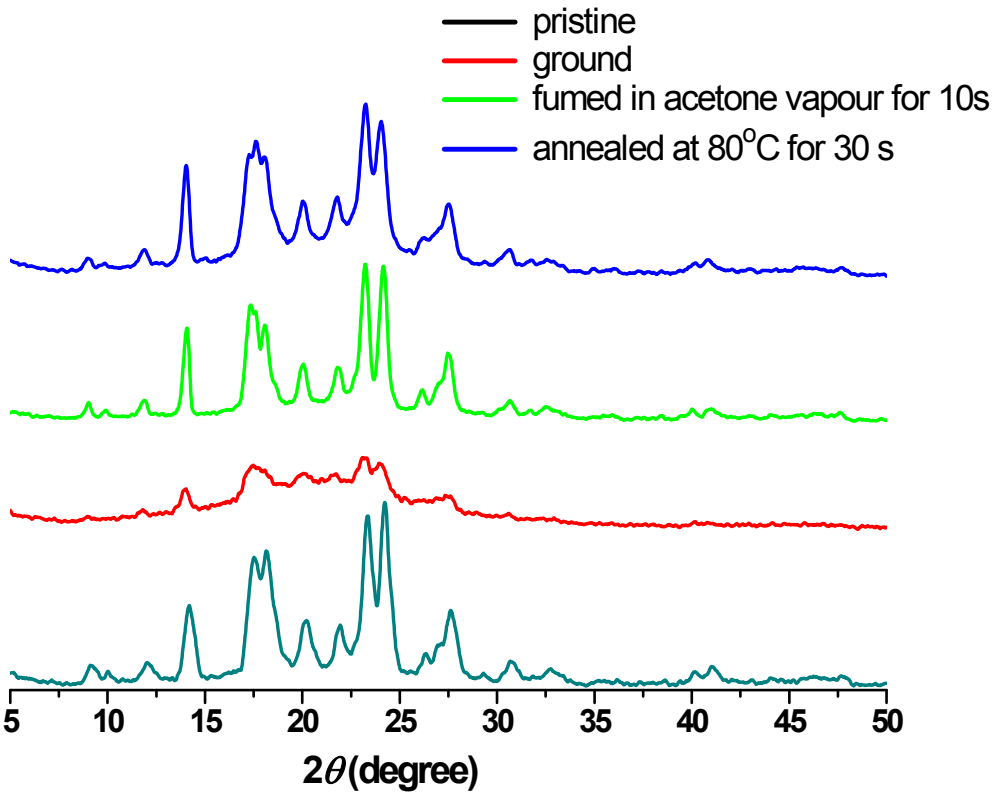


Fig. S14 PXRD patterns of $\mathbf{V_4}$ under different conditions

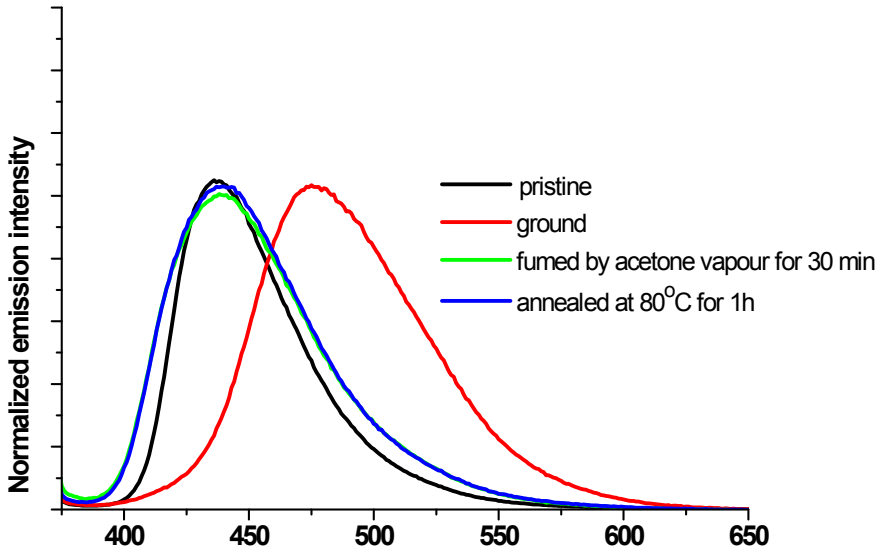


Fig. S15 Solid-state emission spectra of $\mathbf{V_1}$ under different conditions

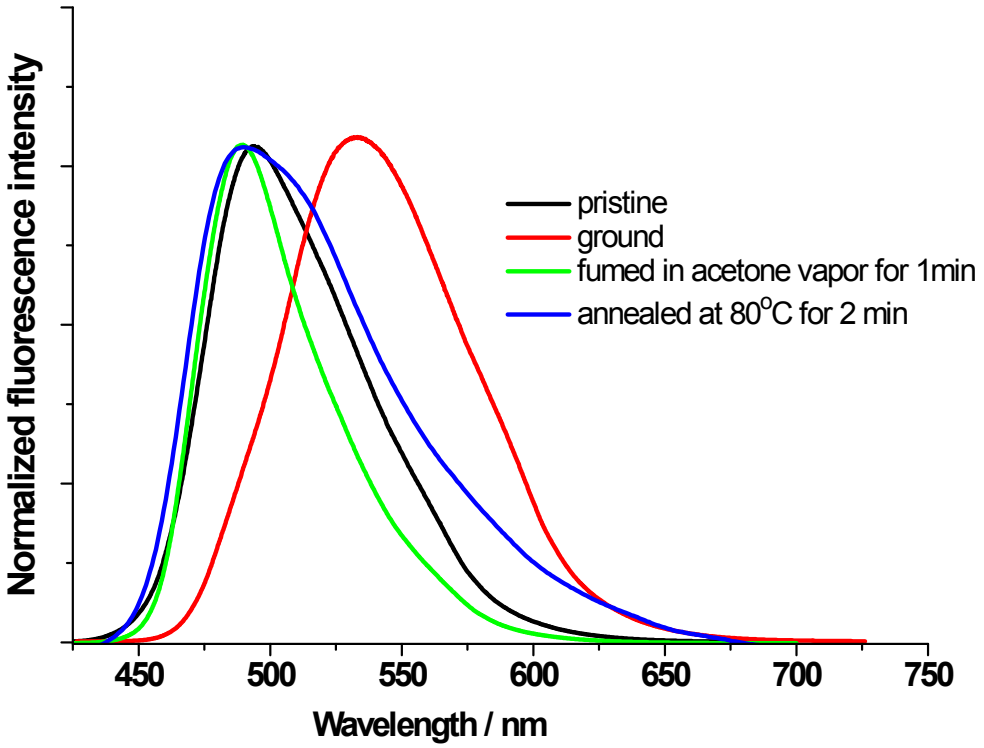


Fig. S16 Solid-state emission spectra of $\mathbf{V_2}$ under different conditions

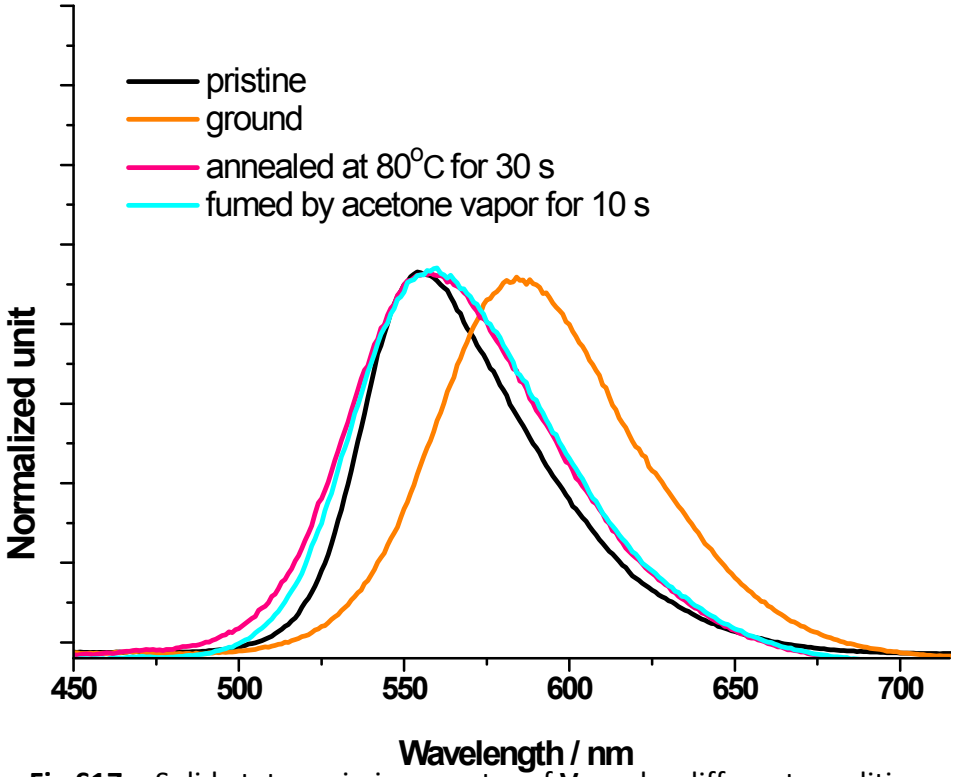


Fig.S17 Solid-state emission spectra of V_4 under different conditions

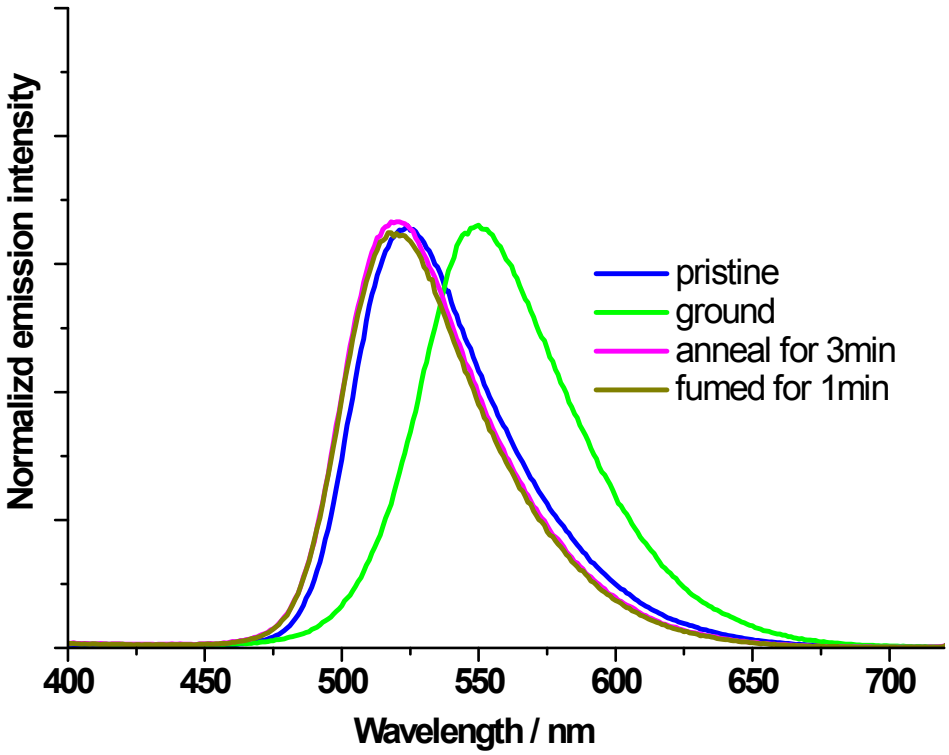


Fig. S18 Solid-state emission spectra of V_3**(G)** under different conditions

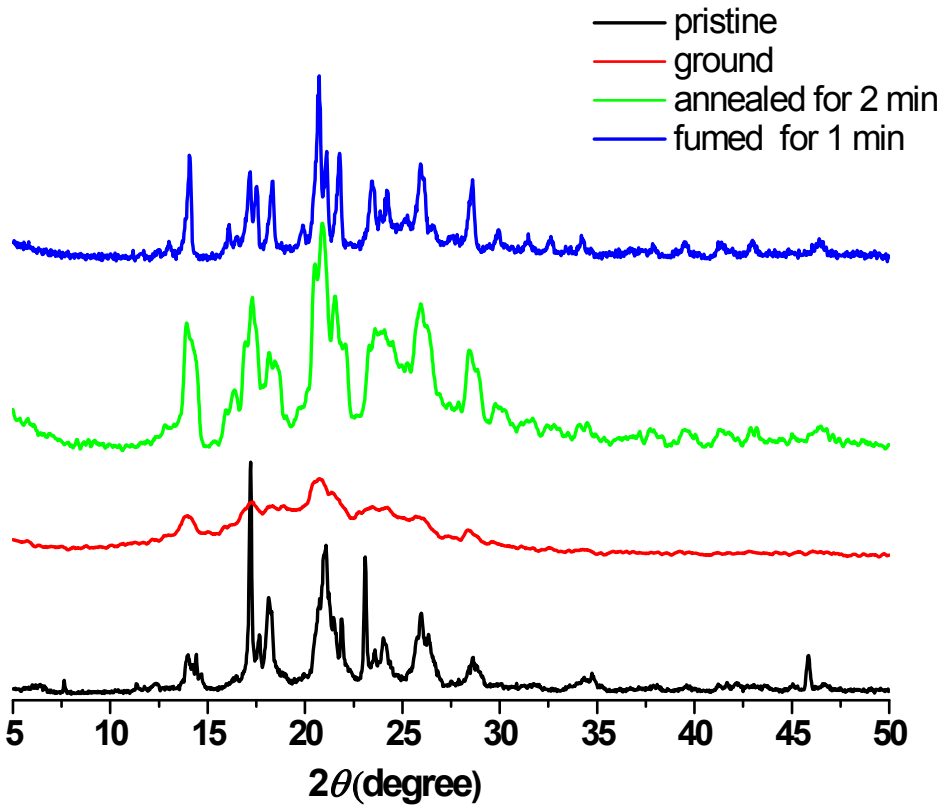


Fig. S19 PXRD patterns of **V_3(G)** under different conditions

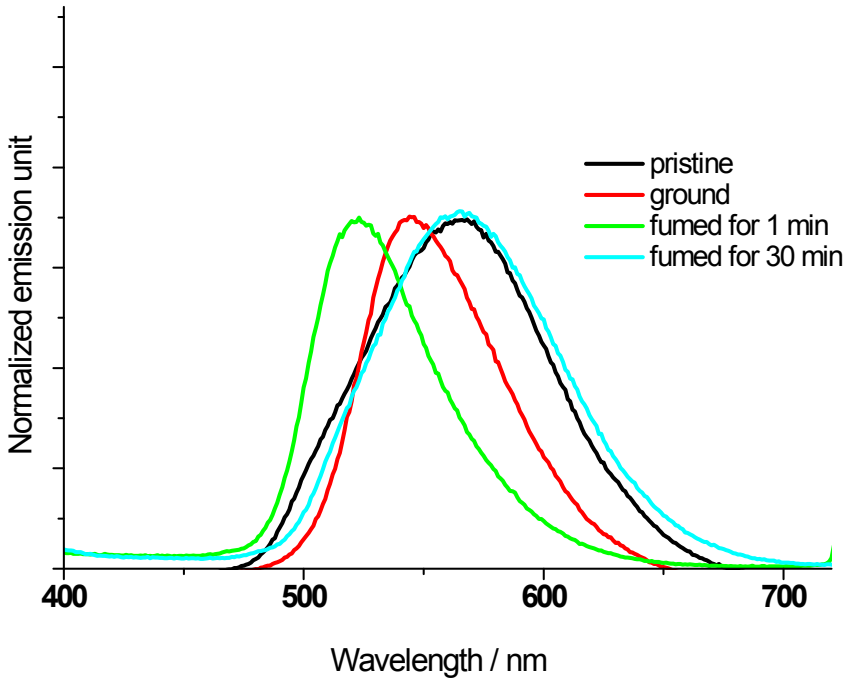


Fig. S20 Solid-state emission spectra of **V_3(O)** under different conditions

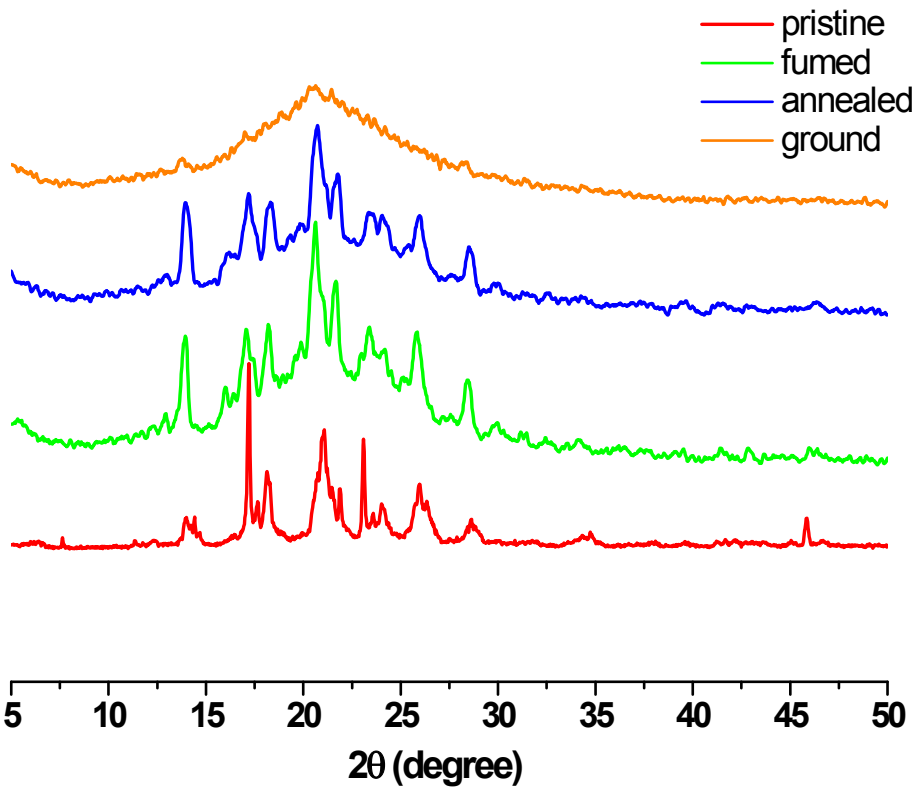


Fig. S21 PXRD patterns of **V_3(O)** under different conditions

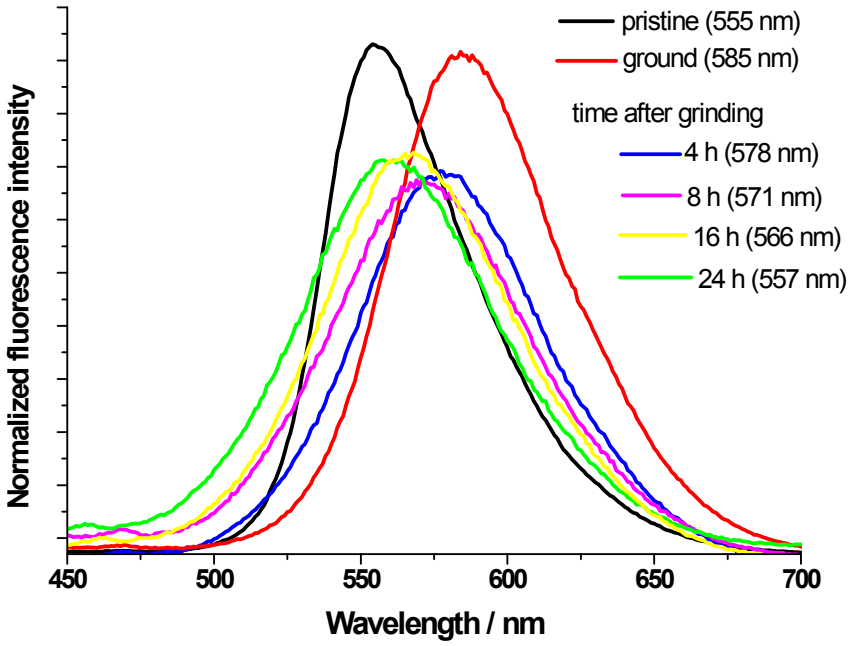


Fig. S22 Solid-state emission spectra of **V_4** before and after grinding as well as those of the ground sample for different time interval

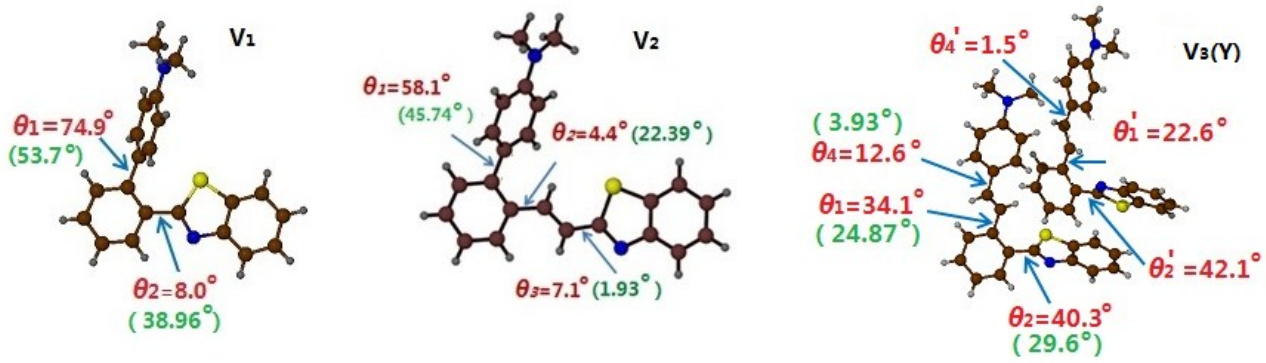
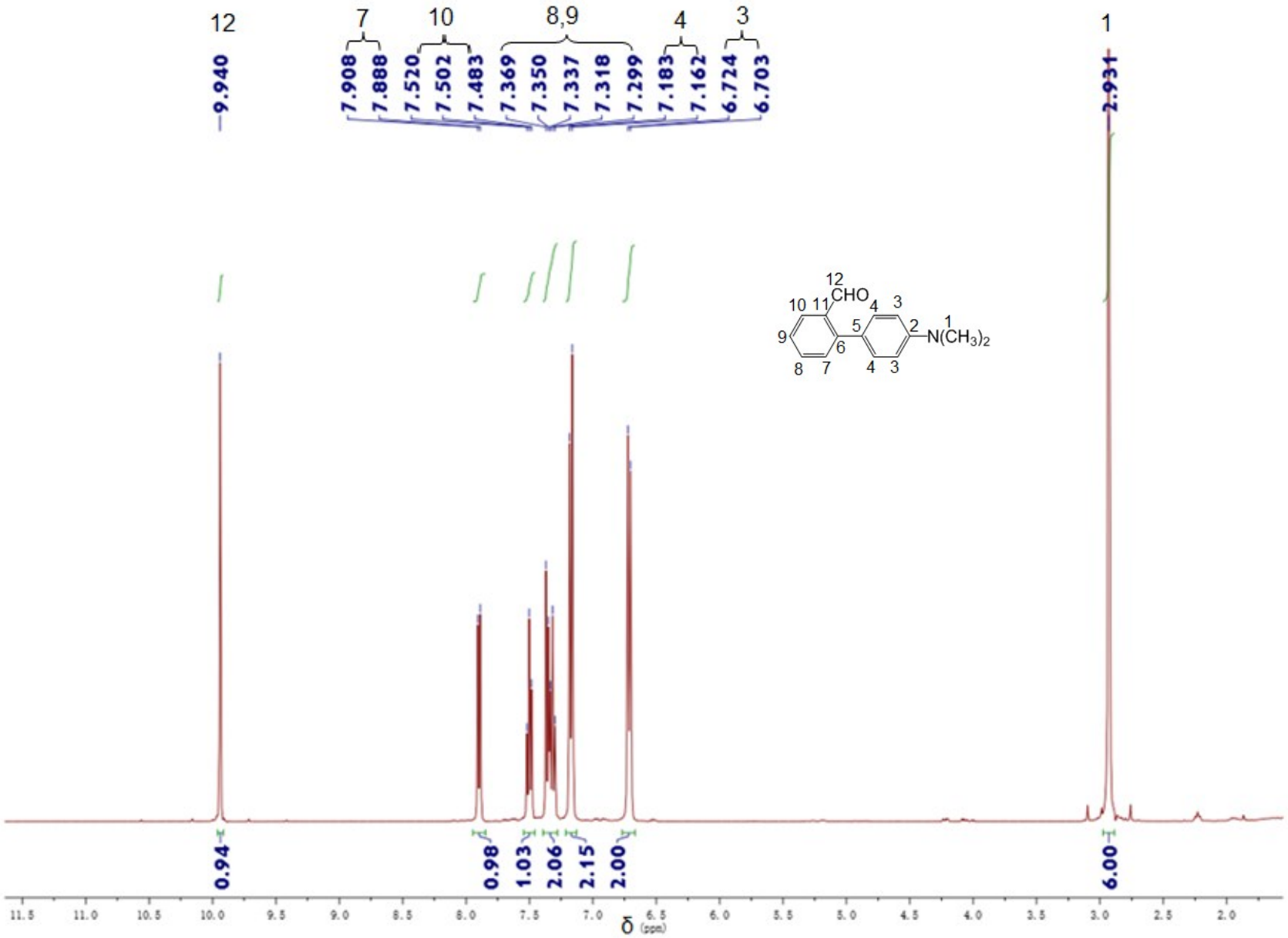
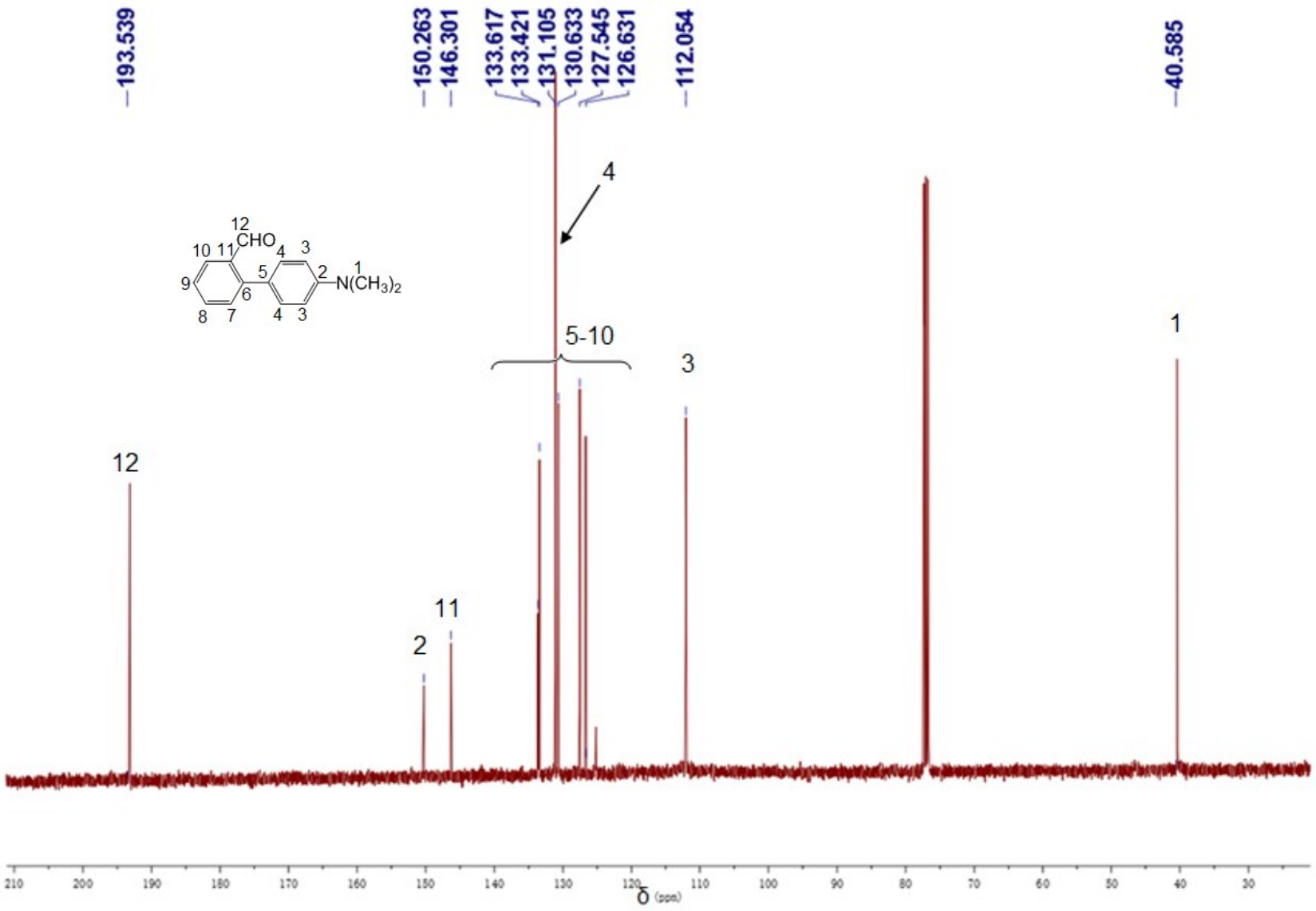
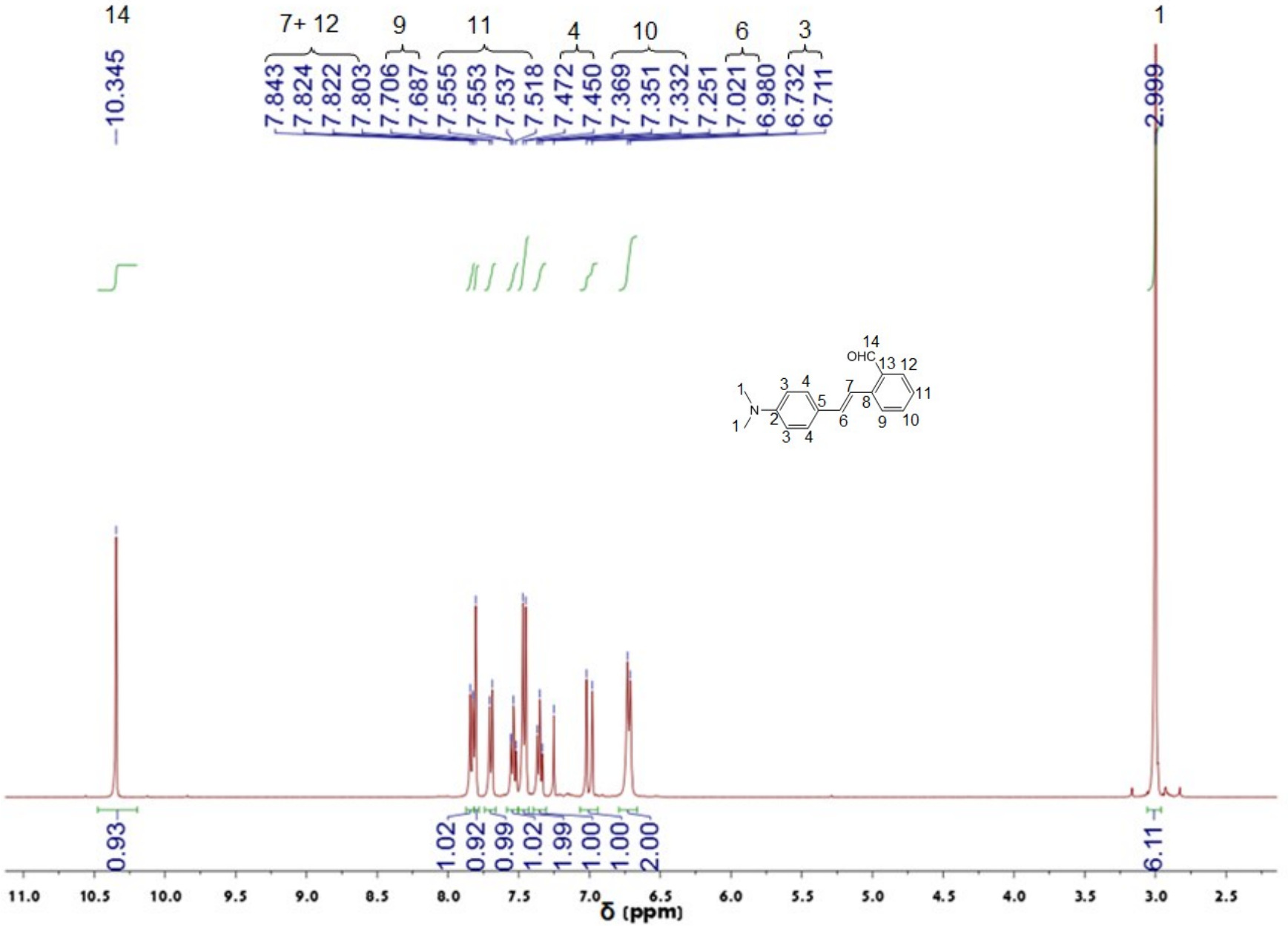
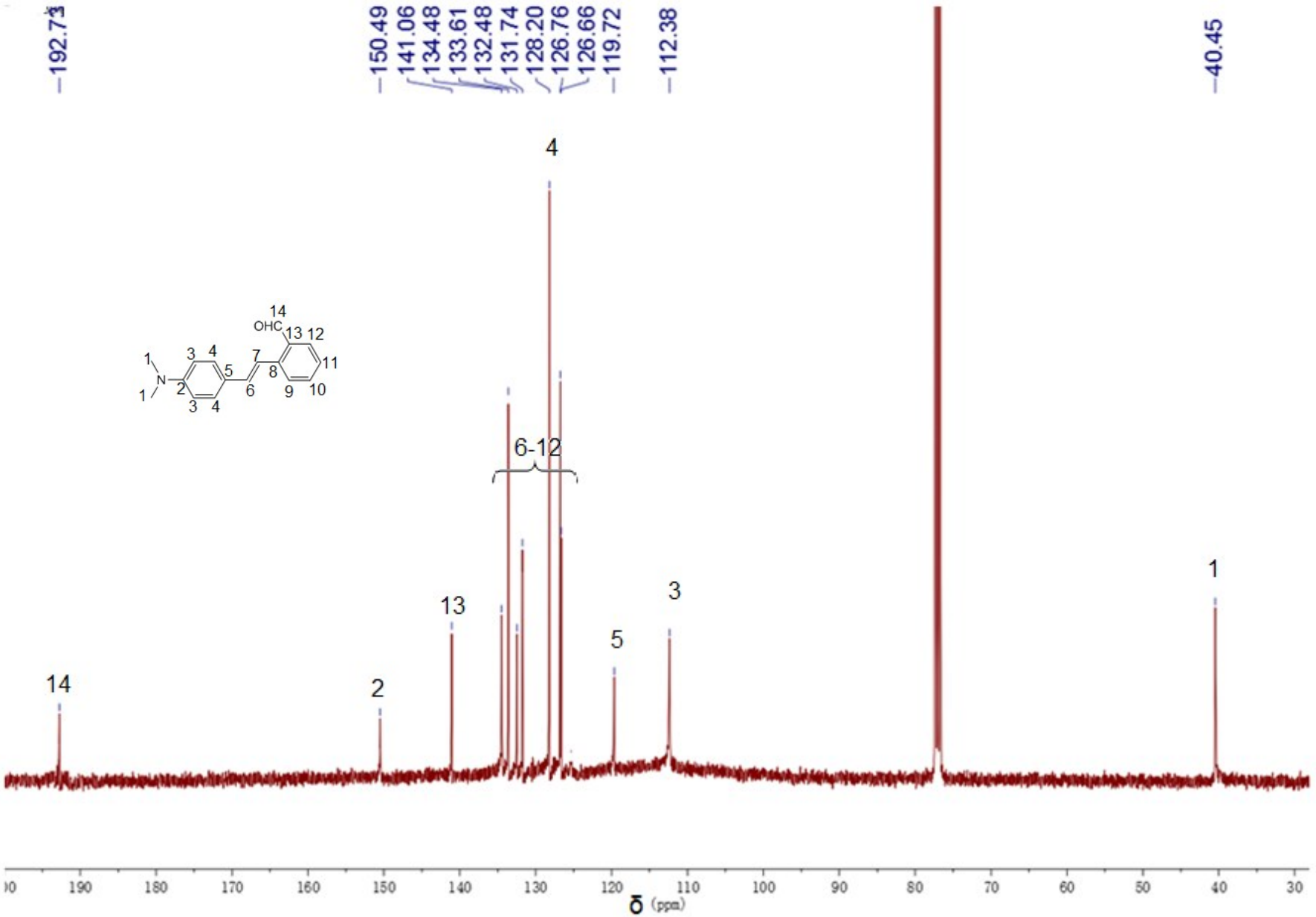


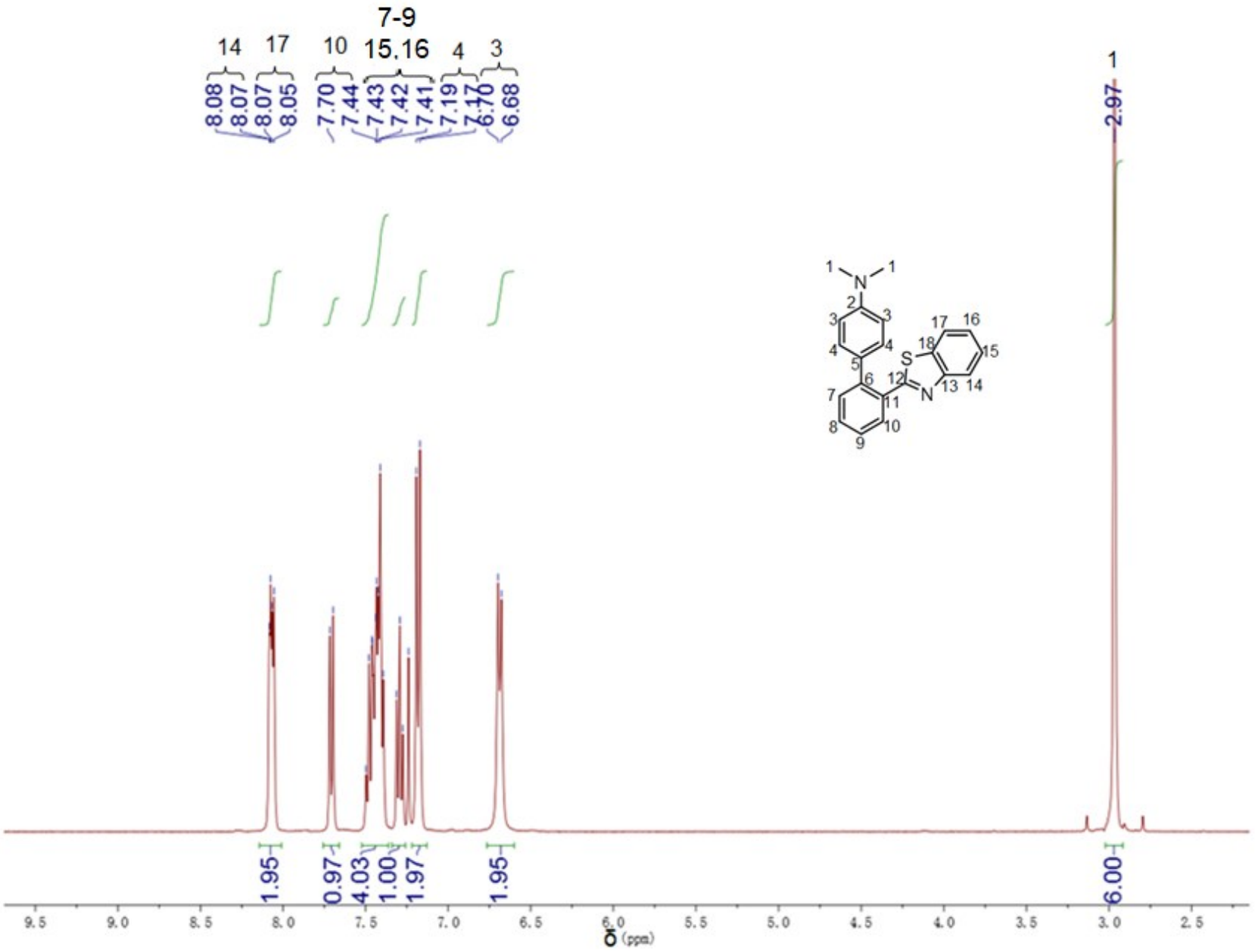
Fig. S23 Molecular geometries of $\mathbf{V_1}$, $\mathbf{V_2}$ and $\mathbf{V_3(Y)}$ in crystalline phase (red data) and gas phase (green data)

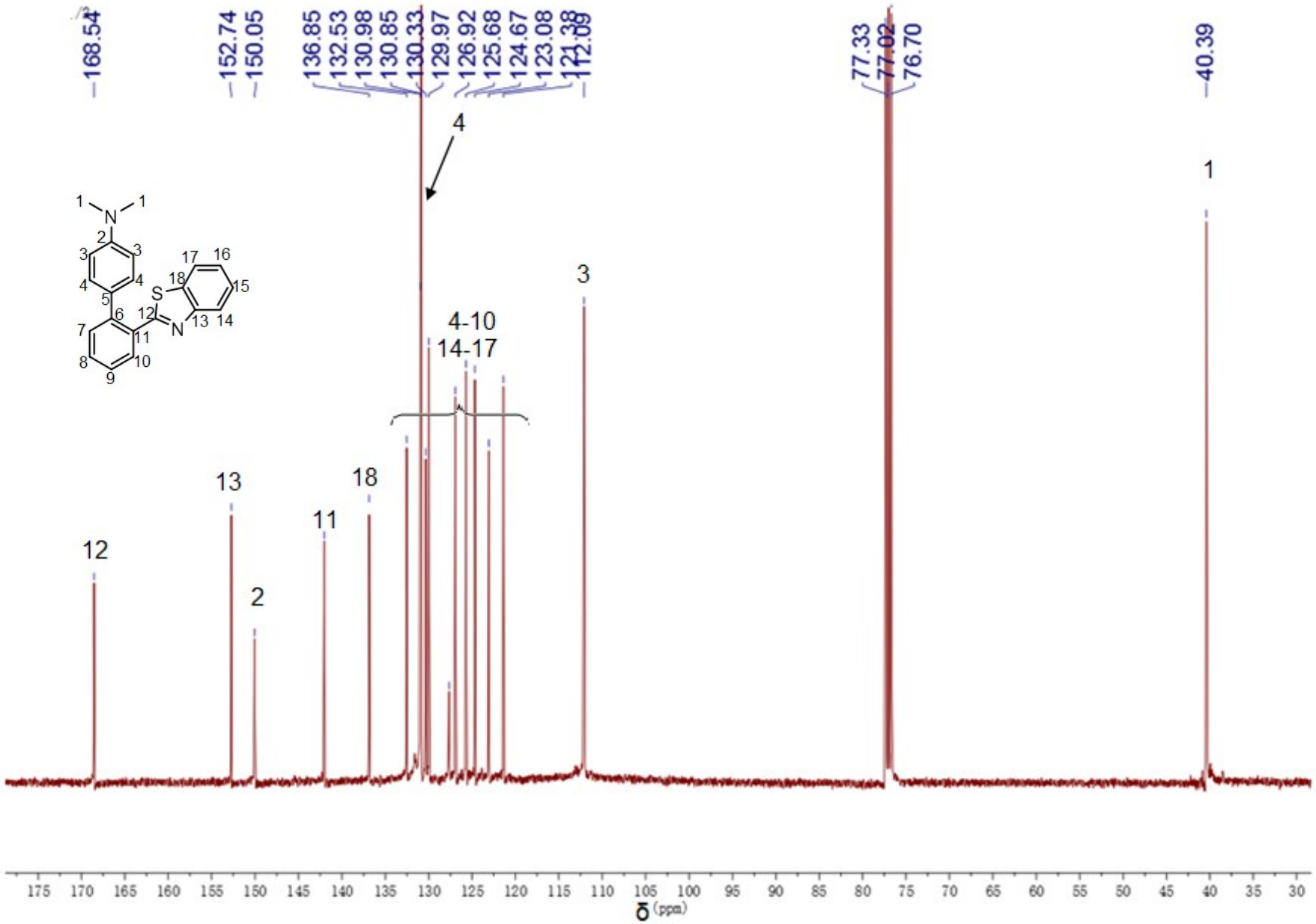

12
7
10
8,9
4
3
1
9.940
7.908
7.888
7.520
7.502
7.483
7.369
7.350
7.337
7.318
7.299
7.183
7.162
6.724
6.703
2.931
0.94
0.98
1.03
2.06
2.15
2.00
6.00
δ (ppm)
CHO
N(CH3)2

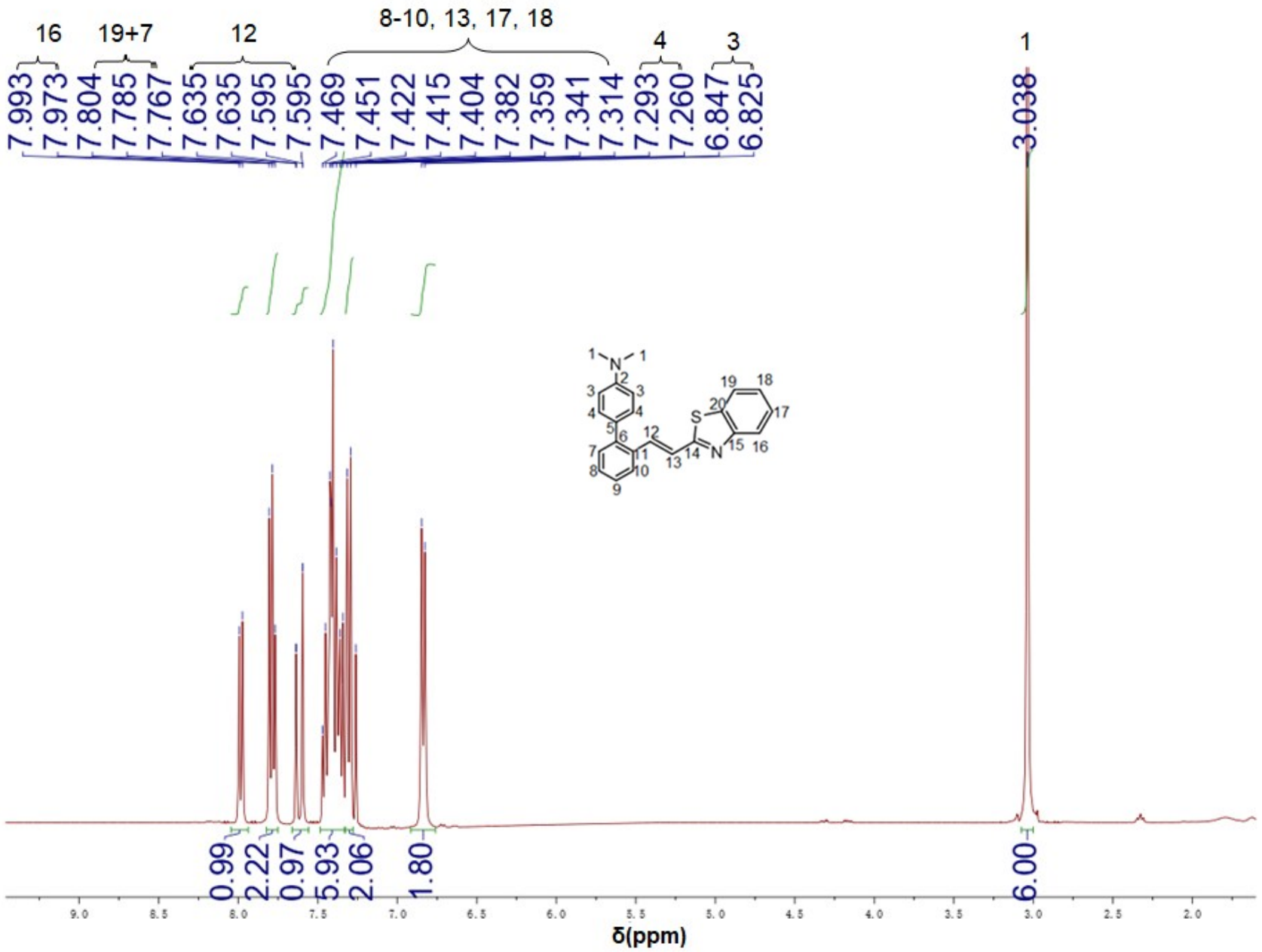

193.539
150.263
146.301
133.617
133.421
131.105
130.633
127.545
126.631
112.054
40.585
12
CHO
10 11
4
3
9
5
2
1
N(CH3)2
6
8 7
4 3
4
5-10
3
1
12
11
2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
δ (ppm)

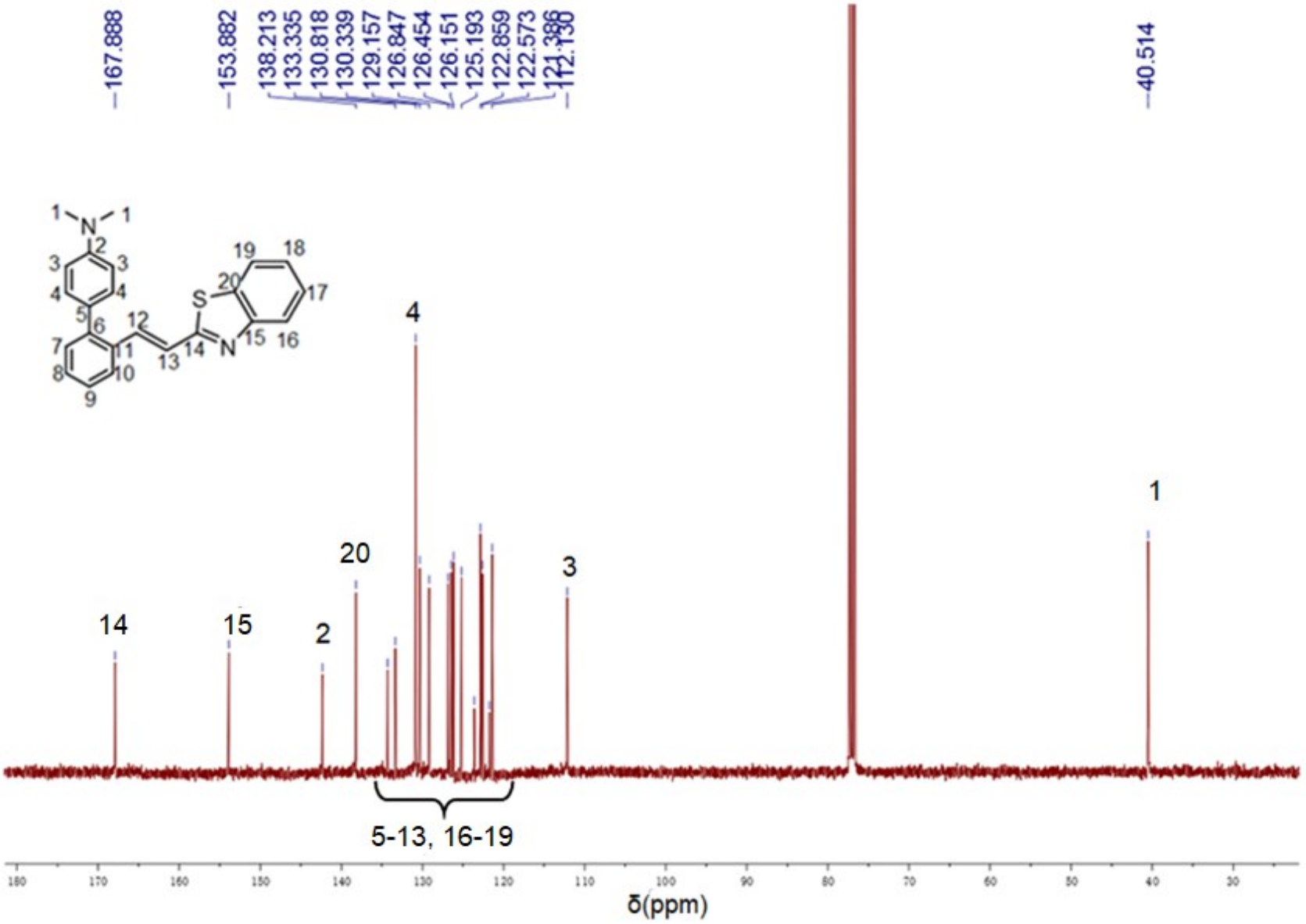

14
10.345
7+ 12
9
11
4
10
6
3
1
2.999
7.843
7.824
7.822
7.803
7.706
7.687
7.555
7.553
7.537
7.518
7.472
7.450
7.369
7.351
7.332
7.251
7.021
6.980
6.732
6.711
OHC
0.93
1.02
0.92
0.99
1.02
1.99
1.00
1.00
2.00
6.11
δ (ppm)


192.73
150.49
141.06
134.48
133.61
132.48
131.74
128.20
126.76
126.66
119.72
112.38
40.45
4
6-12
14
2
13
5
3
1
δ (ppm)


14
17
10
7-9
15,16
4
3
1
8.08
8.07
8.07
8.05
7.70
7.44
7.43
7.42
7.41
7.19
7.17
6.70
6.68
2.97
1.95
0.97
4.03
1.00
1.97
1.95
6.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
δ (ppm)
N
S


168.54
152.74
150.05
136.85
132.53
130.98
130.85
130.33
129.97
126.92
125.68
124.67
123.08
77.33
77.02
76.70
40.39
4
1
3
4-10
14-17
12
13
2
11
18
δ (ppm)


16
19+7
12
8-10, 13, 17, 18
4
3
1
7.993
7.973
7.804
7.785
7.767
7.635
7.635
7.595
7.595
7.469
7.451
7.422
7.415
7.404
7.382
7.359
7.341
7.314
7.293
7.260
6.847
6.825
3.038
0.99
2.22
0.97
5.93
2.06
1.80
6.00
δ(ppm)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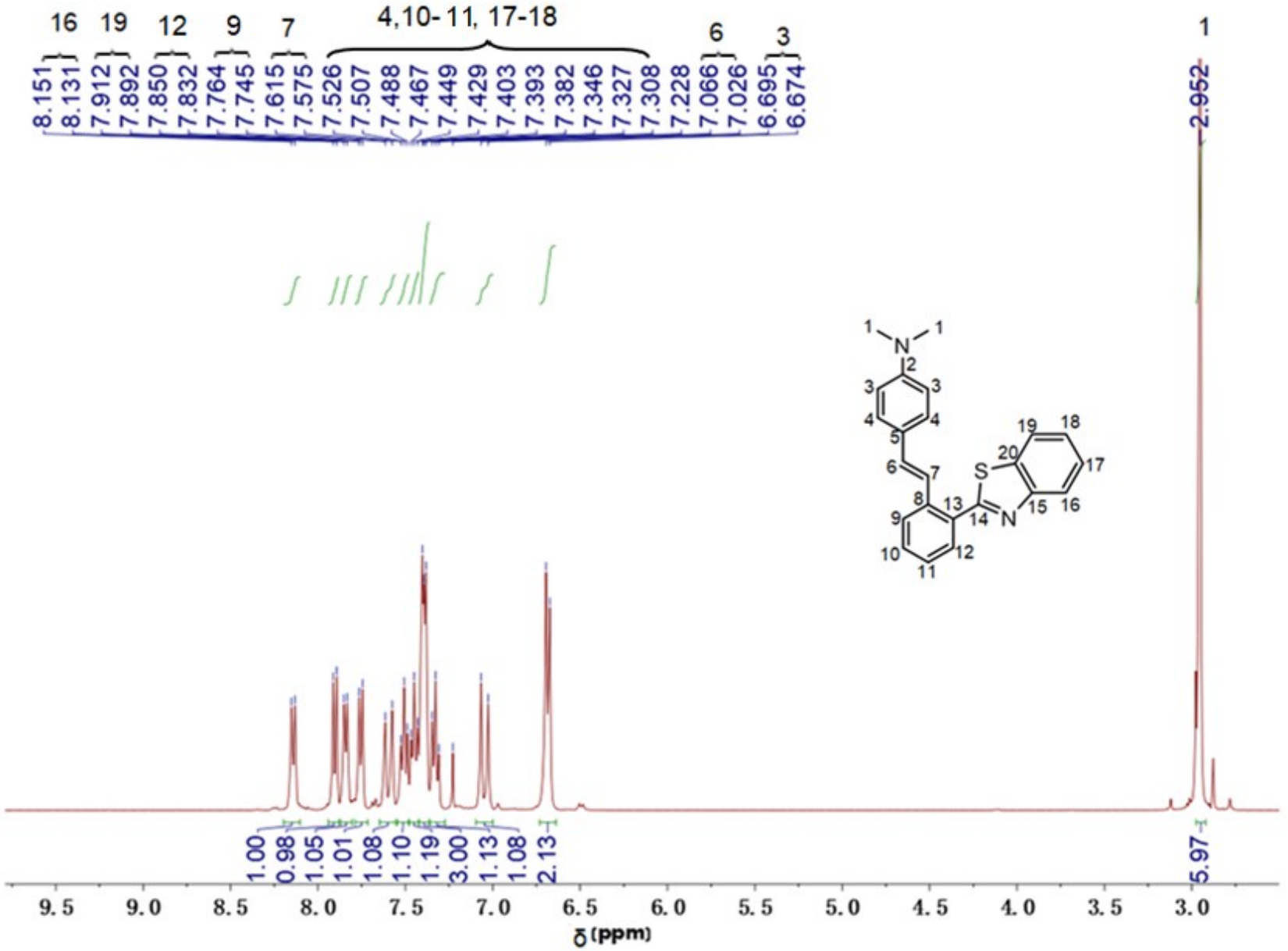
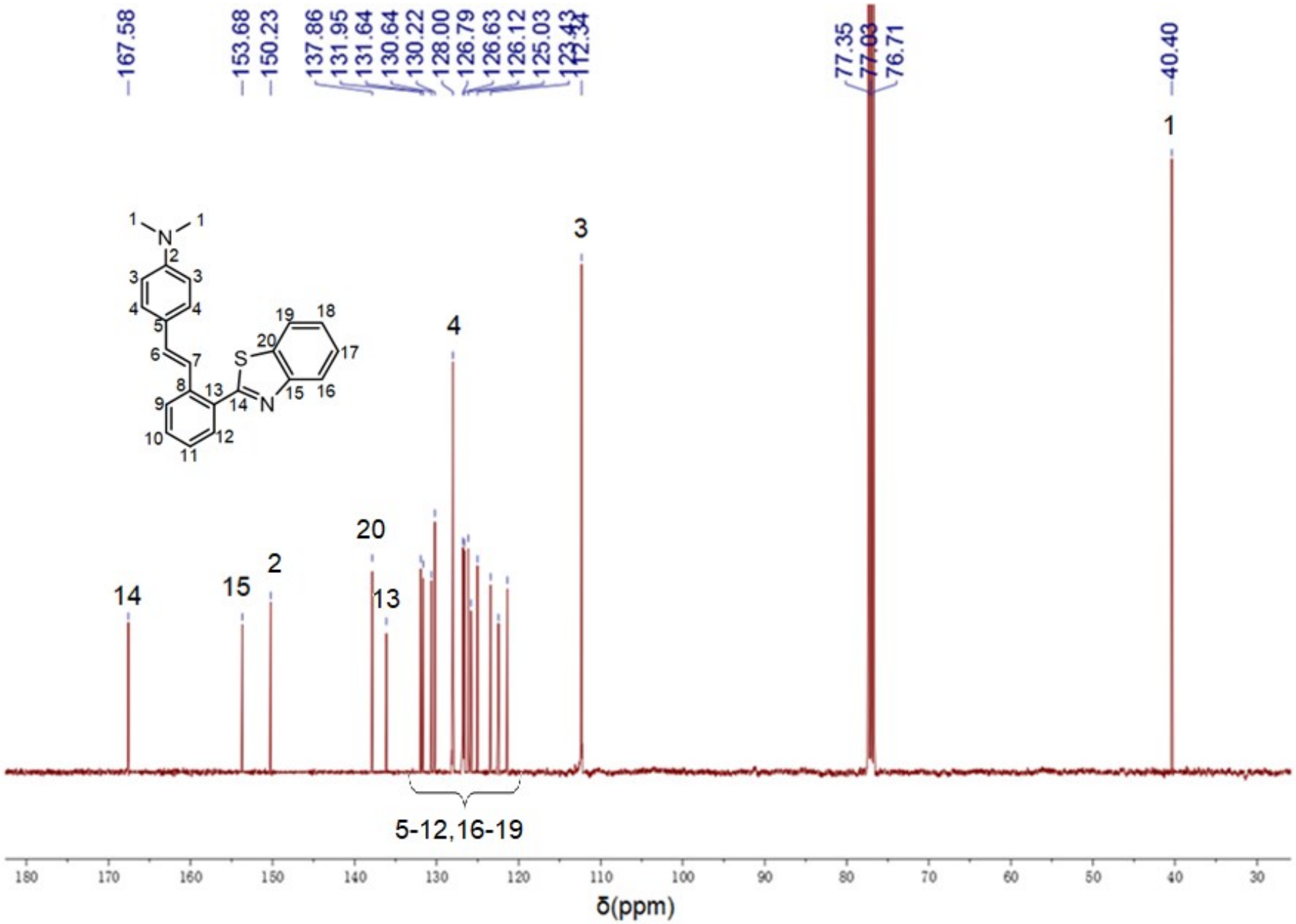
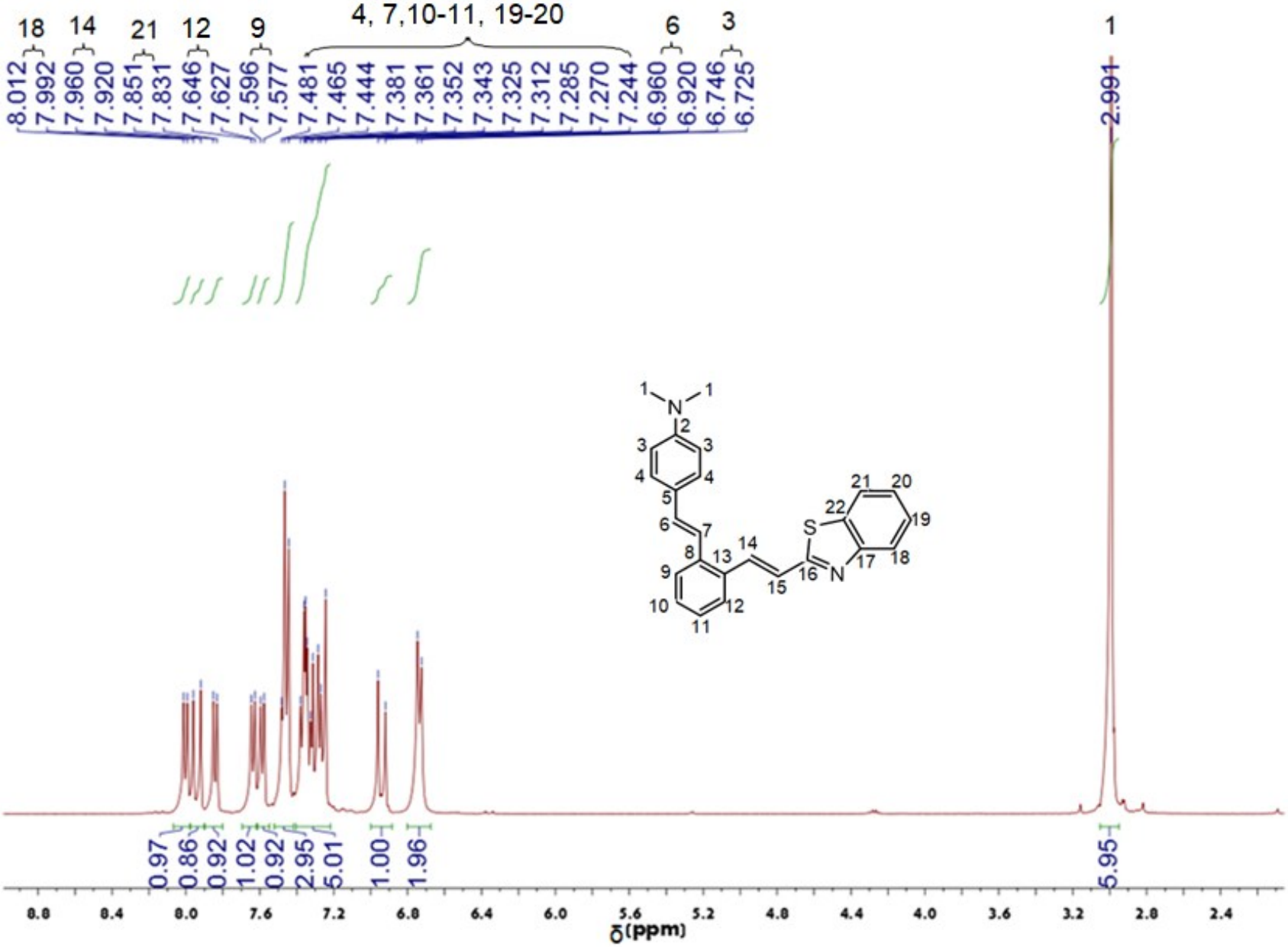
153.882
138.213
133.335
130.818
130.339
129.157
126.847
126.454
126.151
125.193
122.859
122.573
40.514
14
15
2
20
4
3
1
5-13, 16-19
δ(ppm)


16
19
12
9
7
4,10-11, 17-18
6
3
1
8.151
8.131
7.912
7.892
7.850
7.832
7.764
7.745
7.615
7.575
7.526
7.507
7.488
7.467
7.449
7.429
7.403
7.393
7.382
7.346
7.327
7.308
7.228
7.066
7.026
6.695
6.674
2.952
1.00
0.98
1.05
1.01
1.08
1.10
1.19
3.00
1.13
1.08
2.13
5.97
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
δ (ppm)


167.58
153.68
150.23
137.86
131.95
131.64
130.64
130.22
128.00
126.79
126.63
126.12
125.03
77.35
77.03
76.71
40.40
1
3
4
20
2
15
14
13
5-12,16-19
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
δ(ppm)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14
21
12
9
4, 7,10-11, 19-20
6
3
1
8.012
7.992
7.960
7.920
7.851
7.831
7.646
7.627
7.596
7.577
7.481
7.465
7.444
7.381
7.361
7.352
7.343
7.325
7.312
7.285
7.270
7.244
6.960
6.920
6.746
6.725
2.991
0.97
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0.92
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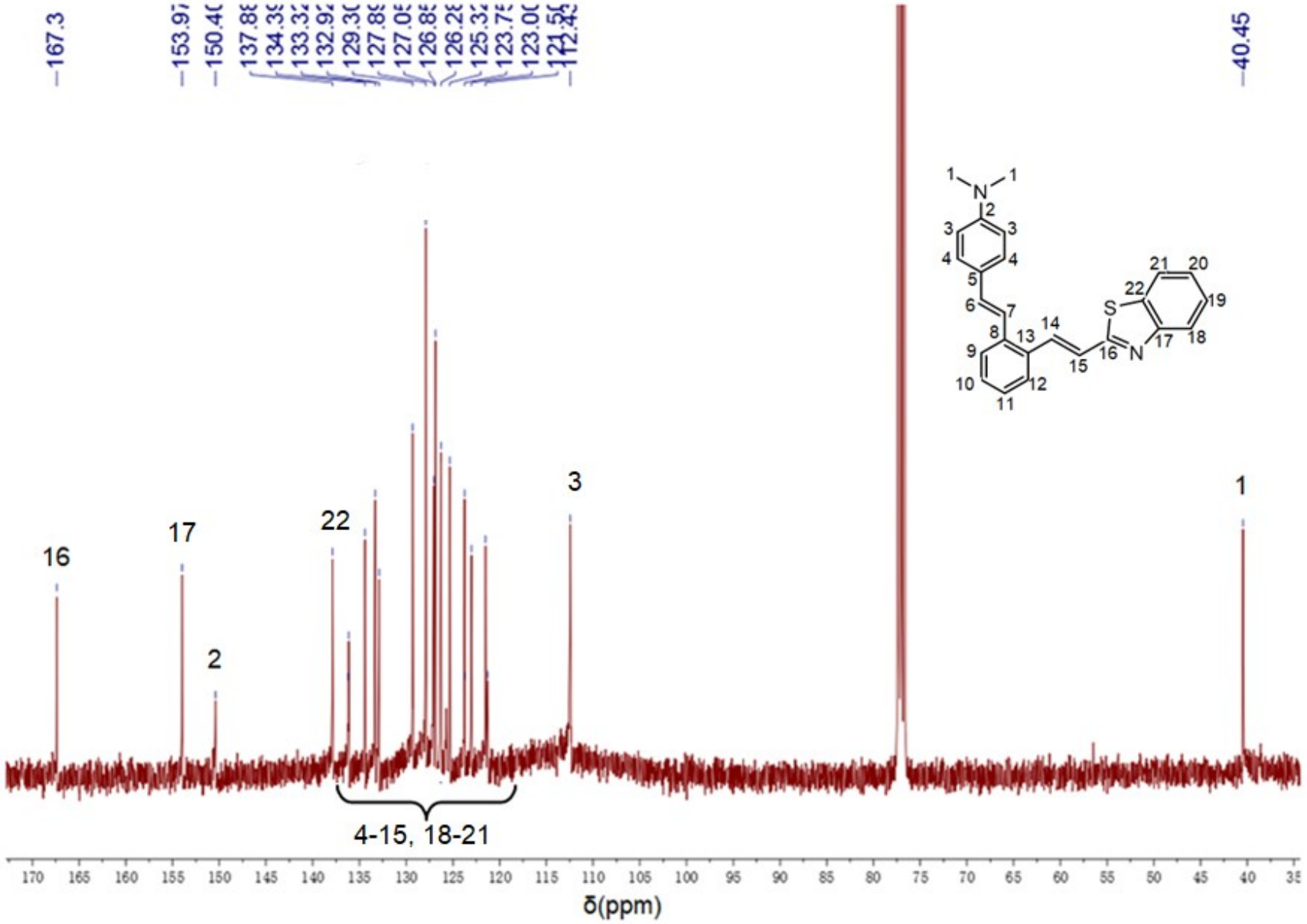
0.92
2.95
5.01
1.00
1.96
5.95
δ(ppm)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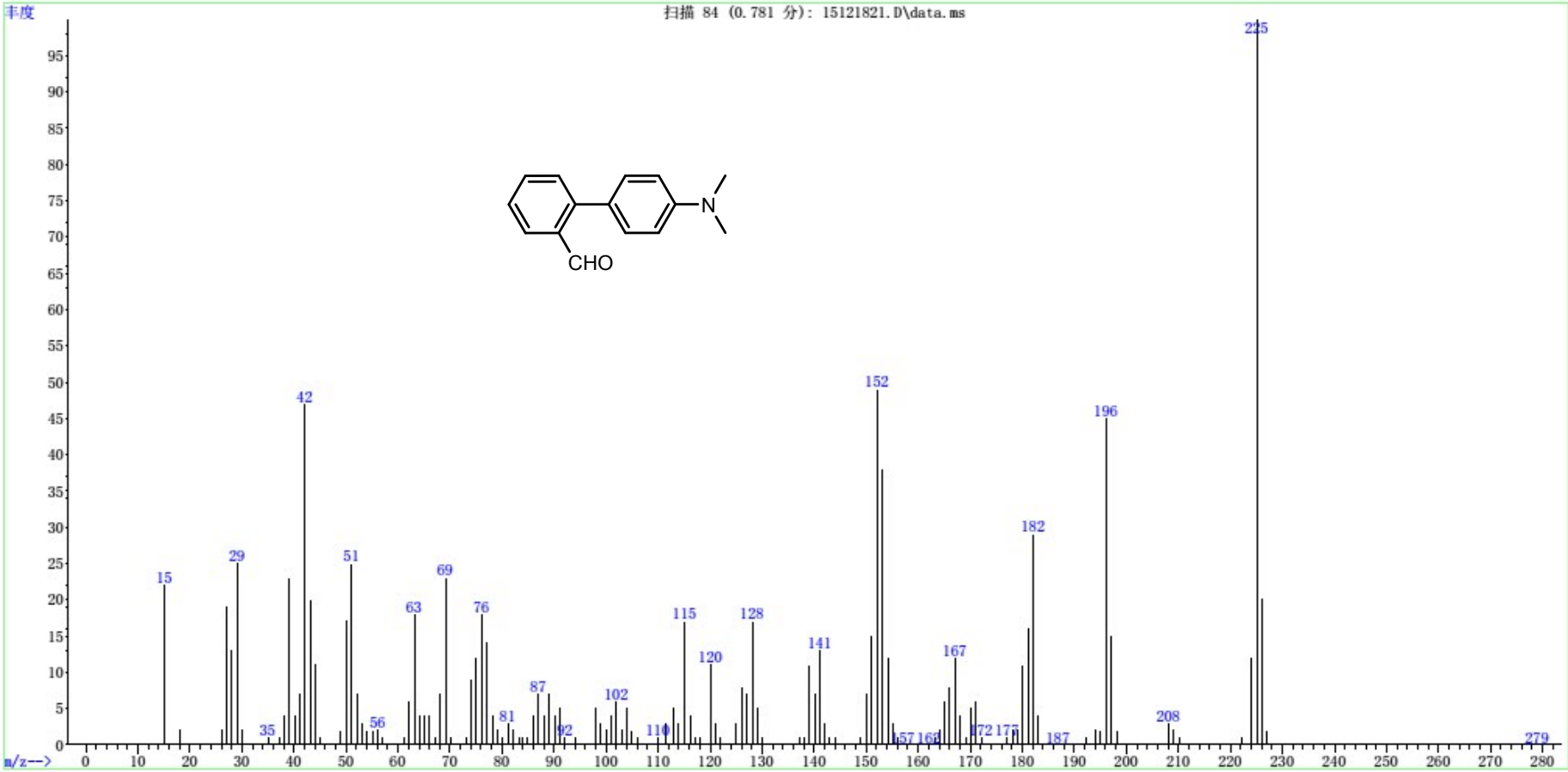
150.4
137.8
134.3
133.3
132.9
129.3
127.8
127.0
126.8
126.2
125.3
123.7
123.0
40.45
16
17
2
22
3
1
4-15, 18-21
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
δ(ppm)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CHO
m/z-->
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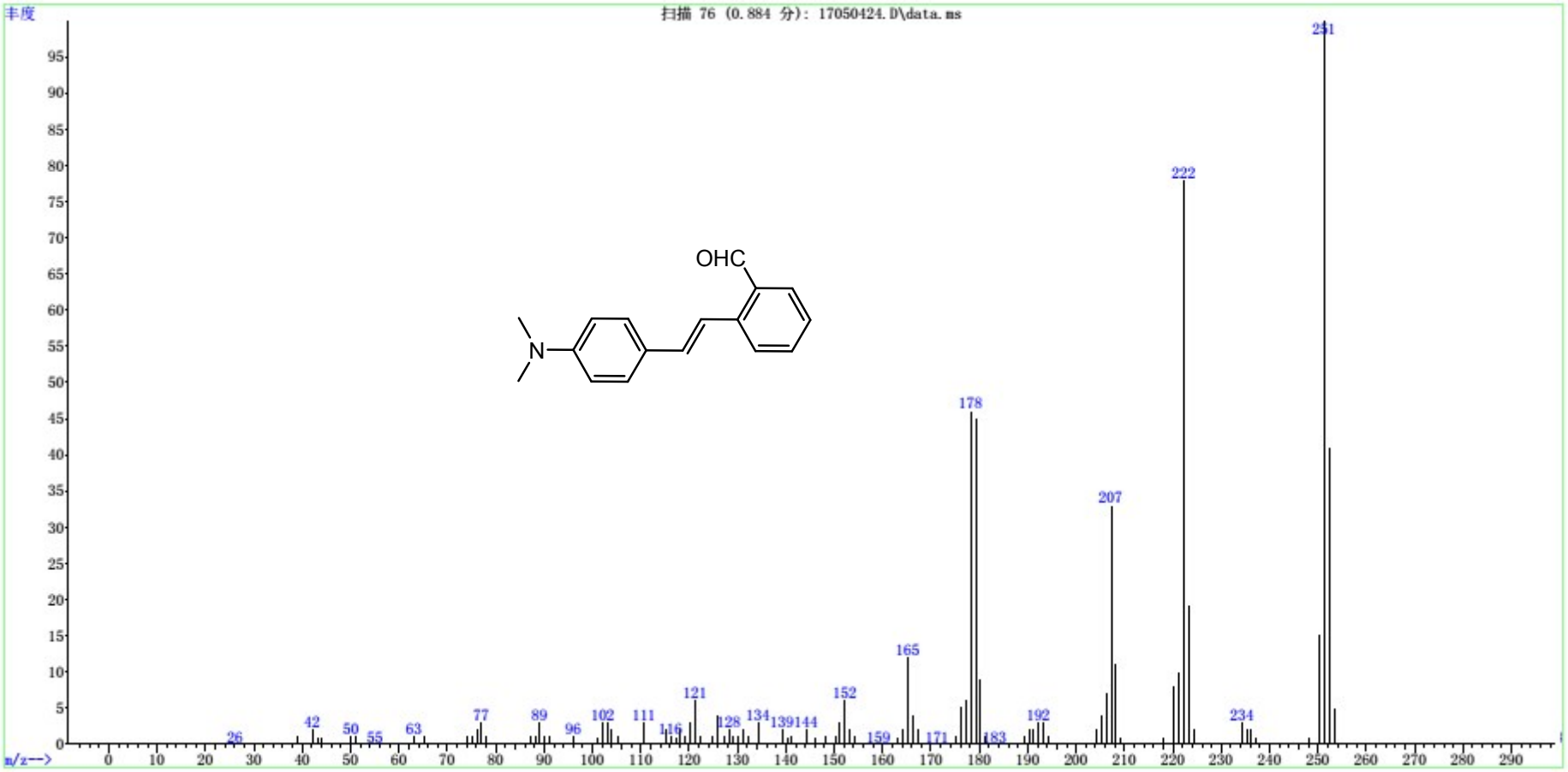
152
196
182
42
29
51
69
63
76
15
115
128
120
141
167
87
102
81
56
35
92
110
208
279
187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207
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192
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50
55
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77
89
96
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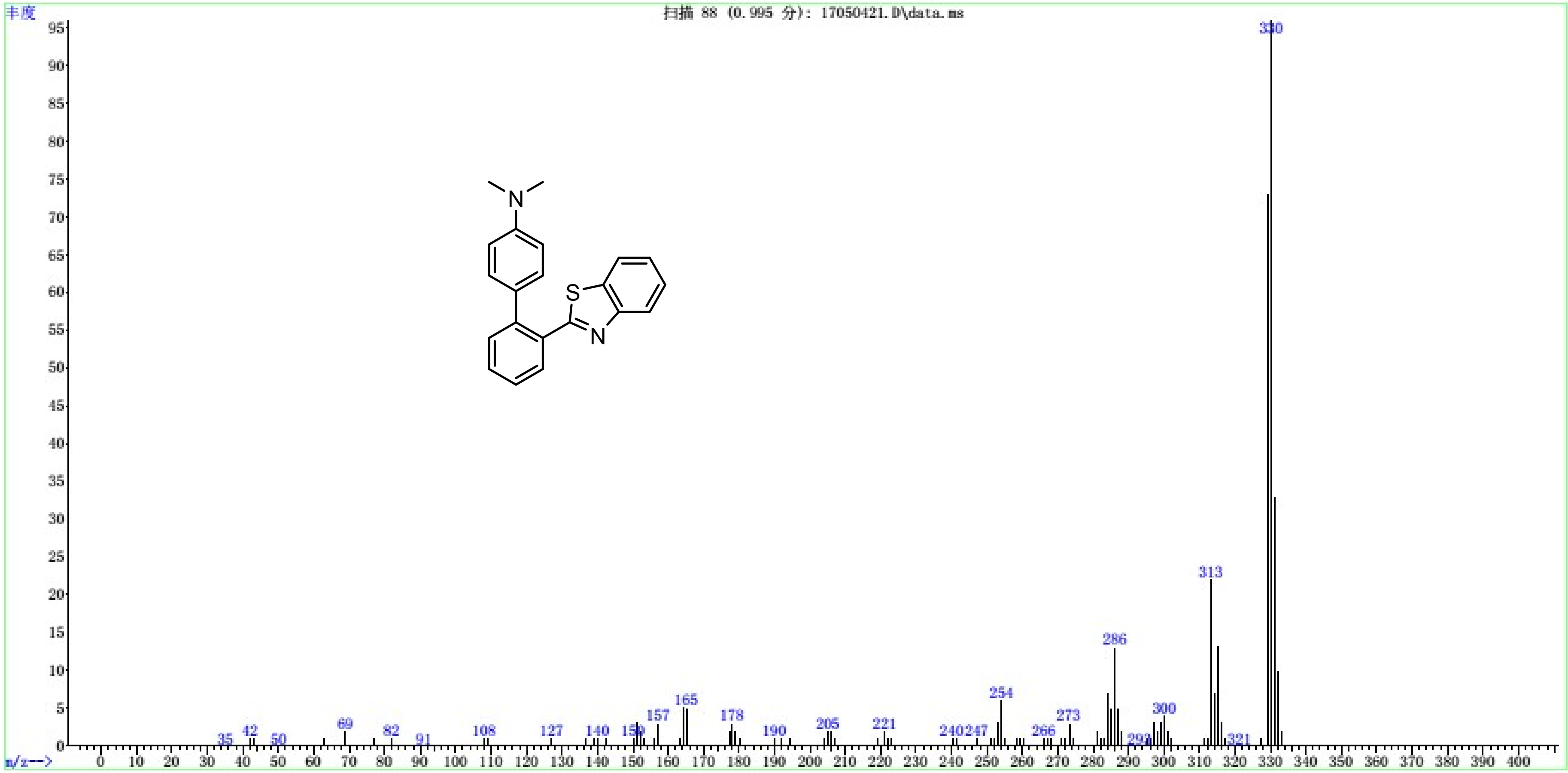
111
116
128
134
139
144
159
171
183



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N
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127
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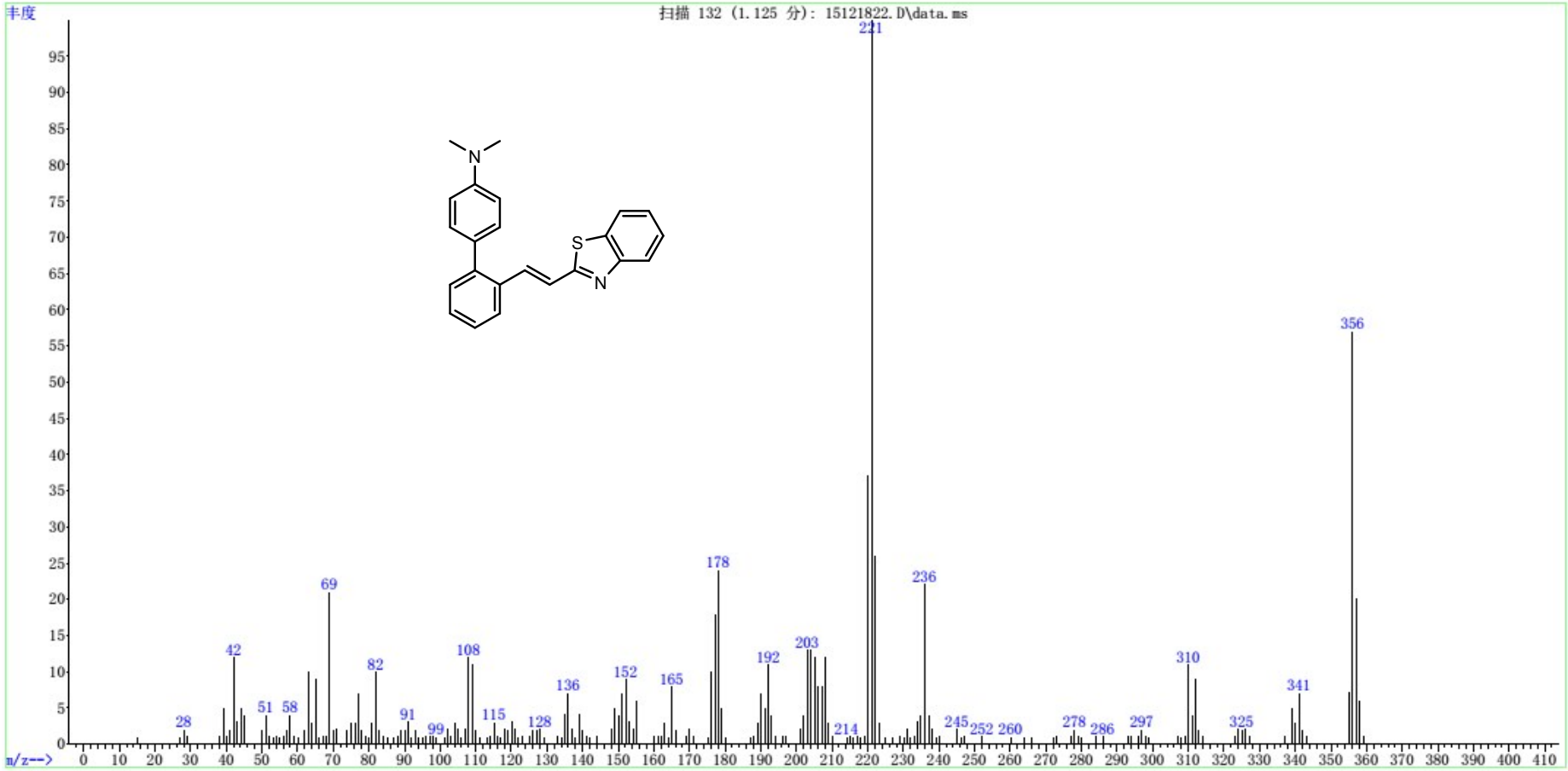
190
240
247
266
42
35
50
91
321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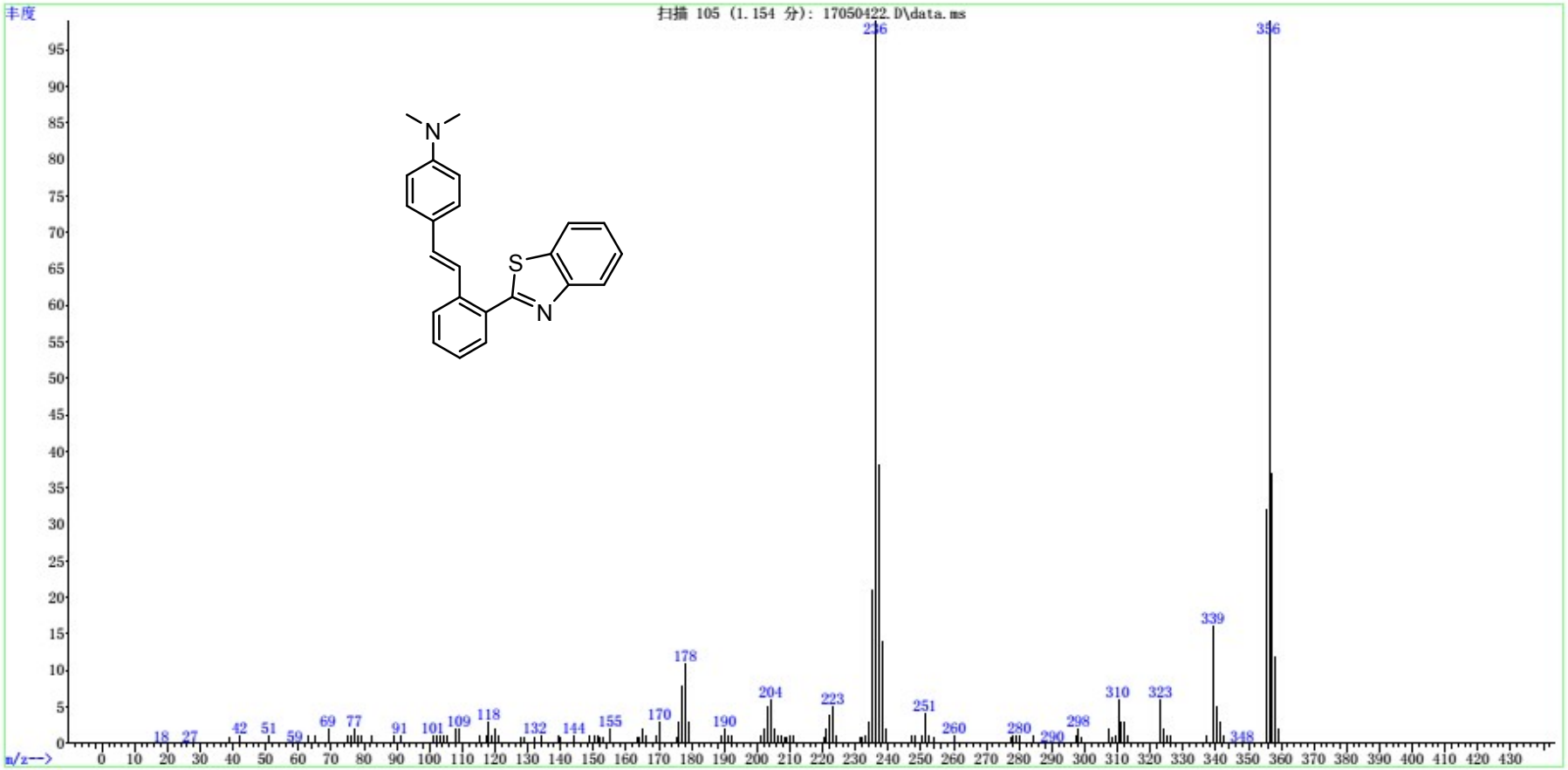
S
N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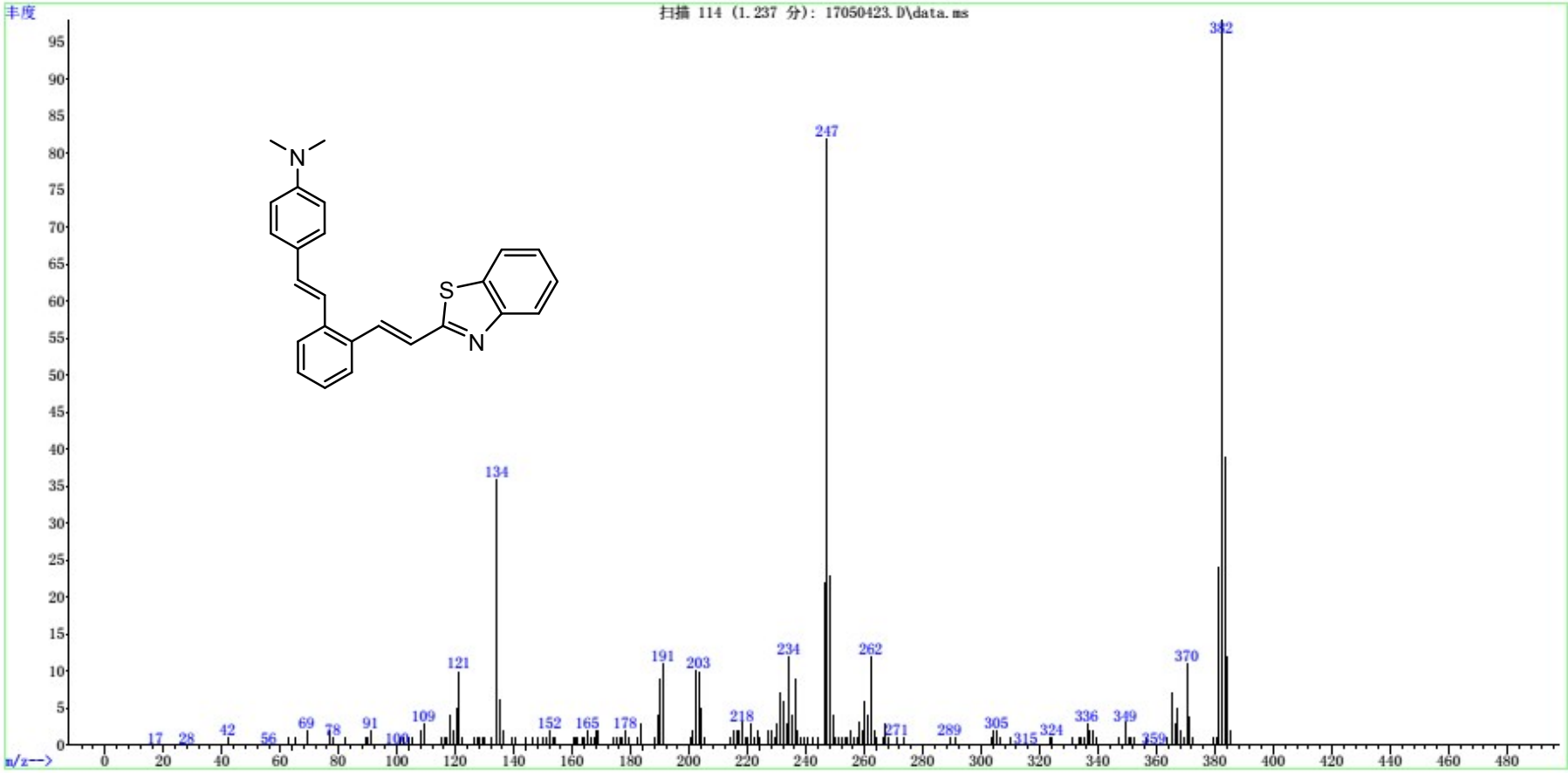
S
N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91
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152
165
178
218
271
289
305
315
324
336
349
359