Electronic supplementary information

How the AIE mechanism is profoundly changed in an ESIPT family: the novel introduction of a tetraphenylethene group onto (*Z*)-3-(quinolin-2-ylmethylene)-3,4-dihydro- quinoxalin-2(1*H*)-one

Ding-Er Wu, Qi-Chao Yao, Min Xia*

Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou 310018, P. R. China
E-mail: xiamin@zstu.edu.cn

Instruments and measurements

All the reagents used 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 DMX400 spectrometer using DMSO-d_6 or $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. 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. Quantum yields in THF solution were measured with fluorescein in 0.1N NaOH aqueous solution (Φ_f=0.91) as the reference. The mass spectra were recorded on a HP 1110 mass spectrometer. Ultrasound irradiation is performed in a KQ250E ultrasound cleaner, whose frequency is 40 KHz and output power is 250 W. The temperature of the water bath is controlled by the addition or removal of water. Transmission electron micrographs (TEM) and electron diffraction (ED) pattern were obtained on a Philips CM-20 TEM instrument. Compound **G** are prepared according to the reported methods [1].

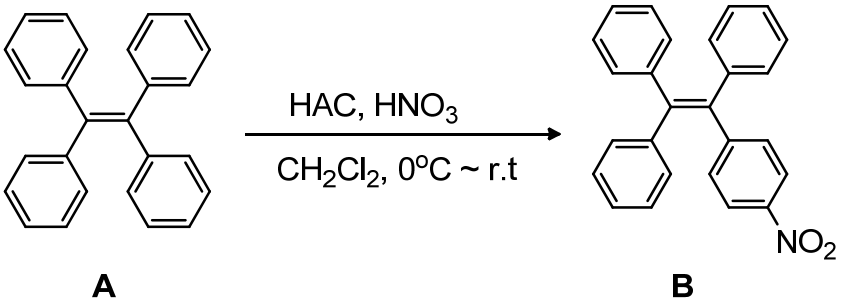
Computational details

The solution-phase geometries of the concerned compound were optimized without any symmetry restrictions in singlet ground state using the density functional theory (DFT) method at the B3LYP level [2] under the polarizable continuum model (PCM)[3]. The 6–31G (d, p) basis set was selected for all the elements. The vibration frequency calculations were performed to ensure that the optimized geometries represented the local minima on the ground-state potential energy surface. All the calculations were carried out with the Gaussian 09

program package in the aid of the GaussView visualization program [4].

The potential energy curves (PECs) of the ground state intramolecular torsion were calculated with energies of the B3LYP/6-31G (d, p) fully optimized structures at the fixed C_3-C_4-C_5-N_2 angle over the -90 ~ 90° range. The PECs of the corresponding excited state intramolecular torsion were obtained by adding the TD-DFT/B3LYP/6-31G (d, p) calculated vertical transition energy of the first singlet excited state to the energy of the ground state..

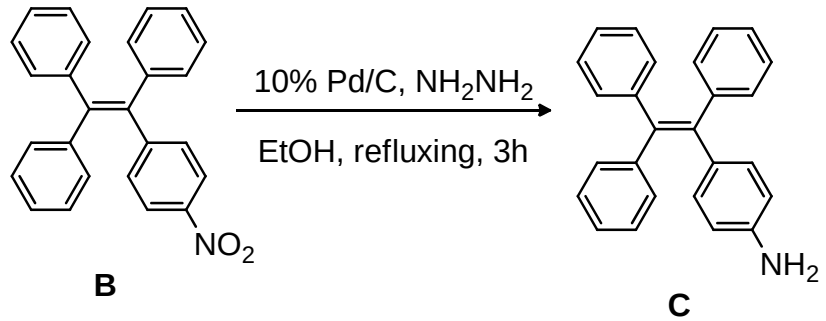
Synthesis and Characterization



Scheme S1 Synthesis of [2-(4-nitrophenyl)ethene-1,1,2-triyl]tribenzene **B**

At 0°C, the mixture of HNO_3 (65 wt%, 0.72 mL) and glacial acetic acid (1 mL) was slowly dropped into the solution of 1,1,2,2-tetraphenylethene **A** (10 mmol, 3.324 g) in CH_2Cl_2(25 mL). The resulting mixture was stirred at 0°C for 30 min and then the ice bath was removed. The mixture was stirred at room temperature for 6 h and poured into water. The formed precipitate was collected and washed by water until the filtrate was neutral. The solid was purified by the column chromatography on silica gel with petroleum ether/CH_2Cl_2 (10:1, v/v) as the eluent.

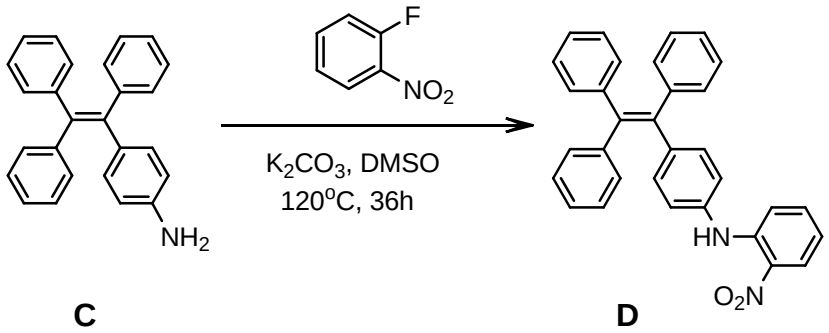
90% yield, m.p. 147.9-149.6°C; ^{1}H NMR (400 MHz, CDCl) δ 7.06(m, 6H), 7.17-7.22(m, 12H), 7.99(d, *J*=8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl) δ 123.05, 127.11, 127.12, 127.37, 127.81, 128.10, 128.11, 131.19, 131.25, 131.27, 132.09, 138.81, 142.53, 142.66, 142.73, 143.87, 145.95, 151.05; EI-MS(70 eV) *m/z*(%) 377(M^+, 100), 252(23), 183(13), 167(28), 105(19), 77(11).



Scheme S2 Synthesis of 4-(1,2,2- triphenylvinyl)aniline **C**

At room temperature, hydrazine hydrate (80 wt%, 8 mmol, 0.5 g) was dropped into the solution of [2-(4-nitrophenyl)ethene-1,1,2-triyl]tribenzene **B** (1 mmol, 0.377 g) and 10% Pd/C (53 mg) in ethanol (5 mL), the mixture was refluxing for 3h and then cooled to room temperature. The solid was filtrated and the filtrate was concentrated on a rotating evaporator. The residue was purified by the column chromatography on silica gel with petroleum ether/CH_2Cl_2 (3:1) to give **C** as a white powder.

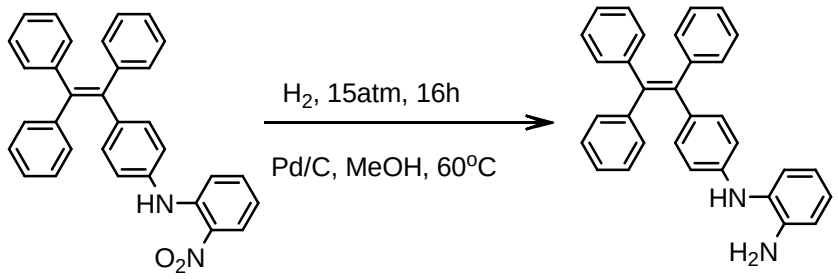
85% yield, m.p. 201.4-202.8°C; ^{1}H NMR (400 MHz, CDCl) δ 3.66(br s, 2H), 6.42(d, *J*=8 Hz, 2H), 6.80(d, *J*=8 Hz, 2H), 7.05-7.12(m, 15H); ^{13}C NMR (100 MHz, CDCl) δ 114.33, 126.05, 126.23, 127.50, 127.53, 127.65, 131.34, 131.39, 131.46, 132.48, 134.05, 139.30, 140.91, 144.15, 144.19, 144.32, 144.68; EI-MS(70 eV) *m/z*(%) 347(M^+, 100), 270(12), 252(13), 180(7), 165(12), 152(6), 93(6), 77(8).



Scheme S3 Synthesis of 2-nitro-*N*-[4-(1,2,2-triphenylvinyl)phenyl]aniline **D**

At room temperature, 1-fluoro-2-nitrobenzene (1.1 mmol, 0.155 g) was added to the mixture of 4-(1,2,2-triphenylvinyl)aniline **C** (1 mmol, 0.347 g) and potassium carbonate (1.2 mmol, 0.165 g) in DMSO (5 mL). The resulting mixture was heating at 120°C for 36 h under the N_2 flow. After cooling to room temperature, the mixture was poured into water and the precipitated dark red solid was filtrated. The solid was purified by the column chromatography on silica gel with petroleum ether/CH_2Cl_2 (4:1) as the eluent.

92% yield, m.p. 182.1-183.8°C; ^{1}H NMR (400 MHz, CDCl) δ 6.76(t, *J*=8 Hz, 1H), 7.00-7.22(m, 20H), 7.36(t, *J*= 8Hz, 1H), 8.19(d, *J*= 8 Hz, 1H), 9.46(s, 1H); ^{13}C NMR (100 MHz, CDCl) δ 116.19, 117.51, 122.93, 126.48, 126.56, 126.62, 127.63, 127.74, 131.25, 131.29, 132.58, 133.15, 135.58, 136.76, 139.98, 140.96, 141.28, 142.62, 143.39, 143.48, 143.59; EI-MS(70 eV) *m/z*(%) 468(M^+, 100), 433(10), 357(15), 341(13), 253(33), 239(21), 178(18), 167(35), 77(15).

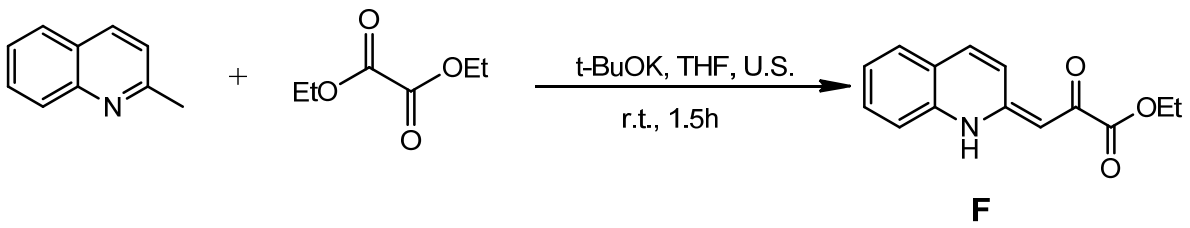


D **E**

Scheme S4 Synthesis of 2-amino-*N*-[4-(1,2,2-triphenylvinyl)phenyl]aniline **E**

At room temperature, 10 wt % Pd/C (5% mmol, 0.053 g) was added to the solution of 2-nitro-*N*-[4-(1,2,2-triphenylvinyl)phenyl]aniline **D** (1 mmol, 0.468 g) in methanol (5 mL). The autoclave was charged with high pure hydrogen to reach 15 atm and the resulting mixture was heating at 60°C for 16 h. After cooling to room temperature and reduction of the pressure, the mixture was filtrated and filtrate was concentrated on a rotating evaporator. The residue was purified by the column chromatography on silica gel with petroleum ether/CH_2Cl_2 (6:1) to give **E** as a white powder.

83% yield, m.p. 164°C (decomp.); ^{1}H NMR (400 MHz, CDCl) δ 6.49(d, *J*=8 Hz, 2H), 6.72-6.78(m, 2H), 6.85(d, *J*=8 Hz, 2H), 6.95-7.01(m, 3H), 7.06-7.14(m, 15H); ^{13}C NMR (100 MHz, CDCl) δ 114.33, 116.28, 119.20, 124.27, 125.35, 126.07, 126.11, 128.25, 127.52, 127.64, 128.58, 131.35, 131.37, 131.45, 132.45, 134.68, 139.49, 140.82, 141.25, 143.41, 144.06, 144.13, 144.28; EI-MS(70 eV) *m/z*(%) 438(M^+, 100), 252(47), 239(28), 219(15), 182(25), 165(28), 107(30), 80(25).

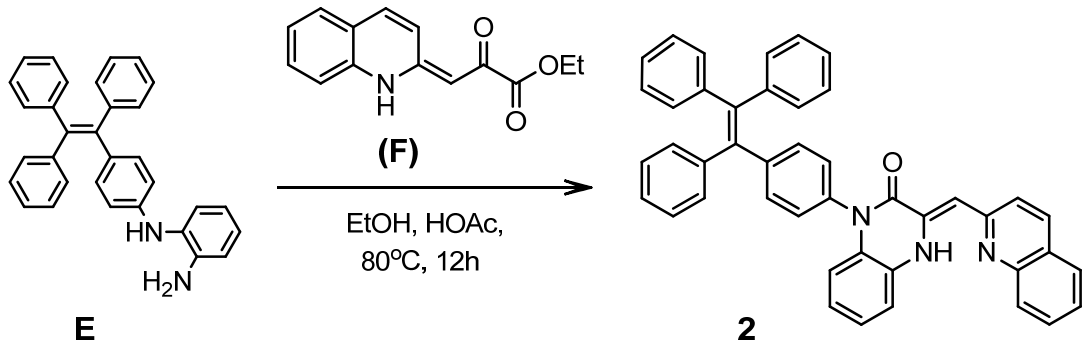


F

Scheme S5 Synthesis of ethyl 2-oxo-3-[quinolin-2(1*H*)-ylidene]propanoate **F**

At room temperature, quinaldine (1 mmol, 0.143 g) was added to the solution of diethyl oxalate (1.2 mmol, 0.175 g) and potassium *t*-butoxide (1.2 mmol, 0.134 g) in anhydrous THF (10 mL). The solution is irradiated in an ultrasound cleaner at 25°C for 1.5 h and the yellow precipitate was collected. The solid was washed by anhydrous ether for several times and then dissolved with 1% HCl aqueous solution. The mixture was extracted by ethyl acetate and the organic layer was dried over anhydrous $NaSO_4$. The filtrate was concentrated on a rotating evaporator. The residue was purified by the column chromatography on silica gel with ethyl acetate/ petroleum ether (4:1) to give **F** as a yellow needle.

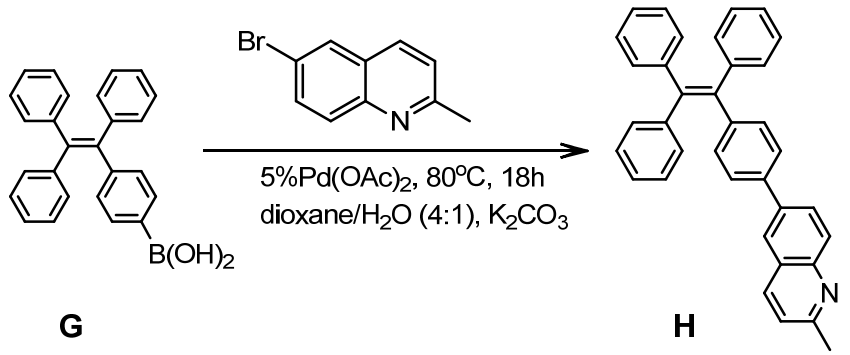
87% yield, m.p. 130.6-132.0 °C; ^{1}H NMR (400 MHz, CDCl) δ 1.38(t, *J*=7.8 Hz, 3H), 4.33(q, *J*=7.8 Hz, 2H), 6.34(s, 1H), 6.98(d, *J*=8 Hz, 1H), 7.36(t, *J*=8 Hz, 1H), 7.52(d, *J*=8 Hz, 1H), 7.60(t, *J*=8 Hz, 2H), 7.83(d, *J*=8 Hz, 1H), 15.81(br s, 1H); ^{13}C NMR (100 MHz, CDCl) δ 14.12,61.53, 93.55, 119.36, 121.70, 124.19, 125.14, 127.73, 131.48, 137.67, 137.77, 155.01, 164.34, 170.20; EI-MS(70 eV) *m/z*(%) 243(M^+, 42), 215(12), 170(100), 142(85), 115(70), 89(13).



Scheme S6 Synthesis of ethyl (*Z*)-3-(quinolin-2-ylmethylene)-1-[4-(1,2,2-triphenylvinyl)phenyl]-3,4-dihydroquinoxalin-2(1*H*)-one **2**

At room temperature, 2-amino-*N*-[4-(1,2,2-triphenylvinyl)phenyl]aniline **E** (1 mmol, 0.438 g) was added to the solution of 2-oxo-3-[quinolin-2(1*H*)-ylidene]propanoate **F** (1.2 mmol, 0.292 g) in ethanol (10 mL). After 1-2 drops of glacial acetic acid was added, the mixture was refluxed at 80°C for 12 h. The bright red solid was filtrated and washed by ethanol and ether for several times. The solid could be further recrystallized in ethanol. The solid is poorly soluble in most deuterated solvents, and its ^{13}C NMR spectrum cannot be available.

65% yield, m.p. 213°C (decomp.); ^{1}H NMR (400 MHz, CDCl) δ 6.31(br s, 1H), 6.55(s, 1H), 6.84(br s, 1H), 7.14(m, 23H), 7.70(br s, 2H), 7.96(br s, 2H), 13.72(br s, 1H); EI-MS(70eV) *m/z*(%) 617(M^+, 23), 4 92(100), 329(15), 253(38), 239(17), 165(20), 77(10).

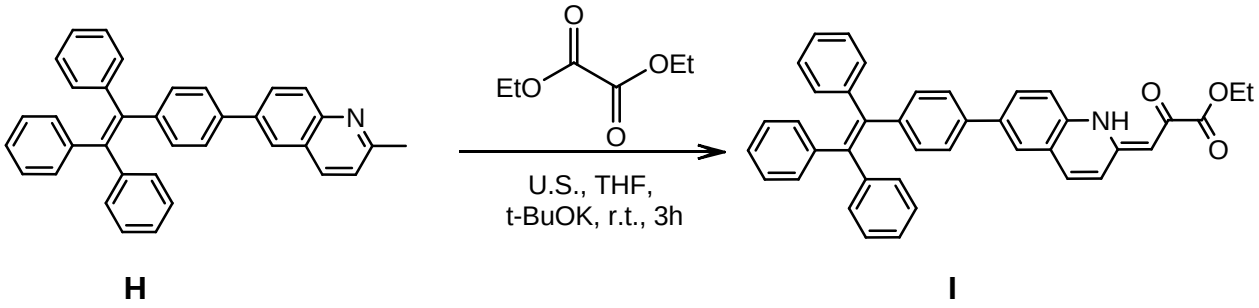


Scheme S7 Synthesis of 2-methyl-6-[4-(1,2,2-triphenylvinyl)phenyl]quinoline **H**

At room temperature and N_2 atmosphere, [4-(1,2,2-triphenylvinyl)phenyl]boronic acid **G** (1 mmol, 0.383 g) was added to the solution of 6-bromo-2-methylquinoline (1.2 mmol, 0.264 g), palladium acetate (0.05 mmol,

11.2 mg), potassium carbonate (1.2 mmol, 0.166 g) in dixoane/H_2O (4:1,v/v, 10 mL). The mixture was heated at 80°C for 18 h. After cooling to room temperature, the mixture was filtrated and the filtrate was diluted with brine. The solution was extracted by dichloromethane and the organic layer was dried over anhydrous $NaSO_4$. The filtrate was concentrated on a rotating evaporator. The residue was purified by the column chromatography on silica gel with ethyl acetate/petroleum ether (1:4) to give **H** as a white powder.

83% yield, m.p. 180.5-182.1°C; ^{1}H NMR (400 MHz, CDCl) δ 2.76(s, 3H), 7.13(m, 17H), 7.29(d, *J*=8.8 Hz, 1H), 7.47(d, *J*=8 Hz, 2H), 7.92(m, 2H), 8.05(t, *J*=8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl) δ 25.33, 122.32, 124.85, 126.39, 126.43, 126.49, 126.51, 126.56, 127.61, 127.68, 127.76, 128.82, 128.87, 131.30, 131.37, 131.91, 136.32, 137.81, 137.97, 140.32, 141.24, 143.09, 143.60, 143.64, 147.08, 158.84; EI-MS(70eV) *m/z*(%) 473(M^+, 100), 394(13), 252(47), 239(21), 197(32), 165(32), 152(13), 115(10), 77(17).

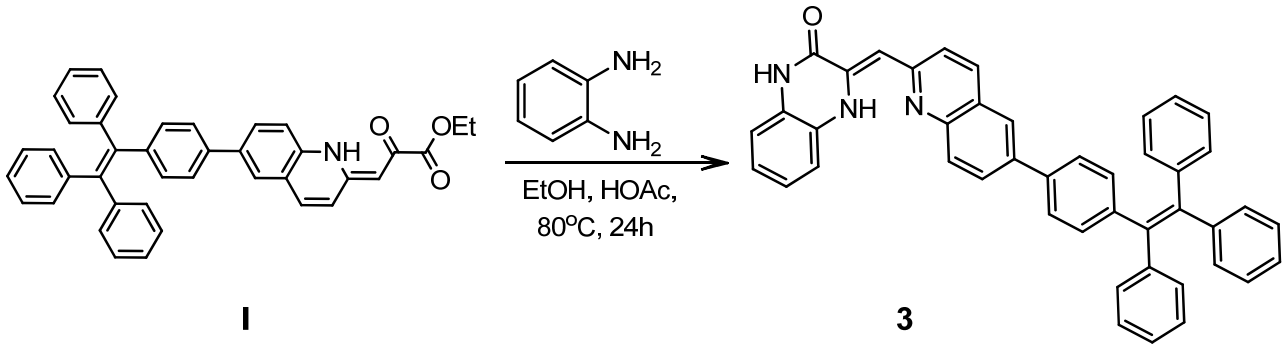


H **I**

Scheme S8 Synthesis of ethyl 2-oxo-3-{6-[4-(1,2,2-triphenylvinyl)phenyl]quinolin-2(1*H*)-ylidene}propanoate **I**

At room temperature, 2-methyl-6-[4-(1,2,2-triphenylvinyl)phenyl]quinoline **H** (1 mmol, 0.473 g) was added to the solution of diethyl oxalate (1.2 mmol, 0.175 g) and potassium *t*-butoxide (1.2 mmol, 0.134 g) in anhydrous THF (10 mL). The solution is irradiated in an ultrasound cleaner at 25°C for 3h and the yellow precipitate was collected. The solid was washed by anhydrous ether for several times and then dissolved with 1% HCl aqueous solution. The mixture was extracted by ethyl acetate and the organic layer was dried over anhydrous $NaSO_4$. The filtrate was concentrated on a rotating evaporator. The residue was purified by the column chromatography on silica gel with ethyl acetate/petroleum ether (1:4) to give **I** as an orange powder.

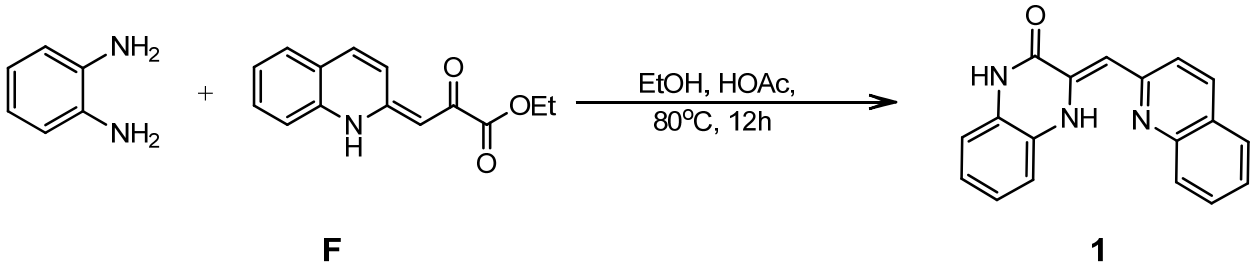
76% yield, m.p. 215.8-216.4°C; ^{1}H NMR (400 MHz, CDCl) δ 1.41(t, *J*=7.2 Hz, 3H), 4.36(q, *J*=7.2 Hz, 2H), 6.40(s, 1H), 7.10(m, 18H), 7.40(d, *J*=8 Hz, 2H), 7.62(d, *J*=8 Hz, 1H), 7.79(s, 1H), 7.84(d, *J*=8 Hz, 1H), 7.90(d, *J*=8 Hz, 1H), 15.82(br s, 1H); ^{13}C NMR (100 MHz, CDCl) δ 14.22, 61.68, 94.17, 120.08, 122.15, 124.68, 125.26, 126.20, 126.53, 126.58, 126.59, 127.66, 127.25, 127.81, 130.75, 131.30, 131.33, 131.37, 132.08, 137.09, 137.24, 137.84, 137.89, 140.16, 141.47, 143.53, 143.57, 143.59, 154.88, 164.43, 169.73; EI-MS(70eV) *m/z*(%) 573(M^+, 33), 545(11), 500(64), 473(100), 394(13), 357(33), 314(27), 301(38), 258(53), 197(10), 165(12), 115(7), 77(10).



I **3**

Scheme S9 Synthesis of (*Z*)-3-{6-[4-(1,2,2-triphenylvinyl)phenyl]quinolin-2-yl}methylene-3,4-dihydroquinoxalin-2(1*H*)-one **3**

At room temperature, ethyl 2-oxo-3-{6-[4-(1,2,2-triphenylvinyl)phenyl]quinolin-2(1*H*)-ylidene} propanoate **I** (1 mmol, 0.573 g) was added to the solution of *o*-phenylenediamine (1.2 mmol, 0.13 g) in ethanol (10 mL). After 1-2 drops of glacial acetic acid was added, the mixture was refluxed at 80°C for 24 h. The bright red solid was filtrated and washed by ethanol and ether for several times. The solid could be further recrystallized in ethanol. The solid is poorly soluble in most deuterated solvents, and its ^{13}C NMR spectrum cannot be available. 55% yield, m.p.314.1-314.6°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.41(s, 1H), 6.97-7.22(m, 20H), 7.49(t, *J*=8 Hz, 2H), 7.77(d, *J*=8 Hz, 2H), 8.03(d, *J*=8 Hz, 1H), 8.20(s, 1H), 8.21(d, *J*=8 Hz, 1H), 8.24(d, *J*=8 Hz, 1H), 11.50(s, 1H), 13.67(s, 1H); EI-MS(70eV) *m/z*(%) 617(M^+, 100), 589(12), 501(10), 473(27), 308(19), 255(12), 131(6), 105(5), 91(6), 77(5).



F **1**

Scheme S10 Synthesis of (*Z*)-3-(isoquinolin-3-ylmethylene)-3,4-dihydroquinoxalin-2(1H)-one **1**

At room temperature, ethyl 2-oxo-3-[quinolin-2(1*H*)-ylidene]propanoate **F** (1 mmol, 0.243 g) was added to the solution of *o*-phenylenediamine (1.2 mmol, 0.13 g) in ethanol (10 mL). After 1-2 drops of glacial acetic acid was added, the mixture was refluxed at 80°C for 12 h. The bright red solid was filtrated and washed by ethanol and ether for several times. The solid could be further recrystallized in ethanol.

73% yield, m.p. 245.5-246.2°C; ^{1}H NMR(400MHz, DMSO-d_6) δ 6.40(s, 1H), 6.99(t, *J*=8 Hz, 1H), 7.06-7.11(m, 2H), 7.44-7.51(m, 3H), 7.75(t, *J*=8 Hz, 1H), 7.87(d, *J*=8 Hz, 1H), 8.20(dd, J_1=8 Hz, J_2=4 Hz, 2H), 11.50(s, 1H), 13.73(s, 1H); ^{13}C NMR(100MHz, DMSO-d_6) δ 94.35, 115.00, 115.21, 121.55, 123.31, 125.09, 125.14, 125.68, 126.35, 126.83, 127.55, 129.81, 135.67, 137.53,145.74, 157.00, 157.05; EI-MS (70 eV) *m/z* (%) 287(M^+, 100), 258(91), 168(10), 143(23), 129(25), 115(10), 101(8), 90(12), 77(10).

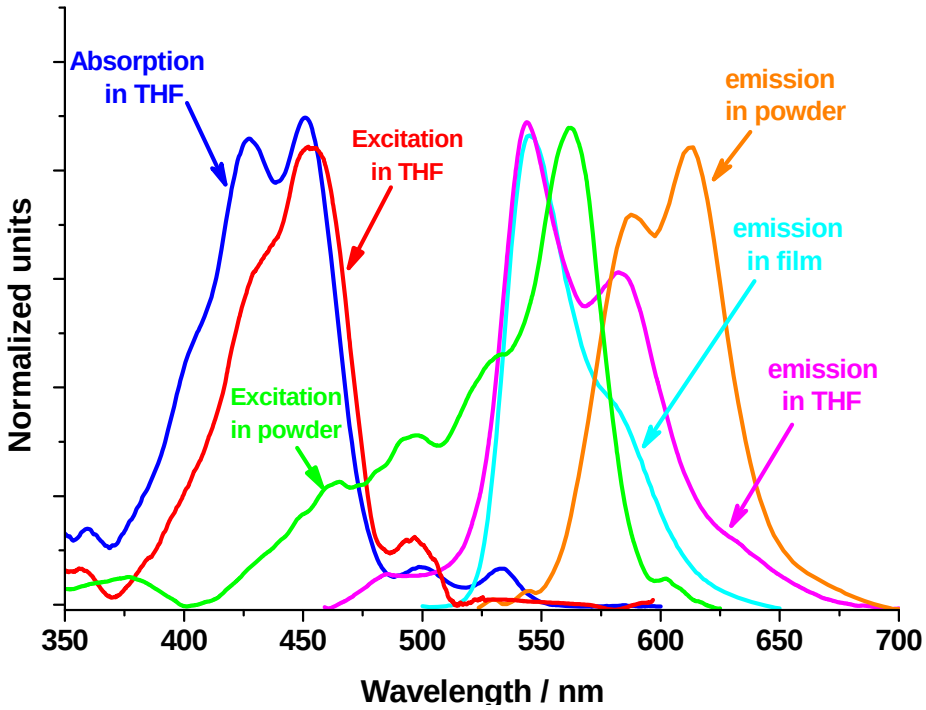


Fig. S1 Absorption and emission (λ_{ex}= 450 nm) spectra of **1** in THF solution, PMMA film and solid state

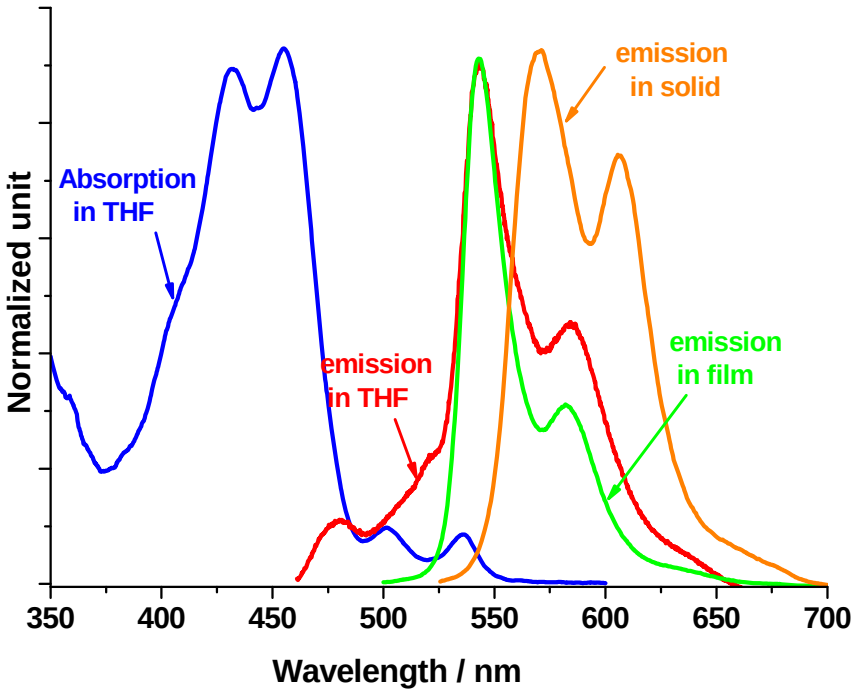


Fig. S2 Absorption and emission (λ_{ex}= 455 nm) spectra of **2** in THF solution, PMMA film and solid state

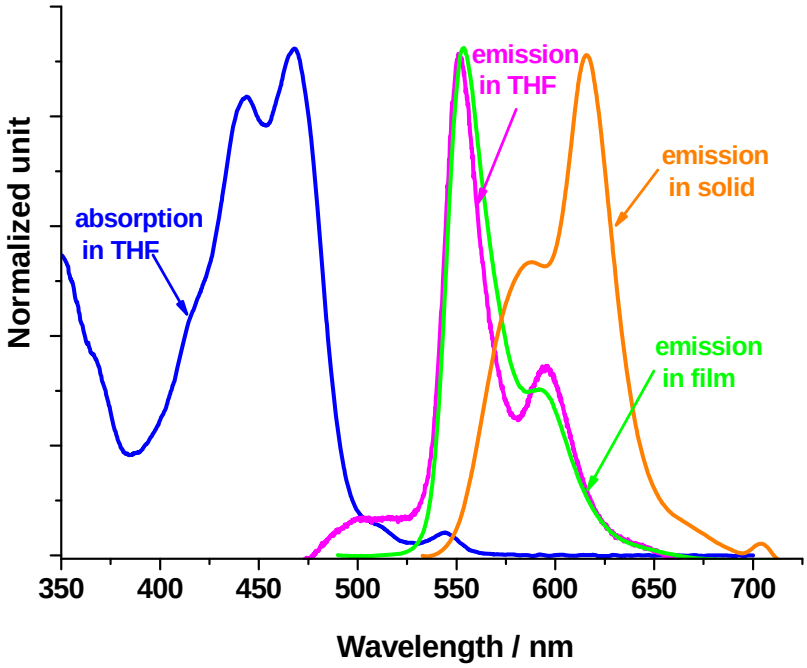


Fig. S3 Absorption and emission (λ_{ex}= 468 nm) spectra of **3** in THF solution, PMMA film and solid state

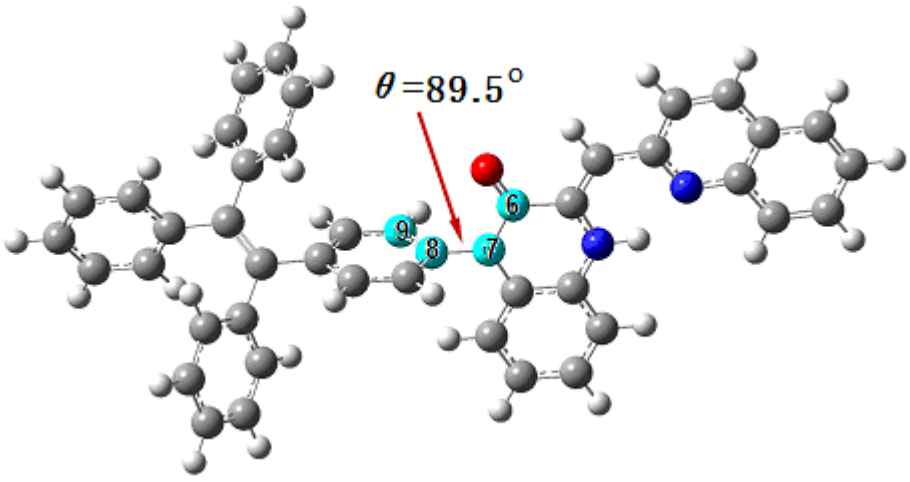


Fig. S4 Geometry of **2N** at ground state

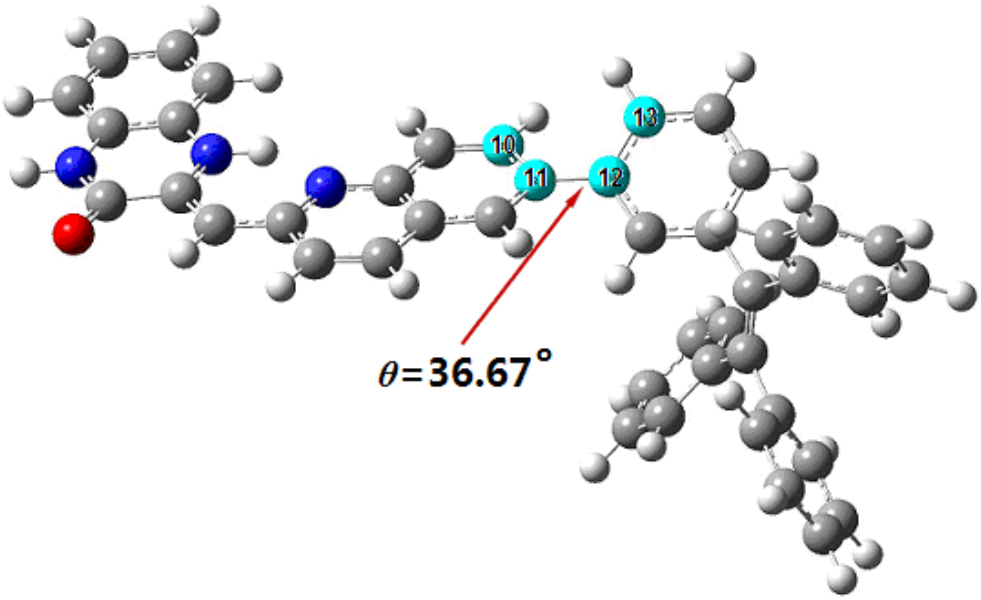


Fig. S5 Geometry of **3N** at ground state

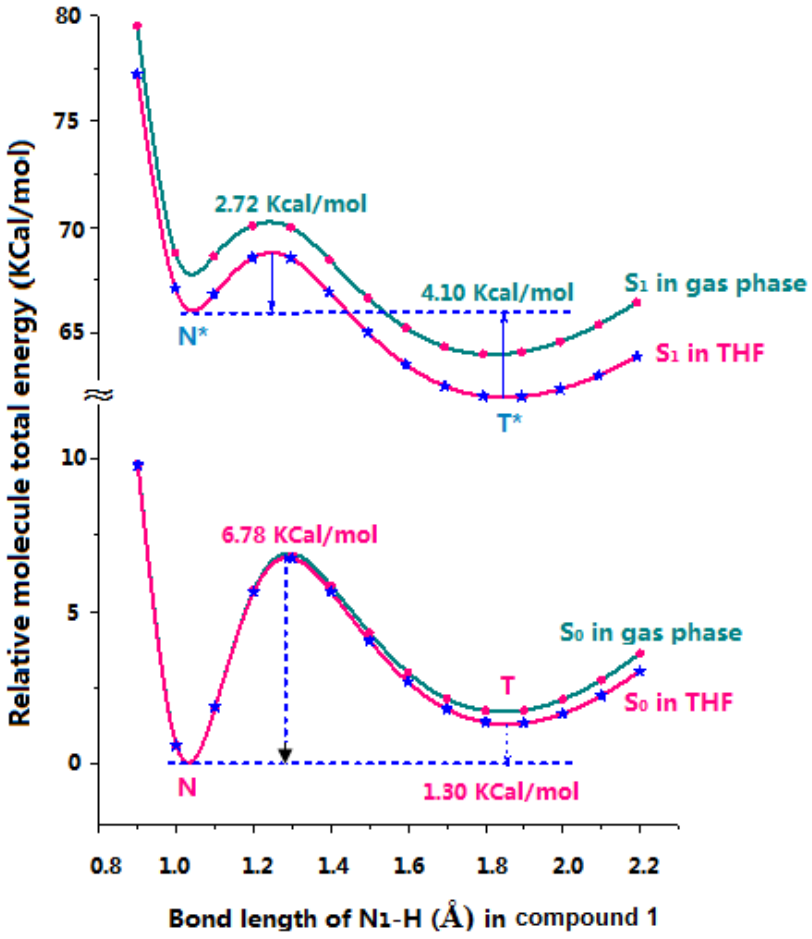


Fig. S6 Relative molecule total energy with varied bond length of N_1-H in compound **1** by TD-DFT calculations at B3LYP/PCM/6-31G(d,p) level in THF and gas phase

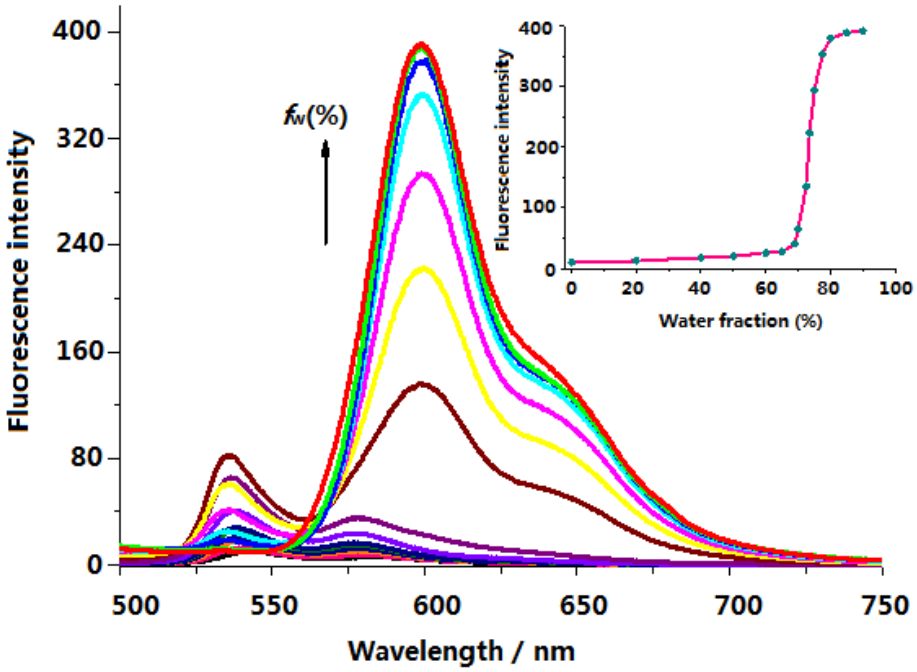


Fig. S7 Emission spectra of **1** (50 μM)in THF/H_2O mixture with varied water content (the inserted is the fluorescence intensity of **1** depending on water fraction in H_2O/THF mixture). Slit width: Ex= 5 nm; Em= 5 nm.

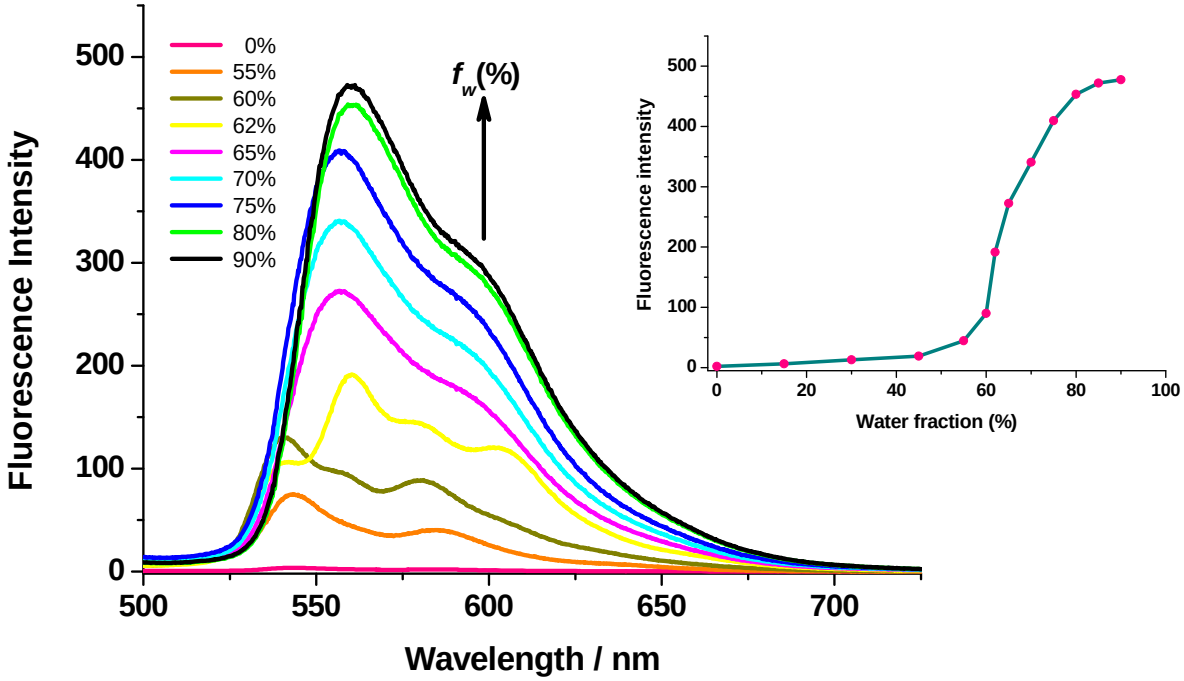


Fig. S8 Emission spectra of **2** (50 μM) in THF/H_2O mixture with varied water content (the inserted is the fluorescence intensity of **2** depending on water fraction in H_2O/THF mixture). Slit width: Ex= 3 nm; Em= 5 nm.

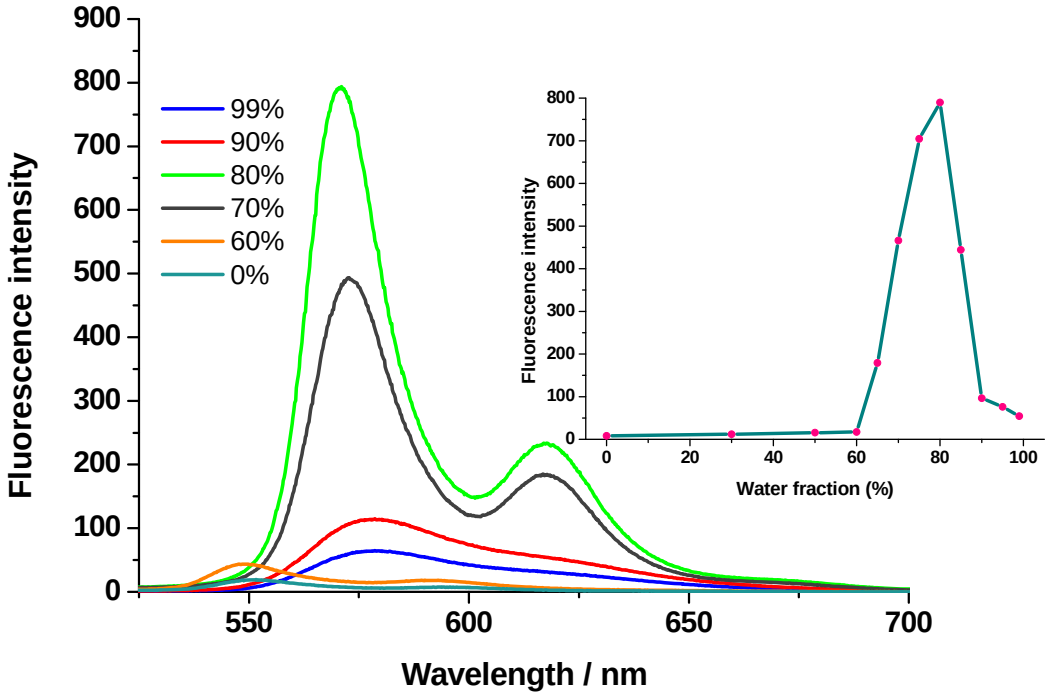


Fig. S9 Emission spectra of **3** (50 μM) in THF/H_2O mixture with varied water content (the inserted is the fluorescence intensity of **3** depending on water fraction in H_2O/THF mixture). Slit width: Ex= 3 nm; Em= 3 nm.

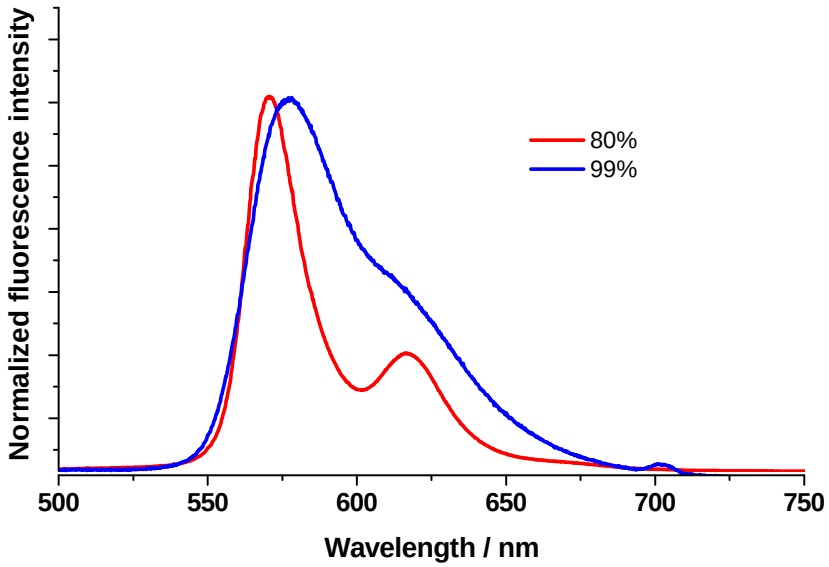


Fig. S10 Normalized emission spectra of **3** (50 μM) in THF/H_2O mixture with different water content

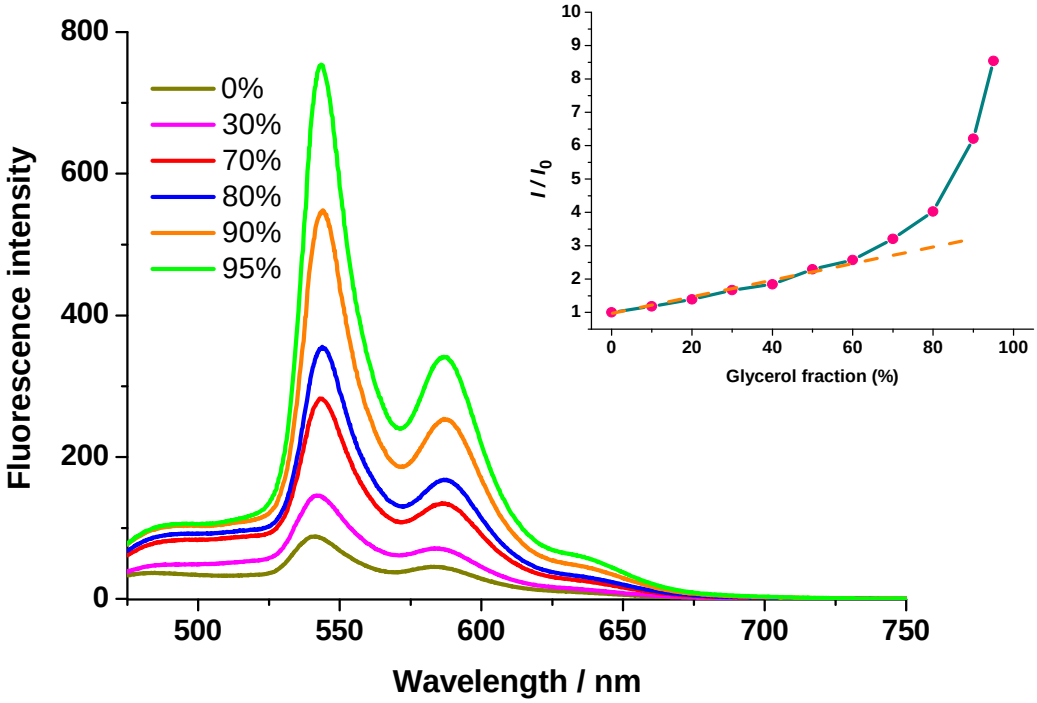


Fig. S11 Emission spectral of **1** (25 μM) in THF/glycerol mixture with varied glycerol fraction (inserted is the intensity change with varied glycerol fraction. I_0 is the intensity in pure THF solution)

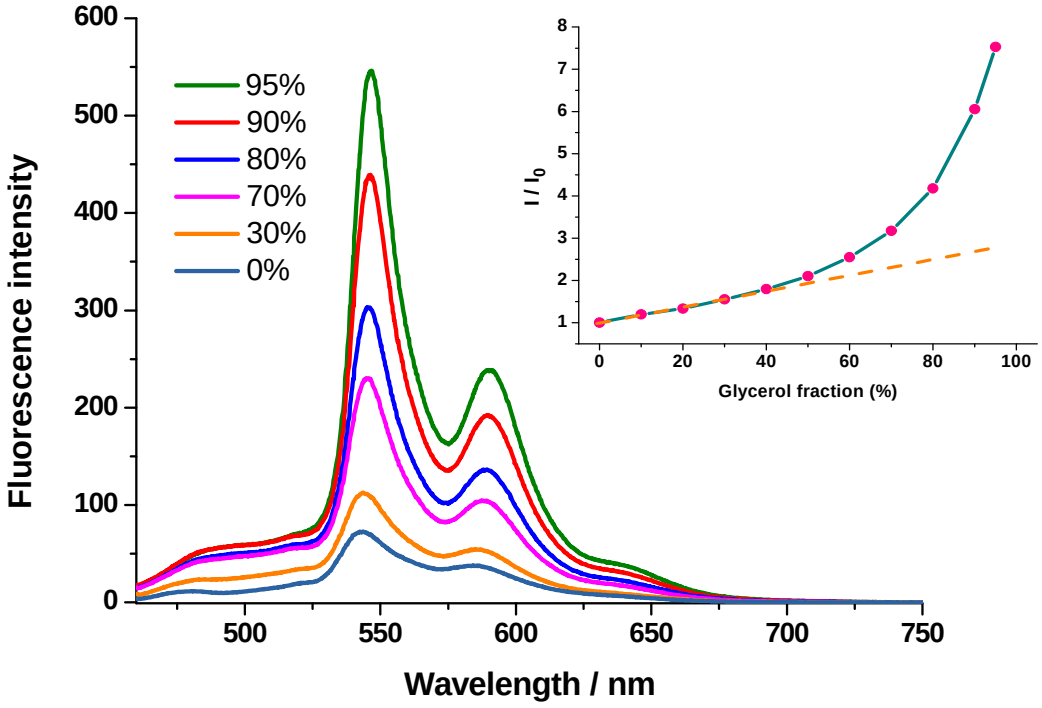


Fig. S12 Emission spectral of **2** (25 μM) in THF/glycerol mixture with varied glycerol fraction (inserted is the intensity change with varied glycerol fraction. I_0 is the intensity in pure THF solution)

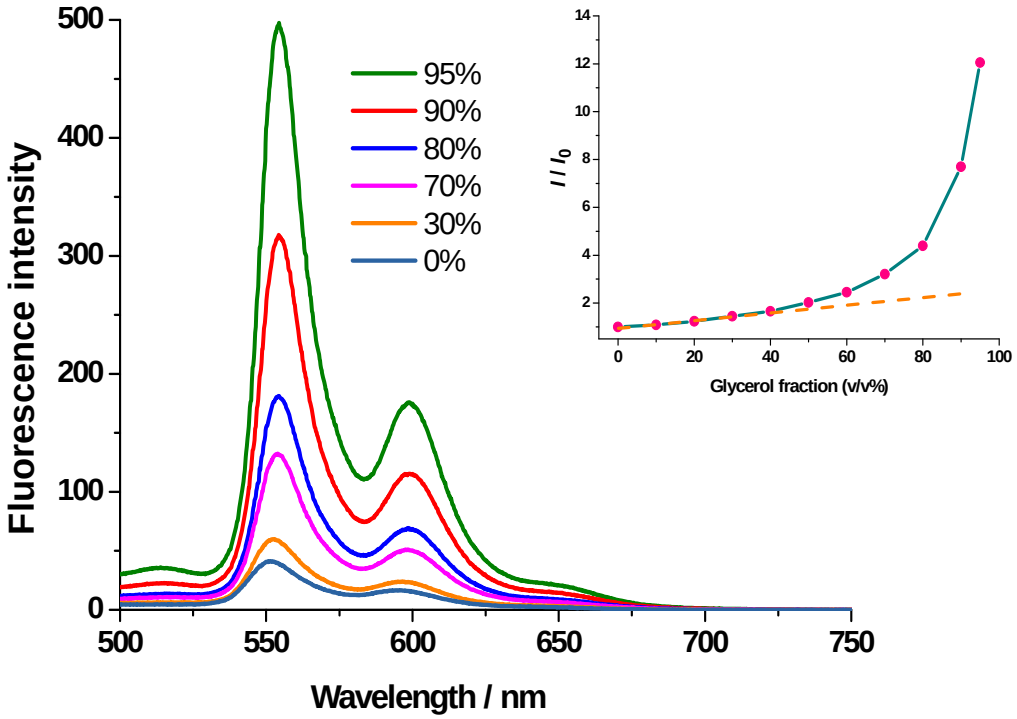
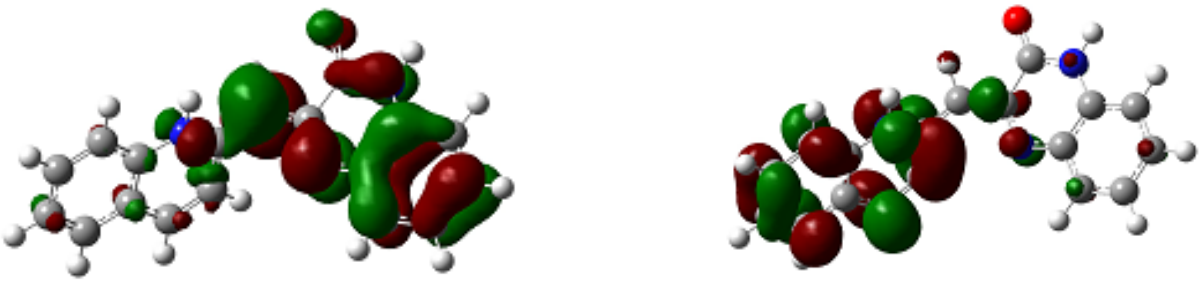


Fig. S13 Emission spectral of **3** (25 μM) in THF/glycerol mixture with varied glycerol fraction (inserted is the intensity change with varied glycerol fraction. I_0 is the intensity in pure THF solution)



HOMO LUMO

Fig. S14 HOMO and LUMO of **1T*** in TICT state (90^o torsion of C_5-C_4 bond)

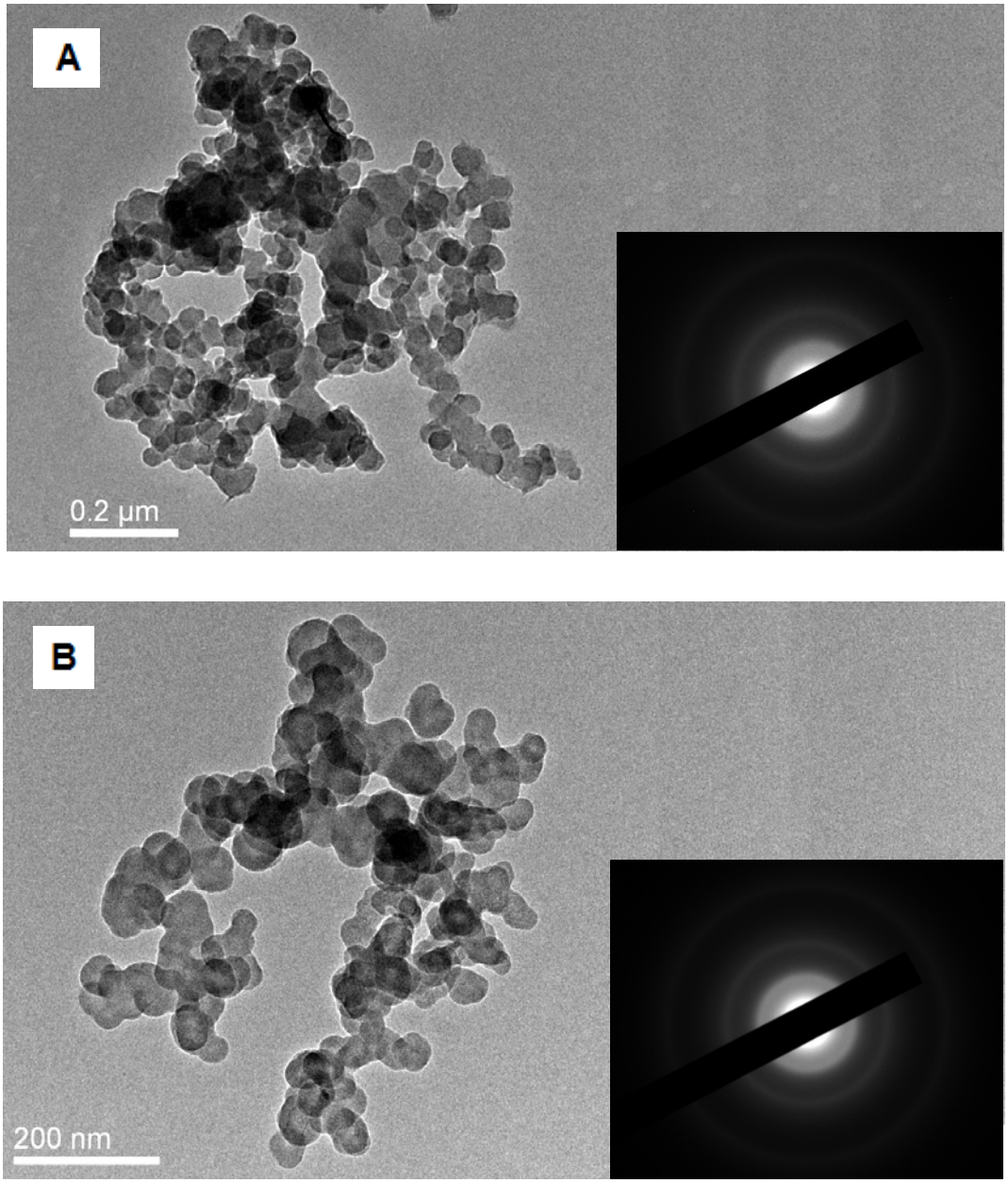
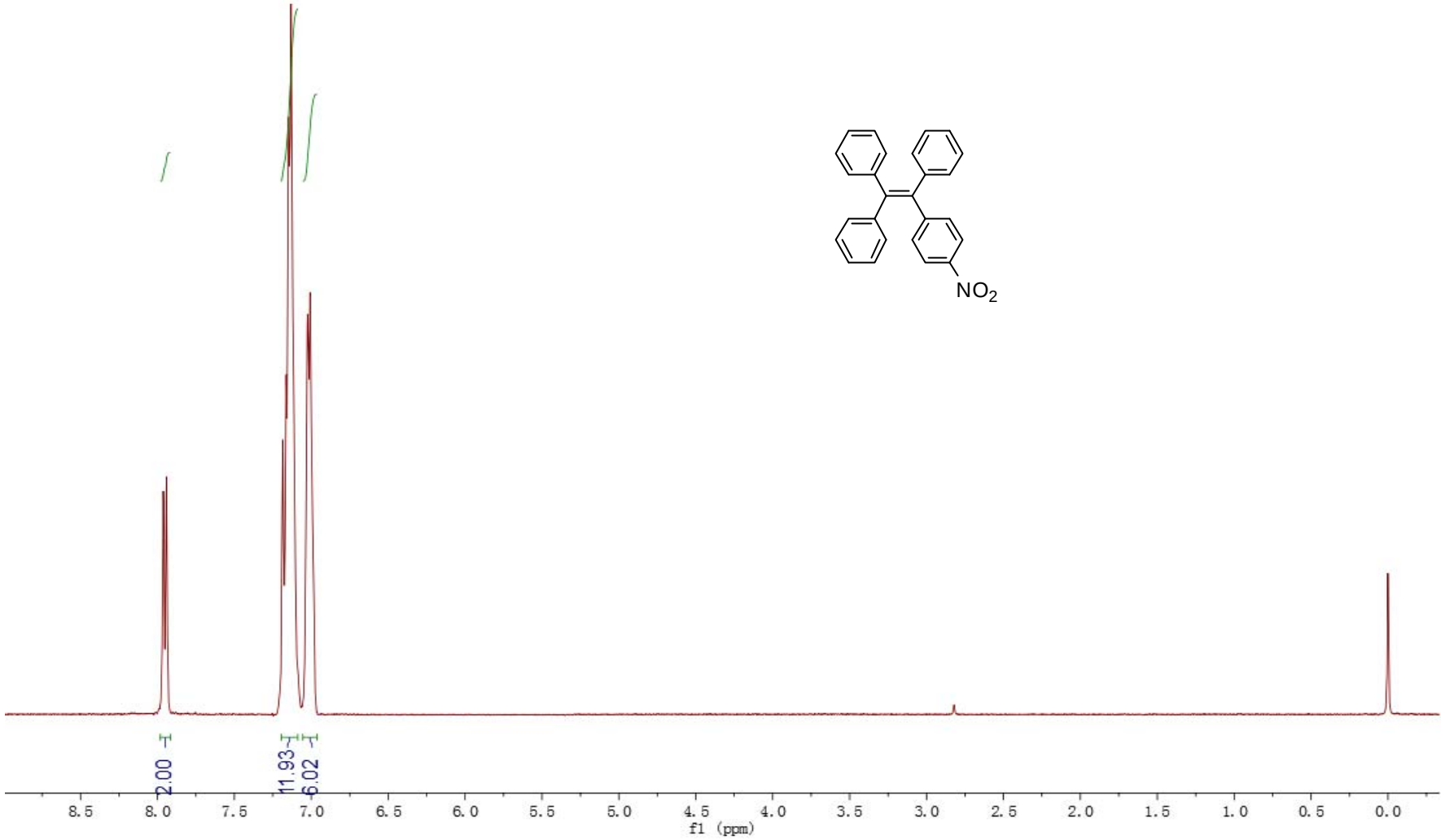
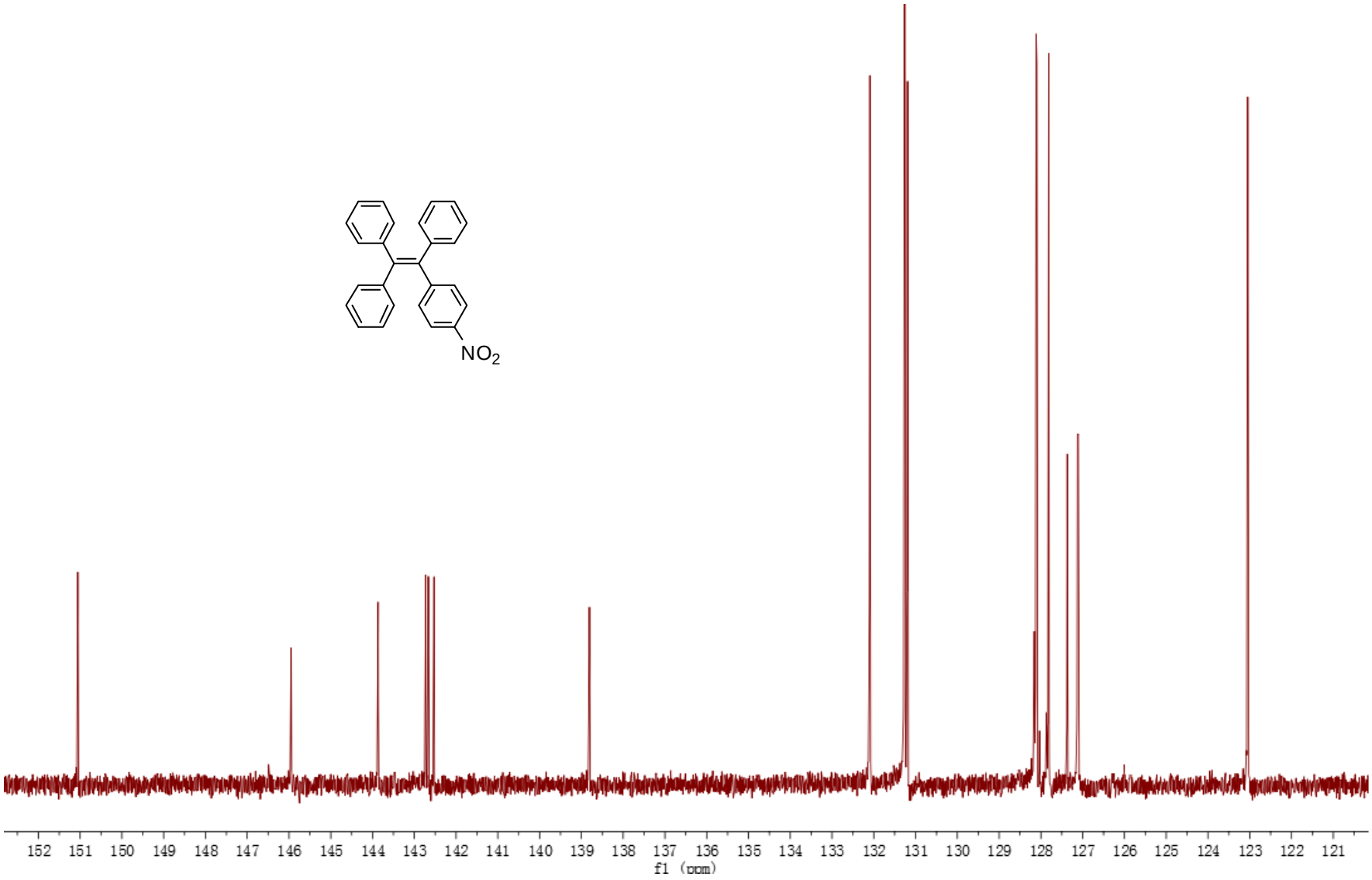
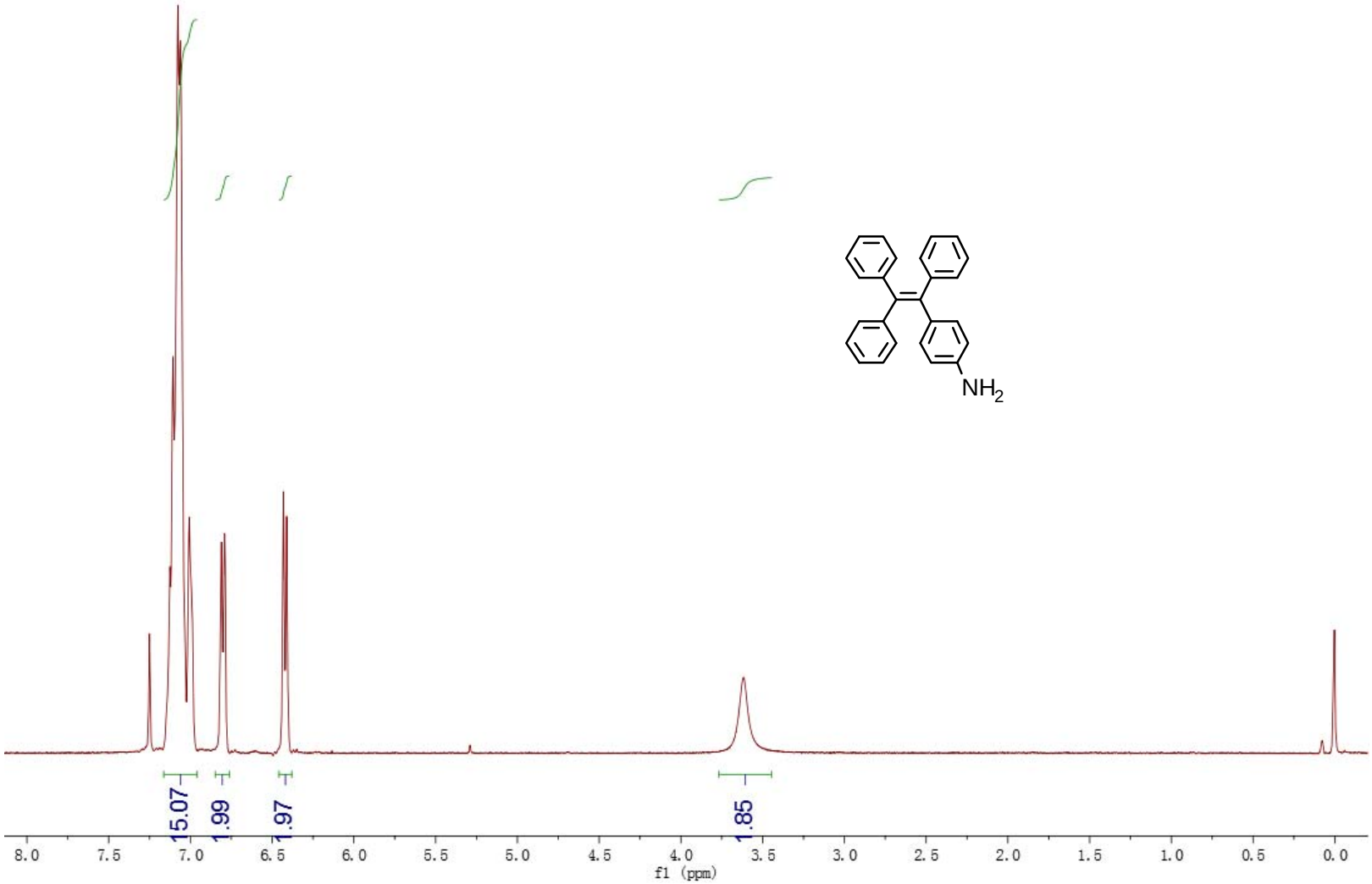
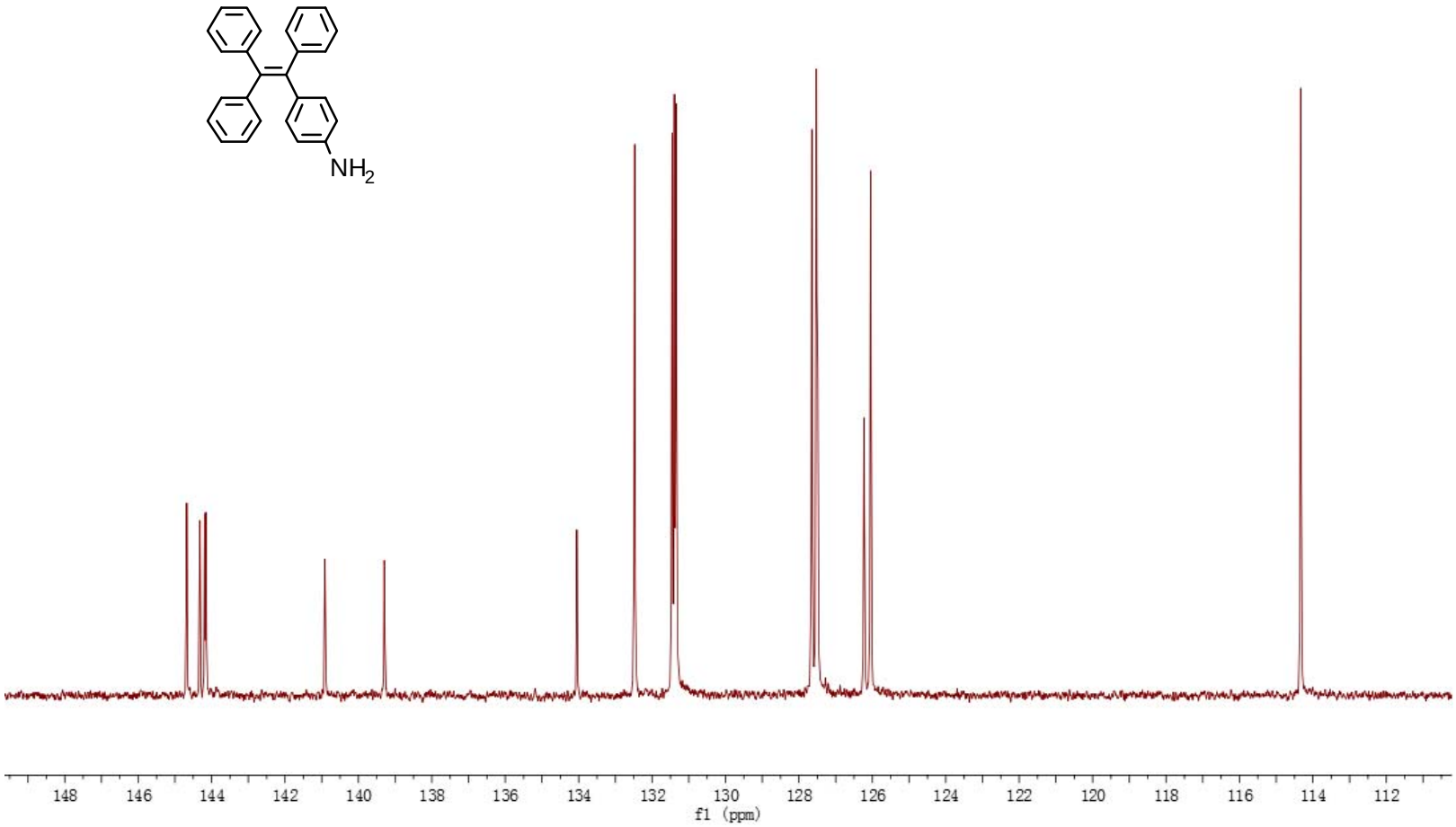


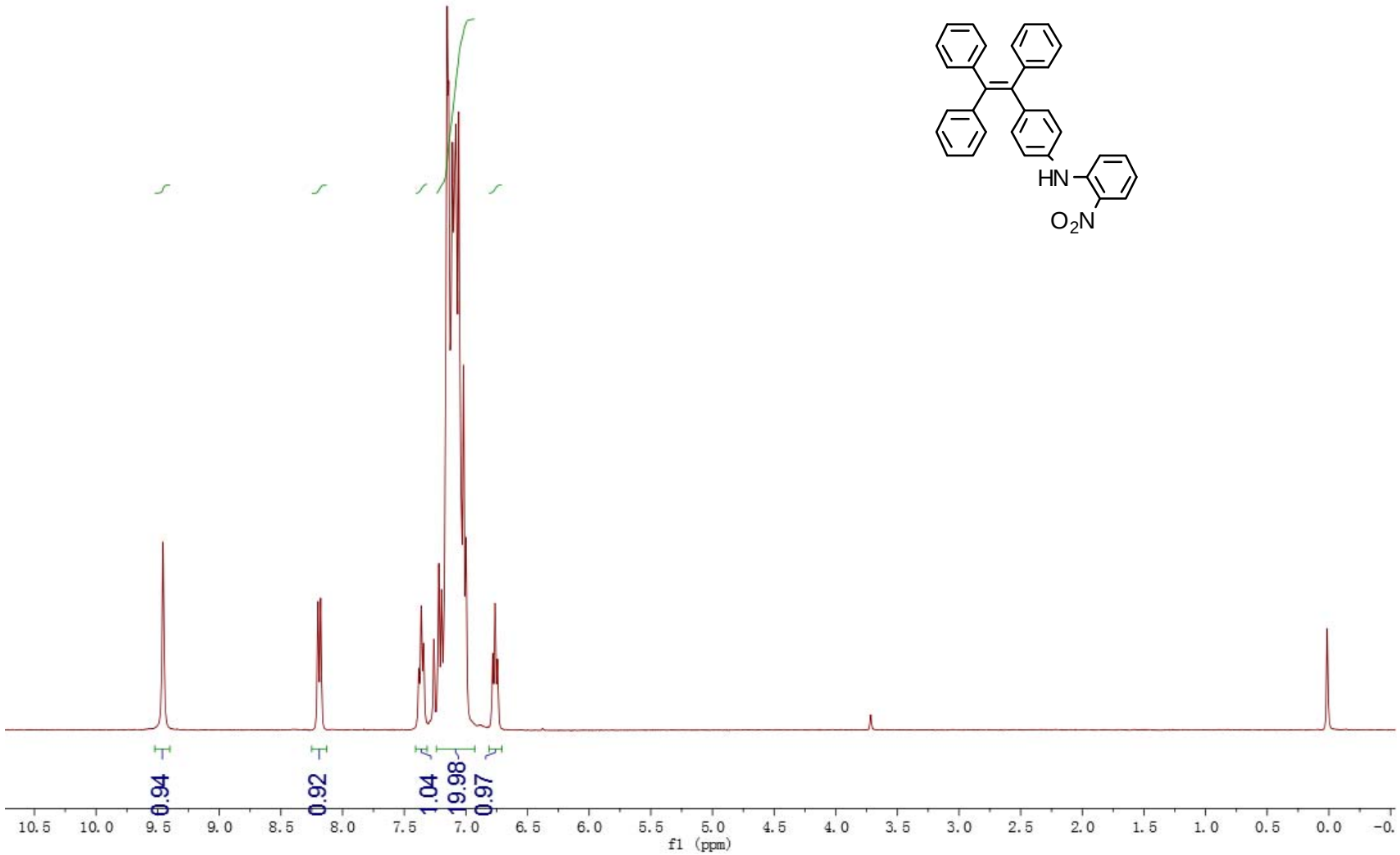
Fig. S15 TEM images and ED patterns of amorphous aggregates of **2** in THF/H_2O mixture with 80% (**A**) and 99% (**B**) water fraction

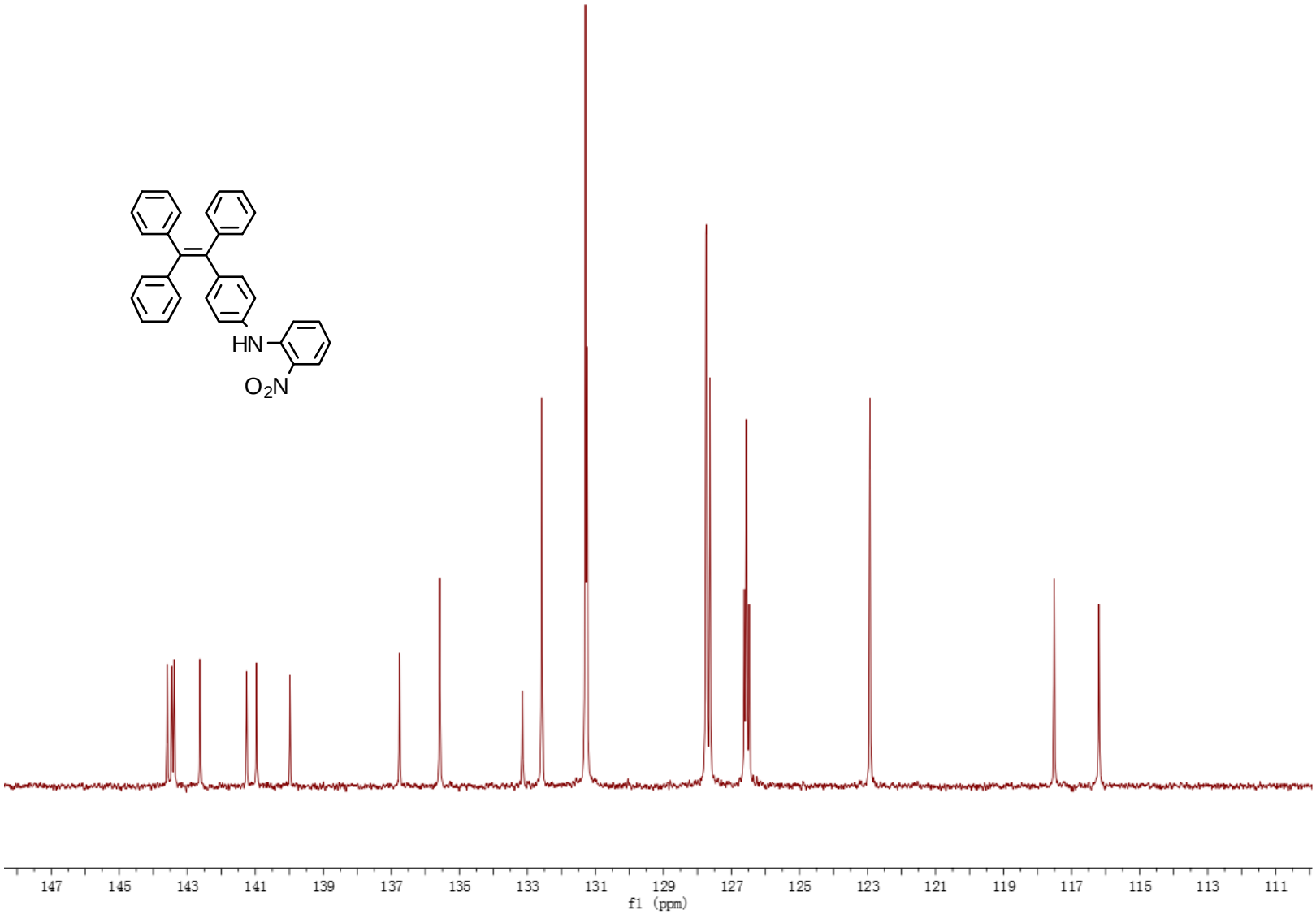

NO2
2.00
11.93
6.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

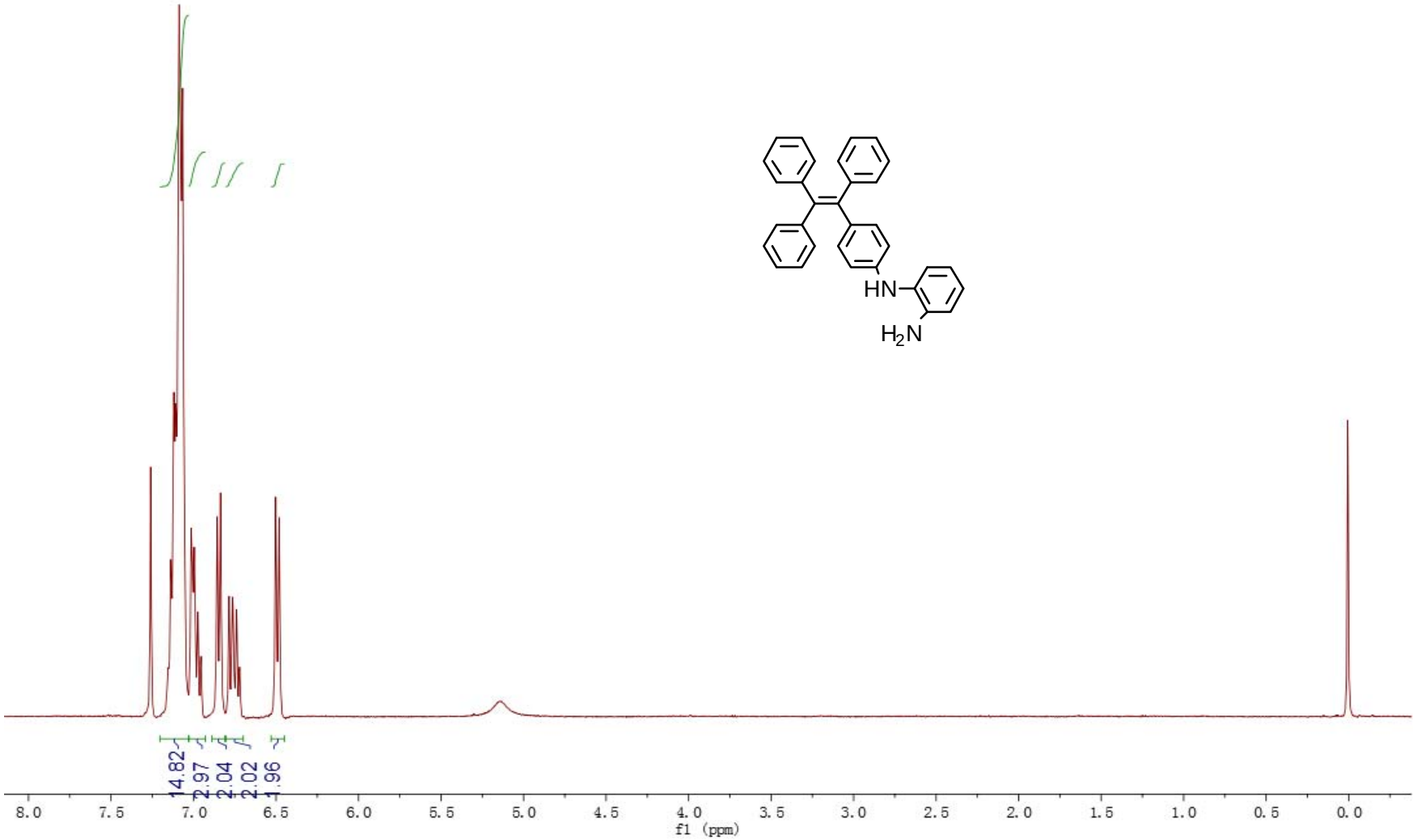

NO2
152 151 150 149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121
f1 (ppm)

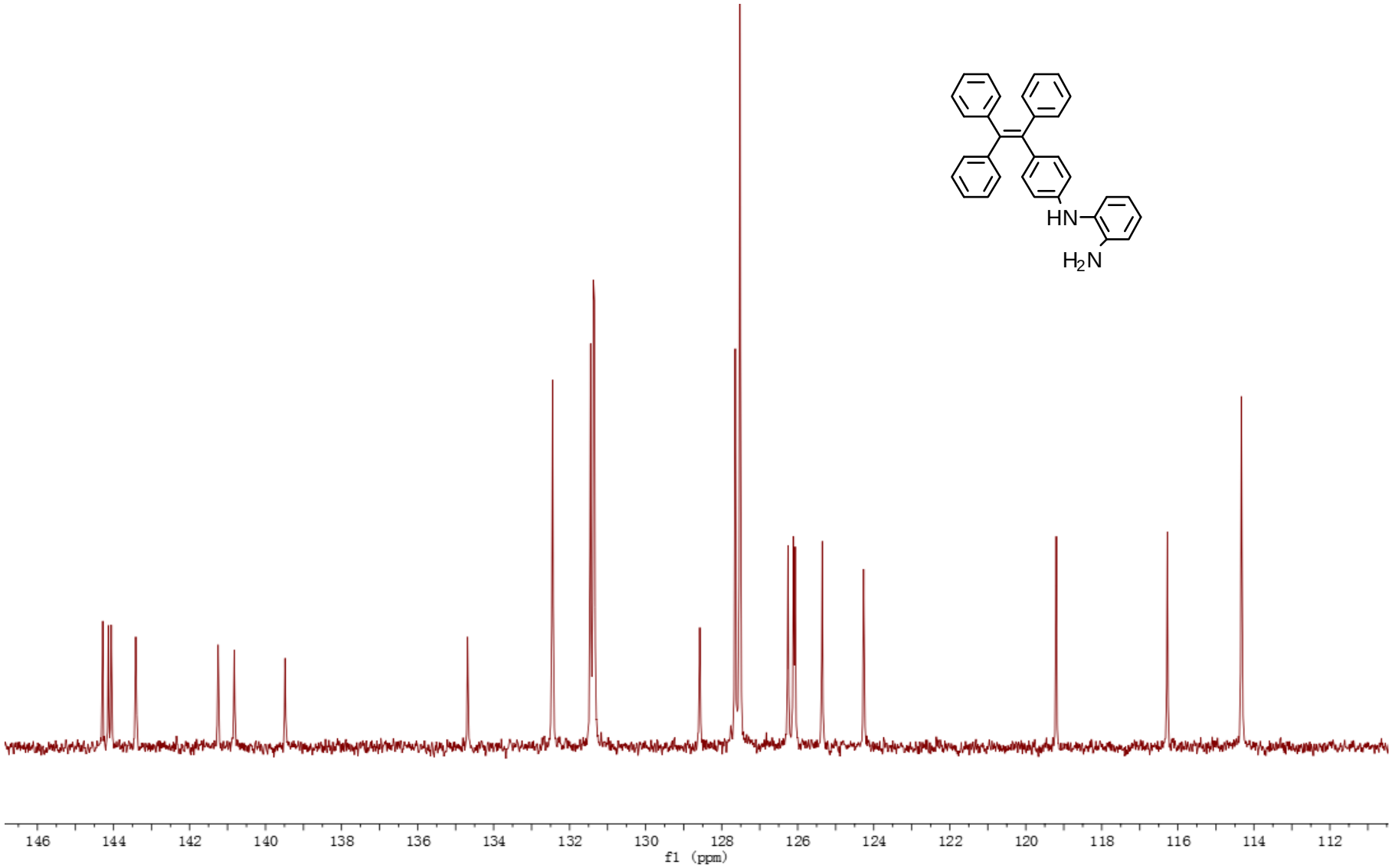

NH2
15.07
1.99
1.97
1.85
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

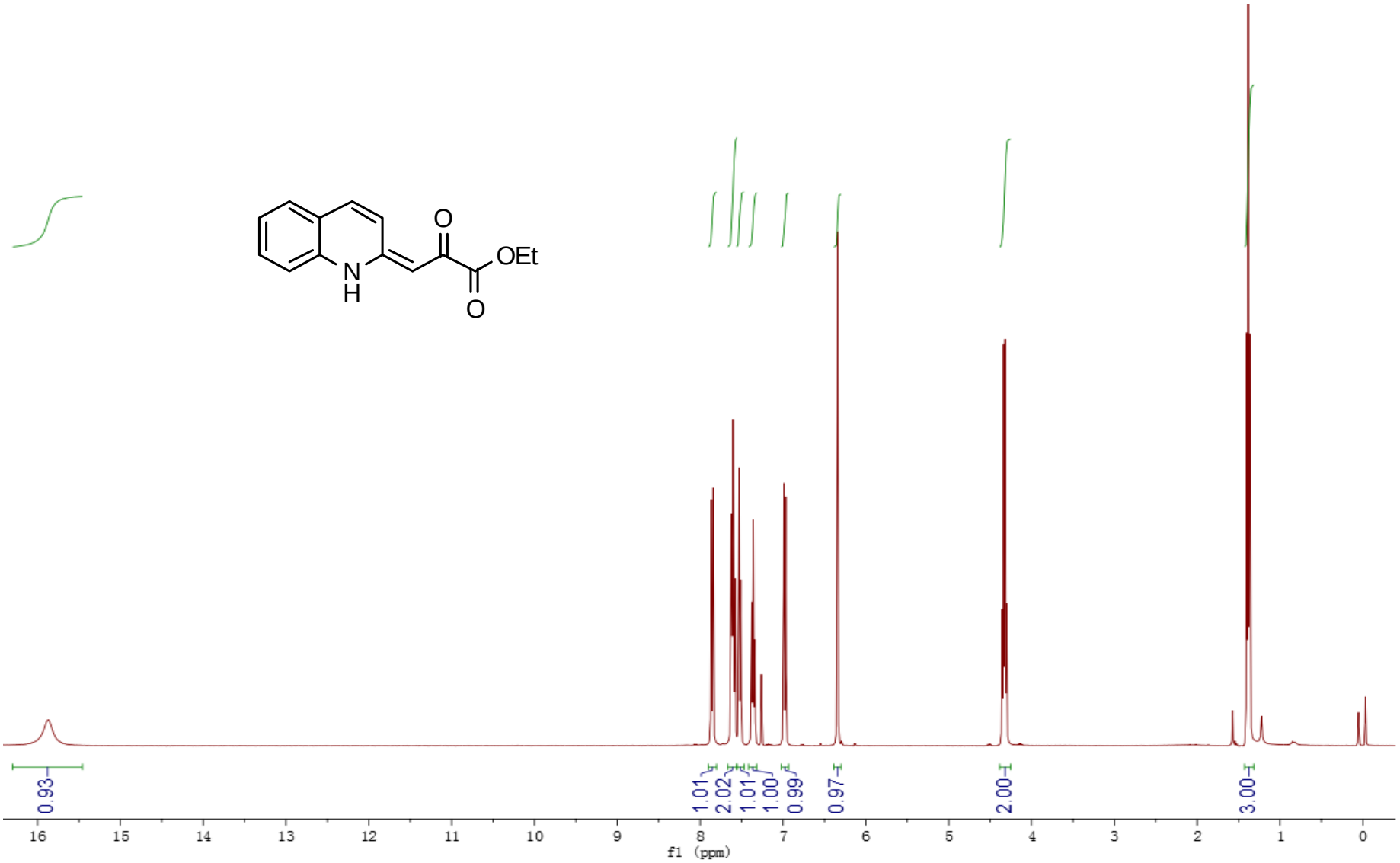

NH2
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112
f1 (ppm)

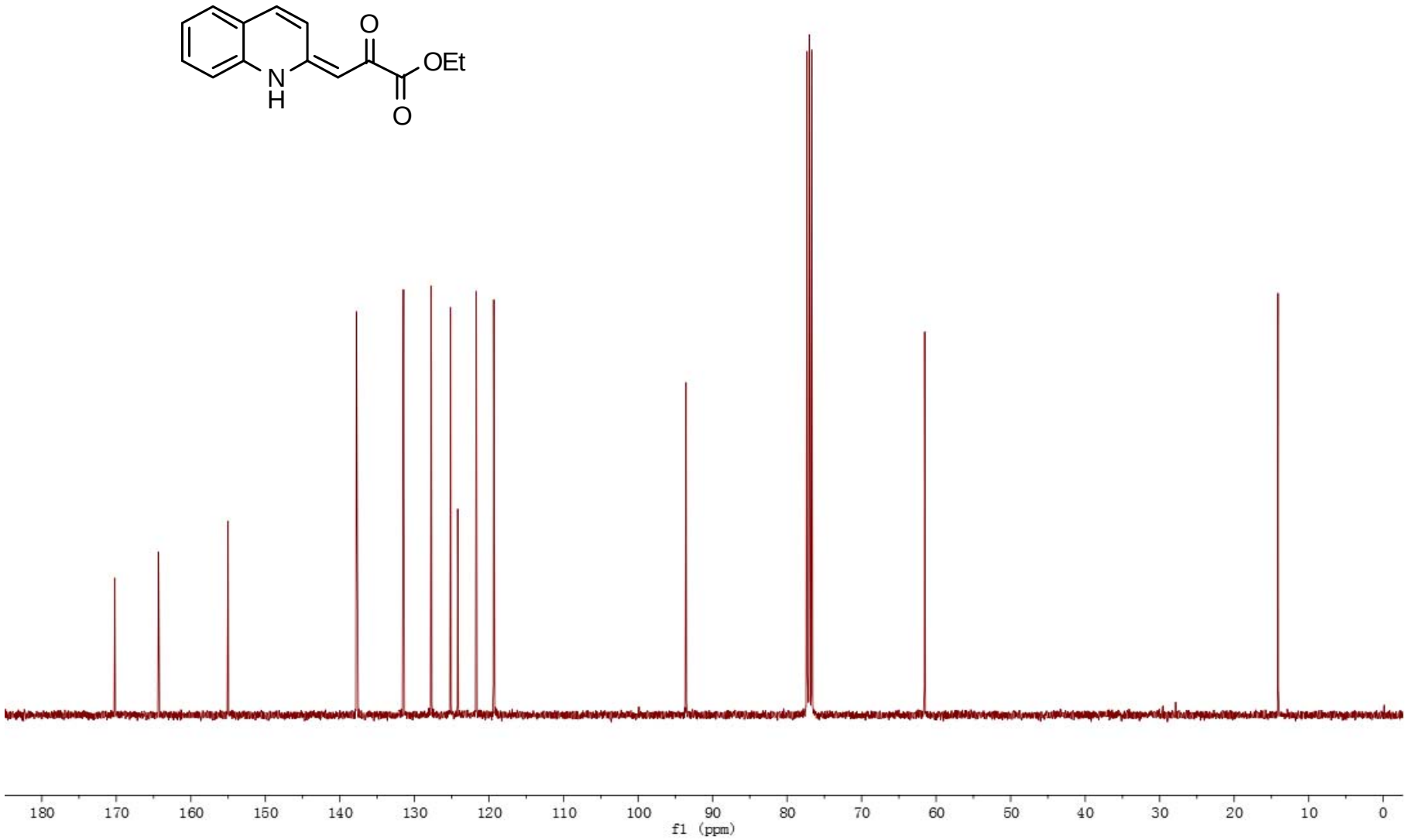

HN
O2N
0.94
0.92
1.04
19.98
0.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

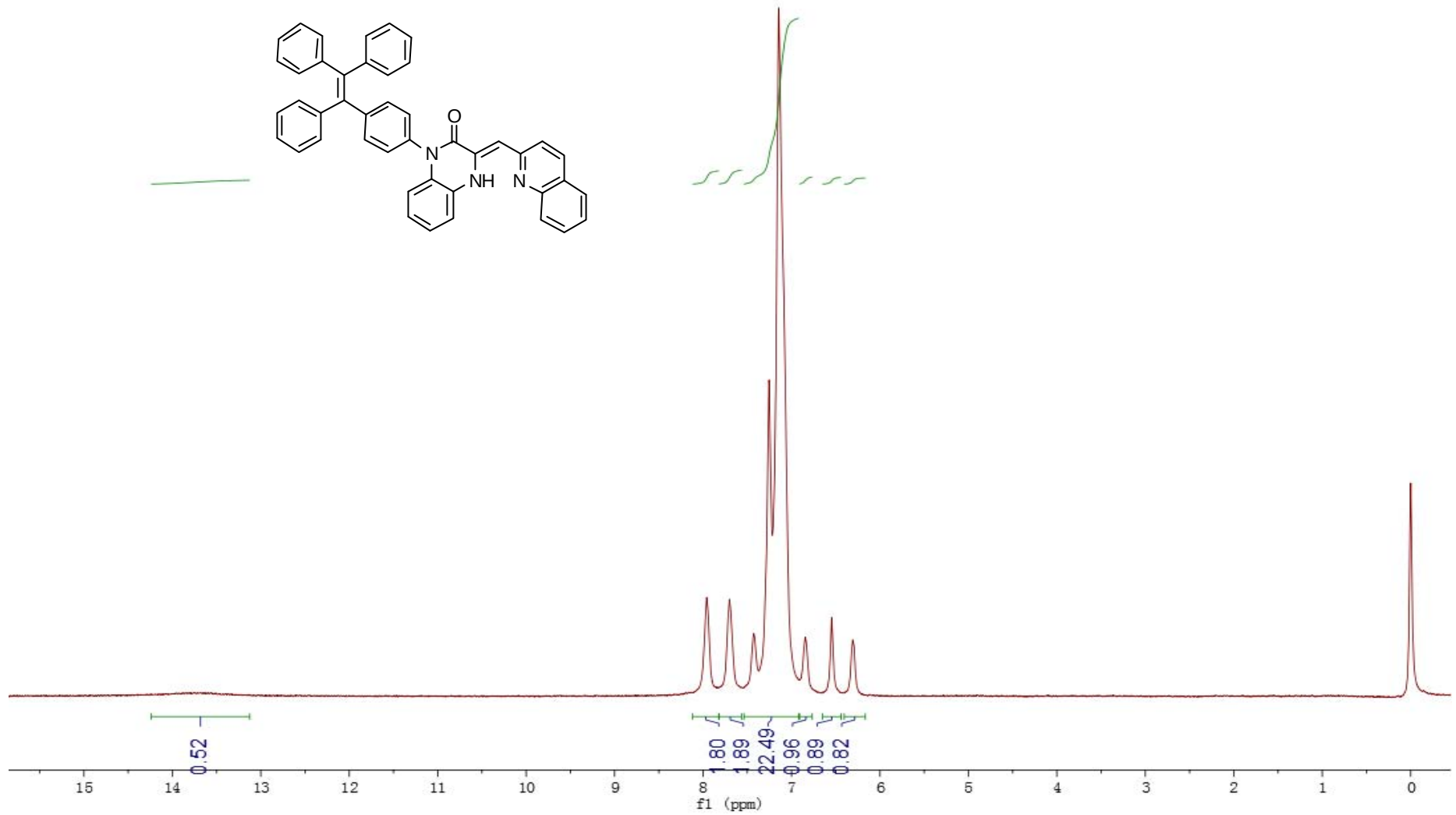

HN
O2N
147
145
143
141
139
137
135
133
131
129
127
125
123
121
119
117
115
113
111
f1 (ppm)

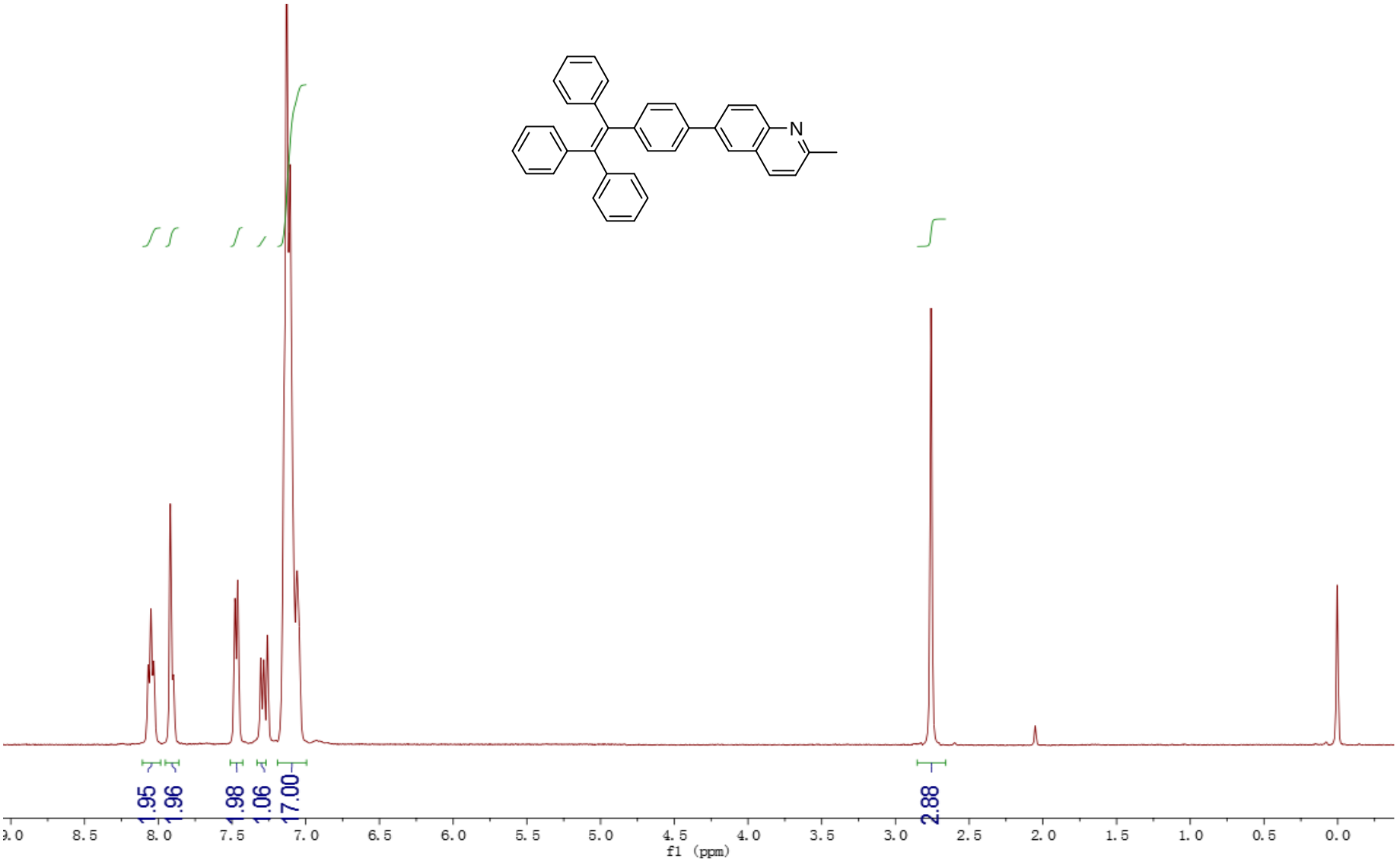

HN
H2N
14.82
2.97
2.04
2.02
1.96
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

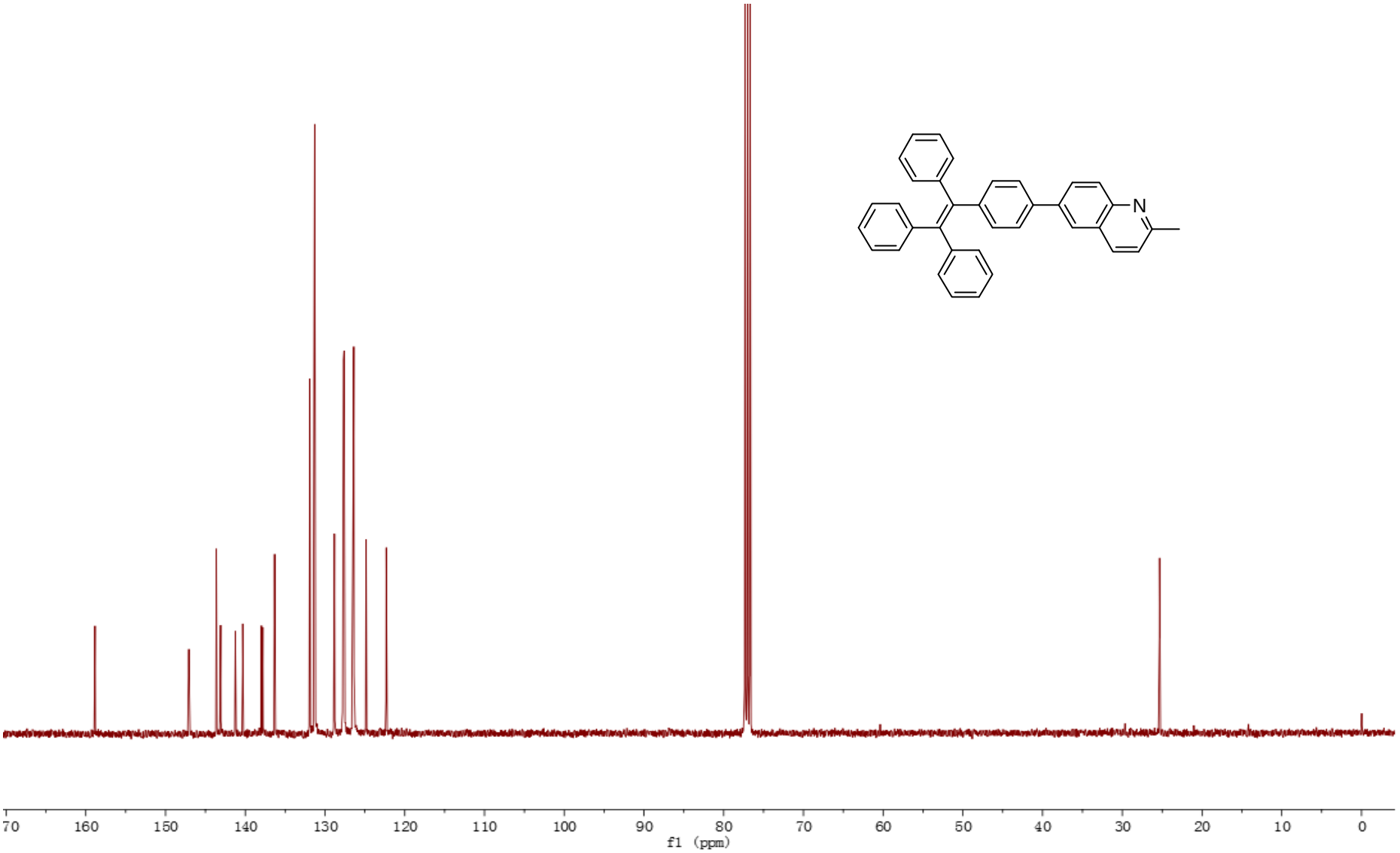

HN
H2N
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112
f1 (ppm)

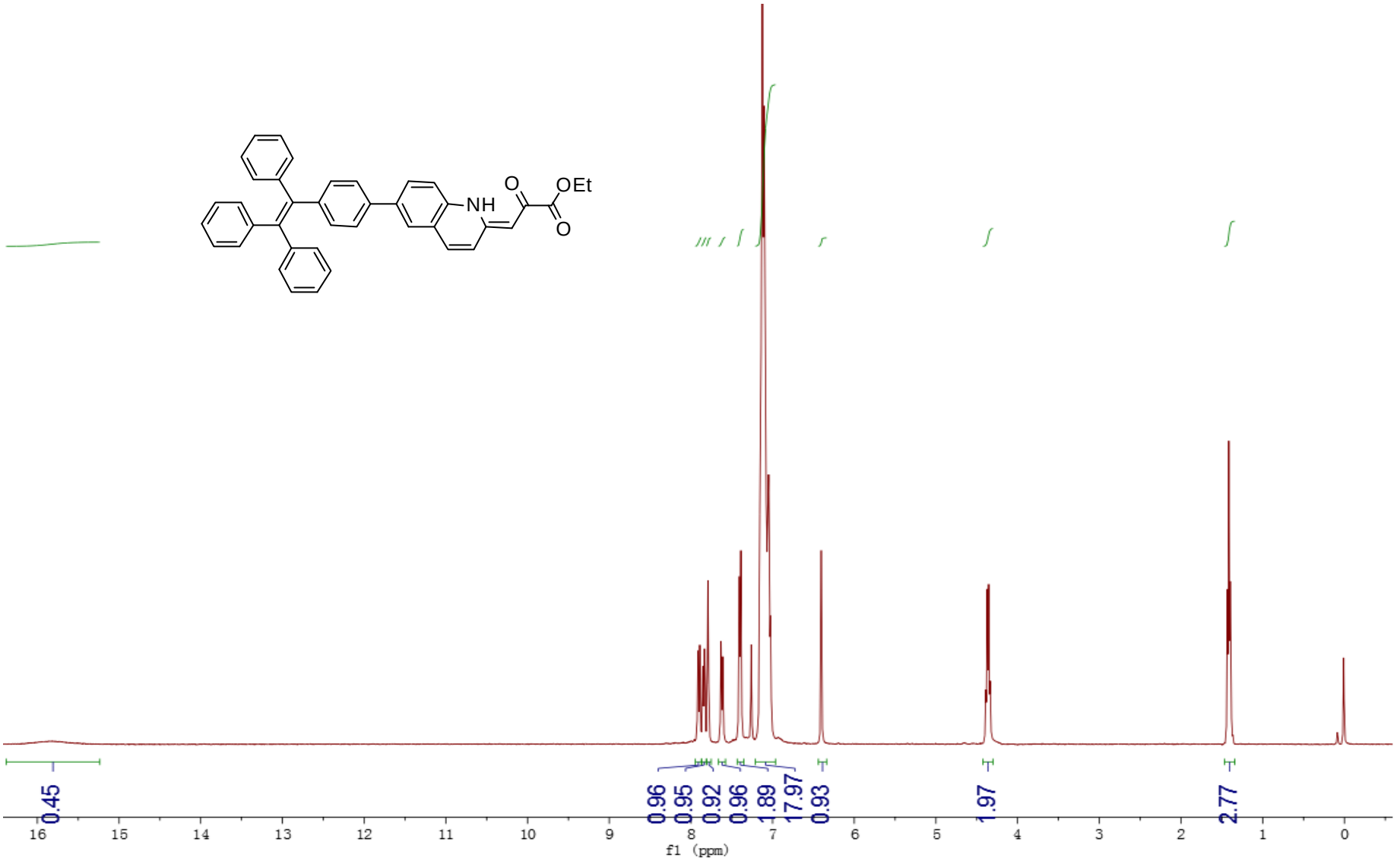

O
OEt
N
H
O
0.93
1.01
2.02
1.01
1.00
0.99
0.97
2.00
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

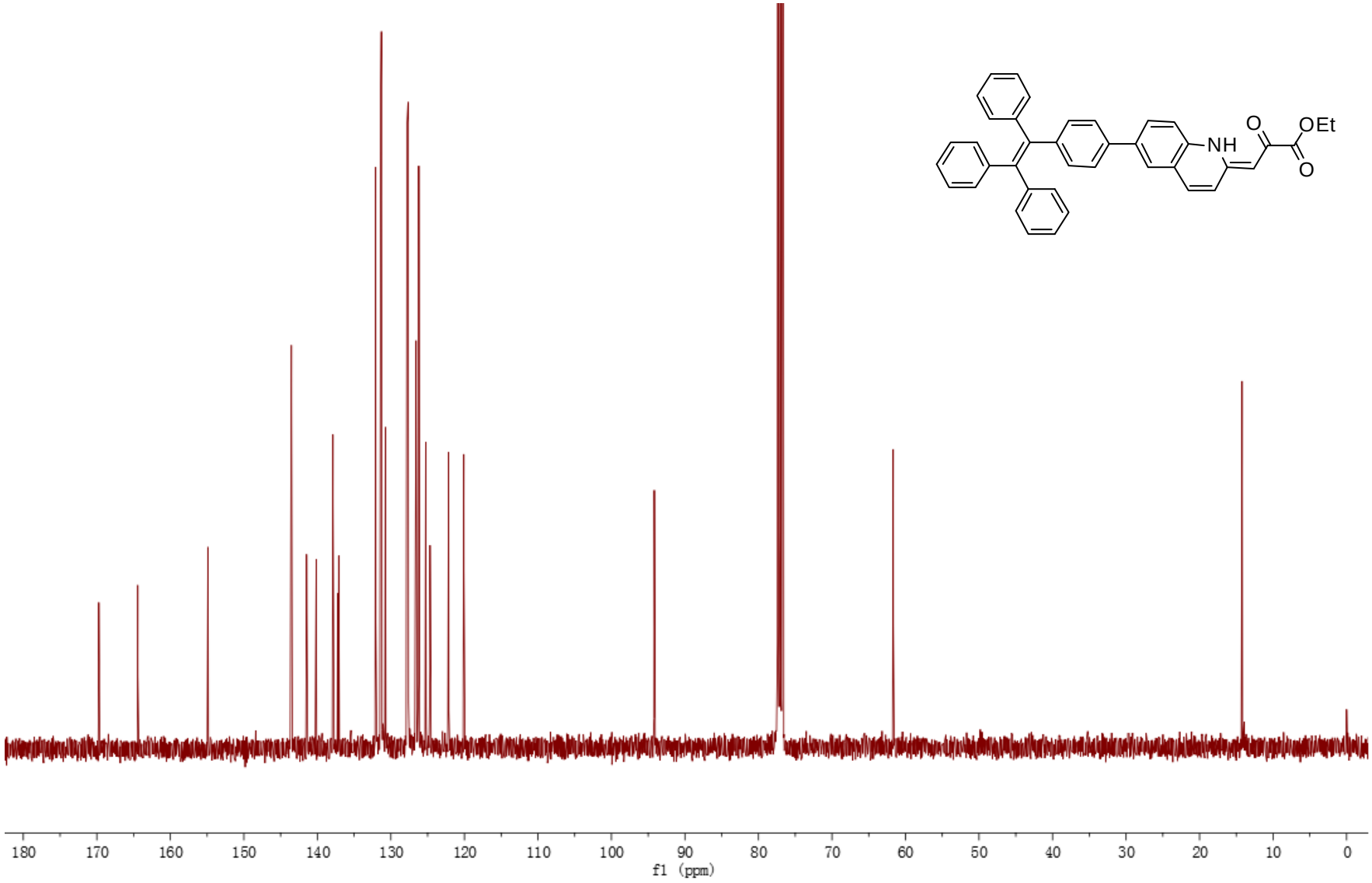

O
OEt
N
H
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

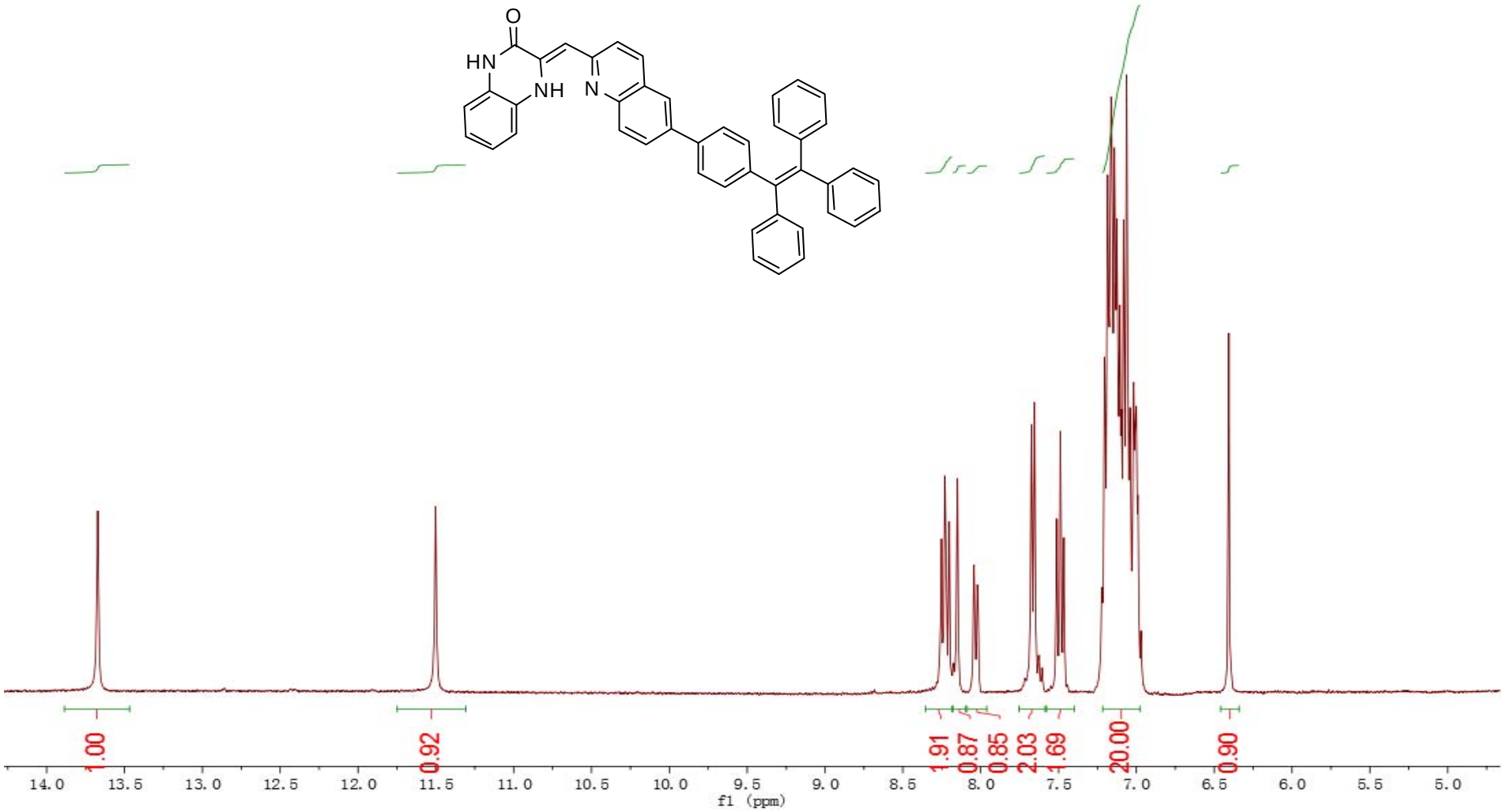

O
N
NH
N
0.52
1.80
1.89
22.49
0.96
0.89
0.82
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

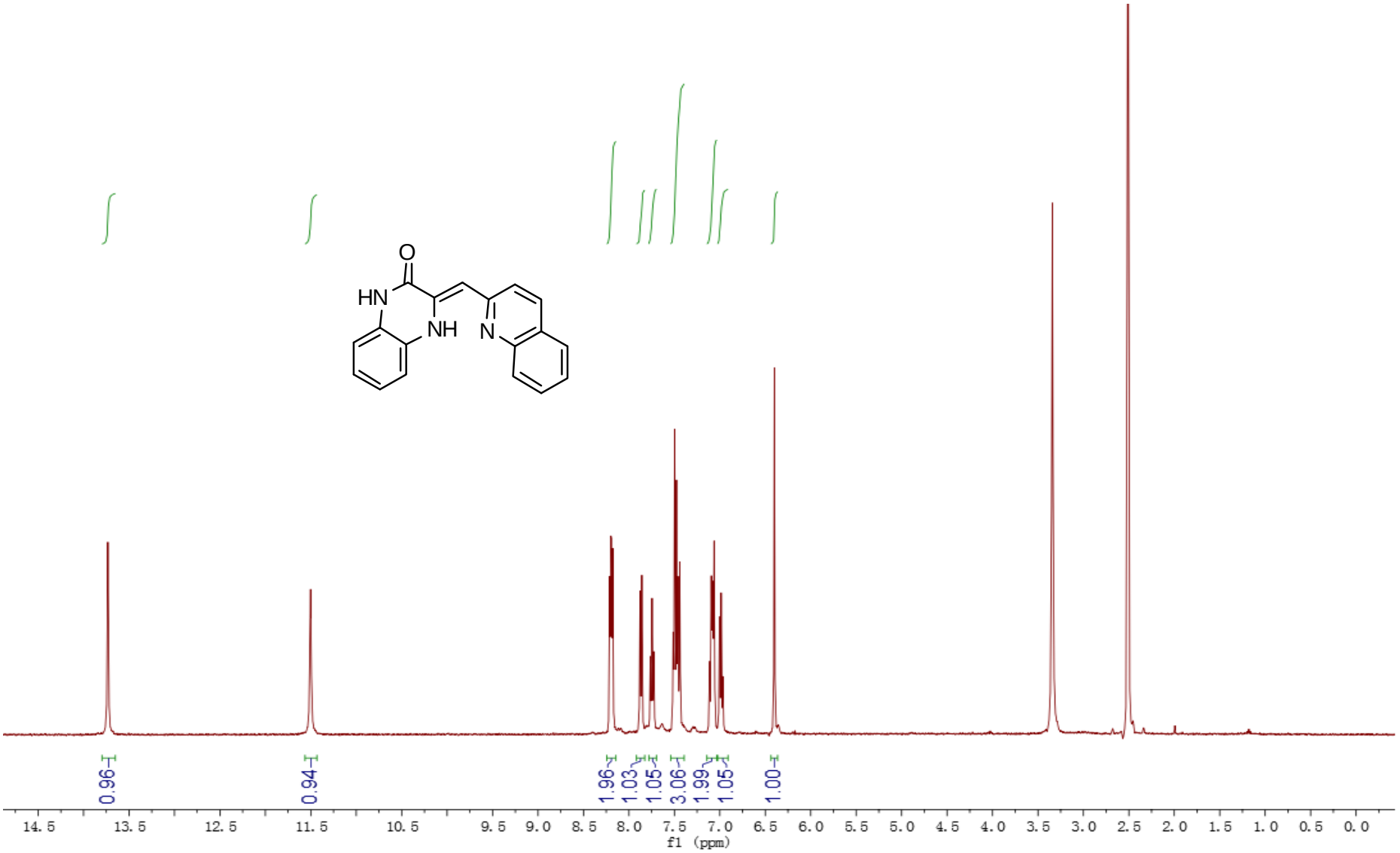

N
1.95
1.96
1.98
1.06
17.00
2.88
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

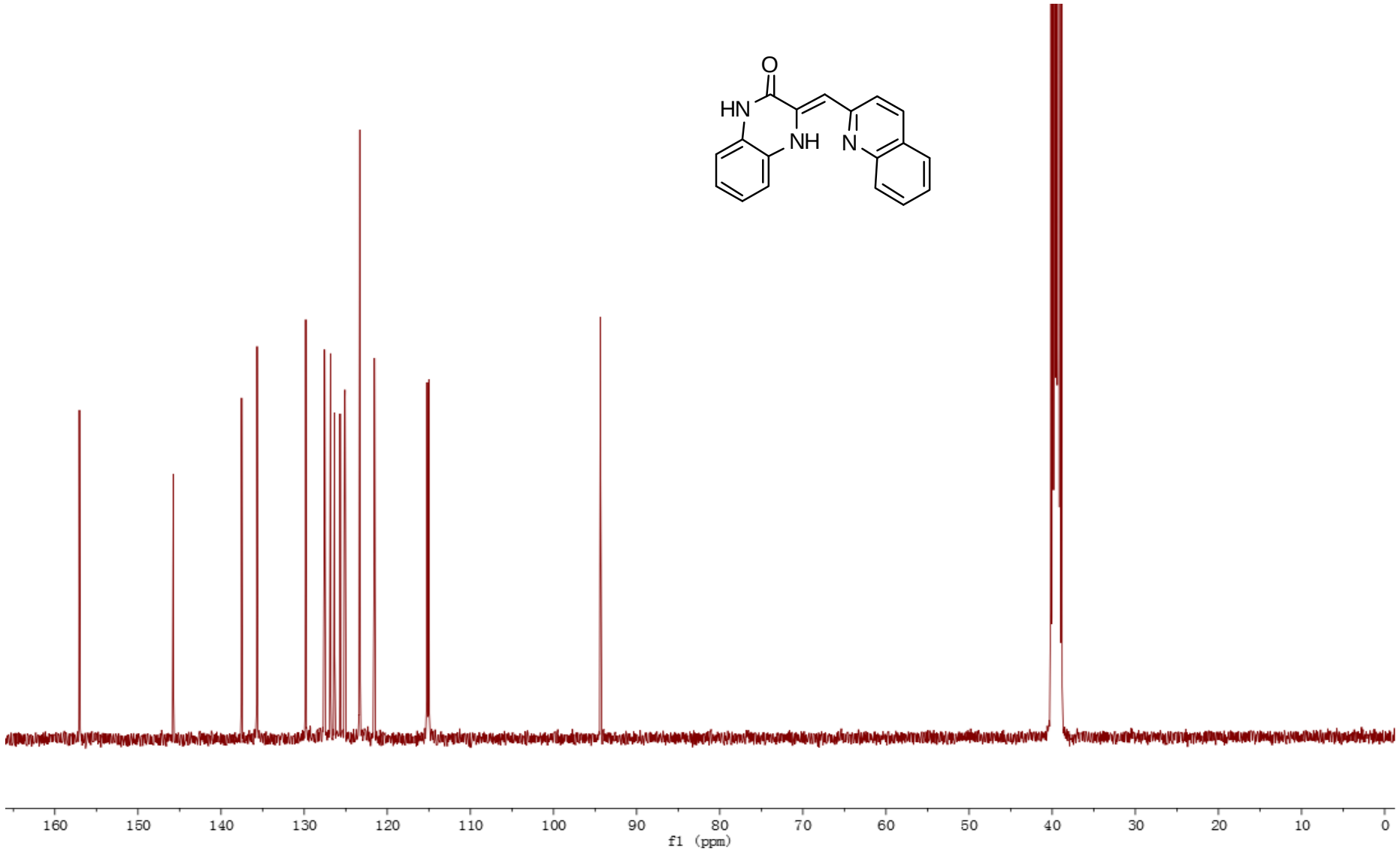

N
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NH
O
OEt
O
0.45
0.96
0.95
0.92
0.96
1.89
17.97
0.93
1.97
2.77
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


NH
O
OEt
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
HN
NH
N
1.00
0.92
1.91
0.87
0.85
2.03
1.69
20.00
0.90
14.0
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
f1 (ppm)


O
HN
NH
N
0.96
0.94
1.96
1.03
1.05
3.06
1.99
1.05
1.00
14.5
13.5
12.5
11.5
10.5
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
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O
HN
NH
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

References

[1] Z. Zhao, S. Chen, J. W. Y. Lam, P. Lu, Y. Zhong, K. S. Wong, H. S. Kwoka and B. Z. Tang, *Chem. Commun*., 2010, **46**, 2221–2223.

[2] (a) A. D. Becke, *J. Chem. Phys*., 1993, **98**, 5648–5652; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785–789.

[3] (a) M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.,* 2003, **24**, 669–681; (b) N. M. O'Boyle, A. L. Tenderholt and K. M. Langner, *J. Comput. Chem.,* 2008, **29**, 839–845.

[4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.