Supporting information

Red Fluorescent Pyrazoline-BODIPY Nanoparticles for Ultrafast and Long-Term Bioimaging

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Synthesis

Synthesis of Compound 1

The compound 1 was synthesized according to the literature method.[1] In a round bottom flask, o-hydroxyacetophenone (2.72 g, 20 mmol) and 4-diethylaminobenzene (3.55 g, 20 mmol) were vigorously stirred in 20 mL ethanol, then 20 mL 10% NaOH solution was dropped. The mixture was stirred and heated at 60 °C for 6 hours, then cooled, neutralized to pH=7 by 1 M HCl. A large amount of precipitate was afforded. After being filtered, and dried by vacuum, a red solid was obtained. The resulting solid was dissolved in DCM/MeOH and froze. A dark-red crystal was obtained. Yield: 4.83g, 82%. ^{1}H NMR (400 MHz, Chloroform-d) δ 13.25 (s, 1H), 7.96 – 7.87 (m, 2H), 7.59 – 7.51 (m, 2H), 7.50 – 7.39 (m, 2H), 7.01 (dd, J = 8.4, 1.2 Hz, 1H), 6.96 – 6.88 (m, 1H),

6.71 – 6.63 (m, 2H), 3.43 (q, J = 7.1 Hz, 4H), 1.21 (t, J = 7.1 Hz, 6H). The ^{1}H NMR spectrum of compound 1 was shown in Fig. S6.

Synthesis of Compound 2

Compound 1 (2.95 g, 10 mmol), phenylhydrazine (1.5 mL, 15 mmol) and glacial acetic acid (20 mL) were added in a 50 mL flask. The mixture was stirred and heated at 85 °C under Ar for 12 h. Then the reaction was dropped into 100 mL ice water and adjusted to neutral by 10% NaOH solution. A large amount of precipitate was afforded. After being filtered, washed with water and EtOH, collected the filter cake and dried by vacuum, a white solid was obtained. The resulting solid was recrystallized from DCM/n-hexane to afford colorless needle crystals. Yield: 2.70g, 70 %. ^{1}H NMR (400 MHz, Chloroform-d) δ 10.87 (s, 1H), 7.25-7.15 (m, 3H), 7.15-7.07 (m, 4H), 7.02 (dd, J= 13.8, 8.4 Hz, 3H), 6.83 (dt, J= 21.8, 7.2 Hz, 2H), 6.61 (d, J= 8.4 Hz, 2H), 5.10 (dd, J= 12.2, 7.6 Hz, 1H), 3.84 (dd, J= 17.2, 12.2 Hz, 1H), 3.30 (q, J= 7.2 Hz, 4H), 3.21 (dd, J= 17.2, 7.6 Hz, 1H), 1.12 (t, J= 7.0 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 157.28, 149.75, 147.50, 144.41, 130.24, 129.09, 128.23, 127.20, 127.08, 119.72, 119.39, 116.72, 116.58, 113.53, 112.15, 63.20, 44.36, 44.11, 12.66. HRMS (ESI): calcd for $[C_{25}H_{27}N_3O, M + H]^+$: 386.2227, measured: 386.2229. The ^{1}H NMR, ^{13}C NMR and HRMS spectra of compound 2 were shown in Fig. S7, S8 and S11, respectively.

Synthesis of Compound 3

In a 50 mL double-necked flask, DMF (1.6 mL, 20 mmol) was stirred vigorously in an ice bath, then phosphorus oxychloride (1.6 mL, 17 mmol) was slowly dropped.

After addition, the mixture was stirred for another hour at room temperature to form golden color Vilsmeier coordination complex. Then 25 mL DMF solution of compound 2 (4.48 g, 15 mmol) was added dropwies. The mixture was heated at 80 °C for 20 h. Then the reaction was stopped and cooled to room temperature. The reactions were dropped into 60 mL water, neutralized with 10% NaOH to pH= 7. A large amount of white precipitate was produced, filtered, and washed with water. The resulting solid was collected and recrystallized with DCM/n-hexane to obtain a pale-yellow solid. Yield: 3.22 g, 52%. ^{1}H NMR (400 MHz, Chloroform-d) δ 10.57 (s, 1H), 9.76 (s, 1H), 7.75-7.66 (m, 2H), 7.35-7.27 (m, 1H), 7.16 (dd, J= 8.0, 1.6 Hz, 1H), 7.11-7.00 (m, 5H), 6.95-6.87 (m, 1H), 6.65-6.57 (m, 2H), 5.29 (dd, J= 12.0, 5.8 Hz, 1H), 3.95 (dd, J= 17.4, 12.0 Hz, 1H), 3.31 (q, J= 7.2 Hz, 4H), 1.13 (t, J= 7.0 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 206.98, 190.52, 157.40, 152.61, 147.80, 147.64, 131.77, 131.23, 128.00, 127.67, 126.74, 126.68, 119.62, 116.85, 115.98, 112.59, 112.06, 61.88, 44.31, 44.11, 30.97, 12.56. HRMS (ESI): calcd for $[C_{26}H_{27}N_3O_2, M + H]^+$: 414.2176, measured: 414.2180. The ^{1}H NMR,^{13}C NMR and HRMS spectra of compound 3 were shown in Fig. S9, S10 and S12, respectively.

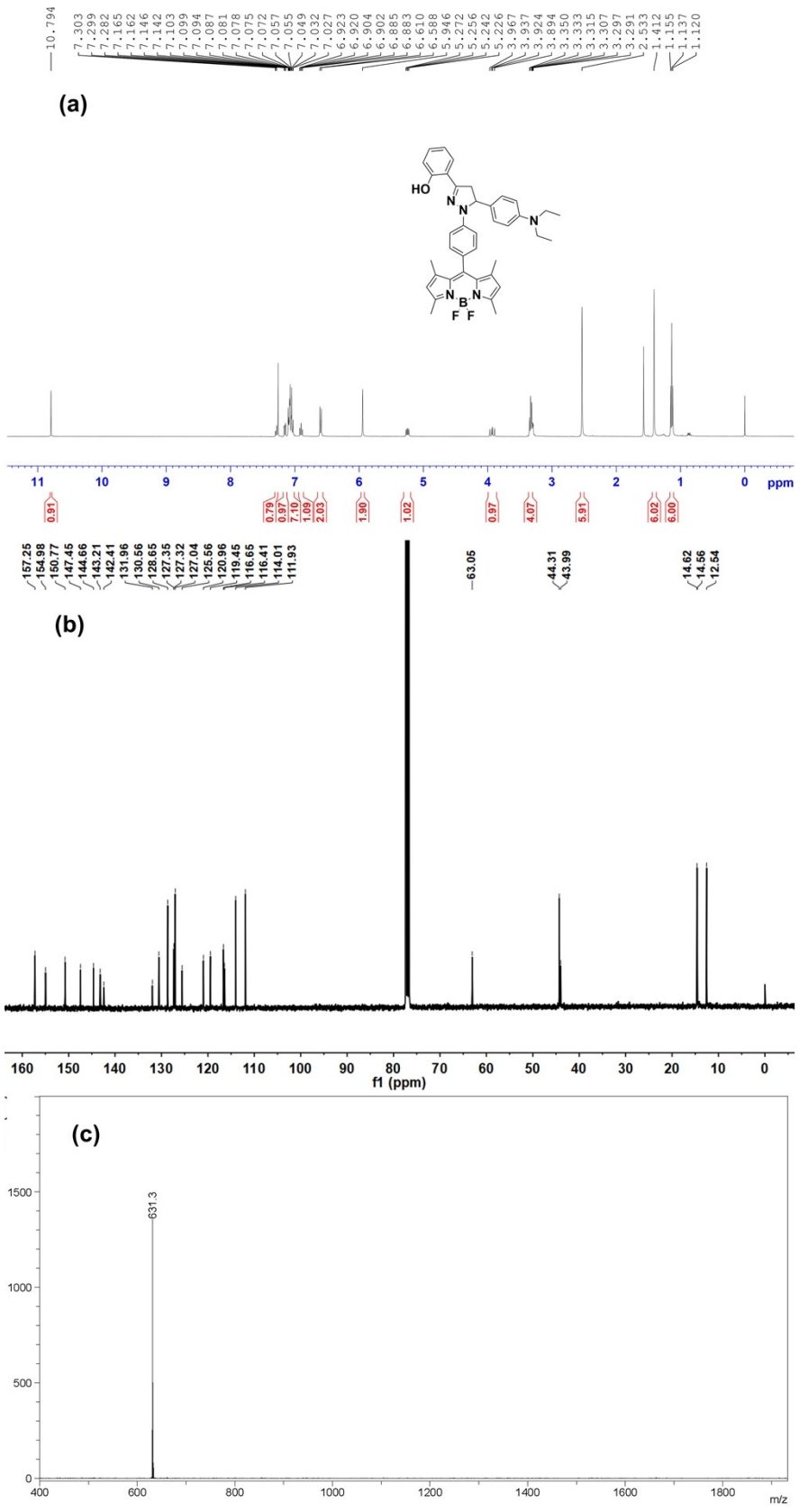

Figure S1. ^{1}H NMR (a), ^{13}C NMR (b), and MALDI-TOF-MS (c) spectrum of PZL-BDP.

Table S1. Crystal data and structure refinement for PZL-BDP.

Compd.	**PZL-BDP**
Empirical formula	C38 H40 B F2 N5 O
Formula weight	631.56
Temperature (K)	153(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
space group	P-1
a (Å)	11.0864(19)
b (Å)	12.741(2)
c (Å)	12.895(2)
α (deg)	87.097(4)
β(deg)	76.513(4)
γ(deg)	70.713(3)
Volume ($Å^3$)	1671.1(5)
Z	2
Calculated density (g/cm3)	1.255
Absorption coefficient (mm^{-1})	0.084
F(000)	668
Crystal size (mm)	0.30 x 0.20 x 0.20
Theta range for data collection	1.69 to 26.39 deg.

Limiting indices	-11<=h<=13, -11<=k<=15, -16<=l<=14
Reflections collected / unique	9644 / 5599 [R(int)= 0.0270]
Completeness to theta= 26.39	97.1 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5599 / 0 / 424
Goodness-of-fit on F^2	0.972
Final R indices [I>2sigma(I)]	R1= 0.0697, wR2= 0.1970
R indices (all data)	R1= 0.1335, wR2= 0.24967
Largest diff. peak and hole ($Å^{-3}$)	0.358 and -0.322 e

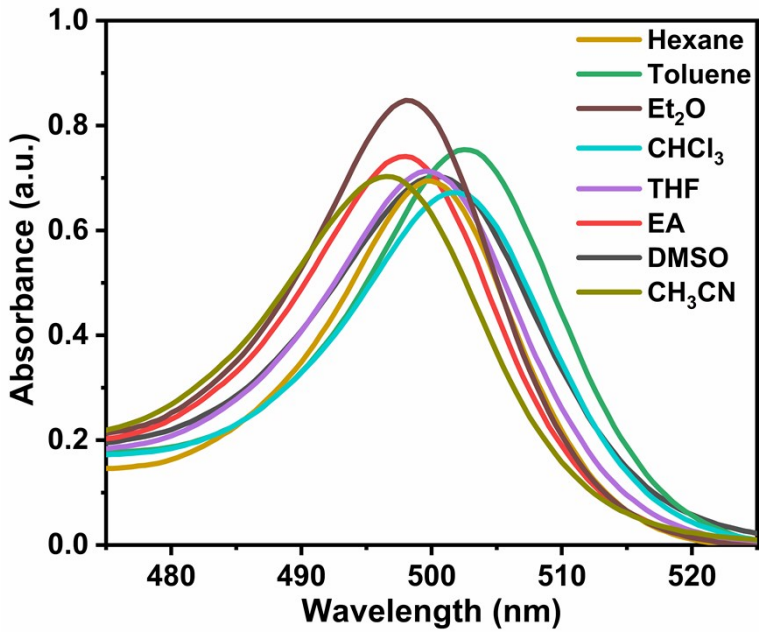

Figure S2. Absorption spectra of PZL-BDP in different solvents.

Table S2 Photophysical of PZL-BDP in different solvents.

Solution	λ_{max}, Abs (nm)	λ_{max}, Em (nm)	Φ_F (%)	$\Delta\lambda$ (nm)
Hexane	499	511	30.6	12
Toluene	503	516	19.0	13
Et_2O	498	587	13.8	89
$CHCl_3$	502	624	7.1	122
THF	500	638	8.1	138
EA	498	646	6.0	148
DMSO	501	/	/	/
CH_3CN	496	/	/	/

Φ_F: fluorescence quantum yield, estimated by quinine sulfate as the standard (QY=0.54).[2, 3]

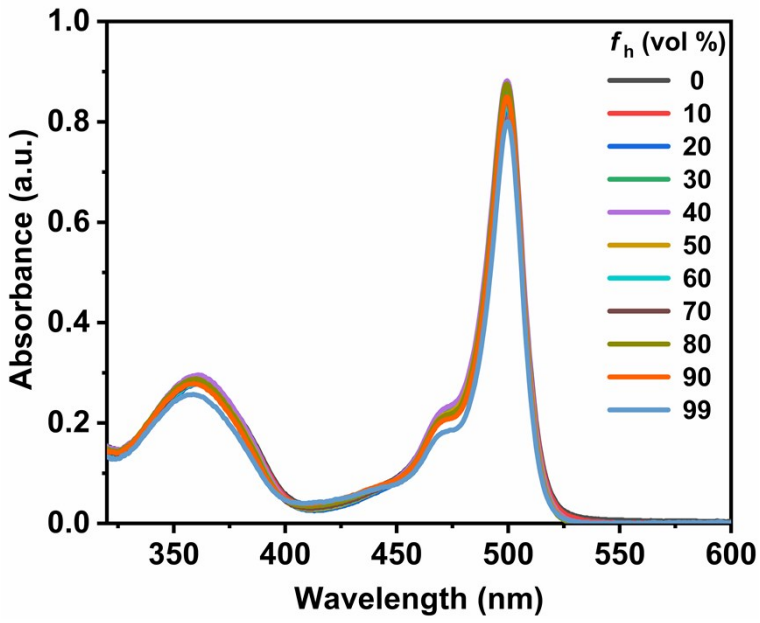

Figure S3. Absorption of PZL-BDP in different ratios of THF and n-Hexane.

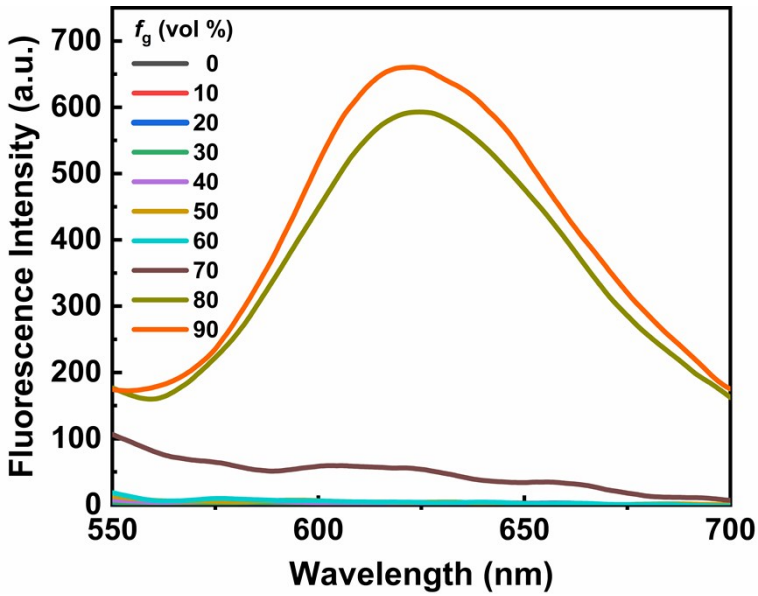

Figure S4. Emission spectra of PZL-BDP in methanol/glycerol mixtures with different fractions of glycerol (f_g). Excitation wavelength: 365 nm.

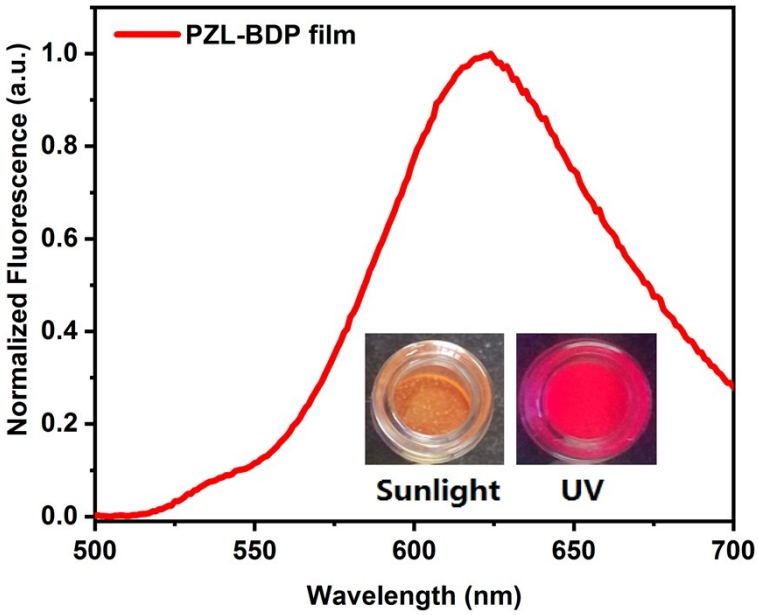

Figure S5. Normalized fluorescence spectra of PZL-BDP spin-coated film under 365 nm excited, the inner graph was PZL-BDP solid under sunlight and a 365 nm UV lamp. Excitation wavelength: 365 nm.

NMR spectra section

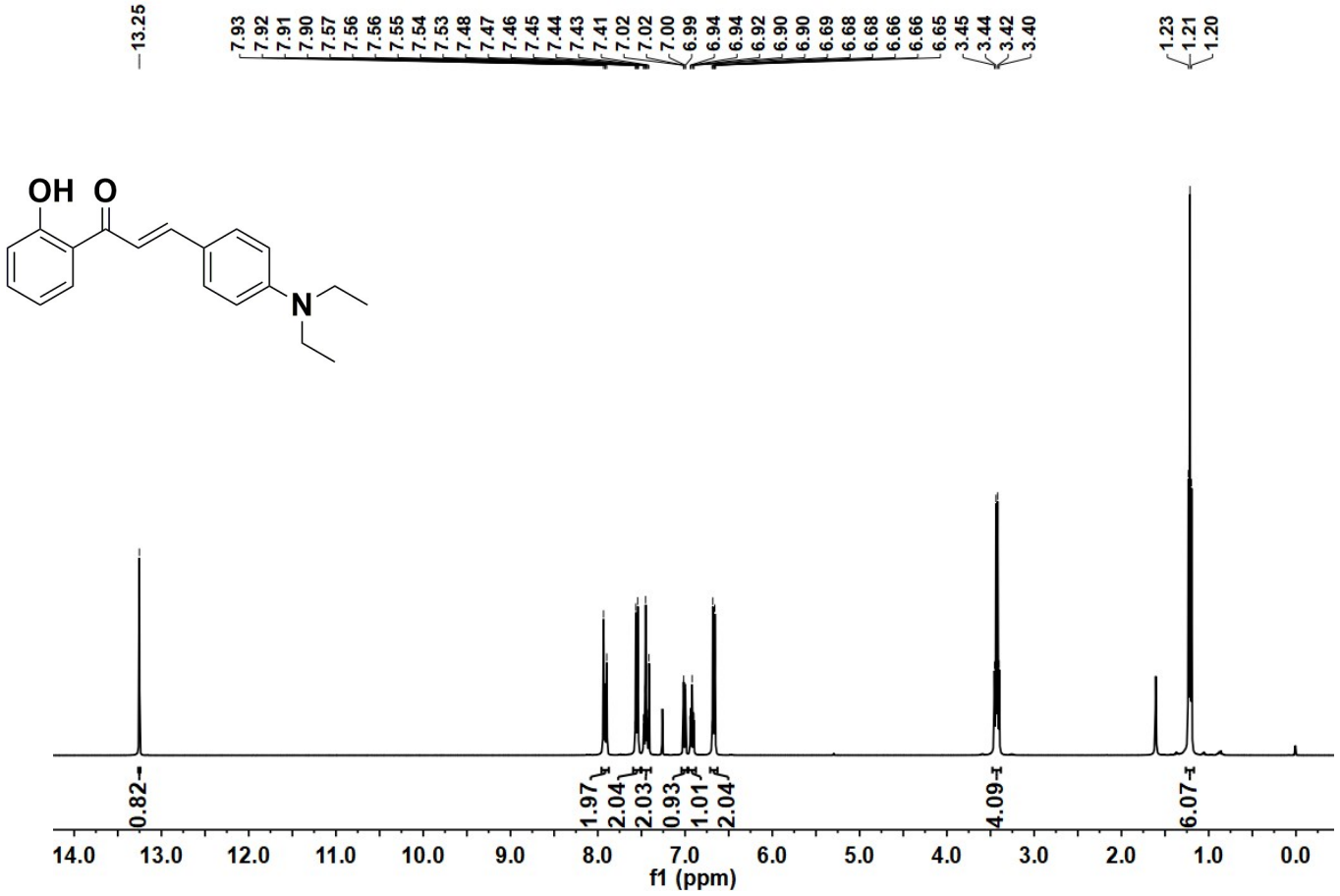

Figure S6. ^{1}H NMR spectrum of compound 1.

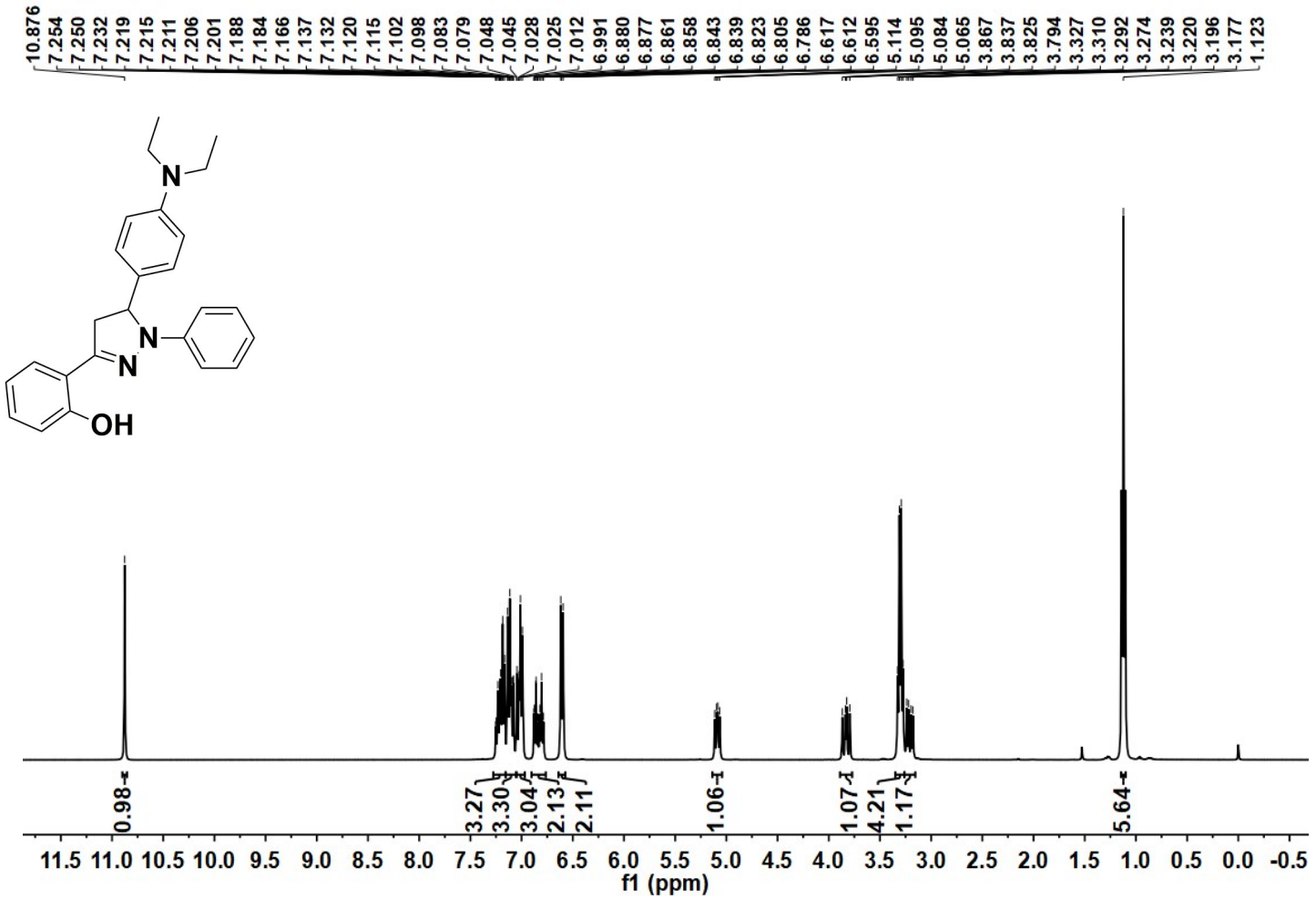

Figure S7. ^{1}H NMR spectrum of compound 2.

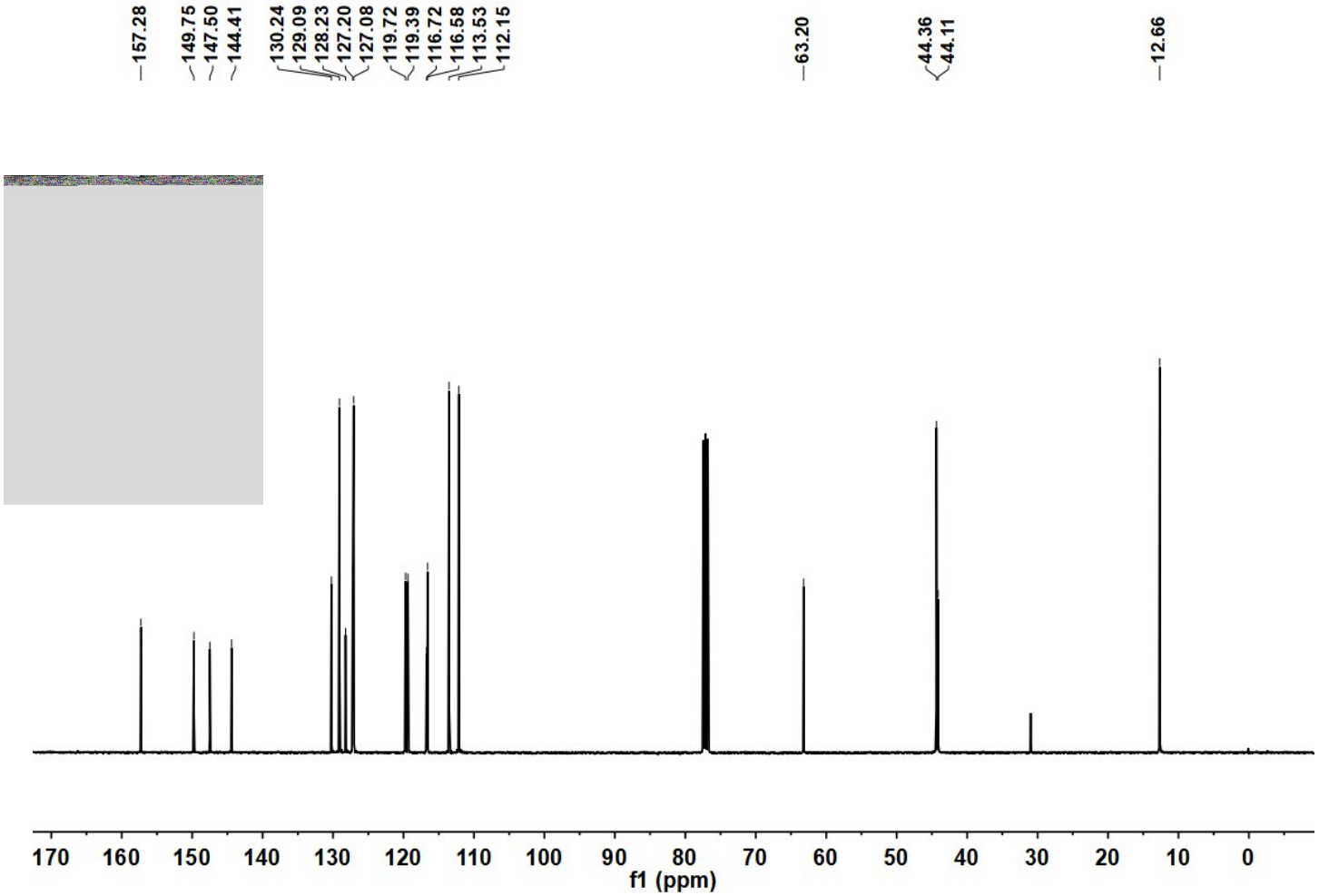

Figure S8. ^{13}C NMR spectrum of compound 2.

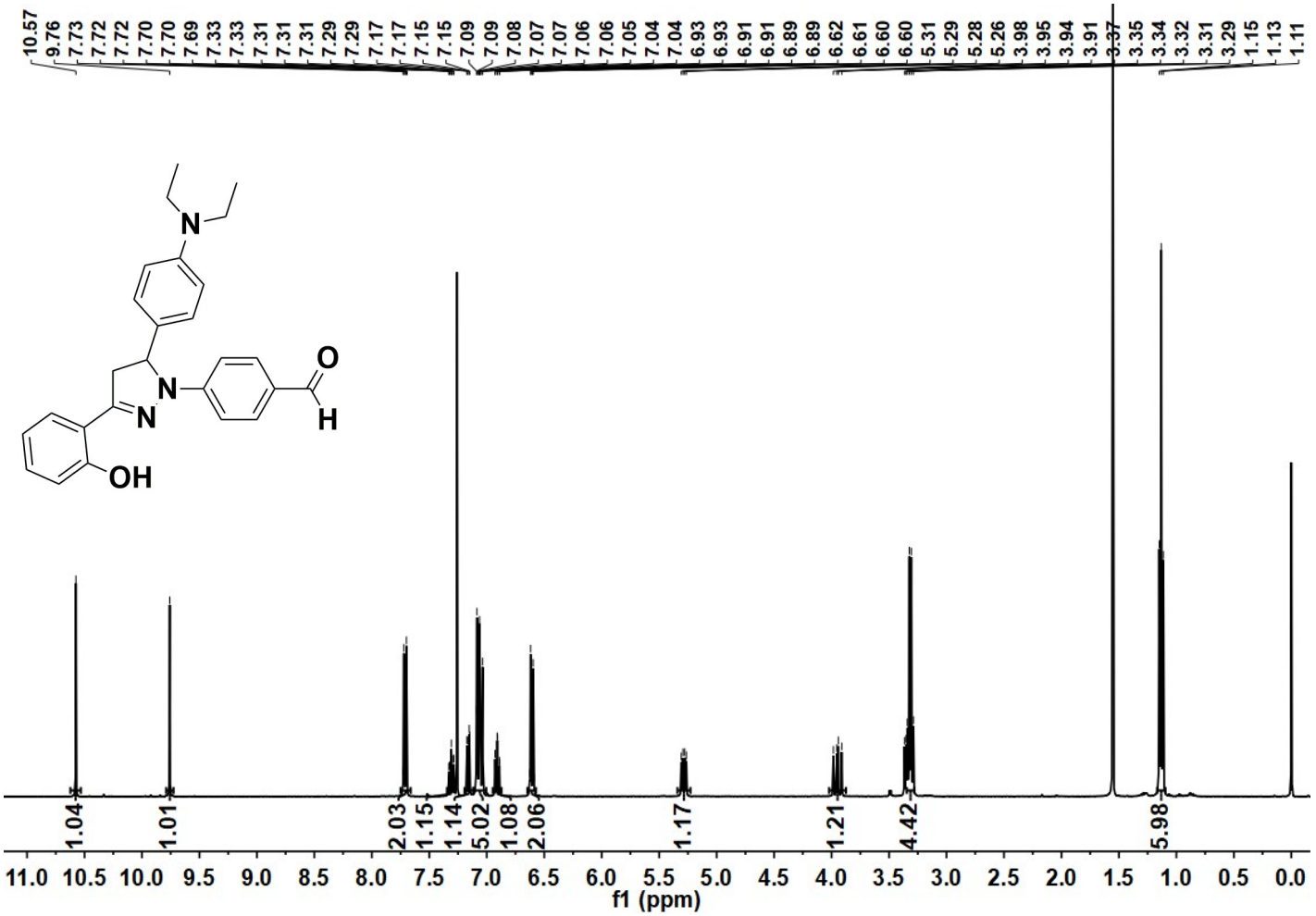

Figure S9. ^{1}H NMR spectrum of compound 3.

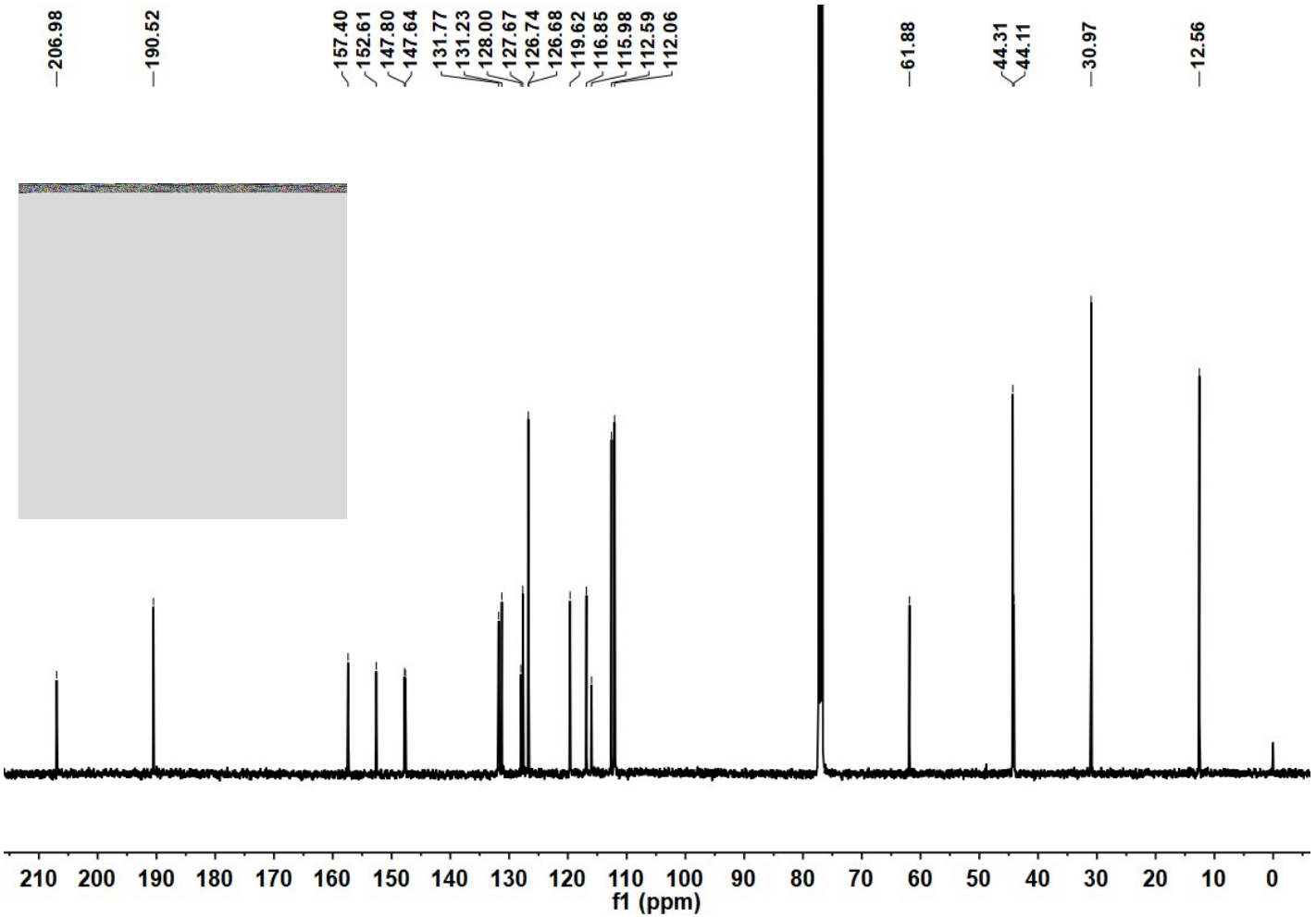

Figure S10. ^{13}C NMR spectrum of compound 3.

HRMS spectra section

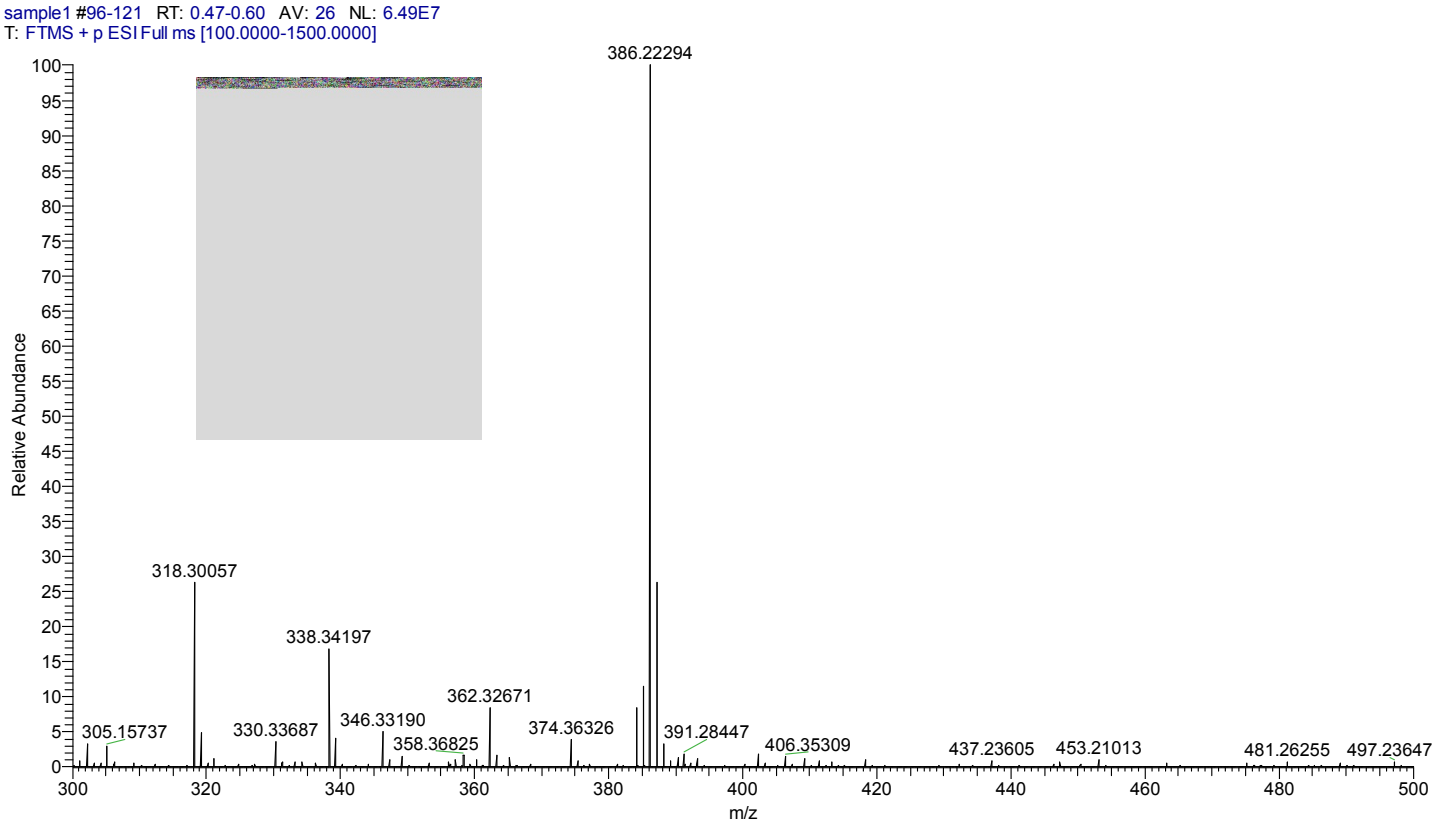

Figure S11. HRMS spectrum of compound 2.

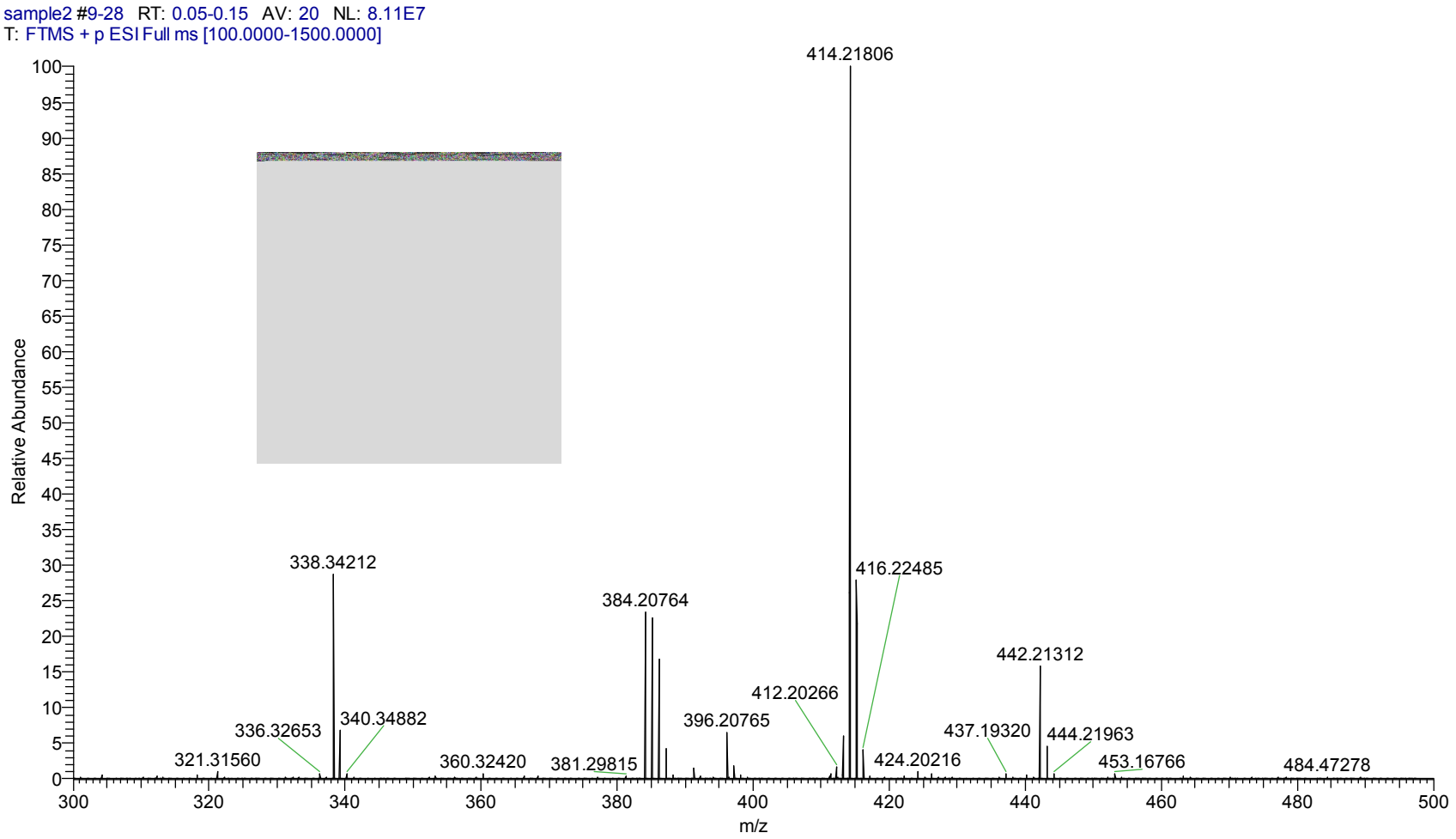

Figure S12. HRMS spectrum of compound 3.

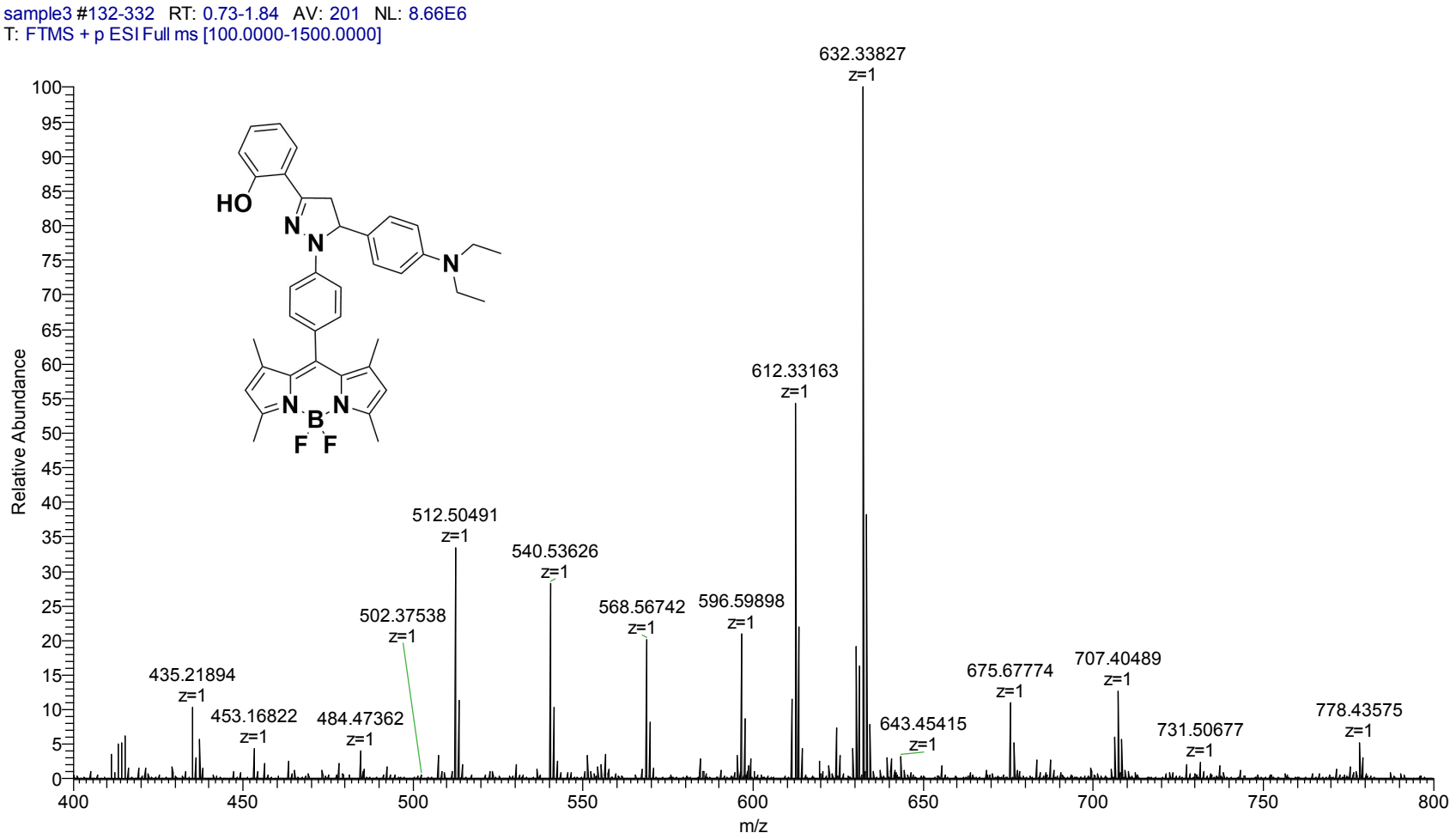

Figure S13. HRMS spectrum of PZL-BDP.

Reference

1. M. Lan, J. Wu, W. Liu, H. Zhang, W. Zhang, X. Zhuang and P. Wang, *Sens. Actuators, B*, 2011, **156**, 332-337.

2. Li D, Huang Z, Shang X, Xia Y, Zhang Y, Li M, et al. Synthesis, photophysical and electrochemical properties of symmetric silicon-linked diphenyl 1,3,4-oxadizole derivatives. *Tetrahedron.* 2015, **71**, 2680-2685.

3. Karstens T, Kobs K. Rhodamine B and rhodamine 101 as reference substances for fluorescence quantum yield measurements. *J. Phys. Chem*. 1980, **84**, 1871-1872.