SUPPORTING INFORMATION

An ideal platform of light-emitting materials from phenothiazine: facile preparation, tunable red/NIR fluorescence, bent geometry promoted AIE behaviour and selective lipid-droplets (LDs) tracking ability

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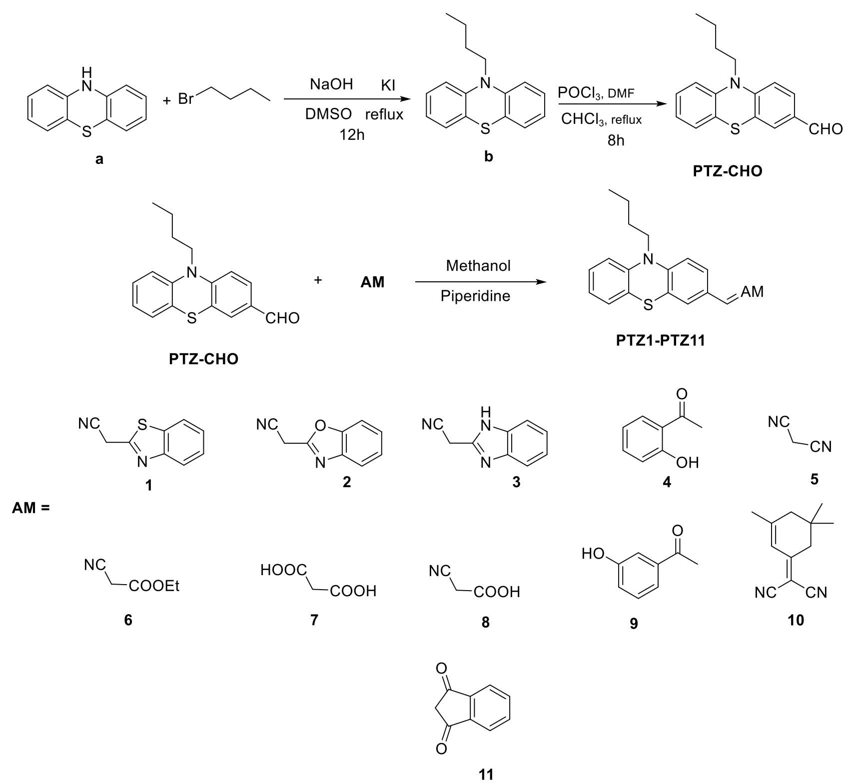
1. Experimental Section

Chemicals and Instrument

All chemicals are commercial available from Energy, J&K, Meryer and Sigma-Aldrich, respectively. The photoluminescence spectra were recorded on a Hitachi F7000 fluorometer. The UV-vis absorption spectra were determined with an Agilent UV2450 spectrometer. The absolute fluorescence quantum yields were obtained on a Hamamatsu Quantarus-QY C11347. NMR spectra were obtained from a Bruker Advance DMX 400 spectrometer. Mass spectra were got on a Bruker Daltonik MicroTOF-Q II mass spectrometer operated with ESI mode. The fluorescent lifetimes were measured on a Fluotime 100 from PicoQuant with PDL 800-B pulsed diode laser. The DFT and TD-DFT calculations were performed on a Gaussian 09 program. The single crystal data was collected on an Oxford Diffraction Xcalibur Atlas Gemini ultra instrument. The bio-imaging experiments were carried out on Opera Phenix/ Operetta CLS from Perkin Elmer, Inc. under 490-515 nm excitation and 570-650 nm emission monitoring range.

Synthesis and Characterization



Synthesis of PTZ-CHO

The synthesis of **PTZ-CHO** was according to the reported method. (S.H. Kim, C. Sakong, J.B. Chang, B. Kim, M.J. Ko, D.H. Kim, K.S. Hong, J.P. Kim,The effect of N-substitution and ethylthio substitution on the performance of phenothiazine donors in dye-sensitized solar cells, Dyes and Pigments 97 (2013), 262-267.)

Synthesis of PTZ1-11

To a solution of **PTZ-CHO** (2.83 g, 10.0 mmol) in methanol was added 10.0 mmol (1.0 equiv.) electron-acceptor compounds, respectively. Catalytic amount of piperidine (0.1 mL) was added into the reaction mixture. The resulting solution was stirred for 12 h. The reaction mixture was filtered and the solid was washed with methanol (20 mL) three times and then purified by re-crystallization in ethyl acetate/ ethanol mixture (v: v = 1:1) to afford compounds **PTZ1- PTZ11** as yellow to dark red solids. (yield: 42.1-90.5 %).

Characterization

PTZ1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-7.88 (m, 3H), 7.70 (s, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.24-7.04 (m, 2H), 7.04-6.79 (m, 3H), 3.90 (t, *J* = 7.0 Hz, 2H), 1.81 (d, *J* = 6.5 Hz, 2H), 1.49 (dd, *J* = 14.9, 7.5 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 185.35, 163.66, 153.28, 148.92, 145.63, 143.24, 134.62, 130.59, 129.44, 127.59, 126.94, 126.49, 125.76, 124.88, 123.59, 123.45, 123.16, 121.64, 117.08, 115.80, 115.11, 101.55, 47.69, 28.83, 20.12, 13.80.

HRMS (ESI) m/z: calcd for $C_{26}H_{21}N_3S_2$ $[M+Na]^+$, 462.1075; found, 462.1009.

PTZ2, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.95 (dt, *J* = 13.0, 6.5 Hz, 1H), 7.84-7.72 (m, 2H), 7.62-7.54 (m, 1H), 7.45-7.35 (m, 2H), 7.18 (dd, *J* = 15.7, 8.0 Hz, 1H), 7.12 (dt, *J* = 10.4, 5.2 Hz, 1H), 7.06-6.86 (m, 3H), 3.92 (d, *J* = 6.4 Hz, 1H), 1.84 (dt, *J* = 14.8, 7.4 Hz, 2H), 1.51 (dq, *J* = 14.7, 7.4 Hz, 2H), 1.00 (dd, *J* = 8.9, 5.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.63, 150.68, 149.22, 147.26, 143.14, 141.78, 130.74, 129.46, 127.63, 127.58, 126.32, 125.77, 125.12, 124.87, 123.66, 123.36, 120.30, 115.84, 115.70, 115.07, 110.59, 95.39, 47.71, 28.80, 20.10, 13.79.

HRMS (ESI) m/z: calcd for $C_{26}H_{21}N_3OS$ $[M+Na]^+$, 446.1303; found, 446.1234.

PTZ3, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.80 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.72 (d, *J* = 1.9 Hz, 1H), 7.64 (s, 2H), 7.34-7.30 (m, 2H), 7.18 (dd, *J* = 11.3, 4.2 Hz, 1H), 7.13 – 7.10 (m, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.91-6.86 (m, 2H), 3.92-3.87 (m, 2H), 2.07 (s, 1H), 1.82 (dt, *J* = 14.8, 7.5 Hz, 2H), 1.50 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.54, 147.22, 145.23, 143.34, 139.38, 133.89, 130.42, 128.59, 127.55, 126.77, 124.79, 123.57, 123.45, 119.18, 119.04, 117.34, 116.20, 115.72, 115.00, 110.51, 110.46, 96.30, 47.60, 28.78, 20.10, 13.79.

HRMS (ESI) m/z: calcd for $C_{26}H_{22}N_4S$ $[M+H]^+$, 423.1643; found, 423.1577.

PTZ4, ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.94 (s, 1H), 7.96-7.88 (m, 1H), 7.81 (d, *J* = 15.3 Hz, 1H), 7.56-7.46 (m, 2H), 7.45-7.38 (m, 2H), 7.21-7.07 (m, 2H), 7.01 (t, *J* = 6.7 Hz, 1H), 6.94 (dd, *J* = 11.6, 4.2 Hz, 2H), 6.92-6.83 (m, 2H), 3.95-3.80 (m, 2H), 1.86-1.74 (m, 2H), 1.46 (dt, *J* = 14.9, 7.5 Hz, 2H), 0.99- 0.91 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.47, 163.59, 147.79, 144.48, 143.98, 136.19, 129.55, 129.30, 128.87, 127.54, 127.51, 126.71, 125.21, 123.76, 123.14, 120.16, 118.80, 118.61, 117.63, 115.71, 115.22, 47.50, 28.89, 20.14, 13.81.

HRMS (ESI) m/z: calcd for $C_{25}H_{23}NO_2S$ $[M-H]^-$, 400.1377; found, 400.1344.

PTZ5, ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, 1H), 7.54-7.45 (m, 2H), 7.18 (dd, *J* = 16.3, 8.4 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.96 (dd, *J* = 18.3, 10.9 Hz, 1H), 6.86 (dd, *J* = 18.3, 8.4 Hz, 2H), 3.89 (t, *J* = 7.2 Hz, 2H), 1.86-1.71 (m, 2H), 1.46 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.00-0.89 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.36, 150.84, 142.48, 131.39, 129.52, 127.82, 127.64, 125.19, 124.98, 124.19, 122.99, 116.10, 114.92, 114.69, 113.58, 47.92, 29.72, 28.75, 20.04, 13.74.

HRMS (ESI) m/z: calcd for $C_{20}H_{17}N_3S$ $[M+H]^+$, 332.1221; found, 332.1205.

PTZ6, ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.86 (dt, *J* = 9.2, 4.6 Hz, 1H), 7.65 (d, *J* = 1.9 Hz, 1H), 7.2-7.05 (m, 2H), 6.91 (dt, *J* = 38.1, 7.9 Hz, 3H), 4.41-4.31 (m, 2H), 3.89 (dd, *J* = 12.6, 5.4 Hz, 2H), 1.87 – 1.72 (m, 2H), 1.52-1.42 (m, 2H), 1.37 (dd, *J* = 14.9, 7.8 Hz, 3H), 1.04-0.87 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.21, 153.21, 149.75, 143.07, 131.34, 130.17, 127.62, 127.59, 125.62, 124.74, 123.72, 123.38, 116.32, 115.87, 114.98, 98.82, 62.43, 47.71, 28.78, 20.08, 14.24, 13.76.

HRMS (ESI) m/z: calcd for $C_{22}H_{22}N_2O_2S$ $[M+Na]^+$, 401.1300; found, 401.1248.

PTZ7, ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 15.8 Hz, 1H), 7.31 (d, *J* = 9.4 Hz, 2H), 7.14 (dd, *J* = 18.5, 7.6 Hz, 2H), 6.85 (dd, *J* = 15.9, 8.0 Hz, 2H), 6.29 (d, *J* = 15.8 Hz, 1H), 3.86 (s, 2H), 1.86-1.69 (m, 2H), 1.53-1.38 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.60, 147.54, 145.91, 144.15, 128.30, 127.45, 126.85, 125.19, 123.93, 123.03, 115.49, 115.19, 114.85, 47.39, 31.96, 29.73, 28.92, 22.73, 20.14, 13.81.

HRMS (ESI) m/z: calcd for $C_{20}H_{19}NO_4S$ $[M+Na]^-$, 392.0932; found, 392.1004.

PTZ8, ^1H NMR (400 MHz, DMSO) δ 7.85 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.67 (s, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.08 (dd, *J* = 16.6, 8.4 Hz, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 3.91 (t, *J* = 6.8 Hz, 2H), 1.73-1.60 (m, 2H), 1.39 (dt, *J* = 14.9, 7.6 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

PTZ8 was synthesized following the literature method. (S.H. Kim, C. Sakong, J.B. Chang, B. Kim, M.J. Ko, D.H. Kim, K.S. Hong, J.P. Kim,The effect of N-substitution and ethylthio substitution on the performance of phenothiazine donors in dye-sensitized solar cells, Dyes and Pigments 97 (2013), 262-267.)

HRMS (ESI) m/z: calcd for $C_{20}H_{18}N_2O_2S$ $[M-H]^-$, 349.1011; found, 349.0988.

PTZ9, ^{1}H NMR (400 MHz, CDCl3) δ 7.66 (s, 2H), 7.53 (dd, J = 21.0, 7.5 Hz, 2H), 7.46 – 7.28 (m, 4H), 7.12 (dd, J = 9.7, 4.3 Hz, 3H), 6.86 (s, 2H), 4.38-3.25 (m, 2H), 1.78 (s, 2H), 1.45 (dq, J = 14.6, 7.4 Hz, 2H), 0.98-0.89 (m, 3H).

^{13}C NMR (100 MHz, CDCl3) δ 157.34, 150.82, 142.47, 134.61, 131.43, 129.44, 127.83, 127.62, 125.80, 125.23, 125.18, 124.97, 124.19, 122.98, 122.93, 118.67, 116.11, 114.91, 114.69, 113.59, 105.48, 47.92, 28.76, 20.04, 13.73.

HRMS (ESI) m/z: calcd for $C_{25}H_{23}NO_2S$ $[M-H]^-$, 400.1371; found, 400.1347.

PTZ10, ^{1}H NMR (400 MHz, CDCl3) δ 7.3-7.26 (m, 1H), 7.24 (s, 1H), 7.14 (ddd, J = 13.2, 8.0, 3.9 Hz, 2H), 6.98-6.89 (m, 2H), 6.84 (td, J = 12.0, 6.1 Hz, 3H), 6.78 (s, 1H), 3.86 (t, J = 7.2 Hz, 2H), 2.57 (s, 2H), 2.42 (s, 2H), 1.85-1.72 (m, 2H), 1.52-1.40 (m, 2H), 1.06 (s, 6H), 0.95 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl3) δ 169.20, 154.18, 146.66, 144.12, 136.07, 130.00, 127.50, 127.47, 127.21, 127.17, 126.19, 125.22, 123.81, 122.98, 122.87, 115.63, 115.38, 113.80, 113.00, 47.44, 45.67, 43.00, 39.21, 32.02, 28.91, 28.05, 25.34, 20.14, 13.83.

HRMS (ESI) m/z: calcd for $C_{29}H_{29}N_3S$ $[M-H]^-$, 450.2004; found, 450.1973.

PTZ11, ^{1}H NMR (400 MHz, CDCl3) δ 8.39-8.27 (m, 2H), 7.99-7.90 (m, 2H), 7.78-7.68 (m, 3H), 7.16-7.07 (m, 2H), 6.95 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 8.1 Hz, 2H), 3.94-3.84 (m, 2H), 1.82 (dt, J = 14.8, 7.5 Hz, 2H), 1.48 (dq, J = 14.7, 7.4 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, CDCl3) δ 190.86, 189.53, 149.82, 145.63, 142.94, 142.40, 139.98, 135.56, 135.02, 133.11, 127.76, 127.55, 127.46, 126.34, 123.80, 123.66, 122.98, 115.80, 114.62, 47.80, 28.82, 20.10, 13.79.

HRMS (ESI) m/z: calcd for C26H21NO2S $[M]^+$, 411.1293; found, 411.1260.

Calculation details

Optimization of chemical structures in ground state

All chemical structures in ground state were optimized in gas phase under 6-31g** with b3lyp hybrid function.

TD-DFT predicted UV absorption peak

UV absorption maximum was predicted by TD-DFT method under def2-TZVP with b3lyp hybrid function (nstate = 20) using PCM solvent model (dichloromethane).

Optimization of chemical structure of PTZ5 in S1 state

The equilibrium geometry of **PTZ5** in S1 state was optimized through TD-DFT method under 6-31g** with b3lyp hybrid function (nstate = 5, root = 1).

2. Figures

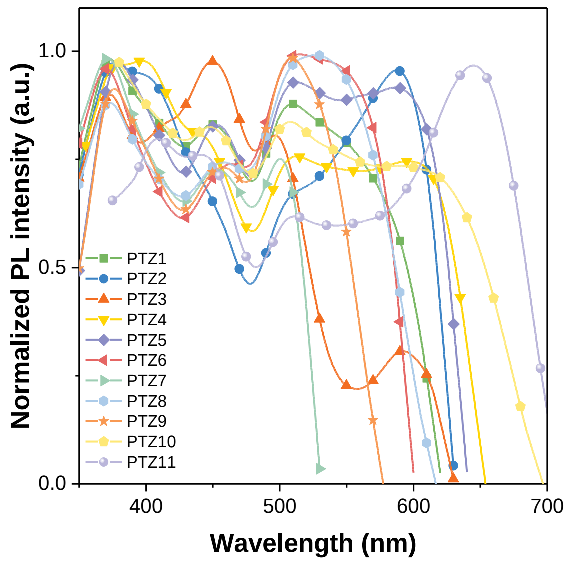


Figure S1. Excitation spectra of photoluminescence of **PTZ-PTZ11** in solid state.

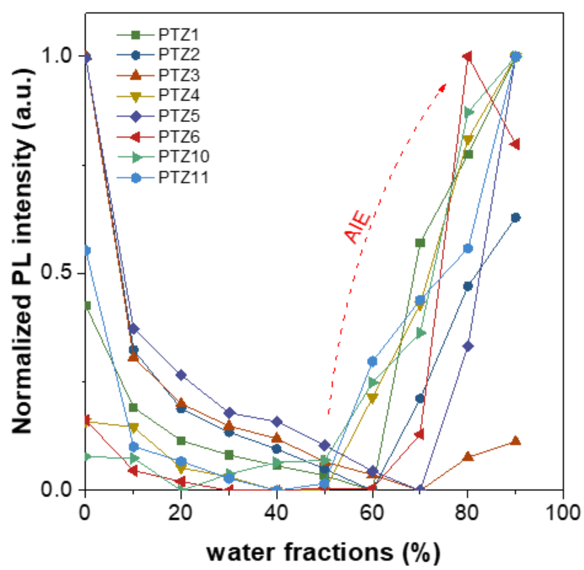


Figure S2. Plots of Normalized PL intensity *versus* water fractions for **PTZ** dyes.

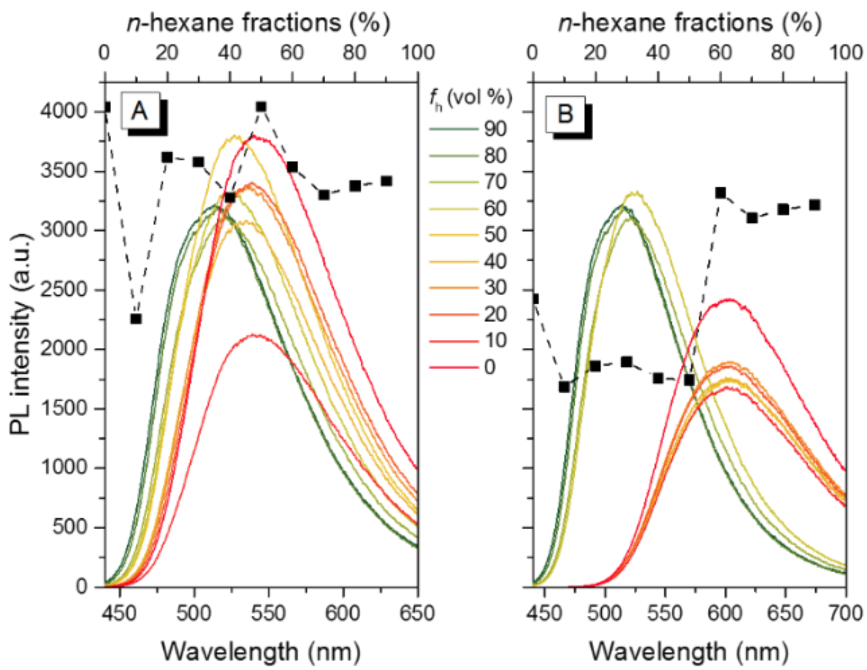


Figure S3. PL spectra (coloured solid lines) and PL intensity versus *n*-hexane fractions plots (black dash lines) of **PTZ7** (A) and **PTZ8** (B) in THF/*n*-hexane mixture with different *n*-hexane fractions.

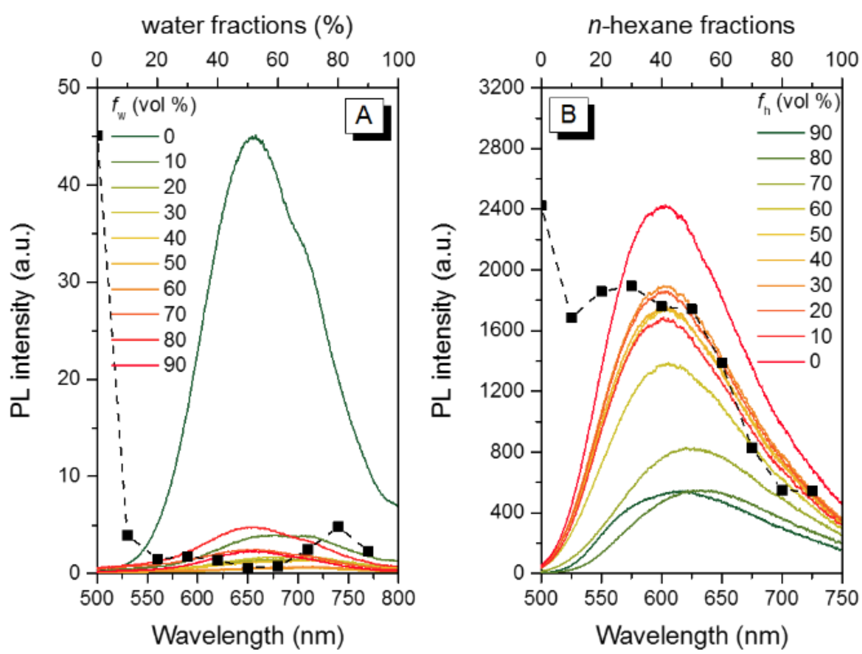


Figure S4. PL spectra and PL intensity versus n-hexane or water fractions plots of **PTZ9** in acetonitrile/water mixture (A) and THF/*n*-hexane mixture (B).

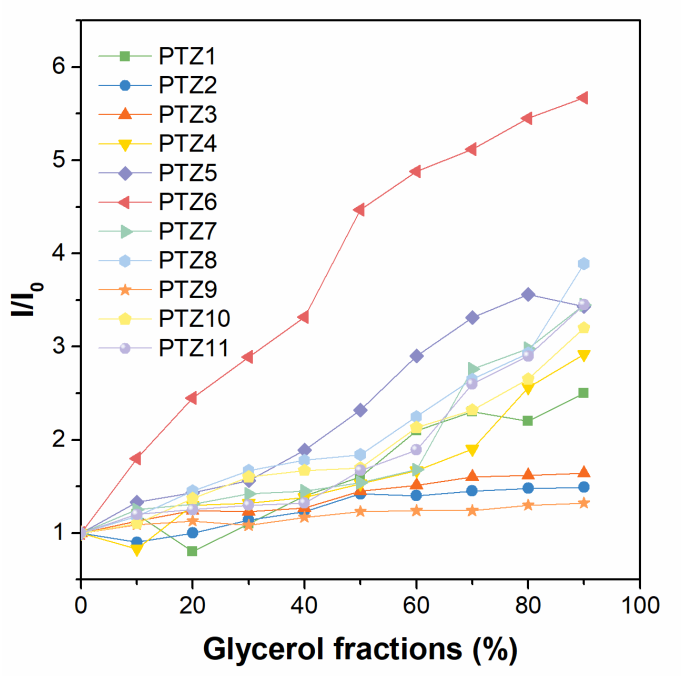


Figure S5. PL intensity change of **PTZ1-PTZ11** dispersed in methanol-glycerol mixtures as a function of the glycerol fractions. I_0 stands for the PL intensity under $f_g = 0$.

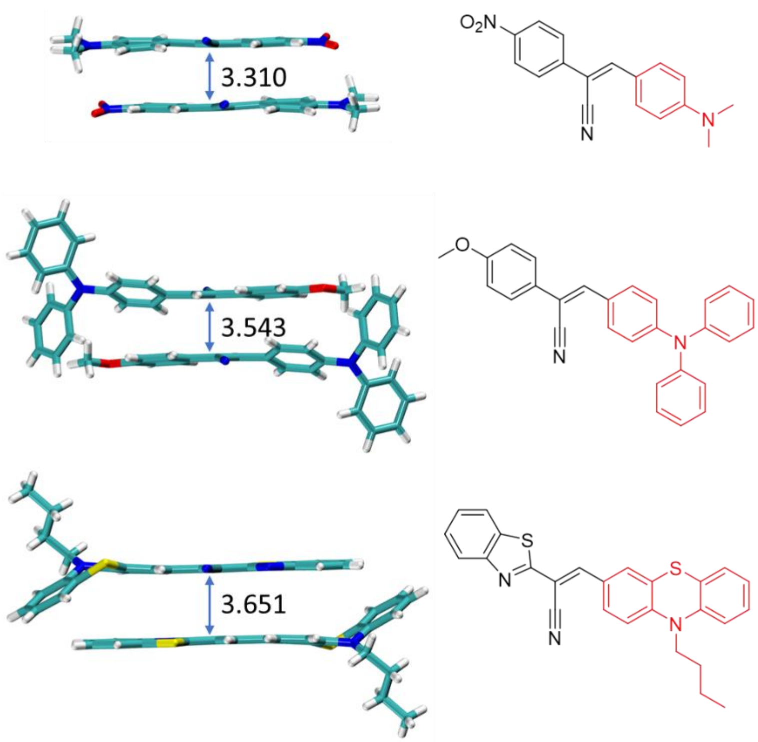


Figure S6. Distances of neighbouring π system of D-π-A structure with different electron donors.

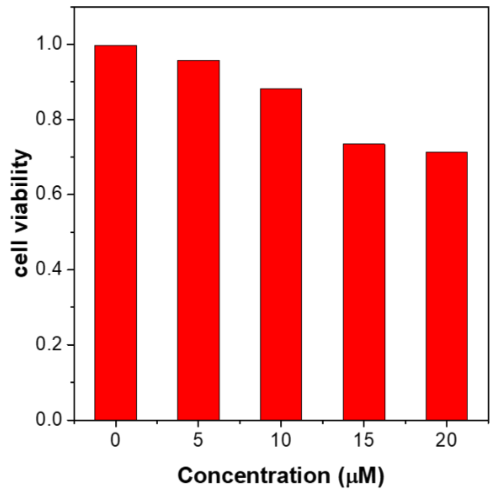


Figure S7. Cytotoxicity of **PTZ6** in HeLa cells determined by MTT assay.

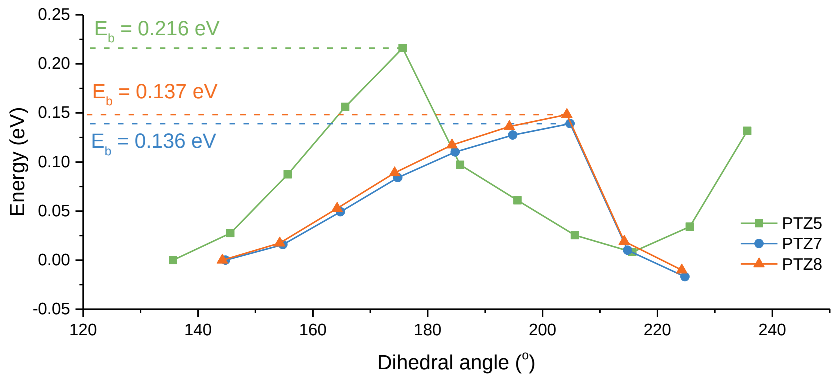


Figure S8. The scanned energy surface of **PTZ5**, **PTZ7** and **PTZ8** in varied dihedral angle between benzene ring A and B.

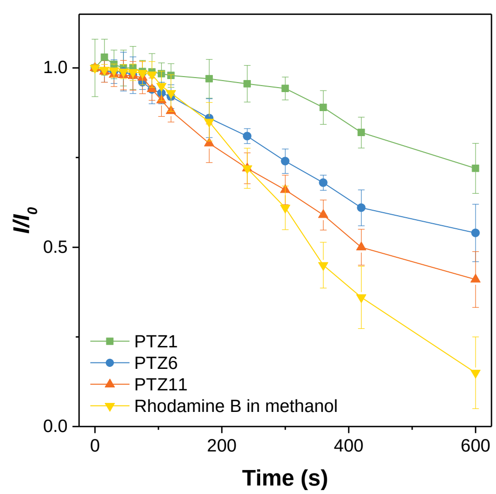


Figure S9. Relative fluorescence intensities of **PTZ1**, **PTZ6** and **PTZ11** in THF-water mixture (80% water) using rhodamine B in methanol as a reference.

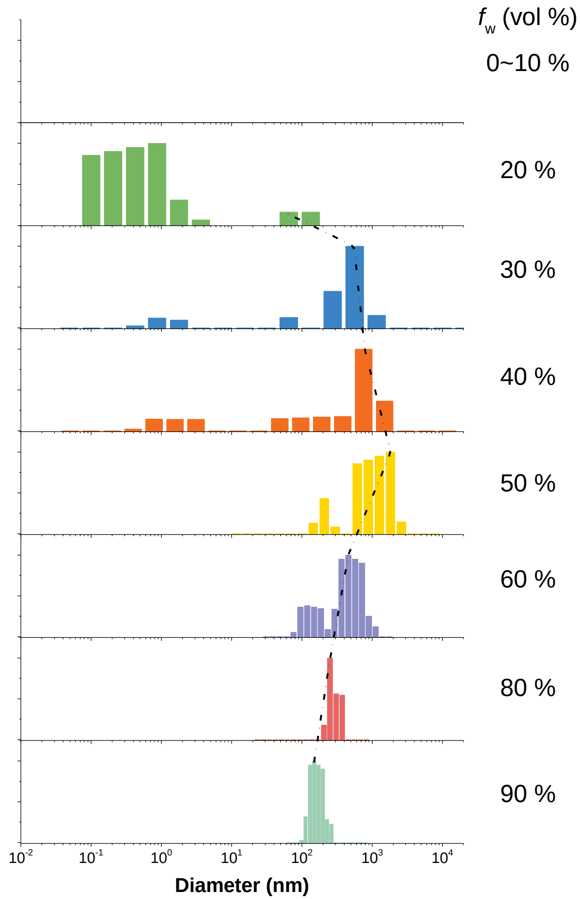


Figure S10. Particle size distribution of **PTZ5** dispersed in THF-water mixture with different water fractions.

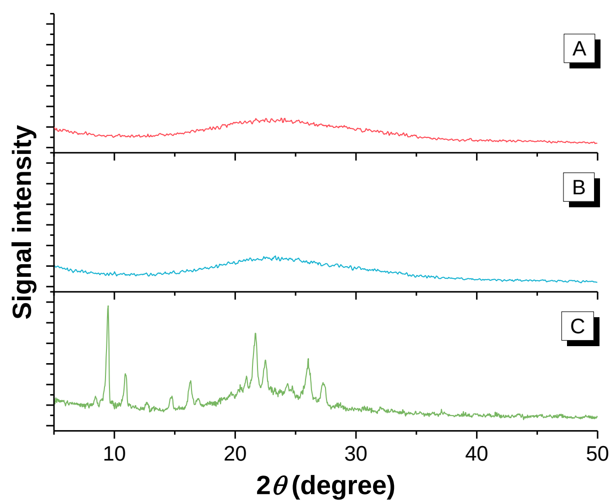
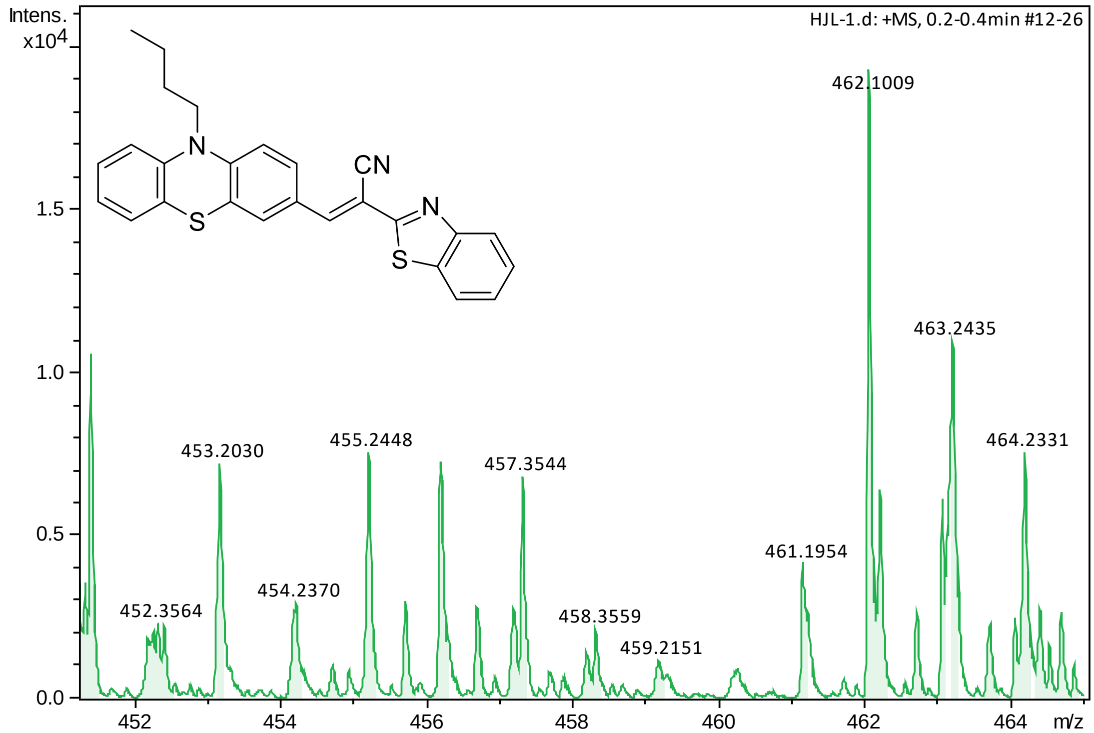


Figure S11. Powder-XRD patterns of **PTZ5** in aggregation (A), amorphous powder (B) and crystalline (C) states.

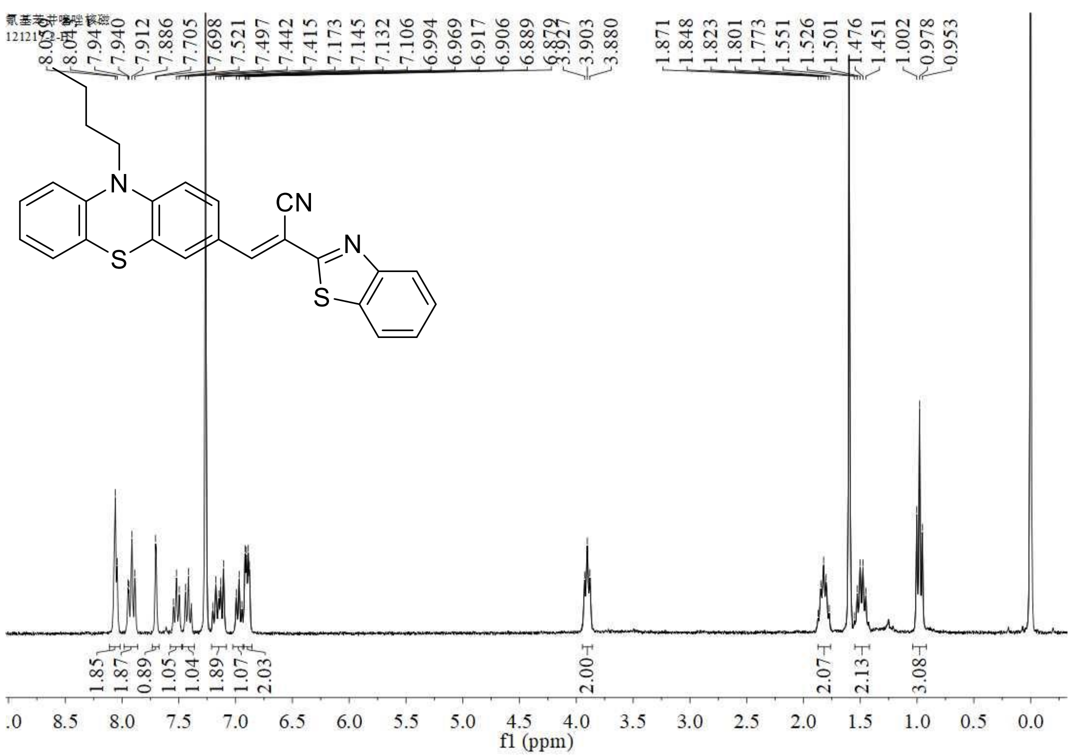
3. NMR and mass spectra

PTZ1

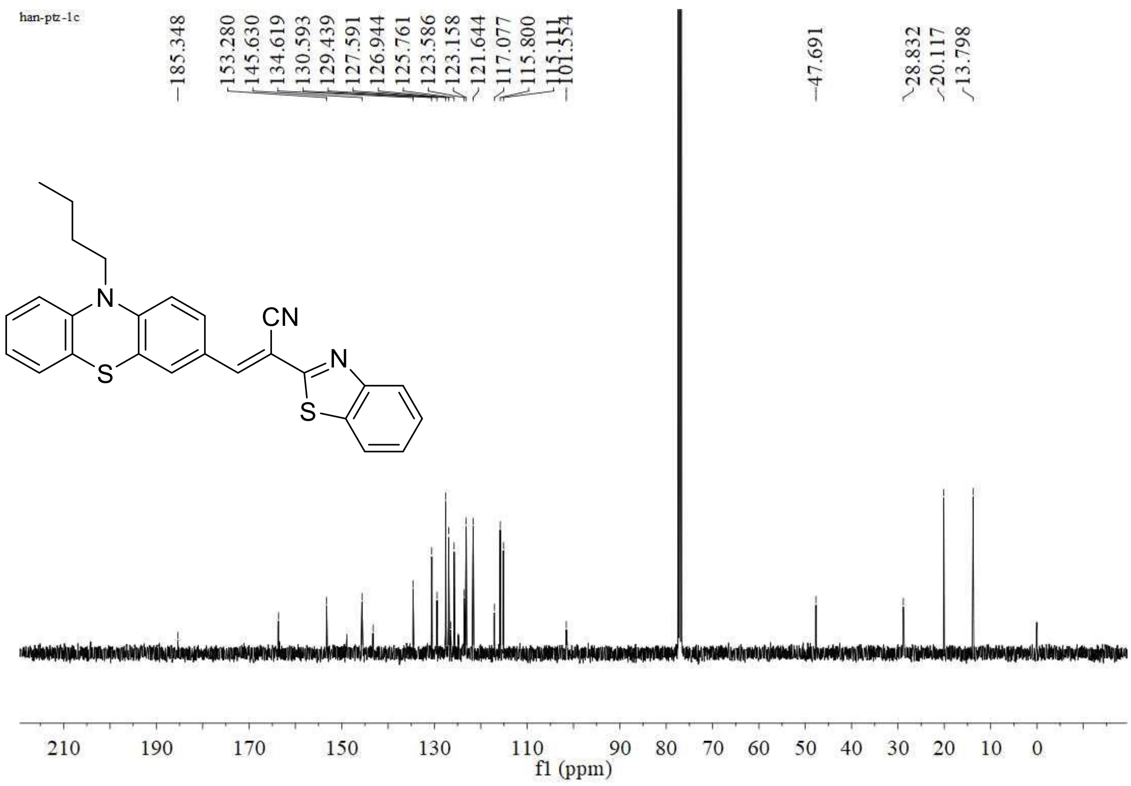
HRMS



^{1}H-NMR

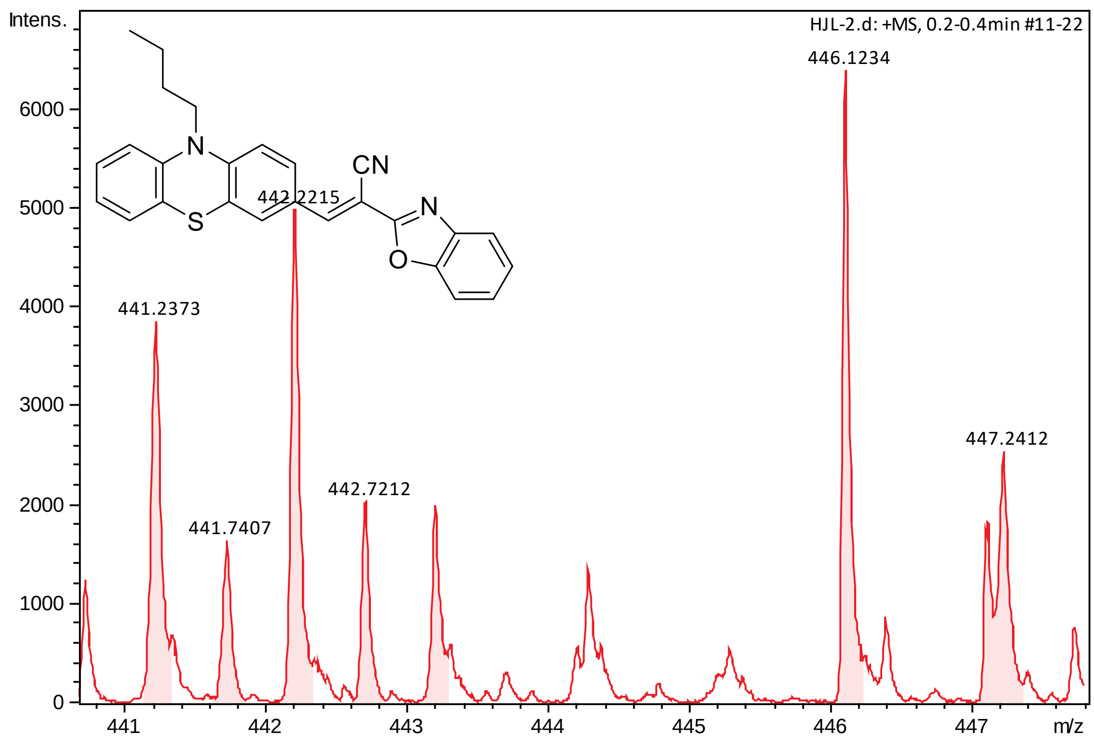


^{13}C-NMR

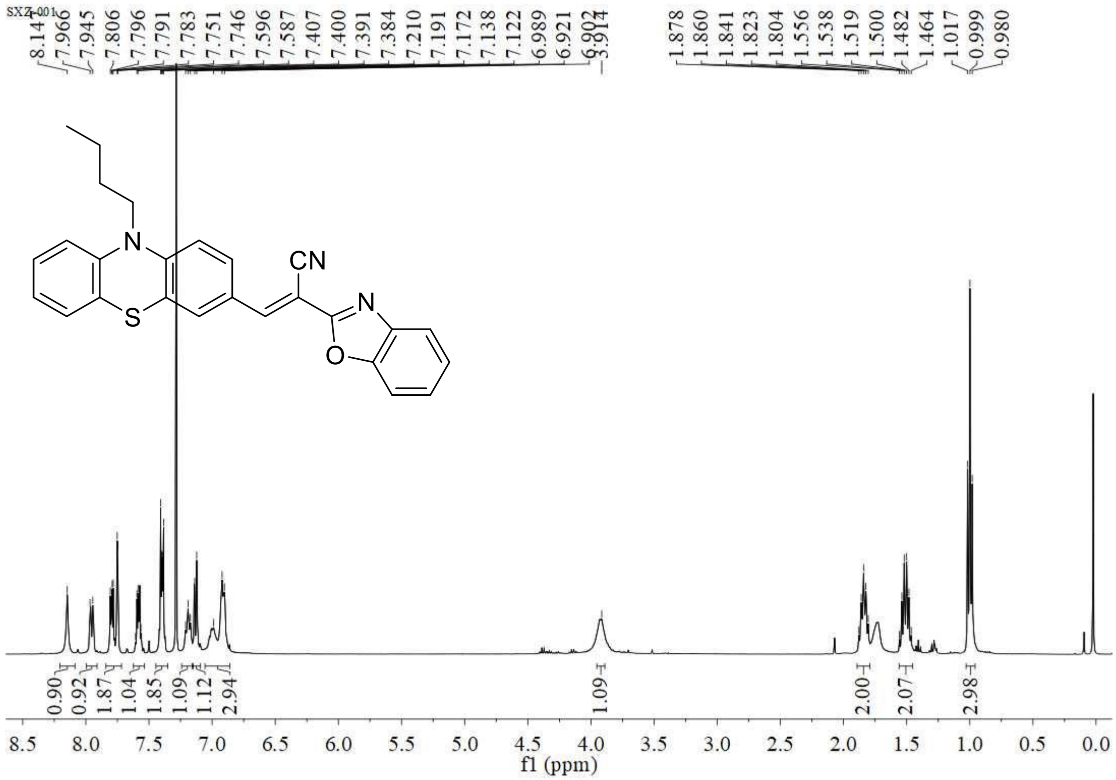


PTZ2

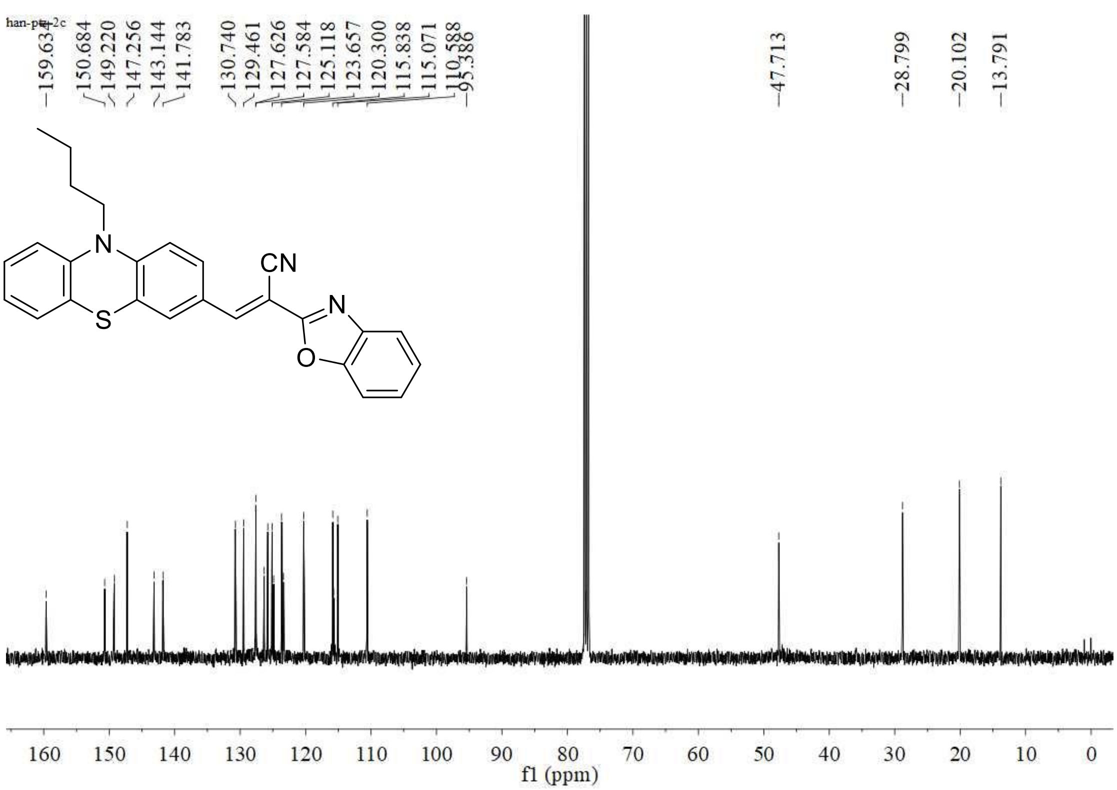
HRMS



[1]H-NMR

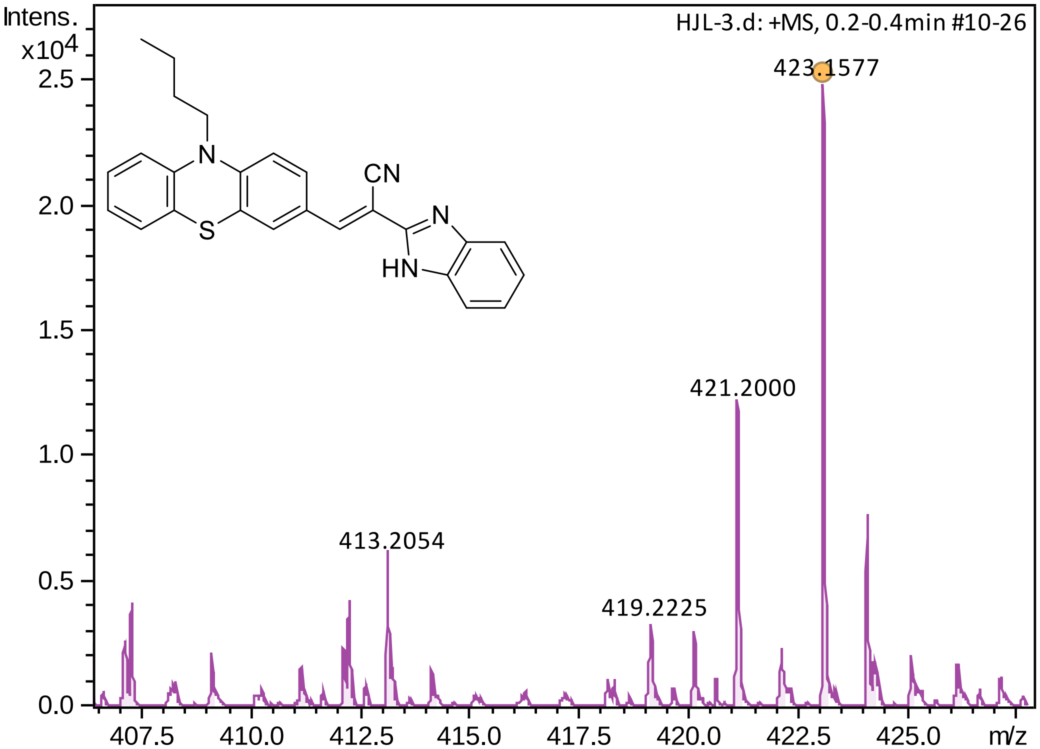


[13]C-NMR

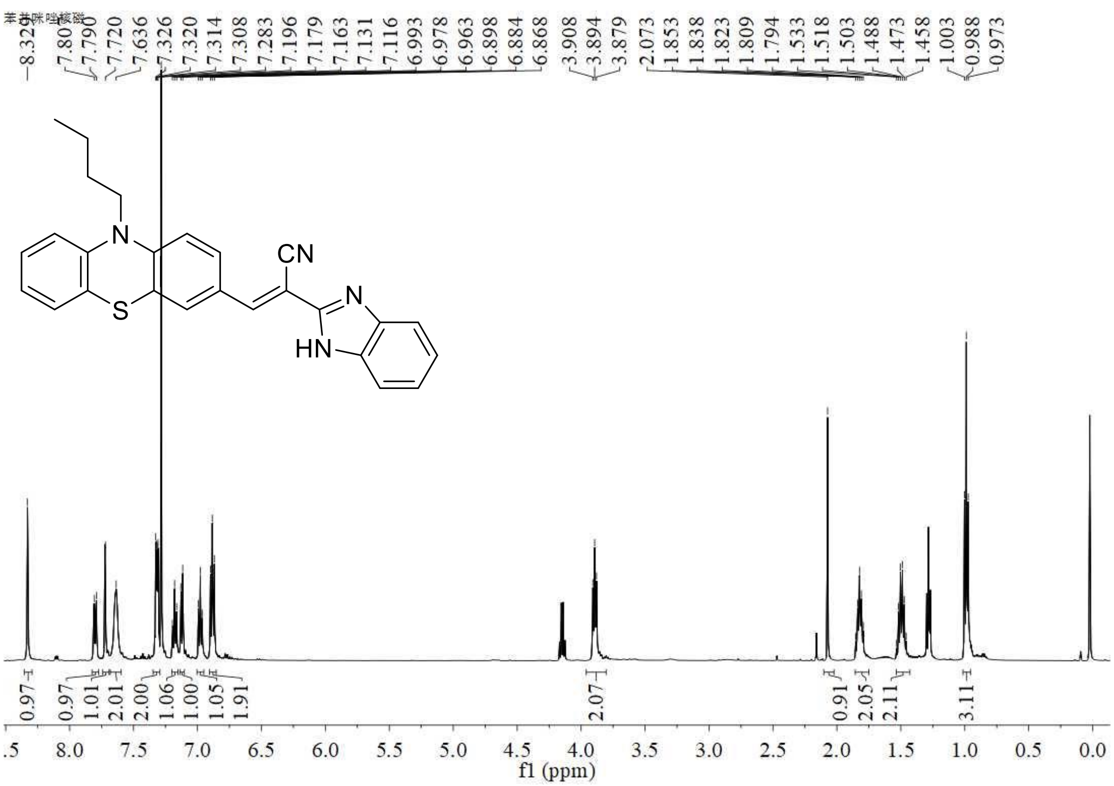


PTZ3

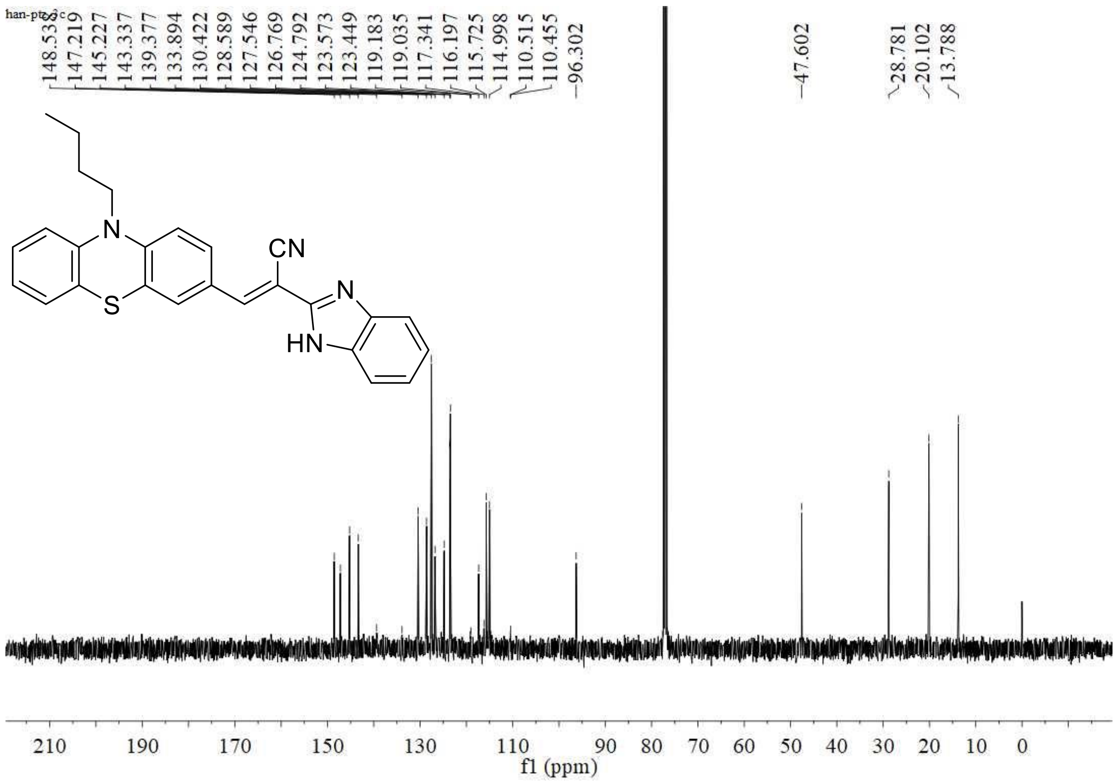
HRMS



^{1}H-NMR

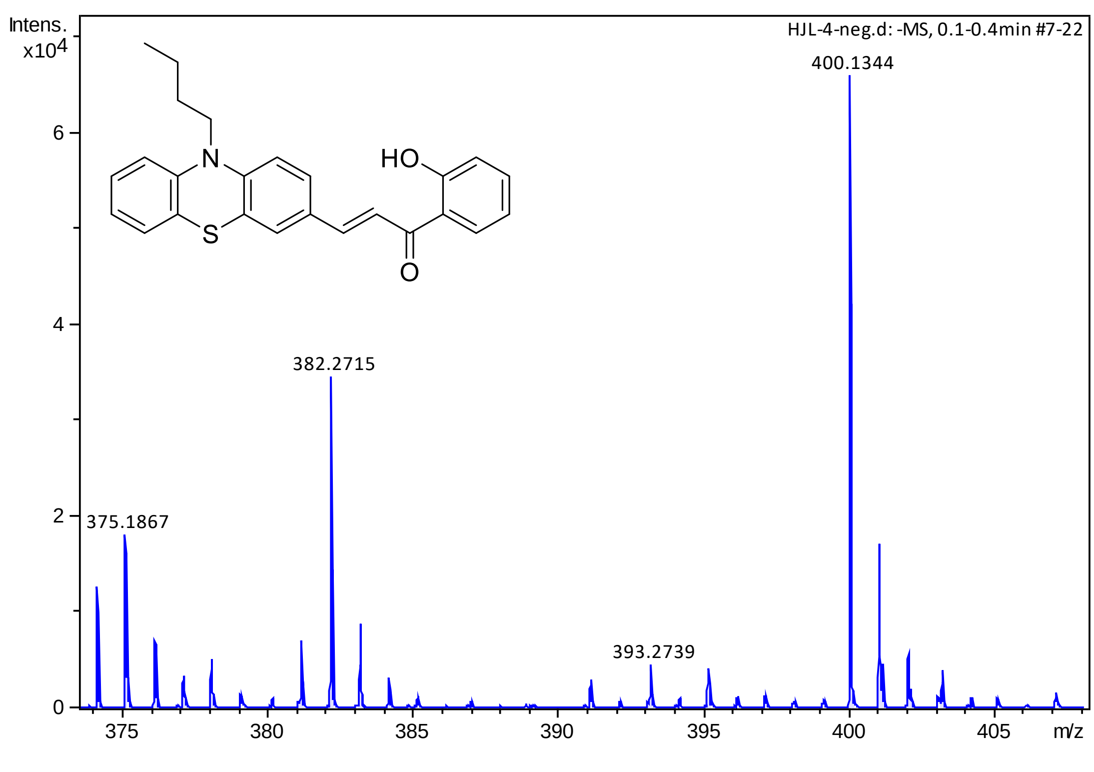


^{13}C-NMR

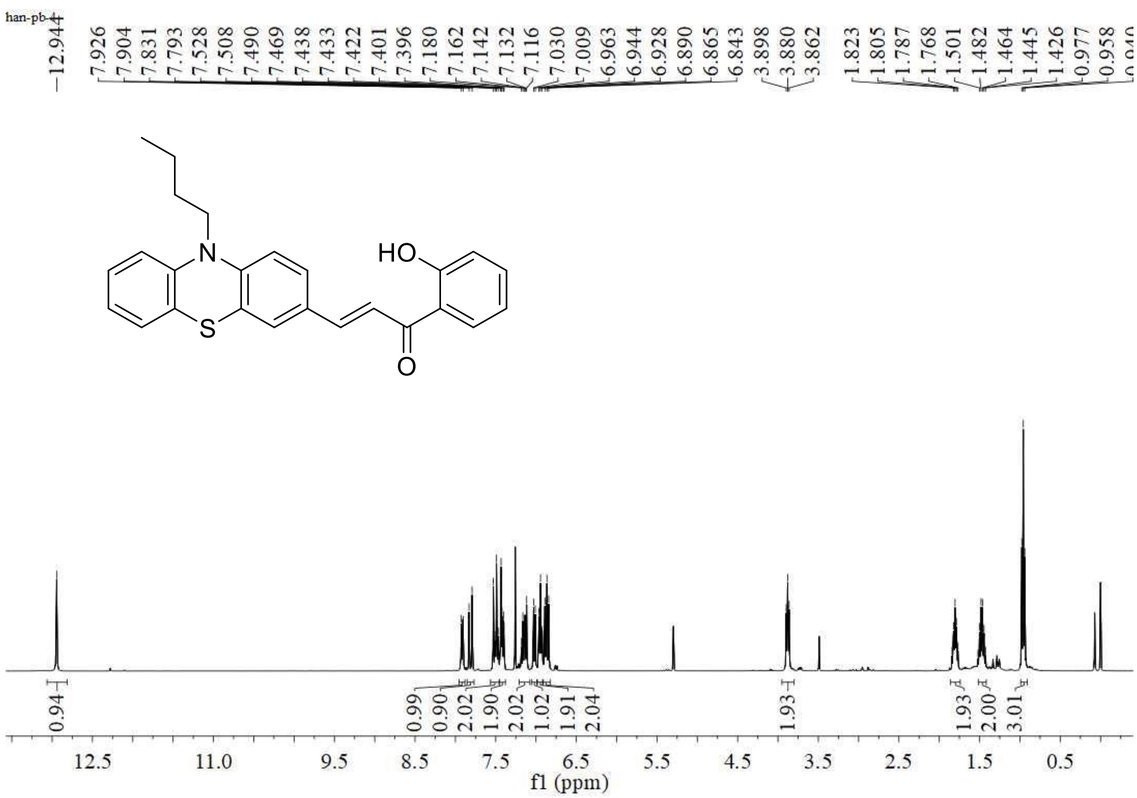


PTZ4

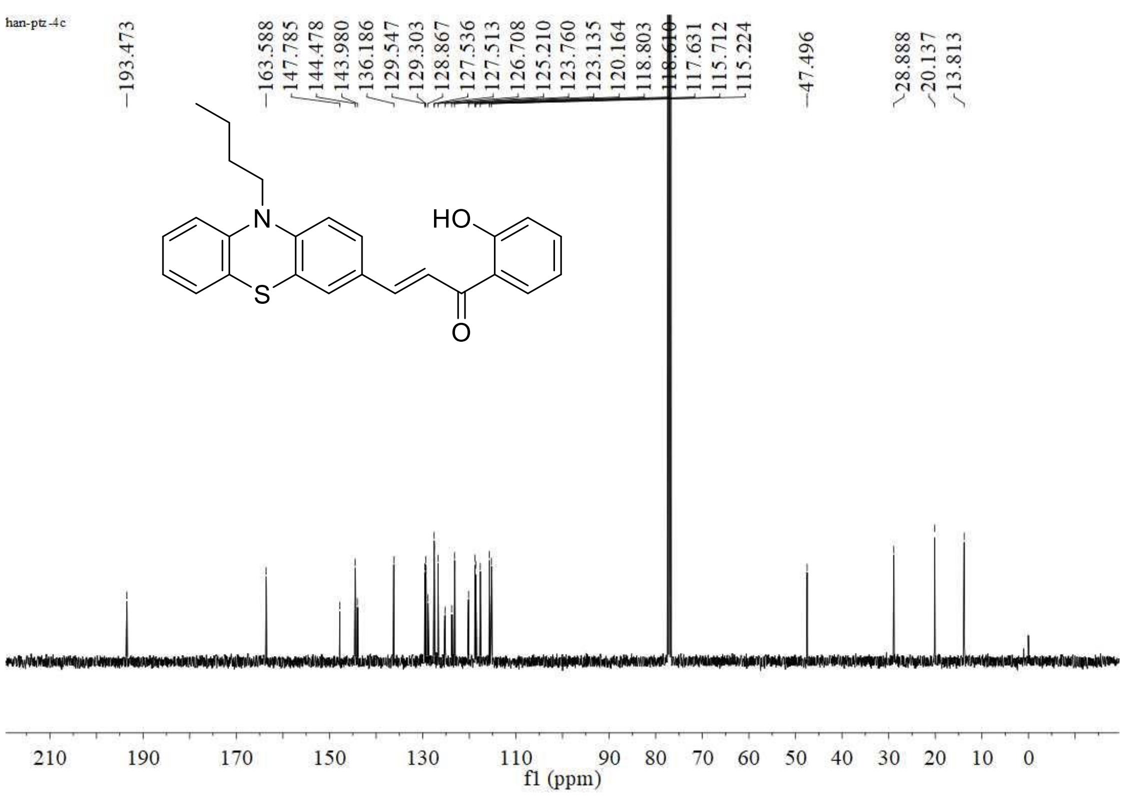
HRMS



^{1}H-NMR

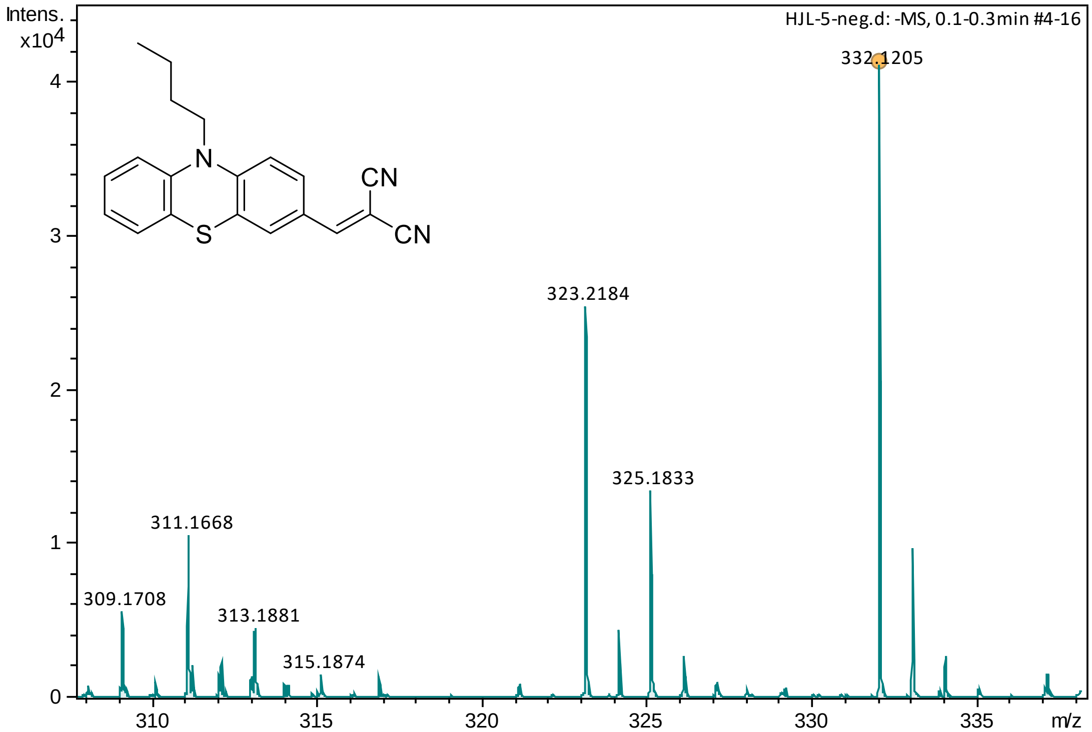


^{13}C-NMR

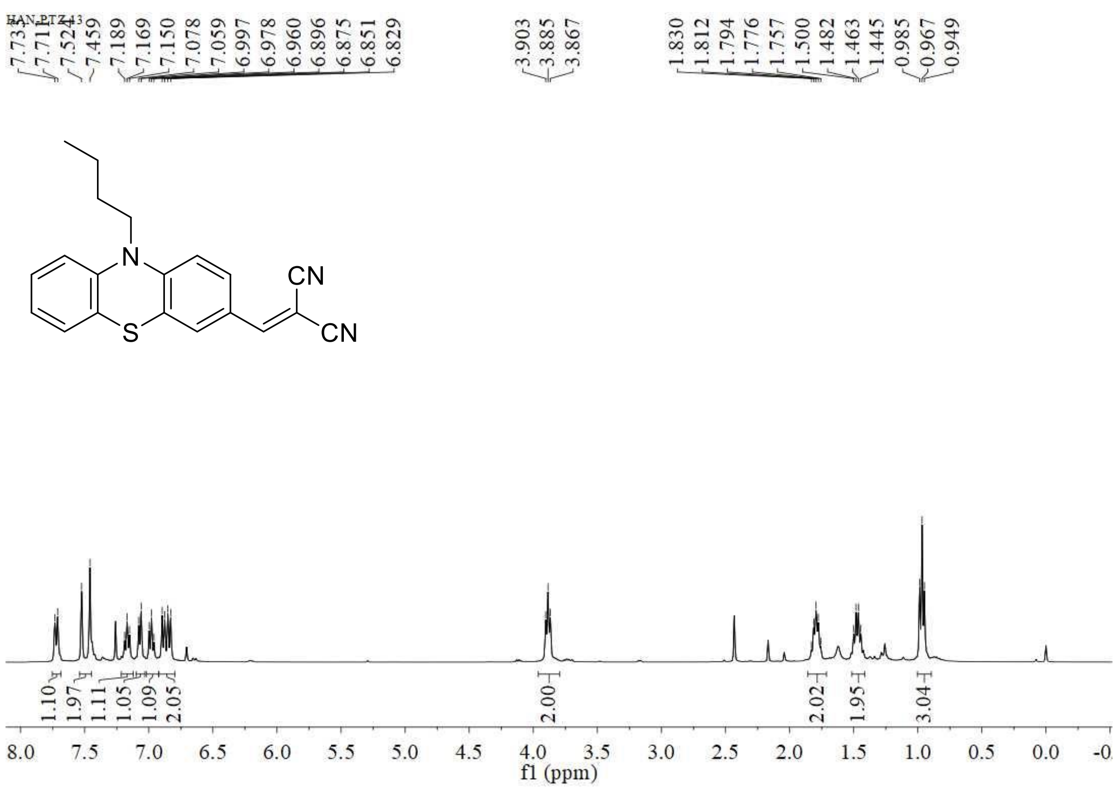


PTZ5

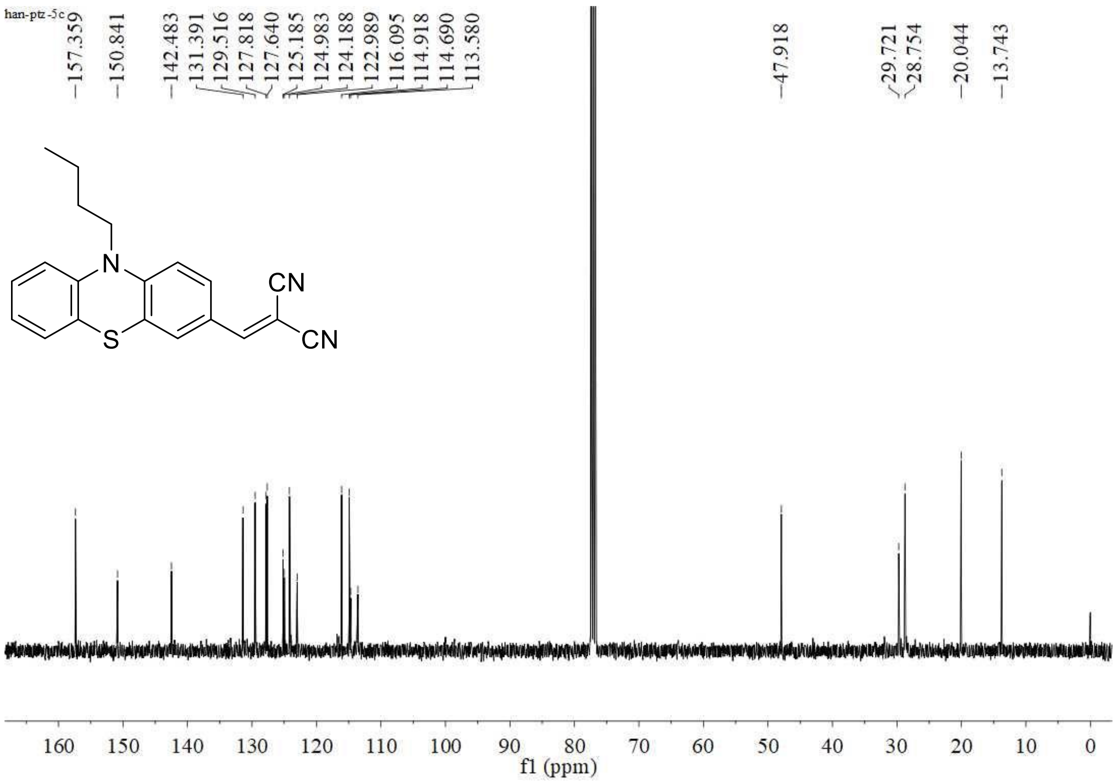
HRMS



^{1}H-NMR

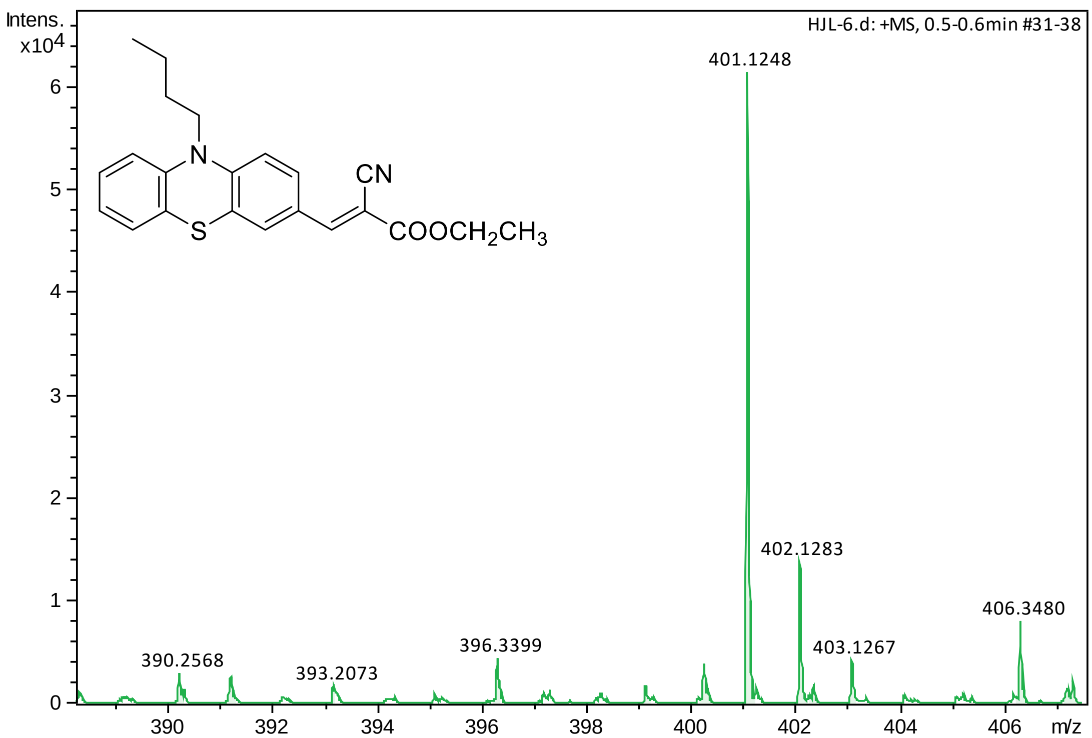


^{13}C-NMR



PTZ6

HRMS



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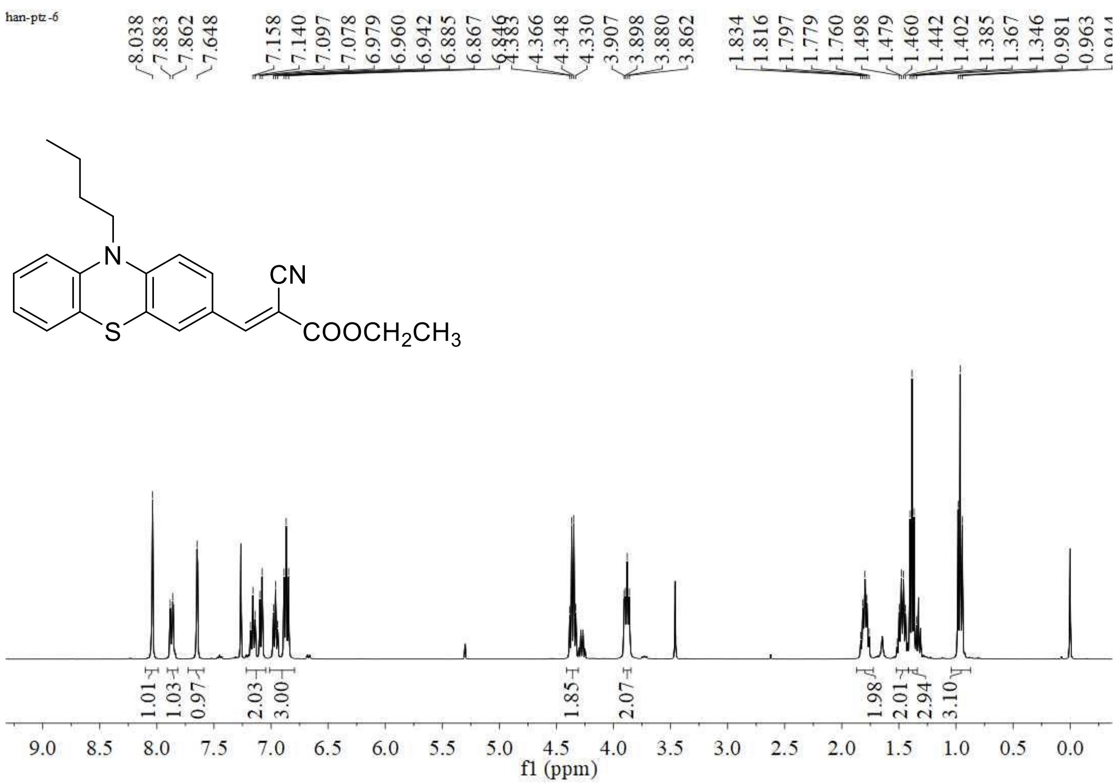

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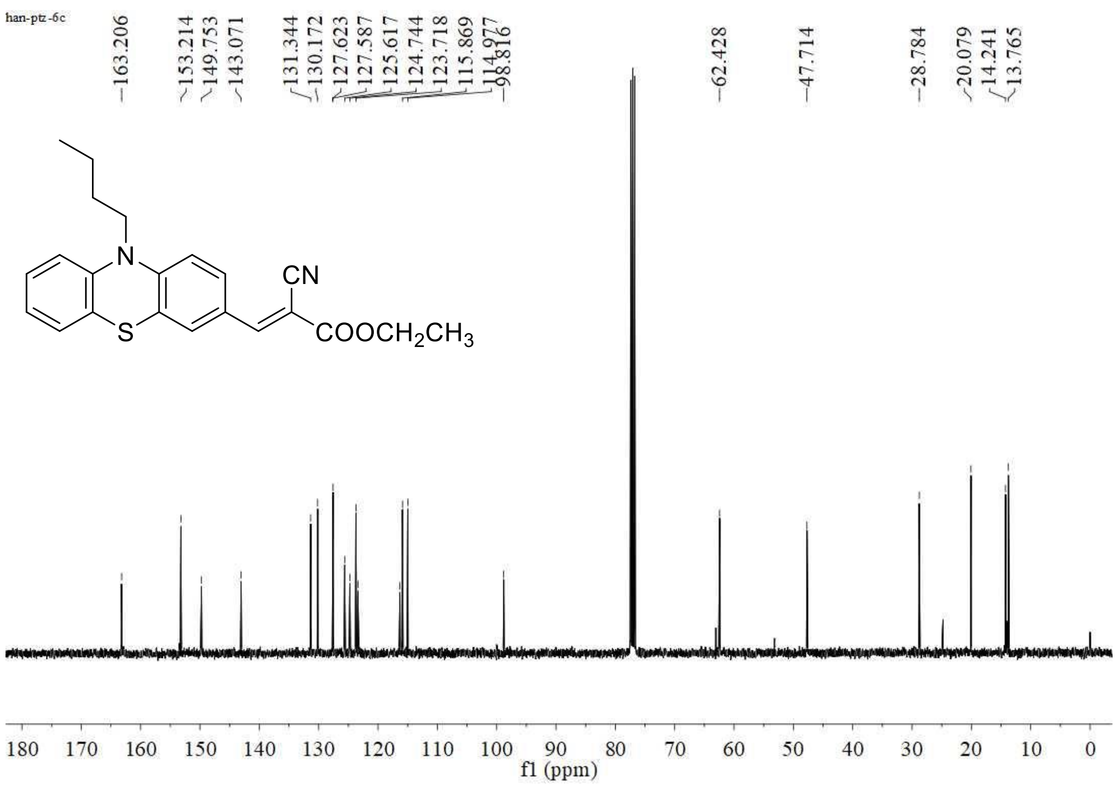
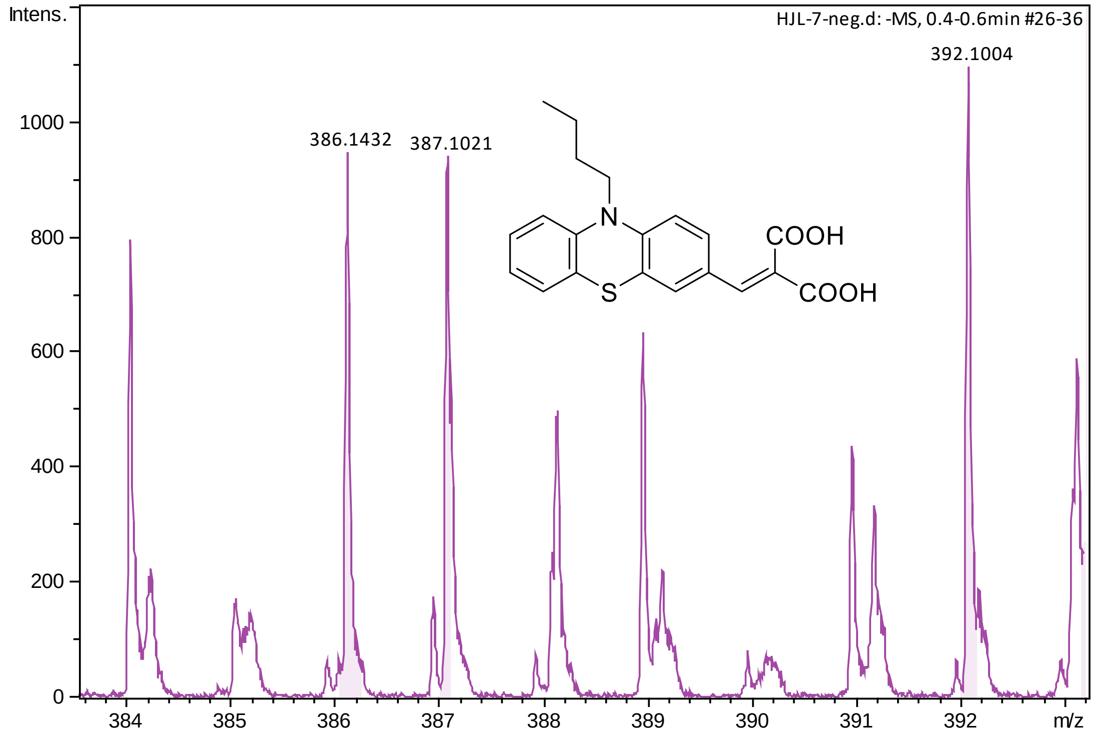


PTZ7

HRMS



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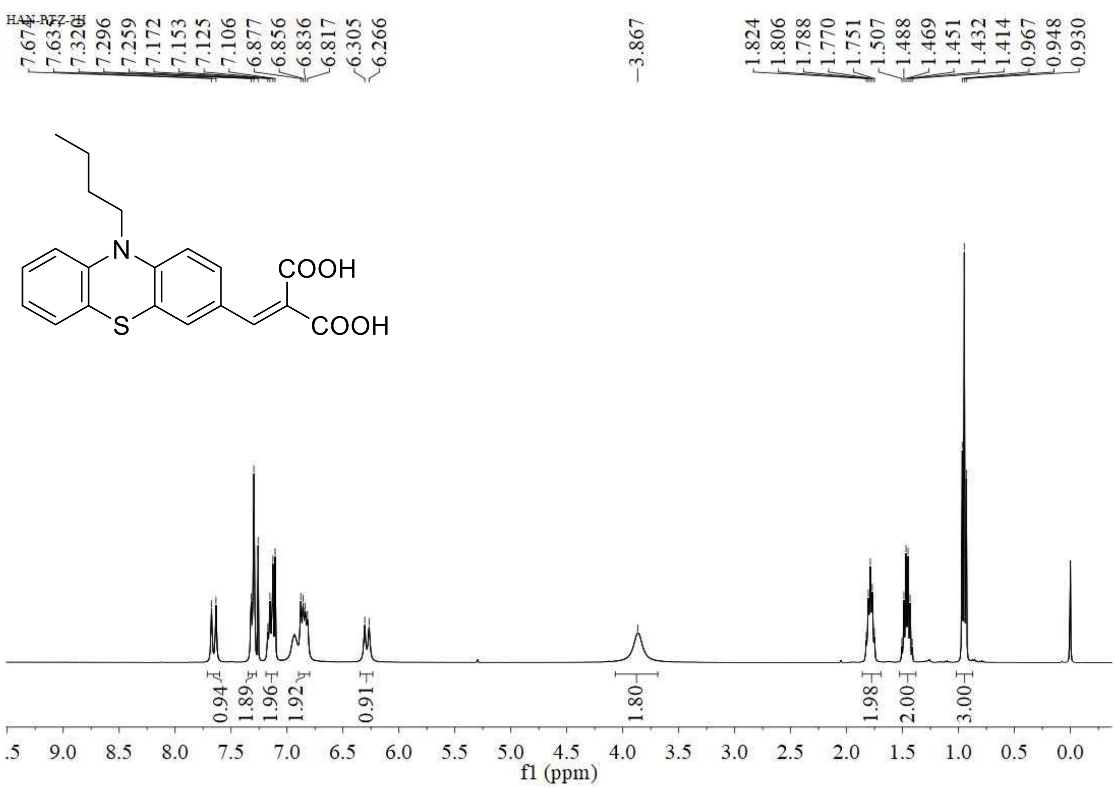

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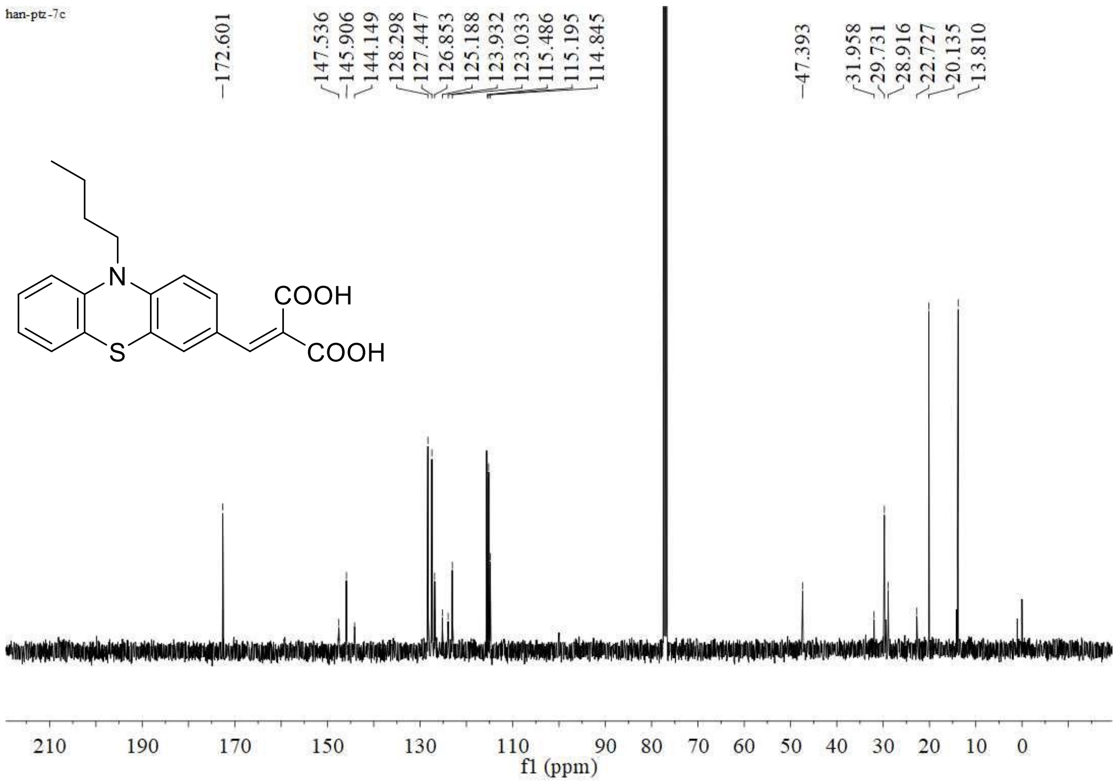
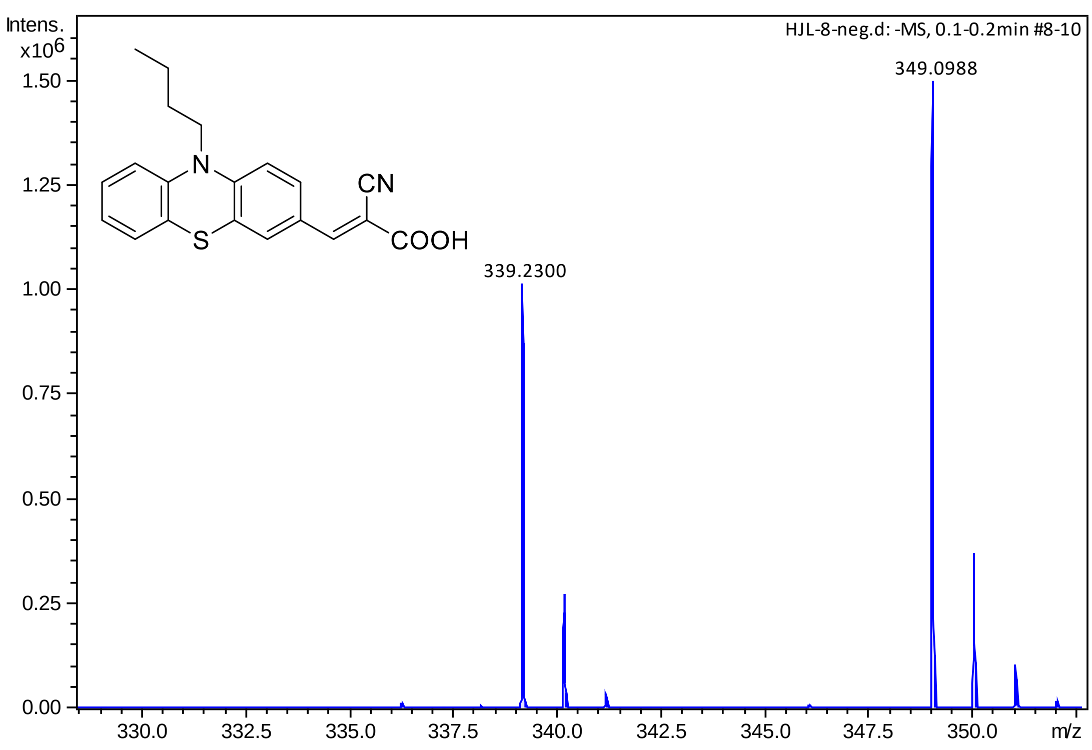
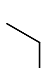


PTZ8

HRMS





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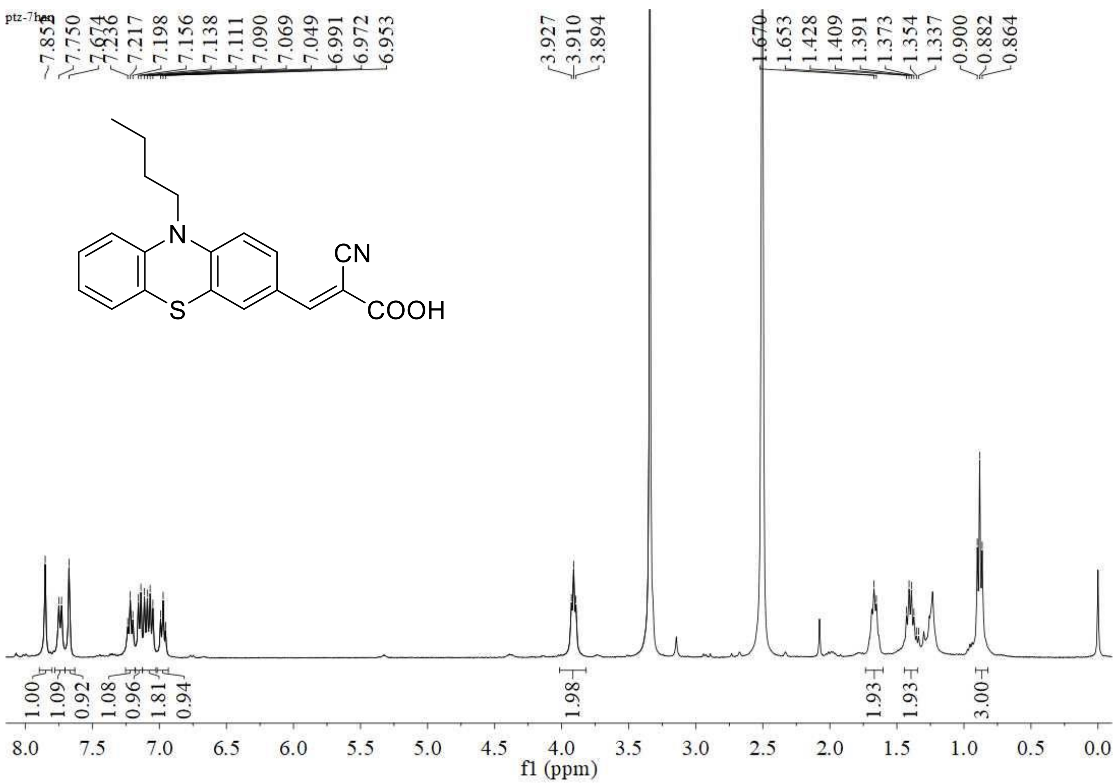
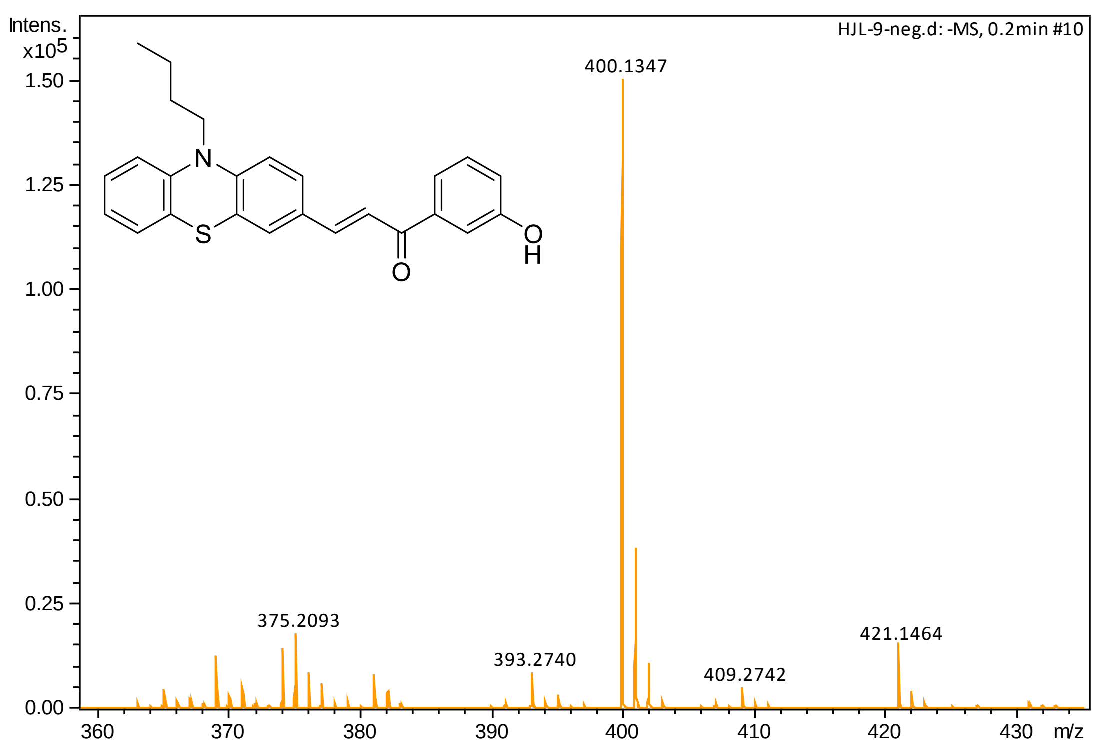
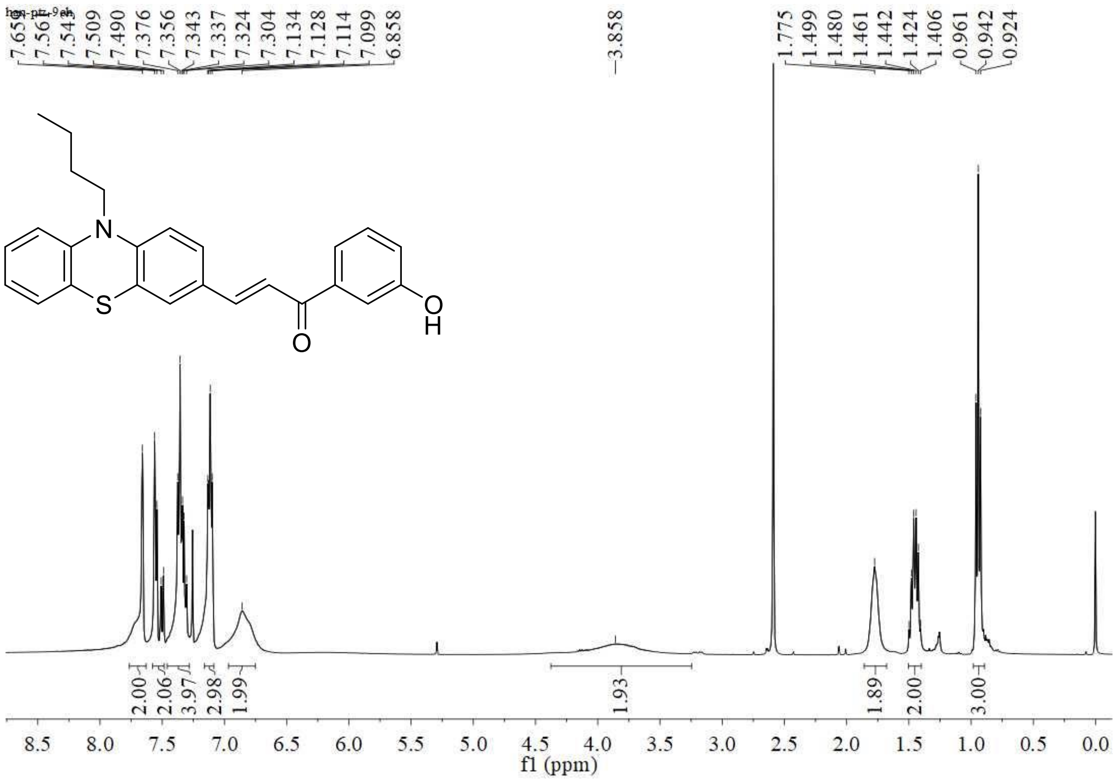


PTZ9

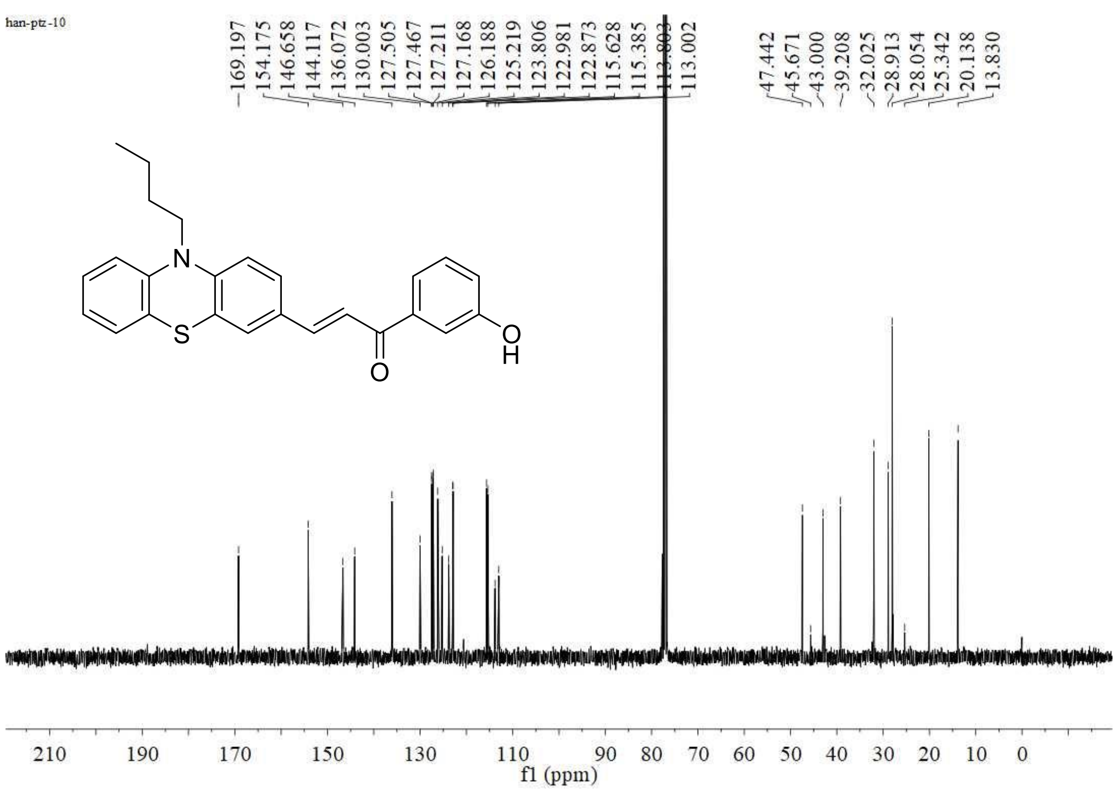
HRMS



^{1}H-NMR

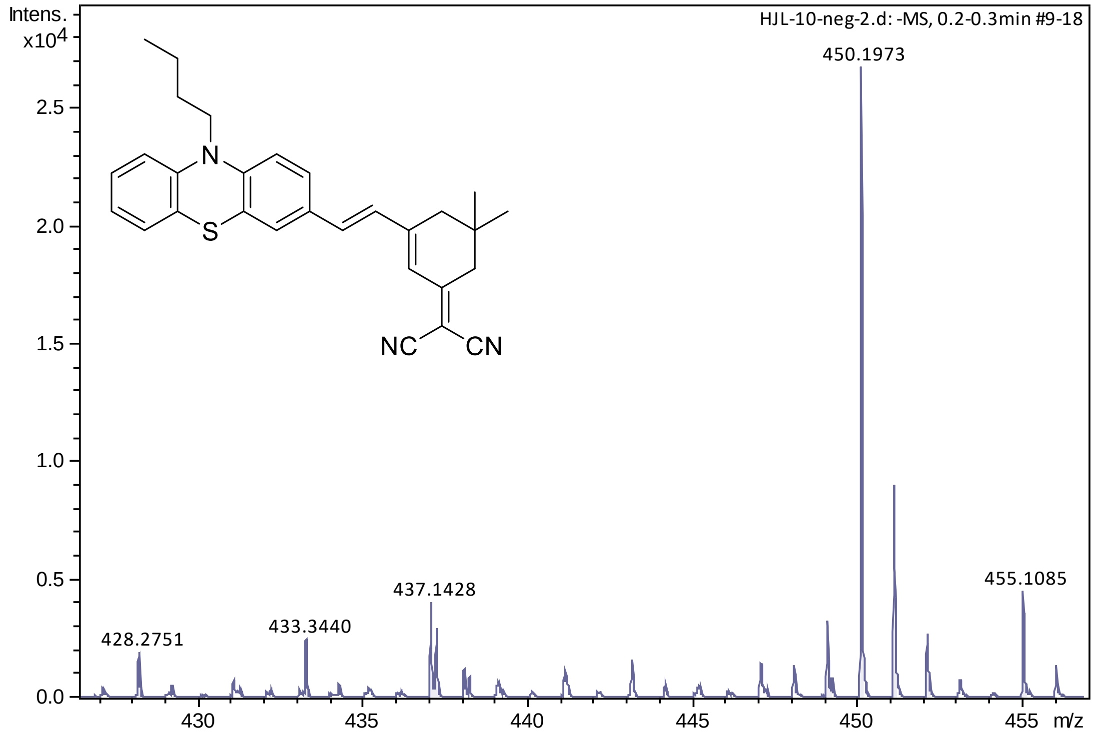


^{13}C-NMR



PTZ10

HRMS



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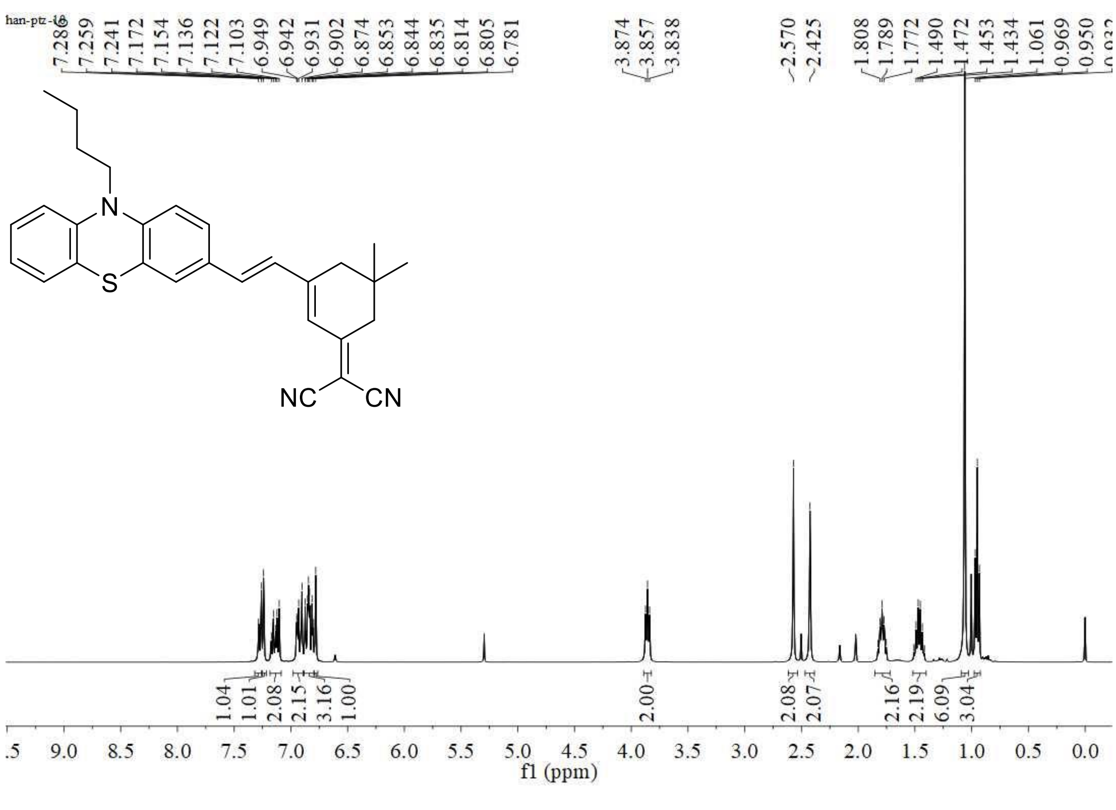

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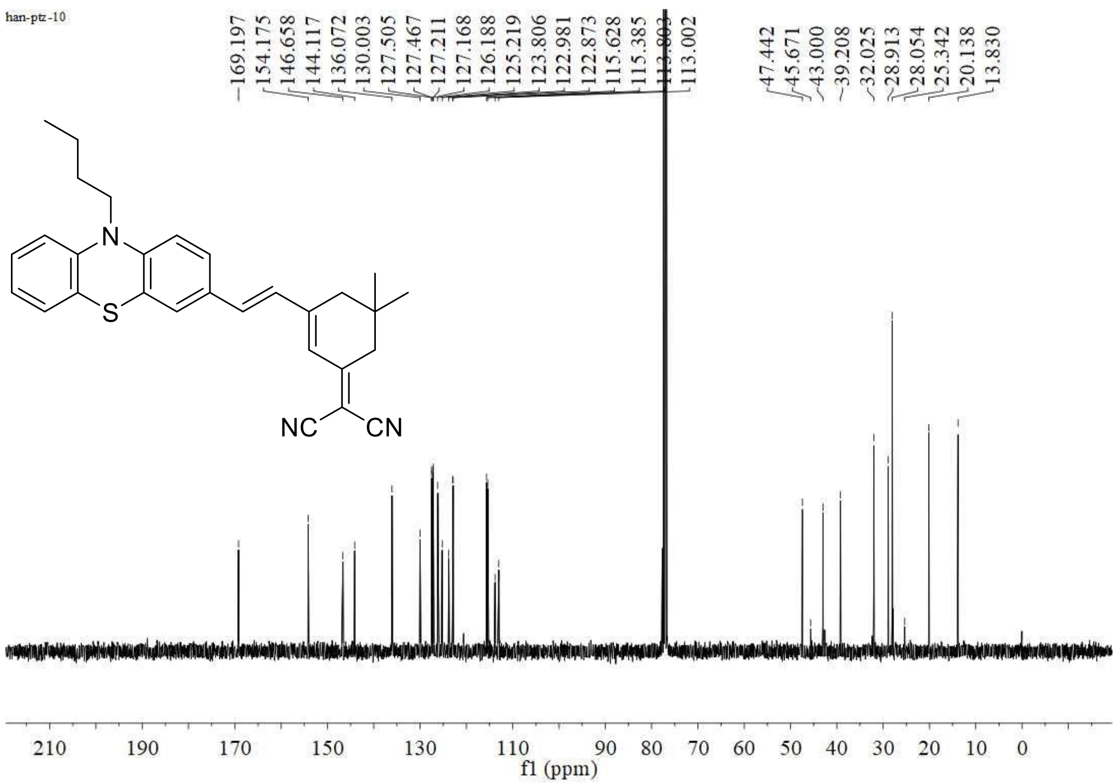
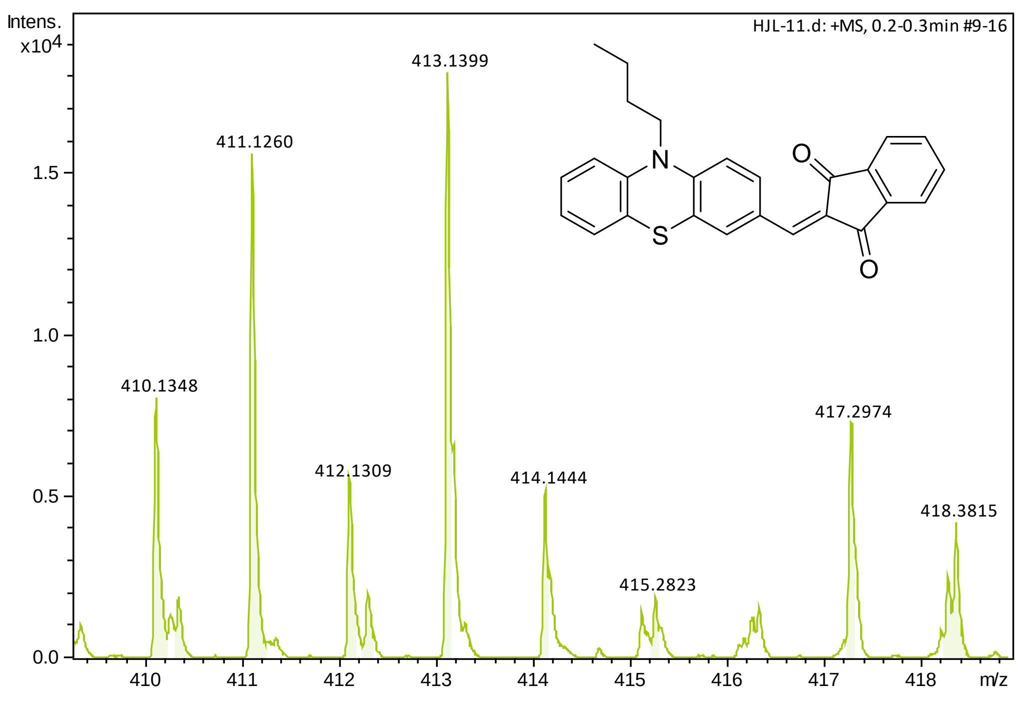
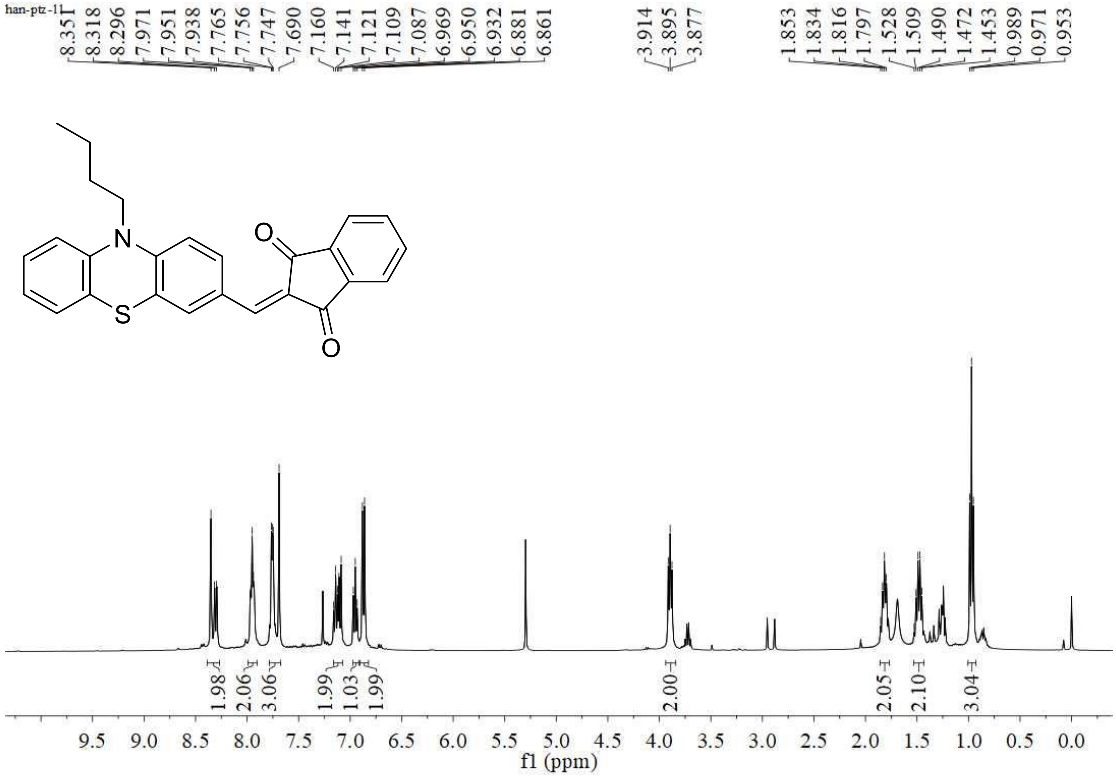


PTZ11

HRMS




han-ptz-11
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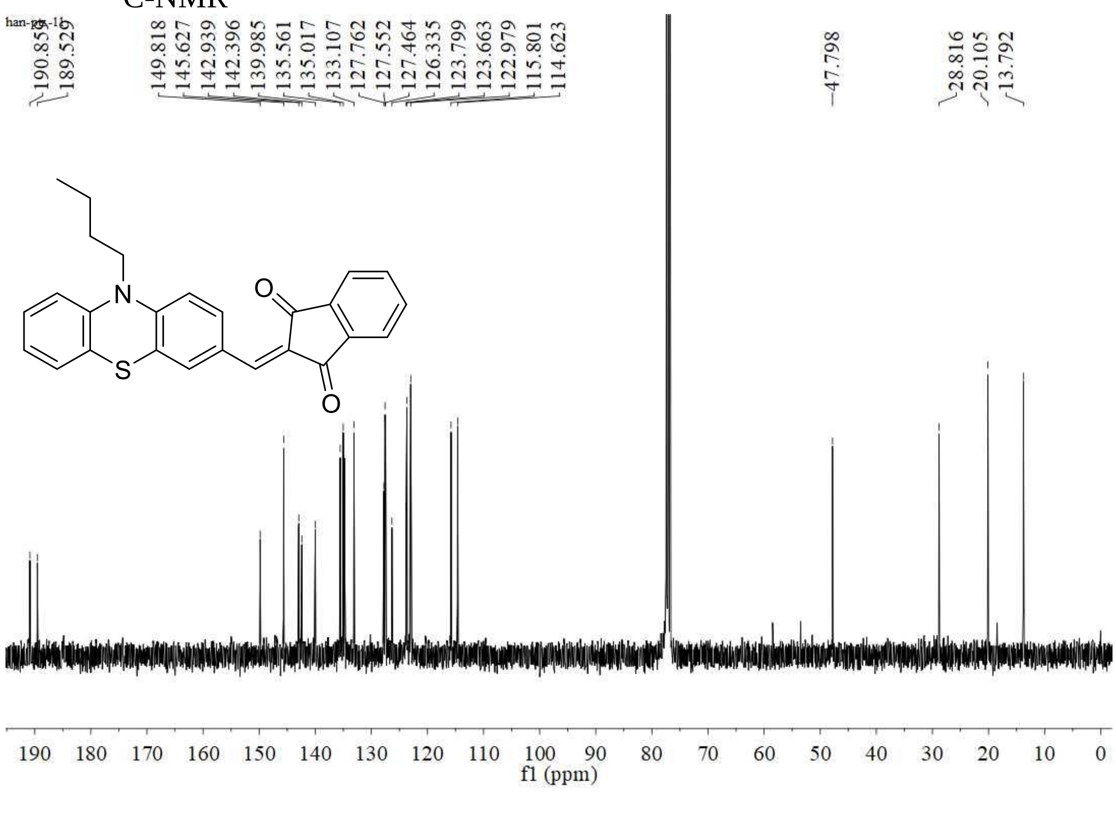
8.318
8.296
7.971
7.951
7.938
7.765
7.756
7.747
7.690
7.160
7.141
7.121
7.109
7.087
6.969
6.950
6.932
6.881
6.861
3.914
3.895
3.877
1.853
1.834
1.816
1.797
1.528
1.509
1.490
1.472
1.453
0.989
0.971
0.953
N
O
S
O
1.98
2.06
3.06
1.99
1.03
1.99
2.00
2.05
2.10
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

^{13}C-NMR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149.818
145.627
142.939
142.396
139.985
135.561
135.017
133.107
127.762
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126.335
123.799
123.663
122.979
115.801
114.623
47.798
28.816
20.105
13.792
N
O
S
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)