Electronic Supplementary Information

Copper dual-atom catalyst mediated C3−H amination of indoles at room temperature

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1. General information

All the obtained products were characterized by melting points (m.p.), ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR, ^{19}F-NMR, high resolution mass spectra (HRMS). Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR, ^{19}F-NMR spectra were obtained on Bruker-500. All the new compounds were further characterized by high resolution mass spectra (HRMS). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; All the reagents were purchased from commercial sources, and used without further purification.

All the reagents were purchased from Bide Pharmatech Ltd. and Energy Chemical. All solvents were purchased from Greagent (Shanghai Titansci incorporated company) and used without further purification. All reactions were heated by metal sand bath (WATTCAS, LAB-500, https://www.wattcas.com). Column chromatography was performed on silica gel (200-300 mesh). Reactions were monitored by using thin layer chromatography (TLC) (Qingdao Jiyida silica gel reagent factory GF254).

Figure S1. Metal sand bath (WATTCAS, LAB-500)

Powder X-ray diffraction (PXRD) data collected using Rigaku Smart Lab diffractometer (9 kW, equipped with Cu X-ray anode and a 2D detector, λ = 1.5406 Å). The patterns were collected in the 2θ range 5-50° with 0.01° data binning using a glass plate sampler. High-resolution PXRD patterns were collected on Rigaku SmartLab diffractometer (3 kW, equipped with Mo X-ray anode, λ = 0.7093 Å). The

patterns were collected in the 2θ range 2-30° with 0.001° data binning in transmission mode using a 0.5-mm borosilicate capillary sample holder. Each pattern was collected at a very slow speed of 0.2° min^{-1} for 120 min in total. This procedure produced good quality patterns of the high signal-to-noise ratio.

The XRF data was collected using Thermo Scientific ARL ADVANT'X IntelliPower X-ray fluorescence spectrometer (Solid-state 3600 W high-frequency generator). All samples were pre-sieved (200 mesh) for better analysis.

The XPS measurements were performed using a Thermo Scientific Nexsa spectrometer (12 kV cathode-biased Al K_α, $h\nu$ = 1486.6 eV) with a spot size of 400 μm at the base pressure < 5 × 10^{-10} mbar. An argon ion gun was used to etch the samples with an etching rate of 0.5 nm s^{-1}. The XPS spectra were obtained at approximately 20 nm depth intervals. The raw data were corrected for substrate charging with the binding energy of the C 1*s* peak at 284.8 eV.

The SEM images were collected using Field Emission Scanning Electron Microscope (TESCAN MAIA3, Brno, Czech Republic) for surface morphology srudy. Before scanning, the samples were coated with a thin layer of gold and then inspected with an accelerating voltage of 5 kV.

The UV-vis measurements were carried out with the obtained samples using Perkin-Elmer Lambda 1050-UV-Vis-NIR spectrophotometer with an Integrating Sphere-150 mm UV-vis-NIR (InGaAs) Module. The equipment was calibrated using Spectralon standard and the reflectance was measured in the 200–900 nm range at an interval of 2 nm.

Brunauer-Emmett-Teller (BET) surface area, pore volume and average pore diameter were determined by N_2 physisorption using a Micromeritics ASAP 2000 automated system.

2. General procedure for the preparation of Cu@USY

Commercial H-USY zeolites (SiO_2:Al_2O_3 = 12, chemical formula $H_nAl_nSi_{192-n}O_{384}$) were purchased from Nankai University Catalyst Co., Ltd. Typical characterization results are displayed on their product website: [http://www.nkcatalyst.com/index.php/en/arc/show/id/57.html]. Briefly, the H-USY samples possess high crystallinity (≥ 80%), a surface area of *ca*. 680 $m^2 \cdot g^{-1}$, and pore size of 7.4 Å.

Cu@USY was synthesized *via* a conventional ion-exchange process. Briefly, 2.0 g H-USY zeolite (SiO_2:Al_2O_3 = 12) was suspended in 0.2 M $Cu(NO_3)_2$ solution (60 mL) for 20 h at 80 °C. Then the solid Cu@USY sample was washed and collected after calcinating at 300 °C for 1 h within a ramping rate of 5 °C min^{-1}.

Table S1. Elemental analysis of Cu@USY by X-ray fluorescence spectroscopy.

Sample	Al(wt%)	Cu(wt%)	Cu/Al molar ratio
Cu@USY	17.95	2.92	0.07

Table S2. Brunauer-Emmett-Teller (BET) surface area analysis of Cu@USY.

Samples	Surface Area			Pore Volume			Pore size (nm) BJH desorption	Pore size (nm) BET desorption
	BET Surface Area m^2/g	t-plot Micropore Area m^2/g	Percent (%)	Single point p/p_0=0.95 Total pore volume cm^3/g	t-plot Micropore cm^3/g	Percent (%)		
Cu@USY	848.3988	794.3603	93.63	0.3835	0.2985	93.63	7.9631	1.8079

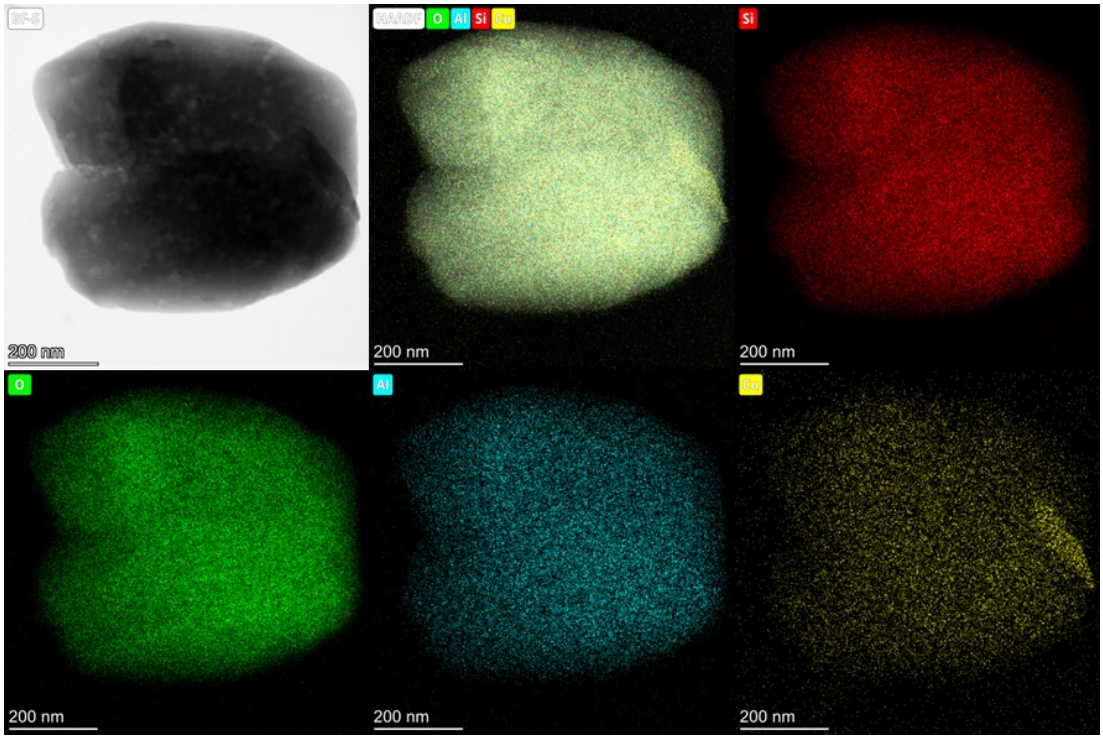


Figure S2. EDX microanalysis of the Cu@USY from high-resolution TEM.

3. Structural and atomic parameters

Table S3. Crystallographic data of the high-resolution XRD measurements of Cu@USY. PXRD data were obtained from Rigaku SmartLab (3 kW, λ = 0.7093 Å).

	Cu@USY
X-ray energy (keV)	17.45
2θ - zero point (°)	0.00517(9)
Space group	*Fd-3m*
Crystal system	Cubic
a (Å)	24.493297
V (Å^3)	14694.058
2θ range for refinement (°)	2-30
Number of parameters	48
Number of *hkl*s	182
Refinement methods	Rietveld
$R_{wp}/R_{exp}/R_p$ (%)	8.809/6.757/7.065

R_{wp}: weighted profile; R_{exp}: expected; R_p: profile.

Table S4. Atomic parameters derived from the PXRD measurements of Cu@USY.

Species	Atom	*x*	*y*	*z*	SOF	B_{eq} (Å^2)
Zeolite framework	Si1	0.12651(14)	0.94510(12)	0.03623(12)	1	1
	O1	0.17510(19)	0.17510(19)	0.9705(3)	1	2
	O2	0.1780(3)	0.1780(3)	0.3132(3)	1	2
	O3	0.25081(16)	0.25081(16)	0.1417(3)	1	2
	O4	0.1049(2)	0.8951(2)	0	1	2
Copper site	Cu1	0.1035(2)	-0.3225(3)	-0.0262(2)	0.07[a]	2
	Cu1’	0.3965(2)	0.4275(3)	0.2238(2)	0.07	2
phenthiozine	C1	0.28(4)	0.43(2)	0.057(18)	0.0539(3)	8
	C2	0.275(15)	0.374(18)	0.066(17)	0.0539(3)	8
	C3	0.27(3)	0.353(16)	0.119(18)	0.0539(3)	8
	C4	0.278(12)	0.388(14)	0.164(17)	0.0539(3)	8
	C5	0.28(5)	0.444(15)	0.156(18)	0.0539(3)	8
	C6	0.29(6)	0.464(18)	0.102(19)	0.0539(3)	8
	N7	0.28(2)	0.365(16)	0.217(17)	0.0539(3)	8
	C8	0.286(14)	0.392(19)	0.266(17)	0.0539(3)	8
	C9	0.29(4)	0.45(2)	0.269(19)	0.0539(3)	8

	S10	0.29(8)	0.492(17)	0.21(2)	0.0539(3)	8
	C11	0.29(3)	0.36(2)	0.315(17)	0.0539(3)	8
	C12	0.30(2)	0.39(3)	0.365(17)	0.0539(3)	8
	C13	0.31(4)	0.44(3)	0.367(19)	0.0539(3)	8
	C14	0.31(6)	0.47(3)	0.32(2)	0.0539(3)	8
Indole	CA1	0.381(4)	0.433(5)	0.332(6)	0.0539(3)	8
molecule	CA2	0.361(4)	0.394(4)	0.298(5)	0.0539(3)	8
	CA3	0.317(4)	0.403(3)	0.267(5)	0.0539(3)	8
	CA4	0.294(3)	0.452(3)	0.270(4)	0.0539(3)	8
	CA5	0.313(4)	0.491(4)	0.303(4)	0.0539(3)	8
	CA6	0.357(5)	0.482(5)	0.335(5)	0.0539(3)	8
	NA7	0.252(3)	0.472(4)	0.245(4)	0.0539(3)	8
	CA8	0.243(4)	0.521(4)	0.260(5)	0.0539(3)	8
	CA9	0.281(5)	0.535(4)	0.297(5)	0.0539(3)	8
	CA10	0.218(4)	0.444(5)	0.206(5)	0.0539(3)	8

a: Based on the elemental analysis of Cu@USY from XRF, the SOF of the mononuclear Cu site was fixed at 0.07.

4. Synthesis of typical product 3aa

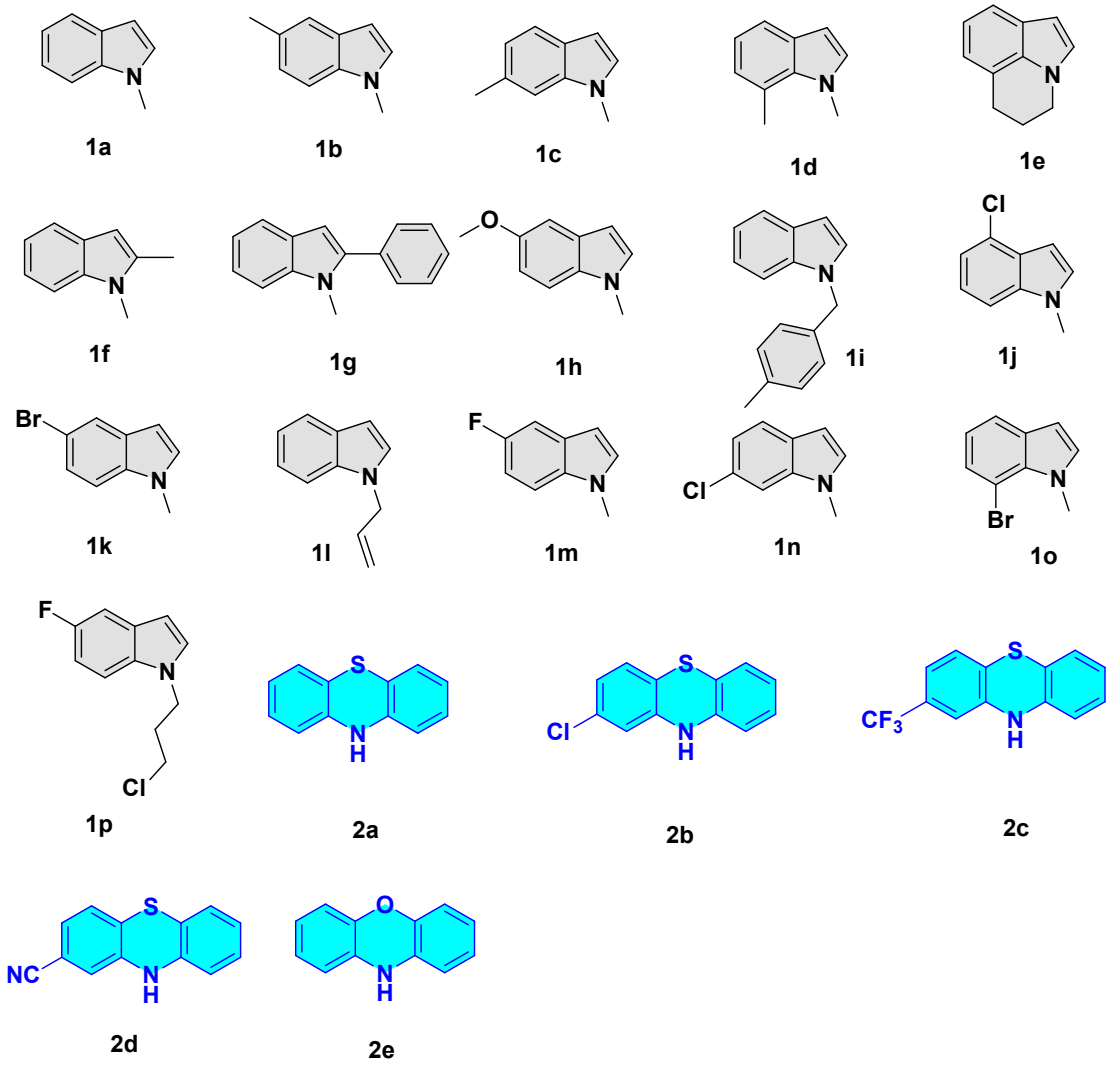
Under oxygen atmosphere, catalyst Cu@USY (100 mg), NaOTf (10 mol%), **1a** (0.39 mmol), **2a** (0.26 mmol) and EtOH (1.5 mL) was added to Schlenk tube (50 mL) along with a magnetic stirrer bar, reaction mixture was stirred at room temperature about 10 h. Then the resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel by using petroleum ether/methylene chloride (3:1), as the eluent to give **3aa** as a white solid (61.4 mg, 72% yield).

5. Substrate preparation

General Procedure for preparation of *N*-substituted indole derivatives (**1b-1d, 1f-1p**).[1] Procedure for preparation of 1,5-dimethyl-1*H*-indole (**1b**): To prepare NaH (0.55 g, 65% dispersion in mineral oil, 15.0 mmol) added in DMF (5 mL), 5-methyl-1*H*-indole (1.31 g, 10.0 mmol) in DMF (5 mL), then add 5-methyl-1*H*-indole solution to NaH at 0 °C. The mixture solution was stirred at 0 °C about 15 min to 1 h naturally to room temperature. After iodomethane (0.83 mL, 13.0 mmol) was added at 0 °C and allowed to warm to room temperature about 30 min. The reaction mixture quenched with saturated NH_4Cl (20 mL), and extracted with ether (3 × 20 mL). The organic layers dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting oil

purified by column chromatography on silica gel (petroleum ether) afforded **1b** as a yellow oil.

Scheme S1. Substrates used for the synthesis of *N*-substituted indoles.



6. Procedure for catalyst recycling

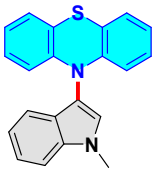
Under oxygen atmosphere, catalyst Cu@USY (100 mg), NaOTf(10 mol%), **1a** (0.39 mmol), **2a** (0.26 mmol) and EtOH (1.5 mL) was added to Schlenk tube (50 mL). The reaction mixture was stirred at room temperature for about 10 h. The catalyst was isolated by centrifugation, washed with EtOH (1.5 mL) for three times. The centrifugal reaction mixture was concentrated in vacuo, the yield was determined by TLC. After that, the centrifugal catalyst directly was reused for the next circular reaction.

7. Synthetic utility.

The preparation of **5pca** was similar to the literature procedures.[2] A mixture of 10-(1-(3-chloropropyl)-5-fluoro-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (**3pc**, 0.26 mmol, 1.0 eq.), triphenylphosphine **4a** (TPP, 0.273 mmol, 1.05 eq.), and potassium iodide (KI, 0.312 mmol, 1.2 eq.) was refluxed with stirring at 85 °C about 48 h in acetonitrile (MeCN) and monitored by TLC. On completion, the mixture was filtered and MeCN removed under vacuum. The crude residue was dissolved in minimal DCM, and the pure product precipitated out of solution by slow addition of diethyl ether, after that filtering and drying. Yield = 32%.

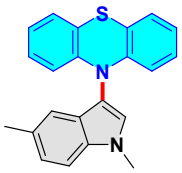
8. Analytical data of the obtained compounds

(1) 10-(1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3aa**)



White solid, (61.4 mg, 72% yield), m.p.: 213-215 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 (dd, *J* = 7.8, 5.3 Hz, 2H), 7.38 – 7.33 (t, *J* =5.0,10.0 Hz ,1H), 7.20 (s, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.11 – 7.05 (m, 2H), 6.86 – 6.79 (m, 4H), 6.49 – 6.43 (m, 2H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 145.38, 136.44, 127.74, 127.11, 126.67, 125.83, 122.63, 122.44, 120.71, 120.17, 119.61, 116.75, 116.26, 110.17, 33.17. HRMS (ESI): Calcd. for $C_{21}H_{16}N_2S$ $[M+H]^+$: 329.1106; found: 329.1101.

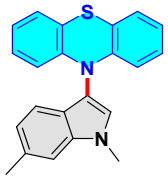
(2) 10-(1,5-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3ba**)



White solid, (71.2 mg, 80% yield), m.p.:188-190 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.4 Hz, 1H), 7.25 (s, 1H),7.17 (d, *J* = 8.8 Hz, 1H), 7.15 (s, 1H), 7.09 – 7.03 (m, 2H), 6.83 (m, *J* = 5.1 Hz, 4H), 6.49 – 6.42 (m, 2H), 3.85 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 145.39, 134.94, 129.60, 127.71, 127.14, 126.63, 126.04, 124.34, 122.37, 120.61, 119.07, 116.28, 116.13, 109.89, 33.20, 21.53. HRMS (ESI): Calcd. for $C_{22}H_{18}N_2S$ $[M+H]^+$: 343.1263; found:

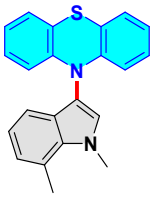
343.1256

(3) 10-(1,6-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3ca**)



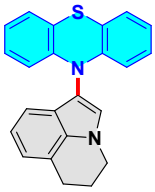
White solid, (75.6 mg, 85% yield), m.p.:198-200 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.0 Hz, 1H), 7.29 (s, 1H), 7.13 (s, 1H), 7.07 (m, 2H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.87 – 6.77 (m, 4H), 6.53 – 6.41 (t, *J* = 5 Hz,2H), 3.85 (s, 3H), 2.58 (s, 3H).^{13}C NMR (125 MHz, Chloroform-*d*) δ 145.43, 136.90, 132.60, 127.11, 127.06, 126.63, 123.65, 122.38, 121.96, 120.62, 119.34, 116.66, 116.24, 110.15, 33.08, 22.04. HRMS (ESI): Calcd. for $C_{22}H_{18}N_2S$ $[M+H]^+$: 343.1263; found: 343.1258.

(4) 10-(1,7-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3da**)



White solid, (64.9 mg, 73% yield); m.p.: 202-204 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.27 (s, 1H), 7.09 (s, 1H), 7.06 – 7.02 (m, 2H), 7.01 – 6.94 (m, 2H), 6.85 – 6.77 (m, 4H), 6.47 – 6.39 (m, 2H), 4.13 (s, 3H), 2.86 (s, 3H).; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 145.29, 135.25, 129.20, 127.12, 127.00, 126.64, 125.31, 122.40, 122.30, 120.64, 120.43, 117.76, 116.52, 116.28, 37.22, 19.95. HRMS (ESI): Calcd. for $C_{22}H_{18}N_2S$ $[M+H]^+$: 343.1263; found: 343.1258.

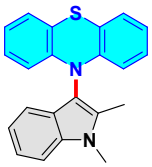
(5) 10-(5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-1-yl)-10*H*-phenothiazine (**3ea**)



White solid, (64.4 mg, 70% yield); m.p.: 188-190 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 7.4 Hz, 1H), 7.20 (s, 1H), 7.10 – 6.98 (m, 4H), 6.82 (m, 4H), 6.54 – 6.43 (m, 2H), 4.27 – 4.18 (t, *J* = 5.0 Hz 2H), 3.10 (t, *J* = 6.1 Hz, 2H), 2.35 (q, *J* = 6.0 Hz, 2H).^{13}C NMR (125 MHz, Chloroform-*d*) δ 145.64, 133.89, 127.13,

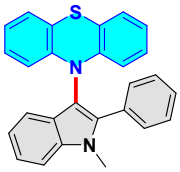
126.67, 125.08, 123.61, 122.58, 122.38, 120.77, 120.53, 119.49, 117.19, 116.76, 116.35, 44.31, 24.69, 22.99.; HRMS (ESI): Calcd. for $C_{23}H_{18}N_2S$ $[M+H]^+$: 355.1263; found: 355.1254.

(6) 10-(1,2-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3fa**)



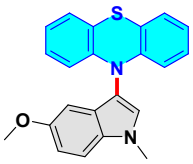
White solid, (44.4 mg, 50% yield); m.p.: 190-193 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 – 7.39 (t, *J* = 10 Hz, 2H), 7.30 – 7.26 (t, *J* = 10 Hz, 1H), 7.14 – 7.09 (t, *J* = 5 Hz ,1H), 7.04 (m, 2H), 6.80 (m, 4H), 6.39 – 6.32 (m, 2H), 3.79 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 144.99, 135.93, 135.04, 127.19, 126.65, 125.55, 122.37, 121.62, 120.73, 120.05, 118.62, 116.10, 113.92, 109.45, 30.08, 9.77. HRMS (ESI): Calcd. for $C_{22}H_{18}N_2S$ $[M+H]^+$: 343.1263; found: 343.1258.

(7) 10-(1-methyl-2-phenyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3ga**)



White solid, (60.0 mg, 57% yield); m.p.: 198-200 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 5.0 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.37 (m, 6H), 7.22 – 7.15 (t, *J* = 10 Hz, 1H), 6.97 (dd, *J* = 7.1, 2.0 Hz, 2H), 6.78 (m, 4H), 6.43 (d, *J* = 5 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 145.02, 138.17, 136.76, 129.89, 129.58, 129.47, 128.59, 128.55, 127.09, 126.61, 125.70, 122.76, 122.29, 120.63, 120.45, 119.55, 117.94, 116.13, 114.52, 110.40, 31.74. HRMS (ESI): Calcd. for $C_{27}H_{20}N_2S$ $[M+H]^+$: 405.1419; found: 405.1413.

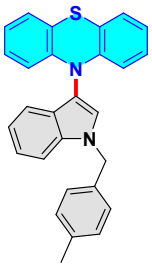
(8) 10-(5-methoxy-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3ha**)



White solid, (61.5 mg, 66% yield); m.p.: 193-195 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 9.1 Hz, 1H), 7.15 (s, 1H), 7.06 (dd, *J* = 5.0, 2H), 6.98

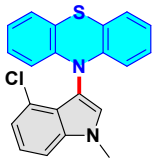
(dd, *J* = 5.1Hz, 1H), 6.83 (m, 5H), 6.50 – 6.43 (dd, *J* = 6.1Hz 2H), 3.85 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 154.69, 145.32, 131.67, 128.05, 127.19, 126.68, 126.38, 122.42, 120.68, 116.33, 116.26, 113.29, 111.14, 100.47, 55.97, 33.34. HRMS (ESI): Calcd. for $C_{22}H_{18}N_2OS$ $[M+H]^+$: 359.1212; found: 359.1206.

(9) 2-chloro-10-(1-(4-methylbenzyl)-1*H*-indol-3-yl)-10*H*-phenothiazine (**3ia**)



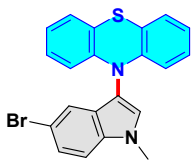
White solid, (54.4 mg, 50% yield); m.p.: 202–205 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 (m, 2H), 7.31 – 7.27 (m, 1H), 7.25 (s, 1H), 7.17 – 7.08 (m, 5H), 7.08 – 7.03 (m, 2H), 6.87 – 6.78 (m, 4H), 6.49 – 6.43 (m, 2H), 5.34 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 145.39, 137.87, 136.10, 133.83, 129.75, 127.21, 127.19, 127.17, 126.71, 126.14, 122.78, 122.47, 120.79, 120.39, 119.77, 117.31, 116.26, 110.73, 50.31, 21.23. HRMS (ESI): Calcd. for $C_{28}H_{22}N_2S$ $[M+H]^+$: 419.1576; found: 419.1567.

(10) 10-(4-chloro-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3ja**)



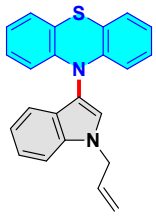
White solid, (40.5 mg, 43% yield); m.p.: 198-200 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.2 Hz, 1H), 7.25 (t, *J* = 7.9 Hz, 1H), 7.21 (s, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 2H), 6.82 (m, 4H), 6.32 (d, *J* = 8.0 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 145.86, 137.72, 128.98, 126.96, 126.36, 126.35, 125.54, 123.43, 122.31, 122.28, 121.35, 120.30, 116.48, 108.62, 33.47. HRMS (ESI): Calcd. for $C_{21}H_{15}ClN_2S$ $[M+H]^+$: 363.0717; found: 363.0712.

(11) 10-(5-bromo-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3ka**)



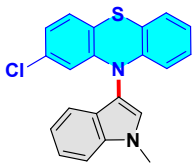
White solid，(31.7 mg, 30% yield); m.p.: 118-120 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 1.8 Hz, 1H), 7.40 (dd, *J* = 8.7,1.4 Hz, 1H), 7.33 (d, *J* = 8.7 Hz, 1H), 7.20 (s, 1H),7.09 – 7.02 (m, 2H), 6.88 – 6.77 (m, 4H), 6.40 – 6.35 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 145.04, 135.13, 129.12, 127.53, 127.21, 126.81, 125.75, 122.65, 121.86, 120.85, 116.27, 116.09, 114.01, 111.79, 33.43. HRMS (ESI): Calcd. for $C_{21}H_{15}BrN_2S$ $[M+H]^+$: 407.0212; found: 407.0204.

(12) 10-(1-allyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3la**)



White solid, (40.5 mg, 44% yield); m.p.: 128-130 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 8.2 Hz, 1H), 7.27 (s, 1H), 7.19 – 7.13 (t, *J* = 10.0 Hz 1H), 7.11 – 7.03 (m, 2H), 6.88 – 6.76 (m, 4H), 6.46 (m, 2H), 6.16 – 5.94 (m, 1H), 5.28 (d, *J* = 10.3 Hz, 1H), 5.18 (d, *J* = 17.1 Hz, 1H), 4.81 (d, *J* = 5.4, Hz, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 145.37, 135.89, 133.12, 127.15, 126.83, 126.71, 126.04, 122.69, 122.47, 120.79, 120.33, 119.75, 118.00, 117.24, 116.23, 110.56, 49.10. HRMS (ESI): Calcd. for $C_{23}H_{18}N_2S$ $[M+H]^+$: 355.1263; found: 355.1257..

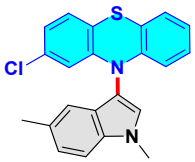
(13) 2-chloro-10-(1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3ab**)



White solid, (48.0 mg, 51% yield); m.p.: 178-180 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 – 7.42 (dd, *J* = 5 Hz,2H), 7.34 (t, *J* = 8.2, Hz, 1H), 7.20 (s, 1H), 7.16 (t, *J* = 7.9, Hz, 1H), 7.06 – 7.00 (m, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.85 – 6.80 (m, 2H), 6.78 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.42 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (125 MHz,

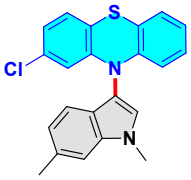
Chloroform-*d*) δ 146.57, 144.71, 136.50, 132.99, 127.69, 127.32, 127.28, 126.69, 125.36, 122.93, 122.85, 122.30, 120.48, 120.43, 119.32, 119.28, 116.58, 116.26, 116.06, 110.29, 33.29. HRMS (ESI): Calcd. for $C_{21}H_{15}ClN_2S$ $[M+H]^+$: 363.0717; found: 363.0709.

(14)2-chloro-10-(1,5-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3bb**)



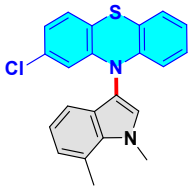
White solid, (78.2 mg, 80% yield); m.p.: 208-210 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.4 Hz, 1H), 7.24 (s, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.15 (s, 1H), 7.04 (t, *J* = 5.5 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.87 – 6.81 (m, 2H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.45 (m, 2H), 3.86 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 146.54, 144.65, 134.98, 132.97, 129.89, 127.62, 127.32, 127.21, 126.62, 125.51, 124.57, 122.84, 122.22, 120.28, 119.13, 118.69, 116.58, 116.24, 115.37, 109.96, 33.27, 21.57. HRMS (ESI): Calcd. For $C_{22}H_{17}ClN_2S$ $[M+H]^+$: 377.0873; found: 377.0867.

(15)2-chloro-10-(1,6-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3cb**)



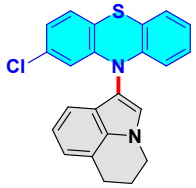
White solid, (74.3 mg, 76% yield); m.p.: 182-184 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.33 (d, *J* = 10.0 Hz 1H), 7.29 (s, 1H), 7.12 (s, 1H), 7.07 – 7.00 (m, 2H), 6.95 (d, *J* = 10.0 Hz 1H), 6.87 – 6.81 (t, *J* = 5.0 Hz 2H), 6.80 (d, *J* = 8.5Hz, 1H), 6.46 (m, 2H), 3.85 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 146.58, 144.72, 136.92, 132.96, 132.77, 127.29, 127.22, 126.94, 126.62, 123.13, 122.85, 122.26, 122.21, 120.29, 119.16, 118.98, 116.55, 116.22, 115.90, 110.23, 33.12, 22.03.; HRMS (ESI): Calcd. for $C_{22}H_{17}ClN_2S$ $[M+H]^+$: 377.0873; found: 377.0867.

(16)2-chloro-10-(1,7-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3db**)



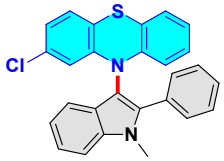
White solid, (79.2 mg, 81% yield); m.p.: 194-196 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.30 – 7.26 (m, 1H), 7.09 (s, 1H), 7.07 – 7.00 (m, 3H), 6.97 – 6.93 (d, *J* = 10.0 Hz 1H), 6.83 (m, 2H), 6.80 (m, 1H), 6.45 (m, 2H), 4.14 (s, 3H), 2.87 (s, 3H). ^{13}C NMR (125MHz, Chloroform-*d*) δ 146.42, 144.55, 135.27, 132.94, 129.05, 127.27, 127.21, 126.61, 126.44, 125.48, 122.86, 122.36, 122.22, 120.67, 120.30, 119.17, 117.33, 116.57, 116.22, 115.70, 37.23, 19.90. HRMS (ESI): Calcd. for $C_{22}H_{17}ClN_2S$ $[M+H]^+$: 377.0873; found: 377.0867.

(17)2-chloro-10-(5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinolin-1-yl)-10*H*-phenothiazine (**3eb**)



White solid, (79.7 mg, 79% yield); m.p.: 183-185 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.28 – 7.25 (d, *J* = 10 Hz 1H), 7.19 (s, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 7.06 – 7.01 (m, 2H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.86 – 6.81 (m, 2H), 6.79 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.50 – 6.46 (m, 2H), 4.26 – 4.20 (t, *J* = 5.0 Hz 2H), 3.10 (t, *J* = 6.1 Hz, 2H), 2.42 – 2.33 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 146.79, 144.94, 133.93, 132.99, 127.30, 127.26, 126.65, 124.97, 123.10, 122.85, 122.65, 122.23, 120.81, 120.45, 119.68, 119.32, 116.83, 116.66, 116.31, 116.00, 44.35, 24.65, 22.92. HRMS (ESI): Calcd. for $C_{23}H_{17}ClN_2S$ $[M+H]^+$: 389.0873; found: 389.0866.

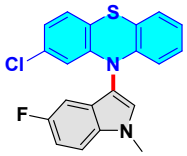
(18)2-chloro-10-(1-methyl-2-phenyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3gb**)



White solid, (51.3 mg, 45% yield); m.p.: 162-164 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.3 Hz, 1H),7.45-7.43(d, *J* = 10.0 Hz,1H)7.40 – 7.35 (m, 6H), 7.24 – 7.17 (m, 1H), 6.95 (m, ,1H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.79 (m, 2H), 6.73

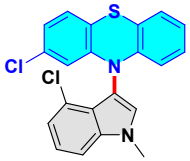
(dd, *J* = 8.1, 2.0 Hz, 1H), 6.43 – 6.471(m, 2H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 146.19, 144.39, 138.09, 136.73, 132.91, 129.84, 129.44, 128.67, 128.65, 127.29, 127.22, 126.62, 125.22, 122.94, 122.79, 122.18, 120.92, 120.15, 119.20, 119.04, 116.47, 116.03, 113.86, 110.54, 31.73. HRMS (ESI): Calcd. for $C_{27}H_{19}ClN_2S$ $[M+H]^+$: 439.1030; found: 439.1025.

(19)2-chloro-10-(5-fluoro-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3mb**)



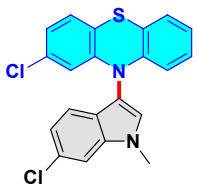
White solid, (63.2 mg, 64% yield); m.p.: 150-152 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 8.7, 4.1 Hz, 1H), 7.24 (s, 1H), 7.13 – 7.04 (m, 2H), 7.07 – 7.00 (m, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.89 – 6.81 (m, 2H), 6.80 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.45 – 6.35 (m, 2H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 158.4 (d, *J* = 236.0 Hz), 146.28, 144.39, 133.06, 133.00, 129.44, 127.36 (d, *J* = 3.8 Hz), 126.79, 125.78, (d, *J* = 9.5 Hz)123.08, 122.44, 120.51, 119.38, 116.39, 116.12, 116.01, 115.97, 111.56 (d, *J* = 26.5Hz), 111.30 (d, *J* = 9.6Hz), 104.95 (d, *J* = 24.0Hz), 33.55. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -122.94. HRMS (ESI): Calcd. for $C_{21}H_{14}ClFN_2S$ $[M+H]^+$: 381.0623; found: 381.0615.

(20) 2-chloro-10-(4-chloro-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3jb**)



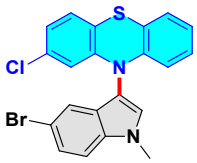
White solid, (61.8 mg, 60% yield); m.p.: 198-200 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.3 Hz, 1H), 7.29 – 7.23 (t, *J* = 8.3 Hz 1H), 7.20 (s, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.03 – 6.98 (m, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.86 – 6.79 (m, 2H), 6.77 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.30 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 146.95, 145.10, 137.73, 132.72, 128.89, 127.14, 126.96, 126.37, 125.32, 123.61, 123.57, 122.77, 122.11, 121.53, 119.90, 118.80, 116.73, 116.42, 115.19, 108.77, 33.51. HRMS (ESI): Calcd. for $C_{21}H_{14}Cl_2N_2S$ $[M+H]^+$: 397.0327; found: 397.0323.

(21) 2-chloro-10-(6-chloro-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (**3nb**)



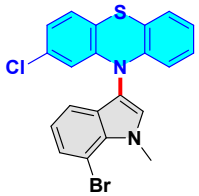
White solid, (67.1 mg, 65% yield); m.p.: 201-203 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 1.8 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.20 (s, 1H), 7.13 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.86 – 6.81 (m, 2H), 6.79 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.37 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 146.30, 144.46, 136.86, 133.02, 129.10, 128.47, 127.38, 127.33, 126.80, 123.88, 123.10, 122.47, 121.33, 120.50, 120.24, 119.35, 116.38, 116.35, 116.12, 110.48, 33.42. HRMS (ESI): Calcd. for $C_{21}H_{14}Cl_2N_2S$ $[M+H]^+$: 397.0327; found: 397.0324.

(22) 10-(5-bromo-1-methyl-1*H*-indol-3-yl)-2-chloro-10*H*-phenothiazine (**3kb**)



White solid, (69.8 mg, 61% yield), m.p.: 185-187 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 (s, 1H), 7.41 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.34 (d, *J* = 8.7 Hz, 1H), 7.21 (s, 1H), 7.03 (m, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.84 (m, 2H), 6.79 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.37 (m, 1H), 6.34 (d, *J* = 2.1 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 146.17, 144.25, 135.17, 133.01, 129.09, 127.39, 126.97, 126.81, 126.00, 123.13, 122.51, 121.51, 120.47, 119.34, 116.36, 116.09, 115.48, 114.26, 111.90, 33.52. HRMS (ESI): Calcd. for $C_{21}H_{14}BrClN_2S$ $[M+H]^+$: 440.9822; found: 440.9816.

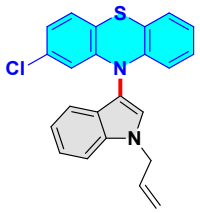
(23) 10-(7-bromo-1-methyl-1*H*-indol-3-yl)-2-chloro-10*H*-phenothiazine (**3ob**)



White solid, (73.2 mg, 64% yield), m.p.: 188-190 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 7.5Hz, 1H), 7.35 (d, *J* = 7.9Hz, 1H), 7.18 (s, 1H), 7.07 – 7.01 (m, 1H), 6.99 – 6.92 (m, 2H), 6.85 – 6.81 (m, 2H), 6.79 (dd, *J* = 8.2, 1.5 Hz, 1H),

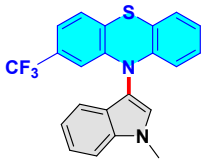
6.36 (m, Hz, 2H), 4.26 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 146.11, 144.28, 133.02, 132.85, 130.74, 128.48, 128.02, 127.37, 127.34, 126.78, 123.11, 122.50, 121.71, 120.50, 119.35, 118.64, 116.46, 116.16, 115.82, 104.98, 37.31. HRMS (ESI): Calcd.for $C_{21}H_{14}BrClN_2S$ $[M+H]^+$: 440.9822; found: 440.9813.

(24) 10-(1-allyl-1*H*-indol-3-yl)-2-chloro-10*H*-phenothiazine (**3lb**)



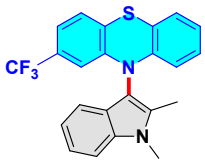
White solid, (40.3 mg, 40% yield), m.p.: 148-150 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 – 7.42 (t, *J* = 10.0 Hz 2H), 7.33 (t, *J* = 7.6 Hz, 1H),7.27(s, 1H) 7.17 (t, *J* = 7.5 Hz, 1H), 7.08 – 7.01 (m, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.90 – 6.79 (m, 2H), 6.79 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.48 – 6.39 (m, 2H), 6.08 (m, 1H), 5.30 (d, *J* = 10.2 Hz, 1H), 5.19 (d, *J* = 17.0 Hz, 1H), 4.82 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 146.52, 144.68, 135.94, 133.03, 133.00, 127.34, 127.29, 126.75, 126.71, 125.54, 122.94, 122.91, 122.32, 120.63, 120.47, 119.42, 119.31, 118.14, 116.53, 116.52, 116.25, 110.65, 49.16.; HRMS (ESI): Calcd. for $C_{23}H_{17}ClN_2S$ $[M+H]^+$: 389.0873; found: 389.0866.

(25) 10-(1-methyl-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (**3ac**)



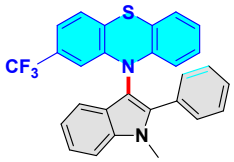
Yellow solid, (75.1 mg, 73% yield), m.p.: 178-180 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.35 (t, *J* = 8.3 Hz, 1H), 7.23 (s, 1H), 7.17 (t, *J* = 8.0, Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.05 (m, 2H), 6.88 – 6.79 (m, 2H), 6.68 (s, 1H), 6.45 – 6.39 (m, 1H), 3.90 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 145.77, 144.71, 136.52, 129.43, (q, *J* = 32.1 Hz,) 127.68, 127.56, 126.76, (d, *J* = 15.5 Hz,) 125.67, 125.26, 125.13，123.01, (d, *J* = 22.4 Hz,) 120.52, 119.83, 119.12, 119.05, (d, *J* = 3.8 Hz,)，119.01，116.71, 115.82, 112.54, (q, *J* = 4.1 Hz,) 110.34, 33.29. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -62.77 HRMS (ESI): Calcd.for $C_{22}H_{15}F_3N_2S$ $[M+H]^+$: 397.0980; found: 397.0974.

(26) 10-(1,2-dimethyl-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (**3fc**)



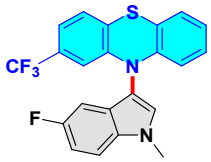
Yellow solid, (71.4 mg, 67% yield), m.p.: 188-190 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.35 (d, *J* = 8.2 Hz 1H), 7.32 – 7.26 (t, *J* = 5.2 Hz ,1H), 7.17 – 7.08 (dd, *J* = 5.2 Hz, 2H), 7.07 – 6.98 (m, 2H), 6.88 – 6.76 (m, 2H), 6.57 (s, 1H), 6.34 – 6.29 (m, 1H), 3.80 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 145.43, 144.27, 136.02, 134.97, 129.52 (q, *J* = 32.1Hz), 127.65, 127.30，126.76 (d, *J* = 14.9 Hz), 125.59, 124.94, 123.04, 121.91, 120.37, 119.80, 119.00 (q, *J* = 3.9 Hz), 118.14, 116.49, 113.04, 112.30 (q, *J* = 3.9 Hz), 109.62, 30.14, 9.81. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -62.79. HRMS (ESI): Calcd. for $C_{23}H_{17}F_3N_2S$ $[M+H]^+$: 411.1137; found: 411.1131.

(27) 10-(1-methyl-2-phenyl-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (**3gc**)



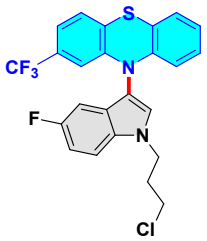
Yellow solid, (85.9 mg, 70% yield), m.p.: 158-160 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.44 – 7.33 (m, 6H), 7.24 – 7.15 (t, *J* = 10.0, Hz 1H), 6.99 (t, *J* = 8.0 Hz, 2H), 6.95 (m, 1H), 6.87 – 6.75 (m, 2H), 6.62 (s, 1H), 6.48 – 6.39 (d, *J* =12, Hz 1H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 145.20, 144.29, 138.18, 136.77, 129.79, 129.35 (d, *J* = 36.2Hz), 128.71, 127.56, 126.66 (d, *J* = 6.5Hz), 125.29, 125.05, 122.99 (d, *J*= 9.2 Hz), 120.96, 119.42, 118.99, 118.90 (d, *J* = 4.0Hz), 116.57, 113.61, 112.26 (d, *J* = 3.9Hz), 110.57, 31.70. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -62.79. HRMS (ESI): Calcd. for $C_{28}H_{19}F_3N_2S$ $[M+H]^+$: 473.1293; found: 473.1291.

(28) 10-(5-fluoro-1-methyl-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (**3mc**)



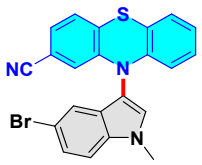
Yellow solid, (69.1 mg, 64% yield), m.p.: 153-155°C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.36 (m, 1H), 7.27 (s, 1H), 7.17 – 7.01 (m, 5H), 6.90 – 6.80 (m, 2H), 6.63 (s, 1H), 6.42 – 6.37 (m, 1H), 3.90 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 158.45 (d, *J* =236.0Hz), 145.50, 144.38, 133.10, 129.54 (d, *J* =17.4Hz), 127.60, 126.88 (d, *J* =13.0Hz), 125.72 (d, *J* =9.5Hz), 123.26, 119.91, 119.21 (q, *J* = 3.9 Hz), 119.17, 116.52, 115.78 (d, *J* = 4.7 Hz), 112.37 (q, *J* = 3.9 Hz), 111.66 (d, *J* = 26.4 Hz), 111.37 (d, *J* = 9.6 Hz), 103.93 (d, *J* = 24.0 Hz), 33.59. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -62.78, -122.94. HRMS (ESI): Calcd. for $C_{22}H_{14}F_4N_2S$ $[M+H]^+$: 415.0886; found: 415.0880.

(29) 10-(1-(3-chloropropyl)-5-fluoro-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (**3pc**)



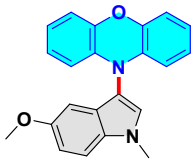
Yellow solid, (74.3 mg, 60% yield), m.p.: 198-200 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 (dd, *J* = 8.8, 4.1 Hz, 1H), 7.38 (s, 1H), 7.15 – 7.05 (m, 4H), 7.07 – 7.01 (m, 2H), 6.90 – 6.83 (m, 2H), 6.57 (s, 1H), 6.41 – 6.34 (m, 1H), 4.44 (t, *J* = 6.4 Hz, 2H), 3.55 – 3.46 (t, *J* = 6.4 Hz, 2H), 2.35 (quint, *J* = 11.8, 6.3 Hz, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 158.50 (d, *J* = 236.7Hz), 145.38, 144.20, 132.25, 129.48(d, *J* = 32.1Hz), 128.76, 127.64, 126.93 (d, *J* = 8.9Hz), 125.98, 125.91, 125.85, 123.33, 119.92, 119.26 (q, *J* = 3.9Hz), 116.36, 116.34, 112.25 (q, *J* = 4.0Hz), 111.96 (d, *J* = 26.5Hz), 111.44 (d, *J* = 9.5Hz), 104.21 (d, *J* = 24.0Hz), 43.60, 41.50, 32.55. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -62.90, -122.47. HRMS (ESI): Calcd. for $C_{24}H_{17}ClF_4N_2S$ $[M+H]^+$: 477.0809; found: 477.0803.

(30) 10-(5-bromo-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine-2-carbonitrile (**3kd**)



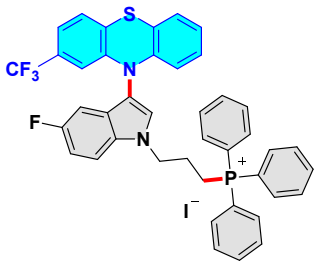
Yellow solid, (48.2 mg, 43% yield), m.p.: 208-210 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 1.9 Hz, 1H), 7.43 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 1H), 7.18 (s, 1H), 7.04 (d, *J* = 1.0 Hz, 2H), 7.01 – 6.96 (m, 1H), 6.88 – 6.80 (m, 2H), 6.48 (s, 1H), 6.40 – 6.33 (m, 1H), 3.90 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 145.40, 143.49, 135.28, 128.87, 127.91, 127.84, 126.99, 126.75, 126.44, 126.25, 125.99, 123.48, 121.15, 119.07, 119.05, 118.25, 116.45, 114.67, 114.46, 112.10, 110.40, 33.55. HRMS (ESI): Calcd. for $C_{22}H_{14}BrN_3S$ $[M+H]^+$: 432.0164; found: 432.0159.

(31) 10-(5-methoxy-1-methyl-1*H*-indol-3-yl)-10*H*-phenoxazine (**3he**)



White solid, (35.6 mg, 40% yield), m.p.: 176-178 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.9 Hz, 1H), 7.10 (s, 1H), 6.95 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.87 (d, *J* = 2.4 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 2H), 6.64 (t, *J* = 7.6 Hz, 2H), 6.61 – 6.55 (t, *J* = 10.0Hz, 2H), 6.13 (d, *J* = 7.8 Hz, 2H), 3.85 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 154.67, 144.47, 134.96, 132.01, 128.34, 125.30, 123.52, 121.18, 115.33, 113.70, 113.42, 112.84, 110.88, 99.93, 55.98, 33.43. HRMS (ESI): Calcd. fo $C_{22}H_{18}N_2O_2$ $[M+H]^+$: 343.1441; found: 343.1437.

(32) (3-(5-fluoro-3-(2-(trifluoromethyl)-10*H*-phenothiazin-10-yl)-1*H*-indol-1-yl)propyl)triphenylphosphonium (**5pca**)



Yellow solid, (69.0 mg, 32% yield), m.p.: 243-245 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 – 7.63 (m, 9H), 7.60 – 7.47 (m, 8H), 7.07 (d, *J* = 7.9 Hz, 1H),

7.03 – 6.90 (m, 4H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.69 (t, *J* = 7.8 Hz, 1H), 6.45 (s, 1H), 6.28 (d, *J* = 8.3 Hz, 1H), 4.81 (t, *J* = 6.7 Hz, 2H), 3.95 – 3.81 (t, *J* = 6.7 Hz ,2H), 2.23 (m, 2H).^{13}C NMR (125 MHz, Chloroform-*d*) δ158.36 (d, *J* = 236.5Hz) 145.33, 144.05, 135.26 (d, *J* = 2.9Hz), 133.59 (d, *J* = 9.9Hz), 132.09, 130.61, 130.51, 128.87, 127.44, 126.84 (d, *J* = 15.8Hz), 123.22, 119.97, 119.05 (d, *J* = 3.9Hz), 117.85, 117.17, 116.36, 112.60(d, *J* = 9.6Hz) , 111.98, 111.77, 103.77 (d, *J* = 23.7Hz), 46.17 (d, *J* = 19.2Hz), 23.55 (d, *J* = 3.5Hz), 20.22 (d, *J* = 52.4Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -62.79, -122.44. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 24.47. HRMS (ESI): Calcd. fo $C_{42}H_{32}F_4IN_2PS$ $[M\text{-}I^-]^+$: 703.1959; found: 703.1943.

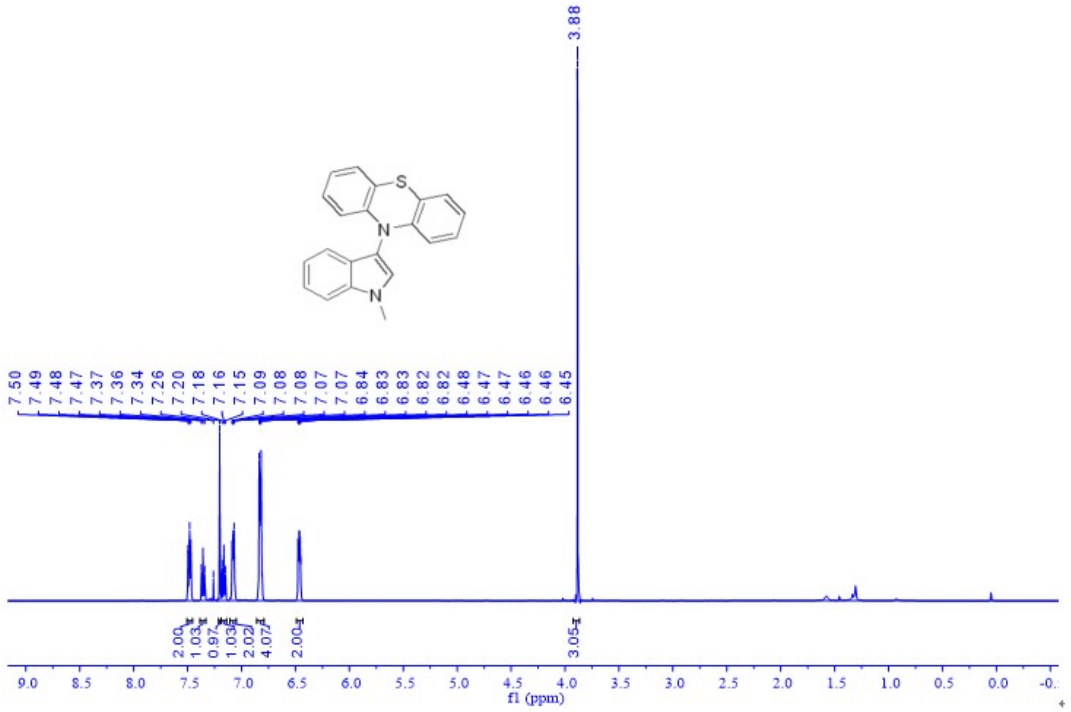
9. References

1 T. Liang, L. Gong, H. Zhao, H. Jiang and M. Zhang, *Chem. Commun.,* 2020, **56**, 2807–2810.

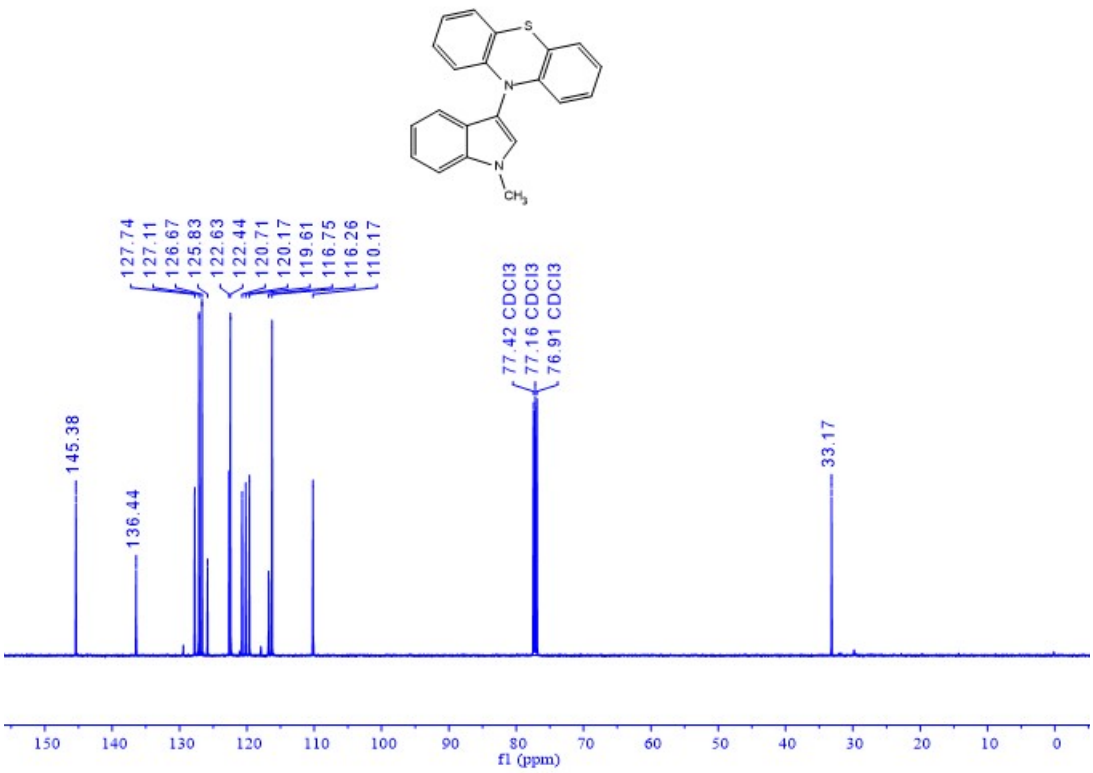
2 M. Li, S. A. Nyantakyi, P. Gopal, D. Aziz, T. Dick and M.-L. Go, *ACS Med. Chem. Lett.,* 2017, **8**, 1165–1170.

10. NMR spectra of the obtained compounds

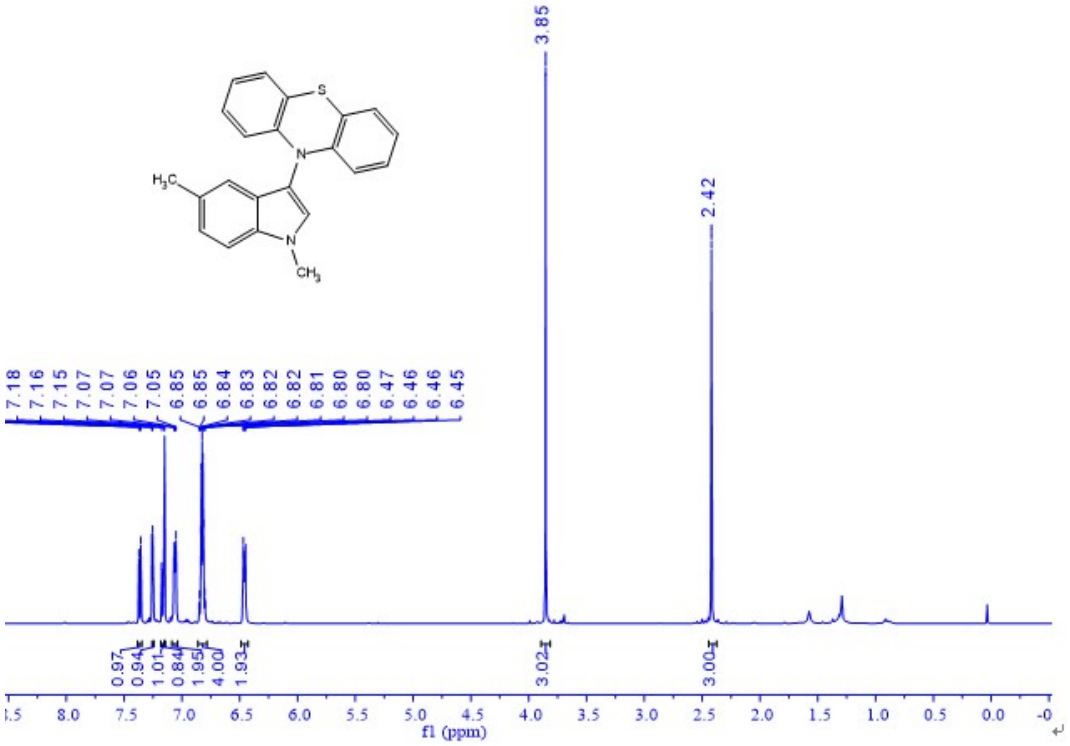
(1) ^{1}H-NMR spectrum of 10-(1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3aa)



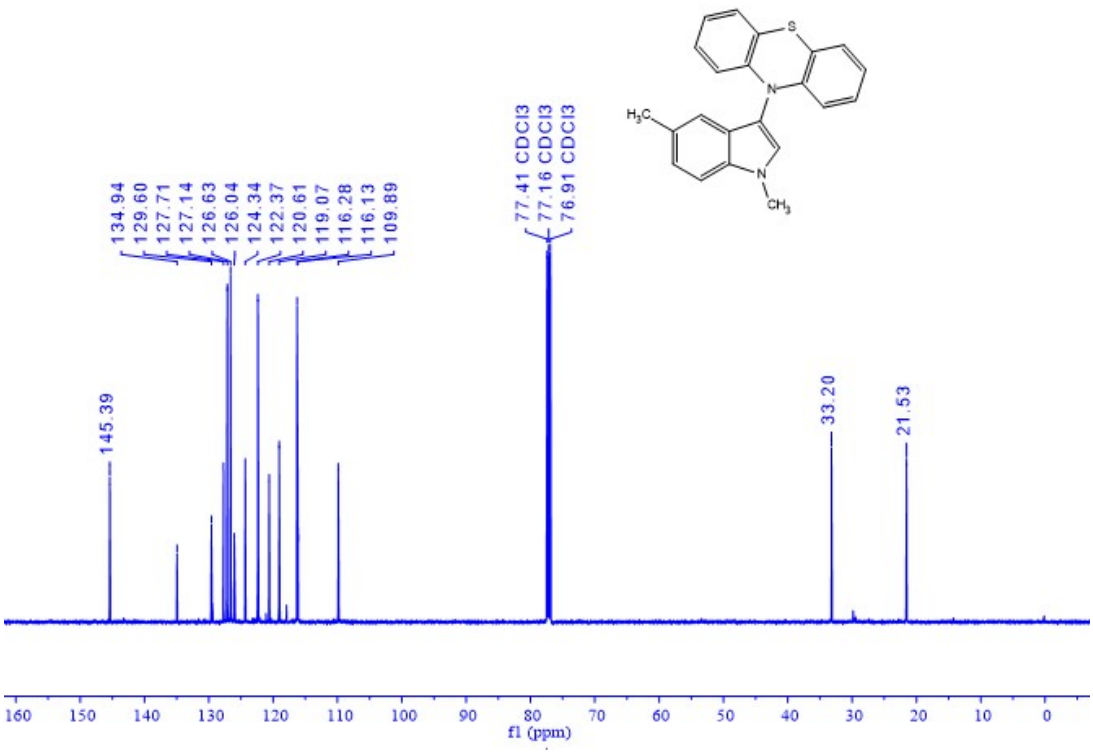
(2) ^{13}C-NMR spectrum of 10-(1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3aa)



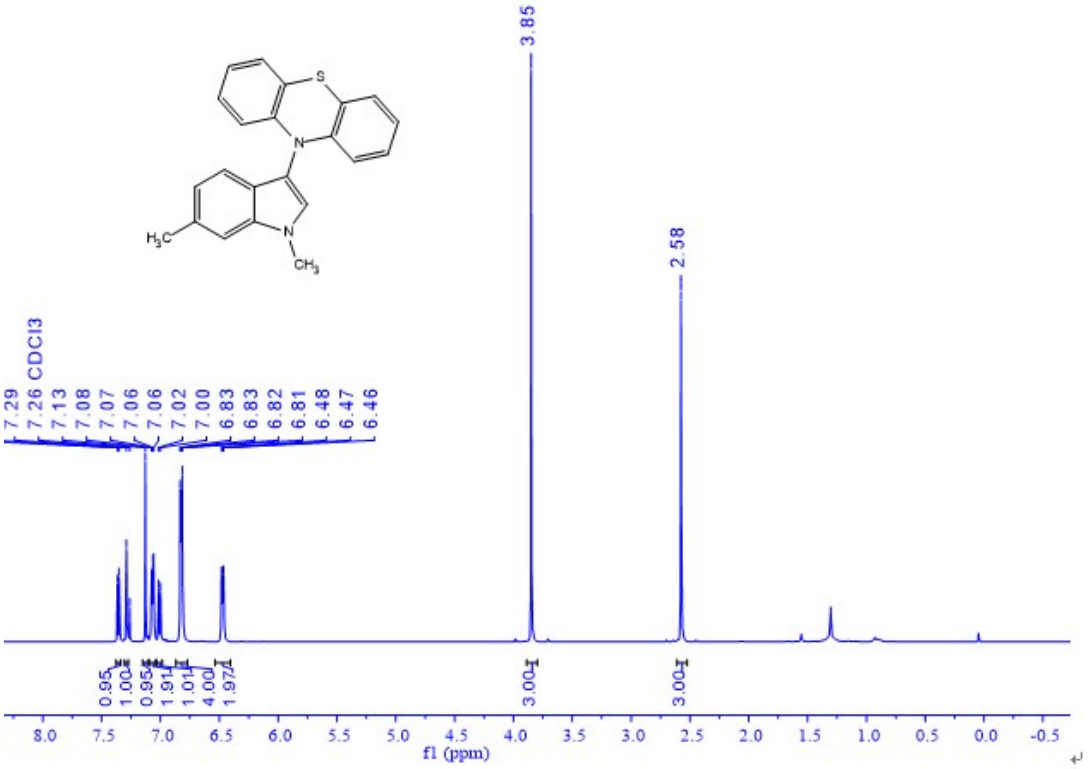
(3) ^{1}H-NMR spectrum of 10-(1,5-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3ba)



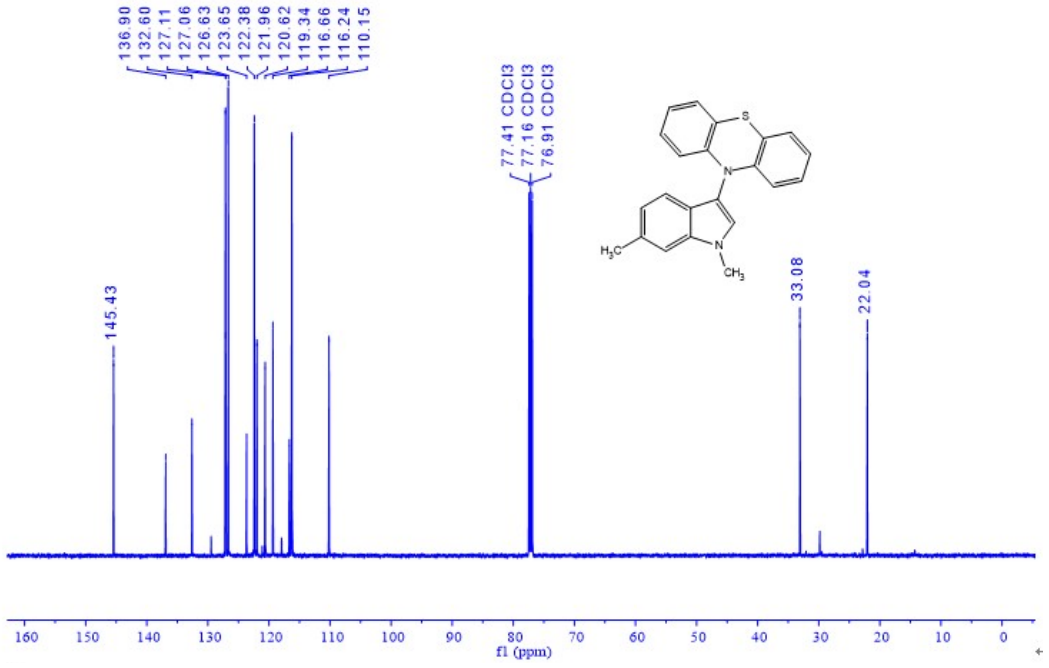
(4) ^{13}C-NMR spectrum of 10-(1,5-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3ba)



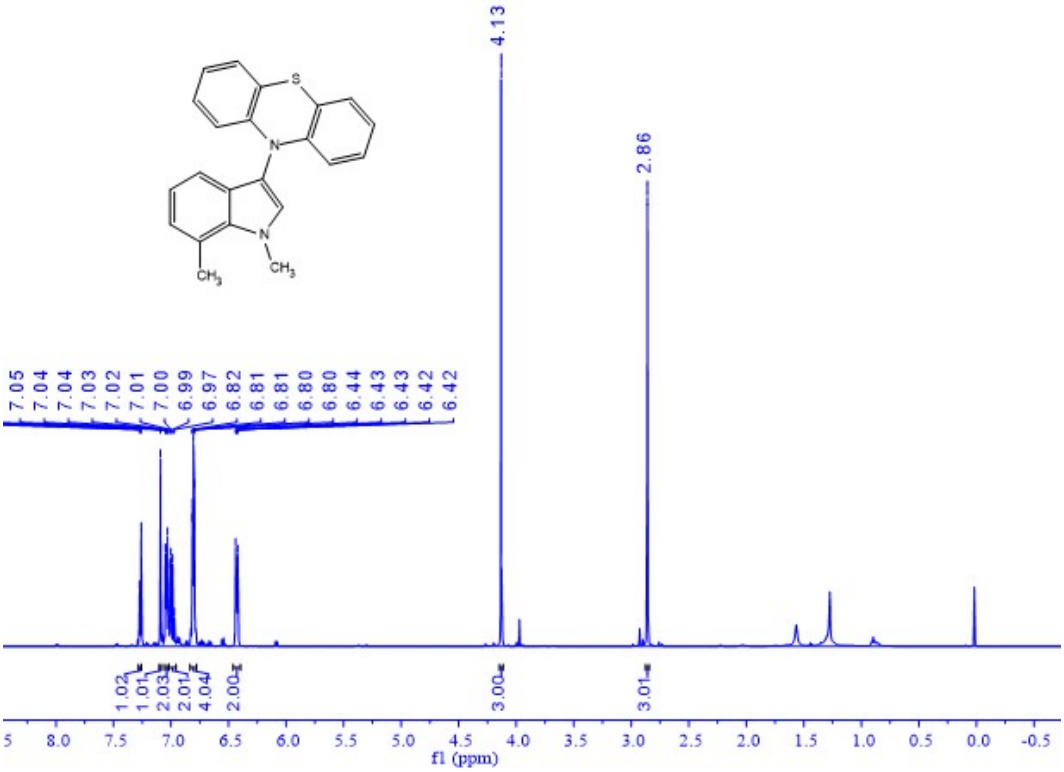
(5) ^{1}H-NMR spectrum of 10-(1,6-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3ca)



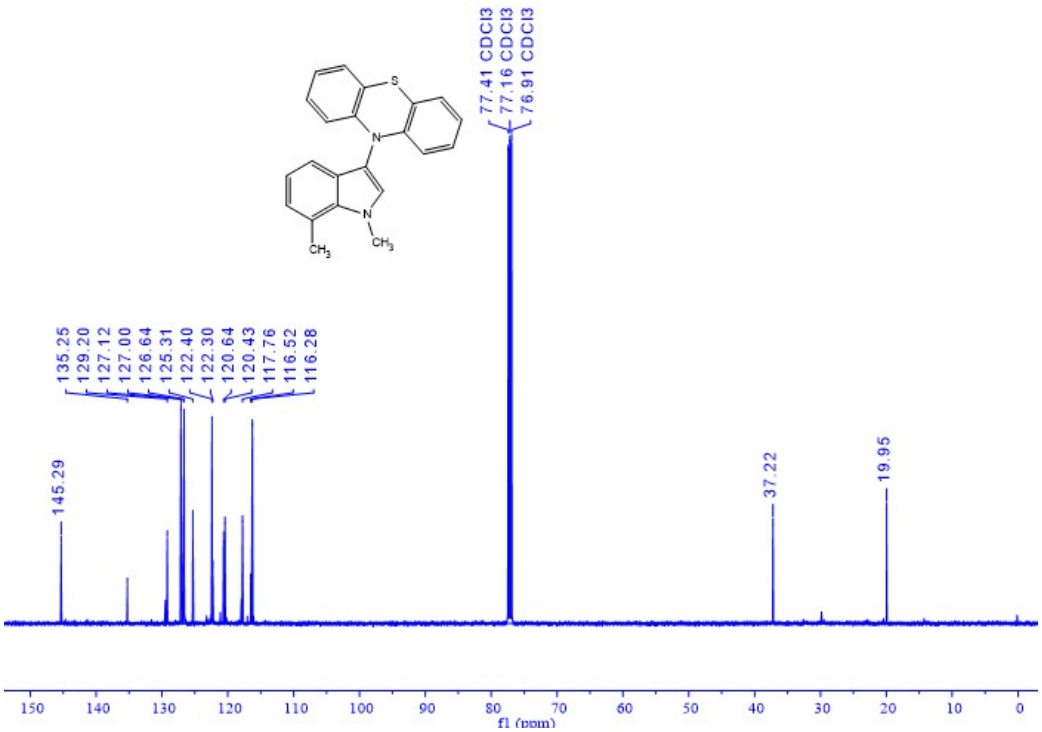
(6) ^{13}C-NMR spectrum of 10-(1,6-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3ca)



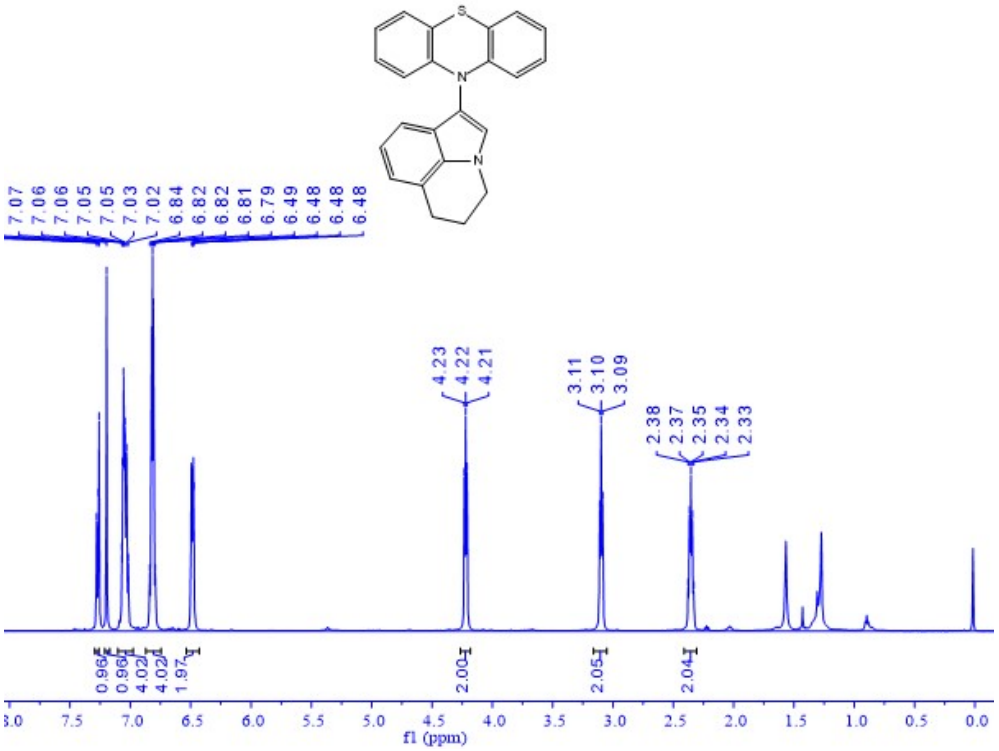
(7) ^{1}H-NMR spectrum of 10-(1,7-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3da)



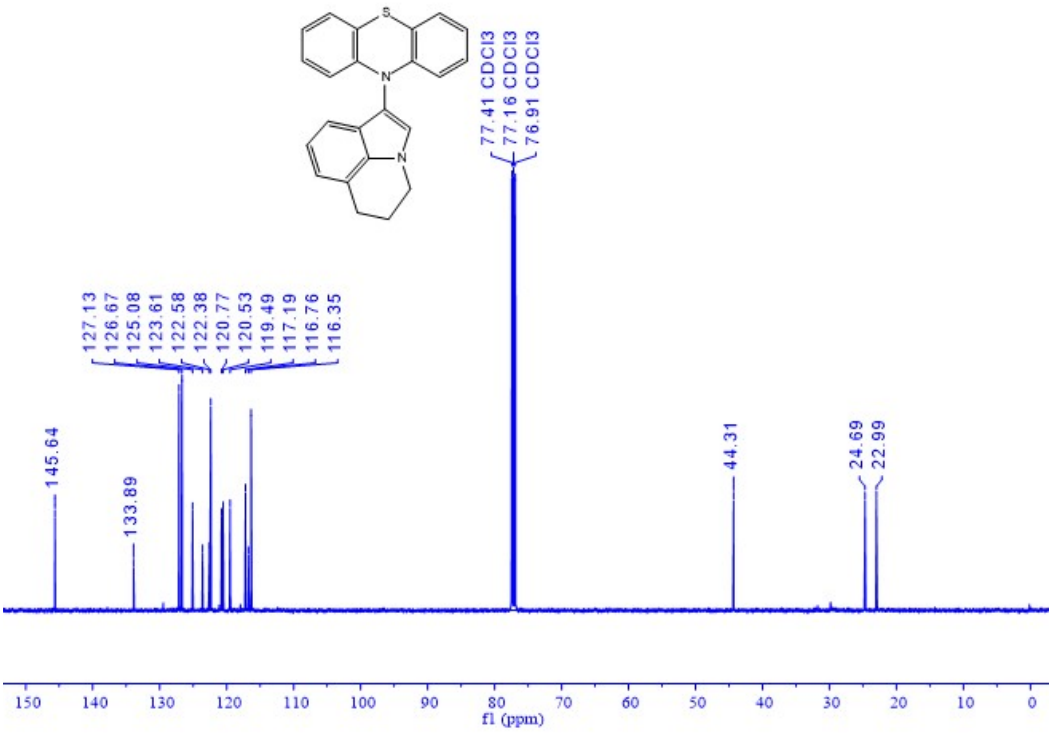
(8) ^{13}C-NMR spectrum of 10-(1,7-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3da)



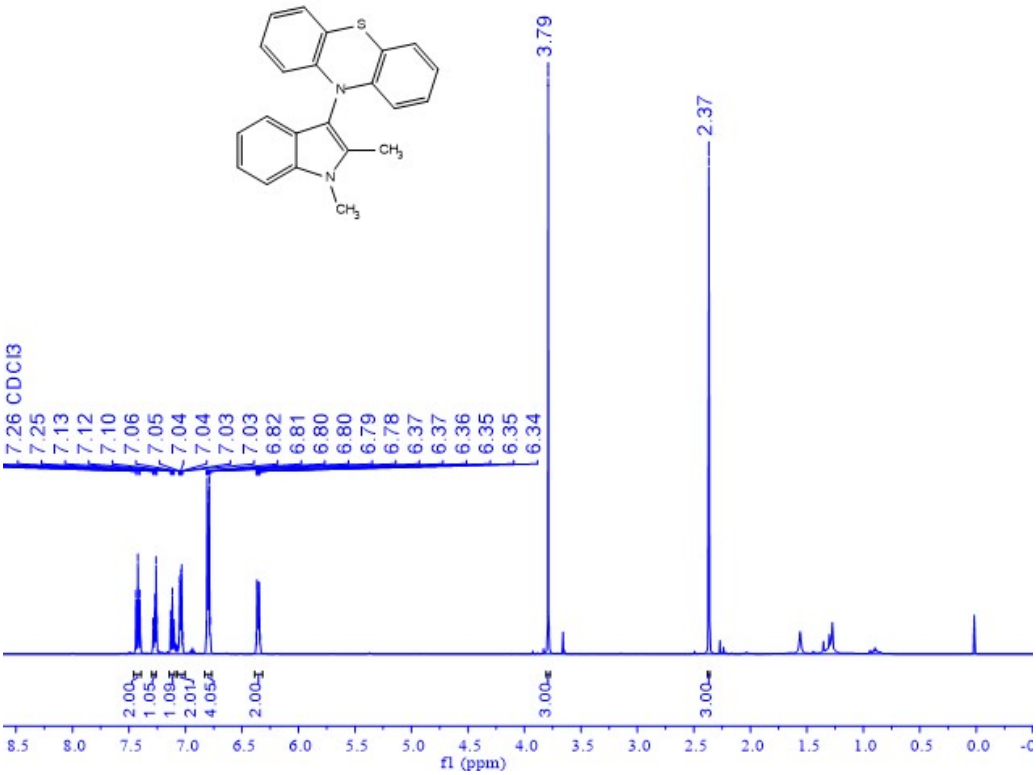
(9) ^{1}H-NMR spectrum of 10-(5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinolin-1-yl)-10*H*-phenothiazine (3ea)



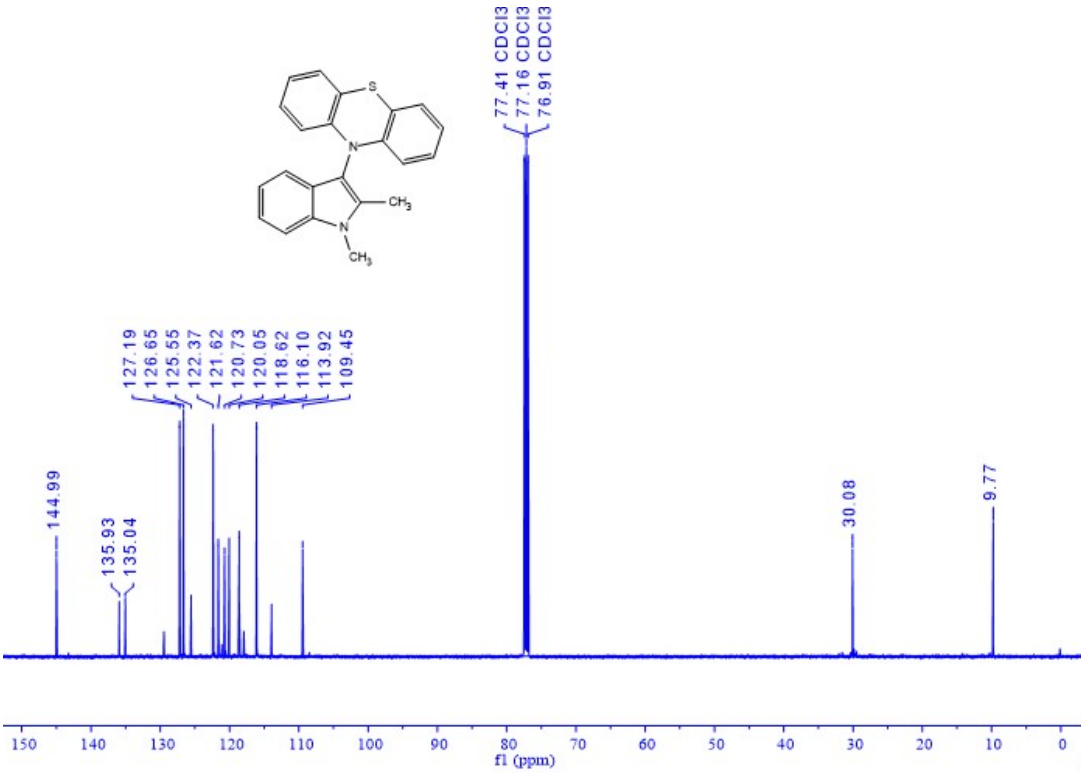
(10) ^{13}C-NMR spectrum of 10-(5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinolin-1-yl)-10*H*-phenothiazine (3ea)



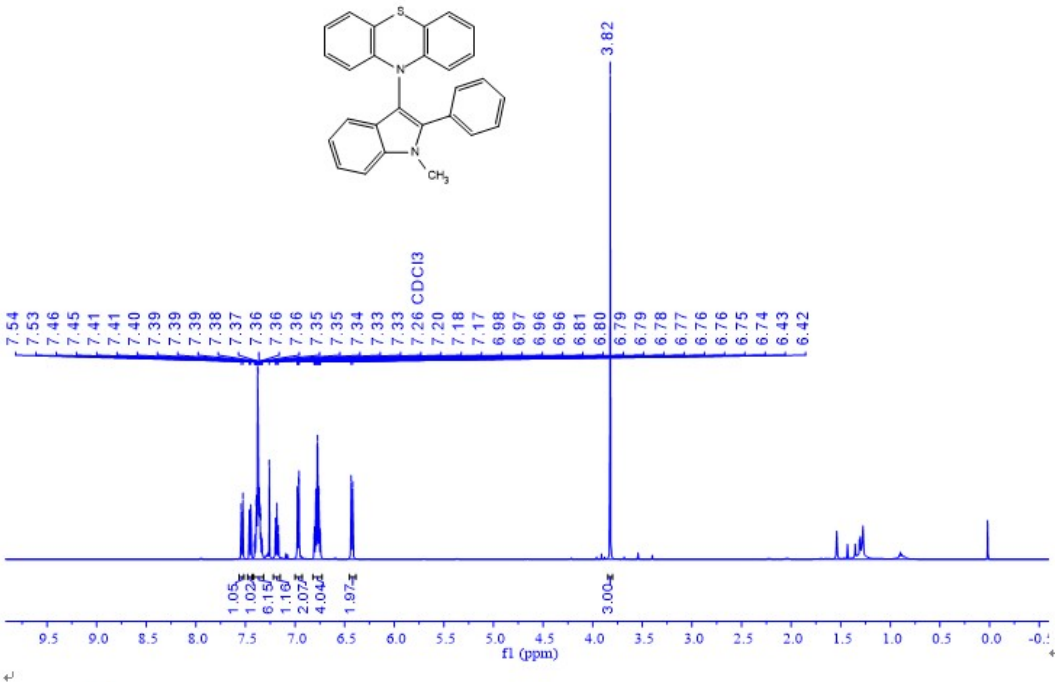
(11) ^{1}H-NMR spectrum of 10-(1,2-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3fa)



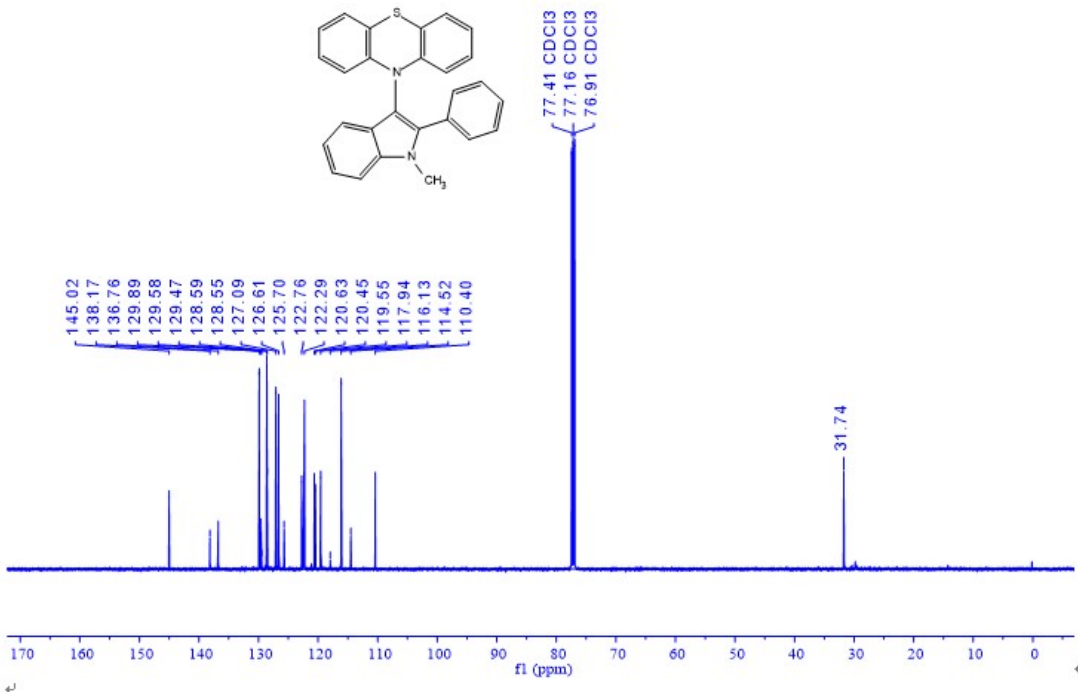
(12) ^{13}C-NMR spectrum of 10-(1,2-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3fa)



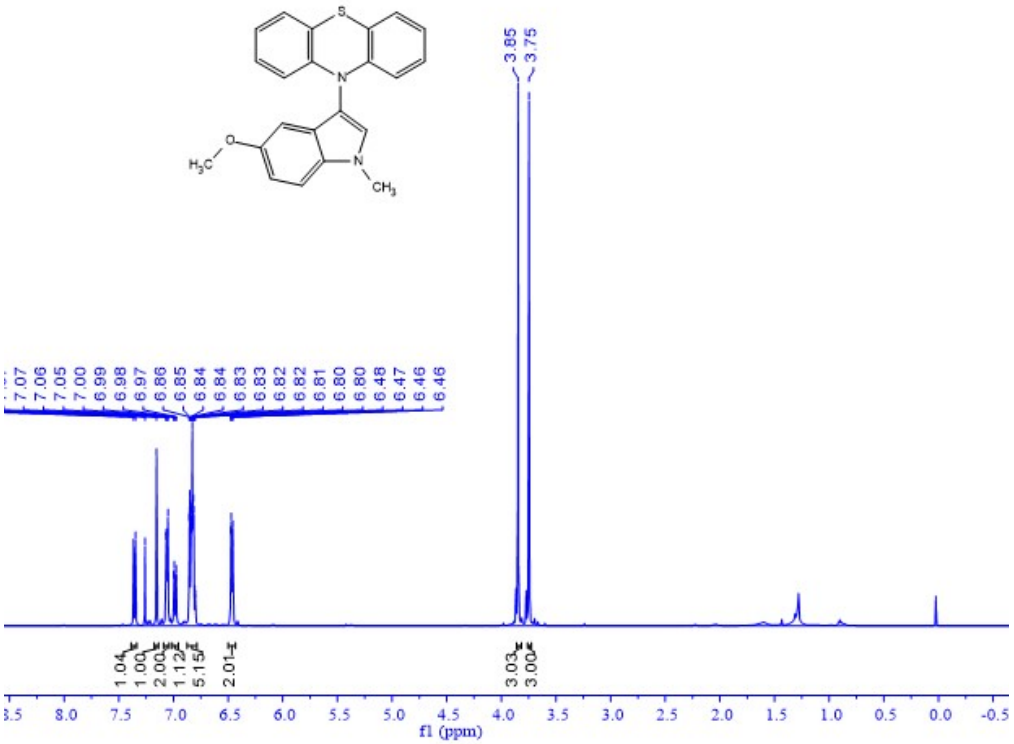
(13) ^{1}H-NMR spectrum of 10-(1-methyl-2-phenyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3ga)



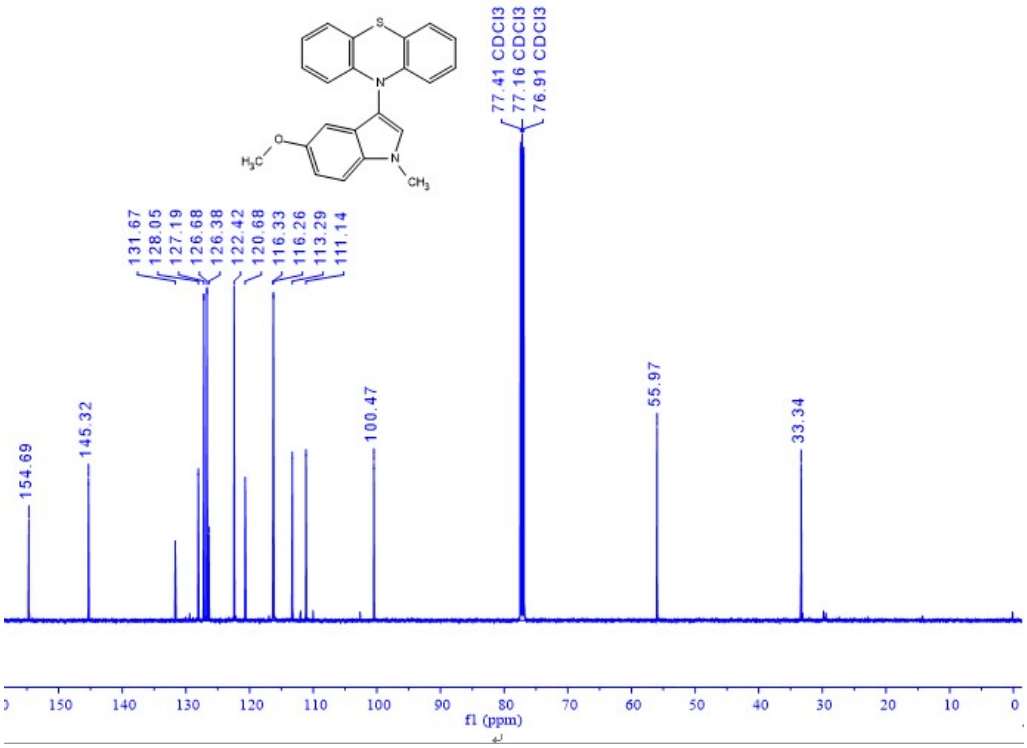
(14) ^{13}C-NMR spectrum of 10-(1-methyl-2-phenyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3ga)



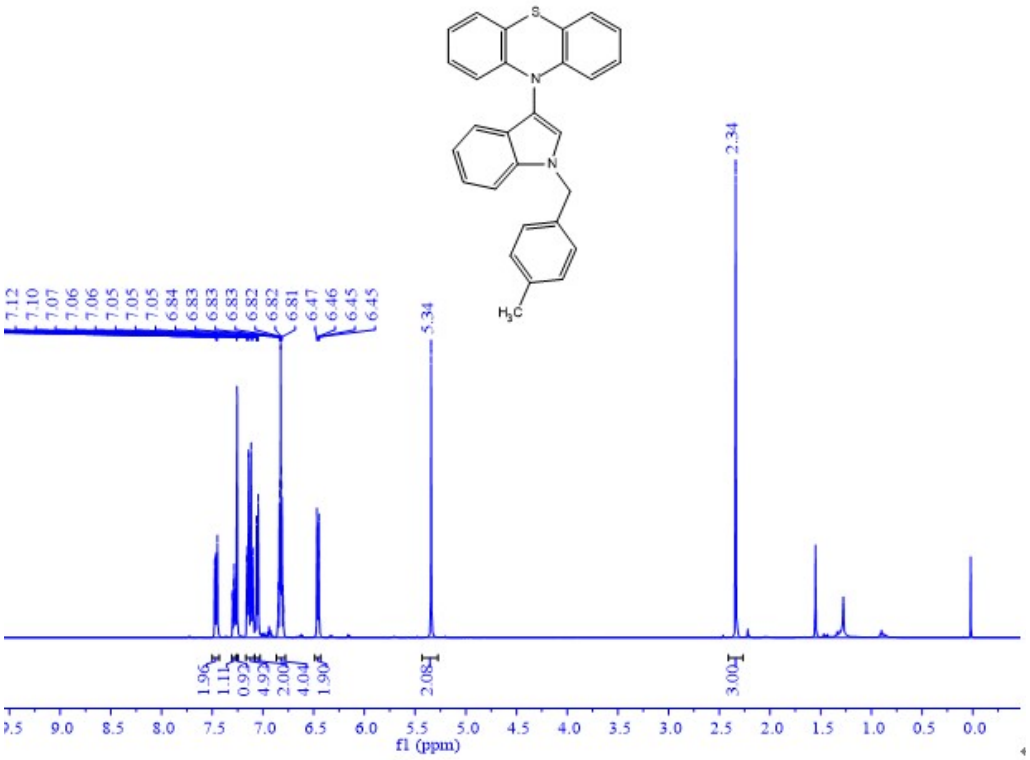
(15) ^{1}H-NMR spectrum of 10-(5-methoxy-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3ha)



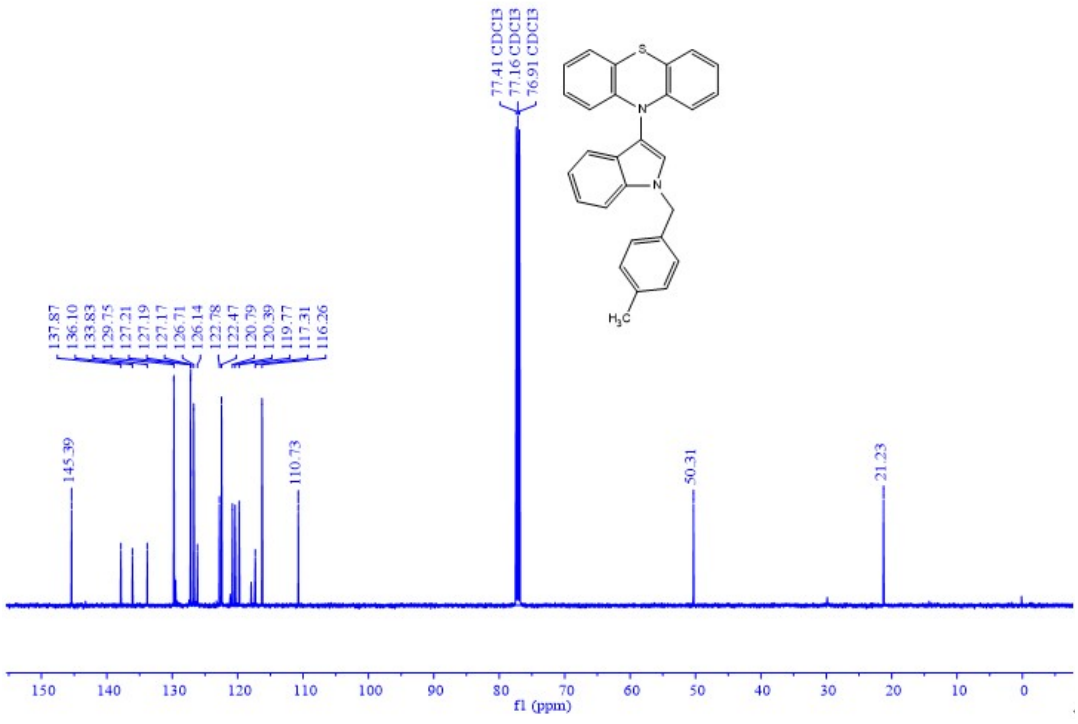
(16) ^{13}C-NMR spectrum of 10-(5-methoxy-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3ha)



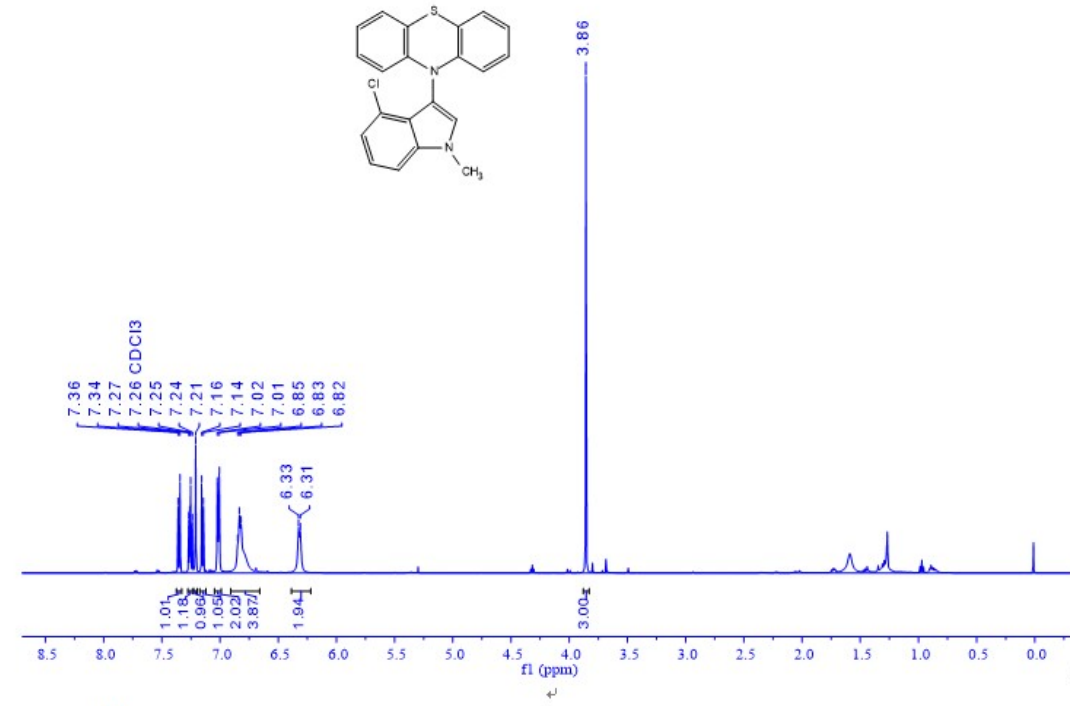
(17) ^{1}H-NMR spectrum of 2-chloro-10-(1-(4-methylbenzyl)-1*H*-indol-3-yl)-10*H*-phenothiazine (3ia)



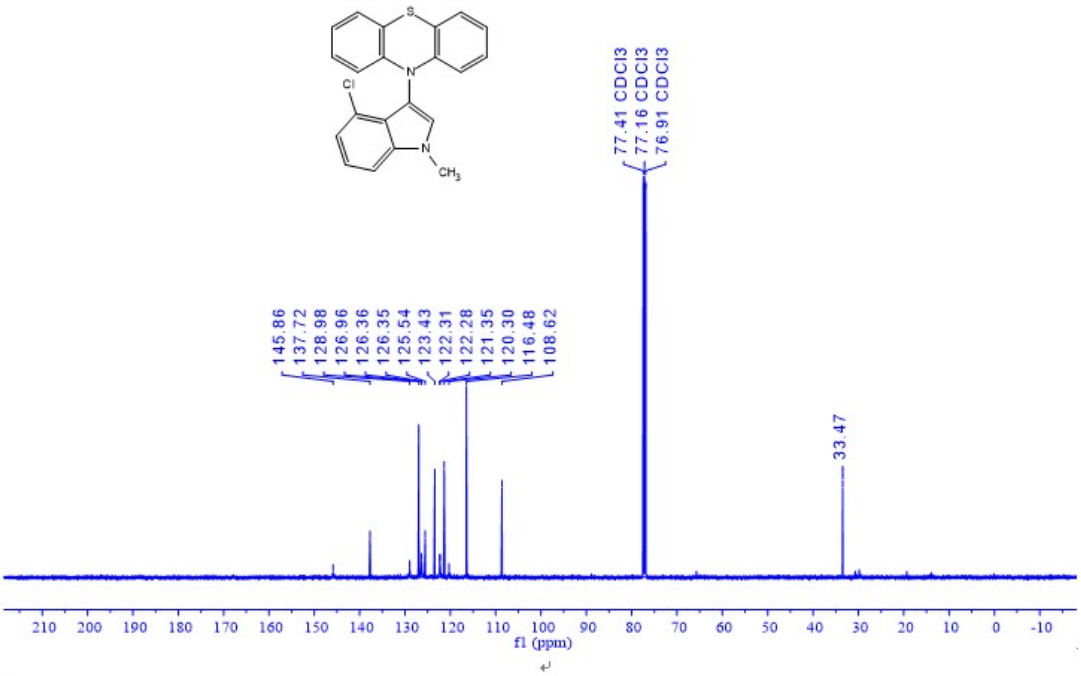
(18) ^{13}C-NMR spectrum of 2-chloro-10-(1-(4-methylbenzyl)-1*H*-indol-3-yl)-10*H*-phenothiazine (3ia)



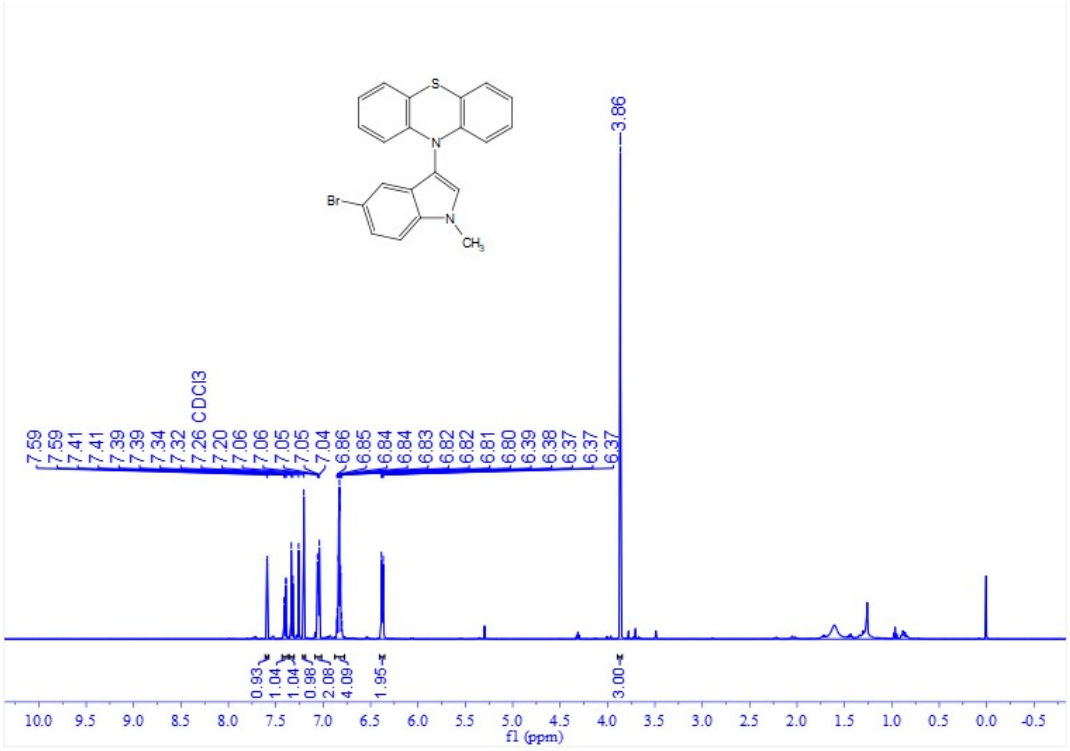
(19) ^{1}H-NMR spectrum of 10-(4-chloro-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3ja)



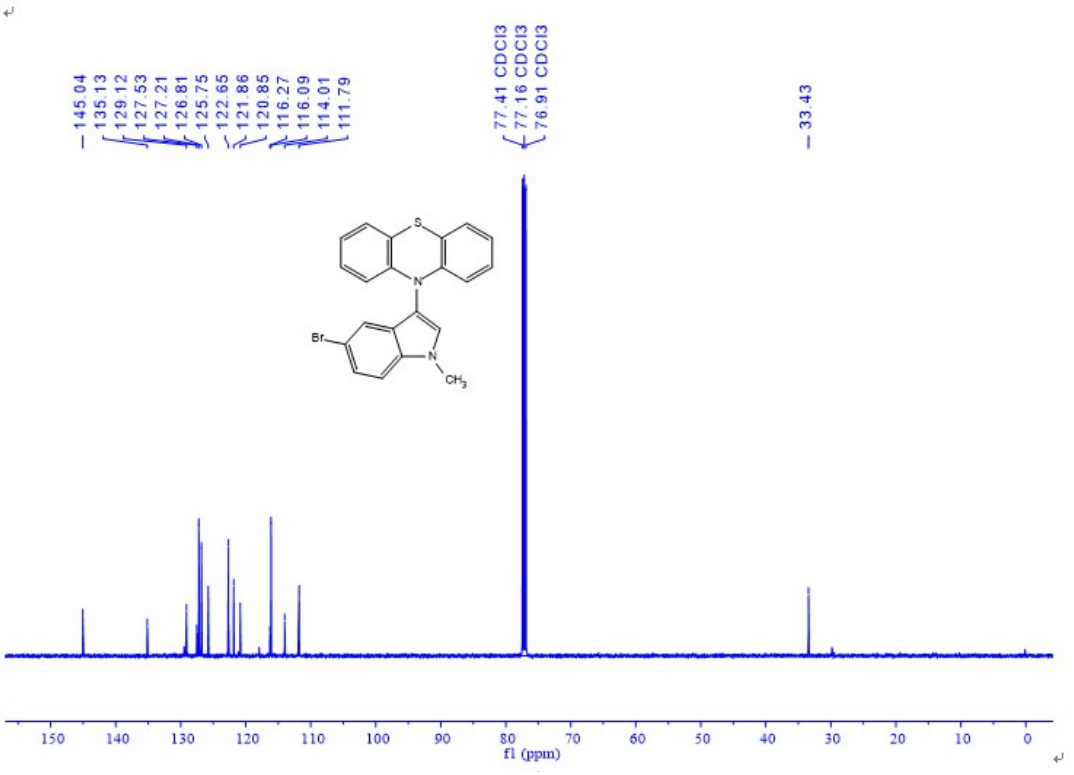
(20) ^{13}C-NMR spectrum of 10-(4-chloro-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3ja)



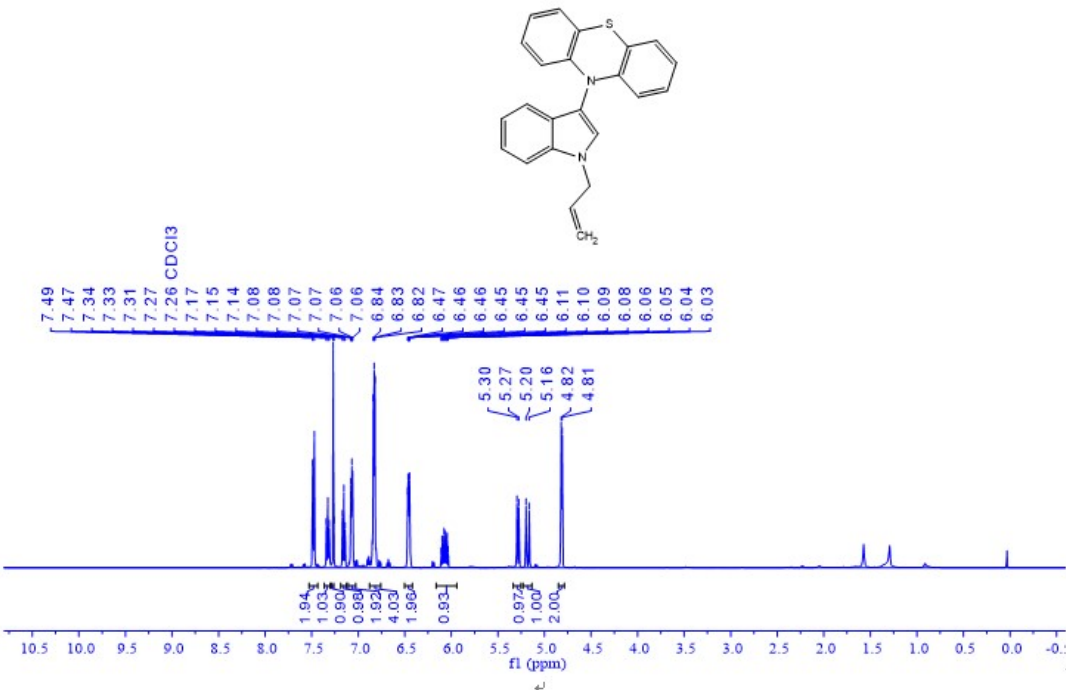
(21) ^{1}H-NMR spectrum of 10-(5-bromo-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3ka)



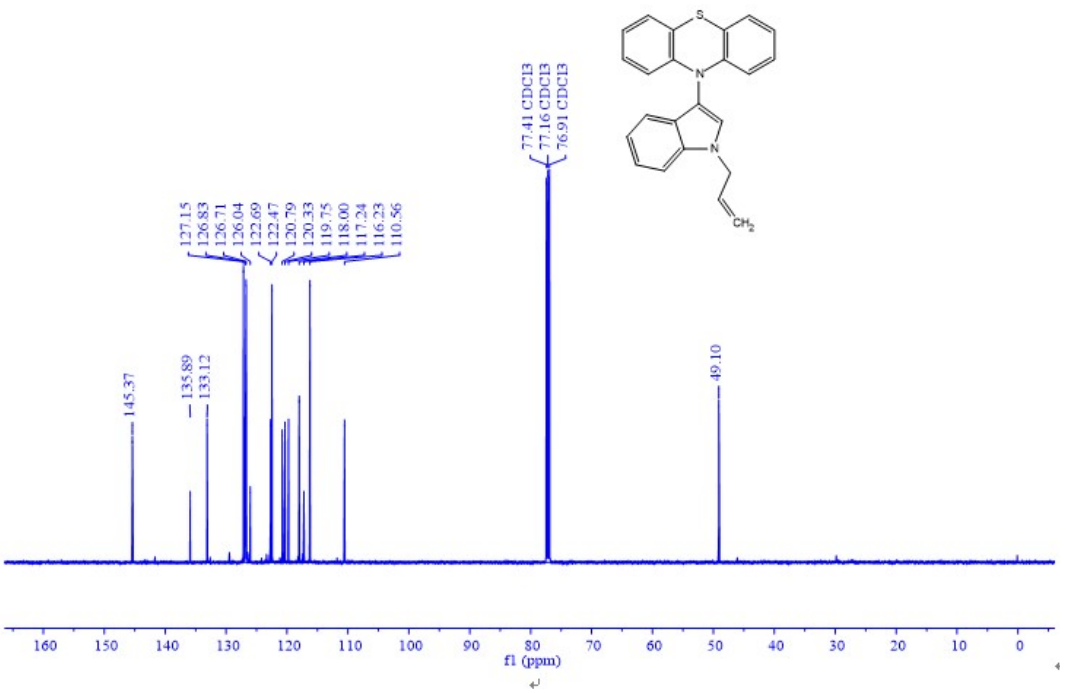
(22) ^{13}C-NMR spectrum of 10-(5-bromo-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3ka)



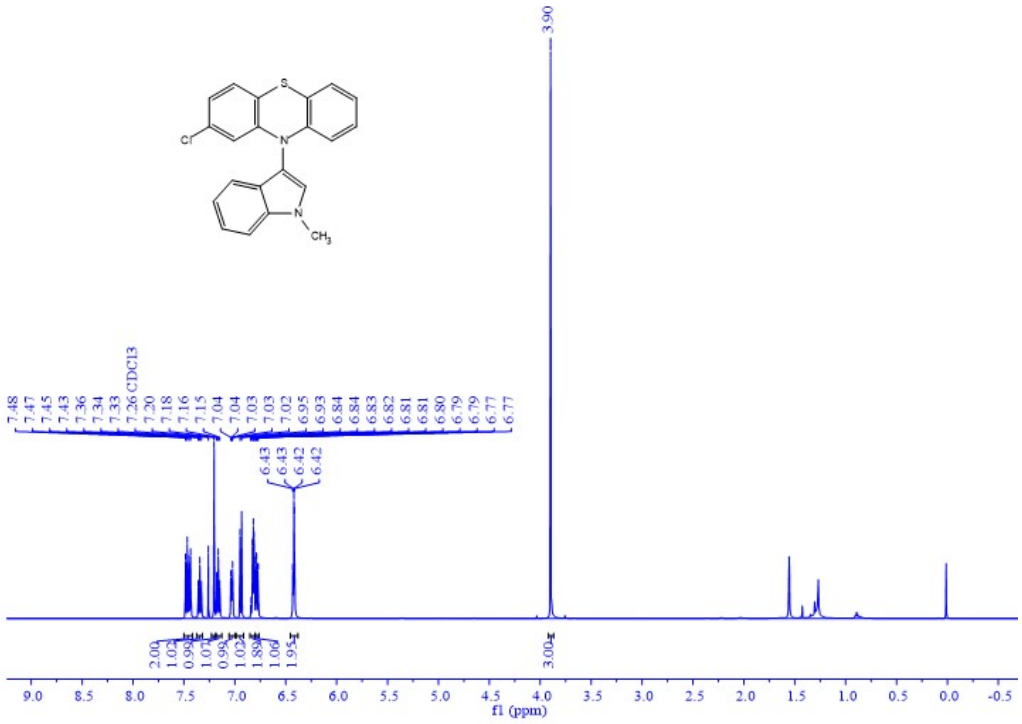
(23) ^{1}H-NMR spectrum of 10-(1-allyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3la)



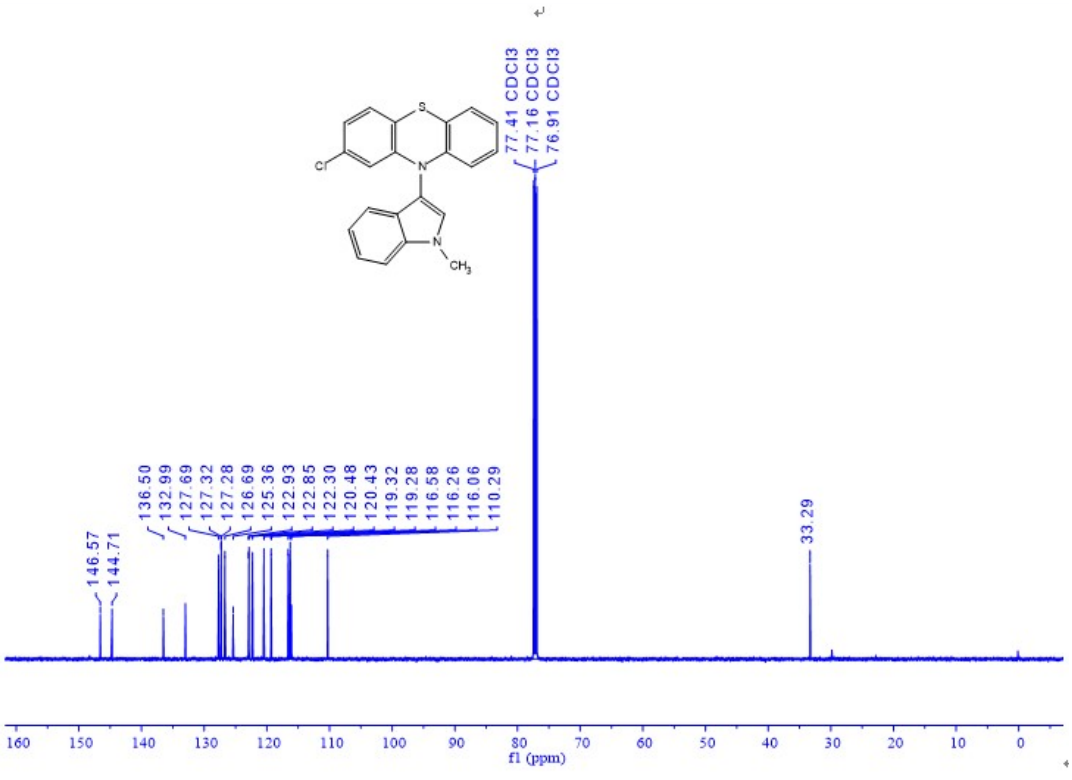
(24) ^{13}C-NMR spectrum of 10-(1-allyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3la)



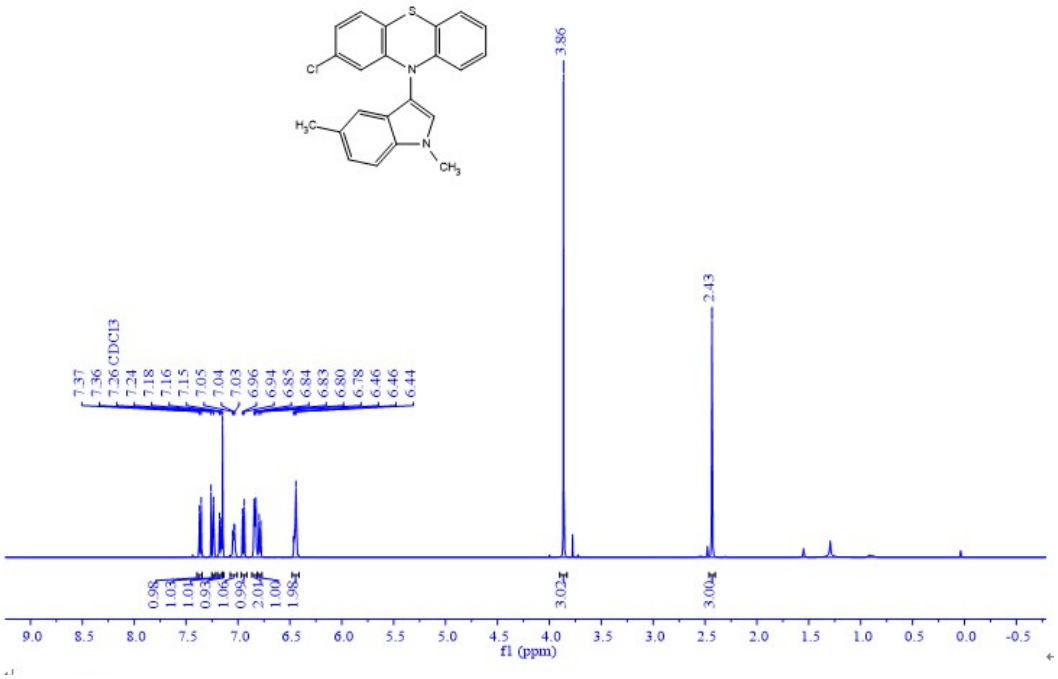
(25) ^{1}H-NMR spectrum of 2-chloro-10-(1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3ab)



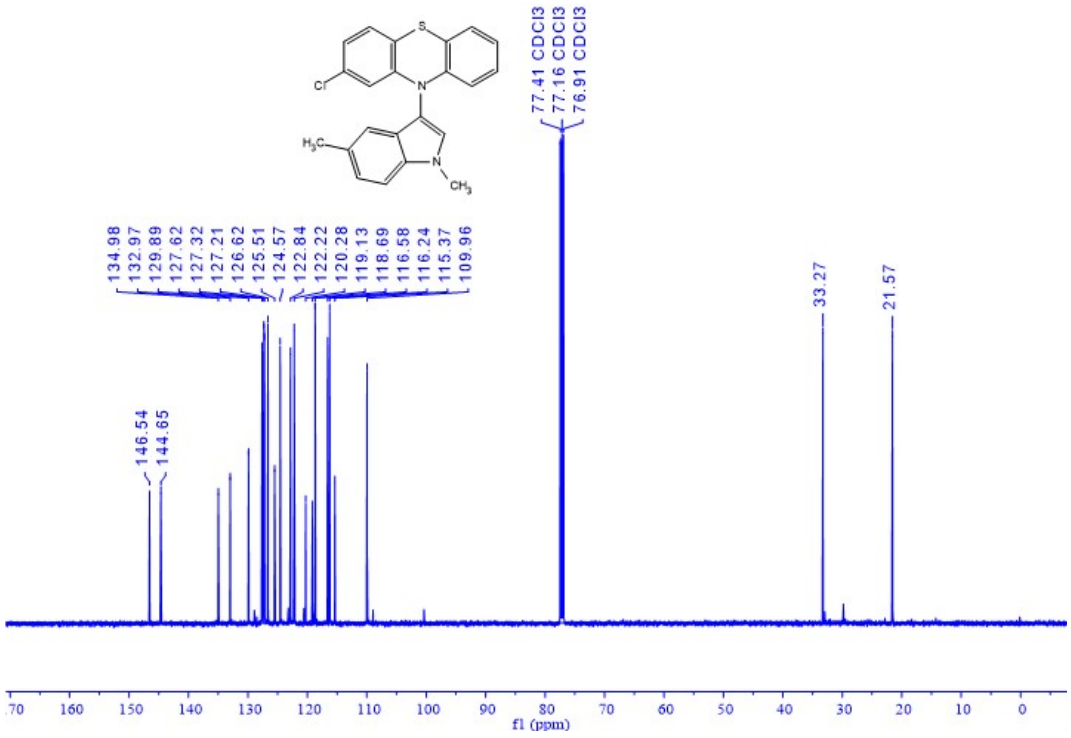
(26) ^{13}C-NMR spectrum of 2-chloro-10-(1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3ab)



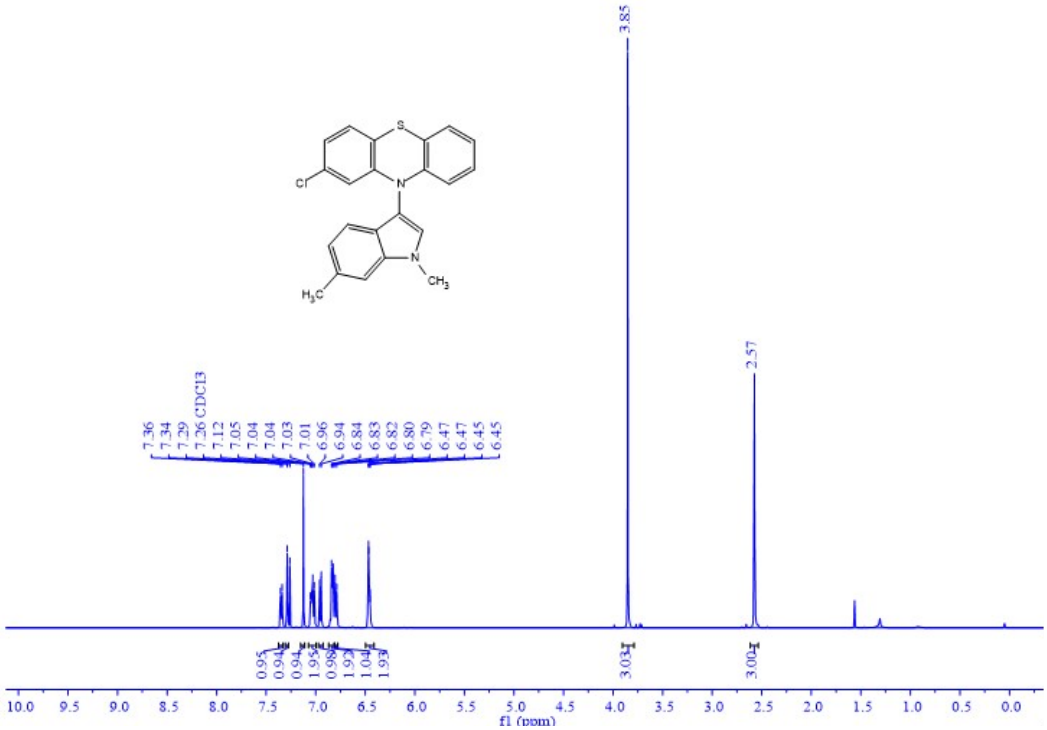
(27) **^{1}H-NMR spectrum of 2-chloro-10-(1,5-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3bb)**



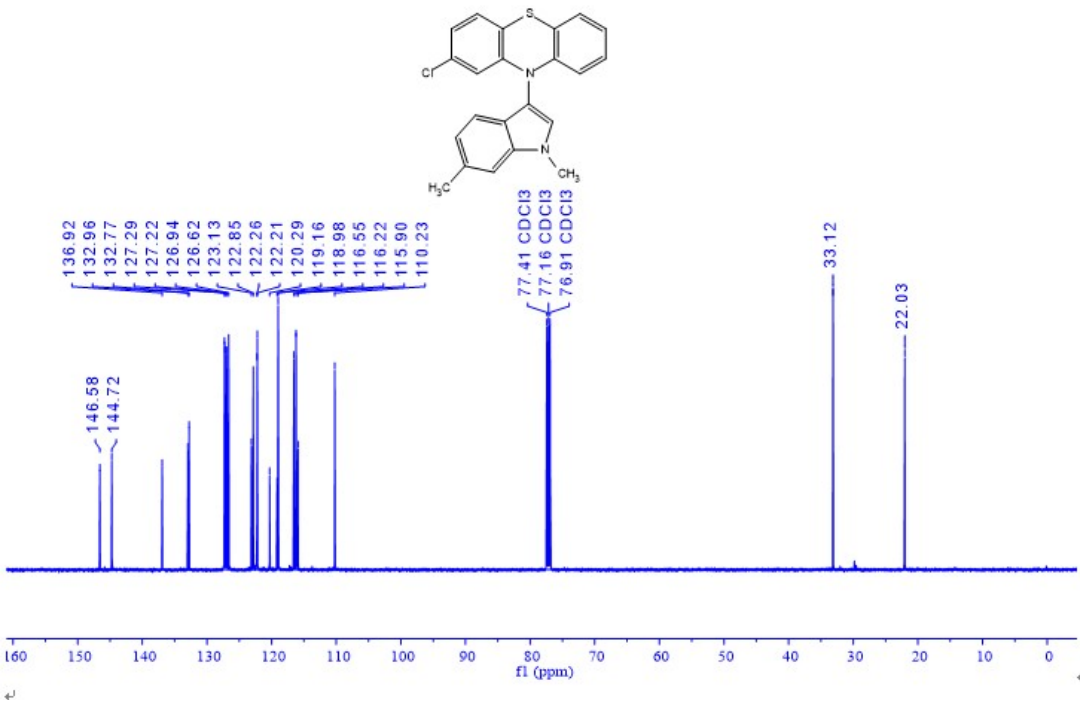
(28) ^{13}C-NMR spectrum of 2-chloro-10-(1,5-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3bb)



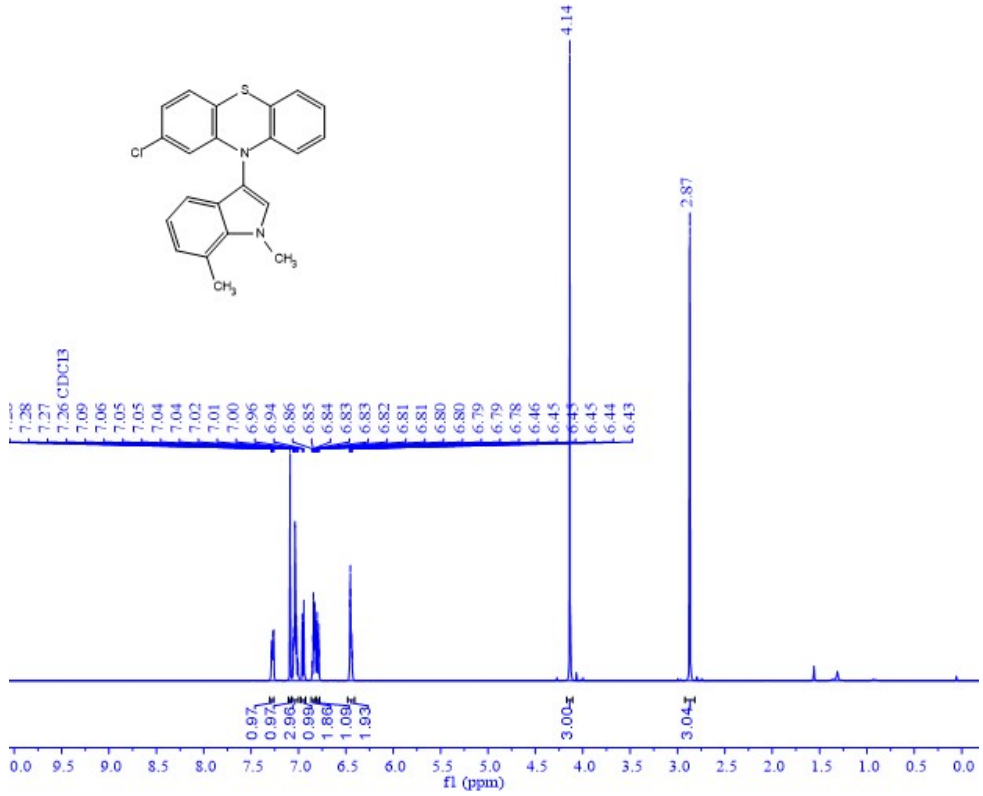
(29) ^{1}H-NMR spectrum of 2-chloro-10-(1,6-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3cb)



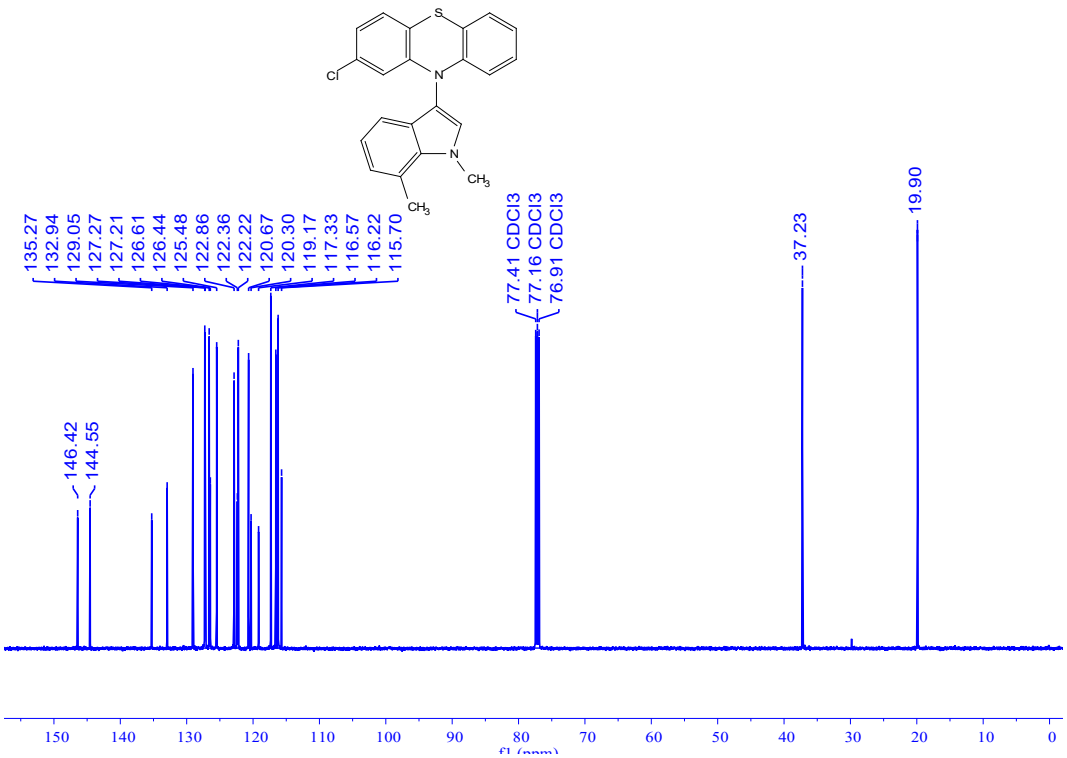
(30) ^{13}C-NMR spectrum of 2-chloro-10-(1,6-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3cb)



(31) ^{1}H-NMR spectrum of 2-chloro-10-(1,7-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3db)

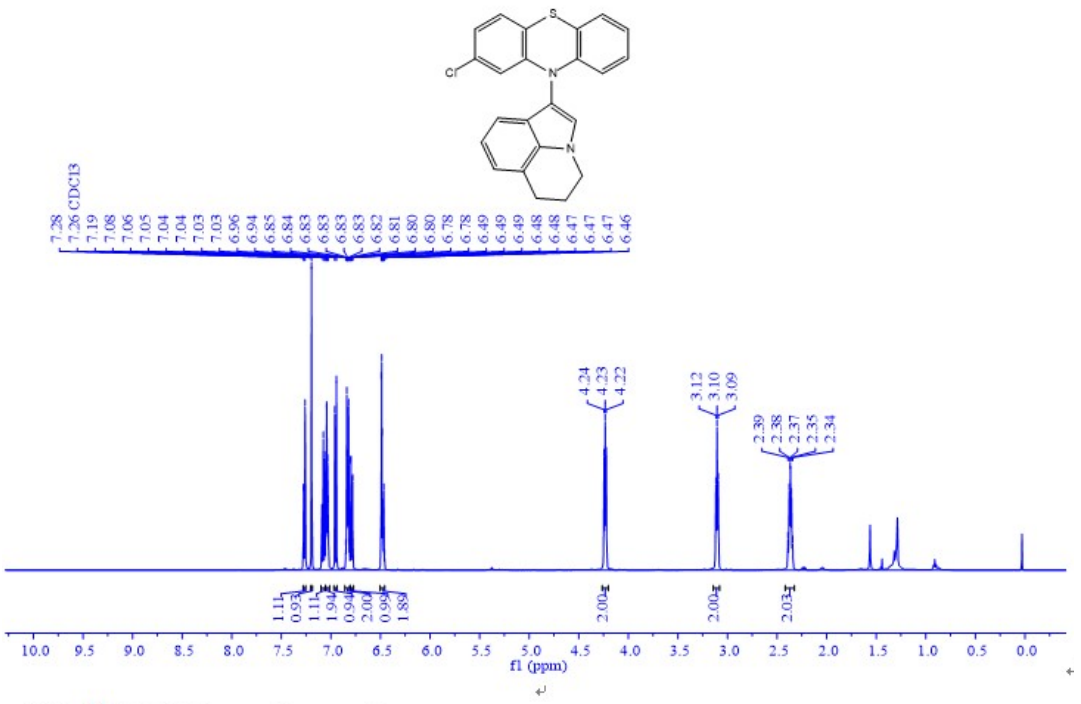


(32) ^{13}C-NMR spectrum of 2-chloro-10-(1,7-dimethyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3db)

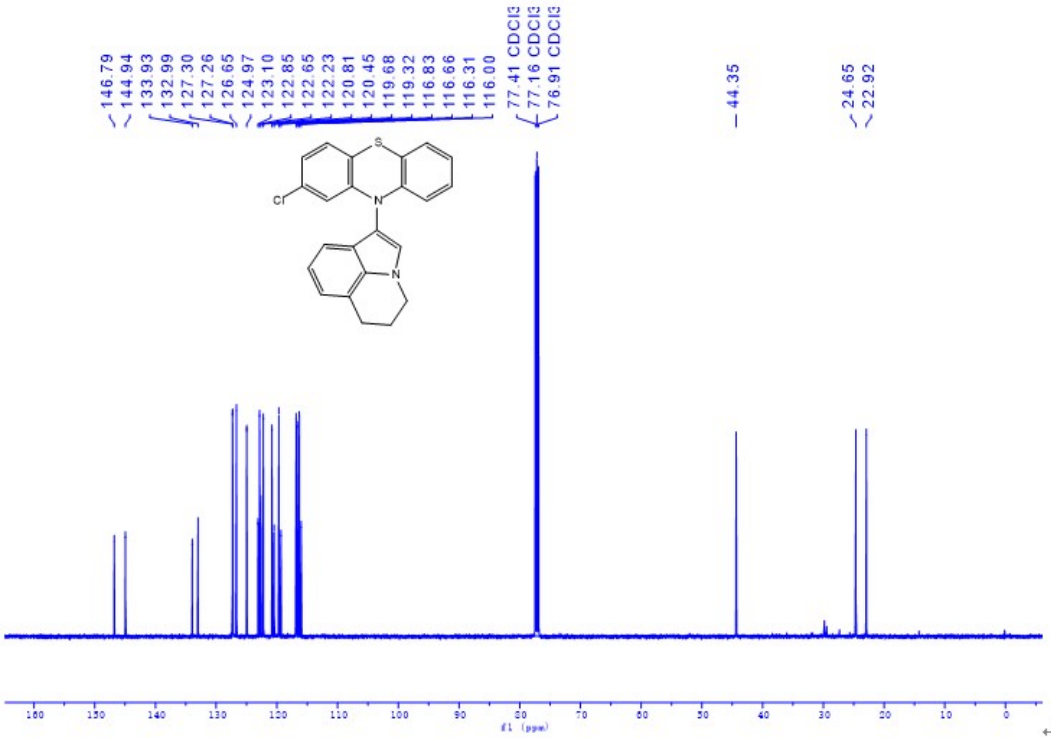


(33) ^{1}H-NMR spectrum of 2-chloro-10-(5,6-dihydro-4*H*-pyrrolo[3,2,1-

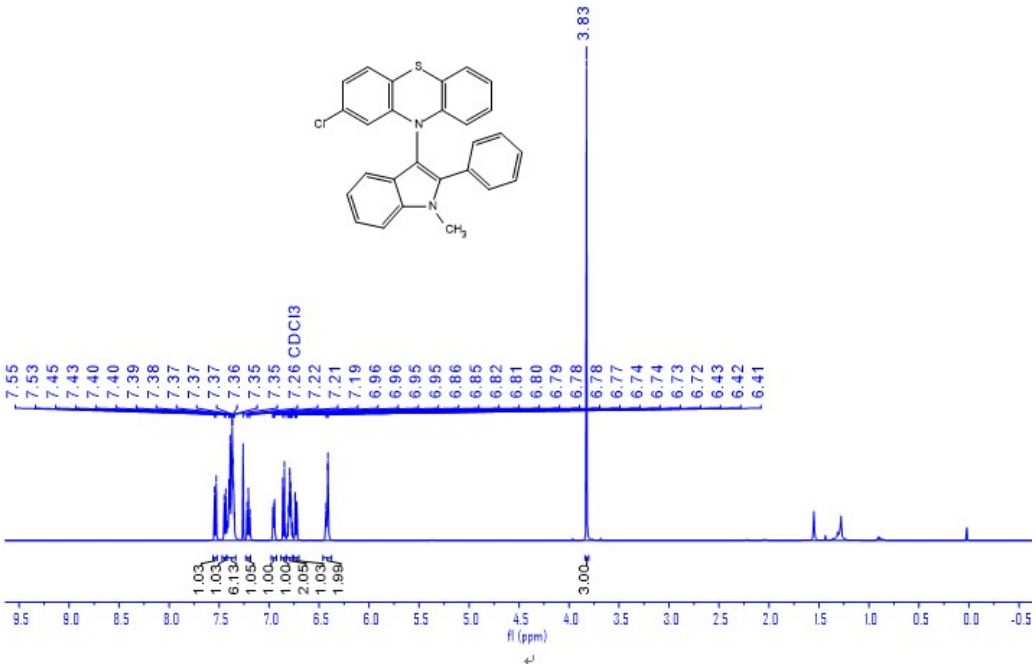
***ij*]quinolin-1-yl)-10*H*-phenothiazine (3eb)**



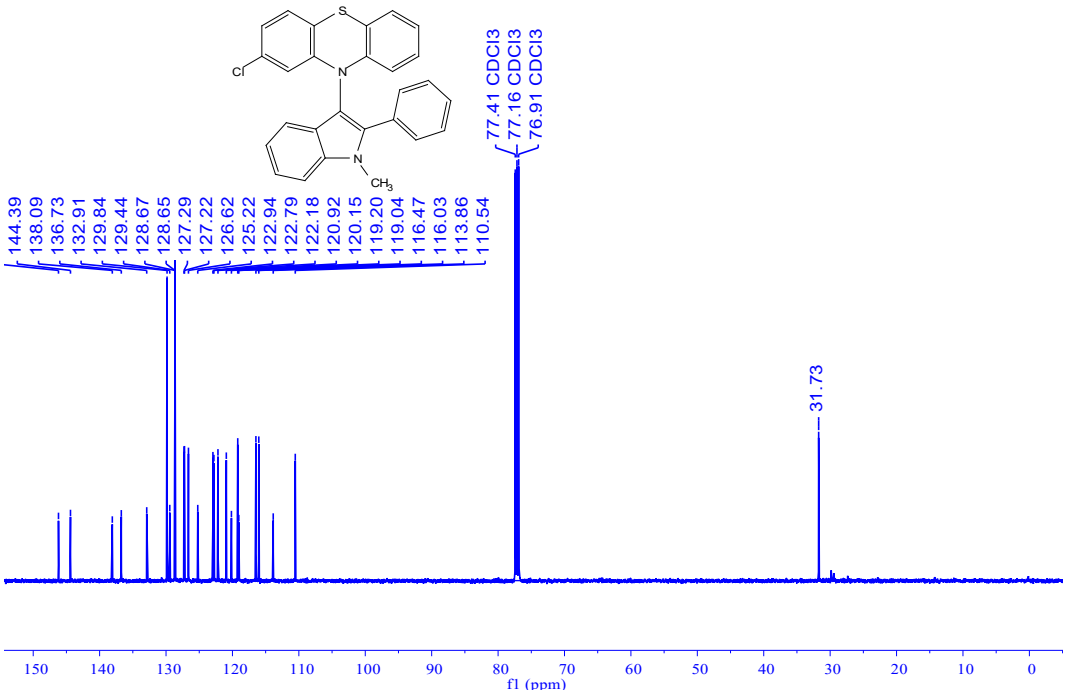
(34) ^{13}C-NMR spectrum of 2-chloro-10-(5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-1-yl)-10*H*-phenothiazine (3eb)



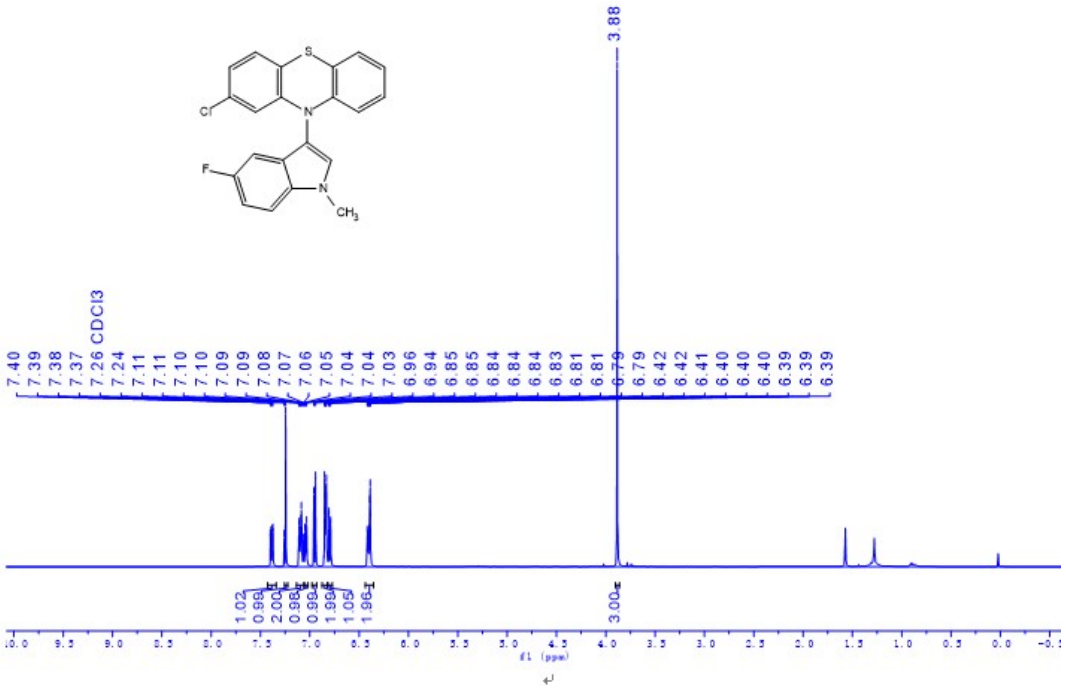
(35) ^{1}H-NMR spectrum of 2-chloro-10-(1-methyl-2-phenyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3gb)



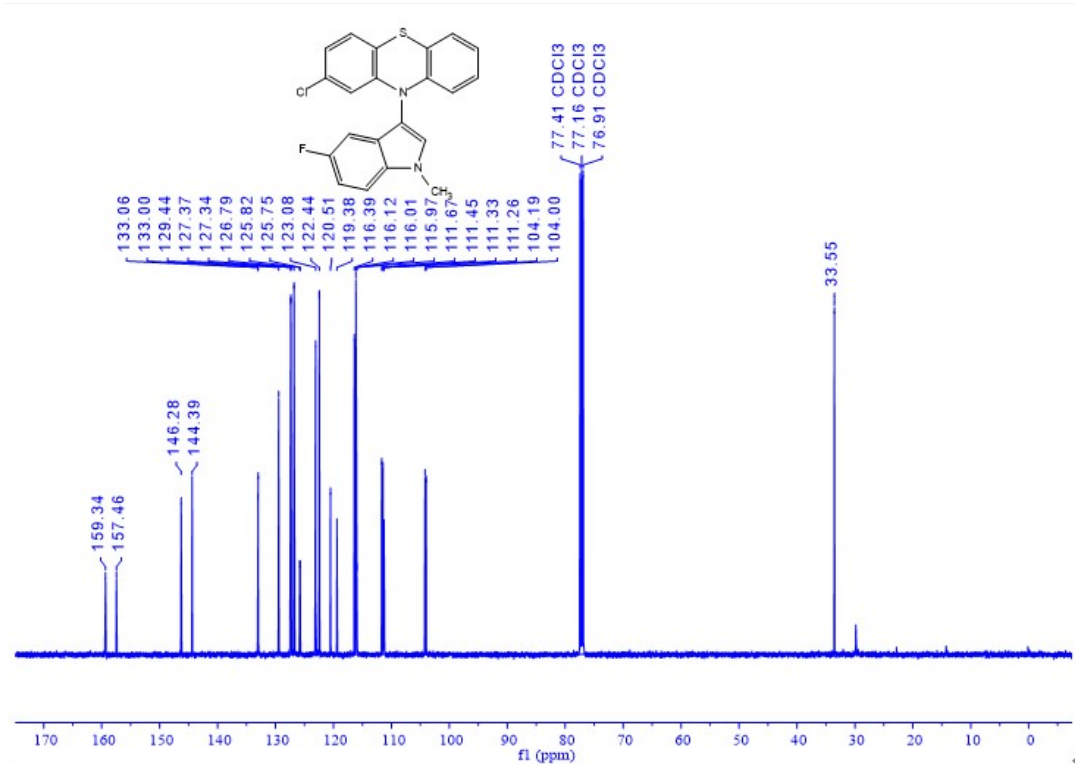
(36) ^{13}C-NMR spectrum of 2-chloro-10-(1-methyl-2-phenyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3gb)



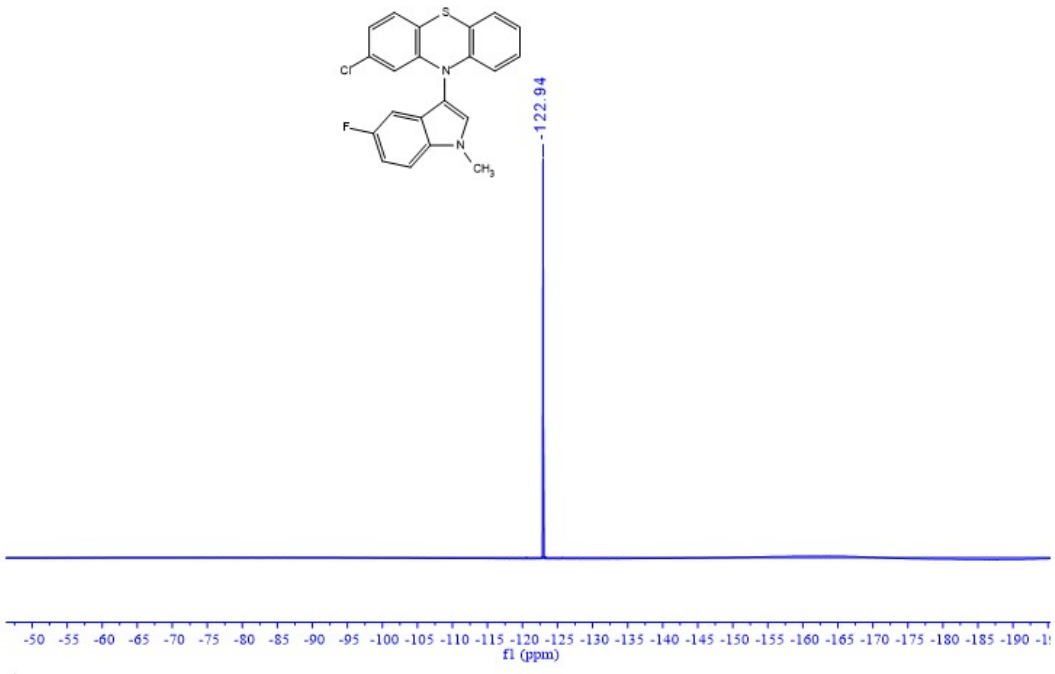
(37) ^{1}H-NMR spectrum of 2-chloro-10-(5-fluoro-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3mb)



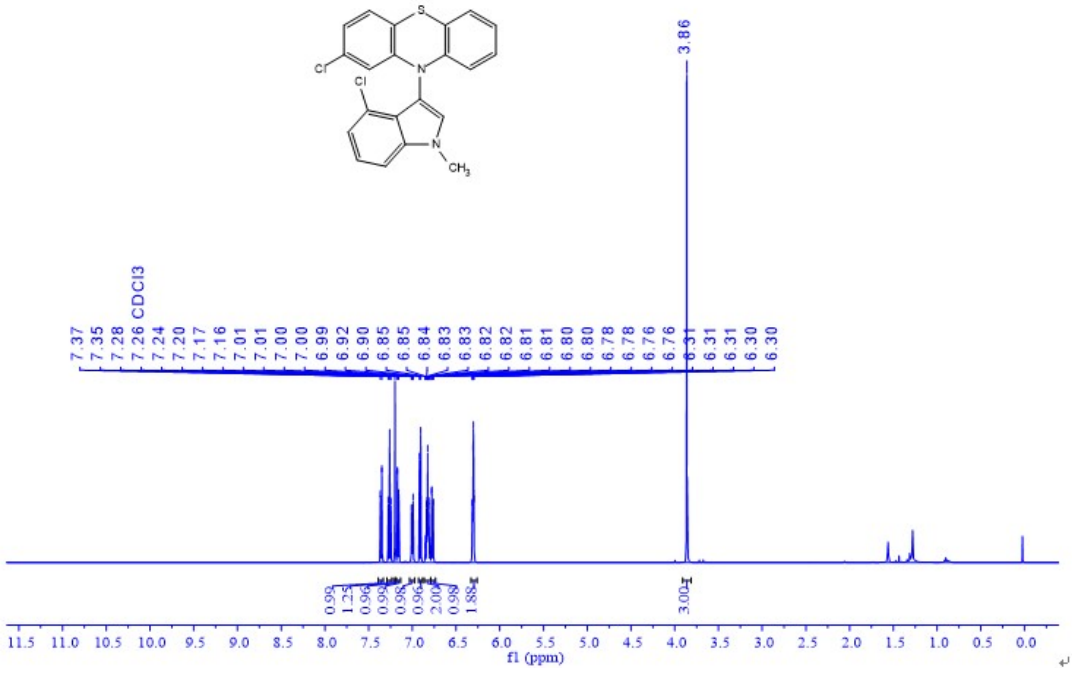
(38) ^{13}C-NMR spectrum of 2-chloro-10-(5-fluoro-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3mb)



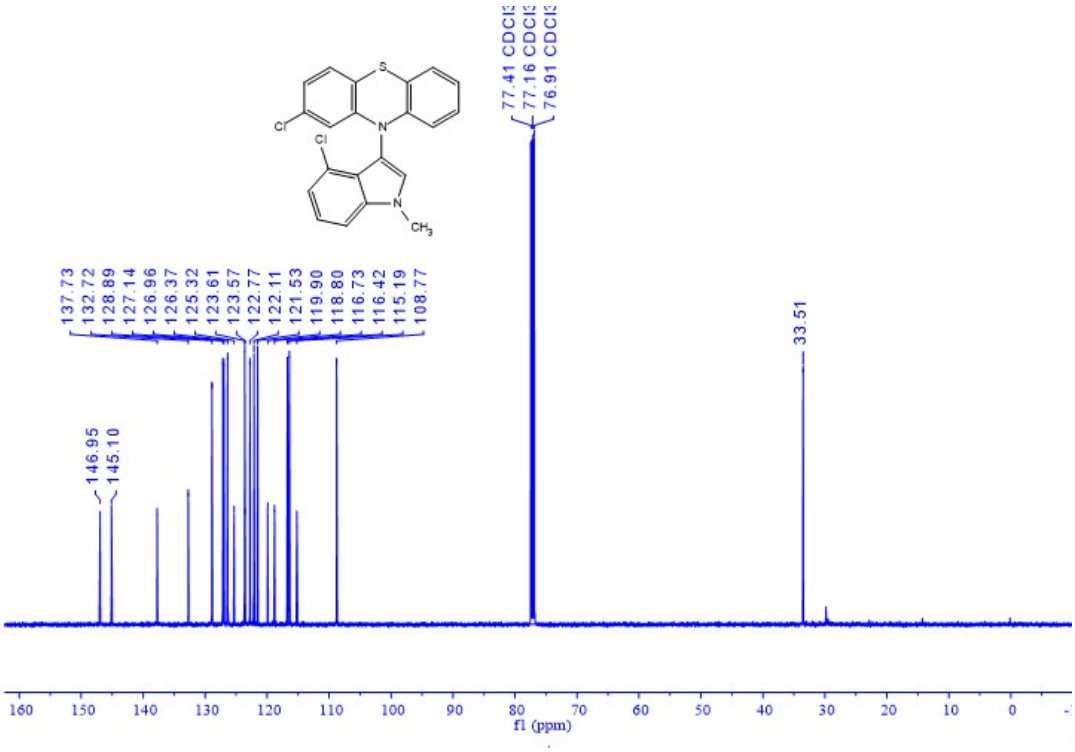
(39) ^{19}F-NMR spectrum of 2-chloro-10-(5-fluoro-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3mb)



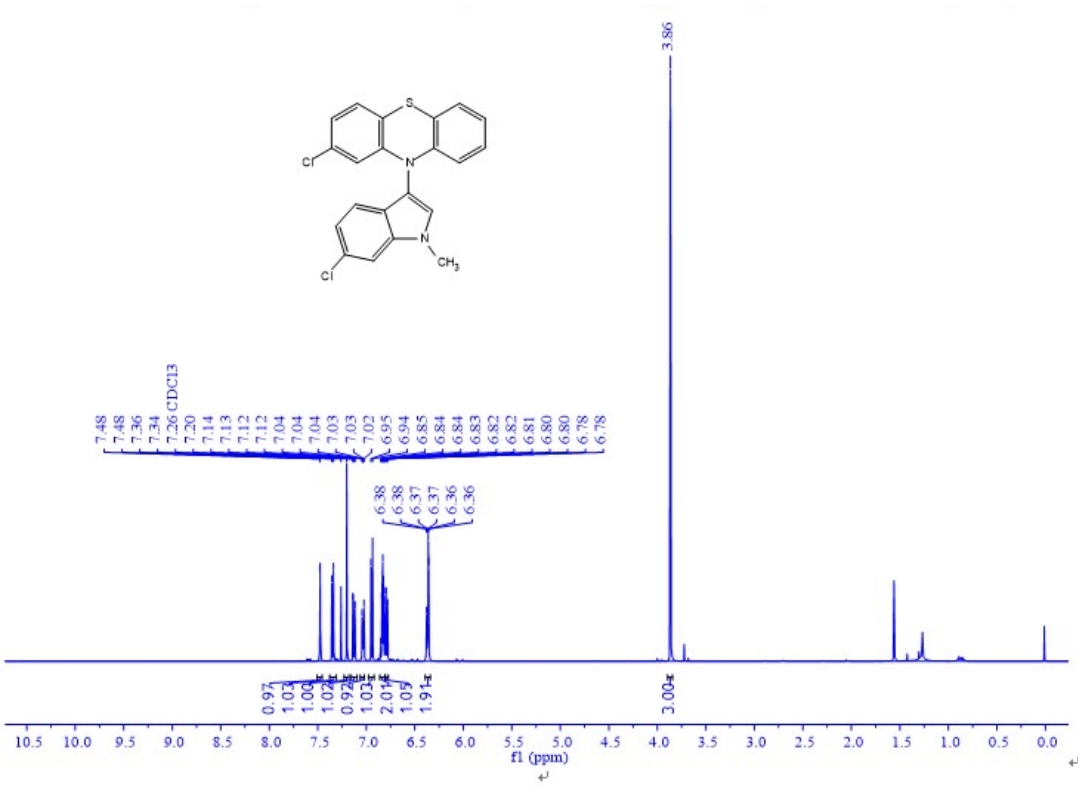
(40) ^{1}H-NMR spectrum of 2-chloro-10-(4-chloro-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3jb)



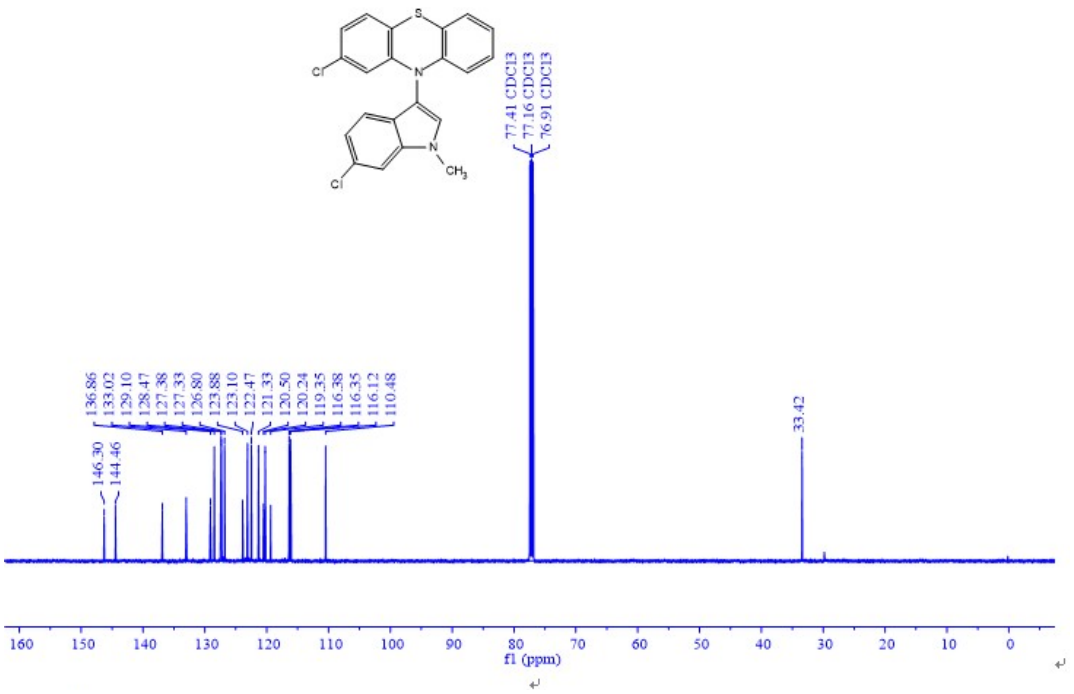
(41) ^{13}C-NMR spectrum of 2-chloro-10-(4-chloro-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3jb)



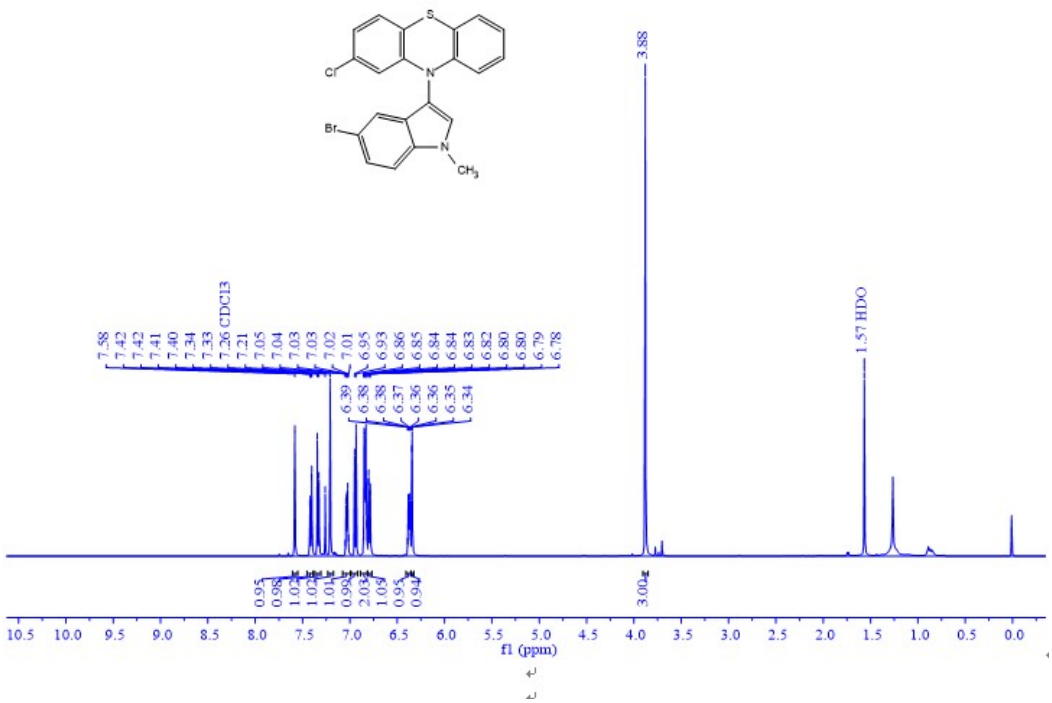
(42) ^{1}H-NMR spectrum of 2-chloro-10-(6-chloro-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3nb)



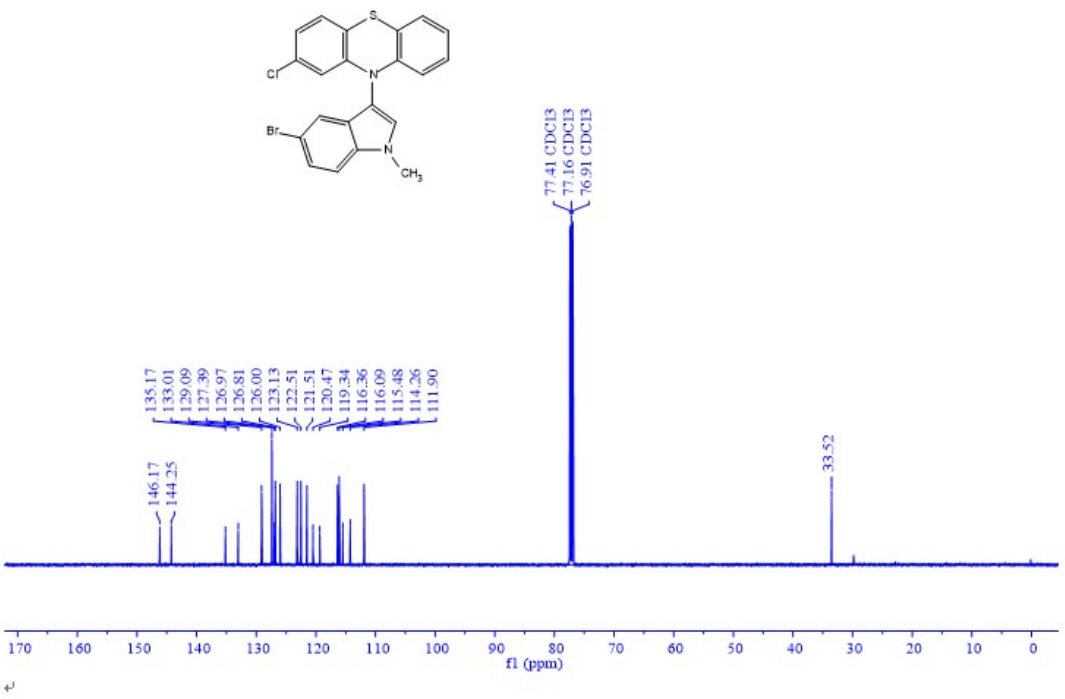
(43) ^{13}C-NMR spectrum of 2-chloro-10-(6-chloro-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine (3nb)



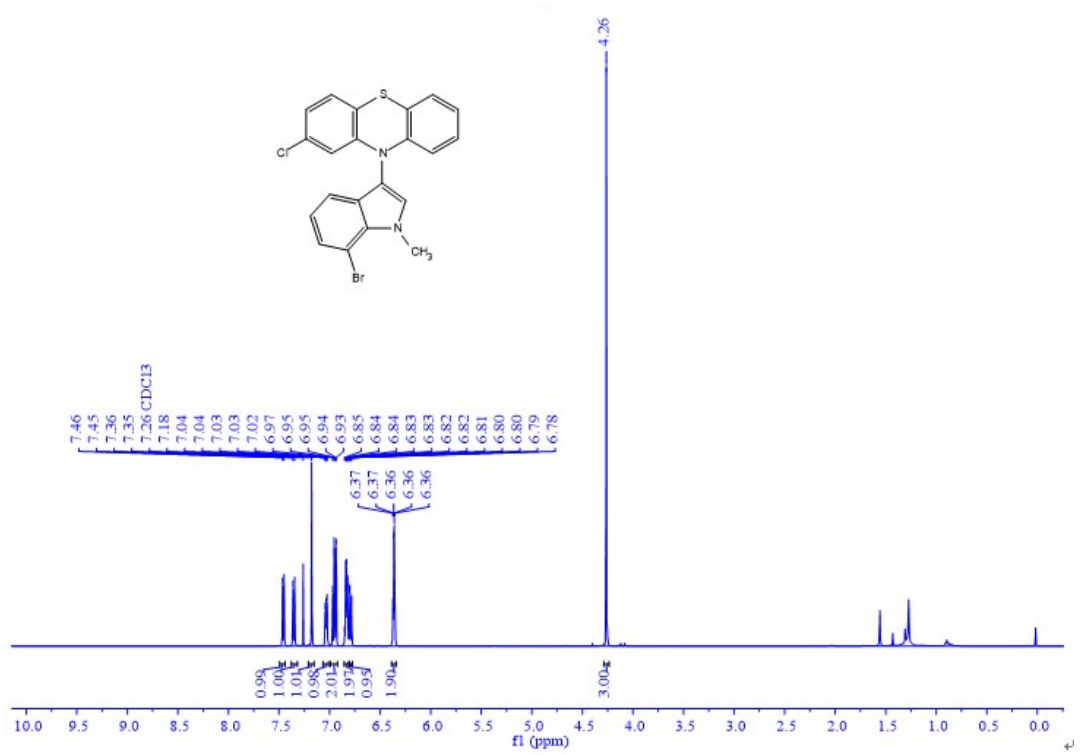
(44) [1]H-NMR spectrum of 10-(5-bromo-1-methyl-1*H*-indol-3-yl)-2-chloro-10*H*-phenothiazine (3kb)



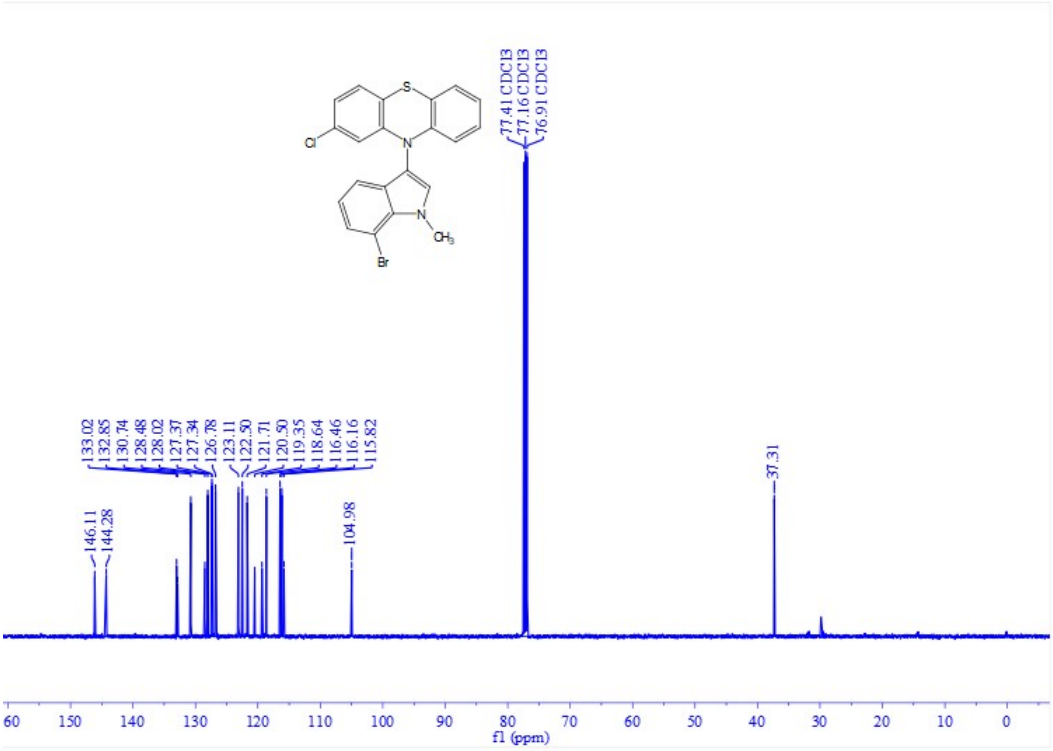
(45) [13]C-NMR spectrum of 10-(5-bromo-1-methyl-1*H*-indol-3-yl)-2-chloro-10*H*-phenothiazine (3kb)



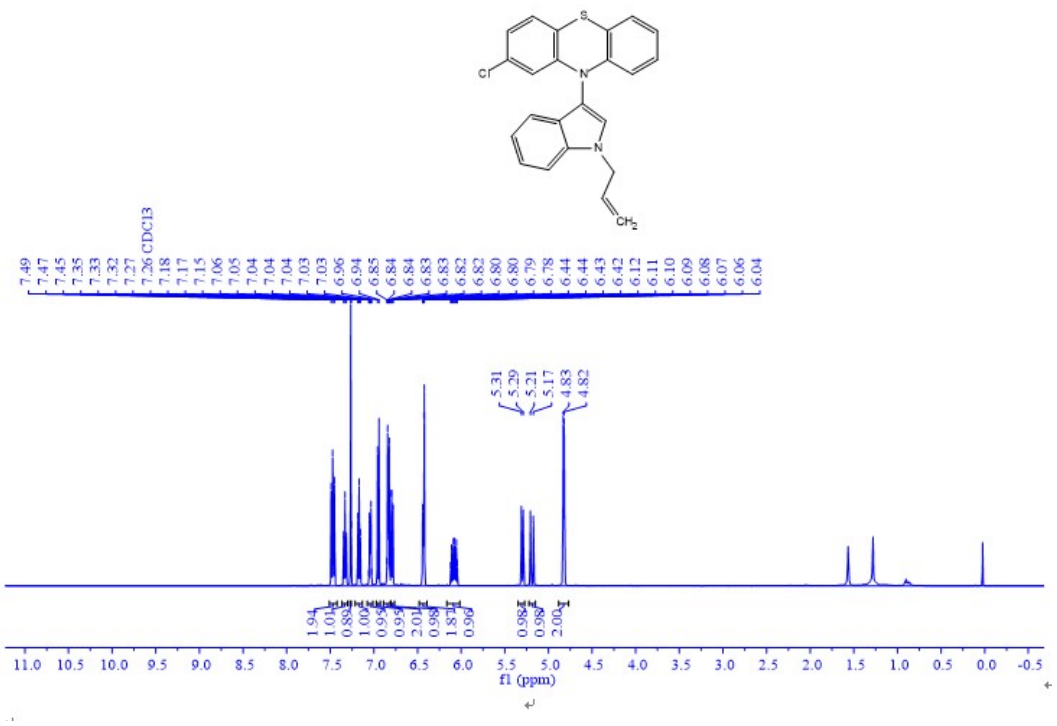
(46) ^{1}H-NMR spectrum of 10-(7-bromo-1-methyl-1*H*-indol-3-yl)-2-chloro-10*H*-phenothiazine (3ob)



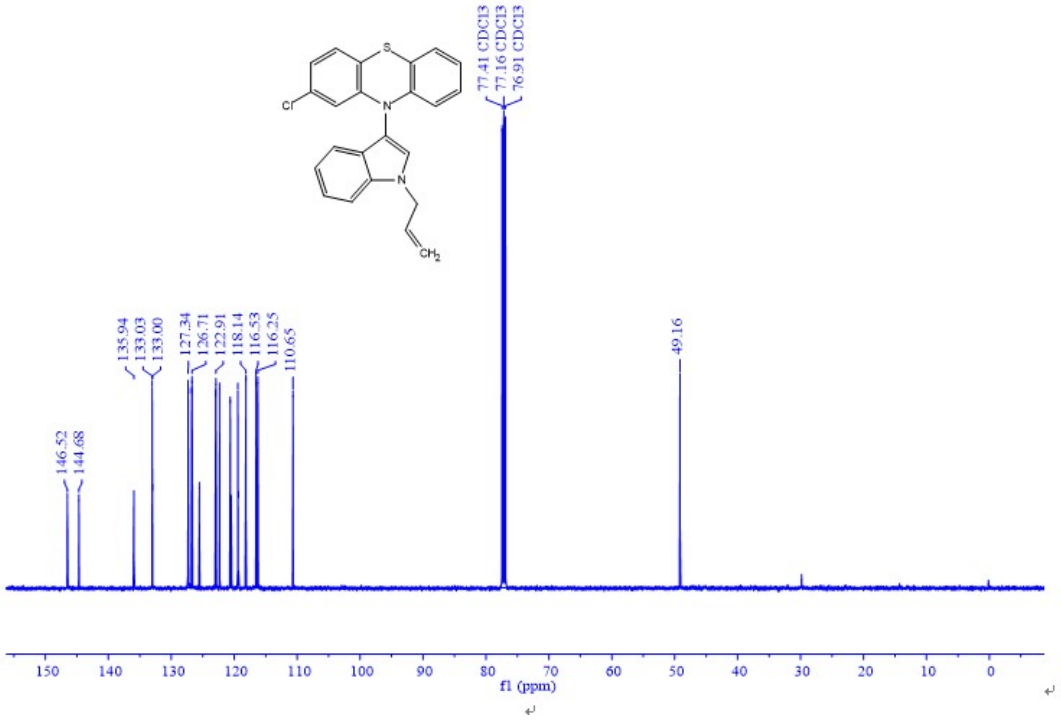
(47) ^{13}C-NMR spectrum of 10-(7-bromo-1-methyl-1*H*-indol-3-yl)-2-chloro-10*H*-phenothiazine (3ob)



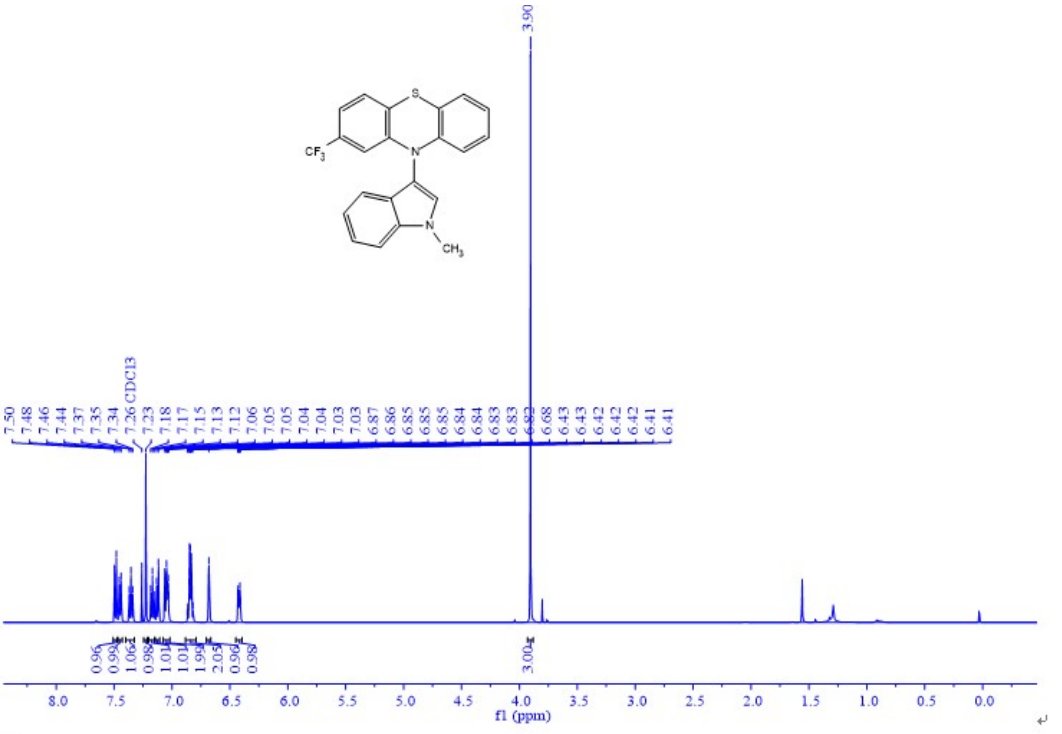
(48) ^{1}H-NMR spectrum of 10-(1-allyl-1*H*-indol-3-yl)-2-chloro-10*H*-phenothiazine (3lb)



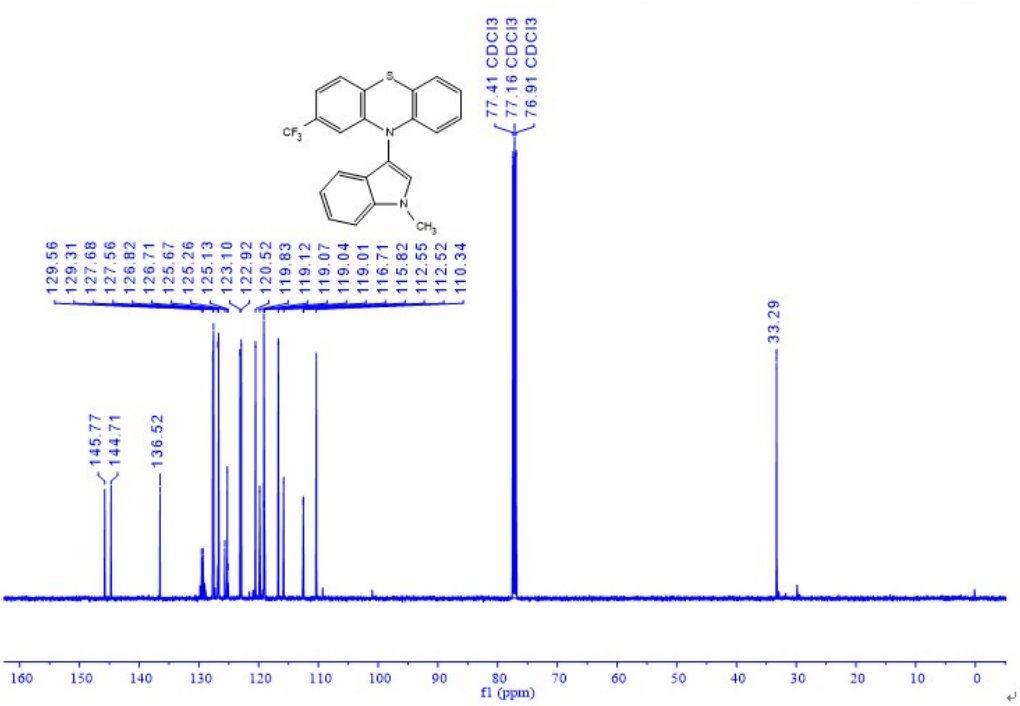
(49) ^{13}C-NMR spectrum of 10-(1-allyl-1*H*-indol-3-yl)-2-chloro-10*H*-phenothiazine (3lb)



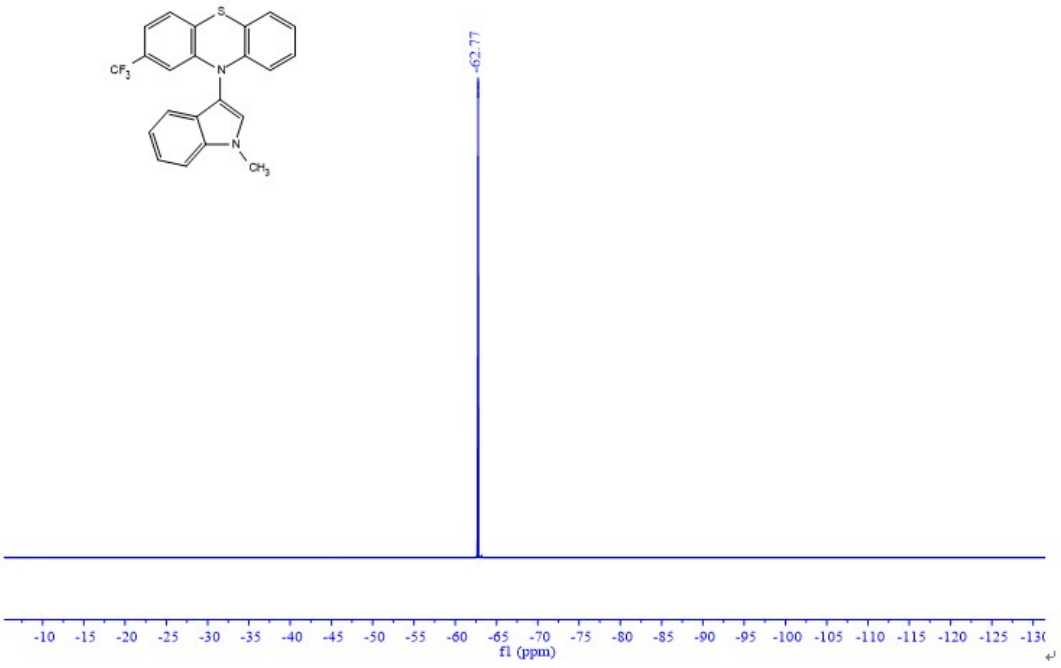
(50) ^{1}H-NMR spectrum of 10-(1-methyl-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (3ac)



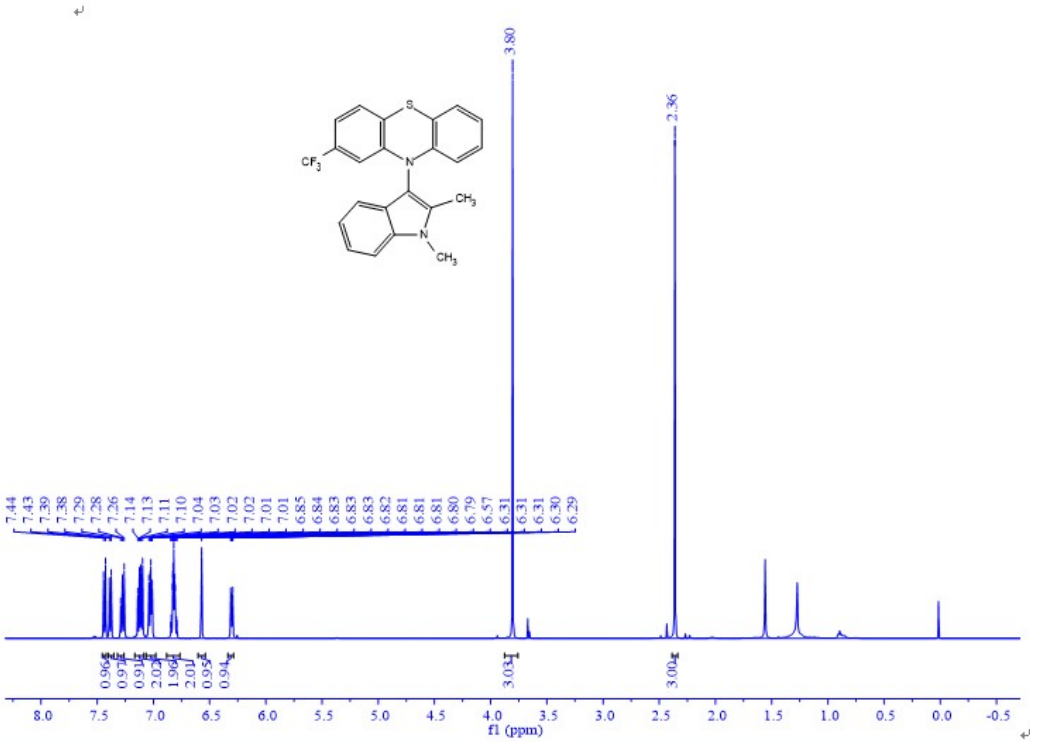
(51) ^{13}C-NMR spectrum of 10-(1-methyl-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (3ac)



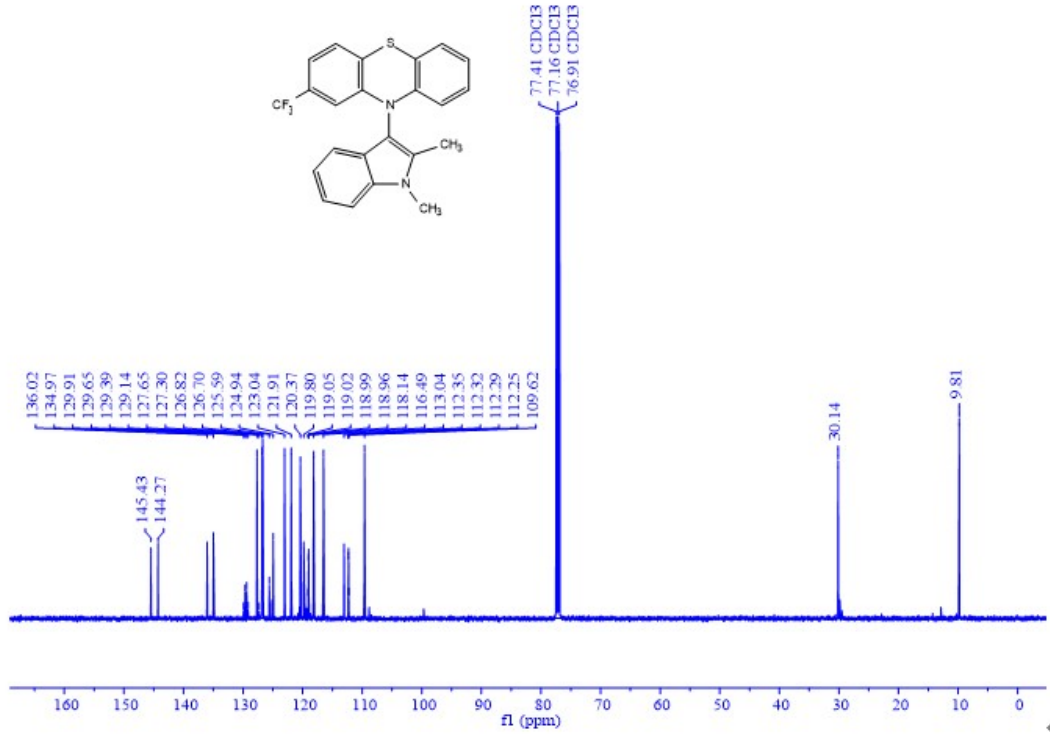
(52) ^{19}F-NMR spectrum of 10-(1-methyl-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (3ac)



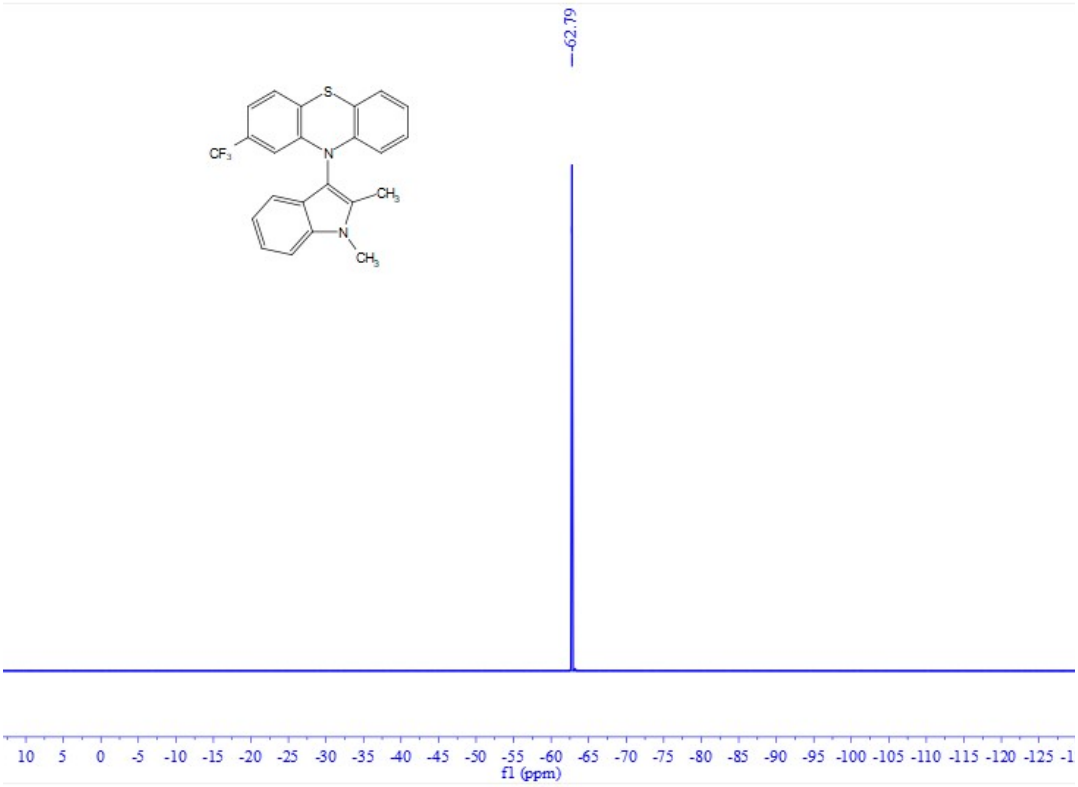
(53) ^{1}H-NMR spectrum of 10-(1,2-dimethyl-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (3fc)



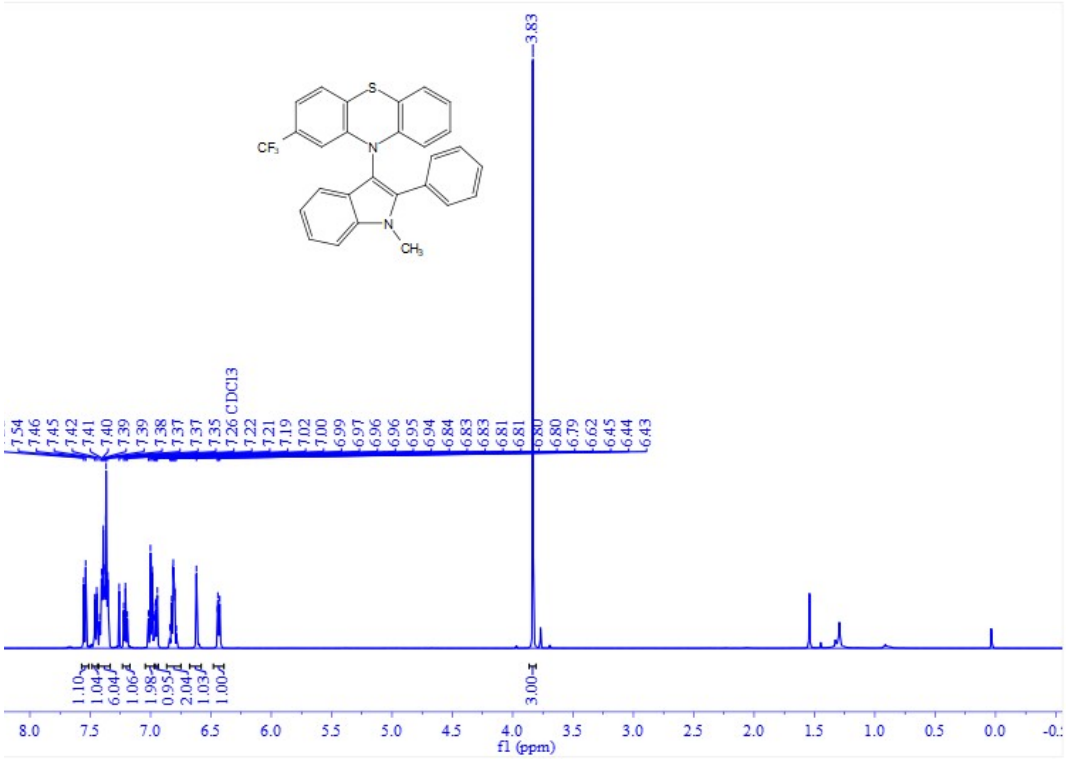
(54) ^{13}C-NMR spectrum of 10-(1,2-dimethyl-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (3fc)



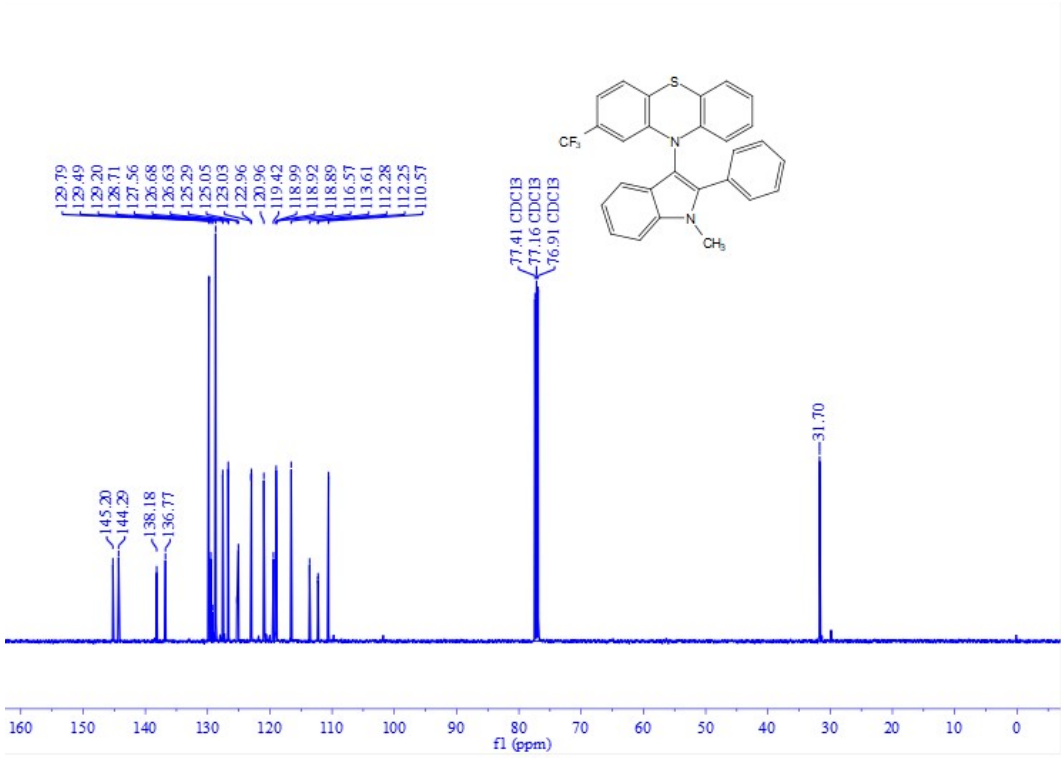
(55) ^{19}F-NMR spectrum of 10-(1,2-dimethyl-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (3fc)



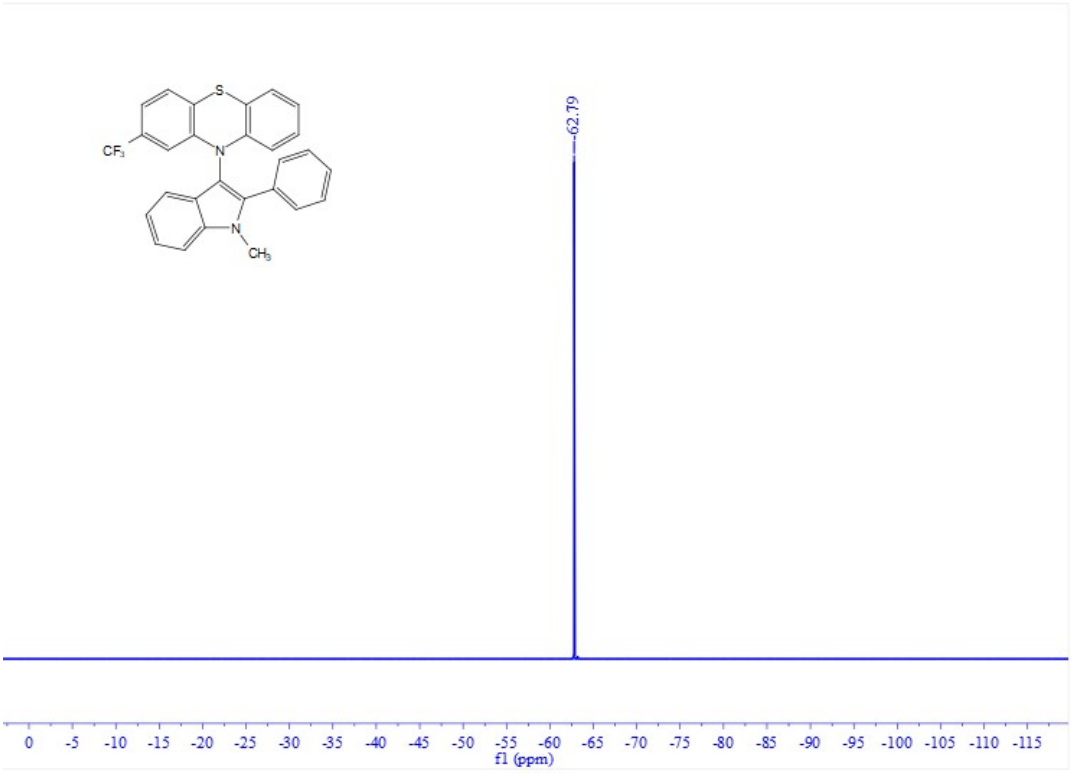
(56) ^{1}H-NMR spectrum of 10-(1-methyl-2-phenyl-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (3gc)



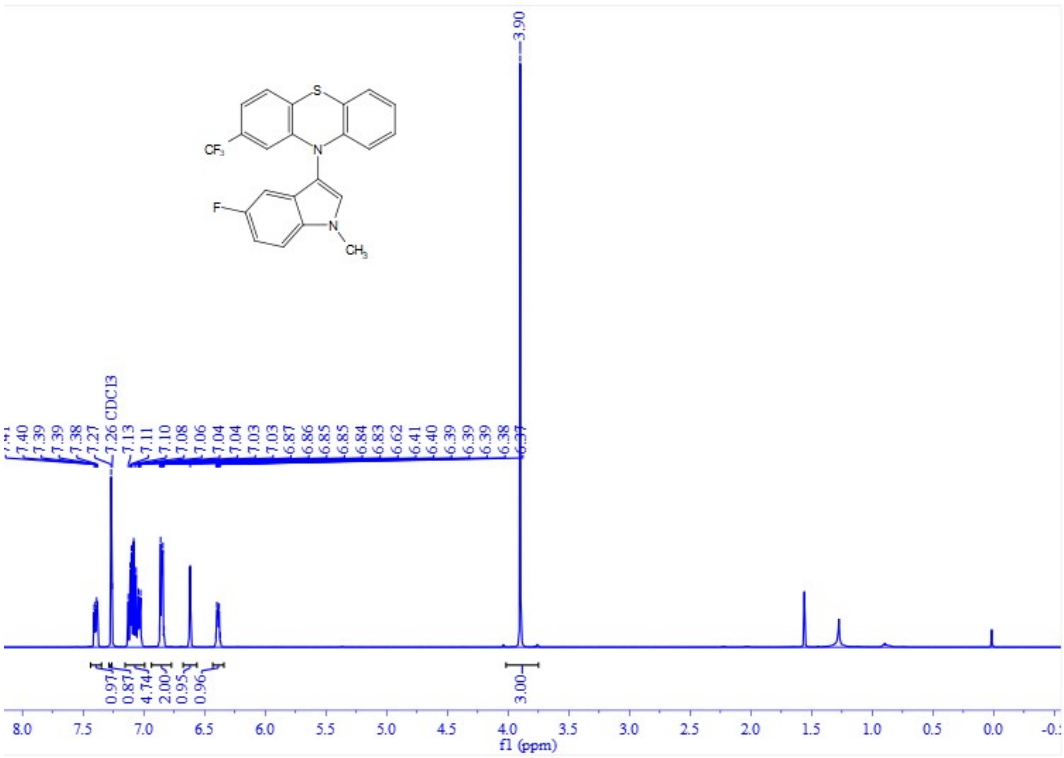
(57) ^{13}C-NMR spectrum of 10-(1-methyl-2-phenyl-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (3gc)



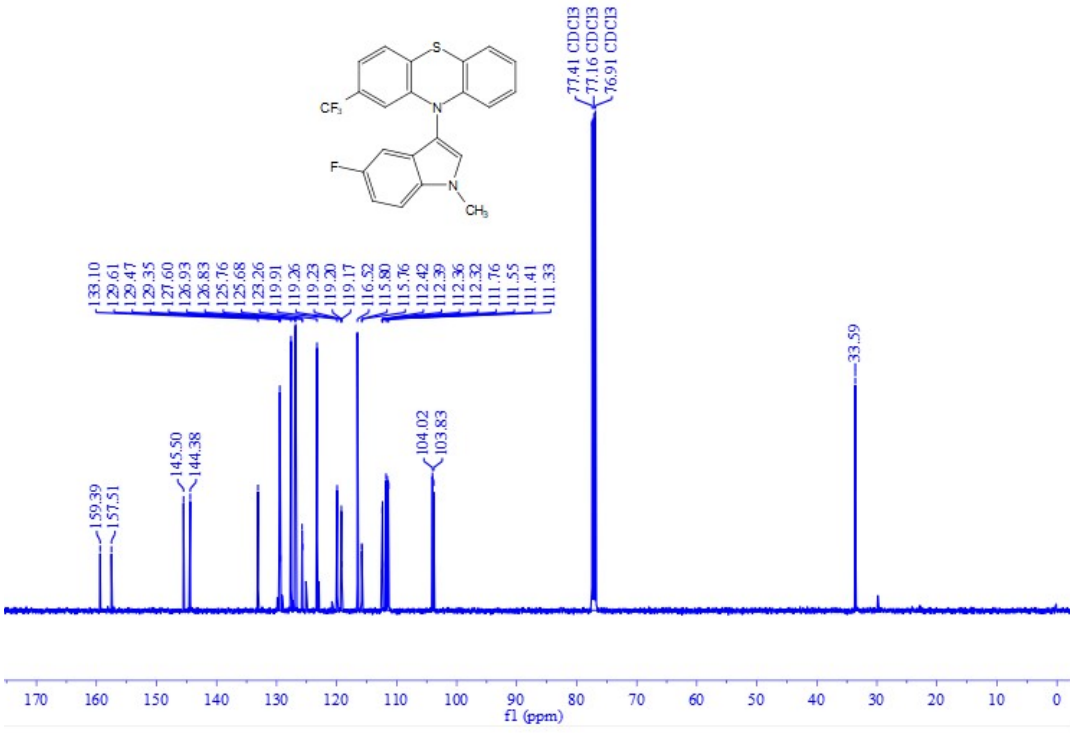
(58) ^{19}F-NMR spectrum of 10-(1-methyl-2-phenyl-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (3gc)



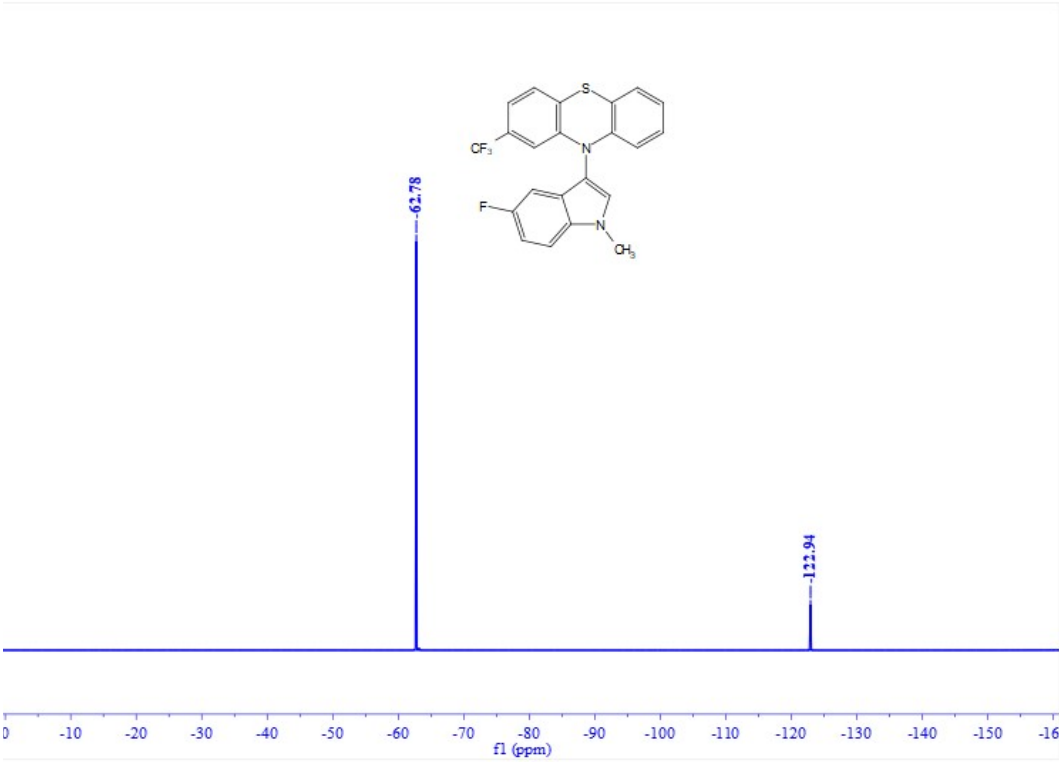
(59) ^{1}H-NMR spectrum of 10-(5-fluoro-1-methyl-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (3mc)



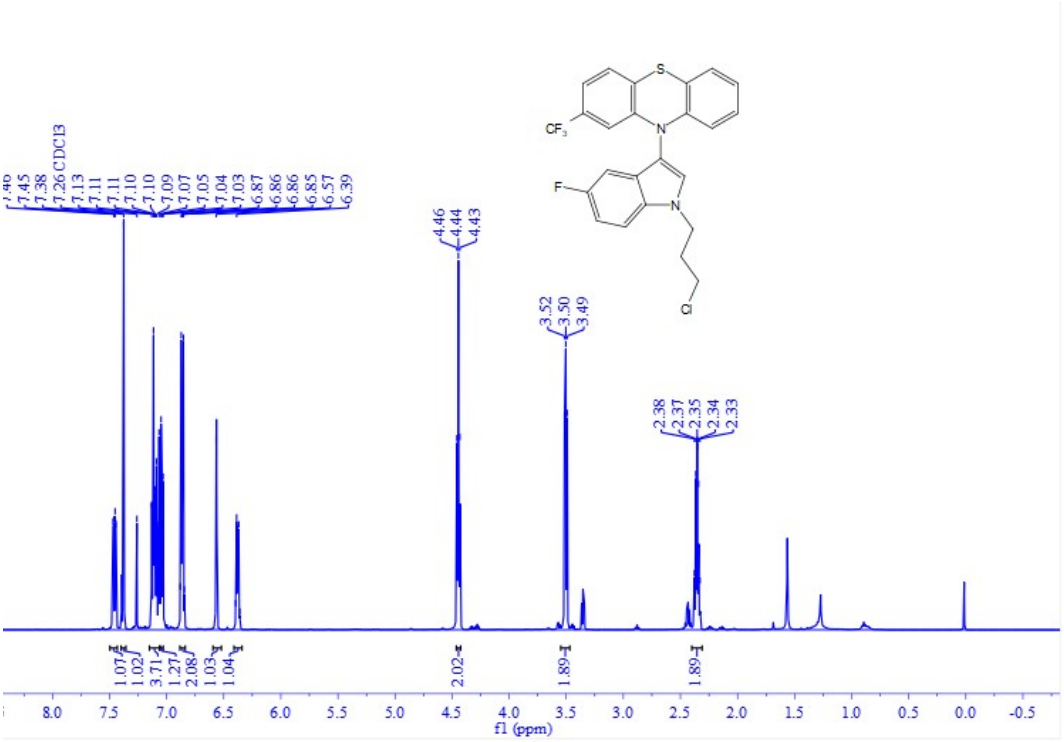
(60) ^{13}C-NMR spectrum of 10-(5-fluoro-1-methyl-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (3mc)



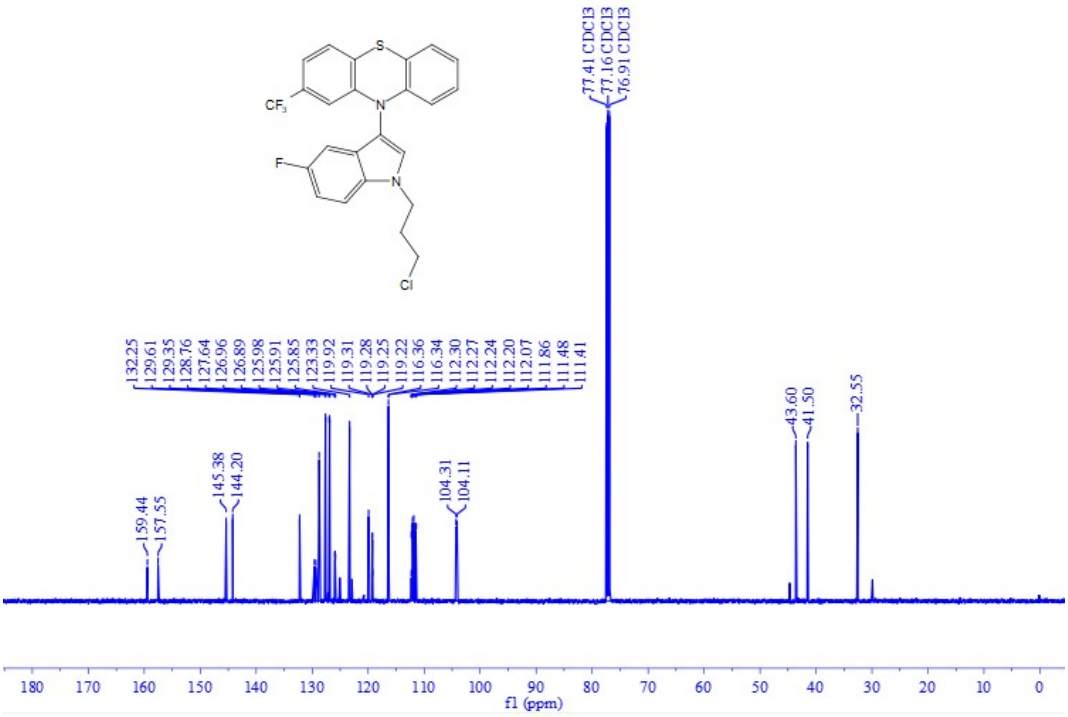
(61) ^{19}F-NMR spectrum of 10-(5-fluoro-1-methyl-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (3mc)



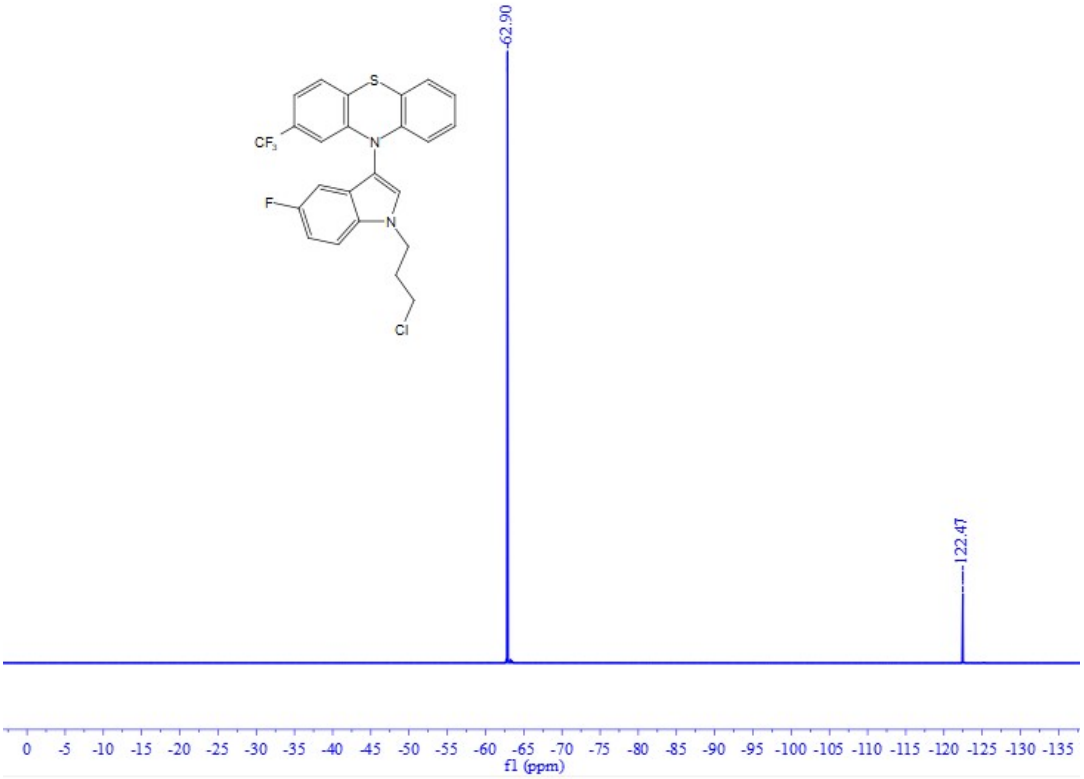
(62) ^{1}H-NMR spectrum of 10-(1-(3-chloropropyl)-5-fluoro-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (3pc)



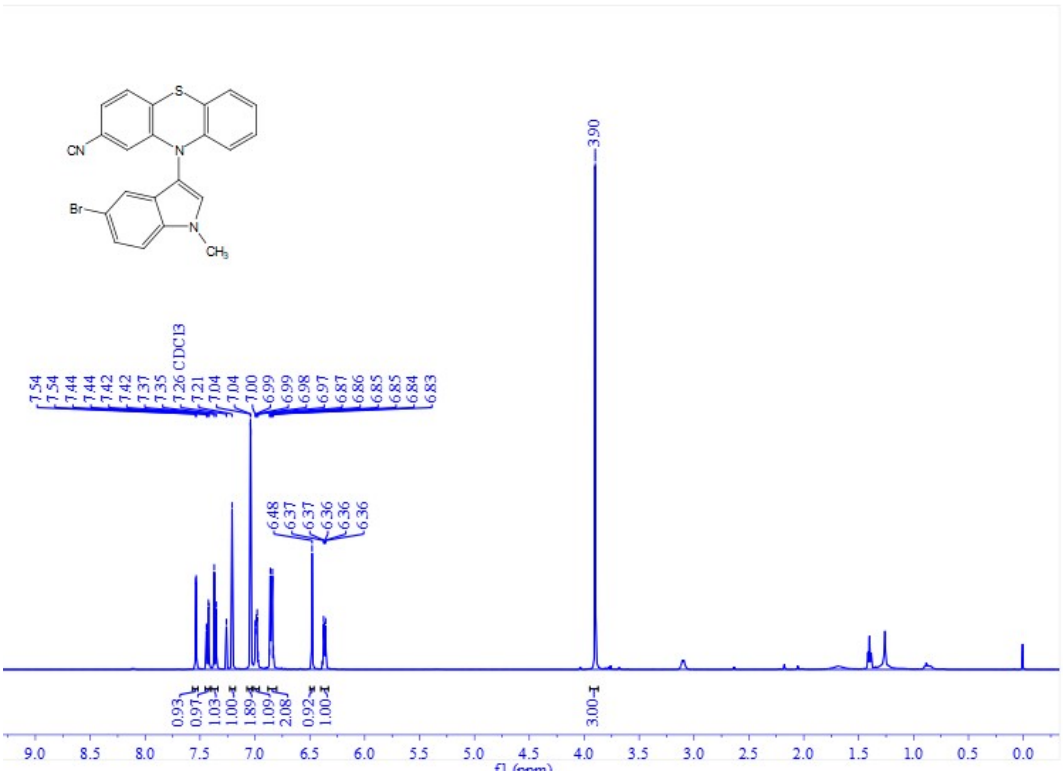
(63) ^{13}C-NMR spectrum of 10-(1-(3-chloropropyl)-5-fluoro-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (3pc)



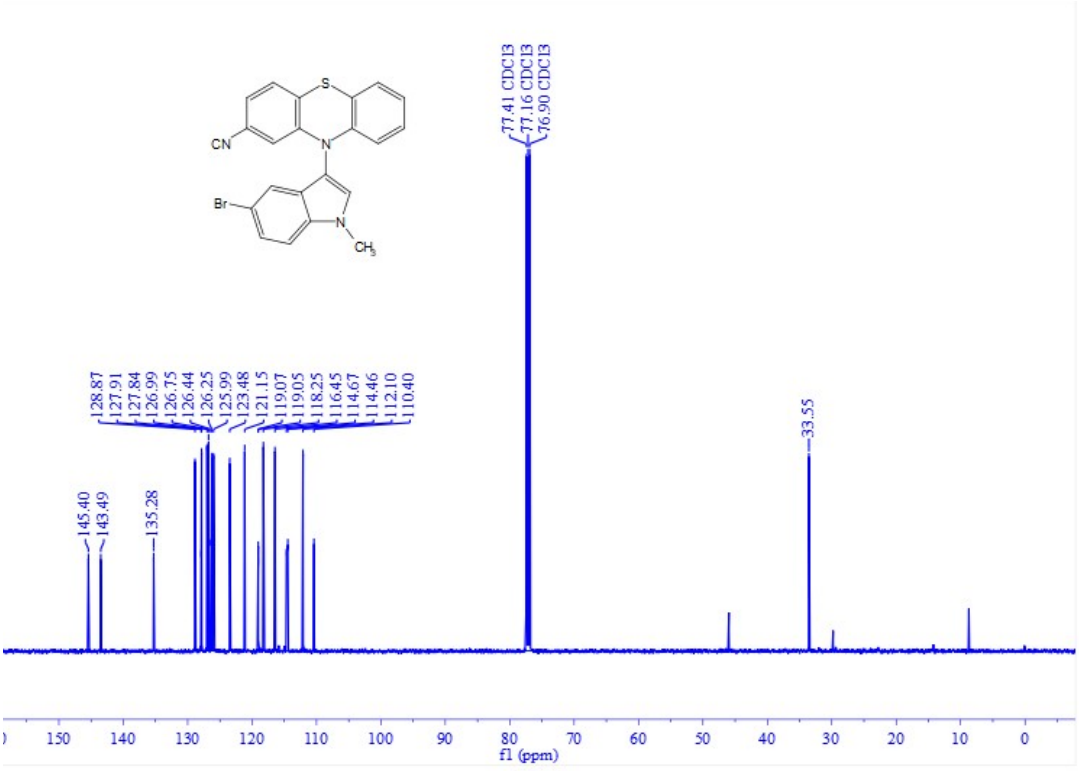
(64) ^{19}F-NMR spectrum of 10-(1-(3-chloropropyl)-5-fluoro-1*H*-indol-3-yl)-2-(trifluoromethyl)-10*H*-phenothiazine (3pc)



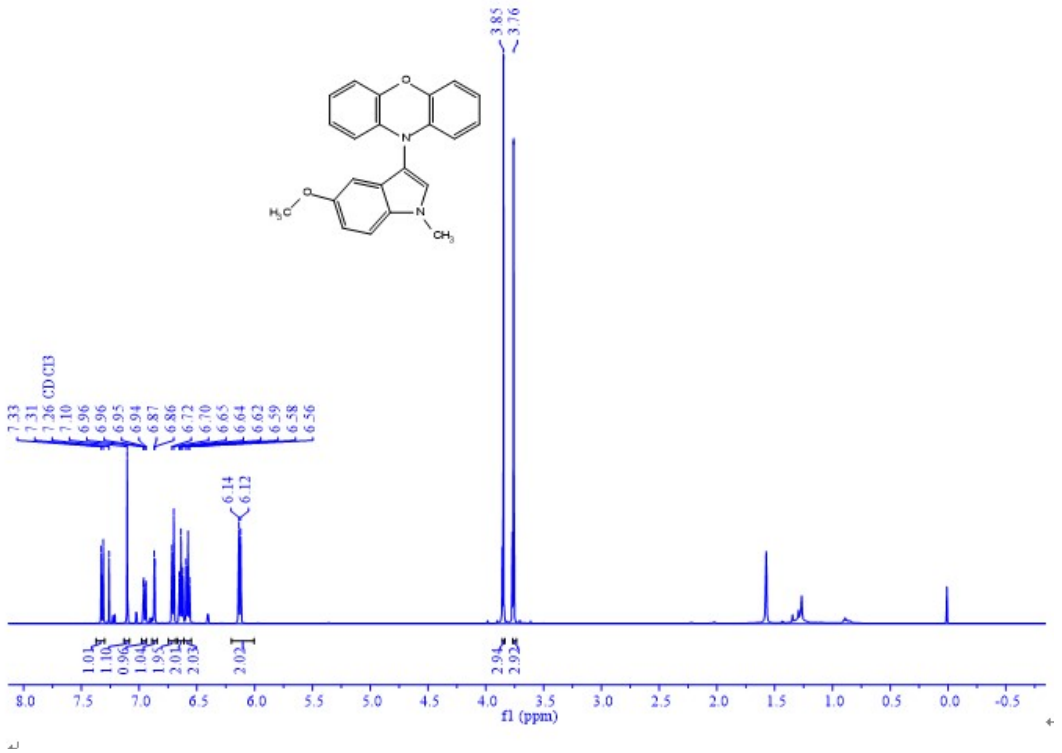
(65) ^{1}H-NMR spectrum of 10-(5-bromo-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine-2-carbonitrile (3kd)



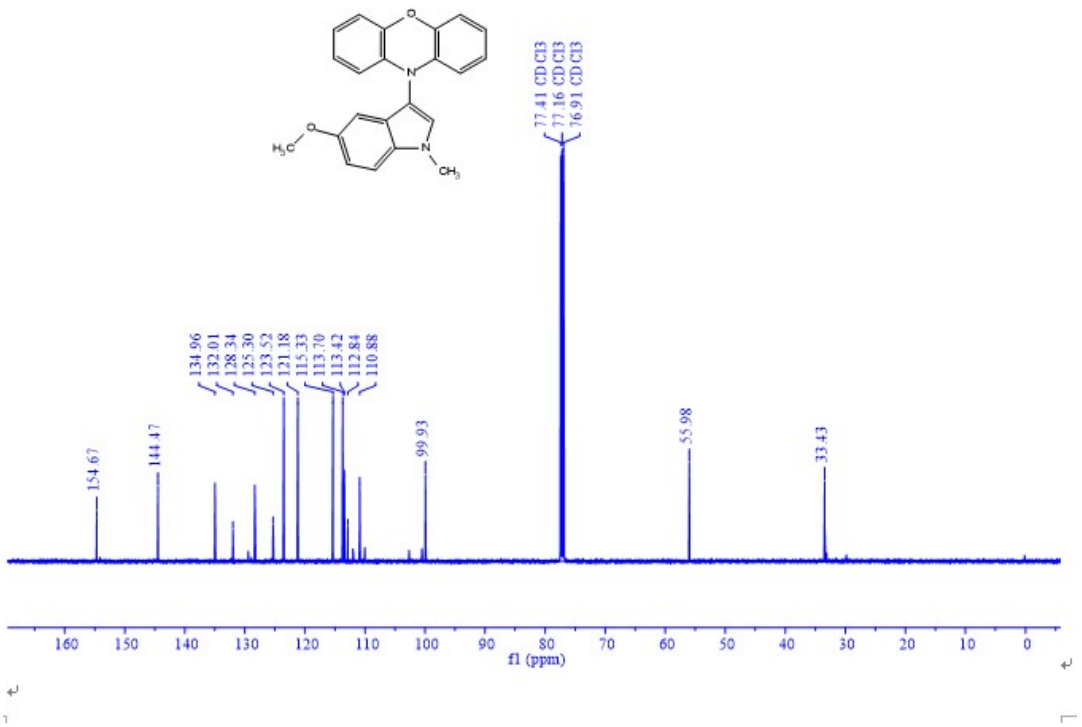
(66) ^{13}C-NMR spectrum of 10-(5-bromo-1-methyl-1*H*-indol-3-yl)-10*H*-phenothiazine-2-carbonitrile (3kd)



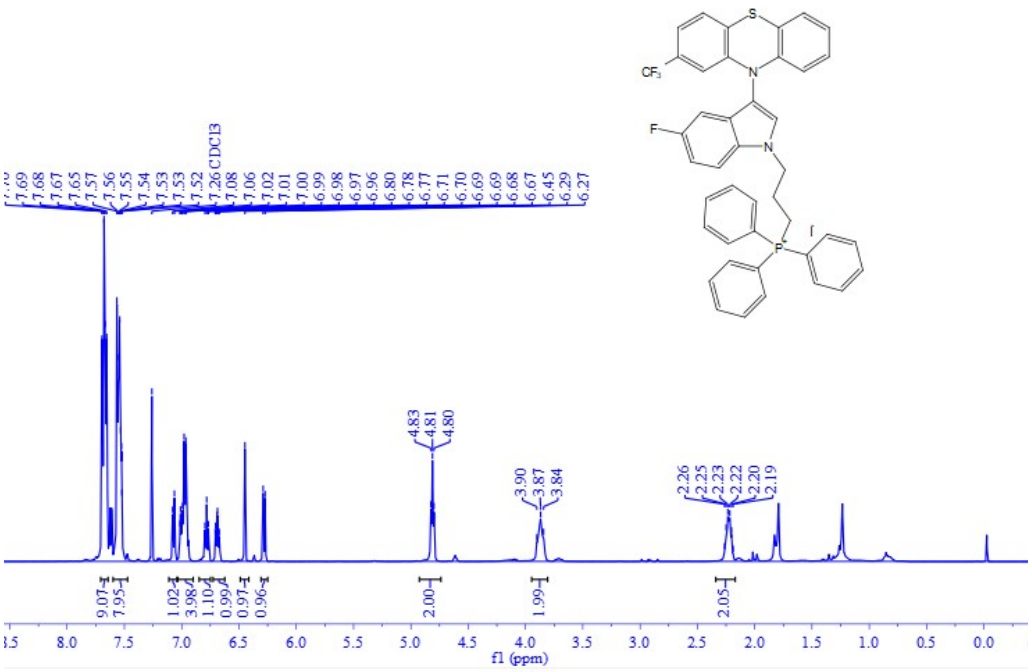
(67) ^{1}H-NMR spectrum of 10-(5-methoxy-1-methyl-1*H*-indol-3-yl)-10*H*-phenoxazine (3he)



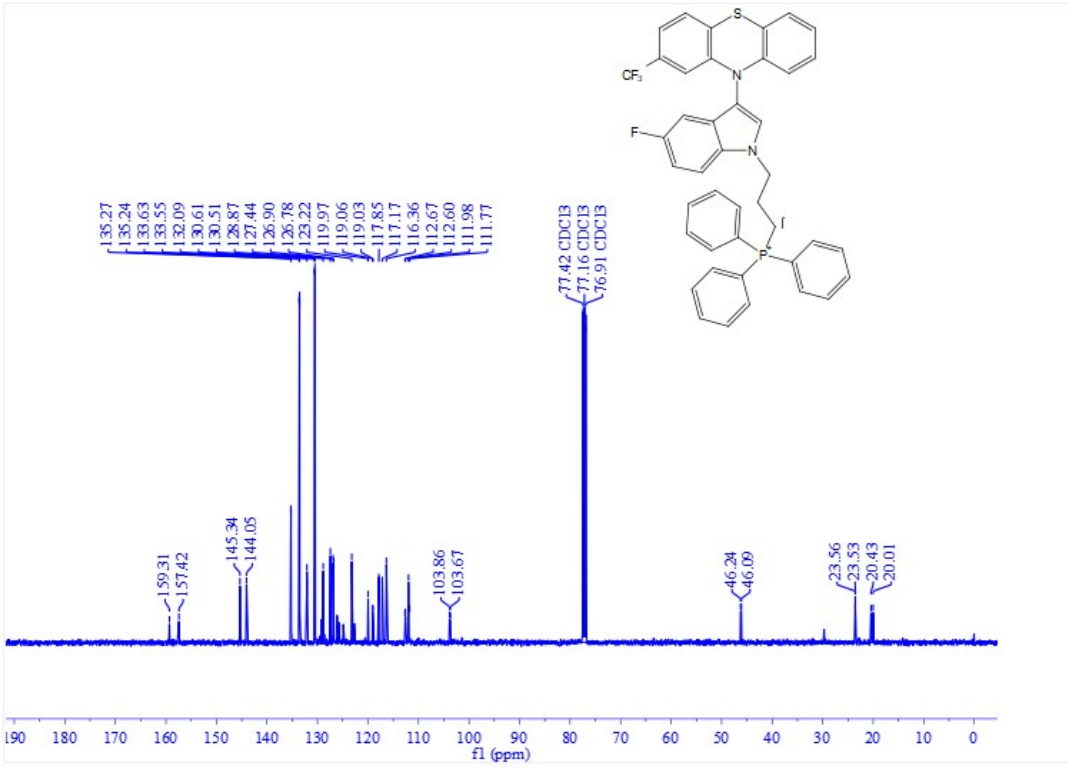
(68) ^{13}C-NMR spectrum of 10-(5-methoxy-1-methyl-1*H*-indol-3-yl)-10*H*-phenoxazine (3he)



(69) ^{1}H-NMR spectrum of (3-(5-fluoro-3-(2-(trifluoromethyl)-10*H*-phenothiazin-10-yl)-1*H*-indol-1-yl)propyl)triphenylphosphonium (5pca)



(70) ^{13}C-NMR spectrum of (3-(5-fluoro-3-(2-(trifluoromethyl)-10*H*-phenothiazin-10-yl)-1*H*-indol-1-yl)propyl)triphenylphosphonium (5pca)



(71) ^{19}F-NMR spectrum of (3-(5-fluoro-3-(2-(trifluoromethyl)-10*H*-phenothiazin-10-yl)-1*H*-indol-1-yl)propyl)triphenylphosphonium (5pca)

(72) ^{31}P-NMR spectrum of (3-(5-fluoro-3-(2-(trifluoromethyl)-10*H*-phenothiazin-10-yl)-1*H*-indol-1-yl)propyl)triphenylphosphonium (5pca)