Supporting Information

Direct Access to Functional Phenazines via Oxidative Annulation of Anilines and *o*-Phenylenediamines with a Reusable Cobalt Catalyst

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1. General information

All the obtained products were characterized by melting points (m.p.), ^{1}H-NMR, ^{13}C-NMR, and mass spectra (MS). the NMR spectra of the known compounds were found to be identical with the ones reported in the literatures. Additionally, all the new compounds were further characterized by high resolution mass spectra (HRMS). Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected. Mass spectra were recorded on Trace ISQ GC/MS, High-resolution mass spectra (HRMS) were recorded on a thermo scientific Q Exactive Ultimate 3000 UPLC spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Bruker-400 or Bruker-500 and referenced to 7.26 ppm for chloroform solvent or 2.54 ppm for dimethyl sulfoxide solvent with TMS as internal standard (0 ppm). 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). 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). 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).

XRD was conducted on a TD-3500 powder diffractometer (Tongda, China) operated at 30 kV and 20 mA, using Cu Kα radiation sources in a Bragg angle range of 10−80°. EPR spectra were recorded on a Bruker X-band A-200 spectrometer. The EPR parameters were set as the following: sweep width 200 G, center field 3511.70 G, sweep time 39.997 s, microwave power 0.20 mW, modulation amplitude 1.000 G, modulation frequency 100 kHz, resolution 1024. The related systems were reacted under the standard conditions for 30 min. Then, the reaction solution was taken out by capillary and analyzed by EPR at room temperature. The samples were taken out by a capillary (borosilicate glass, 0.8-1.1×100 mm), and then recorded by EPR spectrometer at room temperature and parameters.

2. Procedure for the preparation of Co-Nx/NC-800[1]

Cobalt(II) acetate tetrahydrate (126.8 mg, 0.5 mmol) and 1,10-phenanthroline (275.3 mg, 1.5 mmol) (Co:phenanthroline = 1:3 molar ratio) were stirred in ethanol (20 mL) for approximately 20 minutes at room temperature. Then, carbon powder (696 mg) (VULCAN® XC72R, Cabot Corporation Prod. Code XVC72R; CAS No. 1333-86-4) was added and the whole reaction mixture was refluxed for 4 hours. The reaction mixture was cooled to room temperature and the ethanol was removed in vacuo. The solid sample obtained was dried at 60 °C for 12 hours, after which it was grinded to a fine powder. Then, the grinded powder was transferred into a ceramic crucible and placed in the oven. The oven was heated to 800 °C at the rate of 25 °C per minute, and held at 800 °C for 2 hours under argon atmosphere. After heating the oven was switched off and cooled to room temperature. During the whole process argon was constantly passed through the oven.

3. XRD measurements and data of Co-Nx/NC-800

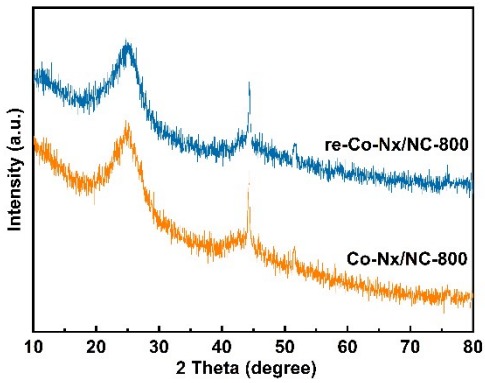
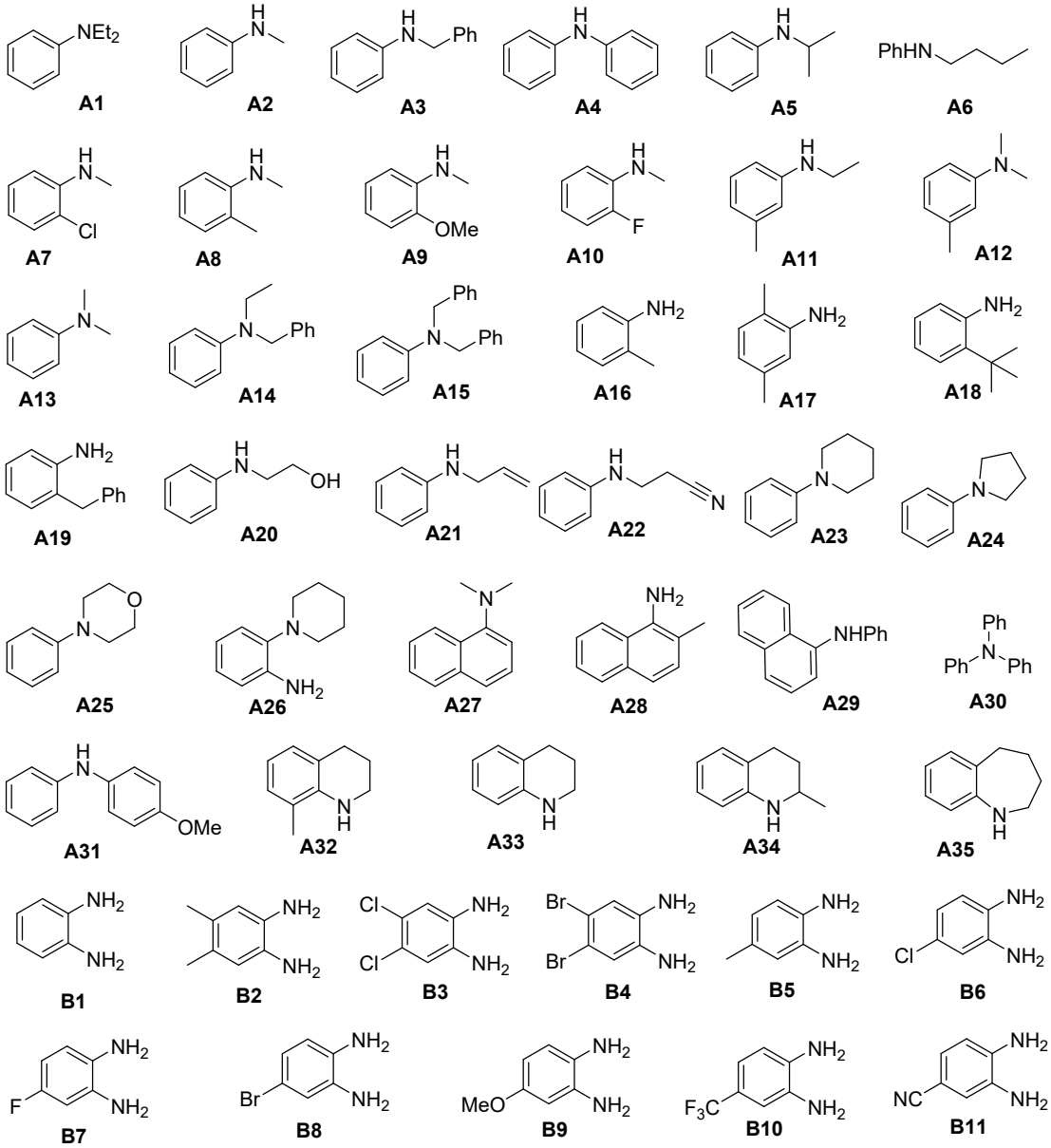


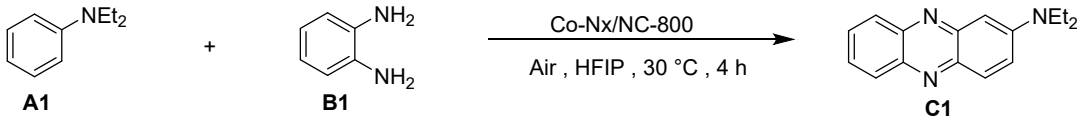
Figure S1. XRD measurements and data of Co-Nx/NC-800

4. Experimental Section



Scheme S1. Substrates employed for the reaction

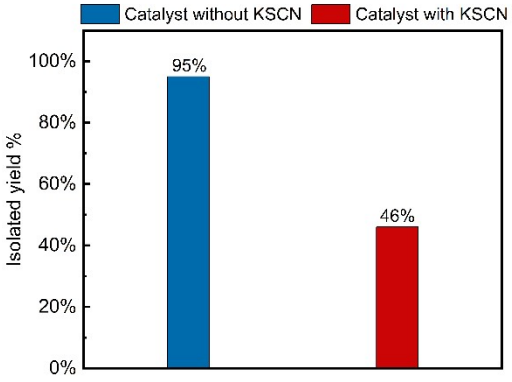
4.1 Typical procedure for the synthesis of product C1



Under air atmosphere, the mixture of Co-Nx/NC-800 (30 mg), *N,N*-diethylaniline **A1** (22.4mg, 0.15 mmol), *o*-phenylenediamine **B1** (16.2mg, 0.15 mmol) and HFIP (1.5 mL) was introduced in a Schlenk tube (50 mL), which was then stirred at 30 ˚C for 4 h. Next, the mixture was extracted with EtOAc (15 mL x 3), and concentrated under vacuum. The residue was purified by column chromatography on silica gel to give the desired product **C1** (ethyl acetate : petroleum ether = 1 : 5, v/v).

4.2 Poisoning experiment

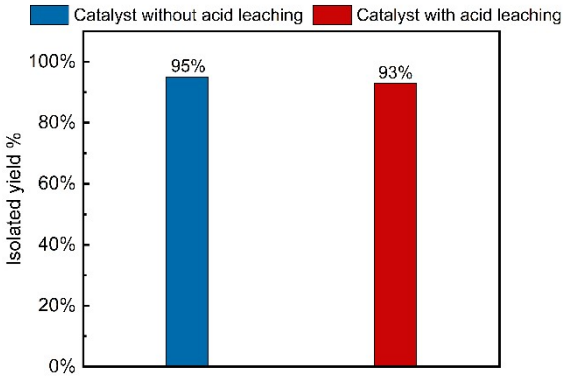
Under air atmosphere, a mixture of Co-Nx/NC-800 (30 mg), arylamines **A1** (0.15 mmol), *o*-Phenylenediamine derivatives **B1** (0.15 mmol), HFIP (1.5 mL) and KSCN (25 mol%) were introduced in a Schlenk tube (50 mL), and then was stirred at 30 ˚C for 4 h. Next, the mixture was extracted with EtOAc for three times, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the product **C1** (EtOAc : petroleum ether = 1:5, v/v).



Scheme S2. KSCN poisoning experiment

4.3 Acid Leaching Experiment

150 mg of the catalyst prepared by the standard procedure were treated with 50 mL of 0.5M H_2SO_4 solution at 90 ˚C for 4 h. Then, the slurry was filtrated with suction filtration on a paper filter with deionized water, dissolved in EtOH and dried under rotary evaporator and vacuum. The activity was estimated via model reaction under the standard condition.



Scheme S3. Acid Leaching Experiment.

4.4 Catalyst and solvent-recycling experiment

Under air atmosphere, a mixture of Co-Nx/NC-800 (30 mg), arylamines **A1** (0.15 mmol), *o*-Phenylenediamine derivatives **B1** (0.15 mmol) and HFIP (1.5 mL) were introduced in a Schlenk tube (50 mL), and then was stirred at 30 ˚C for 4 h. Next, the mixture was extracted with EtOAc for three times, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the product **C1** (ethylacetate : petroleum ether = 1:5, v/v). The catalyst was separated by centrifugation, washed with EtOAc and ethanol for three times, then dried under vacuum at 60 °C for 4 h. After that, the separated catalyst was reused for the next cycle experiment. As for solvent-recycling, HFIP solvent was directly recovered through a rotary evaporator with somewhat loss, which was then reused for the next run of the model reaction and did not affect the product yield.

4.5 Control experiments

(1) Preparation of compound C13-1[2]

The mixture of 1-bromo-2-nitrobenzene (404 mg, 2 mmol), *N*,*N*-dimethyl-1,4-phenylenediamine (2 mmol) and DBU (2 mmol) in DMF (1.5 mL) was stirred at 140 ˚C for 10 hours. After cooling to room temperature, the reaction mixture was extracted with EtOAc for three times and the organic layer was dried over anhydrous sodium sulfate and then concentrated by removing the solvent under vacuum. Finally, the residue was purified via silica gel column chromatography with ethylacetate : petroleum ether (1:40, v/v) as an eluent to afford N^1,N^1-dimethyl-N^4-(2-nitrophenyl)benzene-1,4-diamine.

Next, under N_2 atmosphere, Pd/C (50 mg), EtOH (2 mL) and N^1,N^1-dimethyl-N^4-(2-nitrophenyl)benzene-1,4-diamine were added successively to a Schlenk tube (50 mL) and then equipped with an H_2 balloon at 30 °C for 10 h. The resulting mixture was extracting with EtOAc, dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum. The residue was purified by column chromatography on silica gel, and eluting with ethylacetate : petroleum ether (1:5, v/v) to give the target product **C13-1**. ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.84 (d, J = 7.8 Hz, 1H), 6.77 (d, J = 8.8 Hz, 2H), 6.67 (t, J = 6.0 Hz, 4H), 6.52 (s, 1H), 6.47 (dt, J = 8.4, 4.8 Hz, 1H), 4.64 (s, 2H), 2.78 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 145.42, 140.14, 136.07, 131.32, 121.90, 119.13, 118.90, 117.15, 115.42, 114.81, 41.69.

(2) Detection of aniline radical species

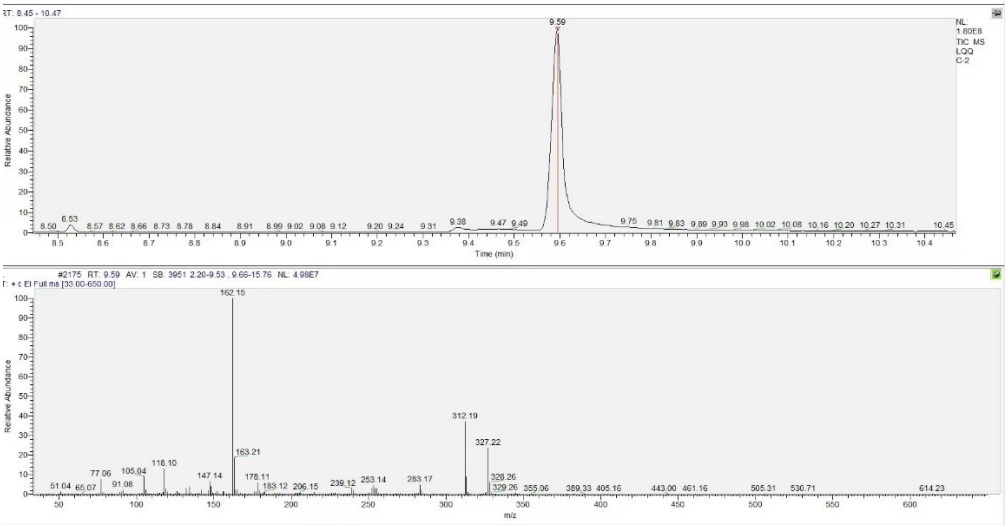
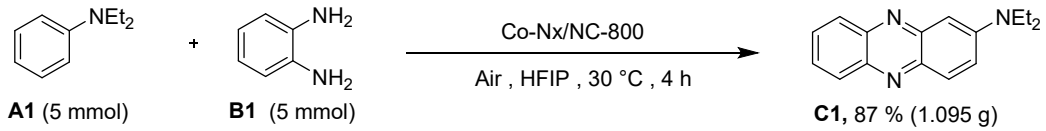


Figure S2. GC-MS analysis for the coupling adduct of 1,1-diphenylethylene-trapping the aniline radical

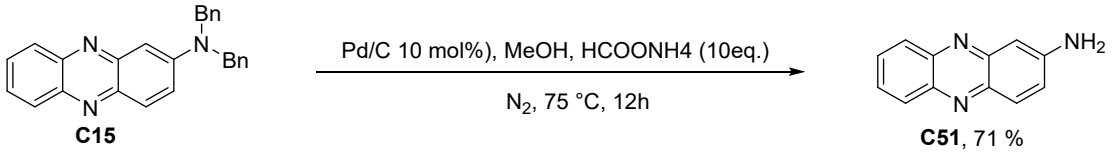
5. Synthetic utility

Gram-scale synthesis of compound C1: Under air atmosphere, Co-Nx/NC-800 (983 mg), *N*,*N*-diethylaniline **A1** (5 mmol), *o*-Phenylenediamine **B1** (5 mmol) and HFIP (33 mL) were introduced in a reaction bulb (100 mL), and then was stirred at 30 ˚C for 4 h. Next, the mixture was extracted with EtOAc for three times, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the desired product **C1** (ethylacetate : petroleum ether = 1:5, v/v).



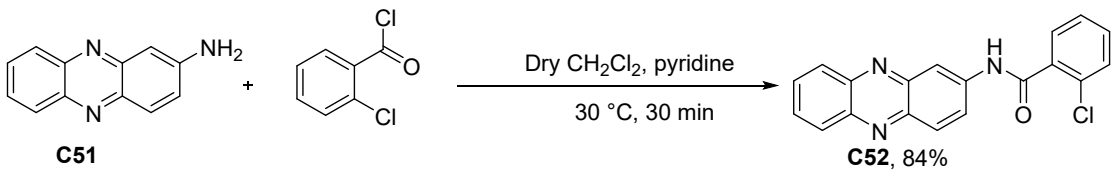
A1 (5 mmol) **B1** (5 mmol) **C1,** 87 % (1.095 g)

Debenzylation of C15 to compound C52: under N_2 atmosphere, Pd/C (10 mol%), **C15** (0.1 mmol, 64.8 g), $HCOONH_4$ (1 mmol, 63 mg), MeOH (0.5 mL) were introduced in a Schlenk tube (50 mL), successively. Then it was stirred at 75 ˚C for 12 h. After cooling down to room temperature, the resulting mixture was extracting with ethyl acetate, dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by column chromatography on silica gel to give **C51** (71% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.05 (d, J = 8.6 Hz, 1H), 7.98 (d, J = 8.6 Hz, 1H), 7.90 (d, J = 9.4 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.45 (dd, J = 9.4, 2.2 Hz, 1H), 6.92 (s, 1H), 6.48 (s, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 151.49, 146.27, 143.68, 140.22, 139.77, 130.61, 130.50, 129.70, 128.49, 127.57, 127.19, 101.67; HRMS (ESI): Calcd. for $C_{12}H_{10}N_3$ $[M+H]^+$: 196.08692; found: 196.08678.



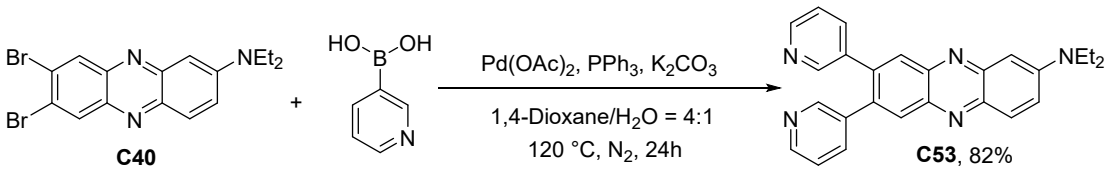
C15 **C51**, 71 %

Derivation of amine C51 to amide C52: 1-aminophenazine **C51** (0.1 mmol, 19.5 mg,) was dissolved in the solution of dry CH_2Cl_2 (2 mL) and anhydrous pyridine (0.1 mL). 2-chlorobenzoyl chloride (1.4 mmol, 245 mg) diluted in CH_2Cl_2 (3 mL), then added dropwise to the above solution. The mixture was stirred at 30 ˚C for 0.5 h, as monitored by TLC until reaction completed, and then the solvent was removed by distillation. The residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (1/1, v/v), and then recrystallized with anhydrous ethanol to give the **C52**. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.17 (s, 1H), 8.83 (s, 1H), 8.23 (t, J = 10.0 Hz, 3H), 8.10 (d, J = 10.0 Hz, 1H), 7.95 - 7.89 (m, 2H), 7.72 (d, J = 10.0 Hz, 1H), 7.63 (d, J = 5.0 Hz, 1H), 7.57 (t, J = 10.0 Hz, 1H), 7.52 (t, J = 10.0 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.32, 144.21, 143.72, 142.50, 141.10, 140.92, 136.91, 132.02, 131.47, 130.60, 130.53, 130.48, 130.28, 129.81, 129.60, 129.49, 127.88, 126.82, 115.06; HRMS (ESI): Calcd. for $C_{19}H_{13}ClN_3O$ $[M+H]^+$: 334.07417; found: 334.07336.



C51 **C52**, 84%

Synthesis of **C53** via Suzuki cross-coupling of **C40** with pyridin-3-ylboronic acid: under nitrogen atmosphere, **C40** (0.1 mmol, 41 mg), boronic acid (0.4 mmol, 49 mg), $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), K_2CO_3 (2 equiv) and 1,4-dioxane/H_2O (4/1) were introduced in a Schlenk tube (50mL), successively. The mixture was stirred at 120 ˚C for 24 hours and cooled to room temperature. The resulting mixture concentrated under vacuum. The residue was purified by column chromatography on silica gel to give the desired product **C53** as a red soild. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.50 (dd, J = 8.8, 4.6 Hz, 2H), 8.45 (d, J = 5.0 Hz, 2H), 8.11 (s, 1H), 8.01 (s, 1H), 7.99 (d, J = 5.0 Hz, 1H), 7.75 (d, J = 9.6 Hz, 1H), 7.62 (t, J = 6.8 Hz, 2H), 7.34 (q, J = 7.0 Hz, 2H), 6.93 (s, 1H), 3.59 (q, J = 7.0 Hz, 4H), 1.23 (t, J = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 150.42, 150.35, 149.35, 148.83, 148.62, 146.59, 143.27, 140.02, 139.73, 139.63, 137.57, 137.56, 136.52, 135.87, 135.80, 131.13, 130.71, 129.86, 124.45, 123.61, 123.58, 100.66, 44.81, 13.09; HRMS (ESI): Calcd. for $C_{26}H_{24}N_5$ $[M+H]^+$: 406.20262; found: 406.20166.



6. Single Crystal X-ray Diffraction of C44

Single crystals of $C_{17}H_{16}ClN_3$ **C44** were red block. X-Ray diffraction data of one these crystals were collected on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 179.99(10) K during data collection. The measurements were performed with Cu-Kα radiation (λ = 1.54184 Å).

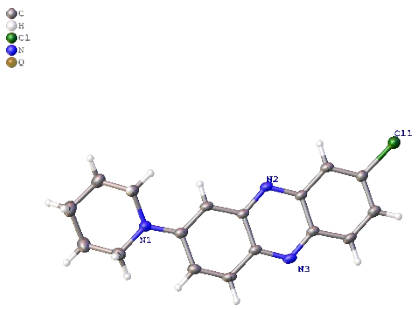


Figure S3. Molecular structure of **C44** (CCDC 2142278)

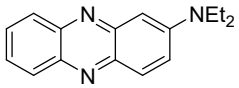
Table S1. Crystal data and structure refinement for **C44.**

Identification code	C44
Empirical formula	$C_{17}H_{16}ClN_3$
Formula weight	297.78
Temperature/K	179.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	6.7166(12)
b/Å	9.3699(17)
c/Å	12.656(2)
α/°	68.667(17)
β/°	79.026(15)
γ/°	72.896(16)

Volume/Å^3	706.0(2)
Z	2
ρ_{calc}g/cm^3	1.401
μ/mm^{-1}	2.351
F(000)	312.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.532 to 147.762
Index ranges	-8 ≤ h ≤ 8, -11 ≤ k ≤ 10, -15 ≤ l ≤ 15
Reflections collected	4355
Independent reflections	2737 [R_{int} = 0.0427, R_{sigma} = 0.0652]
Data/restraints/parameters	2737/3/194
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0670, wR_2 = 0.1771
Final R indexes [all data]	R_1 = 0.0893, wR_2 = 0.1991
Largest diff. peak/hole / e Å^{-3}	0.38/-0.41

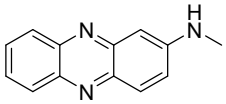
7. Analytical data of the obtained compounds

N,N-diethylphenazin-2-amine (**C1**)



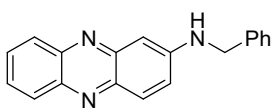
Red solid, m.p.: 100.1 – 101.1 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.06 (d, J = 10.0 Hz, 1H), 7.97 (d, J = 10.0 Hz, 2H), 7.77 (t, J = 5.0 Hz, 1H), 7.71 (dd, J = 9.6 Hz, 2.6 Hz, 1H), 7.65 (t, J = 10.0 Hz, 1H), 6.93 (d, J = 5.0 Hz, 1H), 3.58 - 3.54 (m, 4H), 1.20 (t, J = 10.0 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 148.98, 146.01, 143.91, 140.46, 139.24, 130.60, 130.55, 129.71, 128.45, 127.62, 123.97, 100.81, 44.72, 13.05; HRMS (ESI): Calcd. for $C_{16}H_{18}N_3$ $[M+H]^+$: 252.14952; found: 252.14914.

N-methylphenazin-2-amine (**C2**)



Red solid, m.p.: 165 – 166 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.06 (d, J = 10.0 Hz, 1H), 7.98 (d, J = 10.0 Hz, 1H), 7.88 (d, J = 10.0 Hz, 1H), 7.78 – 7.75 (m, 1H), 7.67 – 7.64 (m, 1H), 7.45 (dd, J = 9.6 Hz, 2.6 Hz, 1H), 7.10 (d, J = 5.0 Hz, 1H), 6.69 (d, J = 2.0 Hz, 1H), 2.89 (d, J = 5.0 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 151.54, 146.64, 143.57, 140.30, 140.13, 130.45, 130.14, 129.63, 128.39, 127.51, 127.38, 97.69, 29.93; HRMS (ESI): Calcd. for $C_{13}H_{12}N_3$ $[M+H]^+$: 210.10257; found: 210.10239.

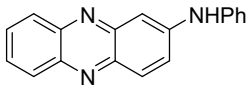
N-benzylphenazin-2-amine (**C3**)



Red solid, m.p.: 98.5 – 99.5 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.05 (d, J = 10.0 Hz, 1H), 7.96 (d, J = 5.0 Hz, 1H), 7.91 (d, J = 10.0 Hz, 1H), 7.75 (t, J = 10.0 Hz, 1H), 7.65 (t, J = 5.0 Hz, 2H), 7.59 (dd, J = 10.0 Hz, 5.0 Hz, 1H), 7.46 (d, J = 10.0 Hz, 2H), 7.37 (t, J = 5.0 Hz, 2H), 7.26 (t, J = 10.0 Hz, 1H), 6.72 (d, J = 5.0 Hz, 1H), 4.50 (d, J = 10.0 Hz, 2H); ^{13}C NMR

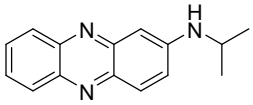
(126 MHz, DMSO-d_6) δ 150.39, 146.34, 143.53, 140.24, 140.21, 139.12, 130.50, 130.27, 129.63, 128.98, 128.40, 127.88, 127.68, 127.50, 99.05, 46.88; HRMS (ESI): Calcd. for $C_{19}H_{16}N_3$ $[M+H]^+$: 286.13387; found: 286.13330.

N-phenylphenazin-2-amine (**C4**)



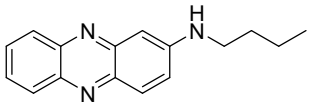
Red solid, m.p.: 193 – 194 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.19 (s, 1H), 8.10 (d, J = 8.6 Hz, 1H), 8.06 - 8.01 (m, 2H), 7.80 (t, J = 6.8 Hz, 1H), 7.73 - 7.69 (m, 2H), 7.49 (s, 1H), 7.44 - 7.39 (m, 4H), 7.09 (t, J = 6.8 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 146.46, 145.80, 143.69, 141.40, 141.03, 140.53, 130.85, 130.76, 129.93, 129.72, 128.73, 128.57, 127.67, 123.24, 120.52, 102.93; HRMS (ESI): Calcd. for $C_{18}H_{14}N_3$ $[M+H]^+$: 272.11822; found: 272.11786.

N-isopropylphenazin-2-amine (**C5**)



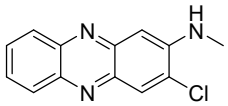
Yellow oil; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.04 (d, *J* = 5.0 Hz, 1H), 7.97 (d, *J* = 5.0 Hz, 1H), 7.87 (d, *J* = 10.0 Hz, 1H), 7.75 (t, *J* = 5.0 Hz, 1H), 7.63 (t, *J* = 10.0 Hz, 1H), 7.46 (d, *J* = 5.0 Hz, 1H), 6.91 (d, *J* = 5.0 Hz, 1H), 6.73 (s, 1H), 3.79 – 3.73 (m, 1H), 1.25 (d, *J* = 5.0 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 149.66, 146.66, 143.62, 140.14, 130.42, 130.24, 129.63, 128.33, 127.85, 127.41, 98.15, 43.89, 22.27; HRMS (ESI): Calcd. for $C_{15}H_{16}N_3$ $[M+H]^+$: 238.13387; found: 238.13354.

N-butylphenazin-2-amine (**C6**)



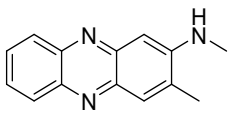
Orange solid, m.p.: 135.4 – 136.4 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.05 (d, *J* = 10.0 Hz, 1H), 7.97 (d, *J* = 10.0 Hz, 1H), 7.87 (d, *J* = 10.0 Hz, 1H), 7.75 (t, *J* = 10.0 Hz, 1H), 7.64 (t, *J* = 10.0 Hz, 1H), 7.48 (dd, *J* = 10.0, 2.0 Hz, 1H), 7.03 (t, *J* = 5.0 Hz, 1H), 6.71 (s, 1H), 3.21 (q, *J* = 5.0 Hz, 2H), 1.67 - 1.62 (m, 2H), 1.48 - 1.40 (m, 2H), 0.94 (t, *J* = 5.0 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 150.71, 146.66, 143.60, 140.26, 140.12, 130.41, 130.16, 129.63, 128.35, 127.57, 127.42, 97.76, 42.84, 30.55, 20.37, 14.22; HRMS (ESI): Calcd. for $C_{16}H_{18}N_3$ $[M+H]^+$:252.14952; found: 252.14937.

3-fluoro-*N*-methylphenazin-2-amine (**C7**)



Orange solid, m.p.: 169 – 170 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.16 (s, 1H), 8.07 (d, J = 5.0 Hz, 1H), 8.01 (d, J = 5.0 Hz, 1H), 7.81 (t, J = 7.4 Hz, 1H), 7.71 (t, J = 7.4 Hz, 1H), 6.89 (s, 1H), 6.79 (q, J = 5.0 Hz, 1H), 2.95 (d, J = 4.8 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 146.93, 144.95, 143.71, 140.65, 138.79, 130.94, 130.05, 129.60, 128.77, 128.63, 128.47, 100.20, 30.55; HRMS (ESI): Calcd. for $C_{13}H_{11}ClN_3$ $[M+H]^+$: 244.06360; found: 244.06325.

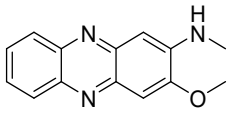
3-chloro-*N*-methylphenazin-2-amine (**C8**)



Red solid, m.p.: 193 – 194 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.05 (d, J = 8.6 Hz, 1H), 7.99 (d, J = 8.6 Hz, 1H), 7.77 (s, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 6.74 (s, 1H), 6.48 – 6.45 (m, 1H), 2.93 (d, J = 4.6 Hz, 3H), 2.40 (s,

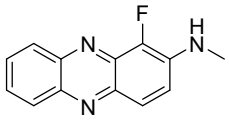
3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 150.88, 145.73, 143.23, 140.30, 140.07, 135.31, 129.87, 129.52, 128.64, 128.42, 127.37, 98.07, 30.50, 18.77; HRMS (ESI): Calcd. for $C_{14}H_{14}N_3$ $[M+H]^+$: 224.11822; found: 224.11769.

N,3-dimethylphenazin-2-amine (**C9**)



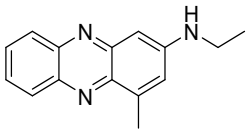
Orange solid, m.p.: 196 – 197 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.02 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 10.0 Hz, 1H), 7.71 (t, J = 5.0 Hz, 1H)), 7.64 (t, J = 10.0 Hz, 1H), 7.28 (s, 1H), 6.73 – 6.71 (m, 1H), 6.70 (s, 1H), 4.07 (s, 3H), 2.92 (d, J = 5.0 Hz, 3H); ^{13}C NMR (126 MHz, DMSO- d_6) δ 154.00, 145.17, 143.67, 142.05, 141.31, 140.18, 128.89, 128.86, 128.32, 127.31, 103.92, 97.83, 56.83, 29.91; HRMS (ESI): Calcd. for $C_{14}H_{14}N_3O$ $[M+H]^+$: 240.11314; found: 240.11266.

1-fluoro-*N*-methylphenazin-2-amine (**C10**)



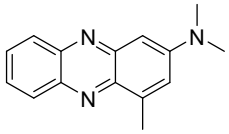
Orange solid, m.p.: 163 – 164 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.07 (d, J = 8.6 Hz, 1H), 8.02 (d, J = 8.6 Hz, 1H), 7.81 - 7.76 (m, 2H), 7.71 (t, J = 7.6 Hz, 1H), 7.13 - 7.09 (m, 1H), 6.89 (d, J = 9.4 Hz, 1H), 2.93 (d, J = 4.8 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 156.66 (d, J = 258.6 Hz), 144.15, 143.00, 142.86, 140.44, 139.38 (d, J = 13.4 Hz), 130.37, 129.24, 128.62, 128.26, 110.78 (d, J = 18.4 Hz), 100.40 (d, J = 5.2 Hz), 29.86; ^{19}F NMR (471 MHz, DMSO-d_6) δ -121.02 (t, J = 11.0 Hz); HRMS (ESI): Calcd. for $C_{13}H_{11}FN_3$ $[M+H]^+$: 228.09315; found: 228.09271.

N-ethyl-4-methylphenazin-2-amine (**C11**)



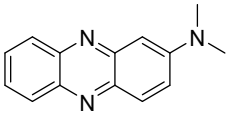
Orange solid, m.p.: 140.4 – 141.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.6 Hz, 1H), 8.04 (d, J = 8.6 Hz, 1H), 7.74 – 7.68 (m, 1H), 7.64 – 7.58 (m, 1H), 7.00 (s, 1H), 6.80 (s, 1H), 4.27 (s, 1H), 3.33 (p, J = 7.0, 6.4 Hz, 2H), 2.78 (s, 3H), 1.34 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.97, 146.48, 143.37, 140.45, 140.14, 138.57, 129.90, 128.11, 127.02, 124.76, 98.30, 38.10, 17.67, 14.32; HRMS (ESI): Calcd. for $C_{15}H_{16}N_3$ $[M+H]^+$: 238.13387; found: 238.13358.

N,*N*,4-trimethylphenazin-2-amine (**C12**)



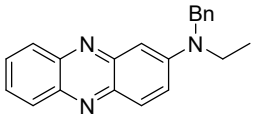
Orange solid, m.p.: 120 – 121 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, J = 8.6 Hz, 1H), 8.01 (d, J = 8.6 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.59 – 7.55 (m, 1H), 7.29 (s, 1H), 6.81 (d, J = 2.4 Hz, 1H), 3.09 (s, 6H), 2.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.86, 145.54, 143.26, 140.22, 139.63, 138.25, 130.02, 129.90, 127.71, 126.89, 121.60, 100.35, 40.25, 18.15; HRMS (ESI): Calcd. for $C_{15}H_{16}N_3$ $[M+H]^+$: 238.13387; found: 238.13348.

N,*N*-dimethylphenazin-2-amine (**C13**)



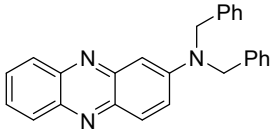
Orange solid, m.p.: 160 – 161 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.08 (d, J = 10.0 Hz, 1H), 8.00 (d, J = 5.0 Hz, 1H), 7.99 (d, J = 5.0 Hz, 1H), 7.80 – 7.77 (m, 2H), 7.68 (t, J = 10.0 Hz, 1H), 6.94 (d, J = 5.0 Hz, 1H), 3.17 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 151.44, 145.66, 143.87, 140.61, 139.36, 130.67, 130.20, 129.70, 128.56, 127.93, 124.15, 101.96, 40.45; HRMS (ESI): Calcd. for $C_{14}H_{14}N_3$ $[M+H]^+$: 224.11822; found: 224.11794.

N-benzyl-*N*-ethylphenazin-2-amine (**C14**)



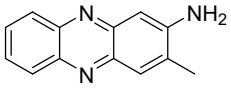
Red solid, m.p.: 100 – 101 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 8.6 Hz, 1H), 8.05 (d, J = 8.6 Hz, 1H), 8.00 (d, J = 9.8 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.53 (dd, J = 9.8, 2.8 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.27 (d, J = 6.8 Hz, 3H), 7.16 (s, 1H), 4.76 (s, 2H), 3.69 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.61, 145.68, 143.86, 140.96, 139.58, 137.55, 130.54, 130.17, 129.55, 128.86, 128.29, 127.48, 127.31, 126.41, 122.95, 102.37, 53.80, 45.81, 12.26; HRMS (ESI): Calcd. for $C_{21}H_{20}N_3$ $[M+H]^+$: 314.16517; found: 314.16470.

N,N-dibenzylphenazin-2-amine (**C15**)



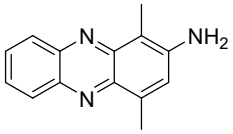
Red solid, m.p.: 172.7 – 173.7°C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.06 (d, J = 5.0 Hz, 1H), 7.97 (t, J = 10.0 Hz, 2H), 7.76 (t, J = 10.0 Hz, 2H), 7.67 (t, J = 10.0 Hz, 1H), 7.36 (d, J = 5.0 Hz, 8H), 7.28 – 7.25 (m, 2H), 6.97 (s, 1H), 4.99 (s, 4H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 149.94, 145.38, 143.81, 140.80, 139.32, 138.39, 130.77, 130.44, 129.69, 129.18, 128.58, 128.19, 127.51, 127.03, 124.21, 103.23, 55.01; HRMS (ESI): Calcd. for $C_{26}H_{22}N_3$ $[M+H]^+$: 376.18082; found: 376.18005.

3-methylphenazin-2-amine (**C16**)



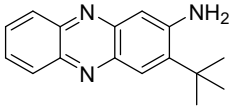
Red oil; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.04 (d, J = 10.0 Hz, 1H), 7.98 (d, J = 10.0 Hz, 1H), 7.80 (s, 1H), 7.73 (t, J = 10.0 Hz, 1H), 7.64 (t, J = 10.0 Hz, 1H), 7.03 (s, 1H), 6.29 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 151.22, 145.41, 143.31, 140.35, 139.90, 135.17, 129.94, 129.59, 128.96, 128.53, 127.43, 102.17, 18.83; HRMS (ESI): Calcd. for $C_{13}H_{12}N_3$ $[M+H]^+$: 210.10257; found: 210.10236.

1,4-dimethylphenazin-2-amine (**C17**)



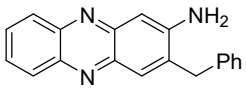
Orange solid, m.p.: 162.6 – 163.6 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.08 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 10.0 Hz, 1H), 7.76 (t, J = 5.0 Hz, 1H), 7.65 (t, J = 5.0 Hz, 1H), 7.36 (s, 1H), 6.09 (s, 2H), 2.69 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 147.72, 144.97, 142.69, 139.65, 138.78, 135.11, 130.16, 129.79, 128.72, 127.31, 125.95, 105.84, 17.75, 10.45; HRMS (ESI): Calcd. for $C_{14}H_{14}N_3$ $[M+H]^+$: 224.11822; found: 224.11798.

3-(tert-butyl)phenazin-2-amine (**C18**)



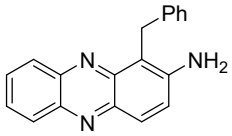
Orange solid, m.p.: 185 – 186°C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.04 (d, J = 10.0 Hz, 1H), 7.98 (d, J = 10.0 Hz, 1H), 7.86 (s, 1H), 7.74 (t, J = 7.2 Hz, 1H), 7.64 (t, J = 5.0 Hz, 1H), 7.12 (s, 1H), 6.20 (s, 2H), 1.51 (s, 9H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 150.71, 145.01, 144.77, 143.80, 140.64, 139.73, 130.17, 129.64, 128.59, 127.46, 126.46, 104.68, 35.56, 29.77; HRMS (ESI): Calcd. for $C_{16}H_{18}N_3$ $[M+H]^+$: 252.14952; found: 252.14922.

3-benzylphenazin-2-amine (**C19**)



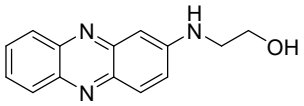
Orange solid, m.p.: 90 - 91 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.99 (t, J = 8.6 Hz, 2H), 7.74 (t, J = 5.0 Hz, 1H), 7.63 (t, J = 5.0 Hz, 1H), 7.50 (s, 1H), 7.37 (d, J = 5.0 Hz, 4H), 7.30 – 7.27 (m, 1H), 7.08 (s, 1H), 6.34 (s, 2H), 4.12 (s, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 150.59, 145.25, 143.50, 140.44, 139.65, 138.91, 138.19, 130.17, 129.81, 129.59, 129.11, 129.07, 128.55, 127.60, 126.95, 102.89, 37.12; HRMS (ESI): Calcd. for $C_{19}H_{16}N_3$ $[M+H]^+$: 286.13387; found: 286.13339.

1-benzylphenazin-2-amine (**C19'**)



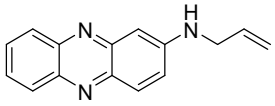
Orange solid, m.p.: 124 - 125 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.08 (d, J = 10.0 Hz, 1H), 8.03 (d, J = 8.6 Hz, 1H), 7.88 (d, J = 10.0 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.68 (t, J = 5.0 Hz, 1H), 7.55 (d, J = 5.0 Hz, 1H), 7.31 (d, J = 7.6 Hz, 2H), 7.17 (t, J = 10.0 Hz, 2H), 7.08 (t, J = 7.2 Hz, 1H), 6.27 (s, 2H), 4.53 (s, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 148.00, 144.52, 143.06, 141.45, 139.91, 130.42, 129.51, 128.99, 128.96, 128.86, 128.45, 127.80, 127.69, 125.89, 111.09, 29.40; HRMS (ESI): Calcd. for $C_{19}H_{16}N_3$ $[M+H]^+$: 286.13387; found: 286.13367.

2-(phenazin-2-ylamino)ethan-1-ol (**C20**)



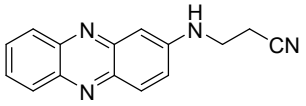
Red solid, m.p.: 176.6 – 177.6 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.04 (d, J = 10.0 Hz, 1H), 7.96 (d, J = 5.0 Hz, 1H), 7.86 (d, J = 10.0 Hz, 1H), 7.75 (t, J = 10.0 Hz, 1H), 7.64 (t, J = 10.0 Hz, 1H), 7.54 (dd, J = 10.0, 5.0 Hz, 1H), 7.18 (t, J = 5.0 Hz, 1H), 6.75 (d, J = 2.0 Hz, 1H), 3.70 (d, J = 5.0 Hz, 2H), 3.31 (q, J = 5.0 Hz, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 150.85, 146.59, 143.55, 140.25, 140.09, 130.47, 130.10, 129.60, 128.31, 127.71, 127.50, 97.84, 59.39, 45.99; HRMS (ESI): Calcd. for $C_{14}H_{14}N_3O$ $[M+H]^+$: 240.11314; found: 240.11290.

N-allylphenazin-2-amine (**C21**)



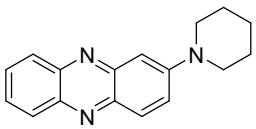
Orange solid, m.p.: 158 – 159 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.06 (d, J = 10.0 Hz, 1H), 7.98 (d, J = 10.0 Hz, 1H), 7.90 (d, J = 10.0 Hz, 1H), 7.77 (t, J = 5.0 Hz, 1H), 7.66 (t, J = 5.0 Hz, 1H), 7.52 (d, J = 10.0 Hz, 1H), 7.25 (s, 1H), 6.75 (s, 1H), 6.01 - 5.95 (m, 1H), 5.35 (d, J = 16.0 Hz, 1H), 5.21 (d, J = 10.0 Hz, 1H), 3.92 (s, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 150.43, 146.44, 143.58, 140.23, 140.20, 135.04, 130.50, 130.21, 129.64, 128.43, 127.64, 127.42, 116.73, 98.82, 45.58; HRMS (ESI): Calcd. for $C_{15}H_{14}N_3$ $[M+H]^+$: 236.11822; found: 236.11777.

3-(phenazin-2-ylamino)propanenitrile (**C22**)



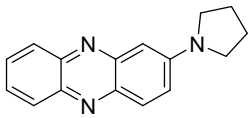
Orange solid, m.p.: 107.6 – 108.6 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.08 (d, J = 10.0 Hz, 1H), 8.00 (d, J = 5.0 Hz, 1H), 7.93 (d, J = 10.0 Hz, 1H), 7.79 (t, J = 10.0 Hz, 1H), 7.69 (t, J = 10.0 Hz, 1H), 7.51 (dd, J = 10.0, 5.0 Hz, 1H), 7.33 (t, J = 5.0 Hz, 1H), 6.89 (d, J = 5.0 Hz, 1H), 3.59 (q, J = 5.0 Hz, 2H), 2.90 (t, J = 5.0 Hz, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 149.76, 146.34, 143.56, 140.41, 140.20, 130.64, 130.48, 129.68, 128.49, 127.95, 127.19, 120.03, 98.99, 39.12, 17.28; HRMS (ESI): Calcd. for $C_{15}H_{13}N_4$ $[M+H]^+$: 249.11347; found: 249.11304.

2-(piperidin-1-yl)phenazine (**C23**)



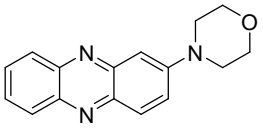
Orange solid, m.p.: 139.5 – 140.5 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.10 (d, J = 10.0 Hz, 1H), 8.04 (d, J = 5.0 Hz, 1H), 7.98 (d, J = 10.0 Hz, 1H), 7.91 (dd, J = 9.6, 2.6 Hz, 1H), 7.81 (t, J = 10.0 Hz, 1H), 7.72 (t, J = 5.0 Hz, 1H), 7.17 (s, 1H), 3.49 (t, J = 5.0 Hz, 4H), 1.68 – 1.65 (m, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 152.21, 145.72, 143.72, 141.07, 139.96, 130.74, 130.07, 129.69, 128.73, 128.45, 126.20, 105.19, 48.96, 25.50, 24.40; HRMS (ESI): Calcd. for $C_{17}H_{18}N_3$ $[M+H]^+$: 264.14952; found: 264.14929.

2-(pyrrolidin-1-yl)phenazine (**C24**)



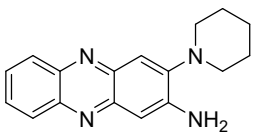
Orange solid, m.p.: 158 – 159 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.06 (d, J = 10.0 Hz, 1H), 7.98 (d, J = 10.0 Hz, 2H), 7.77 (t, J = 10.0 Hz, 1H), 7.66 (t, J = 5.0 Hz, 1H), 7.60 (dd, J = 10.0, 5.0 Hz, 1H), 6.77 (d, J = 5.0 Hz, 1H), 3.48 (t, J = 5.0 Hz, 4H), 2.03 (t, J = 5.0 Hz, 4H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 148.73, 145.83, 143.92, 140.29, 139.45, 130.61, 130.46, 129.69, 128.42, 127.56, 124.72, 100.82, 48.13, 25.52; HRMS (ESI): Calcd. for $C_{16}H_{16}N_3$ $[M+H]^+$: 250.13387; found: 250.13347.

4-(phenazin-2-yl)morpholine (**C25**)



Orange solid, m.p.: 176.7 – 177.7 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.14 (d, J = 5.0 Hz, 1H), 8.08 (d, J = 5.0 Hz, 1H), 8.05 (d, J = 10.0 Hz, 1H), 7.95 (d, J = 10.0 Hz, 1H), 7.84 (t, J = 10.0 Hz, 1H), 7.77 (t, J = 5.0 Hz, 1H), 7.25 (d, J = 5.0 Hz, 1H), 3.81 (t, J = 5.0 Hz, 4H), 3.46 (t, J = 5.0 Hz, 4H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 152.30, 145.37, 143.69, 141.32, 140.13, 130.92, 130.17, 129.73, 128.90, 128.87, 125.51, 105.89, 66.37, 48.01; HRMS (ESI): Calcd. for $C_{16}H_{16}N_3O$ $[M+H]^+$: 266.12879; found: 266.12842.

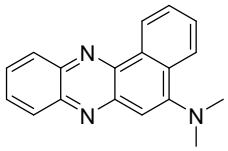
3-(piperidin-1-yl)phenazin-2-amine (**C26**)



Yellow oil; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.01 (d, J = 10.0 Hz, 1H), 7.97 (d, J = 10.0 Hz, 1H), 7.70 (t, J = 5.0 Hz, 1H), 7.63 (t, J = 5.0 Hz, 1H), 7.38 (s, 1H), 7.07 (s, 1H), 6.07 (s, 2H), 3.01 (s, 4H), 1.79 – 1.74 (m, 4H), 1.60 (d, J = 5.0 Hz,

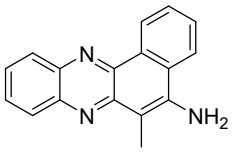
1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 149.68, 148.24, 144.00, 142.54, 141.01, 140.46, 129.21, 129.15, 128.49, 127.44, 115.35, 103.08, 52.53, 26.05, 24.27; HRMS (ESI): Calcd. for $C_{17}H_{19}N_4$ $[M+H]^+$: 279.16042; found: 279.16019.

N,N-dimethylbenzo[*a*]phenazin-5-amine (**C27**)



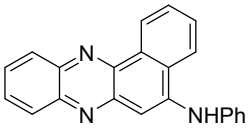
Orange solid, m.p.: 219.6 – 220.6 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.28 (d, J = 7.6 Hz, 1H), 8.27 (d, J = 8.2 Hz, 1H), 8.22 (d, J = 7.8 Hz, 1H), 8.15 (d, J = 8.2 Hz, 1H), 7.91 – 7.83 (m, 4H), 7.29 (s, 1H), 3.01 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.51, 144.89, 143.14, 140.63, 140.45, 131.71, 130.68, 130.24, 129.69, 129.38, 128.74, 128.50, 125.82, 125.72, 110.91, 44.43; HRMS (ESI): Calcd. for $C_{18}H_{16}N_3$ $[M+H]^+$: 274.13387; found: 274.13348.

6-methylbenzo[*a*]phenazin-5-amine (**C28**)



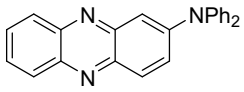
Orange solid, m.p.: 189.8 – 190.8 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.28 (d, J = 8.0 Hz, 1H), 8.41 (d, J = 10.0 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.86 (t, J = 7.6 Hz, 1H), 7.80 (t, J = 5.0 Hz, 2H), 7.70 (t, J = 7.6 Hz, 1H), 6.51 (s, 2H), 2.62 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 145.30, 144.79, 142.91, 139.32, 138.60, 130.26, 130.12, 129.48, 128.46, 128.06, 127.78, 127.42, 125.52, 122.87, 105.80, 11.23; HRMS (ESI): Calcd. for $C_{17}H_{14}N_3$ $[M+H]^+$: 260.11822; found: 260.11798.

N-phenylbenzo[*a*]phenazin-5-amine (**C29**)



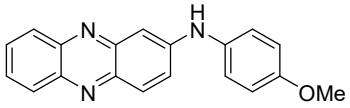
Orange solid, m.p.: 241.8 – 242.8 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.35 (d, J = 5.0 Hz, 1H), 8.90 (s, 1H), 8.57 (d, J = 7.8 Hz, 1H), 8.23 (d, J = 5.0 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.98 - 7.92 (m, 2H), 7.83 (t, J = 5.0 Hz, 1H), 7.77 (t, J = 5.0 Hz, 1H), 7.48 (d, J = 5.0 Hz, 4H), 7.26 (s, 1H), 7.20 - 7.16 (m, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 145.64, 145.16, 143.39, 141.87, 139.99, 139.89, 131.48, 130.55, 130.49, 129.88, 129.67, 129.05, 128.85, 128.45, 128.37, 125.75, 123.96, 123.28, 123.17, 102.51; HRMS (ESI): Calcd. for $C_{22}H_{16}N_3$ $[M+H]^+$: 322.13387; found: 322.13351.

N,N-diphenylphenazin-2-amine (**C30**)



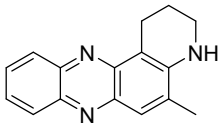
White solid, m.p.: 156.7-157.7 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.13 (d, J = 10.0 Hz, 1H), 8.05 (d, J = 10.0 Hz, 1H), 8.00 (d, J = 5.0 Hz, 1H), 7.83 (t, J = 10.0 Hz, 1H), 7.78 (t, J = 5.0 Hz, 1H), 7.56 (dd, J = 9.6, 2.6 Hz, 1H), 7.46 (t, J = 5.0 Hz, 4H), 7.28 (d, J = 10.0 Hz, 6H), 7.14 (d, J = 2.6 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 149.72, 146.16, 144.88, 143.69, 141.78, 140.80, 131.23, 130.55, 130.44, 129.77, 129.49, 128.99, 128.04, 126.68, 126.03, 112.35; HRMS (ESI): Calcd. for $C_{24}H_{18}N_3$ $[M+H]^+$: 348.14952; found: 348.14871.

N-(4-methoxyphenyl)phenazin-2-amine (**C31**)



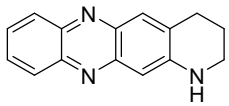
Orange solid, m.p.: 150 – 151 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.96 (s, 1H), 8.09 (d, J = 10.0 Hz, 1H), 8.02 (d, J = 10.0 Hz, 1H), 7.99 (d, J = 10.0 Hz, 1H), 7.79 (t, J = 10.0 Hz, 1H), 7.70 (t, J = 10.0 Hz 1H), 7.64 (dd, J = 9.6, 2.6 Hz, 1H), 7.33 (d, J = 10.0 Hz, 2H), 7.23 (d, J = 2.6 Hz, 1H), 7.03 (d, J = 10.0 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 156.15, 147.89, 146.06, 143.71, 140.76, 140.47, 133.96, 130.77, 130.73, 129.71, 128.63, 128.25, 127.45, 123.60, 115.24, 101.10, 55.78; HRMS (ESI): Calcd. for $C_{19}H_{16}N_3O$ $[M+H]^+$: 302.12879; found: 302.12842.

5-methyl-1,2,3,4-tetrahydropyrido[3,2-*a*]phenazine (**C32**)



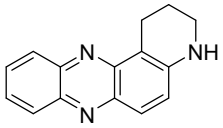
Orange solid, m.p.: 164.7 – 165.7 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.03 (d, J = 10.0 Hz, 1H), 7.99 (d, J = 5.0 Hz, 1H), 7.72 (t, J = 5.0 Hz, 1H), 7.65 (s, 1H), 7.62 (t, J = 5.0 Hz, 1H), 6.42 (s, 1H), 3.41 (s, 2H), 3.19 (t, J = 5.0 Hz, 2H), 2.35 (s, 3H), 1.95 - 1.92(m, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 145.89, 143.23, 142.67, 139.83, 139.79, 134.77, 129.68, 129.41, 128.74, 127.12, 126.85, 106.93, 41.43, 21.72, 20.59, 18.85; HRMS (ESI): Calcd. for $C_{16}H_{16}N_3$ $[M+H]^+$: 250.13387; found: 250.13367.

1,2,3,4-tetrahydropyrido[2,3-*b*]phenazine (**C33**)



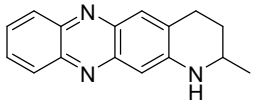
Orange solid, m.p.: 168 – 159 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.99 (d, J = 8.6 Hz, 1H), 7.91 (d, J = 8.6 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.67 (s, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.40 (s, 1H), 6.80 (s, 1H), 3.01 (t, J = 5.0 Hz, 2H), 1.91 - 1.87 (m, 2H), 1.26 - 1.17 (m, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 148.98, 145.42, 143.45, 140.09, 139.81, 134.30, 129.95, 129.56, 128.27, 127.80, 126.96, 100.35, 41.08, 28.48, 21.11; HRMS (ESI): Calcd. for $C_{15}H_{14}N_3$ $[M+H]^+$: 236.11822; found: 236.11787.

1,2,3,4-tetrahydropyrido[3,2-*a*]phenazine (**C33**')



Orange solid, m.p.: 149.9 – 150.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 - 8.09 (m, 2H), 7.82 (d, J = 9.4 Hz, 1H), 7.72 – 7.69 (m, 1H), 7.64 – 7.59 (m, 1H), 7.11 (dd, J = 9.4, 2.0 Hz, 1H), 4.51 (s, 1H), 3.48 - 3.45 (m, 2H), 3.32 (t, J = 6.4 Hz, 2H), 2.12 - 2.06 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.82, 144.14, 143.32, 140.29, 140.22, 129.72, 129.31, 128.83, 128.32, 127.38, 125.64, 109.40, 41.74, 21.10, 21.00; HRMS (ESI): Calcd. for $C_{15}H_{14}N_3$ $[M+H]^+$: 236.11822; found: 236.11787.

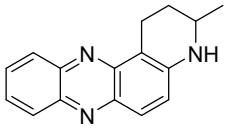
2-methyl-1,2,3,4-tetrahydropyrido[2,3-*b*]phenazine (**C34**)



Orange solid, m.p.: 175.6 – 176.6 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.00 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.6 Hz, 1H), 7.72 – 7.69 (m, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.28 (s, 1H), 6.84 (s, 1H), 3.58 - 3.54 (m, 1H), 3.10 – 2.97 (m, 2H), 2.02 - 1.99 (m, 1H), 1.55 - 1.48 (m, 1H), 1.25 (d, J = 6.4 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 148.95, 145.44, 143.54, 140.17, 139.80, 134.03, 129.94, 129.57, 128.35, 127.61, 127.03, 100.47, 47.09, 29.14, 27.67, 22.46; HRMS (ESI): Calcd.

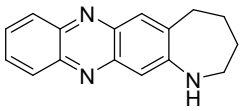
for $C_{16}H_{16}N_3$ $[M+H]^+$: 250.13387; found: 250.13354.

3-methyl-1,2,3,4-tetrahydropyrido[3,2-*a*]phenazine (**C34'**)



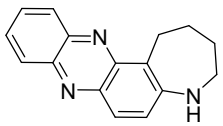
Orange solid, m.p.: 169.8 – 170.8 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.05 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.6 Hz, 1H), 7.79 – 7.75 (m, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.39 (d, J = 9.4 Hz, 1H), 6.97 (s, 1H), 3.55 – 3.51 (m, 1H), 3.40 - 3.38 (m, 1H), 2.99 - 2.93 (m, 1H), 2.06 (d, J = 9.2 Hz, 1H), 1.60 – 1.54 (m, 1H), 1.28 (d, J = 6.2 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 146.36, 144.08, 143.06, 140.25, 139.68, 130.28, 129.56, 128.70, 128.36, 127.27, 126.76, 106.63, 46.59, 28.79, 21.88, 20.74; HRMS (ESI): Calcd. for $C_{16}H_{16}N_3$ $[M+H]^+$: 250.13387; found: 250.13341.

2,3,4,5-tetrahydro-1*H*-azepino[2,3-*b*]phenazine (**C35**)



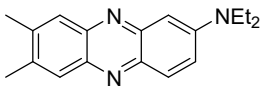
Orange solid, m.p.: 180 – 181 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, J = 8.6 Hz, 1H), 8.09 (d, J = 8.6 Hz, 1H), 7.89 (s, 1H), 7.73 – 7.70 (m, 1H), 7.68 – 7.65 (m, 1H), 7.31 (s, 1H), 4.56 (s, 1H), 3.28 (d, J = 5.4 Hz, 2H), 3.07 (t, J = 5.0 Hz, 2H), 1.89 – 1.88 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.71, 144.16, 143.46, 142.00, 141.84, 140.98, 129.73, 129.57, 129.50, 128.82, 128.30, 111.22, 48.25, 35.70, 30.34, 26.94; HRMS (ESI): Calcd. for $C_{16}H_{16}N_3$ $[M+H]^+$: 250.13387; found: 250.13368.

2,3,4,5-tetrahydro-1*H*-azepino[3,2-*a*]phenazine (**C35'**)



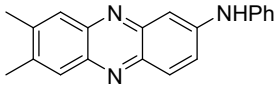
Orange solid, m.p.: 159 – 160 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (dd, J = 15.0, 8.6 Hz, 2H), 7.89 (d, J = 9.2 Hz, 1H), 7.78 – 7.75 (m, 1H), 7.72 – 7.68 (m, 1H), 7.28 (d, J = 3.8 Hz, 1H), 4.37 (s, 1H), 3.71 – 3.69 (m, 2H), 3.43 (t, J = 5.2 Hz, 2H), 2.00 – 1.99 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.13, 144.50, 143.07, 140.73, 140.53, 129.62, 129.35, 129.21, 128.37, 128.18, 127.51, 120.48, 47.34, 30.92, 25.59, 25.06; HRMS (ESI): Calcd. for $C_{16}H_{16}N_3$ $[M+H]^+$: 250.13387; found: 250.13345.

N,N-diethyl-7,8-dimethylphenazin-2-amine (**C36**)



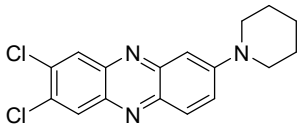
Orange solid, m.p.: 270.4 – 271.4 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.93 (d, J = 9.6 Hz, 1H), 7.81 (s, 1H), 7.74 (s, 1H), 7.65 (dd, J = 9.6, 2.6 Hz, 1H), 6.90 (d, J = 2.6 Hz, 1H), 3.56 (q, J = 7.0 Hz, 4H), 2.46 (d, J = 6.6 Hz, 6H), 1.21 (t, J = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 148.54, 145.54, 143.15, 141.35, 139.84, 138.54, 138.24, 130.37, 128.08, 126.98, 122.99, 101.33, 44.66, 20.62, 20.31, 13.08; HRMS (ESI): Calcd. for $C_{18}H_{22}N_3$ $[M+H]^+$: 280.18082; found: 280.18024.

7,8-dimethyl-*N*-phenylphenazin-2-amine (**C37**)



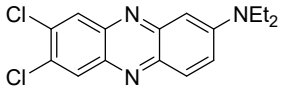
Orange solid, m.p.: 235 – 236 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.06 (s, 1H), 7.99 (d, J = 9.4 Hz, 1H), 7.83 (s, 1H), 7.76 (s, 1H), 7.63 (d, J = 11.2 Hz, 1H), 7.47 (s, 1H), 7.42 - 7.36 (m, 4H), 7.06 (t, J = 7.0 Hz, 1H), 2.45 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 145.76, 145.21, 142.95, 141.68, 140.42, 139.86, 139.30, 130.58, 129.91, 128.03, 127.19, 126.62, 122.88, 120.18, 103.64, 20.60, 20.36; HRMS (ESI): Calcd. for $C_{20}H_{18}N_3$ $[M+H]^+$: 300.14952; found: 300.14926.

2,3-dichloro-7-(piperidin-1-yl)phenazine (**C38**)



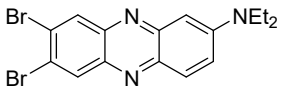
Orange solid, m.p.: 209 – 210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.05 (s, 1H), 7.83 (d, J = 9.6 Hz, 1H), 7.59 (dd, J = 9.8, 2.8 Hz, 1H), 7.03 (s, 1H), 3.46 (t, J = 5.0 Hz, 4H), 1.72 – 1.70 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.35, 145.91, 142.13, 140.48, 139.45, 134.38, 131.73, 129.91, 129.65, 128.69, 125.76, 105.12, 49.13, 25.44, 24.33; HRMS (ESI): Calcd. for $C_{17}H_{16}Cl_2N_3$ $[M+H]^+$: 332.07158; found: 332.07089.

7,8-dichloro-*N,N*-diethylphenazin-2-amine (**C39**)



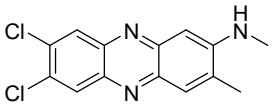
Orange solid, m.p.: 152.1 – 153.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.10 (s, 1H), 7.92 (d, J = 9.7 Hz, 1H), 7.52 (dd, J = 9.8, 2.8 Hz, 1H), 6.92 (d, J = 2.8 Hz, 1H), 3.56 (d, J = 7.2 Hz, 4H), 1.30 (t, J = 7.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.31, 146.28, 142.54, 139.97, 139.07, 134.46, 131.06, 130.55, 129.76, 128.52, 123.51, 100.95, 45.06, 12.79; HRMS (ESI): Calcd. for $C_{16}H_{16}Cl_2N_3$ $[M+H]^+$: 320.07158; found: 320.07101.

7,8-dibromo-*N,N*-diethylphenazin-2-amine (**C40**)



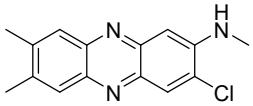
Orange solid, m.p.: 158 – 159 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.43 (s, 1H), 8.34 (s, 1H), 7.93 (d, J = 10.0 Hz, 1H), 7.78 (dd, J = 10.0, 5.0 Hz, 1H), 6.85 (d, J = 5.0 Hz, 1H), 3.59 (q, J = 5.0 Hz, 4H), 1.22 (t, J = 10.0 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 149.80, 146.45, 143.08, 140.03, 139.41, 133.45, 132.16, 130.73, 126.01, 125.24, 122.01, 100.30, 44.89, 13.06; HRMS (ESI): Calcd. for $C_{16}H_{16}Br_2N_3$ $[M+H]^+$: 407.97055; found: 407.96982.

7,8-dichloro-*N*,3-dimethylphenazin-2-amine (**C41**)



Orange solid, m.p.: 282.3 – 283.3 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.28 (s, 1H), 8.19 (s, 1H), 7.74 (s, 1H), 6.72 (q, J = 4.8 Hz, 1H), 6.67 (s, 1H), 2.94 (d, J = 5.0 Hz, 3H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 151.71, 146.18, 141.92, 140.78, 138.70, 136.80, 132.47, 130.02, 129.44, 128.82, 128.64, 97.55, 30.49, 18.81; HRMS (ESI): Calcd. for $C_{14}H_{12}Cl_2N_3$ $[M+H]^+$: 292.04028; found: 292.03967.

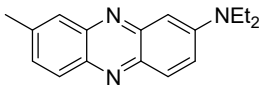
1-chloro-*N*,7,8-trimethylphenazin-2-amine (**C42**)



Orange solid, m.p.: 228 – 229 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.76 (d, J = 10.4 Hz, 2H), 6.95 (s, 1H), 5.00 (d, J = 5.0 Hz, 1H), 3.02 (d, J = 5.0 Hz, 3H), 2.46 (d, J = 4.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.51, 144.15,

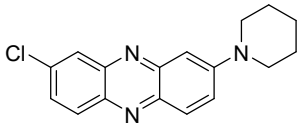
142.95, 141.48, 140.47, 139.11, 138.37, 128.53, 127.88, 127.08, 101.29, 30.46, 20.69, 20.42; HRMS (ESI): Calcd. for $C_{15}H_{15}ClN_3$ $[M+H]^+$: 272.09490; found: 272.09464.

N,N-diethyl-8-methylphenazin-2-amine (**C43**)



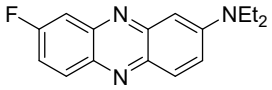
Red oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 9.0 Hz, 2H), 7.75 (s, 1H), 7.44 - 7.38 (m, 2H), 6.96 (s, 1H), 3.50 (q, J = 7.0 Hz, 4H), 2.53 (s, 3H), 1.24 (t, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.79, 145.67, 143.75, 140.81, 139.31, 138.81, 130.28, 130.09, 128.86, 126.27, 122.13, 101.04, 44.89, 22.17, 12.74; HRMS (ESI): Calcd. for $C_{17}H_{20}N_3$ $[M+H]^+$: 266.16517; found: 266.16489.

2-chloro-8-(piperidin-1-yl)phenazine (**C44**)



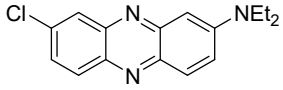
Orange solid, m.p.: 151-152 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.94 (d, J = 9.8 Hz, 1H), 7.64 (dd, J = 9.8, 2.8 Hz, 1H), 7.54 (dd, J = 9.2, 2.2 Hz, 1H), 7.16 (d, J = 2.8 Hz, 1H), 3.49 – 3.46 (m, 4H), 1.75 - 1.69 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.50, 145.99, 143.75, 140.16, 139.63, 135.92, 130.75, 130.03, 129.00, 127.02, 125.45, 105.55, 49.29, 25.46, 24.36; HRMS (ESI): Calcd. for $C_{17}H_{17}ClN_3$ $[M+H]^+$: 298.11055; found: 298.11014.

N,N-diethyl-8-fluorophenazin-2-amine (**C45**)



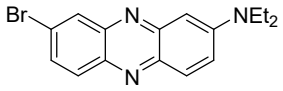
Orange solid, m.p.: 126 – 127 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 8.12 (dd, J = 5.0, 10.0 Hz, 1H), 7.96 (d, J = 10.0 Hz, 1H), 7.71 (d, J = 10.0 Hz, 1H), 7.66 (d, J = 10.0 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 6.88 (s, 1H), 3.58 (q, J = 6.8 Hz, 4H), 1.22 (t, J = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.94 (d, J = 250.8 Hz）, 149.53, 146.20, 144.37 (d, J = 12.6 Hz), 138.87, 137.82, 132.39 (d, J = 10.2 Hz), 130.78, 123.82, 118.60 (d, J = 27.8 Hz), 110.61 (d, J = 20.2 Hz), 100.34, 44.79, 13.04; ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.63.HRMS (ESI): Calcd. for $C_{16}H_{17}FN_3$ $[M+H]^+$: 270.14010; found: 270.13977.

8-chloro-*N,N*-diethylphenazin-2-amine (**C46**)



Orange solid, m.p.: 127-128 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 5.8, 3.4 Hz, 2H), 7.86 (d, J = 9.8 Hz, 1H), 7.43 (t, J = 2.6 Hz, 1H), 7.40 (t, J = 4.0 Hz, 1H), 6.86 (d, J = 2.8 Hz, 1H), 3.47 (q, J = 7.2 Hz, 4H), 1.22 (t, J = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.19, 146.03, 143.73, 139.37, 138.84, 135.84, 130.65, 130.46, 128.11, 126.53, 122.87, 100.77, 44.95, 12.74; HRMS (ESI): Calcd. for $C_{16}H_{17}ClN_3$ $[M+H]^+$: 286.11055; found: 286.11002.

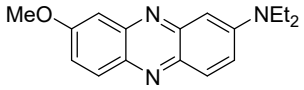
8-bromo-*N,N*-diethylphenazin-2-amine (**C47**)



Orange solid, m.p.: 113.8-114.8 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.93 (t, J = 9.0 Hz, 2H), 7.61 (d, J = 10.8 Hz, 1H), 7.50 (d, J = 12.2 Hz, 1H), 6.95 (s, 1H), 3.55 (q, J = 7.2 Hz, 4H), 1.29 (t, J = 7.2 Hz, 6H); ^{13}C NMR (101 MHz,

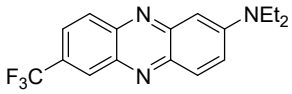
$CDCl_3$) δ 149.23, 146.10, 144.19, 139.50, 139.09, 130.72, 130.58, 130.52, 130.16, 124.33, 123.03, 100.91, 45.00, 12.78; HRMS (ESI): Calcd. for $C_{16}H_{17}BrN_3$ $[M+H]^+$: 330.06003; found: 330.05939.

N,N-diethyl-8-methoxyphenazin-2-amine (**C48**)



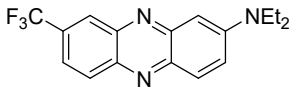
Orange solid, m.p.: 89.9 – 90.9 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.93 (dd, J = 9.4, 4.6 Hz, 2H), 7.61 (dd, J = 9.6, 3.0 Hz, 1H), 7.33 (dd, J = 9.4, 2.8 Hz, 1H), 7.27 (d, J = 2.8 Hz, 1H), 6.88 (s, 1H), 3.96 (s, 3H), 3.57 (q, J = 7.0 Hz, 4H), 1.22 (t, J = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 161.02, 149.10, 145.89, 145.48, 137.34, 137.23, 130.88, 130.59, 122.36, 122.09, 104.71, 100.94, 56.19, 44.71, 13.06; HRMS (ESI): Calcd. for $C_{17}H_{20}N_3O$ $[M+H]^+$: 282.16009; found: 282.15991.

N,N-diethyl-7-(trifluoromethyl)phenazin-2-amine (**C49**)



Orange solid, m.p.: 120.7 -121.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.09 (d, J = 9.0 Hz, 1H), 7.99 (d, J = 9.8 Hz, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.54 (d, J = 9.6 Hz, 1H), 6.99 (s, 1H), 3.57 (q, J = 7.0 Hz, 4H), 1.31 (t, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.61, 146.93, 144.60, 140.42, 138.97, 130.79, 129.43, 128.20 (d, J = 32.8 Hz), 127.82 (d, J = 4.6 Hz), 125.19 (d, J = 3.2 Hz), 124.06 (d, J = 272.2 Hz), 123.54, 100.82, 45.08, 12.75; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.61; HRMS (ESI): Calcd. for $C_{17}H_{17}F_3N_3$ $[M+H]^+$: 320.13691; found: 320.13669.

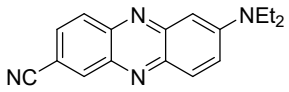
N,N-diethyl-8-(trifluoromethyl)phenazin-2-amine (**C49'**)



Orange solid, m.p.: 111.1 - 112.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.21 (d, J = 9.0 Hz, 1H), 8.03 (d, J = 9.8 Hz, 1H), 7.73 (d, J = 9.0 Hz, 1H), 7.61 (d, J = 10.6 Hz, 1H), 7.03 (s, 1H), 3.60 (q, J = 7.0 Hz, 4H), 1.33 (t, J = 7.0 Hz, 6H);

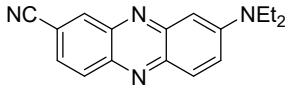
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.30, 146.71, 142.66, 141.10, 140.69, 130.86, 130.62, 126.47 (d, *J* = 5.0 Hz), 124.10, 122.84 – 121.77 (m), 100.93, 45.08, 12.77; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.04; HRMS (ESI): Calcd. for $C_{17}H_{17}F_3N_3$ $[M+H]^+$: 320.13691; found: 320.13638.

7-(diethylamino)phenazine-2-carbonitrile (**C50**)



Red solid, m.p.: 183 - 184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.96 (dd, J = 17.0, 9.4 Hz, 2H), 7.71 (d, J = 8.6 Hz, 1H), 7.55 (d, J = 9.8 Hz, 1H), 6.93 (s, 1H), 3.56 (q, J = 7.2 Hz, 4H), 1.29 (t, J = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.12, 147.05, 144.89, 140.87, 138.90, 136.16, 131.08, 129.71, 129.59, 124.00, 118.90, 109.37, 100.61, 45.21, 12.77; HRMS (ESI): Calcd. for $C_{17}H_{17}N_4$ $[M+H]^+$: 277.14477; found: 277.14462.

8-(diethylamino)phenazine-2-carbonitrile (**C50'**)



Red solid, m.p.: 125 - 126 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.56 (d, J = 1.8 Hz, 1H), 8.20 (d, J = 8.8 Hz, 1H), 8.02 (d, J = 9.8 Hz, 1H), 7.89 – 7.88 (m, 1H), 7.87 (d, J = 2.2 Hz, 1H), 6.94 (d, J = 2.8 Hz, 1H), 3.62 (q, J = 7.0 Hz, 4H), 1.24 (t, J = 10.0 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 149.82, 146.87, 142.64, 141.13, 140.83, 135.11, 131.46, 130.76, 127.05, 126.16, 119.10, 112.70, 100.13, 44.91, 13.04; HRMS (ESI): Calcd. for $C_{17}H_{17}N_4$ $[M+H]^+$: 277.14477; found: 277.14456.

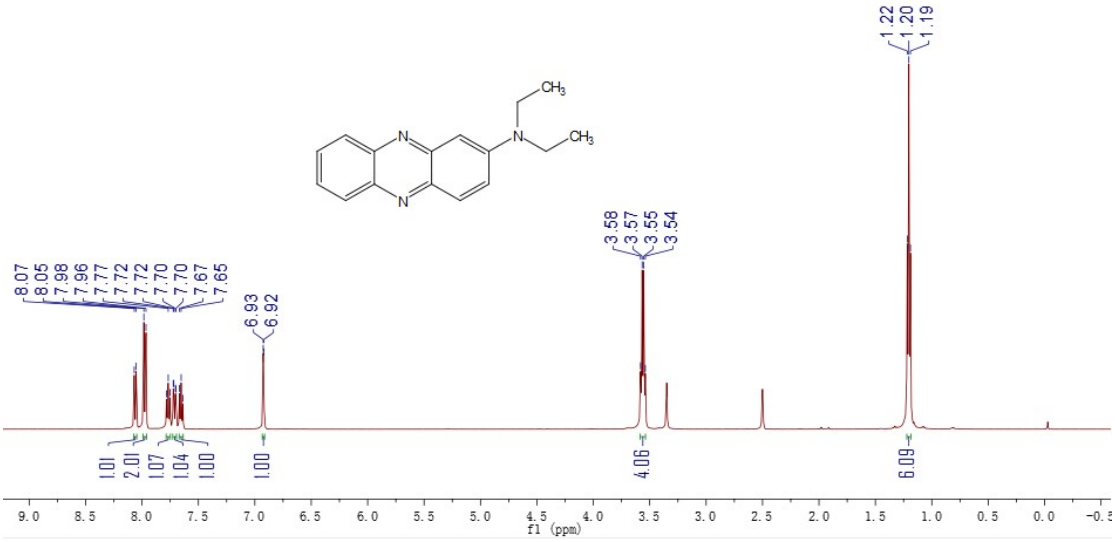
Reference

(1) Westerhaus FA, Jagadeesh RV, Wienhoefer G, Pohl MM, Radnik J, Surkus AE, Rabeah J, Junge K, Junge H, Nielsen M, Brueckner A, Beller M. *Nat Chem*, 2013, 5: 537–543; (b) Tang C, Surkus AE, Chen F, Pohl MM, Agostini G, Schneider M, Junge H, Beller M. *Angew Chem Int Ed*, 2017, 56: 16616–16620

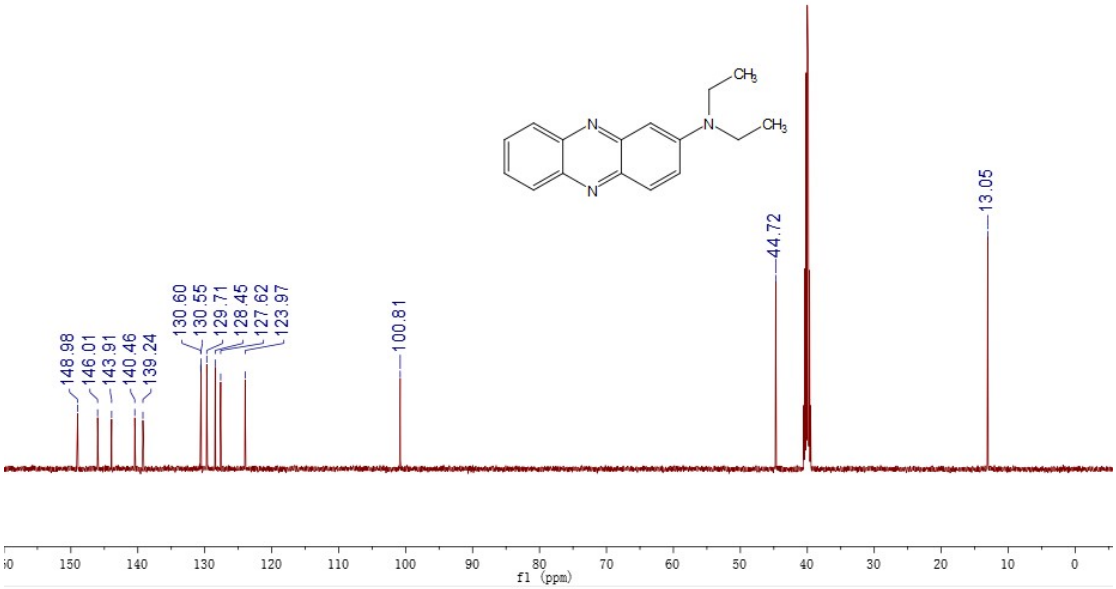
(2) Murakami M, Ohkubo K, Fukuzumi S. *Chem Eur J*, 2010, 16: 7820–7832

NMR spectra of the obtained compounds

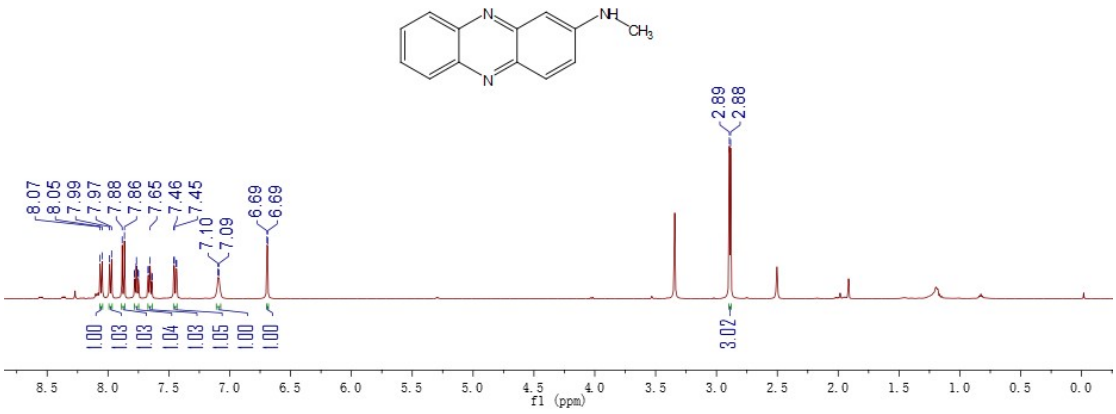
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C1**



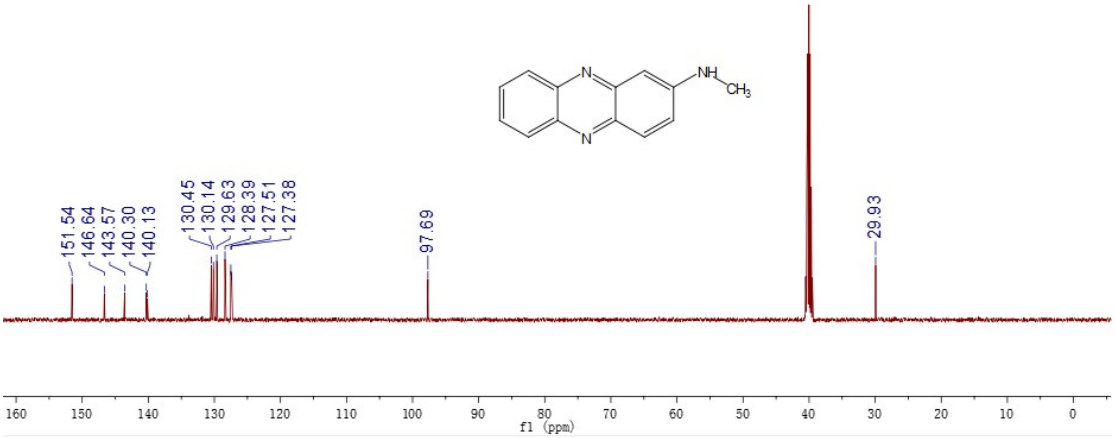
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C1**



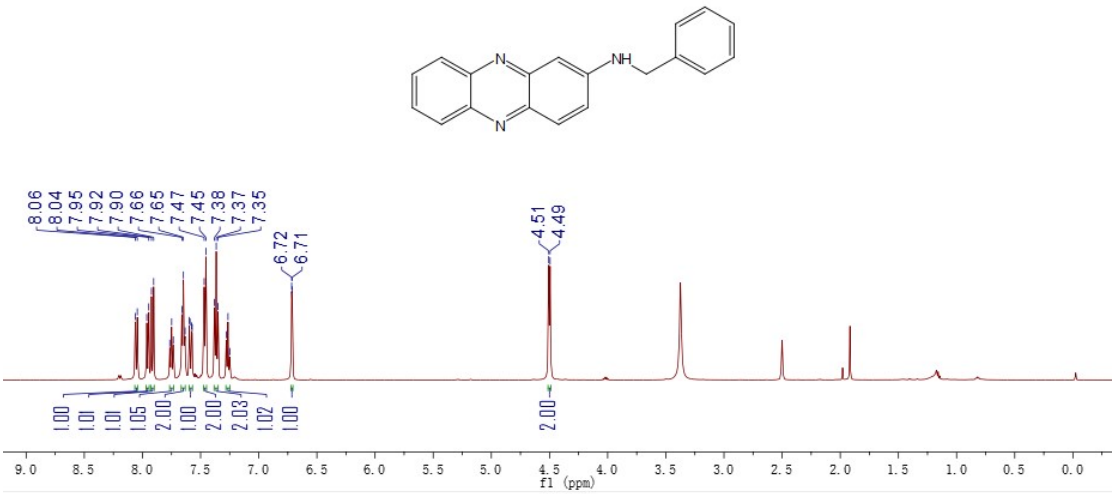
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C2**



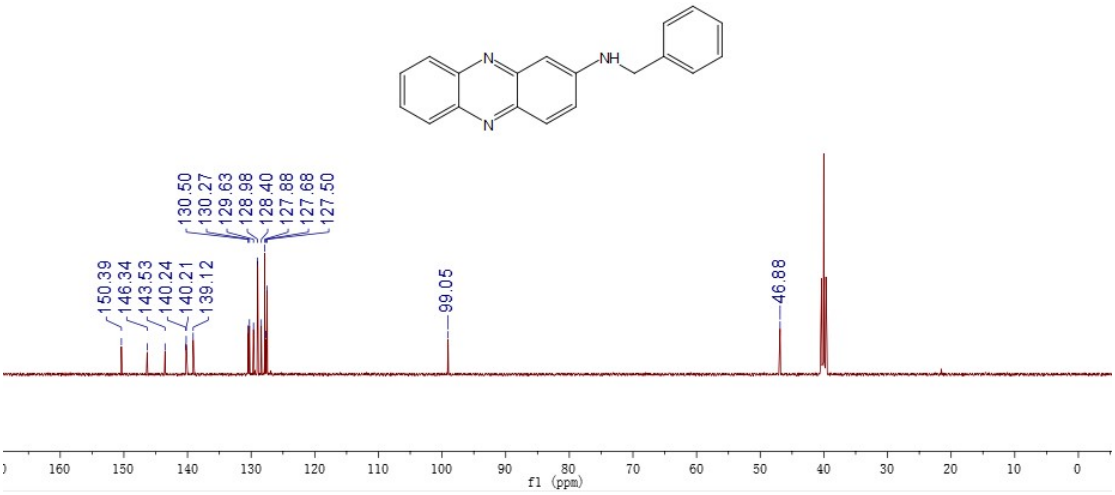
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C2**


N
NH
CH3
N
151.54
146.64
143.57
140.30
140.13
130.45
130.14
129.63
128.39
127.51
127.38
97.69
29.93
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

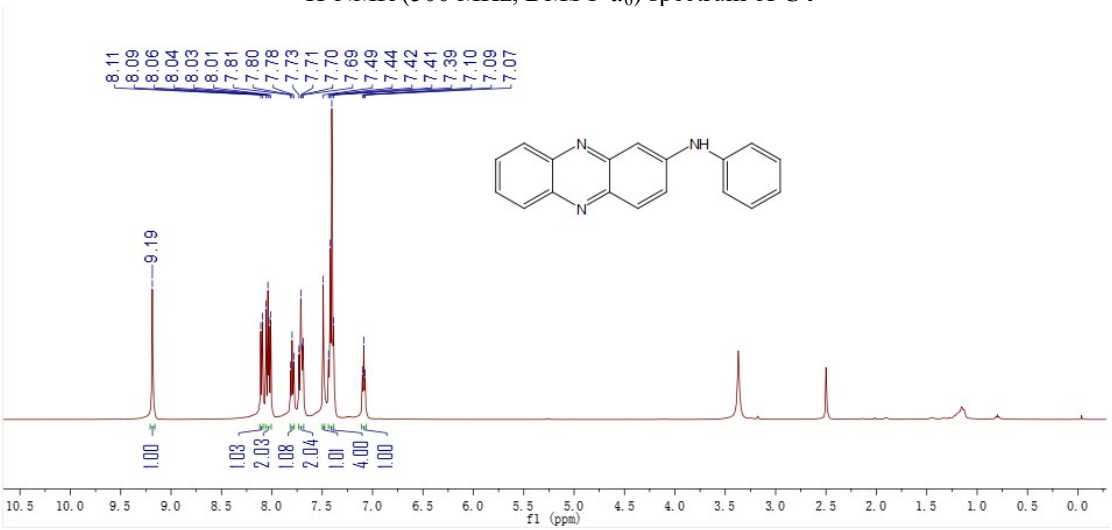
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C3**



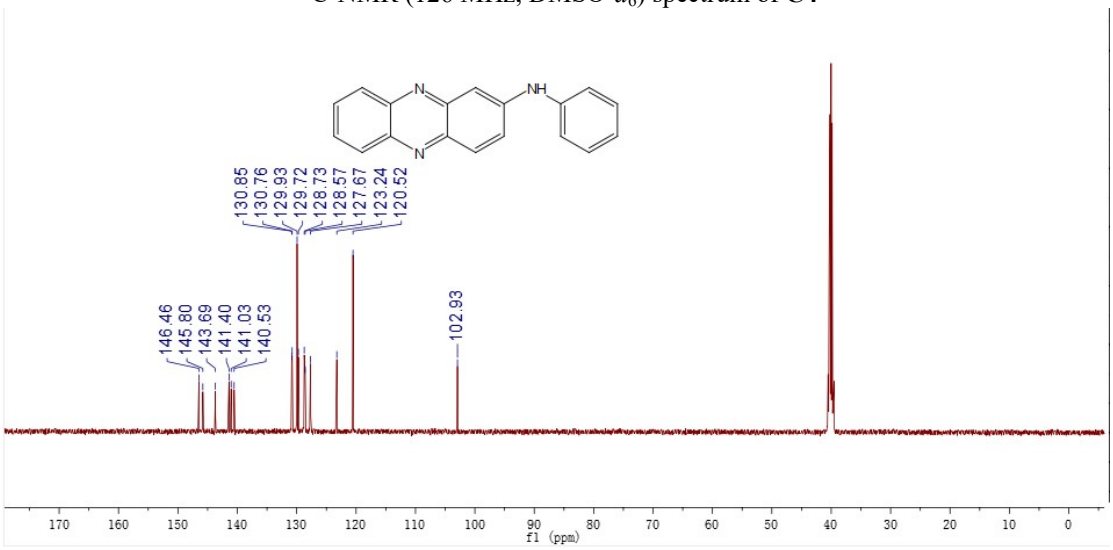
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C3**



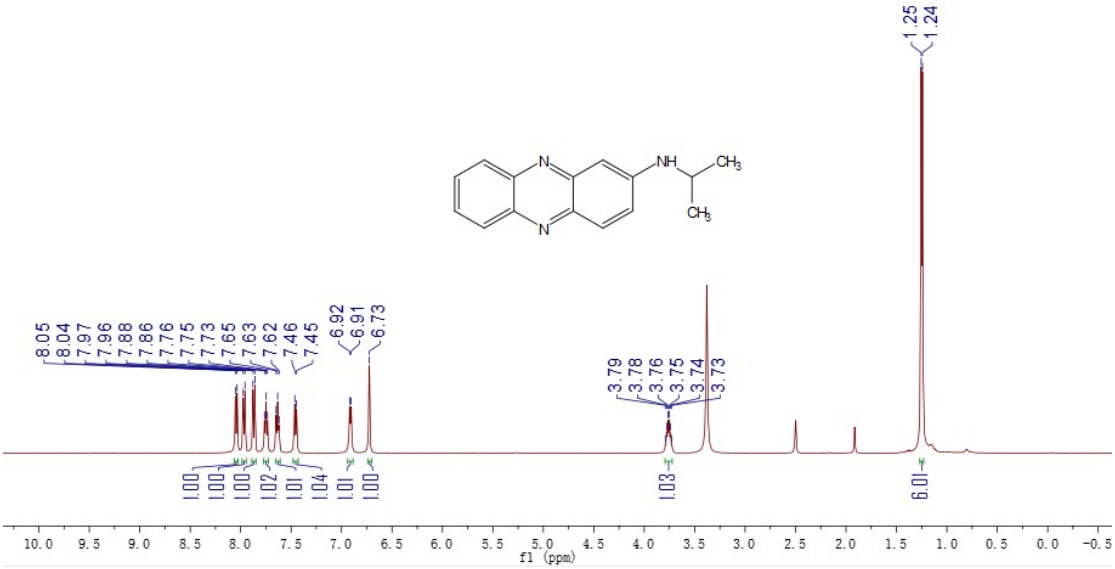
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C4**



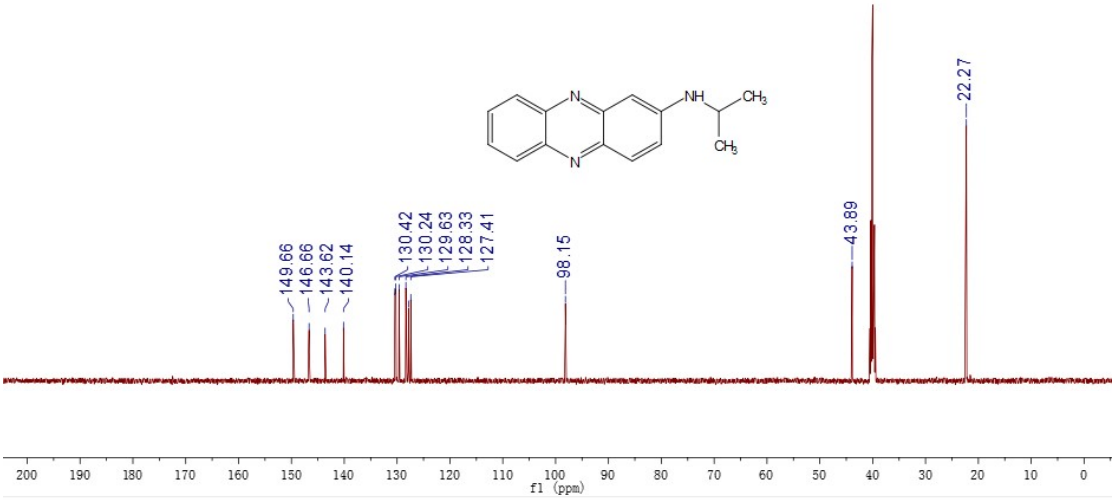
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C4**



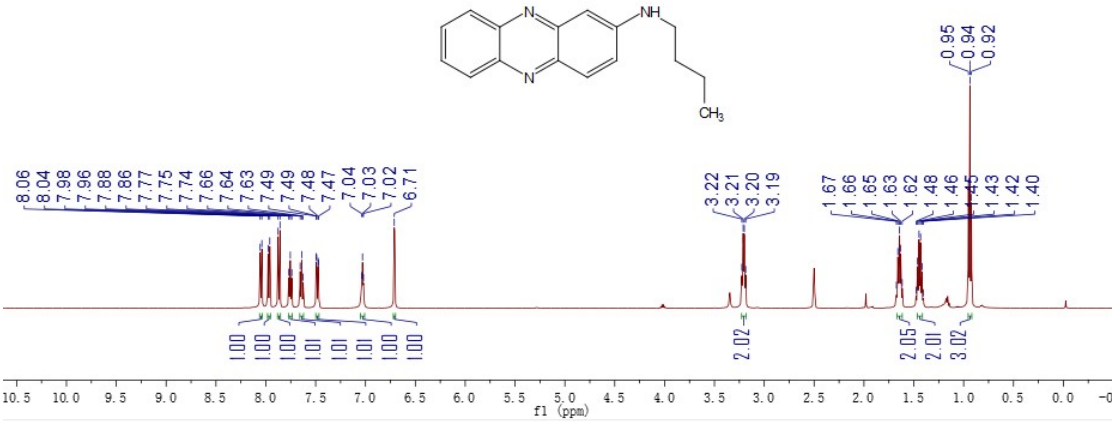
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C5**



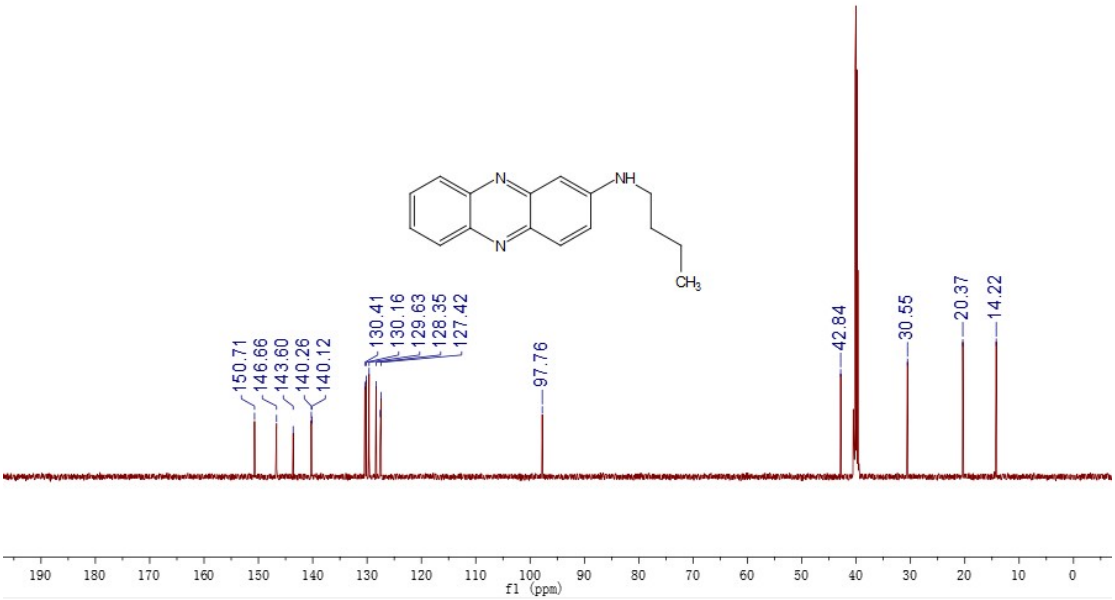
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C5**



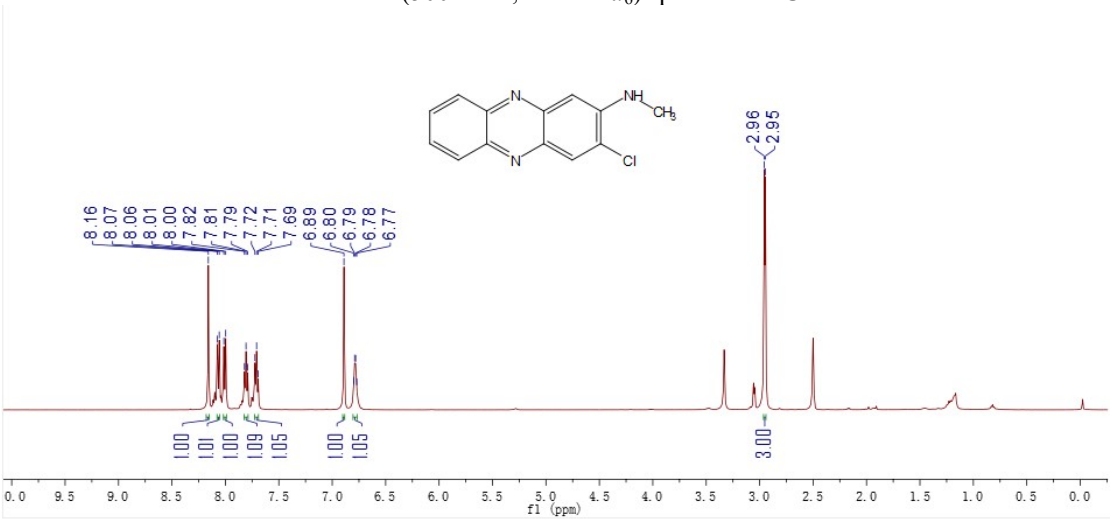
[1]H-NMR (500 MHz, DMSO-d_6) spectrum of **C6**



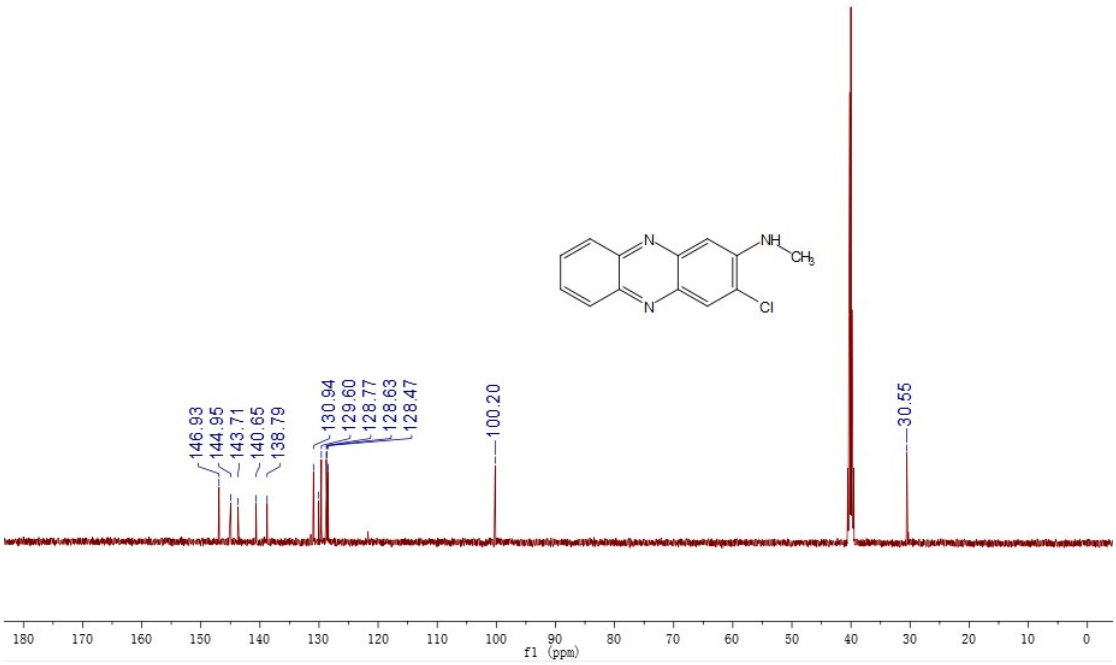
[13]C-NMR (126 MHz, DMSO-d_6) spectrum of **C6**



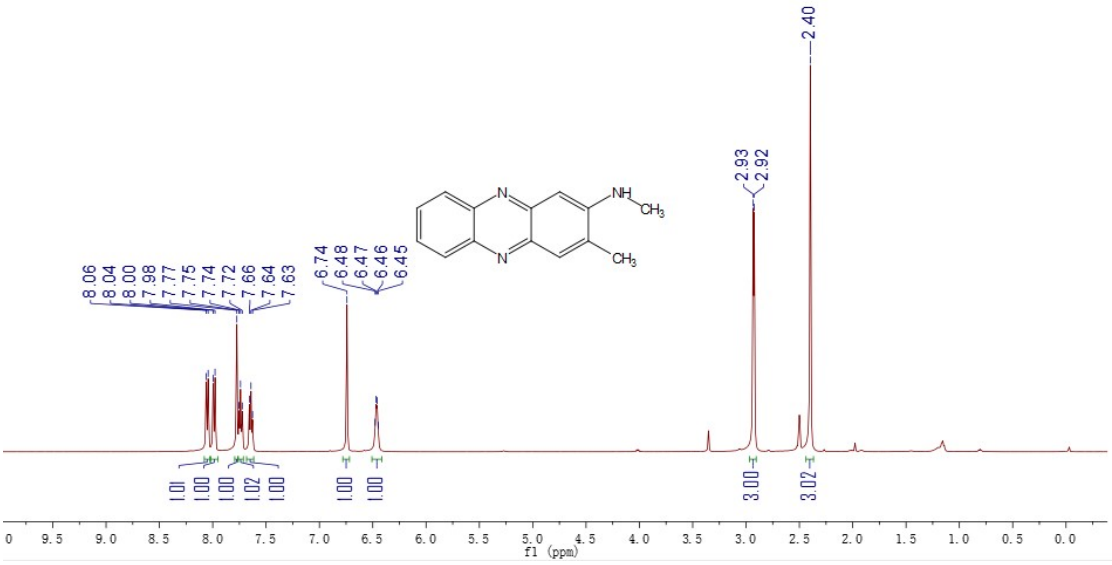
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C7**



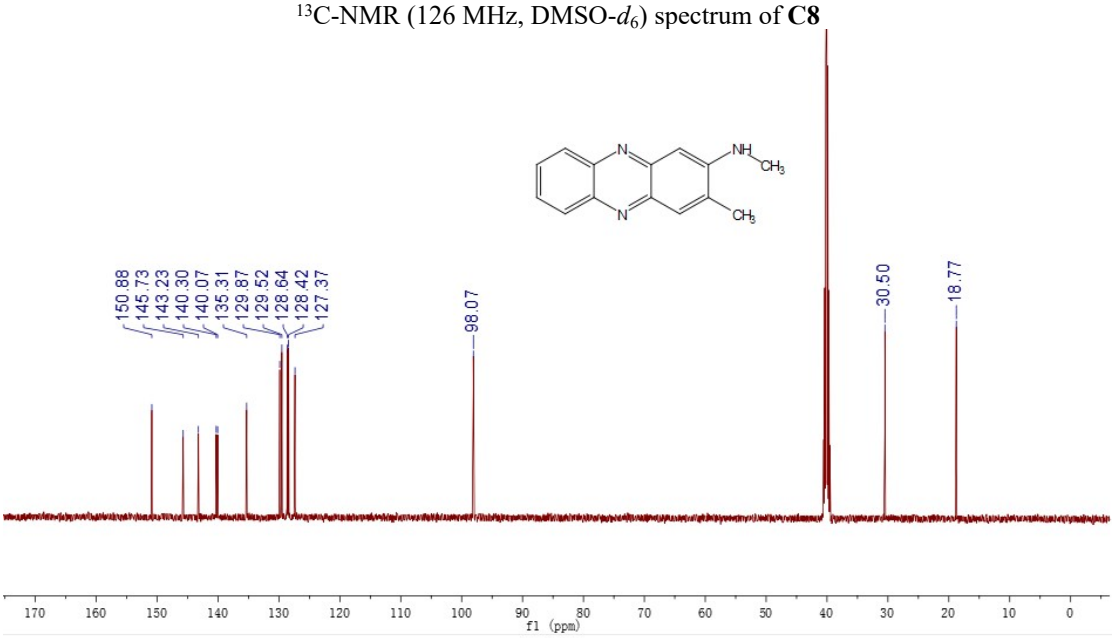
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C7**



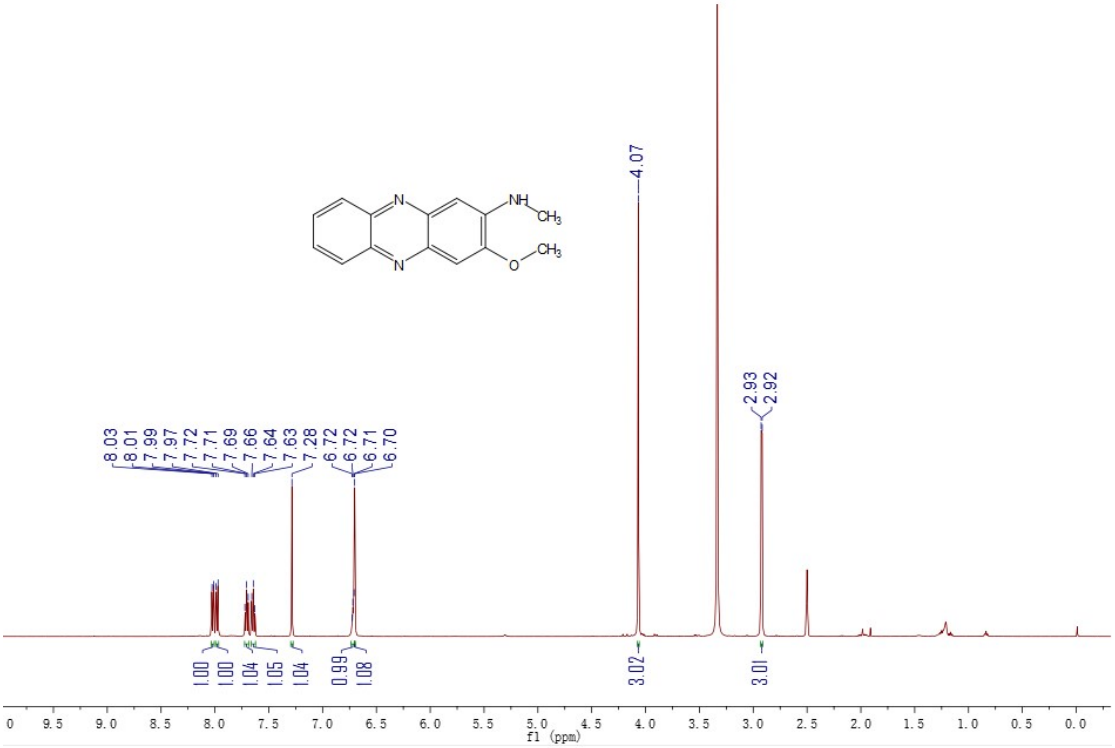
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C8**



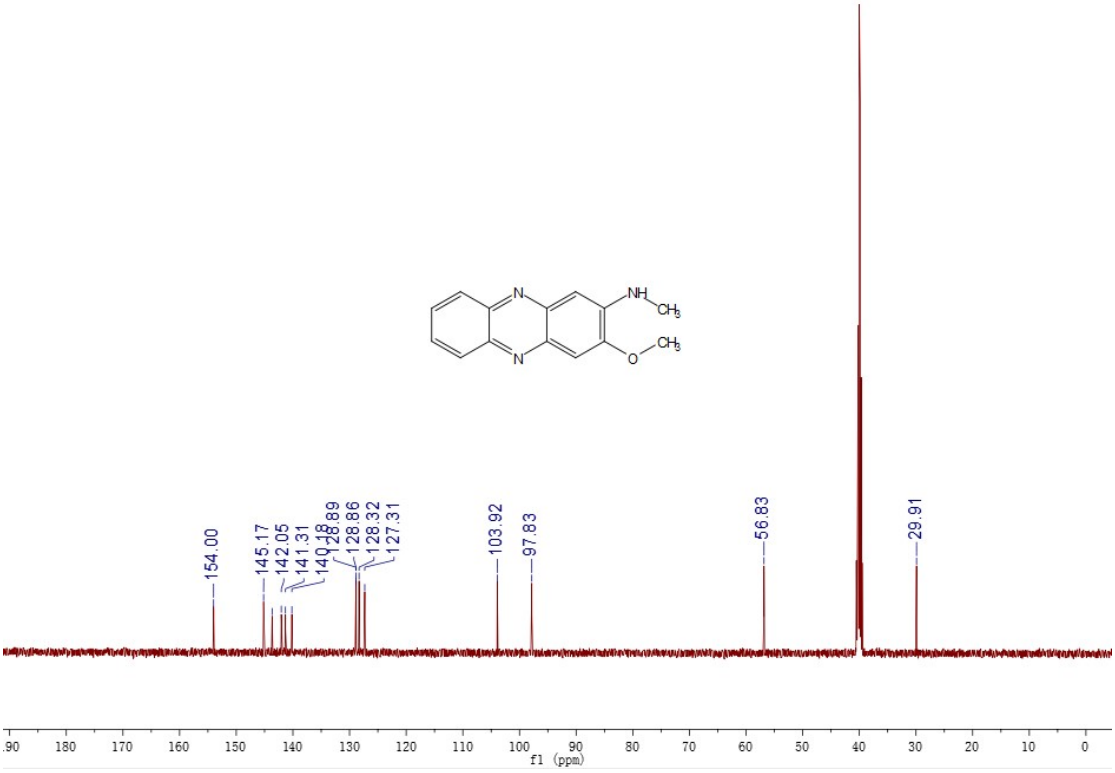
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C8**



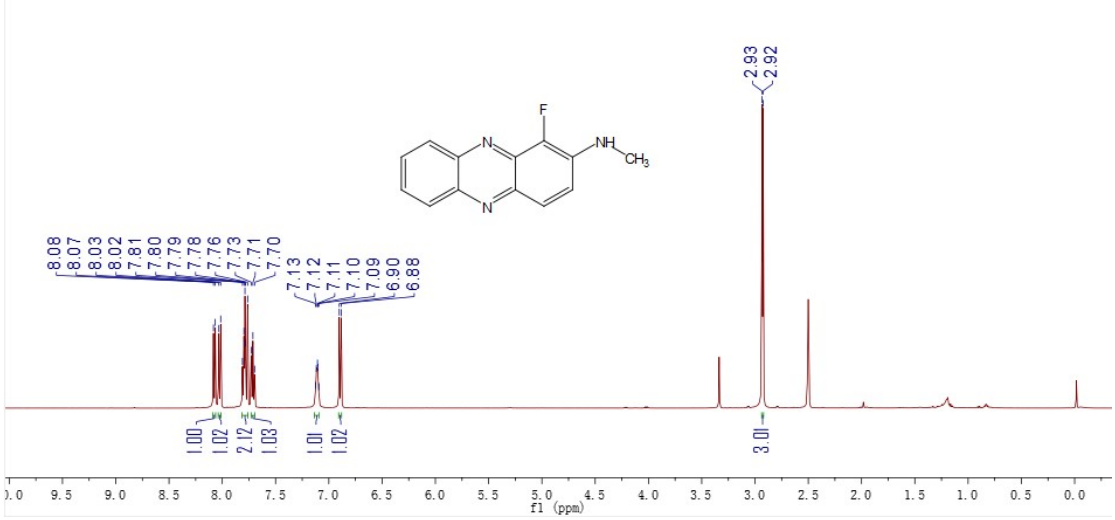
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C9**



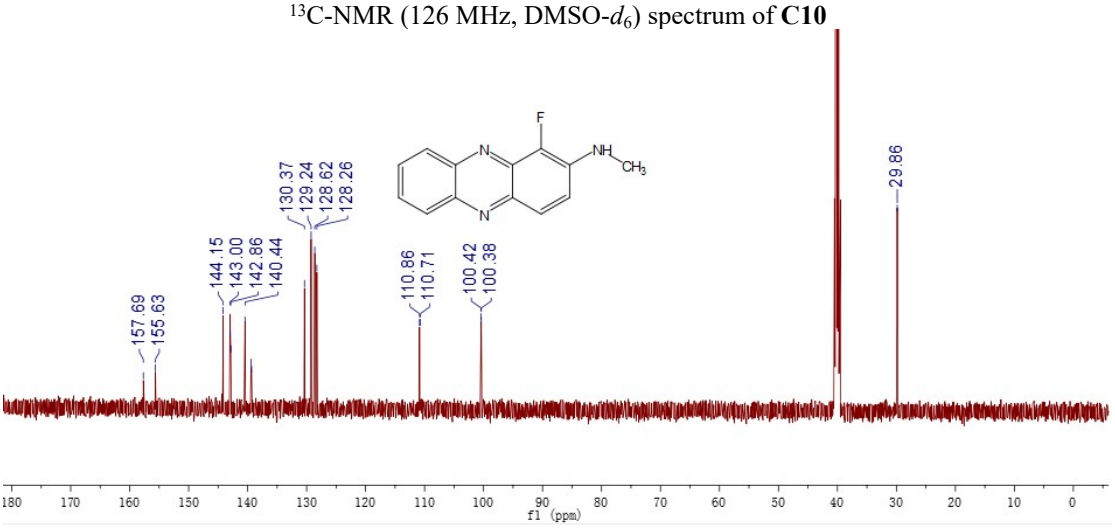
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C9**



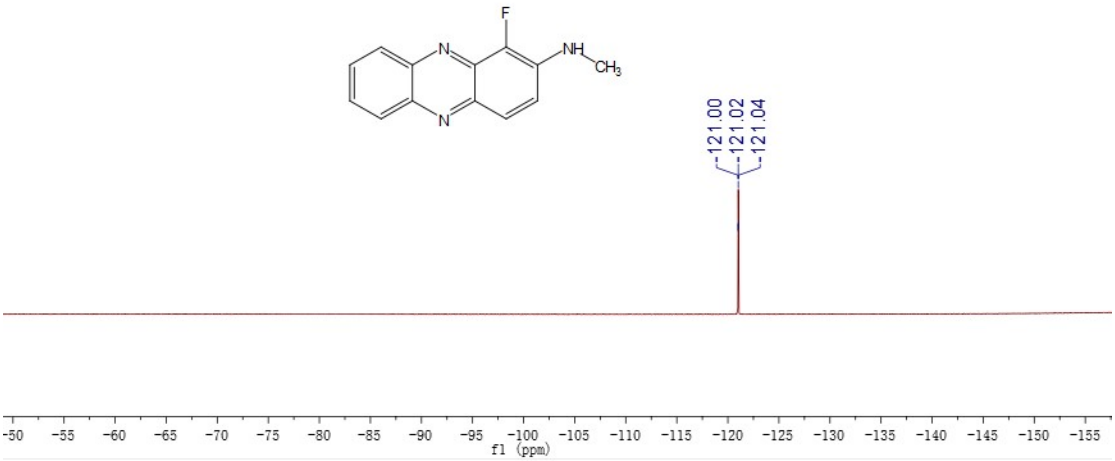
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C10**



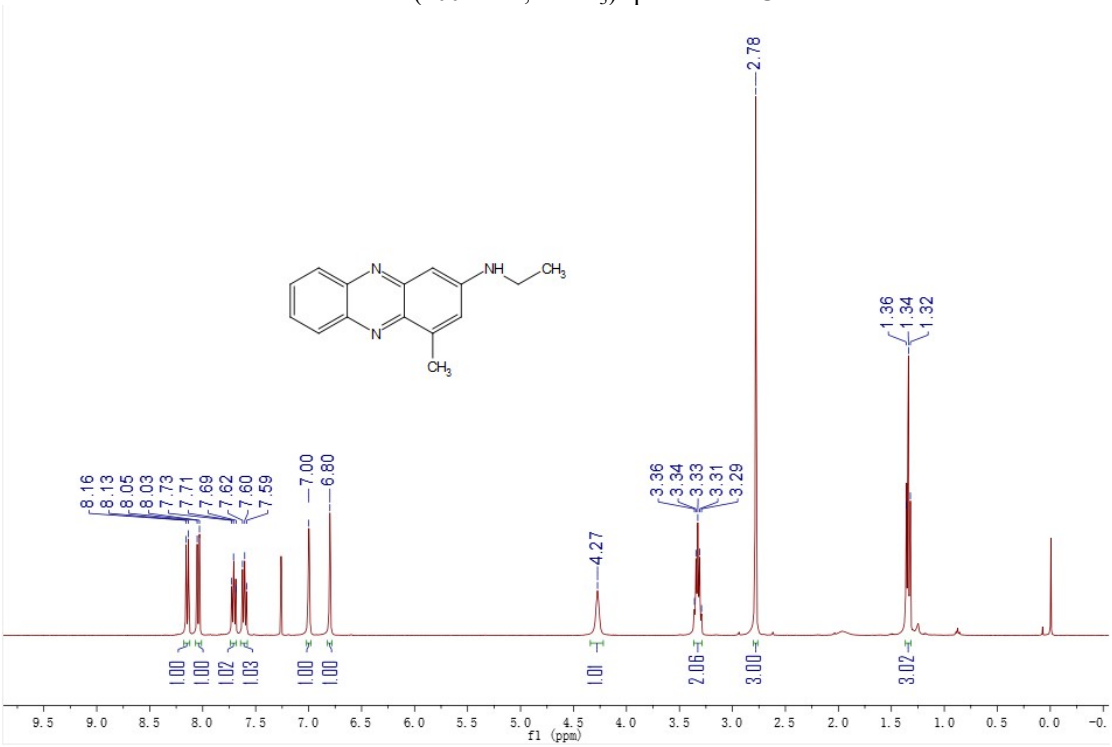
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C10**



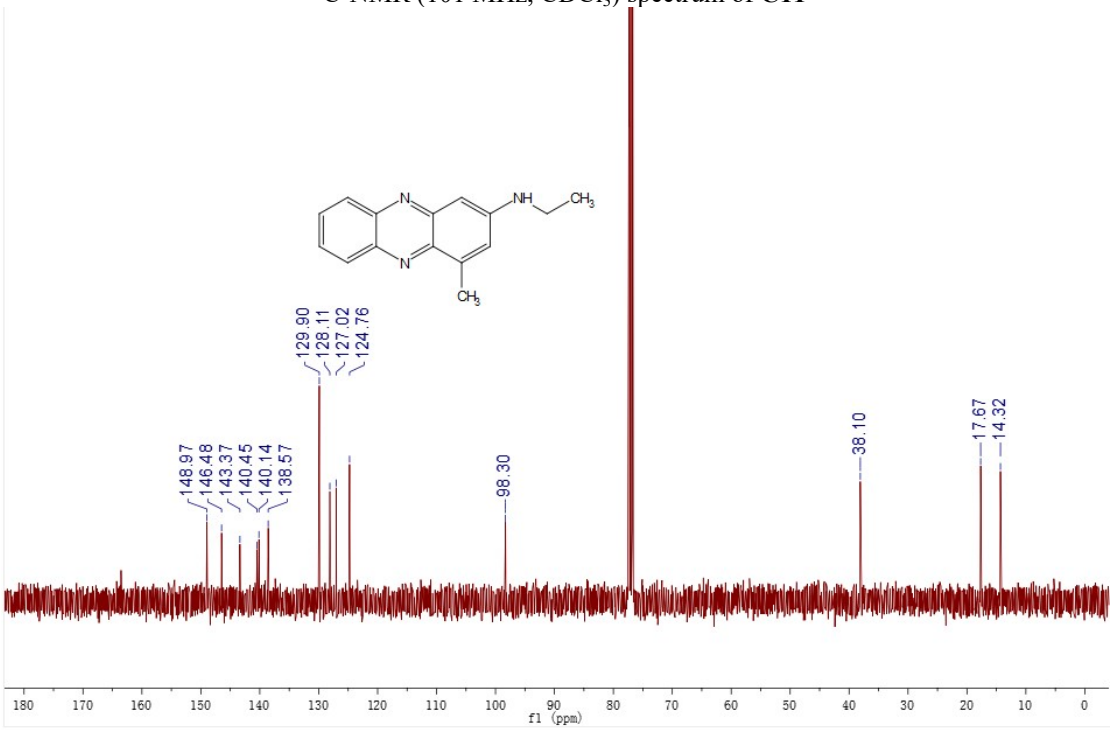
^{19}F-NMR (471 MHz, DMSO-d_6) spectrum of **C10**



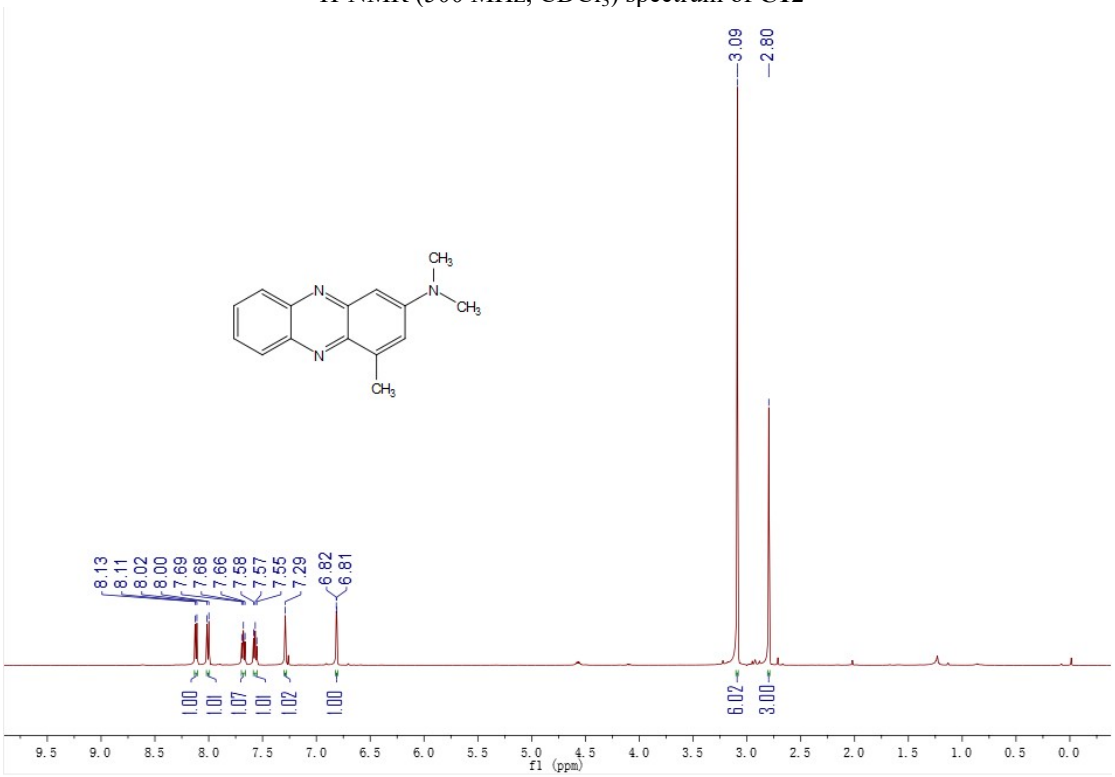
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **C11**



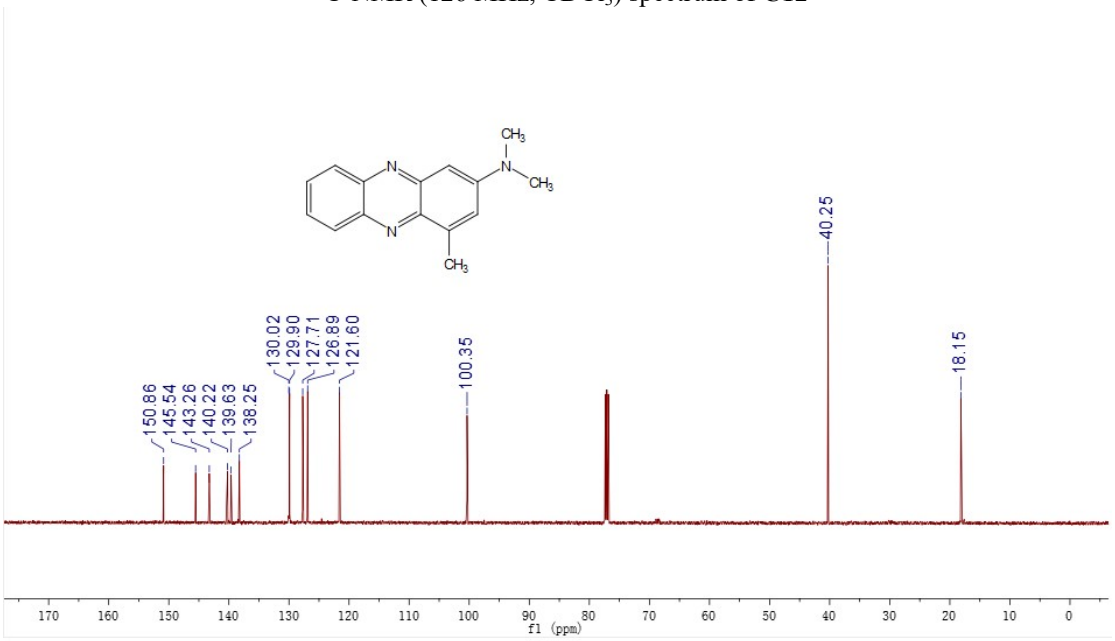
^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **C11**



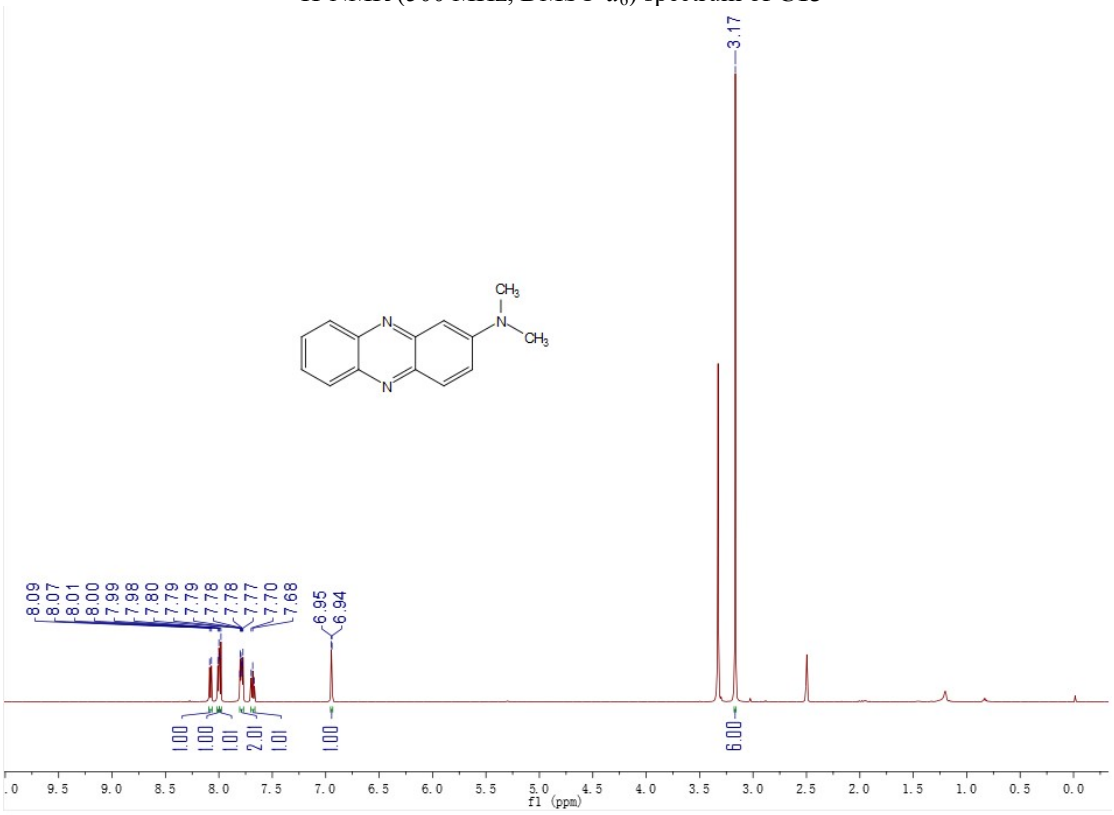
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of **C12**



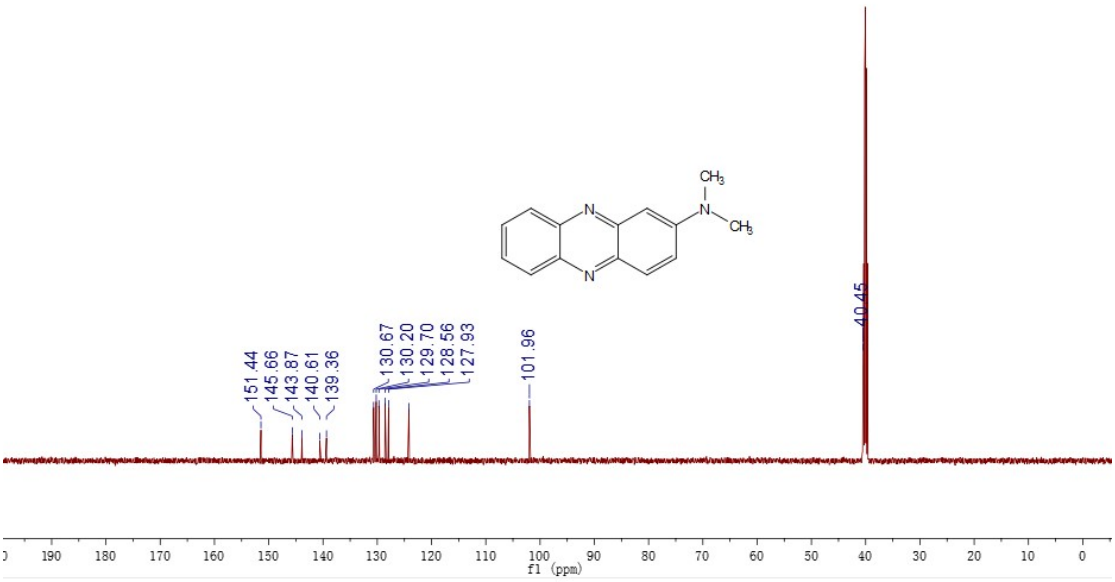
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of **C12**



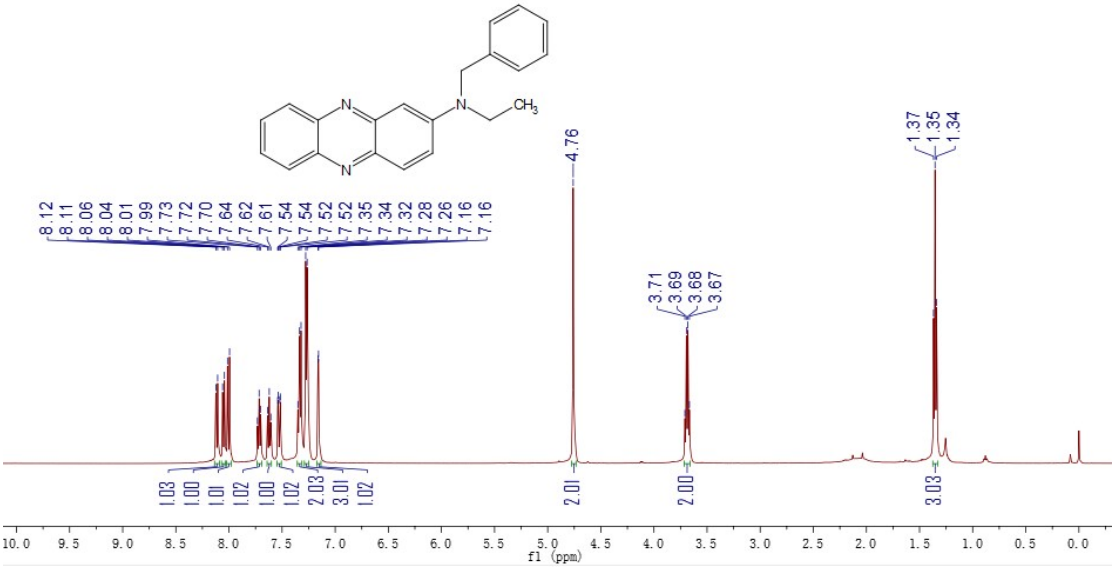
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C13**



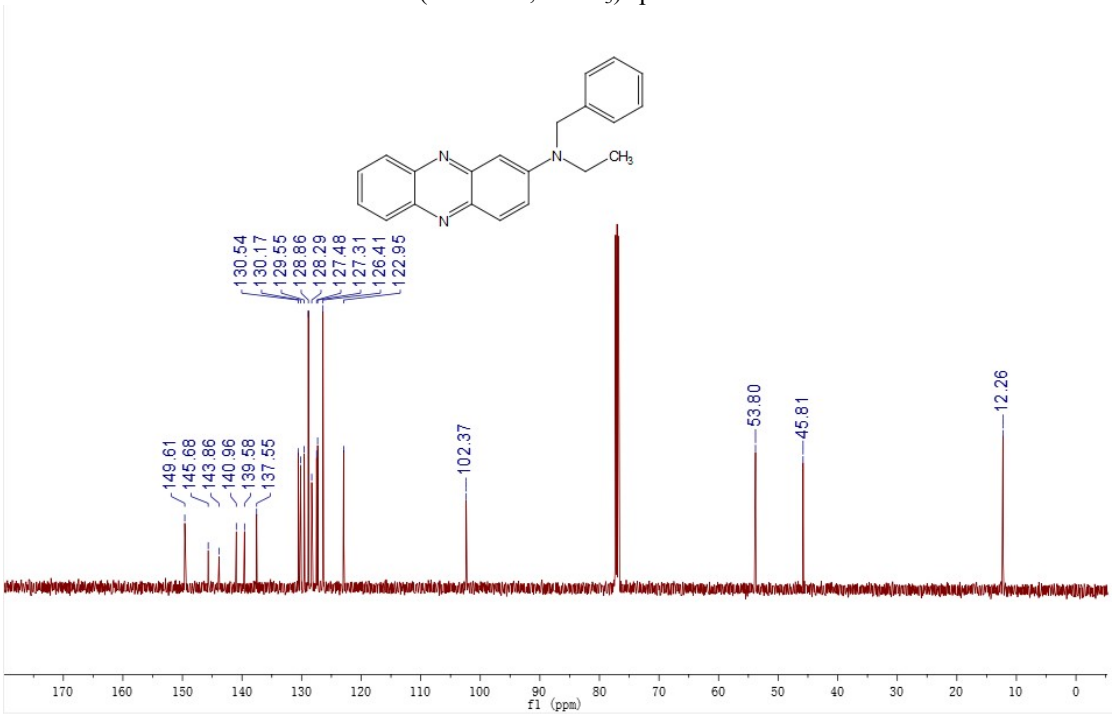
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C13**



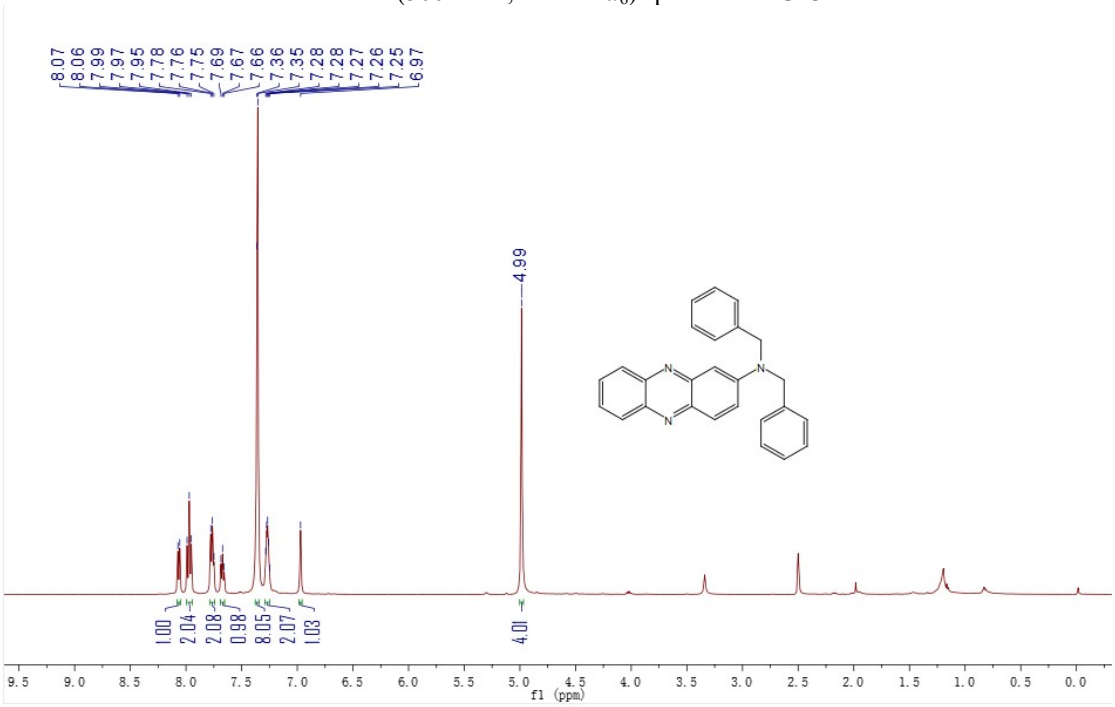
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of **C14**



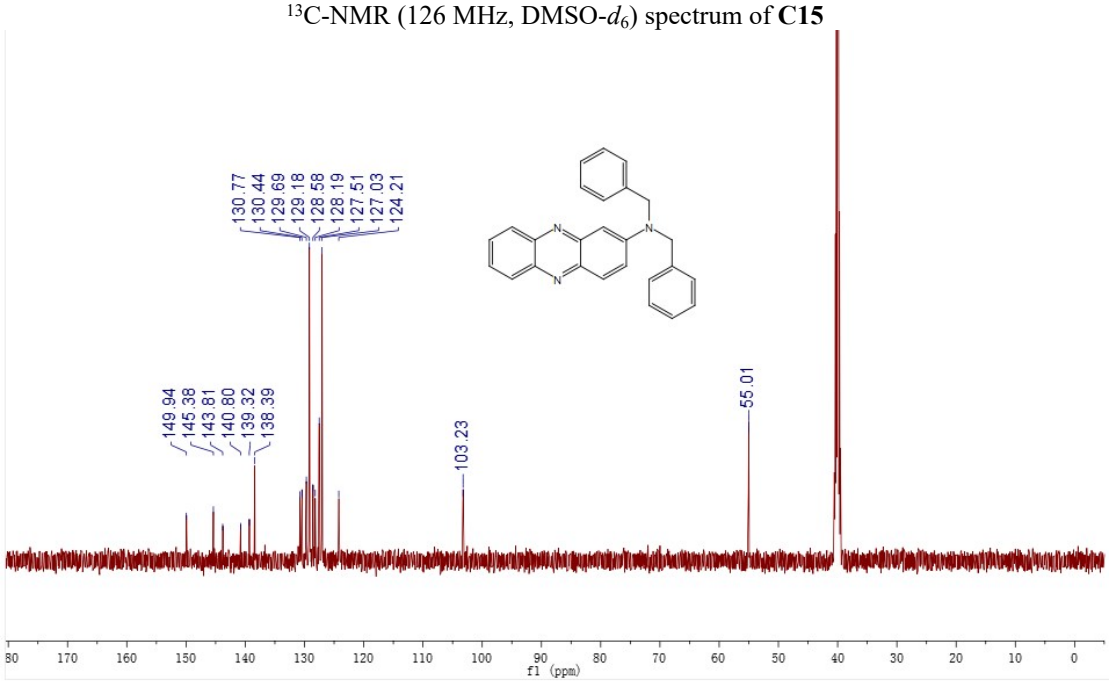
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of **C14**



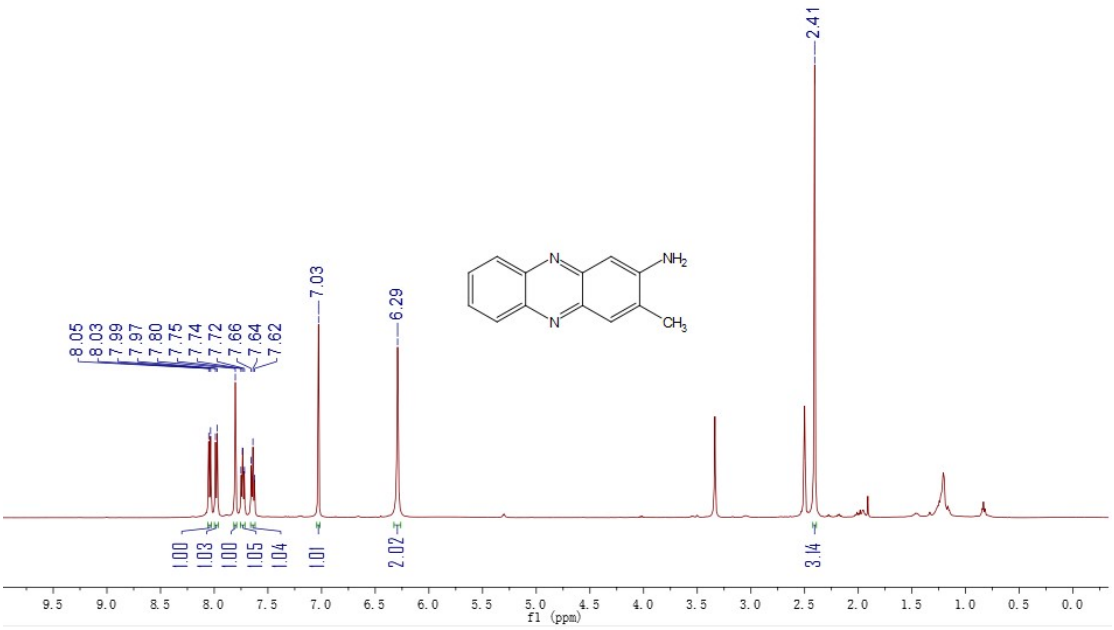
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C15**



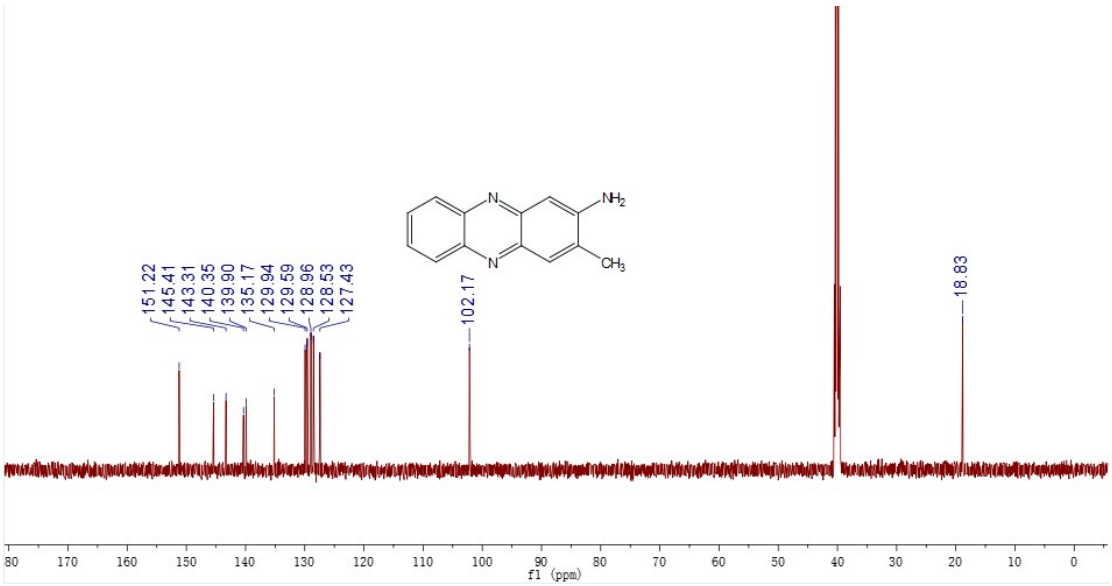
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C15**



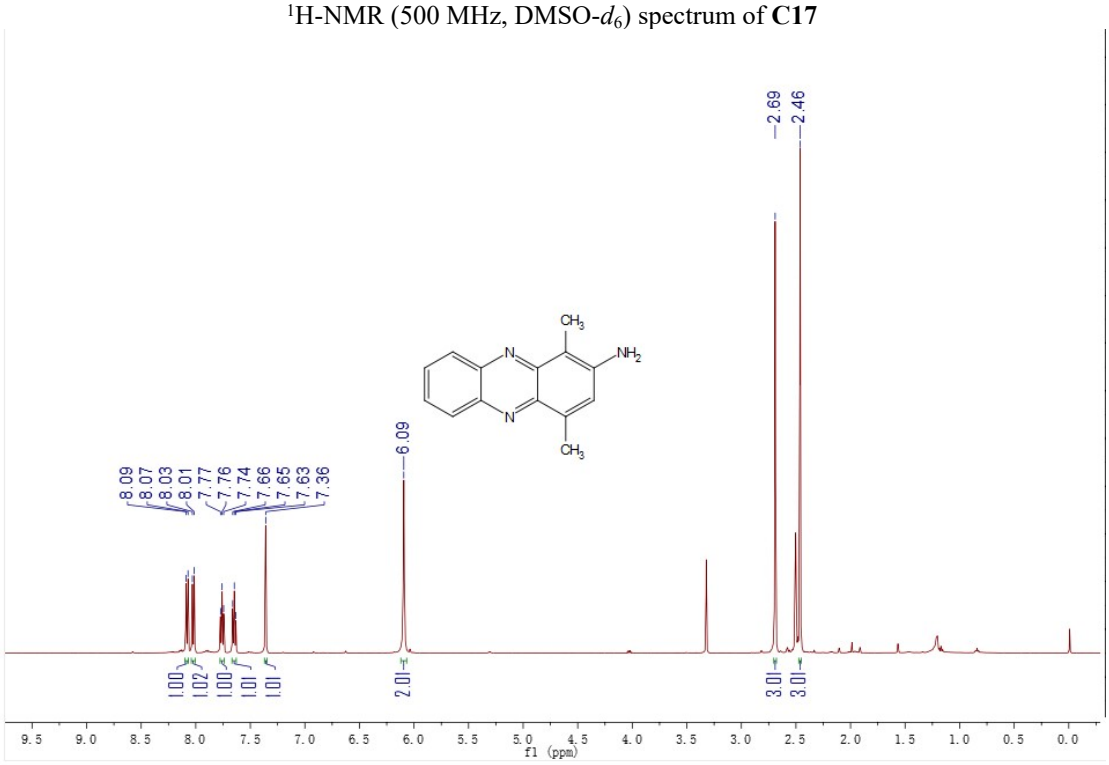
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C16**



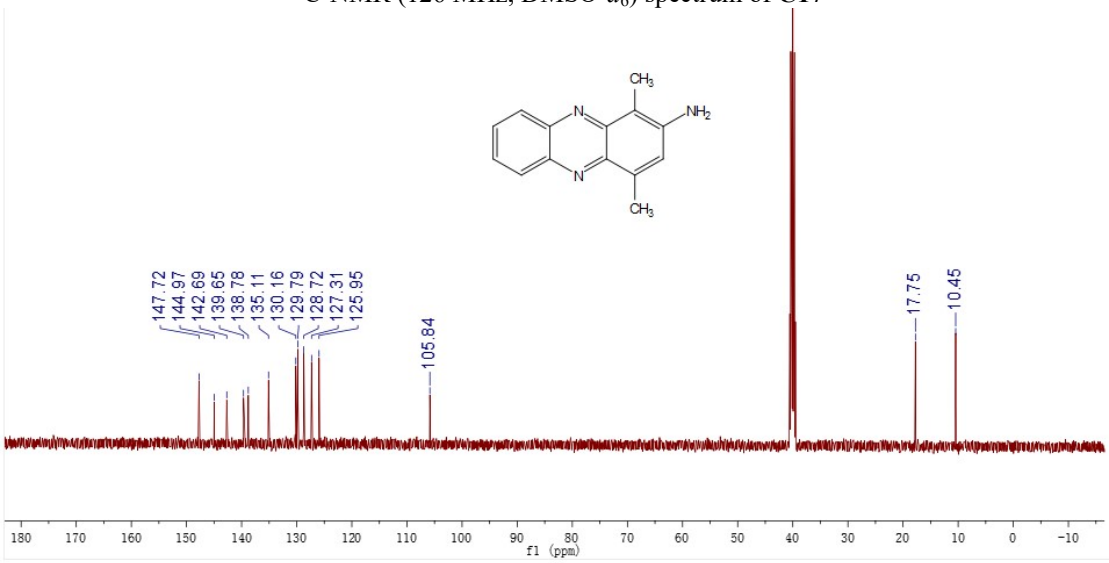
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C16**



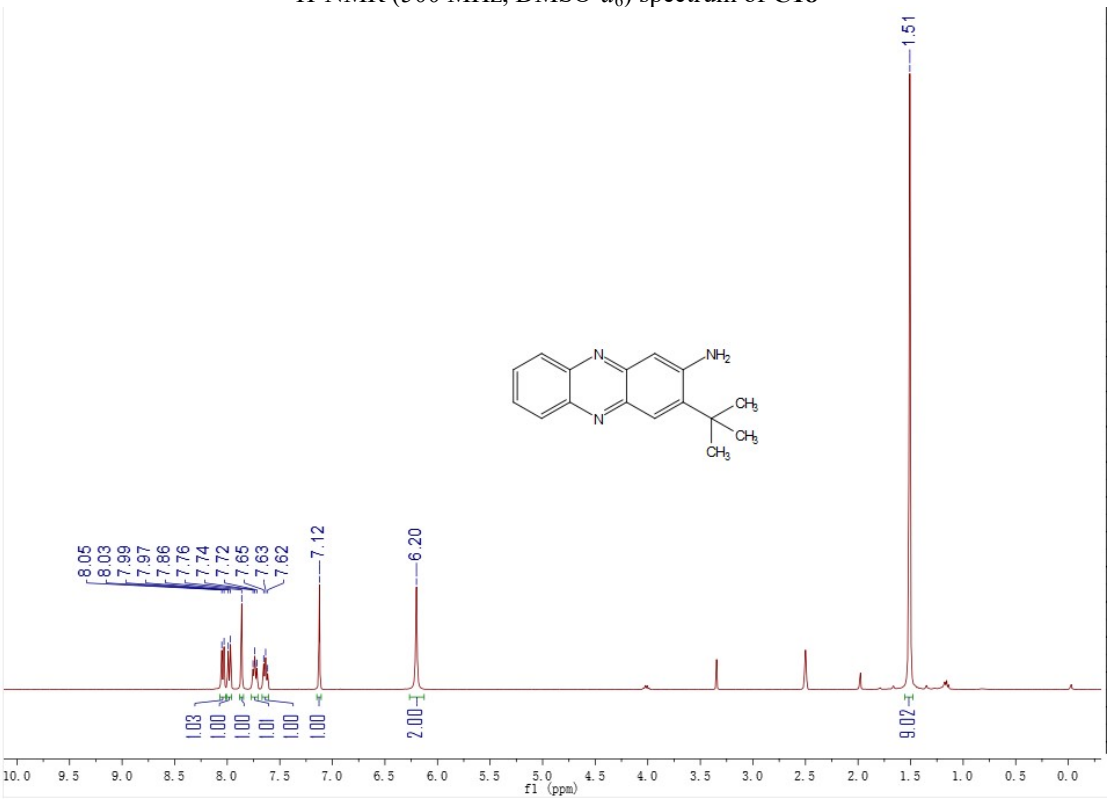
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C17**



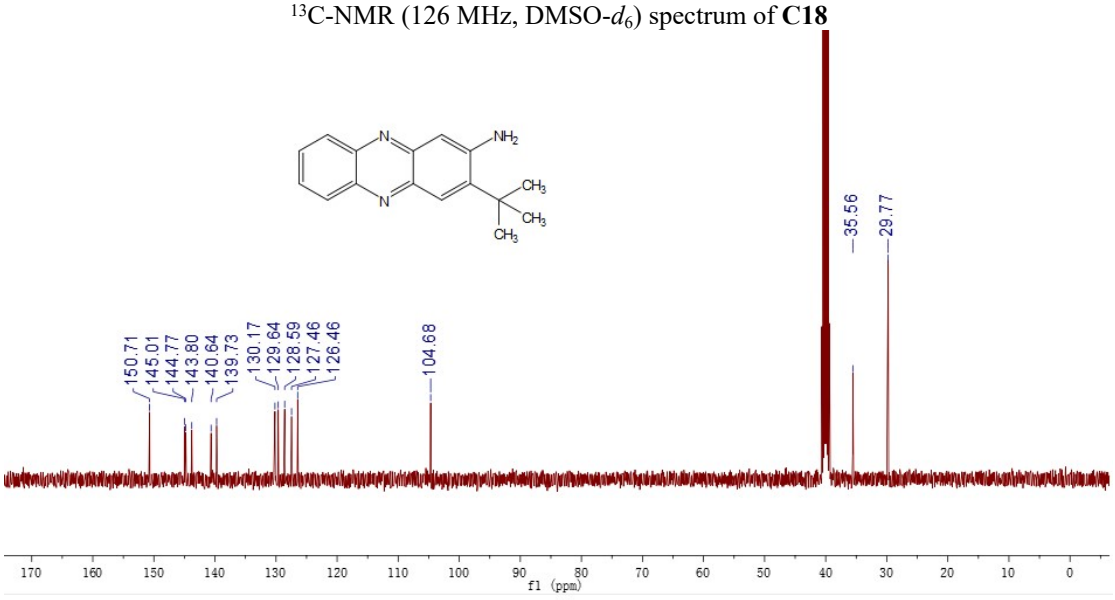
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C17**



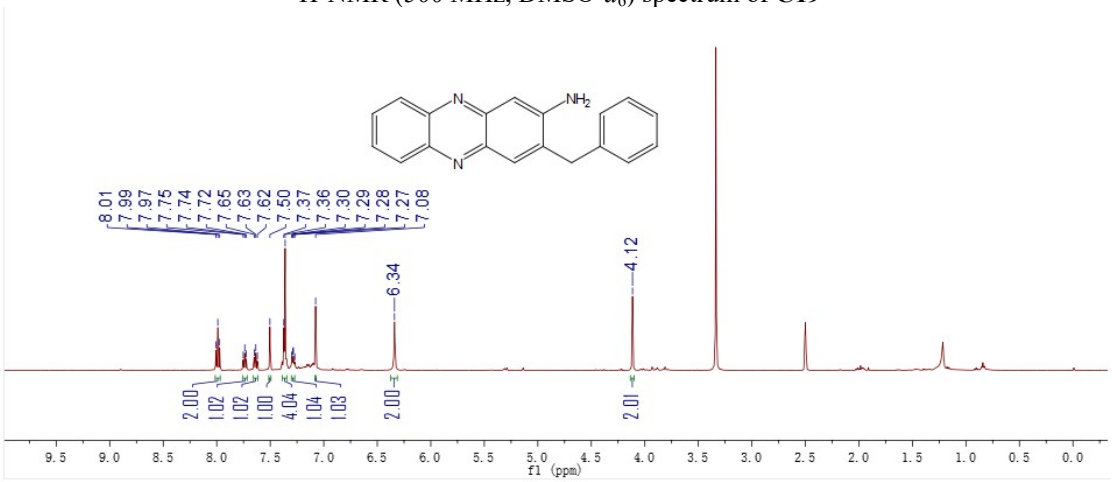
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C18**



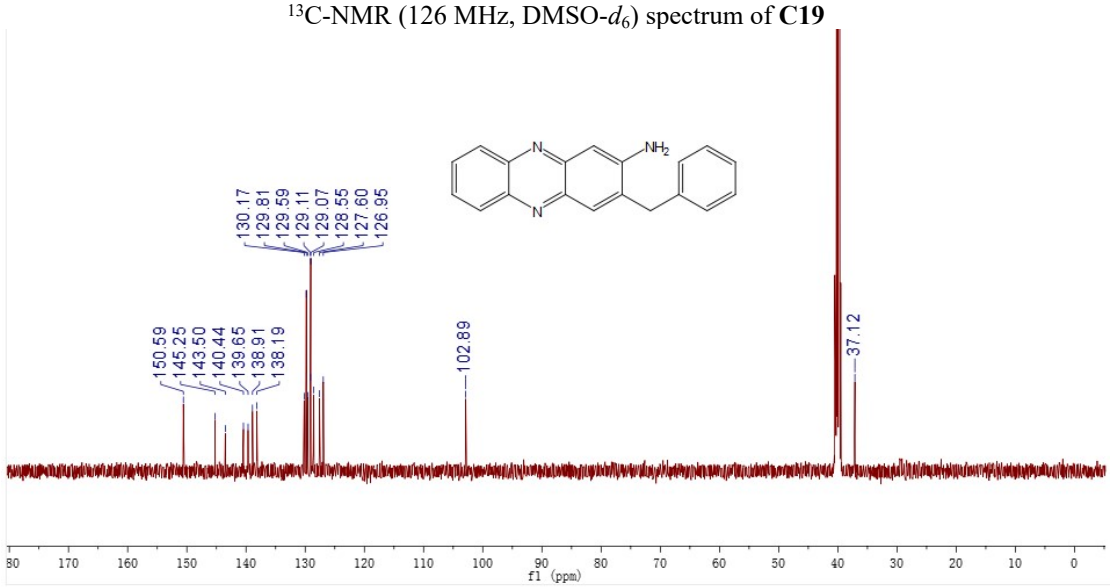
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C18**



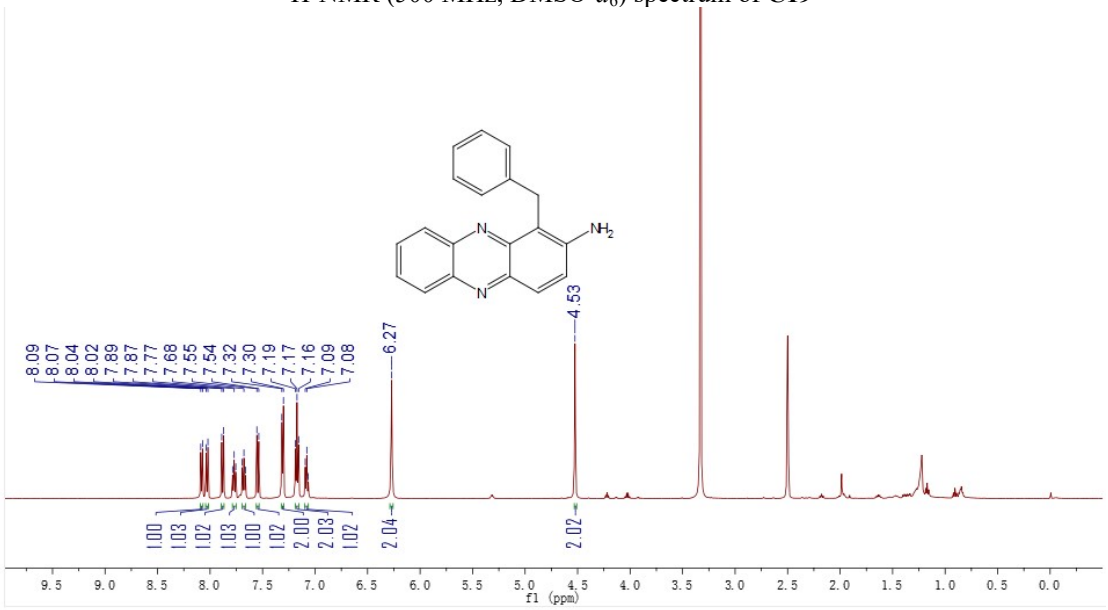
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C19**



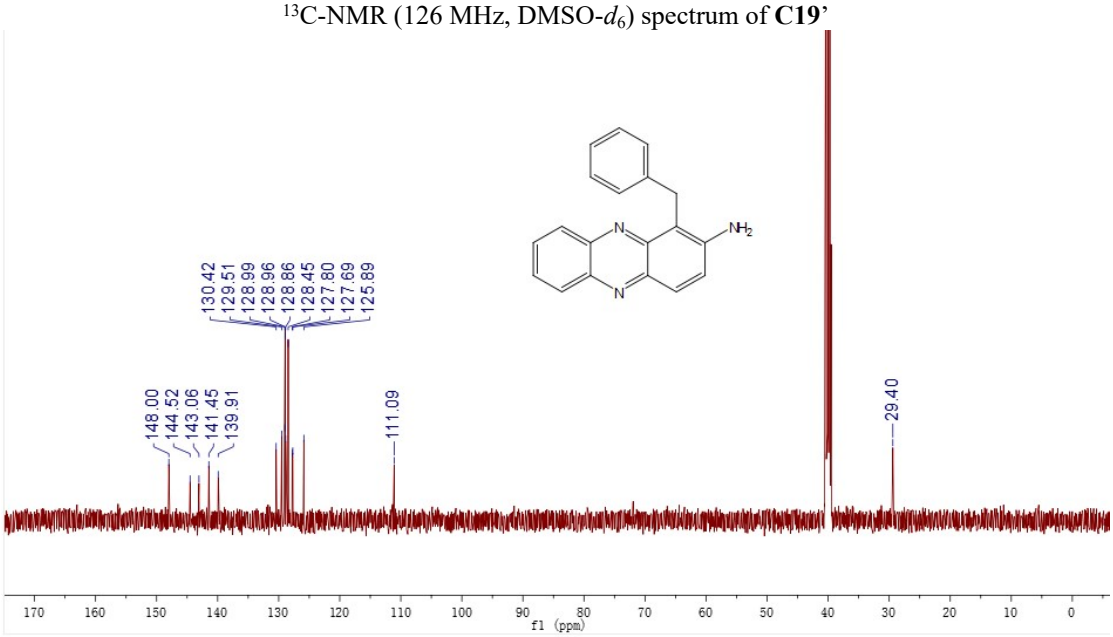
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C19**



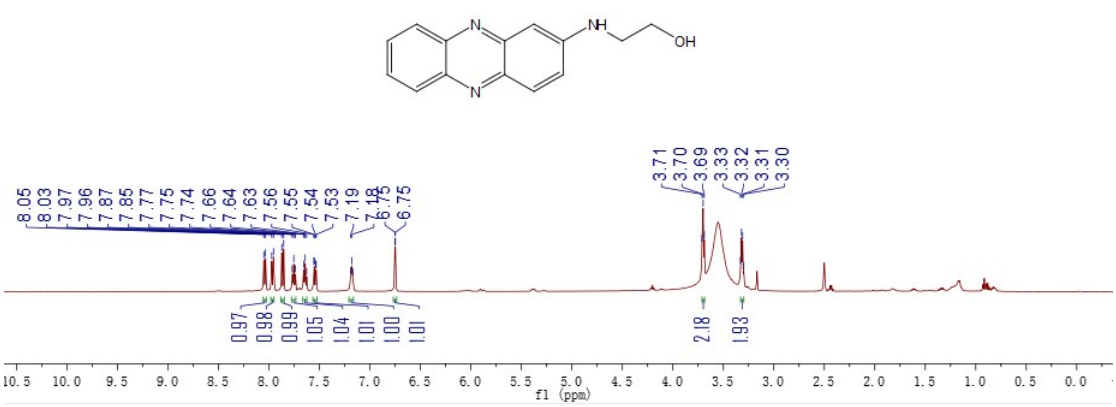
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C19'**



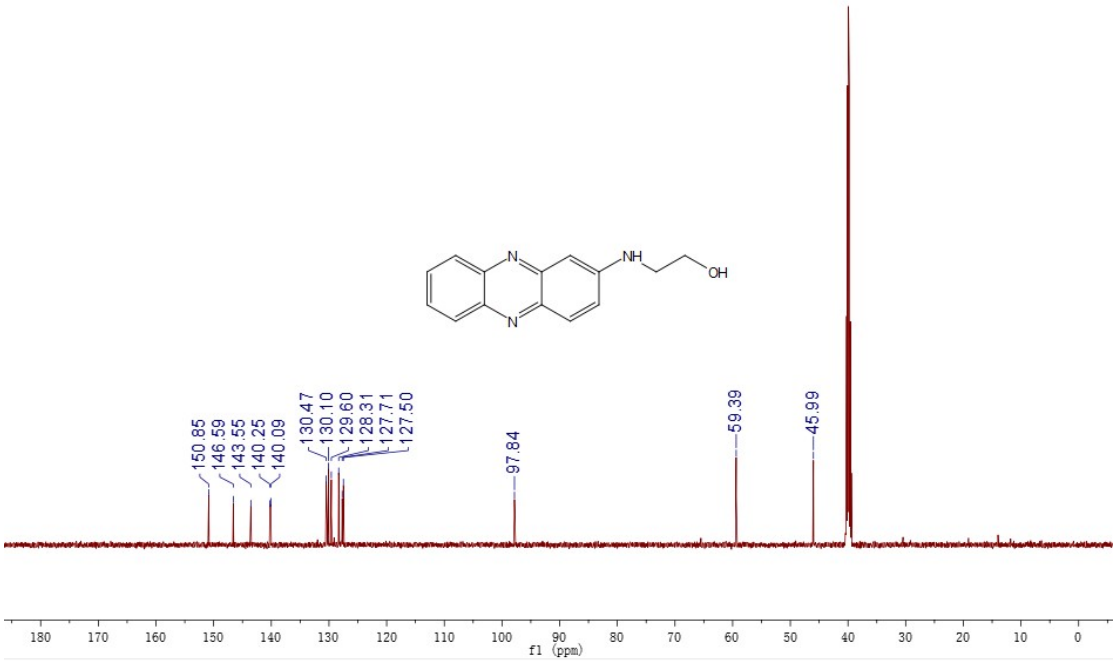
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C19'**



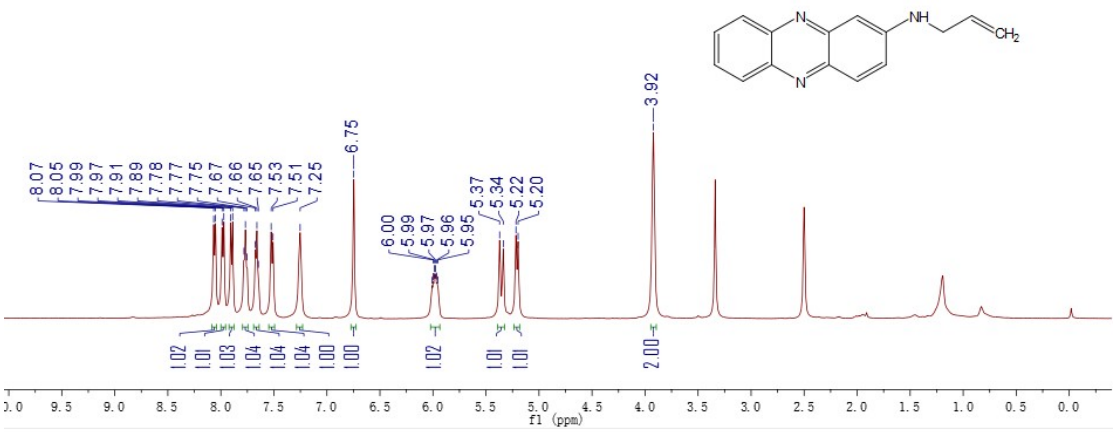
[1]H-NMR (500 MHz, DMSO-d_6) spectrum of **C20**



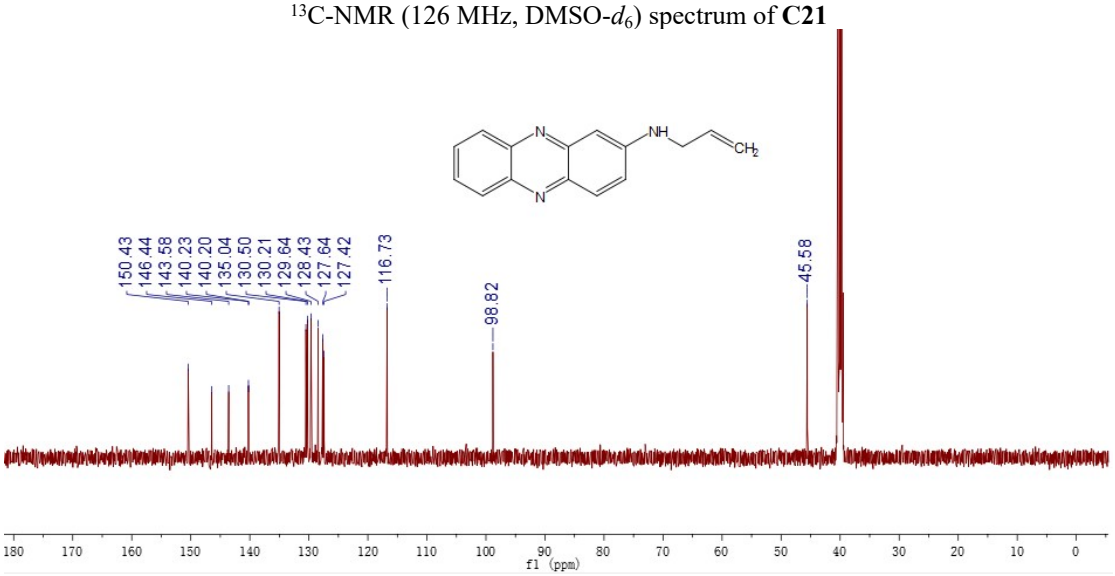
[13]C-NMR (126 MHz, DMSO-d_6) spectrum of **C20**



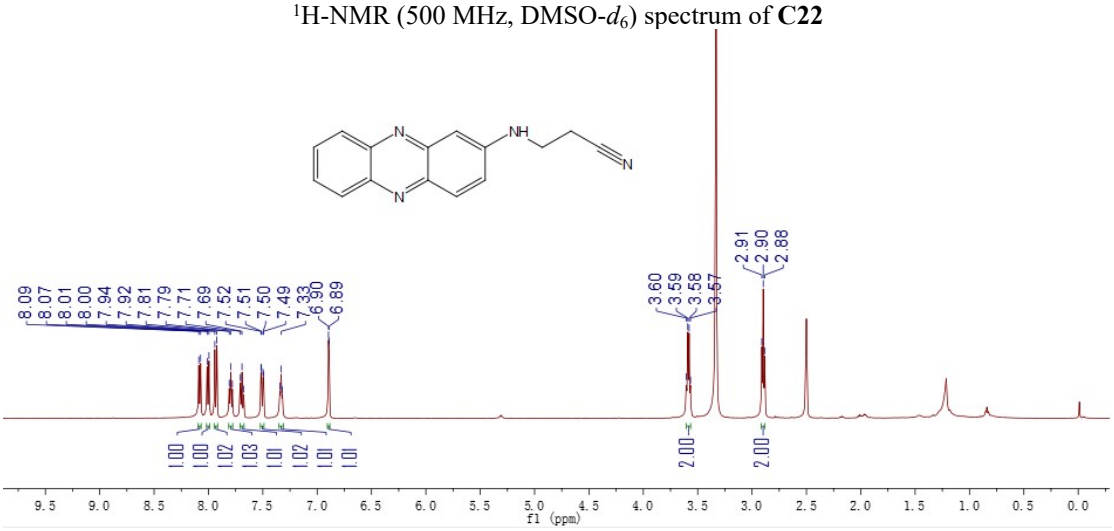
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C21**



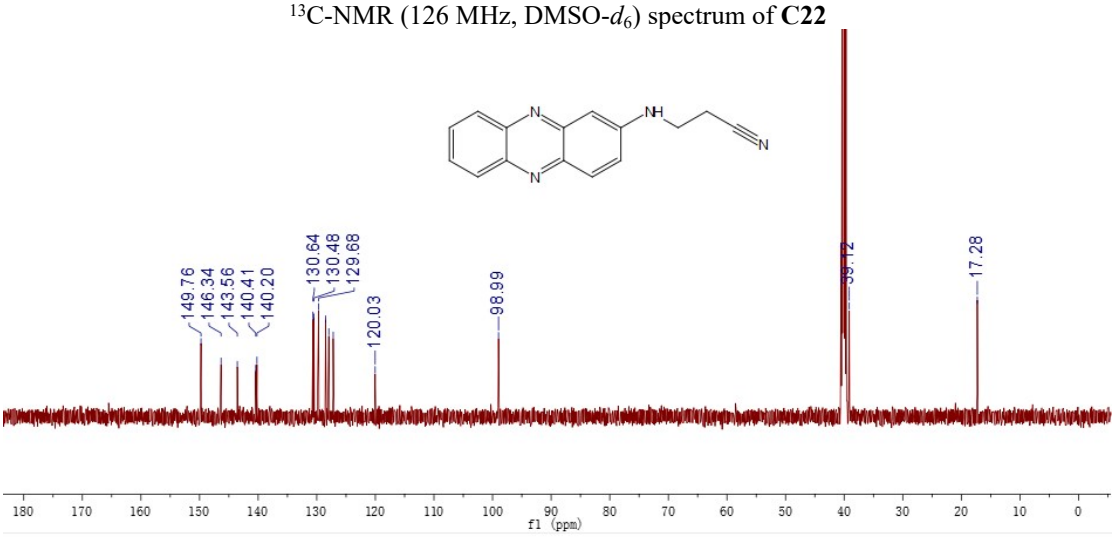
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C21**



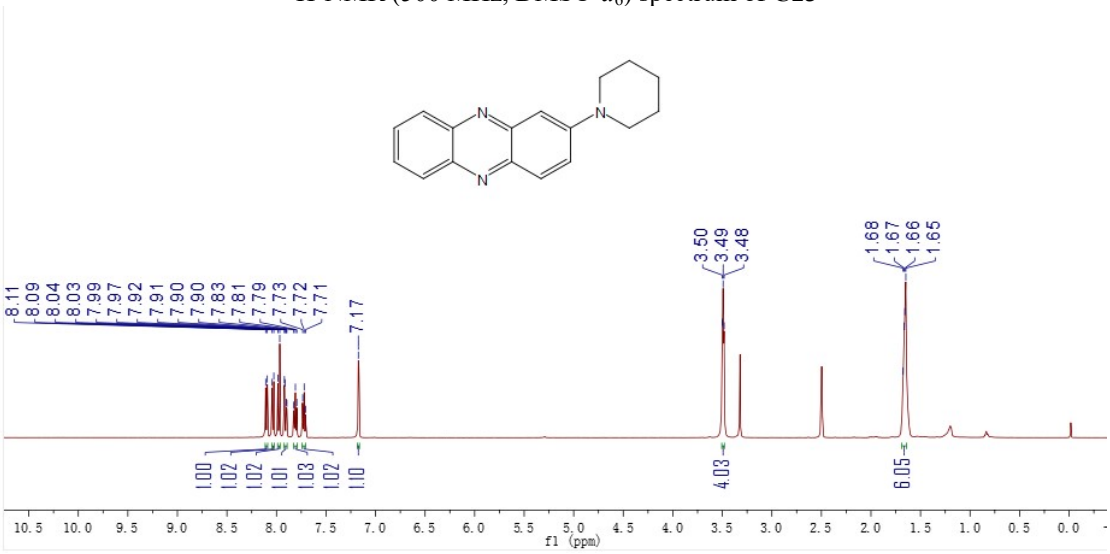
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C22**



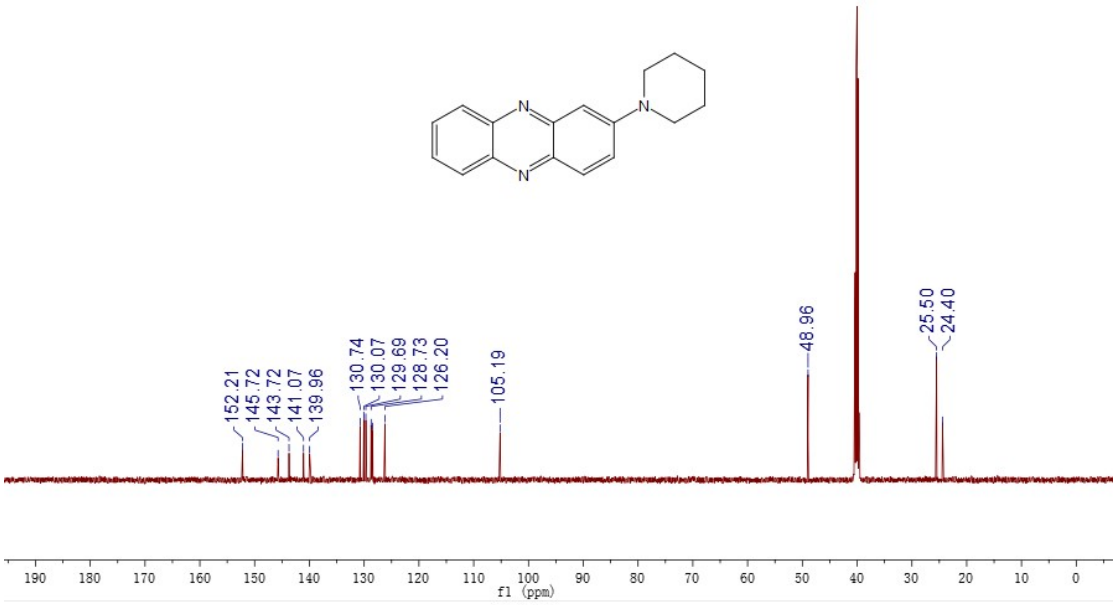
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C22**



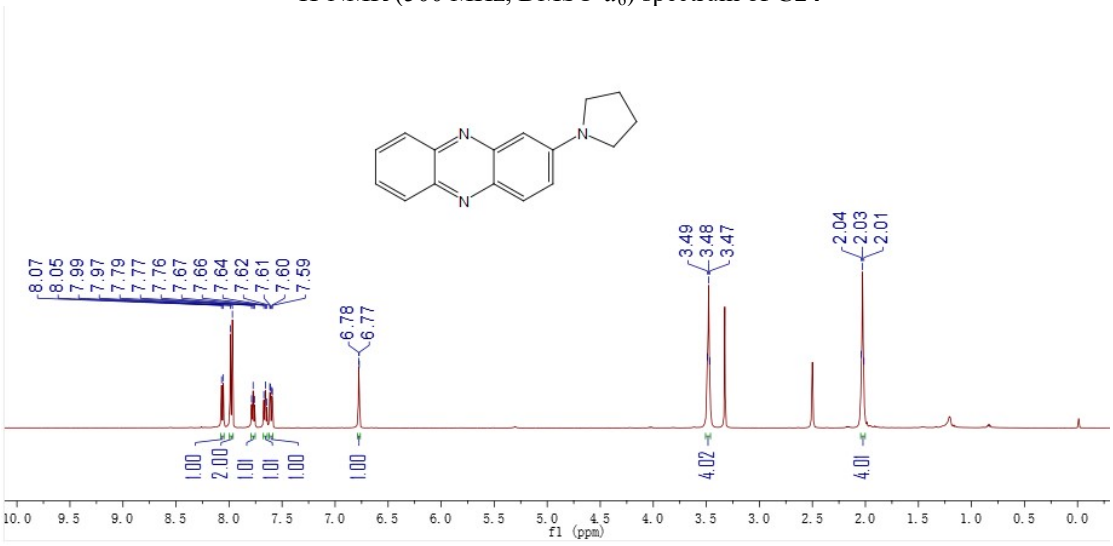
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C23**



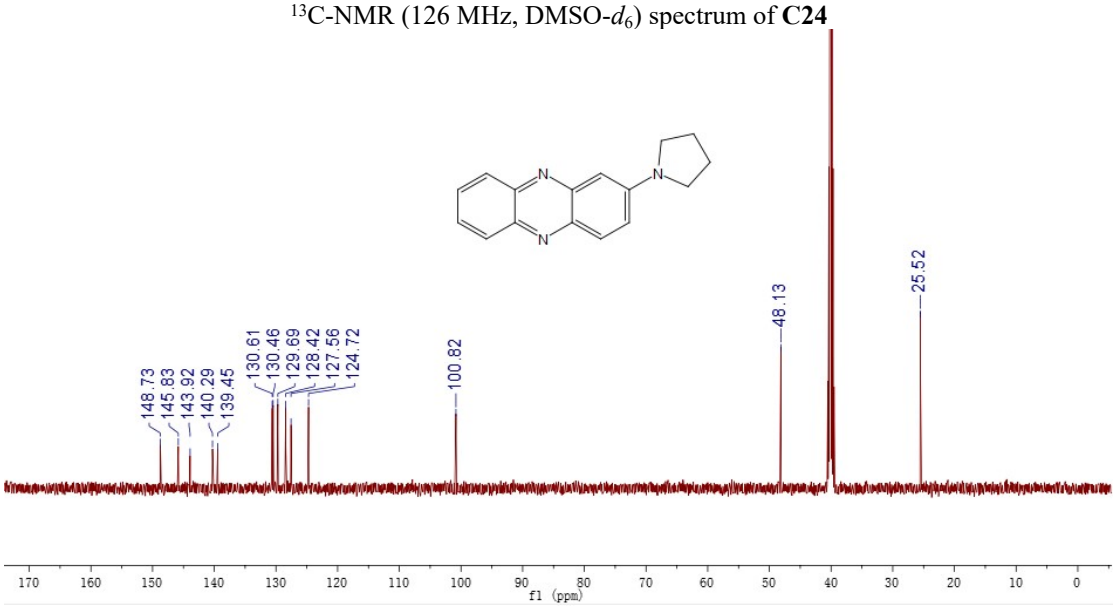
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C23**



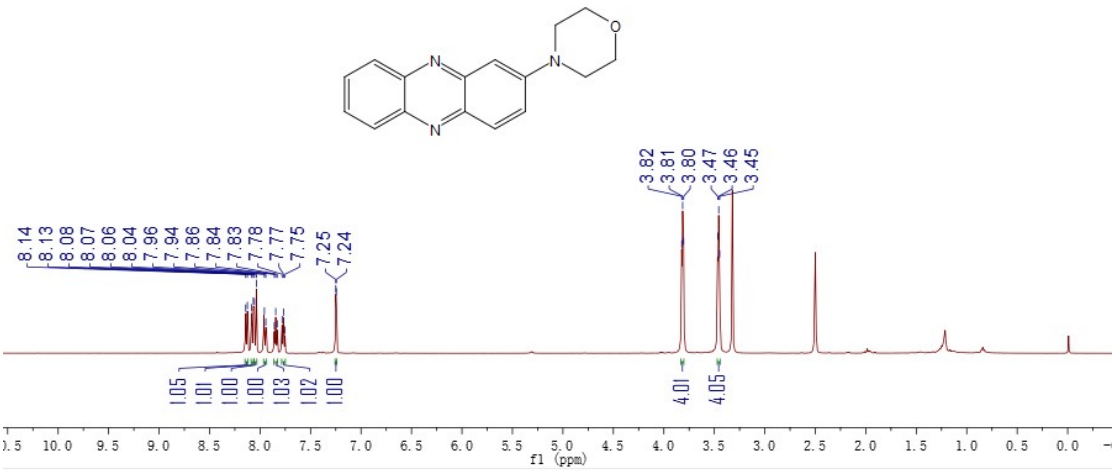
[1]H-NMR (500 MHz, DMSO-d_6) spectrum of **C24**



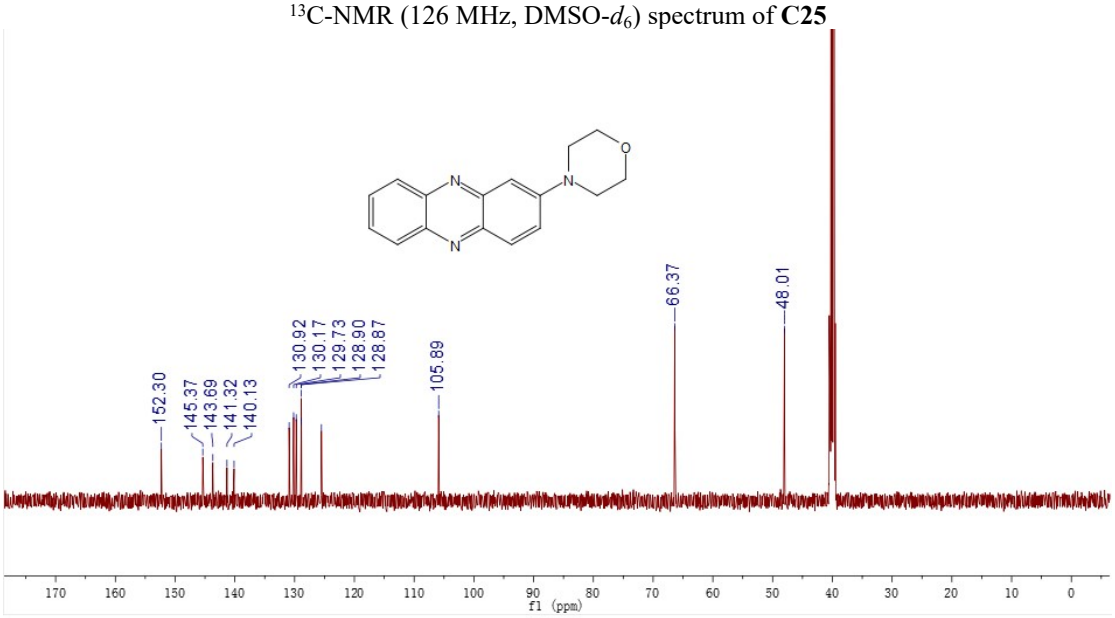
[13]C-NMR (126 MHz, DMSO-d_6) spectrum of **C24**



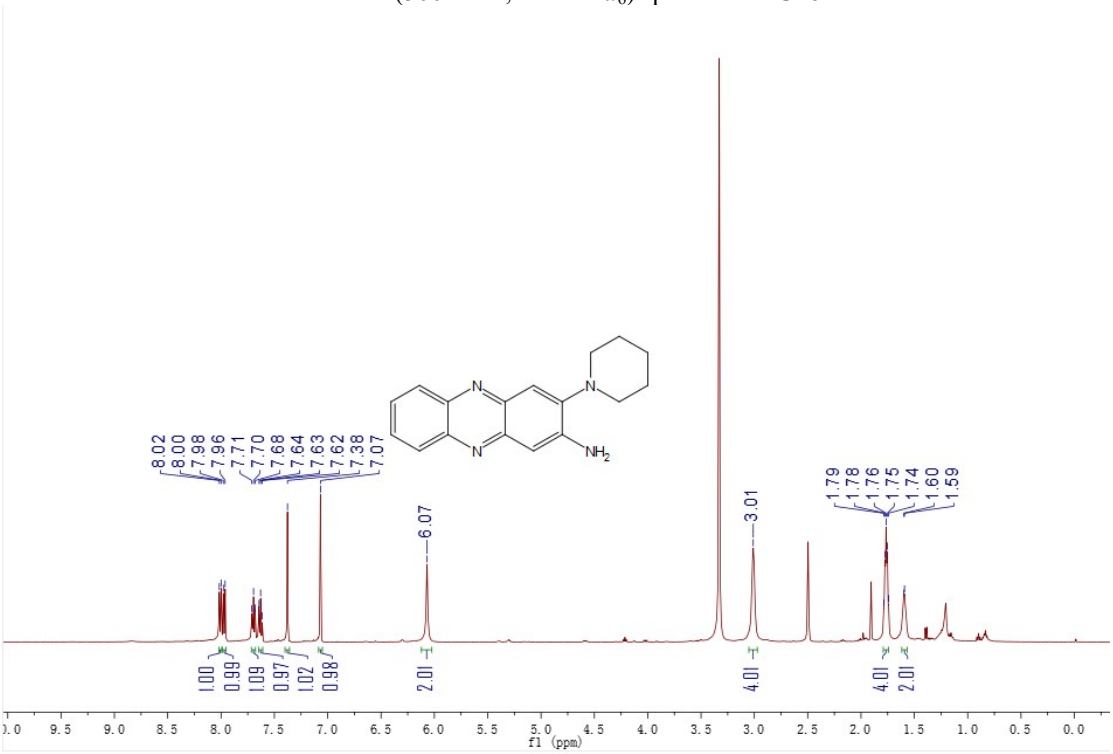
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C25**



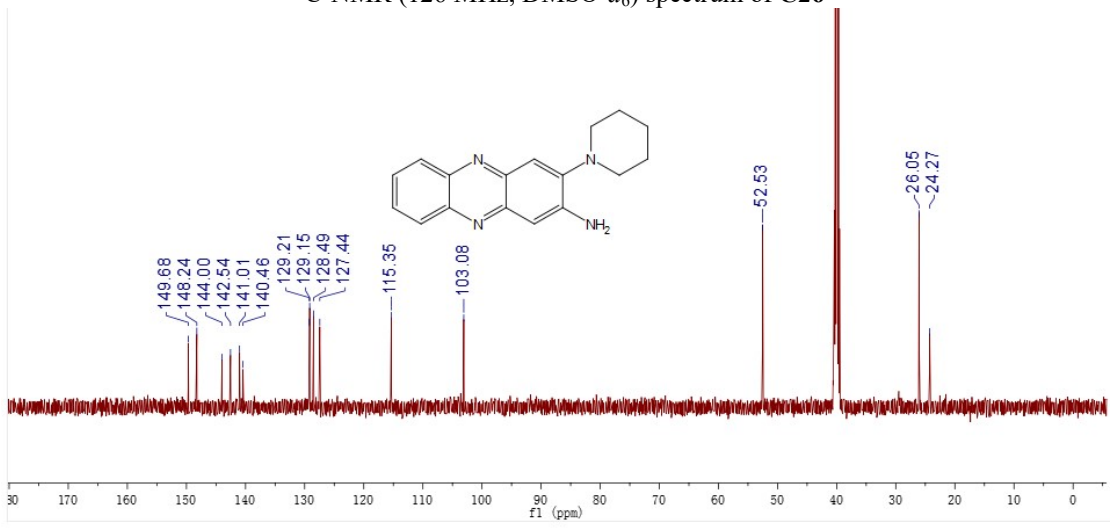
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C25**



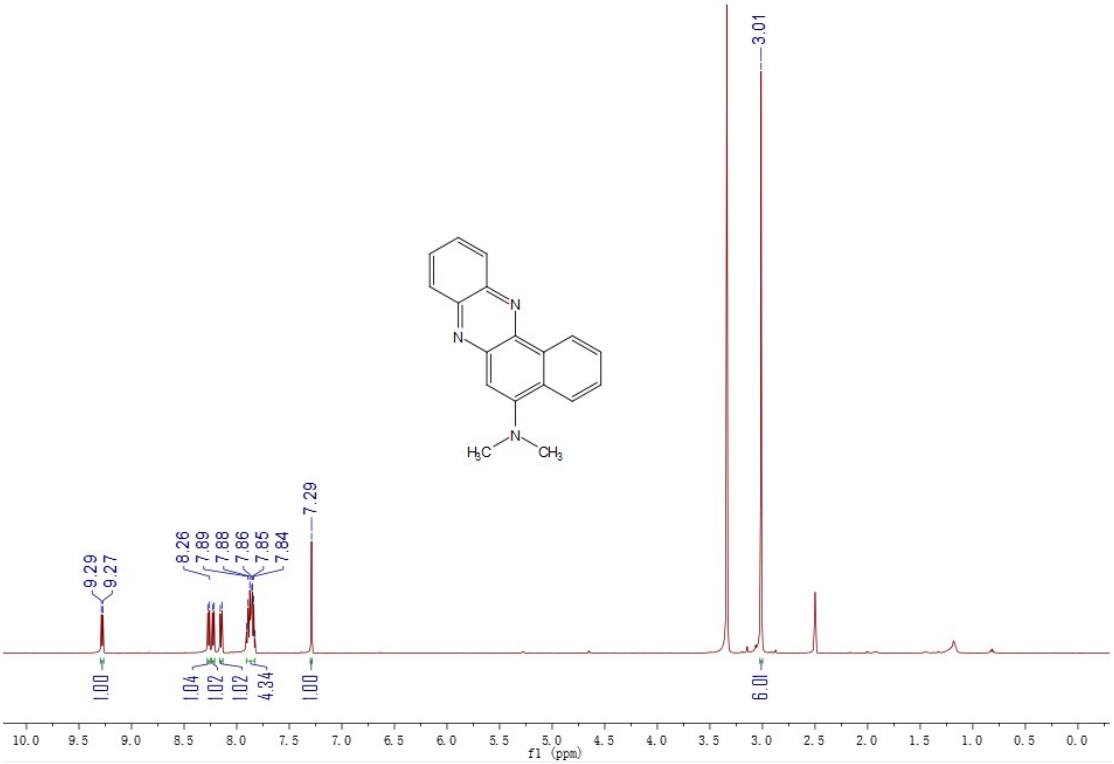
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C26**



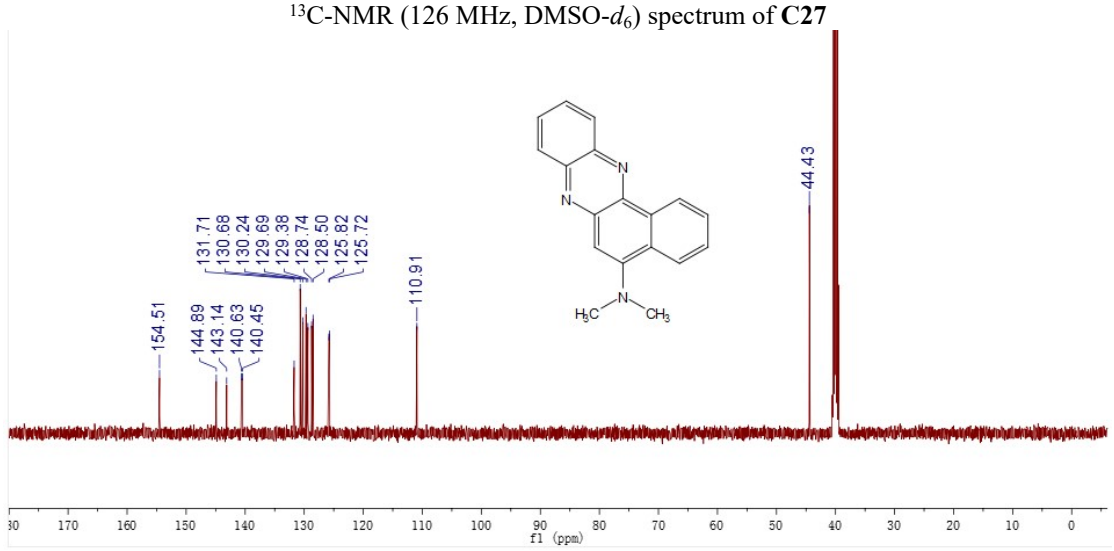
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C26**



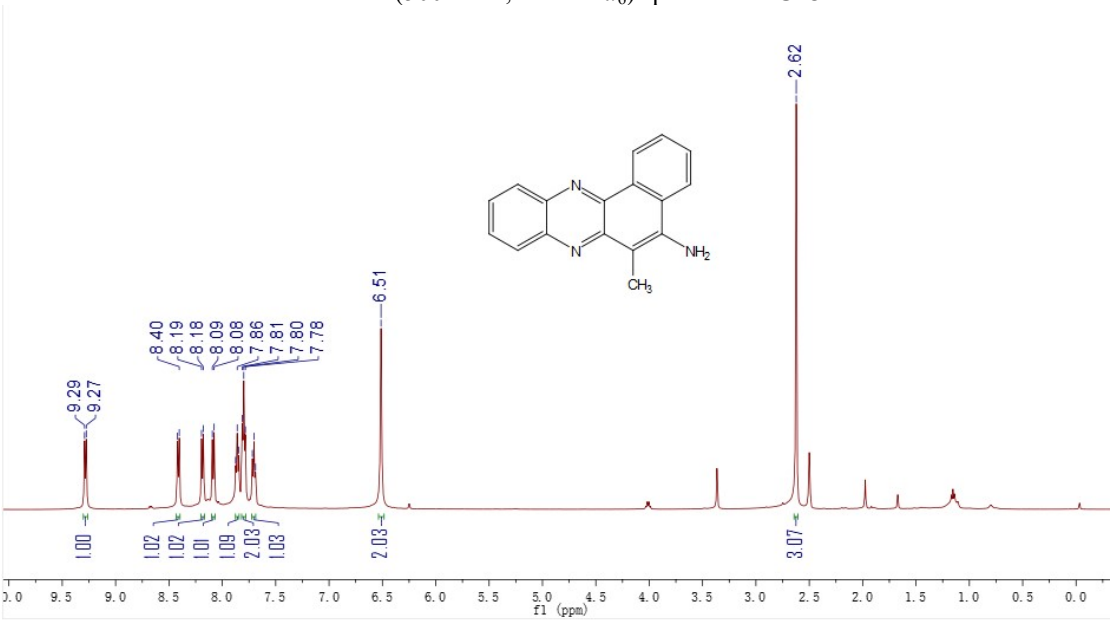
[1]H-NMR (500 MHz, DMSO-d_6) spectrum of **C27**



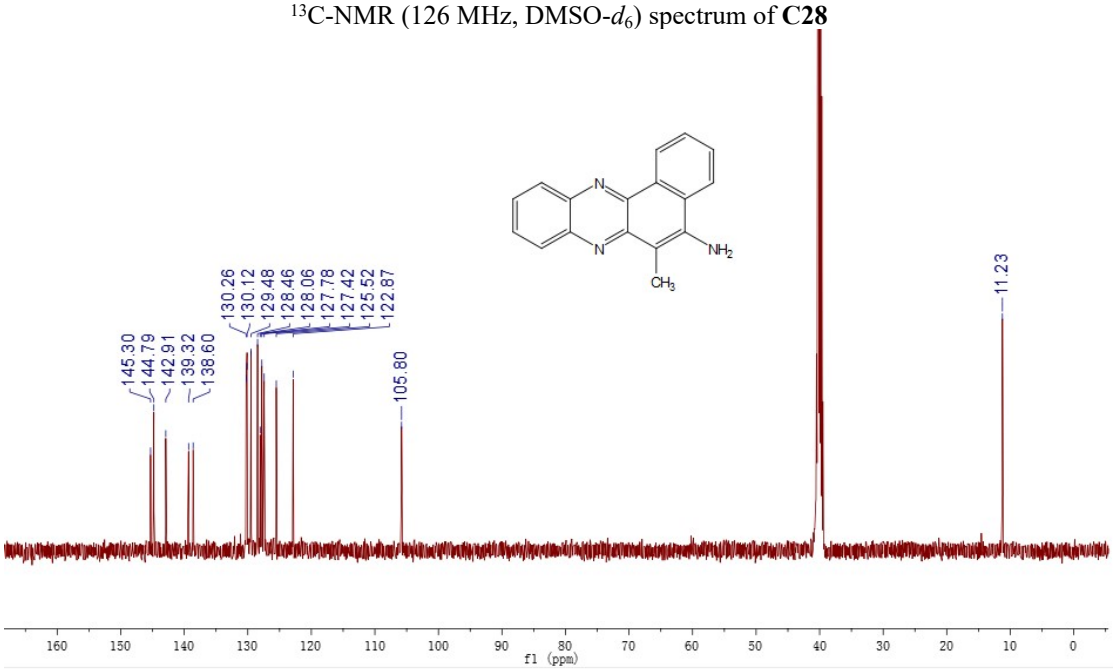
[13]C-NMR (126 MHz, DMSO-d_6) spectrum of **C27**



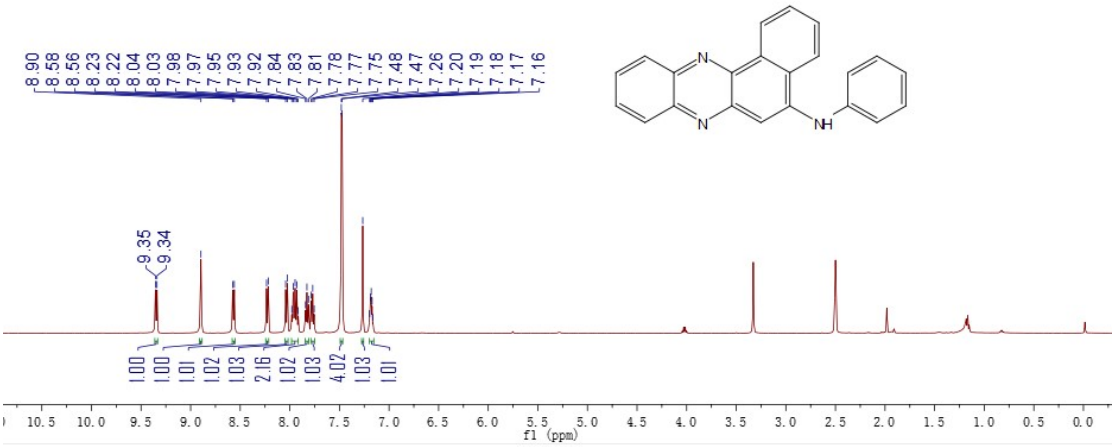
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C28**



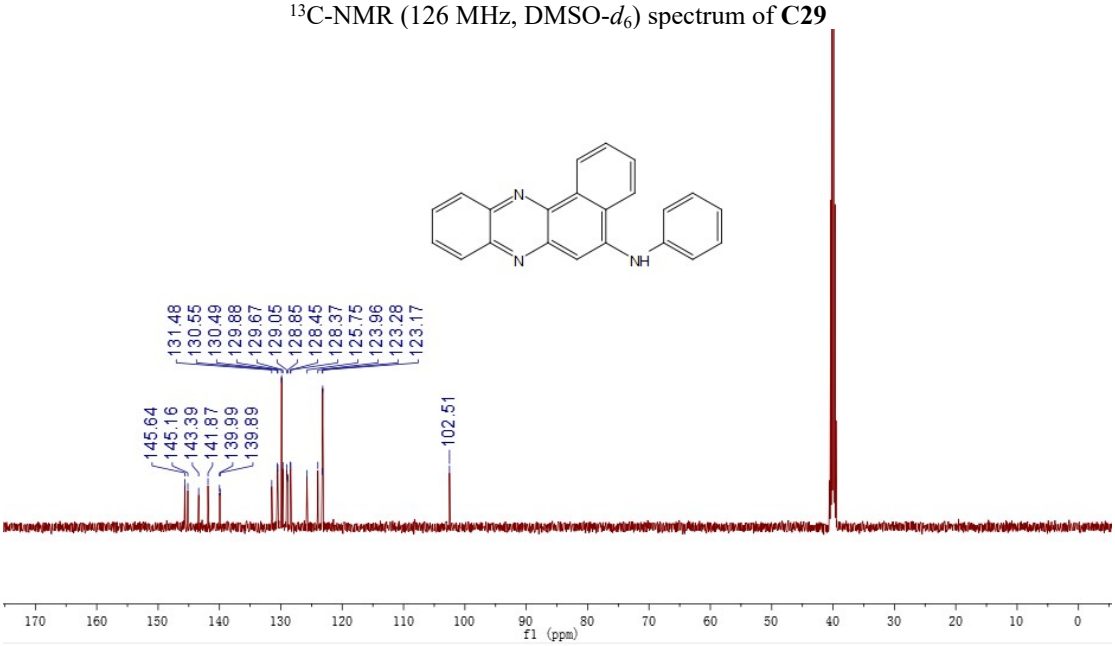
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C28**



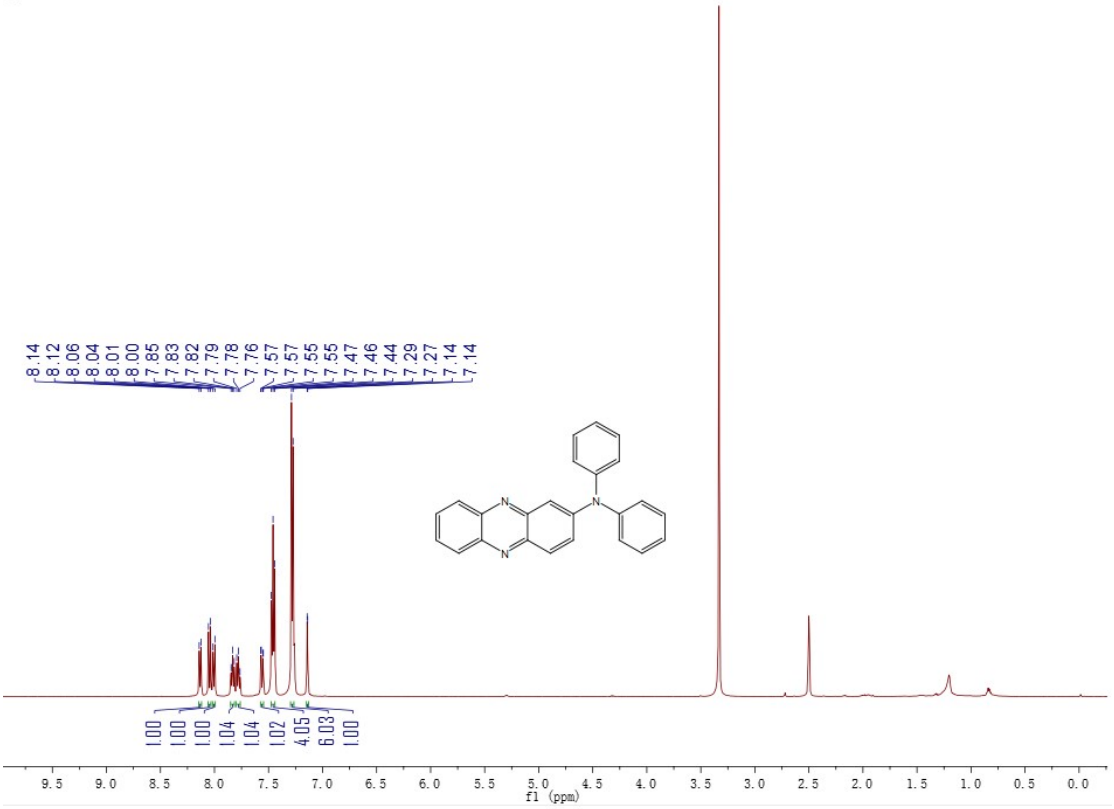
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C29**



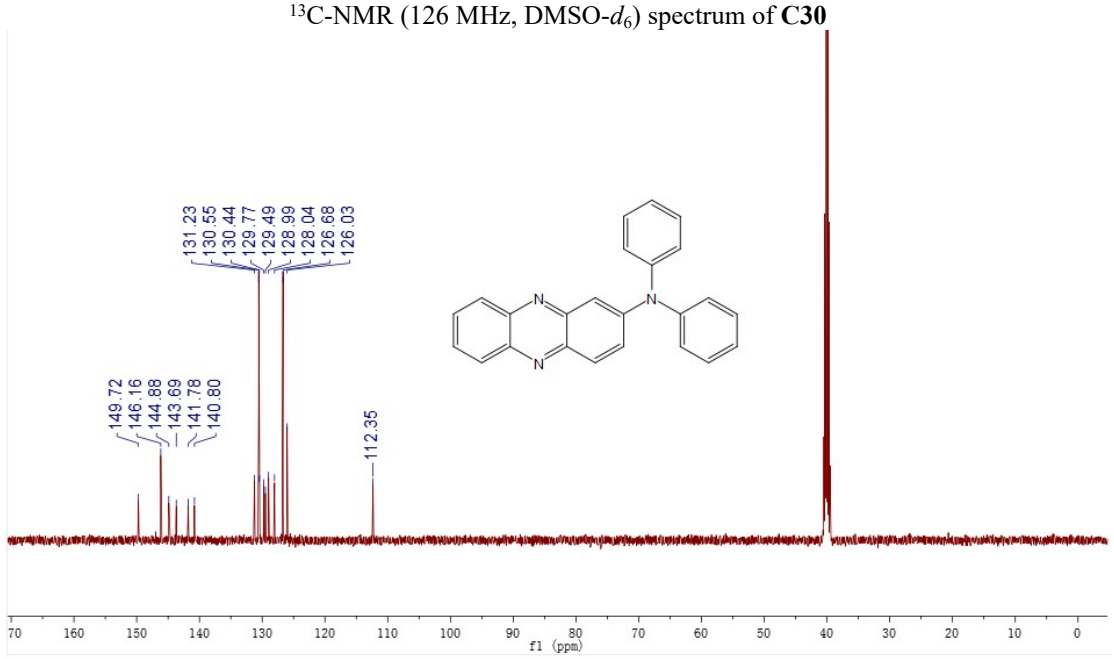
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C29**



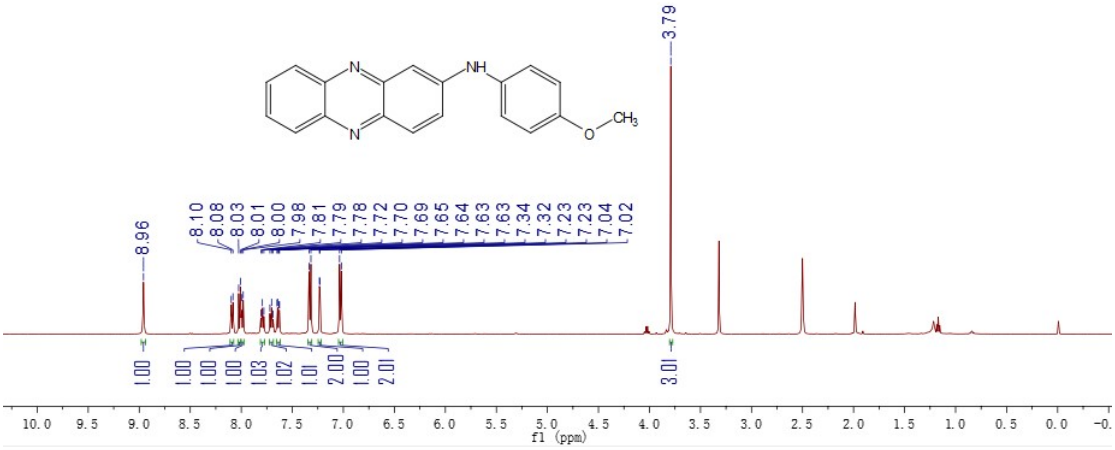
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C30**



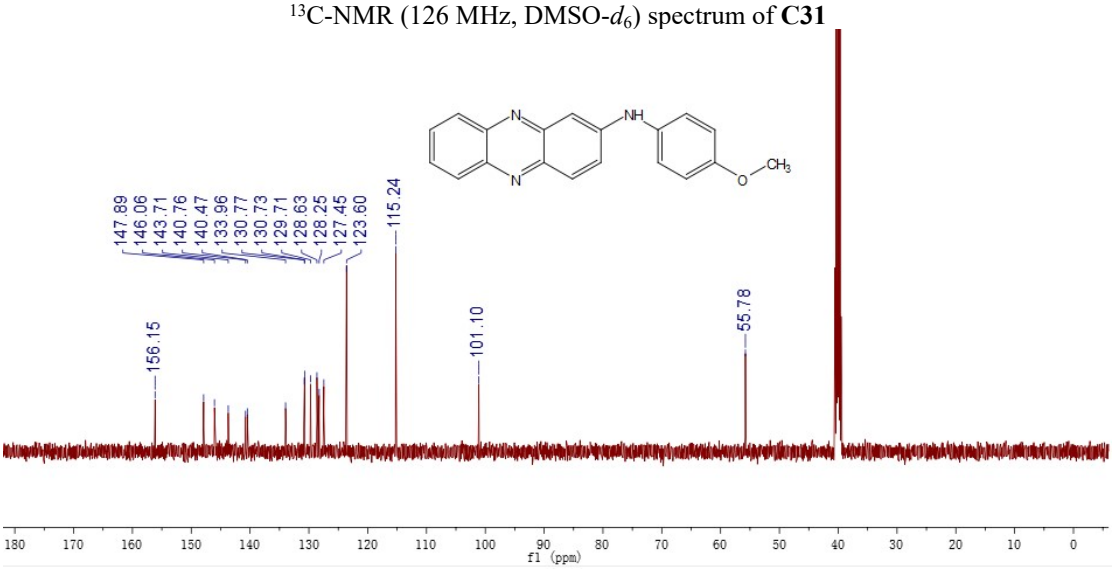
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C30**



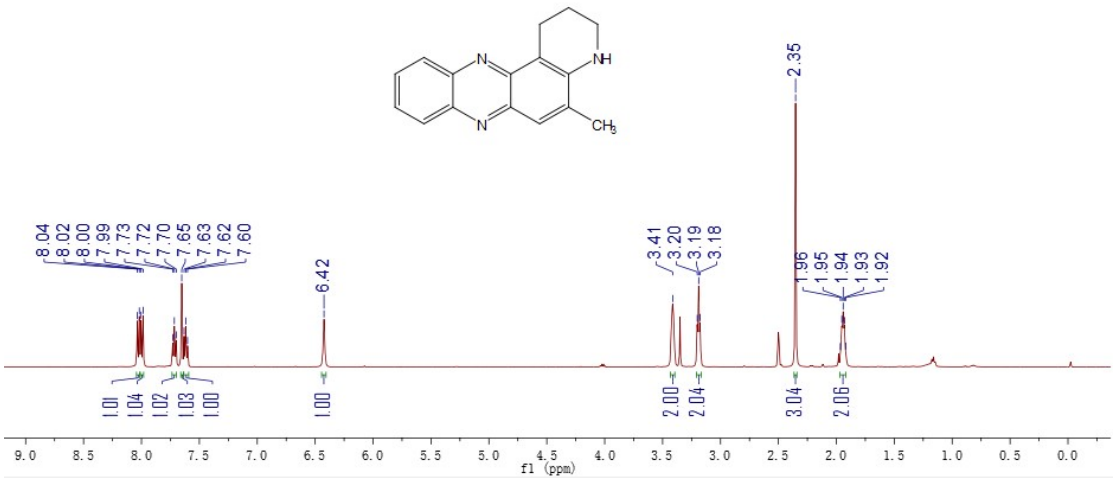
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C31**



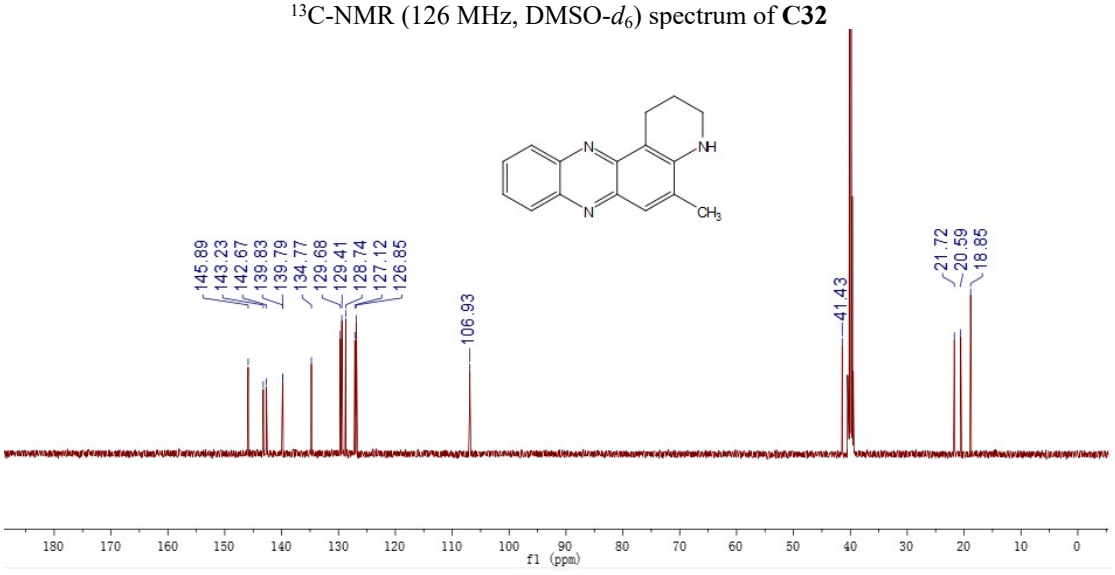
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C31**



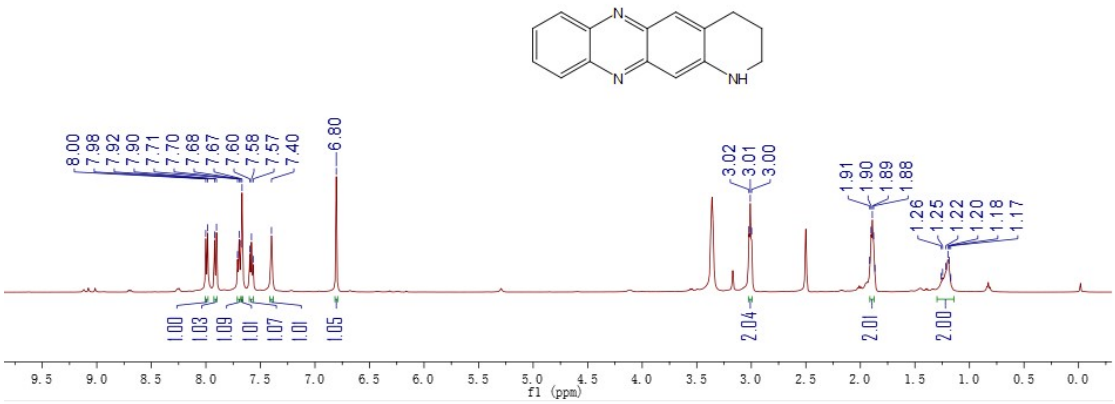
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C32**



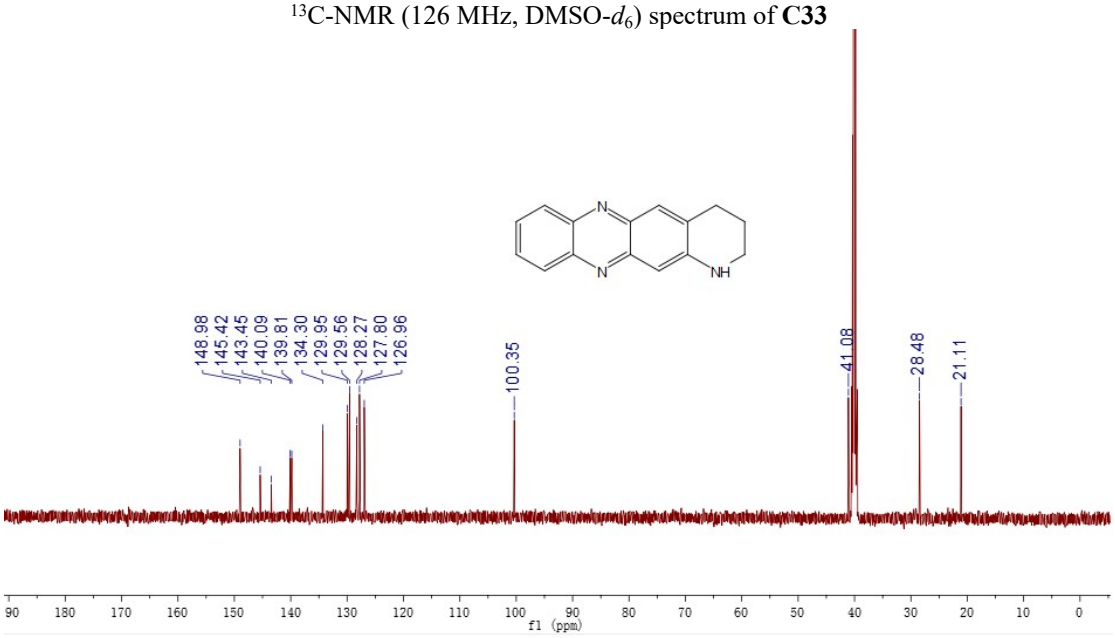
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C32**



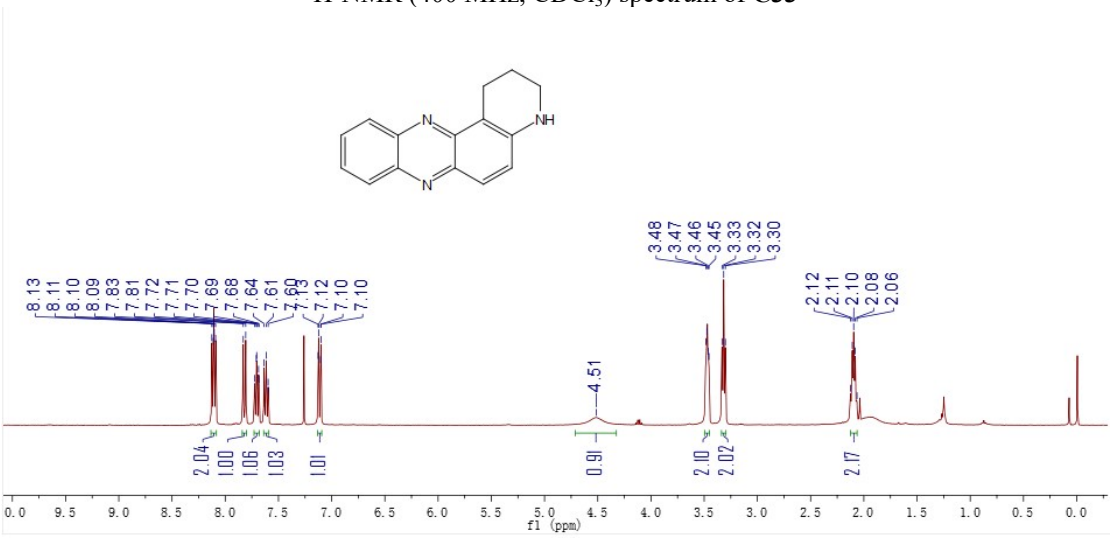
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C33**



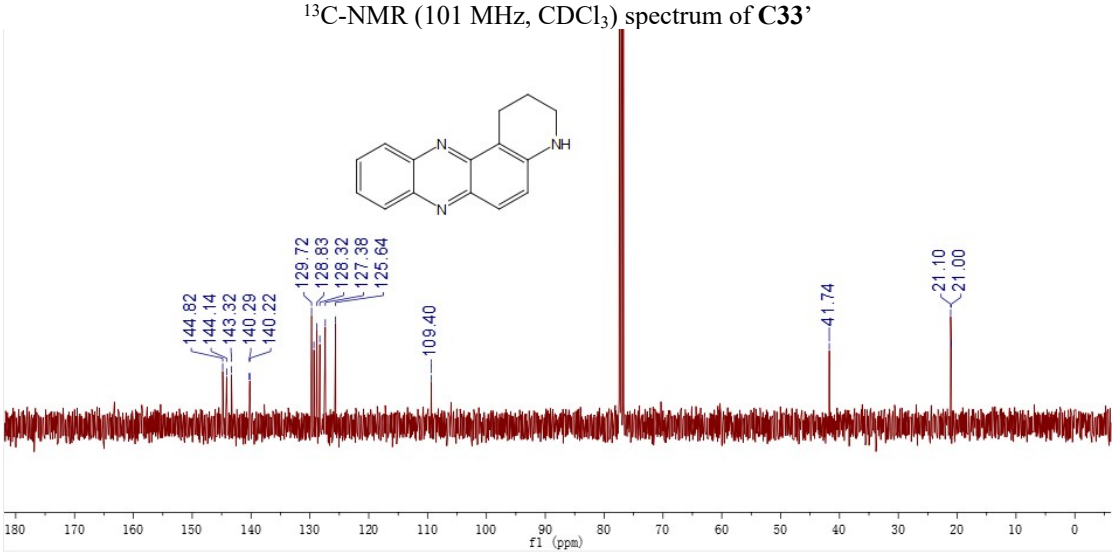
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C33**



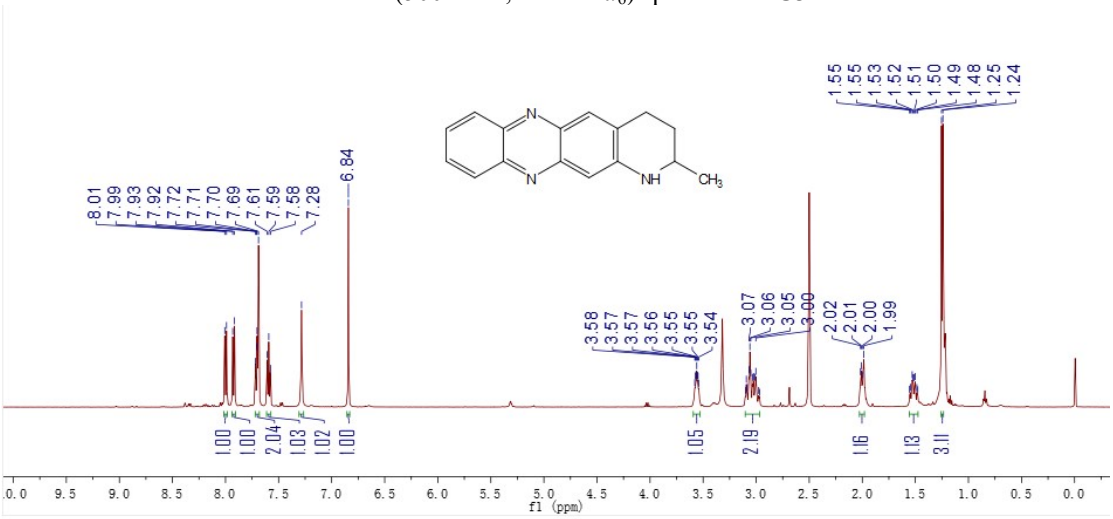
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **C33**'



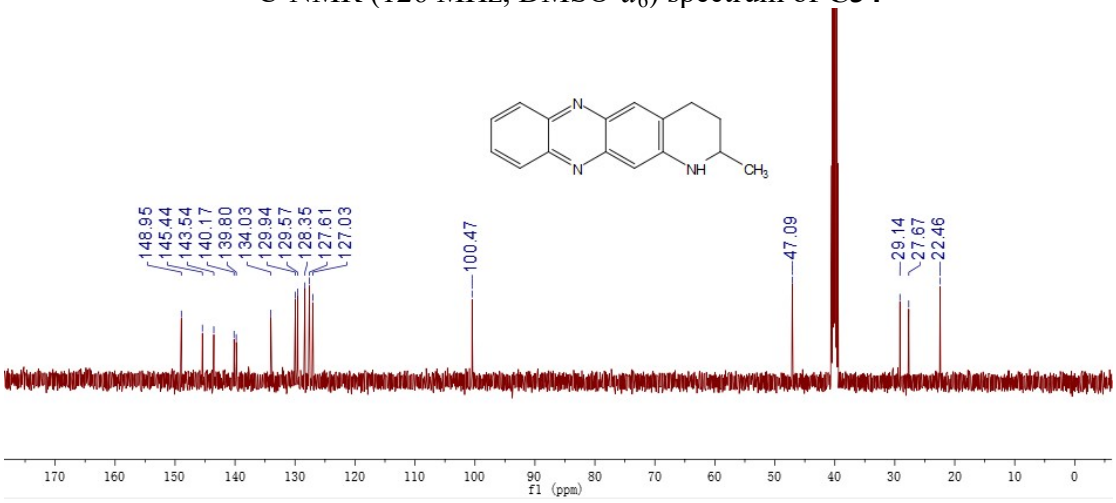
^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **C33**'



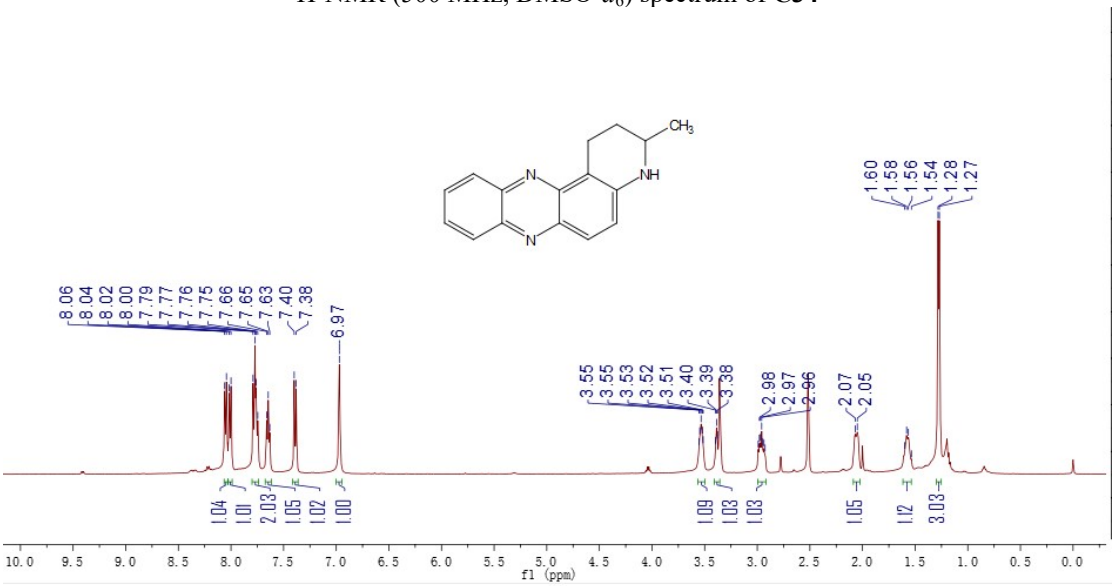
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C34**



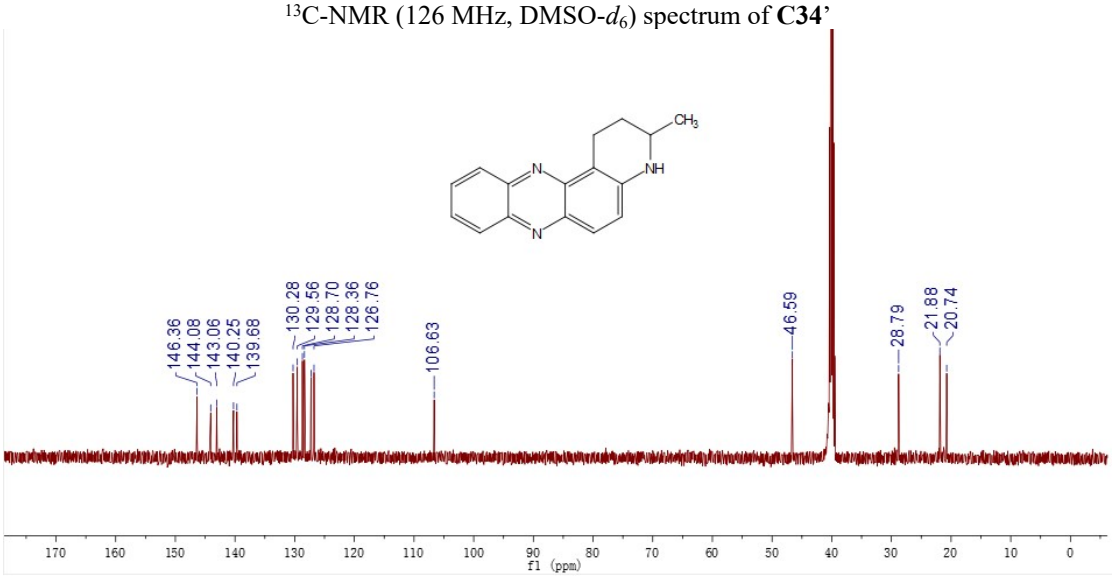
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C34**



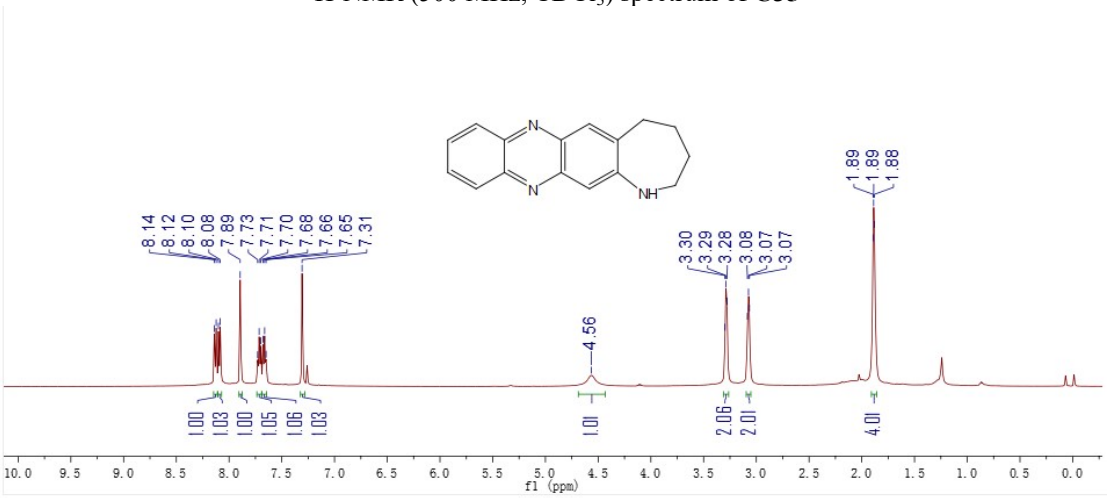
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C34**'



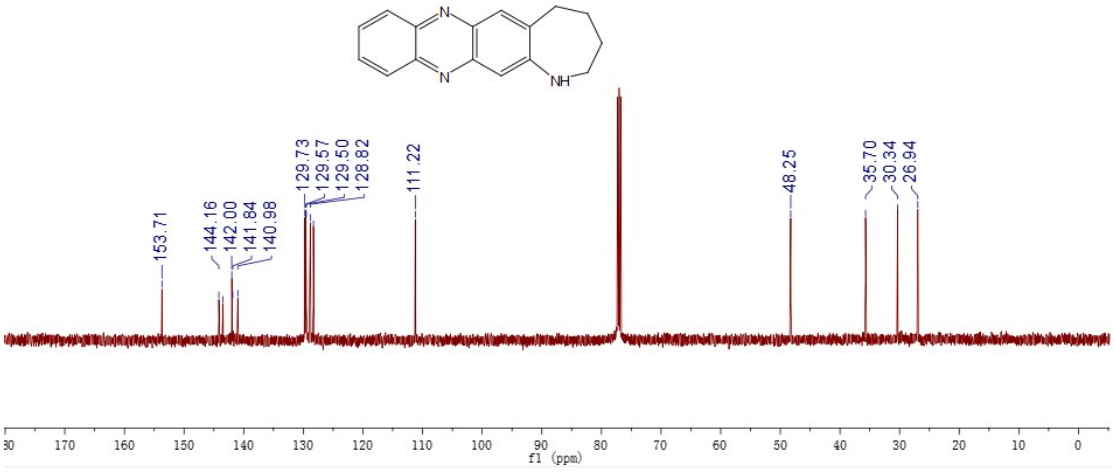
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C34**'



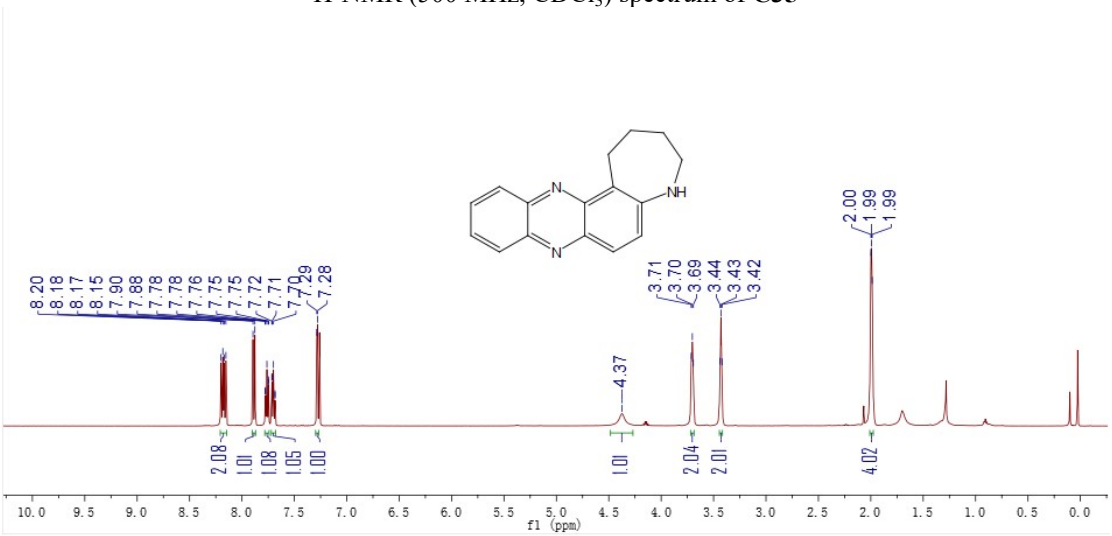
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of **C35**



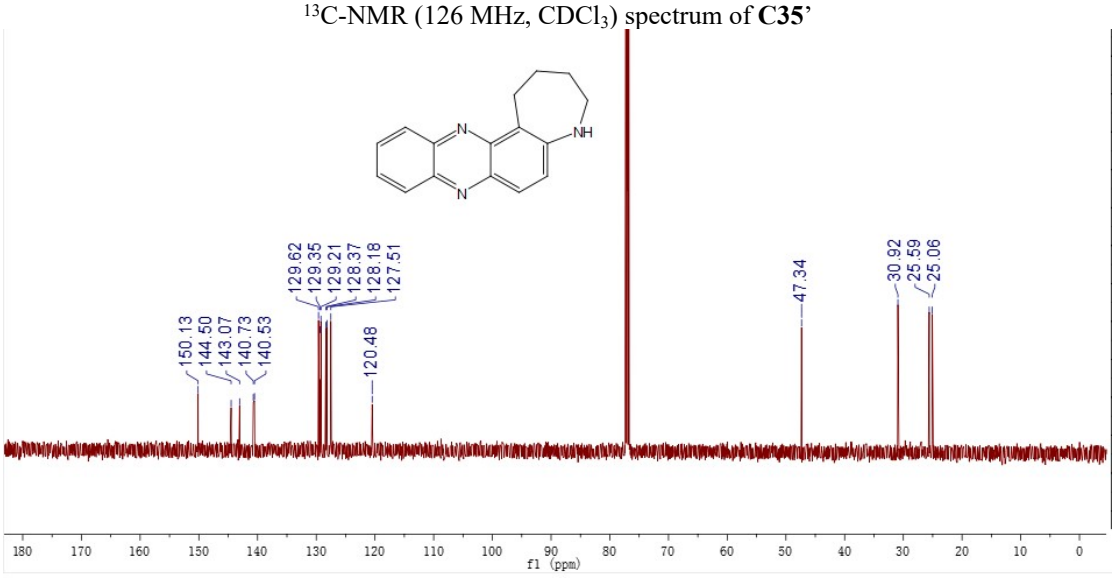
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of **C35**



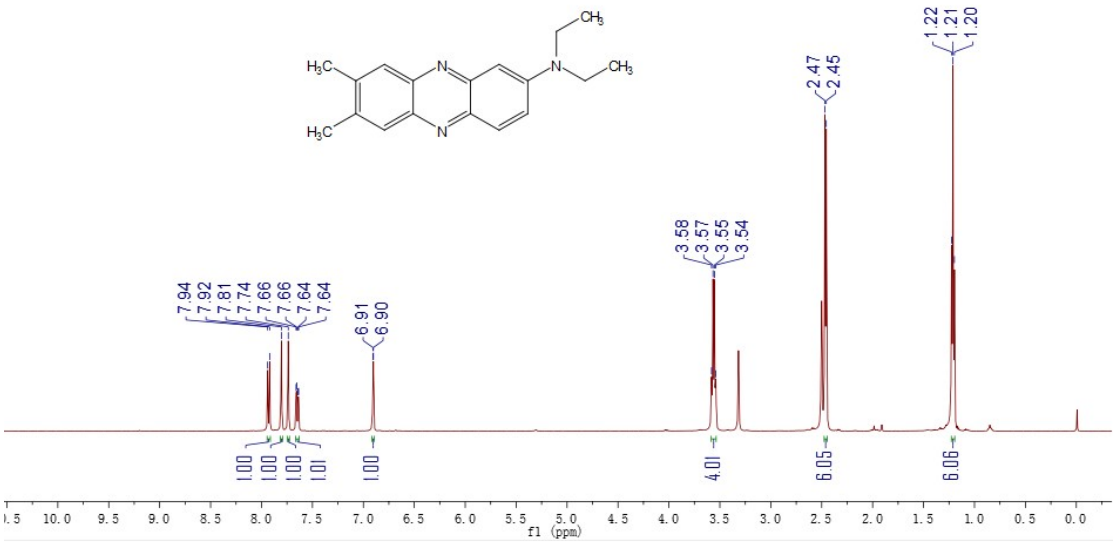
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of **C35'**



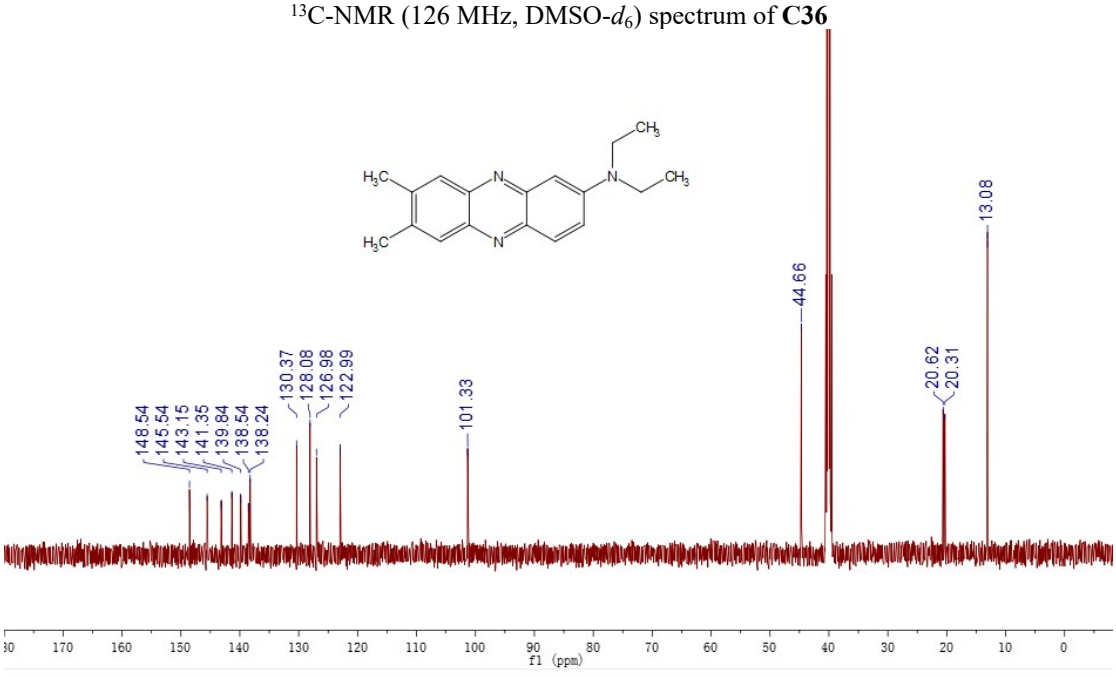
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of **C35'**



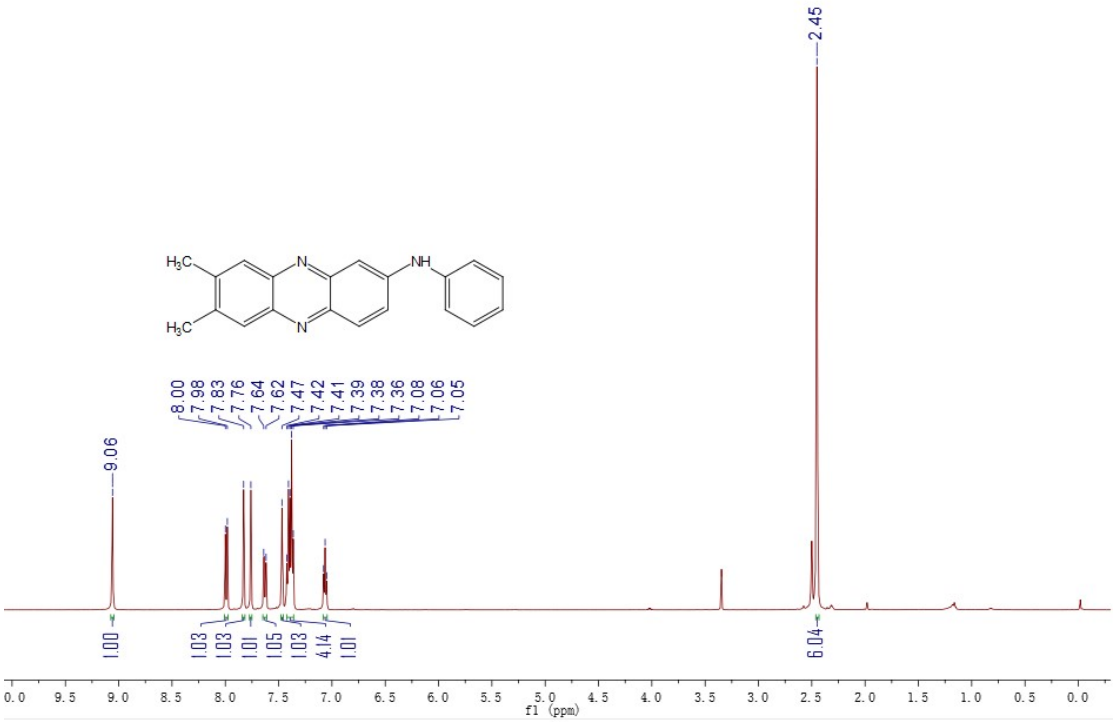
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C36**



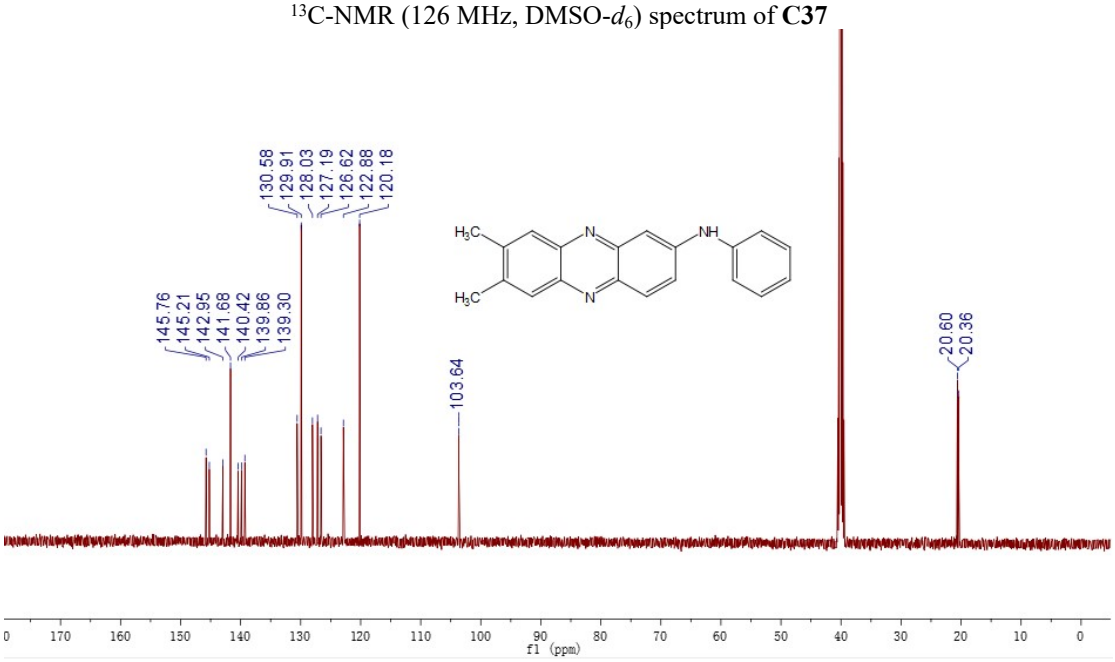
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C36**



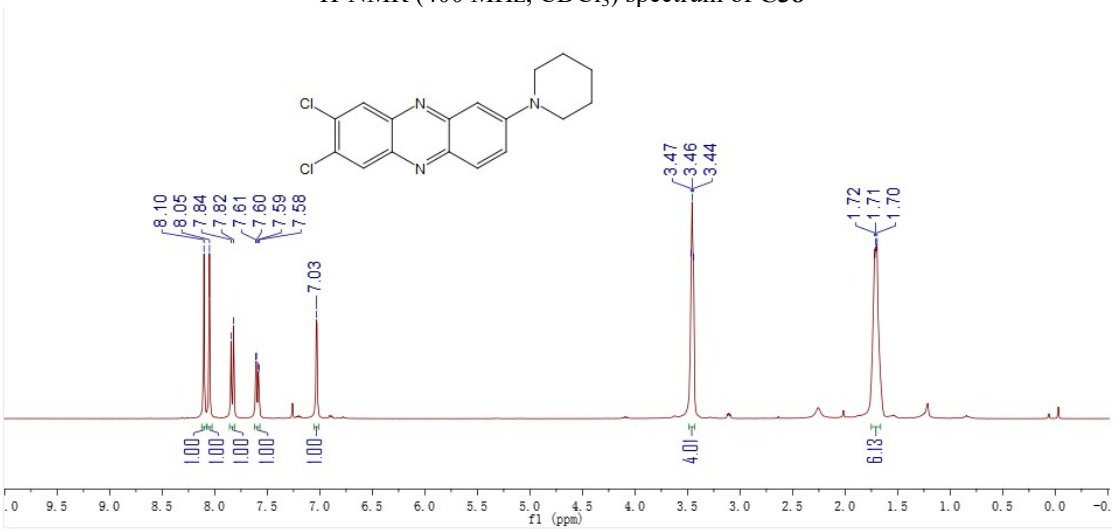
[1]H-NMR (500 MHz, DMSO-d_6) spectrum of **C37**



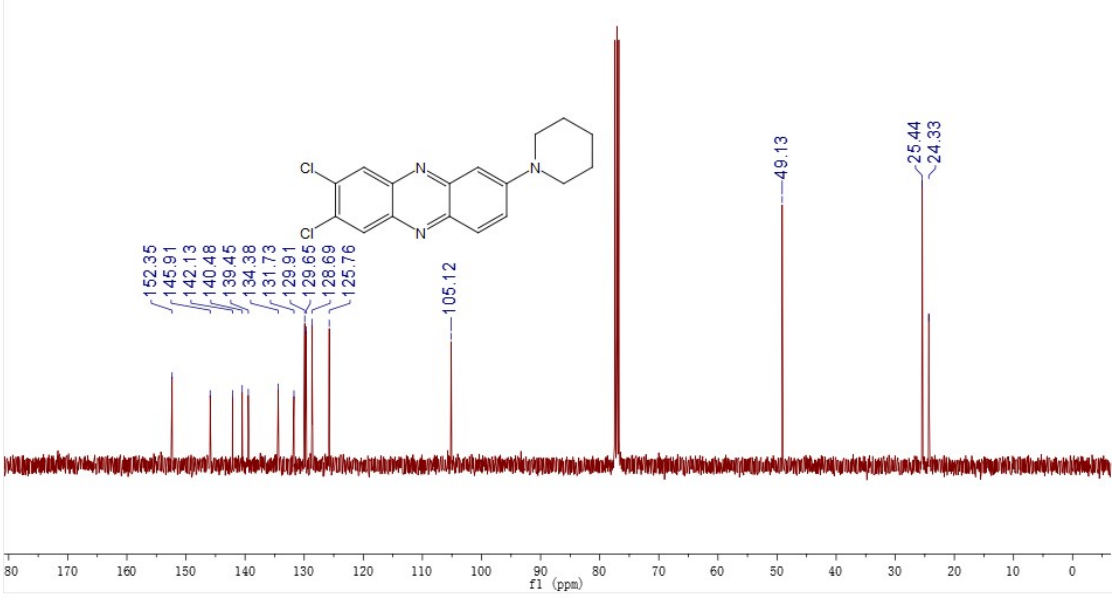
[13]C-NMR (126 MHz, DMSO-d_6) spectrum of **C37**



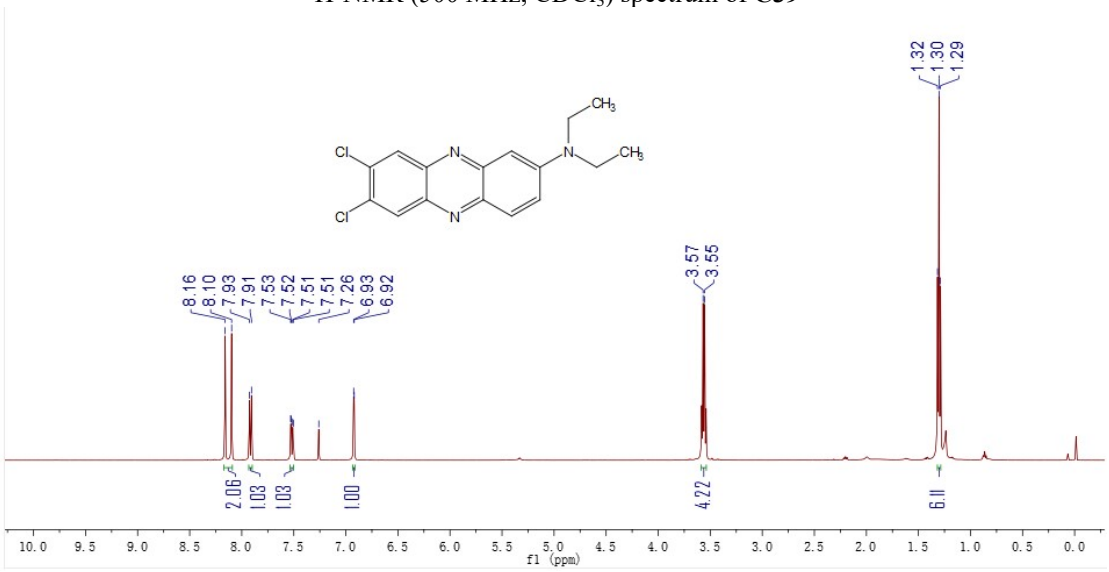
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **C38**



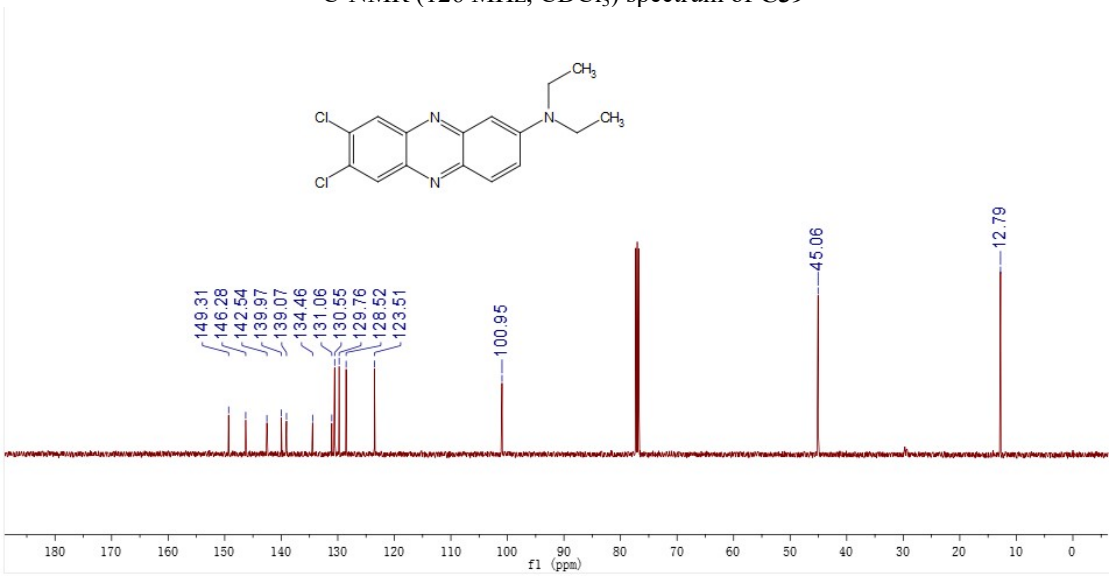
^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **C38**



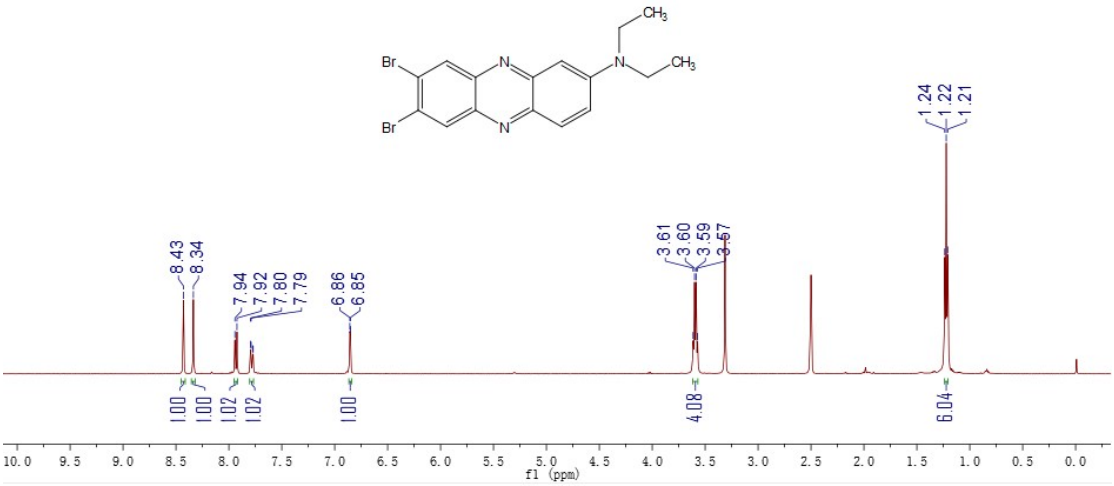
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of **C39**



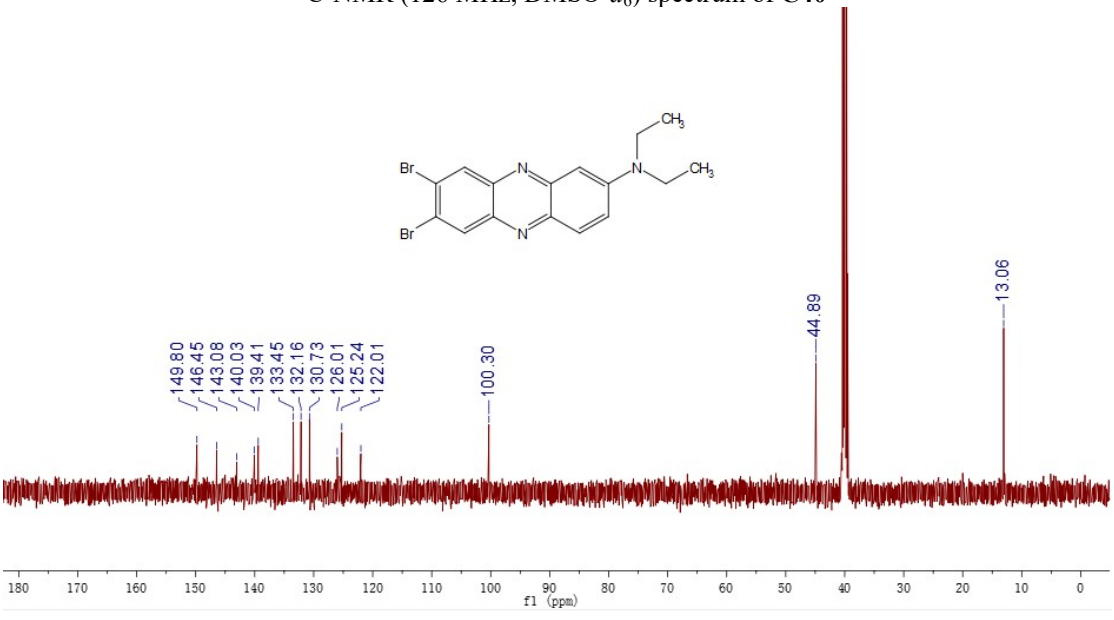
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of **C39**



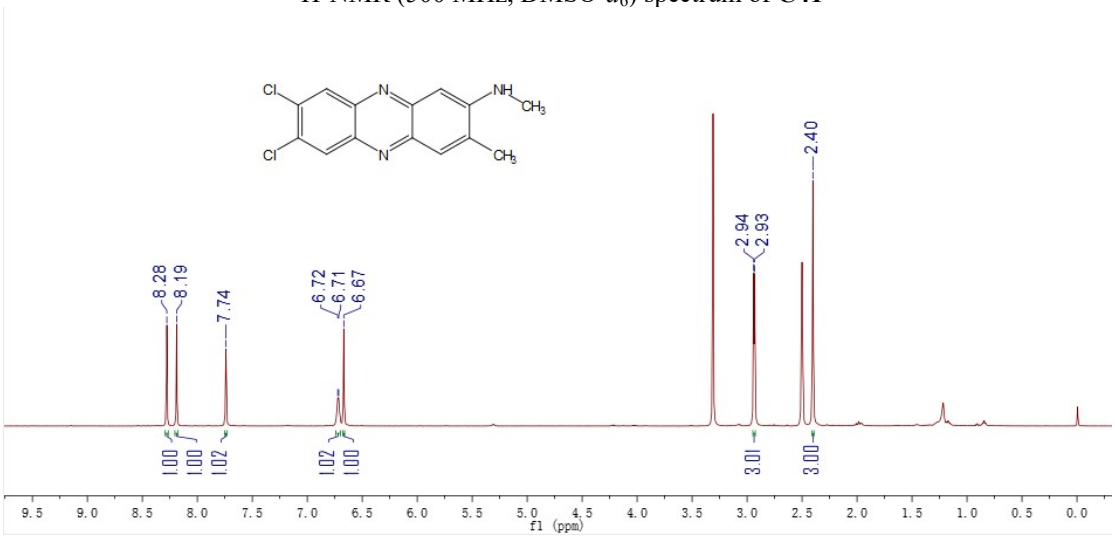
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C40**



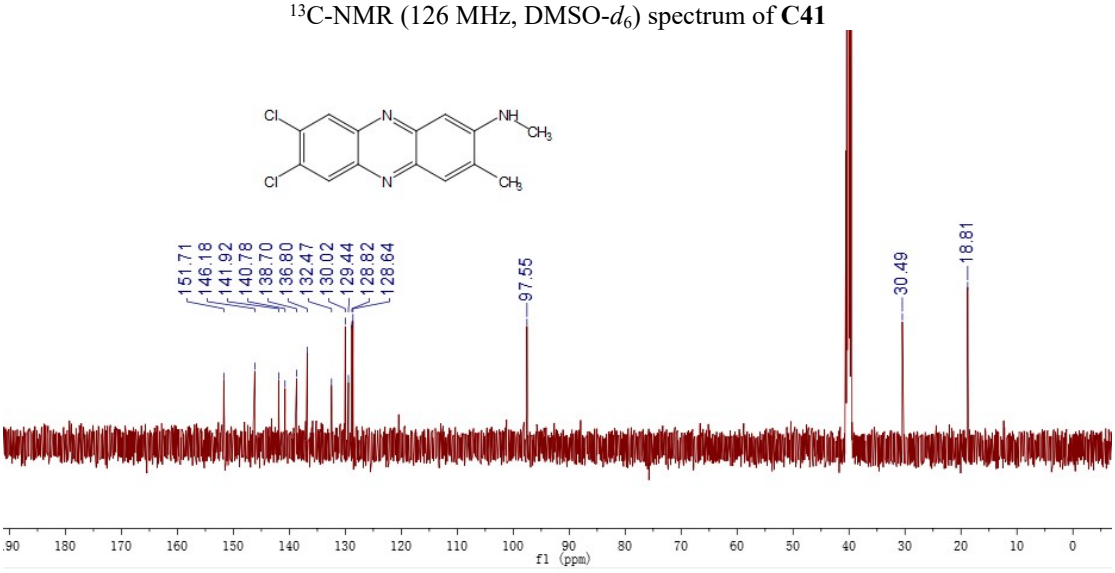
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C40**



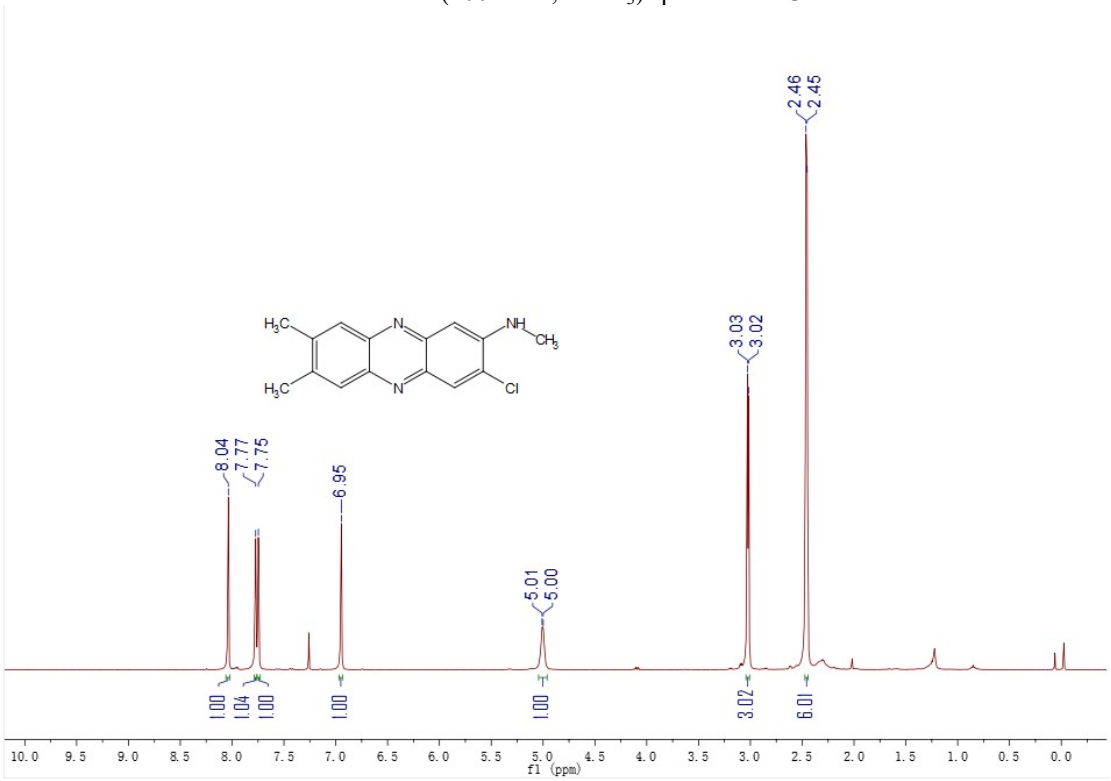
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C41**



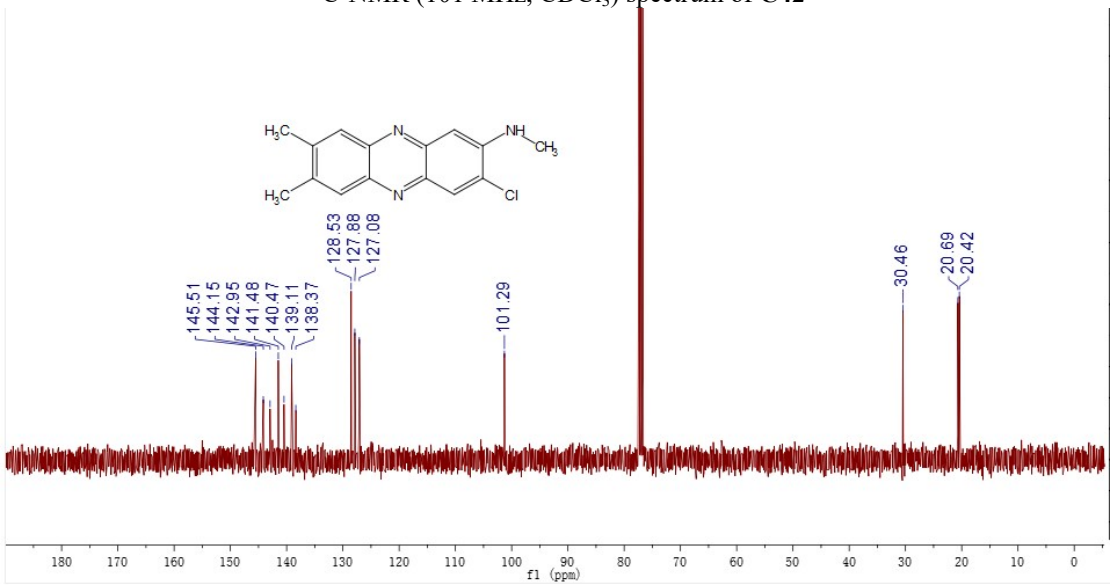
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C41**



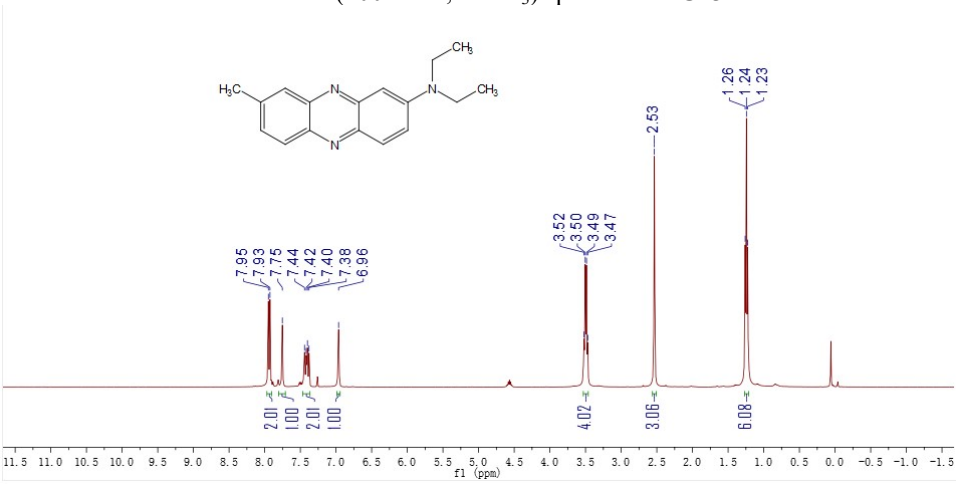
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **C42**



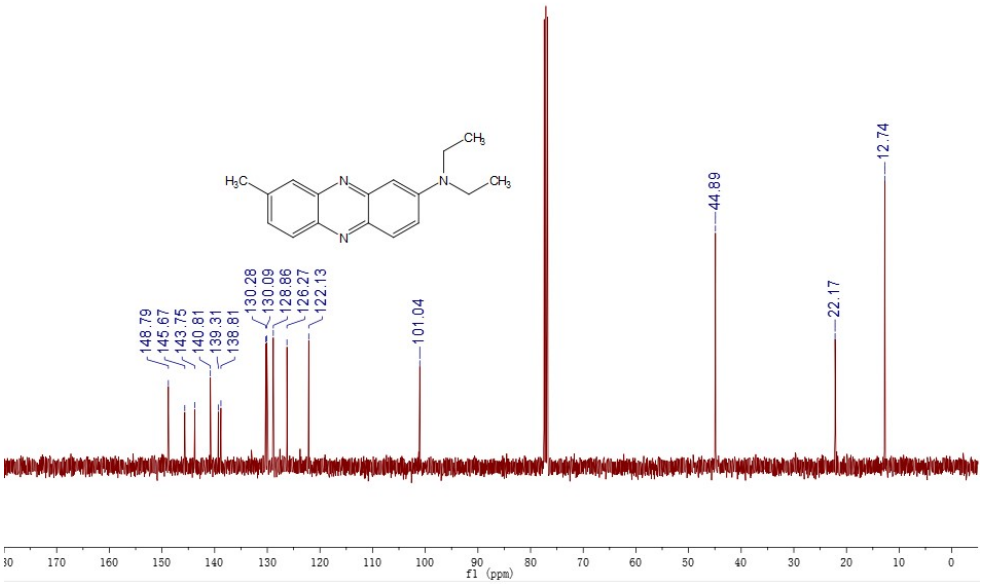
^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **C42**



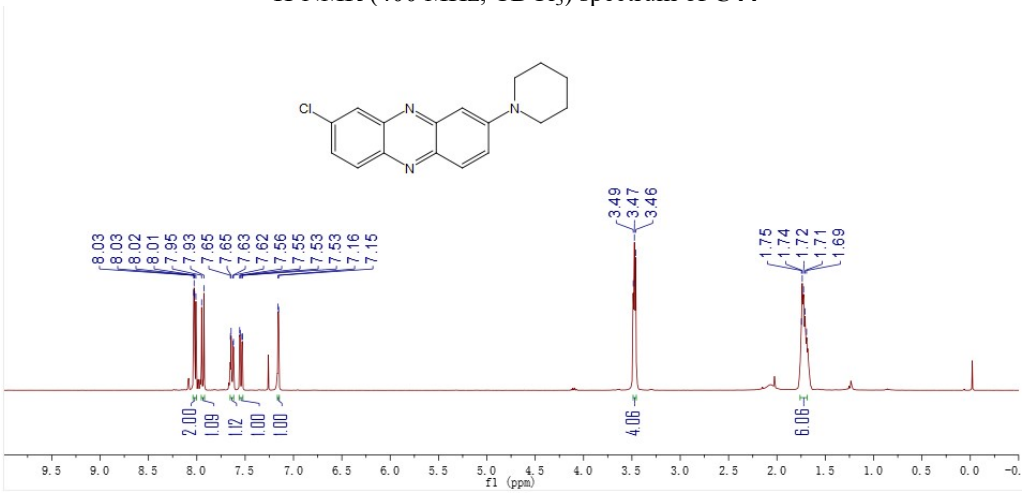
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **C43**



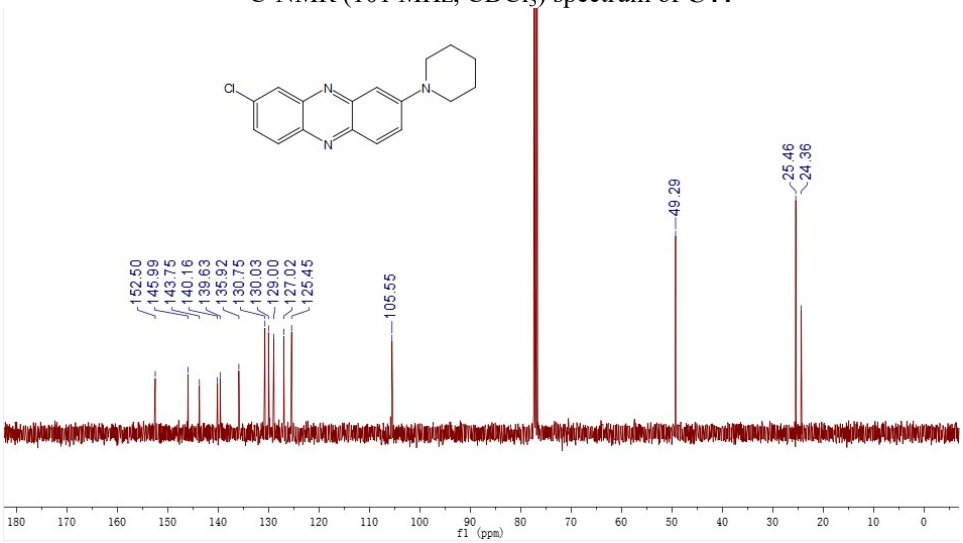
^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **C43**



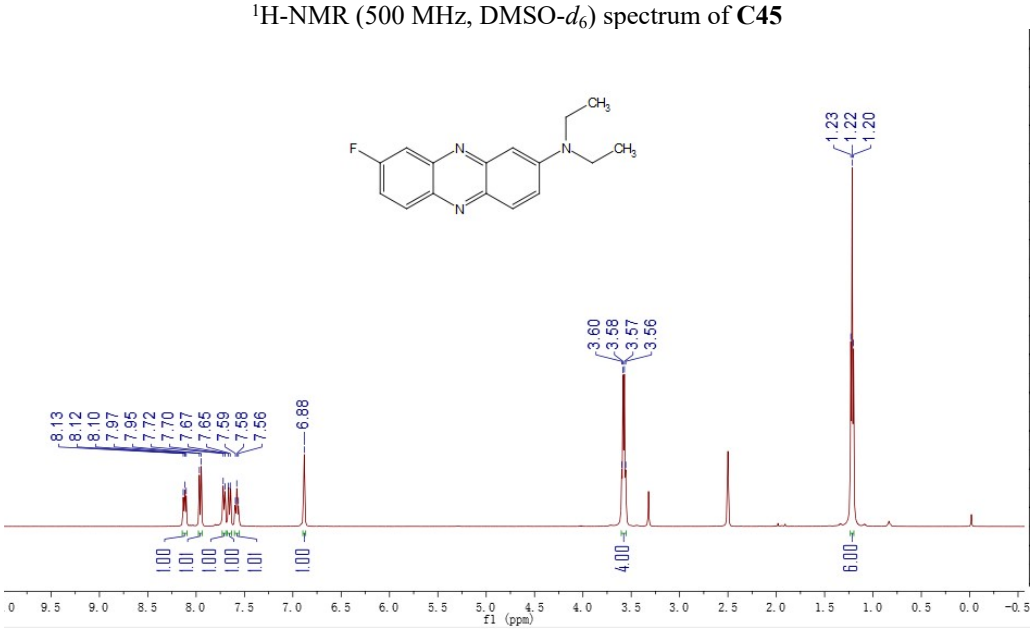
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **C44**



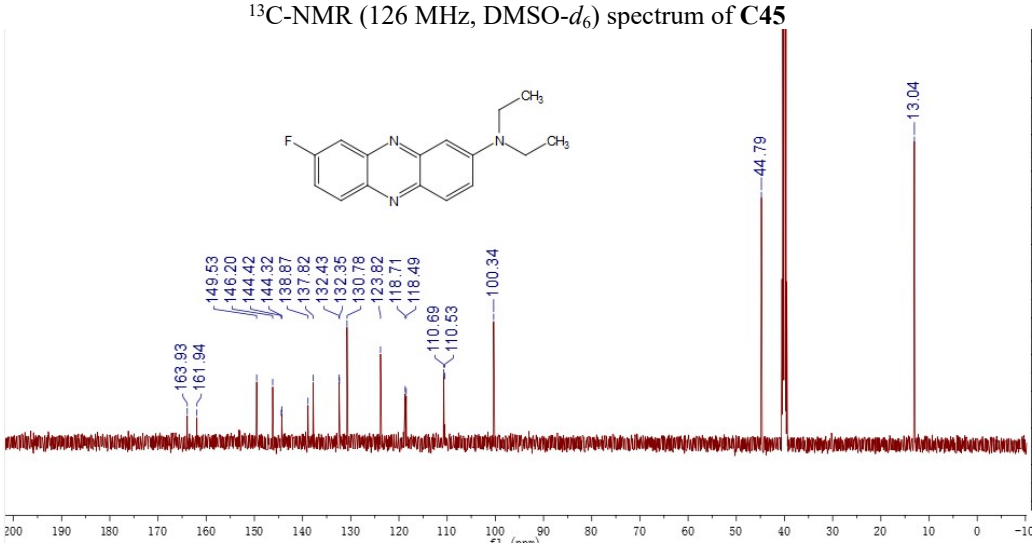
^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **C44**



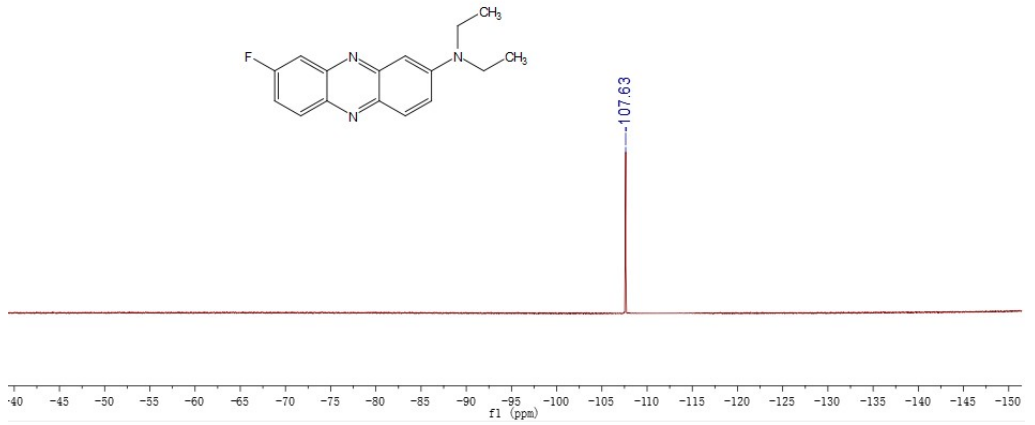
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C45**



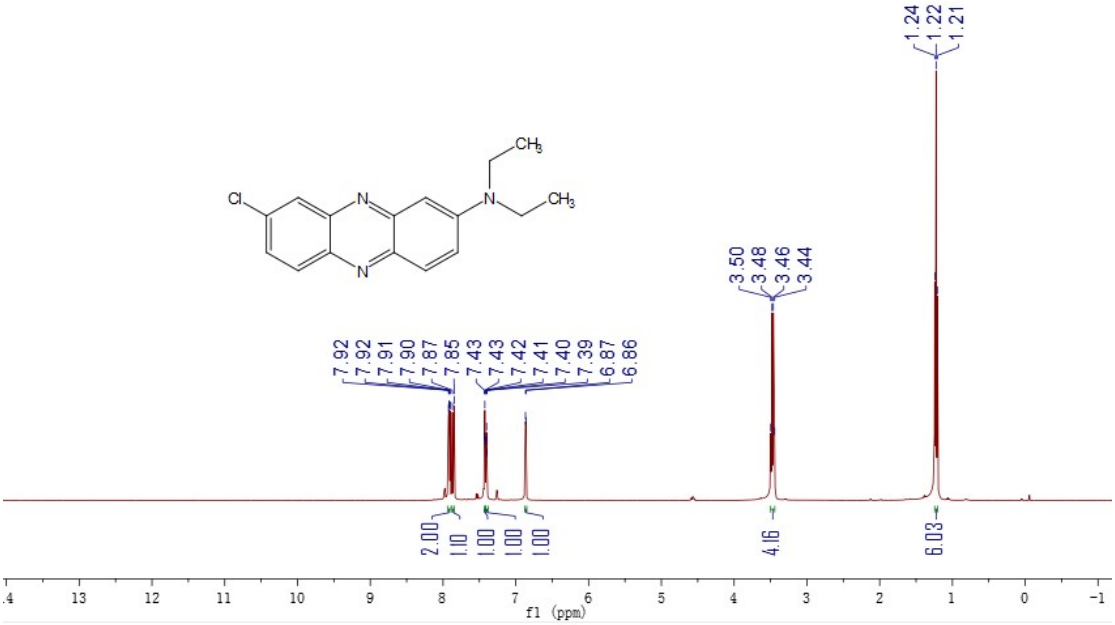
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C45**



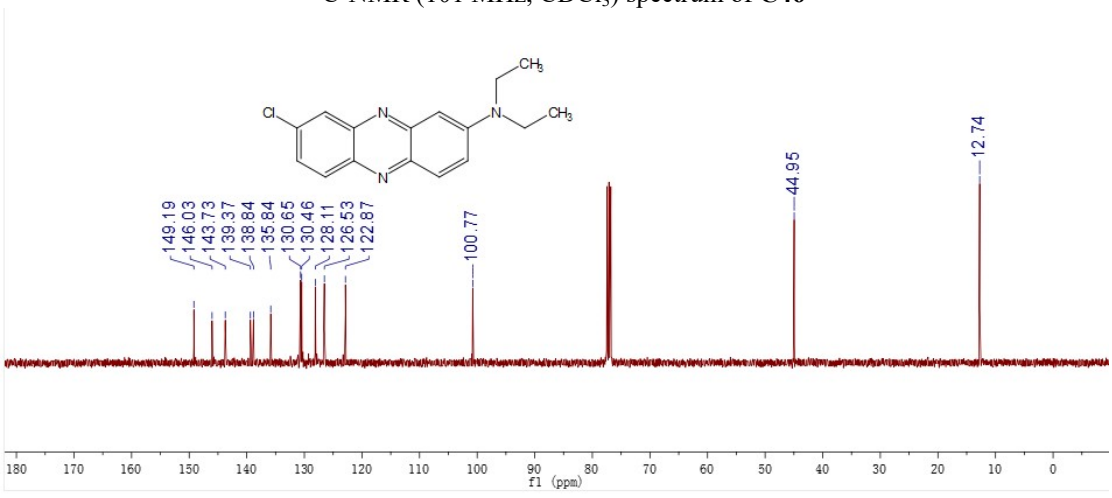
^{19}F-NMR (471 MHz, $CDCl_3$) spectrum of **C45**



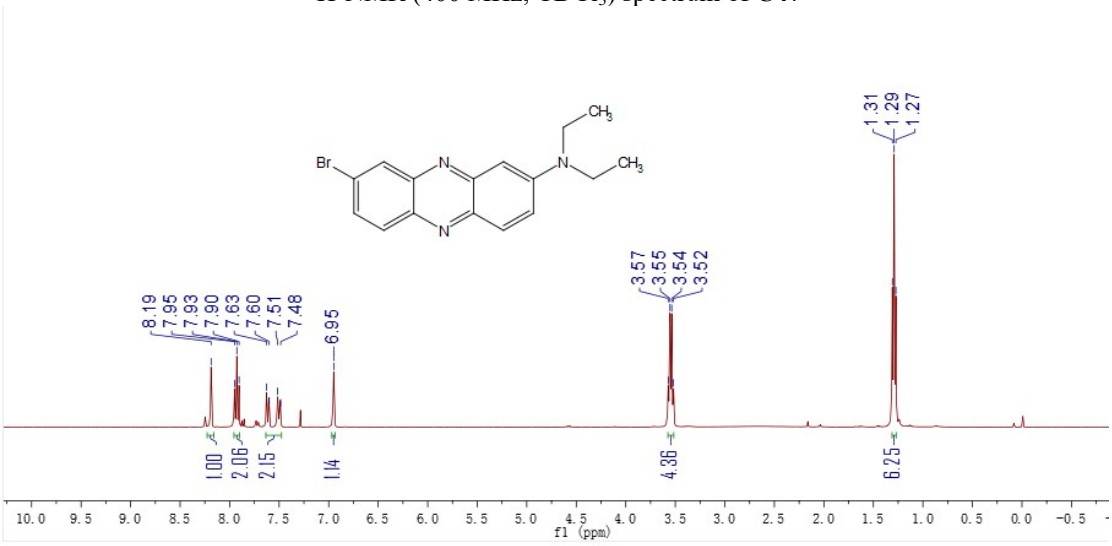
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **C46**



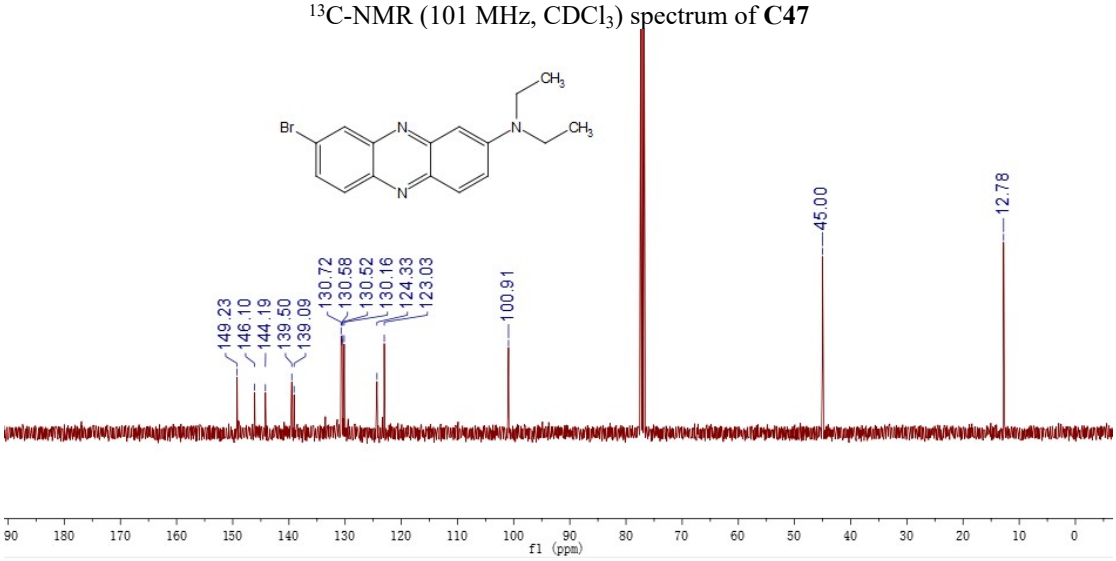
^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **C46**



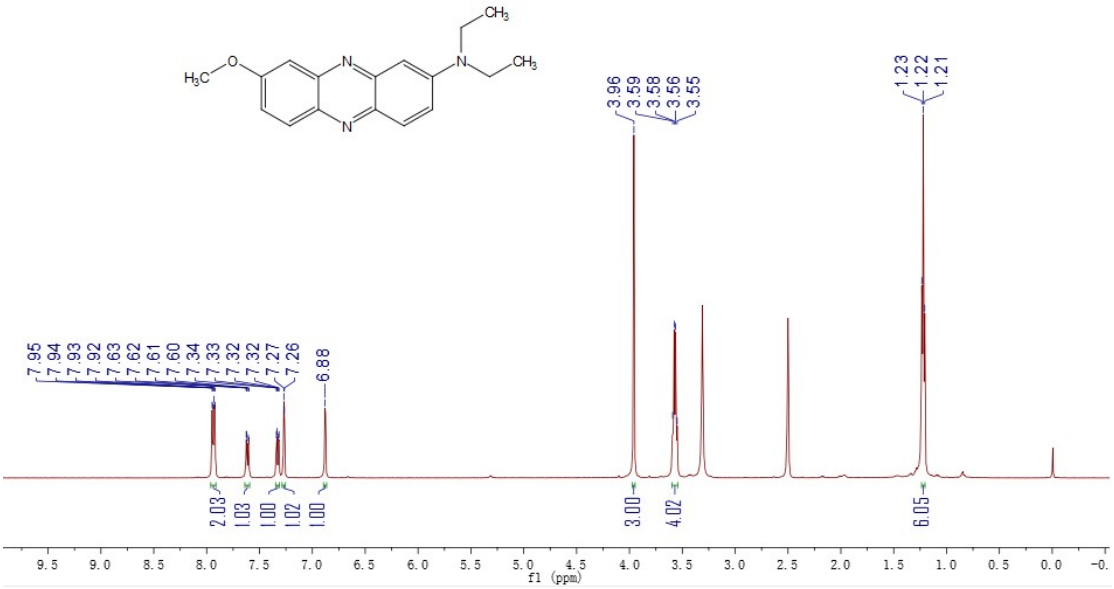
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **C47**



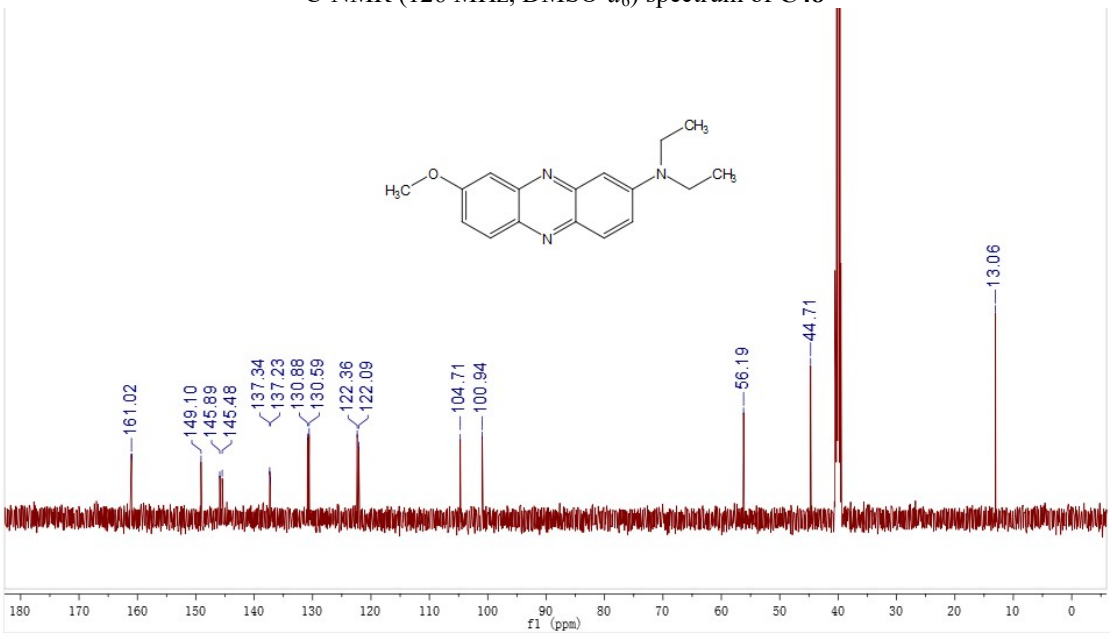
^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **C47**



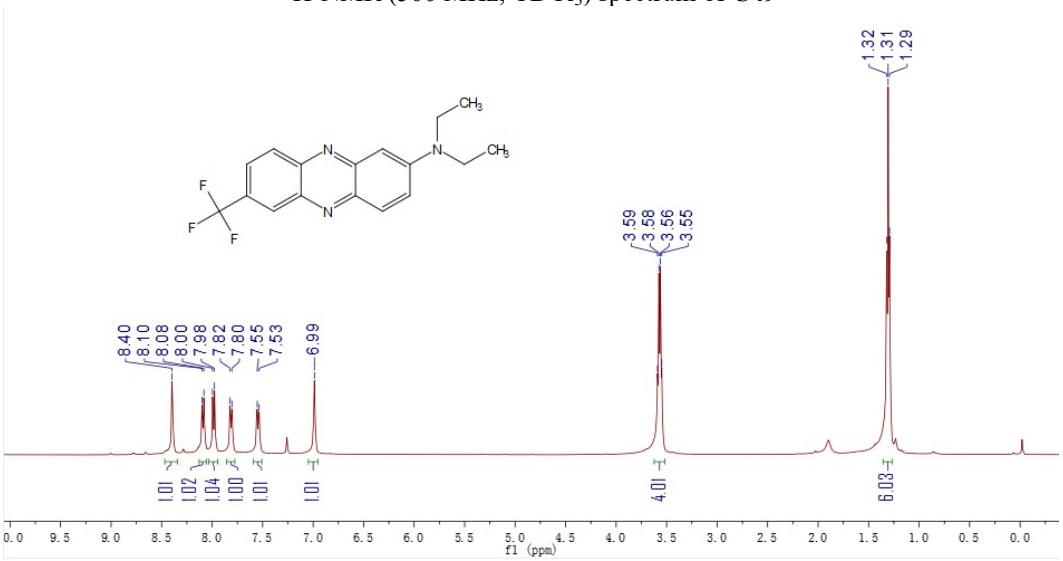
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C48**



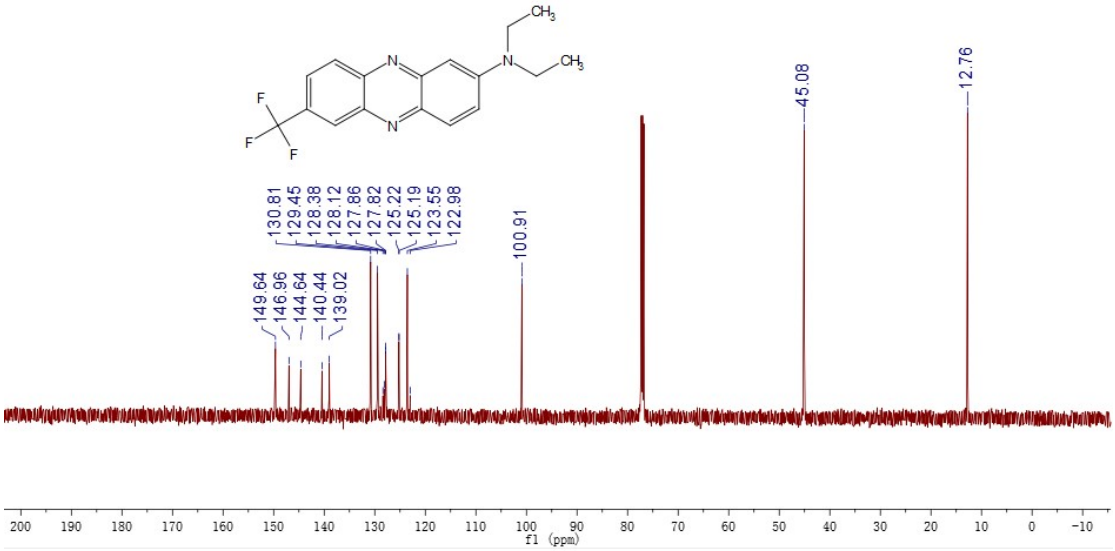
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C48**



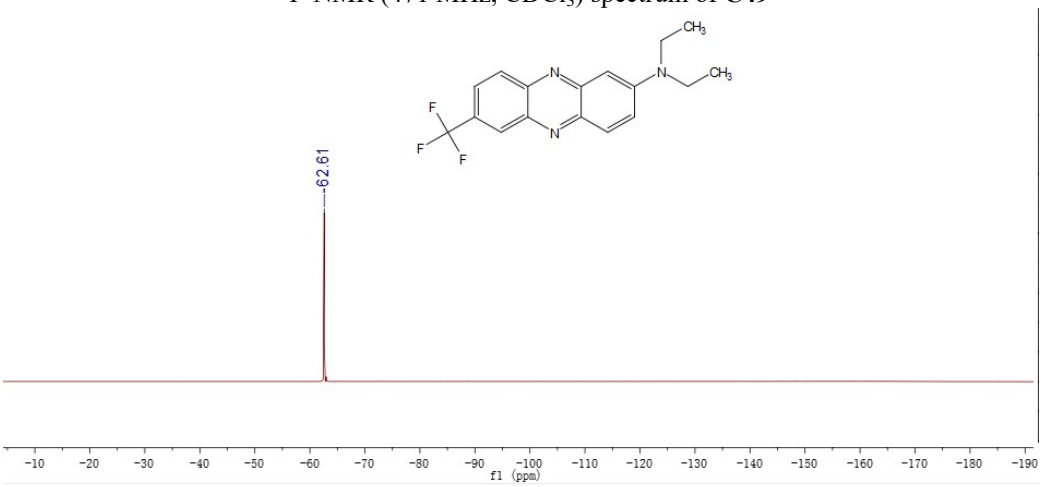
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of **C49**



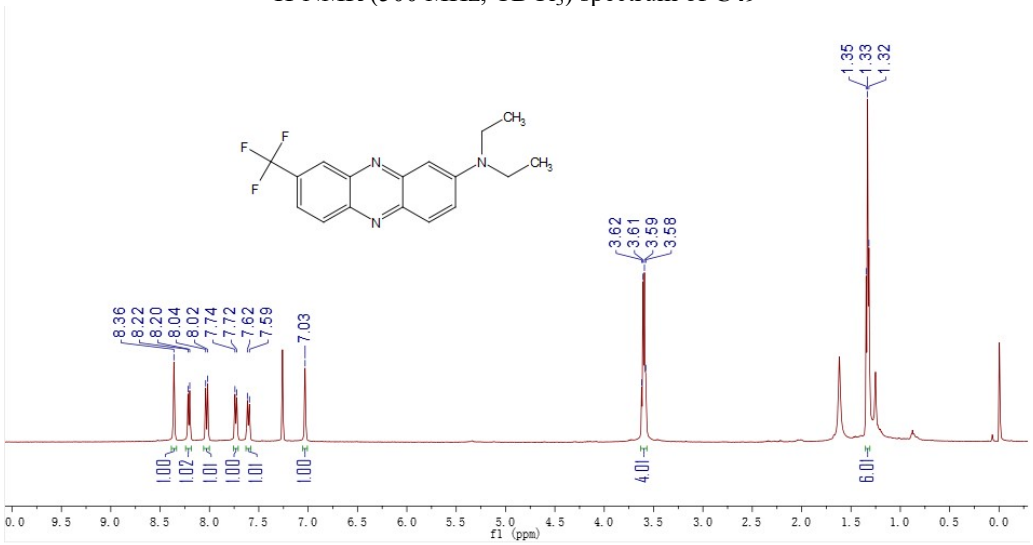
^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **C49**



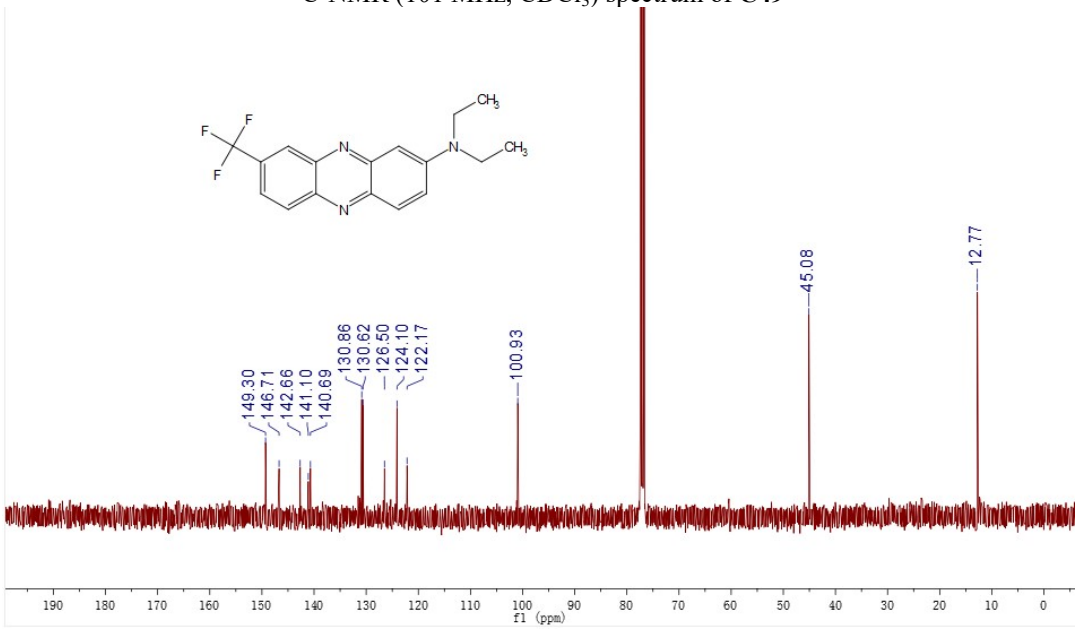
^{19}F-NMR (471 MHz, $CDCl_3$) spectrum of **C49**



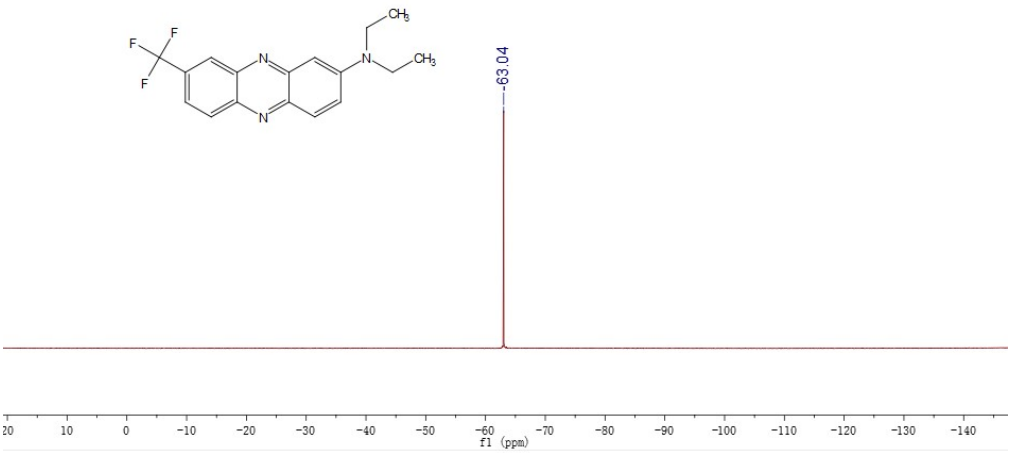
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of **C49'**



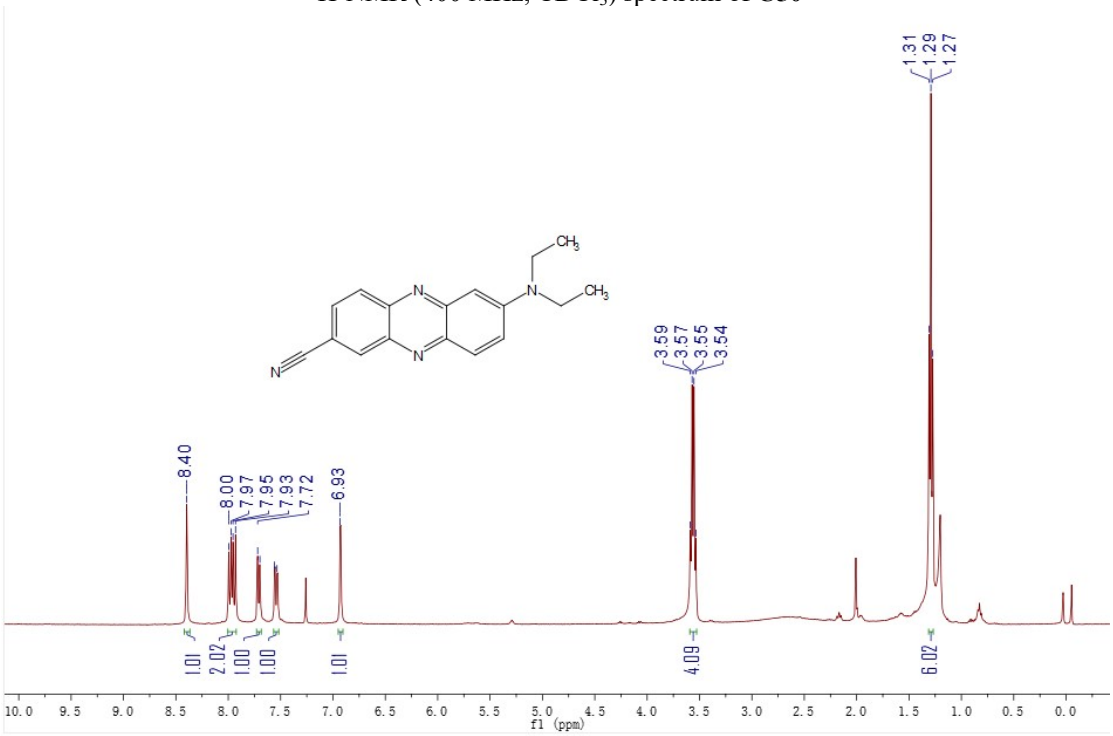
^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **C49'**



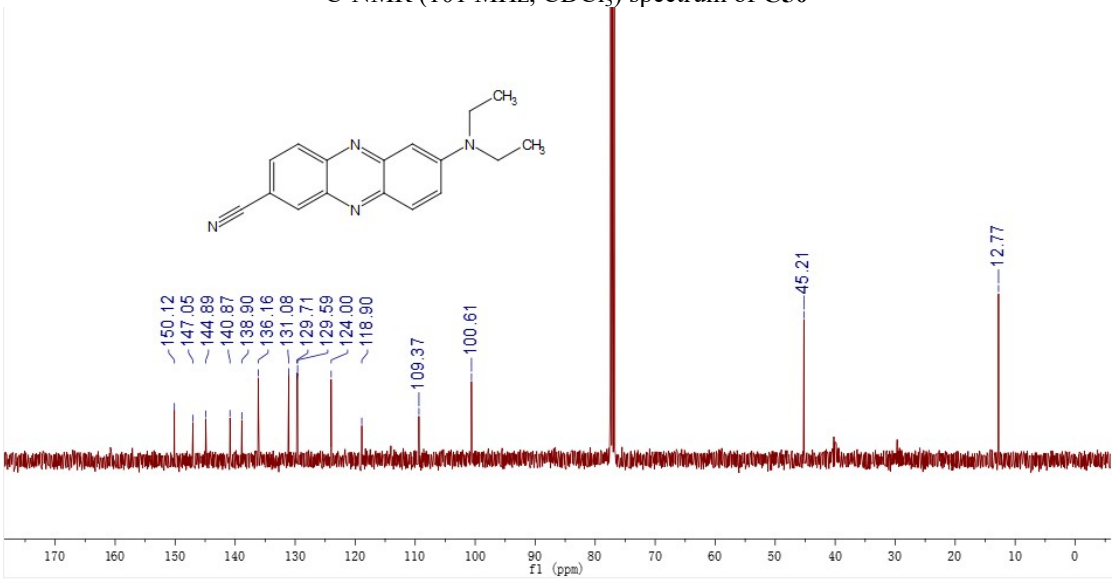
^{19}F-NMR (471 MHz, $CDCl_3$) spectrum of **C49'**



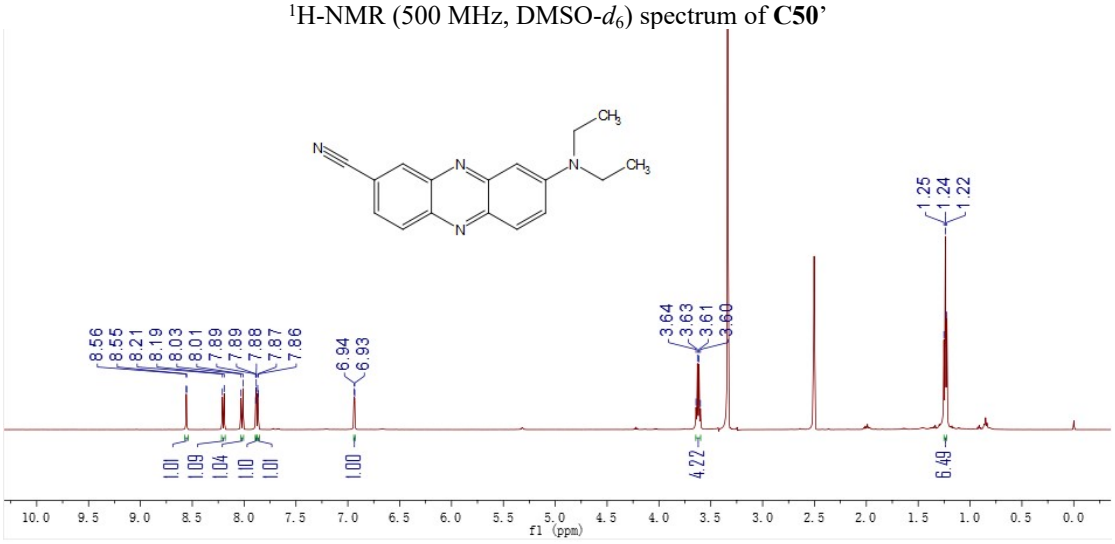
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of **C50**



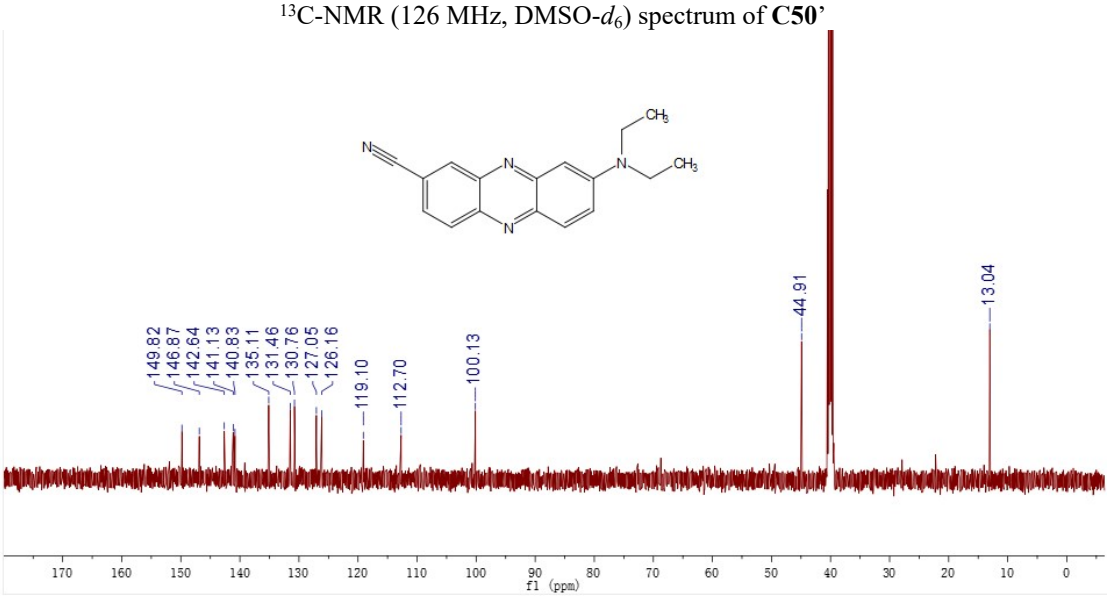
^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of **C50**



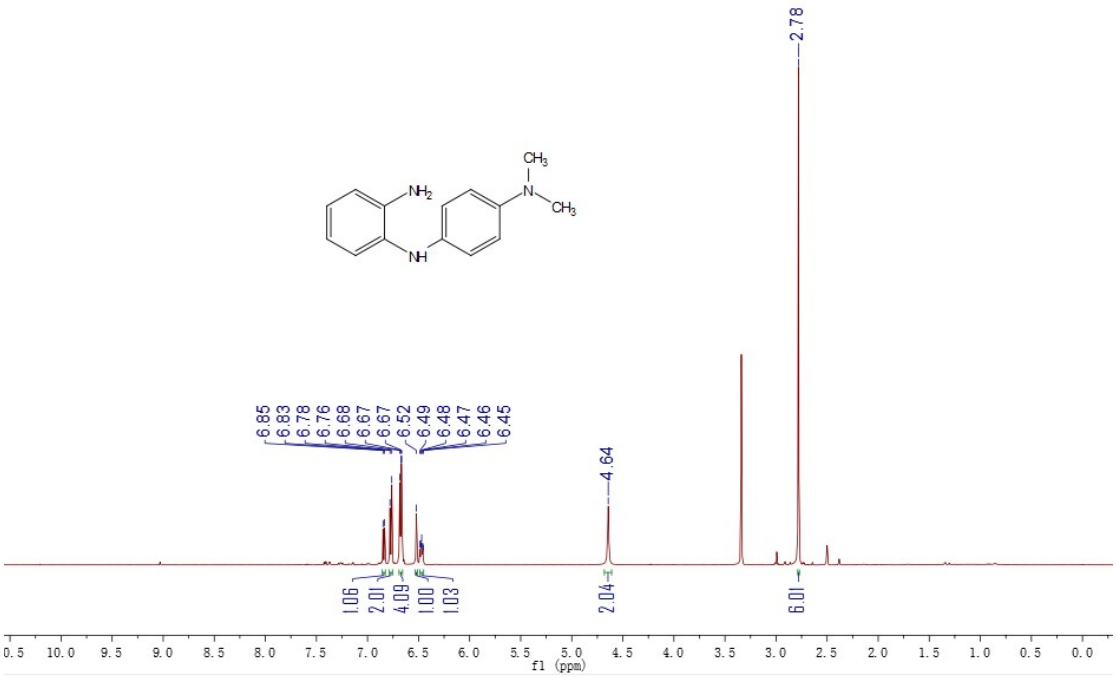
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C50'**



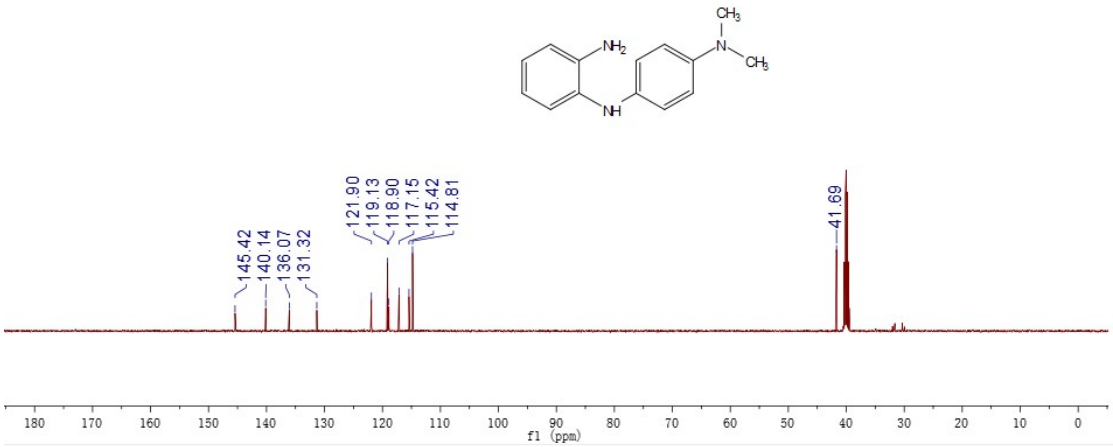
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C50'**



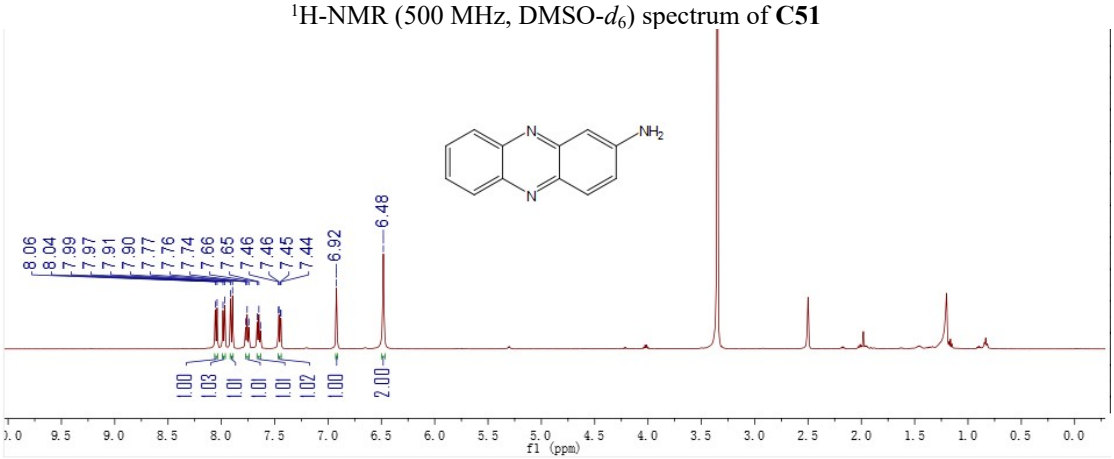
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C13-1**



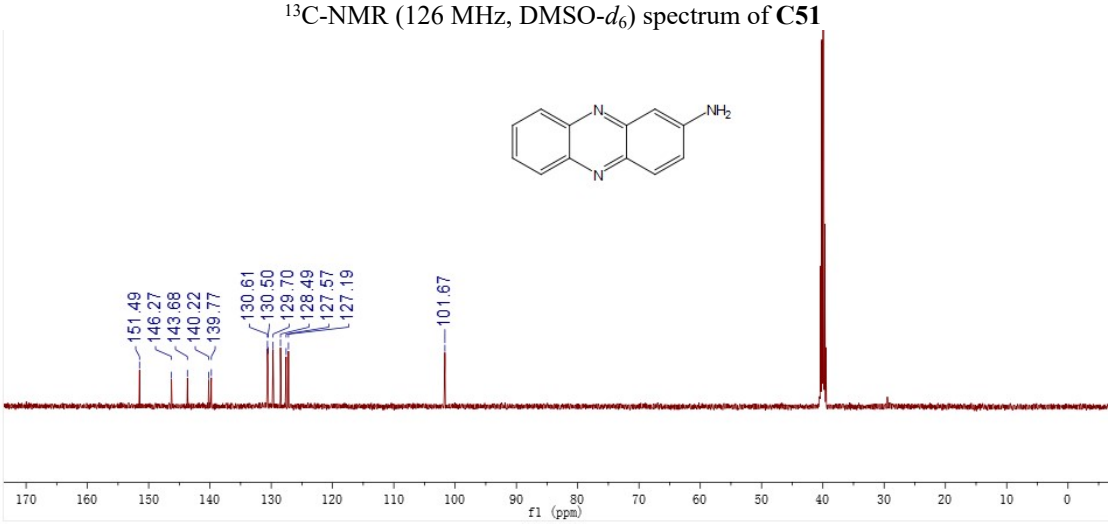
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C13-1**



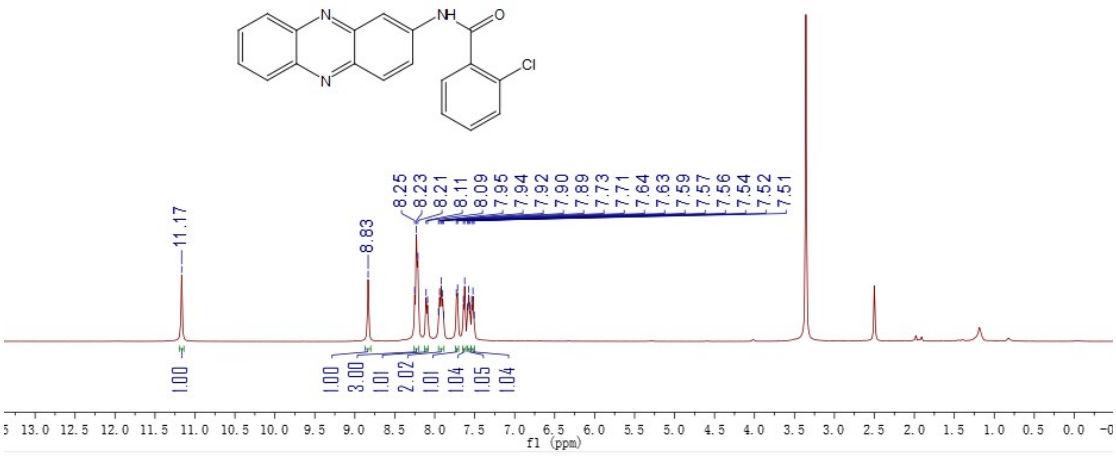
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C51**



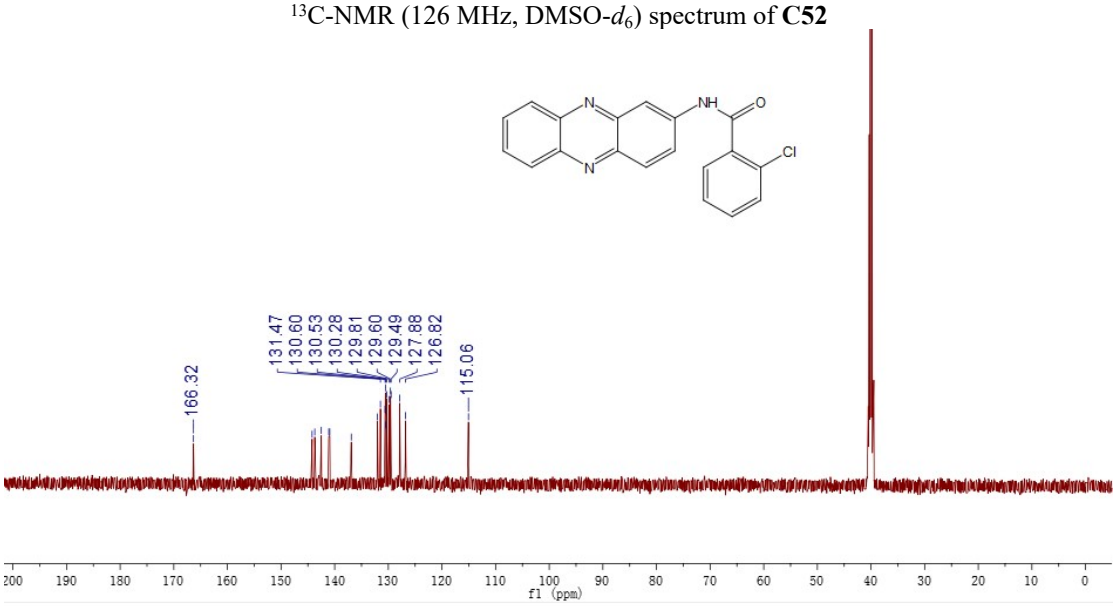
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C51**



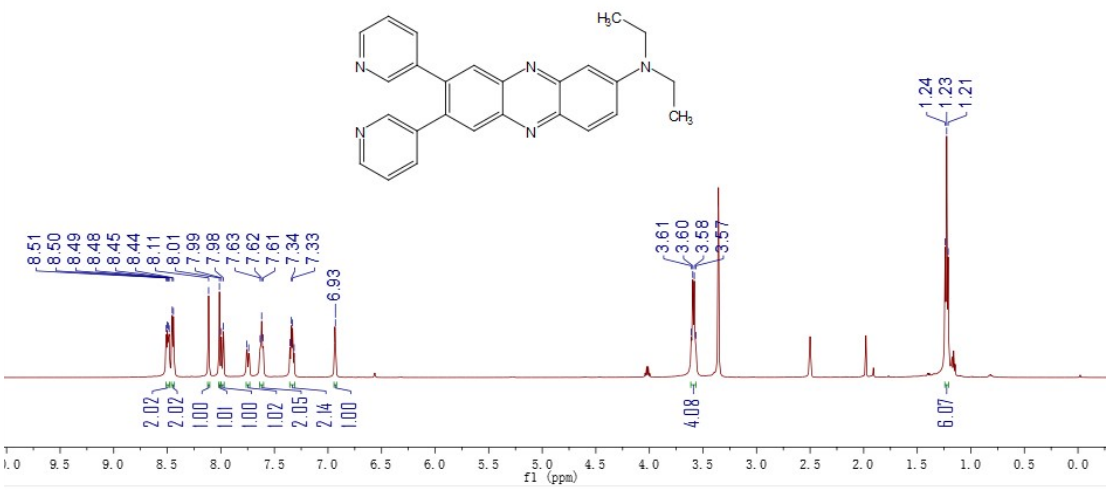
^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C52**



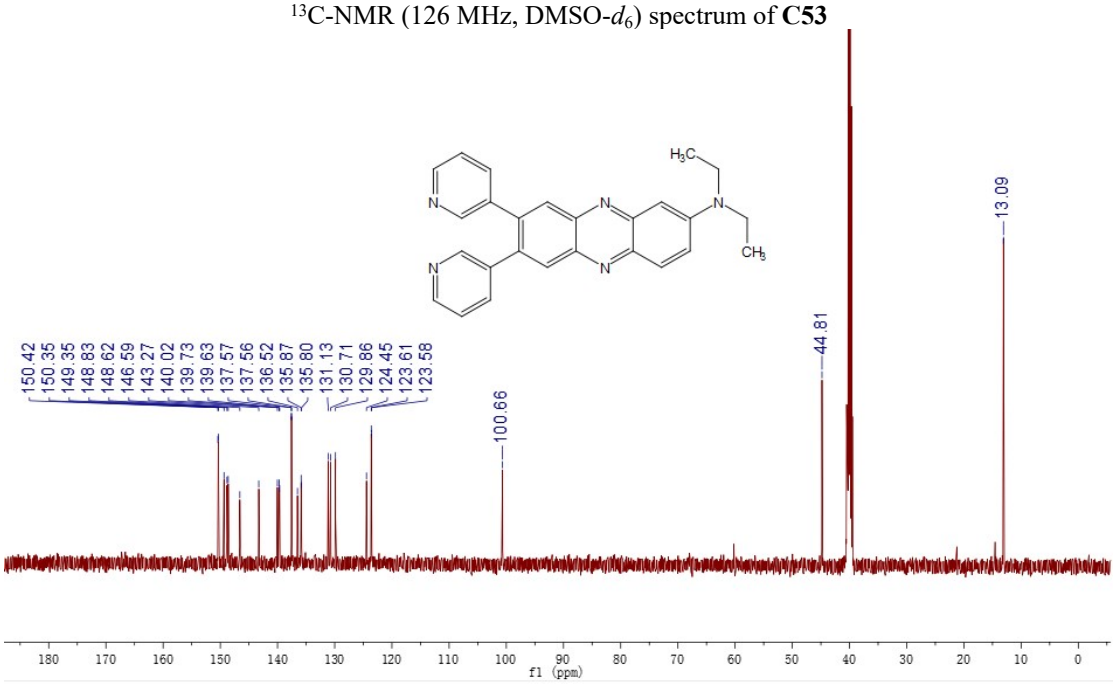
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C52**



^{1}H-NMR (500 MHz, DMSO-d_6) spectrum of **C53**

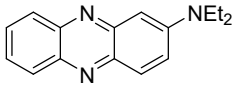


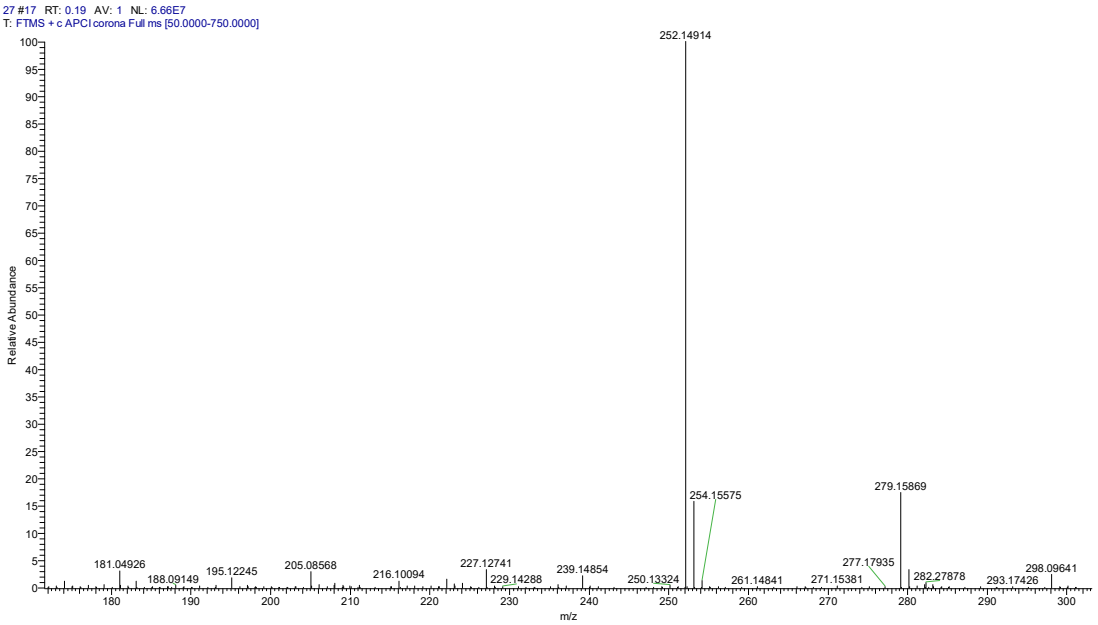
^{13}C-NMR (126 MHz, DMSO-d_6) spectrum of **C53**

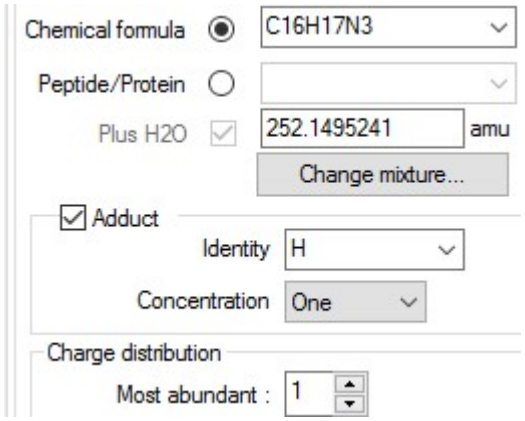


8. HR-MS spectra of the obtained compounds

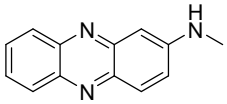
HR-MS spectrum of **C1**

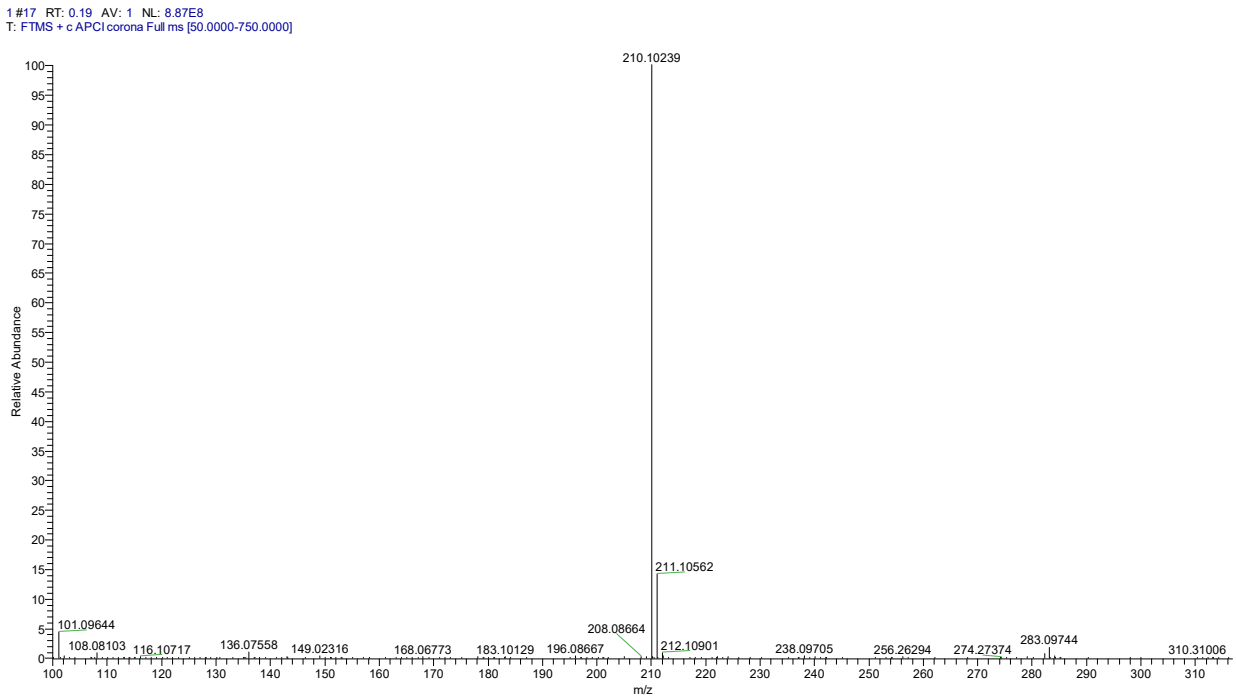


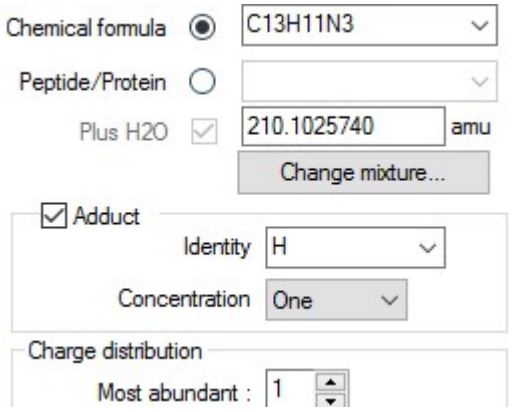




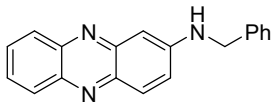
HR-MS spectrum of **C2**

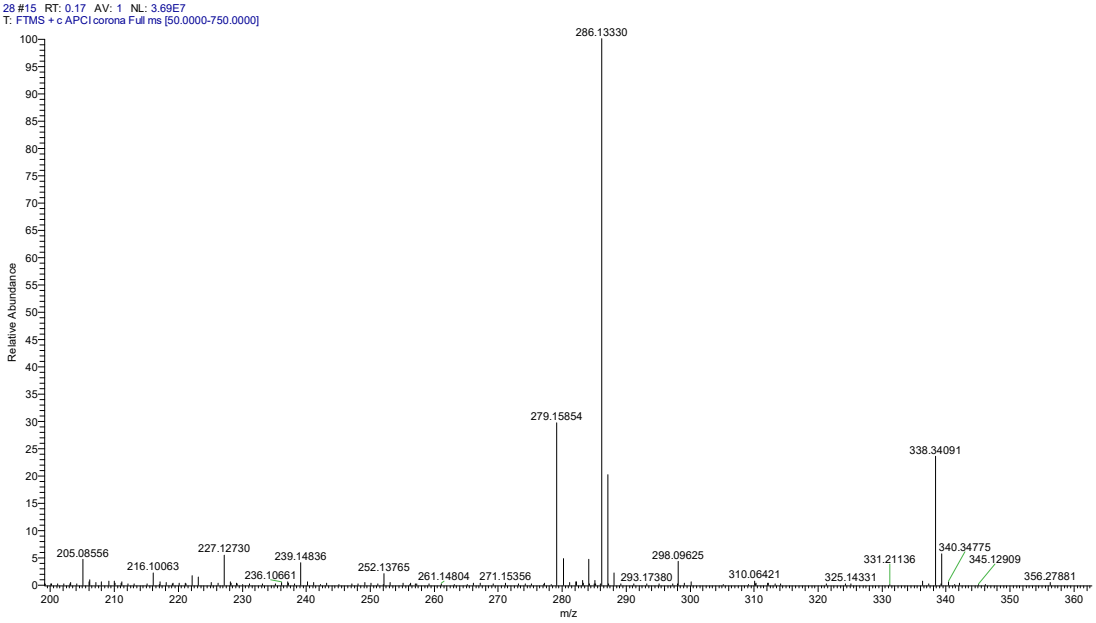


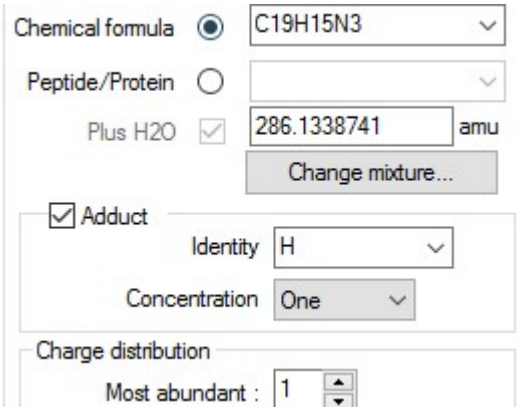




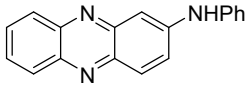
HR-MS spectrum of **C3**

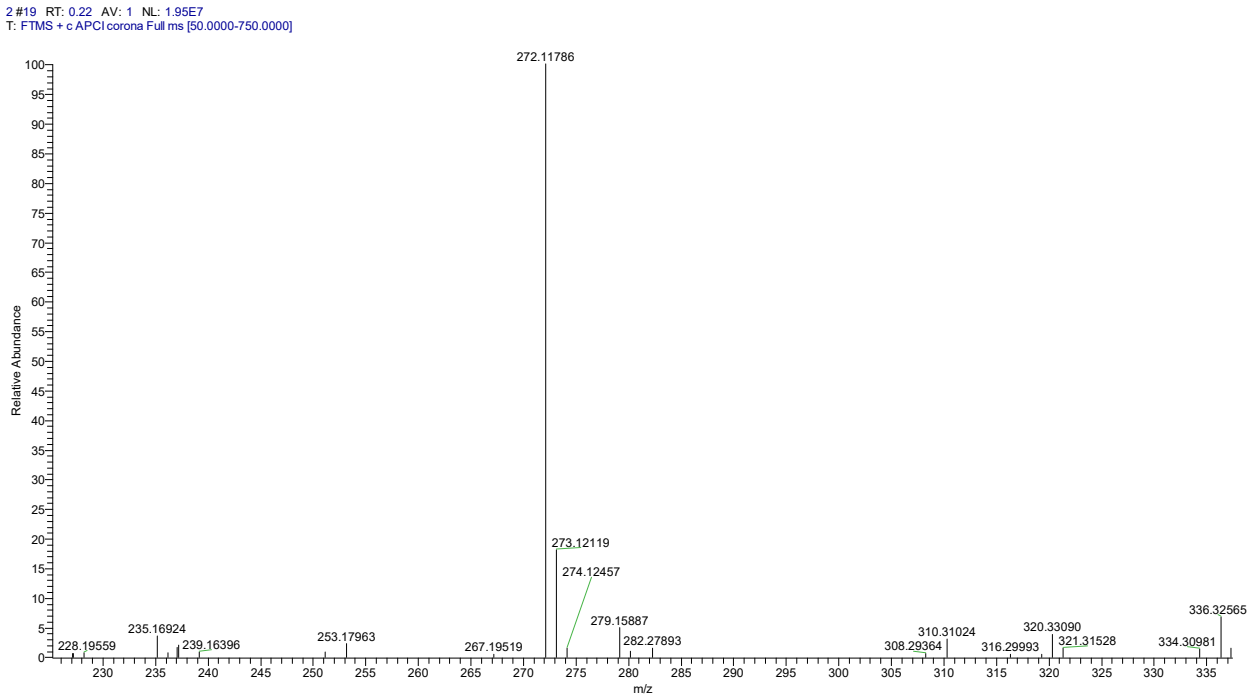


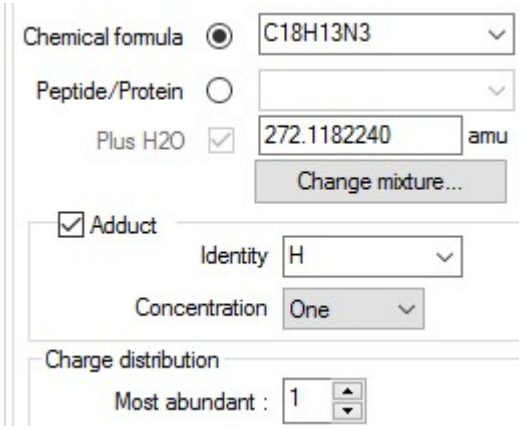




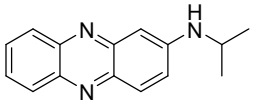
HR-MS spectrum of **C4**

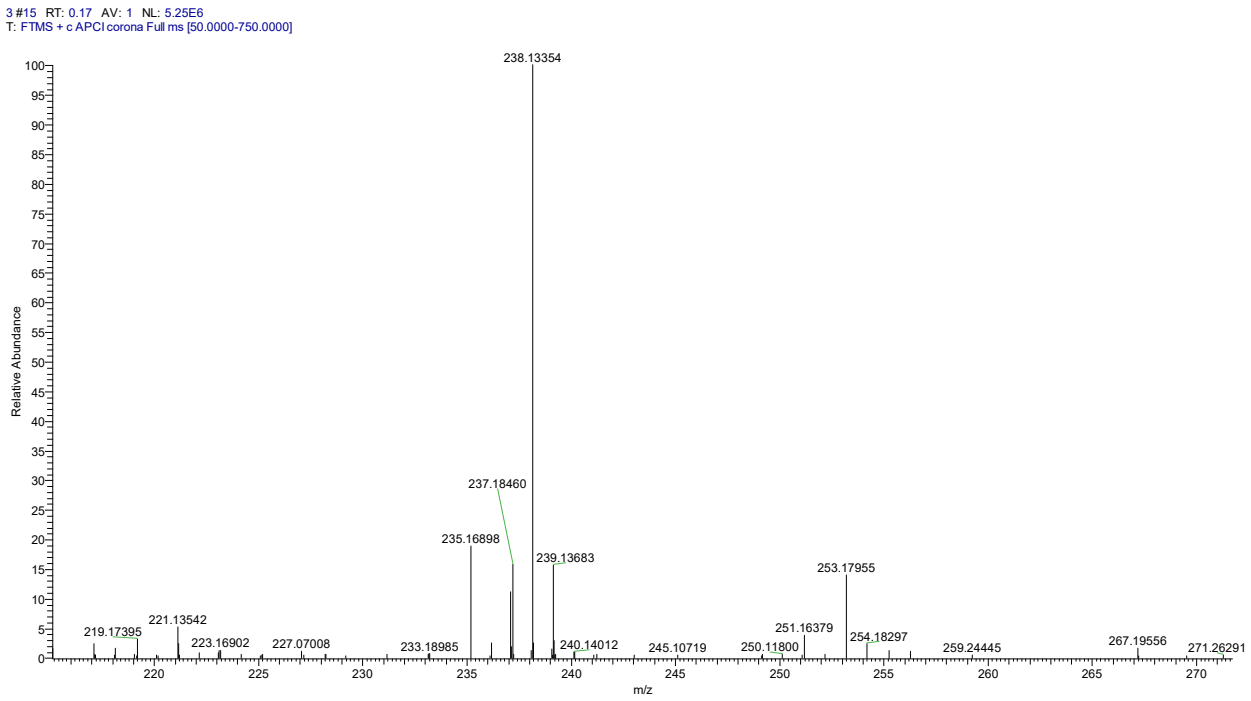


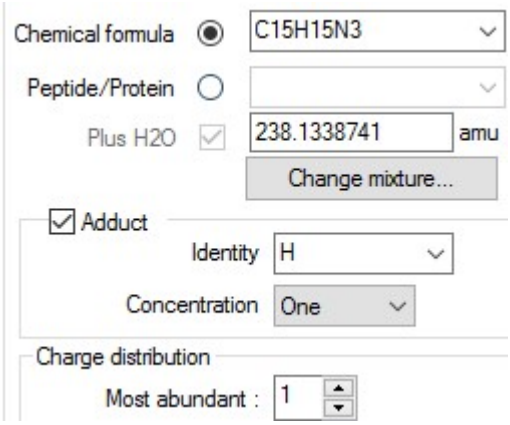




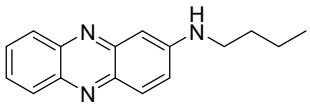
HR-MS spectrum of **C5**

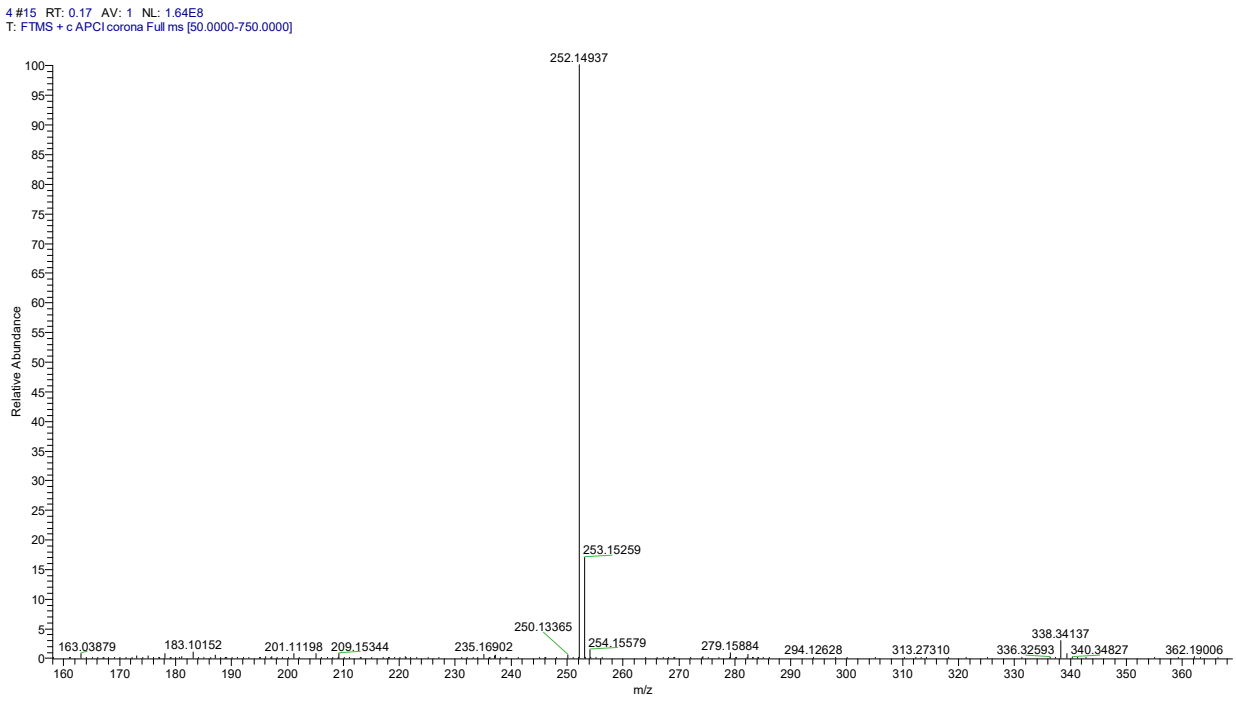


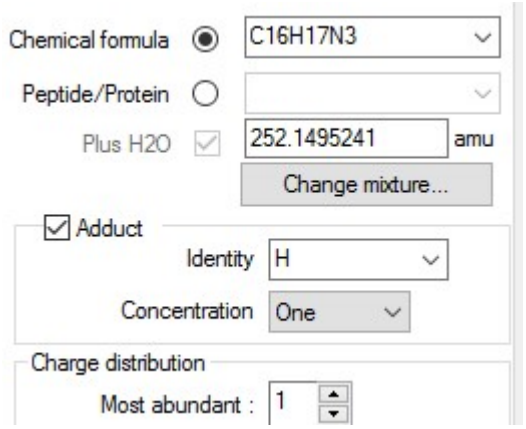




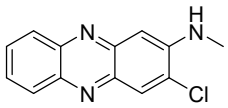
HR-MS spectrum of **C6**

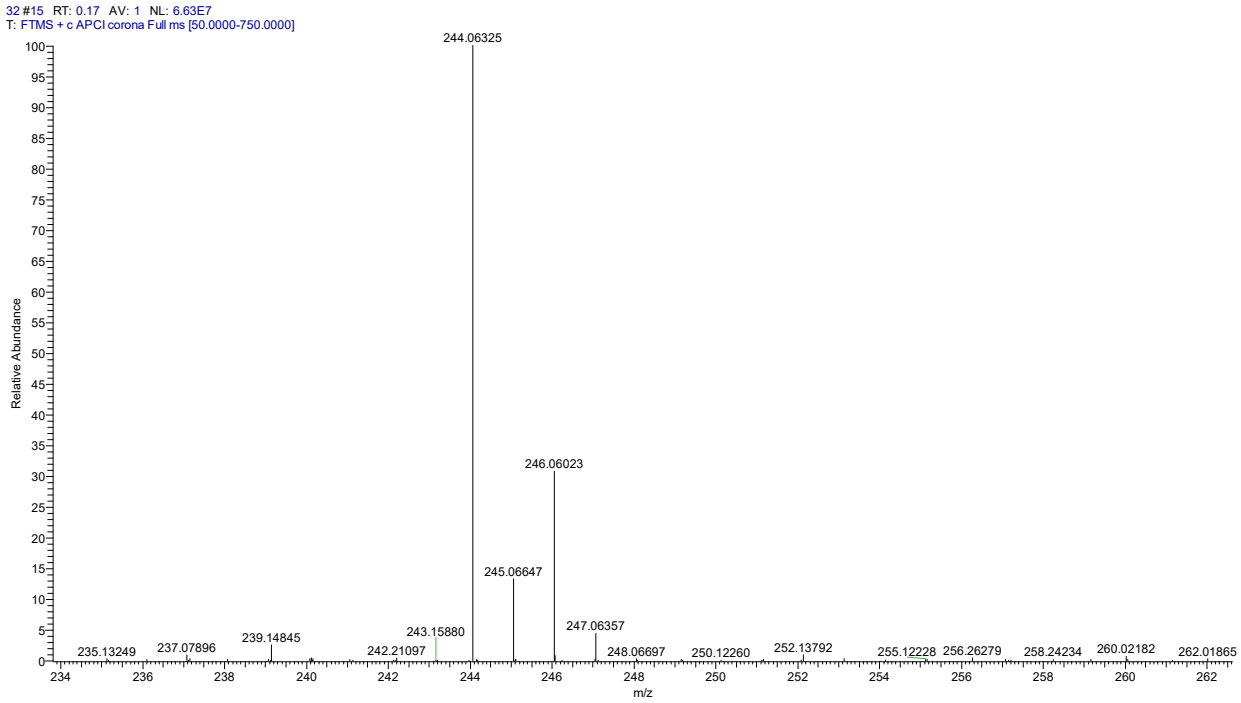


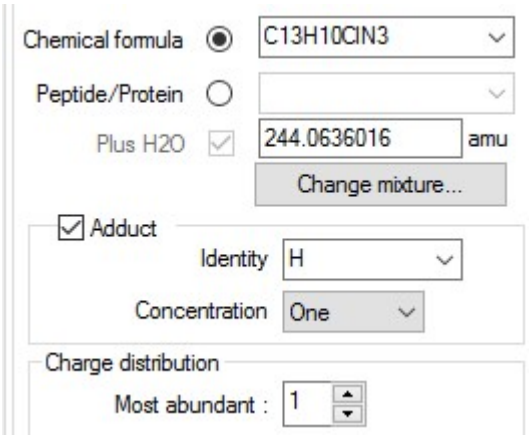




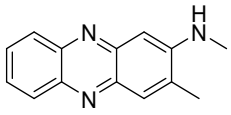
HR-MS spectrum of **C7**

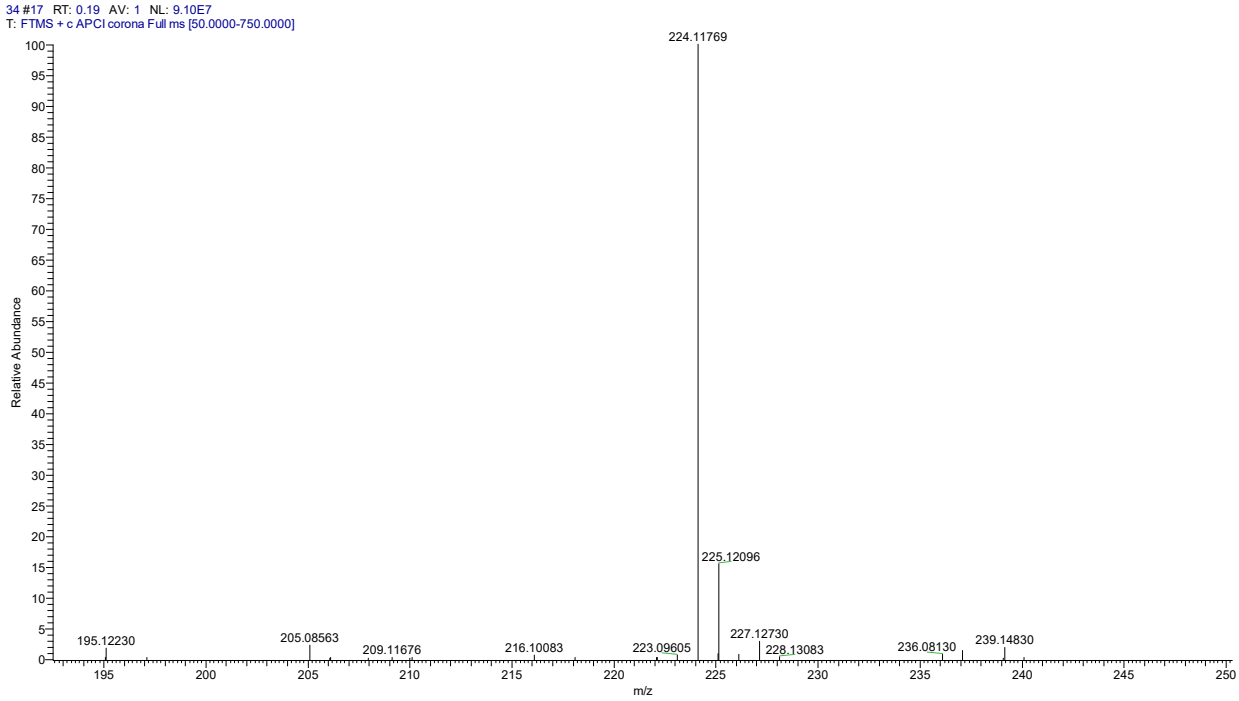


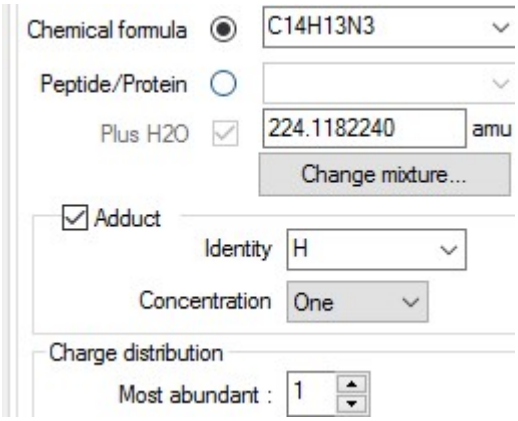




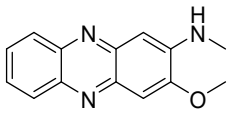
HR-MS spectrum of **C8**

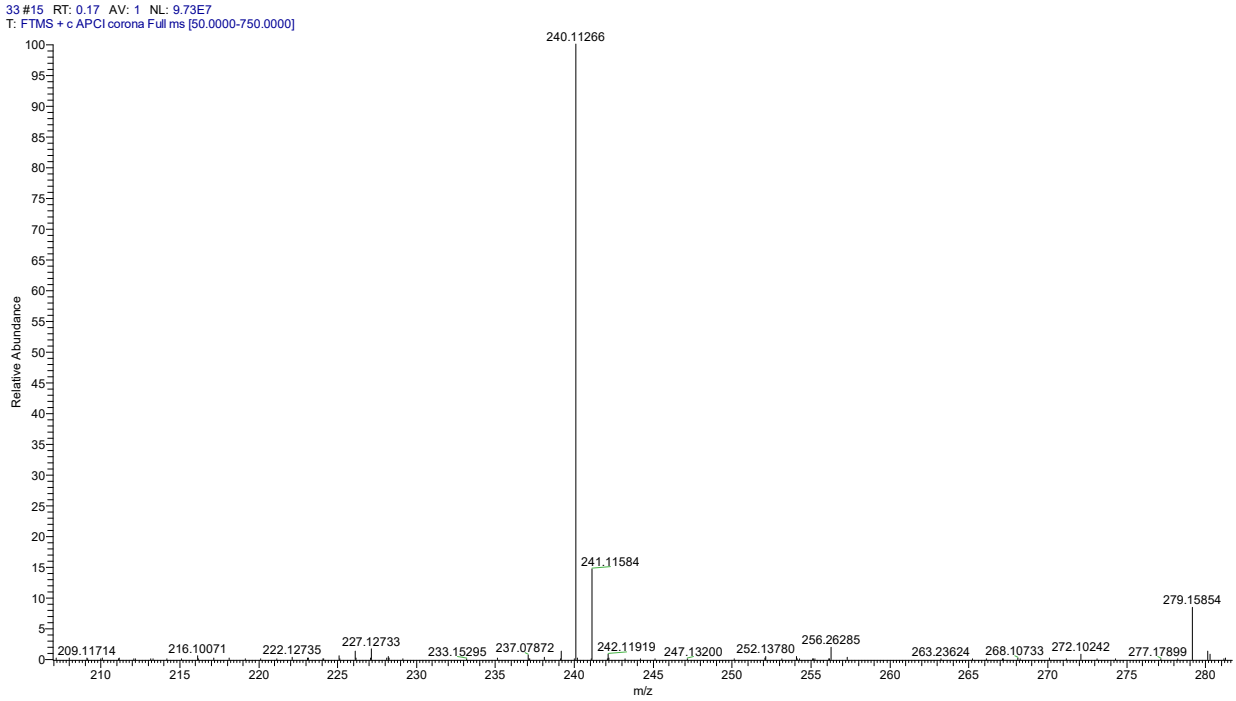


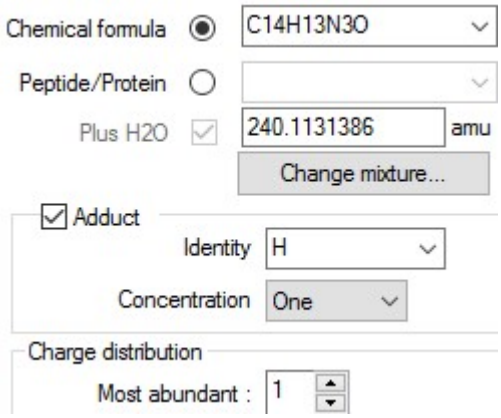




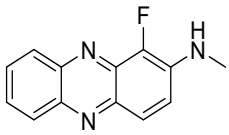
HR-MS spectrum of **C9**

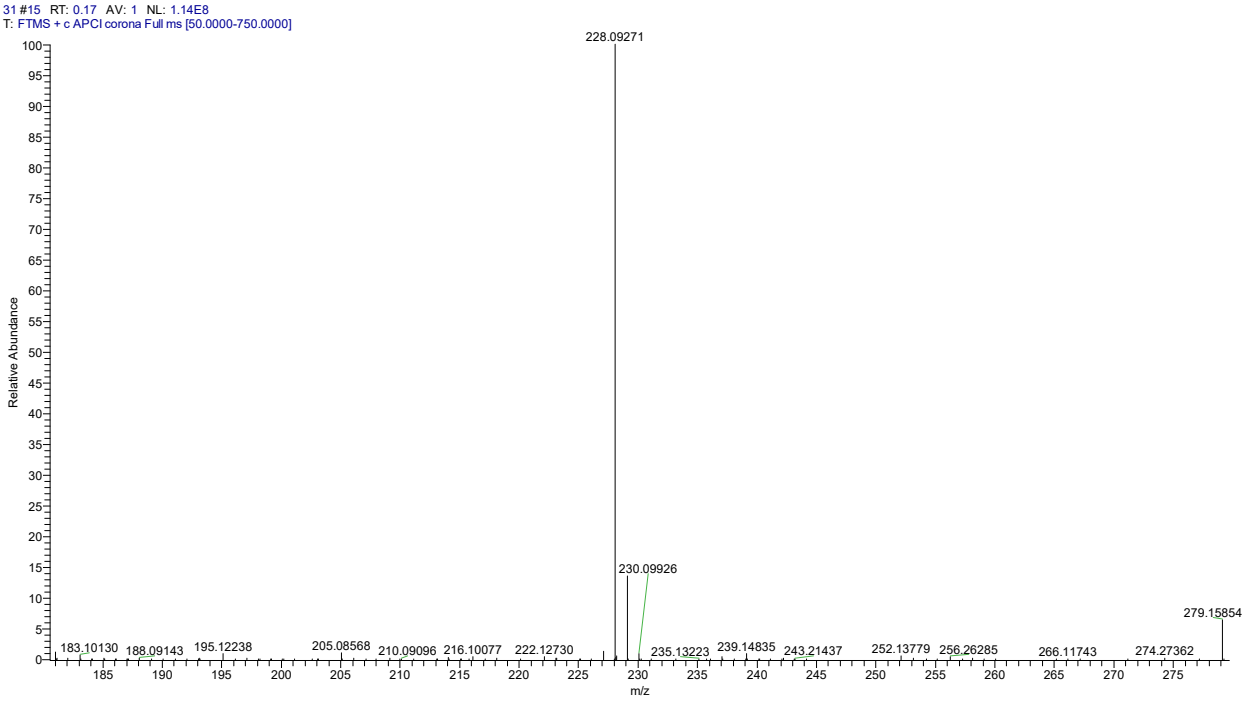


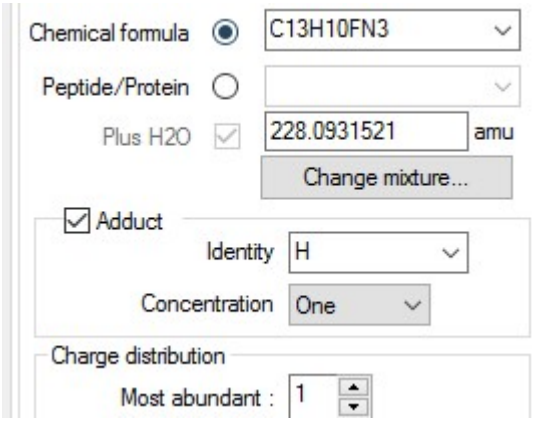




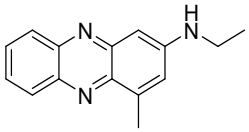
HR-MS spectrum of **C10**

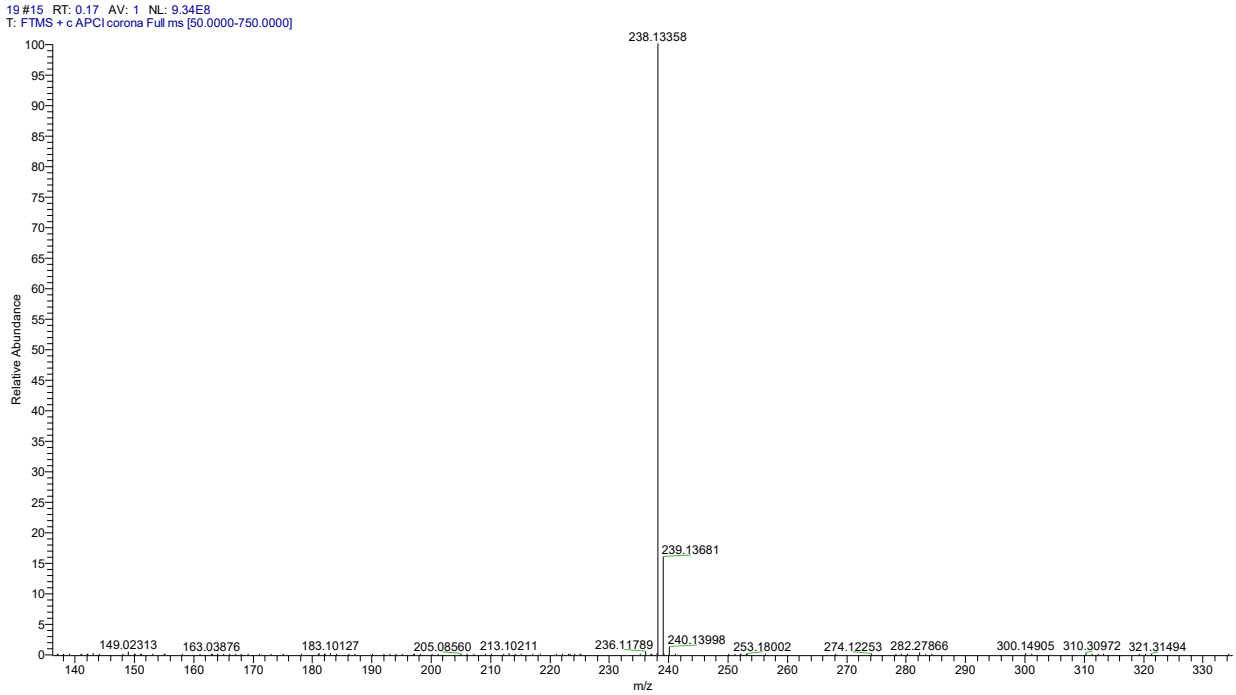


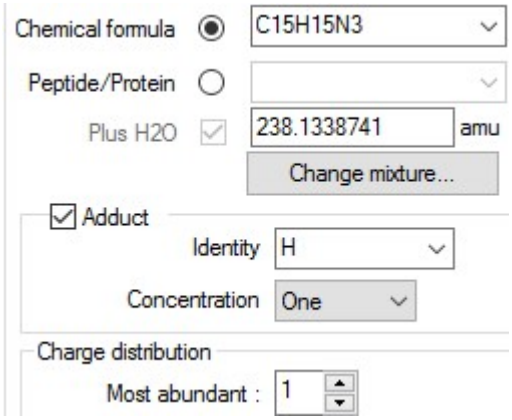




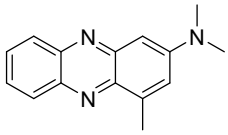
HR-MS spectrum of **C11**

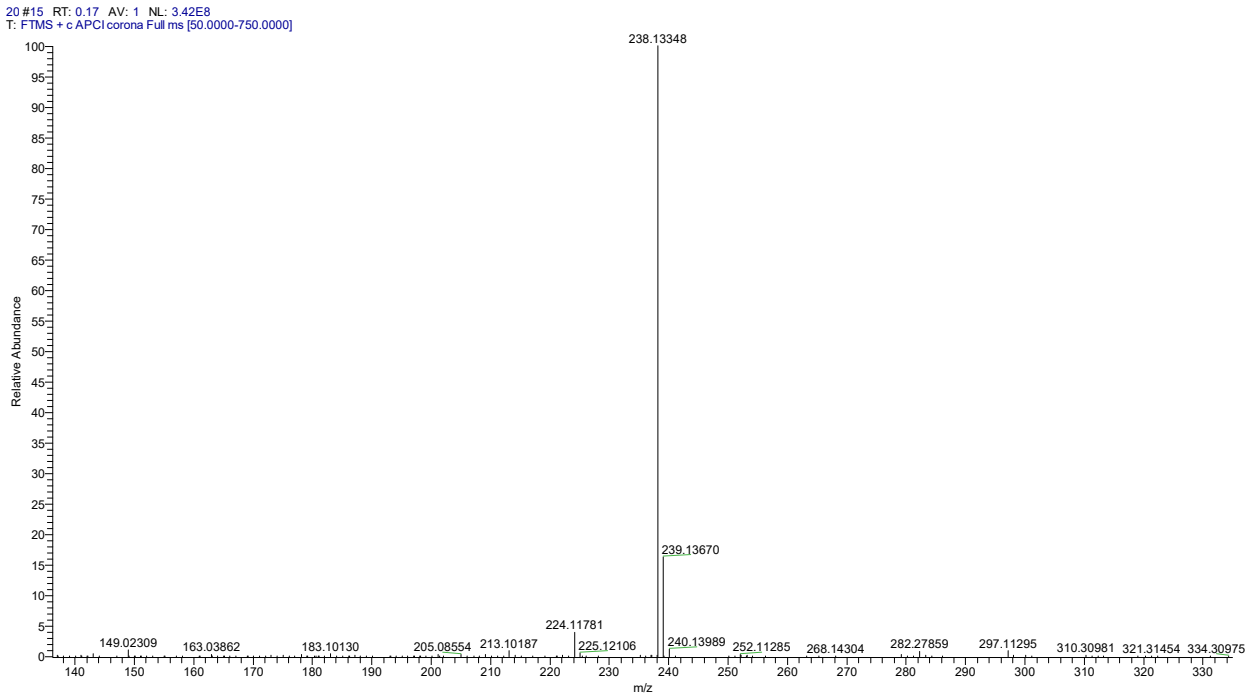




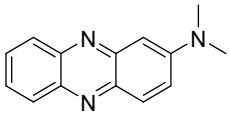


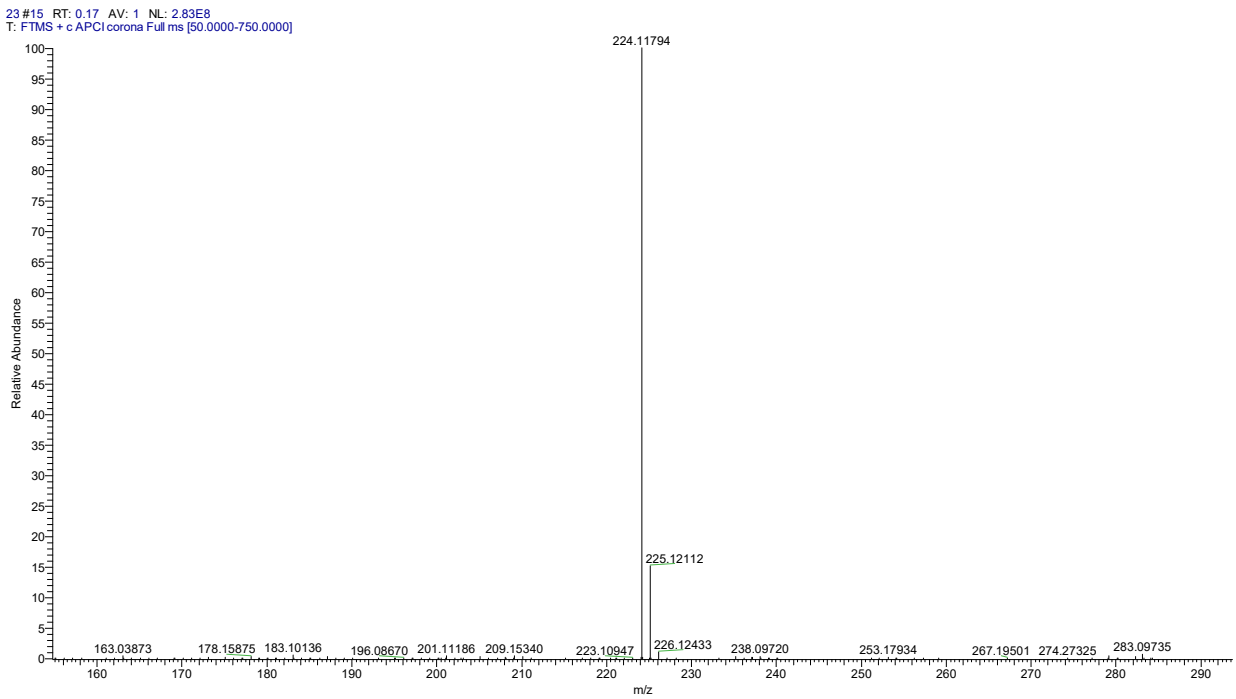
HR-MS spectrum of **C12**

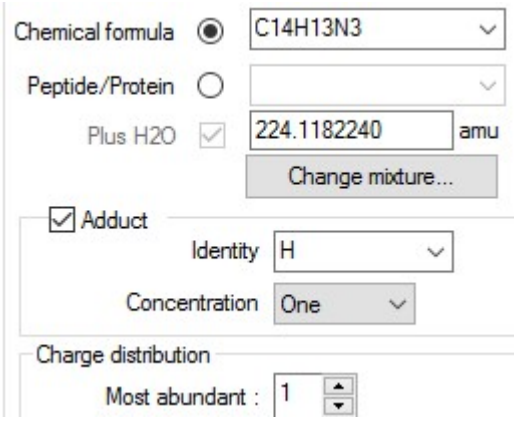




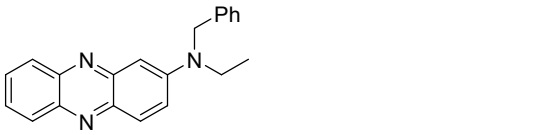
HR-MS spectrum of **C13**

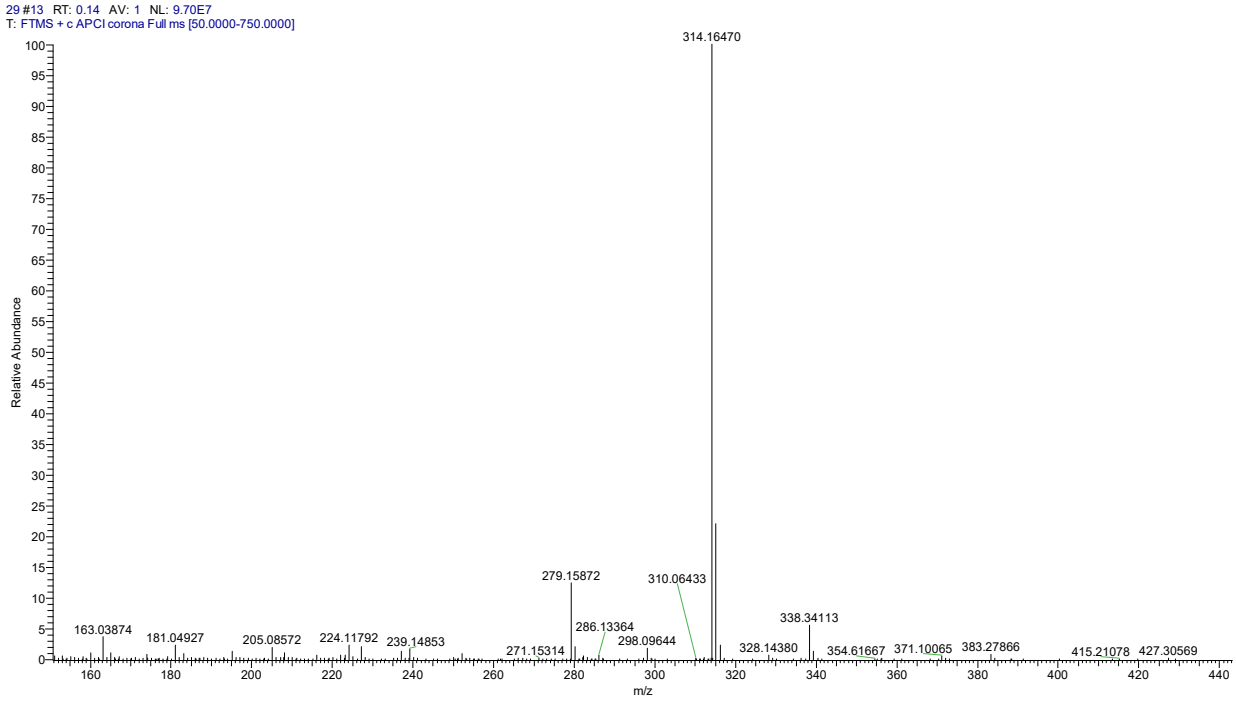


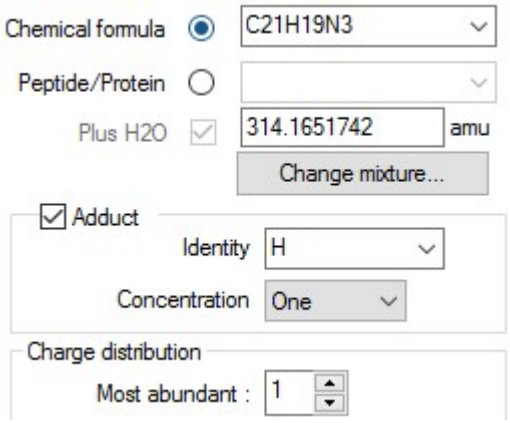




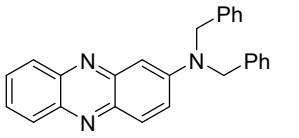
HR-MS spectrum of **C14**

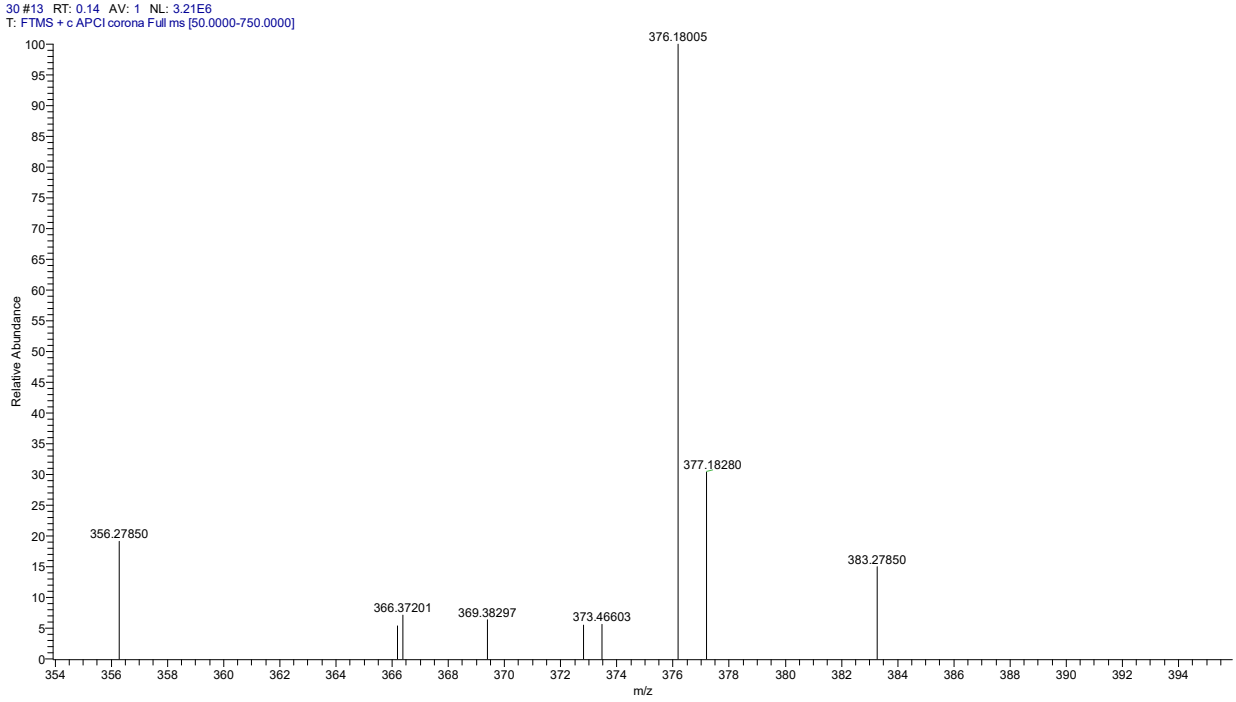


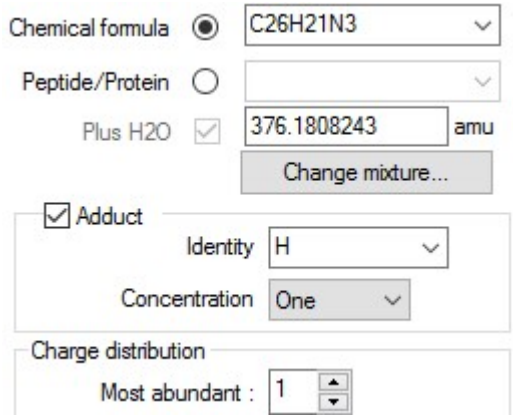




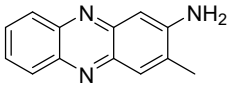
HR-MS spectrum of **C15**

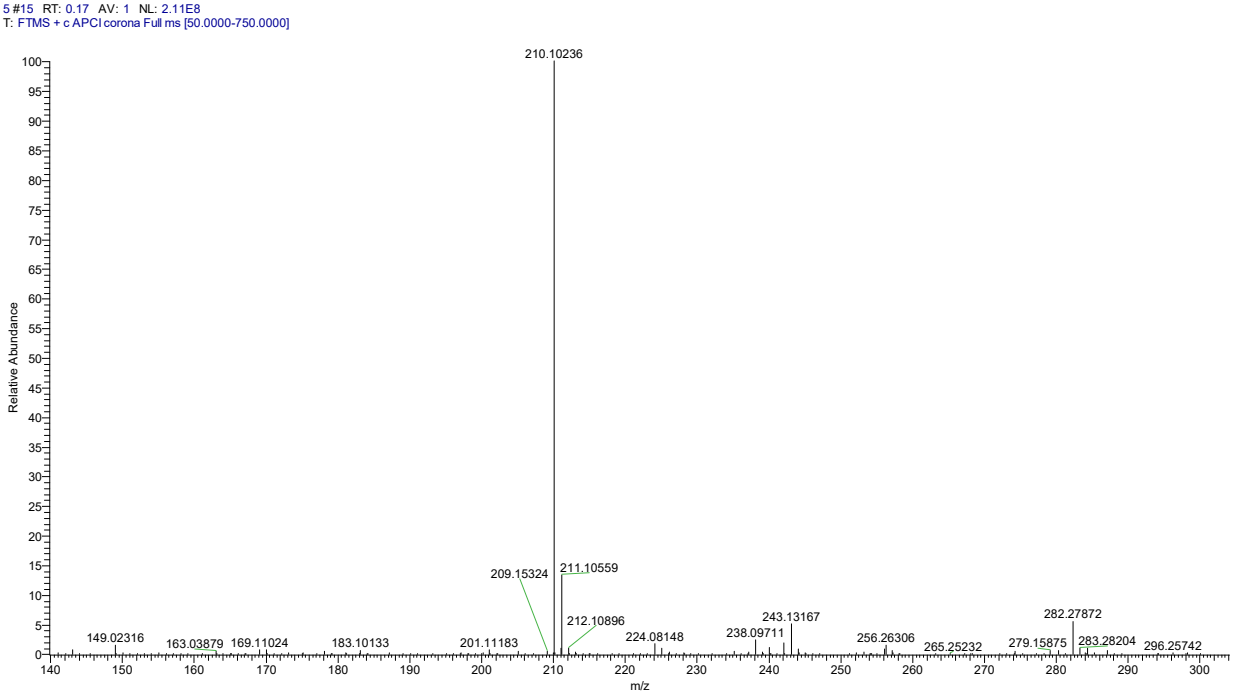


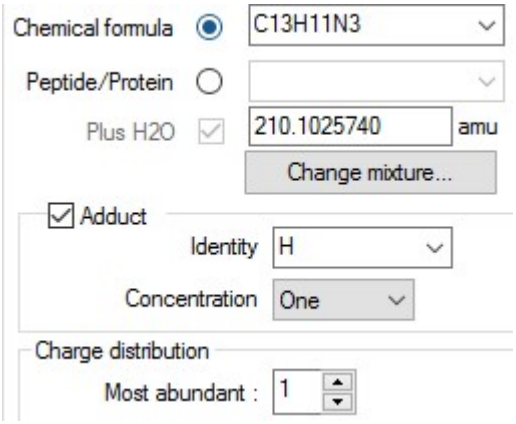




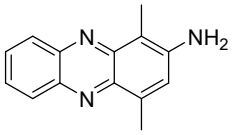
HR-MS spectrum of **C16**

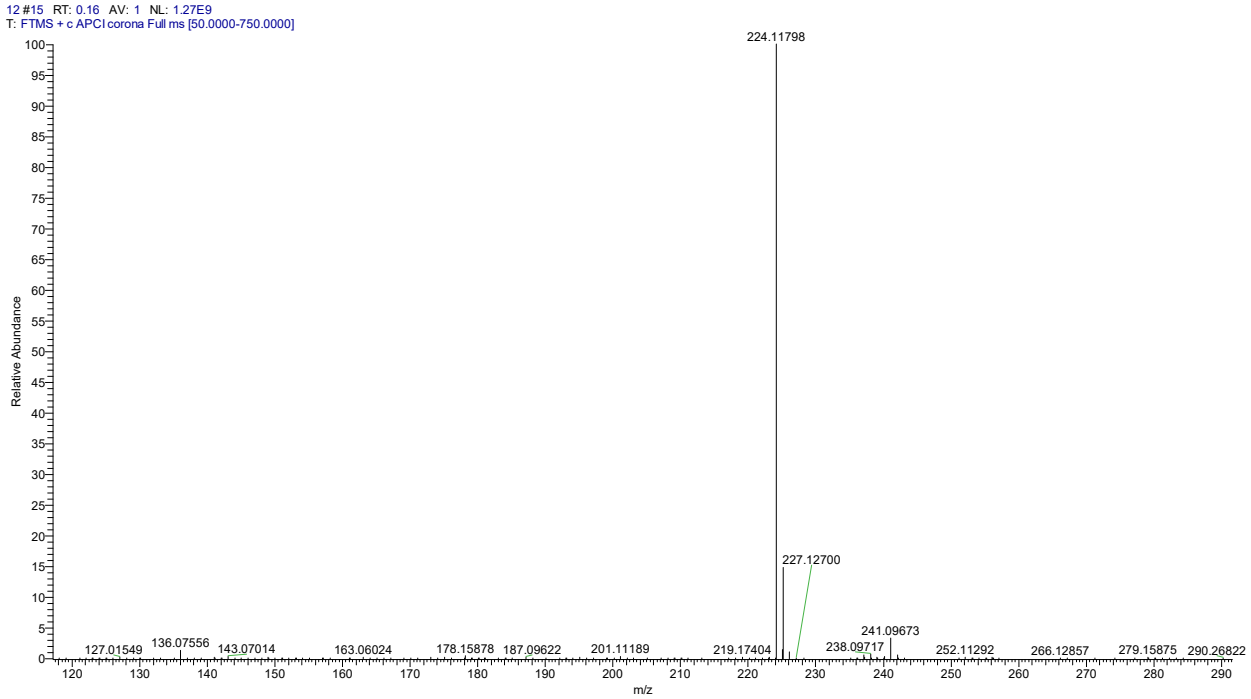


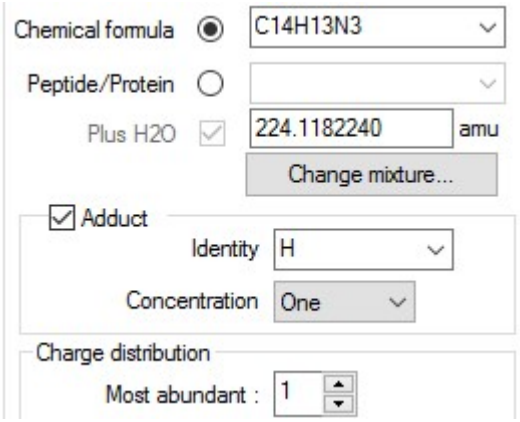




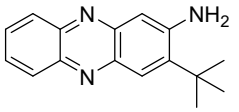
HR-MS spectrum of **C17**

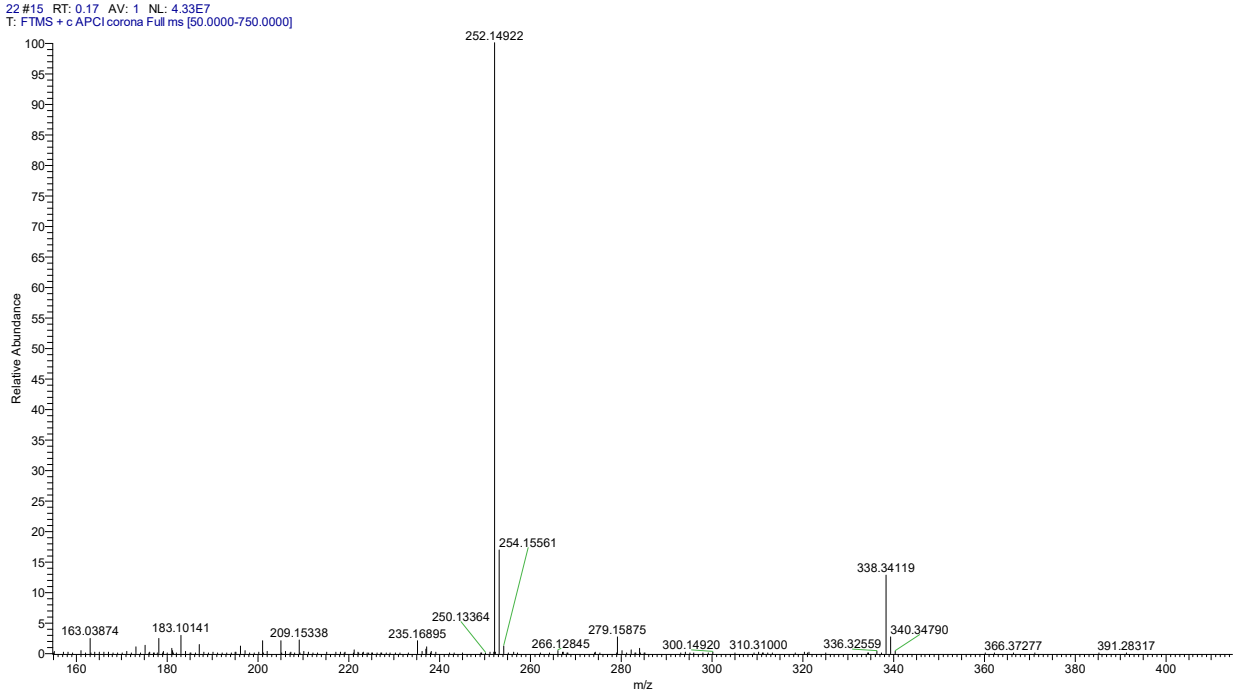


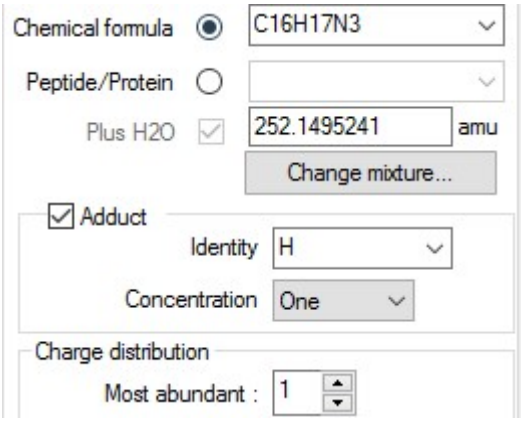




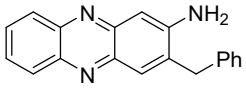
HR-MS spectrum of **C18**

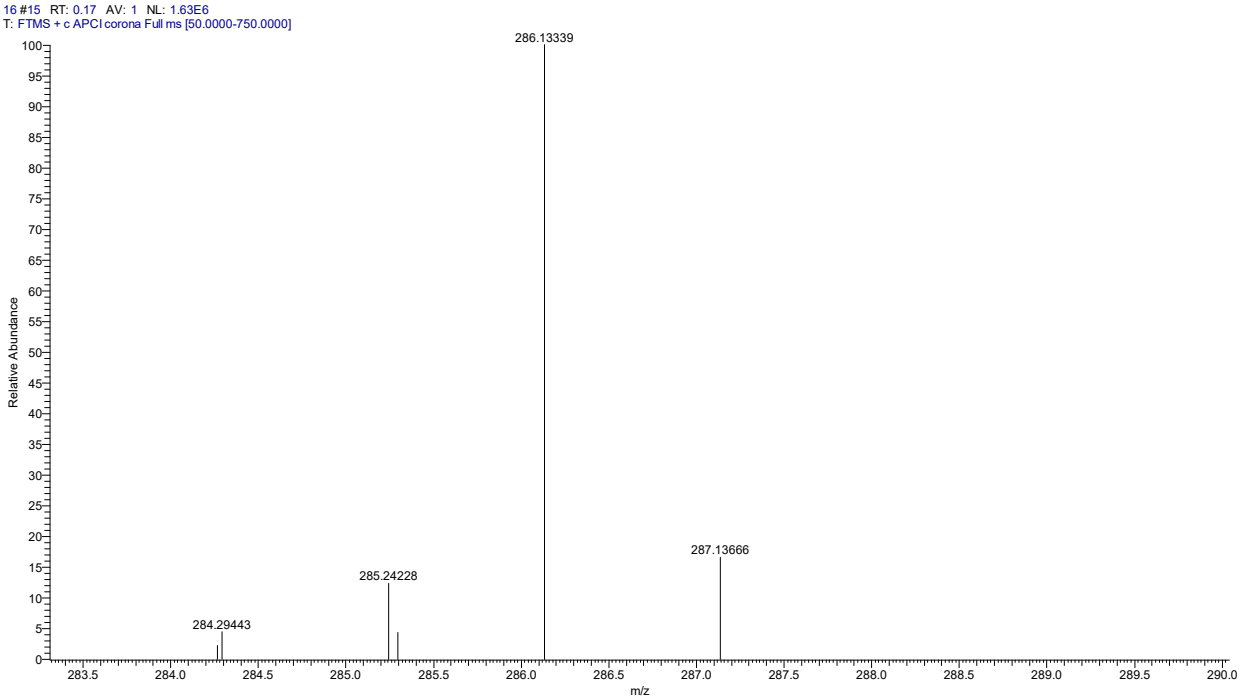


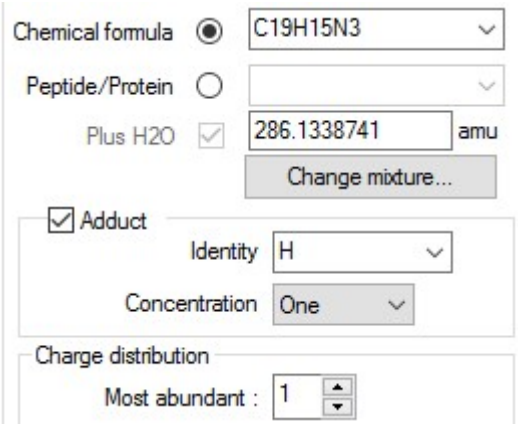




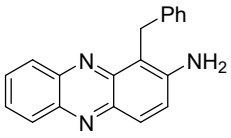
HR-MS spectrum of **C19**

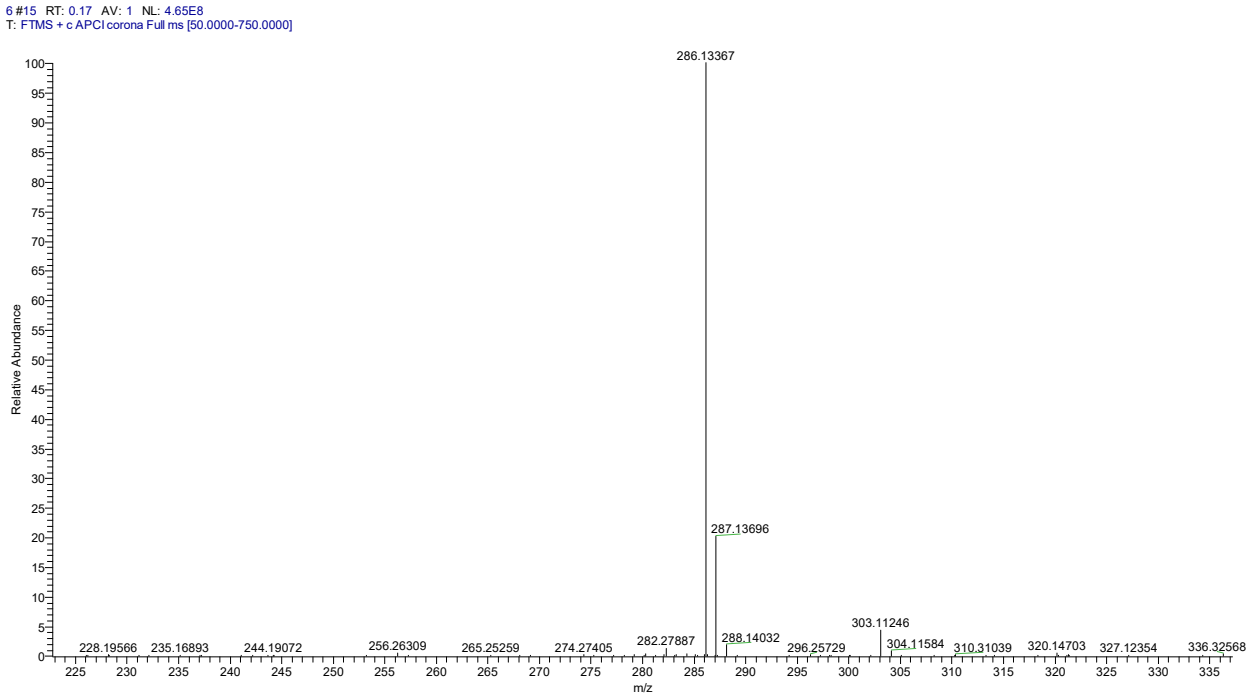


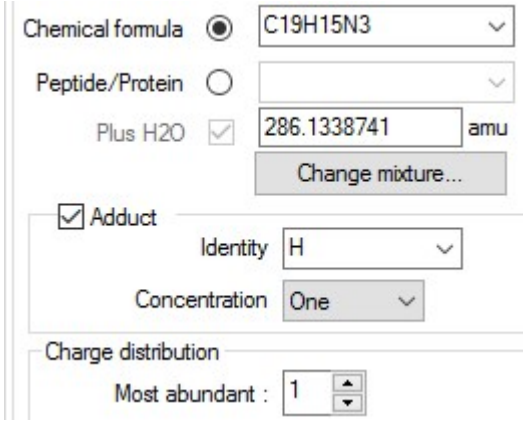




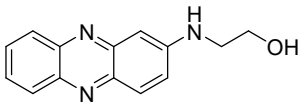
HR-MS spectrum of **C19'**



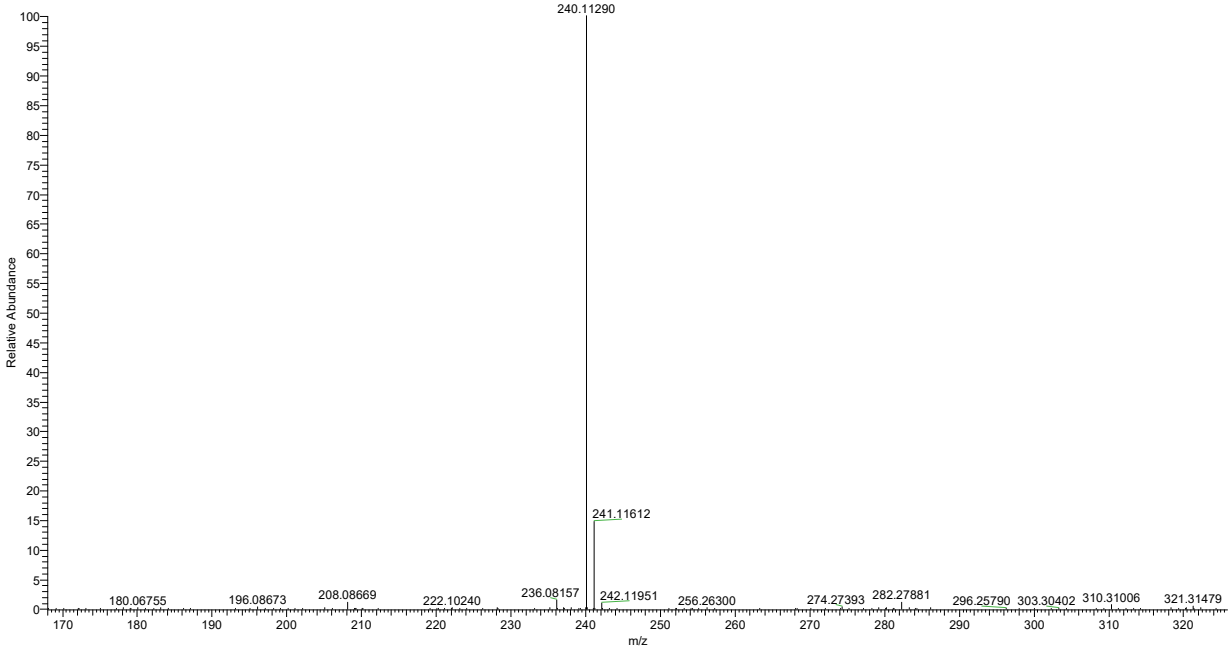


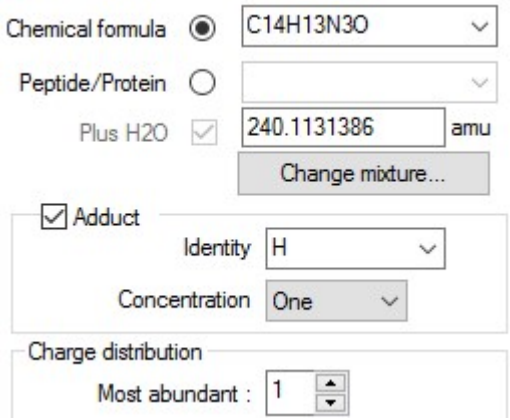


HR-MS spectrum of **C20**

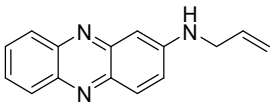


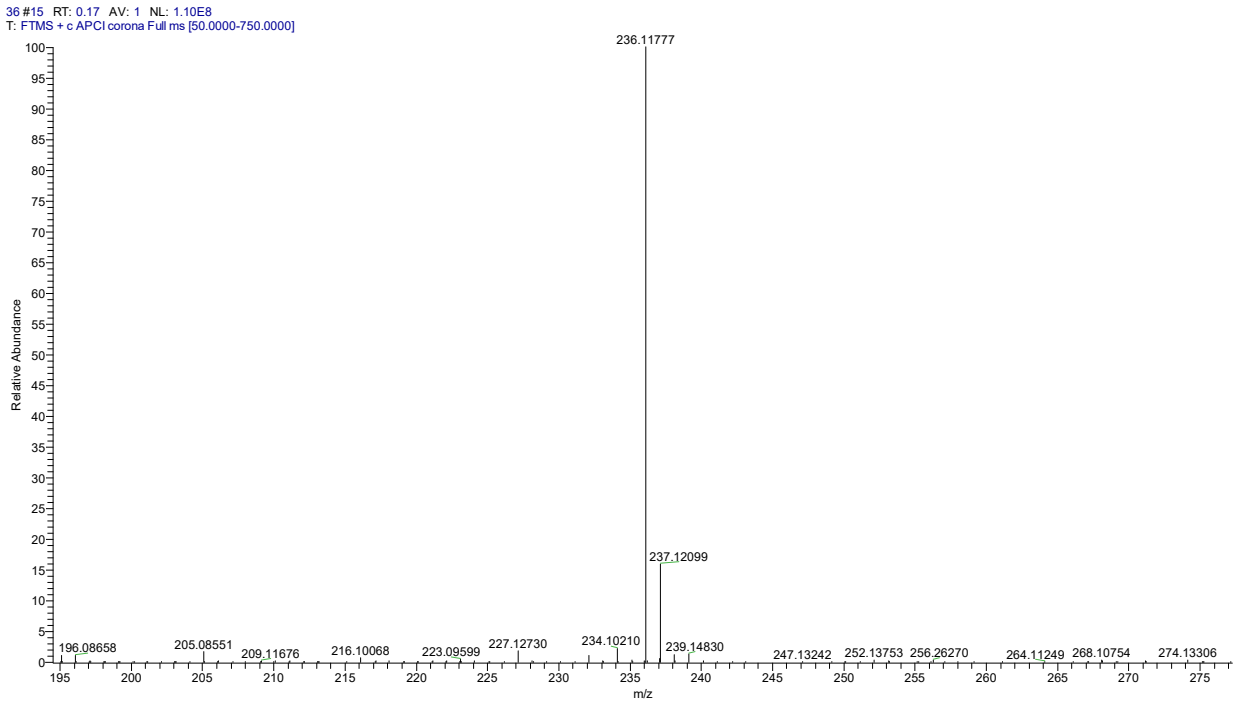
7 #15 RT: 0.17 AV: 1 NL: 5.38E8
T: FTMS + c APCI corona Full ms [50.0000-750.0000]

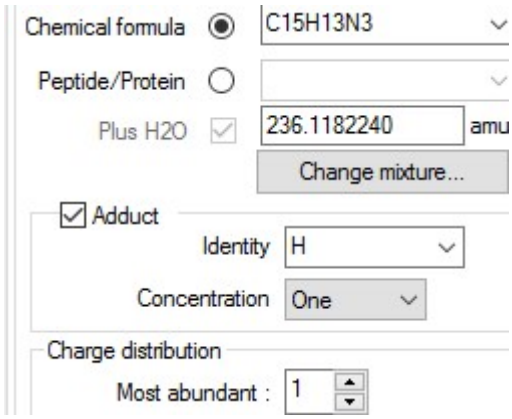




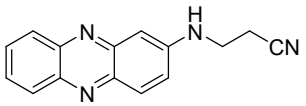
HR-MS spectrum of **C21**

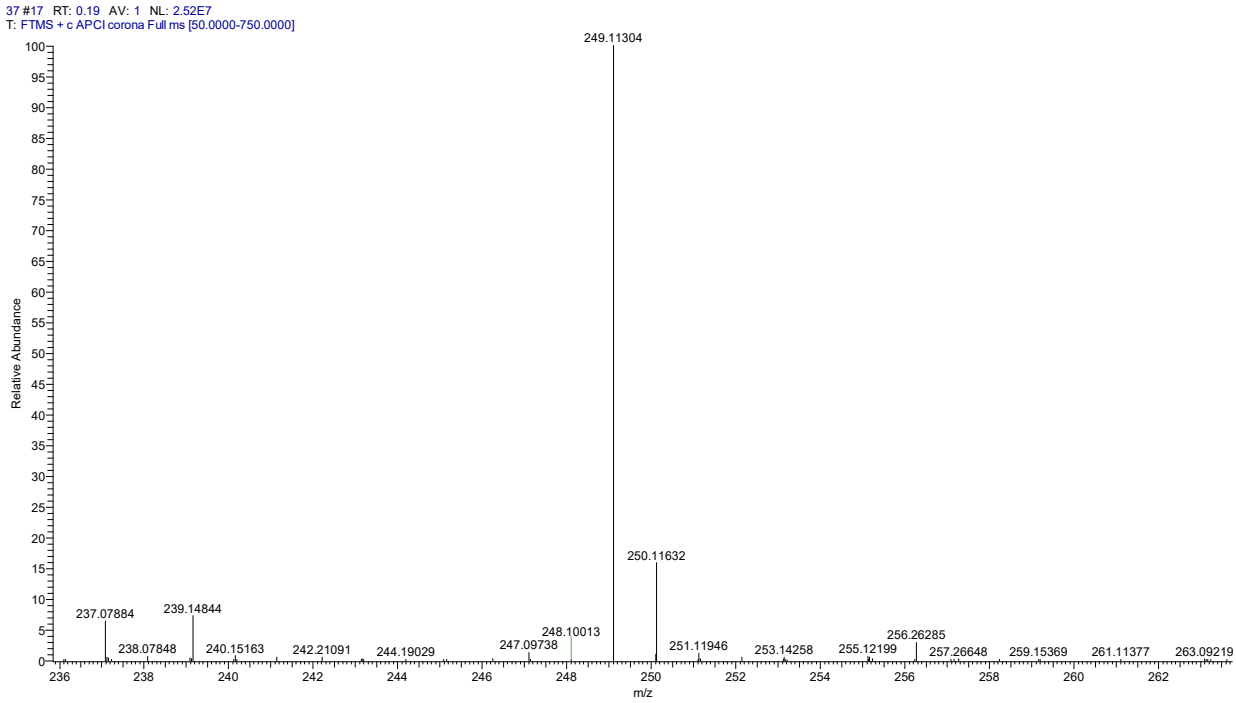


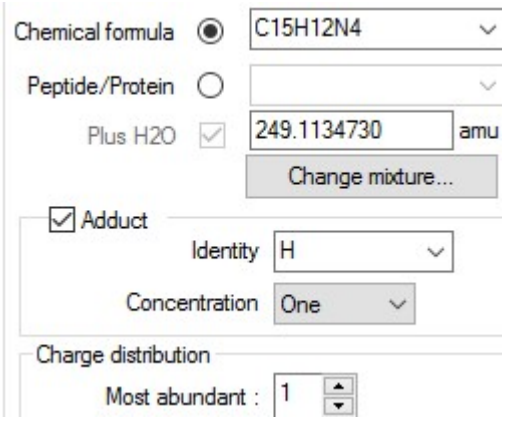




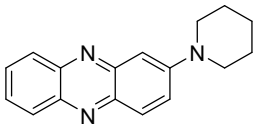
HR-MS spectrum of **C22**

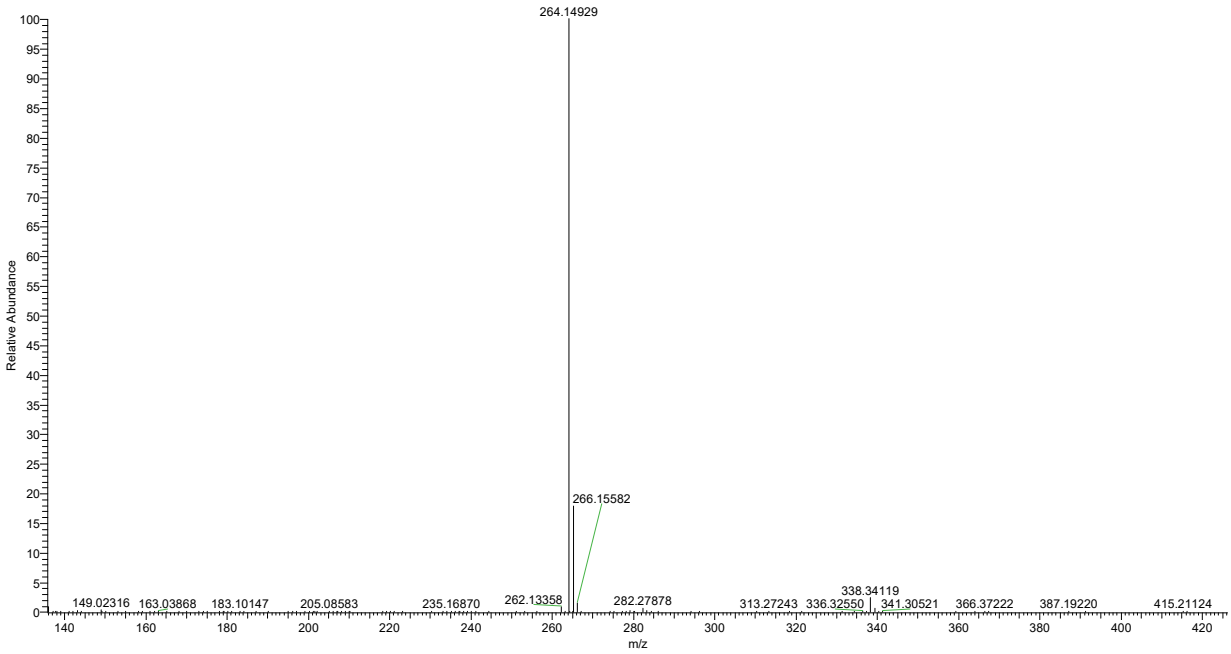


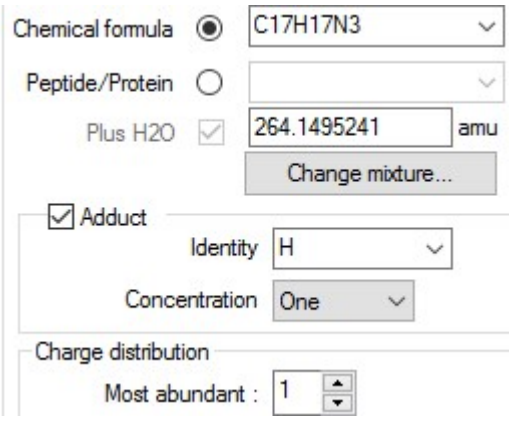




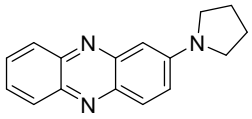
HR-MS spectrum of **C23**

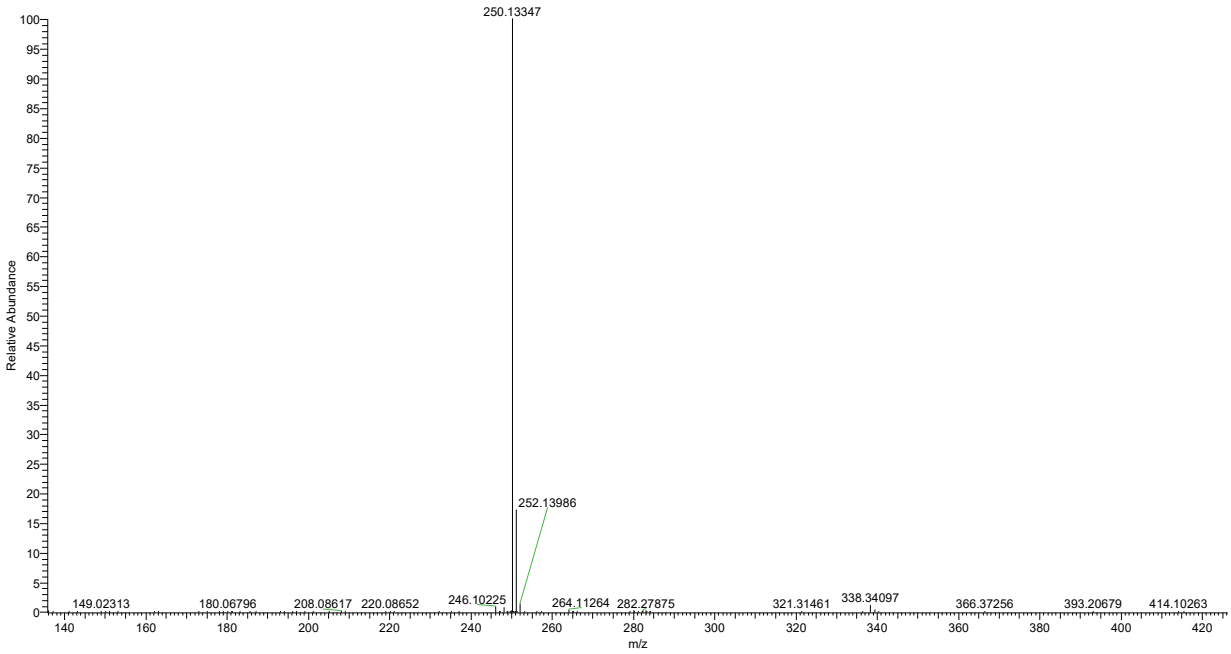


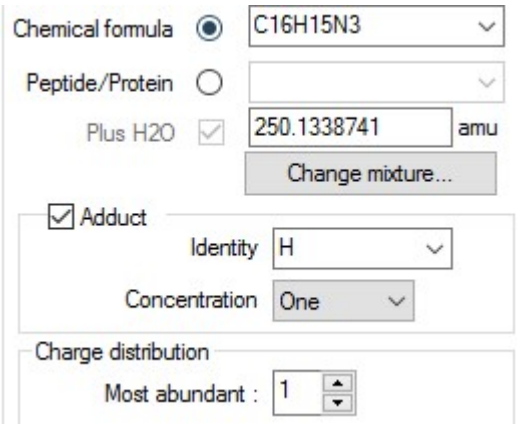




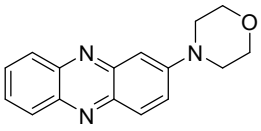
HR-MS spectrum of **C24**

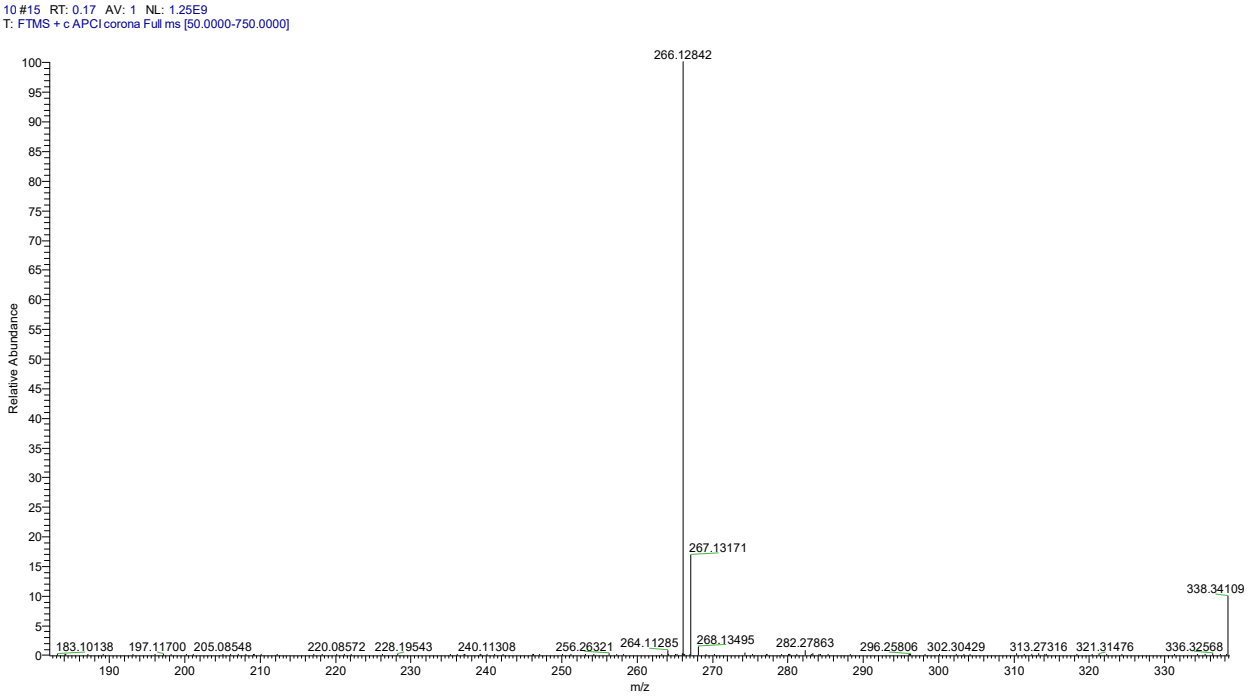


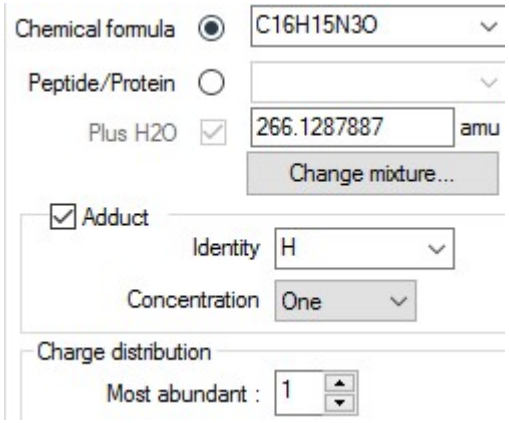




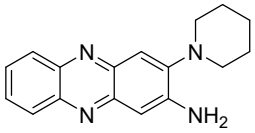
HR-MS spectrum of **C25**

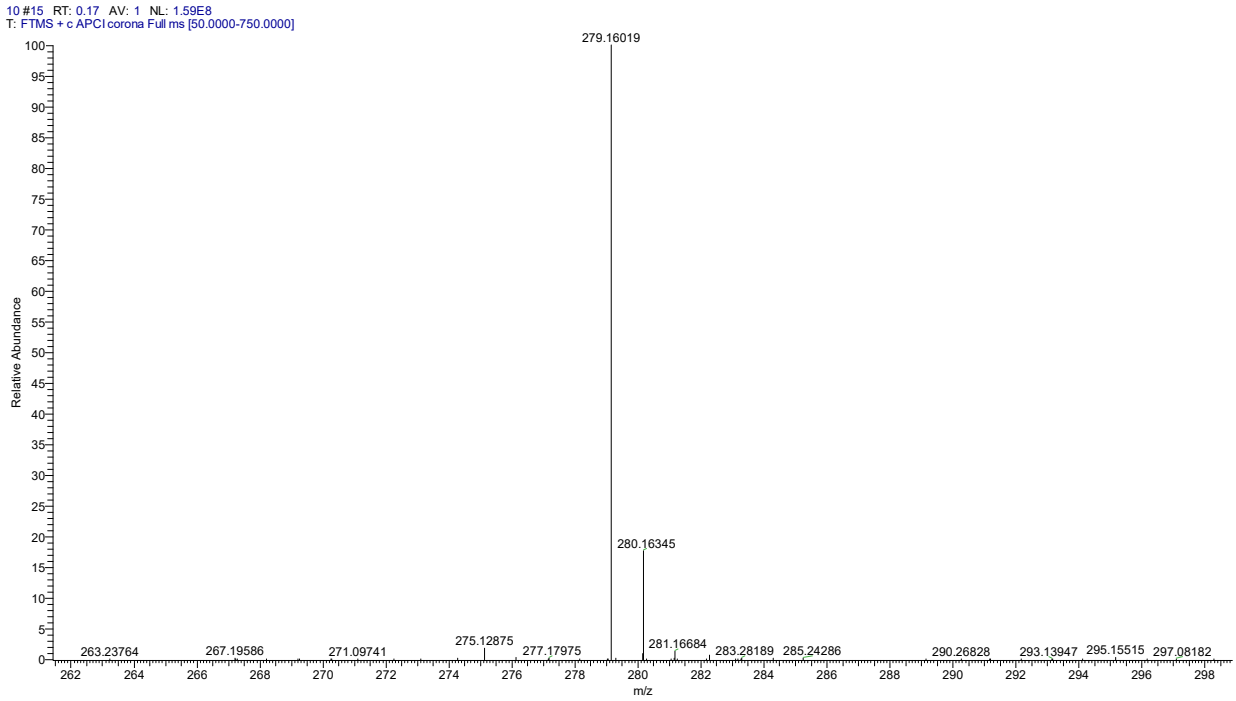


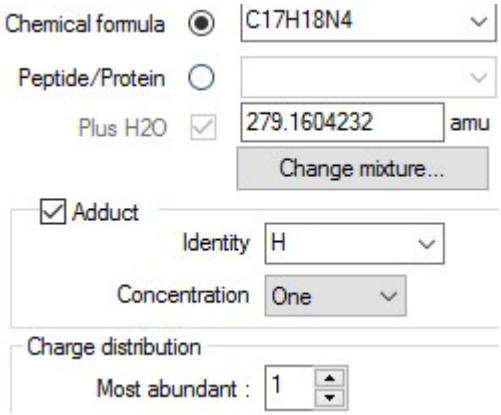




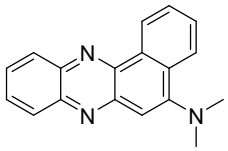
HR-MS spectrum of **C26**

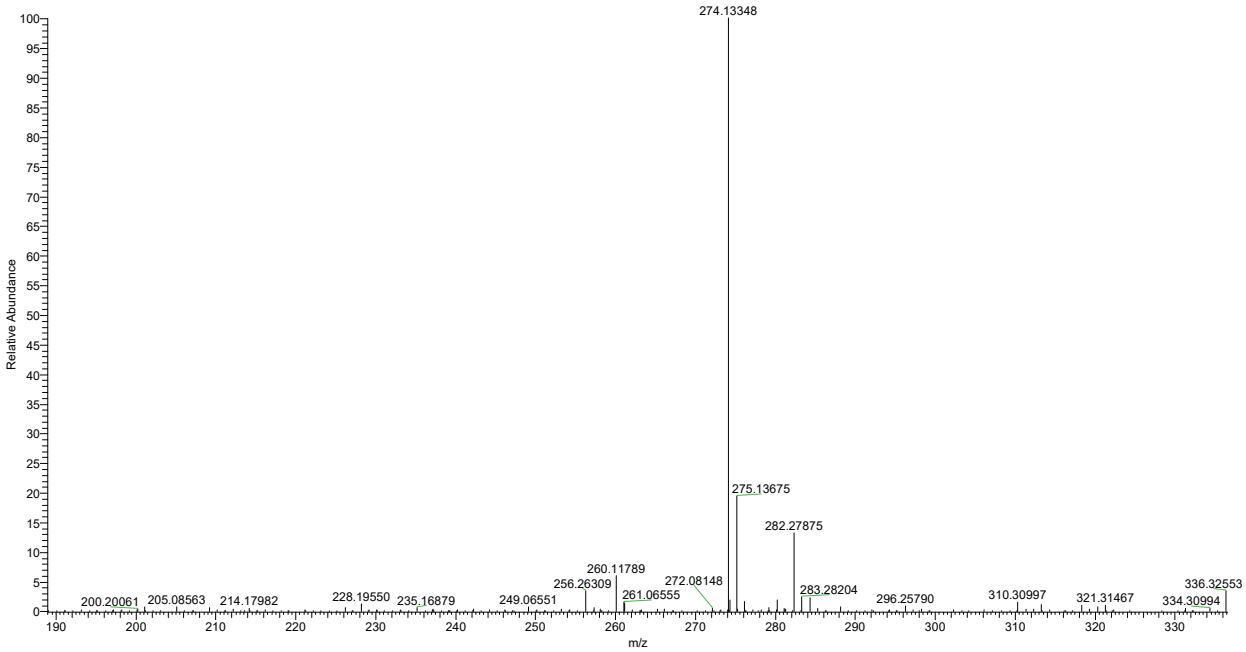


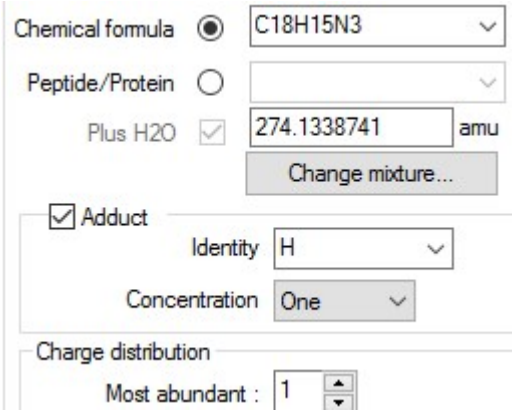




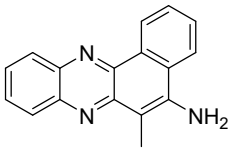
HR-MS spectrum of **C27**

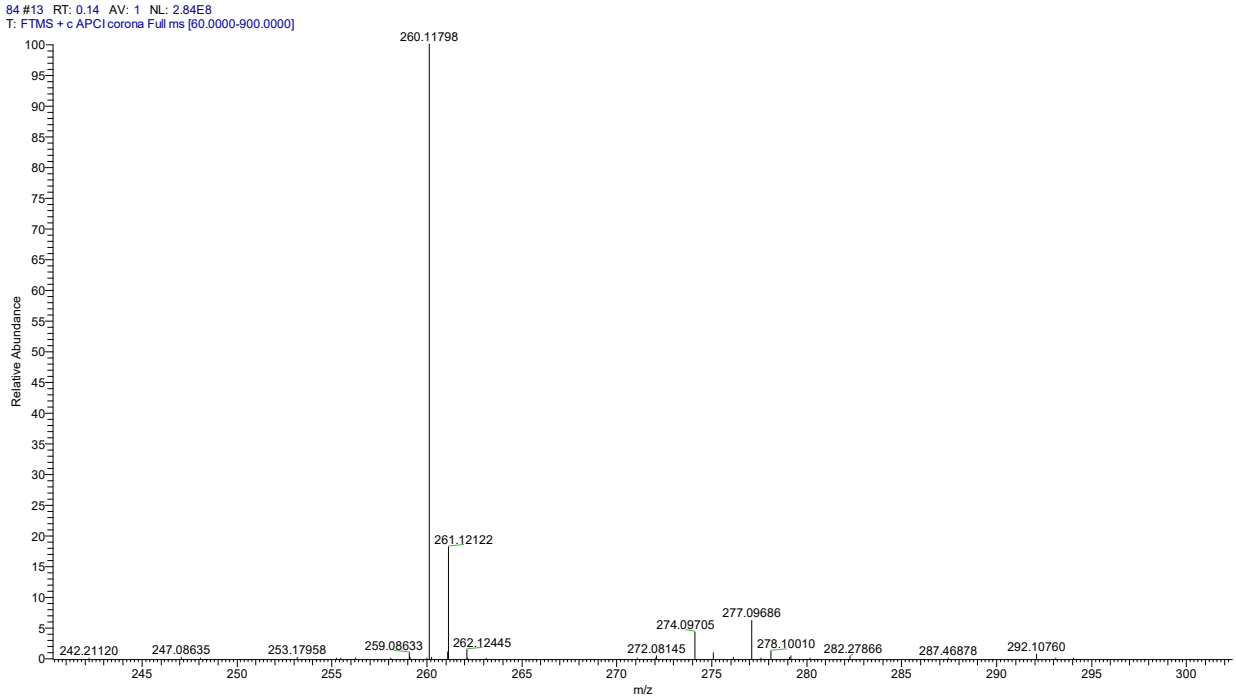


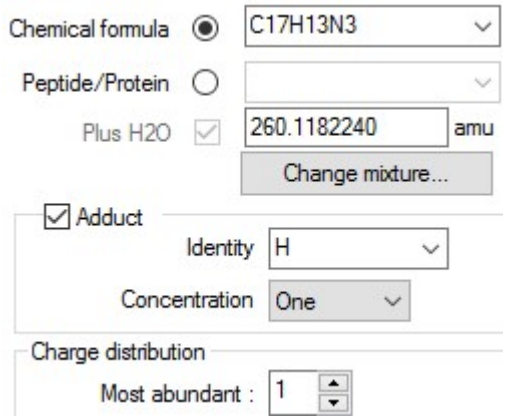




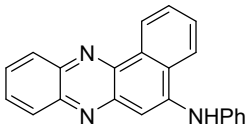
HR-MS spectrum of **C28**

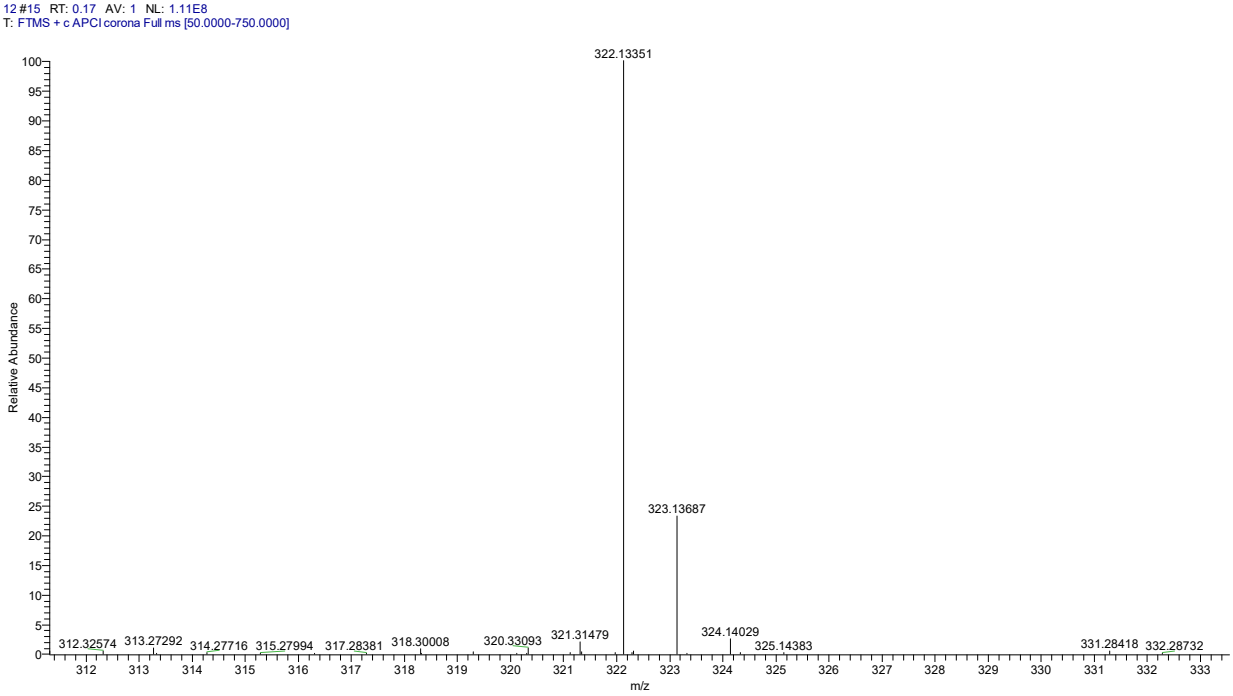


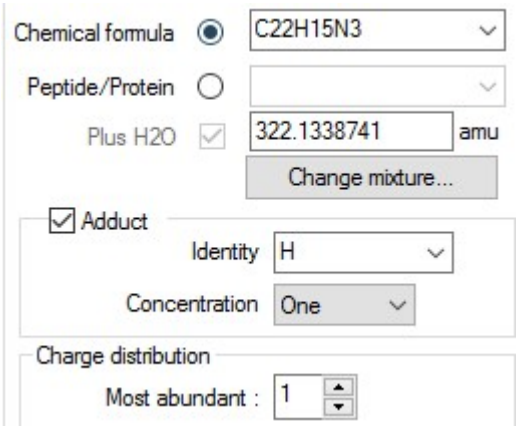




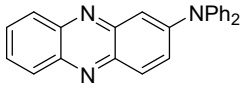
HR-MS spectrum of **C29**

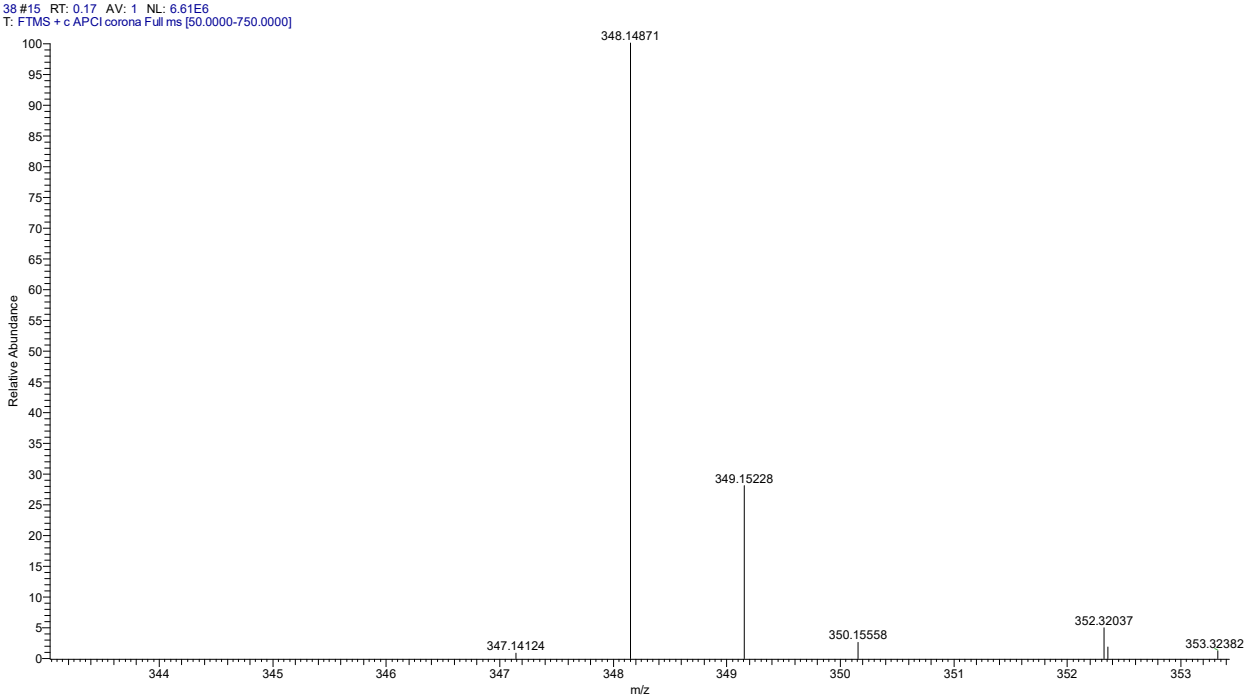


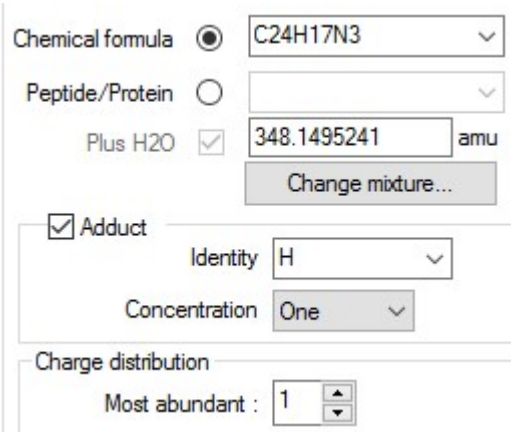




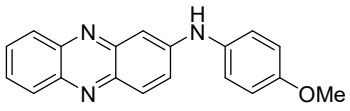
HR-MS spectrum of **C30**

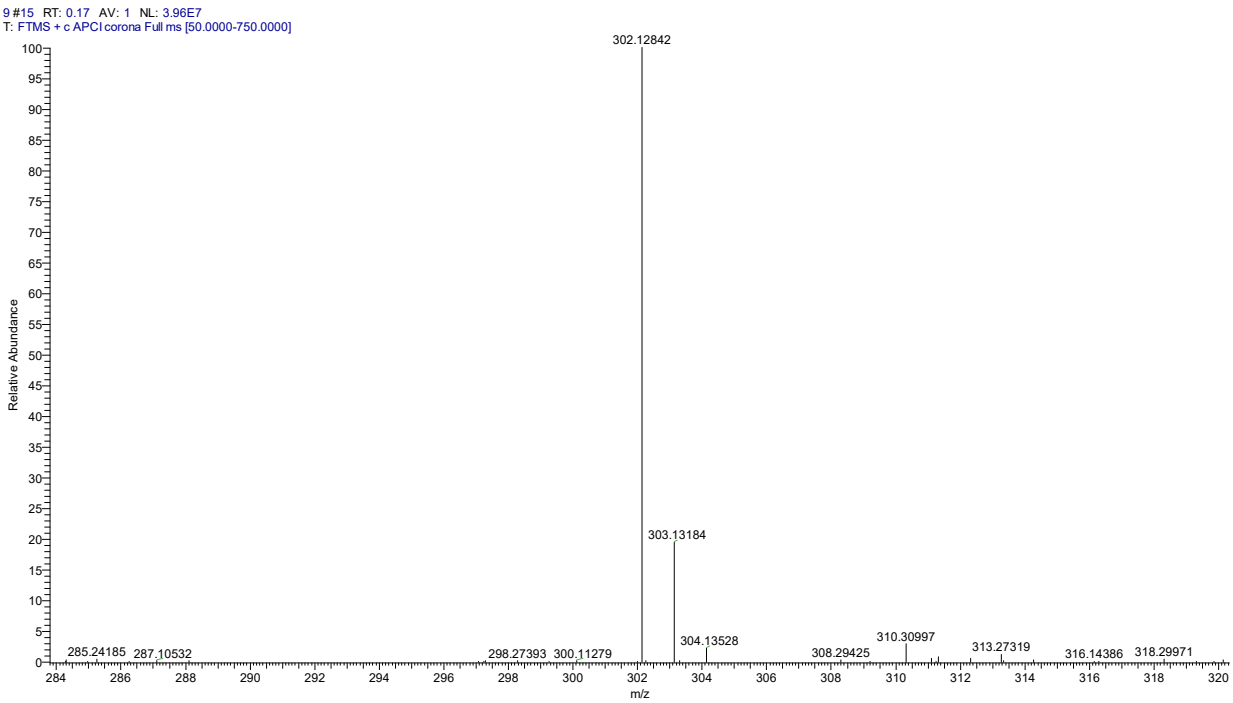


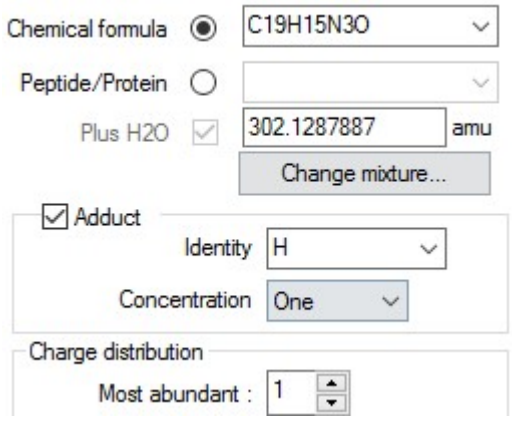




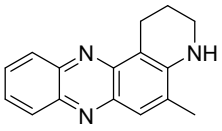
HR-MS spectrum of **C31**

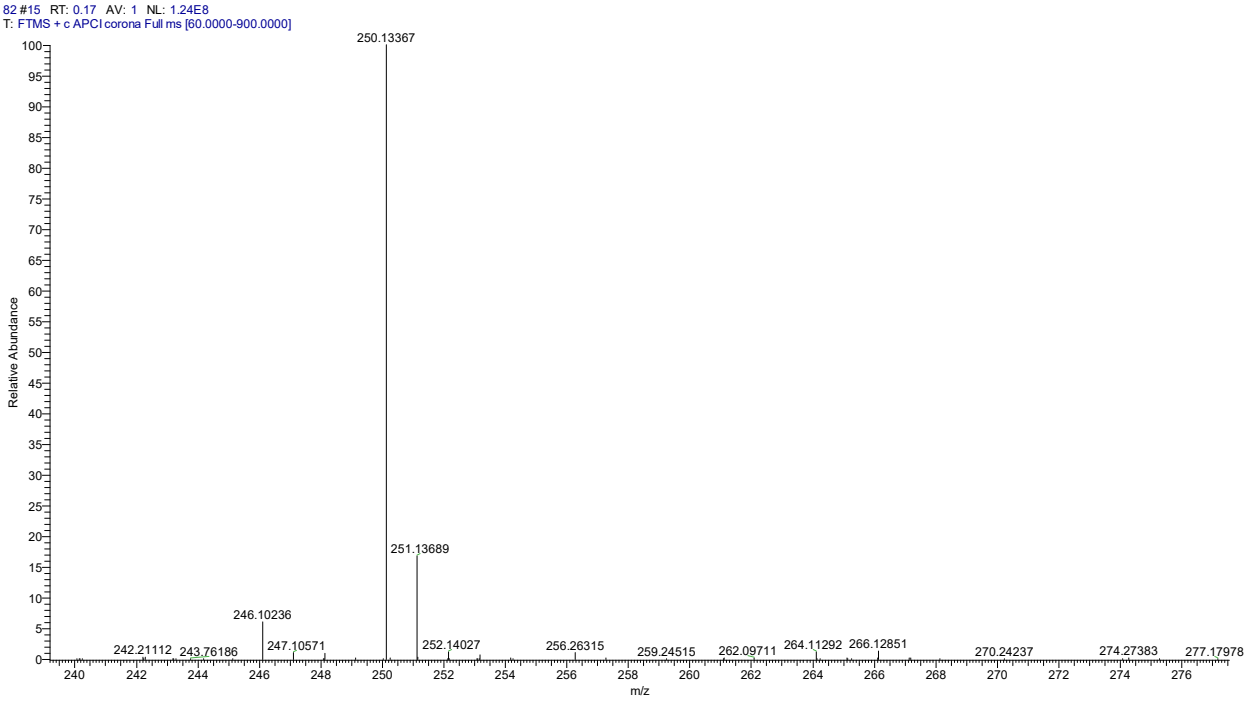


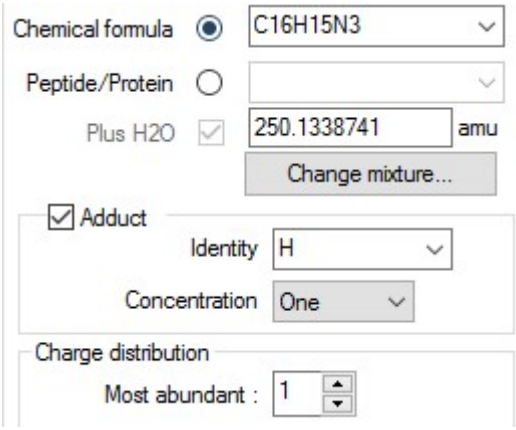




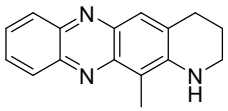
HR-MS spectrum of **C32**

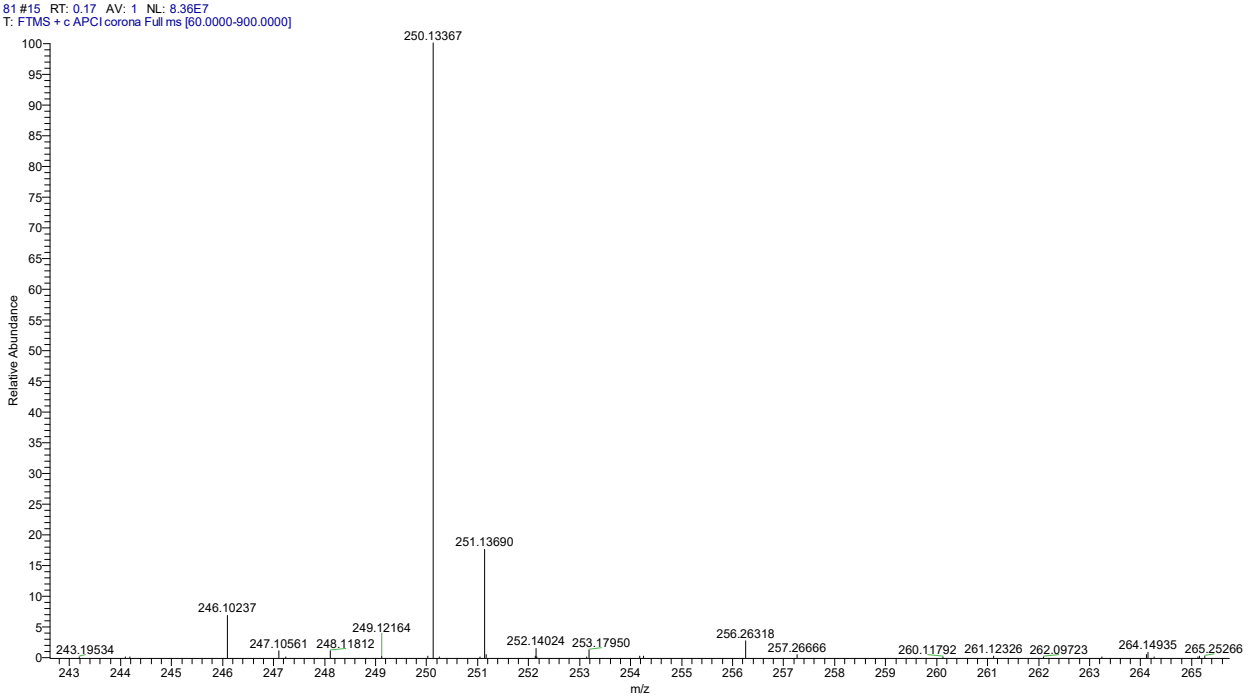




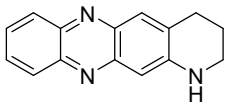


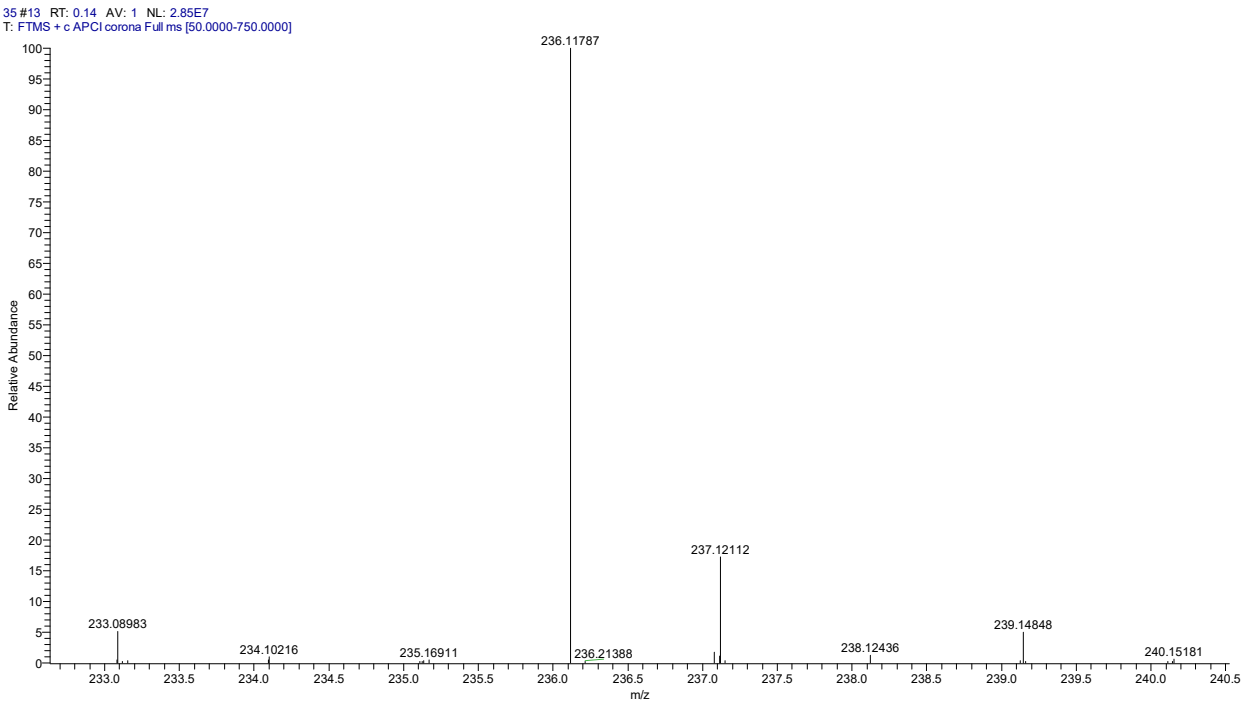
HR-MS spectrum of **C32'**



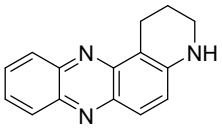


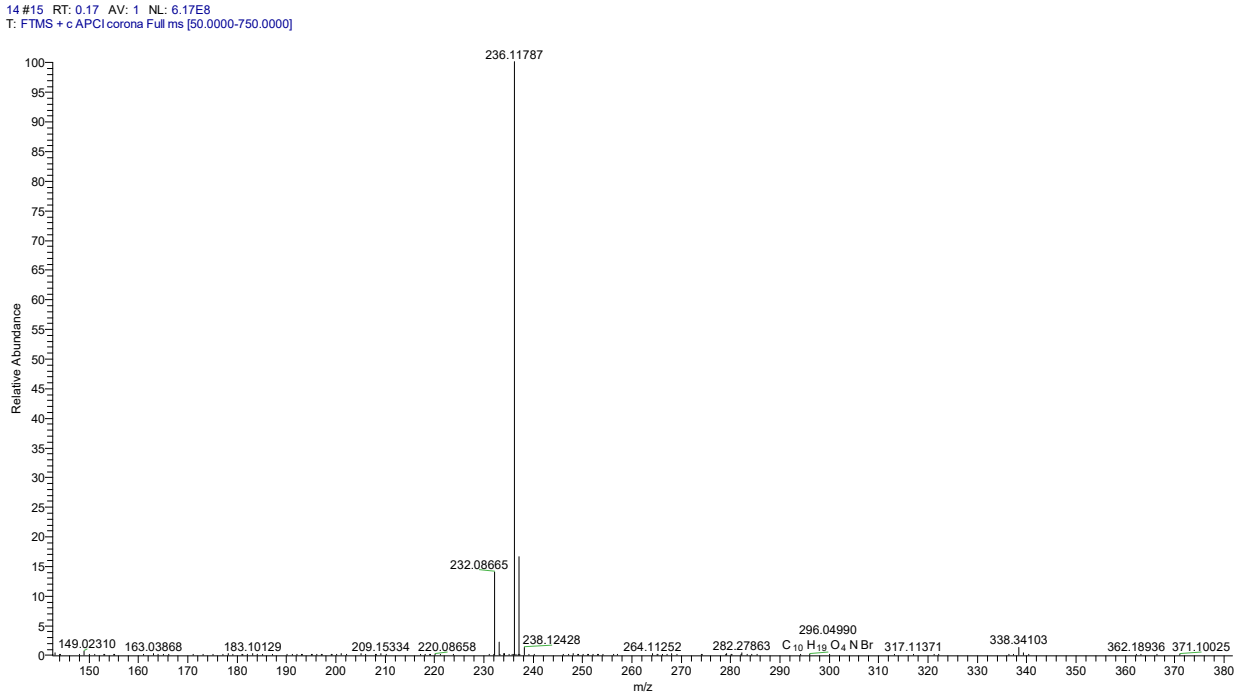
HR-MS spectrum of **C33**

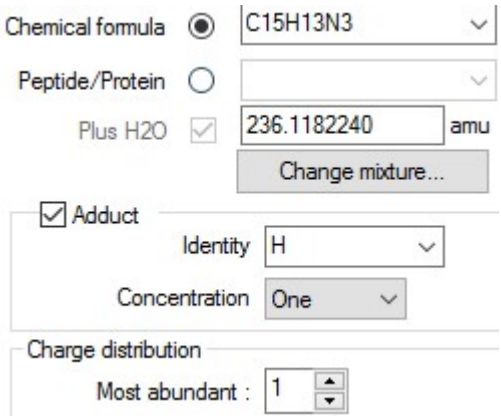




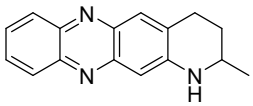
HR-MS spectrum of **C33'**

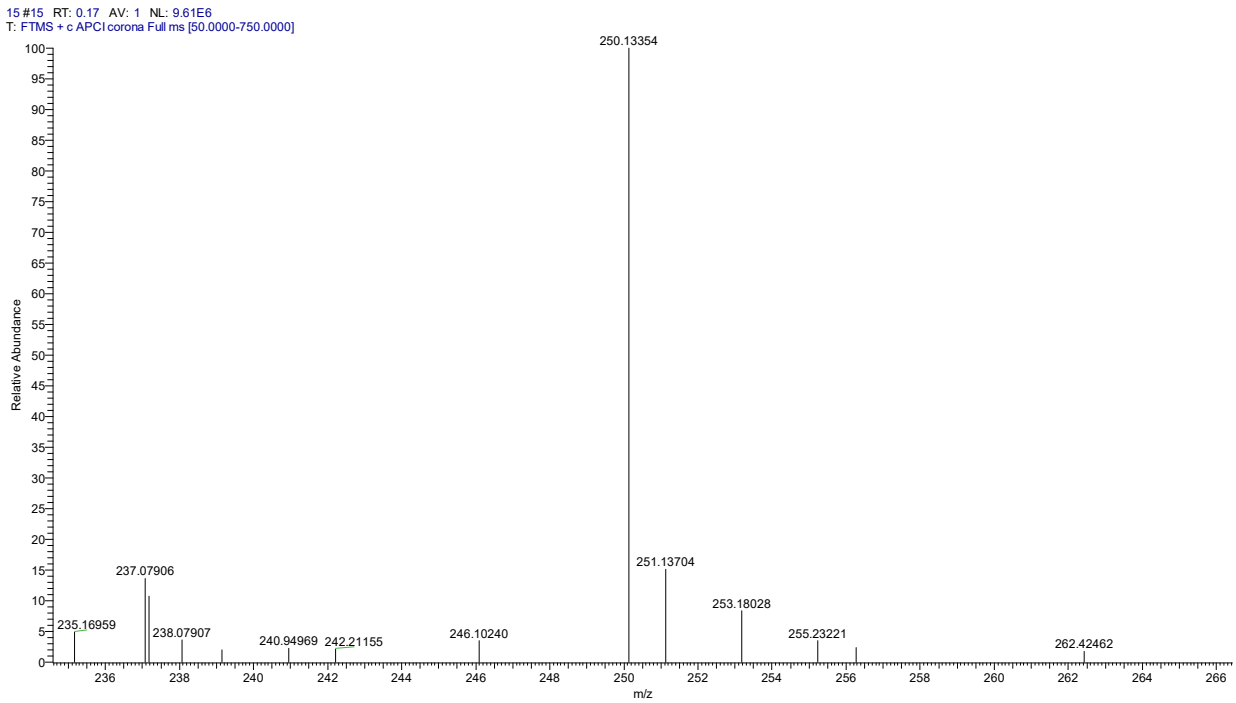


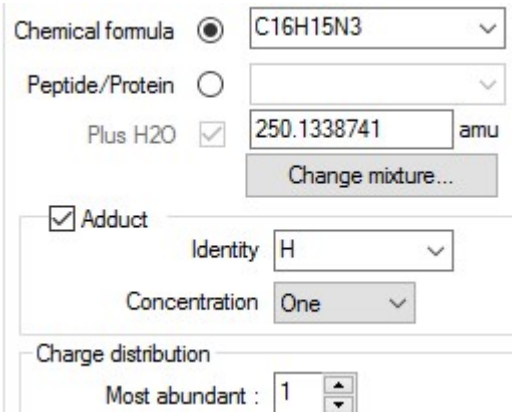




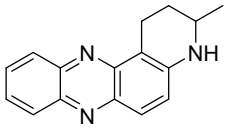
HR-MS spectrum of **C34**

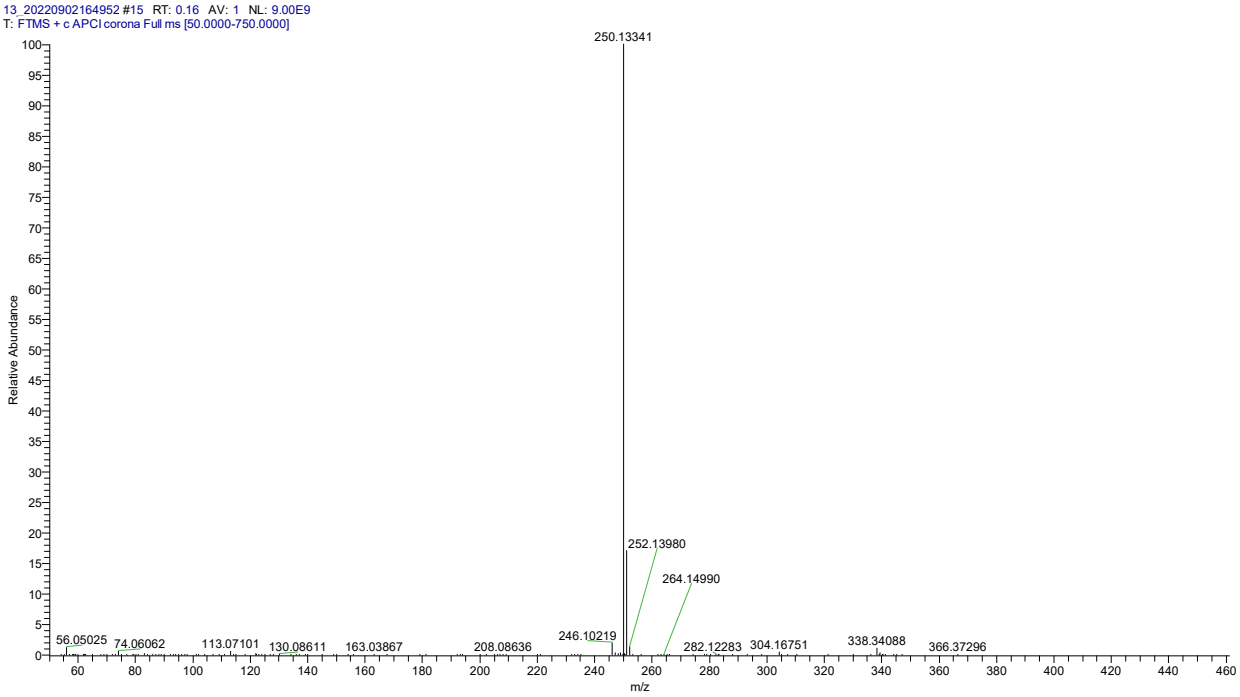




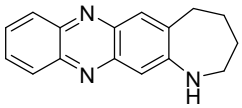


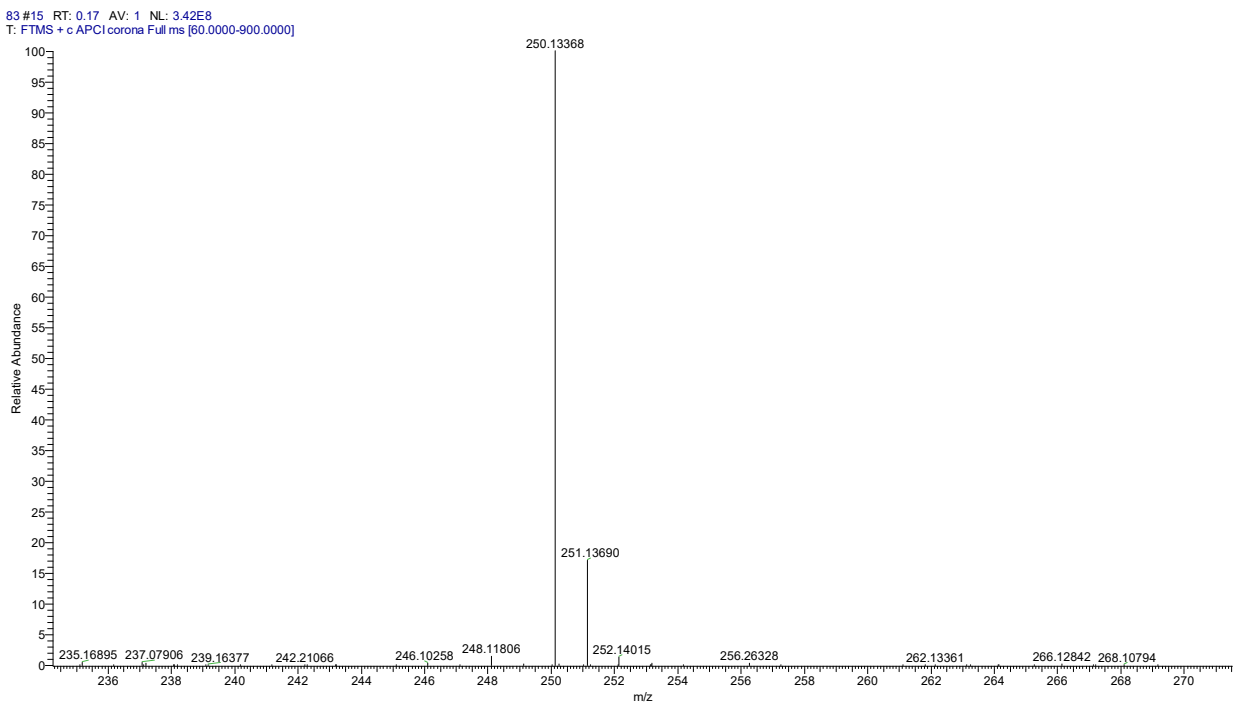
HR-MS spectrum of **C34'**



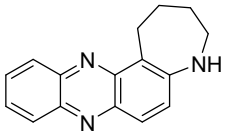


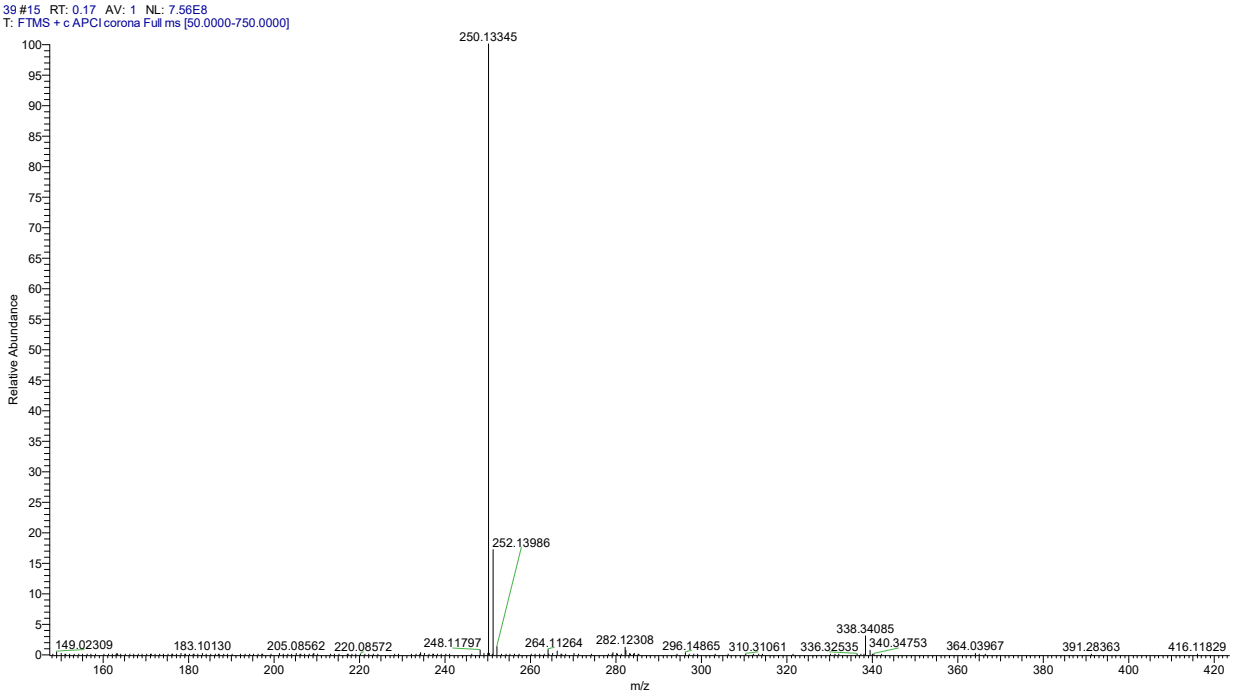
HR-MS spectrum of **C35**

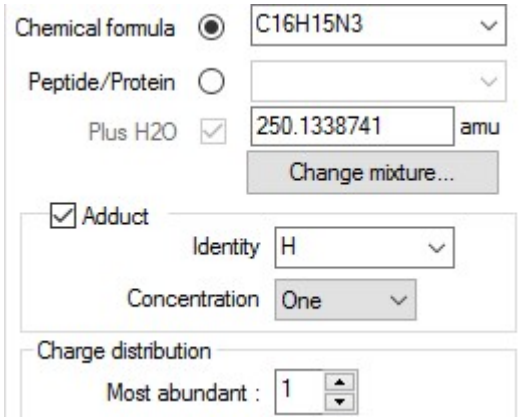




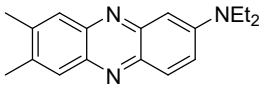
HR-MS spectrum of **C35'**

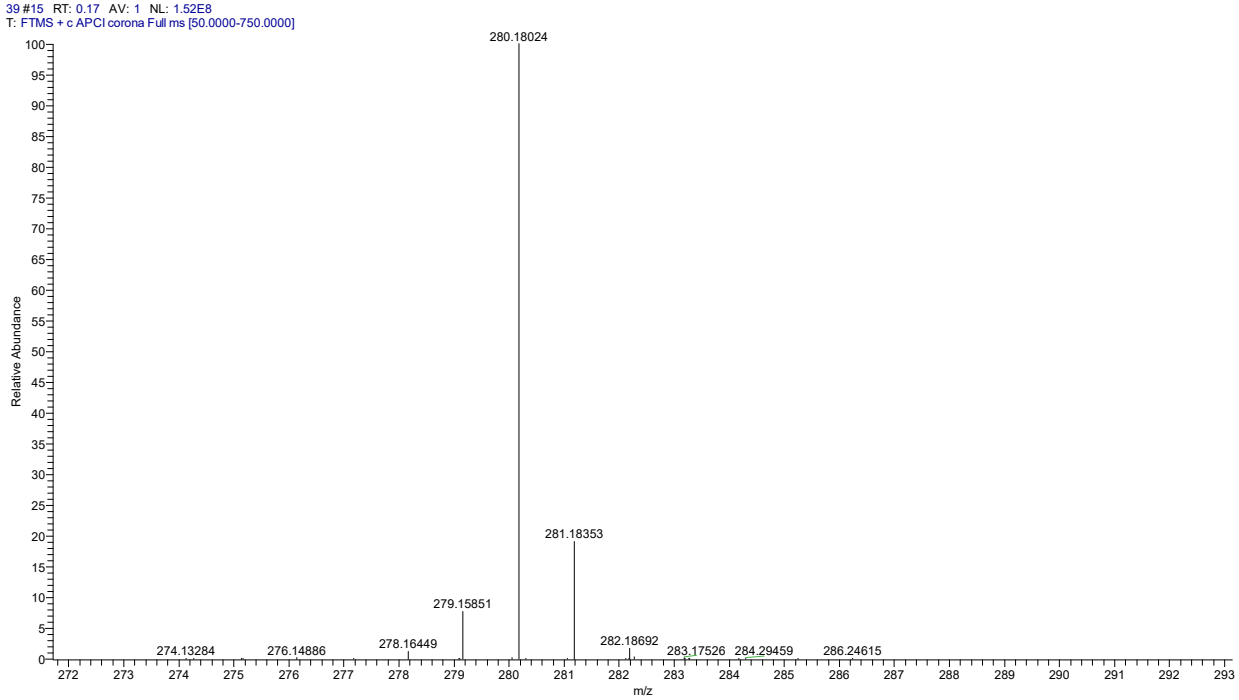


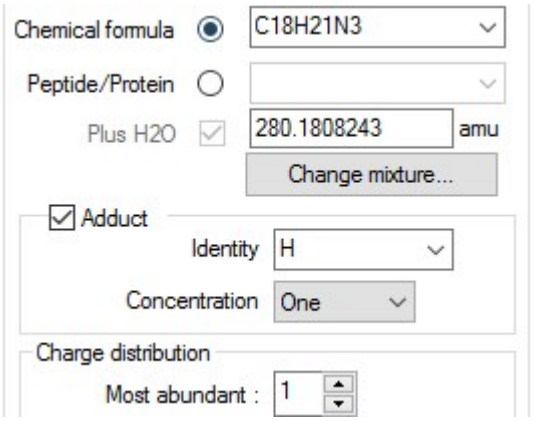




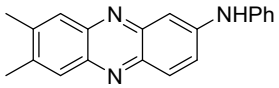
HR-MS spectrum of **C36**

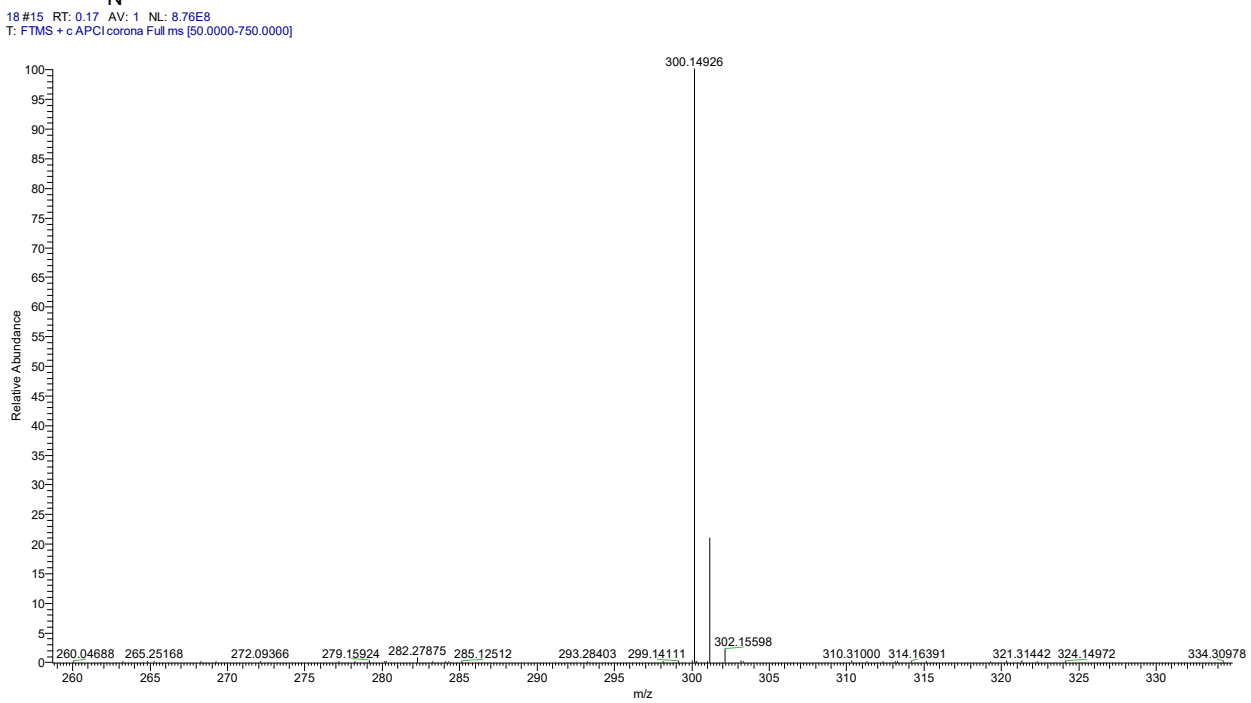


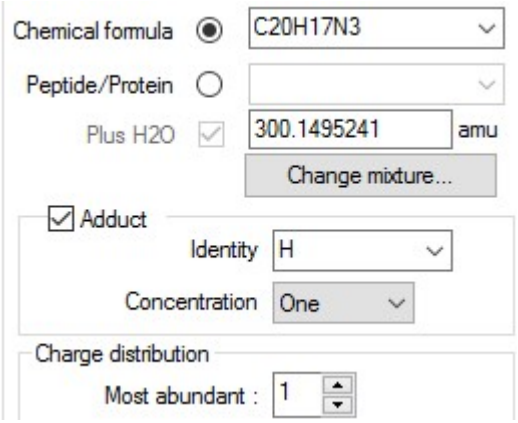




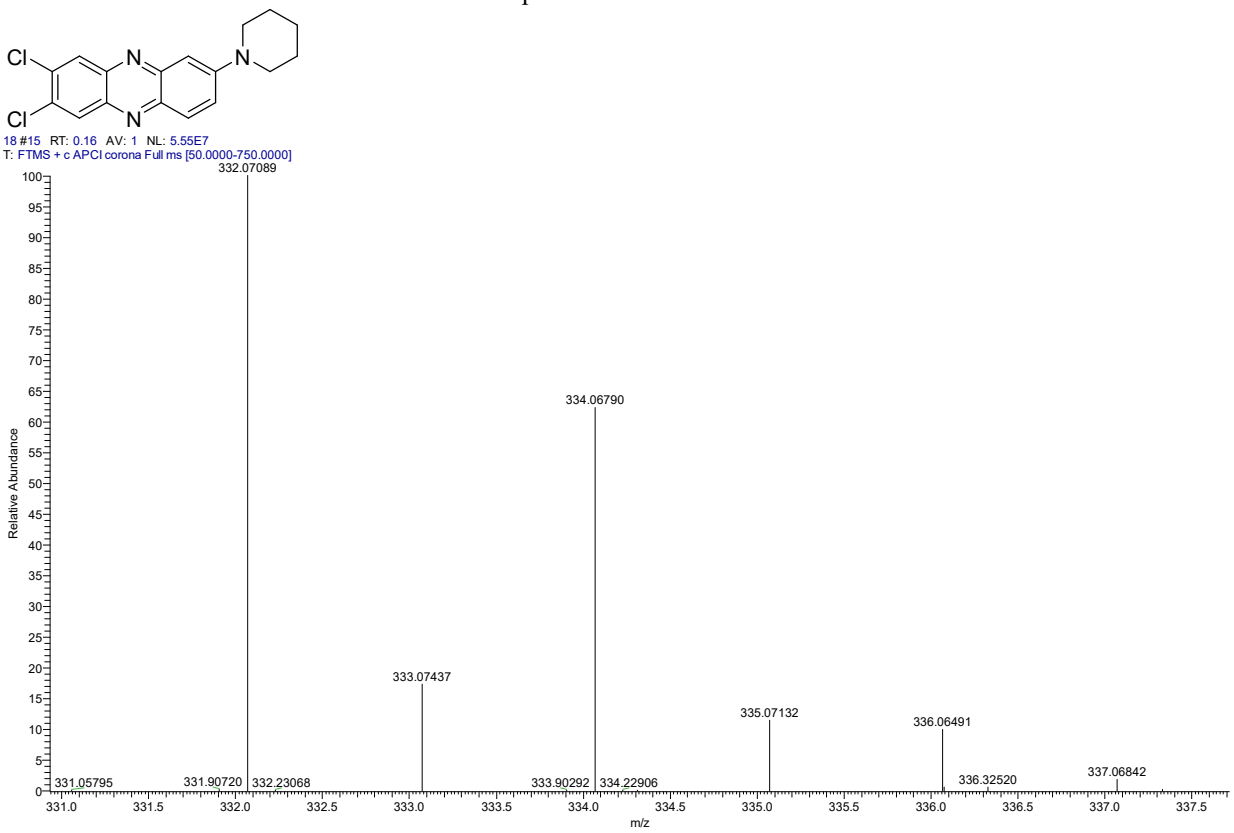
HR-MS spectrum of **C37**

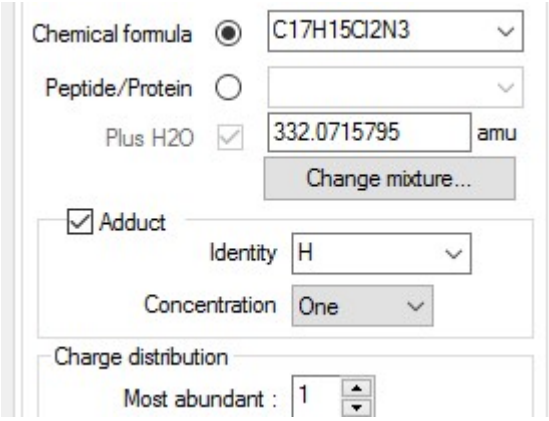




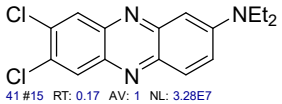


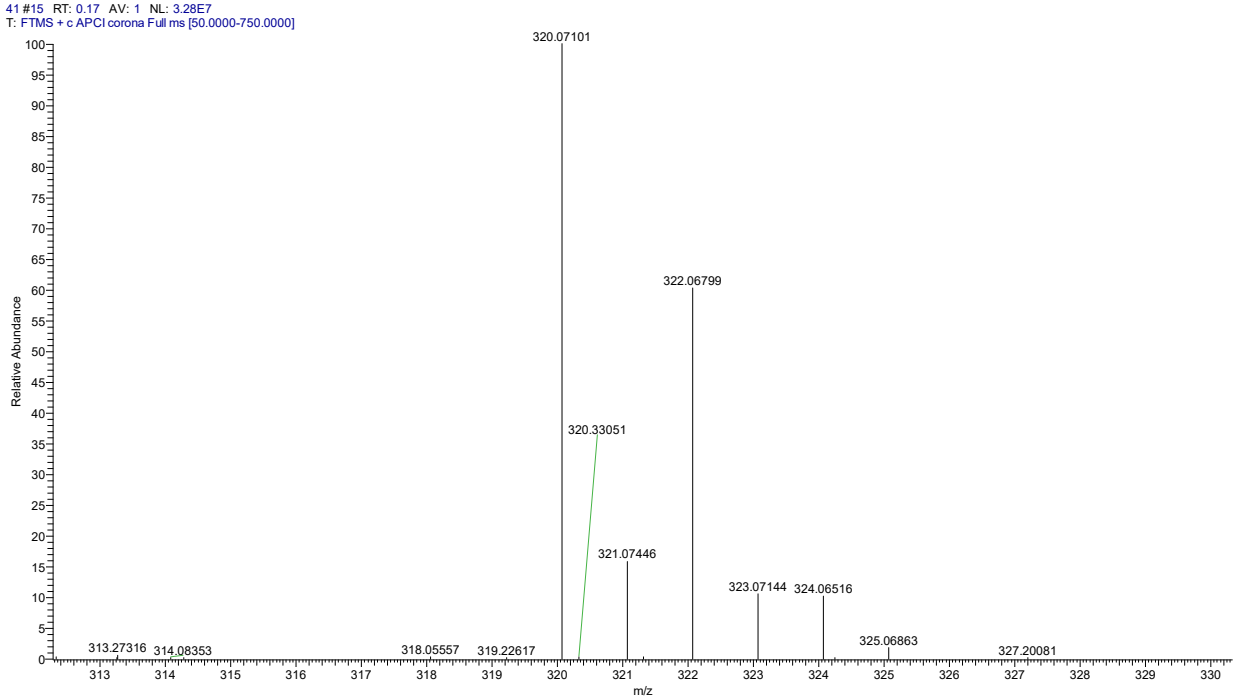
HR-MS spectrum of **C38**

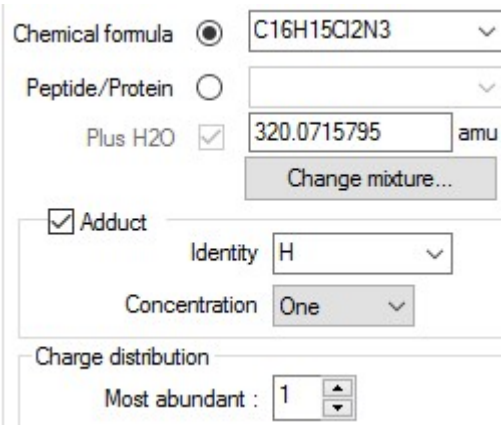




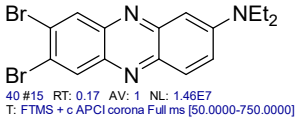
HR-MS spectrum of **C39**

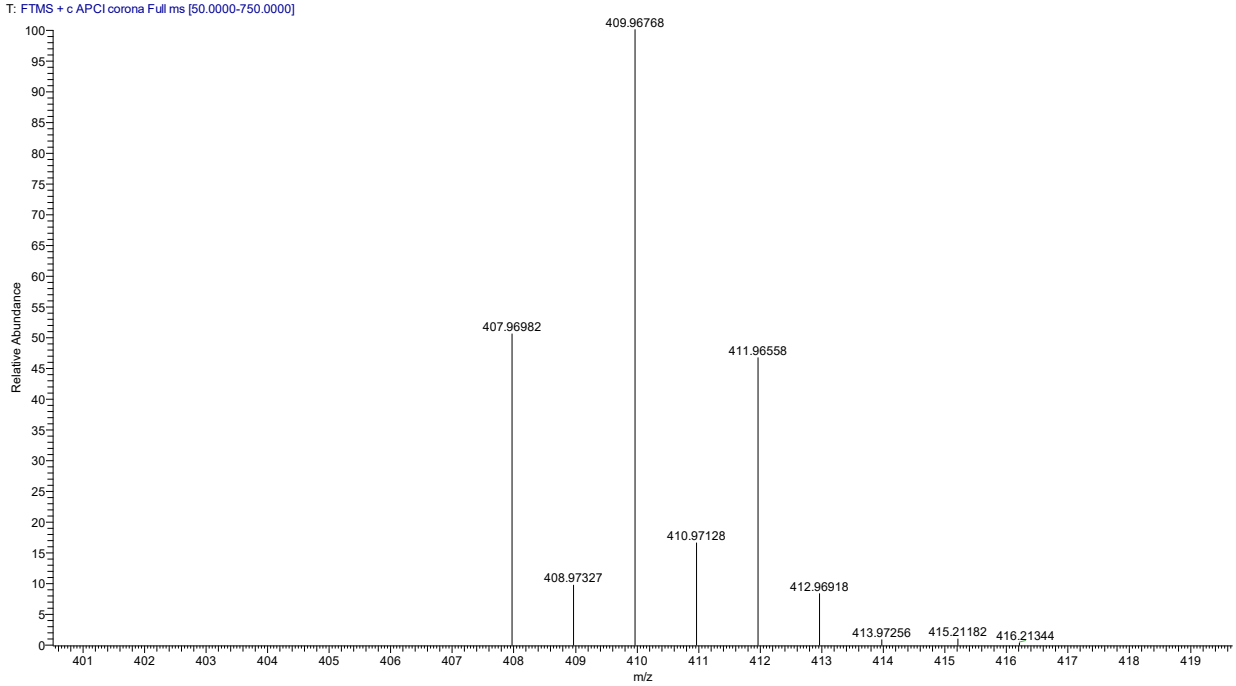


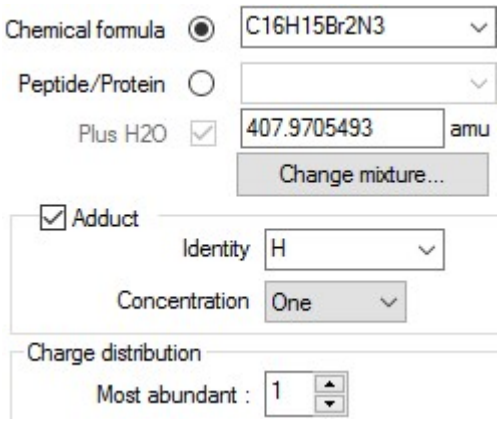




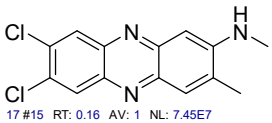
HR-MS spectrum of **C40**

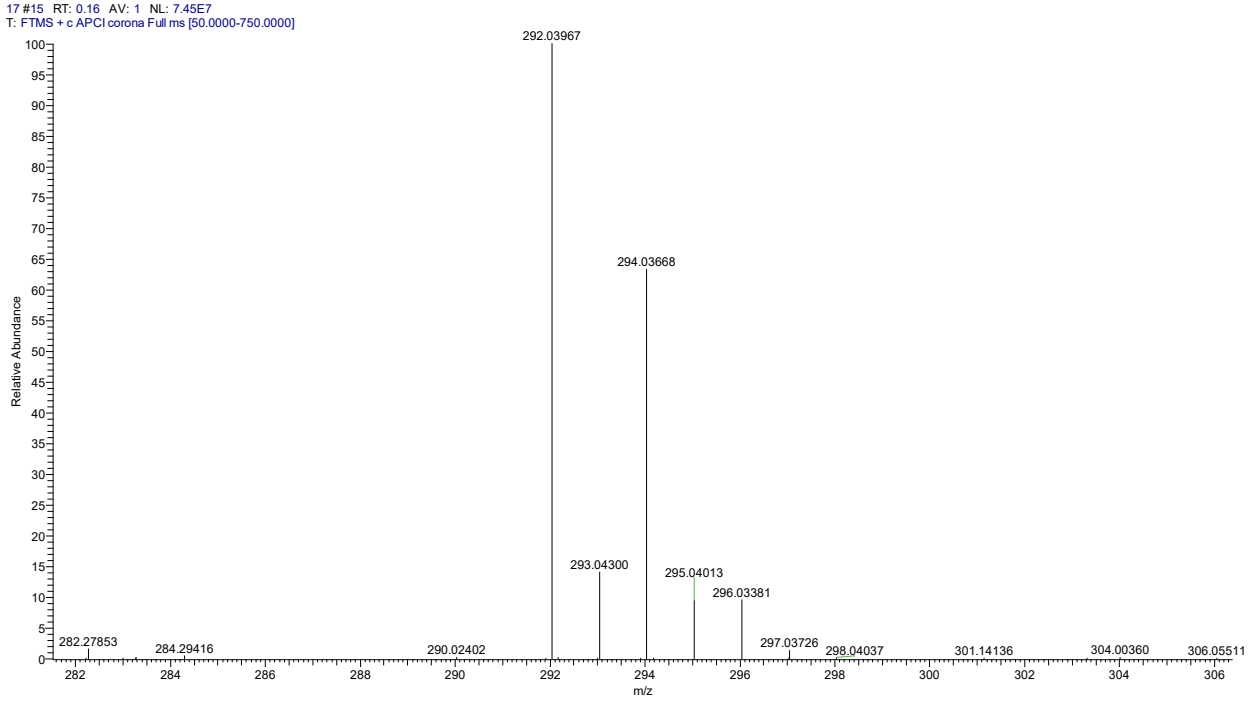


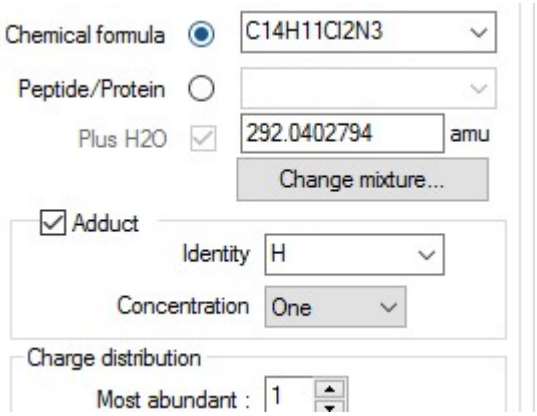




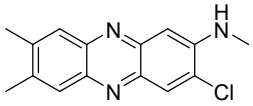
HR-MS spectrum of **C41**



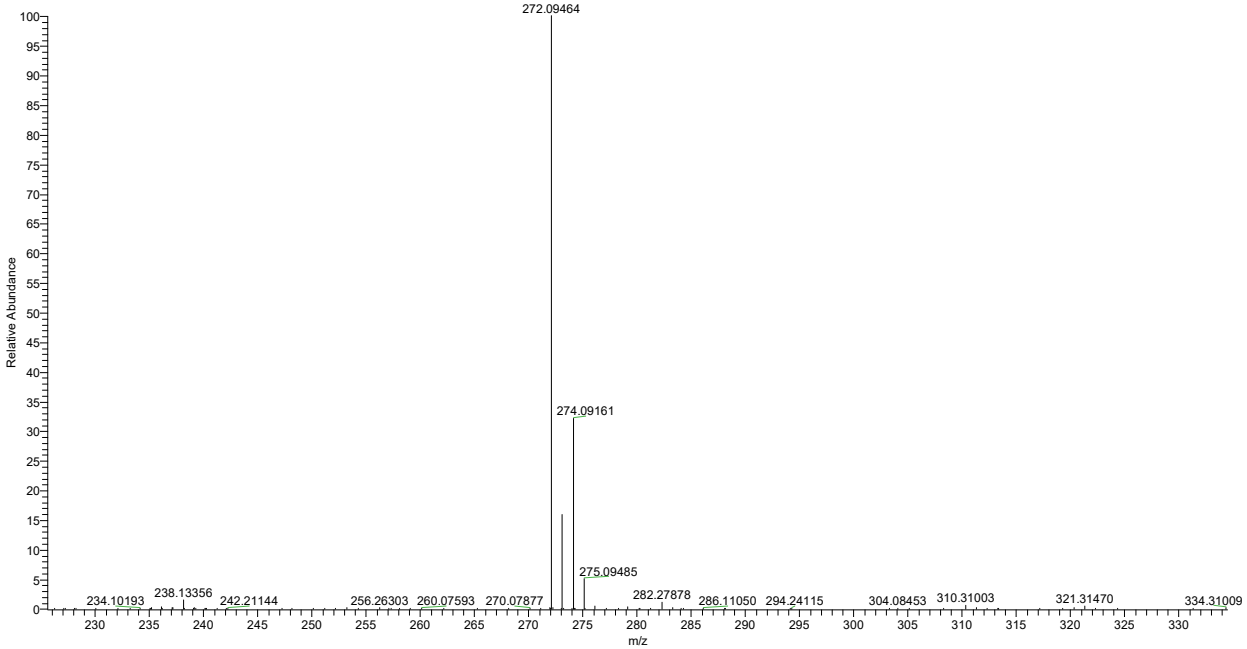


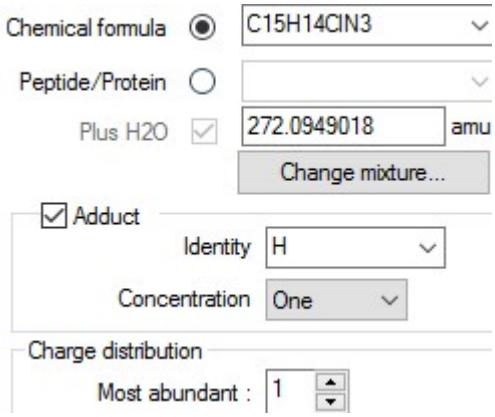


HR-MS spectrum of **C42**

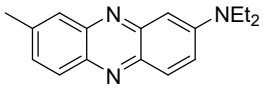


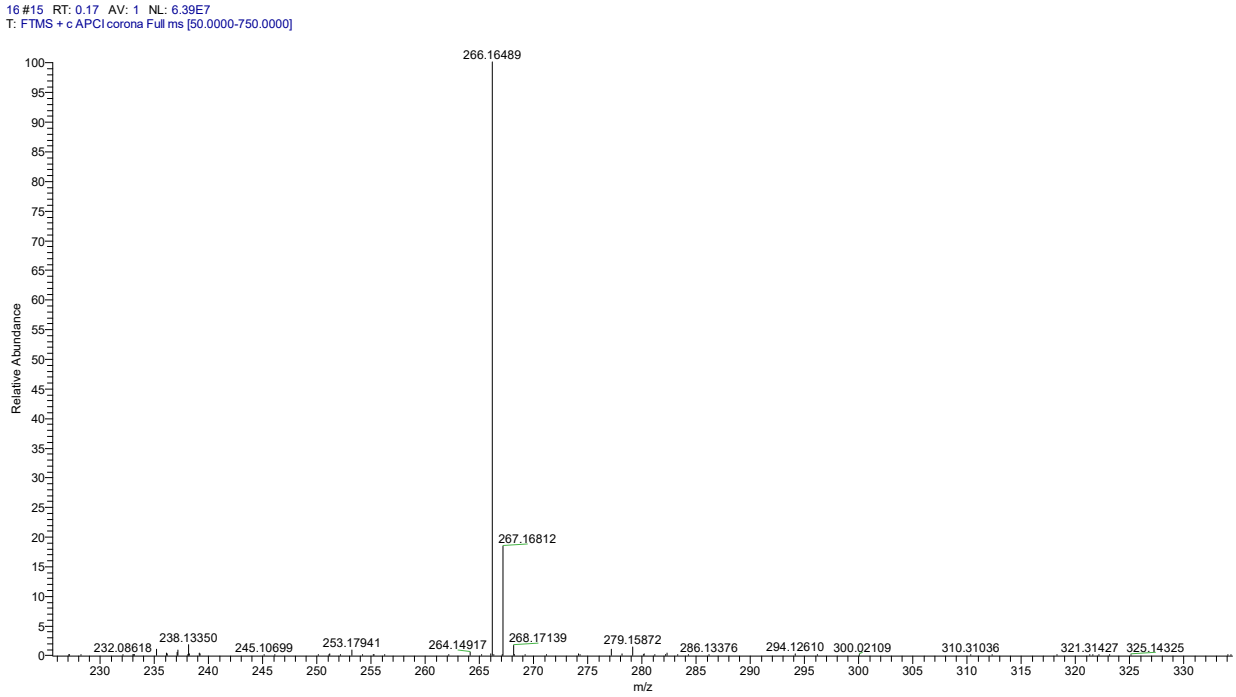
17 #15 RT: 0.17 AV: 1 NL: 4.34E8
T: FTMS + c APCI corona Full ms [50.0000-750.0000]

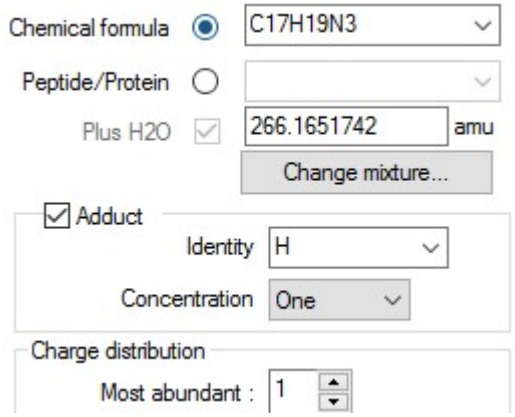




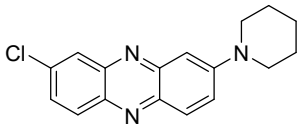
HR-MS spectrum of **C43**

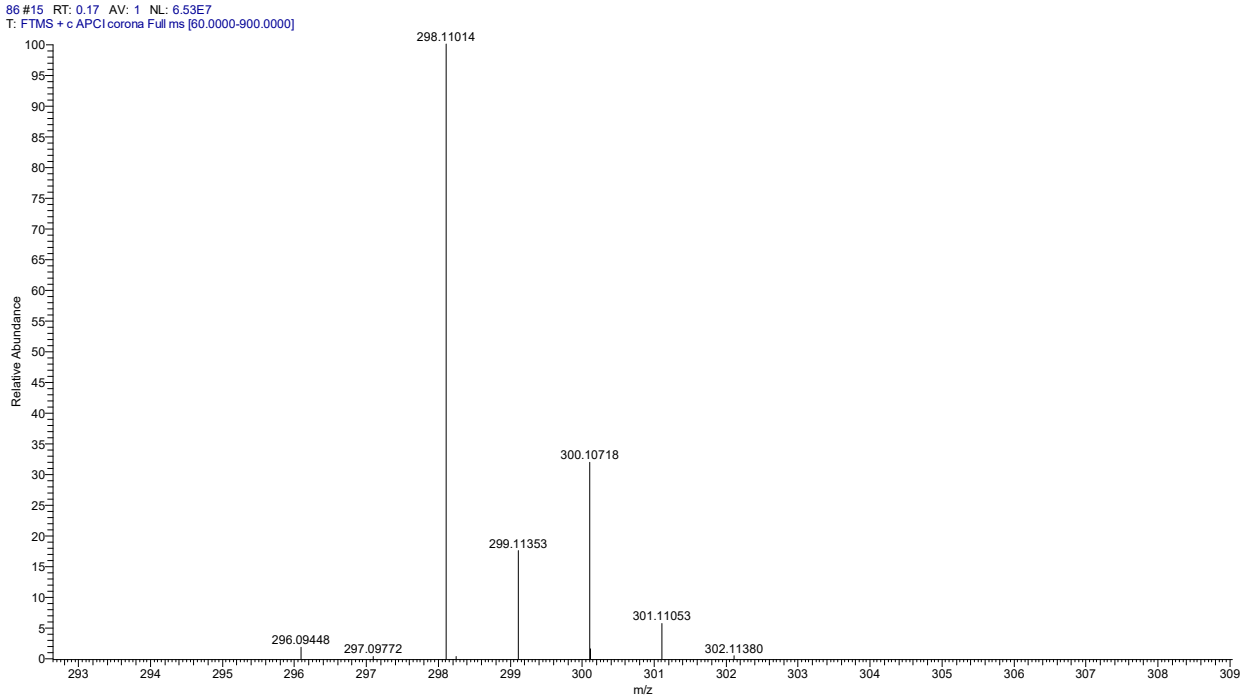


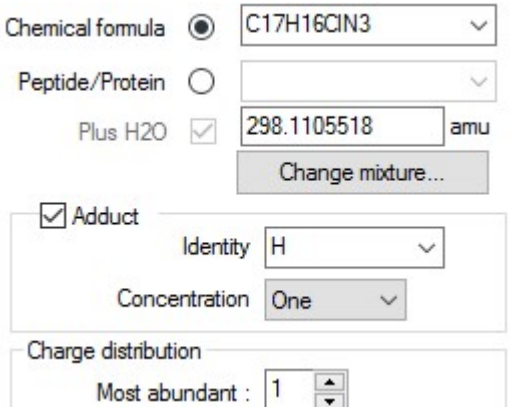




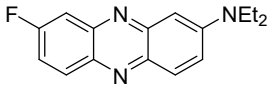
HR-MS spectrum of **C44**

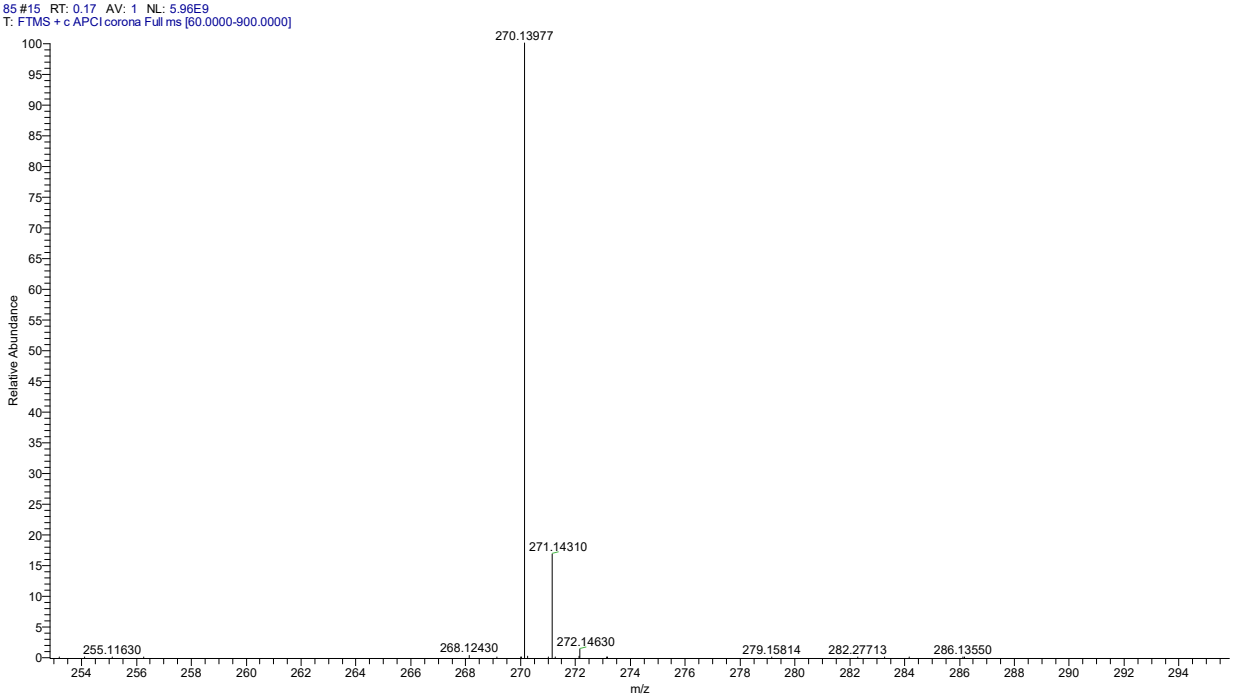


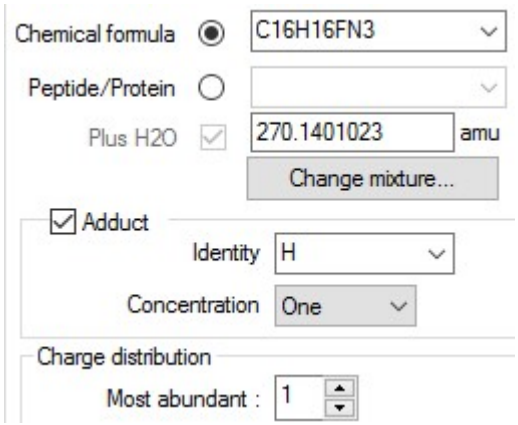




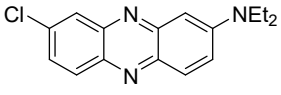
HR-MS spectrum of **C45**

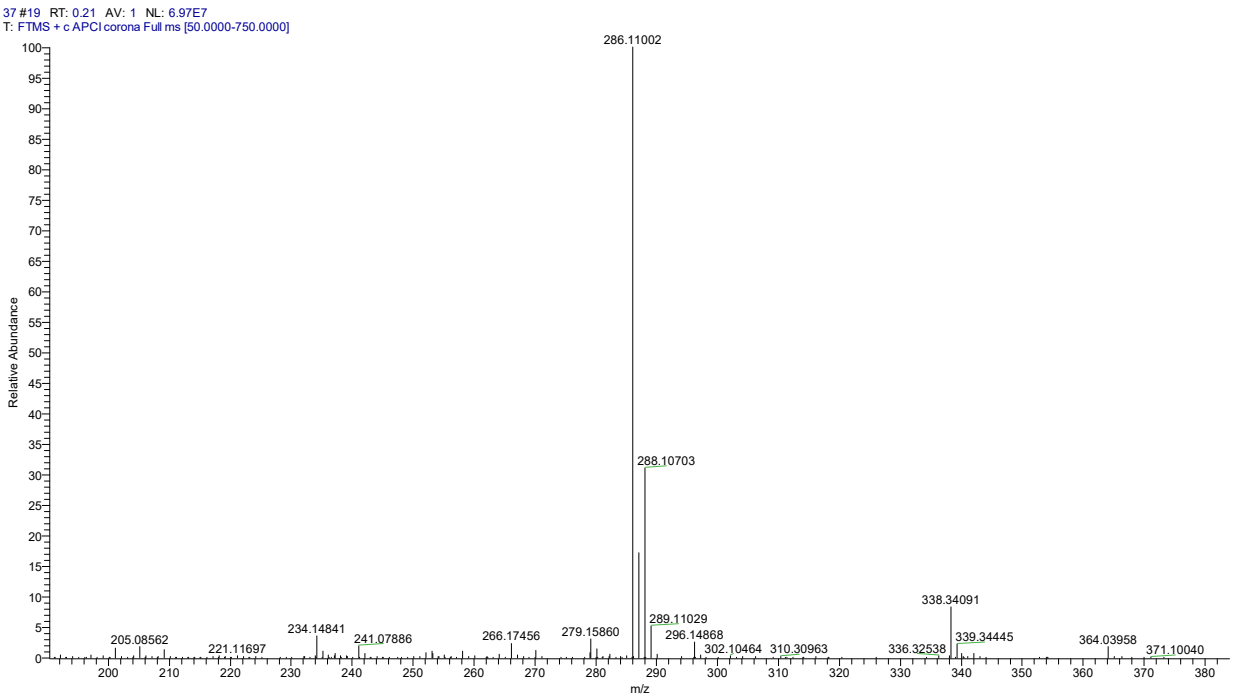


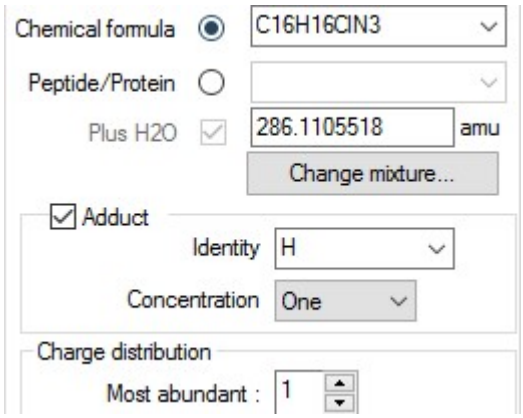




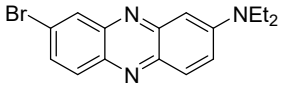
HR-MS spectrum of **C46**

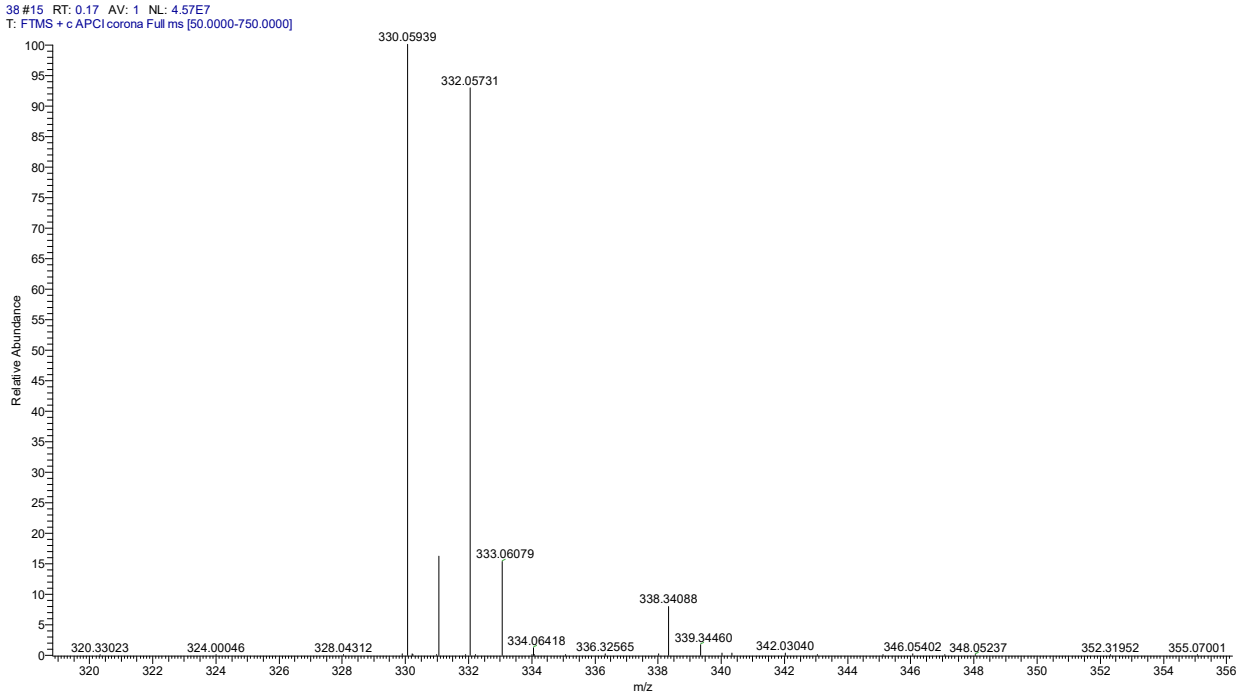


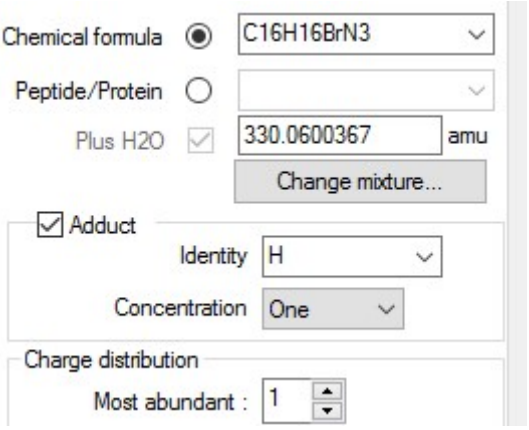




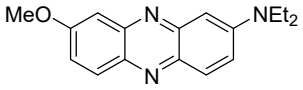
HR-MS spectrum of **C47**

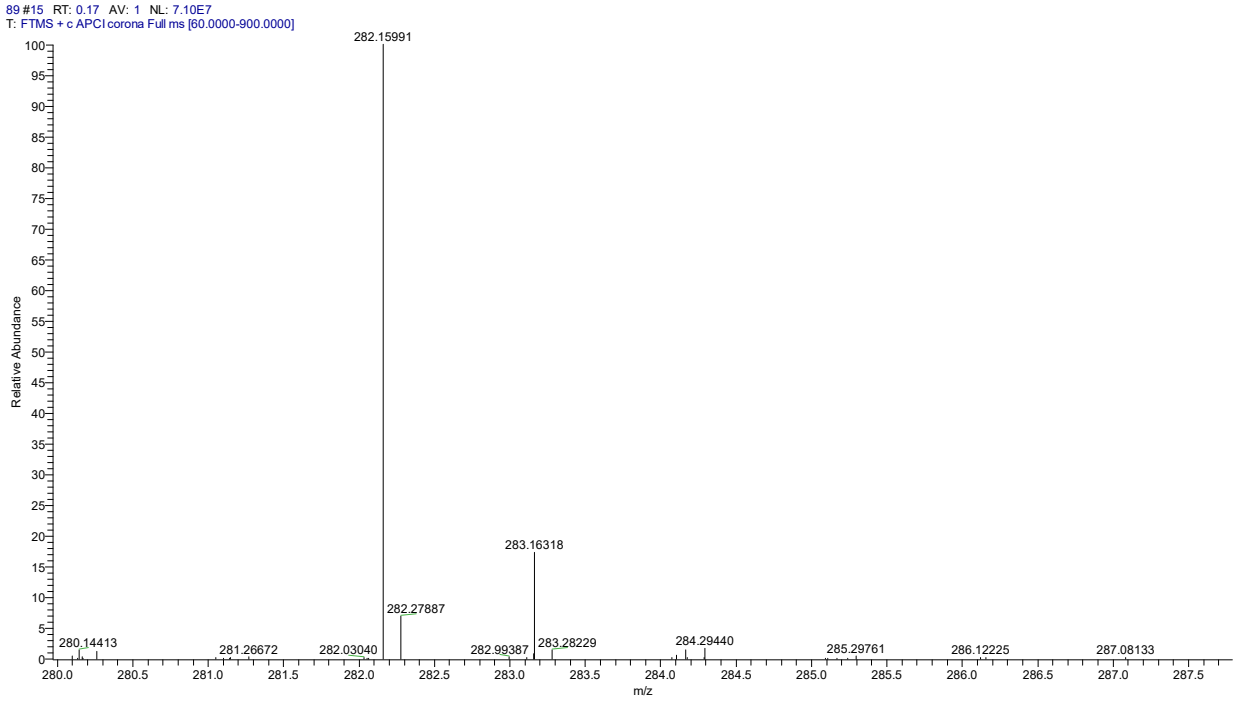


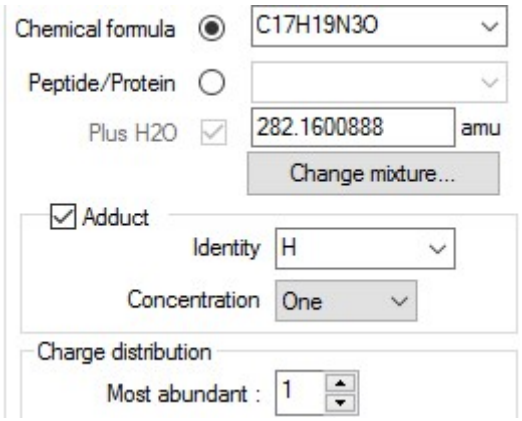




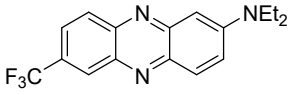
HR-MS spectrum of **C48**

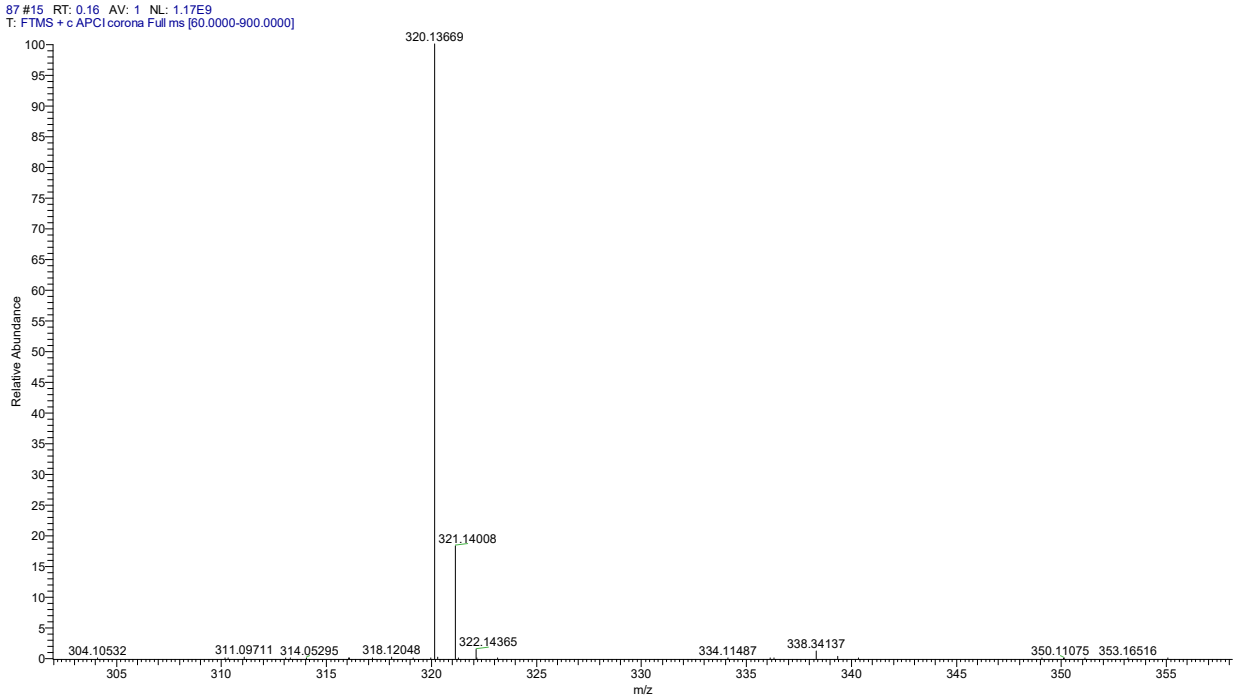


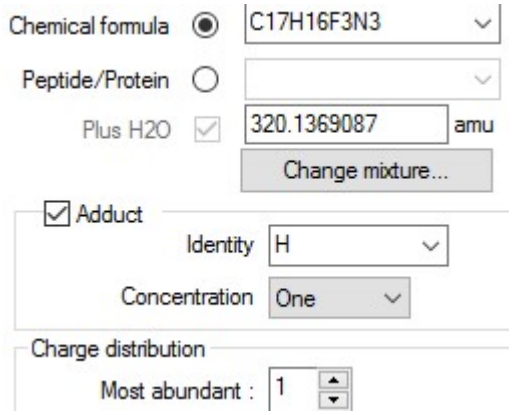




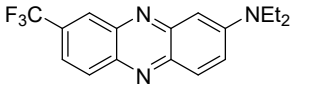
HR-MS spectrum of **C49**

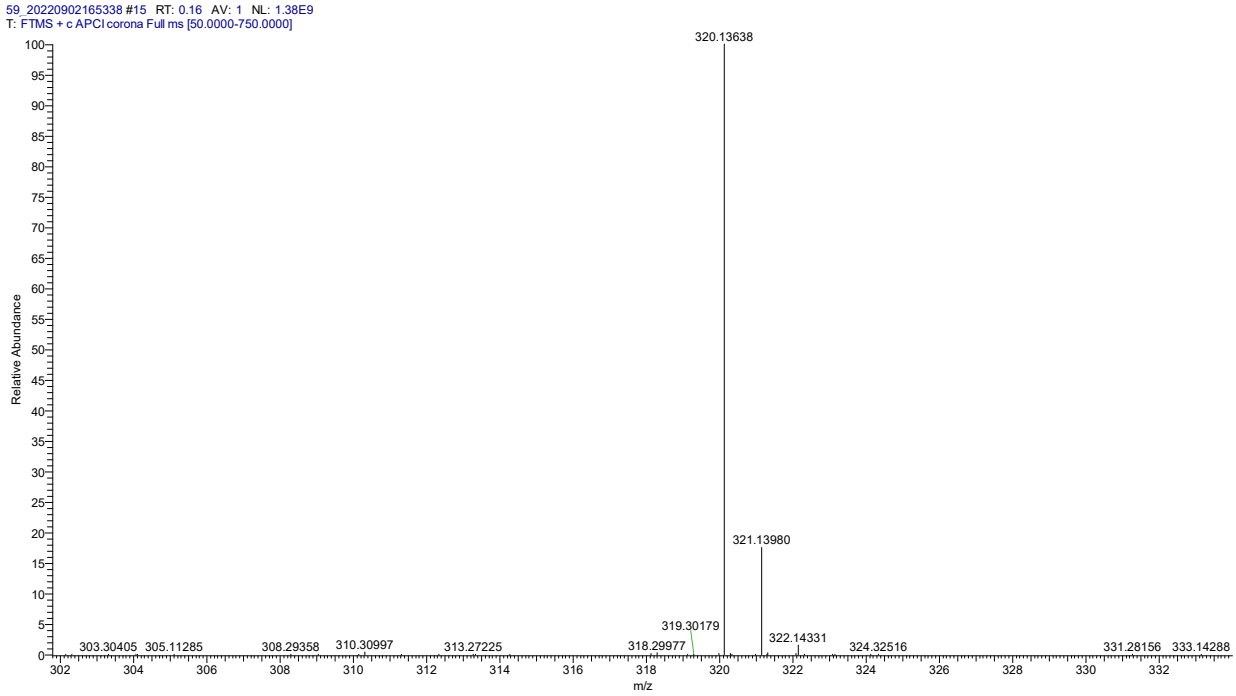


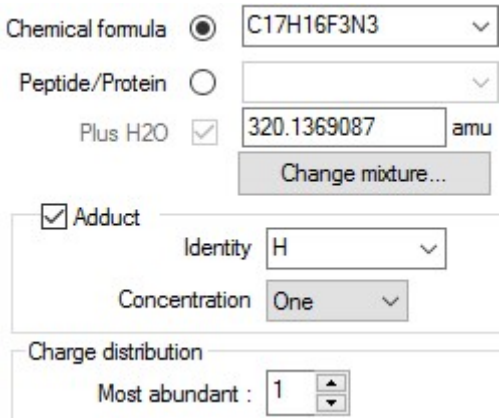




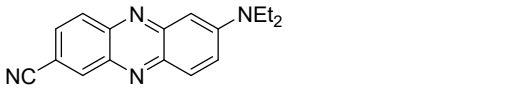
HR-MS spectrum of **C49'**

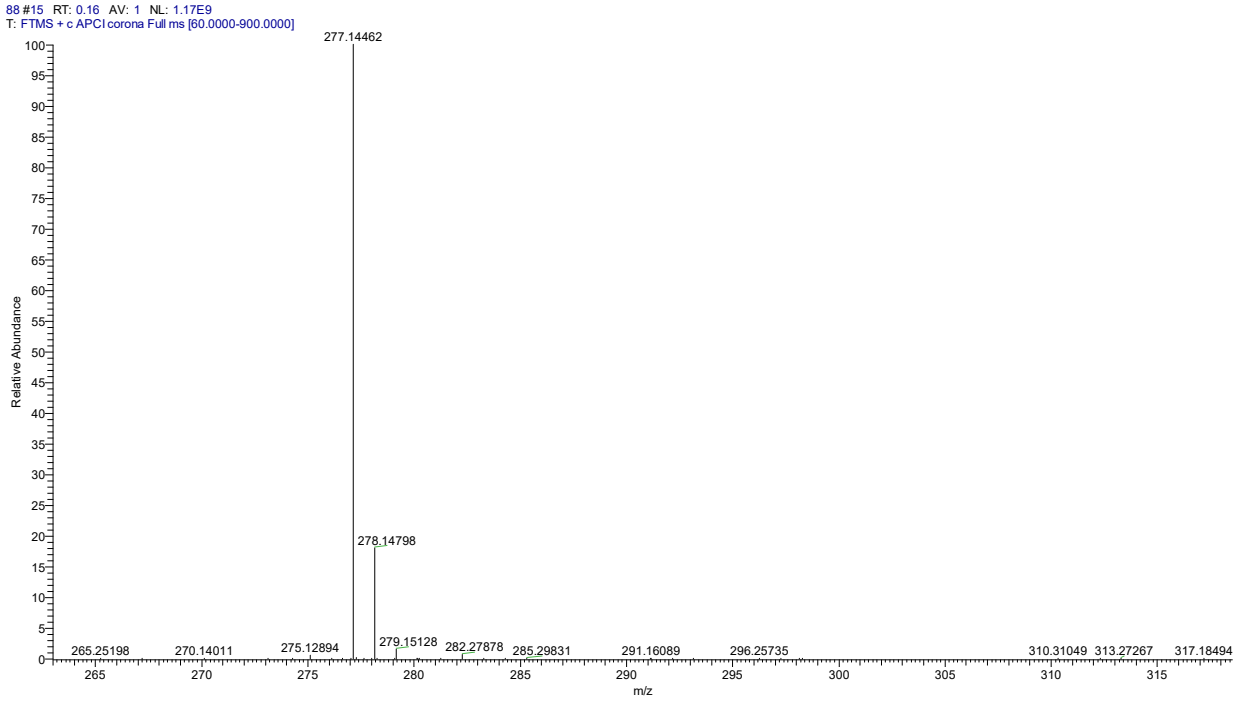


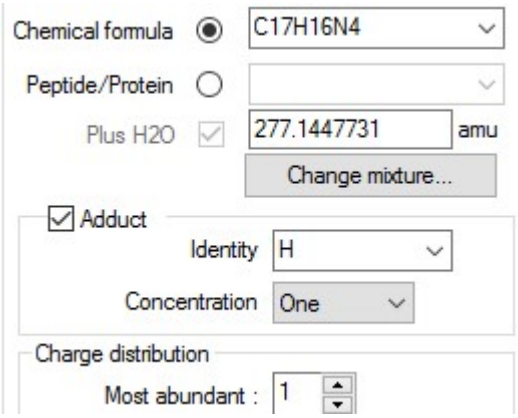




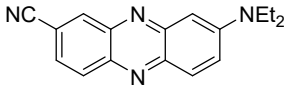
HR-MS spectrum of **C50**

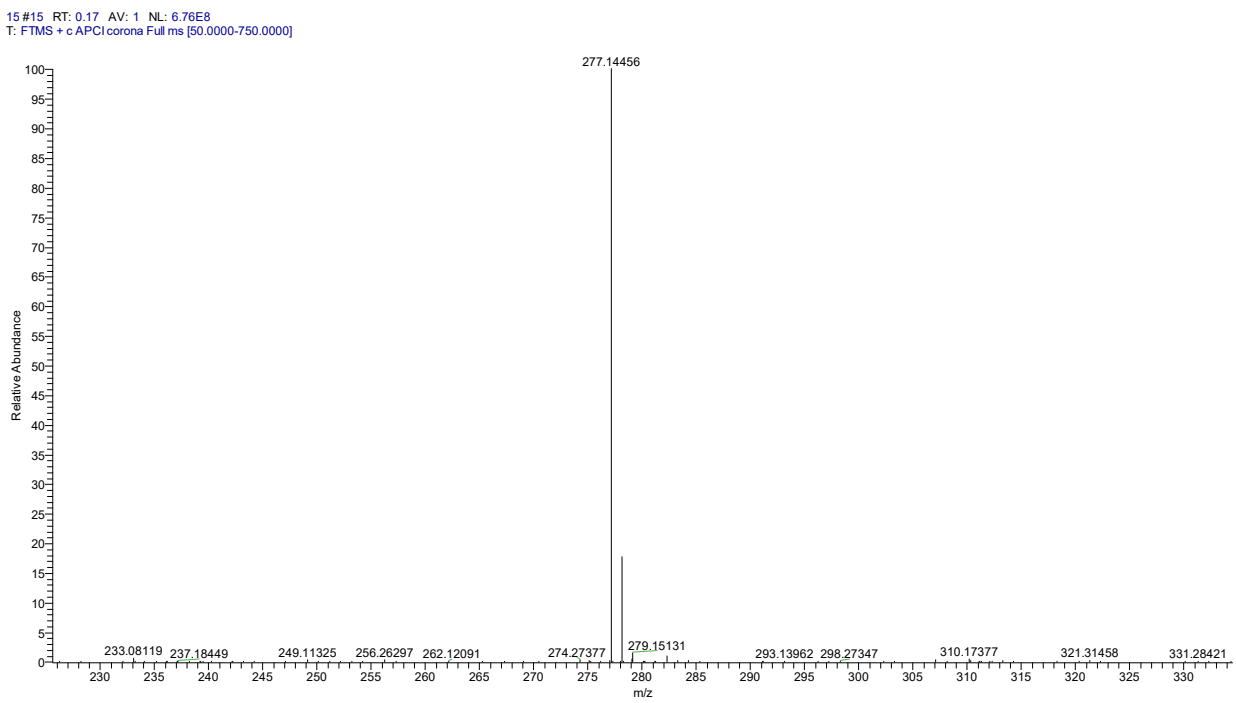


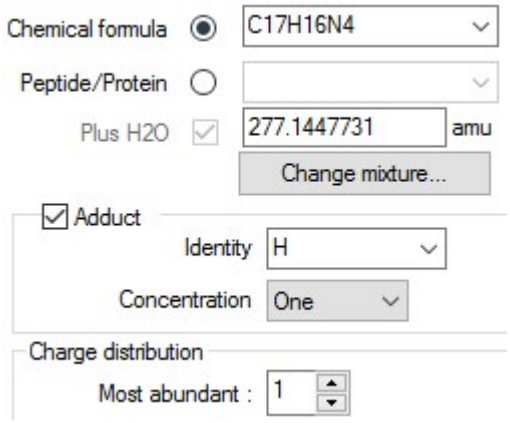




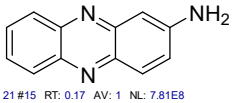
HR-MS spectrum of **C50'**

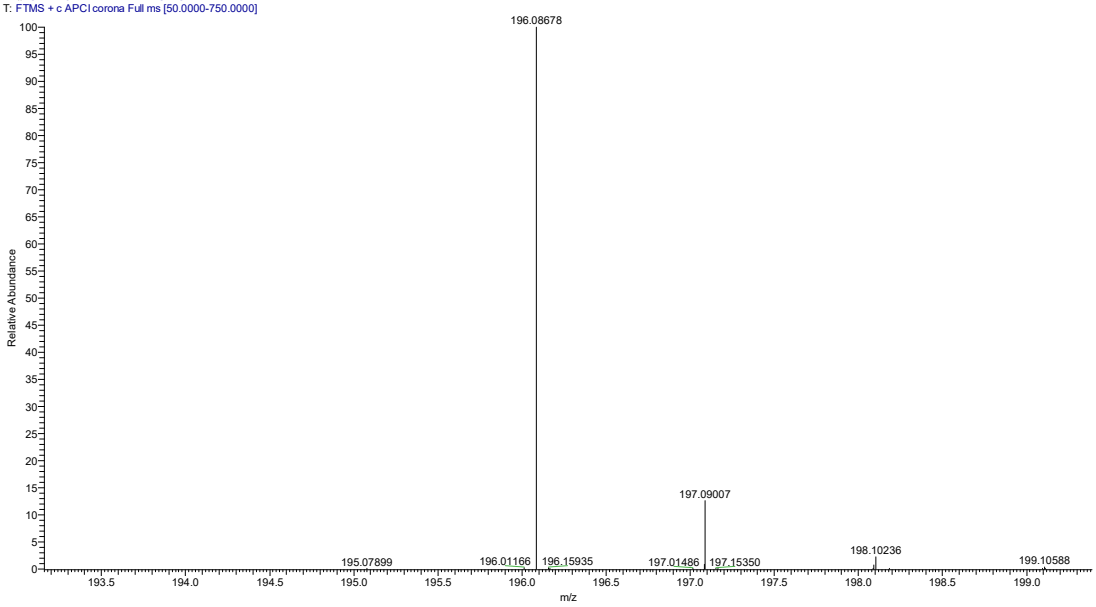


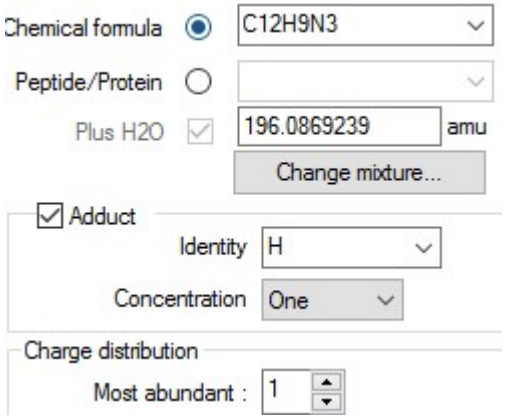




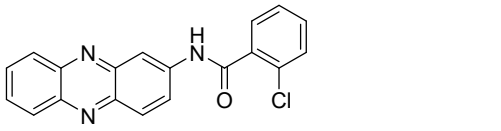
HR-MS spectrum of **C51**

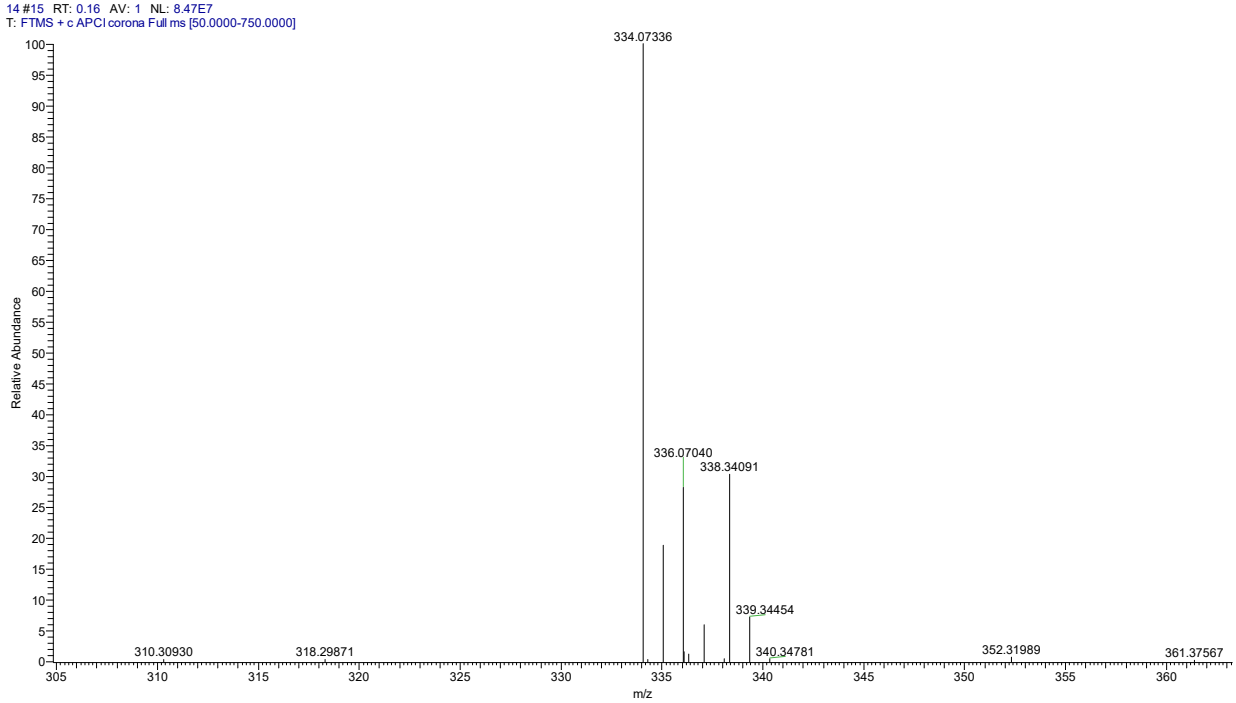


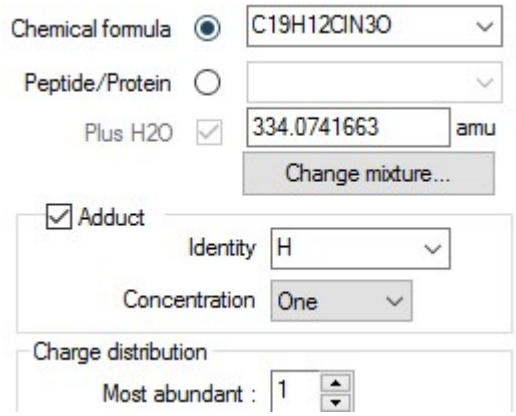




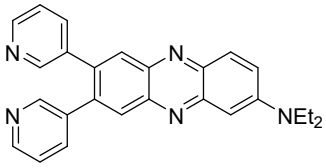
HR-MS spectrum of **C52**

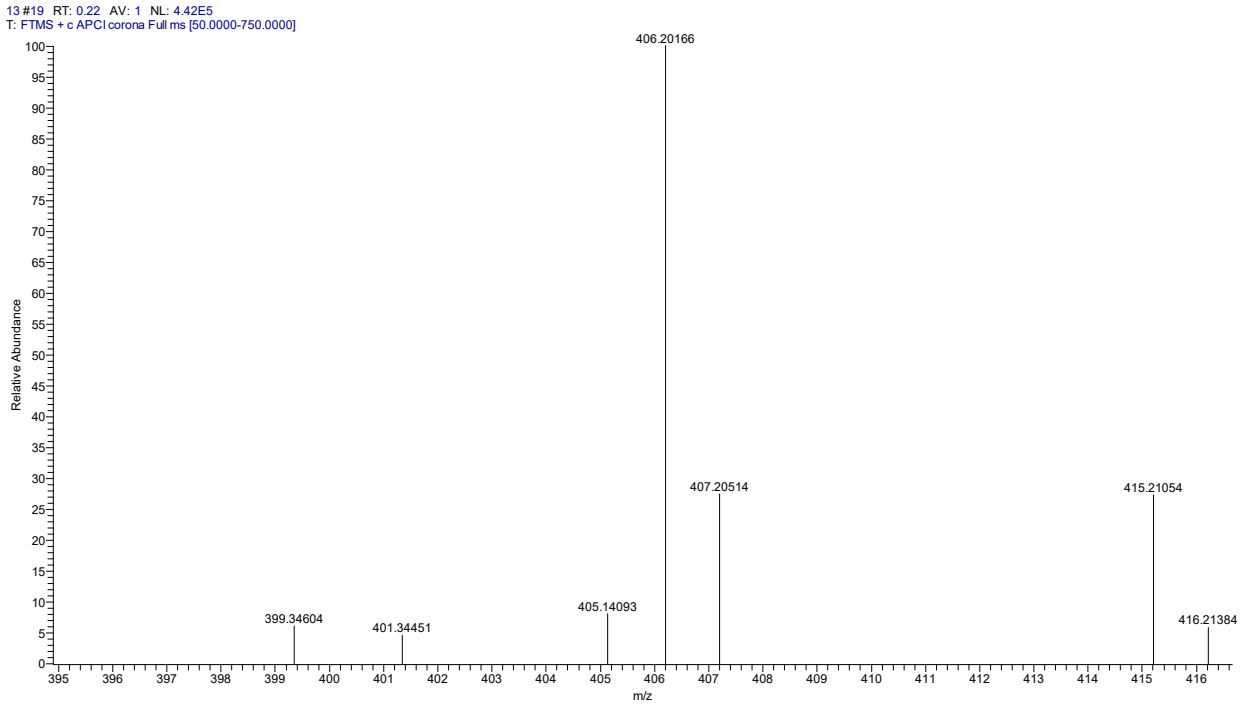


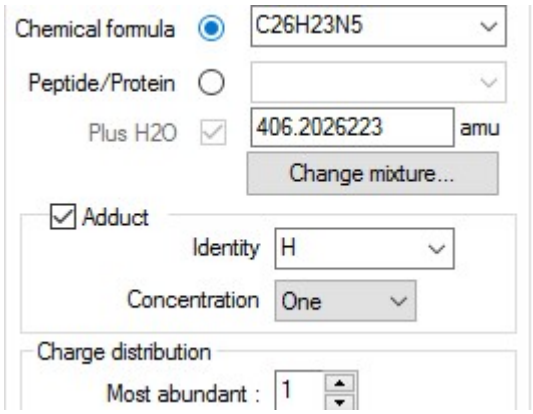




HR-MS spectrum of **C53**







9. DFT calculation

All calculations were carried out using the Gaussian 16 C.01 program package1. The geometry optimizations were performed using hybrid B3LYP exchange correlation2-4, together with the Grimme D3BJ correction term to the electronic energy5,6. The 6-311G** basis set7-9 was used for all atoms. Vibrational frequency calculations were performed to characterize the nature of each stationary point and to make the zero-point energy (ZPE) corrections. A tight convergence (10-12 au) criterion was employed, and the solvent hexafluoropropanol (HFIP) (ε= 5.10) was considered using the SMD10 continuum solvent model (UFF radii).

References

1. Frisch, M. J., et al. Gaussian 16; Gaussian, Inc., Wallingford, CT, 2016.
2. A. D. Becke, *Phys. Rev. A*,1988, **38**, 3098–3100.
3. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.
4. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
5. S. Grimme, J. Anthony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
6. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456−1465.
7. M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees and J. A. Pople, *J. Chem. Phys*., 1982, **77**, 3654–3665.
8. W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys*., 1972, **56**, 2257–2261.
9. P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*., 1973, **28**, 213–222.
10. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.

Table S2. Calculated energies, Mulliken analysis, and WFRT analysis [a]

	C1-2'	**C1-2**
w%[b]	3.99%	14.50%
Δ E/kcal/mol	0.00	-34.74

a. ref [Y. Wang, *J. Comput. Chem.* 2021, **42**, 412-417; Y. Wang, P*hys. Chem. Chem. Phys.*, 2021, **23**, 2331-2348]
b. projection-weighted symmetric orthogonalization (PWSO)%

The calculation for the weights of resonance forms was performed by wave-function-based resonance theory (WFRT) with PWSO approach, the results show that **C1-2** is more stable than **C1-2'** (ΔE = -34.74 kcal/mol), and **C1-2** has a significantly higher distribution ratio (14.50%) than that of **C1-2'** (3.99%).

Table S3. Cartesian coordination and absolute energy for C1-2 and C1-2'.

E +ZPE = -786.7293113 a.u

C	-3.99999900	-0.99375400	0.84595200
C	-2.99681300	-0.55093700	-0.02165000
C	-3.17258300	0.62047100	-0.79098600
C	-4.35758900	1.35033500	-0.60083000
C	-5.33504300	0.91494100	0.27837100
C	-5.16919500	-0.26855600	1.00242200
H	-3.83637500	-1.90540200	1.40955600
H	-4.50687100	2.25912900	-1.17361300
H	-6.24255600	1.49573400	0.39254200
H	-5.93670300	-0.61159500	1.68397300
N	-1.82880000	-1.34866200	-0.17030200
H	-1.98546800	-2.33582800	-0.33593500
C	-0.53877200	-0.98049800	0.03583600
C	0.49897000	-1.91393100	-0.22736200
C	-0.18048200	0.31004300	0.50260000
C	1.81217400	-1.57797600	-0.05742300
H	0.24109900	-2.90846400	-0.57457400
C	1.13331500	0.64450800	0.68195900
H	-0.95422900	1.03065000	0.72189800
C	2.18894100	-0.27816200	0.40376100
H	2.56694400	-2.31750800	-0.27569300
H	1.36324400	1.63840100	1.03474600
N	-2.19646900	1.06484900	-1.66747600
H	-1.61424600	0.35449200	-2.08785100
H	-2.50445600	1.75199100	-2.34036400
N	3.48858400	0.06217600	0.57349200
C	4.58116600	-0.82807300	0.14254100
H	5.48113400	-0.48511900	0.65015700
H	4.38326400	-1.83623100	0.51084900
C	4.79956700	-0.82803200	-1.37025900
H	3.91510000	-1.16838700	-1.91167600
H	5.05536400	0.16918400	-1.73154100
H	5.62564500	-1.49981600	-1.61638700
C	3.87706100	1.38044300	1.10287200
H	4.84078000	1.24976500	1.59472200
H	3.16867900	1.66243700	1.88132400
C	3.97381700	2.46206700	0.02743500
H	4.75992000	2.23505000	-0.69484800
H	3.03298600	2.57644100	-0.51455100
H	4.21633800	3.41919500	0.49584400