Supporting Information

Inherently Chiral *Nor*-Heteracalixarenes: Design and Synthesis via Enantioselective Intramolecular Suzuki-Miyaura Reaction

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1. General information

NMR spectra were recorded on a JEOL ECX-400 400 MHz NMR spectrometers. ^{1}H NMR chemical shifts were reported relative to residual $CDCl_3$ (7.26 ppm), acetone-d_6 (2.09 ppm), tetrachloroethane-d_2 (6.00 ppm) or DMSO-d_6 (2.50 ppm). ^{13}C NMR chemical shifts were reported relative to the central line of $CDCl_3$ (77.16 ppm), acetone-d_6 (29.84 ppm), tetrachloroethane-d_2 (73.78 ppm) or DMSO-d_6 (39.52 ppm). Abbreviations are used in the description of NMR data as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, and br = broad), coupling constant (J, Hz). The high resolution mass spectra (HRMS) were recorded on a GCT-MS Micromass UK spectrometer or a microTOF-Q spectrometer. Infrared spectra were recorded using a PerkinElmer Spectrum 100 FT-IR spectrometer with KBr pellets in the 4000-400 cm^{-1} region. All yields reported were isolated yields. Enantiomeric excesses were determined by HPLC using Daicel chiral stationary phase columns by comparing the samples with the appropriate racemic samples at 25 ^{o}C, column and elution details specified in each entry. The optical rotation was determined by Rudolph Autopol VI Automatic polarimeter. Melting points were uncorrected.

Unless otherwise stated, reagents and solvents were purchased from commercial sources and preserved under argon. More sensitive compounds were stored in a desiccator or glove box if required. Reagents were used without further purification unless otherwise noted. All reactions were performed under argon (or nitrogen) and stirring unless otherwise noted. When needed oven-dried glassware was used (T°>100 °C) or under vacuum with a heat gun (T°>200 °C). Anhydrous solvents were purified and dried following standard procedures. Reactions were monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 F254. Compounds were visualized by UV-light 254 nm and by dipping the plates in an ethanolic phosphomolybdic acid solution followed by heating. Flash column chromatography was performed over silica gel (230-400 mesh).

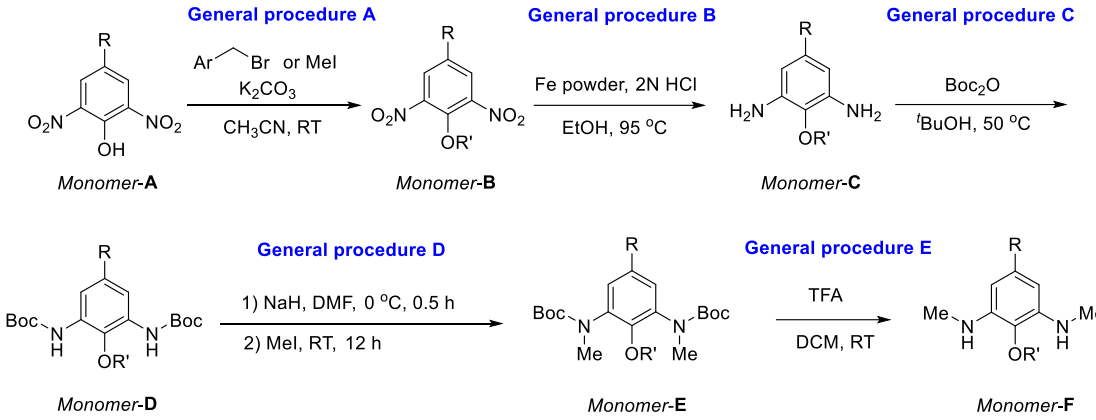
Optical properties: Optical properties were recorded in chromatographic grade acetonitrile. UV-vis absorption spectra were recorded using an Agilent® Cary-5000 UV-vis spectrophotometer at room temperature. Electronic circular dichroism (ECD) spectra were recorded on a JASCO J-815 spectropolarimeter at room temperature in a 1 cm-cuvette. Fluorescence spectra were recorded using an Agilent® Eclipse fluorescence spectrophotometer. Fluorescence quantum yields Ø were measured in diluted solution with an optical density lower than 0.05 using the following equation:

$$\frac{\emptyset_x}{\emptyset_r} = \frac{A_r(\lambda)}{A_x(\lambda)} \times \frac{n_x^2}{n_r^2} \times \frac{D_x}{D_r}$$

Where A is the absorbance at the excitation wavelength (λ), n the refractive index and D the integrated intensity. r and x stand for reference and sample respectively. The fluorescence quantum yields were measured in solution relative to 2-aminopyridine (Ø = 60.0% in 0.1 N H_2SO_4). Excitation of reference and sample compounds was performed at the same wavelength.

The circularly polarized luminescence (CPL) spectra were recorded with a JASCO CPL-200 spectrometer at room temperature.

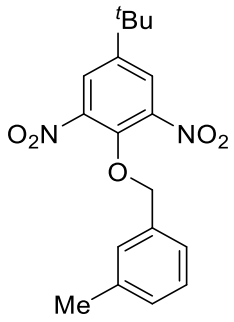
2. Synthesis of *Monomer*



Dinitro compounds (*Monomer*-**A**) are obtained through the nitration reaction of phenol according to reference.[1]

General procedure A: *Monomer*-**A** (30 mmol) and K_2CO_3 (6.2g, 45 mmol, 1.5 equiv) were put into a 500 mL two-necked round bottom flask under N_2 atmosphere. Then CH_3CN (150 mL) and benzyl bromide (36 mmol, 1.2 equiv) were added and the solution was stirred at refluxing temperature overnight. The reaction was quenched with water and extracted with EtOAc. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After solvent evaporation, pure *Monomer*-**B** was obtained by recrystallization.

5-(*tert*-butyl)-2-((3-methylbenzyl)oxy)-1,3-dinitrobenzene (*Monomer*-**B1**)



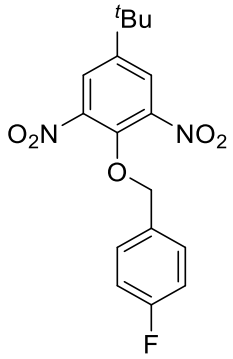
Chemical Formula: $C_{18}H_{20}N_2O_5$; Molecular Weight: 344.3670

8.3 g, 80% yield, yellow solid. M.P. = 86-87 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 2H), 7.28 (m, 3H), 7.19 (m, 1H), 5.16 (s, 2H),

2.38 (s, 3H), 1.38 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.9, 145.6, 143.6, 138.5, 134.8, 129.9, 128.7, 126.4, 126.3, 79.3, 35.4, 30.9, 21.5. **IR** (KBr) *v* 2973, 2873, 1812, 1535, 1349, 1286, 956, 893, 719. **HRMS** (APCI) *m/z* Calcd. for $C_{18}H_{19}N_2O_5^-$ $[M-H]^-$ 343.1299; Found: 343.1288.

5-(*tert*-butyl)-2-((4-fluorobenzyl)oxy)-1,3-dinitrobenzene (*Monomer*-**B2**)

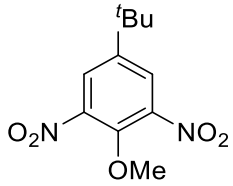


Chemical Formula: $C_{17}H_{17}FN_2O_5$; Molecular Weight: 348.3304

8.3 g, 80% yield, yellow solid. M.P. = 90-91 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 2H), 7.49-7.46 (m, 2H), 7.12-7.06 (m, 2H), 5.17 (s, 2H), 1.39 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.2 (d, J = 247 Hz), 149.2, 145.5, 143.3, 131.3 (d, J = 8 Hz), 130.8 (d, J = 3 Hz), 126.5, 115.7 (d, J = 21 Hz), 78.3, 35.4, 30.9. **IR** (KBr) *v* 2962, 1897, 1532, 1367, 1225, 894, 817, 720. **HRMS** (APCI) *m/z* Calcd. for $C_{17}H_{16}FN_2O_5^-$ $[M-H]^-$ 347.1049; Found: 347.1039.

5-(*tert*-butyl)-2-methoxy-1,3-dinitrobenzene (*Monomer*-**B3**)



Chemical Formula: $C_{11}H_{14}N_2O_5$; Molecular Weight: 254.0903

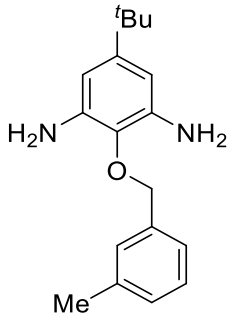
6.1 g, 80% yield, yellow solid. M.P. = 86-87 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 2H), 4.04 (s, 3H), 1.37 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.6, 145.3, 145.1, 126.3, 64.8, 35.3, 31.0. **IR** (KBr) *v* 2962, 2874,

1602, 1531, 1367, 1287, 962, 894, 720. **HRMS** (ESI) *m/z* Calcd. for $C_{11}H_{15}N_2O_5^+$ $[M+H]^+$ 255.0975; Found: 255.0934.

General procedure B: To a sealed tube was added *Mononer*-**B** (2 mmol), Fe powder (1.1 g, 20 mmol, 10 equiv), H_2O (2.5 mL), concentrated HCl (12 N, 0.1 mL), and EtOH (10 mL). The reaction mixture was heated to 95 °C and reacted for 3 h. The reaction was cooled to room temperature, filtered through celite and the filtrate was evaporated under vacuum. The residue was resolved in DCM, washed with brine and dried over anhydrous Na_2SO_4. After solvent evaporation, the residue was subjected to column chromatography on silica gel (PE/EtOAc = 10:1) to give the desired product *Monomer*-**C**.

5-(*tert*-butyl)-2-((3-methylbenzyl)oxy)benzene-1,3-diamine (*Monomer*-**C1**)

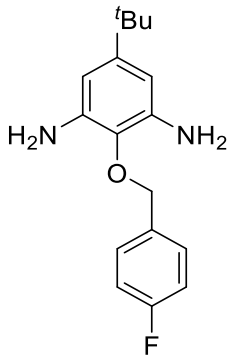


Chemical Formula: $C_{18}H_{24}N_2O$; Molecular Weight: 284.4030

403.8 mg, 71% yield, white solid. M.P. = 110-111 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.31 (m, 3H), 7.20-7.19 (m, 1H), 6.27 (s, 2H), 4.88 (s, 2H), 3.66 (br s, 4H), 2.42 (s, 3H), 1.28 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.3, 139.5, 138.4, 137.8, 132.1, 128.9, 128.8, 128.6, 125.2, 104.1, 73.0, 34.4, 31.5, 21.5. **IR** (KBr) *v* 3413, 3318, 2959, 1615, 1435, 1108, 1027, 887, 833, 751. **HRMS** (ESI) *m/z* Calcd. for $C_{18}H_{25}N_2O^+$ $[M+H]^+$ 285.1961; Found: 285.1964.

5-(*tert*-butyl)-2-((4-fluorobenzyl)oxy)benzene-1,3-diamine (*Monomer*-**C2**)

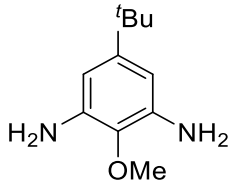


Chemical Formula: $C_{17}H_{21}FN_2O$; Molecular Weight: 288.3664

420.5 mg, 73% yield, white solid. M.P. = 92-93 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2H), 7.10-7.06 (m, 2H), 6.25 (s, 2H), 4.86 (s, 2H), 3.77 (br s, 4H), 1.25 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.3 (d, J = 247 Hz), 149.2, 145.6, 143.4, 131.3 (d, J = 8 Hz), 130.9 (d, J = 4 Hz), 126.5, 115.8 (d, J = 21 Hz), 78.4, 35.4, 31.0. **IR** (KBr) ν 3462, 3373, 2951, 1610, 1519, 1207, 968, 807, 784. **HRMS** (APCI) *m/z* Calcd. for $C_{17}H_{22}FN_2O^+$ $[M+H]^+$ 289.1711; Found: 289.1717.

5-(*tert*-butyl)-2-methoxybenzene-1,3-diamine (*Monomer*-**C3**)

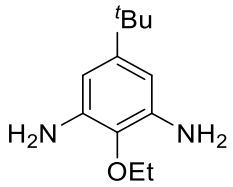


Chemical Formula: $C_{11}H_{18}N_2O$; Molecular Weight: 194.2780

272.0 mg, 70% yield, white solid. M.P. = 90-91 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.28 (s, 2H), 4.07 (br s, 4H), 3.77 (s, 3H), 1.24 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.3, 138.9, 133.2, 104.5, 58.8, 34.4, 31.5. **IR** (KBr) ν 3355, 2958, 2924, 1729, 1538, 1378, 1260, 1050, 807, 782. **HRMS** (ESI) *m/z* Calcd. for $C_{11}H_{19}N_2O^+$ $[M+H]^+$ 195.1492; Found: 195.1492.

5-(*tert*-butyl)-2-ethoxybenzene-1,3-diamine (*Monomer*-**C4**)



Chemical Formula: $C_{12}H_{20}N_2O$; Molecular Weight: 208.3050

307.8 mg, 74% yield, white solid. M.P. = 88-89 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 (s, 2H), 3.94 (q, J = 8.0 Hz, 2H), 3.46 (br s, 4H), 1.40 (t, J = 8.0 Hz, 3H) 1.24 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.1, 139.5, 132.1, 104.1, 66.9, 34.4, 31.5, 16.2. **IR** (KBr) v 3414, 3318, 3198, 2959, 1615, 1361, 1221, 1026, 887, 847. **HRMS** (APCI) *m/z* Calcd. for $C_{12}H_{21}N_2O^+$ $[M+H]^+$ 209.1648; Found: 209.1651.

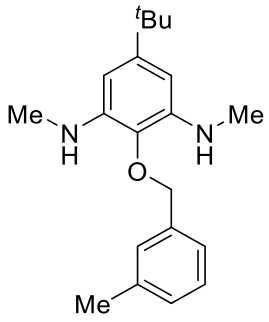
General procedure C: To a round bottom flask was added *Monomer*-**C** (1 mmol), Boc_2O (872.0 mg, 4 mmol, 4 equiv), and ^{t}BuOH (20 mL). The reaction mixture was stirred at 50 ºC for 8 h. The reaction was cooled to room temperature. Solvents were removed under vacuum and the residue was resolved with DCM, washed with saturated $NaHCO_3$ aqueous solution and brine, and dried over anhydrous Na_2SO_4. Solvent evaporation gave the crude product *Monomer*-**D**, which was used directly for the next step without further purification.

General procedure D: To a stirred suspension of NaH (160.0 mg, 4 mmol, 60% dispersion in mineral oil, 4 equiv) in dry DMF (10 mL) was added the above obtained crude product *Monomer*-**D** (approximately 1 mmol) at 0 ºC. After being stirred at 0 ºC for 0.5 h, MeI (570.0 mg, 4 mmol, 4 equiv) was added dropwisely. The mixture was then stirred at room temperature until the starting material was consumed completely (monitored by TLC). The reaction was quenched with H_2O at 0 ºC and the mixture was extracted with DCM. The combined organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to obtained crude product *Monomer*-**E**, which was used for next step without further purification.

General procedure E: To a round bottom flask was added the above obtained crude

Monomer-**E** (approximately 1 mmol), DCM (50 mL), and TFA (10 mL). The mixture was stirred at room temperature for 5 h. Solvents were removed under vacuum and the residue was resolved with DCM (50 mL), washed with saturated Na_2CO_3 aqueous solution and brine, and dried over anhydrous Na_2SO_4. After solvent evaporation, the residue was subjected to column chromatography on silica gel (PE/EtOAc = 20:1) to give the desired product *Monomer*-**F**.

5-(*tert*-butyl)-*N*^{1},*N*^{3}-dimethyl-2-((3-methylbenzyl)oxy)benzene-1,3-diamine (*Monomer*-**F1**)

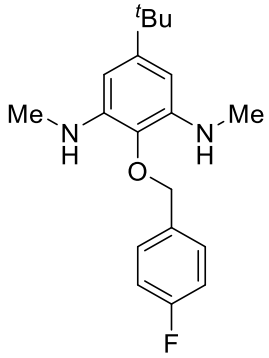


Chemical Formula: $C_{20}H_{28}N_2O$; Molecular Weight: 312.4570

209.3 mg, 67% yield (calculated over 3 steps), red solid. M.P. = 70-71 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 3H), 7.16-7.13 (m, 1H), 6.17 (s, 2H), 4.77 (s, 2H), 3.97 (br s, 2H), 2.81 (s, 6H), 2.37 (s, 3H), 1.33 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.4, 141.8, 138.3, 137.9, 130.9, 128.8, 128.6, 124.9, 98.4, 72.6, 34.9, 31.7, 30.9, 21.5. **IR** (KBr) ν 3418, 2955, 1598, 1415, 1178, 997, 818, 768. **HRMS** (ESI) *m/z* Calcd. for $C_{20}H_{29}N_2O^+$ $[M+H]^+$; 313.2274; Found: 313.2275.

5-(*tert*-butyl)-2-((4-fluorobenzyl)oxy)-*N*^{1},*N*^{3}-dimethylbenzene-1,3-diamine (*Monomer*-**F2**)

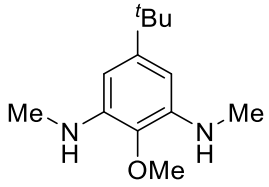


Chemical Formula: $C_{19}H_{25}FN_2O$; Molecular Weight: 316.4204

183.0 mg, 58% yield (calculated over 3 steps), red oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.40 (m, 2H), 7.11-7.07 (m, 2H), 6.17 (s, 2H), 4.78 (s, 2H), 3.96 (s, 2H), 2.82 (s, 6H), 1.33 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.7 (d, J = 245 Hz), 148.6, 141.8, 133.9 (d, J = 3 Hz), 130.8, 129.8 (d, J = 8 Hz), 115.5 (d, J = 21 Hz), 98.5, 71.9, 35.0, 31.7, 30.9. **IR** (KBr) v 3417, 2960, 1588, 1414, 1180, 992, 810, 768. **HRMS** (ESI) *m/z* Calcd. for $C_{19}H_{26}FN_2O^+$ $[M+H]^+$ 317.2024; Found: 317.2025.

5-(*tert*-butyl)-2-methoxy-*N*^{1},*N*^{3}-dimethylbenzene-1,3-diamine (*Monomer*-**F3**)

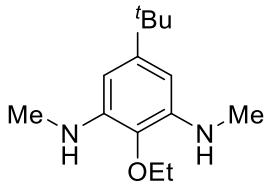


Chemical Formula: $C_{13}H_{22}N_2O$; Molecular Weight: 222.3320

146.4 mg, 66% yield (calculated over 3 steps), red oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.23 (s, 2H), 4.11 (s, 2H), 3.75 (s, 3H), 2.93 (s, 6H), 1.40 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.2, 141.5, 131.5, 98.2, 58.3, 34.9, 31.6, 30.8. **IR** (KBr) v 3417, 2955, 1598, 1415, 1178, 997, 808, 771. **HRMS** (ESI) *m/z* Calcd. for $C_{13}H_{23}N_2O^+$ $[M+H]^+$ 223.1805; Found: 223.1805.

5-(*tert*-butyl)-2-ethoxy-*N*^{1},*N*^{3}-dimethylbenzene-1,3-diamine (*Monomer*-**F4**)

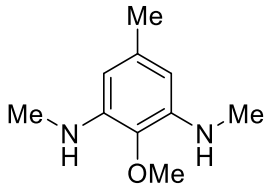


Chemical Formula: $C_{14}H_{24}N_2O$; Molecular Weight: 236.3590

144.2 mg, 61% yield (calculated over 3 steps), red oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (s, 2H), 4.08 (br s, 2H), 3.87 (q, J = 6.8 Hz, 2H), 2.87 (s, 6H), 1.39 (t, J = 6.8 Hz, 3H), 1.33 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.2, 141.8, 131.0, 98.6, 66.6, 34.9, 31.7, 31.0, 16.2. **IR** (KBr) v 3418, 2955, 1598, 1537, 1178, 997, 818, 768. **HRMS** (APCI) *m/z* Calcd. for $C_{14}H_{25}N_2O^+$ $[M+H]^+$ 237.1961; Found: 237.1964.

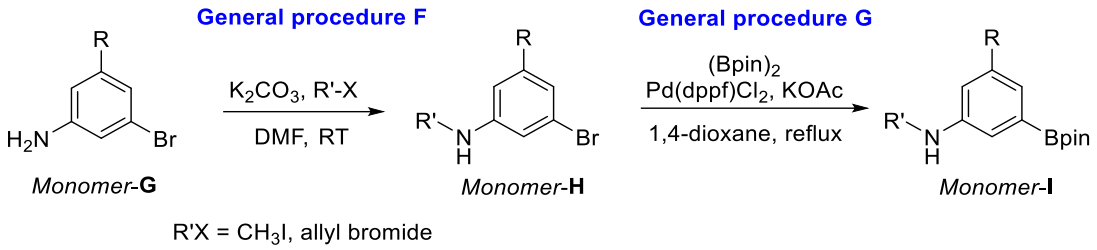
2-methoxy-*N*^{1},*N*^{3},5-trimethylbenzene-1,3-diamine (*Monomer*-**F5**)



Chemical Formula: $C_{10}H_{16}N_2O$; Molecular Weight: 180.2510

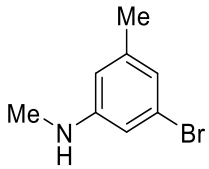
128.0 mg, 71% yield (calculated over 3 steps), red oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (s, 2H), 4.04 (br s, 2H), 3.70 (s, 3H), 2.86 (s, 6H), 2.31 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.0, 135.0, 131.5, 101.6, 58.5, 30.8, 22.1. **IR** (KBr) v 3418, 2924, 2854, 1736, 1674, 1595, 1479, 1356, 1180, 995, 799. **HRMS** (ESI) *m/z* Calcd. for $C_{10}H_{17}N_2O^+$ $[M+H]^+$ 181.1335; Found: 181.1334.



General procedure F: To a mixture of *Monomer*-**G** (10 mmol) and K_2CO_3 (1.5 g, 11 mmol, 1.1 equiv) in DMF (50 mL) was slowly added R'X (10 mmol, 1.0 equiv), and the mixture was stirred at room temperature overnight. The reaction mixture was quenched with H_2O, extracted with EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. The product *Monomer*-**H** was isolated by column chromatography on silica gel (PE/EtOAc = 30:1).

3-bromo-*N*,5-dimethylaniline (*Monomer*-**H1**)

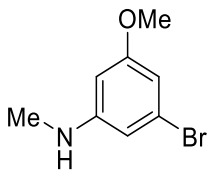


Chemical Formula: $C_8H_{10}BrN$; Molecular Weight: 200.0790

660.0 mg, 33% yield, brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (s, 1H), 6.58 (s, 1H), 6.34 (s, 1H), 3.69 (br s, 1H), 2.81 (s, 3H), 2.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.4, 123.0, 120.7, 112.0, 112.0, 30.5, 21.4. **IR** (KBr) *v* 2966, 870, 1577, 1540, 1456, 1382, 1143, 973, 808, 704. **HRMS** (ESI) *m/z* Calcd. for $C_8H_{11}NBr^+$ $[M+H]^+$ 200.0069; Found: 200.0074.

3-bromo-5-methoxy-*N*-methylaniline (*Monomer*-**H2**)



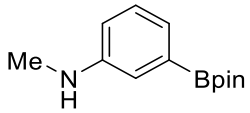
Chemical Formula: $C_8H_{10}BrNO$; Molecular Weight: 216.0780

821.0 mg, 38% yield, brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (s, 1H), 6.37 (s, 1H), 6.05 (s, 1H), 3.75 (s, 4H), 2.79 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.4, 151.4, 123.5, 108.6, 106.0, 97.4, 55.4, 30.7. **IR** (KBr) *v* 3507, 2994, 1770, 1375, 1275, 1246, 913, 764, 748. **HRMS** (ESI) *m/z* Calcd. for $C_8H_{11}NBrO^+$ $[M+H]^+$ 216.0019; Found: 216.0017.

General procedure G: Under argon atmosphere, to a 50 mL round bottom flask was added *Monomer*-**H** (3 mmol), $(Bpin)_2$ (915.0 mg, 3.6 mmol, 1.2 equiv), $Pd(dppf)Cl_2$ (112.0 mg, 0.15 mmol, 5 mol%), KOAc (882.0 mg, 9 mmol, 3 equiv), and dry 1,4-dioxane (30 mL). The mixture was stirred at 100 °C for 12 h. The reaction was quenched with H_2O, extracted with EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent under vacuum, the residue was subjected to column chromatography on silica gel (PE/EtOAc = 10:1) to afford *Monomer*-**I**.

***N*-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline** (*Monomer*-**I1**)

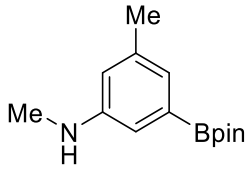


Chemical Formula: $C_{13}H_{20}BNO_2$; Molecular Weight: 233.1180

559.0 mg, 80% yield, red oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, J = 7.2 Hz, 1H), 7.21 (dt, J = 6.8 Hz, 1.2 Hz, 1H), 7.10 (d, J = 2.4 Hz, 1H), 6.74 (ddd, J = 7.6 Hz, 2.8 Hz, 1.6 Hz, 1H), 3.66 (br s, 1H), 2.86 (s, 3H), 1.37 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.8, 128.7, 123.7, 118.5, 115.4, 83.7, 30.8, 24.9. **IR** (KBr) *v* 3410, 2978, 2814, 1604, 1582, 1358, 1144, 1097, 851, 706. **HRMS** (ESI) *m/z* Calcd. for $C_{13}H_{21}NBO_2^+$ $[M+H]^+$ 234.1660; Found: 234.1658.

***N*,3-dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline** (*Monomer*-**I2**)

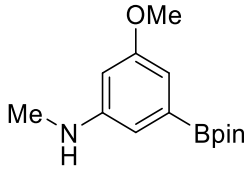


Chemical Formula: $C_{14}H_{22}BNO_2$; Molecular Weight: 247.1450

615.0 mg, 83% yield, red oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 1H), 6.87 (d, J = 2.0 Hz, 1H), 6.54 (s, 1H), 2.84 (s, 3H), 2.29 (s, 3H), 1.34 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.0, 138.5, 124.8, 116.3, 116.0, 83.7, 83.6, 31.1, 25.2, 25.0, 21.5. **IR** (KBr) v 3063, 2966, 1577, 1540, 1474, 1356, 1143, 973, 808, 704. **HRMS** (ESI) *m/z* Calcd. for $C_{14}H_{23}NBO_2^+$ $[M+H]^+$ 248.1816; Found: 248.1819.

3-methoxy-*N*-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (*Monomer*-**I3**)

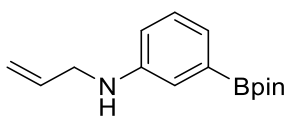


Chemical Formula: $C_{14}H_{22}BNO_3$; Molecular Weight: 263.1440

631.0 mg, 80% yield, red oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71-6.70 (m, 2H), 6.27 (t, J = 2.0 Hz, 1H), 3.81 (s, 4H), 2.83 (s, 3H), 1.34 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.6, 150.5, 112.6, 107.2, 102.0, 83.8, 55.4, 30.9, 25.0. **IR** (KBr) v 2994, 1770, 1759, 1375, 1246, 1057, 913, 764, 748. **HRMS** (ESI) *m/z* Calcd. for $C_{14}H_{23}NBO_3^+$ $[M+H]^+$ 264.1766; Found: 264.1768.

***N*-allyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline** (*Monomer*-**I4**)

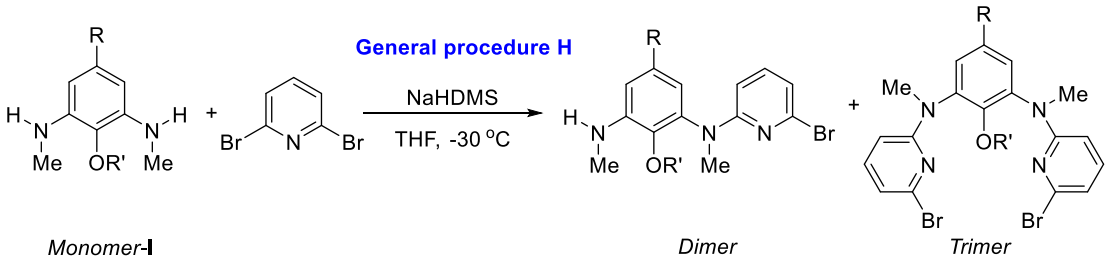


Chemical Formula: $C_{15}H_{22}BNO_2$; Molecular Weight: 259.1560

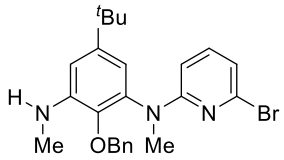
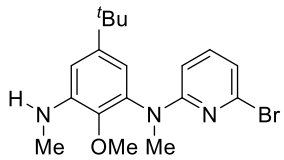
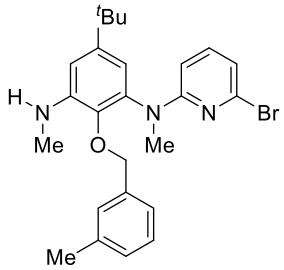
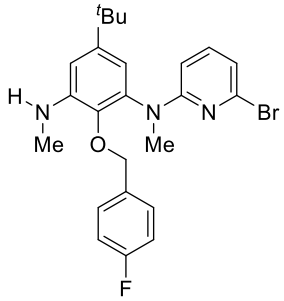
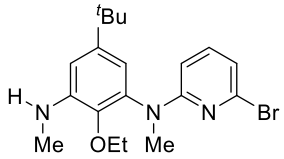
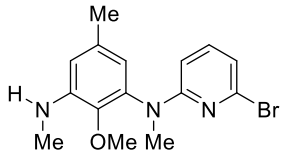
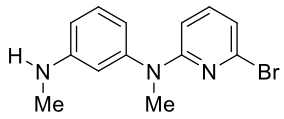
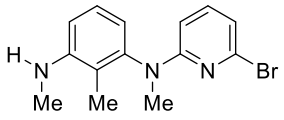
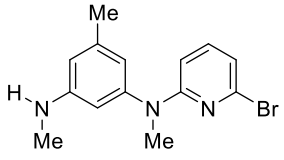
638.0 mg, 83% yield, red oil.

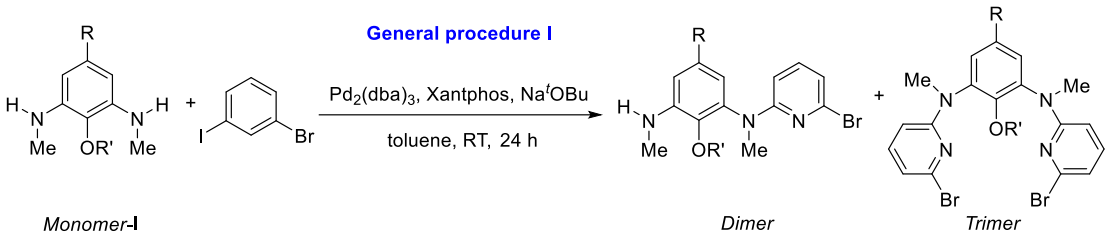
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.17 (m, 2H), 7.09 (d, J = 2.0 Hz, 1H), 6.74 (dt, J = 7.6 Hz, 2.4 Hz, 1H), 6.01-5.92 (m, 1H), 5.31-5.26 (m, 1H), 5.18-5.15 (m, 1H), 3.81-3.80 (m, 3H), 1.35 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.6, 135.6, 128.8, 124.1, 119.5, 116.3, 115.8, 83.8, 46.7, 25.0. **IR** (KBr) v 3404, 2978, 2929, 1603, 1360, 1581, 1145, 964, 852, 788, 706. **HRMS** (ESI) *m/z* Calcd. for $C_{15}H_{23}NBO_2^+$ $[M+H]^+$ 260.1816; Found: 260.1819.

3. Synthesis of *Dimer*

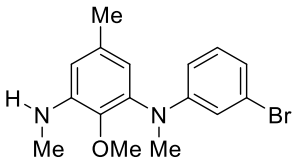
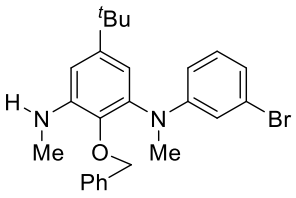


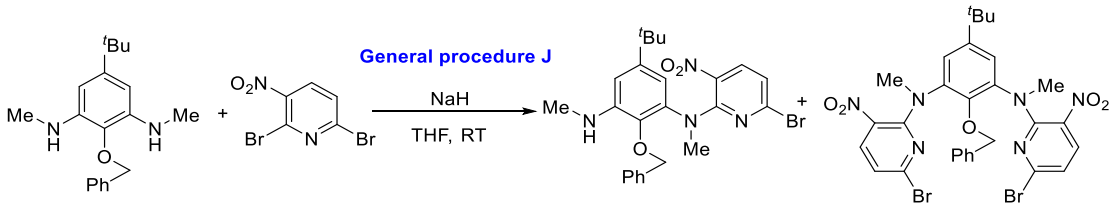
General procedure H: Under argon atmosphere, to a mixture of *Monomer*-**I** (10 mmol, 2.5 equiv) and 2,6-dibromopyridine (950.0 mg, 4 mmol) in dry THF (40 mL) was slowly added NaHMDS (2 mL, 4 mmol, 2.0 M in THF, 1.0 equiv) at -30 ºC. The reaction mixture was stirred at -30 ºC for 12 h. The reaction was quenched with H_2O, extracted with EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent under vacuum, the residue was subjected to column chromatography on silica gel (PE/DCM = 5:1) to give a mixture of *Dimer* and *Trimer*, which was used directly in the next step without purification.

Compound		Ratio of *Dimer* : *Trimer*	Calculated yield of Dimer
Dimer-**1**		>10:1	46%
Dimer-**2**		>10:1	51%
Dimer-**3**		10:1	41%
Dimer-**4**		8:1	40%
Dimer-**5**		10:1	46%
Dimer-**6**		>10:1	62%
Dimer-**7**		7:1	38%
Dimer-**8**		8:1	35%
Dimer-**9**		5:1	40%



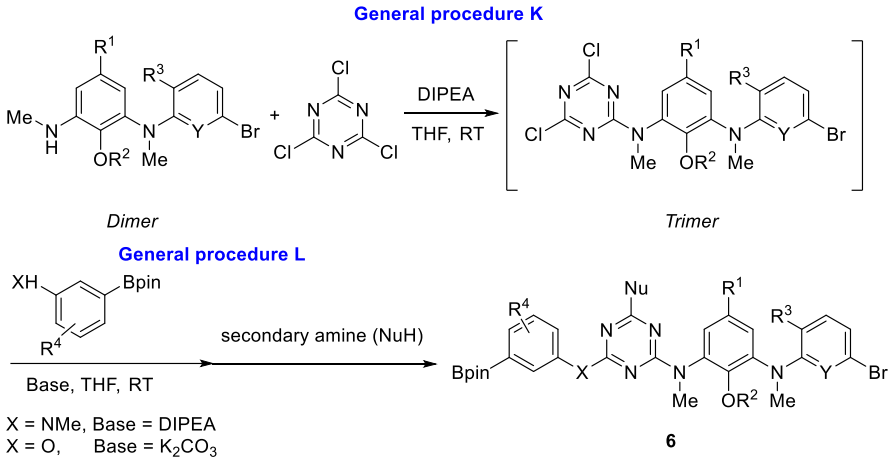
General procedure I: Under argon atmosphere, to a mixture of *Monomer*-**I** (10 mmol, 2.5 equiv), $Pd_2(dba)_3$ (366.3 mg, 0.4 mmol, 10 mol%), Xantphos (462.4 mg, 0.8 mmol, 20 mol%) and Cs_2CO_3 (2.6 g, 8 mmol, 2.0 equiv) in dry toluene (40 mL) was slowly added 1-bromo-3-iodobenzene (1.1 g, 4 mmol) at room temperature and the mixture was stirred for 24 h. The reaction mixture was quenched with H_2O, extracted with EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent under vacuum, the residue was subjected to column chromatography on silica gel (PE/DCM = 5:1) to give a mixture of *Dimer* and *Trimer*, which was used directly in the next step without purification.

Compound		Ratio of *Dimer* : *Trimer*	Calculated yield of Dimer
Dimer-**10**		5:1	36%
Dimer-**11**		5:1	40%



General procedure J: Under argon atmosphere, to a mixture of *Monomer* (1.8 g, 6 mmol, 1.5 equiv) and NaH (160.0 mg, 4 mmol, 60% dispersion in mineral oil, 1.0 equiv) in dry THF (40 mL) was slowly added 2,6-dibromo-3-nitropyridine (1.2 g, 4 mmol) in THF (5 mL). The reaction mixture was stirred at room temperature for 12 h. The reaction was quenched with H_2O, extracted with EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent under vacuum, the residue was isolated by column chromatography on silica gel (PE/EtOAc = 10:1) to give a mixture of *Dimer* and *Trimer* (40% yield of *Dimer*, ratio of *Dimer* : *Trimer* > 10 : 1), which was used directly in the next step without purification.

4. Synthesis of tetramer 6a-6aa and 6ad



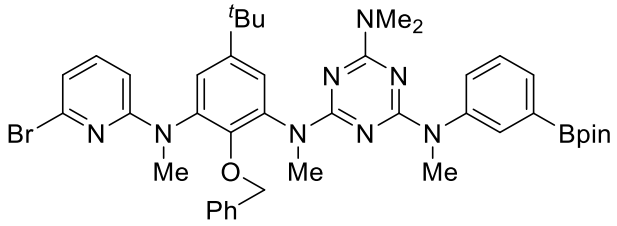
General procedure K: To a 50 mL round bottom flask was added cyanric chloride (40.5 mg, 0.22 mmol, 1.1 equiv), DIPEA (52.0 mg, 0.4 mmol, 2 equiv), and THF (2.5 mL). A solution of *Dimer* (crude product, 0.2 mmol) in 2.5 mL THF was slowly added to the reaction at room temperature. The reaction mixture was quenched with H_2O, extracted with EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. Solvents were evaporated in vacuo to obtained crude *Trimer*, which was used for next step without further purification.

General procedure L: To a round bottom flask was added crude *Trimer* (approximately 0.2 mmol), base (0.3 mmol, 1.5 equiv), aryl borate (0.22 mmol, 1.1 equiv), and THF (10 mL). The reaction mixture was then stirred at 50 °C for 48 h until the starting material was consumed completely. Solvents were removed under vacuum and the residue was resolved with EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. Solvents were evaporated in vacuo to obtain crude product tetramer intermediate, which was used for next step without further purification.

To a round bottom flask was added sequentially the above obtained linear tetramer intermediate (approximately 0.2 mmol), THF (20 mL), and secondary amine (2 mmol, 10 equiv). The mixture was stirred at room temperature until the starting material was consumed completely. Solvents were removed under vacuum and the residue was resolved with EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. After

solvent evaporation, the residue was subjected to column chromatography on silica gel (PE/EtOAc = 20:1) to give the desired linear tetramer **6**.

N^2-(2-(benzyloxy)-3-((6-bromopyridin-2-yl)(methyl)amino)-5-(*tert*-butyl)phenyl)-N^2,N^4,N^4,N^6-tetramethyl-N^6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (6a)

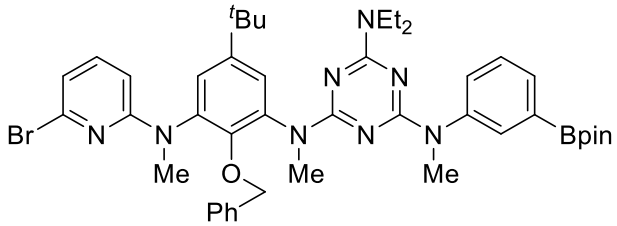


Chemical Formula: $C_{42}H_{52}BBrN_8O_3$; Molecular Weight: 807.6450

129.0 mg, 63% yield (calculated over 3 steps), white solid. M.P. = 72-73 °C

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.77 (s, 1H), 7.56 (d, J = 6.0 Hz, 1H), 7.41 (s, 1H), 7.21-7.17 (m, 5H), 7.09-7.04 (m, 4H), 6.68 (d, J = 7.2 Hz, 1H), 6.09 (d, J = 6.0 Hz, 1H), 4.63 (s, 2H), 3.45 (s, 3H), 3.34 (s, 6H), 3.01 (s, 6H), 1.33 (s, 12H), 1.29 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 166.1, 165.7, 159.1, 149.7, 147.6, 144.9, 140.1, 139.6, 138.5, 138.4, 137.6, 131.2, 130.0, 128.3, 128.2, 127.7, 127.4, 126.6, 124.0, 115.4, 106.9, 83.9, 74.9, 38.1, 37.2, 36.9, 36.0, 34.7, 31.5, 25.1. **IR** (KBr) ν 2978, 2929, 1604, 1582, 1358, 1144, 964, 852, 706. **HRMS** (ESI) *m/z* Calcd. for $C_{42}H_{53}N_8BBrO_3^+$ $[M+H]^+$ 807.3512; Found: 807.3519.

N^2-(2-(benzyloxy)-3-((6-bromopyridin-2-yl)(methyl)amino)-5-(*tert*-butyl)phenyl)-N^4,N^4-diethyl-N^2,N^6-dimethyl-N^6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (6b)

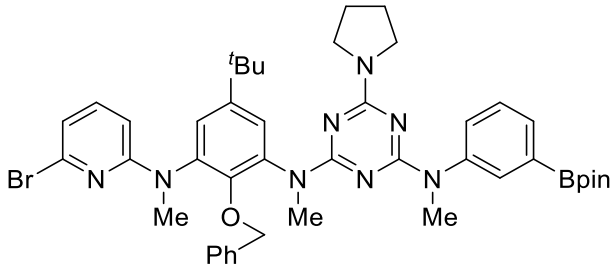


Chemical Formula: $C_{44}H_{56}BBrN_8O_3$; Molecular Weight: 835.6990

107.0 mg, 64% yield (calculated over 3 steps), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.76 (s, 1H), 7.56 (d, J = 7.2 Hz, 1H), 7.16 (d, J = 6.4 Hz, 1H), 7.22-7.17 (m, 5H), 7.10 (d, J = 2.4 Hz, 1H), 7.07-7.03 (m, 3H), 6.69 (d, J = 7.2 Hz, 1H), 6.10 (d, J = 8.0 Hz, 1H), 4.63 (s, 2H), 3.44 (s, 6H), 3.36 (s, 3H), 3.33 (s, 3H), 1.33 (s, 12H), 1.29 (s, 9H), 1.07 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 166.3, 164.7, 159.1, 149.8, 147.4, 144.9, 139.9, 139.7, 138.3, 137.5, 130.9, 129.9, 128.2, 128.1, 127.6, 127.2, 126.7, 124.0, 115.2, 106.7, 83.7, 74.7, 41.3, 37.9, 36.9, 36.5, 34.5, 31.4, 24.9, 13.4. **IR** (KBr) v 2928, 2857, 1577, 1534, 1386, 1144, 973, 808, 705. **HRMS** (ESI) *m/z* Calcd. for $C_{44}H_{57}BBrN_8O_3^+$ $[M+H]^+$ 835.3825; Found: 835.3824.

N^2-(2-(benzyloxy)-3-((6-bromopyridin-2-yl)(methyl)amino)-5-(*tert*-butyl)phenyl)-N^2,N^4-dimethyl-6-(pyrrolidin-1-yl)-N^4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4-diamine (6c)

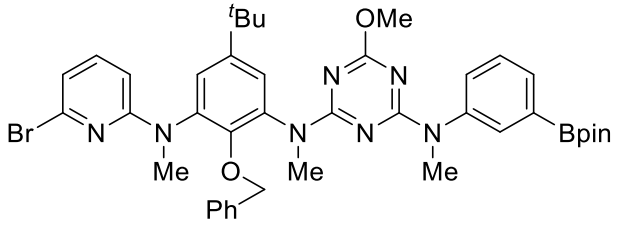


Chemical Formula: $C_{44}H_{54}BBrN_8O_3$; Molecular Weight: 833.6830

93.3 mg, 56% yield (calculated over 3 steps), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.81 (s, 1H), 7.56 (d, J = 7.2 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.23-7.17 (m, 5H), 7.09 (d, J = 2.8 Hz, 1H), 7.08-7.04 (m, 3H), 7.69 (d, J = 3.2 Hz, 1H), 6.09 (d, J = 8.4 Hz, 1H), 4.65 (s, 2H), 3.46 (s, 7H), 3.35 (s, 3H), 3.35 (s, 3H), 1.88 (s, 4H), 1.35 (s, 12H), 1.30 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 166.2, 165.5, 164.1, 159.1, 149.7, 147.5, 145.0, 140.0, 139.8, 138.5, 138.4, 137.6, 132.0, 130.9, 129.9, 128.3, 128.2, 127.7, 127.3, 126.7, 123.9, 115.3, 106.9, 83.9, 74.8, 45.9, 38.1, 37.0, 36.7, 34.7, 31.5, 25.5, 25.1. **IR** (KBr) v 2966, 2870, 1541, 1456, 1382, 1143, 973, 808, 704. **HRMS** (ESI) *m/z* Calcd. for $C_{44}H_{55}BBrN_8O_3^+$ $[M+H]^+$ 833.3668; Found: 833.3665.

N^2-(2-(benzyloxy)-3-((6-bromopyridin-2-yl)(methyl)amino)-5-(*tert*-butyl)phenyl)-6-methoxy-N^2,N^4-dimethyl-N^4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4-diamine (6d)

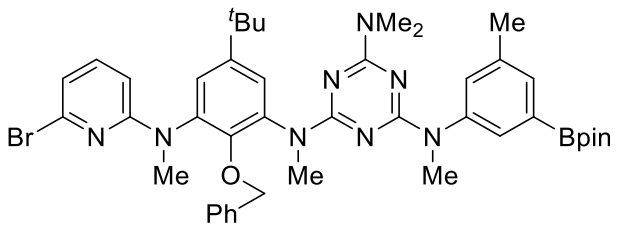


Chemical Formula: $C_{41}H_{49}BBrN_7O_4$; Molecular Weight: 794.6020

82.6 mg, 52% yield (calculated over 3 steps), white solid. M.P. = 71-72 ºC

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.60 (br s, 2H), 7.19-7.13 (m, 7H), 7.09 (dd, J = 8.0 Hz, 7.2 Hz, 1H), 7.01-7.00 (m, 2H), 6.71 (d, J = 7.2 Hz, 1H), 6.15 (br s, 1H), 4.59 (br s, 2H), 3.84-3.68 (m, 3H), 3.51-3.18 (m, 9H), 1.33 (s, 12H), 1.29 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 171.2, 167.3, 158.8, 149.6, 148.0, 144.2, 140.1, 139.0, 138.64, 138.59, 137.4, 132.0, 130.1, 128.3, 128.0, 127.8, 125.7, 124.6, 115.7, 107.0, 84.0, 75.0, 53.8, 38.1, 37.7, 37.4, 34.7, 25.1 . **IR** (KBr) v 2923, 2853, 1584, 1538, 1374, 1349, 1267, 1133, 975, 809, 774. **HRMS** (ESI) *m/z* Calcd. for $C_{41}H_{50}BBrN_7O_4^+$ $[M+H]^+$ 794.3195; Found: 794.3179.

N^2-(2-(benzyloxy)-3-((6-bromopyridin-2-yl)(methyl)amino)-5-(*tert*-butyl)phenyl)-N^2,N^4,N^4,N^6-tetramethyl-N^6-(3-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (6e)

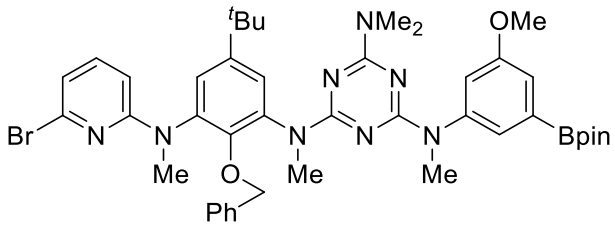


Chemical Formula: $C_{43}H_{54}BBrN_8O_3$; Molecular Weight: 821.6720

95.3 mg, 58% yield (calculated over 3 steps), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.60 (s, 1H), 7.39 (s, 1H), 7.26-7.24 (m, 1H), 7.22-7.21 (m, 1H), 7.17-7.16 (m, 3H), 7.08-7.01 (m, 4H), 6.67 (d, J = 8.0 Hz, 1H), 6.11 (d, J = 8.4 Hz, 1H), 4.64 (s, 2H), 3.41 (s, 3H), 3.31 (s, 3H), 3.29 (s, 3H), 2.95 (s, 6H), 2.29 (s, 3H), 1.31 (s, 12H), 1.26 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 166.4, 166.0, 165.8, 159.1, 149.6, 147.5, 145.0, 140.1, 139.7, 138.5, 138.4, 137.7, 137.1, 131.8, 130.5, 129.6, 128.3, 128.2, 127.8, 126.8, 123.8, 115.4, 106.9, 83.9, 74.8, 38.1, 37.2, 36.8, 35.9, 34.7, 31.5, 29.9, 25.1, 21.3 **IR** (KBr) v 2966, 2870, 1736, 1577, 1540, 1474, 1382, 1143, 973, 808, 704. **HRMS** (ESI) m/z Calcd. for $C_{43}H_{55}N_8BBrO_3^+$ $[M+H]^+$ 821.3668; Found: 821.3670.

N^2-(2-(benzyloxy)-3-((6-bromopyridin-2-yl)(methyl)amino)-5-(*tert*-butyl)phenyl)-N^4-(3-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-N^2,N^4,N^6,N^6-tetramethyl-1,3,5-triazine-2,4,6-triamine (6f)

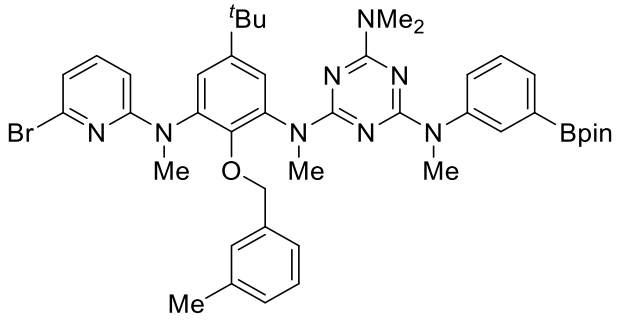


Chemical Formula: $C_{43}H_{54}BBrN_8O_4$; Molecular Weight: 837.6710

103.8 mg, 62% yield (calculated over 3 steps), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.43 (s, 1H), 7.22 (d, J = 2.4 Hz, 1H), 7.19-7.17 (m, 3H), 7.12 (s, 1H), 7.09 (d, J = 2.4 Hz, 1H), 7.08-7.04 (m, 4H), 6.69 (d, J = 7.2 Hz, 1H), 6.14 (d, J = 8.4 Hz, 1H), 4.66 (s, 2H), 3.80 (s, 3H), 3.43 (s, 3H), 3.35 (s, 3H), 3.34 (s, 3H), 2.99 (s, 6H), 1.33 (s, 12H), 1.28 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 166.1, 165.6, 159.1, 158.9, 149.2, 147.4, 146.0, 139.9, 139.4, 138.6, 138.2, 137.3, 129.8, 128.4, 128.2, 127.8, 126.7, 124.9, 123.7, 116.4, 115.3, 106.8, 83.9, 74.7, 55.5, 38.1, 37.2, 36.8, 35.2, 34.7, 31.4, 25.0. **IR** (KBr) v 2965, 2929, 1731, 1579, 1550, 1382, 1517, 1268, 1143, 973, 809. **HRMS** (ESI) m/z Calcd. for $C_{43}H_{55}N_8BBrO_4^+$ $[M+H]^+$ 837.3617; Found: 837.3621.

N^2-(3-((6-bromopyridin-2-yl)(methyl)amino)-5-(*tert*-butyl)-2-((3-methylbenzyl)oxy)phenyl)-N^2,N^4,N^4,N^6-tetramethyl-N^6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (6g)

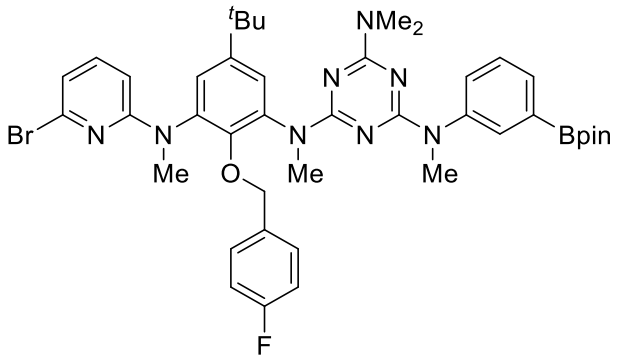


Chemical Formula: $C_{43}H_{54}BBrN_8O_3$; Molecular Weight: 821.6720

118.2 mg, 72% yield (calculated over 3 steps), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.77 (s, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.44-7.40 (m, 1H), 7.21 (s, 2H), 7.09-7.03 (m, 3H), 6.98 (d, J = 7.2 Hz, 1H), 6.84 (s, 2H), 6.69 (d, J = 7.2 Hz, 1H), 6.09 (d, J = 8.0 Hz, 1H), 4.59 (s, 2H), 3.45 (s, 3H), 3.35-3.34 (m, 6H), 3.00 (s, 6H), 2.25 (s, 3H), 1.33 (s, 12H), 1.29 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 166.4, 166.0, 165.7, 159.1, 149.8, 147.5, 145.0, 140.1, 139.7, 138.5, 138.4, 137.9, 137.6, 132.0, 131.0, 130.0, 129.1, 128.5, 128.1, 127.4, 126.7, 125.3, 123.9, 115.3, 106.9, 83.9, 74.9, 38.1, 37.1, 36.8, 35.9, 34.7, 31.5, 25.1, 21.4. **IR** (KBr) ν 2925, 1532, 1490, 1385, 1356, 1143, 973, 808, 705. **HRMS** (ESI) *m/z* Calcd. for $C_{43}H_{55}N_8BBrO_3^+$ $[M+H]^+$ 821.3668; Found: 821.3674.

N^2-(3-((6-bromopyridin-2-yl)(methyl)amino)-5-(*tert*-butyl)-2-((4-fluorobenzyl)oxy)phenyl)-N^2,N^4,N^4,N^6-tetramethyl-N^6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (6h)

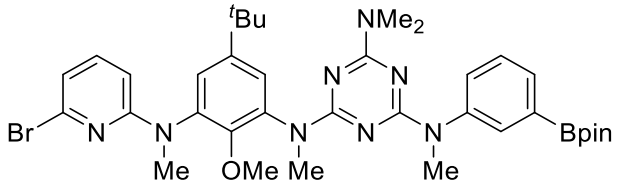


Chemical Formula: $C_{42}H_{51}BFBrN_8O_3$; Molecular Weight: 825.6354

75.9 mg, 46% yield (calculated over 3 steps), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.76 (s, 1H), 7.56 (d, J = 7.2 Hz, 1H), 7.41 (d, J = 6.0 Hz, 1H), 7.23-7.18 (m, 2H), 7.08 (d, J = 2.4 Hz, 1H), 7.04 (t, J = 8.0 Hz, 1H), 6.99-6.96 (m, 2H), 6.82-6.80 (m, 2H), 6.69 (d, J = 7.6 Hz, 1H), 6.03 (d, J = 7.6 Hz, 1H), 4.58 (s, 2H), 3.45 (s, 3H), 3.32 (s, 6H), 3.01 (s, 6H), 1.33 (s, 12H), 1.29 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 166.3, 166.0, 165.7, 162.6 (d, J = 244 Hz), 159.0, 149.4, 147.7, 144.9, 140.0, 139.7, 138.5, 138.4, 133.4 (d, J = 3 Hz), 132.1, 131.1, 130.2 (d, J = 8 Hz), 130.0, 127.4, 126.7, 123.9, 115.4, 115.0 (d, J = 21 Hz), 106.8, 84.0, 74.0, 38.1, 37.1, 36.7, 35.9, 34.7, 31.5, 25.0. **IR** (KBr) v 2921, 2850, 1532, 1470, 1385, 1143, 973, 808, 705. **HRMS** (ESI) *m/z* Calcd. for $C_{42}H_{52}N_8FBBrO_3^+$ $[M+H]^+$ 825.3417; Found: 825.3422.

N^2-(3-((6-bromopyridin-2-yl)(methyl)amino)-5-(*tert*-butyl)-2-methoxyphenyl)-N^2,N^4,N^4,N^6-tetramethyl-N^6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (6i)

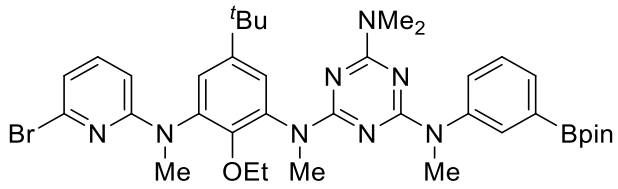


Chemical Formula: $C_{36}H_{48}BBrN_8O_3$; Molecular Weight: 731.5470

102.4 mg, 70% yield (calculated over 3 steps), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.76 (s, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.41 (d, J = 6.4 Hz, 1H), 7.24-7.20 (m, 1H), 7.17 (d, J = 2.0 Hz, 1H), 7.08-7.06 (m, 2H), 6.70 (d, J = 7.6 Hz, 1H), 6.09 (d, J = 8.0 Hz, 1H), 3.49 (s, 3H), 3.43 (s, 3H), 3.40 (s, 3H), 3.35 (s, 3H), 2.99-2.96 (m, 6H), 1.33 (s, 12H), 1.28 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 166.4, 166.1, 165.8, 159.2, 151.1, 147.4, 145.0, 140.2, 139.2, 138.6, 137.8, 132.1, 131.1, 129.9, 127.4, 126.6, 124.1, 115.4, 106.7, 83.9, 60.5, 38.0, 37.1, 36.7, 35.9, 34.7, 31.5, 25.1. **IR** (KBr) v 2928, 1534, 1386, 1356, 1246, 1144, 973, 808, 705. **HRMS** (ESI) m/z Calcd. for $C_{36}H_{49}N_8BBrO_3^+$ $[M+H]^+$ 731.3199; Found: 731.3185.

N^2-(3-((6-bromopyridin-2-yl)(methyl)amino)-5-(*tert*-butyl)-2-ethoxyphenyl)-N^2,N^4,N^4,N^6-tetramethyl-N^6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (6j)

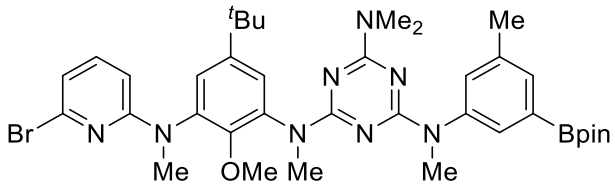


Chemical Formula: $C_{37}H_{50}BBrN_8O_3$; Molecular Weight: 745.5740

83.4 mg, 56% yield (calculated over 3 steps), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.74 (s, 1H), 7.53 (s, 1H), 7.39 (s, 1H), 7.20-7.16 (m, 2H), 7.06 (s, 2H), 6.70-6.69 (m, 1H), 6.10 (s, 1H), 3.66 (s, 2H), 3.40-3.35 (m, 9H), 2.96 (s, 6H), 1.33 (s, 12H), 1.27 (s, 9H), 1.01-1.00 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 166.4, 166.0, 165.8, 159.2, 150.2, 147.1, 145.0, 140.1, 139.5, 138.5, 138.1, 132.1, 131.1, 130.0, 127.4, 126.7, 123.9, 115.2, 106.8, 83.9, 68.8, 38.1, 37.1, 36.7, 35.9, 34.7, 31.5, 25.1, 15.9. **IR** (KBr) v 2925, 1573, 1532, 1385, 1356, 1144, 973, 808, 765. **HRMS** (ESI) m/z Calcd. for $C_{37}H_{51}N_8BBrO_3^+$ $[M+H]^+$ 745.3355; Found: 745.3353.

N^2-(3-((6-bromopyridin-2-yl)(methyl)amino)-5-(*tert*-butyl)-2-methoxyphenyl)-N^2,N^4,N^4,N^6-tetramethyl-N^6-(3-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (6k)

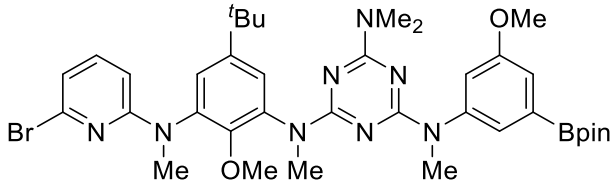


Chemical Formula: $C_{37}H_{50}BBrN_8O_3$; Molecular Weight: 745.5740

71.5 mg, 48% yield (calculated over 3 steps), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.61 (s, 1H), 7.39 (s, 1H), 7.27 (s, 1H), 7.20 (d, J = 2.0 Hz, 1H), 7.10-7.06 (m, 2H), 6.70 (d, J = 7.2 Hz, 1H), 6.14 (d, J = 8.4 Hz, 1H), 3.51 (s, 3H), 3.42 (s, 6H), 3.36 (s, 3H), 3.04-2.96 (m, 6H), 2.31 (s, 3H), 1.33 (s, 9H), 1.28 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 166.4, 166.0, 165.9, 159.2, 151.0, 147.3, 145.0, 140.2, 139.2, 138.5, 137.7, 137.1, 131.8, 130.5, 129.6, 126.6, 124.0, 115.4, 106.7, 83.9, 60.5, 38.1, 37.2, 36.8, 35.8, 34.7, 31.5, 25.1, 21.3. **IR** (KBr) v 2926, 2855, 1532, 1479, 1382, 1248, 1144, 973, 808, 722. **HRMS** (ESI) *m/z* Calcd. for $C_{37}H_{51}N_8BBrO_3^+$ $[M+H]^+$ 745.3355; Found: 745.3363.

N^2-(3-((6-bromopyridin-2-yl)(methyl)amino)-5-(*tert*-butyl)-2-methoxyphenyl)-N^4-(3-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-N^2,N^4,N^6,N^6-tetramethyl-1,3,5-triazine-2,4,6-triamine (6l)



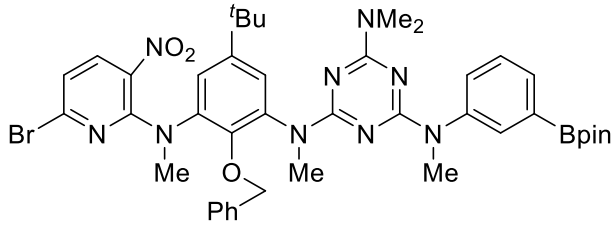
Chemical Formula: $C_{37}H_{50}BBrN_8O_4$; Molecular Weight: 761.5730

82.0 mg, 54% yield (calculated over 3 steps), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.42 (s, 1H), 7.18 (d, J = 2.4 Hz, 1H), 7.11 (s, 1H), 7.08-7.07 (m, 2H), 7.04 (s, 1H), 6.71 (d, J = 7.6 Hz, 1H), 6.14 (d, J = 8.4 Hz, 1H), 3.78 (s, 3H), 3.51 (s, 3H), 3.42 (s, 6H), 3.36 (s, 3H), 2.97 (s, 6H), 1.33 (s, 12H), 1.27 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 166.4, 166.0, 165.8, 159.3, 159.2, 151.0, 147.3, 146.3, 140.2, 139.2, 138.6, 137.7, 126.6, 125.1, 124.0, 116.6, 115.7, 115.4, 106.7,

84.0, 60.5, 55.6, 38.0, 37.2, 36.8, 35.9, 34.7, 31.5, 27.2, 25.1. **IR** (KBr) *v* 2928, 2926, 2855, 1735, 1579, 1403, 1386, 1144, 973, 809, 704. **HRMS** (ESI) *m/z* Calcd. for $C_{37}H_{51}N_8BBrO_4^+$ $[M+H]^+$ 761.3304; Found: 761.3313.

N^2-(2-(benzyloxy)-3-((6-bromo-3-nitropyridin-2-yl)(methyl)amino)-5-(*tert*-butyl)phenyl)-N^2,N^4,N^4,N^6-tetramethyl-N^6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (6m)

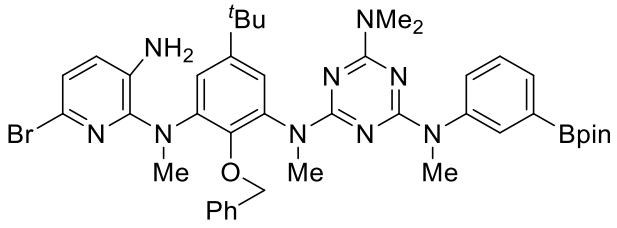


Chemical Formula: $C_{42}H_{51}BBrN_9O_5$; Molecular Weight: 852.6420

112.5 mg, 66% yield (calculated over 3 steps), yellow solid. M.P. = 75-77 ºC

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.81 (s, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 6.8 Hz, 1H), 7.44-7.55 (m, 1H), 7.25-7.22 (m, 4H), 7.11 (d, J = 2.4 Hz, 1H), 7.09-7.08 (m, 2H), 6.94 (d, J = 2.4 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 4.70 (s, 2H), 3.45-3.41 (m, 6H), 3.25 (s, 3H), 2.98 (s, 6H), 1.34 (s, 12H), 1.26 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 166.3, 166.0, 165.8, 151.1, 147.4, 146.8, 145.0, 142.2, 139.3, 138.3, 137.6, 136.2, 134.4, 132.3, 131.1, 129.9, 128.5, 128.3, 127.8, 127.5, 126.9, 120.4, 116.7, 83.9, 74.7, 41.0, 37.1, 36.0, 35.9, 34.7, 31.3, 25.1. **IR** (KBr) *v* 2978, 2931, 1732, 1587, 1519, 1394, 1348, 1142, 975, 808, 775. **HRMS** (ESI) *m/z* Calcd. for $C_{42}H_{52}N_9BBrO_5^+$ $[M+H]^+$ 852.3362; Found: 852.3370.

N^2-(3-((3-amino-6-bromopyridin-2-yl)(methyl)amino)-2-(benzyloxy)-5-(*tert*-butyl)phenyl)-N^2,N^4,N^4,N^6-tetramethyl-N^6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (6n)



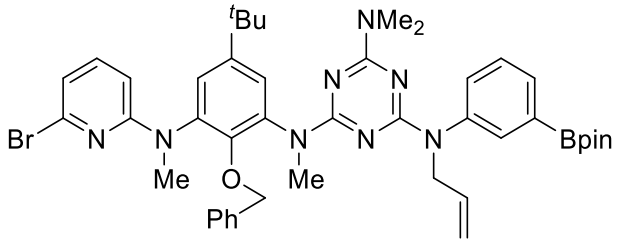
Chemical Formula: $C_{42}H_{53}BBrN_9O_3$; Molecular Weight: 822.6600

Prepared from **6m** under **General procedure B**.

72% yield (calculated yield based on **6m**), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.76 (s, 1H), 7.55 (d, J = 6.8 Hz, 1H), 7.40 (d, J = 7.2 Hz, 1H), 7.24-7.21 (m, 3H), 7.21-7.18 (m, 3H), 7.06 (s, 1H), 6.85 (s, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.60 (d, J = 8.0 Hz, 1H), 4.79 (s, 2H), 3.40 (s, 6H), 3.31 (s, 3H), 2.99 (s, 8H), 1.33 (s, 12H), 1.22 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 166.1, 165.7, 159.1, 149.7, 147.6, 144.9, 140.1, 139.6, 138.5, 138.4, 137.6, 132.0, 131.2, 130.0, 128.3, 128.2, 127.7, 127.4, 126.6, 124.0, 115.4, 106.9, 83.9, 74.9, 38.1, 37.2, 36.9, 36.0, 34.7, 31.5, 25.1. **IR** (KBr) v 3457, 3365, 2963, 2928, 2866, 1546, 1531, 1451, 1385, 1317, 1269, 1143, 964, 808, 705. **HRMS** (ESI) *m/z* Calcd. for $C_{42}H_{54}N_9BBrO_3^+$ $[M+H]^+$ 822.3621; Found: 822.3618.

N^2-allyl-N^4-(2-(benzyloxy)-3-((6-bromopyridin-2-yl)(methyl)amino)-5-(*tert*-butyl)phenyl)-N^4,N^6,N^6-trimethyl-N^2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (6o)



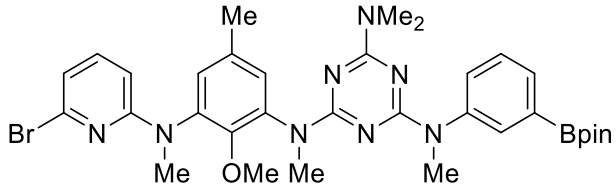
Chemical Formula: $C_{44}H_{54}BBrN_8O_3$; Molecular Weight: 833.6830

76.6 mg, 46% yield (calculated over 3 steps), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.78 (br s, 1H), 7.58 (d, J = 6.8 Hz, 1H), 7.35 (s,

1H), 7.20-7.18 (m, 5H), 7.09 (d, J = 2.0 Hz, 1H), 7.07-7.03 (m, 3H), 6.69 (d, J = 7.6 Hz, 1H), 6.11 (d, J = 8.8 Hz, 1H), 6.00-5.85 (br s, 1H), 5.02-5.01 (m, 2H), 4.63-4.51 (m, 4H), 3.35-3.32 (m, 6H), 3.06-2.97 (m, 6H), 1.32 (s, 9H), 1.29 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 166.4, 166.1, 165.5, 159.1, 149.9, 147.6, 143.9, 140.1, 139.7, 138.5, 137.6, 135.5, 133.5, 131.5, 130.7, 128.32, 128.25, 127.8, 127.5, 126.8, 124.1, 116.1, 115.4, 106.9, 83.9, 74.9, 52.5, 38.1, 36.8, 35.9, 34.7, 31.6, 25.1. **IR** (KBr) v 2960, 2926, 2855, 1735, 1579, 1548, 1403, 1359, 1144, 973, 809, 704. **HRMS** (ESI) m/z Calcd. for $C_{44}H_{55}N_8BBrO_3^+$ $[M+H]^+$ 833.3668; Found: 833.3664.

N^2-(3-((6-bromopyridin-2-yl)(methyl)amino)-2-methoxy-5-methylphenyl)-N^2,N^4,N^4,N^6-tetramethyl-N^6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (6p)

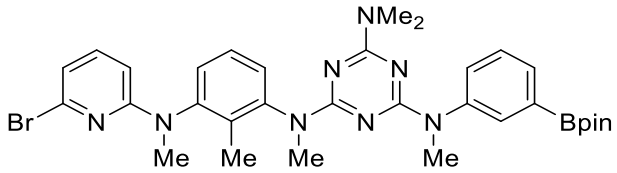


Chemical Formula: $C_{33}H_{42}BBrN_8O_3$; Molecular Weight: 689.4660

95.1 mg, 69% yield (calculated over 3 steps), white solid. M.P. = 72-73 °C

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.75 (s, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.41 (d, J = 6.8 Hz, 1H), 7.22 (s, 1H), 7.07 (t, J = 8.0 Hz, 1H), 6.97 (s, 1H), 6.87 (s, 1H), 6.70 (d, J = 7.6 Hz, 1H), 6.10 (d, J = 7.2 Hz, 1H), 3.47-3.44 (m, 6H), 3.38 (s, 3H), 3.34 (s, 3H), 2.99 (s, 6H), 2.29 (s, 3H), 1.34 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 166.3, 166.1, 165.7, 159.0, 151.4, 145.0, 140.1, 139.7, 138.6, 138.1, 133.7, 132.1, 131.0, 130.0, 129.7, 127.7, 127.3, 115.5, 106.8, 83.9, 60.6, 37.9, 37.0, 36.8, 35.9, 25.1, 20.5. **IR** (KBr) v 2970, 2931, 1579, 1490, 1356, 1144, 976, 910, 868, 809, 705. **HRMS** (ESI) m/z Calcd. for $C_{33}H_{43}N_8BBrO_3^+$ $[M+H]^+$ 689.2729; Found: 689.2726.

N^2-(3-((6-bromopyridin-2-yl)(methyl)amino)-2-methylphenyl)-N^2,N^4,N^4,N^6-tetramethyl-N^6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (6q)

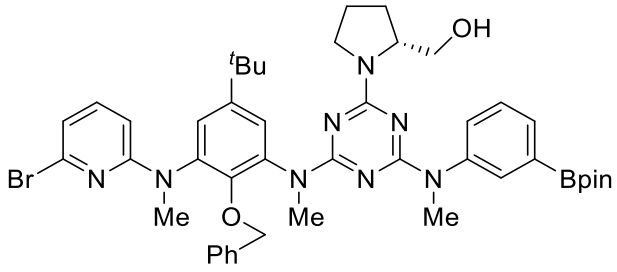


Chemical Formula: $C_{32}H_{40}BBrN_8O_2$; Molecular Weight: 659.4400

67.3 mg, 51% yield (calculated over 3 steps), yellow oil.

^{1}H NMR (400 MHz, DMSO-d_6, 373 K) δ 7.70 (s, 1H), 7.41 (s, 2H), 7.34 (t, J = 8.0 Hz, 1H), 7.22-7.20 (m, 2H), 7.15-7.00 (m, 2H), 6.91-6.85 (m, 1H), 6.74 (d, J = 7.2 Hz, 1H), 3.32-3.27 (m, 6H), 3.06 (s, 3H), 2.90 (br s, 6H), 1.83 (s, 3H), 1.30 (s, 12H). **^{13}C NMR** (100 MHz, DMSO-d_6, 373 K) δ 164.9, 164.6, 157.9, 149.0, 145.5, 143.9, 143.6, 139.0, 134.4, 131.5, 129.9, 128.3, 127.8, 127.4, 127.1, 126.6, 125.9, 121.5, 117.5, 114.4, 114.1, 105.3, 83.2, 82.9, 36.8, 36.1, 36.0, 34.9, 30.4, 29.6, 29.4, 28.4, 24.2, 11.9. **IR** (KBr) v 2926, 2851, 1580, 1487, 1380, 1316, 1144, 970, 810, 705. **HRMS** (ESI) *m/z* Calcd. for $C_{32}H_{41}N_8BBrO_2^+$ $[M+H]^+$ 659.2623; Found: 659.2638.

N^2-(3-((6-bromopyridin-2-yl)(methyl)amino)-2-methoxy-5-methylphenyl)-N^2,N^4,N^4,N^6-tetramethyl-N^6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (6r)



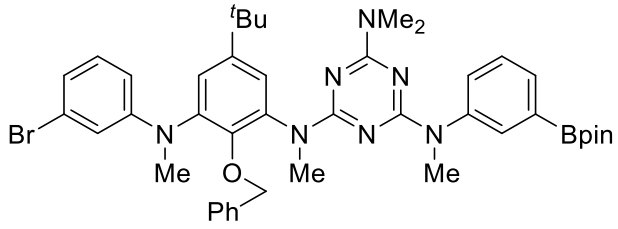
Chemical Formula: $C_{45}H_{56}BBrN_8O_4$; Molecular Weight: 863.7090

84.6 mg, 49% yield, white solid (calculated over 3 steps). M.P. = 76-77 ^{o}C

^{1}H NMR (400 MHz, tetrachloroethane-d_2, 373 K) δ 7.82 (s, 1H), 7.63-7.62 (d, J = 7.2 Hz, 1H), 7.41-7.24 (m, 3H), 7.23-7.20 (m, 3H), 7.18 (d, J = 1.6 Hz, 1H), 7.15-7.09 (m, 3H), 6.74 (d, J = 7.6 Hz, 1H), 6.28 (br s, 1H), 4.69 (s, 2H), 3.74-3.53 (m, 2H), 3.47 (s, 3H), 3.41 (s, 3H), 3.36 (s, 3H), 2.11-2.02 (m, 1H), 1.91-1.77 (m, 2H), 1.68-1.60 (m,

1H), 1.38 (s, 12H), 1.36 (s, 9H). **^{13}C NMR** (100 MHz, tetrachloroethane-d_2, 373 K) δ 165.3, 164.7, 164.5, 158.8, 149.5, 147.6, 144.2, 139.6, 138.6, 138.2, 138.1, 137.4, 132.1, 131.1, 129.2, 127.9, 127.7, 127.3, 127.2, 125.9, 124.3, 115.1, 106.8, 83.6, 74.5, 67.9, 59.8, 47.3, 37.7, 37.0, 36.8, 34.3, 31.1, 29.2, 24.7, 23.5. **IR** (KBr) *v* 2963, 1579, 1532, 1490, 1385, 1316, 1266, 1143, 973, 808, 704. **HRMS** (ESI) *m/z* Calcd. for $C_{45}H_{57}N_8BBrO_4^+$ $[M+H]^+$ 863.3774; Found: 863.3773.

N^2-(2-(benzyloxy)-3-((3-bromophenyl)(methyl)amino)-5-(*tert*-butyl)phenyl)-N^2,N^4,N^4,N^6-tetramethyl-N^6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (6s)

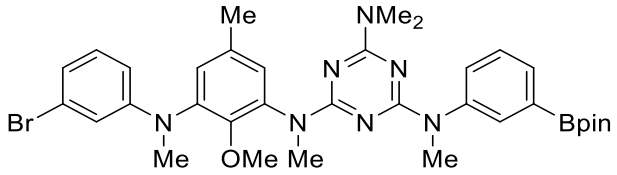


Chemical Formula: $C_{43}H_{53}BBrN_7O_3$; Molecular Weight: 806.6570

55.6 mg, 40% yield (calculated over 3 stpes), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.80 (s, 1H), 7.57 (d, J = 7.2 Hz, 1H), 7.44-7.42 (m, 1H), 7.18-7.17 (m, 4H), 7.08 (d, J = 2.4 Hz, 1H), 7.06-7.03 (m, 2H), 6.99 (t, J = 8.0 Hz, 1H), 6.84-6.82 (m, 1H), 6.79-6.78 (m, 1H), 6.51 (d, J = 8.0 Hz, 1H), 4.63 (s, 2H), 3.45 (s, 3H), 3.35 (s, 3H), 3.14 (s, 3H), 2.98 (s, 6H), 1.34 (s, 12H), 1.28 (s, 9H).**^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 166.4, 166.0, 165.8, 150.9, 149.8, 147.3, 145.0, 140.3, 139.8, 137.9, 131.1, 130.1, 128.4, 128.2, 127.7, 127.5, 126.0, 124.1, 123.3, 120.0, 116.2, 112.2, 83.9, 74.8, 39.4, 37.1, 36.8, 35.9, 34.7, 31.5, 25.1. **IR** (KBr) ν 2963, 1579, 1532, 1490, 1385, 1356, 1316, 1143, 973, 808, 704. **HRMS** (ESI) *m/z* Calcd. for $C_{43}H_{54}N_7BBrO_3^+$ $[M+H]^+$ 806.3559; Found: 806.3558.

N^2-(3-((3-bromophenyl)(methyl)amino)-2-methoxy-5-methylphenyl)-N^2,N^4,N^4,N^6-tetramethyl-N^6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (6t)

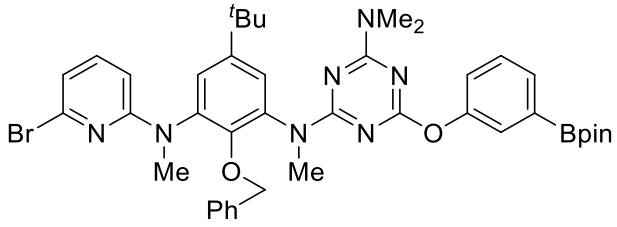


Chemical Formula: $C_{34}H_{43}BBrN_7O_3$; Molecular Weight: 688.4780

63.3 mg, 46% yield (calculated over 3 stpes), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.79 (s, 1H), 7.55 (d, J = 7.2 Hz, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.25-7.20 (m, 1H), 6.99 (t, J = 8.4 Hz, 1H), 6.92 (s, 1H), 6.86 (s, 1H), 6.84-6.82 (m, 2H), 6.54 (d, J = 9.2 Hz, 1H), 3.47-3.44 (m, 6H), 3.34 (s, 3H), 3.20 (s, 3H), 2.98-2.96 (m, 6H), 2.27 (s, 3H), 1.34 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 166.4, 166.0, 165.8, 151.4, 150.9, 145.0, 140.2, 139.8, 133.6, 131.0, 130.2, 129.9, 128.9, 127.8, 127.4, 123.3, 120.2, 116.3, 112.4, 83.9, 60.5, 39.3, 37.1, 36.8, 35.9, 25.1, 20.8. **IR** (KBr) v 2963, 1579, 1532, 1404, 1385, 1143, 973, 808, 704. **HRMS** (ESI) *m/z* Calcd. for $C_{34}H_{44}N_7BBrO_3^+$ $[M+H]^+$ 688.2777; Found: 688.2783.

N^2-(2-(benzyloxy)-3-((6-bromopyridin-2-yl)(methyl)amino)-5-(*tert*-butyl)phenyl)-N^2,N^4,N^4-trimethyl-6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)-1,3,5-triazine-2,4-diamine (6u)



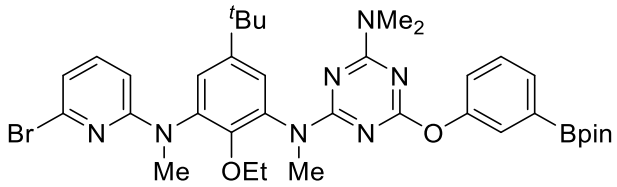
Chemical Formula: $C_{41}H_{49}BBrN_7O_4$; Molecular Weight: 794.6020

95.3 mg, 60% yield (calculated over 3 steps), colorless oil.

^{1}H NMR (400 MHz, tetrachloroethane-d_2, 373 K) δ 7.63-7.62 (m, 2H), 7.42-7.28 (m, 2H), 7.26-7.23 (m, 4H), 7.16-7.13 (m, 2H), 7.08-7.06 (m, 2H), 6.75 (d, J = 7.2 Hz, 1H), 6.18 (d, J = 6.8 Hz, 1H), 4.65 (s, 2H), 3.40 (s, 3H), 3.37 (s, 3H), 3.04 (s, 6H), 1.36 (s, 12H), 1.32 (s, 9H). **^{13}C NMR** (100 MHz, tetrachloroethane-d_2, 373 K) δ 170.5, 167.0,

166.5, 158.5, 154.9, 152.2, 149.1, 147.6, 139.6, 138.38, 138.35, 138.0, 137.1, 130.7, 128.9, 127.6, 127.5, 127.4, 127.0, 125.4, 124.8, 124.1, 121.1, 118.1, 115.3, 106.7, 83.7, 74.5, 37.7, 37.1, 35.9, 34.3, 31.1, 24.7. **IR** (KBr) *v* 2926, 1589, 1534, 1488, 1387, 1144, 1097, 971, 809, 705. **HRMS** (ESI) *m/z* Calcd. for $C_{41}H_{50}N_7BBrO_4^+$ $[M+H]^+$ 794.3195; Found: 794.3211.

N^2-(3-((6-bromopyridin-2-yl)(methyl)amino)-5-(*tert*-butyl)-2-ethoxyphenyl)-N^2,N^4,N^4-trimethyl-6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)-1,3,5-triazine-2,4-diamine (6v)

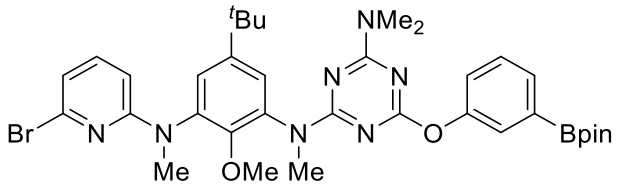


Chemical Formula: $C_{36}H_{47}BBrN_7O_4$; Molecular Weight: 731.2966

93.6 mg, 64% yield (calculated over 3 steps), white solid. M.P. = 71-72 °C

^{1}H NMR (400 MHz, tetrachloroethane-d_2, 373 K) δ 7.61 (d, J = 6.4 Hz, 2H), 7.30-7.26 (m, 2H), 7.17-7.13 (m, 3H), 6.75 (d, J = 7.2 Hz, 1H), 6.16 (d, J = 8.0 Hz, 1H), 3.70 (q, J = 7.2 Hz, 2H), 3.43 (s, 3H), 3.41 (s, 3H), 3.06 (s, 6H), 1.34 (s, 12H), 1.31 (s, 9H), 1.05 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, tetrachloroethane-d_2, 373 K) δ 170.5, 167.1, 166.7, 158.7, 152.3, 149.4, 147.1, 139.6, 138.23, 138.18, 137.8, 130.6, 128.9, 127.8, 127.5, 127.1, 125.3, 124.7, 124.0, 121.2, 118.1, 115.1, 106.6, 83.7, 68.5, 37.6, 36.9, 35.9, 34.2, 31.1, 24.7, 15.4. **IR** (KBr) *v* 2974, 2928, 1585, 1519, 1488, 1347, 1144, 974, 808, 704. **HRMS** (ESI) *m/z* Calcd. for $C_{36}H_{48}N_7BBrO_4^+$ $[M+H]^+$ 732.3039; Found: 732.3033.

N^2-(3-((6-bromopyridin-2-yl)(methyl)amino)-5-(*tert*-butyl)-2-methoxyphenyl)-N^2,N^4,N^4-trimethyl-6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)-1,3,5-triazine-2,4-diamine (6w)

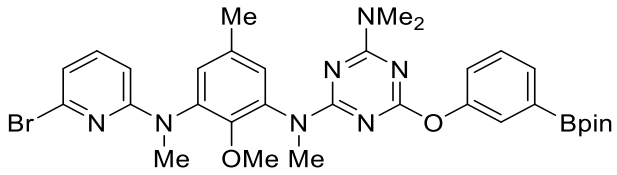


Chemical Formula: $C_{35}H_{45}BBrN_7O_4$; Molecular Weight: 718.5040

93.3 mg, 65% yield (calculated over 3 steps), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.57 (s, 1H), 7.37-7.35 (m, 2H), 7.25-7.24 (m, 1H), 7.22 (d, J = 7.6 Hz, 1H), 6.92 (ddd, J = 8.0 Hz, 2.8 Hz, 1.2 Hz, 1H), 6.72-6.71 (m, 1H), 3.49 (s, 3H), 3.39 (s, 3H), 3.36 (s, 3H), 3.02 (s, 6H), 2.28 (s, 3H), 1.36-1.34 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 167.4, 166.9, 158.9, 155.5, 152.6, 150.7, 147.7, 140.1, 138.7, 138.3, 137.9, 131.0, 129.2, 128.1, 127.1, 125.6, 125.2, 124.7, 121.4, 118.5, 115.6, 106.9, 84.0, 60.6, 37.9, 37.4, 36.2, 31.5, 25.0. **IR** (KBr) v 2977, 2929, 1731, 1586, 1488, 1336, 1189, 976, 809, 733. **HRMS** (ESI) *m/z* Calcd. for $C_{35}H_{46}N_7BBrO_4^+$ $[M+H]^+$ 718.2882; Found: 718.2888.

N^2-(3-((6-bromopyridin-2-yl)(methyl)amino)-2-methoxy-5-methylphenyl)-N^2,N^4,N^4-trimethyl-6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)-1,3,5-triazine-2,4-diamine (6x)



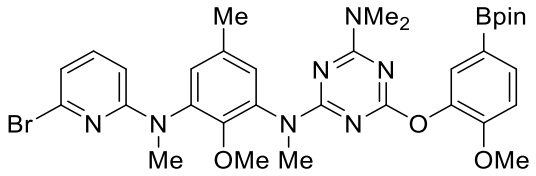
Chemical Formula: $C_{32}H_{39}BBrN_7O_4$; Molecular Weight: 676.4230

78.4 mg, 58% yield (calculated over 3 steps), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.57-7.56 (m, 2H), 7.28-7.20 (m, 2H), 7.11 (t, J = 7.6 Hz, 1H), 6.93-6.89 (m, 2H), 6.72 (d, J = 7.2 Hz, 1H), 6.15 (d, J = 7.2 Hz, 1H), 3.48 (s, 3H), 3.38 (s, 3H), 3.36 (s, 3H), 3.00 (s, 6H), 2.27 (s, 6H), 1.28 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 171.0, 167.4, 167.0, 158.8, 155.3, 152.7, 151.1, 140.1, 138.7, 138.3, 134.1, 131.1, 129.3, 129.2, 129.0, 128.4, 128.2, 127.4, 125.2, 121.3,

118.5, 115.7, 107.0, 84.0, 60.7, 37.9, 37.4, 36.2, 25.1, 20.8. **IR** (KBr) *v* 2921, 2850, 1646, 1581, 1532, 1404, 1356, 1144, 973, 868, 808, 705. **HRMS** (APCI) *m/z* Calcd. for $C_{32}H_{40}N_7BBrO_4^+$ $[M+H]^+$ 676.2413; Found: 676.2426.

N^2-(3-((6-bromopyridin-2-yl)(methyl)amino)-2-methoxy-5-methylphenyl)-6-(2-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)-N^2,N^4,N^4-trimethyl-1,3,5-triazine-2,4-diamine (6y)

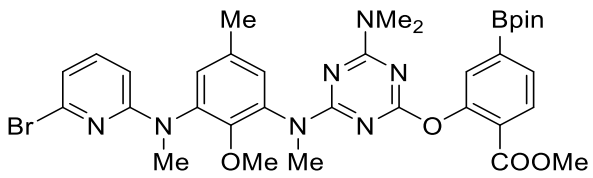


Chemical Formula: $C_{33}H_{41}BBrN_7O_5$; Molecular Weight: 706.4490

93.2 mg, 66% yield (calculated over 3 steps), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.58-7.52 (m, 2H), 7.13 (t, J = 7.2 Hz, 1H), 6.98-6.77 (m, 3H), 6.72 (d, J = 7.2 Hz, 1H), 6.16 (d, J = 8.4 Hz, 1H), 3.74 (s, 3H), 3.46 (s, 3H), 3.37 (s, 3H), 3.30 (s, 3H), 3.00 (s, 6H), 2.25 (s, 3H), 1.31 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 170.9, 167.4, 167.1, 158.8, 154.7, 151.1, 141.9, 140.1, 138.7, 138.3, 133.9, 133.0, 129.5, 129.1, 128.0, 115.7, 111.8, 107.0, 83.8, 60.7, 55.9, 37.9, 37.3, 36.2, 29.9, 25.1, 20.8. **IR** (KBr) *v* 2925, 2854, 1574, 1519, 1347, 1250, 1061, 855, 808, 790. **HRMS** (ESI) *m/z* Calcd. for $C_{34}H_{42}N_7BBrO_5^+$ $[M+H]^+$ 706.2518; Found: 706.2530.

Methyl 2-((4-((3-((6-bromopyridin-2-yl)(methyl)amino)-2-methoxy-5-methylphenyl)(methyl)amino)-6-(dimethylamino)-1,3,5-triazin-2-yl)oxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6z)

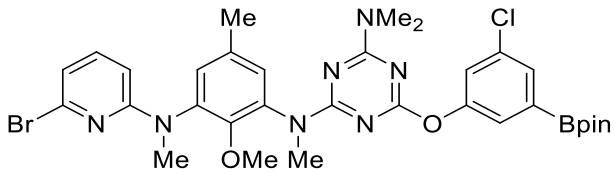


Chemical Formula: $C_{34}H_{41}BBrN_7O_6$; Molecular Weight: 734.4590

76.4 mg, 52% yield (calculated over 3 steps), white solid, M.P. = 77-78 °C

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.83 (s, 1H), 7.63-7.53 (m, 2H), 7.20-7.08 (m, 1H), 6.85 (s, 2H), 6.72 (d, J = 7.6 Hz, 1H), 6.13 (d, J = 7.6 Hz, 1H), 3.70 (s, 3H), 3.44 (s, 3H), 3.36 (s, 3H), 3.32 (s, 3H), 3.01 (s, 6H), 2.24 (s, 3H), 1.33 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 171.0, 167.2, 166.9, 166.0, 158.8, 151.7, 151.0, 140.1, 138.7, 138.3, 134.1, 131.0, 130.2, 129.9, 129.1, 128.1, 127.1, 115.7, 107.1, 84.4, 60.6, 52.0, 37.9, 37.3, 36.3, 25.1, 20.8. **IR** (KBr) v 2978, 2931, 1732, 1587, 1519, 1403, 1348, 1142, 975, 808, 776. **HRMS** (ESI) *m/z* Calcd. for $C_{34}H_{42}N_7BBrO_6^+$ $[M+H]^+$ 734.2468; Found: 734.2464.

N^2-(3-((6-bromopyridin-2-yl)(methyl)amino)-2-methoxy-5-methylphenyl)-6-(3-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)-N^2,N^4,N^4-trimethyl-1,3,5-triazine-2,4-diamine (6aa)



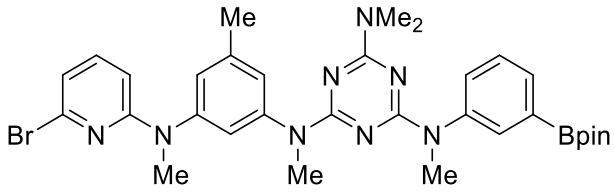
Chemical Formula: $C_{32}H_{38}BBrClN_7O_4$; Molecular Weight: 710.8650

86.6 mg, 61% yield (calculated over 3 steps), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.54 (s, 1H), 7.35 (s, 1H), 7.12-7.08 (m, 2H), 6.94-6.91 (m, 3H), 6.72 (d, J = 7.2 Hz, 1H), 6.19 (d, J = 7.2 Hz, 1H), 3.47 (s, 3H), 3.37 (s, 6H), 3.01 (s, 6H), 2.27 (s, 3H), 1.34 (s, 12H), 1.32 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 170.6, 167.3, 166.9, 158.7, 153.2, 151.0, 140.1, 138.7, 138.3, 134.3, 133.7, 130.9, 128.8, 128.3, 127.0, 126.3, 125.6, 119.8, 118.8, 115.8, 106.9, 84.4, 60.7, 37.9, 37.5, 36.3, 25.0, 20.8. **IR** (KBr) v 2921, 2850, 1658, 1588, 1406, 1340, 1142, 969, 861, 807, 702. **HRMS** (ESI) *m/z* Calcd. for $C_{32}H_{39}N_7BBrClO_4^+$ $[M+H]^+$ 710.2023; Found: 710.2018.

N^2-(3-((6-bromopyridin-2-yl)(methyl)amino)-5-methylphenyl)-N^2,N^4,N^4,N^6-

tetramethyl-N^6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4,6-triamine (6ad)

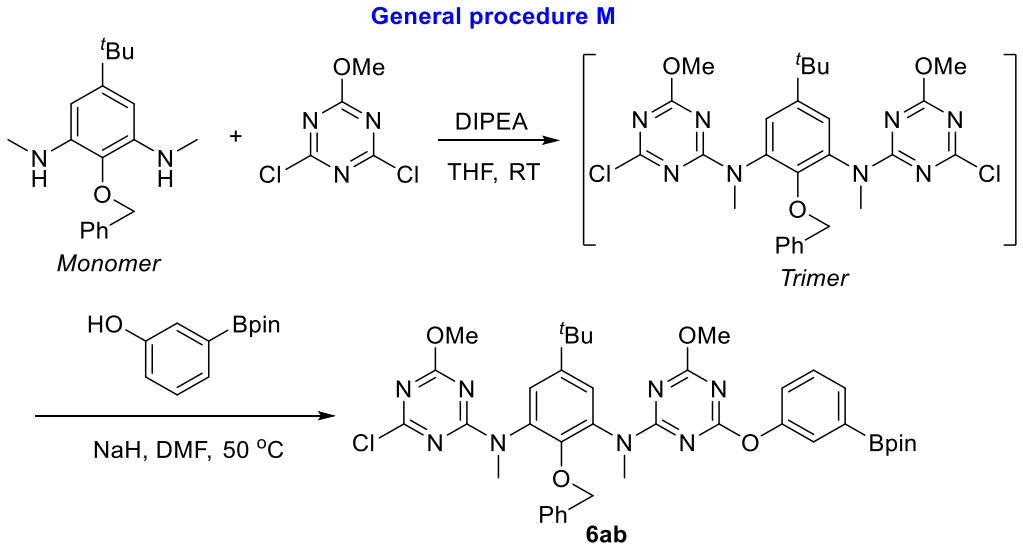


Chemical Formula: $C_{32}H_{40}BBrN_8O_2$; Molecular Weight: 658.2551

65.3 mg, 46% yield (calculated over 3 steps), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.56 (d, J = 7.2 Hz, 1H), 7.43 (d, J = 8.8 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.07-7.03 (m, 3H), 6.80 (s, 1H), 6.70 (d, J = 7.2 Hz, 1H), 6.34 (d, J = 8.4 Hz, 1H), 3.45 (s, 3H), 3.42-3.41 (m, 6H), 2.97 (m, 6H), 2.33 (s, 3H), 1.33 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7, 165.6, 165.6, 159.1, 146.7, 145.3, 144.6, 140.0, 139.6, 138.5, 132.2, 131.2, 129.8, 127.6, 124.8, 123.6, 122.3, 115.5, 107.3, 83.9, 38.5, 37.3, 37.2, 35.9, 25.0, 21.6. **IR** (KBr) ν 2925, 2852, 1657, 1590, 1421, 1341, 1144, 971, 808, 702. **HRMS** (ESI) *m/z* Calcd. For $C_{32}H_{41}N_8BBrO_2^+$ $[M+H]^+$ 659.2638; Found: 659.2642.

5. Synthesis of tetramer 6ab

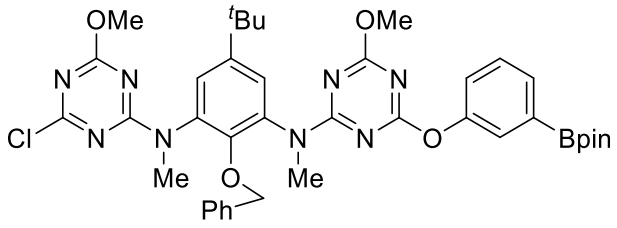


General procedure M: To a 50 mL round bottom flask was added 2,4-dichloro-6-methoxy-1,3,5-triazine (81.0 mg, 0.44 mmol, 2.2 equiv), DIPEA (65.0 mg, 0.5 mmol, 2.5 equiv), and THF (15 mL). A solution of *Monomer* (59.6 mg, 0.2 mmol) in 5 mL THF was slowly added at room temperature and stirred overnight. The reaction mixture was quenched with H_2O and the organic layer was extracted with EtOAc, washed with brine and dried over anhydrous Na_2SO_4. Solvents evaporated in vacuo to obtained crude product *Trimer*, which was used for next step without further purification.

To a round bottom flask was added *Trimer* (crude product, approximately 0.2 mmol), NaH (12.0 mg, 0.3 mmol, 60% dispersion in mineral oil, 1.5 equiv), 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (48.5 mg, 0.22 mmol, 1.1 equiv). To the mixture was added DMF (10 mL) under argon at 0 °C. The mixture was then stirred at room temperature for 12 h until the starting material was consumed completely. The reaction mixture was quenched with H_2O and the organic layer was extracted with EtOAc, washed with brine and dried over anhydrous Na_2SO_4. After solvent evaporation, the residue was subjected to column chromatography on silica gel (PE/EtOAc = 20:1) to give the desired linear tetramer **6ab**.

2-(benzyloxy)-5-(*tert*-butyl)-N^1-(4-chloro-6-methoxy-1,3,5-triazin-2-yl)-N^3-(4-methoxy-6-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)-1,3,5-

triazin-2-yl)-N^1,N^3-dimethylbenzene-1,3-diamine (6ab)

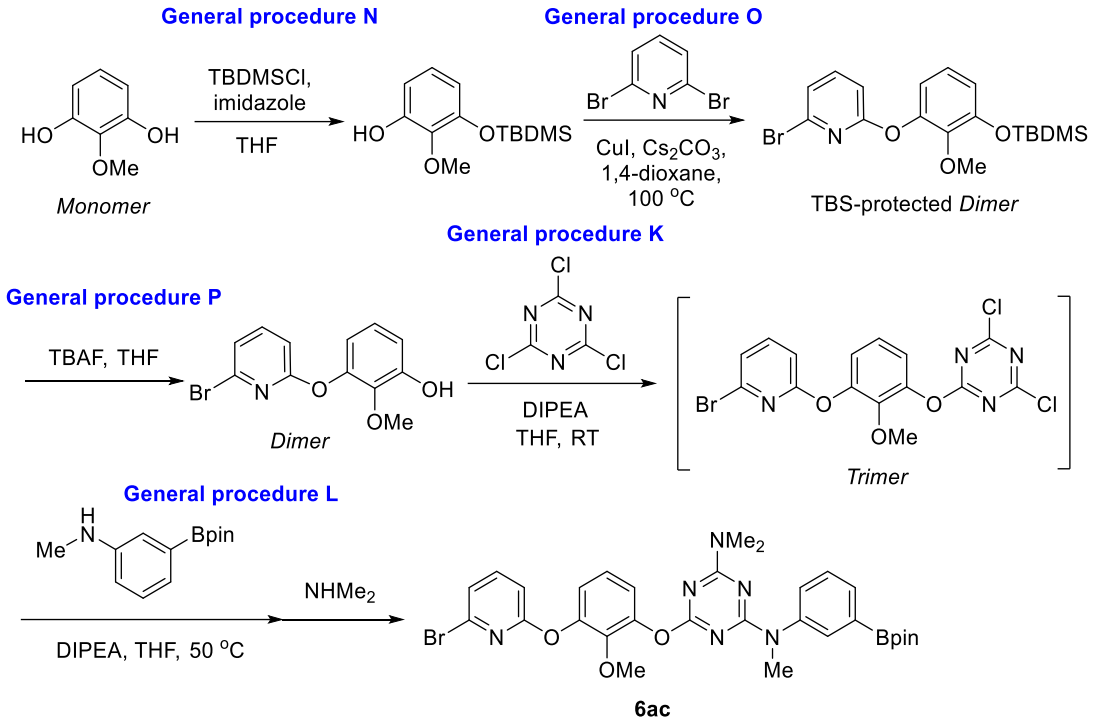


Chemical Formula: $C_{39}H_{46}BClN_8O_6$; Molecular Weight: 769.1070

70.7 mg, 46% yield (calculated over 2 steps), colorless oil.

^{1}H NMR (400 MHz, DMSO-d_6, 373 K) δ 7.58-7.42 (m, 3H), 7.35-7.25 (m, 2H), 7.21-7.16 (m, 4H), 7.03 (d, J = 2.0 Hz, 2H), 4.66 (s, 2H), 3.92-3.66 (m, 6H), 3.32 (s, 6H), 1.31 (s, 12H), 1.27 (s, 9H). **^{13}C NMR** (100 MHz, DMSO-d_6, 373 K) δ 171.2, 167.3, 165.9, 151.3, 146.7, 136.5, 136.2, 135.6, 130.7, 128.5, 127.7, 127.5, 127.2, 126.7, 124.9, 124.2, 83.5, 74.0, 54.2, 53.7, 38.9, 37.5, 37.0, 33.9, 30.6, 27.6, 24.5, 24.2. **IR** (KBr) ν 2925, 2854, 1563, 1466, 1370, 1143, 808, 703. **HRMS** (ESI) *m/z* Calcd. for $C_{39}H_{47}N_8BClO_6^+$ $[M+H]^+$ 769.3395; Found: 769.3401.

6. Synthesis of tetramer 6ac



General procedure N: To a round bottom flask was added *Monomer* 2-methoxybenzene-1,3-diol (700.0 mg, 5 mmol), imidazole (510.0 mg, 7.5 mmol, 1.5 equiv), and THF (10 mL). To the mixture was slowly added TBDMSCl (825.0 mg, 5.5 mmol, 1.1 equiv) at 0 °C. The mixture was then stirred at room temperature for 12 h until the starting material was consumed completely. The reaction mixture was quenched with H_2O and the organic layer was extracted with EtOAc, washed with brine and dried over anhydrous Na_2SO_4. Solvents evaporated in vacuo to obtain the *TBS-protected monomer* as a crude product, which was used for next step without further purification.

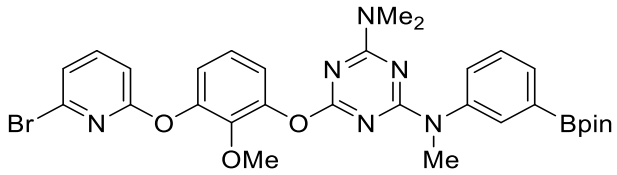
General procedure O: To a round bottom flask was added *TBS-protected monomer* (crude product, approximately 5 mmol), CuI (96 mg, 0.5 mmol, 10 mol%), Cs_2CO_3 (3.3 g, 10 mmol, 2 equiv) and 2,6-dibromopyridine (1.8 g, 7.5 mmol, 1.5 equiv). 1,4-dioxane (30 mL) was added and the reaction was stirred under argon at 100 °C overnight. The reaction mixture was quenched with H_2O and the organic layer was extracted with EtOAc, washed with brine and dried over anhydrous Na_2SO_4. Solvents evaporated in

vacuo to obtain the TBS-protected *Dimer* and trimer as a crude product

General procedure P: To a round bottom flask was added the TBS-protected *Dimer* (crude product, approximately 5 mmol) and THF (10 mL). To the mixture was slowly added the solution of TBAF (5 mL, 5 mmol, 1M in THF, 1.0 equiv). The mixture was then stirred at room temperature for 12 h until the starting material was consumed completely. The reaction mixture was quenched with H_2O and the organic layer was extracted with EtOAc, washed with brine and dried over anhydrous Na_2SO_4. After solvent evaporation, the residue was subjected to column chromatography on silica gel (PE/EtOAc = 10:1) to give the *Dimer*.

The desired tetramer **6ac** was obtained following **General procedure K** and **L.**

6-(3-((6-bromopyridin-2-yl)oxy)-2-methoxyphenoxy)-*N*^{2},*N*^{2},*N*^{4}-trimethyl-*N*^{4}-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine-2,4-diamine (6ac)

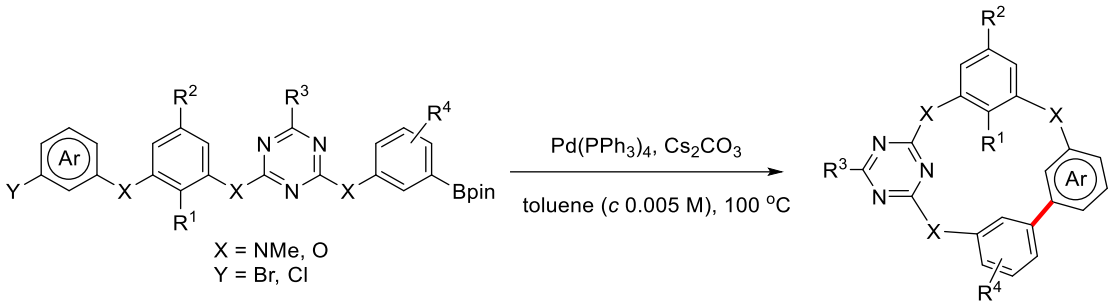


Chemical Formula: $C_{30}H_{34}BBrN_6O_5$; Molecular Weight: 649.3530

53.3 mg, 3% yield (calculated yield based on *Monomer*), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, 333 K) δ 7.72 (s, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.38-7.35 (m, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 7.04-6.98 (m, 2H), 6.98 (t, J = 5.2 Hz, 1H), 6.61 (d, J = 8.0 Hz, 1H), 3.73 (s, 3H), 3.44 (s, 3H), 2.99 (s, 6H), 1.34 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$, 333 K) δ 171.0, 166.9, 163.3, 147.1, 146.9, 145.4, 144.2, 141.1, 139.4, 132.4, 132.0, 129.8, 127.9, 123.1, 122.3, 121.2, 119.8, 108.6, 84.0, 61.3, 37.7, 36.3, 25.1. **IR** (KBr) ν 2976, 2928, 1563, 1466, 1368, 1206, 1144, 809, 704. **HRMS** (ESI) *m/z* Calcd. for $C_{30}H_{35}N_6BBrO_5^+$ $[M+H]^+$ 649.1940; Found: 649.1941.

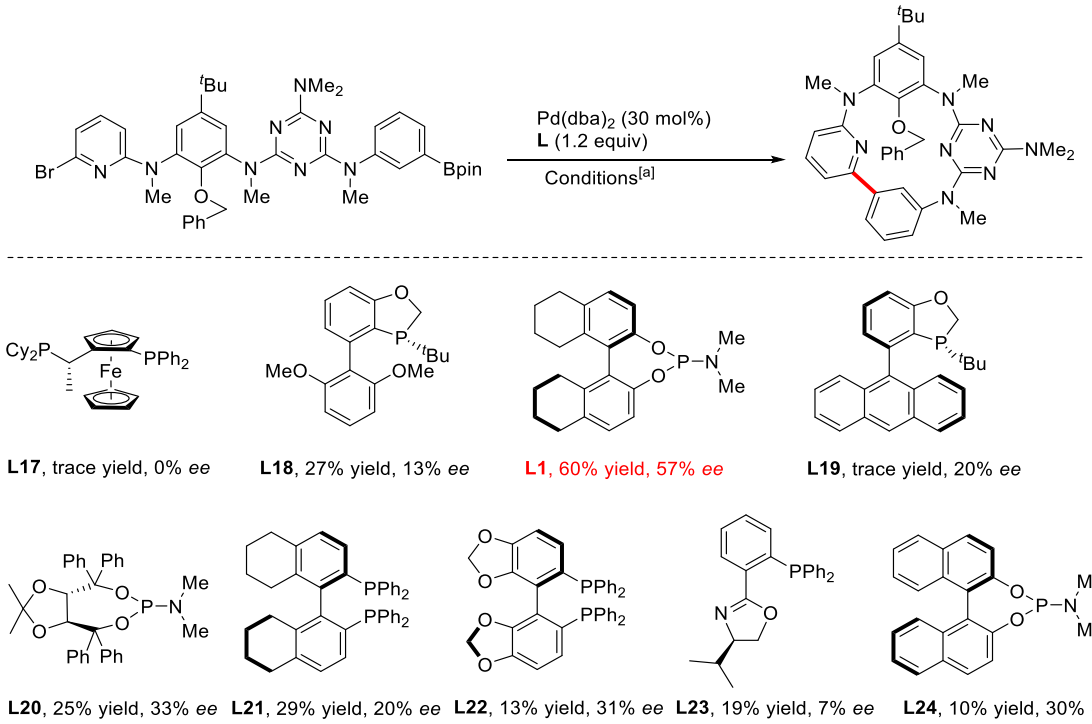
7. Synthesis of racemic 5



A mixture of $Pd(PPh_3)_4$ (15 mg, 0.013 mmol, 25 mol%), Cs_2CO_3 (49 mg, 0.15 mmol, 3 equiv) in dry toluene (8 mL) was heated to 100 °C in a two-neck round bottom flask under argon. To the resulting yellow solution was slowly added linear tetramer **6** (0.05 mmol) in dry toluene (2 mL) with an injection pump during 1 h. The reaction was refluxed for 12 h until the reaction was complete (monitored by TLC). The reaction was cooled to room temperature and filtered through celite. The filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel, eluating with PE/EtOAc 8:1~1:1 to afford *rac*-**5**.

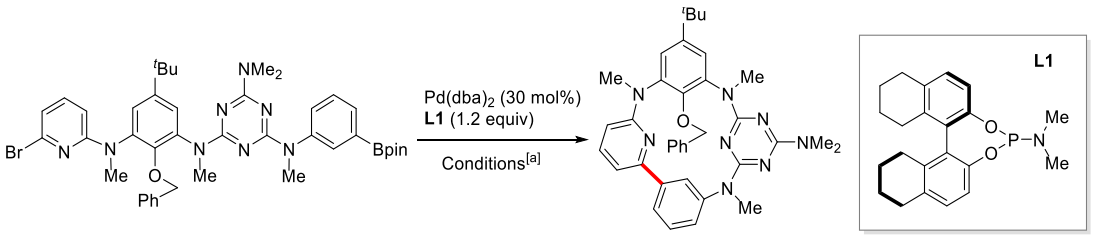
8. Catalytic enantioselective synthesis of 5

Table S1. Optimization of chiral ligands



[a]Conditions: $Pd(dba)_2$ (30 mol%), **L** (1.2 equiv), Cs_2CO_3 (3 equiv), 1,4-dioxane (*c* 0.005 M), Schlenk tube, inert atmosphere, **6** (0.04 mmol) in 1,4-dioxane (2 mL) was added with an injection pump during 1 h, isolated yield.

Table S2. Optimization of reaction conditions using $Pd(dba)_2$/**L1** as chiral catalyst

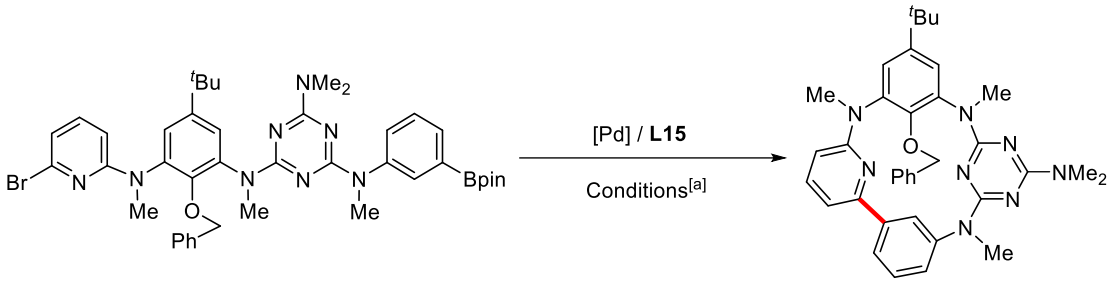


Entry	Solvent	Base	T / °C	Yield / %	*ee* / %
1	1,4-dioxane	Cs_2CO_3	100	60	57
2	Toluene	Cs_2CO_3	100	53	66
3	DMF	Cs_2CO_3	100	40	40
4	THF	Cs_2CO_3	reflux	36	32

5	CH_3CN	Cs_2CO_3	reflux	5	5
6	DME	Cs_2CO_3	reflux	44	0
7	*o*-xylene	Cs_2CO_3	100	54	65
8	*m*-xylene	Cs_2CO_3	100	58	66
9	*p*-xylene	Cs_2CO_3	100	7	33
10	*o*/*m*-xylene = 1:1	Cs_2CO_3	100	31	40
11	xylenes	Cs_2CO_3	100	30	6
12	Benzene	Cs_2CO_3	reflux	NR	ND
13	Toluene	Rb_2CO_3	100	38	18
14	Toluene	K_2CO_3	100	Trace	0
15	Toluene	Na_2CO_3	100	NR	ND
16	Toluene	KO^tBu	100	37	5
17	Toluene	NaO^tBu	100	48	7
18	Toluene	CsOH	100	41	0
19	Toluene	KOH	100	7	19
20	Toluene	NaOH	100	32	24
21	Toluene	K_3PO_4	100	27	20
22	Toluene	K_2HPO_4	100	NR	ND
23	Toluene	KF	100	NR	ND
24	Toluene	KOAc	100	NR	ND

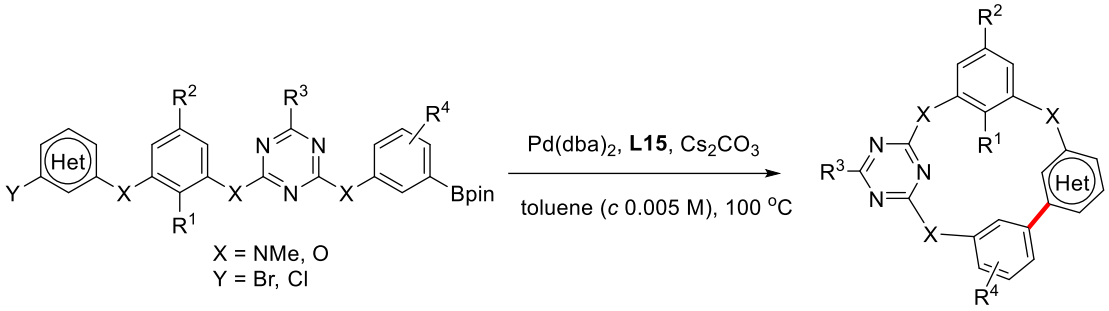
[a]Conditions: $Pd(dba)_2$ (30 mol%), **L1** (1.2 equiv), base (3 equiv), solvent (*c* 0.005 M), Schlenk tube, inert atmosphere, **6** (0.04 mmol) in solvent (2 mL) was added with an injection pump during 1 h, isolated yield.

Table S3. Optimization of reaction conditions using $Pd(dba)_2$/**L15** as chiral catalyst



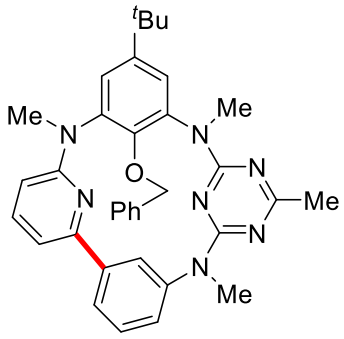
Entry	[Pd] (mol%)	[Pd] / [L]	t / h	Yield / %	*ee* / %
1	$Pd(dba)_2$ (30)	1 : 4	12	66	70
2	$Pd(dba)_2$ (30)	1 : 4.05	12	70	90
3	$Pd(dba)_2$ (25)	1 : 4.05	12	63	91
4	$Pd(dba)_2$ (20)	1 : 4.05	12	63	89
5	$Pd(dba)_2$ (15)	1 : 4.05	12	66	86
6	$Pd(dba)_2$ (15)	1 : 4.05	24	70	87
7	$Pd(dba)_2$ (10)	1 : 4.05	100	47	75
8	$Pd(dba)_2$ (20)	1 : 4.05	100	72	88
9	$PdBr_2$ (25)	1 : 4.05	100	60	75
10	$Pd(CF_3COO)_2$ (30)	1 : 4.05	100	58	80
11	$Pd(OTf)_2(CH_3CN)_2$ (30)	1 : 4.05	100	62	86
12	$Pd_2(dba)_3$ (12)	1 : 4.05	reflux	65	86
13	$PdCl_2(CH_3CN)_2$ (20)	1 : 4.05	100	62	85
14	$Pd(NO_3)_2$ (20)	1 : 4.05	100	trace	85
15	$Pd_2(dba)_3$•toluene (10)	1 : 4.05	100	75	88

[a]Conditions: Catalyst (30 mol%), **L15** (1.2 equiv), base (3 equiv), toluene (*c* 0.005 M), Schlenk tube, inert atmosphere, **6** (0.04 mmol) in toluene (2 mL) was added with an injection pump during 1 h, isolated yield.



A mixture of $Pd(dba)_2$ (7 mg, 0.012 mmol, 30 mol%), **L15** (16 mg, 0.04 mmol, 1.2 equiv), Cs_2CO_3 (39 mg, 0.12 mmol, 3 equiv) in dry toluene (5 mL) was heated to 100 °C in a two-neck round bottom flask under argon. To the resulting yellow solution was slowly added linear tetramer **6** (0.04 mmol) in dry toluene (2 mL) with an injection pump during 1 h. The reaction was refluxed for 12 h until the reaction was complete (monitored by TLC). The reaction was cooled to room temperature and filtered through celite. The filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel, eluating with PE/EtOAc 8:1~1:1 to afford **5**.

6^2-(benzyloxy)-6^5-(*tert*-butyl)-*N*,*N*,3,5,7-pentamethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5a)



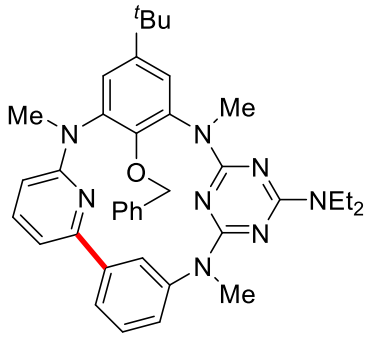
Chemical Formula: $C_{36}H_{40}N_8O$; Molecular Weight: 600.7710

21.0 mg, 70% yield, white solid. M.P. = 238-240 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.22 (t, J = 8.0 Hz, 1H), 7.17-7.15 (m, 1H), 7.13-7.11 (m, 3H), 7.05 (d, J = 2.4 Hz, 1H), 7.05-7.03 (m, 1H), 7.01-7.00 (m, 3H), 6.94 (d, J = 7.2 Hz, 1H), 6.50 (d, J = 8.0 Hz, 1H), 4.92 (d, J = 12.4 Hz, 1H), 4.83 (d, J = 12.0 Hz, 1H), 3.60 (s, 3H), 3.39 (s, 3H), 3.37 (s, 3H), 3.19

(s, 6H), 1.24 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.51, 166.48, 165.4, 157.1, 156.8, 151.2, 146.5, 145.0, 141.0, 140.0, 138.9, 137.8, 137.4, 128.0, 127.5, 127.0, 126.8, 124.1, 123.6, 122.2, 119.6, 119.4, 109.9, 102.7, 74.0, 40.9, 37.9, 37.6, 36.0, 34.5, 31.5. **IR** (KBr) *v* 2926, 2858, 1571, 1533, 1489, 1377, 1244, 807, 778, 733. **HRMS** (ESI) *m/z* Calcd. for $C_{36}H_{41}N_8O^+$ $[M+H]^+$ 601.3398; Found: 601.3388. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 °C, 0.5 mL/min flow rate, detection at 254 nm, t_1 = 10.1 min (minor), t_2 = 21.2 min (major). $[\alpha]_D^{25}$ = -36.2 (*c* = 0.002, CH_3OH) for 90.6% *ee*.

6^2-(benzyloxy)-6^5-(*tert*-butyl)-*N*,*N*-diethyl-3,5,7-trimethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5b)



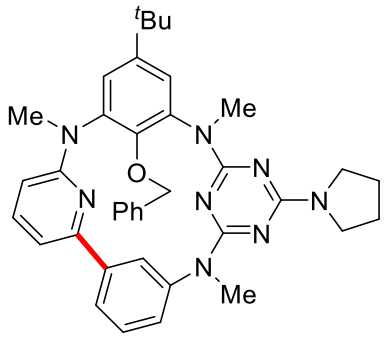
Chemical Formula: $C_{38}H_{44}N_8O$; Molecular Weight: 628.8250

19.5 mg, 62% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.14-7.12 (m, 3H), 7.07 (d, *J* = 2.4 Hz, 1H), 7.05-7.00 (m, 4H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 6.4 Hz, 1H), 4.92 (d, *J* = 12.4 Hz, 1H), 4.82 (d, *J* = 12.0 Hz, 1H), 3.72-3.54 (m, 4H), 3.58 (s, 3H), 3.40 (s, 3H), 3.38 (s, 3H), 1.25 (s, 9H), 1.23-1.21 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 166.5, 164.2, 157.0, 151.2, 146.6, 145.2, 140.9, 139.9, 138.9, 137.9, 137.6, 128.0, 127.5, 127.0, 126.9, 123.9, 123.7, 122.2, 119.5, 119.3, 109.9, 102.9, 74.0, 41.4, 40.9, 37.8, 37.7, 34.5, 31.6, 13.6. **IR** (KBr) *v* 2961, 2926, 2855, 1769, 1558, 1356, 1259, 913, 851, 749. **HRMS** (ESI) *m/z* Calcd. for $C_{38}H_{45}N_8O^+$ $[M+H]^+$ 629.3711; Found: 629.3693. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 °C, 0.5 mL/min flow rate, detection at 254 nm, t_1 = 9.3 min (minor), t_2 = 32.2 min (major). $[\alpha]_D^{25}$ = -31.8 (*c* = 0.002, CH_3OH)

for 90.0% *ee*.

6^2-(benzyloxy)-6^5-(*tert*-butyl)-3,5,7-trimethyl-4^6-(pyrrolidin-1-yl)-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphane (5c)

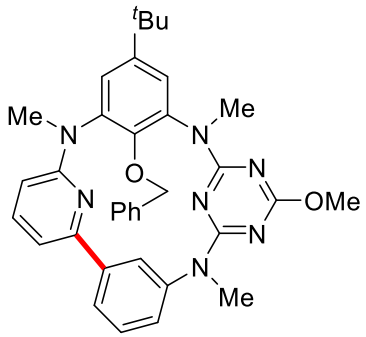


Chemical Formula: $C_{38}H_{42}N_8O$; Molecular Weight: 626.8090

20.7 mg, 66% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 7.2 Hz, 1H), 7.12-7.11 (m, 3H), 7.06-7.04 (m, 2H), 7.01-6.99 (m, 3H), 6.94 (d, J = 7.6 Hz, 1H), 6.51 (d, J = 8.4 Hz, 1H), 4.92 (d, J = 12.4 Hz, 1H), 4.84 (d, J = 12.0 Hz, 1H), 3.62 (t, J = 6.0 Hz, 4H), 3.60 (s, 3H), 3.40 (s, 3H), 3.37 (s, 3H), 1.97 (t, J = 6.4 Hz), 1.24 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 166.3, 163.4, 157.1, 156.8, 151.2, 146.5, 145.1, 141.0, 140.0, 138.9, 137.8, 137.5, 128.0, 127.5, 126.9, 126.8, 123.8, 123.6, 122.2, 119.5, 119.2, 109.9, 102.7, 73.9, 46.0, 40.9, 37.8, 37.6, 34.5, 31.6, 25.6. **IR** (KBr) ν 2923, 2852, 1572, 1519, 1470, 1390, 1255, 966, 780. **HRMS** (APCI) *m/z* Calcd. for $C_{38}H_{43}N_8O^+$ $[M+H]^+$ 627.3554; Found: 627.3540. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 °C, 0.5 mL/min flow rate, detection at 254 nm, t_1 = 12.9 min (minor), t_2 = 43.4 min (major). $[\alpha]_D^{25}$ = -33.6 (c = 0.002, CH_3OH) for 89.0% *ee*.

6^2-(benzyloxy)-6^5-(*tert*-butyl)-4^6-methoxy-3,5,7-trimethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphane (5d)

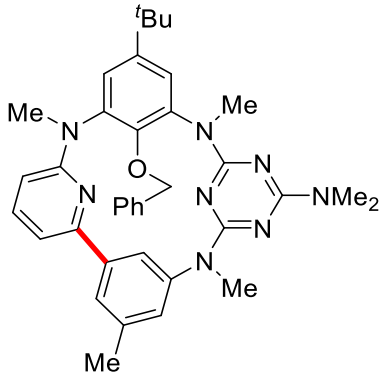


Chemical Formula: $C_{35}H_{37}N_7O_2$; Molecular Weight: 587.7280

21.2 mg, 72% yield, white solid. M.P. = 232-233 ºC

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.89 (s, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.25-7.24 (m, 2H), 7.21-7.19 (m, 5H), 7.14-7.12 (m, 2H), 7.02 (d, J = 7.6 Hz, 1H), 6.77 (d, J = 8.4 Hz, 1H), 5.06 (d, J = 12.0 Hz, 1H), 4.90 (d, J = 12.4 Hz, 1H), 3.99 (s, 3H), 3.66 (s, 3H), 3.54 (s, 3H), 3.46 (s, 3H), 1.29 (s, 9H).**^{13}C NMR** (100 MHz, Acetone-d_6) δ 170.6, 167.4, 167.0, 157.3, 156.4, 151.2, 146.7, 144.7, 141.5, 140.6, 138.6, 138.1, 137.2, 128.0, 127.8, 127.2, 126.9, 124.8, 122.8, 122.5, 120.5, 120.1, 109.6, 103.1, 74.1, 53.1, 40.7, 37.8, 36.8, 34.2, 30.8. **IR** (KBr) ν 2925, 2854, 1731, 1607, 1532, 1372, 1245, 1093, 978, 806, 694. **HRMS** (ESI) *m/z* Calcd. for $C_{35}H_{38}N_7O_2^+$ $[M+H]^+$ 588.3082; Found: 588.3077. **HPLC**: AD-H column, Hexane : *i*-PrOH = 84 : 16, 24 ºC, 0.5 mL/min flow rate, detection at 254 nm, t_1 = 9.7 min (minor), t_2 = 12.5 min (major). $[\alpha]_D^{25}$ = -30.5 (c = 0.002, CH_3OH) for 90.4% *ee*.

6^2-(benzyloxy)-6^5-(*tert*-butyl)-*N*,*N*,2^5,3,5,7-hexamethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5e)

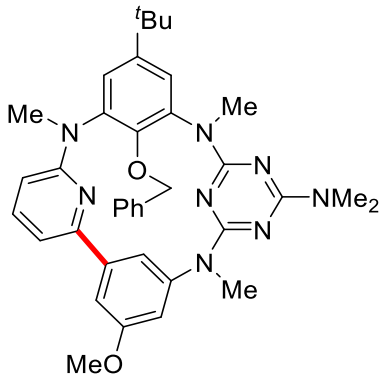


Chemical Formula: $C_{37}H_{42}N_8O$; Molecular Weight: 614.7980

22.1 mg, 72% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.13-7.11 (m, 3H), 7.05 (d, J = 2.4 Hz, 1H), 7.00-6.98 (m, 4H), 6.92 (d, J = 7.2 Hz, 1H), 6.87 (s, 1H), 6.49 (d, J = 8.0 Hz, 1H), 4.91 (d, J = 12.0 Hz, 1H), 4.83 (d, J = 12.0 Hz, 1H), 3.58 (s, 3H), 3.38 (s, 3H), 3.36 (s, 3H), 3.18 (s, 6H), 2.33 (s, 3H), 1.24 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 166.5, 165.3, 159.2, 157.0, 156.8, 151.2, 146.6, 145.9, 141.8, 140.0, 138.9, 137.9, 137.5, 128.0, 127.0, 126.8, 123.6, 122.3, 117.1, 109.8, 106.2, 104.4, 102.9, 74.0, 55.6, 40.9, 37.8, 37.6, 36.0, 34.5, 31.6, 14.3. **IR** (KBr) v 2965, 2925, 2854, 1573, 1537, 1487, 1379, 1247, 1062, 791, 733. **HRMS** (ESI) m/z Calcd. for $C_{37}H_{43}N_8O^+$ $[M+H]^+$ 615.3554; Found: 615.3537. **HPLC**: AD-H column, Hexane : i-PrOH = 80 : 20, 24 ºC, 0.5 mL/min flow rate, detection at 315 nm, t_1 = 11.4 min (minor), t_2 = 20.6 min (major). $[\alpha]_D^{25}$ = -27.8 (c = 0.002, CH_3OH) for 93.0% *ee*.

6^2-(benzyloxy)-6^5-(*tert*-butyl)-2^5-methoxy-*N*,*N*,3,5,7-pentamethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5f)



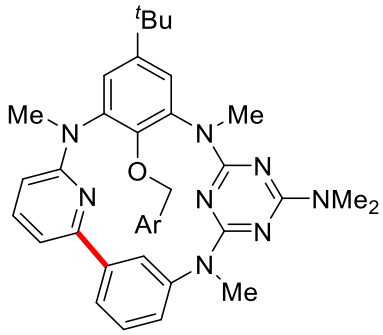
Chemical Formula: $C_{37}H_{42}N_8O_2$; Molecular Weight: 630.7970

23.0 mg, 73% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (dd, J = 2.4 Hz, 1.2 Hz, 1H), 7.54 (dd, J = 8.0 Hz, 7.2 Hz, 1H), 7.12-7.10 (m, 3H), 7.04 (d, J = 2.4 Hz, 1H), 7.00 (d, J = 2.8 Hz, 1H), 6.99-6.96 (m, 2H), 6.92 (d, J = 7.2 Hz, 1H), 6.72 (dd, J = 2.4 Hz, 1.2 Hz, 1H), 6.18 (t, J =

2.4 Hz, 1H), 6.49 (d, J = 8.4 Hz, 1H), 4.88 (d, J = 12.0 Hz, 1H), 4.81 (d, J = 12.0 Hz, 1H), 3.80 (s, 3H), 3.58 (s, 3H), 3.38 (s, 3H), 3.36 (s, 3H), 3.18 (s, 6H), 1.24 (s, 9H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 166.5, 165.4, 159.2, 157.0, 156.8, 151.2, 146.6, 145.9, 141.8, 140.0, 138.9, 137.9, 137.5, 128.0, 127.0, 126.8, 123.6, 122.3, 117.1, 109.8, 106.2, 104.4, 102.9, 74.0, 55.6, 40.9, 37.8, 37.6, 36.0, 34.5, 31.6. **IR** (KBr) v 2960, 2924, 1736, 1577, 1537, 1488, 1390, 1244, 908, 807, 732. **HRMS** (ESI) *m/z* Calcd. for $C_{37}H_{43}N_8O_2^+$ $[M+H]^+$ 631.3504; Found: 631.3507. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 ºC, 0.5 mL/min flow rate, detection at 315 nm, t_1 = 12.5 min (minor), t_2 = 28.7 min (major). $[\alpha]_D^{25}$ = -26.5 (c = 0.002, CH_3OH) for 93.0% *ee*.

6^5-(*tert*-butyl)-*N*,*N*,3,5,7-pentamethyl-6^2-((3-methylbenzyl)oxy)-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5g)



Ar = 3-Me-C_6H_4

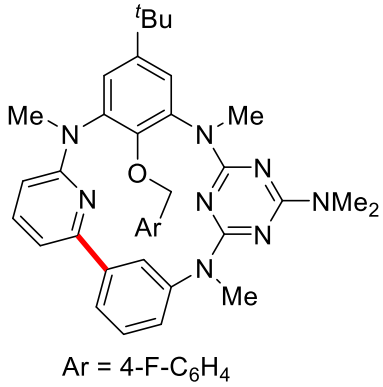
Chemical Formula: $C_{37}H_{42}N_8O$; Molecular Weight: 614.7980

20.6 mg, 67% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.22 (t, J = 8.0 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 7.06-7.04 (m, 2H), 7.02-7.00 (m, 2H), 6.94 (d, J = 7.2 Hz, 2H), 6.83 (s, 1H), 6.79 (d, J = 7.2 Hz, 1H), 6.51 (d, J = 8.4 Hz, 1H), 4.89 (d, J = 12.0 Hz, 1H), 4.79 (d, J = 12.0 Hz, 1H), 3.60 (s, 3H), 3.40 (s, 3H), 3.39 (s, 3H), 3.19 (s, 6H), 2.16 (s, 3H), 1.24 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.48, 166.47, 165.4, 157.1, 156.9, 151.3, 146.5, 145.0, 141.1, 140.0, 138.9, 137.8, 137.7, 137.4, 127.8, 127.7, 127.6, 127.5, 124.3, 123.6, 123.5, 122.2, 119.7, 119.6, 109.9, 102.7, 73.9, 41.0, 38.0, 37.6, 36.0, 34.5, 31.6, 21.3. **IR** (KBr) ν 2955, 2926, 1570, 1535, 1489, 1377, 1244, 808,

778, 698. **HRMS** (ESI) *m/z* Calcd. for $C_{37}H_{43}N_8O^+$ $[M+H]^+$ 615.3554; Found: 615.3559. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 ºC, 0.5 mL/min flow rate, detection at 254 nm, t_1 = 10.2 min (minor), t_2 = 23.6 min (major). $[\alpha]_D^{25}$ = -24.4 (*c* = 0.002, CH_3OH) for 89.7% *ee*.

6^5-(*tert*-butyl)-6^2-((4-fluorobenzyl)oxy)-*N*,*N*,3,5,7-pentamethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5h)

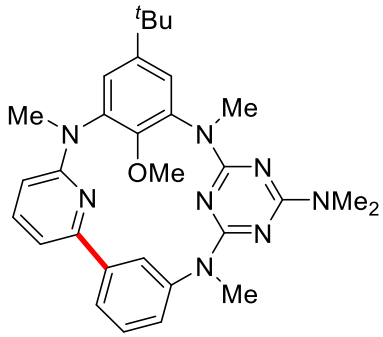


Chemical Formula: $C_{36}H_{39}FN_8O$; Molecular Weight: 618.7614

20.7 mg, 67% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 2.4 Hz, 1.6 Hz, 1H), 7.55 (dd, *J* = 8.4 Hz, 7.6 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.17 (dt, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.06-7.04 (m, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.96-6.93 (m, 3H), 6.82-6.77 (m, 2H), 6.50 (d, *J* = 8.4 Hz, 1H), 4.88 (d, *J* = 12.4 Hz, 1H), 4.79 (d, *J* = 12.0Hz, 1H), 3.60 (s, 3H), 3.38 (s, 6H), 3.19 (s, 6H), 1.24 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.51, 166.49, 165.3, 161.9 (d, *J* = 243 Hz), 157.1, 156.7, 151.1, 146.7, 145.0, 140.9, 140.0, 137.9, 137.4, 134.6 (d, *J* = 3 Hz), 128.4 (d, *J* = 8 Hz), 127.6, 123.9, 123.6, 122.2, 119.7, 119.4, 114.7 (*d*, *J* = 21 Hz), 109.9, 102.8, 73.3, 40.9, 37.9, 37.6, 36.0, 34.5, 31.5. **IR** (KBr) *v* 2920, 2850, 1571, 1532, 1487, 1376, 1140, 970, 808, 705. **HRMS** (ESI) *m/z* Calcd. for $C_{36}H_{40}N_8FO^+$ $[M+H]^+$ 619.3304; Found: 619.3306. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 ºC, 0.5 mL/min flow rate, detection at 260 nm, t_1 = 9.4 min (minor), t_2 = 21.6 min (major). $[\alpha]_D^{25}$ = -25.2 (*c* = 0.002, CH_3OH) for 85.0% *ee*.

6^5-(*tert*-butyl)-6^2-methoxy-*N*,*N*,3,5,7-pentamethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5i)

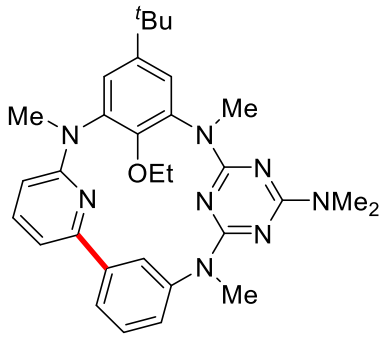


Chemical Formula: $C_{30}H_{36}N_8O$; Molecular Weight: 524.6730

21.0 mg, 80% yield, white solid, M.P. = 226-227 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, J = 2.4 Hz, 1.6 Hz, 1H), 7.57 (dd, J = 8.0 Hz, 7.6 Hz, 1H), 7.22 (t, J = 7.6 Hz, 2H), 7.17 (dt, J = 7.6 Hz, 1.2 Hz, 1H), 7.06-7.03 (m, 1H), 7.03 (d, J = 2.4 Hz, 1H), 6.98 (d, J = 2.4 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.58 (d, J = 8.4 Hz, 1H), 3.63 (s, 3H), 3.59 (s, 3H), 3.48 (s, 3H), 3.46 (s, 3H), 3.20 (s, 6H), 1.23 (s, 9H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.47, 166.45, 165.4, 157.1, 156.7, 152.4, 146.2, 145.1, 140.8, 139.6, 137.9, 137.0, 127.5, 123.8, 123.7, 122.5, 119.7, 119.5, 109.8, 102.6, 60.4, 40.8, 38.0, 37.6, 36.0, 34.5, 31.5. **IR** (KBr) v 2924, 2853, 1571, 1535, 1488, 1378, 1244, 1106, 808, 778. **HRMS** (APCI) *m/z* Calcd. for $C_{30}H_{37}N_8O^+$ $[M+H]^+$ 525.3085; Found: 525.3098. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 ºC, 0.5 mL/min flow rate, detection at 254 nm, t_1 = 11.1 min (minor), t_2 = 27.1 min (major). $[\alpha]_D^{25}$ = -27.3 (c = 0.002, CH_3OH) for 92.0% *ee*.

6^5-(*tert*-butyl)-6^2-ethoxy-*N*,*N*,3,5,7-pentamethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5j)

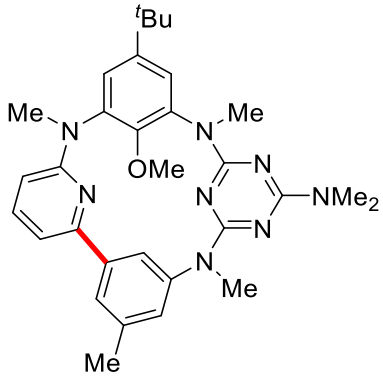


Chemical Formula: $C_{31}H_{38}N_8O$; Molecular Weight: 538.7000

19.9 mg, 74% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.56 (t, J = 8.0 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 7.6 Hz, 1H), 7.05-6.98 (m, 3H), 6.94 (d, J = 7.2 Hz, 1H), 6.56 (d, J = 8.4 Hz, 1H), 3.89 (dq, J = 12.0 Hz, 7.2 Hz, 1H), 3.79 (dq, J = 12.0 Hz, 7.2 Hz, 1H), 3.59 (s, 3H), 3.46 (s, 3H), 3.44 (s, 3H), 3.20 (s, 6H), 1.23 (s, 9H), 0.96 (t, J = 7.2 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 165.4, 157.2, 156.8, 151.4, 146.1, 145.1, 141.0, 139.9, 137.8, 137.4, 127.5, 123.8, 123.6, 122.4, 119.6, 119.2, 109.7, 102.6, 67.9, 40.7, 37.8, 37.7, 36.0, 34.5, 31.6, 16.1. **IR** (KBr) ν 2924, 2853, 1571, 1535, 1378, 1244, 1050, 807, 778, 701. **HRMS** (APCI) *m/z* Calcd. for $C_{31}H_{39}N_8O^+$ $[M+H]^+$ 539.3241; Found: 539.3242. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 ºC, 0.5 mL/min flow rate, detection at 254 nm, t_1 = 8.9 min (minor), t_2 = 16.2 min (major). $[\alpha]_D^{25}$ = -34.0 (c = 0.002, CH_3OH) for 91.8% *ee*.

6^5-(*tert*-butyl)-6^2-methoxy-*N*,*N*,2^5,3,5,7-hexamethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5k)

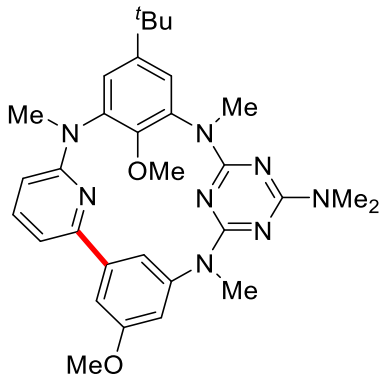


Chemical Formula: $C_{31}H_{38}N_8O$; Molecular Weight: 538.7000

12 mg, 45% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.56 (t, J = 8.0 Hz, 1H), 7.02 (d, J = 2.4 Hz, 1H), 6.98-6.97 (m, 2H), 6.93 (d, J = 7.6 Hz, 1H), 6.86 (s, 1H), 6.56 (d, J = 8.0 Hz, 1H), 3.63 (s, 3H), 3.58 (s, 3H), 3.47 (s, 3H), 3.45 (s, 3H), 3.20 (s, 6H), 2.32 (s, 3H), 1.22 (s, 9H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 165.5, 157.3, 156.8, 152.5, 146.3, 145.2, 140.9, 139.7, 137.9, 137.1, 127.5, 123.9, 123.8, 122.6, 119.7, 119.5, 109.8, 102.7, 60.4, 40.7, 38.0, 37.7, 36.1, 34.5, 31.6. **IR** (KBr) v 2924, 2854, 1573, 1514, 1459, 1367, 1173, 809, 786, 731. **HRMS** (APCI) m/z Calcd. for $C_{31}H_{39}N_8O^+$ $[M+H]^+$ 539.3241; Found: 539.3240. **HPLC**: AD-H column, Hexane : i-PrOH = 80 : 20, 24 ºC, 0.5 mL/min flow rate, detection at 310 nm, t_1 = 12.4 min (minor), t_2 = 24.1 min (major). $[\alpha]_D^{25}$ = -22.0 (c = 0.002, CH_3OH) for 92.0% *ee*.

6^5-(*tert*-butyl)-2^5,6^2-dimethoxy-*N*,*N*,3,5,7-pentamethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5l)



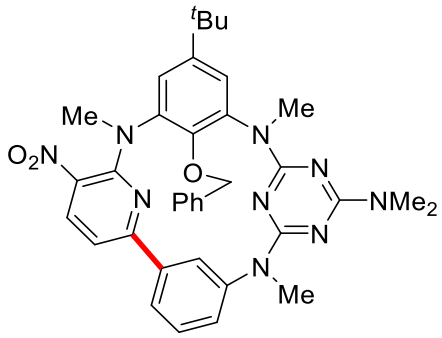
Chemical Formula: $C_{31}H_{38}N_8O_2$; Molecular Weight: 554.6990

16.6 mg, 60% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.03 (d, J = 2.4 Hz, 1H), 6.99 (d, J = 2.4 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 6.73 (s, 1H), 6.61 (t, J = 2.4 =Hz, 1H), 6.58 (d, J = 8.0 Hz, 1H), 3.80 (s, 3H), 3.61 (s, 3H), 3.57 (s, 3H), 3.47 (s, 3H), 3.46 (s, 3H), 3.19 (s, 6H), 1.24 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 166.4,

165.3, 159.2, 157.0, 156.7, 152.3, 146.3, 146.0, 141.6, 139.5, 137.9, 137.0, 123.7, 122.5, 116.8, 109.7, 106.3, 104.4, 102.8, 60.4, 55.5, 40.7, 37.8, 37.6, 36.0, 34.5, 31.6. **IR** (KBr) ν 2925, 2854, 1811, 1573, 1537, 1487, 1379, 1052, 808, 791, 733. **HRMS** (ESI) *m/z* Calcd. for $C_{31}H_{39}N_8O_2^+$ $[M+H]^+$ 555.3191; Found: 555.3196. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 ºC, 0.5 mL/min flow rate, detection at 319 nm, t_1 = 13.7 min (minor), t_2 = 31.9 min (major). $[\alpha]_D^{25}$ = -20.8 (*c* = 0.002, CH_3OH) for 93.1% *ee*.

6^2-(benzyloxy)-6^5-(*tert*-butyl)-*N*,*N*,3,5,7-pentamethyl-1^5-nitro-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5m)

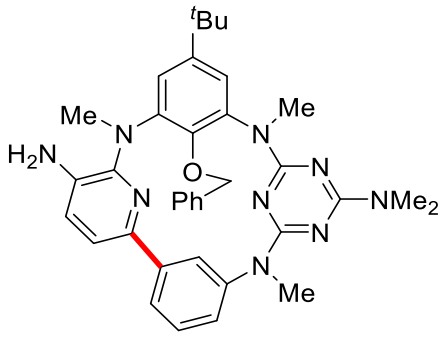


Chemical Formula: $C_{36}H_{39}N_9O_3$; Molecular Weight: 645.7680

22.3 mg, 69% yield, yellow solid. M.P. = 235-236 ºC

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.47 (t, *J* = 1.6 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.30-7.29 (m, 2H), 7.21-7.18 (m, 1H), 7.19 (s, 1H), 7.17-7.16 (m, 2H), 7.16-7.14 (m, 2H), 7.05-7.03 (m, 2H), 5.06 (d, *J* = 11.6 Hz, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 3.50 (s, 3H), 3.37 (s, 3H), 3.31 (s, 3H), 3.14 (s, 6H), 1.25 (s, 9H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 165.53, 165.48, 164.6, 159.2, 149.8, 149.4, 147.0, 144.7, 139.1, 138.3, 137.7, 137.6, 136.2, 130.2, 128.5, 128.1, 127.6, 127.0, 123.6, 122.7, 121.9, 120.4, 119.7, 111.3, 74.0, 37.2, 35.6, 34.4, 31.2. **IR** (KBr) ν 2925, 1724, 1629, 1599, 1578, 1544, 1493, 1399, 1276, 1109, 977, 786. **HRMS** (ESI) *m/z* Calcd. for $C_{36}H_{40}N_9O_3^+$ $[M+H]^+$ 646.3249; Found: 646.3253. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 ºC, 0.5 mL/min flow rate, detection at 254 nm, t_1 = 10.2 min (minor), t_2 = 23.4 min (major). $[\alpha]_D^{25}$ = -17.8 (*c* = 0.002, CH_3OH) for 58.9% *ee*.

6^2-(benzyloxy)-6^5-(*tert*-butyl)-*N*$^{4⁶</sup>$,*N*$^{4⁶</sup>$,3,5,7-pentamethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphane-1^5,4^6-diamine (5n)

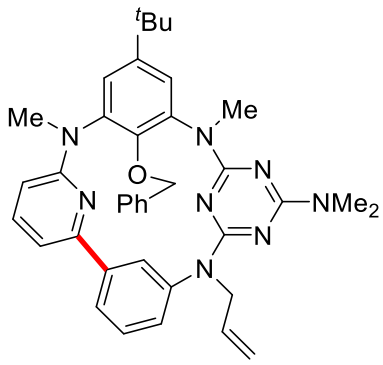


Chemical Formula: $C_{36}H_{41}N_9O$; Molecular Weight: 615.7860

20.3 mg, 66% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 7.23 (t, J = 8.0 Hz, 1H), 7.17-7.14 (m, 2H), 7.11-7.06 (m, 3H), 7.04 (d, J = 8.0 Hz, 1H), 6.98 (ddd, J = 8.4 Hz, 2.8 Hz, 0.8 Hz, 1H), 6.84 (d, J = 2.4 Hz, 1H), 6.80-6.77 (m, 3H), 4.90 (d, J = 12.0 Hz, 1H), 4.67 (d, J = 11.6 Hz, 1H), 3.52 (s, 3H), 3.35 (s, 3H), 3.29 (s, 3H), 3.16 (S, 6H), 1.30 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 166.9 165.2, 149.0, 147.5, 147.3, 146.4, 145.3, 141.9, 140.8, 138.7, 137.4, 132.6, 127.8, 126.9, 126.7, 123.9, 121.6, 120.6, 118.2, 117.2, 116.4, 115.9, 72.5, 39.5, 36.8, 36.0, 35.4, 34.8, 31.6. **IR** (KBr) *v* 3359, 2921, 2851, 1659, 1633, 1573, 1514, 1394, 1367, 1249, 1173, 809, 786. **HRMS** (ESI) *m/z* Calcd. for $C_{36}H_{42}N_9O^+$ $[M+H]^+$ 616.3507; Found: 616.3512. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 °C, 0.5 mL/min flow rate, detection at 273 nm, t_1 = 9.9 min (minor), t_2 = 18.1 min (major). $[\alpha]_D^{25}$ = -21.1 (c = 0.002, CH_3OH) for 73.3% *ee*.

3-allyl-6^2-(benzyloxy)-6^5-(*tert*-butyl)-*N*,*N*,5,7-tetramethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5o)

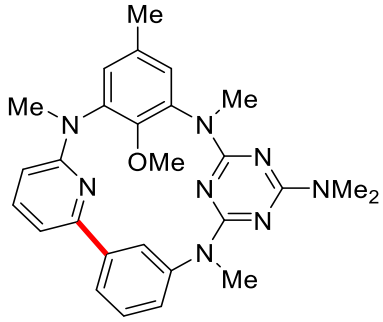


Chemical Formula: $C_{38}H_{42}N_8O$; Molecular Weight: 626.8090

21.0 mg, 67% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.14-7.12 (m, 5H), 7.06 (d, J = 2.4 Hz, 1H), 7.04-7.01 (m, 2H), 6.98 (d, J = 2.4 Hz, 1H), 6.91 (d, J = 7.2 Hz, 1H), 6.49 (d, J = 8.0 Hz, 1H), 6.10-6.00 (m, 1H), 5.24-5.18 (m, 2H), 5.12-5.09 (m, 1H), 4.92 (d, J = 12.4 Hz, 1H), 4.84 (d, J = 12.0 Hz, 1H), 4.33 (dd, J = 16.8 Hz, 4.8 Hz, 1H), 3.39 (s, 3H), 3.36 (s, 3H), 3.16 (s, 6H), 1.24 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 165.7, 165.3, 157.1, 151.2, 146.5, 144.6, 141.3, 140.0, 138.9, 137.8, 137.5, 136.0, 128.0, 127.5, 127.0, 126.7, 125.0, 123.6, 122.0, 120.0, 119.9, 115.3, 110.0, 102.6, 74.1, 53.4, 41.3, 37.5, 36.0, 34.5, 31.5. **IR** (KBr) v 2924, 2853, 1571, 1537, 1390, 1244, 1215, 1061, 807, 780, 697. **HRMS** (APCI) *m/z* Calcd. for $C_{38}H_{43}N_8O^+$ $[M+H]^+$ 627.3554; Found: 627.3558. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 °C, 0.5 mL/min flow rate, detection at 284 nm, t_1 = 9.9 min (minor), t_2 = 22.2 min (major). $[\alpha]_D^{25}$ = -28.3 (c = 0.002, CH_3OH) for 87.6% *ee*.

6^2-methoxy-*N*,*N*,6^5,3,5,7-hexamethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5p)

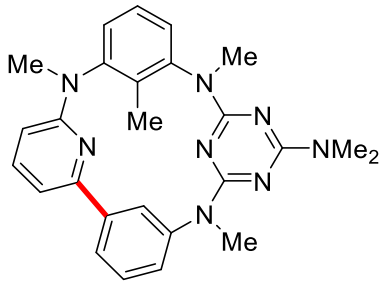


Chemical Formula: $C_{27}H_{30}N_8O$; Molecular Weight: 482.5920

17.4 mg, 72% yield, white solid. M.P. = 232-234 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.57 (dd, J = 8.4 Hz, 7.6 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.16 (dt, J = 7.6 Hz, 1.2 Hz, 1H), 7.02 (ddd, J = 7.6 Hz, 2.4 Hz, 1.2 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.87 (d, J = 2.4 Hz, 1H), 6.83 (d, J = 2.4 Hz, 1H), 6.58 (d, J = 8.4 Hz, 1H), 3.65 (s, 3H), 3.58 (s, 3H), 3.46 (s, 3H), 3.44 (s, 3H), 3.20 (s, 6H), 2.21 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 166.5, 165.4, 157.4, 156.7, 152.7, 145.1, 140.8, 140.3, 138.0, 137.4, 133.2, 127.52, 127.47, 126.3, 123.2, 119.8, 119.3, 109.9, 102.8, 60.6, 40.2, 37.9, 37.5, 36.0, 20.8. **IR** (KBr) v 2922, 2852, 1569, 1488, 1387, 1354, 1277, 805, 785, 699. **HRMS** (ESI) m/z Calcd. for $C_{27}H_{31}N_8O^+$ $[M+H]^+$ 483.2615; Found: 483.2616. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 ºC, 0.5 mL/min flow rate, detection at 254 nm, t_1 = 33.6 min (minor), t_2 = 37.2 min (major). $[\alpha]_D^{25}$ = -38.1 (c = 0.002, CH_3OH) for 95.0% *ee*.

***N*,*N*,6^2,3,5,7-hexamethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5q)**



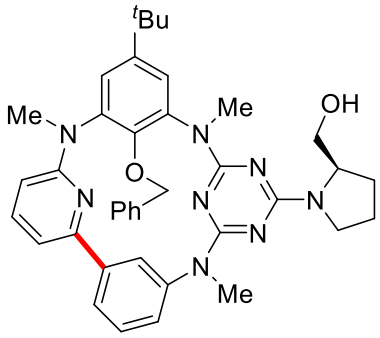
Chemical Formula: $C_{26}H_{28}N_8$; Molecular Weight: 452.5660

13.1 mg, 58% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.21-7.16 (m, 3H), 7.06-7.02 (m, 1H), 7.05 (d, J = 8.4 Hz, 1H), 6.99 (d, J = 7.6 Hz, 1H), 6.97 (d, J = 7.6 Hz), 6.61 (d, J = 8.4 Hz, 1H), 3.60 (s, 3H), 3.48 (s, 3H), 3.45 (s, 3H), 3.22 (s, 6H), 2.12 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 166.0, 165.4, 157.8, 156.3, 147.9, 145.1, 144.3, 140.5, 138.2, 137.6, 127.7, 127.2, 125.5, 124.0, 122.8, 119.9, 119.6, 109.3, 102.9,

39.2, 38.2, 37.4, 36.0, 13.7. **IR** (KBr) *v* 2927, 1629, 1579, 1493, 1453, 1399, 1109, 978, 786, 696. **HRMS** (APCI) *m/z* Calcd. for $C_{26}H_{29}N_8^+$ $[M+H]^+$ 453.2510; Found: 453.2503. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 °C, 0.5 mL/min flow rate, detection at 254 nm, t_1 = 14.4 min (major), t_2 = 18.1 min (minor). $[\alpha]_D^{25}$ = +32.0 (*c* = 0.002, CH_3OH) for 81.6% *ee*.

(*R*)-(1-(6^2-(benzyloxy)-6^5-(tert-butyl)-3,5,7-trimethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphane-4^6-yl)pyrrolidin-2-yl)methanol (5r)

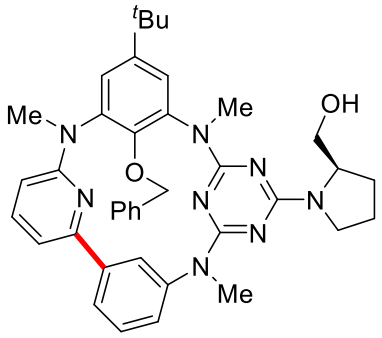


dr = 20:1

Chemical Formula: $C_{39}H_{44}N_8O_2$; Molecular Weight: 656.8350

13.5 mg, 41% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.13 (s, 3H), 7.07-6.94 (m, 6H), 6.51 (d, *J* = 8.4 Hz, 1H), 4.94 (d, *J* = 12.4 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H), 4.42-4.35 (m, 1H), 3.90-3.85 (m, 1H), 3.77-3.65 (m, 2H), 3.60-3.53 (m, 4H), 3.38-3.30 (m, 6H), 2.24-2.10 (m, 1H), 2.05-1.87 (m, 3H), 1.23 (s, 9H). **^{13}C NMR** (100 MHz, DMSO-*d*$_6$) δ 166.0, 165.4, 164.3, 159.1, 150.0, 147.5, 144.9, 139.8, 139.6, 139.0, 138.1, 132.3, 131.0, 129.6, 128.1, 126.4, 124.4, 115.6, 107.3, 84.2, 68.7, 63.5, 59.3, 47.2, 38.3, 37.2, 37.0, 34.7, 31.7, 28.4, 25.3, 23.5. **IR** (KBr) *v* 2926, 1580, 1534, 1488, 1387, 1356, 1316, 1144, 971, 809, 772, 705. **HRMS** (ESI) *m/z* Calcd. for $C_{39}H_{45}N_8O_2^+$ $[M+H]^+$ 657.3660; Found: 657.3651.

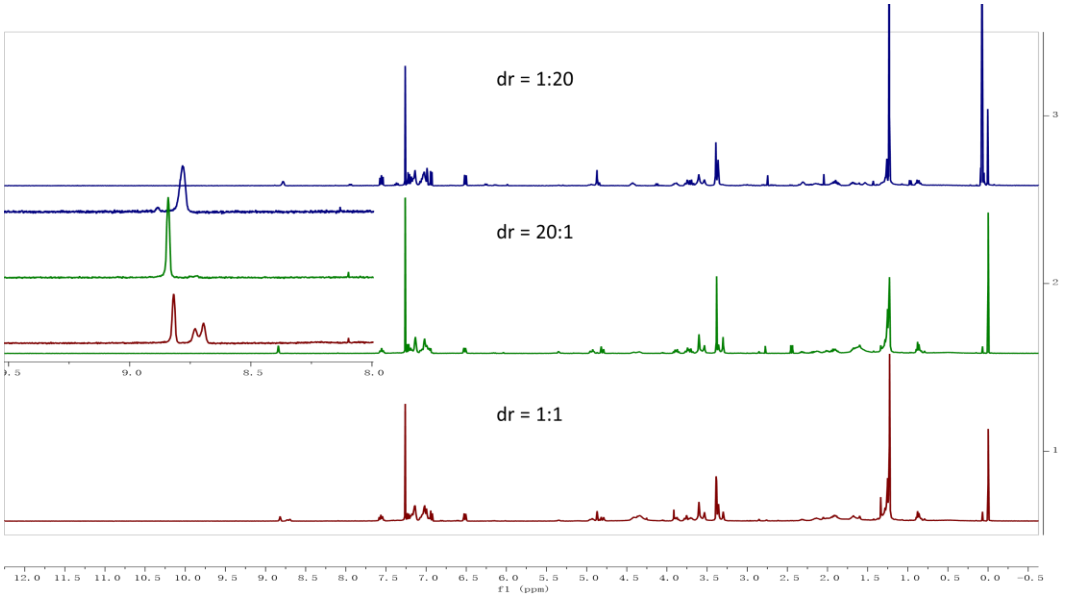


dr = 1:20

Chemical Formula: $C_{39}H_{44}N_8O_2$; Molecular Weight: 656.8350

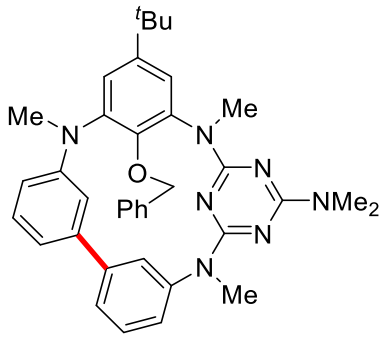
14.0 mg, 50% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.56 (dd, J = 8.0 Hz, 7.2 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.18-7.14 (m, 4H), 7.04-7.00 (m, 4H), 6.99 (d, J = 2.4 Hz, 1H), 6.94 (d, J = 7.2 Hz, 1H), 6.51 (d, J = 8.0 Hz, 1H), 4.98-4.84 (m, 2H), 4.46-4.40 (m, 1H), 3.93-3.86 (m, 1H), 3.77-3.67 (m, 2H), 3.60-3.53 (m, 4H), 3.39-3.36 (m, 6H), 2.30-2.14 (m, 1H), 2.14-2.11 (m, 1H), 1.96-1.85 (m, 2H), 1.23 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 165.7, 165.6, 157.1, 156.6, 151.0, 147.0, 144.8, 141.1, 140.0, 138.0, 128.0, 127.7, 127.1, 126.7, 124.3, 123.4, 122.6, 120.2, 119.9, 110.0, 102.9, 76.8, 74.1, 69.4, 59.9, 47.9, 41.2, 38.2, 37.5, 34.6, 31.5, 29.8, 29.5, 24.1, 22.8. **IR** (KBr) v 2926, 1580, 1534, 1488, 1387, 1356, 1316, 1144, 971, 809, 772, 705. **HRMS** (ESI) m/z Calcd. for $C_{39}H_{45}N_8O_2^+$ $[M+H]^+$ 657.3660; Found: 657.3651.



^{1}H NMR spectra of 5r (dr = 1:1, dr = 20:1, and dr = 1:20)

6^{2}-methoxy-*N*,*N*,6^{5},3,5,7-hexamethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^{6}-amine (5s)



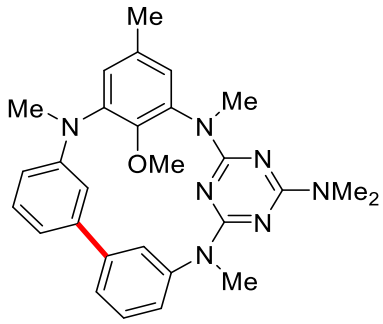
Chemical Formula: $C_{37}H_{41}N_7O$; Molecular Weight: 599.7830

19.1 mg, 64% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (t, J = 1.6 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.16-7.14 (m, 3H), 7.10-7.06 (m, 1H), 7.09 (d, J = 3.2 Hz, 1H), 7.07 (d, J = 2.4 Hz, 1H), 7.03-7.00 (m, 3H), 6.95 (d, J = 7.2 Hz, 1H), 6.77 (dd, J = 8.0 Hz, 2.8 Hz, 1H), 6.67 (dd, J = 2.4 Hz, 1.6 Hz, 1H), 4.97 (d, J = 12.0 Hz, 1H), 4.74 (d, J = 12.0 Hz, 1H), 3.62 (s, 3H), 3.44 (s, 3H), 3.32 (s, 3H), 3.20 (s, 6H), 1.25 (s, 9H). **^{13}C**

NMR (100 MHz, $CDCl_3$) δ 166.9, 166.6, 165.2, 150.0, 147.8, 146.8, 144.7, 142.5, 139.8, 138.4, 137.9, 128.9, 128.1, 127.9, 127.2, 127.1, 124.5, 124.0, 122.9, 119.9, 119.1, 118.5, 114.9, 109.5, 74.2, 41.9, 38.4, 37.7, 36.0, 34.6, 31.5, 31.1. **IR** (KBr) *v* 2924, 2854, 1595, 1532, 1479, 1356, 1212, 1180, 799, 773. **HRMS** (APCI) *m/z* Calcd. for $C_{37}H_{42}N_7O^+$ $[M+H]^+$ 600.3445; Found: 600.3443. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 °C, 0.5 mL/min flow rate, detection at 254 nm, t_1 = 9.4 min (major), t_2 = 10.1 min (minor). $[\alpha]_D^{25}$ = -9.3 (*c* = 0.002, CH_3OH) for 19.1% *ee*.

6^2-methoxy-*N*,*N*,6^5,3,5,7-hexamethyl-3,5,7-triaza-4(2,4)-triazina-1,2,6(1,3)-tribenzenacycloheptaphan-4^6-amine (5t)

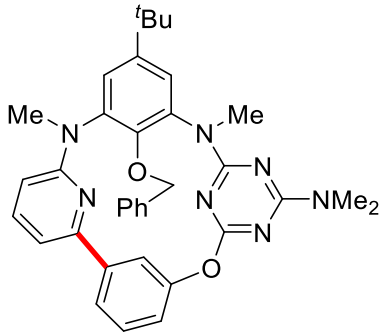


Chemical Formula: $C_{28}H_{31}N_7O$; Molecular Weight: 481.6040

16.8 mg, 70% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (m, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.04 (ddd, *J* = 7.6 Hz, 1.6 Hz, 0.8 Hz, 1H), 6.99 (ddd, *J* = 8.0 Hz, 2.4 Hz, 0.8 Hz, 1H), 6.94 (ddd, *J* = 7.6 Hz, 1.6 Hz, 0.8 Hz, 1H), 6.90-6.88 (m, 2H), 6.80 (dd, *J* = 8.0 Hz, 2.8 Hz, 1H), 6.48-6.47 (m, 1H), 3.67 (s, 3H), 3.61 (s, 3H), 3.45 (s, 3H), 3.42 (s, 3H), 3.20 (s, 6H), 2.22 (s, 3H), 1.25 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 166.6, 165.2, 151.8, 147.3, 144.8, 142.5, 142.3, 140.0, 137.7, 134.4, 129.0, 128.1, 127.9, 127.1, 123.8, 120.0, 118.9, 118.6, 114.8, 109.6, 60.7, 41.0, 38.4, 37.6, 36.0, 20.8. **IR** (KBr) *v* 2924, 2854, 1573, 1514, 1470, 1367, 1249, 1173, 809, 786. **HRMS** (ESI) *m/z* Calcd. for $C_{28}H_{32}N_7O^+$ $[M+H]^+$ 482.2663; Found: 482.2660. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 °C, 0.5 mL/min flow rate, detection at 288 nm, t_1 = 14.6 min (minor), t_2 = 17.4 min (major). $[\alpha]_D^{25}$ = 0 (*c* = 0.002, CH_3OH) for 0% *ee*.

6^2-(benzyloxy)-6^5-(*tert*-butyl)-*N*,*N*,5,7-tetramethyl-3-oxa-5,7-diaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5u)

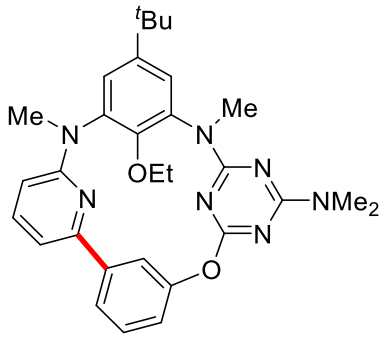


Chemical Formula: $C_{35}H_{37}N_7O_2$; Molecular Weight: 587.7280

20.9 mg, 71% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (dd, J = 2.8 Hz, 1.6 Hz, 1H), 7.57 (dd, J = 8.4 Hz, 7.6 Hz, 1H), 7.32 (dt, J = 7.2 Hz, 1.2 Hz, 1H), 7.22 (t, J = 8.0 Hz, 1H), 7.14-7.19 (m, 4H), 7.07 (s, 2H), 7.02 (d, J = 7.6 Hz, 1H), 6.98 (m, 2H), 6.52 (d, J = 8.4 Hz, 1H), 4.91 (d, J = 12.0 Hz, 1H), 4.80 (d, J = 12.4 Hz, 1H), 3.39 (s, 6H), 3.21 (s, 6H), 1.27 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.5, 166.8, 166.7, 156.8, 155.6, 154.1, 150.8, 147.0, 141.6, 140.1, 138.5, 138.1, 137.0, 128.2, 128.1, 127.2, 126.7, 123.1, 123.0, 120.4, 119.4, 119.1, 109.7, 103.2, 74.1, 40.5, 37.9, 36.6, 34.6, 31.5. **IR** (KBr) v 2922, 2852, 1569, 1488, 1387, 1354, 1277, 1071, 808, 768, 703. **HRMS** (ESI) *m/z* Calcd. for $C_{35}H_{38}N_7O_2^+$ $[M+H]^+$ 588.3082; Found: 588.3090. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 °C, 0.5 mL/min flow rate, detection at 254 nm, t_1 = 10.2 min (minor), t_2 = 21.6 min (major). $[\alpha]_D^{25}$ = +12.3 (c = 0.002, CH_3OH) for 80.0% *ee*.

6^5-(*tert*-butyl)-6^2-ethoxy-*N*,*N*,5,7-tetramethyl-3-oxa-5,7-diaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5v)

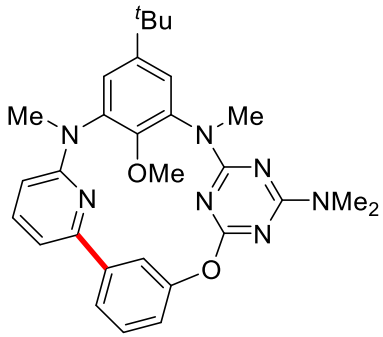


Chemical Formula: $C_{30}H_{35}N_7O_2$; Molecular Weight: 525.6570

17.9 mg, 68% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.20 (t, J = 8.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.04 (s, 2H), 7.01 (d, J = 7.2 Hz, 1H), 6.57 (d, J = 8.4 Hz, 1H), 3.92-3.84 (m, 1H), 3.81-3.73 (m, 1H), 3.49 (s, 3H), 3.45 (s, 3H), 3.23 (s, 6H), 1.25 (s, 9H), 0.99 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.5, 166.9, 166.7, 156.8, 155.7, 154.2, 151.0, 146.4, 141.6, 139.8, 138.0, 136.8, 128.1, 123.1, 120.3, 119.4, 119.1, 109.4, 103.0, 68.0, 40.4, 38.0, 36.6, 34.5, 31.6, 16.1. **IR** (KBr) ν 2954, 2924, 2853, 1736, 1537, 1390, 1147, 982, 807, 780. **HRMS** (ESI) *m/z* Calcd. for $C_{30}H_{36}N_7O_2^+$ $[M+H]^+$ 526.2925; Found: 526.2918. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 ºC, 0.5 mL/min flow rate, detection at 254 nm, t_1 = 12.3 min (minor), t_2 = 25.6 min (major). $[\alpha]_D^{25}$ = +19.9 (c = 0.002, CH_3OH) for 85.0% *ee*.

6^5-(*tert*-butyl)-6^2-methoxy-*N*,*N*,5,7-tetramethyl-3-oxa-5,7-diaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5w)

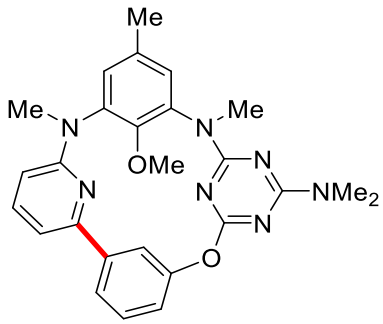


Chemical Formula: $C_{29}H_{33}N_7O_2$; Molecular Weight: 511.6300

23.0 mg, 90% yield, white solid.M.P. = 225-227 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.20 (t, J = 8.0 Hz, 1H), 7.09 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.05 (s, 2H), 7.02 (d, J = 7.2 Hz, 1H), 6.59 (d, J = 8.4 Hz, 1H), 3.64 (s, 3H), 3.51 (s, 3H), 3.47 (s, 3H), 3.23 (s, 6H), 1.25 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.6, 166.9, 166.7, 156.9, 155.6, 154.2, 152.0, 146.7, 141.4, 139.5, 138.2, 136.5, 128.2, 123.4, 120.4, 119.2, 119.2, 109.5, 103.1, 60.4, 40.3, 37.9, 36.6, 34.5, 31.5. **IR** (KBr) v 2924, 2854, 1736, 1573, 1514, 1367, 1251, 1173, 809, 786, 731. **HRMS** (APCI) m/z Calcd. for $C_{29}H_{34}N_7O_2^+$ $[M+H]^+$ 512.2769; Found: 512.2779. **HPLC**: AD-H column, Hexane : i-PrOH = 80 : 20, 24 ºC, 0.5 mL/min flow rate, detection at 254 nm, t_1 = 10.5 min (minor), t_2 = 21.6 min (major). $[\alpha]_D^{25}$ = +22.5 (c = 0.002, CH_3OH) for 91.0% *ee*.

6^2-methoxy-*N*,*N*,6^5,5,7-pentamethyl-3-oxa-5,7-diaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5x)



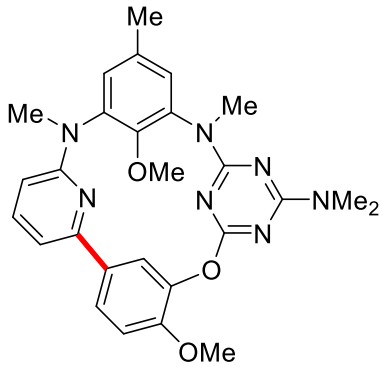
Chemical Formula: $C_{26}H_{27}N_7O_2$; Molecular Weight: 469.5490

22.1 mg, 94% yield, white solid. M.P. = 221-222 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (m, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.02 (ddd, J = 1.2 Hz, 2.4 Hz, 8.4 Hz, 1H), 7.02 (d, J = 7.2 Hz, 1H), 6.89 (s, 2H), 6.59 (d, J = 8.4 Hz, 1H), 3.66 (s, 3H), 3.50 (s, 3H), 3.44 (s, 3H), 3.23 (m, 6H), 2.23 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.6, 166.9, 166.7, 157.1, 155.6, 154.2, 152.3, 141.4, 140.2, 138.2, 136.9, 133.6, 128.3, 127.2, 127.1, 120.5, 119.3, 118.8, 109.6, 103.2, 60.6, 39.9, 37.8, 36.6, 20.9. **IR** (KBr) ν 2922, 2852, 1569,

1519, 1488, 1387, 1354, 1277, 992, 805, 785. **HRMS** (ESI) *m/z* Calcd. for $C_{26}H_{28}N_7O_2^+$ $[M+H]^+$ 470.2299; Found: 470.2296. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 °C, 0.5 mL/min flow rate, detection at 326 nm, t_1 = 20.3 min (minor), t_2 = 33.8 min (major). $[\alpha]_D^{25}$ = +9.7 (*c* = 0.001, CH_3OH) for 89.2% *ee*.

2^4,6^2-dimethoxy-*N*,*N*,6^5,5,7-pentamethyl-3-oxa-5,7-diaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5y)

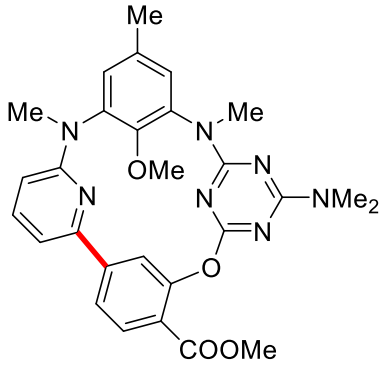


Chemical Formula: $C_{27}H_{29}N_7O_3$; Molecular Weight: 499.5750

15.0 mg, 60% yield, white solid. M.P. = 230-231 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 2.0 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.27-7.25 (m, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 5.2 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 1H), 3.85 (s, 3H), 3.65 (s, 3H), 3.49 (s, 3H), 3.43 (s, 3H), 3.22 (s, 6H), 2.24 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.6, 166.9, 166.8, 157.1, 155.6, 152.4, 149.8, 143.2, 140.3, 138.1, 136.9, 133.5, 133.1, 127.2, 127.1, 120.4, 119.5, 110.5, 109.0, 102.4, 60.6, 56.0, 39.9, 37.8, 36.5, 25.0, 20.9. **IR** (KBr) ν 2964, 2925, 1712, 1574, 1514, 1395, 1368, 1246, 1162, 952, 816, 787. **HRMS** (ESI) *m/z* Calcd. for $C_{27}H_{30}N_7O_3.^+$ $[M+H]^+$ 500.2405; Found: 500.2413. **HPLC**: AD-H column, Hexane : *i*-PrOH = 75 : 25, 24 °C, 0.5 mL/min flow rate, detection at 254 nm, t_1 = 11.5 min (minor), t_2 = 12.9 min (major). $[\alpha]_D^{25}$ = +4.6 (*c* = 0.002, CH_3OH) for 94.7% *ee*.

Methyl 4^6-(dimethylamino)-6^2-methoxy-6^5,5,7-trimethyl-3-oxa-5,7-diaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphane-2^4-carboxylate (5z)

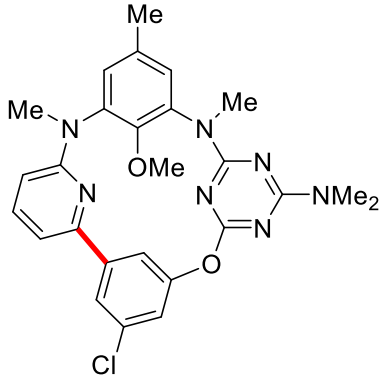


Chemical Formula: $C_{28}H_{29}N_7O_4$; Molecular Weight: 527.5850

21.9 mg, 83% yield, white solid. M.P. = 230-231 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.28 (s, 1H), 7.02 (d, J = 7.2 Hz, 1H), 6.88 (d, J = 17.6 Hz, 2H), 6.63 (d, J = 8.0 Hz, 1H), 3.88 (s, 3H), 3.64 (s, 3H), 3.49 (s, 3H), 3.44 (s, 3H), 3.23 (s, 6H), 2.24 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.2, 167.0, 166.7, 166.5, 157.1, 154.9, 152.9, 152.3, 145.4, 140.0, 138.3, 137.0, 133.7, 131.0, 127.2, 126.9, 120.8, 120.1, 120.0, 110.1, 103.9, 60.7, 52.2, 40.2, 37.7, 36.6, 25.0, 20.9. **IR** (KBr) v 2922, 2852, 1731, 1574, 1493, 1396, 1345, 1246, 1095, 806, 779. **HRMS** (ESI) m/z Calcd. for $C_{28}H_{30}N_7O_4^+$ $[M+H]^+$ 528.2354; Found: 528.2352. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 ºC, 0.5 mL/min flow rate, detection at 254 nm, t_1 = 12.3 min (minor), t_2 = 17.3 min (major). $[\alpha]_D^{25}$ = +20.0 (c = 0.002, CH_3OH) for 94.9% *ee*.

2^5-chloro-6^2-methoxy-*N*,*N*,6^5,5,7-pentamethyl-3-oxa-5,7-diaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5aa)

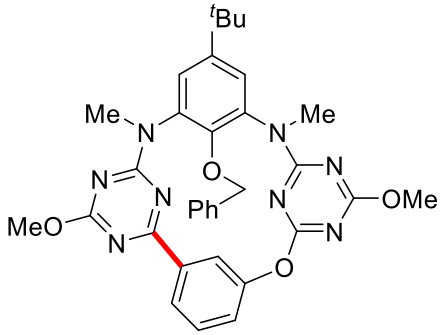


Chemical Formula: $C_{26}H_{26}N_7O_2Cl$; Molecular Weight: 503.9910

16.6 mg, 66% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (dd, J = 1.2 Hz, 2.4 Hz, 1H), 7.60 (dd, J = 7.4 Hz, 8.4 Hz, 1H), 7.27 (dd, J = 1.6 Hz, 1.2 Hz, 1H), 7.08 (dd, J = 2.4 Hz, 3.2 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 6.89 (s, 2H), 6.62 (d, J = 8.0 Hz, 1H), 3.64 (s, 3H), 3.49 (s, 3H), 3.45 (s, 3H), 3.24-3.20 (m, 6H), 2.24 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 166.8, 166.6, 157.0, 154.5, 154.3, 152.2, 142.7, 140.0, 138.4, 136.8, 133.8, 133.3, 127.2, 127.1, 120.7, 119.3, 117.3, 109.6, 103.8, 60.7, 40.0, 37.8, 36.6, 20.9. **IR** (KBr) ν 2925, 2854, 1574, 1505, 1395, 1347, 1250, 1061, 855, 808, 790. **HRMS** (ESI) *m/z* Calcd. for $C_{26}H_{27}N_7O_2Cl^+$ $[M+H]^+$ 504.1909; Found: 504.1916. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 ºC, 0.5 mL/min flow rate, detection at 315 nm, t_1 = 11.5 min (minor), t_2 = 22.3 min (major). $[\alpha]_D^{25}$ = -7.4 (c = 0.002, CH_3OH) for 89.7% *ee*.

6^2-(benzyloxy)-6^5-(*tert*-butyl)-1^6,4^6-dimethoxy-5,7-dimethyl-3-oxa-5,7-diaza-1,4(2,4)-ditriazina-2,6(1,3)-dibenzenacycloheptaphane (5ab)



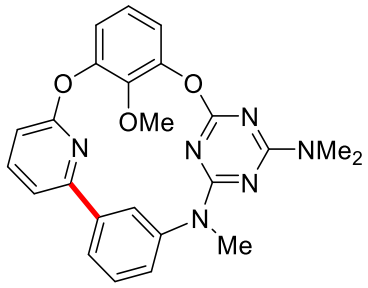
Chemical Formula: $C_{33}H_{34}N_8O_4$; Molecular Weight: 606.6870

13.1 mg, 54% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.87 (d, J = 7.2 Hz, 1H), 7.34-7.29 (m, 2H), 7.19-7.17 (m, 4H), 7.13-7.12 (m, 1H), 7.02 (br, s, 2H), 4.86 (s, 2H), 4.07 (s, 3H), 4.05 (s, 3H), 3.53 (s, 3H), 3.41 (s, 3H), 1.29 (s, 9H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.3, 173.1, 172.0, 168.2, 152.9, 149.7, 148.3, 137.5, 137.0, 129.8, 128.5, 127.7, 126.4, 125.8, 119.4, 116.9, 73.9, 55.0, 37.0, 34.4, 31.4, 31.1. **IR** (KBr) ν 2923, 2853, 1573, 1492, 1395, 1299, 1055, 807. **HRMS** (ESI) *m/z* Calcd. for $C_{33}H_{35}N_8O_4^+$ $[M+H]^+$

607.2776; Found: 607.2767. **HPLC**: IB-N5 column, Hexane : *i*-PrOH = 80 : 20, 24 ºC, 0.5 mL/min flow rate, detection at 264 nm, t_1 = 13.8 min (minor), t_2 = 18.3 min (major). $[\alpha]_D^{25}$ = -6.2 (*c* = 0.002, CH_3OH) for 65.7% *ee*.

6^2-methoxy-*N*,*N*,3-trimethyl-5,7-dioxa-3-aza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5ac)

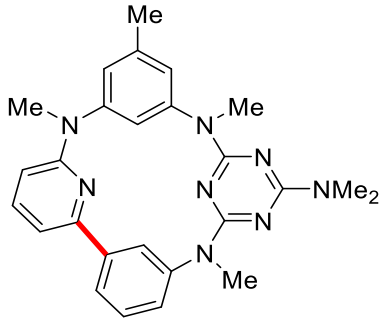


Chemical Formula: $C_{24}H_{22}N_6O_3$; Molecular Weight: 442.4790

6.6 mg, 59% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, *J* = 2.0 Hz, 1.6 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.25-7.21 (m, 2H), 7.11 (ddd, *J* = 8.0 Hz, 2.4 Hz, 1.2 Hz, 1H), 7.05 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.99-6.92 (m, 2H), 6.90 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 3.83 (s, 3H), 3.64 (s, 3H), 3.24 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 166.8, 166.5, 161.9, 156.1, 148.0, 147.3, 145.1, 144.3, 139.8, 139.8, 128.0, 125.0, 123.1, 120.8, 120.8, 120.7, 120.6, 114.2, 107.5, 77.5, 77.2, 76.8, 61.0, 38.6, 36.7, 36.6. **IR** (KBr) ν 2926, 2854, 1588, 1488, 1356, 1292, 1072, 808. **HRMS** (ESI) m/z Calcd. for $C_{24}H_{23}N_6O_3^+$ $[M+H]^+$ 443.1826; Found: 443.1827. **HPLC**: AD-H column, Hexane : *i*-PrOH = 80 : 20, 24 ºC, 0.5 mL/min flow rate, detection at 284 nm, t_1 = 11.8 min (major), t_2 = 14.7 min (minor). $[\alpha]_D^{25}$ = -12.0 (*c* = 0.002, CH_3OH) for 64.2% *ee*.

***N*,*N*,6^5,3,5,7-hexamethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-4^6-amine (5ad)**

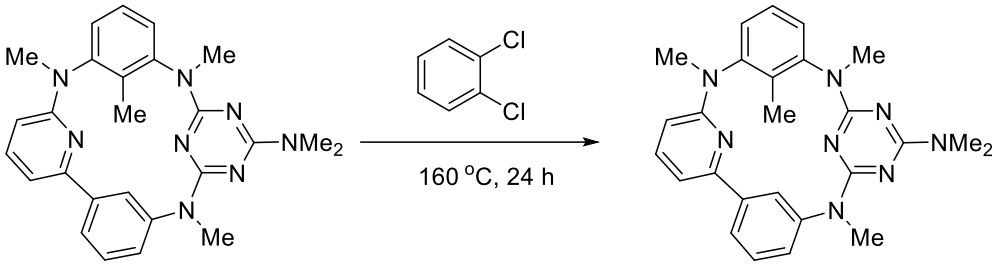


Chemical Formula: $C_{26}H_{28}N_8$; Molecular Weight: 452.2437

49% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, J = 1.6 Hz, 2.8 Hz, 1H), 7.58 (dd, J = 8.4 Hz, 7.6 Hz, 1H), 7.35 (t, J = 2.8 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.18 (dt, J = 1.6 Hz, 7.6 Hz, 1H), 7.03 (ddd, J = 1.2 Hz, 2.4 Hz, 7.6 Hz, 1H), 7.00 (d, J = 7.6 Hz, 1H), 6.80 (d, J = 6.0 Hz, 1H), 6.58 (d, J = 8.4 Hz, 1H), 3.58 (s, 3H), 3.46 (s, 3H), 3.43 (s, 3H), 3.19 (s, 6H), 2.28 (s, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 166.1, 165.3, 157.8, 156.2, 147.3, 145.0, 144.6, 140.6, 139.6, 138.3, 128.0, 127.8, 124.4, 122.9, 122.3, 119.6, 118.9, 110.0, 103.4, 40.6, 37.9, 37.8, 36.0, 21.5. **IR** (KBr) ν 2962, 2920, 1582, 1533, 1482, 1382, 1241, 1144, 972, 808, 705. **HRMS** (ESI) *m/z* Calcd. For $C_{26}H_{28}N_8^+$ $[M+H]^+$ 453.2492; Found: 453.2488.

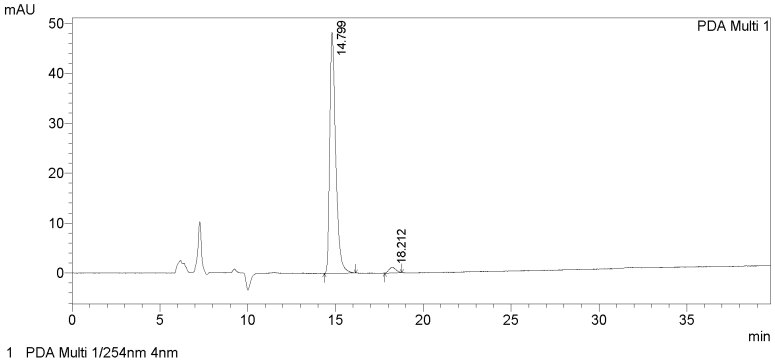
9. Inversion barrier test



95% *ee*

To a sealed tube was added **5q** (1 mg, 95% *ee*) and *o*-dichlorobenzene (5 mL). The mixture was heated to 160 °C for 24 h. The mixture was cooled to room temperature and measured the *ee* value.

0 h

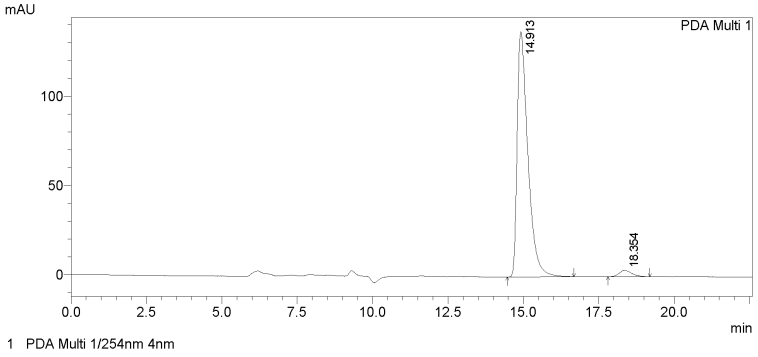


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.799	1142944	48255	97.318	97.648
2	18.212	31501	1162	2.682	2.352
Total		1174446	49417	100.000	100.000

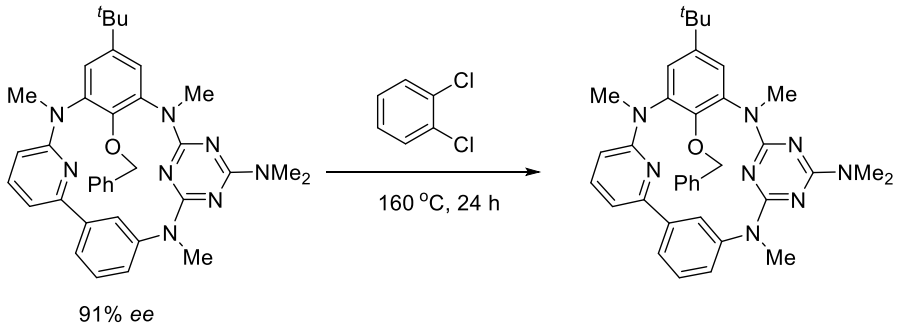
24 h



PeakTable

PDA Ch1 254nm 4nm

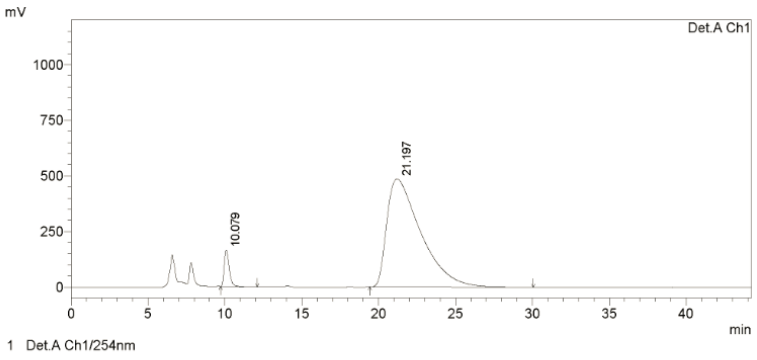
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.913	3390956	137342	97.051	97.501
2	18.354	103032	3520	2.949	2.499
Total		3493989	140863	100.000	100.000



91% *ee*

To a sealed tube was added **5a** (1 mg, 91% *ee*) and *o*-dichlorobenzene (5 mL). The mixture was heated to 160 °C for 24 h. The mixture was cooled to room temperature and measured the *ee* value.

0 h

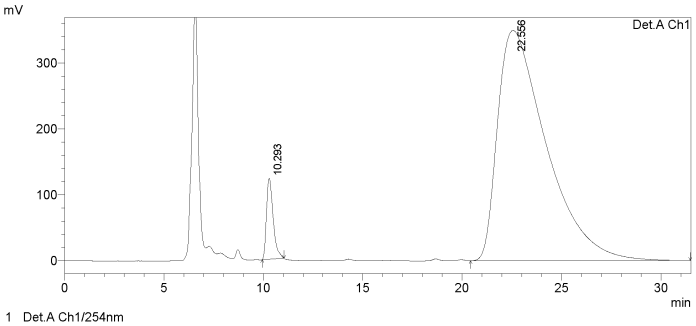


PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.079	3693747	164070	4.710	25.252
2	21.197	74730408	485652	95.290	74.748
Total		78424155	649722	100.000	100.000

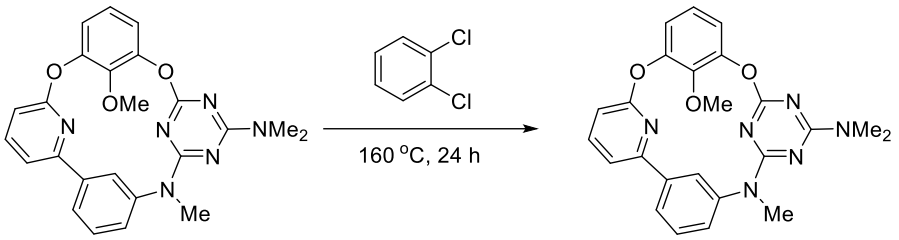
24 h



PeakTable

检测器 A Ch1 254nm

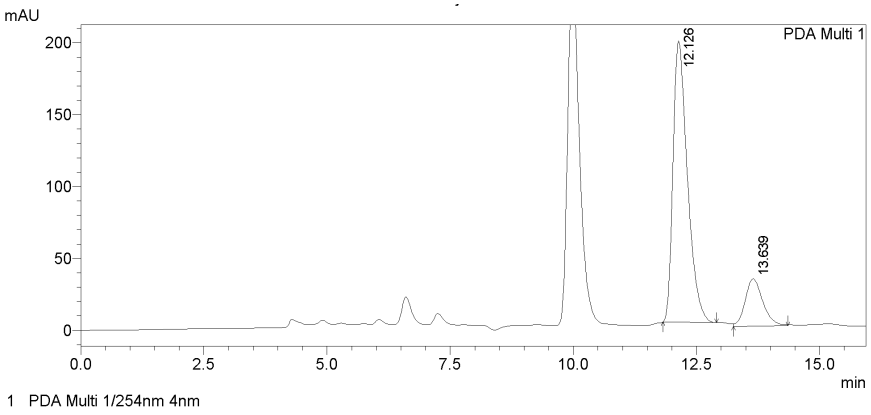
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.293	2879207	122755	4.612	25.989
2	22.556	59551841	349573	95.388	74.011
Total		62431048	472329	100.000	100.000



66% *ee*

To a sealed tube was added **5ac** (1 mg, 66% *ee*) and *o*-dichlorobenzene (5 mL). The mixture was heated to 160 °C for 24 h. The mixture was cooled to room temperature and measured the *ee* value.

0 h

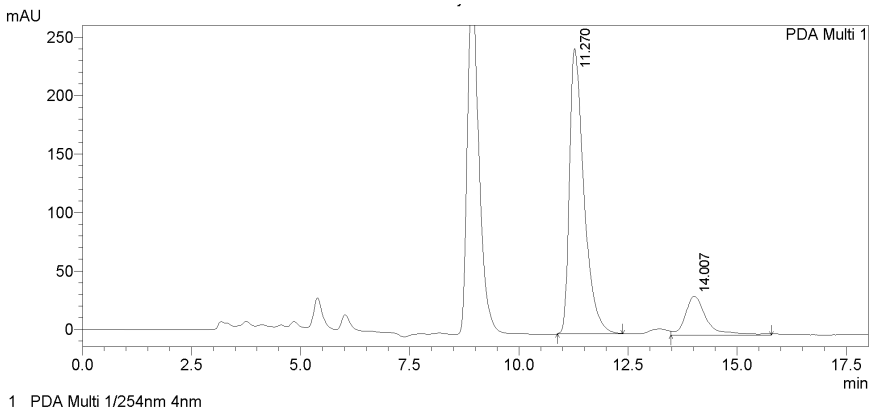


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.126	3985575	195540	82.902	85.543
2	13.639	821977	33046	17.098	14.457
Total		4807552	228586	100.000	100.000

24 h

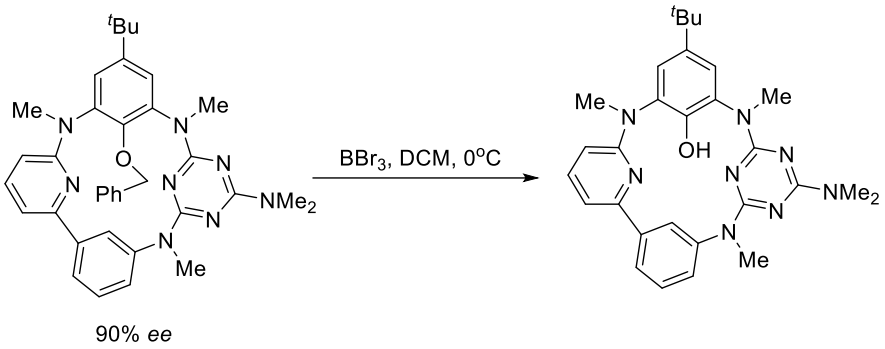


PeakTable

PDA Ch1 254nm 4nm

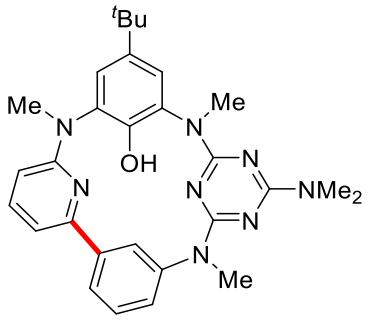
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.270	5628979	243958	83.032	87.939
2	14.007	1150286	33458	16.968	12.061
Total		6779265	277416	100.000	100.000

10. Synthesis and measurement of kinetics of racemization of enantiomers 5ae



Debenzylation reaction: Under argon atmosphere, to a mixture of **5a** (60 mg, 0.1 mmol, *ee* = 90%) in dry DCM (10 mL) was slowly added BBr_3 (0.1 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 5 h. The reaction was quenched with H_2O, and extracted with EtOAc, washed with brine, and dried over anhydrous Na_2SO_4. After solvent evaporation, the residue was chromatographed with a silica gel column (PE/EtOAc = 3:1) to afford **5ae**, which was totally racemized during the reaction and purification.

6^5-(tert-butyl)-4^6-(dimethylamino)-3,5,7-trimethyl-3,5,7-triaza-4(2,4)-triazina-1(2,6)-pyridina-2,6(1,3)-dibenzenacycloheptaphan-6^2-ol (5ae)

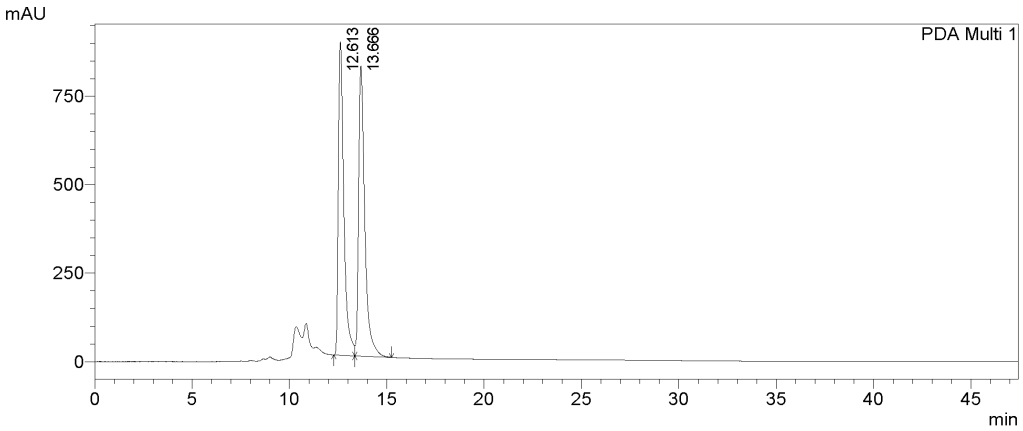


Chemical Formula: $C_{29}H_{34}N_8O$; Molecular Weight: 510.6460

8.8 mg, 40% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (t, *J* = 1.6 Hz, 1H), 7.67 (dd, *J* = 8.0 Hz, 7.6 Hz, 1H), 7.30-7.24 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.09 (ddd, *J* = 7.6 Hz, 2.4 Hz, 1.2 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.99 (d, *J* = 2.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 3.55 (s, 3H), 3.52 (s, 3H), 3.45 (s, 3H), 3.21 (s, 6H), 1.25 (s, 9H). **^{13}C NMR** (100 MHz,

$CDCl_3$) δ 167.4, 166.2, 165.2, 157.4, 156.1, 147.4, 145.7, 143.2, 139.3, 138.8, 137.9, 134.0, 128.0, 122.6, 122.1, 119.9, 119.6, 109.9, 104.4, 40.9, 38.3, 36.0, 34.4, 31.6. **IR** (KBr) ν 2926, 2854, 1588, 1488, 1356, 1292, 1072, 808. **HRMS** (APCI) m/z Calcd. for $C_{29}H_{35}N_8O^+$ $[M+H]^+$ 511.2928; Found: 511.2934. **HPLC**: IBN5 column, hexane: CH_2Cl_2: *i*-PrOH: = 80 : 15 : 5, 24 ºC, 0.4 mL/min flow rate, detection at 254 nm, t_1 = 12.6 min, t_2 = 13.7 min.



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.613	17448915	885643	49.067	51.936
2	13.666	18112555	819621	50.933	48.064
Total		35561470	1705264	100.000	100.000

Figure S1. HPLC analysis of (±) **5ae**. (chiral column, IBN5; mobile phase, hexane: CH_2Cl_2: ^{i}PrOH: = 80 : 15 : 5, 24 ºC, flow rate, 0.4 mL/min).

Enantioenriched **5ae** was obtained by resolution of racemic **5ae** by chiral HPLC under the conditions described in Figure S1.

10.1 Measurement of the racemization barrier of 5ae for in CH_3CN at different temperatures

Measurement of kinetics of the racemization barrier of **5ae** was carried out according to literature method.[2]

A solution of **5ae** (89.0% ee, resoluted by chiral HPLC, 1.0 g/L) was kept in the range of 288 K-308 K. At a specific temperature, a very small amount of sample was pipetted at different time intervals and enantiomeric excess value (ee_t) was analyzed by chiral HPLC analysis. Plot of $\ln(ee_o/ee_t)$ against time gave a straight line, and a rate constant (k) for racemization was obtained from the slope. After measuring rate constants at different temperature, the Eyring plot of $\ln(k/T)$ against 1/T gave enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) of activation for racemization.

308K		305.5K		303K		300.5K		298K	
t/s	$\ln(ee_0/ee_t)$	t/s	$\ln(ee_0/ee_t)$	t/s	$\ln(ee_0/ee_t)$	t/s	$\ln(ee_0/ee_t)$	t/s	$\ln(ee_0/ee_t)$
0	0	0	0	0	0	0	0	0	0
1740	0.058351	1800	0.042358	1980	0.03102	2400	0.02601	4080	0.0305
3300	0.107176	3960	0.091013	4320	0.068823	4680	0.052	7980	0.060132
6660	0.210861	7200	0.162012	7860	0.124673	8460	0.09305	11880	0.08685
8280	0.273394	10800	0.25134	10020	0.16138	11280	0.1212	14880	0.11508
10140	0.314563	14400	0.3018	13080	0.20114	16080	0.18052	19920	0.17103

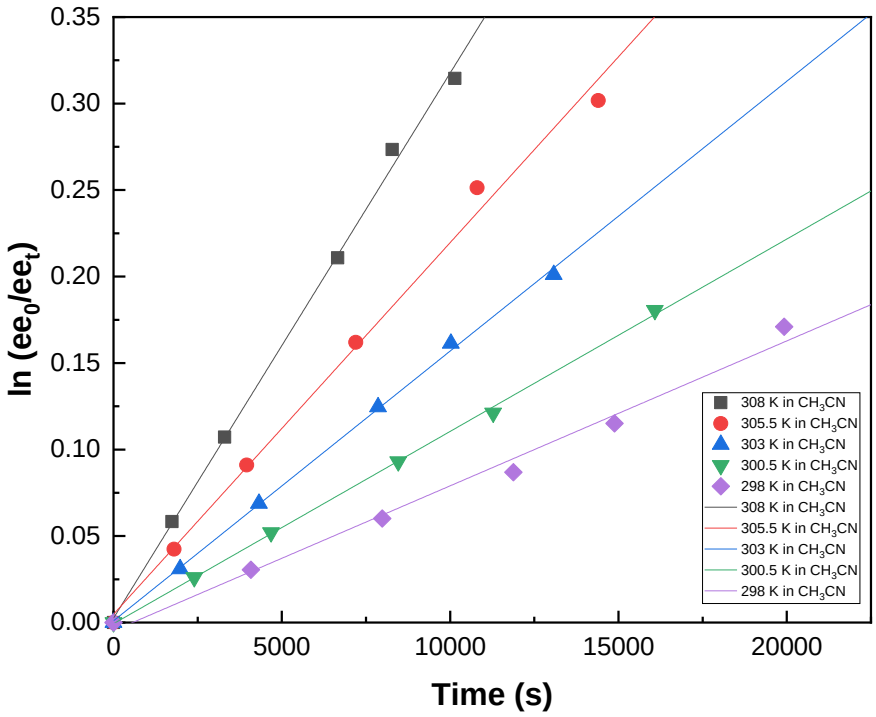


Figure S2. Rate equations for racemic reaction at 308 K, 305.5 K, 303 K, 300.5 K, 298 K in CH_3CN.

Equation: $\ln(ee_0/ee_t) = 2kt$.

T (K)	308	305.5	303	300.5	298
k (10^{-5}, s^{-1})	1.57549	1.07419	0.77978	0.55594	0.41887
R^2	0.998	0.994	0.998	0.999	0.989

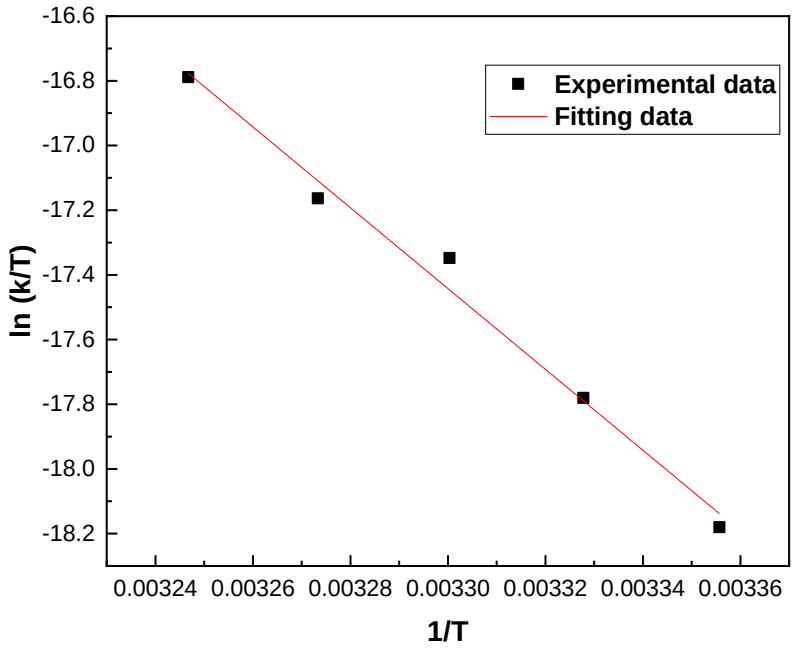


Figure S3. Erying plot analysis and rate constant data for the enantiomerization of **5ae** in the CH_3CN. Errors in $\Delta H^{\#}$ and $\Delta S^{\#}$ are expressed as 95% confidence limits.

$$\text{Erying equation:}\quad \ln\frac{k}{T} = -\frac{\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R} + \ln\frac{k_B}{h}$$

Slope = -12493.75034; Intercept = 23.8871, $R^2 = 0.987$

$\Delta H^{\#} = 24.83 \pm 1.61$ kcal mol^{-1}, $\Delta S^{\#} = 1.0 \pm 5.33$ cal mol^{-1} K^{-1}

10.2 Measurement of the racemization barrier of 5ae for in ^{i}PrOH at different temperatures

308K		303K		298K		293K		288K	
t/s	$\ln(ee_0/ee_t)$	t/s	$\ln(ee_0/ee_t)$	t/s	$\ln(ee_0/ee_t)$	t/s	$\ln(ee_0/ee_t)$	t/s	$\ln(ee_0/ee_t)$
0	0	0	0	0	0	0	0	0	0
2520	0.26848	1800	0.09979	4080	0.15043	1800	0.03694	100800	0.59884
4920	0.52193	3960	0.20378	7980	0.24574	4440	0.04495	117480	0.77319
6720	0.68898	7200	0.45119	11880	0.31985	10800	0.158	168540	1.10966
8520	0.94681	10800	0.64409	14880	0.56241	22200	0.36772	181740	1.25276
10560	1.11976	14400	0.96788	19920	0.73304	28920	0.39999	198600	1.36898
12420	1.33767	18000	1.16203	24180	0.88332	77040	1.10966	205380	1.37102

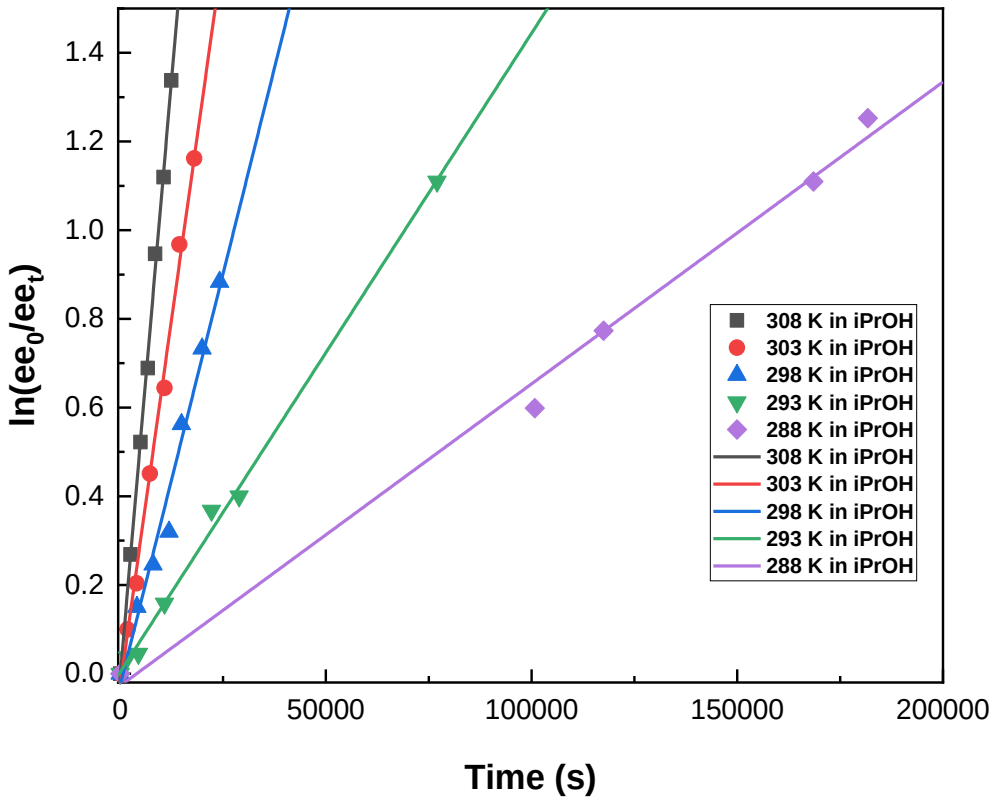


Figure S4. Rate equations for racemic reaction at 308 K, 303 K, 298 K, 293 K, 288 K in ^{i}PrOH.

Equation: $\ln(ee_0/ee_t) = 2kt$.

T (K)	308	303	298	293	288
k (10^{-5}, s^{-1})	5.3873	3.3063	1.8562	0.7203	0.3404
R^2	0.998	0.995	0.979	0.997	0.993

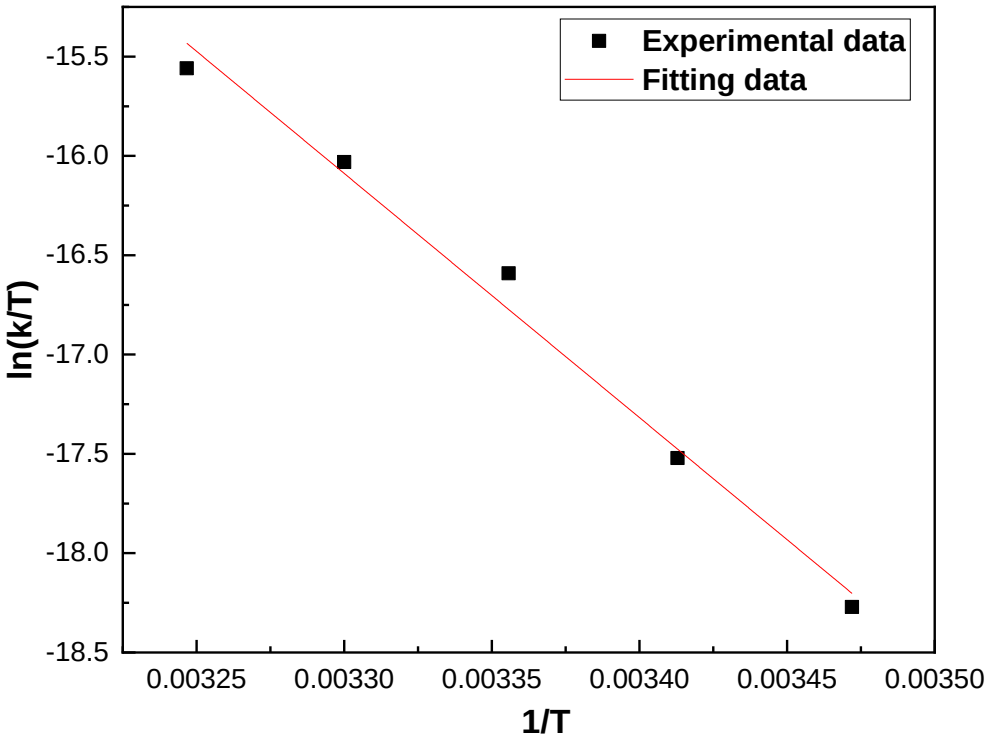


Figure S5. Eyring plot analysis and rate constant data for the enantiomerization of **5ae** in the ^{i}PrOH. Errors in $\Delta H^{\#}$ and $\Delta S^{\#}$ are expressed as 95% confidence limits.

$$\text{Erying equation:}\quad \ln\frac{k}{T} = -\frac{\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R} + \ln\frac{k_B}{h}$$

Slope = -12291.57093; Intercept = 24.47384, R^2 = 0.9879

$\Delta H^{\#}$ = 24.42 ± 1.36 kcal mol^{-1}, $\Delta S^{\#}$ = 1.42 ± 5.24 cal mol^{-1} K^{-1}

11. Crystallographic data

Table S4. Crystal data and structure refinement for (*cS*)-**5p**.

Identification code	14-TM-20230310_auto
Empirical formula	$C_{27}H_{30}N_8O$
Formula weight	482.59
Temperature/K	172.99(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.3425(2)
b/Å	12.0823(2)
c/Å	10.7603(2)
α/°	90
β/°	111.053(2)
γ/°	90
Volume/Å^3	1254.86(4)
Z	2
ρcalcg/cm^3	1.277

μ/mm^{-1}	0.659
F(000)	512.0
Crystal size/mm^3	0.6 × 0.5 × 0.3
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.806 to 156.024
Index ranges	$-12 \leq h \leq 12$, $-15 \leq k \leq 15$, $-13 \leq l \leq 13$
Reflections collected	23451
Independent reflections	5147 [R_{int} = 0.0372, R_{sigma} = 0.0285]
Data/restraints/parameters	5147/1/332
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0324, wR_2 = 0.0826
Final R indexes [all data]	R_1 = 0.0339, wR_2 = 0.0835
Largest diff. peak/hole / e $Å^{-3}$	0.15/-0.16
Flack parameter	-0.03(10)

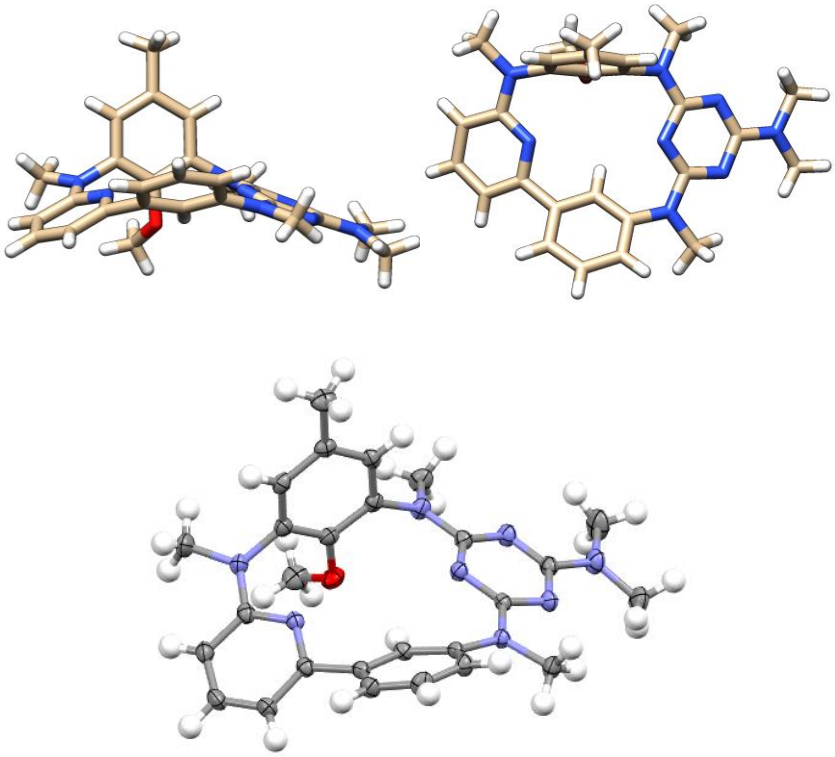


Figure S6. X-ray molecular structures of (*cS*)-**5p**. Oak ridge thermal ellipsoid plot (ORTEP) diagram of (*cS*)-**5p**. Thermal ellipsoids are shown at the 50% probability level.

Table S5. Crystal data and structure refinement for (*cR*)-**5w**.

Identification code	5w-20240307-1_auto
Empirical formula	$C_{30}H_{35}Cl_2N_7O_2$
Formula weight	596.55
Temperature/K	172.99(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.11960(10)
b/Å	10.25230(10)
c/Å	15.3641(2)
α/°	90
β/°	108.4350(10)
γ/°	90
Volume/Å^3	1512.21(3)
Z	2
ρ_{calc}g/cm^3	1.310
μ/mm^{-1}	2.251

F(000)	628.0
Crystal size/mm^3	0.35 × 0.2 × 0.15
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.064 to 153.264
Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-19 \leq l \leq 19$
Reflections collected	29091
Independent reflections	6207 [R_{int} = 0.0374, R_{sigma} = 0.0292]
Data/restraints/parameters	6207/1/378
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0477, wR_2 = 0.1276
Final R indexes [all data]	R_1 = 0.0494, wR_2 = 0.1290
Largest diff. peak/hole / e $Å^{-3}$	0.63/-0.58
Flack parameter	0.019(8)

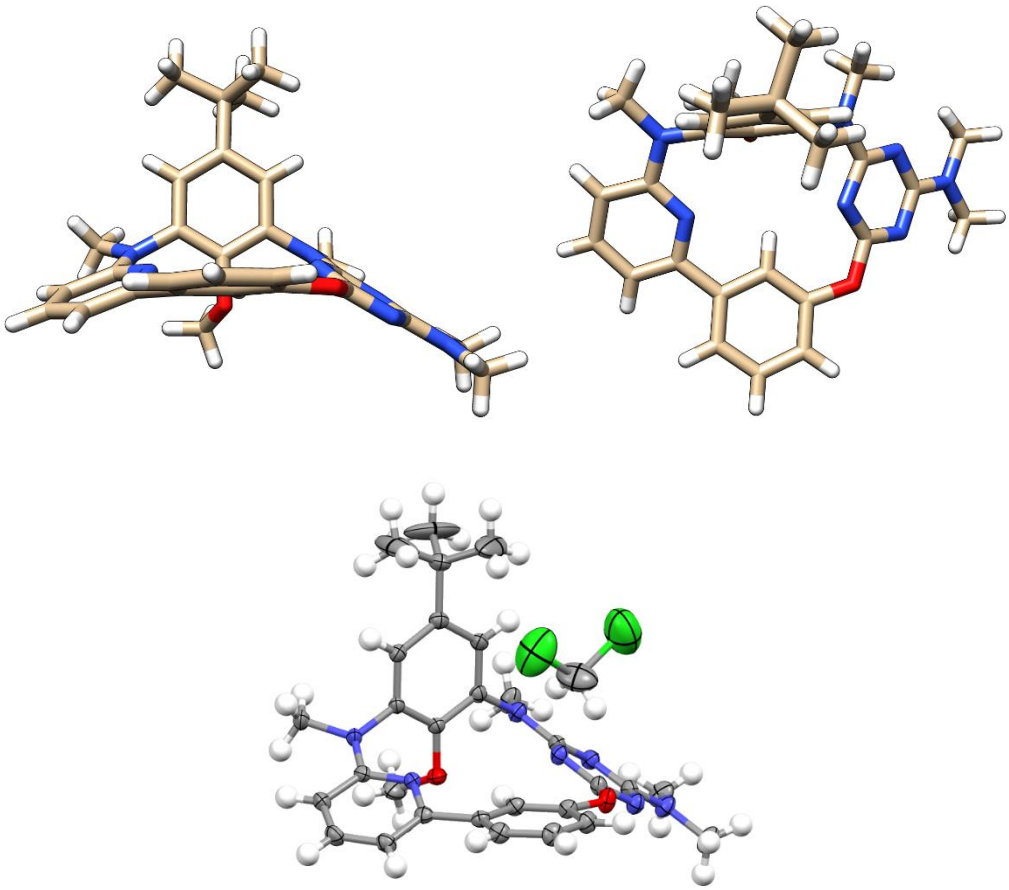


Figure S7. X-ray molecular structures of (*cR*)-**5w**. Oak ridge thermal ellipsoid plot (ORTEP) diagram of (*cR*)-**5w**. Thermal ellipsoids are shown at the 50% probability level.

12. Copies of UV-vis spectra and fluorescence spectra

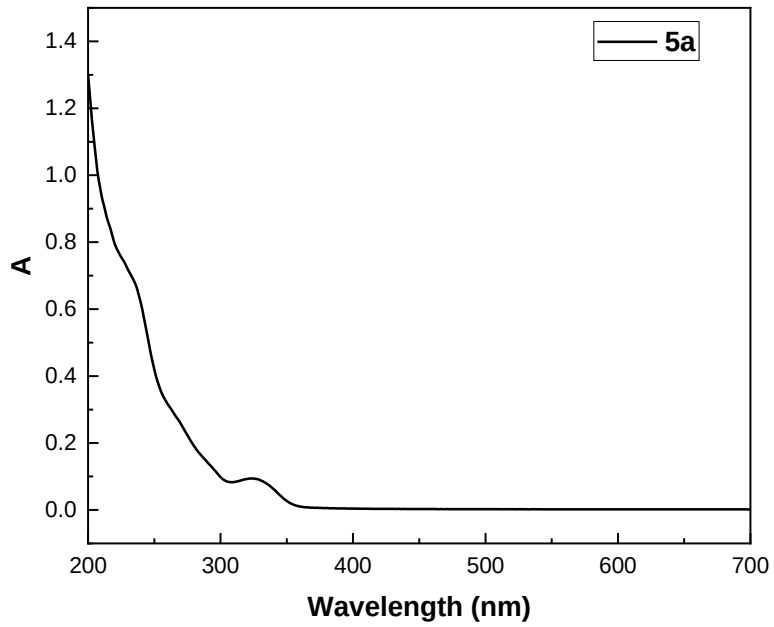


Figure S8. UV-vis spectrum of **5a** in CH_3CN at 25 ºC, the concentration was 5×10^{-5} M

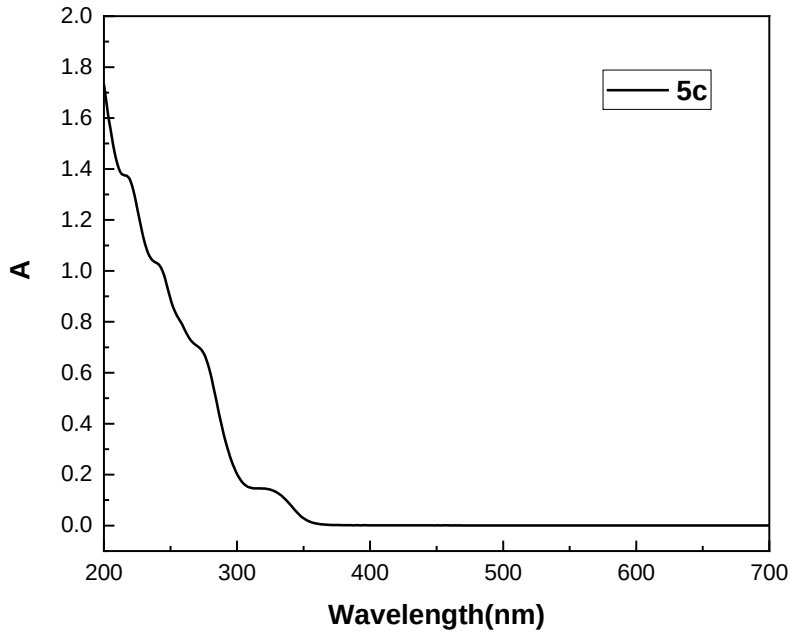


Figure S9. UV-vis spectrum of **5c** in CH_3CN at 25 ºC, the concentration was 6×10^{-5} M

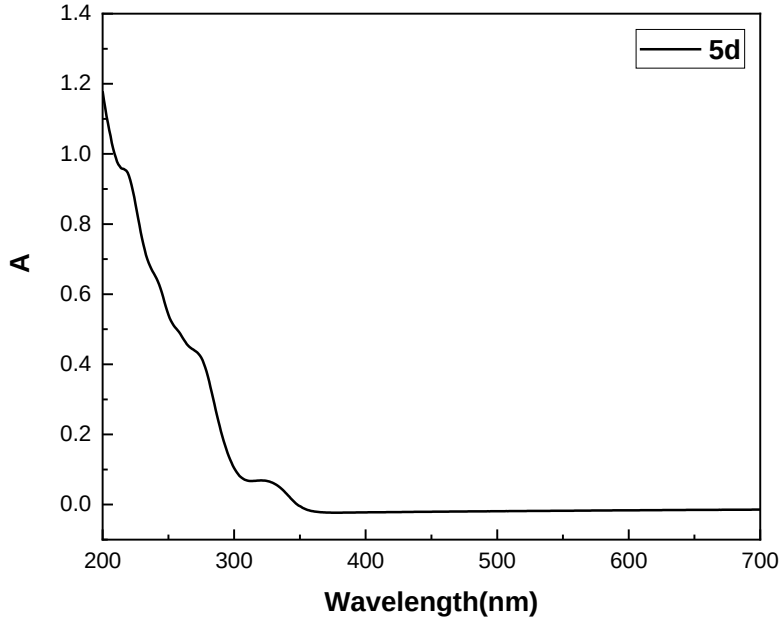


Figure S10. UV-vis spectrum of **5d** in CH_3CN at 25 ºC, the concentration was 4×10^{-5} M

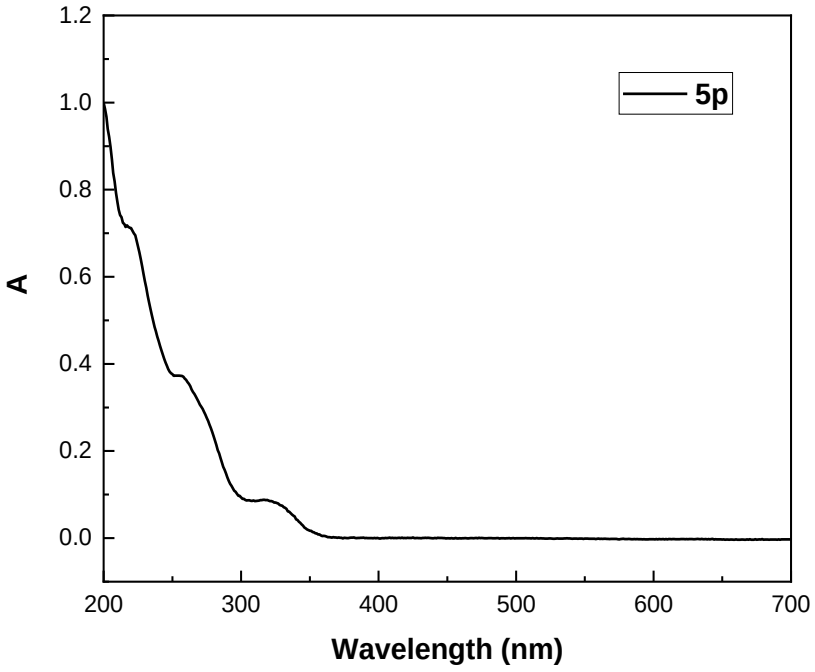


Figure S11. UV-vis spectrum of **5p** in CH_3CN at 25 ºC, the concentration was 4×10^{-5} M

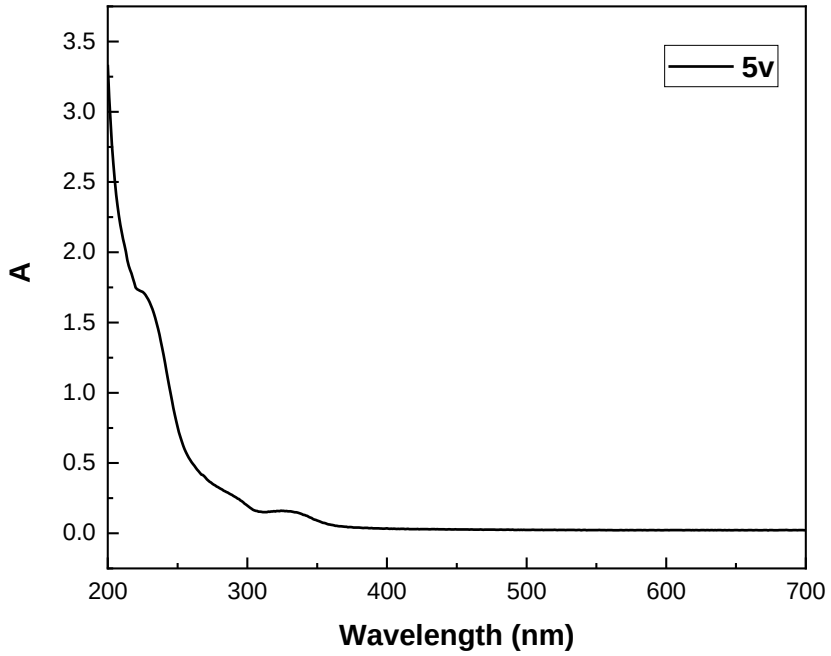


Figure S12. UV-Vis spectrum of **5v** in CH_3CN at 25 ºC, the concentration was 1×10^{-4} M

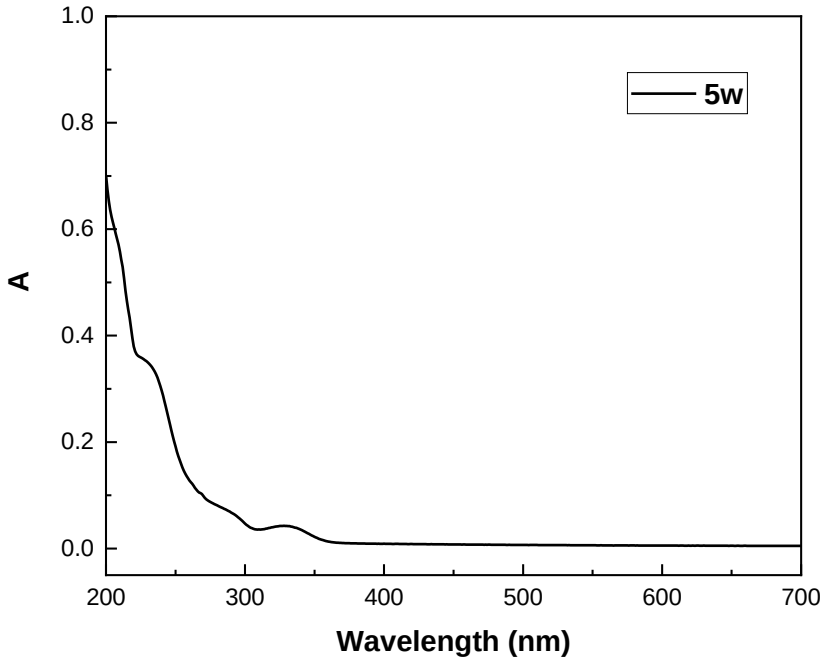


Figure S13. UV-Vis spectrum of **5w** in CH_3CN at 25 ºC, the concentration was 2×10^{-5} M

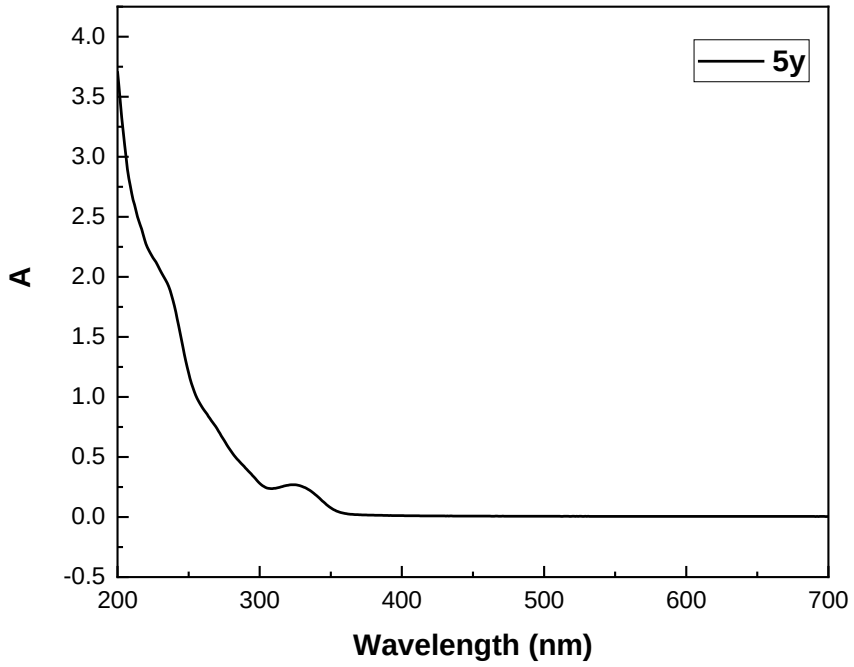


Figure S14. UV-Vis spectrum of **5y** in CH_3CN at 25 ºC, the concentration was 1×10^{-4} M

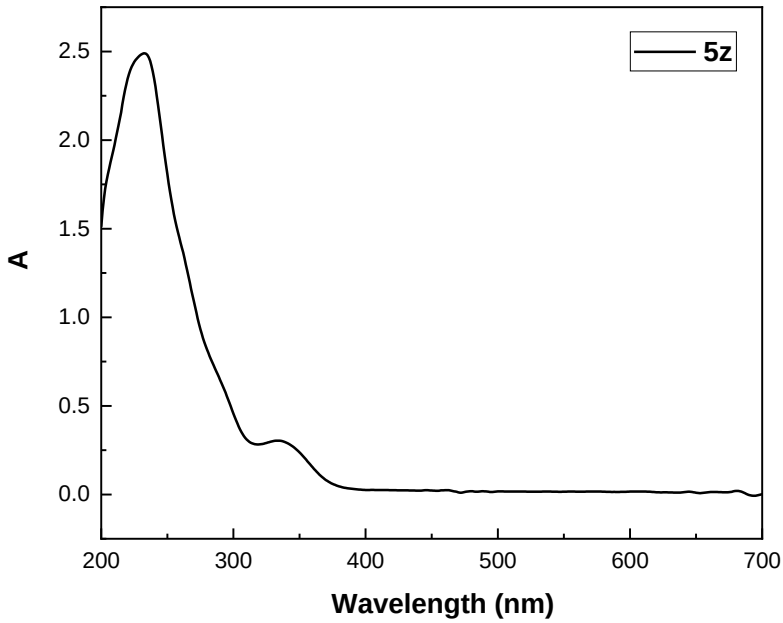


Figure S15. UV-Vis spectrum of **5z** in CH_3CN at 25 ºC, the concentration was 6×10^{-5} M

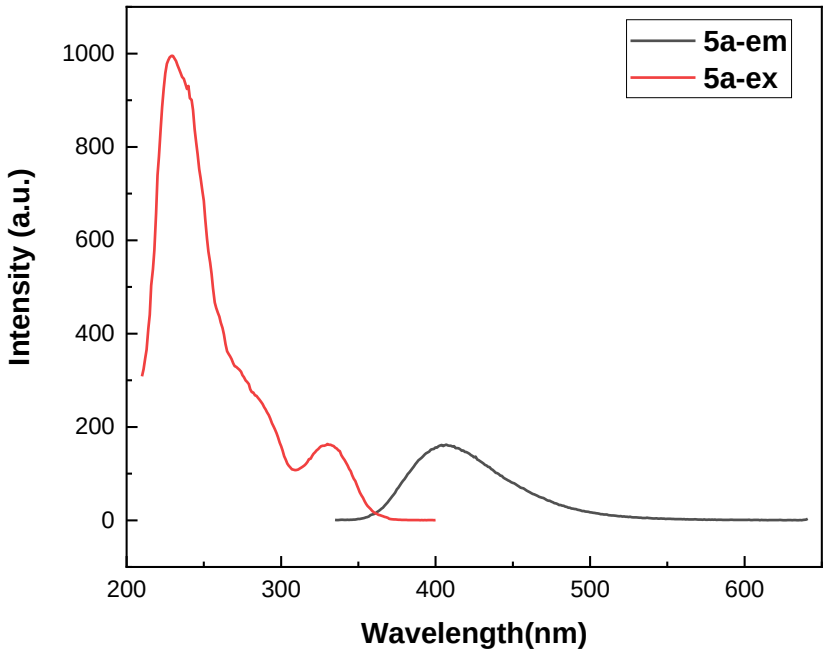


Figure S16. Fluorescence spectrum of **5a** in CH_3CN at 25 °C, the concentration was 1×10^{-5} M

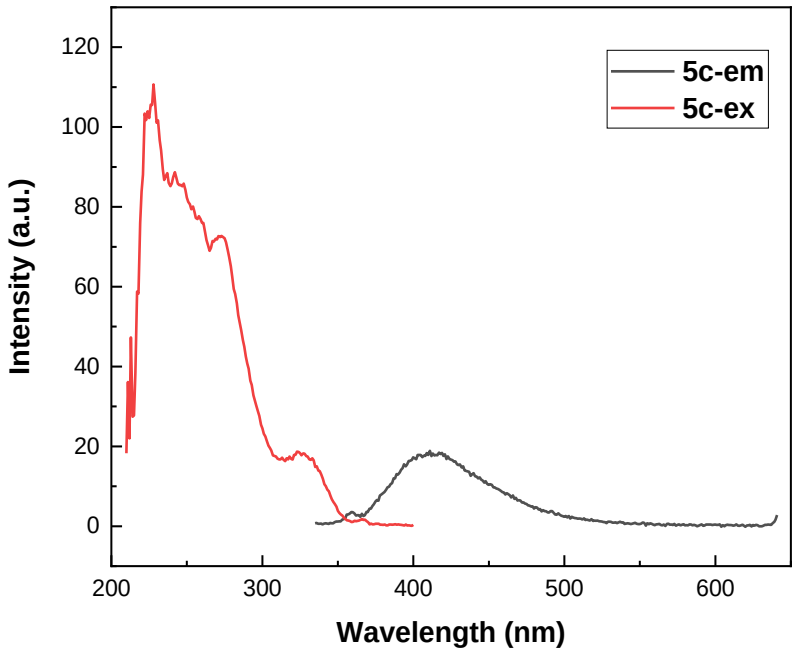


Figure S17. Fluorescence spectrum of **5c** in CH_3CN at 25 °C, the concentration was 5×10^{-6} M

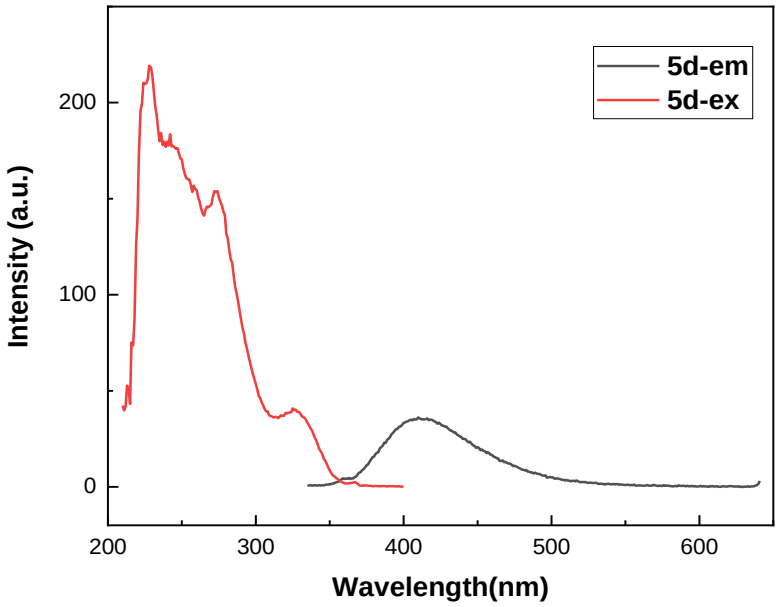


Figure S18. Fluorescence spectrum of **5d** in CH_3CN at 25 °C, the concentration was 5×10^{-6} M

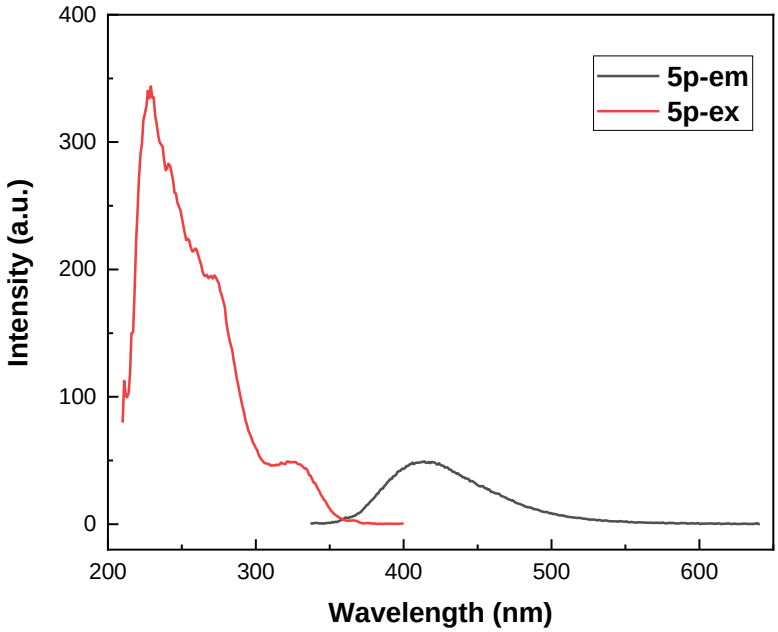


Figure S19. Fluorescence spectrum of **5p** in CH_3CN at 25 °C, the concentration was 5×10^{-6} M

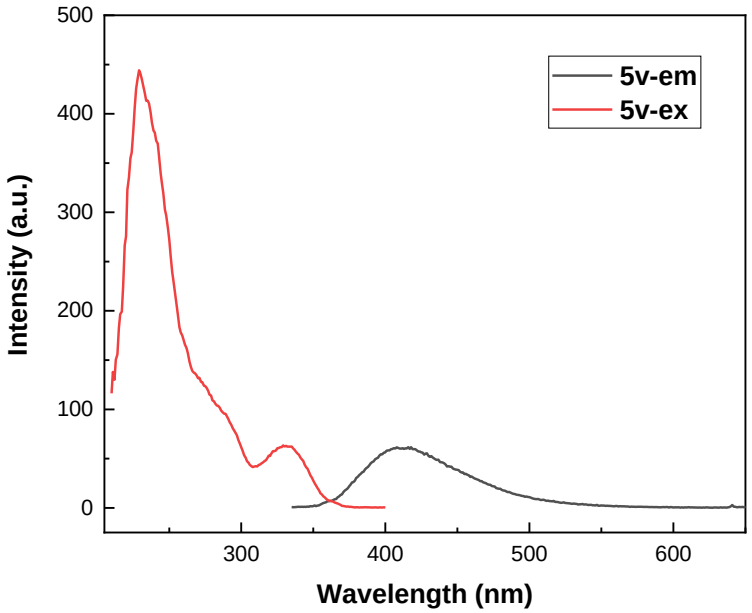


Figure S20. Fluorescence spectrum of **5w** in CH_3CN at 25 °C, the concentration was 5×10^{-6} M

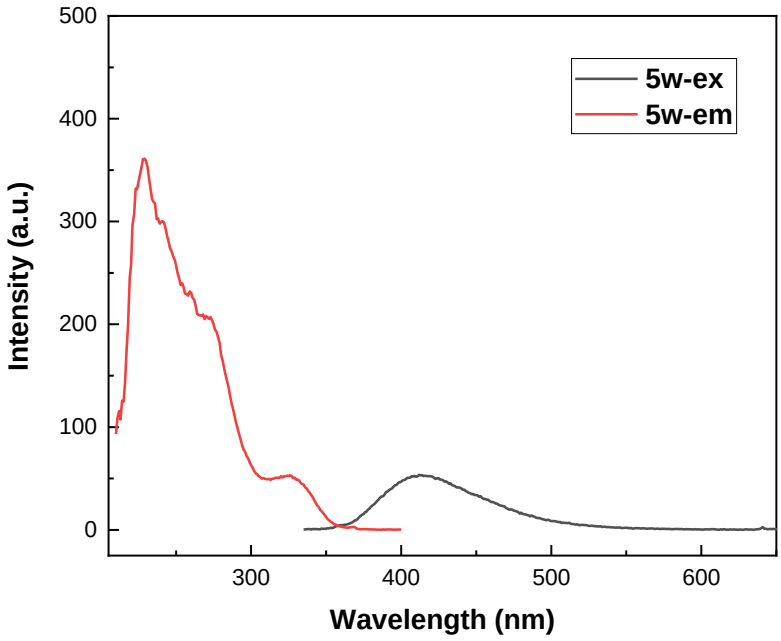


Figure S21. Fluorescence spectrum of **5w** in CH_3CN at 25 °C, the concentration was 5×10^{-6} M

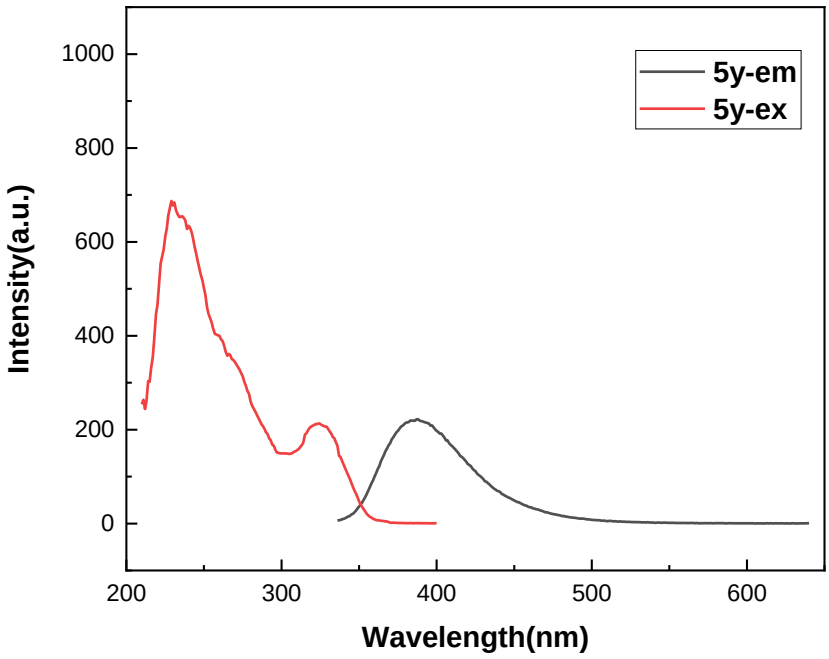


Figure S22. Fluorescence spectrum of **5y** in CH_3CN at 25 °C, the concentration was 1×10^{-5} M

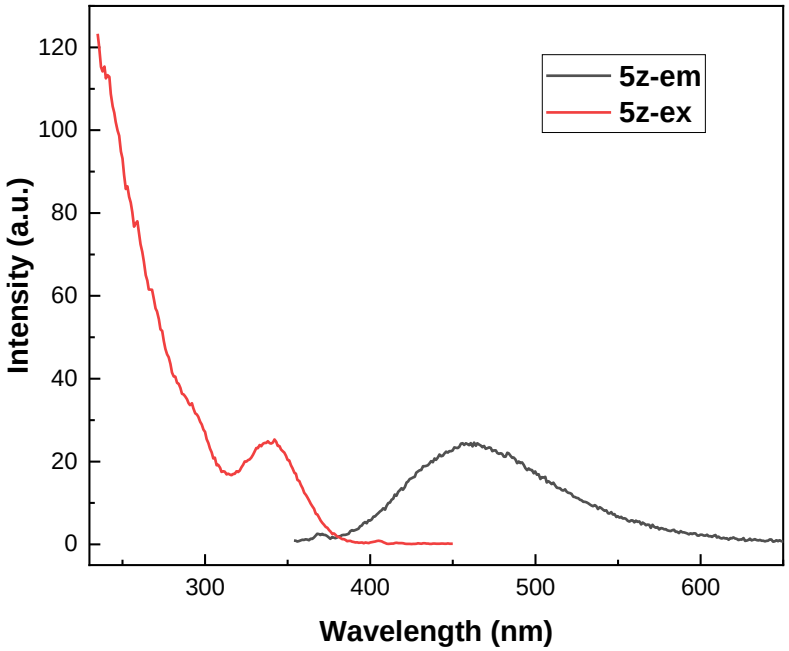


Figure S23. Fluorescence spectrum of **5z** in CH_3CN at 25 °C, the concentration was 1×10^{-6} M

Table S6. Summary of the UV-vis and fluorescence spectra.

Compd	λ_{abs} (nm) [ε_{max} (cm^{-1} M^{-1})]	λ_{ex} (nm)	λ_{em} (nm)	$\Phi^{[a]}$ (%)
5a	325 (1860)	328	410	21.5
5c	326 (1850)	326	409	15.6
5d	328 (1740)	326	408	11.0
5p	321 (1900)	325	413	18.3
5v	326 (1600)	326	408	20.1
5w	325 (1800)	328	410	15.2
5y	323 (1440)	327	411	21.5
5z	340 (1680)	342	462	12.5

[a]Quantum yield determined in solution, using 2-aminopyridine as reference $\phi_{ref} = 0.6$ in 0.1 N H_2SO_4.

13. Copies of CD and CPL spectra

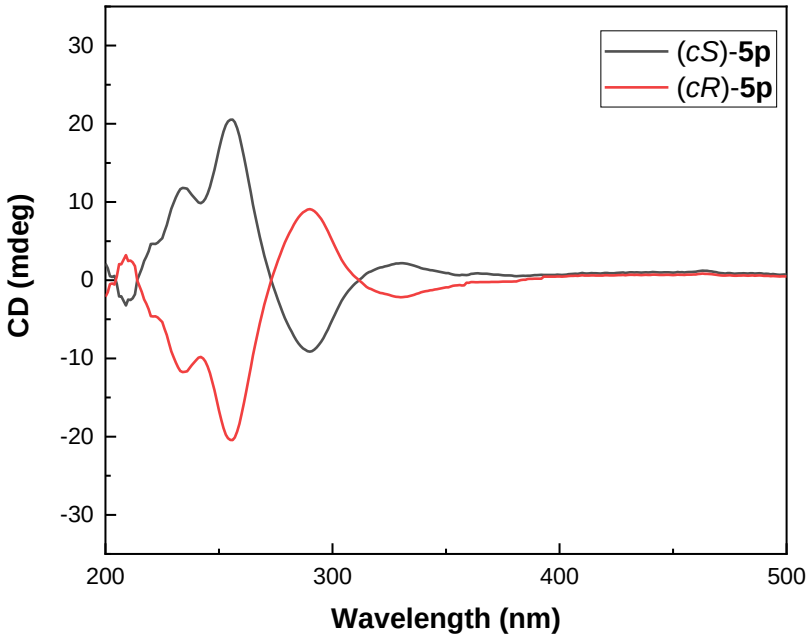


Figure S24. CD spectrum of (*cR*)-**5p** and (*cS*)-**5p** in CH_3CN at 25 °C (c 5×10^{-6} M)

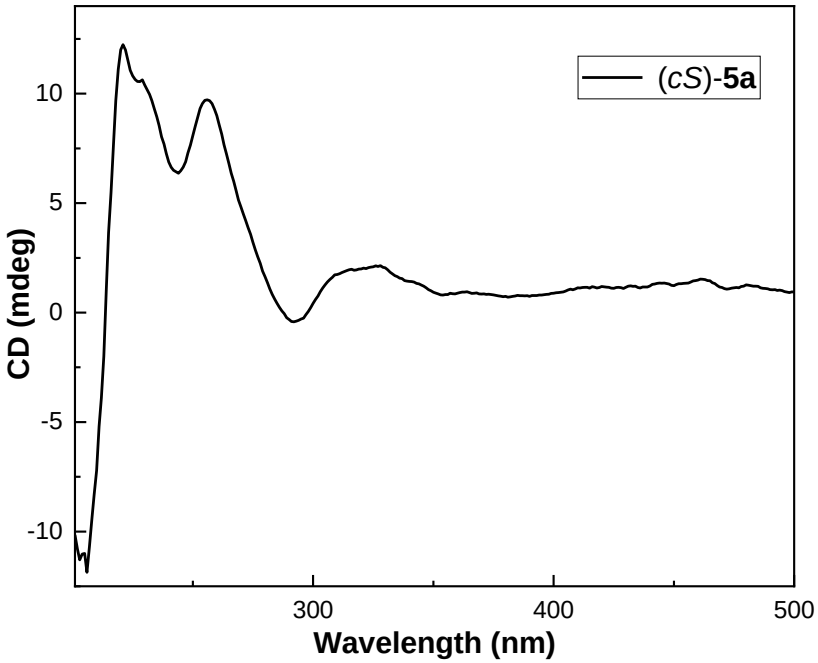


Figure S25. CD spectrum of (*cS*)-**5a** in CH_3CN at 25 °C (c 5×10^{-6} M)

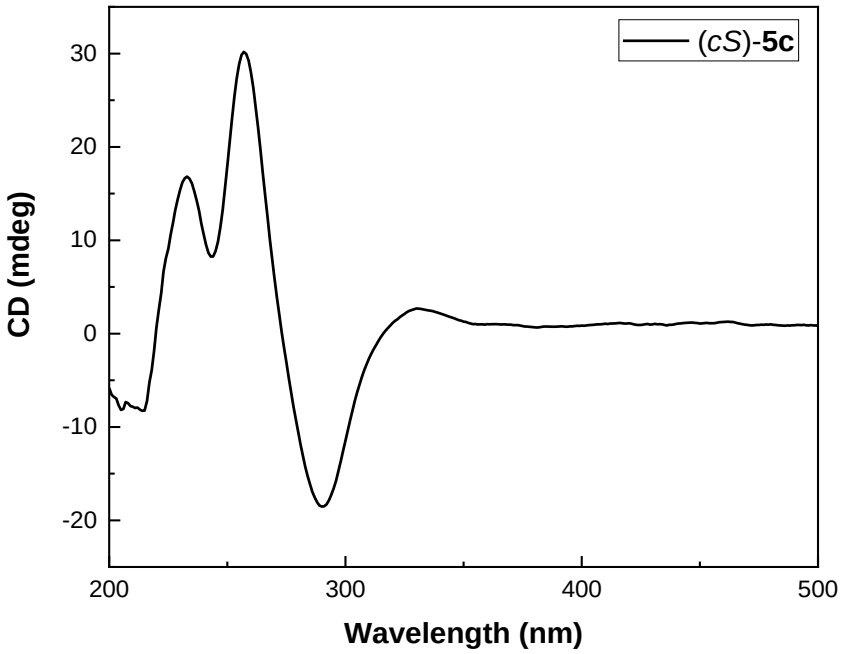


Figure S26. CD spectrum of (*cS*)-**5c** in CH_3CN at 25 °C (*c* 5×10^{-6} M)

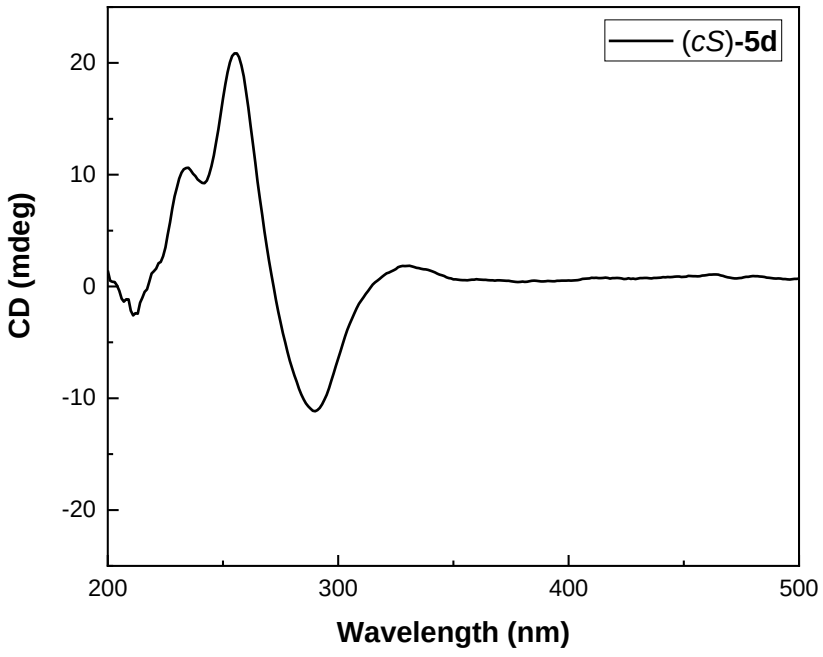


Figure S27. CD spectrum of (*cS*)-**5d** in CH_3CN at 25 °C (*c* 5×10^{-6} M)

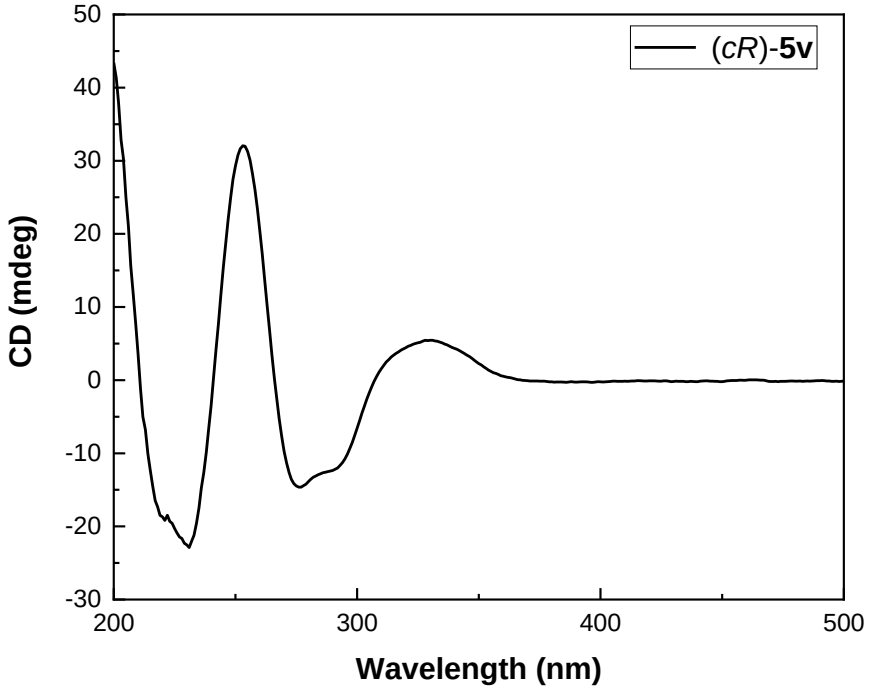


Figure S28. CD spectrum of (c*R*)-**5v** in CH_3CN at 25 °C (2×10^{-6} M)

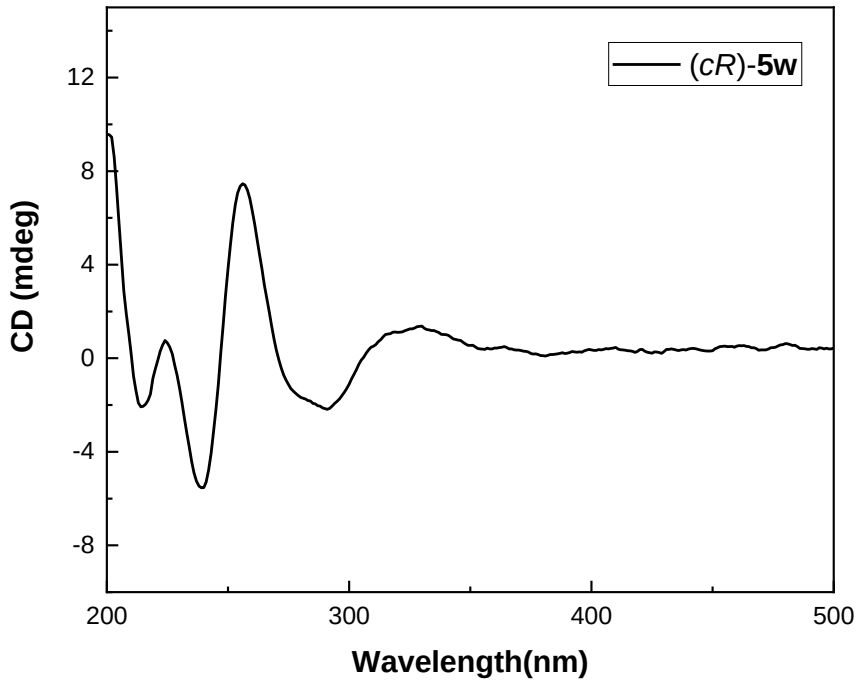


Figure S29. CD spectrum of (c*R*)-**5w** in CH_3CN at 25 °C (2×10^{-6} M)

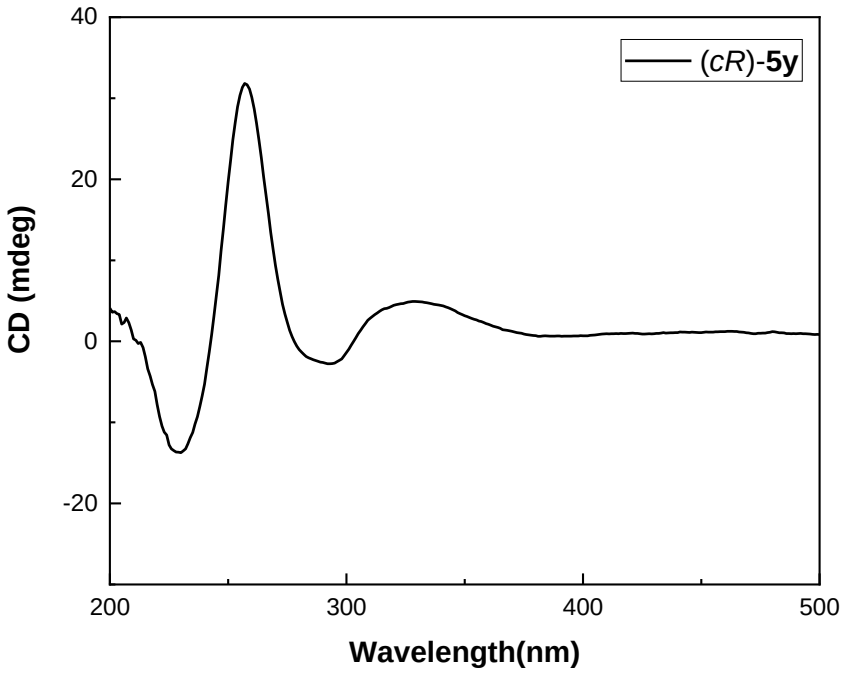


Figure S30. CD spectrum of (c*R*)-**5y** in toluene at 25 °C (5×10^{-6} M)

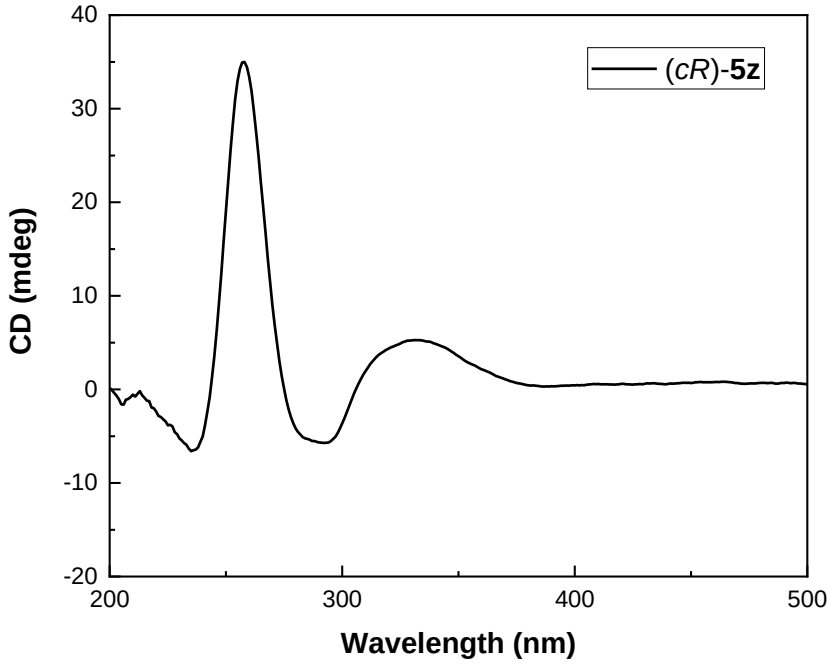


Figure S31. CD spectrum of (c*R*)-**5z** in CH_3CN at 25 °C (5×10^{-6} M)

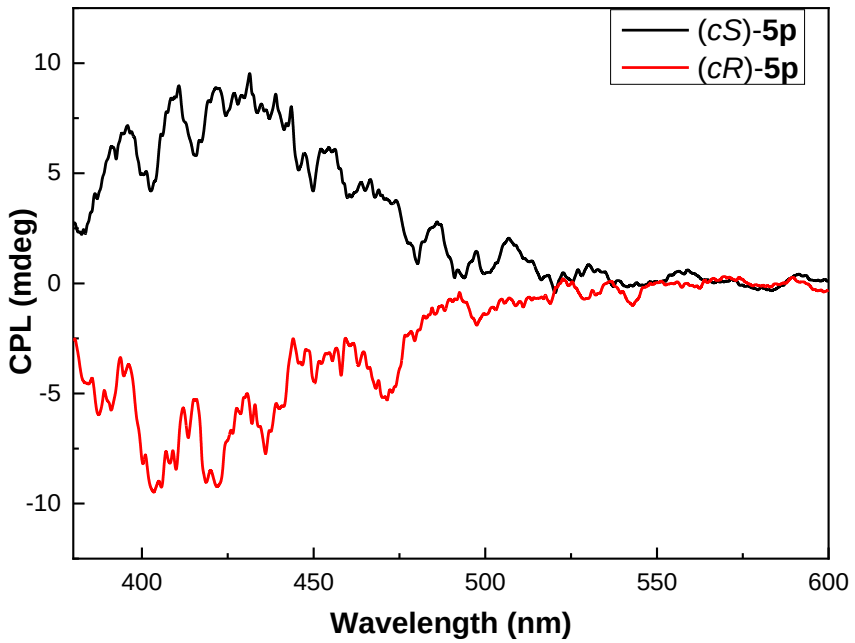


Figure S32. CPL spectrum of (*cR*)-**5p** and (*cS*)-**5p** in CH_3CN at 25 °C (*c* 1×10^{-4} M)

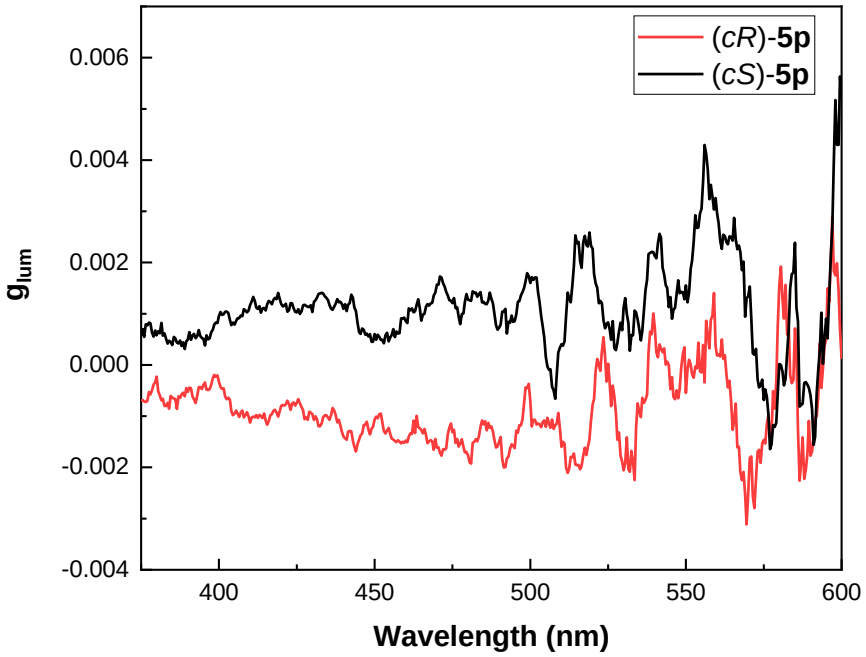


Figure S33. CPL(g_{lum}) of (*cR*)-**5p** and (*cS*)-**5p** in CH_3CN at 25 °C (*c* 1×10^{-4} M)

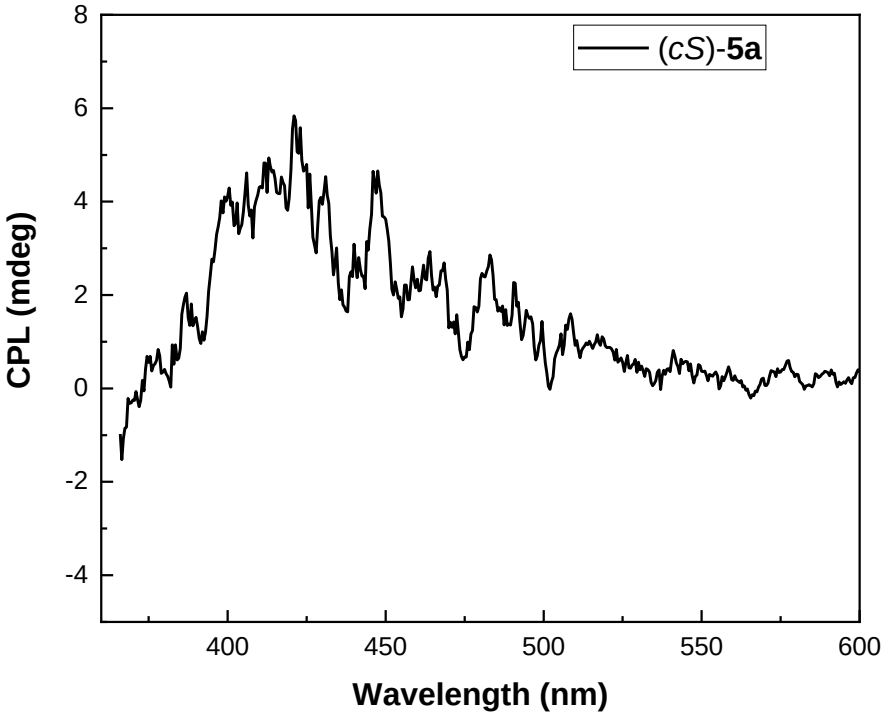


Figure S34. CPL spectrum of (*cS*)-**5a** in CH_3CN at 25 °C (*c* 1×10^{-4} M)

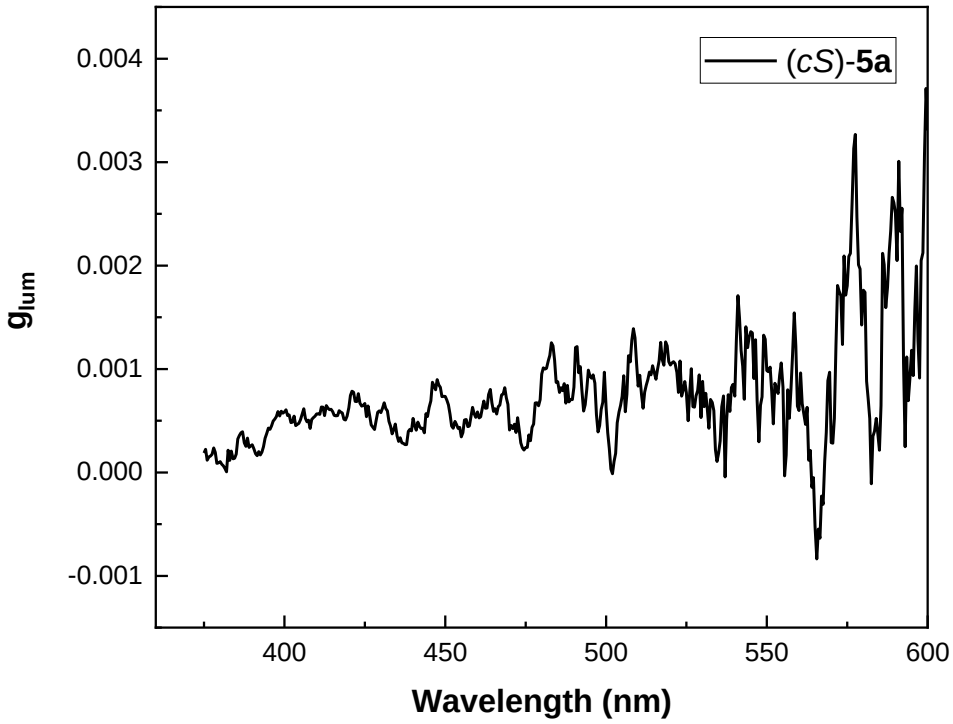


Figure S35. CPL(g_{lum}) of (*cS*)-**5a** in CH_3CN at 25 °C (*c* 1×10^{-4} M)

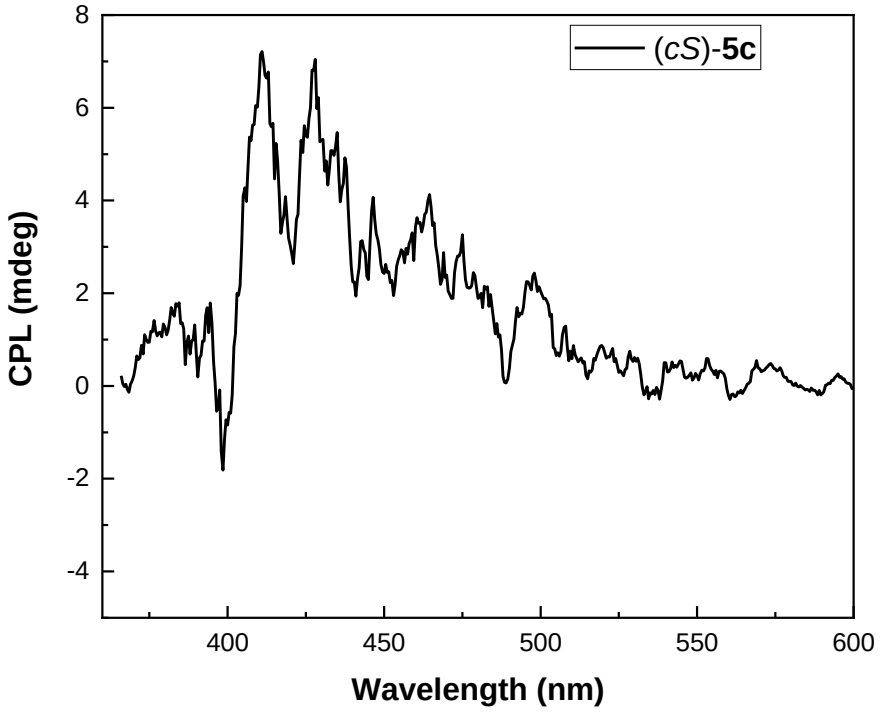


Figure S36. CPL spectrum of (*cS*)-**5c** in CH_3CN at 25 °C (*c* 1×10^{-4} M)

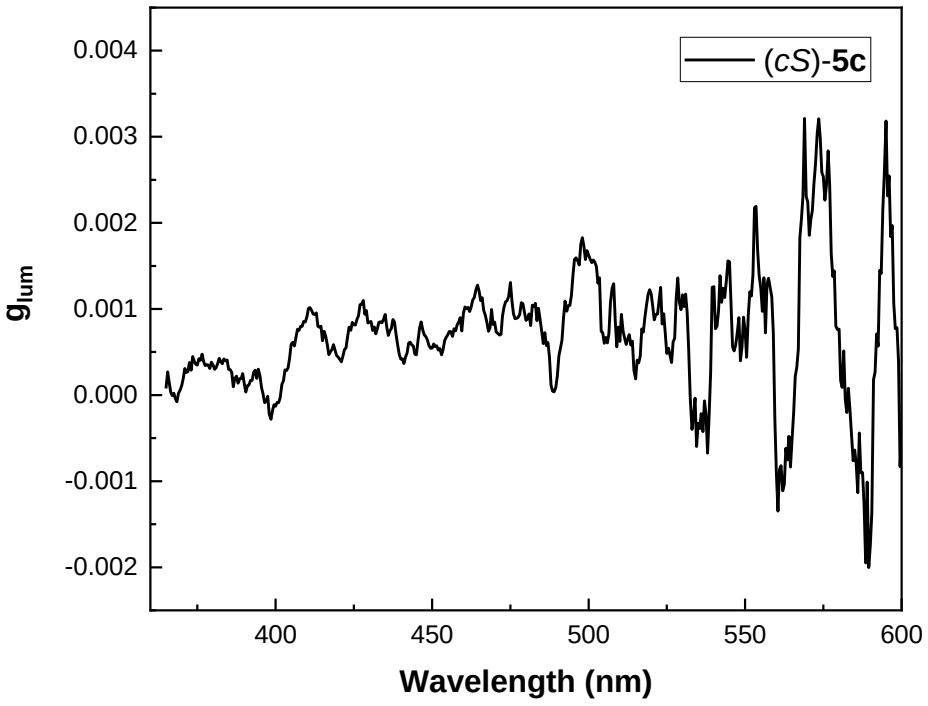


Figure S37. CPL(g_{lum}) of (*cS*)-**5c** in CH_3CN at 25 °C (*c* 1×10^{-4} M)

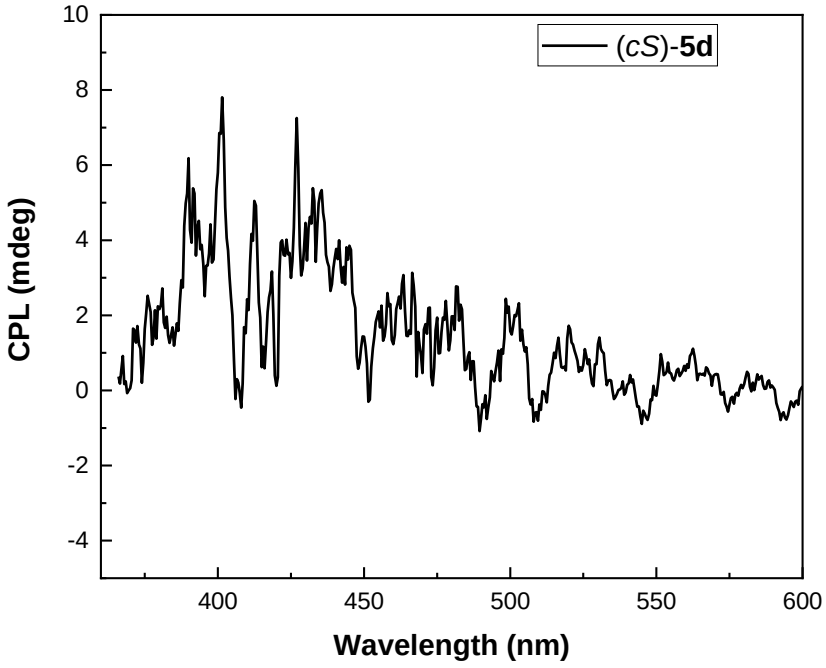


Figure S38. CPL spectrum of (*cS*)-**5d** in CH_3CN at 25 °C (*c* 1×10^{-4} M)

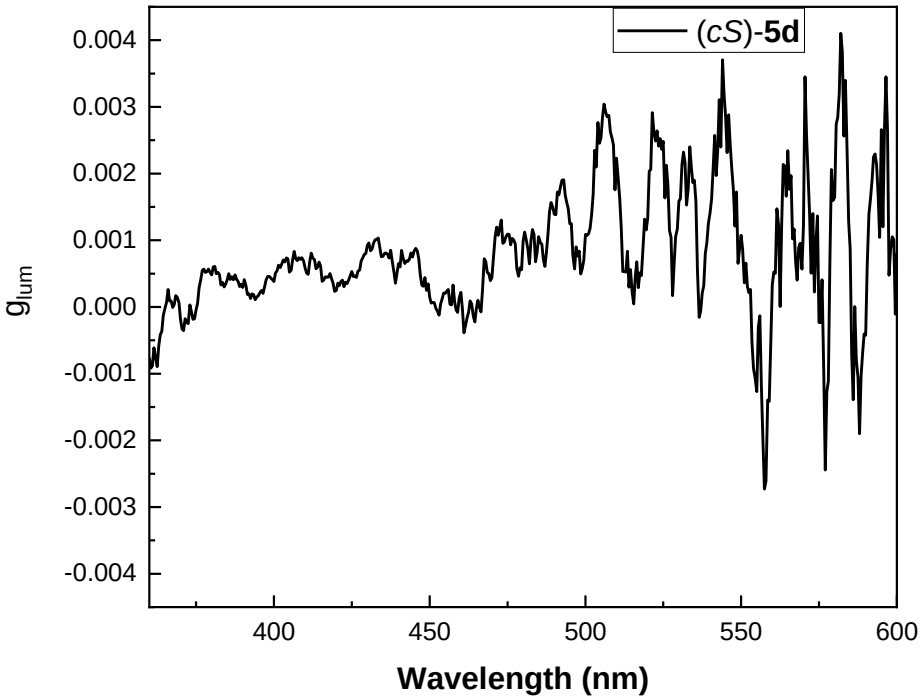


Figure S39. CPL(g_{lum}) of (*cS*)-**5d** in CH_3CN at 25 °C (*c* 1×10^{-4} M)

Table S7. Summary of the g_{abs} for CD, g_{lum} and B_{CPL} for CPL .

Compd.	CD g_{abs}	CPL g_{lum}	B_{CPL}
(*cS*)-**5p**	1.1×10^{-3} (256 nm); -2.4×10^{-3} (291 nm); 1.1×10^{-3} (330 nm)	1.3×10^{-3} (411 nm)	0.65
(*cR*)-**5p**	1.1×10^{-3} (256 nm); 2.5×10^{-3} (291 nm); -1.0×10^{-3} (330 nm)	-1.1×10^{-3} (410 nm)	0.65
(*cS*)-**5a**	1.7×10^{-3} (256 nm); -2.0×10^{-3} (291 nm); 1.7×10^{-3} (328 nm)	0.8×10^{-3} (421 nm)	0.40
(*cS*)-**5c**	1.2×10^{-3} (257 nm); -2.3×10^{-3} (290 nm); 7.8×10^{-4} (330 nm)	1.0×10^{-3} (411 nm)	0.38
(*cS*)-**5d**	1.7×10^{-3} (254 nm); -2.6×10^{-3} (291 nm); 8.0×10^{-4} (328 nm)	0.9×10^{-3} (428 nm)	0.35
(*cR*)-**5v**	1.0×10^{-3} (252 nm); -1.1×10^{-3} (291 nm); 8.2×10^{-4} (330 nm)	---	---
(*cR*)-**5w**	1.7×10^{-3} (254 nm); -2.6×10^{-3} (291 nm); 8.0×10^{-4} (328 nm)	---	---
(*cR*)-**5y**	6.2×10^{-4} (256 nm); -6.0×10^{-4} (295 nm); 6.8×10^{-4} (327nm)	---	---
(*cR*)-**5z**	1.3×10^{-3} (258 nm); -5×10^{-4} (292 nm); 9.5×10^{-4} (333 nm)	---	---

[a] B_{CPL} value was calculated based on the formula: $B_{CPL} = \varepsilon \times \Phi_F \times g_{lum}/2$.

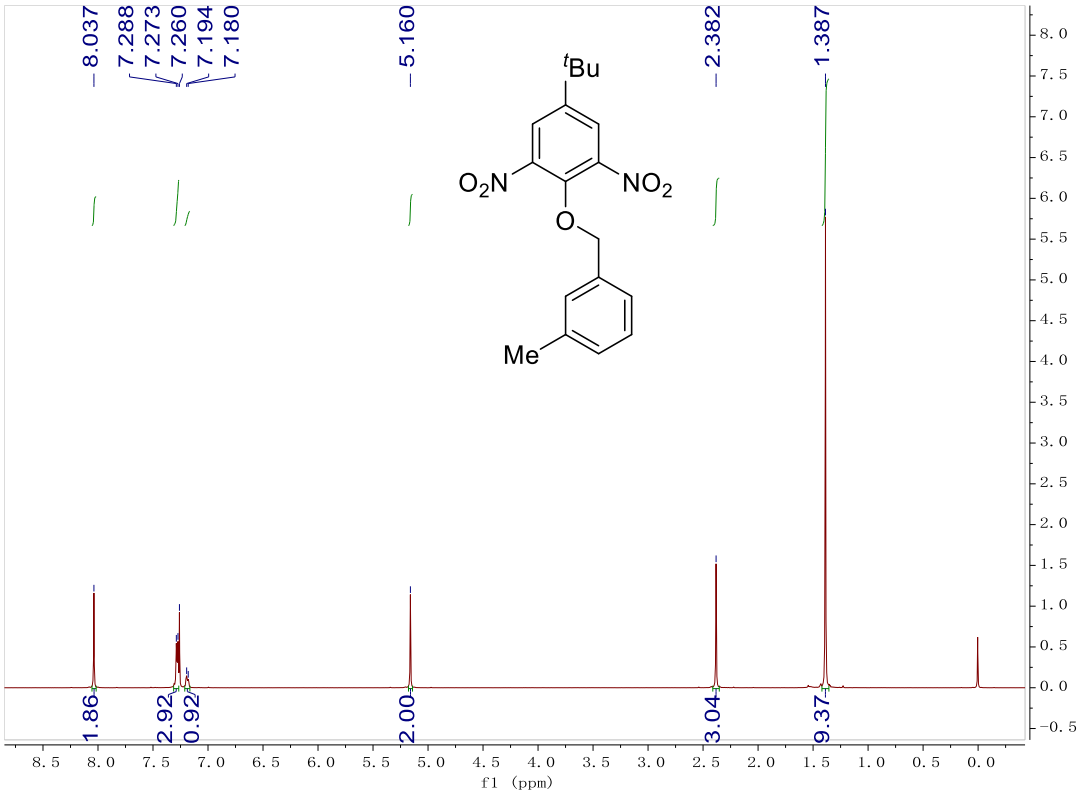
14. References

[1] S. Tong, J.-T. Li, D.-D. Liang, Y.-E. Zhang, Q.-Y. Feng, X. Zhang, J. Zhu, M.-X. Wang, *J. Am. Chem. Soc*. **2020**, *142*, 14432-14436.

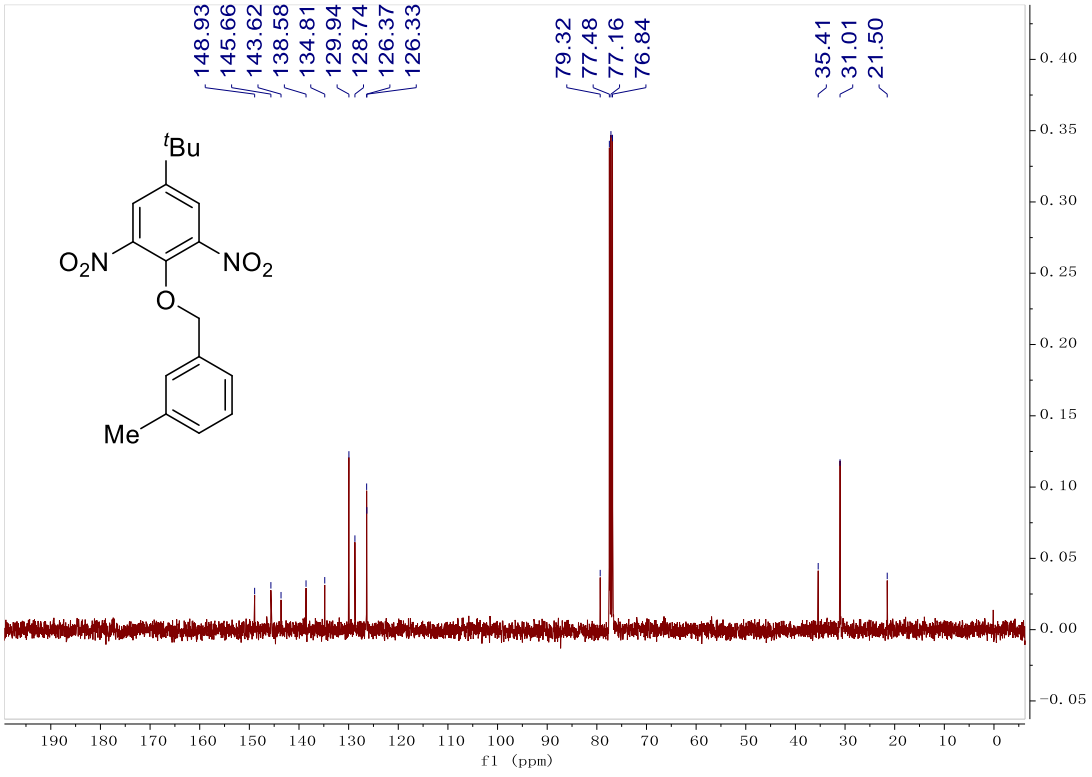
[2] J.-T. Li, L.-X. Wang, D.-X. Wang, L. Zhao, M.-X. Wang, *J. Org. Chem.* **2014***, 79,* 2178-2188.

15. Copies of ^{1}H and ^{13}C NMR spectra

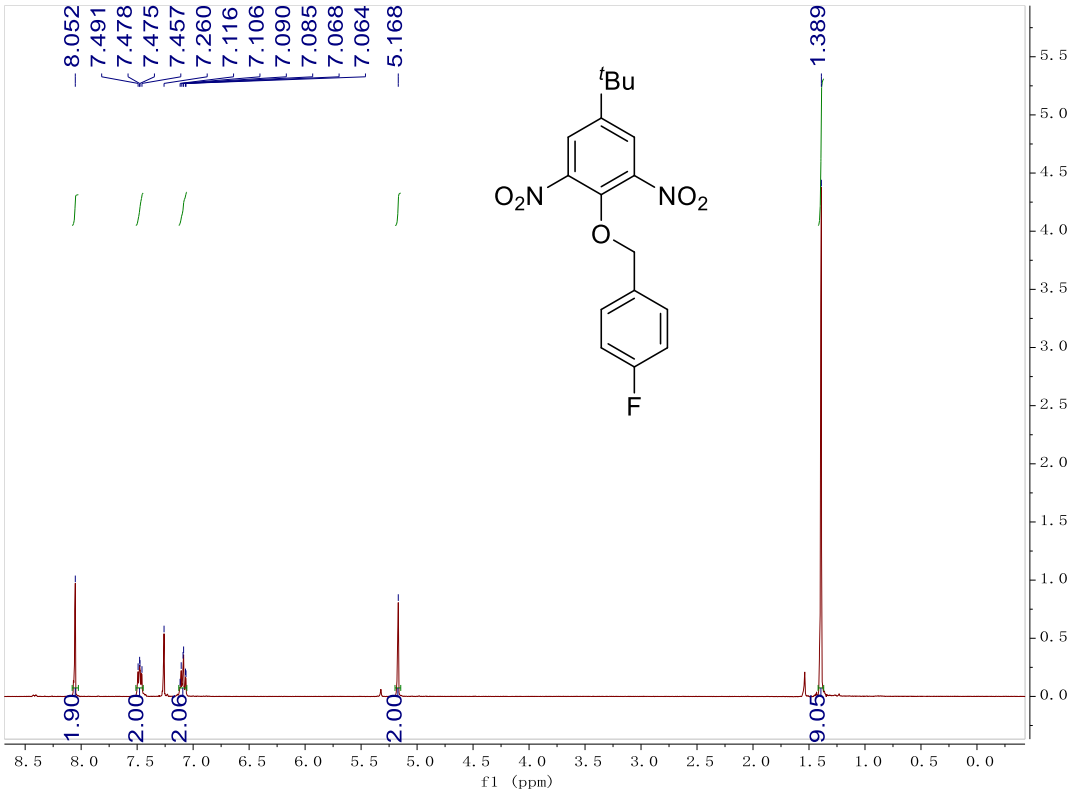
^{1}H NMR spectrum of *Monomer*-**B1** in $CDCl_3$ at 298 K



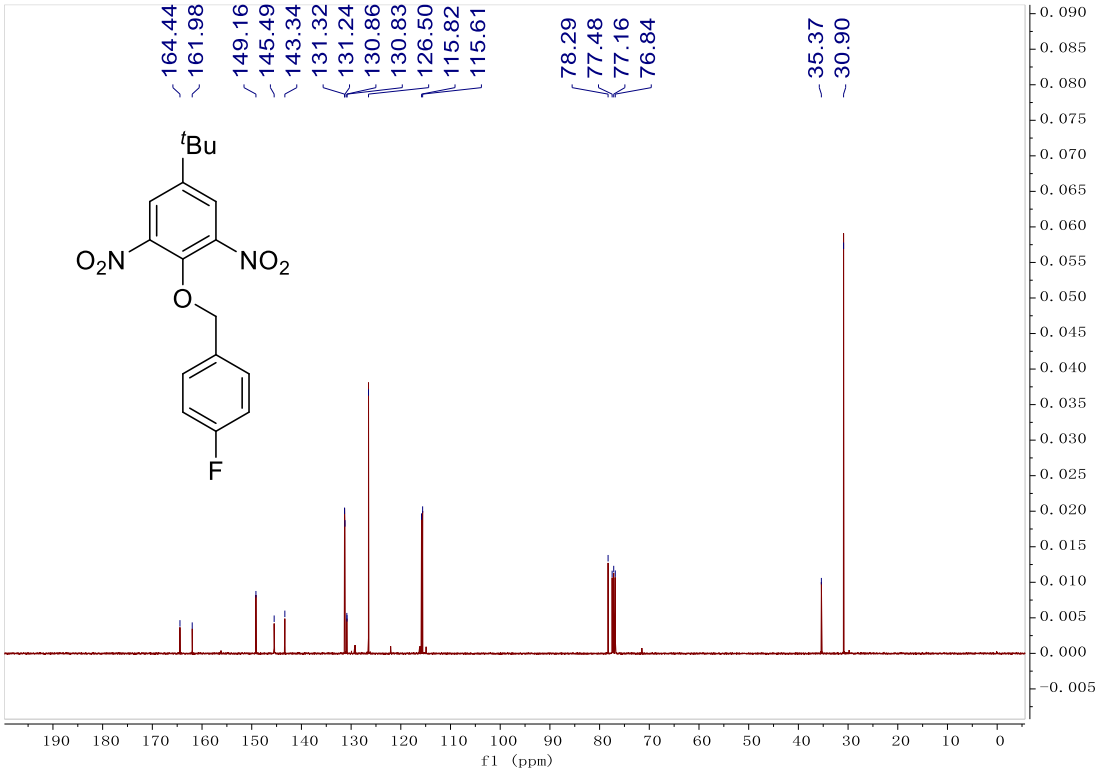
^{13}C NMR spectrum of *Monomer*-**B1** in $CDCl_3$ at 298 K



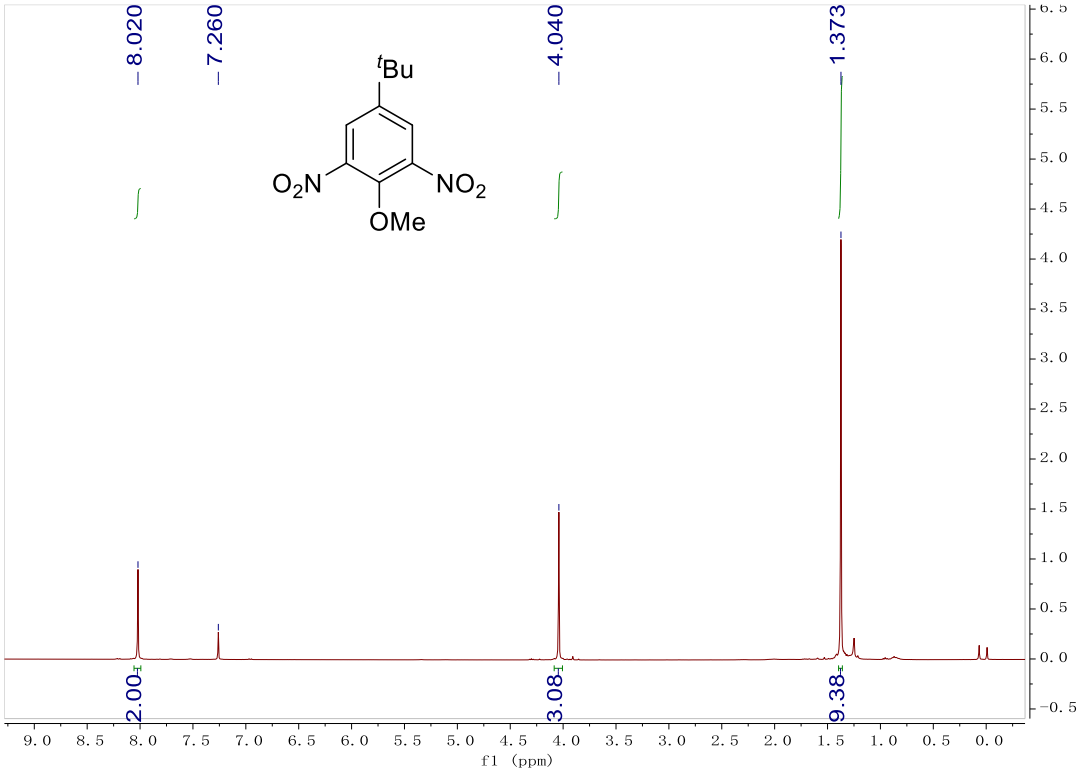
^{1}H NMR spectrum of *Monomer*-**B2** in $CDCl_3$ at 298 K



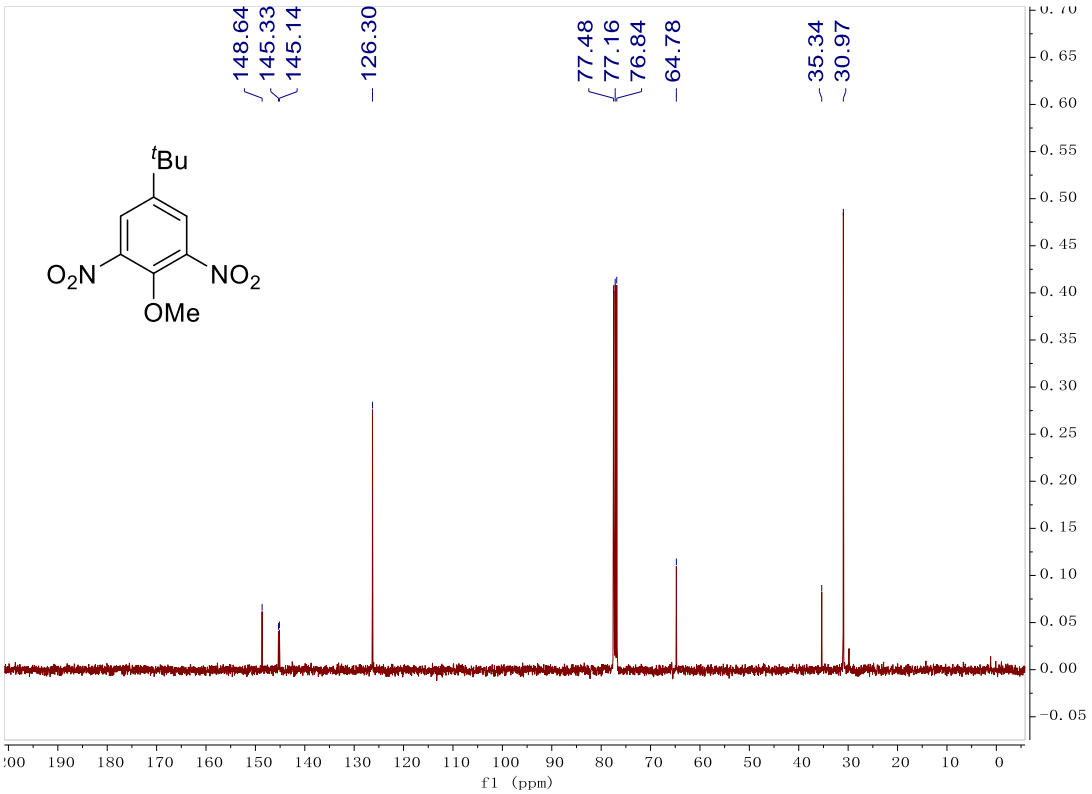
^{13}C NMR spectrum of *Monomer*-**B2** in $CDCl_3$ at 298 K



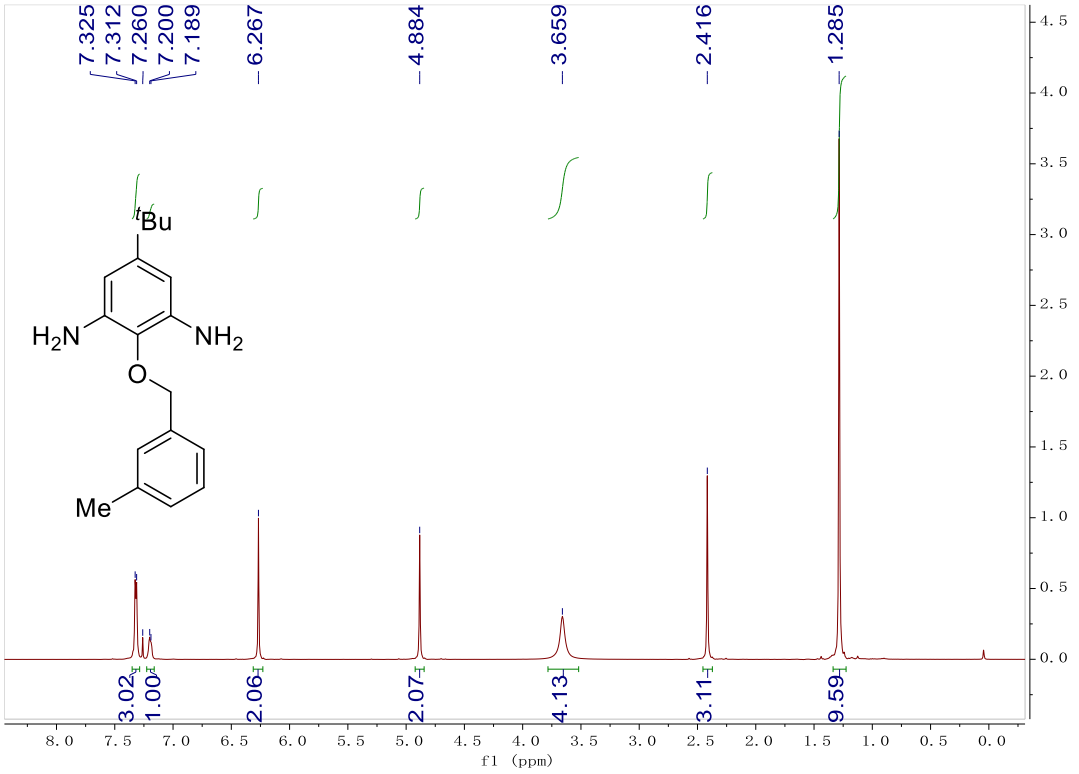
^{1}H NMR spectrum of *Monomer*-**B3** in $CDCl_3$ at 298 K



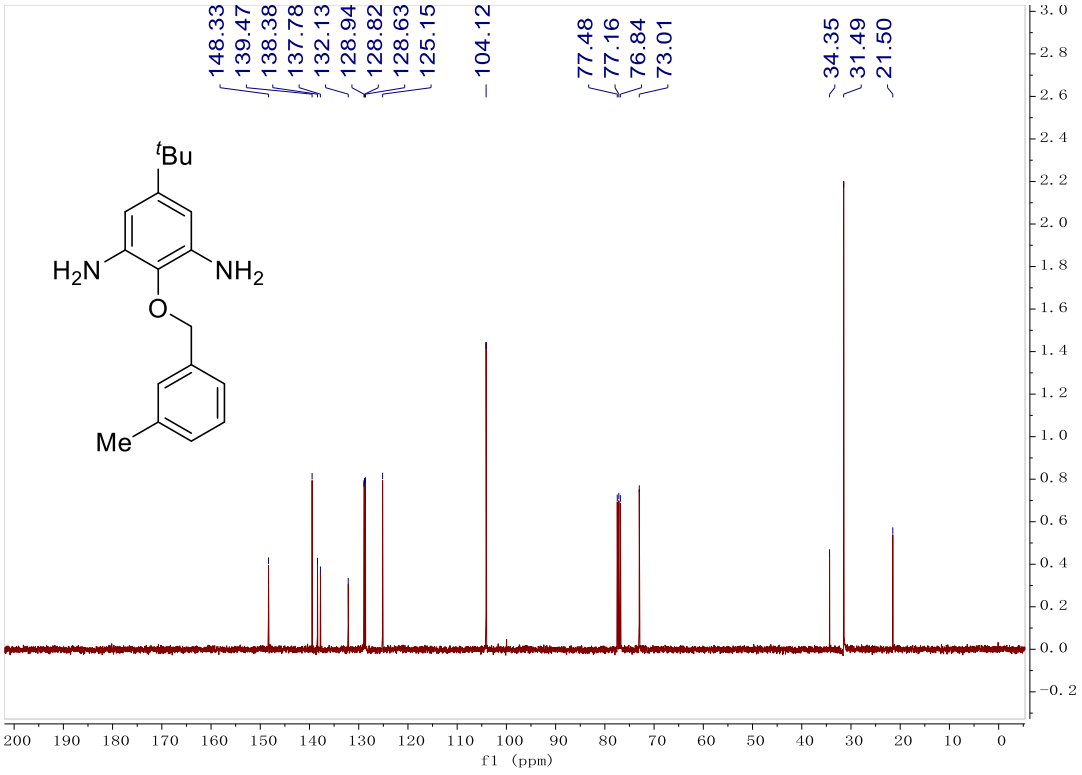
^{13}C NMR spectrum of *Monomer*-**B3** in $CDCl_3$ at 298 K



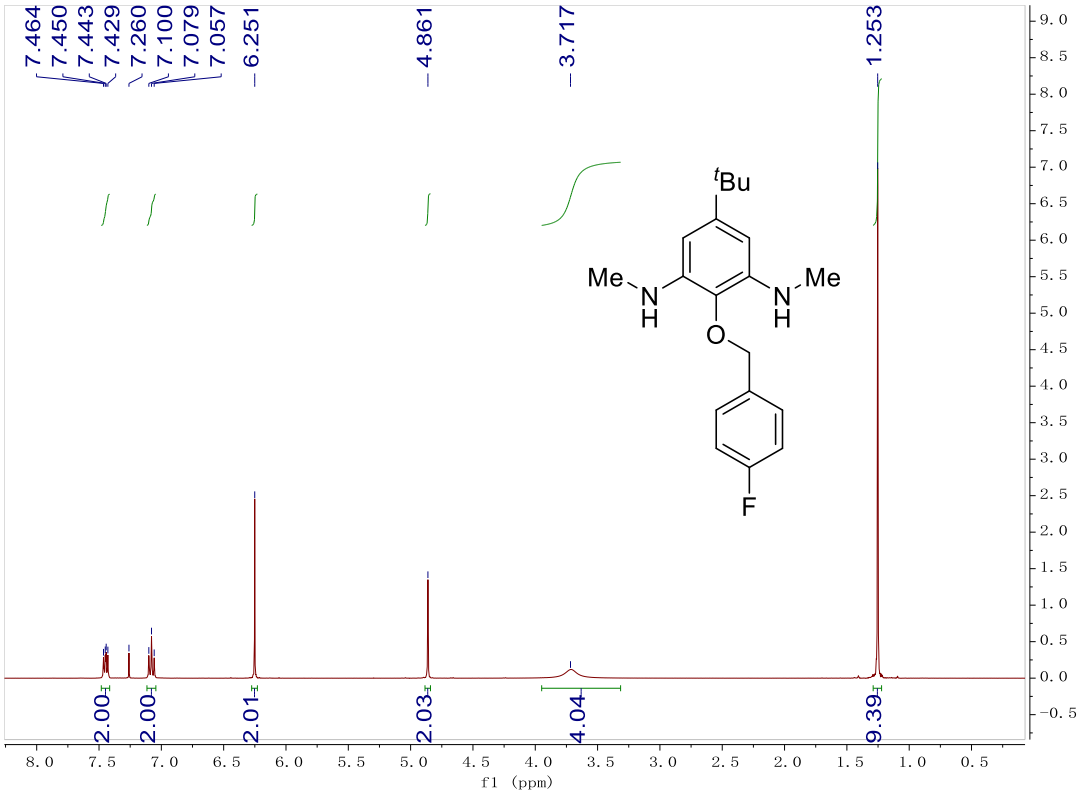
^{1}H NMR spectrum of *Monomer*-**C1** in $CDCl_3$ at 298 K



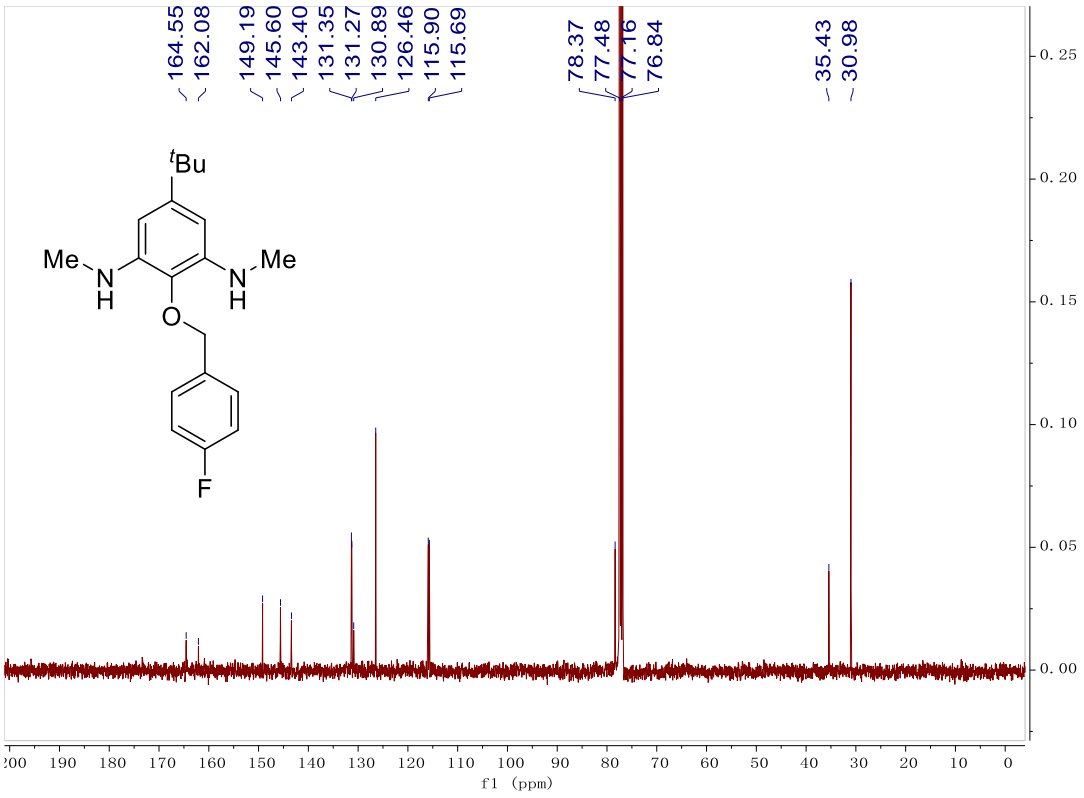
^{13}C NMR spectrum of *Monomer*-**C1** in $CDCl_3$ at 298 K



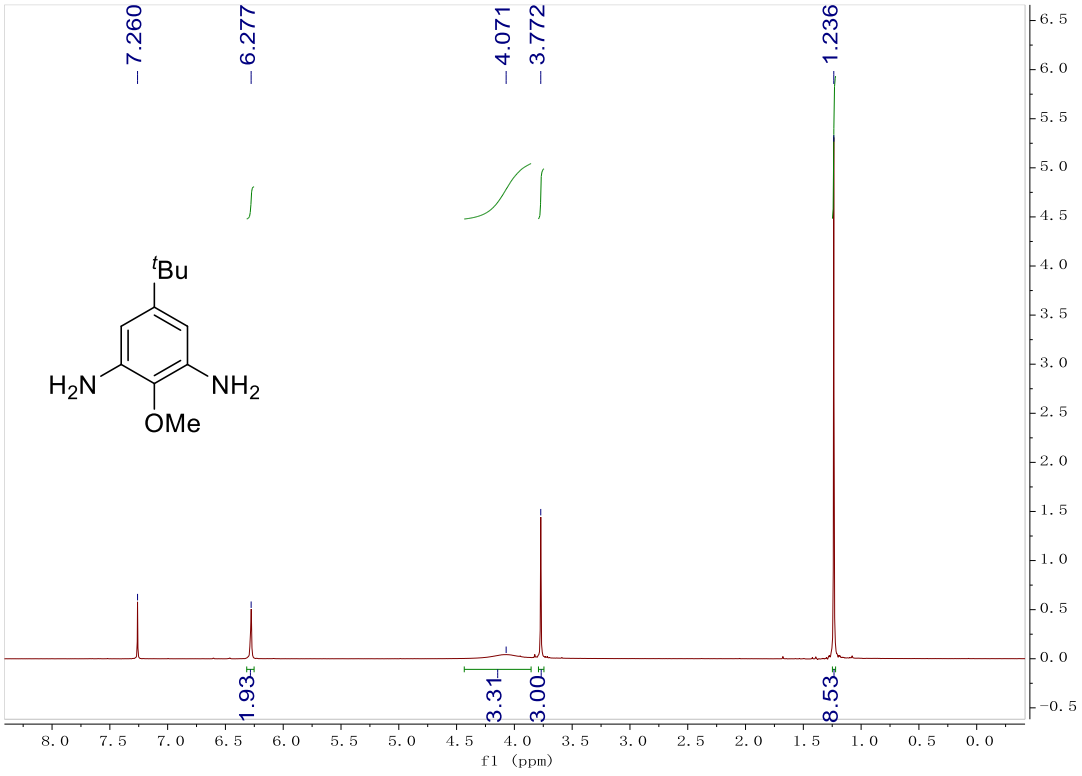
^{1}H NMR spectrum of *Monomer*-**C2** in $CDCl_3$ at 298 K



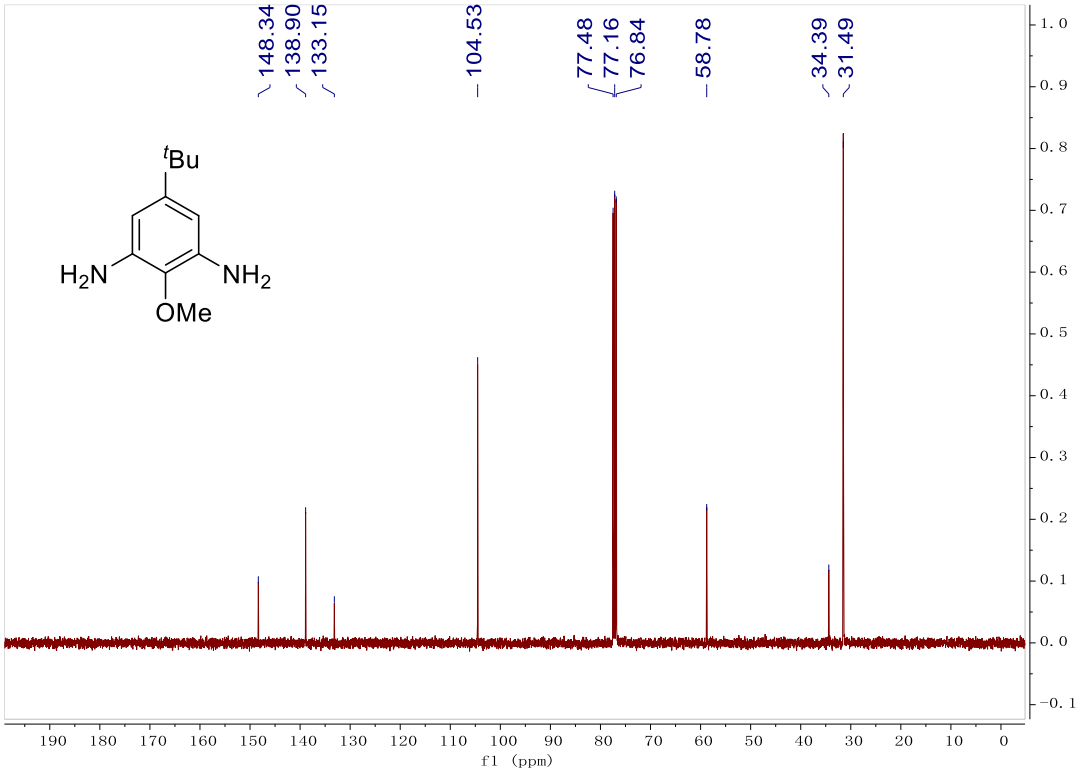
^{13}C NMR spectrum of *Monomer*-**C2** in $CDCl_3$ at 298 K



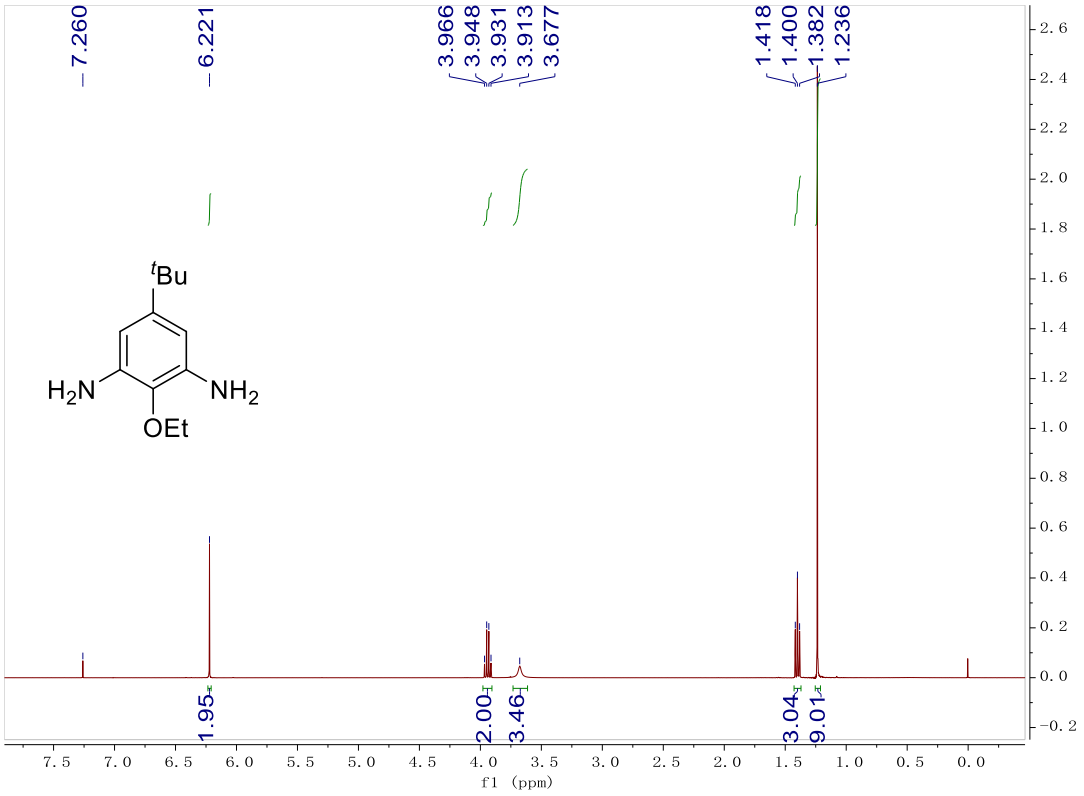
^{1}H NMR spectrum of *Monomer*-**C3** in $CDCl_3$ at 298 K



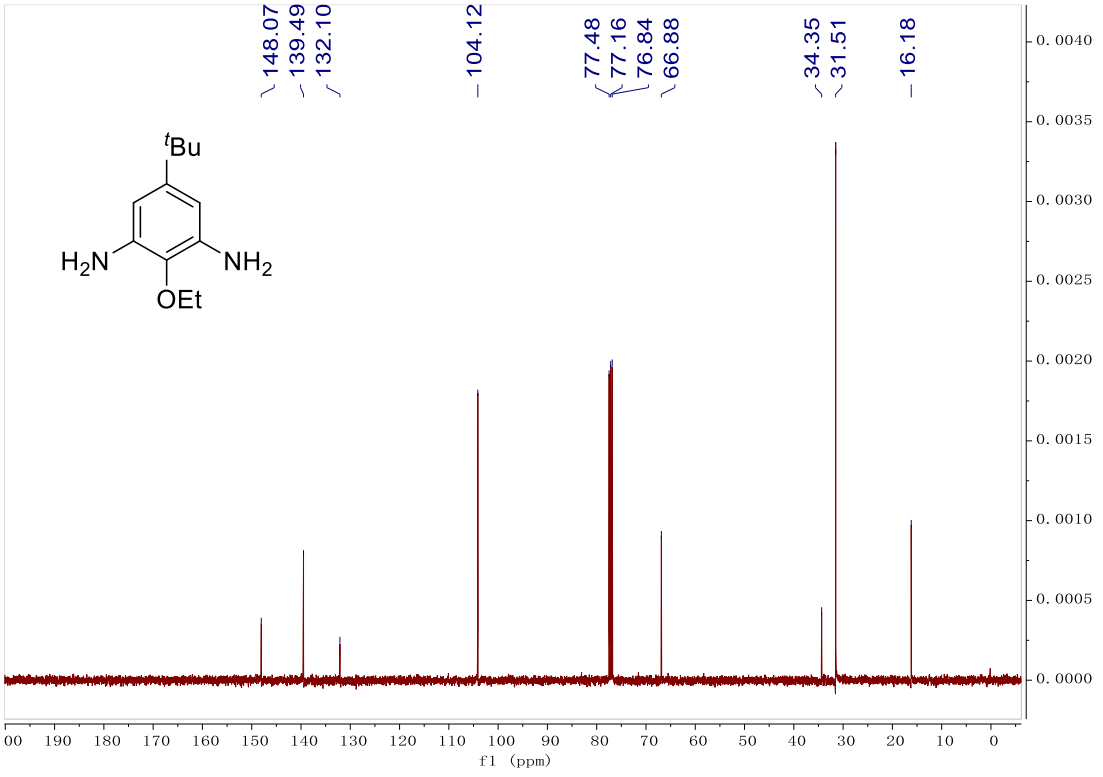
^{13}C NMR spectrum of *Monomer*-**C3** in $CDCl_3$ at 298 K



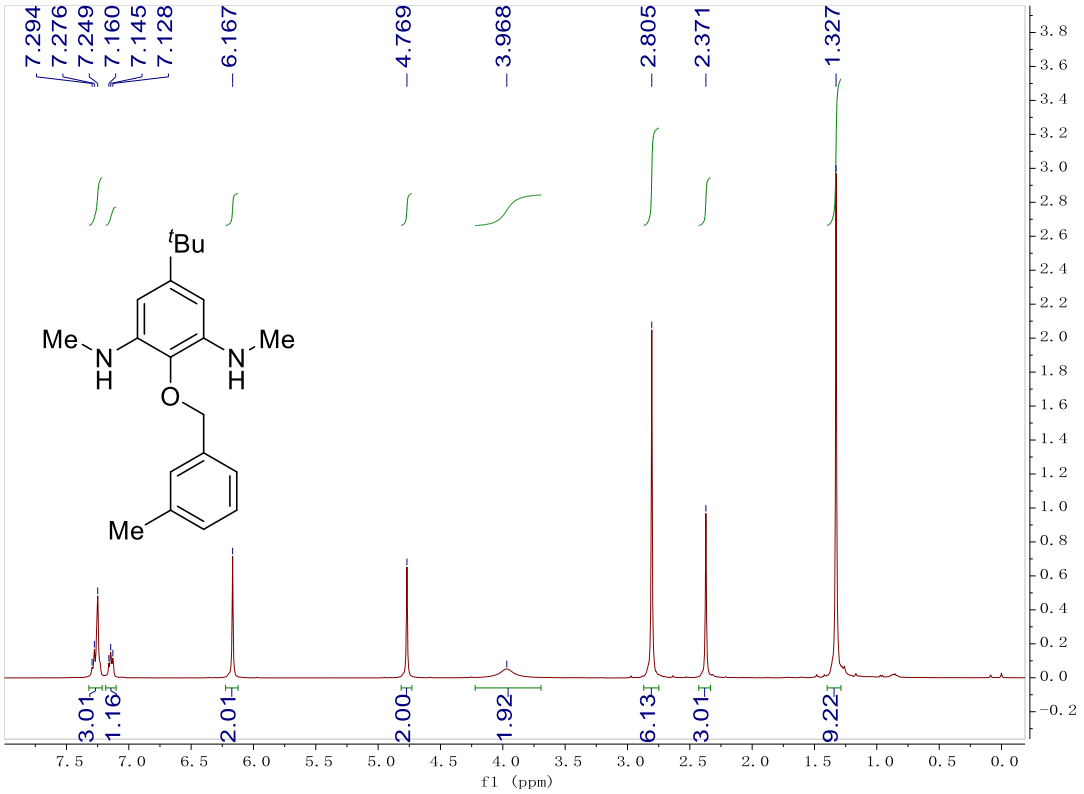
^{1}H NMR spectrum of *Monomer*-**C4** in $CDCl_3$ at 298 K



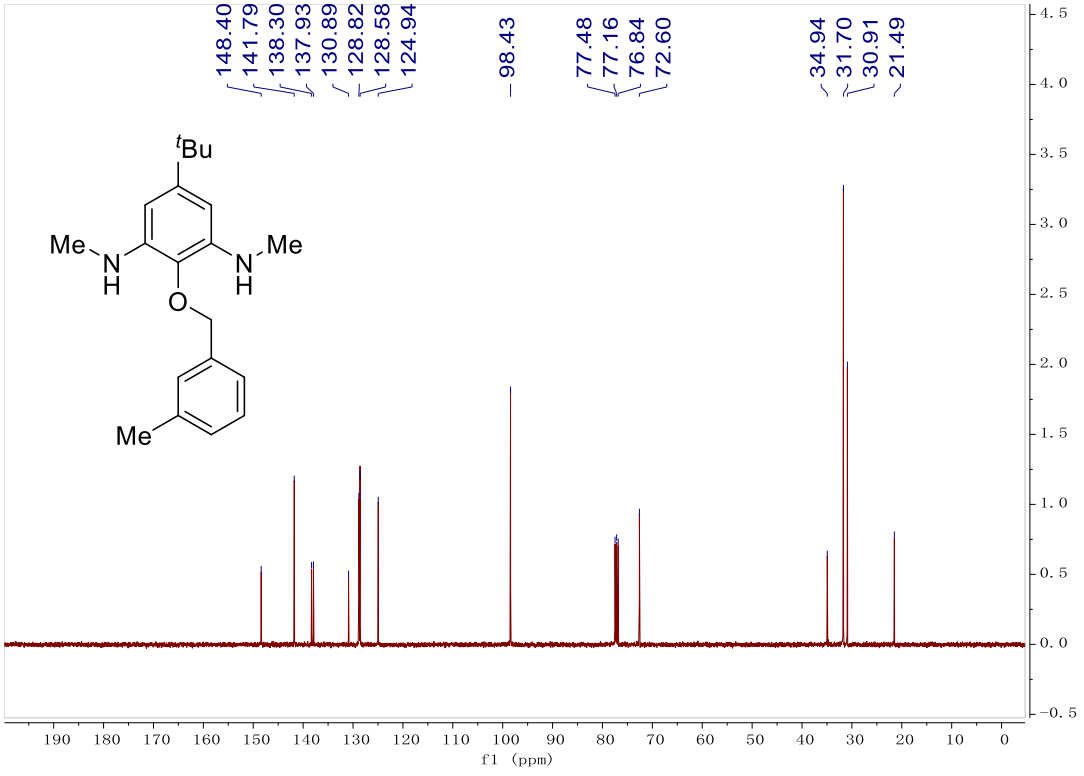
^{13}C NMR spectrum of *Monomer*-**C4** in $CDCl_3$ at 298 K



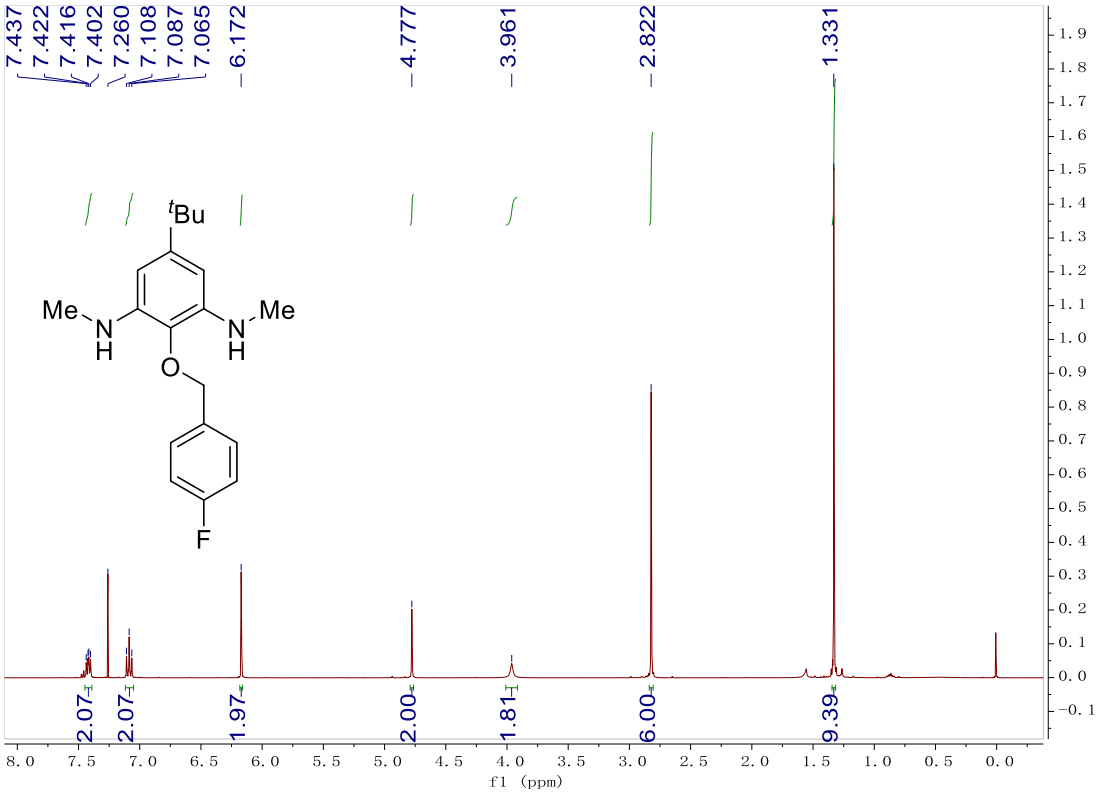
^{1}H NMR spectrum of *Monomer*-**F1** in $CDCl_3$ at 298 K



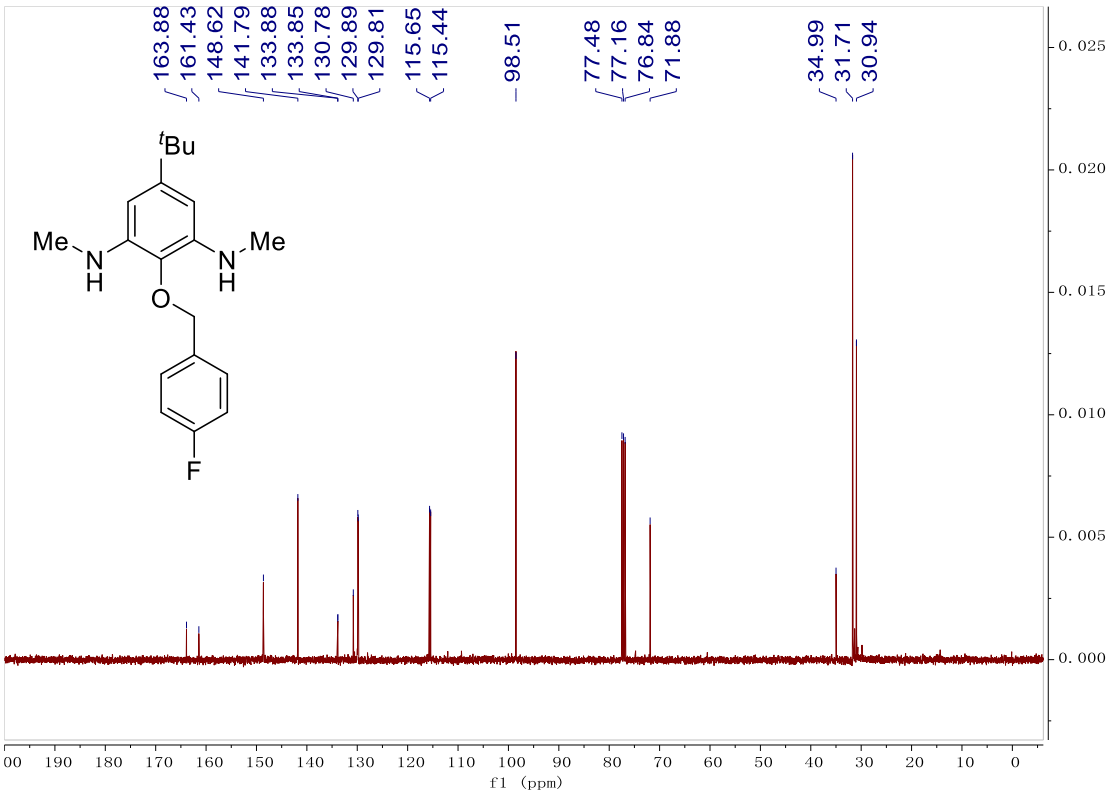
^{13}C NMR spectrum of *Monomer*-**F1** in $CDCl_3$ at 298 K



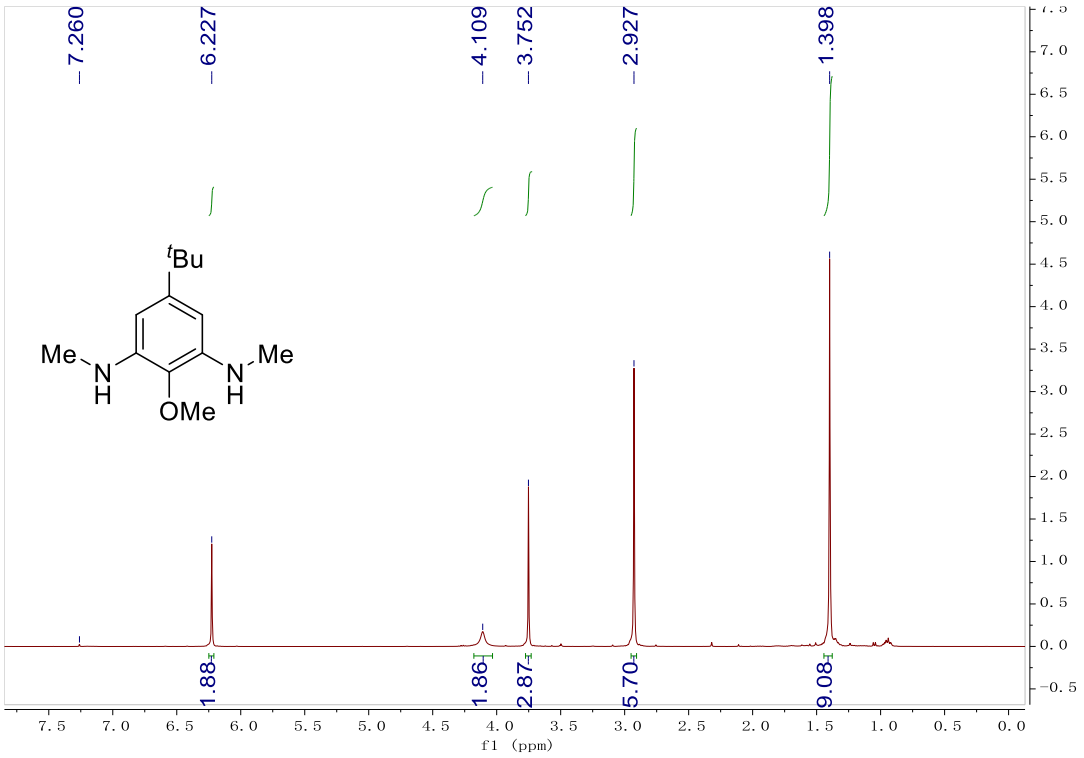
^{1}H NMR spectrum of *Monomer*-**F2** in $CDCl_3$ at 298 K



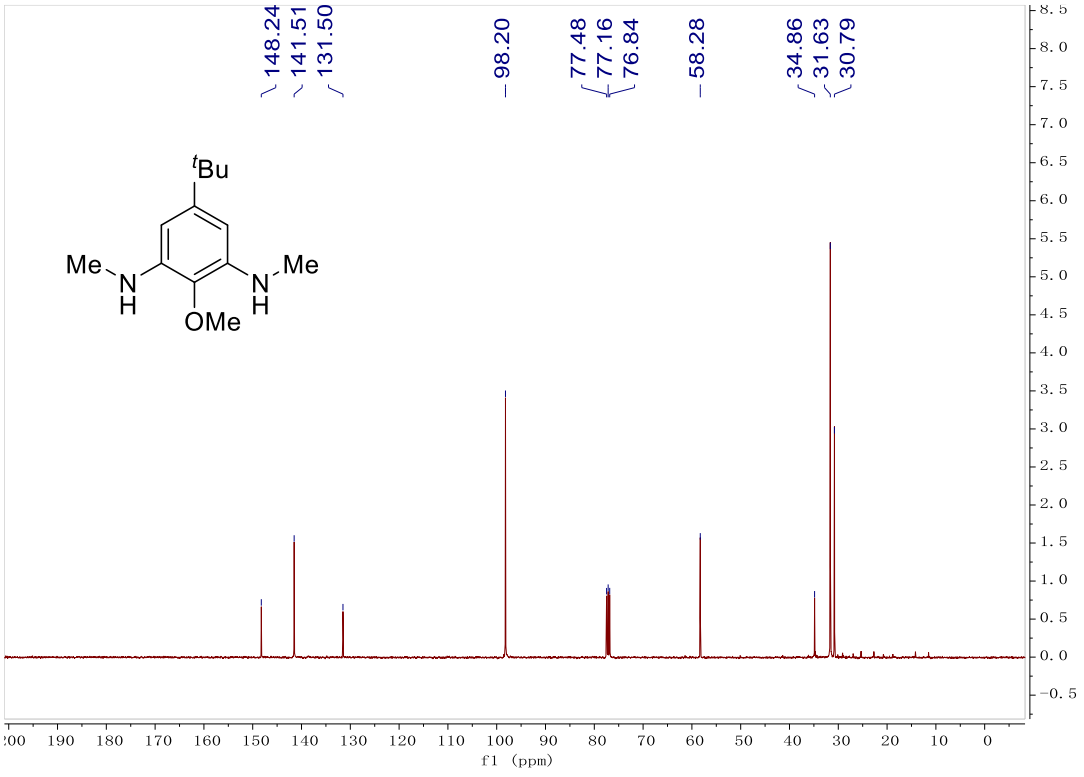
^{13}C NMR spectrum of *Monomer*-**F2** in $CDCl_3$ at 298 K



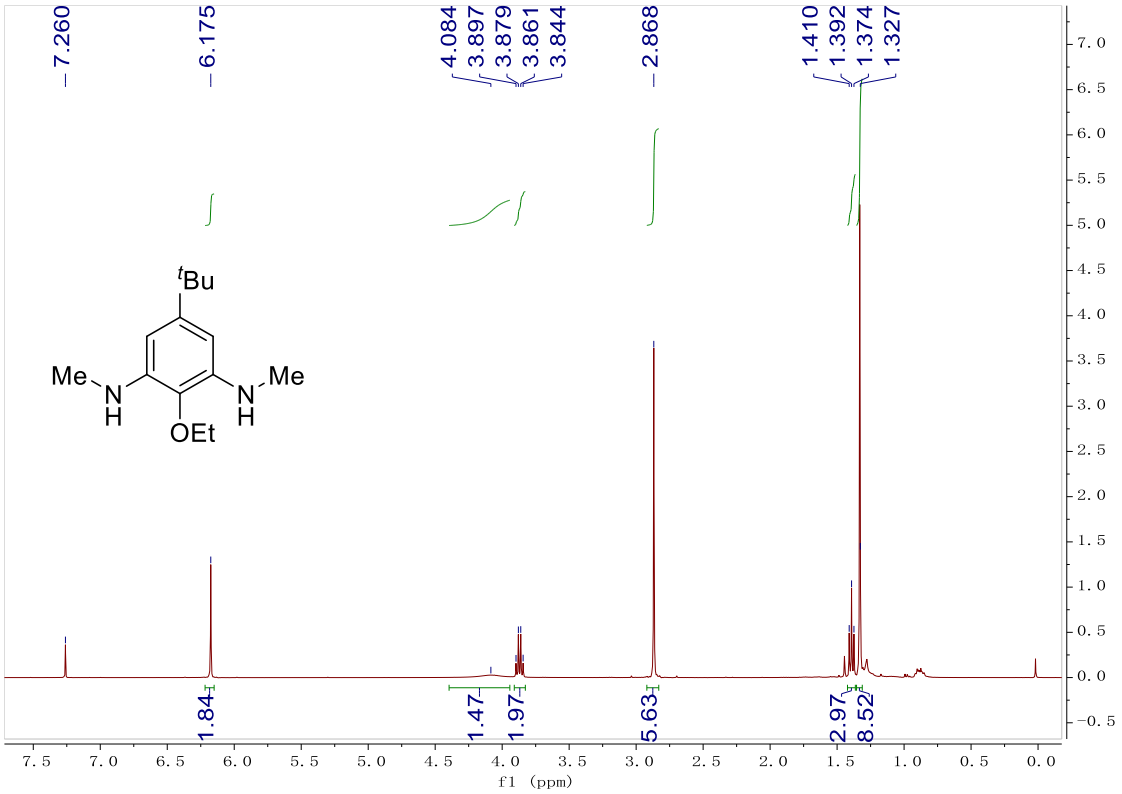
^{1}H NMR spectrum of *Monomer*-**F3** in $CDCl_3$ at 298 K



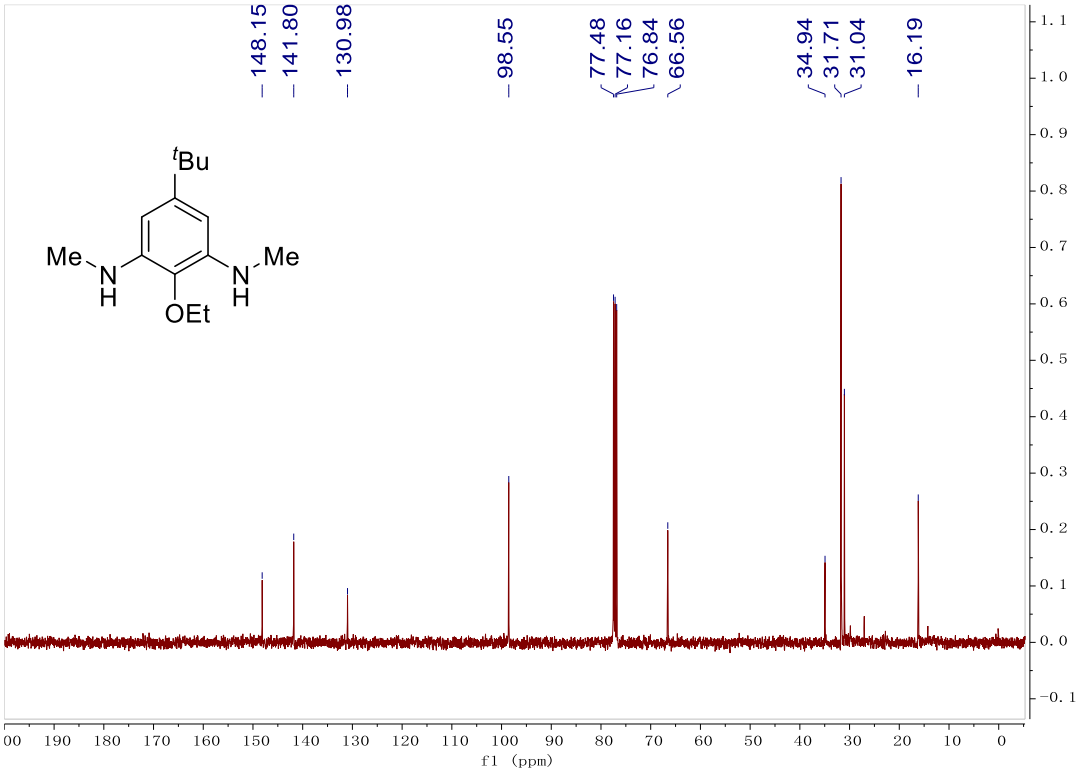
^{13}C NMR spectrum of *Monomer*-**F3** in $CDCl_3$ at 298 K



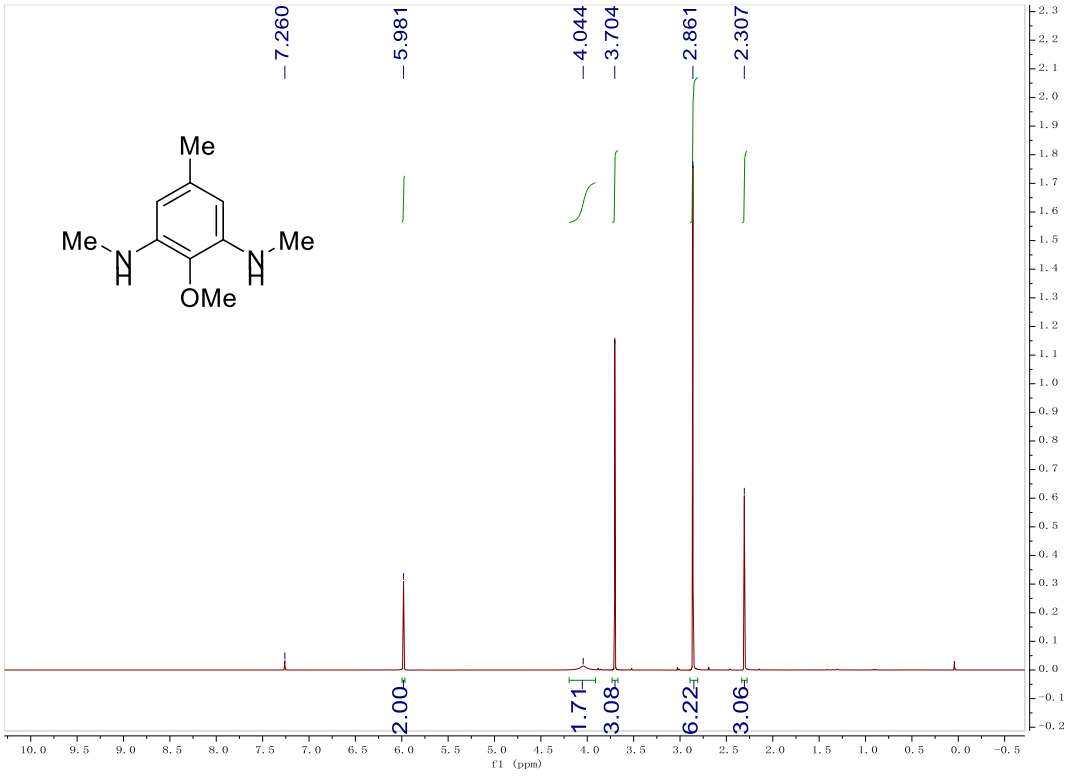
^{1}H NMR spectrum of *Monomer*-**F4** in $CDCl_3$ at 298 K



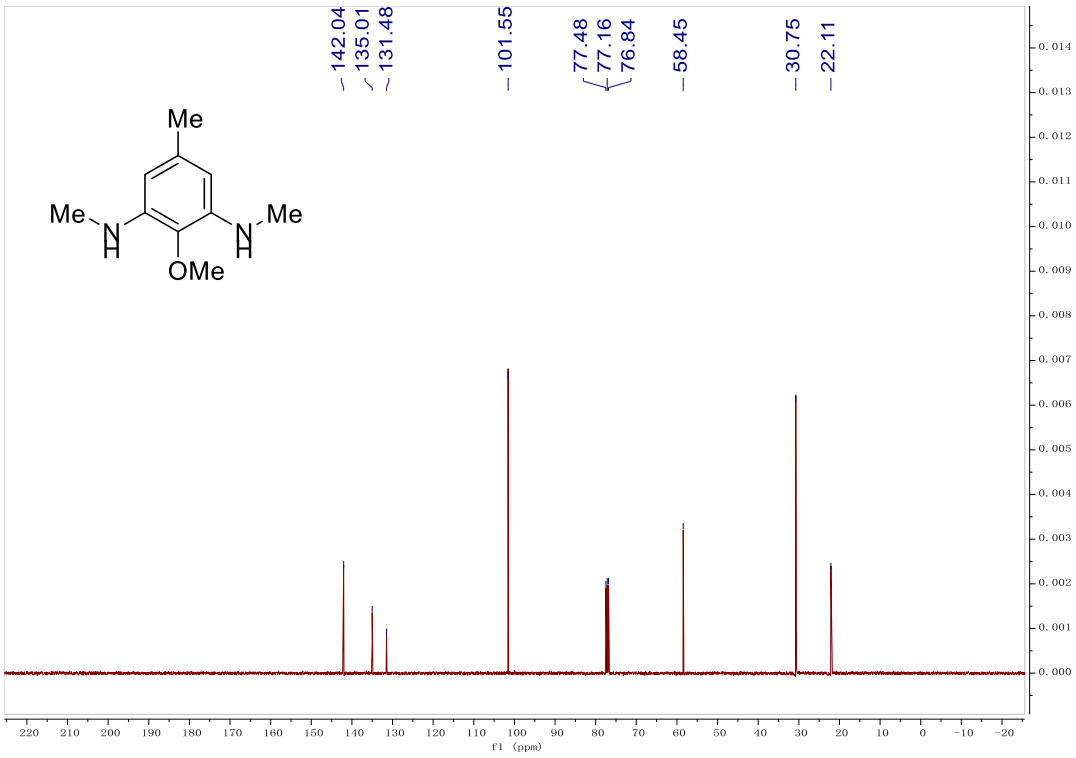
^{13}C NMR spectrum of *Monomer*-**F4** in $CDCl_3$ at 298 K



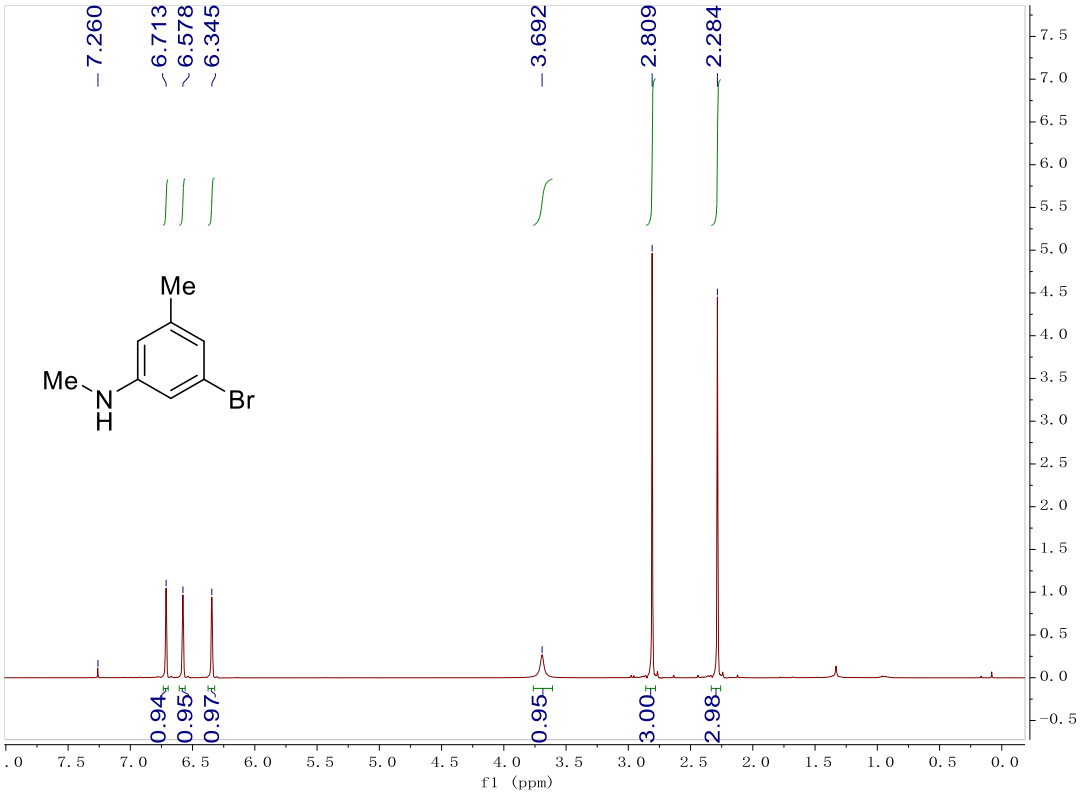
^{1}H NMR spectrum of *Monomer*-**F5** in $CDCl_3$ at 298 K



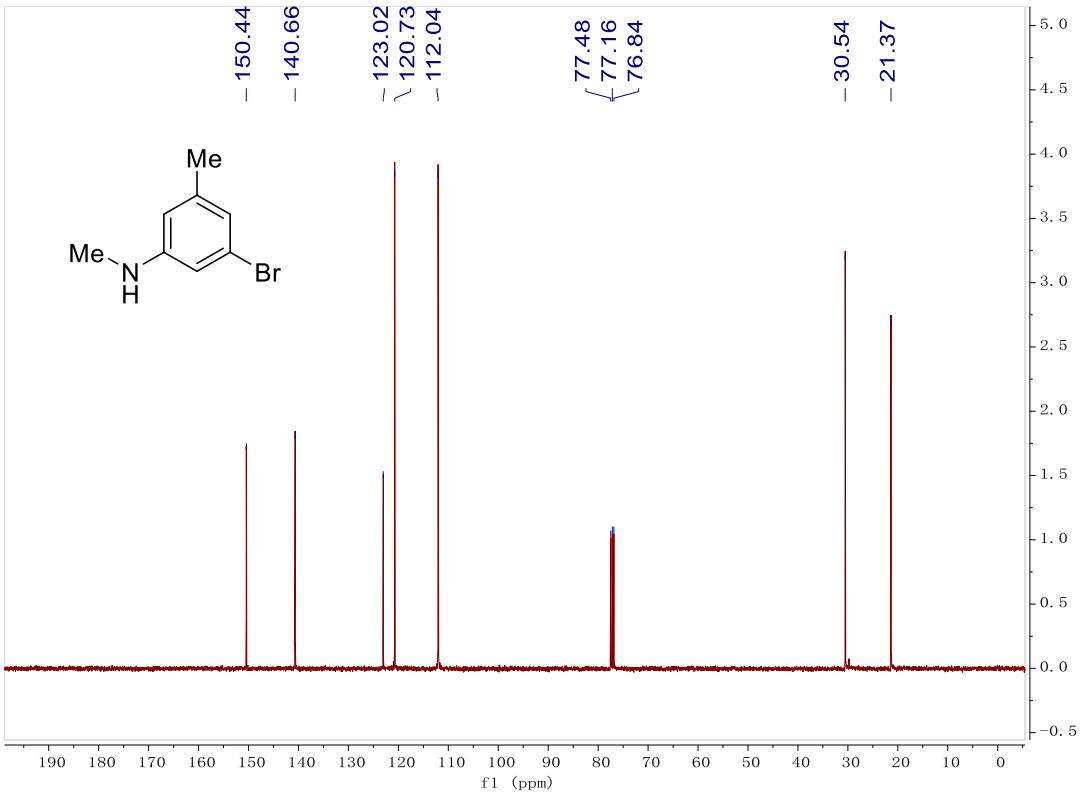
^{13}C NMR spectrum of *Monomer*-**F5** in $CDCl_3$ at 298 K



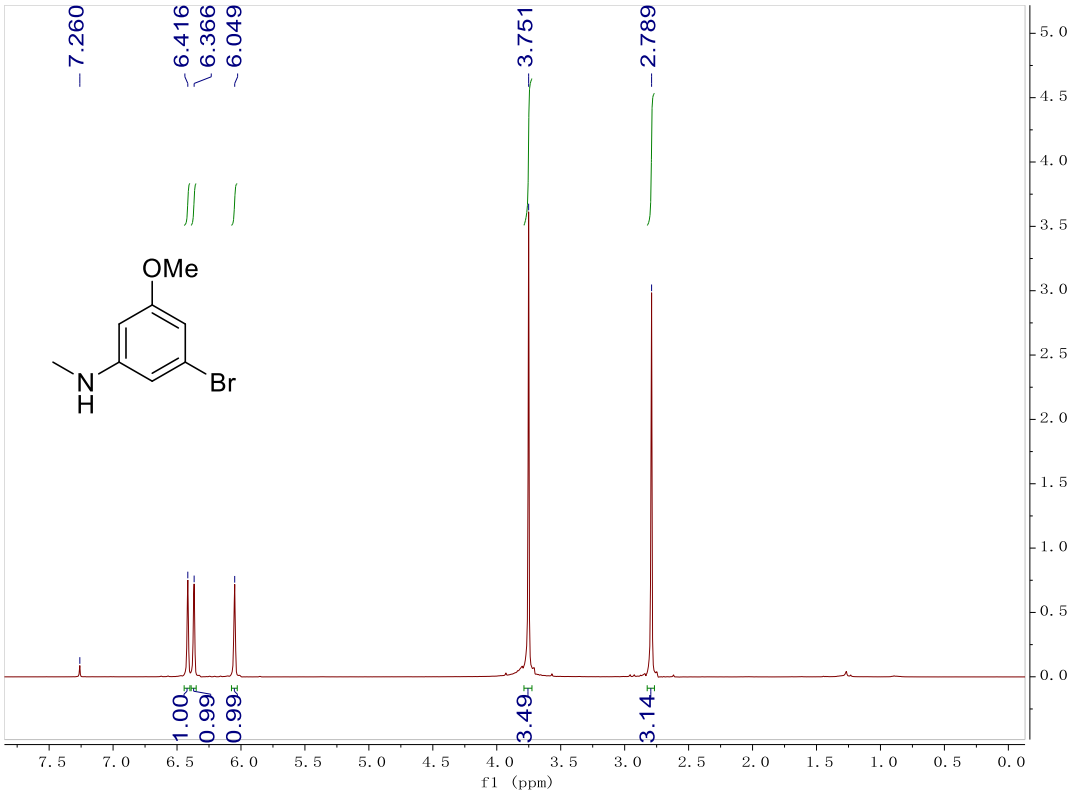
^{1}H NMR spectrum of *Monomer*-**H1** in $CDCl_3$ at 298 K



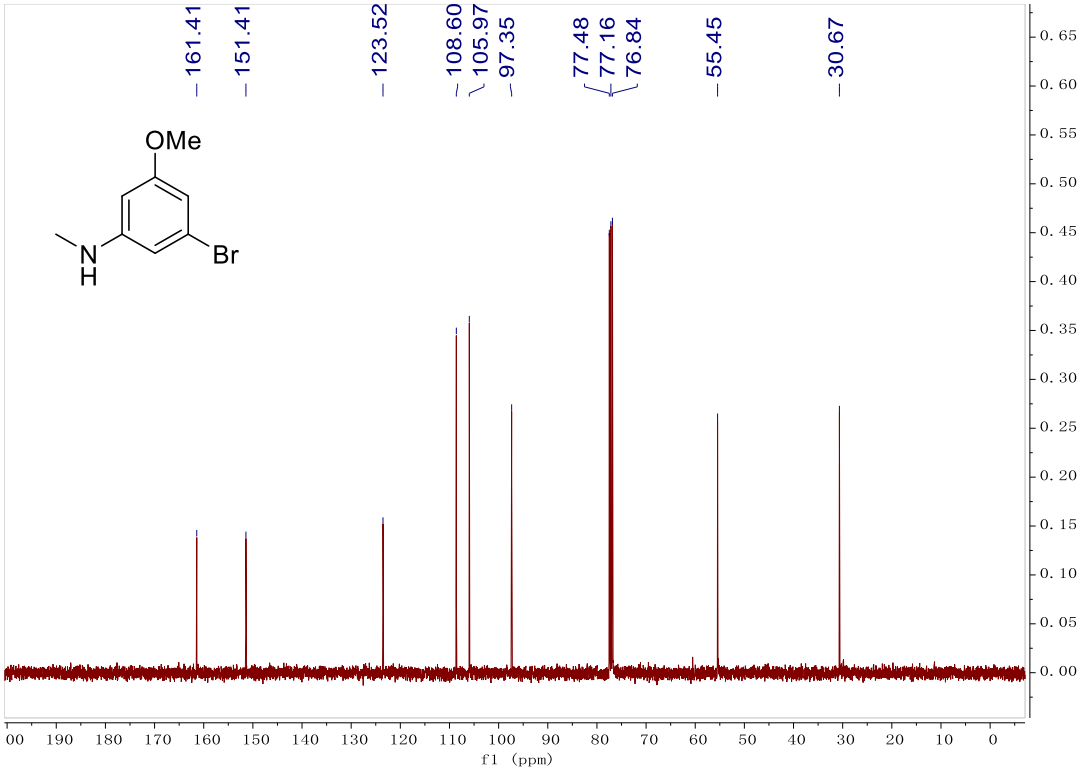
^{13}C NMR spectrum of *Monomer*-**H1** in $CDCl_3$ at 298 K



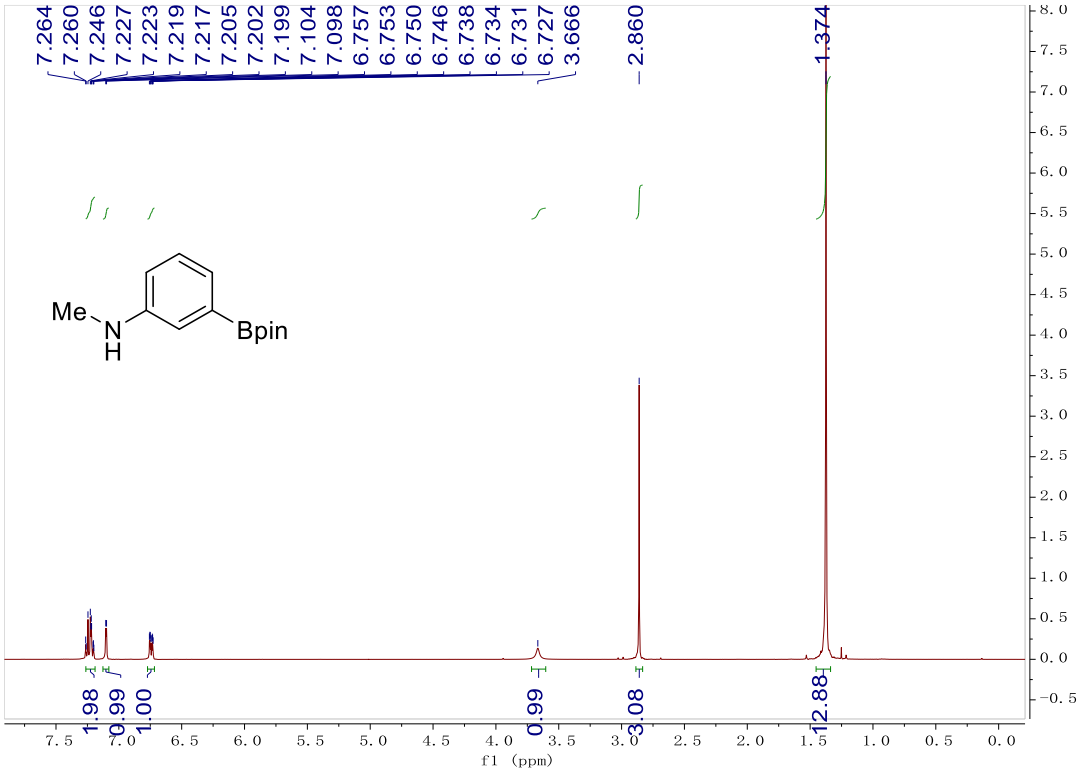
^{1}H NMR spectrum of *Monomer*-**H2** in $CDCl_3$ at 298 K



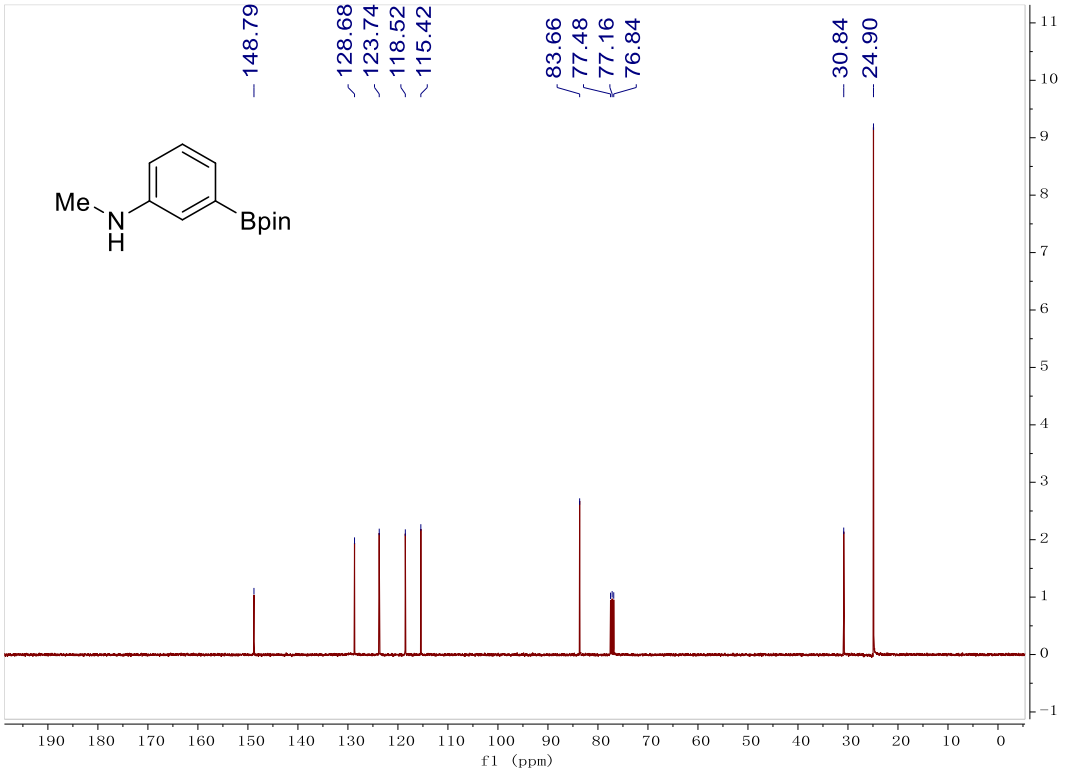
^{13}C NMR spectrum of *Monomer*-**H2** in $CDCl_3$ at 298 K



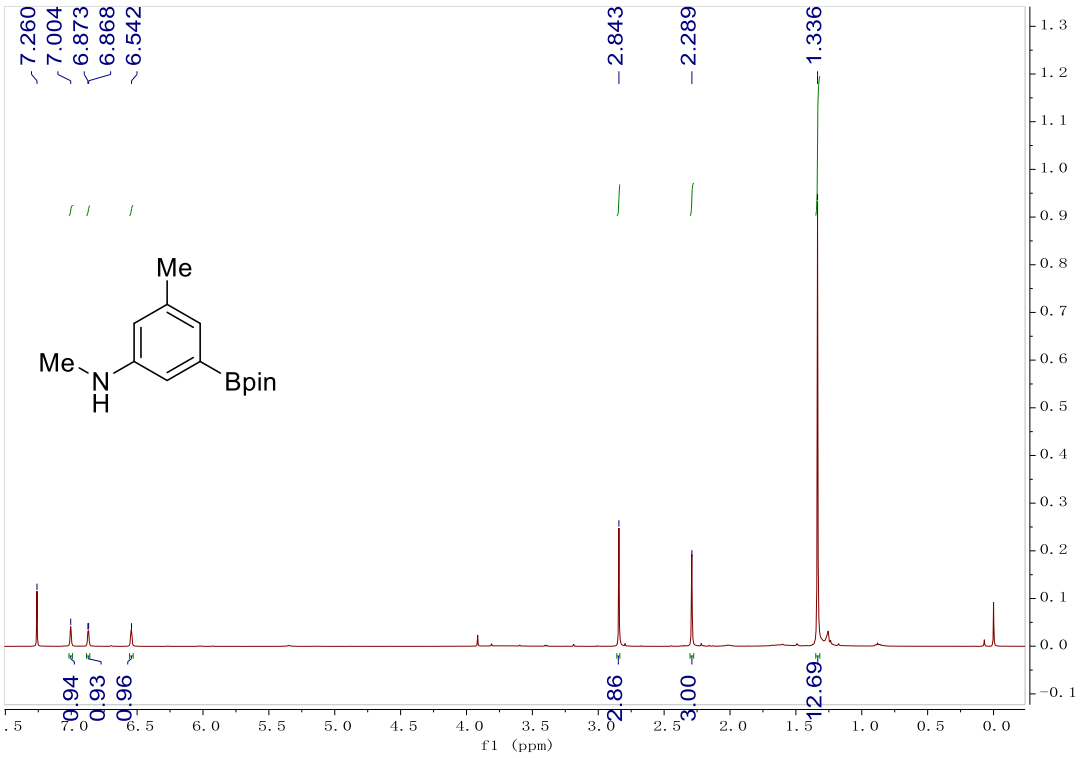
^{1}H NMR spectrum of *Monomer*-**I1** in $CDCl_3$ at 298 K



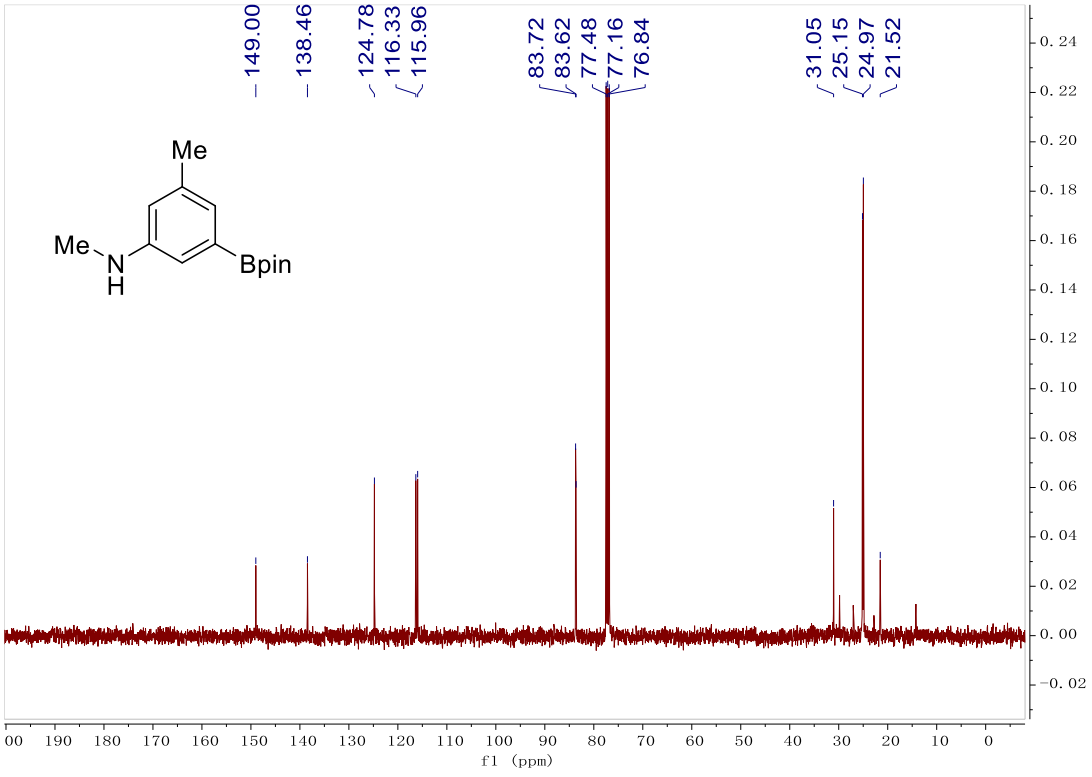
^{13}C NMR spectrum of *Monomer*-**I1** in $CDCl_3$ at 298 K



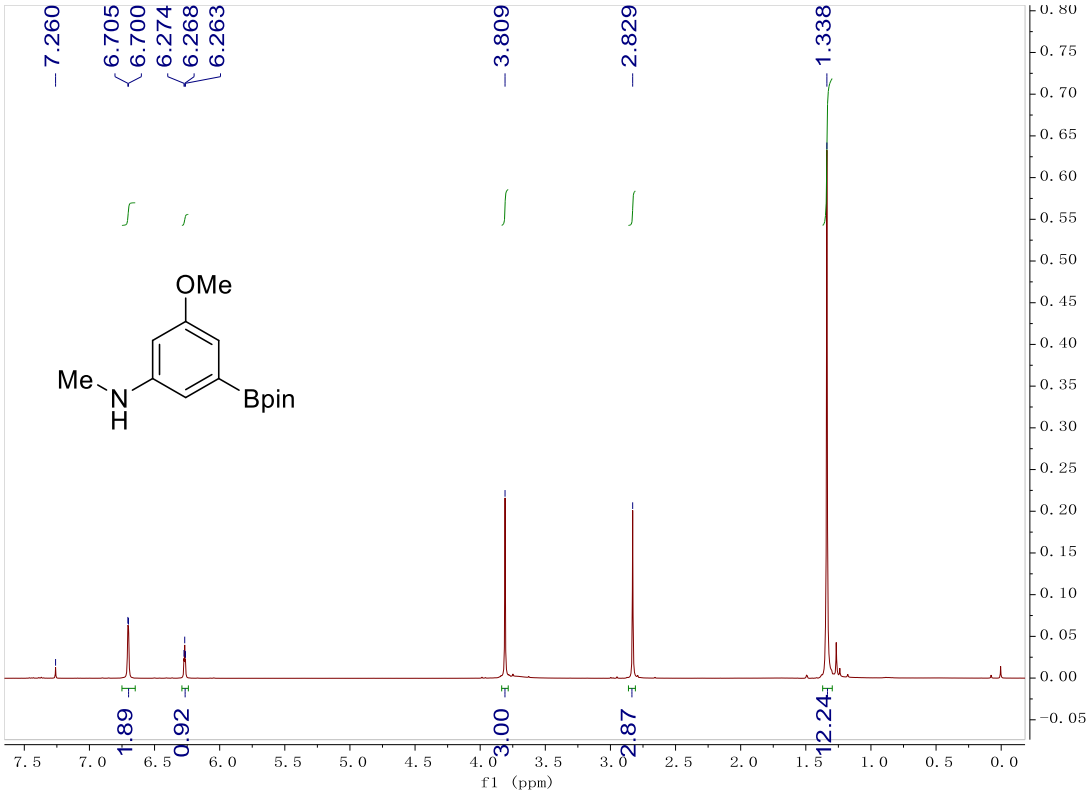
^{1}H NMR spectrum of *Monomer*-**I2** in $CDCl_3$ at 298 K



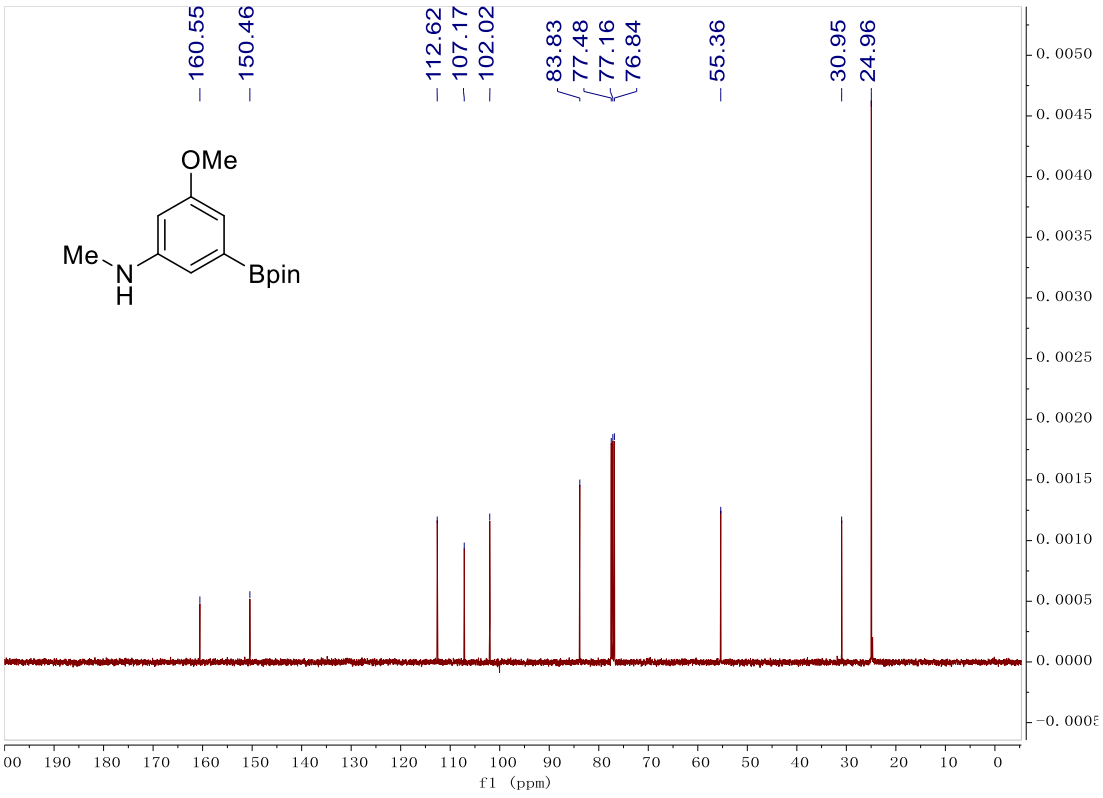
^{13}C NMR spectrum of *Monomer*-**I2** in $CDCl_3$ at 298 K



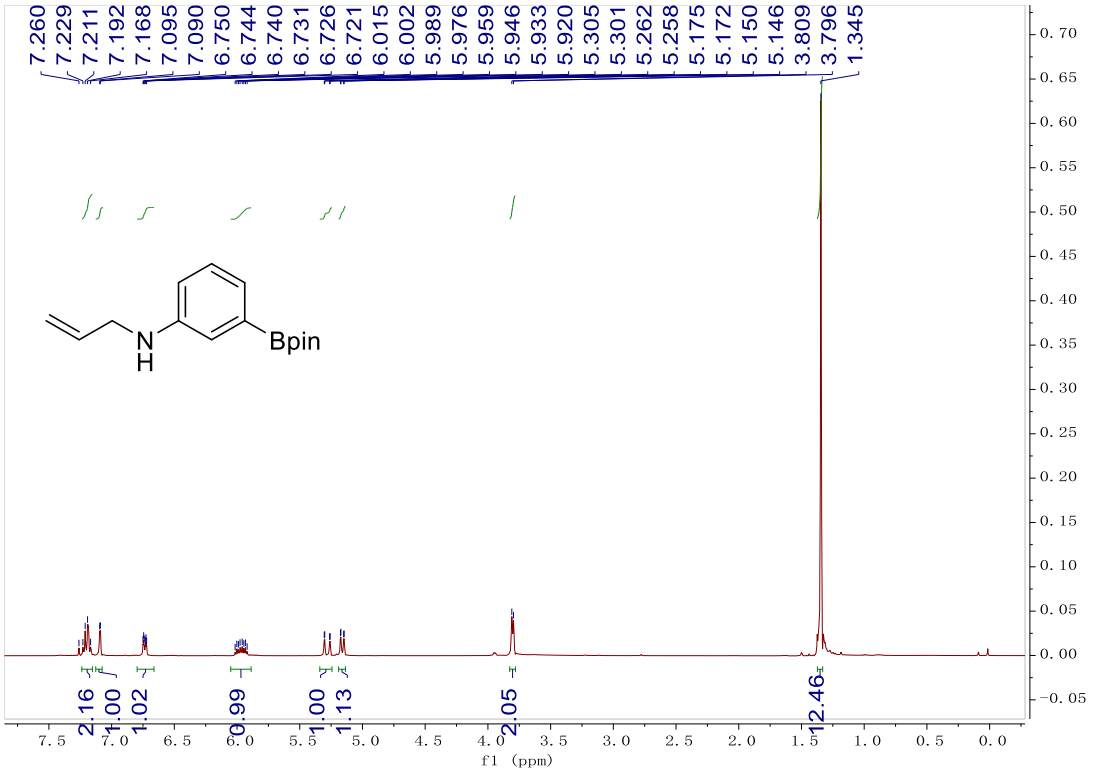
^{1}H NMR spectrum of *Monomer*-**I3** in $CDCl_3$ at 298 K



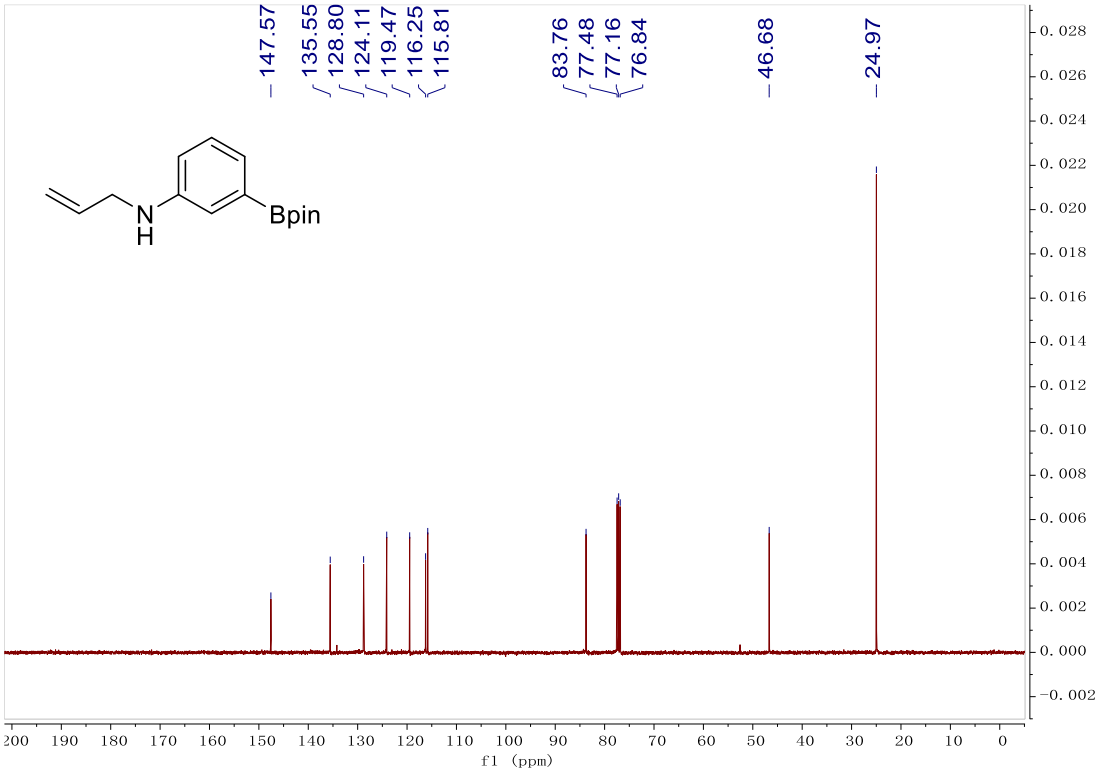
^{13}C NMR spectrum of *Monomer*-**I3** in $CDCl_3$ at 298 K



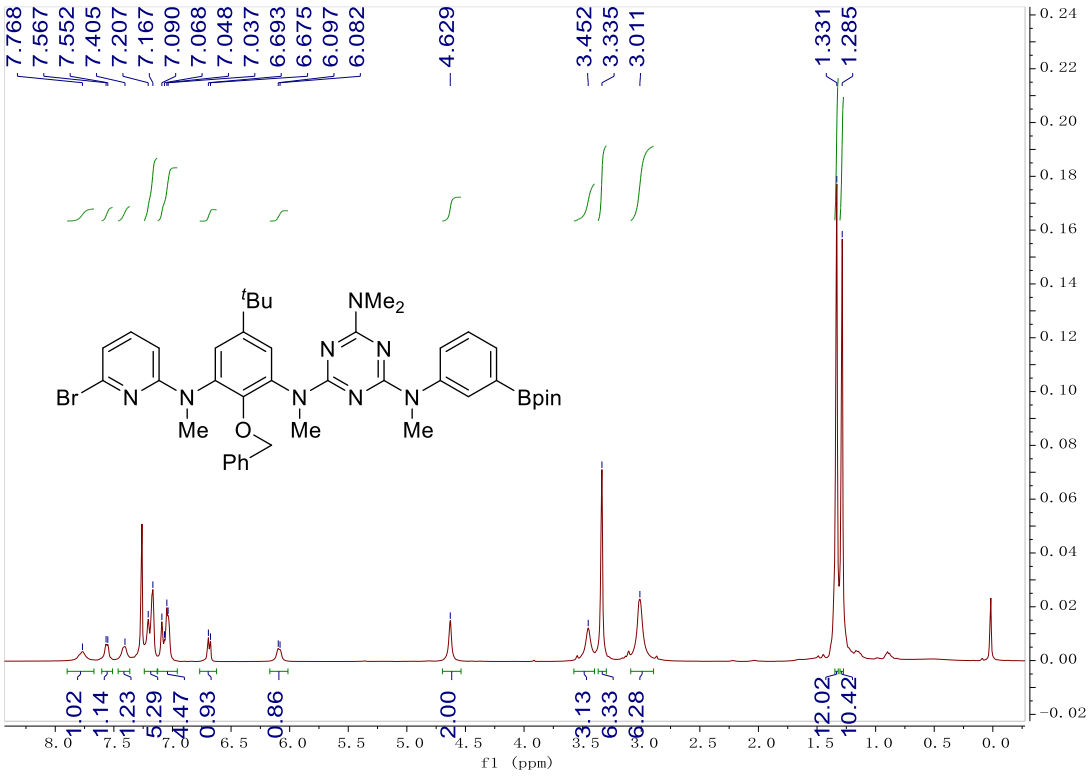
^{1}H NMR spectrum of *Monomer*-**I4** in $CDCl_3$ at 298 K



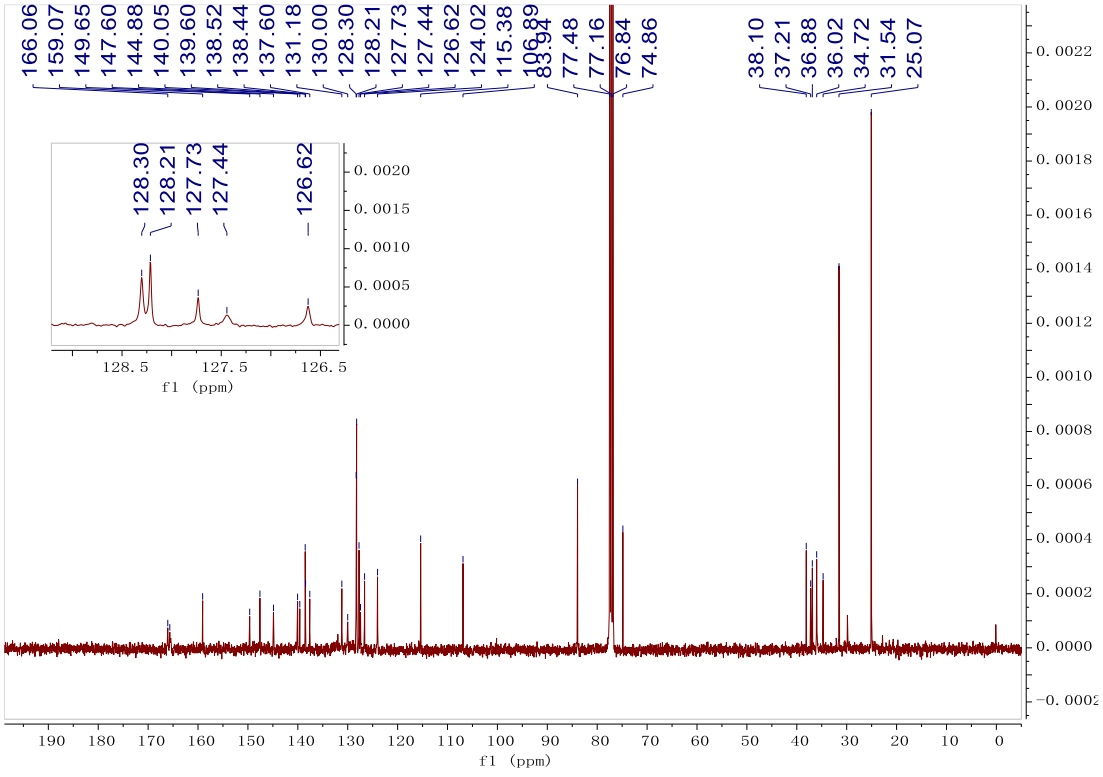
^{13}C NMR spectrum of *Monomer*-**I4** in $CDCl_3$ at 298 K



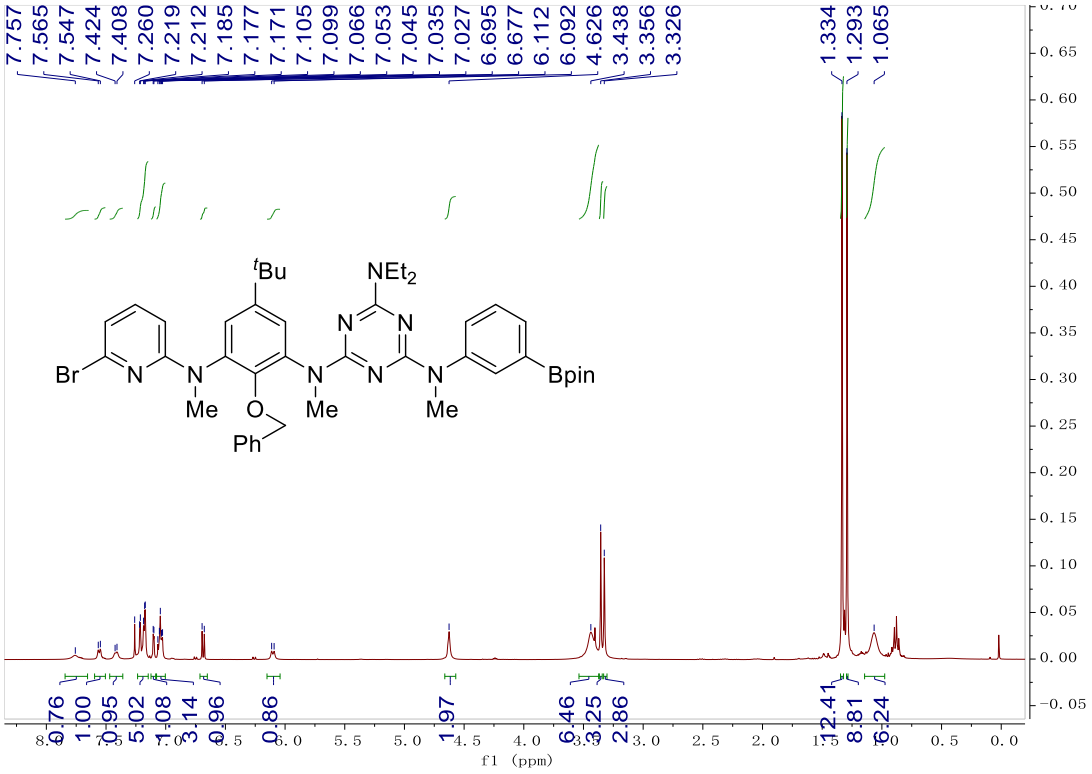
^{1}H NMR spectrum of **6a** in $CDCl_3$ at 333 K



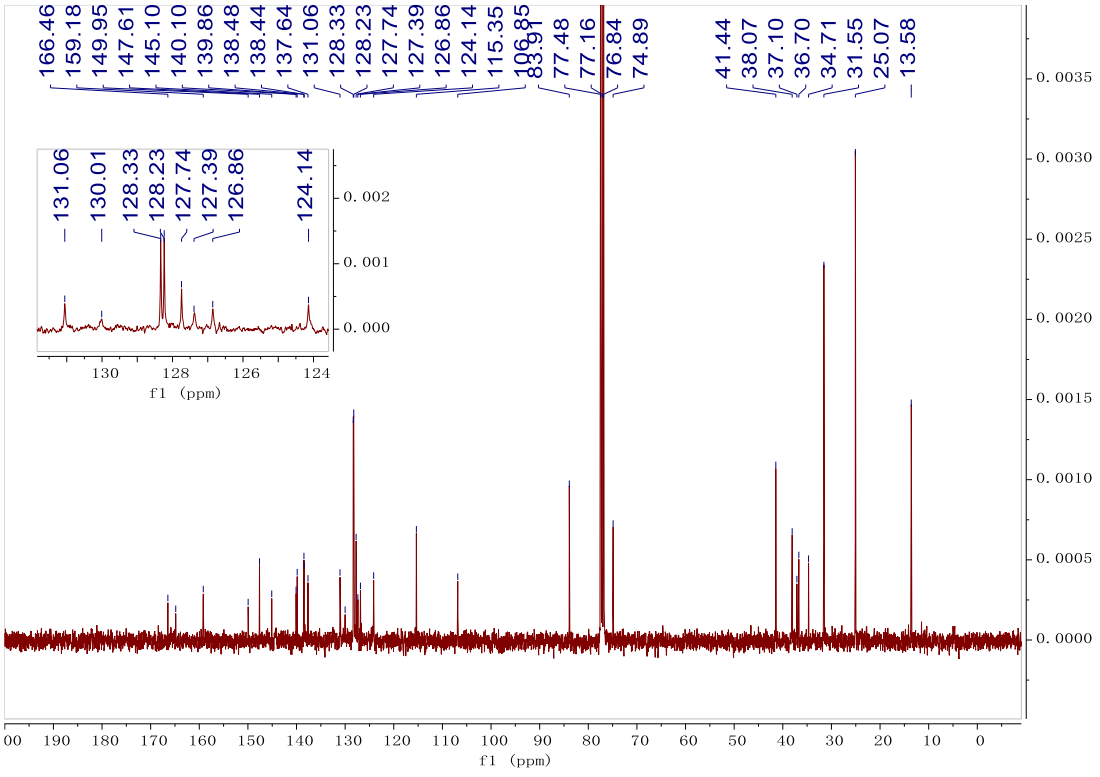
^{13}C NMR spectrum of **6a** in $CDCl_3$ at 333 K



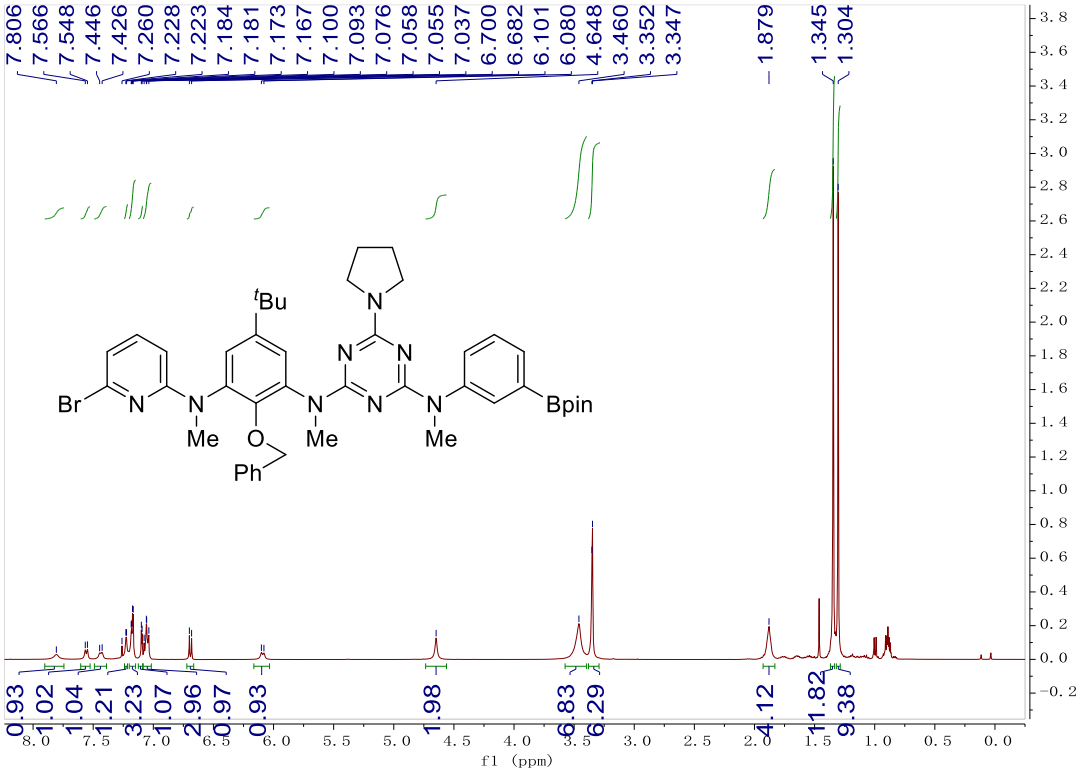
^{1}H NMR spectrum of **6b** in $CDCl_3$ at 333 K



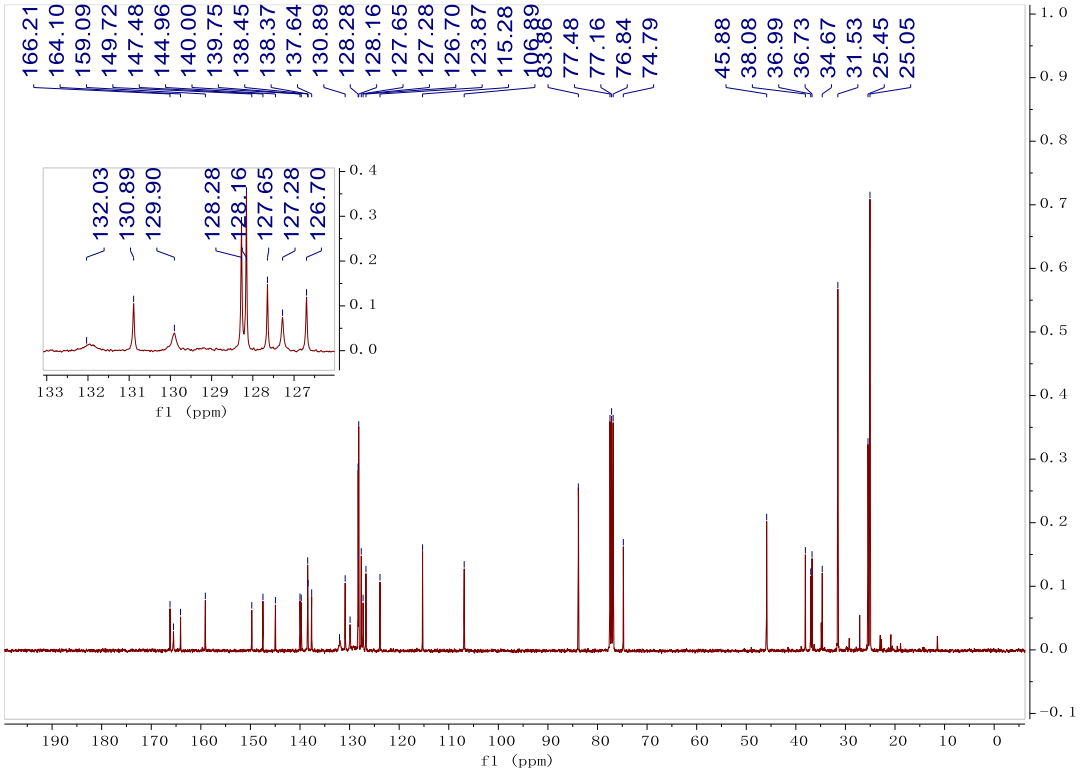
^{13}C NMR spectrum of **6b** in $CDCl_3$ at 333 K



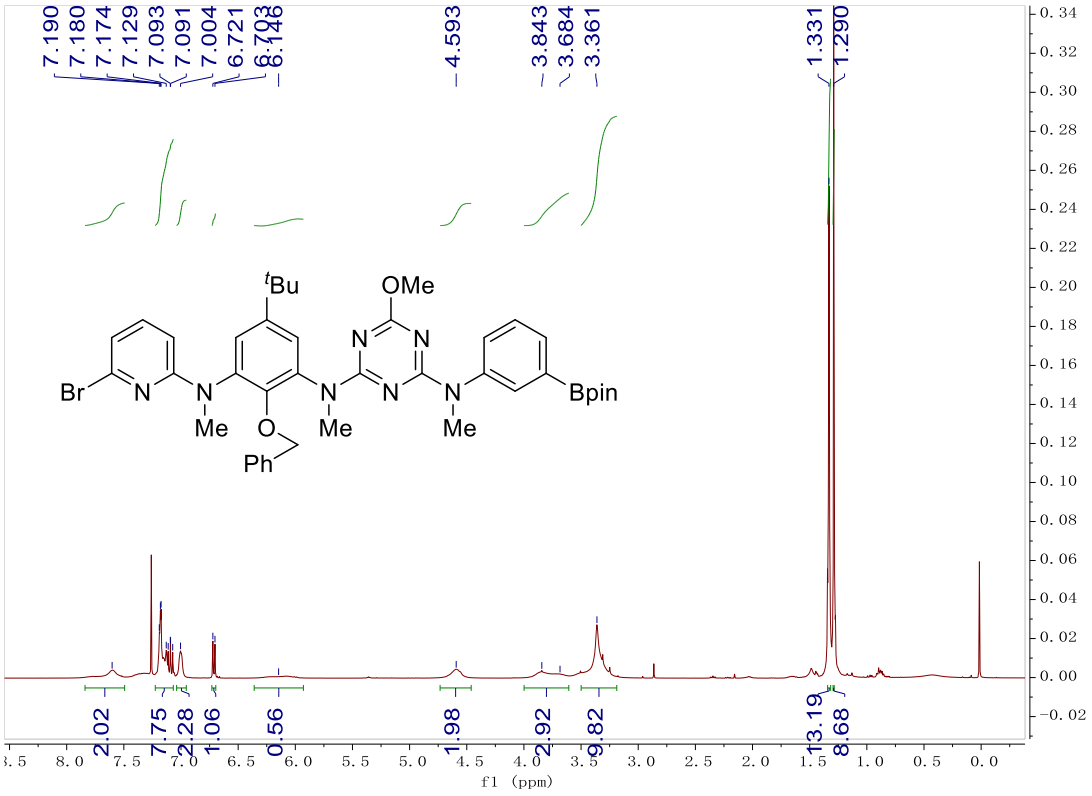
^{1}H NMR spectrum of **6c** in $CDCl_3$ at 333 K



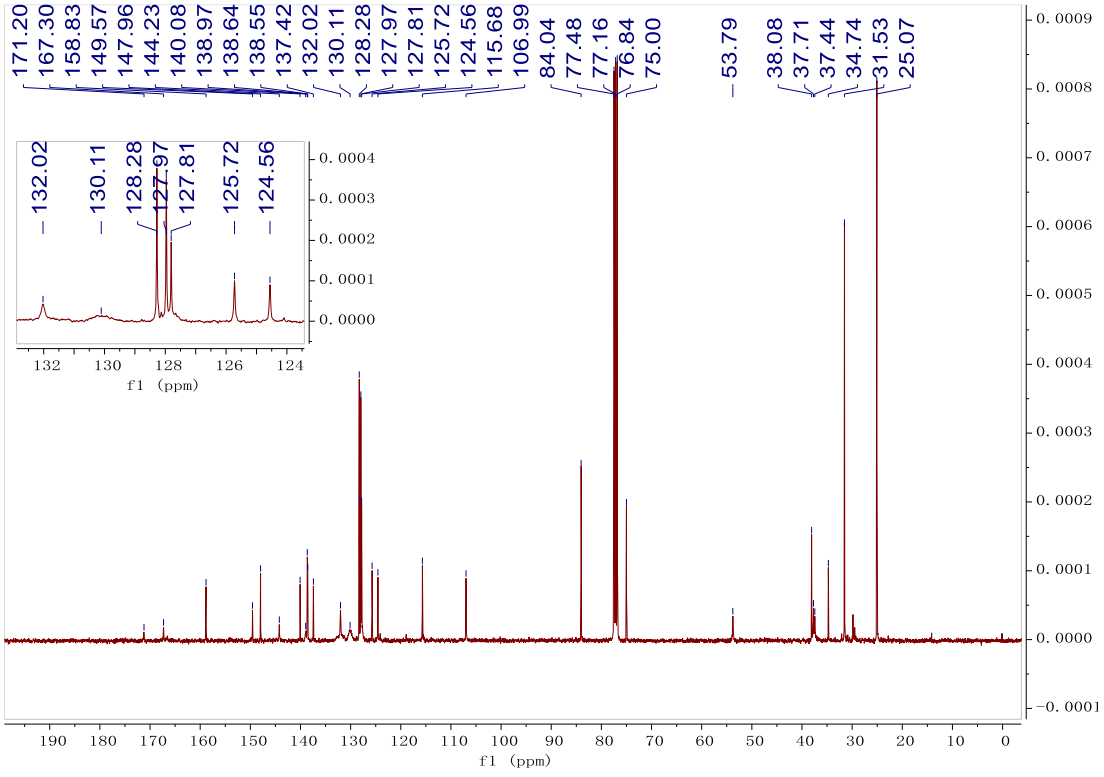
^{13}C NMR spectrum of **6c** in $CDCl_3$ at 333 K



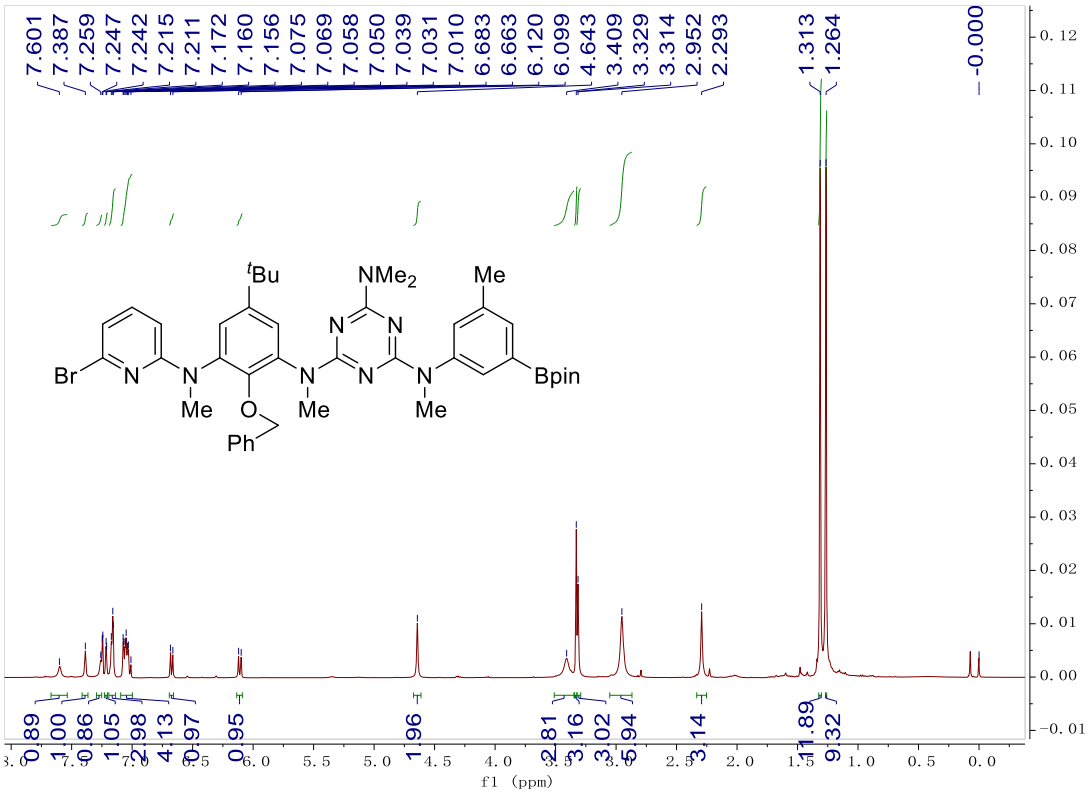
^{1}H NMR spectrum of **6d** in $CDCl_3$ at 333 K



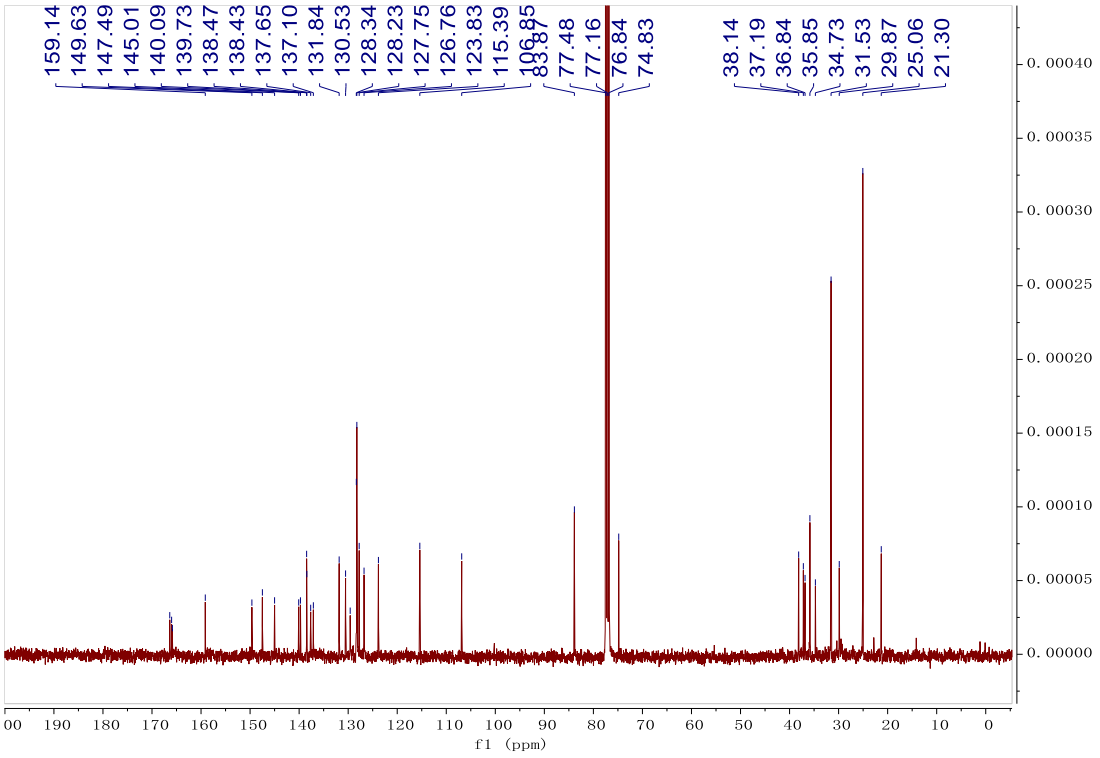
^{13}C NMR spectrum of **6d** in $CDCl_3$ at 333 K



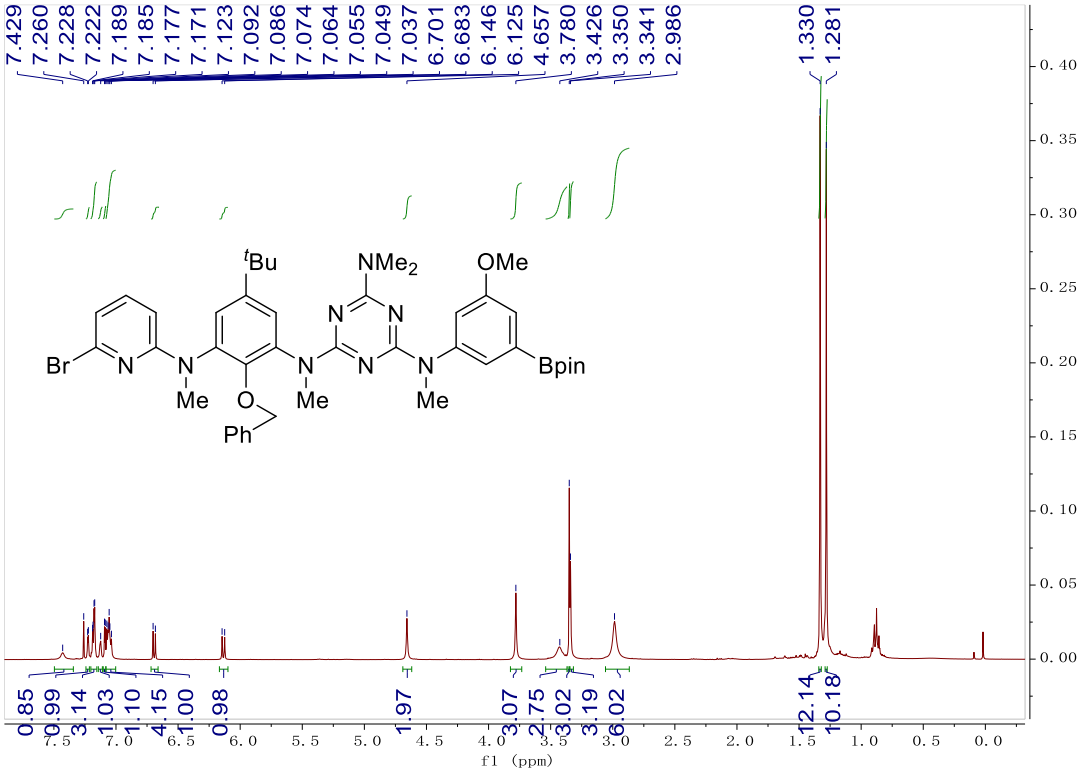
^{1}H NMR spectrum of **6e** in $CDCl_3$ at 333 K



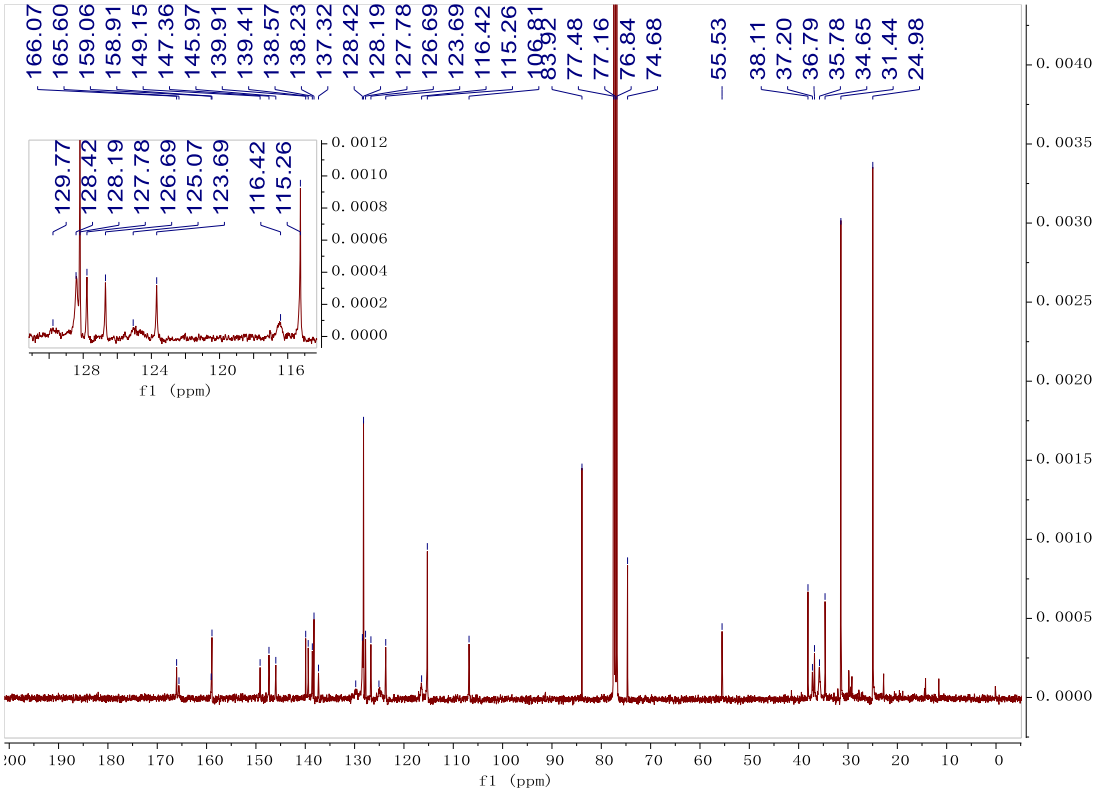
^{13}C NMR spectrum of **6e** in $CDCl_3$ at 333 K



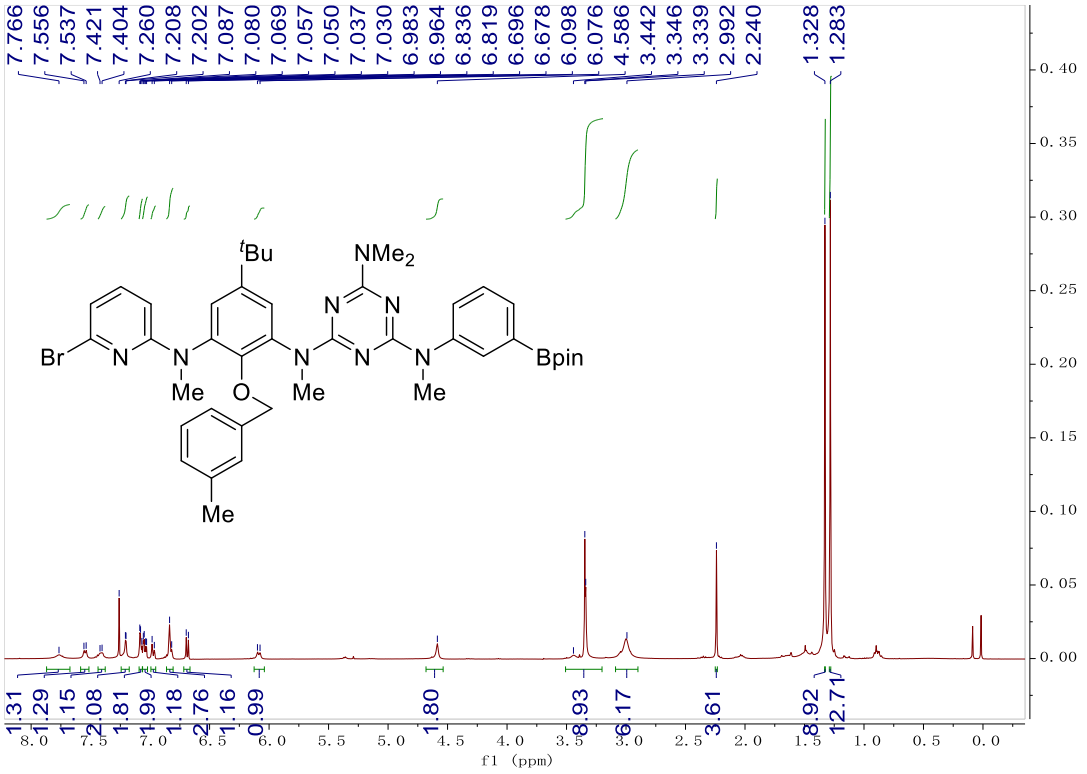
^{1}H NMR spectrum of **6f** in $CDCl_3$ at 333 K



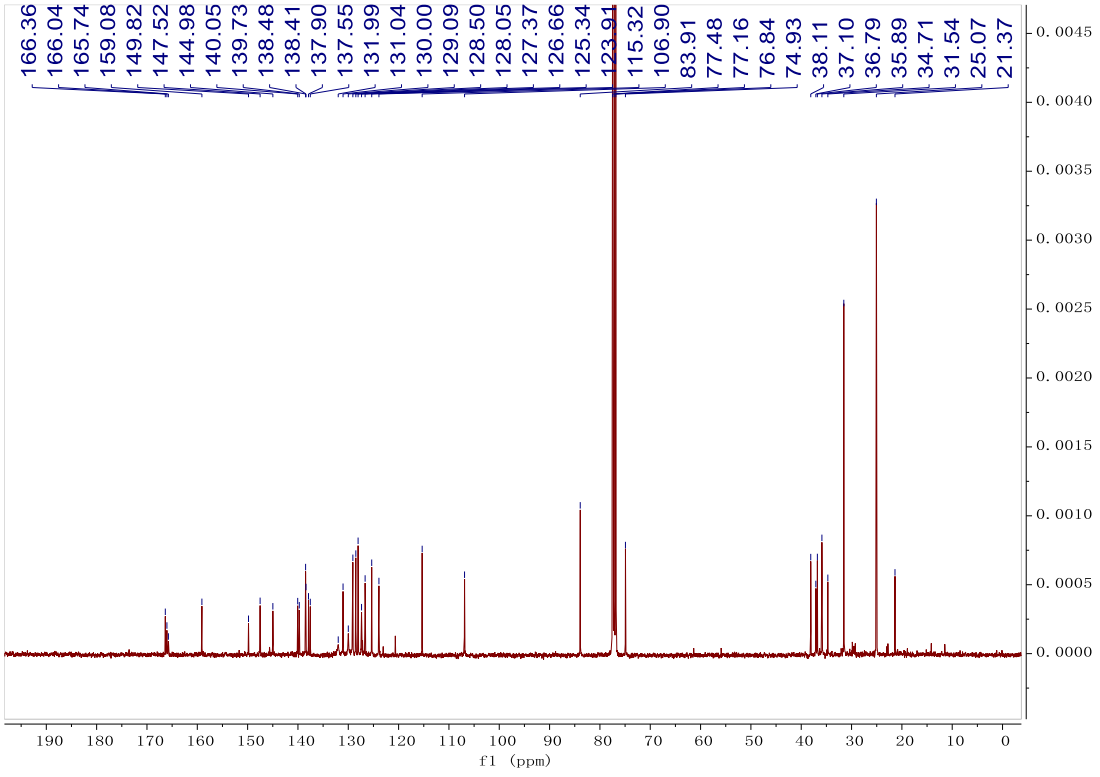
^{13}C NMR spectrum of **6f** in $CDCl_3$ at 333 K



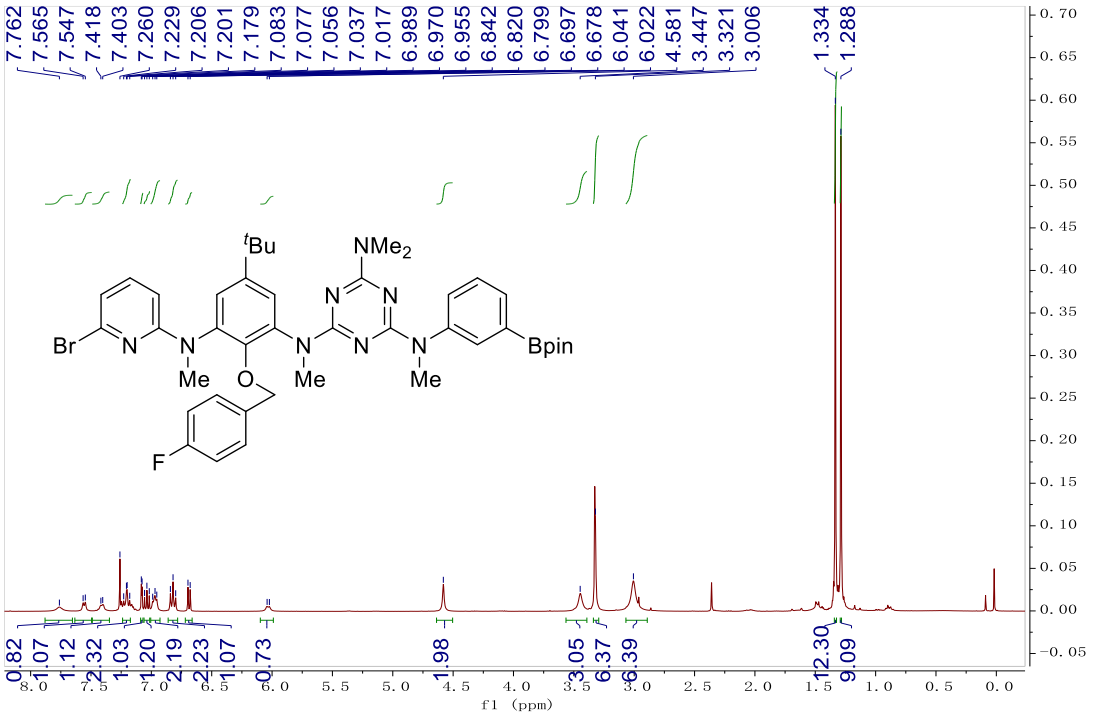
^{1}H NMR spectrum of **6g** in $CDCl_3$ at 333 K



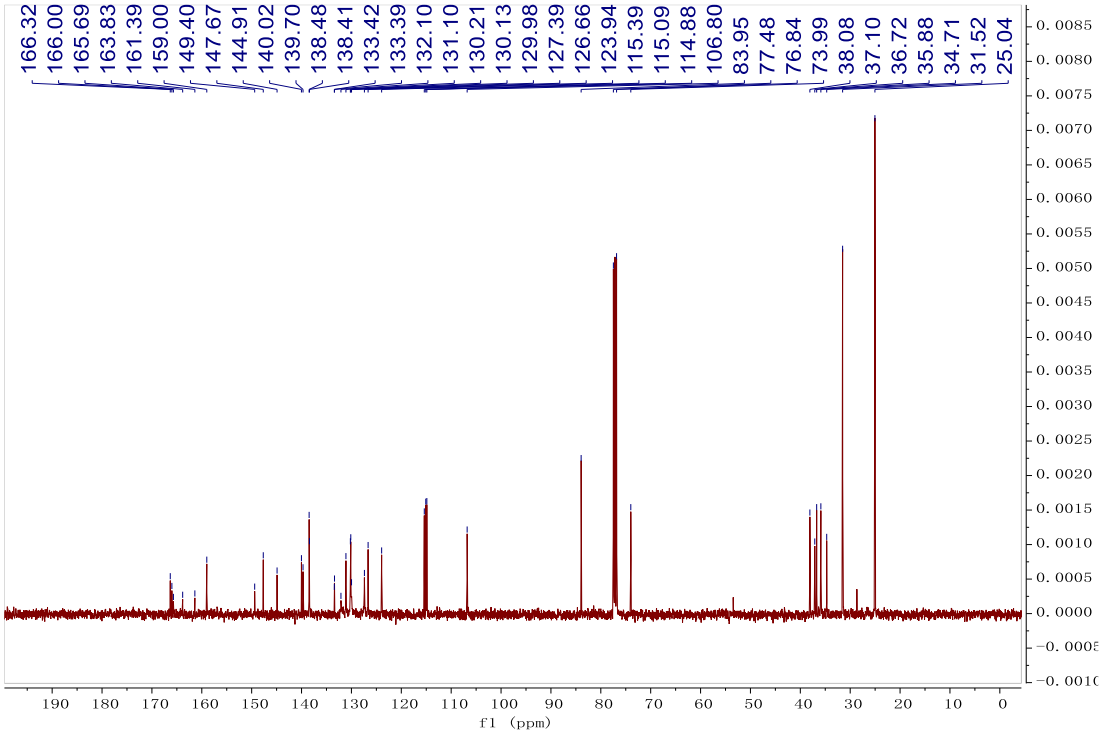
^{13}C NMR spectrum of **6g** in $CDCl_3$ at 333 K



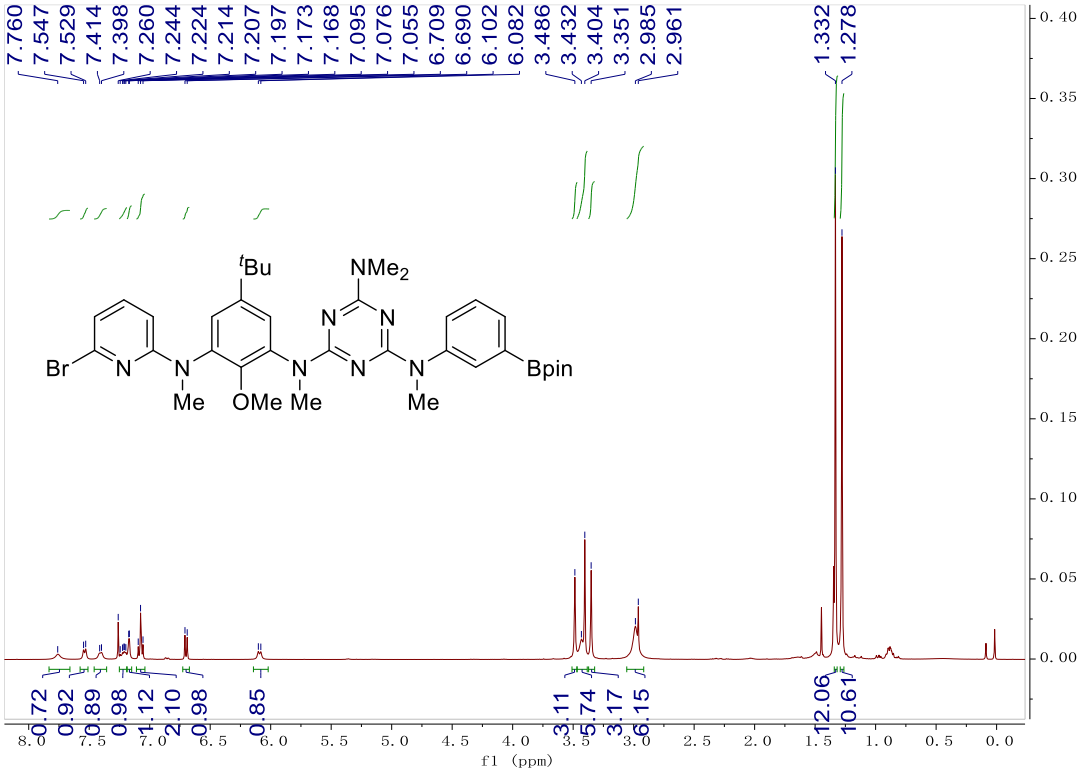
^{1}H NMR spectrum of **6h** in $CDCl_3$ at 333 K



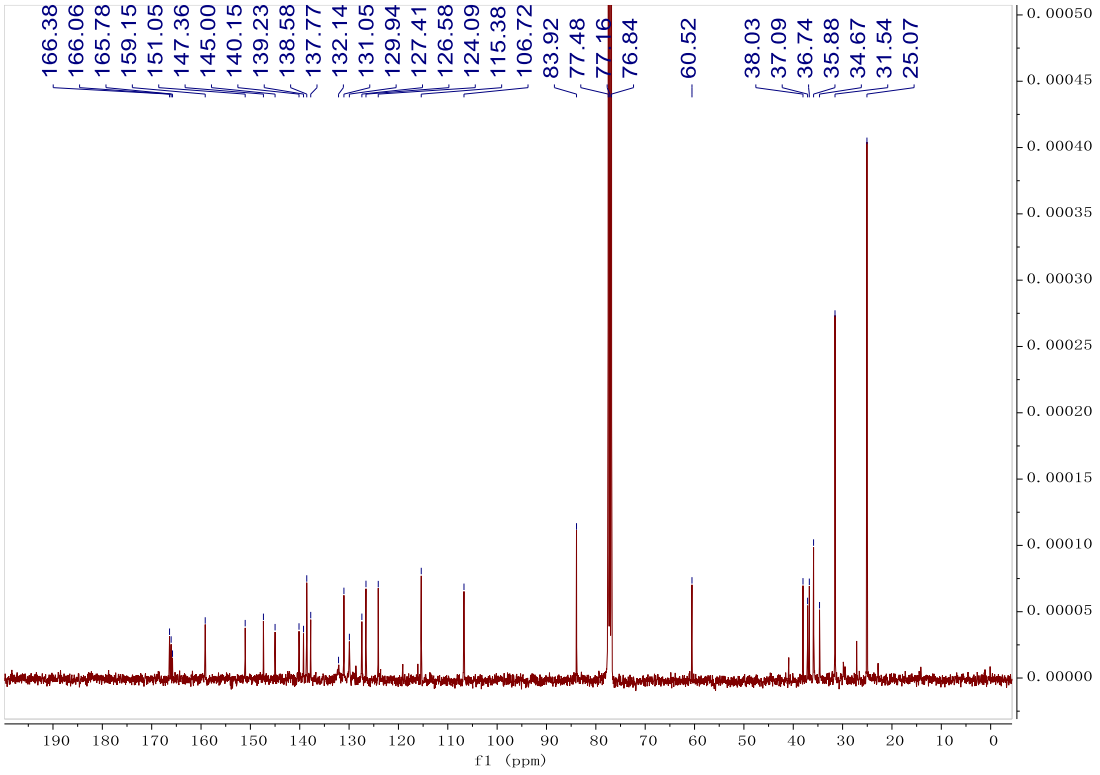
^{13}C NMR spectrum of **6h** in $CDCl_3$ at 333 K



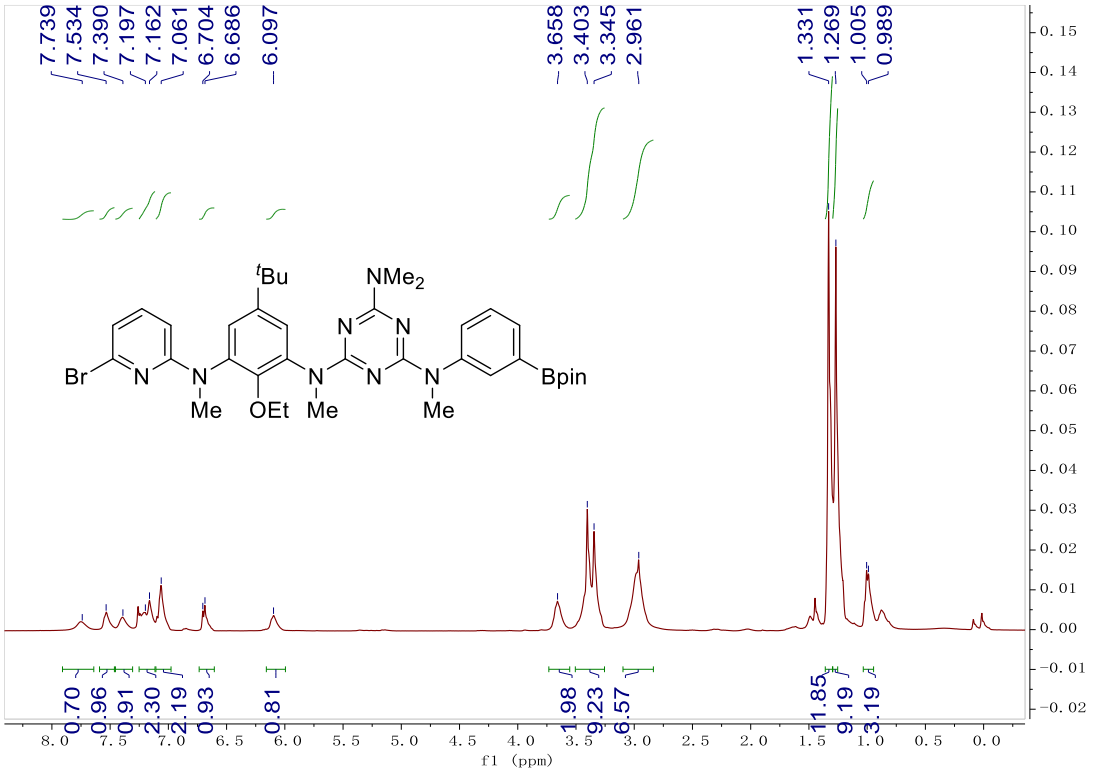
^{1}H NMR spectrum of **6i** in $CDCl_3$ at 333 K



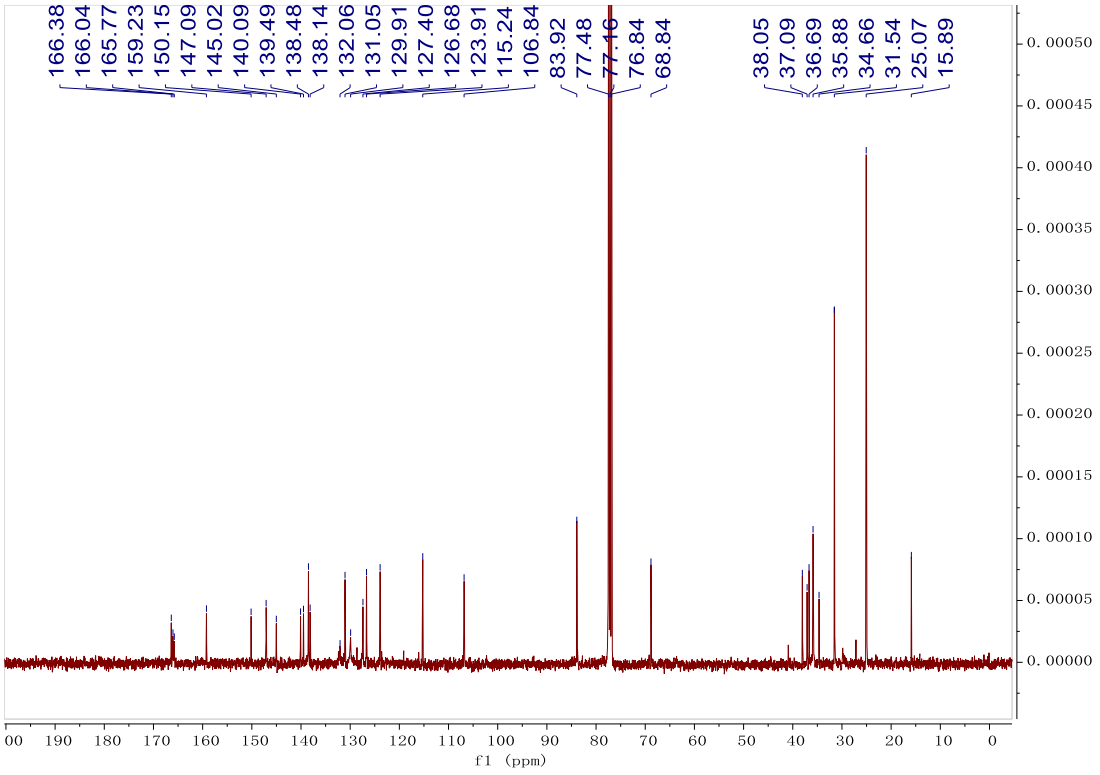
^{13}C NMR spectrum of **6i** in $CDCl_3$ at 333 K



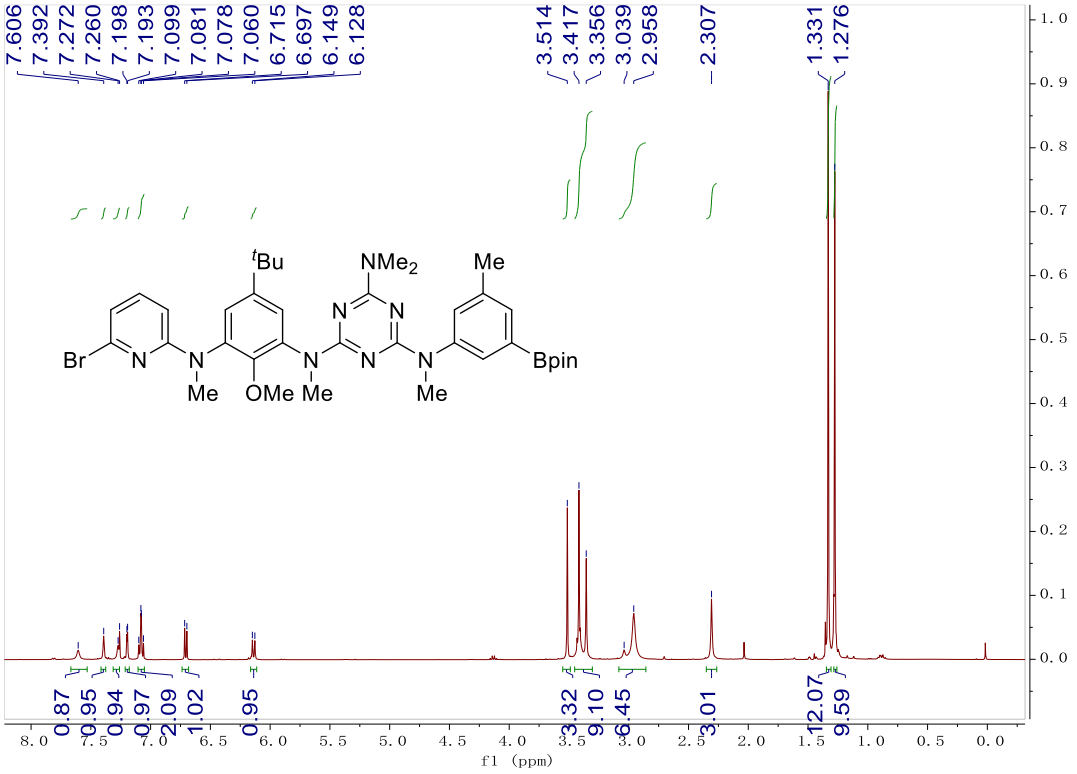
^{1}H NMR spectrum of **6j** in $CDCl_3$ at 333 K



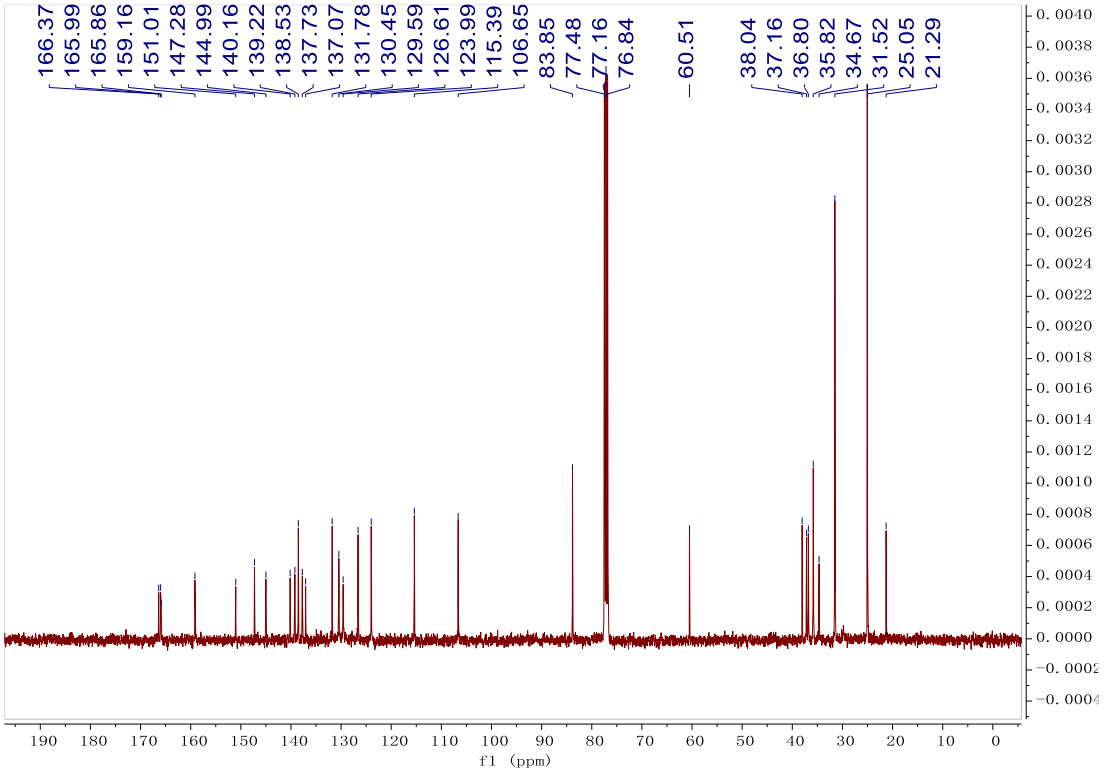
^{13}C NMR spectrum of **6j** in $CDCl_3$ at 333 K



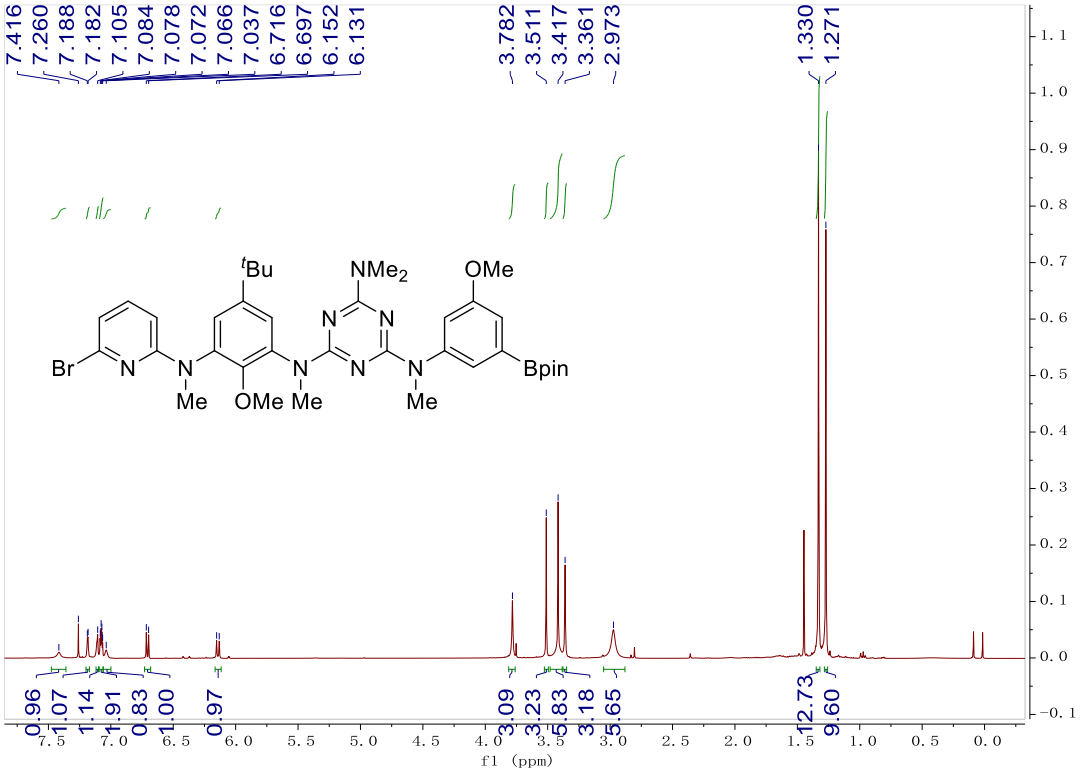
^{1}H NMR spectrum of **6k** in $CDCl_3$ at 333 K



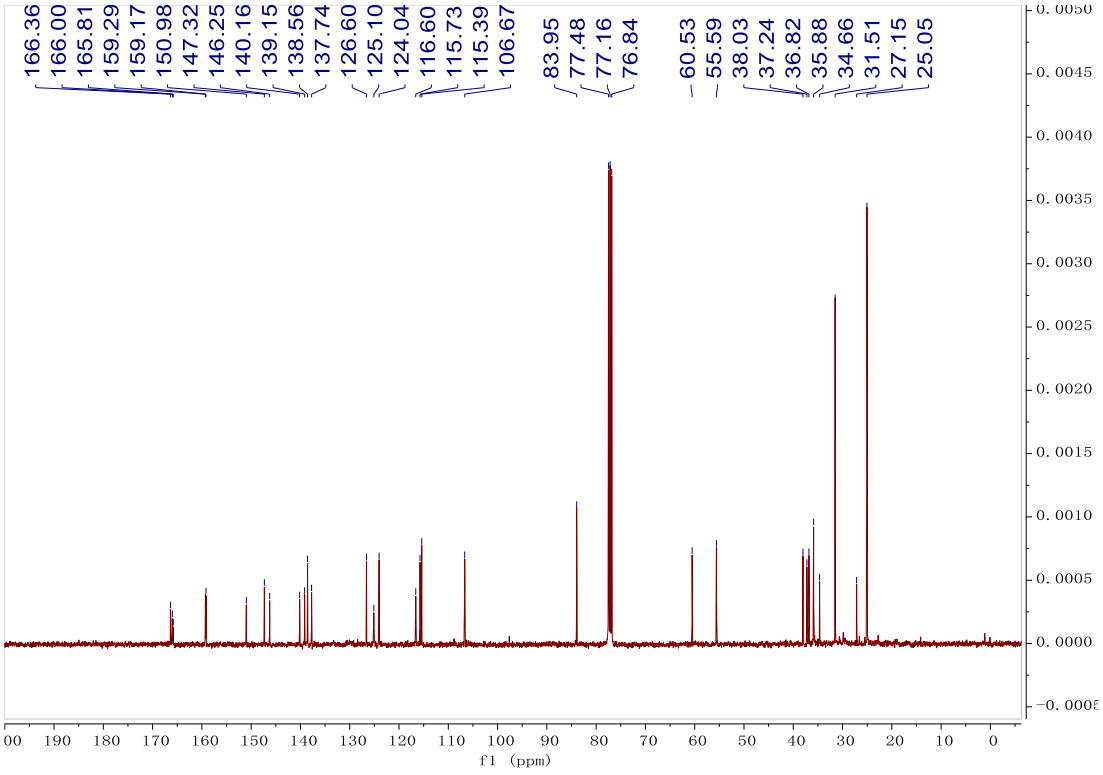
^{13}C NMR spectrum of **6k** in $CDCl_3$ at 333 K



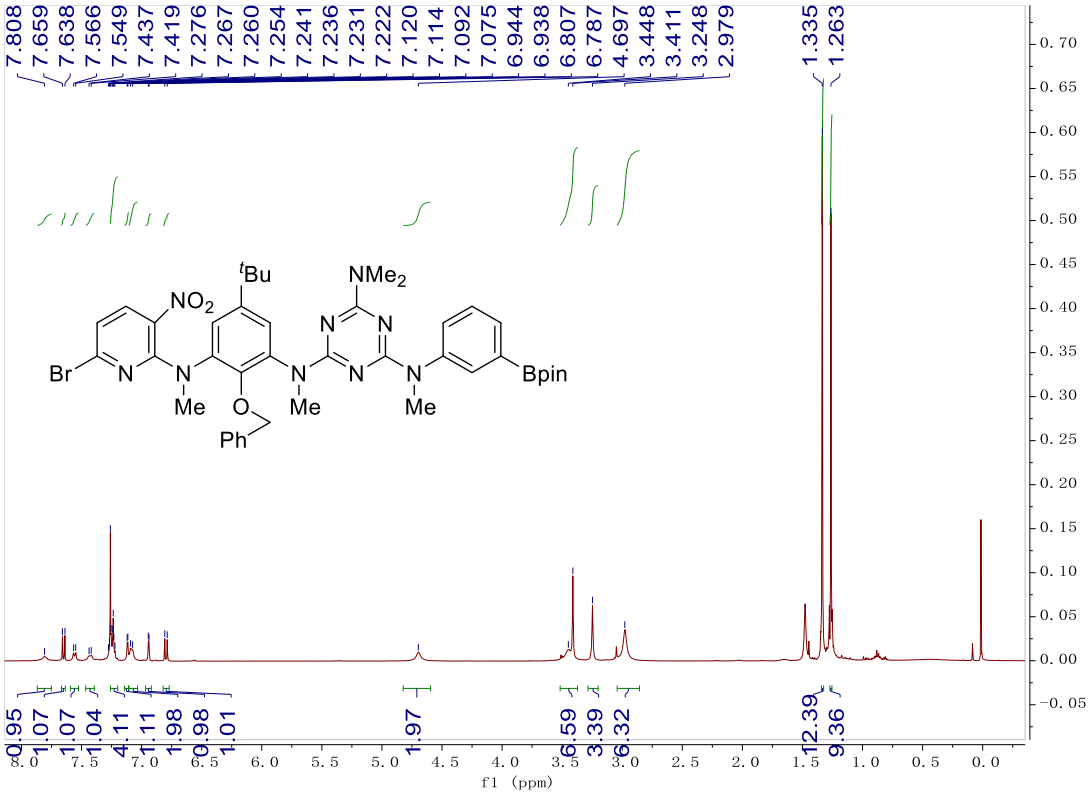
^{1}H NMR spectrum of **6l** in $CDCl_3$ at 333 K



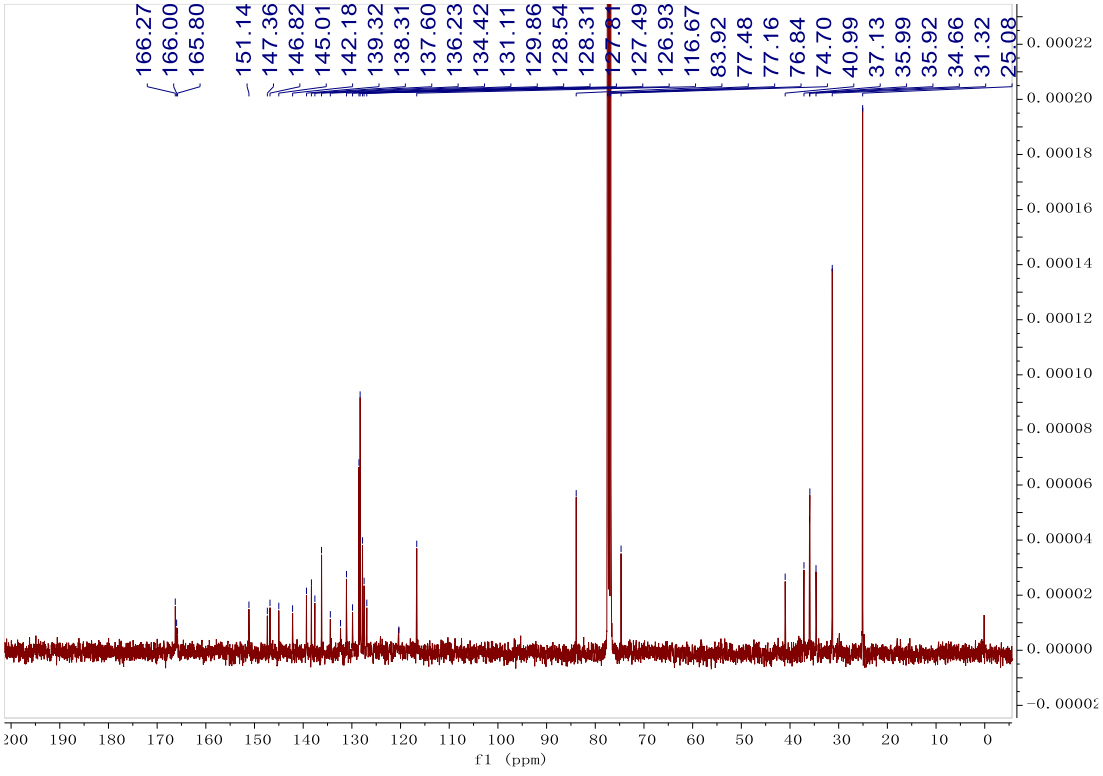
^{13}C NMR spectrum of **6l** in $CDCl_3$ at 333 K



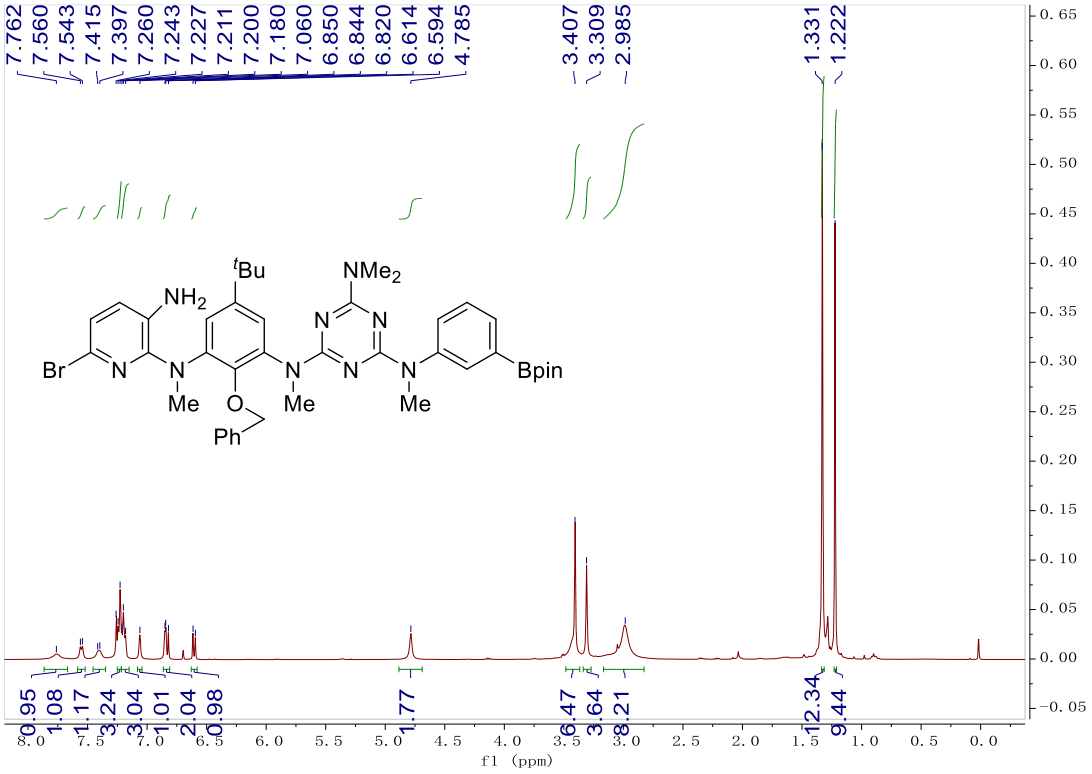
^{1}H NMR spectrum of **6m** in $CDCl_3$ at 333 K



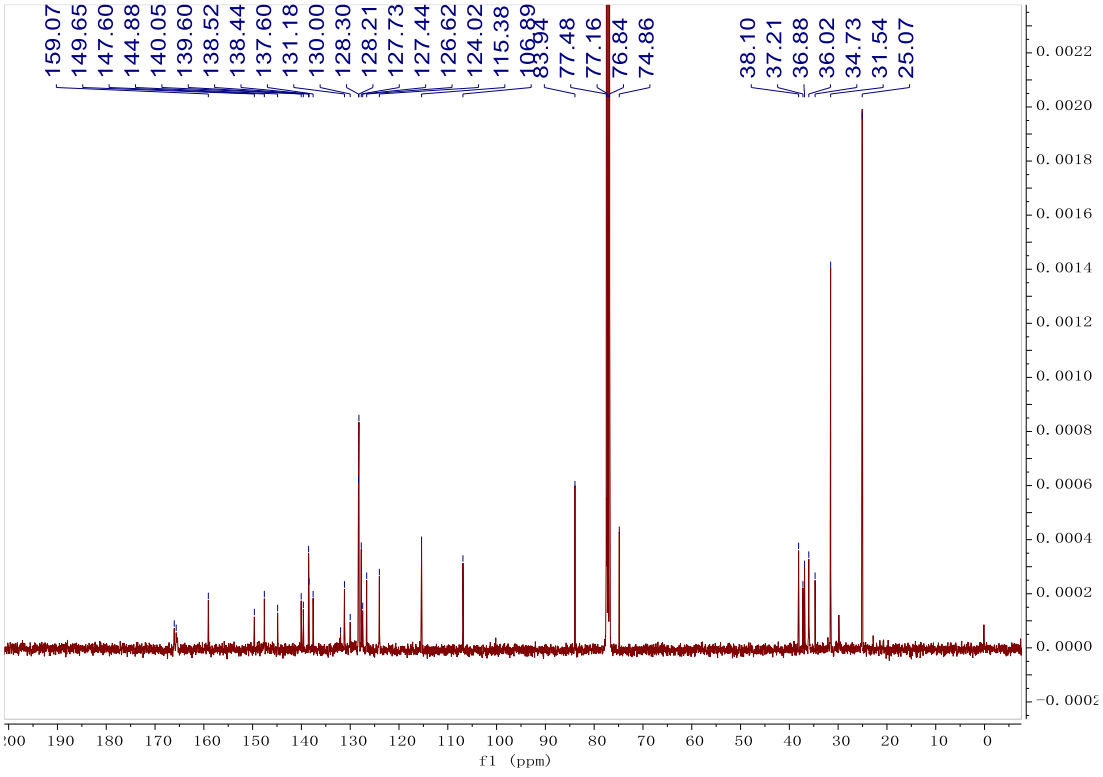
^{13}C NMR spectrum of **6m** in $CDCl_3$ at 333 K



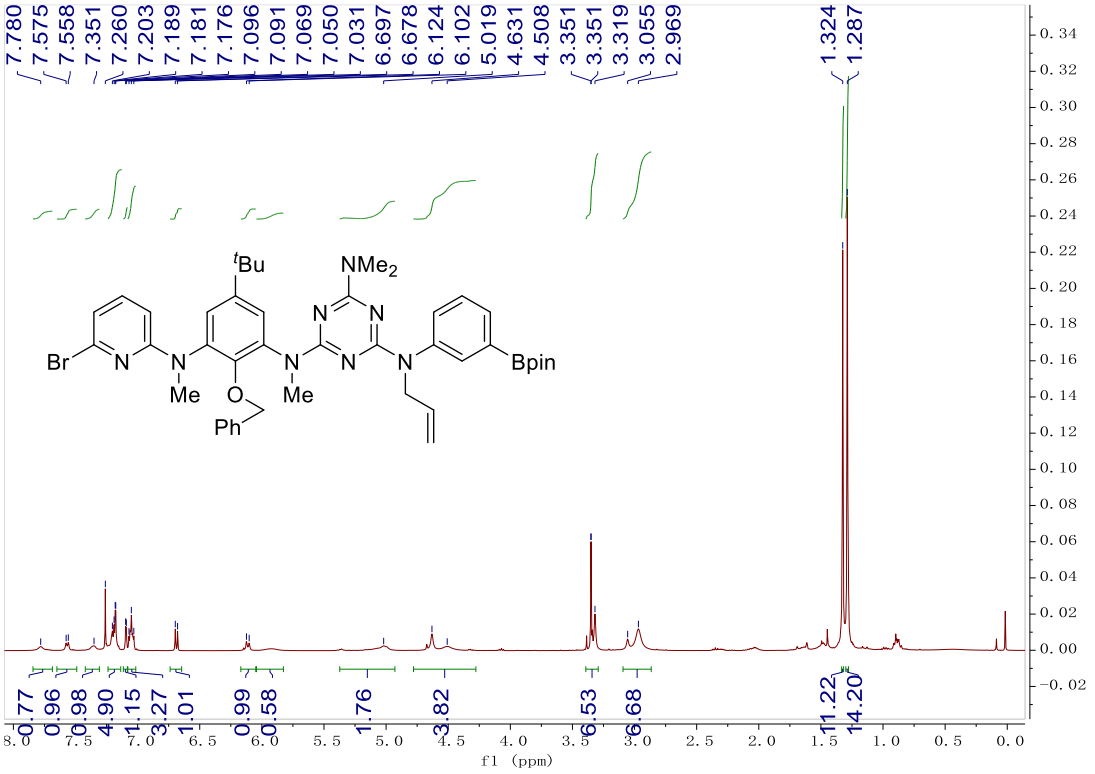
^{1}H NMR spectrum of **6n** in $CDCl_3$ at 333 K



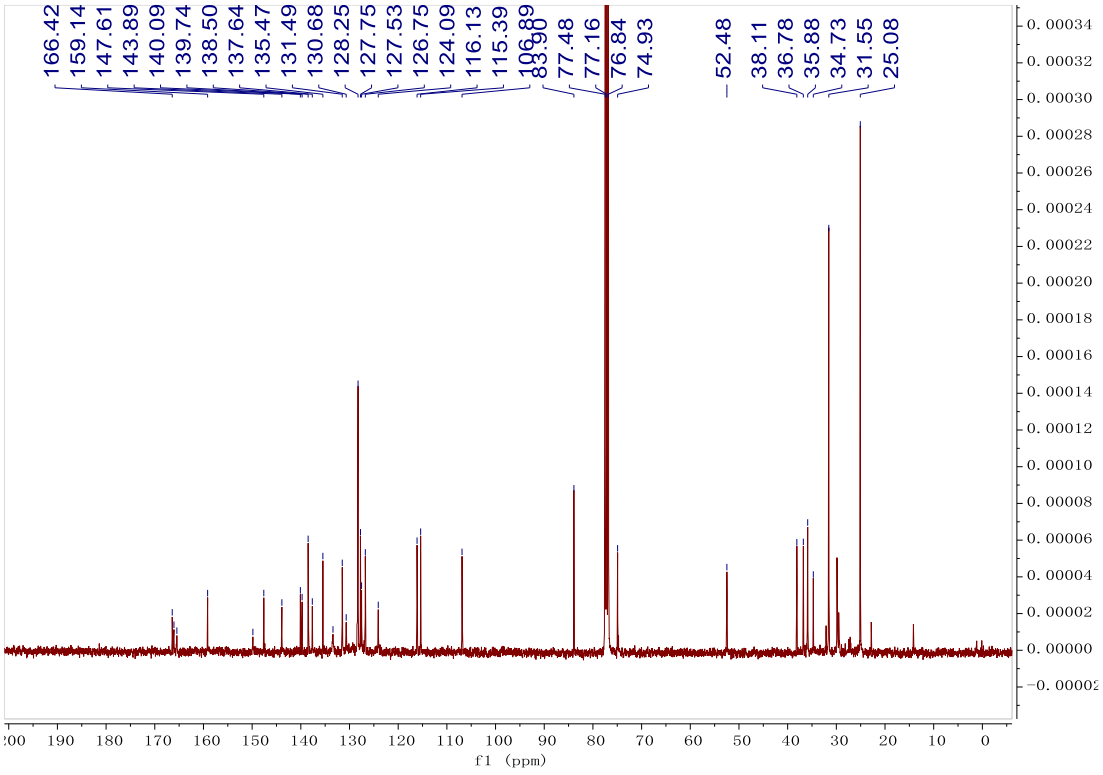
^{13}C NMR spectrum of **6n** in $CDCl_3$ at 333 K



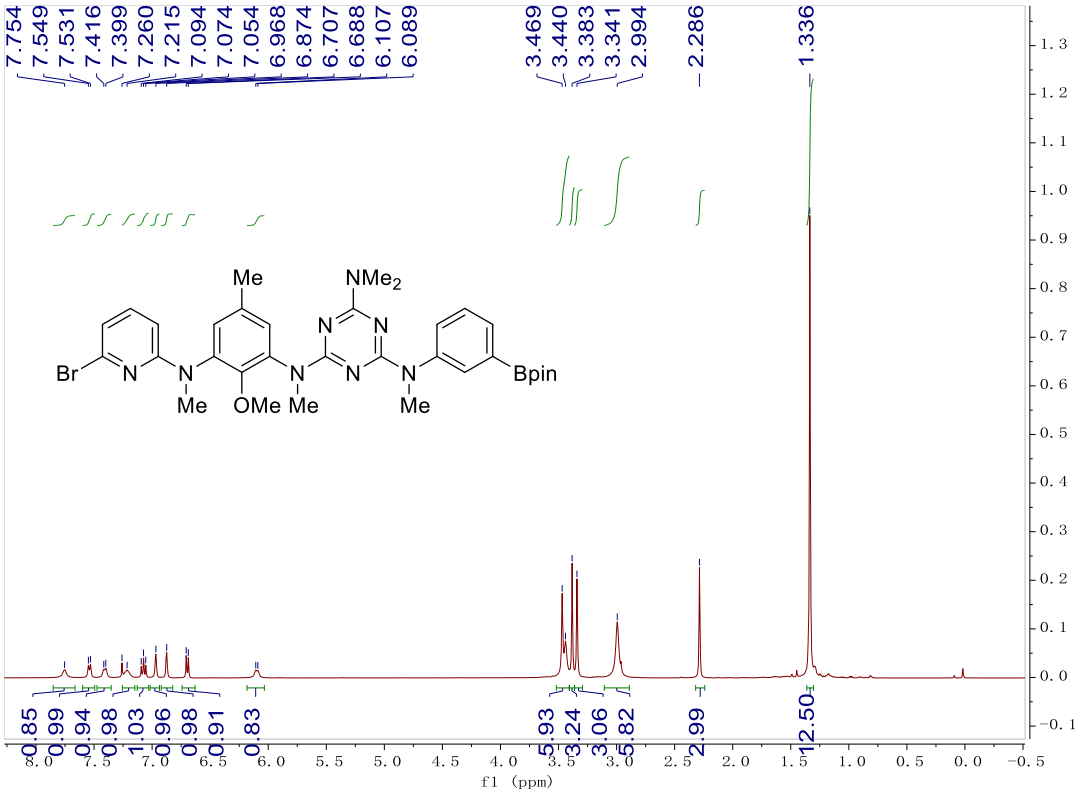
^{1}H NMR spectrum of **6o** in $CDCl_3$ at 333 K



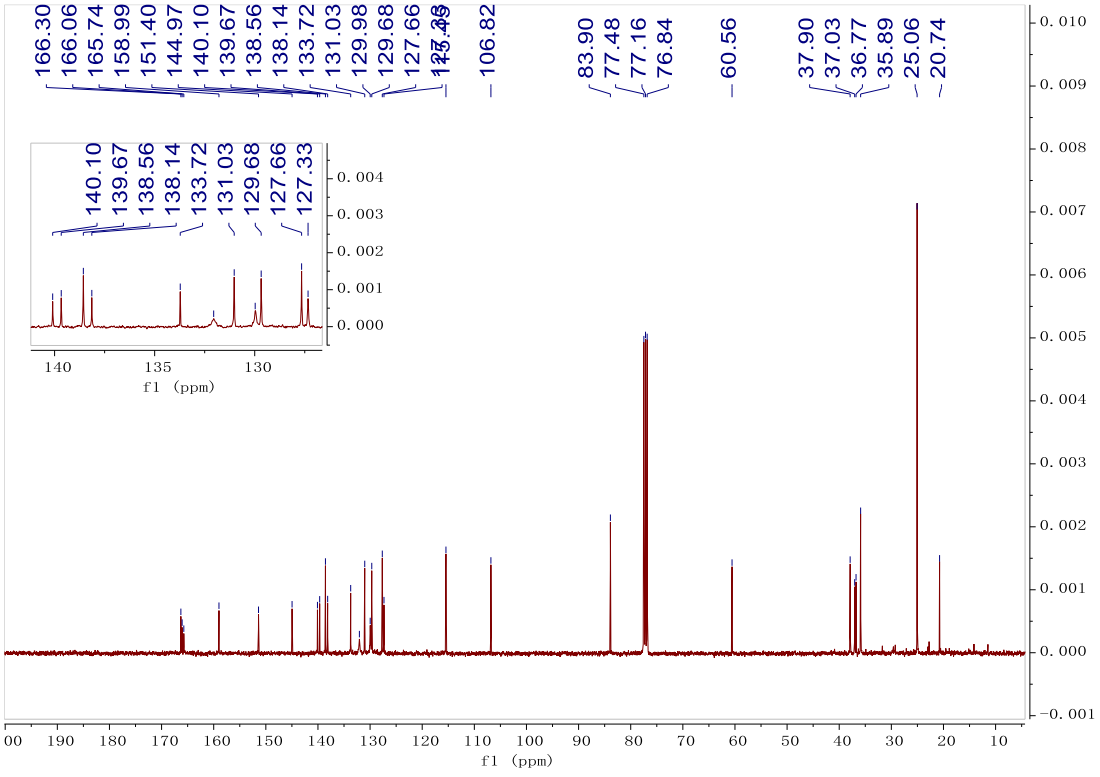
^{13}C NMR spectrum of **6o** in $CDCl_3$ at 333 K



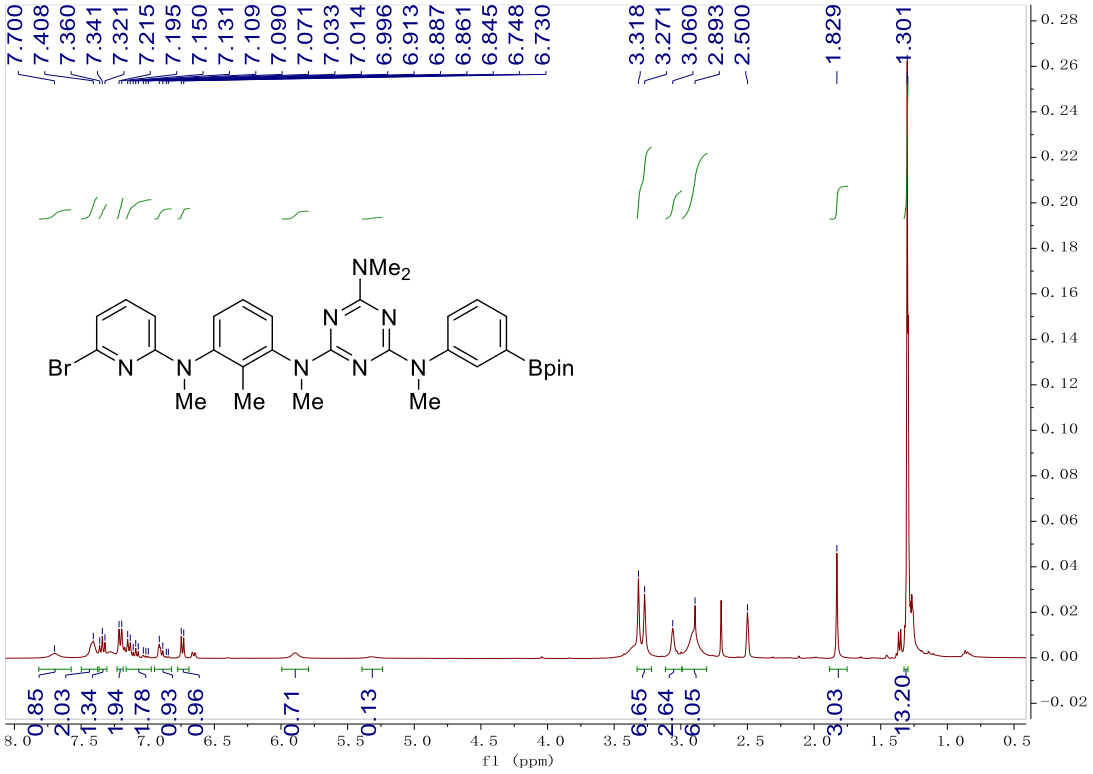
^{1}H NMR spectrum of **6p** in $CDCl_3$ at 333 K



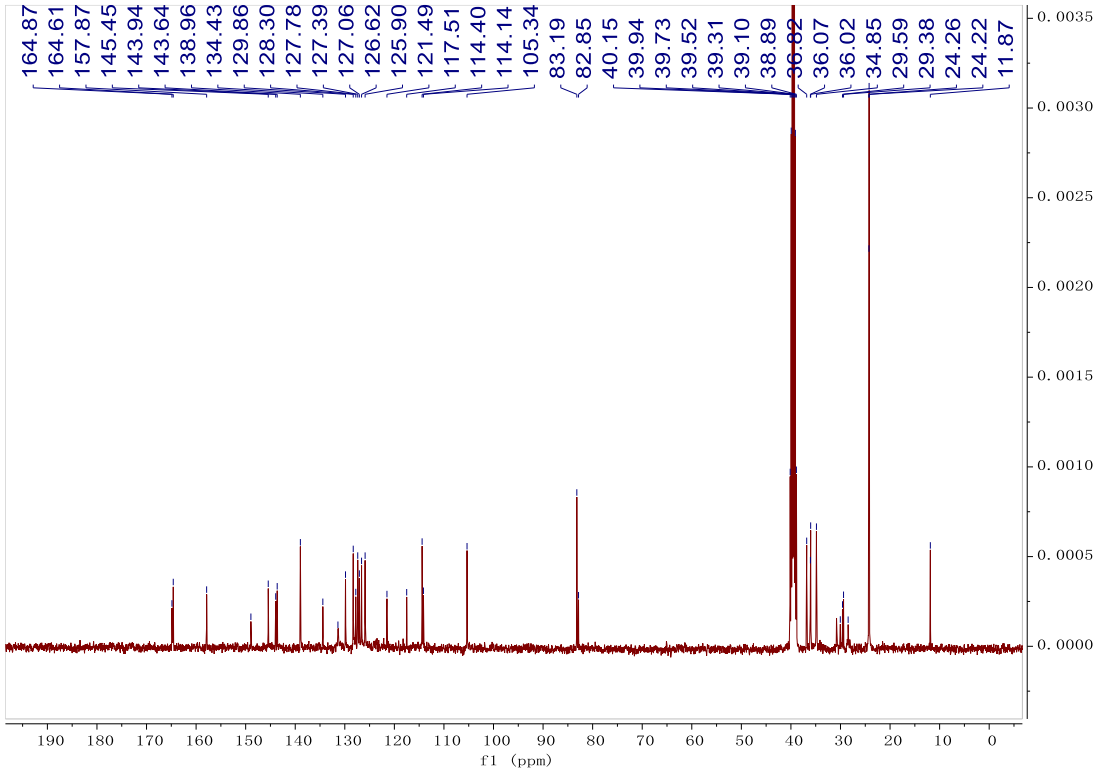
^{13}C NMR spectrum of **6p** in $CDCl_3$ at 333 K



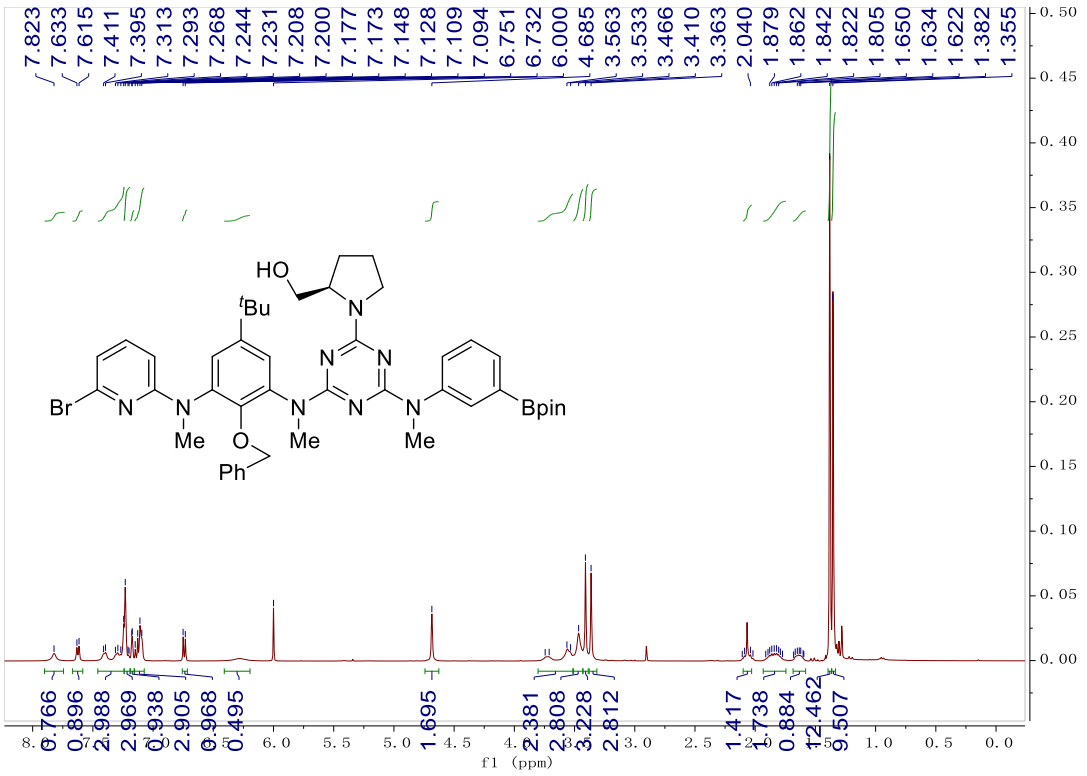
^{1}H NMR spectrum of **6q** in DMSO-d_6 at 373 K



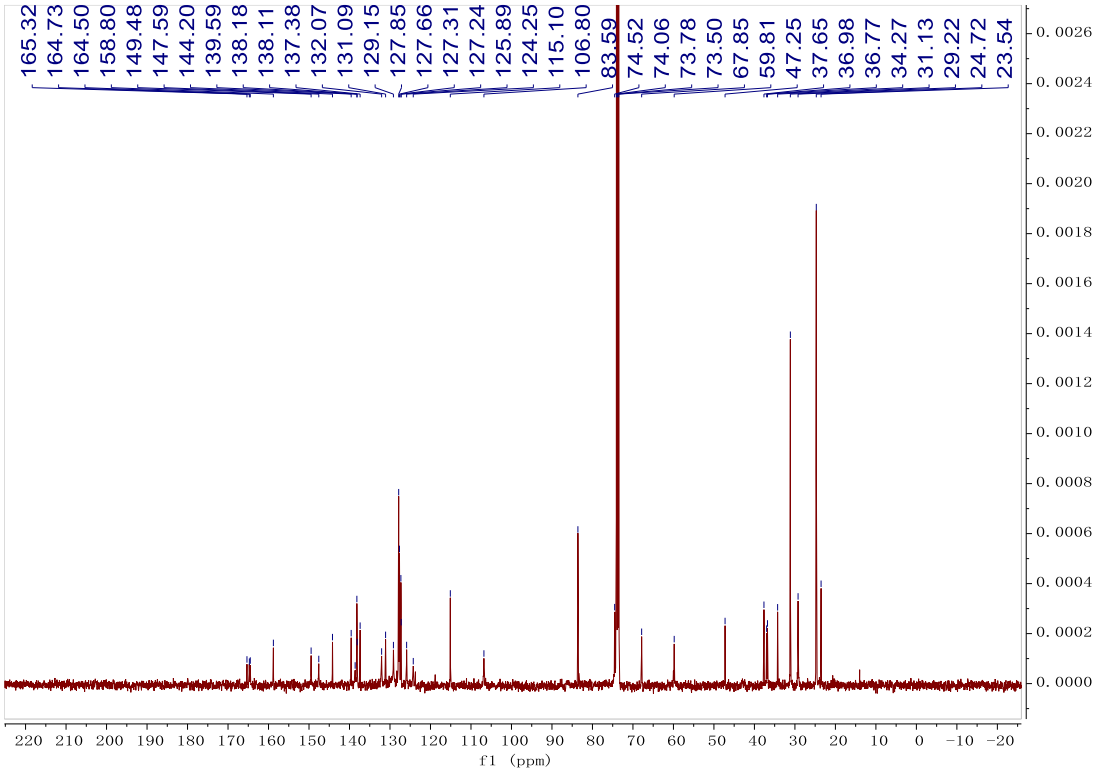
^{13}C NMR spectrum of **6q** in DMSO-d_6 at 373 K



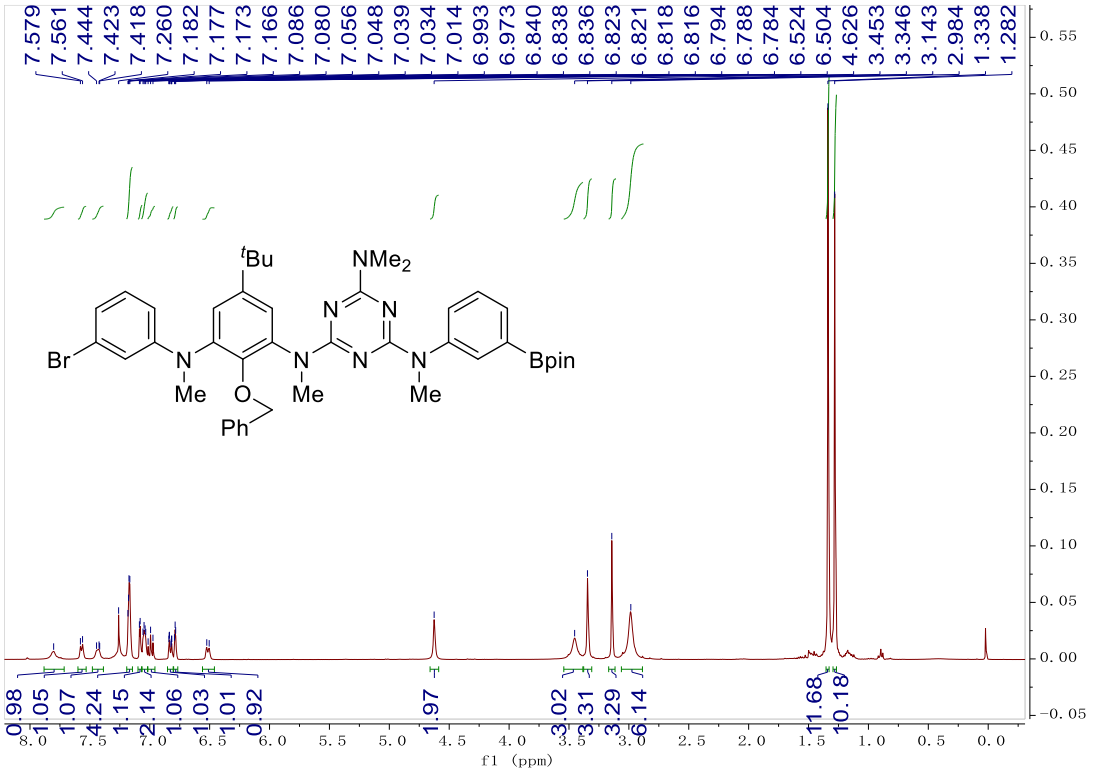
^{1}H NMR spectrum of **6r** in $C_2D_2Cl_4$ at 373 K



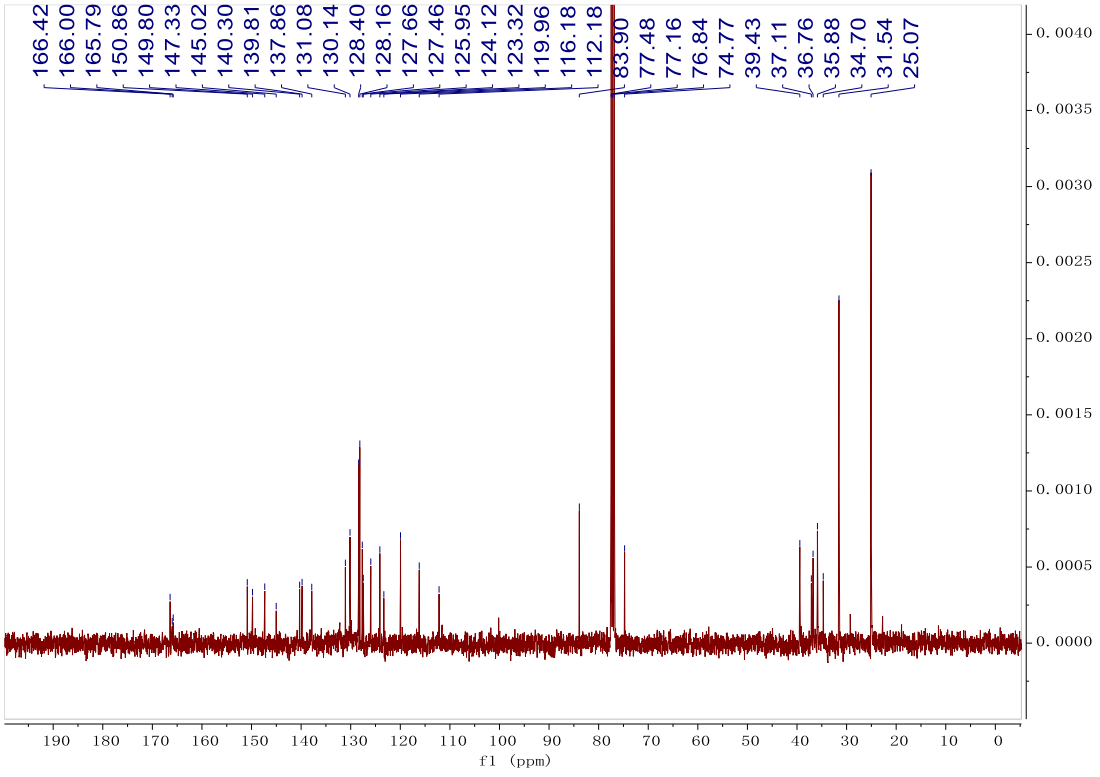
^{13}C NMR spectrum of **6r** in $C_2D_2Cl_4$ at 373 K



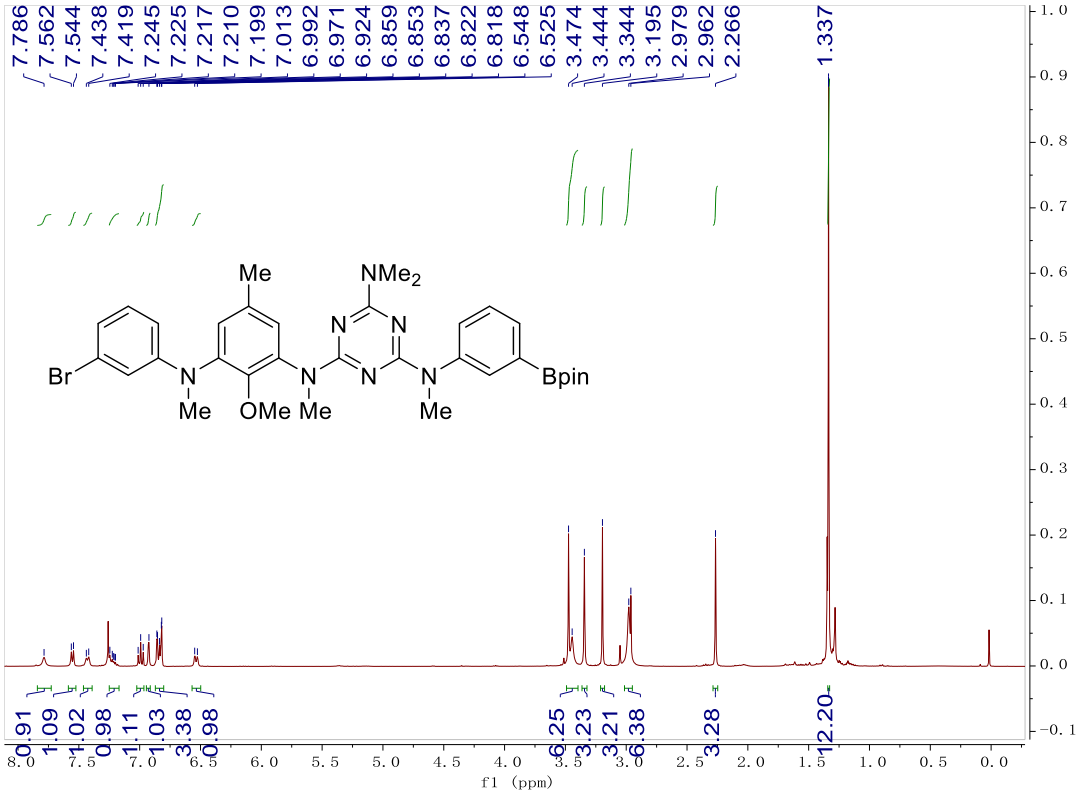
^{1}H NMR spectrum of **6s** in $CDCl_3$ at 333 K



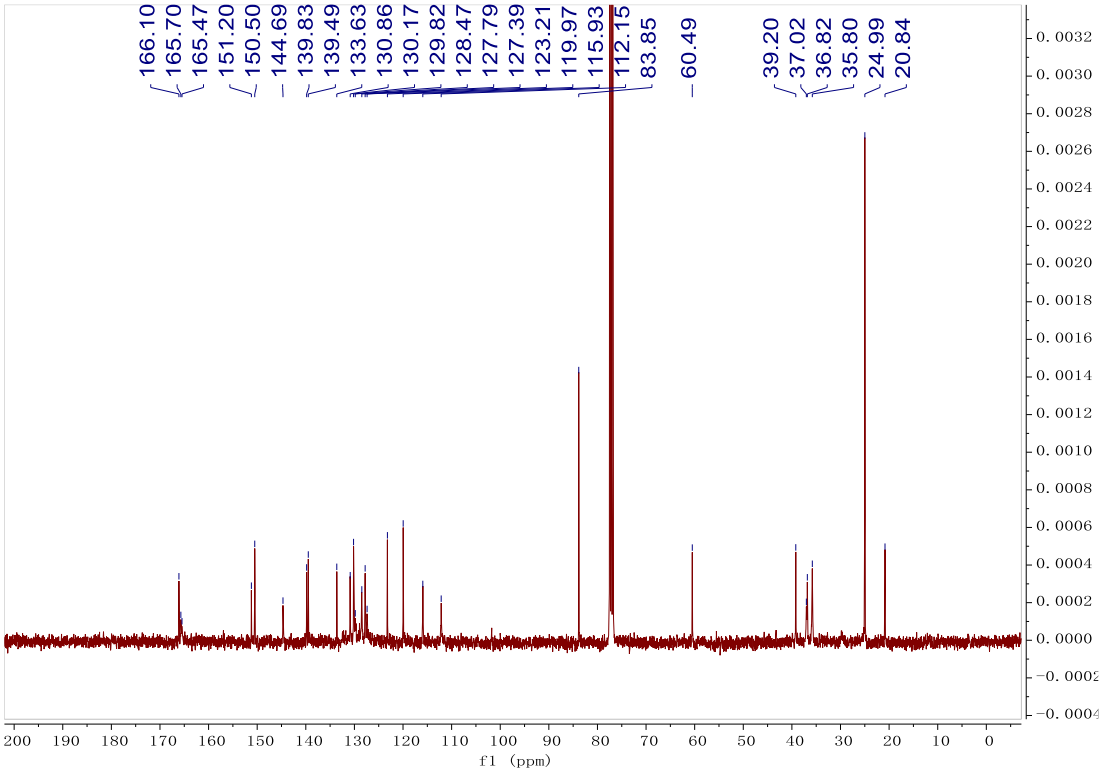
^{13}C NMR spectrum of **6s** in $CDCl_3$ at 333 K



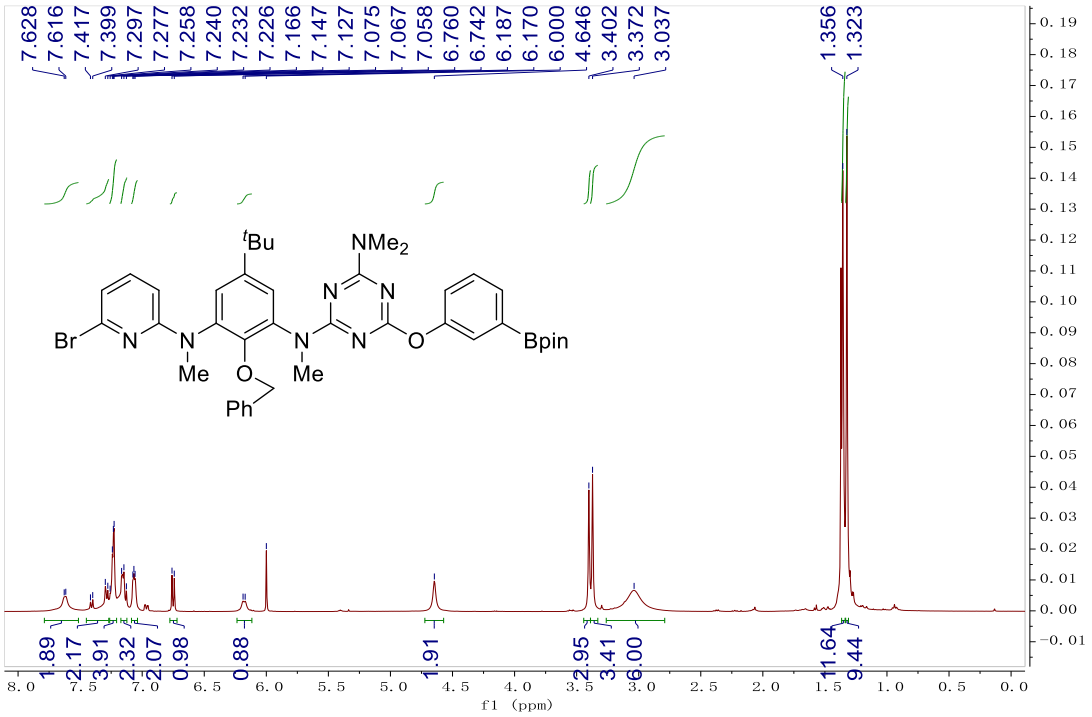
^{1}H NMR spectrum of **6t** in $CDCl_3$ at 333 K



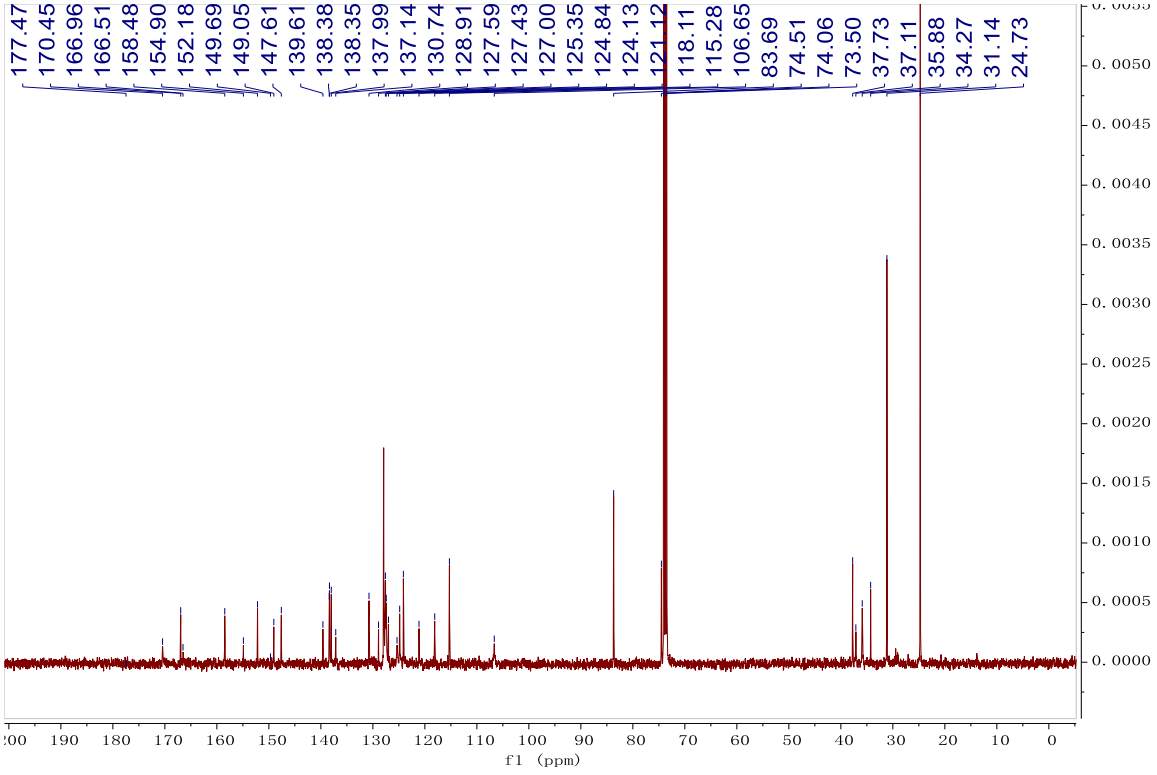
^{13}C NMR spectrum of **6t** in $CDCl_3$ at 333 K



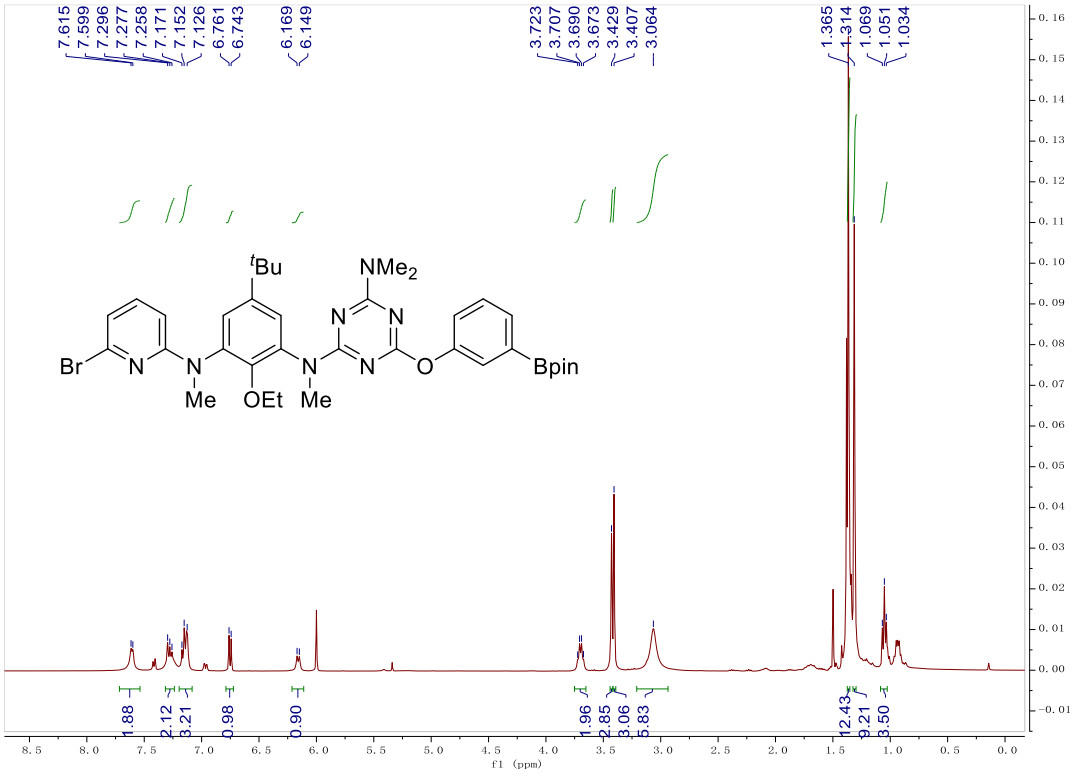
^{1}H NMR spectrum of **6u** in $C_2D_2Cl_4$ at 373 K



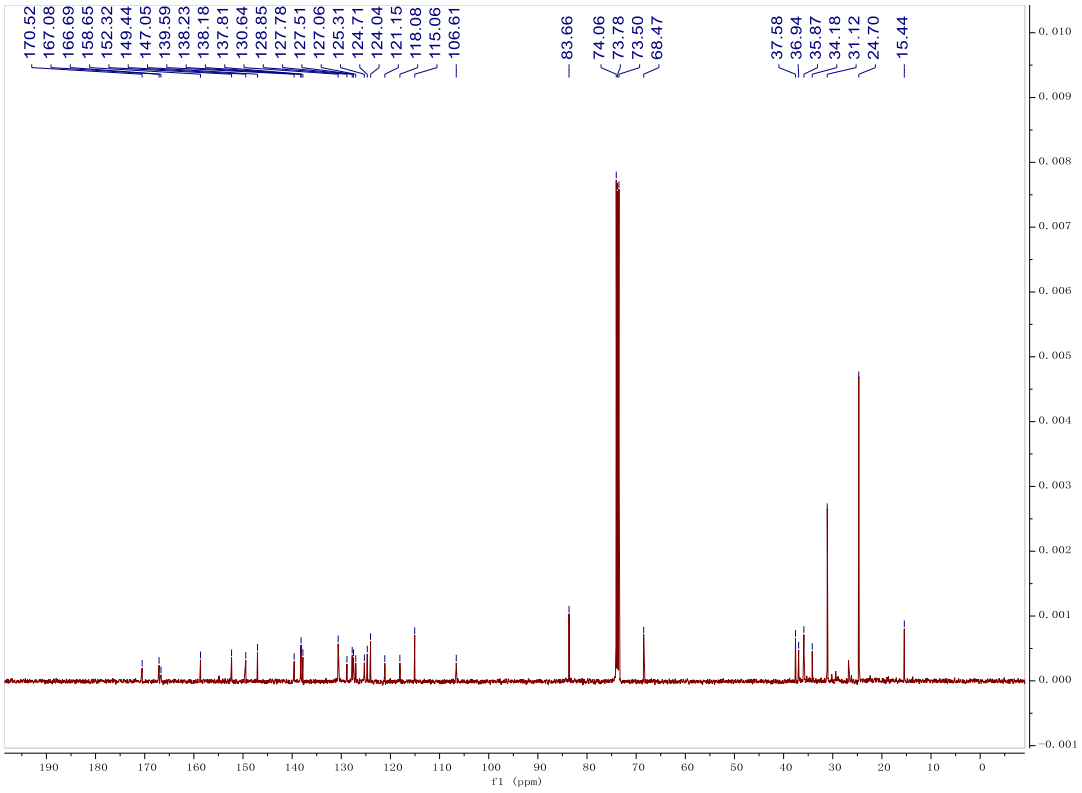
^{13}C NMR spectrum of **6u** in $C_2D_2Cl_4$ at 373 K



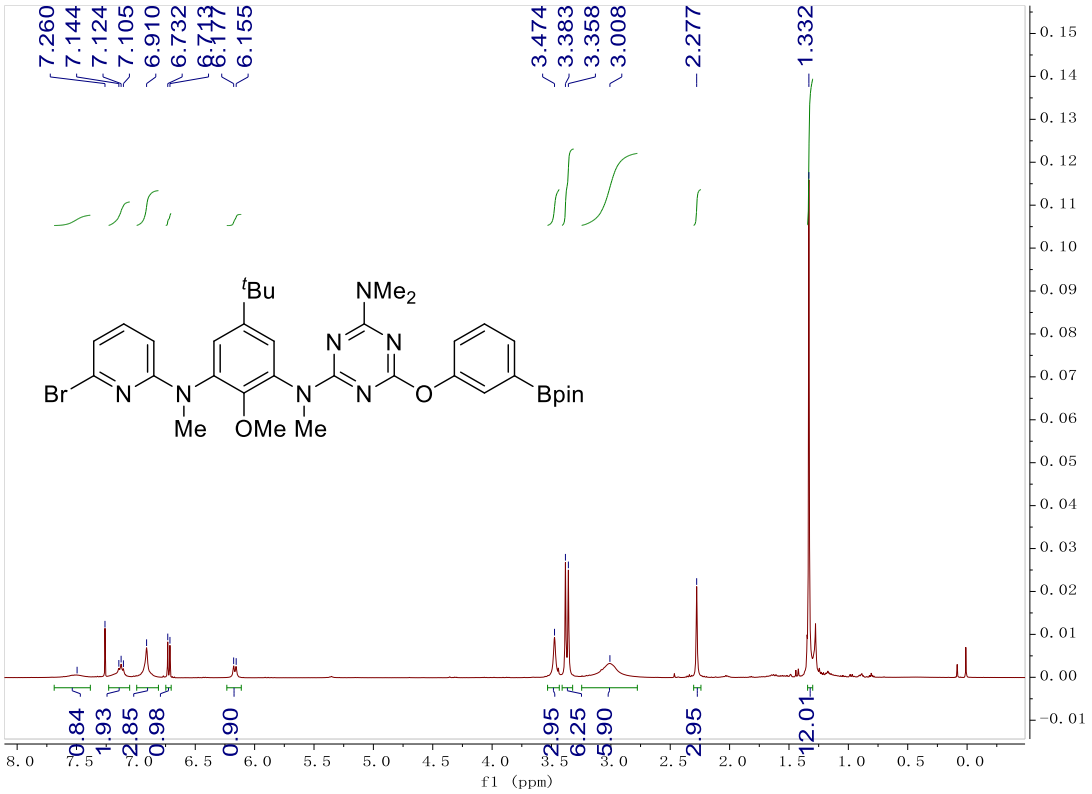
^{1}H NMR spectrum of **6v** in $C_2D_2Cl_4$ at 373 K



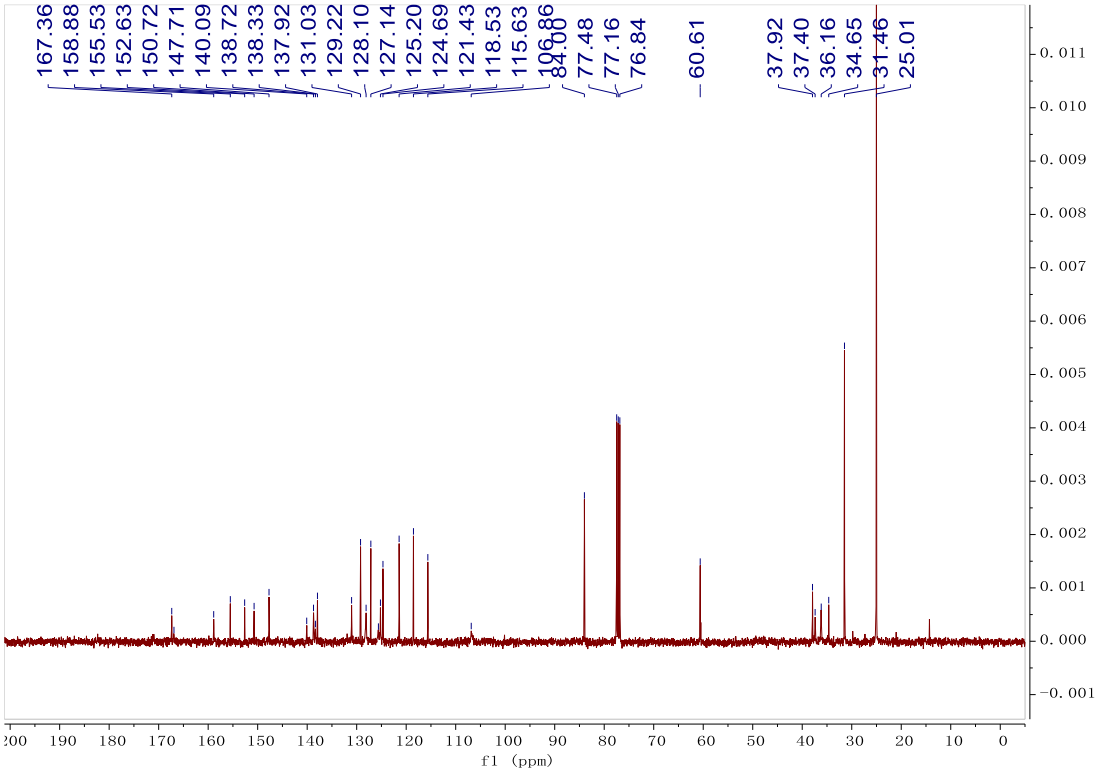
^{13}C NMR spectrum of **6v** in $C_2D_2Cl_4$ at 373 K



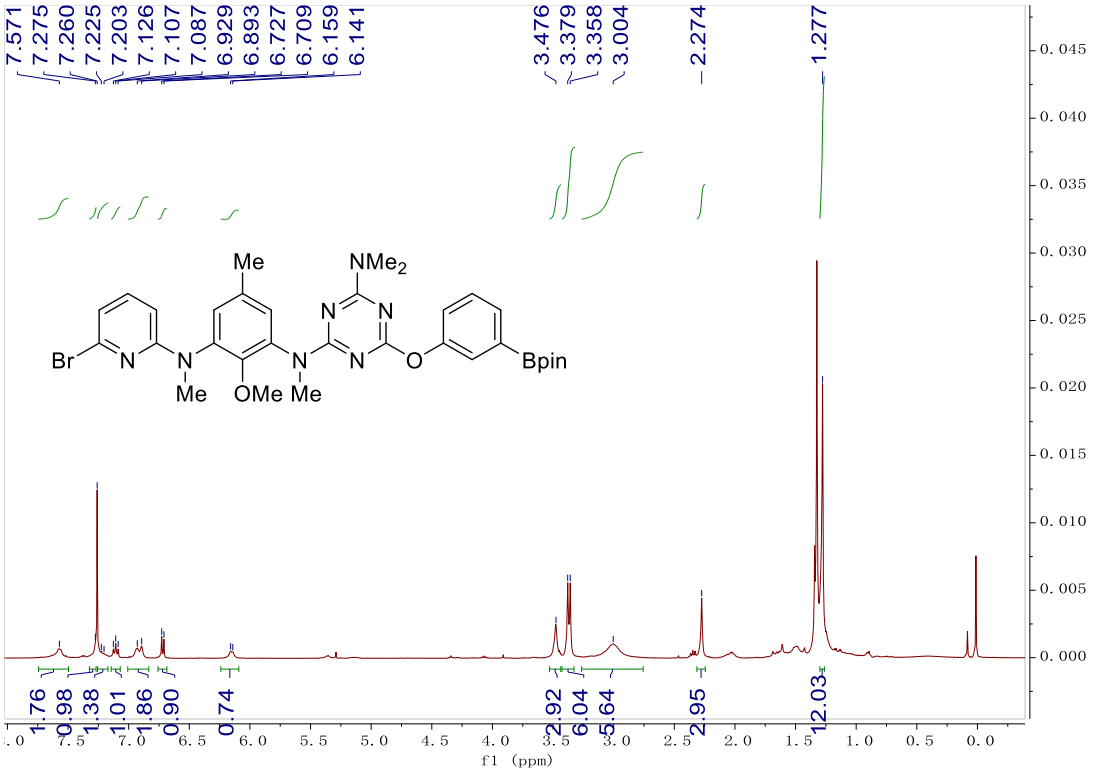
^{1}H NMR spectrum of **6w** in $CDCl_3$ at 333 K



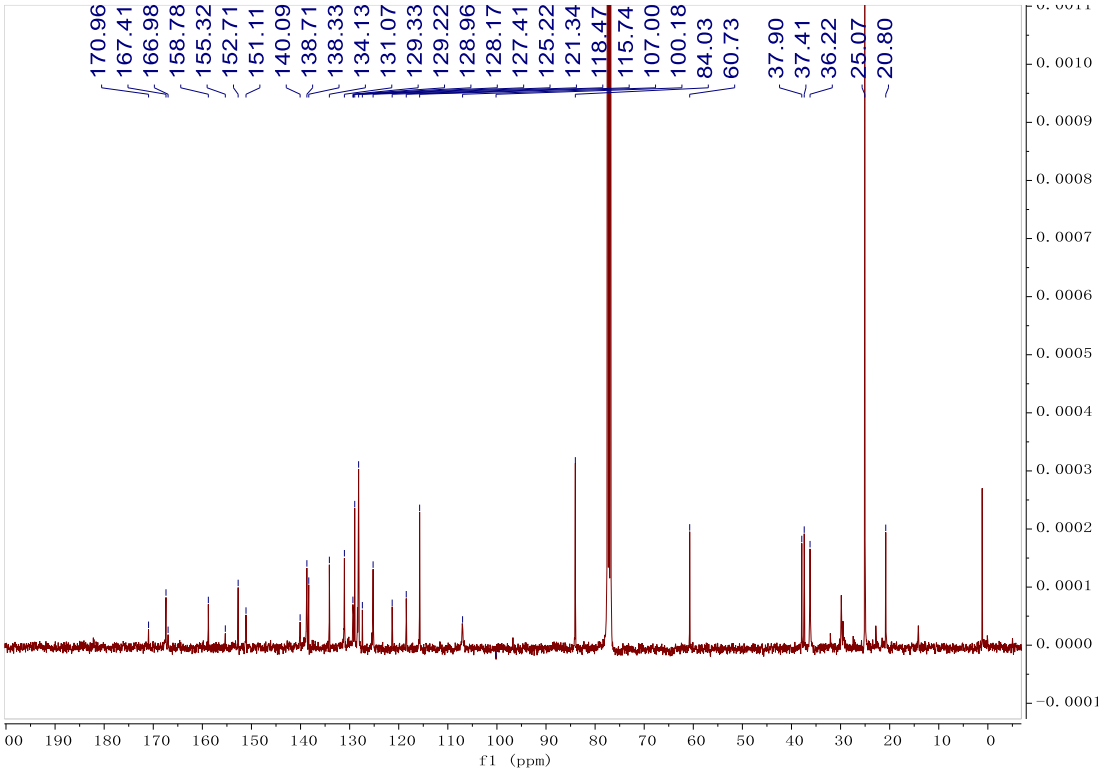
^{13}C NMR spectrum of **6w** in $CDCl_3$ at 333 K



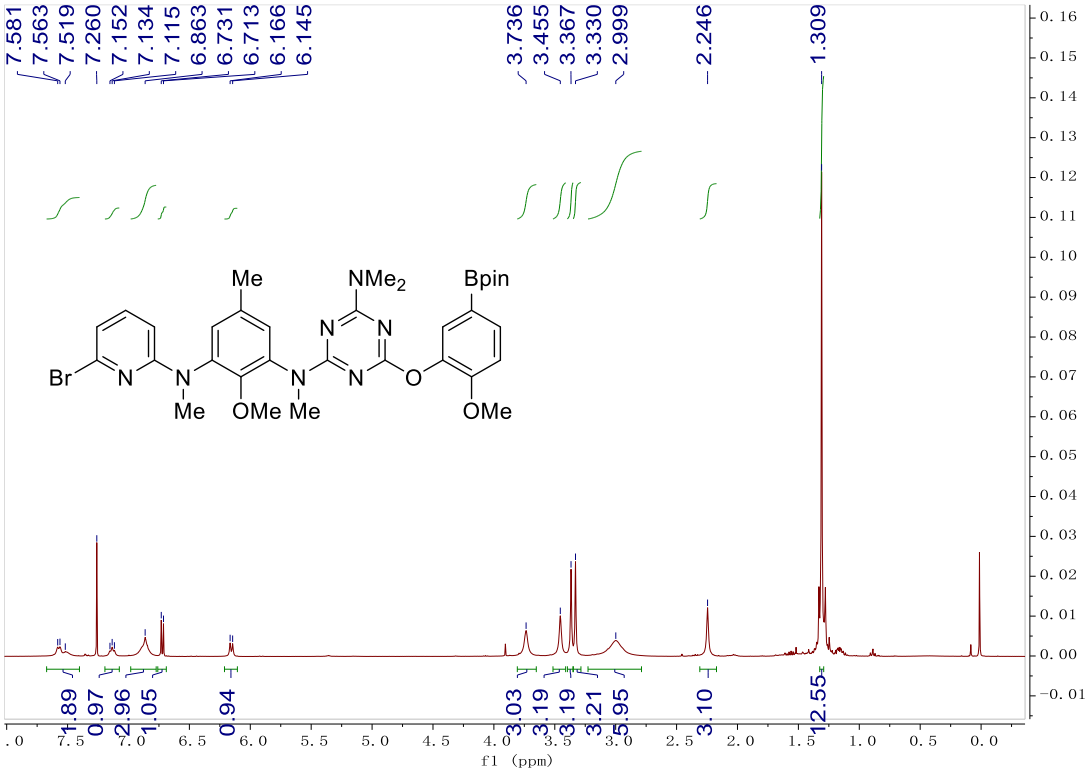
^{1}H NMR spectrum of **6x** in $CDCl_3$ at 333 K



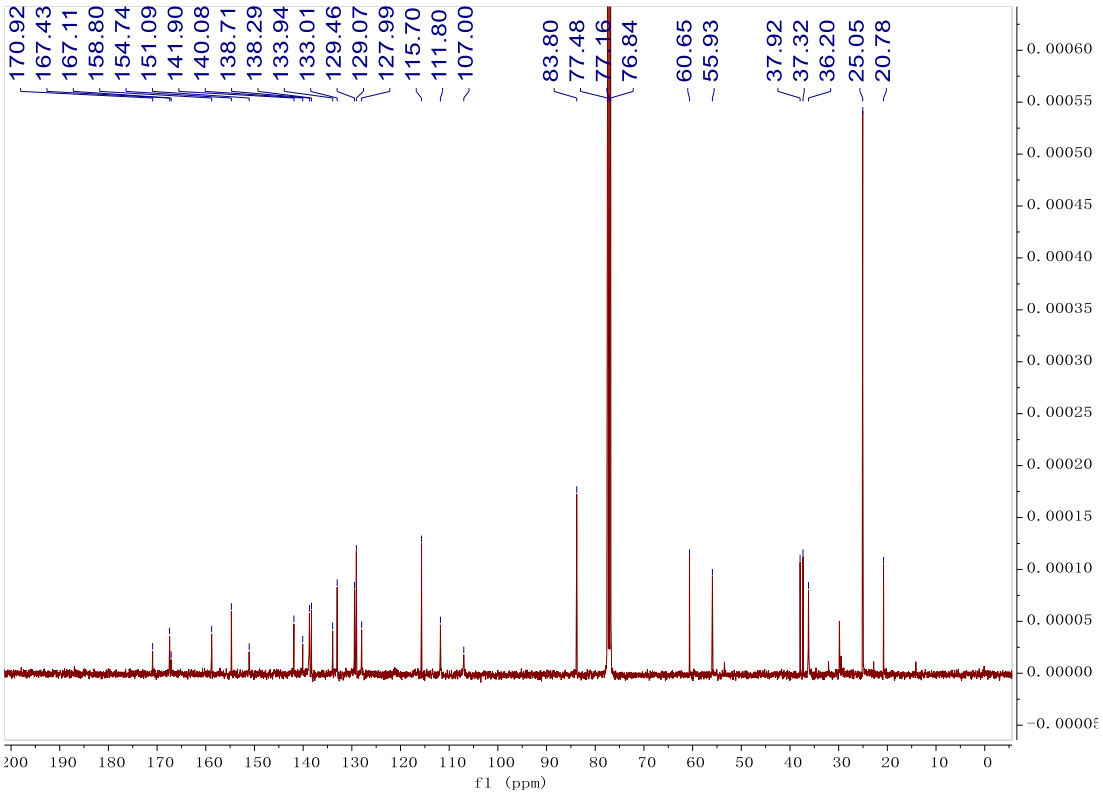
^{13}C NMR spectrum of **6x** in $CDCl_3$ at 333 K



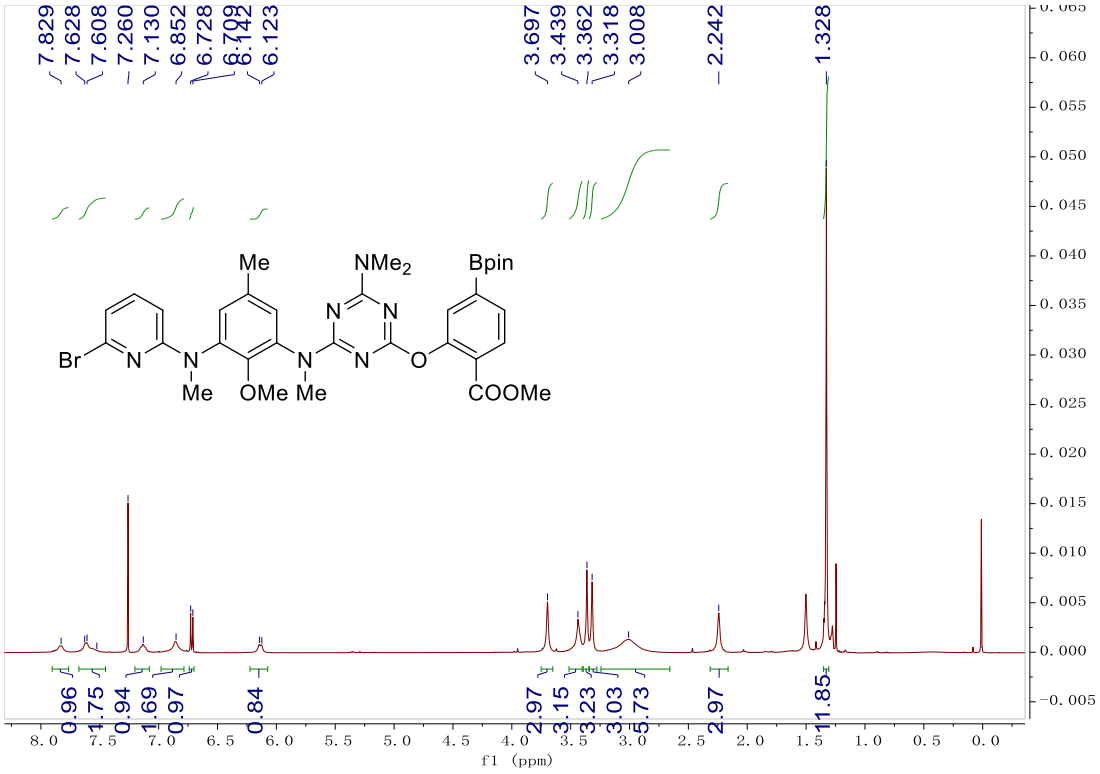
^{1}H NMR spectrum of **6y** in $CDCl_3$ at 333 K



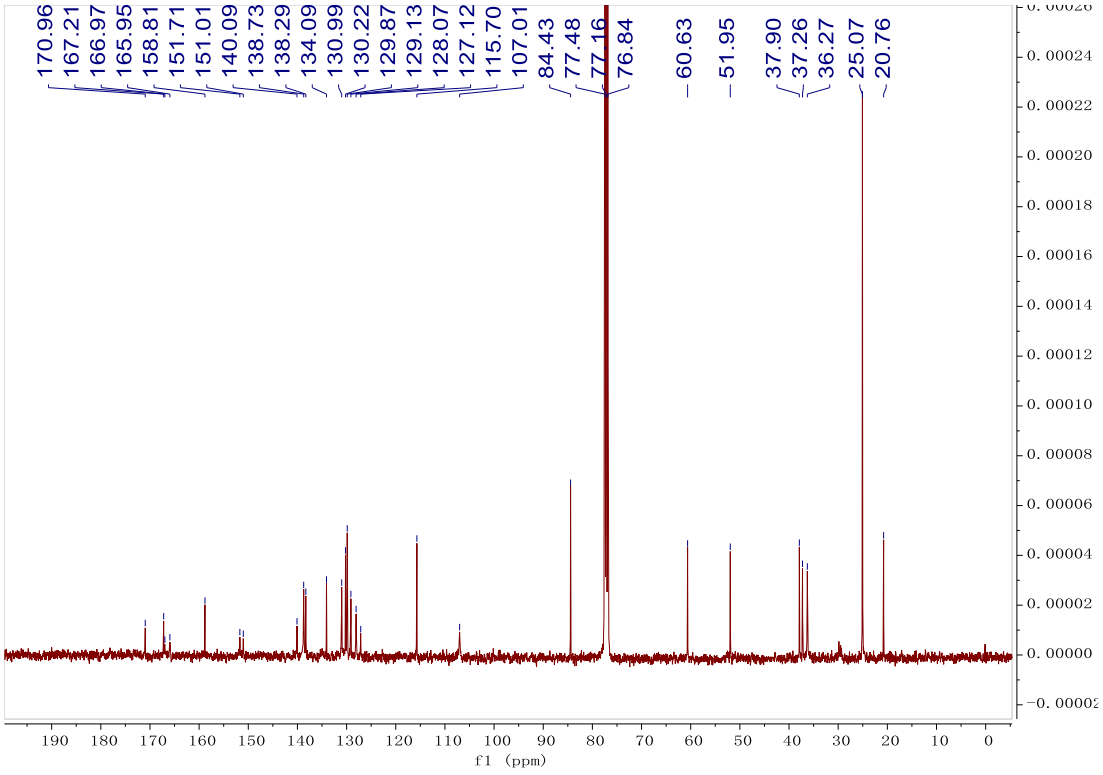
^{13}C NMR spectrum of **6y** in $CDCl_3$ at 333 K



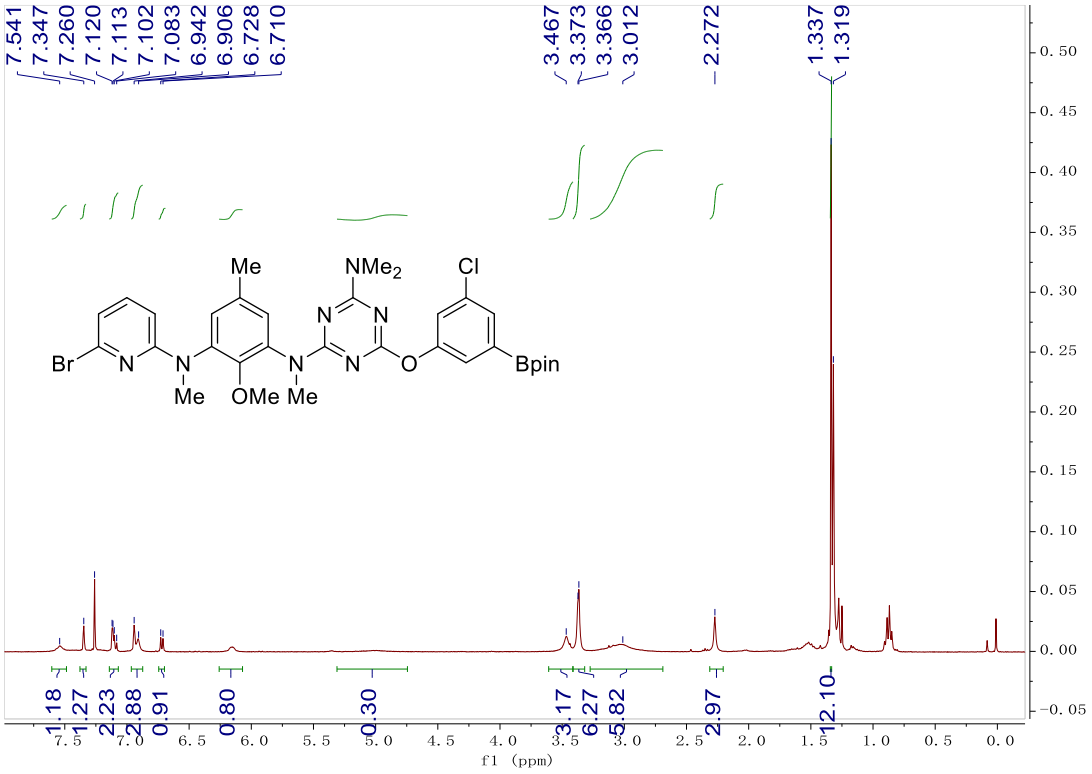
^{1}H NMR spectrum of **6z** in $CDCl_3$ at 333 K



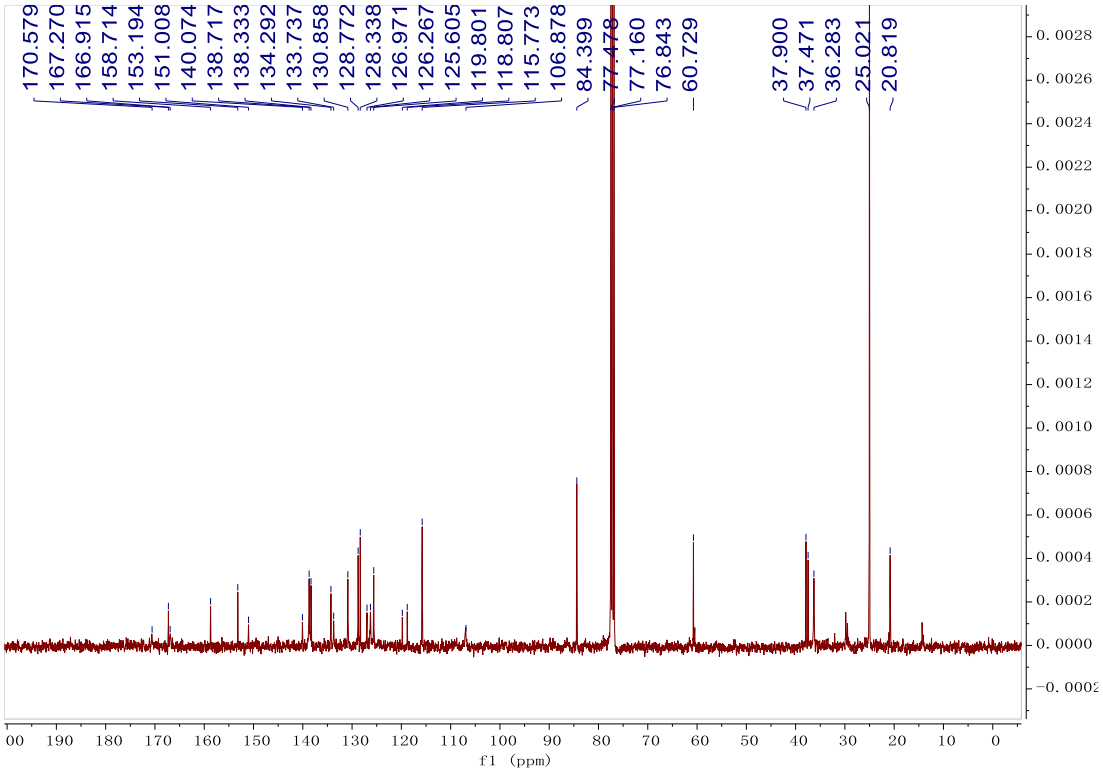
^{13}C NMR spectrum of **6z** in $CDCl_3$ at 333 K



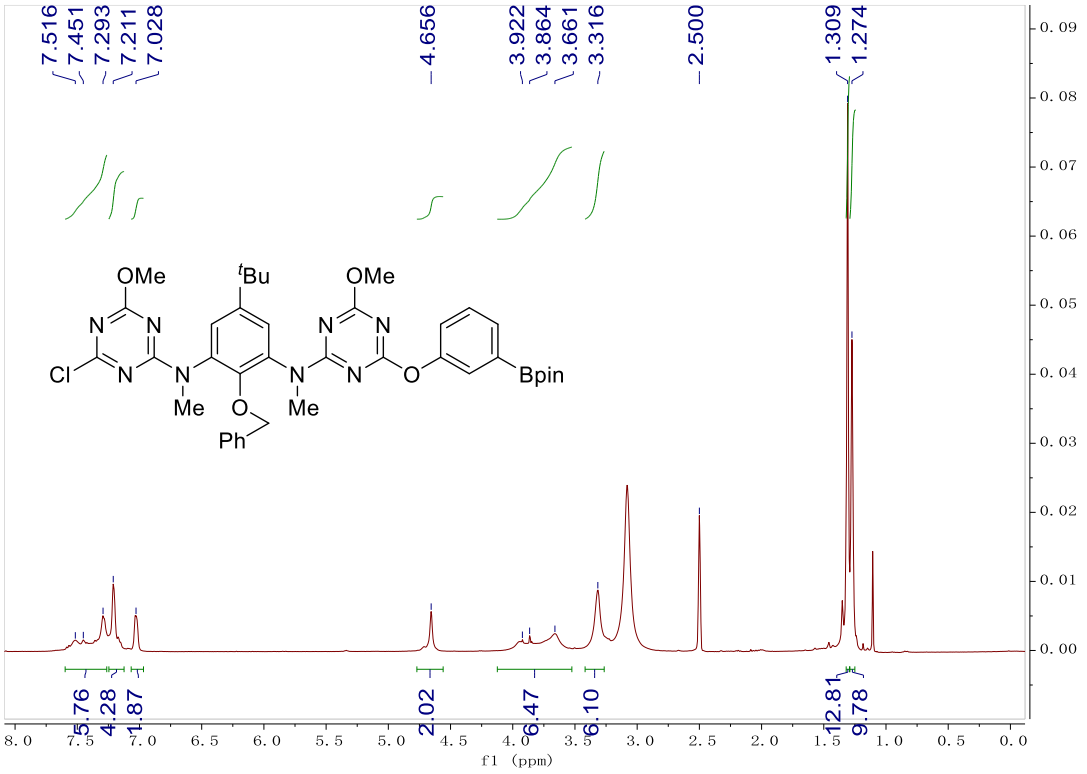
^{1}H NMR spectrum of **6aa** in $CDCl_3$ at 333 K



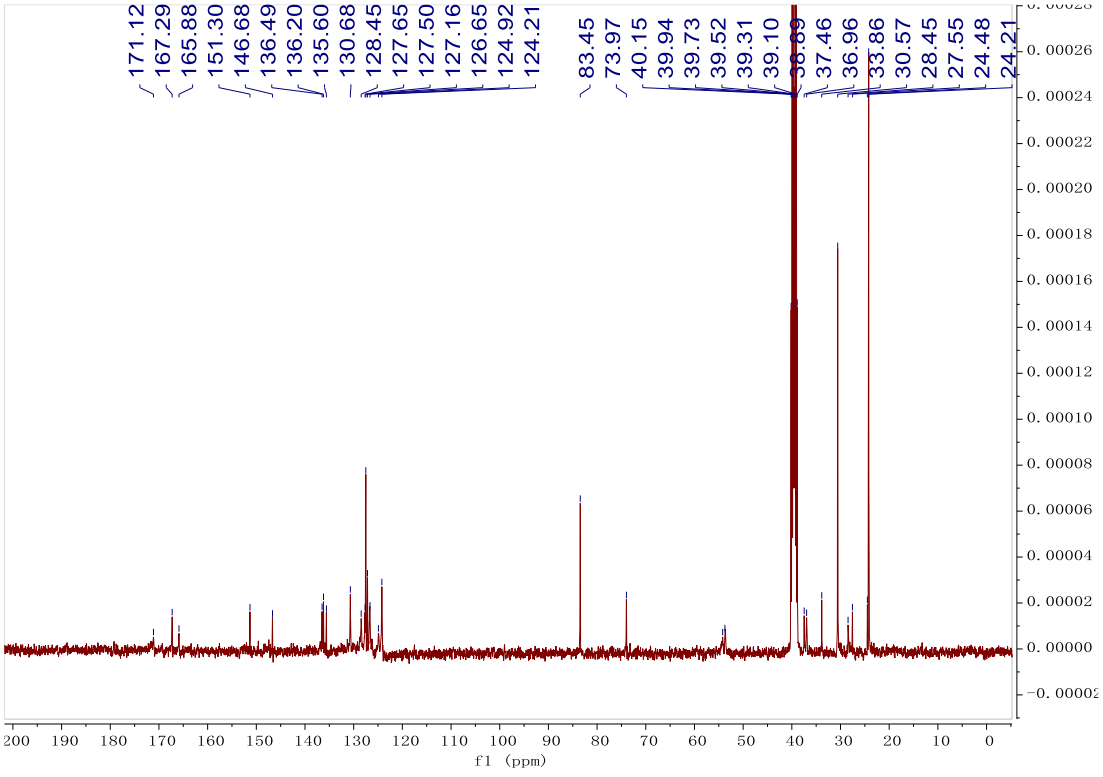
^{13}C NMR spectrum of **6aa** in $CDCl_3$ at 333 K



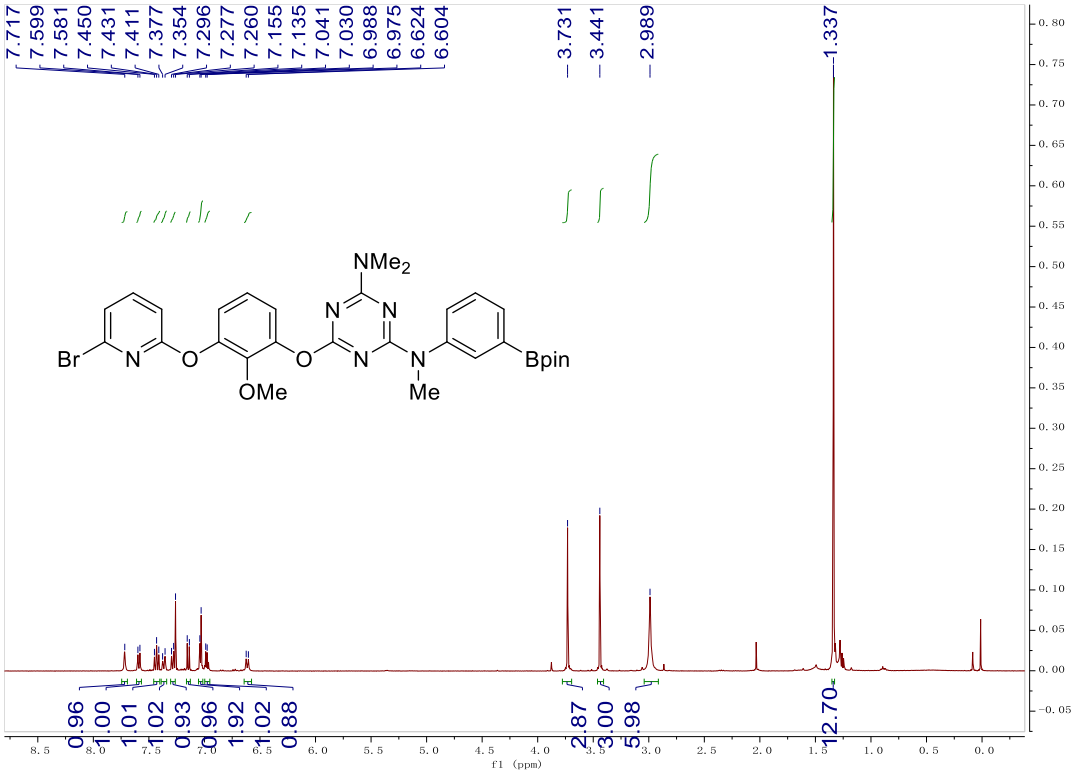
^{1}H NMR spectrum of **6ab** in DMSO-d_6 at 373 K



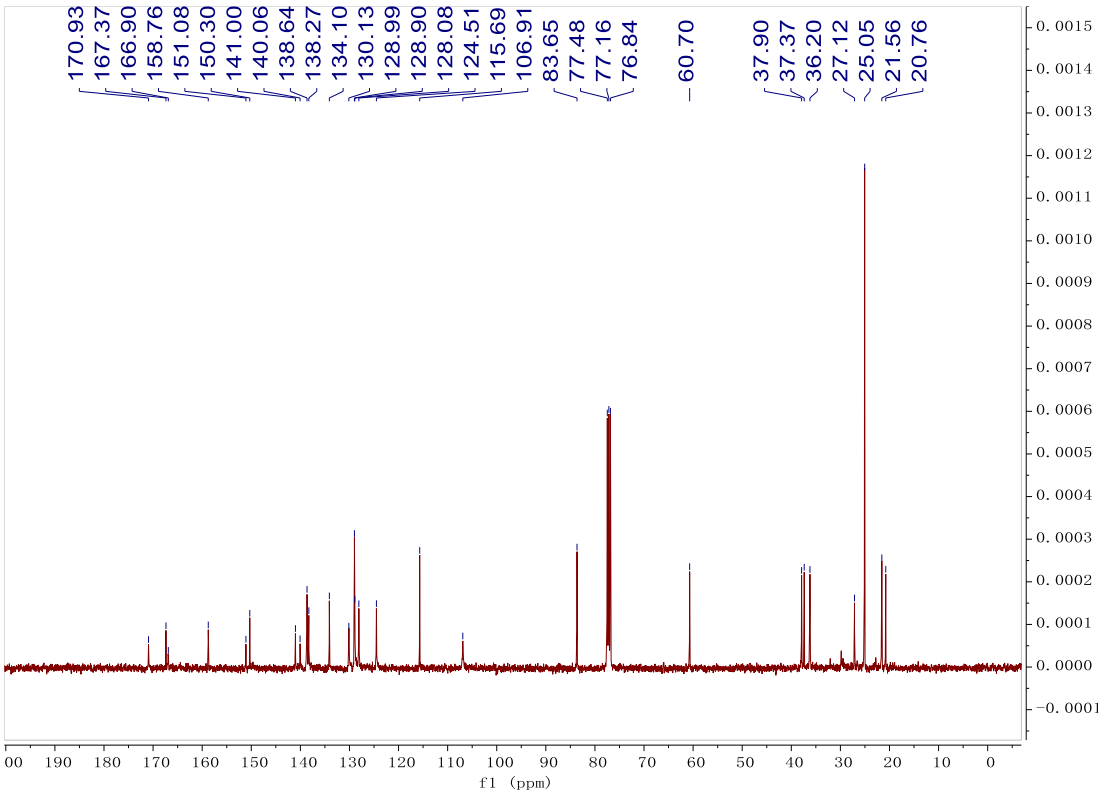
^{13}C NMR spectrum of **6ab** in DMSO-d_6 at 373 K



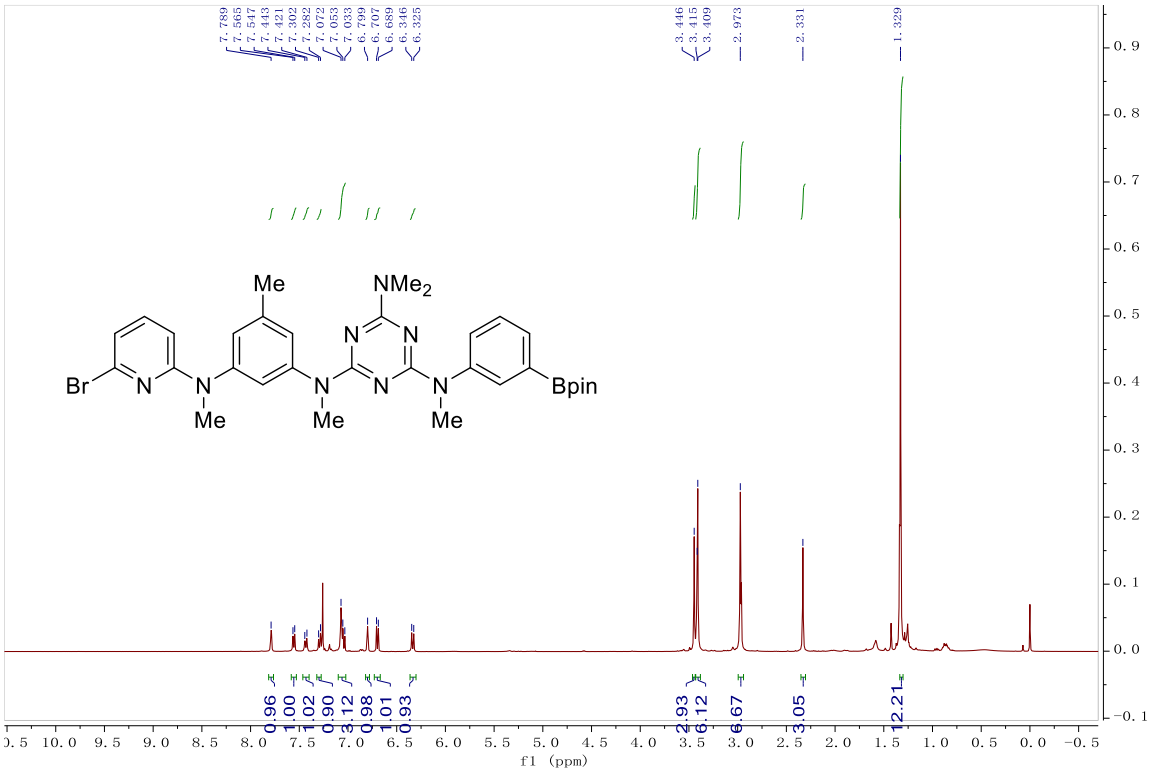
^{1}H NMR spectrum of **6ac** in $CDCl_3$ at 333 K



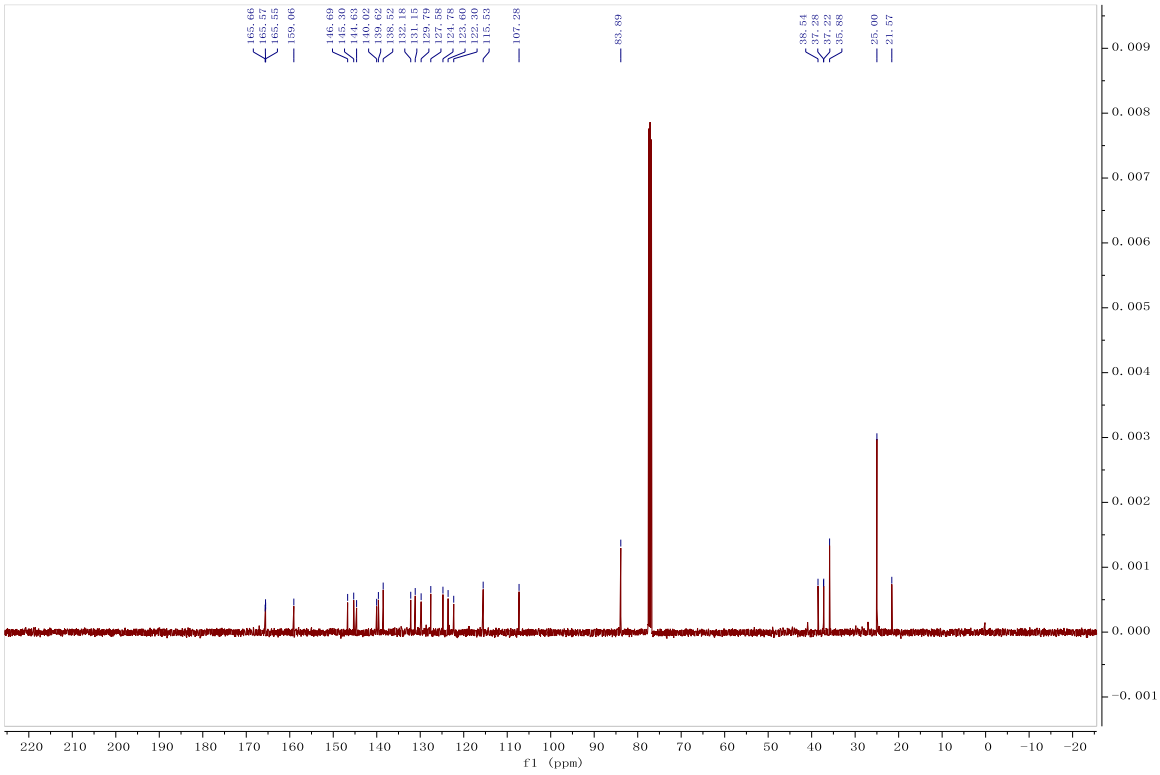
^{13}C NMR spectrum of **6ac** in $CDCl_3$ at 333 K



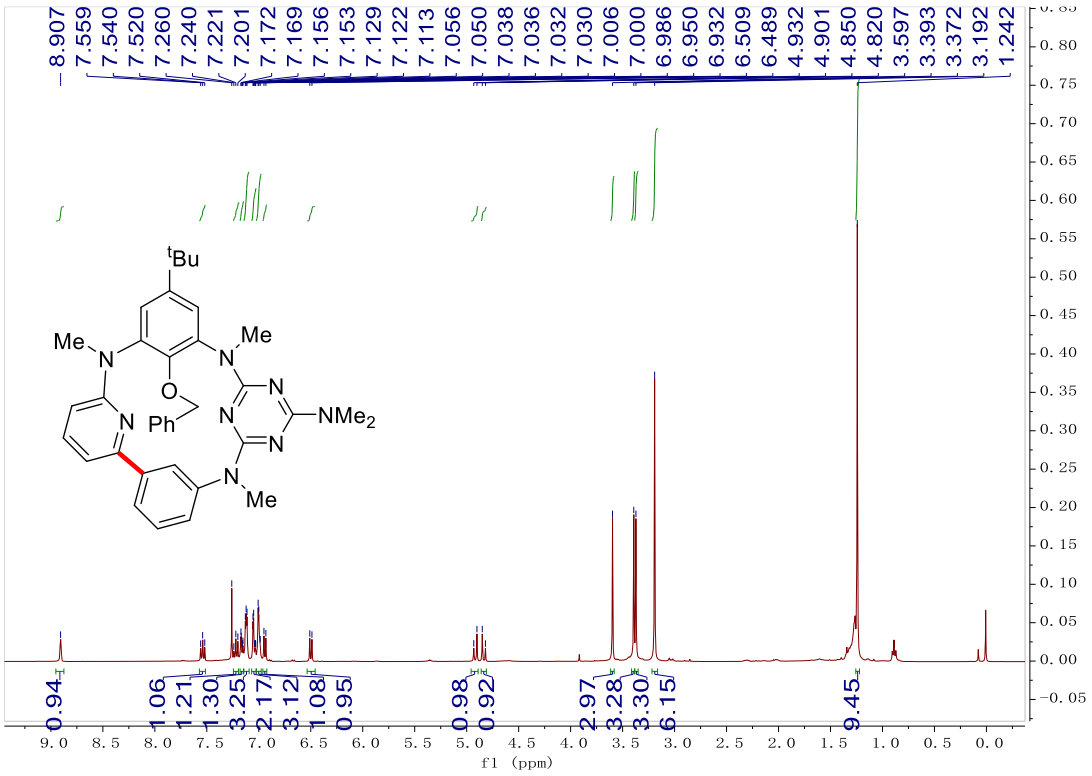
^{1}H NMR spectrum of **6ad** in $CDCl_3$ at 298 K



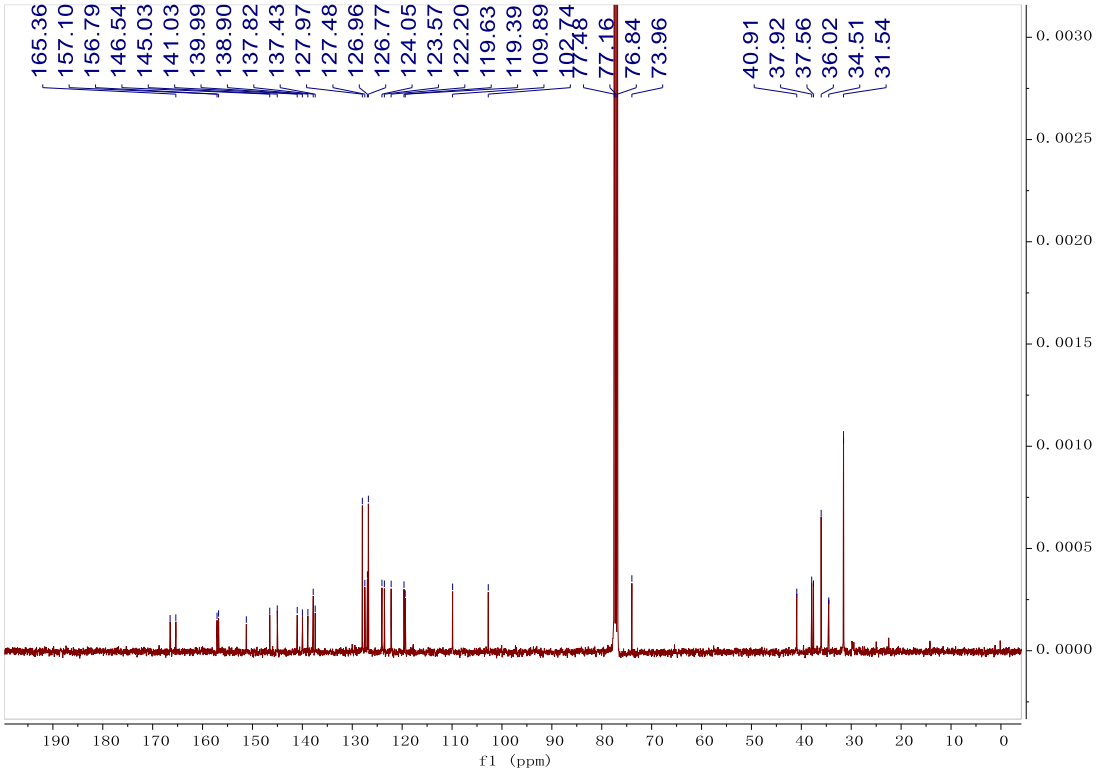
^{13}C NMR spectrum of **6ad** in $CDCl_3$ at 333 K



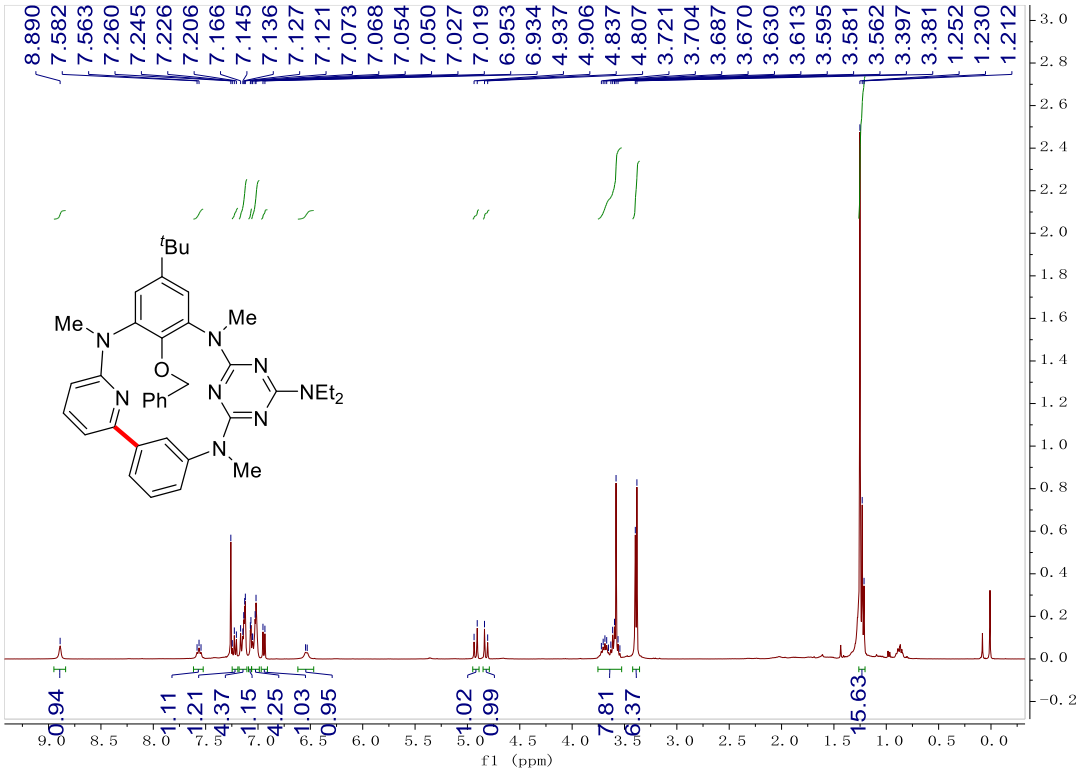
^{1}H NMR spectrum of **5a** in $CDCl_3$ at 298 K



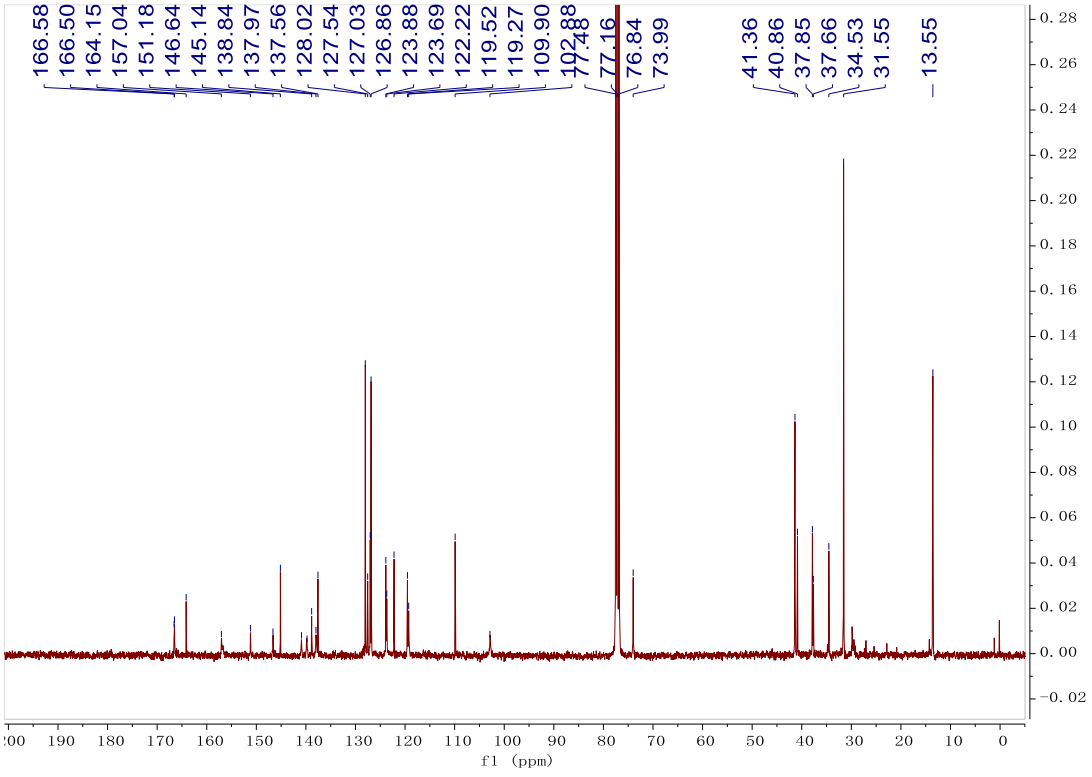
^{13}C NMR spectrum of **5a** in $CDCl_3$ at 298 K



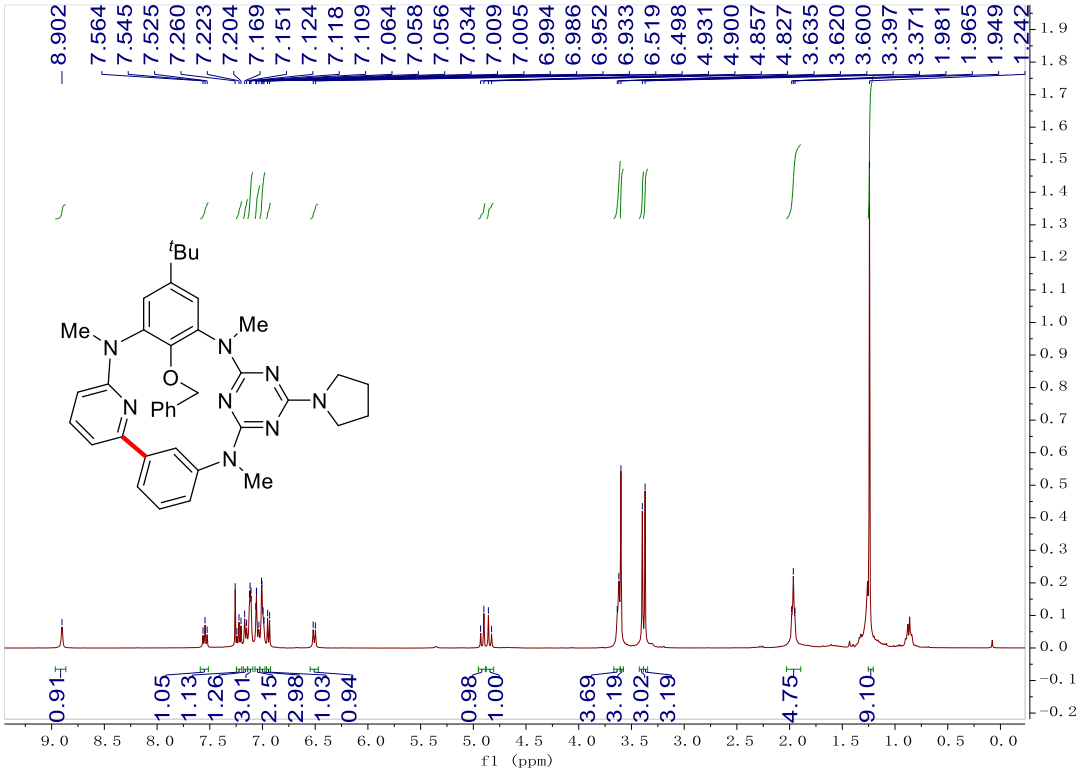
^{1}H NMR spectrum of **5b** in $CDCl_3$ at 298 K



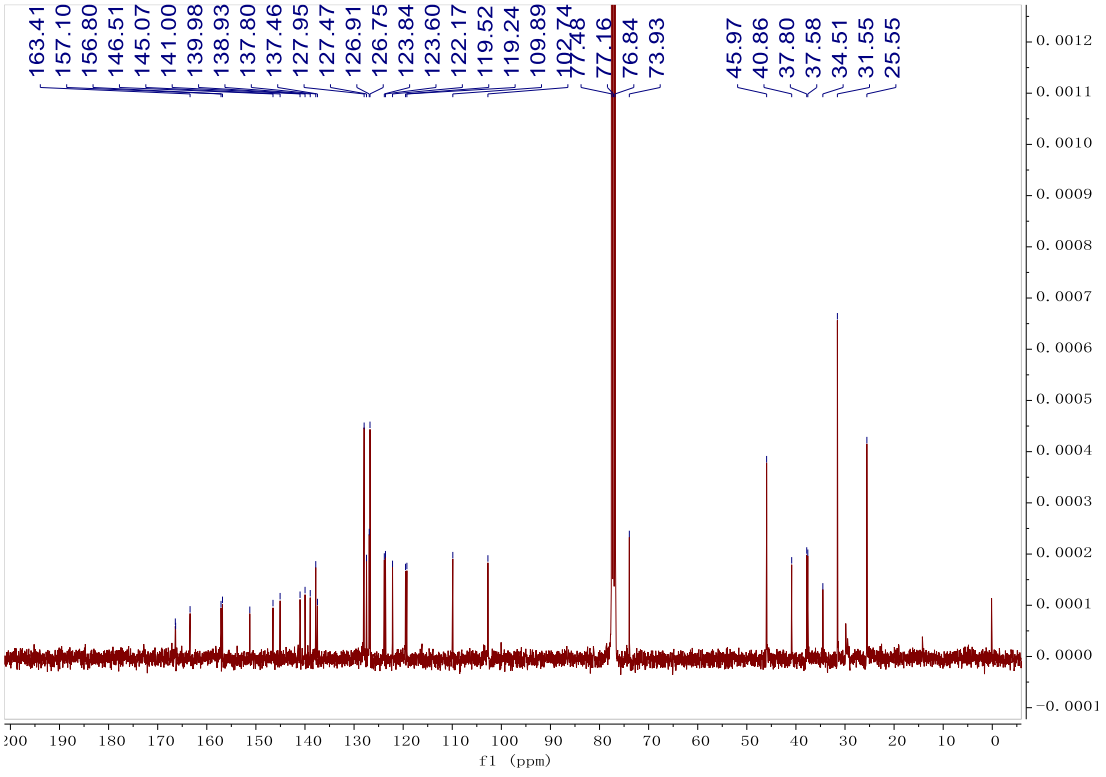
^{13}C NMR spectrum of **5b** in $CDCl_3$ at 298 K



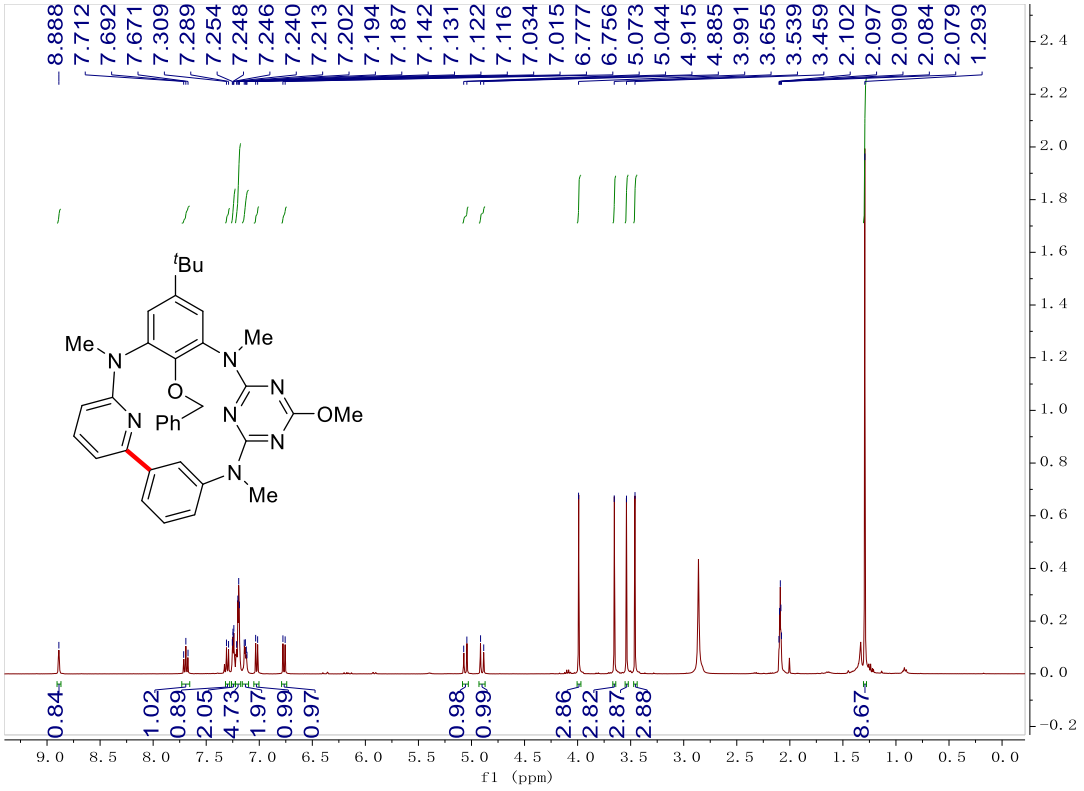
^{1}H NMR spectrum of **5c** in $CDCl_3$ at 298 K



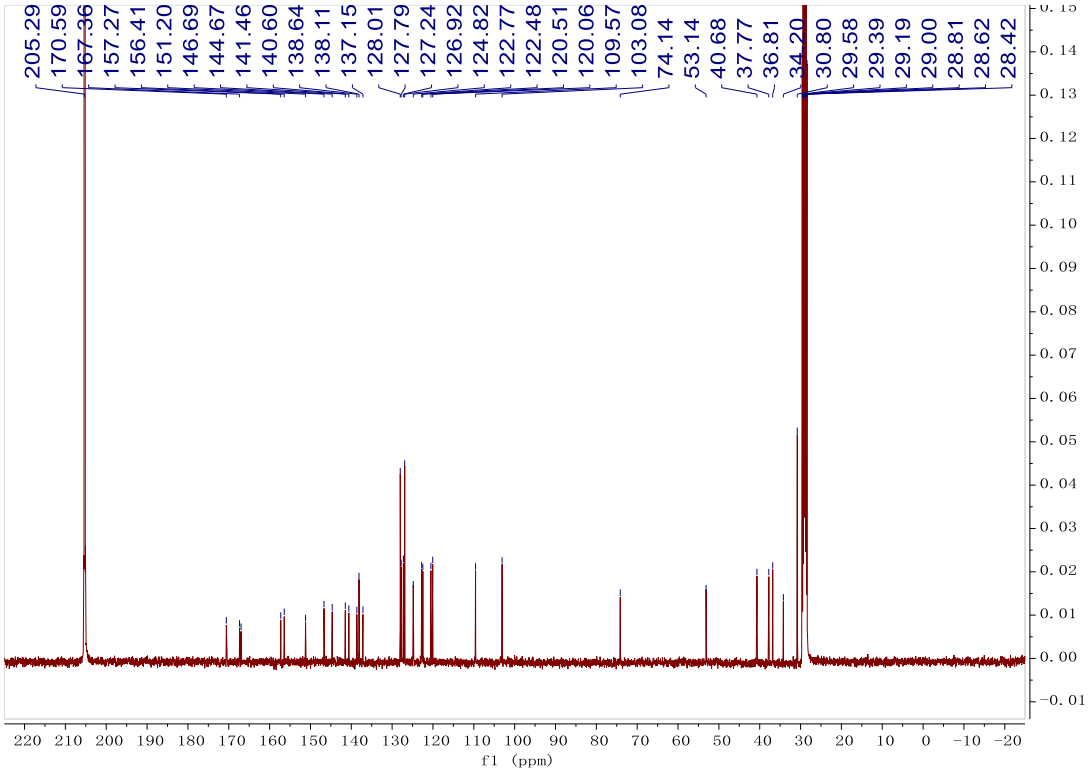
^{13}C NMR spectrum of **5c** in $CDCl_3$ at 298 K



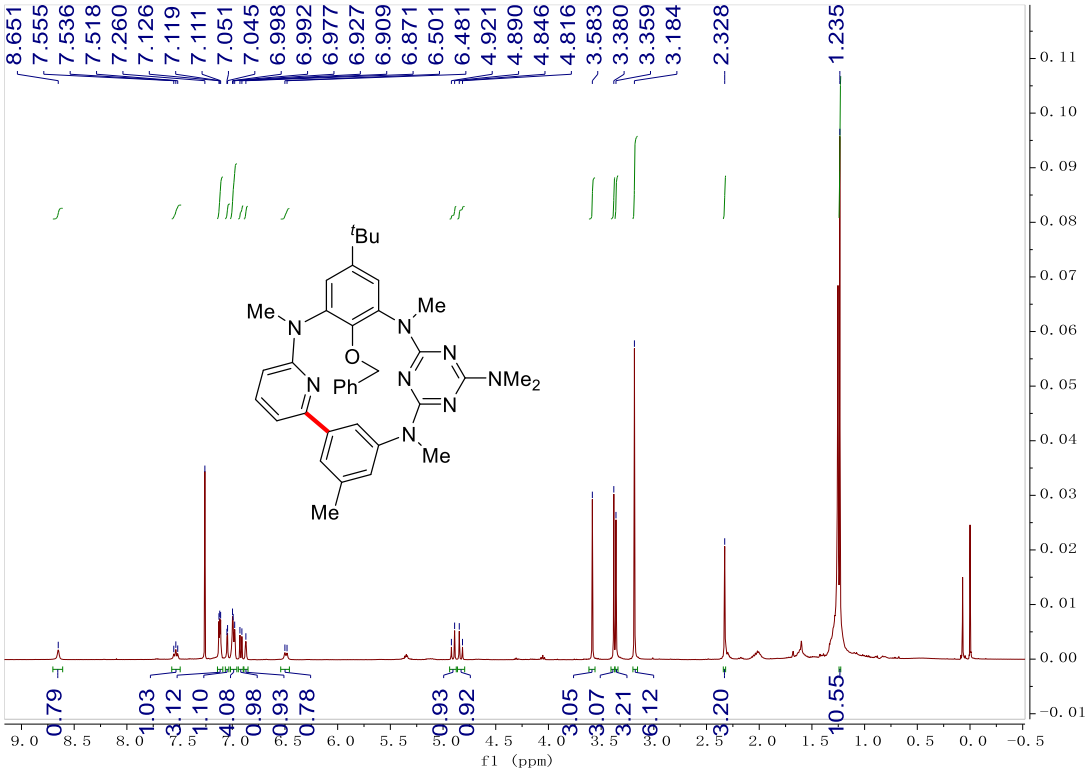
^{1}H NMR spectrum of **5d** in acetone-d_6 at 298 K



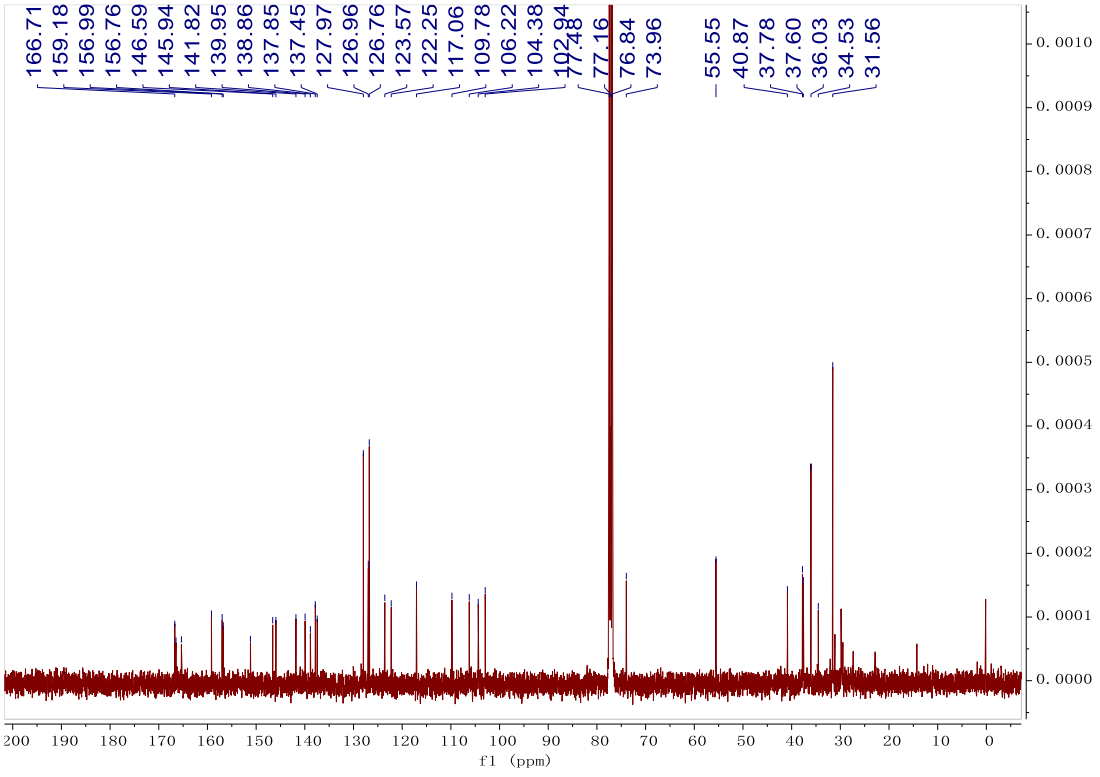
^{13}C NMR spectrum of **5d** in acetone-d_6 at 298 K



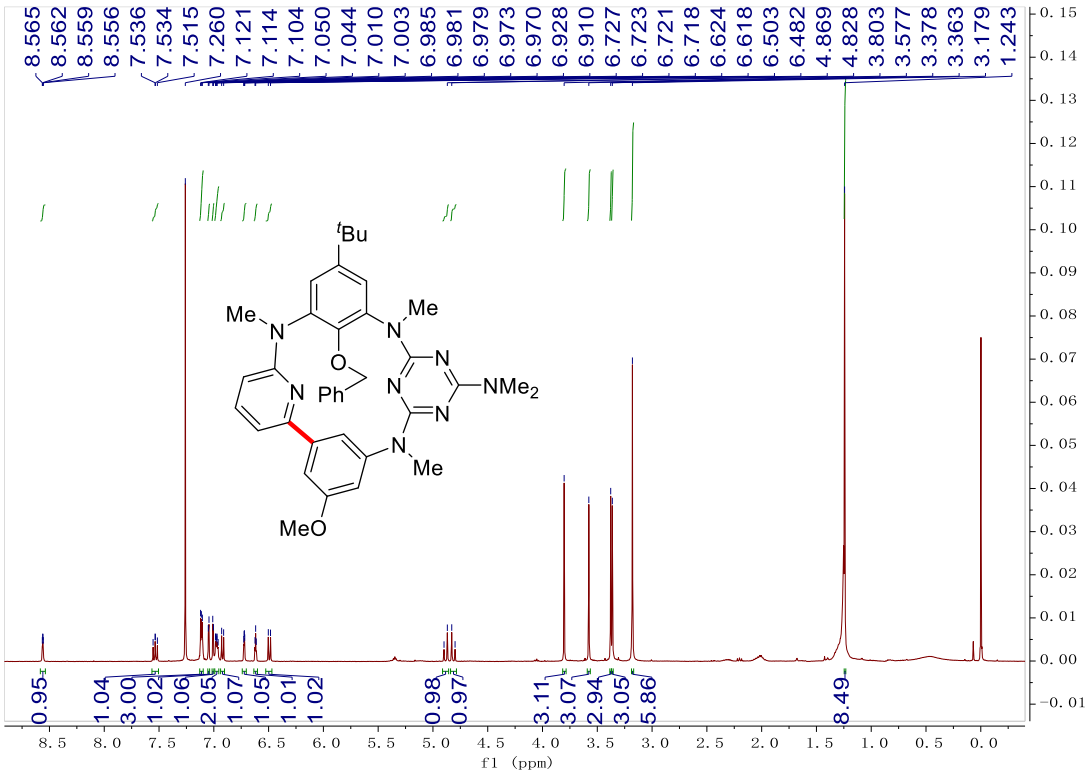
^{1}H NMR spectrum of **5e** in $CDCl_3$ at 298 K



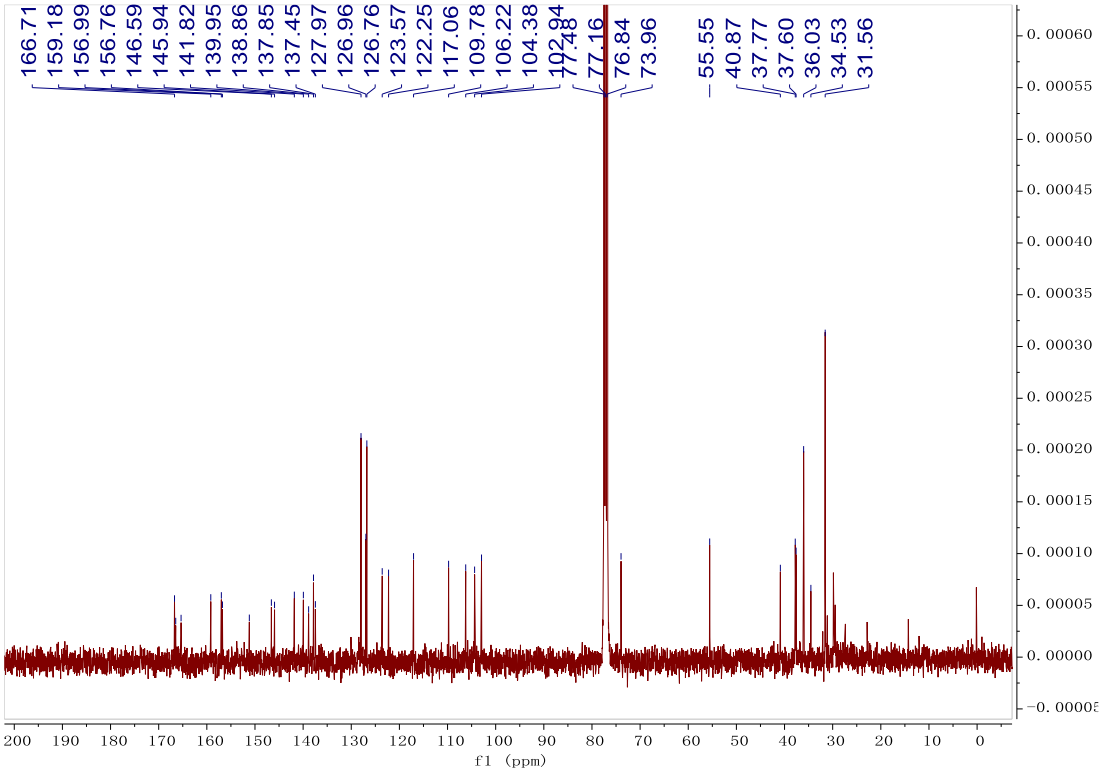
^{13}C NMR spectrum of **5e** in $CDCl_3$ at 298 K



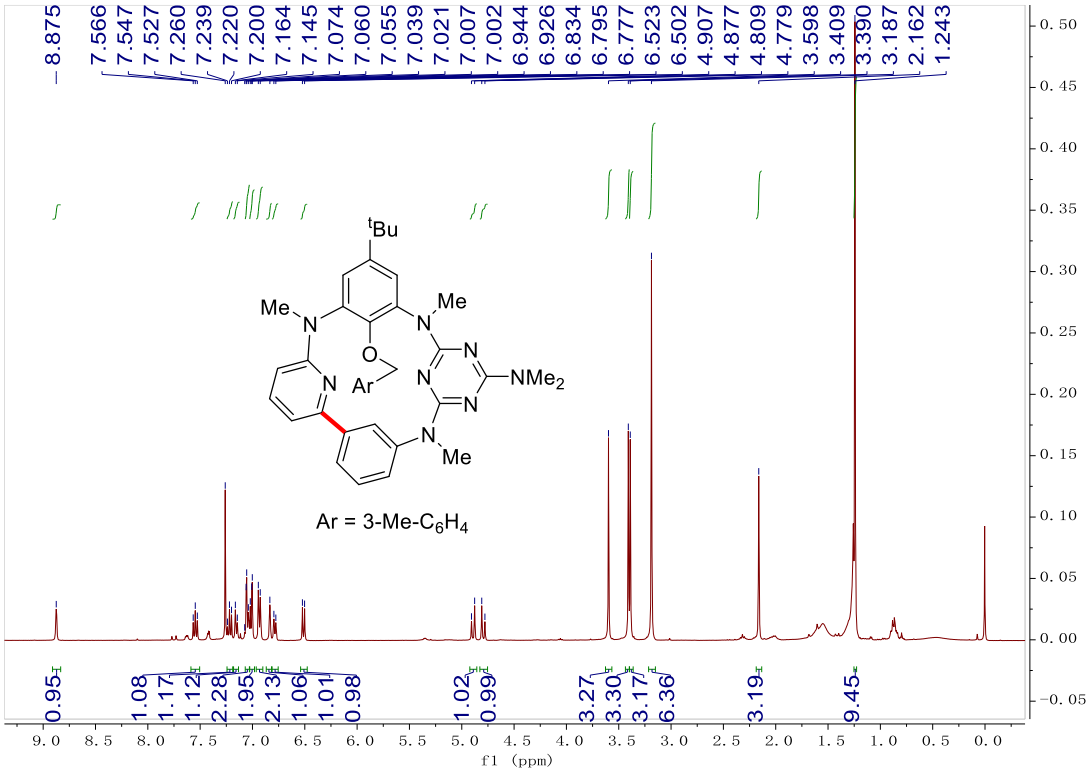
^{1}H NMR spectrum of **5f** in $CDCl_3$ at 298 K



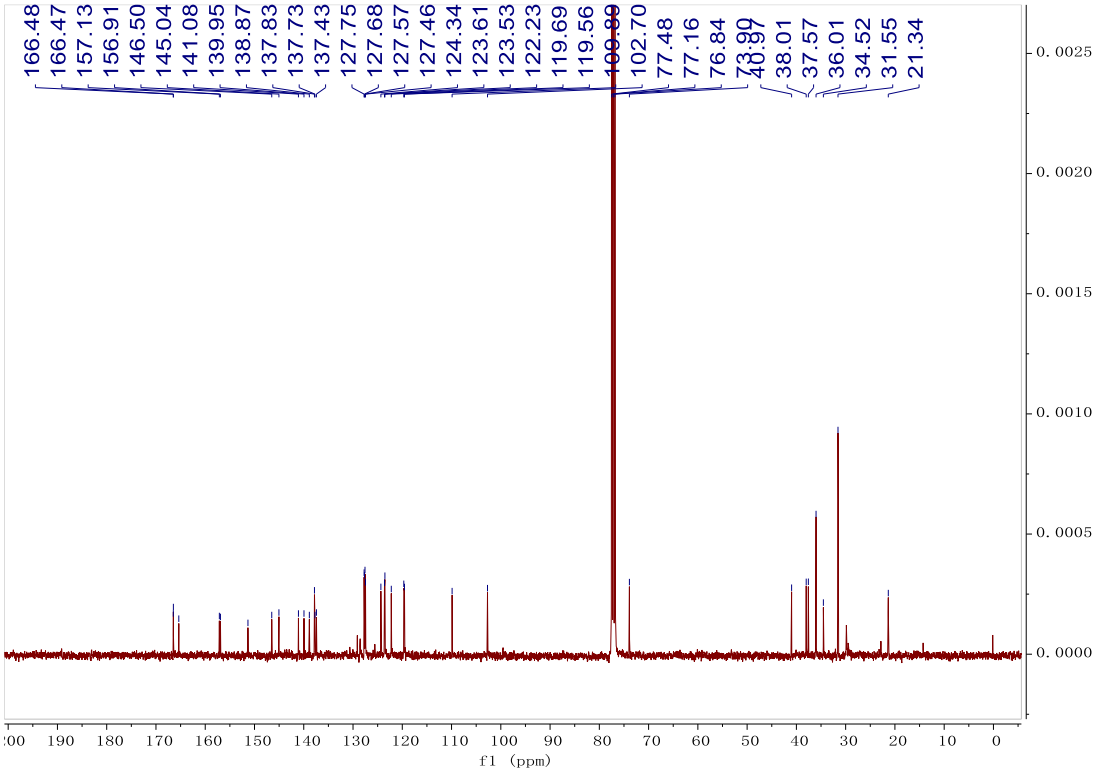
^{13}C NMR spectrum of **5f** in $CDCl_3$ at 298 K



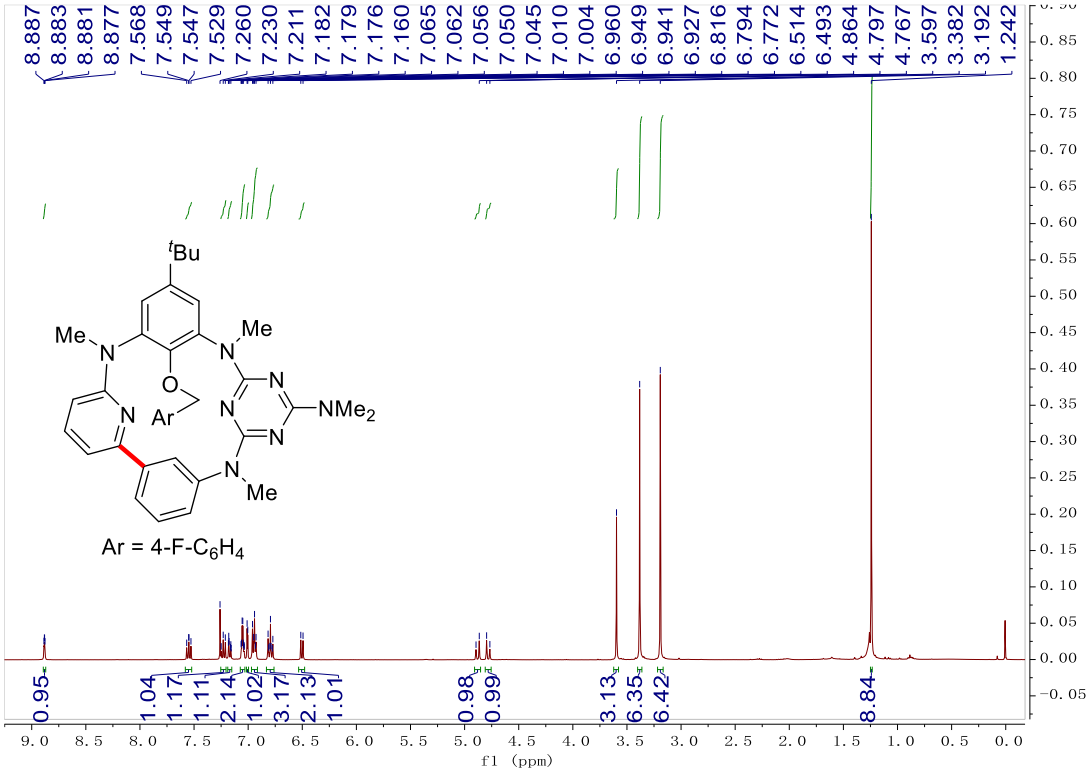
^{1}H NMR spectrum of **5g** in $CDCl_3$ at 298 K



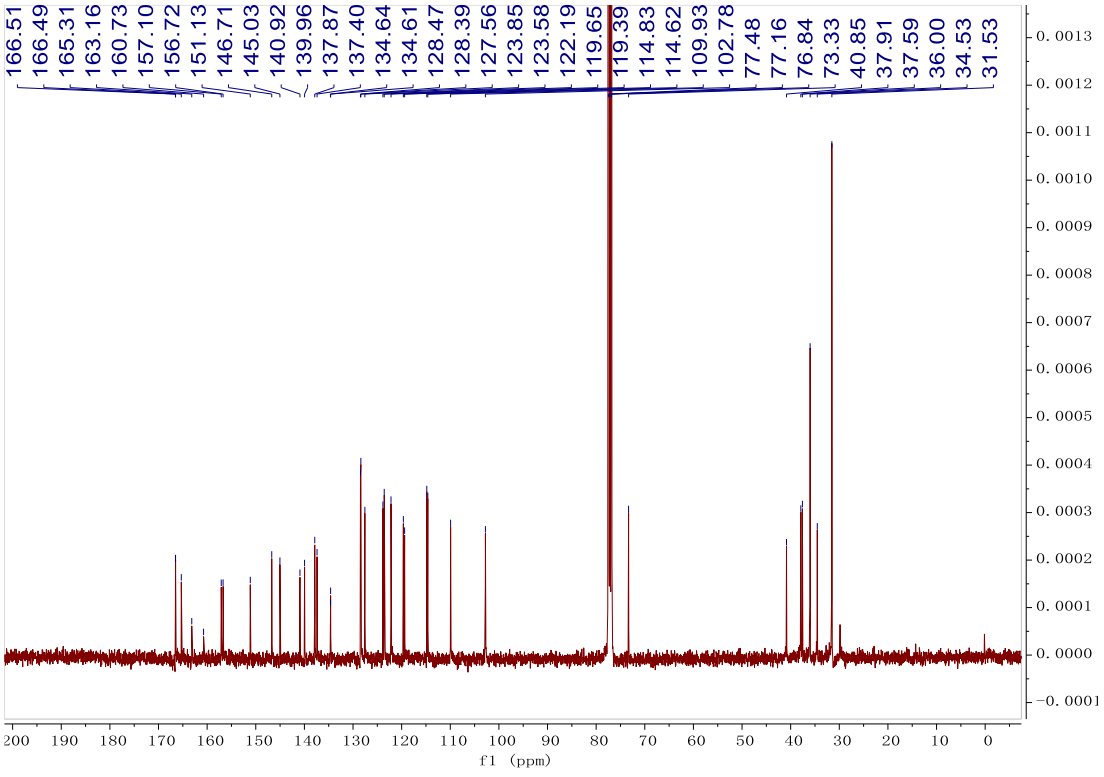
^{13}C NMR spectrum of **5g** in $CDCl_3$ at 298 K



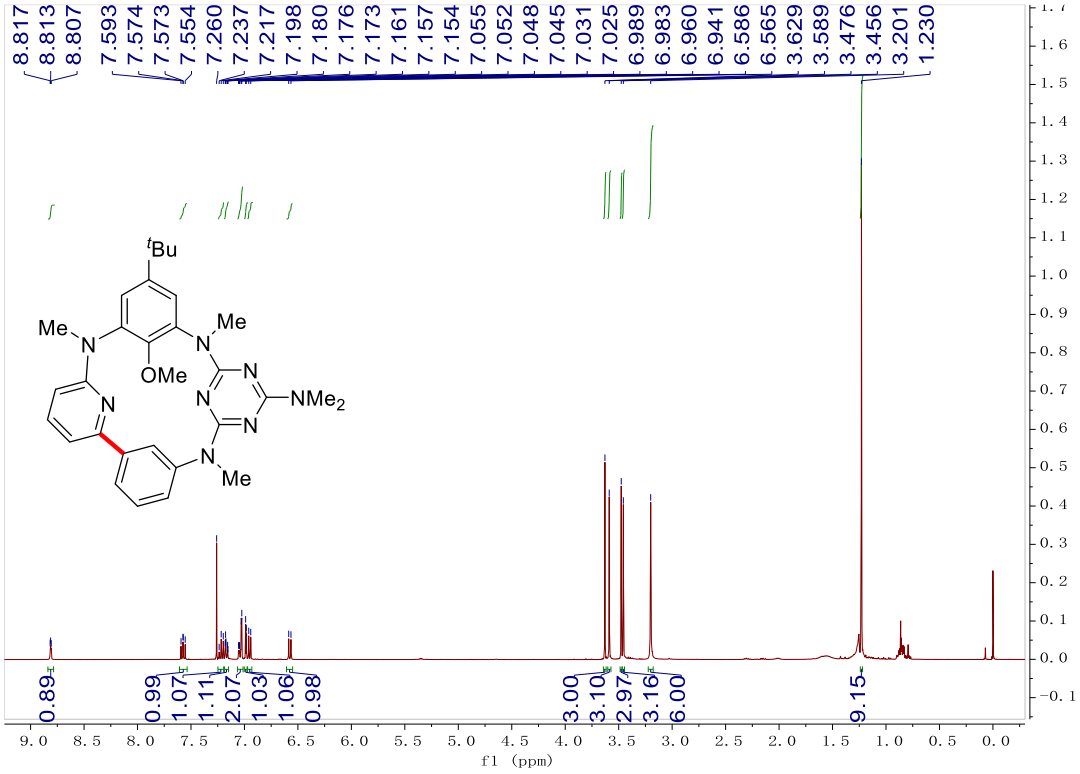
^{1}H NMR spectrum of **5h** in $CDCl_3$ at 298 K



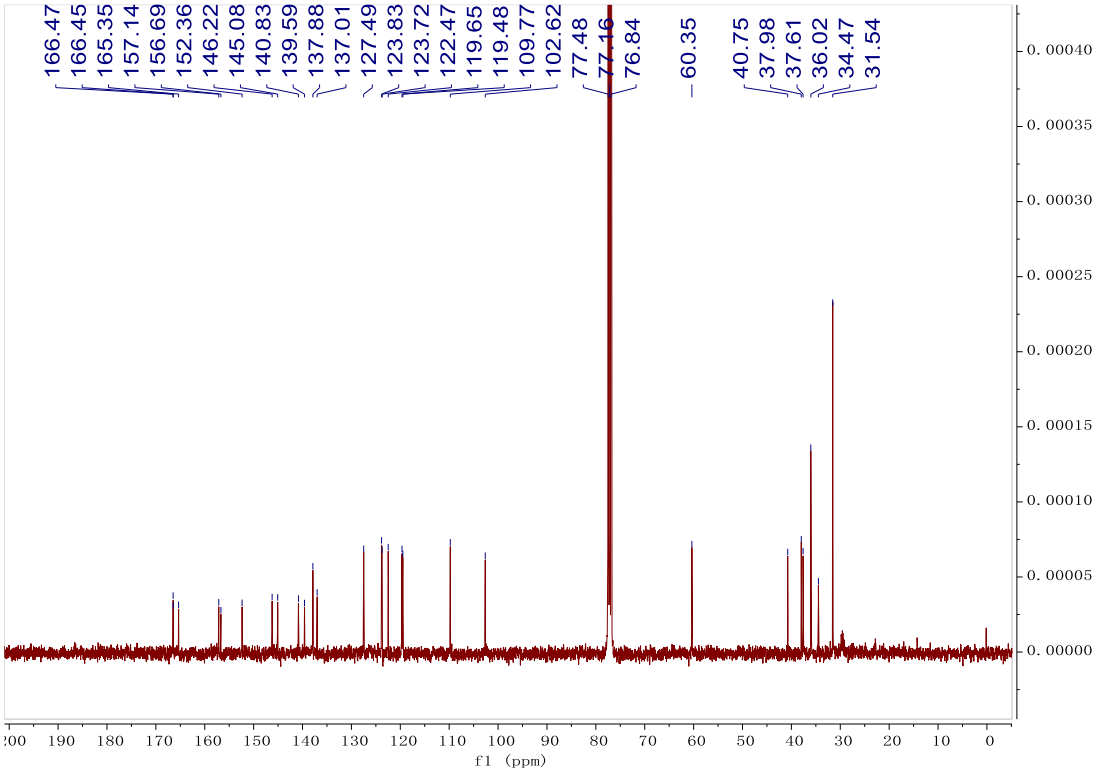
^{13}C NMR spectrum of **5h** in $CDCl_3$ at 298 K



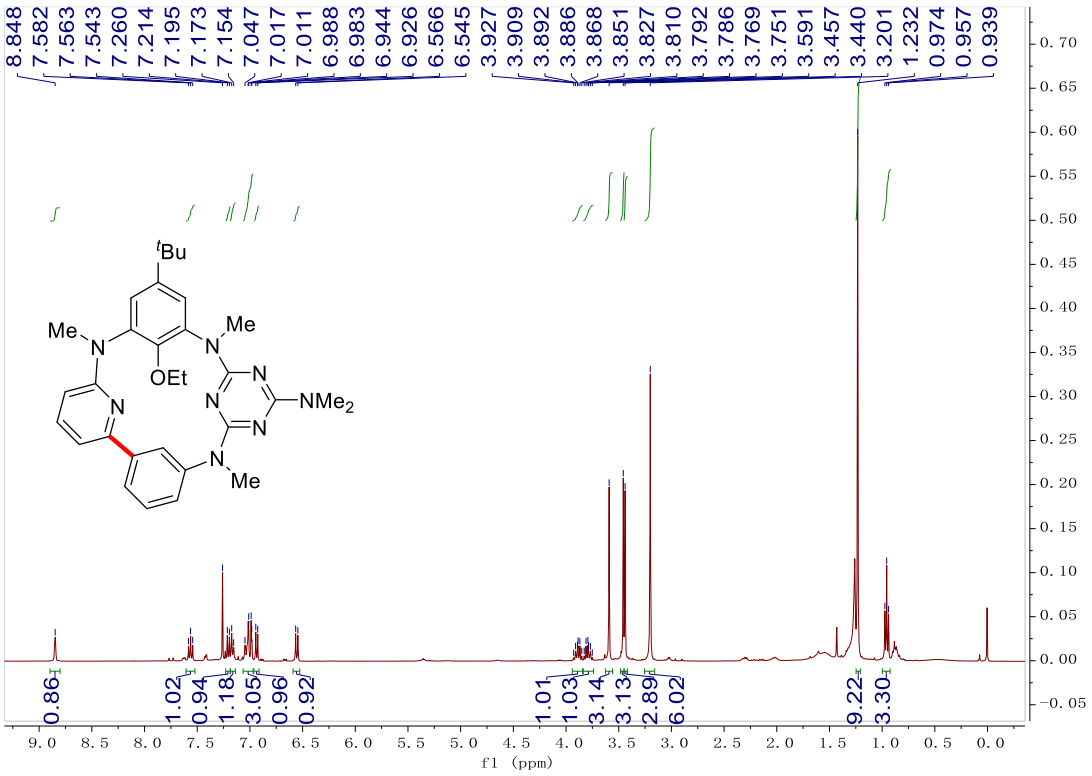
^{1}H NMR spectrum of **5i** in $CDCl_3$ at 298 K



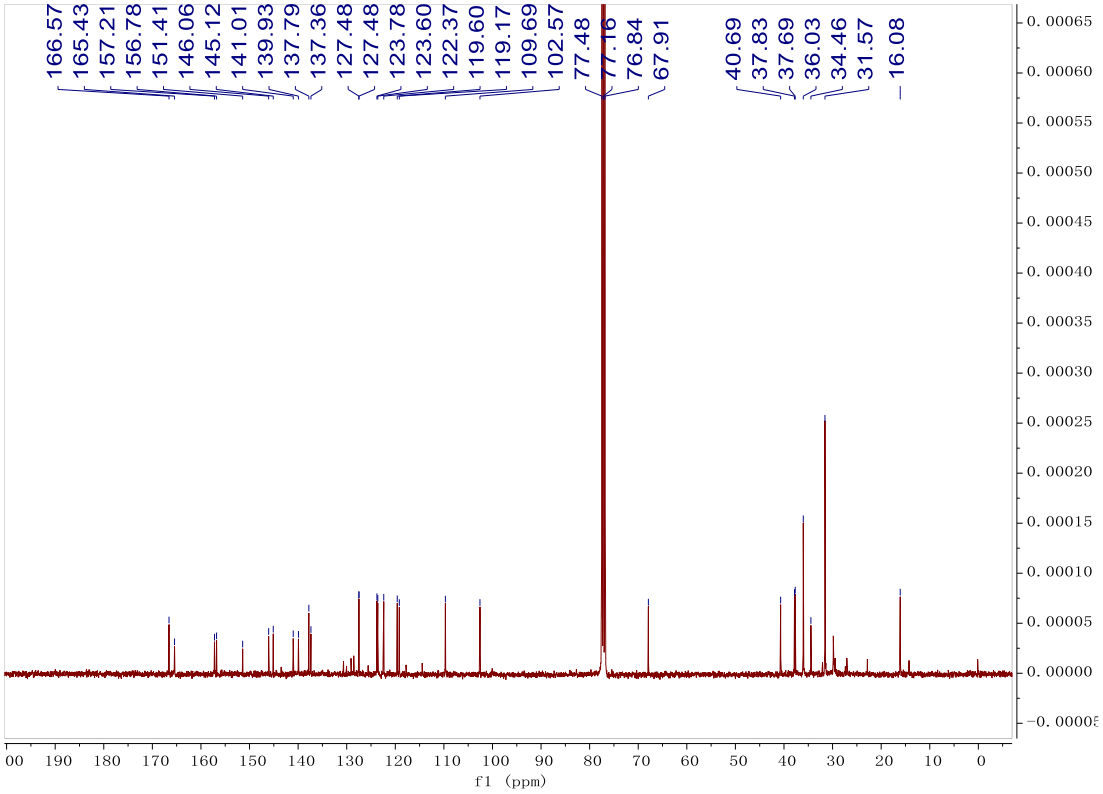
^{13}C NMR spectrum of **5i** in $CDCl_3$ at 298 K



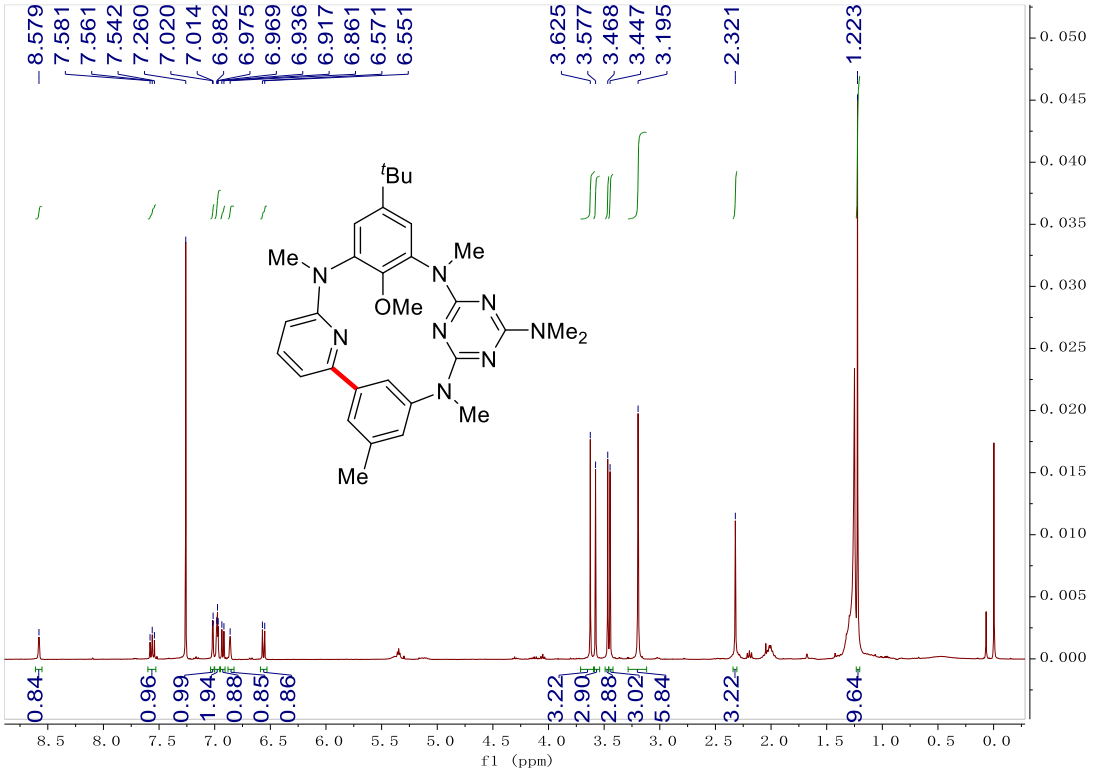
^{1}H NMR spectrum of **5j** in $CDCl_3$ at 298 K



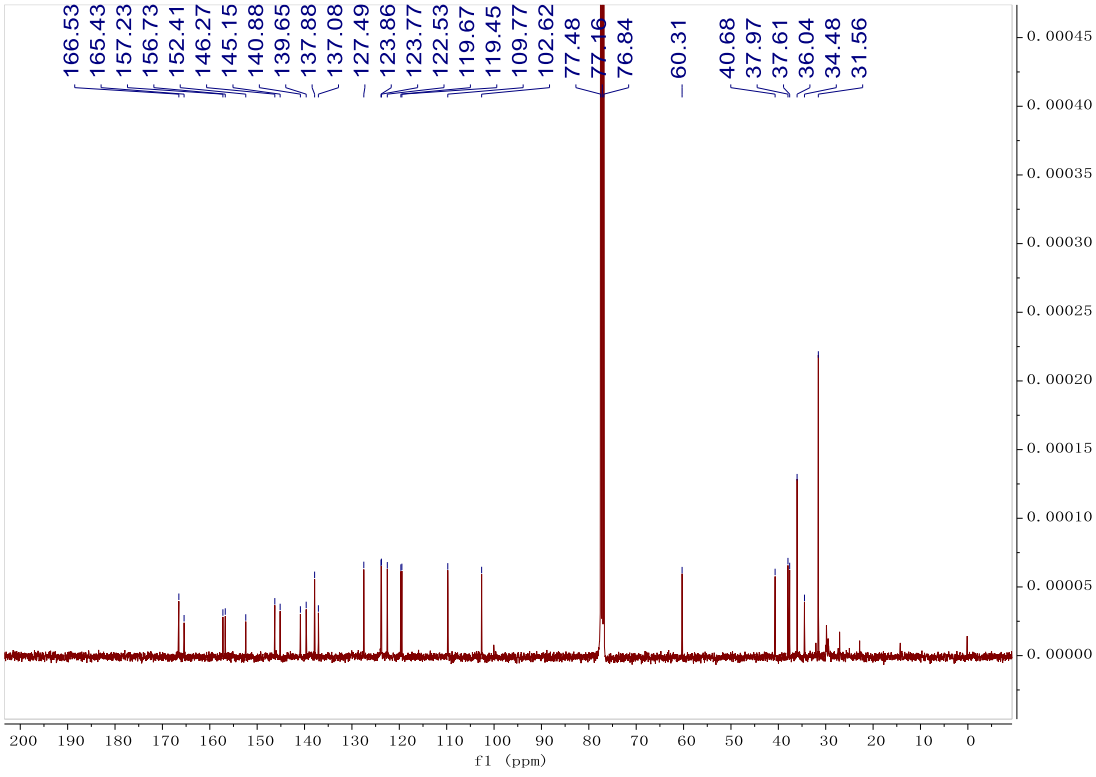
^{13}C NMR spectrum of **5j** in $CDCl_3$ at 298 K



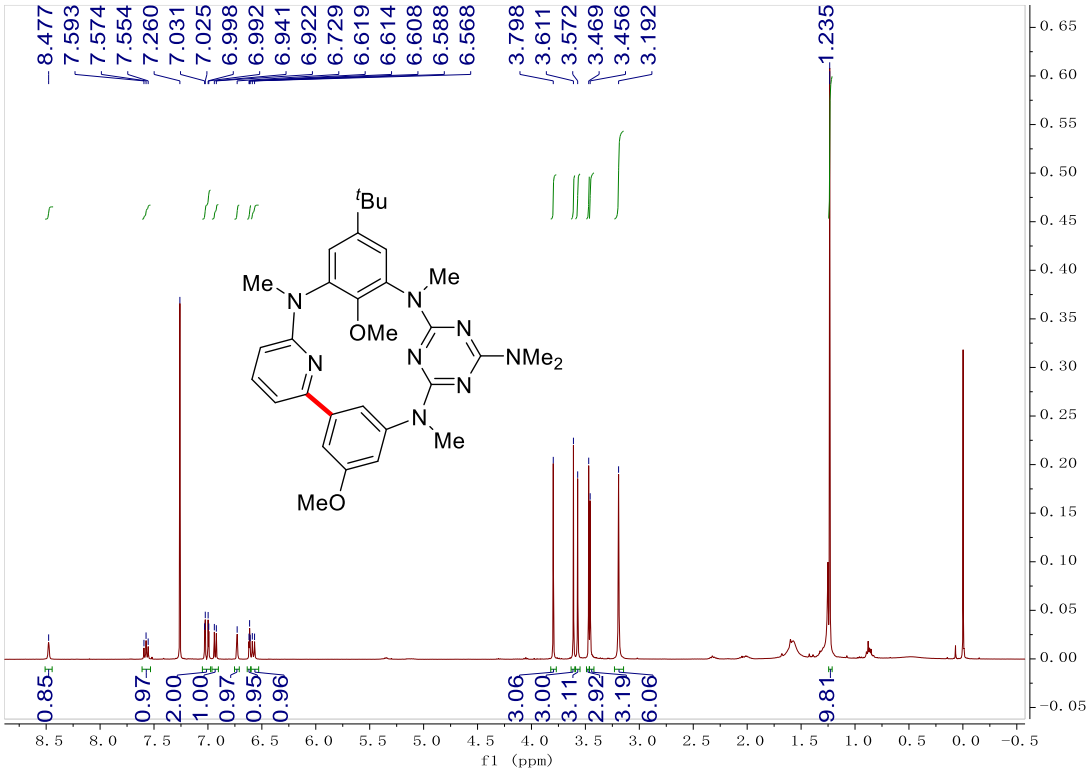
^{1}H NMR spectrum of **5k** in $CDCl_3$ at 298 K



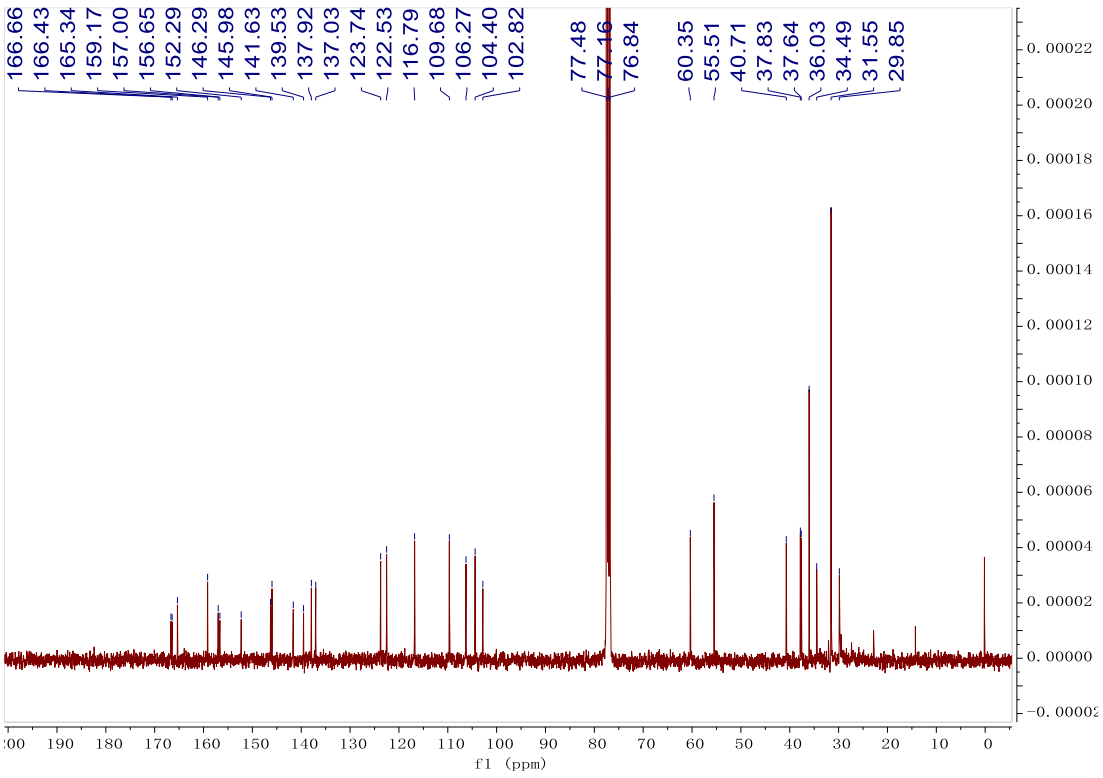
^{13}C NMR spectrum of **5k** in $CDCl_3$ at 298 K



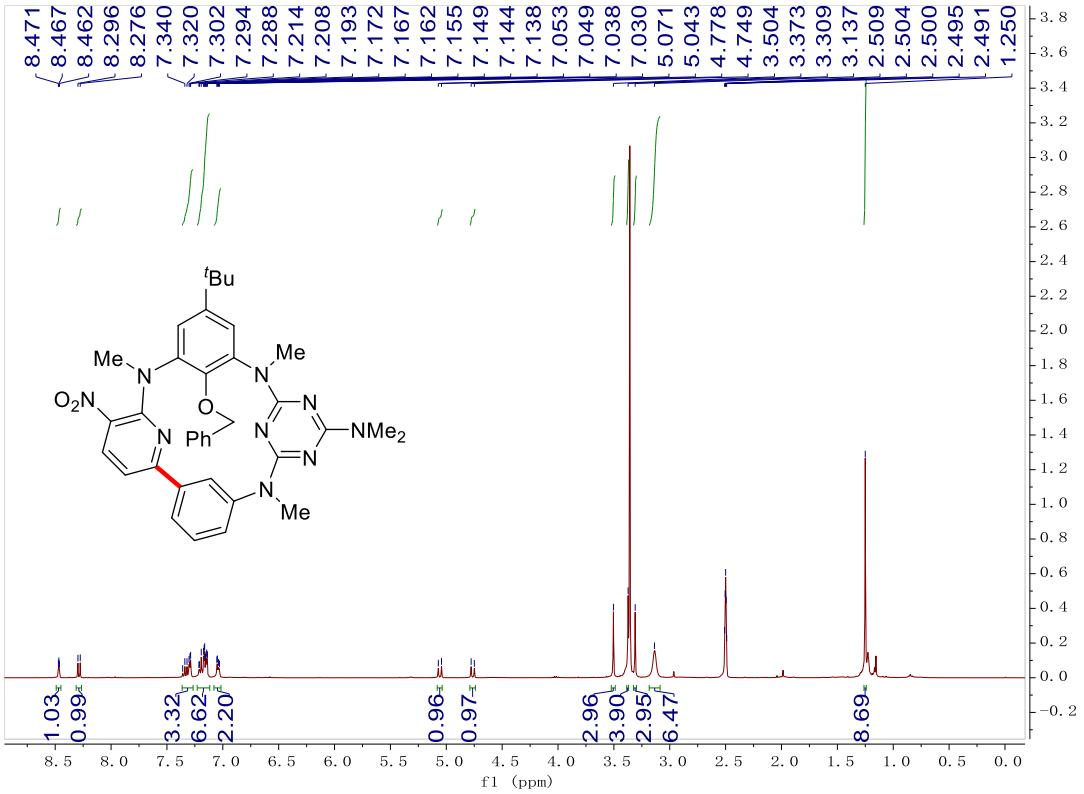
^{1}H NMR spectrum of **5l** in $CDCl_3$ at 298 K



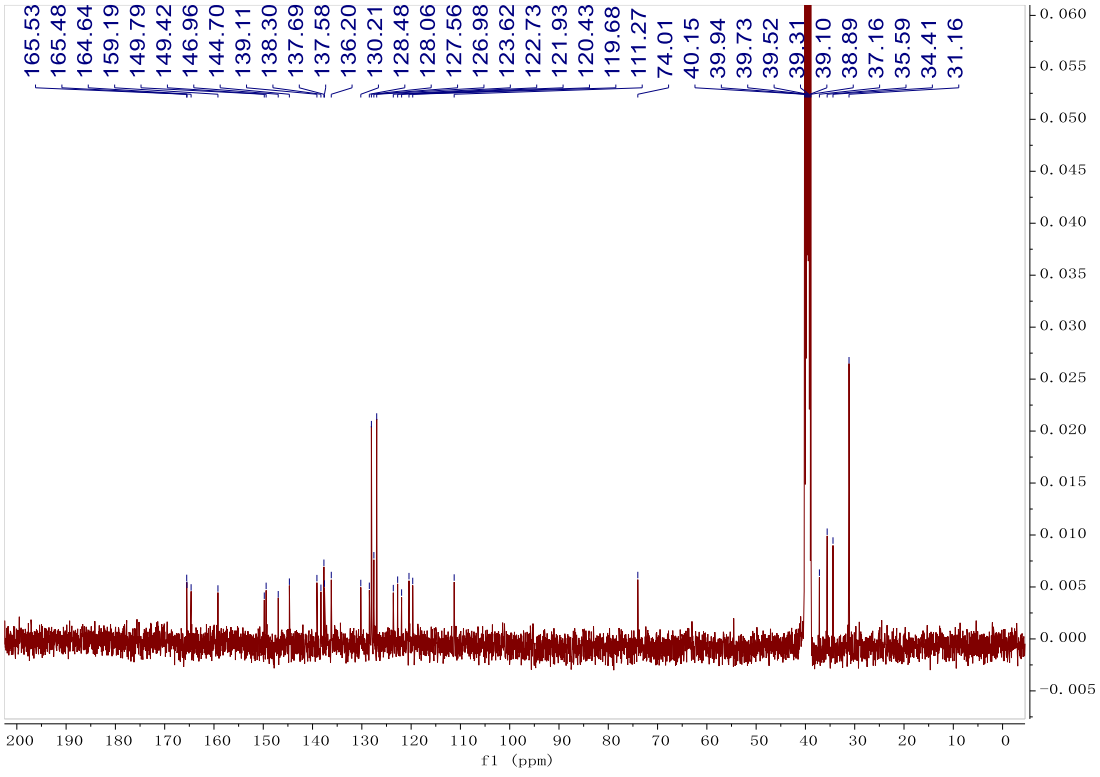
^{13}C NMR spectrum of **5l** in $CDCl_3$ at 298 K



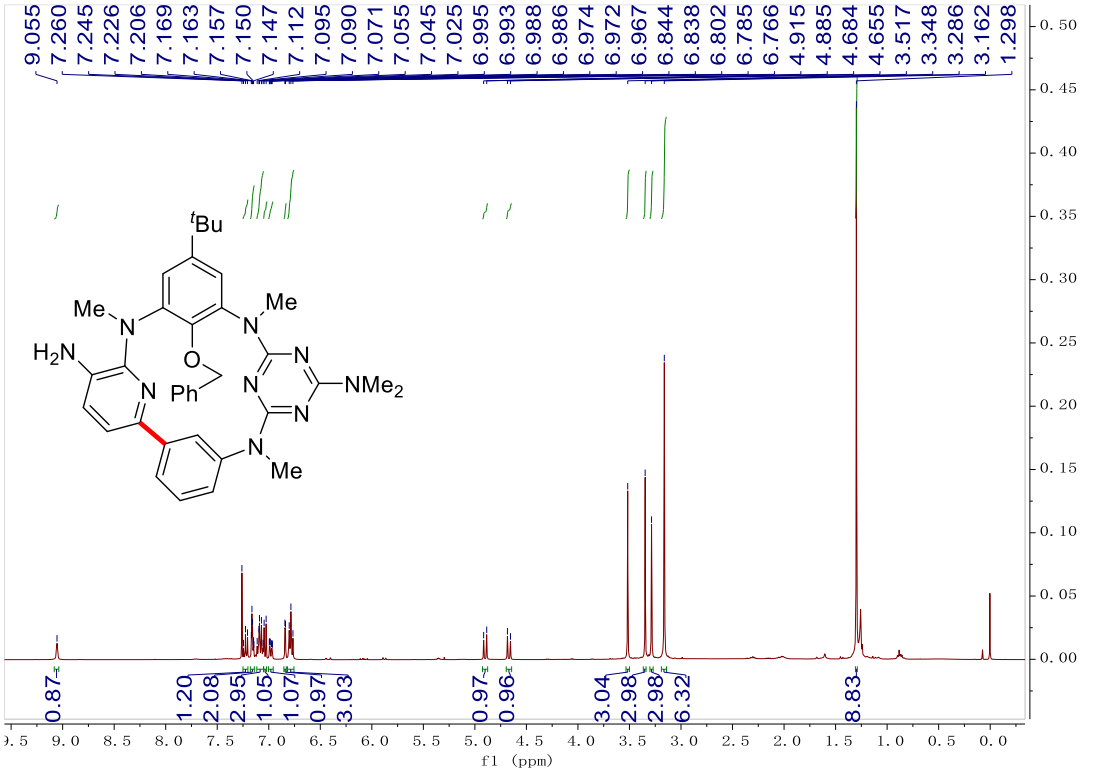
^{1}H NMR spectrum of **5m** in DMSO-d_6 at 298 K



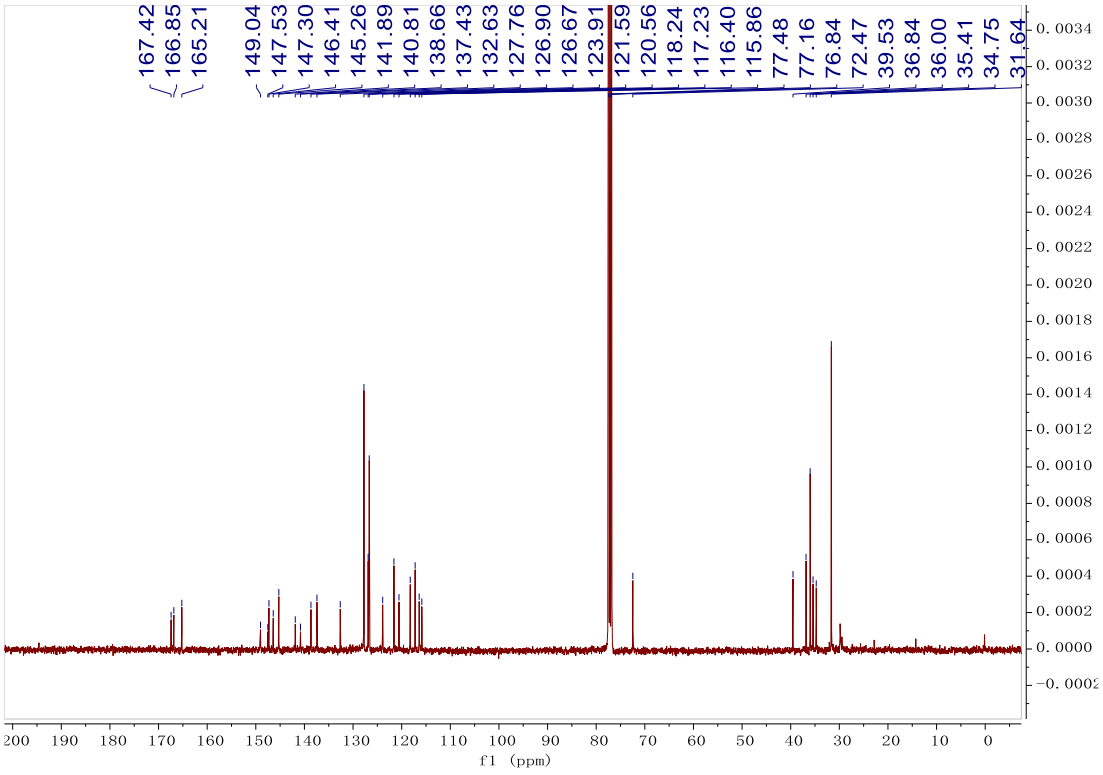
^{13}C NMR spectrum of **5m** in DMSO-d_6 at 298 K



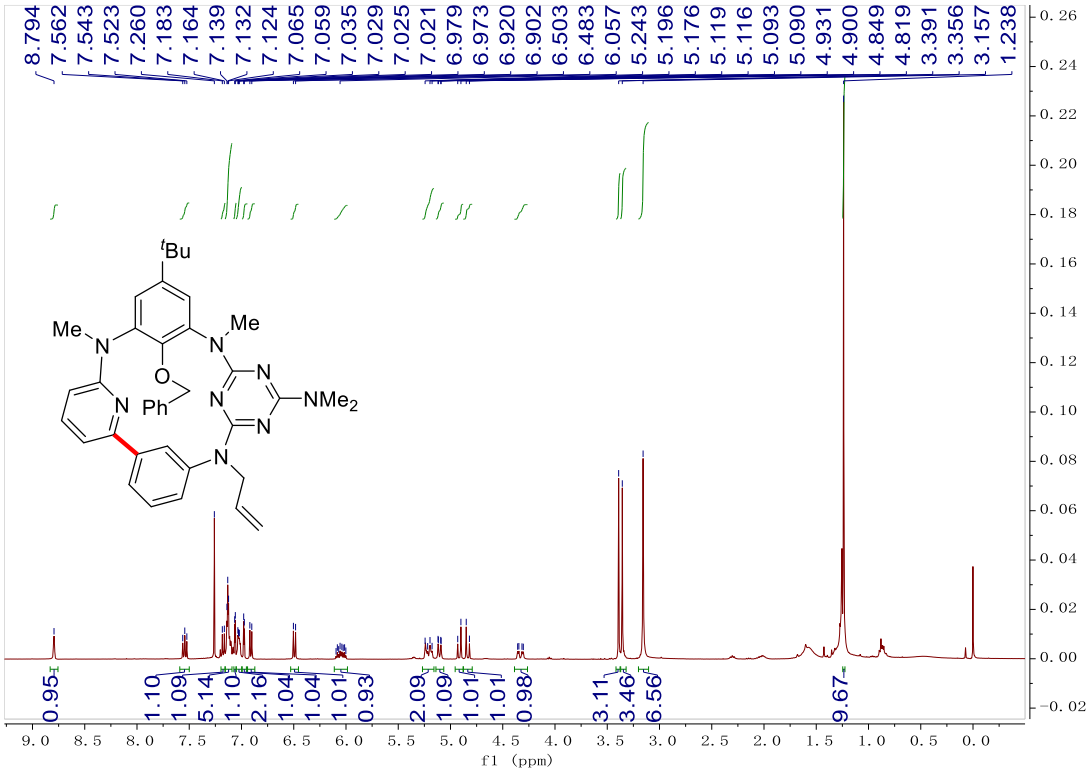
^{1}H NMR spectrum of **5n** in $CDCl_3$ at 298 K



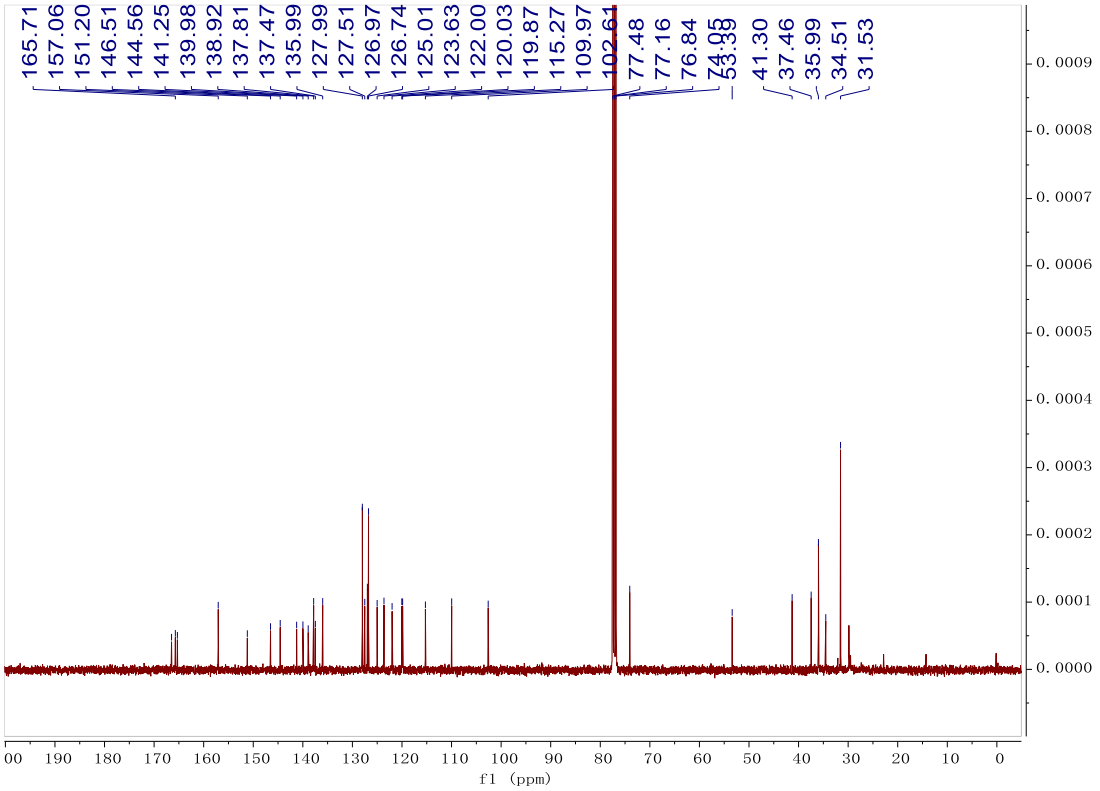
^{13}C NMR spectrum of **5n** in $CDCl_3$ at 298 K



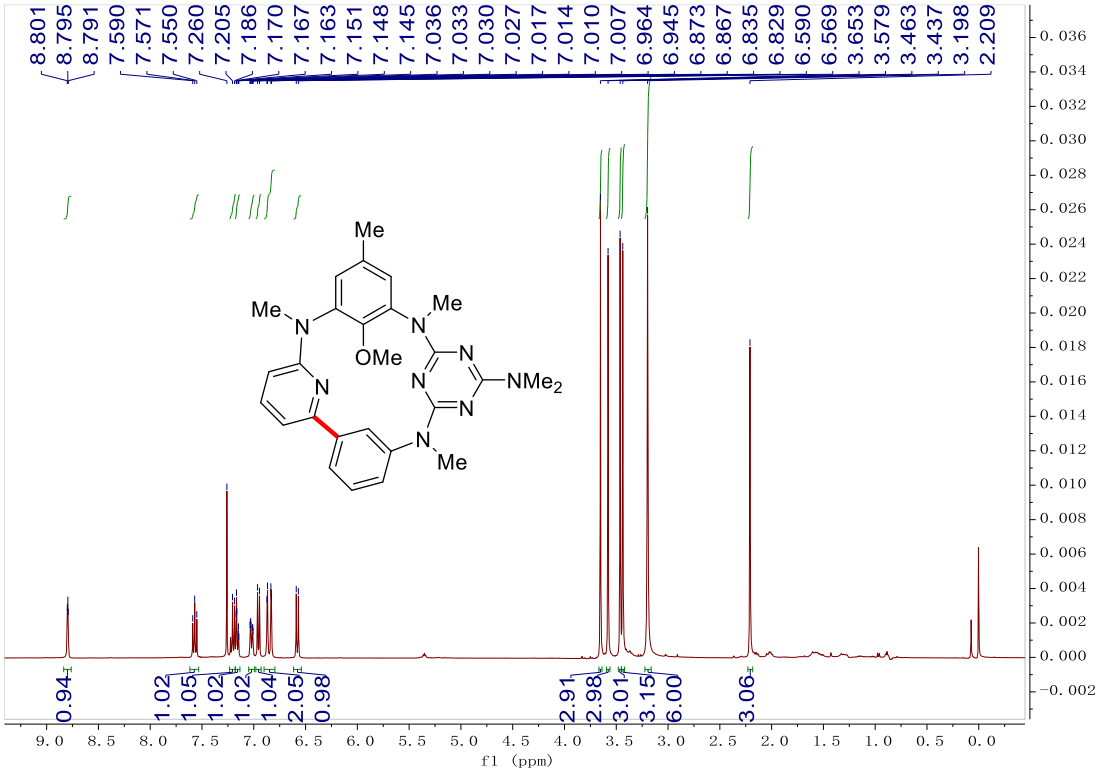
^{1}H NMR spectrum of **5o** in $CDCl_3$ at 298 K



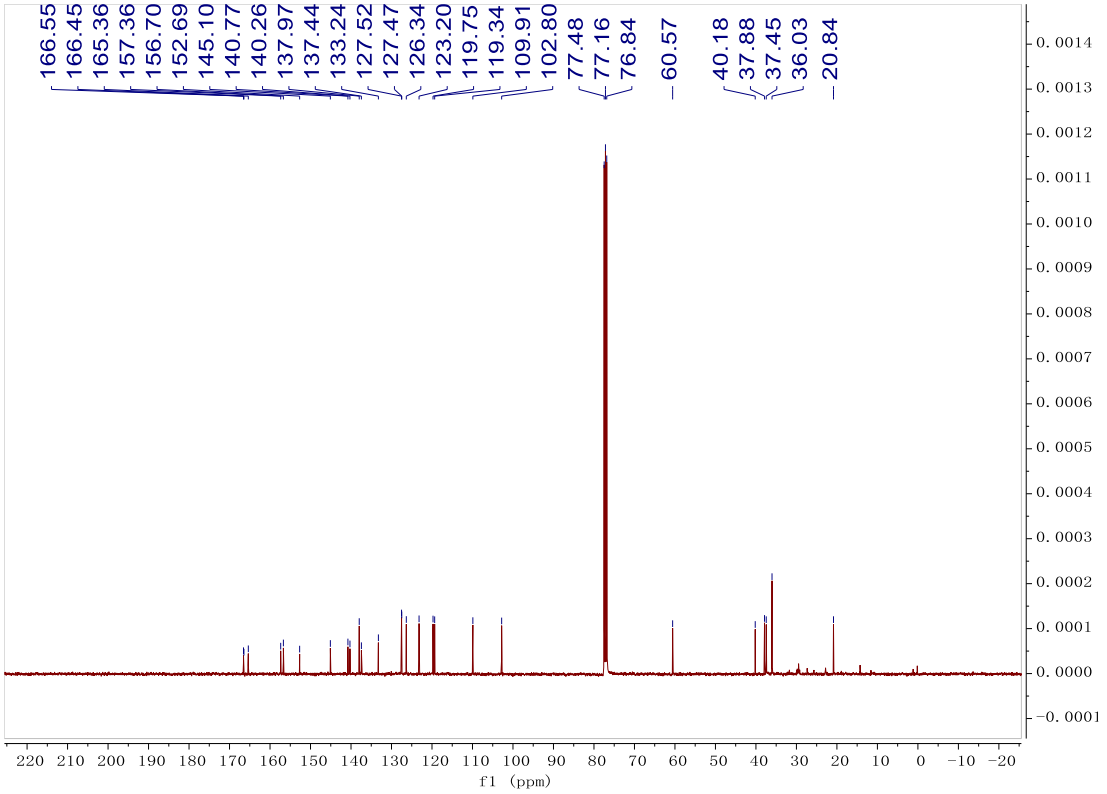
^{13}C NMR spectrum of **5o** in $CDCl_3$ at 298 K



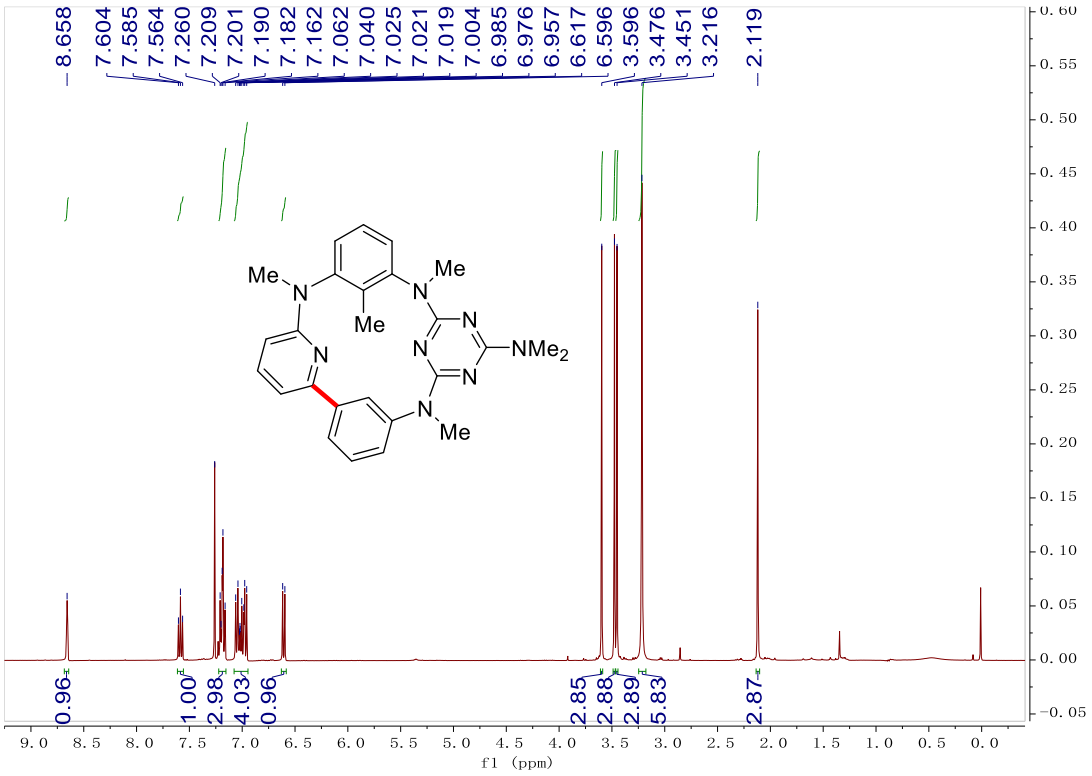
^{1}H NMR spectrum of **5p** in $CDCl_3$ at 298 K



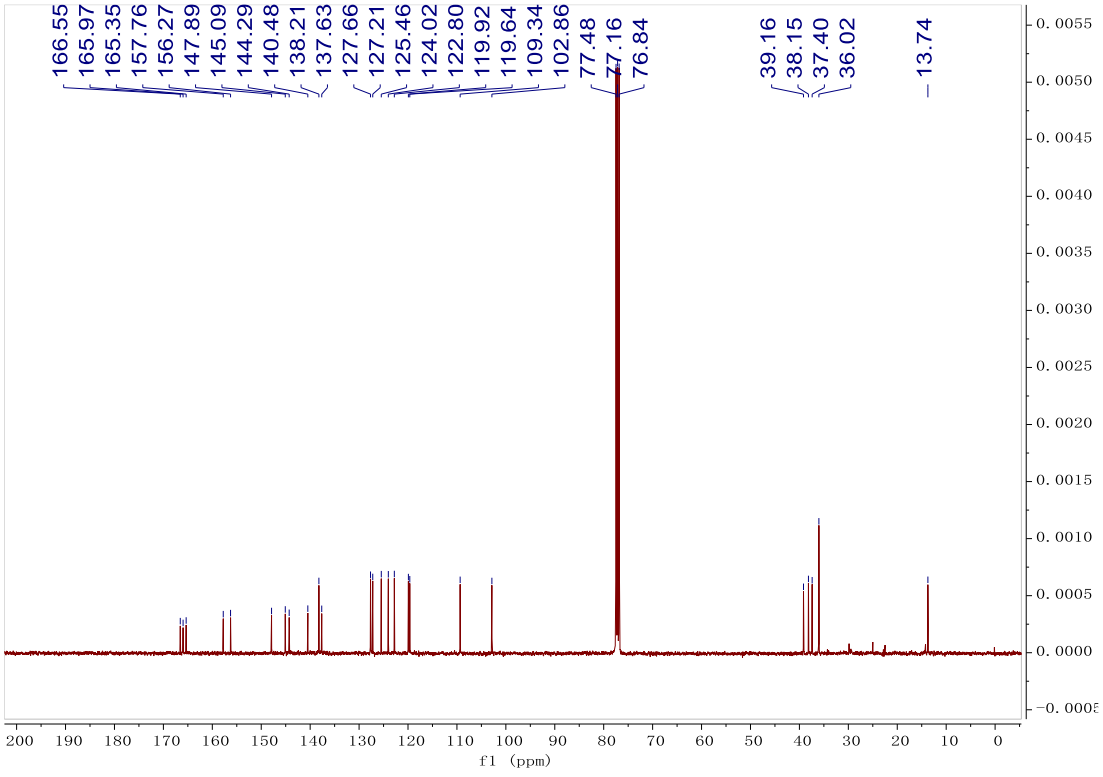
^{13}C NMR spectrum of **5p** in $CDCl_3$ at 298 K



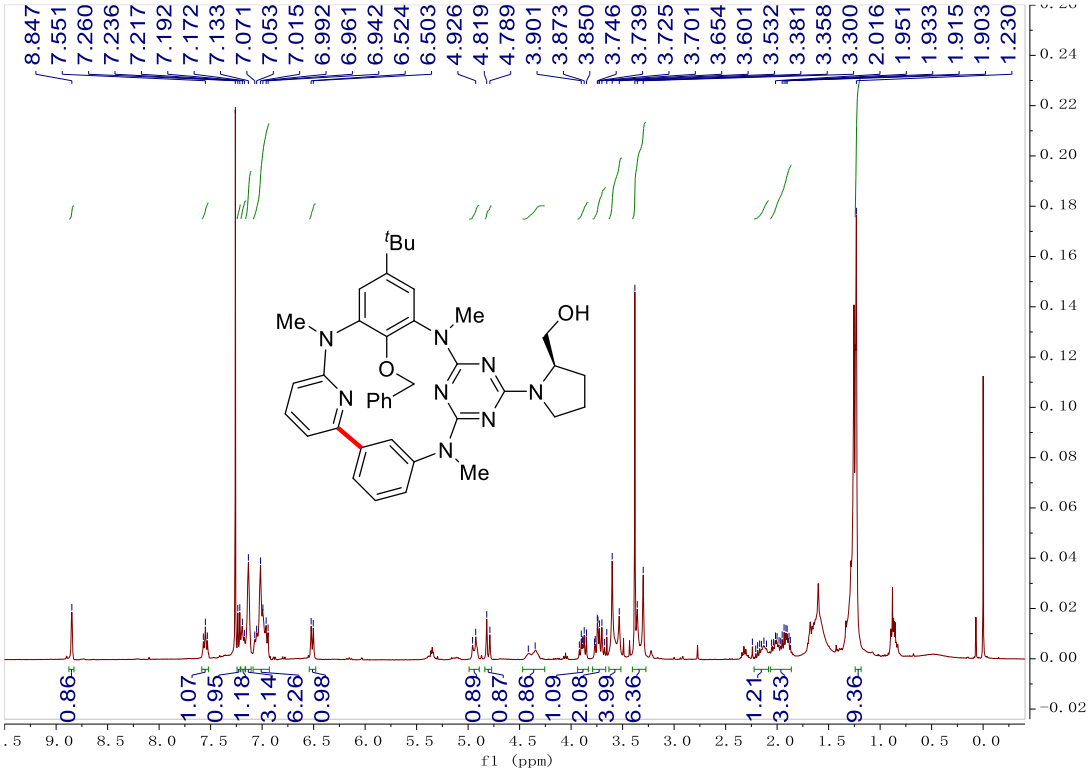
^{1}H NMR spectrum of **5q** in $CDCl_3$ at 298 K



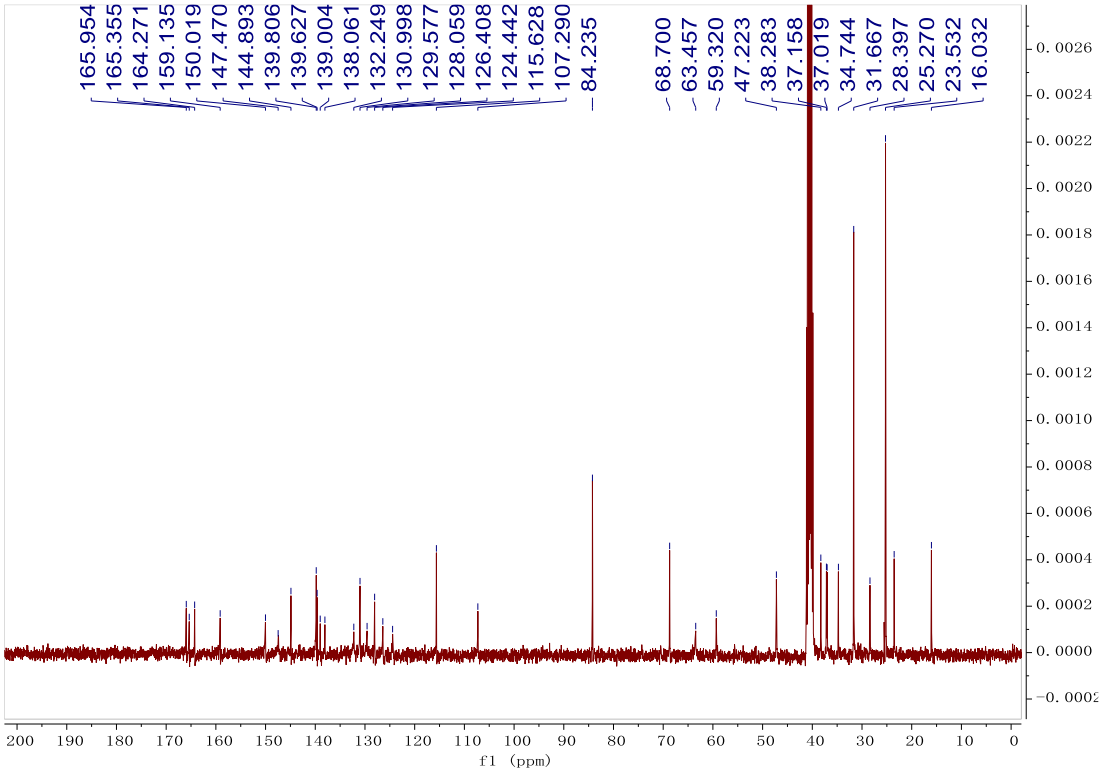
^{13}C NMR spectrum of **5q** in $CDCl_3$ at 298 K



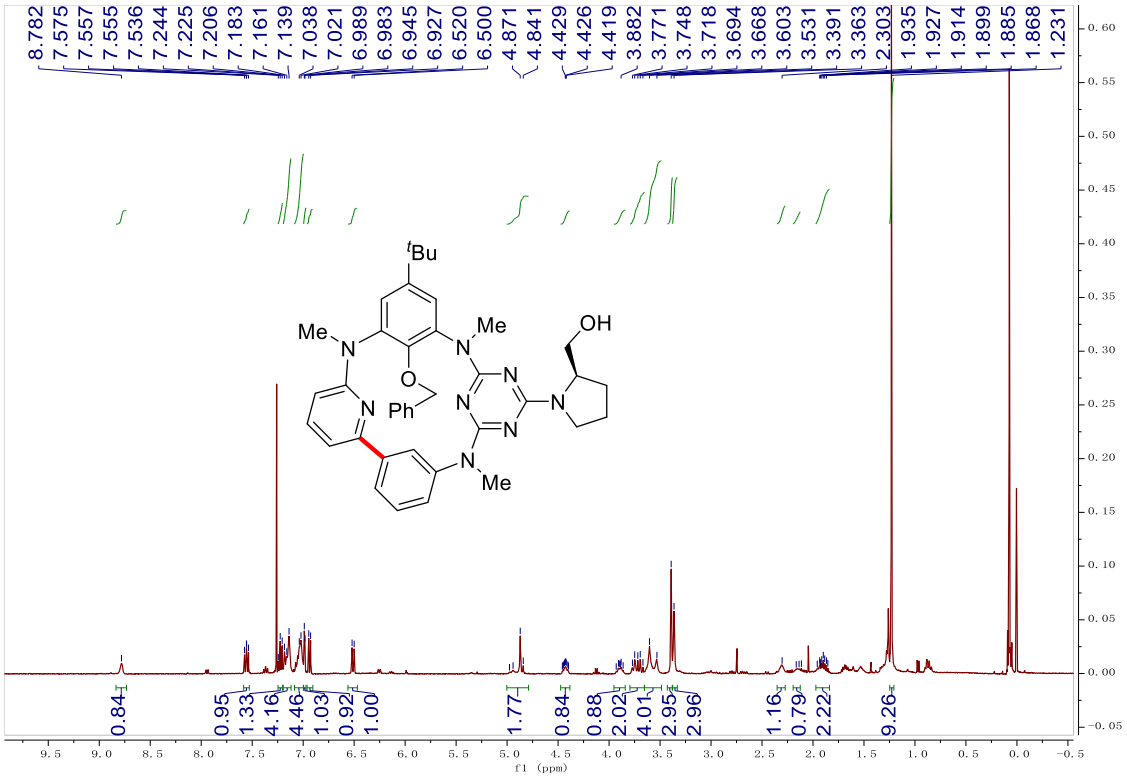
^{1}H NMR spectrum of **5r** (dr = 20 : 1) in $CDCl_3$ at 298 K



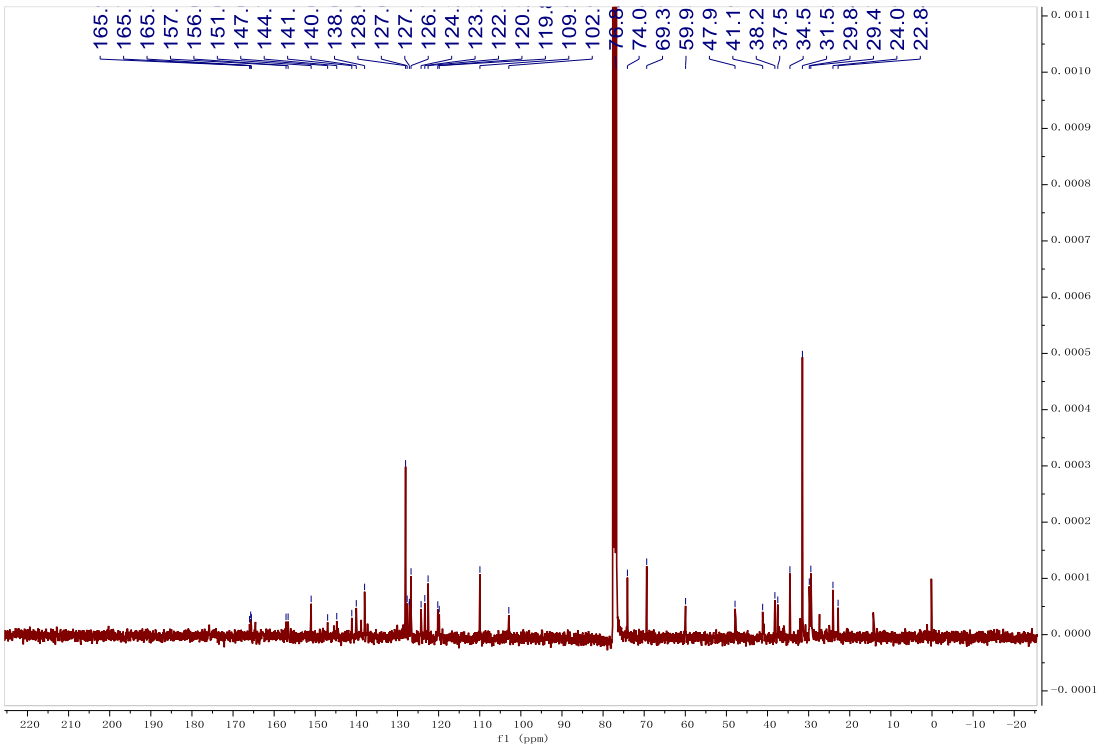
^{13}C NMR spectrum of **5r** (dr = 20 : 1) in DMSO-d_6 at 298 K



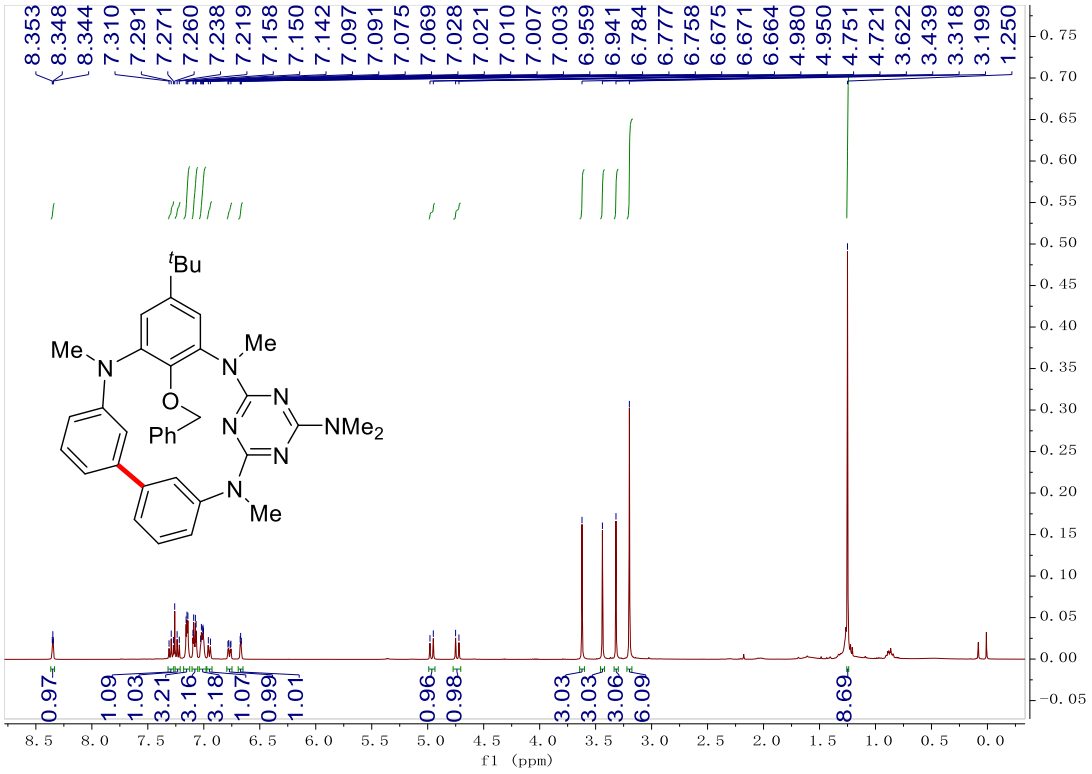
^{1}H NMR spectrum of **5r** (dr = 1 : 20) in $CDCl_3$ at 298 K



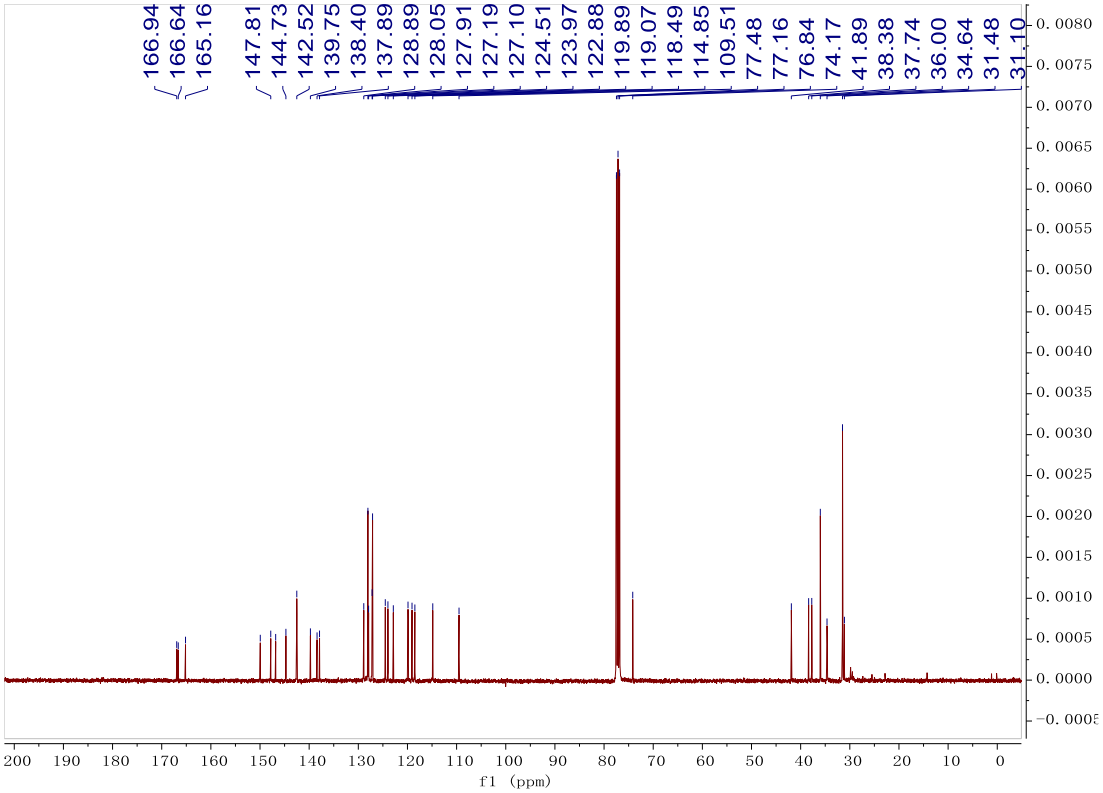
^{13}C NMR spectrum of **5r** (dr = 1 : 20) in $CDCl_3$ at 298 K



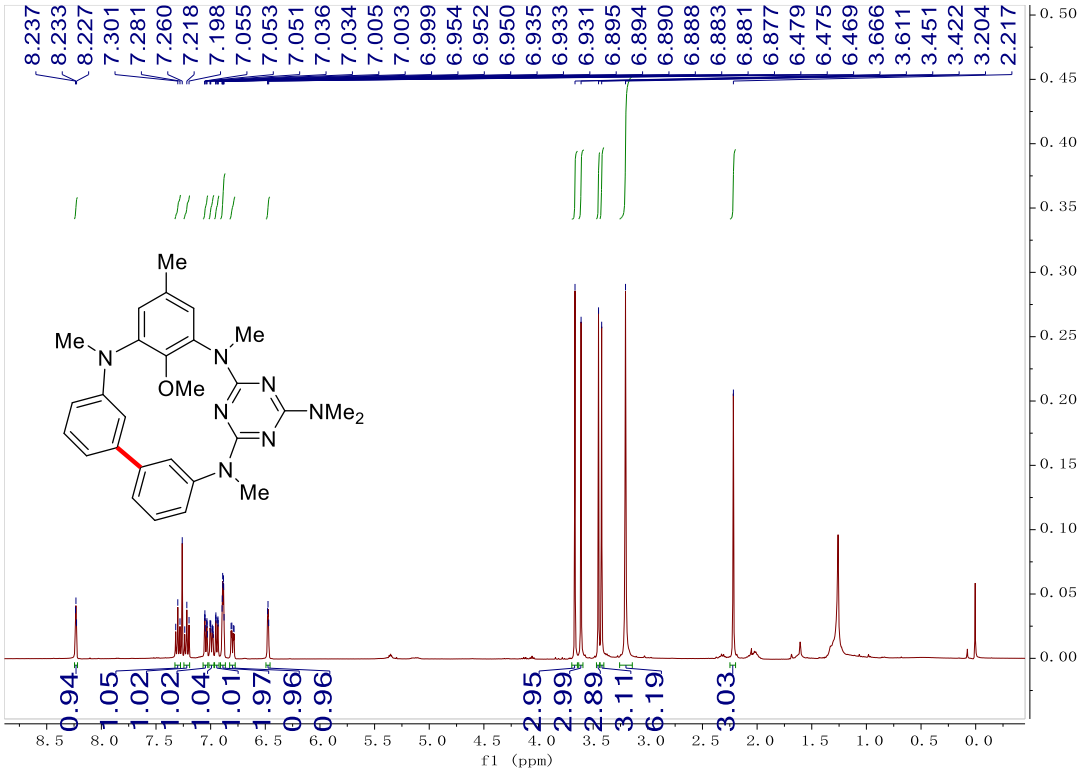
^{1}H NMR spectrum of **5s** in $CDCl_3$ at 298 K



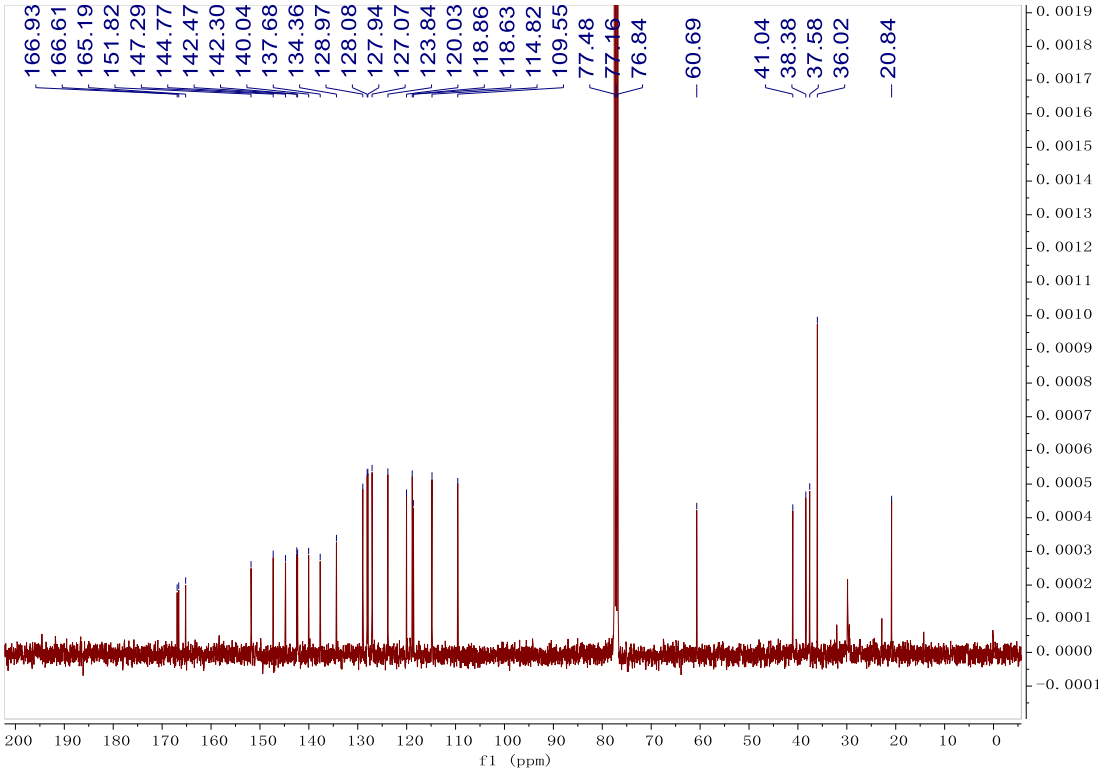
^{13}C NMR spectrum of **5s** in $CDCl_3$ at 298 K



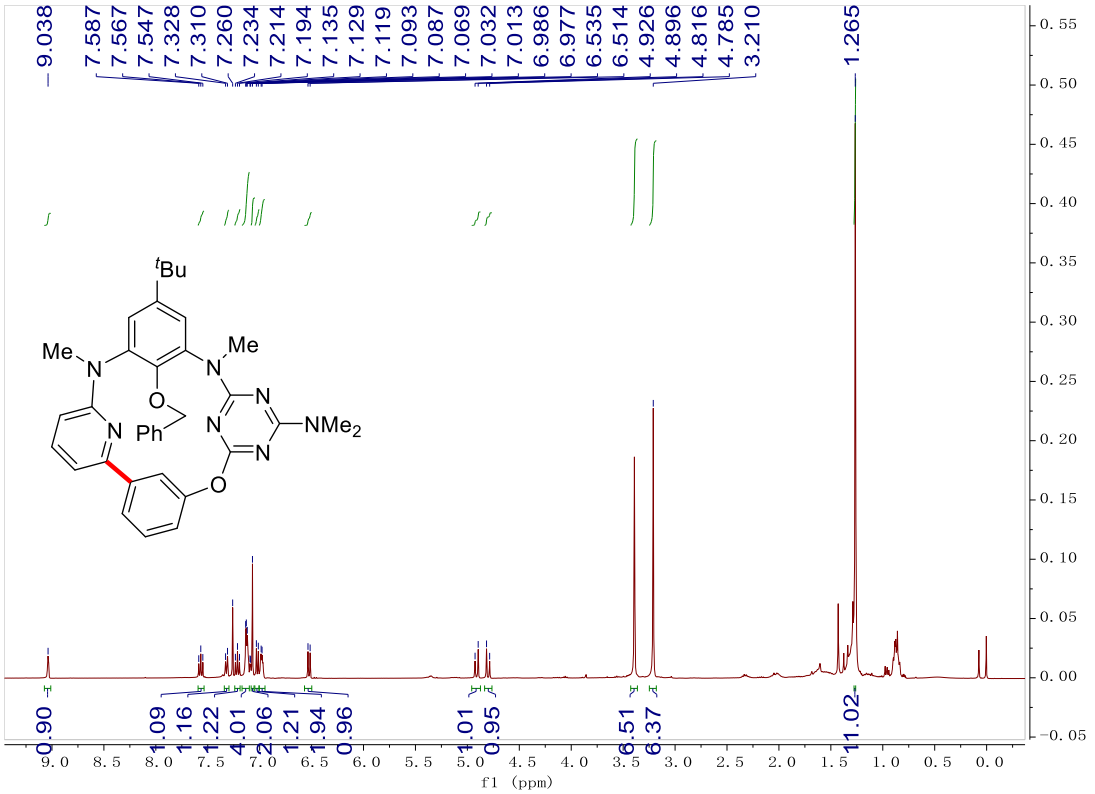
^{1}H NMR spectrum of **5t** in $CDCl_3$ at 298 K



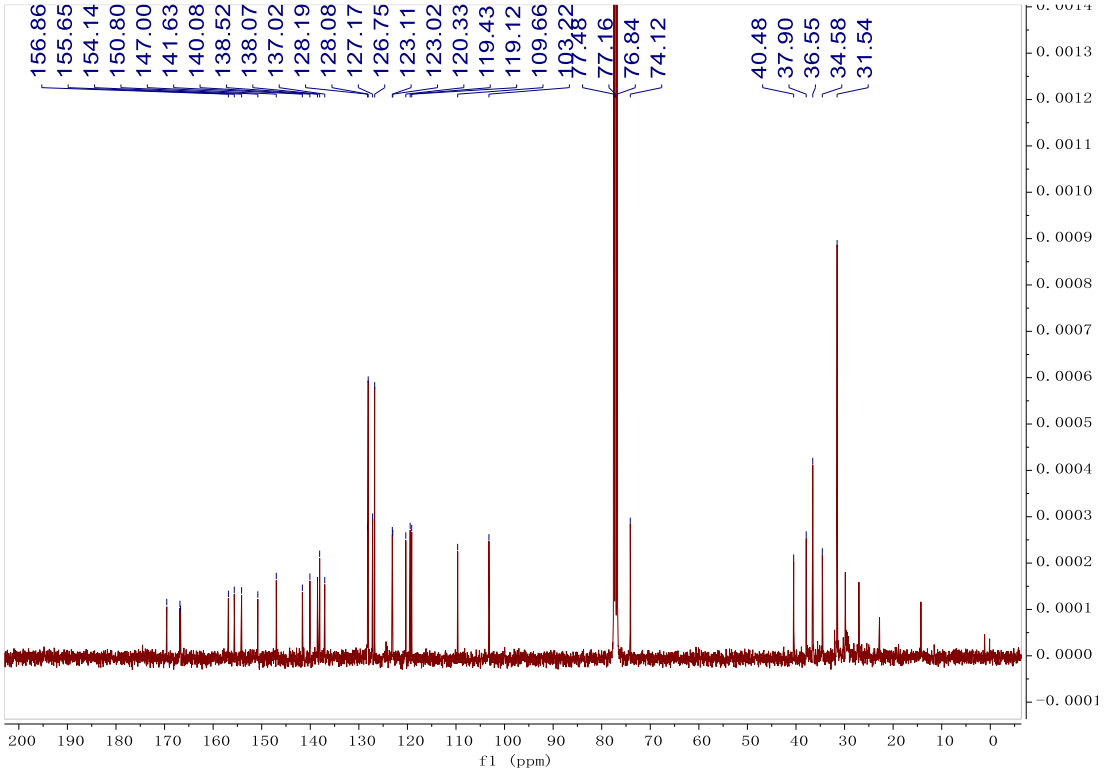
^{13}C NMR spectrum of **5t** in $CDCl_3$ at 298 K



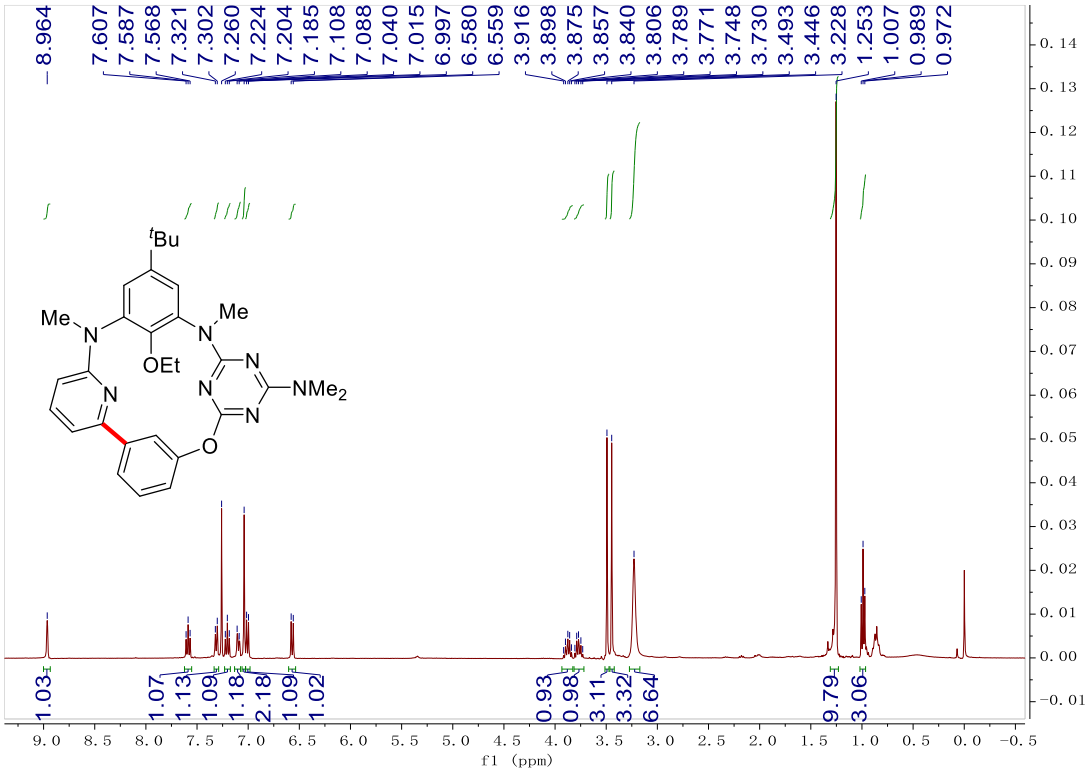
^{1}H NMR spectrum of **5u** in $CDCl_3$ at 298 K



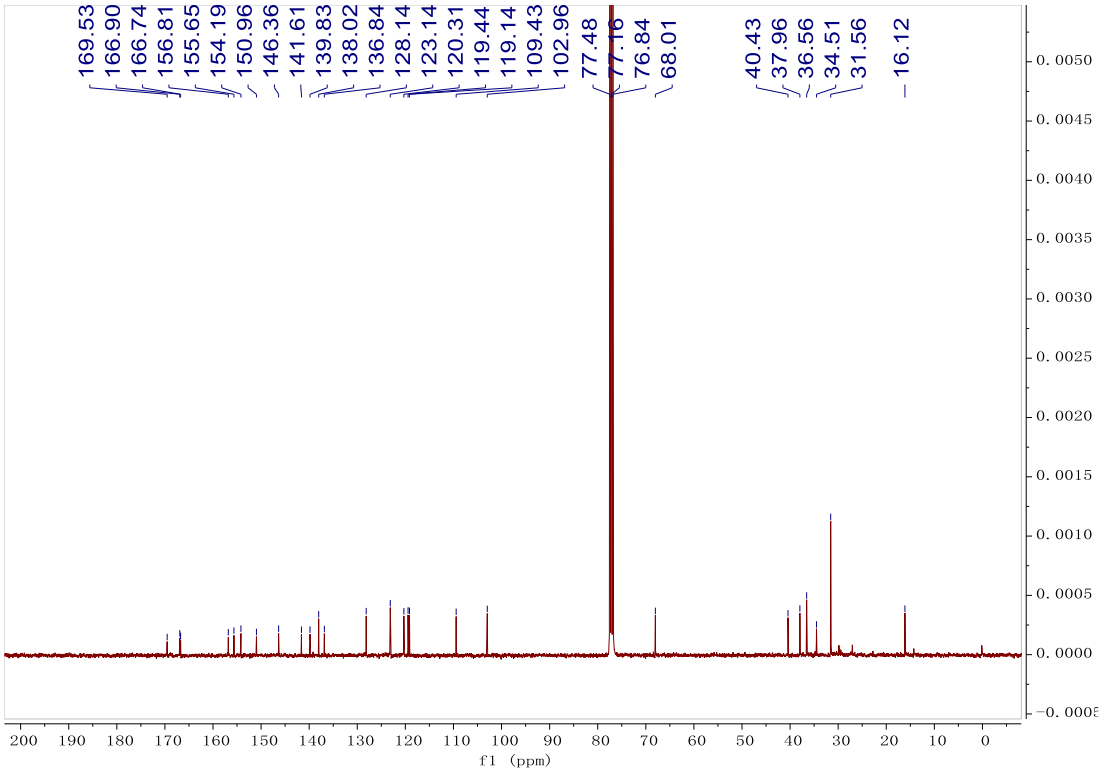
^{13}C NMR spectrum of **5u** in $CDCl_3$ at 298 K



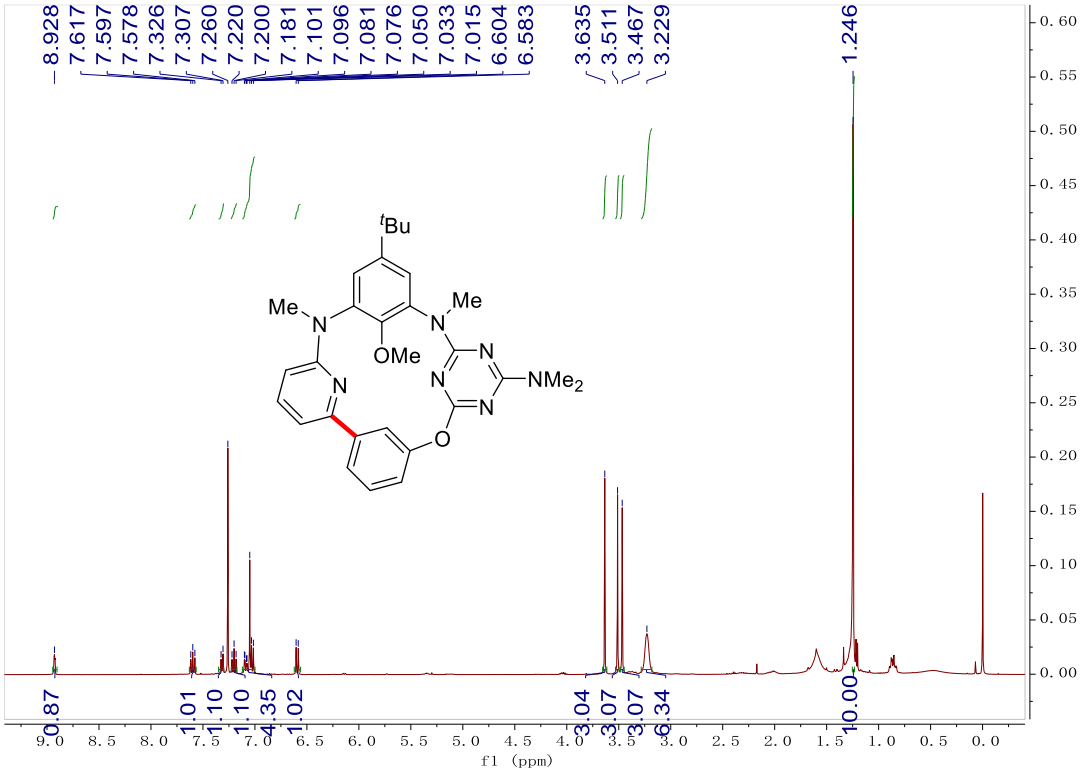
^{1}H NMR spectrum of **5v** in $CDCl_3$ at 298 K



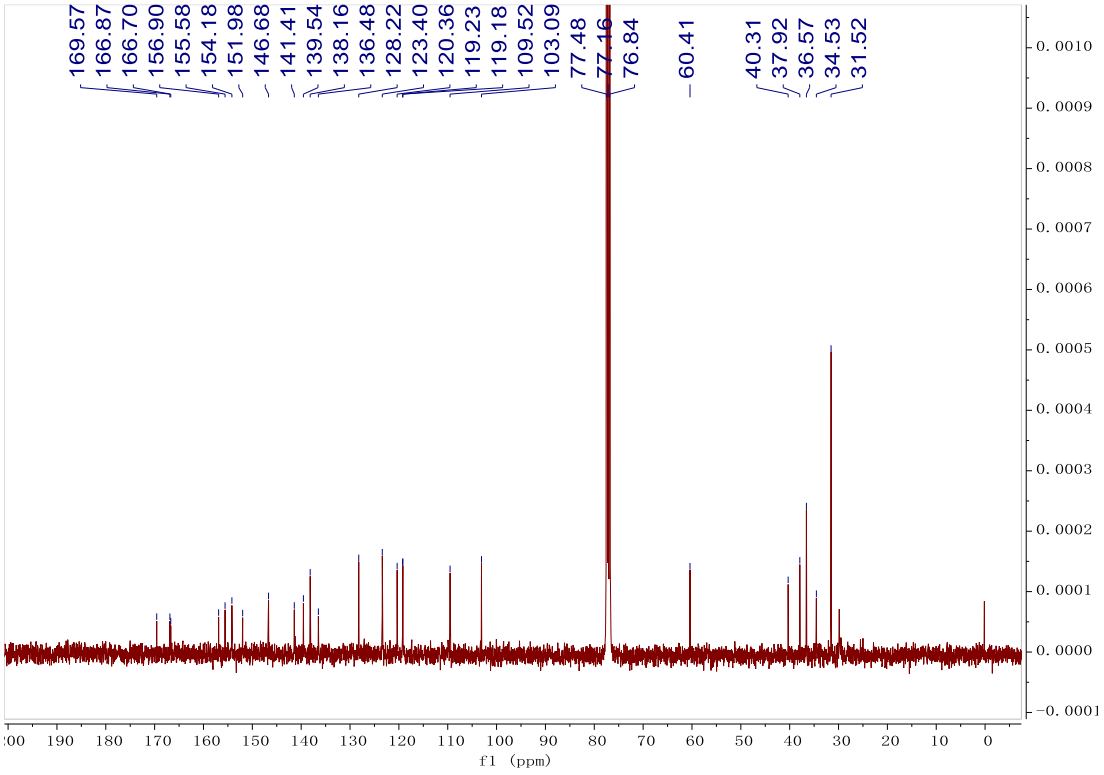
^{13}C NMR spectrum of **5v** in $CDCl_3$ at 298 K



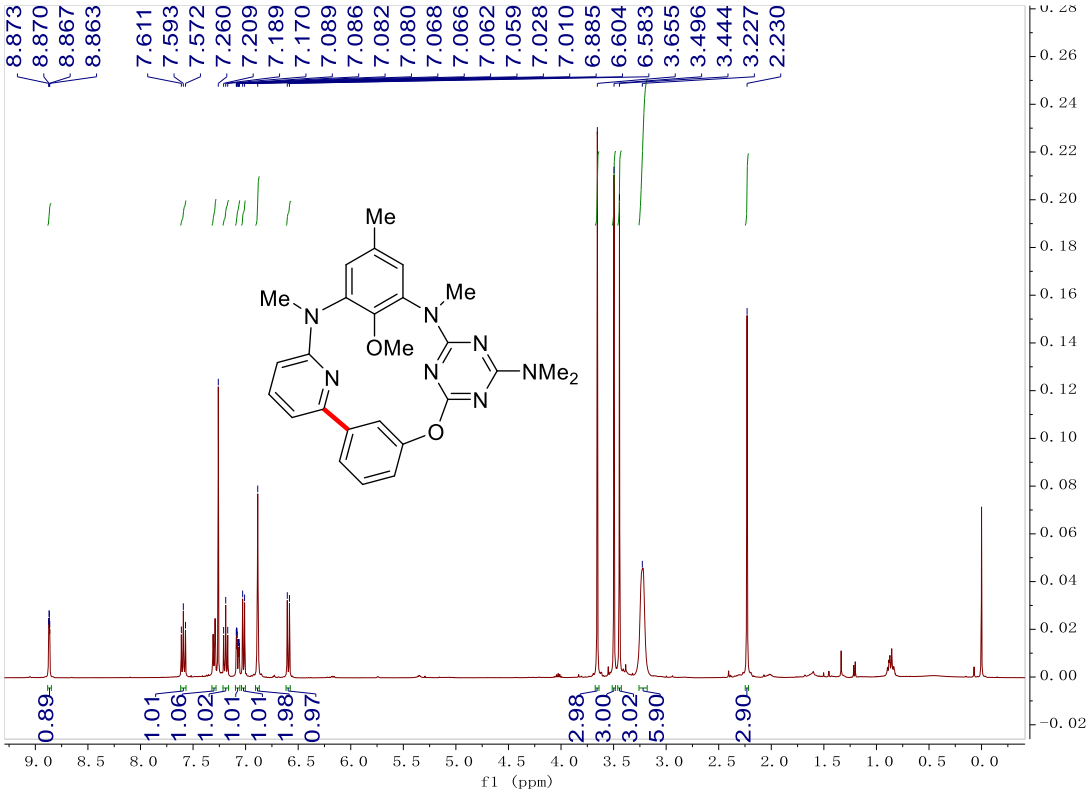
^{1}H NMR spectrum of **5w** in $CDCl_3$ at 298 K



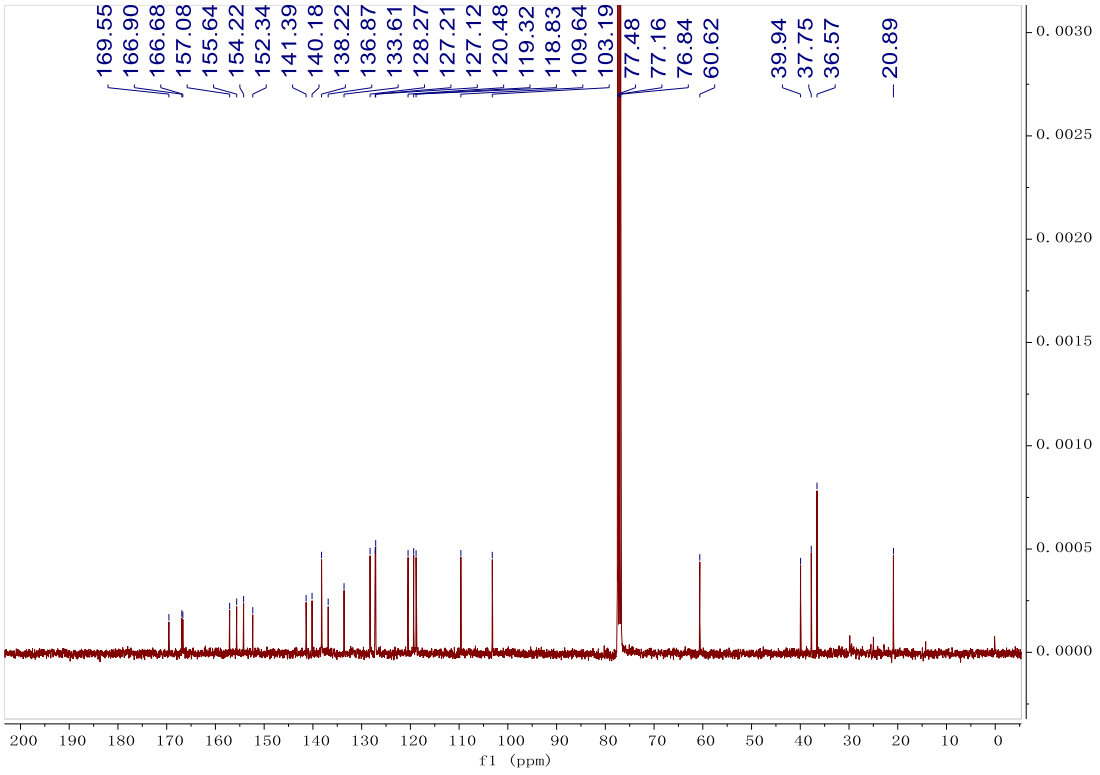
^{13}C NMR spectrum of **5w** in $CDCl_3$ at 298 K



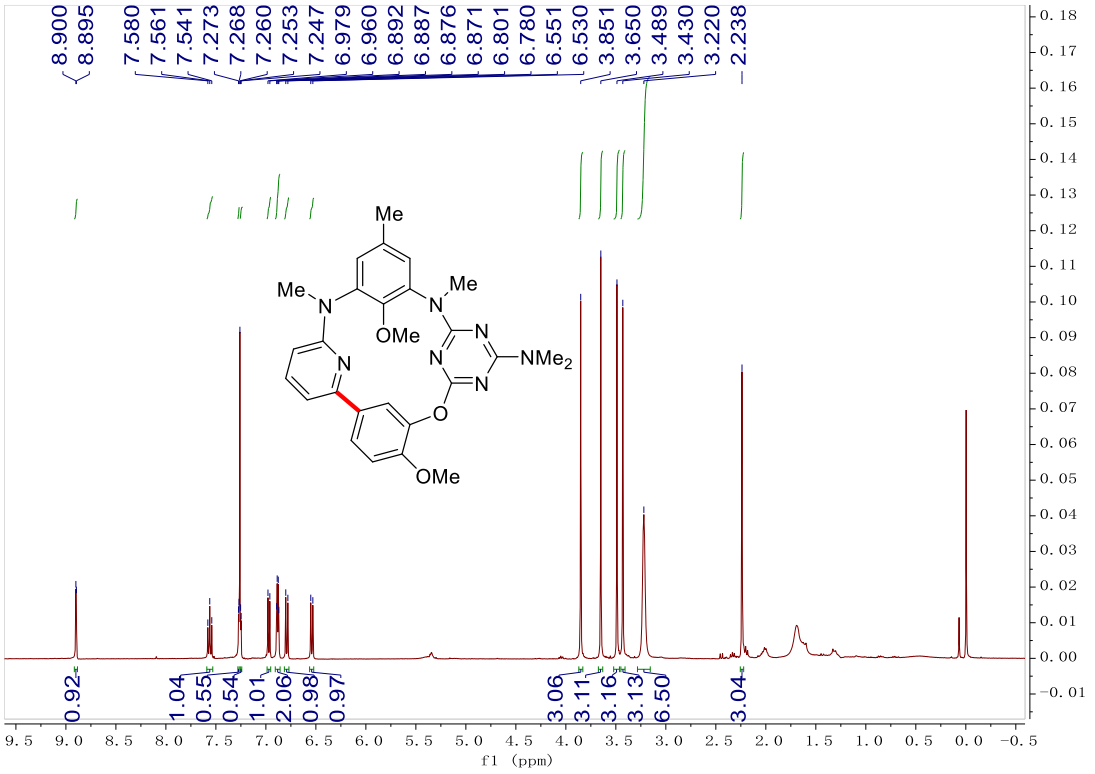
^{1}H NMR spectrum of **5x** in $CDCl_3$ at 298 K



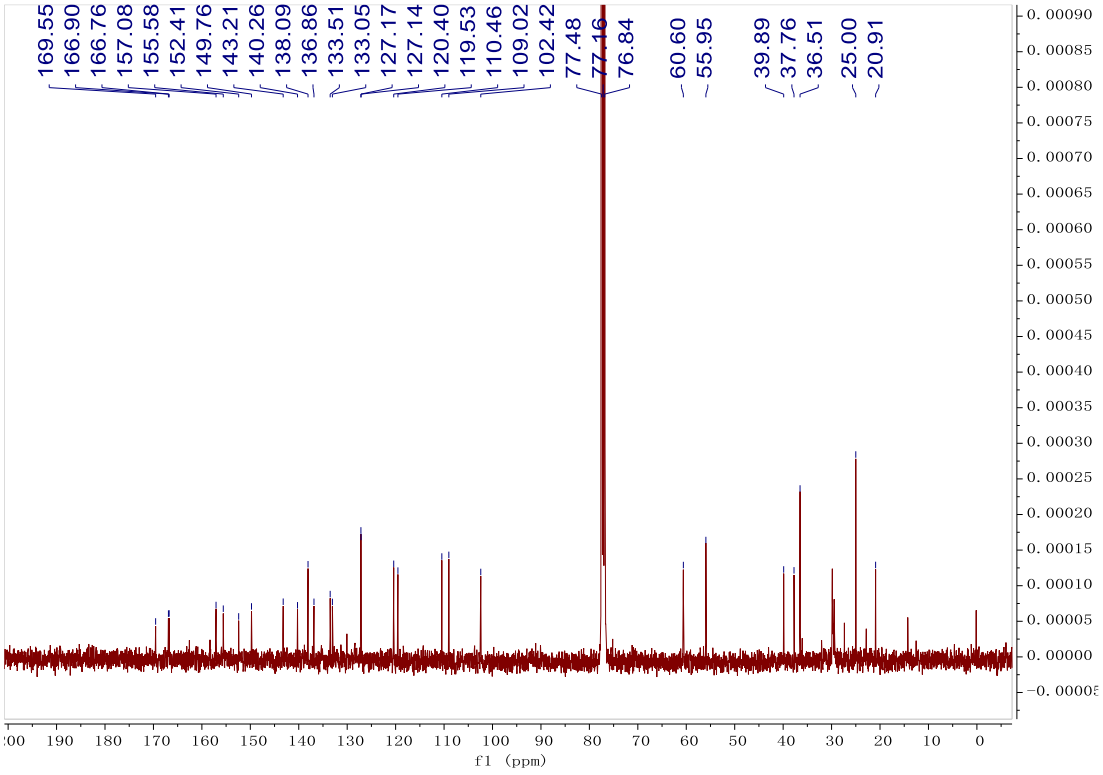
^{13}C NMR spectrum of **5x** in $CDCl_3$ at 298 K



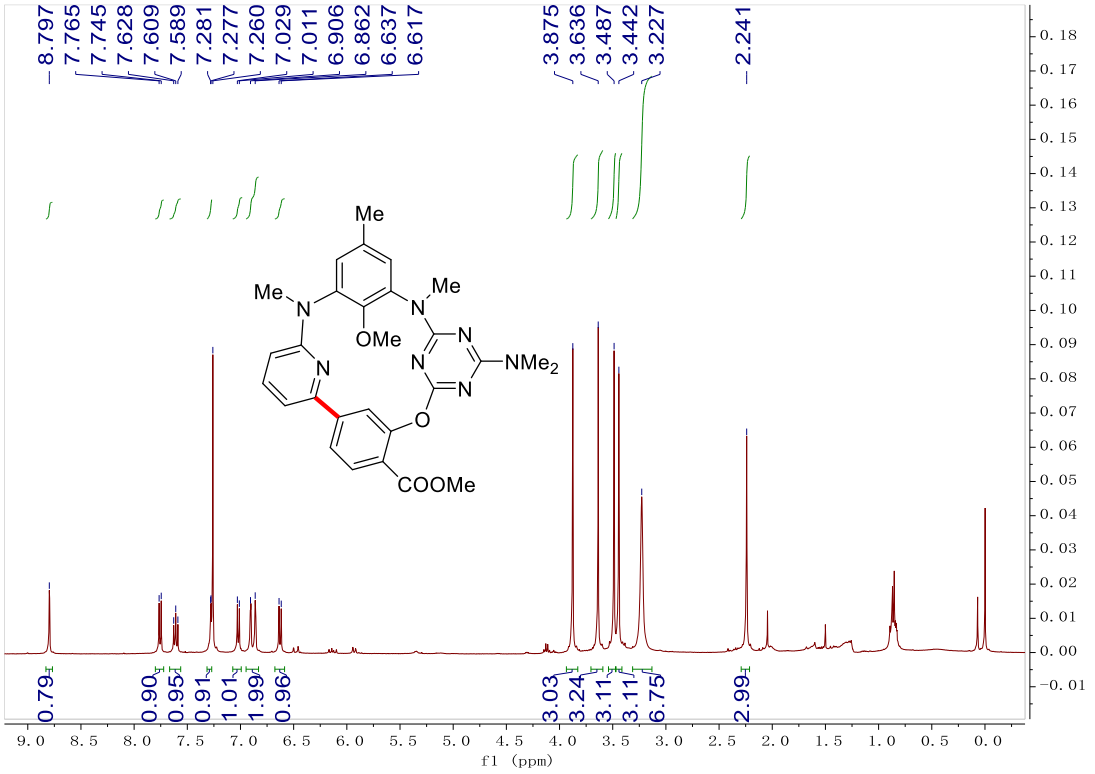
^{1}H NMR spectrum of **5y** in $CDCl_3$ at 298 K



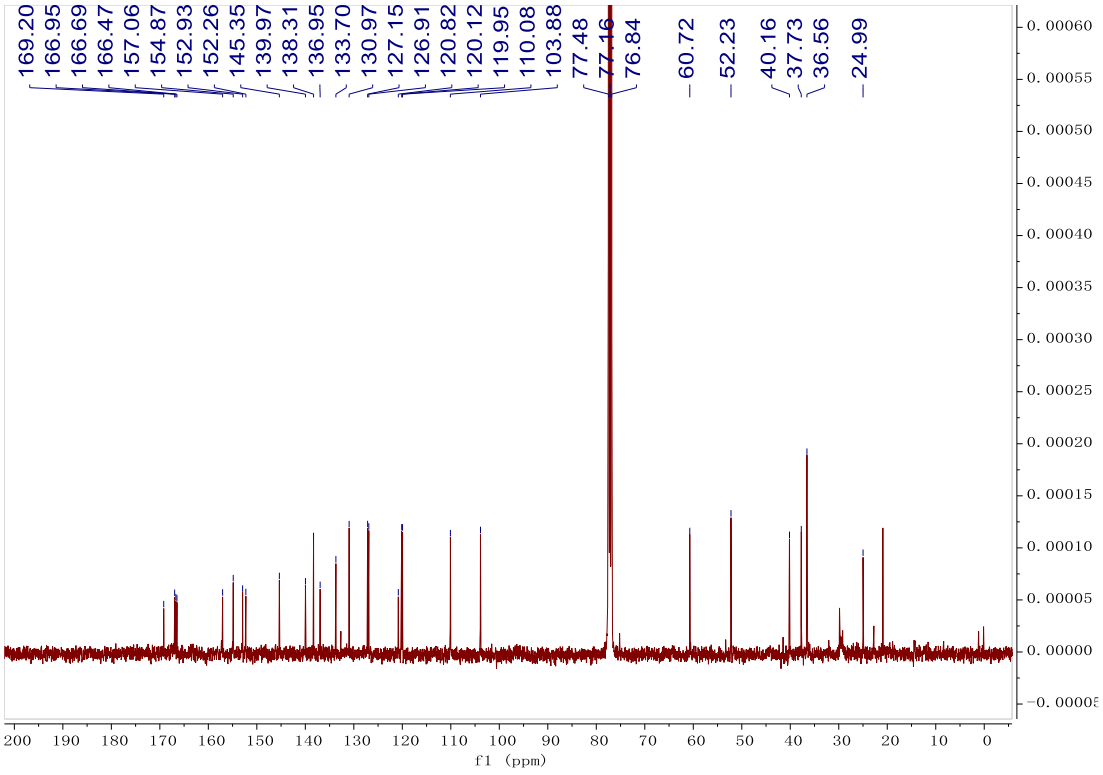
^{13}C NMR spectrum of **5y** in $CDCl_3$ at 298 K



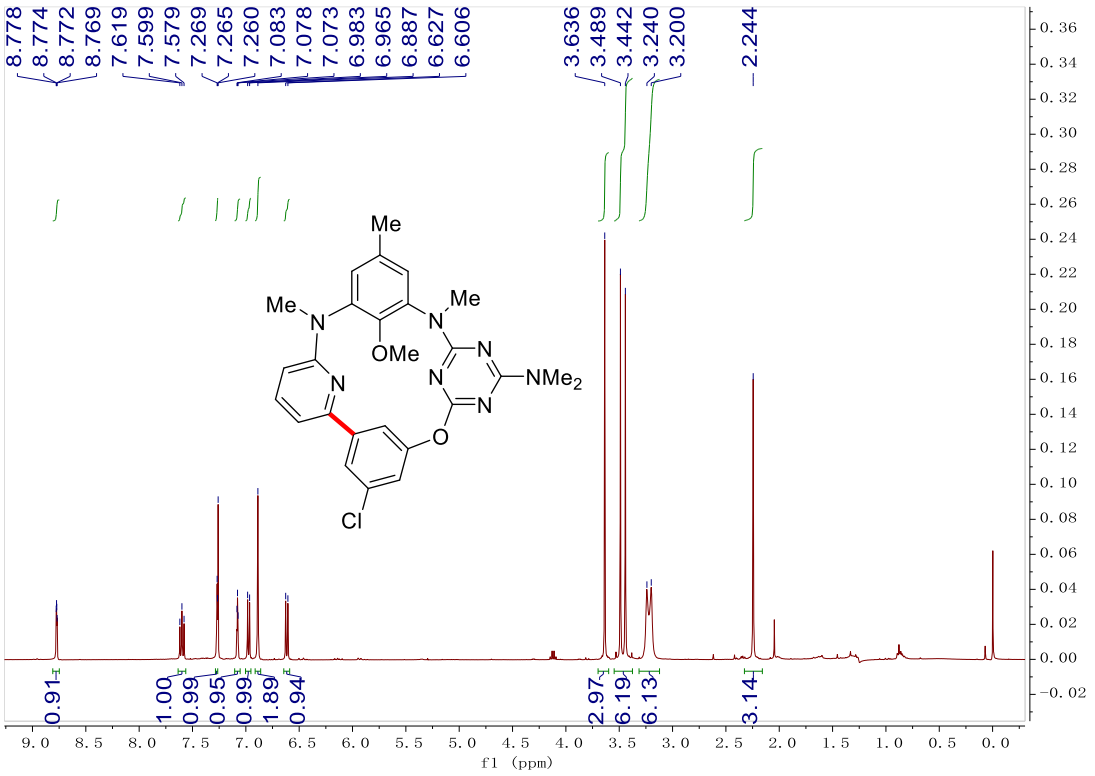
^{1}H NMR spectrum of **5z** in $CDCl_3$ at 298 K



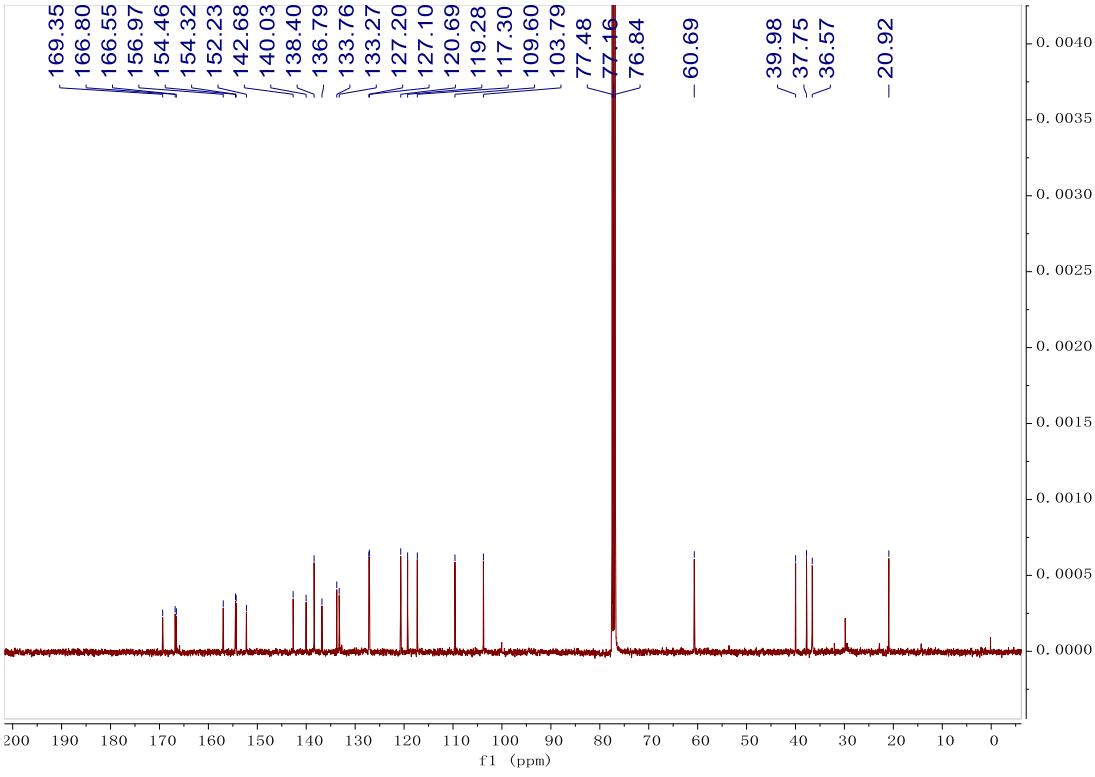
^{13}C NMR spectrum of **5z** in $CDCl_3$ at 298 K



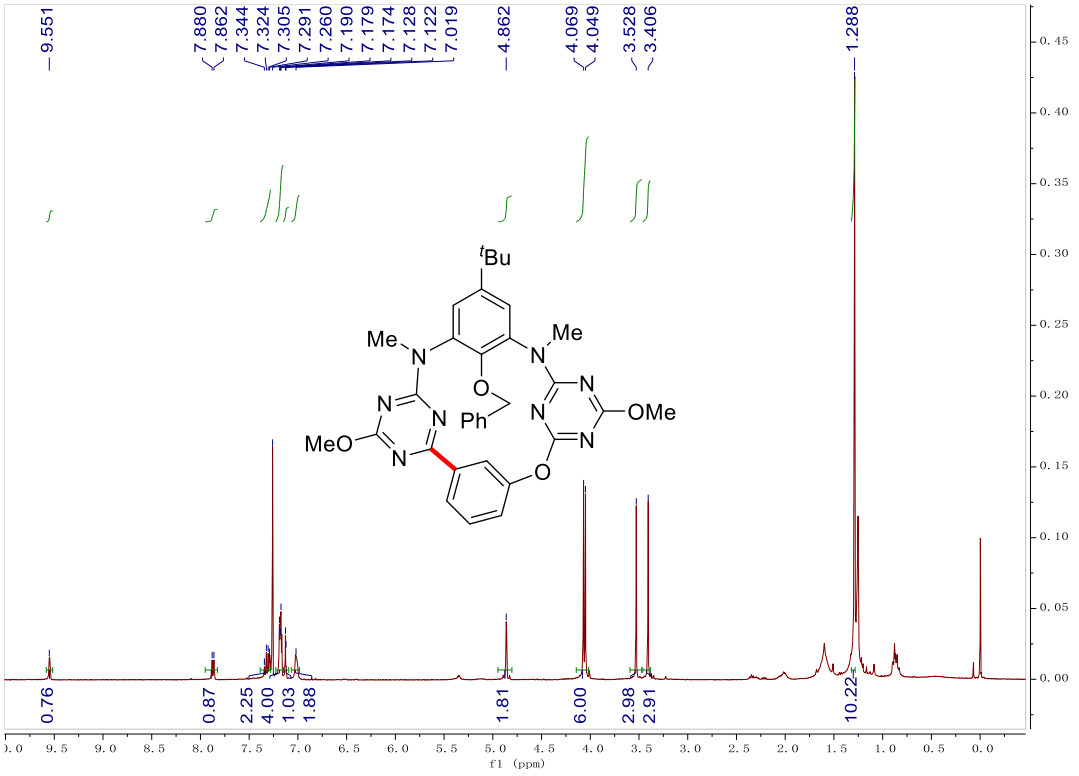
^{1}H NMR spectrum of **5aa** in $CDCl_3$ at 298 K



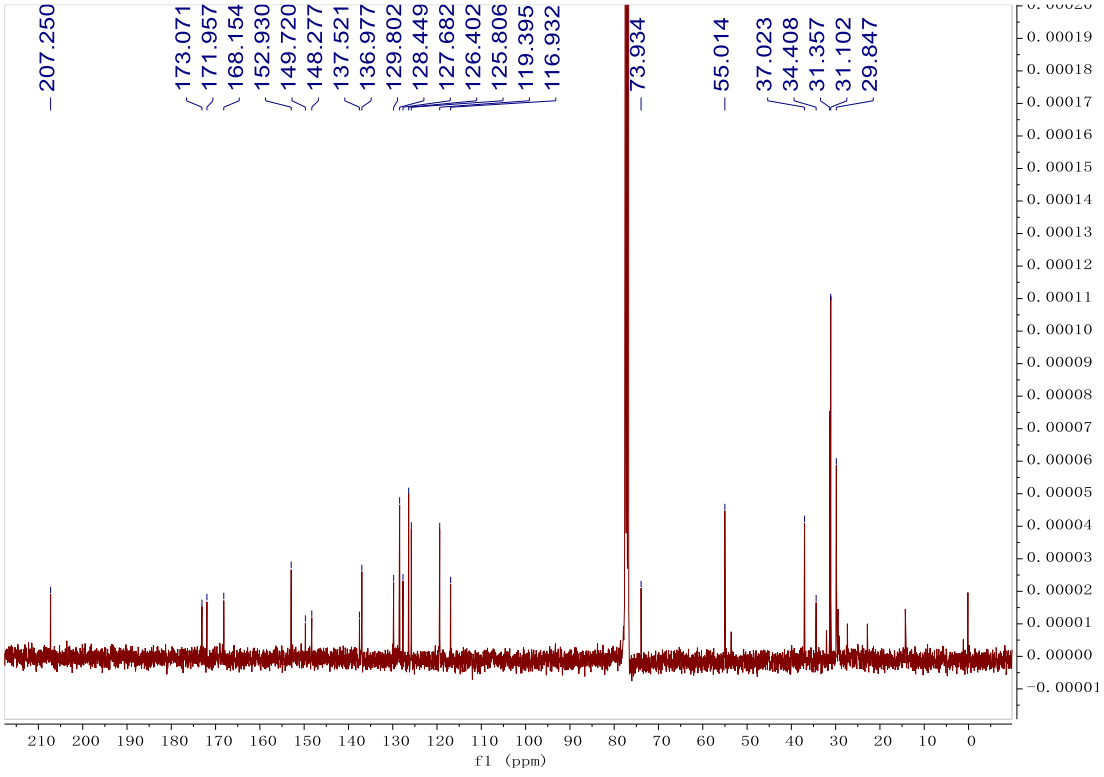
^{13}C NMR spectrum of **5aa** in $CDCl_3$ at 298 K



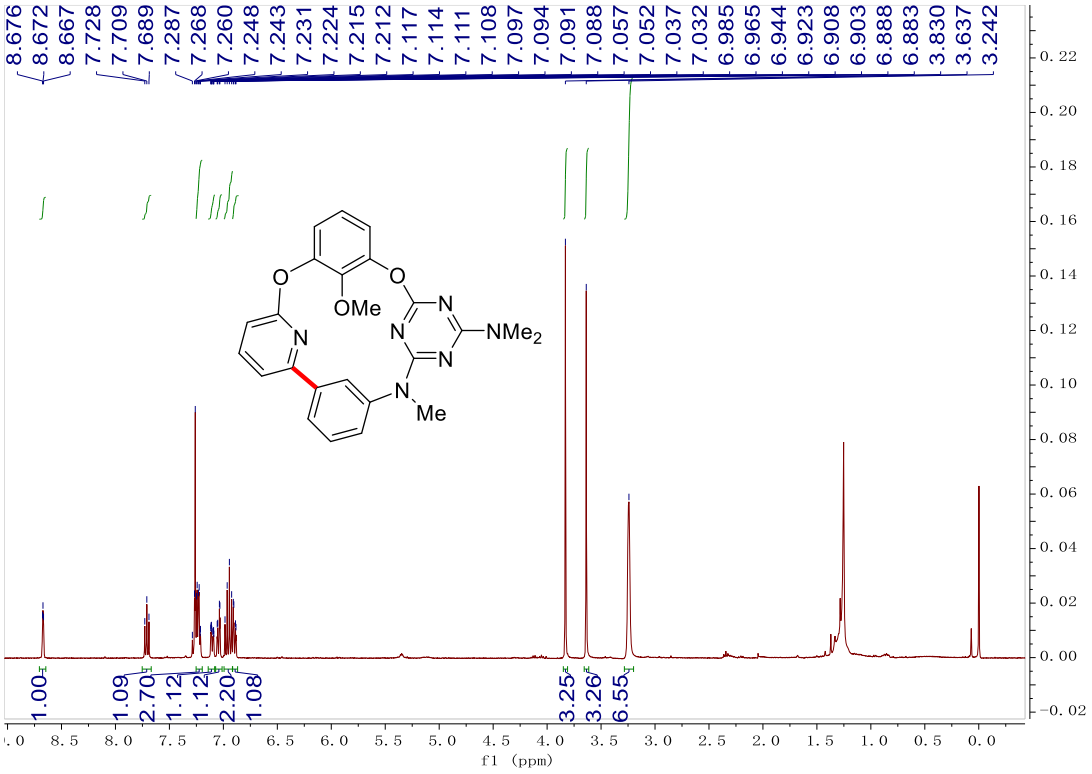
^{1}H NMR spectrum of **5ab** in $CDCl_3$ at 298 K



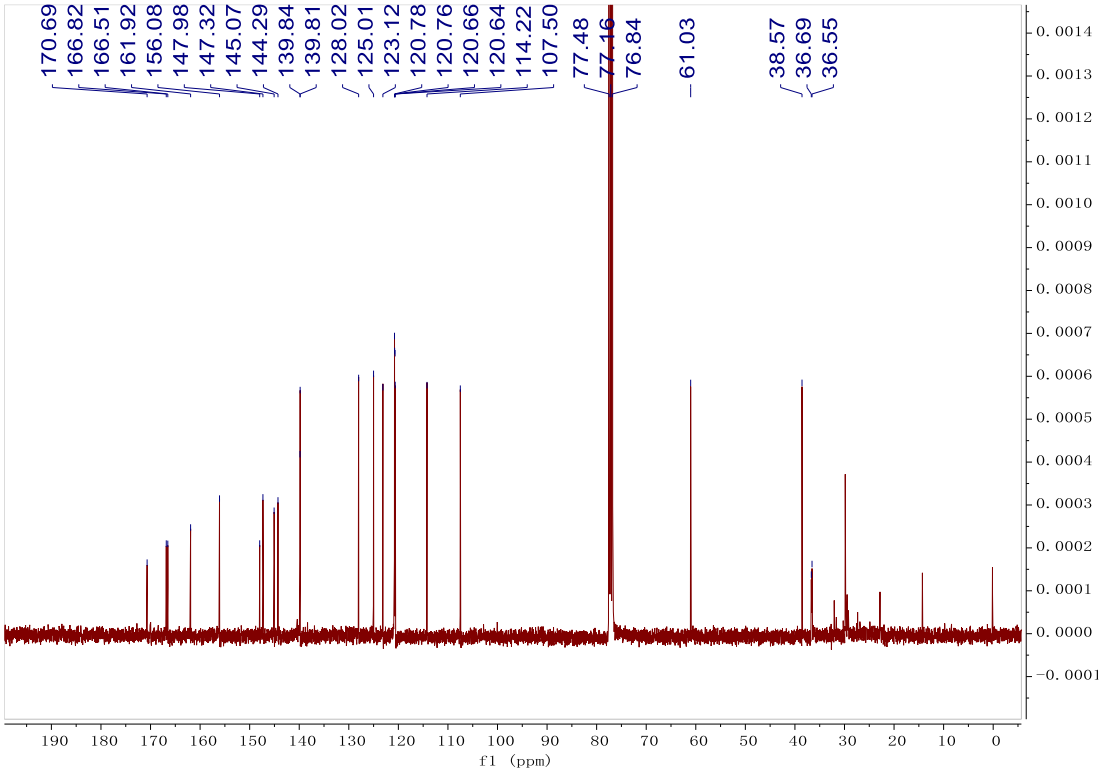
^{13}C NMR spectrum of **5ab** in $CDCl_3$ at 298 K



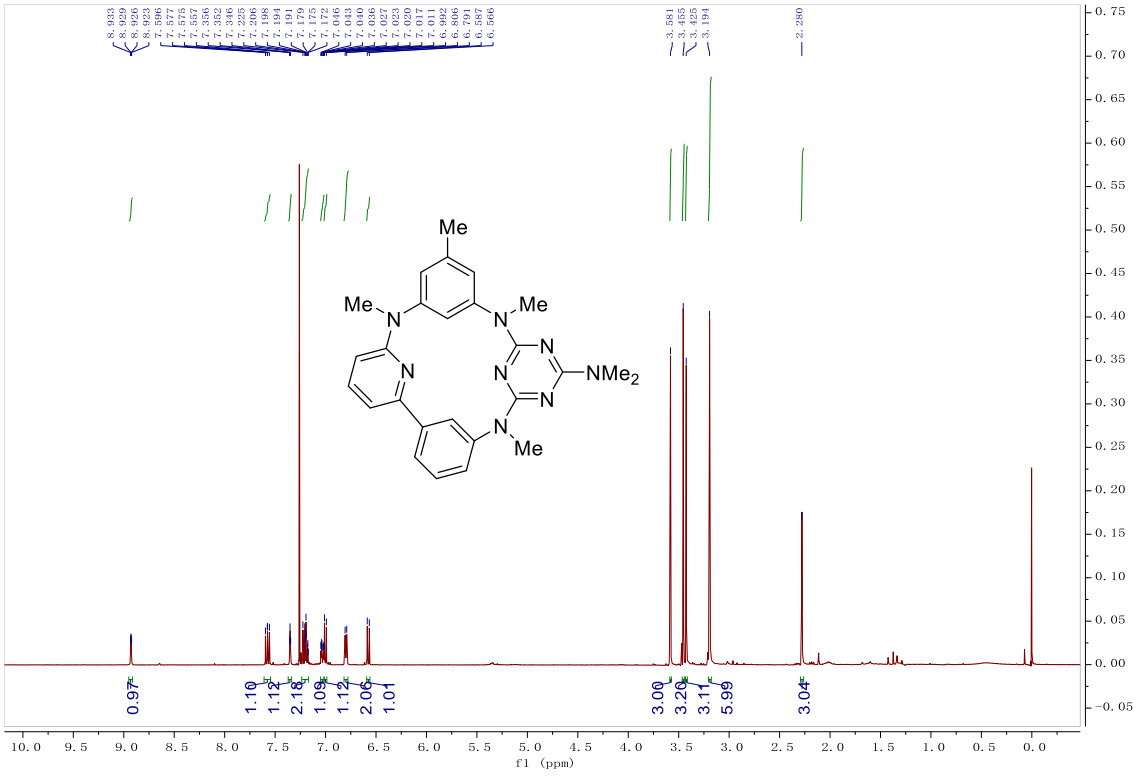
^{1}H NMR spectrum of **5ac** in $CDCl_3$ at 298 K



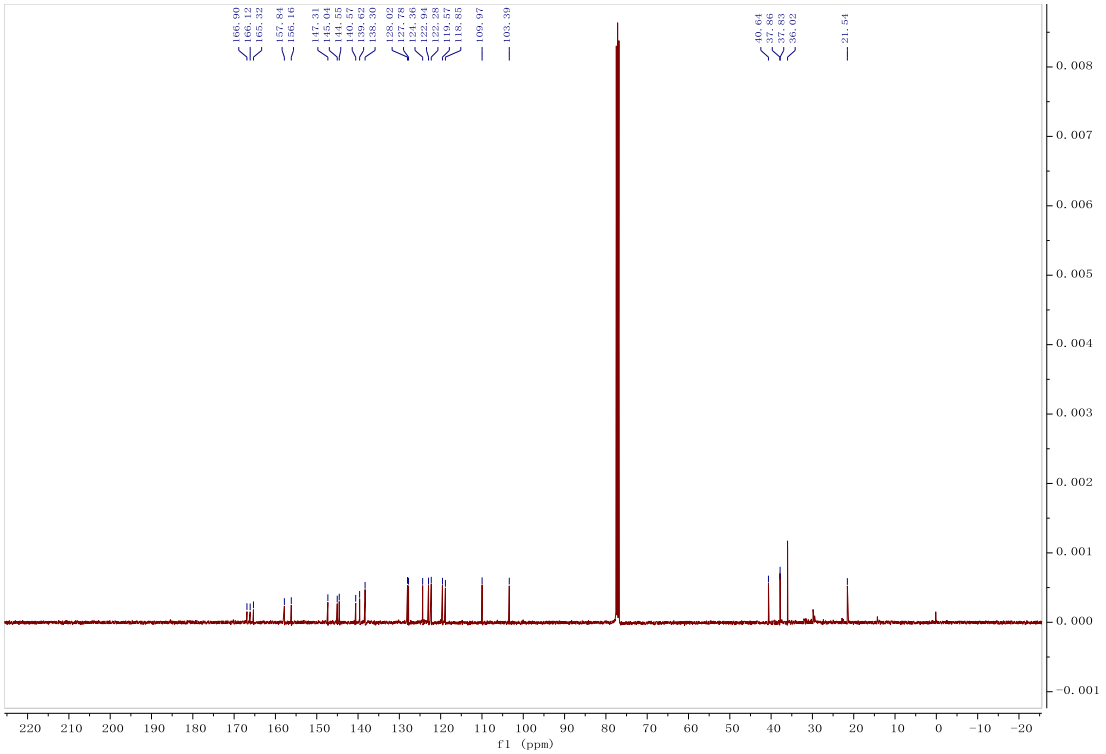
^{13}C NMR spectrum of **5ac** in $CDCl_3$ at 298 K



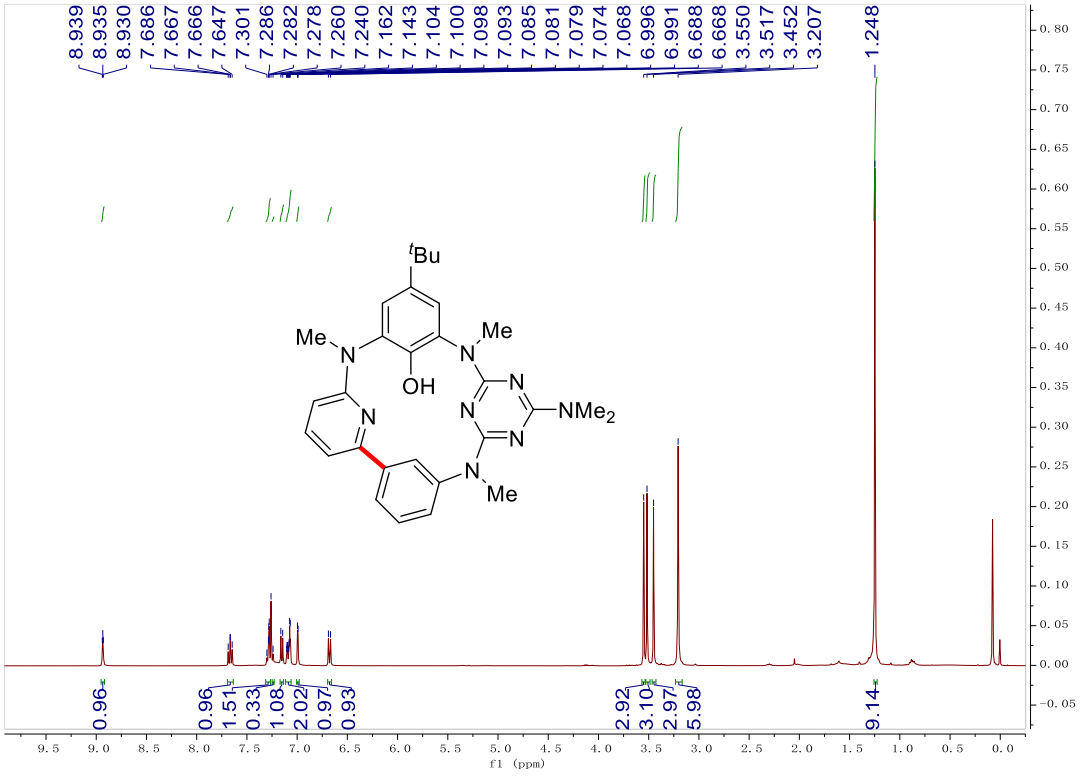
^{1}H NMR spectrum of **5ad** in $CDCl_3$ at 298 K



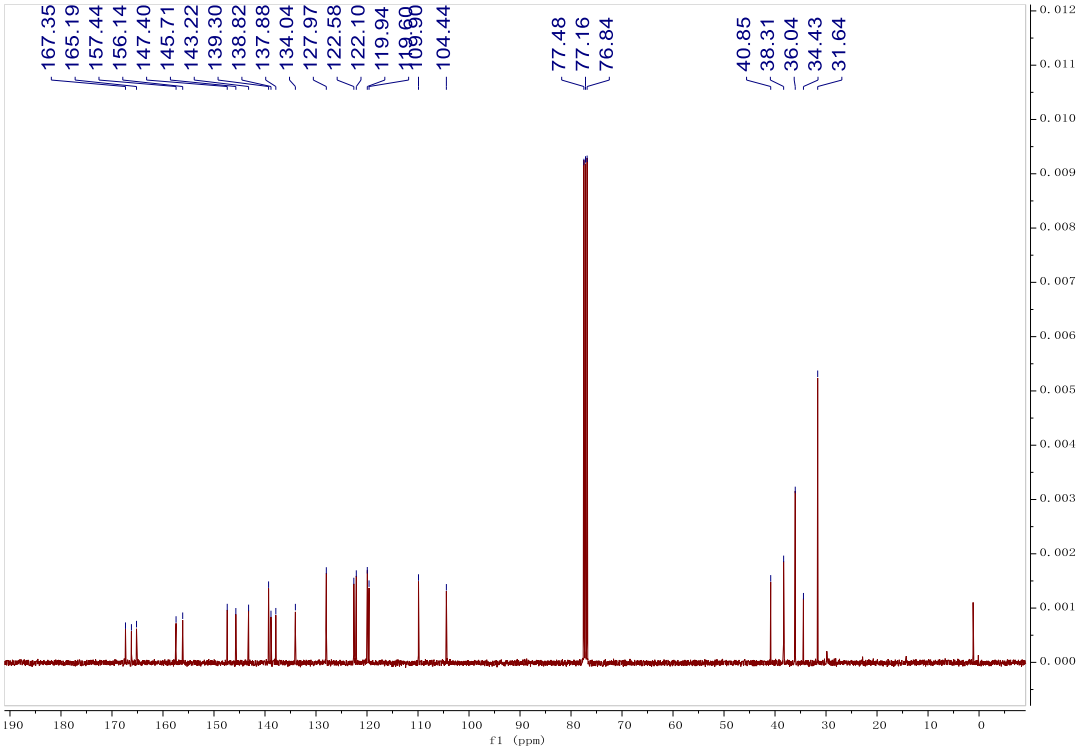
^{13}C NMR spectrum of **5ad** in $CDCl_3$ at 298 K



^{1}H NMR spectrum of **5ae** in $CDCl_3$ at 298 K

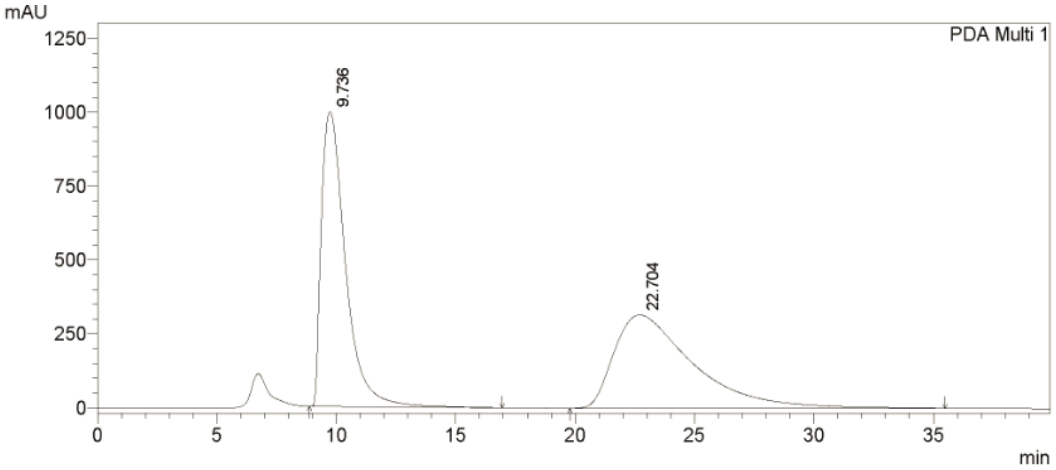


^{13}C NMR spectrum of **5ae** in $CDCl_3$ at 298 K



16. Copies of HPLC chromatograms

5a

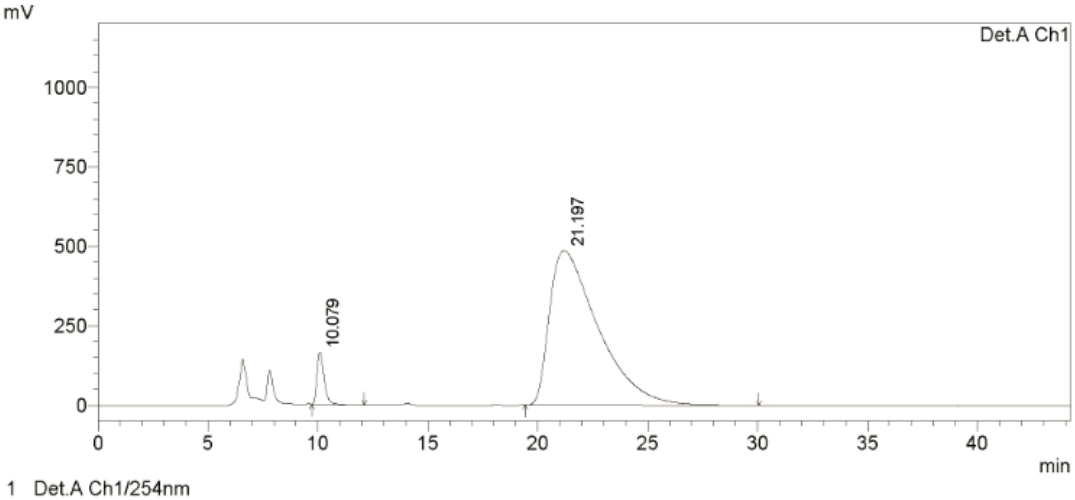


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.736	69979159	997564	49.129	75.951
2	22.704	72461477	315868	50.871	24.049
Total		142440636	1313432	100.000	100.000



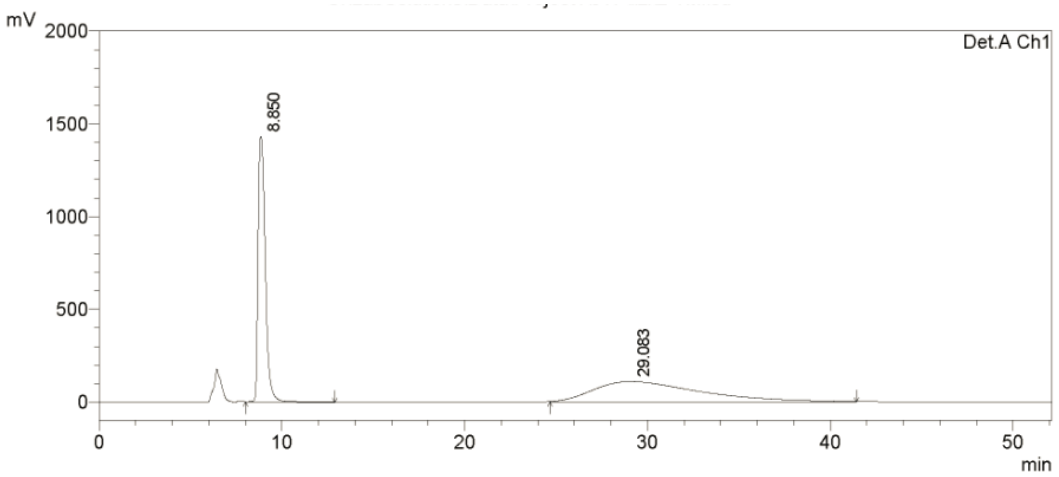
1 Det.A Ch1/254nm

PeakTable

檢測器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.079	3693747	164070	4.710	25.252
2	21.197	74730408	485652	95.290	74.748
Total		78424155	649722	100.000	100.000

5b

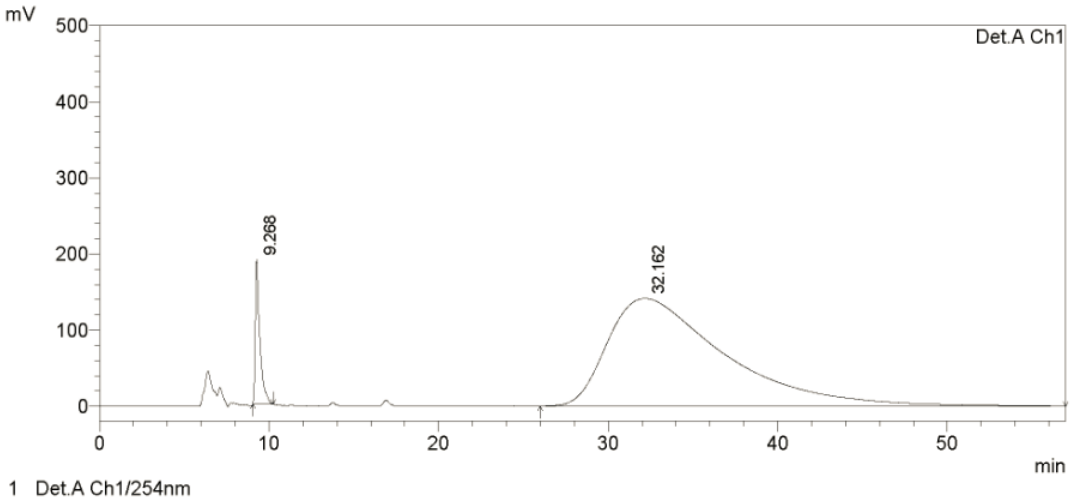


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.850	39349927	1433171	46.580	92.883
2	29.083	45128623	109814	53.420	7.117
Total		84478549	1542985	100.000	100.000



1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

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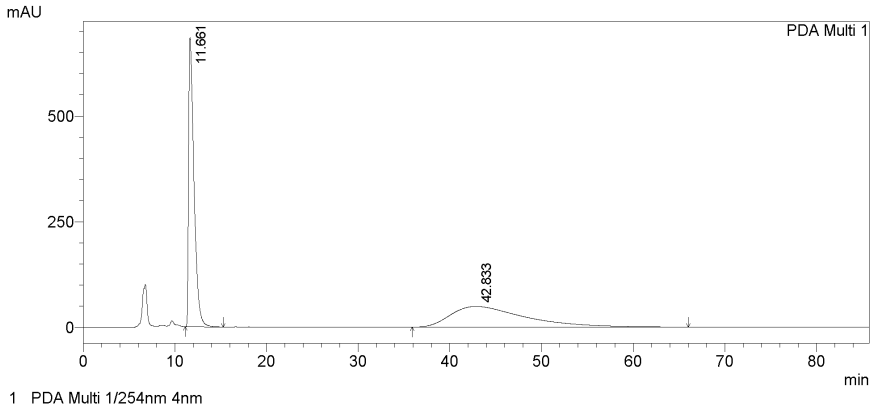
1	9.268	3581716	190035	5.020	57.338
2	32.162	67766947	141393	94.980	42.662
Total		71348663	331428	100.000	100.000

5c

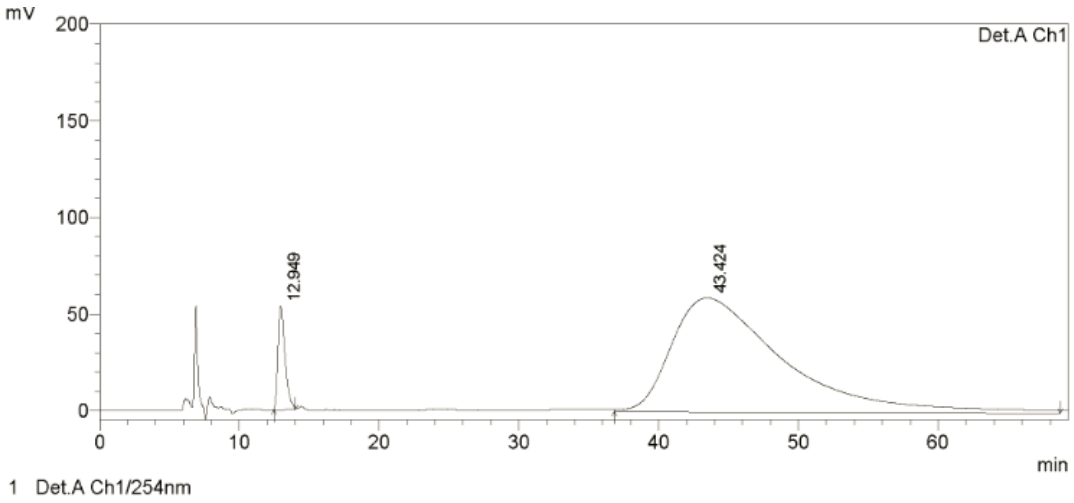


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.661	28057025	684201	50.159	93.290
2	42.833	27878730	49213	49.841	6.710
Total		55935755	733414	100.000	100.000



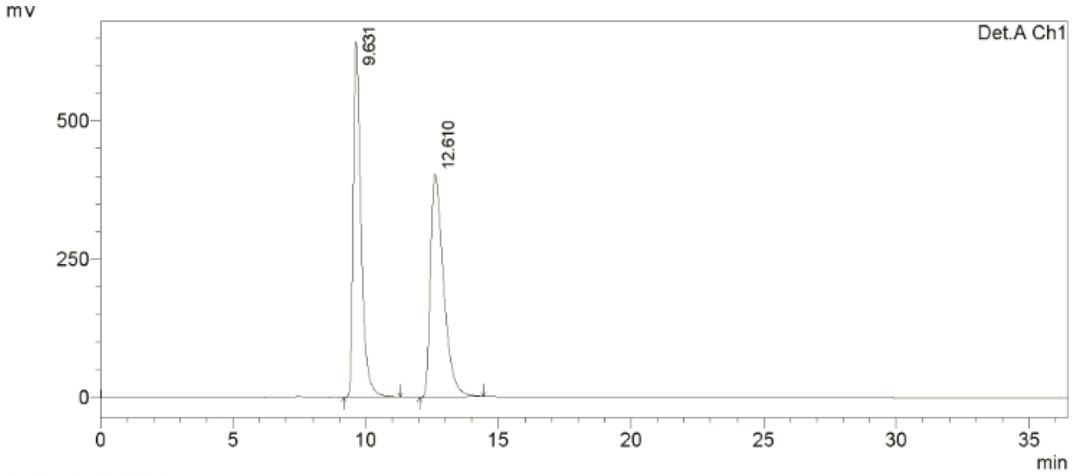
1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.949	1920232	53922	5.516	47.726
2	43.424	32894032	59062	94.484	52.274
Total		34814265	112983	100.000	100.000

5d

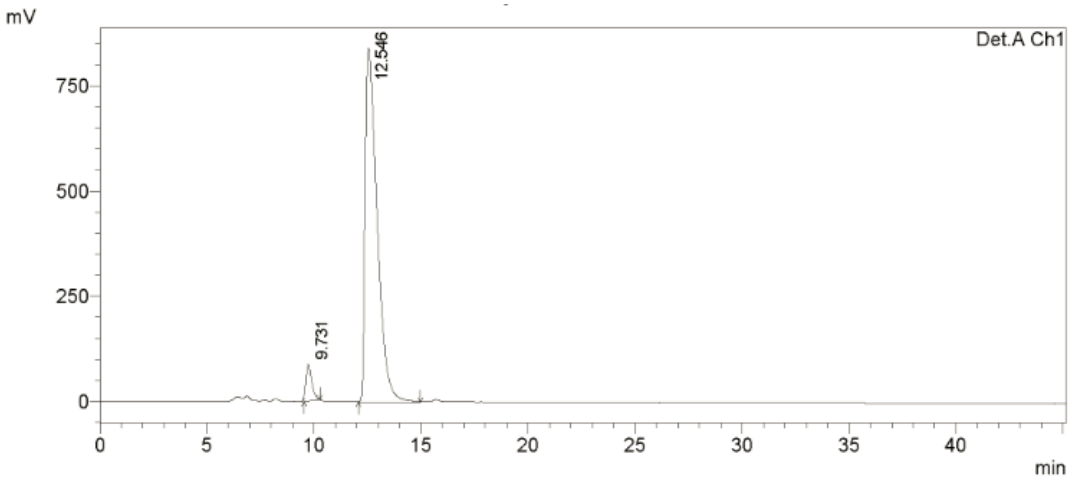


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.631	13262446	642311	49.047	61.450
2	12.610	13777825	402951	50.953	38.550
Total		27040271	1045262	100.000	100.000



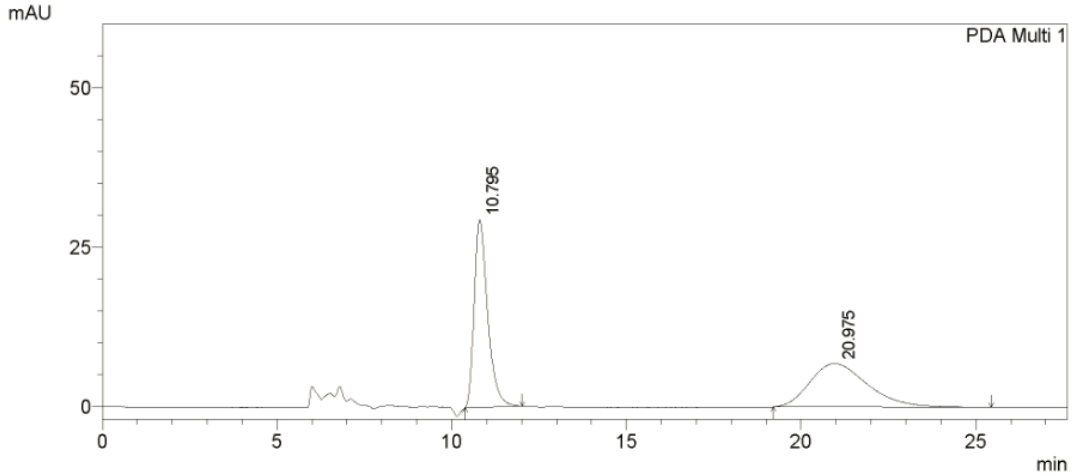
1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.731	1647919	87566	4.798	9.425
2	12.546	32695919	841529	95.202	90.575
Total		34343839	929095	100.000	100.000

5e

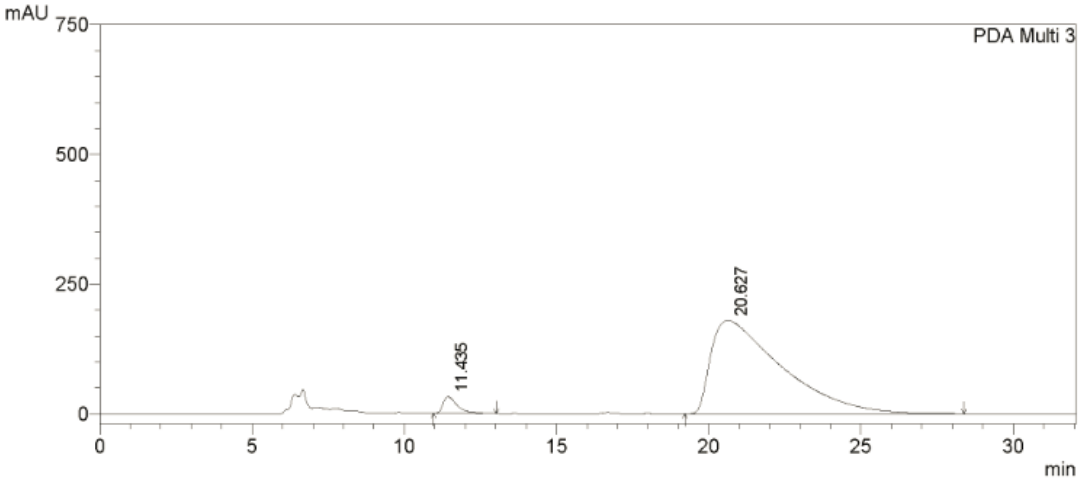


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.795	793714	29394	50.451	81.172
2	20.975	779536	6818	49.549	18.828
Total		1573251	36212	100.000	100.000



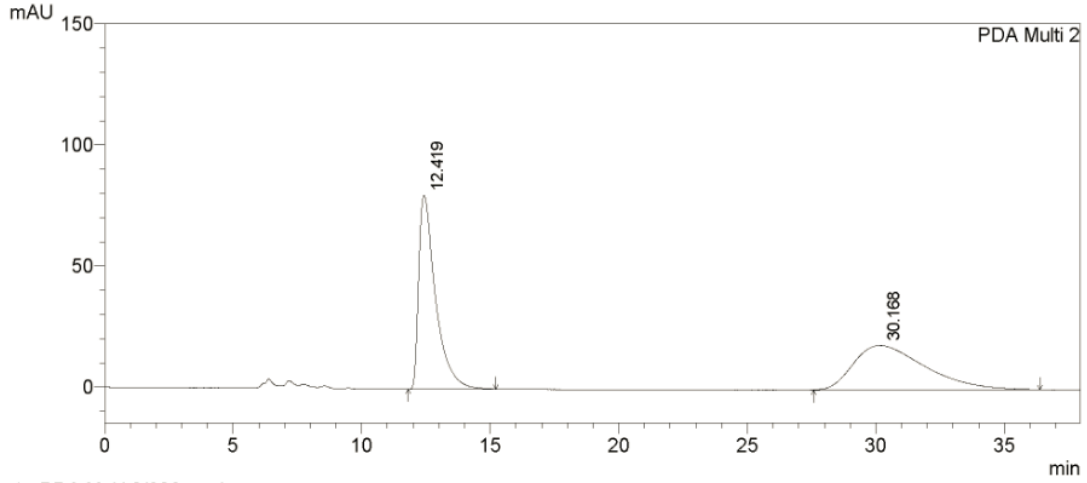
1 PDA Multi 3/315nm 4nm

PeakTable

PDA Ch3 315nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.435	1056501	32025	3.509	15.121
2	20.627	29051696	179769	96.491	84.879
Total		30108196	211794	100.000	100.000

5f

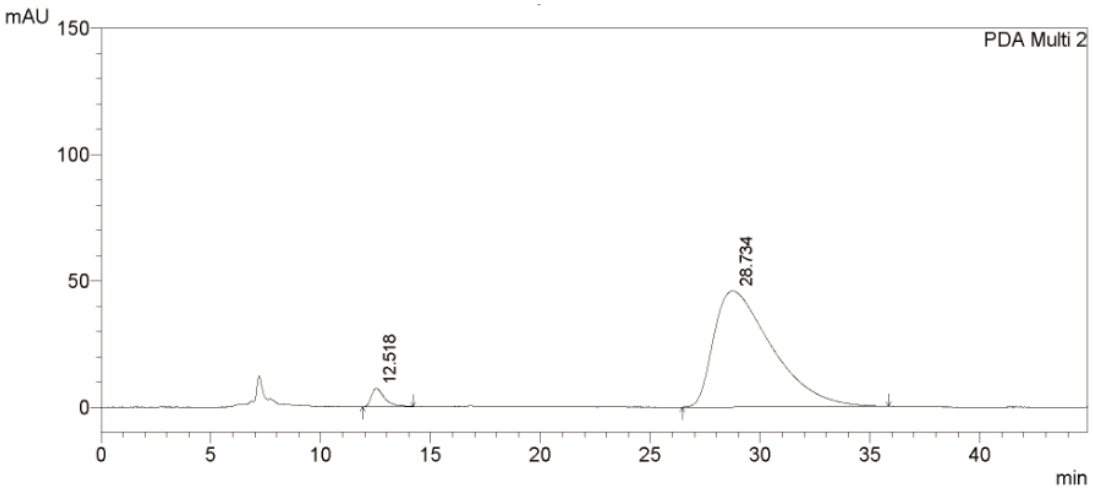


1 PDA Multi 2/328nm 4nm

PeakTable

PDA Ch2 328nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.419	3652182	80264	50.538	81.373
2	30.168	3574495	18373	49.462	18.627
Total		7226677	98637	100.000	100.000



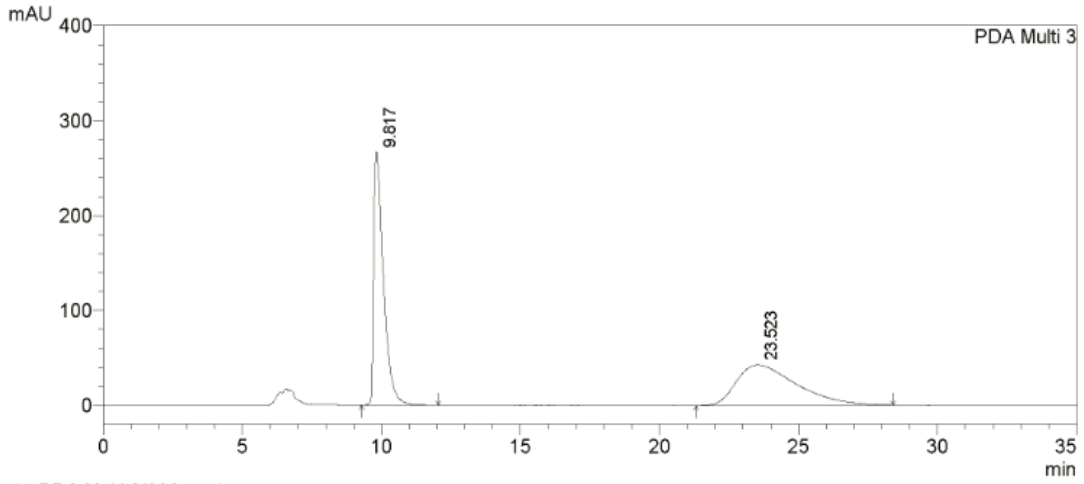
1 PDA Multi 2/315nm 4nm

PeakTable

PDA Ch2 315nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.518	306466	7219	3.504	13.578
2	28.734	8440570	45950	96.496	86.422
Total		8747035	53169	100.000	100.000

5g

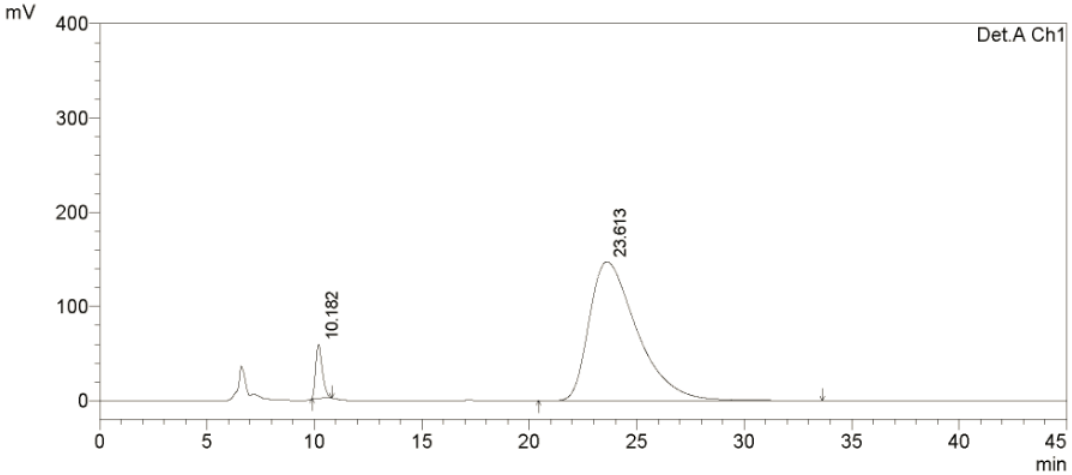


1 PDA Multi 3/320nm 4nm

PeakTable

PDA Ch3 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.817	6532798	267105	50.456	86.231
2	23.523	6414593	42651	49.544	13.769
Total		12947390	309756	100.000	100.000



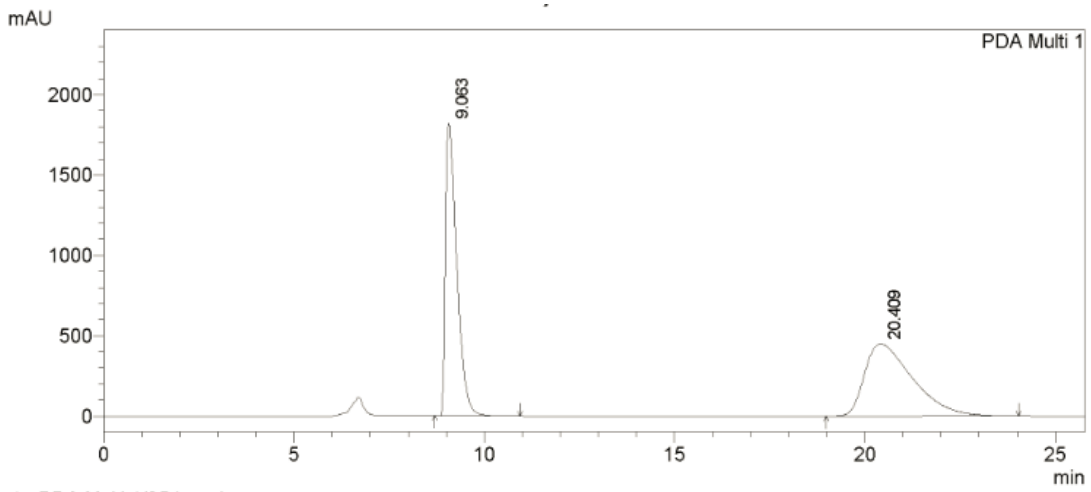
1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.182	1231457	57159	5.126	27.948
2	23.613	22792259	147363	94.874	72.052
Total		24023717	204522	100.000	100.000

5h

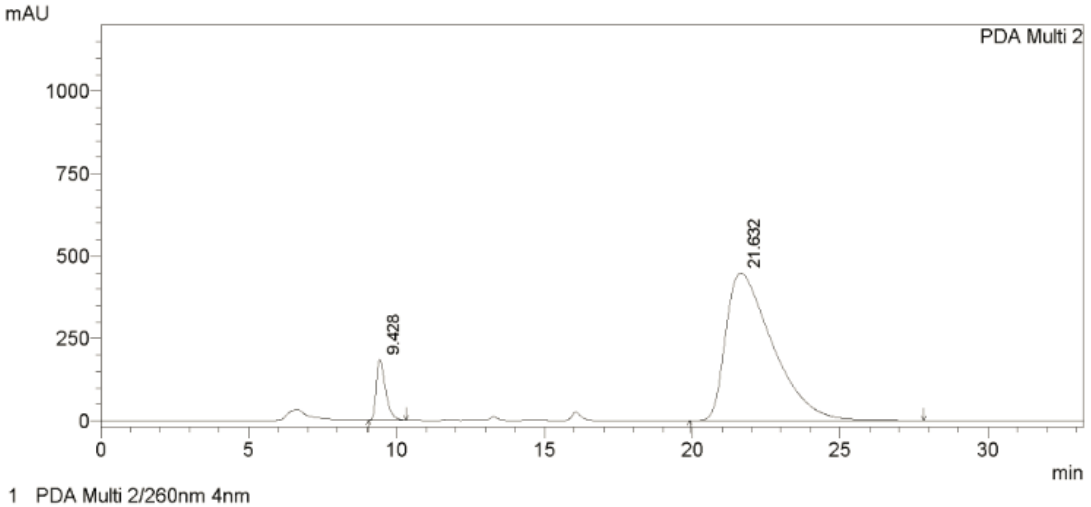


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.063	37865449	1820362	49.061	80.216
2	20.409	39314782	448957	50.939	19.784
Total		77180231	2269319	100.000	100.000



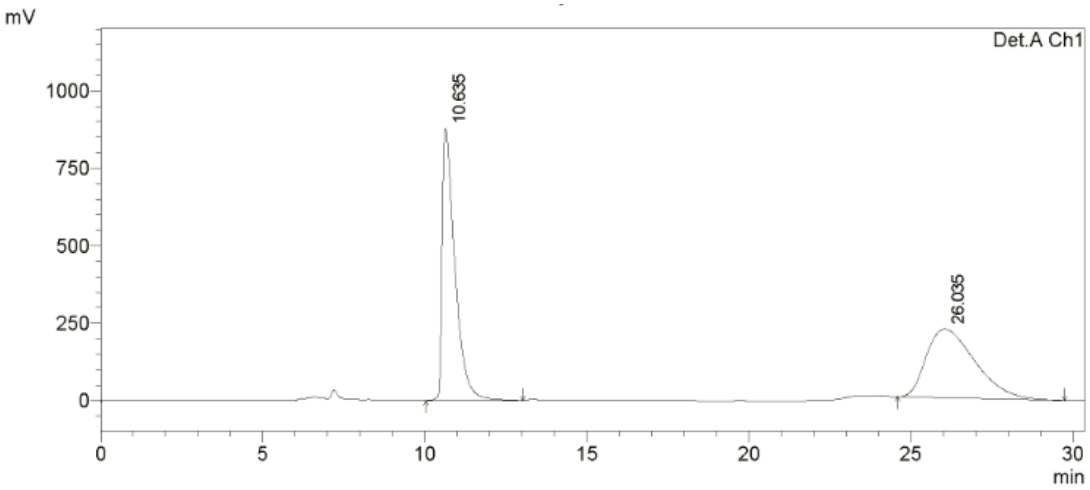
1 PDA Multi 2/260nm 4nm

PeakTable

PDA Ch2 260nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.428	3990555	183548	7.497	29.083
2	21.632	49236856	447570	92.503	70.917
Total		53227411	631118	100.000	100.000

5i

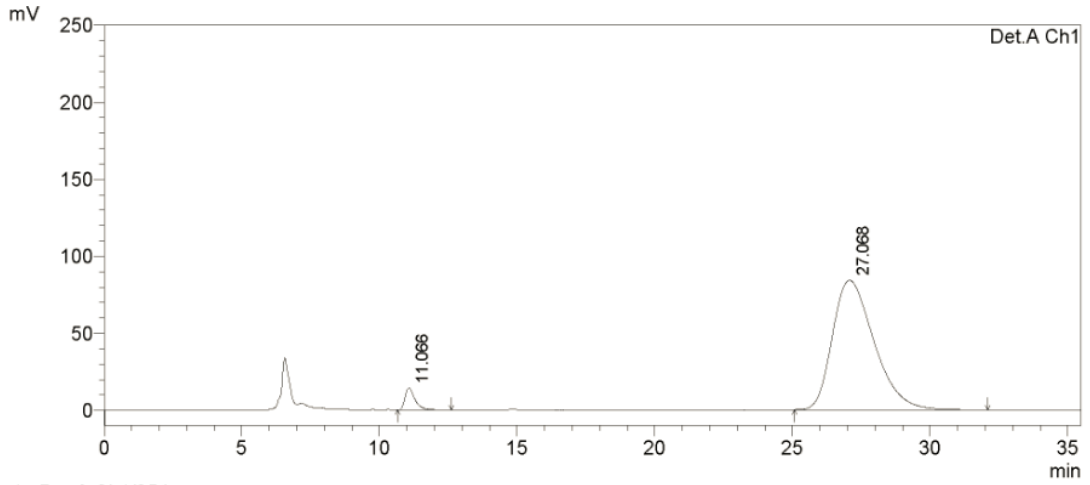


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.635	23896963	878428	50.818	79.843
2	26.035	23127962	221762	49.182	20.157
Total		47024925	1100189	100.000	100.000



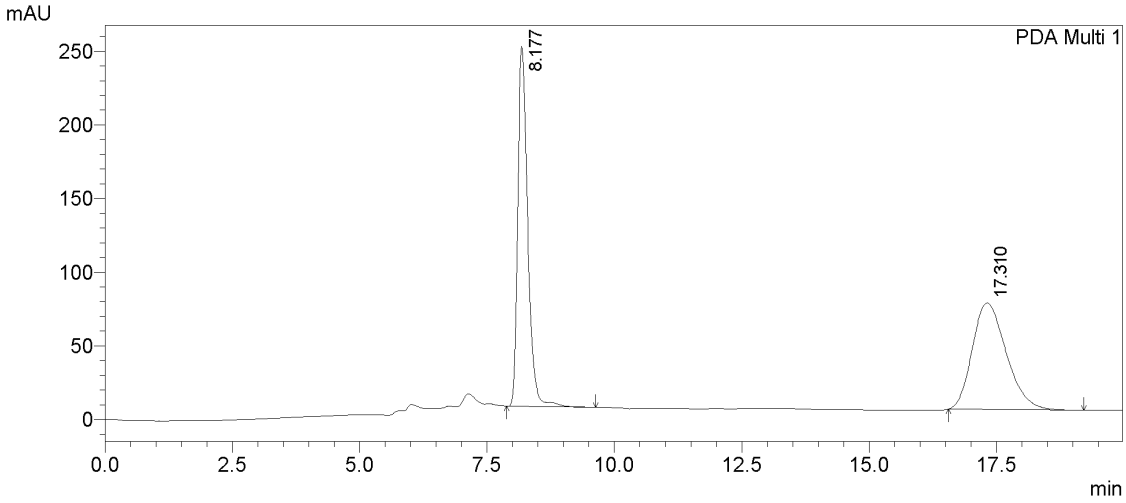
1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.066	366134	14275	3.978	14.516
2	27.068	8838869	84064	96.022	85.484
Total		9205003	98339	100.000	100.000

5j

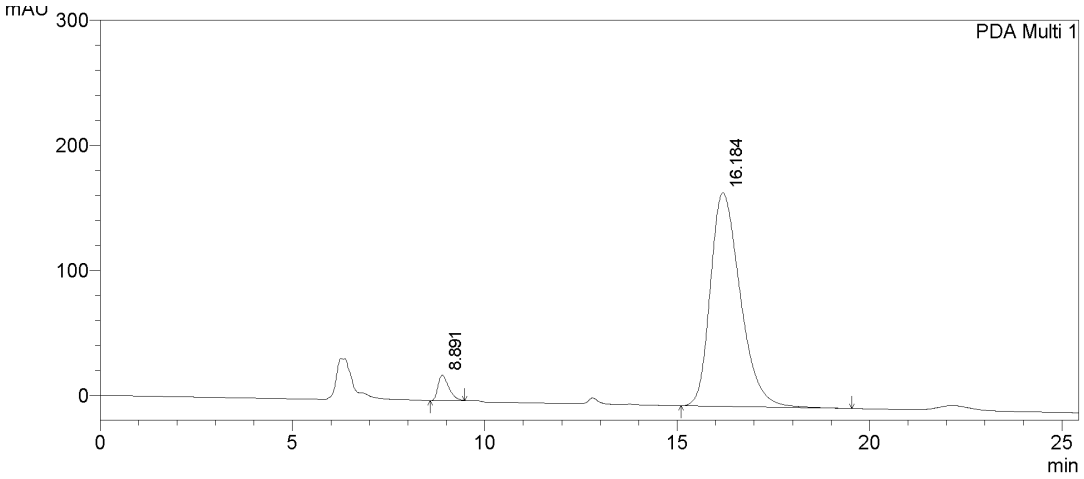


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.177	3324062	244218	49.772	77.136
2	17.310	3354517	72387	50.228	22.864
Total		6678579	316605	100.000	100.000



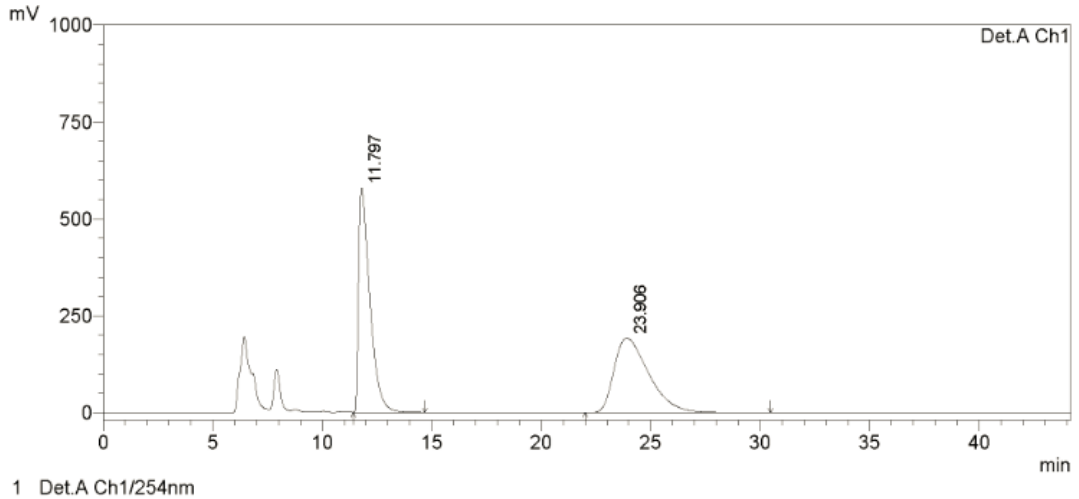
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.891	398138	20357	4.122	10.637
2	16.184	9260804	171023	95.878	89.363
Total		9658942	191379	100.000	100.000

5k

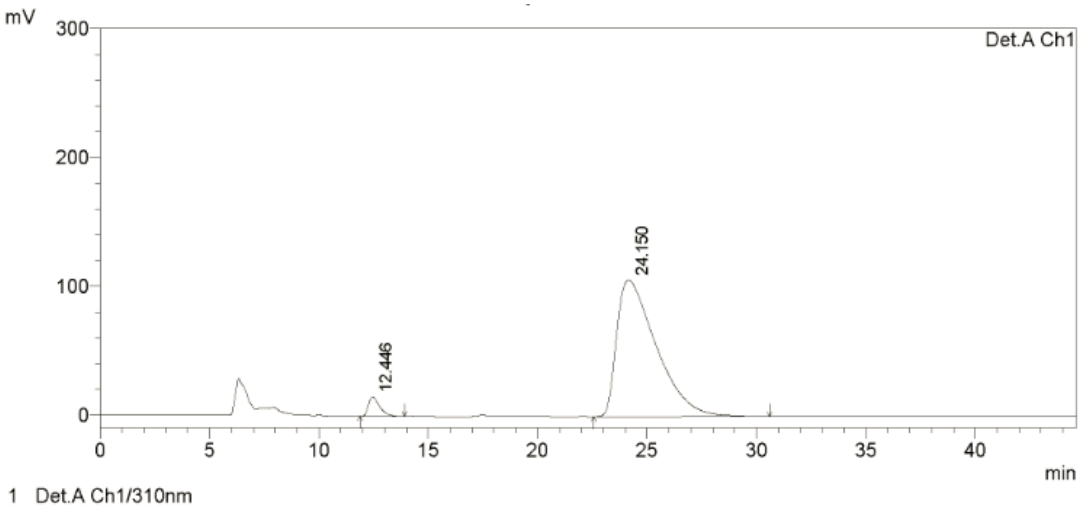


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.797	20738915	578117	49.323	75.009
2	23.906	21308112	192616	50.677	24.991
Total		42047027	770732	100.000	100.000



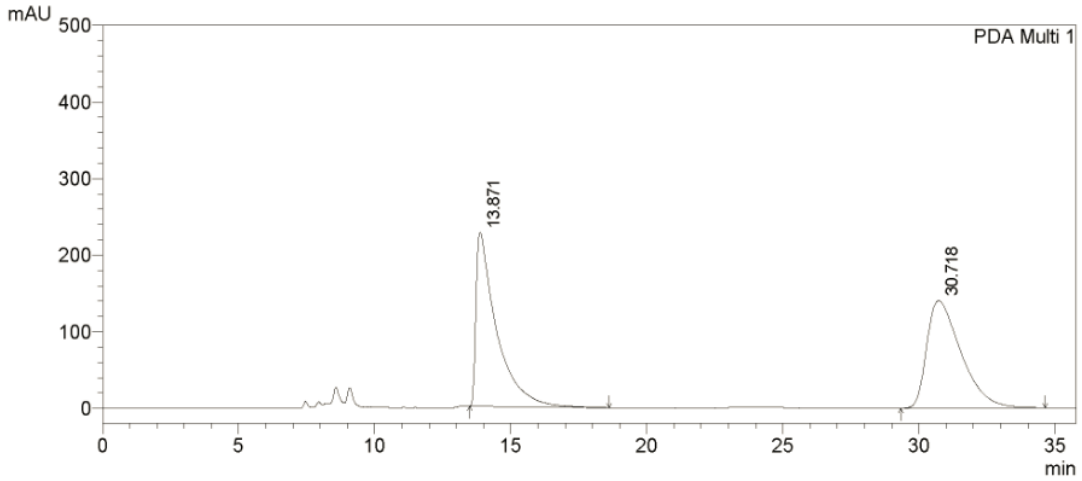
1 Det.A Ch1/310nm

PeakTable

检测器 A Ch1 310nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.446	549969	15191	3.987	12.548
2	24.150	13242421	105868	96.013	87.452
Total		13792389	121059	100.000	100.000

5l

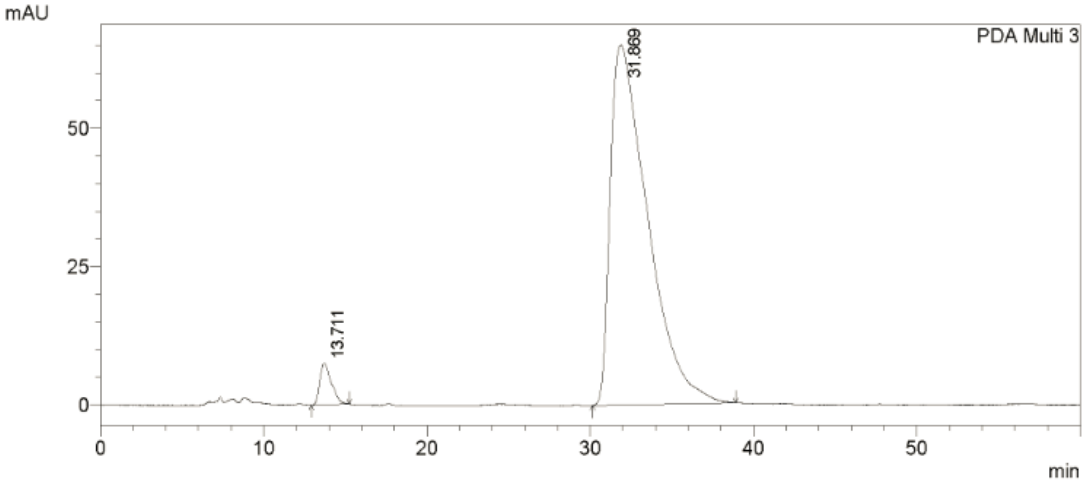


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.871	11866112	226808	49.164	61.772
2	30.718	12269827	140364	50.836	38.228
Total		24135939	367172	100.000	100.000



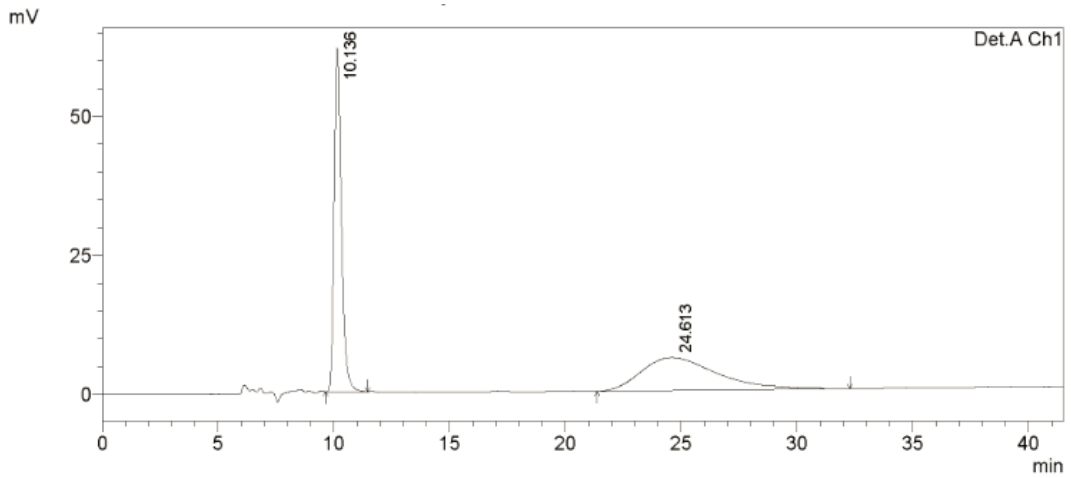
1 PDA Multi 3/319nm 4nm

PeakTable

PDA Ch3 319nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.711	372039	7516	3.467	10.358
2	31.869	10359867	65050	96.533	89.642
Total		10731906	72567	100.000	100.000

5m

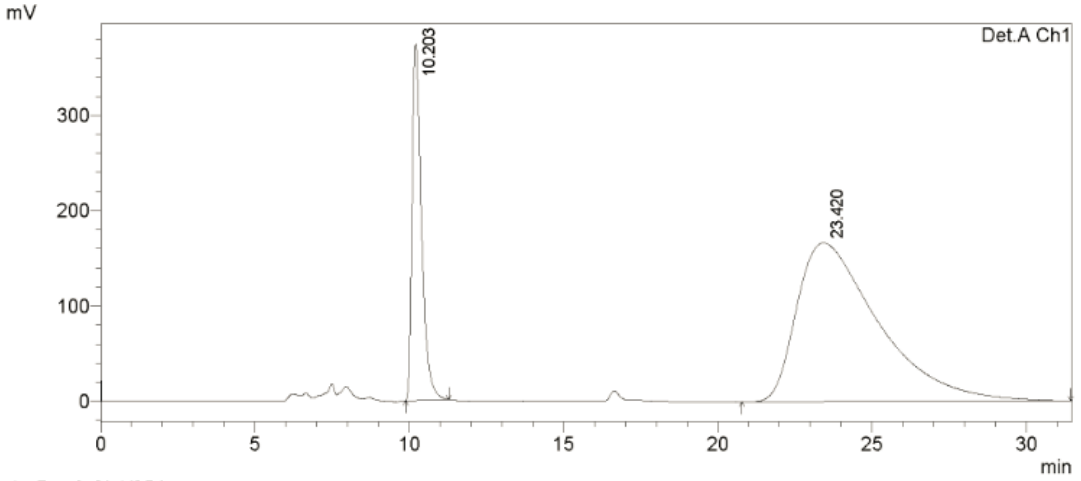


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.136	1356923	61761	50.112	91.253
2	24.613	1350882	5920	49.888	8.747
Total		2707805	67681	100.000	100.000



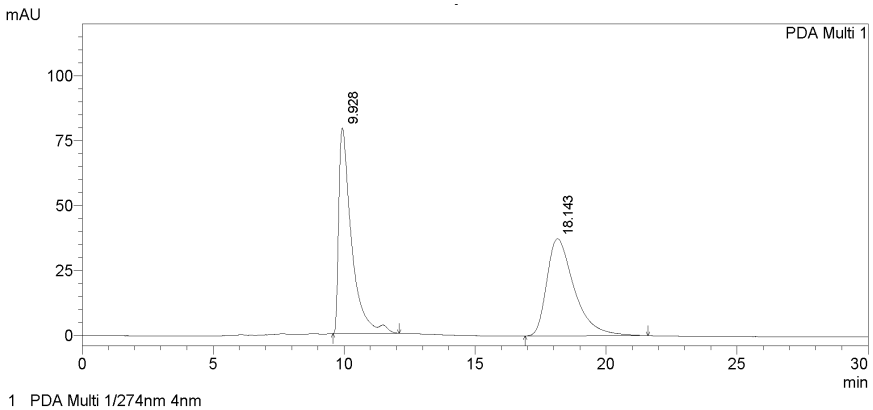
1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.203	7942882	373558	20.535	69.149
2	23.420	30737224	166665	79.465	30.851
Total		38680106	540223	100.000	100.000

5n

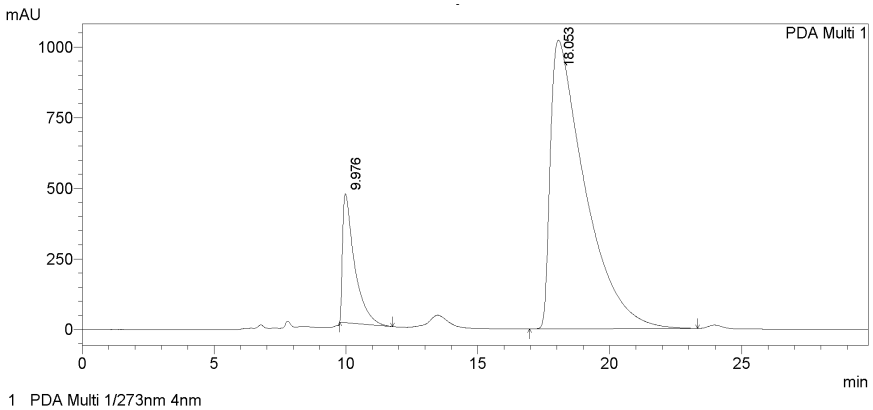


1 PDA Multi 1/274nm 4nm

PeakTable

PDA Ch1 274nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.928	2694249	79195	49.709	67.924
2	18.143	2725824	37399	50.291	32.076
Total		5420073	116595	100.000	100.000



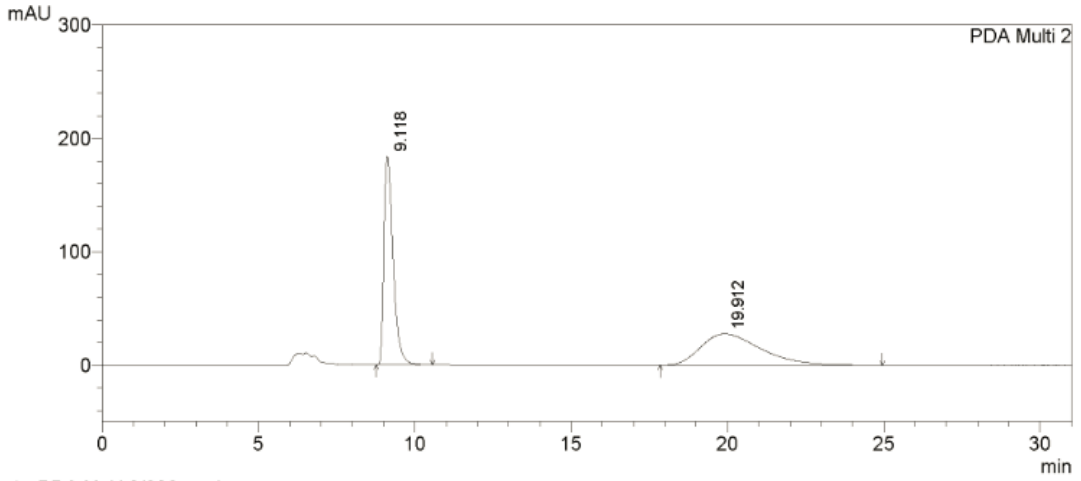
1 PDA Multi 1/273nm 4nm

PeakTable

PDA Ch1 273nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.976	14372106	457266	13.353	30.916
2	18.053	93259337	1021773	86.647	69.084
Total		107631443	1479039	100.000	100.000

5o

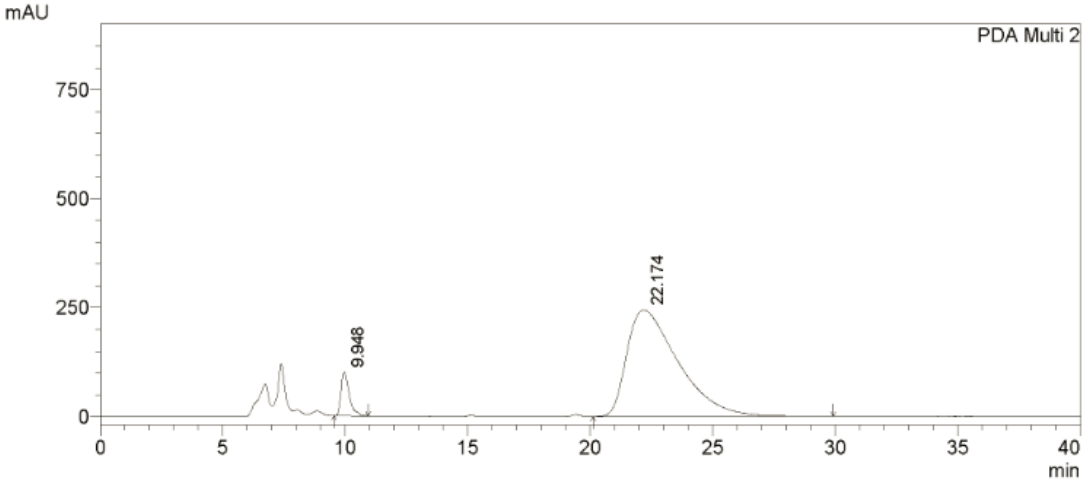


1 PDA Multi 2/320nm 4nm

PeakTable

PDA Ch2 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.118	3773048	184129	50.077	86.873
2	19.912	3761417	27823	49.923	13.127
Total		7534466	211951	100.000	100.000



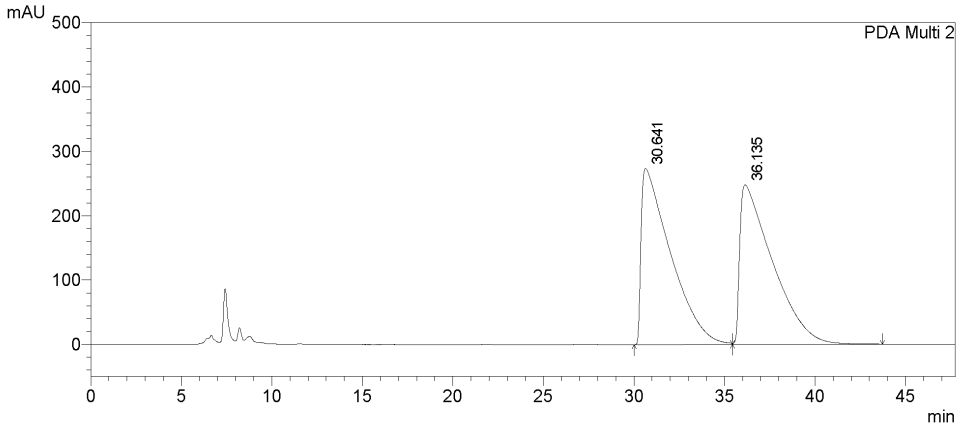
1 PDA Multi 2/284nm 4nm

PeakTable

PDA Ch2 284nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.948	2357032	100586	6.202	29.146
2	22.174	35648022	244525	93.798	70.854
Total		38005053	345110	100.000	100.000

5p

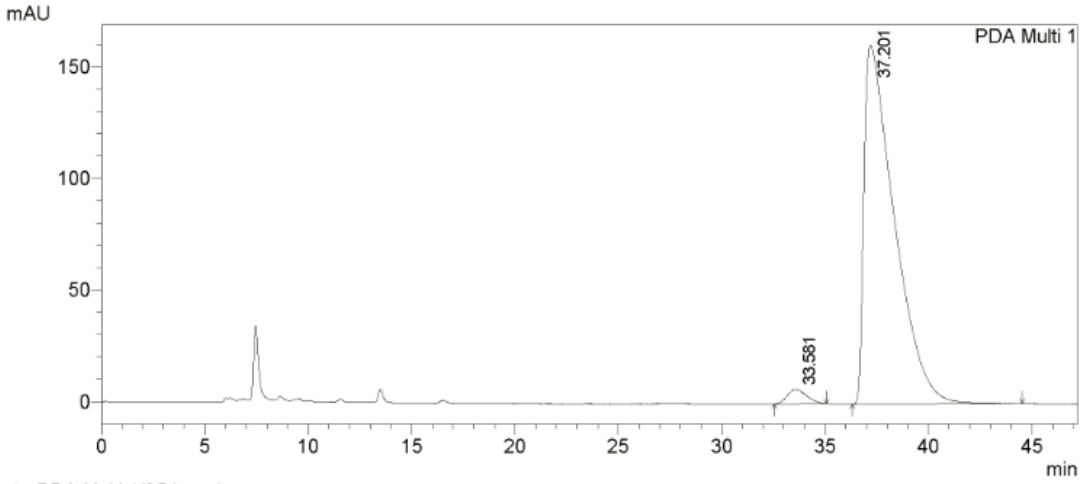


1 PDA Multi 2/268nm 4nm

PeakTable

PDA Ch2 268nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.641	30859702	273854	49.844	52.479
2	36.135	31053042	247983	50.156	47.521
Total		61912744	521836	100.000	100.000



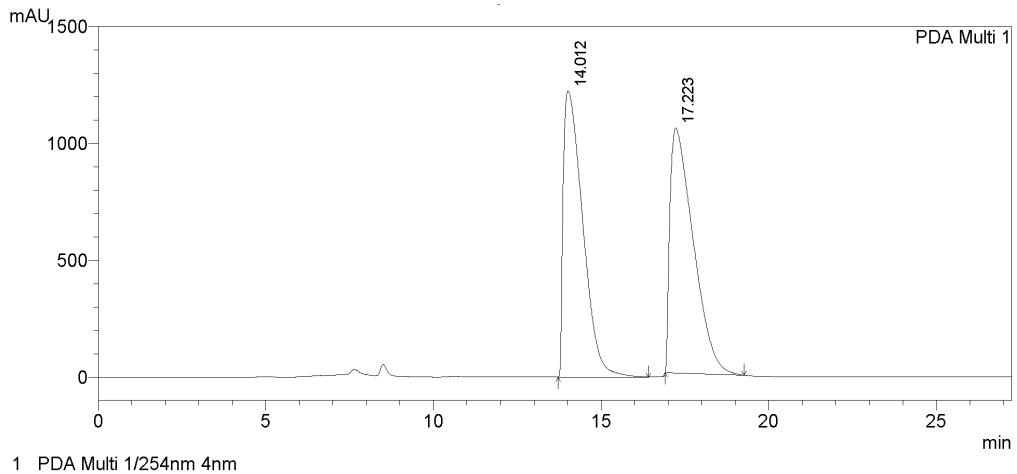
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.581	417952	6460	2.493	3.865
2	37.201	16349598	160684	97.507	96.135
Total		16767549	167144	100.000	100.000

5q

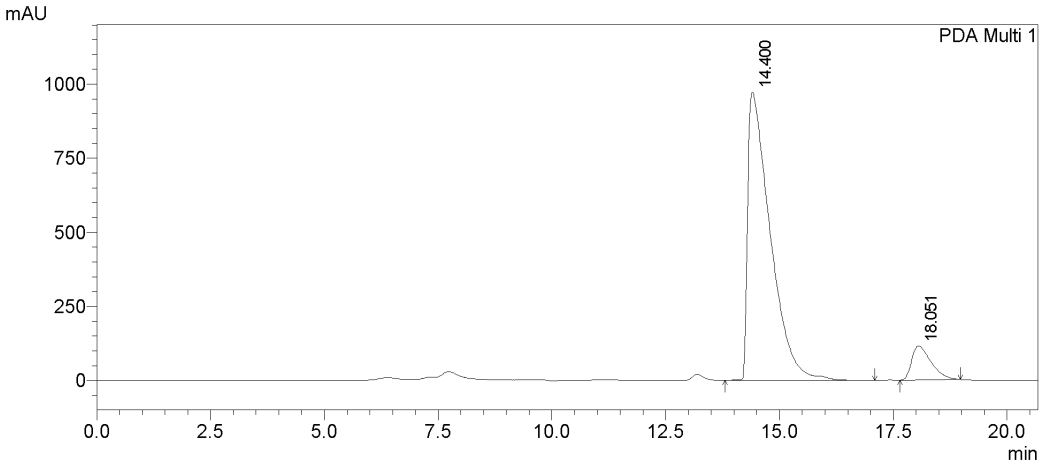


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.012	49711551	1226362	49.402	53.853
2	17.223	50914734	1050872	50.598	46.147
Total		100626284	2277234	100.000	100.000



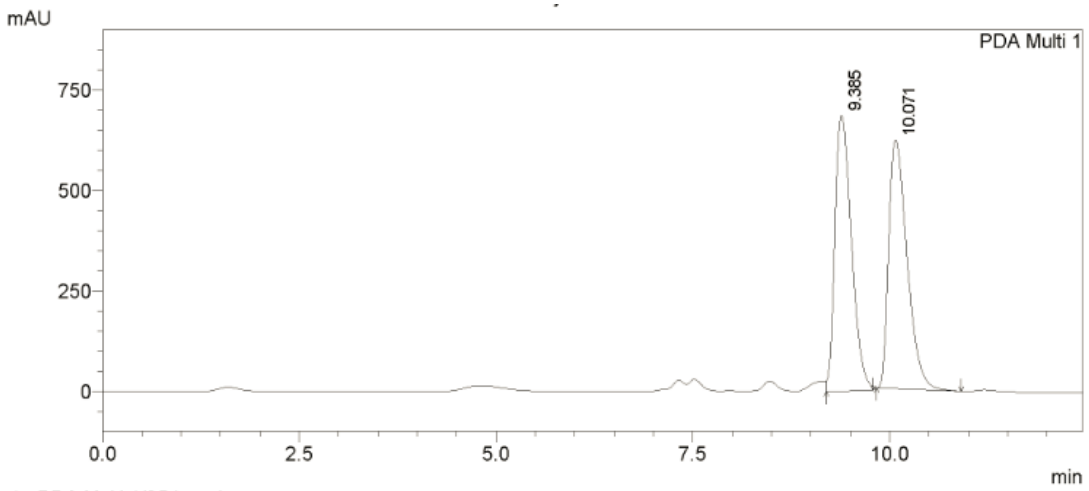
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.400	33493084	973102	90.803	89.454
2	18.051	3392253	114717	9.197	10.546
Total		36885336	1087819	100.000	100.000

5s

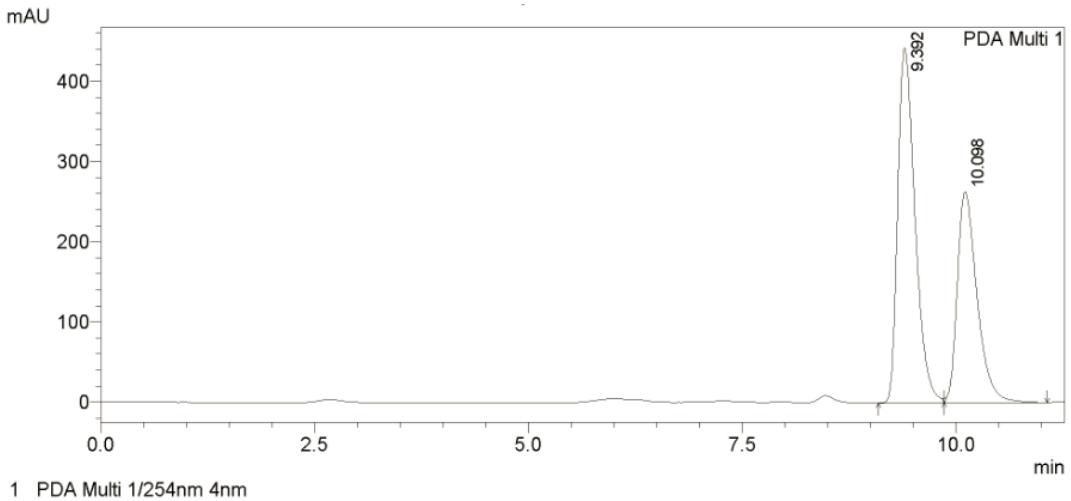


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.385	10013169	686750	49.819	52.562
2	10.071	10085797	619804	50.181	47.438
Total		20098966	1306554	100.000	100.000



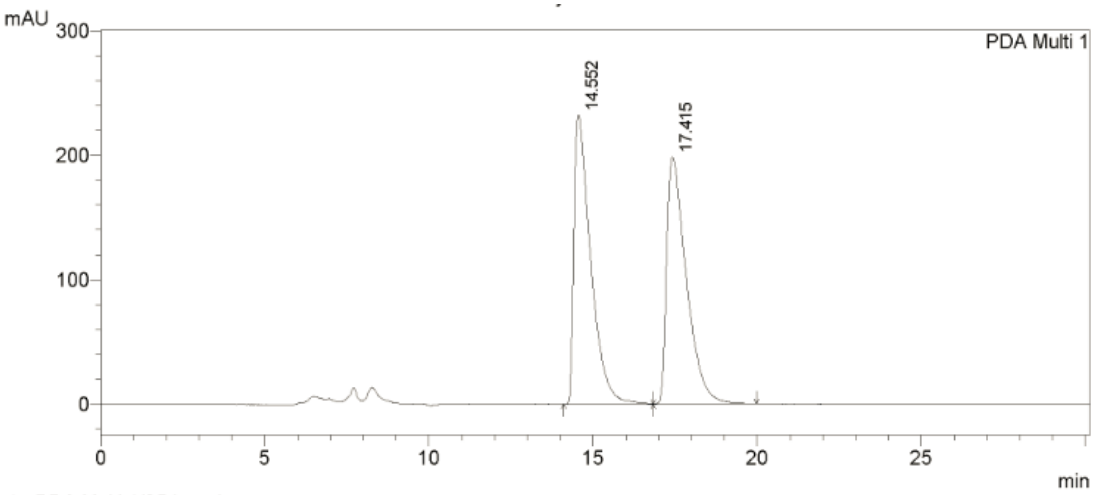
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.392	6217130	442897	59.549	62.720
2	10.098	4223211	263258	40.451	37.280
Total		10440342	706155	100.000	100.000

5t

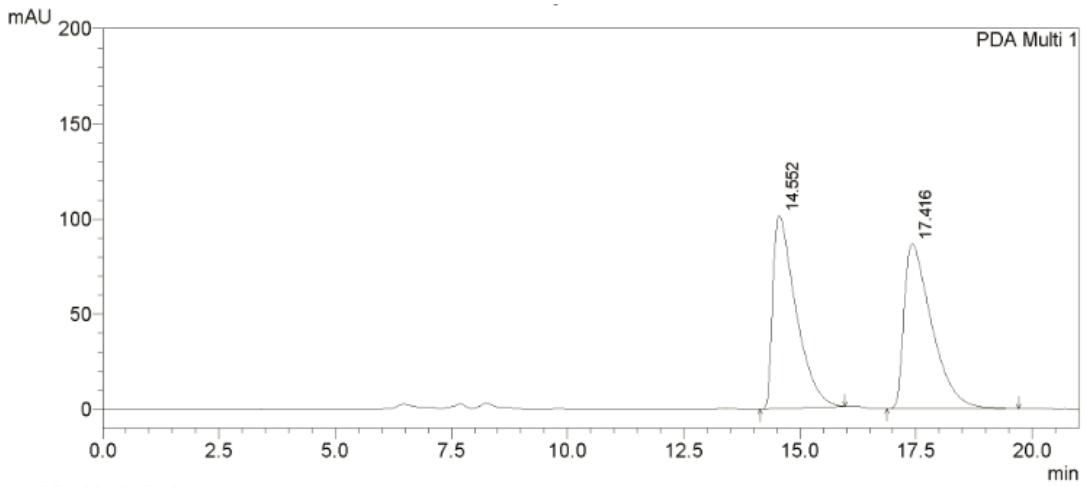


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.552	8250819	231942	49.950	53.942
2	17.415	8267313	198042	50.050	46.058
Total		16518132	429984	100.000	100.000



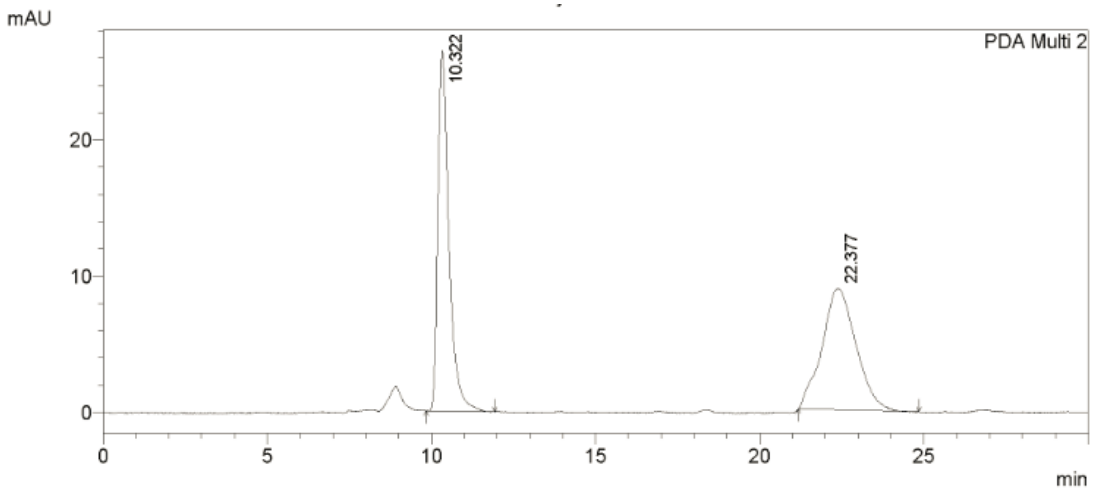
1 PDA Multi 1/288nm 4nm

PeakTable

PDA Ch1 288nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.552	3506407	101361	49.315	53.913
2	17.416	3603847	86649	50.685	46.087
Total		7110254	188009	100.000	100.000

5u

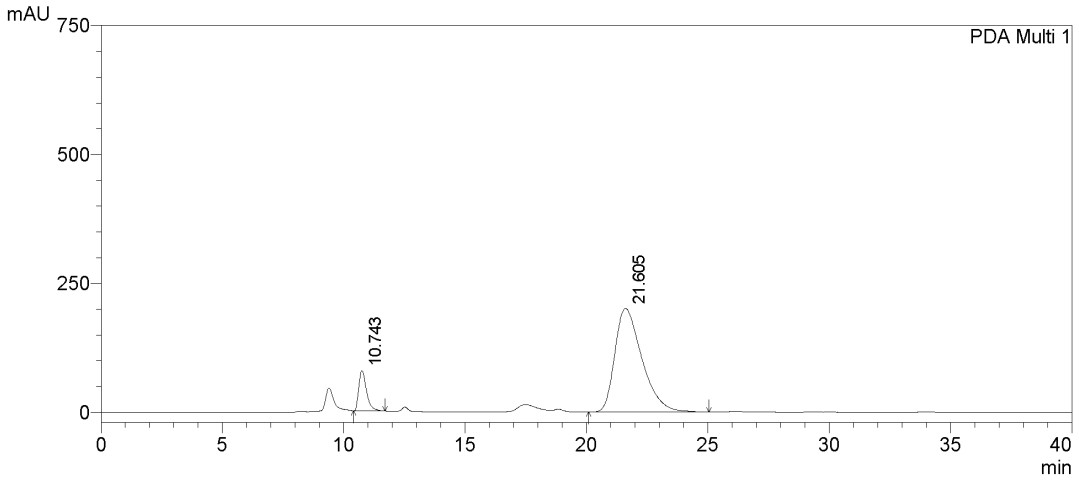


1 PDA Multi 2/326nm 4nm

PeakTable

PDA Ch2 326nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.322	622309	26448	49.167	74.791
2	22.377	643398	8914	50.833	25.209
Total		1265707	35363	100.000	100.000



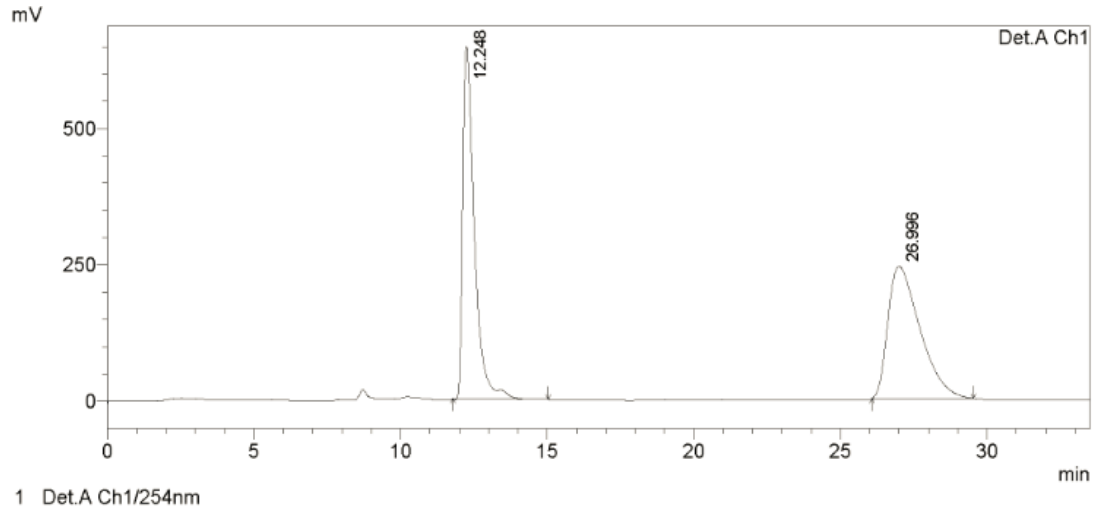
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.743	1739240	78057	10.018	27.989
2	21.605	15621158	200830	89.982	72.011
Total		17360398	278888	100.000	100.000

5v

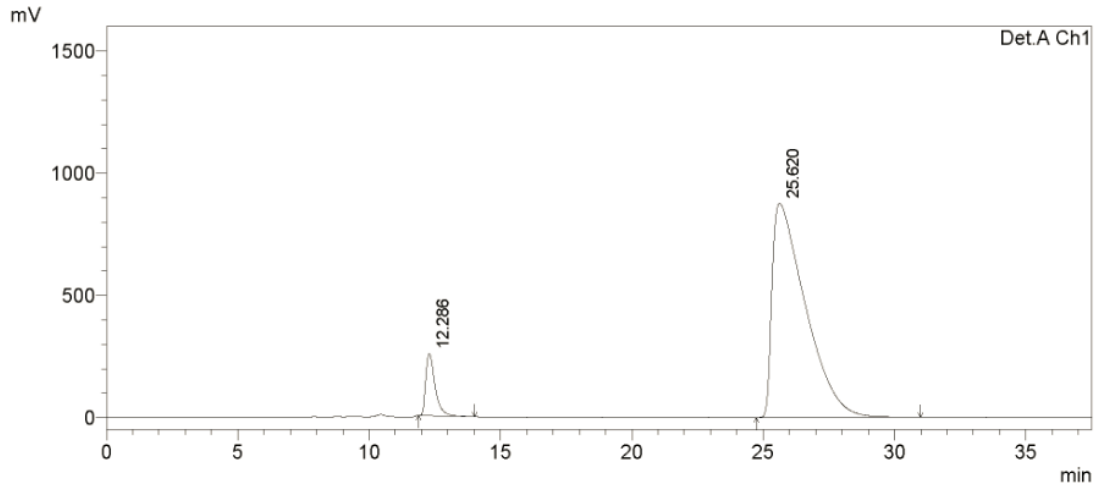


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.248	17829515	645775	49.161	72.711
2	26.996	18438237	242362	50.839	27.289
Total		36267752	888137	100.000	100.000



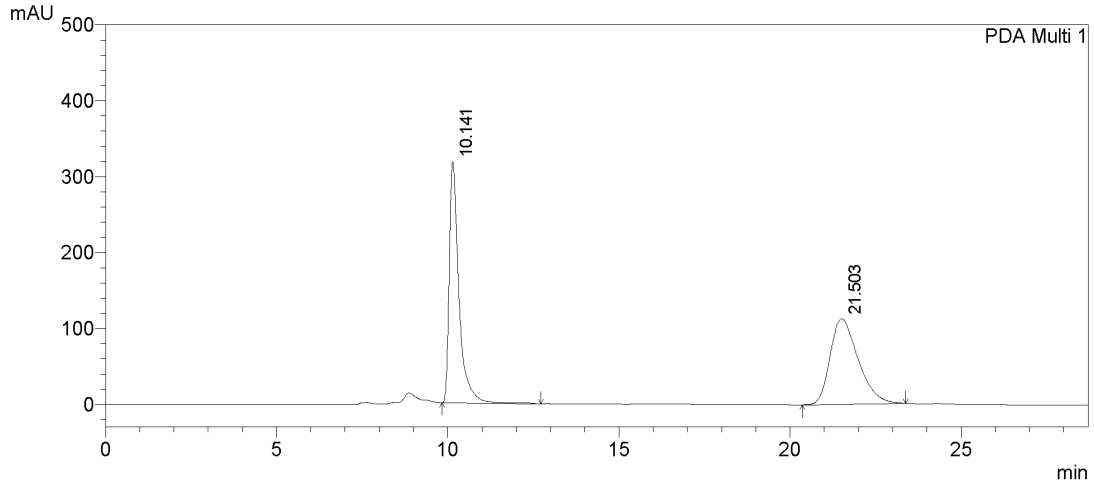
1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.286	6302171	255286	7.525	22.532
2	25.620	77444884	877722	92.475	77.468
Total		83747055	1133009	100.000	100.000

5w

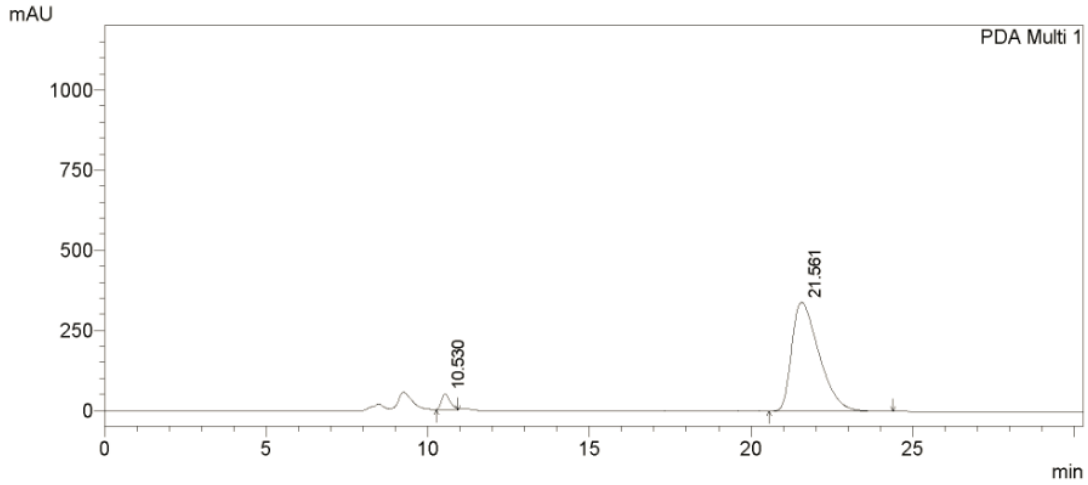


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.141	6318941	317664	49.609	73.835
2	21.503	6418674	112568	50.391	26.165
Total		12737614	430232	100.000	100.000



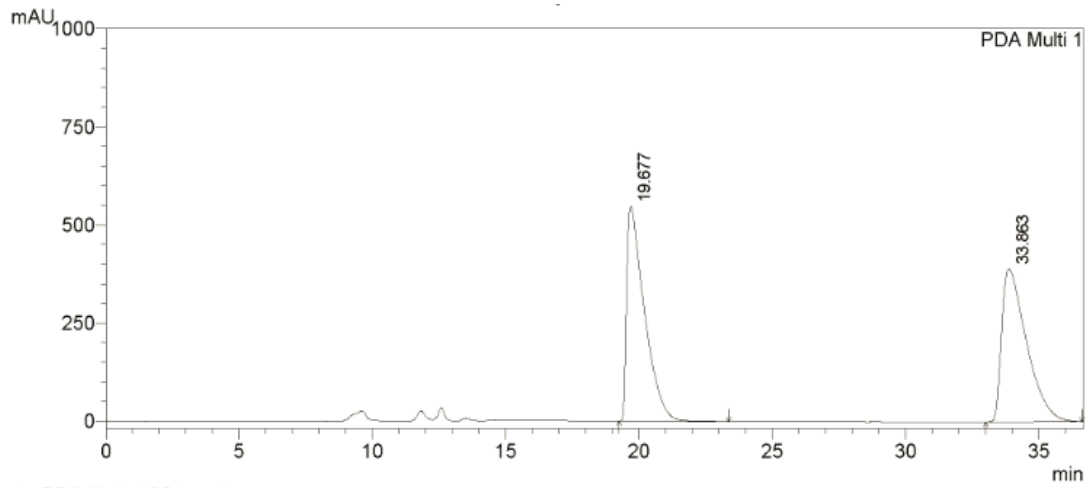
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.530	938692	49951	4.496	12.820
2	21.561	19941558	339674	95.504	87.180
Total		20880250	389625	100.000	100.000

5x

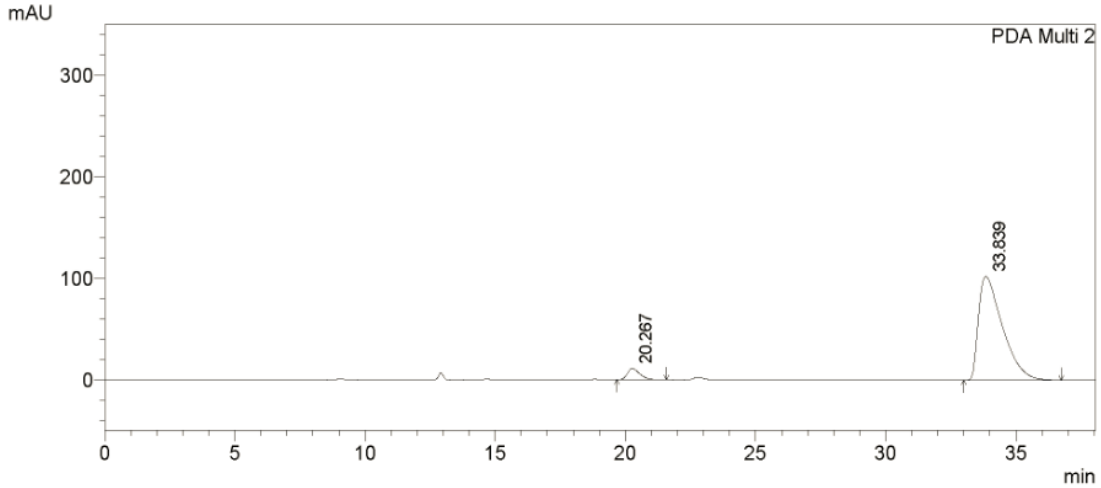


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.677	25362632	546684	50.165	58.403
2	33.863	25196284	389376	49.835	41.597
Total		50558916	936060	100.000	100.000



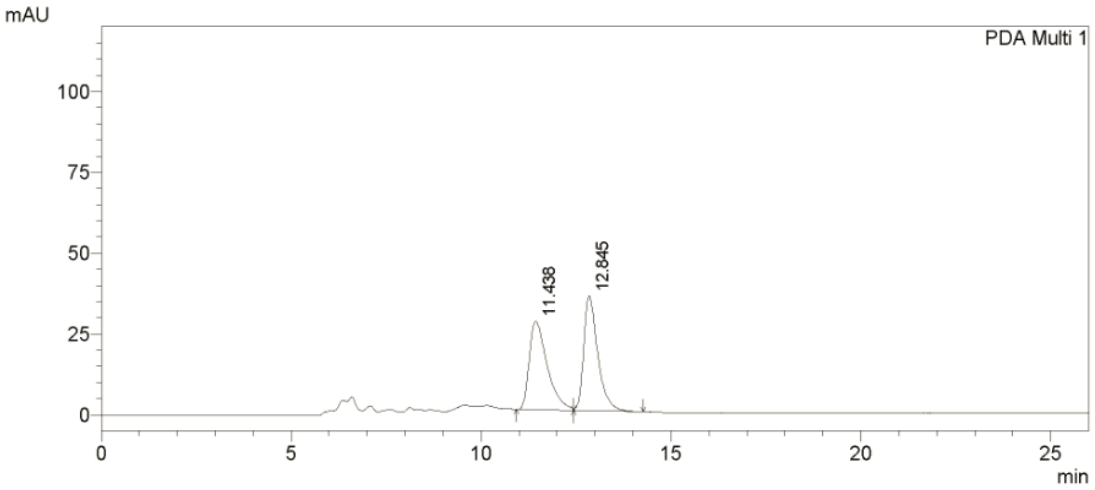
1 PDA Multi 2/326nm 4nm

PeakTable

PDA Ch2 326nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.267	375215	11066	5.422	9.762
2	33.839	6544956	102292	94.578	90.238
Total		6920170	113358	100.000	100.000

5y

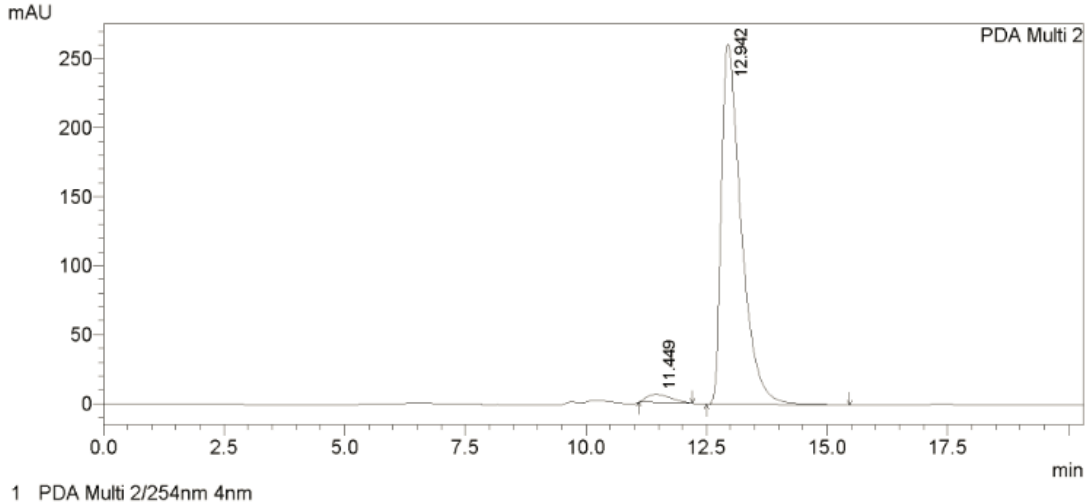


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.438	903882	27398	49.607	43.541
2	12.845	918213	35526	50.393	56.459
Total		1822096	62924	100.000	100.000



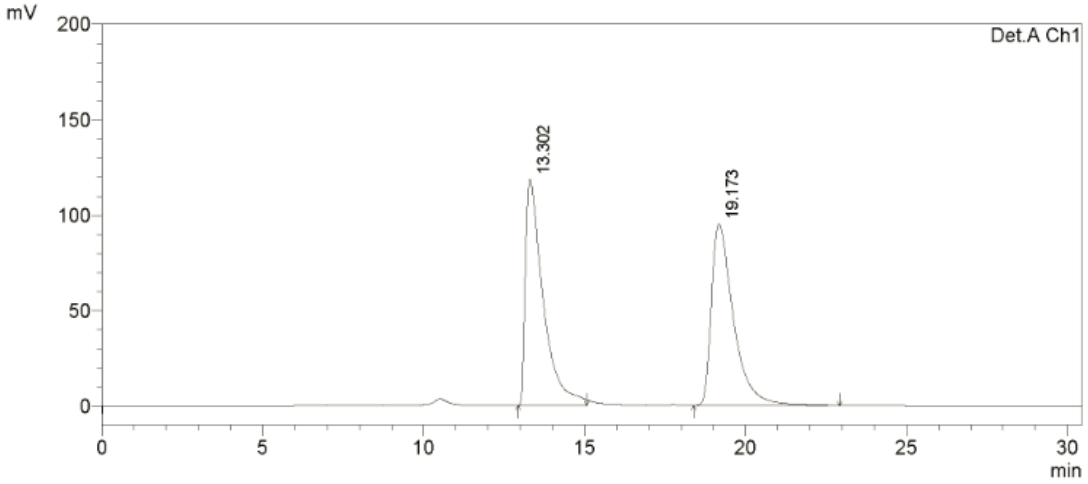
1 PDA Multi 2/254nm 4nm

PeakTable

PDA Ch2 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.449	204097	5892	2.658	2.208
2	12.942	7474562	260945	97.342	97.792
Total		7678659	266837	100.000	100.000

5z

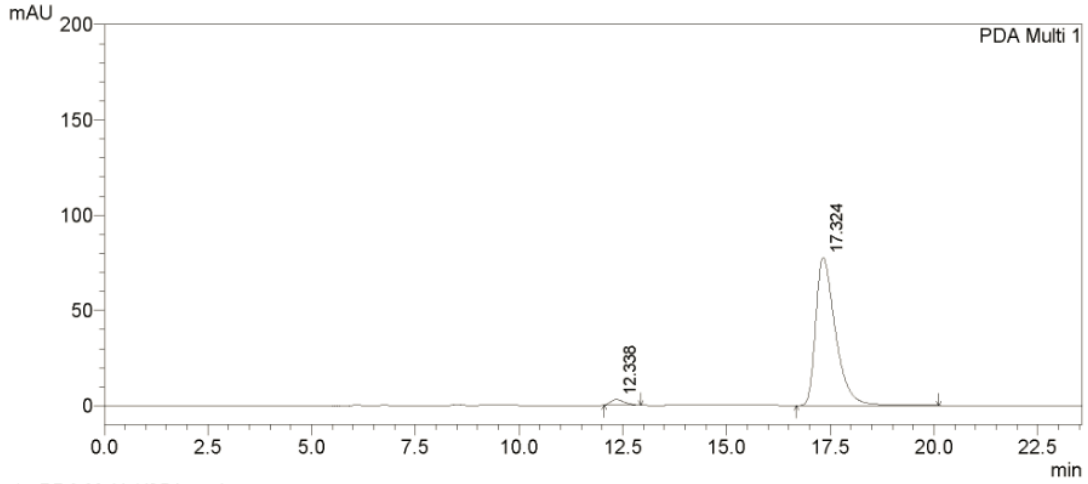


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.302	4556795	118578	50.127	55.489
2	19.173	4533632	95120	49.873	44.511
Total		9090427	213698	100.000	100.000



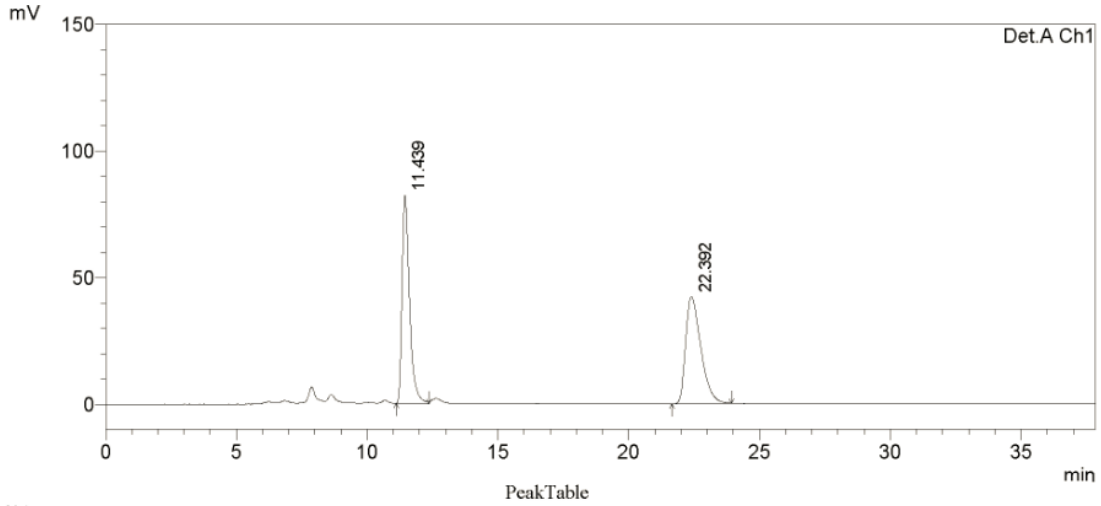
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.338	68533	2958	2.542	3.659
2	17.324	2626989	77901	97.458	96.341
Total		2695522	80860	100.000	100.000

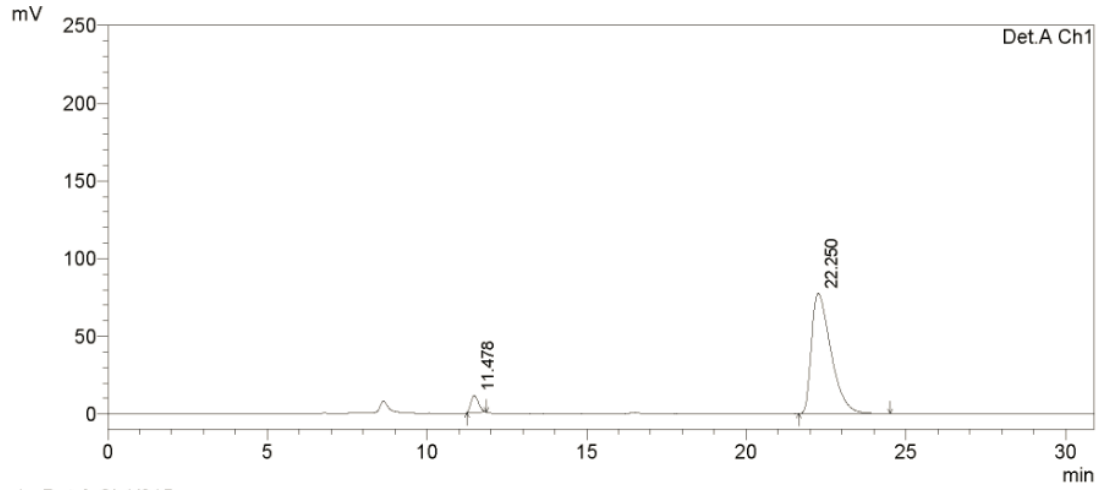
5aa



PeakTable

检测器 A Ch1 315nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.439	1644319	82213	49.017	66.048
2	22.392	1710263	42262	50.983	33.952
Total		3354582	124474	100.000	100.000



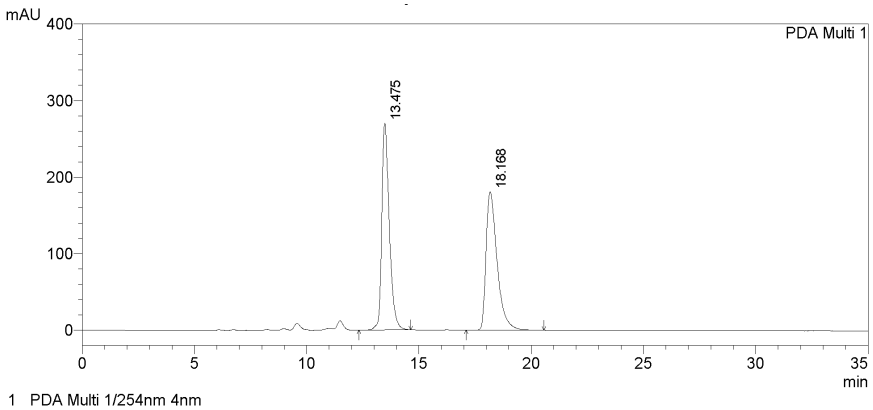
1 Det.A Ch1/315nm

PeakTable

检测器 A Ch1 315nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.478	178861	10871	5.153	12.315
2	22.250	3291878	77401	94.847	87.685
Total		3470739	88272	100.000	100.000

5ab

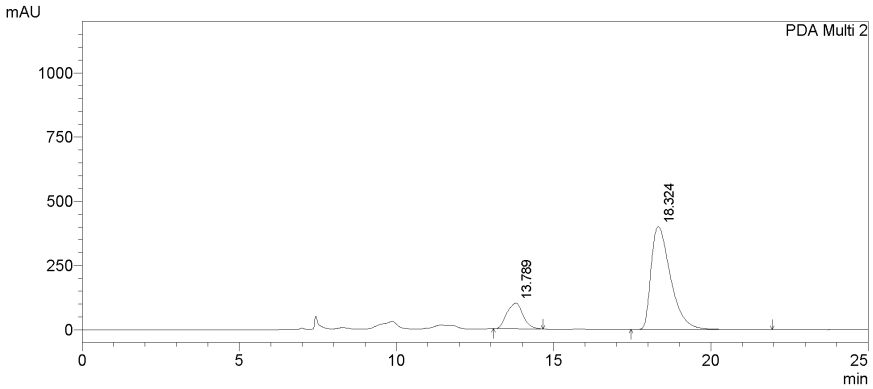


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.475	6298006	270082	50.349	59.880
2	18.168	6210780	180960	49.651	40.120
Total		12508786	451042	100.000	100.000



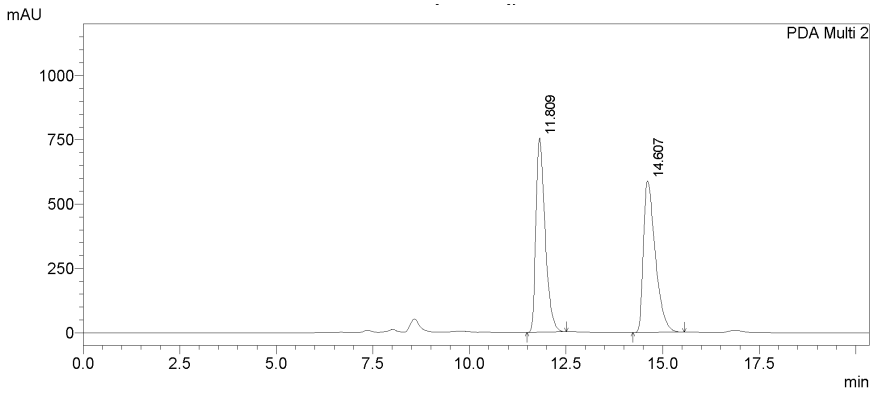
1 PDA Multi 2/264nm 4nm

PeakTable

PDA Ch2 264nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.789	3580095	100456	17.150	20.053
2	18.324	17295614	400482	82.850	79.947
Total		20875710	500938	100.000	100.000

5ac

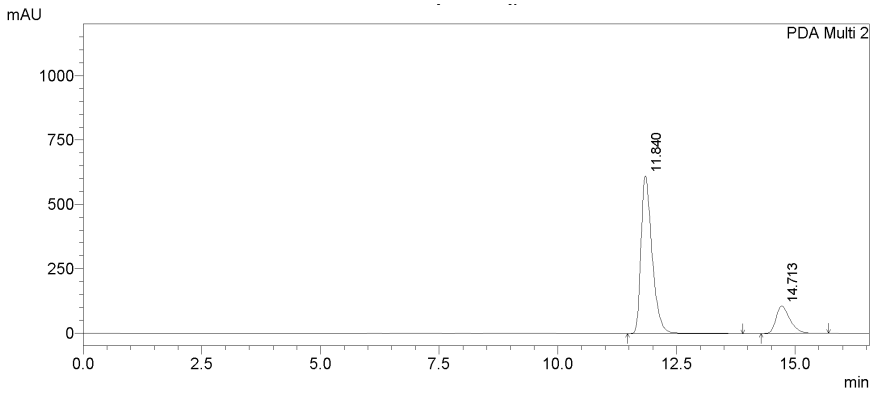


1 PDA Multi 2/284nm 4nm

PeakTable

PDA Ch2 284nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.809	12476349	754660	49.718	56.173
2	14.607	12617628	588791	50.282	43.827
Total		25093976	1343451	100.000	100.000



1 PDA Multi 2/284nm 4nm

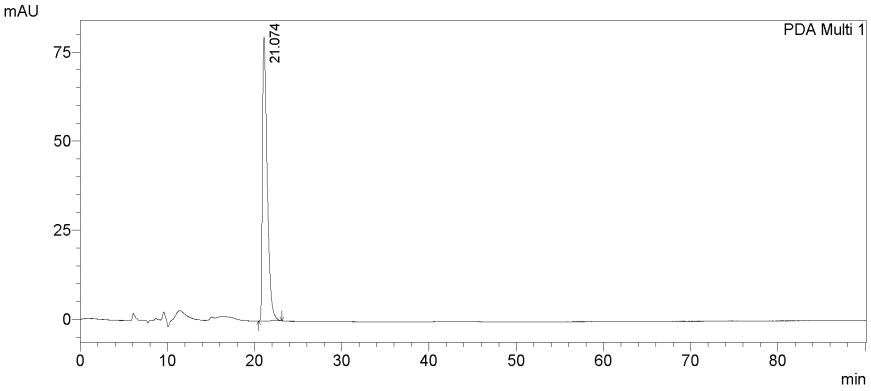
PeakTable

PDA Ch2 284nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.840	9931649	610996	82.112	85.185
2	14.713	2163653	106266	17.888	14.815
Total		12095302	717262	100.000	100.000

5ad (cannot be resolved into enantiomers)

AD-H



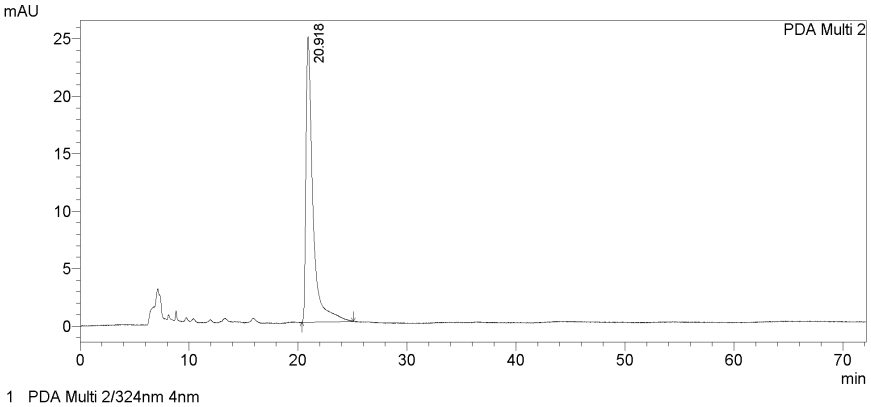
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.074	3011988	79799	100.000	100.000
Total		3011988	79799	100.000	100.000

IA



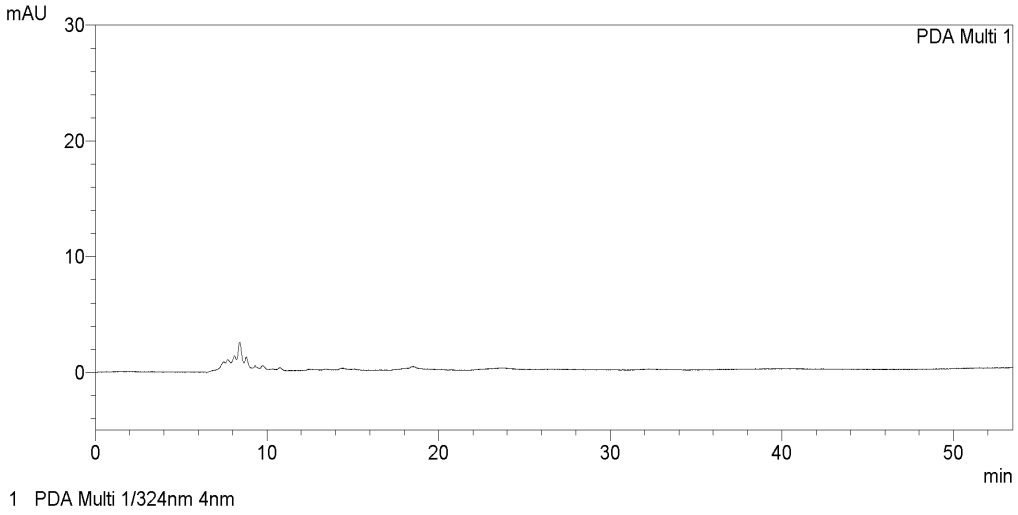
1 PDA Multi 2/324nm 4nm

PeakTable

PDA Ch2 324nm 4nm

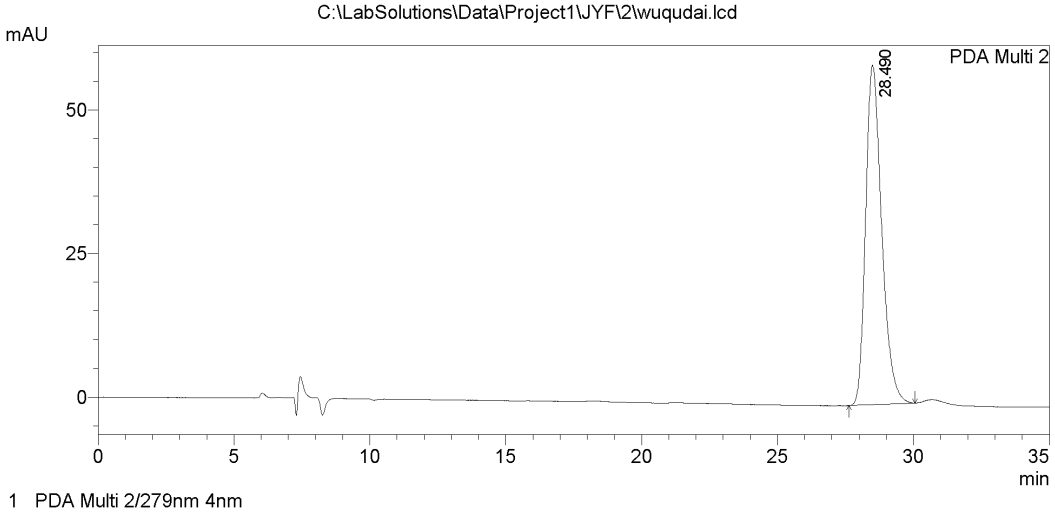
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.918	1099963	24868	100.000	100.000
Total		1099963	24868	100.000	100.000

ID



1 PDA Multi 1/324nm 4nm

IBN5



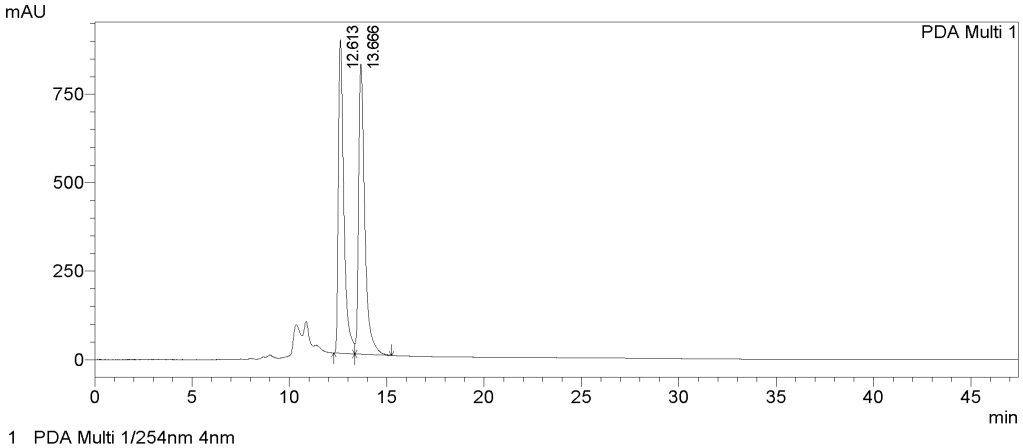
1 PDA Multi 2/279nm 4nm

PeakTable

PDA Ch2 279nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.490	2434781	59159	100.000	100.000
Total		2434781	59159	100.000	100.000

5ae



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.613	17448915	885643	49.067	51.936
2	13.666	18112555	819621	50.933	48.064
Total		35561470	1705264	100.000	100.000