
Supporting Information

**Synthesis of Easy-modified and Useful Dibenzo-[*b,d*]azepines by
Palladium(II)-Catalyzed Cyclization/Addition with a Green Solvent.**

Hua Cheng,^{abd} Rongqi Liu,^a Shengyang Fang,^a Zixiang Li,^a Denggao Zhang^a, Xi Zhang,^d
Wenfei Chen,^c Huixin Chen,^c Leyi Kang,^d Juan Wang,^c Yulong Xu,^d Shaoli Song,^b and
Liming Shao,^a

^a School of Pharmacy, Fudan University, 826 Zhangheng Road, Zhangjiang Hi-tech Park, Pudong, Shanghai,
201203, China

^b China Department of Nuclear Medicine, Fudan University Shanghai Cancer Center, No.270, Dong'an Road, Xuhui
District, Shanghai 200032, China

^c School of Medicine, Shanghai University, Shanghai 200444, China

^d Massachusetts General Hospital, Harvard Medical School, Charlestown, MA 02129, USA

Contents

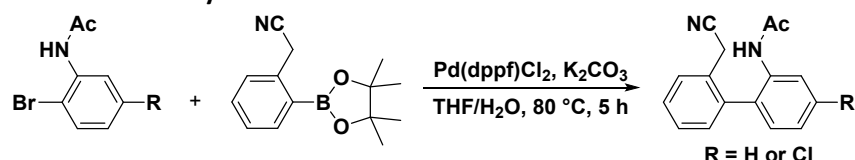
1.General	2
2.General Method for the Synthesis of 1a and 4a	2
3 Characterization Data of Products 1a and 4a	2
4. General Method for the Synthesis of Dibenzo-[<i>b,d</i>]azepines products.....	3
5. Characterization Data of Products 3a–3q and 5a–5h	3
6. Large-Scale Experiment.....	15
7. General Method for the Synthesis of 6a and 7a	15
8. Characterization Data of Products 6a and 7a	16
9. Synthesis Method and Characterization Data of Products 8a , 8b and 8c	17

10. Characterization Data of Controlled Experiment Intermediate C:.....	18
11. NMR Spectra for Compounds of this paper.....	19

1. General

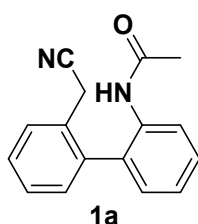
All raw reagents were bought from commercial sources and used as received. All reagents were purchased from Sigma Aldrich or Fluorochem and used as received. All reactions apart from where noted were carried out in air. All flash column chromatography was carried out using silica purchased from Fluorochem using the solvent system noted. ^1H NMR spectra were recorded at 400 MHz using a Bruker Avance III spectrometer. ^{13}C NMR spectra were recorded at 600 MHz using a Bruker Avance III spectrometer. All coupling constants are reported in Hertz (Hz). In cases where it was required 2D NMR techniques were used to confirm compound identity. Chemical shifts are reported in ppm and are referenced to residual solvent peaks; CHCl_3 (^1H 7.26 ppm, ^{13}C 77.0 ppm).

2. General Method for the Synthesis of 1a and 4a



To the solution of *N*-(2-bromophenyl)acetamide (1 eq) (*N*-(2-bromophenyl)acetamide was bought from commercial source and *N*-(2-bromo-5-chlorophenyl)acetamide was prepared according to the procedures reported in the literature Tetrahedron, 2011, 67, 5806-5810), (2-(2-(cyanomethyl)phenyl)-4,5,5-trimethyl-1,3,2-dioxaborolan-4-yl)methylum (1.5 eq) (prepared according to the procedures reported in the patent US 2017/0158704 A1), K_2CO_3 (2 eq) in the solvent ($\text{THF} : \text{H}_2\text{O} = 5:1$) was added $\text{Pd}(\text{dppf})\text{Cl}_2$ (0.1 eq). Then the mixture was stirred at 80 °C for 5 h under N_2 atmosphere. The reaction was then cooled to room temperature and diluted with H_2O , extracted three times with EA, dried by Na_2SO_4 and evaporated under a vacuum. The crude material was purified by column chromatography to give the desired product.

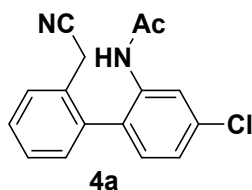
3. Characterization Data of Products 1a and 4a



Synthesised according to the general method, the crude material was purified by column chromatography (PE : EA = 5:1) to give the desired product as a yellow liquid in 72% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.26 (d, $J = 8.2$ Hz, 1H), 7.64 (d, $J = 7.3$ Hz, 1H), 7.54 – 7.40 (m, 3H), 7.27 (brd, $J = 7.3$ Hz, 1H), 7.22 (t, $J = 7.4$ Hz, 1H), 7.14 (brd, $J = 7.5$ Hz, 1H), 6.68 (s, 1H), 3.50 (d, $J = 18.5$ Hz, 1H), 3.44 (d, $J = 18.5$ Hz, 1H), 1.98 (s, 3H).

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}$, 251.1106; found, 251.1114.

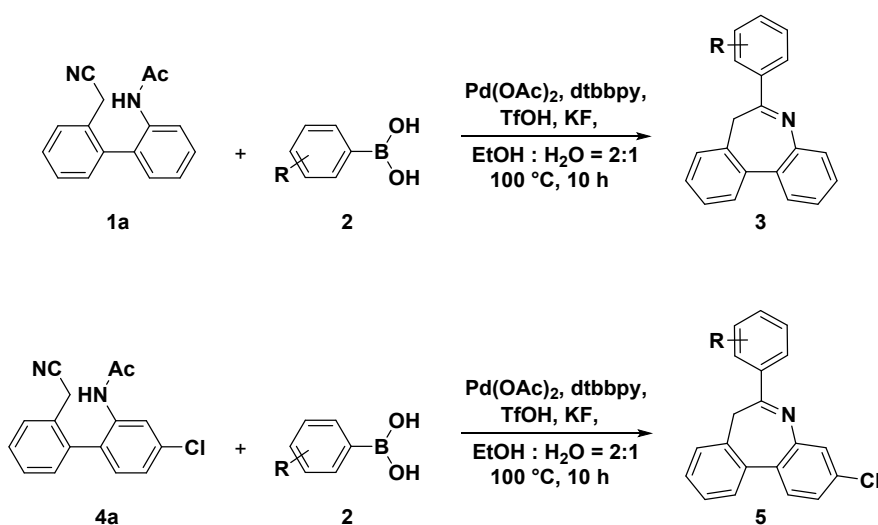


Synthesised according to the general method, the crude material was purified by column chromatography (PE : EA = 5:1) to give the desired product as a yellow liquid in 42% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.43 (s, 1H), 7.64 (d, J = 7.4 Hz, 1H), 7.53 (td, J = 7.6, 1.6 Hz, 1H), 7.48 (td, J = 7.5, 1.3 Hz, 1H), 7.25 (brd, J = 7.4 Hz, 1H), 7.19 (dd, J = 8.2, 2.1 Hz, 1H), 7.07 (d, J = 8.2 Hz, 1H), 6.66 (s, 1H), 3.49 (d, J = 18.4 Hz, 1H), 3.42 (d, J = 18.4 Hz, 1H), 1.98 (s, 3H).

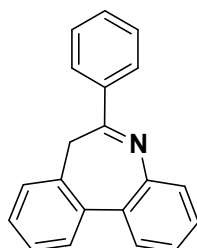
HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{NCl}$, 285.0716; found, 285.0720.

4. General Method for the Synthesis of Dibenzo-*[b,d]*azepines products



To the solution of **1a** (100 mg, 0.4 mmol, 1 eq) or **4a** (122 mg, 0.4 mmol, 1 eq), arylboronic acid **2** (0.6 mmol, 1.5 eq), KF (47 mg, 0.8 mmol, 2 eq), dtbbpy (11 mg, 0.04 mmol, 0.1 eq) in mix solvent (EtOH : H_2O = 1:2, 4 mL) was added TfOH (0.35 mL, 4 mmol, 10 eq) slowly, then the mixture was stirred at Ar at 100 °C for 10 h, and the reaction is a tube sealing reaction. After cooling to room temperature, the reaction was neutralized by saturated NaHCO_3 , then extracted three times with EA, dried by Na_2SO_4 and evaporated under a vacuum. The crude material was purified by column chromatography to afford products **3a–3q** and **5a–5h**.

5. Characterization Data of Products **3a–3q** and **5a–5h**



3a 6-phenyl-7H-dibenzo[*b,d*]azepine

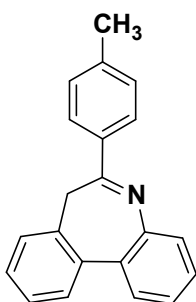
Synthesised according to the general method, after addition of the **1a** (100 mg, 0.4 mmol) and

phenylboronic acid (73 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 91% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.09 (dd, J = 6.7, 2.9 Hz, 2H), 7.74 (dd, J = 7.9, 1.5 Hz, 1H), 7.71 (dq, J = 7.0, 2.2 Hz, 1H), 7.54 (dd, J = 8.1, 1.5 Hz, 1H), 7.49 (dd, J = 7.1, 1.5 Hz, 1H), 7.46 (d, J = 3.5 Hz, 2H), 7.38 (d, J = 2.6 Hz, 3H), 7.31 (ddd, J = 8.2, 7.2, 1.5 Hz, 1H), 4.35 (d, J = 12.4 Hz, 1H), 3.04 (d, J = 12.5 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 163.80, 137.85, 136.98, 136.52, 131.46, 130.51, 129.43, 128.55, 128.46, 128.24, 127.99, 127.78, 127.10, 126.93, 126.88, 124.56, 36.43.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{N}$, 270.1204; found, 270.1210.



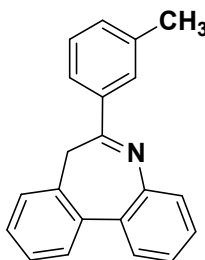
3b 6-(*p*-tolyl)-7*H*-dibenzo[*b,d*]azepine

Synthesised according to the general method, after addition of the **1a** (100 mg, 0.4 mmol) and *p*-tolylboronic acid (82 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 89% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, J = 6.0 Hz, 2H), 7.71 (dd, J = 10.6, 5.1 Hz, 2H), 7.49 (dd, J = 19.8, 7.2 Hz, 2H), 7.35 (d, J = 2.8 Hz, 3H), 7.29 (d, J = 7.8 Hz, 1H), 7.25 (d, J = 4.6 Hz, 2H), 4.33 (dd, J = 12.3, 2.2 Hz, 1H), 3.00 (dd, J = 12.4, 2.0 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 163.51, 146.55, 140.77, 137.03, 136.65, 135.19, 131.42, 129.41, 129.26, 128.40, 128.14, 127.94, 127.72, 126.98, 126.91, 126.85, 124.28, 36.30, 21.38.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{N}$, 284.1434; found, 284.1424.



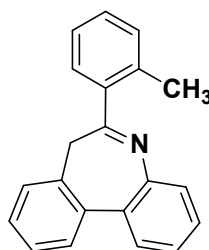
3c 6-(*m*-tolyl)-7*H*-dibenzo[*b,d*]azepine

Synthesised according to the general method, after addition of the **1a** (100 mg, 0.4 mmol) and *m*-tolylboronic acid (82 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 90% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 9.0 Hz, 2H), 7.77 – 7.68 (m, 2H), 7.54 (d, J = 7.9 Hz, 1H), 7.48 (dd, J = 9.2, 3.6 Hz, 1H), 7.40 – 7.27 (m, 5H), 7.26 (d, J = 2.3 Hz, 1H), 4.34 (dd, J = 12.4, 1.9 Hz, 1H), 3.02 (dd, J = 12.3, 1.8 Hz, 1H), 2.42 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 164.01, 138.16, 136.97, 136.58, 131.42, 131.32, 129.41, 128.61, 128.41, 128.20, 127.74, 127.05, 126.91, 125.10, 124.47, 36.52, 21.46.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{N}$, 284.1434; found, 284.1427.



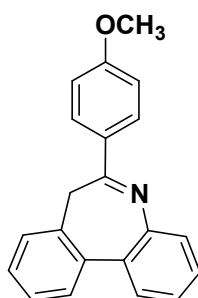
3d 6-(*o*-tolyl)-7H-dibenzo[*b,d*]azepine

Synthesised according to the general method, after addition of the **1a** (100 mg, 0.4 mmol) and *o*-tolylboronic acid (82 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 78% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.75 (t, J = 8.4 Hz, 2H), 7.53 – 7.45 (m, 2H), 7.45 – 7.40 (m, 1H), 7.40 – 7.34 (m, 1H), 7.34 – 7.31 (m, 1H), 7.29 (d, J = 7.3 Hz, 2H), 7.19 (dd, J = 15.2, 7.8 Hz, 3H), 3.93 (d, J = 11.9 Hz, 1H), 3.21 (d, J = 11.8 Hz, 1H), 2.23 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 167.52, 136.64, 136.07, 135.86, 131.15, 130.84, 129.39, 128.91, 128.52, 128.21, 127.99, 127.79, 127.20, 127.15, 126.72, 125.70, 124.70, 41.08, 20.09.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{N}$, 284.1434; found, 284.1421.



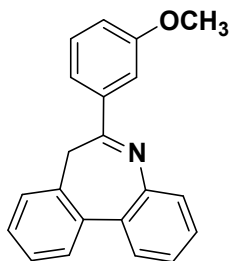
3e 6-(4-methoxyphenyl)-7H-dibenzo[*b,d*]azepine

Synthesised according to the general method, after addition of the **1a** (100 mg, 0.4 mmol) and 4-methoxyphenylboronic acid (91 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 30:1) to give the desired product as a yellow liquid in 75% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.15 – 8.02 (m, 2H), 7.71 (dd, J = 12.0, 5.3 Hz, 2H), 7.56 – 7.42 (m, 2H), 7.35 (s, 3H), 7.31 – 7.23 (m, 1H), 7.02 – 6.92 (m, 2H), 4.32 (d, J = 12.3 Hz, 1H), 3.84 (s, 3H), 2.99 (d, J = 12.3 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 161.59, 137.08, 136.61, 131.41, 129.71, 129.41, 128.41, 128.13, 127.74, 126.99, 126.88, 126.81, 124.17, 113.88, 55.38, 36.14.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{NO}$, 300.1383; found, 300.1366.



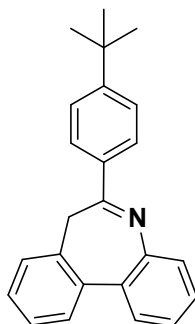
3f 6-(3-methoxyphenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the **1a** (100 mg, 0.4 mmol) and 3-methoxyphenylboronic acid (91 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 30:1) to give the desired product as a yellow liquid in 80% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.77 – 7.65 (m, 3H), 7.63 (s, 1H), 7.52 (d, J = 7.4 Hz, 1H), 7.47 (t, J = 7.2 Hz, 1H), 7.37 (t, J = 5.2 Hz, 4H), 7.30 (t, J = 7.4 Hz, 1H), 7.00 (d, J = 6.5 Hz, 1H), 4.32 (d, J = 12.4 Hz, 1H), 3.86 (s, 3H), 3.02 (d, J = 12.4 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 163.37, 159.79, 146.36, 139.39, 136.95, 136.58, 131.42, 129.44, 128.42, 128.23, 127.74, 127.05, 126.94, 126.87, 124.49, 120.42, 116.67, 112.87, 55.37, 36.50.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{NO}$, 300.1383; found, 300.1379.



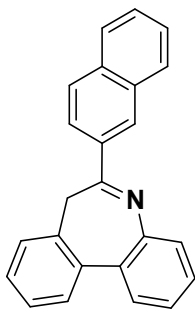
3g 6-(4-(tert-butyl)phenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the **1a** (100 mg, 0.4 mmol) and 4-*tert*-butylbenzeneboronic acid (107 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 91% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, J = 6.9 Hz, 2H), 7.77 – 7.67 (m, 2H), 7.56 – 7.43 (m, 4H), 7.36 (s, 3H), 7.32 – 7.26 (m, 1H), 4.35 (d, J = 12.3 Hz, 1H), 3.01 (d, J = 12.4 Hz, 1H), 1.33 (s, 9H).

^{13}C NMR (151 MHz, CDCl_3) δ 162.78, 153.27, 146.02, 136.46, 136.09, 134.55, 130.82, 128.82, 127.80, 127.53, 127.15, 127.12, 126.38, 126.35, 126.30, 124.93, 123.68, 35.63, 34.22, 30.56.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{23}\text{N}$, 326.1903; found, 326.1899.



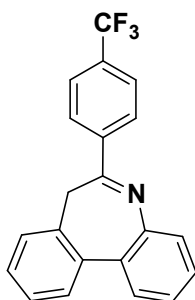
3h 6-(naphthalen-2-yl)-7H-dibenzo[*b,d*]azepine

Synthesised according to the general method, after addition of the **1a** (100 mg, 0.4 mmol) and naphthalen-2-ylboronic acid (103 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 74% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.55 (s, 1H), 8.25 (d, J = 8.6 Hz, 1H), 7.98 (dd, J = 8.2, 4.7 Hz, 1H), 7.87 (dd, J = 12.8, 7.3 Hz, 2H), 7.79 – 7.71 (m, 2H), 7.59 – 7.48 (m, 4H), 7.46 – 7.42 (m, 1H), 7.38 (dd, J = 5.1, 3.9 Hz, 2H), 7.32 (t, J = 7.5 Hz, 1H), 4.53 (d, J = 12.5 Hz, 1H), 3.11 (d, J = 12.4 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 163.36, 146.63, 137.05, 136.63, 135.31, 134.32, 132.98, 131.41, 129.46, 128.97, 128.47, 128.30, 128.25, 128.15, 127.80, 127.66, 127.26, 127.07, 127.02, 126.91, 126.42, 125.04, 124.49, 36.30.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{17}\text{N}$, 320.1434; found, 320.1433.



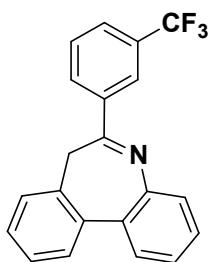
3i 6-(4-(trifluoromethyl)phenyl)-7H-dibenzo[*b,d*]azepine

Synthesised according to the general method, after addition of the **1a** (100 mg, 0.4 mmol) and 4-(trifluoromethyl)phenylboronic acid (114 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 45% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, J = 6.1 Hz, 2H), 7.78 – 7.67 (m, 4H), 7.54 – 7.46 (m, 2H), 7.36 (dd, J = 18.7, 5.0 Hz, 4H), 4.31 (d, J = 12.3 Hz, 1H), 3.06 (d, J = 12.7 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 162.03, 146.07, 141.28, 136.91, 136.19, 131.38, 129.50, 128.62, 128.42, 128.20, 127.91, 127.30, 126.99, 126.76, 125.50, 125.48, 124.96, 36.40.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{14}\text{F}_3\text{N}$, 338.1151; found, 338.1144.



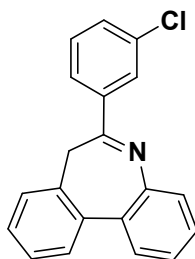
3j 6-(3-(trifluoromethyl)phenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the **1a** (100 mg, 0.4 mmol) and 3-(trifluoromethyl)phenylboronic acid (114 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 40% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.36 (s, 1H), 8.26 (d, J = 7.6 Hz, 1H), 7.81 – 7.66 (m, 3H), 7.63 – 7.46 (m, 3H), 7.45 – 7.29 (m, 4H), 4.32 (d, J = 12.2 Hz, 1H), 3.06 (d, J = 12.5 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 161.81, 146.08, 138.76, 136.94, 136.17, 131.38, 131.17, 131.00, 129.50, 129.07, 128.62, 128.43, 127.91, 127.30, 126.99, 126.86, 126.84, 126.76, 124.90, 124.76, 124.74, 123.08, 36.25.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{14}\text{F}_3\text{N}$, 338.1151; found, 338.1144.



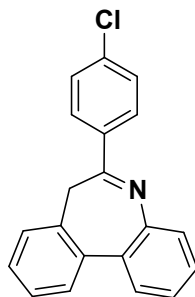
3k 6-(3-chlorophenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the **1a** (100 mg, 0.4 mmol) and 3-chlorophenylboronic acid (94 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 66% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.07 (s, 1H), 7.96 (d, J = 7.1 Hz, 1H), 7.77 – 7.67 (m, 2H), 7.57 – 7.45 (m, 2H), 7.45 – 7.28 (m, 6H), 4.32 – 4.21 (m, 1H), 3.03 (d, J = 12.5 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 161.96, 146.08, 139.75, 136.88, 136.22, 134.71, 131.35, 130.31, 129.71, 129.44, 128.51, 128.34, 128.05, 127.83, 127.20, 126.94, 126.77, 125.94, 124.76, 36.27.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{14}\text{ClN}$, 304.0888; found, 304.0860.



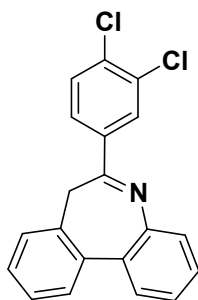
3l 6-(4-chlorophenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the **1a** (100 mg, 0.4 mmol) and 4-chlorophenylboronic acid (94 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 85% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.07 – 8.00 (m, 2H), 7.77 – 7.68 (m, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.45 – 7.28 (m, 6H), 4.28 (d, J = 12.5 Hz, 1H), 3.02 (d, J = 12.5 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 163.16, 143.15, 140.29, 137.04, 136.77, 136.58, 131.45, 129.46, 128.86, 128.45, 128.25, 127.79, 127.23, 127.13, 127.09, 126.98, 126.88, 124.48, 36.33.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{14}\text{ClN}$, 304.0888; found, 304.0883.



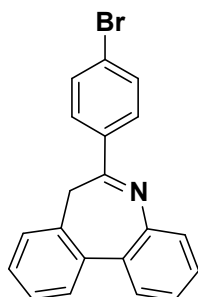
3m 6-(3,4-dichlorophenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the **1a** (100 mg, 0.4 mmol) and 3,4-dichlorophenylboronic acid (114 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 68% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.19 (s, 1H), 7.94 (d, J = 8.7 Hz, 1H), 7.80 – 7.68 (m, 2H), 7.52 (dd, J = 10.7, 7.0 Hz, 3H), 7.40 (dd, J = 12.6, 8.8 Hz, 4H), 4.29 – 4.21 (m, 1H), 3.04 (d, J = 12.5 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 166.29, 145.59, 139.45, 136.61, 136.32, 131.97, 131.11, 130.39, 130.30, 129.79, 129.32, 128.52, 128.16, 127.86, 127.36, 127.27, 126.95, 126.87, 125.04, 40.63.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{13}\text{Cl}_2\text{N}$, 338.0498; found, 338.0480.



3n 6-(4-bromophenyl)-7H-dibenzo[b,d]azepine

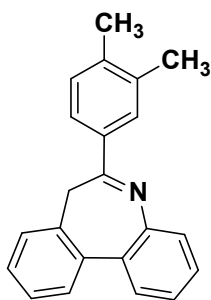
Synthesised according to the general method, after addition of the **1a** (100 mg, 0.4 mmol) and 4-bromophenylboronic acid (120 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 89% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, J = 8.4 Hz, 2H), 7.73 (dd, J = 11.9, 6.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.50 (dd, J = 8.3, 7.0 Hz, 2H), 7.36 (ddd, J = 19.6, 10.6, 5.9 Hz, 4H), 4.27 (d, J = 12.5 Hz, 1H), 3.02 (d, J = 12.4 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 162.19, 146.26, 136.95, 136.58, 136.40, 136.32, 131.36, 129.46,

129.25, 128.74, 128.53, 128.29, 127.83, 127.17, 126.91, 126.74, 124.63, 36.21.

HRMS m/z : $[M + H]^+$ calcd for $C_{20}H_{14}BrN$, 348.0382; found, 348.0374.



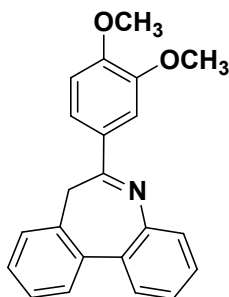
3o 6-(3,4-dimethylphenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the **1a** (100 mg, 0.4 mmol) and 3,4-dimethylphenylboronic acid (90 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 84% yield.

1H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.78 (m, 2H), 7.72 (dd, J = 9.9, 5.1 Hz, 2H), 7.55 – 7.43 (m, 2H), 7.35 (d, J = 2.9 Hz, 3H), 7.32 – 7.27 (m, 1H), 7.21 (d, J = 4.9 Hz, 1H), 4.34 (dd, J = 12.3, 2.8 Hz, 1H), 2.99 (dd, J = 12.3, 2.8 Hz, 1H), 2.31 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.76, 146.62, 139.55, 137.02, 136.86, 136.70, 135.56, 131.40, 129.74, 129.40, 129.11, 128.36, 128.13, 127.70, 126.95, 126.91, 126.87, 125.47, 124.23, 36.33, 19.87, 19.74.

HRMS m/z : $[M + H]^+$ calcd for $C_{22}H_{19}N$, 298.1590; found, 298.1585.



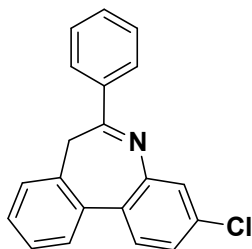
3p 6-(3,4-dimethoxyphenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the **1a** (100 mg, 0.4 mmol) and 3,4-dimethoxyphenylboronic acid (109 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 25:1) to give the desired product as a yellow liquid in 80% yield.

1H NMR (400 MHz, Chloroform- d) δ 7.71 (q, J = 7.2, 6.4 Hz, 4H), 7.56 – 7.41 (m, 2H), 7.39 – 7.27 (m, 4H), 6.92 (d, J = 8.3 Hz, 1H), 4.34 (d, J = 12.3 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 2.99 (d, J = 12.4 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.75, 151.41, 149.15, 146.57, 137.04, 136.62, 131.38, 130.60, 129.42, 128.40, 128.16, 127.75, 127.00, 126.88, 126.79, 124.21, 121.34, 110.59, 110.17, 55.95, 35.94.

HRMS m/z : $[M + H]^+$ calcd for $C_{22}H_{19}NO_2$, 330.1489; found, 330.1489.



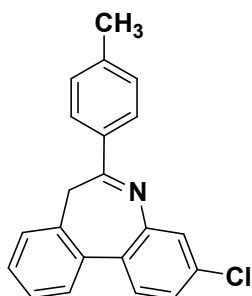
5a 3-chloro-6-phenyl-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the **4a** (122 mg, 0.4 mmol) and phenylboronic acid (73 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 89% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.01 (s, 2H), 7.58 (d, J = 11.3 Hz, 2H), 7.46 (s, 1H), 7.38 (s, 3H), 7.30 (s, 3H), 7.18 (d, J = 8.6 Hz, 1H), 4.29 (d, J = 12.4 Hz, 1H), 2.90 (s, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 164.40, 147.32, 137.55, 136.21, 136.10, 133.15, 130.69, 130.55, 129.87, 128.56, 128.50, 128.22, 127.96, 127.19, 127.04, 126.46, 124.53, 36.37.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{NCl}$, 304.0815; found, 304.0814.



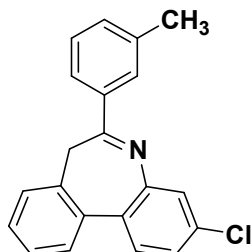
5b 3-chloro-6-(p-tolyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the **4a** (122 mg, 0.4 mmol) and *p*-tolylboronic acid (82 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 90% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.89 (s, 2H), 7.53 (d, J = 11.2 Hz, 2H), 7.45 (d, J = 9.8 Hz, 1H), 7.28 (s, 3H), 7.16 (d, J = 17.7 Hz, 3H), 4.23 (d, J = 11.1 Hz, 1H), 2.83 (d, J = 11.0 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 164.23, 147.46, 141.10, 136.26, 136.11, 134.73, 133.09, 130.50, 129.86, 129.28, 128.42, 128.16, 127.97, 127.10, 127.01, 126.43, 124.32, 36.21, 21.36.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{ClN}$, 318.0971; found, 318.0982.



5c 6-(m-tolyl)-7H-dibenzo[b,d]azepine

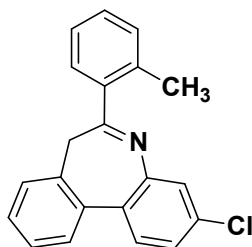
Synthesised according to the general method, after addition of the **4a** (122 mg, 0.4 mmol) and *m*-

tolylboronic acid (82 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 87% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.72 (p, J = 8.3, 7.6 Hz, 2H), 7.50 (d, J = 21.9 Hz, 2H), 7.41 (s, 1H), 7.21 (d, J = 8.3 Hz, 4H), 7.10 (d, J = 23.6 Hz, 2H), 4.22 (d, J = 13.3 Hz, 1H), 2.80 (s, 1H), 2.25 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 165.09, 149.53, 139.16, 137.52, 136.27, 136.10, 133.15, 131.57, 130.55, 129.87, 128.61, 128.49, 128.42, 128.20, 127.18, 127.08, 126.46, 125.13, 124.50, 36.50, 21.45.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{ClN}$, 318.0971; found, 318.0990.



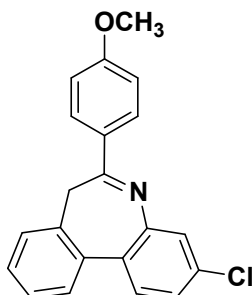
5d 3-chloro-6-(*o*-tolyl)-7*H*-dibenzo[*b,d*]azepine

Synthesised according to the general method, after addition of the **4a** (122 mg, 0.4 mmol) and *o*-tolylboronic acid (82 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 80% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, J = 8.5 Hz, 2H), 7.53 (s, 1H), 7.40 (d, J = 5.5 Hz, 2H), 7.31 (d, J = 9.7 Hz, 3H), 7.23 (d, J = 6.1 Hz, 3H), 3.98 (dd, J = 12.5, 4.3 Hz, 1H), 3.18 (dd, J = 12.0, 4.3 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 168.55, 146.75, 139.86, 135.97, 135.84, 135.78, 133.17, 130.94, 130.55, 129.55, 129.07, 128.49, 128.27, 127.96, 127.32, 126.29, 125.71, 124.73, 40.93, 20.58.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{ClN}$, 318.0971; found, 318.0972.



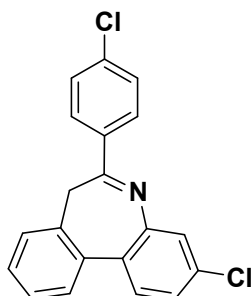
5e 3-chloro-6-(4-methoxyphenyl)-7*H*-dibenzo[*b,d*]azepine

Synthesised according to the general method, after addition of the **4a** (122 mg, 0.4 mmol) and 4-methoxyphenylboronic acid (91 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 30:1) to give the desired product as a yellow liquid in 79% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 14.5 Hz, 2H), 7.41 (s, 1H), 7.23 (s, 3H), 7.11 (d, J = 8.6 Hz, 1H), 6.84 (d, J = 18.7 Hz, 2H), 4.21 (d, J = 12.5 Hz, 1H), 3.72 (s, 3H), 2.82 (d, J = 12.4 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 163.13, 161.75, 147.56, 136.27, 136.17, 133.09, 130.51, 130.00, 129.84, 129.74, 128.40, 128.17, 127.65, 127.09, 126.97, 126.40, 124.16, 55.31, 36.06.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{ClNO}$, 334.0920; found, 334.0930.



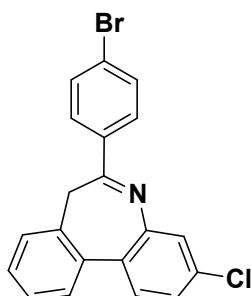
5f 3-chloro-6-(4-chlorophenyl)-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the **4a** (122 mg, 0.4 mmol) and 4-chlorophenylboronic acid (94 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 89% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 27.6 Hz, 2H), 7.54 (d, J = 27.4 Hz, 2H), 7.38 (s, 2H), 7.28 (s, 3H), 7.13 (s, 1H), 4.16 (d, J = 32.6 Hz, 1H), 2.87 (d, J = 32.8 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 163.50, 146.24, 136.97, 135.89, 133.27, 130.58, 129.84, 129.31, 128.80, 128.62, 128.33, 127.35, 126.95, 126.46, 124.76, 36.21.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{13}\text{Cl}_2\text{N}$, 338.0425; found, 338.0430.



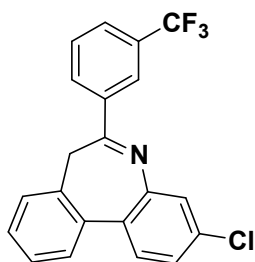
5g 6-(4-bromophenyl)-3-chloro-7H-dibenzo[b,d]azepine

Synthesised according to the general method, after addition of the **4a** (122 mg, 0.4 mmol) and 4-bromophenylboronic acid (120 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 88% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.81 (t, J = 9.2 Hz, 2H), 7.53 (s, 2H), 7.42 (s, 2H), 7.24 (s, 3H), 7.14 (s, 1H), 4.15 (d, J = 23.0 Hz, 1H), 2.85 (d, J = 15.2 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 163.18, 147.90, 136.33, 136.19, 135.92, 133.27, 132.16, 130.59, 129.51, 128.63, 128.33, 127.36, 127.07, 126.64, 125.49, 124.79, 36.81.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{13}\text{BrClN}$, 381.9920; found, 381.9921.



5h 3-chloro-6-(3-(trifluoromethyl)phenyl)-7H-dibenzo[*b,d*]azepine

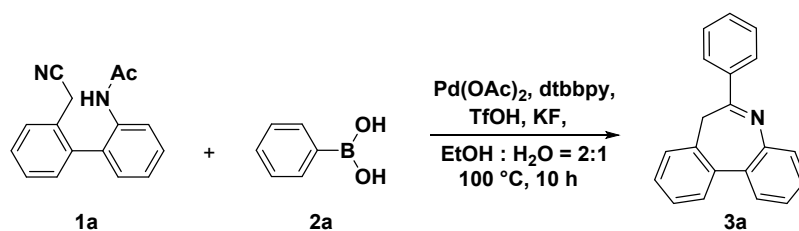
Synthesised according to the general method, after addition of the **4a** (122 mg, 0.4 mmol) and 3-(trifluoromethyl)phenylboronic acid (114 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow liquid in 43% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 34.9 Hz, 2H), 7.62 (s, 3H), 7.52 (s, 1H), 7.35 (d, *J* = 6.3 Hz, 3H), 7.19 (s, 1H), 4.30 (dd, *J* = 30.3, 12.8 Hz, 1H), 2.88 (s, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 162.73, 146.85, 137.98, 136.08, 135.80, 133.40, 131.06, 130.64, 129.88, 129.16, 128.79, 128.44, 127.50, 127.20, 126.98, 126.55, 125.07, 124.82, 36.85.

HRMS *m/z*: [M + H]⁺ calcd for C₂₁H₁₄F₃ClN, 372.0689; found, 372.0690.

6. Large-Scale Experiment



Synthesised according to the general method, and the amount of material is magnified tenfold. After addition of the **1a** (1.0 g, 4 mmol) and phenylboronic acid (0.7 g, 6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using an oil bath. The crude material was purified by column chromatography (PE : EA = 40:1) to give the desired product as a yellow solid in 85% yield. The product are shown below.

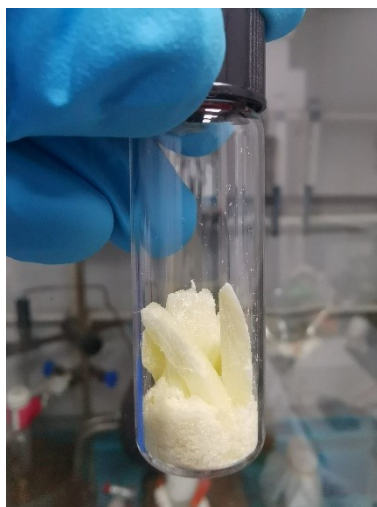
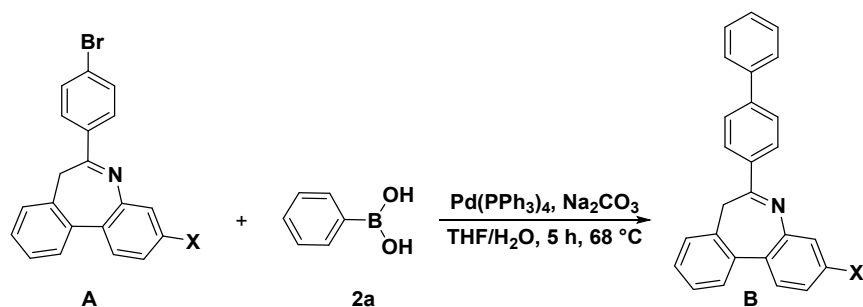


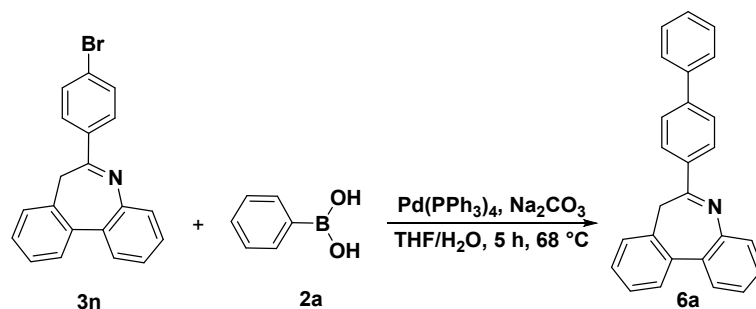
Fig. S1 The product of large-scale experiment

7. General Method for the Synthesis of 6a and 7a



To the solution of **A** (0.3 mmol, 1 eq) and **2a** (0.45 mmol, 1.5 eq) in the THF/H₂O (THF : H₂O = 5:1, 4.8 mL) was added Pd(PPh₃)₄ (0.03 mmol, 0.1 eq) and Na₂CO₃ (0.6 mmol, 2 eq), heated to 68 °C, then stirred at N₂ atmosphere for about 5 h. The reaction was then cooled to room temperature and diluted with H₂O, extracted three times with EA, dried by Na₂SO₄ and evaporated under a vacuum. The crude material was purified by column chromatography to give the desired product.

8. Characterization Data of Products 6a and 7a

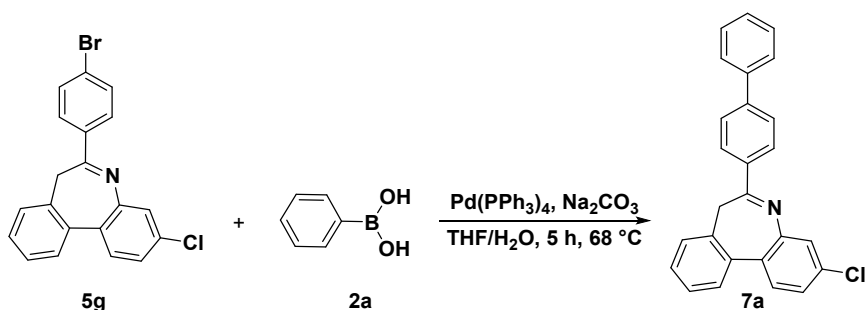


Synthesised according to the general method. The crude material was purified by column chromatography (PE : EA = 60:1) to give the desired product as a yellow liquid in 86% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 4.9 Hz, 2H), 7.80 – 7.68 (m, 4H), 7.67 – 7.56 (m, 3H), 7.48 (dd, *J* = 6.9, 2.8 Hz, 3H), 7.40 (t, *J* = 4.6 Hz, 4H), 7.34 (d, *J* = 5.9 Hz, 1H), 4.41 (d, *J* = 12.3 Hz, 1H), 3.08 (d, *J* = 12.2 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 162.36, 146.21, 136.94, 136.83, 136.31, 131.71, 131.36, 129.48, 128.54, 128.31, 127.84, 127.19, 126.90, 126.75, 125.09, 124.68, 36.20.

HRMS *m/z*: [M + H]⁺ calcd for C₂₆H₁₉N, 346.1590; found, 346.1587.



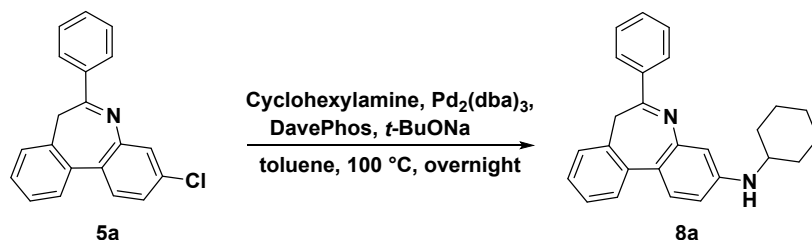
Synthesised according to the general method. The crude material was purified by column chromatography (PE : EA = 60:1) to give the desired product as a yellow liquid in 63% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.09 (t, J = 7.8 Hz, 2H), 7.58 (d, J = 22.7 Hz, 6H), 7.47 (d, J = 10.1 Hz, 1H), 7.40 (s, 2H), 7.32 (s, 4H), 7.19 (d, J = 15.5 Hz, 1H), 4.34 (dt, J = 12.6, 6.8 Hz, 1H), 2.94 (dt, J = 12.6, 6.6 Hz, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 162.88, 146.63, 143.45, 139.14, 136.34, 136.25, 133.22, 130.59, 129.92, 128.88, 128.56, 128.51, 128.29, 127.86, 127.27, 127.13, 127.08, 126.53, 124.56, 36.32.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{19}\text{N}$, 380.1128; found, 380.1187.

9. Synthesis Method and Characterization Data of Products 8a, 8b and 8c

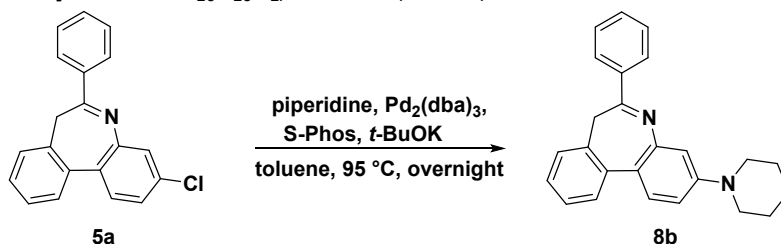


To a solution of **5a** (42.5 mg, 0.14 mmol, 1 eq) in toluene was added Dave-Phos (4.4 mg, 0.011 mmol, 0.08 eq), $\text{Pd}_2(\text{dba})_3$ (6.4 mg, 0.007 mmol, 0.05 eq), $t\text{-BuONa}$ (19.4 mg, 0.2 mmol, 1.4 eq), cyclohexylamine (16.9 mg, 0.17 mmol, 1.2 eq) and the mixture was stirred overnight at 100 °C under nitrogen atmosphere. The reaction mixture was then cooled to room temperature and quenched with water, extracted three times with EA, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (PE : EA = 30:1) to give the desired product as a yellow oil in 54% yield.

^1H NMR (400 MHz, CD_3OD) δ 8.04 – 7.95 (m, 2H), 7.58 (dd, J = 7.5, 1.1 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.45 (dd, J = 6.4, 3.7 Hz, 3H), 7.35 (dd, J = 7.2, 1.3 Hz, 1H), 7.32 – 7.23 (m, 2H), 6.66 (dd, J = 6.1, 2.4 Hz, 2H), 4.32 (d, J = 12.3 Hz, 1H), 3.31 (s, 1H), 2.98 (d, J = 12.2 Hz, 1H), 2.09 (t, J = 14.4 Hz, 2H), 1.79 (d, J = 13.3 Hz, 2H), 1.67 (d, J = 12.7 Hz, 1H), 1.49 – 1.35 (m, 2H), 1.30 – 1.17 (m, 3H).

^{13}C NMR (151 MHz, CD_3OD) δ 166.19, 149.24, 148.28, 139.52, 138.72, 136.60, 131.52, 131.15, 129.61, 129.07, 128.37, 128.16, 128.10, 127.94, 122.04, 113.32, 109.65, 52.92, 38.04, 34.31, 34.19, 27.13, 26.26.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{26}\text{N}_2$, 367.2169; found, 367.2171.



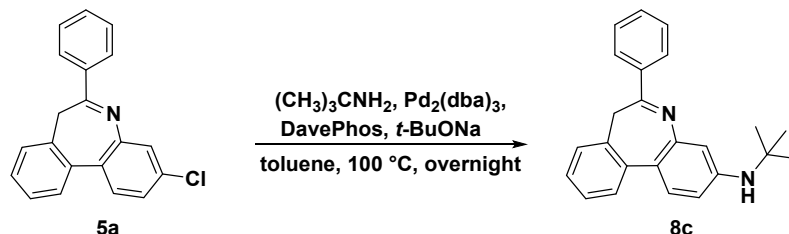
To a solution of **5a** (42.5 mg, 0.14 mmol, 1 eq) in toluene was added S-Phos (2.9 mg, 0.007 mmol, 0.05 eq), $\text{Pd}_2(\text{dba})_3$ (7.7 mg, 0.008 mmol, 0.06 eq), $t\text{-BuOK}$ (31.4 mg, 0.28 mmol, 2 eq), piperidine (17.9 mg, 0.21 mmol, 1.5 eq) and the mixture was stirred overnight at 100 °C under nitrogen atmosphere. The reaction mixture was then cooled to room temperature and quenched with water, extracted three times with EA, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (PE : EA = 30:1) to give the desired product as a yellow oil in 86% yield.

^1H NMR (400 MHz, CD_3OD) δ 8.03 (d, J = 2.9 Hz, 2H), 7.61 (d, J = 5.5 Hz, 2H), 7.45 (s, 3H), 7.38 (s,

1H), 7.32 (d, $J = 3.0$ Hz, 2H), 6.99 (d, $J = 14.2$ Hz, 2H), 4.36 (d, $J = 12.5$ Hz, 1H), 3.26 (s, 4H), 2.96 (d, $J = 12.2$ Hz, 1H), 1.73 (s, 4H), 1.63 (s, 2H).

^{13}C NMR (151 MHz, CD_3OD) δ 166.32, 152.99, 148.07, 139.39, 138.24, 137.04, 131.60, 131.03, 129.63, 129.10, 128.64, 128.61, 128.23, 128.04, 124.43, 115.72, 113.68, 51.55, 37.82, 26.80, 25.43.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{24}\text{N}_2$, 353.2012; found, 353.2010.



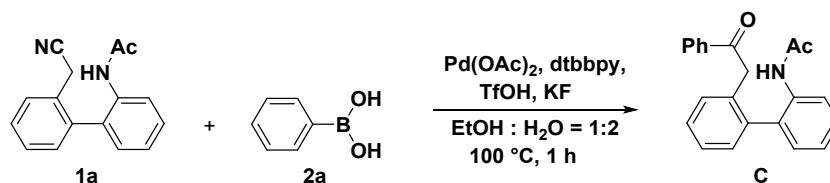
Synthesised according to the general method same as **8a**. The crude material was purified by column chromatography (PE : EA = 30:1) to give the desired product as a yellow oil in 47% yield.

^1H NMR (400 MHz, CD_3OD) δ 8.01 (ddd, $J = 4.0, 2.2, 0.6$ Hz, 2H), 7.61 (dd, $J = 7.2, 1.4$ Hz, 1H), 7.52 (d, $J = 8.6$ Hz, 1H), 7.48 – 7.43 (m, 3H), 7.37 (dd, $J = 7.0, 1.6$ Hz, 1H), 7.34 – 7.26 (m, 2H), 6.92 (d, $J = 2.4$ Hz, 1H), 6.84 (ddd, $J = 8.4, 2.4, 0.6$ Hz, 1H), 4.35 (d, $J = 12.3$ Hz, 1H), 2.99 (d, $J = 12.3$ Hz, 1H), 1.39 (s, 9H).

^{13}C NMR (151 MHz, CD_3OD) δ 166.32, 148.27, 147.84, 139.44, 138.46, 136.84, 131.57, 130.75, 129.62, 129.09, 128.54, 128.42, 128.20, 127.99, 123.76, 117.37, 114.77, 52.56, 37.94, 30.14.

HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{24}\text{N}_2$, 341.2012; found, 341.2014.

10. Characterization Data of Controlled Experiment Intermediate C

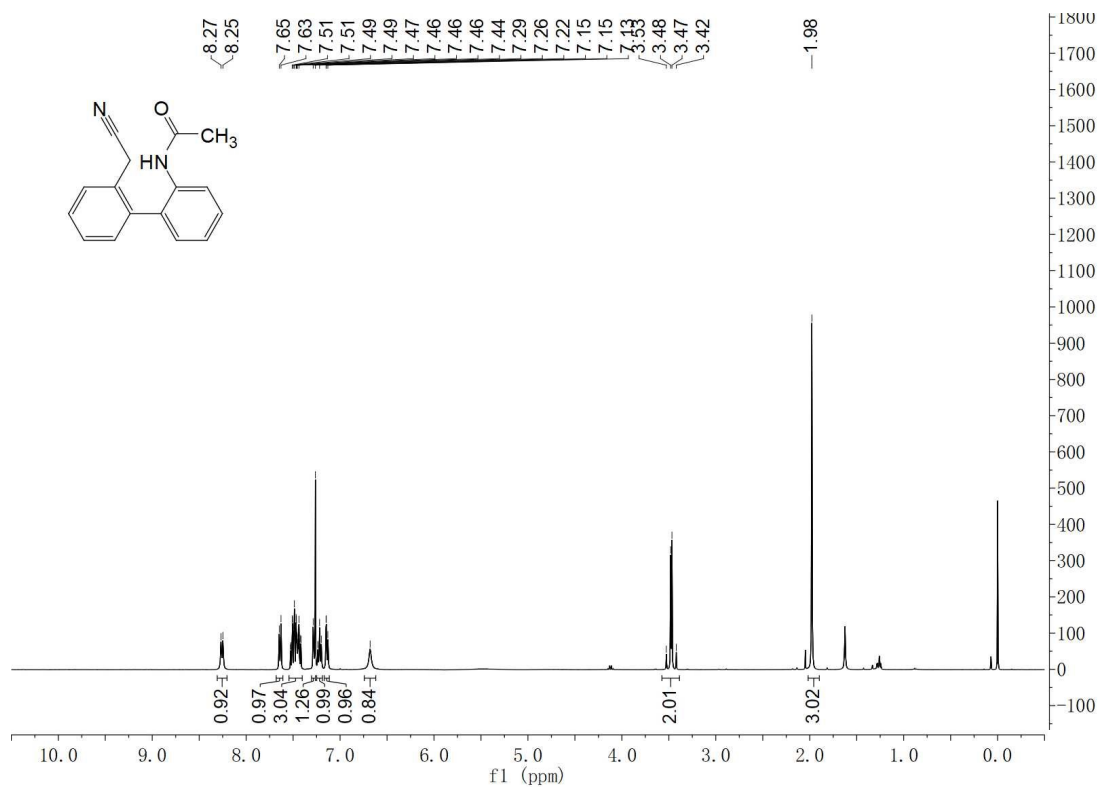
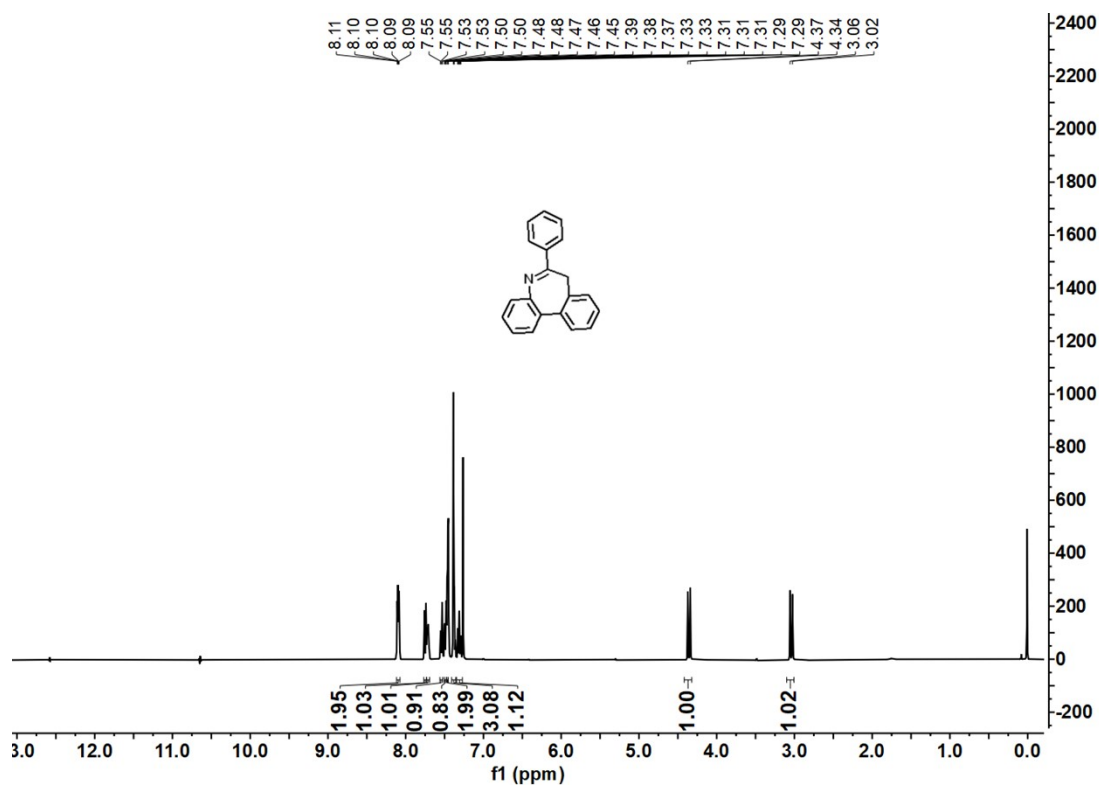


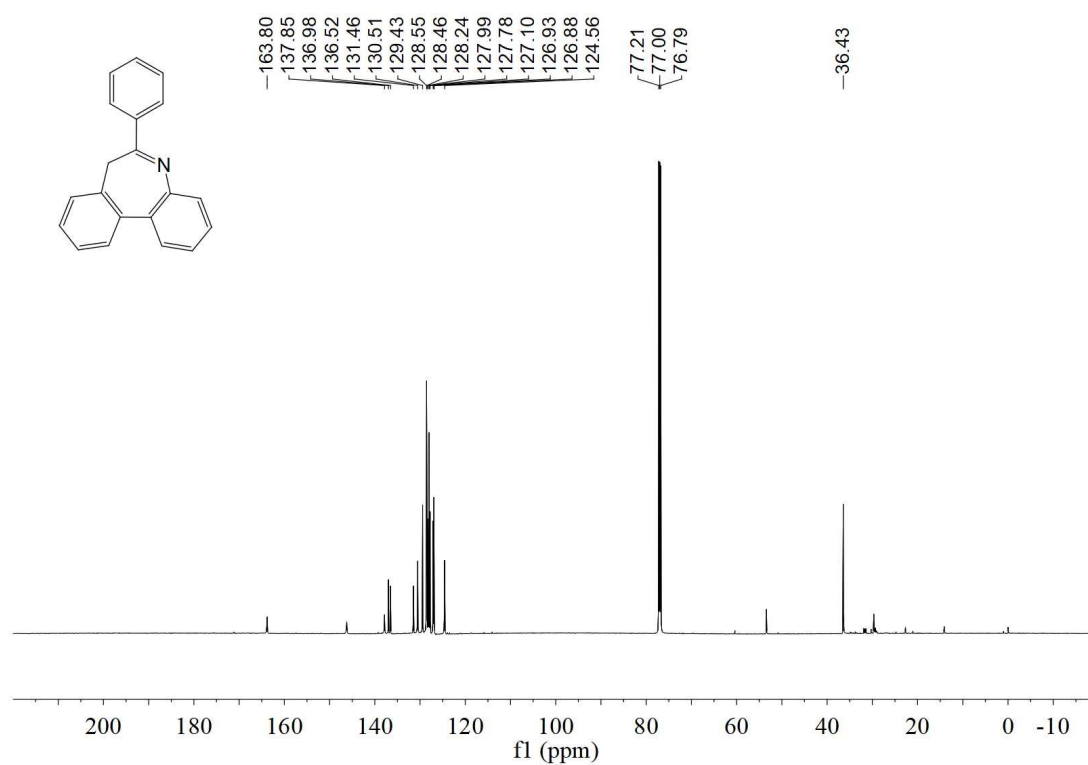
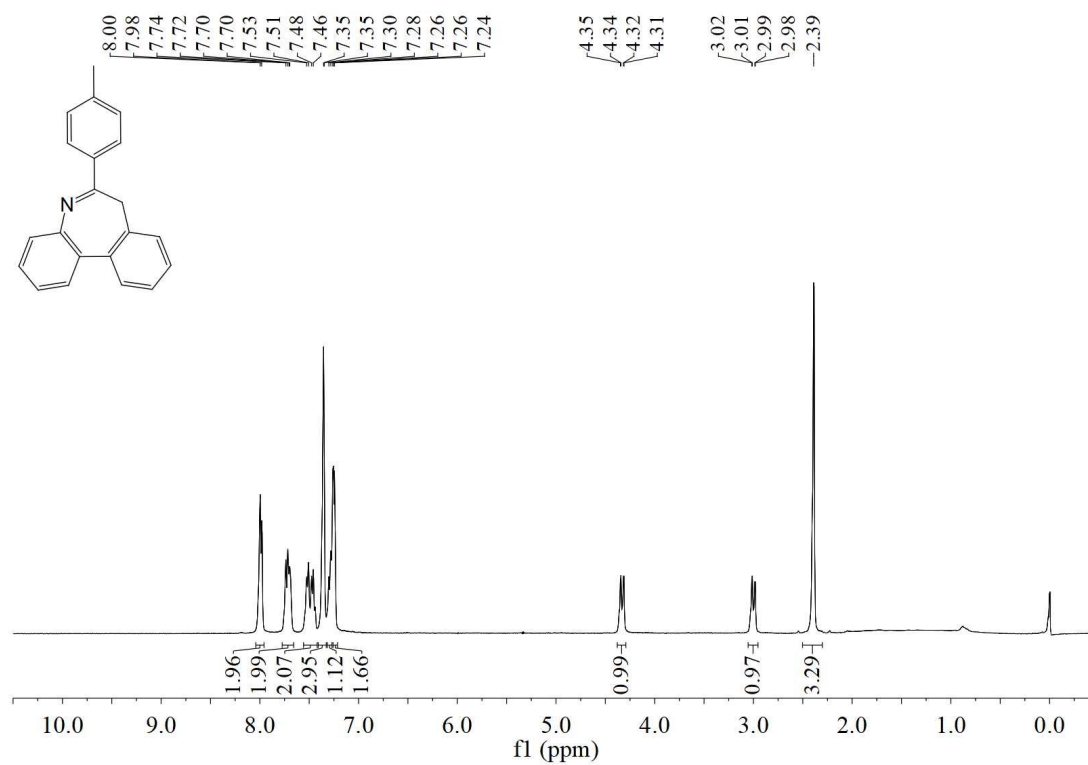
Synthesised according to the general method for the synthesis of dibenzo- $[b,d]$ azepines products, after addition of the **1a** (100 mg, 0.4 mmol) and phenylboronic acid (73 mg, 0.6 mmol) with other reagents, the reaction mixture was heated to 100 °C in a sealed tube using a hotplate only for 1 hour in order to capture the intermediate **C**. The crude material was purified by column chromatography (PE : EA = 2:1) to give the desired product as a yellow oil in 18% yield.

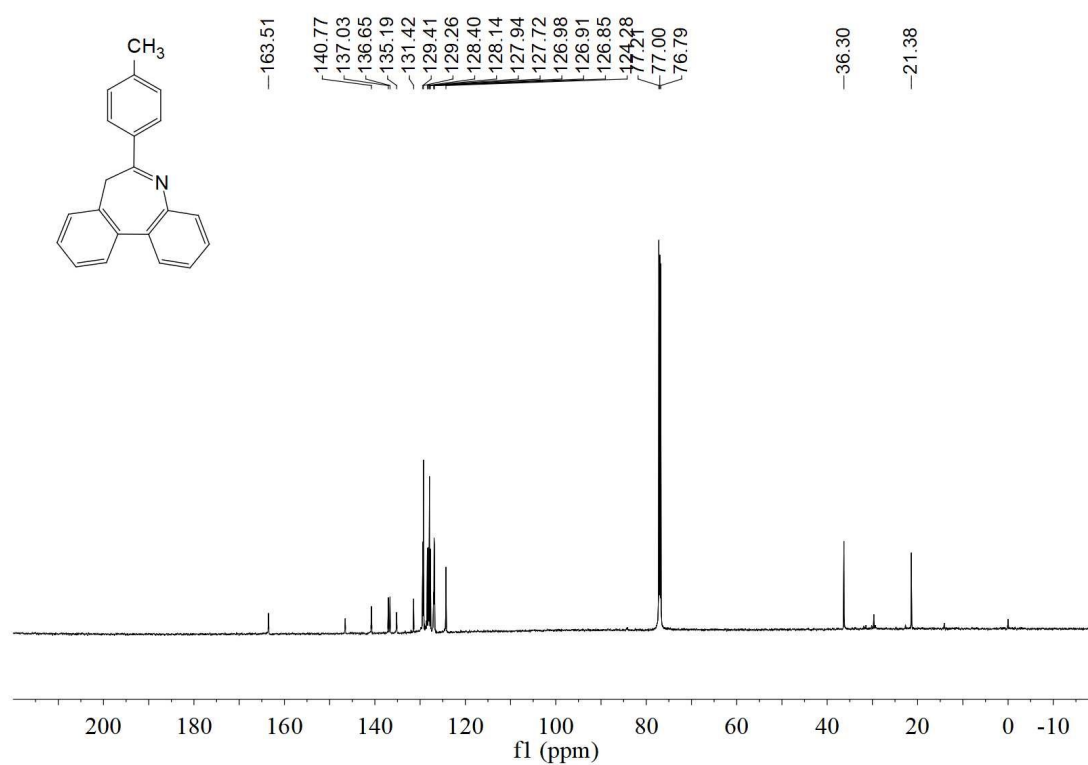
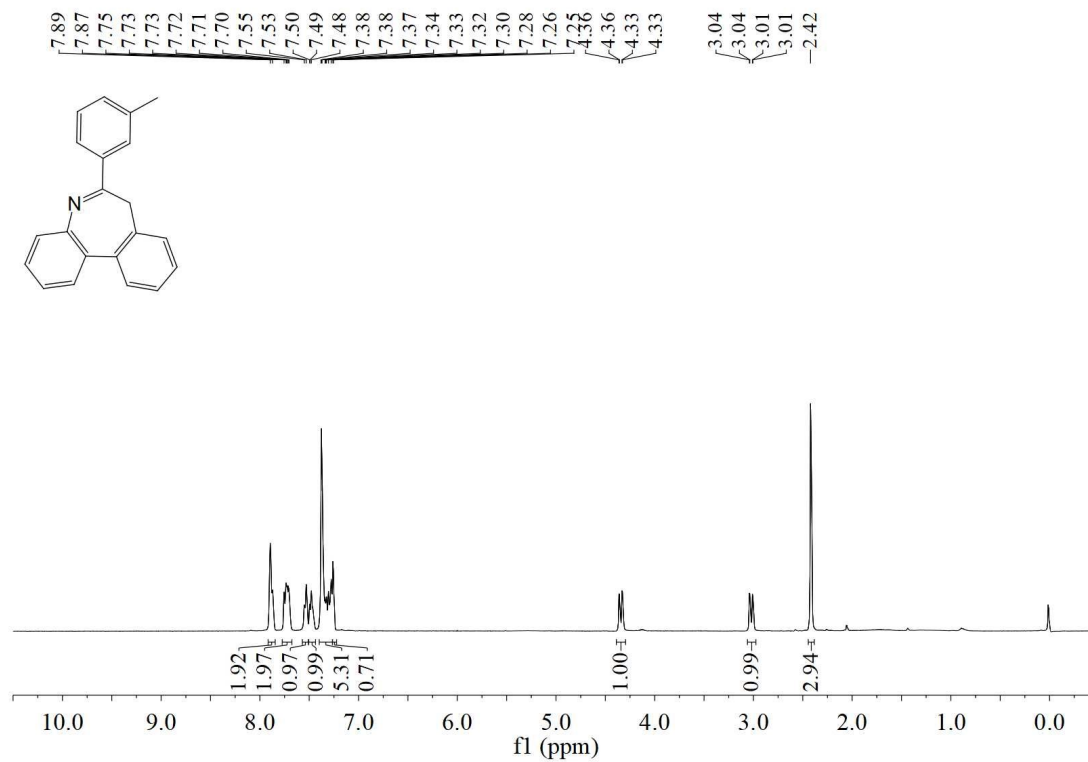
^1H NMR (400 MHz, CD_3OD) δ 7.79 (d, $J = 7.4$ Hz, 2H), 7.66 (d, $J = 8.1$ Hz, 1H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.41 – 7.34 (m, 4H), 7.31 (dd, $J = 7.2, 1.4$ Hz, 1H), 7.29 – 7.25 (m, 1H), 7.21 – 7.17 (m, 1H), 7.16 – 7.09 (m, 2H), 4.21 (dd, $J = 107.0, 17.5$ Hz, 2H), 1.93 (s, 3H).

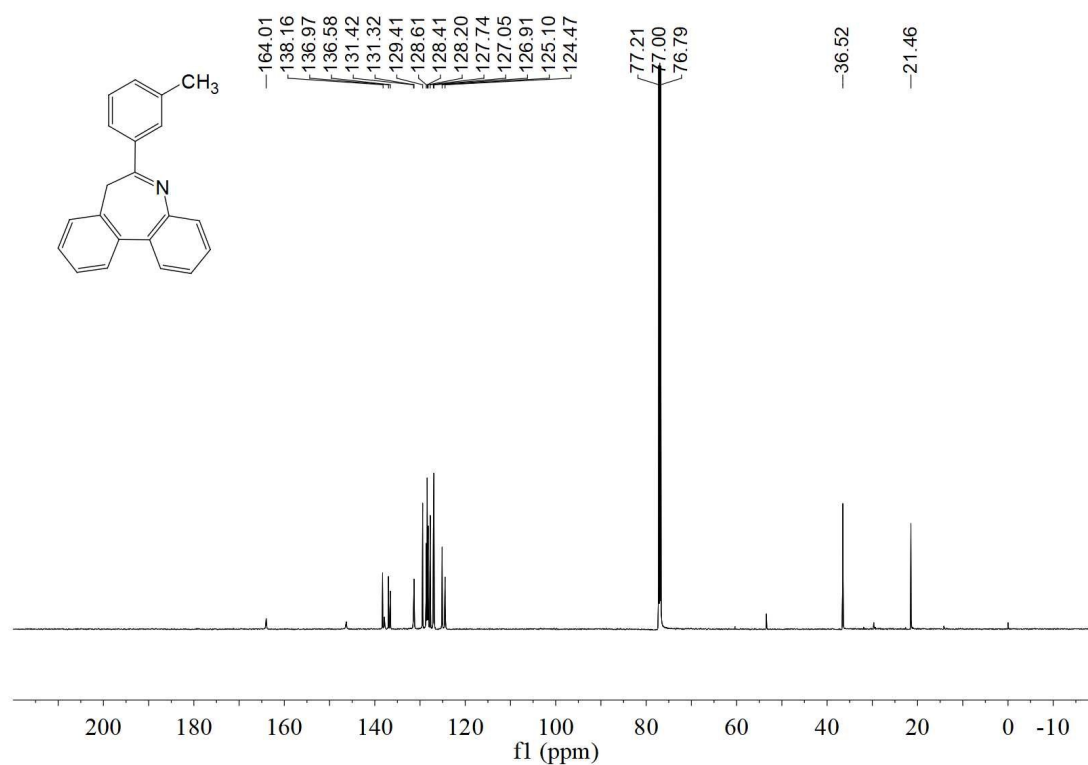
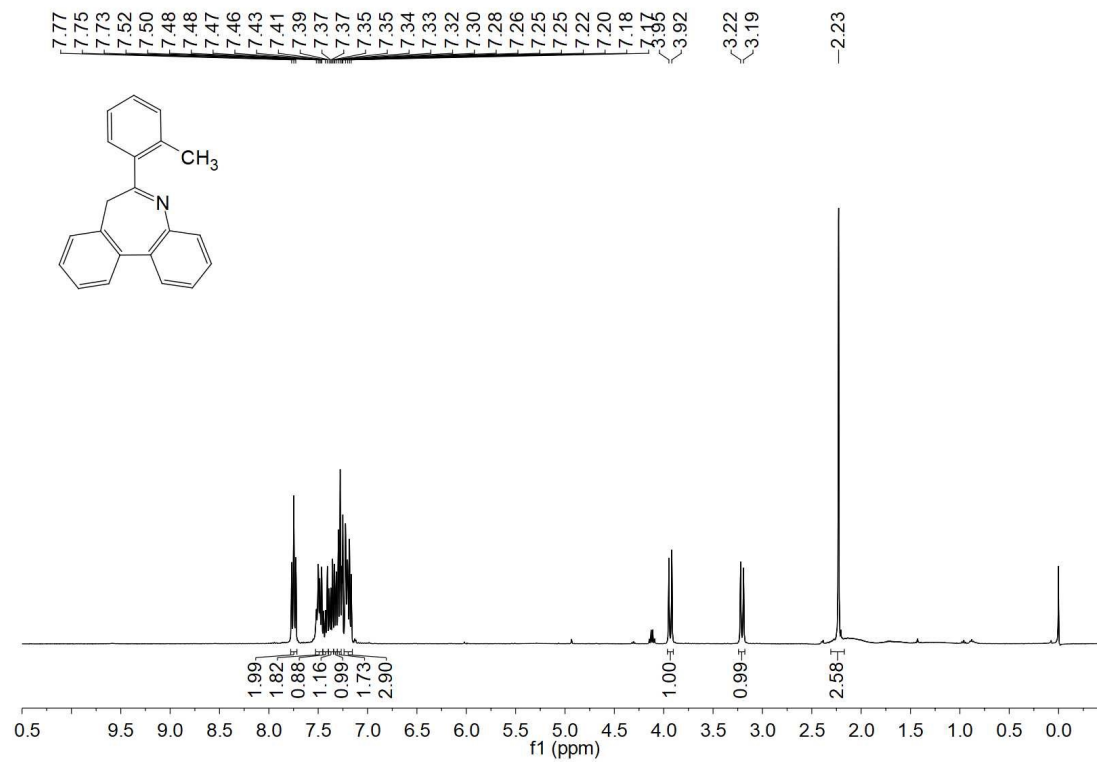
^{13}C NMR (151 MHz, CD_3OD) δ 200.72, 171.83, 140.15, 137.90, 136.46, 136.23, 135.27, 134.43, 132.30, 131.48, 131.31, 129.63, 129.22, 129.20, 129.18, 128.18, 126.54, 126.19, 49.43, 49.28, 49.14, 49.00, 48.86, 48.72, 48.57, 43.94, 23.33.

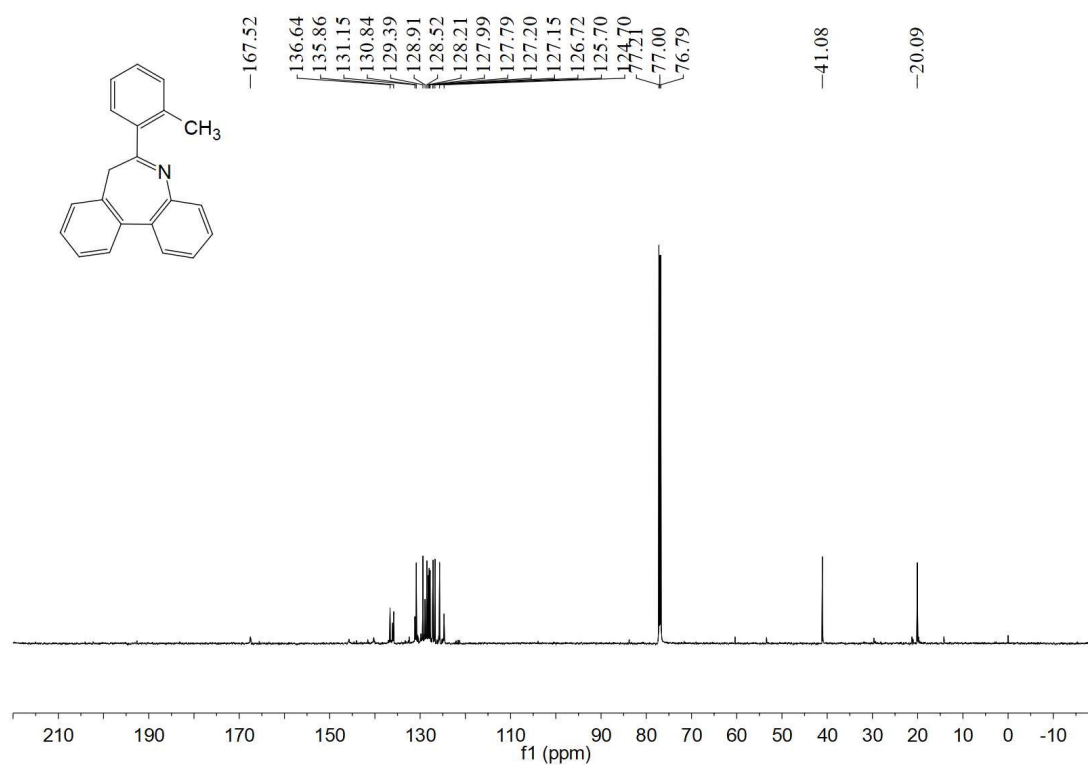
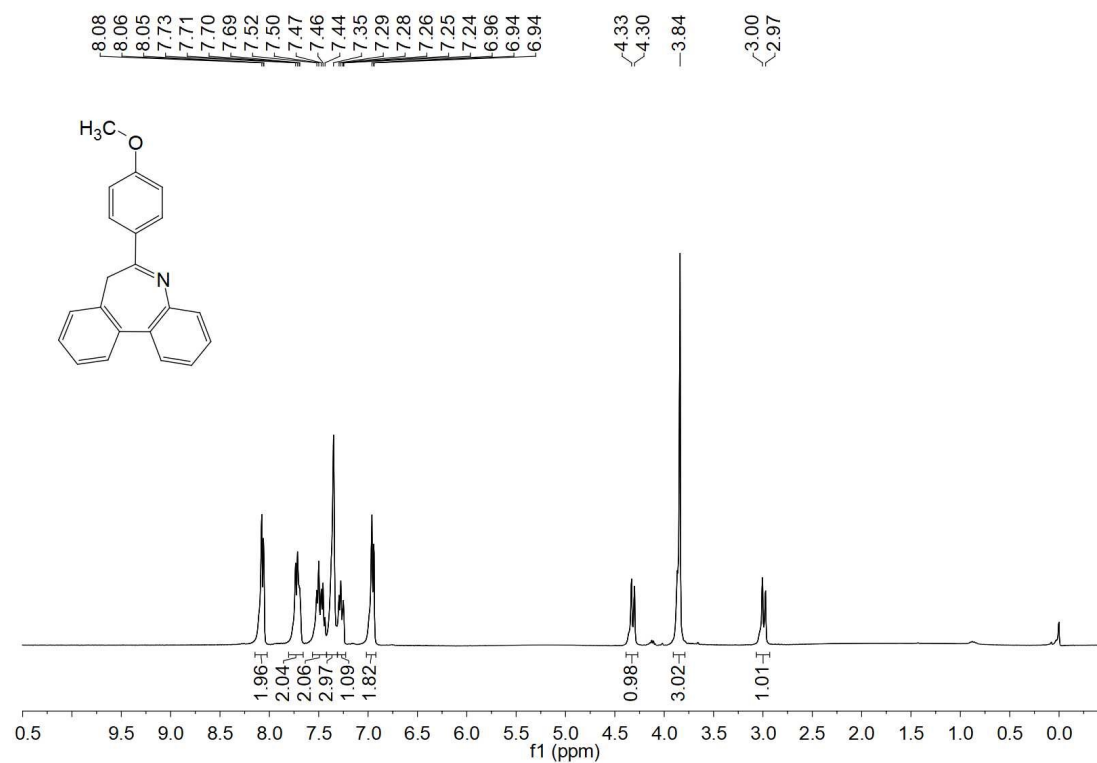
HRMS m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{19}\text{N}$, 330.1489; found, 330.1488.

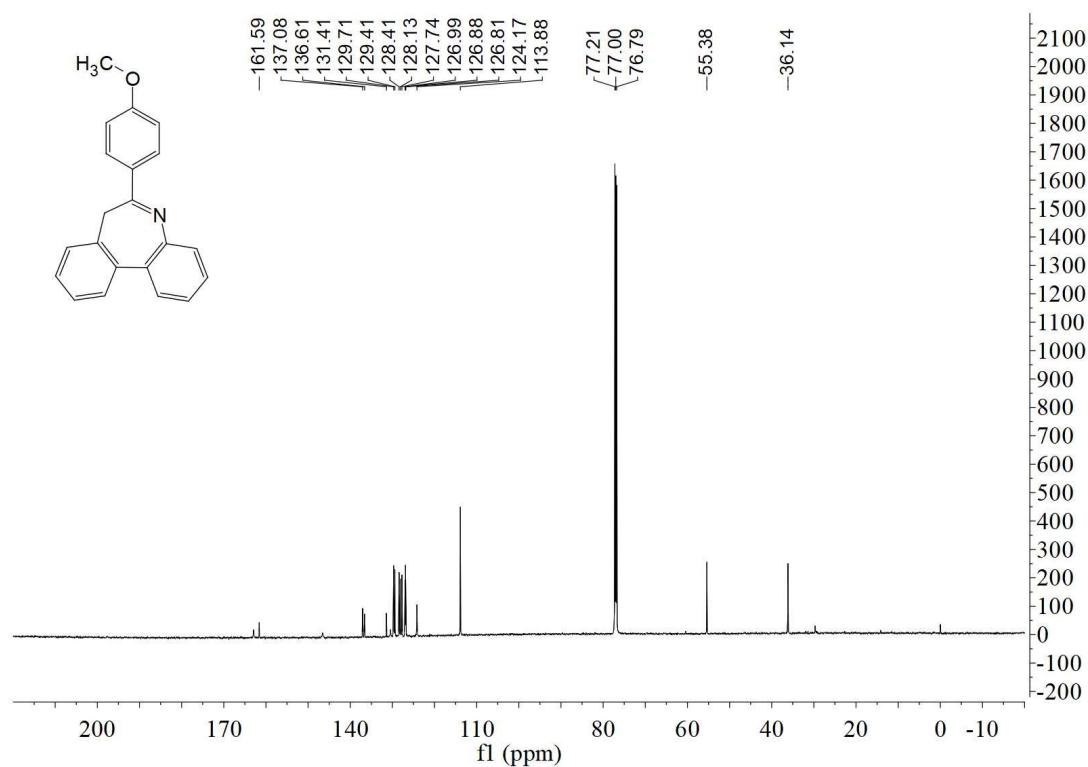
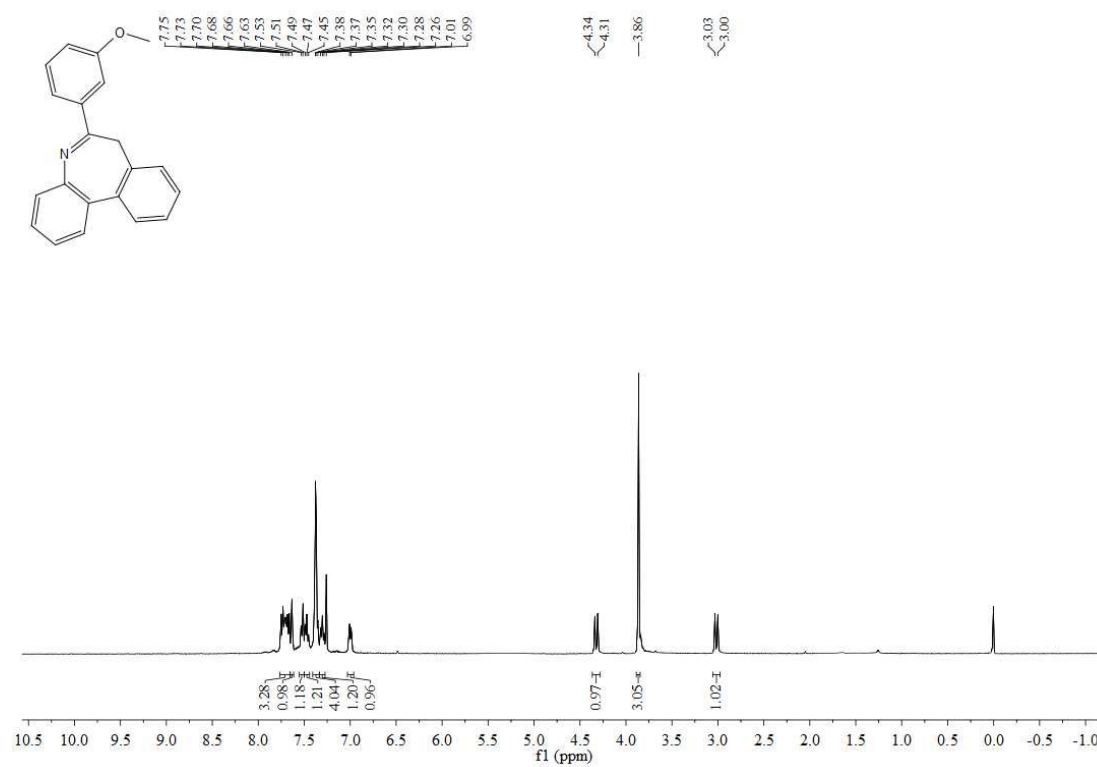
11. NMR Spectra for Compounds of this paper:**¹H NMR Spectra of Compound 1a:****¹H NMR Spectra of Compound 3a:**

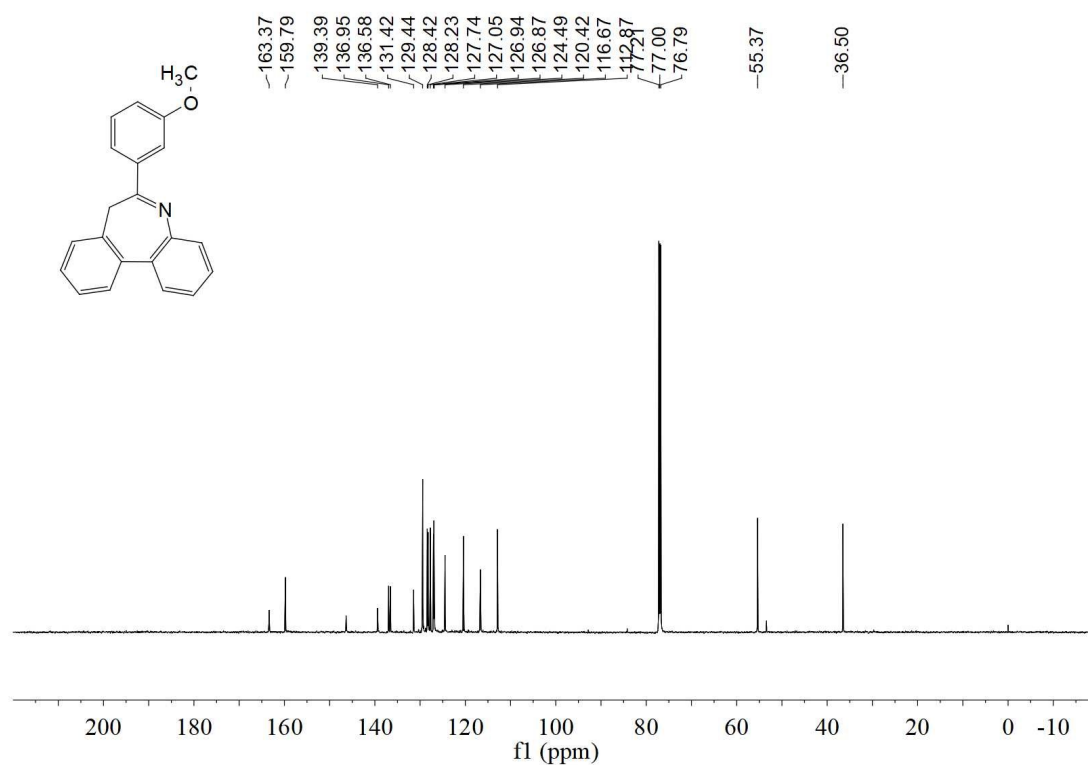
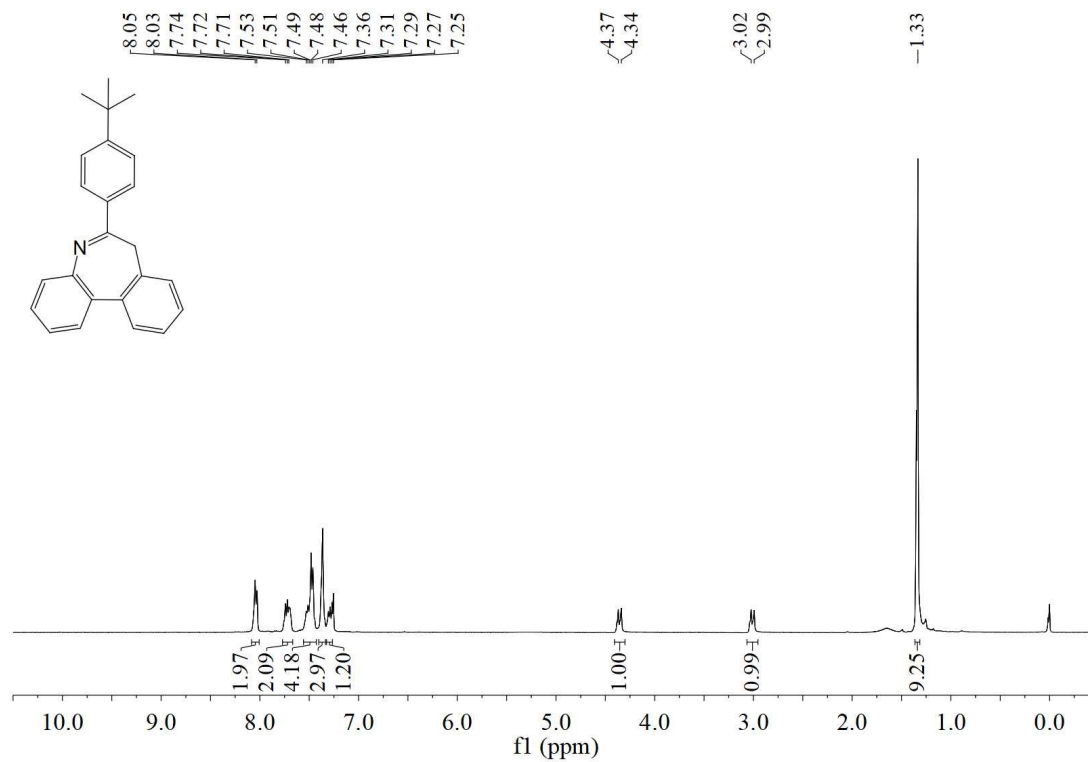
^{13}C NMR Spectra of Compound **3a:** **^1H NMR Spectra of Compound **3b**:**

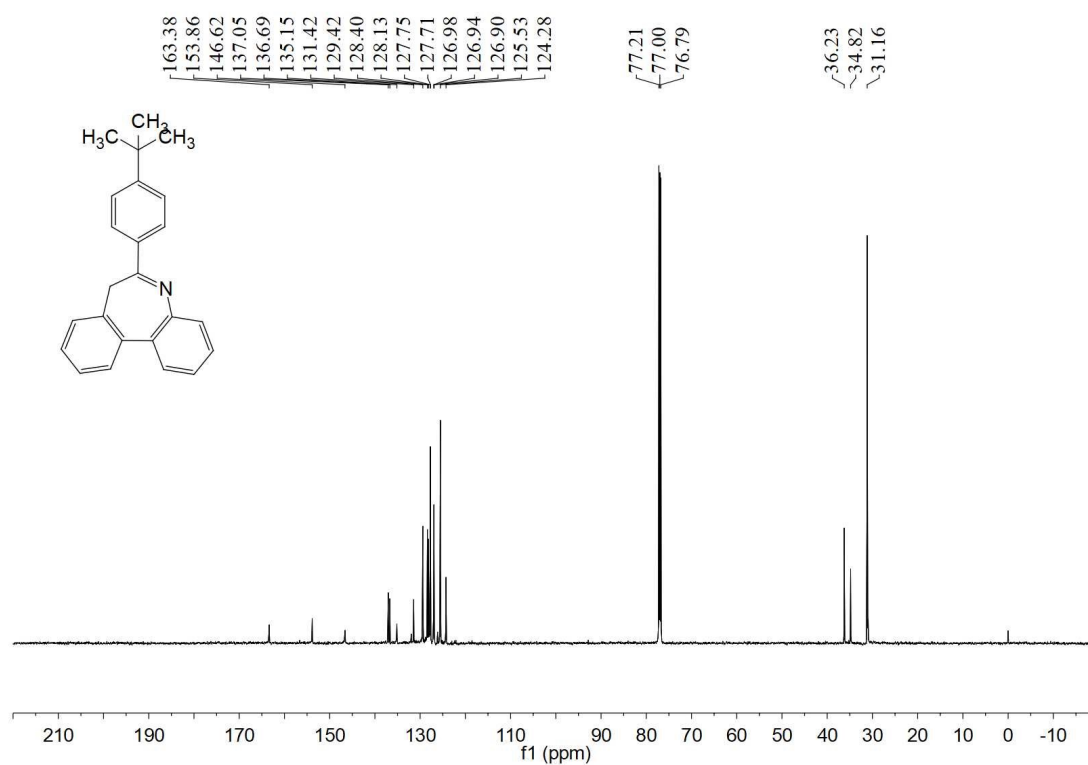
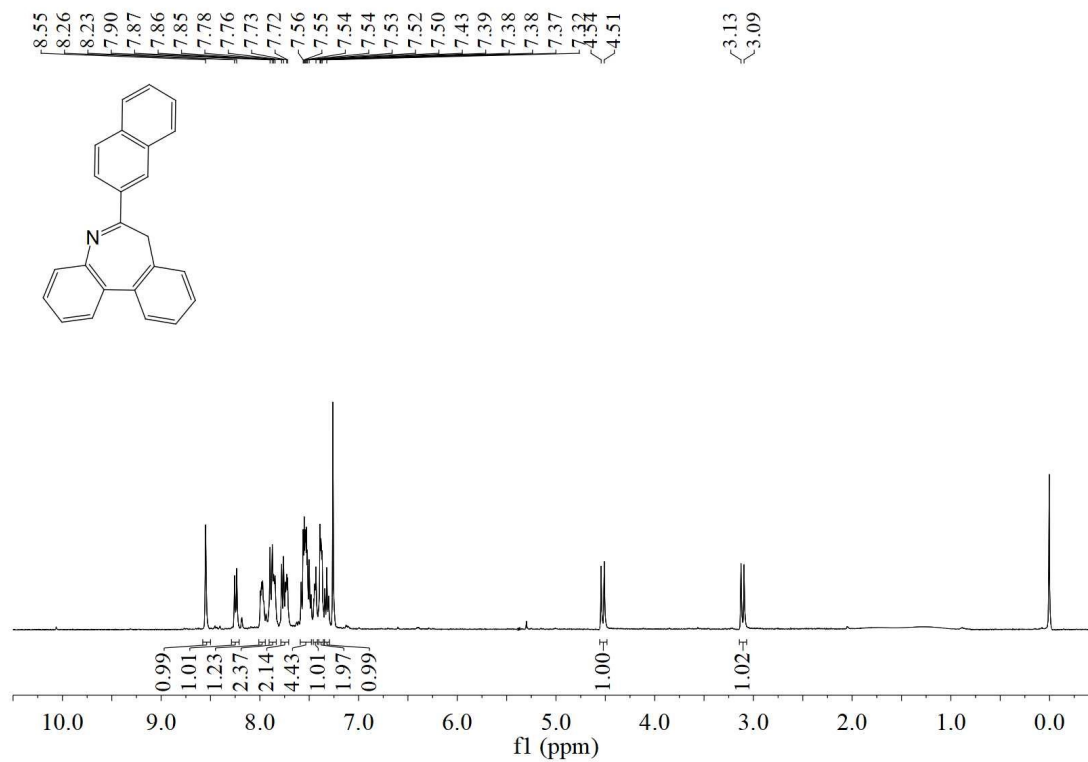
¹³C NMR Spectra of Compound 3b:**¹H NMR Spectra of Compound 3c:**

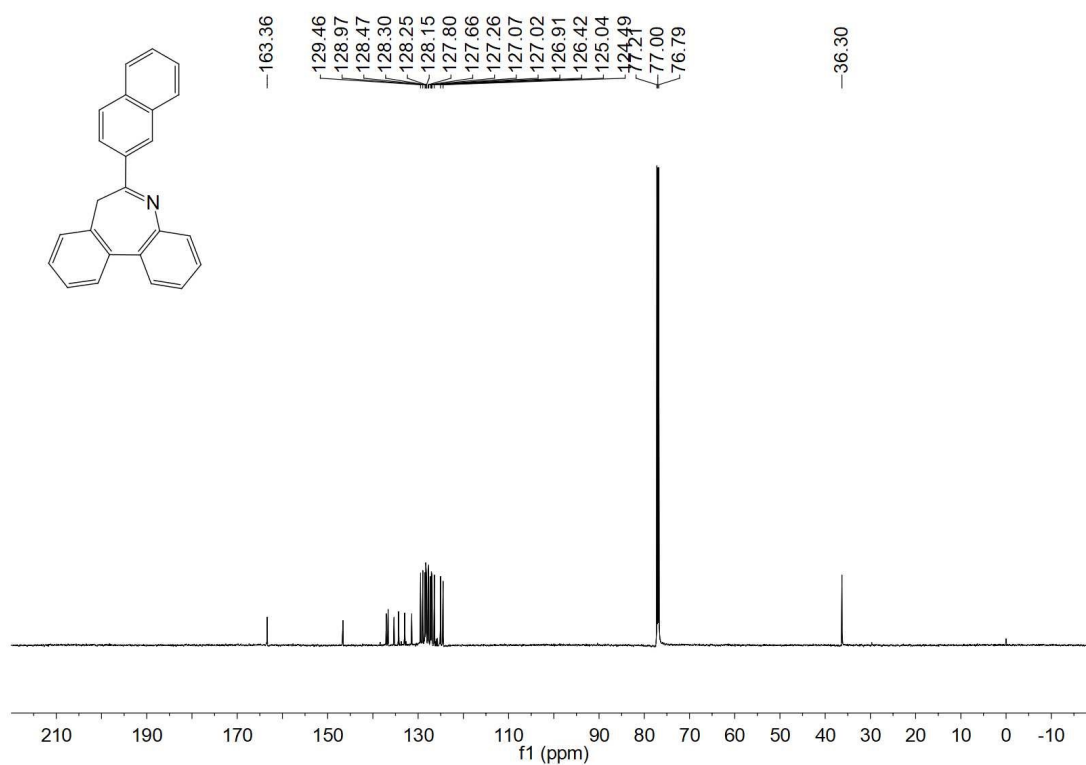
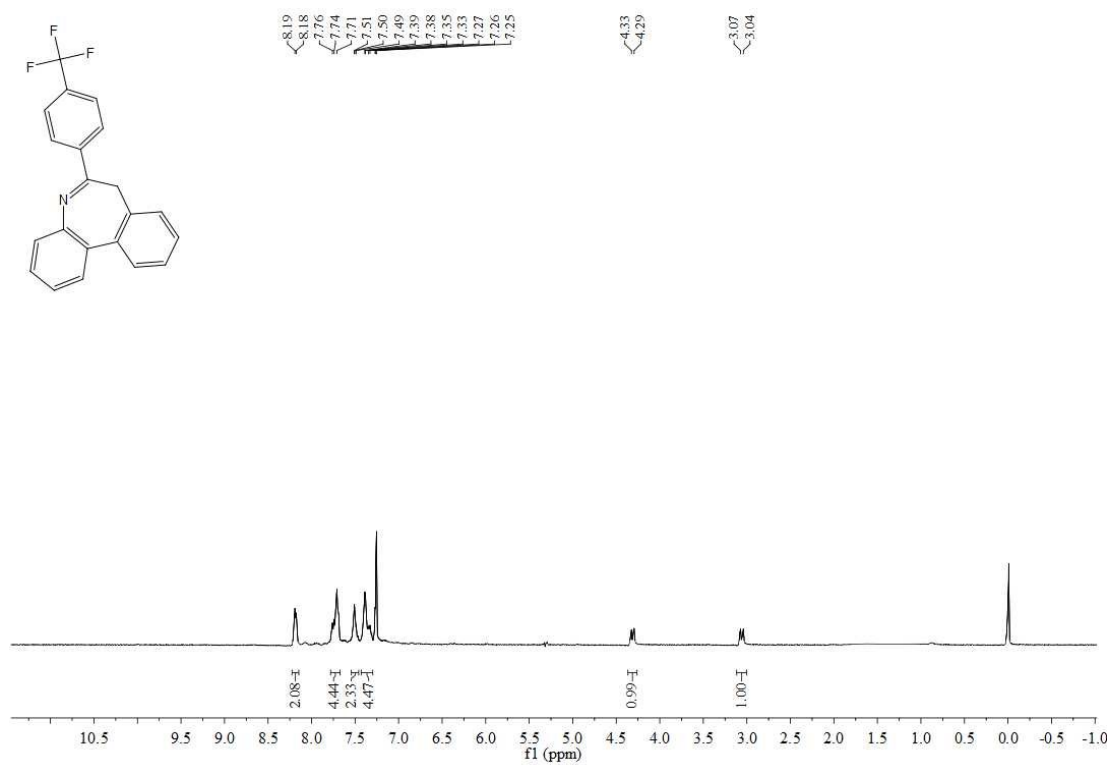
^{13}C NMR Spectra of Compound **3c:** **^1H NMR Spectra of Compound **3d**:**

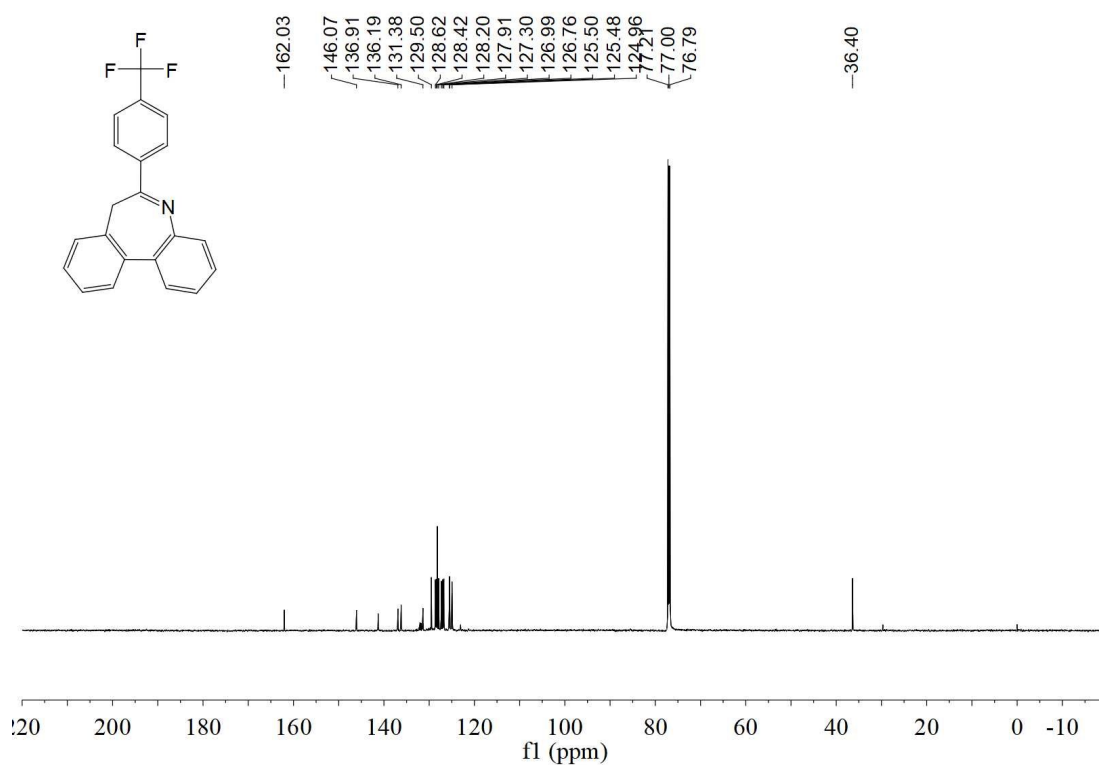
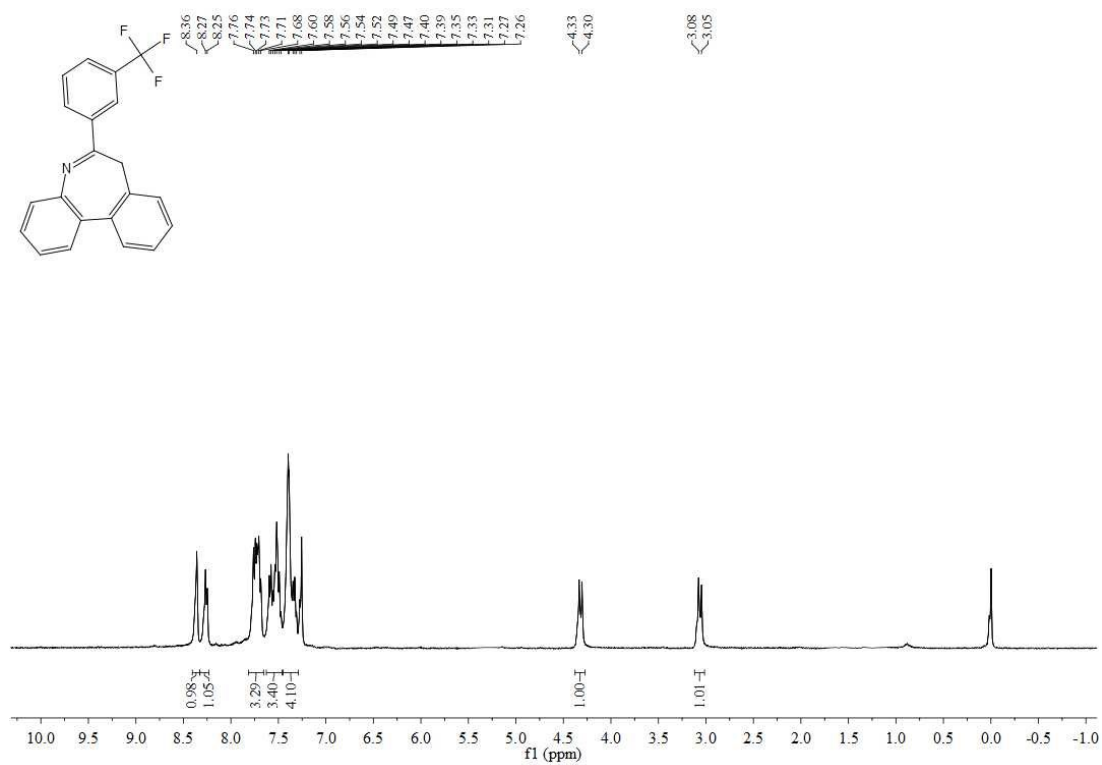
¹³C NMR Spectra of Compound 3d:**¹H NMR Spectra of Compound 3e:**

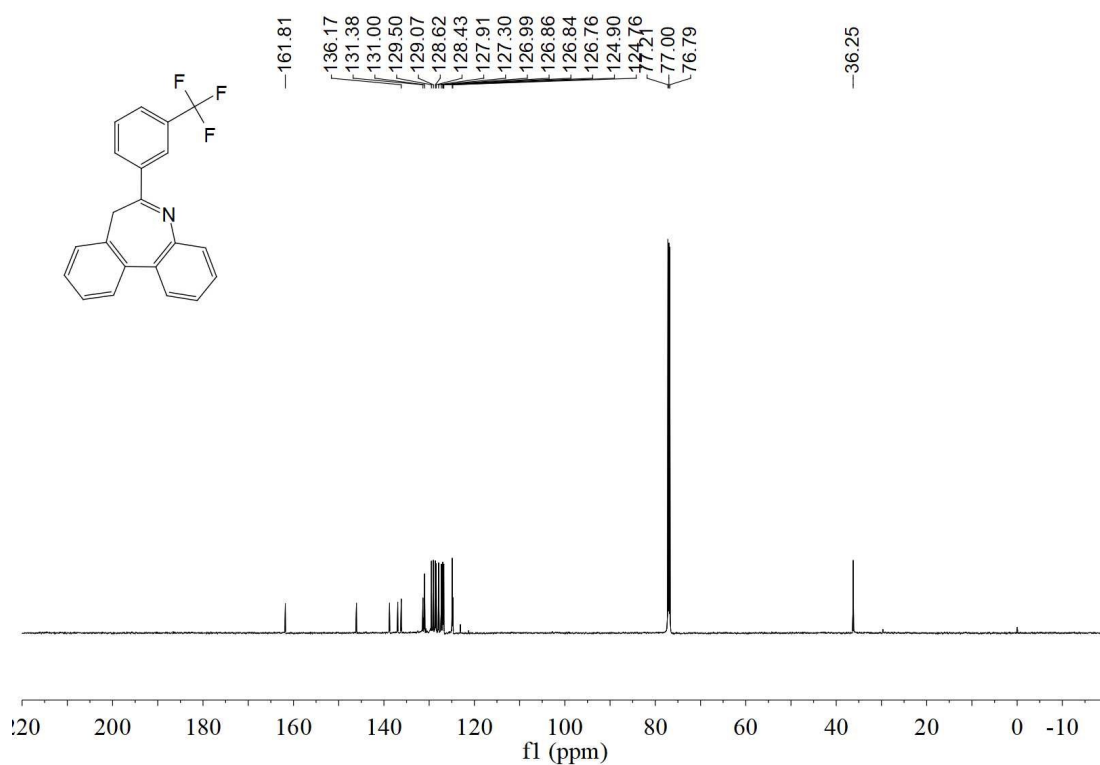
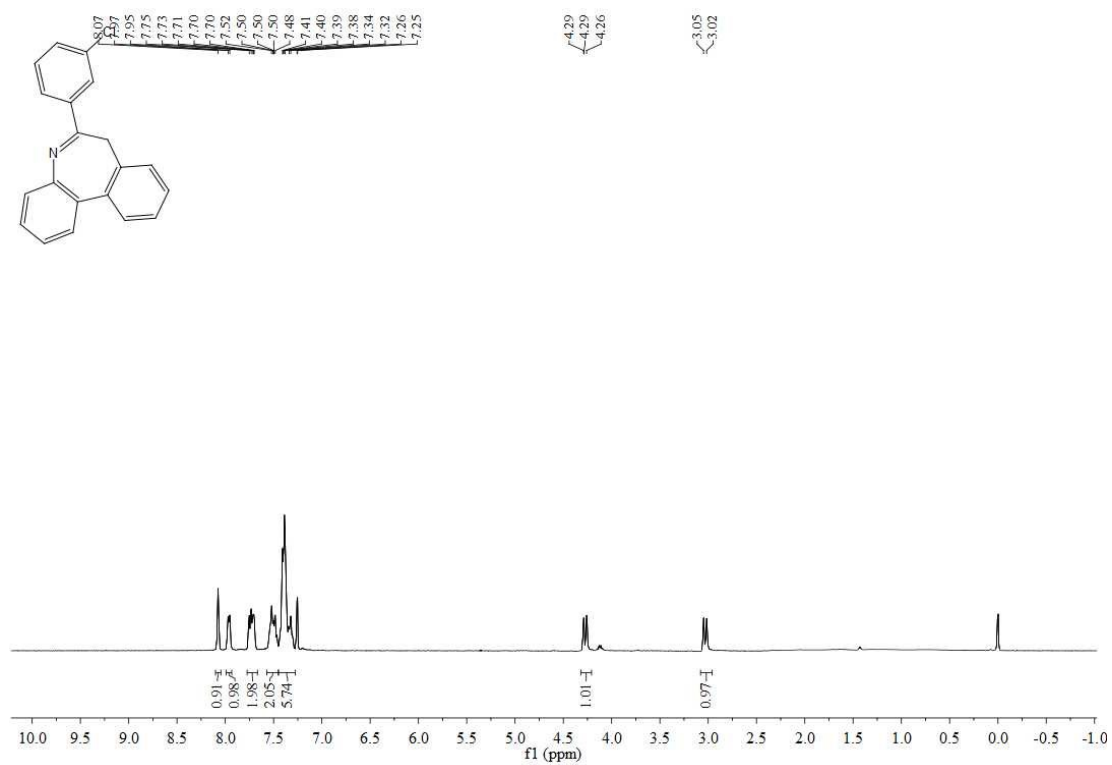
¹³C NMR Spectra of Compound **3e**:¹H NMR Spectra of Compound **3f**:

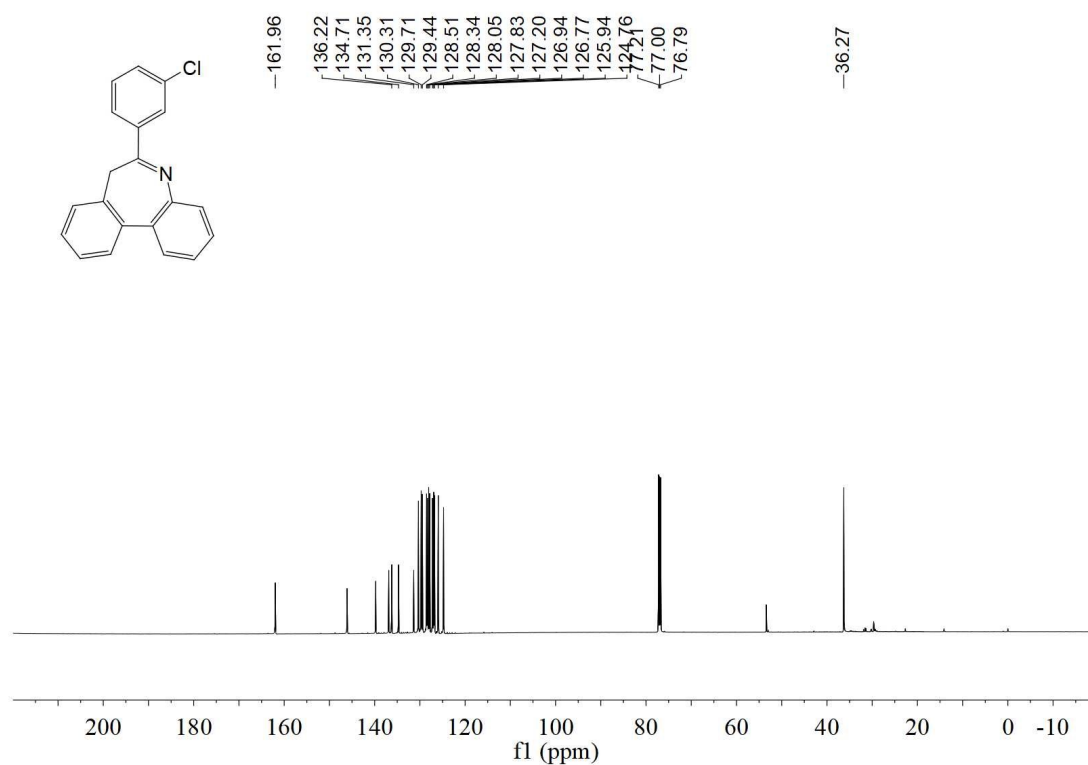
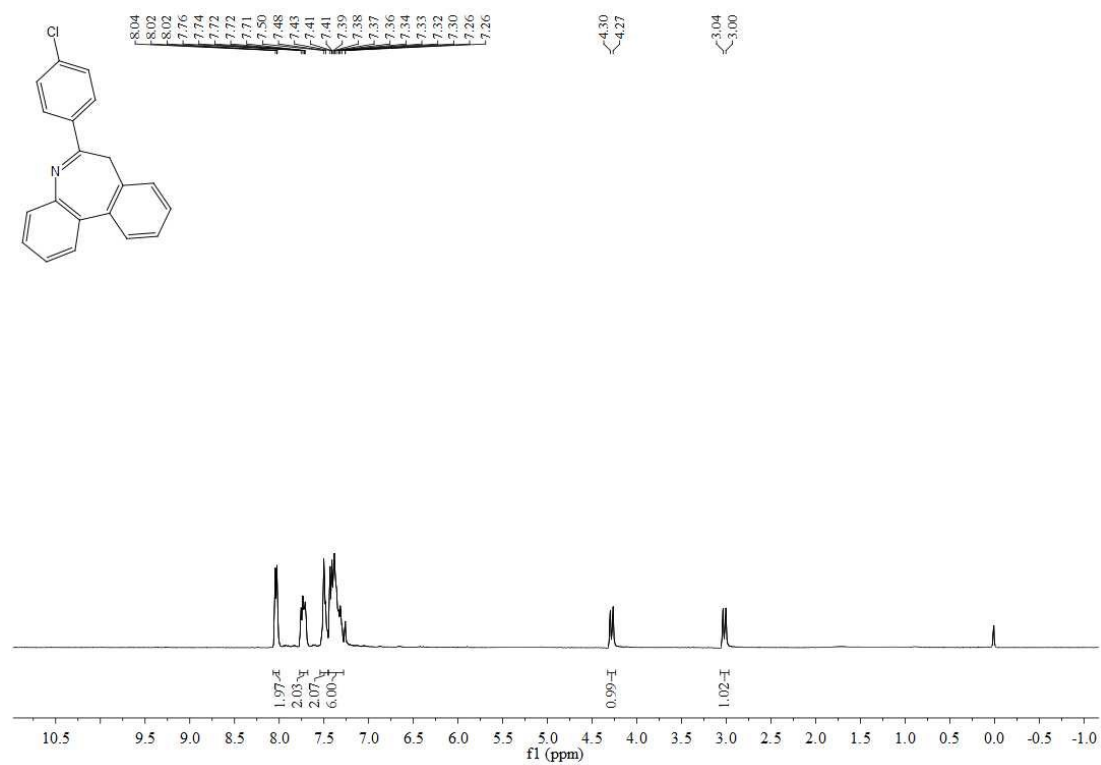
¹³C NMR Spectra of Compound **3f:****¹H NMR Spectra of Compound **3g**:**

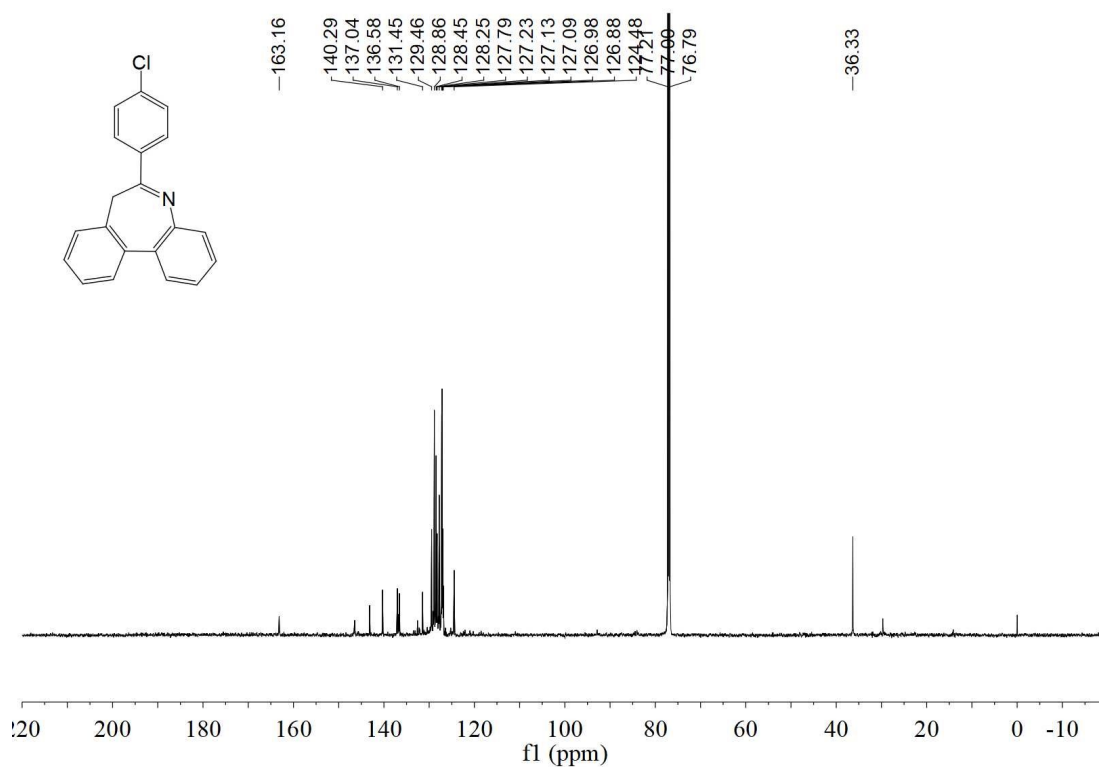
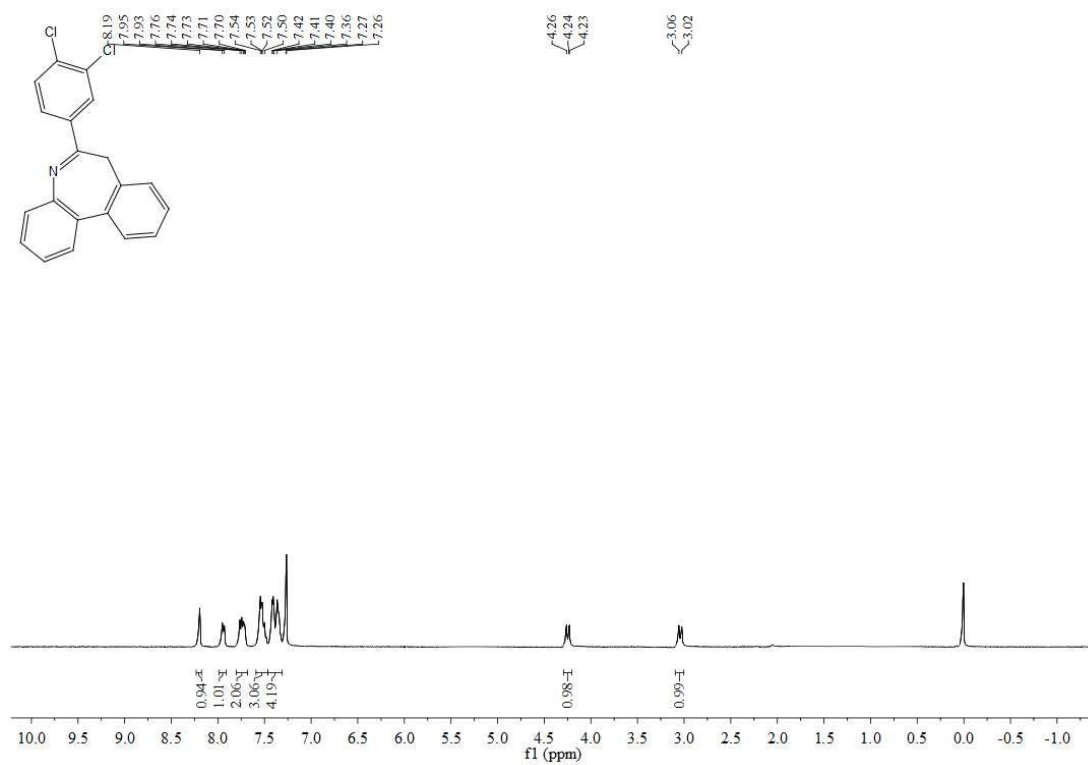
¹³C NMR Spectra of Compound 3g:**¹H NMR Spectra of Compound 3h:**

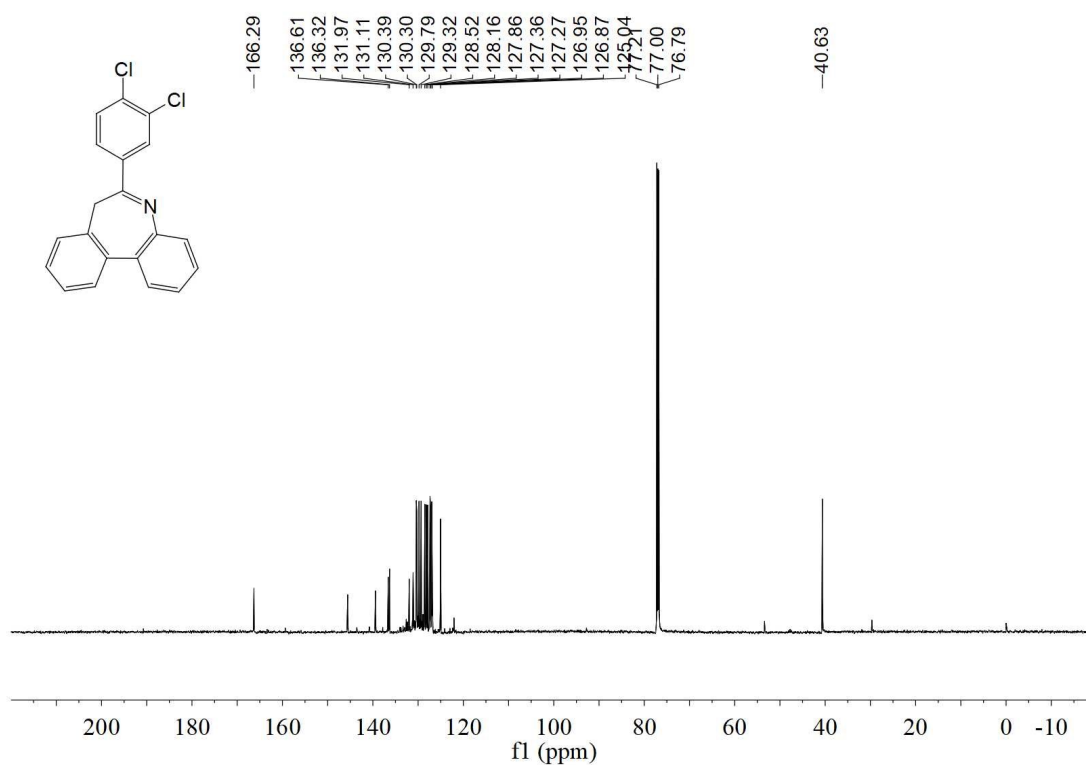
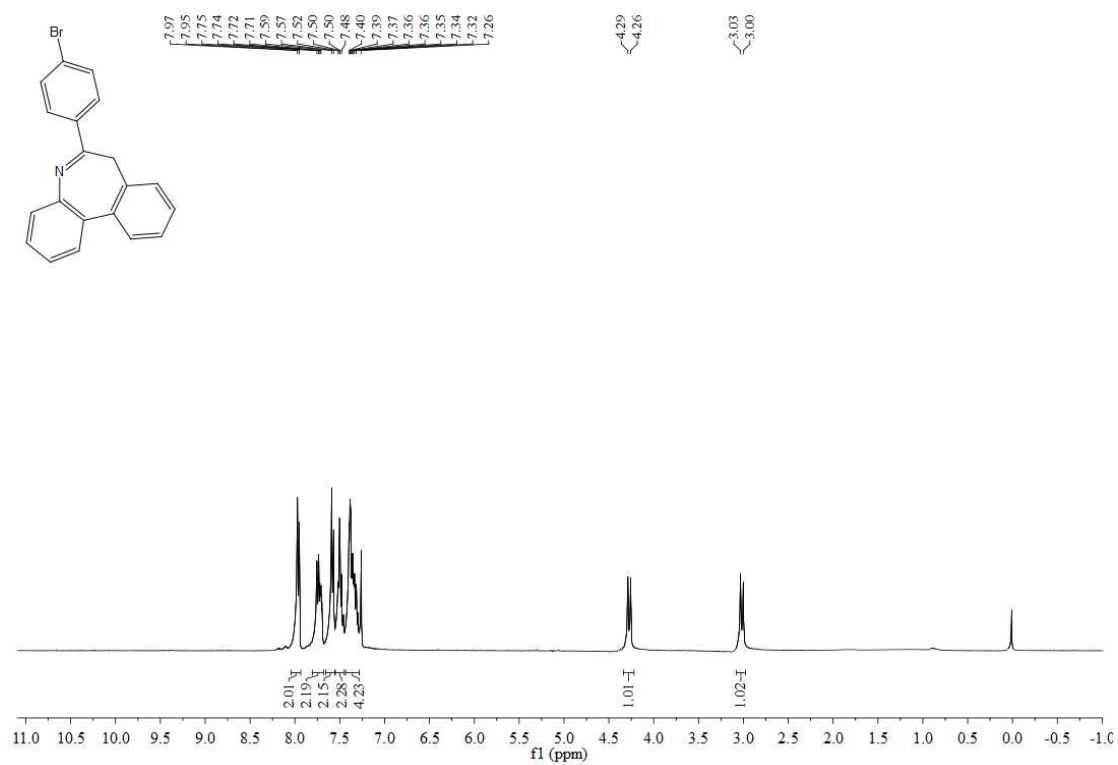
^{13}C NMR Spectra of Compound **3h:** **^1H NMR Spectra of Compound **3i**:**

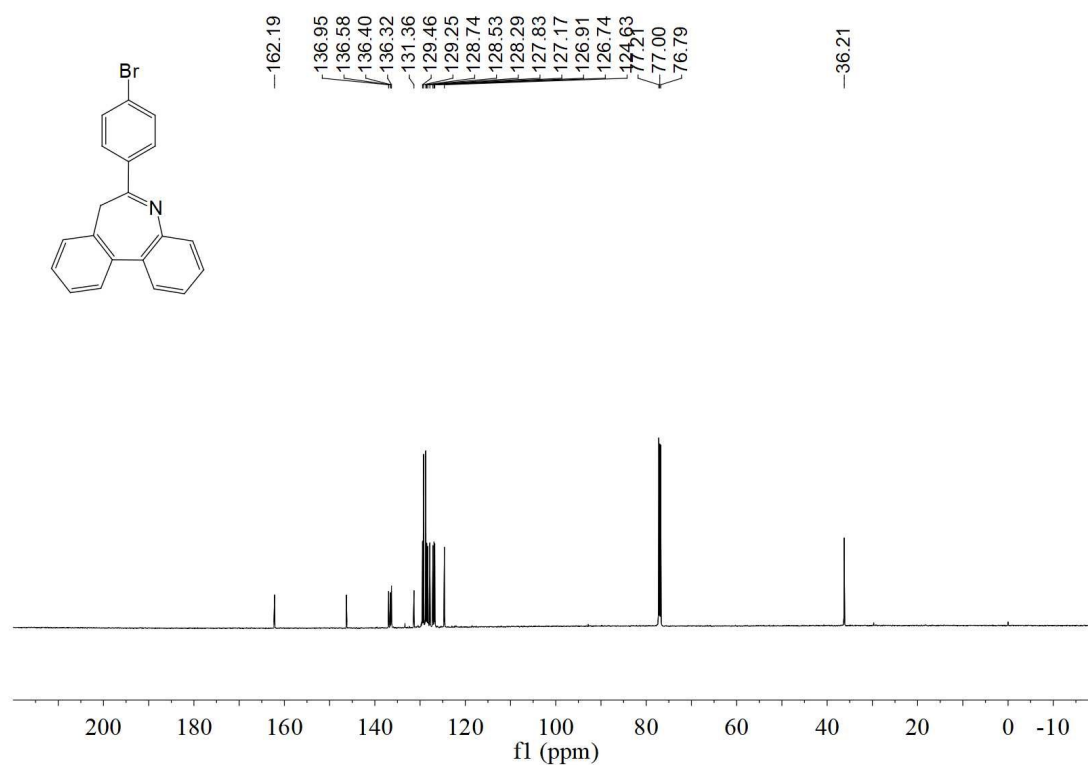
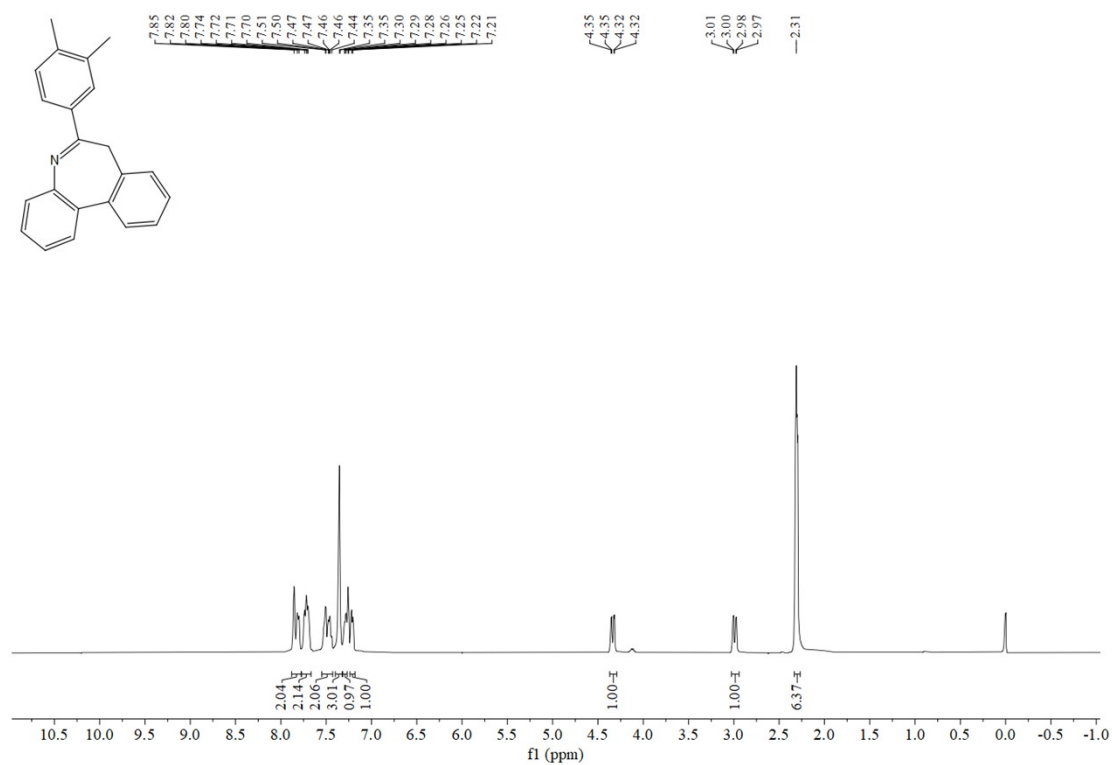
¹³C NMR Spectra of Compound 3i:**¹H NMR Spectra of Compound 3j:**

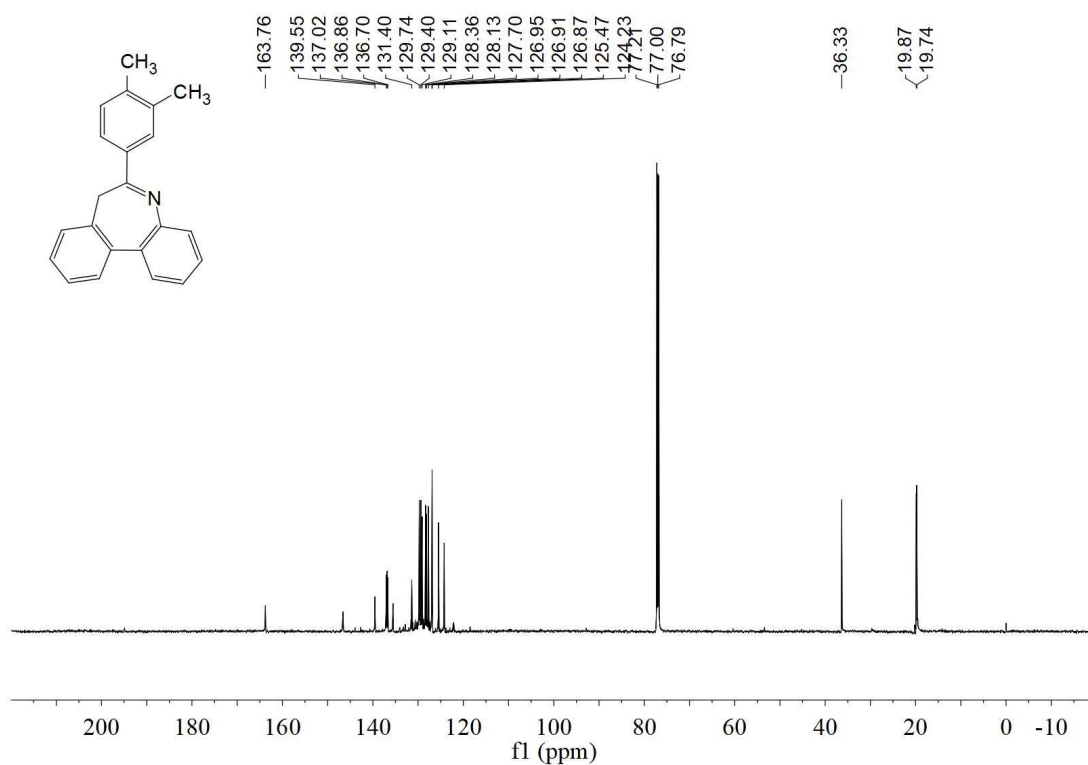
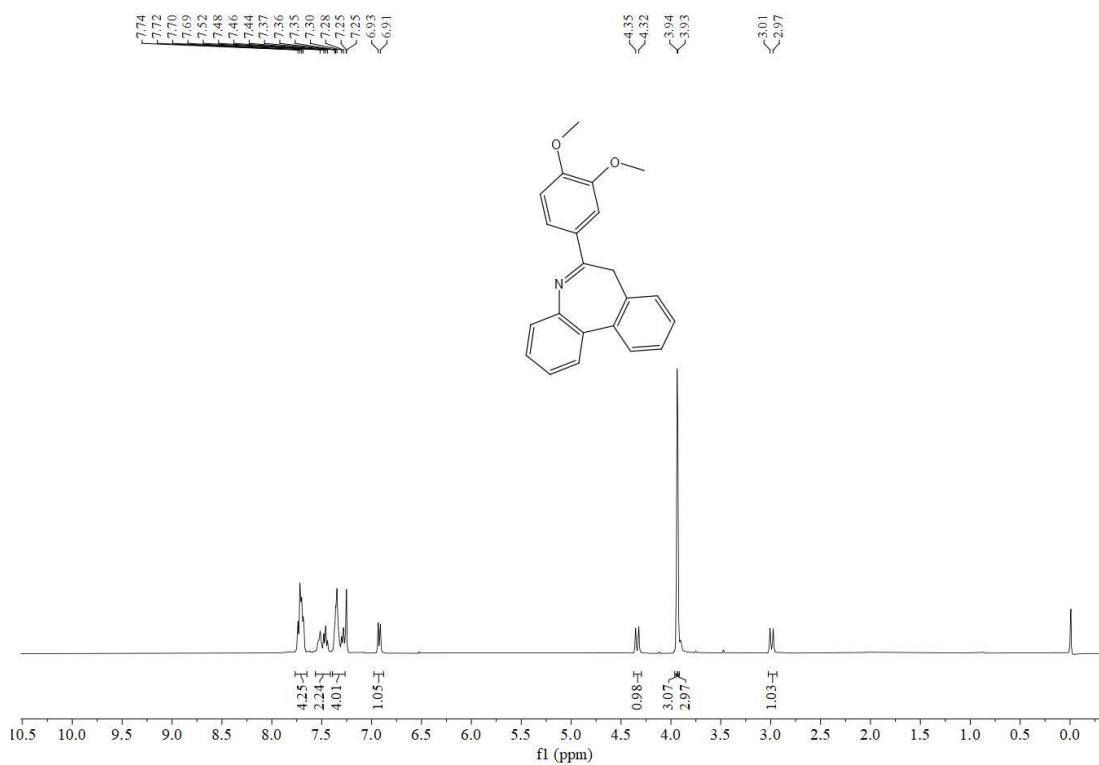
¹³C NMR Spectra of Compound 3j:**¹H NMR Spectra of Compound 3k:**

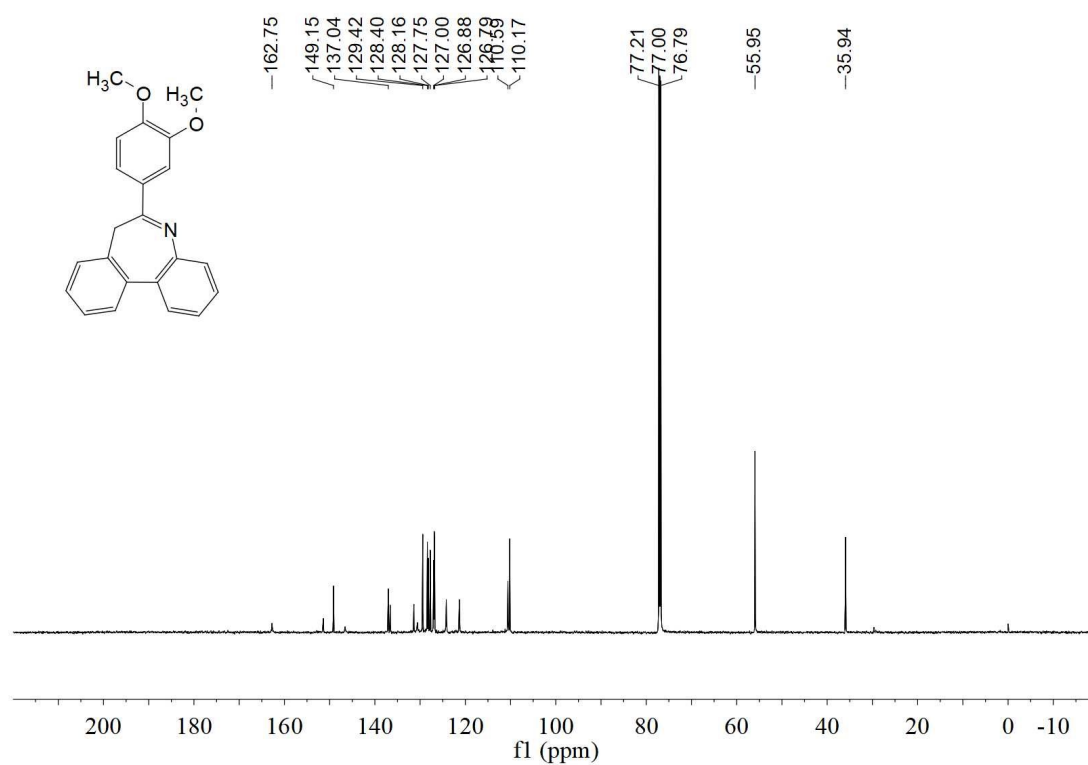
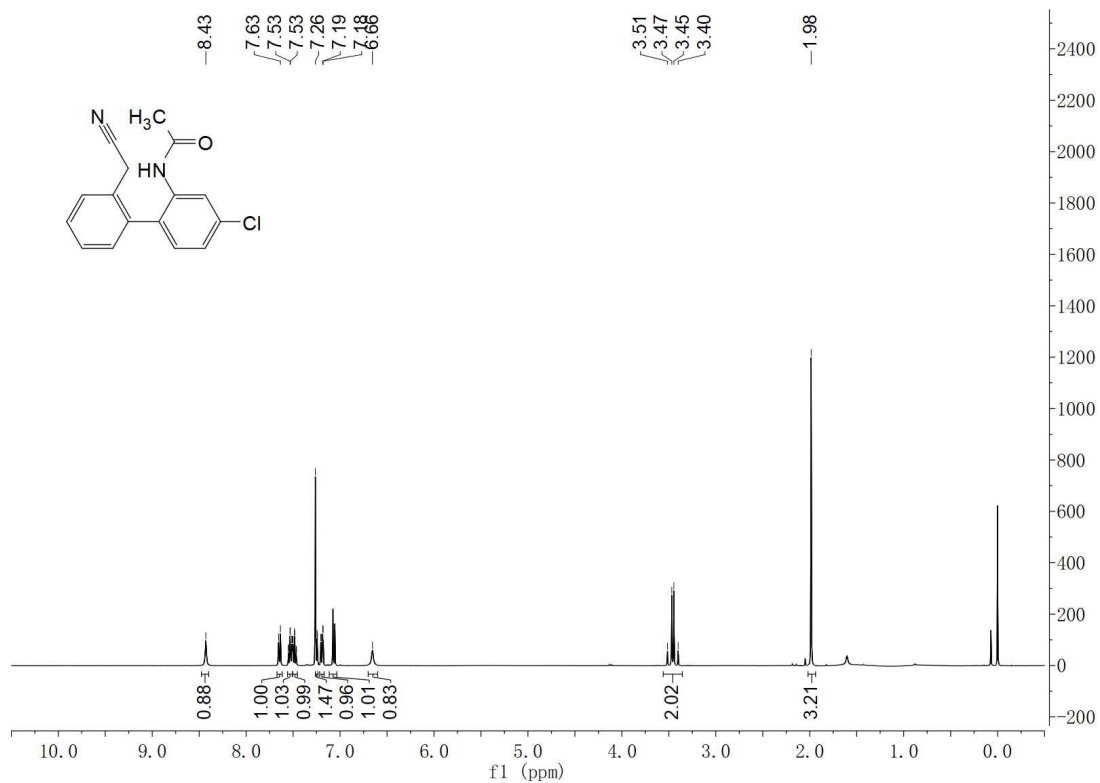
^{13}C NMR Spectra of Compound **3k:** **^1H NMR Spectra of Compound **3l**:**

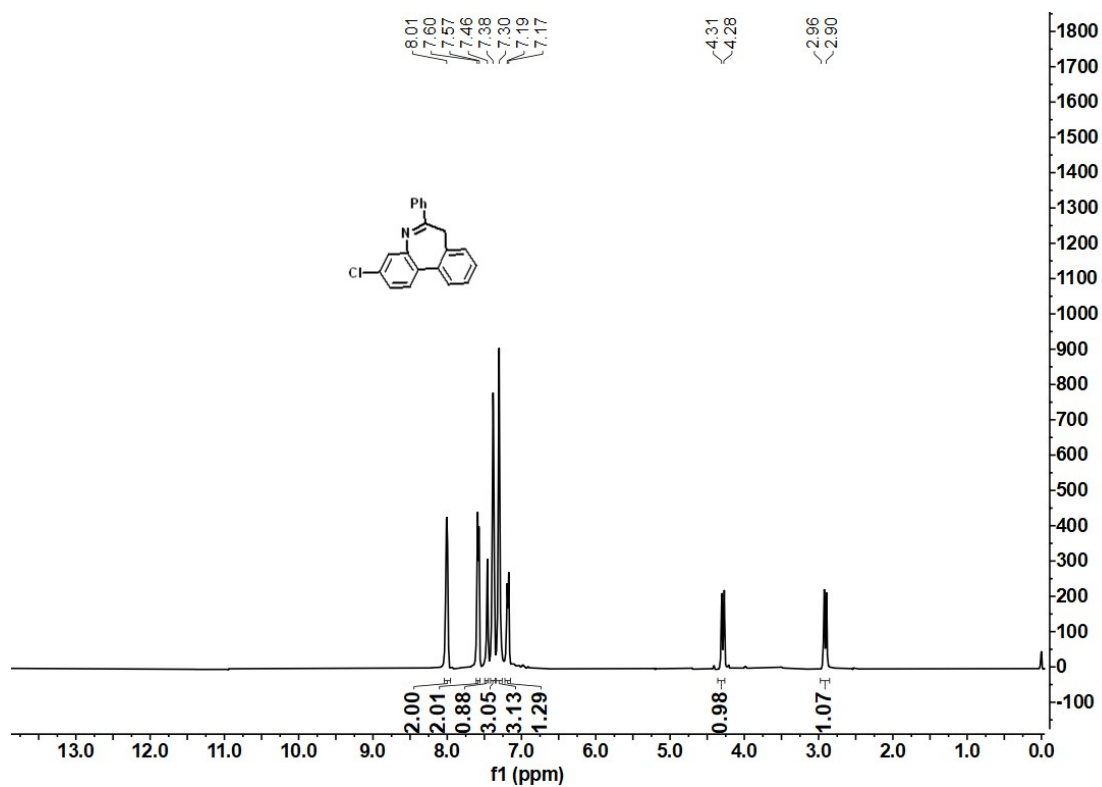
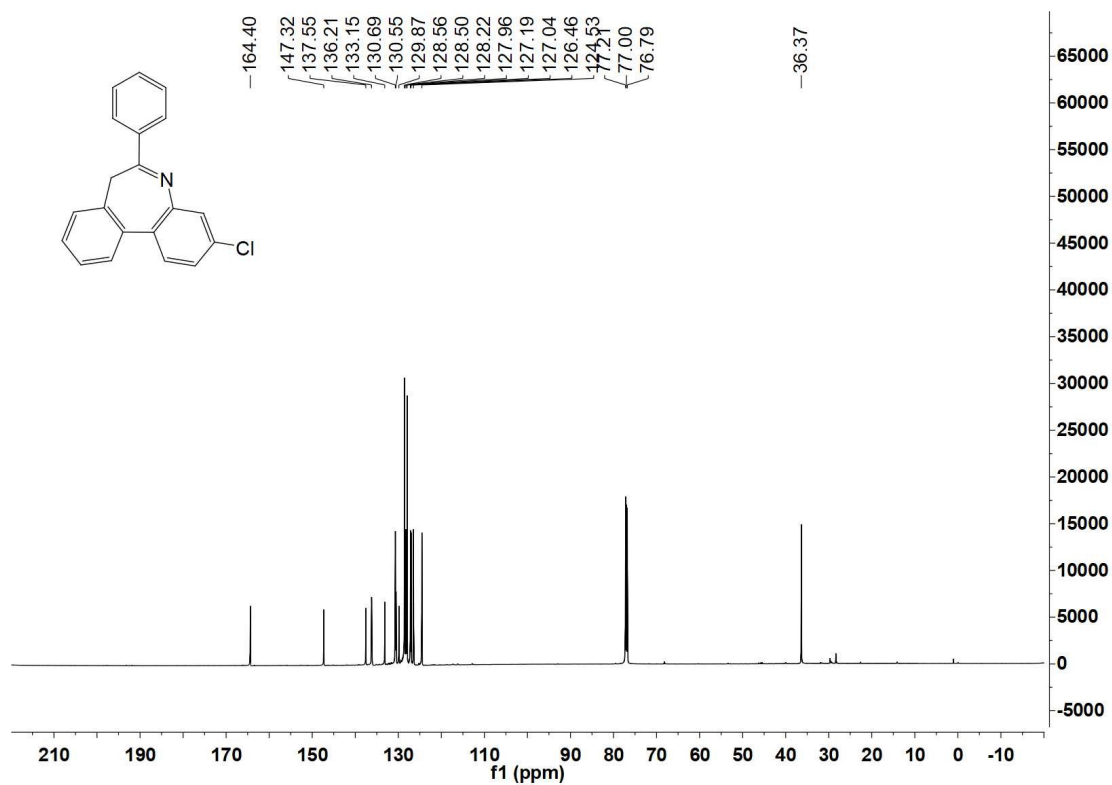
^{13}C NMR Spectra of Compound **3l:** **^1H NMR Spectra of Compound **3m**:**

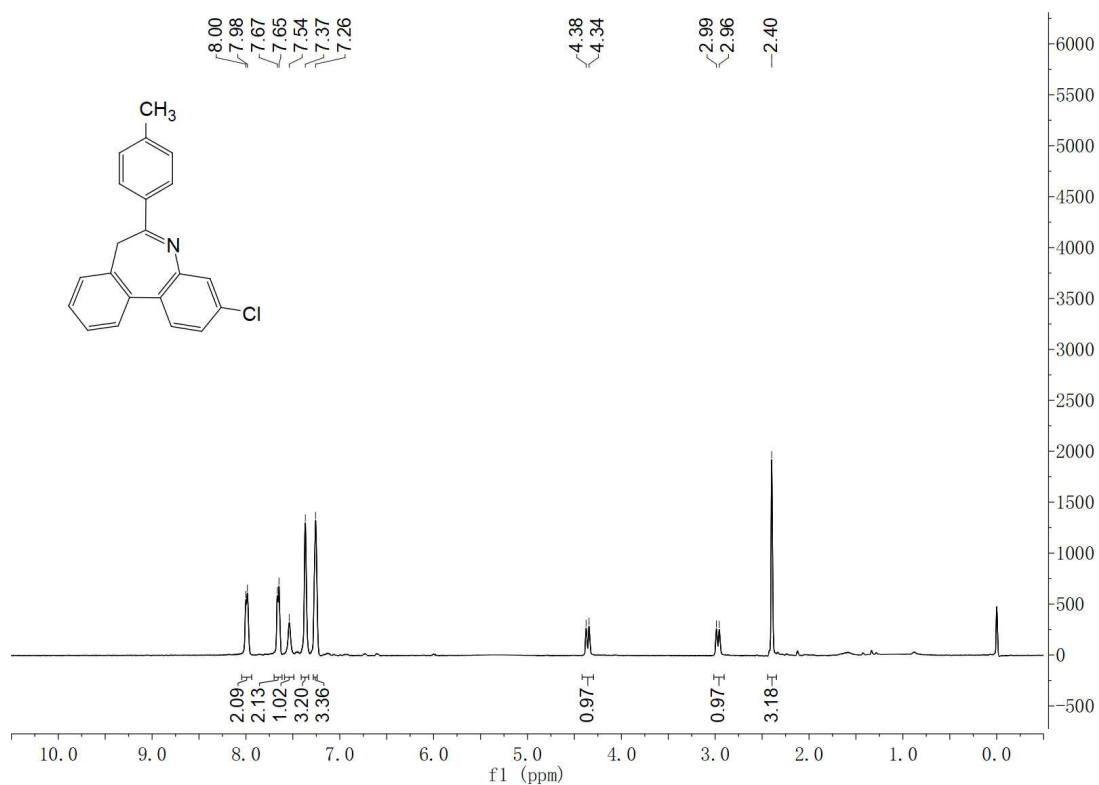
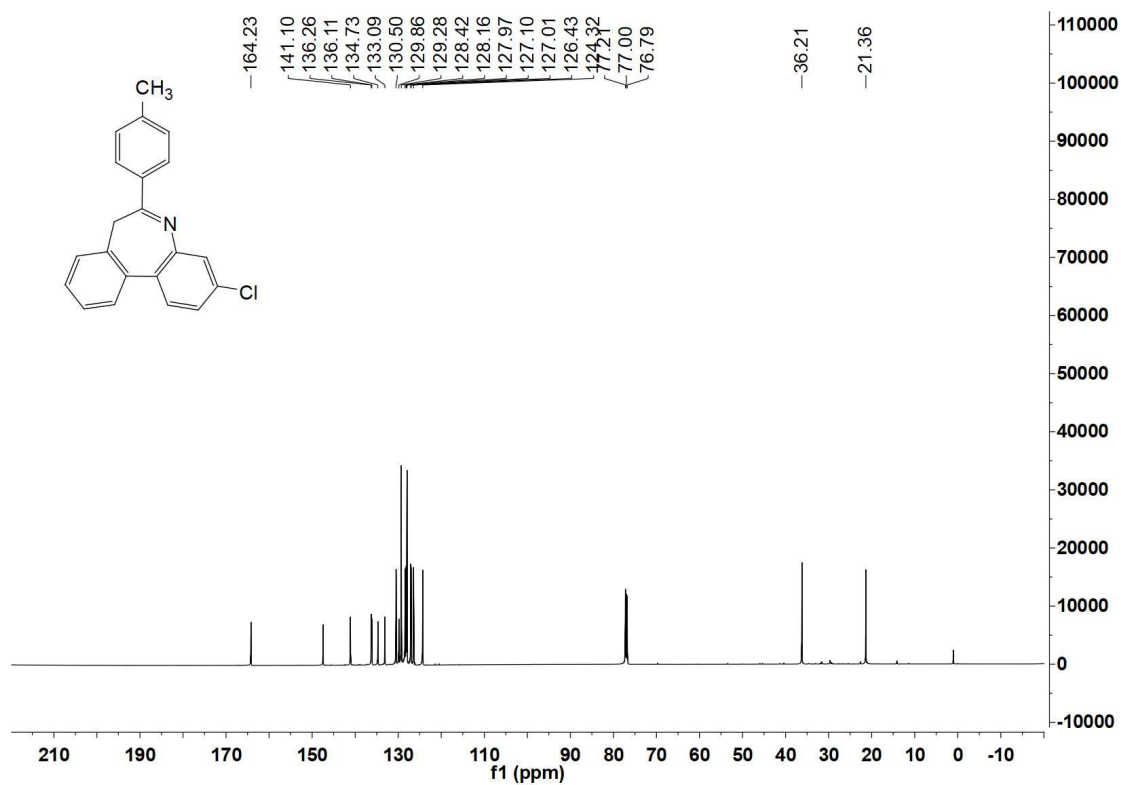
¹³C NMR Spectra of Compound 3m:**¹H NMR Spectra of Compound 3n:**

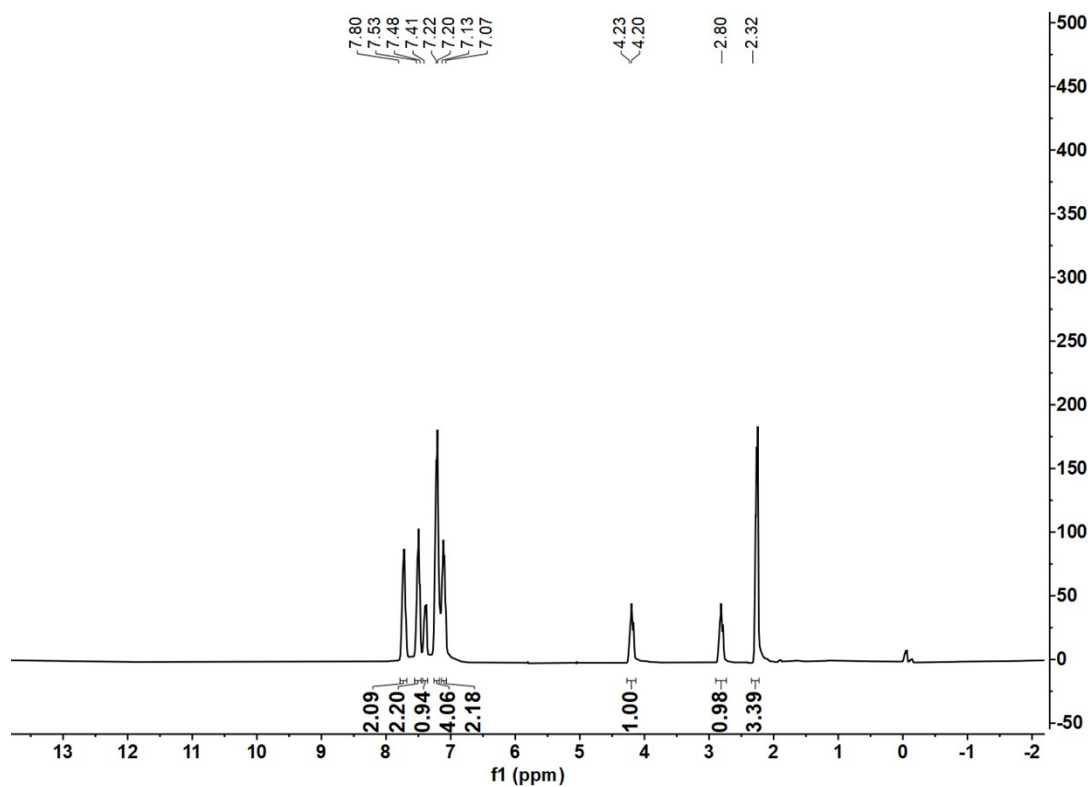
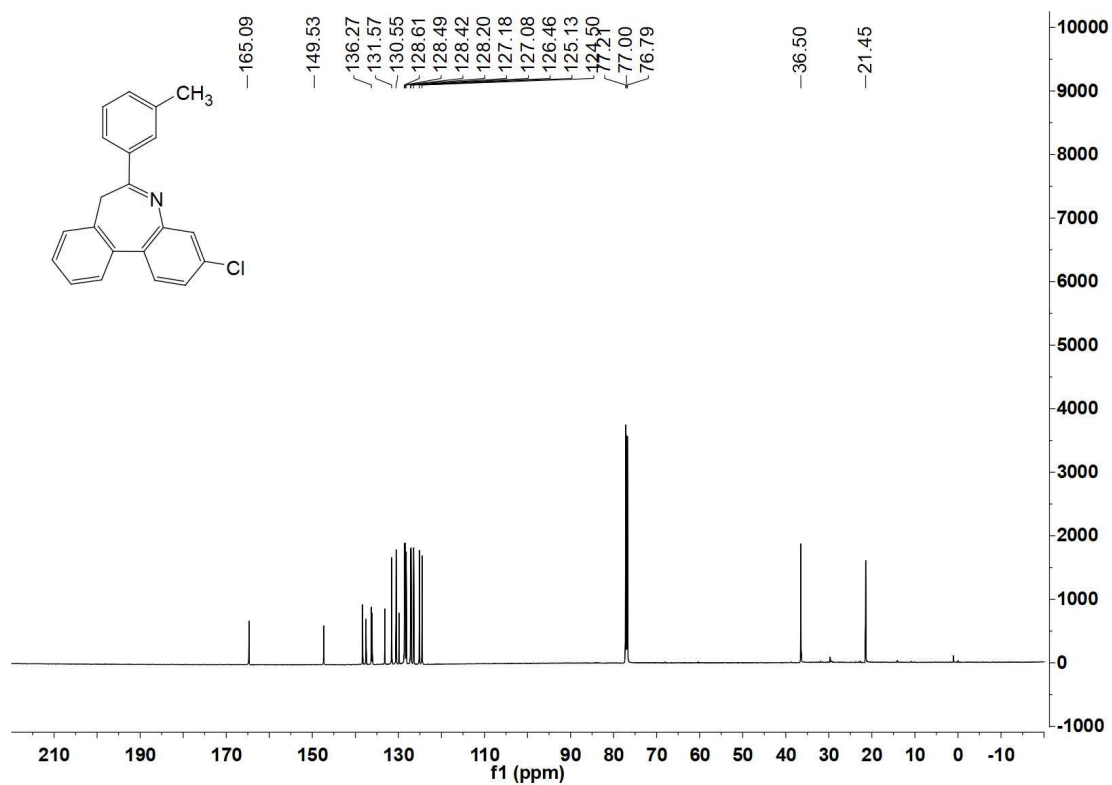
^{13}C NMR Spectra of Compound **3n:** **^1H NMR Spectra of Compound **3o**:**

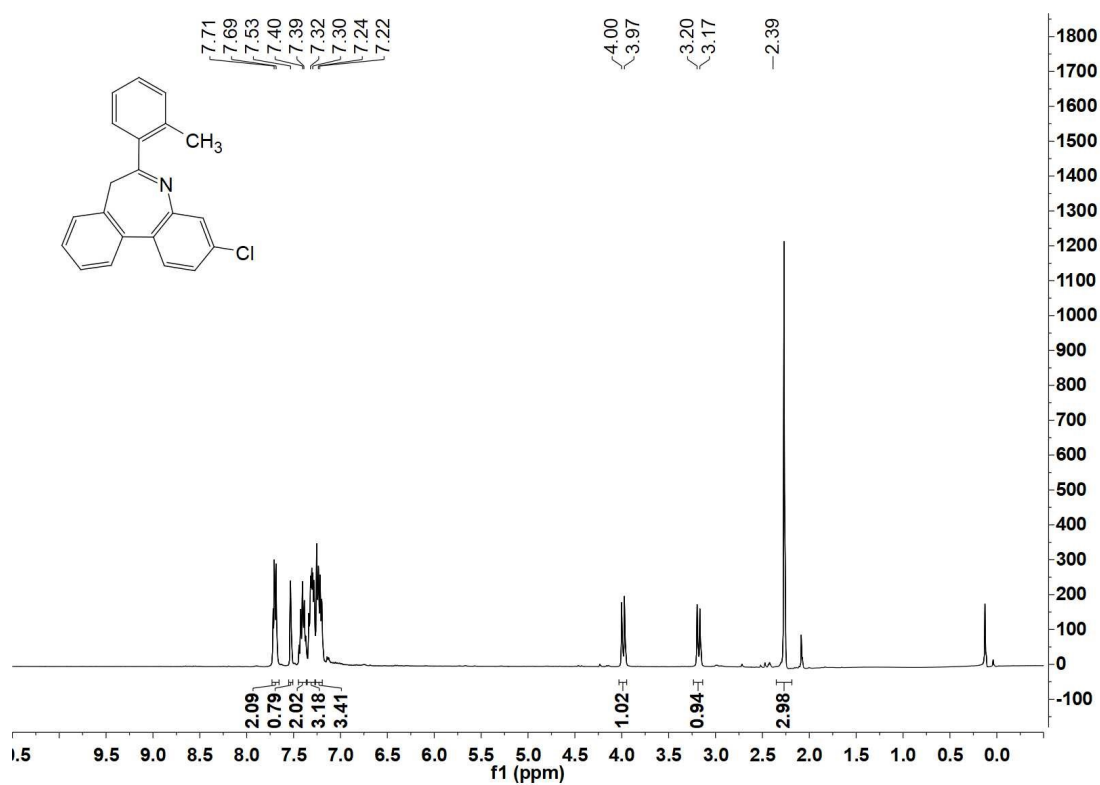
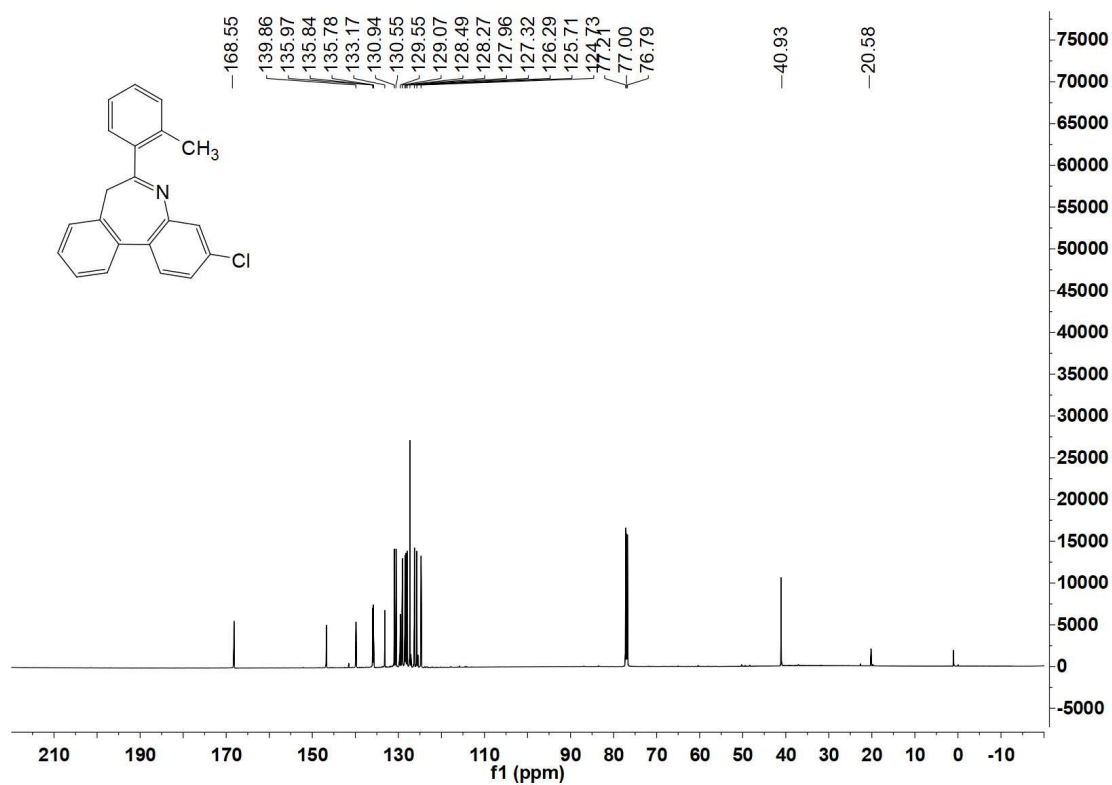
^{13}C NMR Spectra of Compound **3o:** **^1H NMR Spectra of Compound **3p**:**

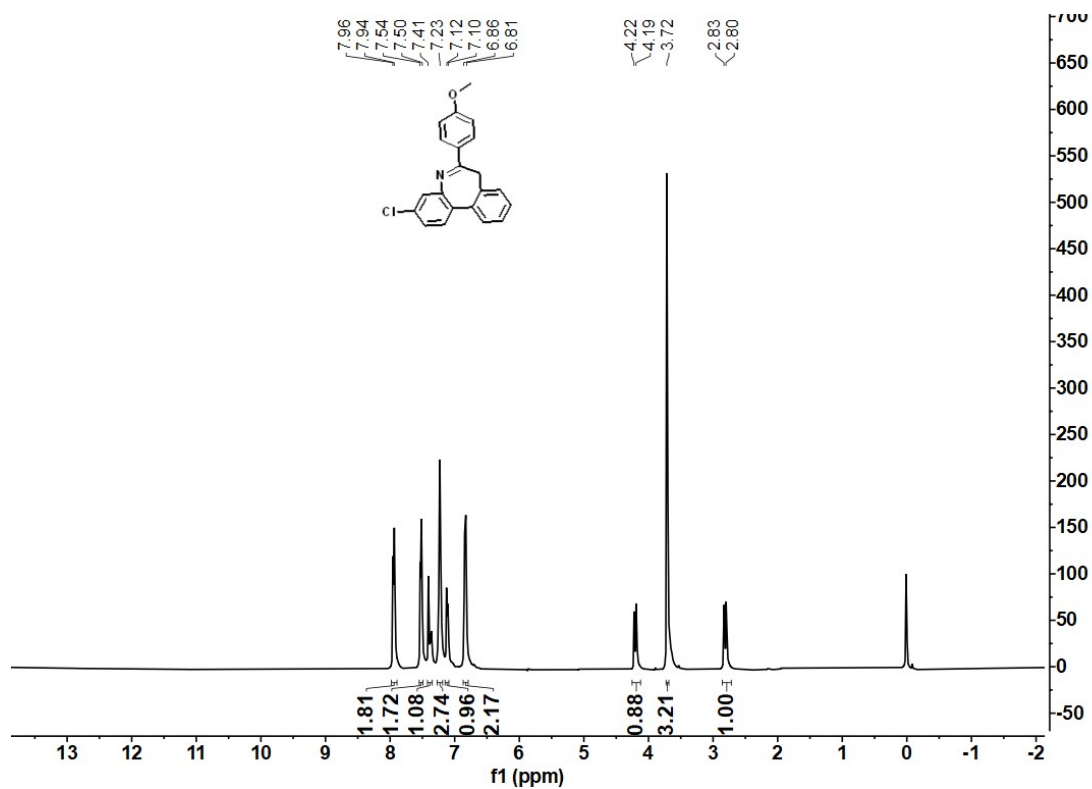
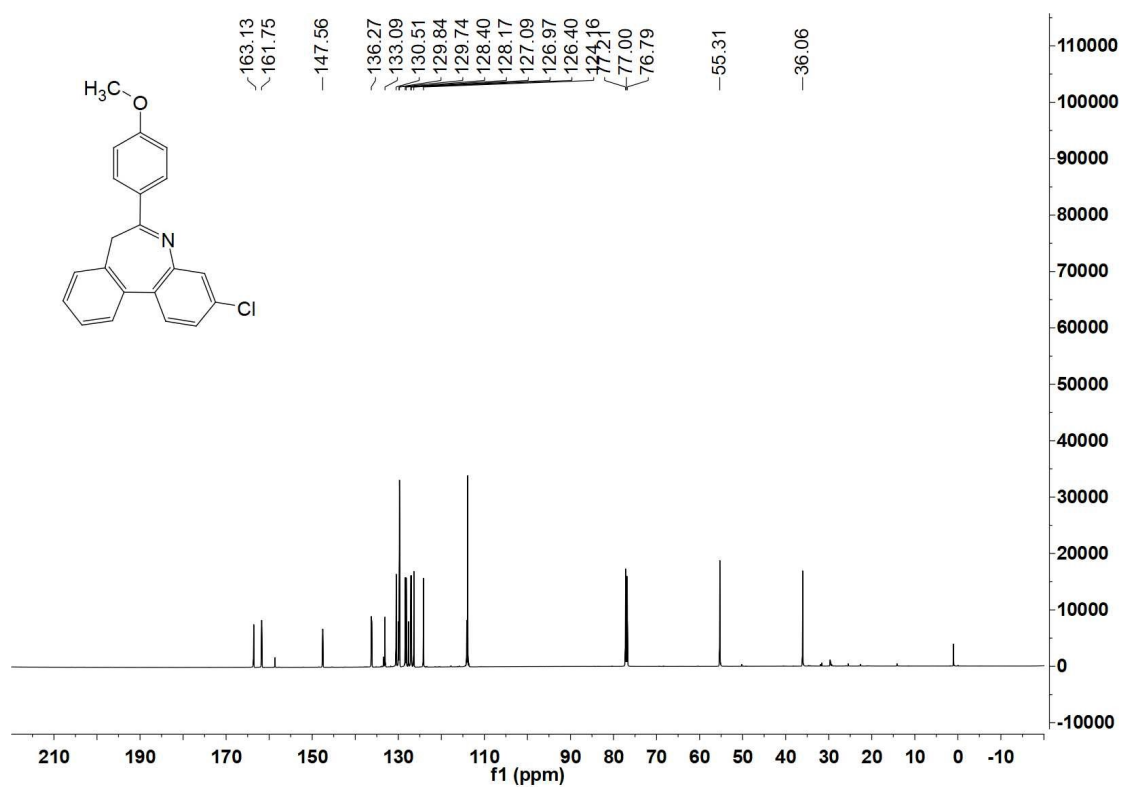
¹³C NMR Spectra of Compound 3p:**¹H NMR Spectra of Compound 4a:**

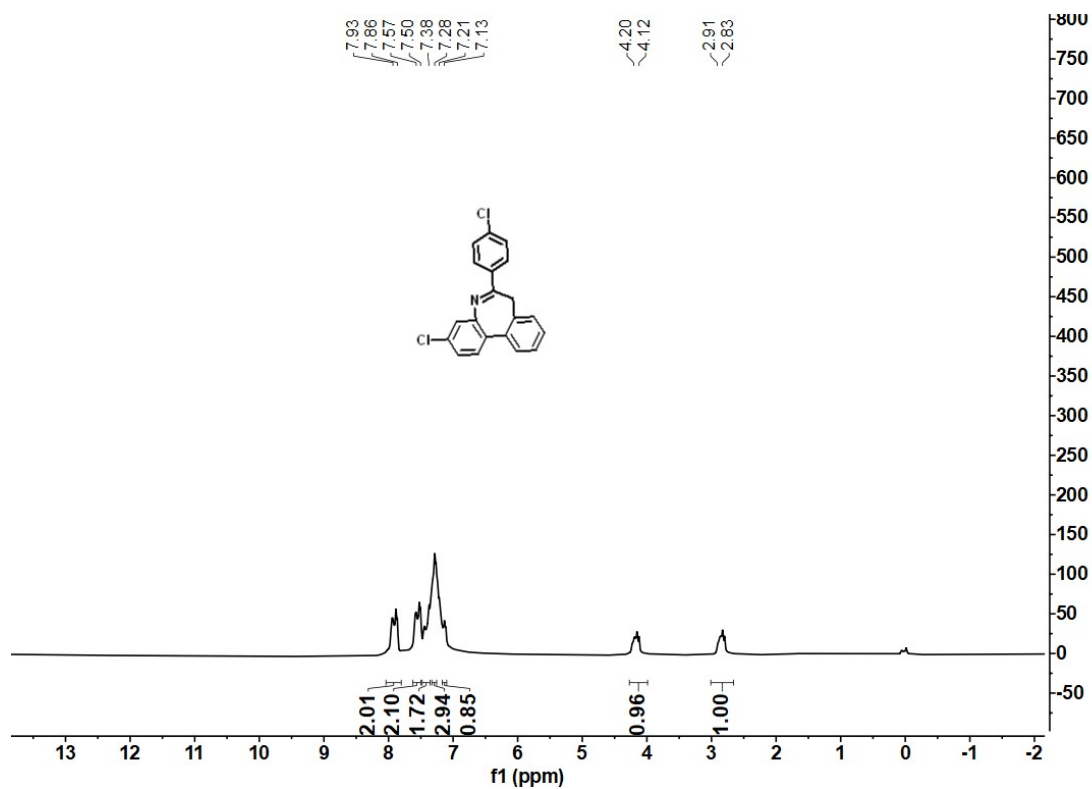
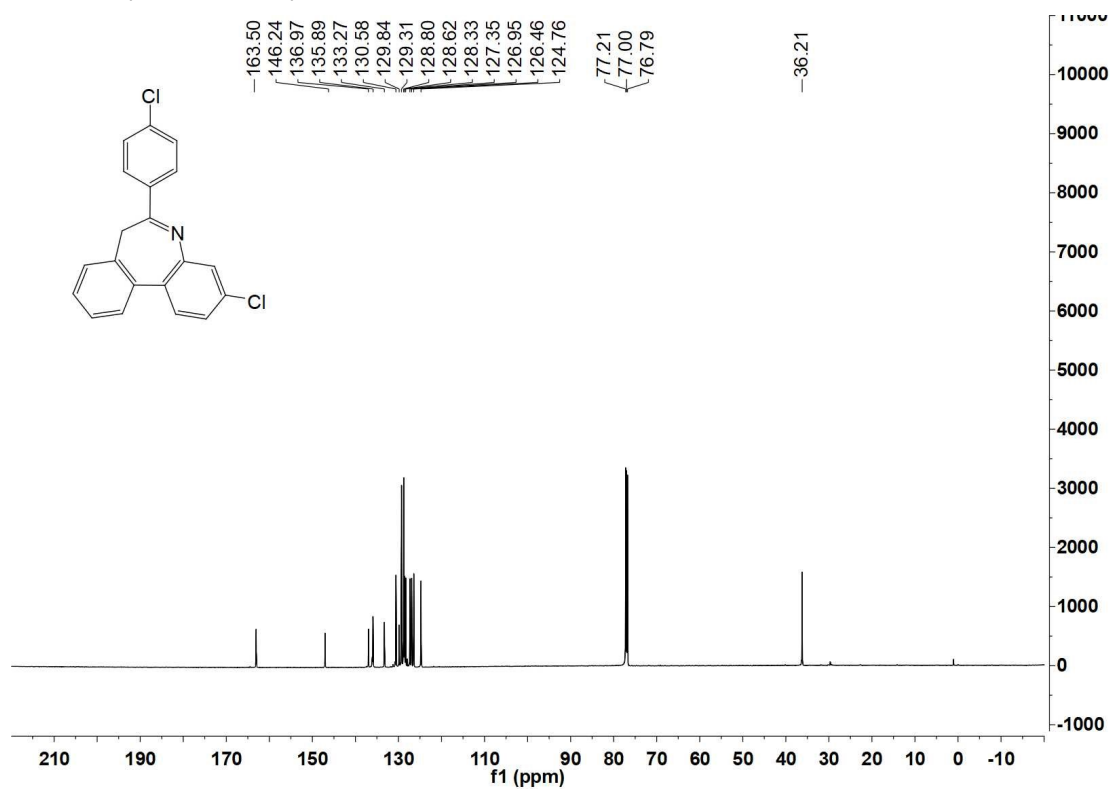
¹H NMR Spectra of Compound **5a**:¹³C NMR Spectra of Compound **5a**:

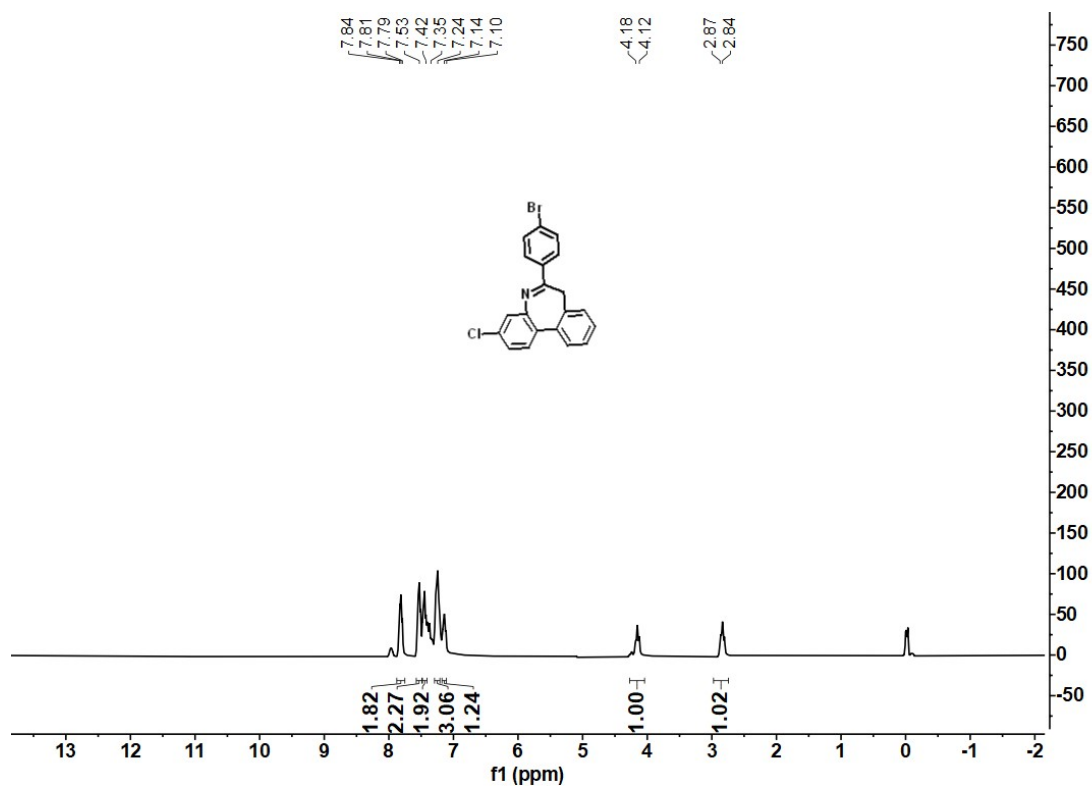
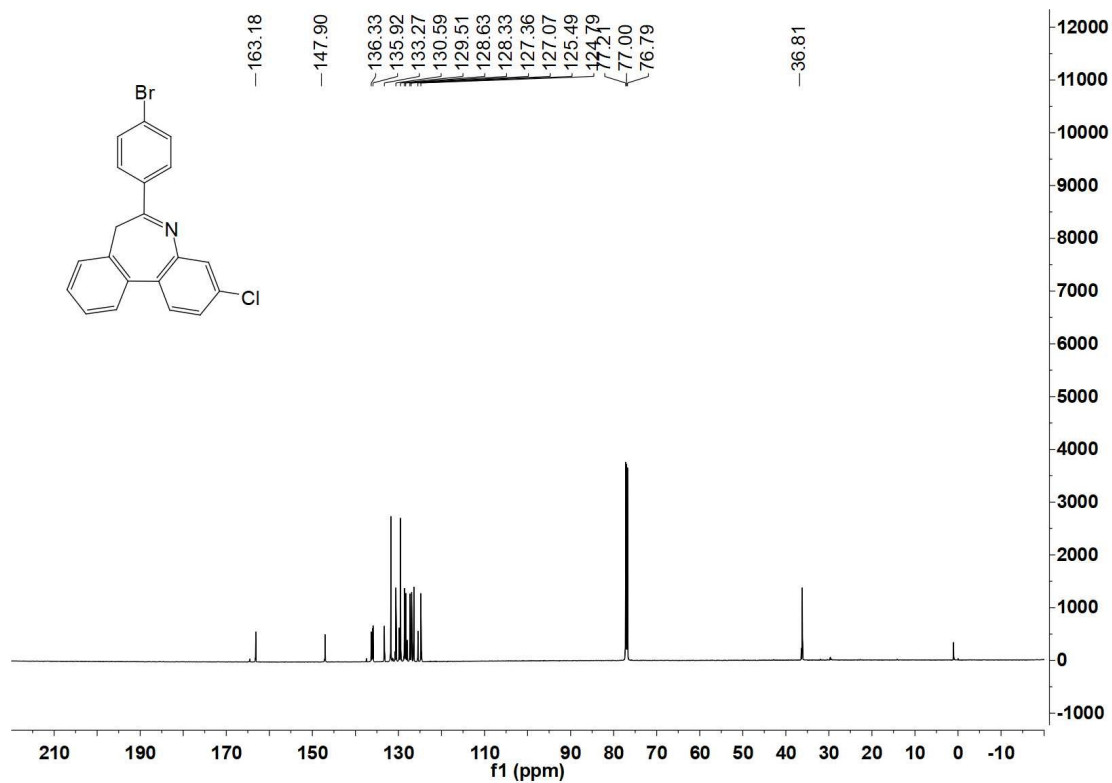
¹H NMR Spectra of Compound 5b:**¹³C NMR Spectra of Compound 5b:**

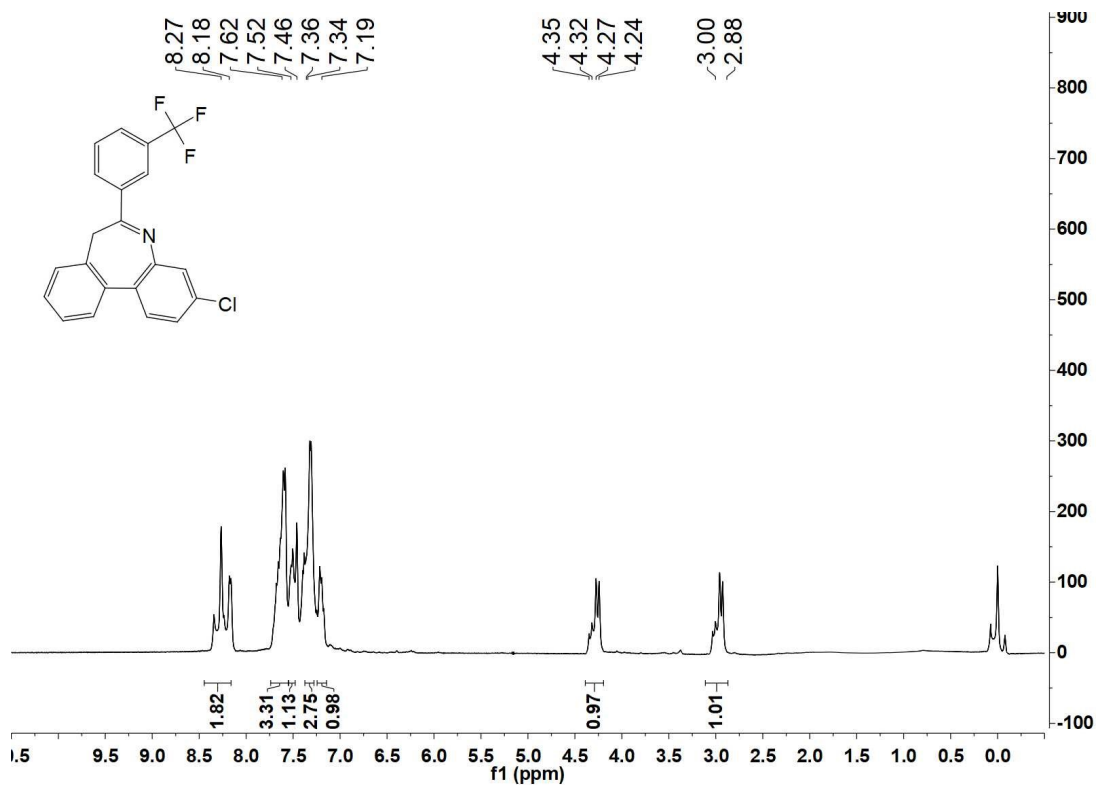
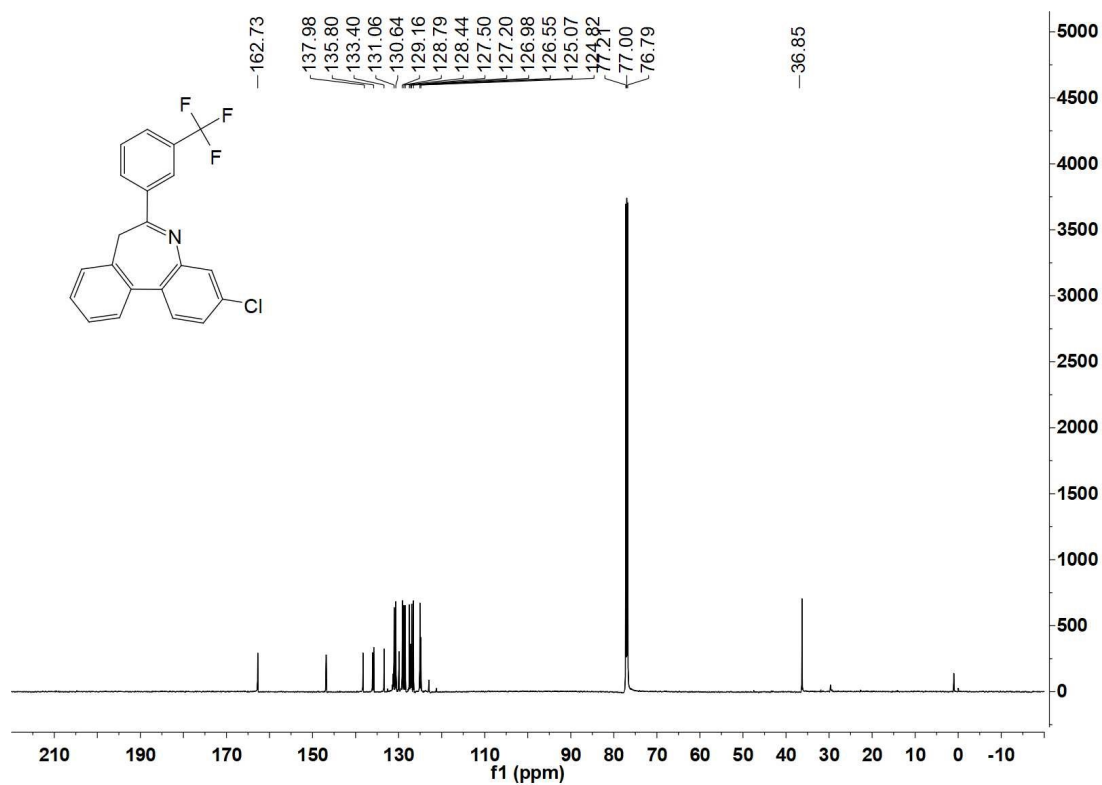
¹H NMR Spectra of Compound **5c**:¹³C NMR Spectra of Compound **5c**:

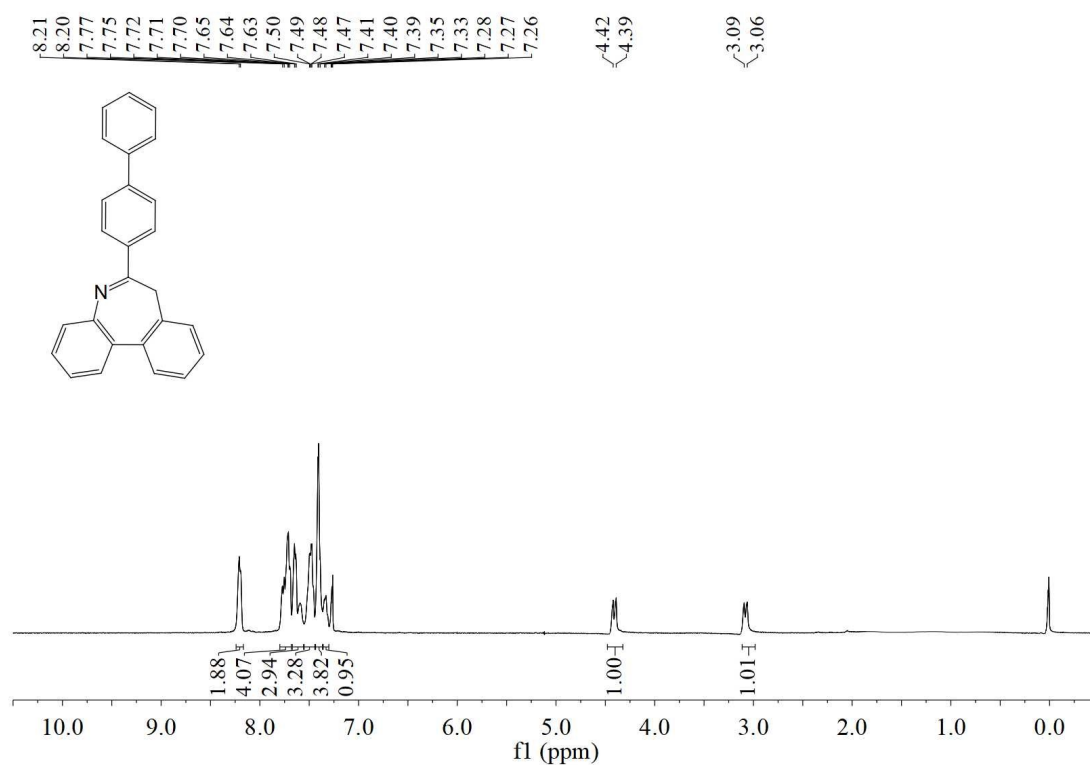
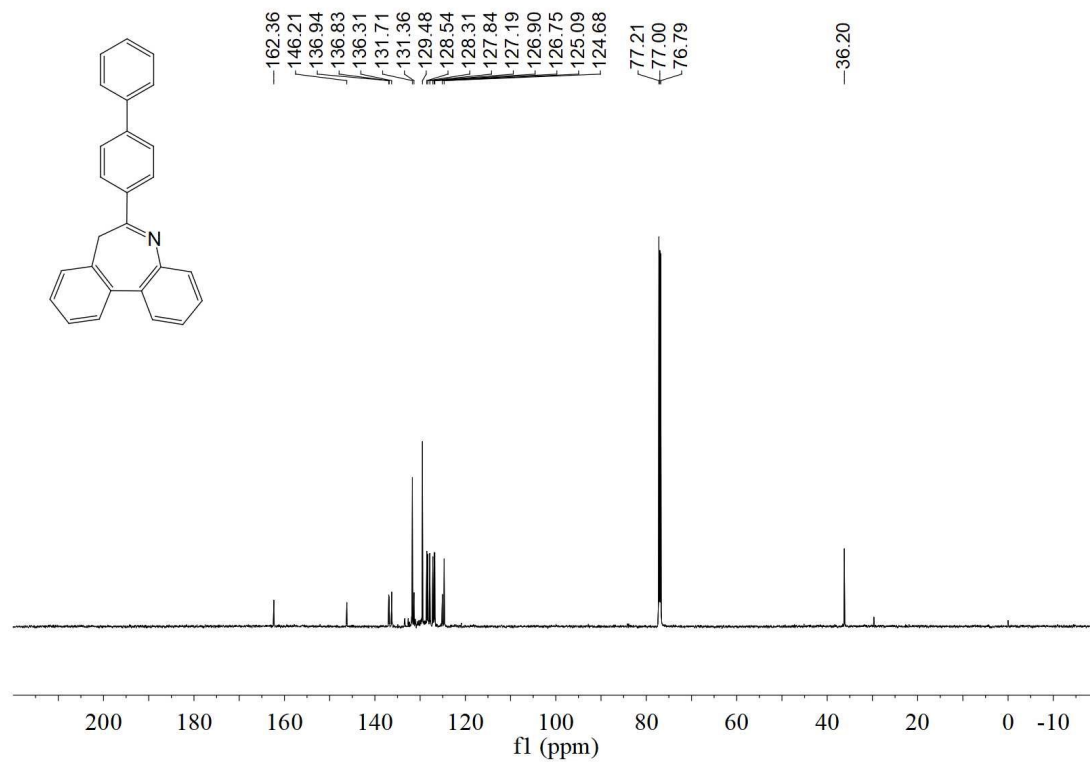
¹H NMR Spectra of Compound **5d**:¹³C NMR Spectra of Compound **5d**:

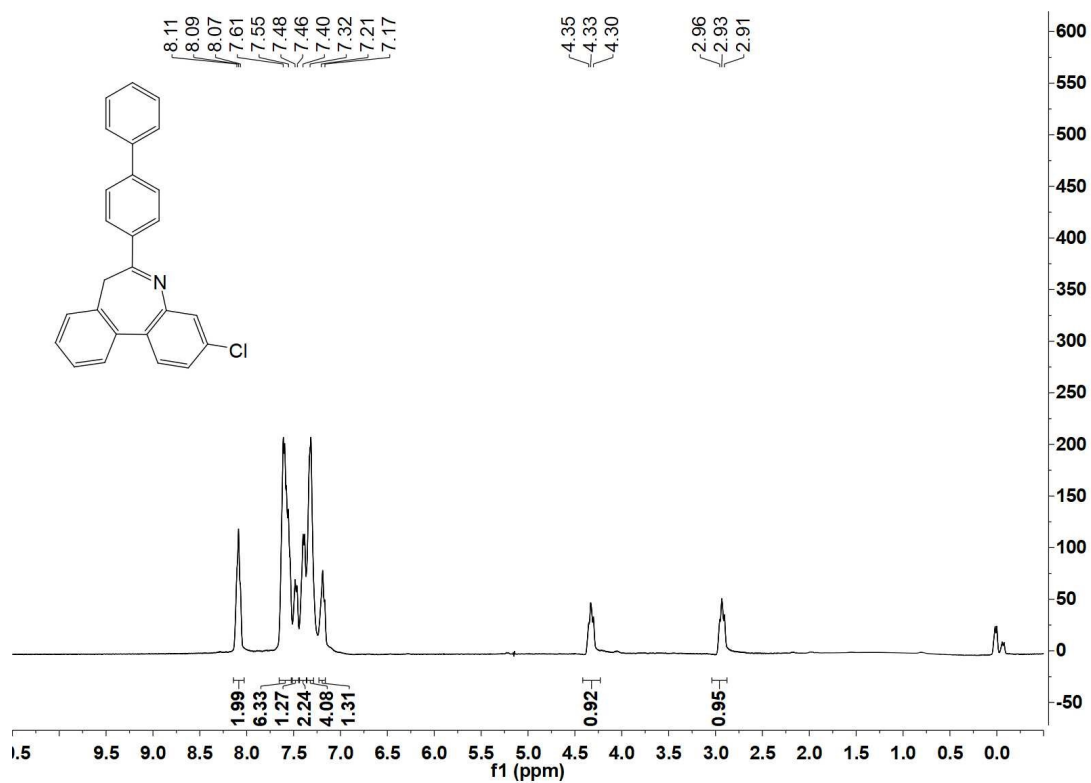
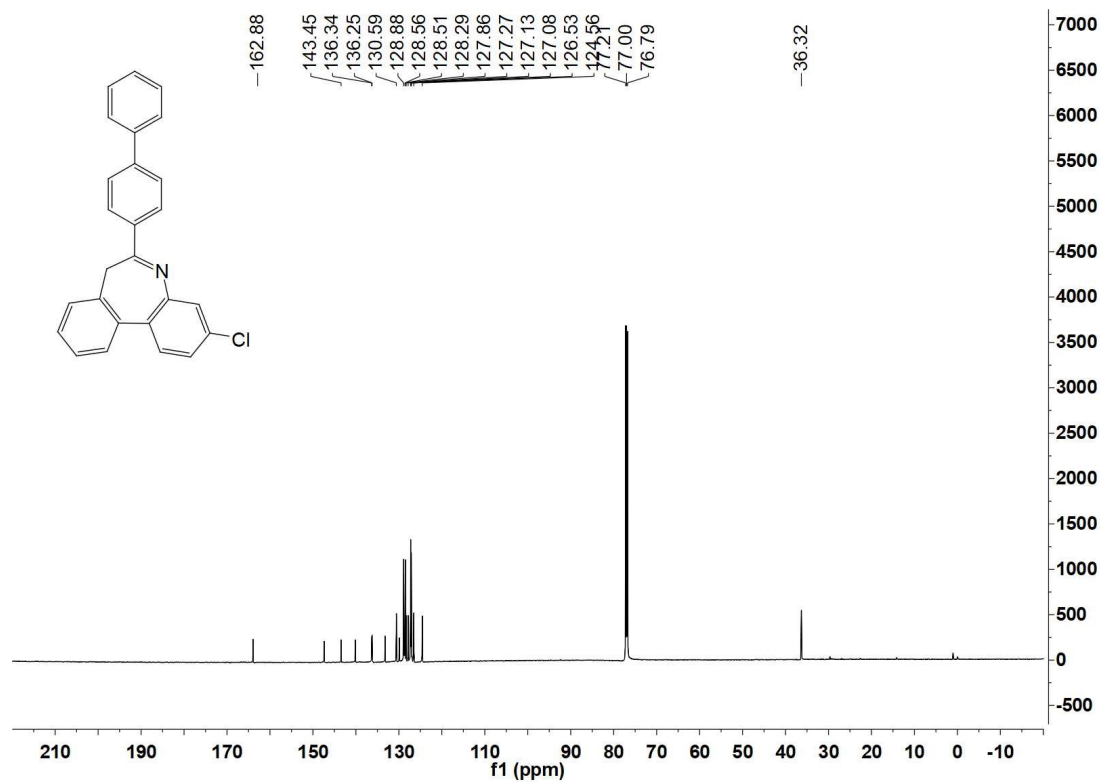
¹H NMR Spectra of Compound **5e**:¹³C NMR Spectra of Compound **5e**:

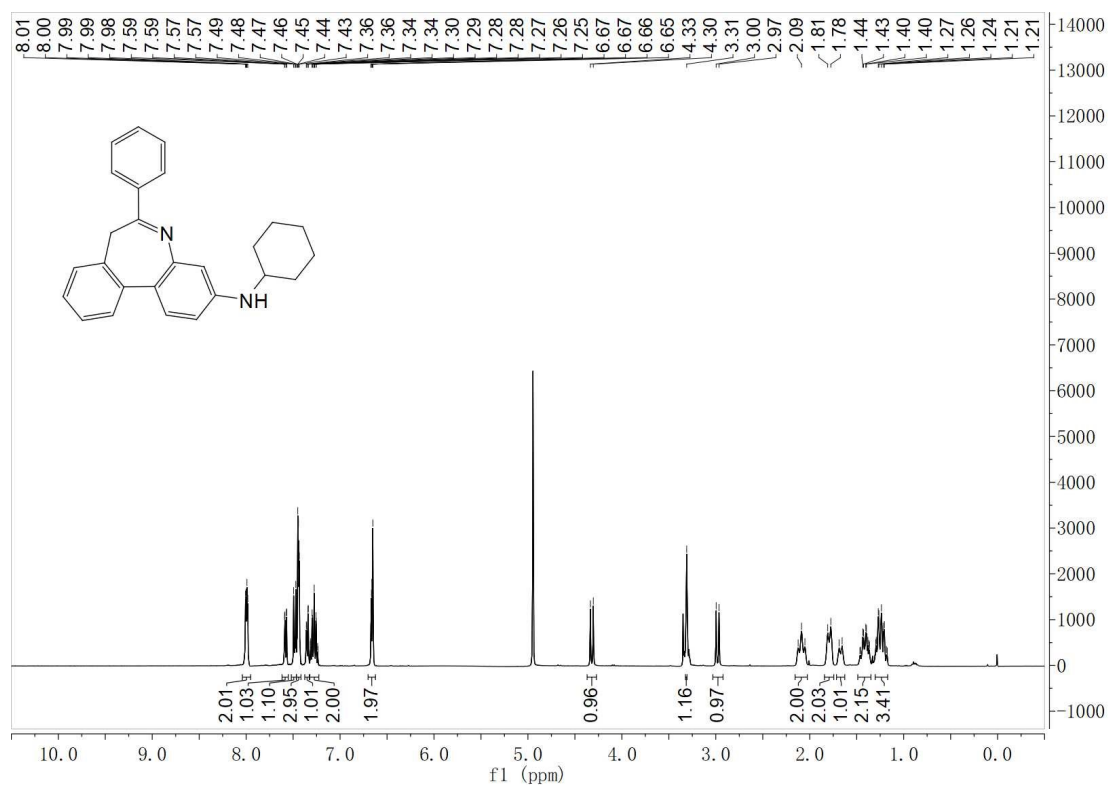
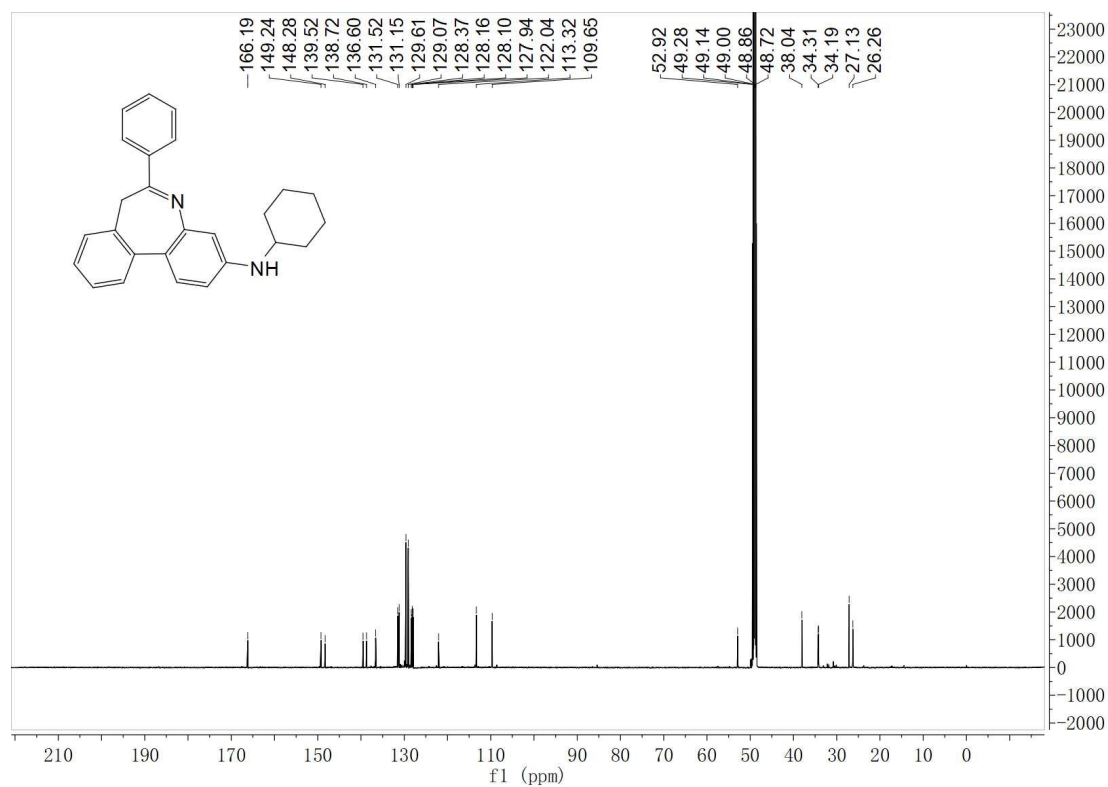
¹H NMR Spectra of Compound 5f:**¹³C NMR Spectra of Compound 5f:**

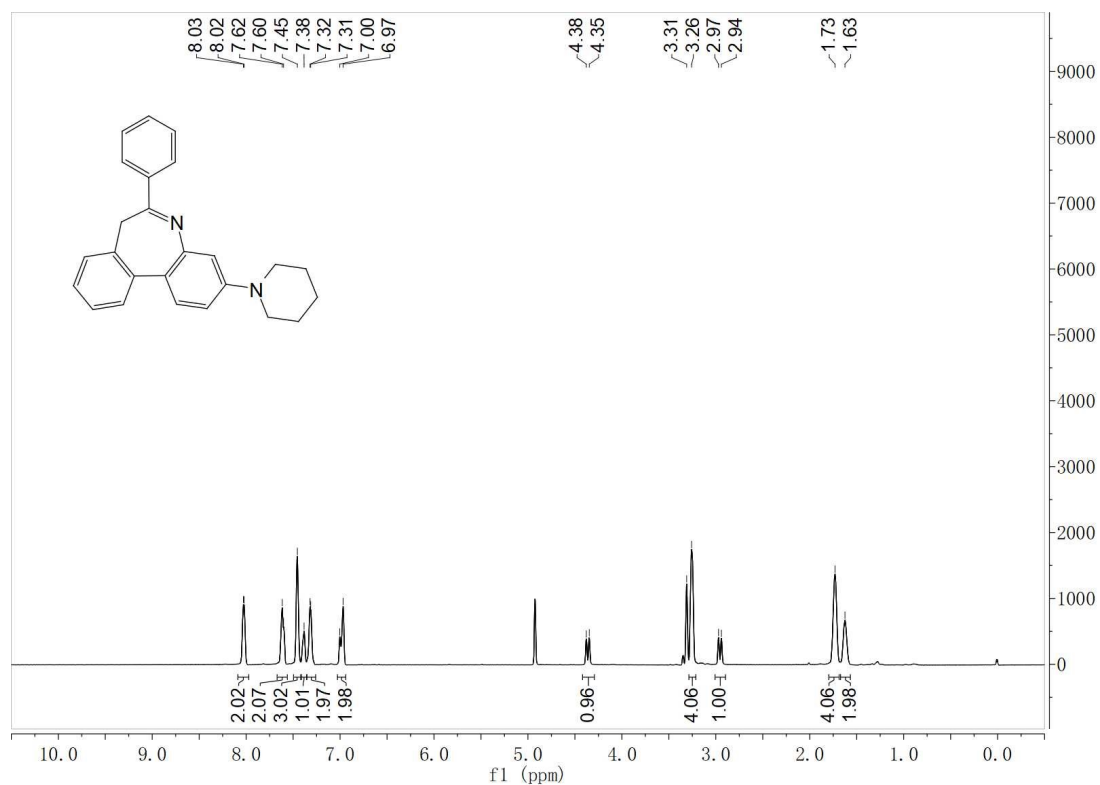
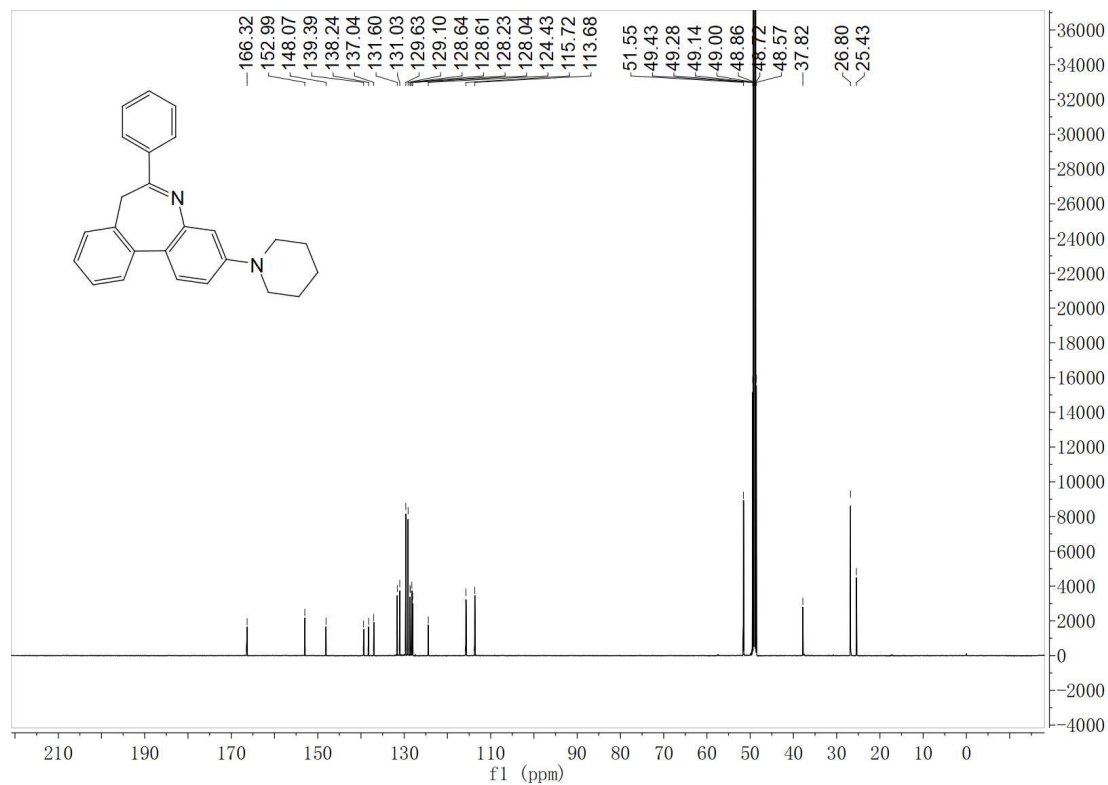
¹H NMR Spectra of Compound 5g:**¹³C NMR Spectra of Compound 5g:**

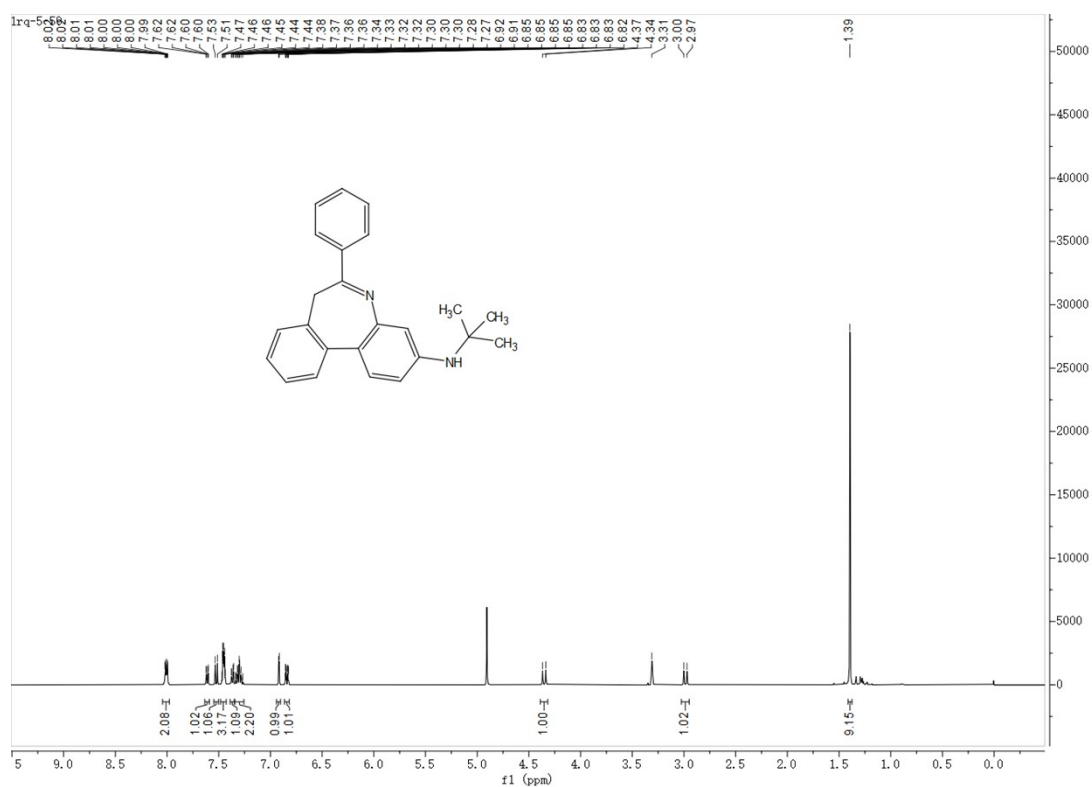
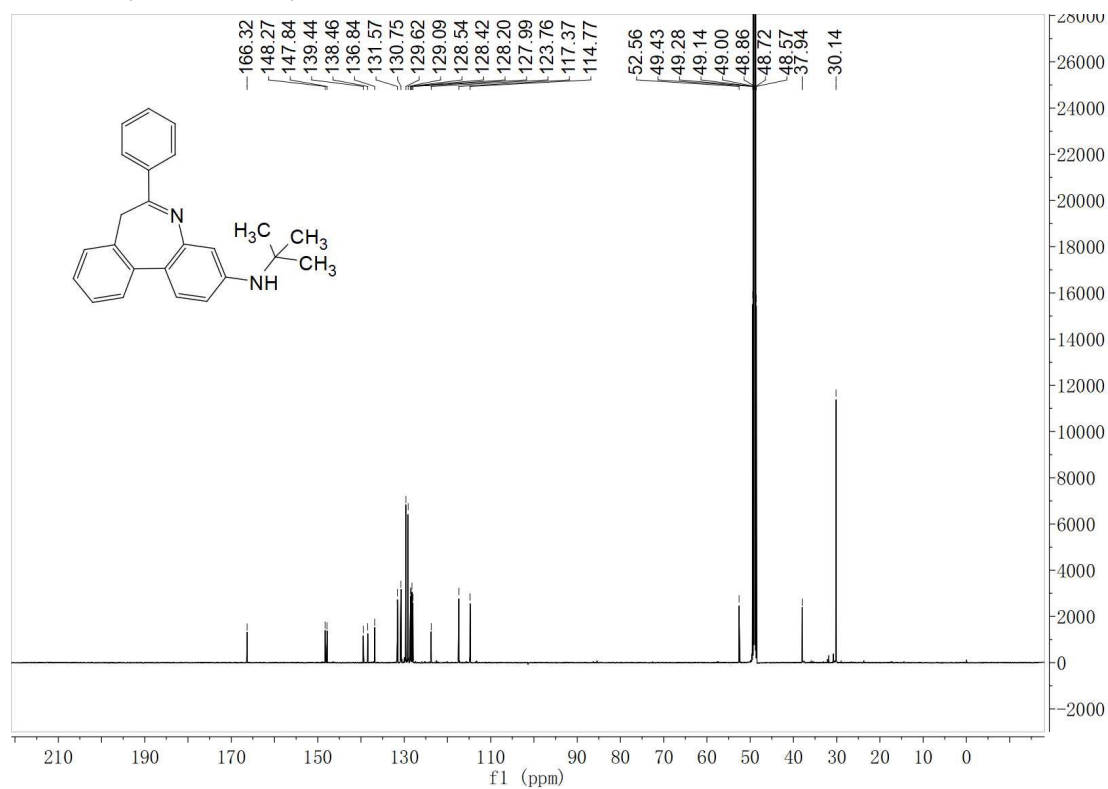
¹H NMR Spectra of Compound **5h**:¹³C NMR Spectra of Compound **5h**:

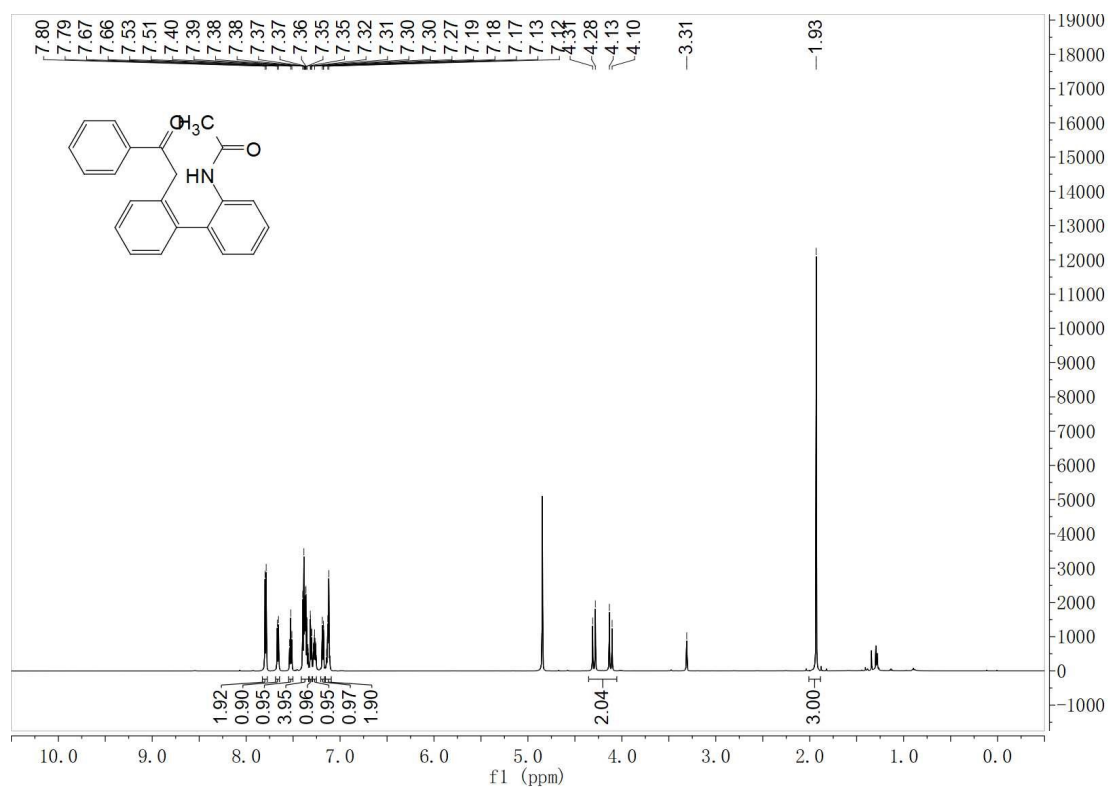
¹H NMR Spectra of Compound 6a:**¹³C NMR Spectra of Compound 6a:**

¹H NMR Spectra of Compound 7a:**¹³C NMR Spectra of Compound 7a:**

¹H NMR Spectra of Compound 8a:**¹³C NMR Spectra of Compound 8a:**

¹H NMR Spectra of Compound **8b:****¹³C NMR Spectra of Compound **8b**:**

¹H NMR Spectra of Compound 8c:**¹³C NMR Spectra of Compound 8c:**

¹H NMR Spectra of intermediate C:¹³C NMR Spectra of intermediate C: