

Supporting Information:

## **Modular 2,3-diaryl-2*H*-azirines synthesis from ketoxime acetates via Cs<sub>2</sub>CO<sub>3</sub>-mediated cyclization**

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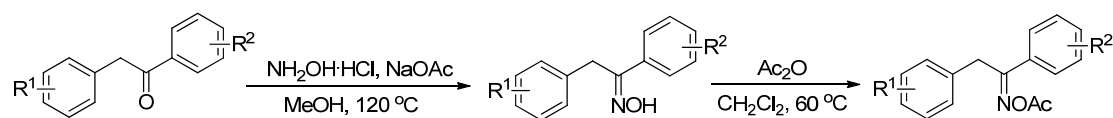
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## 1. General Information

Column chromatography was carried out on silica gel.  $^1\text{H}$  NMR spectra were recorded on 400 MHz in  $\text{CDCl}_3$  and  $^{13}\text{C}$  NMR spectra were recorded on 100 MHz in  $\text{CDCl}_3$ . The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All new products were further characterized by HRMS; copies of their  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra are provided. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. The ketones were in all cases prepared by Friedel-Crafts reactions.

## 2. Typical Procedure for Preparation of Ketoxime Acetates

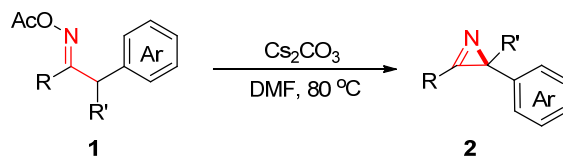


The mixture of ketone (5 mmol),  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (6 mmol, 416.9 mg) and  $\text{NaOAc}$  (7.5 mmol, 615.0 mg) was stirred in  $\text{MeOH}$  (20 mL) at  $120\text{ }^\circ\text{C}$  oil bath. After completion of the reaction (detected by TLC), the reaction mixture was cooled to room temperature, diluted with  $\text{EtOAc}$  (25 mL  $\times$  2) and washed with brine (20 mL). The organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated in vacuo to afford crude ketoximes. The desired ketoximes were obtained by recrystallization (hexanes).

Then, the mixture of ketoxime and acetic anhydride (2.0 equiv) was stirred in dichloromethane at  $60\text{ }^\circ\text{C}$  for 2-3 h and monitored by TLC until reaction completion. The reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$  (25 mL) and washed with  $\text{H}_2\text{O}$  (20 mL) and brine (10 mL). The organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated in vacuo. The crude product was purified by recrystallization (hexanes) to afford corresponding ketoxime acetates.

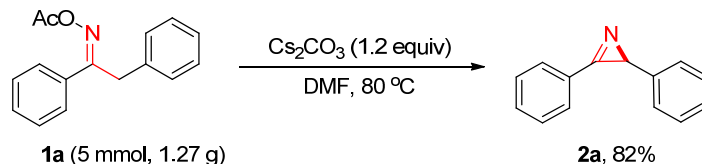
### 3. Typical Procedure for the Synthesis of 2*H*-Azirines

#### A: General experimental procedure for the preparation of 2*H*-azirines **2**



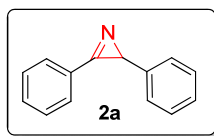
In a 10 mL round bottom flask, ketoxime acetate **1** (0.2 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.24 mmol, 78.2 mg) were stirred in *N,N*-dimethylformamide (DMF, 1 mL) at 80 °C under Ar. After completion of the reaction (detected by TLC), the reaction mixture was cooled to room temperature, extracted with ethyl acetate (2 × 10 mL) and washed with brine (10 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo. The residue was purified by column chromatography on silica gel with hexanes/ethyl acetate (v/v = 50:1) as the eluent to afford the corresponding 2*H*-azirine **2**.

#### B: Typical procedure for the preparation of **2a** on 5 mmol scale

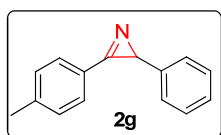


In a 50 mL round bottom flask, 1,2-diphenylethanone oxime acetate **1a** (5 mmol, 1.27 g), Cs<sub>2</sub>CO<sub>3</sub> (6 mmol, 1.95 g) were stirred in *N,N*-dimethylformamide (DMF, 15 mL) at 80 °C under Ar. After completion of the reaction (detected by TLC), the reaction mixture was cooled to room temperature, extracted with ethyl acetate and washed with brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo. The crude product was purified by recrystallization (hexanes and ethyl acetate) to afford corresponding 2,3-diphenyl-2*H*-azirine **2a** in 82% yield (790 mg).

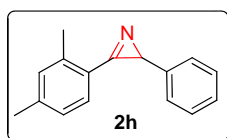
#### 4. Spectroscopic Data for 2*H*-Azirines



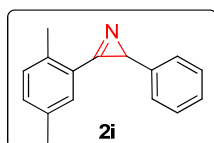
**2a:** Yield 93% (35.9 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J$  = 7.6 Hz, 2H), 7.60-7.52 (m, 3H), 7.30-7.24 (m, 3H), 7.15 (d,  $J$  = 7.2 Hz, 2H), 3.32 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.4, 140.8, 133.2, 129.9, 129.2, 128.2, 127.0, 126.0, 124.0, 34.4. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{14}\text{H}_{11}\text{NNa}$ :  $[\text{M}+\text{Na}]^+$  216.0784. Found: 216.0786.



**2g:** Yield 92% (38.0 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (dd,  $J$  = 2.4, 8.0 Hz, 2H), 7.35-7.33 (m, 2H), 7.27-7.22 (m, 3H), 7.15-7.12 (m, 2H), 3.29 (s, 1H), 2.44 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.8, 144.0, 141.0, 129.9, 129.9, 128.2, 126.9, 126.0, 121.1, 34.1, 21.8. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{15}\text{H}_{13}\text{NNa}$ :  $[\text{M}+\text{Na}]^+$  230.0940. Found: 230.0951.

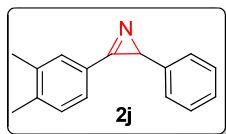


**2h:** Yield 81% (35.7 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J$  = 7.6 Hz, 1H), 7.27 (t,  $J$  = 6.4 Hz, 2H), 7.22 (d,  $J$  = 6.8 Hz, 1H), 7.17 (s, 1H), 7.14-7.11 (m, 3H), 3.18 (s, 1H), 2.66 (s, 3H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.0, 143.5, 141.4, 141.1, 131.9, 131.8, 128.2, 127.0, 126.8, 125.9, 119.6, 32.5, 21.7, 19.8. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{16}\text{H}_{15}\text{NNa}$ :  $[\text{M}+\text{Na}]^+$  244.1097. Found: 244.1102.

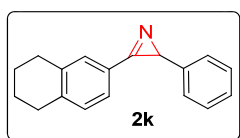


**2i:** Yield 89% (39.4 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (s, 1H), 7.30-7.23 (m, 5H), 7.14 (d,  $J$  = 7.6 Hz, 2H), 3.20 (s, 1H), 2.64 (s, 3H), 2.34 (s, 3H).

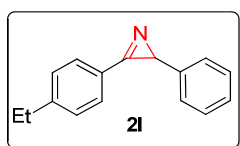
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5, 141.4, 138.1, 135.9, 133.6, 132.1, 130.9, 128.2, 126.8, 125.9, 122.1, 32.7, 20.6, 19.4. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{16}\text{H}_{15}\text{NNa}$ :  $[\text{M}+\text{Na}]^+$  244.1097. Found: 244.1107.



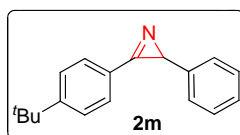
**2j**: Yield 87% (38.5 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (s, 1H), 7.64 (d,  $J = 8.0$  Hz, 1H), 7.31-7.22 (m, 4H), 7.14 (d,  $J = 6.8$  Hz, 2H), 3.28 (s, 1H), 2.34 (s, 3H), 2.32 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.8, 142.8, 141.1, 137.8, 130.8, 130.5, 128.2, 127.5, 126.9, 126.0, 121.4, 34.1, 20.2, 19.6. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{16}\text{H}_{15}\text{NNa}$ :  $[\text{M}+\text{Na}]^+$  244.1097. Found: 244.1100.



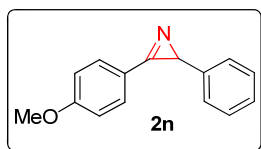
**2k**: Yield 87% (43.0 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (dd,  $J = 1.6, 8.0$  Hz, 1H), 7.59 (s, 1H), 7.29-7.22 (m, 4H), 7.15-7.13 (m, 2H), 3.27 (s, 1H), 2.84-2.80 (m, 4H), 1.83-1.80 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 143.4, 141.2, 138.3, 130.7, 130.0, 128.2, 126.8, 126.7, 126.0, 121.0, 34.1, 29.8, 29.1, 22.7, 22.7. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{18}\text{H}_{17}\text{NNa}$ :  $[\text{M}+\text{Na}]^+$  270.1253. Found: 270.1263.



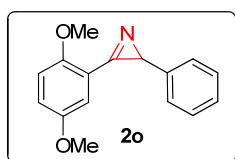
**2l**: Yield 90% (39.6 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 8.0$  Hz, 2H), 7.37 (d,  $J = 8.0$  Hz, 2H), 7.27-7.22 (m, 3H), 7.15 (d,  $J = 6.8$  Hz, 2H), 3.29 (s, 1H), 2.74 (q,  $J = 7.6$  Hz, 2H), 1.28 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 150.2, 141.0, 130.0, 128.8, 128.2, 126.9, 126.0, 121.4, 34.2, 29.1, 15.2. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{16}\text{H}_{15}\text{NNa}$ :  $[\text{M}+\text{Na}]^+$  244.1097. Found: 244.1002.



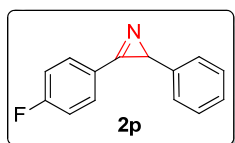
**2m**: Yield 86% (42.8 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 8.4$  Hz, 2H), 7.56 (d,  $J = 8.4$  Hz, 2H), 7.27-7.24 (m, 3H), 7.16-7.14 (m, 2H), 3.29 (s, 1H), 1.36 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.8, 157.0, 141.0, 129.7, 128.2, 126.9, 126.2, 126.0, 121.1, 35.3, 34.1, 31.0. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{18}\text{H}_{19}\text{NNa}$ :  $[\text{M}+\text{Na}]^+ 272.1410$ . Found: 272.1420.



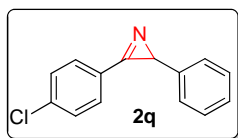
**2n**: Yield 85% (37.9 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 8.8$  Hz, 2H), 7.27-7.22 (m, 3H), 7.15-7.13 (m, 2H), 7.04 (d,  $J = 8.4$  Hz, 2H), 3.88 (s, 3H), 3.27 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.4, 162.0, 141.2, 131.8, 128.2, 126.8, 126.0, 116.3, 114.7, 55.5, 34.0. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{15}\text{H}_{13}\text{NONa}$ :  $[\text{M}+\text{Na}]^+ 246.0889$ . Found: 246.0900.



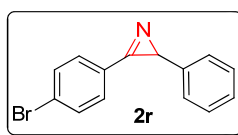
**2o**: Yield 85% (43.0 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29-7.25 (m, 2H), 7.23-7.21 (m, 1H), 7.18-7.14 (m, 2H), 7.10 (dd,  $J = 3.2, 9.2$  Hz, 1H), 6.97 (d,  $J = 9.2$  Hz, 1H), 3.89 (s, 3H), 3.76 (s, 3H), 3.19 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.6, 154.2, 153.4, 141.3, 128.0, 126.7, 126.0, 120.7, 116.1, 113.0, 112.7, 56.3, 55.9, 32.5. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{16}\text{H}_{15}\text{NO}_2\text{Na}$ :  $[\text{M}+\text{Na}]^+ 276.0995$ . Found: 276.1004.



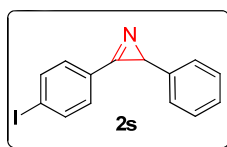
**2p**: Yield 75% (31.5 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (dd,  $J = 5.6, 8.8$  Hz, 2H), 7.30-7.22 (m, 5H), 7.14 (dd,  $J = 1.6, 8.0$  Hz, 2H), 3.33 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6 (d,  $J_{\text{CF}} = 253.9$  Hz), 162.5, 140.5, 132.2 (d,  $J_{\text{CF}} = 9.2$  Hz), 128.3, 127.2, 126.0, 120.4, 116.7 (d,  $J_{\text{CF}} = 22.3$  Hz), 34.5. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{14}\text{H}_{10}\text{FNNa}$ :  $[\text{M}+\text{Na}]^+ 234.0689$ . Found: 234.0698.



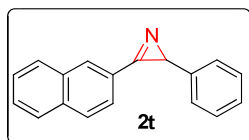
**2q:** Yield 70% (31.8 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 8.4$  Hz, 2H), 7.53 (d,  $J = 8.4$  Hz, 2H), 7.29-7.24 (m, 3H), 7.14-7.12 (m, 2H), 3.33 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.8, 140.4, 139.5, 131.0, 129.7, 128.3, 127.2, 126.0, 122.5, 34.6. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{14}\text{H}_{10}\text{ClNNa}$ :  $[\text{M}+\text{Na}]^+$  250.0394. Found: 250.0401.



**2r:** Yield 72% (39.0 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (d,  $J = 8.0$  Hz, 2H), 7.70 (d,  $J = 8.0$  Hz, 2H), 7.29-7.25 (m, 3H), 7.13 (d,  $J = 7.2$  Hz, 2H), 3.34 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.0, 140.3, 132.7, 131.1, 128.3, 128.1, 127.2, 126.0, 122.9, 34.6. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{14}\text{H}_{10}\text{BrNNa}$ :  $[\text{M}+\text{Na}]^+$  293.9889. Found: 293.9891.

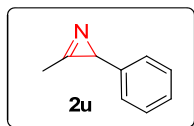


**2s:** Yield 61% (38.7 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J = 8.4$  Hz, 2H), 7.61 (d,  $J = 8.4$  Hz, 2H), 7.28-7.25 (m, 3H), 7.12 (dd,  $J = 1.6, 8.0$  Hz, 2H), 3.33 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.2, 140.3, 138.6, 131.0, 128.3, 127.2, 126.0, 123.4, 100.7, 34.6. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{14}\text{H}_{10}\text{INNa}$ :  $[\text{M}+\text{Na}]^+$  341.9750. Found: 341.9751.

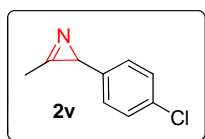


**2t:** Yield 92% (44.6 mg); White solid; mp 76-77  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (s, 1H), 8.05 (d,  $J = 8.4$  Hz, 1H), 8.00 (d,  $J = 8.4$  Hz, 1H), 7.90 (d,  $J = 8.0$  Hz, 2H), 7.61 (t,  $J = 7.2$  Hz, 1H), 7.55 (t,  $J = 7.6$  Hz, 1H), 7.30-7.24 (m, 3H), 7.21-7.19

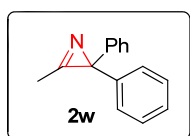
(m, 2H), 3.41 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.4, 140.8, 135.5, 132.8, 132.1, 129.3, 129.0, 128.6, 128.3, 128.0, 127.1, 127.1, 126.1, 124.5, 121.3, 34.6. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{18}\text{H}_{13}\text{NNa}$ :  $[\text{M}+\text{Na}]^+$  266.0940. Found: 266.0949.



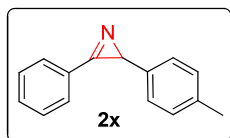
**2u**: Yield 70% (18.4 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (t,  $J = 7.6$  Hz, 2H), 7.16 (t,  $J = 7.6$  Hz, 1H), 6.99 (d,  $J = 7.2$  Hz, 2H), 2.82 (s, 1H), 2.45 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 141.1, 128.2, 126.8, 125.5, 33.3, 12.8. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_9\text{H}_{10}\text{N}$ :  $[\text{M}+\text{H}]^+$  132.0808. Found: 132.0806.



**2v**: Yield 63% (20.7 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18 (d,  $J = 8.0$  Hz, 2H), 6.91 (d,  $J = 8.0$  Hz, 2H), 2.78 (s, 1H), 2.44 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 139.7, 132.4, 128.3, 126.8, 32.7, 12.8. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_9\text{H}_9\text{ClN}$ :  $[\text{M}+\text{H}]^+$  166.0418. Found: 166.0423.



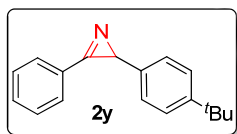
**2w**: Yield 84% (34.8 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (d,  $J = 7.6$  Hz, 4H), 7.18 (d,  $J = 7.2$  Hz, 2H), 7.13 (d,  $J = 7.2$  Hz, 4H), 2.49 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4, 141.7, 128.3, 127.8, 126.9, 42.7, 12.8. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{15}\text{H}_{13}\text{NNa}$ :  $[\text{M}+\text{Na}]^+$  230.0940. Found: 230.0947.



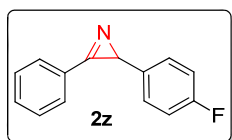
**2x**: Yield 83% (34.5 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91-7.88 (m, 2H), 7.59-7.51 (m, 3H), 7.10-7.03 (m, 4H), 3.30 (s, 1H), 2.31 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.7, 137.8, 136.7, 133.0, 129.8, 129.2, 128.9, 126.0, 124.2, 34.3,



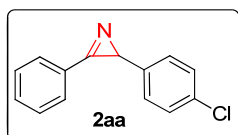
21.1. HRMS Calcd (ESI)  $m/z$  for  $C_{15}H_{13}NNa$ :  $[M+Na]^+$  230.0940. Found: 230.0945.



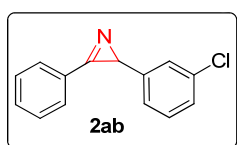
**2y**: Yield 87% (43.1 mg); Colourless oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.84 (d,  $J = 8.4$  Hz, 2H), 7.56 (d,  $J = 8.4$  Hz, 2H), 7.27-7.22 (m, 3H), 7.16-7.14 (m, 2H), 3.29 (s, 1H), 1.36 (s, 9H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  162.9, 157.0, 141.0, 129.7, 128.2, 126.9, 126.2, 126.1, 121.1, 35.3, 34.1, 31.1. HRMS Calcd (ESI)  $m/z$  for  $C_{18}H_{19}NNa$ :  $[M+Na]^+$  272.1410. Found: 272.1418.



**2z**: Yield 73% (30.7 mg); Colourless oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.90 (d,  $J = 7.2$  Hz, 2H), 7.62 (t,  $J = 7.2$  Hz, 1H), 7.56 (t,  $J = 7.2$  Hz, 2H), 7.11 (t,  $J = 8.4$  Hz, 2H), 6.97 (t,  $J = 8.4$  Hz, 2H), 3.31 (s, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  163.5 (d,  $J = 25.2$  Hz), 160.9, 136.5, 133.3, 129.8, 129.3, 127.5 (d,  $J = 8.2$  Hz), 123.8, 115.2 (d,  $J = 21.6$  Hz), 33.8. HRMS Calcd (ESI)  $m/z$  for  $C_{14}H_{10}FNNa$ :  $[M+Na]^+$  234.0689. Found: 234.0693.

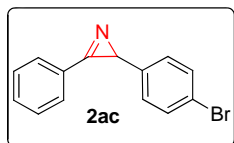


**2aa**: Yield 80% (36.2 mg); Colourless oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.88 (d,  $J = 6.8$  Hz, 2H), 7.61-7.53 (m, 3H), 7.24 (d,  $J = 8.0$  Hz, 2H), 7.07 (d,  $J = 8.0$  Hz, 2H), 3.29 (s, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  163.2, 139.4, 133.3, 132.7, 129.9, 129.3, 128.4, 127.3, 123.6, 33.7. HRMS Calcd (ESI)  $m/z$  for  $C_{14}H_{10}ClNNa$ :  $[M+Na]^+$  250.0394. Found: 250.0403.

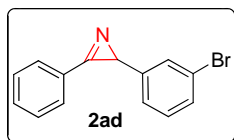


**2ab**: Yield 84% (38.0 mg); Colourless oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.80 (d,  $J =$

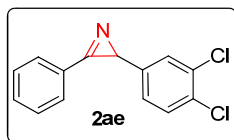
7.2 Hz, 2H), 7.54-7.44 (m, 3H), 7.10 (s, 2H), 7.02 (s, 1H), 6.95 (s, 1H), 3.18 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 143.0, 134.3, 133.4, 129.9, 129.5, 129.3, 127.1, 125.9, 124.2, 123.4, 33.7. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{14}\text{H}_{10}\text{ClNNa}$ :  $[\text{M}+\text{Na}]^+$  250.0394. Found: 250.0402.



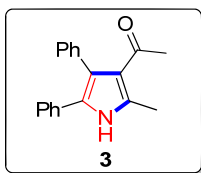
**2ac**: Yield 88% (47.6 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 7.2$  Hz, 2H), 7.61 (t,  $J = 7.2$  Hz, 1H), 7.55 (t,  $J = 7.2$  Hz, 2H), 7.39 (d,  $J = 8.0$  Hz, 2H), 7.02 (d,  $J = 8.0$  Hz, 2H), 3.28 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1, 139.9, 133.4, 131.3, 129.9, 129.3, 127.6, 123.5, 120.8, 33.8. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{14}\text{H}_{10}\text{BrNNa}$ :  $[\text{M}+\text{Na}]^+$  293.9889. Found: 293.9899.



**2ad**: Yield 82% (44.5 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 7.6$  Hz, 2H), 7.62-7.60 (m, 1H), 7.56 (t,  $J = 7.2$  Hz, 2H), 7.36 (d,  $J = 8.0$  Hz, 1H), 7.27 (s, 1H), 7.14 (t,  $J = 7.6$  Hz, 1H), 7.07 (d,  $J = 7.2$  Hz, 1H), 3.26 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 143.3, 133.4, 130.1, 130.0, 129.8, 129.3, 128.9, 124.6, 123.4, 122.6, 33.7. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{14}\text{H}_{10}\text{BrNNa}$ :  $[\text{M}+\text{Na}]^+$  293.9889. Found: 293.9903.

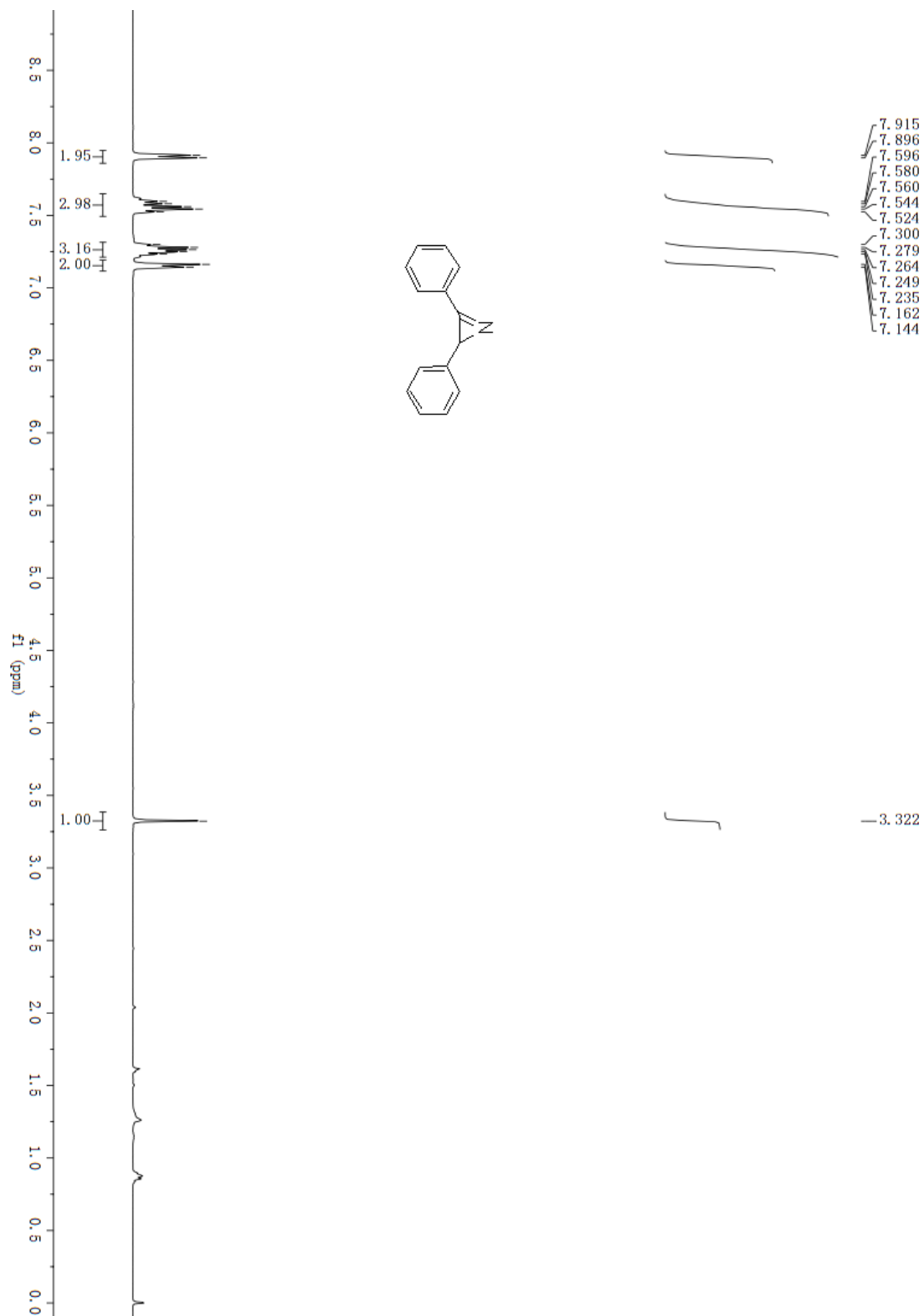
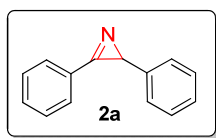


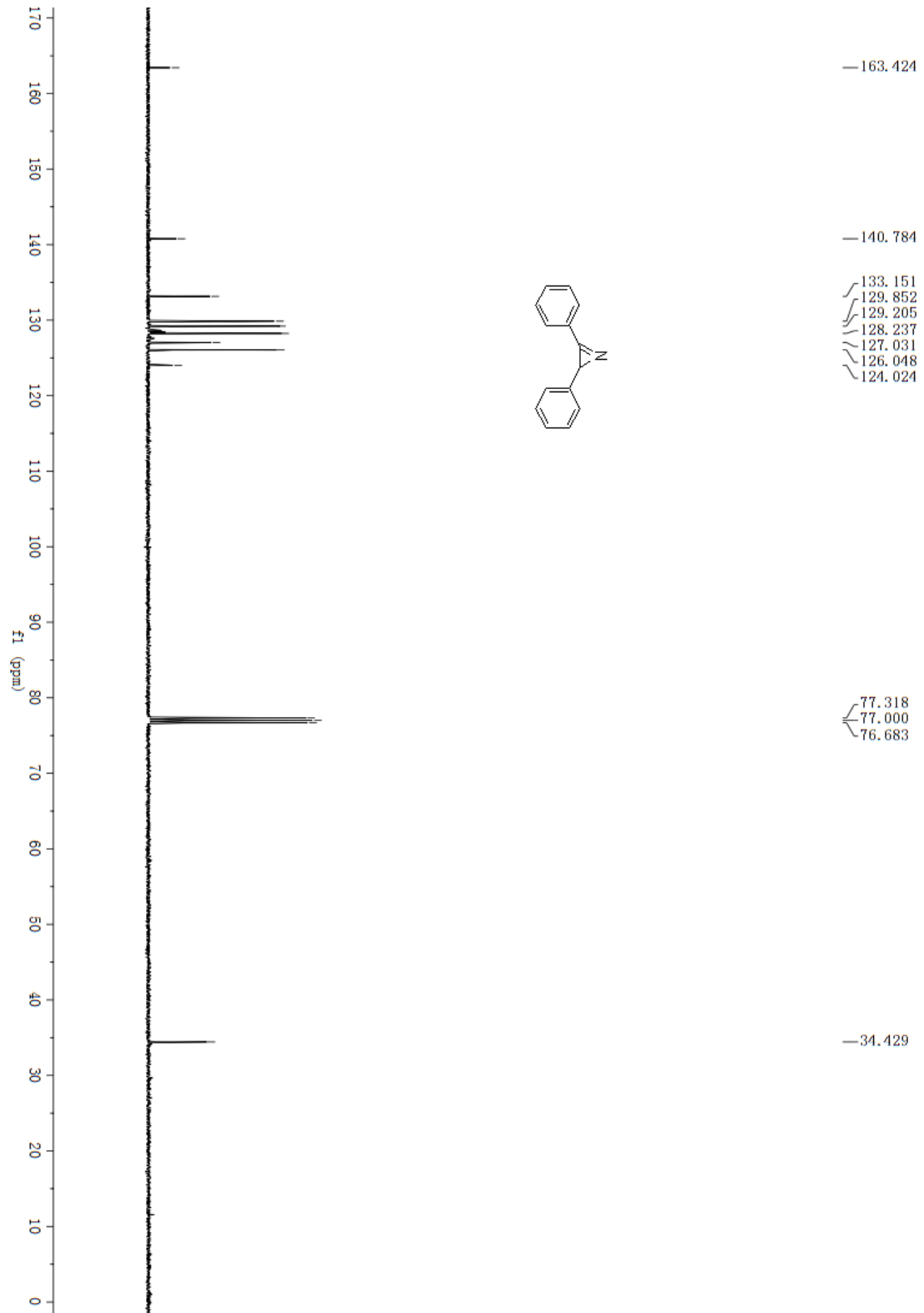
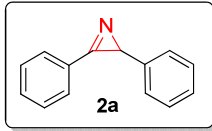
**2ae**: Yield 81% (42.2 mg); Colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 7.6$  Hz, 2H), 7.63 (t,  $J = 6.8$  Hz, 1H), 7.57 (t,  $J = 7.6$  Hz, 2H), 7.34 (d,  $J = 8.4$  Hz, 1H), 7.22 (s, 1H), 6.98 (d,  $J = 7.6$  Hz, 1H), 3.25 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.8, 141.4, 133.6, 132.5, 130.9, 130.2, 130.0, 129.4, 127.7, 125.2, 123.2, 33.2. HRMS Calcd (ESI)  $m/z$  for  $\text{C}_{14}\text{H}_9\text{Cl}_2\text{NNa}$ :  $[\text{M}+\text{Na}]^+$  284.0004. Found: 284.0011.

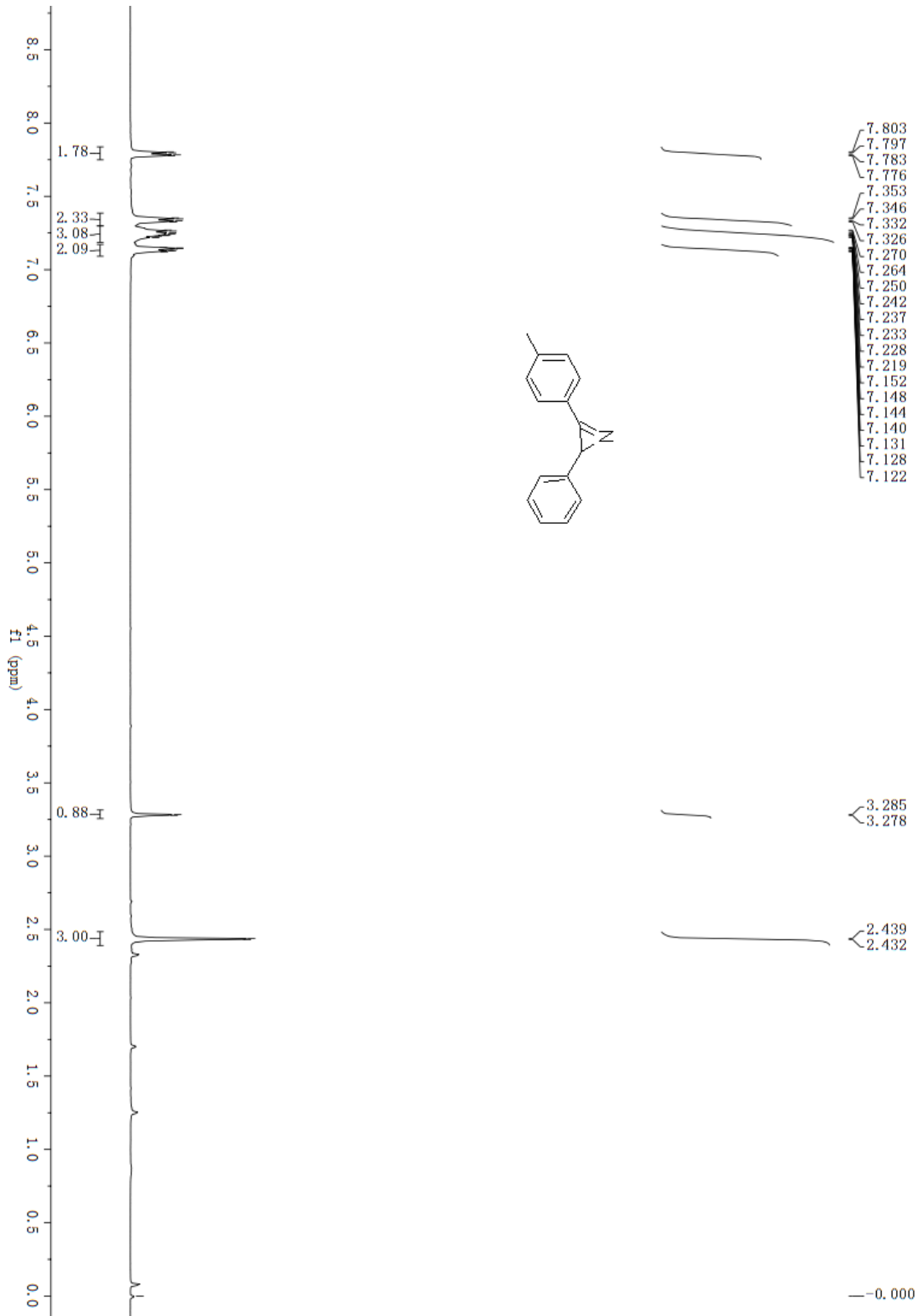
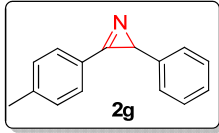


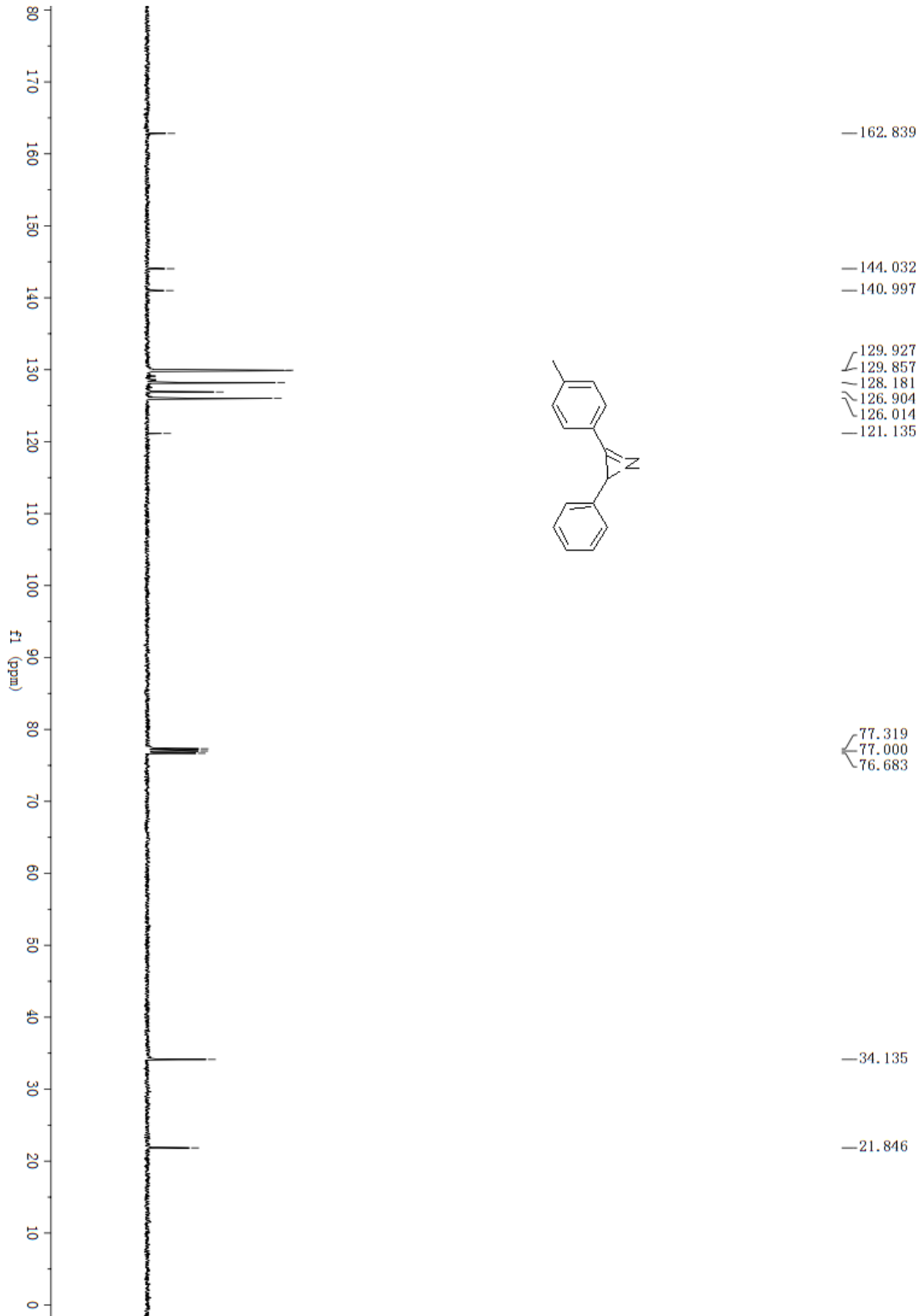
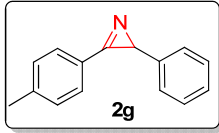
**3:** Yield 97% (53.6 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.89 (s, 1H), 7.35-7.31 (m, 3H), 7.29-7.27 (m, 2H), 7.20-7.14 (m, 3H), 7.13-7.10 (m, 2H), 2.59 (s, 3H), 1.87 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.3, 136.5, 135.3, 132.0, 130.8, 128.4, 127.0, 127.0, 126.6, 126.5, 122.8, 122.7, 30.8, 14.3.

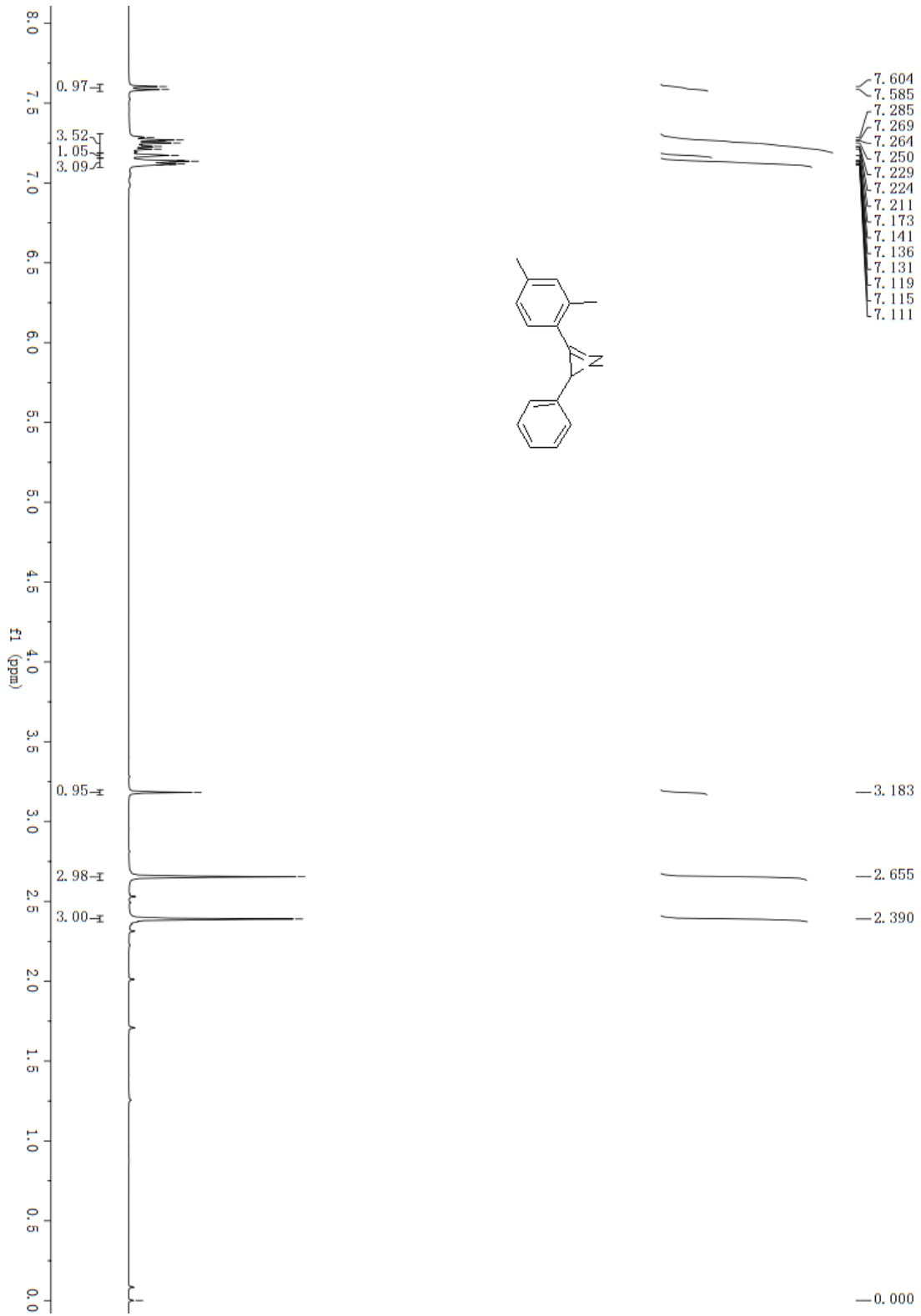
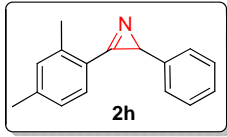
## 5. Appendix (Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra)



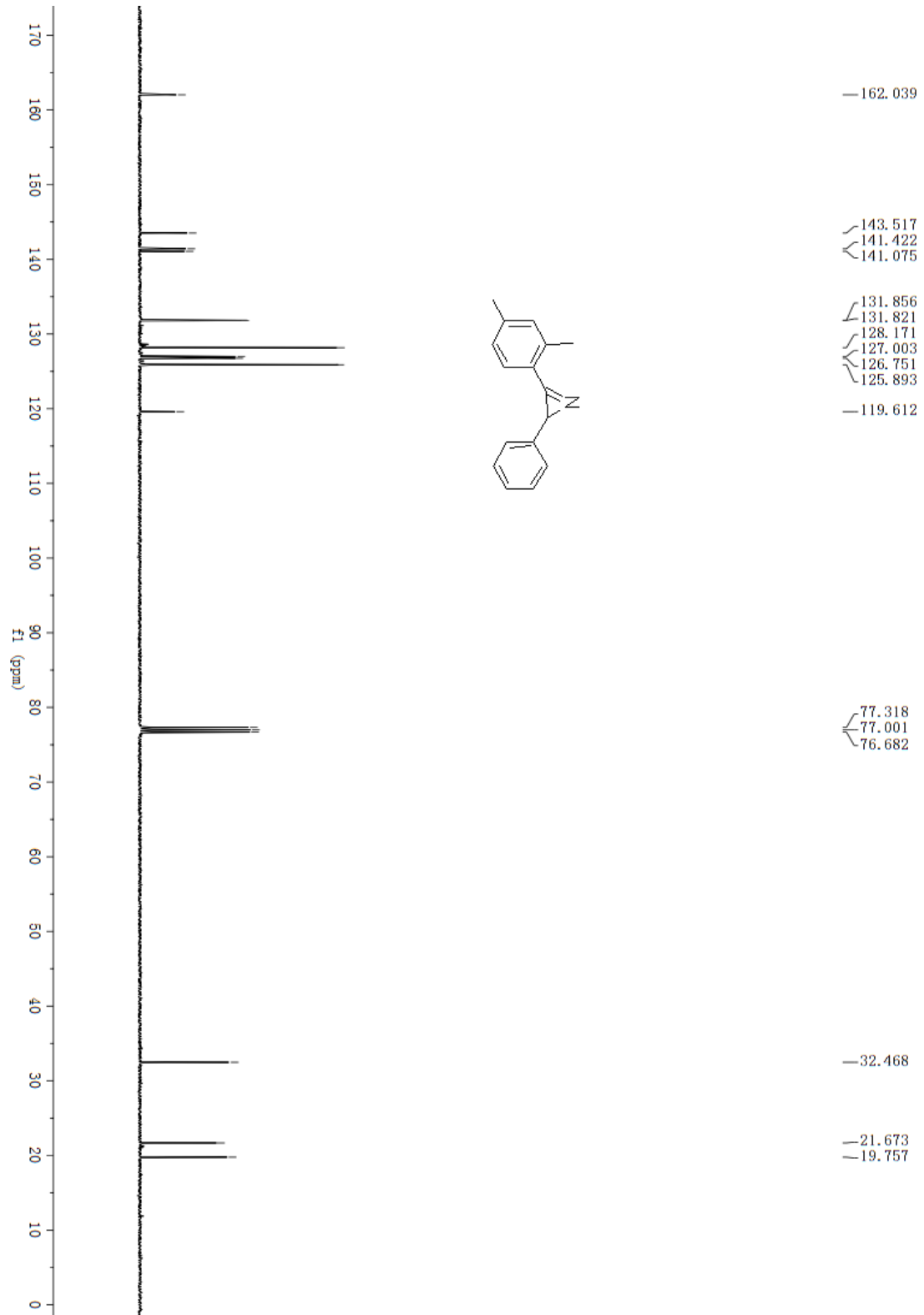
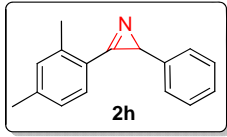


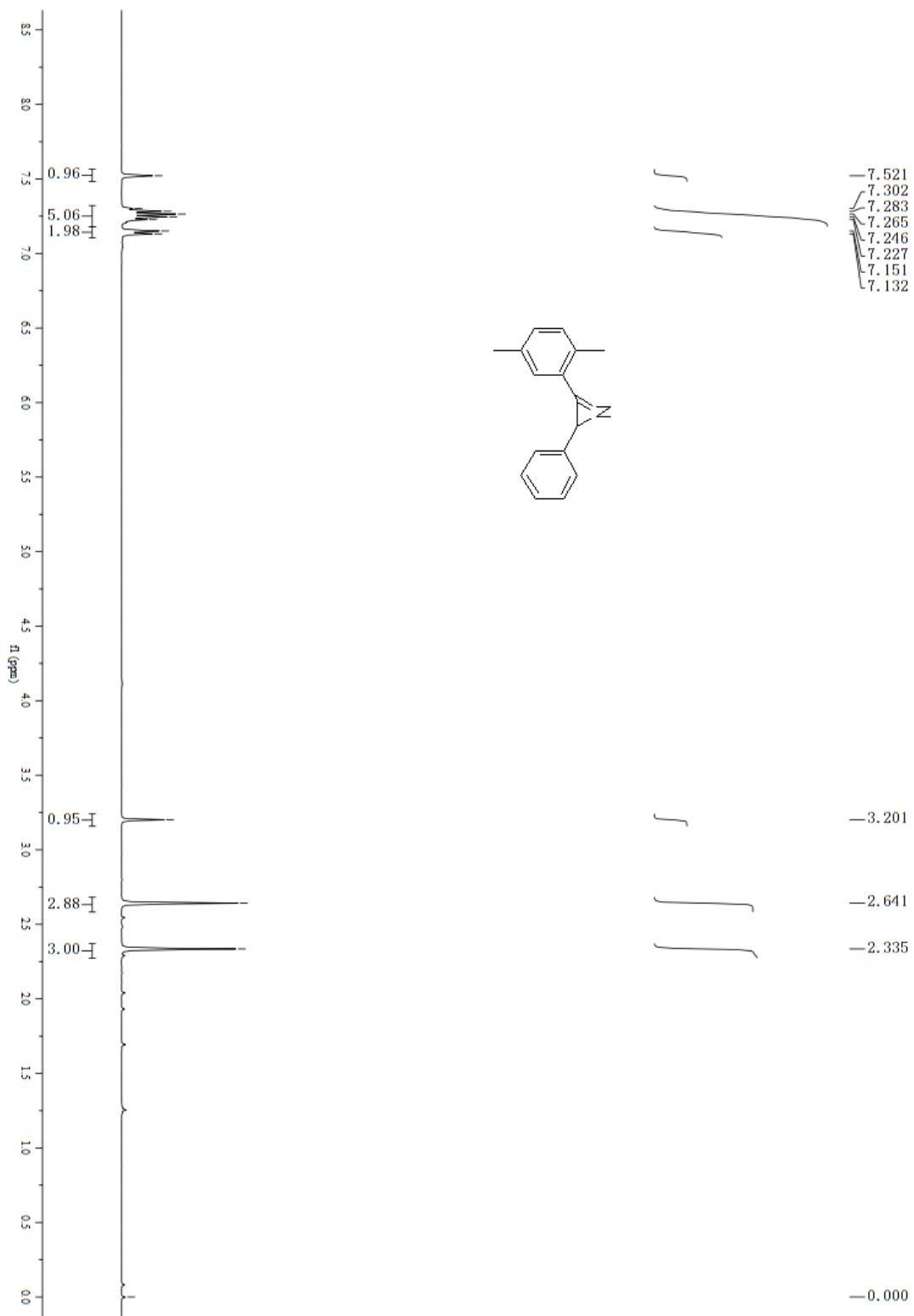
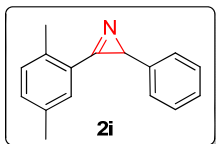


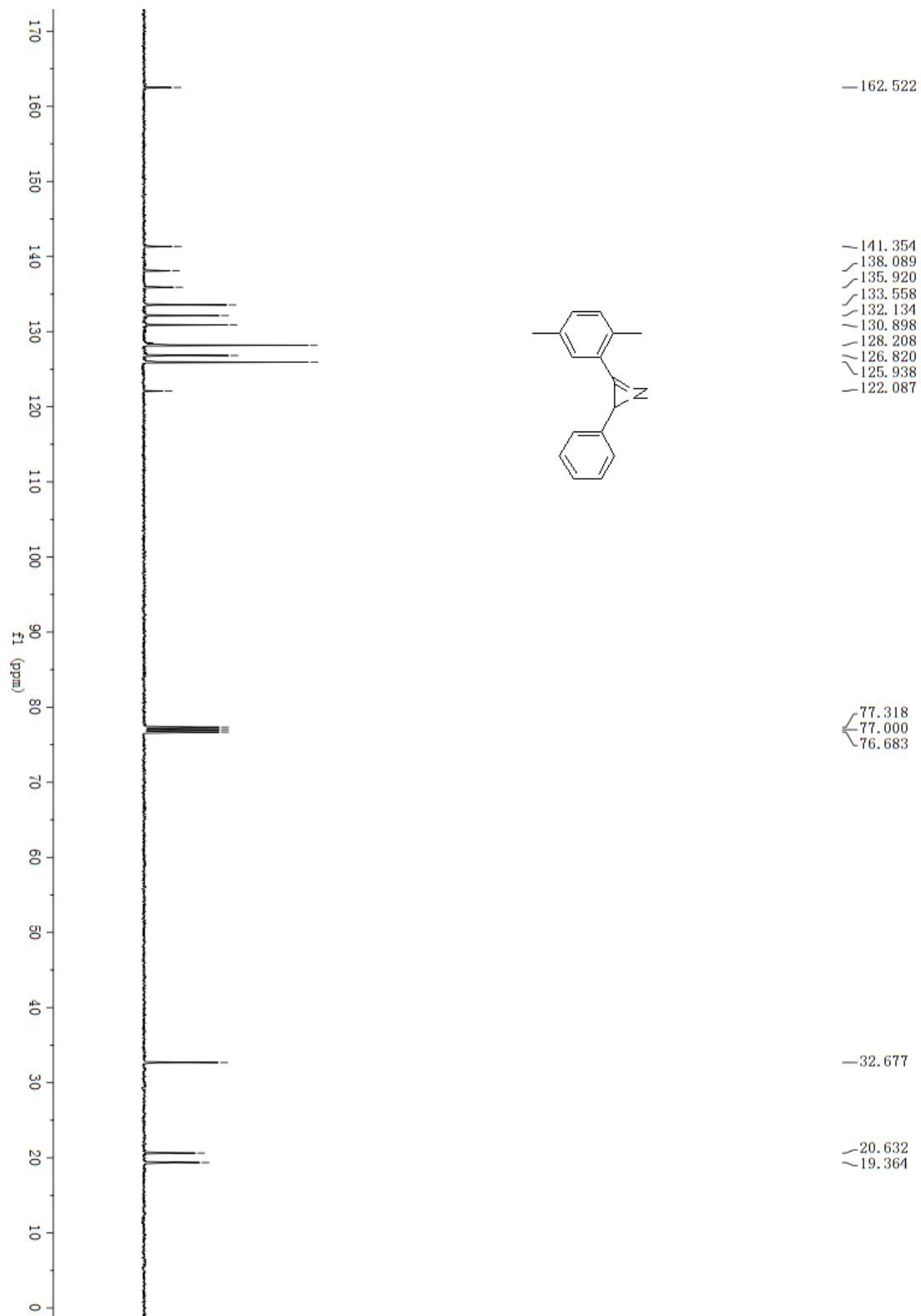
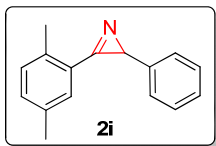


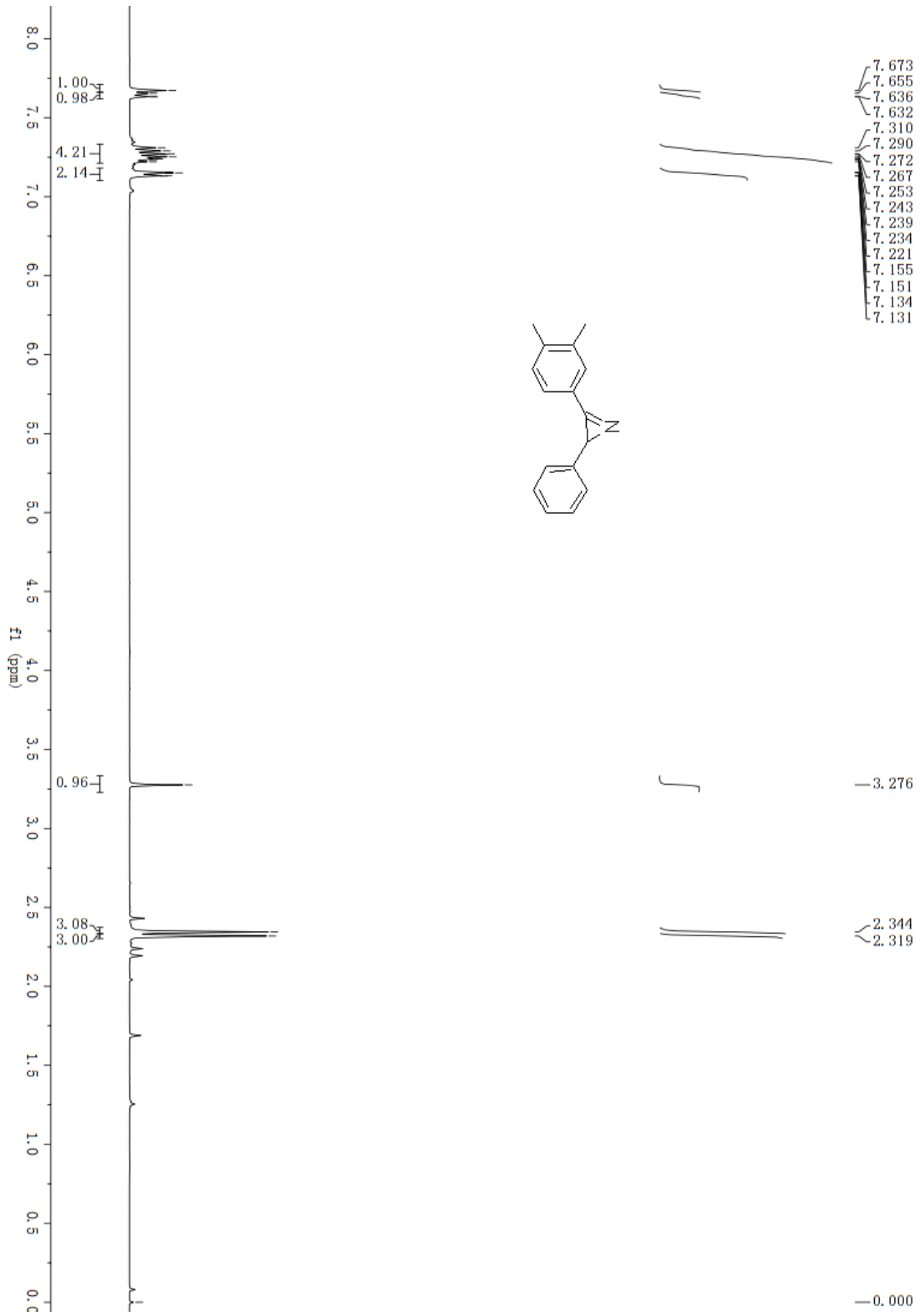
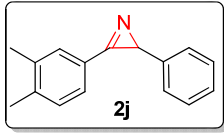


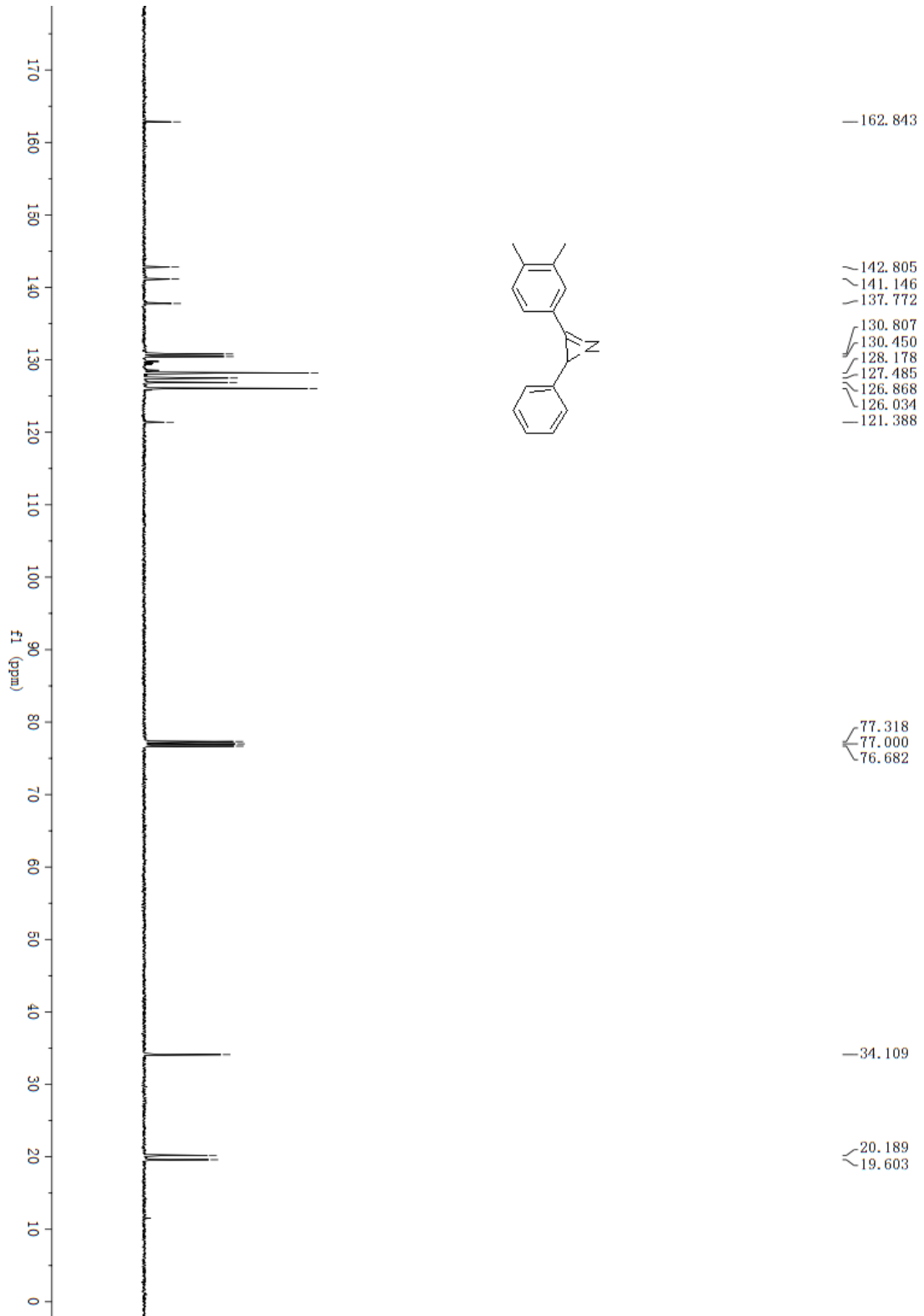
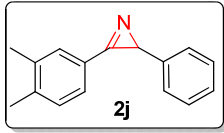


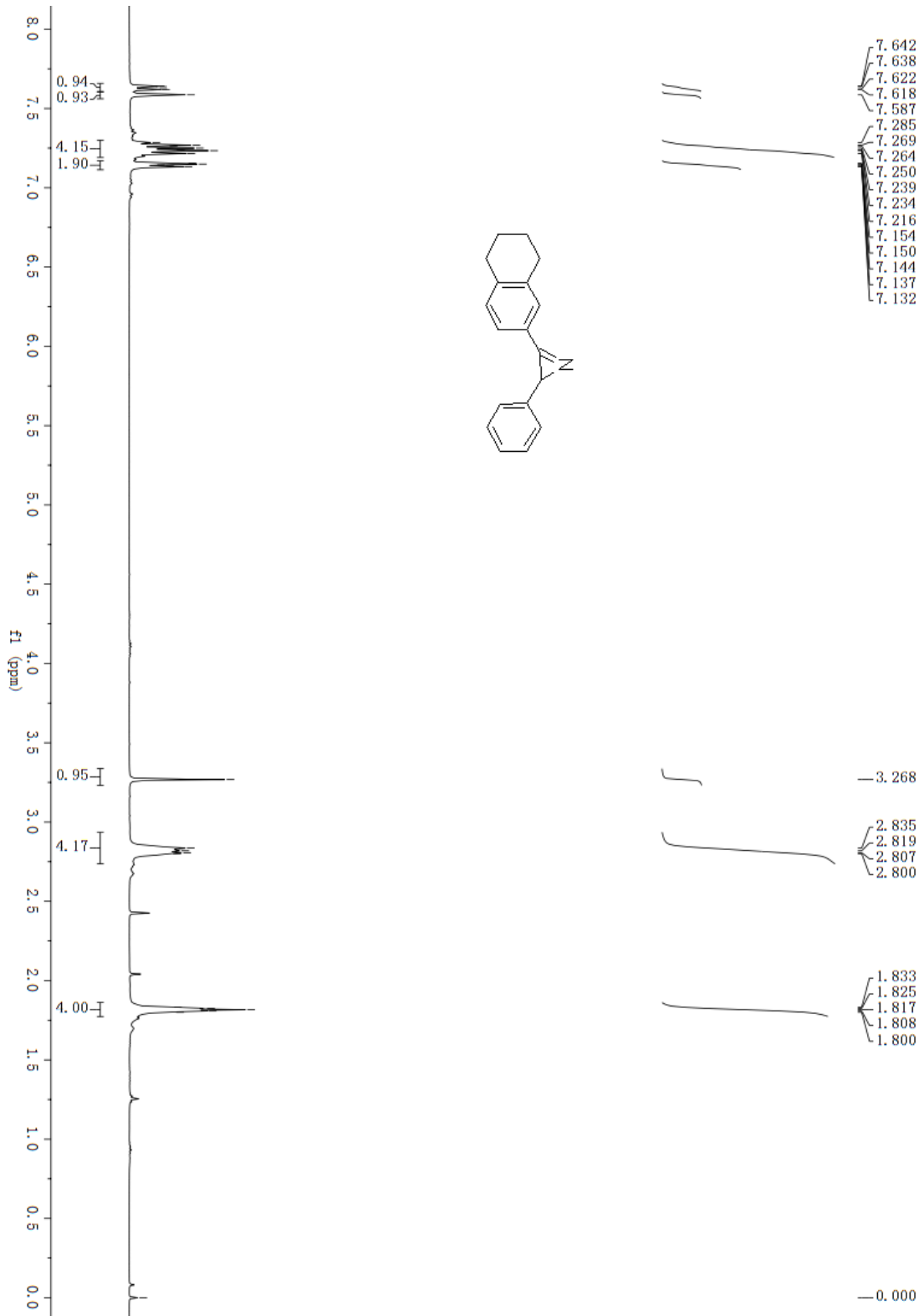
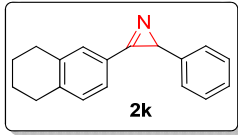


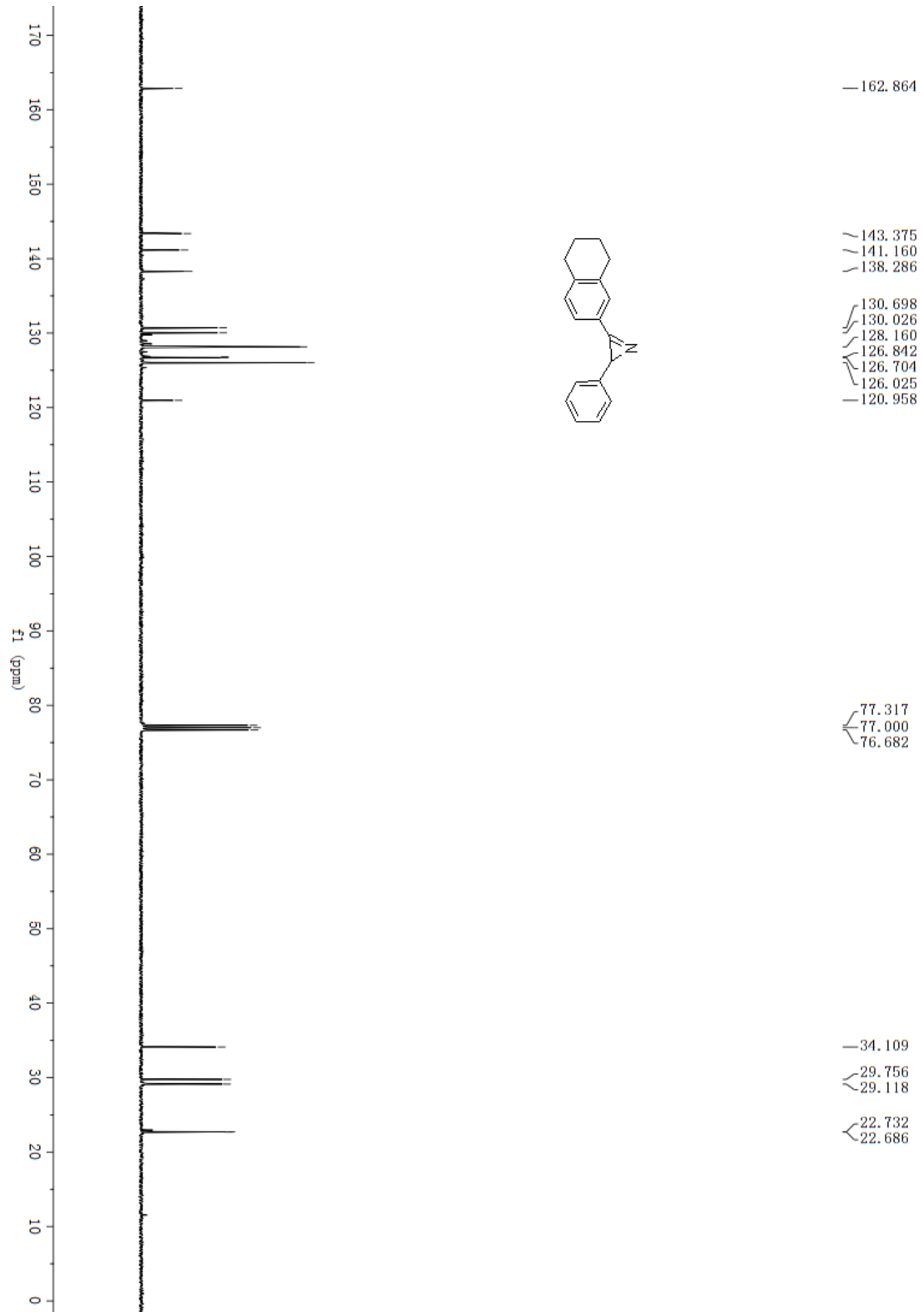
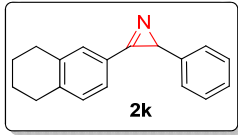


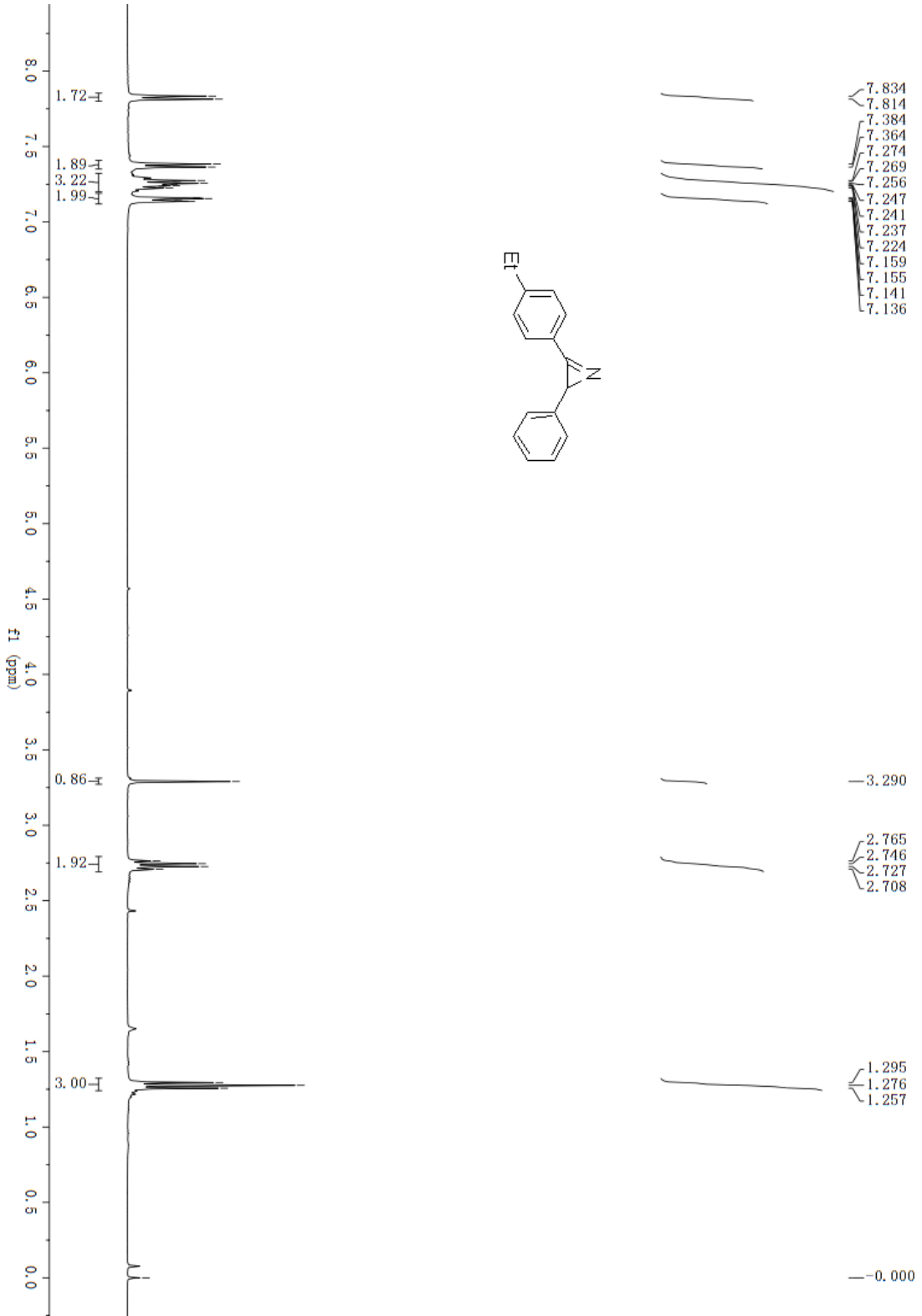
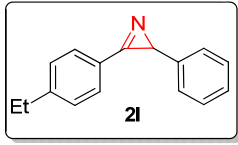




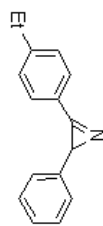
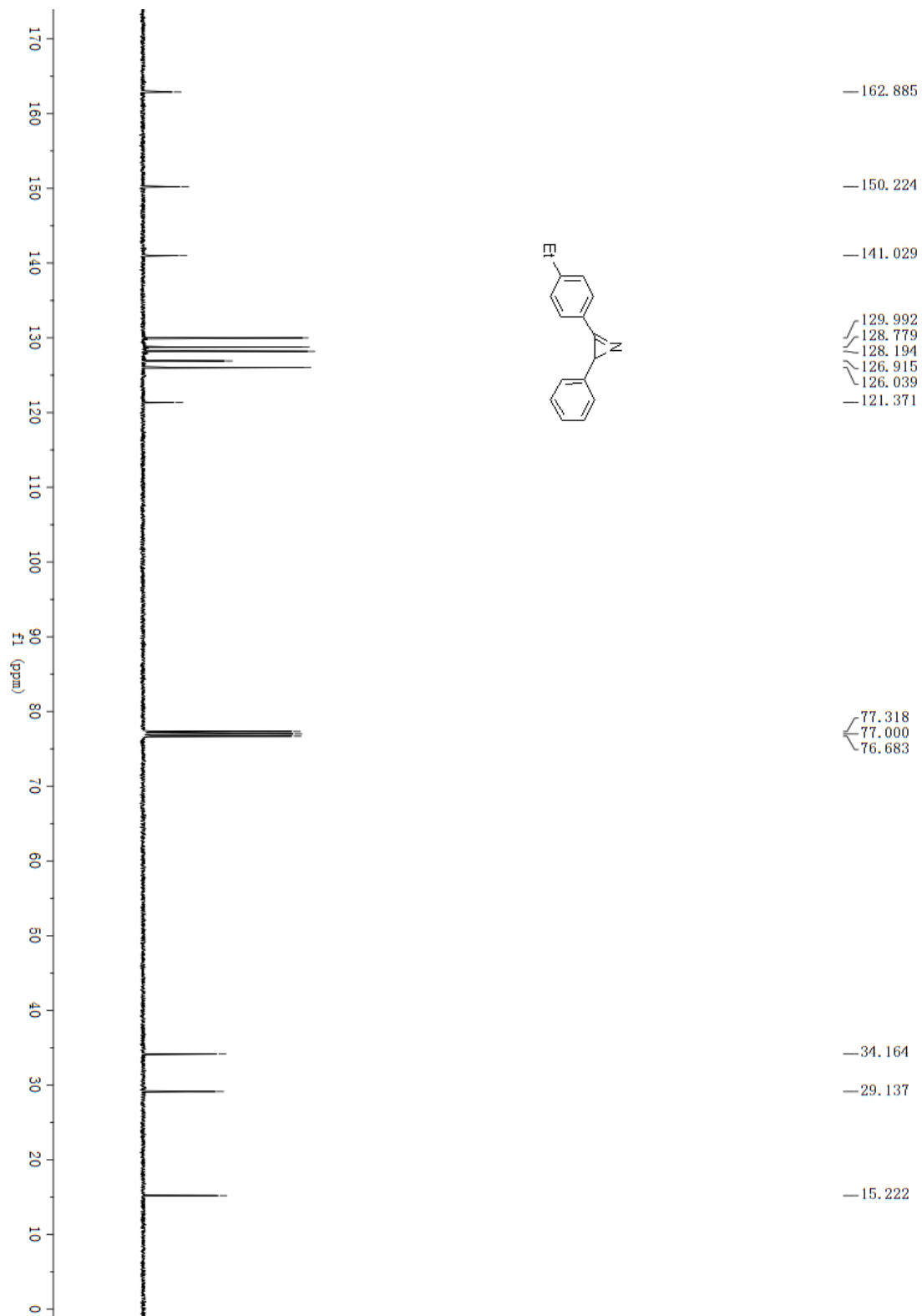
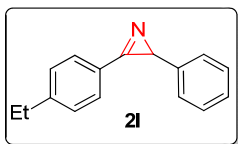


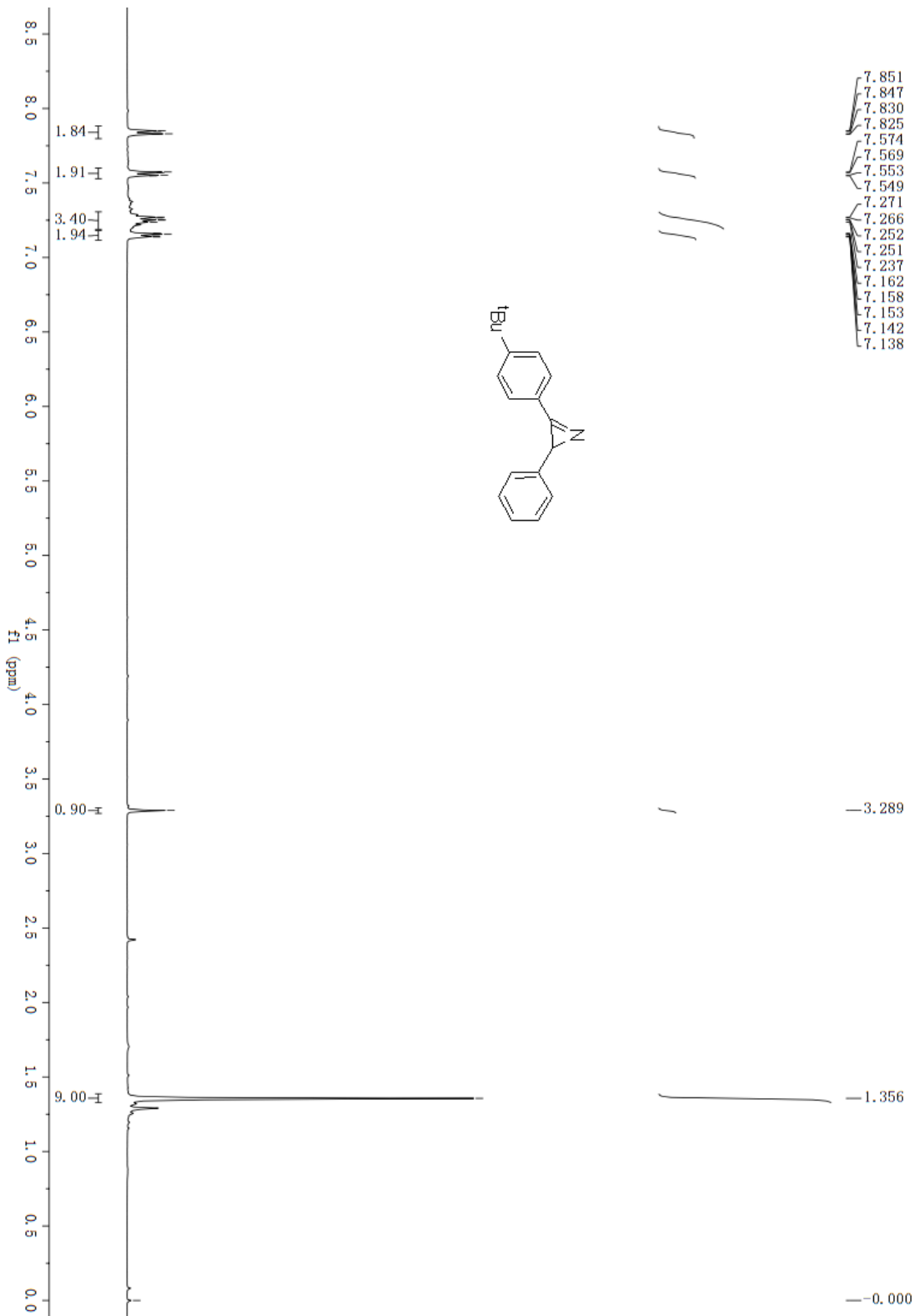
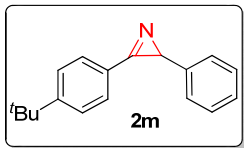


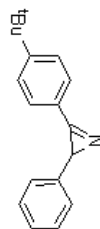
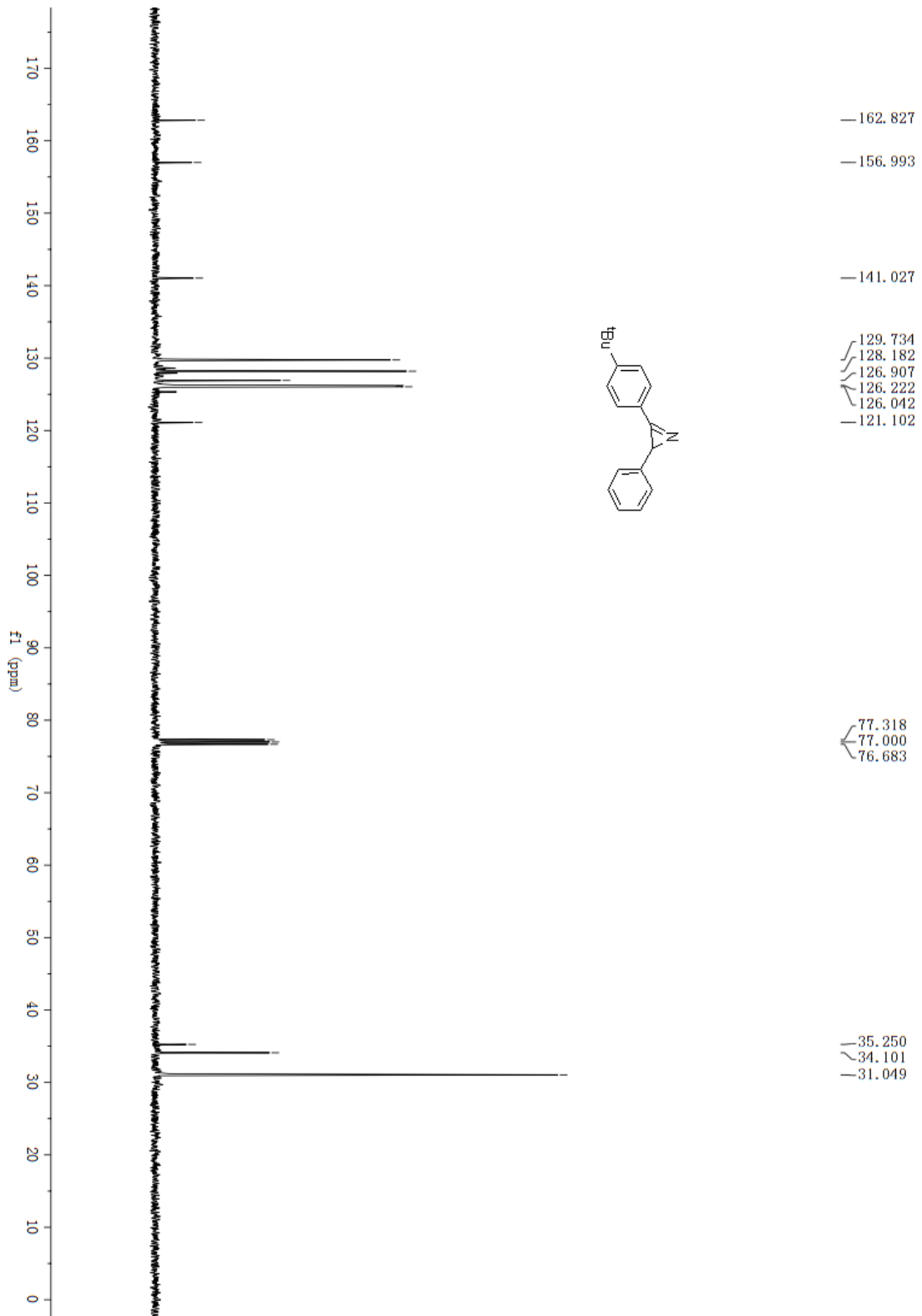
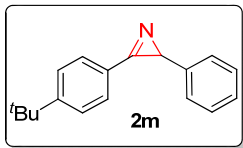


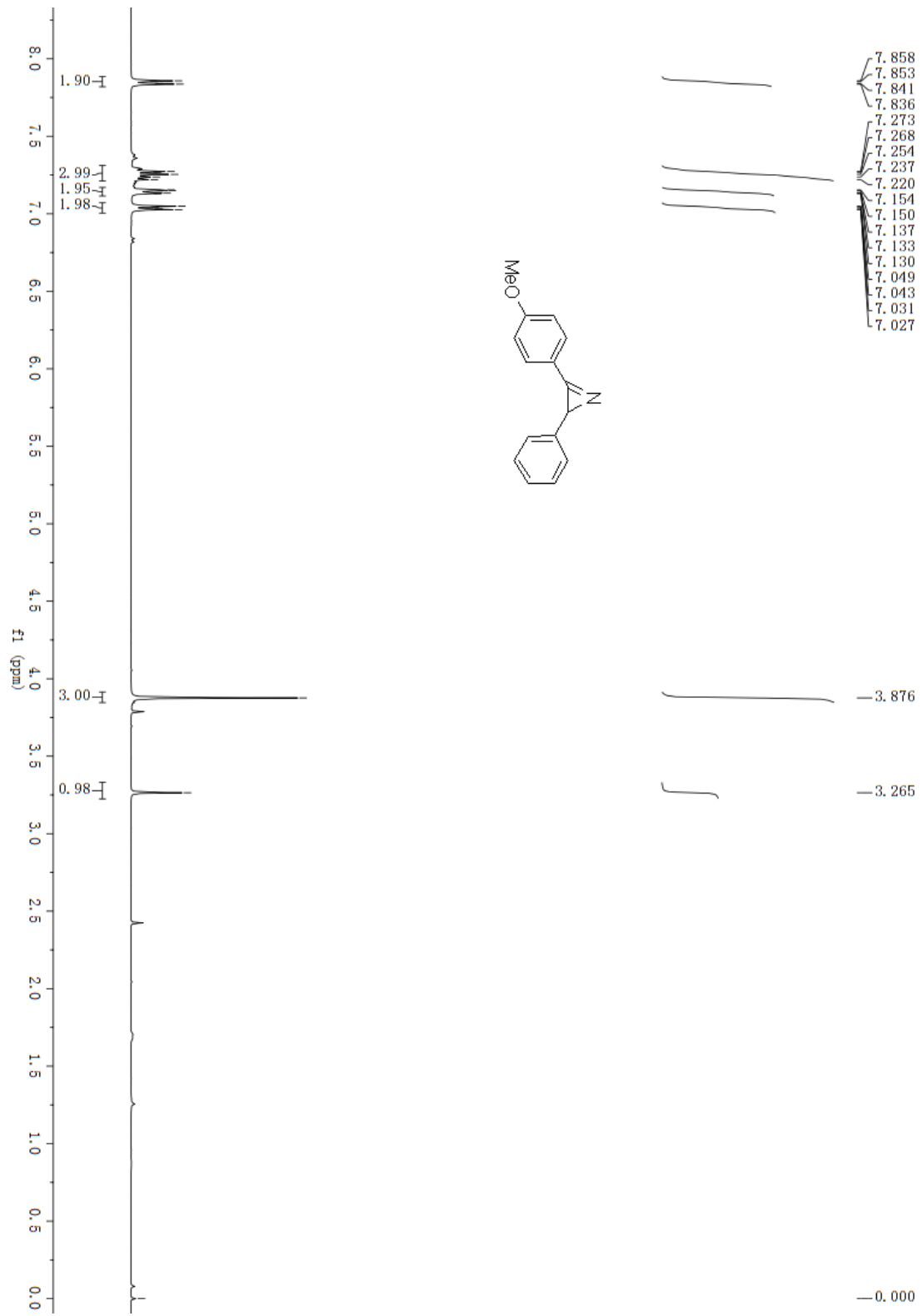
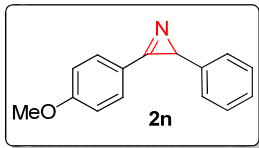


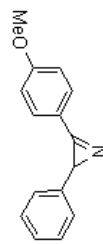
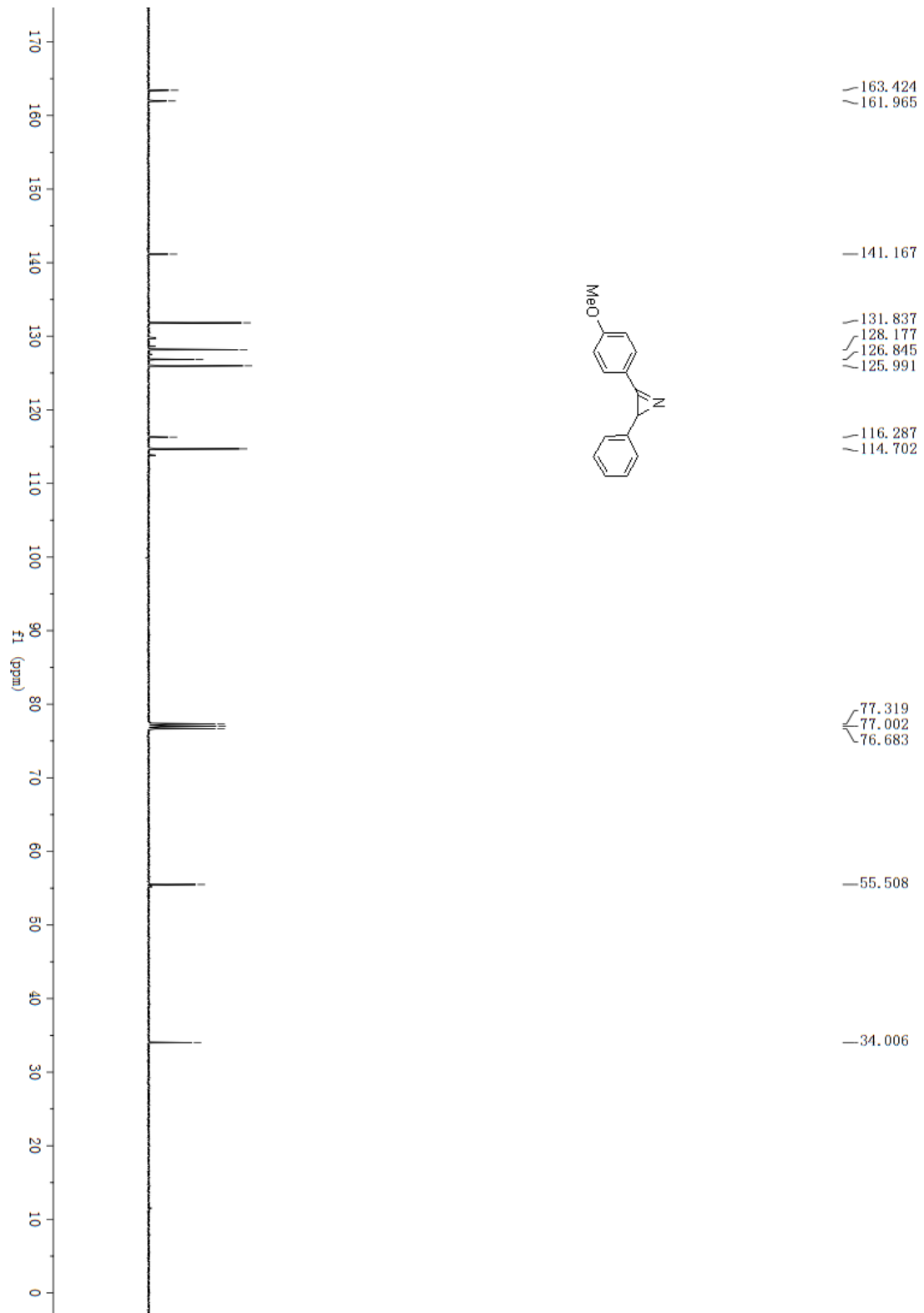
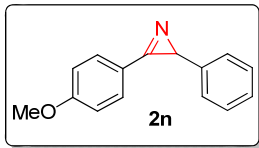


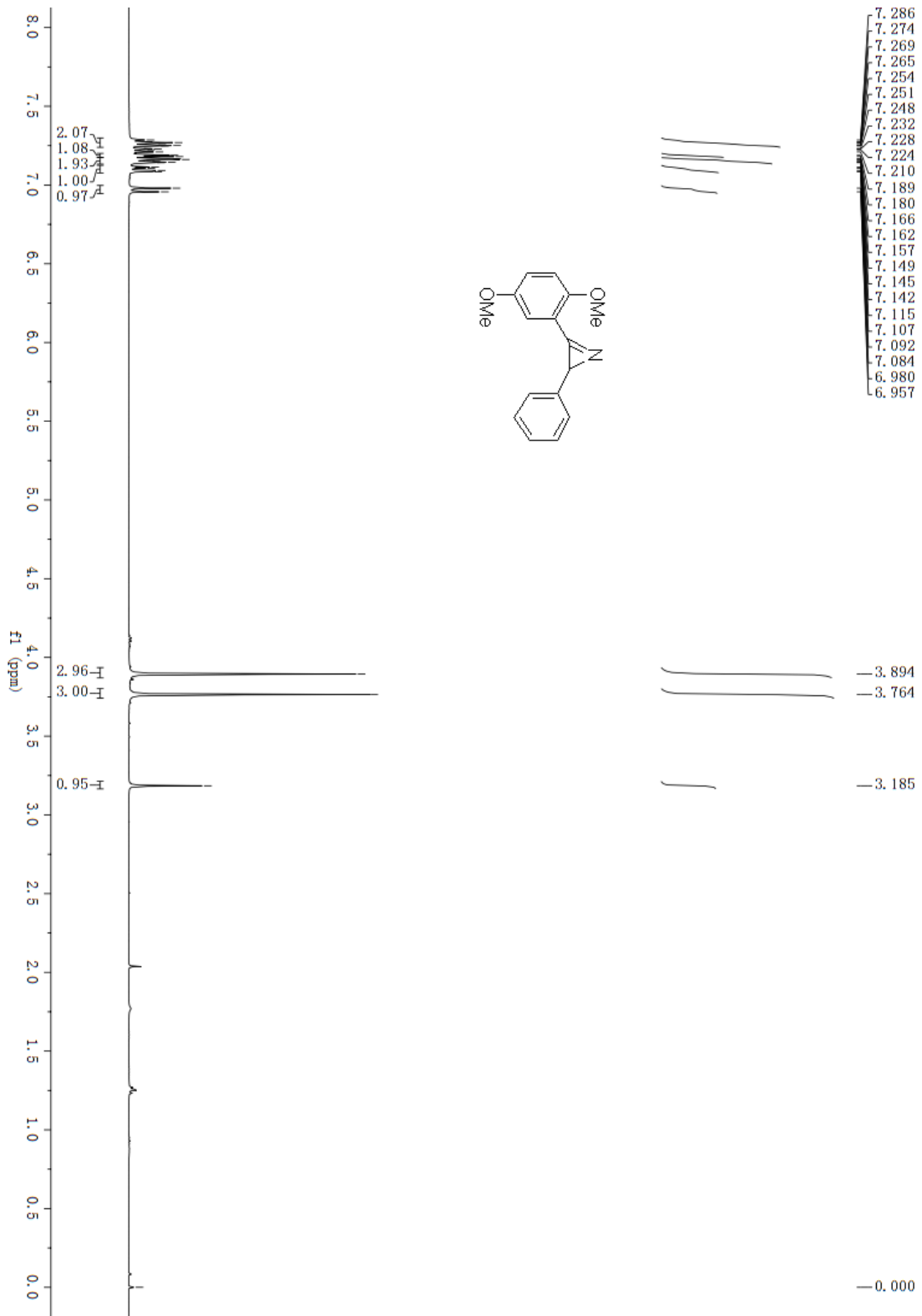
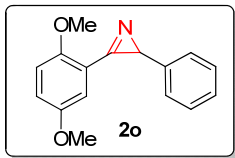


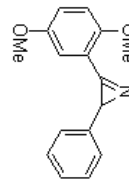
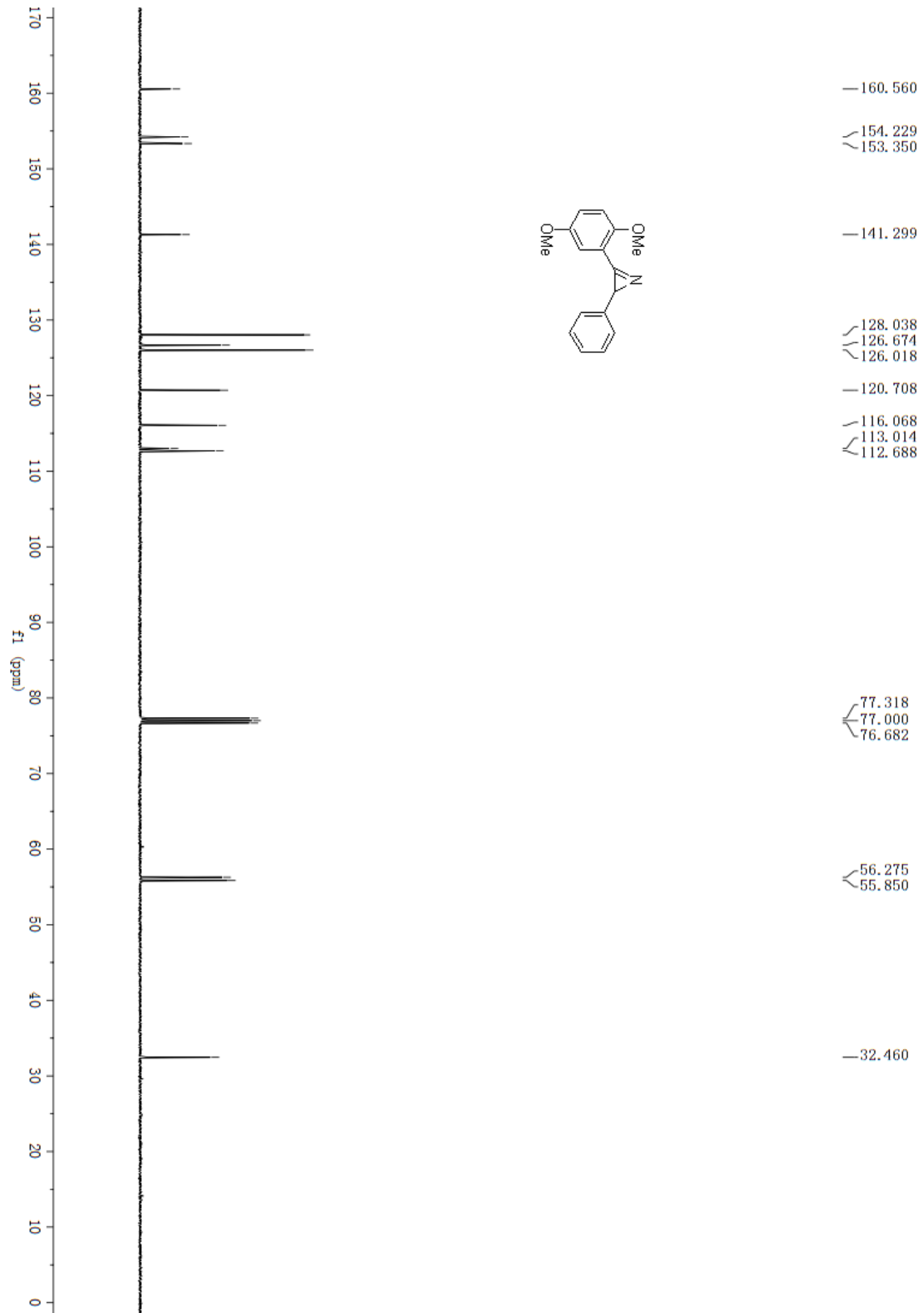
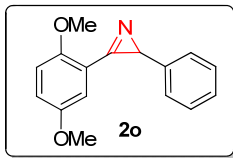


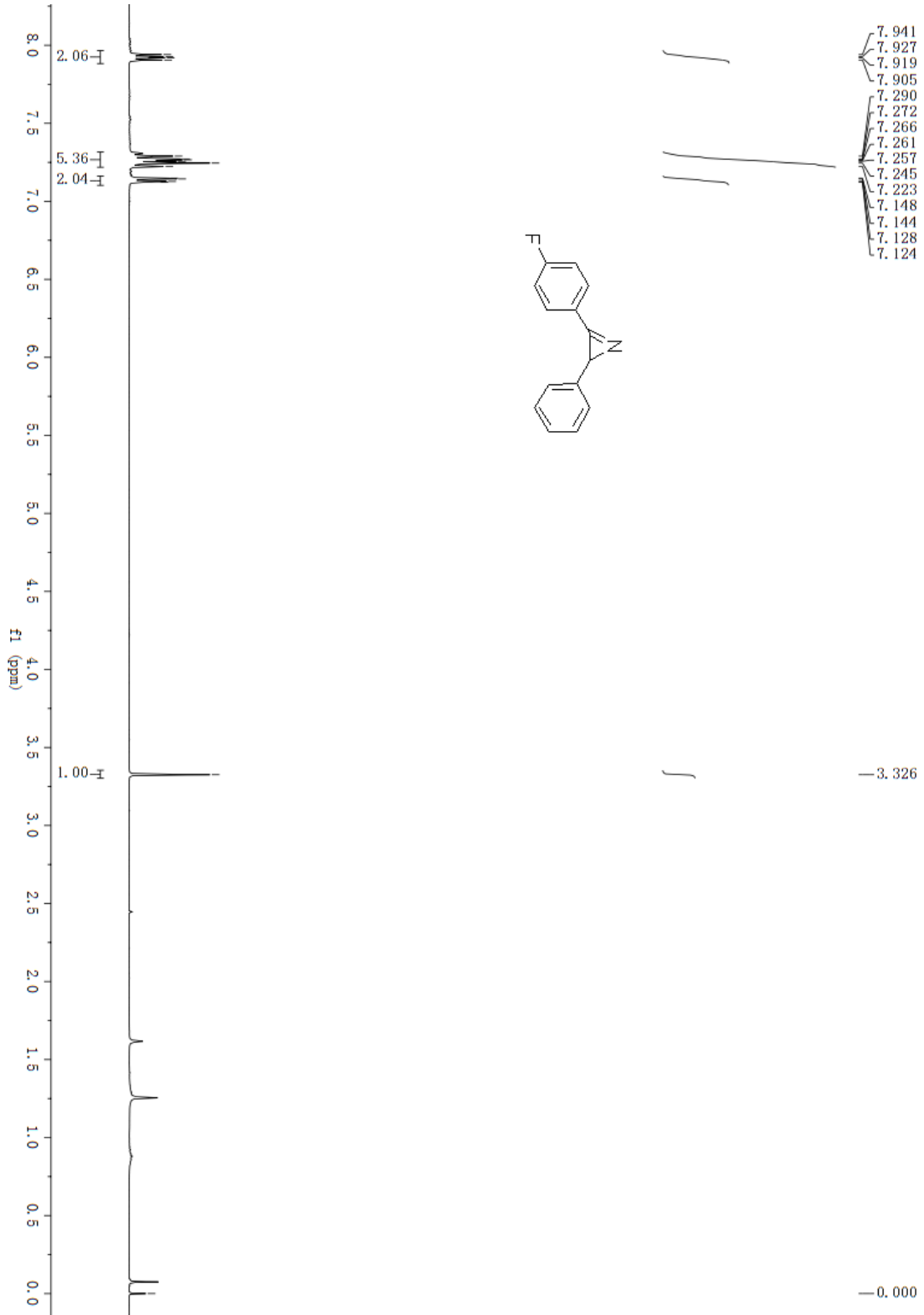
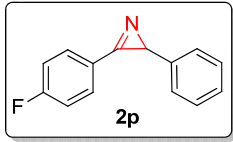




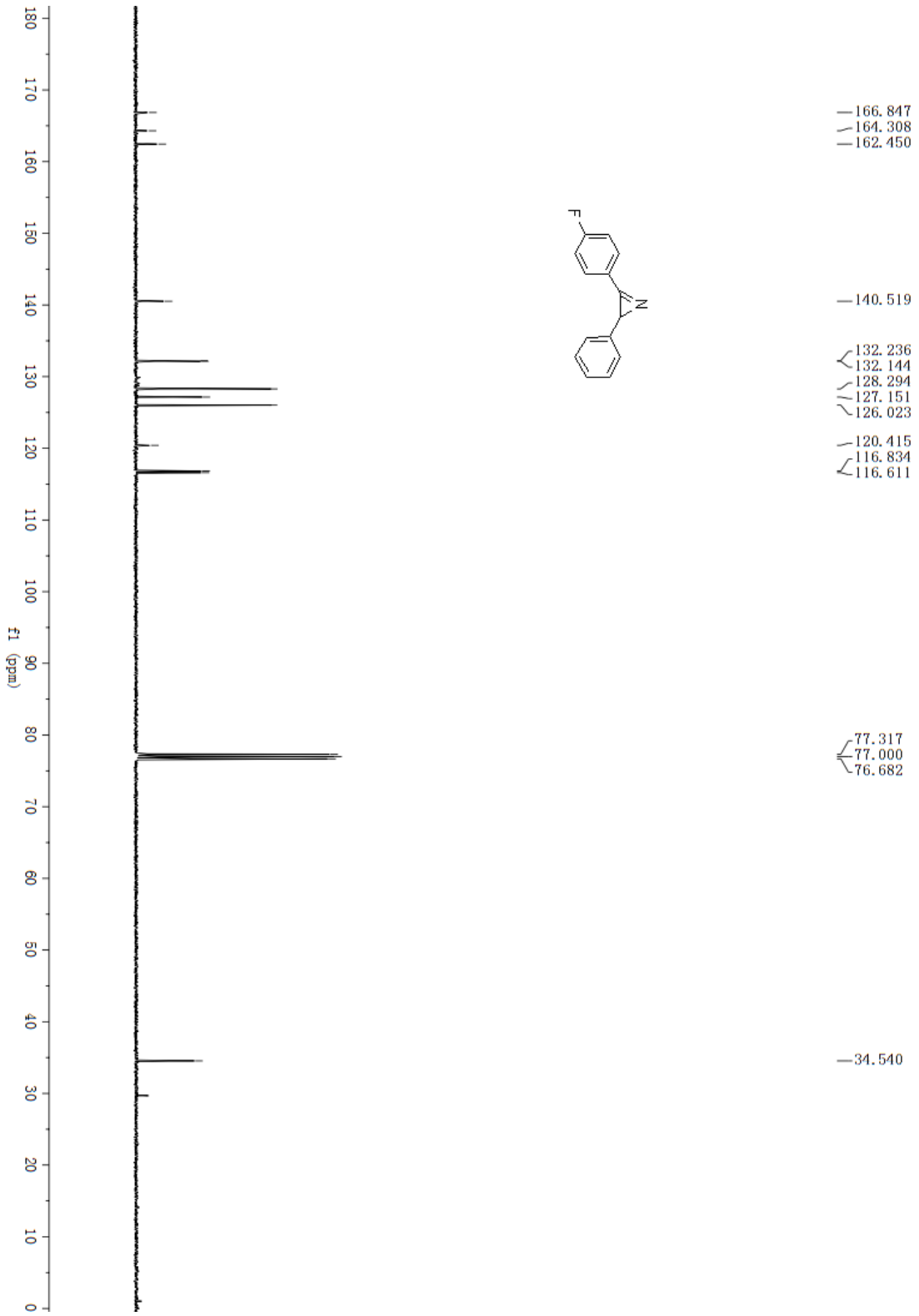
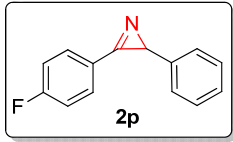


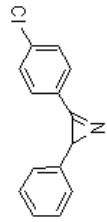
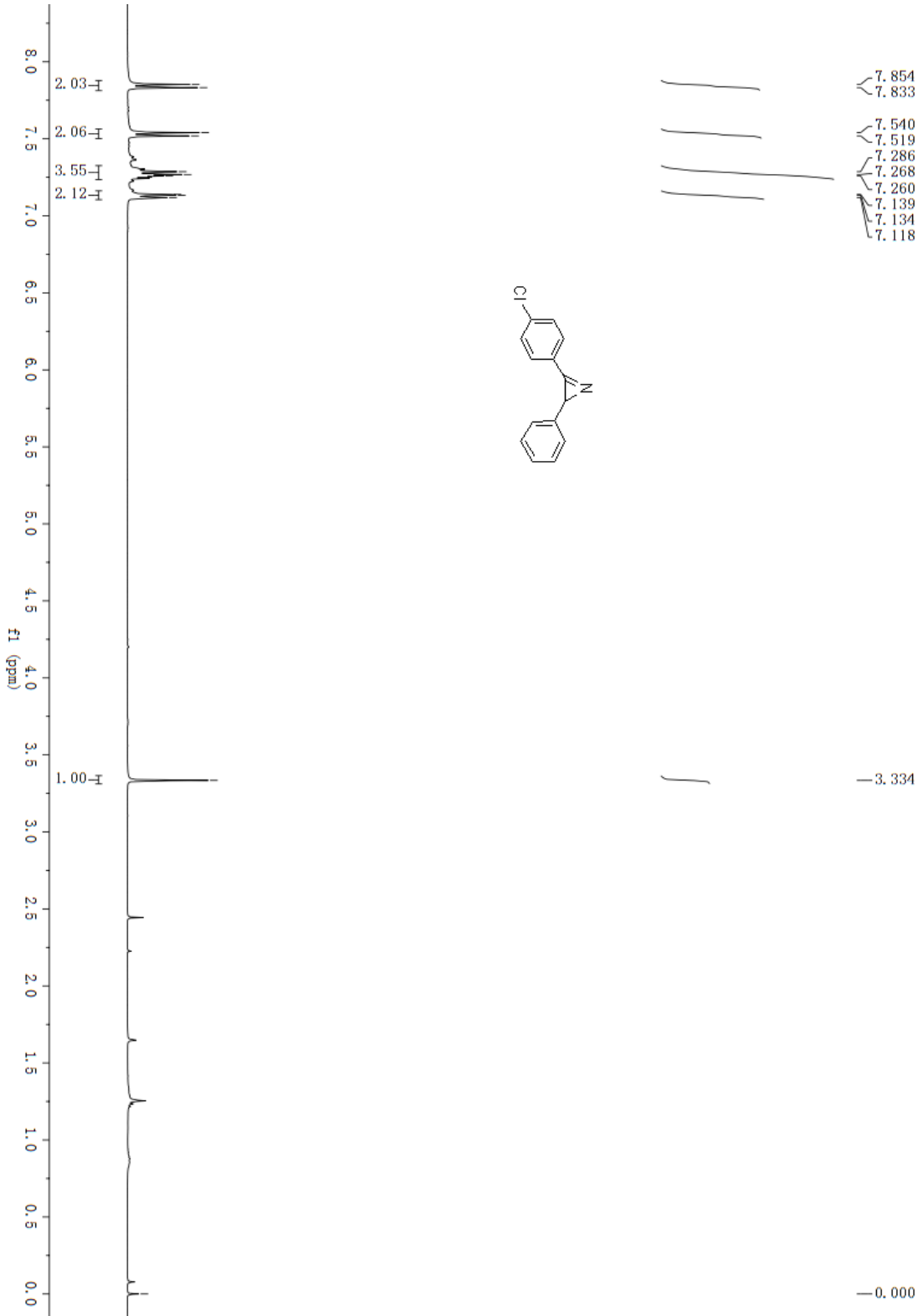
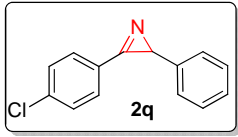


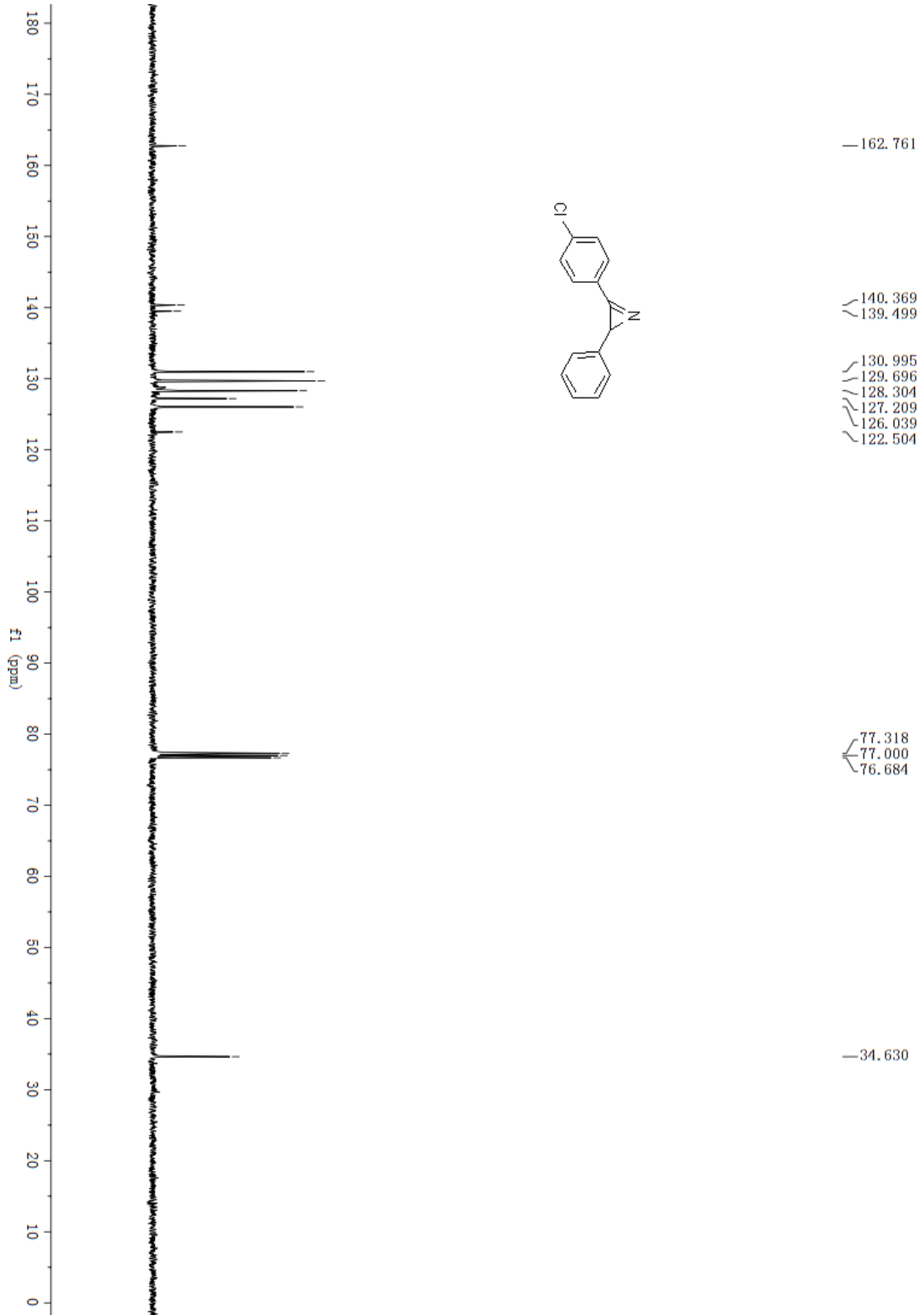
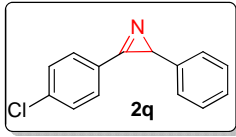


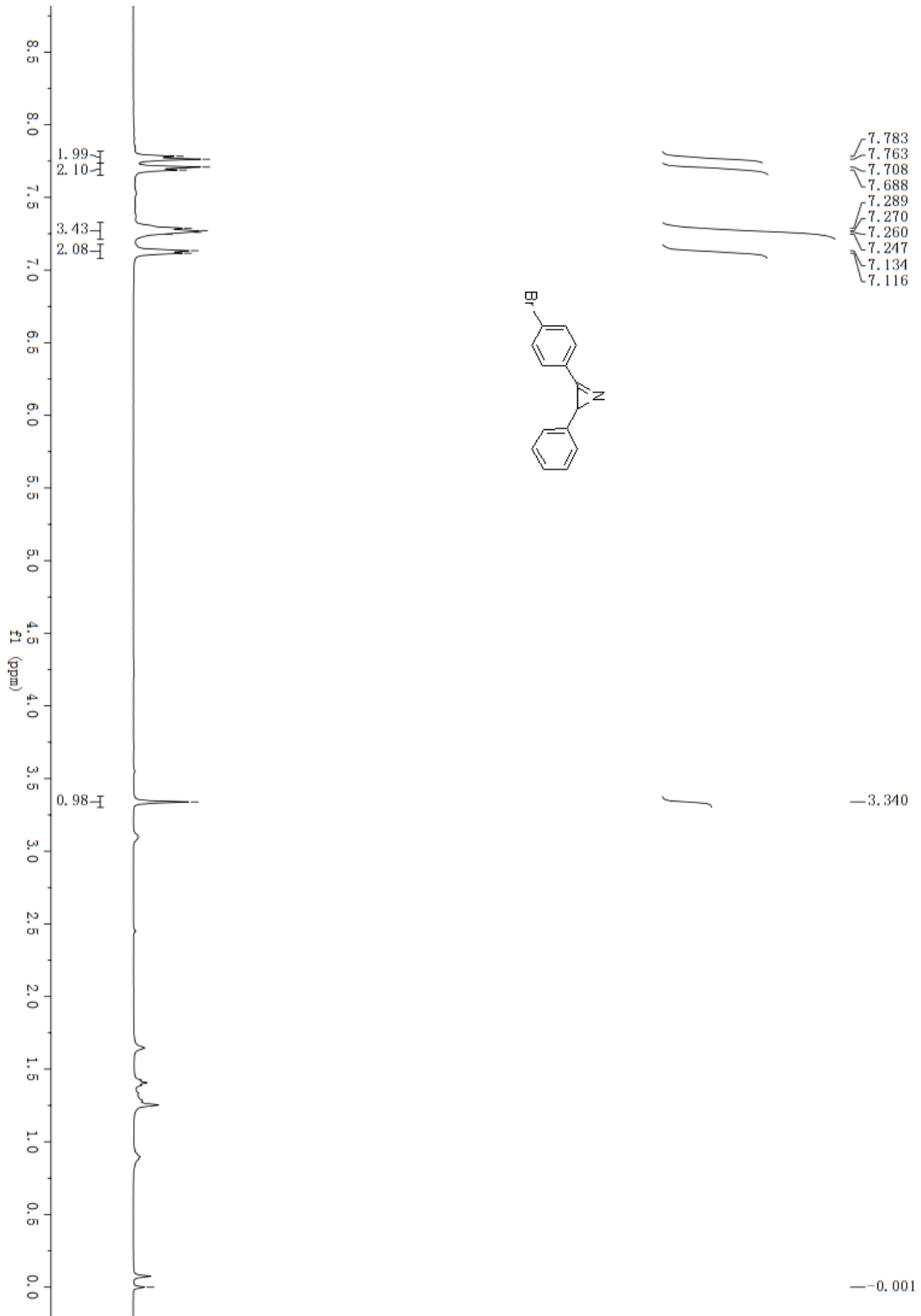
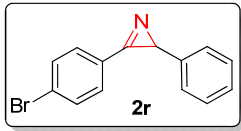


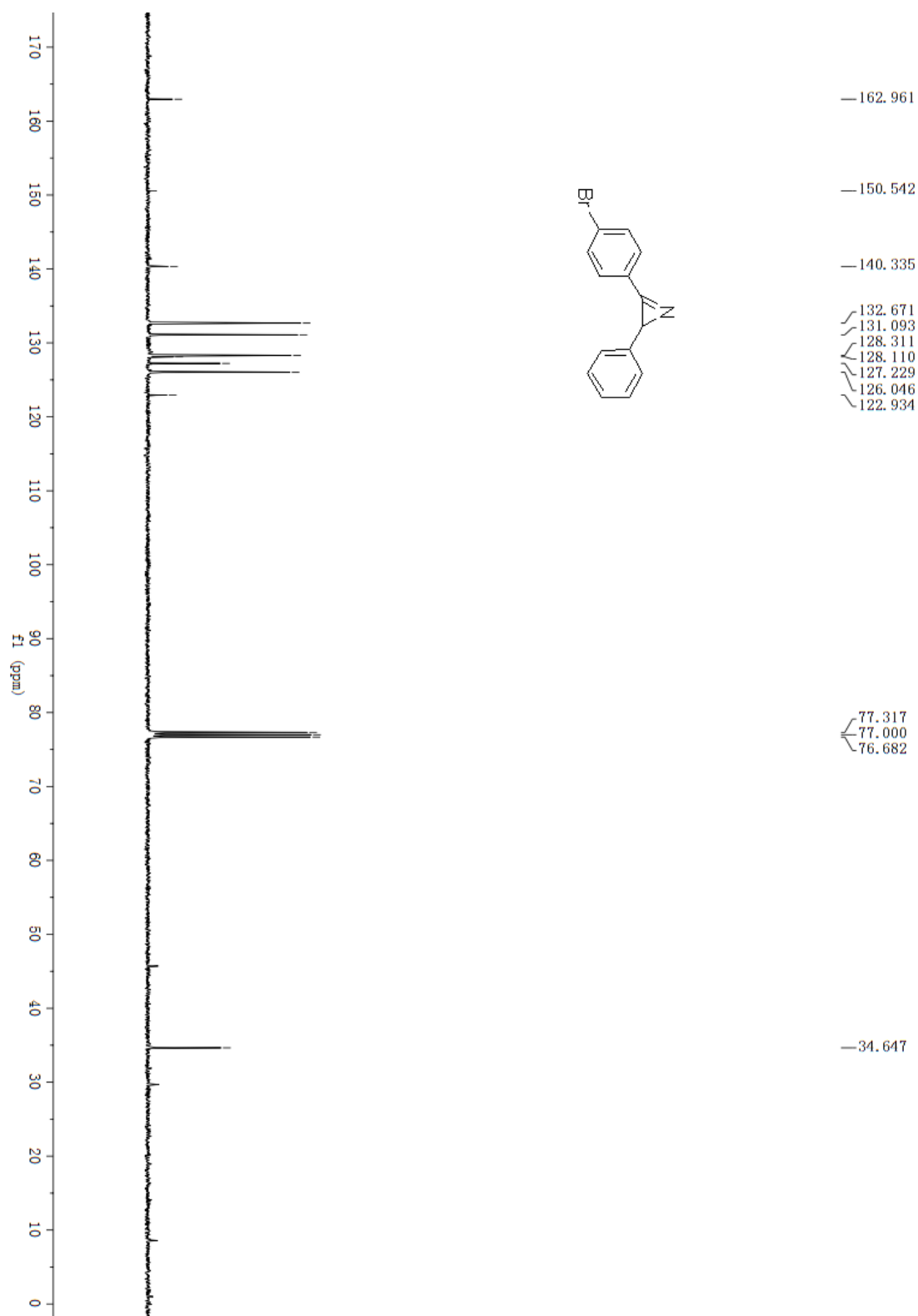
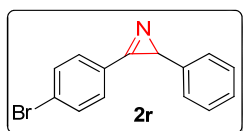


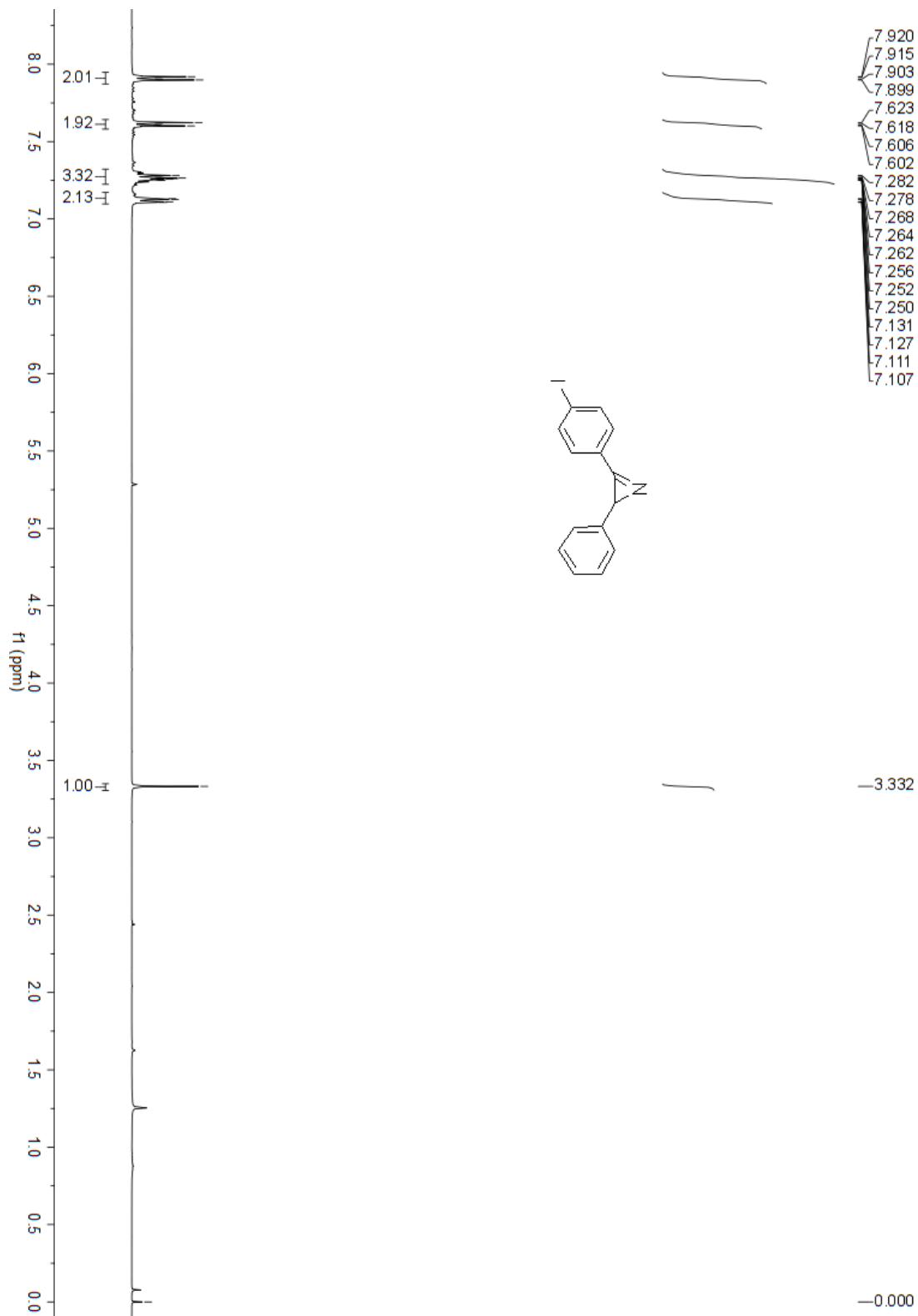
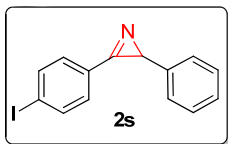


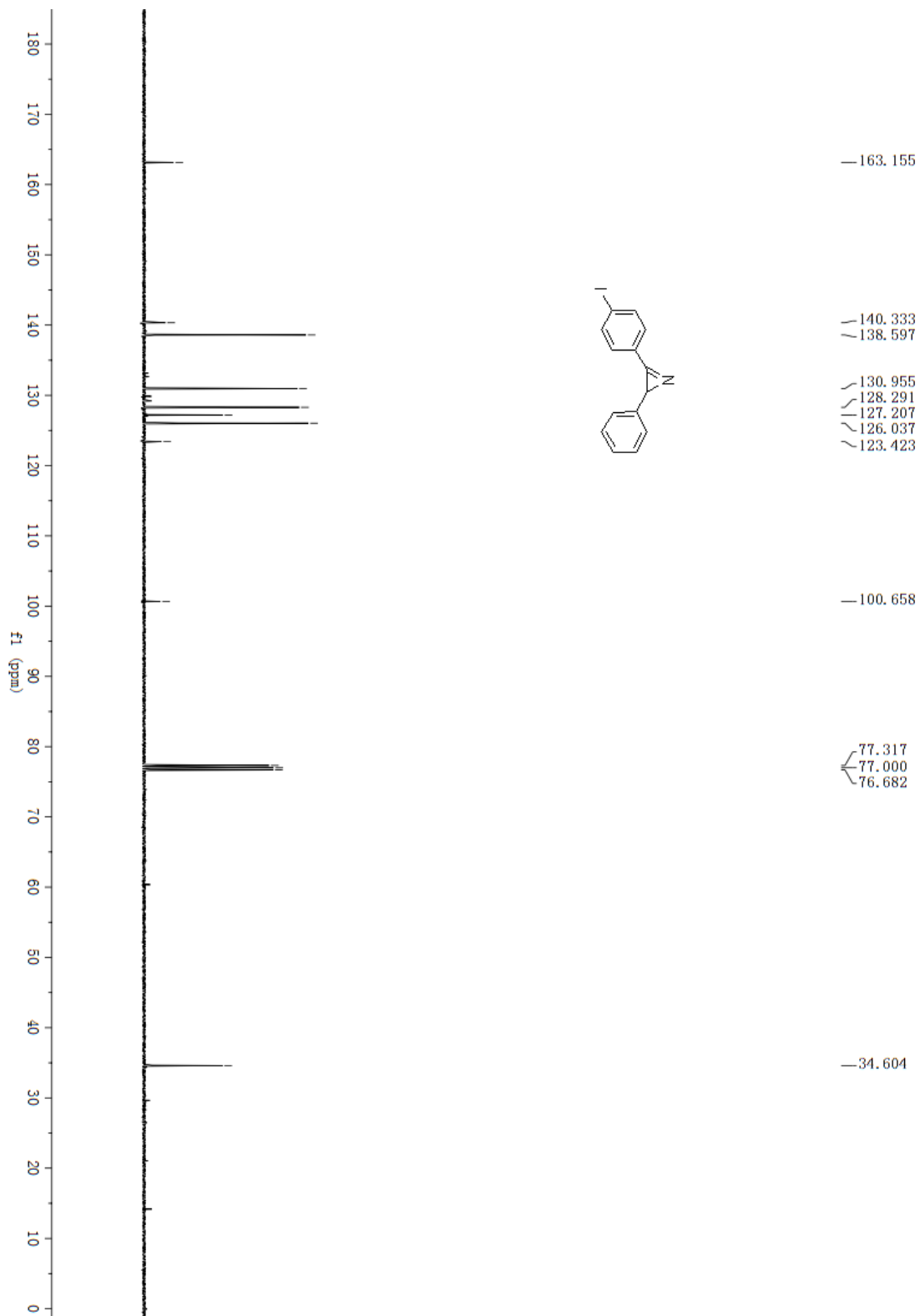
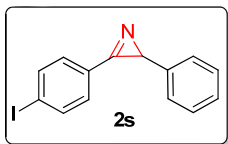


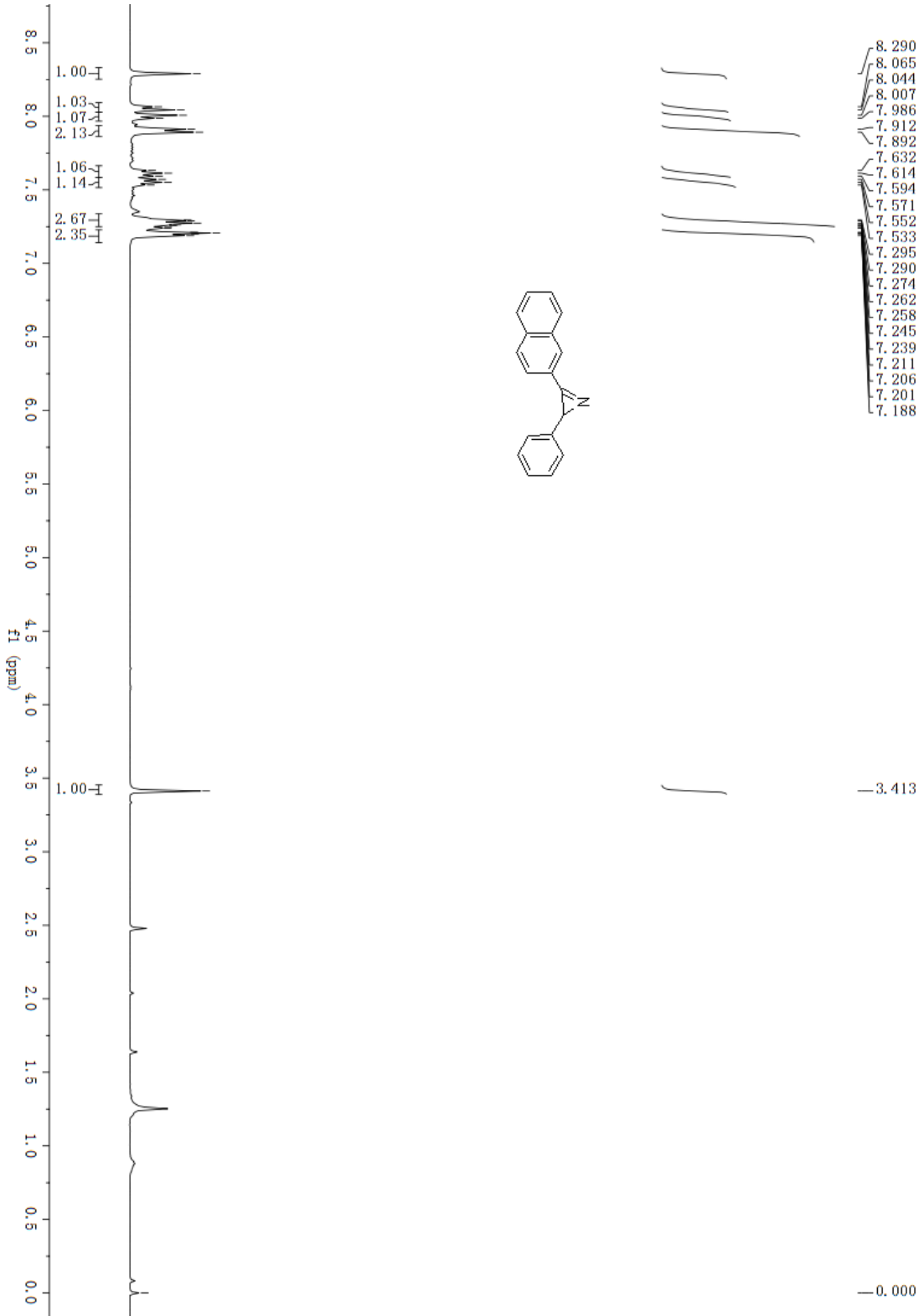
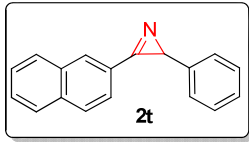




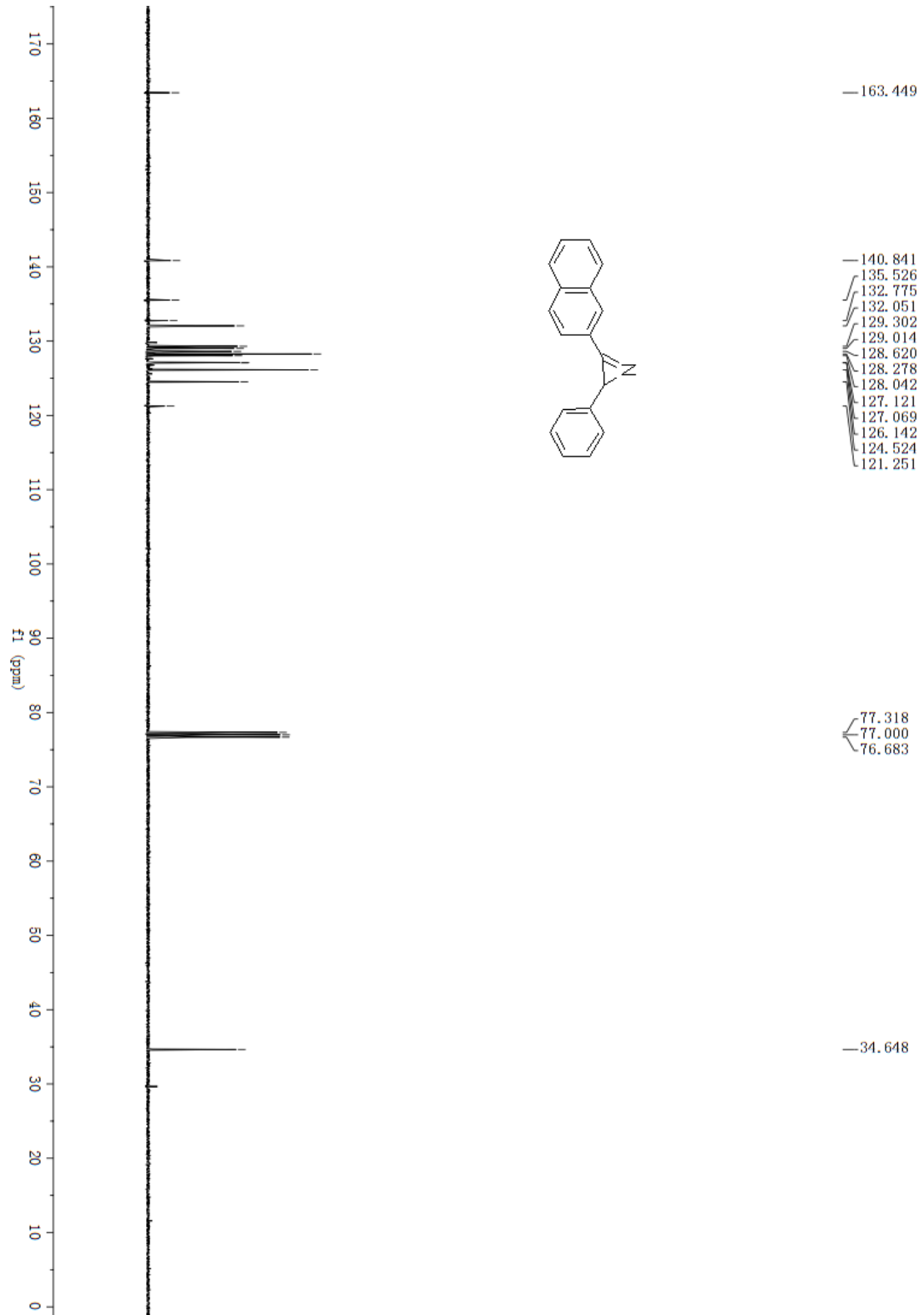
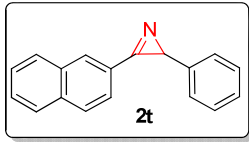


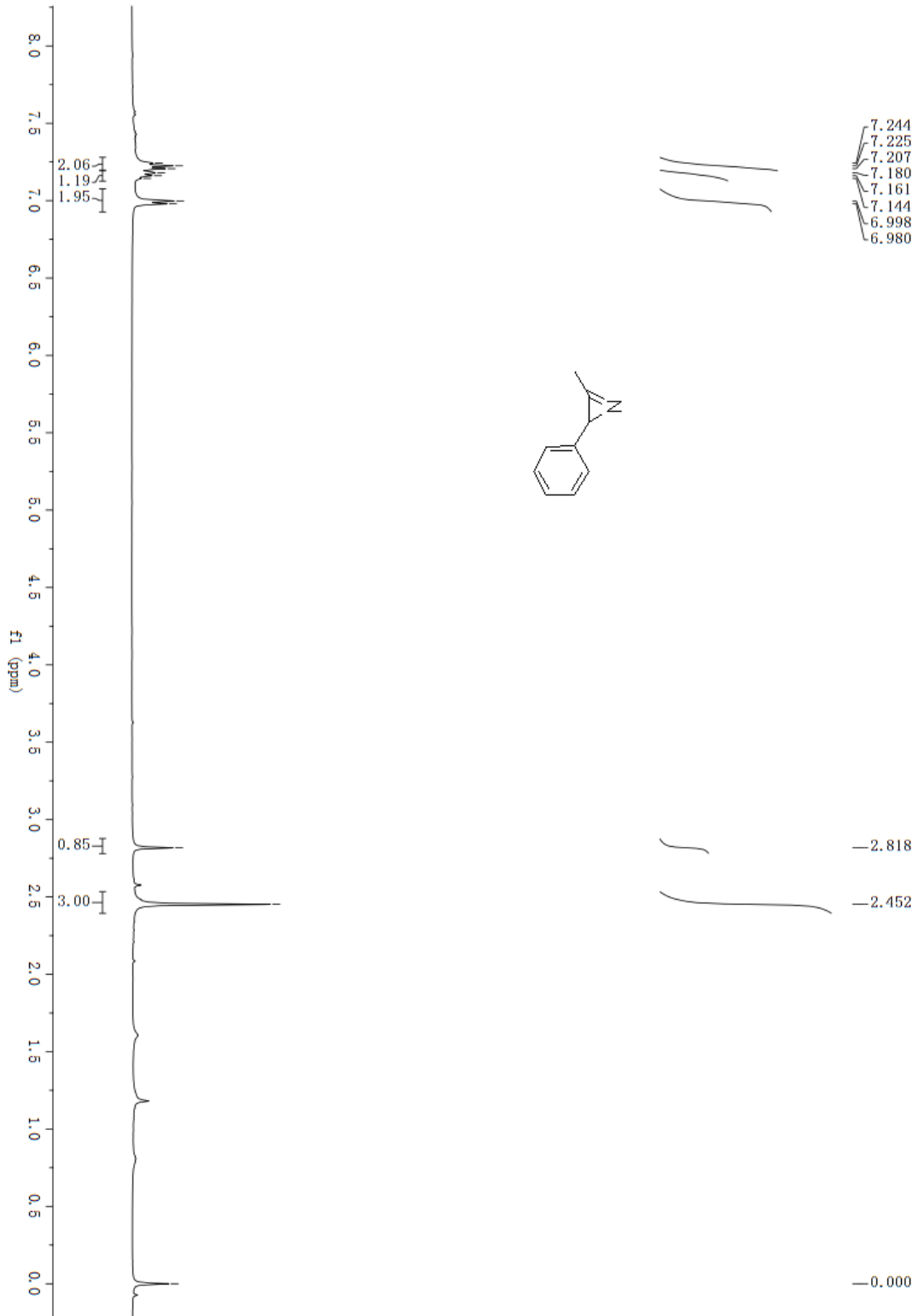
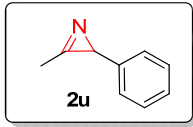


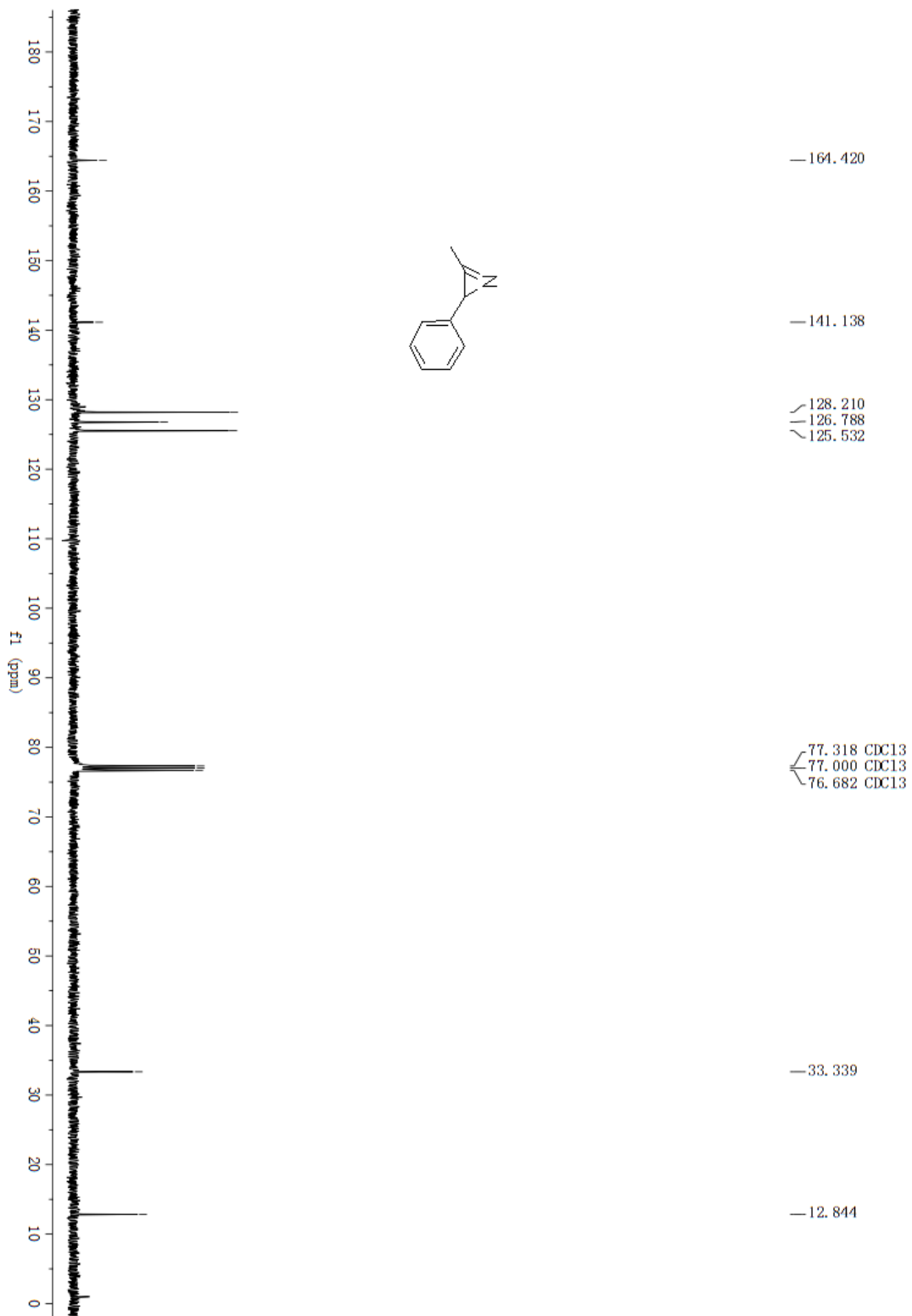
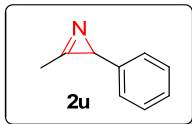


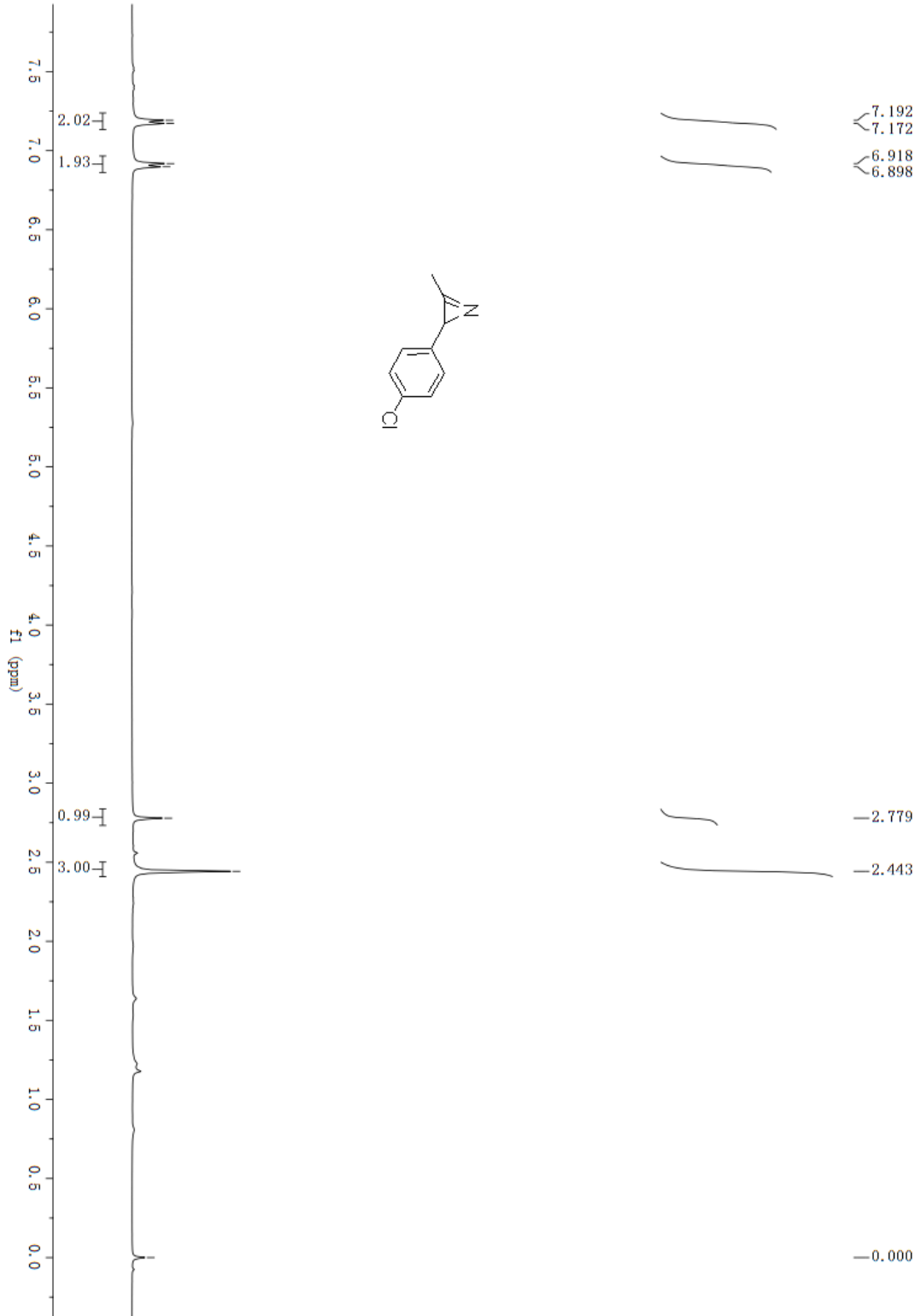
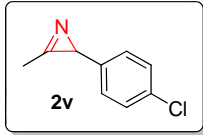


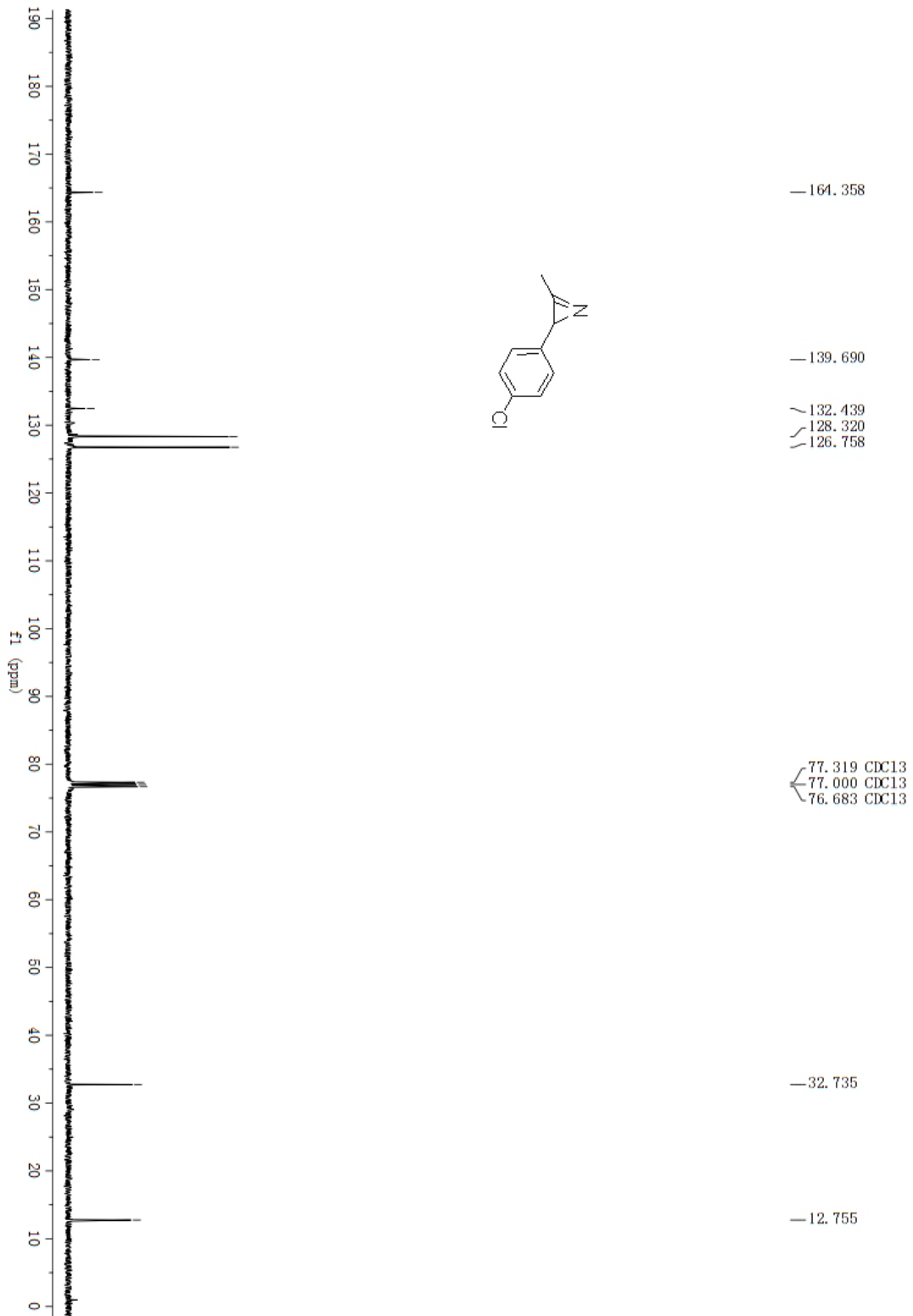
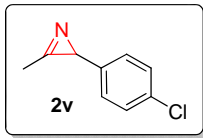


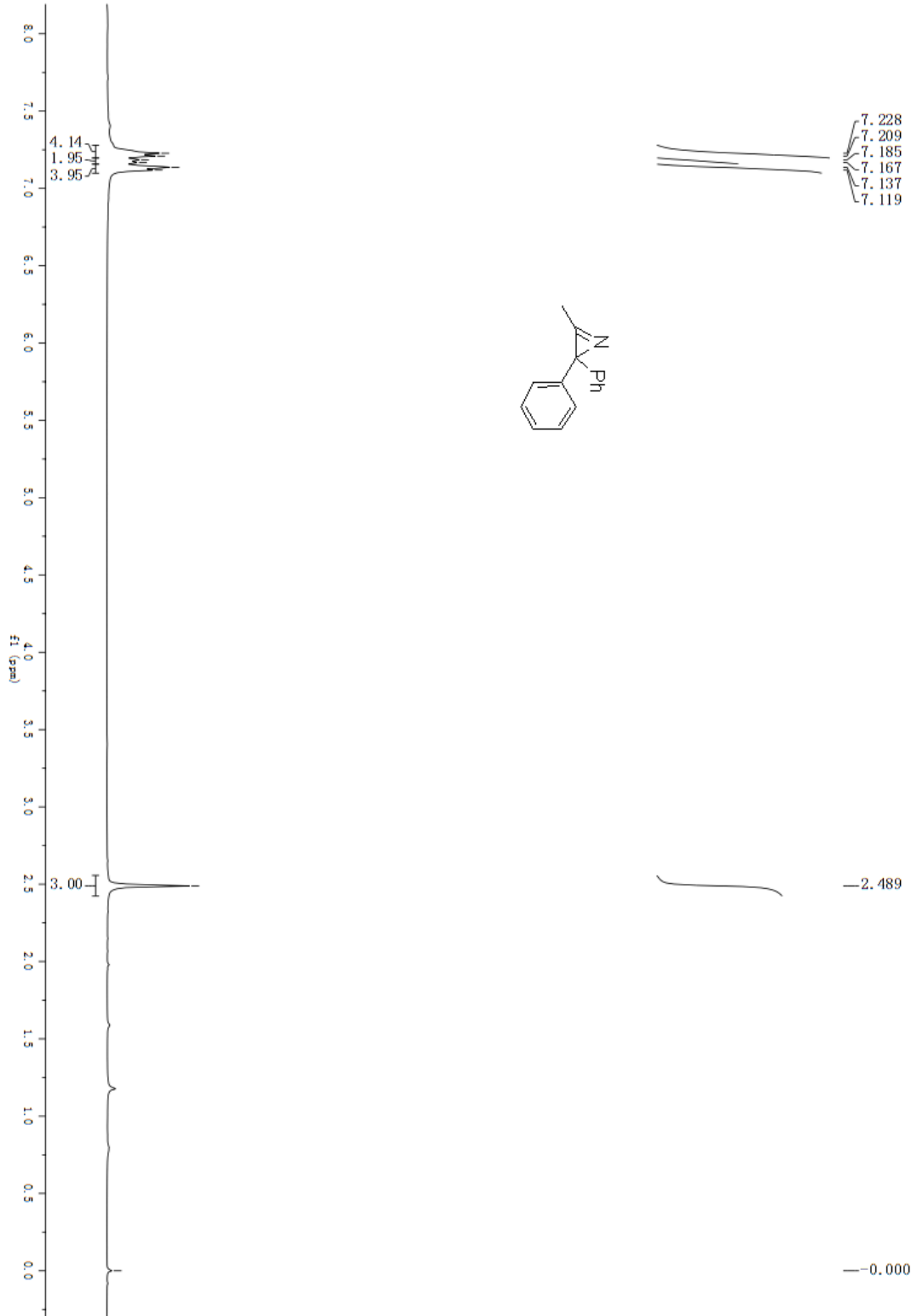
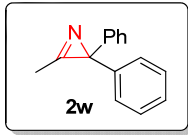


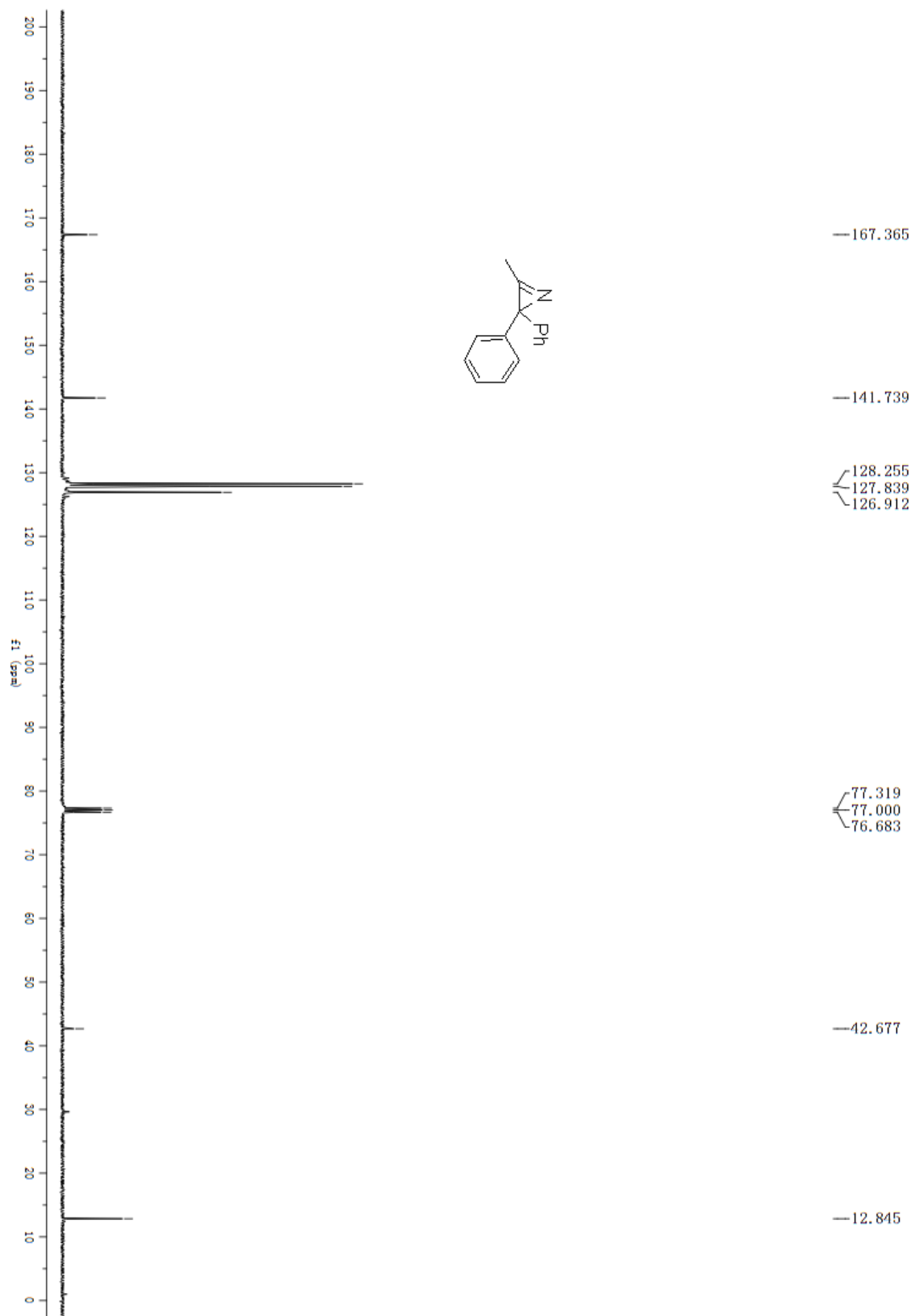
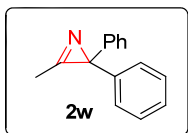


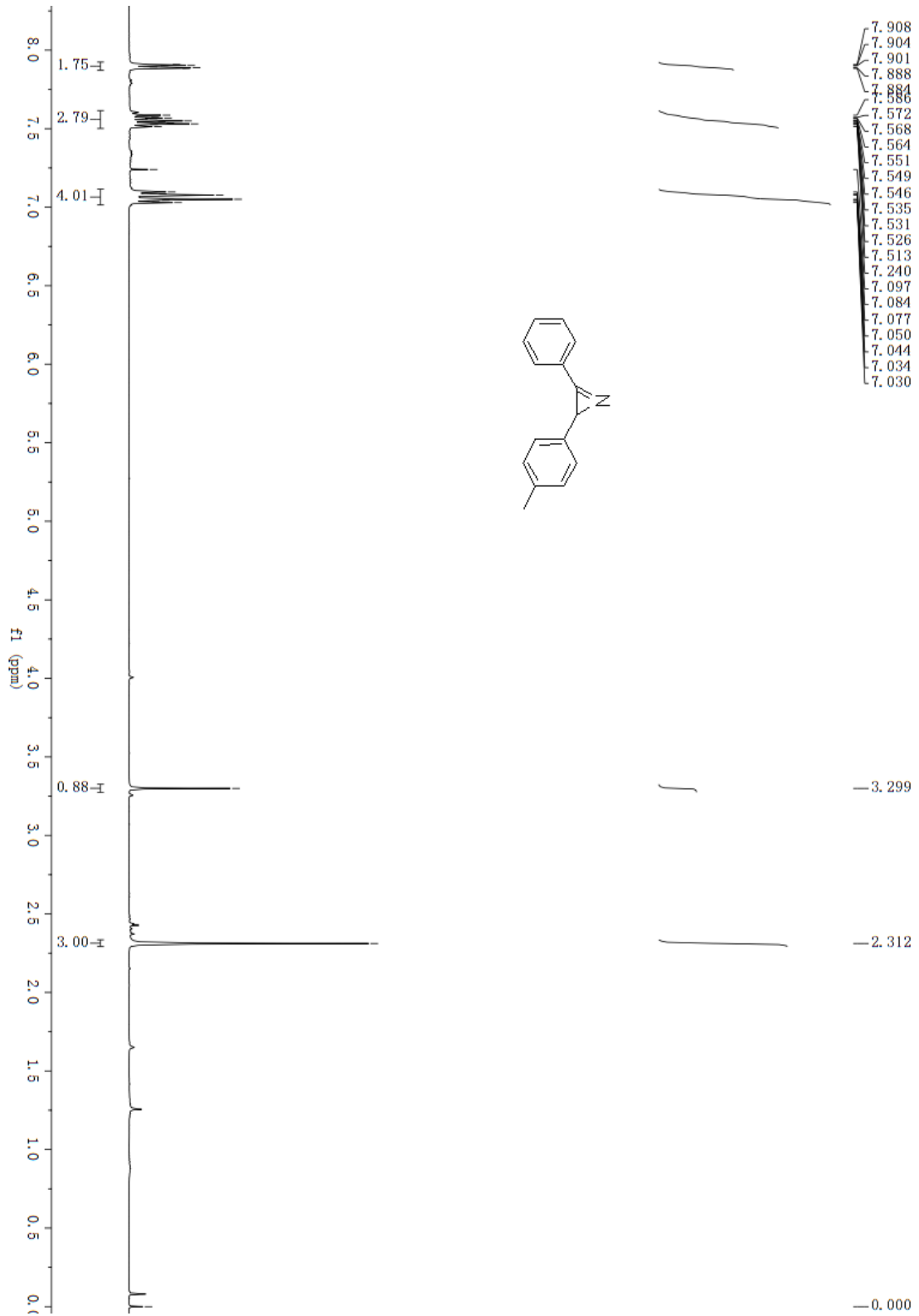
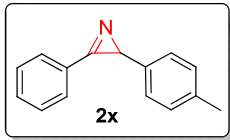




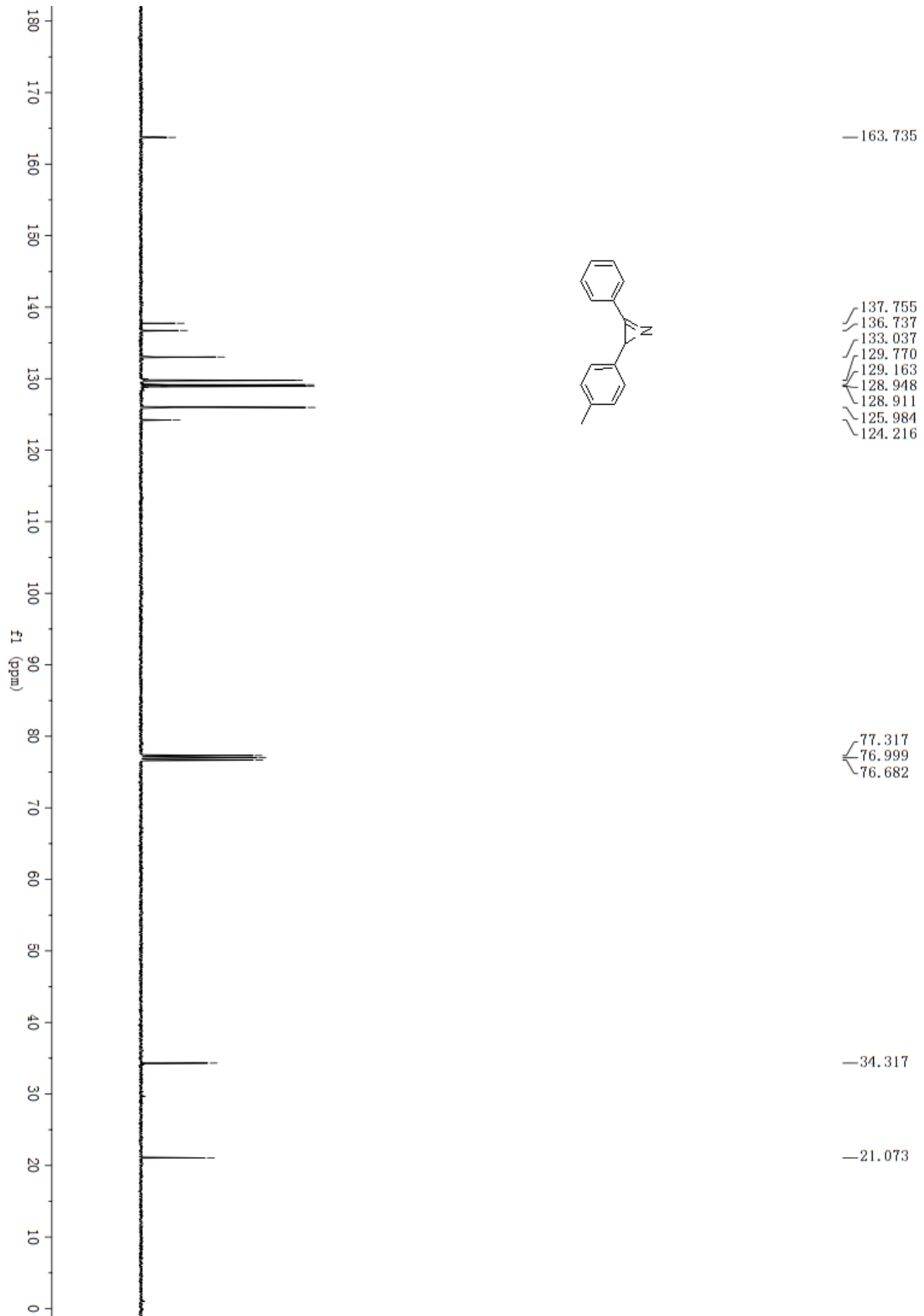
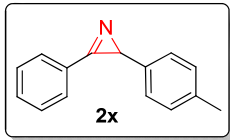


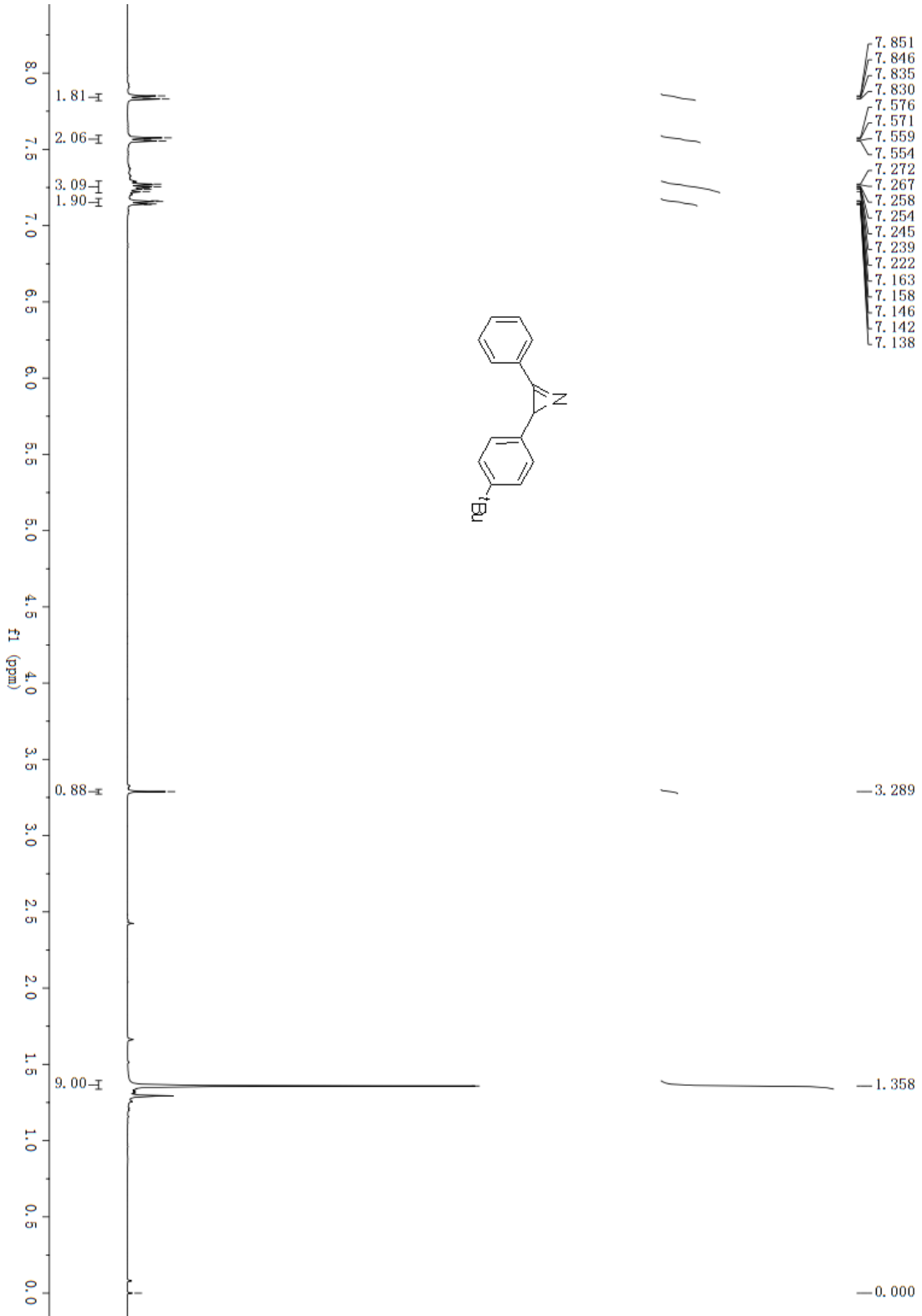
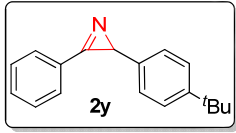


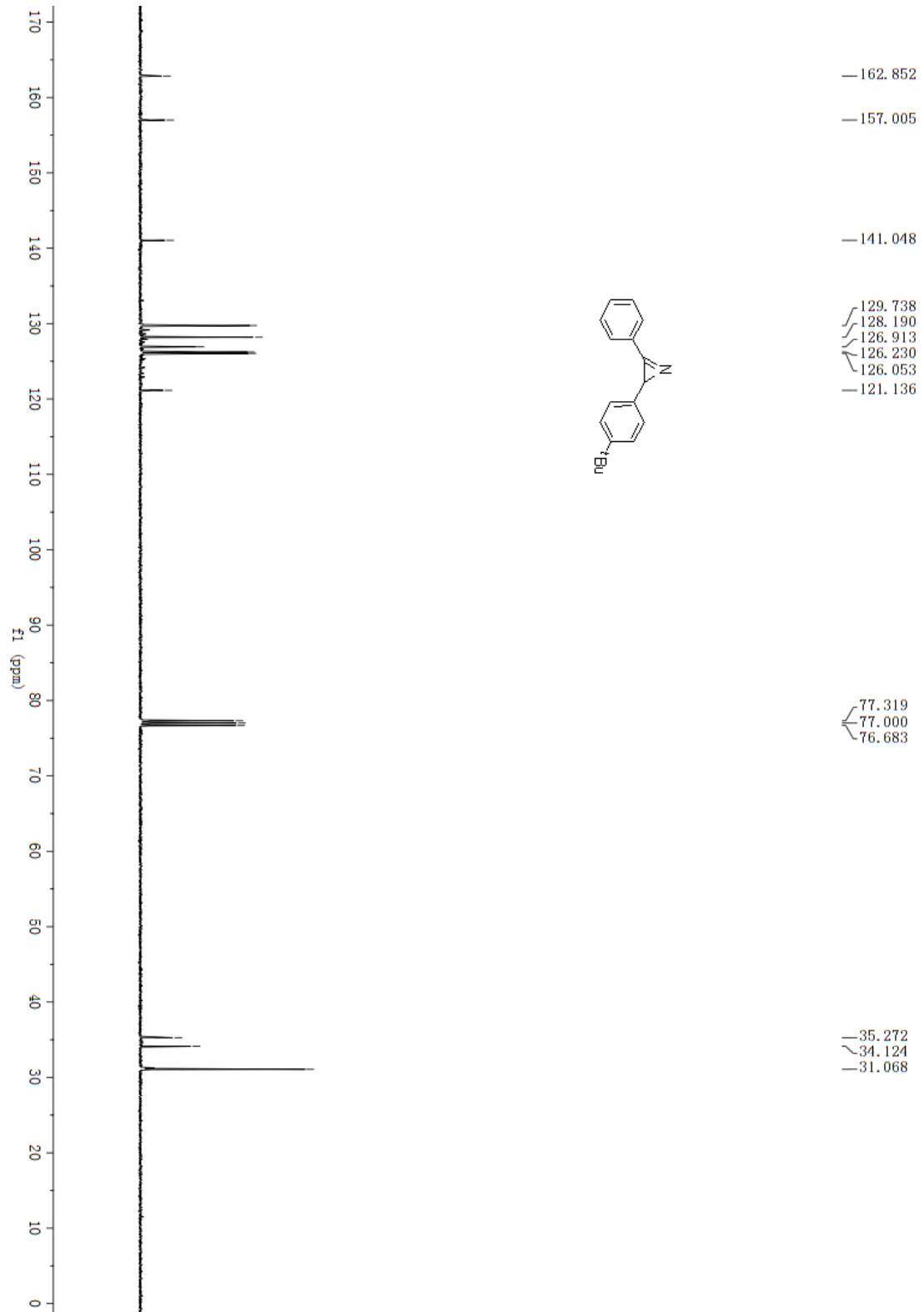
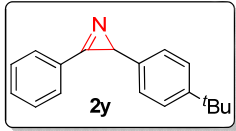


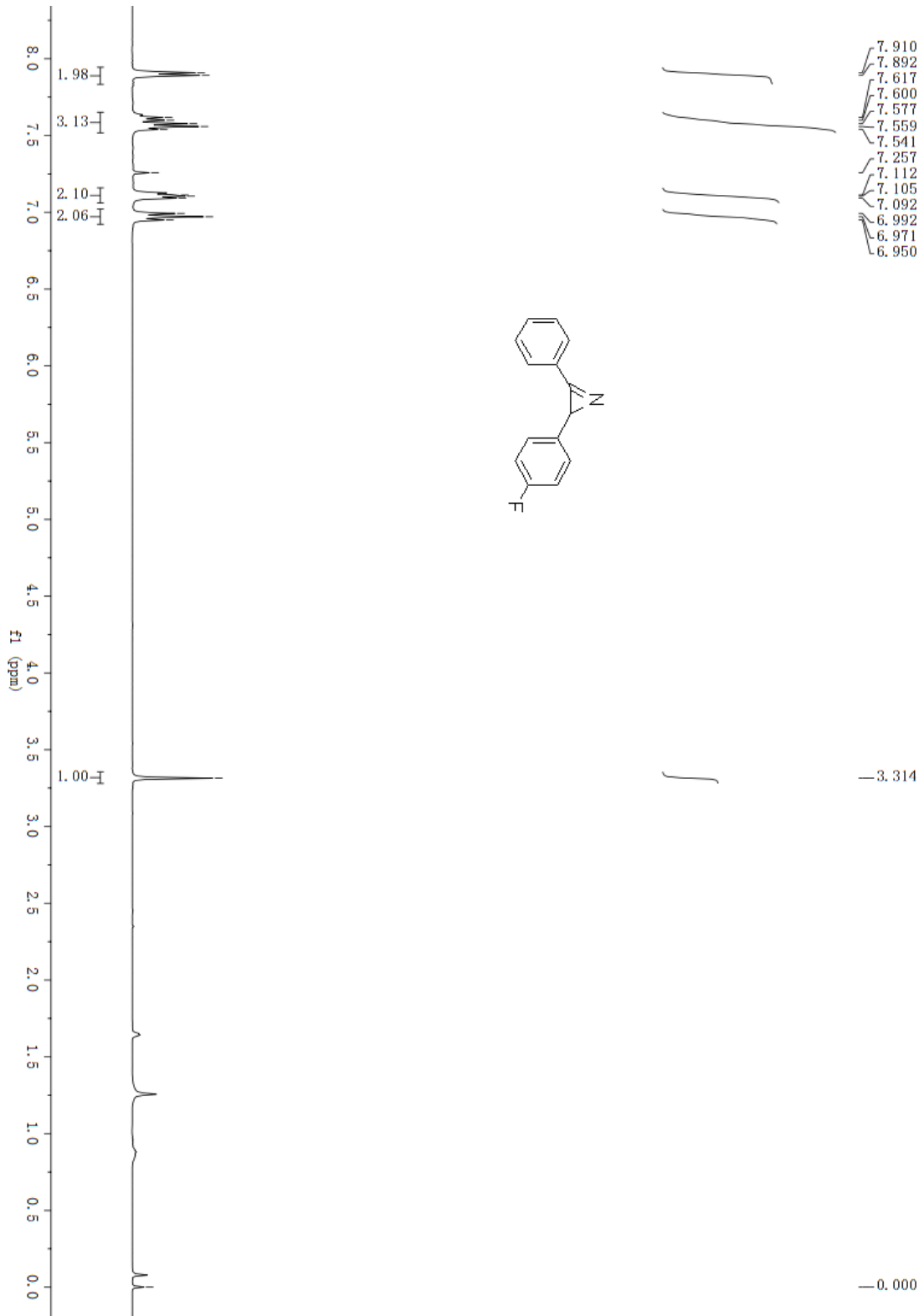
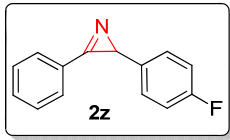


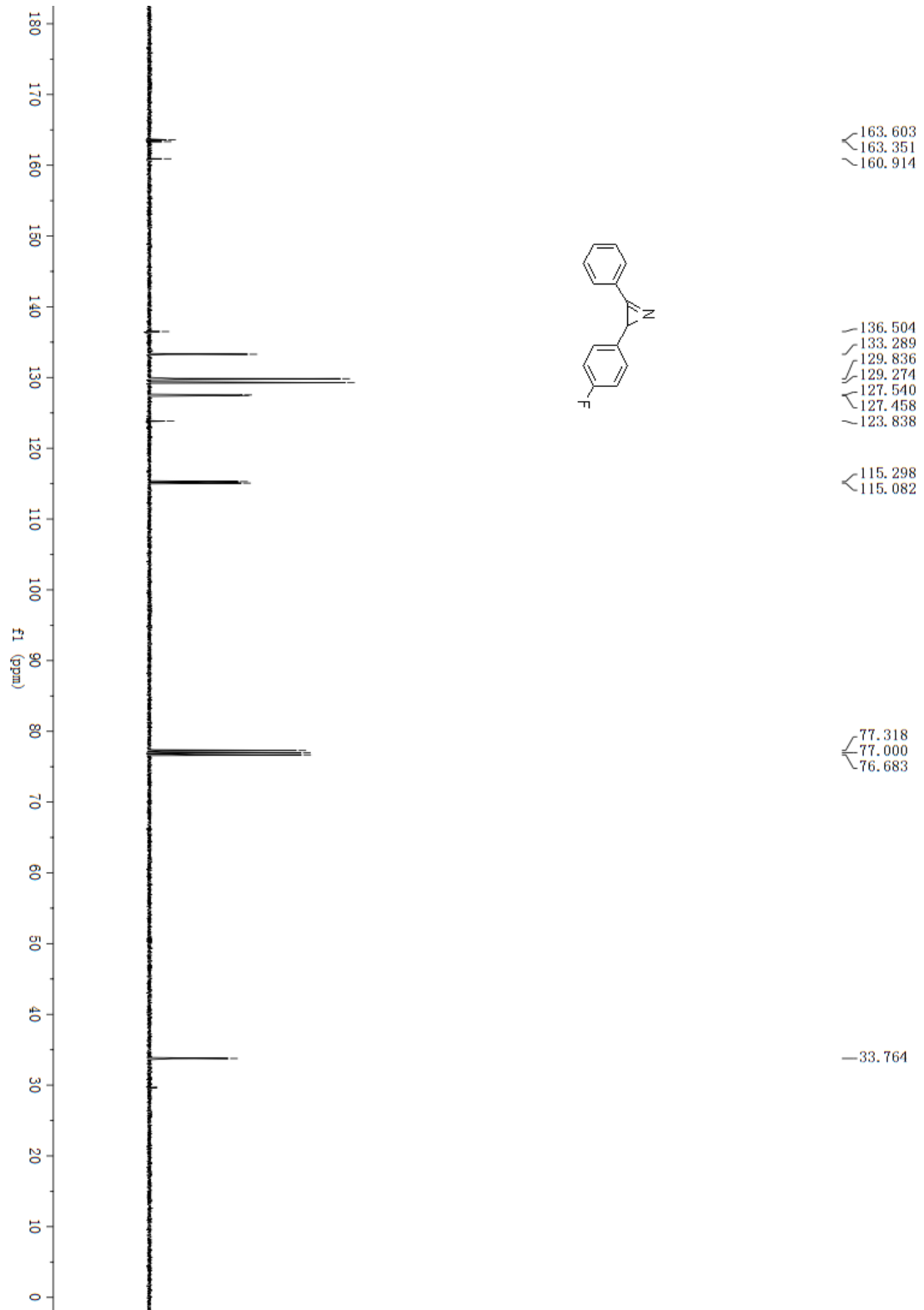
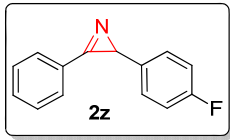


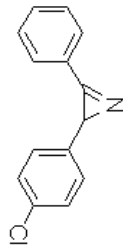
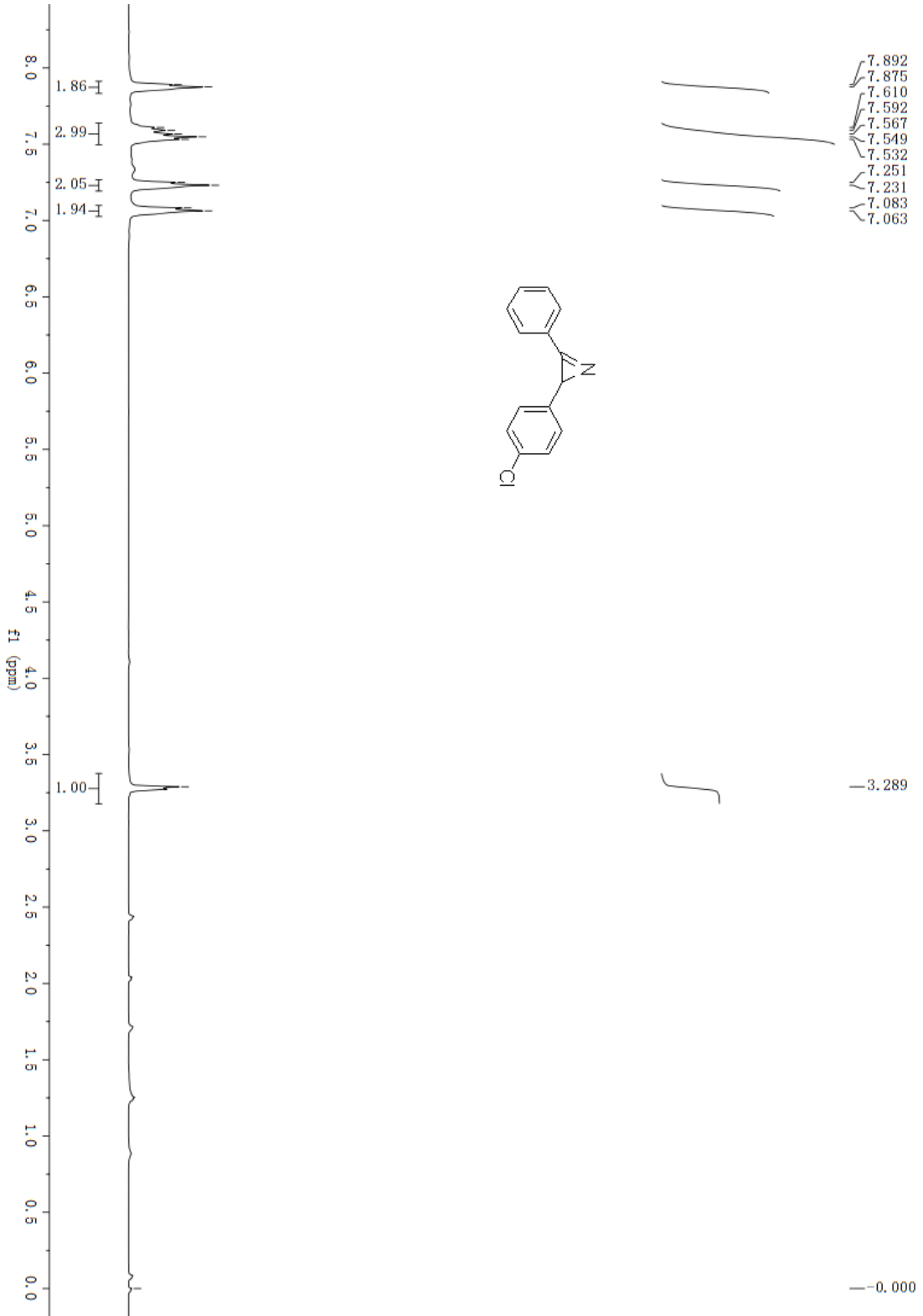
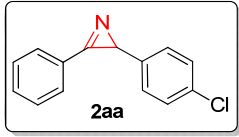


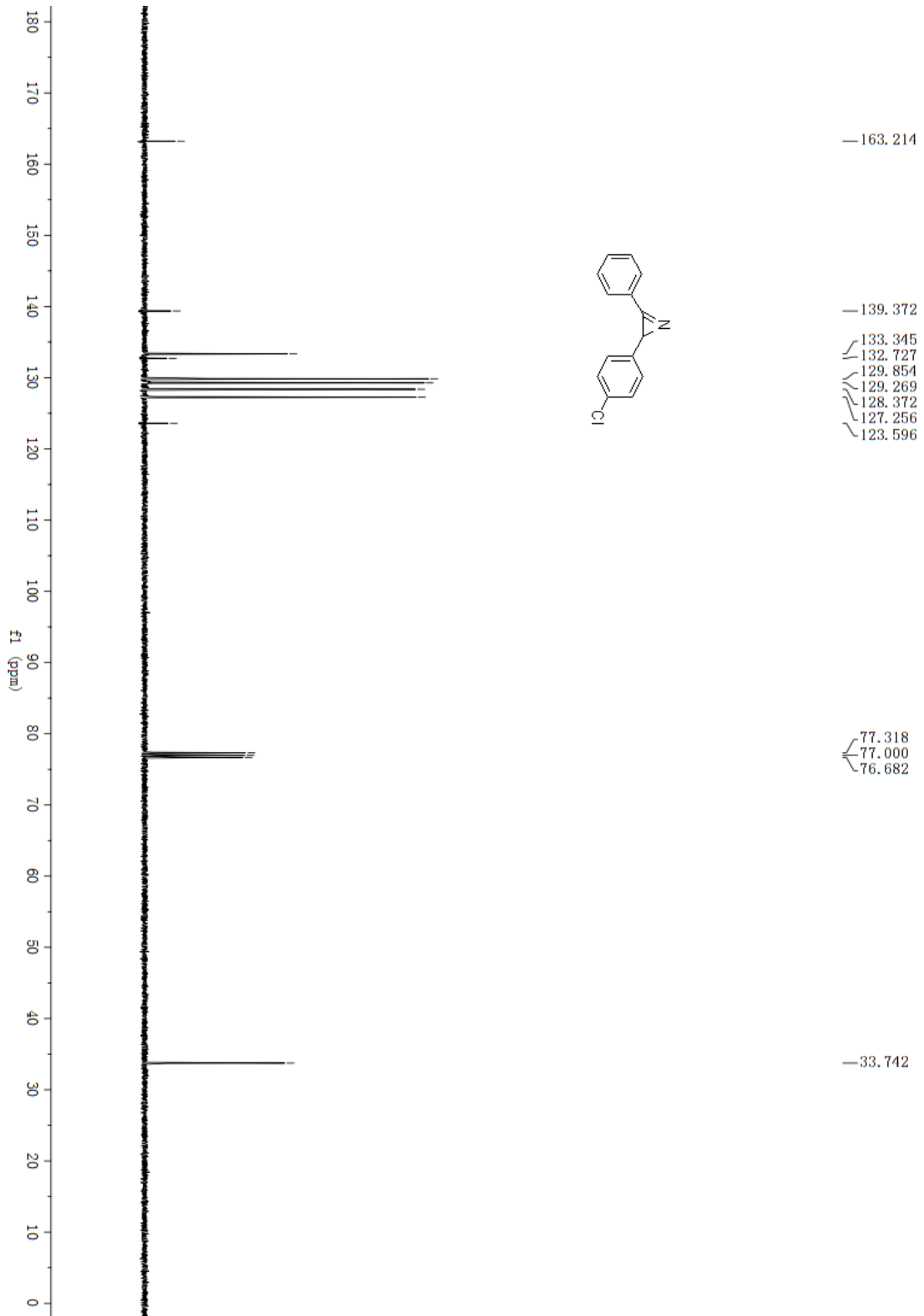
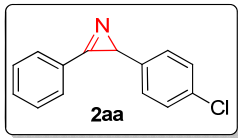


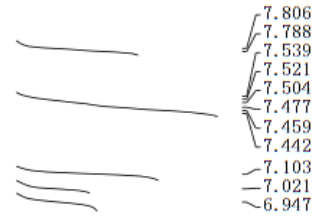
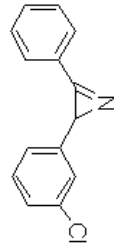
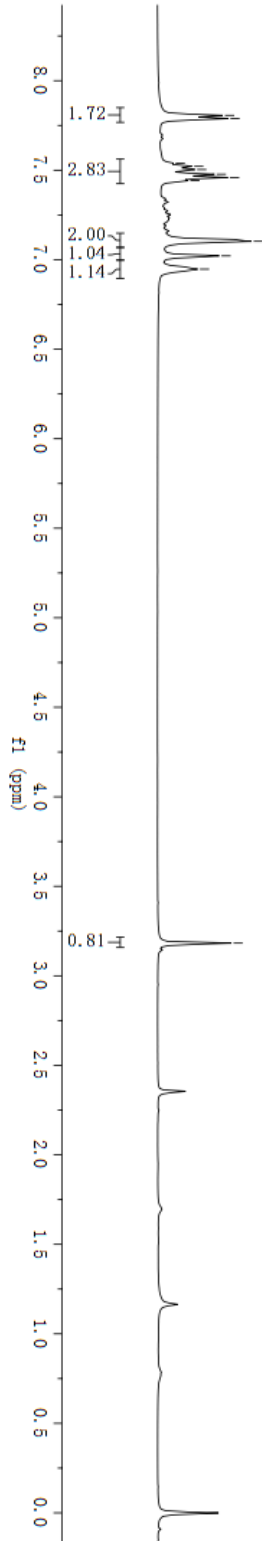
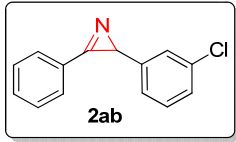












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