# Synthesis of dibenzo[*b,d*]azepine skeleton via a catalyst-free ring expansion domino reaction

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**Supplementary Information**

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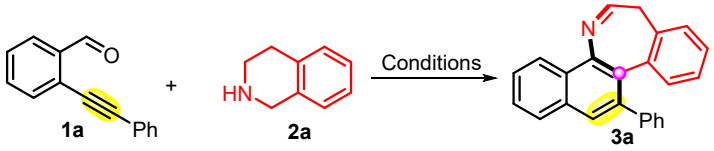
# 1. General Experimental

Unless otherwise mentioned, all materials were commercially obtained and used without further purification. *o*-alkynylarylaldehydes (**1**)[1-2] were synthesized according to previously described methods. The $^{1}H$ NMR, $^{13}C$ NMR, and $^{19}F$ NMR spectra were recorded at 500 MHz, 126 MHz, 471 MHz, respectively, on a Bruker AM500 MHz with chemical shift values in ppm relative to TMS (δH 0.00 and δC 0.0) as internal standard. The coupling constants *J*, are reported in Hertz (Hz). All melting points were determined on a SGW X-4A melting point instrument without correction. High-resolution mass spectra (HRMS) were recorded on Q-Exactive plus Orbitrap (ESI) or HP-5989A instrument.. Infrared spectra (IR) were recorded on Spectrum TWO. Reactions were monitored by thin layer chromatography (TLC), on glass plates coated with silica gel with Fluorescent indicator (Huanghai, HSGF254) and visualized with UV light at 254 nm. Flash chromatography was performed on silica gel (Huanghai, 300-400) using petroleum ether (PE)-ethyl acetate (EA) as eluent. The structure of product **3c** (CCDC file number 2272052) was further confirmed by X-ray diffraction collected on a diffractometer with graphite-monochromated Cu Kα radiation.

# 2 Optimization of the reaction conditions

**Table S1.** Optimization of the reaction conditions[a]




| Entry[a] | Oxidant (equiv.) | Additive (1 equiv.) | Solvent (2 mL) | Temperature (°C) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | Air | -- | 1,4-Dioxane | 100 | 0 |
| 2 | Air | -- | DMSO | 100 | 0 |
| 3 | Air | -- | DMF | 100 | 48 |
| 4 | Air | -- | NMP | 100 | 0 |
| 5 | Air | -- | DME | 100 | 0 |
| 6 | Air | -- | MeCN | 80 | 0 |
| 7 | Air | -- | Dichloroethane | 80 | 0 |
| 8 | Air | -- | Xylenes | 100 | 67 |
| 9 | Air | -- | Toluene | 100 | 81 |
| 10 | Air | -- | THF | Reflux | 0 |
| 11[c] | None | -- | Toluene | 100 | 0 |
| 12 | $O_2$ | -- | Toluene | 100 | 78 |
| 13 | $KIO_3$ (2) | -- | Toluene | 100 | 65 |
| 14 | DTBP (2) | -- | Toluene | 100 | 73 |
| 15 | $MnO_2$ (2) | -- | Toluene | 100 | 46 |
| 16 | Air | $NaHCO_3$ | Toluene | 100 | 58 |
| 17 | Air | $K_2CO_3$ | Toluene | 100 | 0 |
| 18 | Air | $AlCl_3$ | Toluene | 100 | Trace |
| 19 | Air | *n*-$Bu_4NI$ | Toluene | 100 | 38 |
| 20 | Air | $(Ph_3P)_2PdCl_2$ | Toluene | 100 | 71 |
| 21 | Air | $NiCl_2$ | Toluene | 100 | 32 |
| 22 | Air | $Cu(OAc)_2$ | Toluene | 100 | 69 |
| 23 | Air | -- | Toluene | rt | 0 |
| 24 | Air | -- | Toluene | 80 | 35 |

| | | | | | |
|---|---|---|---|---|---|
| 25 | Air | -- | Toluene | 90 | 71 |
| 26 | Air | -- | Toluene | 110 | 63 |
| 27[d] | Air | | Toluene | 100 | 76 |

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), and solvent (1 mL) in air reacted for 4 h.

[b]Isolated yield. [c] Under $N_2$. [d] Reaction time: 8 h.

# 3 Control experiments

To further understand this oxidative ring expansion reaction, several preliminary experiments were performed (Figure S1). When the common radical scavenger 2,2,6,6-tetramethylpiperidine (TEMPO), butylated hydroxytoluene (BHT), and 1,1-diphenylethylene (DPE) were utilized in this reaction system under standard conditions, the product **3a** was provided in 72%, 59% and 54% yields, respectively, implying that the transformation may not proceed via a radical process (Figure S1a). Moreover, the reaction of reduction compound **7** under the optimal conditions afford **3a** in 95% yield (Figure S1b). The addition to template reaction with TMSCN (2.0 equiv.) produced **11** in 76% yield (Figure S1c). Futhermore, intermediate **A** (alcohol) was detected by HRMS under standard reaction conditions (Figure S2). According to the above experimental results, intermediate **A** (alcohol), **B** (imine) and compound **7** may be an important intermediate in this reaction.

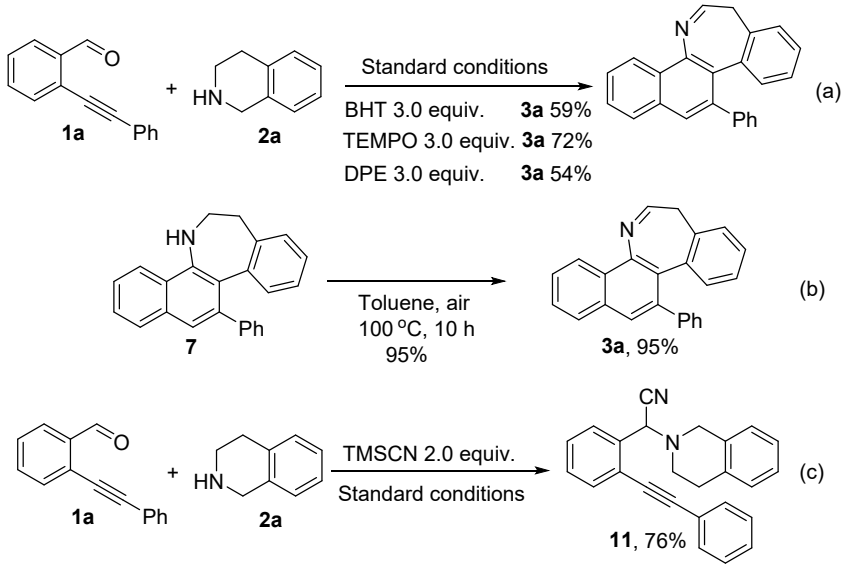



**Figure S1** Control experiments

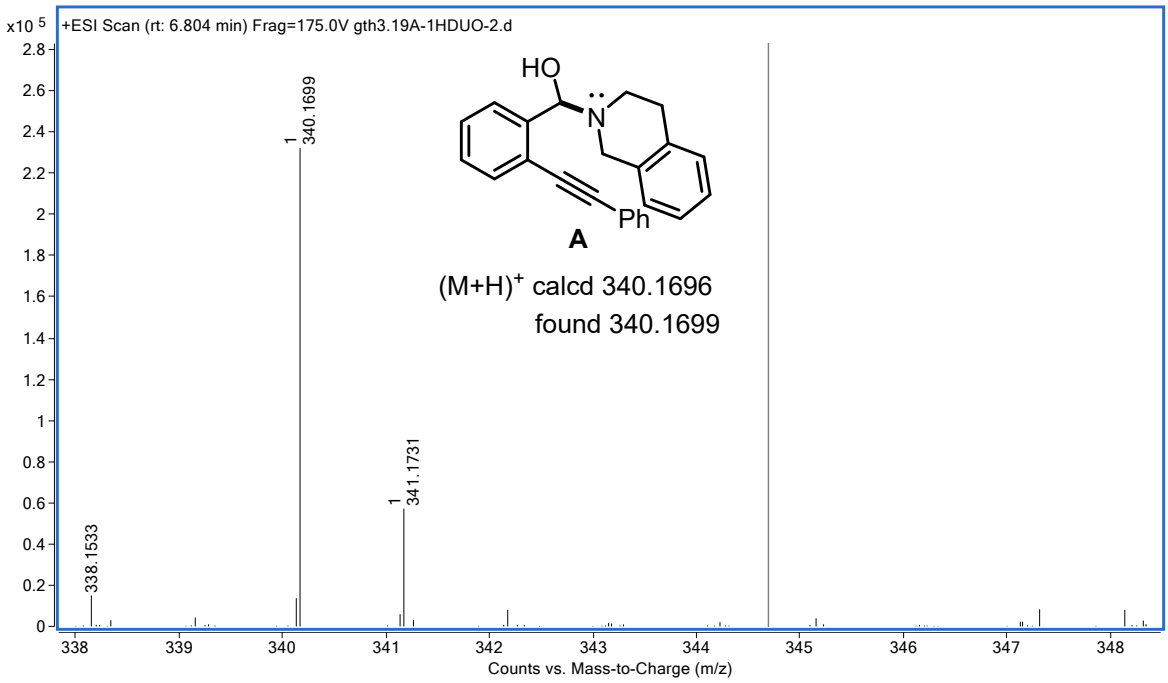
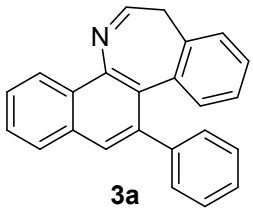



**Figure S2** HRMS of standard reaction solution

# 4. General procedure for the synthesis of dibenzo[*b,d*]azepines 3, 4, and isoindoline derivatives 6

## General procedure for the synthesis of dibenzo[*b,d*]azepines 3 and 4

1 mL Toluene, (**1**, 0.4 mmol (2.0 equiv.)), and (**2**, 0.2 mmol), were added into the dry thick-walled glass pressure tube. The mixture was stirred in a preheated oil bath in air at 100 °C for 4 h. Then the reaction was cooled down to room temperature, diluted with 20 mL ethyl acetate and washed with 10 mL $H_2O$. The aqueous layer was extracted twice with ethyl acetate (5 mL) and the combined organic phase was dried over $Na_2SO_4$. After evaporation of the solvents the residue was purified by flash column chromatography (silica gel, PE–EA) to afford the desired products **3** and **4**.




**3a**

8-phenyl-3H-benzo[d]naphtho[1,2-b]azepine

**3a** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1).

Yellow solid, mp 174-176 °C.

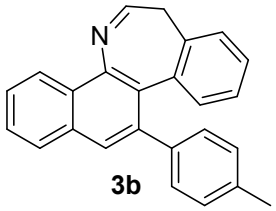
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.46 – 8.44 (m, 1H), 7.94 (t, *J* = 4.5 Hz, 1H), 7.76 – 7.74 (m, 1H), 7.62 (s, 1H), 7.75 – 7.43 (m, 2H), 7.15 – 7.05 (m, 7H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.70 (t, *J* = 7.5 Hz, 1H), 3.60 – 3.57 (m, 1H), 2.82 – 2.79 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.5, 143.0, 142.1, 140.0, 136.7, 134.3, 133.1, 132.7, 130.1, 128.9,

128.1, 127.7, 127.6, 127.3, 127.1, 126.6, 126.5, 126.4, 126.3, 125.2, 125.0, 38.0.

**IR (KBr):** 1625, 1482, 1378, 1256, 891, 765, 750, 702, 650 $cm^{-1}$.

**HRMS for $C_{24}H_{18}N^+$ $(M+H)^+$**: calcd. 320.14338, found 320.14355.




**3b**

8-(p-tolyl)-3H-benzo[d]naphtho[1,2-b]azepine

**3b** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1).

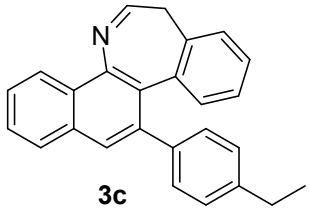
Yellow solid, mp 94-96 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.55 – 8.53 (m, 1H), 8.03 (t, *J* = 5.0 Hz, 1H), 7.84 – 7.82 (m, 1H), 7.70 (s, 1H), 7.56 – 7.52 (m, 2H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.18 – 7.15 (m, 1H), 7.01 – 6.94 (m, 5H), 6.81 (t, *J* = 7.5 Hz, 1H), 3.68 – 3.65 (m, 1H), 2.91 – 2.87 (m, 1H), 2.29 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.5, 142.0, 140.1, 139.9, 136.7, 136.1, 134.4, 133.1, 132.7, 129.9, 128.9, 128.8, 127.6, 127.6, 127.2, 127.1, 126.7, 126.3, 126.2, 125.2, 125.0, 38.0, 21.2.

**IR (KBr):** 2971, 1627, 1510, 1478, 1378, 1069, 819, 749, 686 $cm^{-1}$.

**HRMS for $C_{25}H_{20}N^+$ $(M+H)^+$**: calcd. 334.15903, found 334.15906.




**3c**

8-(4-ethylphenyl)-3H-benzo[d]naphtho[1,2-b]azepine

**3c** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1).

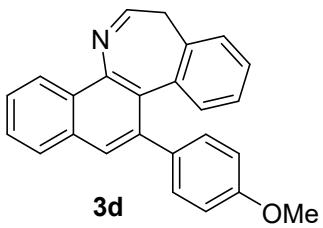
Yellow solid, mp 114-116 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.46 – 8.44 (m, 1H), 7.96 (t, *J* = 5.0 Hz, 1H), 7.77 – 7.76 (m, 1H), 7.63 (s, 1H), 7.49 – 7.45 (m, 2H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.0 Hz, 1H), 7.00 – 6.94 (m, 4H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 3.64 – 3.60 (m, 1H), 2.85 – 2.82 (m, 1H), 2.52 (q, *J* = 7.5 Hz, 2H), 1.13 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.5, 142.6, 142.0, 140.3, 139.9, 136.7, 134.5, 133.2, 132.8, 130.0, 128.9, 127.6, 127.6, 127.6, 127.3, 127.1, 126.8, 126.3, 126.2, 125.2, 125.0, 38.1, 28.6, 15.6.

**IR (KBr):** 2970, 1625, 1450, 1373, 1170, 885, 831, 750, 685 $cm^{-1}$.

**HRMS for $C_{26}H_{22}N^+$ $(M+H)^+$**: calcd. 348.17468, found 348.17462.




**3d**

8-(4-methoxyphenyl)-3H-benzo[d]naphtho[1,2-b]azepine

**3d** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1).

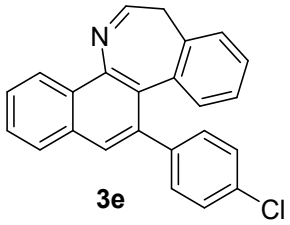
Yellow solid, mp 162-164 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.45 – 8.43 (m, 1H), 7.96 – 7.93 (m, 1H), 7.75 – 7.74 (m, 1H), 7.60 (s, 1H), 7.46 – 7.45 (m, 2H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.0 Hz, 1H), 6.98 – 6.94 (m, 2H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 2H), 3.65 (s, 3H), 3.61 – 3.58 (m, 1H), 2.82 – 2.79 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.5, 158.4, 142.0, 139.5, 136.7, 135.4, 134.4, 133.1, 132.8, 131.1, 128.8, 127.6, 127.6, 127.1, 127.1, 126.7, 126.3, 126.2, 125.2, 125.1, 113.6, 55.3, 38.1.

**IR (KBr):** 2964, 1625, 1605, 1510, 1280, 1247, 1181, 1030, 871, 832, 758 cm$^{-1}$.

**HRMS for $C_{25}H_{20}NO^+$ $(M+H)^+$**: calcd. 350.15394, found 350.15393.




**3e**

8-(4-chlorophenyl)-3H-benzo[d]naphtho[1,2-b]azepine

**3e** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1).

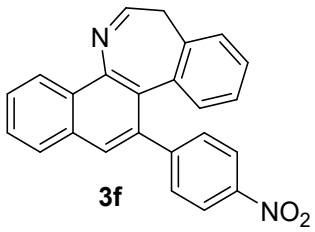
Yellow solid, mp 112-114 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.45 – 8.43 (m, 1H), 7.94 (t, *J* = 5.0 Hz, 1H), 7.75 – 7.73 (m, 1H), 7.56 (s, 1H), 7.49 – 7.44 (m, 2H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.12 – 7.07 (m, 3H), 6.98 – 6.94 (m, 2H), 6.80 – 6.73 (m, 2H), 3.61 – 3.58 (m, 1H), 2.79 – 2.76 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.6, 142.2, 141.5, 138.6, 136.8, 134.0, 133.1, 132.6, 132.6, 131.3, 129.0, 128.3, 127.8, 127.7, 127.3, 126.6, 126.4, 126.3, 125.3, 125.2, 38.0.

**IR (KBr):** 2969, 1626, 1488, 1377, 1090, 1012, 826, 758, 727, 683 cm$^{-1}$.

**HRMS for $C_{24}H_{17}ClN^+$ $(M+H)^+$**: calcd. 354.10440, found 354.10498.




**3f**

8-(4-nitrophenyl)-3H-benzo[d]naphtho[1,2-b]azepine

**3f** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1 to 10:1).

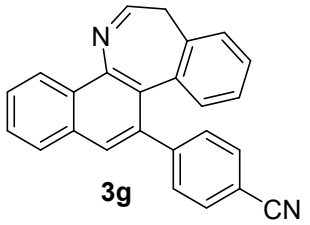
Yellow solid, mp 122-124 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.48 – 8.47 (m, 1H), 8.00 (t, *J* = 5.0 Hz, 3H), 7.83 – 7.81 (m, 1H), 7.64 (s, 1H), 7.56 – 7.52 (m, 2H), 7.25 – 7.15 (m, 4H), 6.78 – 6.72 (m, 2H), 3.73 – 3.69 (m, 1H), 2.87 – 2.84 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.9, 150.1, 146.4, 142.4, 137.6, 136.9, 133.6, 133.1, 132.5, 130.8, 129.4, 128.2, 127.9, 127.7, 127.6, 127.3, 126.8, 125.9, 125.5, 125.3, 123.4, 38.1.

**IR (KBr):** 2969, 1594, 1512, 1340, 1105, 849, 757, 707, 650 cm$^{-1}$.

**HRMS for $C_{24}H_{17}N_2O_2^+$ (M+H)$^+$**: calcd. 365.12845, found 365.12854.




**3g**

4-(3H-benzo[d]naphtho[1,2-b]azepin-8-yl)benzonitrile

**3g** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1).

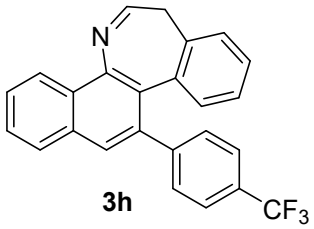
Yellow solid, mp 112-114 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.87 (dd, *J* = 4.0, 2.0 Hz, 1H), 8.79 – 8.76 (m, 1H), 7.98 (t, *J* = 5.0 Hz, 1H), 7.93 (s, 1H), 7.39 – 7.36 (m, 1H), 7.20 – 7.09 (m, 7H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.76 – 6.73 (m, 1H), 3.69 – 3.66 (m, 1H), 2.84 – 2.81 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 159.5, 151.3, 147.5, 143.6, 142.2, 141.8, 136.5, 133.8, 133.7, 133.0, 130.0, 128.3, 128.2, 128.0, 127.3, 126.9, 126.4, 125.2, 124.4, 121.3, 38.1.

**IR (KBr):** 2968, 2224, 1626, 1603, 1479, 1377, 1049, 837, 748, 686 cm$^{-1}$.

**HRMS for $C_{25}H_{17}N_2^+$ (M+H)$^+$**: calcd. 345.13862, found 345.13907.




**3h**

8-(4-(trifluoromethyl)phenyl)-3H-benzo[d]naphtho[1,2-b]azepine

**3h** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1 to 10:1).

Yellow solid, mp 135-137 °C.

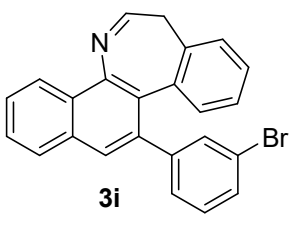
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.48 – 8.46 (m, 1H), 7.99 (t, *J* = 5.0 Hz, 1H), 7.81 – 7.79 (m, 1H), 7.63 (s, 1H), 7.55 – 7.49 (m, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.23 – 7.13 (m, 4H), 6.78 – 6.74 (m, 2H), 3.69 – 3.66 (m, 1H), 2.87 – 2.83 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.8, 146.8, 142.3, 138.5, 136.9, 133.8, 133.1, 132.6, 130.4, 129.2, 128.7 (q, $J_{C\text{-}F}$ = 32.8 Hz), 128.0, 127.8, 127.6, 127.4, 126.9, 126.6, 126.2, 125.4, 125.3, 125.0 (q, $J_{C\text{-}F}$ = 2.5 Hz), 124.4 (q, $J_{C\text{-}F}$ = 273.4 Hz), 38.1.

**$^{19}$F NMR (470 MHz, $CDCl_3$):** δ -62.2.

**IR (KBr):** 2987, 1625, 1323, 1164, 1108, 1063, 837, 760, 678 cm$^{-1}$.

**HRMS for $C_{25}H_{17}F_3N^+$ (M+H)$^+$**: calcd. 388.13076, found 388.13089.




**3i**

8-(3-bromophenyl)-3H-benzo[d]naphtho[1,2-b]azepine

**3i** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1).

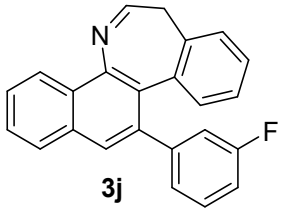
White solid, mp 194-196 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.55 (d, *J* = 1.5 Hz, 1H), 8.06 (t, *J* = 5.0 Hz, 1H), 7.78 (d, *J* = 3.5 Hz, 1H), 7.69 (s, 1H), 7.50 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.29 – 7.20 (m, 4H), 7.16 – 7.12 (m, 2H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.84 – 6.81 (m, 1H), 3.77 – 3.73 (m, 1H), 2.93 – 2.89 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 159.1, 142.7, 141.3, 140.3, 136.7, 134.0, 133.1, 132.3, 130.9, 130.1, 129.8, 129.2, 128.2, 128.0, 127.6, 126.9, 126.7, 126.4, 125.2, 124.4, 38.1.

**IR (KBr):** 2972, 1632, 1471, 1404, 1376, 1253, 1172, 1063, 887, 790, 761, 719 $cm^{-1}$.

**HRMS for $C_{24}H_{17}BrN^+$ $(M+H)^+$**: calcd. 398.05389, found 398.05377.




**3j**

8-(3-fluorophenyl)-3H-benzo[d]naphtho[1,2-b]azepine

**3j** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1).

White solid, mp 79-81 °C.

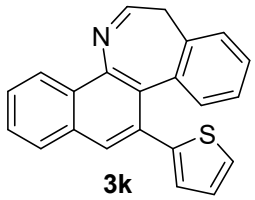
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.56 – 8.54 (m, 1H), 8.04 (t, *J* = 5.0 Hz, 1H), 7.84 (dd, *J* = 7.0, 1.5 Hz, 1H), 7.70 (s, 1H), 7.59 – 7.54 (m, 2H), 7.25 (d, *J* = 7.0 Hz, 1H), 7.21 – 7.18 (m, 1H), 7.16 – 7.12 (m, 1H), 6.93 – 6.82 (m, 5H), 3.71 – 3.68 (m, 1H), 2.90 – 2.86 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 162.6 (d, $J_{C\text{-}F}$ = 245.7 Hz), 158.7, 145.3 (d, $J_{C\text{-}F}$ = 7.6 Hz), 142.2, 138.6 (d, $J_{C\text{-}F}$ = 2.5 Hz), 136.8, 134.0, 132.9, 132.6, 129.5 (d, $J_{C\text{-}F}$ = 7.6 Hz), 129.1, 127.9, 127.7, 127.3, 127.3, 126.7, 126.5, 126.3, 125.9, 125.3, 125.2, 117.9 (d, $J_{C\text{-}F}$ = 21.4 Hz), 113.4 (d, $J_{C\text{-}F}$ = 21.4 Hz), 38.0.

**$^{19}$F NMR (470 MHz, $CDCl_3$):** δ -113.5.

**IR (KBr):** 3058, 1626, 1578, 1480, 1261, 1176, 954, 861, 785, 749, 702 $cm^{-1}$.

**HRMS for $C_{24}H_{17}FN^+$ $(M+H)^+$**: calcd. 338.13395, found 338.13406.




**3k**

8-(thiophen-2-yl)-3H-benzo[d]naphtho[1,2-b]azepine

**3k** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1).

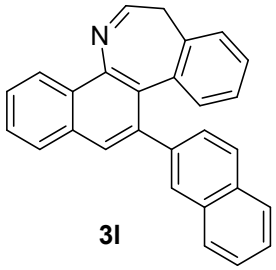
White solid, mp 133-135 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.45 – 8.43 (m, 1H), 7.96 (t, *J* = 5.0 Hz, 1H), 7.76 – 7.75 (m, 2H), 7.49 – 7.45 (m, 2H), 7.20 – 7.15 (m, 2H), 7.11 – 7.09 (m, 2H), 6.86 – 6.83 (m, 1H), 6.80 – 6.78 (m, 1H), 6.63 – 6.62 (m, 1H), 3.62 – 3.39 (m, 1H), 2.83 – 2.79 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.9, 145.0, 142.0, 136.9, 134.1, 132.6, 132.4, 132.1, 129.3, 128.0, 127.9, 127.7, 127.3, 127.2, 127.0, 126.9, 126.7, 126.3, 125.7, 125.3, 125.2, 38.0.

**IR (KBr):** 2970, 1624, 1477, 1254, 1047, 835, 818, 750, 699 $cm^{-1}$.

**HRMS for $C_{22}H_{16}NS^+$ $(M+H)^+$**: calcd. 326.09980, found 326.09976.




**3l**

8-(naphthalen-2-yl)-3H-benzo[d]naphtho[1,2-b]azepine

**3l** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1 to 10:1).

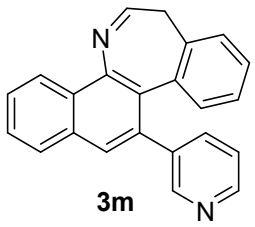
Yellow solid, mp 116-118 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.48 – 8.47 (m, 1H), 7.96 (t, *J* = 5.0 Hz, 1H), 7.78 – 7.76 (m, 2H), 7.72 (s, 1H), 7.70 – 7.68 (m, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.44 (m, 3H), 7.36 – 7.30 (m, 2H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.58 (t, *J* = 7.5 Hz, 1H), 3.64 – 3.61 (m, 1H), 2.87 – 2.84 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.6, 142.1, 140.8, 139.8, 136.7, 134.3, 133.7, 133.1, 132.8, 132.1, 129.0, 128.7, 128.3, 128.1, 127.8, 127.7, 127.2, 127.1, 126.6, 126.5, 126.4, 126.1, 125.9, 125.3, 38.1.

**IR (KBr):** 2969, 1626, 1504, 1477, 1253, 1067, 854, 818, 746, 690 $cm^{-1}$.

**HRMS for $C_{28}H_{20}N^+$ $(M+H)^+$**: calcd. 370.15903, found 370.15918.




**3m**

8-(pyridin-3-yl)-3H-benzo[d]naphtho[1,2-b]azepine

**3m** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1).

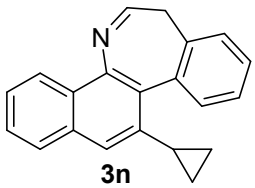
Yellow solid, mp 92-94 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.43 (d, *J* = 7.5 Hz, 1H), 8.34 – 8.30 (m, 2H), 7.90 (t, *J* = 5.0 Hz, 1H), 7.73 – 7.71 (m, 1H), 7.55 (s, 1H), 7.47 – 7.42 (m, 2H), 7.23 – 7.20 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.07 – 7.04 (m, 1H), 6.97 – 6.95 (m, 1H), 6.70 (d, *J* = 4.0 Hz, 2H), 3.58 – 3.55 (m, 1H), 2.76 – 2.73 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.7, 150.4, 147.6, 142.3, 138.6, 137.1, 136.9, 135.9, 133.5, 133.1, 132.5, 129.1, 127.9, 127.7, 127.5, 127.3, 126.8, 126.6, 126.2, 125.2, 125.2, 122.8, 37.9.

**IR (KBr):** 3022, 1626, 1477, 1404, 1321, 1024, 898, 760, 750, 713, 655 $cm^{-1}$.

**HRMS for $C_{23}H_{17}N_2^+$ $(M+H)^+$**: calcd. 321.13862, found 321.13840.



**3n**

8-cyclopropyl-3H-benzo[d]naphtho[1,2-b]azepine

**3n** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1 to 10:1).

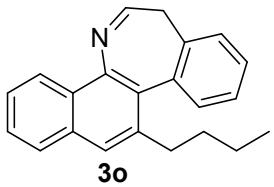
Yellow oil.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.38 – 8.37 (m, 1H), 7.93 (t, *J* = 5.0 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.67 – 7.65 (m, 1H), 7.42 – 7.38 (m, 2H), 7.28 – 7.17 (m, 4H), 3.52 – 3.48 (m, 1H), 2.66 – 2.62 (m, 1H), 2.03 – 1.97 (m, 1H), 1.02 – 0.98 (m, 1H), 0.79 – 0.74 (m, 1H), 0.72 – 0.67 (m, 2H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.7, 141.3, 139.2, 137.3, 134.0, 132.8, 132.1, 128.7, 127.9, 127.9, 127.0, 126.8, 126.5, 125.6, 125.1, 125.0, 120.6, 38.0, 16.2, 13.2, 8.9.

**IR (KBr):** 3004, 1626, 1479, 1427, 1377, 1020, 955, 748, 689 $cm^{-1}$.

**HRMS for $C_{21}H_{18}N^+$ $(M+H)^+$**: calcd. 284.14338, found 284.14322.



**3o**

8-butyl-3H-benzo[d]naphtho[1,2-b]azepine

**3o** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1 to 10:1).

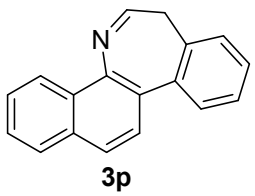
Yellow oil.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.39 – 8.37 (m, 1H), 7.89 – 7.87 (m, 1H), 7.68 – 7.66 (m, 1H), 7.49 (s, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.22 (t, *J* = 7.0 Hz, 1H), 7.16 – 7.11 (m, 2H), 2.43 – 3.40 (m, 1H), 3.01 – 2.95 (m, 1H), 2.71 – 2.65 (m, 1H), 2.61 – 2.58 (m, 1H), 1.36 – 1.20 (m, 2H), 1.08 – 1.00 (m, 2H), 0.63 (t, *J* = 7.0 Hz, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.9, 141.6, 138.5, 137.5, 134.0, 132.9, 131.1, 128.0, 127.9, 127.9, 127.0, 126.7, 126.5, 125.5, 125.4, 125.2, 125.0, 37.8, 34.5, 33.4, 22.4, 13.9.

**IR (KBr):** 2926, 1625, 1479, 1452, 1376, 1008, 926, 853, 749, 646 $cm^{-1}$.

**HRMS for $C_{22}H_{22}N^+$ $(M+H)^+$**: calcd. 300.17468, found 300.17484.



**3p**

3H-benzo[d]naphtho[1,2-b]azepine

**3p** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1).

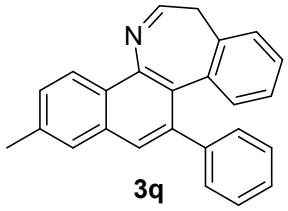
Yellow oil.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.47 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.94 (t, *J* = 5.0 Hz, 1H), 7.85 – 7.83 (m, 1H), 7.79 – 7.77 (m, 2H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.42 – 7.38 (m, 2H), 7.31 – 7.29 (m, 1H), 3.72 – 3.69 (m, 1H), 2.65 – 2.62 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 156.6, 141.4, 136.9, 135.6, 133.0, 129.9, 129.2, 128.4, 127.7, 127.5, 127.4, 127.2, 126.9, 126.8, 126.4, 125.1, 125.0, 28.2

**IR (KBr):** 2924, 1630, 1481, 1377, 1285, 1079, 873, 819, 760, 736, 679 $cm^{-1}$.

**HRMS for $C_{18}H_{14}N^+$ $(M+H)^+$**: calcd. 244.11208, found 244.11237.




**3q**

11-methyl-8-phenyl-3H-benzo[d]naphtho[1,2-b]azepine

**3q** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1).

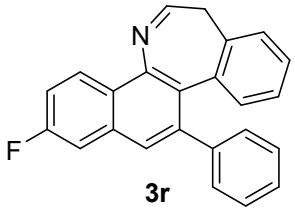
Yellow solid, mp 222-224 °C.

**$^{1}$H NMR (500 MHz, $CDCl_3$)** δ 8.43 (d, $J$ = 9.0 Hz, 1H), 8.06 (t, $J$ = 5.0 Hz, 1H), 7.65 (s, 2H), 7.41 (dd, $J$ = 8.5, 1.0 Hz, 1H), 7.28 – 7.15 (m, 7H), 6.92 (d, $J$ = 7.5 Hz, 1H), 6.82 (t, $J$ = 7.5 Hz, 1H), 3.74 – 3.71 (m, 1H), 2.96 – 2.92 (m, 1H), 2.55 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.5, 143.2, 142.0, 140.0, 137.0, 136.7, 134.4, 133.2, 133.0, 130.1, 128.7, 128.1, 127.6, 127.1, 126.9, 126.8, 126.5, 126.3, 126.0, 125.1, 125.0, 38.1, 21.8.

**IR (KBr):** 2919, 1624, 1480, 1380, 1073, 904, 831, 762, 701, 640 $cm^{-1}$.

**HRMS for $C_{25}H_{20}N^+$ $(M+H)^+$**: calcd. 334.15903, found 334.15900.




**3r**

11-fluoro-8-phenyl-3H-benzo[d]naphtho[1,2-b]azepine

**3r** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1).

Yellow solid, mp 198-200 °C.

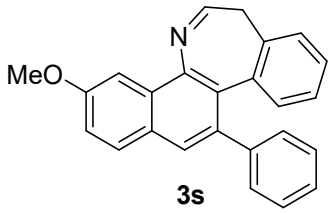
**$^{1}$H NMR (500 MHz, $CDCl_3$)** δ 8.57 – 8.54 (m, 1H), 8.06 (t, $J$ = 5.0 Hz, 1H), 7.65 (s, 1H), 7.46 (dd, $J$ = 9.5, 2.0 Hz, 1H), 7.32 (td, $J$ = 8.5, 2.5 Hz, 1H), 7.27 (d, $J$ = 7.5 Hz, 1H), 7.22 – 7.14 (m, 6H), 6.91 (d, $J$ = 8.0 Hz, 1H), 6.82 (t, $J$ = 7.5 Hz, 1H), 3.75 – 3.72 (m, 1H), 2.94 – 2.91 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 161.7 (d, $J_{C\text{-}F}$ = 248.2 Hz), 158.9, 142.7, 142.1, 141.3, 136.6, 134.1, 133.7 (d, $J_{C\text{-}F}$ = 10.1 Hz), 133.1, 130.0, 128.1, 128.1, 127.7, 126.7, 126.5 (d, $J_{C\text{-}F}$ = 5.0 Hz), 126.4, 126.1, 125.9, 125.1, 116.2 (d, $J_{C\text{-}F}$ = 23.9 Hz), 110.8 (d, $J_{C\text{-}F}$ = 20.2 Hz), 38.1.

**$^{19}$F NMR (470 MHz, $CDCl_3$):** δ -114.0.

**IR (KBr):** 2980, 1625, 1556, 1480, 1382, 1219, 1144, 963, 892, 837, 756, 702 $cm^{-1}$.

**HRMS for $C_{24}H_{17}FN^+$ $(M+H)^+$**: calcd. 338.13395, found 338.13339.




**3s**

12-methoxy-8-phenyl-3H-benzo[d]naphtho[1,2-b]azepine

**3s** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1).

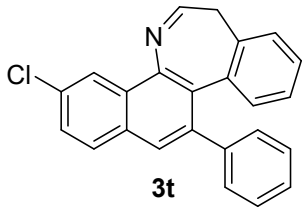
Yellow solid, mp 193-195 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.45 (d, *J* = 9.0 Hz, 1H), 8.02 (t, *J* = 5.0 Hz, 1H), 7.62 (s, 1H), 7.24 – 7.14 (m, 9H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.79 (t, *J* = 7.5 Hz, 1H), 3.90 (s, 3H), 3.69 – 3.66 (m, 1H), 2.93 – 2.90 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.8, 158.5, 143.1, 142.1, 140.6, 136.5, 134.4, 134.1, 133.1, 130.1, 128.1, 127.4, 127.0, 126.5, 126.4, 126.3, 125.0, 124.8, 124.0, 118.6, 106.0, 55.4, 38.1.

**IR (KBr):** 2929, 1620, 1479, 1388, 1230, 1169, 1024, 900, 832, 773, 705 $cm^{-1}$.

**HRMS for $C_{25}H_{20}NO^+$ $(M+H)^+$**: calcd. 350.15394, found 350.15396.




**3t**

12-chloro-8-phenyl-3H-benzo[d]naphtho[1,2-b]azepine

**3t** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1).

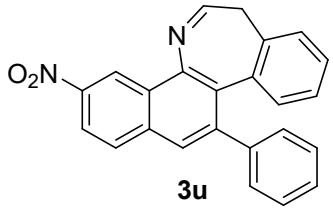
White solid, mp 193-195 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.55 (d, *J* = 1.5 Hz, 1H), 8.06 (t, *J* = 5.0 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.69 (s, 1H), 7.50 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.23 – 7.14 (m, 6H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 3.77 – 3.73 (m, 1H), 2.93 – 2.89 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 159.1, 142.7, 141.3, 140.3, 136.7, 134.0, 133.1, 132.3, 130.9,, 130.1, 129.8, 129.2, 128.2, 128.0, 127.6, 126.9, 126.7, 126.4, 125.2, 124.4, 38.1.

**IR (KBr):** 2973, 1626, 1473, 1375, 1085, 1037, 885, 806, 770, 716, 701 $cm^{-1}$.

**HRMS for $C_{24}H_{17}ClN^+$ $(M+H)^+$**: calcd. 354.10440, found 354.10437.




**3u**

12-nitro-8-phenyl-3H-benzo[d]naphtho[1,2-b]azepine

**3u** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1).

Yellow solid, mp 250-252 °C.

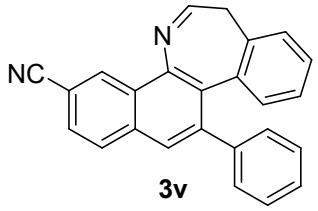
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 9.45 (d, *J* = 2.0 Hz, 1H), 8.25 (dd, *J* = 9.0, 2.5 Hz, 1H), 8.07 (t, *J* = 5.0

Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.72 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.09 (m, 6H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.81 – 6.77 (m, 1H), 3.78 – 3.75 (m, 1H), 2.87 – 2.84 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 160.2, 145.8, 144.3, 143.5, 142.1, 136.7, 135.3, 133.6, 133.0, 130.0, 129.1, 128.5, 128.4, 128.4, 128.3, 127.3, 126.7, 126.7, 125.4, 122.7, 120.7, 38.2.

**IR (KBr):** 2968, 1619, 1515, 1336, 1099, 920, 898, 777, 741, 703 $cm^{-1}$.

**HRMS for $C_{24}H_{17}N_2O_2^+$ $(M+H)^+$**: calcd. 365.12845, found 365.12836.




**3v**

8-phenyl-3H-benzo[d]naphtho[1,2-b]azepine-12-carbonitrile

**3v** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1).

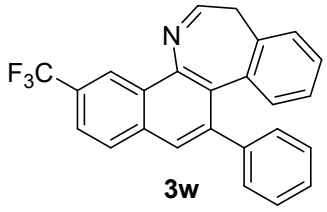
Yellow solid, mp 224-226 °C.

**$^{1}$H NMR (500 MHz, $CDCl_3$)** δ 8.90 (s, 1H), 8.02 (t, *J* = 5.0 Hz, 1H), 7.84 (t, *J* = 8.5 Hz, 1H), 7.66 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.07 (m, 7H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.77 (t, *J* = 7.5 Hz, 1H), 3.75 – 3.71 (m, 1H), 2.84 – 2.81 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 160.0, 143.5, 142.2, 142.1, 136.7, 134.0, 133.6, 133.0, 131.9, 129.9, 128.7, 128.3, 128.3, 128.3, 127.7, 127.2, 126.8, 126.6, 125.3, 119.7, 109.4, 38.1.

**IR (KBr):** 2921, 2223, 1720, 1631, 1374, 1072, 918, 889, 817, 781, 742, 707 $cm^{-1}$.

**HRMS for $C_{25}H_{17}N_2^+$ $(M+H)^+$**: calcd. 345.13862, found 345.13913.




**3w**

8-phenyl-12-(trifluoromethyl)-3H-benzo[d]naphtho[1,2-b]azepine

**3w** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1 to 10:1).

Yellow solid, mp 202-204 °C.

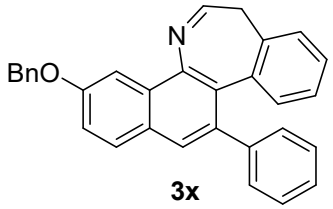
**$^{1}$H NMR (500 MHz, $CDCl_3$)** δ 8.82 (s, 1H), 8.03 (t, *J* = 5.0 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.17 – 7.08 (m, 6H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.77 (t, *J* = 7.5 Hz, 1H), 3.73 – 3.70 (m, 1H), 2.86 – 2.83 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 159.6, 142.6, 142.5, 142.4, 136.8, 134.0, 133.9, 133.1, 130.0, 128.6, 128.3, 128.2, 128.1, 127.9, 127.0, 126.9, 126.5, 125.3, 124.7 (q, $J_{C\text{-}F}$ = 272.2 Hz), 123.4 (q, $J_{C\text{-}F}$ = 5.0 Hz), 122.8 (q, $J_{C\text{-}F}$ = 3.8 Hz), 38.1.

**$^{19}$F NMR (470 MHz, $CDCl_3$):** δ -61.9.

**IR (KBr):** 2970, 1632, 1431, 1326, 1298, 1248, 1124, 1077, 914, 889, 823, 755, 707 $cm^{-1}$.

**HRMS for $C_{25}H_{17}F_3N^+$ $(M+H)^+$**: calcd. 388.13076, found 388.13092.




**3x**

12-(benzyloxy)-8-phenyl-3H-benzo[d]naphtho[1,2-b]azepine

**3x** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1).

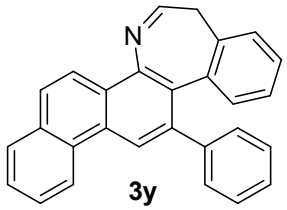
Yellow solid, mp 93-95 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.01 (t, *J* = 5.0 Hz, 1H), 7.89 (d, *J* = 7.0 Hz, 1H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.61 (s, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.0 Hz, 2H), 7.29 – 7.21 (m, 4H), 7.15 – 7.08 (m, 5H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 5.21 – 5.15 (m, 2H), 3.69 – 3.66 (m, 1H), 2.91 – 2.88 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.5, 157.5, 143.2, 141.2, 137.7, 137.1, 136.8, 134.5, 133.3, 130.2, 130.2, 129.4, 128.7, 128.3, 128.2, 128.1, 128.0, 127.7, 127.3, 127.1, 126.4, 126.3, 125.1, 120.1, 104.7, 70.3, 38.2.

**IR (KBr):** 3028, 1619, 1495, 1381, 1254, 1217, 1193, 1012, 885, 749, 698 $cm^{-1}$.

**HRMS for $C_{31}H_{24}NO^+$ $(M+H)^+$**: calcd. 426.18524, found 426.18542.




**3y**

14-phenyl-9H-benzo[d]phenanthro[1,2-b]azepine

**3y** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1 to 10:1).

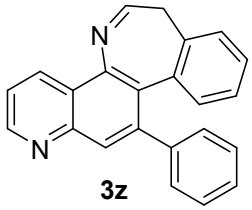
White solid, mp 198-200 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.70 (d, *J* = 7.5 Hz, 1H), 8.55 – 8.53 (m, 2H), 8.08 (t, *J* = 5.0 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.24 – 7.15 (m, 7H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.80 (t, *J* = 7.5 Hz, 1H), 3.66 – 3.63 (m, 1H), 2.95 – 2.92 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 159.1, 143.4, 142.5, 140.3, 137.1, 134.4, 133.2, 132.5, 130.3, 130.0, 129.5, 128.7, 128.2, 127.7, 127.5, 127.2, 127.0, 126.9, 126.7, 126.6, 126.3, 125.1, 123.4, 123.0, 122.3, 37.9.

**IR (KBr):** 2976, 1628, 1509, 1371, 1285, 1245, 1073, 879, 836, 765, 755, 702 $cm^{-1}$.

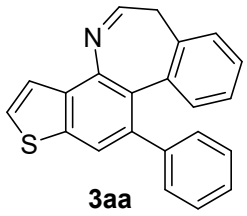
**HRMS for $C_{28}H_{20}N^+$ $(M+H)^+$**: calcd. 370.15903, found 370.15900.




**3z**

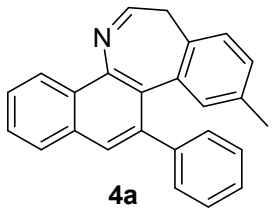
12-phenyl-7H-benzo[4,5]azepino[2,3-f]quinoline

**3z** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1).
Yellow solid, mp 87-89 °C.
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.87 (dd, *J* = 4.0, 2.0 Hz, 1H), 8.79 – 8.77 (m, 1H), 7.98 (t, *J* = 5.0 Hz, 1H), 7.93 (s, 1H), 7.39 – 7.36 (m, 1H), 7.20 – 7.07 (m, 7H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.76 – 6.73 (m, 1H), 3.69 – 3.66 (m, 1H), 2.84 – 2.81 (m, 1H).
**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 159.5, 151.3, 147.5, 143.6, 142.2, 141.8, 136.5, 133.8, 133.7, 133.0, 130.0, 128.3, 128.2, 128.0, 127.3, 126.9, 126.4, 125.2, 124.4, 121.3, 38.1.
**IR (KBr):** 2969, 1628, 1598, 1462, 1375, 1071, 1052, 886, 825, 770, 759, 700 $cm^{-1}$.
**HRMS for $C_{23}H_{17}N_2^+$ (M+H)$^+$**: calcd. 321.13862, found 321.13904.



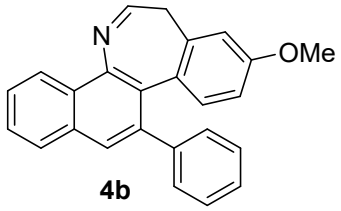
**3aa**

11-phenyl-6H-benzo[d]thieno[2',3':5,6]benzo[1,2-b]azepine
**3aa** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1).
Yellow solid, mp 92-94 °C.
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.98 (t, *J* = 5.0 Hz, 1H), 7.70 (s, 1H), 7.67 (d, *J* = 6.0 Hz, 1H), 7.41 (d, *J* = 5.0 Hz, 1H), 7.19 – 7.04 (m, 7H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.75 – 6.72 (m, 1H), 3.63 – 3.60 (m, 1H), 2.95 – 2.92 (m, 1H).
**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 160.0, 143.0, 141.2, 139.3, 139.1, 136.9, 135.4, 134.4, 133.3, 130.3, 128.2, 127.5, 126.6, 126.5, 126.4, 126.1, 125.2, 123.2, 121.7, 38.0.
**IR (KBr):** 2968, 1625, 1486, 1427, 1321, 1074, 829, 757, 735, 699 $cm^{-1}$.
**HRMS for $C_{22}H_{16}NS^+$ (M+H)$^+$**: calcd. 326.09980, found 326.10010.



**4a**

6-methyl-8-phenyl-3H-benzo[d]naphtho[1,2-b]azepine
**4a** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1).
White solid, mp 80-82 °C.
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.46 – 8.44 (m, 1H), 7.98 (t, *J* = 5.0 Hz, 1H), 7.79 – 7.78 (m, 1H), 7.65 (s, 1H), 7.51 – 7.47 (m, 2H), 7.16 – 7.06 (m, 6H), 6.92 (d, *J* = 8.0 Hz, 1H), 7.63 (s, 1H), 3.61 – 3.58 (m, 1H), 2.82 – 2.78 (m, 1H), 1.84 (s, 3H).
**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.8, 143.1, 142.1, 140.1, 134.6, 134.2, 134.0, 132.7, 130.1, 129.0, 128.5, 128.0, 127.7, 127.1, 127.1, 126.7, 126.5, 126.4, 126.1, 125.3, 37.7, 20.9.
**IR (KBr):** 3021, 2919, 1630, 1481, 1071, 888, 815, 791, 700 $cm^{-1}$.
**HRMS for $C_{25}H_{20}N^+$ (M+H)$^+$**: calcd. 334.15903, found 334.15939.




**4b**

5-methoxy-8-phenyl-3H-benzo[d]naphtho[1,2-b]azepine

**4b** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1).

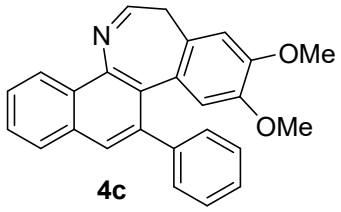
White solid, mp 144-146 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.52 (d, *J* = 8.0 Hz, 1H), 7.99 (t, *J* = 5.0 Hz, 1H), 7.83 – 7.81 (m, 1H), 7.68 (s, 1H), 7.56 – 7.50 (m, 2H), 7.22 – 7.15 (m, 5H), 6.81 (d, *J* = 8.5 Hz, 1H), 6.75 (d, *J* = 2.5 Hz, 1H), 6.36 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.69 (s, 3H), 3.63 – 3.60 (m, 1H), 2.90 – 2.86 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 159.4, 158.0, 143.1, 141.6, 139.9, 137.9, 134.2, 132.4, 130.0, 129.0, 128.1, 127.6, 127.3, 127.1, 126.9, 126.4, 126.3, 125.1, 111.4, 110.9, 55.2, 38.3.

**IR (KBr):** 2969, 1602, 1499, 1261, 1244, 1153, 1124, 1050, 1007, 897, 815, 770, 755 $cm^{-1}$.

**HRMS for $C_{25}H_{20}NO^+$ $(M+H)^+$**: calcd. 350.15394, found 350.15341.




**4c**

5,6-dimethoxy-8-phenyl-3H-benzo[d]naphtho[1,2-b]azepine

**4c** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1 to 10:1).

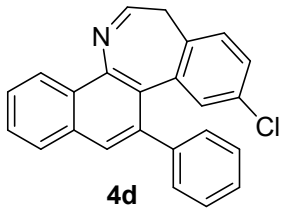
Yellow solid, mp 108-110 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.53 (d, *J* = 8.0 Hz, 1H), 8.00 (t, *J* = 5.0 Hz, 1H), 7.85 – 7.83 (m, 1H), 7.71 (s, 1H), 7.58 – 7.53 (m, 2H), 7.24 – 7.18 (m, 5H), 6.74 (s, 1H), 6.38 (s, 1H), 3.87 (s, 3H), 3.63 – 3.60 (m, 1H), 3.18 (s, 3H), 2.79 – 2.76 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 157.5, 148.9, 146.1, 143.4, 141.7, 139.8, 132.3, 130.0, 129.2, 129.0, 128.3, 127.6, 127.1, 126.9, 126.5, 126.4, 126.4, 126.2, 125.2, 116.1, 108.8, 55.8, 55.4, 37.5.

**IR (KBr):** 2954, 1604, 1510, 1463, 1346, 1260, 1209, 1124, 1043, 868, 782, 753, 701 $cm^{-1}$.

**HRMS for $C_{26}H_{22}NO_2^+$ $(M+H)^+$**: calcd. 380.16451, found 380.16458.




**4d**

6-chloro-8-phenyl-3H-benzo[d]naphtho[1,2-b]azepine

**4d** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1).

Yellow solid, mp 140-142 °C.

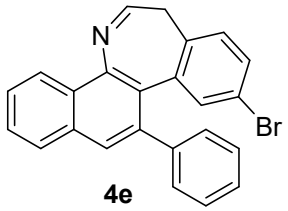
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.44 (dd, *J* = 6.0, 3.5 Hz, 1H), 7.97 (t, *J* = 5.0 Hz, 1H), 7.80 – 7.78 (m,

1H), 7.66 (s, 1H), 7.52 – 7.50 (m, 2H), 7.18 – 7.07 (m, 7H), 6.81 (d, *J* = 2.0 Hz, 1H), 3.64 – 3.61 (m, 1H), 2.82 – 2.79 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.4, 142.4, 142.4, 139.7, 135.8, 135.1, 132.9, 132.9, 130.9, 130.1, 128.8, 128.3, 127.7, 127.7, 127.5, 127.5, 127.4, 126.9, 126.6, 125.3, 125.3, 37.5.

**IR (KBr):** 2962, 1625, 1471, 1372, 1260, 1049, 883, 809, 753, 701 $cm^{-1}$.

**HRMS for $C_{24}H_{17}ClN^+$ $(M+H)^+$**: calcd. 354.10440, found 354.10486.




**4e**

6-bromo-8-phenyl-3H-benzo[d]naphtho[1,2-b]azepine

**4e** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1).

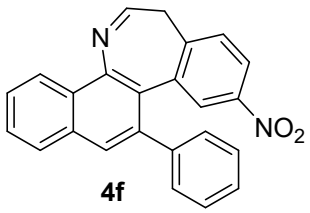
Yellow solid, mp 95-97 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.45 – 8.42 (m, 1H), 7.97 (t, *J* = 5.0 Hz, 1H), 7.81 – 7.78 (m, 1H), 7.66 (s, 1H), 7.52 – 7.49 (m, 2H), 7.24 – 7.19 (m, 4H), 7.05 (d, *J* = 8.5 Hz, 3H), 6.96 (d, *J* = 2.0 Hz, 1H), 3.63 – 3.60 (m, 1H), 2.80 – 2.76 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.3, 142.4, 142.3, 139.7, 136.1, 135.9, 135.6, 132.9, 130.6, 130.1, 128.8, 128.3, 127.8, 127.7, 127.5, 127.4, 127.0, 126.6, 125.3, 125.2, 118.8, 37.5.

**IR (KBr):** 2971, 1628, 1474, 1324, 1080, 886, 807, 765, 700 $cm^{-1}$.

**HRMS for$C_{24}H_{17}BrN^+$ $(M+H)^+$**: calcd. 398.05389, found 398.05408.




**4f**

6-nitro-8-phenyl-3H-benzo[d]naphtho[1,2-b]azepine

**4f** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 5:1 to 2:1).

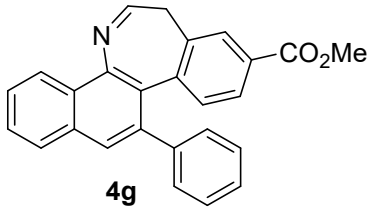
Yellow solid, mp 223-225 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.44 – 8.41 (m, 1H), 7.94 – 7.89 (m, 2H), 7.77 – 7.75 (m, 1H), 7.70 (d, *J* = 2.5 Hz, 1H), 7.66 (s, 1H), 7.52 – 7.49 (m, 2H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.13 – 7.08 (m, 5H), 3.78 – 3.75 (m, 1H), 2.90 – 2.86 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 157.1, 145.2, 142.5, 142.3, 141.7, 139.4, 135.4, 133.0, 130.0, 128.6, 128.5, 128.1, 127.8, 127.8, 127.7, 127.2, 126.8, 125.2, 124.7, 122.2, 38.0.

**IR (KBr):** 2988, 1632, 1516, 1343, 1285, 1104, 1070, 910, 898, 755, 701 $cm^{-1}$.

**HRMS for $C_{24}H_{17}N_2O_2^+$ $(M+H)^+$**: calcd. 365.12845, found 365.12820.




**4g**

methyl 8-phenyl-3H-benzo[d]naphtho[1,2-b]azepine-5-carboxylate

**4g** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1 to 10:1).

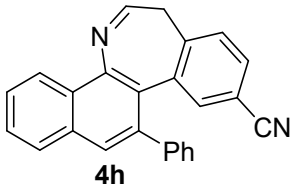
White solid, mp 108-110 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.47 – 8.45 (m, 1H), 8.02 (t, *J* = 5.0 Hz, 1H), 7.93 (d, *J* = 1.5 Hz, 1H), 7.82 – 7.80 (m, 1H), 7.67 (s, 1H), 7.54 – 7.51 (m, 2H), 7.40 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.15 – 7.07 (m, 5H), 6.93 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 3H), 3.78 – 3.75 (m, 1H), 2.93 – 2.90 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 167.1, 158.4, 142.5, 142.5, 139.7, 139.0, 136.7, 133.2, 133.0, 130.1, 129.1, 128.8, 128.3, 127.8, 127.6, 127.6, 126.8, 126.7, 125.9, 125.7, 125.3, 52.3, 38.0.

**IR (KBr):** 2948, 1716, 1629, 1434, 1294, 1267, 1194, 1104, 888, 786, 746, 701 $cm^{-1}$.

**HRMS for $C_{26}H_{20}NO_2^+$ $(M+H)^+$**: calcd. 378.14886, found 378.14893.




**4h**

8-phenyl-3H-benzo[d]naphtho[1,2-b]azepine-6-carbonitrile

**4h** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1 to 10:1).

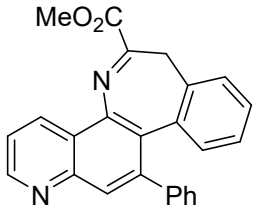
White solid, mp 202-204 °C.

**$^1$H NMR (500 MHz, DMSO-$d_6$)** δ 8.45 (d, *J* = 8.0 Hz, 1H), 8.13 (t, *J* = 5.0 Hz, 1H), 8.05 (d, *J* = 7.5 Hz, 1H), 7.86 (s, 1H), 7.72 – 7.64 (m, 4H), 7.33 - 7.29 (m, 5H), 7.19 (s, 1H), 4.10 – 4.07 (m, 1H), 2.99 – 2.95 (m, 1H).

**$^{13}$C NMR (126 MHz, DMSO-$d_6$)** δ 159.6, 142.1, 141.7, 141.7, 139.2, 135.9, 134.6, 132.6, 130.7, 130.0, 128.3, 128.1, 128.0, 127.9, 127.7, 126.9, 126.9, 126.7, 124.6, 124.3, 118.4, 107.7, 37.5.

**IR (KBr):** 2227, 1633, 1479, 1419, 914, 855, 763, 707 $cm^{-1}$.

**HRMS for $C_{25}H_{17}N_2^+$ $(M+H)^+$**: calcd. 345.13862, found 345.13834.



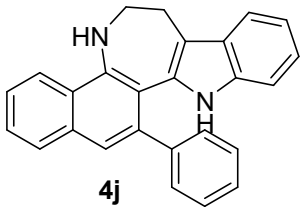

**4i**

methyl 12-phenyl-7H-benzo[4,5]azepino[2,3-f]quinoline-6-carboxylate

**4i** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1).

White solid, mp 97-99 °C.

**$^1$H NMR (500 MHz, DMSO-$d_6$)** δ 9.05 – 9.04 (m, 1H), 8.80 (d, *J* = 8.5 Hz, 1H), 7.94 (s, 1H), 7.71 – 7.69 (m, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.33 – 7.25 (m, 6H), 6.90 – 6.85 (m, 2H), 4.50 (d, *J* = 10.5 Hz, 1H), 3.88 (s, 3H), 2.97 (d, *J* = 12.0 Hz, 1H).
**$^{13}$C NMR (126 MHz, DMSO-$d_6$)** δ 163.2, 157.1, 151.8, 146.8, 143.1, 141.6, 140.6, 137.1, 133.0, 132.9, 132.1, 129.8, 128.7, 128.3, 128.3, 127.7, 127.2, 126.9, 125.3, 123.7, 122.1, 53.1, 35.4.
**IR (KBr):** 2922, 1717, 1435, 1199, 1102, 1025, 890, 771, 750 cm$^{-1}$.
**HRMS for $C_{25}H_{19}N_2O_2^+$ (M+H)$^+$**: calcd. 379.14410, found 379.14352.




**4j**

1-phenyl-7,8,9,14-tetrahydronaphtho[1',2':2,3]azepino[4,5-b]indole
**4j** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1 to 10:1).
Yellow solid, mp 211-213 °C.
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.82 – 7.80 (m, 1H), 7.75 – 7.73 (m, 1H), 7.50 – 7.48 (m, 2H), 7.46-7.44 (m, 1H), 7.41 – 7.38 (m, 3H), 7.32 – 7.25 (m, 3H), 7.14 (s, 1H), 6.97 – 6.94 (m, 2H), 6.79 – 6.77 (m, 1H), 5.27 (s, 1H), 3.77 (t, *J* = 7.0 Hz, 2H), 3.24 (t, *J* = 7.0 Hz, 2H).
**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 148.0, 142.7, 138.6, 135.2, 132.6, 131.8, 129.3, 129.1, 128.8, 128.4, 127.6, 126.4, 126.1, 125.0, 123.4, 122.2, 120.0, 119.0, 118.4, 114.4, 114.2, 110.1, 49.2, 28.6.
**IR (KBr):** 2904, 1565, 1439, 1354, 1167, 1077, 861, 762, 743, 696 cm$^{-1}$.
**HRMS for $C_{26}H_{21}N_2^+$ (M+H)$^+$**: calcd. 361.16993, found 361.16937.

## General procedure for the synthesis of isoindoline derivatives 6

1 mL Toluene, 2-cyanobenzaldehydes (**5**, 0.4 mmol (2.0 equiv.)), and THIQs (**2**, 0.2 mmol), were added into the dry thick-walled glass pressure tube. The mixture was stirred in a preheated oil bath at 100 °C in air for 4 h. Then the reaction was cooled down to room temperature, diluted with 20 mL ethyl acetate and washed with 10 mL $H_2O$. The aqueous layer was extracted twice with ethyl acetate (5 mL) and the combined organic phase was dried over $Na_2SO_4$. After evaporation of the solvents the residue was purified by flash column chromatography (silica gel, PE–EA) to afford the desired products **6**.

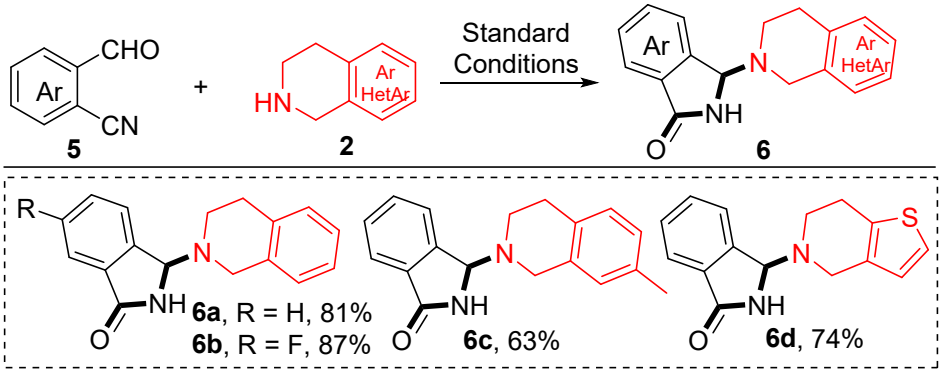
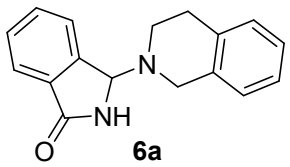



**Figure S3** The synthesis of isoindoline derivatives **6**




**6a**

3-(3,4-dihydroisoquinolin-2(1H)-yl)isoindolin-1-one

**6a** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1).

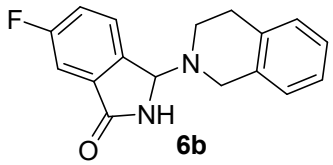
White solid, mp 180-182 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.24 (s, 1H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.51 – 7.41 (m, 3H), 7.02 – 6.98 (m, 3H), 6.84 (d, *J* = 7.5 Hz, 1H), 5.57 (s, 1H), 3.78 (d, *J* = 15.0 Hz, 1H), 3.52 (d, *J* = 14.5 Hz, 1H), 2.90 – 2.65 (m, 4H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ171.4, 144.3, 134.5, 134.3, 132.8, 132.4, 129.3, 128.9, 126.7, 126.2, 125.8, 124.0, 123.6, 76.4, 49.6, 46.0, 29.7.

**IR (KBr):** 2987, 1691, 1654, 1465, 1416, 1315, 1197, 1131, 1081, 982, 835, 739 $cm^{-1}$.

**HRMS for $C_{17}H_{17}N_2O^+$ $(M+H)^+$**: calcd. 265.13354, found 265.13336.




**6b**

3-(3,4-dihydroisoquinolin-2(1H)-yl)-6-fluoroisoindolin-1-one

**6b** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1 to 1:1).

White solid, mp 197-199 °C.

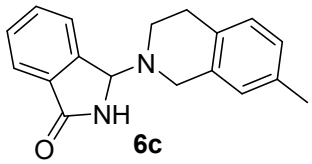
**$^1$H NMR (500 MHz, DMSO-$d_6$)** δ 9.15 (s, 1H), 7.61 – 7.58 (m, 1H), 7.50 – 7.44 (m, 2H), 7.11 – 7.05 (m, 3H), 6.97 (d, *J* = 7.0 Hz, 1H), 5.66 (s, 1H), 3.74 (d, *J* = 15.0 Hz, 1H), 3.52 (d, *J* = 15.0 Hz, 1H), 2.83 – 2.72 (m, 3H), 2.62 – 2.57 (m, 1H).

**$^{13}$C NMR (126 MHz, DMSO-$d_6$)** δ 168.1 (d, $J_{C\text{-}F}$ = 3.8 Hz), 162.9 (d, $J_{C\text{-}F}$ = 245.7 Hz), 140.1, 135.4 (d, $J_{C\text{-}F}$ = 8.8 Hz), 134.5, 134.1, 128.6, 126.5, 126.0, 125.8 (d, $J_{C\text{-}F}$ = 8.8 Hz), 125.6, 119.3 (d, $J_{C\text{-}F}$ = 23.9 Hz), 109.3 (d, $J_{C\text{-}F}$ = 23.9 Hz), 74.8, 49.0, 45.2, 29.1.

**$^{19}$F NMR (470 MHz, DMSO-$d_6$):** δ -112.3.

**IR (KBr):** 2901, 1700, 1483, 1445, 1348, 1233, 1050, 1025, 823, 761, 738 $cm^{-1}$.

**HRMS for $C_{17}H_{16}FN_2O^+$ $(M+H)^+$**: calcd. 283.12412, found 283.12408.




**6c**

3-(7-methyl-3,4-dihydroisoquinolin-2(1H)-yl)isoindolin-1-one

**6c** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 3:1 to 1:1).

Yellow solid, mp 195-197 °C.

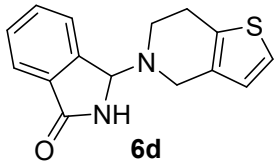
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 7.5 Hz, 1H), 7.52 – 7.50 (m, 2H), 7.47 – 7.43 (m, 1H), 7.33 (s, 1H), 6.92 – 6.86 (m, 2H), 6.68 (s, 1H), 5.57 (s, 1H), 3.73 (d, *J* = 14.5 Hz, 1H), 3.47 (d, *J* = 14.5 Hz, 1H), 2.90 – 2.63 (m, 4H), 2.17 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 170.9, 144.3, 135.4, 134.2, 132.6, 132.5, 131.1, 129.4, 128.8, 127.3,

127.2, 124.0, 123.7, 76.3, 49.5, 46.3, 29.3, 21.1.

**IR (KBr):** 2919, 1679, 1467, 1358, 1230, 1137, 1106, 1049, 996, 789, 757, 745 $cm^{-1}$.

**HRMS for $C_{18}H_{19}N_2O^+$ $(M+H)^+$**: calcd. 279.14919, found 279.14923.




**6d**

3-(6,7-dihydrothieno[3,2-c]pyridin-5(4H)-yl)isoindolin-1-one

**6d** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 3:1 to 1:1).

Yellow solid, mp 186-188 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.87 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.53 – 7.51 (m, 2H), 7.47 – 7.44 (m, 1H), 6.98 (d, *J* = 5.0 Hz, 1H), 6.58 (d, *J* = 5.5 Hz, 1H), 5.6 (s, 1H), 3.70 (d, *J* = 14.0 Hz, 1H), 3.47 (d, *J* = 14.0 Hz, 1H), 2.94 – 2.71 (m, 4H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 171.2, 144.2, 133.4, 133.3, 132.6, 132.5, 129.4, 125.3, 124.0, 123.7, 123.1, 76.3, 47.1, 46.2, 26.1.

**IR (KBr):** 2911, 1684, 1351, 1314, 1235, 1169, 1119, 990, 909, 795, 724 $cm^{-1}$.

**HRMS for $C_{15}H_{15}N_2OS^+$ $(M+H)^+$**: calcd. 271.08996, found 271.08997.

## 5. General procedure for the derivatization of 3a

To demonstrate the utility of this method, further transformations of dibenzo[b,d]azepines product were pursued. The imine bond could be readily reduced to produced product **7** in 92% yield, which has the potential to be converted into diverse *N*-substituted dibenzo[b,d]azepine derivatives. Besides, many natural products contain a lactams ring. Thus, oxidation reaction was performed on **3a**. To our delight, dibenzo[b,d]azepin-2-one **8** could be efficiently produced in 86% yield. Furthermore, the reaction of 1-naphthol with **3a** result in the bifunctional aminonaphthol **9** in 83% yield. And the ring closures of **3a** with solution of HCHO as cyclizing agent, affording new oxazine derivatives **10** in 74% yield.

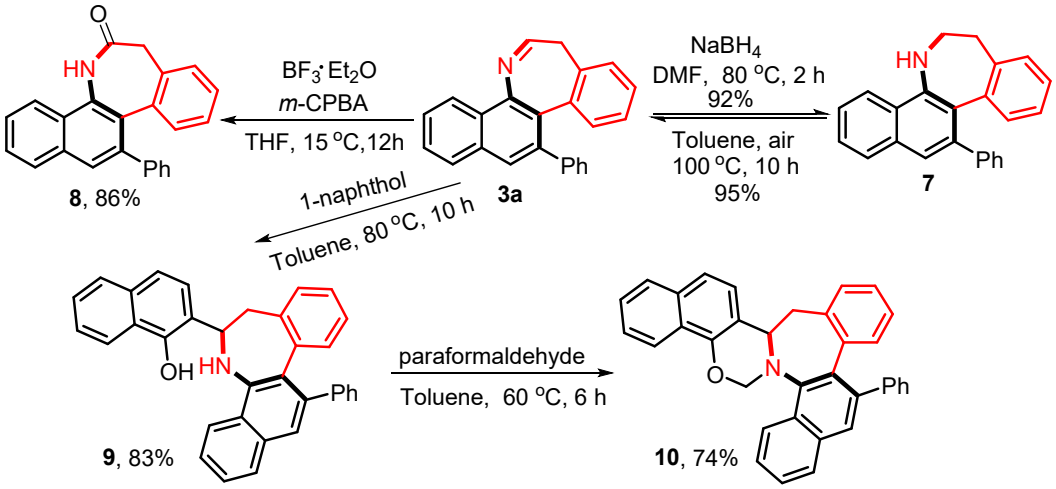


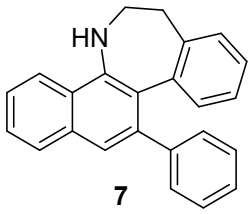

**Figure S4** The derivatization of **3a**

1 mL DMF, **3a** (0.2 mmol), and $NaBH_4$ (0.2 mmol (7.6 mg, 1.0 equiv.)) were added into the dry

thick-walled glass pressure tube and stirred at 80 °C for 2 h. Then the reaction was cooled down to room temperature, diluted with 20 mL ethyl acetate and washed with 10 mL $H_2O$. The aqueous layer was extracted twice with ethyl acetate (5 mL) and the combined organic phase was dried over $Na_2SO_4$. After evaporation of the solvents the residue was purified by flash column chromatography (silica gel, petroleum ether–ethyl acetate, 30:1 to 20:1) to afford the reduction product **7**.

1 mL THF, **3a** (0.2 mmol), $BF_3{\cdot}Et_2O$ (0.4 mmol, 56.8 mg) and 3-chloroperoxybenzoic acid (*m*-CPBA, 69.0 mg, 0.4 mmol) were added into the dry thick-walled glass pressure tube and stirred at 15 °C for 12 h. Then the reaction was diluted with 20 mL ethyl acetate and washed with 10 mL $H_2O$. The aqueous layer was extracted twice with ethyl acetate (5 mL) and the combined organic phase was dried over $Na_2SO_4$. After evaporation of the solvents the residue was purified by flash column chromatography (silica gel, petroleum ether–ethyl acetate, 2:1) to afford the dibenzo[*b,d*]azepin-2-one **8**.

1 mL toluene, **3a** (0.2 mmol), and 1-naphthalenol (28.8 mg, 0.2 mmol) were added into the dry thick-walled glass pressure tube and stirred in air at 80 °C for 10 h. Then the reaction was cooled down to room temperature, diluted with 20 mL ethyl acetate and washed with 10 mL $H_2O$. The aqueous layer was extracted twice with ethyl acetate (5 mL) and the combined organic phase was dried over $Na_2SO_4$. After evaporation of the solvents the residue was purified by flash column chromatography (silica gel, petroleum ether–ethyl acetate, 30:1) to afford the bifunctional aminonaphthol **9**. Then, paraformaldehyde (18.0 mg, 0.6 mmol), **9** (0.2 mmol), and 1 mL toluene were added into the dry thick-walled glass pressure tube and stirred in air at 60 °C for 6 h. The reaction was further diluted with 20 mL ethyl acetate and washed with 10 mL $H_2O$. The aqueous layer was extracted twice with ethyl acetate (5 mL) and the combined organic phase was dried over $Na_2SO_4$. After evaporation of the solvents the residue was purified by flash column chromatography (silica gel, petroleum ether–ethyl acetate, 120:1) to afford the oxazine **10**.




**7**

8-phenyl-2,3-dihydro-1H-benzo[d]naphtho[1,2-b]azepine

**7** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1).

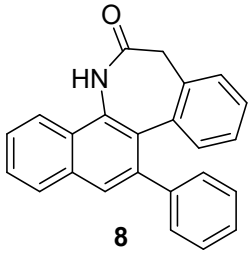
Yellow oil.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.10 – 7.99 (m, 1H), 7.80 – 7.78 (m, 1H), 7.61 (s, 1H), 7.44 – 7.39 (m, 2H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.14 – 7.04 (m, 6H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 7.5 Hz, 1H), 3.87 – 3.83 (m, 1H), 3.74 – 3.68 (m, 1H), 3.40 (s, 1H), 3.03 – 2.96 (m, 1H), 2.68 – 2.65 (m, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 142.1, 140.9, 139.9, 139.6, 139.4, 134.0, 131.7, 130.1, 130.0, 128.8, 128.1, 128.0, 127.5, 127.0, 126.5, 126.4, 126.2, 125.7, 125.2, 121.6, 55.6, 33.0.

**IR (KBr):** 3054, 2920, 1493, 1340, 1116, 1030, 906, 728 $cm^{-1}$.

**HRMS for $C_{24}H_{20}N^+$ $(M+H)^+$**: calcd. 322.15903, found 322.15900.




**8**

8-phenyl-1,3-dihydro-2H-benzo[d]naphtho[1,2-b]azepin-2-one

**8** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2:1).

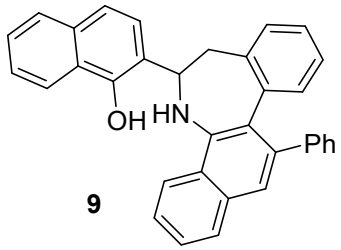
Yellow solid, mp 260-262 °C.

**$^1$H NMR (500 MHz, DMSO-$d_6$)** δ 10.3 (s, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.86 (s, 1H), 7.67 – 7.62 (m, 2H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.26 – 7.15 (m, 6H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 7.5 Hz, 1H), 3.69 – 3.53 (m, 2H).

**$^{13}$C NMR (126 MHz, DMSO-$d_6$)** δ 172.1, 141.8, 139.4, 136.7, 134.9, 133.3, 132.8, 131.9, 129.7, 128.2, 128.1, 127.9, 127.8, 127.3, 127.2, 126.8, .126.7, 126.6, 126.1, 125.5, 123.4, 41.9.

**IR (KBr):** 2923, 1659, 1418, 1353, 1141, 882, 751, 718, 696 cm$^{-1}$.

**HRMS for $C_{24}H_{18}NO^+$ $(M+H)^+$**: calcd. 336.13829, found 336.15756.




**9**

2-(8-phenyl-2,3-dihydro-1H-benzo[d]naphtho[1,2-b]azepin-2-yl)naphthalen-1-ol

**9** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1).

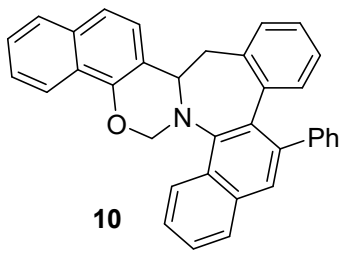
Yellow solid, mp 168-170 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 9.99 (s, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.83 – 7.80 (m, 2H), 7.70 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.13 – 7.06 (m, 6H), 6.90 – 6.84 (m, 2H), 6.72 – 6.66 (m, 2H), 5.35 (d, *J* = 6.5 Hz, 1H), 4.67 (s, 1H), 3.46 – 3.42 (m, 1H), 2.77 (d, *J* = 13.5 Hz, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 153.6, 141.6, 139.9, 138.6, 138.2, 136.6, 133.9, 133.8, 131.5, 130.4, 130.0, 129.2, 129.0, 128.1, 127.5, 127.2, 127.1, 126.9, 126.8, 126.6, 126.5, 126.5, 126.4, 125.6, 125.0, 122.7, 120.4, 118.8, 117.0, 71.8, 40.2.

**IR (KBr):** 2906, 1601, 1374, 882, 802, 755, 698 cm$^{-1}$.

**HRMS for $C_{34}H_{24}NO^-$ $(M-H)^-$**: calcd. 462.18524, found 462.18552.




**10**

13-phenyl-18,18a-dihydro-6H-benzo[d]naphtho[2,1-f]naphtho[2',1':5,6][1,3]oxazino[3,4-a]azepine

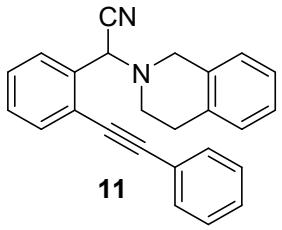
**10** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 120:1).

Yellow solid, mp 154-156 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.22 – 8.20 (m, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.83 – 7.82 (m, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.42 (m, 3H), 7.35 – 7.28 (m, 3H), 7.14 – 7.06 (m, 5H), 6.69 – 6.66 (m, 3H), 6.59 – 6.56 (m, 1H), 5.35 (d, *J* = 6.5 Hz, 1H), 4.83 (d, *J* = 8.0 Hz, 1H), 4.34 (d, *J* = 8.0 Hz, 1H), 3.52 – 3.48 (m, 1H), 3.08 (d, *J* = 13.5 Hz, 1H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 151.3, 141.7, 141.7, 139.9, 138.5, 137.1, 136.2, 134.3, 133.1, 132.1, 131.9, 130.1, 129.1, 128.9, 128.3, 128.0, 127.5, 126.9, 126.9, 126.8, 126.7, 126.3, 125.9, 125.6, 125.5, 124.9, 124.3, 121.7, 120.7, 118.3, 79.8, 64.6, 39.8.

**IR (KBr):** 2923, 1575, 1372, 1254, 1073, 1010, 804, 748, 699 $cm^{-1}$.




**11**

2-(3,4-dihydroisoquinolin-2(1H)-yl)-2-(2-(phenylethynyl)phenyl)acetonitrile

**10** was purified by silica gel chromatography (petroleum ether/ethyl acetate = 50:1).

Yellow solid, mp 103- 105 °C.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 7.61 – 7.59 (m, 1H), 7.49 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.35 – 7.26 (m, 4H), 7.24 – 7.20 (m, 3H), 7.01 – 6.95 (m, 3H), 6.87 – 6.85 (m, 1H), 5.34 (s. 1H), 3.72 (dd, *J* = 14.0 Hz, 2H), 2.88 – 2.72 (m, 4H)

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 134.7, 133.8, 133.6, 133.1, 131.5, 129.1, 128.8, 128.7, 128.6, 128.4, 128.4, 126.6, 126.4, 125.8, 123.9, 122.7, 115.7, 95.2, 86.4, 60.6, 52.1, 48.1, 29.3

**HRMS for $C_{25}H_{21}N_2^+$ $(M+H)^+$**: calcd. 349.16993, found 349.16953.

## Reference:

(1) Malkov, A. V.; Westwater, M.-M.; Gutnov, A.; Ramírez-López, P.; Friscourt, F.; Kadlčíkova, A.; Hodačová, J.; Rankovic, Z.; Kotora, M; Kočovský, P. New pyridine *N*-oxides as chiral organocatalysts in the asymmetric allylation of aromatic aldehydes. *Tetrahedron*, 2**008**, *64*, 11335-11348.

(2) Liu, Y.; Feng, X.; Liu, Y.; Lin, H.; Li, Y.; Gong, Y.; Cao,L.; Chen, L. Carbonyl-directed addition of *N*-alkylhydroxylamines to unactivated alkynes: regio- and stereoselective synthesis of ketonitrones. *Org. Lett.* **2019**, *21*, 382-386

# 6. X-ray diffraction analysis of compound 3a

Sample preparation:

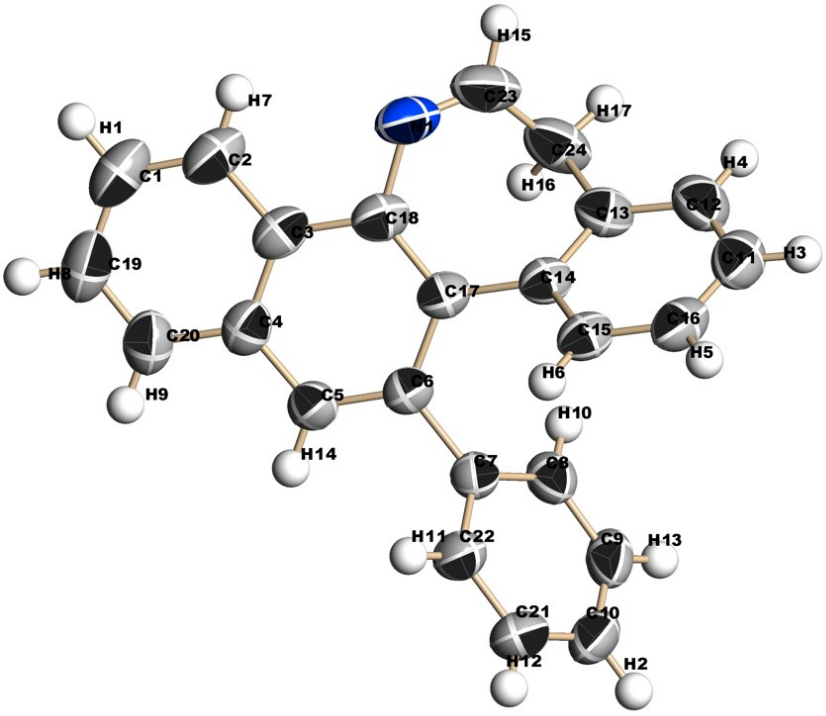
The method for crystal growth is slow volatilization using petroleum ether (PE)-ethyl acetate (EA) mixture as a solvent.

Crystal measurement for compound **3a**:

A specimen of $C_{24}H_{17}N$ was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a d8 venture system (cu $k_{\alpha}$, $\lambda$ = 1.54178 Å).

The total exposure time was 1.76 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 15879 reflections to a maximum θ angle of 65.13° (0.85 Å resolution), of which 2942 were independent (average redundancy 5.397, completeness = 99.9%, $R_{int}$ = 12.08%, $R_{sig}$ = 7.54%) and 1997 (67.88%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.2109(2) Å, b = 13.5877(3) Å, c = 15.4845(3) Å, β = 90.6590(10)°, volume = 1727.45(7) $Å^3$, are based upon the refinement of the XYZ-centroids of 7474 reflections above 20 σ(I) with 6.505° < 2θ < 130.2°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.838.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/n 1, with Z = 4 for the formula unit, $C_{24}H_{17}N$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 226 variables converged at R1 = 4.16%, for the observed data and wR2 = 11.61% for all data. The goodness-of-fit was 1.039. The largest peak in the final difference electron density synthesis was 0.098 $e^-/Å^3$ and the largest hole was -0.157 $e^-/Å^3$ with an RMS deviation of 0.034 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.228 $g/cm^3$ and F(000), 672 $e^-$.




Plots are drawn at 50% probability level.

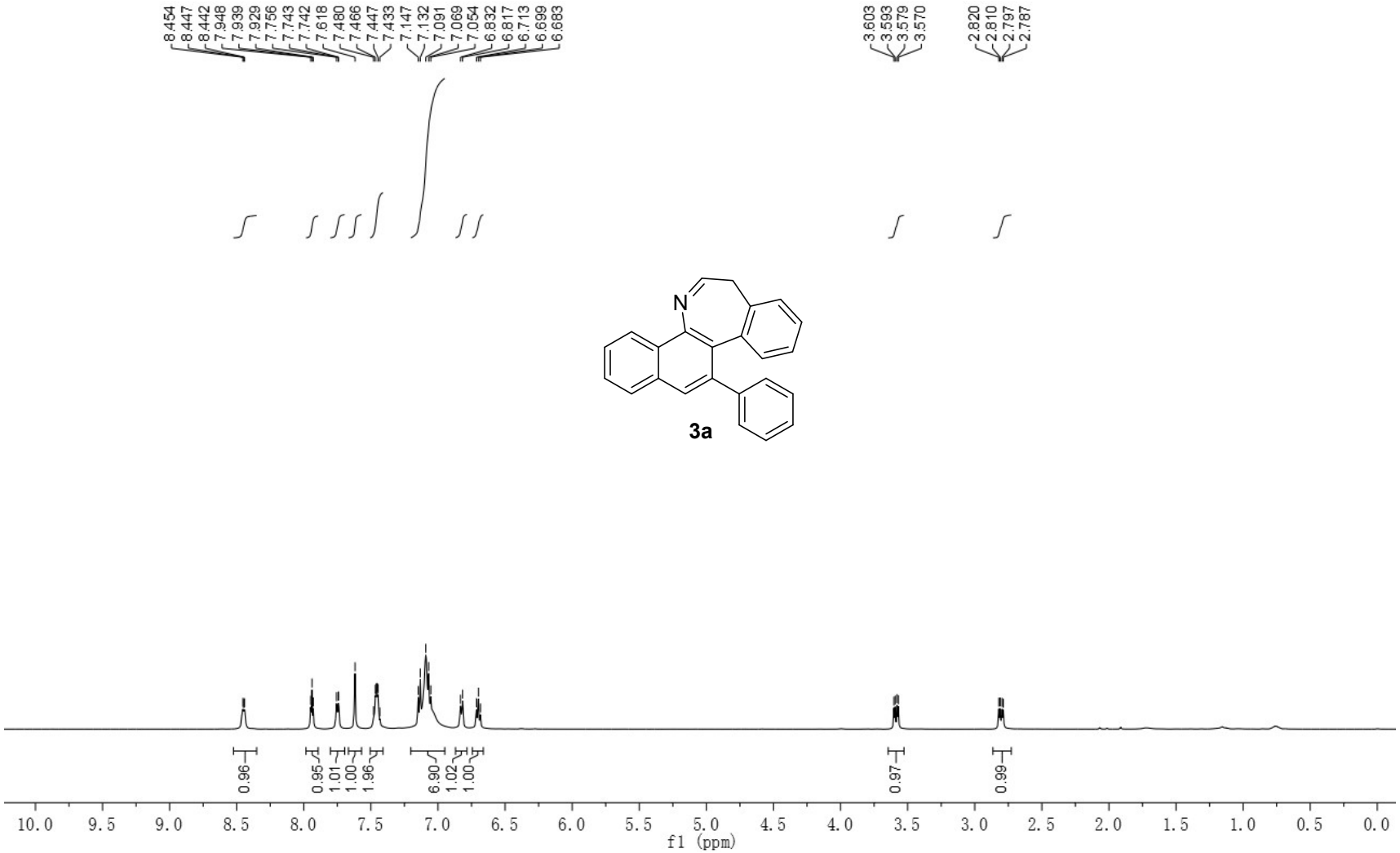
**Table S2.** Crystal data and structure refinement for **3a**

| | |
|---|---|
| Identification code | 20230412_GTH_319_A_1 |
| Chemical formula | $C_{24}H_{17}N$ |
| Formula weight | 319.38 g/mol |
| Temperature | 303(2) K |
| Wavelength | 1.54178 Å |

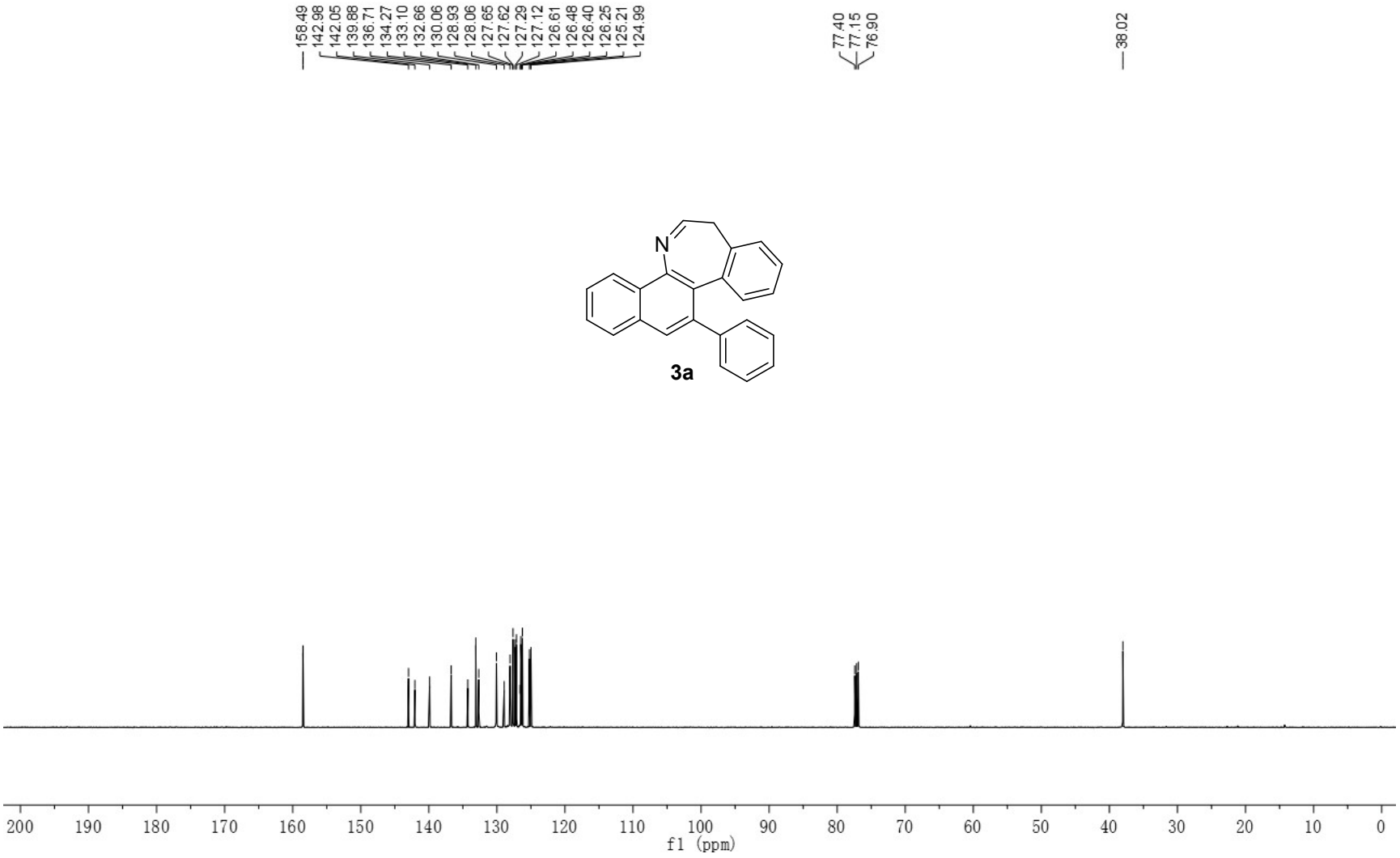
| | |
|---|---|
| Crystal system | monoclinic |
| Space group | P 1 21/n 1 |
| Unit cell dimensions | a = 8.2109 Å α = 90° |
| | b = 13.5877(3) Å β = 90.6590(10)° |
| | c = 15.4845 Å γ = 90° |
| Volume | 15.4845 $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.228 $g/cm^3$ |
| Absorption coefficient | 0.542 $mm^{-1}$ |
| F(000) | 672 |
| Diffractometer | d8 venture |
| Theta range for data collection | 4.33 to 65.13° |
| Index ranges | -9<=h<=9, -15<=k<=15, -18<=l<=18 |
| Reflections collected | 15879 |
| Independent reflections | 2942 [R(int) = 0.1208] |
| Coverage of independent reflections | 99.9% |
| Absorption correction | Multi-Scan |
| Structure solution technique | direct methods |
| Structure solution program | SHELXT 2018/2 (Sheldrick, 2018) |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Refinement program | SHELXL-2018/3 (Sheldrick, 2018) |
| Function minimized | $\Sigma w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 2942 / 0 / 226 |
| Goodness-of-fit on $F^2$ | 1.039 |
| Final R indices | 1997 data; I>2σ(I) R1 = 0.0416, wR2 = 0.1049 |
| | all data R1 = 0.0722, wR2 = 0.1161 |
| Weighting scheme | $w=1/[\sigma^2(F_o^2)+(0.0500P)^2+0.1230P]$ where $P=(F_o^2+2F_c^2)/3$ |
| Largest diff. peak and hole | 0.098 and -0.157 $eÅ^{-3}$ |
| R.M.S. deviation from mean | 0.034 $eÅ^{-3}$ |

## 7. Copies of $^1H$ and $^{13}C$ NMR Spectra

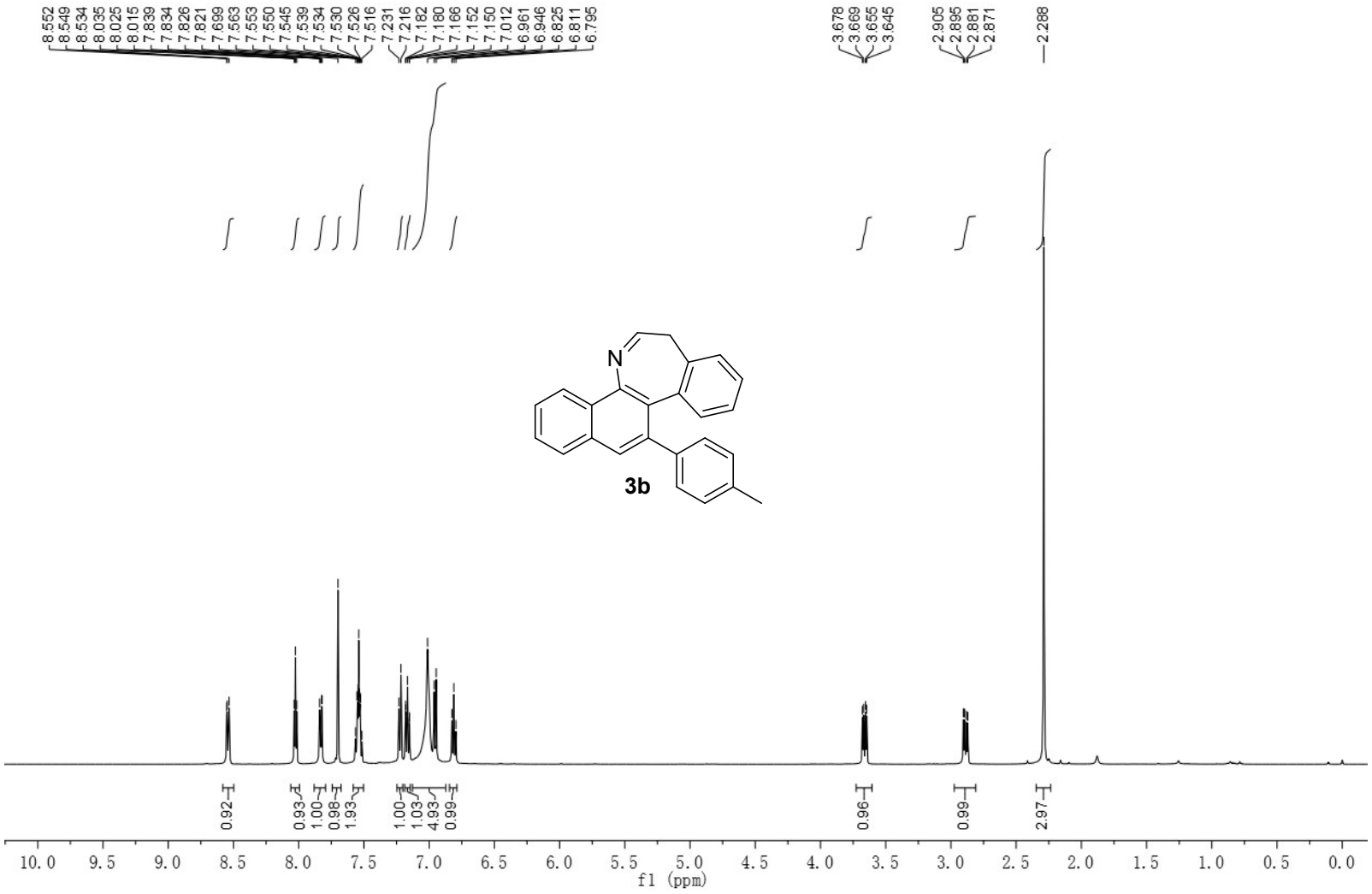
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3a**



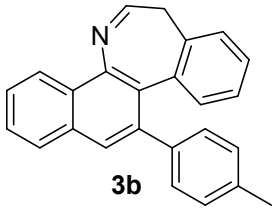
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3a**



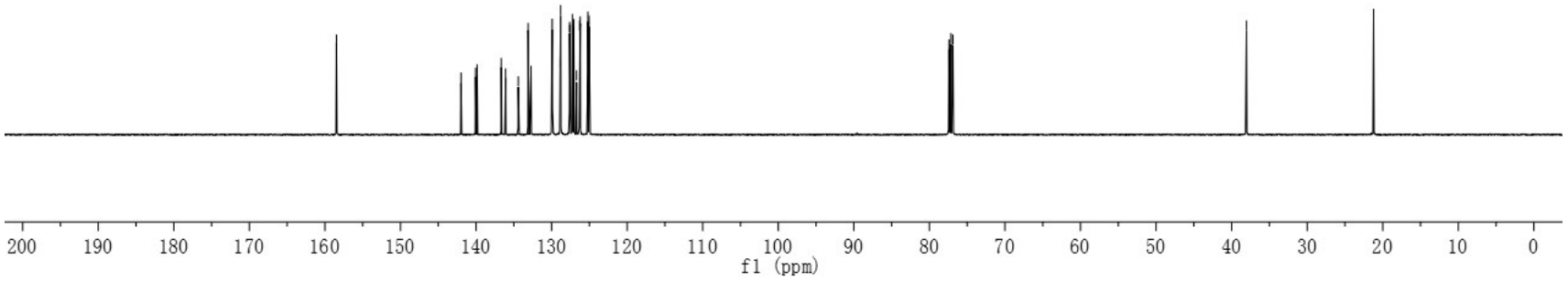
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3b**



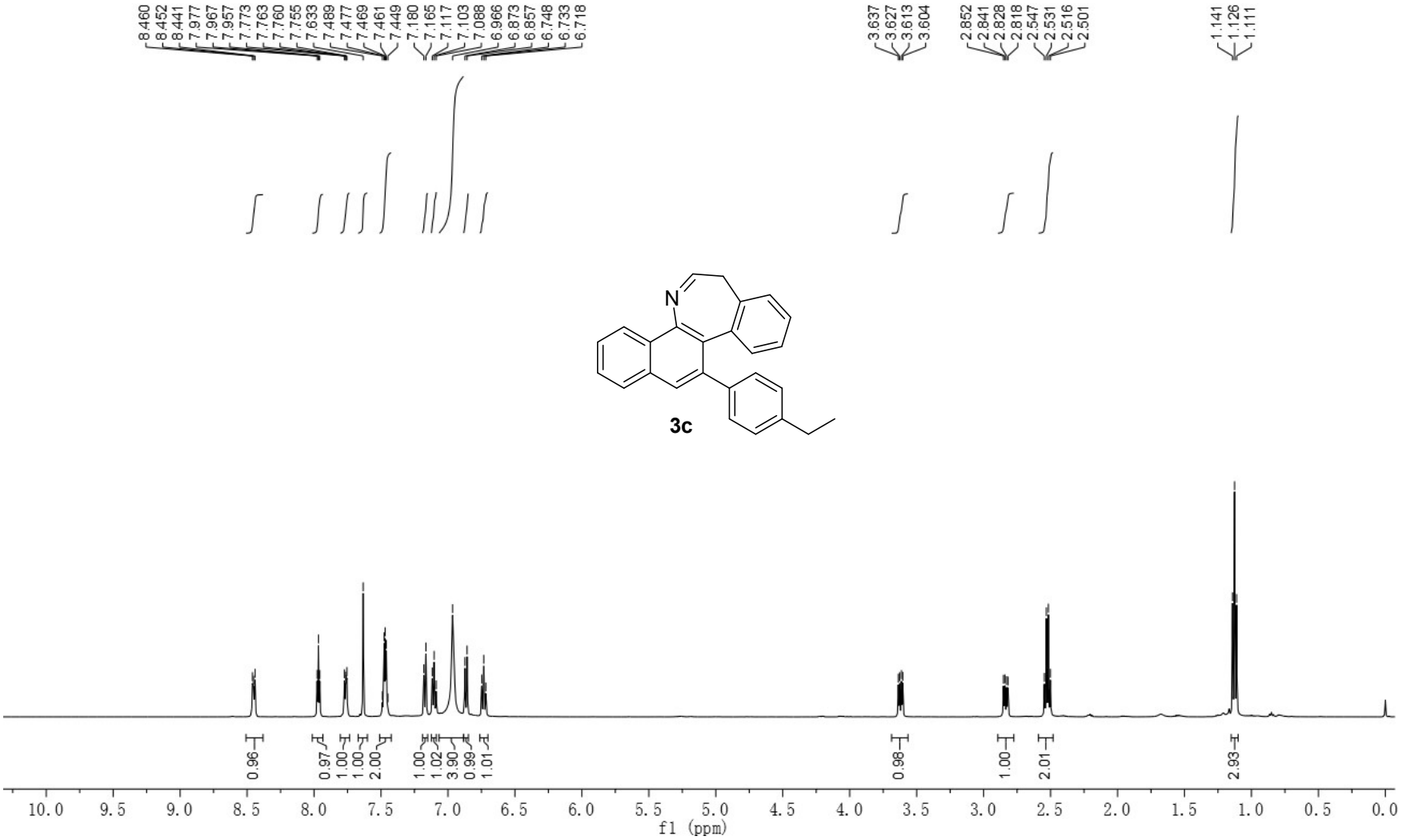
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3b**

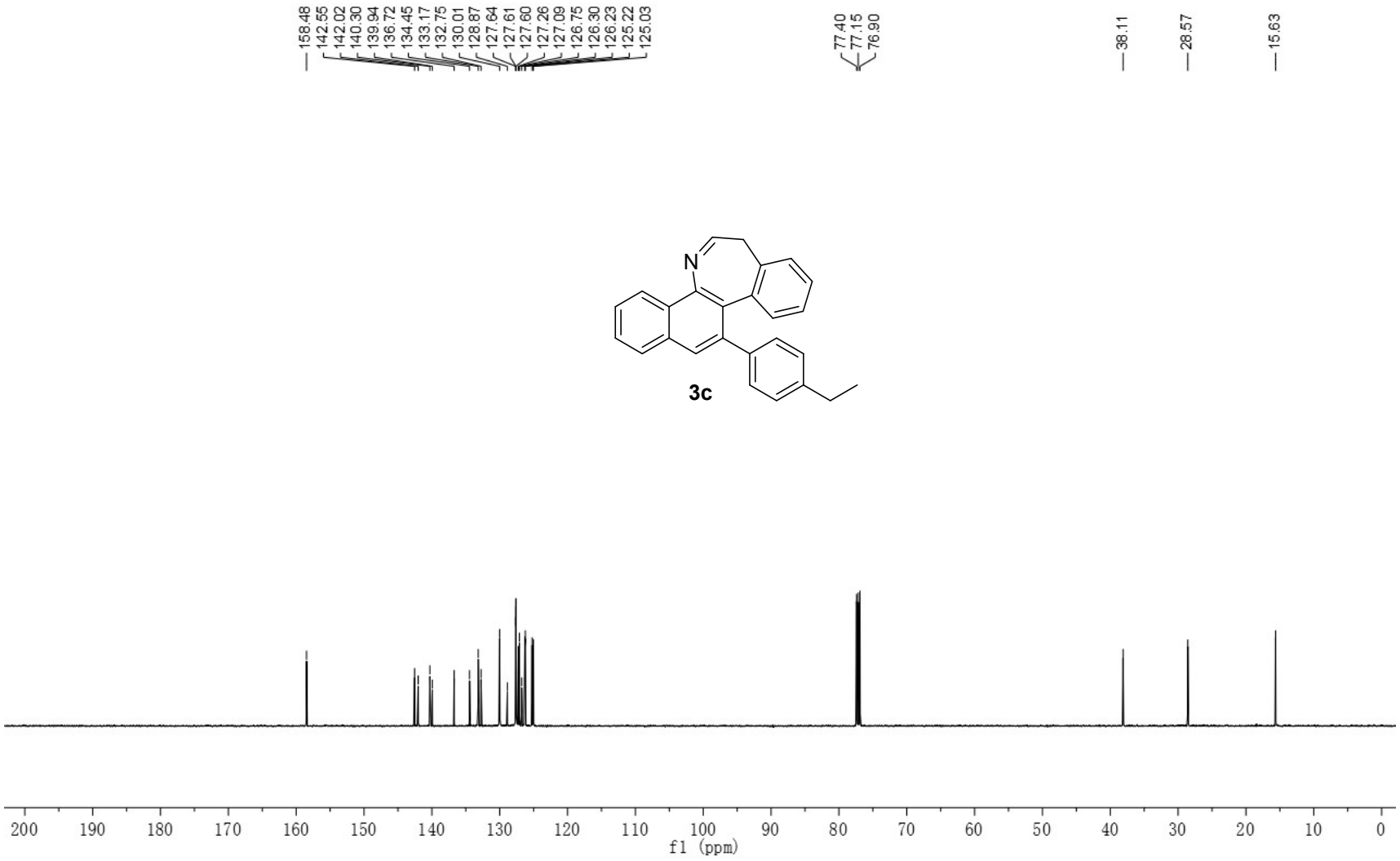

**3b**



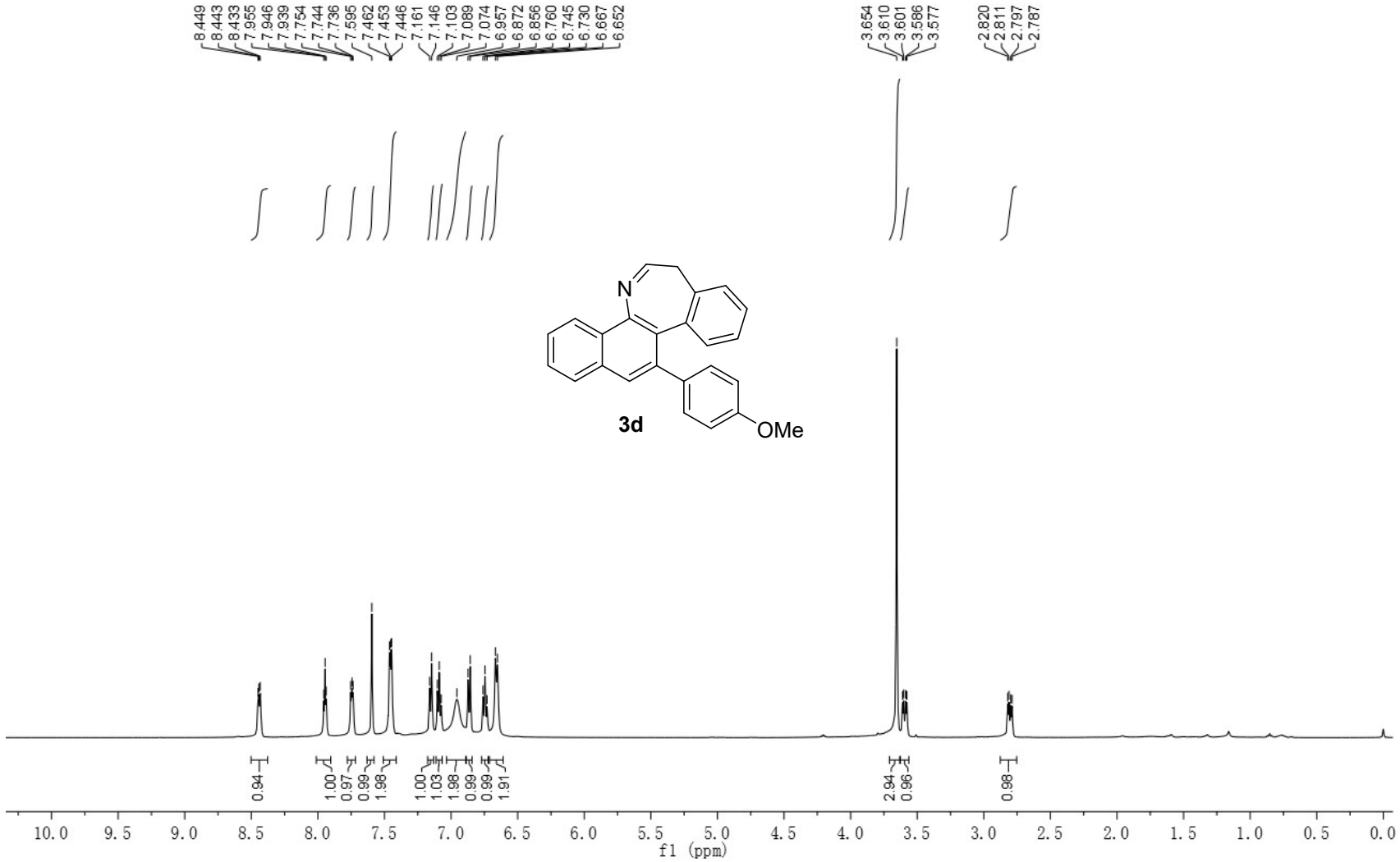
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3c**



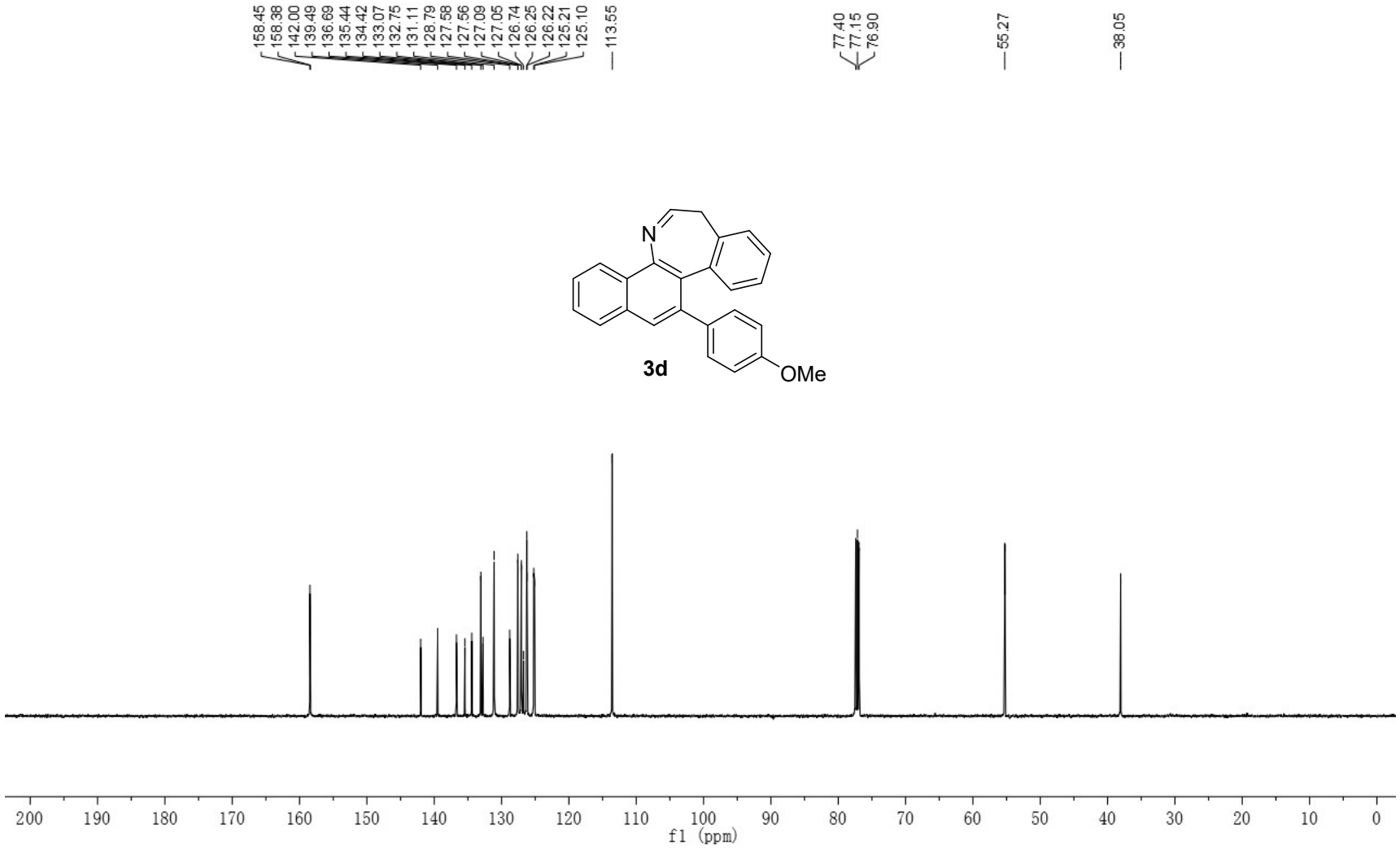
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3c**



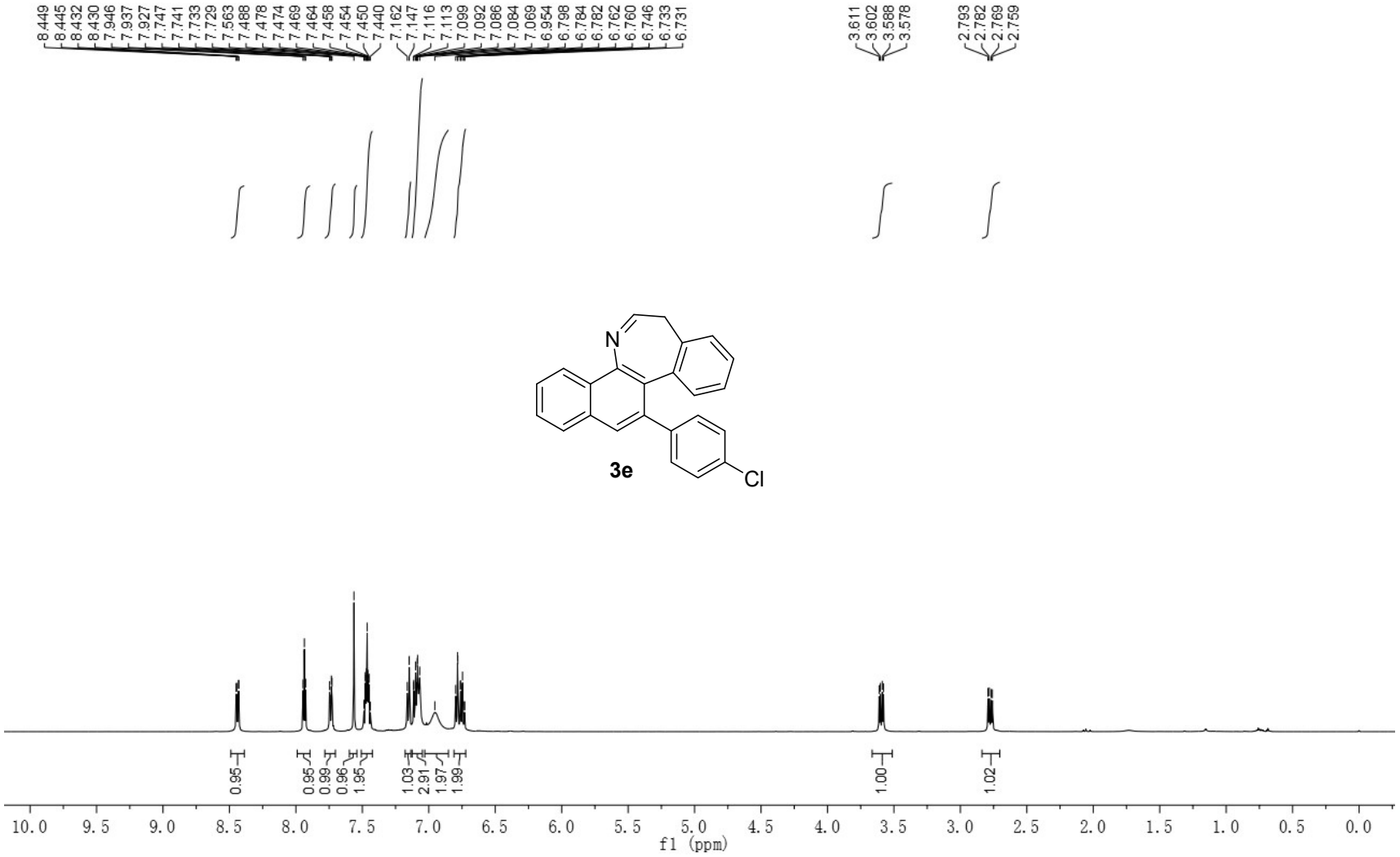
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3d**



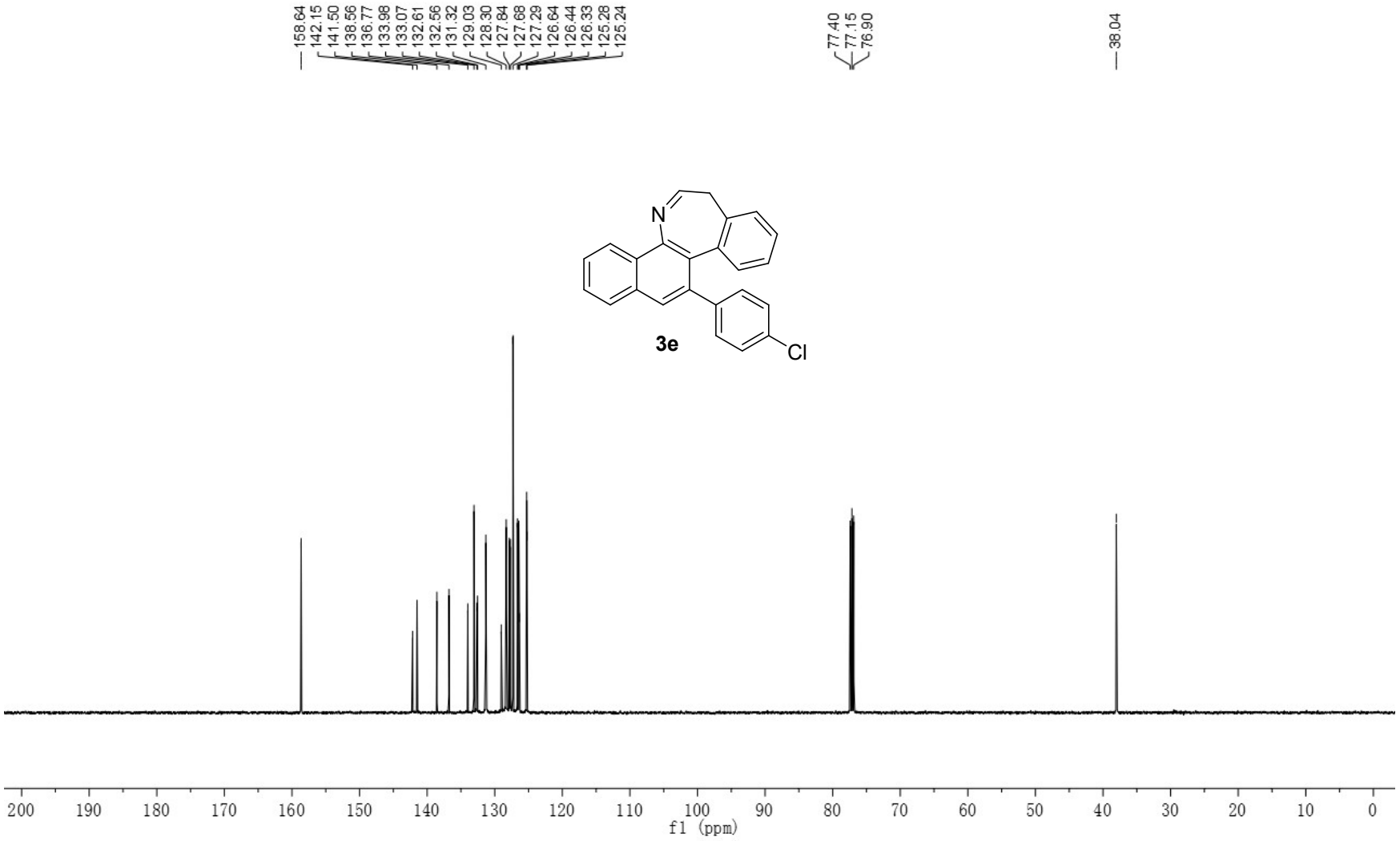
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3d**



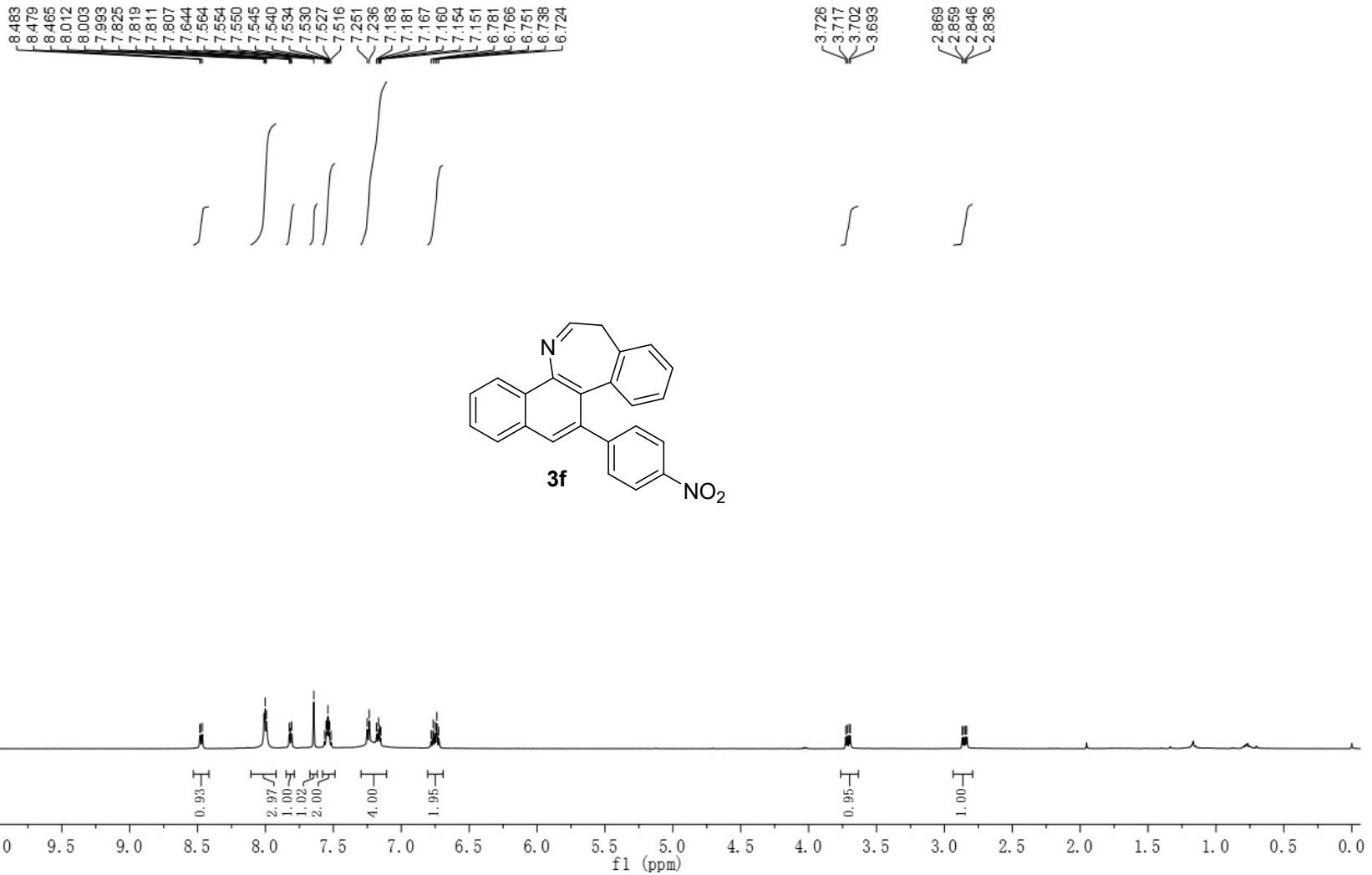
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3e**



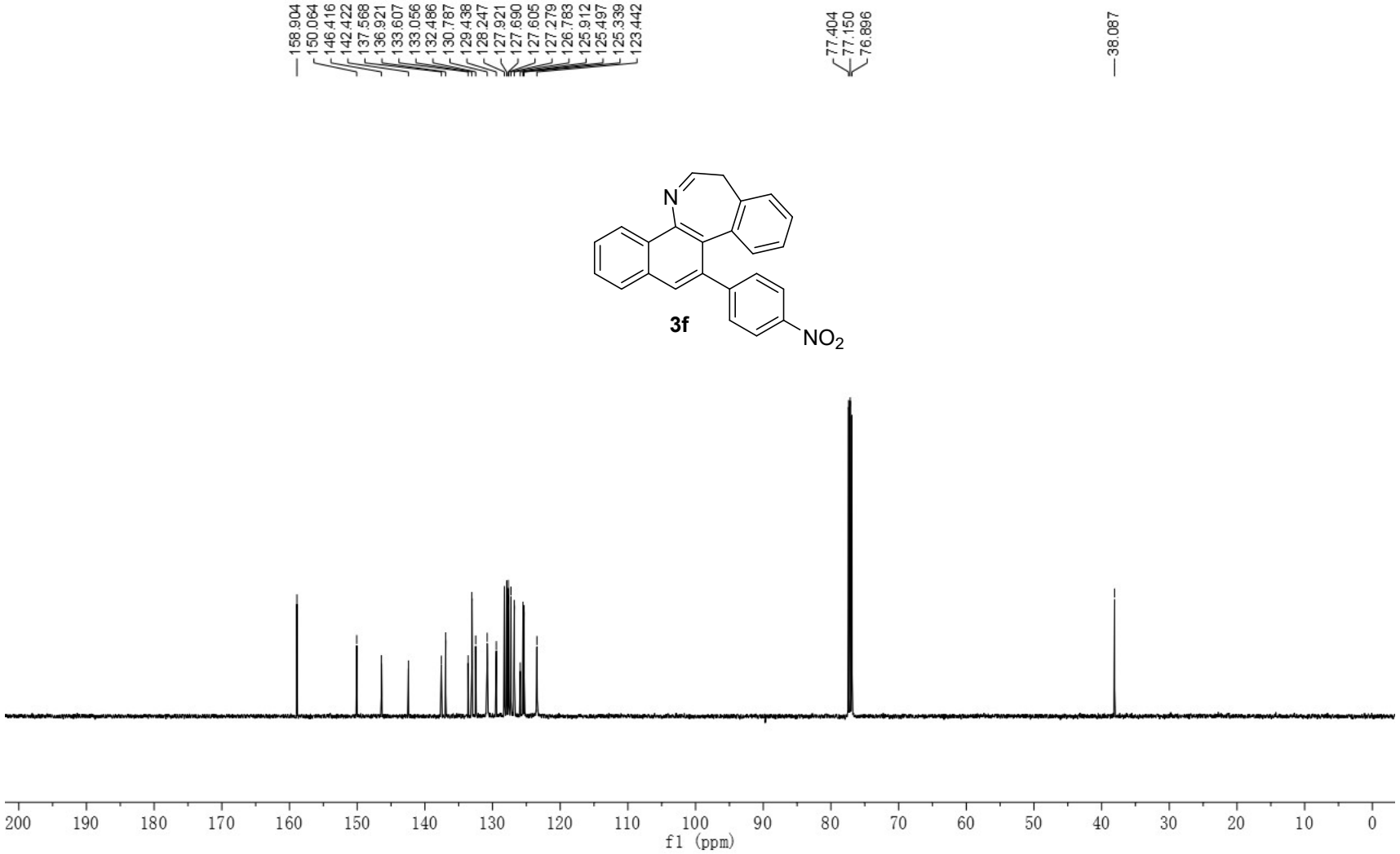
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3e**



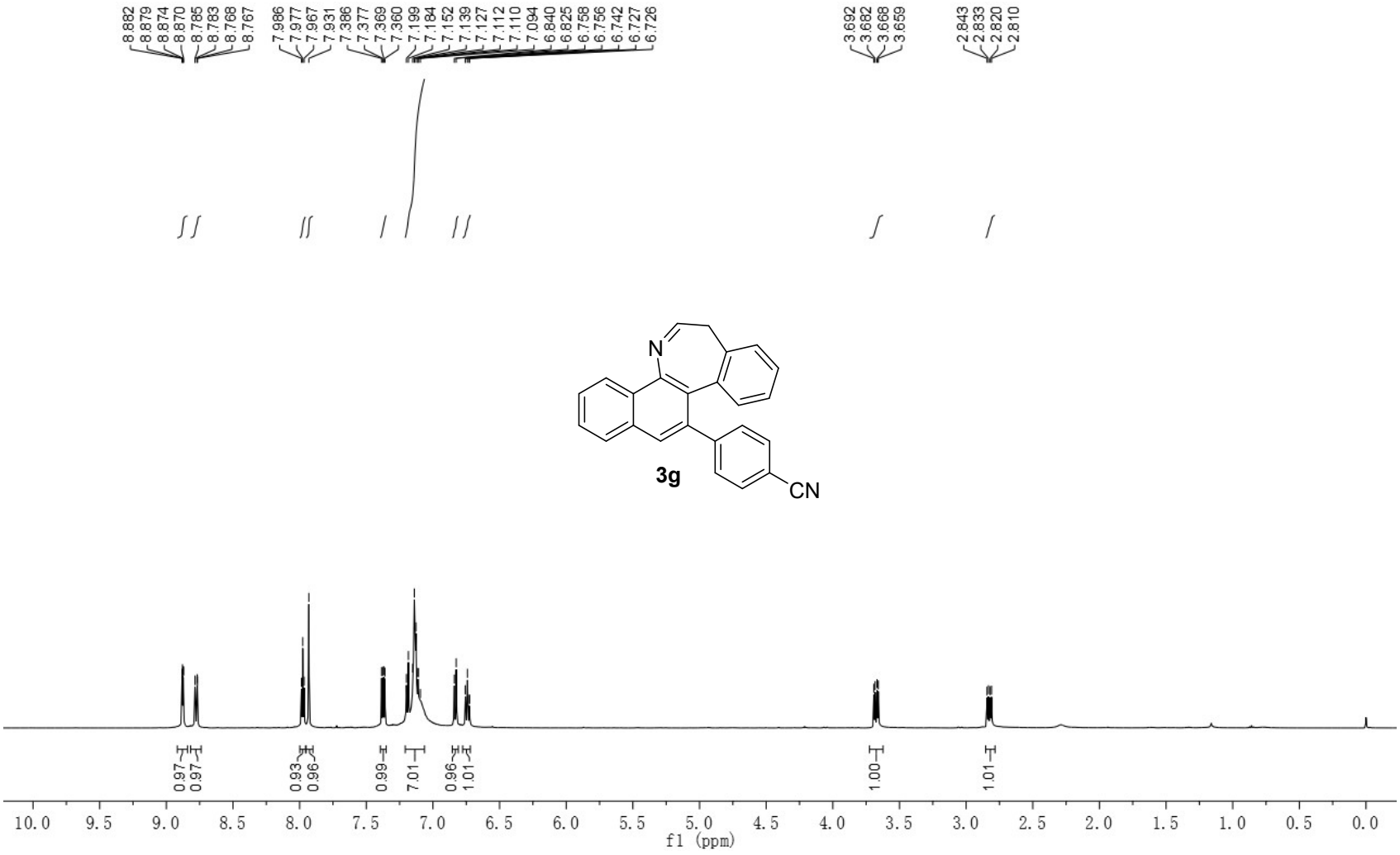
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3f**



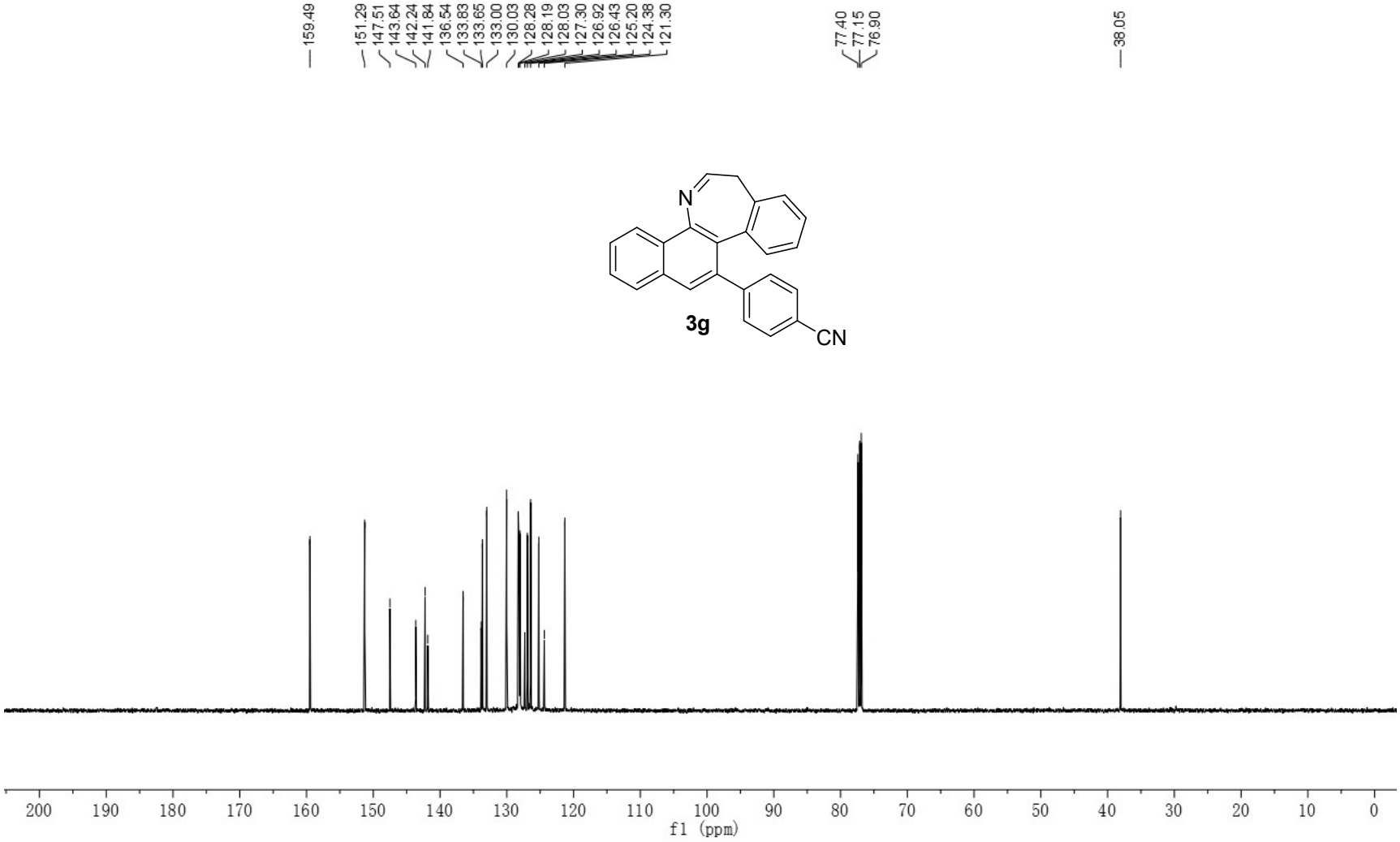
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3f**



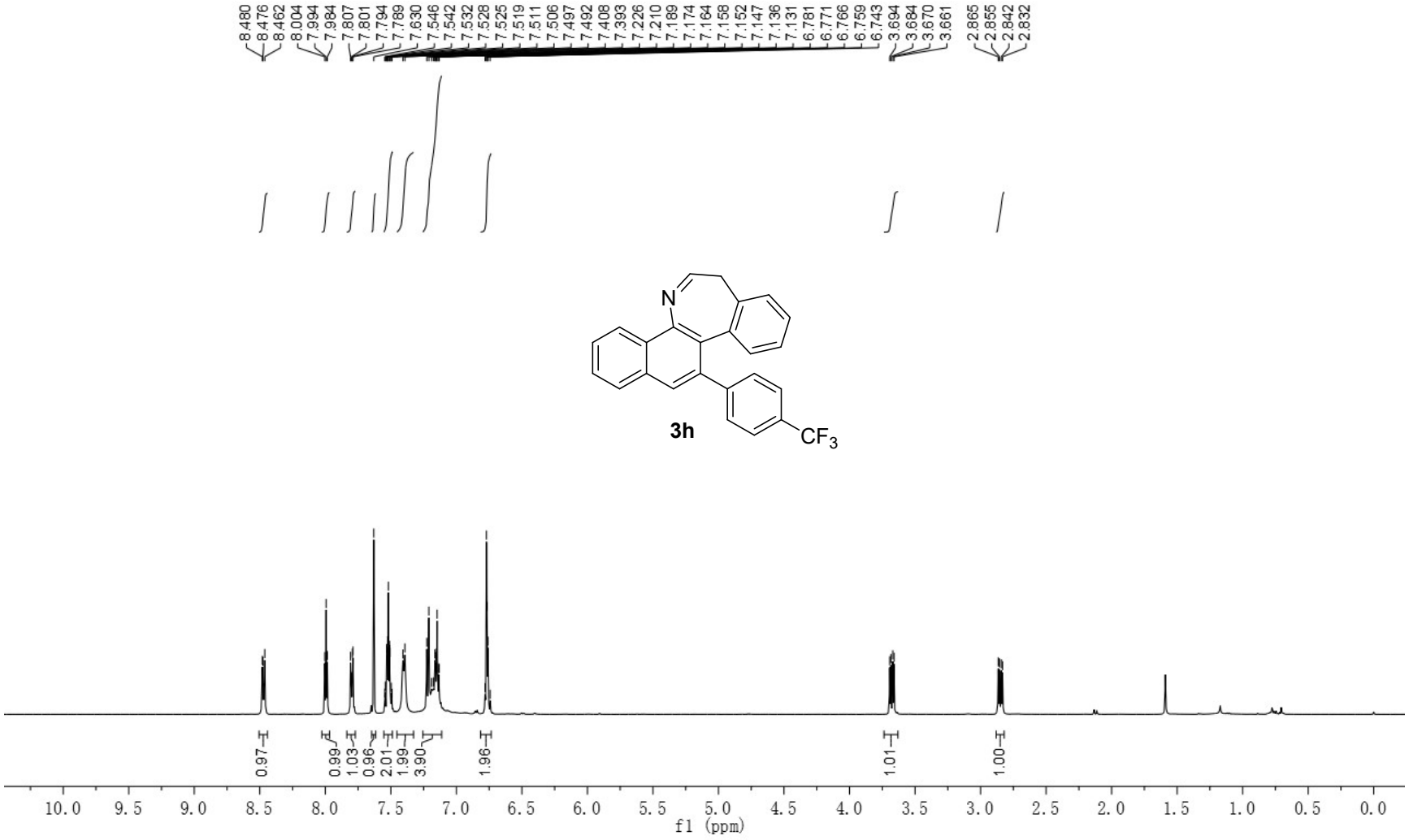
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3g**



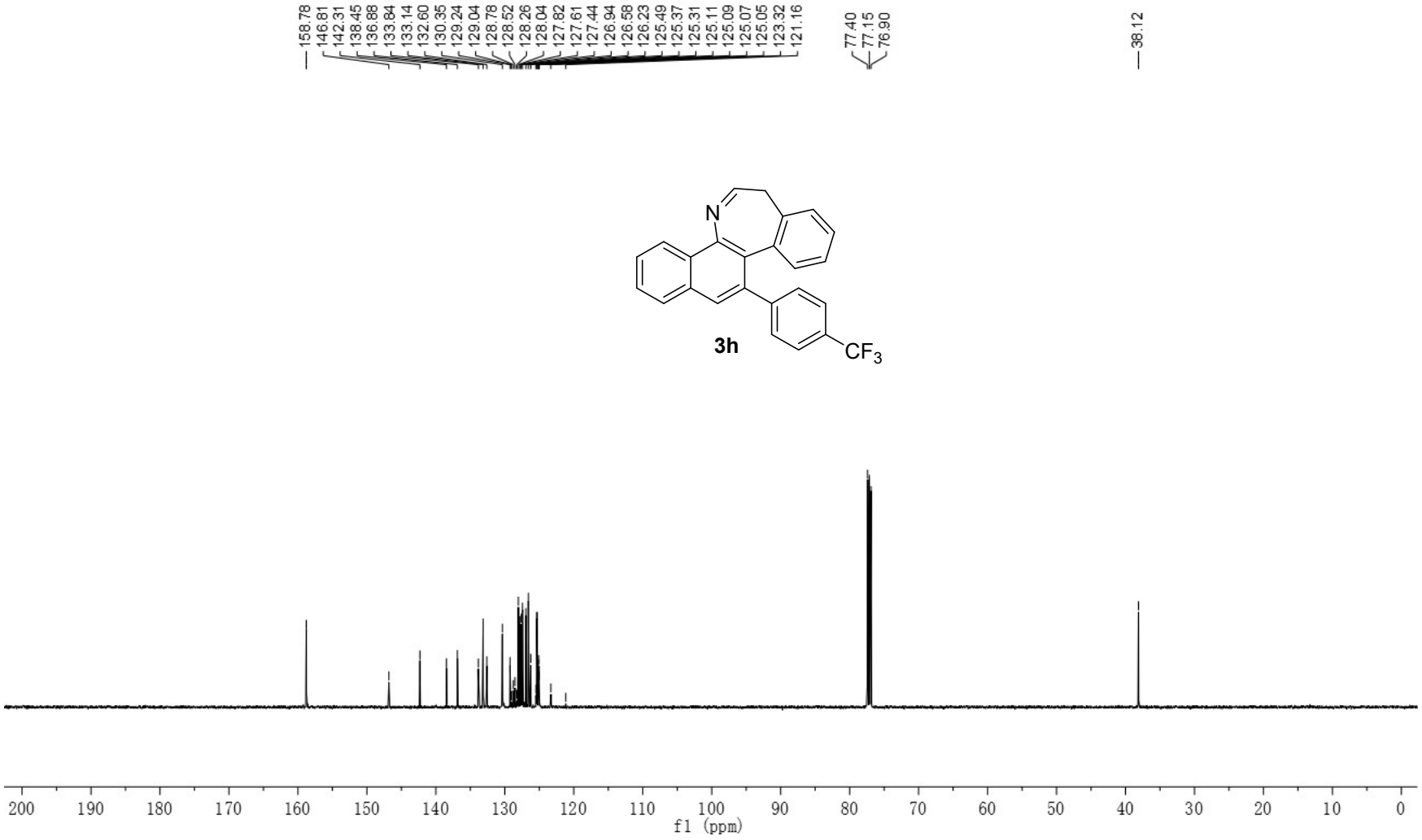
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3g**



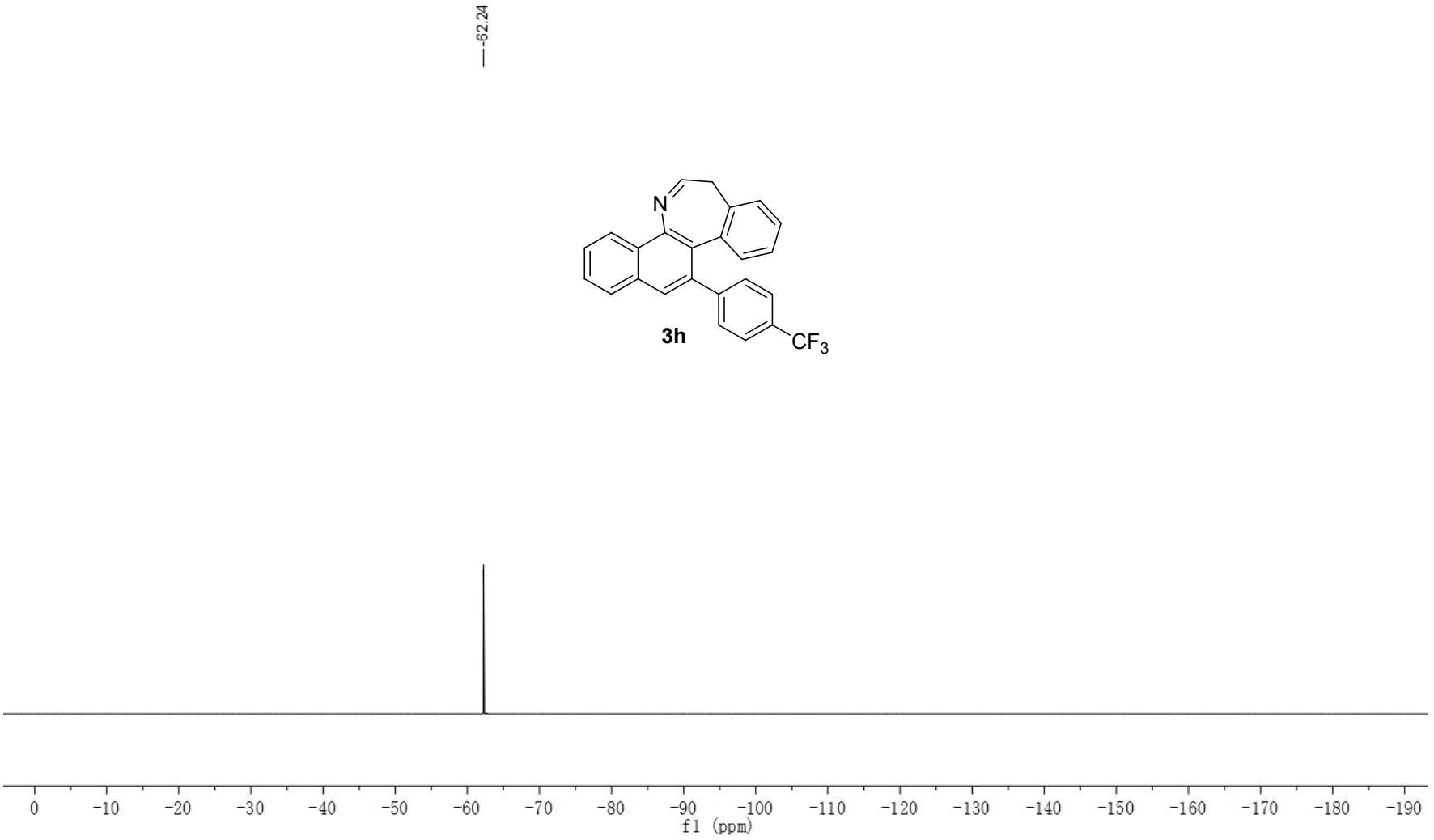
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3h**



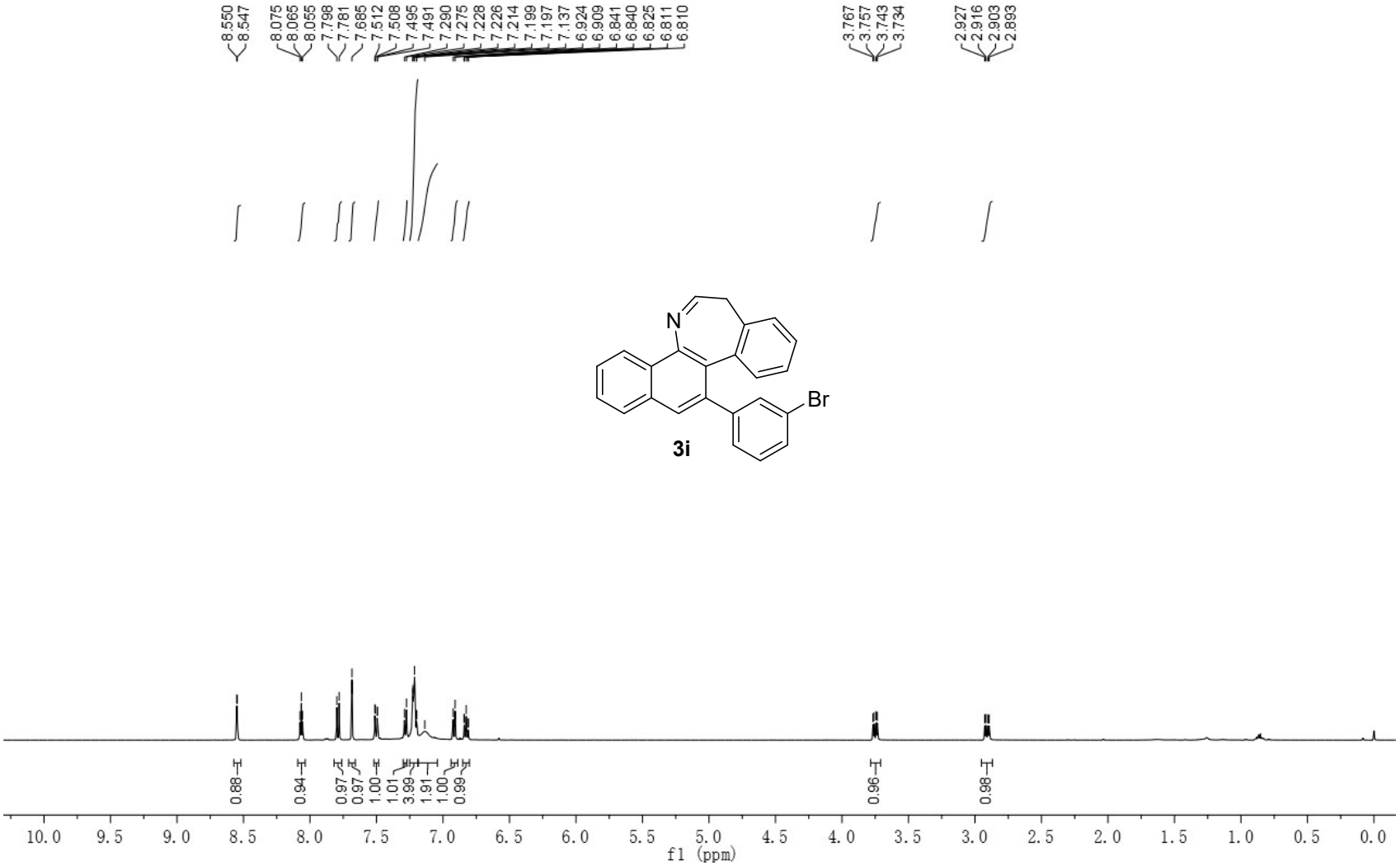
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3h**



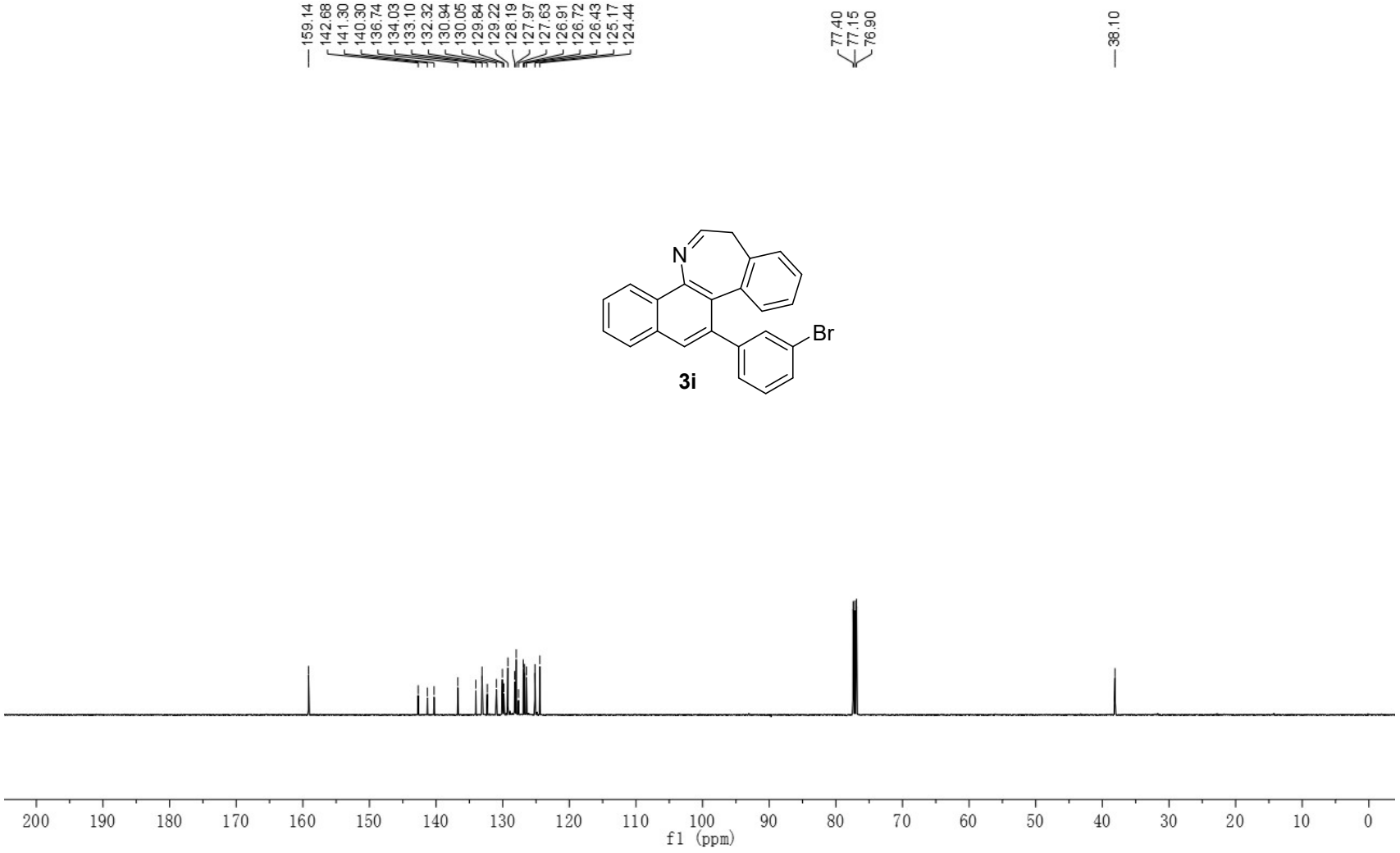
$^{19}$F NMR (471 MHz, $CDCl_3$) of **3h**



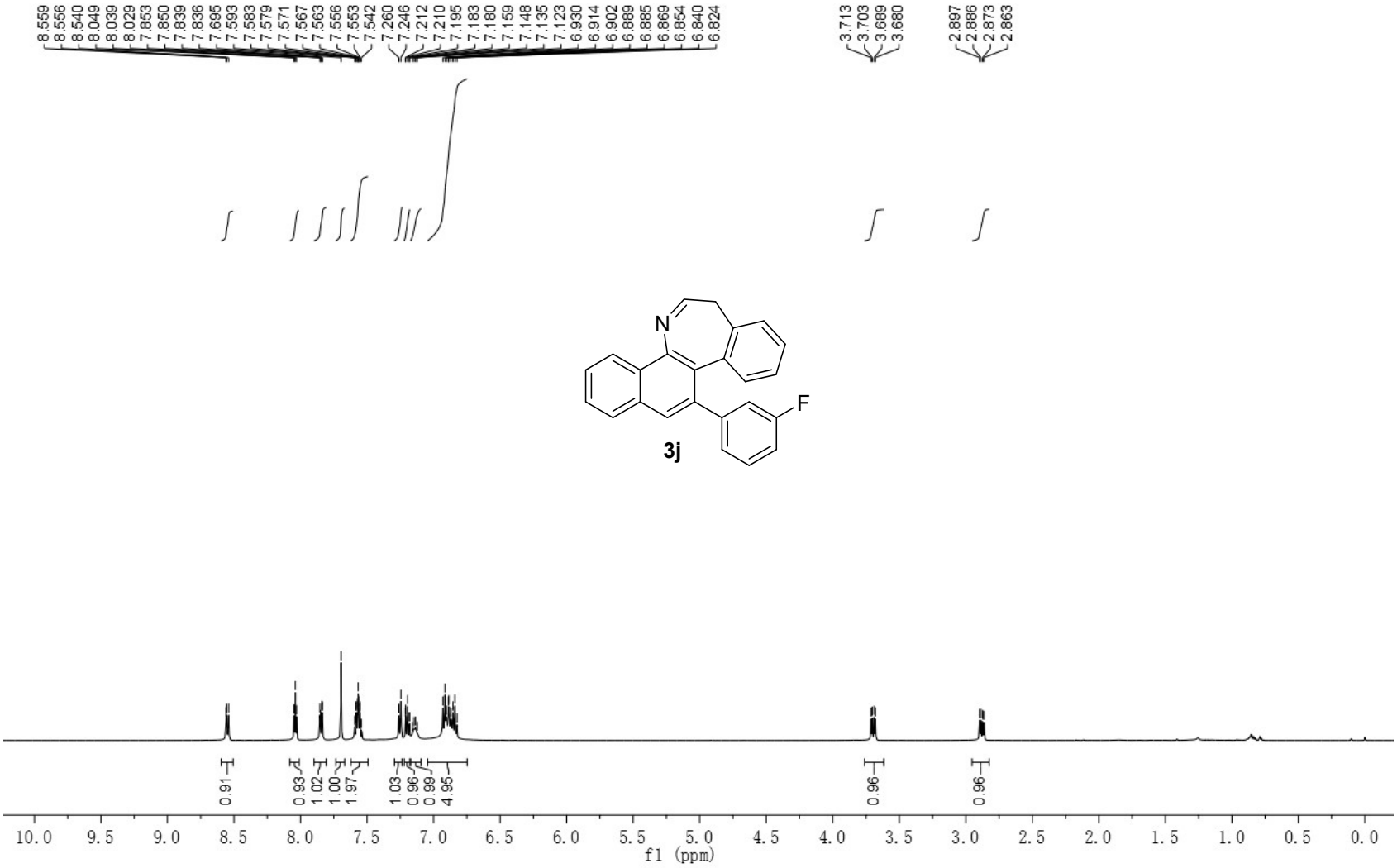
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3i**



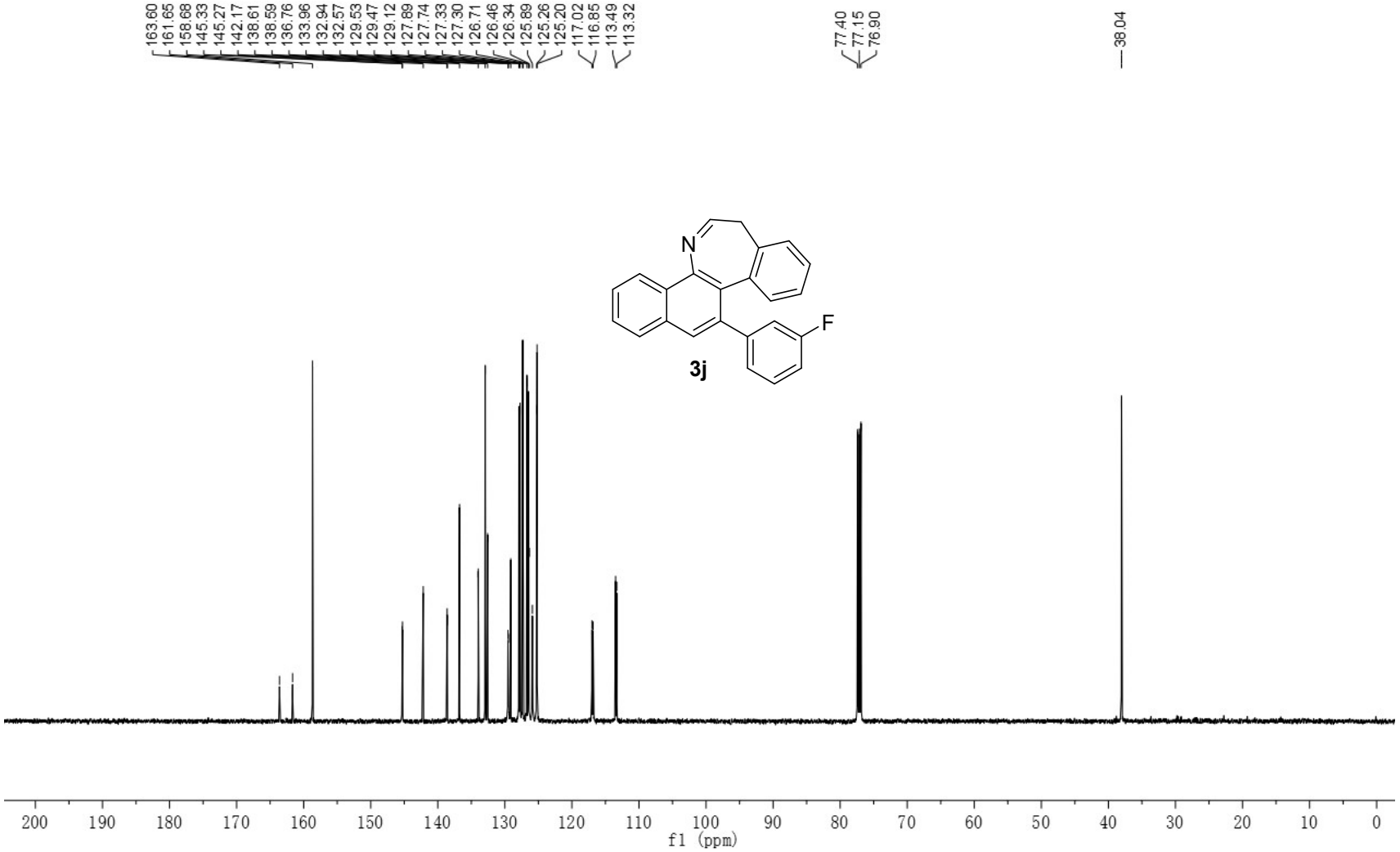
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3i**



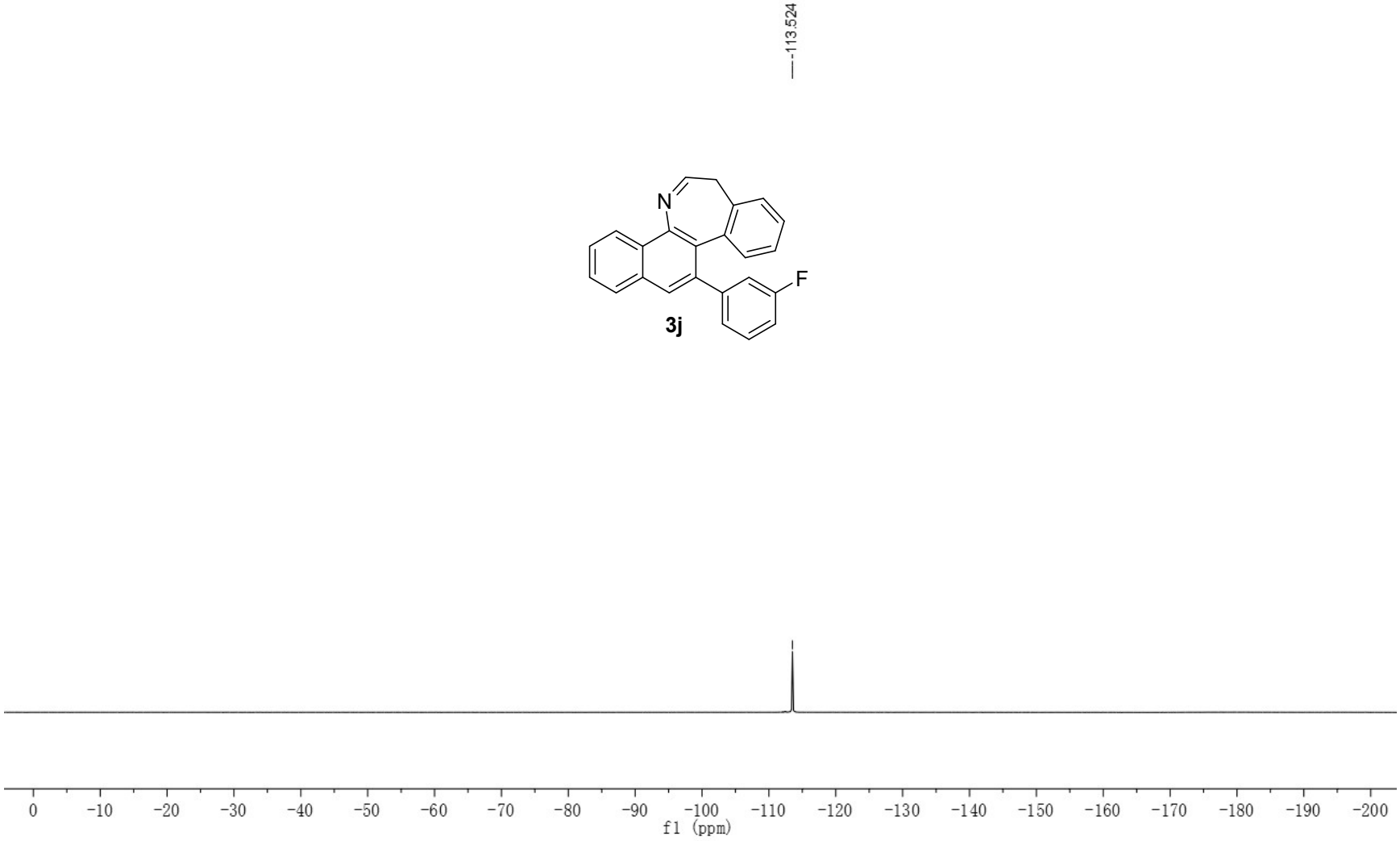
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3j**



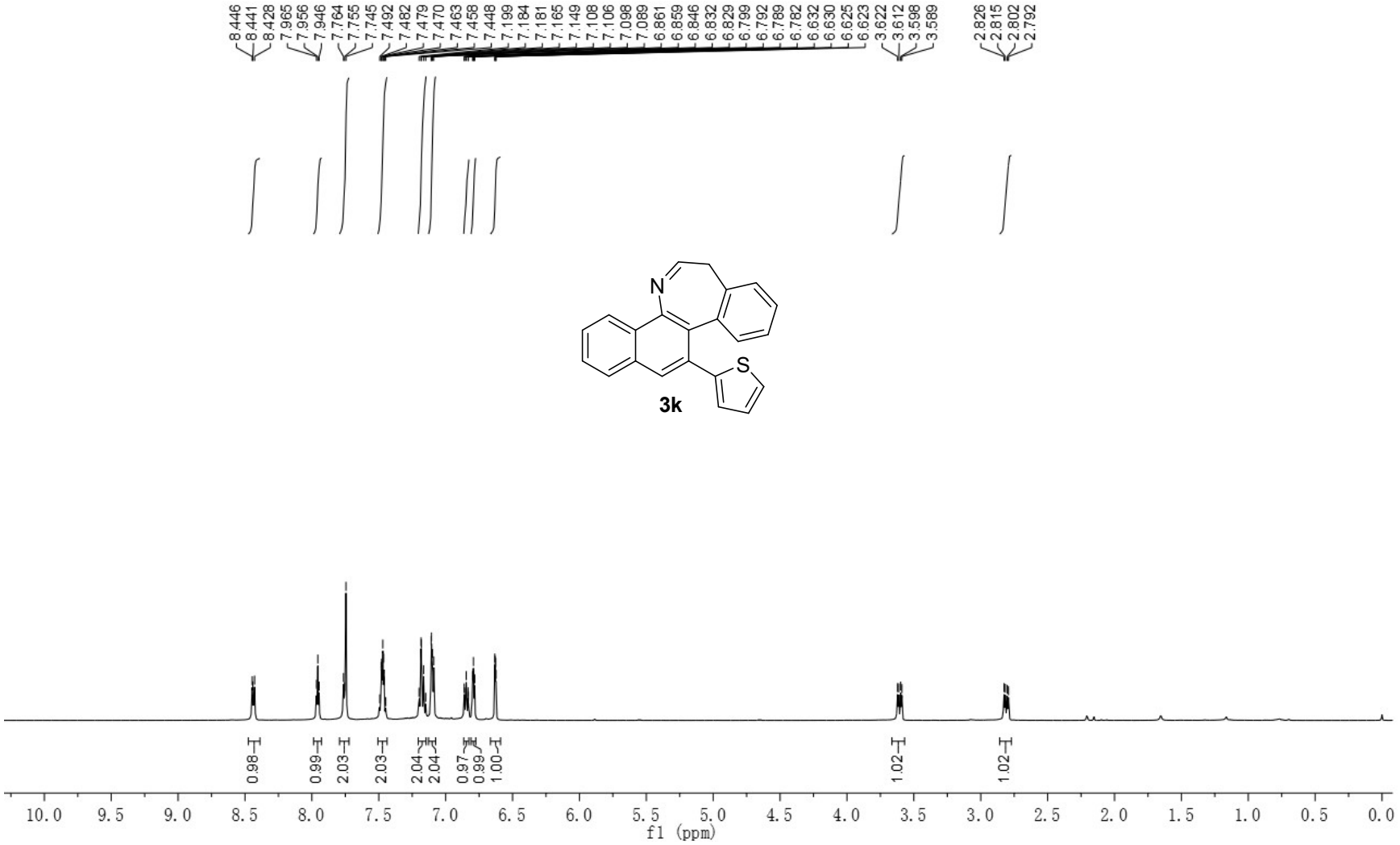
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3j**



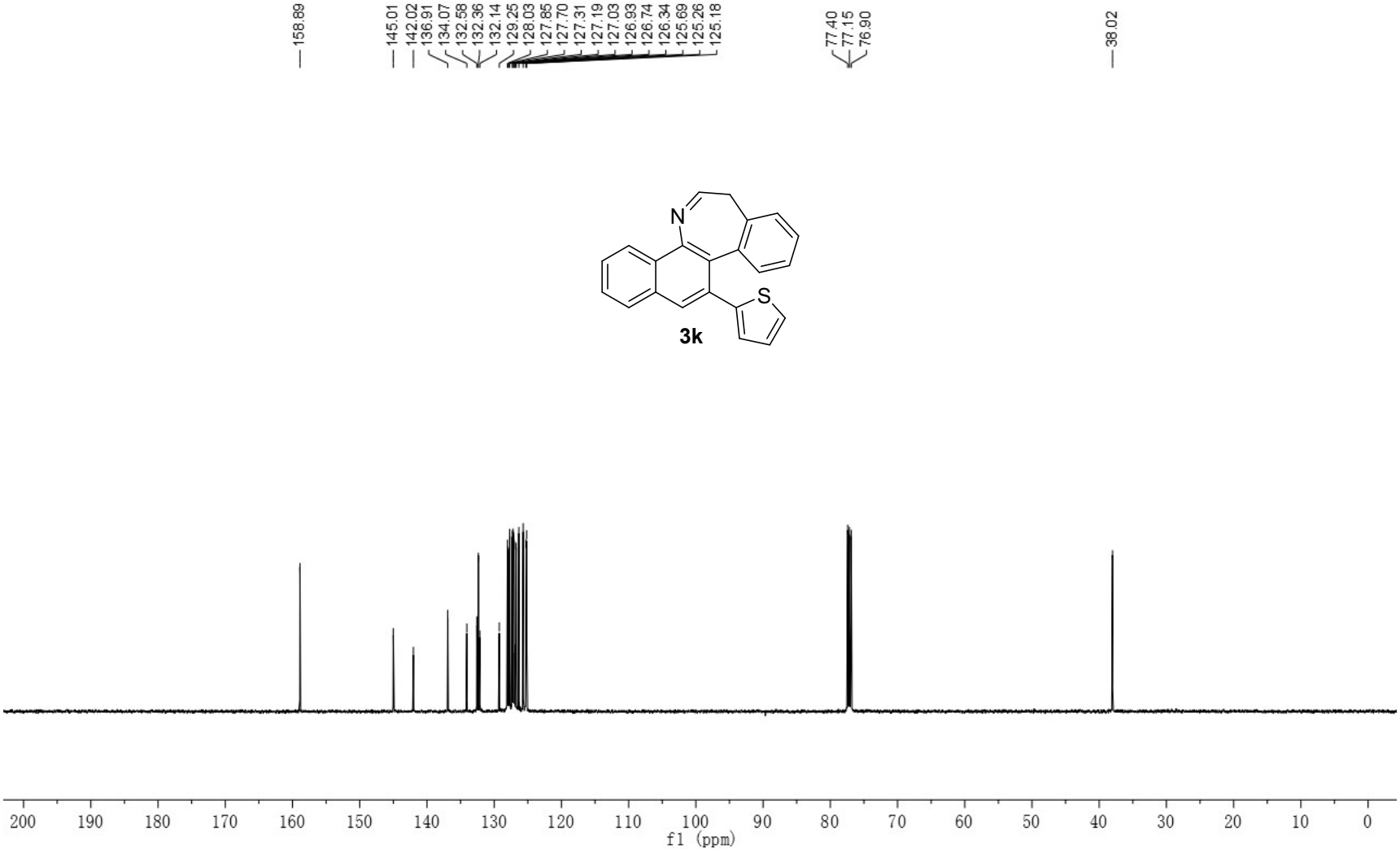
$^{19}F$ NMR (471 MHz, $CDCl_3$) of **3j**



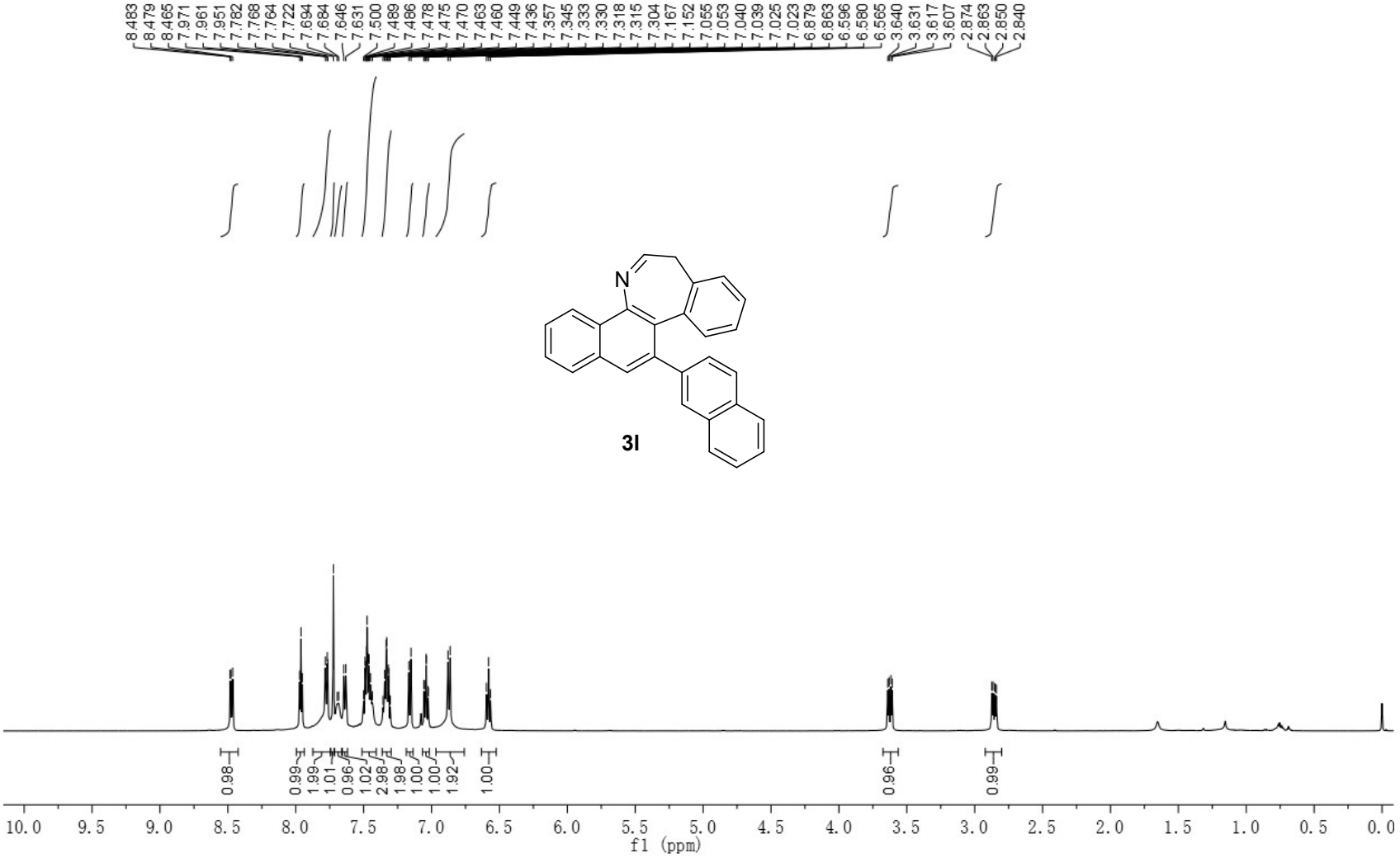
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3k**



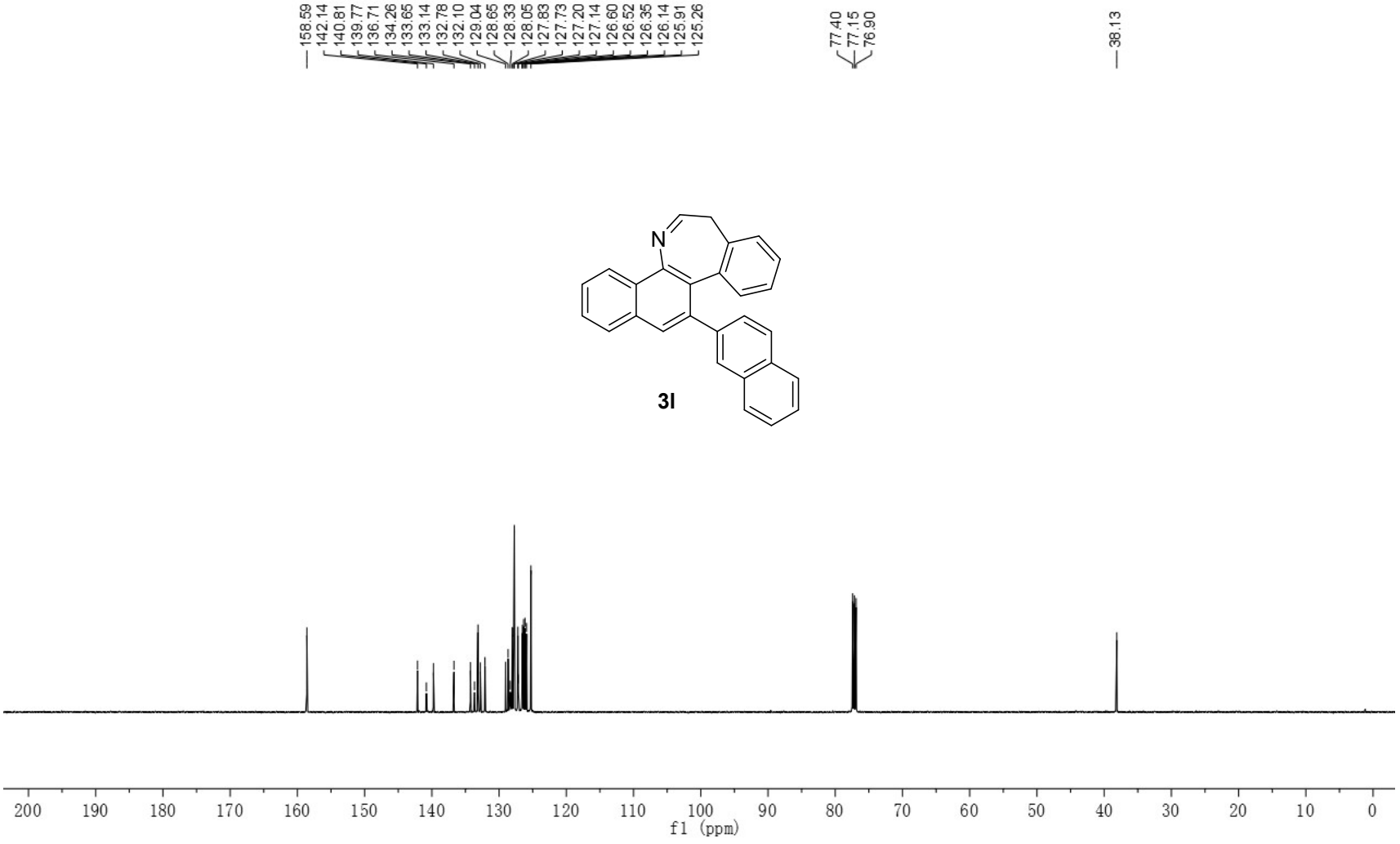
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3k**



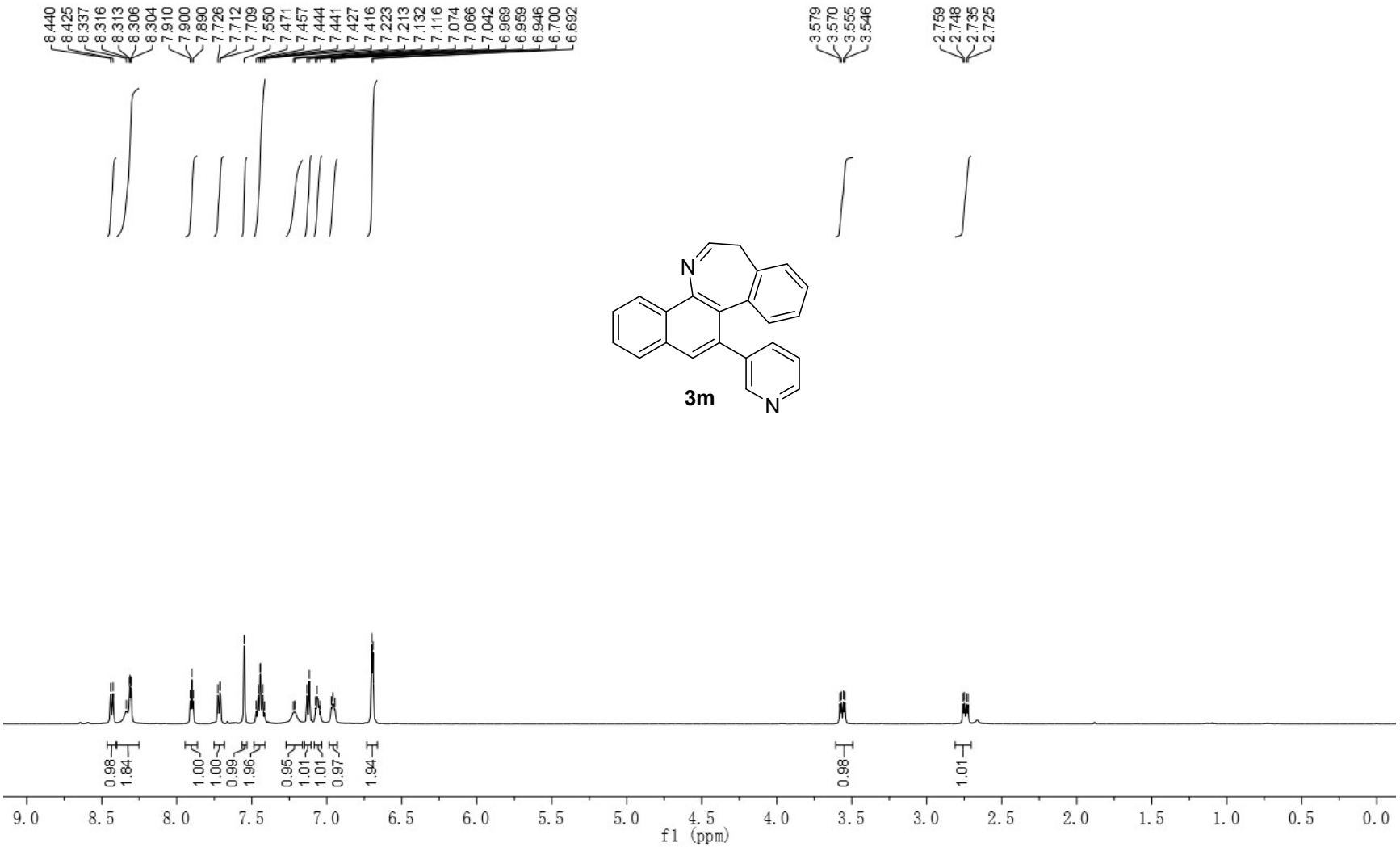
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3l**



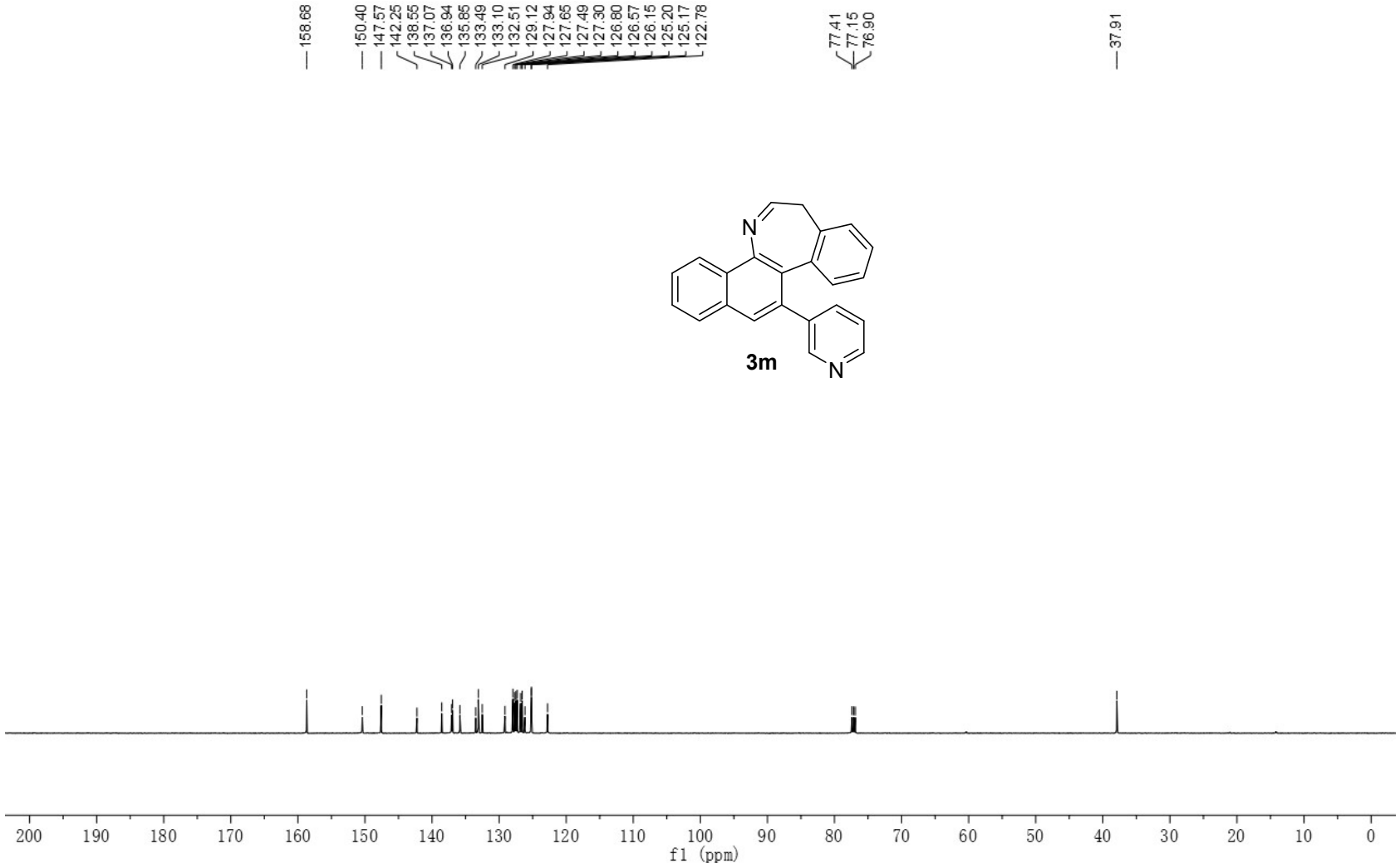
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3l**



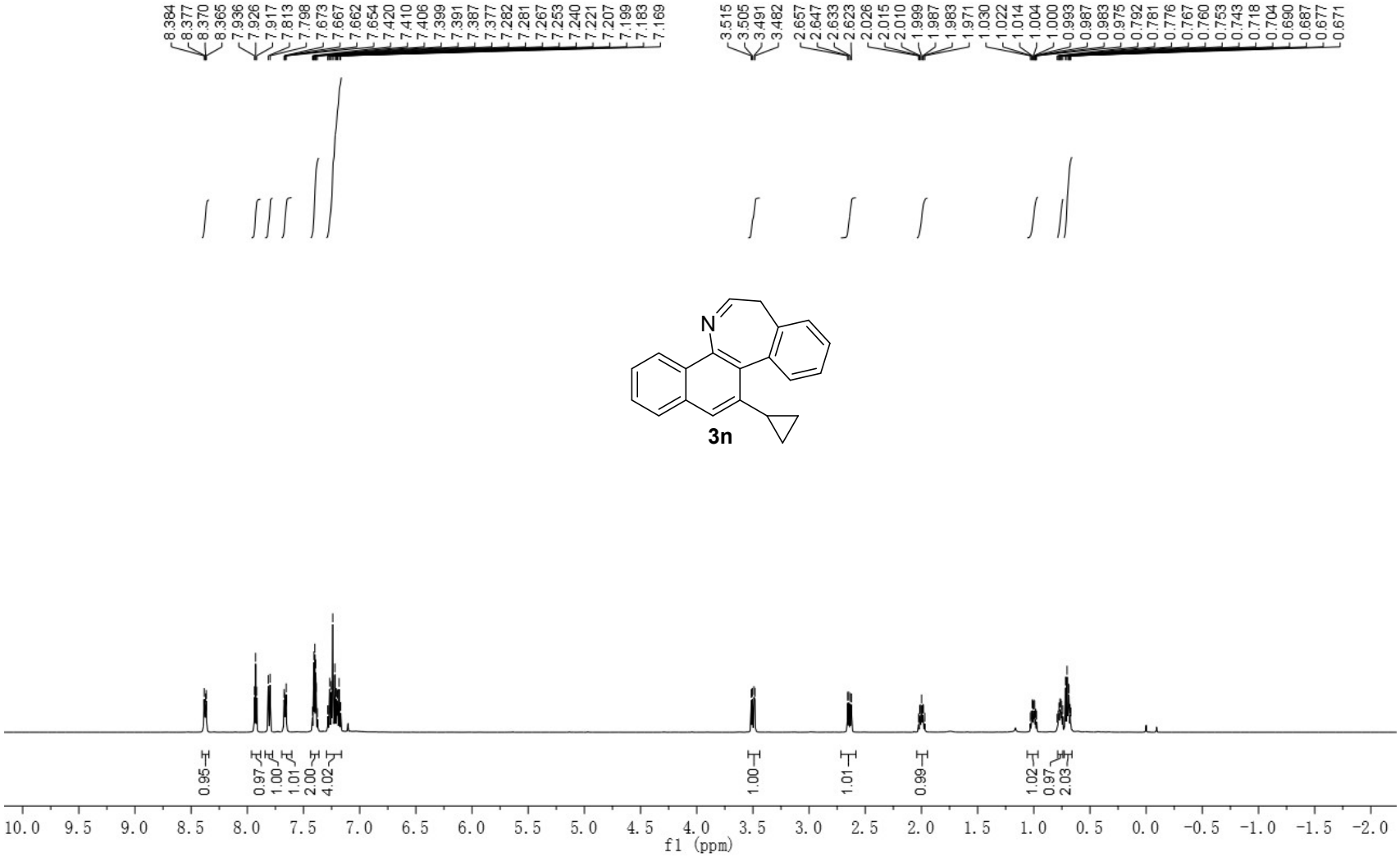
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3m**



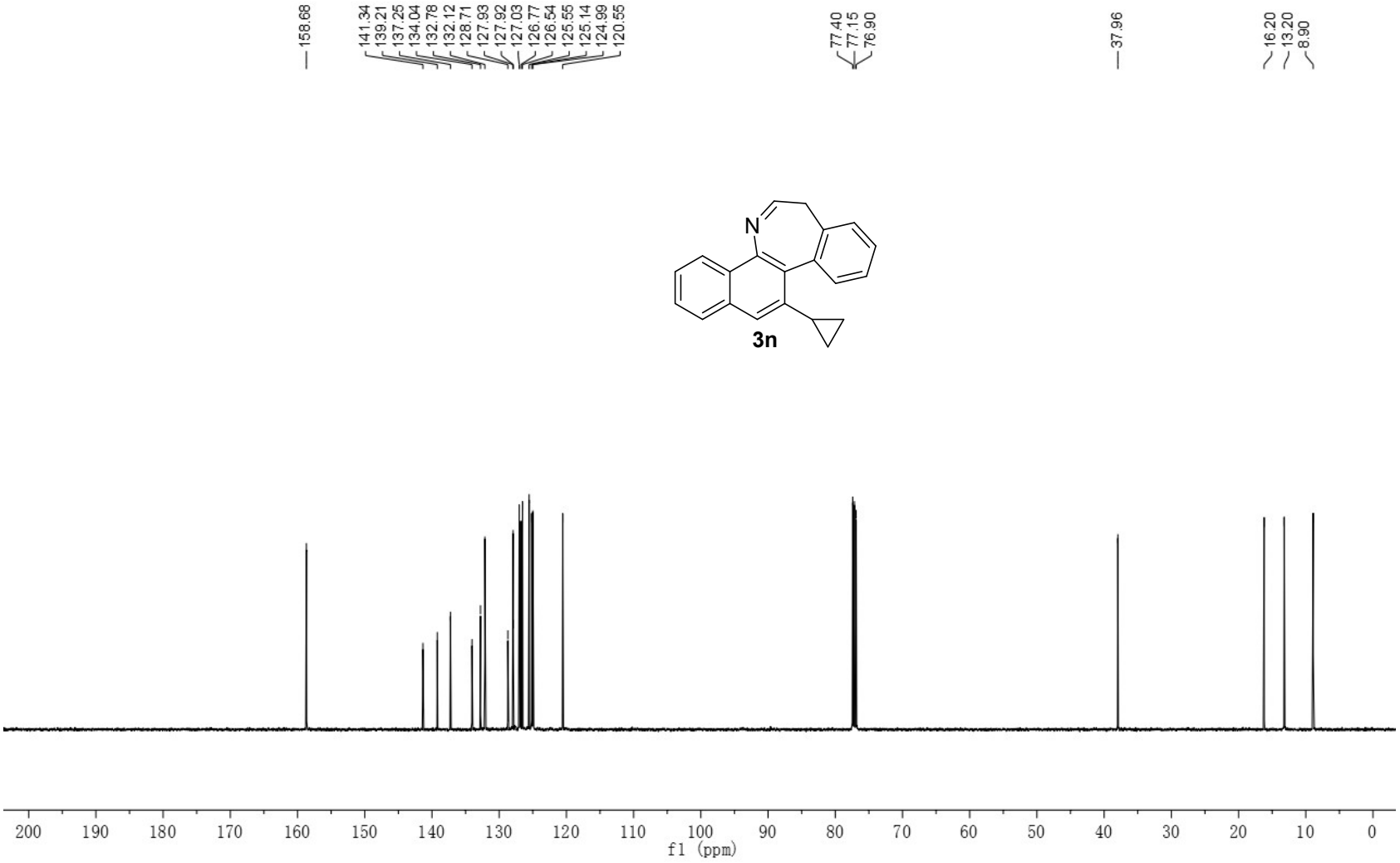
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3m**



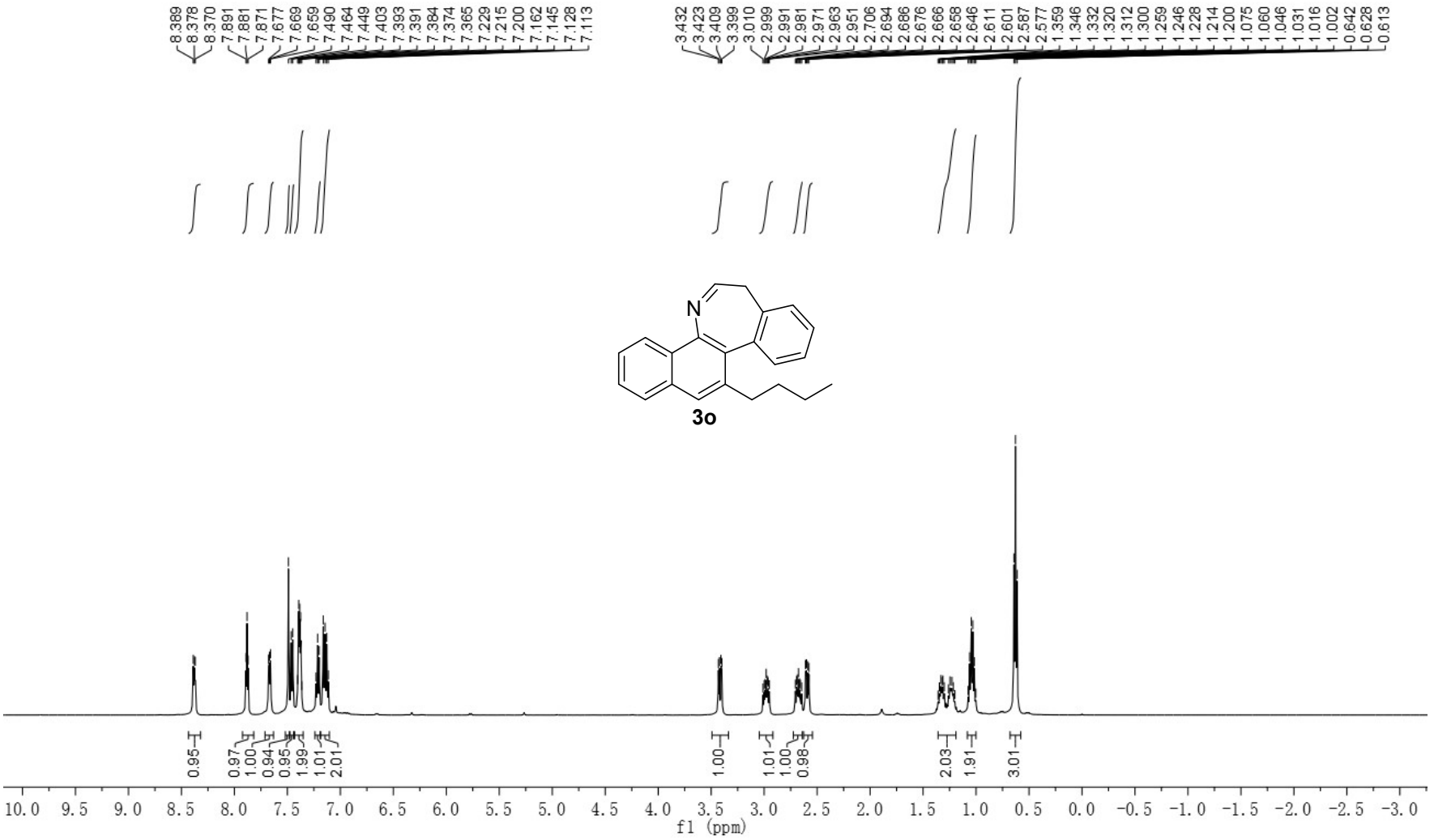
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3n**



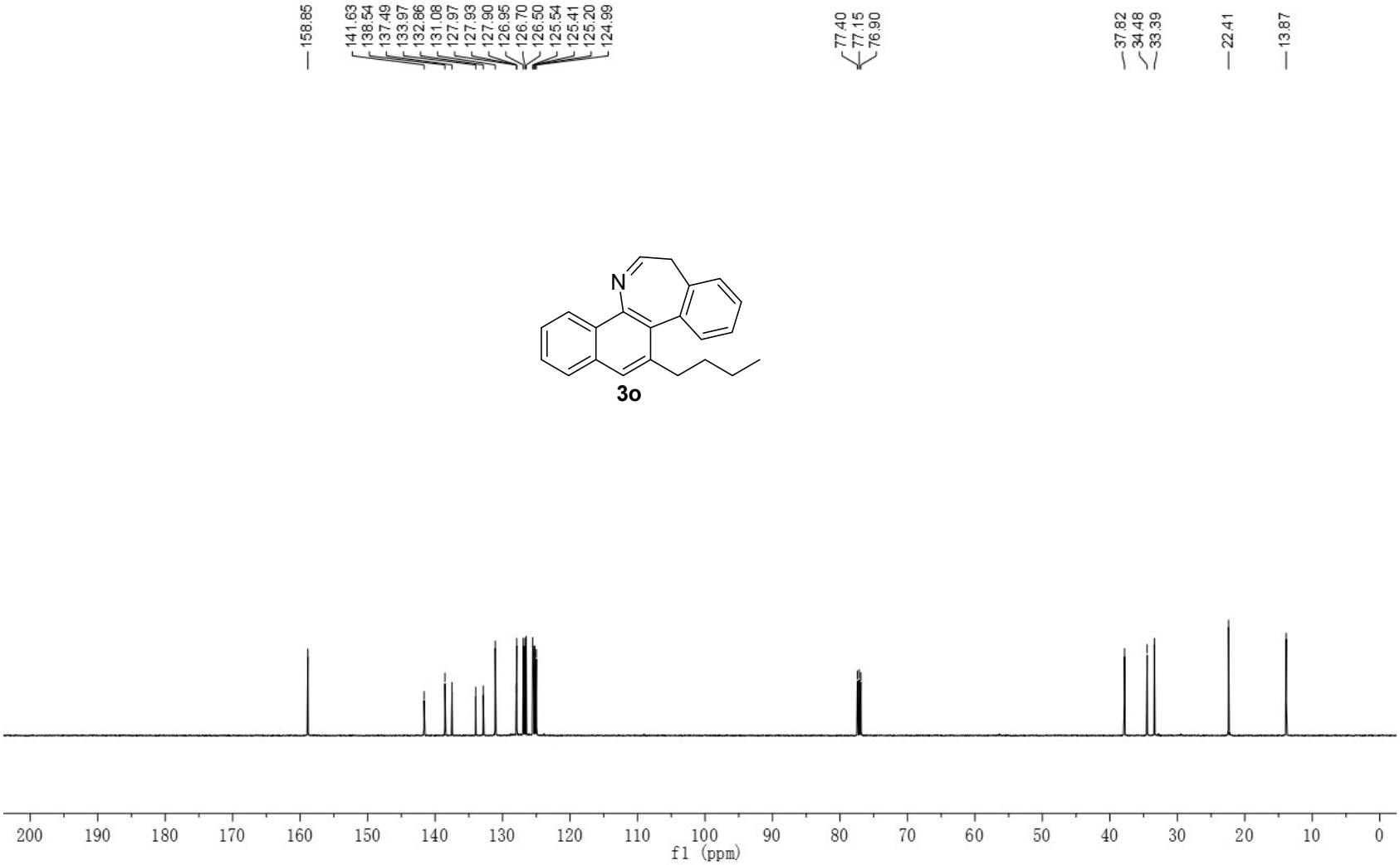
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3n**



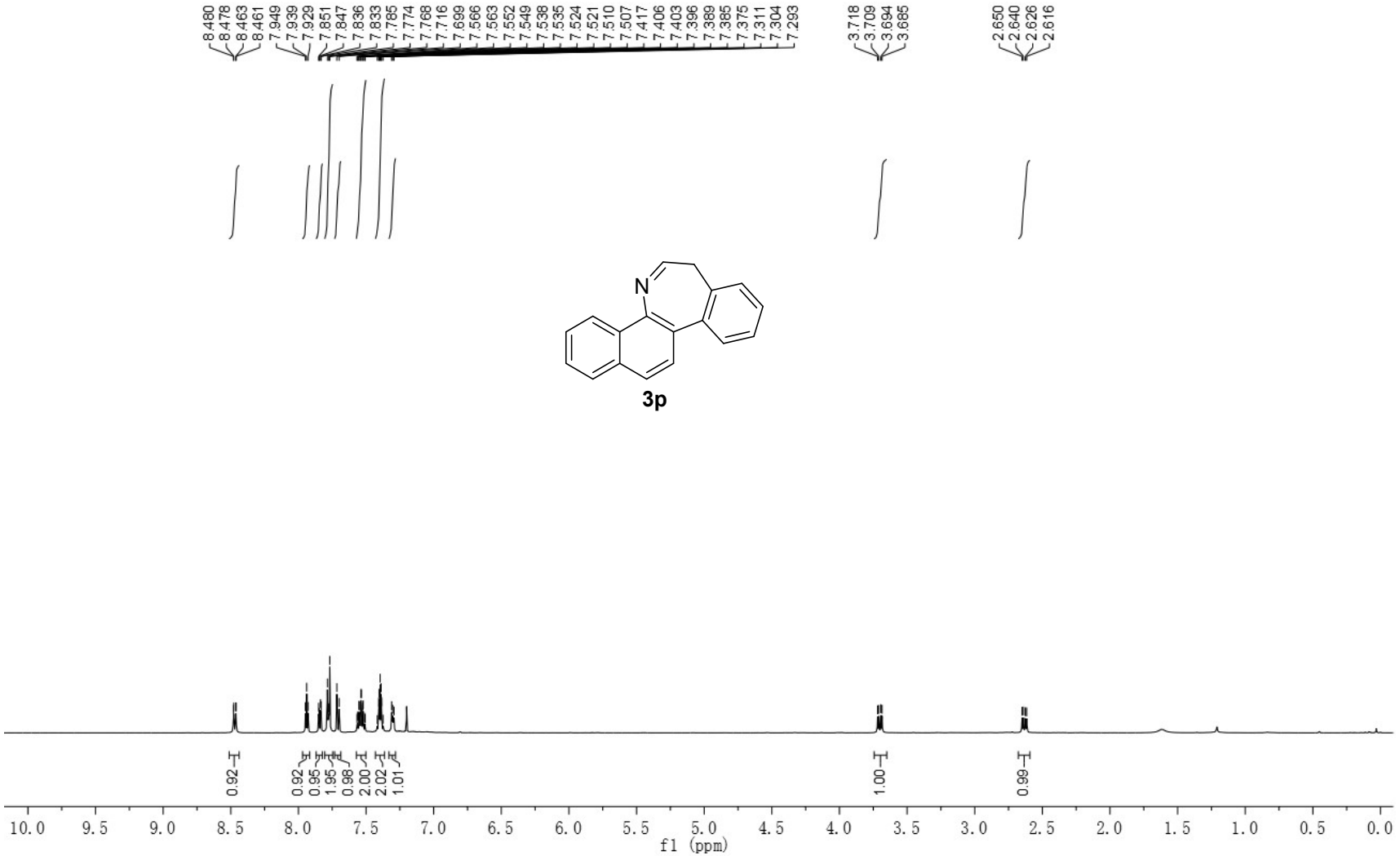
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3o**



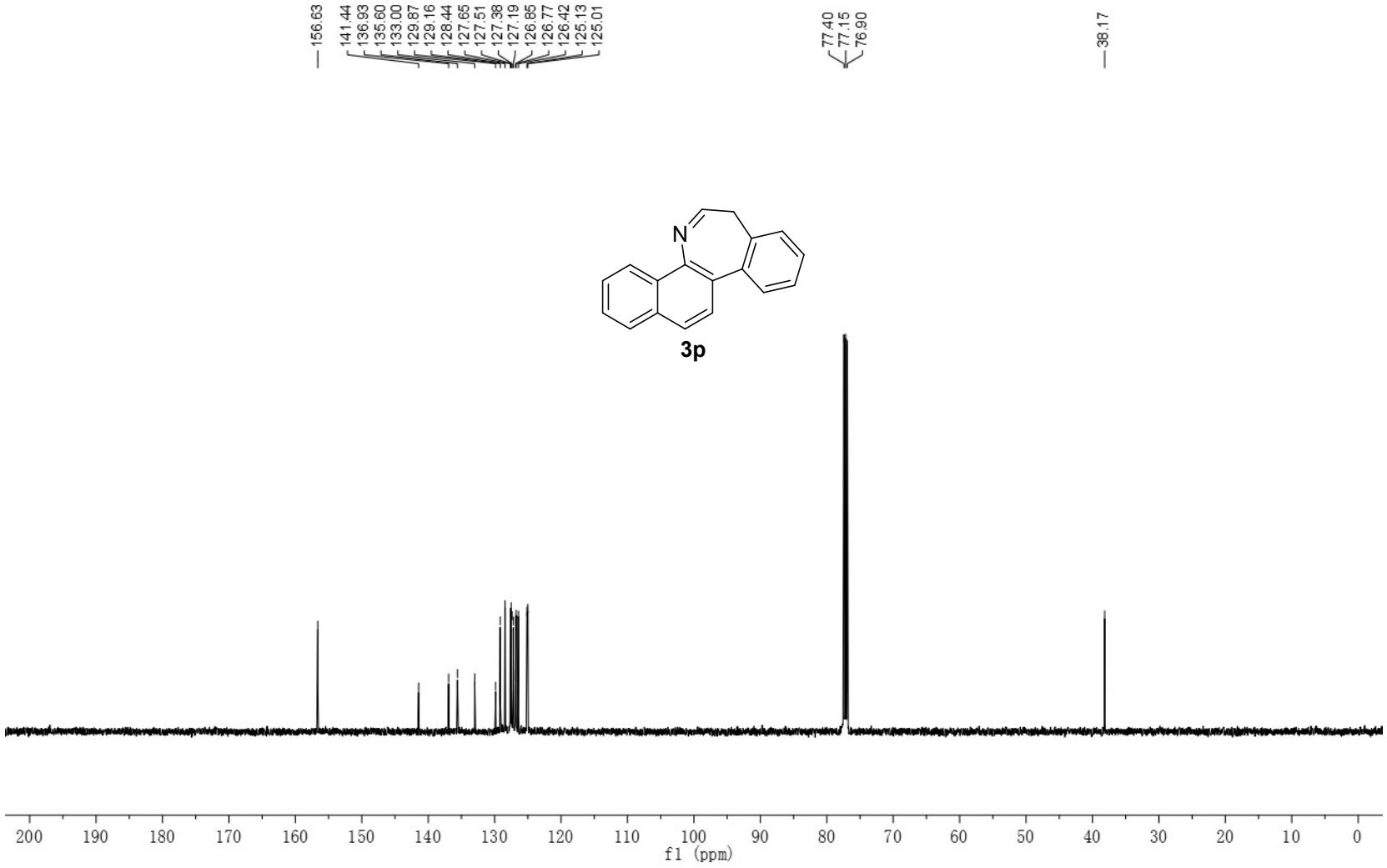
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3o**



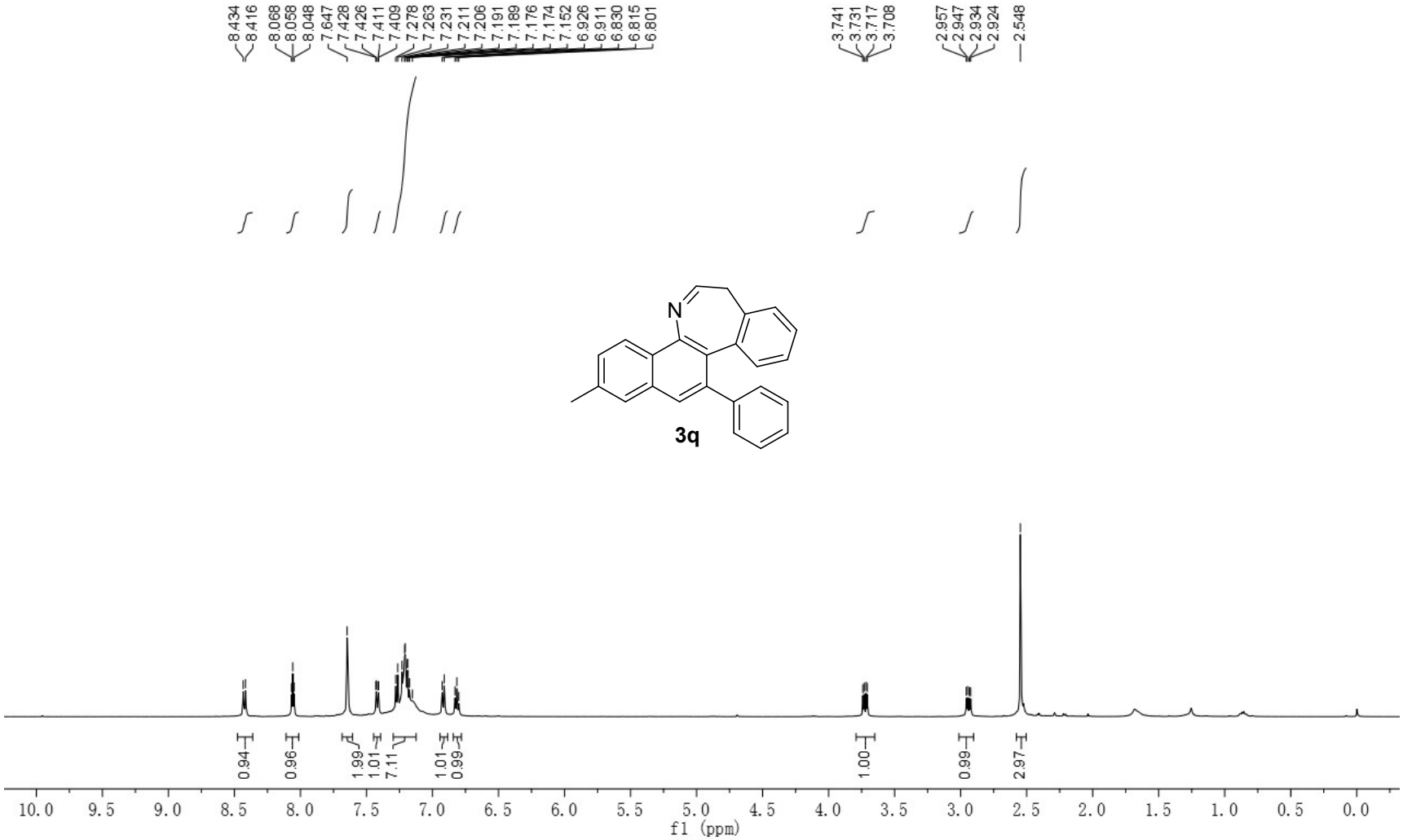
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3p**



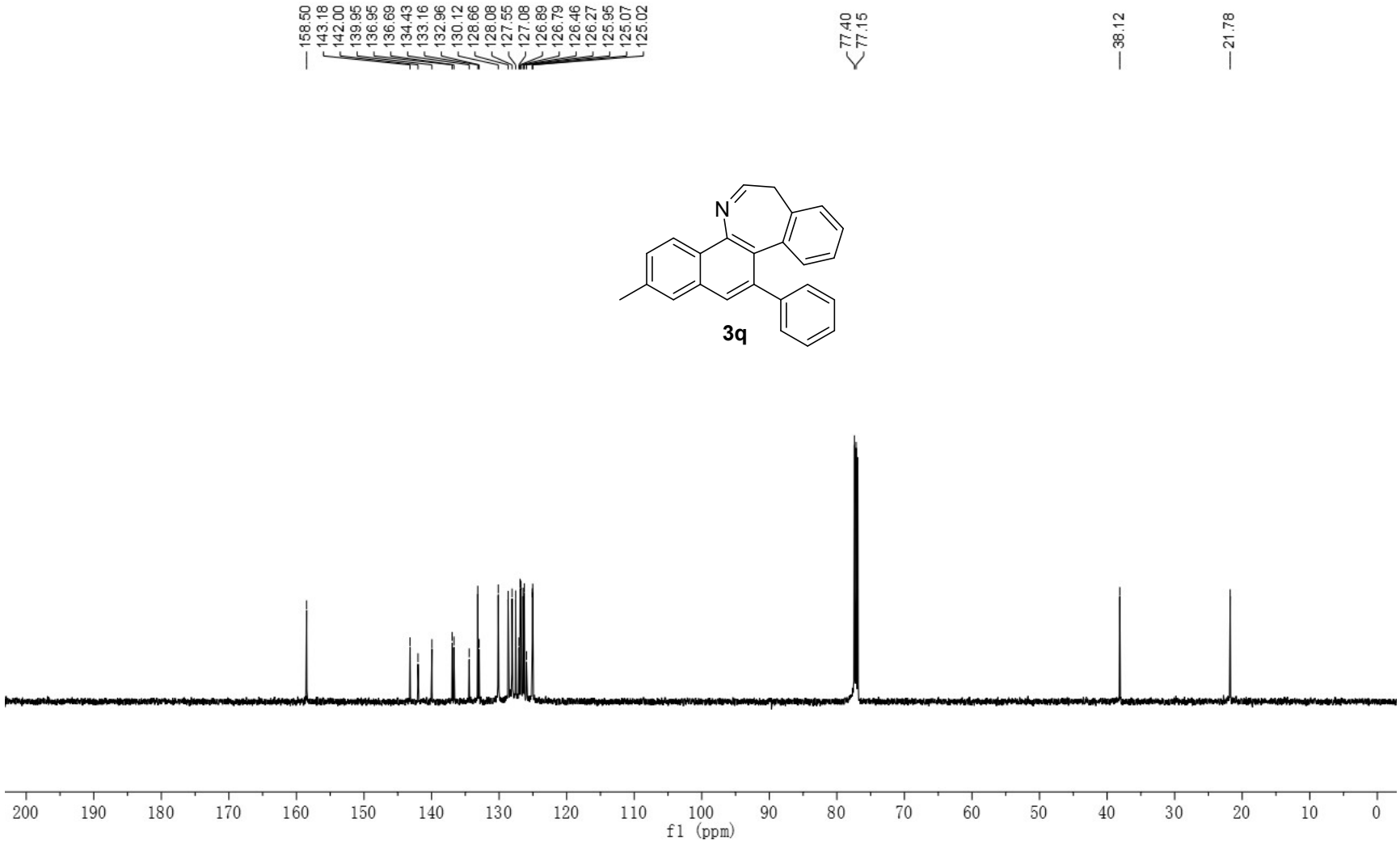
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3p**



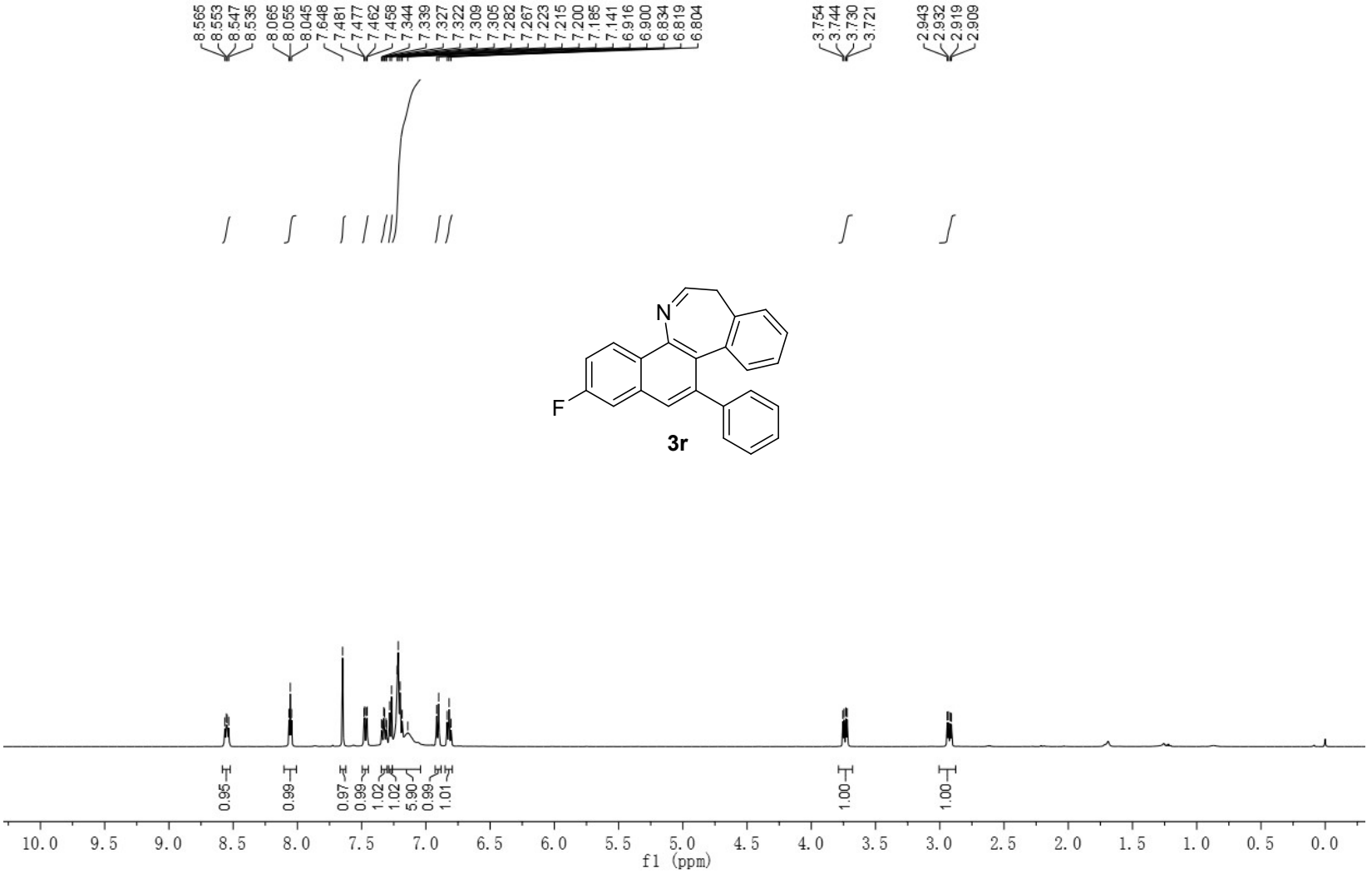
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3q**



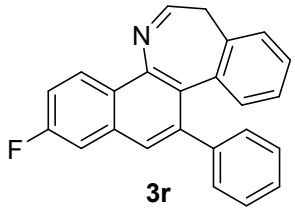
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3q**



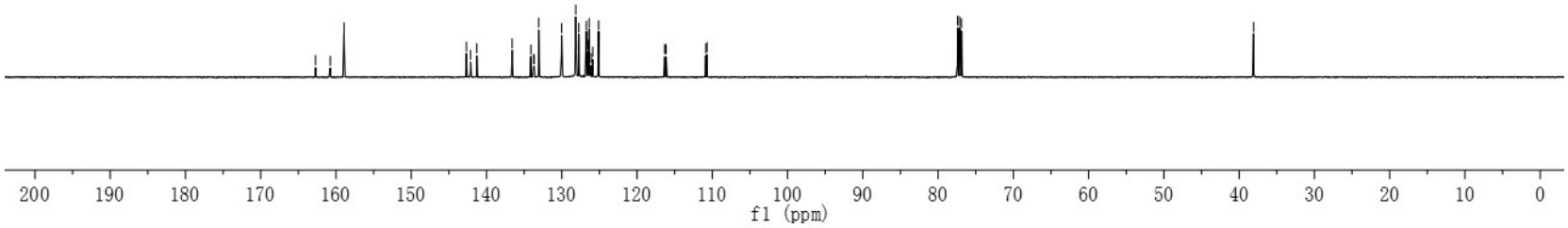
$^1$H NMR (500 MHz, $CDCl_3$) of **3r**



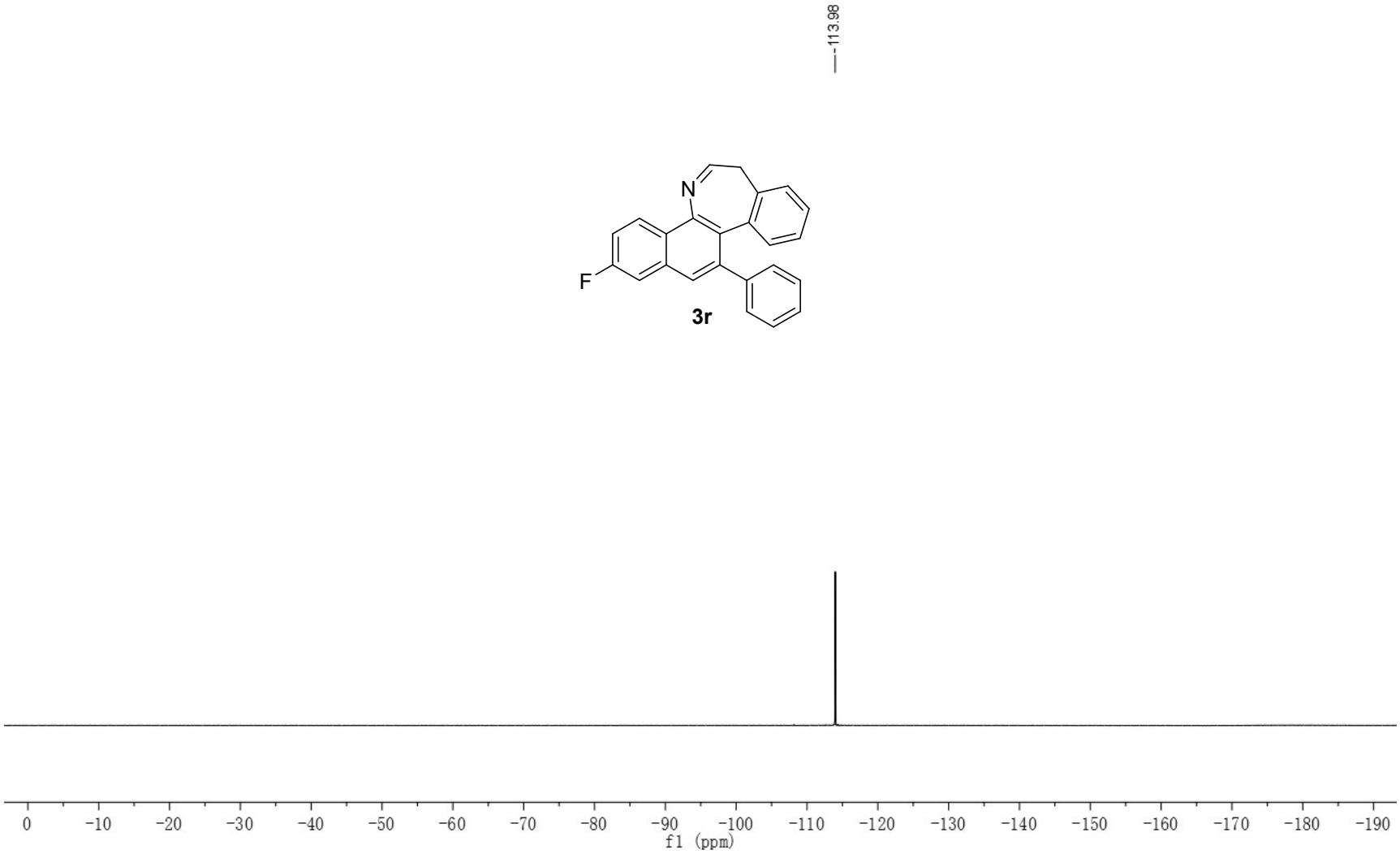
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3r**

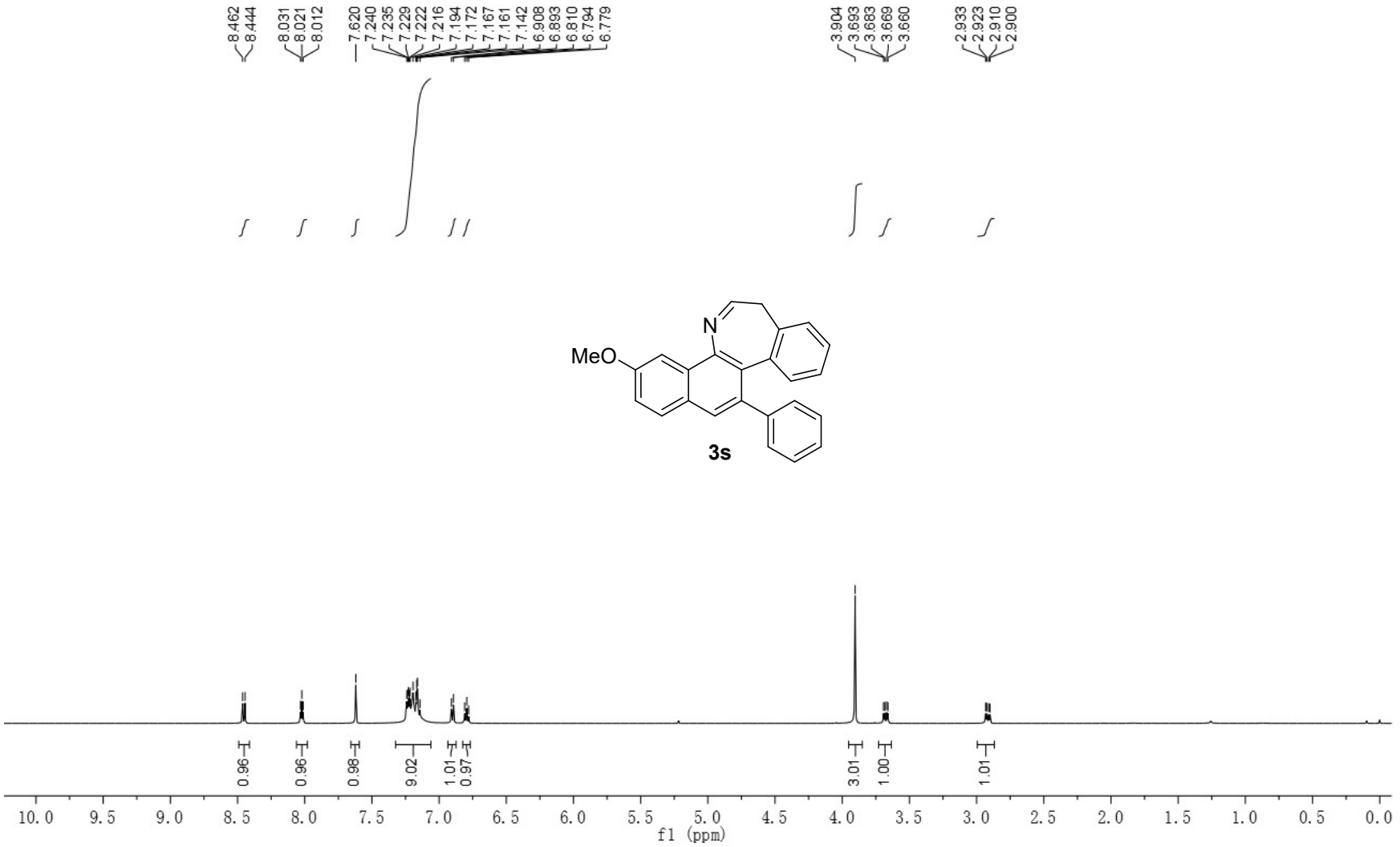

**3r**



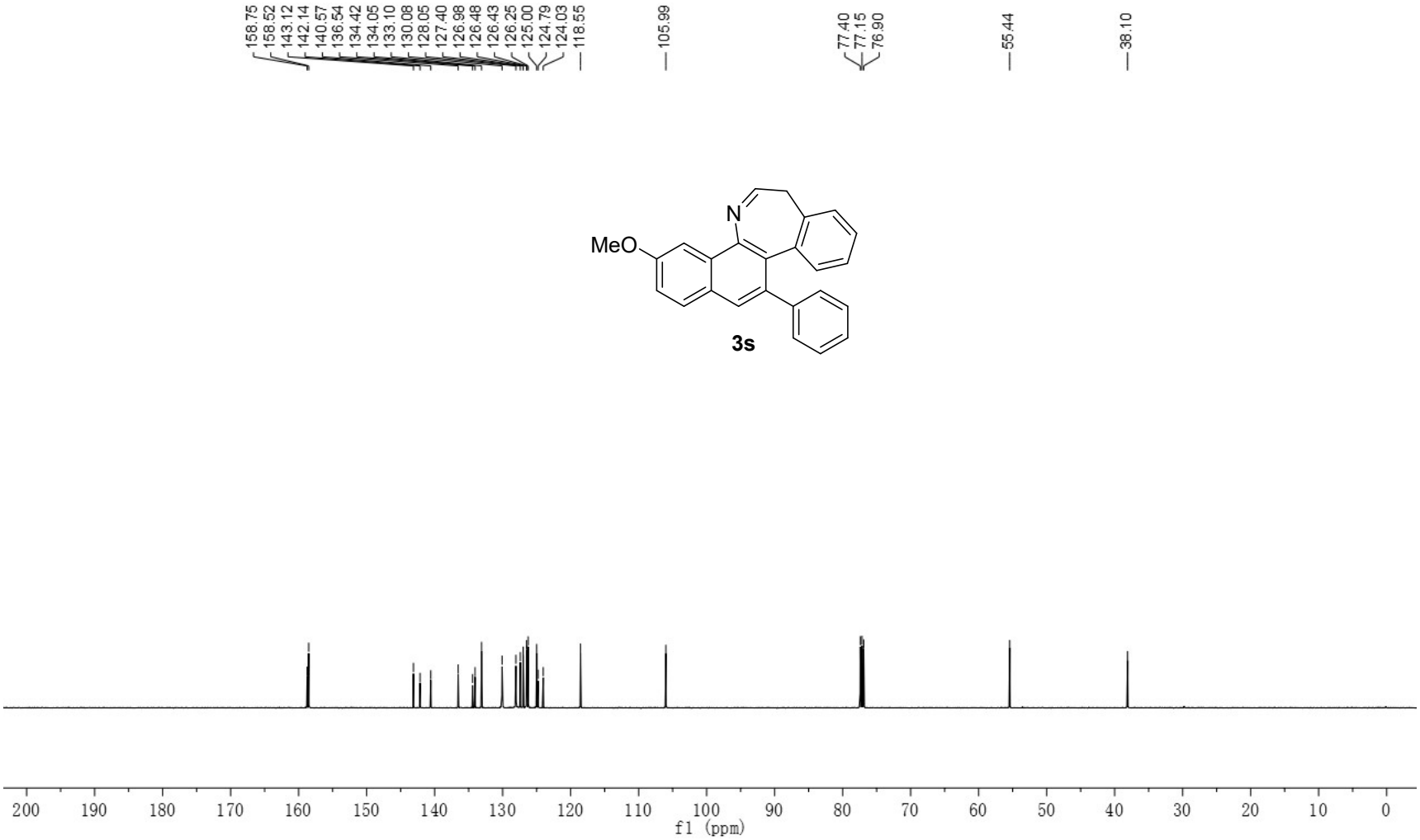
$^{19}F$ NMR (471 MHz, $CDCl_3$) of **3r**



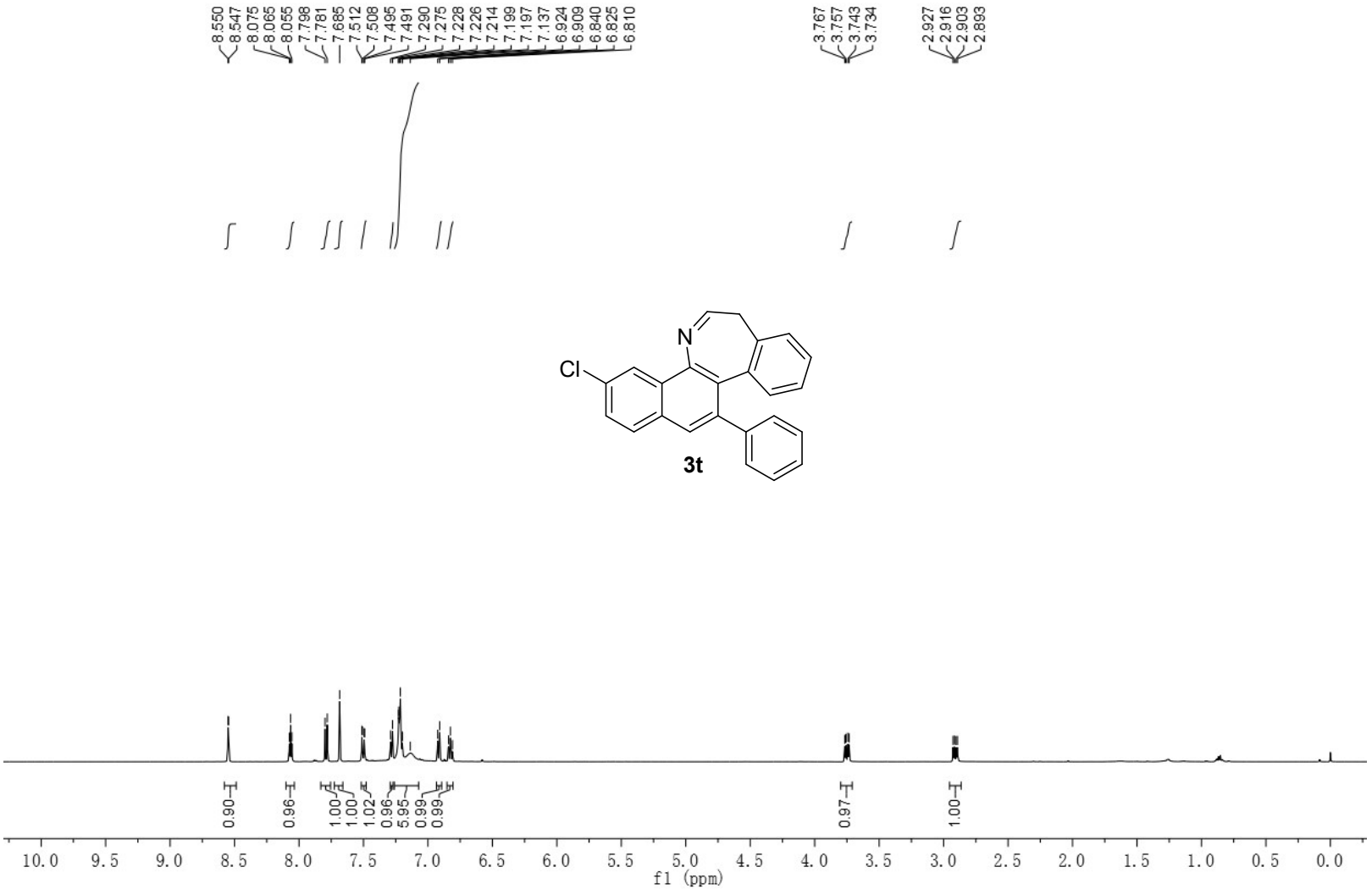
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3s**



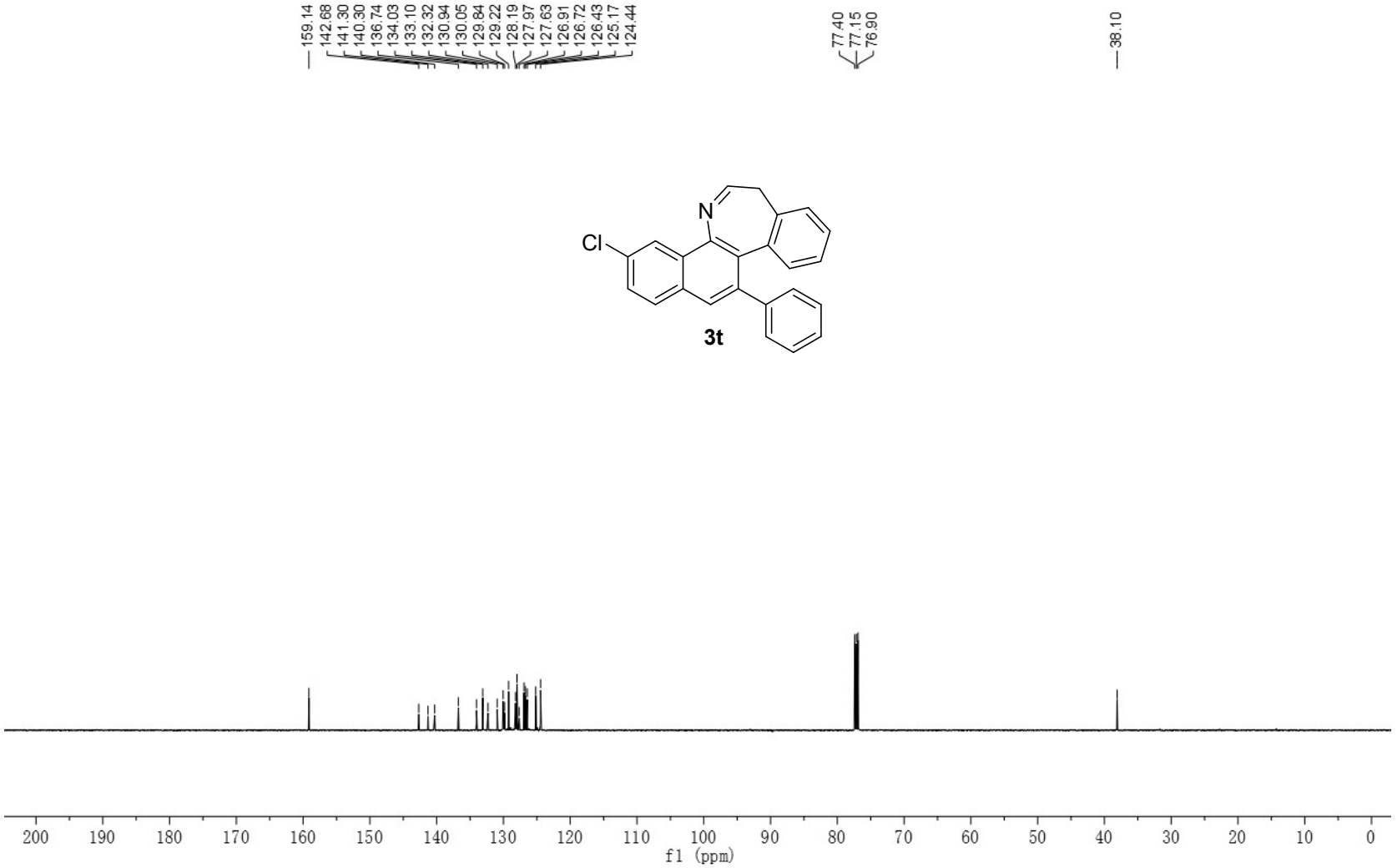
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3s**



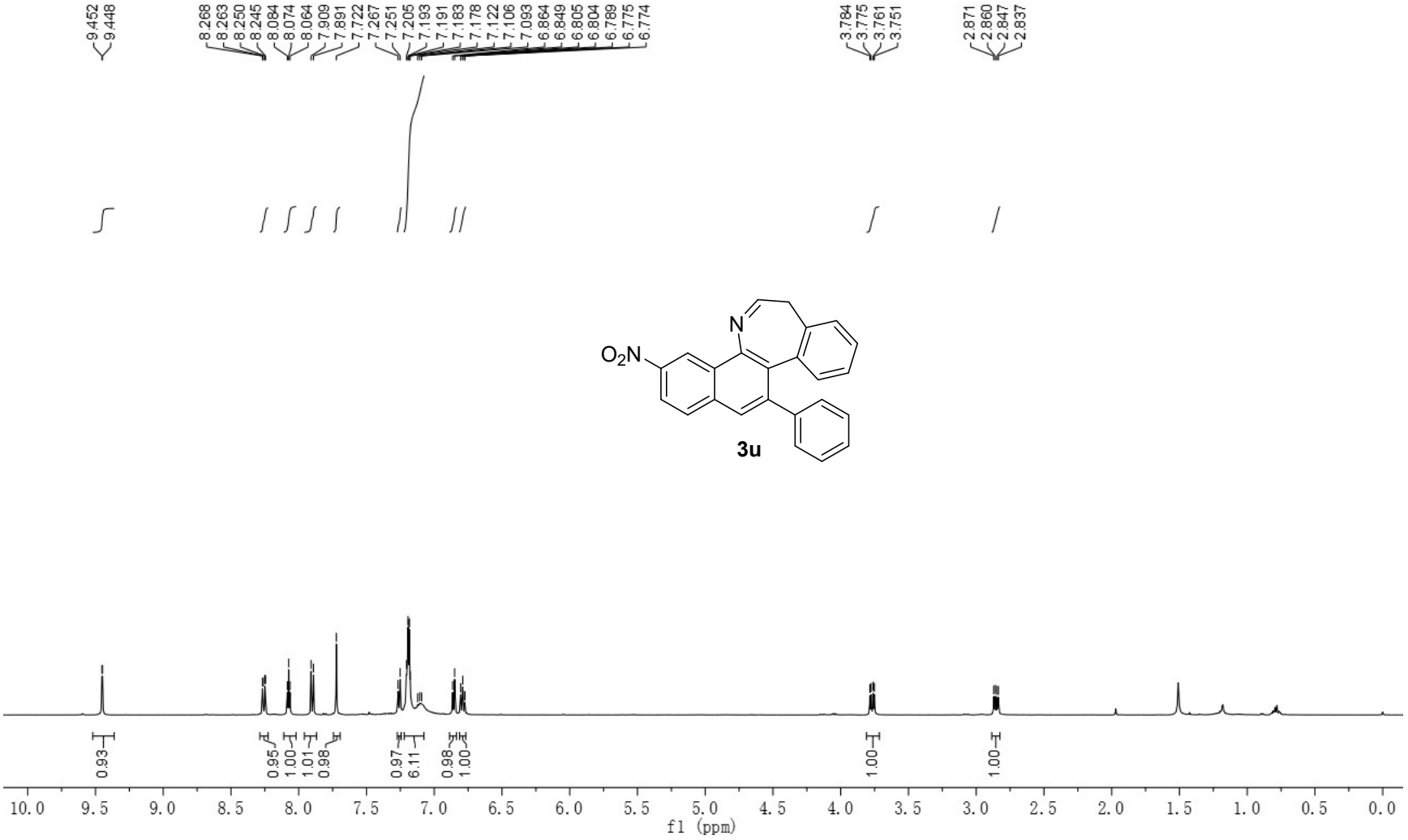
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3t**



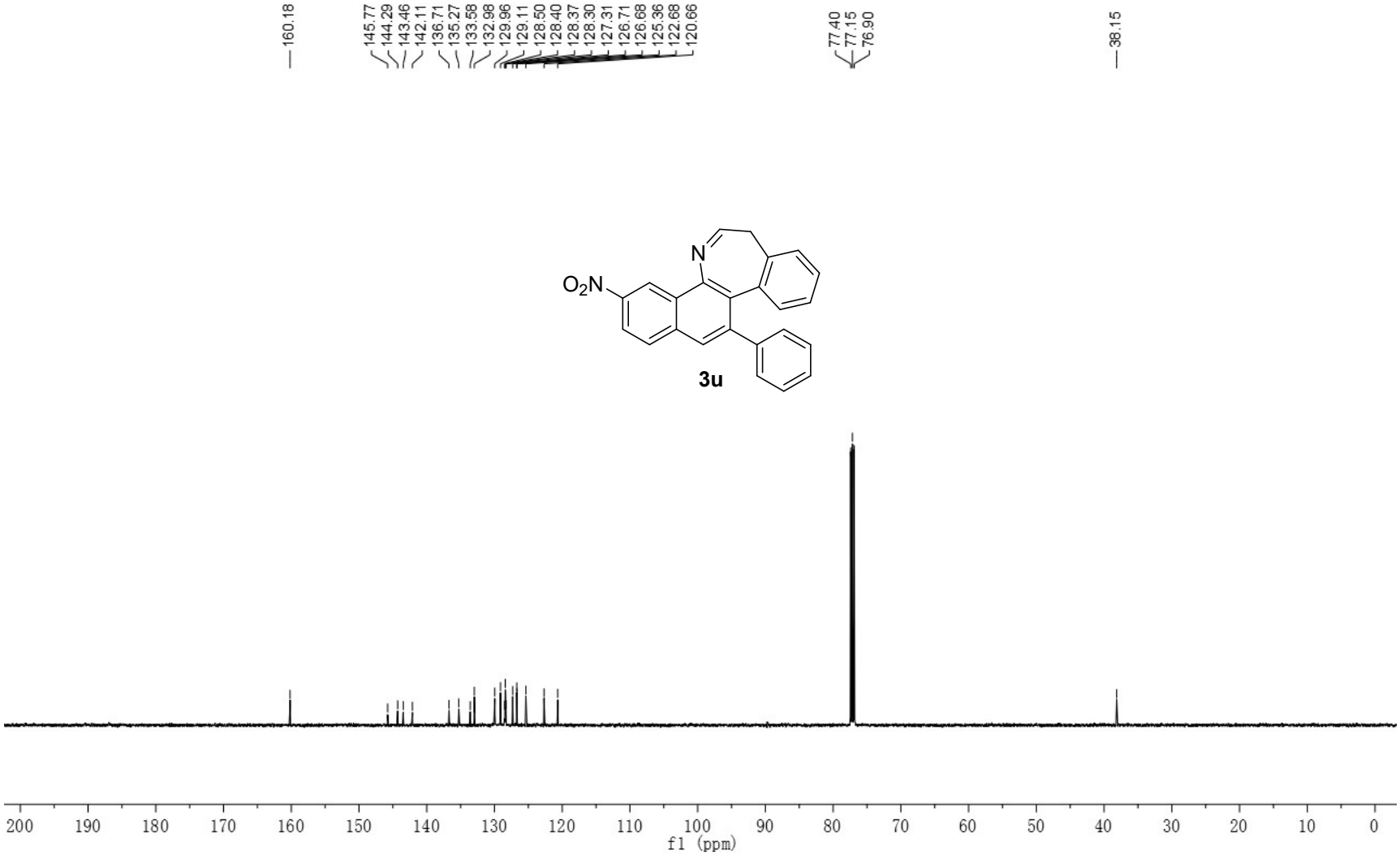
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3t**



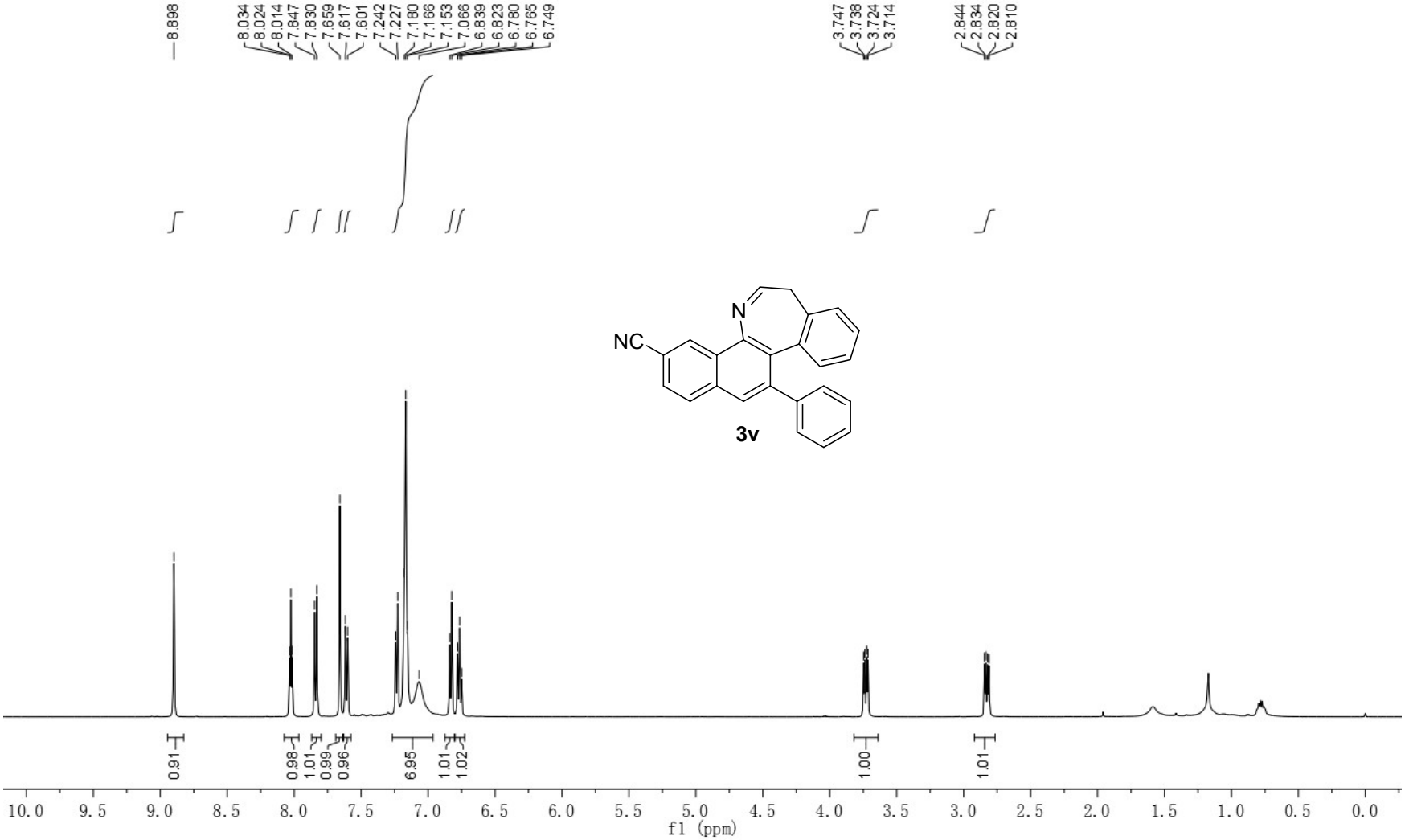
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3u**



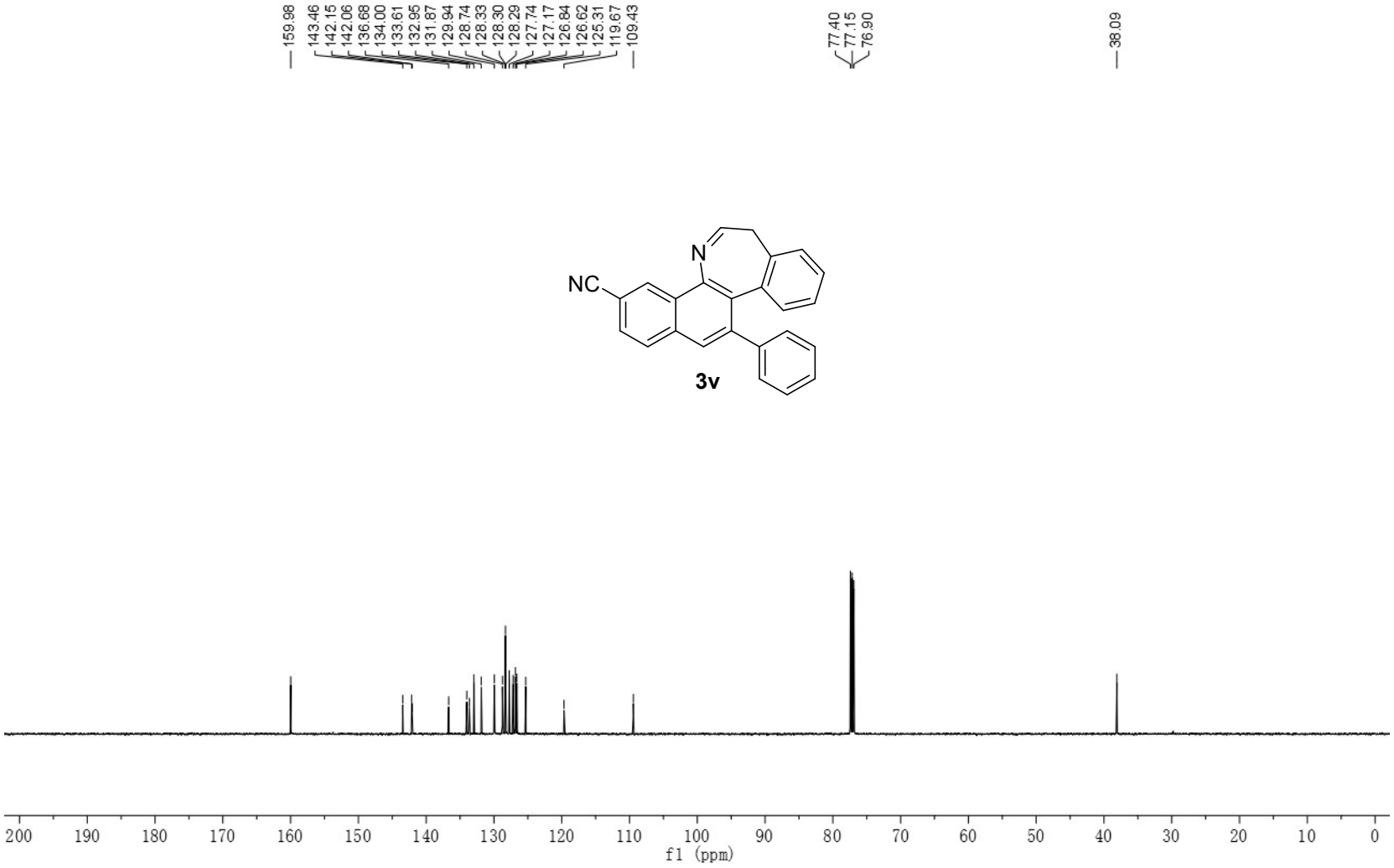
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3u**



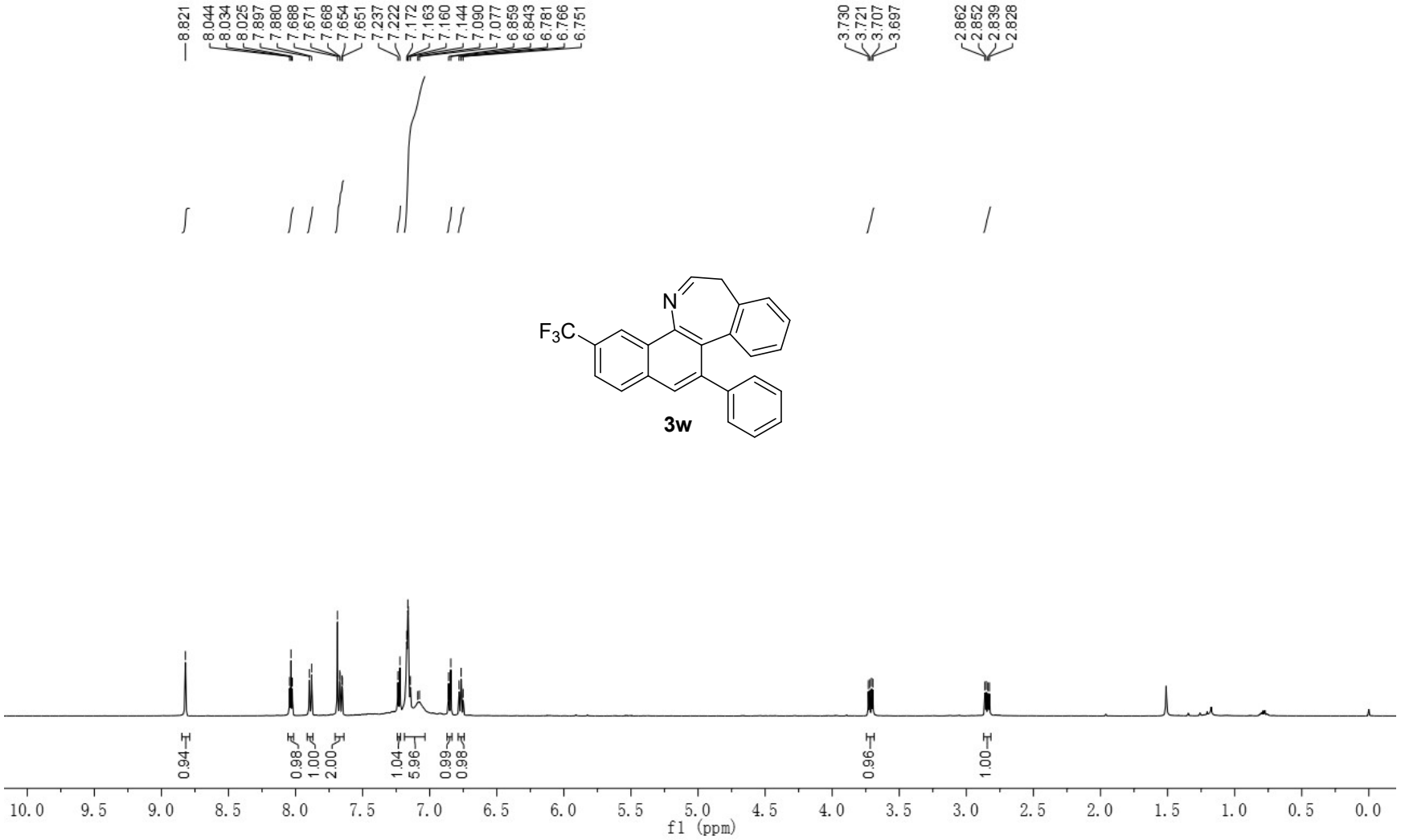
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3v**



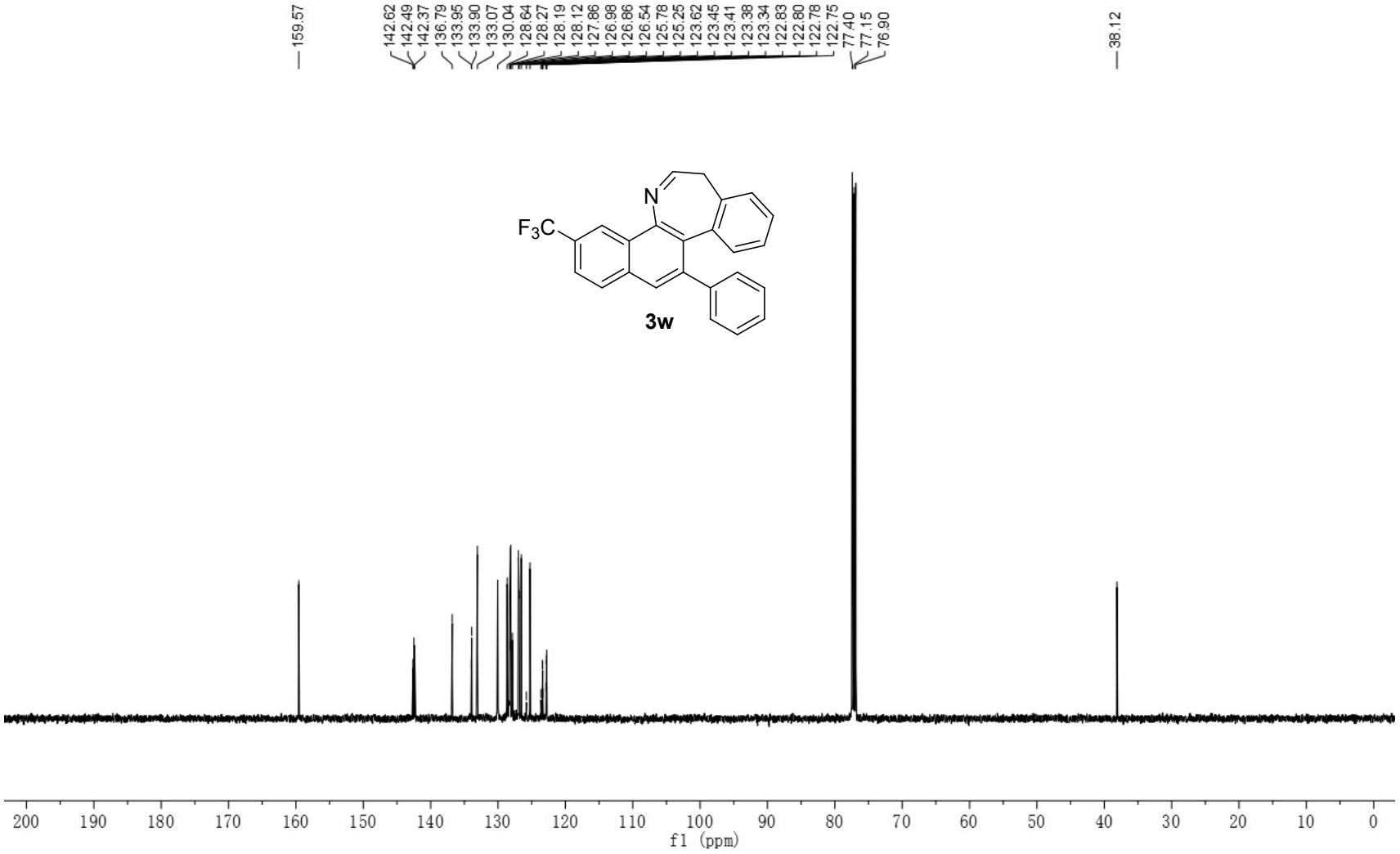
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3v**



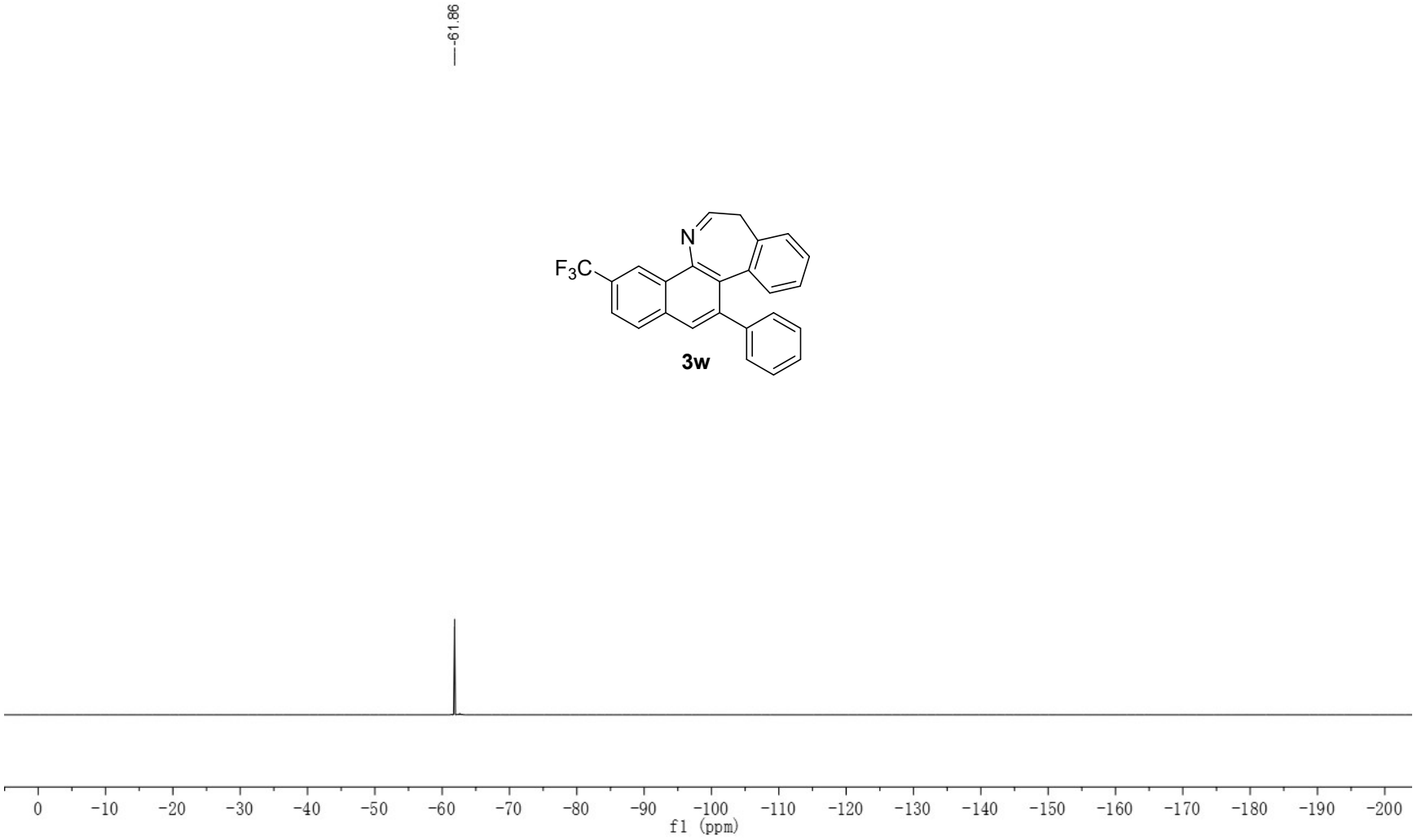
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3w**



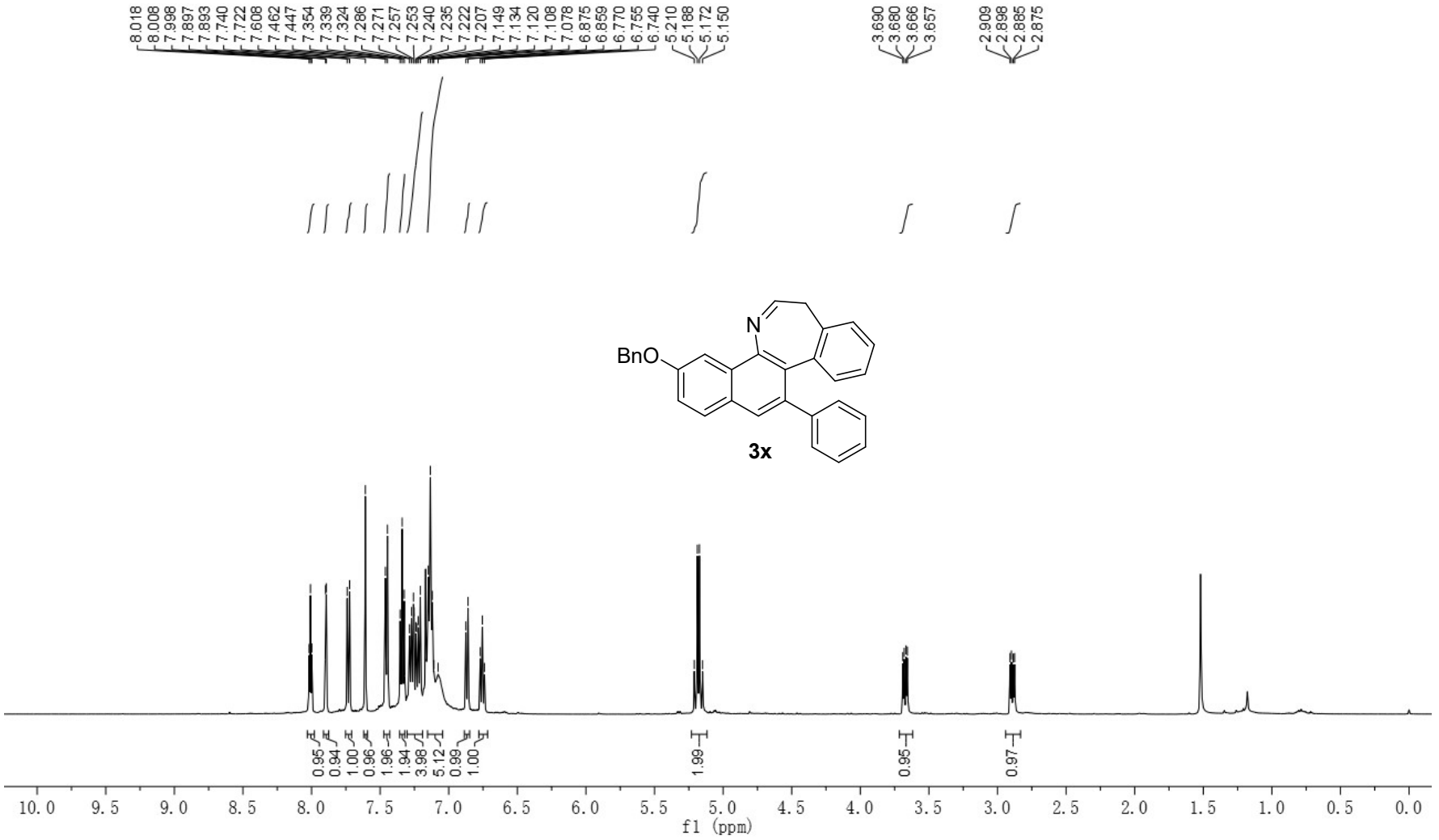
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3w**



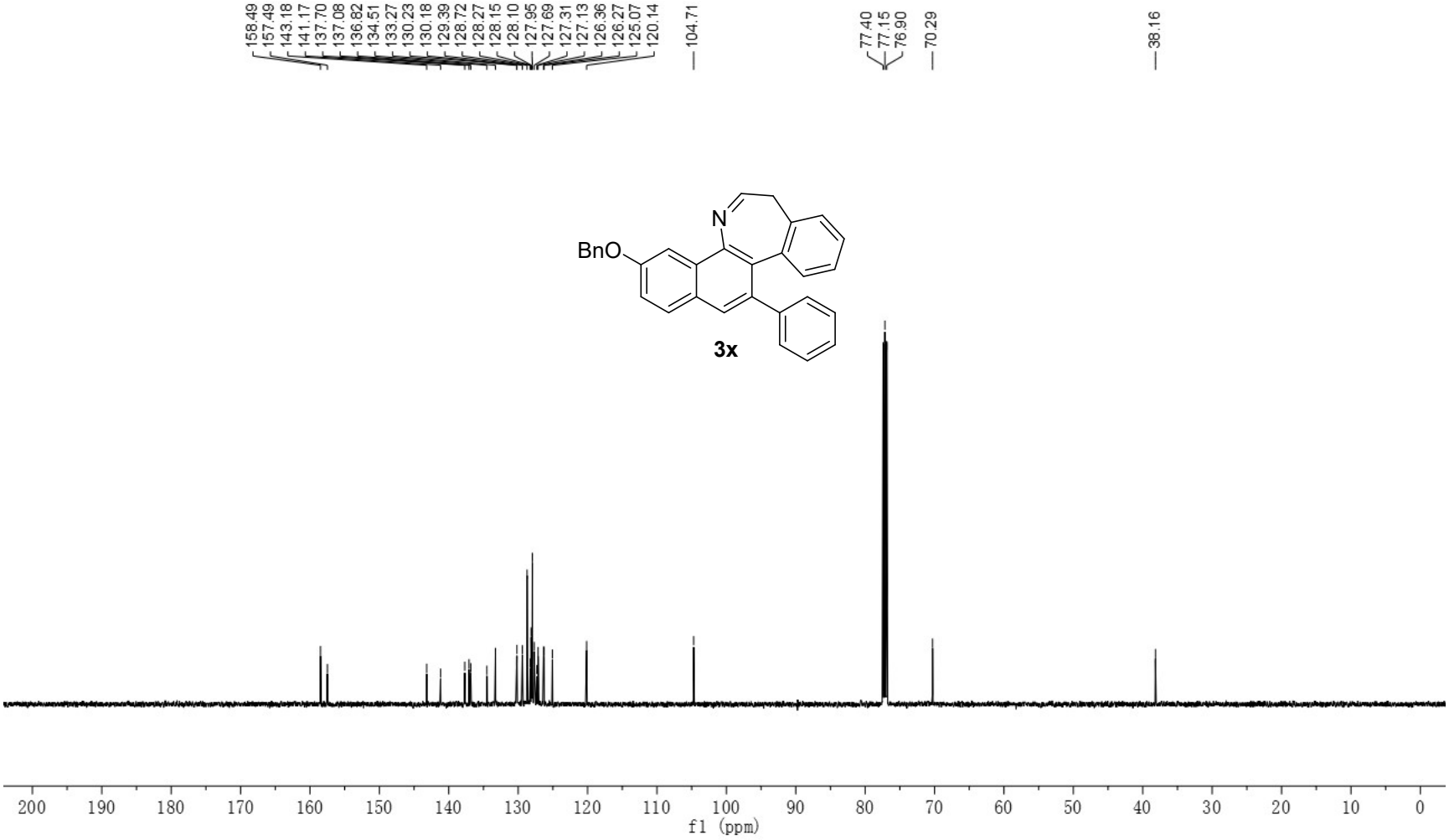
$^{19}F$ NMR (471 MHz, $CDCl_3$) of **3w**



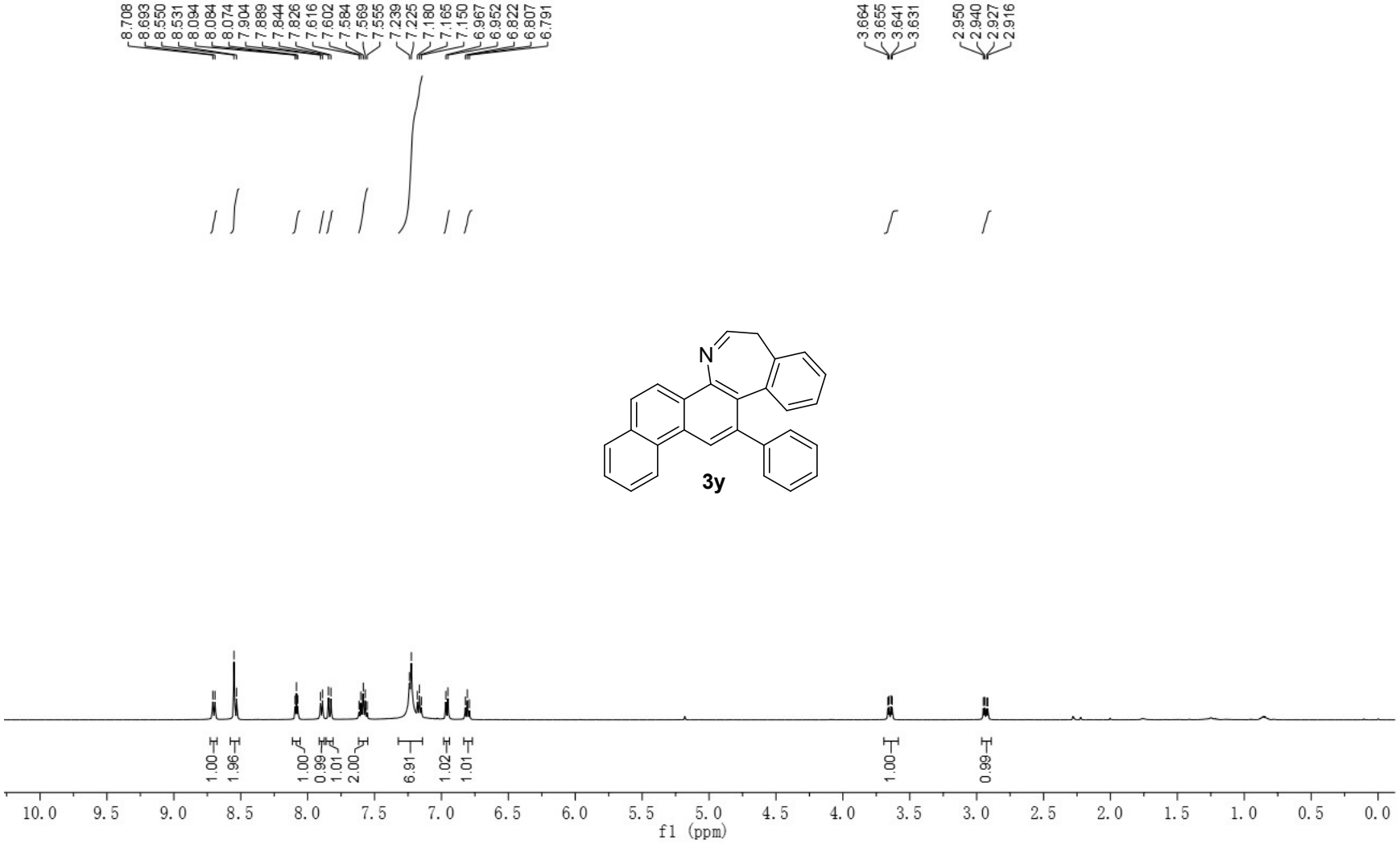
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3x**



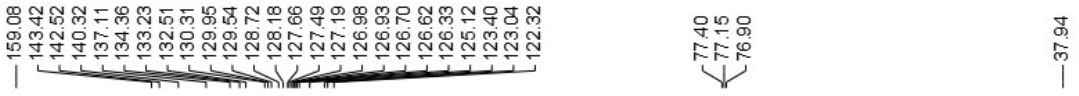
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3x**

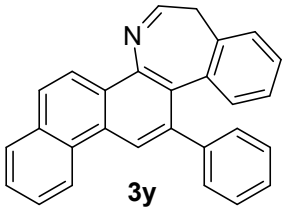


$^{1}$H NMR (500 MHz, $CDCl_3$) of **3y**

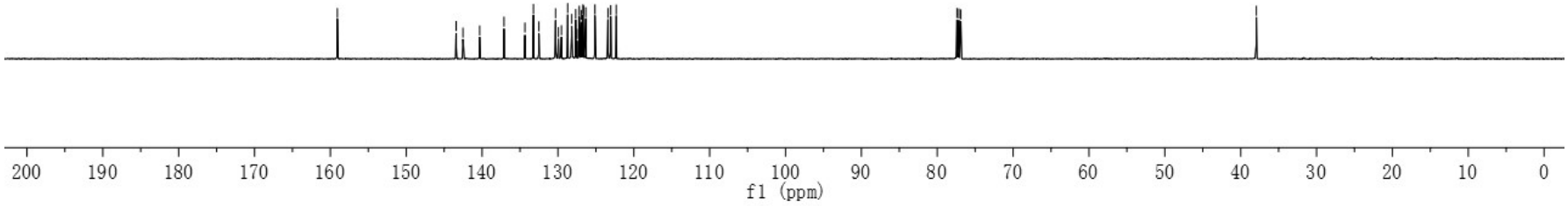


$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3y**

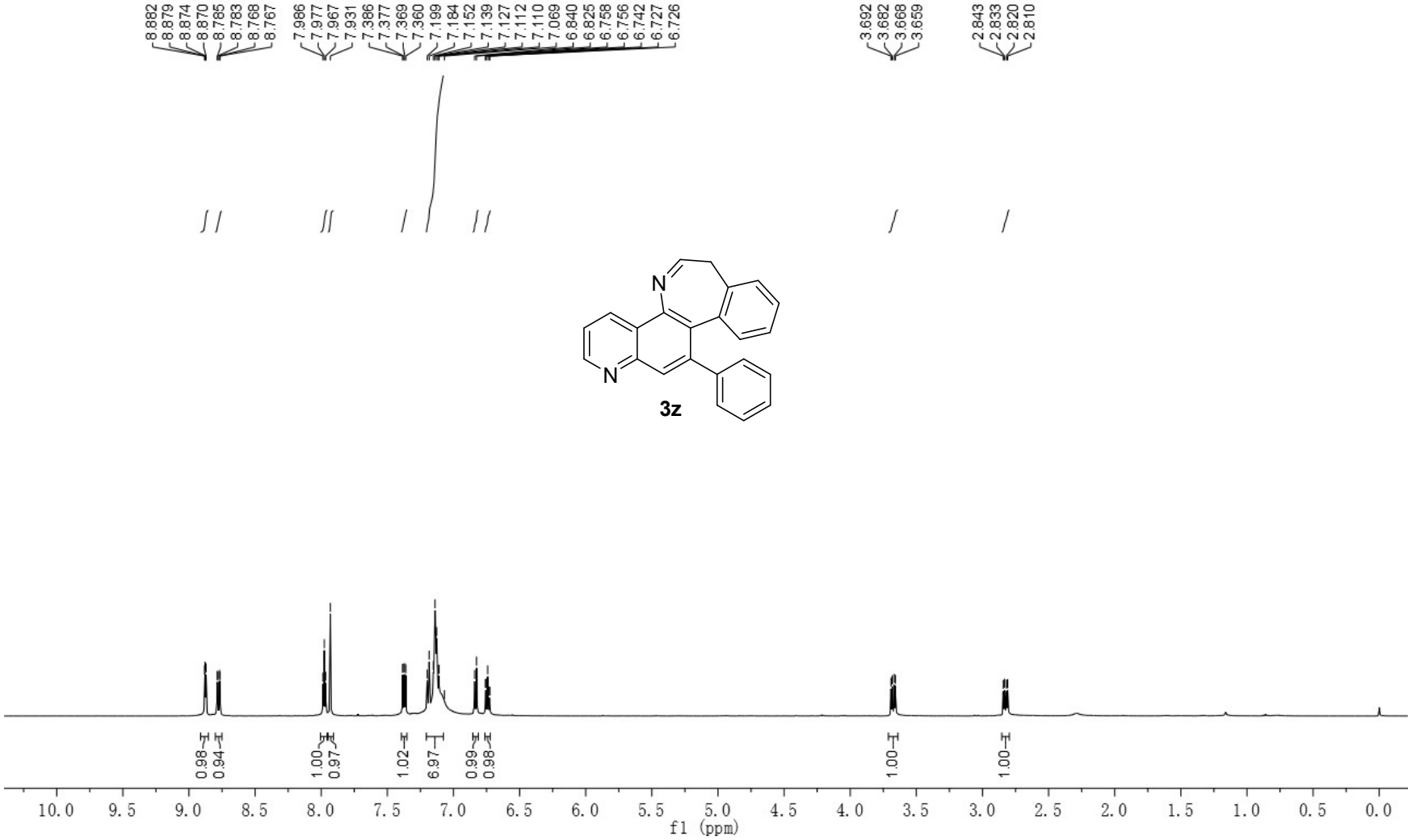


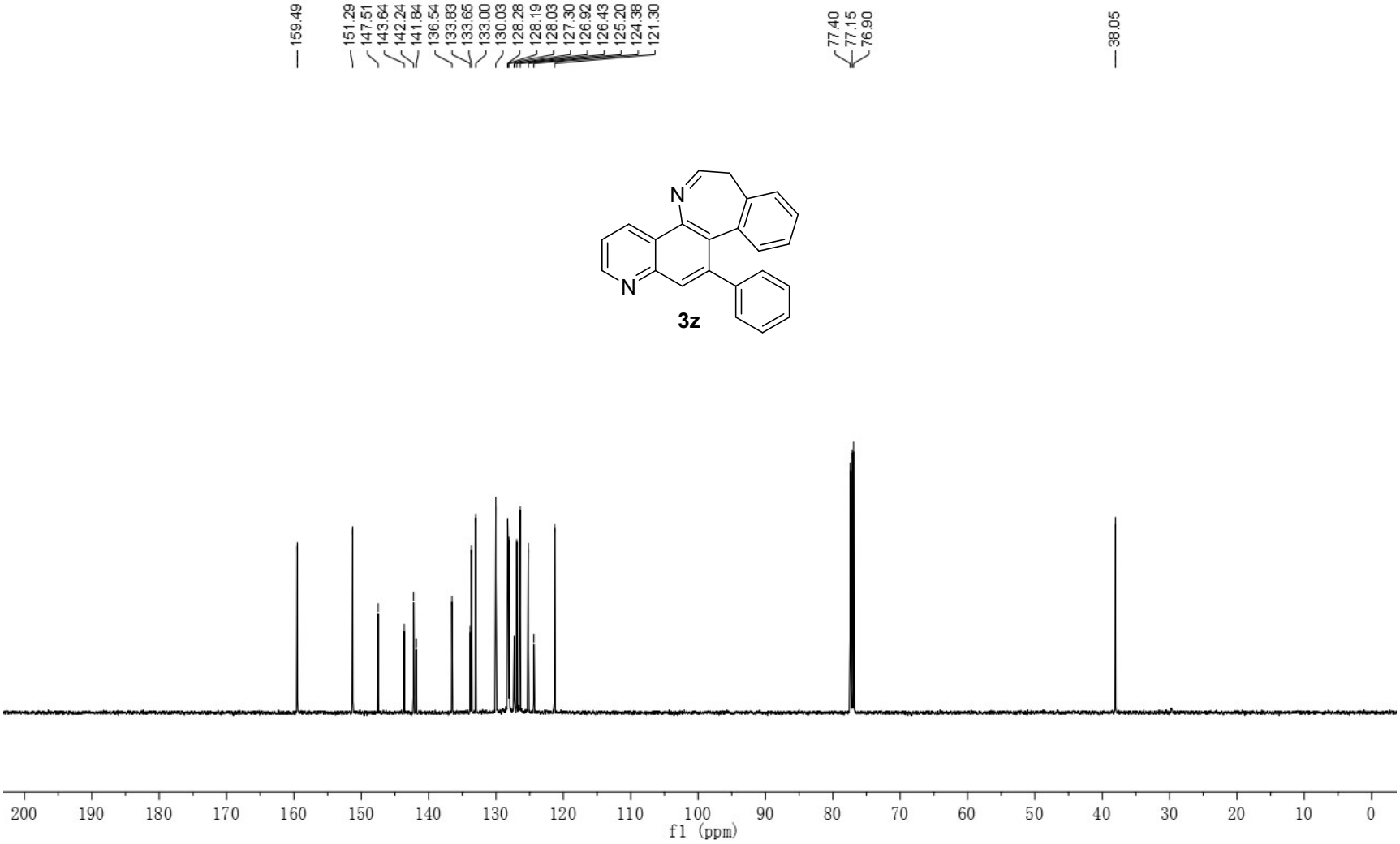

**3y**



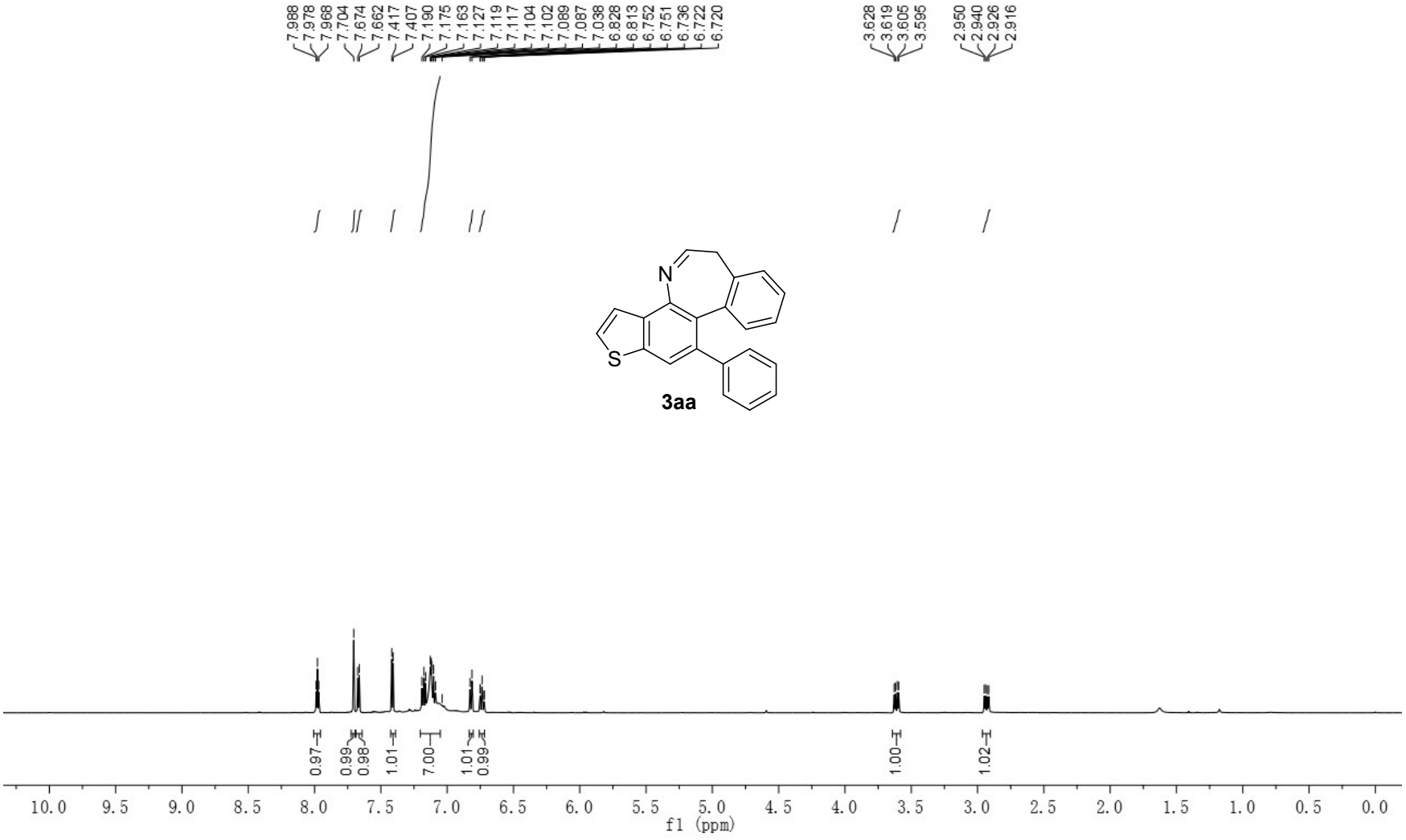
$^1$H NMR (500 MHz, $CDCl_3$) of **3z**



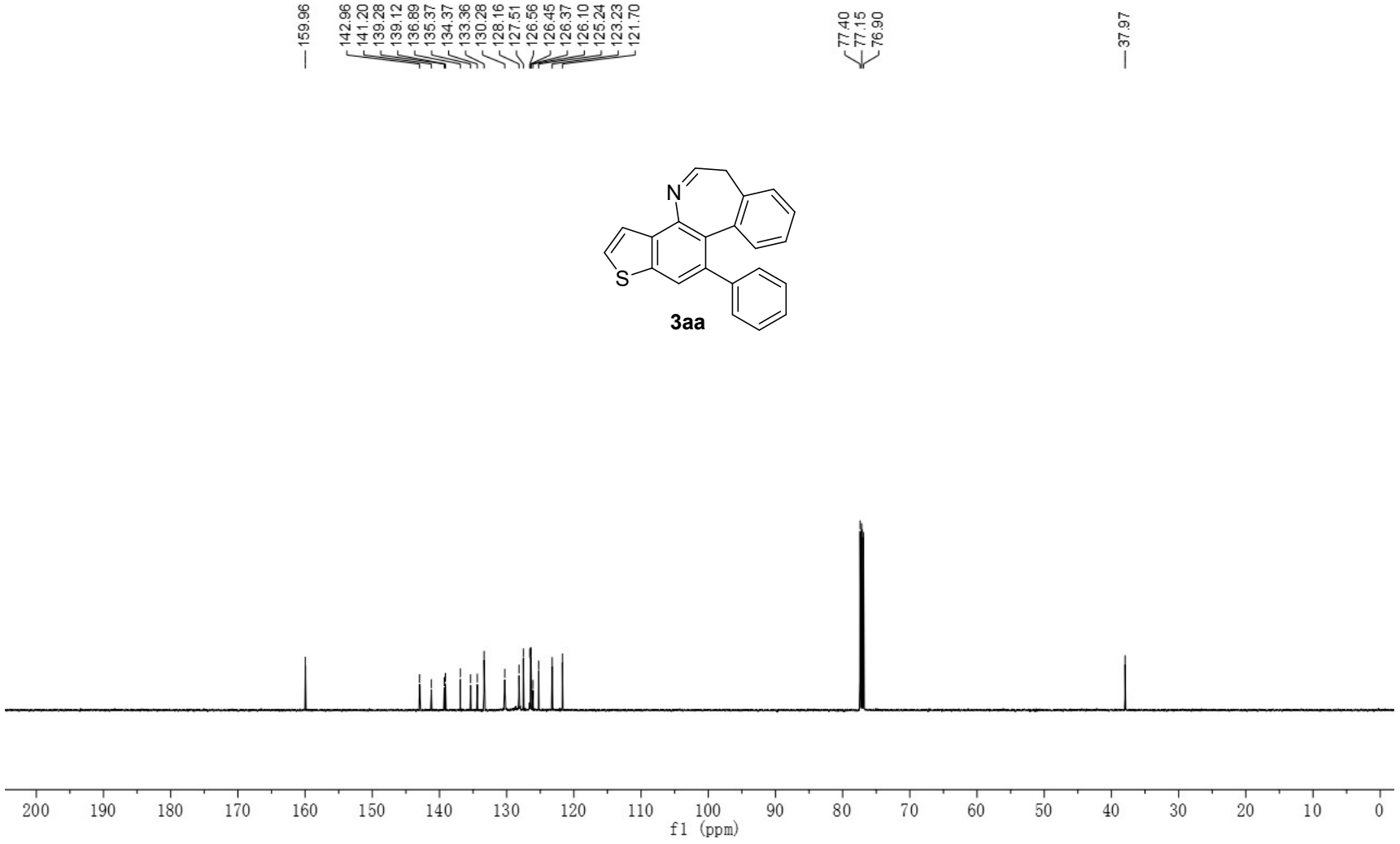
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3z**



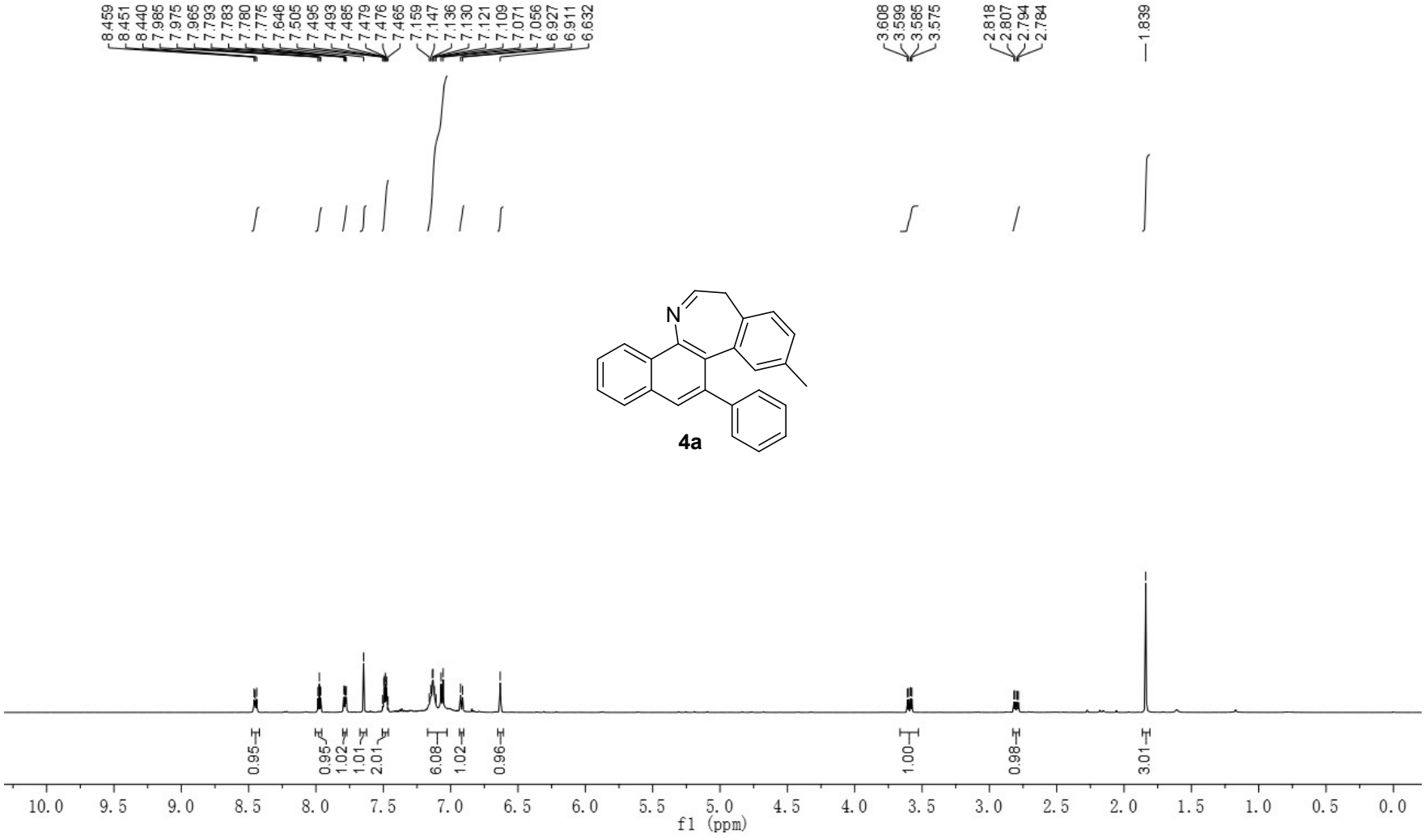
$^{1}$H NMR (500 MHz, $CDCl_3$) of **3aa**



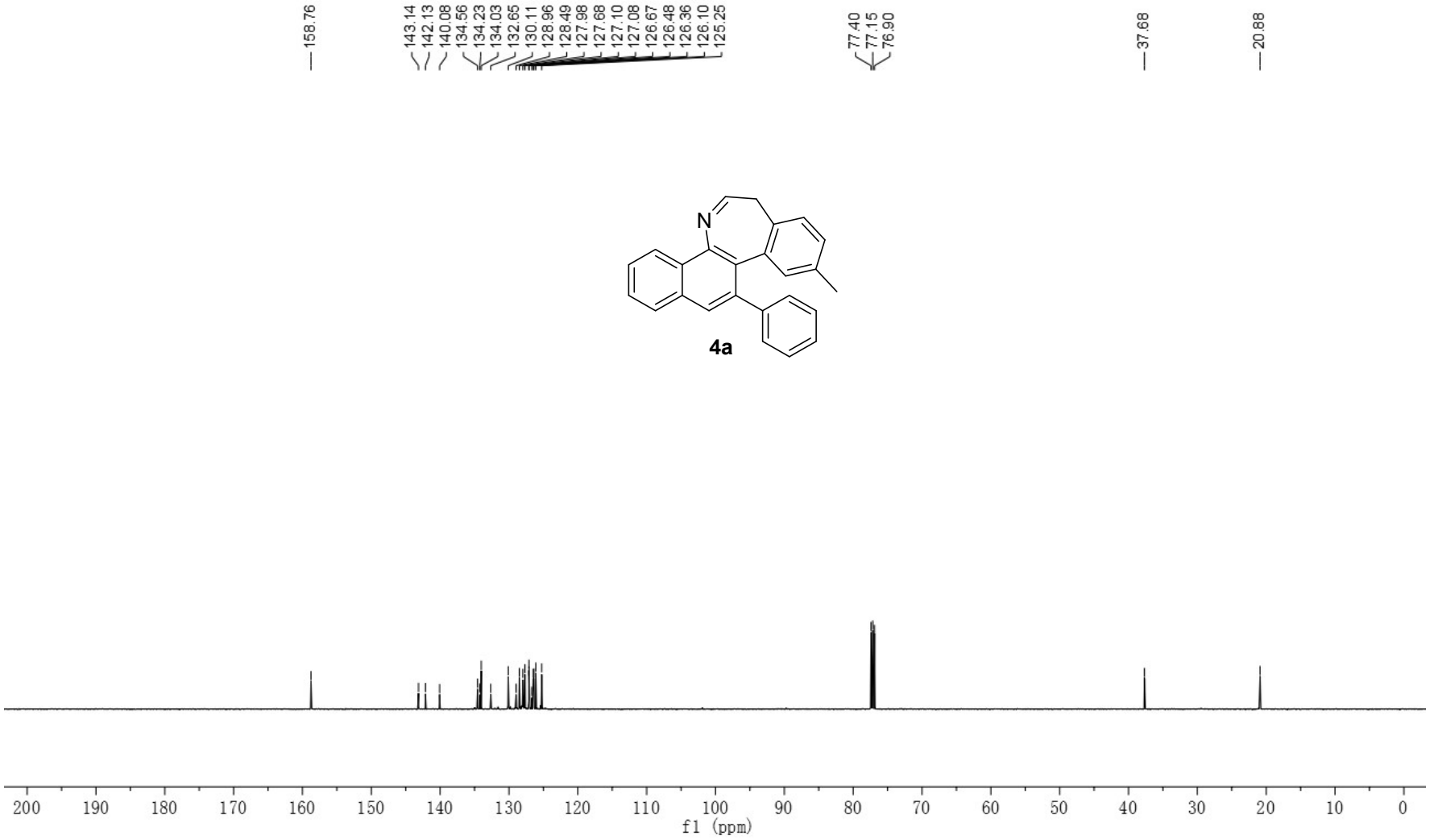
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **3aa**



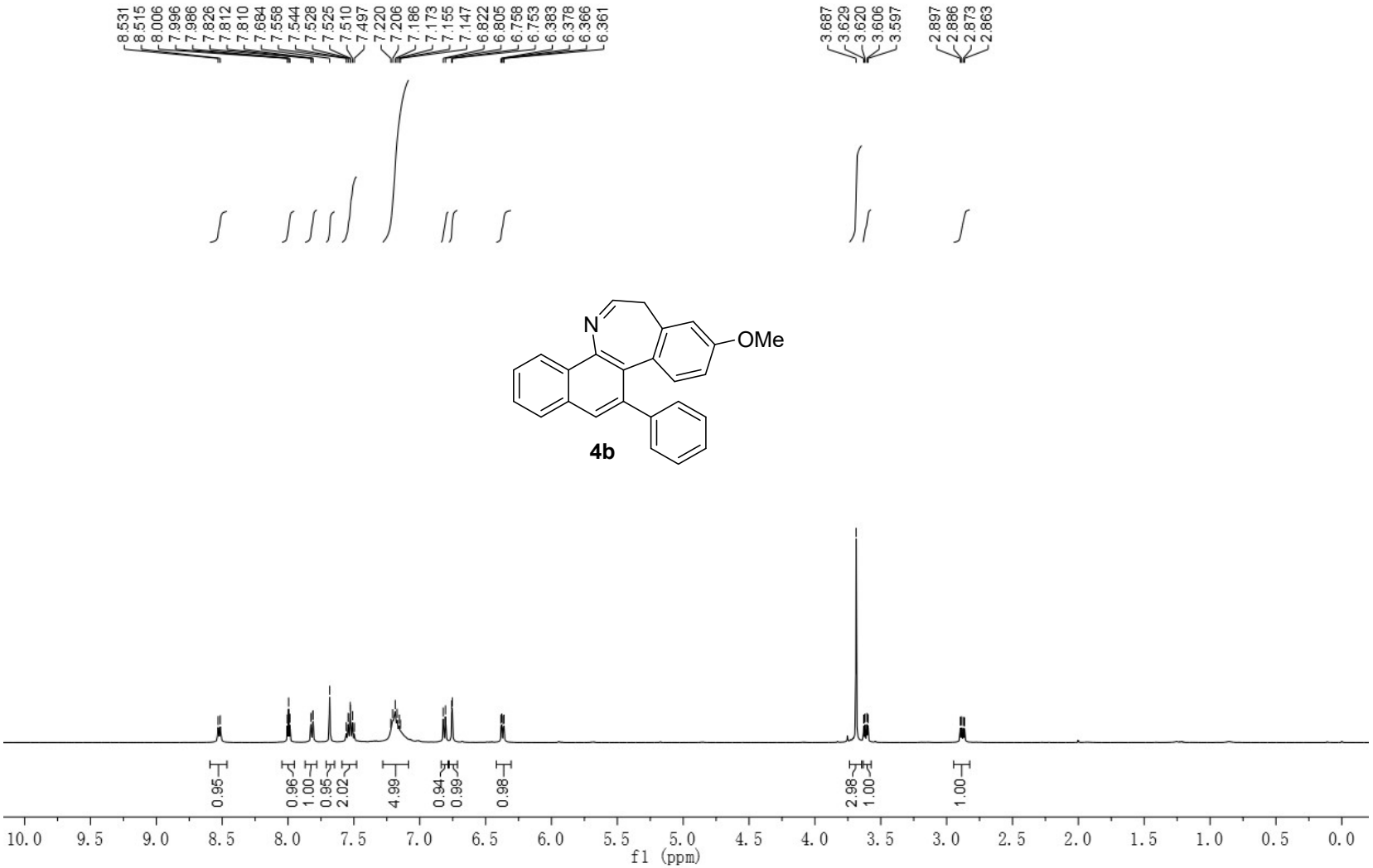
$^{1}$H NMR (500 MHz, $CDCl_3$) of **4a**



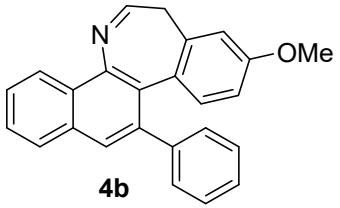
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **4a**



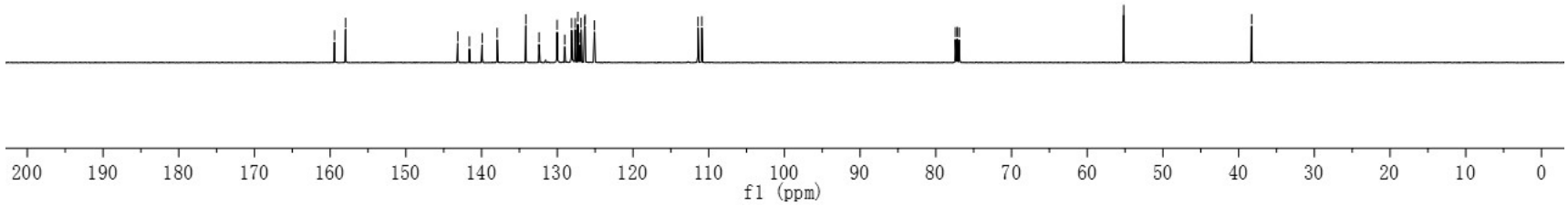
$^{1}$H NMR (500 MHz, $CDCl_3$) of **4b**



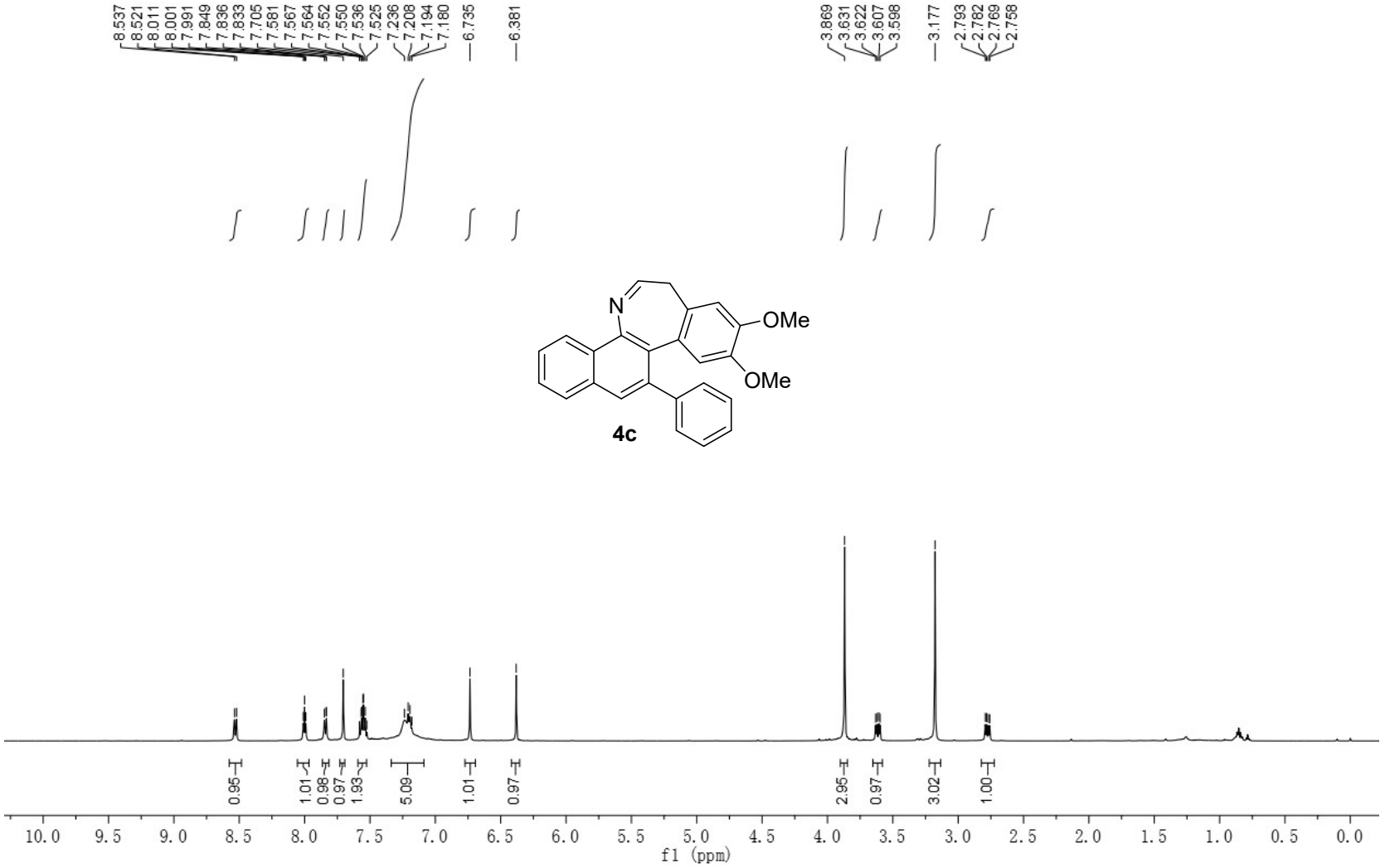
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **4b**

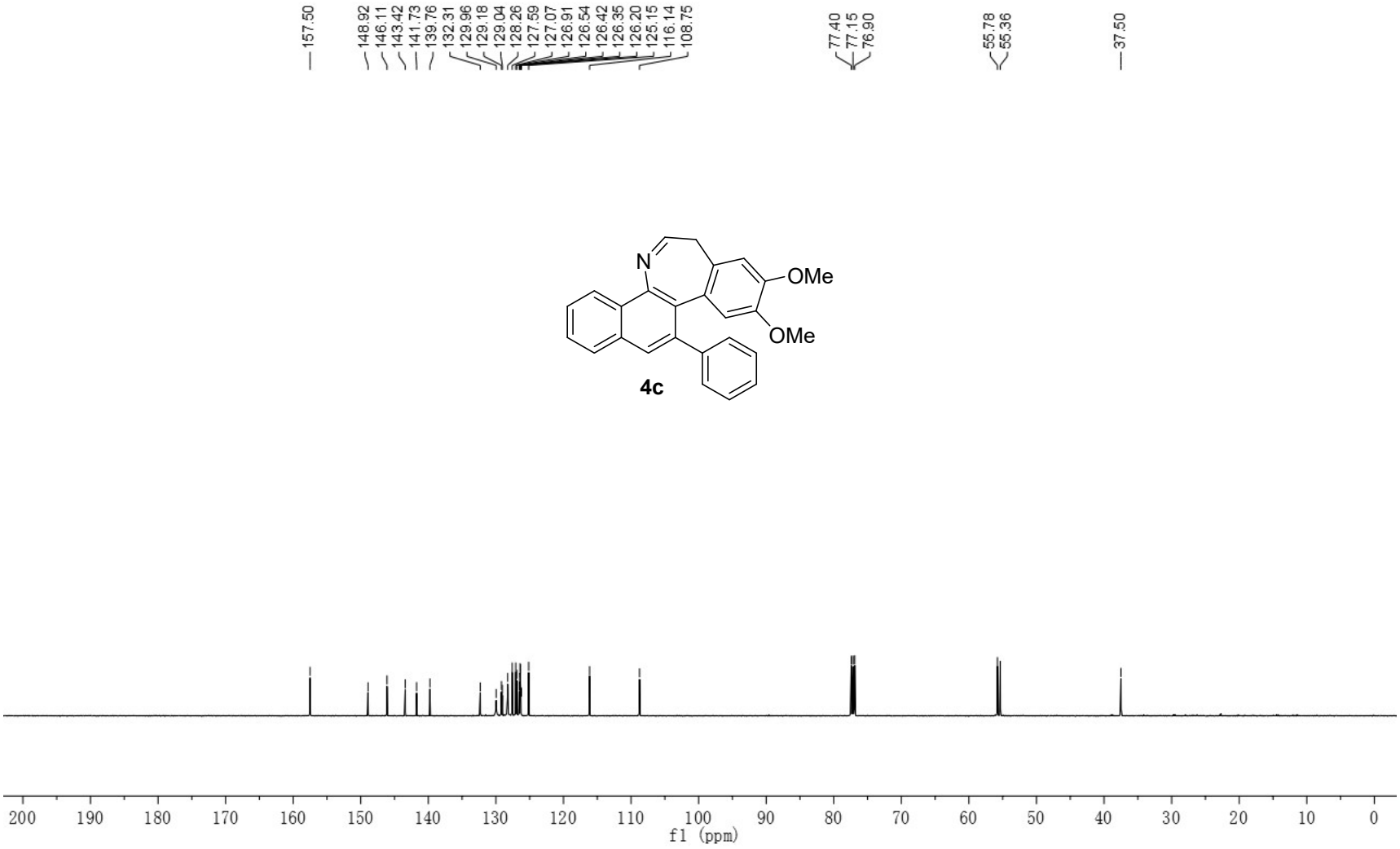

**4b**



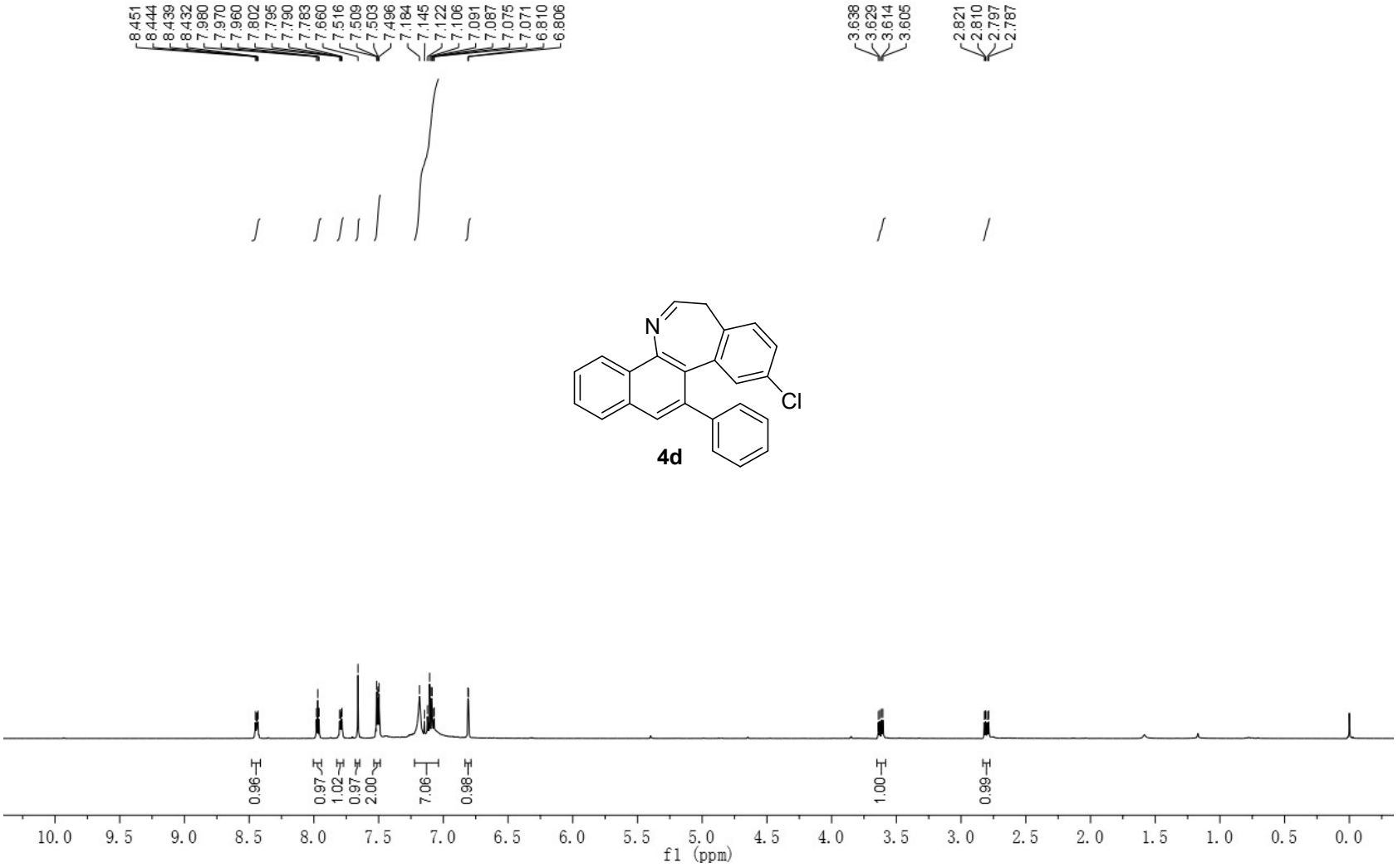
$^{1}$H NMR (500 MHz, $CDCl_3$) of **4c**



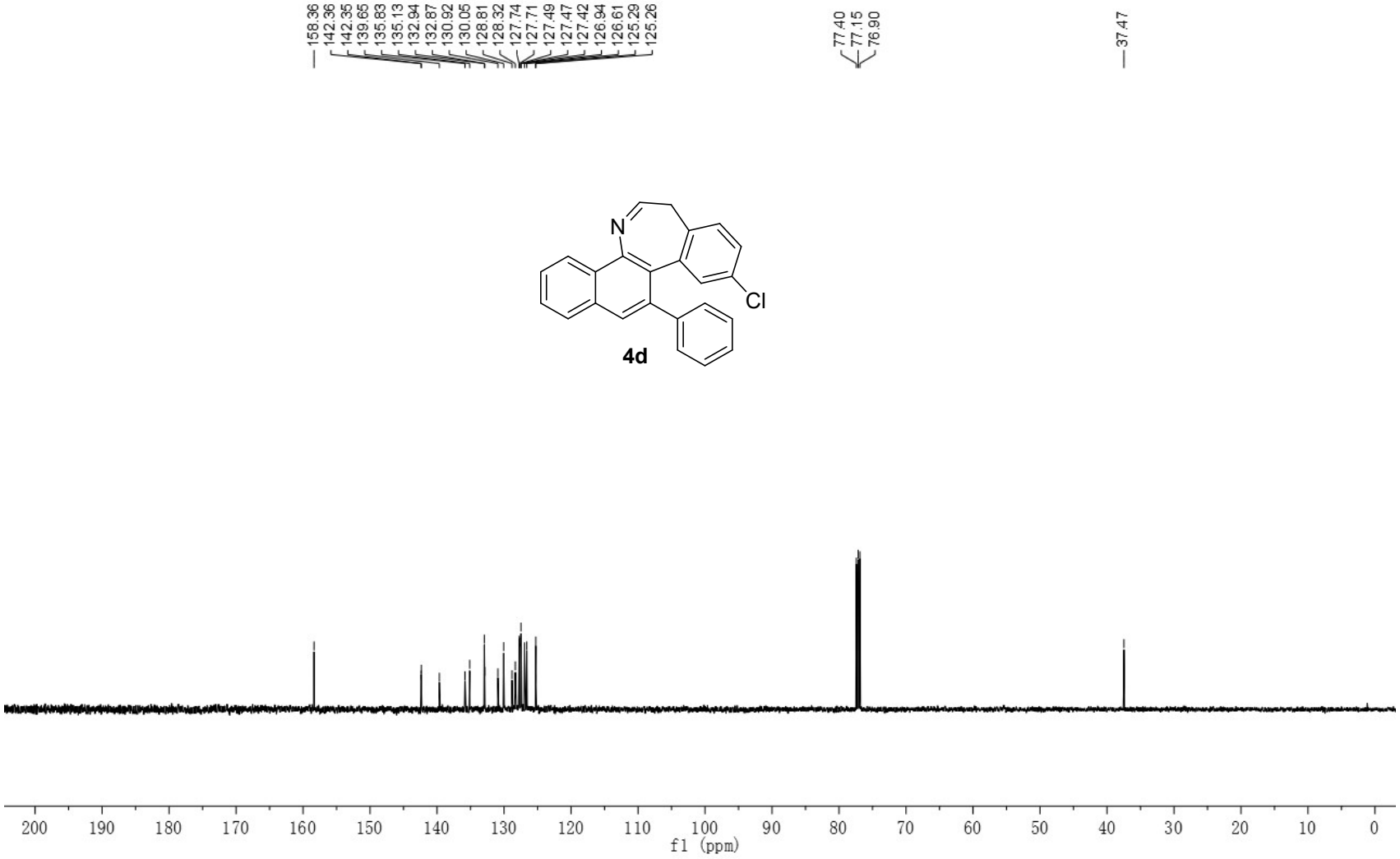
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **4c**



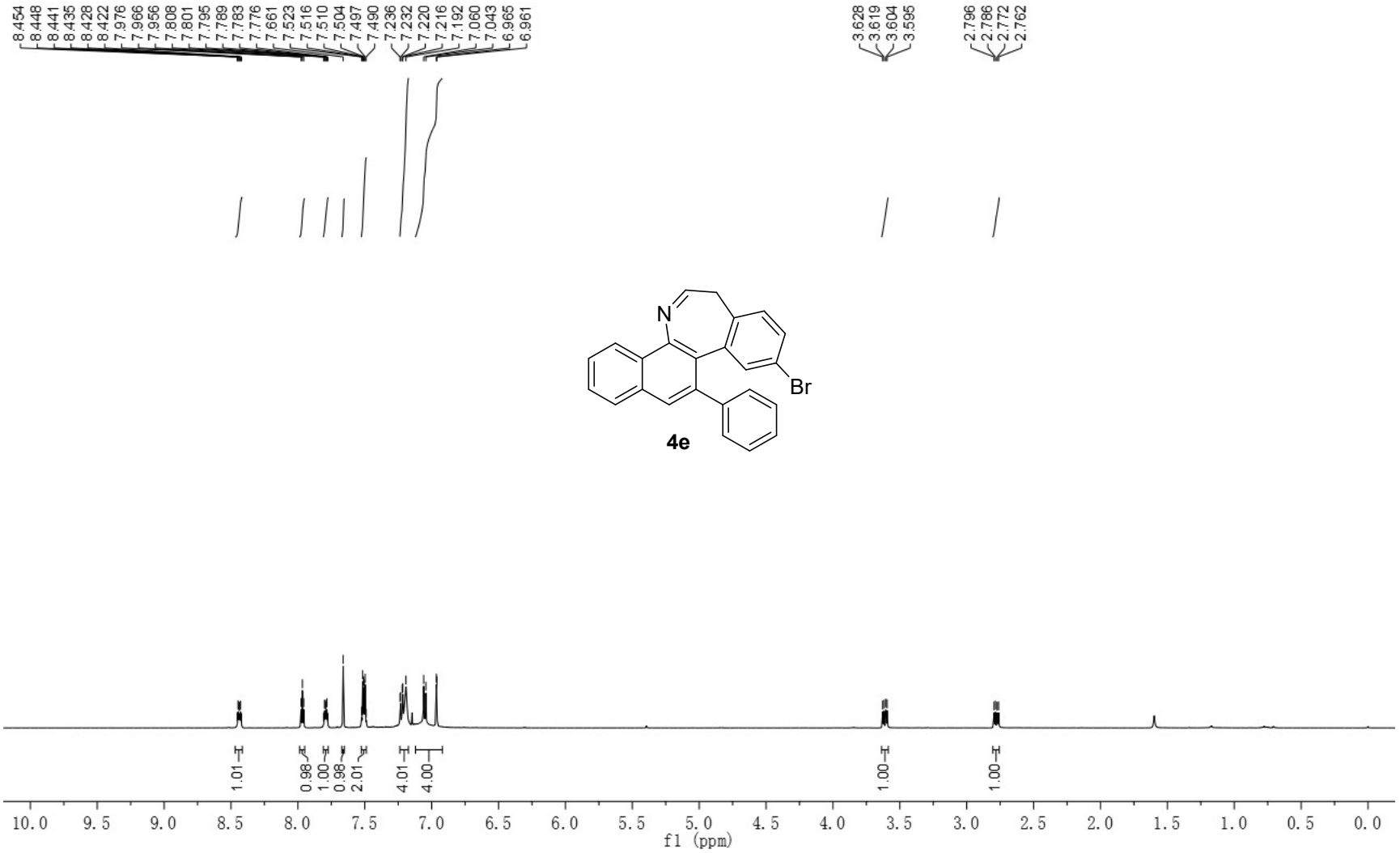
$^{1}$H NMR (500 MHz, $CDCl_3$) of **4d**



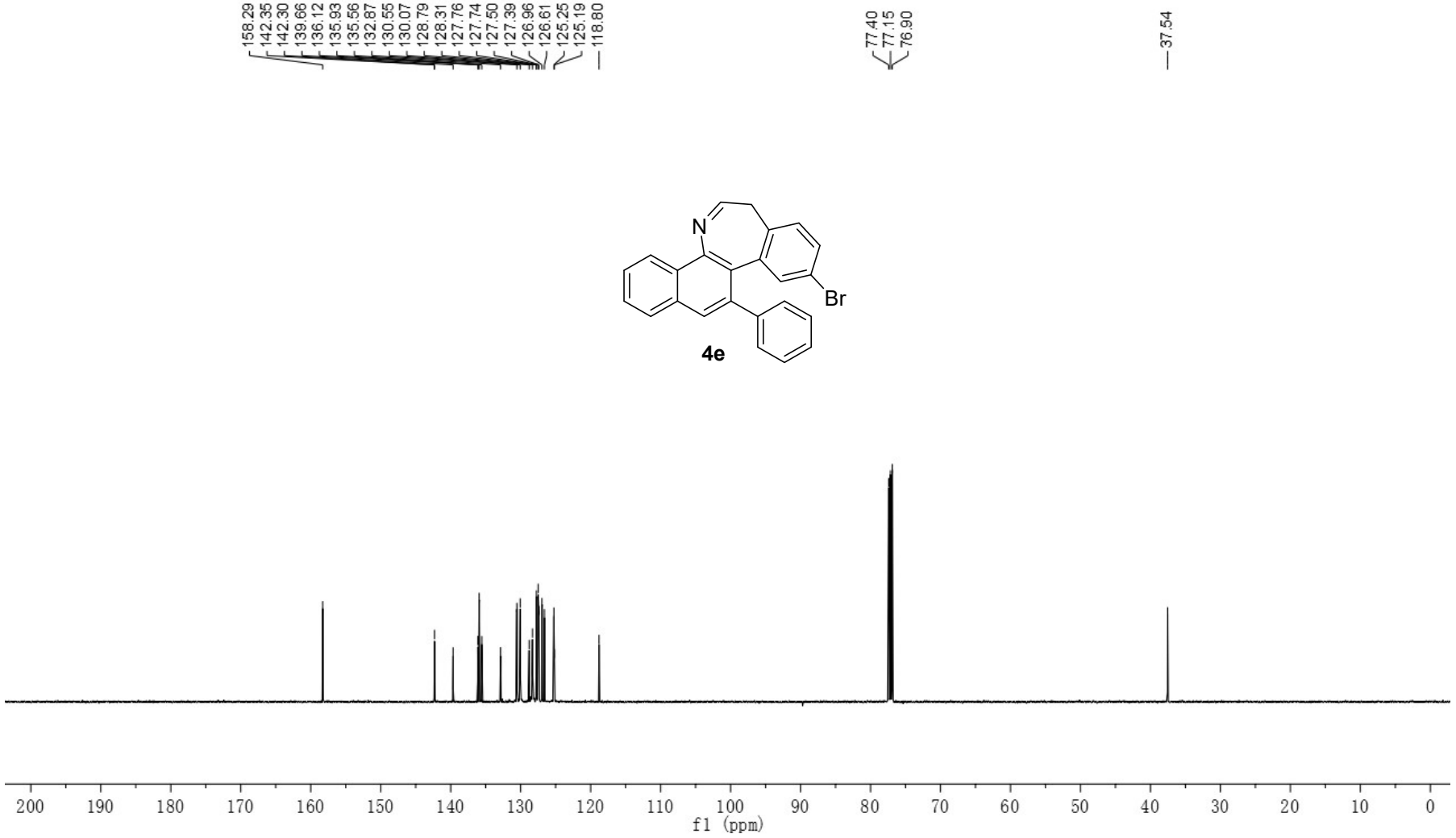
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **4d**



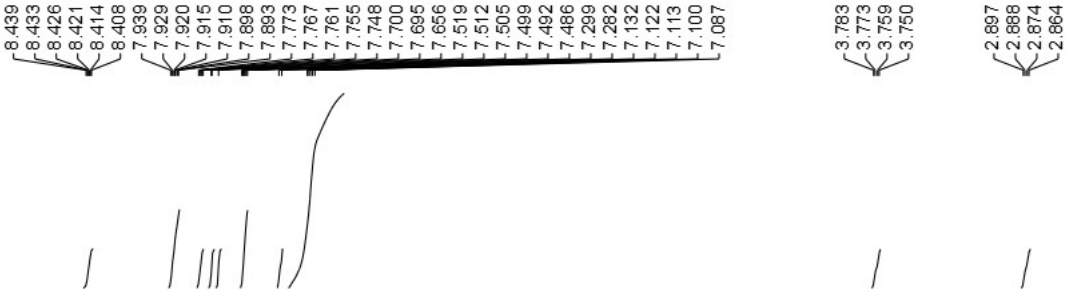
$^1$H NMR (500 MHz, $CDCl_3$) of **4e**

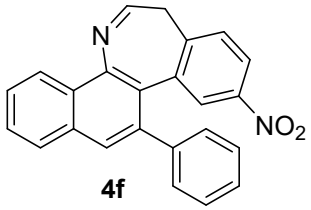


$^{13}C$ NMR (126 MHz, $CDCl_3$) of **4e**

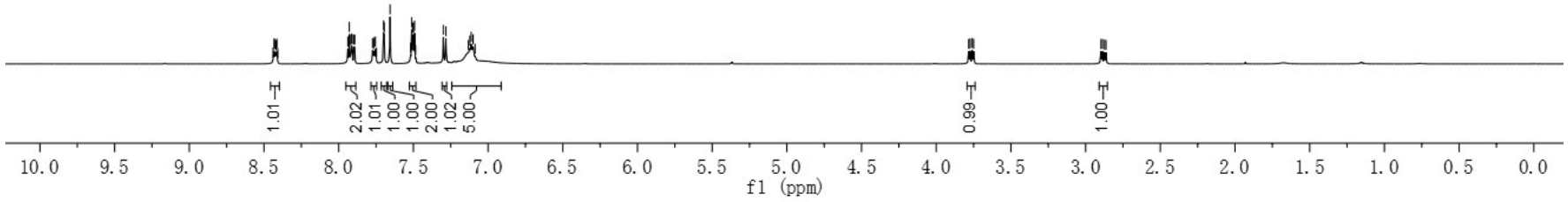


$^{1}$H NMR (500 MHz, $CDCl_3$) of **4f**



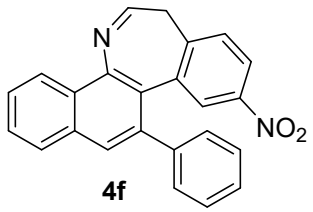

**4f**



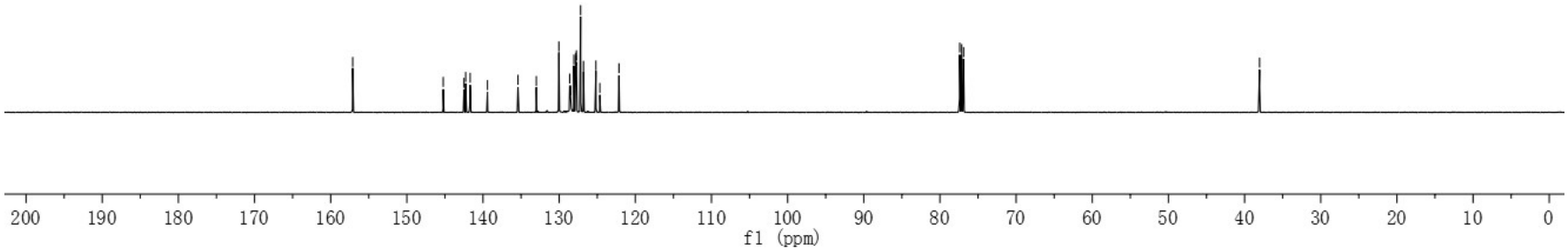
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **4f**



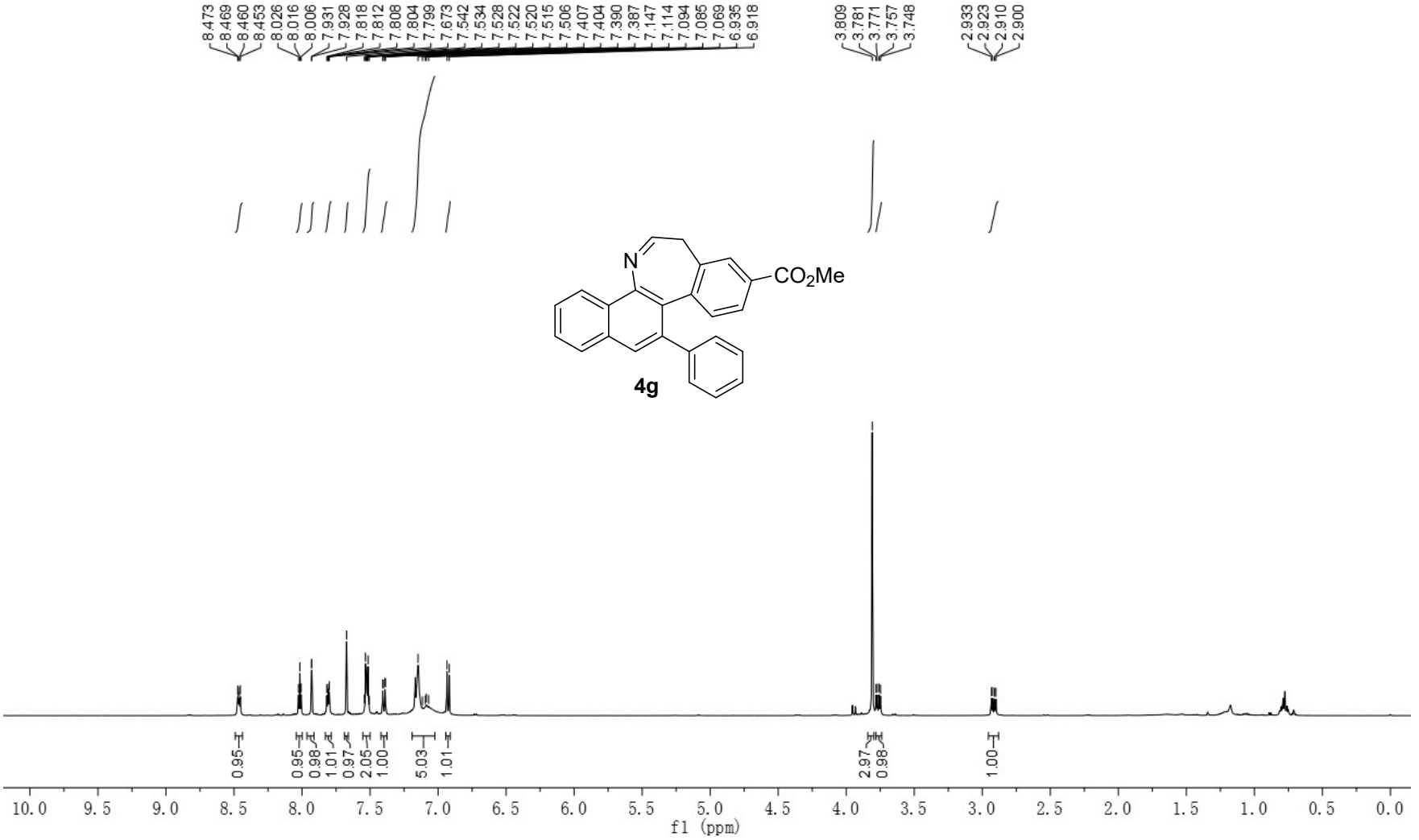


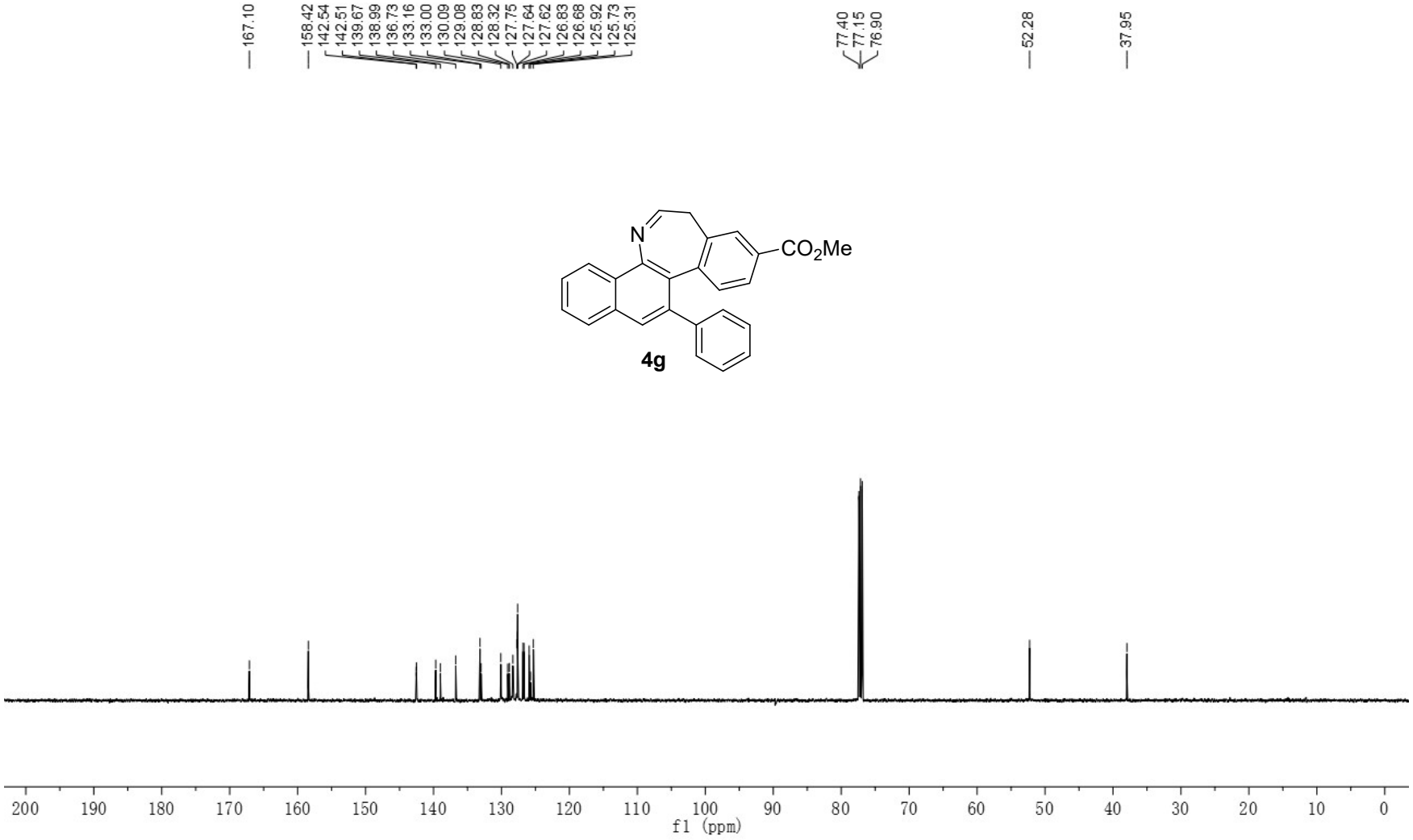

**4f**



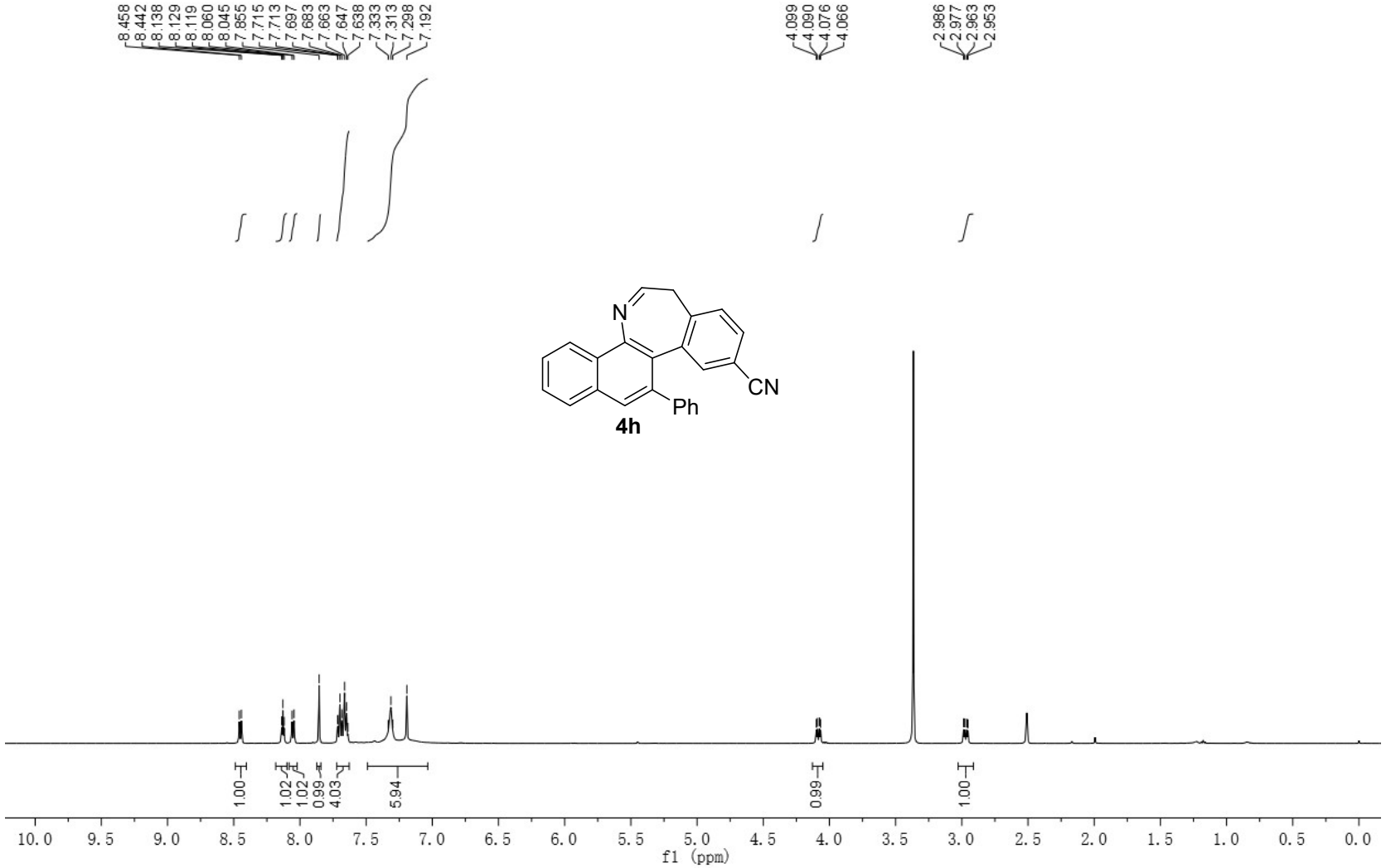
$^{1}$H NMR (500 MHz, $CDCl_3$) of **4g**



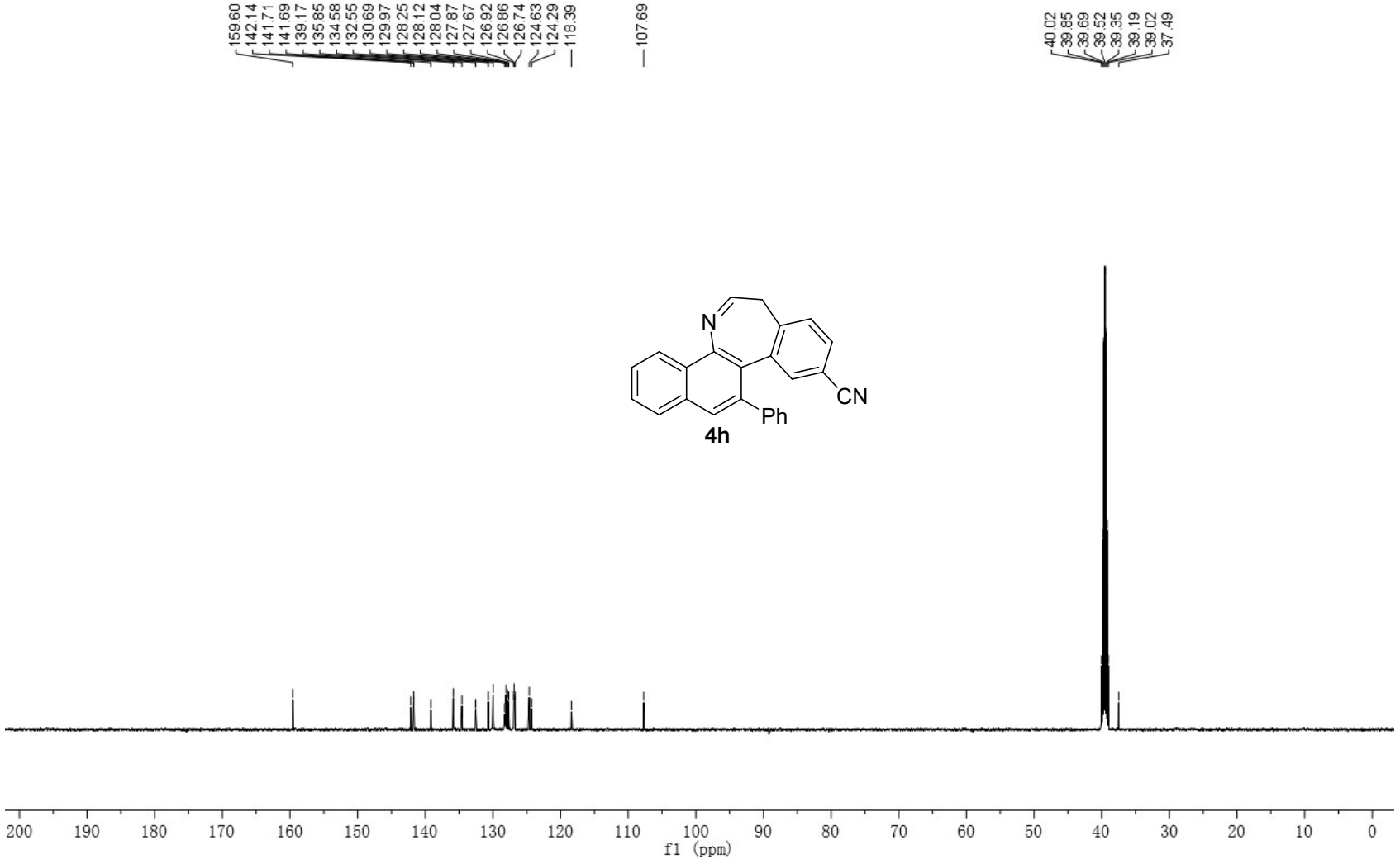
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **4g**



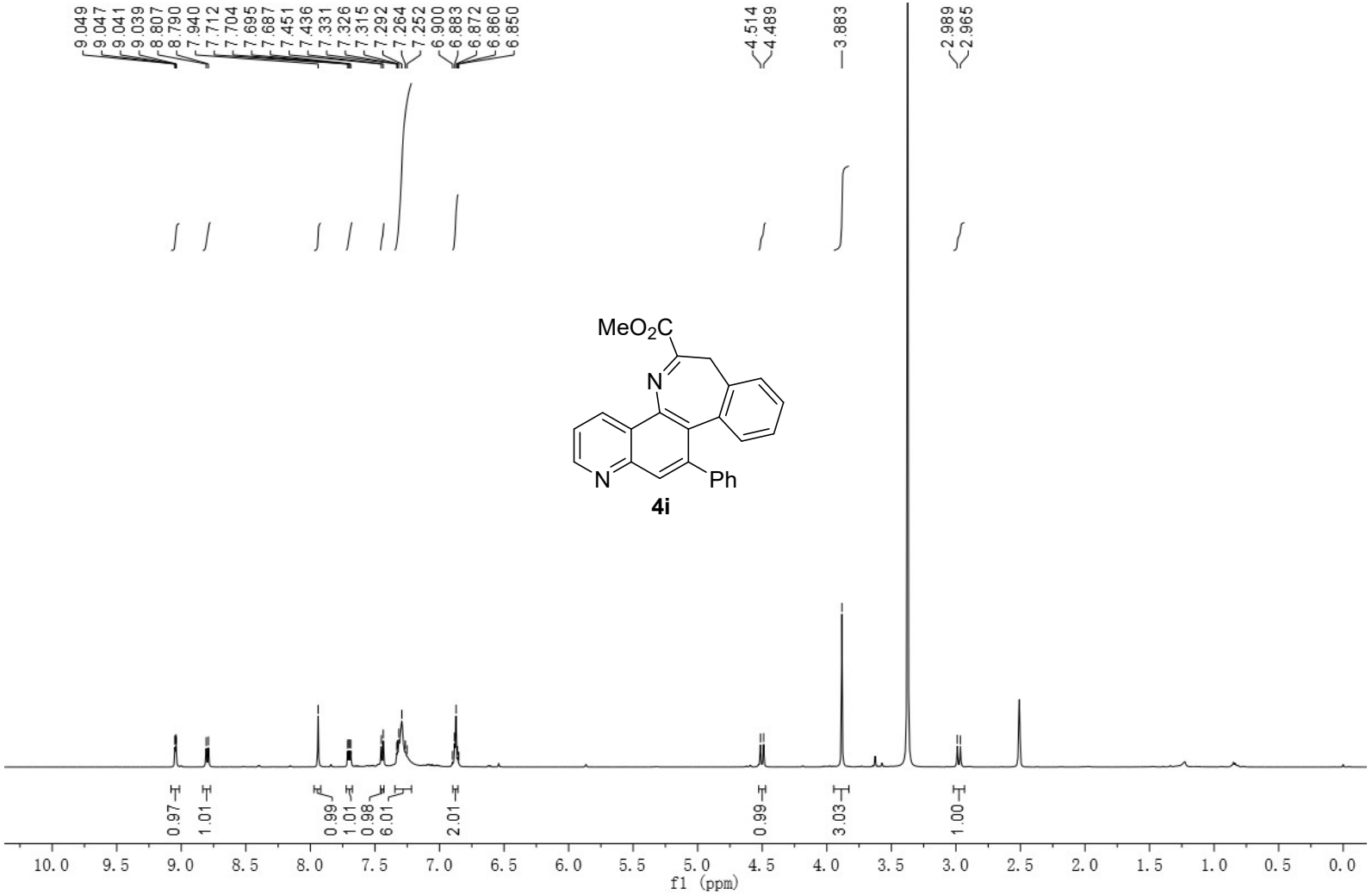
$^{1}$H NMR (500 MHz, DMSO-$d_6$) of **4h**



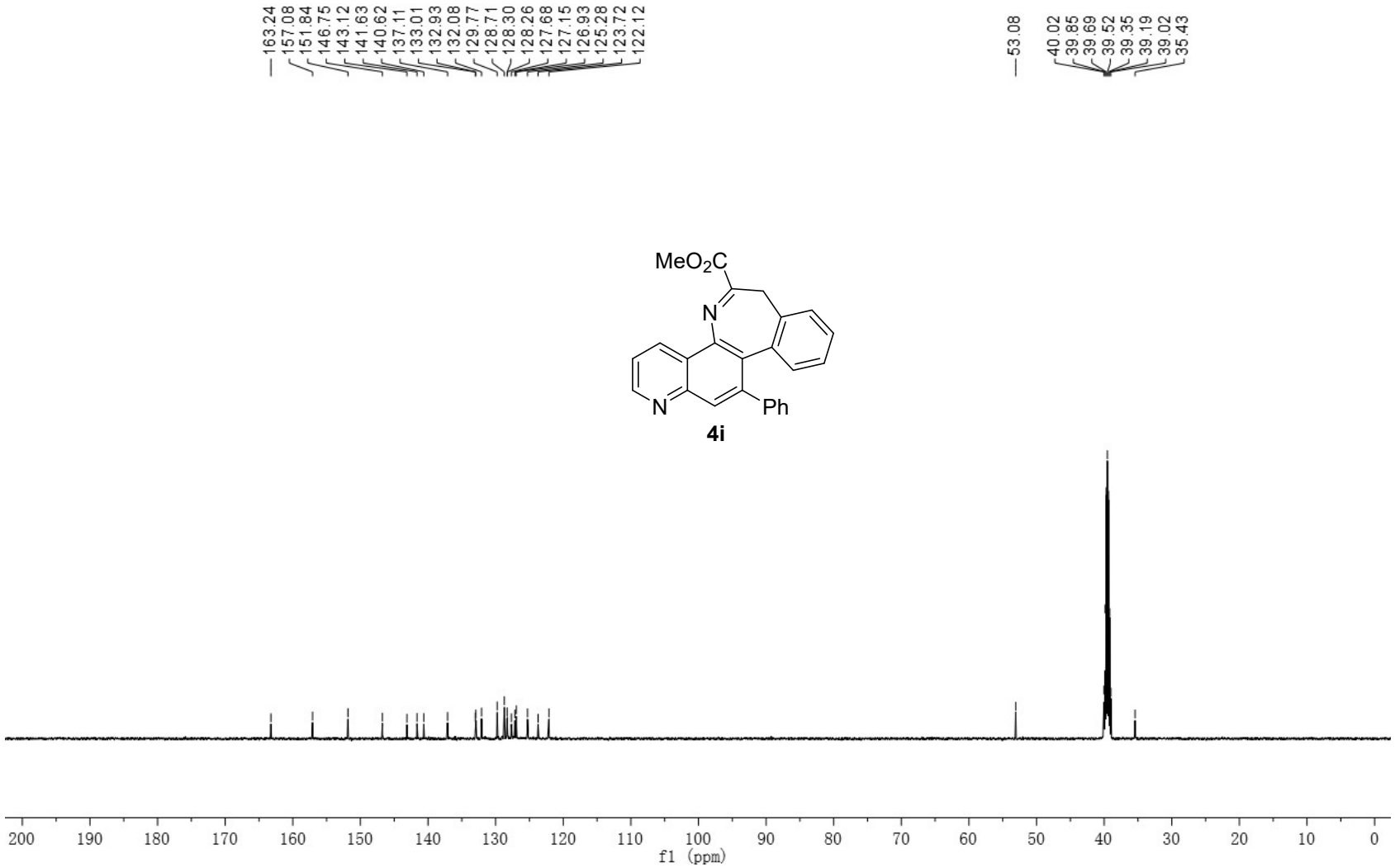
$^{13}$C NMR (126 MHz, DMSO-$d_6$) of **4h**



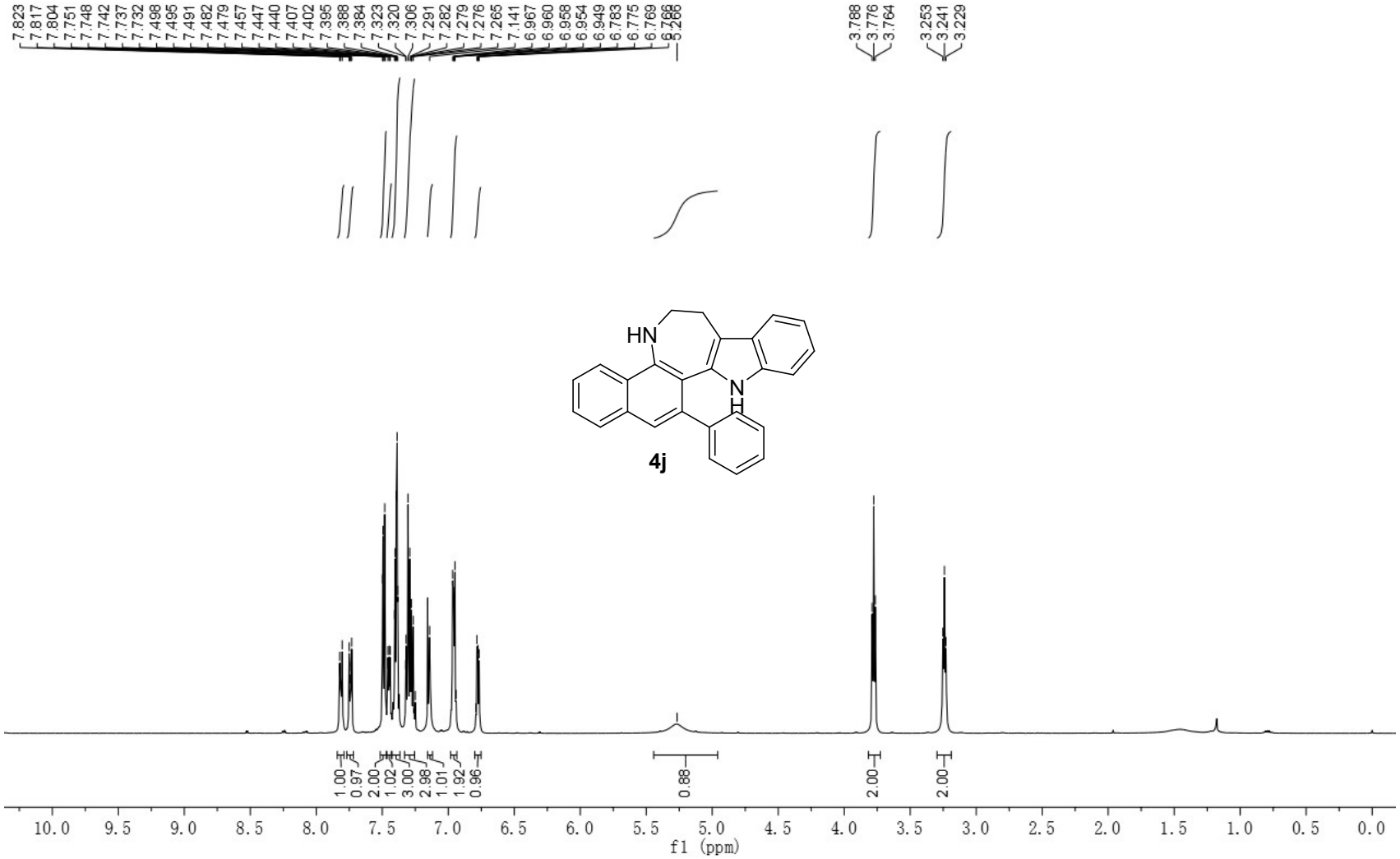
$^{1}$H NMR (500 MHz, DMSO-$d_6$) of **4i**



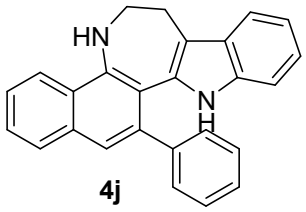
$^{13}$C NMR (126 MHz, DMSO-$d_6$) of **4i**



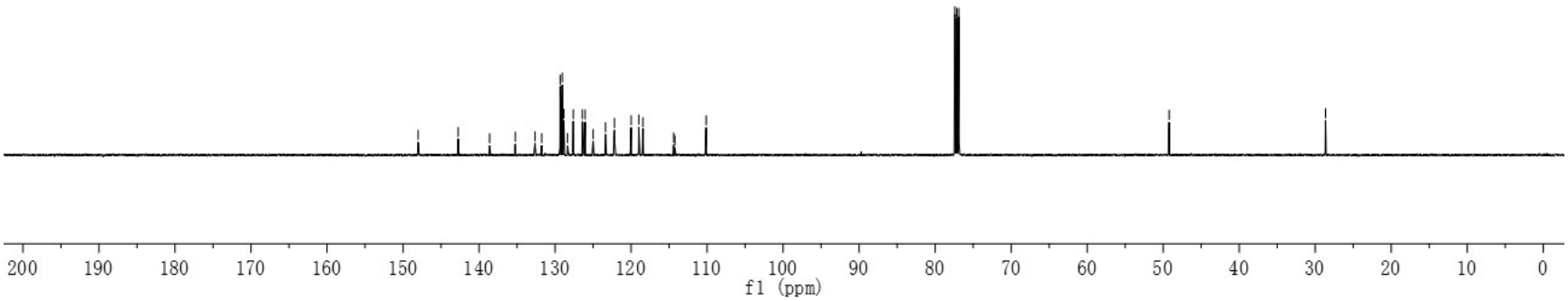
$^{1}$H NMR (500 MHz, $CDCl_3$) of **4j**



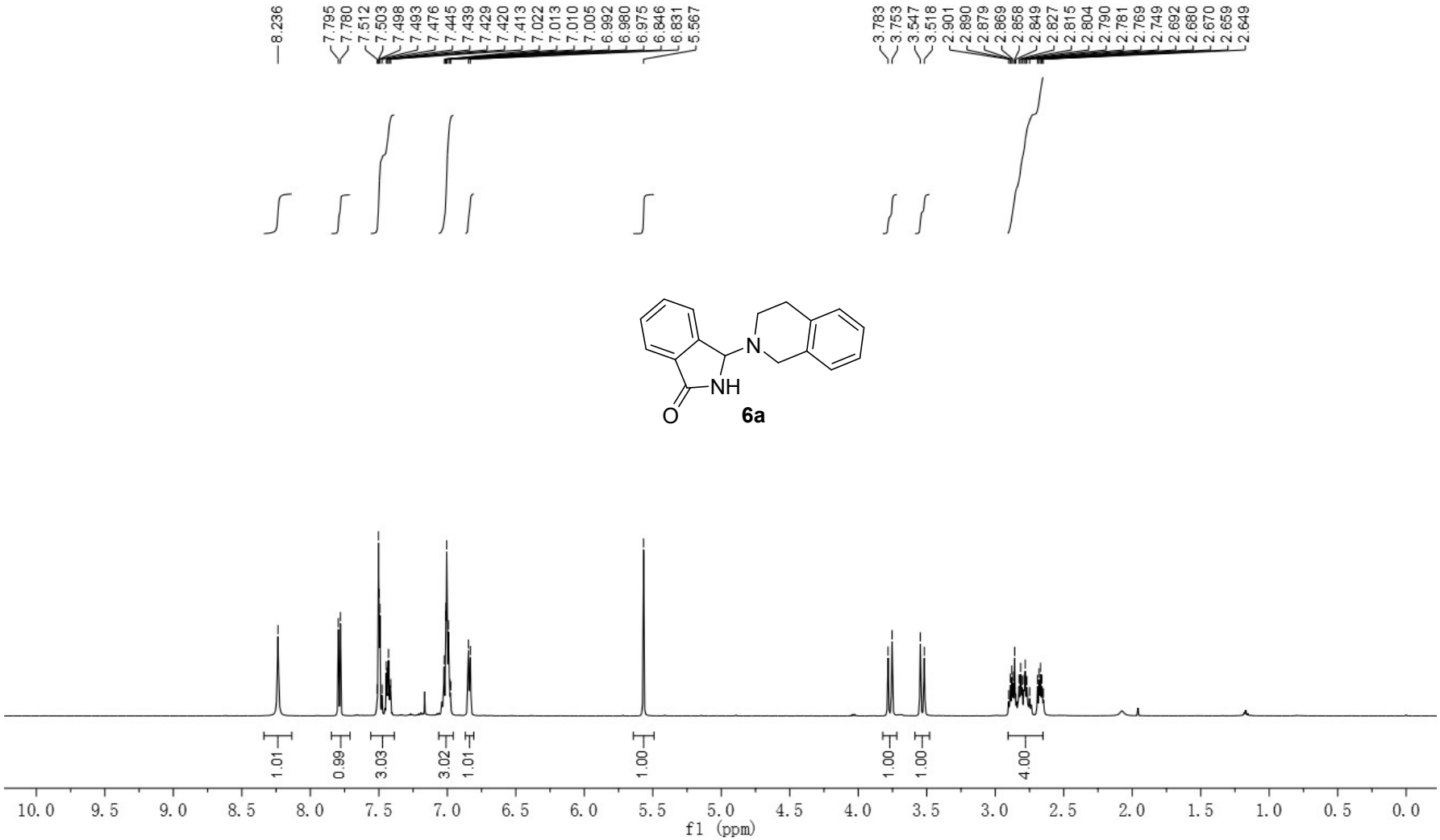
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **4j**

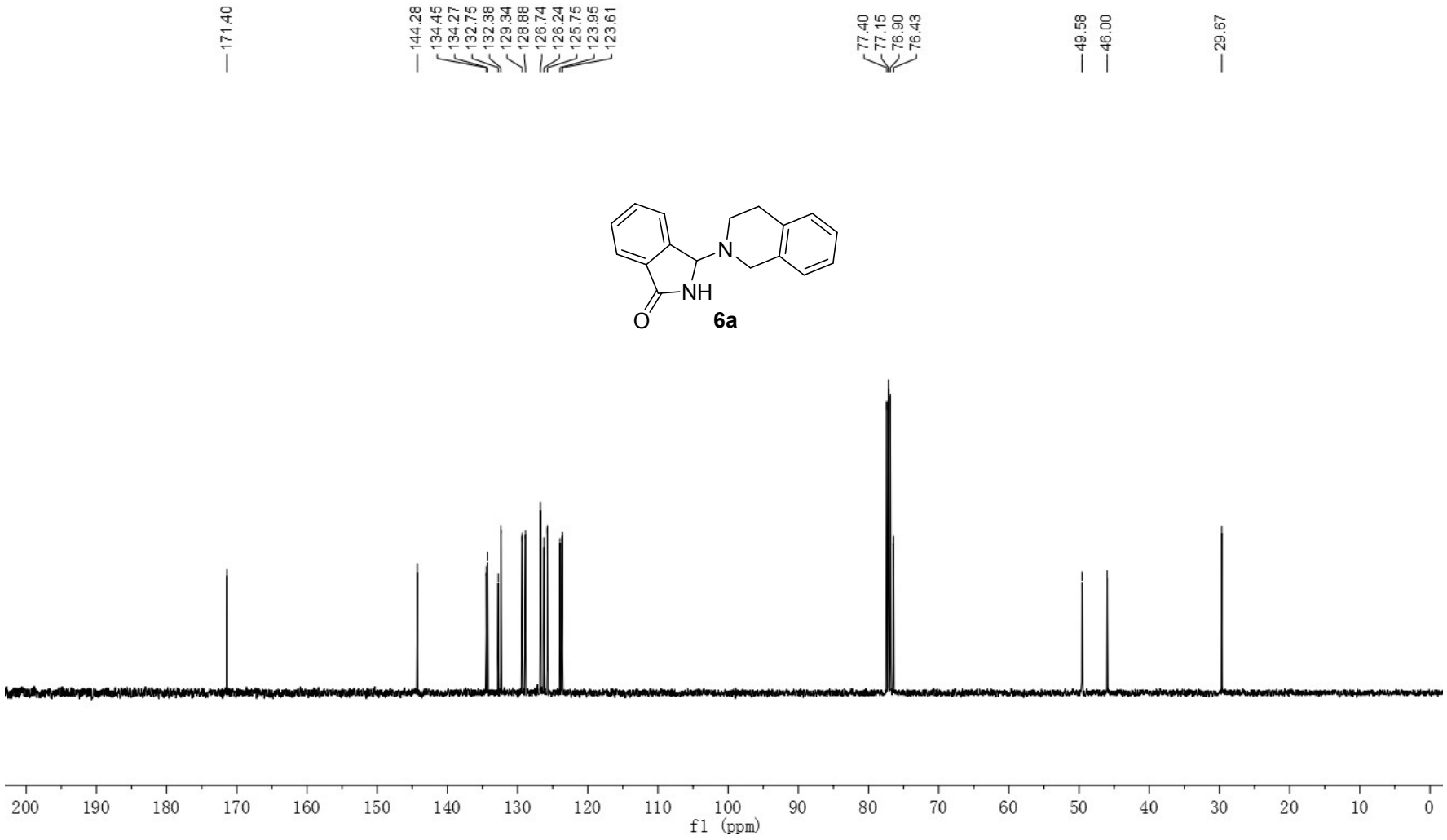

**4j**



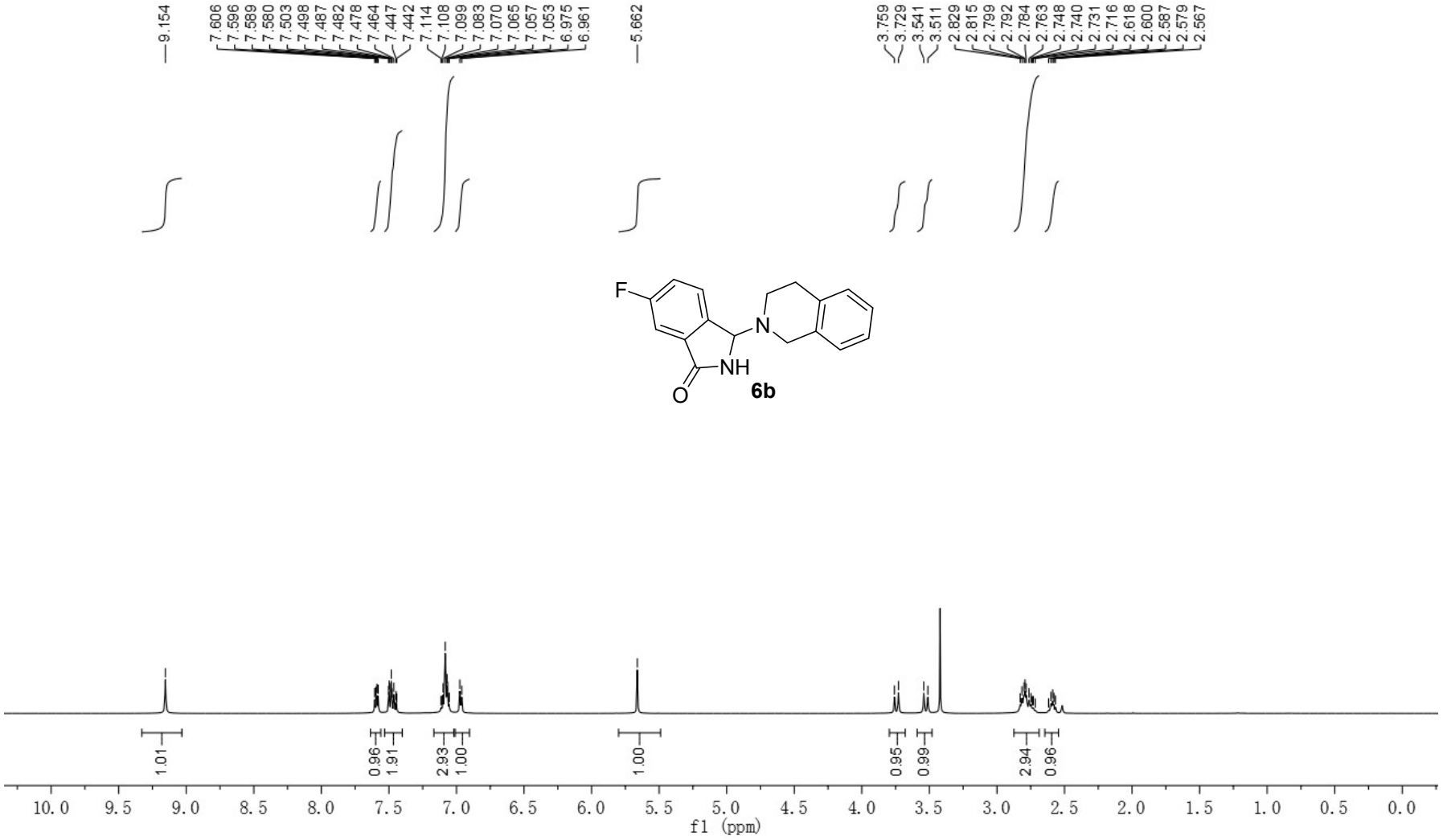
$^{1}$H NMR (500 MHz, $CDCl_3$) of **6a**



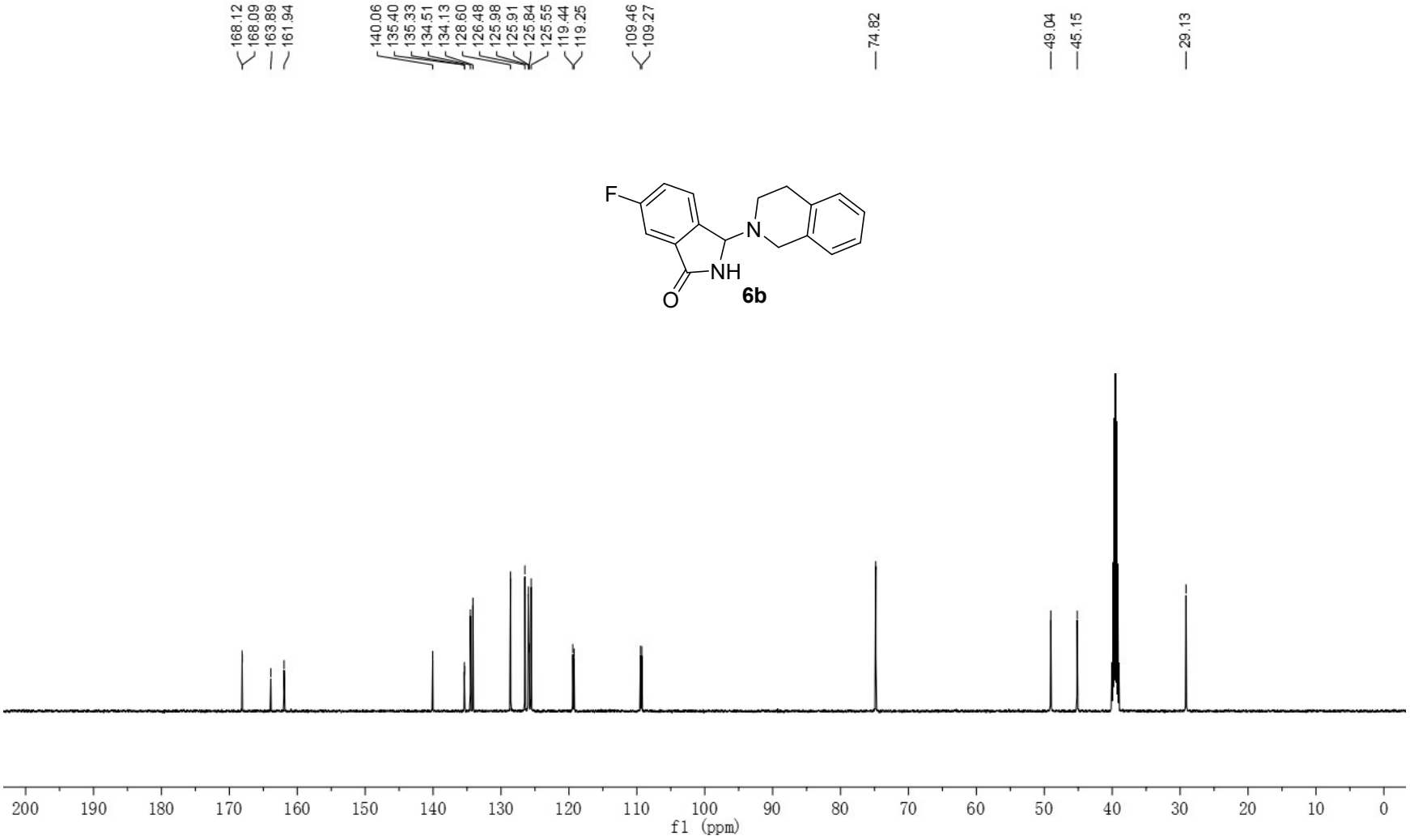
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **6a**



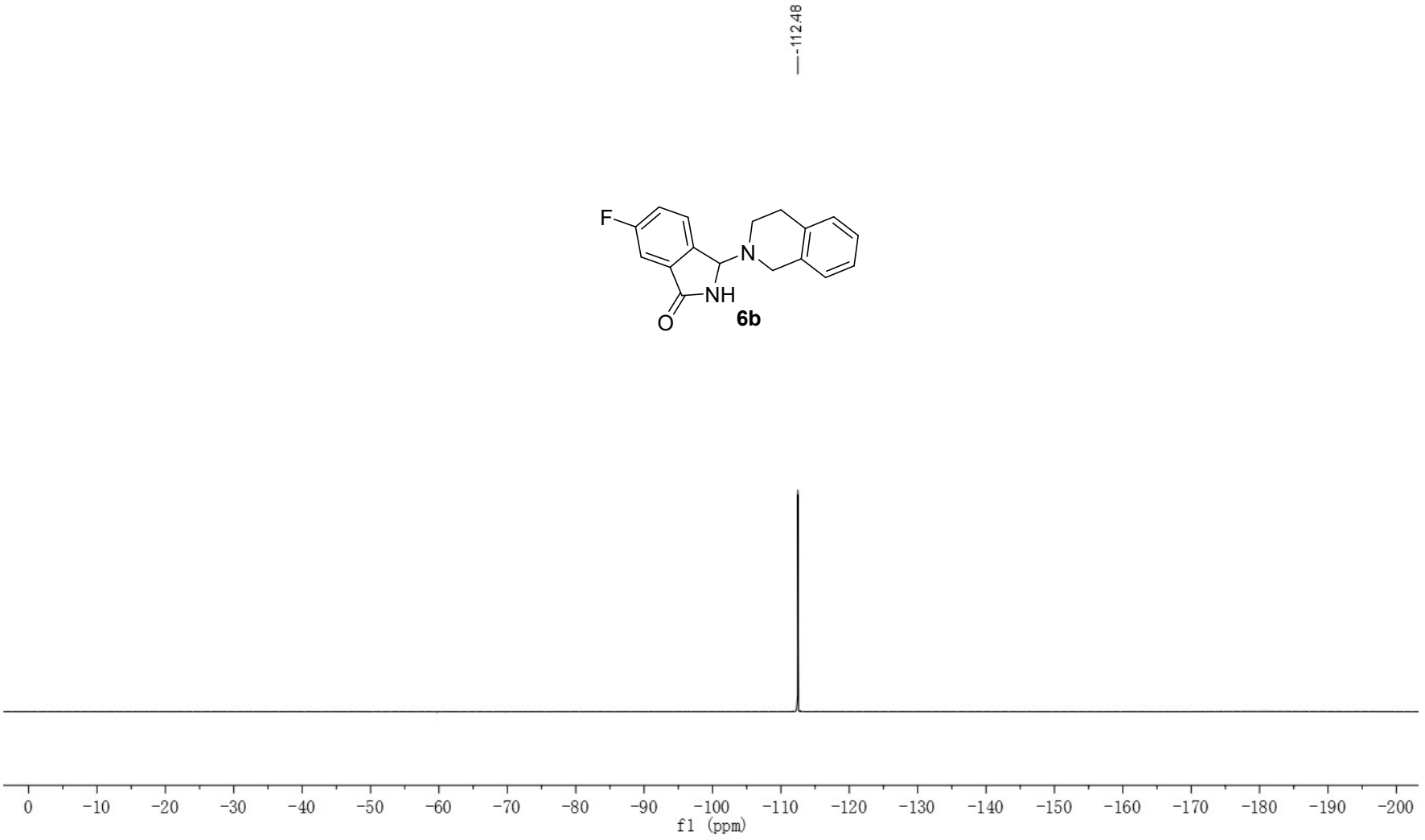
$^{1}$H NMR (500 MHz, $CDCl_3$) of **6b**



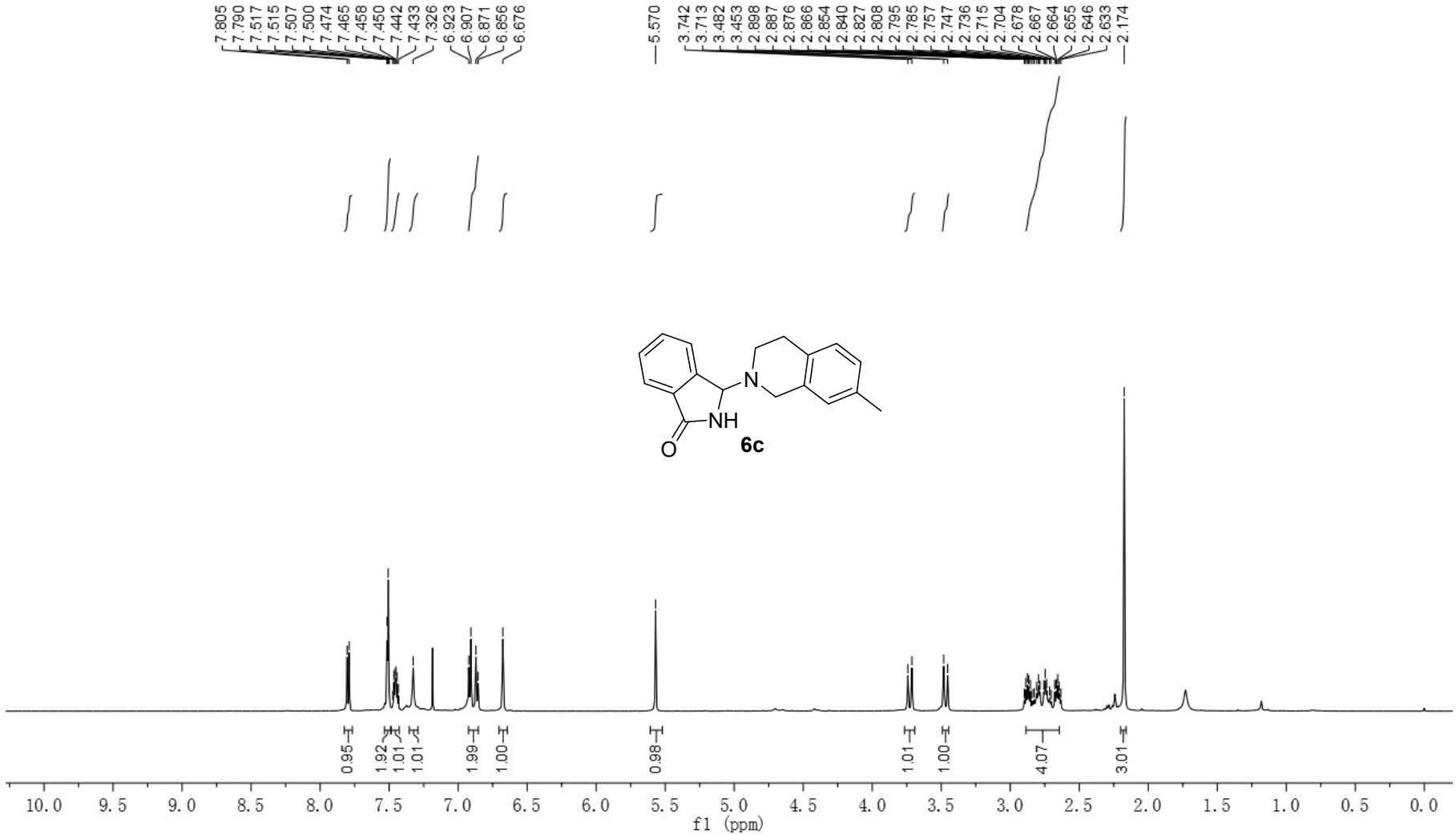
$^{13}$C NMR (126 MHz, DMSO-$d_6$) of **6b**



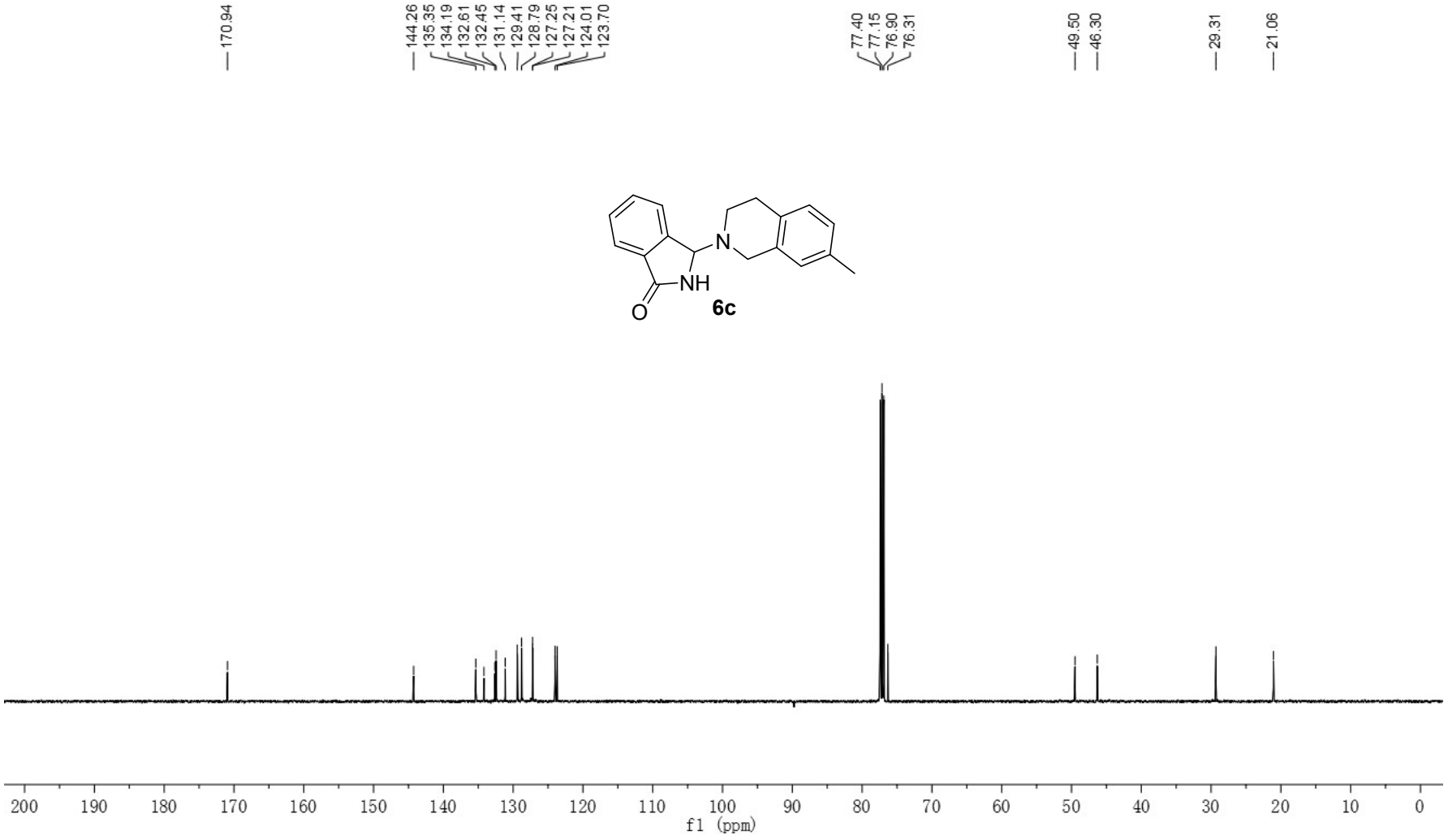
$^{19}$F NMR (471 MHz, DMSO-$d_6$) of **6b**



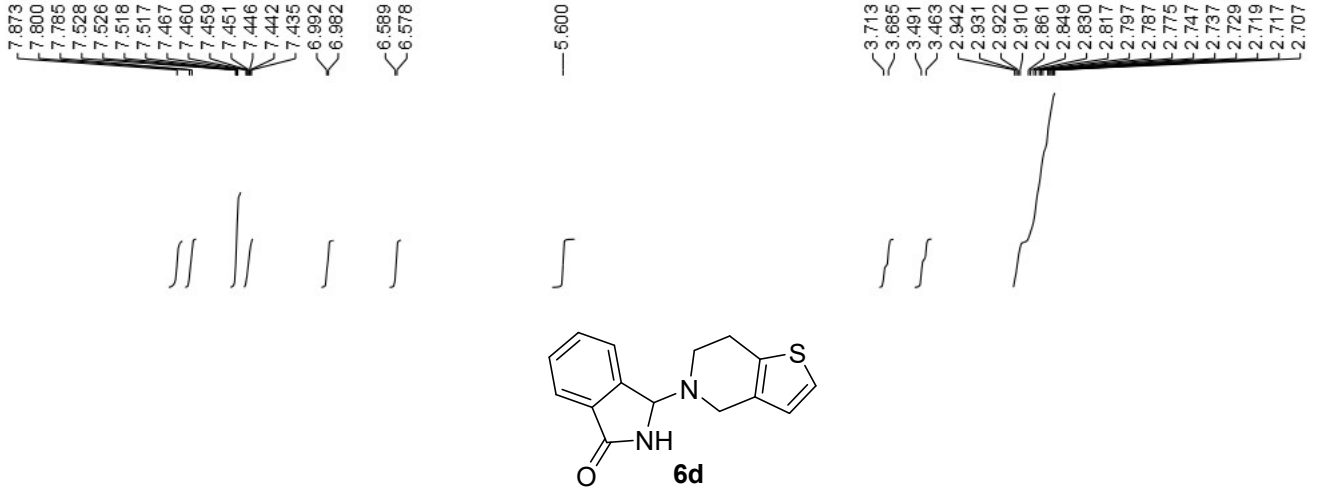
$^{1}$H NMR (500 MHz, $CDCl_3$) of **6c**

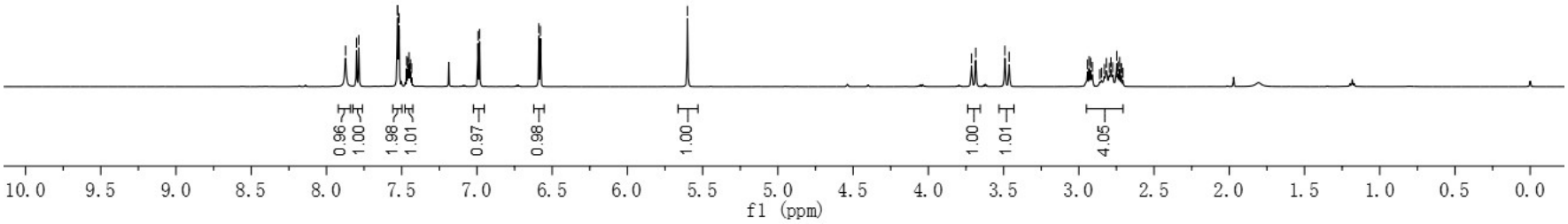


$^{13}C$ NMR (126 MHz, $CDCl_3$) of **6c**

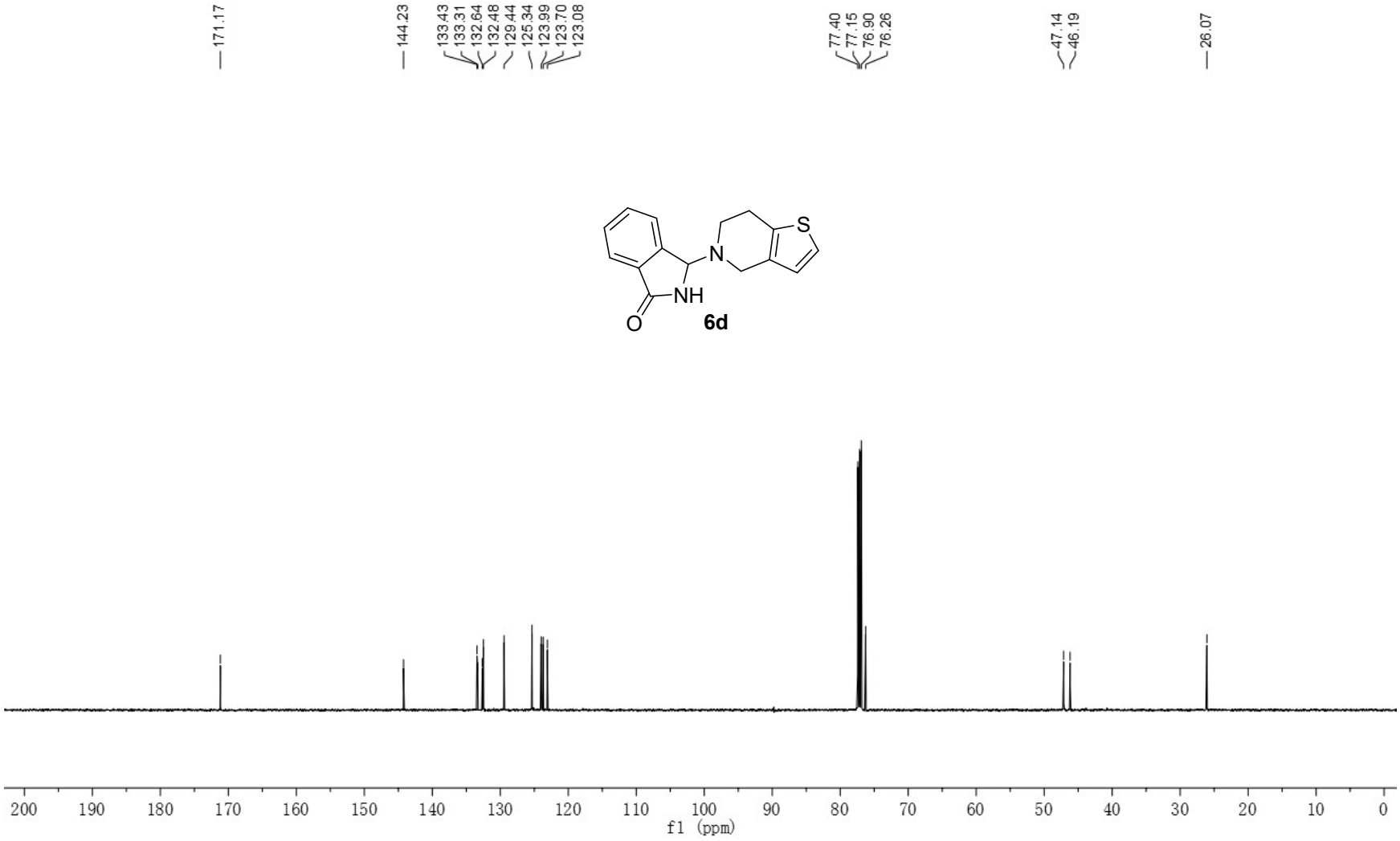


$^1$H NMR (500 MHz, $CDCl_3$) of **6d**

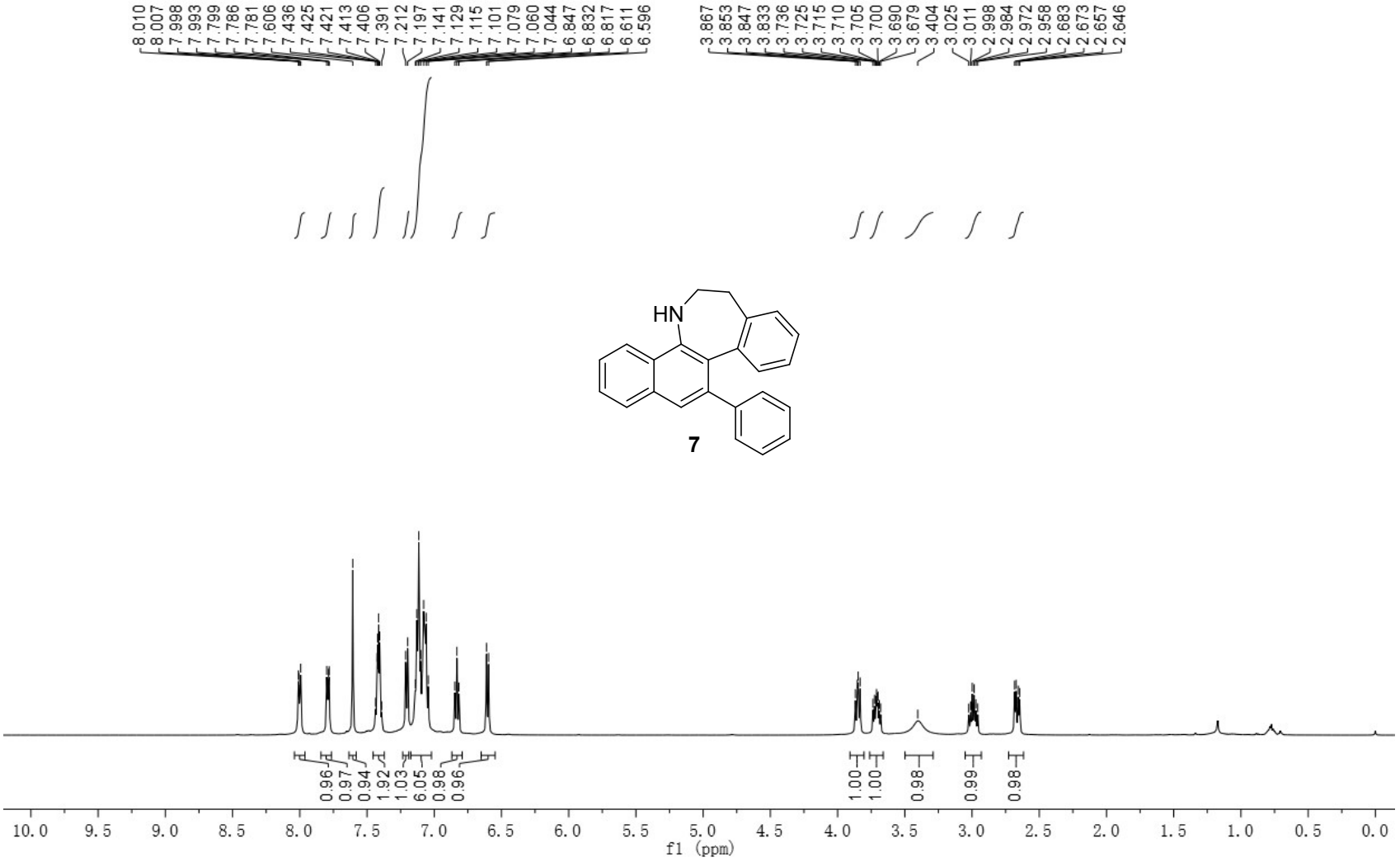


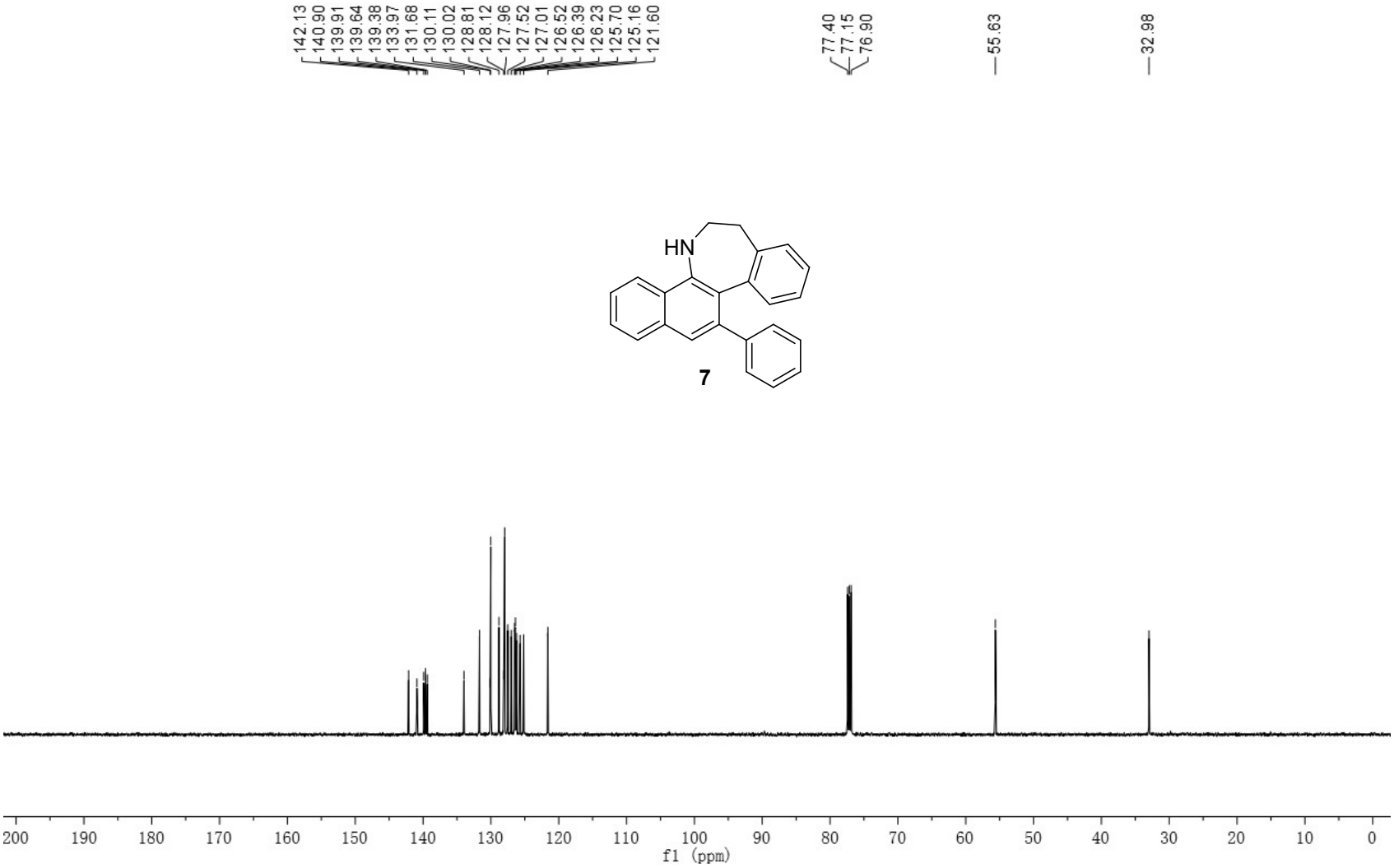
$^{13}C$ NMR (126 MHz, $CDCl_3$) of **6d**



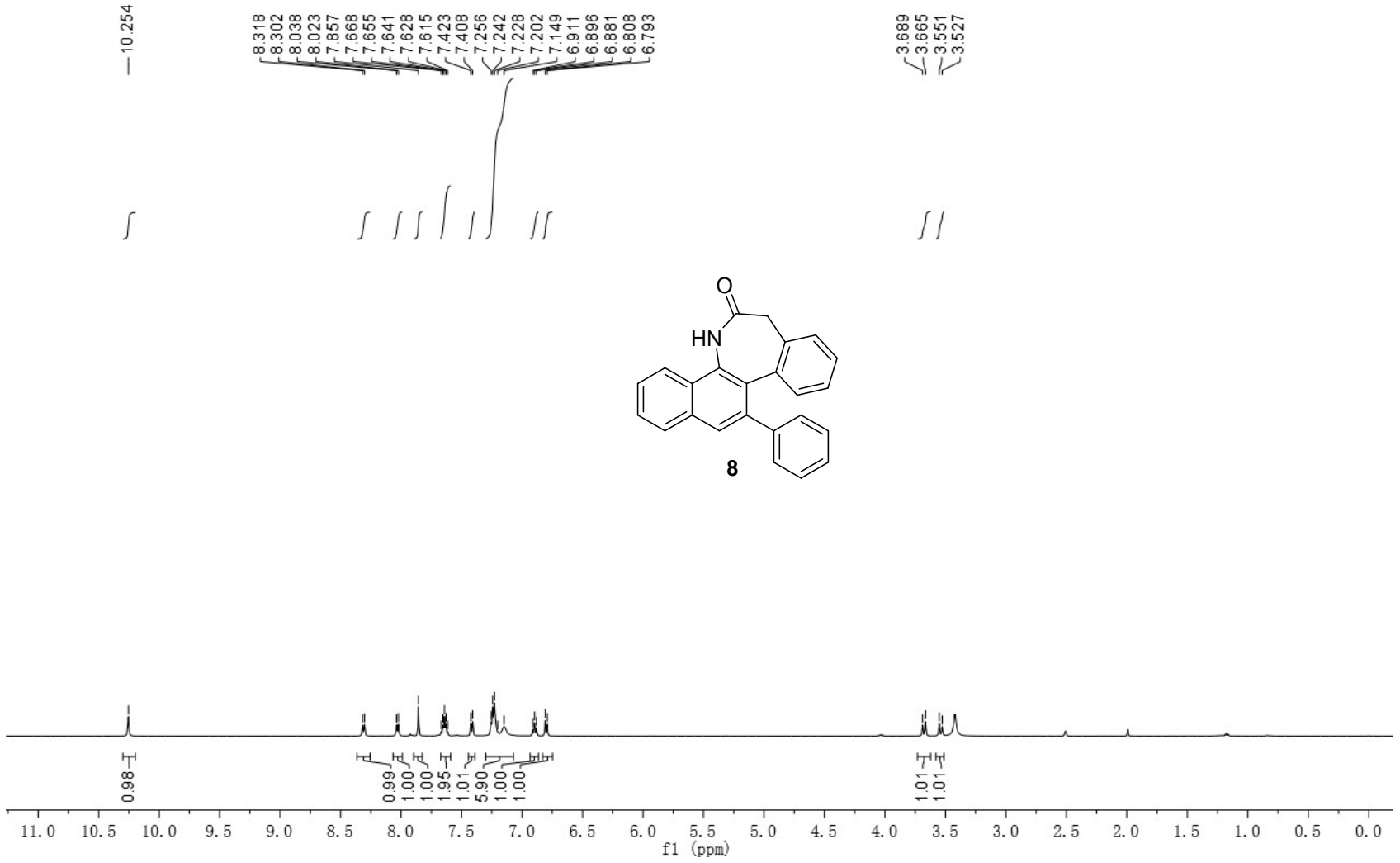
$^{1}$H NMR (500 MHz, $CDCl_3$) of **7**



$^{13}C$ NMR (126 MHz, $CDCl_3$) of **7**

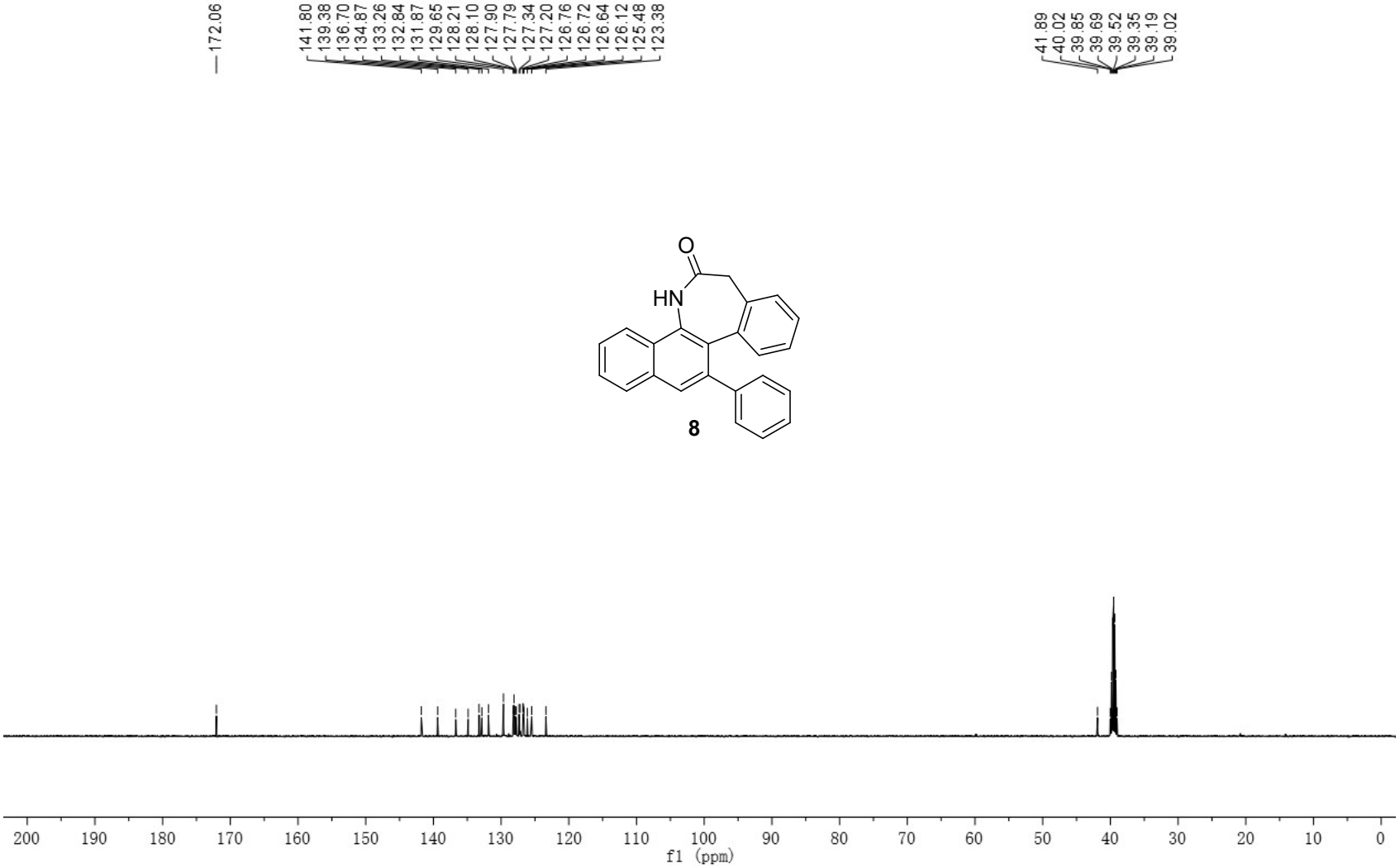


$^{1}$H NMR (126 MHz, DMSO-$d_6$) of **8**

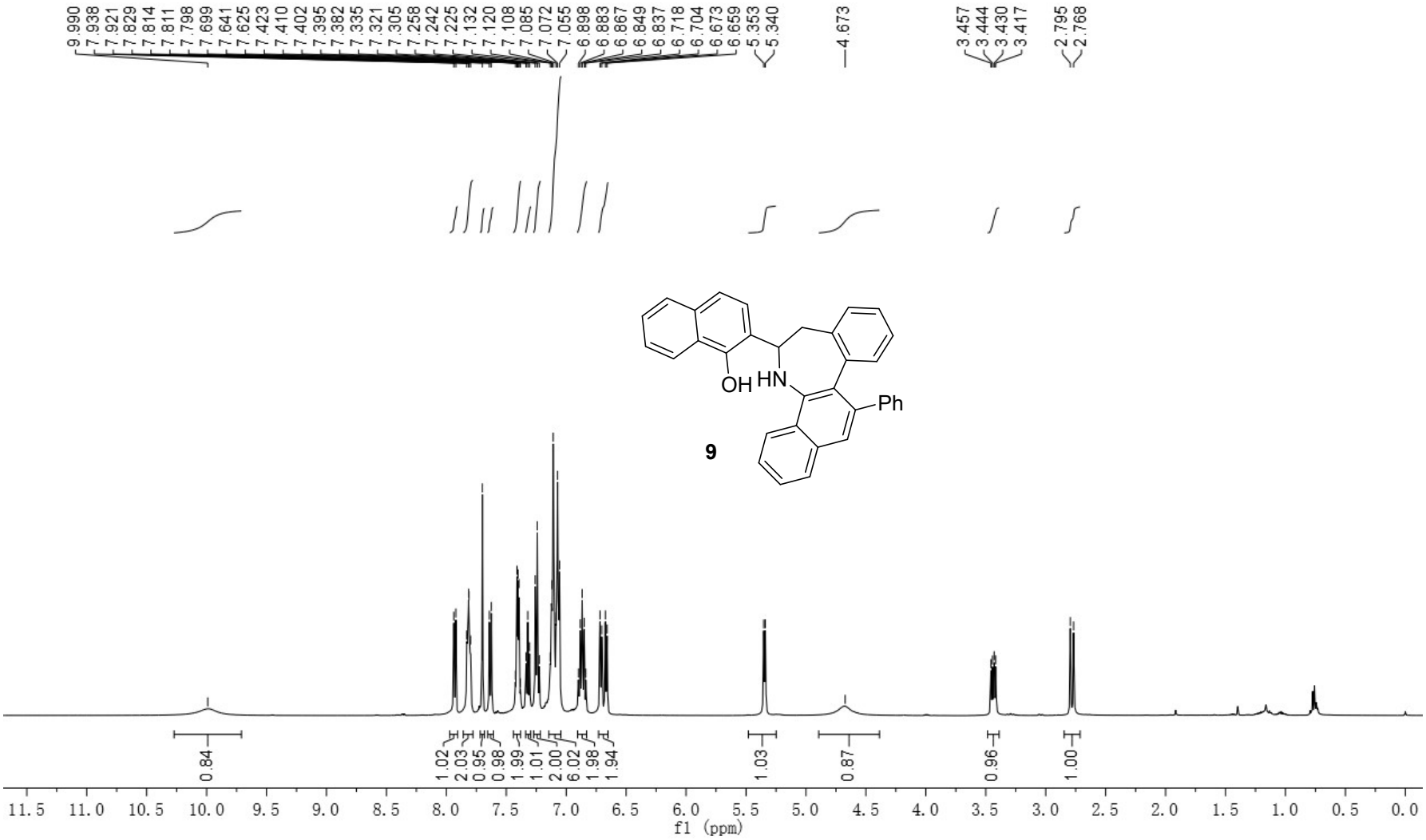



**8**

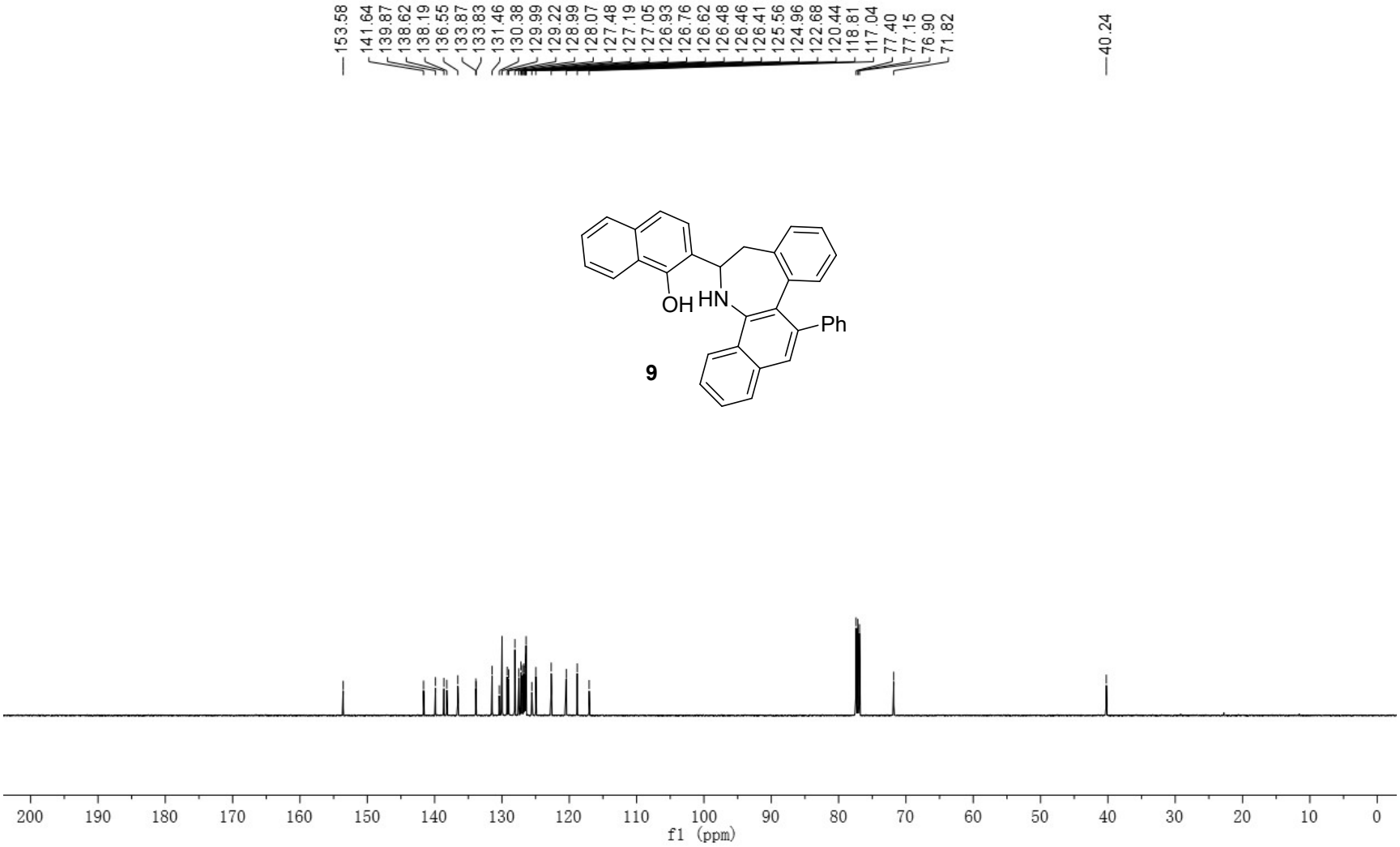
$^{13}$C NMR (126 MHz, DMSO-$d_6$) of **8**



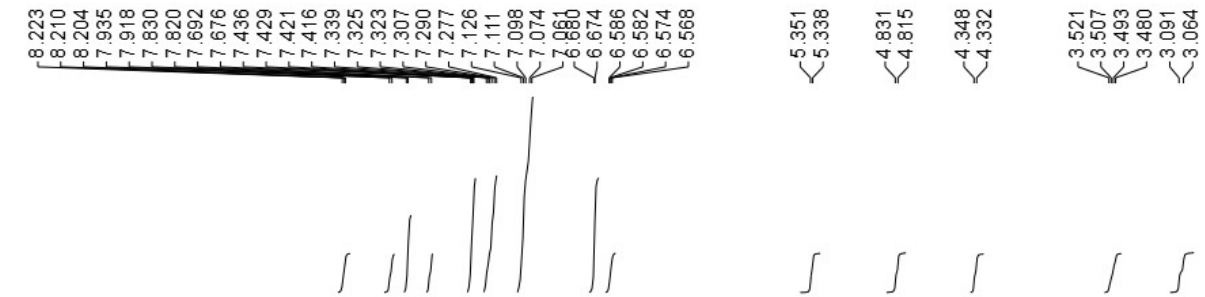
$^{1}$H NMR (126 MHz, $CDCl_3$) of **9**

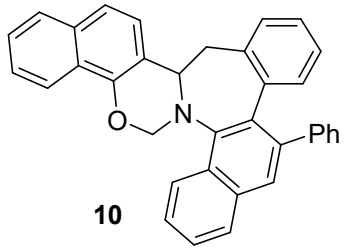


$^{13}C$ NMR (126 MHz, $CDCl_3$) of **9**

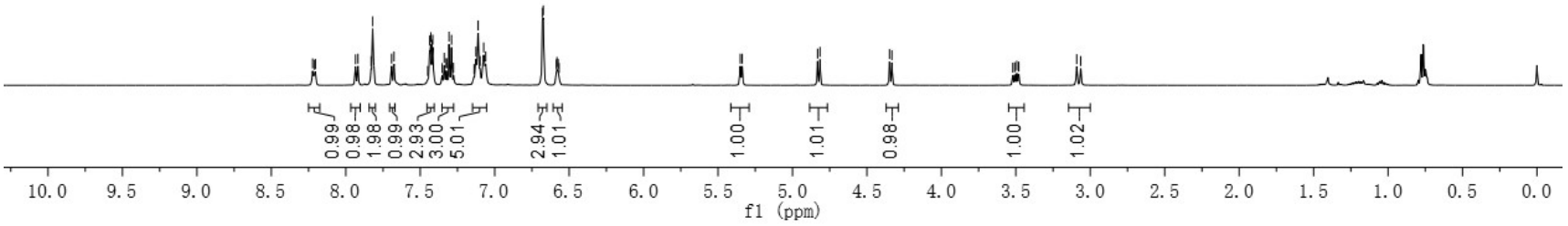


$^1$H NMR (126 MHz, $CDCl_3$) of **10**




**10**



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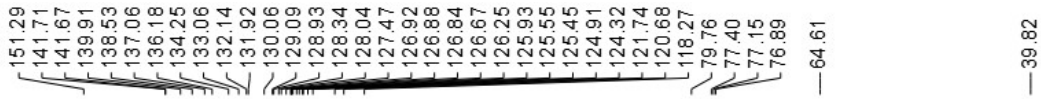
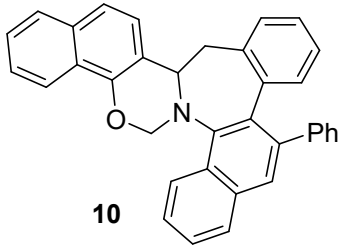
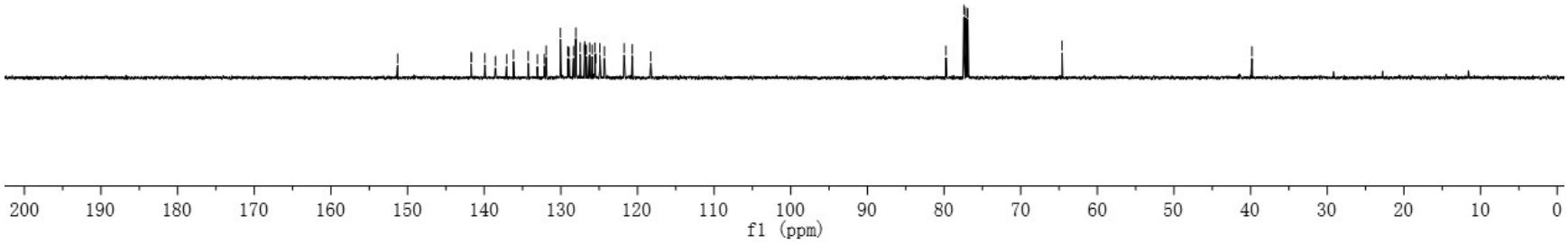
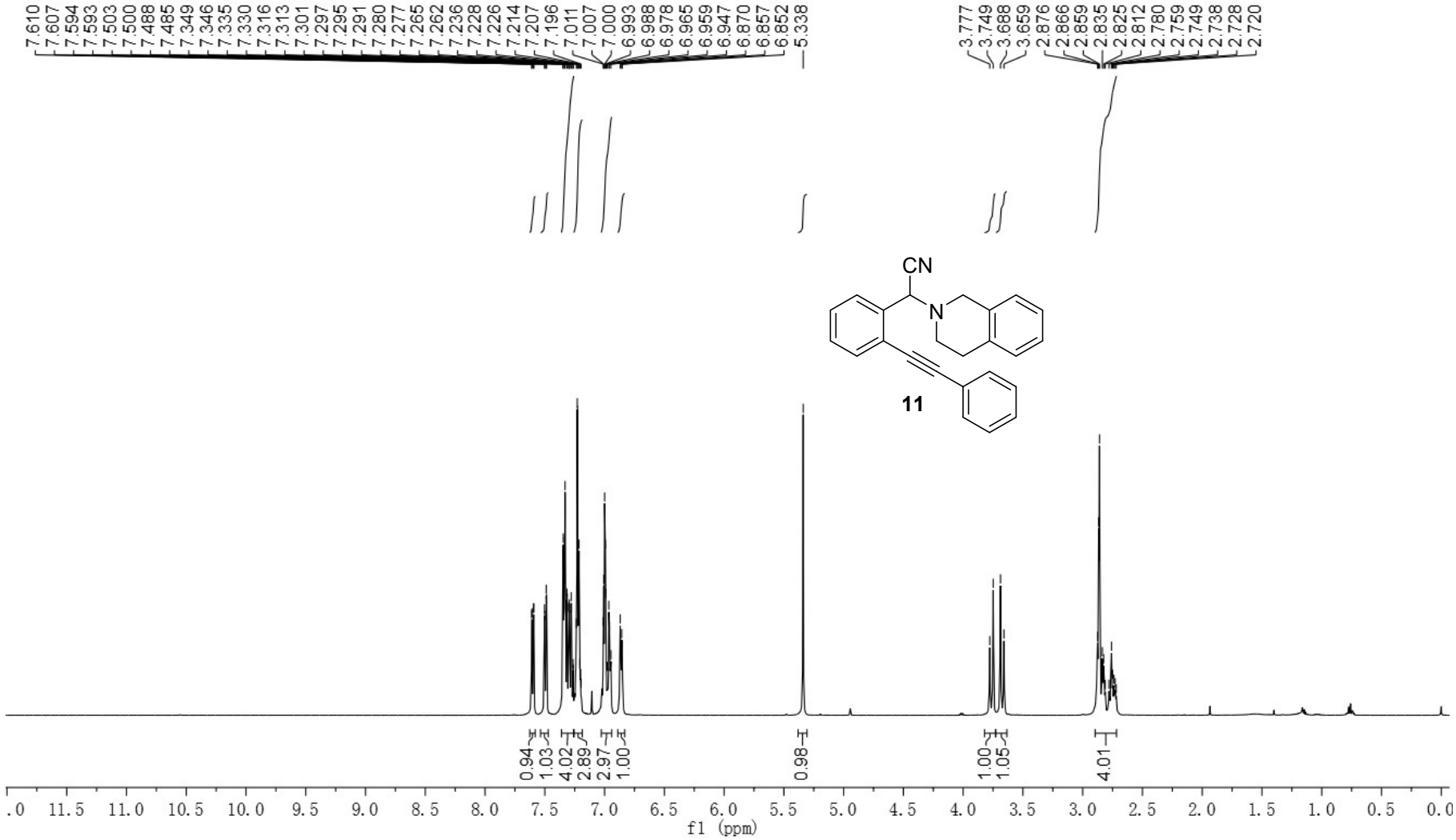


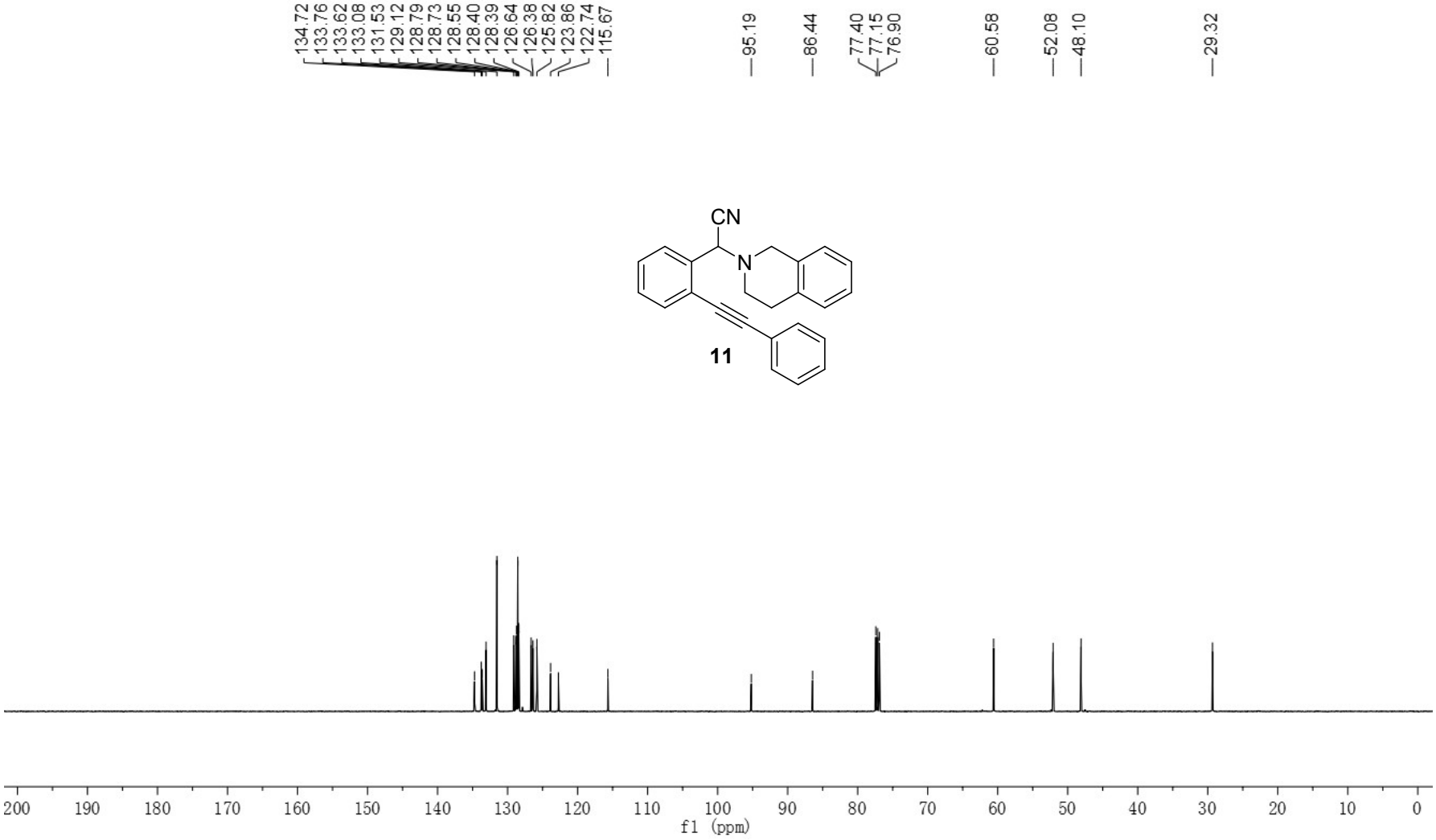

**10**



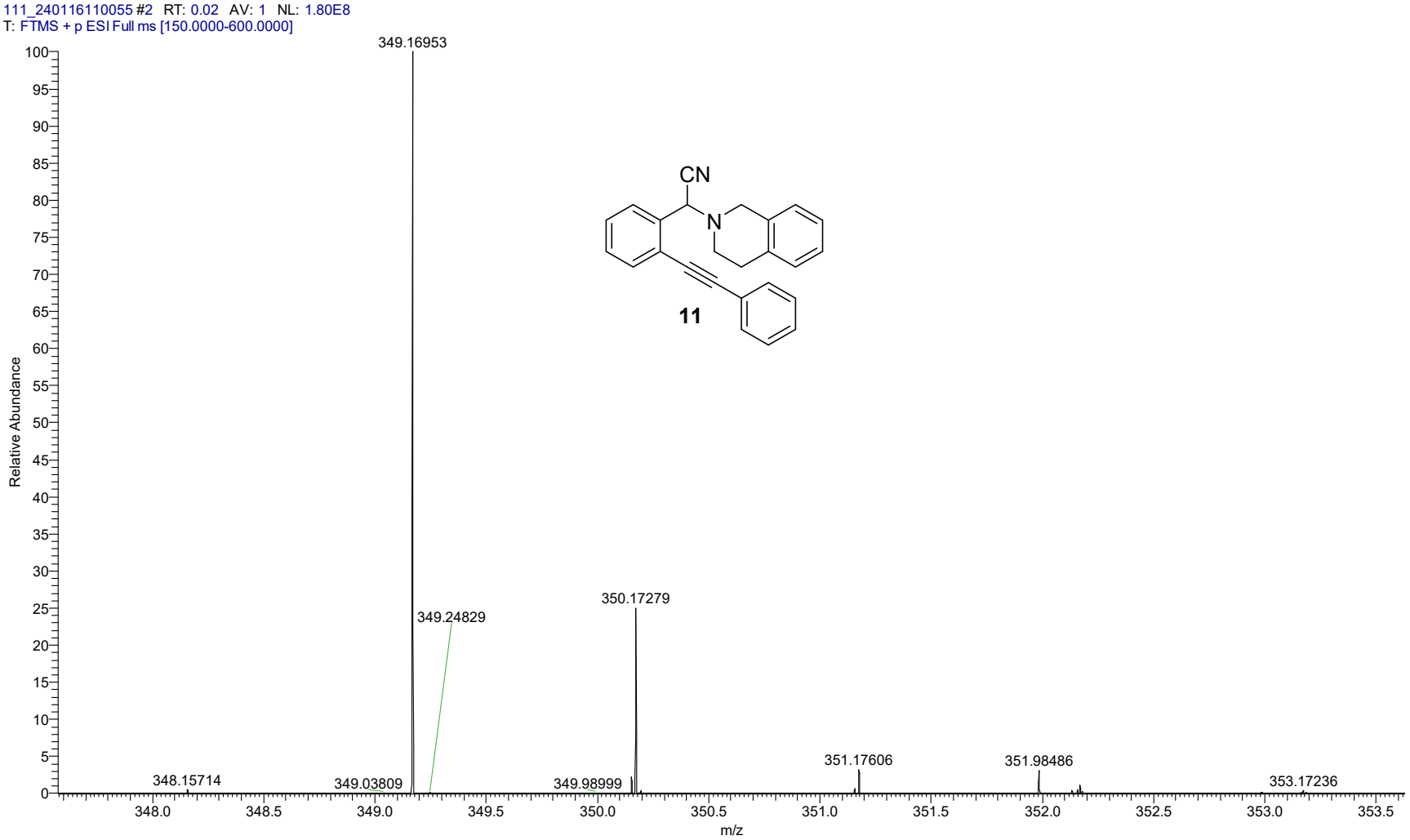
$^{1}$H NMR (126 MHz, $CDCl_3$) of **11**



$^{13}C$ NMR (126 MHz, $CDCl_3$) of **11**



**HRMS** of **11**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T: FTMS + p ESI Full ms [150.0000-600.0000]
349.16953
CN
N
11
Relative Abundance
350.17279
349.24829
348.15714
349.03809
349.98999
351.17606
351.98486
353.17236
m/z