

## Supporting Information for

Single Cu(I)-photosensitizer Enabling Combination of Energy-Transfer and Photoredox Catalysis for the Synthesis of Benzo[b]fluorenols from 1,6-Enynes

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## 1. General Information

Unless otherwise noted, all reactions were carried out in flame-dried reaction vessels with Teflon screw caps under nitrogen. Solvents were purified and dried according to standard methods prior to use. Unless otherwise stated, all reagents were purchased from commercial suppliers and used as received. Flash column chromatography was performed on silica gel (200-300 mesh) with the indicated eluent solvents. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light.

Melting points are uncorrected.  $^1\text{H}$  NMR spectra were recorded on a spectrometer at 25 °C in  $\text{CDCl}_3$  at 500 MHz, with TMS as internal standard.  $^{13}\text{C}$  NMR spectra were recorded on a spectrometer at 25 °C in  $\text{CDCl}_3$  at 125 MHz.  $^{19}\text{F}$  NMR spectra were recorded on a spectrometer at 25 °C in  $\text{CDCl}_3$  at 565 MHz, with  $\text{CF}_3\text{COOH}$  as internal standard. Chemical shifts ( $\delta$ ) are expressed in ppm and coupling constants  $J$  are given in Hz. The following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, br = broad and all combinations thereof can be explained by their integral parts. High resolution mass spectra (HRMS) were obtained on a Bruker micro TOF-Q II instrument with APCI source or Agilent 6200 series TOF/6500 series Q-TOF instrument with ESI source or Waters GCT Premier TOF MS with EI source.

## 2. Preparation of Substrates and Catalyst

### 2.1 General procedure for the preparation of 1

#### Synthesis of 1-(2-iodophenyl)ethan-1-one

To a solution of PTSA (35.9 g, 189 mmol) in MeCN (200 mL) was added 1-(2-aminophenyl)ethan-1-one (8.50 g, 62.9 mmol). The resulting suspension of amine salt was cooled to 0-5 °C. A solution of NaNO<sub>2</sub> (8.68 g, 126 mmol) and KI (25.95 g, 157.3 mmol) in H<sub>2</sub>O (20.0 mL) were added dropwise. The reaction mixture was stirred for 10 min, then allowed to warm to ambient temperature and stirred until the total amine was consumed. To the reaction mixture was then added H<sub>2</sub>O (50.0 mL), NaHCO<sub>3</sub> (until pH = 9-10) and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The reaction mixture was extracted with ethyl acetate and purified by column chromatography (EtOAc/hexane = 20 : 1) to afford pure 2-iodoacetophenone as a pale-yellow oil (14.5 g, 94%).

#### Synthesis of 1-(2-(phenylethynyl)phenyl)ethan-1-one

Et<sub>3</sub>N (1.96 g, 19.4 mmol), 2-iodoacetophenone (2.50 g, 10.2 mol), and phenylacetylene (1.31 g, 12.8 mmol) were added to a mixture of CuI (97 mg, 0.51 mmol) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (143 mg, 0.204 mmol) in Et<sub>3</sub>N (40 mL). Upon stirring for 12 h at 50 °C in an oil bath, the yellow reaction mixture turned black. Saturated aqueous NH<sub>4</sub>Cl (70 mL) was added at room temperature and the mixture was extracted with EtOAc (3 × 40 mL). The combined organic extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated on a rotary evaporator. 1-(2-(phenylethynyl)phenyl)ethan-1-one was isolated by flash column chromatography (petroleum ether/EtOAc = 50 : 1) as an orange oil (1.80 g, 80%).

#### Typical procedure for the synthesis of (E)-3-phenyl-1-(2-(phenylethynyl)phenyl)prop-2-en-1-one (1a)

A solution of NaOH (0.49 g, 12.3 mmol) in water (10 mL) and ethanol (10 mL) was cooled to 0 °C and 1-(2-(phenylethynyl)phenyl)ethan-1-one (1.80 g, 8.18 mmol) and benzaldehyde (0.87 g, 8.18 mmol) were slowly added successively. The reaction mixture was allowed to warm to room temperature overnight. After 12 h the reaction mixture was diluted with diethyl ether (100 mL), the organic phase was separated and

washed with saturated aqueous  $\text{NH}_4\text{Cl}$  and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated and the crude mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20: 1) to afford the desired product **1a** as a yellow solid (2.27 g, 90%).

1,6-Enynes **1a-j**, **1q-1z** were prepared according to this procedure.

#### **General procedure for the synthesis of 1,6-enyne 1p**

$\text{Et}_3\text{N}$  (1.96 g, 19.4 mmol), 2-bromo-5-methoxybenzaldehyde (2.18 g, 10.2 mmol), and phenylacetylene (1.31 g, 12.8 mmol) were added to a mixture of  $\text{CuI}$  (97 mg, 0.51 mmol) and  $\text{PdCl}_2(\text{PPh}_3)_2$  (143 mg, 0.204 mmol) in  $\text{Et}_3\text{N}$  (40 mL). Upon stirring for 12 h at 50 °C in an oil bath, the yellow reaction mixture turned black. Saturated aqueous  $\text{NH}_4\text{Cl}$  (70 mL) was added at room temperature and the mixture was extracted with EtOAc (3 × 40 mL). The combined organic extract was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated on a rotary evaporator. 5-methoxy-2-(phenylethynyl)benzaldehyde was isolated by flash column chromatography (petroleum ether/EtOAc = 50 : 1) as an orange oil (2.04 g, 85%).

5-methoxy-2-(phenylethynyl)benzaldehyde (1.18 g, 5 mmol) was then dissolved in dry THF (20 ml) followed by the addition of methyl magnesium bromide (5.5 mL, 1mol/L in THF, 5.5 mmol) at 0 °C under inert atmosphere. The reaction mixture was allowed to come at room temperature and stirred for 2 hours until completion of the reaction as indicated by TLC. Subsequently, the reaction mixture was quenched with saturated ammonium chloride solution and then extracted with EtOAc and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The organic layer was concentrated under reduced pressure, then dissolved in DCM and Dess-Martin periodinane (2.12 g, 5 mmol) was added to this solution. The reaction mixture was stirred at room temperature until completion of the reaction as indicated by TLC. Then the reaction mixture was filtered through celite and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/EtOAc = 20 : 1) to get pure 1-(5-methoxy-2-(phenylethynyl)phenyl)ethan-1-one as an orange oil (0.88 g, 70%).

A solution of  $\text{NaOH}$  (0.35 g, 8.75 mmol) in water (3.5 mL) and ethanol (7 mL) was cooled to 0 °C and 1-(5-methoxy-2-(phenylethynyl)phenyl)ethan-1-one (0.88 g,

3.5 mmol) and benzaldehyde (0.41 g, 3.9 mmol) were slowly added successively. The reaction mixture was allowed to warm to room temperature overnight. After 12 h the reaction mixture was diluted with diethyl ether (50 mL), the organic phase was separated and washed with saturated aqueous  $\text{NH}_4\text{Cl}$  and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated and the crude mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10 : 1 ) to afford the desired product **1p** as a yellow oil (1.06 g, 90%).

1,6-Enynes **1k-p** were prepared according to this procedure.

#### **General procedure for the synthesis of Substrate 1za**

To a stirred solution under argon atmosphere of 1-(2-iodophenyl)ethan-1-one (2.46 g, 10 mmol) in DMF (40 mL) was added styrene (5.20 g, 50 mmol),  $\text{Na}_2\text{CO}_3$  (2.12 g, 20 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (0.12 g, 0.1 mmol). The reaction mixture was heated to  $120^\circ\text{C}$  in an oil bath for 18 h. Then the reaction was allowed to cool to room temperature. Water and EtOAc were added, the organic phase was separated and washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under reduced pressure to give the crude product which was further purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20 : 1 ) to afford the desired product (E)-1-(2-styrylphenyl)ethan-1-one as a yellow oil (2.0 g, 90%).

A solution of NaOH (0.35 g, 8.75 mmol) in water (3.5 mL) and ethanol (7 mL) was cooled to  $0^\circ\text{C}$  and (E)-1-(2-styrylphenyl)ethan-1-one (0.78 g, 3.5 mmol) and benzaldehyde (0.41 g, 3.9 mmol) were slowly added successively. The reaction mixture was allowed to warm to room temperature overnight. After 12 h the reaction mixture was diluted with diethyl ether (50 mL), the organic phase was separated and washed with saturated aqueous  $\text{NH}_4\text{Cl}$  and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated and the crude mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20 : 1 ) to afford the desired product **1za** as a yellow oil (0.92 g, 85%).

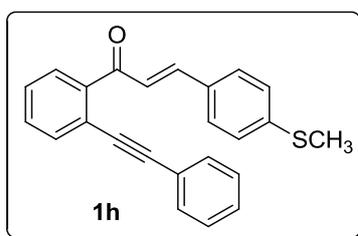
#### **General procedure for the synthesis of 1,6-enyne 1zb**

To a 25 mL Schlenk tube were added cinnamyl 3-phenylpropiolate (0.6 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.75 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (5 mol %)

and CsF (2 equiv), the tube was evacuated and refilled with N<sub>2</sub> for three times. Then MeCN (6 mL) was added under nitrogen atmosphere. The reaction was stirred at 60 °C until complete consumption of starting material as monitored by TLC. After the reaction was finished, the mixture was filtered by a crude column with ethyl acetate as eluent, followed by evaporation in vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the desired product **1zb**.

Substrates **1a-1g**, **1i**, **1j**, **1n**, **1o**, **1q**, **1r**, **1t-1x**, and **1zb** are known compounds and their NMR spectra are consistent with the documented data (**1a**<sup>1</sup>, **1b-1d**<sup>2</sup>, **1e**<sup>1</sup>, **1f**<sup>3</sup>, **1g**<sup>4</sup>, **1i**<sup>5</sup>, **1j**<sup>5</sup>, **1n**<sup>4</sup>, **1o**<sup>4</sup>, **1q**<sup>1</sup>, **1r**<sup>2</sup>, **1t**<sup>5</sup>, **1u-1w**<sup>2</sup>, **1x**<sup>6</sup>, **1zb**<sup>7</sup>). Substrates **1h**, **1k-1m**, **1p**, **1s**, **1y**, **1z**, and **1za** were unknown compounds and their analytical data are listed as follows:

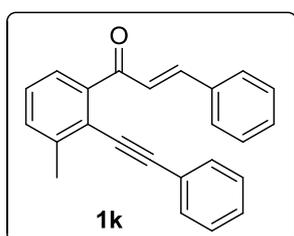
**(E)-3-(4-(methylthio)phenyl)-1-(2-(phenylethynyl)phenyl)prop-2-en-1-one (1h)**



Yellow solid, m.p. 83-85 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.72-7.66 (m, 3H), 7.55-7.50 (m, 4H), 7.47-7.44 (m, 1H), 7.40-7.38 (m, 2H), 7.31-7.28 (m, 1H), 7.26-7.23 (m, 2H), 7.22-7.20 (m, 2H), 2.51 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 193.6, 143.9, 142.4, 142.1,

133.2, 131.5, 131.4, 130.8, 128.9, 128.7, 128.6, 128.4, 128.3, 125.9, 124.9, 122.7, 121.5, 95.4, 88.01 15.1. **HRMS** (ESI) m/z: [M+Na]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>18</sub>NaOS<sup>+</sup> 377.0971; Found 377.0973.

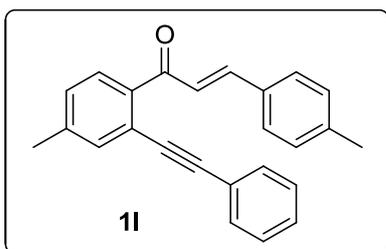
**(E)-1-(3-methyl-2-(phenylethynyl)phenyl)-3-phenylprop-2-en-1-one (1k)**



Yellow solid, m.p. 72-74 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.71-7.65 (m, 3H), 7.55-7.49 (m, 4H), 7.46-7.44 (m, 1H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.31-7.19 (m, 5 H), 2.51 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 193.6, 143.9, 142.4, 142.1, 133.2, 131.5, 131.4, 130.8, 128.9, 128.7, 128.6, 128.4, 128.3, 125.9,

124.9, 122.7, 121.5, 95.4, 88.0, 15.1. **HRMS** (ESI) m/z: [M+Na]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>18</sub>NaO<sup>+</sup> 345.1250; Found 345.1254.

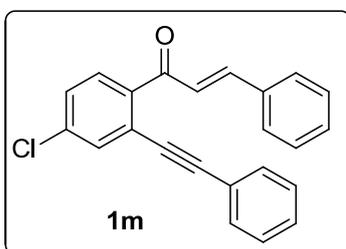
**(E)-1-(4-methyl-2-(phenylethynyl)phenyl)-3-(p-tolyl)prop-2-en-1-one (1l)**



Yellow solid, m.p. 124-126 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.71 (d,  $J = 16.0$  Hz, 1H), 7.65 (d,  $J = 8.0$  Hz, 1H), 7.58 (d,  $J = 16.0$  Hz, 1H), 7.52-7.49 (m, 3H), 7.40-7.38 (m, 2H), 7.30-7.21 (m, 4H), 7.21, 7.17 (d,  $J = 8.0$  Hz, 2H), 2.43 (s, 3H), 2.38 (s, 3H).  $^{13}\text{C NMR}$

(125 MHz,  $\text{CDCl}_3$ ):  $\delta$  193.3, 144.1, 141.3, 140.9, 139.3, 133.8, 132.3, 131.6, 129.6, 129.3, 129.1, 128.5, 128.5, 128.2, 124.9, 122.9, 121.6, 95.0, 88.4, 21.5, 21.2. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{25}\text{H}_{21}\text{O}^+$  337.1587; Found 337.1608.

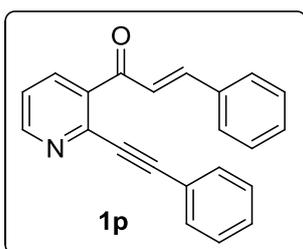
**(E)-1-(4-chloro-2-(phenylethynyl)phenyl)-3-phenylprop-2-en-1-one (1m)**



Yellow solid, m.p. 88-90 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.73 (d,  $J = 16.0$  Hz, 1H), 7.67 (d,  $J = 8.0$  Hz, 1H), 7.65 (d,  $J = 2.0$  Hz, 1H), 7.62-7.60 (m, 2H), 7.58 (d,  $J = 16.0$  Hz, 1H), 7.43-7.35 (m, 6H), 7.32-7.29 (m, 1H), 7.24-7.21 (m, 2H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  192.3,

144.7, 140.1, 137.0, 134.8, 132.8, 131.7, 130.7, 130.3, 129.0, 128.9, 128.7, 128.6, 128.3, 125.4, 123.4, 122.2, 96.7, 86.8. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{23}\text{H}_{15}\text{ClNaO}^+$  365.0704; Found 365.0713.

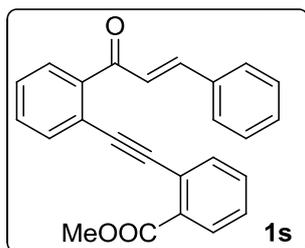
**(E)-3-phenyl-1-(2-(phenylethynyl)pyridin-3-yl)prop-2-en-1-one (1p)**



Brown solid, m.p. 69-71 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.77 (dd,  $J_1 = 4.5$  Hz,  $J_2 = 2.0$  Hz, 1 H), 8.01 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 2.0$  Hz, 1H), 7.75 (d,  $J = 16.0$  Hz, 1H), 7.63-7.60 (m, 3H), 7.43-7.35 (m, 6H), 7.32-7.28 (m, 1H), 7.22-7.19 (m, 2H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  192.2, 151.9, 145.3,

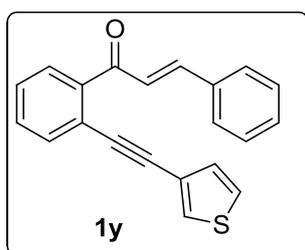
140.8, 138.1, 136.7, 134.5, 132.0, 130.9, 129.4, 129.0, 128.7, 128.3, 125.1, 122.8, 121.6, 95.5, 87.7. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{22}\text{H}_{15}\text{NNaO}^+$  332.1046; Found 332.1055.

**methyl 2-((2-cinnamoylphenyl)ethynyl)benzoate (1s)**



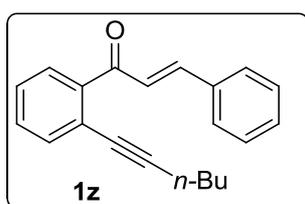
Brown solid, m.p. 70-72 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.95 (dd,  $J_1 = 7.8$  Hz,  $J_2 = 1.2$  Hz, 1H), 7.76-7.70 (m, 3H), 7.62-7.58 (m, 3H), 7.55-7.52 (m, 1H), 7.48-7.45 (m, 1H), 7.42 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 1.2$  Hz, 1H), 7.39-7.25 (m, 5H), 3.93 (s, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  193.5, 166.4, 144.4, 141.8, 134.9, 134.1, 133.6, 131.6, 131.5, 130.9, 130.5, 130.5, 128.9, 128.8, 128.6, 128.5, 128.2, 125.9, 123.2, 121.7, 94.2, 92.7, 52.2. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{25}\text{H}_{18}\text{NaO}_3^+$  389.1148; Found 389.1154.

**(E)-3-phenyl-1-(2-(thiophen-3-ylethynyl)phenyl)prop-2-en-1-one (1y)**



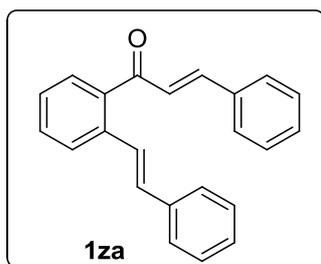
Yellow solid, m.p. 100-102 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.73-7.69 (m, 2H), 7.65-7.56 (m, 4H), 7.53-7.49 (m, 1H), 7.47-7.43 (m, 1H), 7.41-7.34 (m, 4H), 7.20 (dd,  $J_1 = 5.0$  Hz,  $J_2 = 3.0$  Hz, 1H), 7.02 (dd,  $J_1 = 5.0$  Hz,  $J_2 = 1.0$  Hz, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  193.6, 144.3, 141.8, 134.9, 133.1, 130.9, 130.6, 129.7, 129.2, 128.9, 128.8, 128.5, 128.3, 125.8, 125.4, 121.8, 121.7, 90.8, 87.5. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{21}\text{H}_{14}\text{NaOS}^+$  337.0658; Found 337.0666.

**(E)-1-(2-(hex-1-yn-1-yl)phenyl)-3-phenylprop-2-en-1-one (1z)**



Yellow liquid.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.63-7.59 (m, 4H), 7.52-7.50 (m, 1H), 7.47-7.42 (m, 2H), 7.40-7.35 (m, 4H), 2.34 (t,  $J = 7.0$  Hz, 2H), 1.46-1.40 (m, 2H), 1.36-1.29 (m, 2H), 0.78 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.4, 144.1, 142.1, 135.0, 133.2, 130.5, 130.5, 128.9, 128.7, 128.4, 128.3, 127.6, 126.1, 122.4, 97.2, 79.1, 30.6, 22.0, 19.3, 13.5. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{21}\text{H}_{20}\text{NaO}^+$  311.1406; Found 311.1415.

**(E)-3-phenyl-1-(2-((E)-styryl)phenyl)prop-2-en-1-one (1za)**



Yellow liquid.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.81 (d,  $J = 8.0$  Hz, 1H), 7.59-7.49 (m, 7H), 7.46 (d,  $J = 16.0$  Hz, 1H), 7.42-7.37 (m, 4 H), 7.35-7.32 (m, 2H), 7.26-7.25 (m, 1H), 7.21 (d,  $J = 16.0$  Hz, 1H), 7.11 (d,  $J = 11.0$  Hz, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.1, 146.0, 138.6, 137.1, 136.6, 134.6, 131.5, 130.8, 130.7, 129.0, 128.6, 128.5, 128.5, 127.9, 127.1, 126.9, 126.8, 126.4, 126.3. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{23}\text{H}_{18}\text{NaO}^+$  333.1250; Found 333.1259.

## 2.2 Synthesis of photosensitizer (PS1-S3)

$[\text{Cu}(2,9\text{-dimethyl-4,7-diphenyl-1,10-phenanthroline})(\text{xantphos})]\text{PF}_6^-$  (PS1)<sup>7</sup> was prepared according to the reported procedure: In an oven-dried Schlenk tube,  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6^-$  (373.0 mg, 1.0 mmol) and Xantphos (579.0 mg, 1.0 mmol) were dissolved in dry DCM (20 mL) at room temperature. The resulting solution was stirred at reflux overnight. The reaction mixture was then allowed to cool to room temperature and the 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (360.0 mg, 1.0 mmol) was added at room temperature dissolved in a minimal amount of DCM. The resulting mixture was then heated to reflux in an oil bath for another 3 hours until no further color change was observed (at this point red to yellow solution was obtained). The reaction mixture was then allowed to cool to room temperature and *n*-hexane was added to precipitate the product. It was filtered and washed with *n*-hexane. The resulting solid was further purified by recrystallization in a DCM/*n*-hexane mixture at 4 °C.

PS2, PS3 were also prepared according to this procedure.

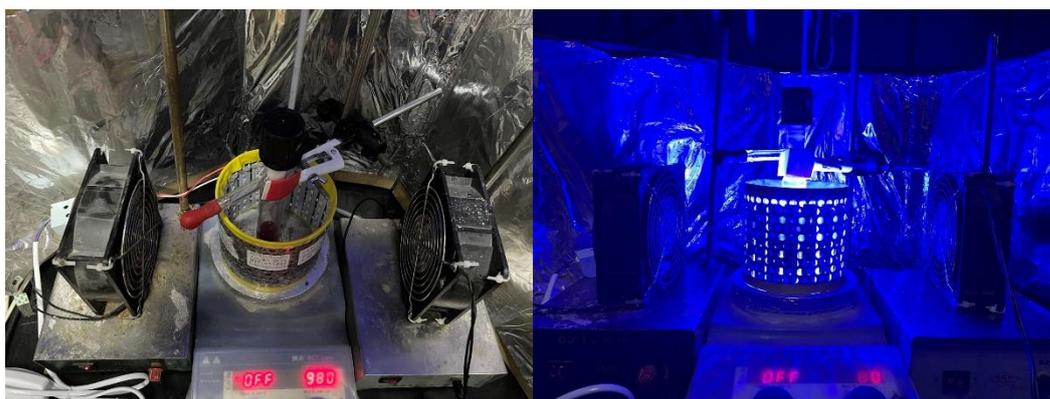
## 3. Typical Procedure for the Synthesis of Benzo[b]fluorenols

### 3.1 Experimental details and characterization of products 2

To a 25 mL Schlenk tube were added **1** (0.3 mmol) and PS1 (0.015 mmol, 17.0 mg), the tube was evacuated and refilled with  $\text{N}_2$  for three times. Then  $\text{Me}_2\text{NH}$  (0.9 mmol, 0.45 mL, 2 M in THF) and 6 mL MeCN was added under nitrogen atmosphere.

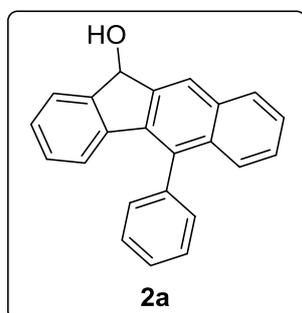
The reaction mixture was irradiated at a distance of 3 cm from 15 W blue LED light. The reaction mixture was stirred at room temperature for 20 h. Upon completion, the reaction mixture concentrated under vacuum and the residue was purified by column chromatography on silica gel (200-300 mesh), eluting with the indicated mixture of ethyl acetate (EA)/ petroleum ether (PE) to give pure product **2**.

### Reaction setup



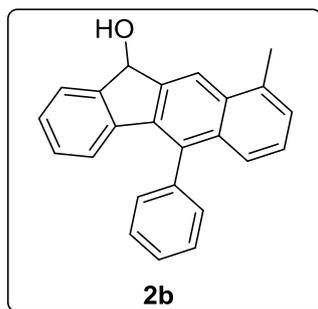
**Figure S1. Reaction Setup.** Light irradiation was performed using 15 W blue LED strips (18 LED's/ft, purchased from Solid Apollo) with 420 nm light. The strips were wrapped around on the inside walls of a meshy cask. The Schlenk tube was placed in the center of the meshy cask. The reaction mixture was irradiated at a distance of 3 cm from 15 W blue LED strips. Two fans were used to control the reaction temperature at 25 °C.

### 5-phenyl-11H-benzo[b]fluoren-11-ol (**2a**)<sup>8</sup>



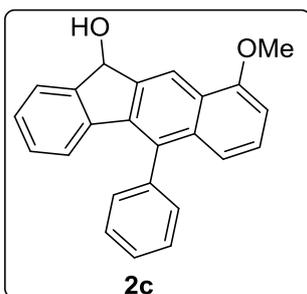
**2a** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (79.5 mg, 86%). m.p.: 74-76 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.10 (s, 1H), 7.90 (d, *J* = 8 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.63-7.59 (m, 3H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.51-7.47 (m, 1), 7.43-7.39 (m, 2H), 7.38-7.36 (m, 1H), 7.28-7.25 (m, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.42 (d, *J* = 8 Hz, 1H), 5.77 (s, 1H), 2.34 (s, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 146.5, 143.5, 139.8, 138.4, 135.1, 133.8, 133.8, 133.1, 130.0, 129.7, 129.1, 129.0, 128.8, 128.3, 127.9, 127.8, 126.4, 126.2, 125.8, 125.2, 123.9, 123.4, 74.3.

### 9-methyl-5-phenyl-11H-benzo[b]fluoren-11-ol (**2b**)



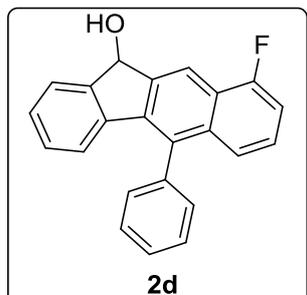
**2b** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (60.9 mg, 63%). m.p.: 167-169 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.33 (s, 1H), 7.65 (d,  $J = 7.5$  Hz, 1H), 7.63-7.59 (m, 3H), 7.43-7.37 (m, 3H), 7.35 (d,  $J = 6.5$  Hz, 1H), 7.32-7.25 (m, 2H), 7.09 (t,  $J = 7$  Hz, 1H), 6.39 (d,  $J = 7.5$  Hz, 1H), 5.80 (s, 1H), 2.81 (s, 3H), 2.25 (s, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.6, 143.4, 139.9, 138.8, 134.8, 134.6, 134.4, 134.0, 132.3, 130.0, 129.8, 129.1, 129.0, 128.9, 127.9, 127.8, 126.8, 125.8, 125.2, 124.9, 123.5, 120.2, 74.7, 19.9. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{24}\text{H}_{18}\text{NaO}$  345.1250; Found 345.1247.

### 9-methoxy-5-phenyl-11H-benzo[b]fluoren-11-ol (**2c**)



**2c** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (87.2 mg, 86%). m.p.: 176-178 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.61 (s, 1H), 7.66 (d,  $J = 7.5$  Hz, 1H), 7.62-7.56 (m, 3H), 7.41-7.38 (m, 2H), 7.30 (t,  $J = 8$  Hz, 1H), 7.28-7.25 (m, 1H), 7.11-7.06 (m, 2H), 6.83 (d,  $J = 7.5$  Hz, 1H), 6.39 (d,  $J = 8$  Hz, 1H), 5.79 (s, 1H), 4.03 (s, 3H), 2.29 (s, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.7, 146.8, 142.9, 139.9, 138.8, 135.6, 135.0, 133.6, 130.1, 129.8, 129.1, 129.0, 128.9, 128.0, 127.8, 126.1, 125.2, 125.1, 123.5, 118.9, 118.1, 104.1, 74.6, 55.7. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{24}\text{H}_{18}\text{NaO}_2$  361.1199; Found 361.1198.

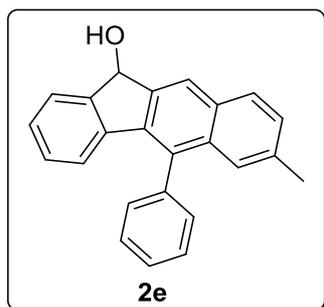
### 9-fluoro-5-phenyl-11H-benzo[b]fluoren-11-ol (**2d**)



**2d** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (60.6 mg, 62%). m.p.: 138-140 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.41 (s, 1H), 7.65 (d,  $J = 7.0$  Hz, 1H), 7.62-7.60 (m, 3H), 7.40-7.35 (m, 2H), 7.31-7.27 (m, 3H), 7.18-7.14 (m, 1H), 7.09 (t,  $J = 7.5$  Hz, 1H), 6.40 (d,  $J = 8.0$  Hz, 1H), 5.78 (s, 1H), 2.24 (s, 1H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.2 (C-F,  $^1J_{\text{C-F}} = 250.0$  Hz), 146.6, 144.0, 139.5, 138.2, 136.1, 135.6 (C-F,

$^4J_{C-F} = 3.8$  Hz), 133.67 (C-F,  $^4J_{C-F} = 2.5$  Hz), 129.9, 129.7, 129.2, 129.2, 129.0, 128.4, 128.1, 125.8 (C-F,  $^3J_{C-F} = 8.8$  Hz), 125.2, 123.7, 123.2 (C-F,  $^2J_{C-F} = 16.3$  Hz), 122.3 (C-F,  $^4J_{C-F} = 3.8$  Hz), 116.6 (C-F,  $^3J_{C-F} = 6.3$  Hz), 109.6 (C-F,  $^2J_{C-F} = 20.0$  Hz), 74.4.  **$^{19}F$  NMR** (565 MHz,  $CDCl_3$ ):  $\delta$  -122.52. **HRMS** (ESI)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{23}H_{15}FNaO$  349.0999; Found 349.0997.

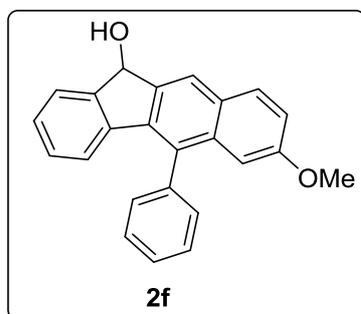
#### 7-methyl-5-phenyl-11H-benzo[b]fluoren-11-ol (**2e**)<sup>8</sup>



**2e** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (76.3 mg, 79%). m.p.: 180-182 °C.  **$^1H$  NMR** (500 MHz,  $CDCl_3$ ):  $\delta$  8.06 (s, 1H), 7.81 (d,  $J = 8.5$  Hz, 1H), 7.64-7.61 (m, 4H), 7.42-7.40 (m, 1H), 7.39-7.37 (m, 1H), 7.33 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.5$  Hz, 1H), 7.29 (s, 1H), 7.27-7.23 (m, 1H), 7.07 (t,  $J = 8.0$  Hz, 1H),

6.36 (d,  $J = 8.0$  Hz, 1H), 5.77 (s, 1H), 2.42 (s, 3H), 2.20 (s, 1H).  **$^{13}C$  NMR** (125 MHz,  $CDCl_3$ ):  $\delta$  146.6, 142.6, 1394.0, 138.6, 136.0, 135.3, 134.1, 133.3, 131.4, 130.1, 129.8, 129.1, 129.1, 128.9, 128.2, 128.0, 127.9, 127.8, 125.5, 125.1, 123.7, 123.5, 74.4, 21.9.

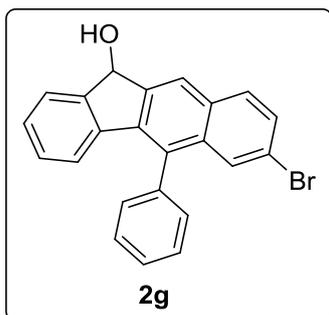
#### 7-methoxy-5-phenyl-11H-benzo[b]fluoren-11-ol (**2f**)



**2f** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (58.8 mg, 58%). m.p.: 176-178 °C.  **$^1H$  NMR** (500 MHz,  $CDCl_3$ ):  $\delta$  8.00 (s, 1H), 7.77 (d,  $J = 9.0$  Hz, 1H), 7.64-7.56 (m, 4H), 7.42-7.40 (m, 1H), 7.36-7.34 (m, 1H), 7.27-7.23 (m, 1H), 7.14 (dd,  $J_1 = 8.5$  Hz,  $J_2 = 2.5$  Hz, 1H), 7.07 (t,  $J = 8.0$  Hz, 1H),

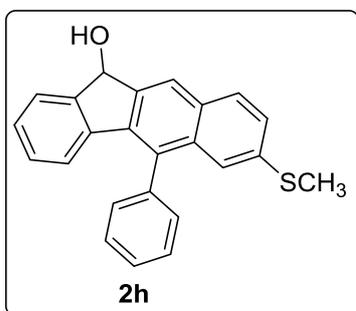
6.82 (d,  $J = 2.5$  Hz, 1H), 6.37 (d,  $J = 8.0$  Hz, 1H), 5.72 (s, 1H), 3.70 (s, 3H), 2.37 (s, 1H).  **$^{13}C$  NMR** (125 MHz,  $CDCl_3$ ):  $\delta$  157.9, 146.7, 141.4, 139.9, 138.6, 135.7, 135.2, 132.8, 130.0, 129.7, 129.2, 129.2, 128.8, 128.6, 127.9, 127.9, 125.1, 123.7, 123.5, 117.8, 105.6, 74.4, 55.1. **HRMS** (ESI)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{24}H_{18}NaO_2$  361.1199; Found 361.1200.

#### 7-bromo-5-phenyl-11H-benzo[b]fluoren-11-ol (**2g**)<sup>9</sup>



**2g** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (62.5 mg, 54%). m.p.: 195-197 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.06 (s, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.65-7.64 (m, 2H), 7.63-7.59 (m, 3H), 7.55 (dd, *J*<sub>1</sub> = 8.5 Hz, *J*<sub>2</sub> = 2.0 Hz, 1H), 7.40-7.32 (m, 2H), 7.29-7.26 (m, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.36 (d, *J* = 7.5 Hz, 1H), 5.76 (d, *J* = 9.0 Hz, 1H), 2.21 (d, *J* = 9.5 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 146.5, 144.1, 139.4, 137.6, 136.3, 135.2, 133.1, 131.6, 130.0, 129.9, 129.7, 129.4, 129.3, 129.2, 129.1, 128.6, 128.4, 128.3, 125.2, 123.9, 123.7, 120.7, 74.4.

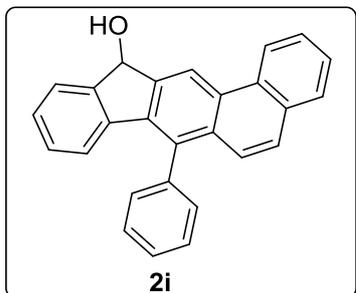
#### 7-(methylthio)-5-phenyl-11H-benzo[b]fluoren-11-ol (**2h**)



**2h** was isolated via column chromatography (eluent EA/PE = 1:3 (V/V)) as white solid (90.3 mg, 85%). m.p.: 126-128 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.02 (s, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.62-7.56 (m, 3H), 7.40-7.34 (m, 3H), 7.29-7.24 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.39 (d, *J* = 8.0 Hz, 1H), 5.75 (s, 1H),

2.39 (s, 3H), 2.25 (d, *J* = 4.0 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 146.6, 143.0, 139.8, 138.2, 136.6, 135.9, 134.4, 132.9, 131.0, 130.0, 129.8, 129.2, 129.2, 129.0, 128.6, 128.1, 128.0, 125.3, 125.2, 123.8, 123.6, 122.4, 74.4, 15.6. **HRMS** (APCI) *m/z*: [M-H<sub>2</sub>O+H]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>17</sub>S 337.1045; Found 337.1052.

#### 7-phenyl-12H-indeno[1,2-b]phenanthren-12-ol (**2i**)

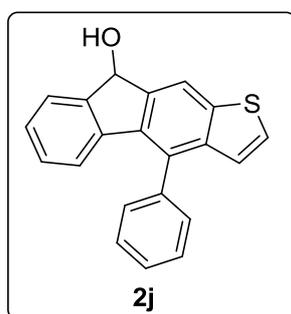


**2i** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (72.0 mg, 67%). m.p.: 185-187 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 9.03 (s, 1H), 8.82 (d, *J* = 8.5 Hz, 1H), 7.89-7.88 (m, 1H), 7.72-7.68 (m, 2H), 7.66-7.59 (m, 5H), 7.50 (d, *J* = 9.5 Hz, 1H),

7.46-7.41 (m, 2H), 7.29-7.26 (m, 1H), 7.11-7.08 (m, 1H), 6.39 (d, *J* = 7.5 Hz, 1H), 5.85 (d, *J* = 2 Hz, 1H), 2.20 (d, *J* = 2 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 146.7, 144.2, 140.0, 138.8, 136.0, 134.8, 132.1, 131.8, 130.5, 130.1, 130.1, 129.9, 129.2, 129.2, 129.0, 128.5, 128.0, 127.9, 127.1, 126.8, 126.8, 125.1, 124.7, 123.4, 123.1, 118.9, 75.0.

**HRMS** (ESI)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{27}H_{18}NaO$  381.1250; Found 381.1250.

#### 4-phenyl-9H-fluoreno[2,3-b]thiophen-9-ol (**2j**)

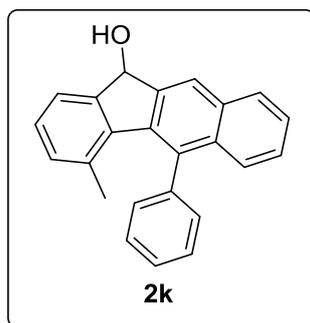


**2j** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (65.0 mg, 69%). m.p.: 145-147 °C.

**<sup>1</sup>H NMR** (500 MHz,  $CDCl_3$ ):  $\delta$  8.11 (d,  $J = 0.5$  Hz, 1H), 7.62 (d,  $J = 7.5$  Hz, 1H), 7.59-7.53 (m, 3H), 7.47-7.42 (m, 2H), 7.39 (d,  $J = 5.5$  Hz, 1H), 7.25-7.22 (m, 1H), 7.09-7.06 (m, 1H), 7.01 (dd,  $J_1 = 5.5$  Hz,  $J_2 = 0.5$  Hz, 1H), 6.60 (d,  $J = 8.0$  Hz,

1H), 5.68 (d,  $J = 3.0$  Hz, 1H), 2.22 (d,  $J = 9.5$  Hz, 1H). **<sup>13</sup>C NMR** (125 MHz,  $CDCl_3$ ):  $\delta$  146.2, 143.2, 140.7, 139.9, 139.2, 138.7, 133.9, 132.2, 129.6, 129.2, 128.9, 128.8, 128.0, 127.5, 126.5, 125.1, 123.6, 122.8, 118.5, 74.4. **HRMS** (APCI)  $m/z$ :  $[M-H_2O+H]^+$ : Calcd for  $C_{21}H_{13}S$  297.0732; Found 297.0750.

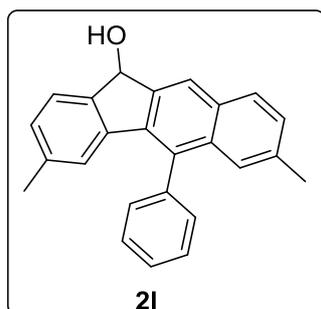
#### 4-methyl-5-phenyl-11H-benzo[b]fluoren-11-ol (**2k**)



**2k** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (67.6 mg, 70%). m.p.: 158-160 °C. **<sup>1</sup>H NMR** (500 MHz,  $CDCl_3$ ):  $\delta$  8.12 (s, 1H), 7.89 (d,  $J = 8$  Hz, 1H), 7.68 (d,  $J = 8.5$  Hz, 1H), 7.53 (d,  $J = 7.5$  Hz, 1H), 7.51-7.46 (m, 5H), 7.43-7.42 (m, 1H), 7.39-7.36 (m, 1H), 7.24 (t,  $J = 7.5$  Hz, 1H), 7.01 (d,  $J = 2.5$  Hz, 1H), 5.72

(s, 1H), 2.22 (d,  $J = 1.5$  Hz, 1H), 1.43 (s, 3H). **<sup>13</sup>C NMR** (125 MHz,  $CDCl_3$ ):  $\delta$  147.5, 144.4, 141.0, 139.0, 137.1, 135.1, 134.5, 134.2, 133.1, 132.9, 132.1, 132.0, 128.3, 128.3, 128.1, 128.0, 127.6, 127.1, 126.1, 125.9, 124.0, 122.6, 74.2, 22.0. **HRMS** (APCI)  $m/z$ :  $[M-H_2O+H]^+$  Calcd for  $C_{24}H_{17}$  305.1325; Found 305.1302.

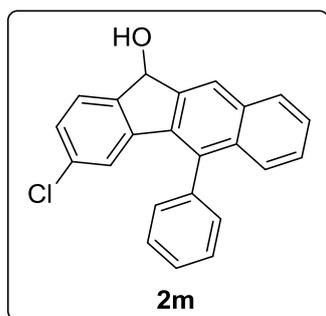
#### 3,7-dimethyl-5-phenyl-11H-benzo[b]fluoren-11-ol (**2l**)



**2l** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (72.6 mg, 72%). m.p.: 200-202 °C. **<sup>1</sup>H NMR** (500 MHz,  $CDCl_3$ ):  $\delta$  8.05 (s, 1H), 7.81 (d,  $J = 8.0$  Hz, 1H), 7.64-7.60 (m, 3H), 7.53 (d,  $J = 7.5$  Hz, 1H), 7.42-7.37 (m, 2H), 7.34-7.30 (m, 2H), 7.08 (d,  $J = 8.0$  Hz, 1H), 6.10 (s, 1H), 5.74 (s, 1H), 2.42 (s, 3H), 2.13 (s,

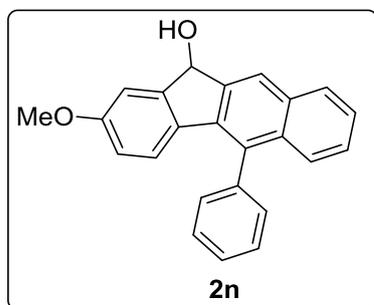
3H), 2.11 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.8, 143.2, 140.2, 138.7, 138.6, 136.0, 135.4, 134.0, 133.2, 131.4, 130.1, 129.9, 129.1, 129.0, 128.7, 128.2, 128.0, 127.7, 125.5, 124.8, 124.3, 123.7, 74.2, 21.9, 21.7. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{25}\text{H}_{20}\text{NaO}$  359.1406; Found 359.1406.

### 3-chloro-5-phenyl-11H-benzo[b]fluoren-11-ol (2m)



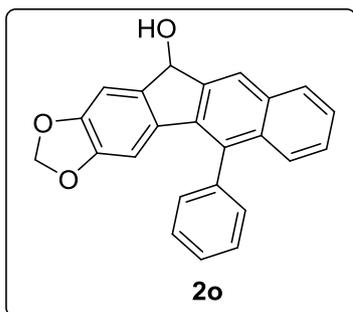
**2m** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (48.3 mg, 47%). m.p.: 108-110 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.10 (s, 1H), 7.91 (d,  $J$  = 8.0 Hz, 1H), 7.64-7.61 (m, 3H), 7.56-7.49 (m, 3H), 7.43-7.40 (m, 1H), 7.39-7.34 (m, 2H), 7.22 (dd,  $J_1$  = 8.0 Hz,  $J_2$  = 2.0 Hz, 1H), 6.28 (d,  $J$  = 2.0 Hz, 1H), 5.74 (s, 1H), 2.22 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.7, 143.5, 141.6, 137.8, 134.8, 134.6, 134.1, 133.8, 133.4, 129.8, 129.5, 129.3, 129.2, 128.3, 128.2, 127.9, 126.6, 126.5, 126.2, 126.1, 124.1, 123.7, 73.9. HRMS (APCI)  $m/z$ :  $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{14}\text{Cl}$  325.0779; Found 325.0797.

### 2-methoxy-5-phenyl-11H-benzo[b]fluoren-11-ol (2n)



**2n** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (84.2 mg, 83%). m.p.: 155-157 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.06 (s, 1H), 7.99 (d,  $J$  = 8.0 Hz, 1H), 7.62-7.55 (m, 3H), 7.50 (d,  $J$  = 8.5 Hz, 1H), 7.47-7.44 (m, 1H), 7.41-7.37 (m, 3H), 7.20 (d,  $J$  = 7.5 Hz, 1H), 6.62 (dd,  $J_1$  = 8.5 Hz,  $J_2$  = 2.5 Hz, 1H), 6.29 (d,  $J$  = 9.0 Hz, 1H), 5.73 (d,  $J$  = 10.0 Hz, 1H), 3.81 (s, 3H), 2.18 (d,  $J$  = 10.0 Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.0, 148.5, 143.7, 138.6, 135.2, 134.0, 132.6, 132.5, 132.4, 130.8, 129.9, 129.2, 129.1, 128.3, 127.8, 126.2, 126.2, 125.4, 124.4, 123.8, 115.2, 110.3, 74.4, 55.5. HRMS (APCI)  $m/z$ :  $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$  Calcd for  $\text{C}_{24}\text{H}_{17}\text{O}$  321.1274; Found 321.1271.

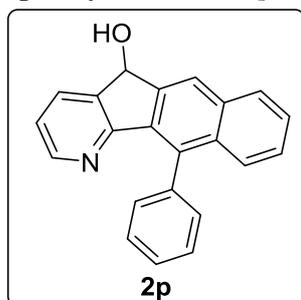
### 5-phenyl-11H-benzo[6,7]fluoreno[2,3-d][1,3]dioxol-11-ol (2o)



**2o** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (71.8 mg, 68%). m.p.: 125-127 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): 8.00 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.60-7.57 (m, 3H), 7.49-7.43 (m, 2H), 7.39-7.33 (m, 3H), 7.06 (s, 1H), 5.84 (dd, *J*<sub>1</sub> = 13 Hz, *J*<sub>2</sub> = 1.5 Hz, 2H), 5.76 (s, 1H), 5.59 (s, 1H), 2.24

(s, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 148.4, 147.9, 144.0, 141.1, 138.3, 135.1, 134.0, 134.0, 132.6, 132.4, 130.1, 129.9, 129.2, 129.2, 128.3, 128.0, 126.3, 126.3, 125.6, 123.6, 105.8, 104.0, 101.3, 74.2. **HRMS** (ESI) C<sub>24</sub>H<sub>15</sub>O<sub>3</sub> for [M-H]<sup>-</sup>: calcd 351.1027, found 351.1028.

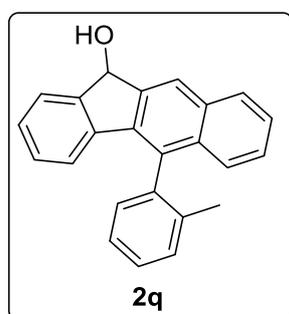
#### 11-phenyl-5H-benzo[5,6]indeno[1,2-b]pyridin-5-ol (**2p**)



**2p** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (52.8 mg, 57%). m.p.: 168-170 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.29 (d, *J* = 5.0 Hz, 1H), 8.12 (s, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.58-7.50 (m, 4H), 7.44-

7.40 (m, 3H), 7.02 (dd, *J*<sub>1</sub> = 7.5 Hz, *J*<sub>2</sub> = 4.5 Hz, 1H), 5.75 (d, *J* = 8.0 Hz, 1H), 2.37 (s, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 159.5, 150.6, 143.3, 140.0, 137.6, 135.4, 134.2, 134.1, 133.7, 132.4, 130.6, 130.3, 128.3, 128.0, 127.9, 127.3, 127.2, 126.5, 126.4, 124.1, 121.7, 72.3. **HRMS** (APCI) *m/z*: [M-H<sub>2</sub>O+H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>14</sub>N 292.1121; Found 292.1130.

#### 5-(*o*-tolyl)-11H-benzo[*b*]fluoren-11-ol (**2q**)

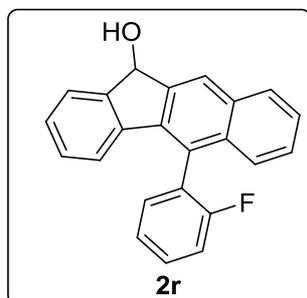


**2q** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (74.3 mg, 77%). m.p.: 80-82 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.11 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.53-7.48 (m, 3H), 7.47-7.39 (m, 3H), 7.29-7.20 (m, 2H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.36 (d, *J* = 8.0 Hz, 1H), 5.80 (d, *J* = 8.0 Hz, 1H), 2.35 (s, 1H), 1.97

(d, *J* = 19 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 146.4, 143.7, 139.9, 137.7, 137.0, 135.1, 133.4, 133.3, 133.2, 130.4, 130.1, 129.2, 128.5, 128.2, 128.0, 126.6, 126.4, 126.0,

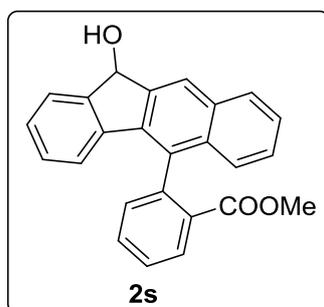
125.9, 125.1, 123.8, 123.0, 77.3, 19.6. **HRMS** (ESI)  $m/z$ :  $[M+Na]^+$  Calcd for  $C_{24}H_{18}NaO$  345.1250; Found 345.1250.

#### 5-(2-fluorophenyl)-11H-benzo[b]fluoren-11-ol (**2r**)



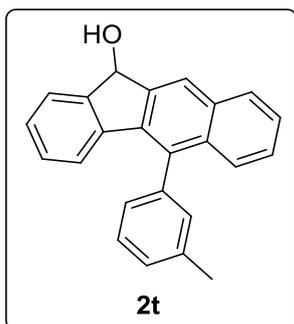
**2r** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (61.6 mg, 63%). m.p.: 196-198 °C.  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  8.14 (s, 1H), 7.92 (d,  $J$  = 8.0 Hz, 1H), 7.66 (d,  $J$  = 7.5 Hz, 1H), 7.63-7.58 (m, 1H), 7.52-7.48 (m, 2H), 7.45-7.34 (m, 4H), 7.31-7.28 (m, 1H), 7.13 (t,  $J$  = 8.0 Hz, 1H), 6.53 (t,  $J$  = 7.5 Hz, 1H), 5.79 (s, 1H), 2.28 (s, 1H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  160.5 (C-F,  $^1J_{C-F}$  = 245.0 Hz), 146.6, 143.6, 139.6, 136.1, 133.7, 133.3, 132.2 (C-F,  $^3J_{C-F}$  = 2.5 Hz), 130.3 (C-F,  $^3J_{C-F}$  = 8.8 Hz), 129.2, 128.5, 128.3, 126.8, 126.6, 126.0, 125.8, 125.6 (C-F,  $^2J_{C-F}$  = 17.5 Hz), 125.3, 124.9 (C-F,  $^4J_{C-F}$  = 3.8 Hz), 124.7, 122.8, 116.3 (C-F,  $^2J_{C-F}$  = 21.3 Hz), 74.4.  $^{19}F$  NMR (565 MHz,  $CDCl_3$ )  $\delta$  -114.06. **HRMS** (APCI)  $m/z$ :  $[M-H_2O+H]^+$  Calcd for  $C_{23}H_{14}F$  309.1074; Found 309.1076.

#### methyl 2-(11-hydroxy-11H-benzo[b]fluoren-5-yl)benzoate (**2s**)



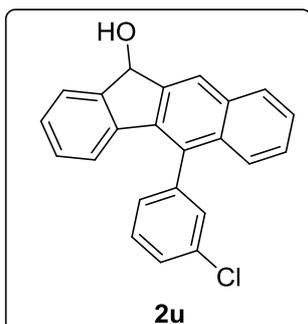
**2s** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (49.4 mg, 47%). m.p.: 190-192 °C.  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  8.62 (dd,  $J_1$  = 7.8 Hz,  $J_2$  = 1.4 Hz, 1H), 8.10 (s, 1H), 7.91 (d,  $J$  = 7.9 Hz, 1H), 7.75-7.72 (m, 1H), 7.70-7.67 (m, 1H), 7.64 (d,  $J$  = 7.5 Hz, 1H), 7.48-7.44 (m, 1H), 7.38-7.33 (m, 3H), 7.24 (t,  $J$  = 7.5 Hz, 1H), 7.05 (t,  $J$  = 7.5 Hz, 1H), 6.22 (d,  $J$  = 7.5 Hz, 1H), 5.81 (d,  $J$  = 4.0 Hz, 1H), 3.41 (s, 3H), 2.24 (d,  $J$  = 6.0 Hz, 1H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  166.6, 146.5, 143.4, 139.9, 139.8, 134.6, 133.7, 133.2, 133.0, 133.0, 131.7, 131.1, 131.0, 129.0, 128.4, 128.3, 127.9, 126.2, 125.9, 125.7, 125.24, 123.8, 122.9, 74.5, 51.8. **HRMS** (APCI)  $m/z$ :  $[M-H_2O+H]^+$  Calcd for  $C_{25}H_{17}O_2$  349.1223; Found 349.1203.

#### 5-(*m*-tolyl)-11H-benzo[b]fluoren-11-ol (**2t**)



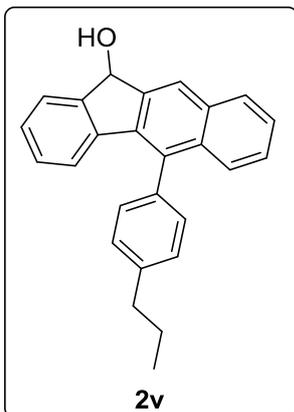
**2t** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (64.7 mg, 67%). m.p.: 176-178 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.09 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.51-7.47 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.28-7.22 (m, 2H), 7.18 (d, *J* = 8.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.47 (d, *J* = 7.5 Hz, 1H), 5.77 (d, *J* = 6.5 Hz, 1H), 2.49 (s, 1.5 H), 2.47 (s, 1.5H), 2.38 (s, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 146.5, 143.6, 139.9, 138.7, 138.3, 135.1, 134.0, 133.2, 130.6, 130.4, 128.9, 128.6, 128.3, 127.9, 127.0, 126.7, 126.5, 126.2, 125.8, 125.2, 123.8, 123.6, 74.4, 21.5. **HRMS** (APCI) *m/z*: [M-H<sub>2</sub>O+H]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>17</sub> 305.1325; Found 305.1314.

#### 5-(3-chlorophenyl)-11H-benzo[b]fluoren-11-ol (**2u**)



**2u** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (81.2 mg, 79%). m.p.: 135-137 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.11-8.10 (m, 1H), 7.91-7.89 (m, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.60-7.58 (m, 1H), 7.57-7.53 (m, 1H), 7.51-7.48 (m, 2H), 7.45-7.39 (m, 2H), 7.33-7.26 (m, 2H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 5.76 (d, *J* = 6.0 Hz, 1H), 2.37 (d, *J* = 8.5 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 146.6, 143.6, 140.4, 139.4, 135.2, 135.1, 133.6, 133.1, 132.1, 130.4, 130.2, 123.0, 129.1, 128.4, 128.2, 128.2, 126.5, 126.1, 126.0, 125.3, 124.4, 123.4, 74.3. **HRMS** (APCI) *m/z*: [M-H<sub>2</sub>O+H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>14</sub>Cl 325.0779; Found 325.0768.

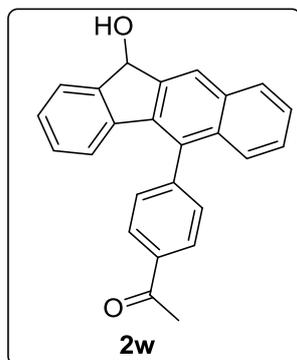
#### 5-(4-propylphenyl)-11H-benzo[b]fluoren-11-ol (**2v**)



**2v** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (73.5 mg, 70%). m.p.: 145-147 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.11 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.50-7.47 (m, 1H), 7.42-7.38 (m, 3H), 7.32-7.25 (m, 3H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.43 (d, *J* = 8.0 Hz, 1H), 5.80 (d, *J* = 8.5 Hz, 1H), 2.80 (t, *J* = 7.5 Hz, 2H), 2.14 (d, *J* = 9.5 Hz, 1H), 1.87-

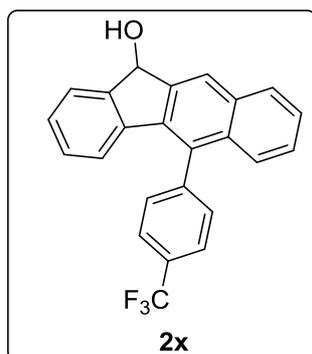
1.80 (m, 2H), 1.08 (t,  $J = 7.5$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.5, 143.6, 142.3, 140.0, 135.6, 135.3, 134.2, 133.2, 129.8, 129.6, 129.2, 129.2, 128.9, 128.3, 127.9, 126.6, 126.2, 125.8, 125.1, 123.8, 123.6, 74.5, 37.9, 24.6, 13.8. HRMS (APCI)  $m/z$ :  $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$  Calcd for  $\text{C}_{26}\text{H}_{21}$  333.1638; Found 333.1656.

#### 1-(4-(11-hydroxy-11H-benzo[b]fluoren-5-yl)phenyl)ethan-1-one (2w)



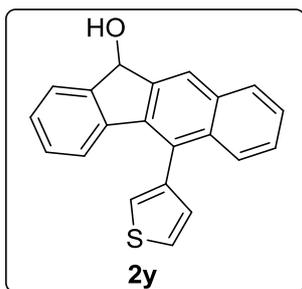
**2w** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (83.0 mg, 79%). m.p.: 158-160 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.15 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.5$  Hz, 1H), 8.11 (dd,  $J_1 = 7.5$  Hz,  $J_2 = 1.5$  Hz, 1H), 8.09 (s, 1H), 7.88 (d,  $J = 8.5$  Hz, 1H), 7.63 (d,  $J = 7.5$  Hz, 1H), 7.50-7.46 (m, 2H), 7.41 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.5$  Hz, 1H), 7.39-7.36 (m, 2H), 7.25 (t,  $J = 7.5$  Hz, 1H), 7.06 (t,  $J = 7.5$  Hz, 1H), 6.37 (d,  $J = 7.5$  Hz, 1H), 5.73 (s, 1H), 2.84 (d,  $J = 10$  Hz, 1H), 2.72 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.1, 146.7, 143.9, 143.7, 139.4, 136.6, 135.0, 133.4, 133.1, 132.4, 130.6, 130.3, 129.2, 129.1, 129.0, 128.5, 128.3, 126.5, 126.0, 126.0, 125.4, 124.5, 123.3, 74.2, 26.8. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{25}\text{H}_{18}\text{NaO}_2$  373.1199; Found 373.1202.

#### 5-(4-(trifluoromethyl)phenyl)-11H-benzo[b]fluoren-11-ol (2x)



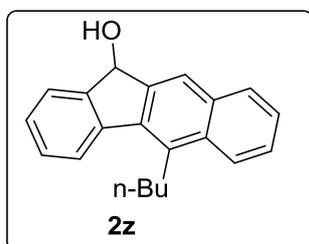
**2x** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (63.2 mg, 56%). m.p.: 145-147 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.13 (s, 1H), 7.92 (d,  $J = 8.0$  Hz, 1H), 7.89-7.88 (m, 2H), 7.67 (d,  $J = 7.5$  Hz, 1H), 7.56-7.49 (m, 3H), 7.44-7.39 (m, 2H), 7.31-7.28 (m, 1H), 7.13-7.10 (m, 1H), 6.37 (d,  $J = 7.5$  Hz, 1H), 5.78 (s, 1H), 2.24 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.6, 143.6, 142.5, 139.3, 135.2, 133.5, 133.1, 132.1, 130.7, 130.4, 130.3 (C-F,  $^2J_{\text{C-F}} = 32.5$  Hz), 129.1, 128.5, 128.4, 126.6, 126.1 (C-F,  $^3J_{\text{C-F}} = 2.5$  Hz), 126.1, 125.9, 125.4, 124.6, 124.3 (C-F,  $^1J_{\text{C-F}} = 271.3$  Hz), 123.2, 74.2.  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.26. HRMS (APCI)  $m/z$ :  $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$  Calcd for  $\text{C}_{24}\text{H}_{14}\text{F}_3$  359.1042; Found 359.1039.

#### 5-(thiophen-3-yl)-11H-benzo[b]fluoren-11-ol (2y)



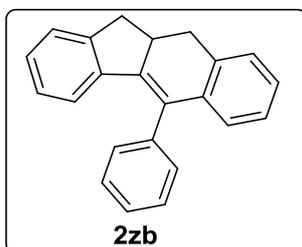
**2y** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (84.8 mg, 90%). m.p.: 135-137 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): 8.08 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.65-7.61 (m, 3H), 7.51-7.48 (m, 1H), 7.45-7.42 (m, 1H), 7.33-7.27 (m, 2H), 7.18-7.11 (m, 2H), 6.55 (d, *J* = 7.5 Hz, 1H), 5.75 (s, 1H), 2.30 (s, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 146.5, 143.6, 139.8, 138.2, 136.2, 134.4, 133.2, 129.5, 129.2, 128.7, 128.4, 128.2, 126.6, 126.4, 126.3, 125.9, 125.2, 124.2, 123.8, 123.3, 74.4. **HRMS** (ESI) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>14</sub>NaOS 337.0658; Found 337.0659.

#### 5-butyl-11H-benzo[b]fluorene-11-ol (**2z**)



**2z** was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (21.6 mg, 25%). m.p.: 192-194 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.18 (d, *J* = 8.5 Hz, 1H), 7.98 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 7.0 Hz, 1H), 7.58-7.54 (m, 1H), 7.51-7.48 (m, 2H), 7.42-7.39 (m, 1H), 5.73 (d, *J* = 6.0 Hz, 1H), 3.51-3.41 (m, 2H), 2.02 (d, *J* = 7.5 Hz, 1H), 1.83-1.77 (m, 2H), 1.72-1.64 (m, 2H), 1.08 (t, *J* = 7.5 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 146.8, 144.0, 140.5, 134.9, 134.2, 133.6, 133.4, 129.5, 129.0, 127.8, 126.3, 125.7, 125.6, 124.0, 123.9, 122.8, 74.4, 31.8, 28.3, 23.4, 14.1. **HRMS** (APCI) *m/z*: [M-H<sub>2</sub>O+H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>19</sub> 271.1481; Found 271.1493.

#### 5-phenyl-10a,11-dihydro-10H-benzo[b]fluorene (**2zb**)



**2zb** was isolated via column chromatography (PE) as white solid (15.0 mg, 17%). m.p.: 50-52 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.58-7.46 (m, 4H), 7.33-7.29 (m, 3H), 7.19-7.12 (m, 3H), 6.92 (t, *J* = 7.5 Hz), 6.87 (dd, *J*<sub>1</sub> = 7.5 Hz, *J*<sub>2</sub> = 1.5 Hz, 2H), 6.39 (d, *J* = 8.0 Hz, 1H), 3.40 (dd, *J*<sub>1</sub> = 16 Hz, *J*<sub>2</sub> = 3 Hz), 3.23-3.12 (m, 2H), 2.88 (t, *J* = 14.0 Hz, 1H), 2.78 (dd, *J*<sub>1</sub> = 16.0 Hz, *J*<sub>2</sub> = 2.0 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 147.4, 142.0, 139.5, 139.1, 137.6, 135.2, 130.8, 129.3, 129.1, 127.9, 127.6, 127.4, 126.5, 126.4, 126.3, 125.9, 125.1, 124.3, 38.5, 37.8, 35.7. **HRMS** (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>18</sub><sup>+</sup> 294.1403; Found 294.1390.

### 3.2 1 mmol-scale synthesis of **2a**

Procedure: To a 25 mL Schlenk tube were added (E)-3-aryl-1-(2-(2-arylethynyl)phenyl)prop-2-en-1-one **1a** (1.0 mmol, 308 mg) and [Cu(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)(xantphos)]PF<sub>6</sub><sup>-</sup> (0.015 mmol, 113.0 mg), the tube was evacuated and refilled with N<sub>2</sub> for three times. Then Me<sub>2</sub>NH (3.0 mmol, 1.5 ml, 2 M in THF) and 20 ml MeCN were added under nitrogen atmosphere. The reaction mixture was stirred at room temperature under 15 W blue LED light for 20 h. Upon completion, the reaction mixture concentrated under vacuum and the residue was purified by column chromatography on silica gel (200-300 mesh), eluting with the indicated mixture of ethyl acetate (EA)/petroleum ether (PE) to give pure product **2a** (246 mg, yield: 80%).

## 4. Mechanistic Studies

### 4.1 Radical scavenging experiment

Procedure: The radical scavenging experiment was carried out on the model reaction of **1a** under the standard reaction conditions except with the addition of 2.0 equivalents radical scavengers. Thus, in the presence of 2.0 equivalents of TEMPO, BHT or 1,1-diphenylethylene, **2a** was obtained in 87%, 85% and 86% yield, respectively.

### 4.2 Subjection of **1a** to the standard reaction conditions except in the absence of Me<sub>2</sub>NH

Procedure: To a 25 mL Schlenk tube were added **1a** (92.4 mg, 0.3 mmol) and PS1 (17.0 mg, 0.015 mmol), the tube was evacuated and refilled with N<sub>2</sub> for three times. Then 6 mL MeCN was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from 15 W blue LED light. The reaction mixture was stirred at room temperature for 20 h. Upon separation and purification, 95% yield of **3a** and 0% yield of **2a** were obtained.

### 4.3. The model reaction of **1a** was quenched in midway to trap possible

## **intermediate**

Procedure: To a 25 mL Schlenk tube were added **1a** (92.4 mg, 0.3 mmol) and PS1 (17.0 mg, 0.015 mmol), the tube was evacuated and refilled with N<sub>2</sub> for three times. Then Me<sub>2</sub>NH (0.9 mmol, 0.45 ml, 2 M in THF) and 6 mL MeCN was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from 15 W blue LED light. The reaction mixture was stirred at room temperature for 4 h. After separation and purification, it was found that the reaction gave **2a** as the major product in 37% yield along with 10% yield of byproduct **3a**.

### **4.4. Intermediate determining experiments**

#### **Synthesis and isolation of intermediates **3a**<sup>10</sup>**

Compound **1a** (0.4 mmol), Cu(0) powder (1.28 mg, 5 mol %), Selectfluor (283.4 mg, 0.8 mmol, 2 equiv.), and CH<sub>3</sub>CN (4 mL) were added to a flask (10 mL). The reaction mixture was stirred at room temperature for 3 h. When the reaction was complete, the mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and filtered through Celite. The solvent was evaporated under vacuum, and the residue was purified by column chromatography on silica gel (100–200 mesh) using petroleum ether/EtOAc (10:1, v/v) as eluent to give pure **3a**.

#### **Subjection of intermediate **3a** to the standard reaction conditions and its conversion to **2a****

Procedure: To a 25 mL Schlenk tube were added 5-phenyl-11H-benzo[b]fluoren-11-one **3a** (0.3 mmol, 91.9 mg) and PS 1 (0.015 mmol, 17.0 mg), the tube was evacuated and refilled with N<sub>2</sub> for three times. Then Me<sub>2</sub>NH (0.9 mmol, 0.45 ml, 2.0 M in THF) and 6 mL MeCN were added under nitrogen atmosphere. The reaction mixture was stirred at room temperature under 15 W blue LED light. Upon completion, the reaction mixture concentrated under vacuum and the residue was purified by column chromatography on silica gel (200-300 mesh), eluting with the indicated mixture of ethyl acetate (EA)/ petroleum ether (PE) to give pure product **2a** in 93% (86.0 mg) yield.

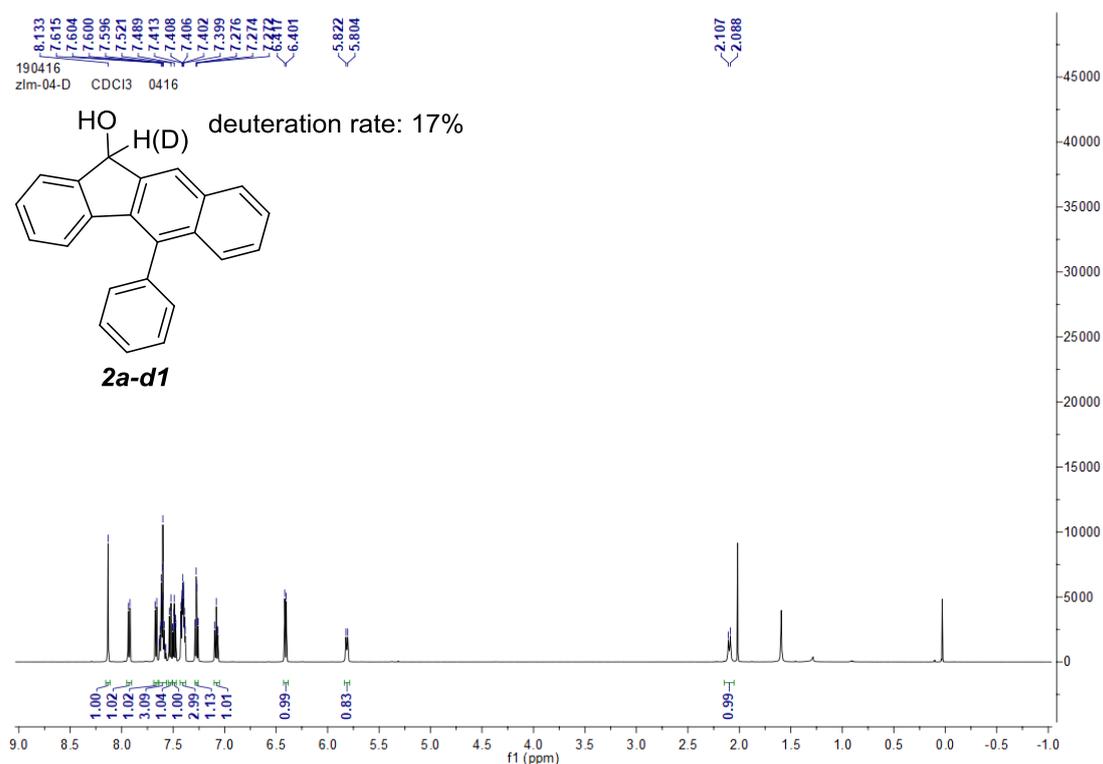
### **4.5. Deuterium-labeling experiments**

#### **Deuteration experiment of D<sub>2</sub>O**

Procedure: To a 25 mL Schlenk tube were added (E)-3-phenyl-1-(2-

(phenylethynyl)phenyl)prop-2-en-1-one **1a** (0.3 mmol, 92.4 mg) and [Cu(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)(xantphos)]PF<sub>6</sub><sup>-</sup> (0.015 mmol, 17.0 mg), the tube was evacuated and refilled with N<sub>2</sub> for three times. Then Me<sub>2</sub>NH (0.9 mmol, 0.45 mL, 2.0 M in THF), D<sub>2</sub>O (0.9 mmol, 18 mg) and 6 mL MeCN were added under nitrogen atmosphere. The reaction mixture was stirred at room temperature under 15 W blue LED light. Upon completion, the reaction mixture concentrated under vacuum and the residue was purified by column chromatography on silica gel (200-300 mesh), eluting with the indicated mixture of ethyl acetate (EA)/ petroleum ether (PE) to give pure product **2a-d1** (80.4 mg, 87%) The <sup>1</sup>H NMR spectra of **2a-d1** and the calculated D-incorporated rates are listed as below:

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of **2a-d1** obtained from the above-mentioned experiment: Product was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.13 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.63-7.57 (m, 3H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.51-7.47 (m, 1H), 7.43-7.38 (m, 3H), 7.27 (dt, *J*<sub>1</sub> = 7.5 Hz, *J*<sub>2</sub> = 1 Hz, 1H), 7.10-7.07 (m, 1H), 6.41 (d, *J* = 8.0 Hz, 1H), 5.81 (d, *J* = 9.0 Hz, 0.83H), 2.10 (d, *J* = 9.0 Hz, 1H).



**Synthesis and isolation of (E)-3-(phenyl-d<sub>5</sub>)-1-(2-(phenylethynyl)phenyl)prop-2-**

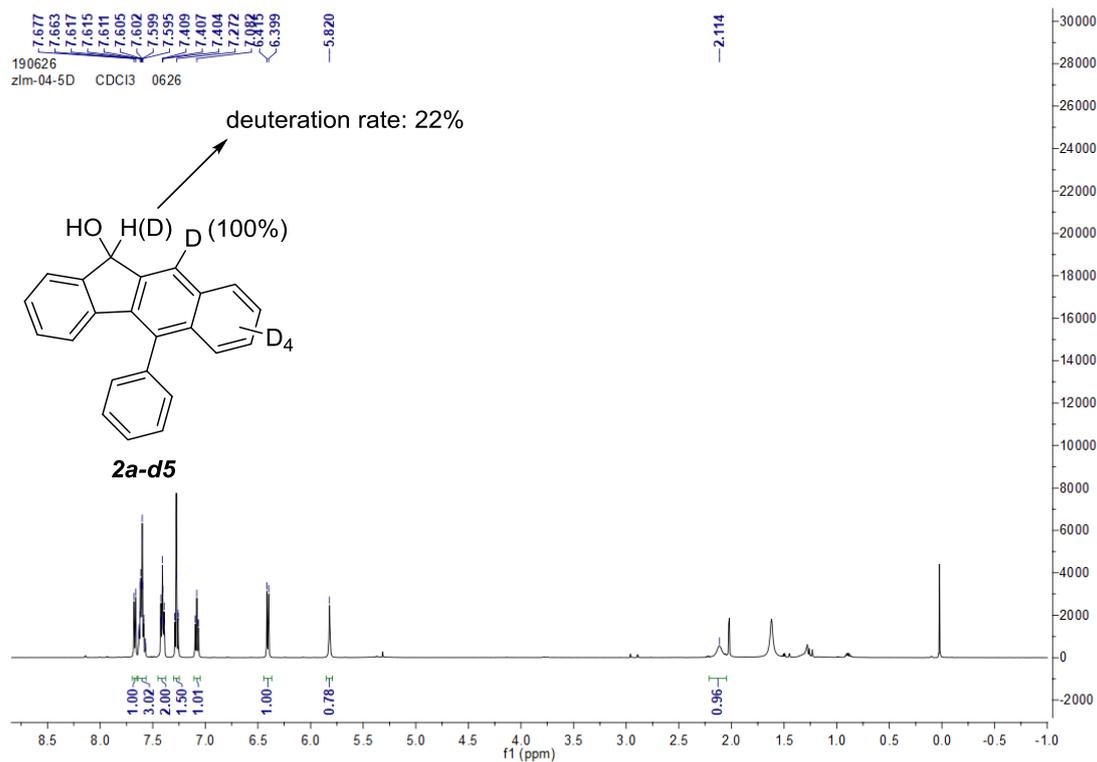
### **en-1-one-3-d (1a-d<sub>6</sub>)**

A solution of NaOH (0.008 g, 3.0 mmol) in water (2 mL) and ethanol (2 mL) was cooled to 0 °C and 1-(2-(phenylethynyl)phenyl)ethan-1-one (0.44 g, 2.0 mmol) and benzaldehyde-*d*<sub>6</sub> (0.23 g, 2.0 mmol) were slowly added successively. The reaction mixture was allowed to warm to room temperature overnight. After 12 h the reaction mixture was diluted with diethyl ether (25 mL), the organic phase was separated and washed with saturated aqueous NH<sub>4</sub>Cl and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the crude mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20: 1) to afford the desired product **1a-d<sub>6</sub>** as a yellow solid (0.56 g, 89%).

### **Subjection of 1a-d<sub>6</sub> to the standard reaction conditions and its conversion to 2a-d<sub>6</sub>**

Procedure: To a 25 mL Schlenk tube were added (E)-3-(phenyl-*d*<sub>5</sub>)-1-(2-(phenylethynyl)phenyl)prop-2-en-1-one-3-d **1a-d<sub>6</sub>** (0.3 mmol, 94.2 mg) and [Cu(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)(xantphos)]PF<sub>6</sub><sup>-</sup> (0.015 mmol, 17.0 mg), the tube was evacuated and refilled with N<sub>2</sub> for three times. Then Me<sub>2</sub>NH (0.9 mmol, 0.45 mL, 2.0 M in THF) and 6 mL MeCN were added under nitrogen atmosphere. The reaction mixture was stirred at room temperature under 15 W blue LED light. Upon completion, the reaction mixture concentrated under vacuum and the residue was purified by column chromatography on silica gel (200-300 mesh), eluting with the indicated mixture of ethyl acetate (EA)/ petroleum ether (PE) to give pure product **2a-d<sub>6</sub>** (79.8 mg, 85%). <sup>1</sup>H NMR spectra of **2a-d<sub>6</sub>** and the calculated D-incorporated rates are listed as below:

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) of **2a-d<sub>6</sub>** obtained from the above-mentioned experiment: Product was isolated via column chromatography (eluent EA/PE = 1:5 (V/V)) as white solid (79.8 mg, 85%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.67 (d, *J* = 7.0 Hz, 1H), 7.63-7.57 (m, 3H), 7.42-7.39 (m, 2H), 7.29-7.26 (m, 1H), 7.10-7.06 (m, 1H), 6.41 (d, *J* = 8.0 Hz, 1H), 5.82 (s, 0.78 H), 2.11 (s, 1H).



#### 4.6 Cyclic Voltammetry experiments of **3a**

A solution of **3a** in MeCN (0.001 M) was tested with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte. The solutions were degassed with a flow of argon for 20 minutes prior to the measurement. As shown in Figure 1, the reduction potential of **3a**  $E_{p/2} = -1.24$  (V vs Ag/AgCl),  $-1.26$  (V vs SCE).

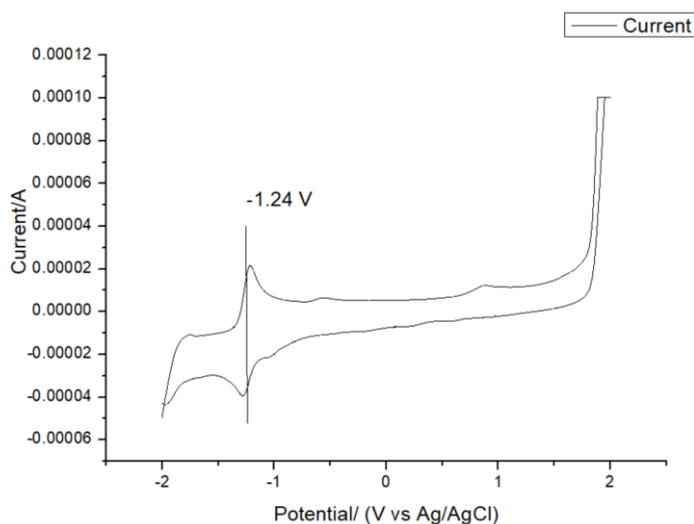
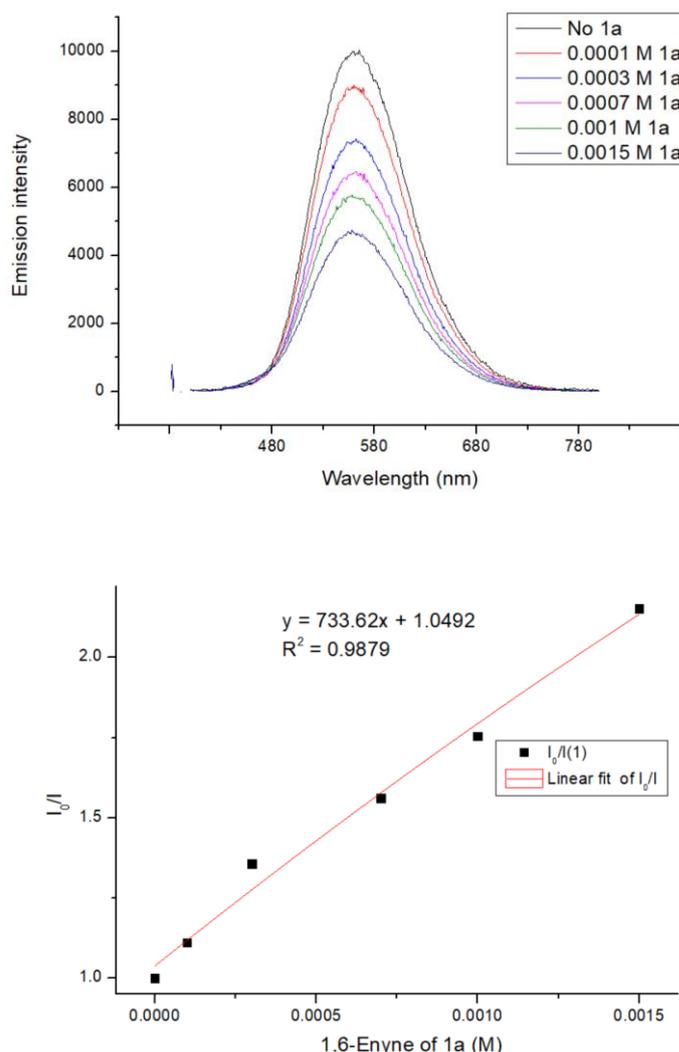


Figure S2. The Cyclic Voltammetry of **3a**

#### 4.7 Stern-Volmer experiments

Stern-Volmer quenching experiment were carried out with freshly prepared

solution of  $1 \times 10^{-4}$  M [Cu(2,9-methyl-4,7-diphenyl-1,10-phenanthroline) (xantphos)]PF<sub>6</sub><sup>-</sup> (PS 1) and quenched by 1,6-ynes **1a** in MeCN at room temperature under Ar atmosphere. The solutions were irradiated at 387 nm and luminescence was measured at 560 nm.



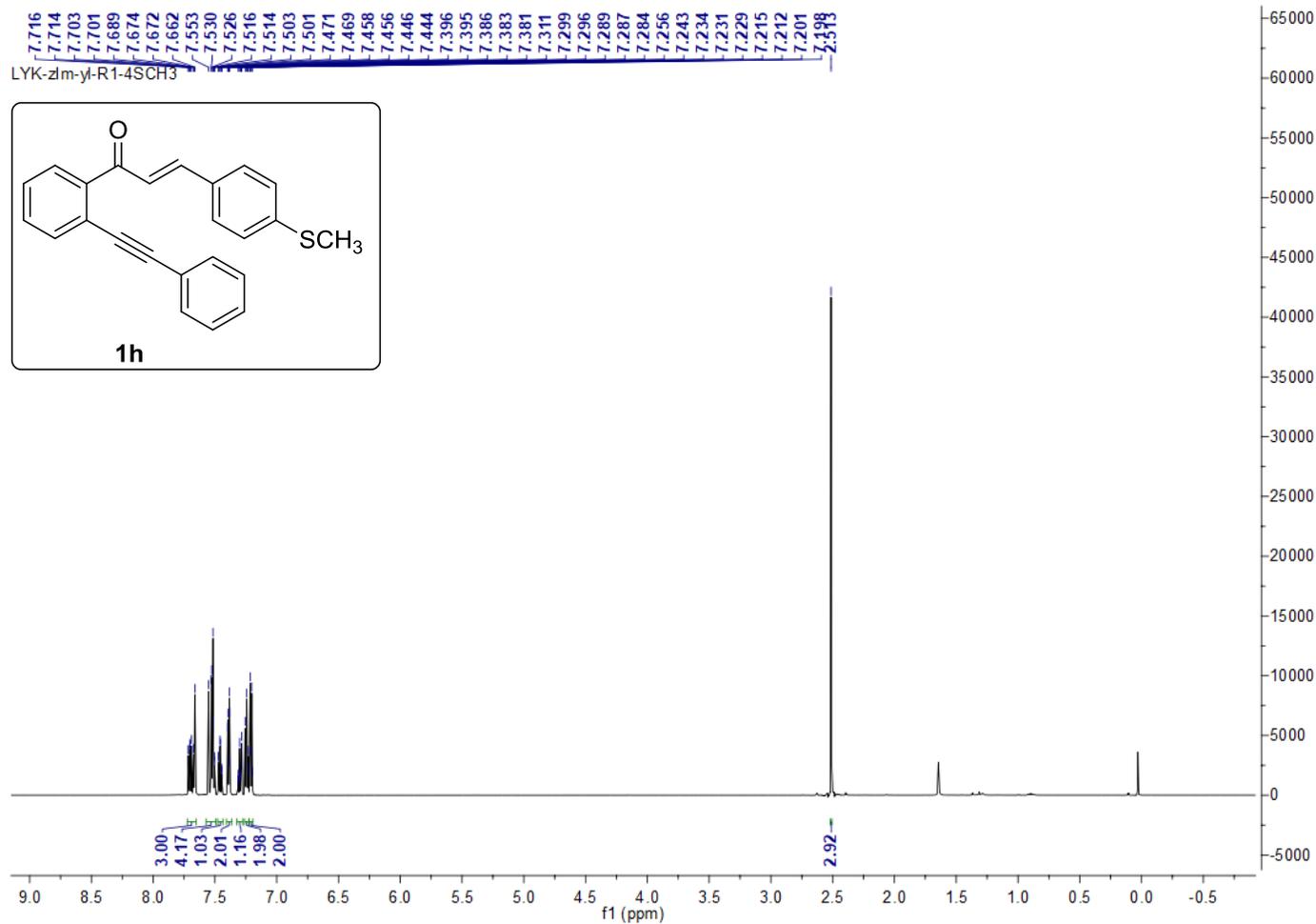
**Figure S3. Stern-Volmer plot of PS 1 quenching with varying concentration of 1a**

## 5. References

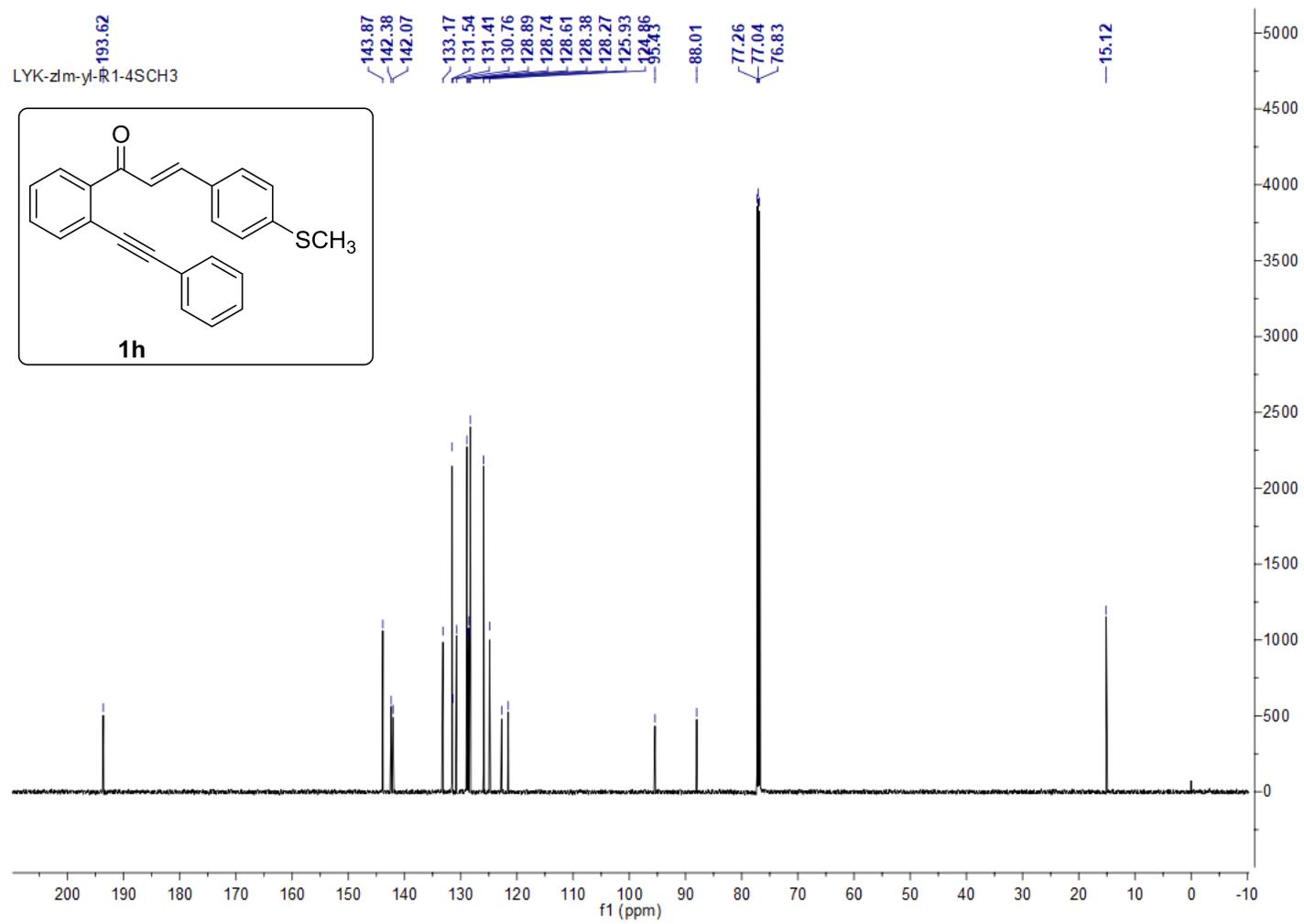
1. Wang, Z.-Q.; Zhang, W.-W.; Gong, L.-B.; Tang, R.-Y.; Yang, X.-H.; Liu, Y.; Li, J.-H. Copper-Catalyzed Intramolecular Oxidative 6-exo-trig Cyclization of 1,6-Enynes with H<sub>2</sub>O and O<sub>2</sub>. *Angew. Chem., Int. Ed.* **2011**, *50*, 8968-8973.

2. Zheng, L.; Zhou, B.; Jin, H.; Li, Ting.; Liu Y. Radical-Triggered Tandem Cyclization of 1,6-Enynes with H<sub>2</sub>O: A Way to Access Strained 1H-Cyclopropa[b]naphthalene-2,7-diones. *Org. Lett.* **2018**, *20*, 7053–7056.
3. Wu, Y.-N.; Fu, R.; Wang, N.-N.; Hao, W.-J.; Li, G.; Tu, S.-J.; and Jiang, B. Catalytic Sulfur-Enabled Dehydrobicyclization of 1,6-Enynes toward Arylated Indeno[1,2-c]thiophenes. *J. Org. Chem.* **2016**, *81*, 4762–4770.
4. Mandala, M.; Balamurugan, R. Triflic acid-Mediated Expedient Synthesis of Benzo[a]fluorenes and Fluorescent Benzo[a]fluorenones. *Adv. Synth. Catal.* **2018**, *360*, 1453-1465.
5. Akbar, S.; Tamilarasan, V. J.; Srinivasan, K. Iodine-mediated synthesis of benzo[a]fluorenones from yne-enones. *RSC Adv.* **2019**, *9*, 23652–23657.
6. Pi, S.-F.; Tang, B.-X.; Li, J.-H.; Liu, Y.-L.; Liang, Y. Palladium-Catalyzed Decarboxylative Coupling of Allylic Alkynoates with Arynes. *Org. Lett.* **2009**, *11*, 2309–2312.
7. Mejia, E.; Luo, S.-P.; Karnahl, M.; Friedrich, A.; Tschierlei, S.; Surkus, A.-E.; Junge, H.; Gladiali, S.; Lochbrunner, S.; Beller, M. A Noble-Metal-Free System for Photocatalytic Hydrogen Production from Water. *Chem. Eur. J.* **2013**, *19*, 15972-15978.
8. Zhao, Q.; Hu, Q.; Wen, L.; Wu, M.; Hu, Y. Fused Benzo[b]fluorenols: Palladium-Catalyzed Intramolecular Dehydroaromatization and Carbonyl Reduction. *Adv. Synth. Catal.* **2012**, *354*, 2113-2116.
9. Hao W.-J., Zhou P., Yang, Z., Jiang B., Zhang J.-P., Tu S.-J. Base-controlled 1,6-enyne-bicyclization: divergent synthesis of benzo[b]fluorenones and benzo[b]fluorenols. *Tetrahedron* **2016**, *72*, 2206-2212.
10. Zhang, J.; Zhang, H.-F.; Shi, D.-D.; Jin, H.-W.; Liu, Y.-K. Facile and Diverse Synthesis of Benzo[b]fluorenone Derivatives through a Copper/Selectfluor-Catalyzed Tandem Annulation of 1,6-Enynes. *Eur. J. Org. Chem.* **2016**, *33*, 5545-5558.

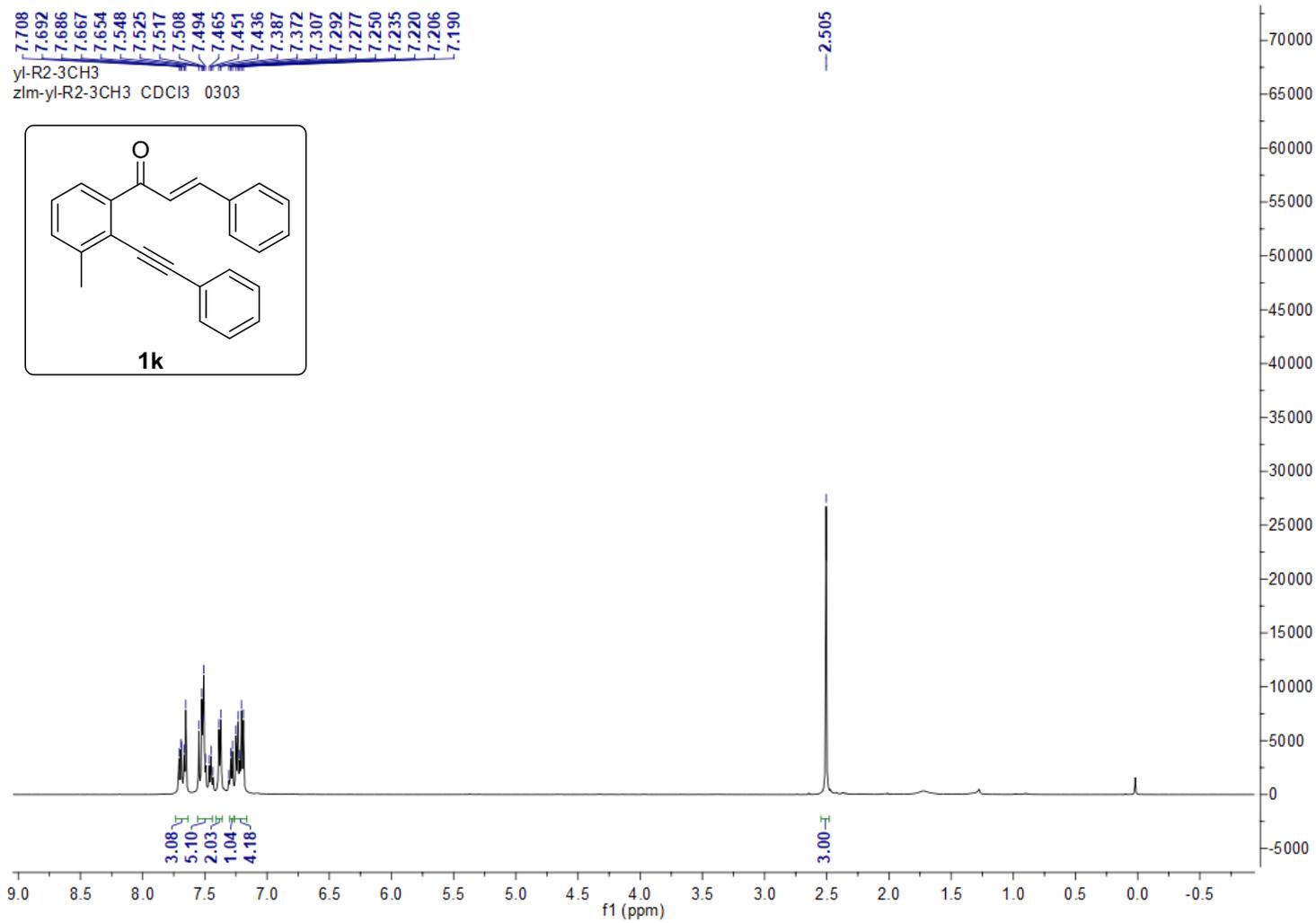
## 6. Copies of $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ NMR Spectra $^1\text{H}$ NMR (500 MHz, $\text{CDCl}_3$ ) spectrum of compound 1h



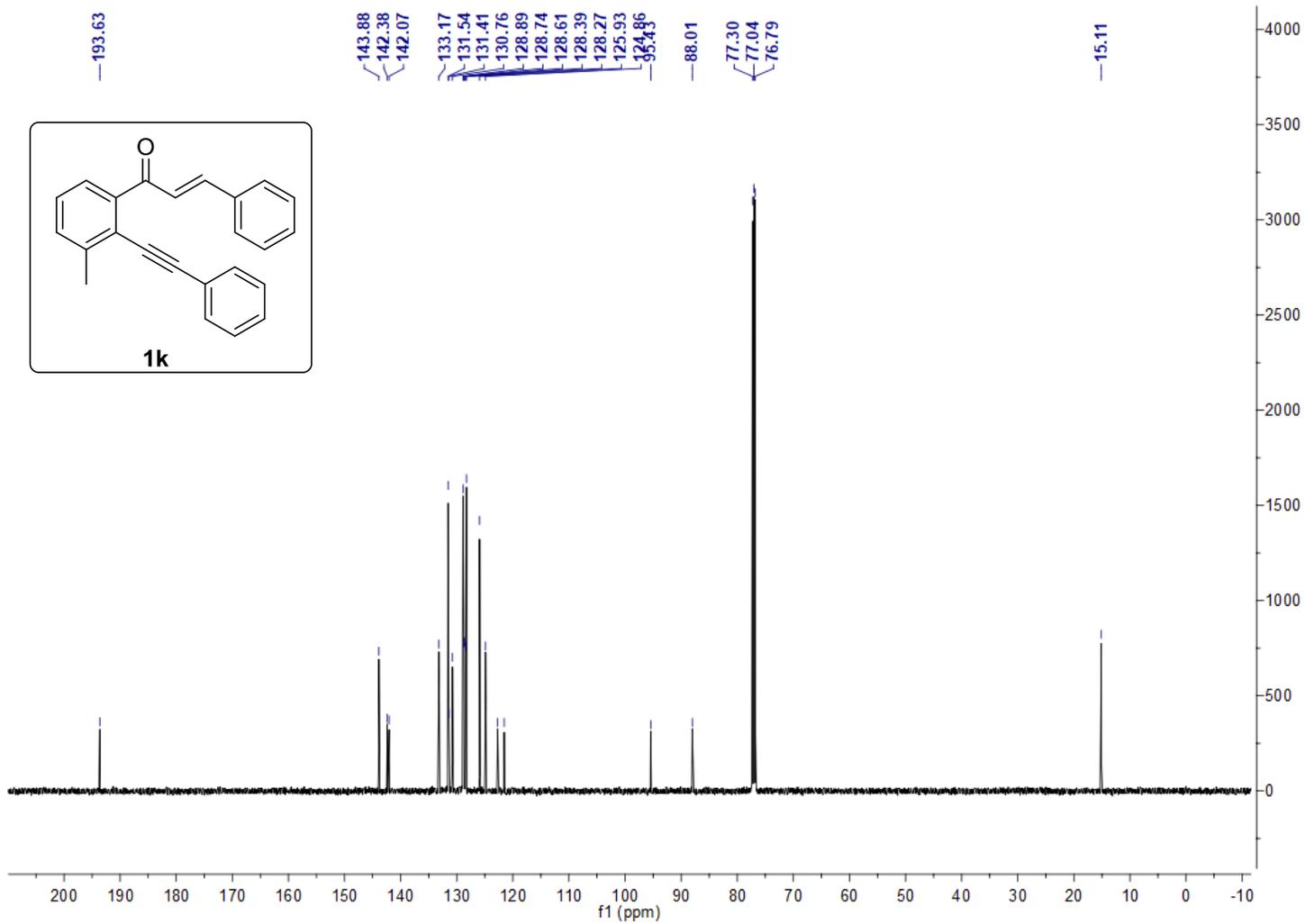
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 1h



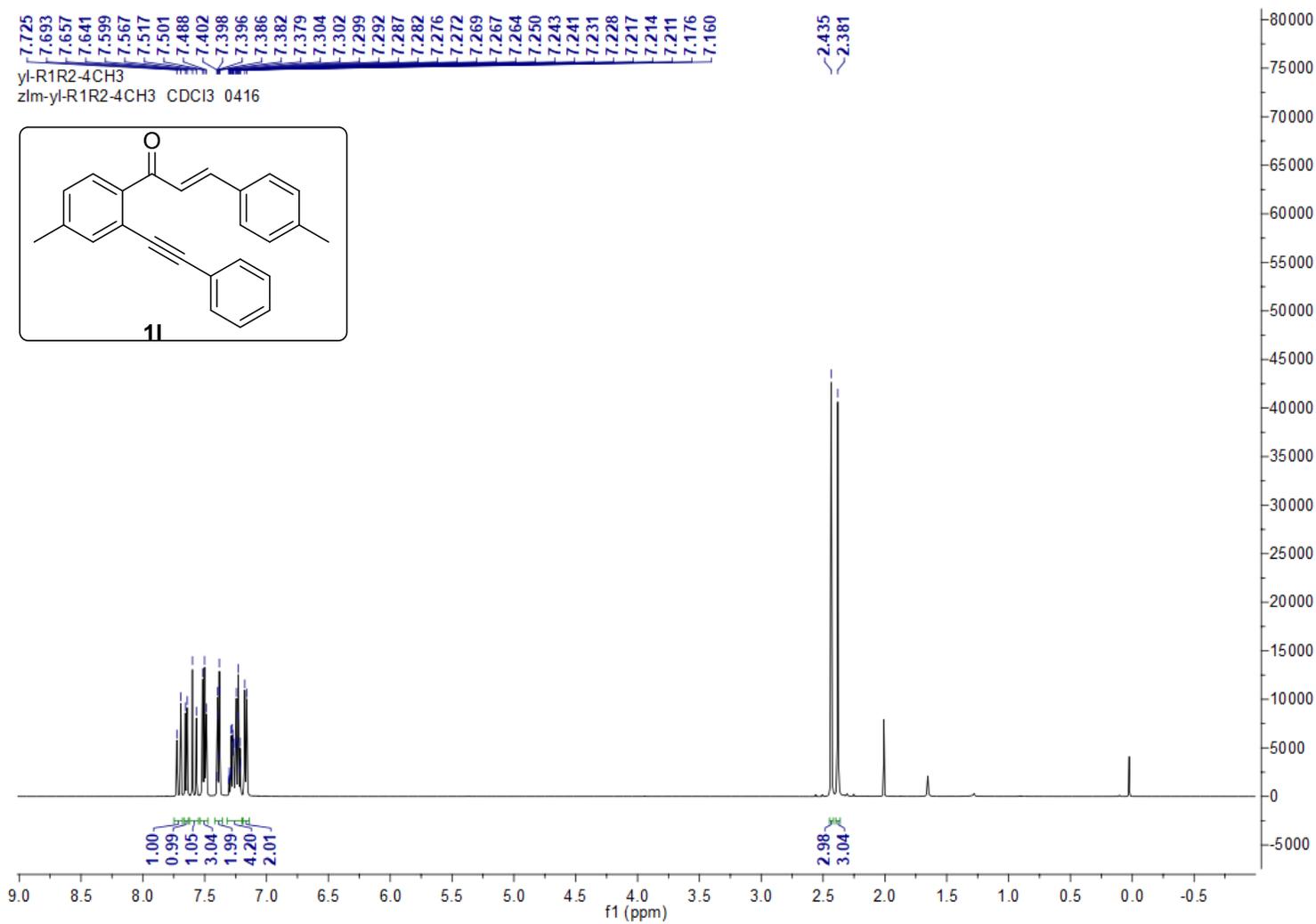
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 1k



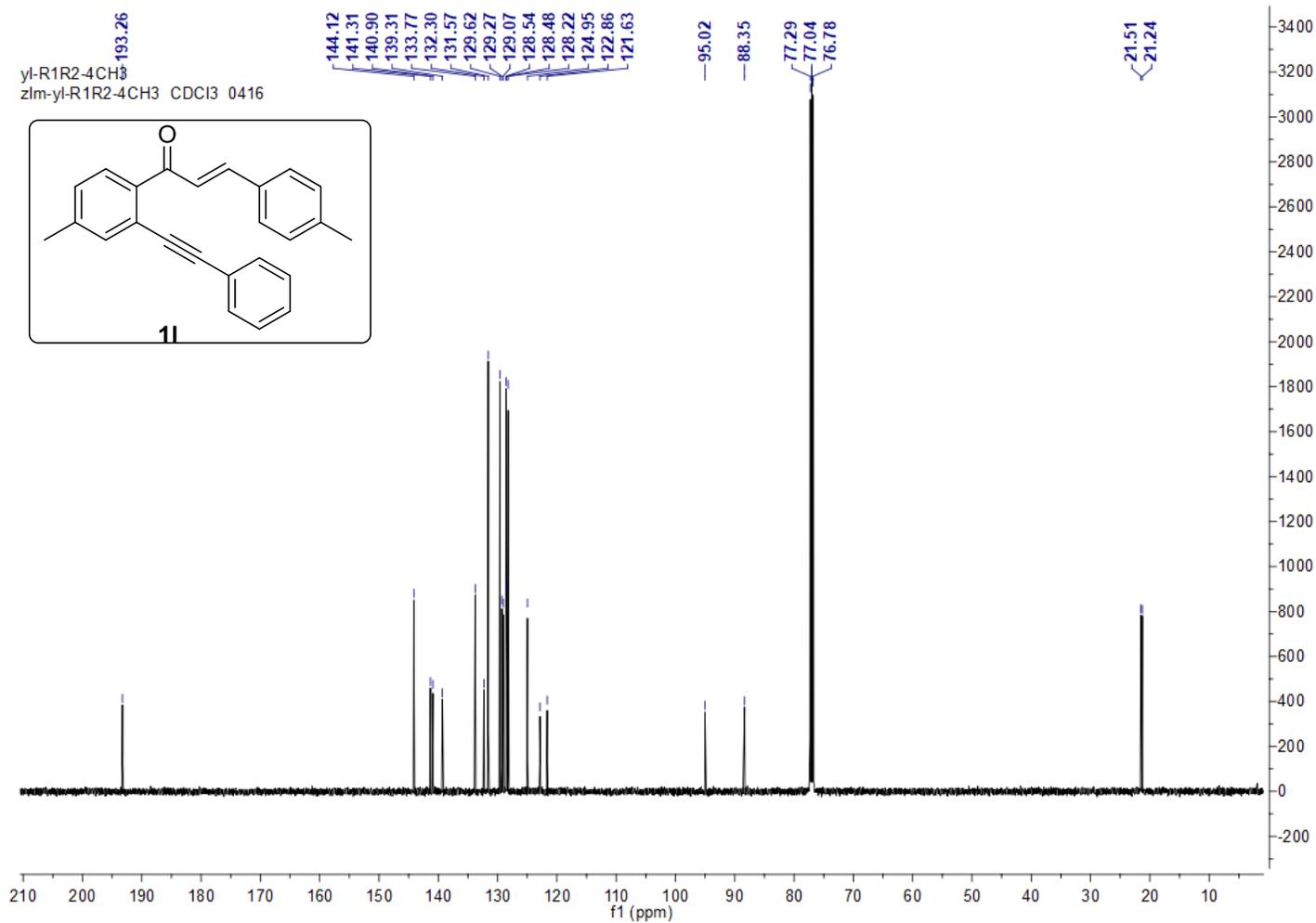
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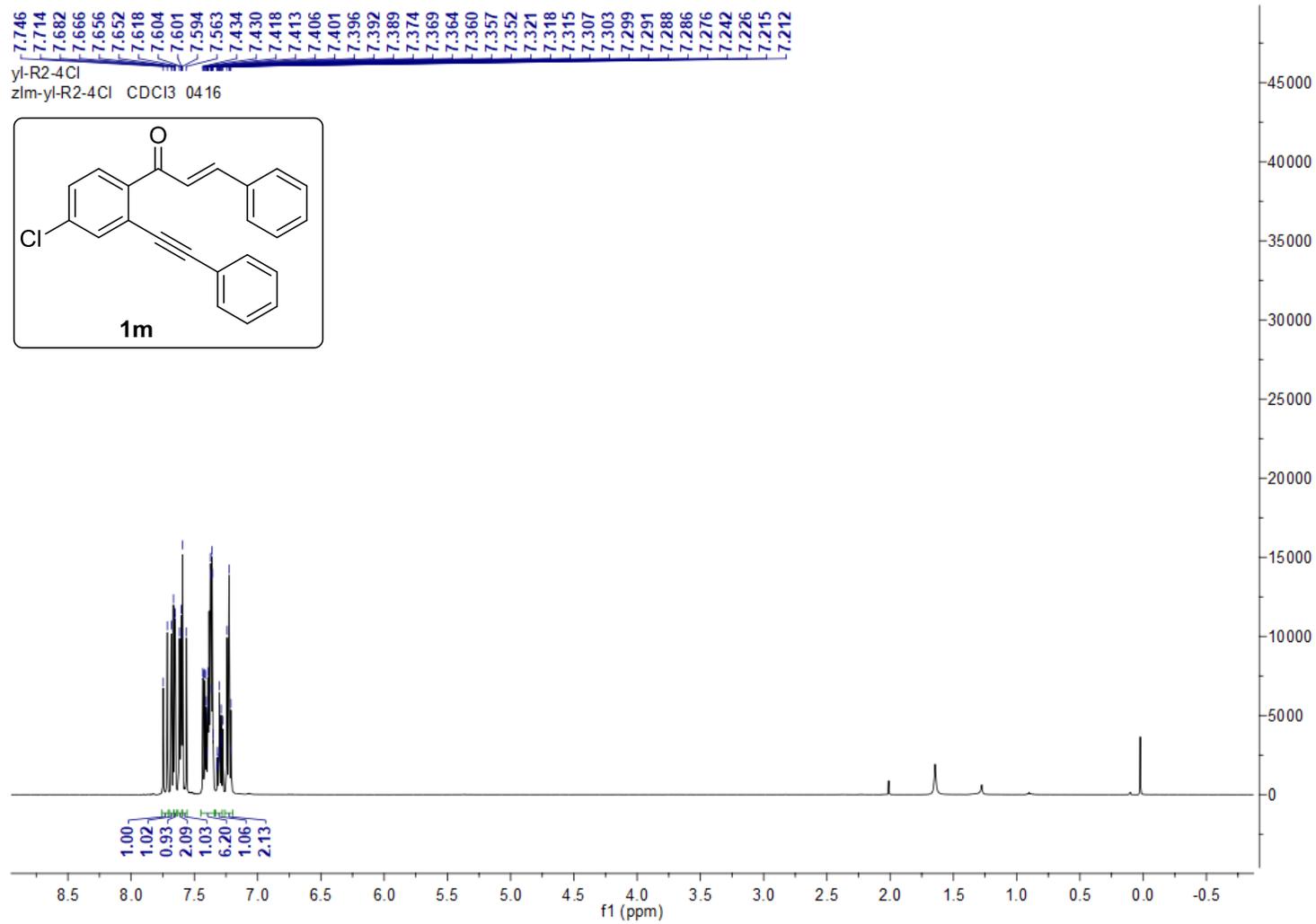
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 11



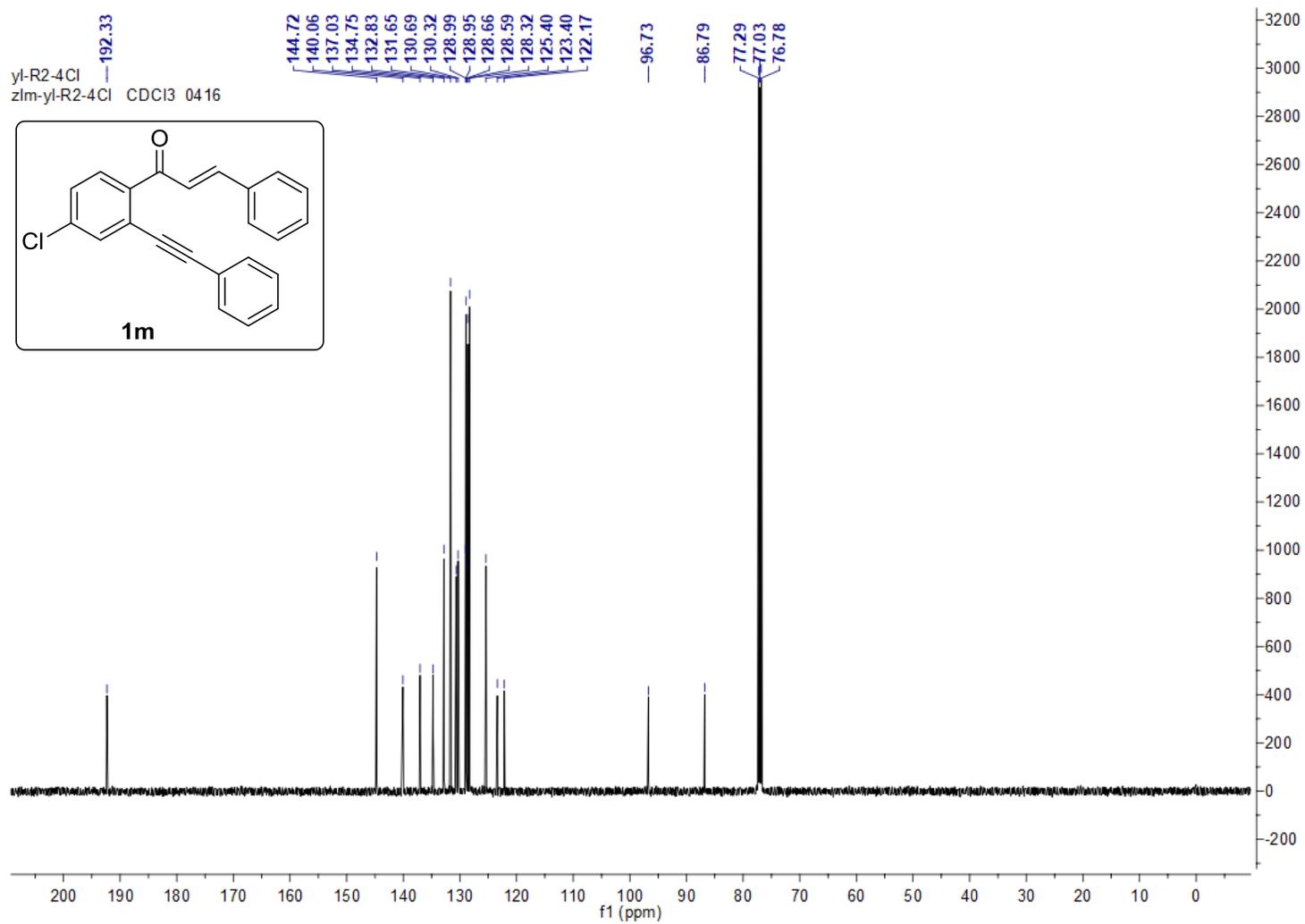
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 11



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 1m

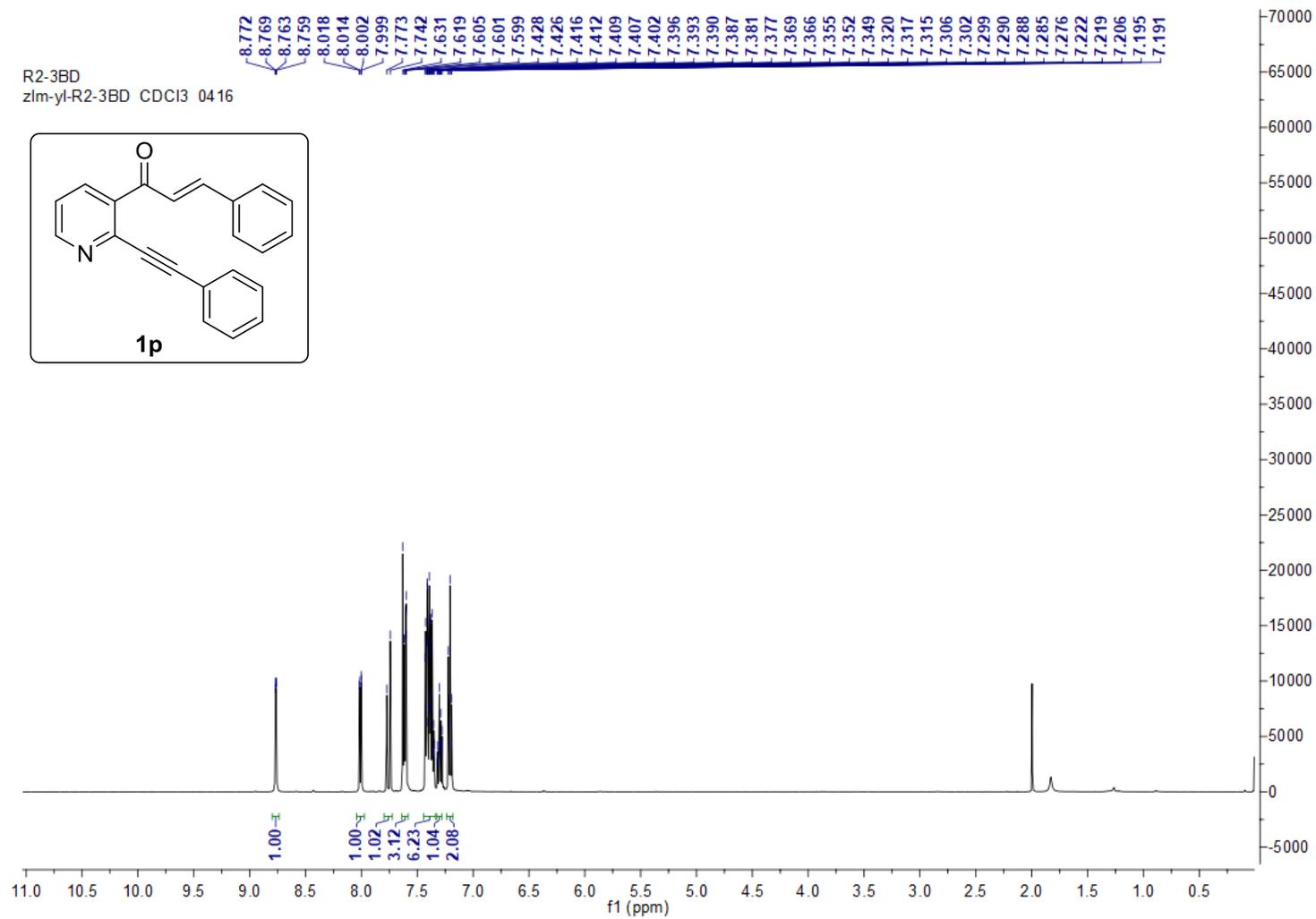
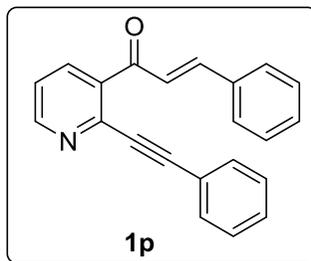


<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 1m

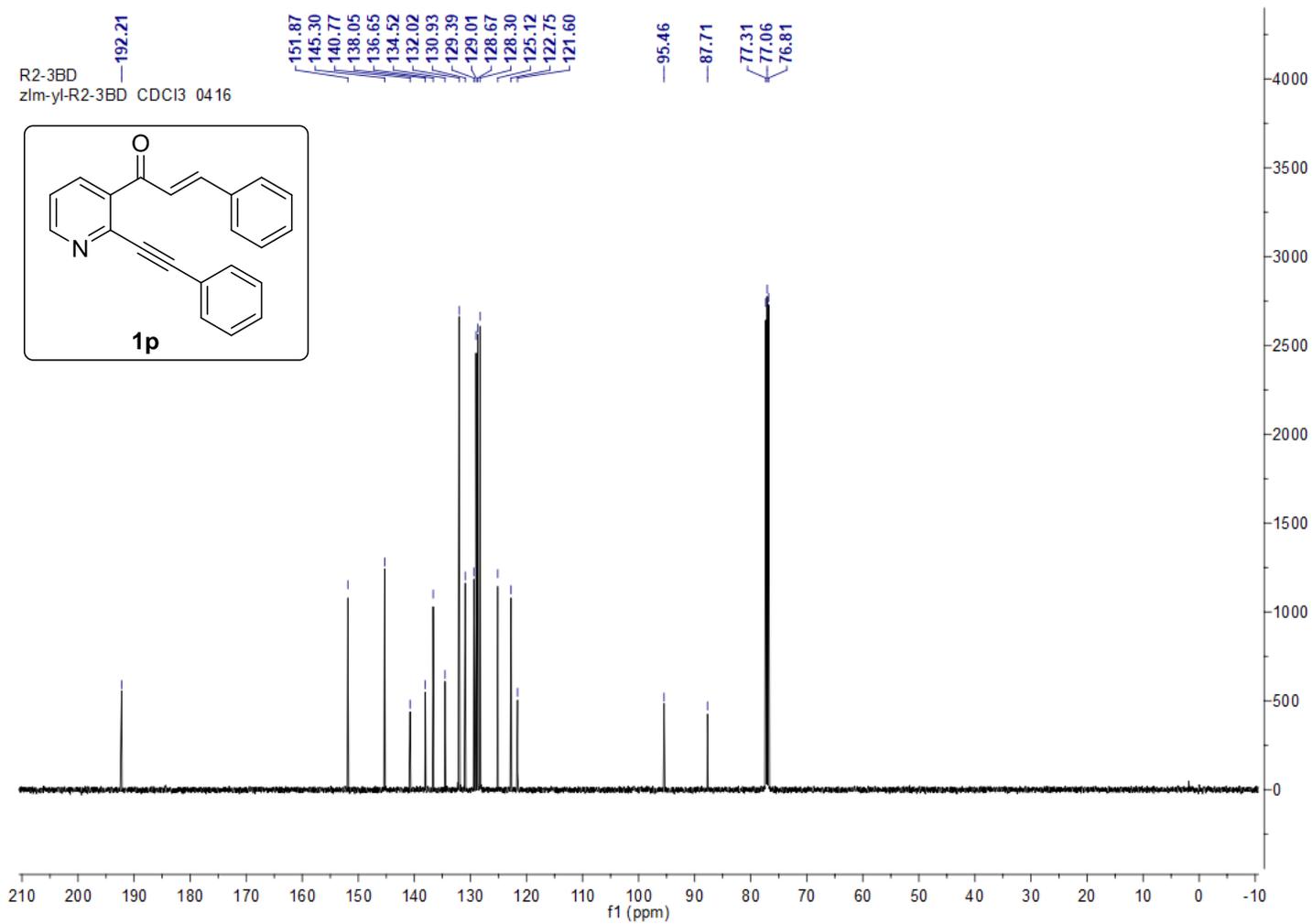


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 1p

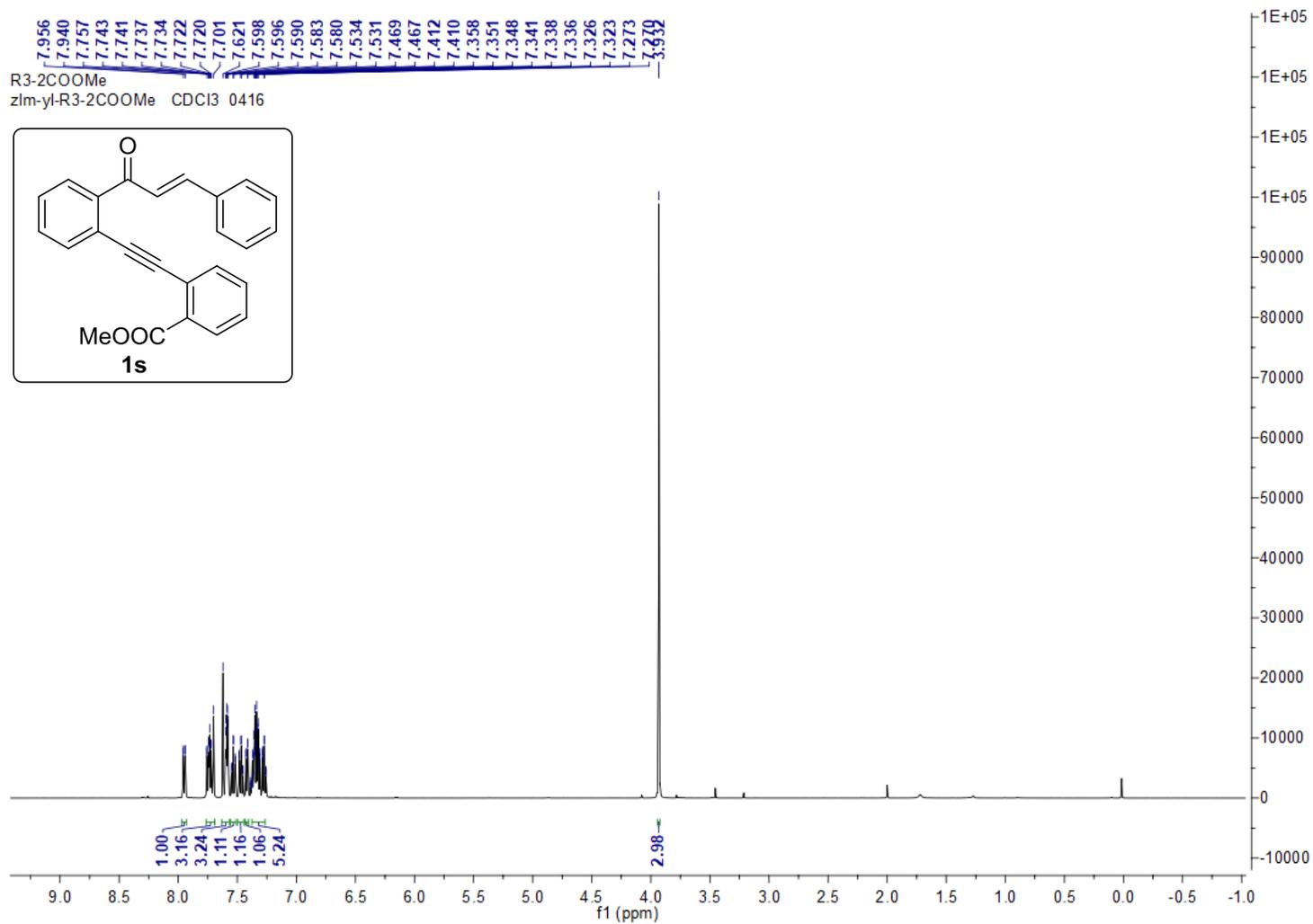
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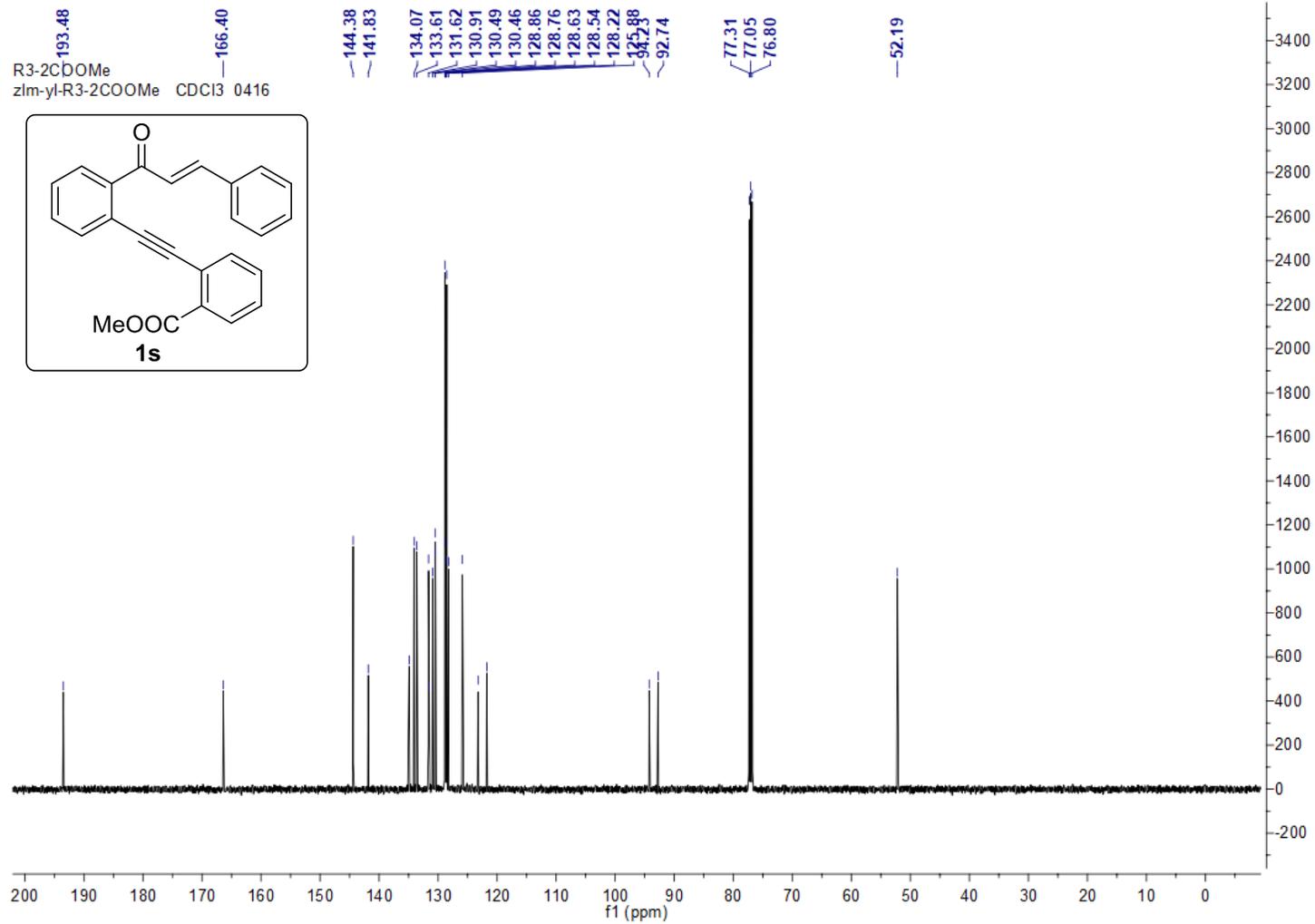
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 1p



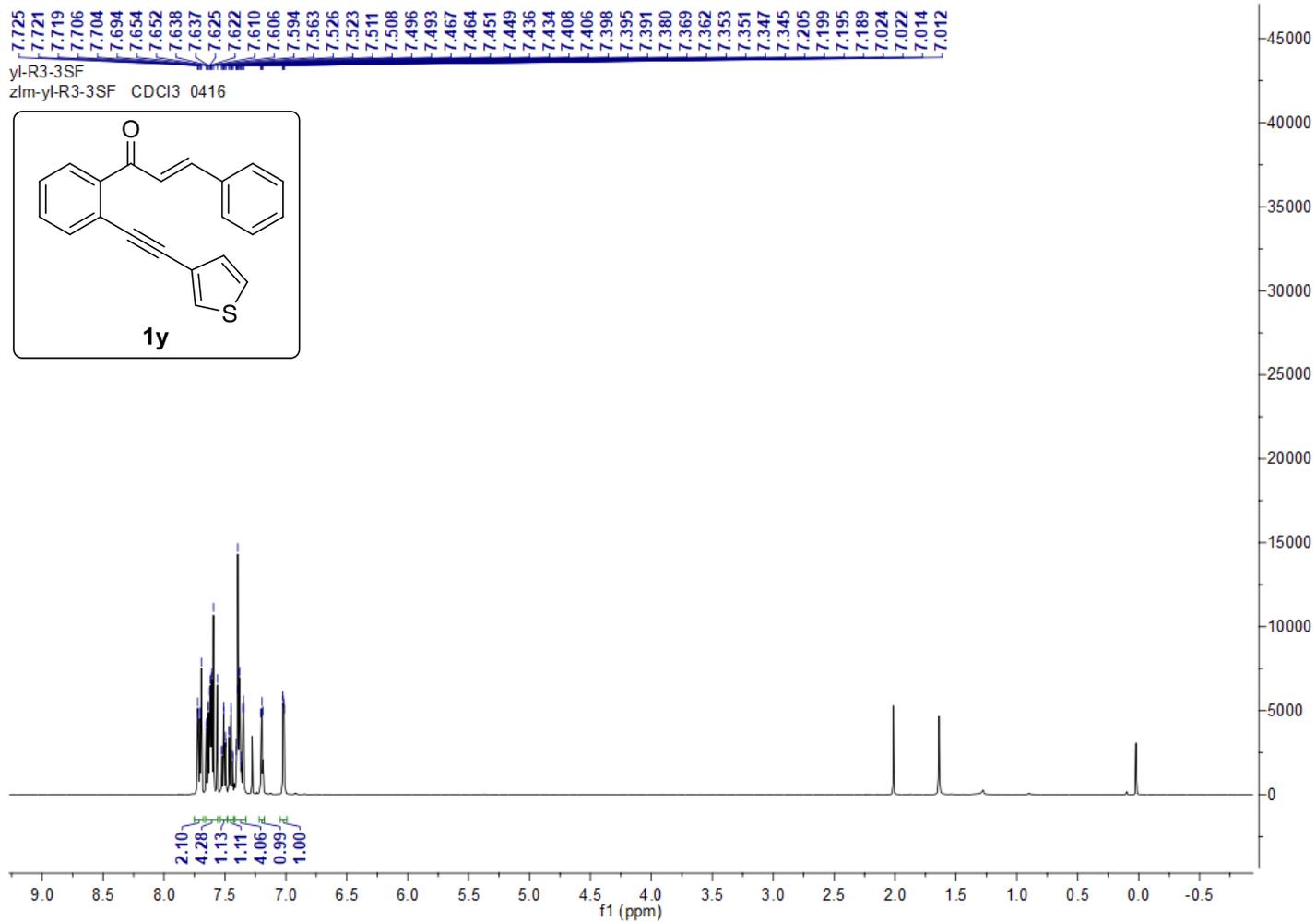
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 1s



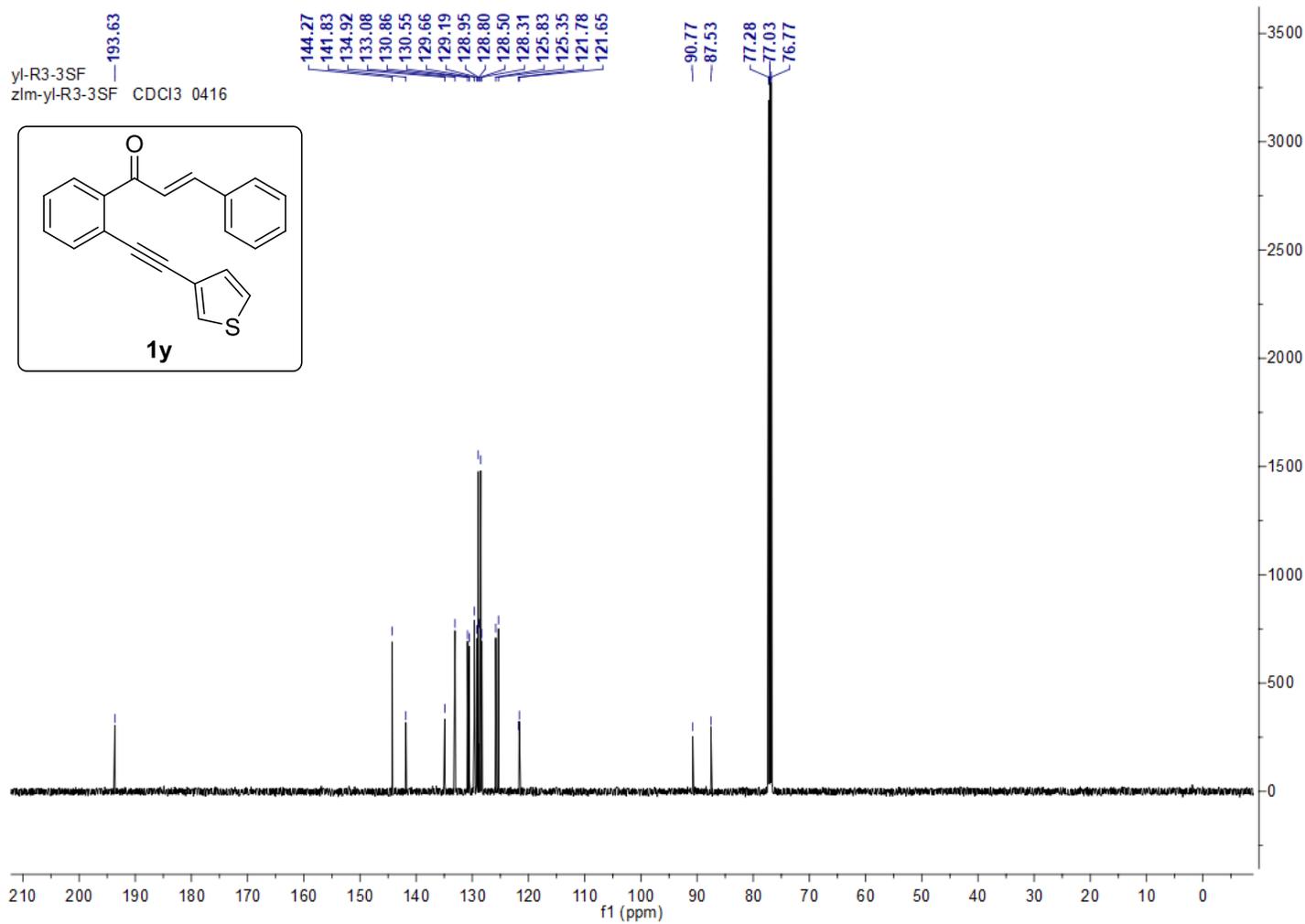
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 1s



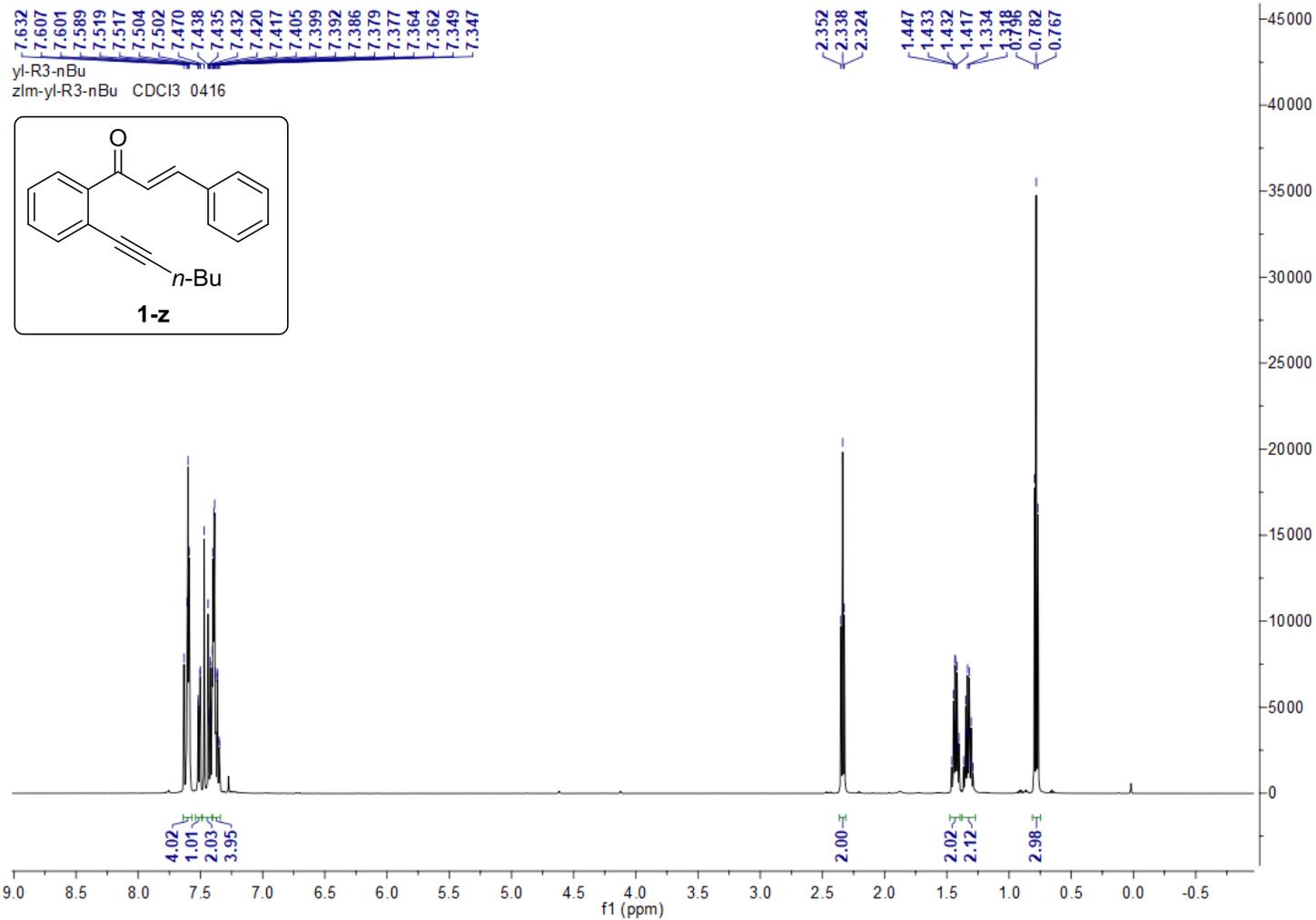
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 1y



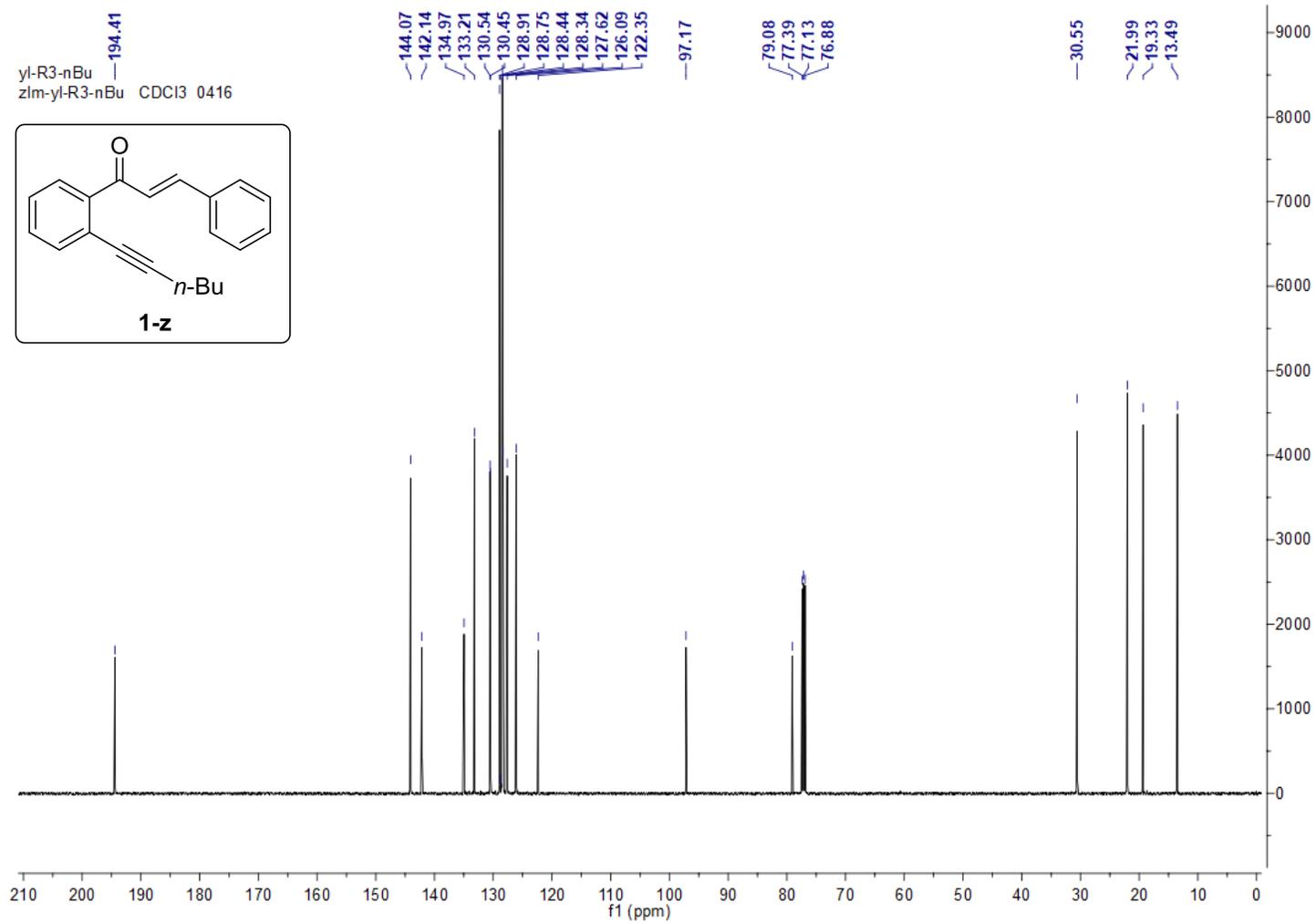
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 1y



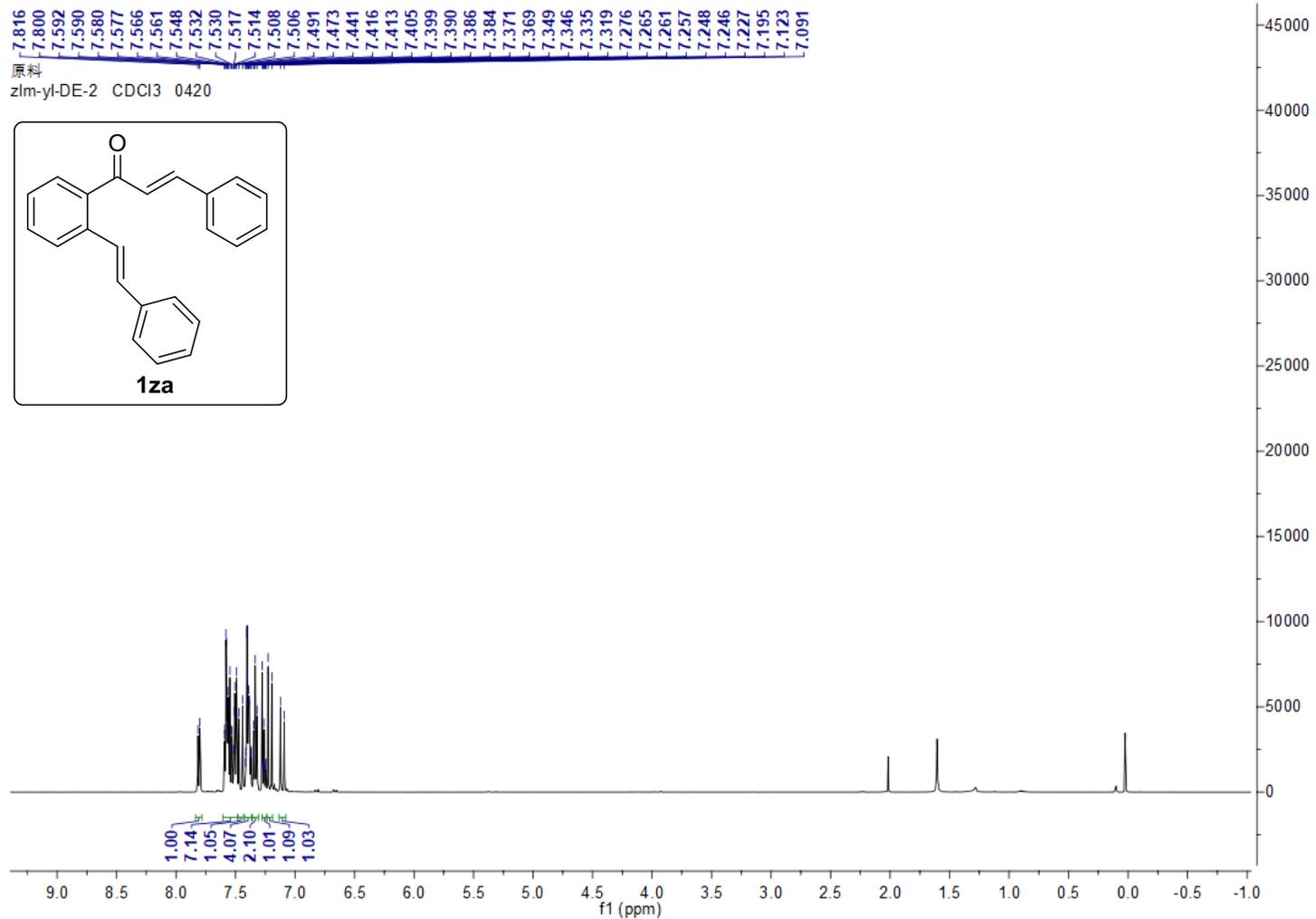
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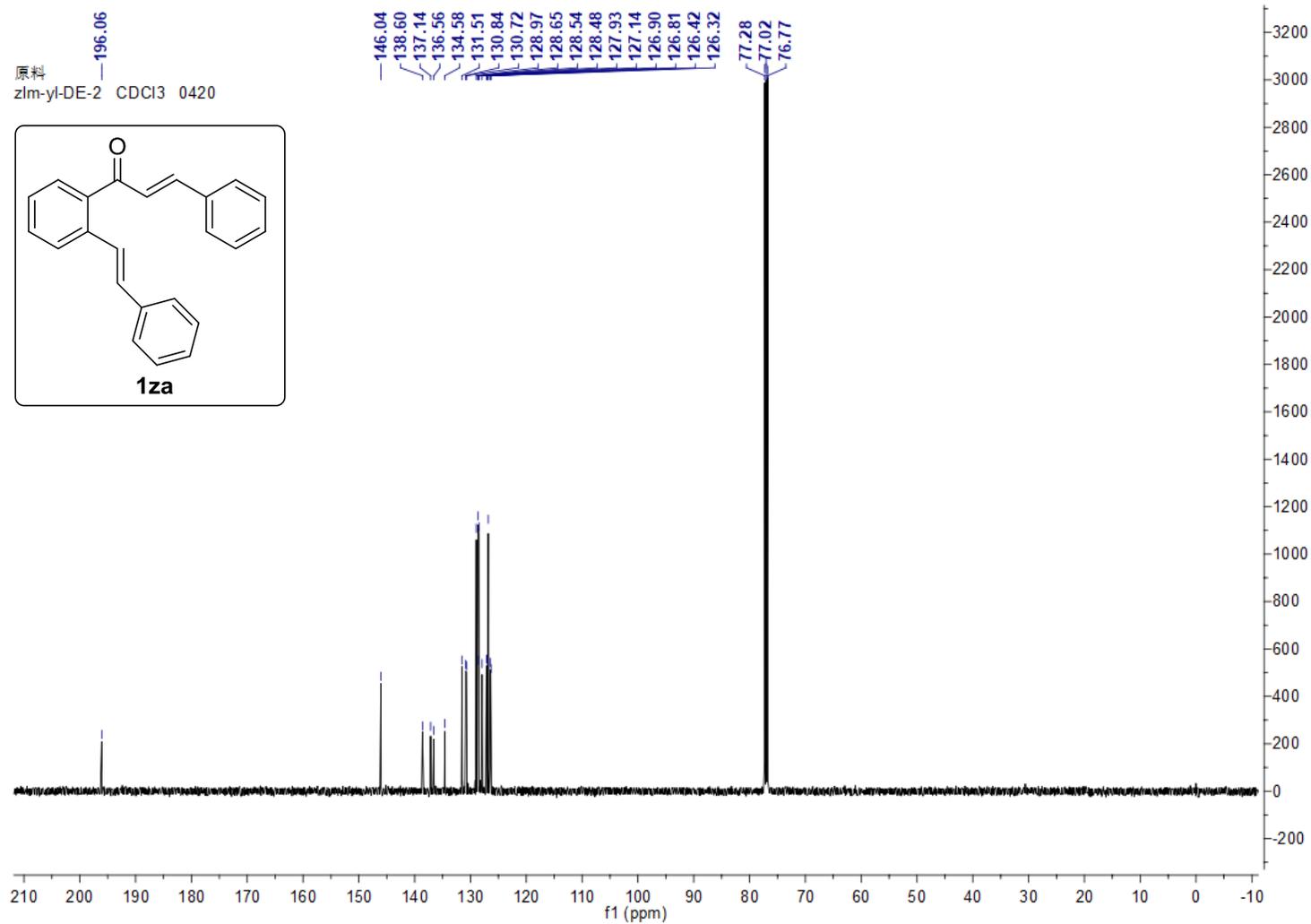
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 1z



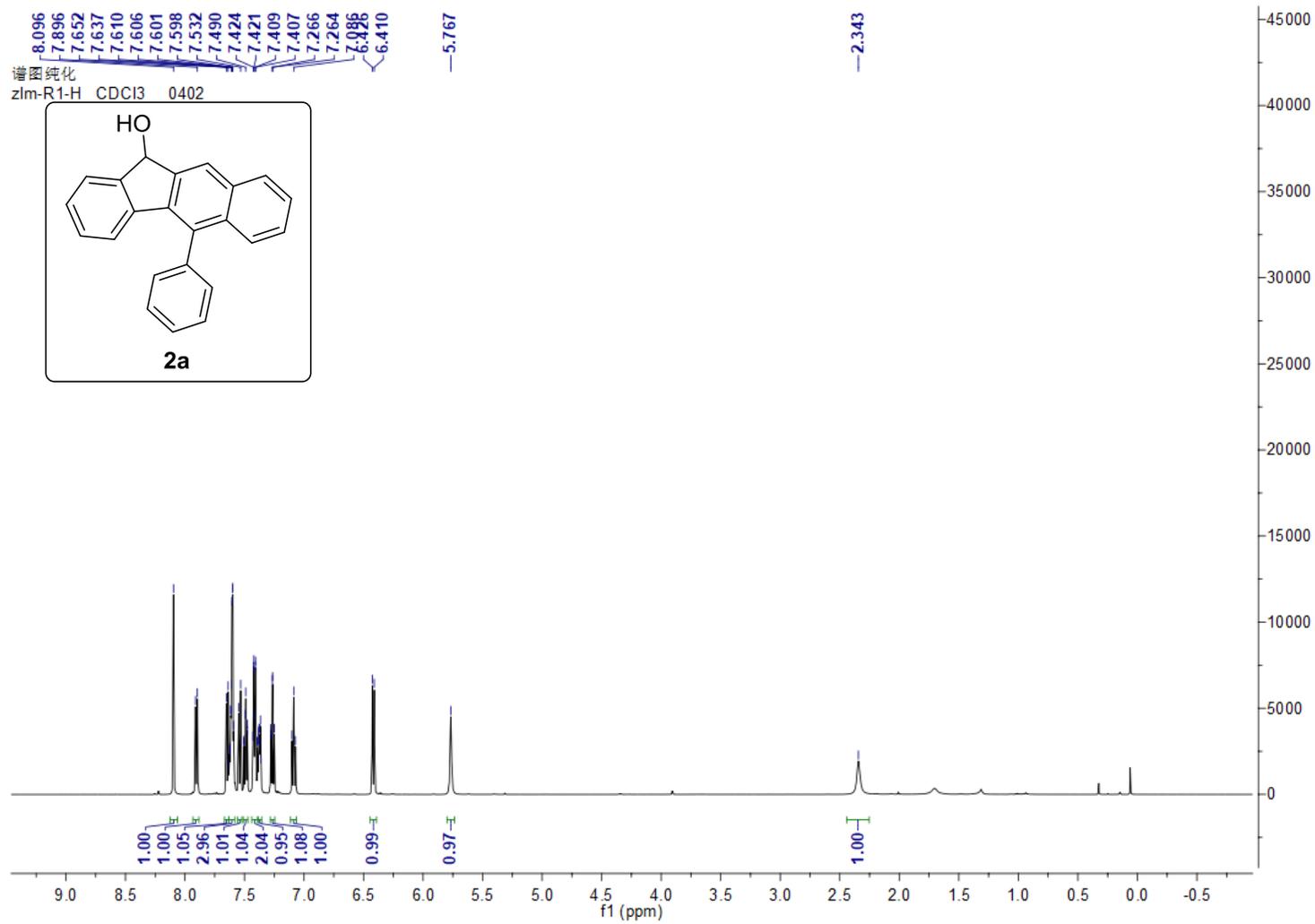
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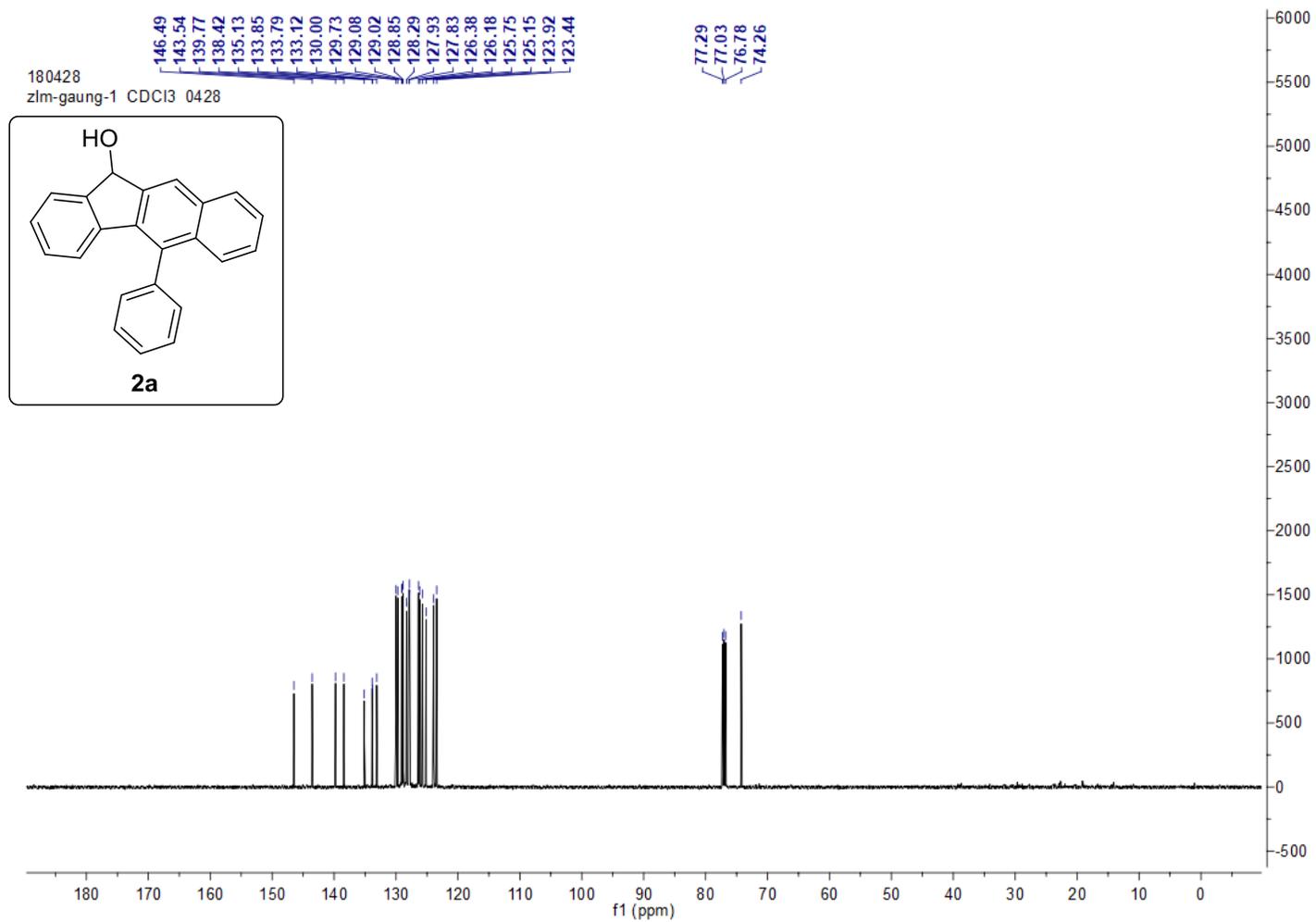
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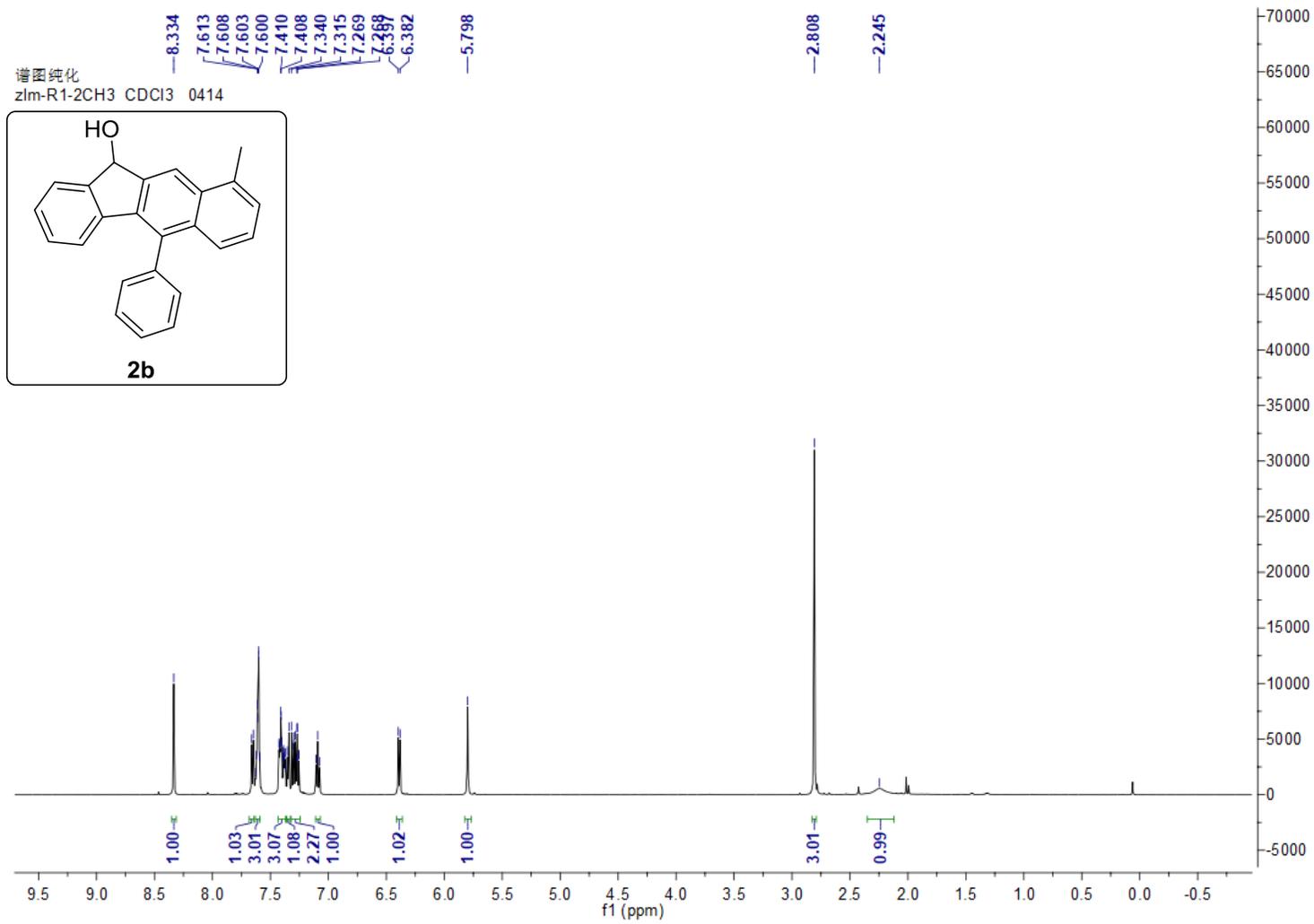
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2a



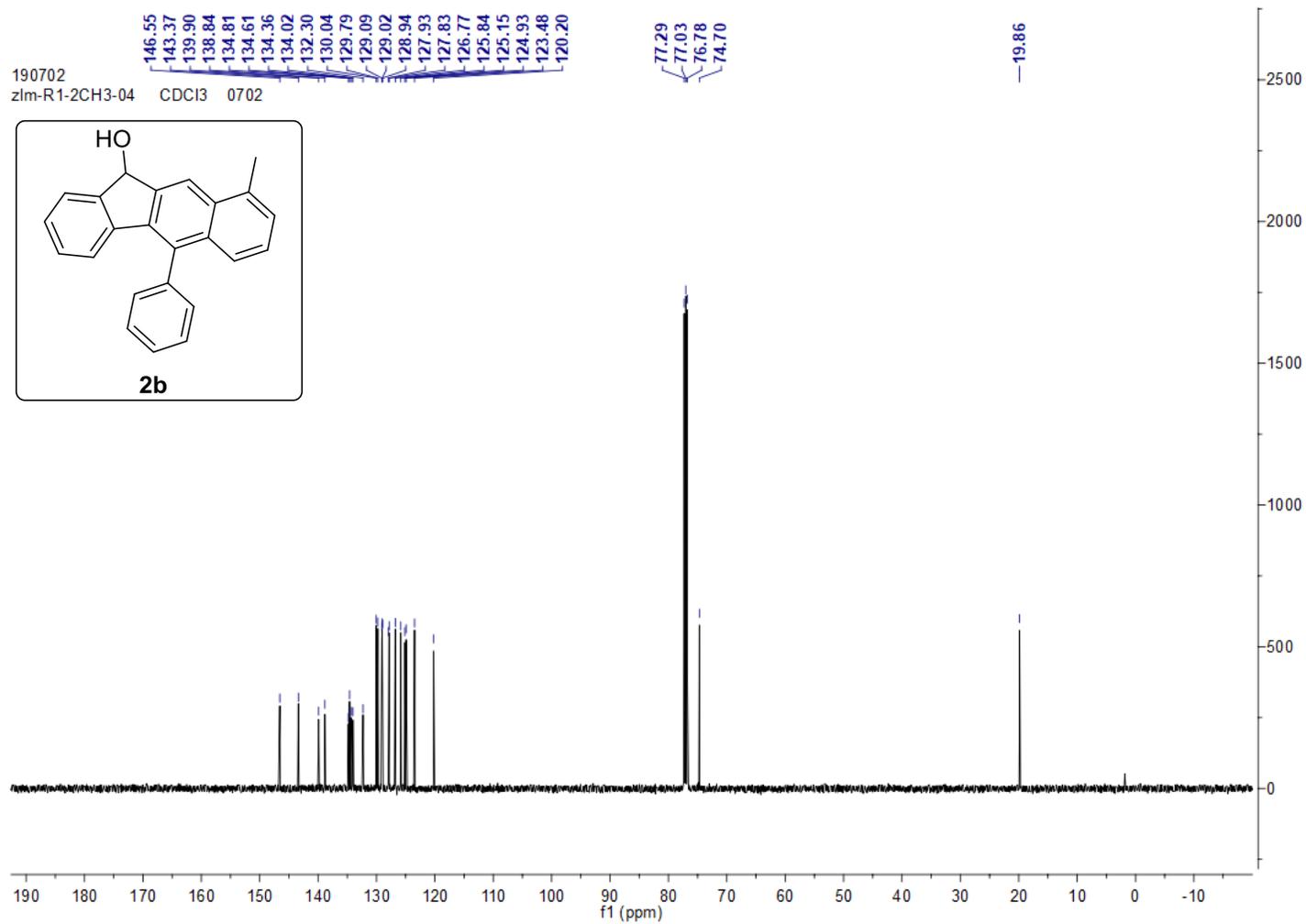
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2a



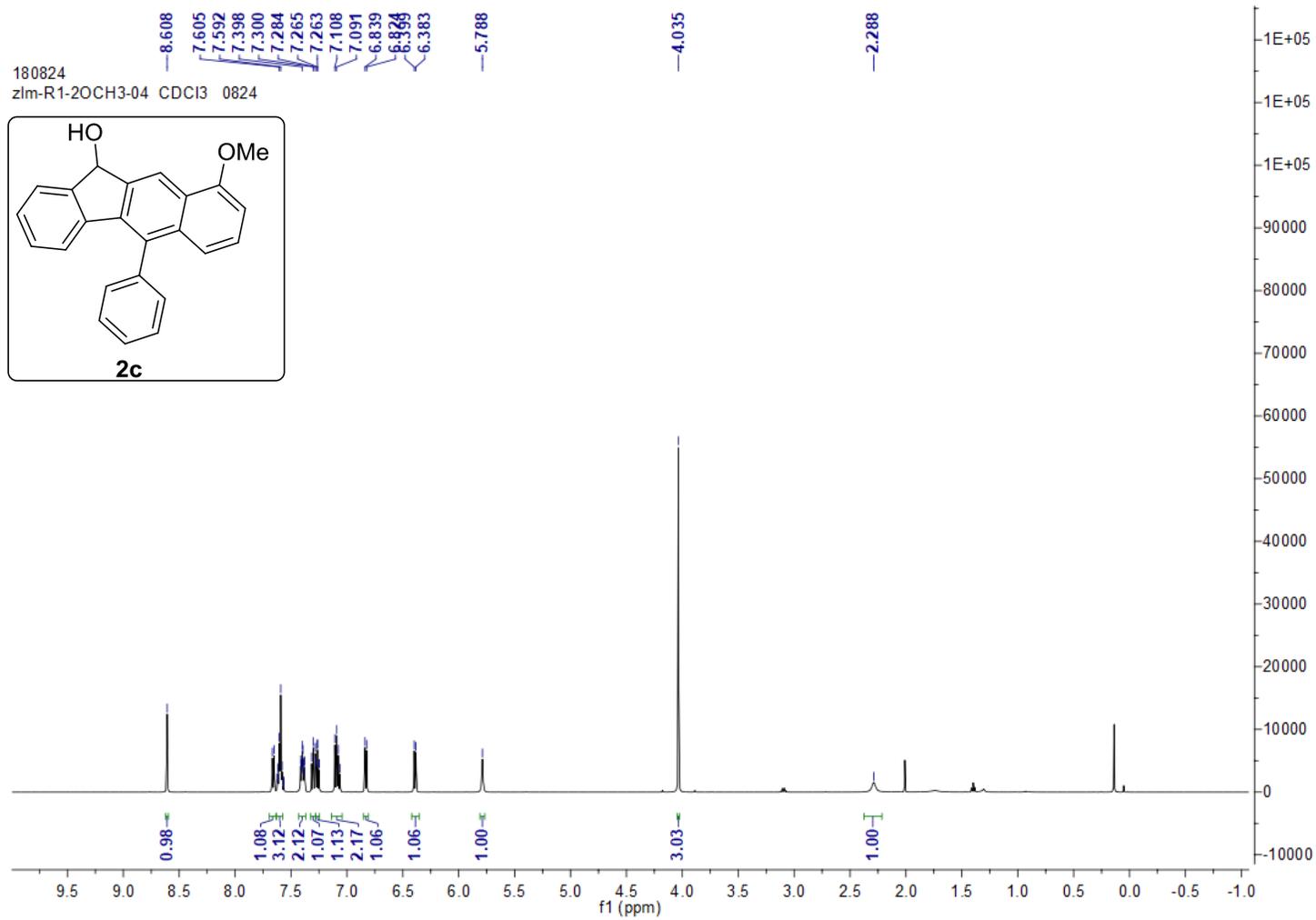
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2b



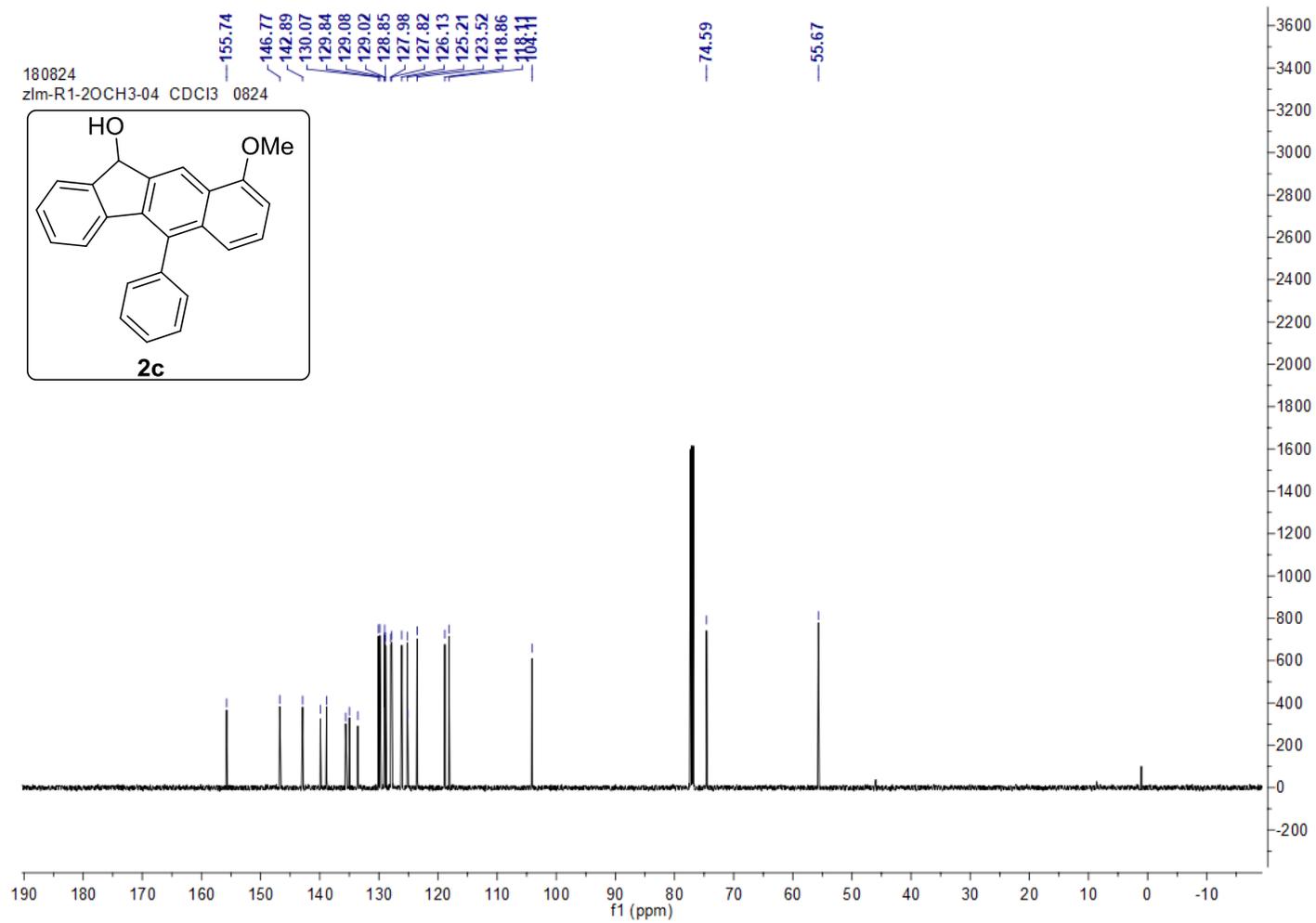
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2b



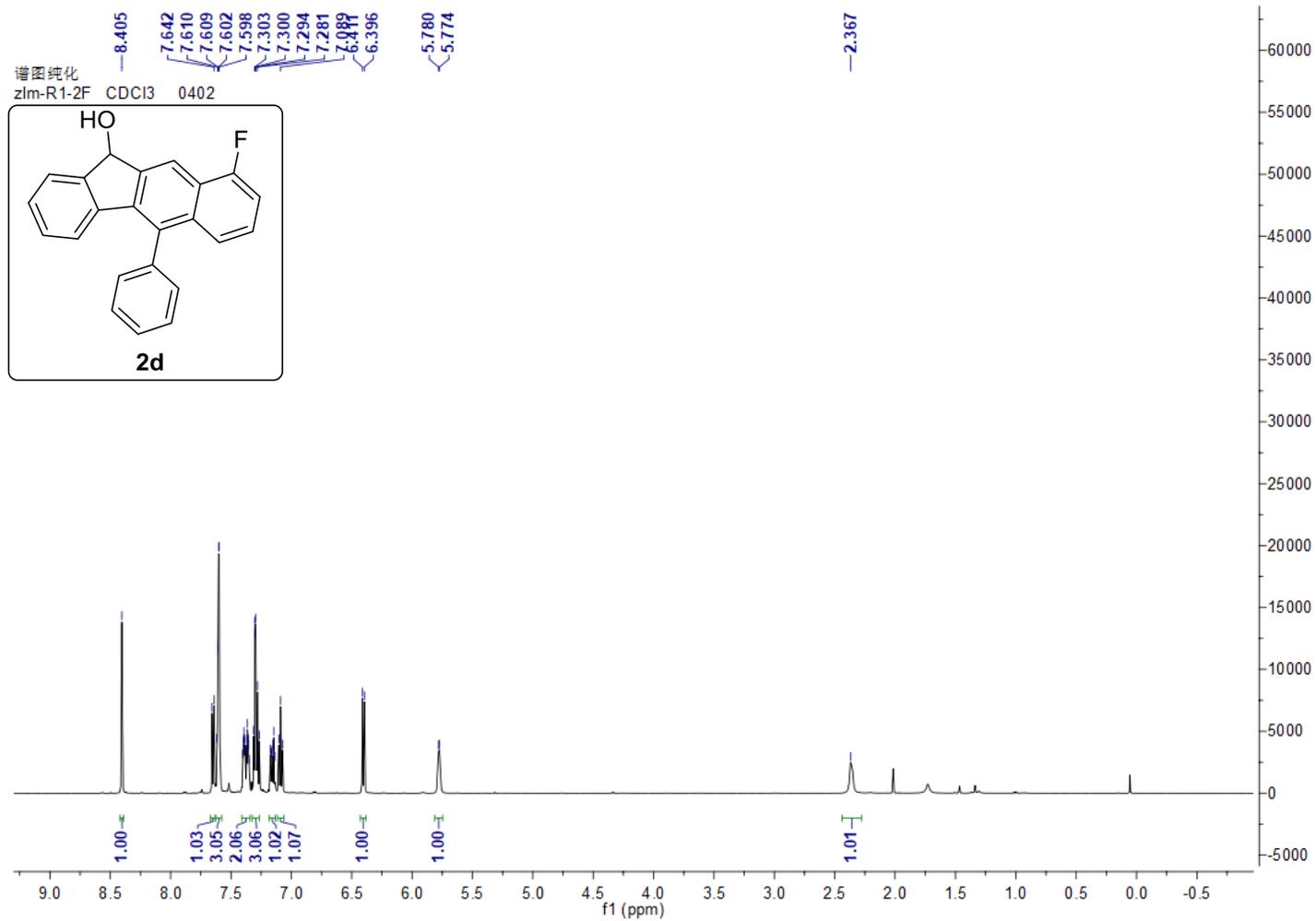
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2c



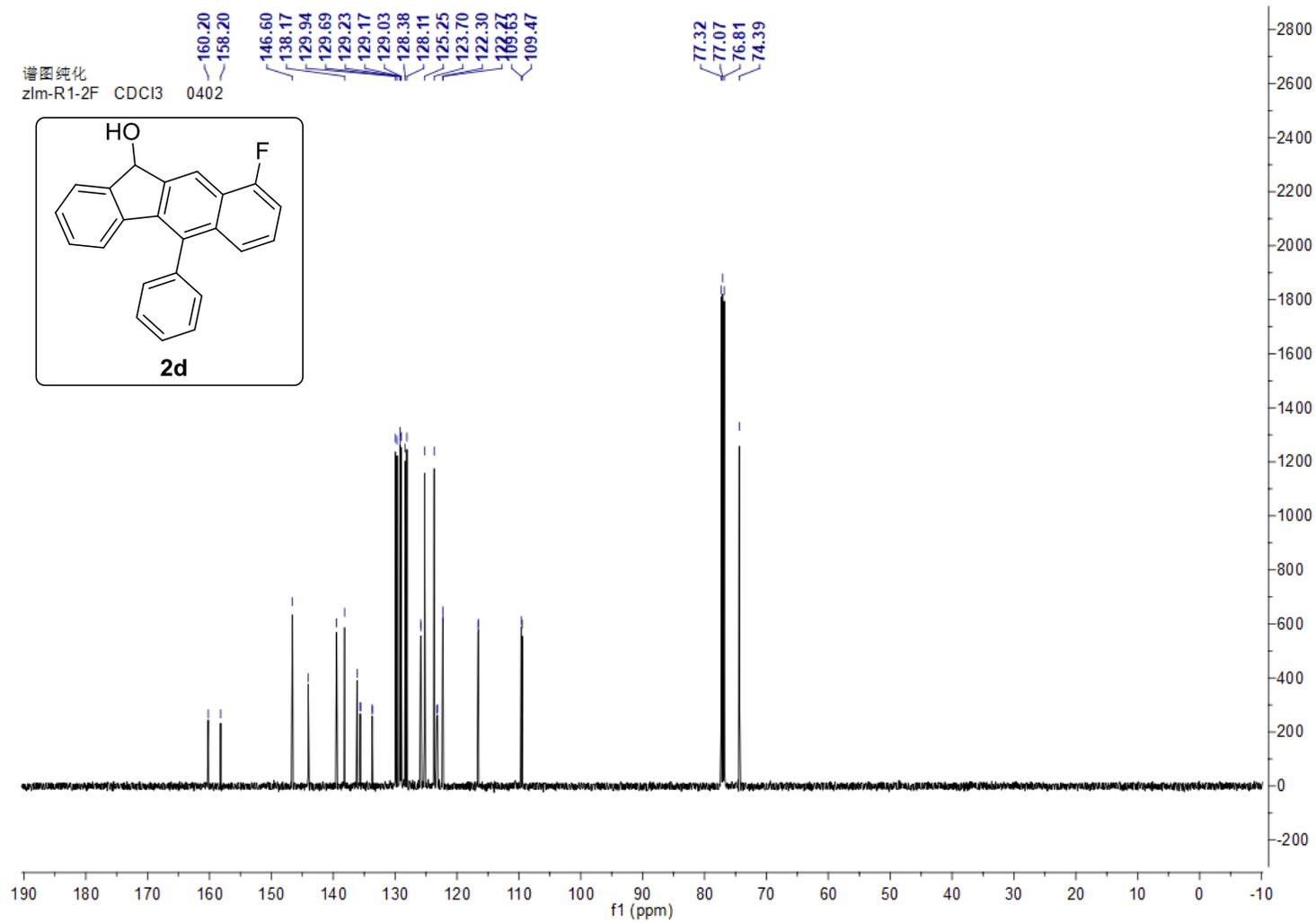
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2c



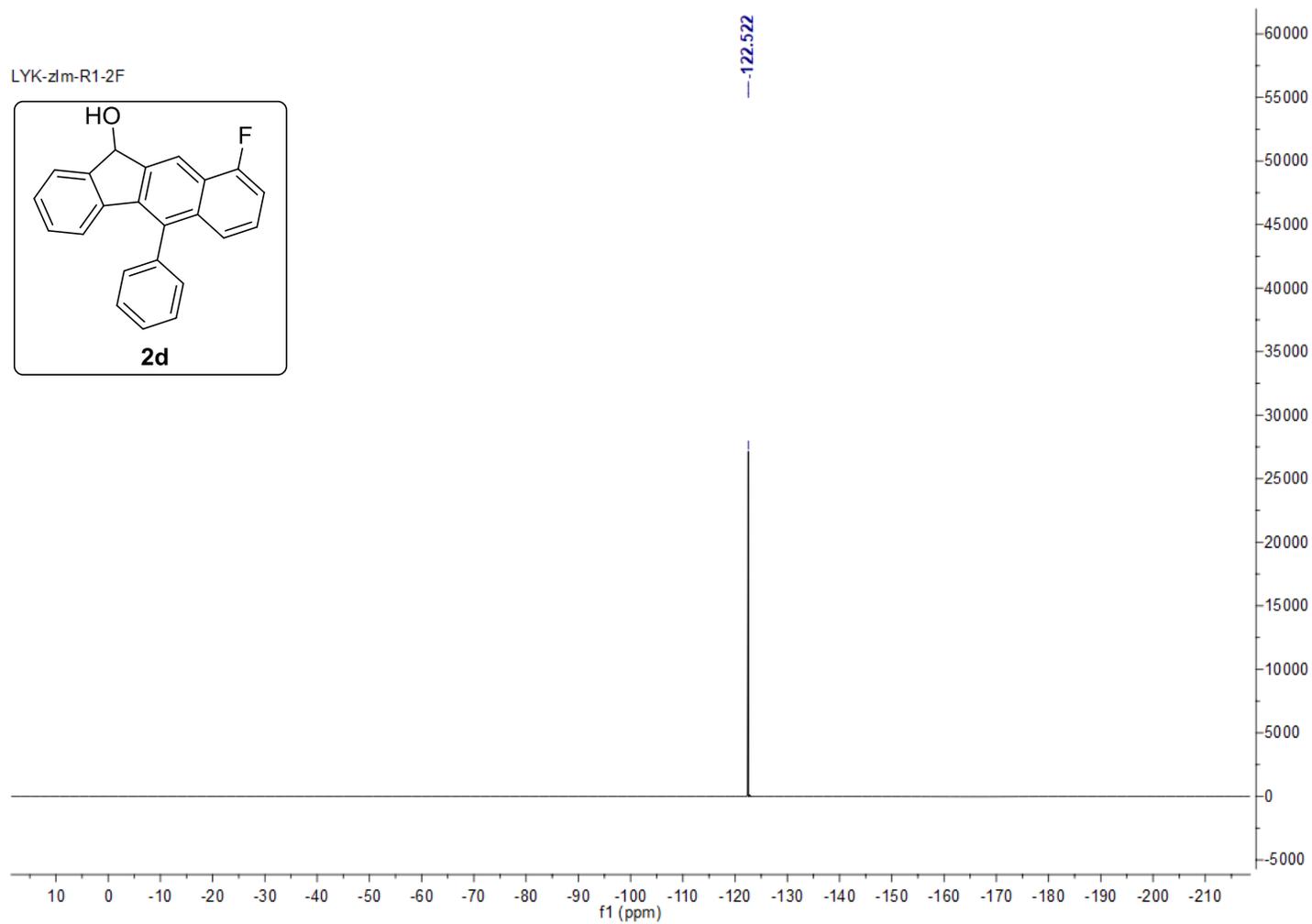
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2d



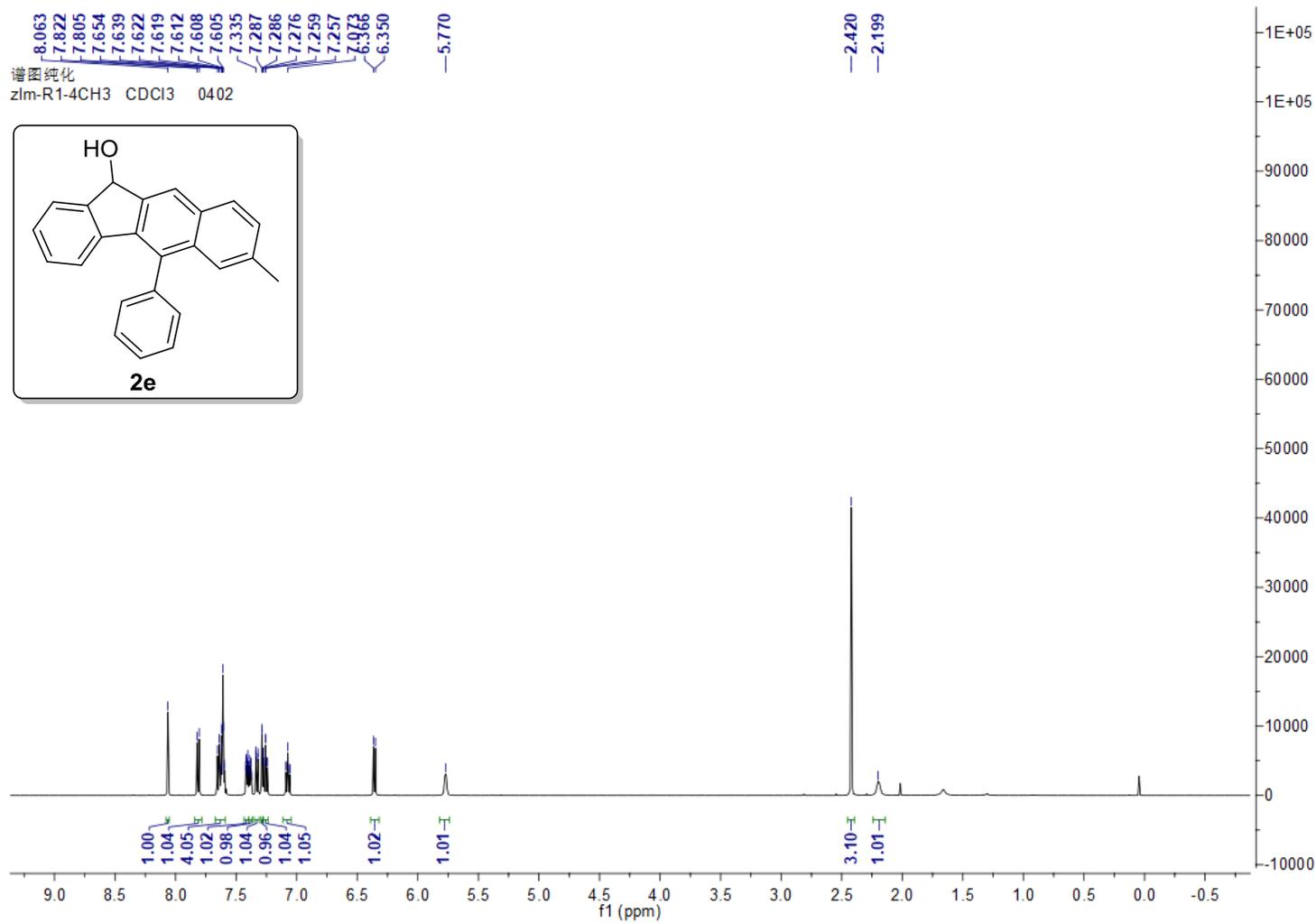
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2d



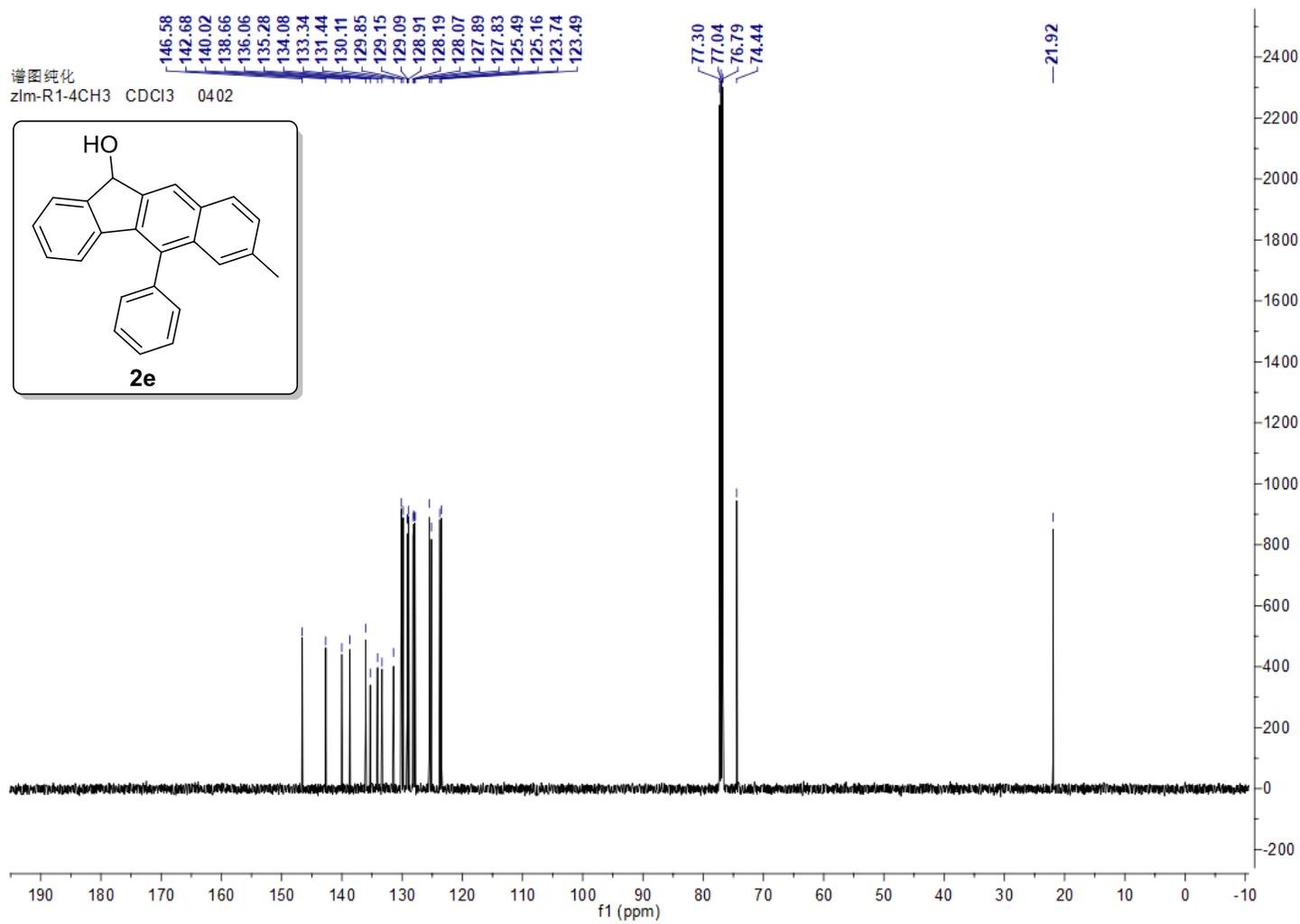
<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) spectrum of compound 2d



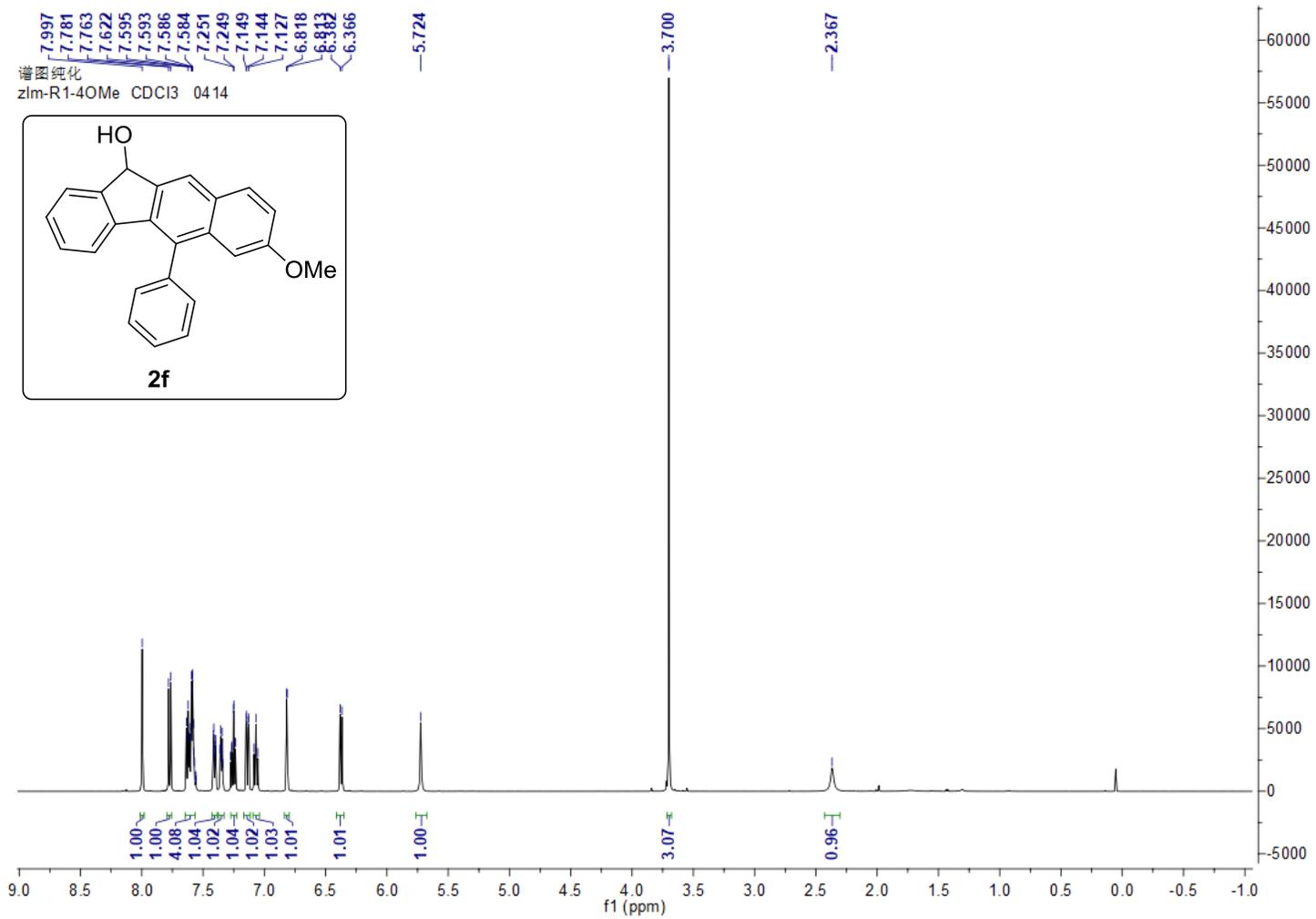
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2e



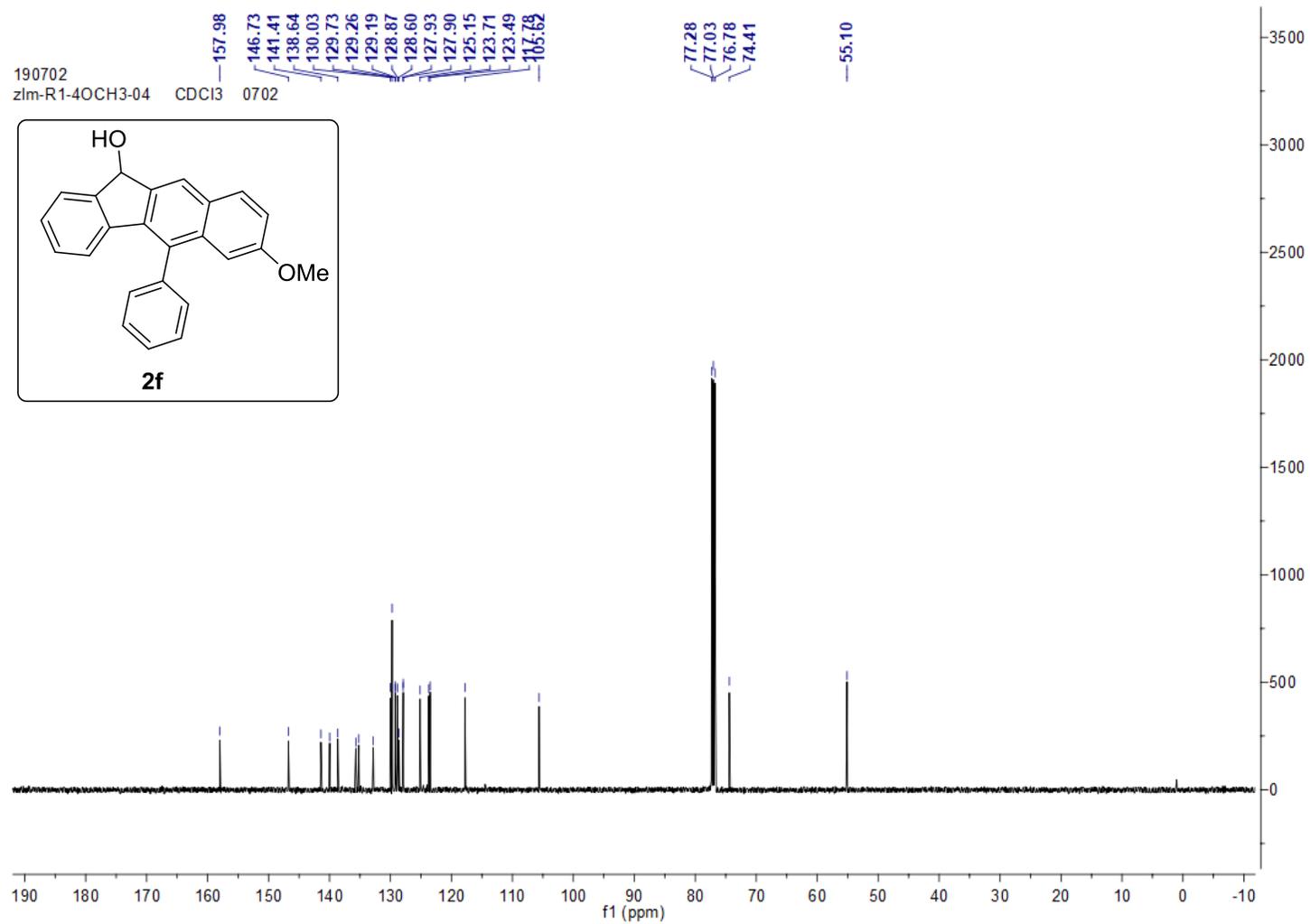
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2e



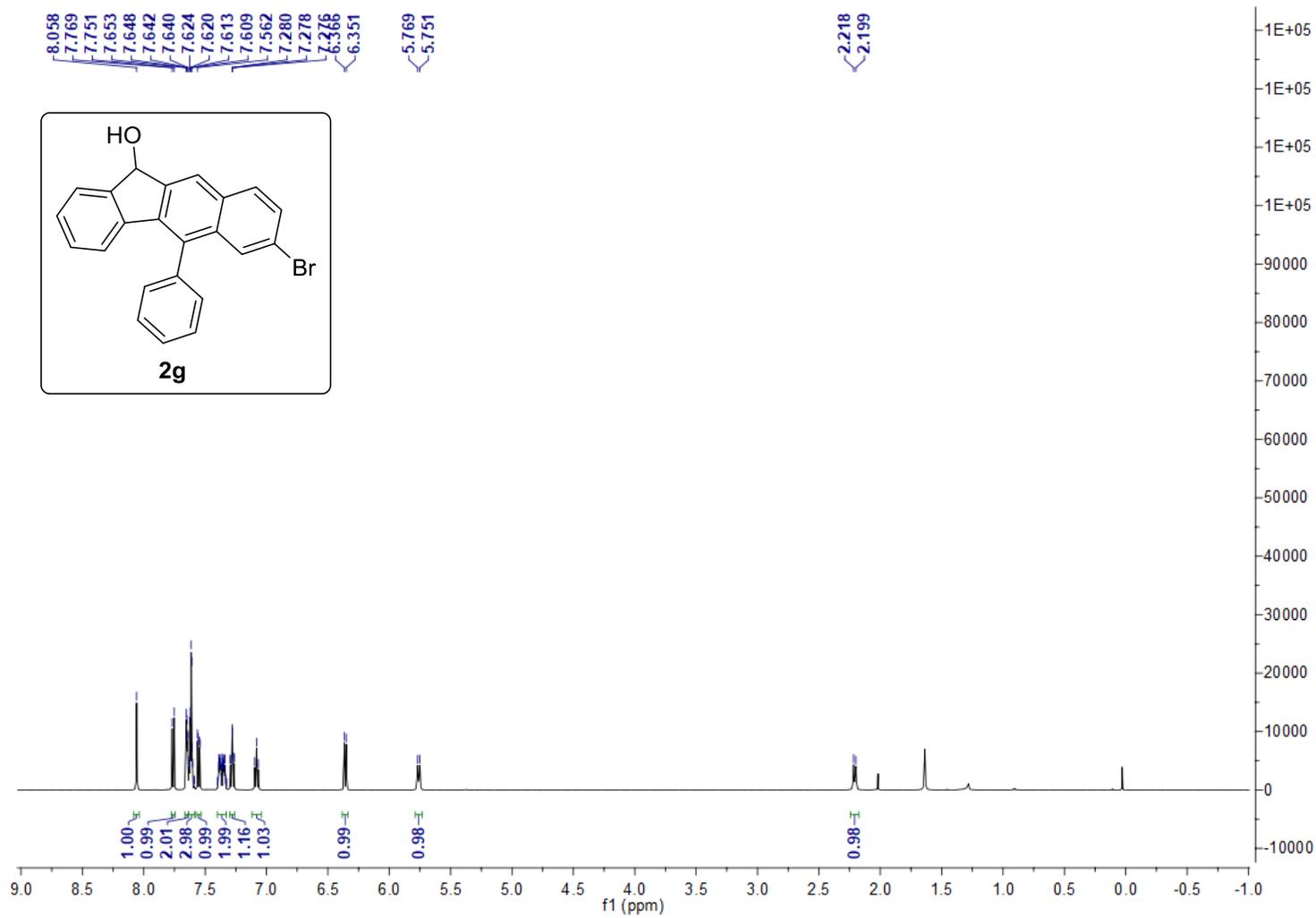
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2f



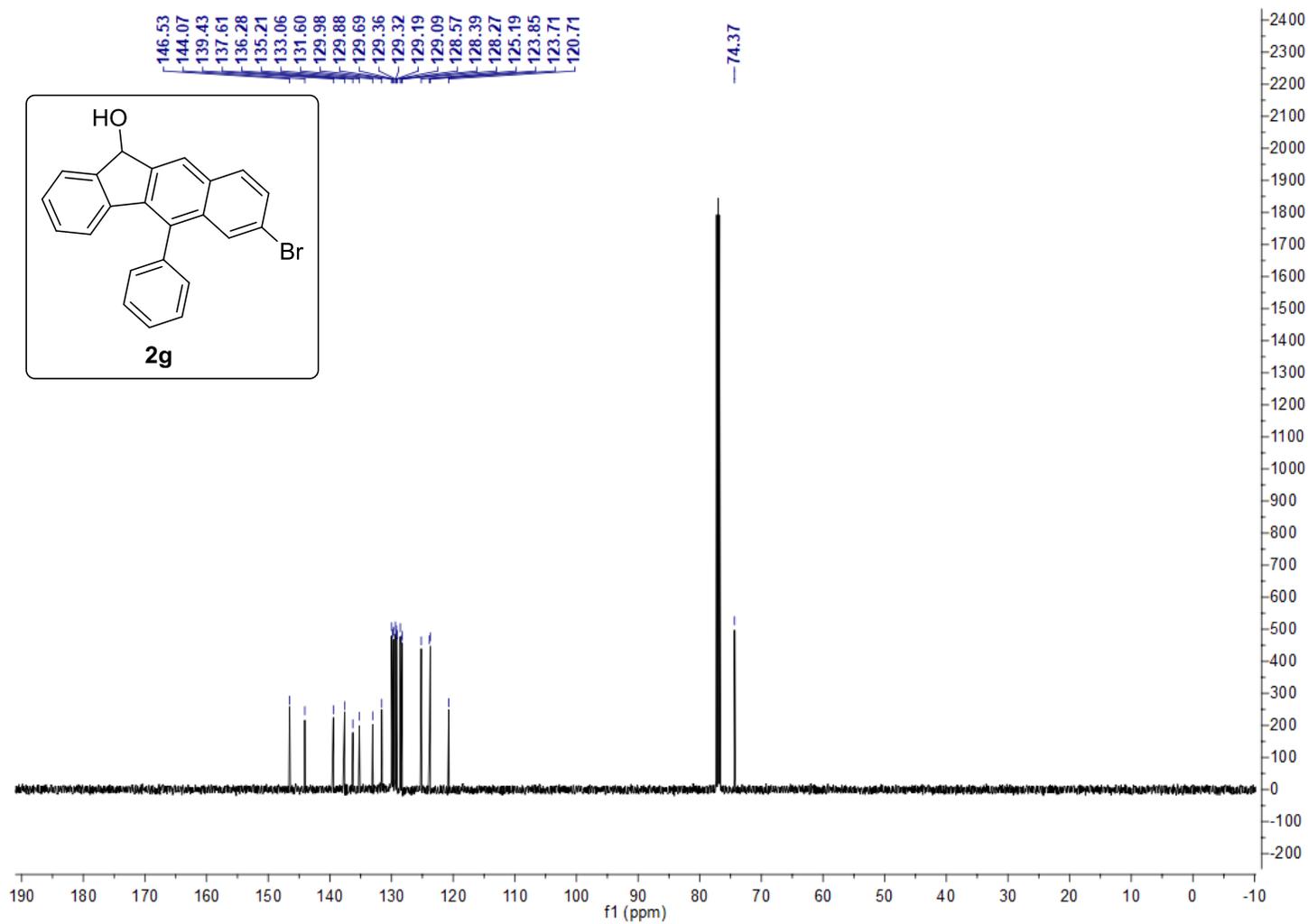
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2f



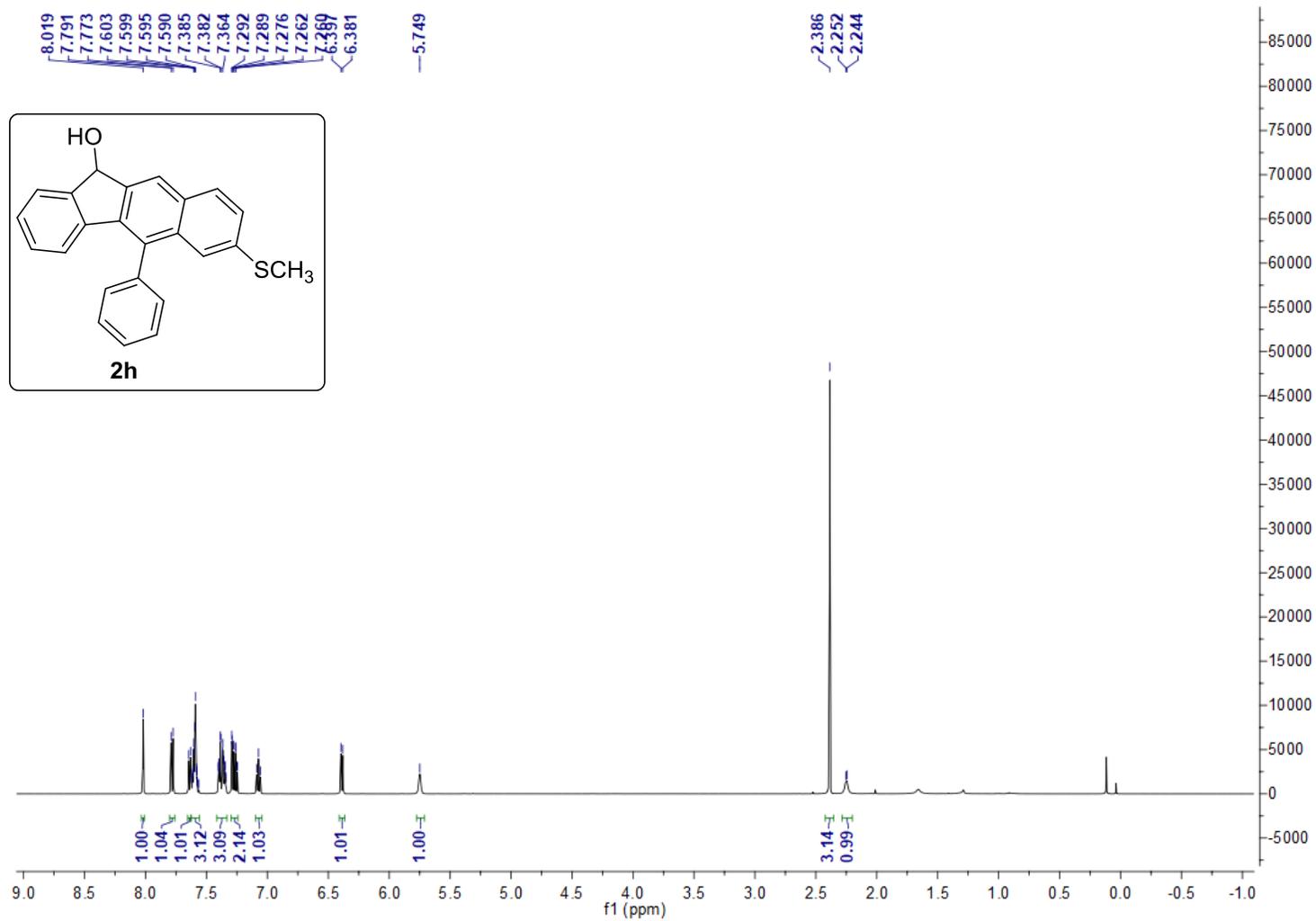
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2g



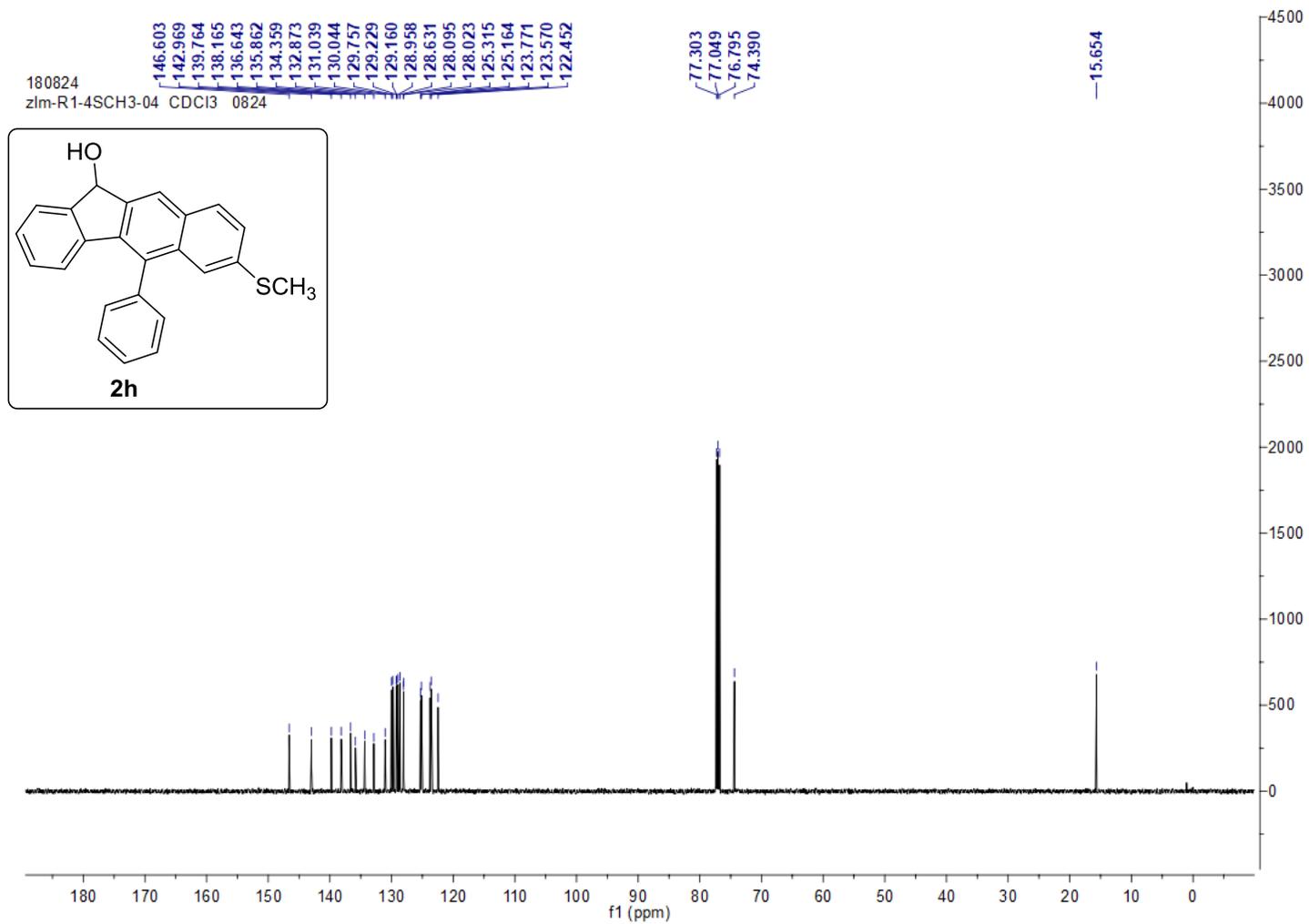
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2g



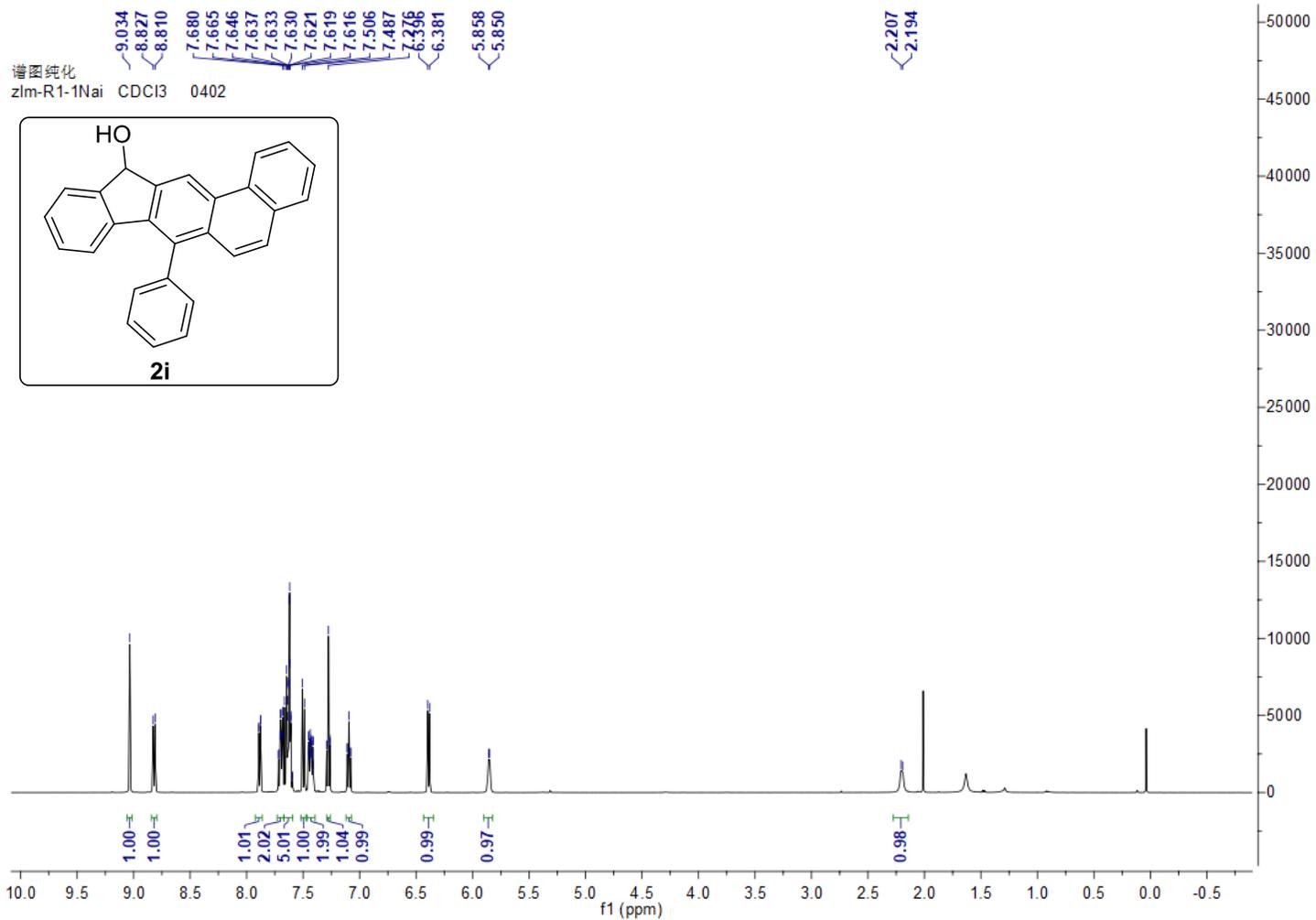
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2h



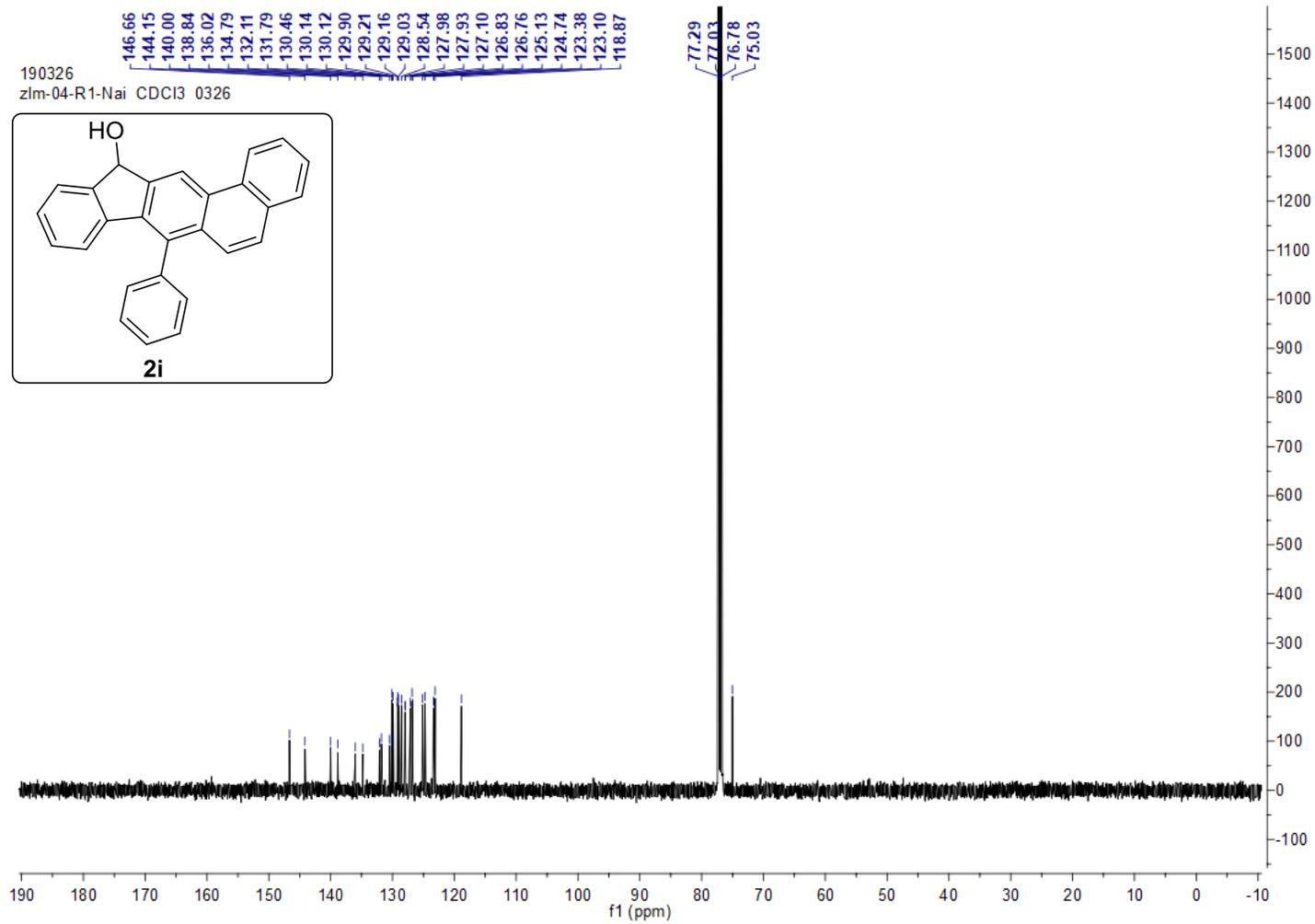
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2h



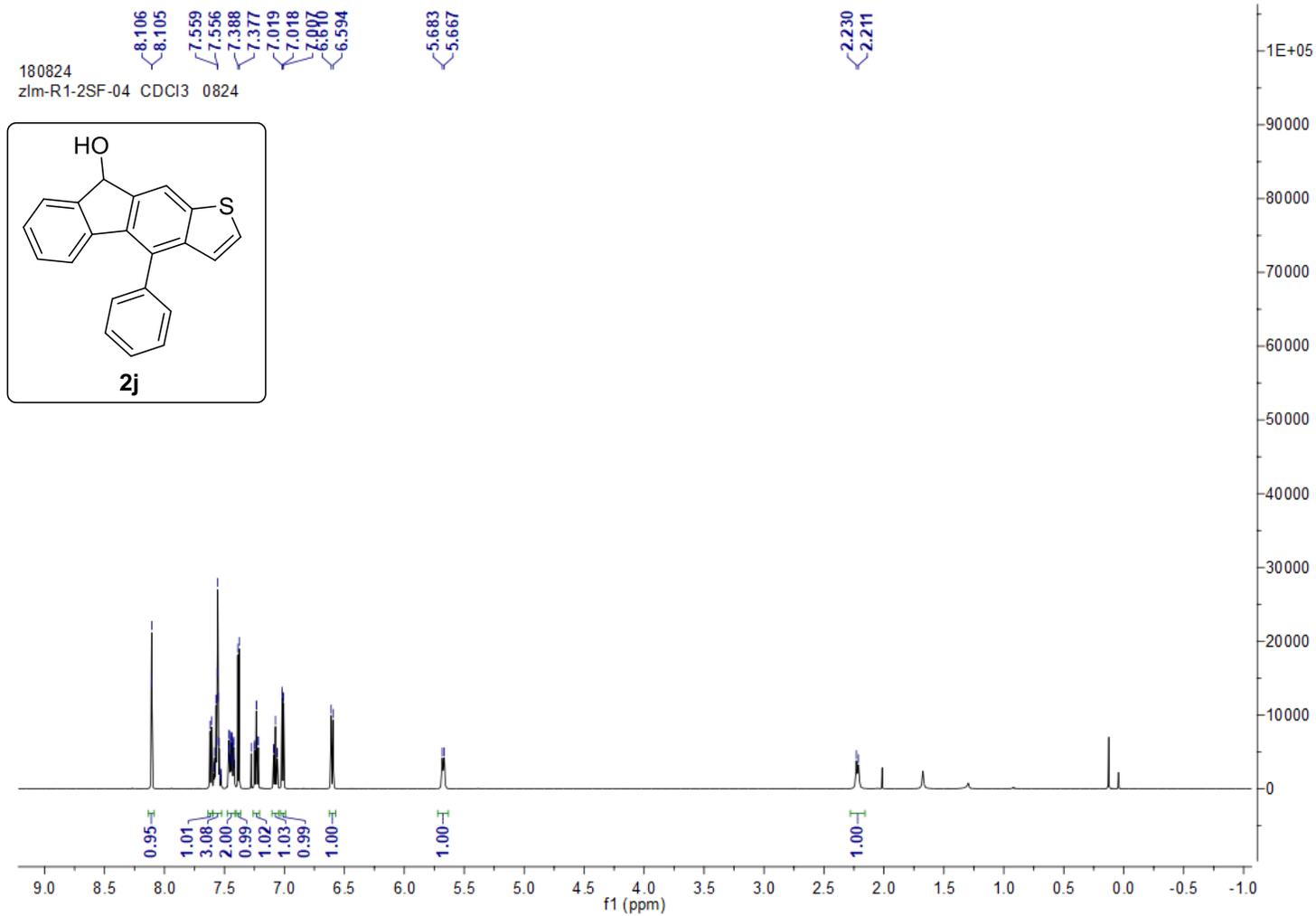
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2i**



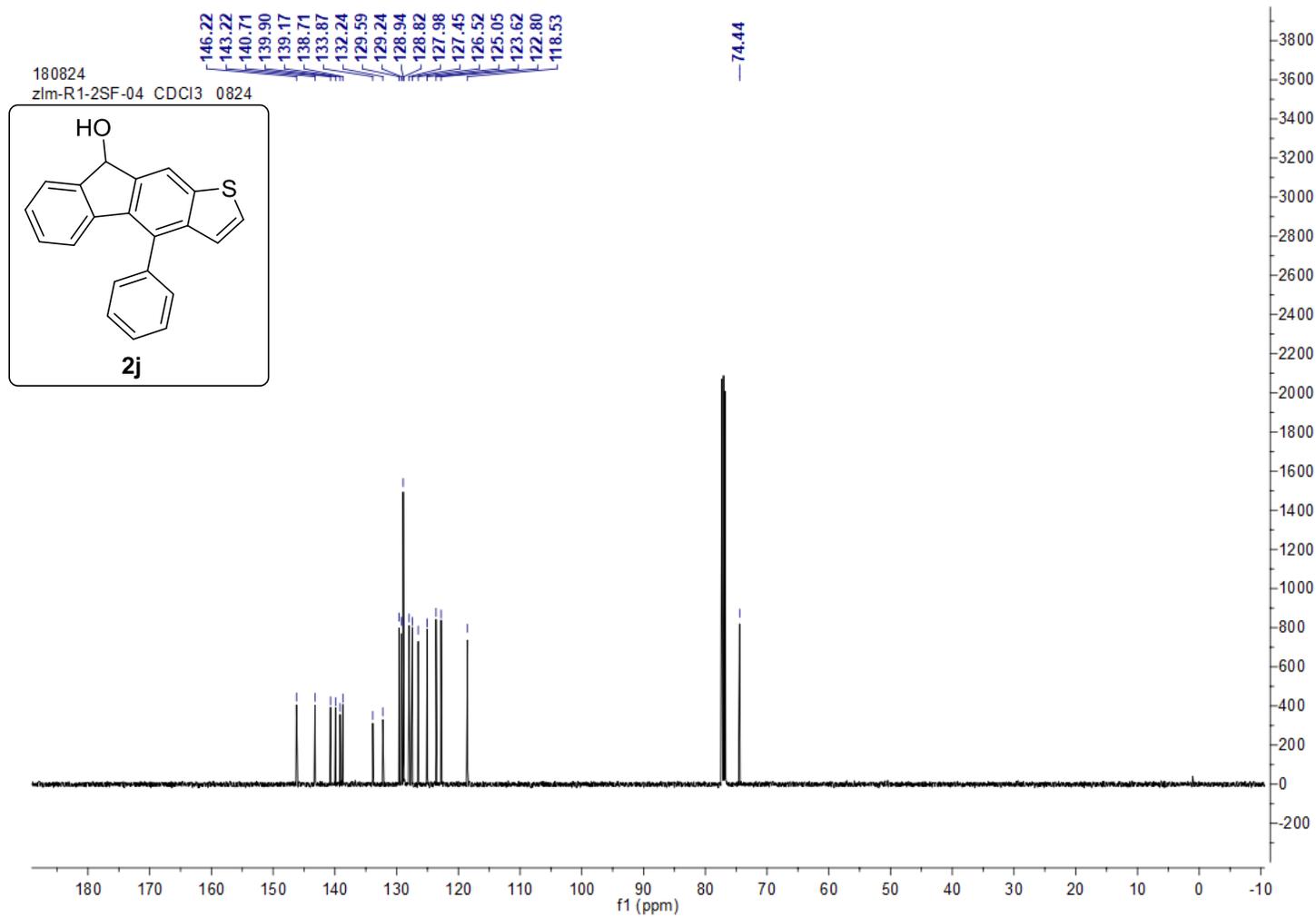
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2i



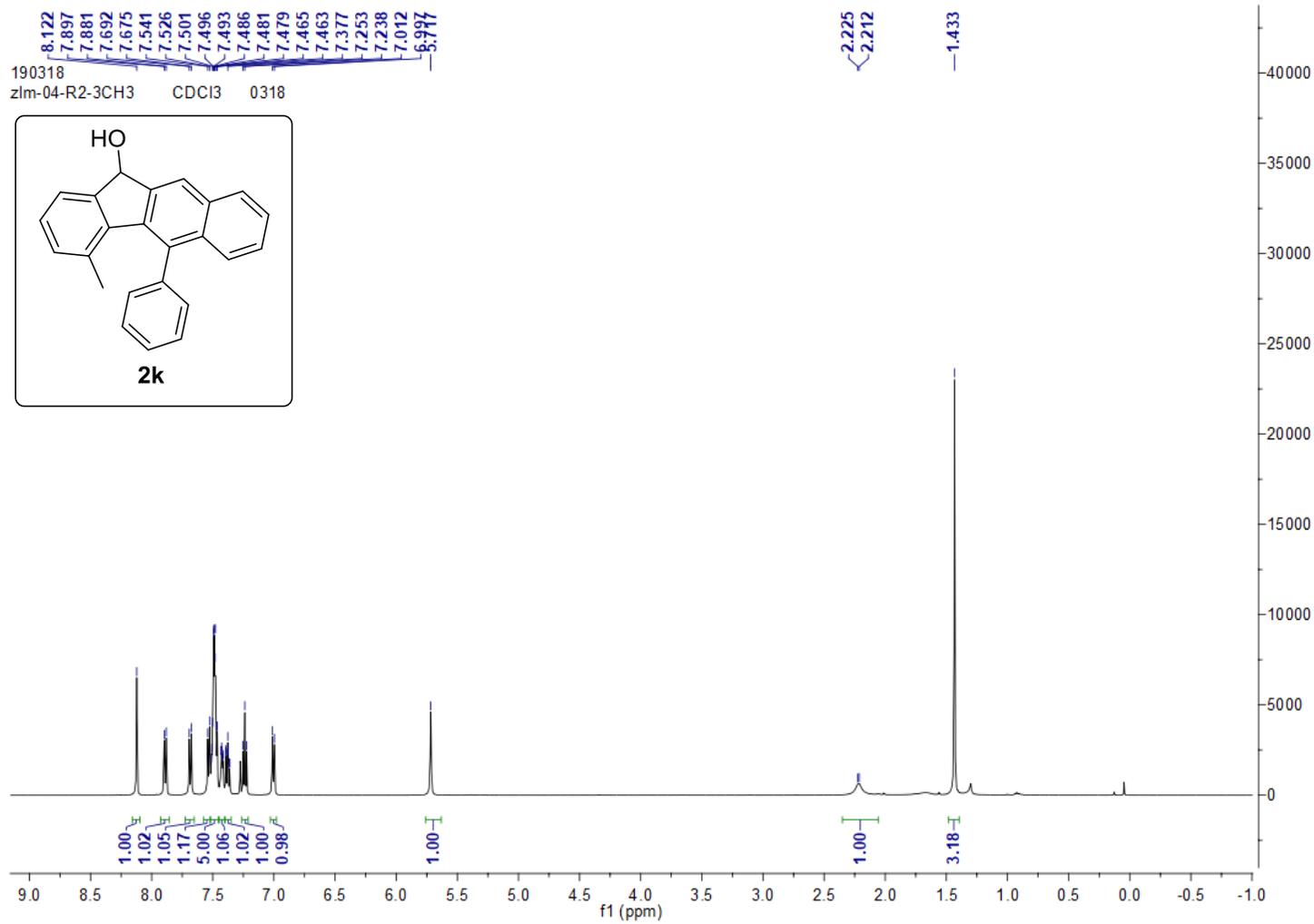
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2j**



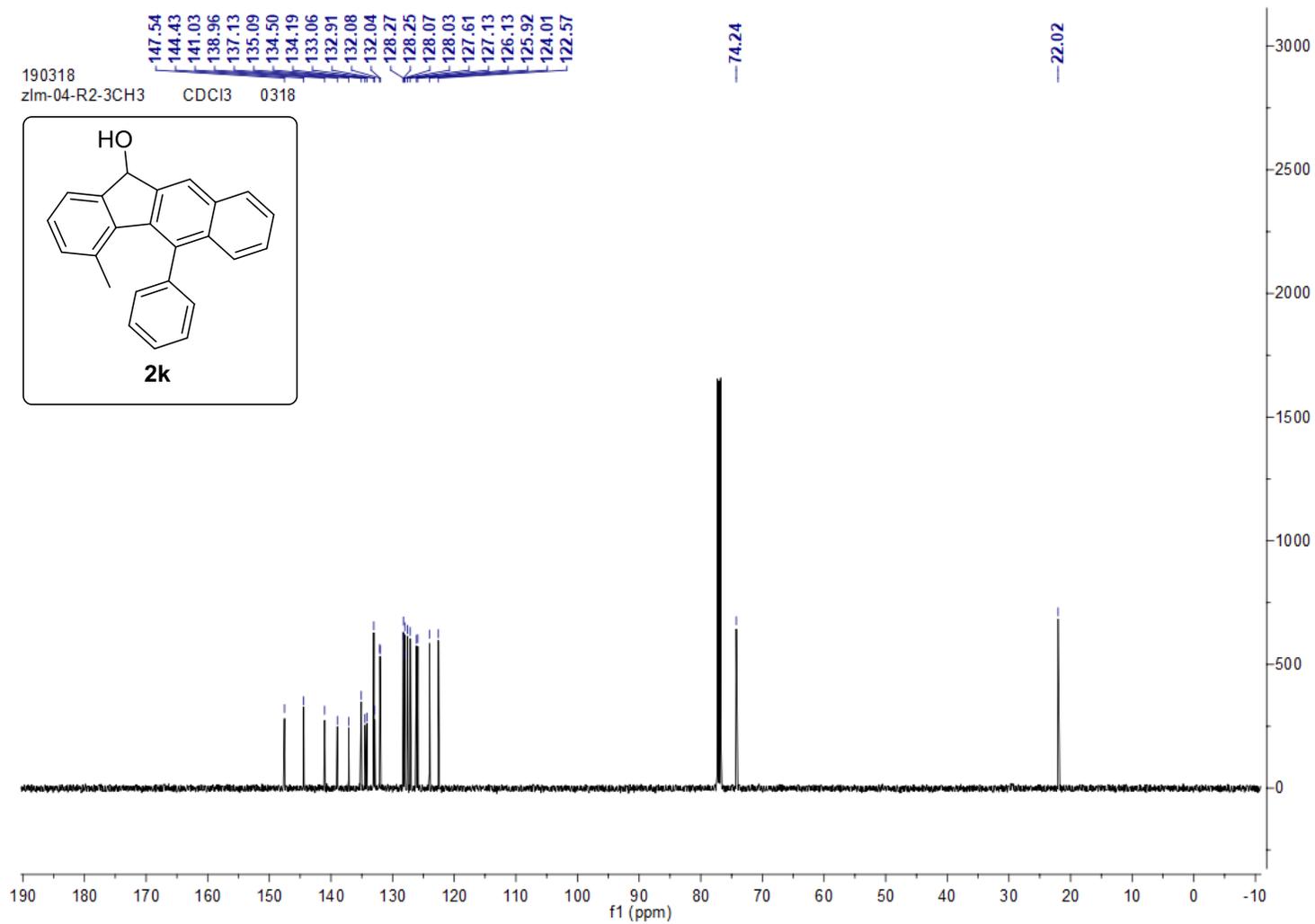
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2j



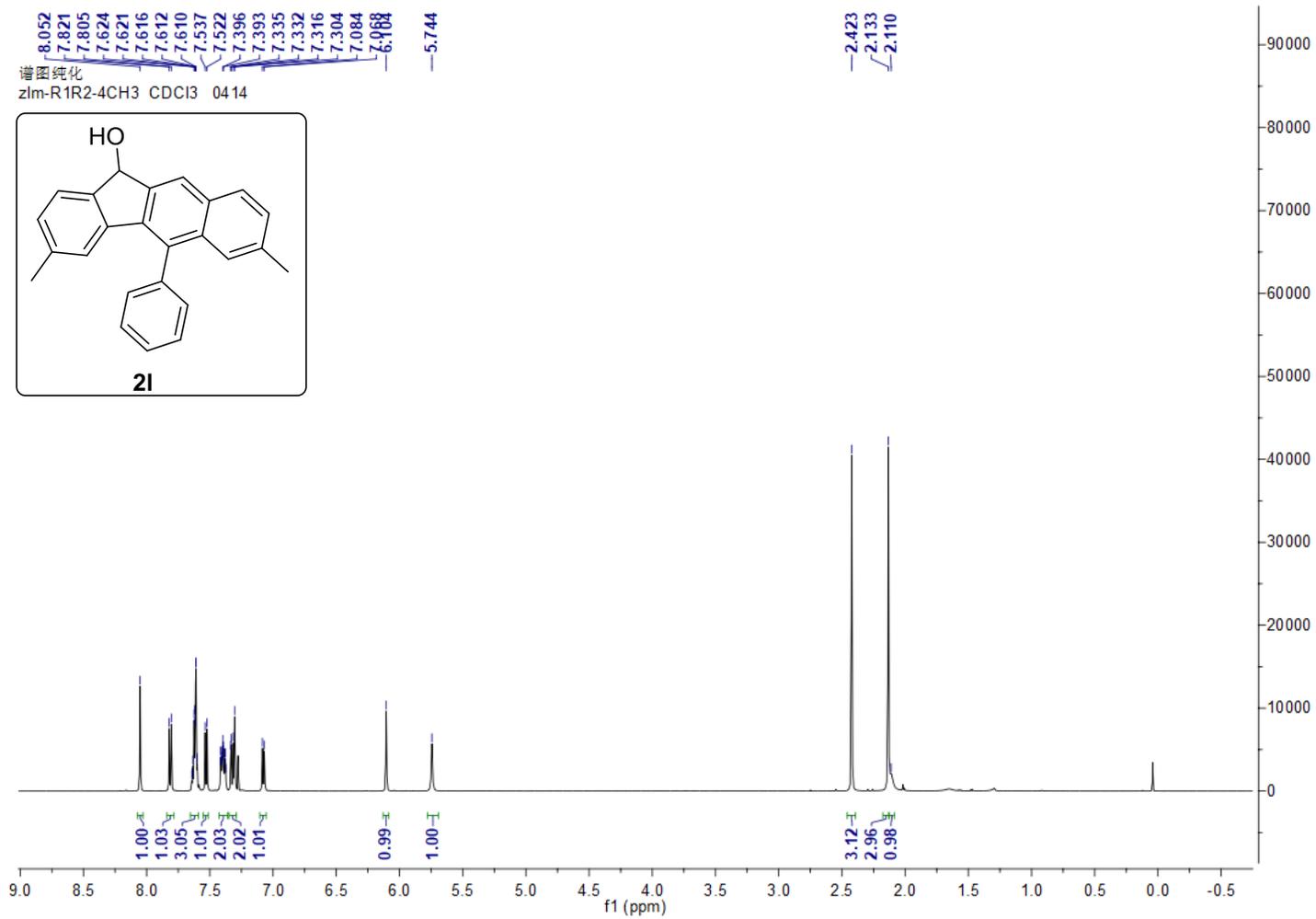
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2k



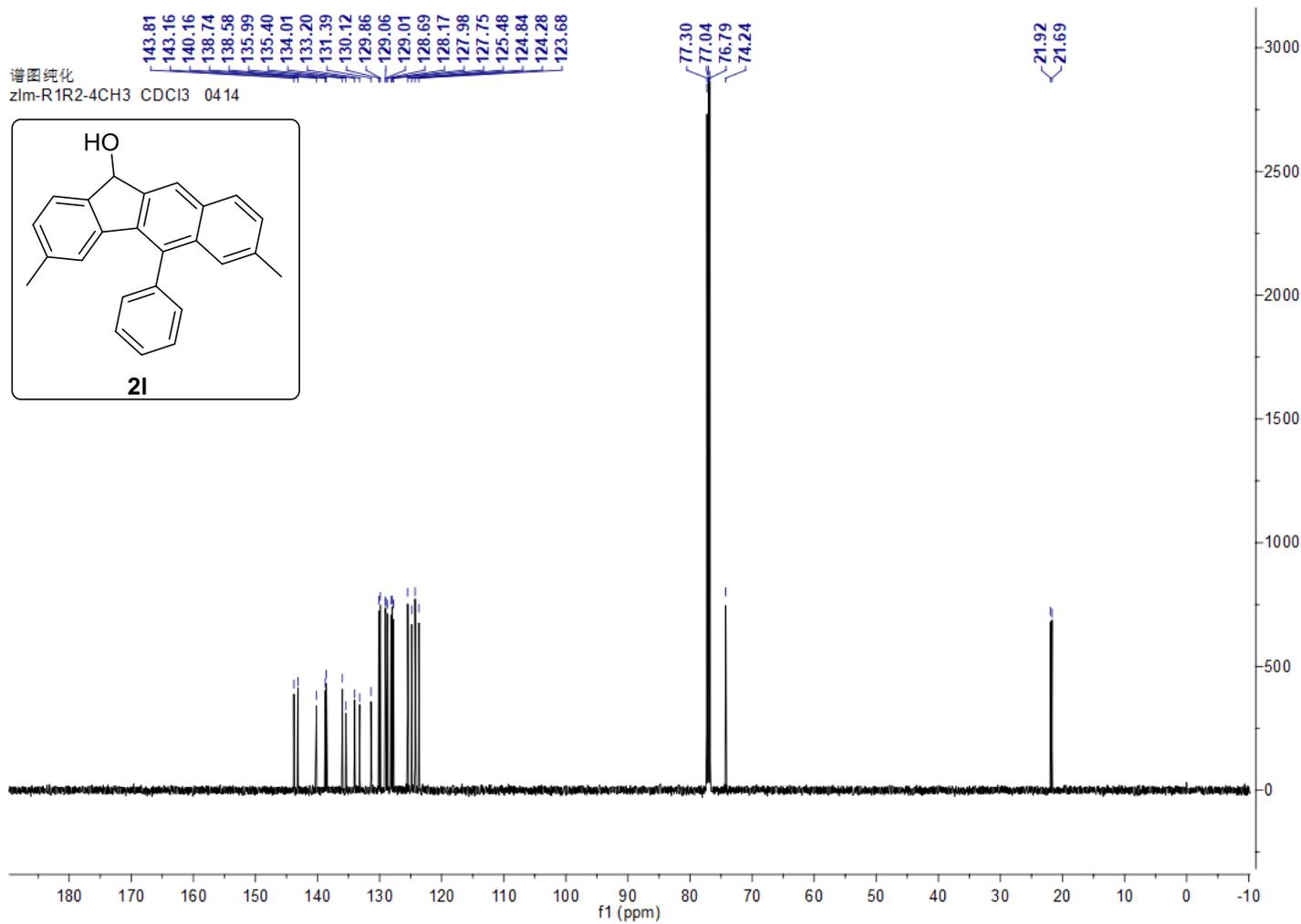
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2k



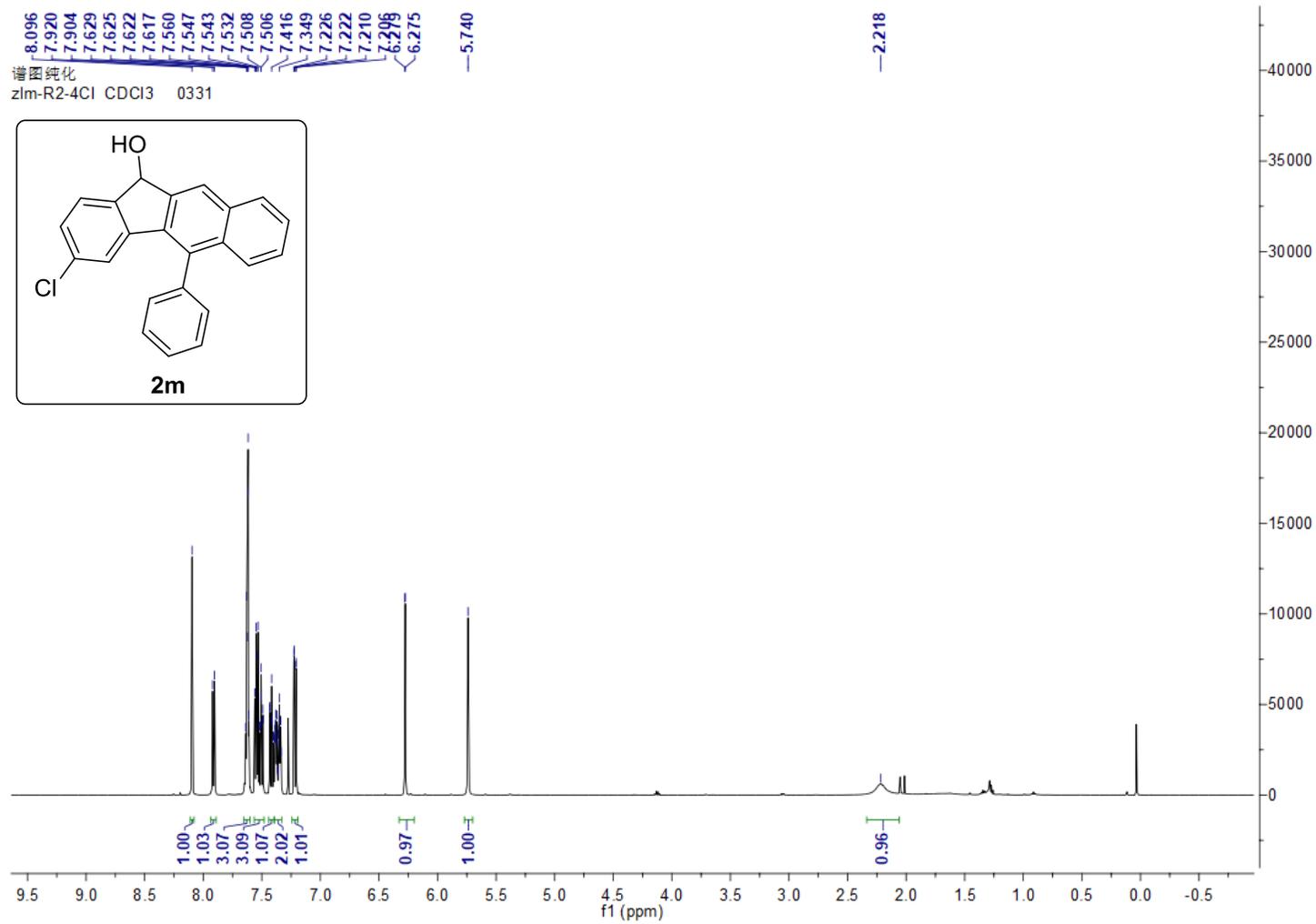
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 21



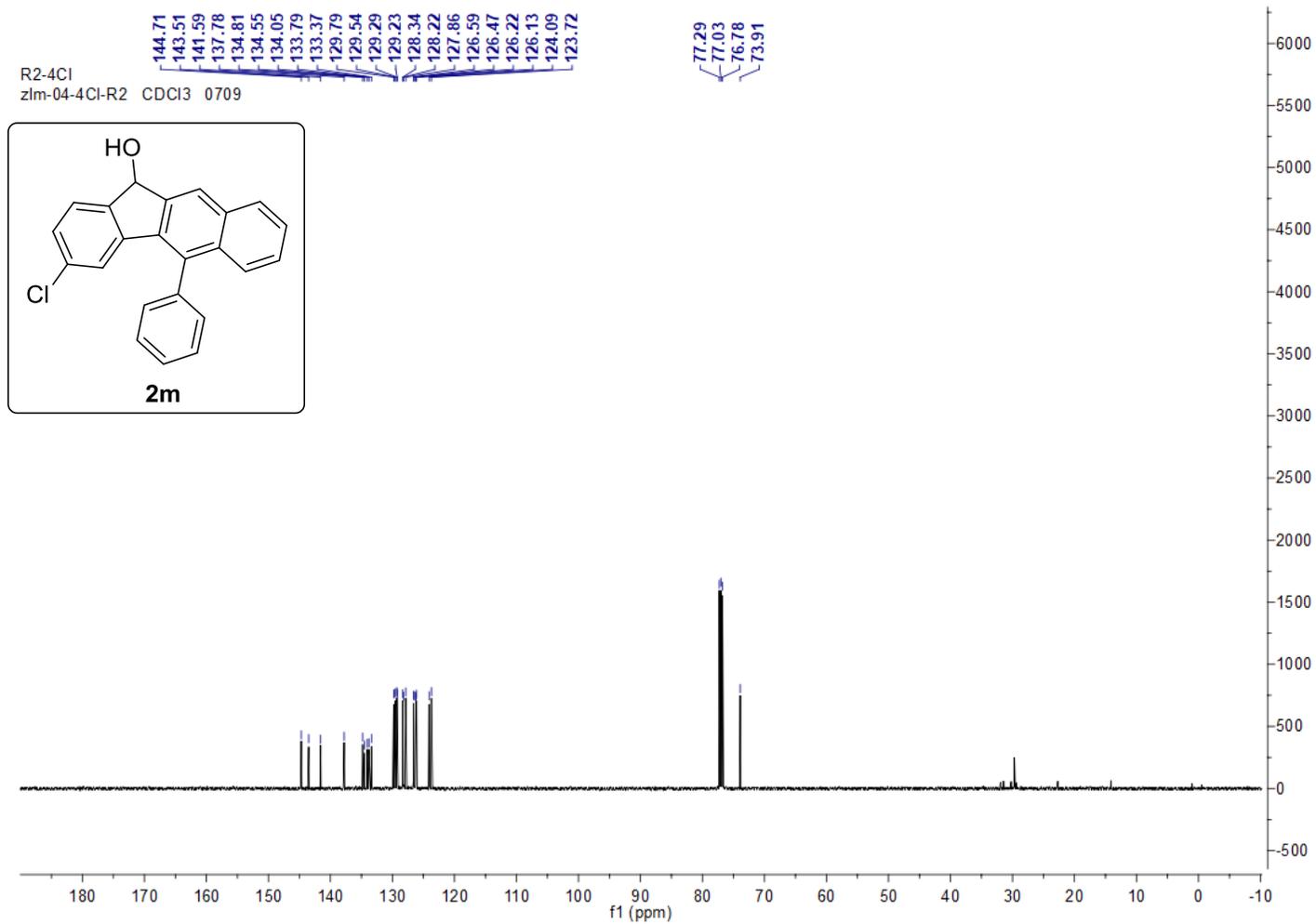
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 21



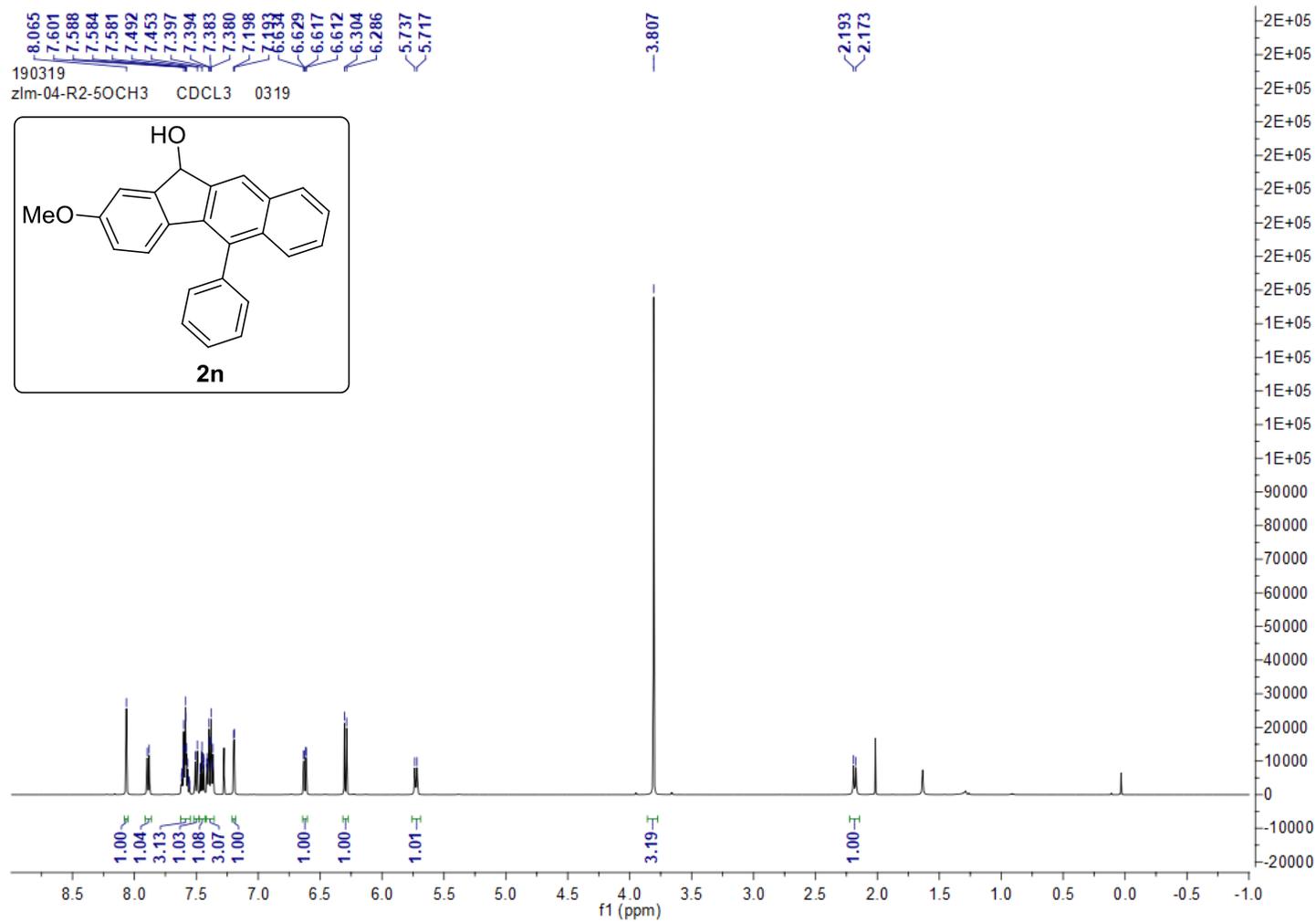
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2m



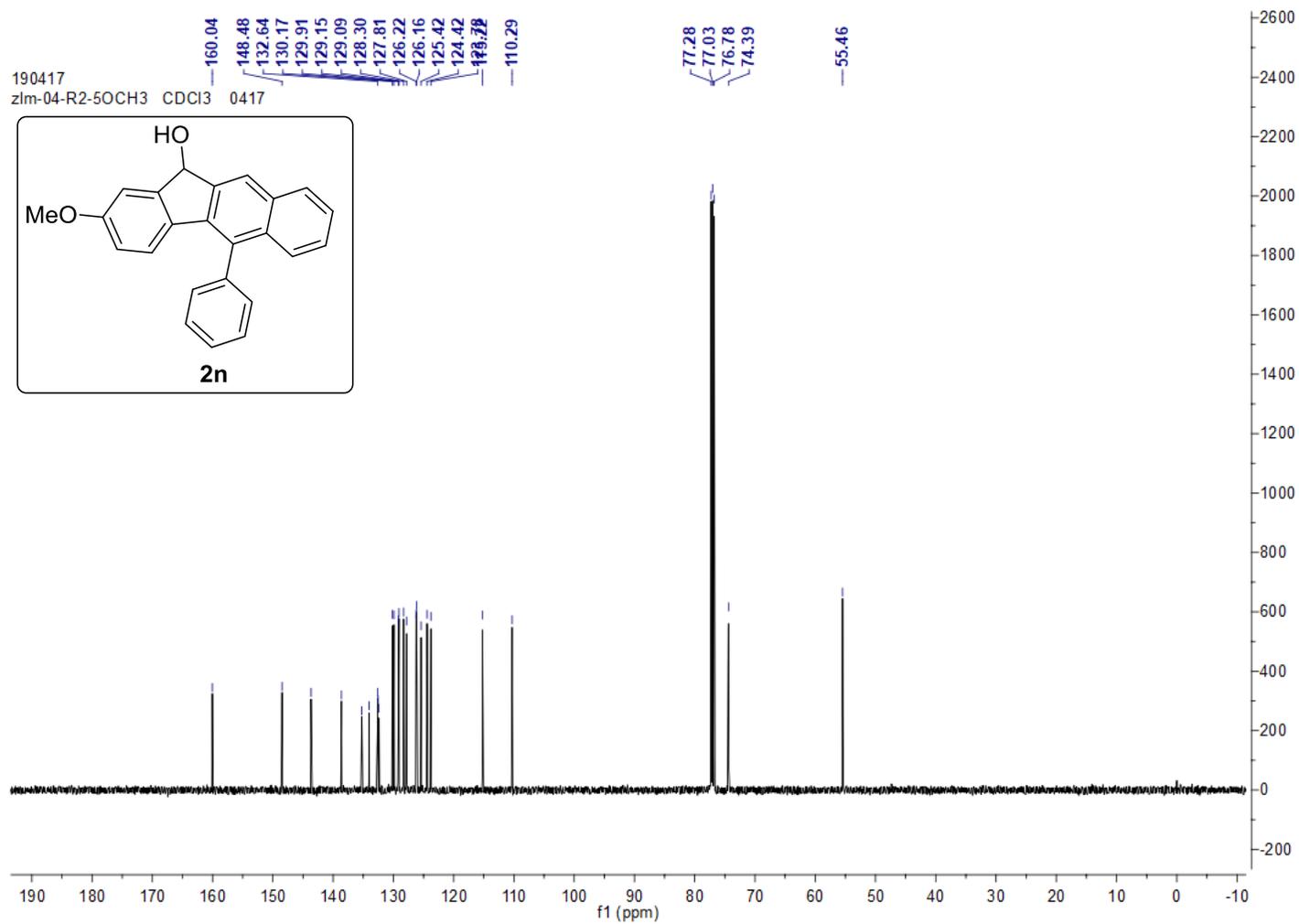
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2m



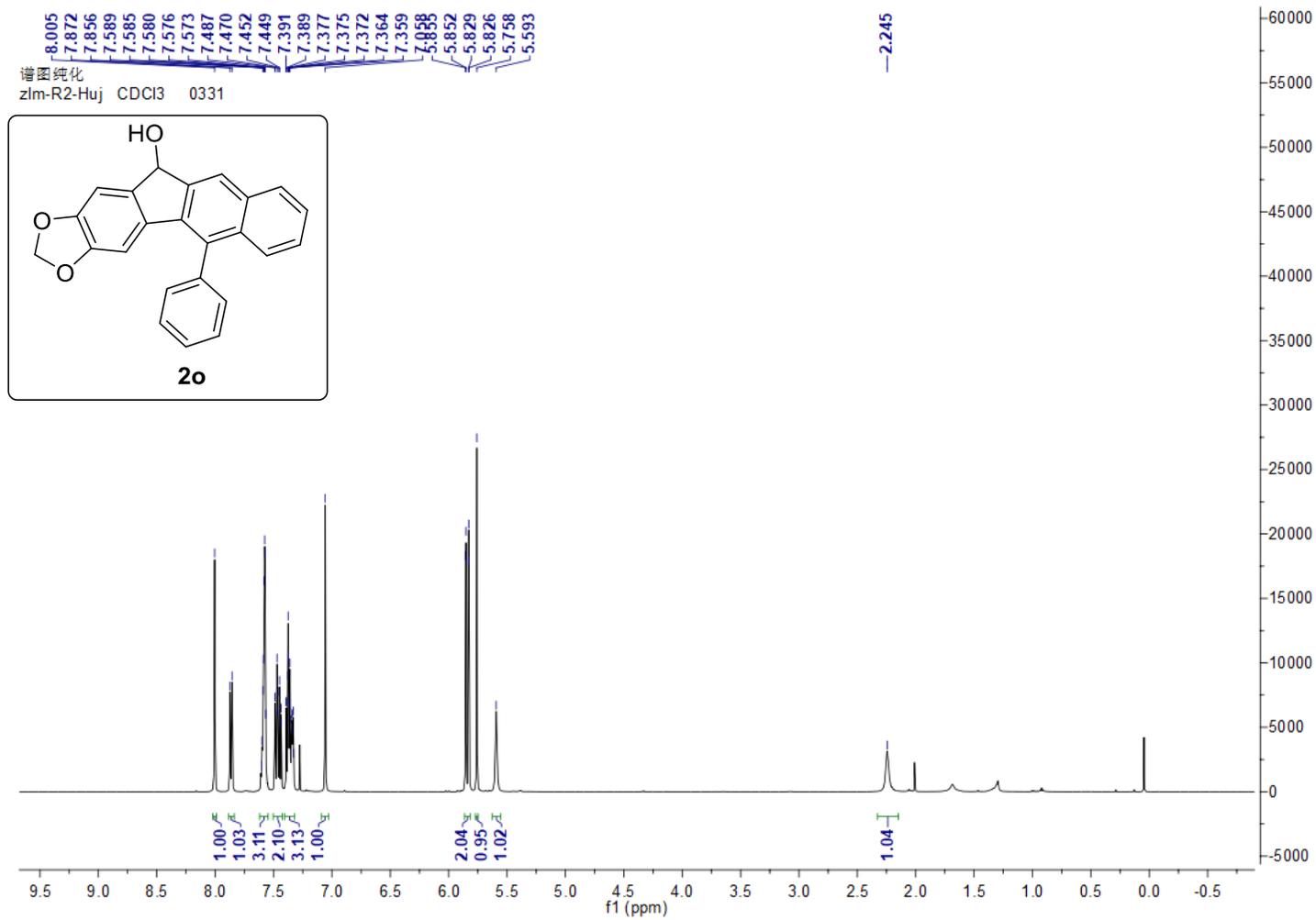
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2n



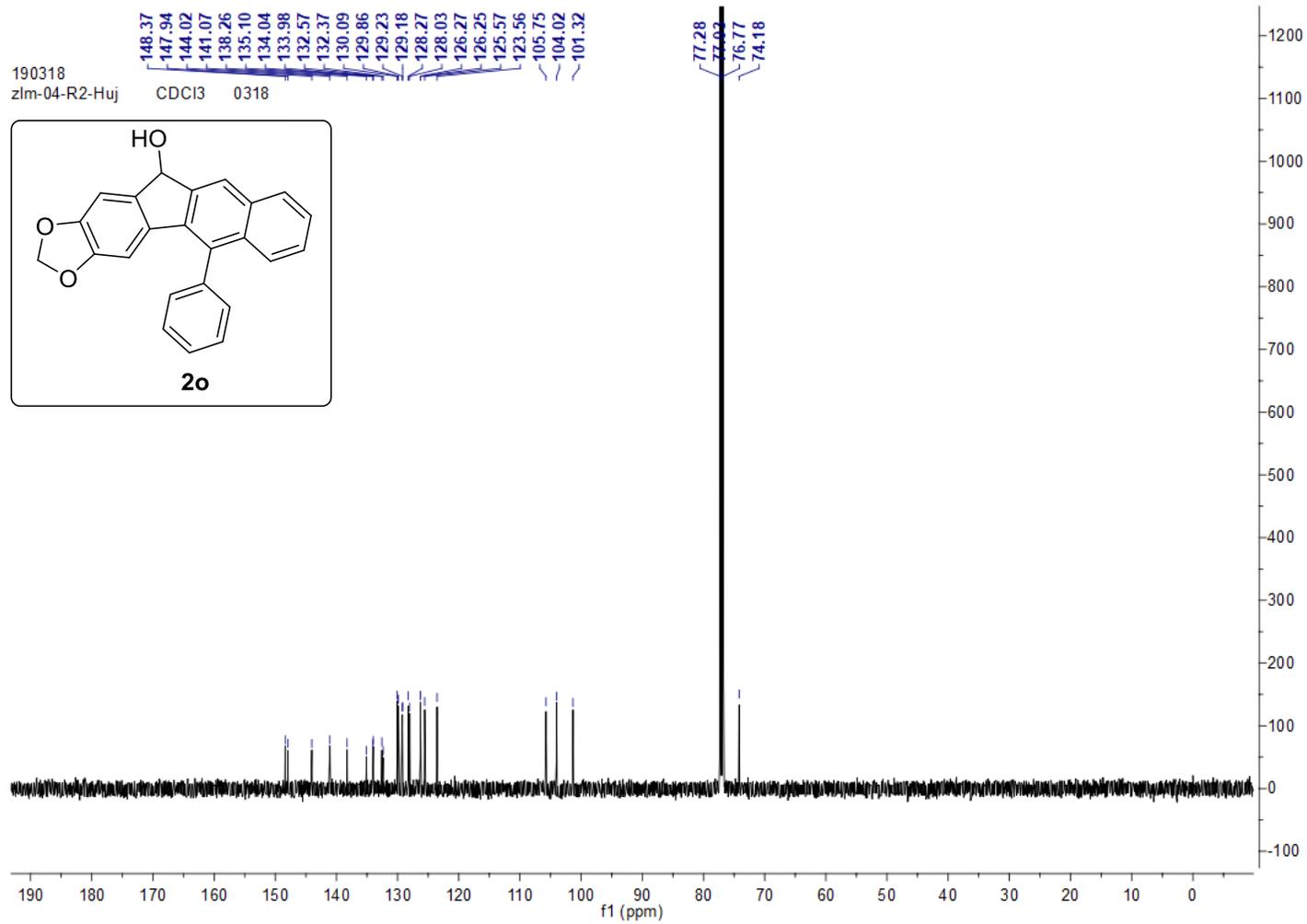
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2n



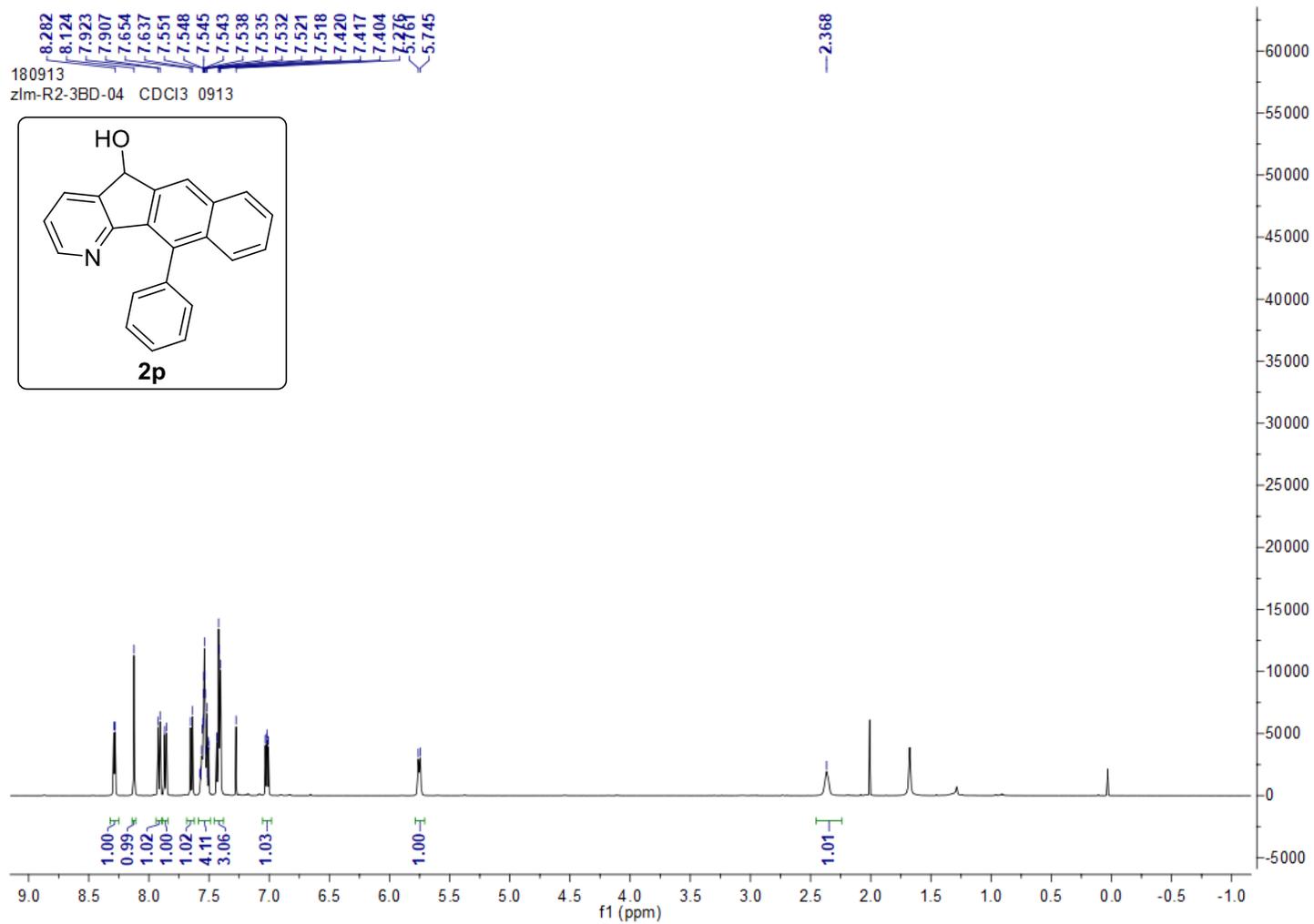
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2o



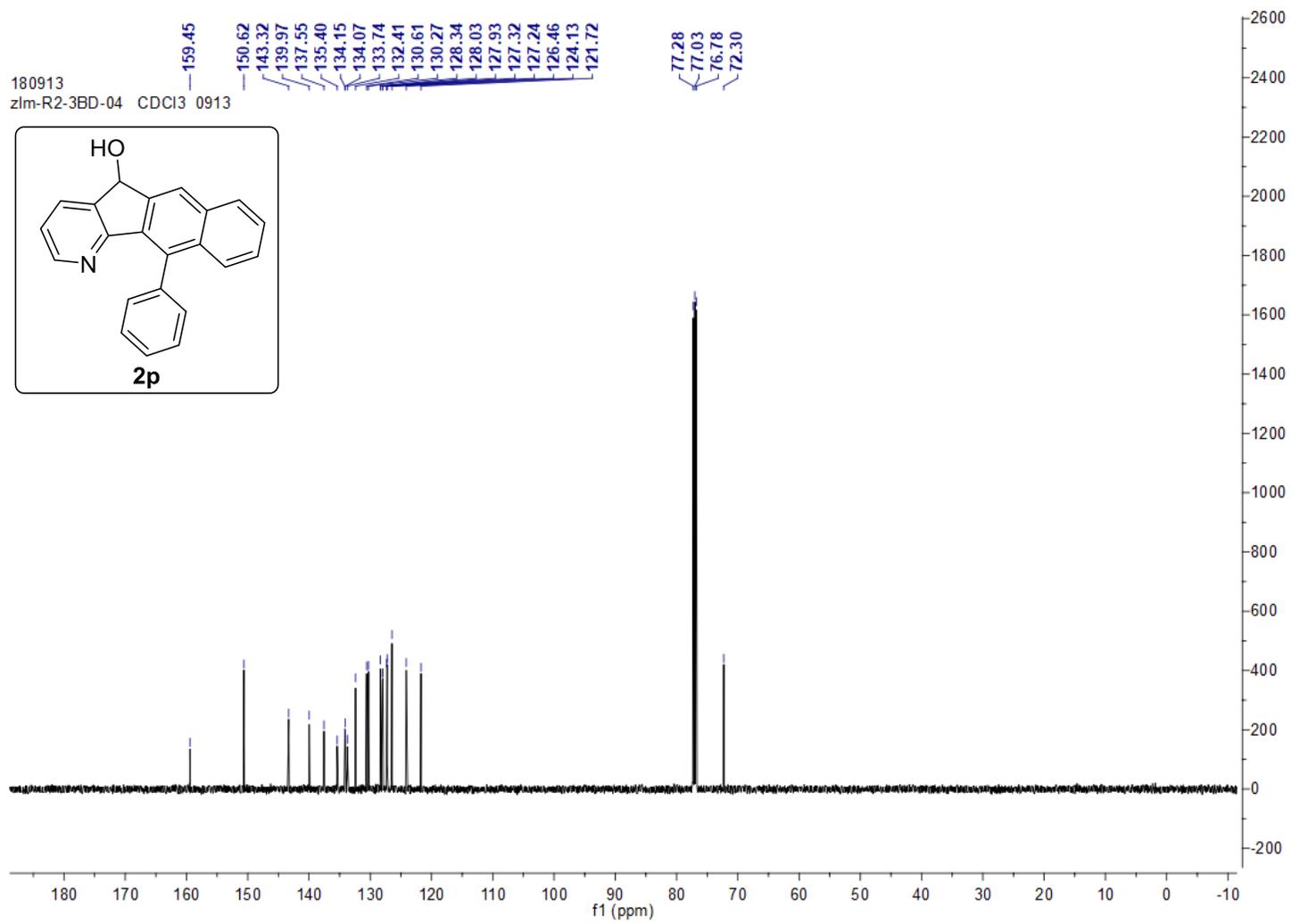
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2o



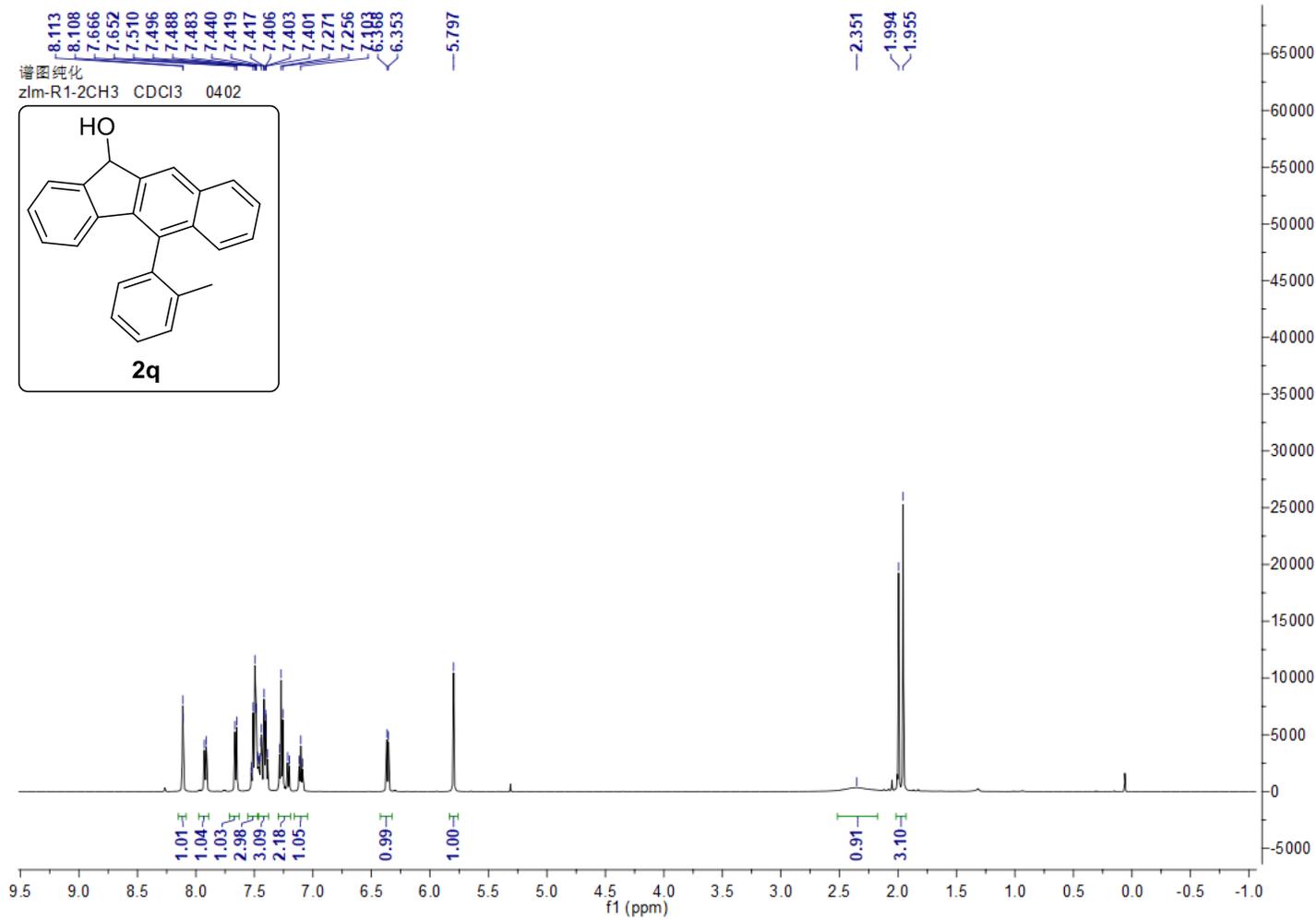
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2p



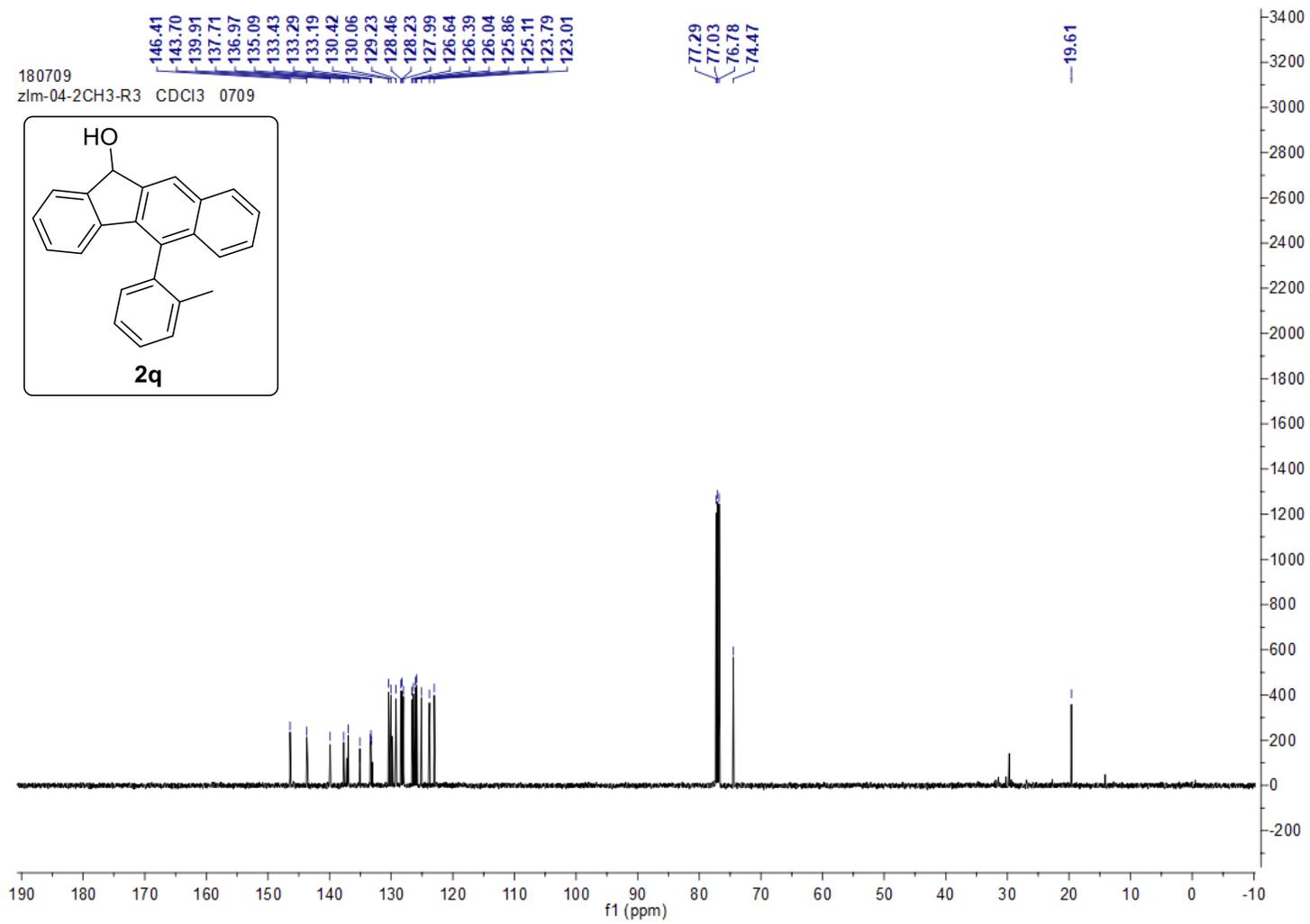
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2p



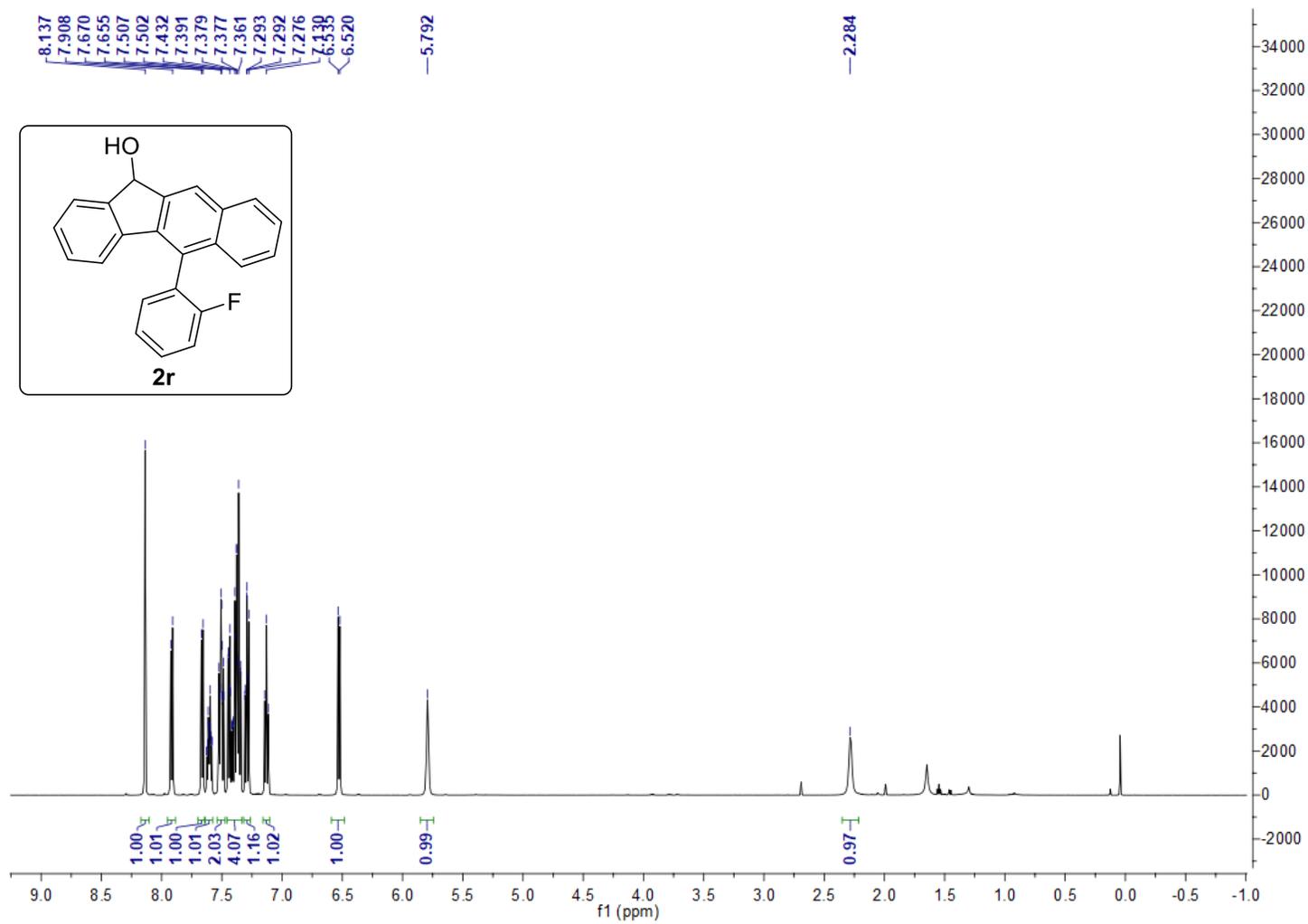
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2q



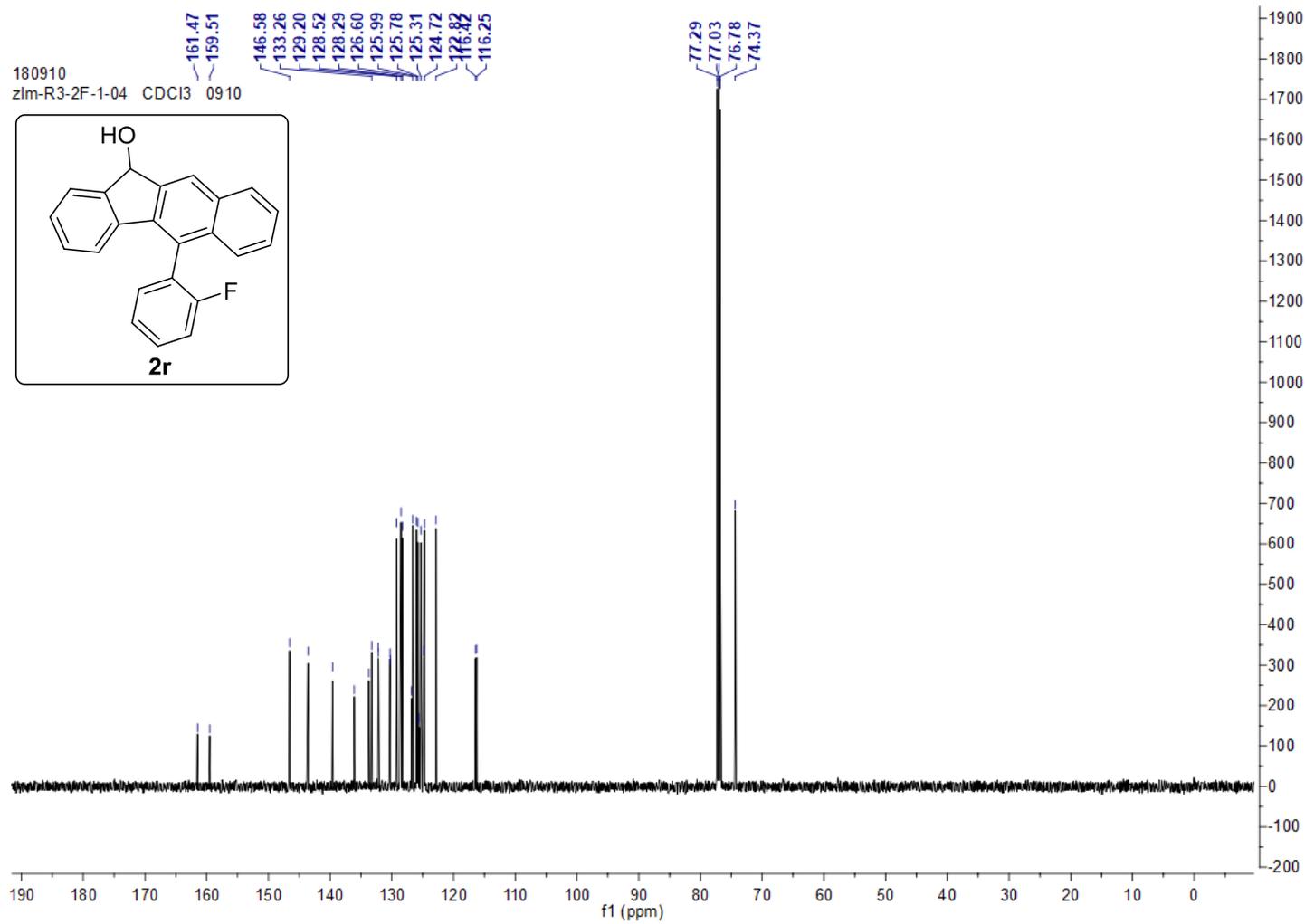
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2q



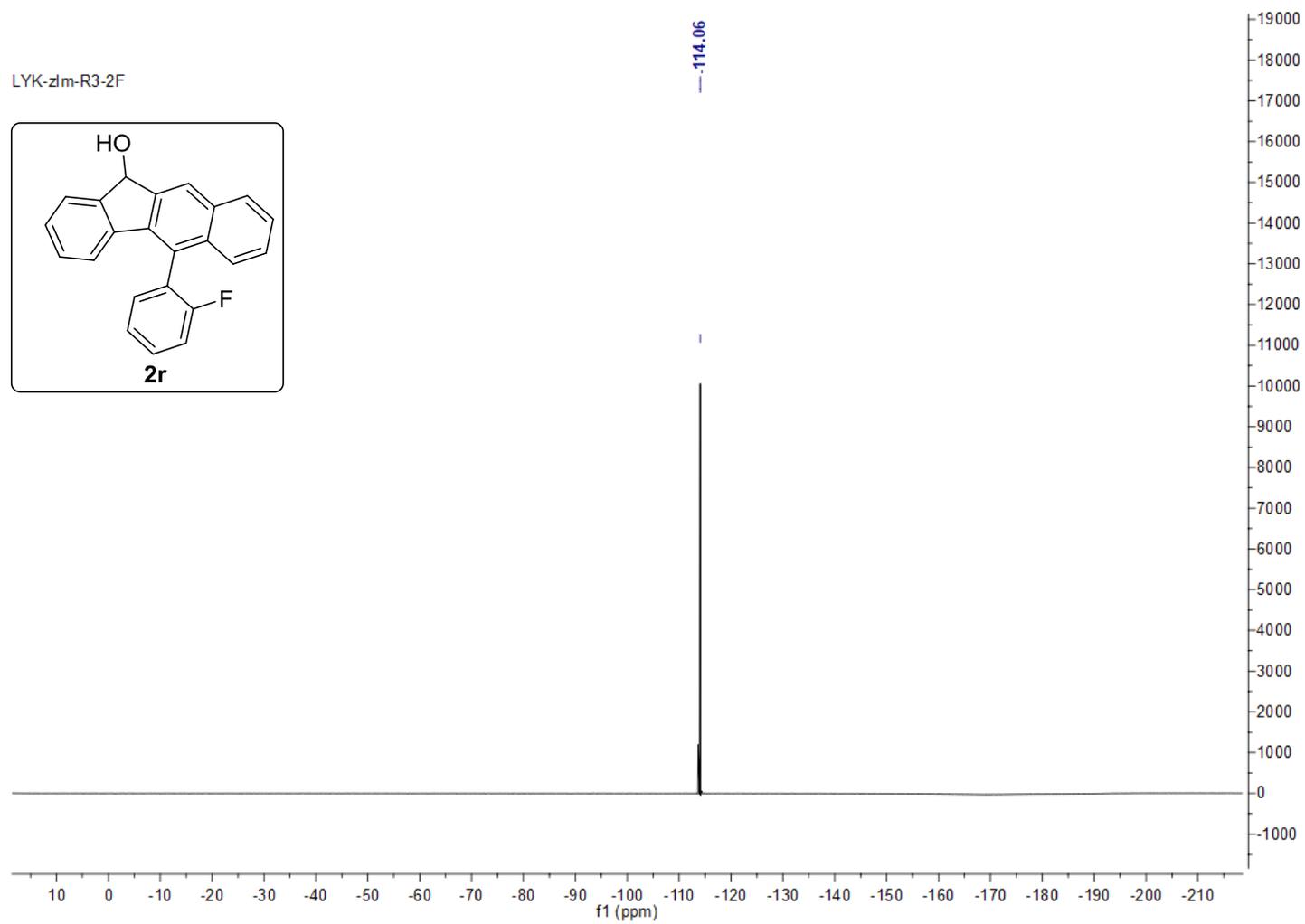
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2r



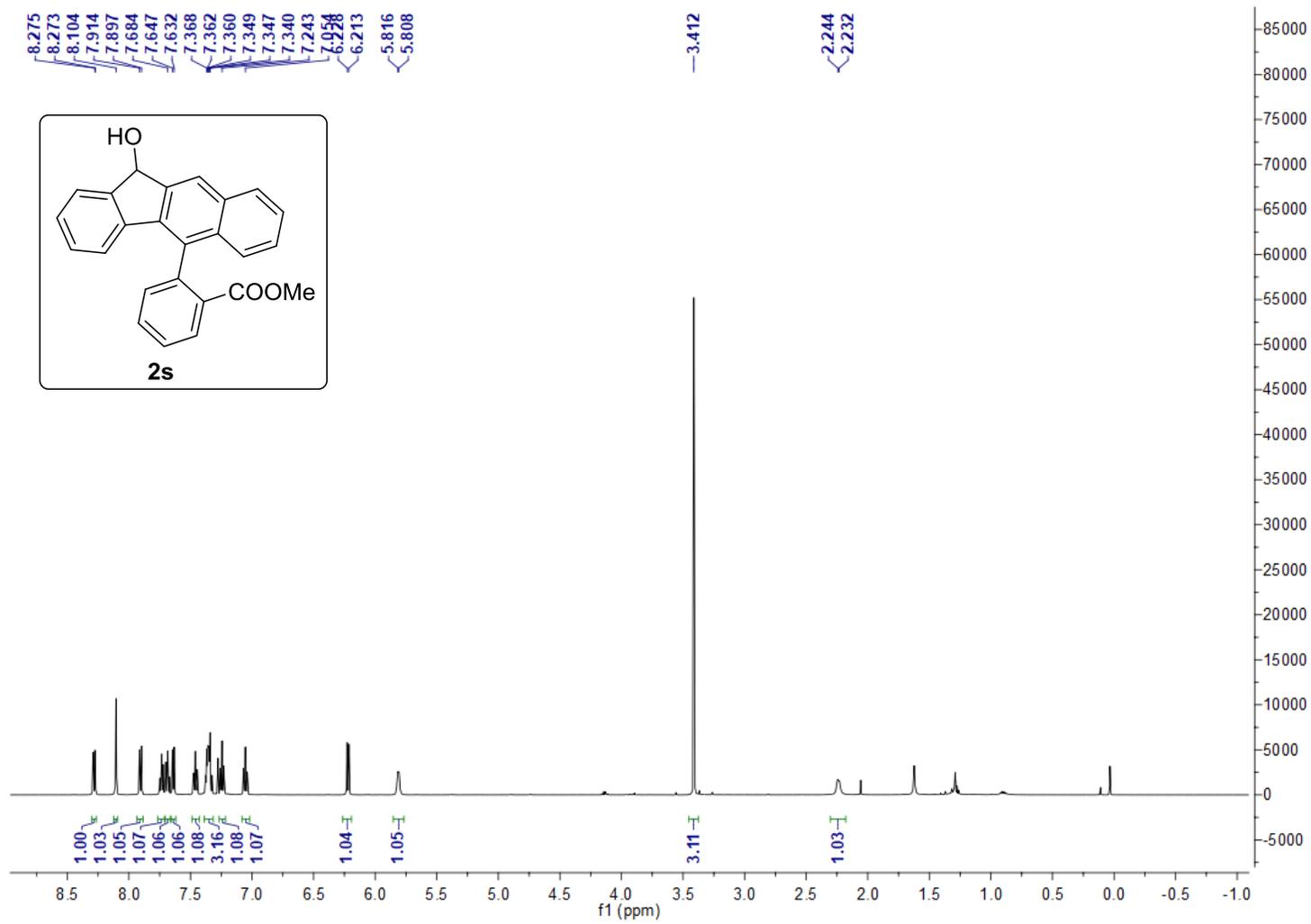
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2r



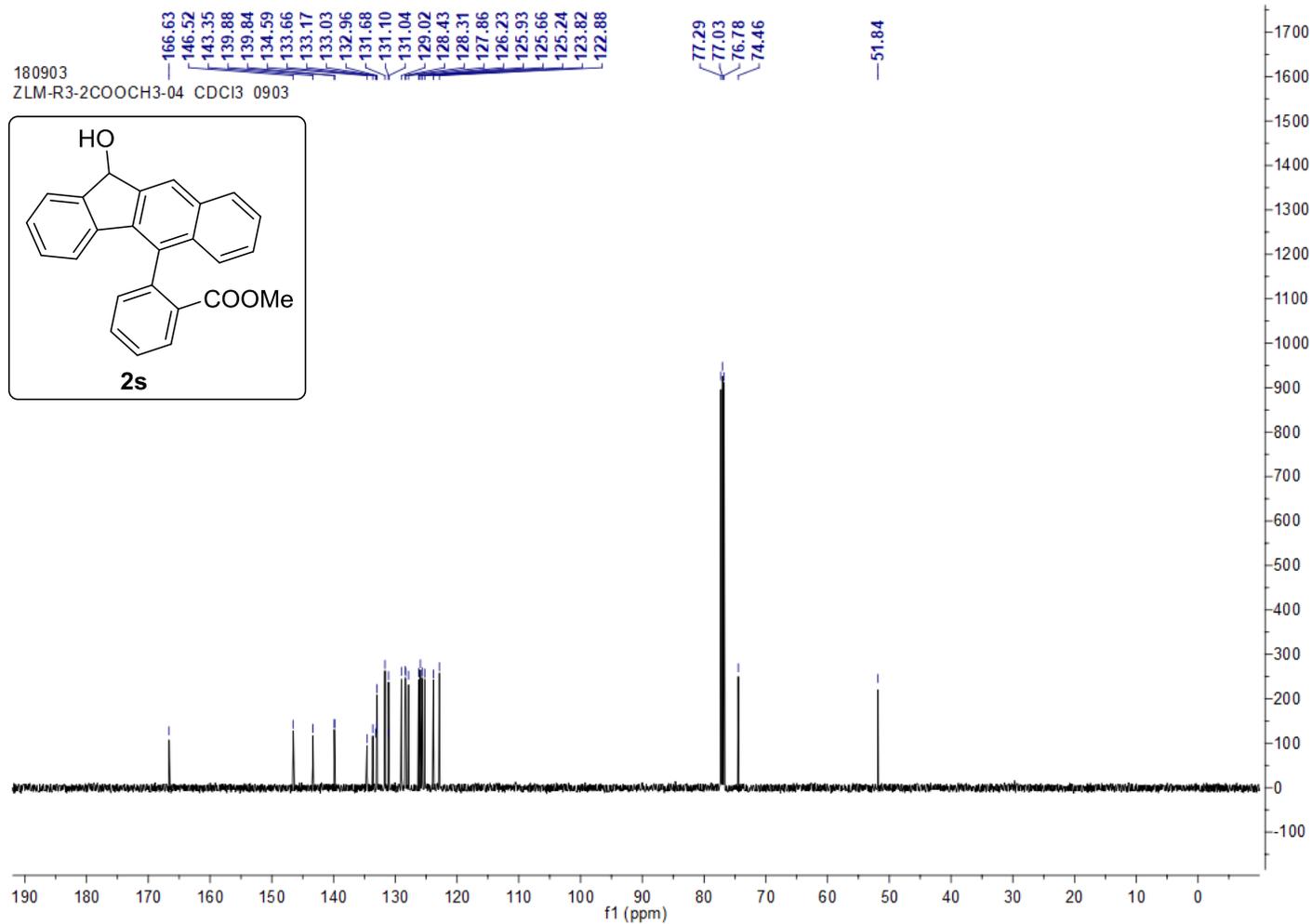
**<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) spectrum of compound 2r**



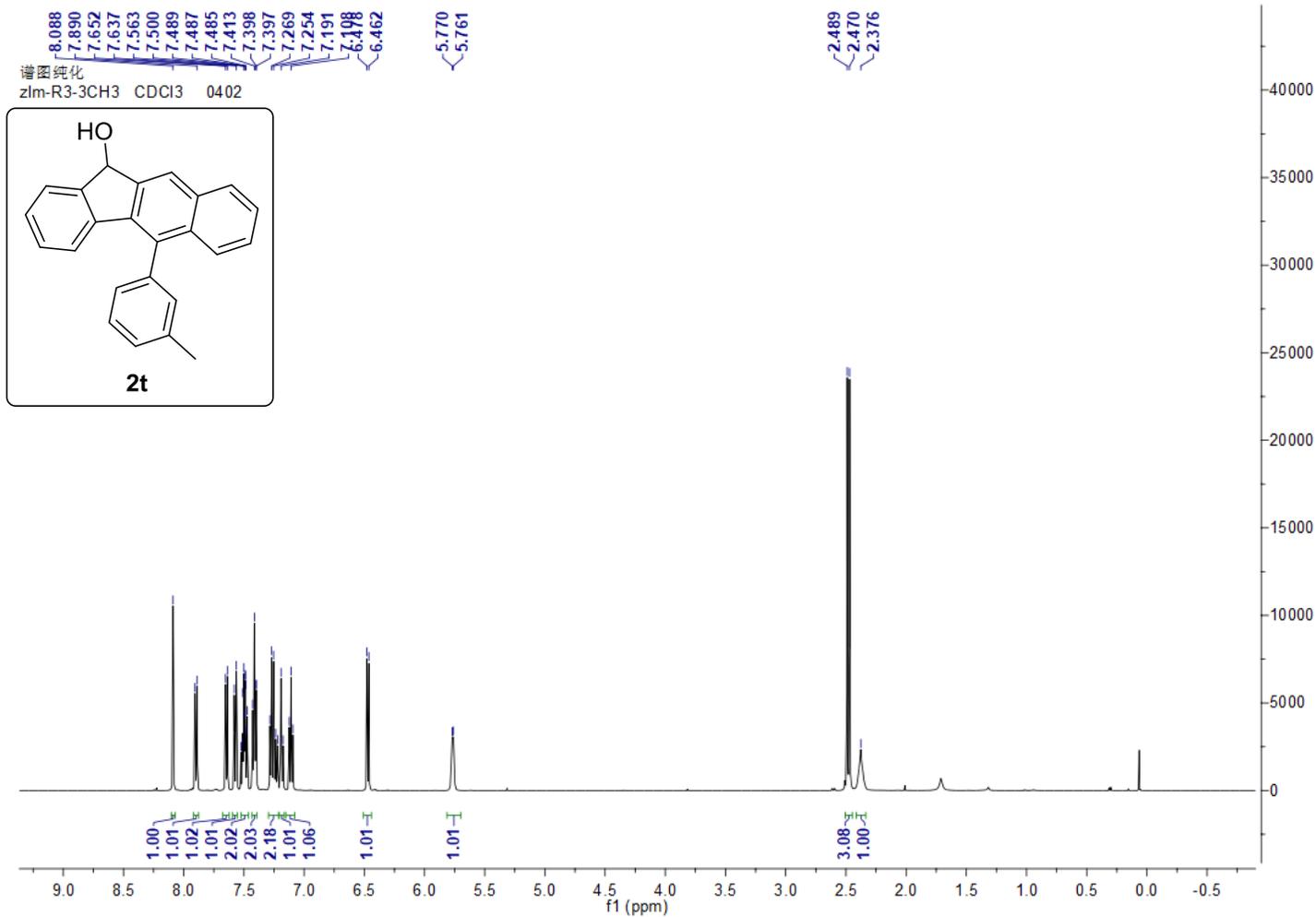
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2s



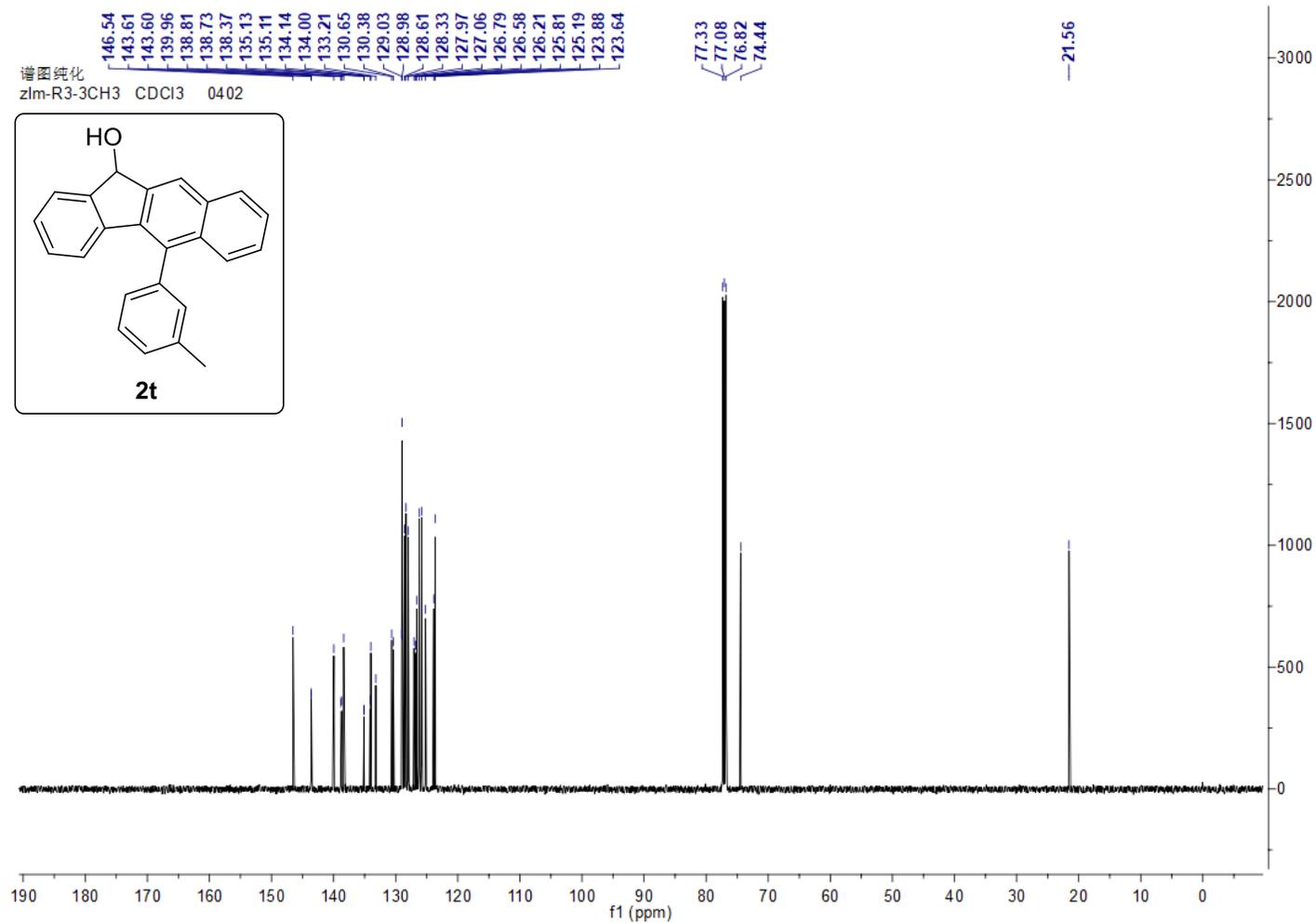
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2s



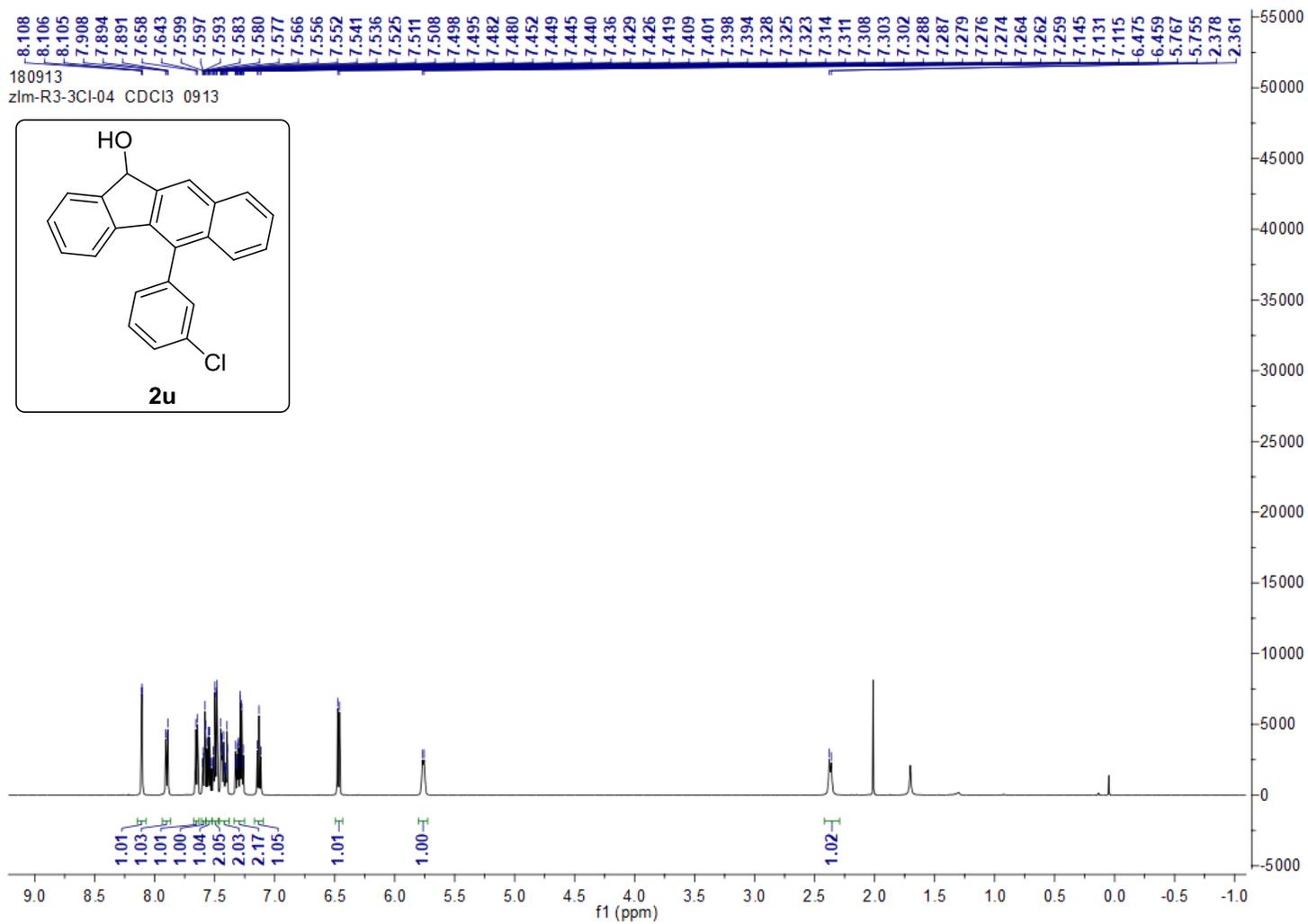
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2t



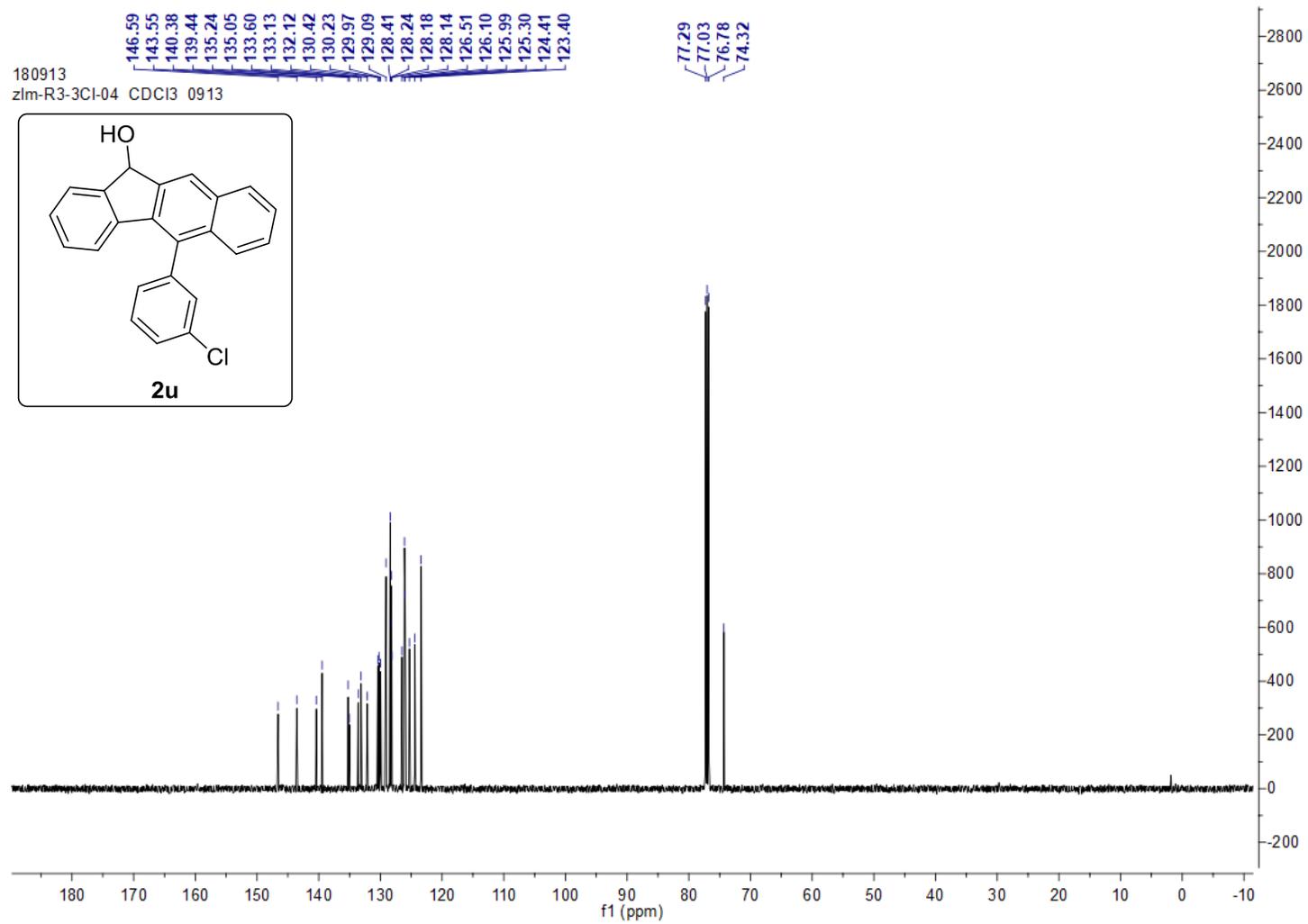
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2t



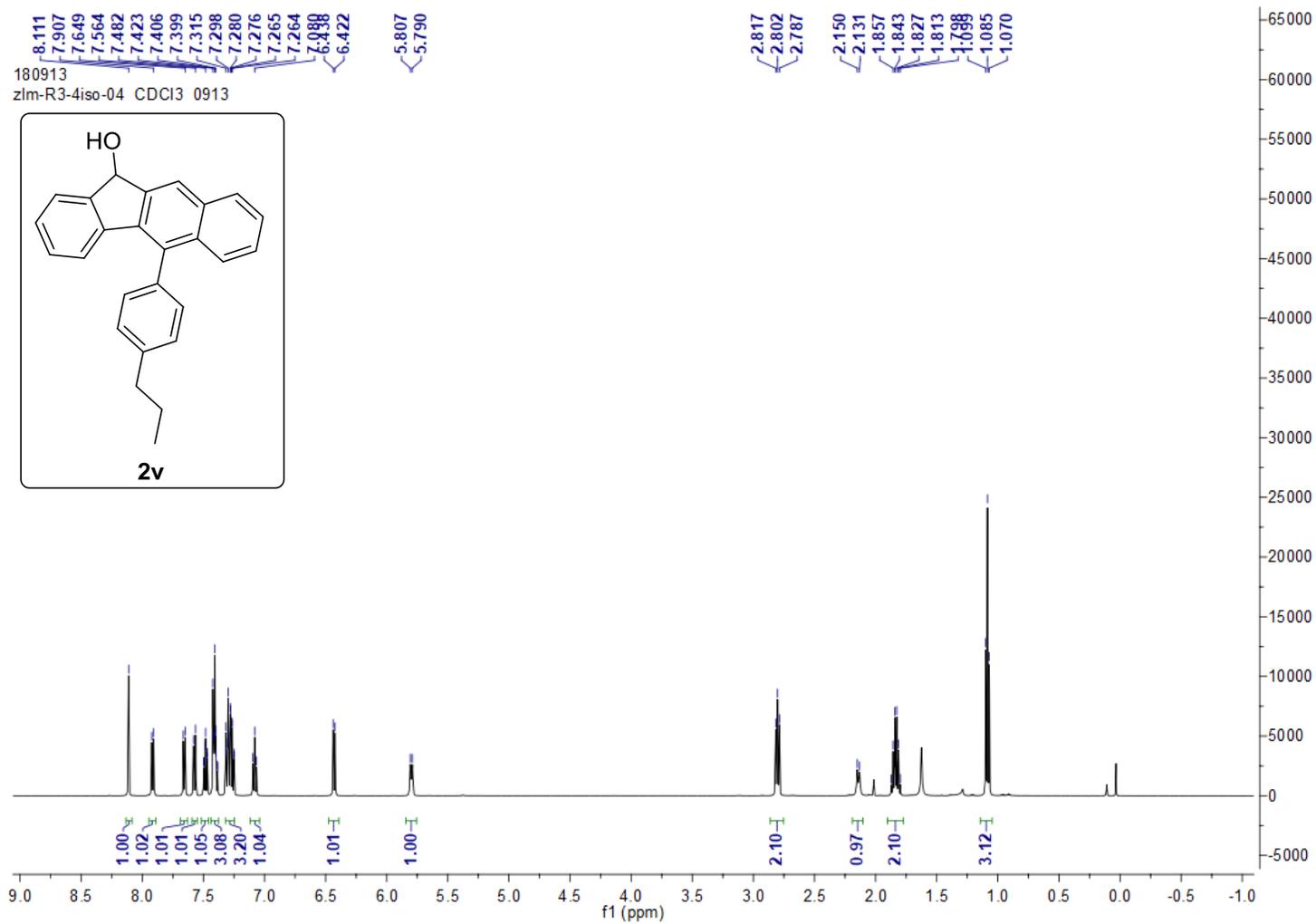
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2u



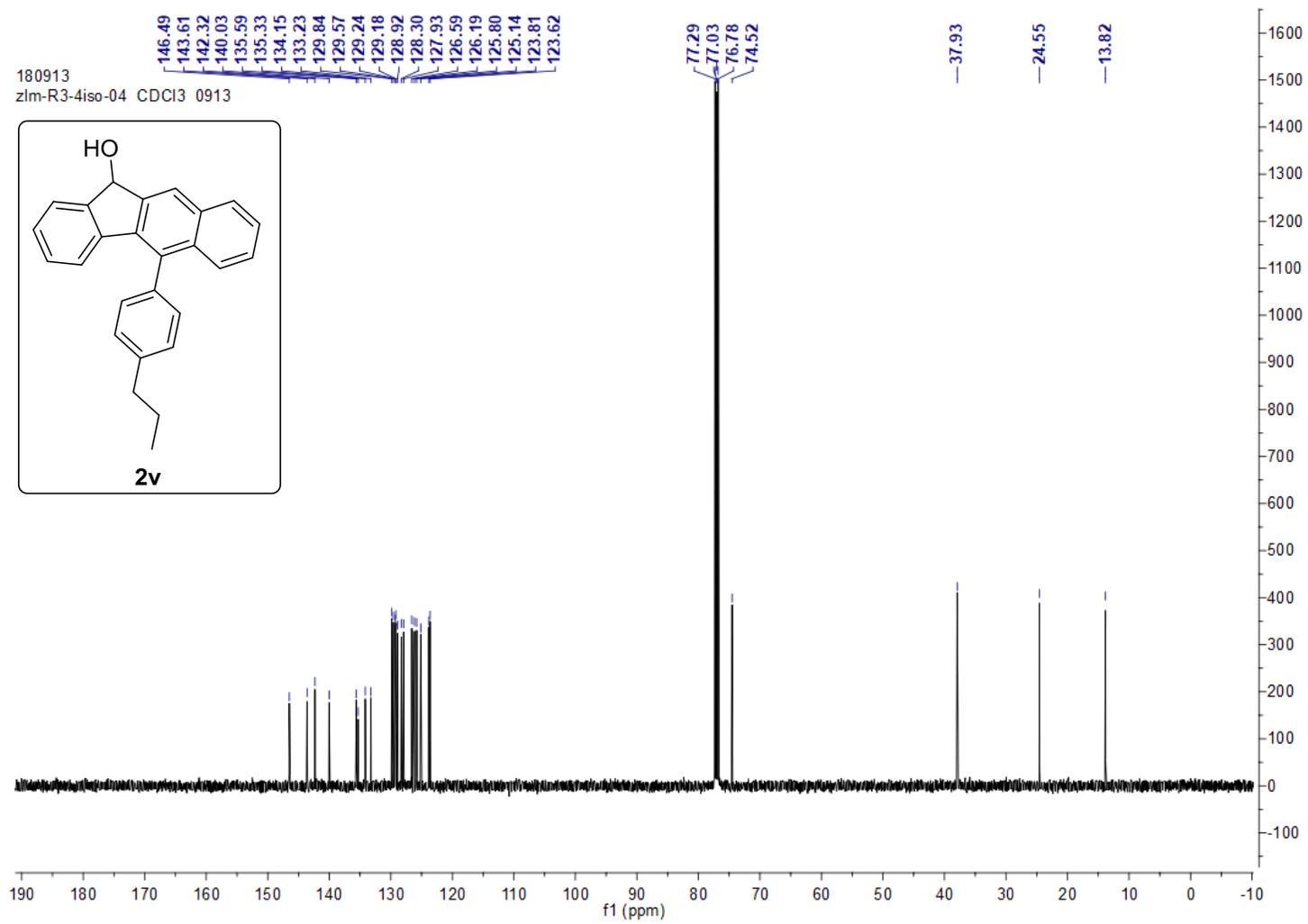
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2u



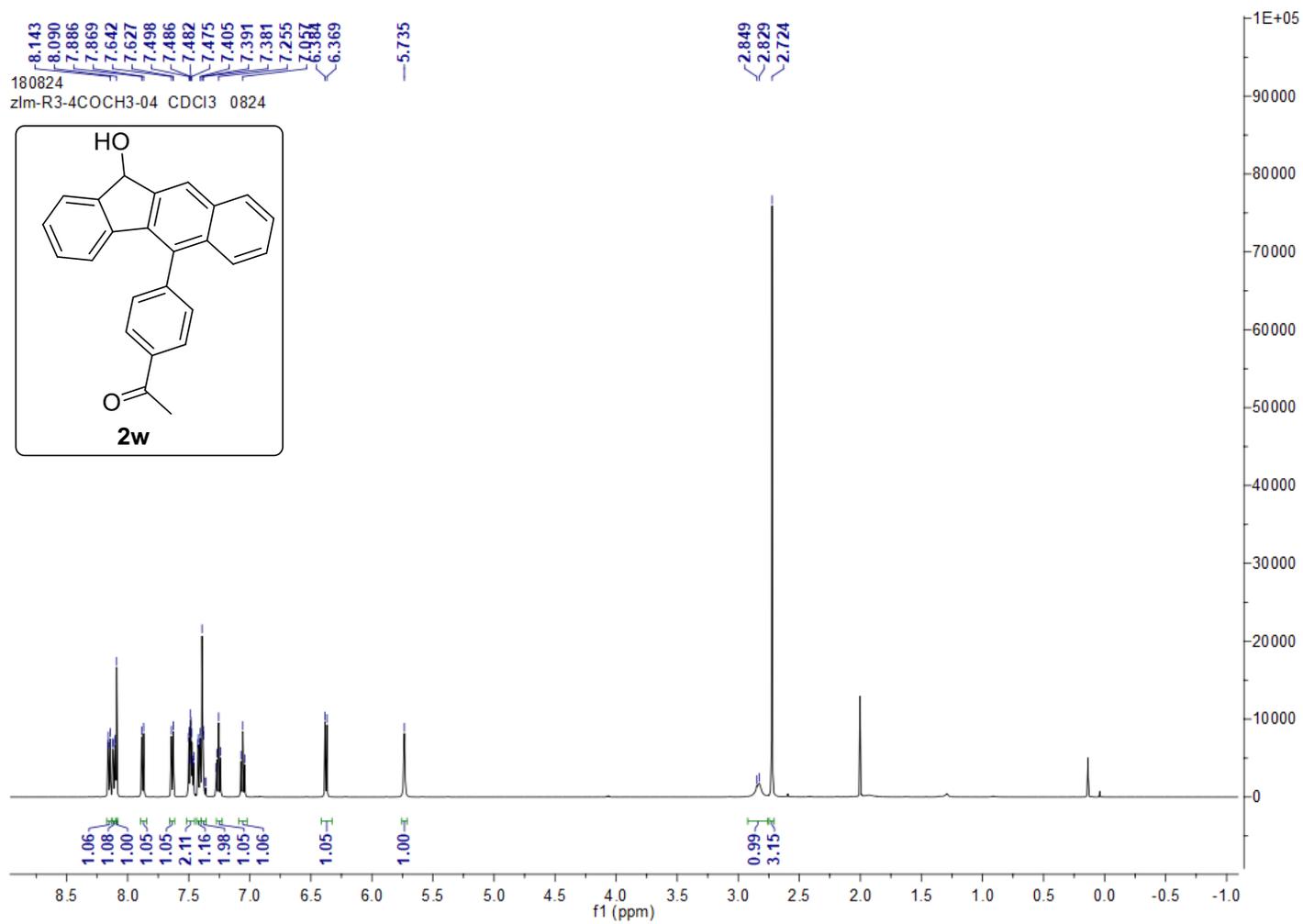
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2v



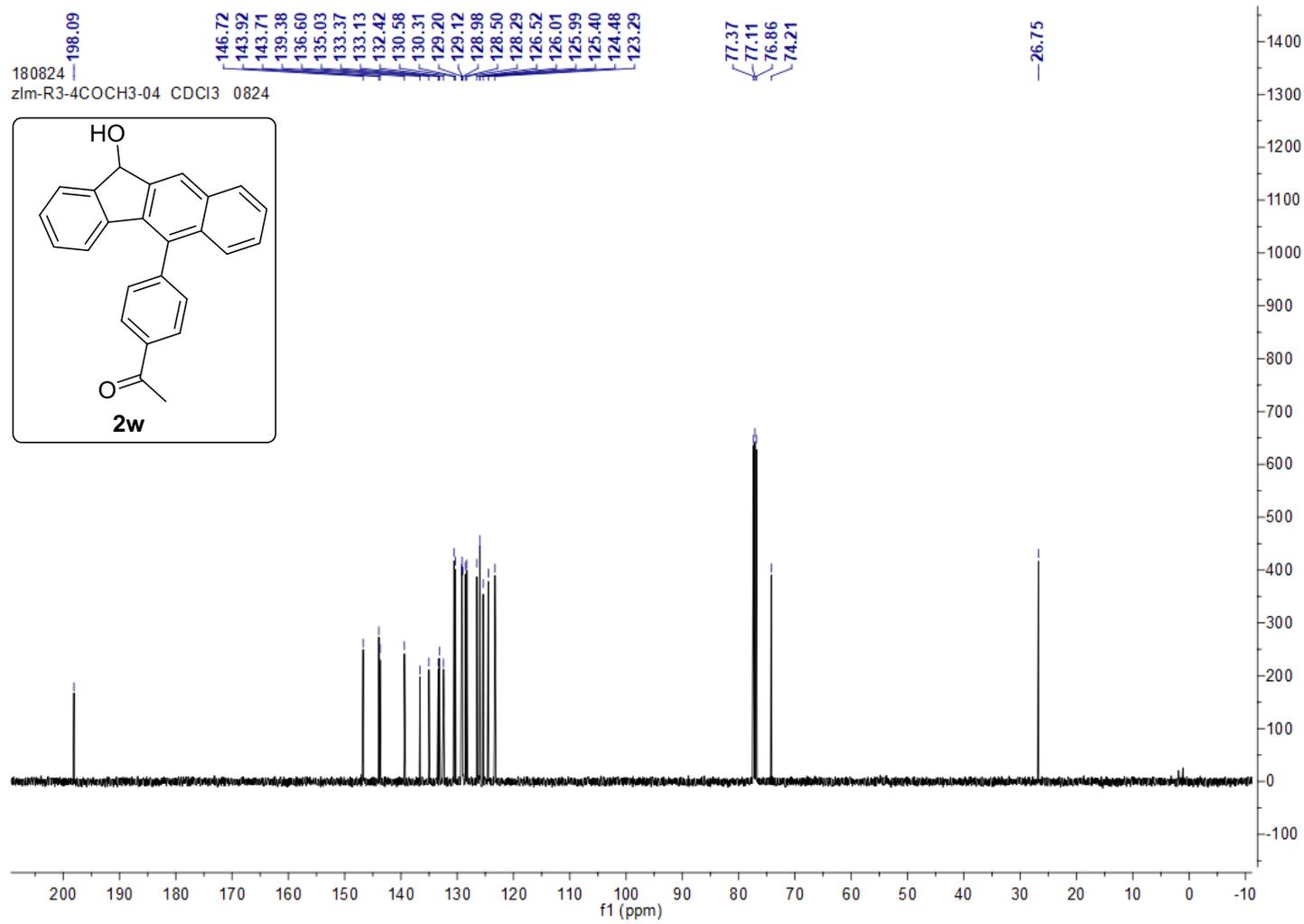
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2v



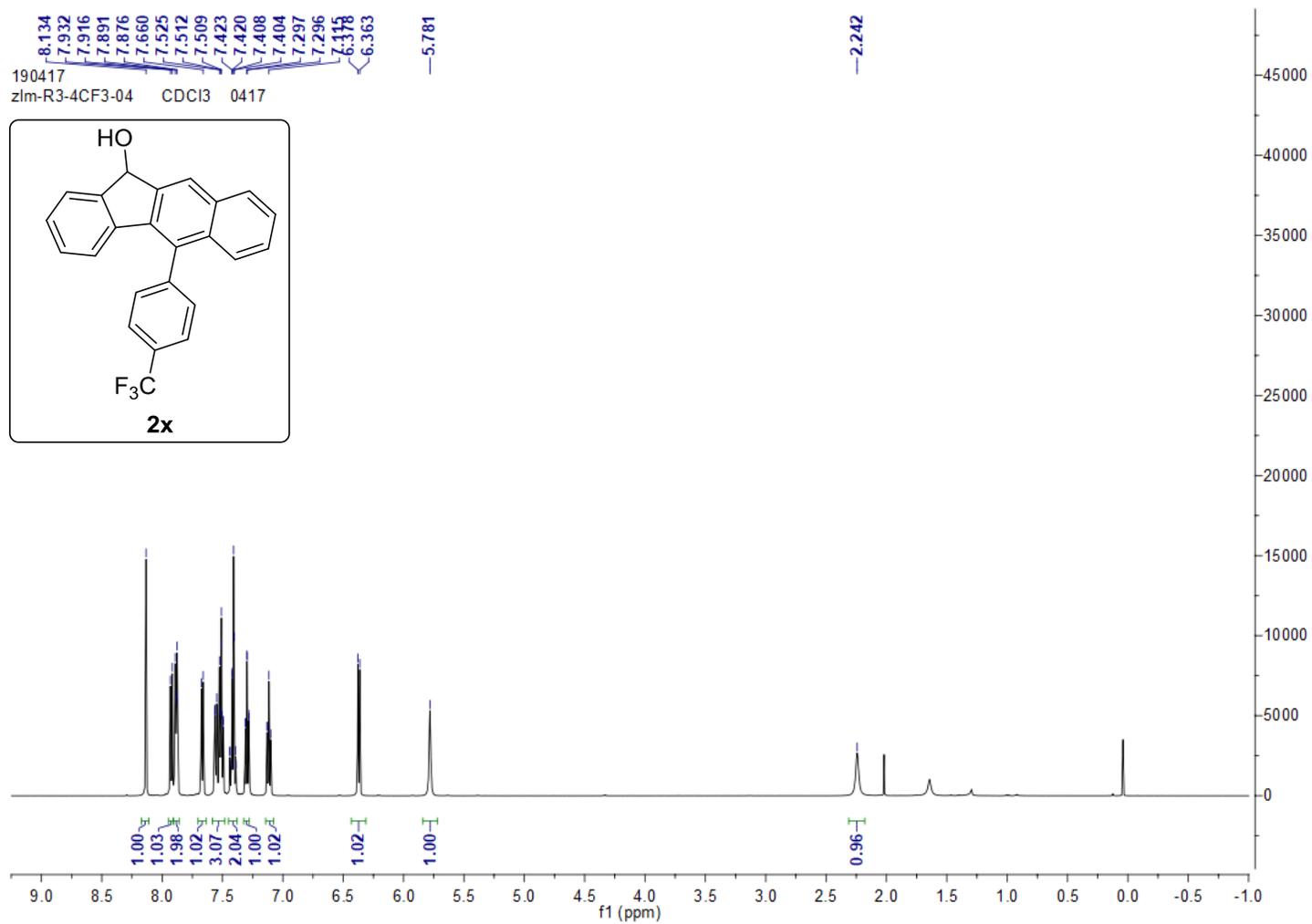
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2w



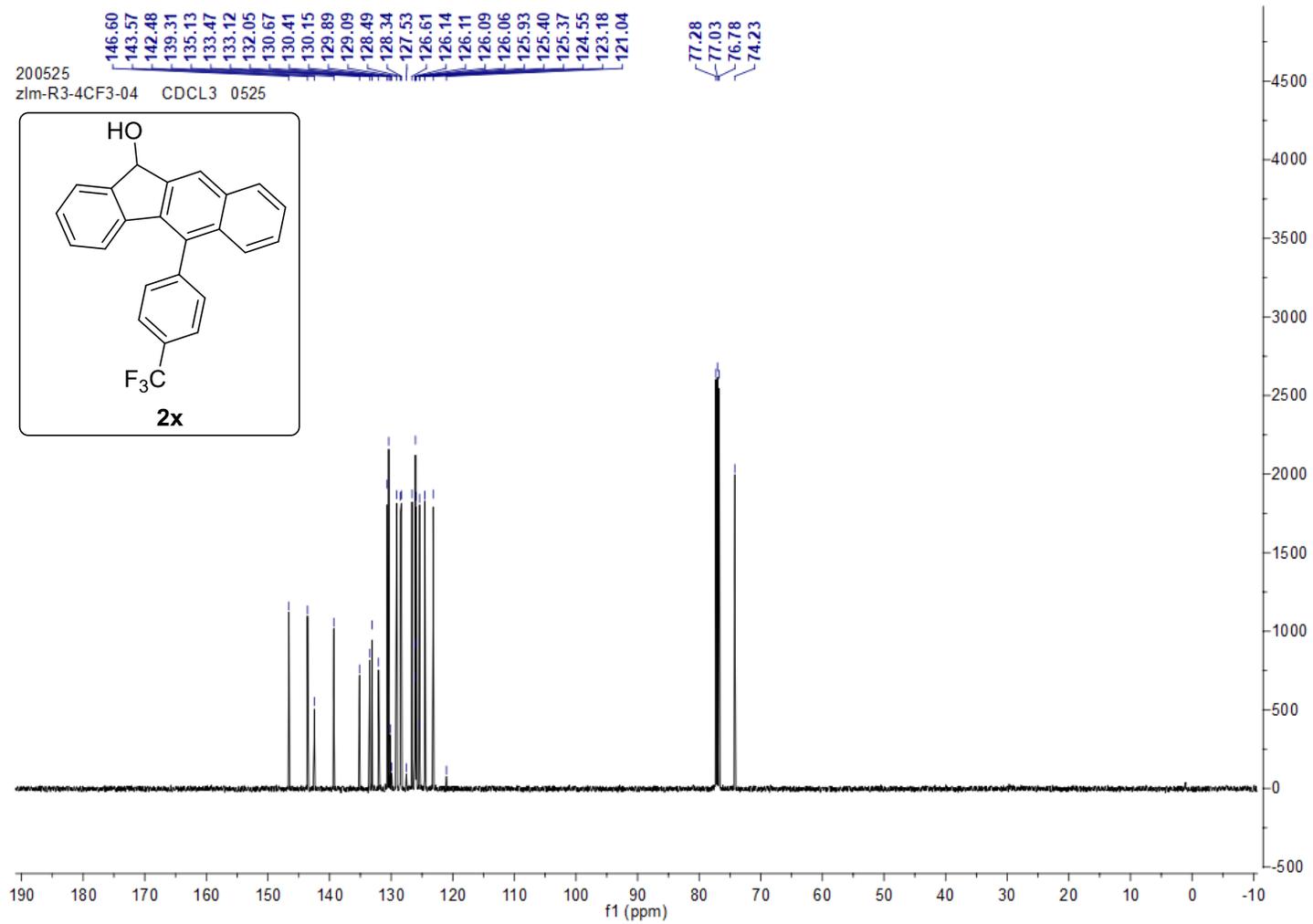
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2w



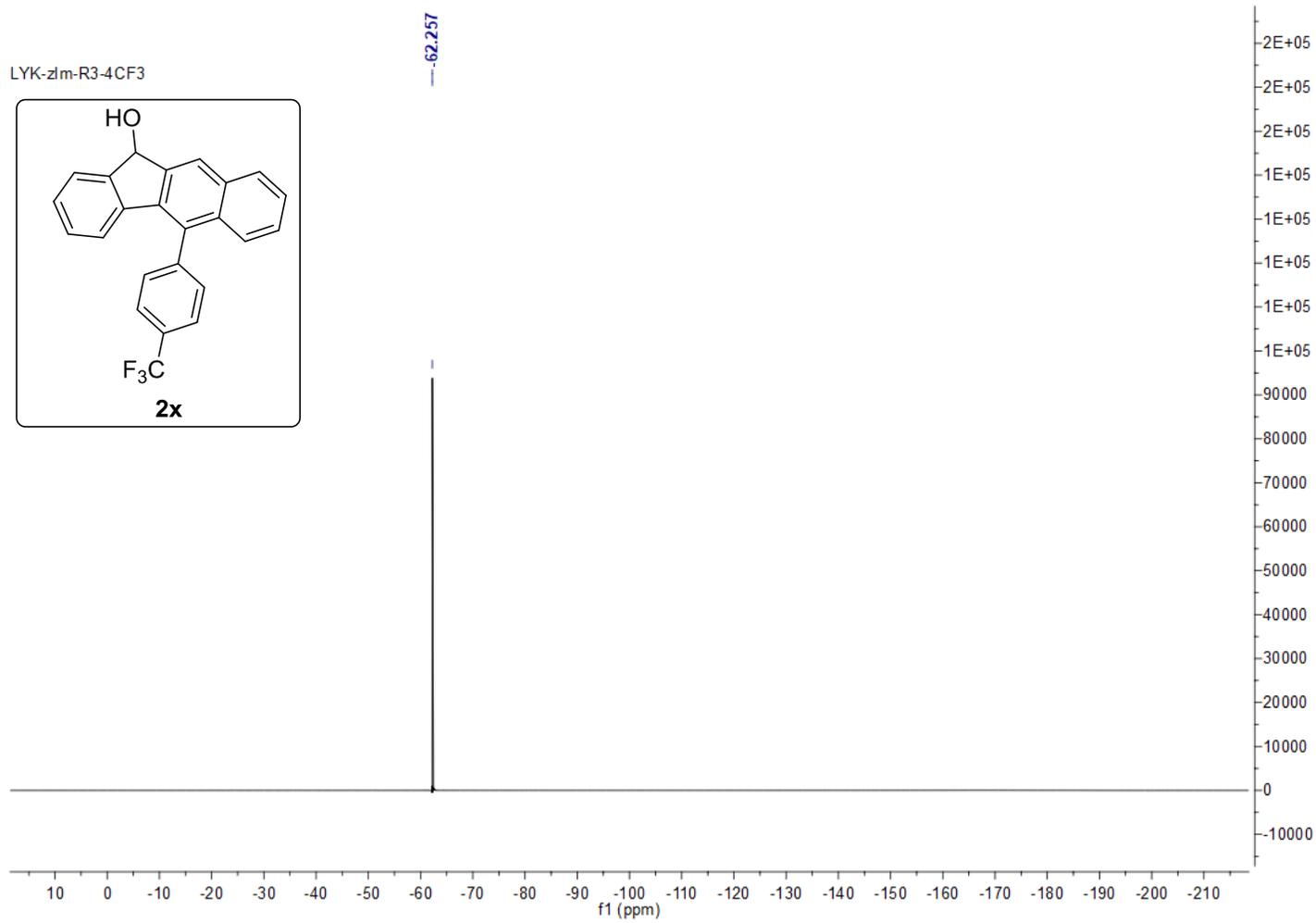
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2x**



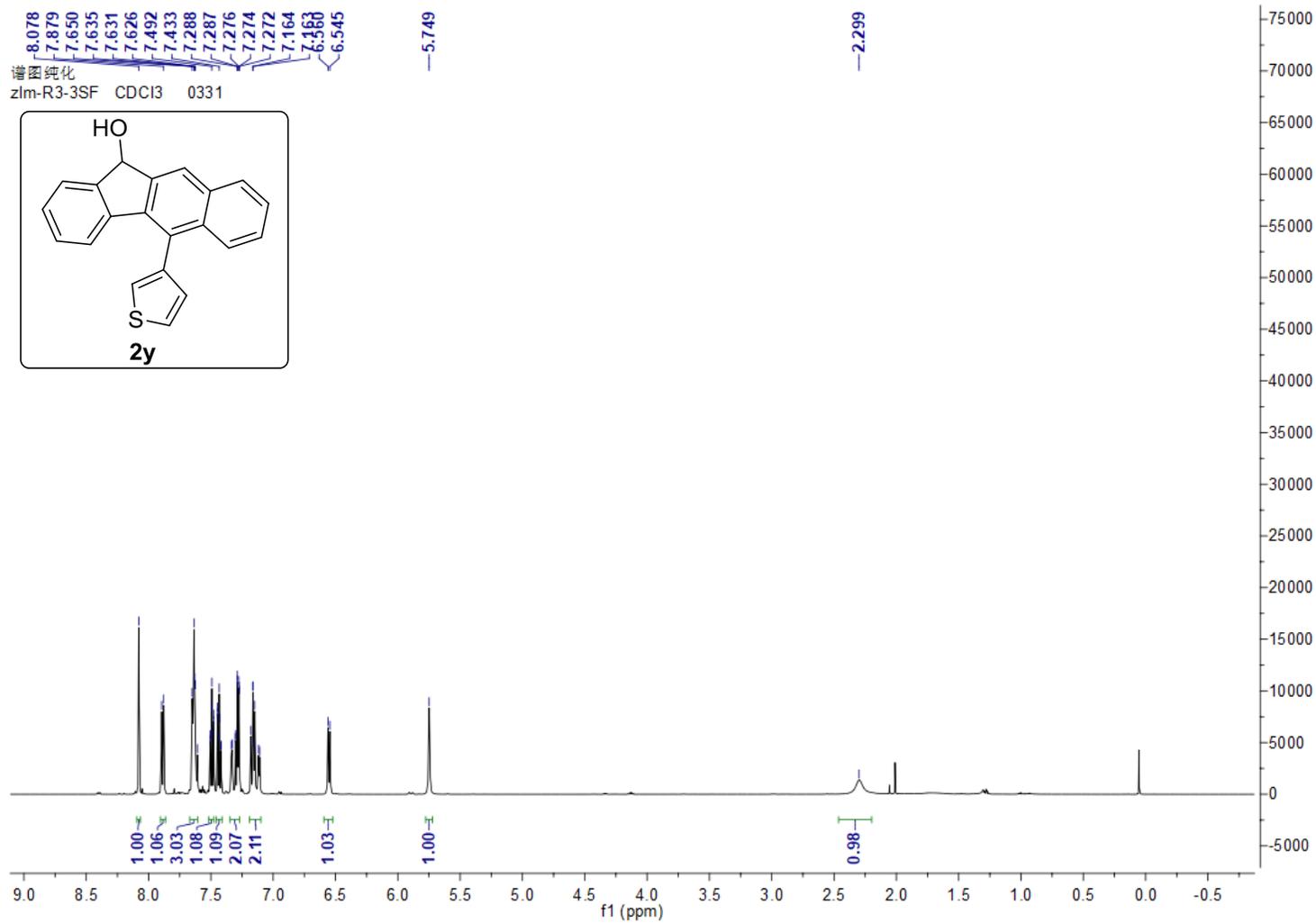
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2x



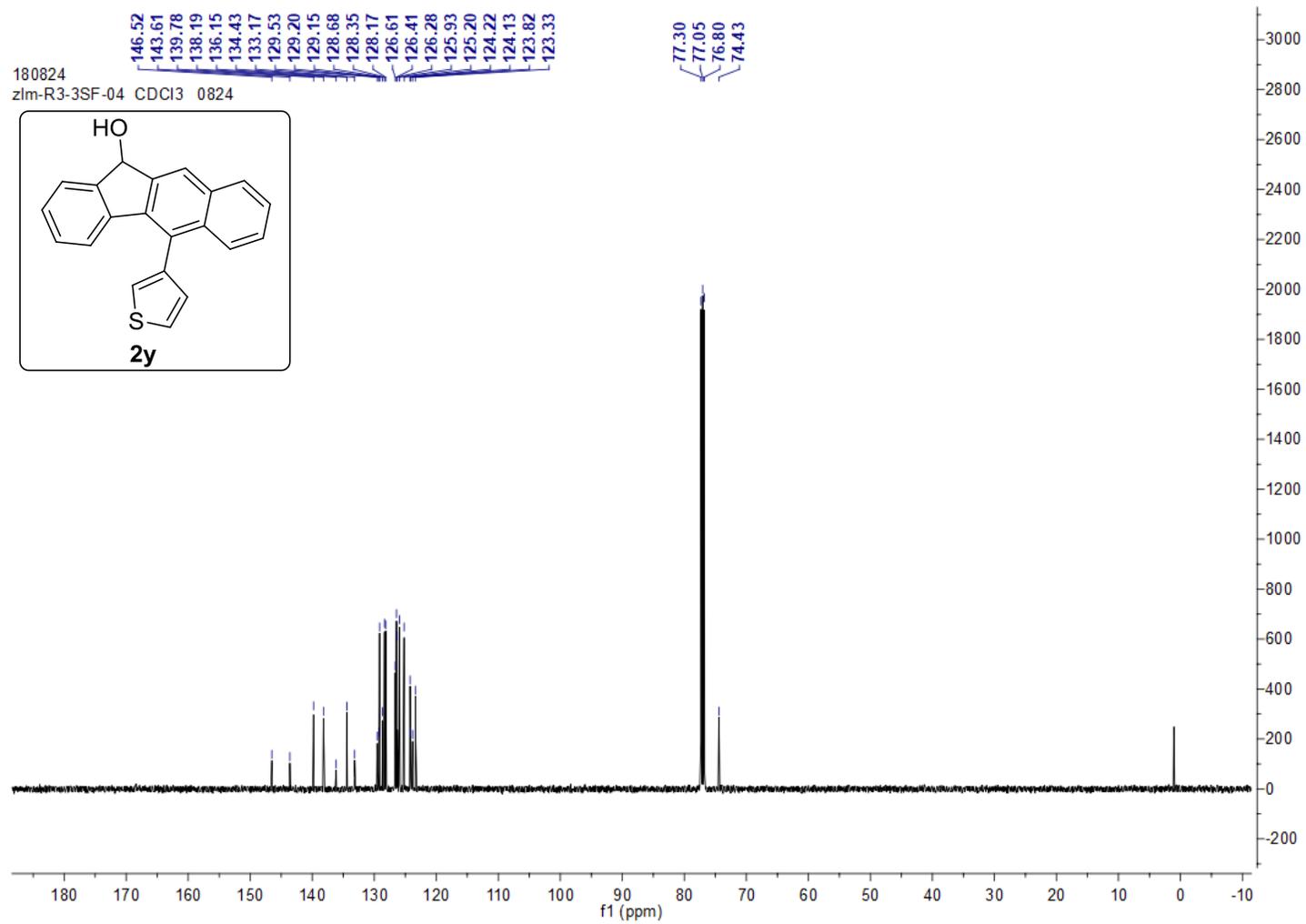
**<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) spectrum of compound 2x**



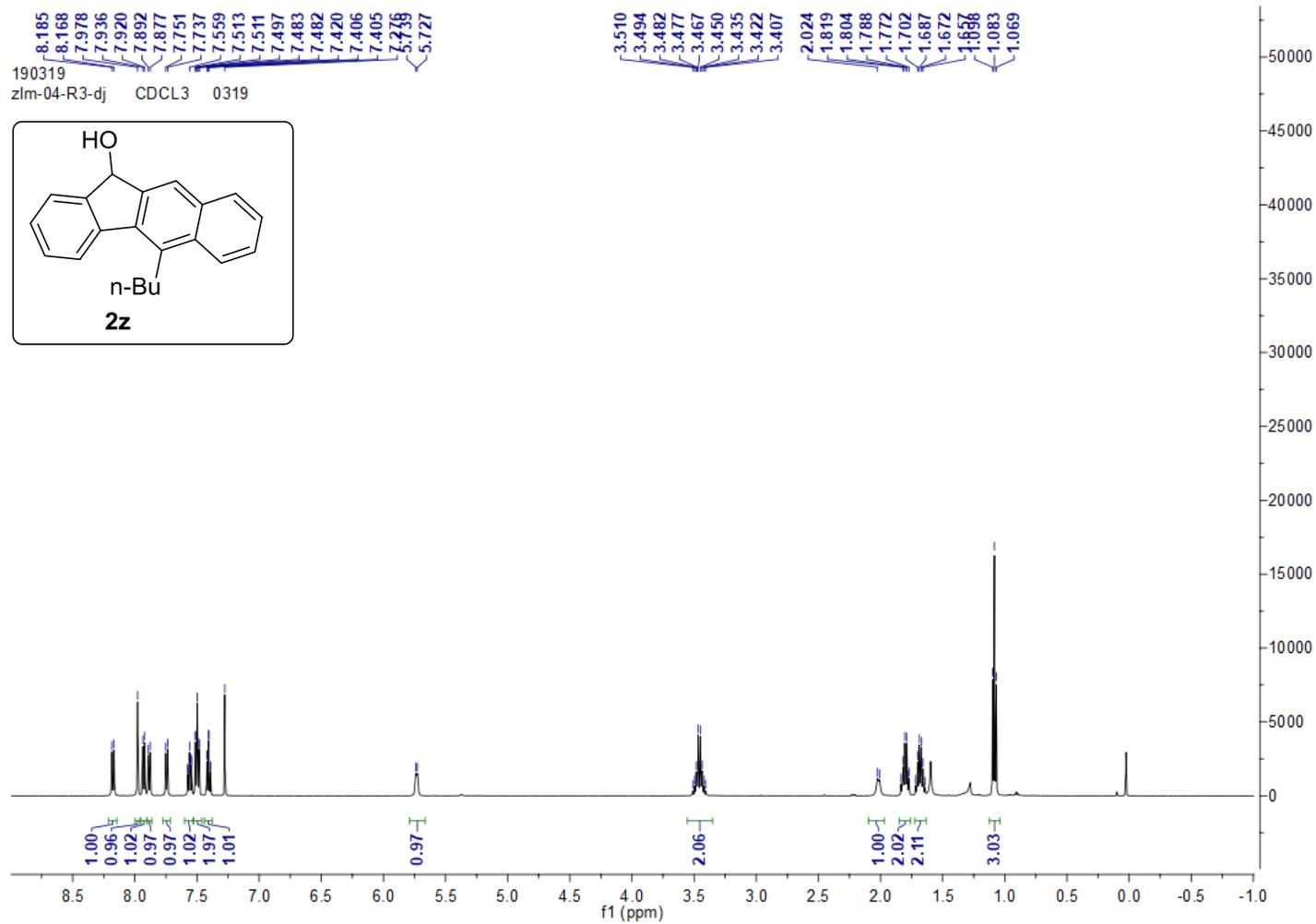
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2y



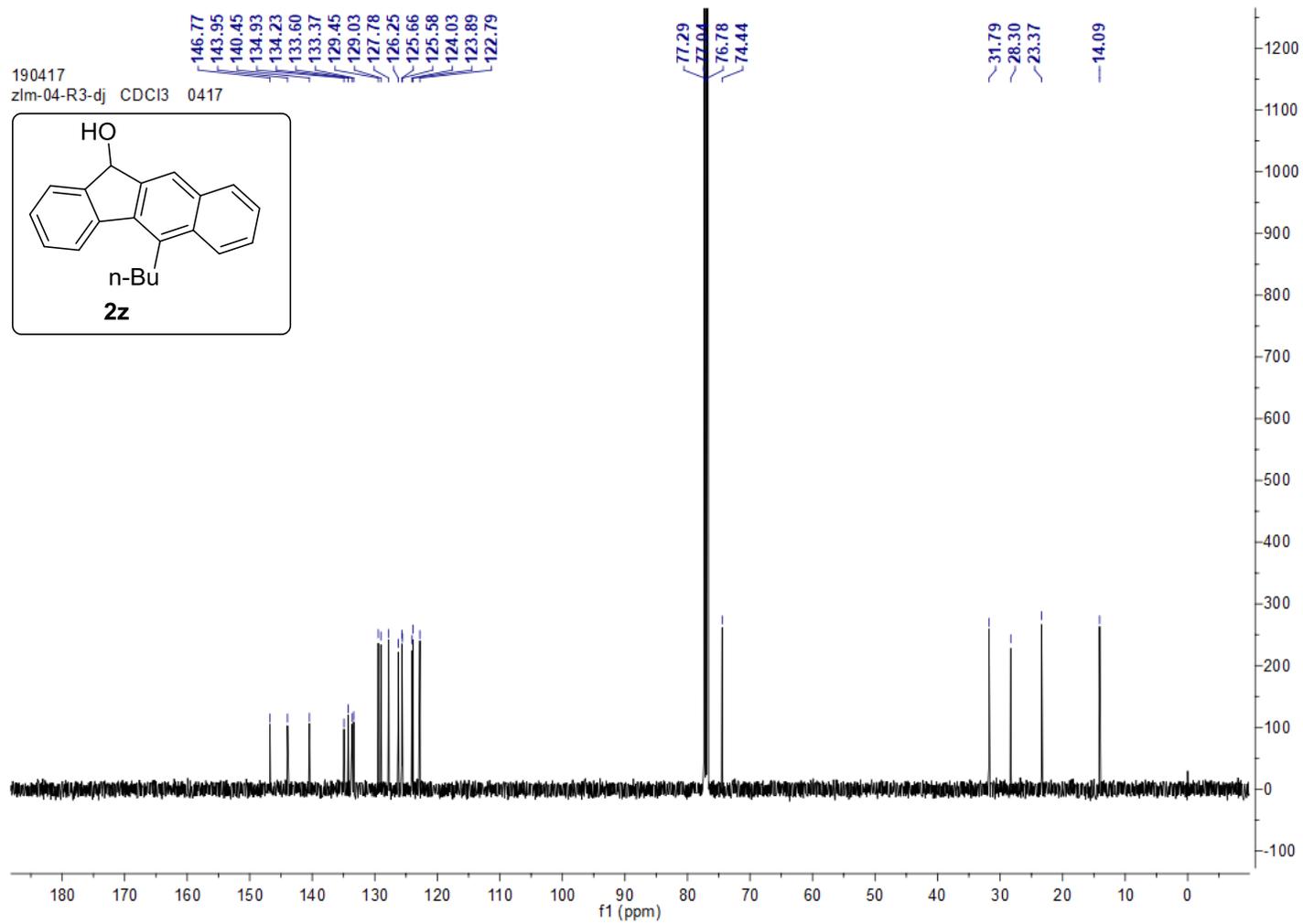
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2y



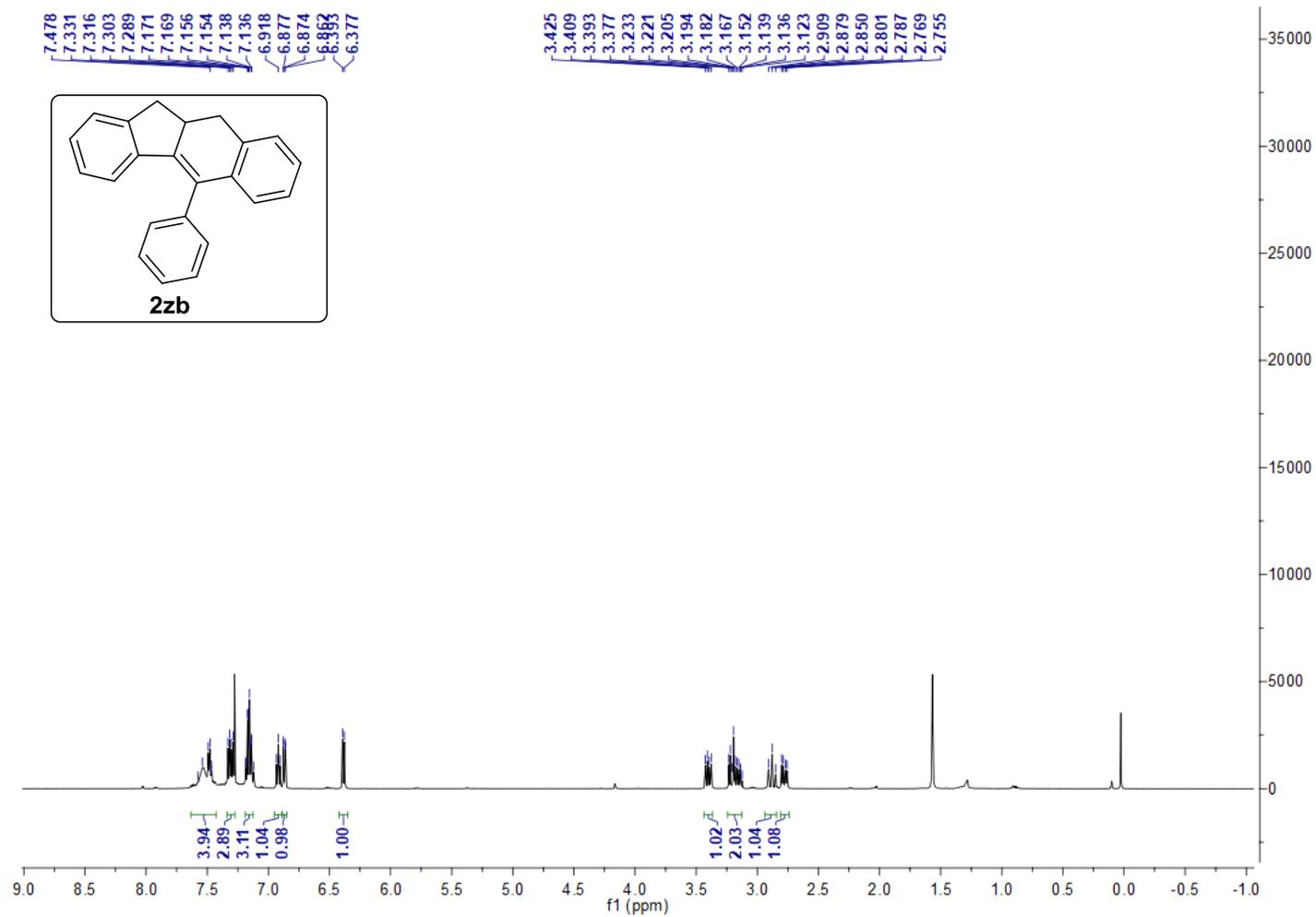
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2z



<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2z



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of compound 2zb



<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of compound 2zb

