

## *Supporting information*

# **Mild ketyl radical generation and coupling with alkynes enabled by Cr catalysis: stereoselective access to *E*-exocyclic allyl alcohols**

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## 1. Materials and Methods

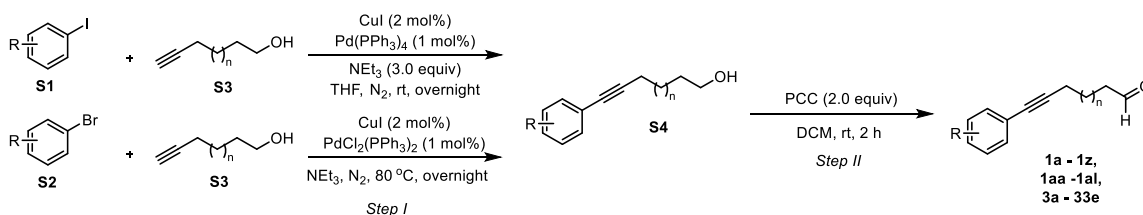
**Methods.** All reactions dealing with air- or moisture-sensitive compounds were carried out in a flame-dried and sealed Schlenk tube under atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with silica gel (0.25 mm, 230–400 mesh) containing a fluorescent indicator (Merck), or phosphomolybdic acid hydrate or  $\text{KMnO}_4$  staining solutions and followed by heating. Flash silica gel column chromatography was performed on silica gel 60 N (spherical and neutral, 140–325 mesh). NMR spectra were measured on a Bruker AVANCE III HD spectrometer and reported in parts per million (ppm).  $^1\text{H}$  NMR spectra were recorded at 400 MHz in  $\text{CDCl}_3$  were referenced internally to tetramethylsilane as standard,  $^{13}\text{C}$  NMR spectra were recorded at 100 MHz and referenced to the solvent resonance.  $^{19}\text{F}$  NMR spectra are not calibrated by an internal reference. Melting points were determined with a Hanon Instruments MP300. Analytical gas chromatography (GC) was carried out on an Agilent Technologies 7890B GC-system, equipped with FID detector and a J&W GC column (0.32 mm  $\times$  30 m  $\times$  0.25  $\mu\text{m}$ ). The methods were used by starting with the injection temperature  $T_0$ ; after holding the related temperature for 3 min, the column was heated to temperature  $T_1$  (ramp). (GC Method:  $T_0 = 50\text{ }^\circ\text{C}$ ,  $T_1 = 280\text{ }^\circ\text{C}$ , ramp = 15  $^\circ\text{C}/\text{min}$ ). GC-MS spectra were recorded on an Agilent Technologies 7890B GC-system with an Agilent 5977B MSD and a HP-5MS column (0.25 mm  $\times$  30 m  $\times$  0.25  $\mu\text{m}$ ). The major signals are quoted in  $m/z$  with the relative intensity in parentheses. The methods were used by starting with the injection temperature  $T_0$ ; after holding this temperature for 3 min, the column was heated to the temperature  $T_1$  (ramp). (GC-MS Method:  $T_0 = 50\text{ }^\circ\text{C}$ ,  $T_1 = 280\text{ }^\circ\text{C}$ , ramp = 15  $^\circ\text{C}/\text{min}$ ). High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with ESI ionization source. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (X500R, USA) equipped with ESI ionization source and TOF mass analyzer. Source temperature: 500  $^\circ\text{C}$ , Ion source gas: 55 psi, Spray voltage: 5500 V, Declustering potential: 80 V, Collision energy: 10 V, TOF start mass: 100 Da, TOF stop mass: 300 Da. Single crystal X-ray diffraction (X-ray) was recorded on the Bruker APEX-II CCD diffractometer. The crystal was kept at 285.0 K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement

package using Least Squares minimisation.

**Materials.** Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, Energy Chemical and other commercial suppliers and used as received. DME were purchased from Adamas (Water  $\leq$  30 ppm (by K.F.), 99.0%, SafeDry, with molecular sieves, Safeseal), EA, CH<sub>3</sub>CN and DMF were dried with activated molecular sieves and degassed with N<sub>2</sub>, THF were dried over sodium by refluxing for overnight and freshly distilled prior to use. CrCl<sub>2</sub> (99.99%), CrCl<sub>3</sub> (99.99%), Cr(acac)<sub>3</sub> (99.99%) and Cr(OAc)<sub>3</sub> (99.99%) were purchased from Aldrich Inc. and used as received.

## 2. General Procedure in the Preparation of Substrates

### Procedure A in the preparation of alkynyl aldehydes:

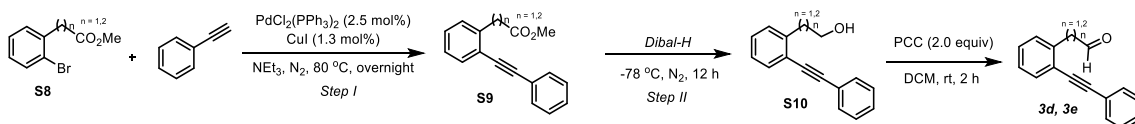


**Step I:** The reactions using iodoarenes were performed with the reported procedure.<sup>1</sup> Pd(PPh<sub>3</sub>)<sub>4</sub> (0.08 mmol) and CuI (0.16 mmol) were added to the round bottom flask, then triethylamine (30 mL), THF (5 mL), iodobenzene **S1** (16 mmol) and alkynyl alcohol **S3** (8 mmol) were added under atmosphere of N<sub>2</sub>. The reaction mixture was stirred at room temperature for overnight. The mixture was filtration and the volatiles were removed under vacuum, the crude mixture was purified by flash column chromatography on silica gel to afford the alkynyl alcohol **S4**.

The reactions using bromoarenes were performed with the reported procedure.<sup>2</sup> A mixture of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.08 mmol), CuI (0.16 mmol), bromobenzene **S2** (10.4 mmol), alkynyl alcohol **S3** (8 mmol) and triethylamine (20 mL) were stirred under atmosphere of nitrogen at 80 °C for overnight. The mixture was filtration and the volatiles were removed under vacuum, the crude mixture was purified by flash column chromatography on silica gel to afford the alkynyl alcohol **S4**.

**Step II:** The reaction was performed according to the reported procedure.<sup>3</sup> Alkynyl

alcohol **S4** (5.0 mmol) was slowly added into a solution of PCC (10.0 mmol, 2.0 equiv) in 30 mL of CH<sub>2</sub>Cl<sub>2</sub> and stirred at room temperature for 2 h. The mixture was filtration and the volatiles were removed under vacuum, the crude mixture was purified by flash column chromatography on silica gel to afford the alkenyl aldehydes **1a-1z**, **1aa-1al** and **3a-3e**.

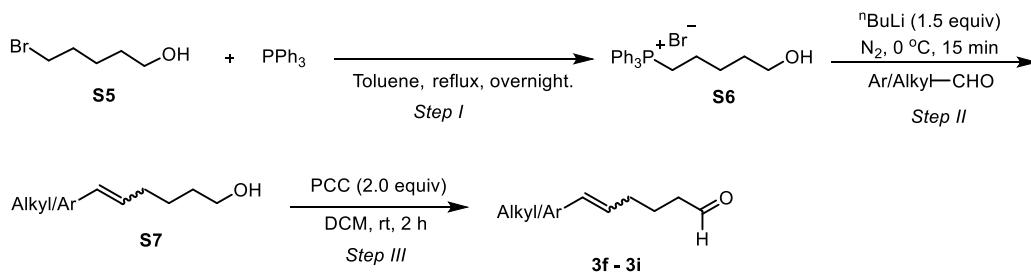


**Step I:** The reaction was performed according to the reported procedure.<sup>4</sup> Phenylacetylene (7 mmol) was slowly added into a mixture of **S8** (5 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.125 mmol), CuI (0.0625 mmol), and Et<sub>3</sub>N (20 mL) under N<sub>2</sub> atmosphere and stirred at 80 °C for overnight. After cooling to room temperature, H<sub>2</sub>O were added, and the aqueous layer was extracted by ethyl acetate. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then filtration and removal of volatiles under vacuum. The crude mixture was purified by flash column chromatography on silica gel to afford **S9**.

**Step II:** The reaction was performed according to the reported procedure.<sup>5</sup> Diisobutylaluminium hydride (1.0 M in toluene) (2.1 equiv) was added drowsily into a solution of ester **S9** (5 mmol, 1 equiv) in dichloromethane (20 mL) at -78 °C and stirred for 12 h. Subsequently, 1 M aqueous solution of hydrochloric acid was added, and diluted with 20 mL of ethyl acetate. The organic phase was extracted with ethyl acetate, and the combined organic layers were washed by 1M HCl, water and saturated solution of NaCl. After drying over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtration and removal of volatiles under vacuum, the crude mixture was used without any further purification.

**Step III:** The reaction was performed according to the reported procedure.<sup>3</sup> Alkenyl alcohol **S10** (5.0 mmol) was slowly added into a solution of PCC (10.0 mmol, 2.0 equiv) in 30 mL CH<sub>2</sub>Cl<sub>2</sub> and stirred at room temperature for 2 h. After filtration and removal of volatiles under vacuum, the crude mixture was purified by flash column chromatography on silica gel to afford the alkenyl aldehydes **3d** and **3e**.

#### Procedure B in the preparation of alkenyl aldehydes:



**Step I:** The reaction was performed according to the reported procedure.<sup>6</sup> To a flask with bromide alkyl alcohol **S5** (25.1 mmol) in toluene (10 mL) was added  $\text{PPh}_3$  (27.52 mmol), and the mixture was refluxed for overnight. After cooling to room temperature, the mixture was filtered and washed with cold ether to afford **S6** as white solid.

**Step II:** The reaction was performed according to the reported procedure.<sup>6</sup>  ${}^n\text{BuLi}$  (1.6 M in hexanes, 8.1 mL, 13 mmol) was slowly added into a suspension of **S6** (10 mmol) in THF (30 mL) at  $0\text{ }^\circ\text{C}$ . A solution of aldehyde (8 mmol) in THF (5 mL) was added after 30 min and slowly warmed to room temperature for another 2 h. After quenching by saturated aqueous solution of  $\text{NH}_4\text{Cl}$  and extraction with ethyl acetate, the combined organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and filtered and concentrated under vacuum. The crude mixture was purified by flash column chromatography on silica to afford **S7**.

**Step III:** The reaction was performed according to the reported procedure.<sup>3</sup> Alkenyl alcohol **S7** (5.0 mmol) was slowly added into a solution of PCC (10.0 mmol, 2.0 equiv) in 30 mL  $\text{CH}_2\text{Cl}_2$  and stirred at room temperature for 2 h. After filtration and removal of volatiles under vacuum, the residue mixture was purified by flash column chromatography on silica gel to afford the alkenyl aldehydes **3f-3i**.

### 3. Table S1 Optimization of Reaction Conditions

Entry	Variation from the standard conditions	Yield of <b>2a</b> (%) <sup>a</sup>	Recovery of <b>1a</b> (%) <sup>a</sup>
1	none	87 (99/1) <sup>b</sup>	0
2	No CrCl <sub>2</sub> or dtbpy	<i>n.d.</i> , <i>trace</i>	96, 92
3	No Mn or Cp <sub>2</sub> ZrCl <sub>2</sub>	<i>n.d.</i> , <i>n.d.</i>	97, 95
4	Other Cr salts: CrCl <sub>3</sub> , CrCl <sub>3</sub> (THF) <sub>3</sub> , Cr(acac) <sub>3</sub> , Cr(OAc) <sub>3</sub>	68, 64, 43, 38	28, 31, 51, 58
5	Other solvents: EA, CH <sub>3</sub> CN, THF, DMF	41, 39, 76, <i>n.d.</i>	52, 58, 0, 97
6	No LiCl	68	29
7	5 mol % CrCl <sub>2</sub> + dtbpy	58	38
8	<i>rt</i> instead of 40 °C	39	60
9	TMSCl instead of Cp <sub>2</sub> ZrCl <sub>2</sub>	27	70
10	Cp <sub>2</sub> ZrHCl instead of Cp <sub>2</sub> ZrCl <sub>2</sub>	<i>n.d.</i>	97
11	0.2 M instead of 0.1M	79	0
12	1.0 equiv Mn instead of 2.0 equiv Mn	43	52
13	100 mol% CrCl <sub>2</sub> /dtbpy without Mn or Cp <sub>2</sub> ZrCl <sub>2</sub>	0, 0	98, 96
14	Other reductant (Zn, Al or Mg) instead of Mn	42 (25) <sup>c</sup> , <i>n.d.</i> or 21 (18) <sup>c</sup>	18, 95, 30
15	Other ligand ( <b>L1-4</b> ) instead of dtbpy	69 (83/17) <sup>b</sup> , 78 (90/10) <sup>b</sup> 69 (87/13) <sup>b</sup> or 45 (77/23) <sup>b</sup>	25, 19, 17, 50
16	FeCl <sub>2</sub> , CoCl <sub>2</sub> , NiCl <sub>2</sub> , CuCl <sub>2</sub> , AuCl <sub>3</sub> , AgCl, RuCl <sub>3</sub> ·6H <sub>2</sub> O, VCl <sub>3</sub> , MoCl <sub>3</sub> or WCl <sub>6</sub> instead of CrCl <sub>2</sub>	4 (1/1) <sup>b</sup> , 18 (8/1) <sup>b</sup> , 12 (2/1) <sup>b</sup> , 6 (1/2) <sup>b</sup> , 4, 6 (2/1) <sup>b</sup> , 4, 10, 16 (1/1) <sup>b</sup> or 8 (1/1) <sup>b</sup>	90, 78, 92, 90, 91, 90, 91, 79, 80, 89

**L1**

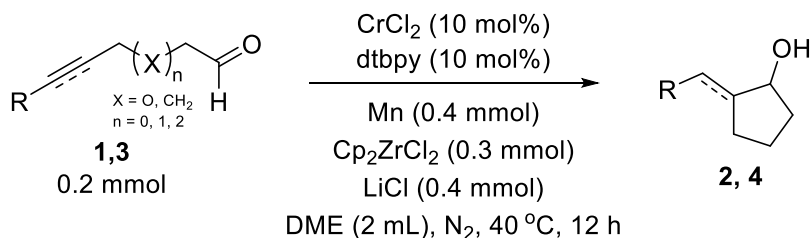
**L2**

**L3**

**L4**

<sup>a</sup>Isolated yield. <sup>b</sup>The ration of *E/Z* was determined by GC-MS. <sup>c</sup>Dialkynyl-containing diol **6**.

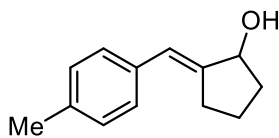
### 4. General Procedure of Cr-Catalyzed Ketyl Radical Couplings in the Synthesis of *E*-exocyclic Allyl Alcohols



**1** or **3** (0.2 mmol), CrCl<sub>2</sub> (10 mol%, 0.02 mmol), dtbpy (10 mol%, 0.02 mmol), Mn (22 mg, 0.4 mmol), Cp<sub>2</sub>ZrCl<sub>2</sub> (88 mg, 0.3 mmol), LiCl (17 mg, 0.4 mmol) and DME (2 mL) were

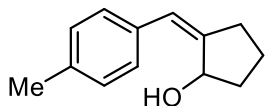
added into a dried Schlenk tube and the resulting mixture stirred at 40 °C for 12 h. After colling to room temperature, 0.2 mL of H<sub>2</sub>O was added and the resulting mixture was stirred for 15 min. After filtration and washing by ethyl acetate, the volatiles were removed under vacuum. The crude mixture was purified by flash column chromatography on silica gel to afford the exocyclic products **2** and **4**. The stereoselectivity of exocyclic *E*-isomer relative to *Z*-isomer was determined by GC-MS analysis prior to purification.

## 5. Analytical Data of the Products



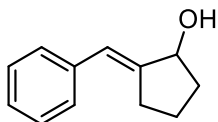
### (*E*)-2-(4-methylbenzylidene)cyclopentan-1-ol (**2a**)

The general procedure was applied to 6-(*p*-tolyl)hex-5-ynal (37 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as colorless oil (33 mg, 87% yield) (*E/Z* = 99/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.26 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.55 (q, *J* = 2.6 Hz, 1H), 4.59 (t, *J* = 5.6 Hz, 1H), 2.78–2.67 (m, 1H), 2.61–2.51 (m, 1H), 2.34 (s, 3H), 2.02–1.89 (m, 2H), 1.79–1.60 (m, 2H), 1.57 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 146.8, 136.8, 134.9, 129.0, 128.3, 123.6, 77.5, 34.9, 29.4, 22.7, 21.2. HRMS (ESI<sup>+</sup>): calcd for C<sub>13</sub>H<sub>17</sub>O [M+H]<sup>+</sup> 189.1274, found 189.1281. Spectroscopic data are in accordance with those described in the literature.<sup>7</sup>



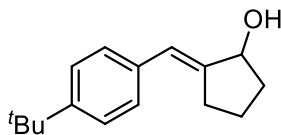
### (*Z*)-2-(4-methylbenzylidene)cyclopentan-1-ol (**2a'**)

White solid. Melting point = 39–40 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.38 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.45 (q, *J* = 2.1 Hz, 1H), 4.88–4.85 (m, 1H), 2.68–2.60 (m, 1H), 2.46–2.37 (m, 1H), 2.34 (s, 3H), 1.92–1.82 (m, 3H), 1.74–1.66 (m, 1H), 1.63 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 146.2, 136.6, 134.4, 129.3, 128.2, 125.6, 71.6, 36.9, 33.3, 22.2, 21.2. HRMS (ESI<sup>+</sup>): calcd for C<sub>13</sub>H<sub>17</sub>O [M+H]<sup>+</sup> 189.1274, found 189.1279.



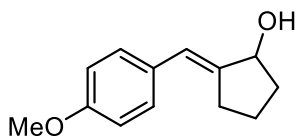
**(E)-2-benzylidenecyclopentan-1-ol (2b)**

The general procedure was applied to 6-phenylhex-5-ynal (34 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as white solid (30 mg, 86% yield) (*E/Z* = 99/1). Melting point = 41–42 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.38–7.31 (m, 4H), 7.24–7.19 (m, 1H), 6.58 (m, 1H), 4.62–4.57 (m, 1H), 2.79–2.68 (m, 1H), 2.63–2.53 (m, 1H), 2.03–1.91 (m, 2H), 1.79–1.61 (m, 2H), 1.59 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 147.8, 137.8, 128.4, 128.9, 126.6, 123.7, 77.4, 34.9, 29.4, 22.6. HRMS (ESI<sup>+</sup>): calcd for C<sub>12</sub>H<sub>15</sub>O [M+H]<sup>+</sup> 175.1117, found 175.1120. Spectroscopic data are in accordance with those described in the literature.<sup>7</sup>



**(E)-2-(4-(*tert*-butyl)benzylidene)cyclopentan-1-ol (2c)**

The general procedure was applied to 6-(4-(*tert*-butyl)phenyl)hex-5-ynal (46 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as colorless oil (41 mg, 89% yield) (*E/Z* = 99/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.37 (d, *J* = 8.9 Hz, 2H), 7.31 (d, *J* = 8.9 Hz, 2H), 6.56 (q, *J* = 2.6 Hz, 1H), 4.61–4.56 (m, 1H), 2.79–2.68 (m, 1H), 2.63–2.53 (m, 1H), 2.03–1.89 (m, 2H), 1.79–1.61 (m, 2H), 1.58 (br, 1H), 1.32 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 149.6, 147.1, 134.9, 128.2, 125.3, 123.3, 34.9, 34.5, 31.3, 29.7, 29.4, 22.6. HRMS (ESI<sup>+</sup>): calcd for C<sub>16</sub>H<sub>23</sub>O [M+H]<sup>+</sup> 231.1743, found 231.1747. Spectroscopic data are in accordance with those described in the literature.<sup>8</sup>

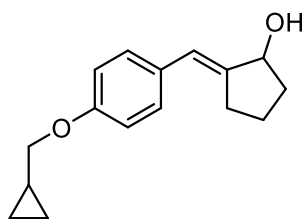


**(E)-2-(4-methoxybenzylidene)cyclopentan-1-ol (2d)**

The general procedure was applied to 6-(4-methoxyphenyl)hex-5-ynal (40 mg, 0.2 mmol).

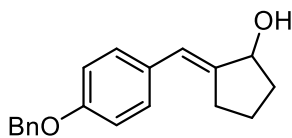


The crude product was purified by column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as white solid. (33 mg, 81% yield) (*E/Z* = 96/4). Melting point = 80–81 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.30 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.53 (q, *J* = 2.6 Hz, 1H), 4.60–4.56 (m, 1H), 3.81 (s, 3H), 2.76–2.66 (m, 1H), 2.59–2.50 (m, 1H), 2.03–1.87 (m, 2H), 1.78–1.62 (m, 2H), 1.59 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 147.4, 136.7, 134.8, 128.8, 126.5, 123.1, 34.9, 29.7, 29.4, 22.6, 15.9. HRMS (ESI<sup>+</sup>): calcd for C<sub>13</sub>H<sub>17</sub>O<sub>2</sub> [M+H]<sup>+</sup> 205.1223, found 205.1225. Spectroscopic data are in accordance with those described in the literature.<sup>7</sup>



**(*E*)-2-(4-(cyclopropylmethoxy)benzylidene)cyclopentan-1-ol (2e)**

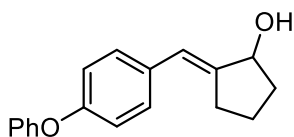
The general procedure was applied to 6-(4-cyclopropoxyphenyl)hex-5-ynal (46 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as white solid. (39 mg, 81% yield) (*E/Z* = 99/1). Melting point = 88–89 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.29 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.52 (q, *J* = 2.6 Hz, 1H), 4.60–4.55 (m, 1H), 3.81 (d, *J* = 6.8 Hz, 2H), 2.76–2.65 (m, 1H), 2.59–2.49 (m, 1H), 2.04–1.88 (m, 2H), 1.78–1.62 (m, 2H), 1.59 (br, 1H), 1.29–1.28 (m, 1H), 0.67–0.61 (m, 2H), 0.37–0.32 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 157.8, 145.5, 130.5, 129.6, 129.0, 123.3, 114.5, 77.5, 72.8, 34.9, 29.3, 22.7, 10.3, 3.2. HRMS (ESI<sup>+</sup>): calcd for C<sub>16</sub>H<sub>21</sub>O<sub>2</sub> [M+H]<sup>+</sup> 245.1536, found 245.1541.



**(*E*)-2-(4-(benzyloxy)benzylidene)cyclopentan-1-ol (2f)**

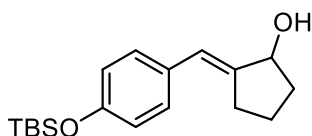
The general procedure was applied to 6-(4-(benzyloxy)phenyl)hex-5-ynal (56 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as colorless oil. (45 mg, 80% yield) (*E/Z* = 96/4). <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.45–7.33 (m, 5H), 7.33–7.28 (m, 2H), 6.98–6.93 (m, 2H), 6.52 (q,  $J$  = 2.6 Hz, 1H), 5.08 (s, 2H), 4.60–4.55 (m, 1H), 2.77–2.66 (m, 1H), 2.59–2.49 (m, 1H), 2.04–1.87 (m, 2H), 1.80–1.61 (m, 2H), 1.57 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 157.5, 145.7, 137.0, 130.9, 129.7, 128.6, 128.0, 127.5, 123.2, 114.8, 77.5, 70.0, 34.9, 29.3, 22.7. HRMS (ESI<sup>+</sup>): calcd for C<sub>19</sub>H<sub>21</sub>O<sub>2</sub> [M+H]<sup>+</sup> 281.1536, found 281.1540.



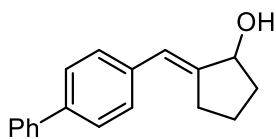
**(E)-2-(4-phenoxybenzylidene)cyclopentan-1-ol (2g)**

The general procedure was applied to 6-(4-phenoxyphenyl)hex-5-ynal (53 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as colorless oil. (44 mg, 83% yield) ( $E/Z$  = 96/4). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.36–7.30 (m, 4H), 7.13–7.08 (m, 1H), 7.04–6.96 (m, 4H), 6.56 (q,  $J$  = 2.56 Hz, 1H), 4.62–4.57 (m, 1H), 2.77–2.67 (m, 1H), 2.61–2.51 (m, 1H), 2.04–1.90 (m, 2H), 1.80–1.61 (m, 2H), 1.60 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 157.2, 155.9, 146.8, 133.0, 129.8, 129.8, 123.3, 123.0, 119.0, 118.7, 77.4, 34.9, 29.3, 22.6. HRMS (ESI<sup>+</sup>): calcd for C<sub>18</sub>H<sub>19</sub>O<sub>2</sub> [M+H]<sup>+</sup> 267.1380, found 267.1384.



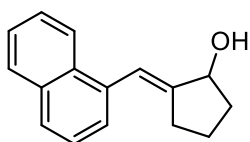
**(E)-2-(4-((tert-butyldimethylsilyl)oxy)benzylidene)cyclopentan-1-ol (2h)**

The general procedure was applied to 6-(4-((tert-butyldimethylsilyl)oxy)phenyl)hex-5-ynal (60 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as colorless oil (53 mg, 87% yield) ( $E/Z$  = 94/6). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.31 (d,  $J$  = 8.6 Hz, 2H), 6.89 (d,  $J$  = 8.6 Hz, 2H), 6.52 (q,  $J$  = 2.6 Hz, 1H), 4.60–4.54 (m, 1H), 2.76–2.62 (m, 1H), 2.59–2.48 (m, 1H), 2.02–1.87 (m, 2H), 1.80–1.60 (m, 2H), 1.57 (br, 1H), 0.98 (s, 9H), 0.20 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 154.5, 145.6, 131.1, 129.6, 123.4, 112.0, 34.9, 29.7, 29.3, 25.7, 22.7, 18.2, -4.4. HRMS (ESI<sup>+</sup>): calcd for C<sub>18</sub>H<sub>19</sub>O<sub>2</sub>Si [M+H]<sup>+</sup> 305.1931, found 305.1931.



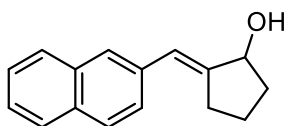
**(E)-2-([1,1'-biphenyl]-4-ylmethylene)cyclopentan-1-ol (2i)**

The general procedure was applied to 6-([1,1'-biphenyl]-4-yl)hex-5-ynal (50 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as white solid (44 mg, 88% yield) (*E/Z* = 99/1). Melting point = 96–97 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.63–7.57 (m, 4H), 7.47–6.41 (m, 4H), 7.37–7.31 (m, 1H), 6.62 (q, *J* = 2.6 Hz, 1H), 4.62 (t, *J* = 5.7 Hz, 1H), 2.84–2.73 (m, 1H), 2.68–2.58 (m, 1H), 2.06–1.93 (m, 2H), 1.82–1.62 (m, 2H), 1.57 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.1, 140.7, 139.3, 136.8, 128.9, 128.8, 127.3, 127.0, 127.0, 123.3, 77.5, 34.9, 29.5, 22.6. HRMS (ESI<sup>+</sup>): calcd for C<sub>18</sub>H<sub>19</sub>O [M+H]<sup>+</sup> 215.1430, found 215.1433.



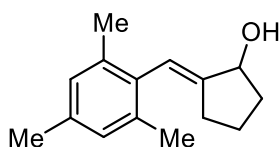
**(E)-2-(naphthalen-1-ylmethylene)cyclopentan-1-ol (2j)**

The general procedure was applied to ethyl 6-(naphthalen-1-yl)hex-5-ynal (44 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as white solid (38 mg, 85% yield) (*E/Z* = 96/4). Melting point = 92–93 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.09–8.04 (m, 1H), 7.87–7.83 (m, 1H), 7.78–7.73 (m, 1H), 7.51–7.47 (m, 2H), 7.47–7.45 (m, 2H), 7.18 (q, *J* = 2.5 Hz, 1H), 4.75–4.70 (m, 1H), 2.66–2.56 (m, 1H), 2.48–2.38 (m, 1H), 2.09–2.00 (m, 1H), 1.94–1.85 (m, 1H), 1.76–1.67 (m, 2H), 1.60 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 145.0, 134.7, 133.6, 131.7, 128.5, 127.3, 125.9, 125.8, 125.7, 125.3, 124.4, 120.7, 35.2, 29.7, 28.8, 22.2. HRMS (ESI<sup>+</sup>): calcd for C<sub>16</sub>H<sub>17</sub>O [M+H]<sup>+</sup> 225.1274, found 225.1277. Spectroscopic data are in accordance with those described in the literature.<sup>8</sup>



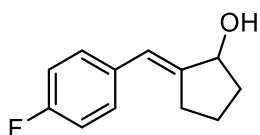
**(E)-2-(naphthalen-2-ylmethylene)cyclopentan-1-ol (2k)**

The general procedure was applied to 6-(naphthalen-2-yl)hex-5-ynal (44 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as white solid. (39 mg, 87% yield) (*E/Z* = 95/5). Melting point = 95–96 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.83–7.78 (m, 4H), 7.52 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.49–7.42 (m, 2H), 6.74 (q, *J* = 2.7 Hz, 1H), 4.67–4.63 (m, 1H), 2.91–2.80 (m, 1H), 2.75–2.65 (m, 1H), 2.06–1.95 (m, 2H), 1.83–1.65 (m, 2H), 1.62 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.3, 135.4, 133.5, 132.2, 128.0, 127.8, 127.6, 127.2, 126.8, 126.1, 125.8, 123.8, 77.5, 34.9, 29.5, 22.6. HRMS (ESI<sup>+</sup>): calcd for C<sub>16</sub>H<sub>17</sub>O [M+H]<sup>+</sup> 225.1274, found 225.1277. Spectroscopic data are in accordance with those described in the literature.<sup>8</sup>



**(*E*)-2-(2,4,6-trimethylbenzylidene)cyclopentan-1-ol (2l)**

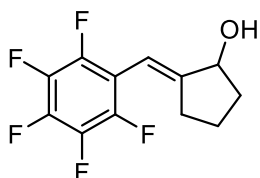
The general procedure was applied to 6-mesitylhex-5-ynal (43 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as colorless oil (36 mg, 83% yield) (*E/Z* = 98/2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 6.86 (s, 2H), 7.46–7.43 (m, 1H), 4.64–4.59 (m, 1H), 2.27 (s, 3H), 2.17 (s, 6H), 2.14–2.06 (m, 1H), 2.02–1.88 (m, 2H), 1.87–1.76 (m, 1H), 1.73–1.58 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 149.3, 136.0, 135.6, 134.0, 128.0, 121.9, 75.6, 35.6, 29.7, 28.1, 21.9, 21.0, 20.1. HRMS (ESI<sup>+</sup>): calcd for C<sub>15</sub>H<sub>21</sub> [M+H]<sup>+</sup> 217.1587, found 217.1590. Spectroscopic data are in accordance with those described in the literature.<sup>7</sup>



**(*E*)-2-(4-fluorobenzylidene)cyclopentan-1-ol (2m)**

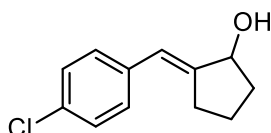
The general procedure was applied to 6-(4-fluorophenyl)hex-5-ynal (38 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as colorless oil (35 mg, 90% yield) (*E/Z* = 99/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.35–7.29 (m, 2H), 7.05–6.99 (m, 2H), 6.54 (q, *J* = 2.1 Hz, 1H), 4.59 (t,

$J = 5.7$  Hz, 1H), 2.74–2.64 (m, 1H), 2.59–2.49 (m, 1H), 2.03–1.90 (m, 2H), 1.80–1.61 (m, 2H), 1.59 (br, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 161.5$  (d,  $J = 247.4$  Hz), 147.3 (d,  $J = 1.8$  Hz), 133.9 (d,  $J = 3.3$  Hz), 129.9 (d,  $J = 8.1$  Hz), 122.6, 115.2 (d,  $J = 21.4$  Hz), 77.3, 34.9, 29.2, 22.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -115.4$ . HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{12}\text{H}_{14}\text{FO}$   $[\text{M}+\text{H}]^+$  193.1023, found 193.1027. Spectroscopic data are in accordance with those described in the literature.<sup>8</sup>



**(E)-2-((perfluorophenyl)methylene)cyclopentan-1-ol (2n)**

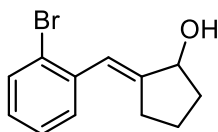
The general procedure was applied to 6-(perfluorophenyl)hex-5-ynal (52 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as yellow solid. (49 mg, 92% yield) ( $E/Z = 98/2$ ). Melting point = 82–83 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 6.32$ –6.28 (m, 1H), 4.64–4.56 (m, 1H), 2.42–2.32 (m, 1H), 2.32–2.21 (m, 1H), 2.13–2.03 (m, 1H), 1.93–1.83 (m, 1H), 1.69–1.63 (m, 2H), 1.25 (br, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 156.7$ , 107.2, 76.0, 35.3, 29.7, 29.0 (t,  $J = 3.9$  Hz), 21.4.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -139.5$  (dd,  $J = 22.5$ , 8.2 Hz), -156.6 (t,  $J = 20.4$  Hz), -162.91–163.07 (m). HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{12}\text{H}_{10}\text{F}_5\text{O}$   $[\text{M}+\text{H}]^+$  265.0646, found 265.0651.



**(E)-2-(4-chlorobenzylidene)cyclopentan-1-ol (2o)**

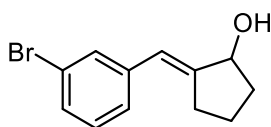
The general procedure was applied to 6-(4-chlorophenyl)hex-5-ynal (41 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as white solid (37 mg, 89% yield) ( $E/Z = 99/1$ ). Melting point = 84–85 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.29$ –7.22 (m, 4H), 6.49 (q,  $J = 2.7$  Hz, 1H), 4.58–4.52 (m, 1H), 2.72–2.60 (m, 1H), 2.56–2.46 (m, 1H), 1.99–1.89 (m, 2H), 1.76–1.60 (m, 2H), 1.59 (br, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 148.4$ , 136.2, 132.2, 129.6, 128.5,

122.5, 77.3, 34.9, 29.4, 22.5. HRMS (ESI<sup>+</sup>): calcd for C<sub>12</sub>H<sub>14</sub>ClO [M+H]<sup>+</sup> 209.0728, found 209.0732. Spectroscopic data are in accordance with those described in the literature.<sup>8</sup>



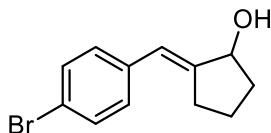
**(E)-2-(2-bromobenzylidene)cyclopentan-1-ol (2p)**

The general procedure was applied to 6-(2-bromophenyl)hex-5-ynal (50 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as colorless oil. (46 mg, 91% yield) (*E/Z* = 98/2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.57 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.41 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.27 (dt, *J* = 7.4, 1.5 Hz, 1H), 7.07 (dt, *J* = 7.6, 1.8 Hz, 1H), 6.77 (q, *J* = 2.6 Hz, 1H), 4.65–4.60 (m, 1H), 2.66–2.56 (m, 1H), 2.53–2.40 (m, 1H), 2.04–1.86 (m, 2H), 1.78 (br, 1H), 1.72–1.62 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 150.0, 137.4, 132.7, 129.5, 128.1, 127.0, 124.3, 122.7, 76.7, 34.8, 28.7, 22.3. HRMS (ESI<sup>+</sup>): calcd for C<sub>12</sub>H<sub>14</sub>BrO [M+H]<sup>+</sup> 253.0223, found 253.0227. Spectroscopic data are in accordance with those described in the literature.<sup>8</sup>



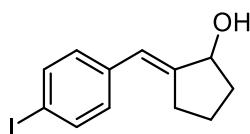
**(E)-2-(3-bromobenzylidene)cyclopentan-1-ol (2q)**

The general procedure was applied to 6-(3-bromophenyl)hex-5-ynal (50 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as colorless oil (46 mg, 92% yield) (*E/Z* = 98/2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.50 (t, *J* = 1.9 Hz, 1H), 7.35–7.32 (m, 1H), 7.28–7.25 (m, 1H), 7.22–7.17 (m, 1H), 6.50 (q, *J* = 2.6 Hz, 1H), 4.61–4.55 (m, 1H), 2.77–2.65 (m, 1H), 2.62–2.51 (m, 1H), 2.05–1.92 (m, 2H), 1.79–1.62 (m, 2H), 1.59 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 149.5, 139.9, 131.1, 129.8, 129.5, 127.0, 122.5, 122.3, 77.2, 34.9, 29.3, 22.4. HRMS (ESI<sup>+</sup>): calcd for C<sub>12</sub>H<sub>14</sub>BrO [M+H]<sup>+</sup> 253.0223, found 253.0226. Spectroscopic data are in accordance with those described in the literature.<sup>8</sup>



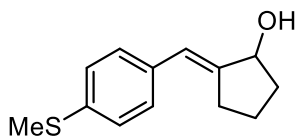
**(E)-2-(4-bromobenzylidene)cyclopentan-1-ol (2r)**

The general procedure was applied to 6-(4-bromophenyl)hex-5-ynal (50 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as yellow solid. (45 mg, 90% yield) (*E/Z* = 95/5). Melting point = 84–85 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.42 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.51 (q, *J* = 2.5 Hz, 1H), 4.60–4.55 (m, 1H), 2.73–2.62 (m, 1H), 2.58–2.48 (m, 1H), 2.03–1.92 (m, 2H), 1.79–1.62 (m, 2H), 1.60 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.6, 136.7, 131.4, 129.9, 122.5, 120.4, 77.3, 34.9, 29.4, 22.4. HRMS (ESI<sup>+</sup>): calcd for C<sub>12</sub>H<sub>14</sub>BrO [M+H]<sup>+</sup> 253.0223, found 253.0226. Spectroscopic data are in accordance with those described in the literature.<sup>8</sup>



**(E)-2-(4-iodobenzylidene)cyclopentan-1-ol (2s)**

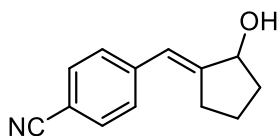
The general procedure was applied to 6-(4-iodophenyl)hex-5-ynal (59 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as colorless oil. (37 mg, 62% yield) (*E/Z* = 94/6). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.65 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.49 (q, *J* = 2.6 Hz, 1H), 4.60–4.54 (m, 1H), 2.73–2.63 (m, 1H), 2.58–2.48 (m, 1H), 2.01–1.91 (m, 2H), 1.79–1.60 (m, 2H), 1.58 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.9, 137.4, 137.3, 130.2, 122.6, 91.8, 77.2, 34.9, 29.4, 22.4. HRMS (ESI<sup>+</sup>): calcd for C<sub>12</sub>H<sub>14</sub>IO [M+H]<sup>+</sup> 301.0084, found 301.0089.



**(E)-2-(4-(methylthio)benzylidene)cyclopentan-1-ol (2t)**

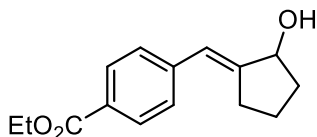
The general procedure was applied to 6-(4-(methylthio)phenyl)hex-5-ynal (44 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA =

5/1) to afford the title compound as white solid. (39 mg, 88% yield) (*E/Z* = 99/1). Melting point = 83–84 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.28 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.53 (q, *J* = 2.6 Hz, 1H), 4.61–4.56 (m, 1H), 2.76–2.63 (m, 1H), 2.60–2.50 (m, 1H), 2.49 (s, 3H), 2.03–1.90 (m, 2H), 1.79–1.61 (m, 2H), 1.58 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 147.4, 136.7, 134.8, 128.8, 126.5, 123.1, 34.9, 29.7, 29.4, 22.6, 15.9. HRMS (ESI<sup>+</sup>): calcd for C<sub>13</sub>H<sub>17</sub>OS [M+H]<sup>+</sup> 221.0995, found 221.0998.



**(*E*)-4-((2-hydroxycyclopentylidene)methyl)benzonitrile (2u)**

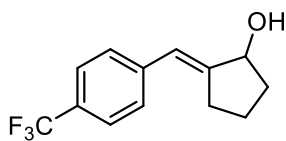
The general procedure was applied to 4-(6-oxohex-1-yn-1-yl)benzonitrile (39 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 2/1) to afford the title compound as colorless oil. (36 mg, 90% yield) (*E/Z* = 97/3). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.61 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 6.59 (q, *J* = 2.5 Hz, 1H), 4.63–4.58 (m, 1H), 2.77–2.65 (m, 1H), 2.65–2.54 (m, 1H), 2.07–1.93 (m, 2H), 1.81–1.68 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 151.9, 142.4, 132.1, 128.8, 122.1, 109.7, 77.2, 34.8, 29.7, 29.6, 22.2. HRMS (ESI<sup>+</sup>): calcd for C<sub>13</sub>H<sub>14</sub>NO [M+H]<sup>+</sup> 200.1070, found 200.1072.



**Ethyl (*E*)-4-((2-hydroxycyclopentylidene)methyl)benzoate (2v)**

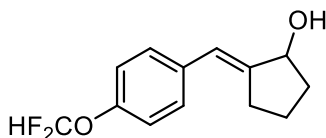
The general procedure was applied to ethyl 4-(6-oxohex-1-yn-1-yl)benzoate (49 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as colorless oil (46 mg, 93% yield) (*E/Z* = 96/4). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.00 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 6.61 (q, *J* = 2.5 Hz, 1H), 4.63–4.58 (m, 1H), 4.37 (q, *J* = 7.12 Hz, 2H), 2.80–2.68 (m, 1H), 2.66–2.56 (m, 1H), 2.04–1.03 (m, 2H), 1.80–1.65 (m, 2H), 1.63 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 166.5, 150.5, 142.3, 129.6, 128.3, 128.2, 122.9, 60.9, 34.8, 29.7, 29.6, 22.4, 14.4. HRMS (ESI<sup>+</sup>): calcd for C<sub>15</sub>H<sub>19</sub>O<sub>3</sub> [M+H]<sup>+</sup> 247.1329, found 247.1332.





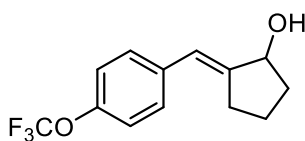
**(E)-2-(4-(trifluoromethyl)benzylidene)cyclopentan-1-ol (2w)**

The general procedure was applied to 6-(4-(trifluoromethyl)phenyl)hex-5-ynal (48 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as colorless oil (44 mg, 90% yield) (*E/Z* = 94/6). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.61 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 6.63 (q, *J* = 2.6 Hz, 1H), 4.65–4.60 (m, 1H), 2.80–2.70 (m, 1H), 2.67–2.56 (m, 1H), 2.07–1.96 (m, 2H), 1.82–1.65 (m, 2H), 1.64 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 150.5, 141.3, 128.5, 125.3, 125.23 (d, *J* = 12.1 Hz), 125.21, 122.4, 77.2, 34.8, 29.4, 22.3. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -62.4. HRMS (ESI<sup>+</sup>): calcd for C<sub>13</sub>H<sub>14</sub>F<sub>3</sub>O [M+H]<sup>+</sup> 243.0991, found 243.0996. Spectroscopic data are in accordance with those described in the literature.<sup>8</sup>



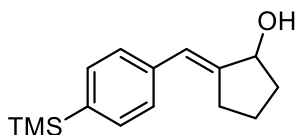
**(E)-2-(4-(difluoromethoxy)benzylidene)cyclopentan-1-ol (2x)**

The general procedure was applied to 6-(4-(difluoromethoxy)phenyl)hex-5-ynal (48 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as colorless oil. (39 mg, 81% yield) (*E/Z* = 99/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.34 (d, *J* = 8.7 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.55 (q, *J* = 2.6 Hz, 1H), 6.50 (t, *J* = 74.1 Hz, 1H), 4.61–4.56 (m, 1H), 2.75–2.65 (m, 1H), 2.60–2.50 (m, 1H), 2.02–1.92 (m, 2H), 1.80–1.63 (m, 2H), 1.62 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 149.6 (t, *J* = 2.8 Hz), 148.0, 135.2, 129.7, 122.5, 119.4, 115.9 (t, *J* = 260.3 Hz), 77.3, 34.9, 29.3, 22.5. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -80.7. HRMS (ESI<sup>+</sup>): calcd for C<sub>13</sub>H<sub>15</sub>F<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 241.1035, found 241.1040.



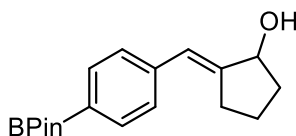
**(E)-2-(4-(trifluoromethoxy)benzylidene)cyclopentan-1-ol (2y)**

The general procedure was applied to 6-(4-(trifluoromethoxy)phenyl)hex-5-ynal (51 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as colorless oil (46 mg, 90% yield) (*E/Z* = 94/6). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.37 (d, *J* = 8.9 Hz, 2H), 7.18 (d, *J* = 8.9 Hz, 2H), 6.56 (q, *J* = 2.5 Hz, 1H), 4.62–4.56 (m, 1H), 2.75–2.65 (m, 1H), 2.61–2.51 (m, 1H), 2.02–1.92 (m, 2H), 1.79–1.60 (m, 2H), 1.58 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.7, 136.5, 129.6, 122.2, 120.8, 77.3, 34.9, 29.7, 29.3, 22.4, 14.2. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ = -57.8. HRMS (ESI<sup>+</sup>): calcd for C<sub>13</sub>H<sub>14</sub>F<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 259.0940, found 259.0944. Spectroscopic data are in accordance with those described in the literature.<sup>8</sup>



**(E)-2-(4-(trimethylsilyl)benzylidene)cyclopentan-1-ol (2z)**

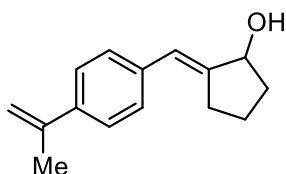
The general procedure was applied to 6-(4-(trimethylsilyl)phenyl)hex-5-ynal (49 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as white solid. (42 mg, 85% yield) (*E/Z* = 98/2). Melting point = 87 - 88 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.51 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 6.57 (q, *J* = 2.5 Hz, 1H), 4.60 (t, *J* = 5.9 Hz, 1H), 2.80–2.70 (m, 1H), 2.64–2.54 (m, 1H), 2.03–1.91 (m, 2H), 1.79–1.63 (m, 2H), 1.58 (br, 1H), 0.27 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.2, 138.8, 138.2, 133.4, 127.7, 123.7, 77.4, 34.9, 29.4, 22.6, -1.12. HRMS (ESI<sup>+</sup>): calcd for C<sub>15</sub>H<sub>23</sub>OSi [M+H]<sup>+</sup> 247.1513, found 247.1515.



**(E)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzylidene)cyclopentan-1-ol (2aa)**

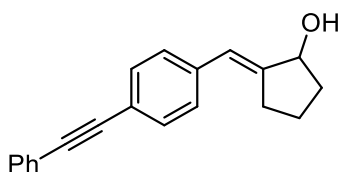
The general procedure was applied to 6-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)hex-5-ynal (49 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as colorless oil.

(44 mg, 74% yield) (*E/Z* = 95/5). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.78 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 6.59 (q, *J* = 2.6 Hz, 1H), 4.62–4.57 (m, 1H), 2.80–2.70 (m, 1H), 2.64–2.54 (m, 1H), 2.02–1.91 (m, 2H), 1.79–1.63 (m, 2H), 1.57 (br, 1H), 1.34 (s, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 149.0, 140.5, 134.8, 127.7, 123.7, 83.8, 77.2, 76.9, 34.9, 29.5, 24.9, 22.5. HRMS (ESI<sup>+</sup>): calcd for C<sub>18</sub>H<sub>26</sub>BO<sub>3</sub> [M+H]<sup>+</sup> 301.1970, found 301.1972.



**(*E*)-2-(4-(prop-1-en-2-yl)benzylidene)cyclopentan-1-ol (2ab)**

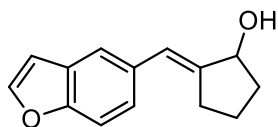
The general procedure was applied to 6-(4-(prop-1-en-2-yl)phenyl)hex-5-ynal (42 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as white solid. (36 mg, 83% yield) (*E/Z* = 94/6). Melting point = 85–86 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.46 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 6.57 (q, *J* = 2.7 Hz, 1H), 5.40 (dd, *J* = 1.6, 0.9 Hz, 1H), 5.09–5.07 (m, 1H), 4.62–4.57 (m, 1H), 2.80–2.70 (m, 1H), 2.64–2.54 (m, 1H), 2.16–1.14 (m, 3H), 2.04–1.91 (m, 2H), 1.81–1.61 (m, 2H), 1.59 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 147.8, 142.8, 139.3, 136.9, 128.3, 125.4, 123.4, 112.3, 77.4, 34.9, 29.5, 22.6, 21.7. HRMS (ESI<sup>+</sup>): calcd for C<sub>15</sub>H<sub>19</sub>O [M+H]<sup>+</sup> 215.1430, found 215.1436.



**(*E*)-2-(4-(phenylethynyl)benzylidene)cyclopentan-1-ol (2ac)**

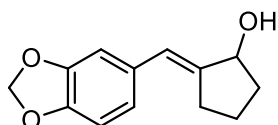
The general procedure was applied to 6-(4-(phenylethynyl)phenyl)hex-5-ynal (54 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as white solid. (43 mg, 78% yield) (*E/Z* = 98/2). Melting point = 90–92 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.54–7.48 (m, 4H), 7.37–7.32 (m, 5H), 6.57 (q, *J* = 2.6 Hz, 1H), 4.63–4.57 (m, 1H), 2.80–2.70 (m, 1H), 2.65–2.55 (m, 1H), 2.04–1.93 (m, 2H), 1.81–1.70 (m, 1H), 1.70–1.62 (m, 1H), 1.59 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.9, 137.8, 131.6, 131.6, 128.4, 128.36, 128.34, 123.3, 123.2, 121.3, 89.9,

89.6, 77.4, 34.9, 29.6, 22.5. HRMS (ESI<sup>+</sup>): calcd for C<sub>20</sub>H<sub>19</sub>O [M+H]<sup>+</sup> 275.1430, found 275.1432.



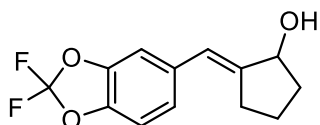
**(E)-2-(benzofuran-5-ylmethylene)cyclopentan-1-ol (2ad)**

The general procedure was applied to 6-(benzofuran-5-yl)hex-5-ynal (42 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as colorless oil. (36 mg, 85% yield) (*E/Z* = 97/3). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.61 (d, *J* = 2.2 Hz, 1H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.31 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.75 (dd, *J* = 2.4, 0.9 Hz, 1H), 6.70–6.67 (m, 1H), 4.65–4.59 (m, 1H), 2.82–2.72 (m, 1H), 2.66–2.56 (m, 1H), 2.05–1.92 (m, 2H), 1.80–1.63 (m, 2H), 1.22 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 153.8, 146.5, 145.4, 132.8, 127.6, 125.3, 123.9, 120.7, 111.1, 106.7, 35.0, 29.7, 29.4, 22.7. HRMS (ESI<sup>+</sup>): calcd for C<sub>14</sub>H<sub>15</sub>O<sub>2</sub> [M+H]<sup>+</sup> 215.1067, found 215.1070.



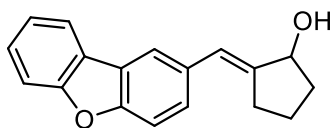
**(E)-2-(benzo[*d*][1,3]dioxol-5-ylmethylene)cyclopentan-1-ol (2ae)**

The general procedure was applied to ethyl 6-(benzo[*d*][1,3]dioxol-5-yl)hex-5-ynal (43 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 2/1) to afford the title compound as colorless oil. (37 mg, 85% yield) (*E/Z* = 99/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 6.90–6.88 (m, 1H), 6.84–6.78 (m, 2H), 6.49 (q, *J* = 2.6 Hz, 1H), 5.96 (s, 2H), 4.59–4.54 (m, 1H), 2.74–2.63 (m, 1H), 2.58–2.48 (m, 1H), 2.03–1.88 (m, 2H), 1.79–1.63 (m, 2H), 1.59 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 147.7, 146.2, 146.0, 132.2, 123.5, 122.6, 108.3, 108.3, 101.0, 77.5, 34.9, 29.3, 22.6. HRMS (ESI<sup>+</sup>): calcd for C<sub>13</sub>H<sub>15</sub>O<sub>3</sub> [M+H]<sup>+</sup> 219.1016, found 219.1020.



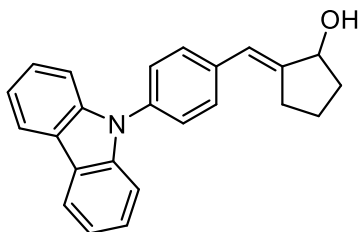
**(E)-2-((2,2-difluorobenzo[*d*][1,3]dioxol-5-yl)methylene)cyclopentan-1-ol (2af)**

The general procedure was applied to 6-(2-methylbenzo[*d*][1,3]dioxol-5-yl)hex-5-ynal (50 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as colorless oil. (45 mg, 88% yield) (*E/Z* = 98/2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.09–7.08 (m, 1H), 7.05–6.99 (m, 2H), 6.52 (q, *J* = 2.6 Hz, 1H), 4.60–4.55 (m, 1H), 2.72–2.62 (m, 1H), 2.58–2.48 (m, 1H), 2.02–1.93 (m, 2H), 1.79–1.69 (m, 1H), 1.68–1.64 (m, 1H), 1.25 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.0, 143.0 (d, *J* = 174.3 Hz), 134.2, 131.6482 (d, *J* = 512.0 Hz), 131.6481, 124.1, 122.5, 109.2, 108.9, 77.2, 34.9, 29.7, 29.3, 22.4. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -50.0. HRMS (ESI<sup>+</sup>): calcd for C<sub>13</sub>H<sub>13</sub>F<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 255.0827, found 255.0827.



**(E)-2-(dibenzo[*b,d*]furan-2-ylmethylene)cyclopentan-1-ol (2ag)**

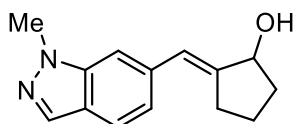
The general procedure was applied to 6-(dibenzo[*b,d*]furan-2-yl)hex-5-ynal (52 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as yellow oil. (38 mg, 72% yield) (*E/Z* = 98/2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.96–7.93 (m, 1H), 7.93 (d, *J* = 2.0 Hz, 1H), 7.58–7.51 (m, 2H), 7.48–7.43 (m, 2H), 7.35 (td, *J* = 7.5, 1.1 Hz, 1H), 6.74 (q, *J* = 2.6 Hz, 1H), 4.67–4.62 (m, 1H), 2.88–2.78 (m, 1H), 2.72–2.62 (m, 1H), 2.07–1.94 (m, 2H), 1.85–1.75 (m, 1H), 1.75–1.66 (m, 1H), 1.60 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 156.6, 155.0, 146.8, 132.9, 128.0, 127.2, 124.4, 124.2, 123.7, 122.8, 120.6, 120.2, 111.8, 111.4, 77.5, 35.0, 29.4, 22.7. HRMS (ESI<sup>+</sup>): calcd for C<sub>18</sub>H<sub>17</sub>O<sub>2</sub> [M+H]<sup>+</sup> 265.1223, found 265.1226.



**(E)-2-(4-(9*H*-carbazol-9-yl)benzylidene)cyclopentan-1-ol (2ah)**

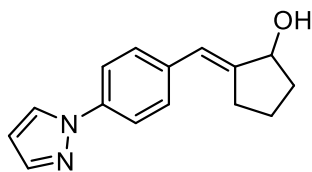
The general procedure was applied to 6-(4-(9*H*-carbazol-9-yl)phenyl)hex-5-ynal (77 mg,

0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as white solid. (53 mg, 78% yield) (*E/Z* = 97/3). Melting point = 96–97 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.15 (dt, *J* = 7.8, 1.08 Hz, 2H), 7.61–7.52 (m, 4H), 7.45–7.39 (m, 4H), 7.32–7.27 (m, 2H), 6.69 (q, *J* = 2.6 Hz, 1H), 4.69–4.64 (m, 1H), 2.88–2.78 (m, 1H), 2.73–2.65 (m, 1H), 2.06–1.98 (m, 2H), 1.86–1.75 (m, 1H), 1.75–1.66 (m, 1H), 1.60 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.7, 140.8, 137.0, 135.9, 129.8, 126.9, 126.0, 123.4, 122.8, 120.3, 112.0, 110.0, 34.9, 29.7, 29.53, 22.5. HRMS (ESI<sup>+</sup>): calcd for C<sub>24</sub>H<sub>22</sub>NO [M+H]<sup>+</sup> 340.1696, found 340.1699.



**(*E*)-2-((1-methyl-1*H*-indazol-6-yl)methylene)cyclopentan-1-ol (2ai)**

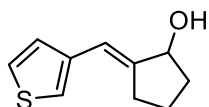
The general procedure was applied to 6-(1-methyl-1*H*-indazol-6-yl)hex-5-ynal (45 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as white solid. (37 mg, 82% yield) (*E/Z* = 96/4). Melting point = 88–89 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.93 (d, *J* = 1.1 Hz, 1H), 7.66 (dd, *J* = 8.4, 0.84 Hz, 1H), 7.32 (s, 1H), 7.18 (dd, *J* = 8.4, 1.5 Hz, 1H), 6.73 (q, *J* = 2.6 Hz, 1H), 4.66–4.61 (m, 1H), 4.06 (s, 3H), 2.87–2.76 (m, 1H), 2.71–2.60 (m, 1H), 2.05–1.95 (m, 2H), 1.83–1.69 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.5, 140.3, 136.2, 132.6, 124.0, 122.7, 122.0, 120.7, 108.0, 77.4, 35.4, 34.9, 29.6, 22.5. HRMS (ESI<sup>+</sup>): calcd for C<sub>14</sub>H<sub>17</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 229.1335, found 229.1341.



**(*E*)-2-(4-(1*H*-pyrazol-1-yl)benzylidene)cyclopentan-1-ol (2aj)**

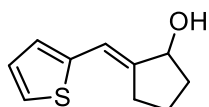
The general procedure was applied to 6-(4-(1*H*-pyrazol-1-yl)phenyl)hex-5-ynal (47 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as white solid. (41 mg, 85% yield) (*E/Z* = 97/3). Melting point = 91–92 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.92 (d, *J* = 2.5 Hz, 1H), 7.7 (d, *J* = 1.9 Hz, 1H), 7.68–7.64 (m, 2H), 7.46–7.41 (m, 2H), 6.59 (q, *J* = 2.6 Hz, 1H), 6.47

(t,  $J = 2.1$  Hz, 1H), 4.61 (t,  $J = 5.8$  Hz, 1H), 2.80–2.70 (m, 1H), 2.65–2.55 (m, 1H), 2.05–1.93 (m, 2H), 1.81–1.73 (m, 1H), 1.72–1.65 (m, 1H), 1.25 (br, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 148.2, 141.1, 138.4, 136.1, 129.4, 126.6, 122.7, 119.0, 107.6, 76.8, 34.9, 29.4, 22.5$ . HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  241.1335, found 241.1338.



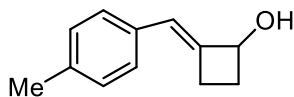
**(E)-2-(thiophen-3-ylmethylene)cyclopentan-1-ol (2ak)**

The general procedure was applied to 6-(thiophen-3-yl)hex-5-ynal (36 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as colorless oil. (29 mg, 80% yield) ( $E/Z = 96/4$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.29$  (dd,  $J = 5.00, 3.04$  Hz, 1H), 7.19–7.14 (m, 2H), 6.62 (q,  $J = 2.7$  Hz, 1H), 4.60–4.55 (m, 1H), 2.73–2.64 (m, 1H), 2.58–2.48 (m, 1H), 2.03–1.91 (m, 2H), 1.79–1.61 (m, 2H), 1.56 (br, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 146.6, 139.4, 128.1, 125.2, 122.3, 117.8, 77.0, 35.3, 29.6, 22.4$ . HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{10}\text{H}_{13}\text{OS}$   $[\text{M}+\text{H}]^+$  181.0682, found 181.0686.



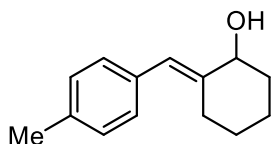
**(E)-2-(thiophen-2-ylmethylene)cyclopentan-1-ol (2al)**

The general procedure was applied to 6-(thiophen-2-yl)hex-5-ynal (36 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as white solid. (30 mg, 84% yield) ( $E/Z = 96/4$ ). Melting point = 46–47 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.27$  (d,  $J = 5.0$  Hz, 1H), 7.05–6.99 (m, 2H), 6.81 (q,  $J = 2.4$  Hz, 1H), 4.63–4.60 (m, 1H), 2.72–2.62 (m, 1H), 2.57–2.47 (m, 1H), 2.07–1.92 (m, 2H), 1.83–1.73 (m, 1H), 1.80–1.61 (m, 1H), 1.60 (br, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 145.9, 141.8, 127.0, 126.4, 125.2, 117.1, 76.9, 35.6, 29.8, 22.4$ . HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{10}\text{H}_{13}\text{OS}$   $[\text{M}+\text{H}]^+$  181.0682, found 181.0685. Spectroscopic data are in accordance with those described in the literature.<sup>8</sup>



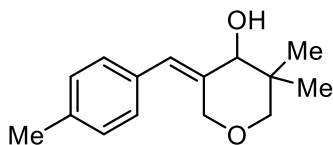
**(E)-2-(4-methylbenzylidene)cyclobutan-1-ol (4a)**

The general procedure was applied to 5-(*p*-tolyl)pent-4-ynal (34 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as white solid. (16 mg, 47% yield) (*E/Z* = 99/1). Melting point = 84–86 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.18–1.11 (m, 4H), 6.40 (q, *J* = 2.4 Hz, 1H), 4.87–4.80 (m, 1H), 2.83–2.73 (m, 1H), 2.70–2.60 (m, 1H), 2.55–2.46 (m, 1H), 2.37 (s, 3H), 1.98–1.91 (m, 1H), 1.62 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 146.8, 136.5, 134.0, 129.2, 127.7, 112.0, 72.3, 32.0, 25.1, 21.2. HRMS (ESI<sup>+</sup>): calcd for C<sub>12</sub>H<sub>15</sub>O [M+H]<sup>+</sup> 175.1117, found 175.1119. Spectroscopic data are in accordance with those described in the literature.<sup>9</sup>



**(E)-2-(4-methylbenzylidene)cyclohexan-1-ol (4b)**

The general procedure was applied to 7-(*p*-tolyl)hept-6-ynal (40 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as white solid. (29 mg, 73% yield) (*E/Z* = 99/1). Melting point = 48–50 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.15–7.10 (m, 4H), 6.32 (d, *J* = 2.3 Hz, 1H), 4.84–4.81 (m, 1H), 2.65–2.55 (m, 1H), 2.34 (s, 3H), 2.19–2.13 (m, 1H), 1.94–1.77 (m, 3H), 1.62–1.55 (m, 3H), 1.26 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 142.2, 136.3, 134.2, 128.9, 128.7, 125.2, 65.9, 34.2, 32.4, 28.0, 21.1, 20.3. HRMS (ESI<sup>+</sup>): calcd for C<sub>14</sub>H<sub>19</sub>O [M+H]<sup>+</sup> 203.1430, found 203.1435. Spectroscopic data are in accordance with those described in the literature.<sup>9</sup>

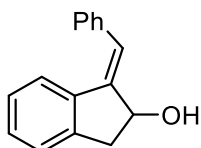


**(E)-3,3-dimethyl-5-(4-methylbenzylidene)tetrahydro-2H-pyran-4-ol (4c)**

The general procedure was applied to 2,2-dimethyl-3-((3-(*p*-tolyl)prop-2-yn-1-

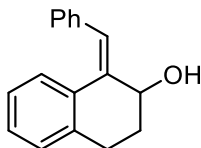


yl)oxy)propanal (46 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as white solid. (33 mg, 71% yield) (*E/Z* = 97/3). Melting point = 57–58 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.14 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.58 (s, 1H), 4.56 (d, *J* = 12.8 Hz, 1H), 4.16 (dd, *J* = 12.8, 1.1 Hz, 1H), 3.97 (s, 1H), 3.63 (dd, *J* = 11.6, 1.0 Hz, 1H), 3.31 (d, *J* = 11.2 Hz, 1H), 2.34 (s, 3H), 1.60 (br, 1H), 1.01 (s, 3H), 0.96 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 137.1, 136.8, 133.4, 129.0, 129.0, 125.2, 78.7, 75.3, 65.2, 38.3, 23.2, 21.2, 19.0. HRMS (ESI<sup>+</sup>): calcd for C<sub>15</sub>H<sub>21</sub>O<sub>2</sub> [M+H]<sup>+</sup> 233.1536, found 233.1536.



**(*E*)-1-benzylidene-2,3-dihydro-1*H*-inden-2-ol (4d)**

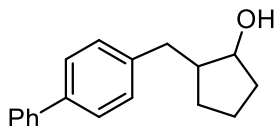
The general procedure was applied to 2-(2-(phenylethynyl)phenyl)acetaldehyde (44 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as yellow oil. (38 mg, 85% yield) (*E/Z* = 91/9). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.44–7.39 (m, 2H), 7.37–7.32 (m, 2H), 7.32–7.23 (m, 3H), 7.18 (dt, *J* = 4.6, 1.3 Hz, 1H), 6.81 (d, *J* = 1.9 Hz, 1H), 4.95 (t, *J* = 6.4 Hz, 1H), 3.35–3.27 (m, 1H), 2.95–2.87 (m, 1H), 1.95 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 145.6, 143.8, 137.3, 137.2, 128.9, 128.5, 128.3, 127.3, 126.4, 125.5, 124.5, 124.3, 76.5, 40.6. HRMS (ESI<sup>+</sup>): calcd for C<sub>16</sub>H<sub>15</sub>O [M+H]<sup>+</sup> 223.1117, found 223.1118.



**(*E*)-1-benzylidene-1,2,3,4-tetrahydronaphthalen-2-ol (4e)**

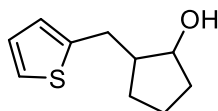
The general procedure was applied to 1-(3-methylbut-3-en-1-yl)-2-(phenylethynyl)benzene (47 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as white solid. (39 mg, 83% yield) (*E/Z* = 99/1). Melting point = 108–109 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.28–7.17 (m, 6H), 7.17–7.10 (m, 2H), 6.88–6.83 (m, 1H), 6.71 (s, 1H), 4.60–4.56 (m,

1H), 3.14–3.04 (m, 1H), 2.97–2.88 (m, 1H), 2.17–2.08 (m, 1H), 2.15–2.04 (m, 1H), 1.67 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 139.9, 137.71, 137.69, 132.2, 130.0, 129.1, 128.6, 128.3, 127.8, 126.9, 125.0, 124.4, 72.6, 31.6, 26.0. HRMS (ESI<sup>+</sup>): calcd for C<sub>17</sub>H<sub>17</sub>O [M+H]<sup>+</sup> 237.1274, found 237.1278.



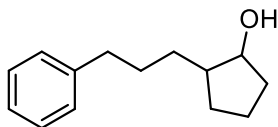
#### 2-([1,1'-biphenyl]-4-ylmethyl)cyclopentan-1-ol (4f)

The general procedure was applied to 6-([1,1'-biphenyl]-4-yl)hex-5-enal (50 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as white solid. (43 mg, 85% yield). (*dr* = 95:5). Melting point = 84–85 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.61–7.58 (m, 2H), 7.55–7.51 (m, 2H), 7.46–7.41 (m, 2H), 7.36–7.30 (m, 3H), 4.16–4.12 (m, 1H), 2.95–2.87 (m, 1H), 2.77–2.70 (m, 1H), 2.11–2.00 (m, 1H), 1.92–1.82 (m, 2H), 1.79–1.67 (m, 2H), 1.67–1.54 (m, 2H), 1.29 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 141.12, 141.06, 138.7, 129.2, 128.7, 127.1, 127.03, 127.00, 74.4, 47.6, 35.2, 34.9, 28.8, 21.9. HRMS (ESI<sup>+</sup>): calcd for C<sub>18</sub>H<sub>21</sub>O [M+H]<sup>+</sup> 253.1587, found 253.1590.



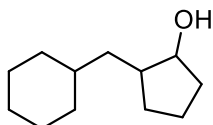
#### 2-(thiophen-2-ylmethyl)cyclopentan-1-ol (4g)

The general procedure was applied to 6-(thiophen-2-yl)hex-5-enal (36 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as colorless oil. (27 mg, 74% yield). (*dr* = 85:15). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.12 (dd, *J* = 5.1, 1.4 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.84–6.81 (m, 1H), 4.18 (t, *J* = 4.4 Hz, 1H), 3.08 (dd, *J* = 14.8, 8.12 Hz, 1H), 2.91 (dd, *J* = 14.8, 7.12 Hz, 1H), 2.11–2.00 (m, 1H), 1.90–1.75 (m, 3H), 1.70–1.63 (m, 1H), 1.28 (br, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 144.6, 126.7, 124.5, 123.1, 74.2, 47.9, 34.9, 29.6, 29.0, 21.9. HRMS (ESI<sup>+</sup>): calcd for C<sub>10</sub>H<sub>15</sub>OS [M+H]<sup>+</sup> 183.0838, found 183.0839.



#### 2-(3-phenylpropyl)cyclopentan-1-ol (4h)

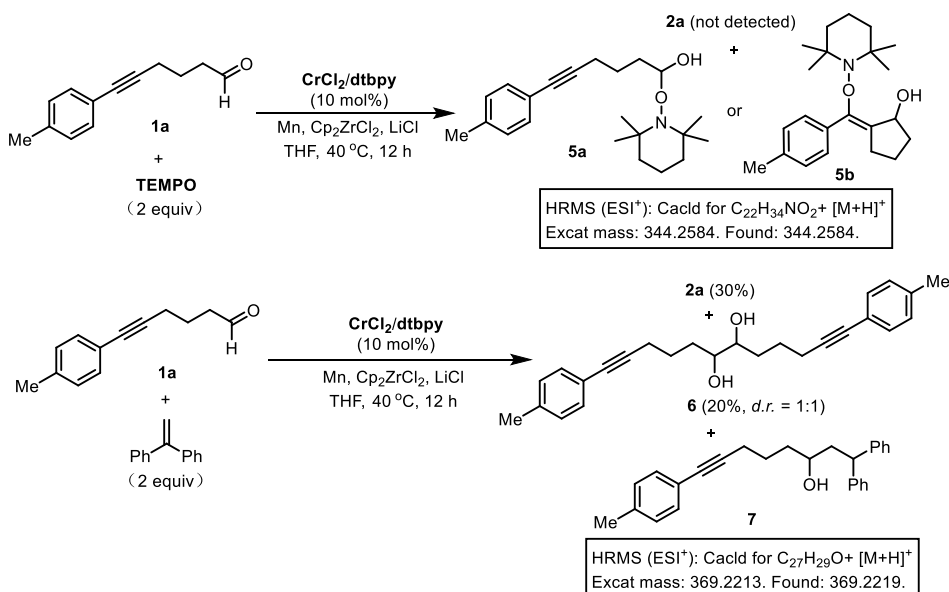
The general procedure was applied to 8-phenyloct-5-enal (40 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as colorless oil. (26 mg, 65% yield). (*dr* = 60:40).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.30–7.26 (m, 2H), 7.20–7.17 (m, 3H), 4.15–4.11 (m, 1H), 2.66–2.61 (m, 2H), 1.81–1.64 (m, 7H), 1.58–1.50 (m, 2H), 1.45–1.34 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 128.5, 128.4, 128.3, 125.7, 74.9, 45.8, 36.3, 34.8, 30.6, 28.8, 28.7, 21.8. HRMS ( $\text{ESI}^+$ ): calcd for  $\text{C}_{14}\text{H}_{21}\text{O}$   $[\text{M}+\text{H}]^+$  205.1587, found 205.1589. Spectroscopic data are in accordance with those described in the literature.<sup>10</sup>



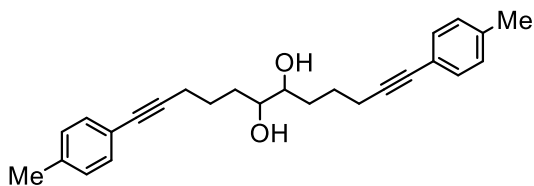
#### 2-(cyclohexylmethyl)cyclopentan-1-ol (4i)

The general procedure was applied to 6-cyclohexylhex-5-enal (36 mg, 0.2 mmol). The crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as colorless oil. (25 mg, 70% yield). (*dr* = 58:42).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.77 (q,  $J$  = 5.24 Hz, 1H), 1.93–1.85 (m, 2H), 1.79–1.75 (m, 1H), 1.74–1.65 (m, 5H), 1.63–1.56 (m, 2H), 1.53–1.50 (m, 2H), 1.37–1.29 (m, 2H), 1.20–1.10 (m, 3H), 1.09–1.01 (m, 1H), 0.96–0.78 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 79.8, 45.4, 41.9, 36.2, 34.5, 34.3, 33.0, 30.2, 26.7, 26.5, 26.4, 21.8. HRMS ( $\text{ESI}^+$ ): calcd for  $\text{C}_{12}\text{H}_{23}\text{O}$   $[\text{M}+\text{H}]^+$  183.1743, found 183.1746.

## 6. Radical Scavenger Experiments



**1a** (0.2 mmol), CrCl<sub>2</sub> (10 mol%, 0.02 mmol), dtbpy (10 mol%, 0.02 mmol), Mn (22 mg, 0.4 mmol), Cp<sub>2</sub>ZrCl<sub>2</sub> (88 mg, 0.3 mmol), LiCl (17 mg, 0.4 mmol), DME (2 mL) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (0.4 mmol, 2 equiv) or 1,1-diphenylethylene (0.4 mmol, 2 equiv) were added into a dried Schlenk tubes and stirred at 40 °C for 12 h. After cooling to room temperature, 0.2 mL of H<sub>2</sub>O was added and stirred for 15 min (the compounds **5a** or **5b** and **7** was detected by HRMS analysis). The crude mixture was purified by flash column chromatography on silica gel to afford the related compounds.



### 1,12-di-*p*-tolyl-dodeca-1,11-diyne-6,7-diol (**6**)

Colorless oil. *dr* = 1:1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.25–7.21 (d, *J* = 8.2 Hz, 2H), 7.14–7.11 (d, *J* = 8.0 Hz, 2H), 7.09–7.04 (m, 4H), 5.00–4.97 (m, 1H), 4.74–4.69 (m, 1H), 2.43–2.38 (m, 3H), 2.33 (s, 6H), 2.22–2.12 (m, 1H), 2.08–1.97 (m, 1H), 1.88–1.80 (m, 2H), 1.80–1.64 (m, 5H), 1.60 (br, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 144.0, 139.4, 137.5, 137.5, 136.4, 131.4, 129.1, 128.9, 128.6, 120.8, 89.1, 81.1, 74.1, 71.6, 36.6, 35.3, 31.8, 25.1, 22.7, 21.4, 21.2, 19.2. HRMS (ESI<sup>+</sup>): calcd for C<sub>26</sub>H<sub>31</sub>O<sub>2</sub> [M+H]<sup>+</sup> 375.2319, found

375.2330.

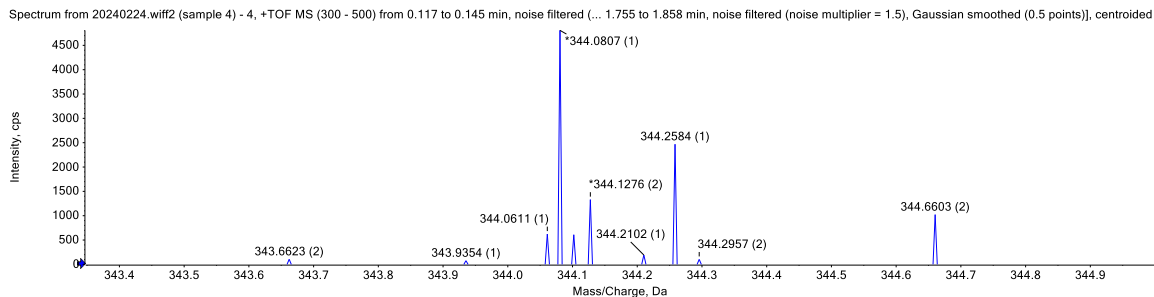


Figure S1: Image for HRMS analysis of **5a** or **5b**.

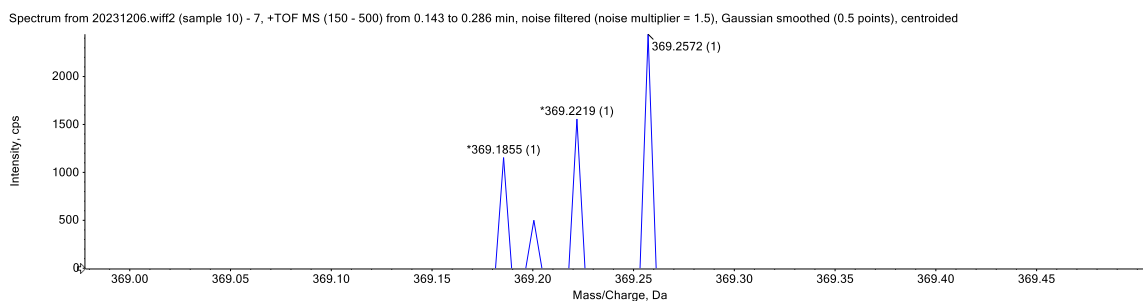


Figure S2: Image for HRMS analysis of **7**.

## 7. Cyclic Voltammetry

Linear Sweep Voltammetry was performed on electrochemical analyzer. The voltametric cell consisted of glassy carbon electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. The measurements were varied out under atmosphere of nitrogen by using a solution of sample with a concentration of 0.1 M in MeCN containing tetrabutylammonium perchlorate ( $[\text{Bu}_4\text{N}]^+[\text{ClO}_4]^-$ ) as a supporting electrolyte (0.1 M).

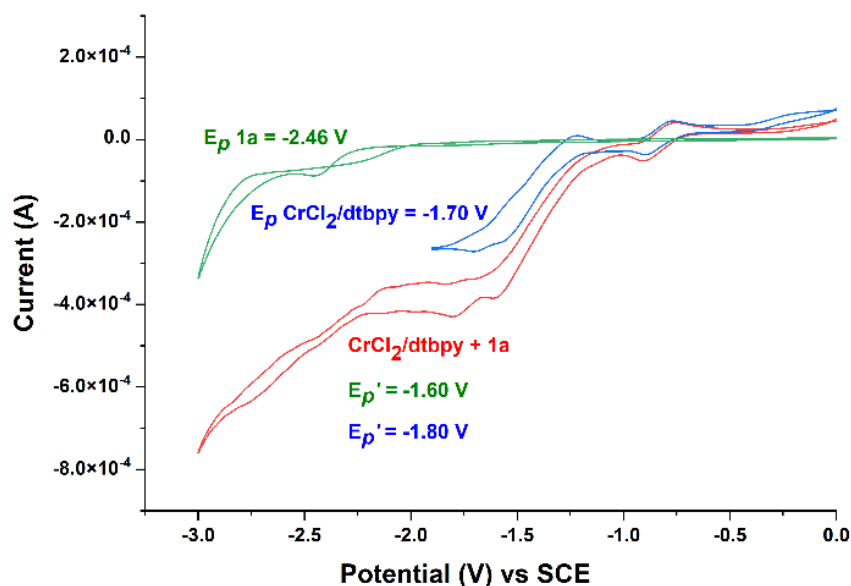
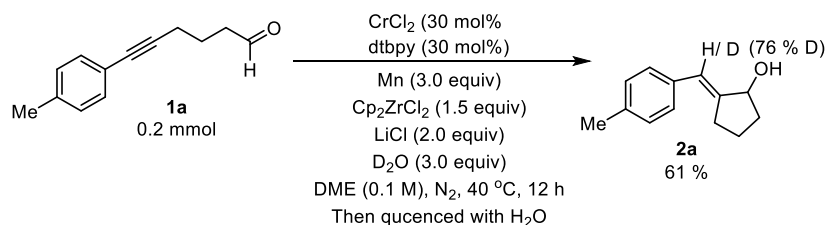


Figure S3. Measurements of the reduction potentials

## 8. Exploring the Hydrogen Source of Vinyl Group



**1a** (0.2 mmol),  $\text{CrCl}_2$  (30 mol%, 0.06 mmol), dtbpy (30 mol%, 0.06 mmol), Mn (33 mg, 0.6 mmol),  $\text{Cp}_2\text{ZrCl}_2$  (88 mg, 0.3 mmol), LiCl (17 mg, 0.4 mmol),  $\text{D}_2\text{O}$  (0.6 mmol) and DME (2 mL) were added into a Schlenk tube and the resulting mixture was stirred at 40 °C for 12 h. After cooling to room temperature, 0.2 mL of  $\text{H}_2\text{O}$  was added and the resulting mixture was stirred for 15 min. The crude mixture was purified by flash column chromatography on silica gel to afford **2a** in 61% yield. The incorporation of 76% of deuterium into the vinyl group was detected by  $^1\text{H}$  NMR analysis.

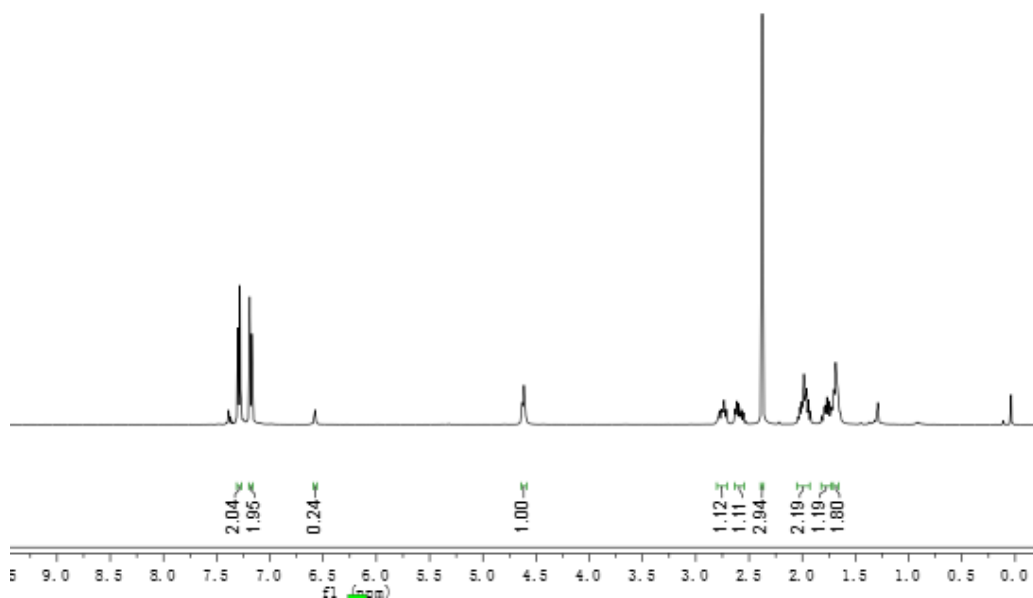
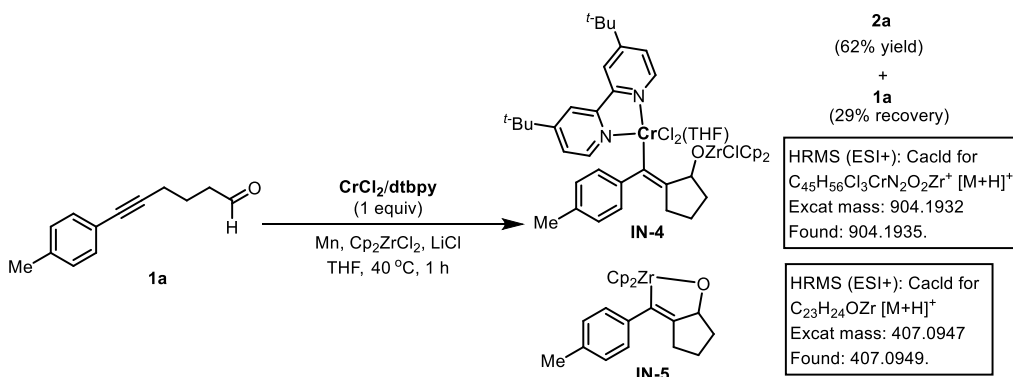


Figure S4:  $^1\text{H}$  NMR spectra of **2a** with the incorporation of 76% of deuterium.

## 9. Analysis of the Related Intermediates by HRMS Technique



**1a** (0.2 mmol),  $\text{CrCl}_2$  (0.2 mmol), dtbpy (0.2 mmol), Mn (22 mg, 0.4 mmol),  $\text{Cp}_2\text{ZrCl}_2$  (88 mg, 0.3 mmol), LiCl (17 mg, 0.4 mmol) and DME (2 mL) were added into a dried Schlenk tube and the resulting mixture was stirred at 40 °C for 1 h. After removal of the volatiles under vacuum, the resulting residue was analyzed by HRMS technique. While the crude compounds were purified by flash column chromatography on silica gel to afford the product **2a** in 62% yield with 29% recovery of **1a**.

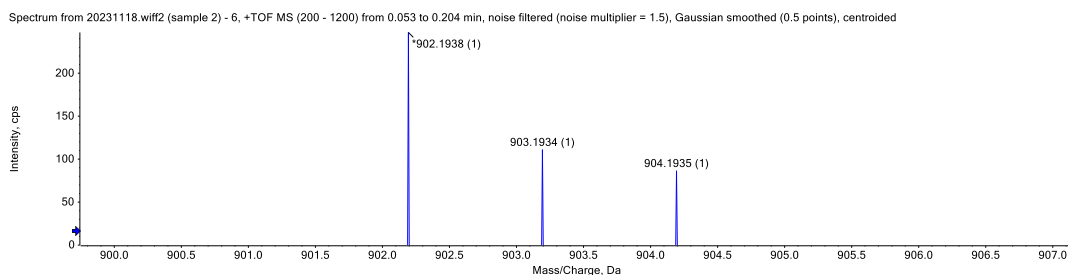


Figure S5: Image for HRMS analysis of Intermediate IN-4.

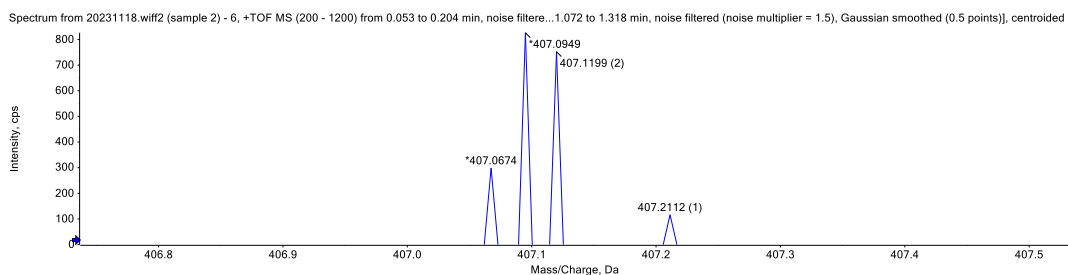
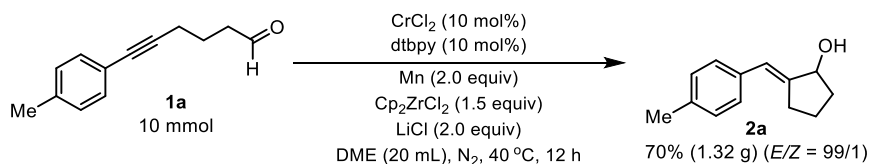


Figure S6: Image for HRMS analysis of Intermediate IN-5.

## 10. Synthetic Applications

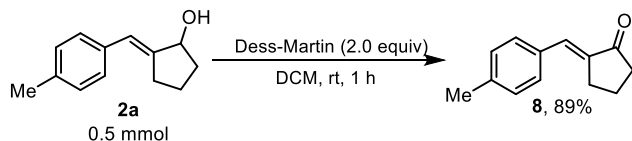
### Gram-Scale Reaction:



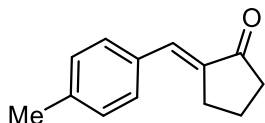
**1a** (10.0 mmol, 1.86 g),  $\text{CrCl}_2$  (1.0 mmol), dtbpy (1.0 mmol), Mn (1.1 g, 20 mmol),  $\text{Cp}_2\text{ZrCl}_2$  (4.4 g, 15 mmol), LiCl (0.8 g, 20 mmol) and DME (20 mL) were added into a dried Schlenk tube (50 mL) and the resulting mixture was stirred at 40 °C for 12 h. After cooling to room temperature, 10.0 mL of  $\text{H}_2\text{O}$  was added and the resulting mixture was stirred for 15 min. After filtration and washing by ethyl acetate, the volatiles were removed under vacuum, the crude mixture was purified by flash column chromatography on silica gel to afford **2a** in 70% yield (1.32 g) (*E/Z* = 99/1).

### Late-stage functionalization of **2a**:



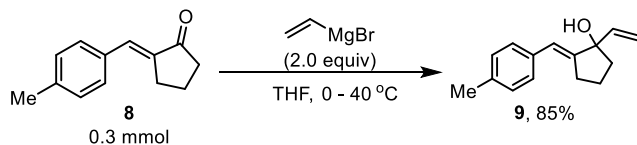


Dess-Martin (1.0 mmol, 0.4 g) was slowly added into a solution of **2a** (0.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) and stirred at room temperature for 1 h. After quenching the reaction with saturated  $\text{Na}_2\text{S}_2\text{O}_3$  (aq) and washing by saturated  $\text{NaHCO}_3$  (aq), the organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the volatiles under vacuum, the crude product was purified by column chromatography on silica gel (PE/EA = 20/1) to afford (*E*)-2-(4-methylbenzylidene)cyclopentan-1-one (**8**) as yellow solid (83 mg, 89% yield).



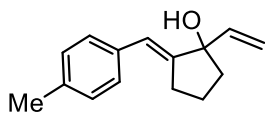
**(*E*)-2-(4-methylbenzylidene)cyclopentan-1-one (8)**

White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.44 (d,  $J$  = 8.3 Hz, 2H), 7.37 (t,  $J$  = 2.8 Hz, 1H), 7.22 (d,  $J$  = 8.1 Hz, 2H), 2.97 (dt,  $J$  = 7.4, 2.8 Hz, 2H), 2.40 (t,  $J$  = 8.0 Hz, 2H), 2.38 (s, 3H), 2.07–1.98 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 208.2, 139.7, 135.1, 132.8, 132.4, 130.6, 129.5, 37.8, 29.4, 21.5, 20.2. HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{13}\text{H}_{15}\text{O}$  [ $\text{M}+\text{H}$ ]<sup>+</sup> 187.1117, found 187.1121. Spectroscopic data are in accordance with those described in the literature.<sup>8</sup>



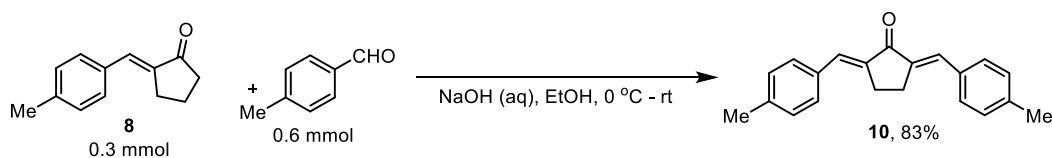
To a solution of the ketone **8** (56 mg, 0.3 mmol) in dry THF (1 mL) added vinylmagnesium bromide (1.0 M in THF, 0.6 mL, 0.6 mmol) dropwise at 0 °C. After stirring for 20 min, the reaction mixture was slowly heated to 40 °C. After quenching by saturated aqueous solution of  $\text{NH}_4\text{Cl}$  and extraction with ethyl acetate, the combined organic layers were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration and removal of volatiles under vacuum, the crude product was purified by column chromatography on silica gel (PE/EA = 5/1) to afford (*E*)-2-(4-methylbenzylidene)-1-vinylcyclopentan-1-ol (**9**) as a colorless oil (55 mg,

85%).

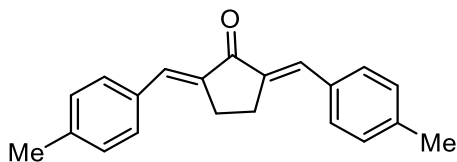


**(E)-2-(4-methylbenzylidene)-1-vinylcyclopentan-1-ol (9)**

Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.25 (d,  $J$  = 8.2 Hz, 2H), 7.16-7.12 (d,  $J$  = 8.1 Hz, 2H), 6.37 (t,  $J$  = 2.7 Hz, 1H), 5.98 (dd,  $J$  = 17.2, 6.7 Hz, 1H), 5.44 (dd,  $J$  = 17.1, 1.6 Hz, 1H), 5.22 (dd,  $J$  = 10.5, 1.6 Hz, 1H), 2.90–2.81 (m, 1H), 2.67–2.55 (m, 1H), 2.34 (s, 3H), 2.07–1.96 (m, 1H), 1.88–1.79 (m, 3H), 1.25 (br, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.3, 142.5, 136.5, 134.8, 129.0, 128.5, 123.9, 113.0, 83.2, 40.4, 30.4, 22.8, 21.2. HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{15}\text{H}_{19}\text{O}$   $[\text{M}+\text{H}]^+$  215.1430, found 215.1437.



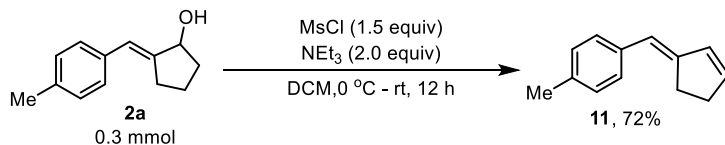
$\text{NaOH}(\text{aq})$  (5 mL, 0.1 M) was slowly added into a solution of **8** (56 mg, 0.3 mmol) and *p*-tolualdehyde (72 mg, 0.6 mmol) in EtOH (5 mL) at 0 °C and the mixture was warmed to room temperature. After quenching by  $\text{H}_2\text{O}$  and extraction with ethyl acetate, the combined organic layers were then washed with brine, and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration and removal of volatiles under vacuum, the crude product was purified by column chromatography on silica gel (PE/EA = 20/1) to afford 2,5-bis((*E*)-4-methylbenzylidene)cyclopentan-1-one (**10**) as yellow solid (72 mg, 83%).



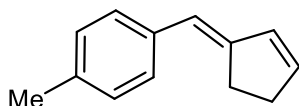
**2,5-bis((E)-4-methylbenzylidene)cyclopentan-1-one (10)**

Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.57 (s, 2H), 7.50 (d,  $J$  = 8.2 Hz, 4H), 7.25 (d,  $J$  = 8.9 Hz, 4H), 3.09 (t,  $J$  = 1.1 Hz, 4H), 2.40 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 196.5, 139.8, 136.6, 133.7, 133.2, 130.8, 129.6, 26.6, 21.5. HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{21}\text{H}_{21}\text{O}$   $[\text{M}+\text{H}]^+$  289.1587, found 289.1589. Spectroscopic data are in accordance with

those described in the literature.<sup>8</sup>

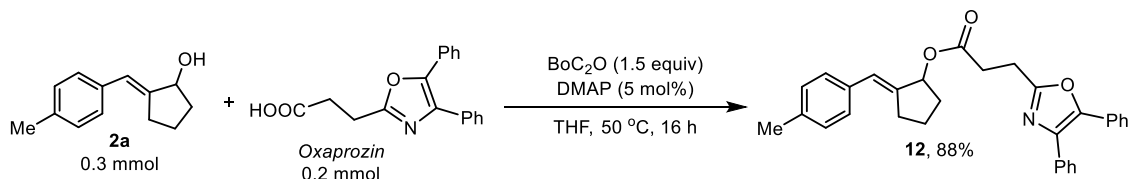


To a solution of **2a** (56 mg, 0.3 mmol) in dry DCM at 0 °C added triethylamine (0.6 mmol) and MsCl (0.3 mmol). The mixture was stirred at room temperature for 12 h. After quenching with saturated aqueous solution of NaHCO<sub>3</sub> and extraction by DCM, the combined organic layers were washed by brine, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and removal of the volatiles under vacuum, the crude product was purified by column chromatography on silica gel (PE) to afford (*E*)-1-(cyclopent-2-en-1-ylidenemethyl)-4-methylbenzene (**11**) as white solid (37 mg, 72%).



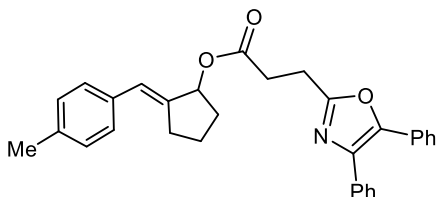
**(E)-1-(cyclopent-2-en-1-ylidenemethyl)-4-methylbenzene (11)**

White solid. Melting point = 46 - 48 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.27 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.34 (t, *J* = 2.8 Hz, 1H), 6.31–6.28 (m, 1H), 6.16–6.12 (m, 1H), 2.86–2.81 (m, 2H), 2.67–2.63 (m, 2H), 2.33 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.6, 137.2, 136.8, 136.0, 135.4, 129.1, 127.8, 119.5, 33.3, 28.8, 21.2. HRMS (ESI<sup>+</sup>): calcd for C<sub>13</sub>H<sub>15</sub> [M+H]<sup>+</sup> 171.1168, found 171.1170.



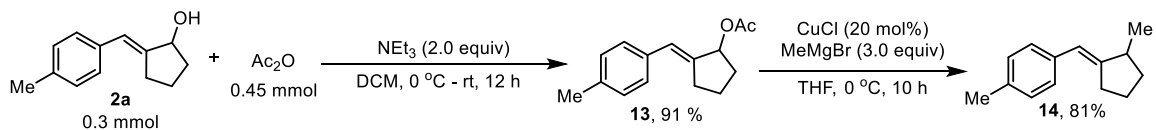
**2a** (56 mg, 0.3 mmol), oxaprozin (60 mg, 0.2 mmol), BoC<sub>2</sub>O (0.3 mmol), DMAP (0.01 mmol) and THF (2 mL) were added into a Schlenk tube (20 mL) and the mixture was stirred at 50 °C for 16 h. After removal of the volatiles under vacuum, the crude mixture was purified by column chromatography on silica gel (PE/EA = 5/1) to afford (*E*)-2-(4-methylbenzylidene)cyclopentyl 3-(4,5-diphenyloxazol-2-yl)propanoate (**12**) as colorless

oil (82 mg, 88%).

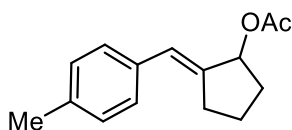


**(E)-2-(4-methylbenzylidene)cyclopentyl 3-(4,5-diphenyloxazol-2-yl)propanoate (12)**

Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.63–7.59 (m, 2H), 7.57–7.52 (m, 2H), 7.35–7.29 (m, 6H), 7.20 (d,  $J$  = 8.3 Hz, 2H), 7.11 (d,  $J$  = 8.9 Hz, 2H), 7.60–7.56 (m, 1H), 5.72–5.67 (m, 1H), 3.20 (t,  $J$  = 7.3 Hz, 2H), 2.93 (t,  $J$  = 7.8 Hz, 2H), 2.74–2.64 (m, 1H), 2.57–2.47 (m, 1H), 2.33 (s, 3H), 1.99–1.88 (m, 2H), 1.83–1.74 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 171.8, 161.9, 145.4, 141.7, 136.7, 135.2, 134.7, 132.5, 129.0, 128.6, 128.6, 128.6, 128.55, 128.4, 128.0, 127.9, 126.7, 126.5, 79.9, 32.4, 31.6, 29.6, 23.7, 23.5, 21.2. HRMS (ESI $^+$ ): calcd for  $\text{C}_{31}\text{H}_{30}\text{NO}_3$   $[\text{M}+\text{H}]^+$  464.2220, found 464.2223.

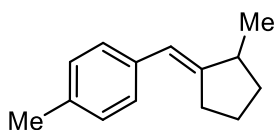


$\text{Ac}_2\text{O}$  (0.45 mmol) was slowly added into a solution of **2a** (56 mg, 0.3 mmol) and triethylamine (0.6 mmol) in dry DCM (5 mL) at 0 °C. The mixture was then slowly warmed to room temperature and stirred for 12 h. After quenching with saturated aqueous solution of  $\text{NaHCO}_3$  and extraction with DCM, the combined organic layers were washed with brine, and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration and removal of the volatiles under vacuum, the crude product was purified by column chromatography on silica gel (PE) to afford (*E*)-2-(4-methylbenzylidene)cyclopentyl acetate (**13**) as colorless oil (63 mg, 91 %). Subsequently,  $\text{MeMgBr}$  (1.0 M in THF, 0.6 mL, 0.6 mmol) was slowly added into a solution of **13** (0.2 mmol) and  $\text{CuCl}$  (0.04 mmol) in THF (3 mL) and the mixture was stirred at 0 °C for 10 h. After quenching with saturated aqueous solution of  $\text{NH}_4\text{Cl}$  and extraction by ethyl acetate, the combined organic layers were washed with brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration and removal of volatiles under vacuum, the crude product was purified by column chromatography on silica gel (PE) to afford (*E*)-1-methyl-4-((2-methylcyclopentylidene)methyl)benzene (**14**) as colorless oil (30 mg, 81%).



**(E)-2-(4-methylbenzylidene)cyclopentyl acetate (13)**

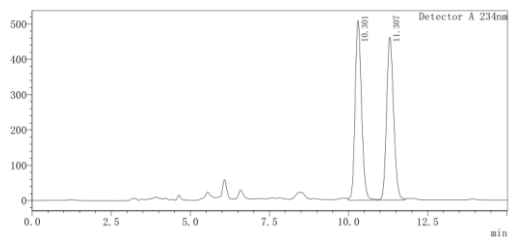
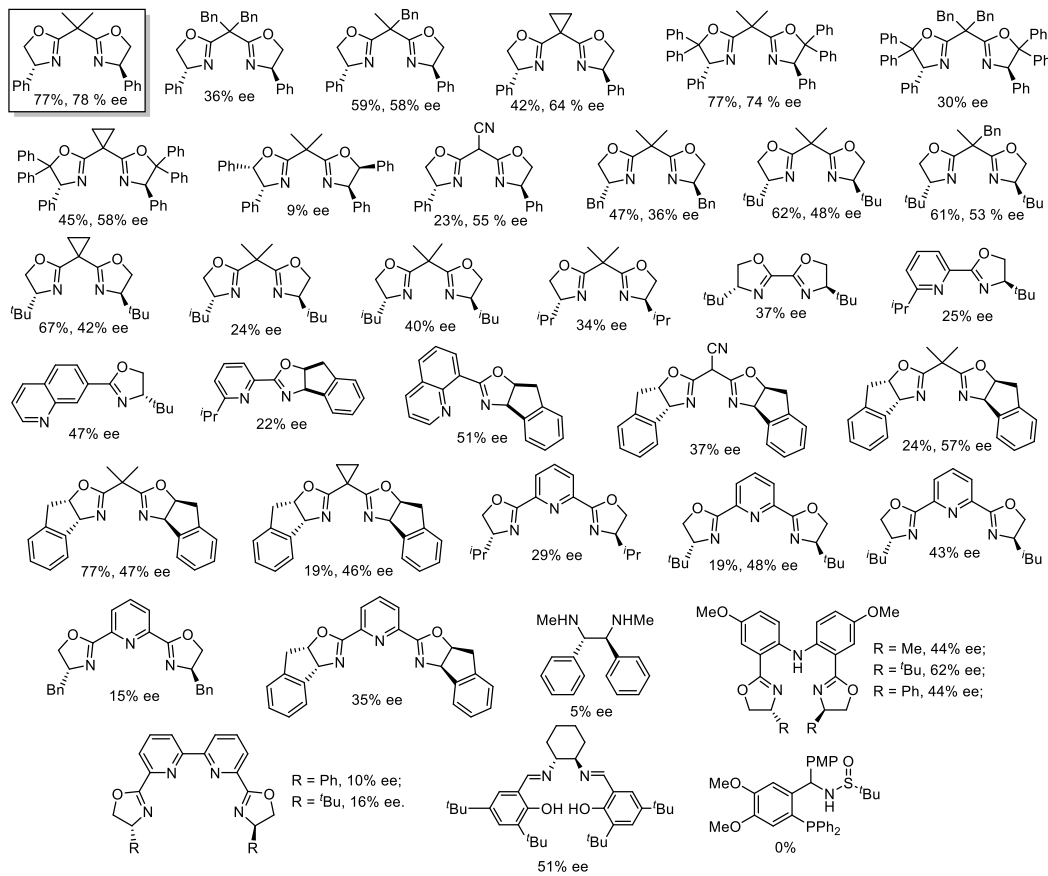
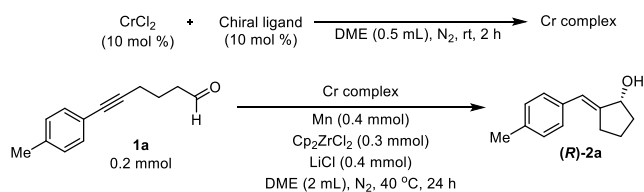
Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.25 (d,  $J$  = 8.16 Hz, 2H), 7.13 (d,  $J$  = 7.8 Hz, 2H), 6.58 (q,  $J$  = 2.1 Hz, 1H), 5.66–5.63 (m, 1H), 2.77–2.67 (m, 1H), 2.59–2.50 (m, 1H), 2.33 (s, 3H), 2.08 (s, 3H), 2.00–1.90 (m, 2H), 1.82–1.72 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 171.0, 141.9, 136.6, 134.7, 129.0, 128.6, 126.4, 79.3, 32.4, 29.6, 23.5, 21.5, 21.2. HRMS (ESI $^+$ ): calcd for  $\text{C}_{15}\text{H}_{19}\text{O}_2$   $[\text{M}+\text{H}]^+$  231.1380, found 231.1387.



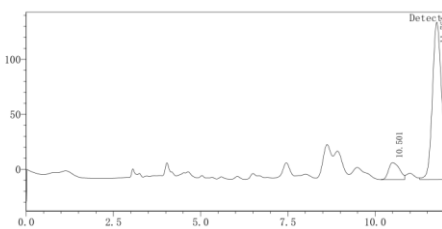
**(E)-1-methyl-4-((2-methylcyclopentylidene)methyl)benzene (14)**

Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.21 (d,  $J$  = 8.2 Hz, 2H), 7.15 (d,  $J$  = 7.9 Hz, 2H), 6.19 (q,  $J$  = 2.6 Hz, 1H), 2.68–2.50 (m, 3H), 2.32 (s, 3H), 1.94–1.78 (m, 2H), 1.69–1.56 (m, 1H), 1.28–1.89 (m, 1H), 1.17 (d,  $J$  = 6.72 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 150.7, 136.2, 135.2, 128.9, 128.0, 119.9, 40.9, 34.7, 31.6, 24.8, 21.1, 19.4. HRMS (ESI $^+$ ): calcd for  $\text{C}_{14}\text{H}_{19}$   $[\text{M}+\text{H}]^+$  187.1481, found 187.1486.

# 11. Table S2 Cr-Catalyzed Asymmetric Ketyl Radical Coupling with Alkyne



Detector A 234nm				
峰号	保留时间	面积	高度	浓度
1	10.301	7192695	508212	50.224
2	11.307	7128611	461009	49.776
总计		14321305	969221	



Detector A 234nm				
峰号	保留时间	面积	高度	浓度
1	10.501	332779	15346	11.088
2	11.764	2668597	142994	88.912
总计		3001375	158340	

HPLC conditions: DAICEL Chiralpak OD-H column, Hexane/<sup>i</sup>PrOH = 95/5, 254 nm, 1.0 mL/min, 25 °C.

## 12. The Crystallographic Data for the Compound of 2n

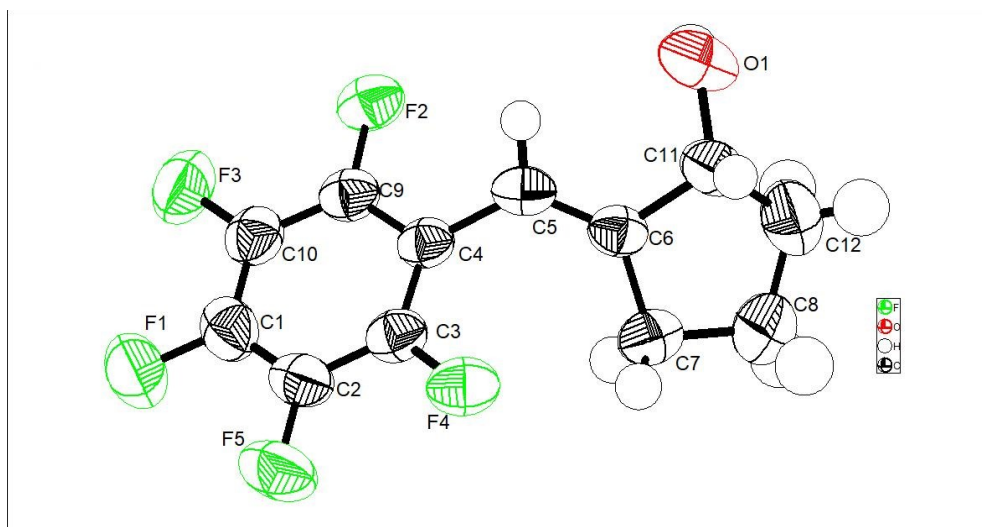


Figure S7: . X-ray structures of **2n** (ellipsoids set at 50% probability).

**Table S3** Crystal data and structure refinement for **2n**.

Identification code	<b>2n</b>
Empirical formula	C <sub>12</sub> H <sub>9</sub> F <sub>5</sub> O
Formula weight	264.19
Temperature/K	285.0
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	4.915(3)
b/Å	11.218(7)
c/Å	20.402(14)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	1124.8(12)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.560
μ/mm <sup>-1</sup>	0.154
F(000)	536.0
Crystal size/mm <sup>3</sup>	0.48 × 0.12 × 0.02
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.144 to 55.612
Index ranges	-6 ≤ h ≤ 6, -14 ≤ k ≤ 13, -26 ≤ l ≤ 23
Reflections collected	9067
Independent reflections	2622 [R <sub>int</sub> = 0.0865, R <sub>sigma</sub> = 0.0815]
Data/restraints/parameters	2622/0/164
Goodness-of-fit on F <sup>2</sup>	1.026

Final R indexes [ $I \geq 2\sigma(I)$ ]  $R_1 = 0.0546$ ,  $wR_2 = 0.1253$   
 Final R indexes [all data]  $R_1 = 0.1124$ ,  $wR_2 = 0.1573$   
 Largest diff. peak/hole /  $e \text{ \AA}^{-3}$  0.19/-0.21  
 Flack parameter 0.8(9)

**Table S4 Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for 2n.  $U_{eq}$  is defined as 1/3 of the trace of the orthogonalised  $U_{IJ}$  tensor.**

Atom	x	y	z	$U_{eq}$
F1	10796(8)	3167(3)	8646.5(16)	99.8(11)
F2	8550(5)	1713(2)	6574.3(14)	69.1(8)
F3	11621(6)	1610(3)	7658.0(18)	88.6(10)
F4	3658(6)	4926(2)	7479.4(15)	75.0(8)
F5	6778(8)	4837(3)	8547.5(16)	93.6(11)
O1	2044(7)	2923(3)	5140(2)	82.1(12)
C1	9255(11)	3221(5)	8108(3)	69.0(13)
C2	7235(11)	4072(4)	8055(3)	64.3(13)
C3	5693(9)	4111(4)	7495(2)	57.2(11)
C4	6042(9)	3351(3)	6972(2)	51.2(10)
C5	4328(9)	3321(4)	6385(2)	55.2(11)
C6	3508(9)	4231(4)	6020(2)	53.7(11)
C7	4294(13)	5522(4)	6070(3)	74.4(15)
C8	3568(19)	6055(5)	5415(3)	118(3)
C9	8101(9)	2504(4)	7056(2)	54.2(11)
C10	9665(10)	2437(4)	7602(3)	61.8(12)
C11	1822(10)	4074(4)	5418(3)	67.4(13)
C12	2820(20)	5056(6)	4971(3)	110(2)

**Table S5 Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for 2n. The Anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$ .**

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
F1	118(3)	106(2)	76(2)	9.8(19)	-30(2)	-17(2)
F2	76.0(17)	54.8(13)	76.4(19)	-8.5(14)	8.1(15)	6.9(13)
F3	87.4(19)	74.6(18)	104(2)	16.8(17)	-13.0(19)	14.6(18)
F4	76.8(17)	67.1(16)	81(2)	-17.8(15)	12.4(18)	10.5(15)
F5	122(3)	94(2)	64(2)	-27.5(17)	8.0(19)	-12(2)
O1	52.9(17)	97(3)	96(3)	-43(2)	-4.7(19)	5.3(18)
C1	78(3)	73(3)	56(3)	11(3)	-4(3)	-19(3)
C2	79(3)	60(3)	53(3)	-7(3)	8(3)	-16(3)



**Table S5 Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for 2n. The Anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$ .**

Atom	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
C3	62(3)	49(2)	60(3)	-1(2)	10(3)	-3(2)
C4	54(2)	44(2)	56(3)	2(2)	4(2)	-7.4(19)
C5	54(2)	50(2)	62(3)	-11(2)	10(2)	-9(2)
C6	51(2)	53(2)	58(3)	-10(2)	2(2)	1(2)
C7	92(3)	53(2)	78(4)	-3(3)	-2(3)	-3(3)
C8	178(8)	77(4)	101(5)	19(4)	-40(6)	-11(5)
C9	58(2)	48(2)	57(3)	-1(2)	10(2)	-6(2)
C10	64(3)	56(2)	66(3)	8(2)	2(3)	-6(2)
C11	57(3)	73(3)	72(3)	-21(3)	-9(3)	7(2)
C12	149(7)	102(5)	79(5)	14(4)	-35(4)	-15(5)

**Table S6 Bond Lengths for 2n.**

Atom Atom	Length/ $\text{\AA}$	Atom Atom	Length/ $\text{\AA}$
F1 C1	1.336(6)	C4 C5	1.465(6)
F2 C9	1.342(5)	C4 C9	1.399(6)
F3 C10	1.341(5)	C5 C6	1.325(6)
F4 C3	1.355(5)	C6 C7	1.502(6)
F5 C2	1.340(5)	C6 C11	1.492(7)
O1 C11	1.414(5)	C7 C8	1.507(8)
C1 C2	1.382(7)	C8 C12	1.488(8)
C1 C10	1.371(7)	C9 C10	1.355(7)
C2 C3	1.372(7)	C11 C12	1.512(8)
C3 C4	1.377(6)		

**Table S7 Bond Angles for 2n.**

Atom Atom Atom	Angle/ $^\circ$	Atom Atom Atom	Angle/ $^\circ$
F1 C1 C2	120.2(5)	C5 C6 C11	122.7(4)
F1 C1 C10	120.5(5)	C11 C6 C7	108.2(4)
C10 C1 C2	119.3(5)	C6 C7 C8	105.1(5)
F5 C2 C1	120.3(5)	C12 C8 C7	107.5(5)
F5 C2 C3	120.8(5)	F2 C9 C4	118.5(4)
C3 C2 C1	119.0(5)	F2 C9 C10	118.2(4)
F4 C3 C2	116.7(4)	C10 C9 C4	123.3(4)
F4 C3 C4	119.5(4)	F3 C10 C1	119.0(5)

**Table S7 Bond Angles for 2n.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C3	C4	123.8(4)	F3	C10	C9	121.0(5)
C3	C4	C5	125.2(4)	C9	C10	C1	120.0(5)
C3	C4	C9	114.5(4)	O1	C11	C6	113.2(4)
C9	C4	C5	120.1(4)	O1	C11	C12	113.4(5)
C6	C5	C4	128.0(4)	C6	C11	C12	103.4(4)
C5	C6	C7	128.7(4)	C8	C12	C11	105.1(5)

**Table S8 Torsion Angles for 2n.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F1	C1	C2	F5	-1.1(7)	C3	C4	C9	C10	-0.9(6)
F1	C1	C2	C3	179.6(5)	C4	C5	C6	C7	5.9(8)
F1	C1	C10	F3	0.5(7)	C4	C5	C6	C11	178.0(4)
F1	C1	C10	C9	-179.6(4)	C4	C9	C10	F3	-179.8(4)
F2	C9	C10	F3	0.4(6)	C4	C9	C10	C1	0.4(7)
F2	C9	C10	C1	-179.4(4)	C5	C4	C9	F2	3.5(6)
F4	C3	C4	C5	-1.4(6)	C5	C4	C9	C10	-176.3(4)
F4	C3	C4	C9	-176.5(4)	C5	C6	C7	C8	160.9(6)
F5	C2	C3	F4	-2.2(6)	C5	C6	C11	O1	-22.5(7)
F5	C2	C3	C4	-179.7(4)	C5	C6	C11	C12	-145.6(5)
O1	C11	C12	C8	-156.0(6)	C6	C7	C8	C12	-9.0(9)
C1	C2	C3	F4	177.1(4)	C6	C11	C12	C8	-33.0(8)
C1	C2	C3	C4	-0.4(7)	C7	C6	C11	O1	151.1(4)
C2	C1	C10	F3	-179.7(4)	C7	C6	C11	C12	28.0(6)
C2	C1	C10	C9	0.2(7)	C7	C8	C12	C11	26.3(9)
C2	C3	C4	C5	176.0(4)	C9	C4	C5	C6	-137.6(5)
C2	C3	C4	C9	0.9(6)	C10	C1	C2	F5	179.1(5)
C3	C4	C5	C6	47.5(7)	C10	C1	C2	C3	-0.2(7)
C3	C4	C9	F2	178.9(4)	C11	C6	C7	C8	-12.1(6)

**Table S9 Hydrogen Atom Coordinates ( $\text{\AA} \times 10^4$ ) and Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for 2n.**

Atom	x	y	z	U(eq)
H1	3563	2841	4980	123
H5	3741	2572	6251	66
H7A	6227	5602	6155	89

**Table S9 Hydrogen Atom Coordinates ( $\text{\AA}\times 10^4$ ) and Isotropic Displacement Parameters ( $\text{\AA}^2\times 10^3$ ) for 2n.**

Atom	x	y	z	U(eq)
H7B	3295	5911	6420	89
H8A	2049	6600	5462	142
H8B	5106	6491	5239	142
H11	-88	4225	5528	81
H12A	4389	4792	4721	132
H12B	1402	5298	4668	132

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# 14. $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ NMR Spectra

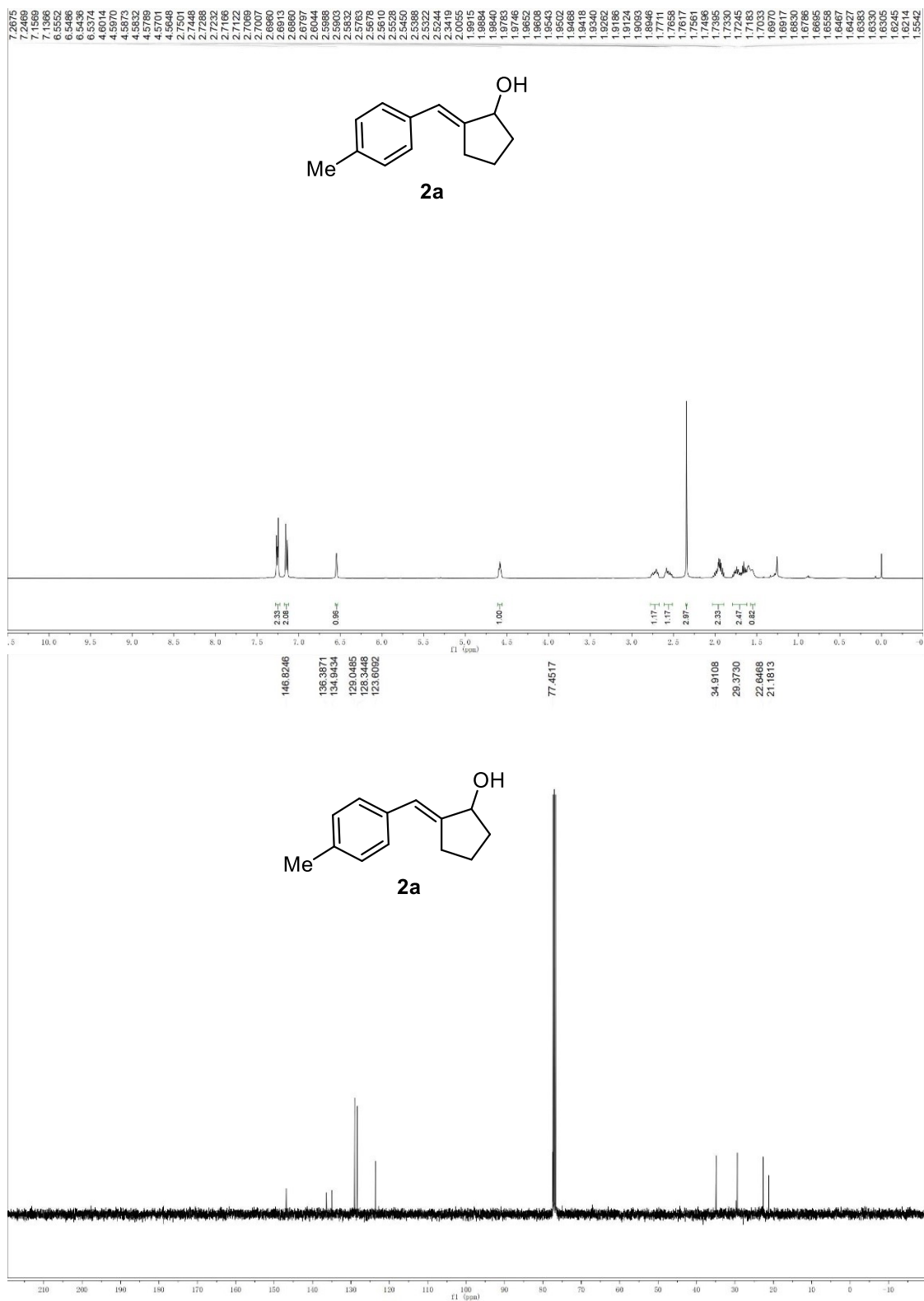
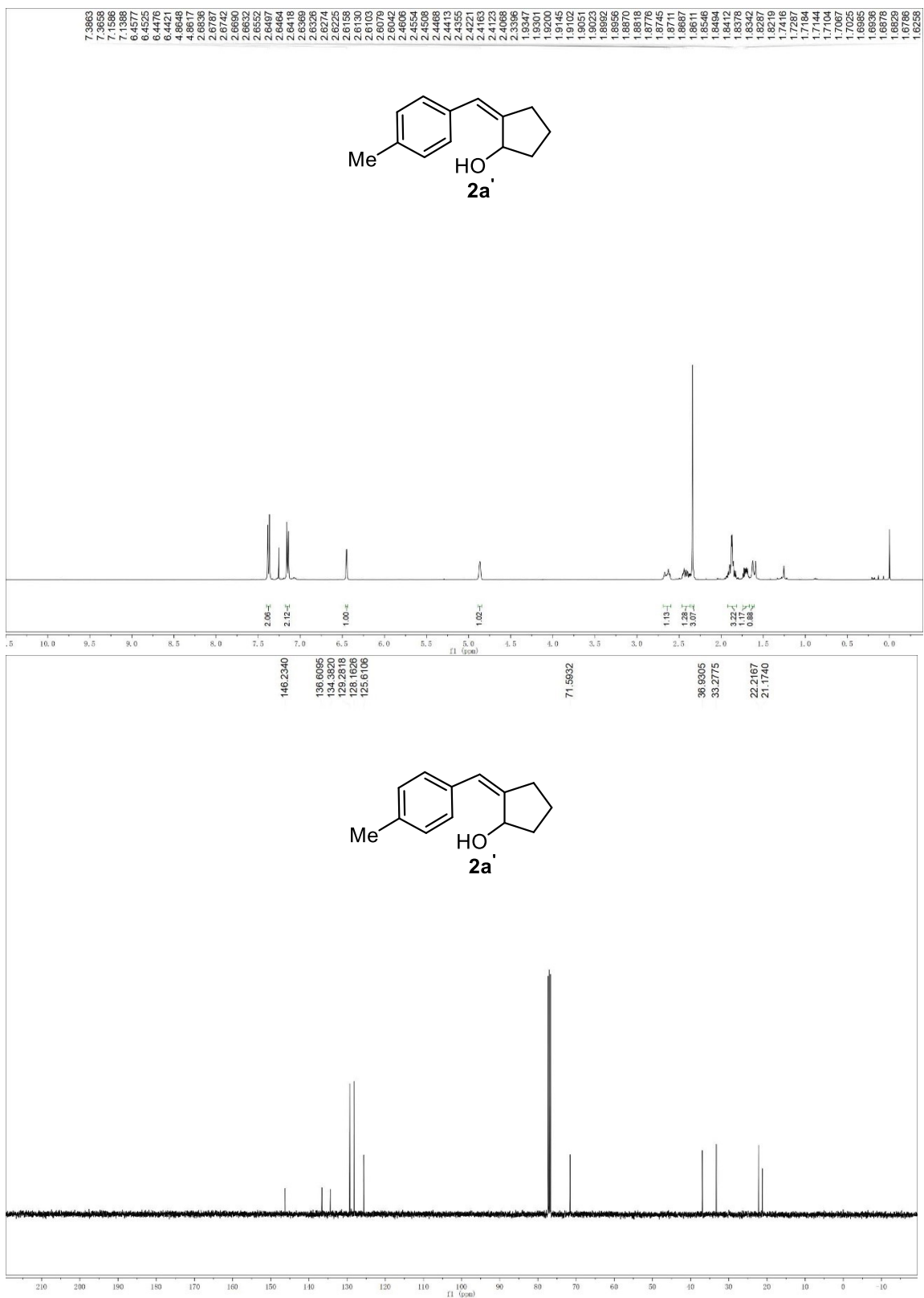


Figure S8.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  (100 MHz,  $\text{CDCl}_3$ ) NMR spectra for compound **2a**



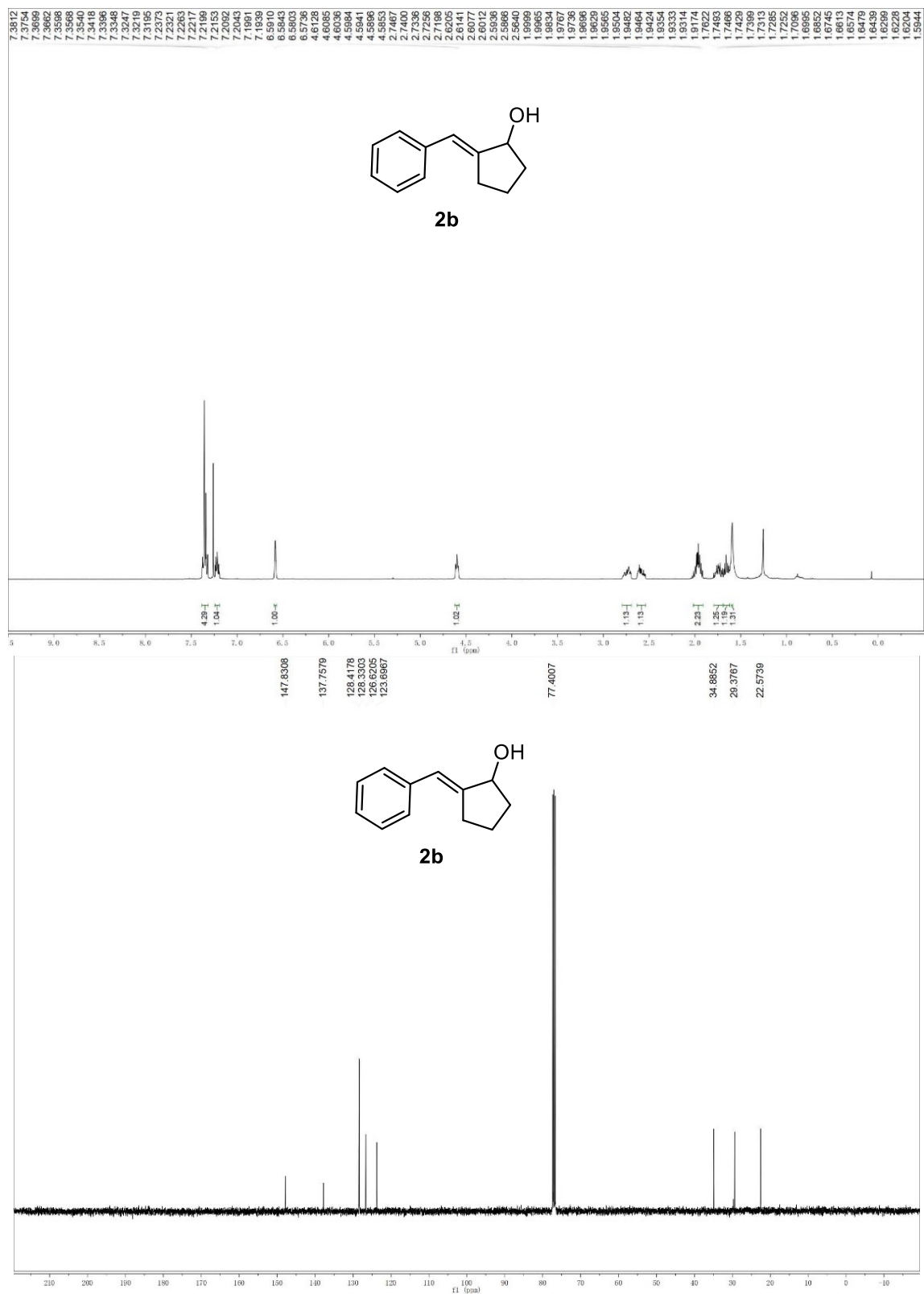


Figure S10. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2b**

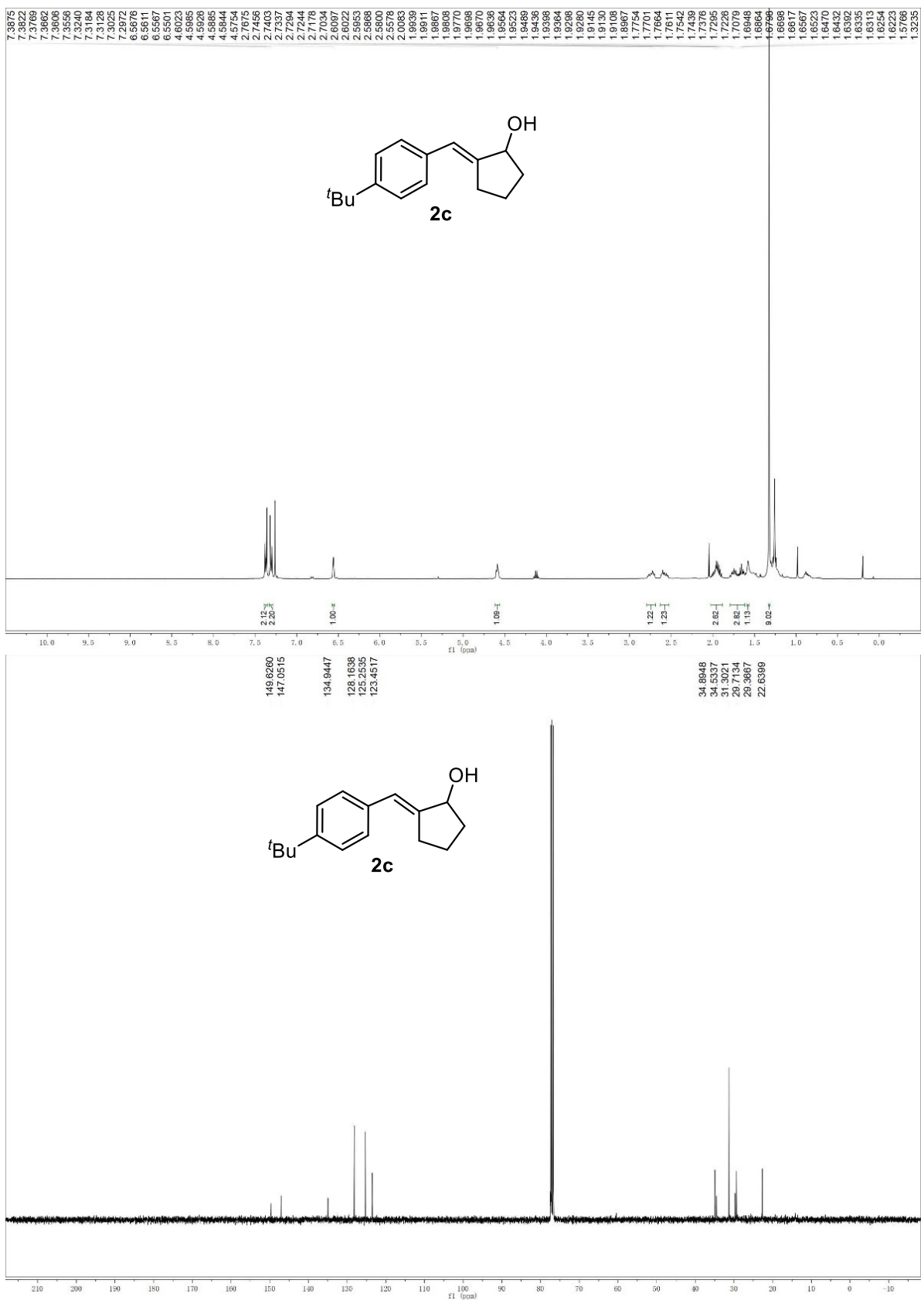


Figure S11. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2c**



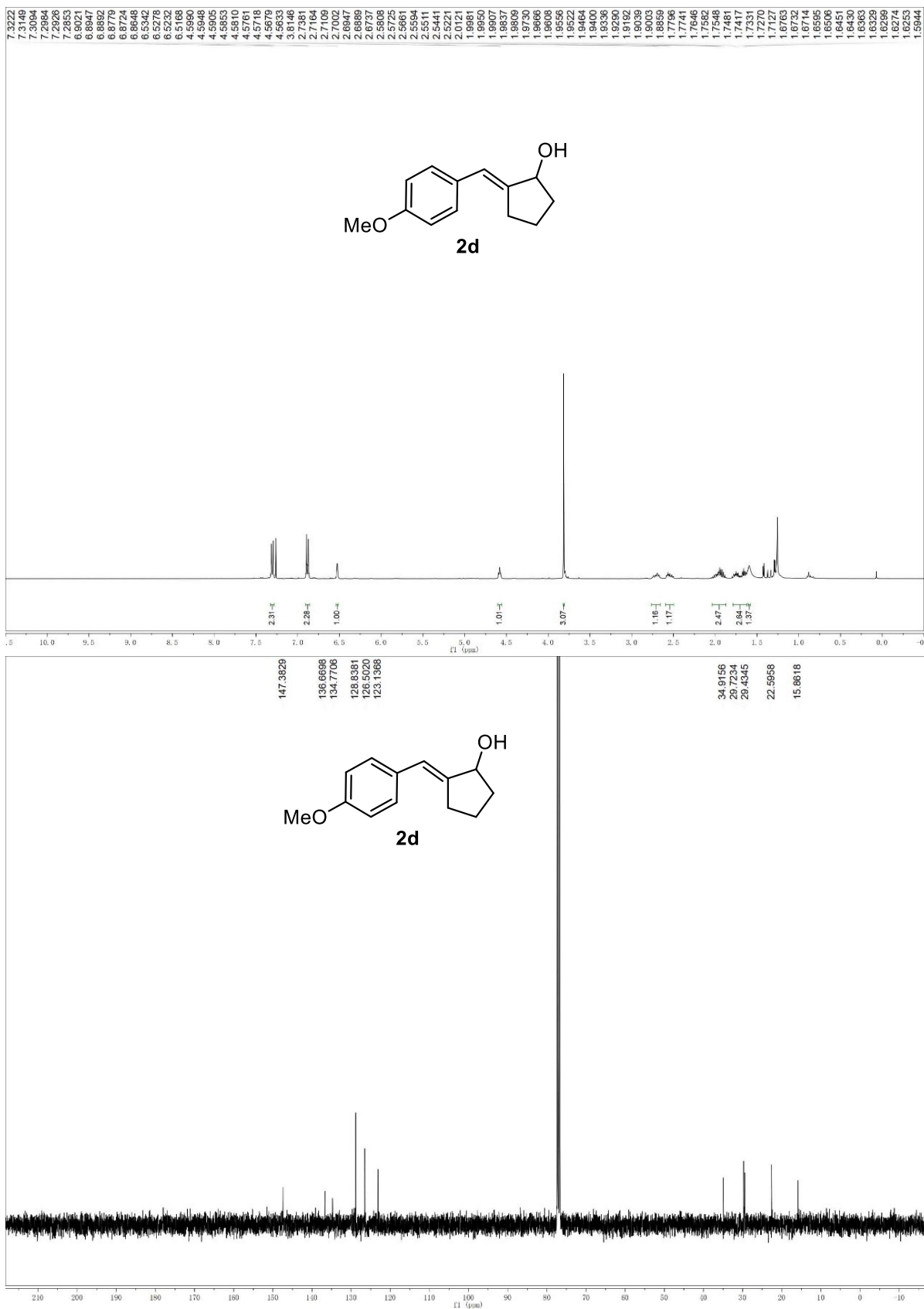


Figure S12. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound 2d

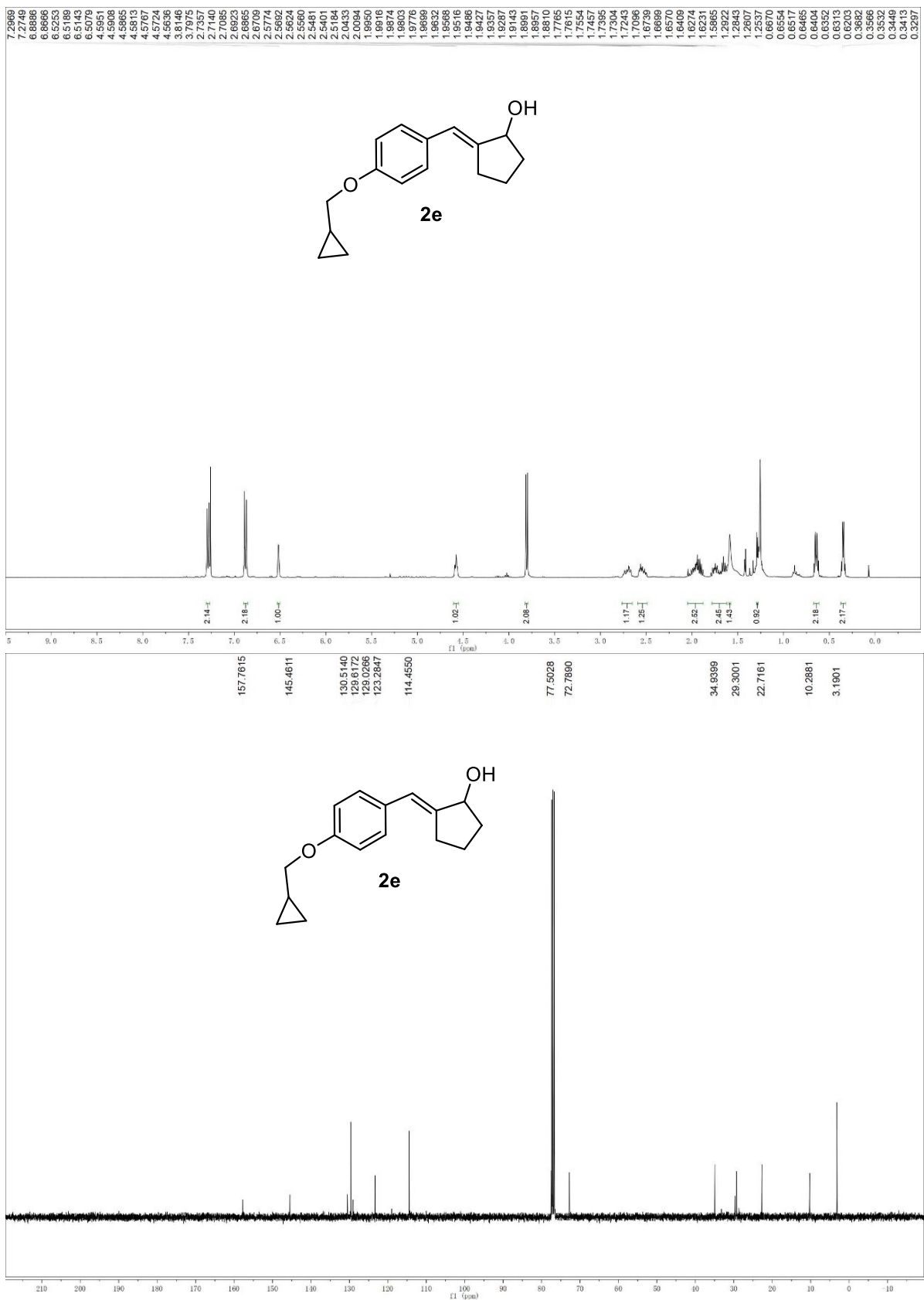


Figure S13. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound 2e

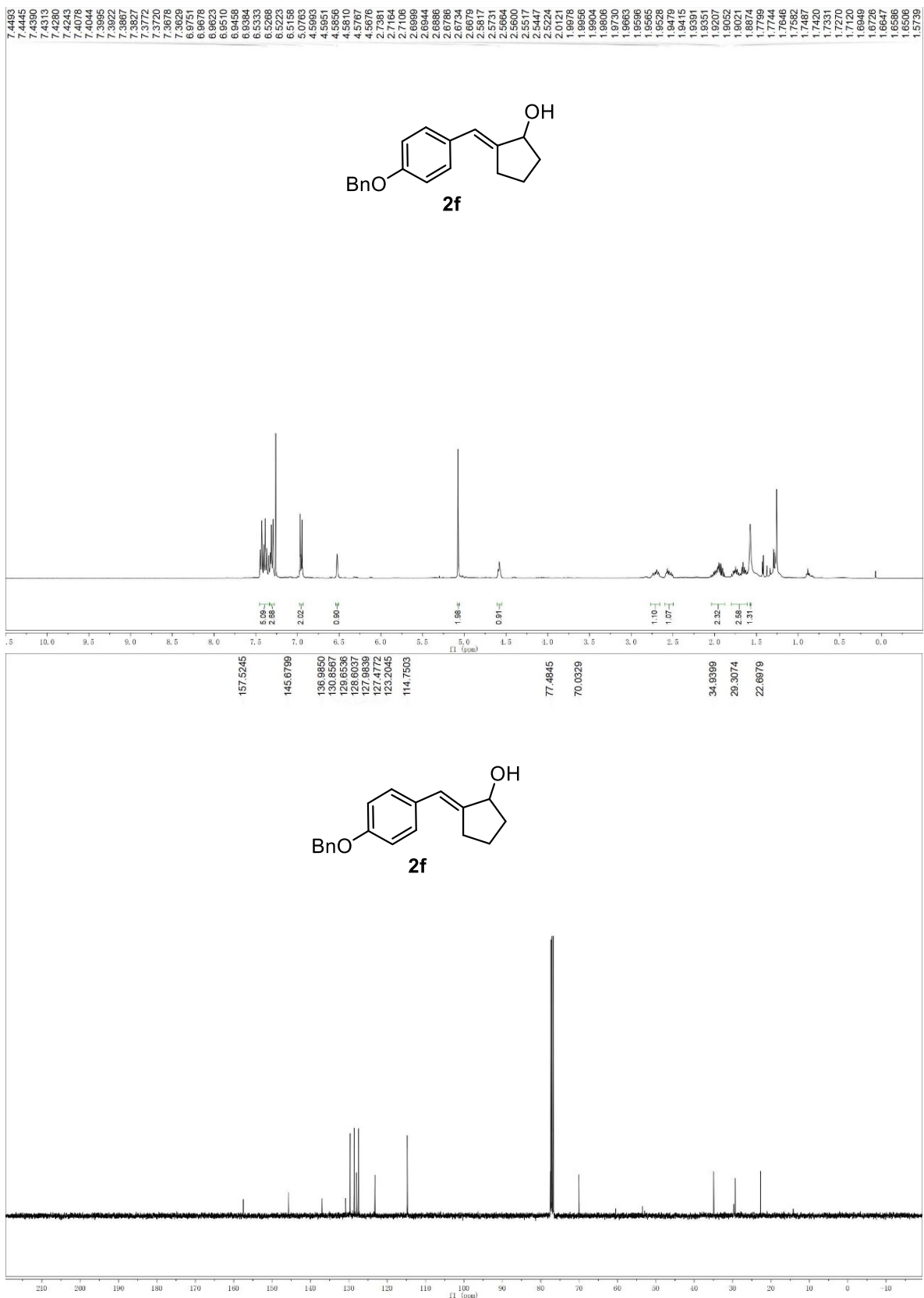


Figure S14. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2f**

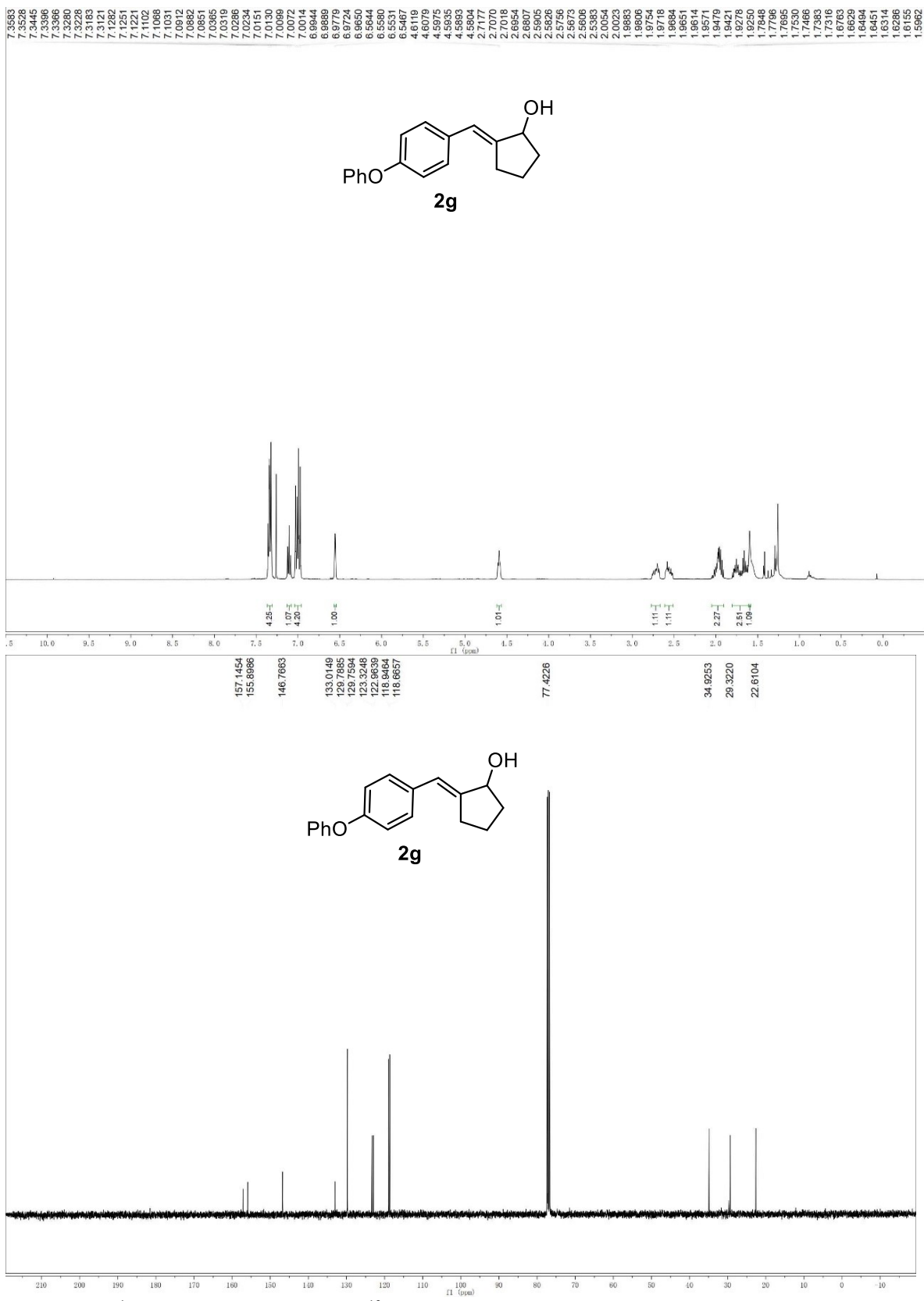


Figure S15.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  (100 MHz,  $\text{CDCl}_3$ ) NMR spectra for compound **2g**

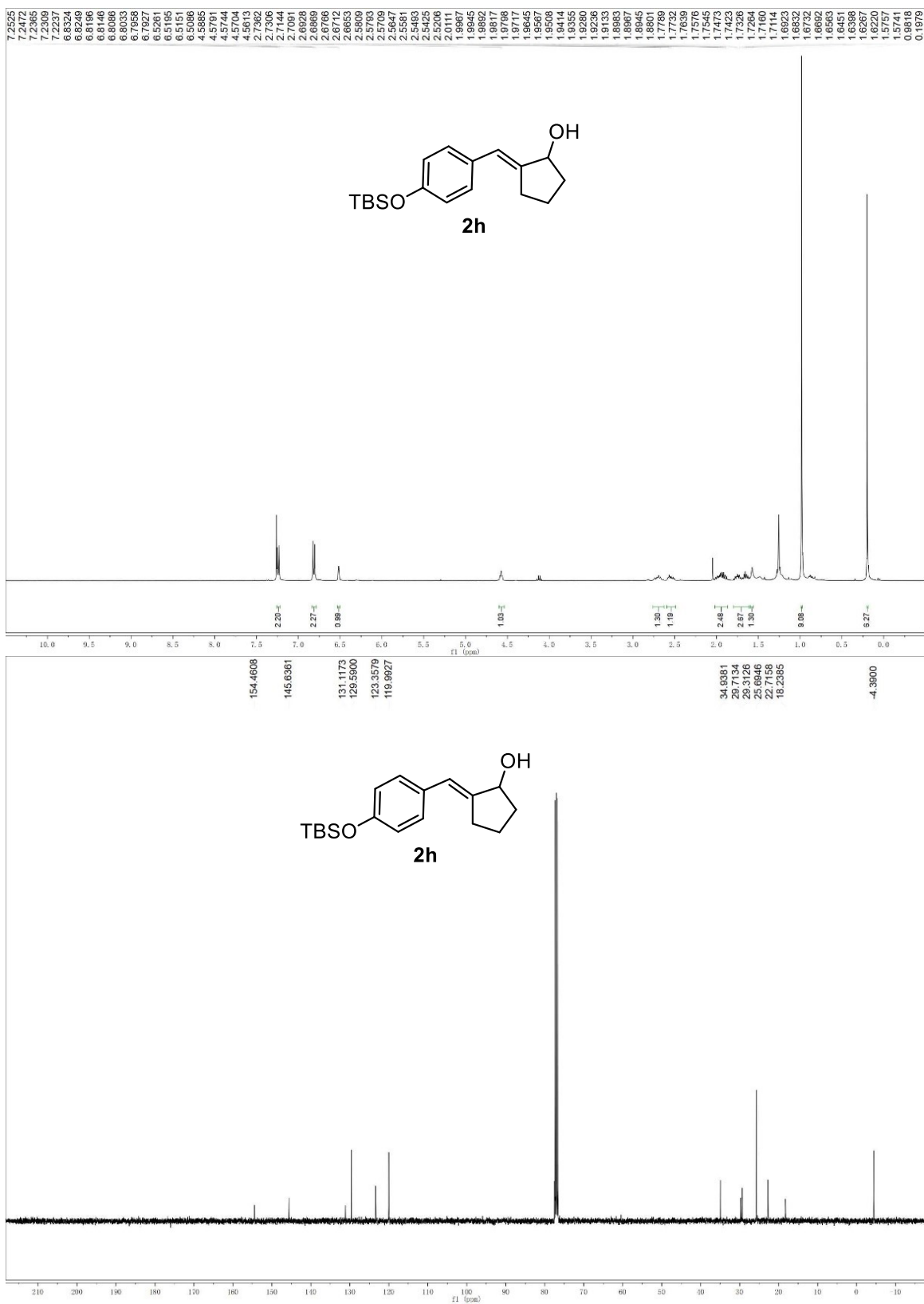


Figure S16. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2h**

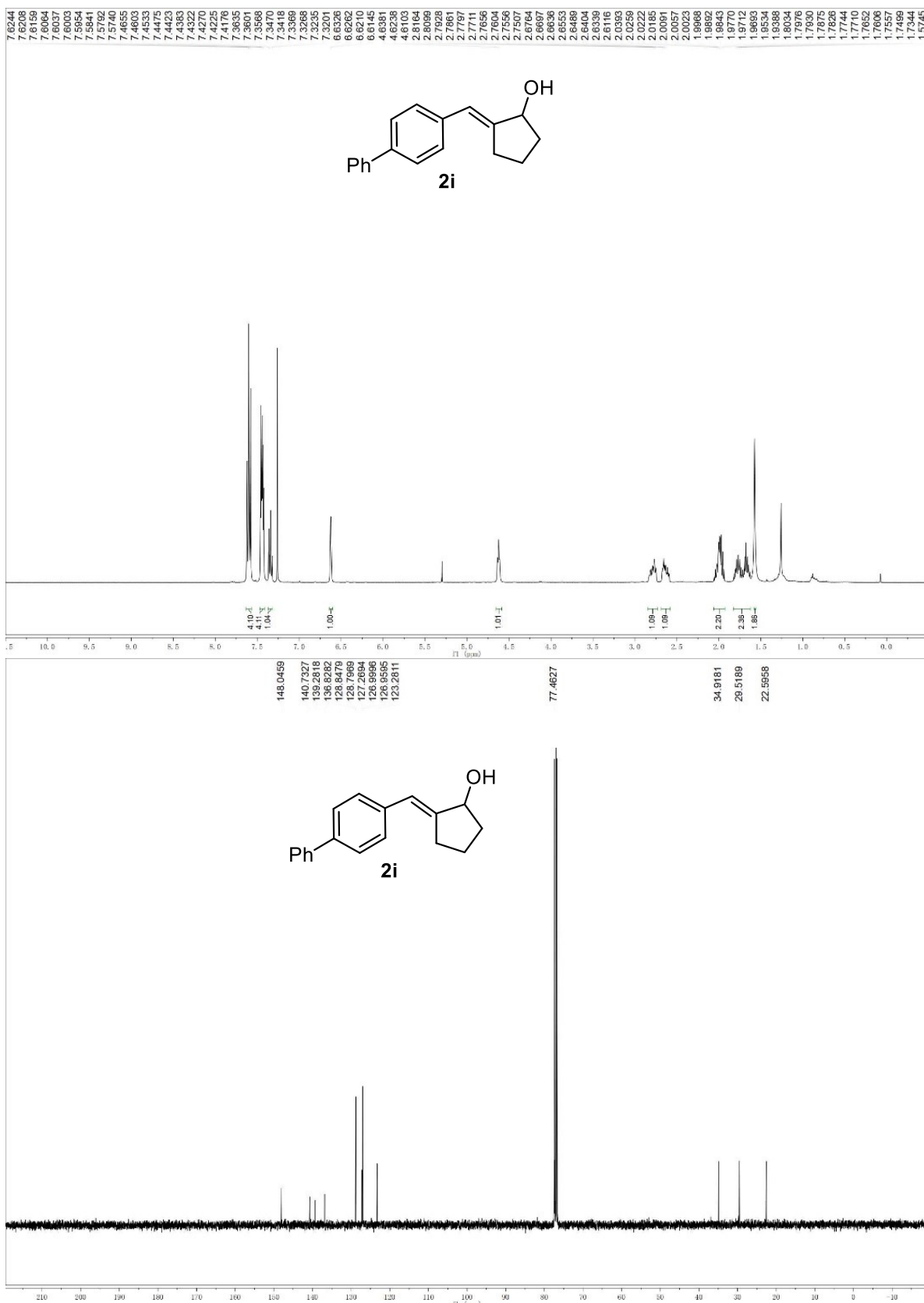


Figure S17. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2i**



Figure S18. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2j**





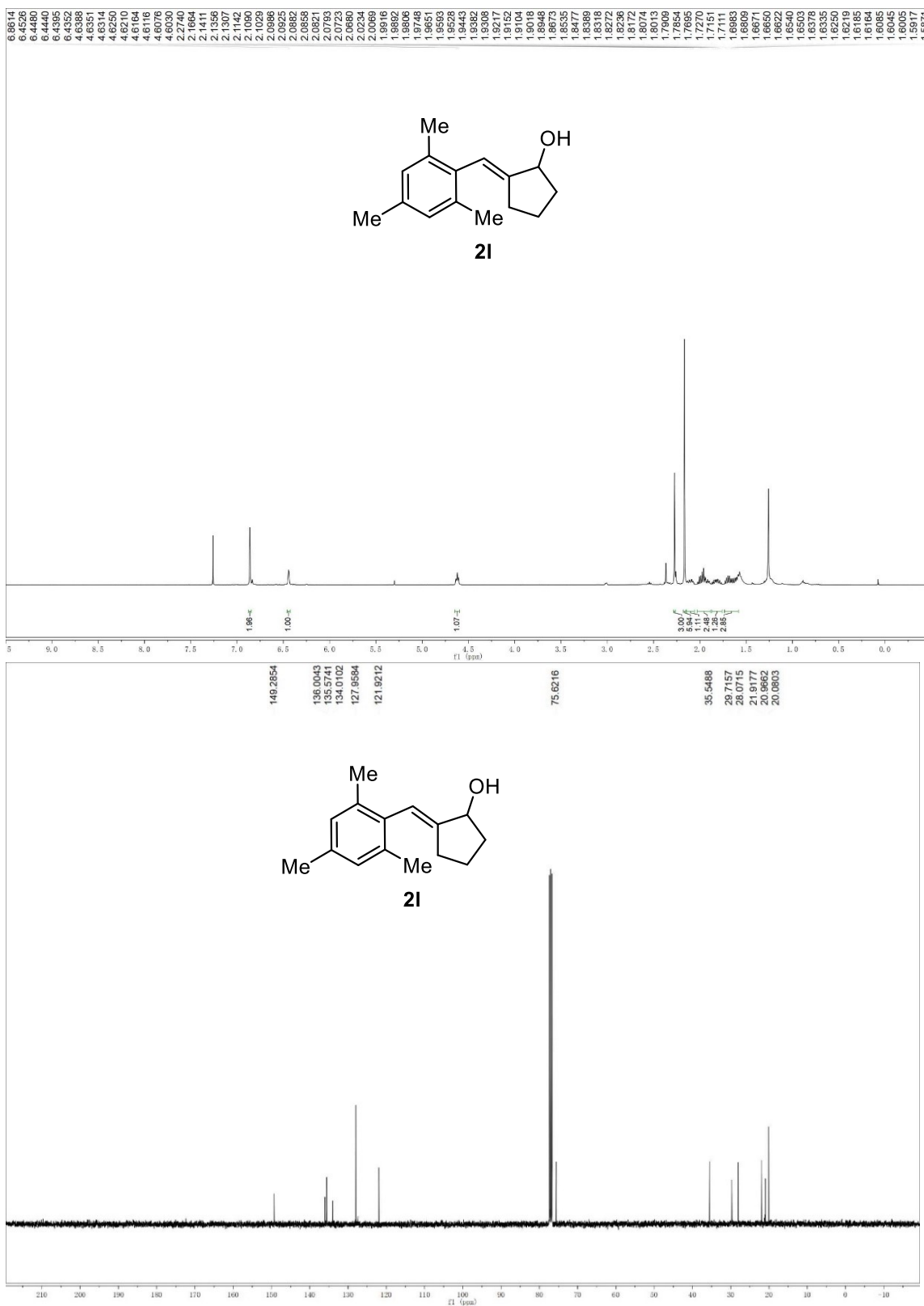
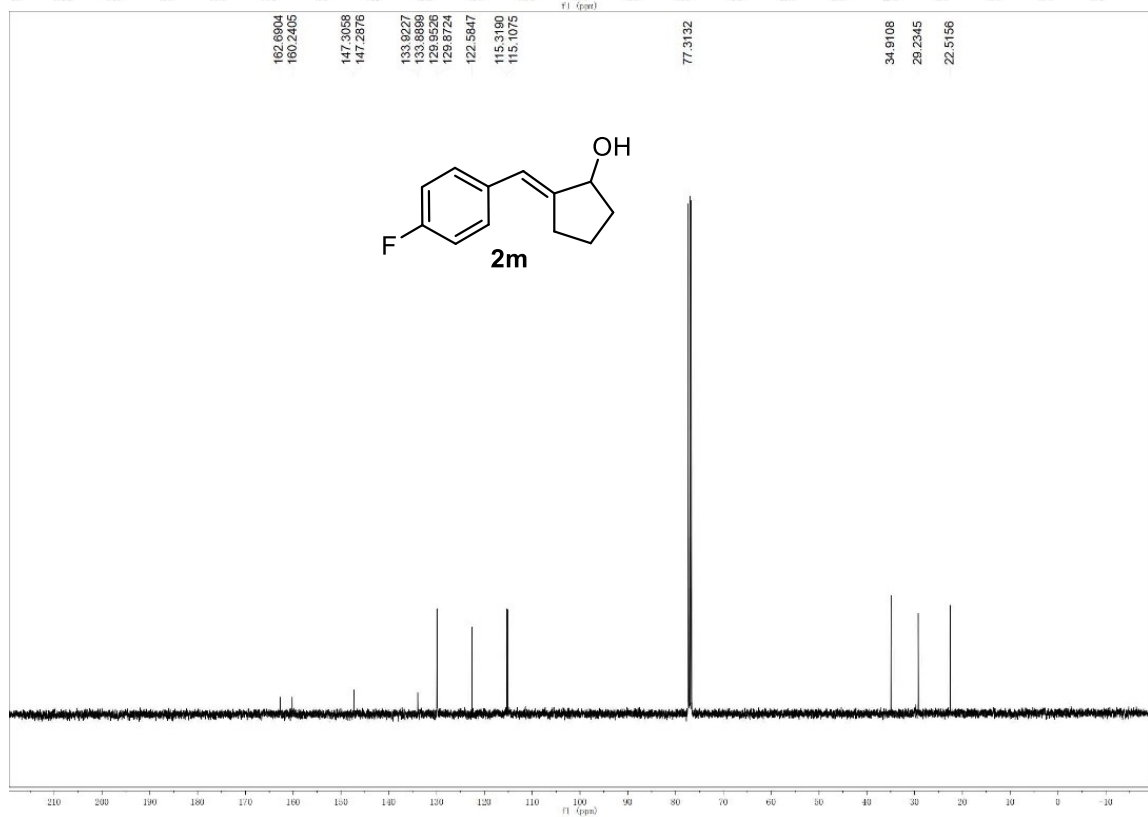
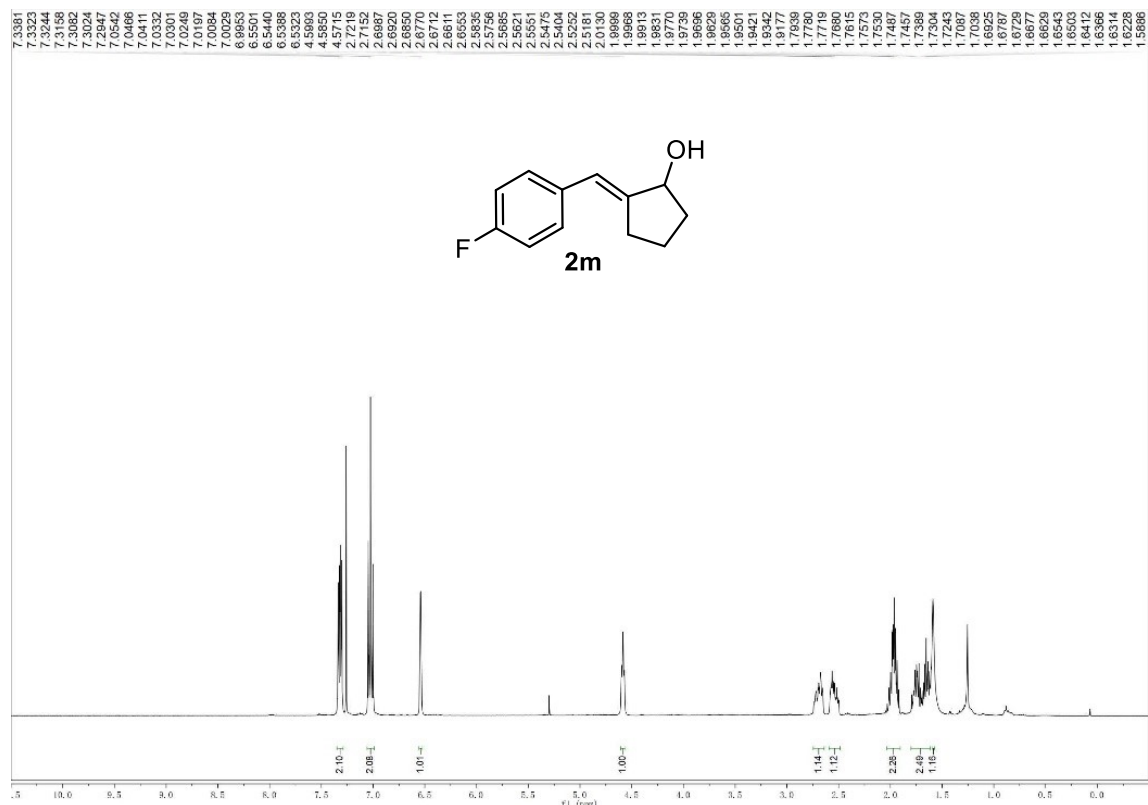


Figure S20.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  (100 MHz,  $\text{CDCl}_3$ ) NMR spectra for compound **2I**



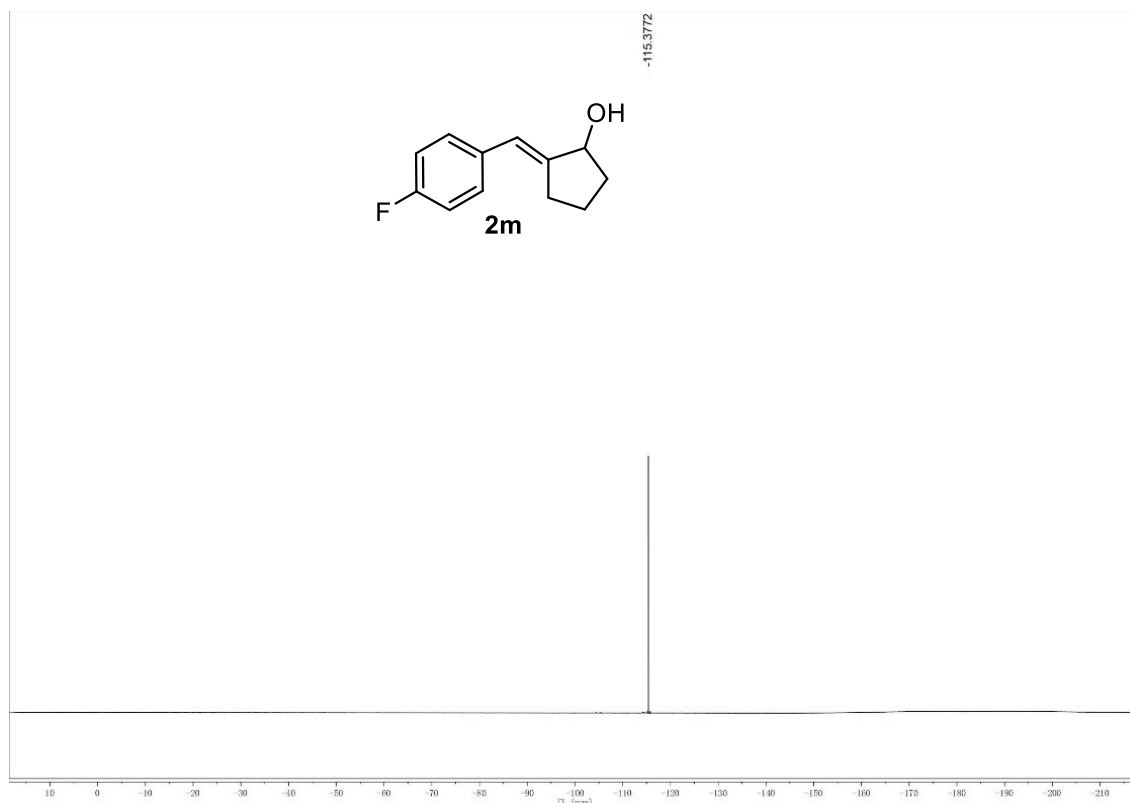
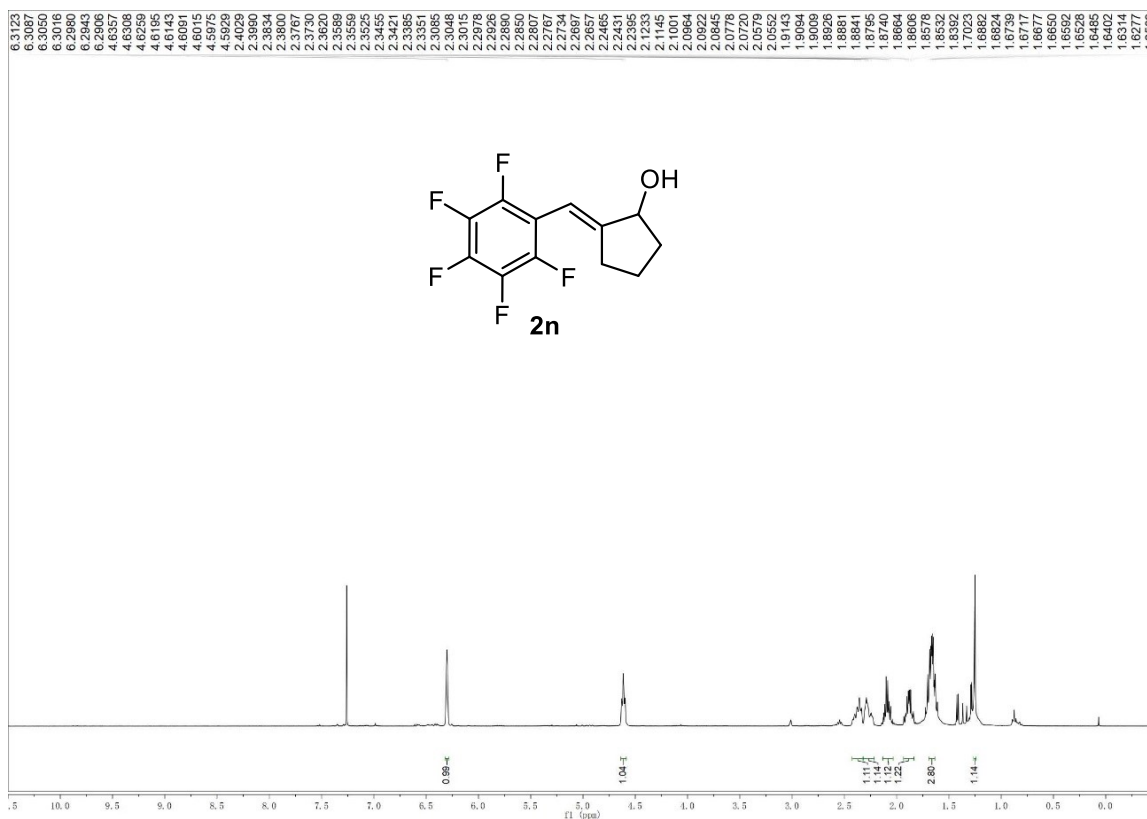


Figure S21.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ ),  $^{13}\text{C}$  (100 MHz,  $\text{CDCl}_3$ ) and  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) NMR spectra for compound **2m**



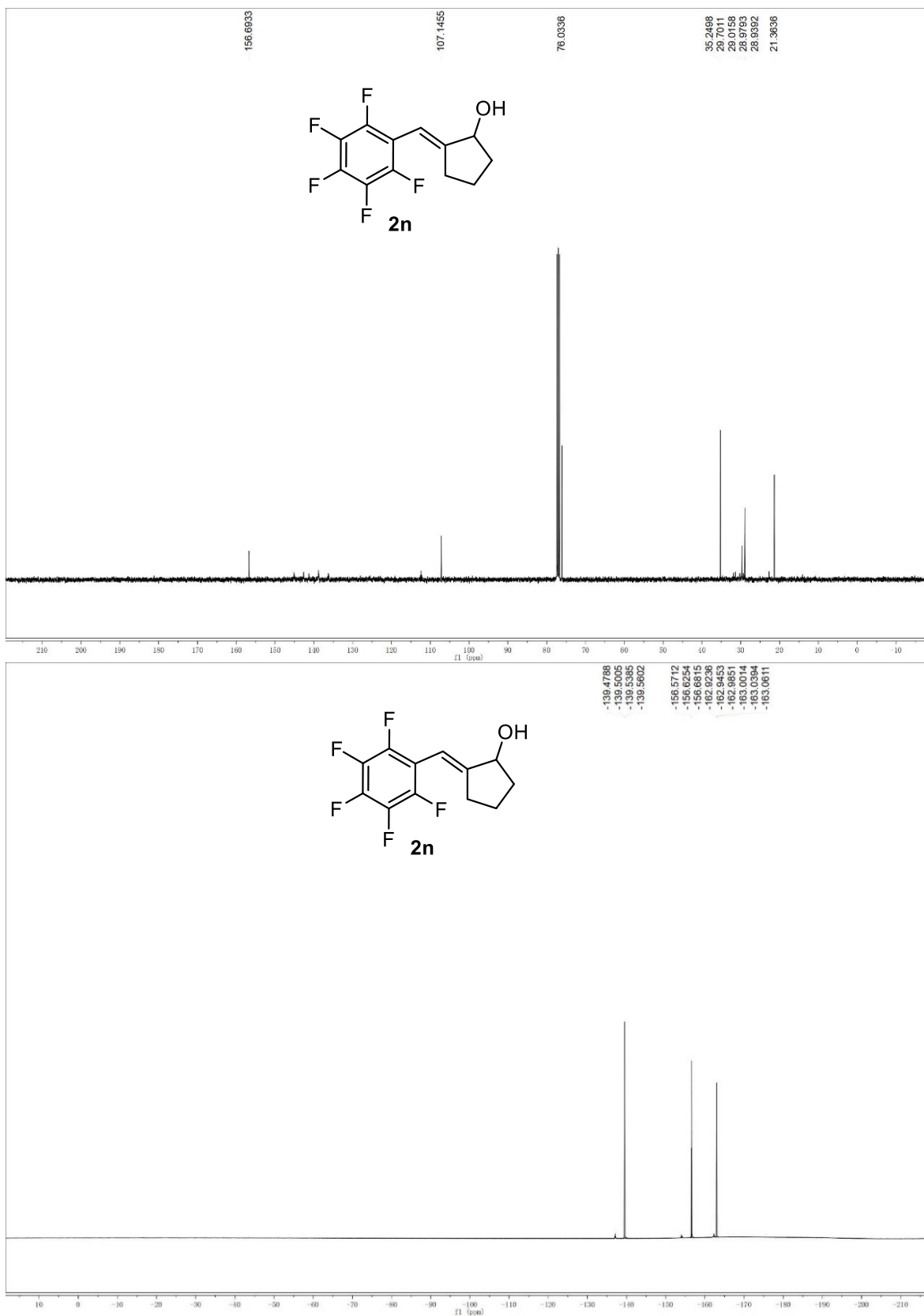


Figure S22. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) and <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2n**

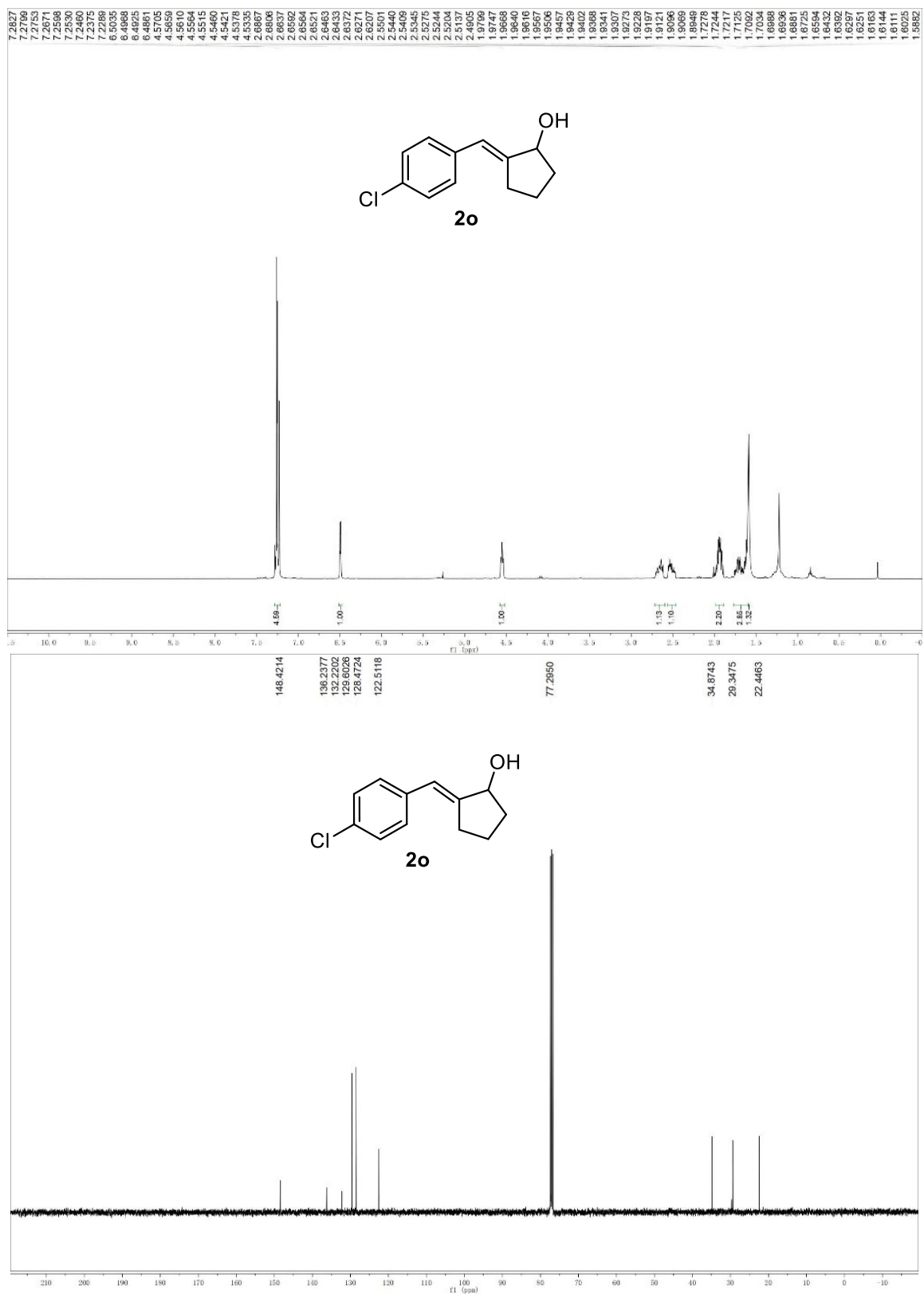


Figure S23. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2o**

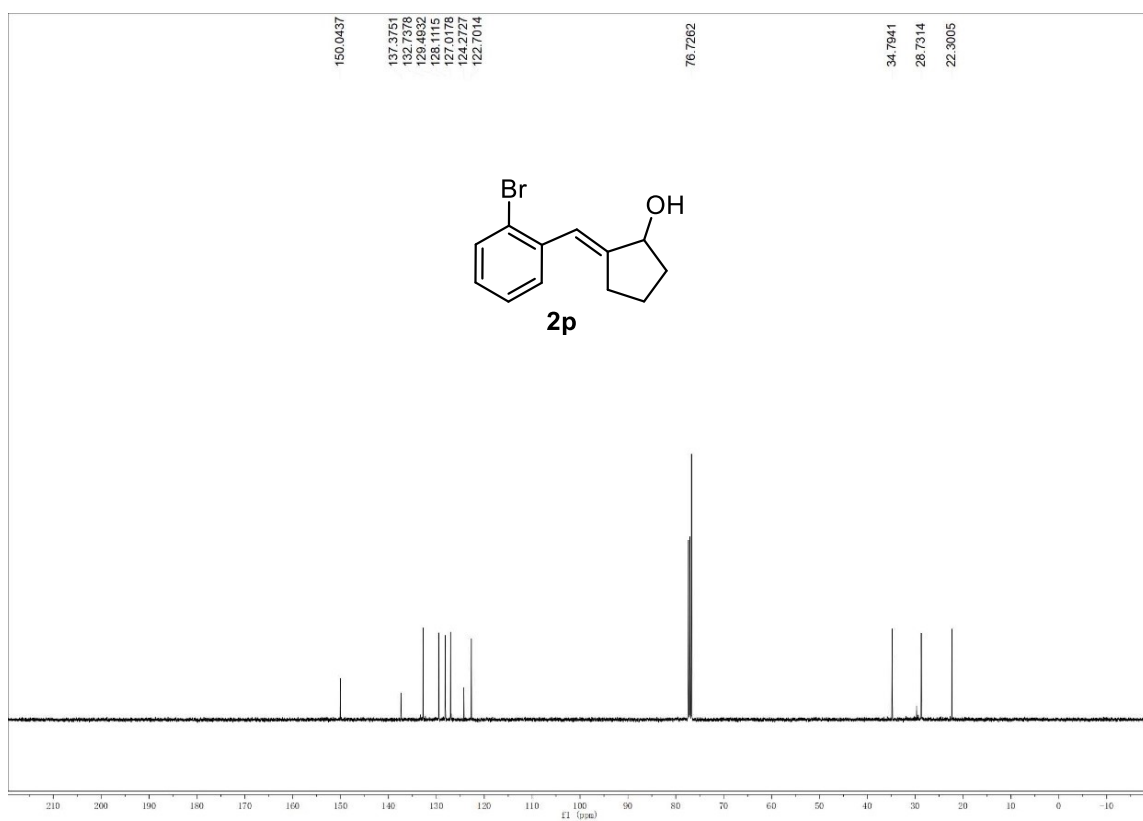
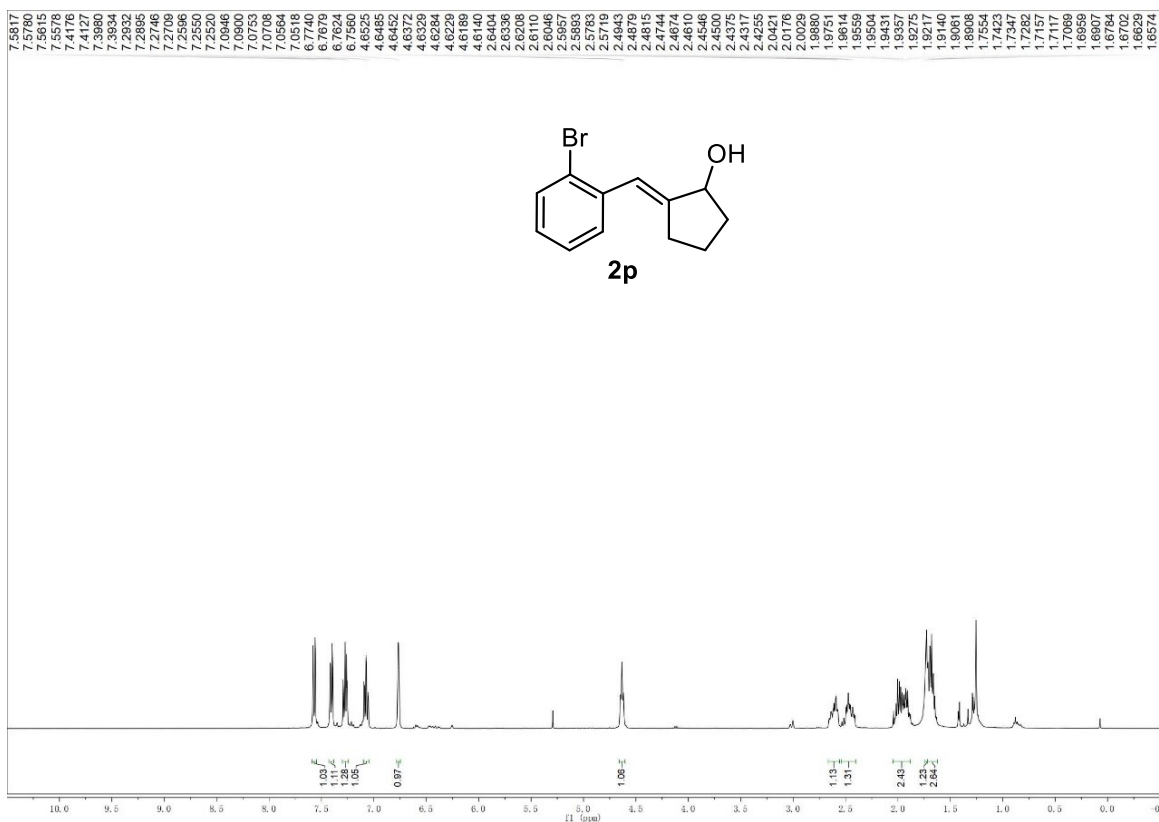


Figure S24. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2p**

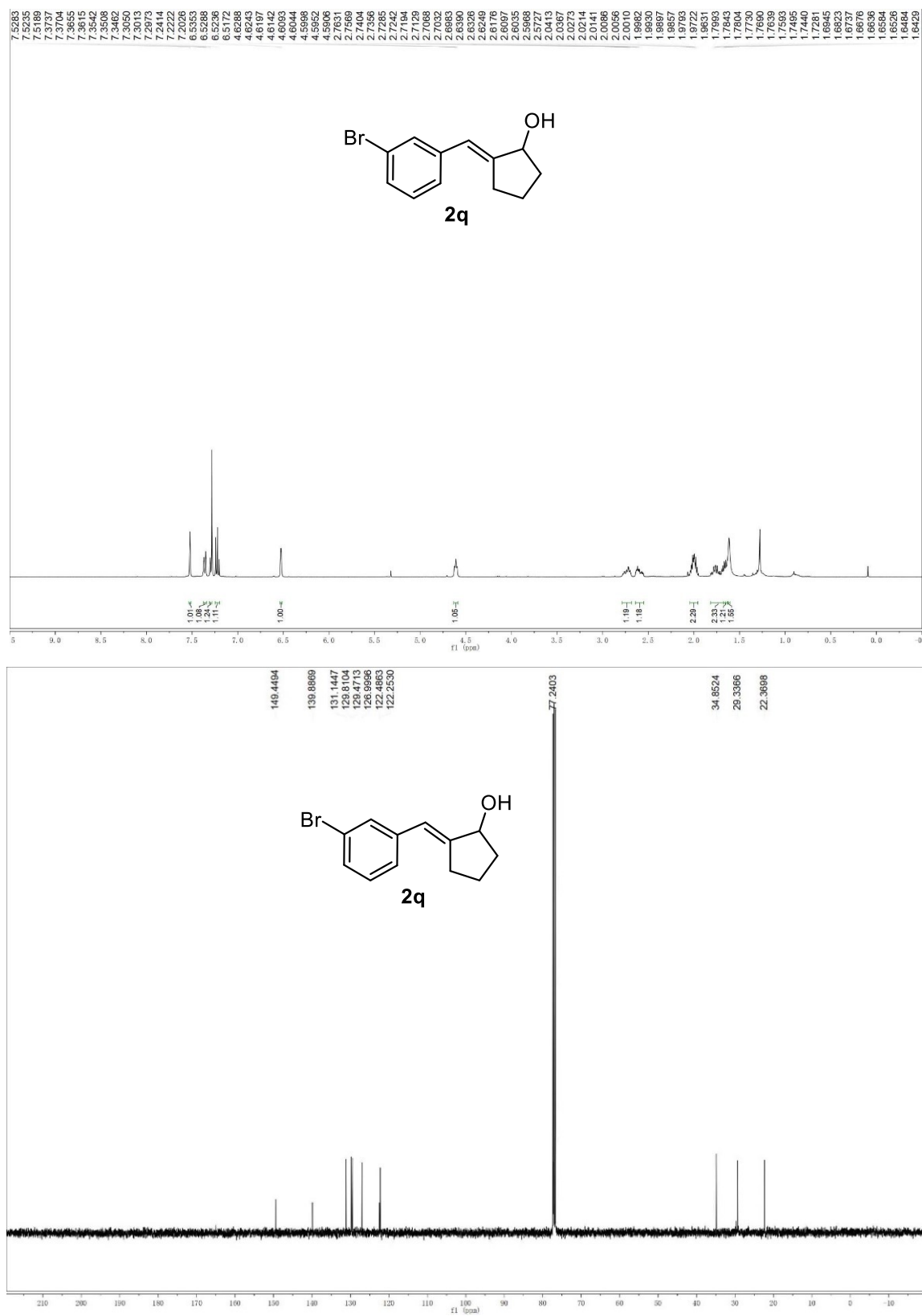


Figure S25. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2q**

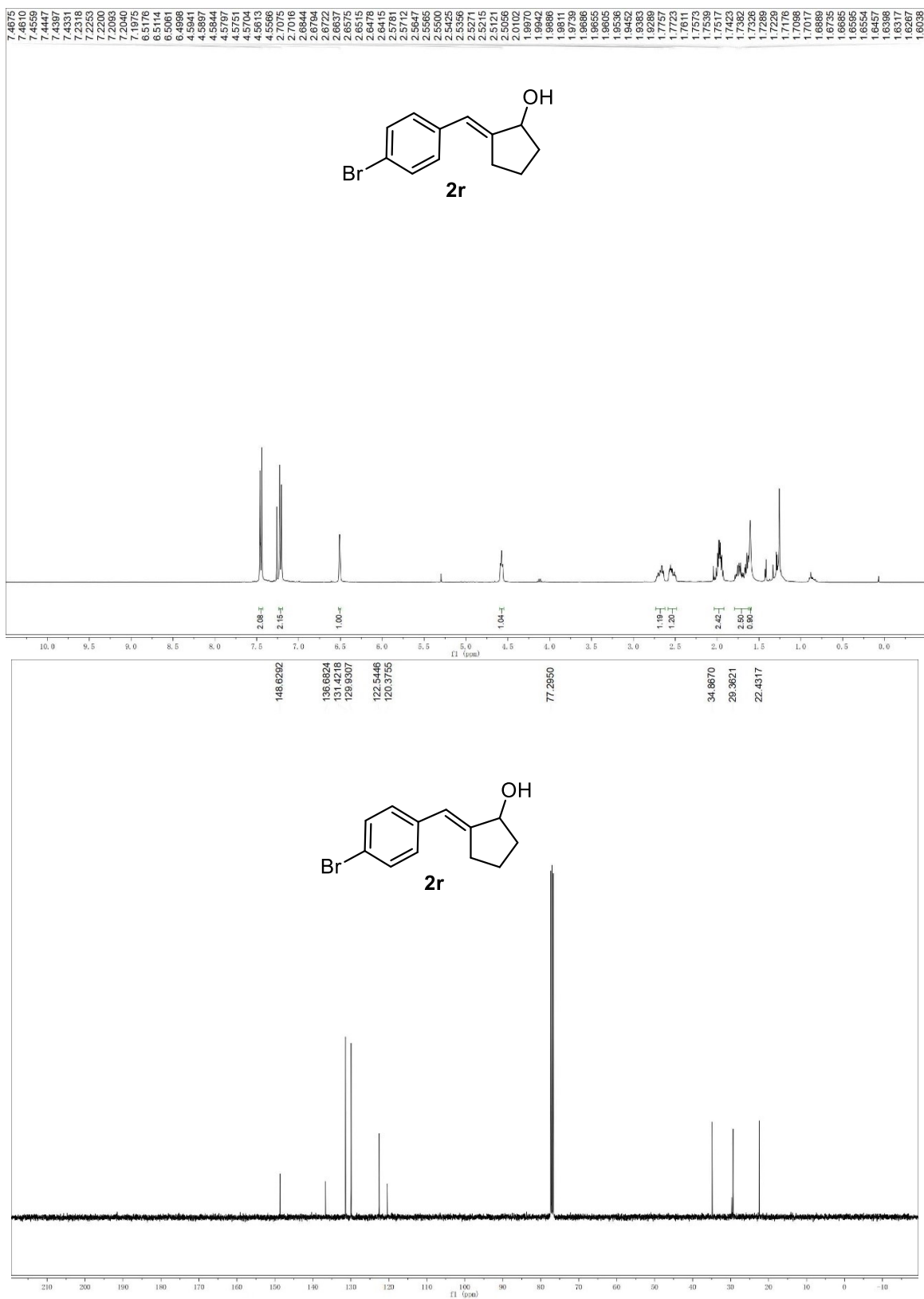


Figure S26.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  (100 MHz,  $\text{CDCl}_3$ ) NMR spectra for compound **2r**



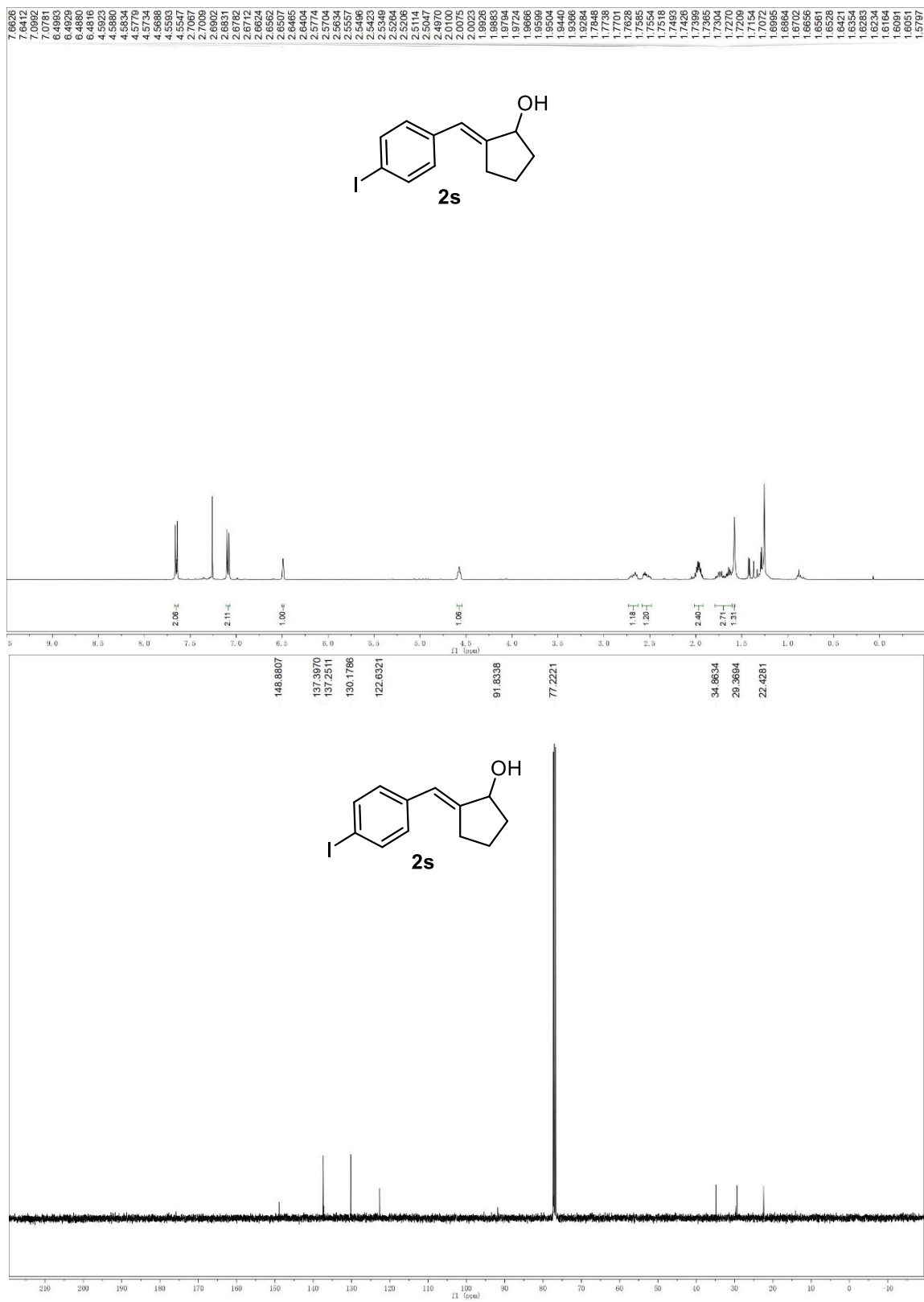


Figure S27. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2s**

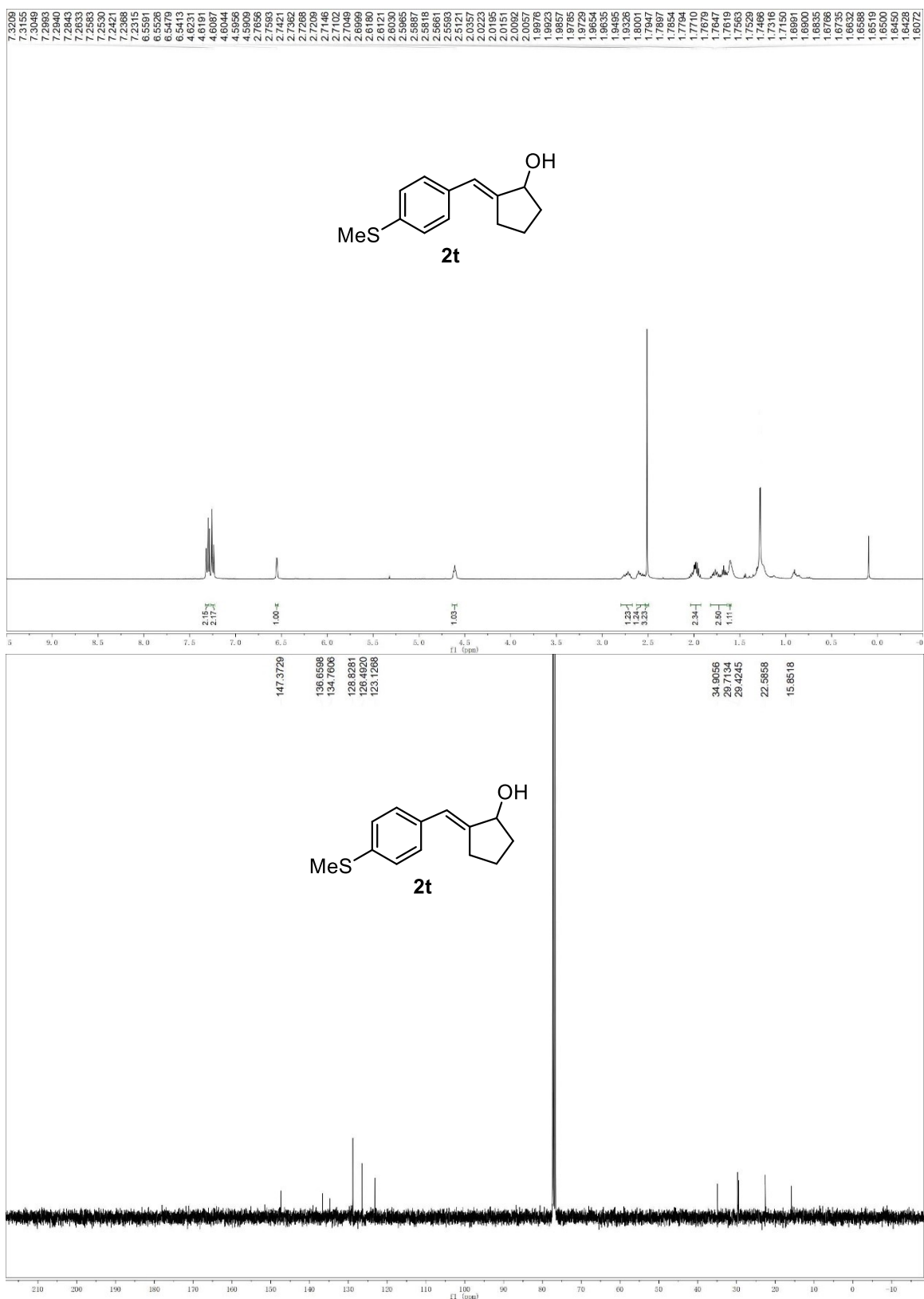


Figure S28. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2t**

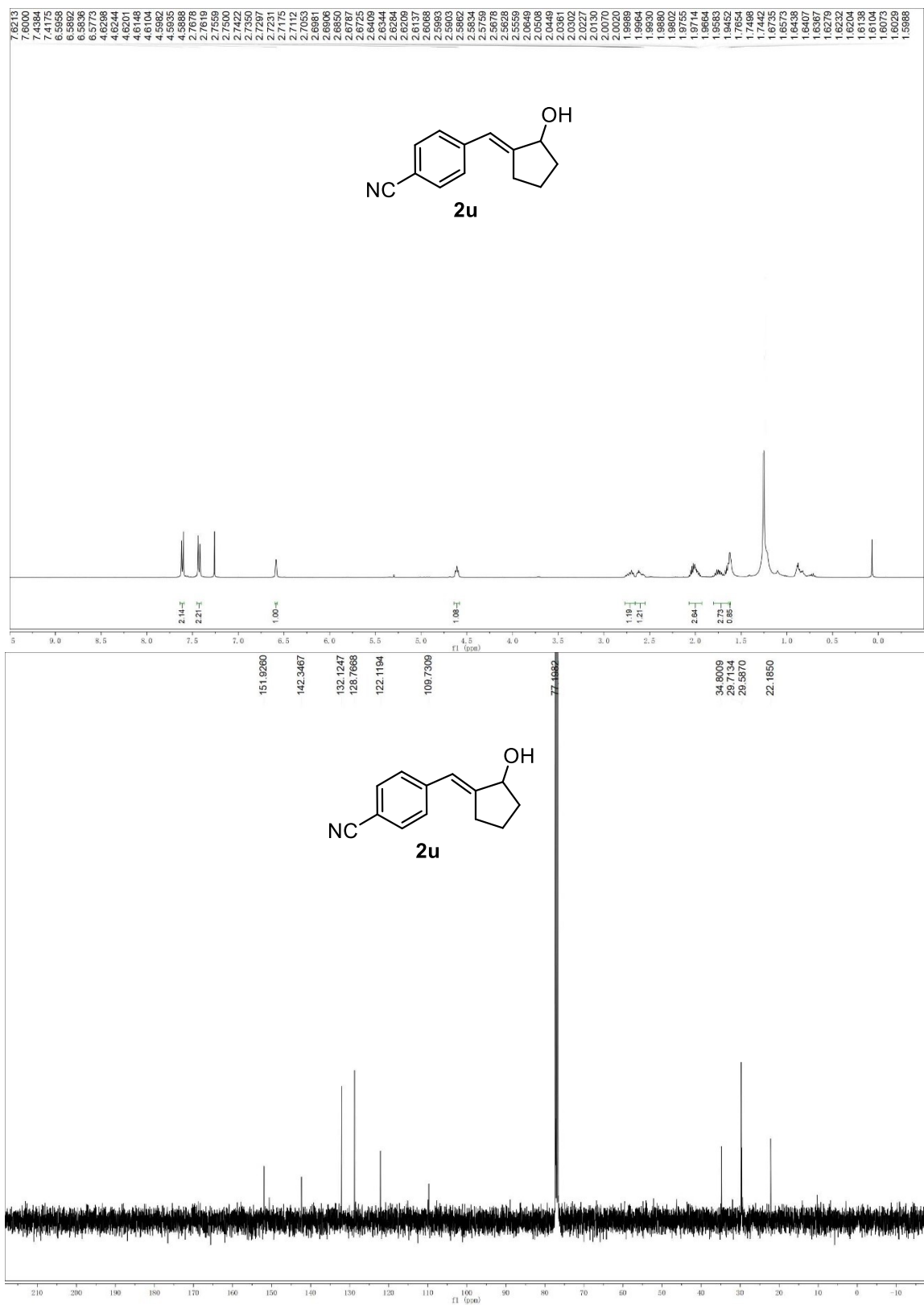


Figure S29.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  (100 MHz,  $\text{CDCl}_3$ ) NMR spectra for compound **2u**

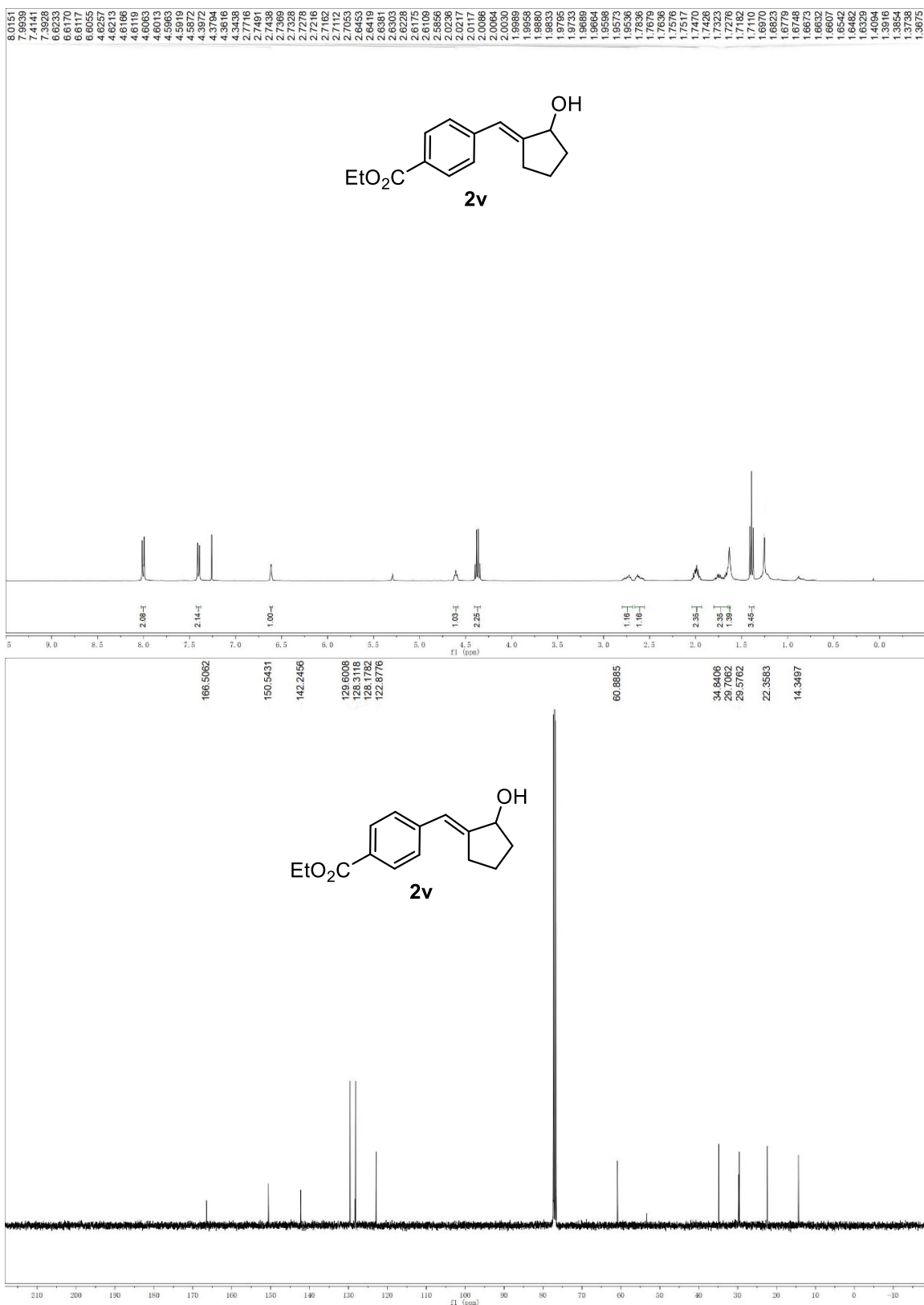
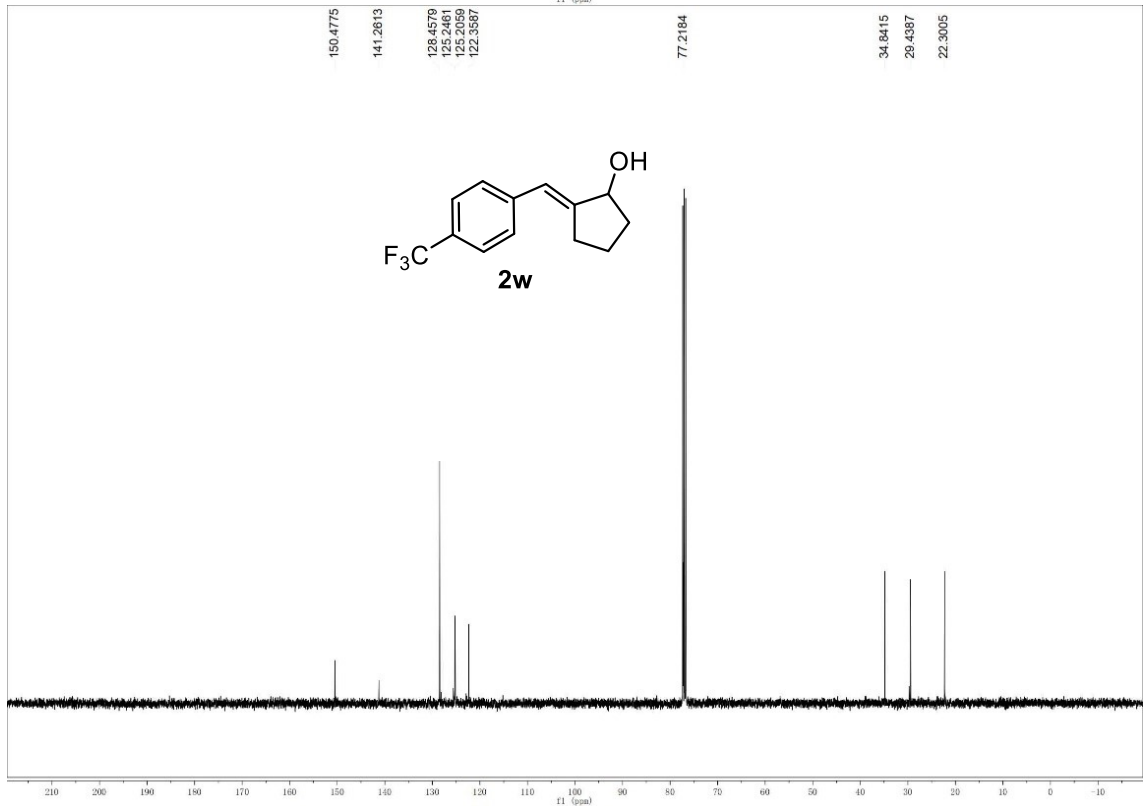
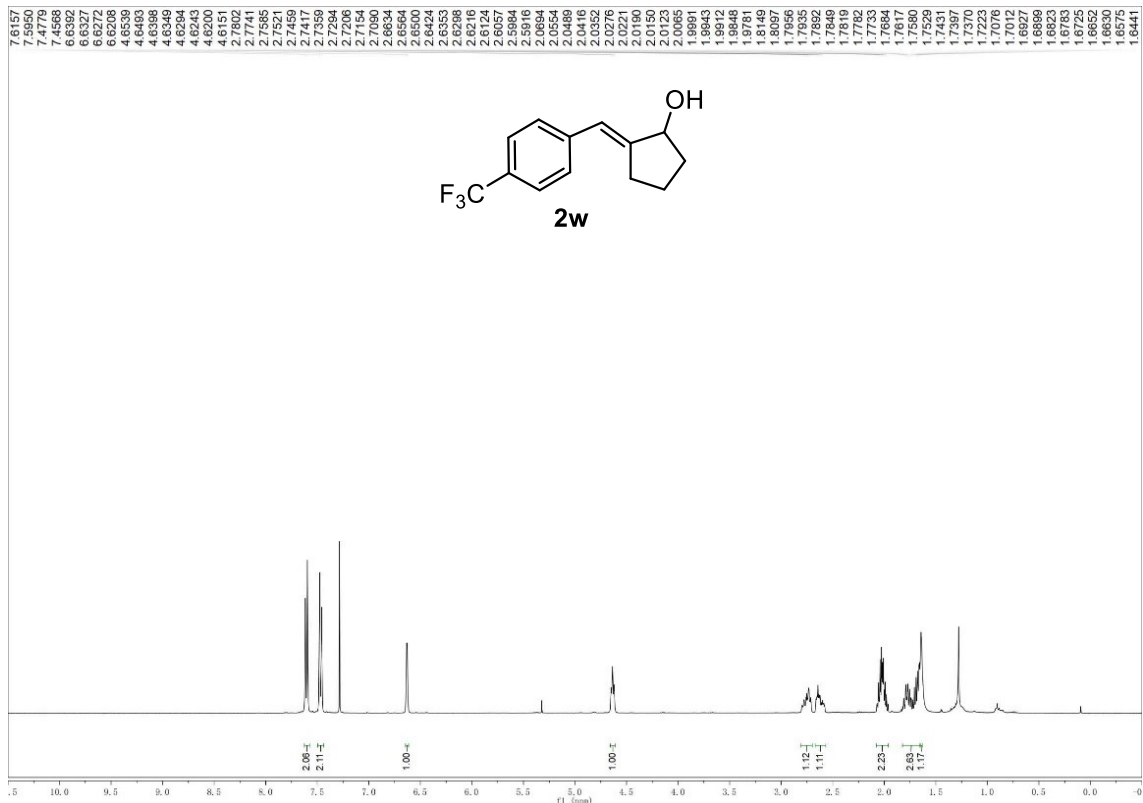


Figure S30. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound 2v



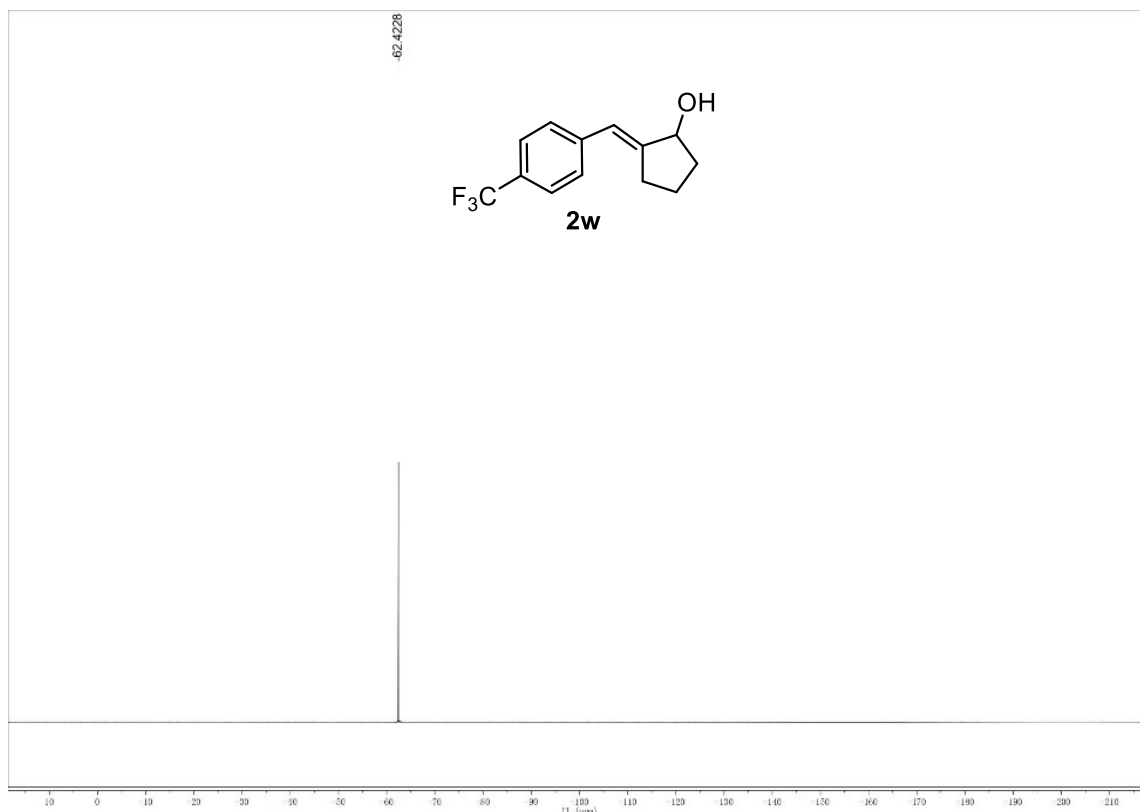
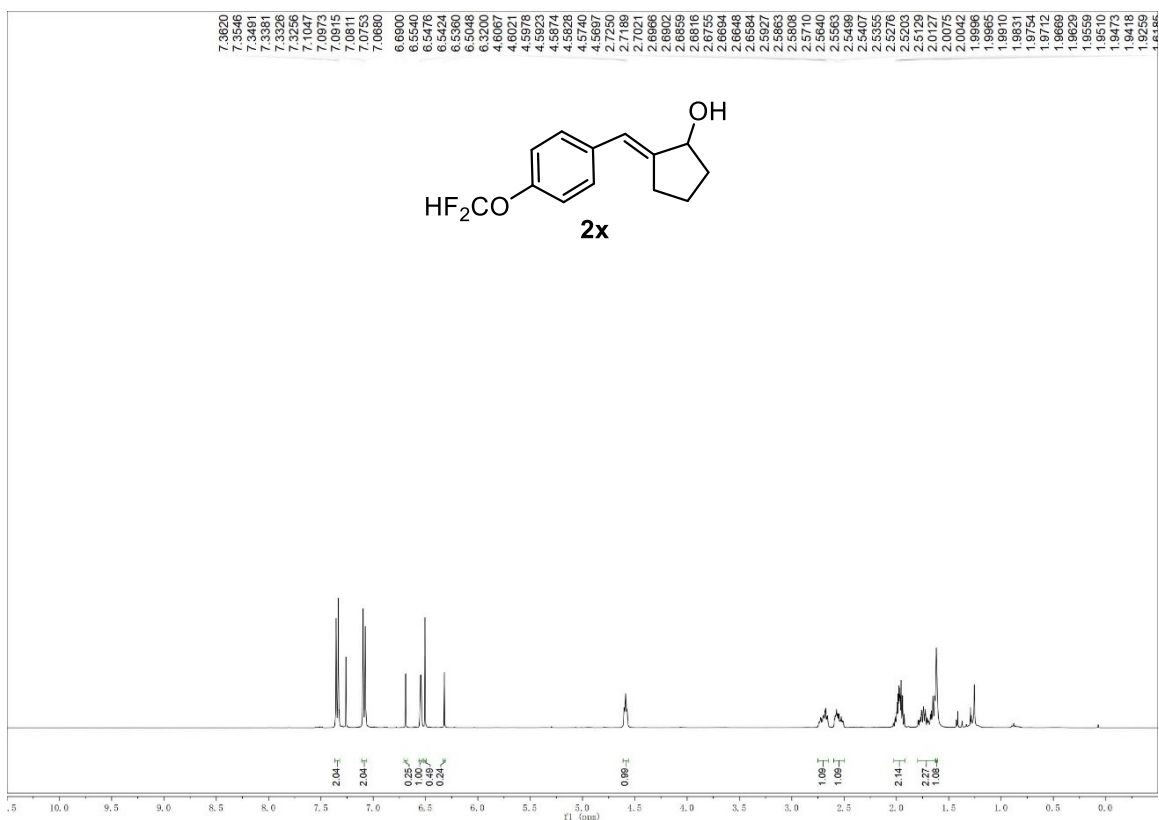


Figure S31. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) and <sup>19</sup>F (376 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2w**



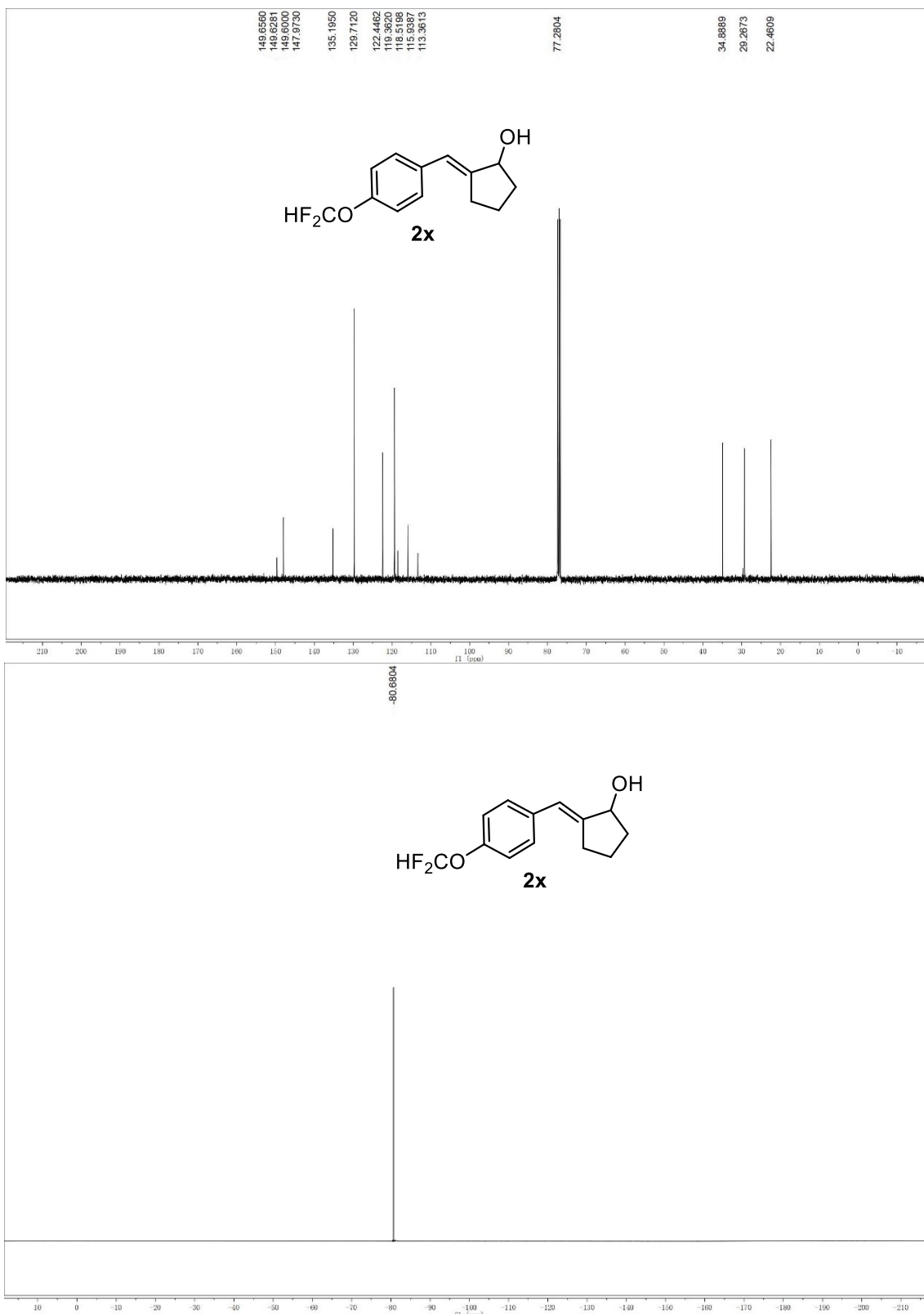
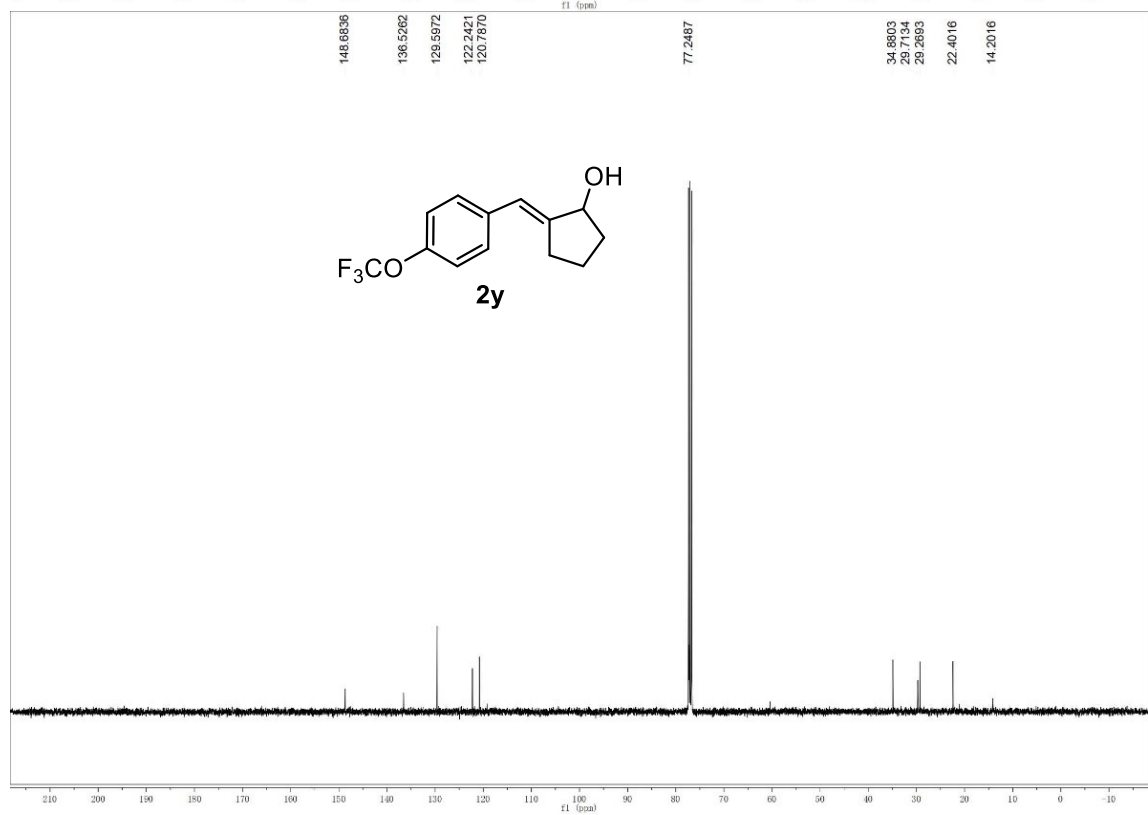
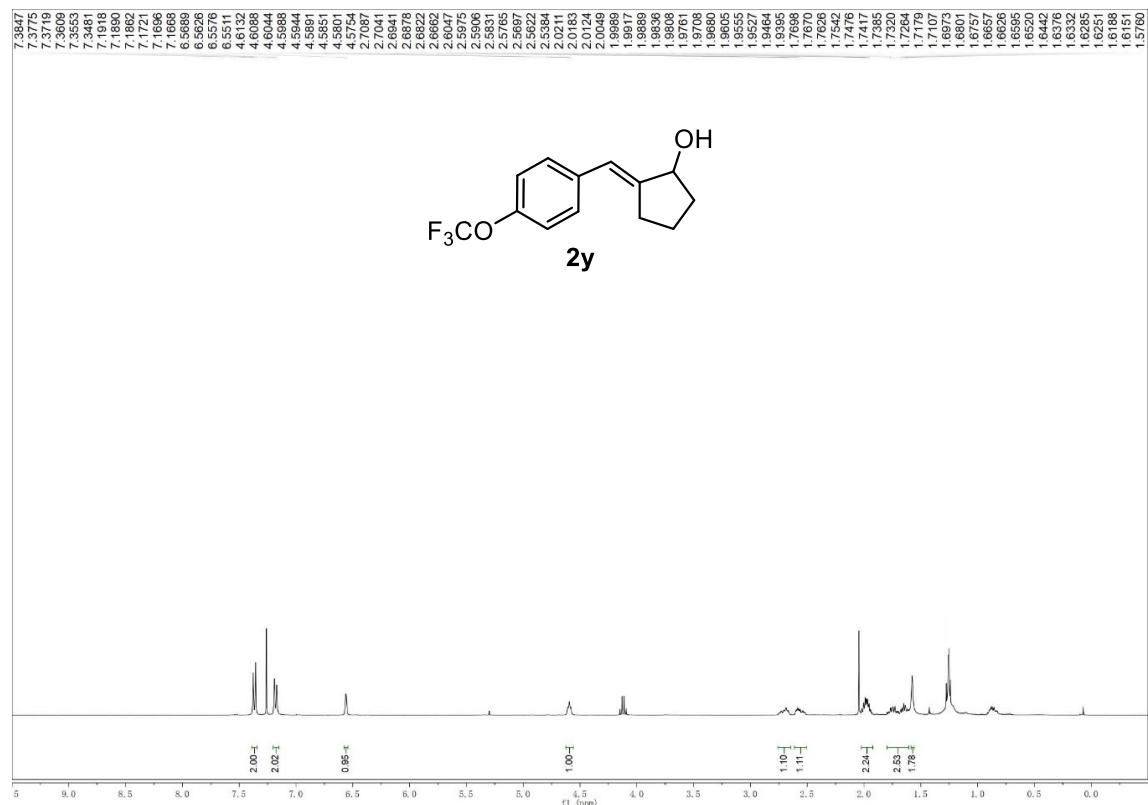


Figure S32. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) and <sup>19</sup>F (376 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2x**





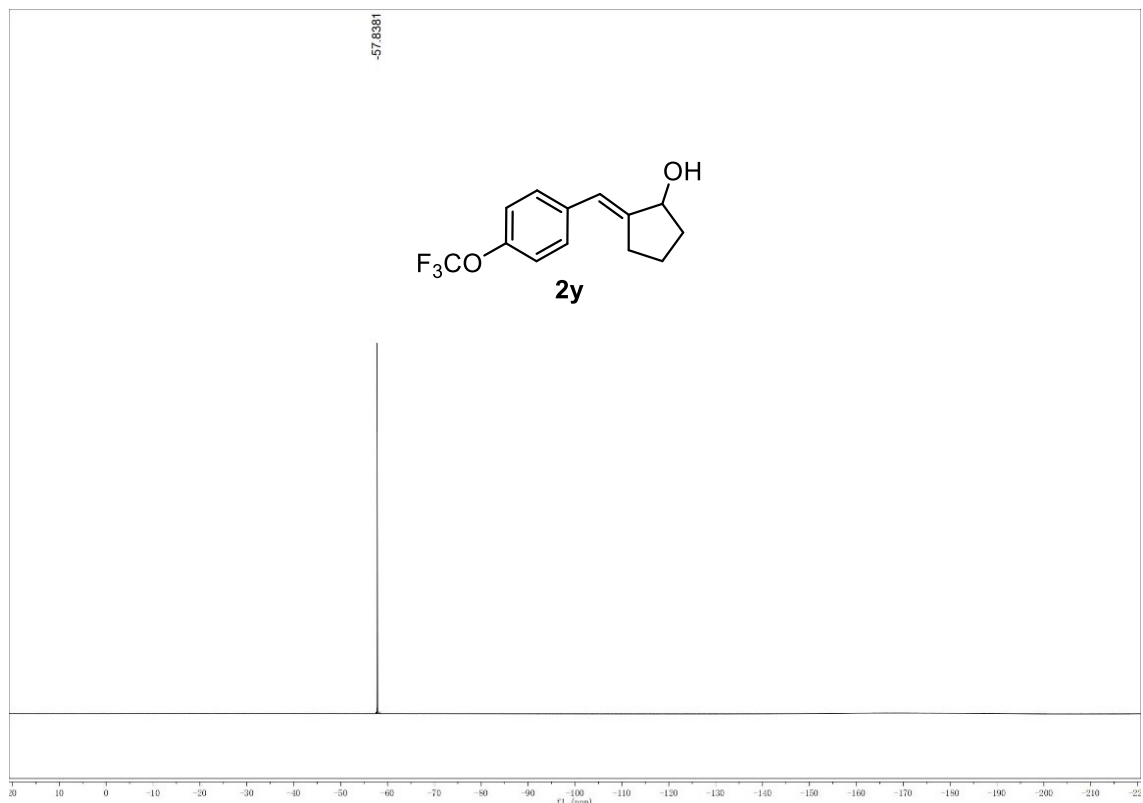
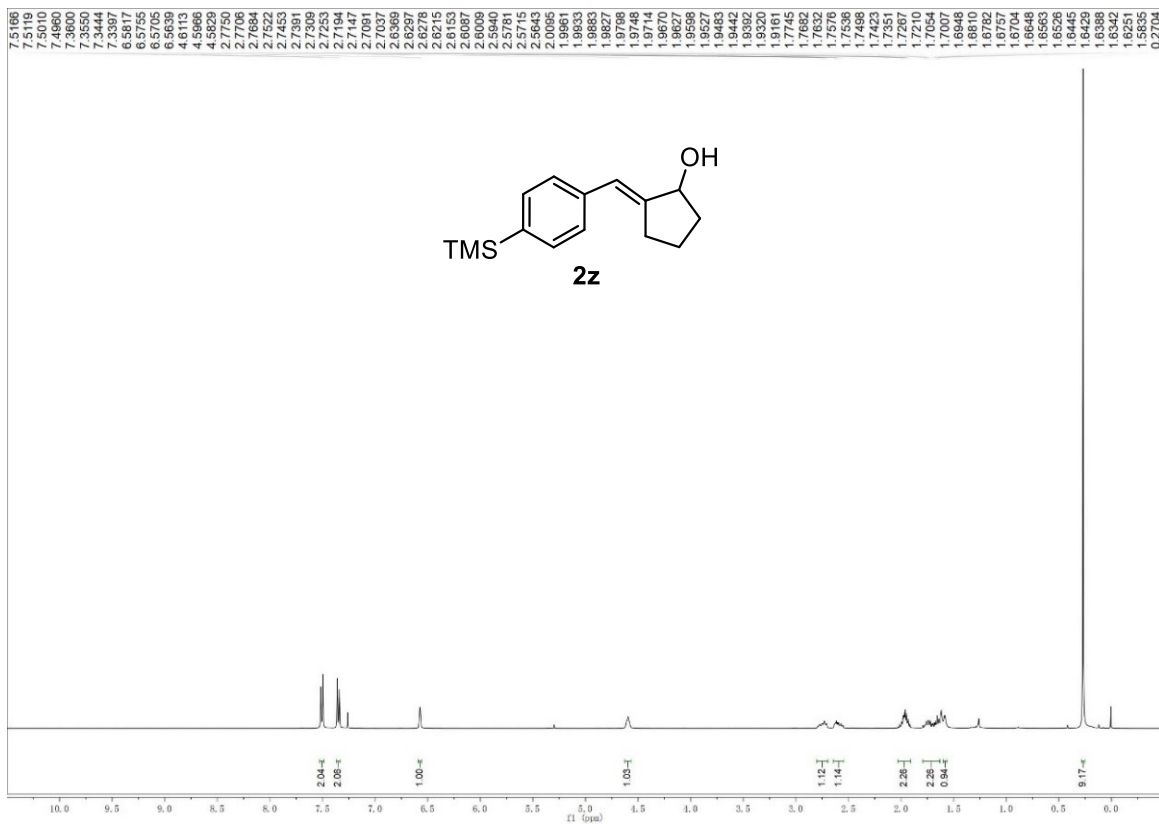


Figure S33.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ ),  $^{13}\text{C}$  (100 MHz,  $\text{CDCl}_3$ ) and  $^{19}\text{F}$  (376 MHz,  $\text{CDCl}_3$ ) NMR spectra for compound **2y**



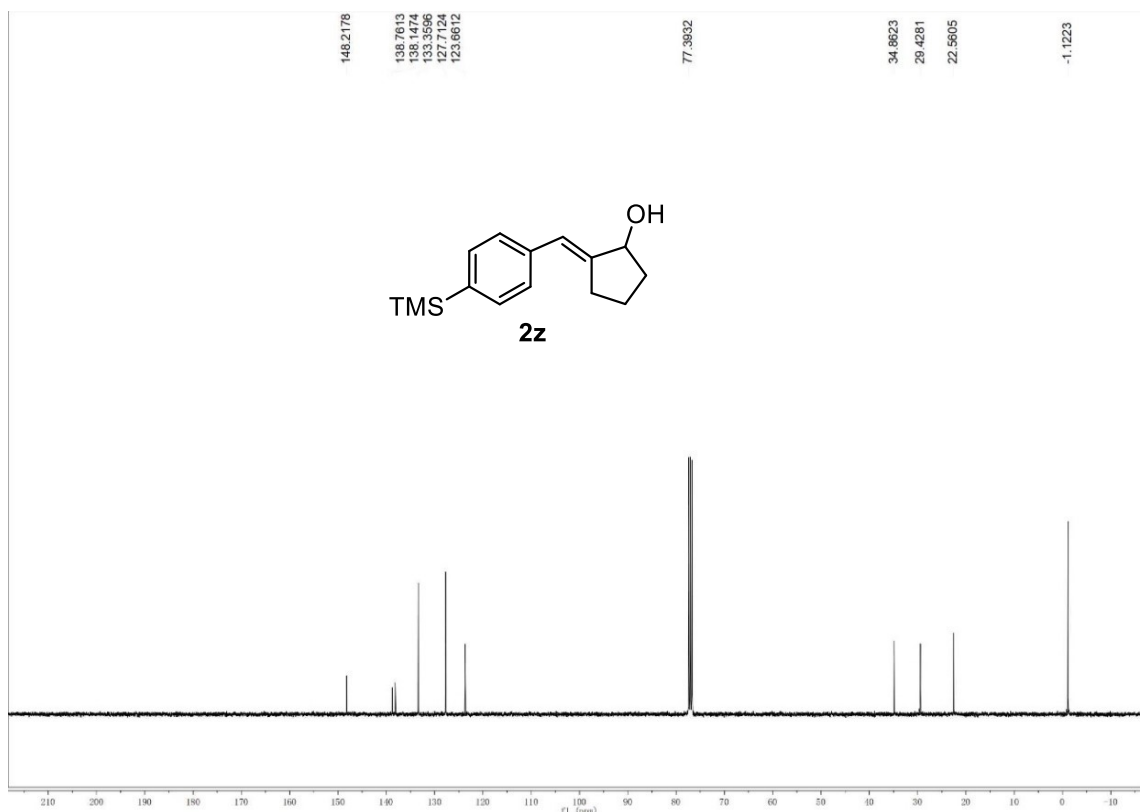
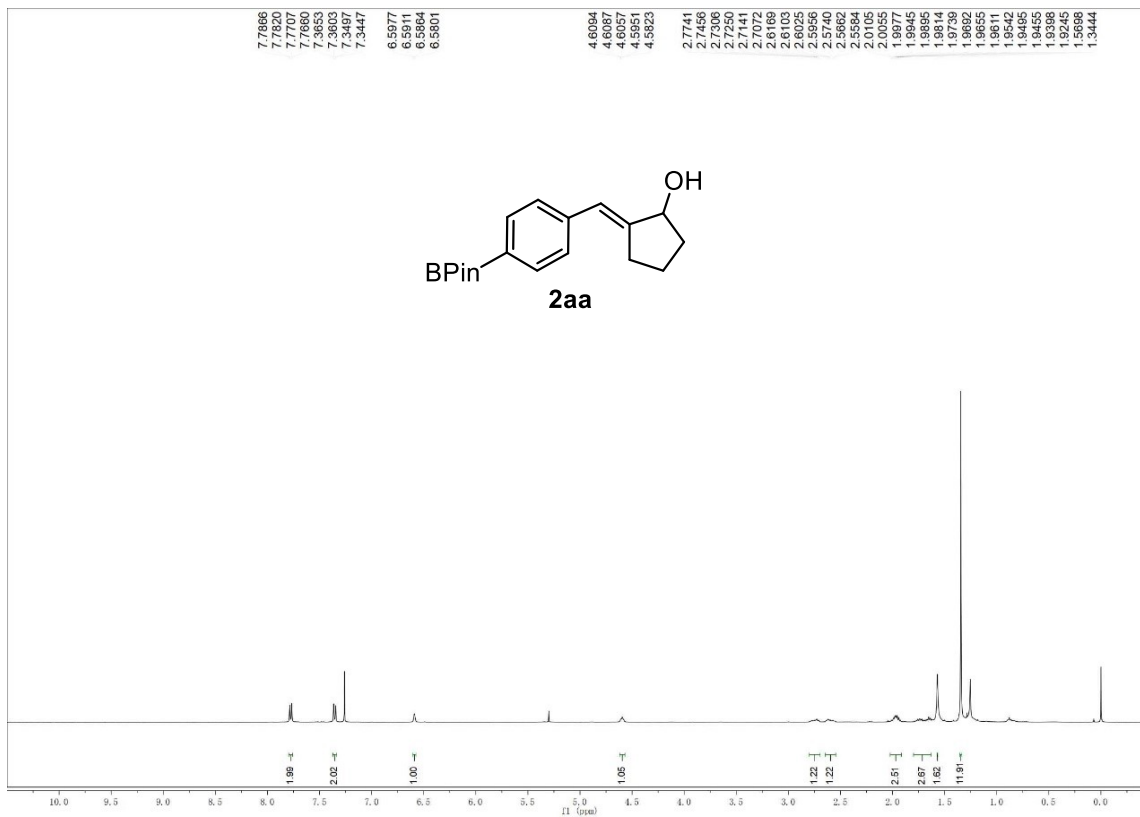


Figure S34. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2z**



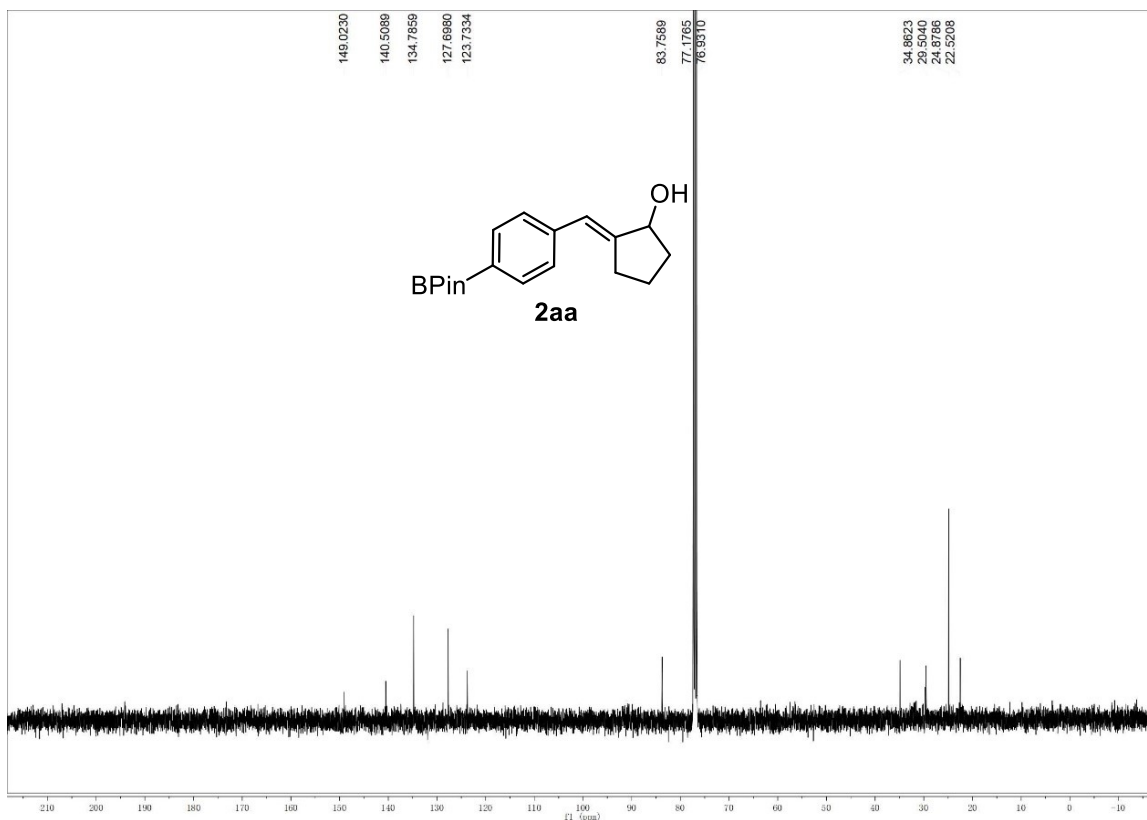
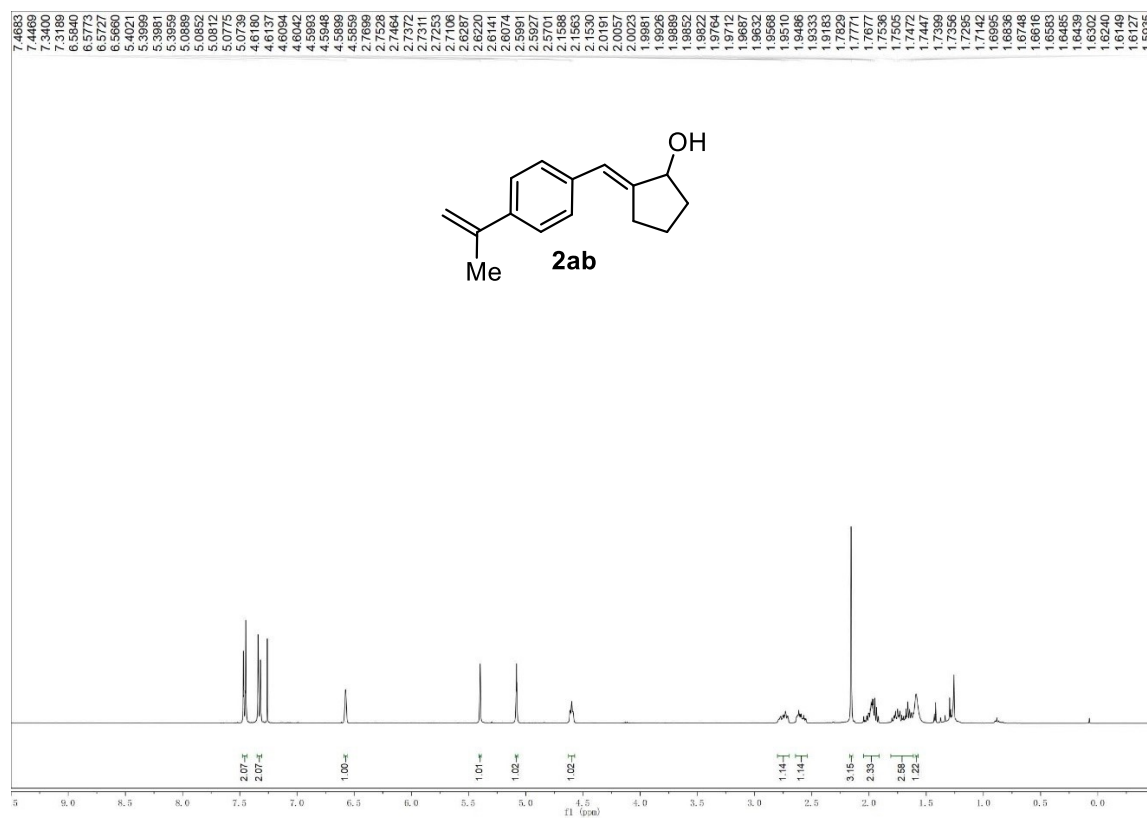


Figure S35.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  (100 MHz,  $\text{CDCl}_3$ ) NMR spectra for compound **2aa**



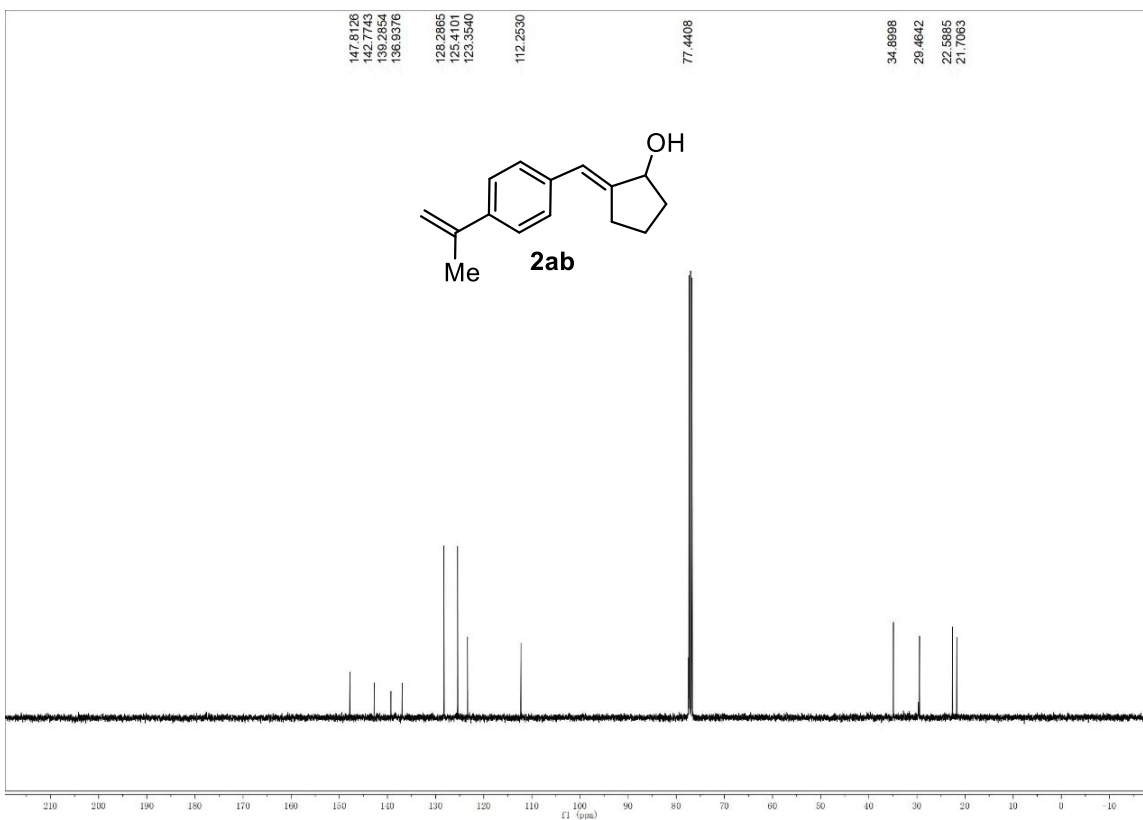
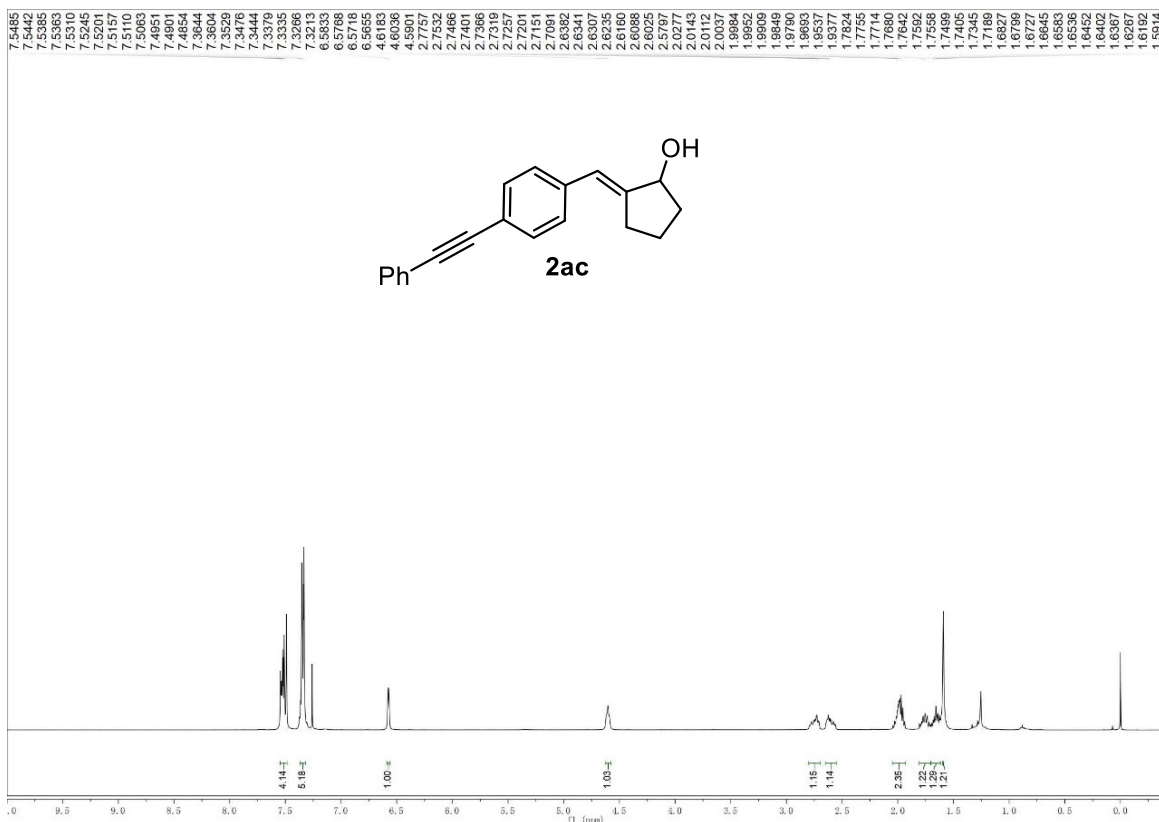


Figure S36. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2ab**



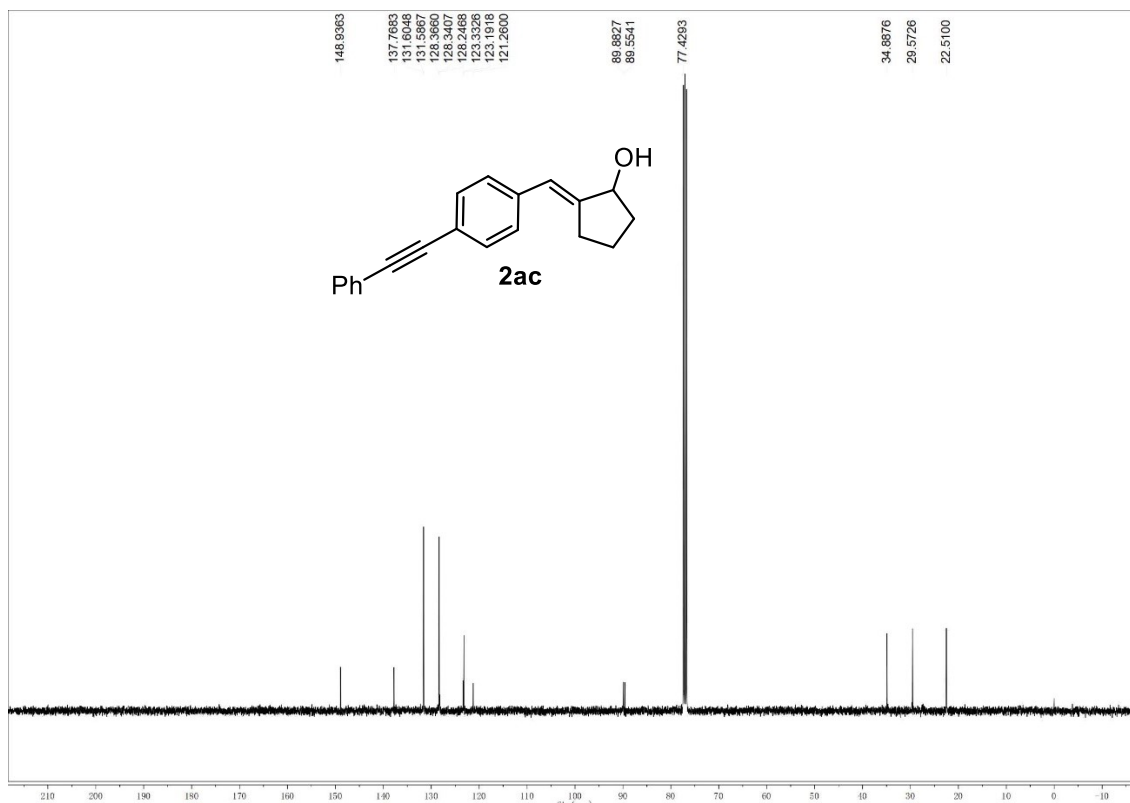
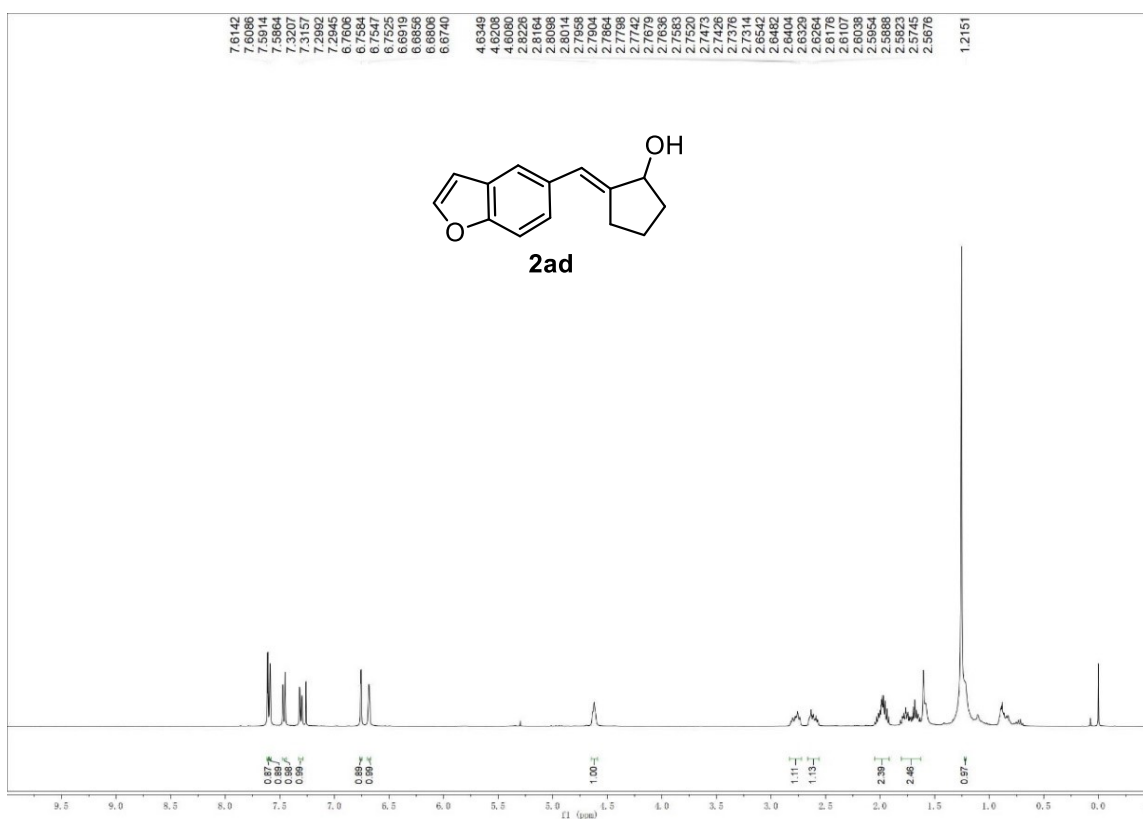


Figure S37. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2ac**



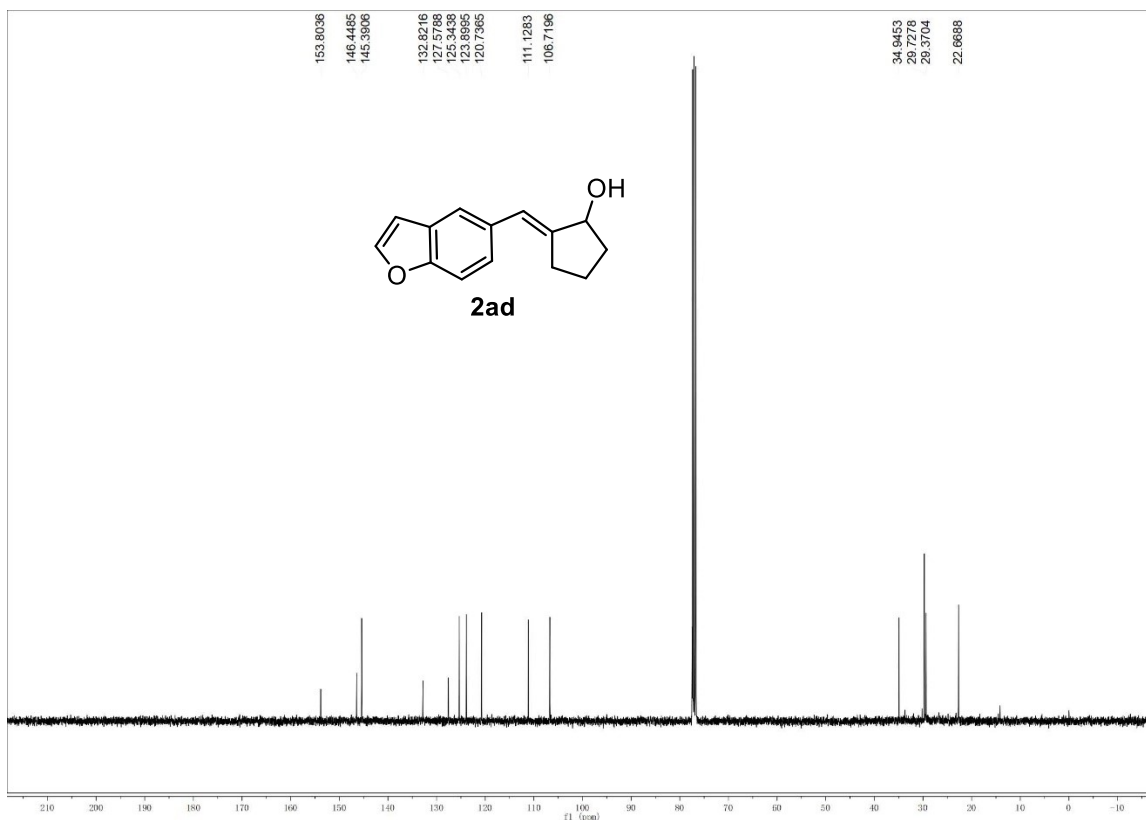
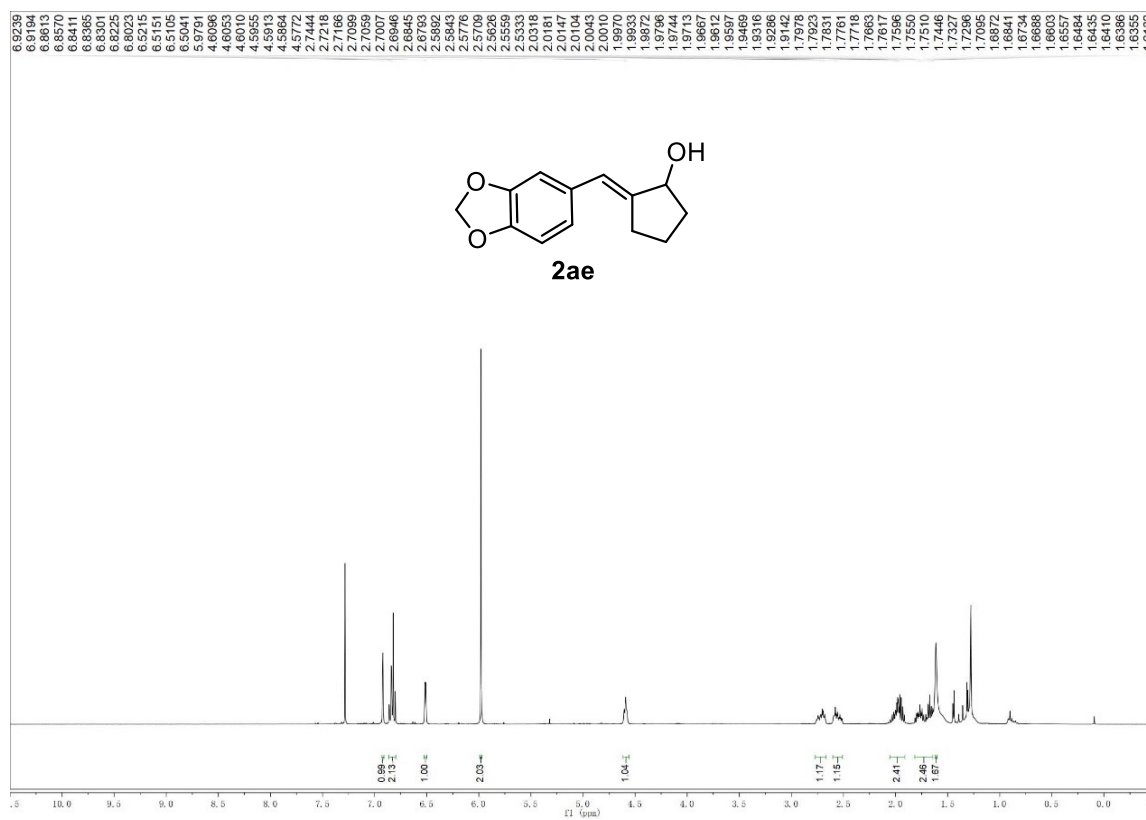


Figure S38. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2ad**



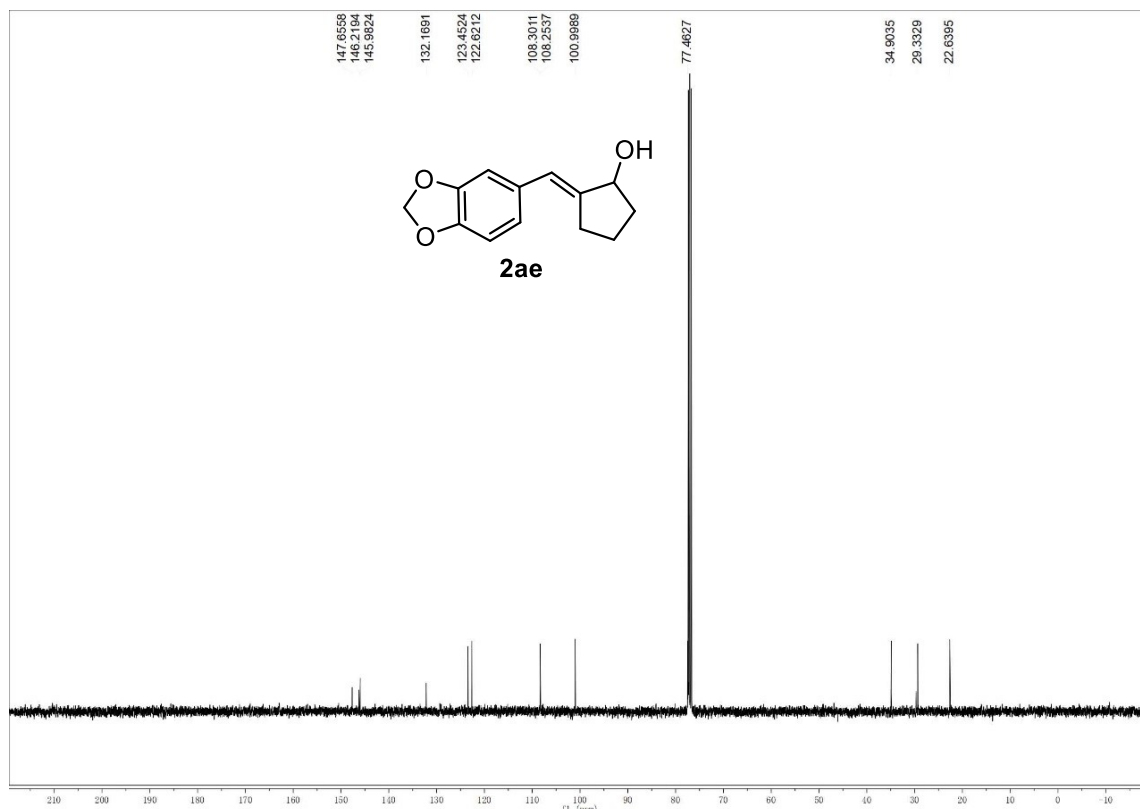
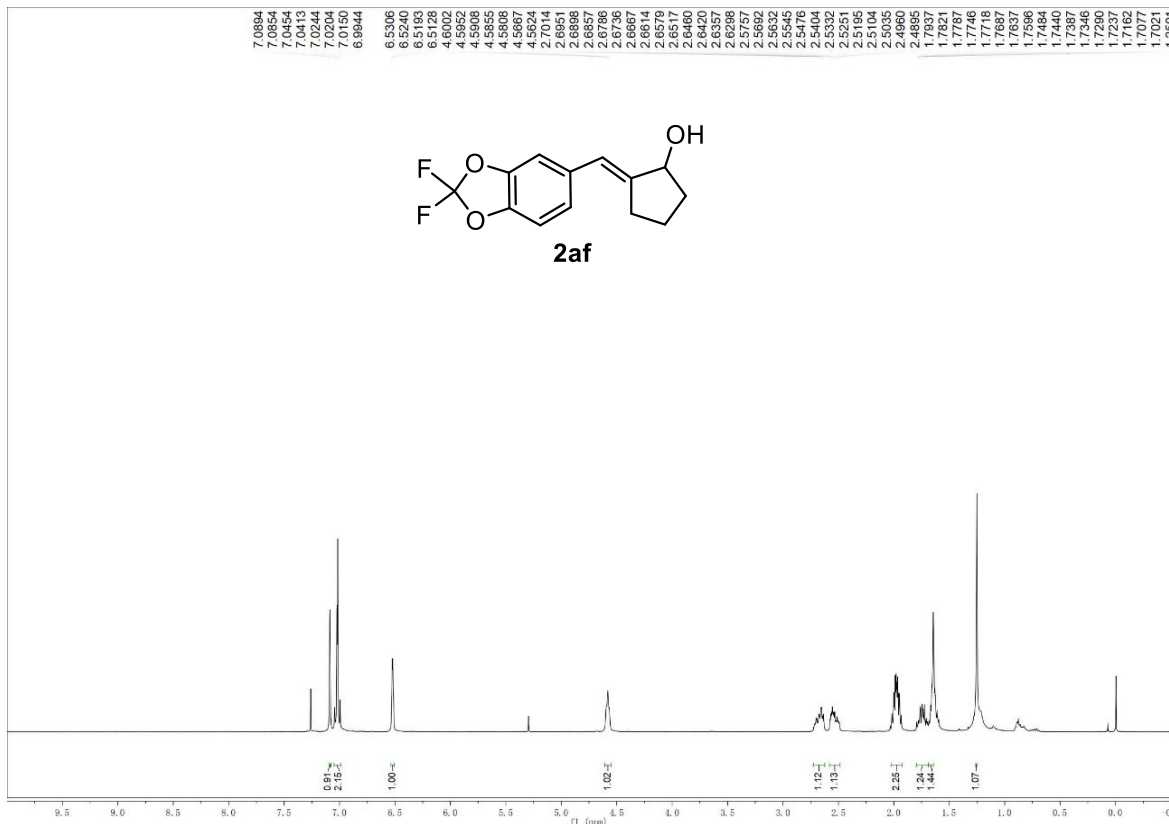


Figure S39. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2ae**



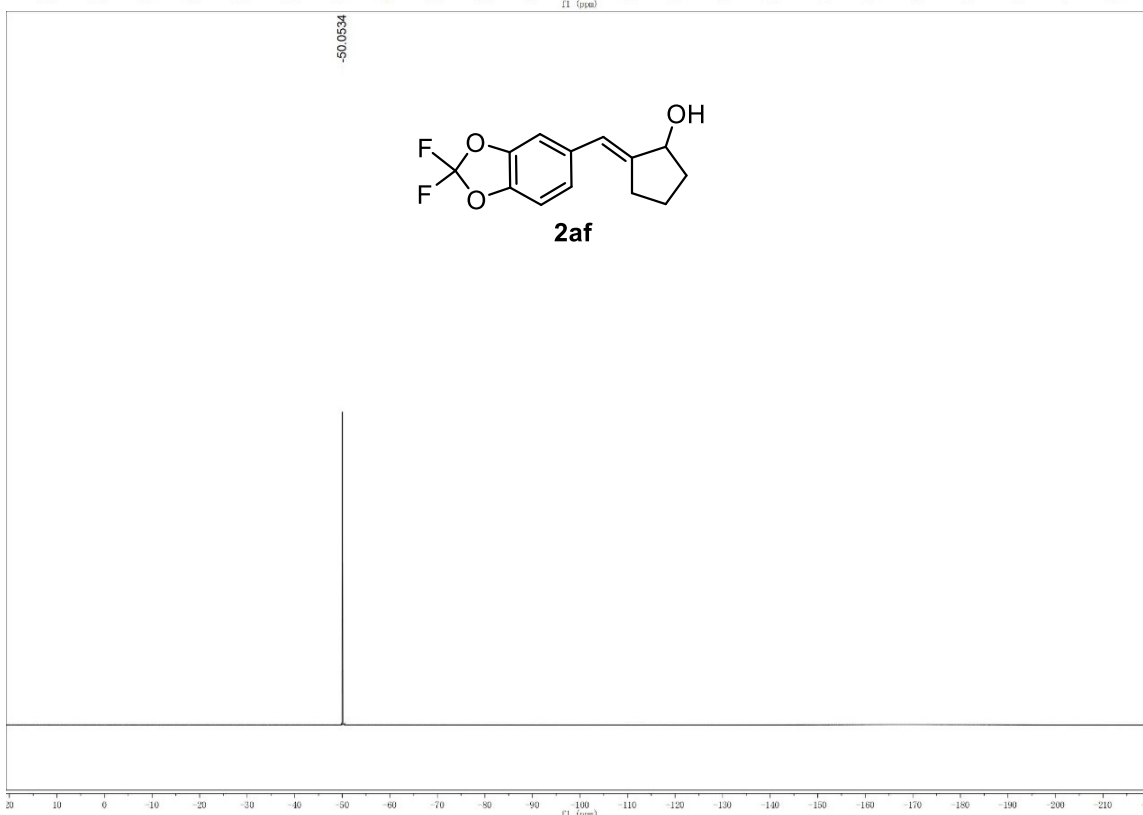
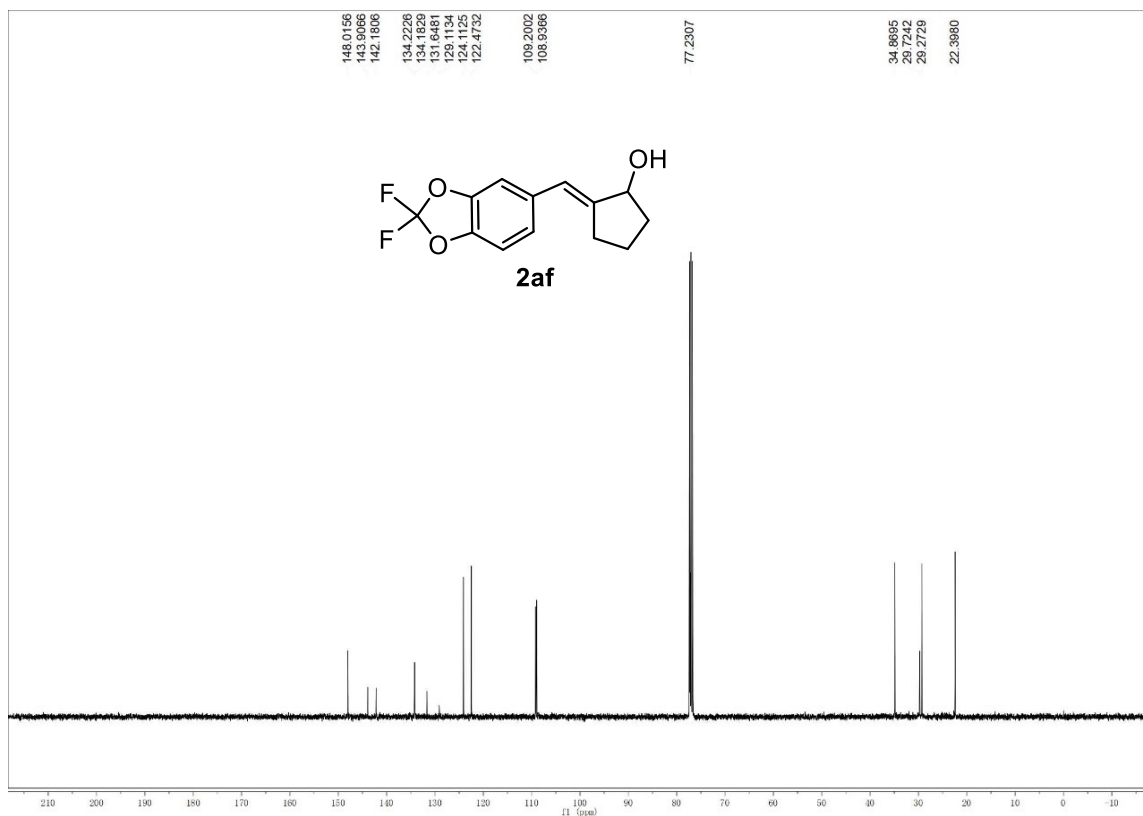


Figure S40. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) and <sup>19</sup>F (376 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2af**



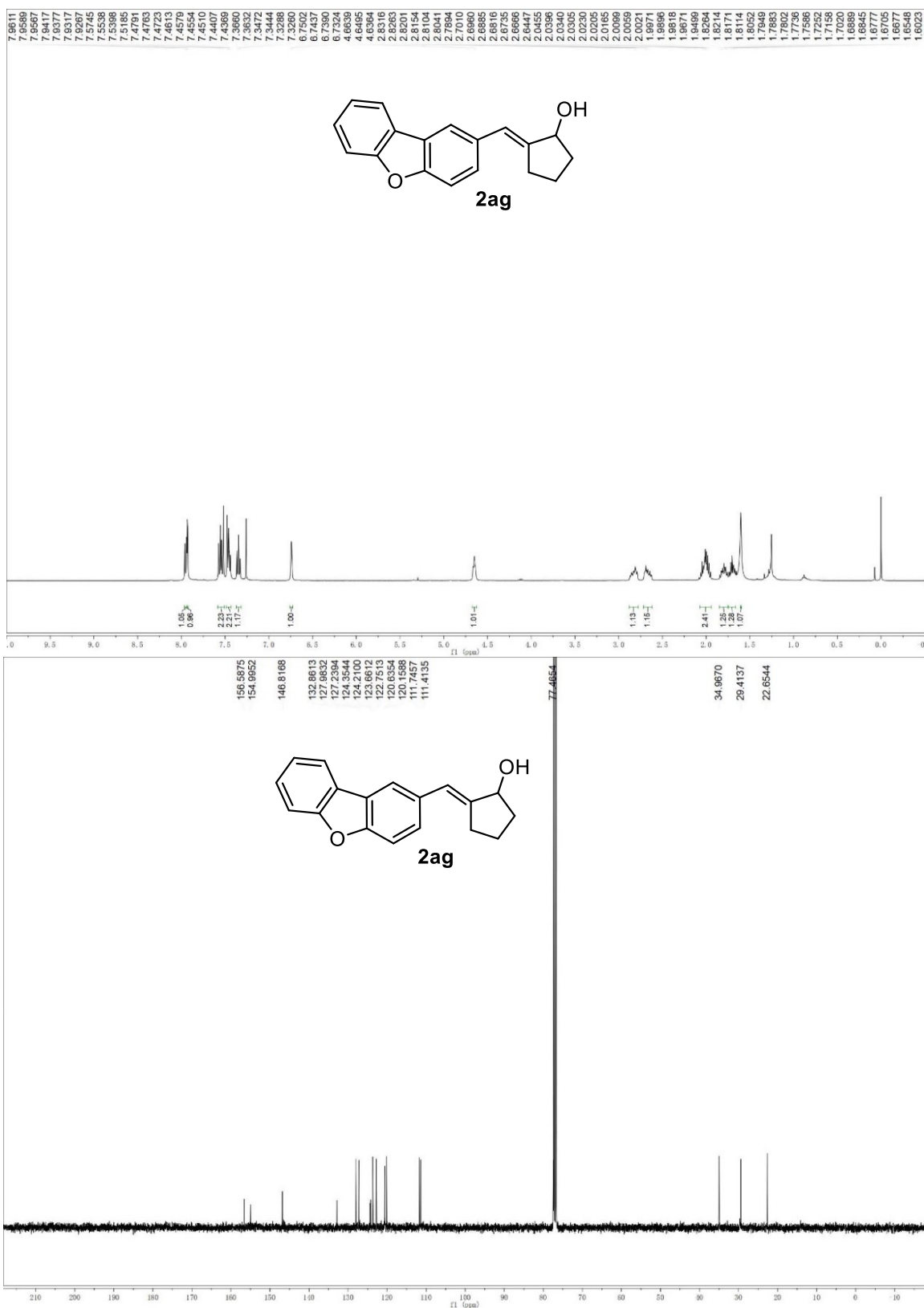


Figure S41. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2ag**

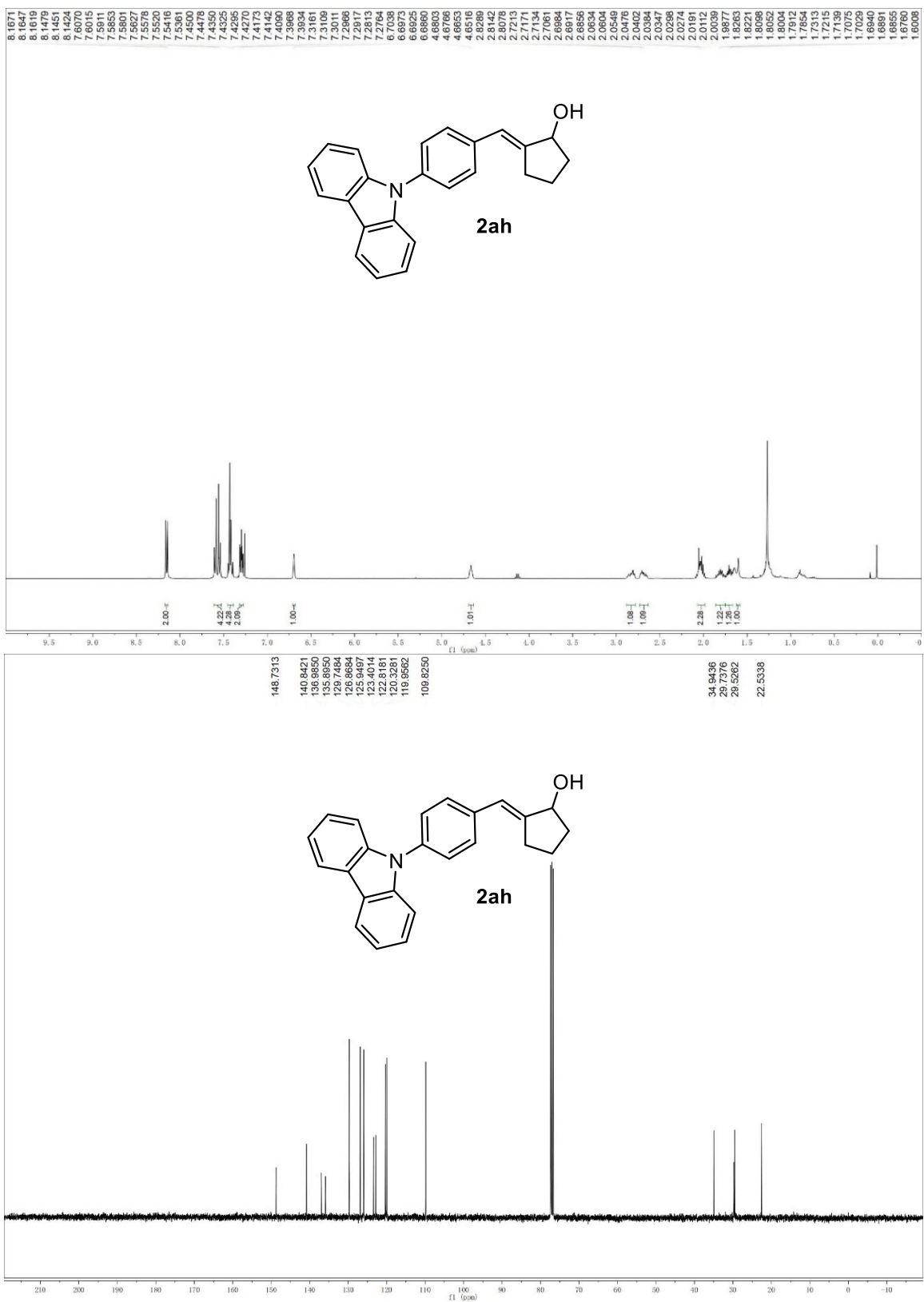


Figure S42. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2ah**



Figure S43. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound 2ai

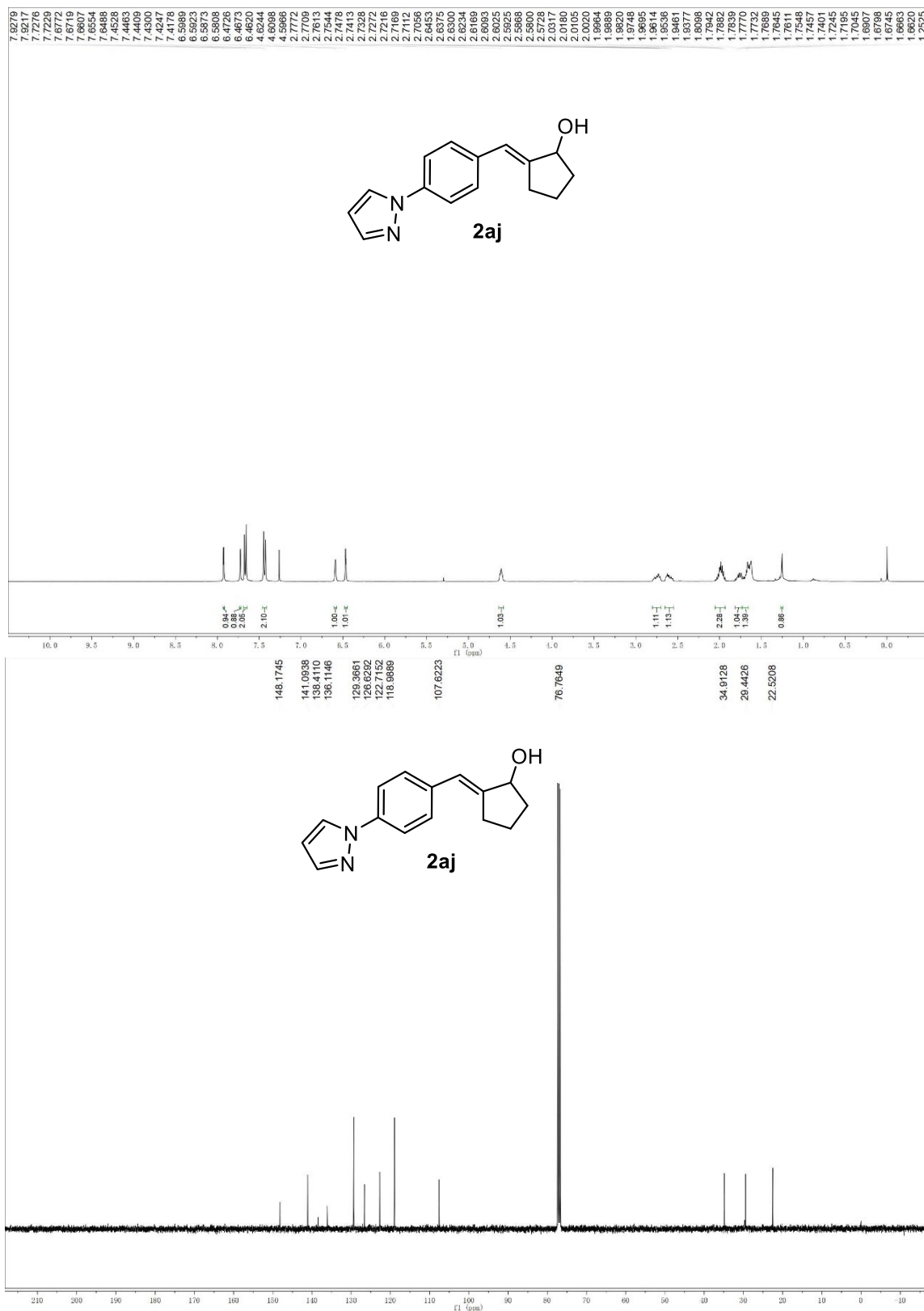


Figure S44. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2aj**

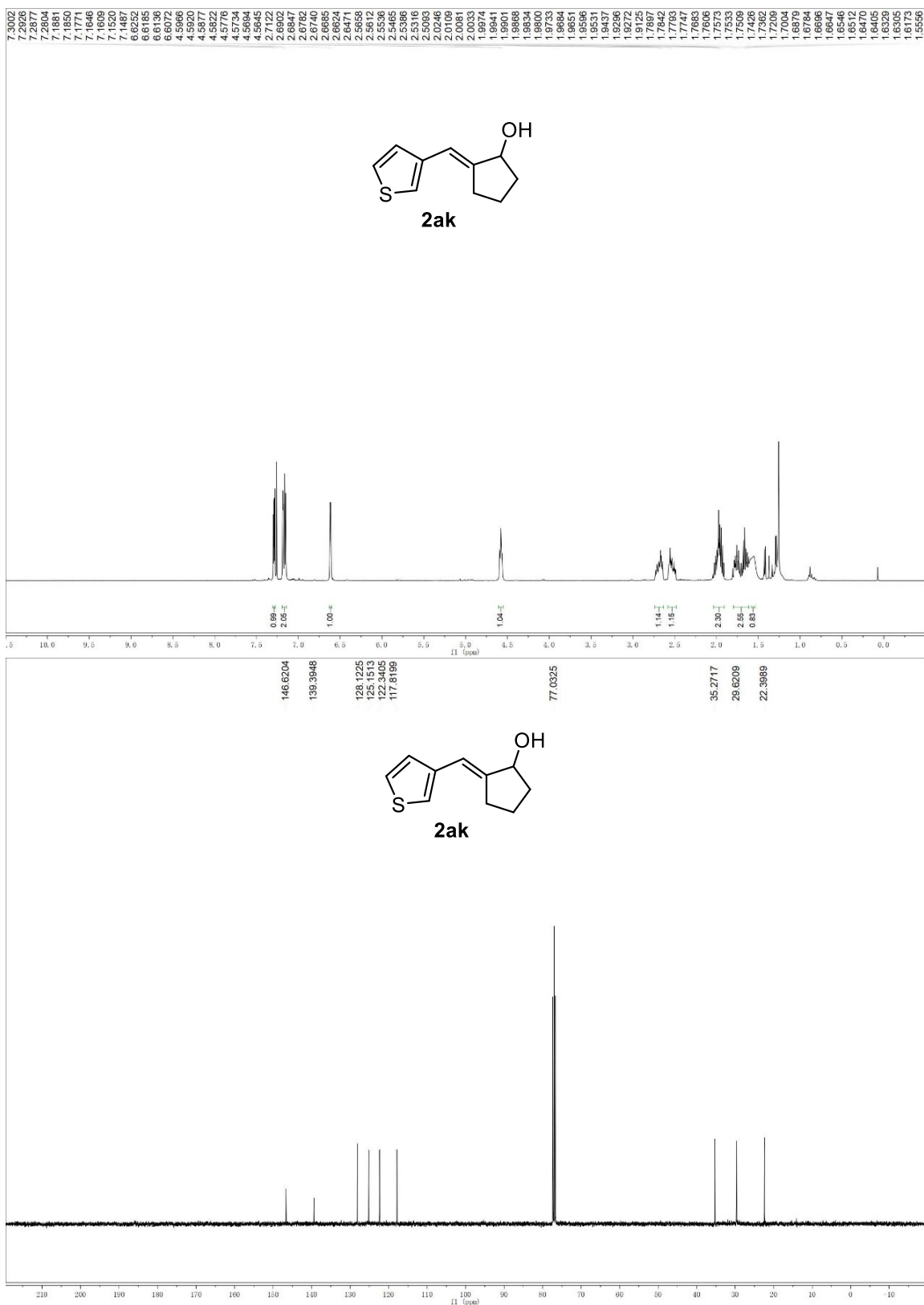


Figure S45. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2ak**

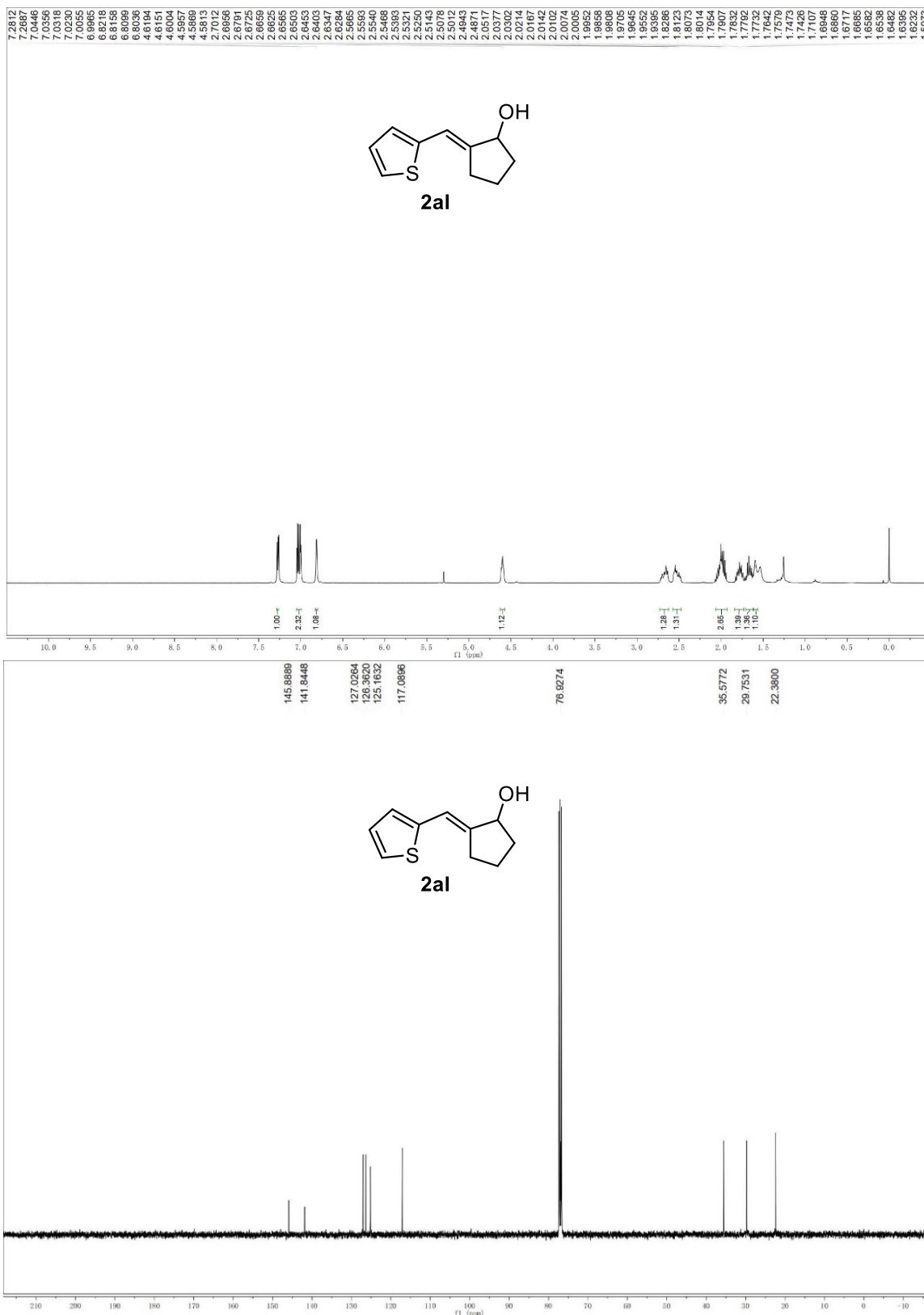


Figure S46. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **2al**

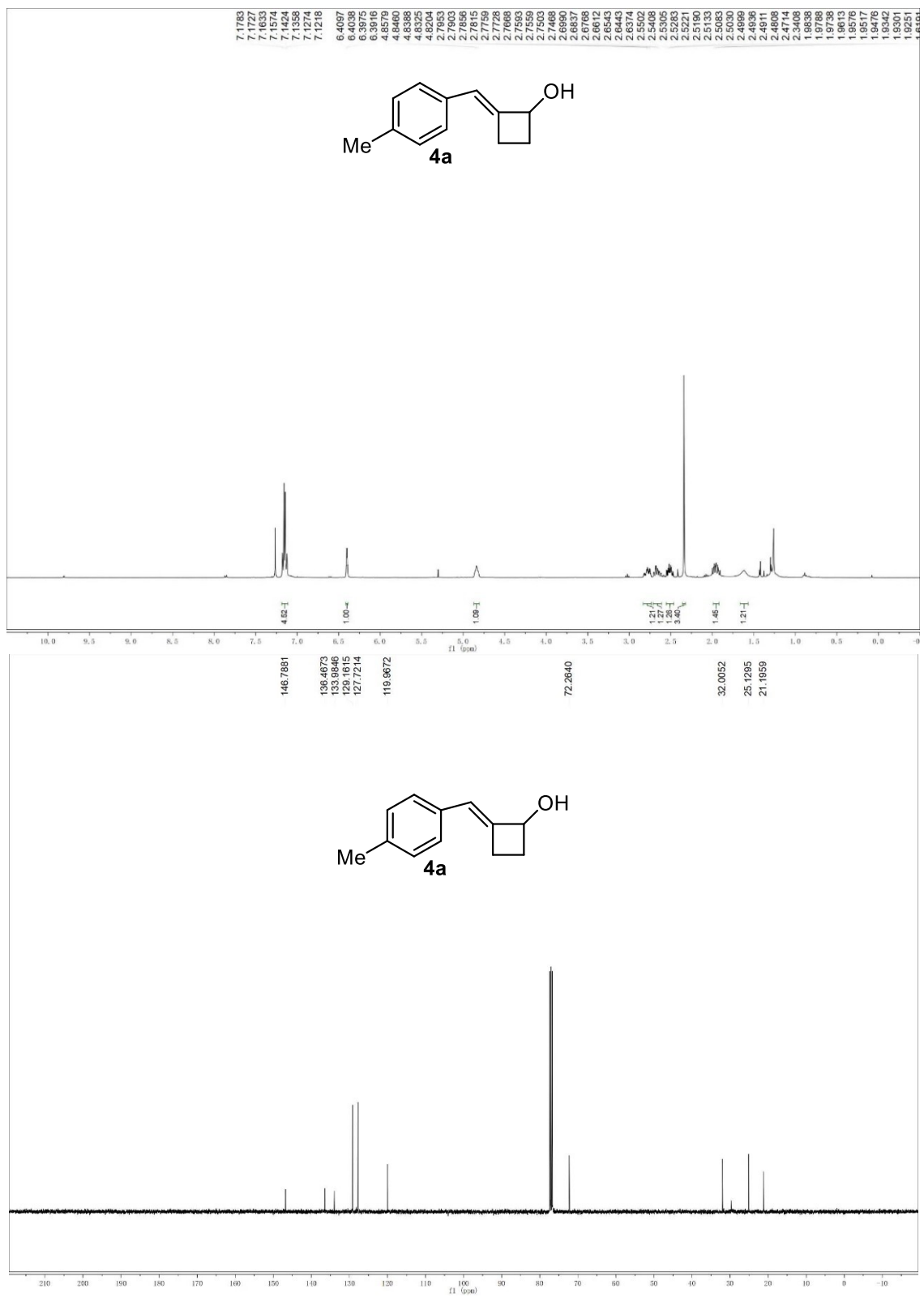


Figure S47. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **4a**

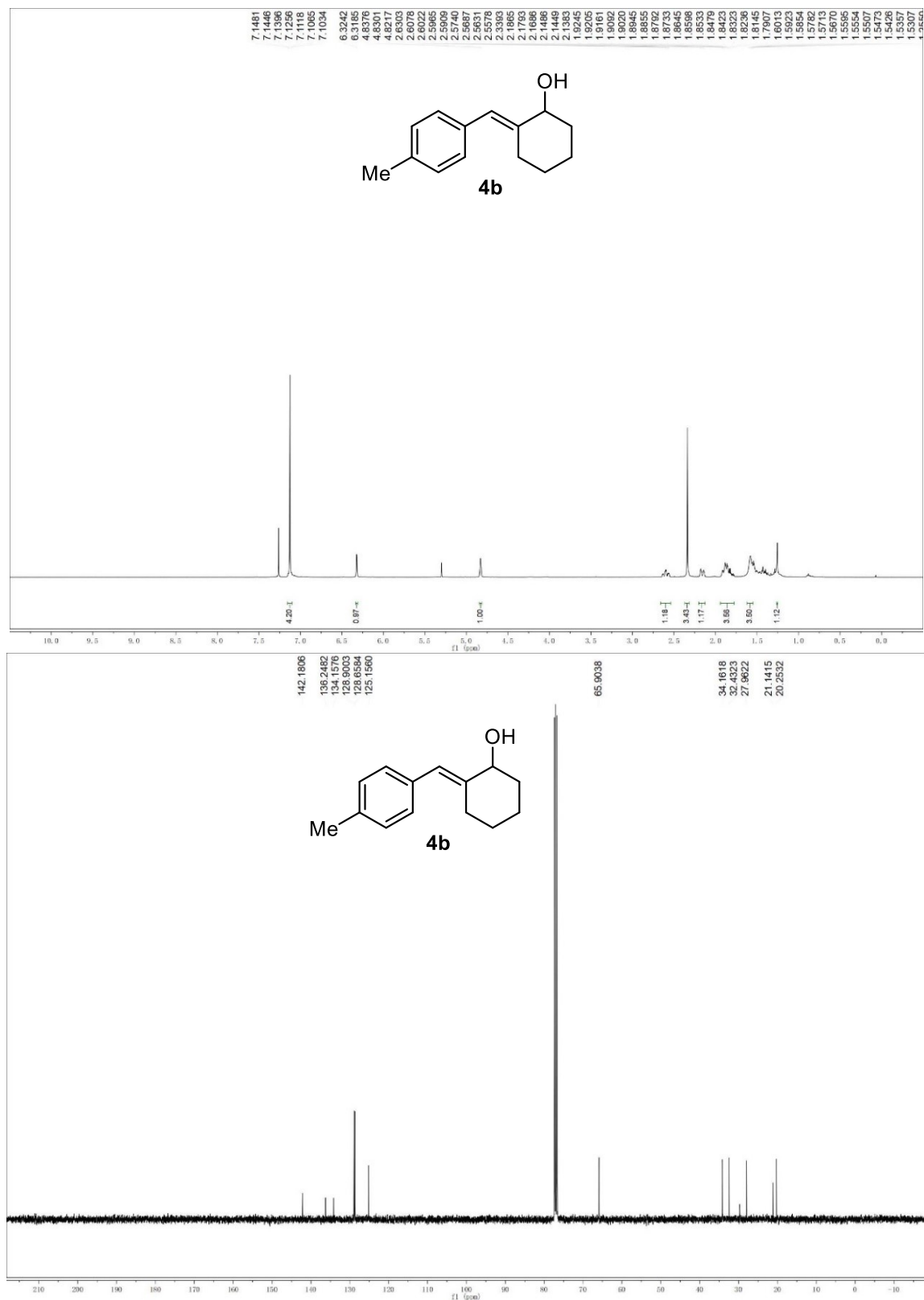


Figure S48. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **4b**



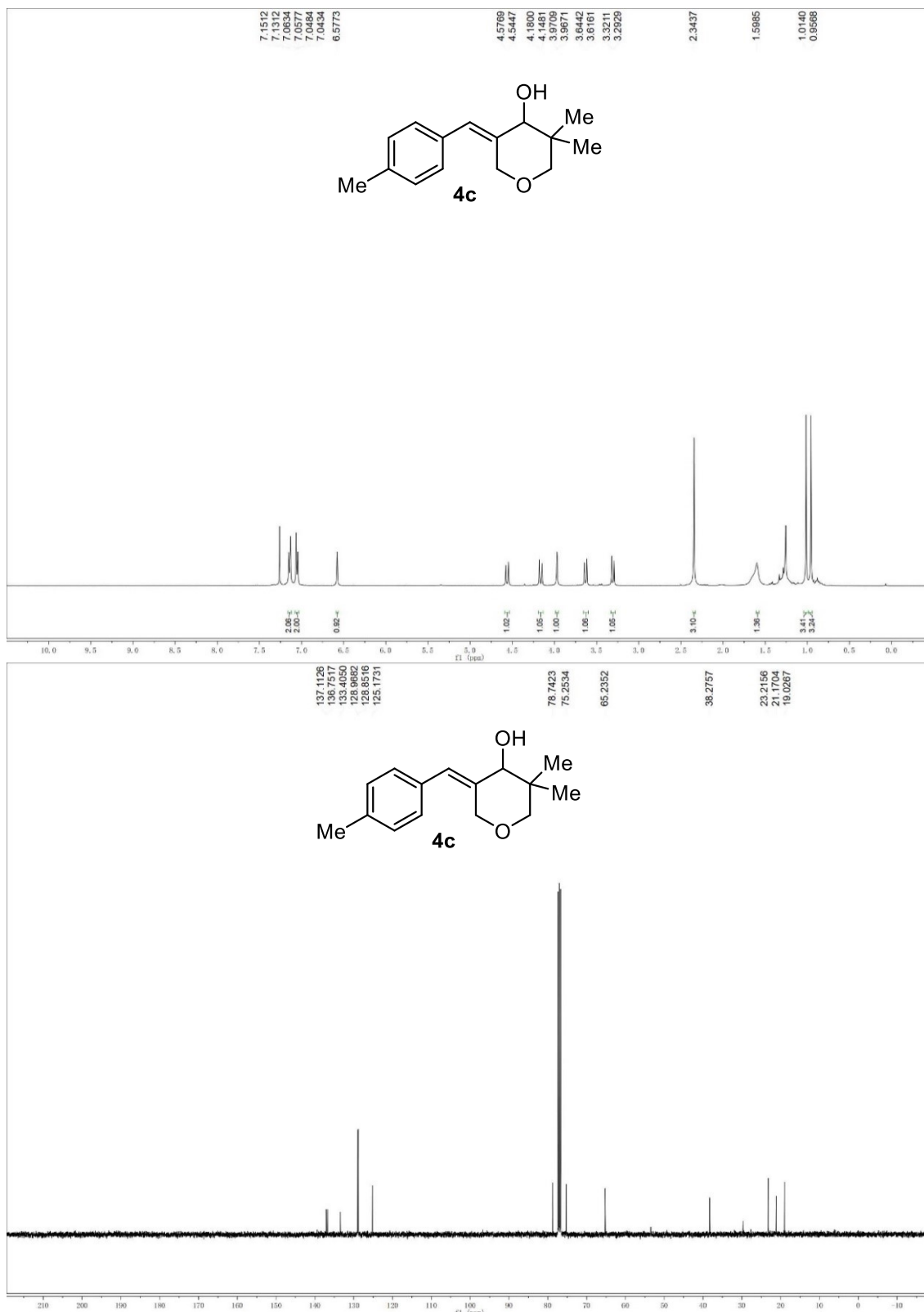


Figure S49. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **4c**

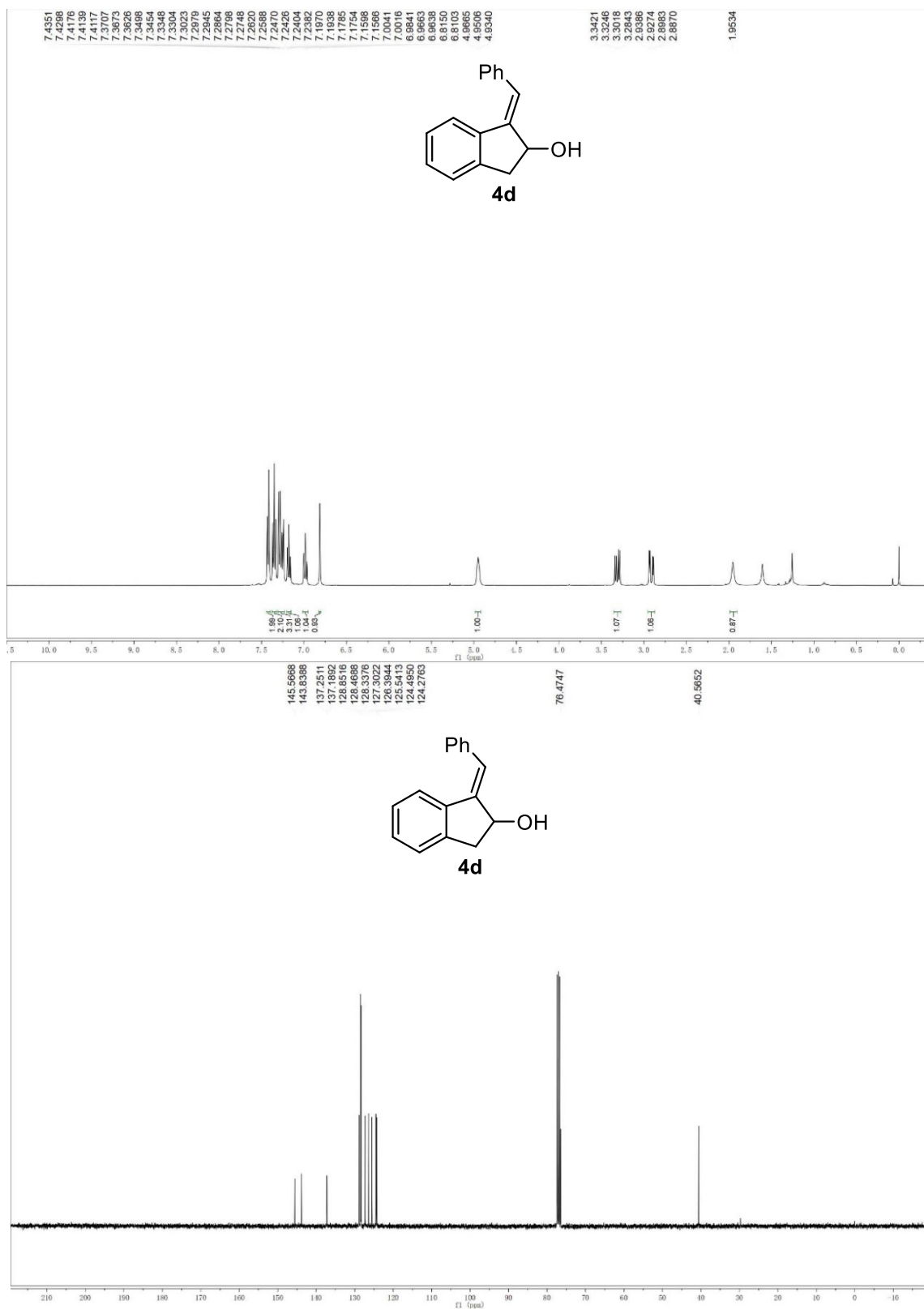


Figure S50. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **4d**

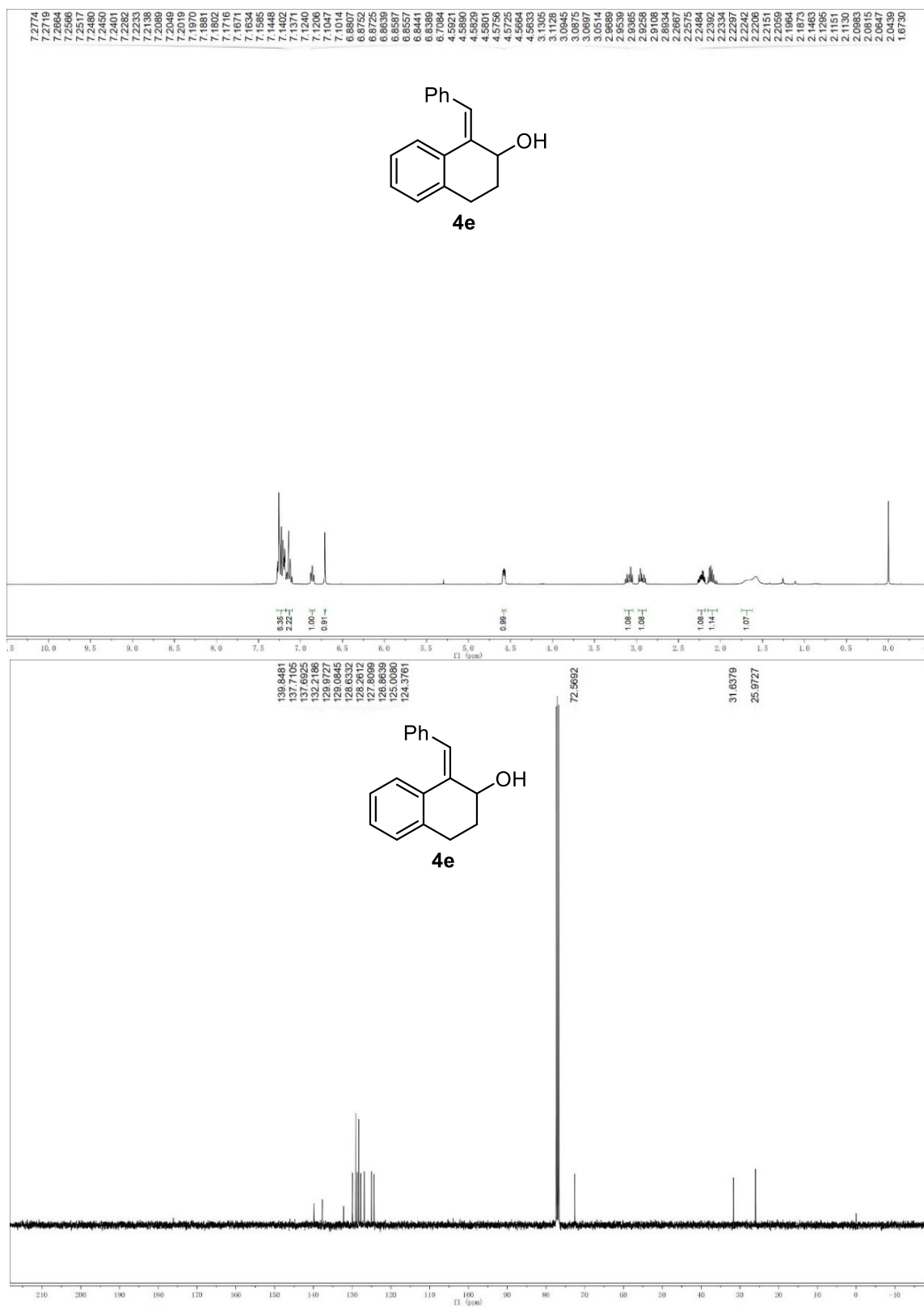


Figure S51. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **4e**

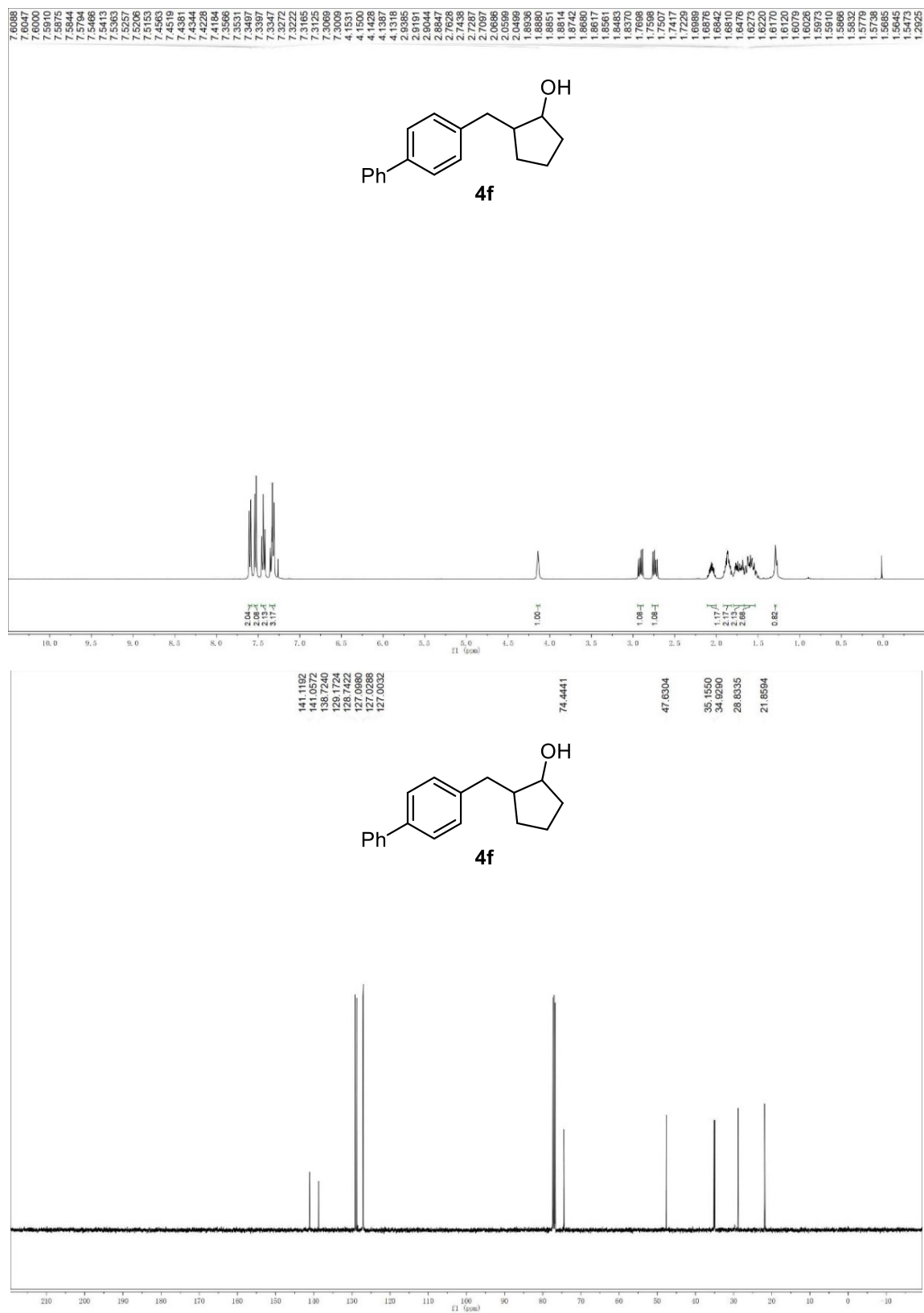


Figure S52. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **4f**

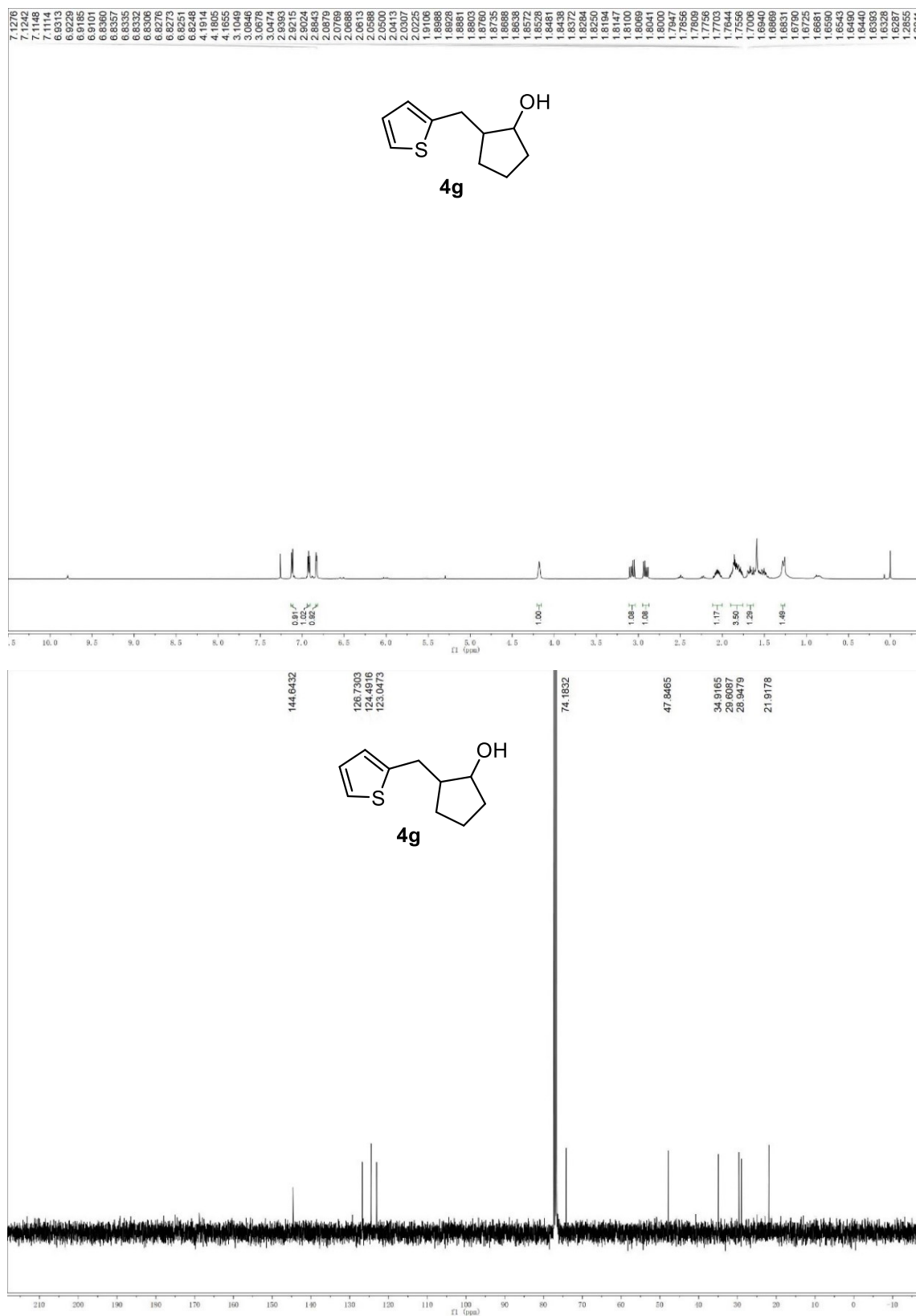


Figure S53. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **4g**

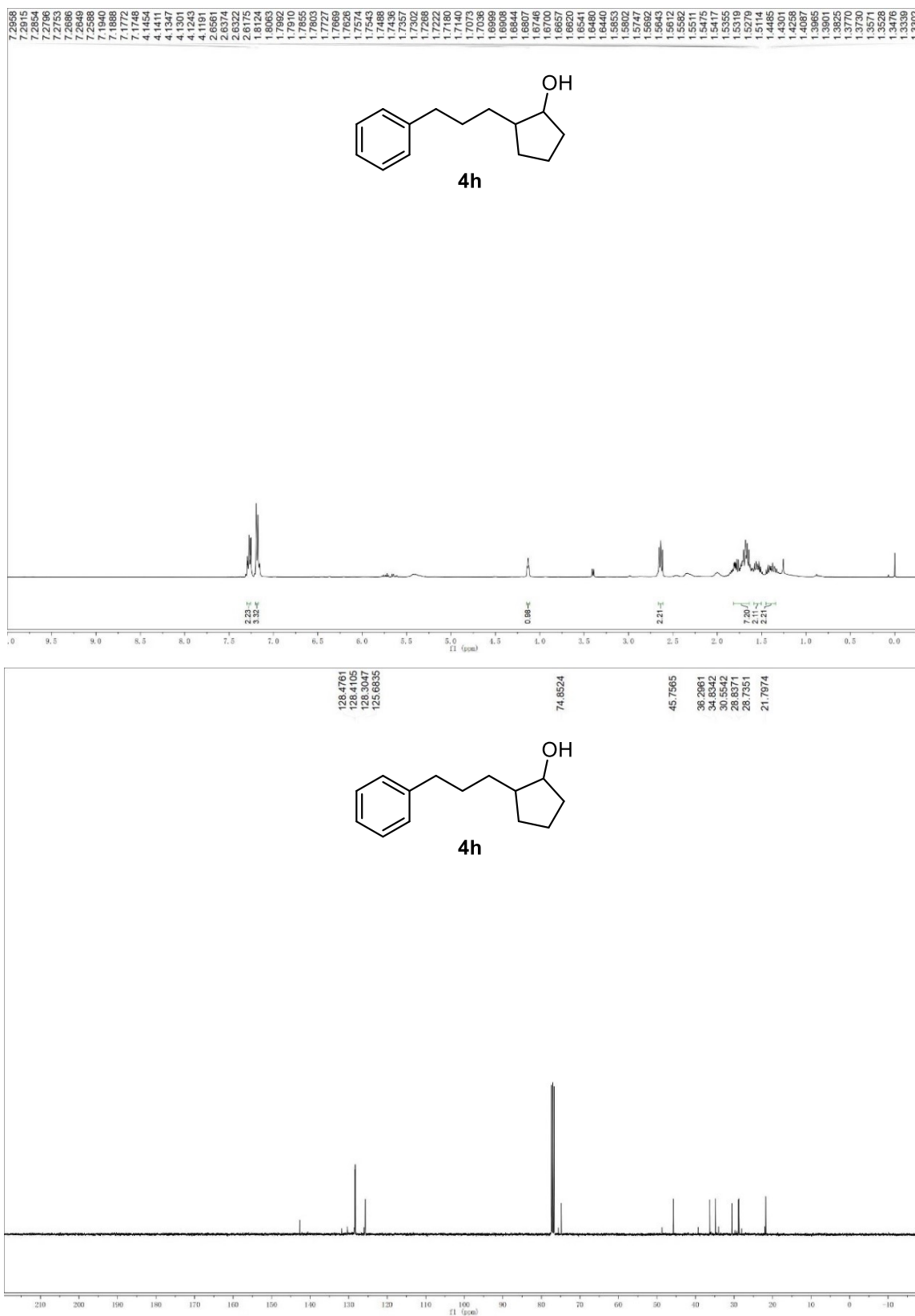


Figure S54. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **4h**

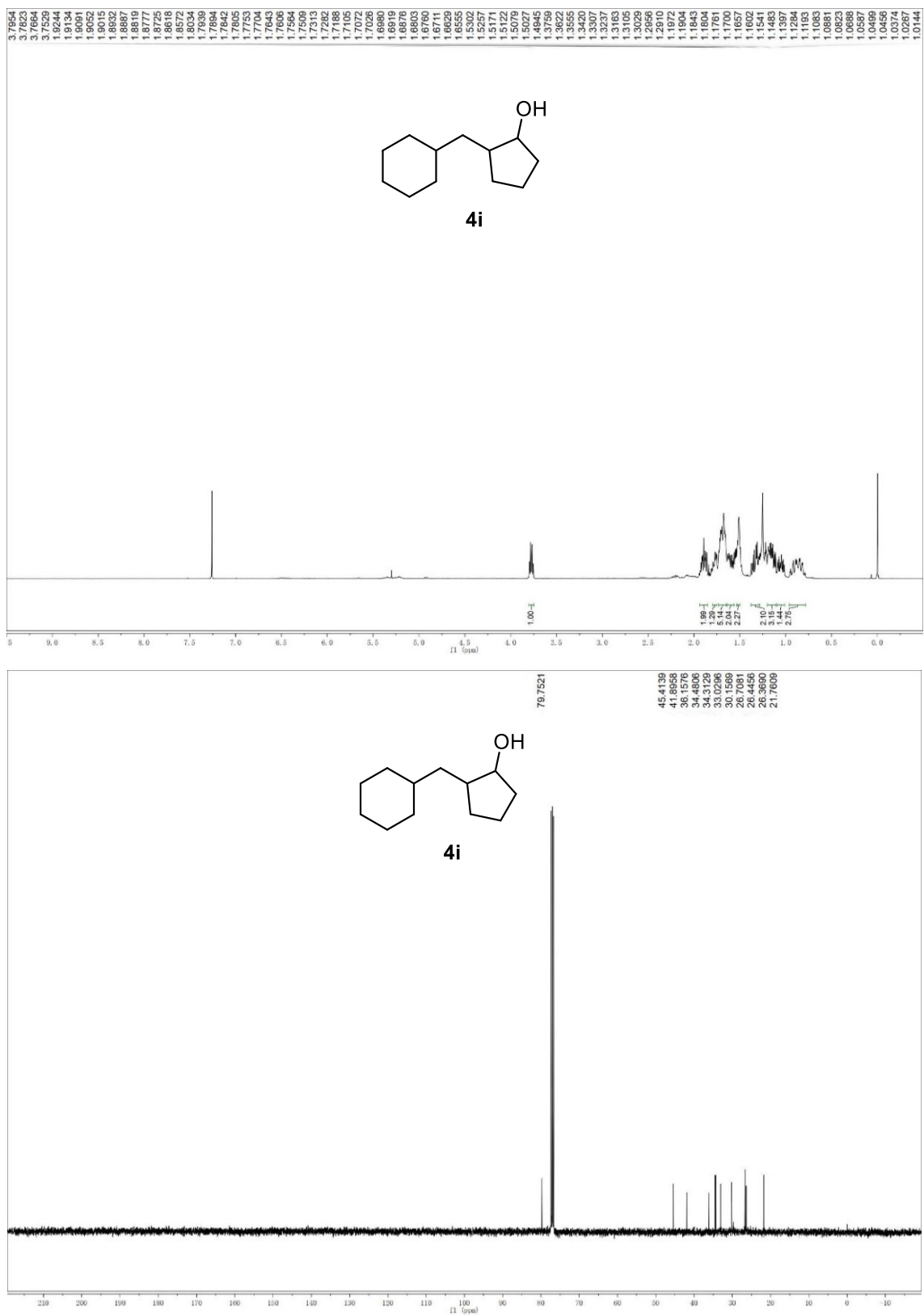


Figure S55.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  (100 MHz,  $\text{CDCl}_3$ ) NMR spectra for compound **4i**

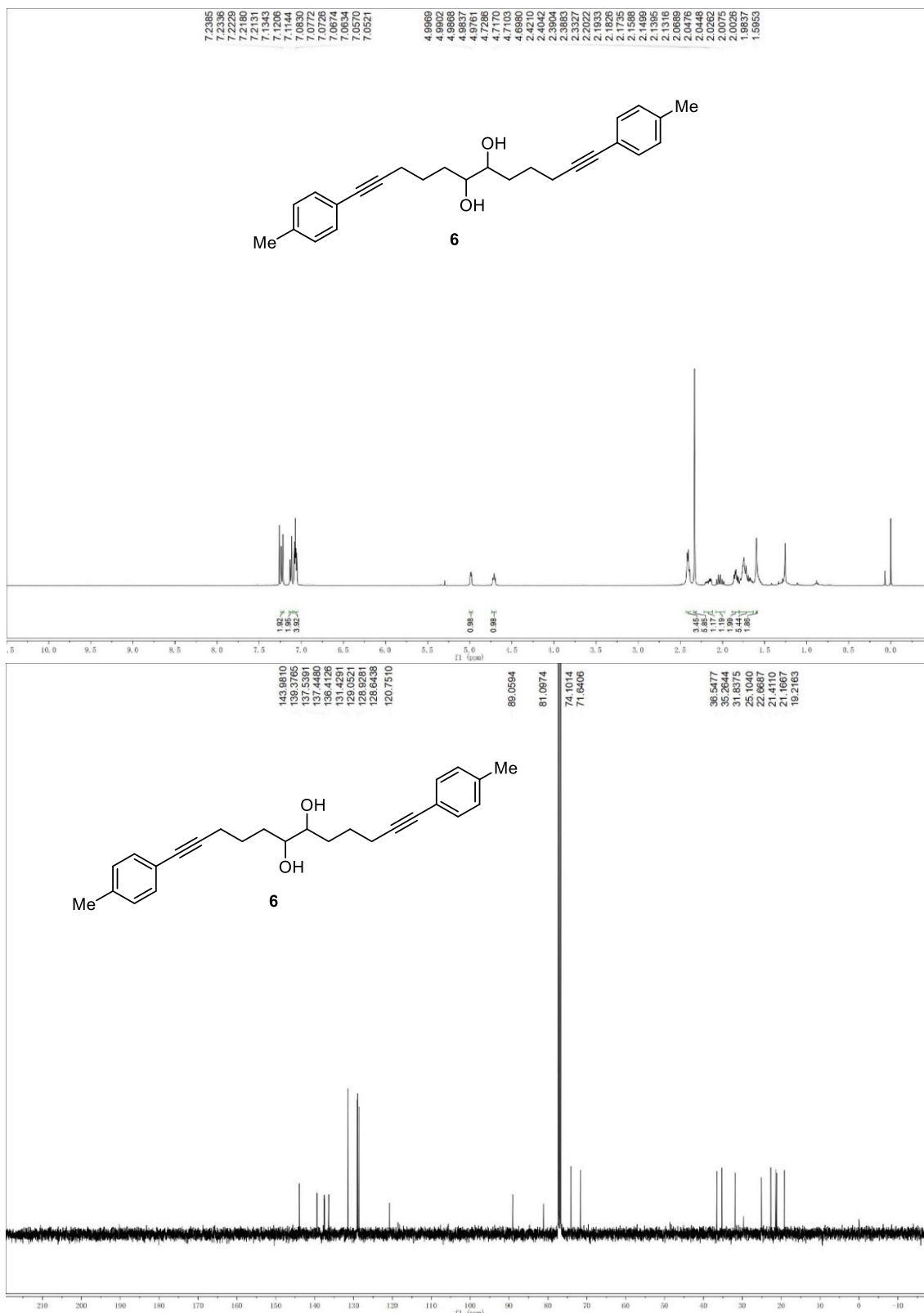


Figure S56. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **6**



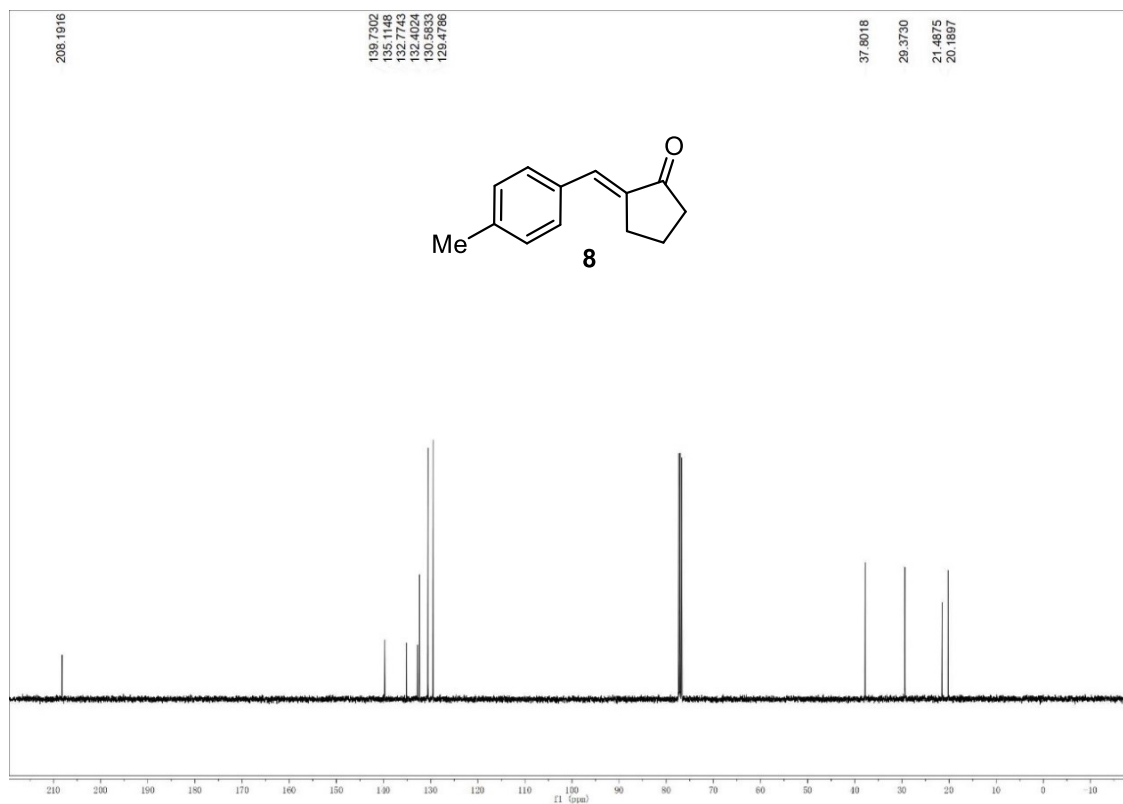
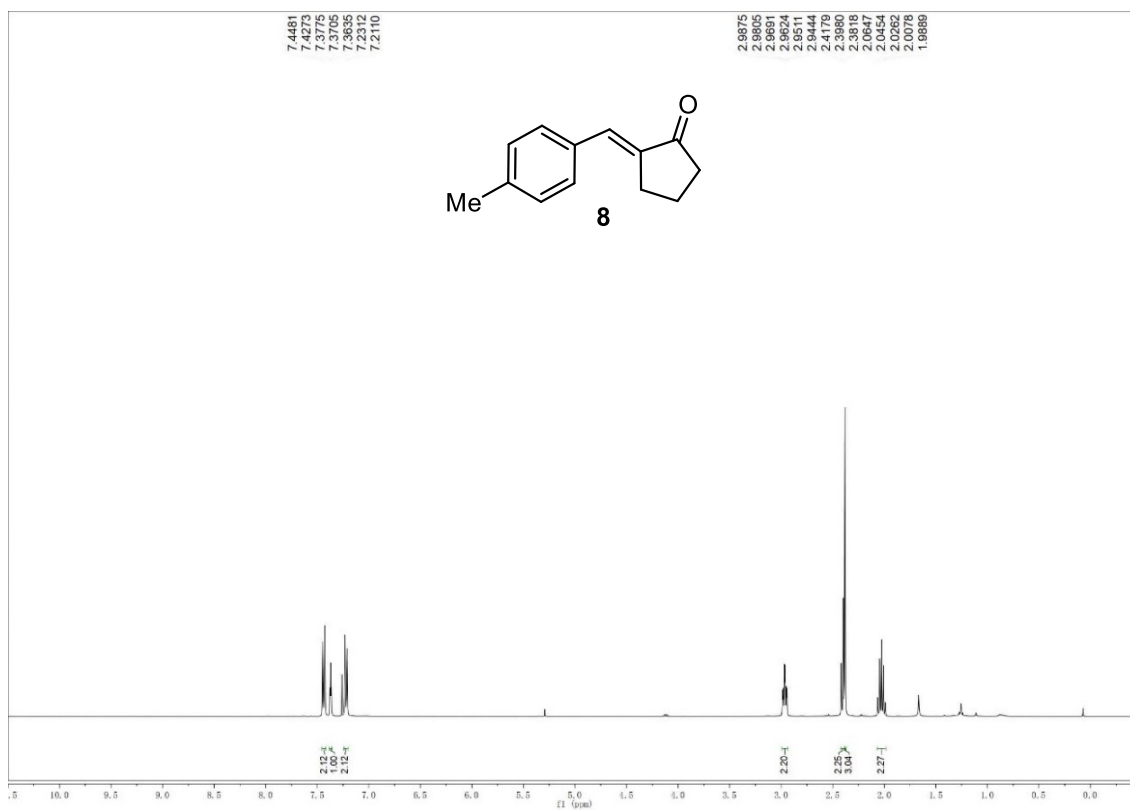


Figure S57. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **8**

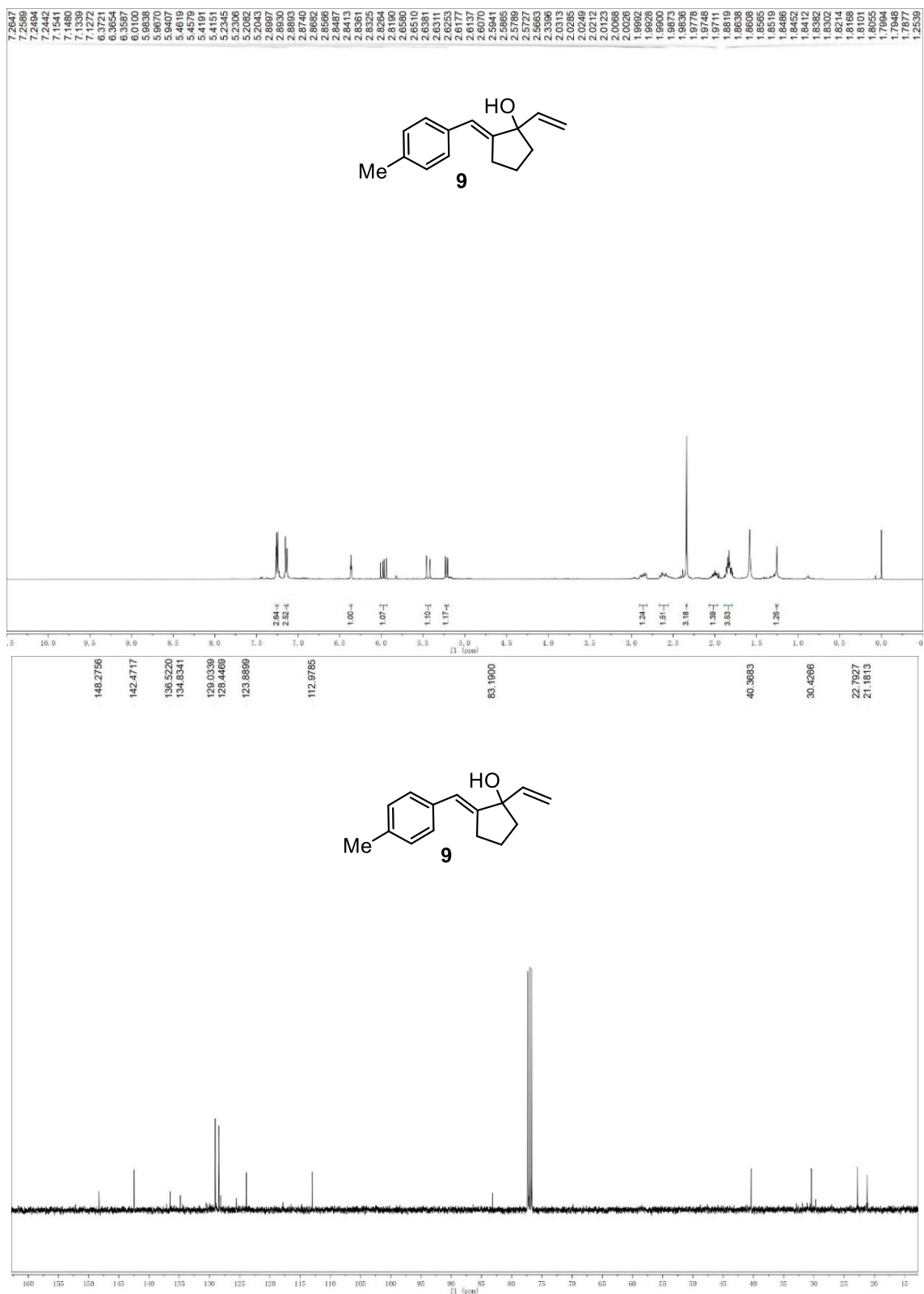


Figure S58. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **9**

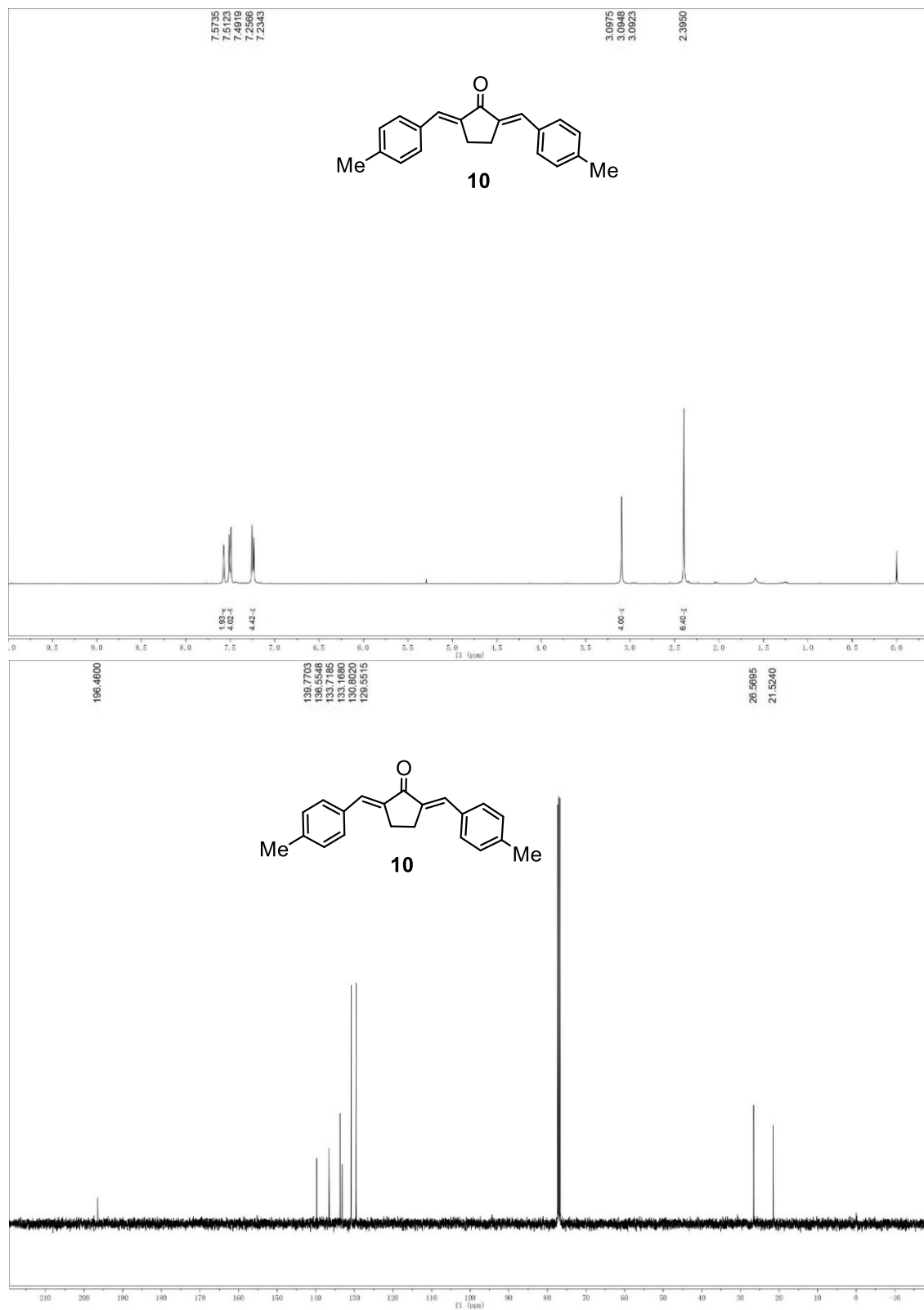


Figure S59. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **10**



Figure S60. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **11**

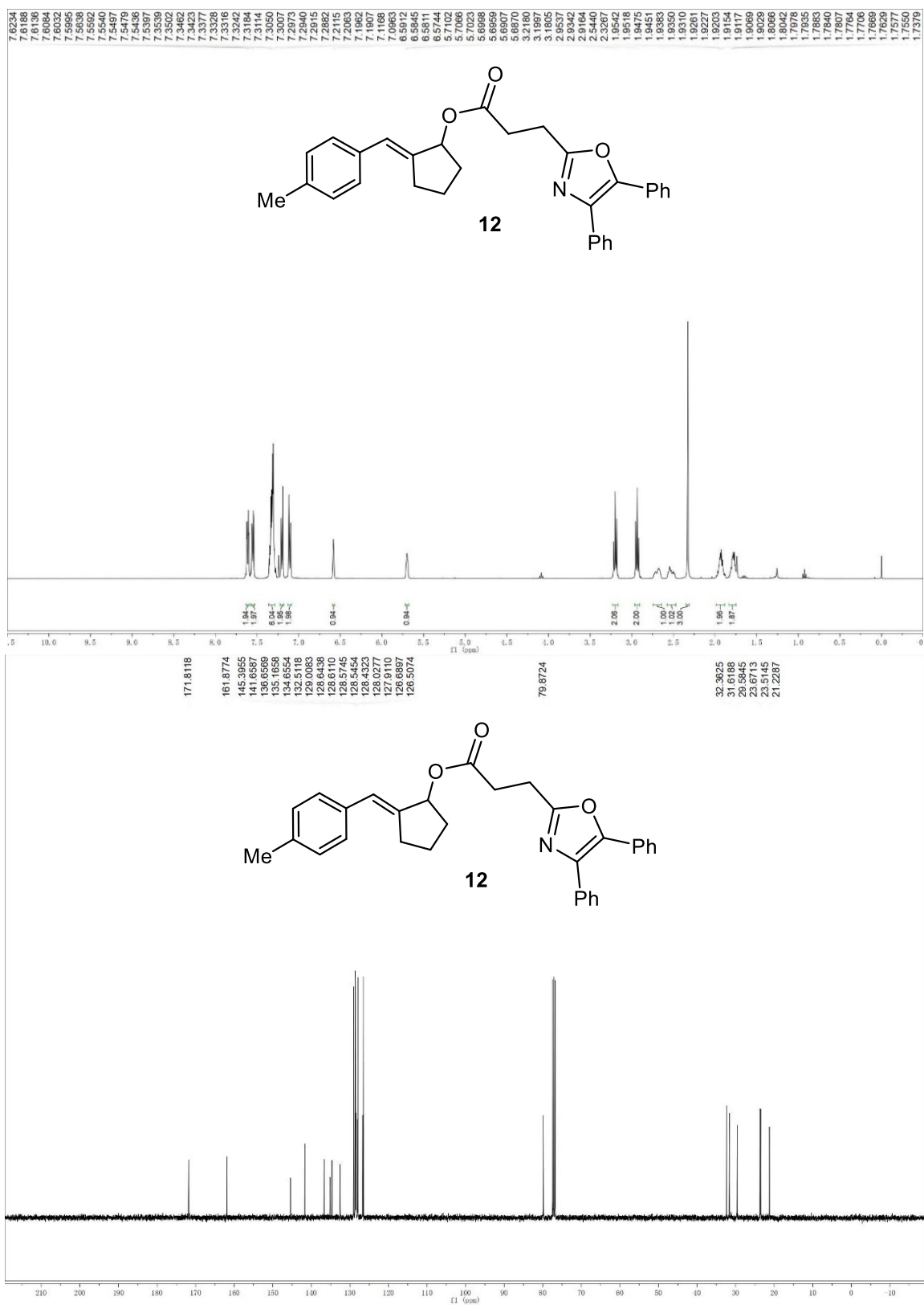


Figure S61. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **12**

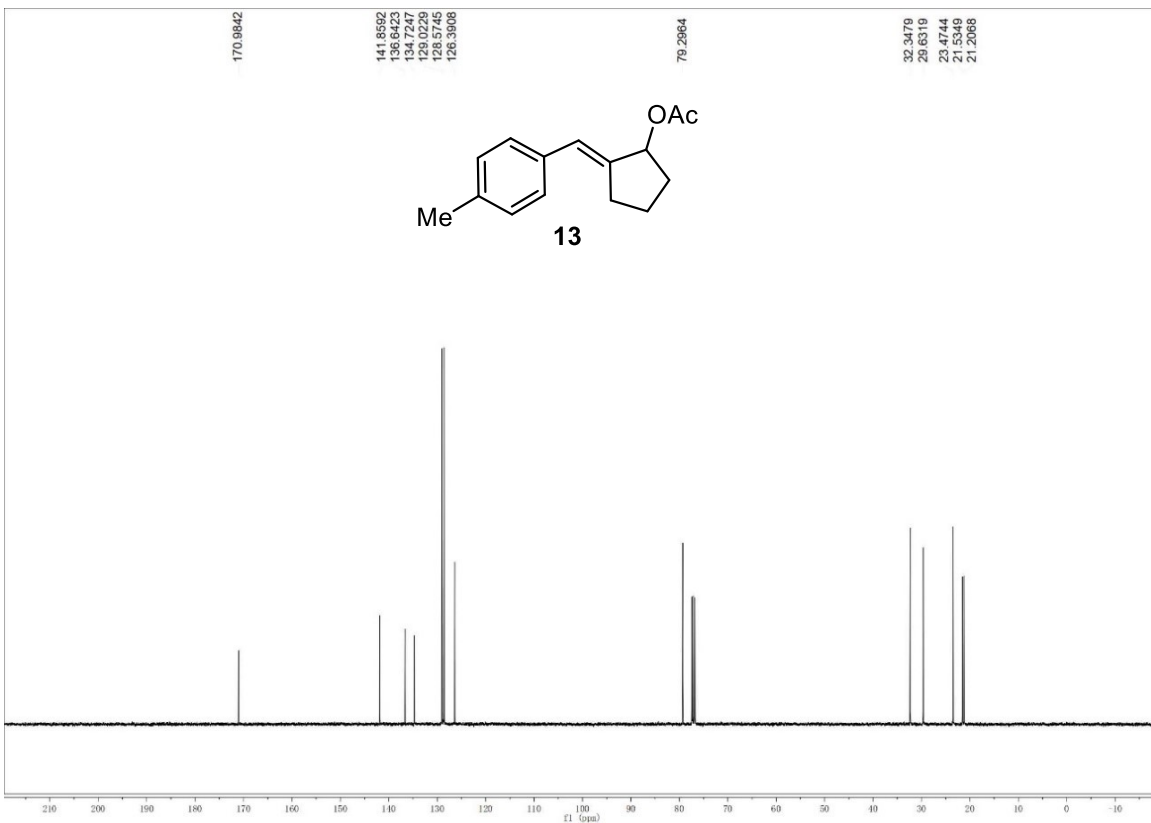
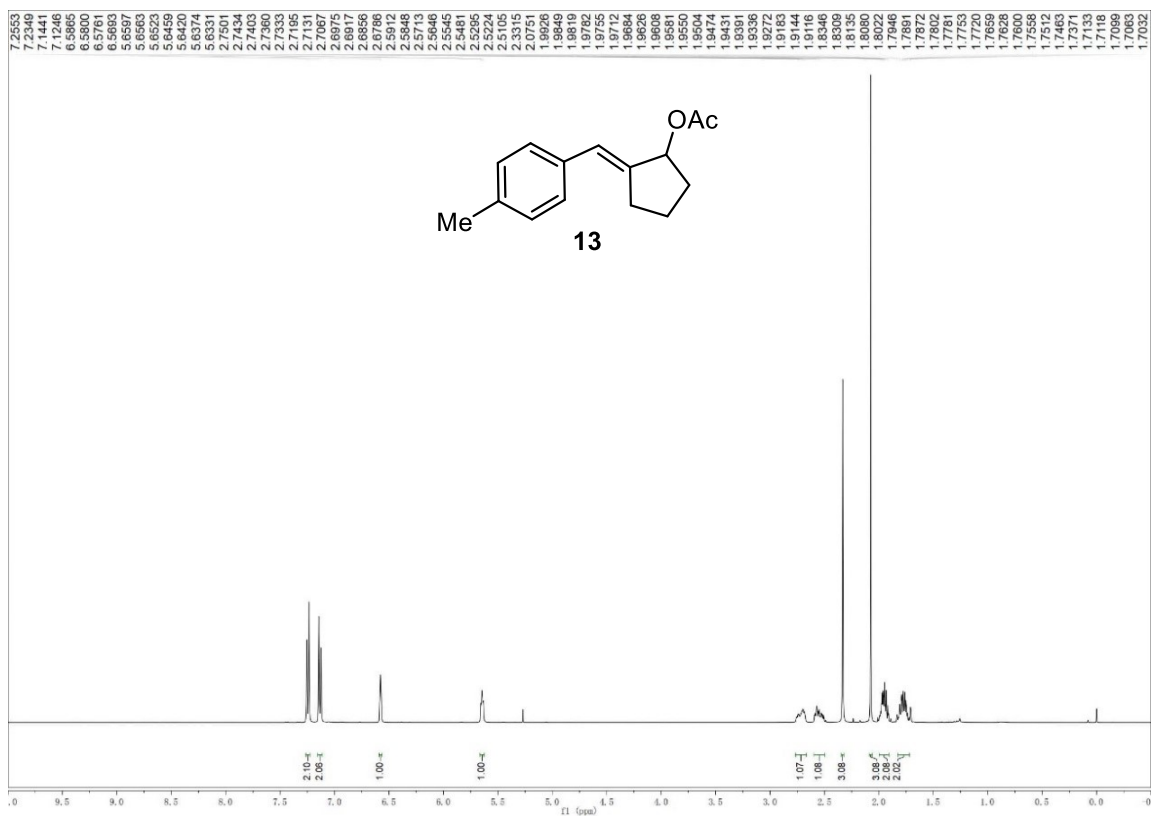


Figure S62.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  (100 MHz,  $\text{CDCl}_3$ ) NMR spectra for compound **13**

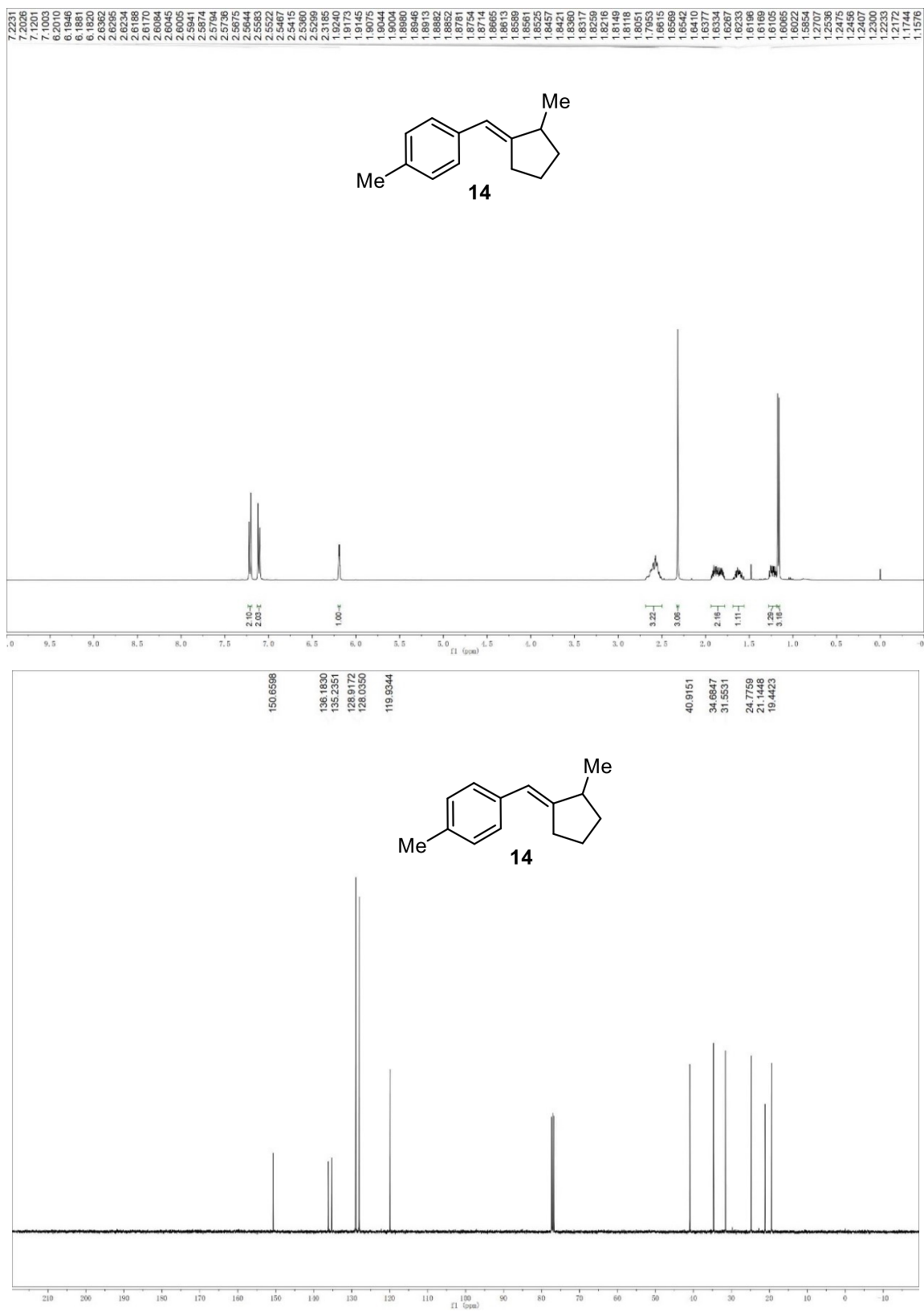


Figure S63. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>) NMR spectra for compound **14**