

# Supporting Information

## Aromatization-driven cascade [1,5]-hydride transfer/cyclization for synthesis of spirochromanes

Lianyi Cao,<sup>a,c</sup> Fangzhi Hu,<sup>a,b</sup> Jiacheng Dong,<sup>b</sup> Xiao-Mei Zhang,<sup>\*,a</sup> Shuai-Shuai Li<sup>\*,a,b</sup>

<sup>a</sup> Asymmetric Synthesis and Chiraltechnology Key Laboratory of Sichuan Province, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, China.

<sup>b</sup> College of Chemistry and Pharmaceutical Sciences, Qingdao Agricultural University, Changcheng Rd. #700, Qingdao 266109, P. R. China.

<sup>c</sup> University of Chinese Academy of Sciences, Beijing, China.

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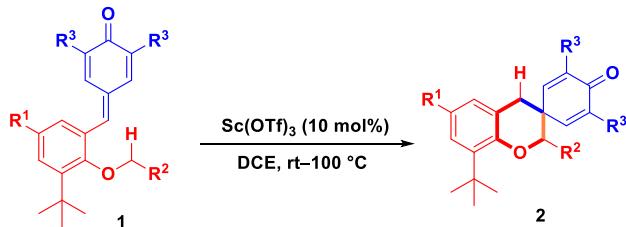
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## 1. General Information

Unless otherwise noted, all reagents and solvents were purchased from the commercial sources and used as received. Thin layer chromatography (TLC) was used to monitor the reaction on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. The products were purified by flash column chromatography (300-400 mesh silica gel/200-300 mesh basic alumina) eluted with the gradient of petroleum ether, ethyl acetate and dichloromethane. Proton nuclear magnetic resonance spectra (<sup>1</sup>H NMR) were recorded on a Bruker 300 MHz NMR spectrometer and a Bruker 400 MHz NMR spectrometer (CDCl<sub>3</sub> as solvent). The chemical shifts were reported in parts per million (ppm), downfield from SiMe<sub>4</sub> ( $\delta$  0.0) and relative to the signal of chloroform-*d* ( $\delta$  7.26, singlet). Multiplicities were afforded as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet) or m (multiplets). The number of protons for a given resonance is indicated by nH. Coupling constants were reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (<sup>13</sup>C NMR) was referenced to the appropriate residual solvent peak. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. *Para*-quinone methide derivatives were prepared according to literature.<sup>1</sup>

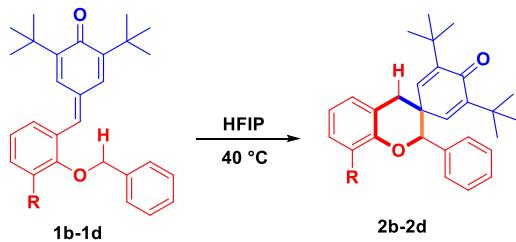
## 2. General Procedure

### 2.1 General Procedure for the Synthesis of products 2a, 2e-2zd



A reaction tube was charged with *p*-QMs **1** (0.1 mmol) and Sc(OTf)<sub>3</sub> (10 mol%) in 1.0 mL of DCE. The mixture was stirred at room temperature to 100 °C under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether, from 1:100 to 1:25) to give the desired product.

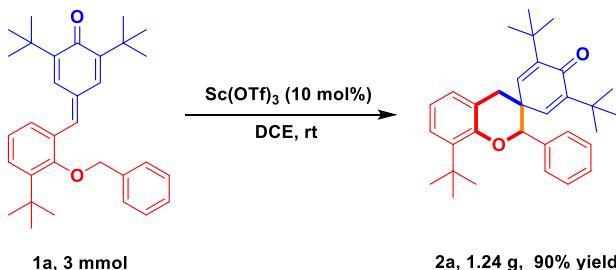
### 2.2 General Procedure for the Synthesis of products 2b-2d



A reaction tube was charged with *p*-QMs **1b-1d** (0.1 mmol) in 1.0 mL of HFIP. The mixture was stirred at 40 °C under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether, from 1:100) to give the desired products **2b-2d**.

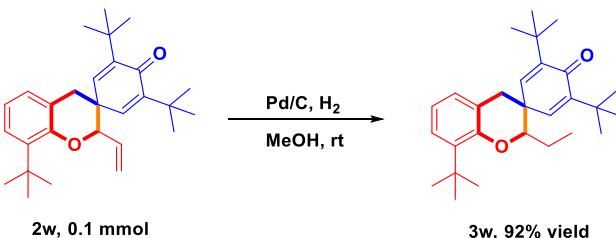
### 3. Large Scale Synthesis and Synthetic Transformations

#### 3.1 Large Scale Synthesis of **2a**



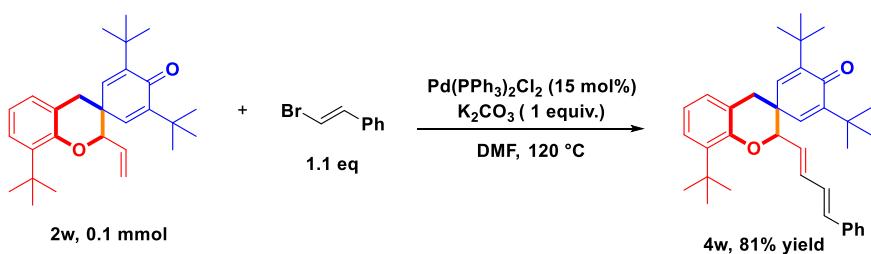
A round-bottom flask was charged with *p*-QM **1a** (3 mmol) and  $\text{Sc}(\text{OTf})_3$  (10 mol%) in 30.0 mL of DCE. The mixture was stirred at room temperature under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:100) to give the desired product **2a** in 90% yield.

#### 3.2 The Detailed Procedure for the Synthesis of **3w**



A reaction tube was charged with spirochromanes **2w** (0.1 mmol) and 5% by wt  $\text{Pd/C}$  (10 % by wt relative to **2w**) in 1.0 mL of MeOH. The tube was equipped with a magnetic stir bar, and the suspension was sealed with a septum under an atmosphere of  $\text{H}_2$  supplied via a balloon. Upon completion of the reaction as indicated by TLC analysis, the suspension was filtered through a pad of Celite. The filtrate was concentrated in vacuum. The residue was directly purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:100) to give the desired product **3w** in 92% yield.

#### 3.3 The Detailed Procedure for the Synthesis of **4w**

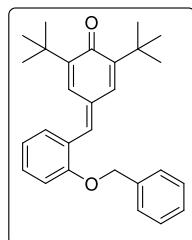


A sealed tube was charged with spirochromanes **2w** (0.1 mmol),  $\beta$ -bromostyrene (1.1 equiv.),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (15 mol%),  $\text{K}_2\text{CO}_3$  (1 equiv.), and DMF (1 mL). The mixture was stirred at 120 °C. Upon completion of the reaction as indicated by TLC analysis,  $\text{H}_2\text{O}$  (3 mL) was added dropwise to the system at 0 °C and the resulting solution was extracted with EtOAc (5 mL  $\times$  3). The combined organic extracts were dried with anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The

residue was directly purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:80) to afford the desired product **4w** in 81% yield.

#### 4. Characterization Data of Products

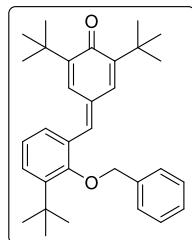
##### **4-(2-(benzyloxy)benzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1a')**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1a'** as a yellow solid (1.1 g, 55% yield), m.p.: 148.1–149.8 °C.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.42 (m, 9H), 7.10 – 6.98 (m, 3H), 5.17 (s, 2H), 1.35 (s, 9H), 1.31 (s, 9H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 186.8, 157.6, 149.0, 147.4, 139.0, 136.7, 135.4, 132.2, 131.7, 130.9, 128.8, 128.6, 128.2, 127.5, 125.5, 120.9, 112.5, 70.5, 35.5, 35.1, 29.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>33</sub>O<sub>2</sub><sup>+</sup> 401.2475; found: 401.2484.

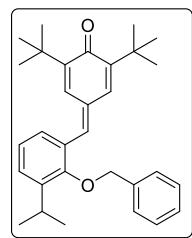
##### **4-(2-(benzyloxy)-3-(tert-butyl)benzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1a)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1a** as a light yellow solid (2.65 g, 58% yield), m.p.: 108.5–110.5 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 2.2 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.40 – 7.32 (m, 5H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.20 – 7.09 (m, 1H), 6.92 (d, *J* = 2.3 Hz, 1H), 4.90 (s, 2H), 1.47 (s, 9H), 1.31 (s, 9H), 1.29 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 186.8, 158.2, 149.2, 147.8, 143.7, 140.0, 137.4, 135.1, 131.7, 130.6, 130.0, 128.6, 128.6, 128.1, 127.6, 123.7, 76.7, 35.6, 35.4, 35.1, 31.0, 29.7, 29.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>41</sub>O<sub>2</sub><sup>+</sup> 457.3101; found: 457.3145.

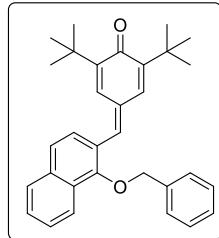
##### **4-(2-(benzyloxy)-3-isopropylbenzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1c)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1c** as a yellow solid (487 mg, 22% yield), m.p.: 108.1–108.6 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 2.1 Hz, 1H), 7.41 – 7.29 (m, 7H), 7.29 – 7.24 (m, 1H), 7.24 – 7.17 (m, 1H), 6.96 (d, *J* = 2.3 Hz, 1H), 4.83 (s, 2H), 3.43 (hept, *J* = 6.7 Hz, 1H), 1.34 (s, 9H), 1.30 (s, 9H), 1.27 (s, 3H), 1.25 (s, 3H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 186.8, 155.8, 149.2, 147.8, 142.9, 139.4, 137.1, 135.2, 132.1, 129.8, 129.6, 128.7, 128.5, 128.2, 124.6, 77.2, 35.6, 35.1, 29.7, 26.8, 23.8. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>38</sub>O<sub>2</sub><sup>+</sup> 443.2945; found: 443.2954.

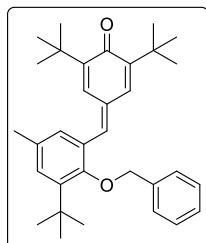
**4-((1-(benzyloxy)naphthalen-2-yl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1d)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1d** as a orange-yellow solid (924 mg, 41% yield), m.p.: 124.6–125.3 °C.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 7.3 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.60 – 7.48 (m, 4H), 7.44 (d, *J* = 7.4 Hz, 3H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.35 – 7.29 (m, 1H), 7.00 (s, 1H), 5.07 (s, 2H), 1.36 (s, 9H), 1.30 (s, 9H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 186.5, 155.1, 149.2, 147.7, 138.9, 136.9, 135.4, 135.3, 132.0, 128.7, 128.7, 128.6, 128.5, 128.2, 128.2, 127.6, 126.8, 125.6, 124.3, 122.9, 77.8, 35.6, 35.2, 29.7. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>34</sub>O<sub>2</sub><sup>+</sup> 451.2632; found: 451.2635.

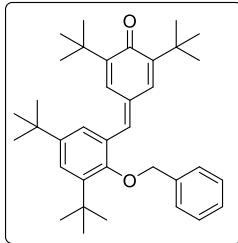
**4-(2-(benzyloxy)-3-(tert-butyl)-5-methylbenzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1e)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1e** as a yellow solid (1.11 g, 47% yield), m.p.: 149.3–150.1 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 2.1 Hz, 1H), 7.46 – 7.31 (m, 5H), 7.29 – 7.19 (m, 2H), 7.11 (s, 1H), 6.93 (d, *J* = 2.2 Hz, 1H), 4.87 (s, 2H), 2.38 (s, 3H), 1.47 (s, 9H), 1.33 (s, 9H), 1.30 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 186.7, 156.0, 149.0, 147.8, 143.3, 140.1, 137.5, 135.0, 132.8, 131.7, 130.9, 129.7, 129.4, 128.8, 128.6, 128.0, 127.6, 76.8, 35.5, 35.3, 35.1, 31.0, 29.7, 21.3. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>43</sub>O<sub>2</sub><sup>+</sup> 471.3258; found: 471.3267.

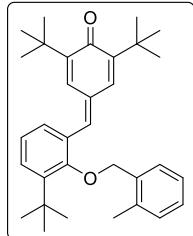
**4-(2-(benzyloxy)-3,5-di-tert-butylbenzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1f)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1f** as a yellow solid (1.15 g, 45% yield), m.p.: 168.4–169.5 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 2.1 Hz, 1H), 7.47 (d, *J* = 2.3 Hz, 1H), 7.45 – 7.33 (m, 5H), 7.33 – 7.29 (m, 2H), 6.94 (d, *J* = 2.2 Hz, 1H), 4.91 (s, 2H), 1.49 (s, 9H), 1.37 (s, 9H), 1.34 (s, 9H), 1.33 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 186.8, 156.1, 149.2, 147.8, 145.9, 142.7, 140.9, 137.7, 135.2, 131.4, 129.2, 128.7, 128.6, 128.0, 127.8, 127.5, 125.9, 76.8, 35.6, 35.1, 34.8, 31.7, 31.1, 29.8, 29.7. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>36</sub>H<sub>49</sub>O<sub>2</sub><sup>+</sup> 513.3727; found: 513.3734.

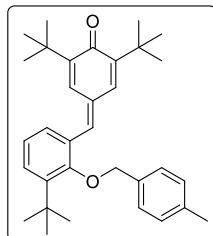
#### 2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((2-methylbenzyl)oxy)benzylidene)cyclohexa-2,5-dien-1-one (**1g**)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1g** as a yellow solid (1.11 g, 47% yield), m.p.: 115.4–116.8 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.59 – 7.49 (m, 2H), 7.44 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.31 – 7.22 (m, 3H), 7.21 – 7.10 (m, 3H), 6.76 (d, *J* = 2.1 Hz, 1H), 4.93 (s, 2H), 2.21 (s, 3H), 1.46 (s, 9H), 1.31 (s, 9H), 1.28 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 186.7, 158.9, 149.2, 147.6, 143.6, 140.3, 135.9, 135.3, 135.1, 131.5, 130.6, 130.3, 130.0, 128.5, 128.3, 127.8, 127.6, 126.1, 123.6, 75.2, 35.6, 35.3, 35.1, 30.9, 29.7, 29.6, 19.2. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>43</sub>O<sub>2</sub><sup>+</sup> 471.3258; found: 471.3256.

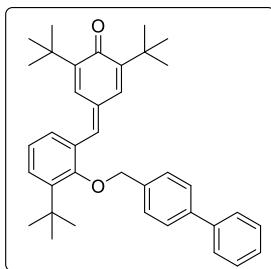
#### 2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((4-methylbenzyl)oxy)benzylidene)cyclohexa-2,5-dien-1-one (**1i**)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1i** as a yellow solid (1.06 g, 45% yield), m.p.: 121.3–121.8 °C.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.49 (s, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.24 (m, 4H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.14 (t, *J* = 7.9 Hz, 1H), 6.94 (s, 1H), 4.86 (s, 2H), 2.37 (s, 3H), 1.47 (s, 9H), 1.33 (s, 9H), 1.29 (s, 9H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 186.8, 158.3, 149.1, 147.8, 143.7, 140.1, 137.9, 135.1, 134.4, 131.6, 130.6, 130.1, 129.3, 128.6, 127.7, 123.6, 76.7, 35.6, 35.4, 35.1, 31.0, 29.7, 29.7, 21.4. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>43</sub>O<sub>2</sub><sup>+</sup> 471.3258; found: 471.3266.

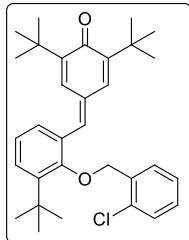
**4-(2-([1,1'-biphenyl]-4-ylmethoxy)-3-(tert-butyl)benzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1j)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1j** as a light yellow solid (1.23 g, 46% yield), m.p.: 179.6–180.8 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.1 Hz, 4H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.50 – 7.43 (m, 5H), 7.41 – 7.34 (m, 1H), 7.30 (d, *J* = 5.7 Hz, 2H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 2.1 Hz, 1H), 4.96 (s, 2H), 1.51 (s, 9H), 1.33 (s, 9H), 1.31 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 186.8, 158.1, 149.2, 148.0, 143.8, 141.1, 140.9, 139.8, 136.4, 135.0, 131.8, 130.6, 130.0, 129.0, 128.7, 128.6, 128.1, 127.5, 127.4, 127.3, 123.7, 76.4, 35.6, 35.4, 35.1, 31.0, 29.7. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>38</sub>H<sub>45</sub>O<sub>2</sub><sup>+</sup> 533.3414; found: 533.3427.

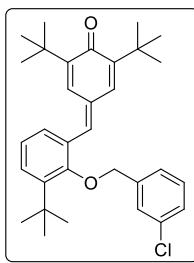
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((2-chlorobenzyl)oxy)benzylidene)cyclohexa-2,5-dien-1-one (1k)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1k** as a yellow solid (1.05 g, 43% yield), m.p.: 123.5–124.8 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.44 (td, *J* = 3.6, 1.8 Hz, 2H), 7.37 – 7.23 (m, 4H), 7.20 – 7.11 (m, 2H), 6.77 (d, *J* = 2.5 Hz, 1H), 5.01 (s, 2H), 1.47 (s, 9H), 1.30 (s, 9H), 1.27 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 186.8, 158.2, 149.2, 147.7, 143.7, 139.4, 135.6, 134.9, 132.1, 132.1, 130.5, 130.1, 129.4, 129.0, 128.8, 128.5, 128.5, 127.0, 123.8, 73.9, 35.5, 35.4, 35.0, 31.0, 29.7, 29.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>40</sub>ClO<sub>2</sub><sup>+</sup> 491.2711; found: 491.2717.

**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((3-chlorobenzyl)oxy)benzylidene)cyclohexa-2,5-dien-1-one (1l)**

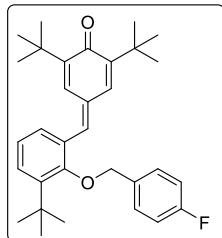


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1l** as a yellow solid (1.03 g, 42% yield), m.p.: 116.5–117.5 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.48 – 7.41 (m, 2H), 7.38 (s, 1H), 7.33 – 7.29 (m, 2H), 7.28 – 7.24 (m, 2H), 7.21 (s, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 2.5 Hz, 1H), 4.86 (s, 2H), 1.46 (s, 9H),

1.31 (s, 9H), 1.29 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*)  $\delta$  186.7, 157.9, 149.4, 148.1, 143.7, 139.4, 134.8, 132.0, 130.6, 130.0, 129.9, 128.9, 128.4, 128.2, 127.6, 125.6, 123.9, 75.8, 35.6, 35.4, 35.1, 31.0, 29.7, 29.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>40</sub>ClO<sub>2</sub><sup>+</sup> 491.2711; found: 491.2717.

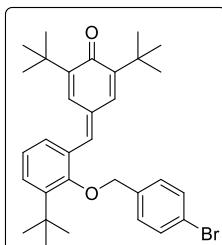
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((4-fluorobenzyl)oxy)benzylidene)cyclohexa-2,5-dien-1-one (1m)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1m** as a yellow solid (1.04 g, 44% yield), m.p.: 141.3–142.1 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*)  $\delta$  7.47 (d, *J* = 2.2 Hz, 1H), 7.44 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.30 – 7.25 (m, 1H), 7.23 (s, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.10 – 7.01 (m, 2H), 6.93 (d, *J* = 2.3 Hz, 1H), 4.86 (s, 2H), 1.47 (s, 9H), 1.33 (s, 9H), 1.29 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*)  $\delta$  186.7, 162.6 (d, *J* = 246.4 Hz), 157.9, 149.3, 148.0, 143.7, 139.7, 134.8, 133.2 (d, *J* = 3.4 Hz), 131.8, 130.5, 130.0, 129.4 (d, *J* = 8.0 Hz), 128.7, 128.6, 123.8, 115.5 (d, *J* = 21.4 Hz), 76.0, 35.6, 35.4, 35.1, 31.0, 29.7. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>40</sub>FO<sub>2</sub><sup>+</sup> 475.3007; found: 475.3027.

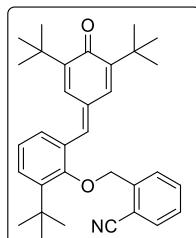
**4-(2-((4-bromobenzyl)oxy)-3-(tert-butyl)benzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1n)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1n** as a yellow solid (1.09 g, 41% yield), m.p.: 135.7–136.8 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*)  $\delta$  7.50 (d, *J* = 2.0 Hz, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.31 – 7.22 (m, 3H), 7.20 (s, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 2.2 Hz, 1H), 4.84 (s, 2H), 1.45 (s, 9H), 1.32 (s, 9H), 1.29 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*)  $\delta$  186.7, 157.8, 149.3, 148.1, 143.7, 139.5, 136.4, 134.8, 131.9, 131.7, 130.6, 129.9, 129.1, 128.7, 128.5, 123.9, 122.0, 75.8, 35.6, 35.4, 35.1, 31.0, 29.7. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>40</sub>BrO<sub>2</sub><sup>+</sup> 535.2206; found: 535.2211.

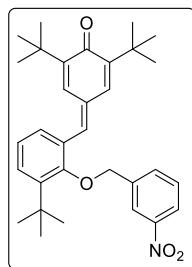
**2-((2-(tert-butyl)-6-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenoxy)methyl)benzonitrile (1o)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:50) afforded the product **1o** as a light yellow solid (674 mg, 28% yield), m.p.: 131.5–132.8 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 2H), 7.47 – 7.34 (m, 3H), 7.25 (d, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 2.2 Hz, 1H), 5.09 (s, 2H), 1.45 (s, 9H), 1.27 (s, 18H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 186.7, 157.4, 149.2, 147.8, 143.6, 141.2, 139.0, 134.8, 133.0, 132.9, 132.3, 130.4, 129.9, 128.6, 128.4, 128.4, 124.2, 117.2, 110.7, 74.1, 35.5, 35.4, 35.1, 31.0, 29.6, 29.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>40</sub>NO<sub>2</sub><sup>+</sup> 482.3054; found: 482.3056.

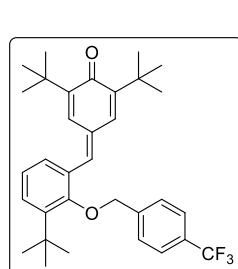
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((3-nitrobenzyl)oxy)benzylidene)cyclohexa-2,5-dien-1-one (1p)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:50) afforded the product **1p** as a orange solid (902 mg, 36% yield), m.p.: 185.1–186.7 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 8.29 (s, 1H), 8.23 – 8.15 (m, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.45 (dt, *J* = 4.7, 1.9 Hz, 2H), 7.27 (d, *J* = 6.0 Hz, 1H), 7.23 – 7.14 (m, 2H), 6.89 (d, *J* = 2.2 Hz, 1H), 4.99 (s, 2H), 1.46 (s, 9H), 1.29 (s, 9H), 1.28 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 186.7, 157.4, 149.5, 148.3, 143.7, 139.5, 138.9, 134.5, 133.2, 132.2, 130.7, 129.9, 129.6, 128.8, 128.3, 124.2, 123.0, 122.2, 75.1, 35.6, 35.4, 35.1, 31.0, 29.7, 29.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>40</sub>NO<sub>4</sub><sup>+</sup> 502.2952; found: 502.2954.

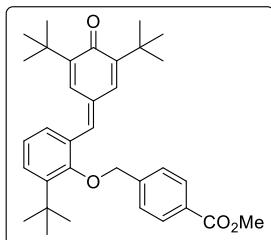
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((4-(trifluoromethyl)benzyl)oxy)benzylidene)cyclohexa-2,5-dien-1-one (1q)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:80) afforded the product **1q** as a yellow solid (603 mg, 23% yield), m.p.: 148.8–150.5 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.48 – 7.41 (m, 2H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.22 – 7.13 (m, 2H), 6.86 (d, *J* = 2.1 Hz, 1H), 4.96 (s, 2H), 1.45 (s, 9H), 1.29 (s, 9H), 1.28 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 186.7, 157.7, 149.4, 148.1, 143.7, 141.4, 139.2, 134.7, 132.0, 130.6, 129.9, 128.7, 128.4, 128.0 (q, *J* = 298.3 Hz), 127.3, 125.6 (q, *J* = 3.8 Hz), 124.0, 75.6, 35.6, 35.4, 35.1, 30.9, 29.7, 29.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>40</sub>F<sub>3</sub>O<sub>2</sub><sup>+</sup> 525.2975; found: 525.2985.

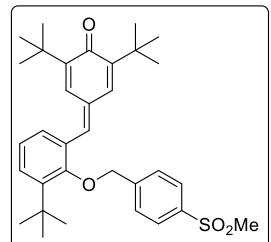
**methyl 4-((2-(tert-butyl)-6-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene) methyl) phenoxy) methyl) benzoate (1r)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:50) afforded the product **1r** as a yellow solid (746 mg, 29% yield), m.p.: 126.2–127.1 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.49 – 7.40 (m, 4H), 7.30 – 7.23 (m, 1H), 7.17 (dd, *J* = 14.7, 6.9 Hz, 2H), 6.85 (d, *J* = 2.2 Hz, 1H), 4.96 (s, 2H), 3.93 (s, 3H), 1.45 (s, 9H), 1.29 (s, 18H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 186.7, 166.9, 157.9, 149.3, 148.0, 143.7, 142.6, 139.4, 134.8, 132.0, 130.6, 129.9, 128.7, 128.4, 127.0, 123.9, 76.0, 52.2, 35.6, 35.4, 35.1, 31.0, 29.7, 29.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>43</sub>O<sub>4</sub><sup>+</sup> 515.3156; found: 515.3160.

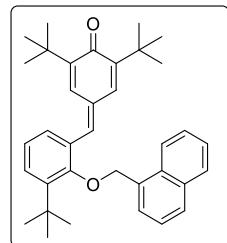
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((4-(methylsulfonyl)benzyl)oxy)benzylidene)cyclohexa-2,5-dien-1-one (1s)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:30) afforded the product **1s** as a light yellow solid (989 mg, 37% yield), m.p.: 192.9–193.7 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.38 (m, 2H), 7.30 – 7.23 (m, 1H), 7.22 – 7.12 (m, 2H), 6.89 (d, *J* = 2.2 Hz, 1H), 4.97 (s, 2H), 3.06 (s, 3H), 1.45 (s, 9H), 1.29 (s, 9H), 1.25 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 186.7, 157.2, 149.3, 148.2, 143.7, 143.6, 140.2, 138.8, 134.6, 132.2, 130.6, 129.7, 128.8, 128.5, 127.9, 127.7, 124.1, 75.2, 44.6, 35.5, 35.4, 35.1, 30.9, 29.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>43</sub>O<sub>4</sub>S<sup>+</sup> 535.2877; found: 535.2877.

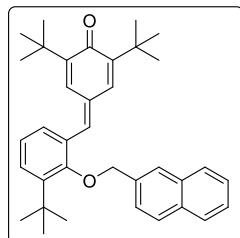
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-(naphthalen-1-ylmethoxy)benzylidene)cyclohexa-2,5-dien-1-one (1t)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1t** as a light yellow solid (1.22 g, 48% yield), m.p.: 142.2–143.1 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 8.02 – 7.93 (m, 1H), 7.93 – 7.86 (m, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.56 – 7.43 (m, 5H), 7.28 (t, *J* = 6.2 Hz, 1H), 7.19 (dd, *J* = 15.6, 7.8 Hz, 2H), 6.67 (d, *J* = 2.4 Hz, 1H), 5.41 (s, 2H), 1.50 (s, 9H), 1.33 (s, 9H), 1.23 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 186.7, 158.9, 149.2, 147.5, 143.7, 140.1, 135.0, 133.7, 133.4, 131.7, 130.9, 130.7, 130.3, 128.9, 128.7, 128.6, 128.4, 126.4, 126.0, 125.7, 125.4, 123.7, 123.5, 75.5, 35.6, 35.3, 35.0, 31.0, 29.7, 29.5. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>36</sub>H<sub>43</sub>O<sub>2</sub><sup>+</sup> 507.3258; found: 507.3264.

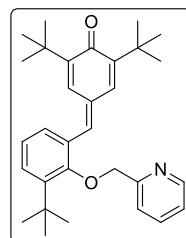
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-(naphthalen-2-ylmethoxy)benzylidene)cyclohexa-2,5-dien-1-one (1u)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1u** as a light yellow solid (1.29 g, 51% yield), m.p.: 119.6–121.3 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.92 – 7.79 (m, 4H), 7.57 – 7.43 (m, 5H), 7.31 (d, *J* = 6.9 Hz, 2H), 7.18 (t, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 2.2 Hz, 1H), 5.08 (s, 2H), 1.51 (s, 9H), 1.31 (s, 9H), 1.29 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 186.8, 158.3, 149.3, 147.9, 143.8, 140.0, 135.0, 134.9, 133.4, 133.2, 131.8, 130.6, 130.1, 128.7, 128.6, 128.4, 128.1, 127.9, 126.5, 126.3, 125.5, 123.7, 76.9, 35.6, 35.4, 35.1, 31.0, 29.7, 29.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>36</sub>H<sub>43</sub>O<sub>2</sub><sup>+</sup> 507.3258; found: 507.3256.

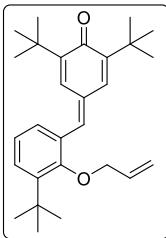
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-(pyridin-2-ylmethoxy)benzylidene)cyclohexa-2,5-dien-1-one (1v)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:30) afforded the product **1v** as a yellow solid (480 mg, 21% yield), m.p.: 116.3–117.5 °C.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 4.8 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 5.9 Hz, 2H), 7.25 (q, *J* = 5.9 Hz, 3H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.83 (s, 1H), 5.05 (s, 2H), 1.47 (s, 9H), 1.29 (s, 9H), 1.26 (s, 9H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 186.8, 157.7, 157.5, 149.2, 149.1, 147.6, 143.5, 139.3, 136.9, 134.9, 132.1, 130.7, 129.9, 128.6, 128.5, 123.9, 122.7, 121.1, 76.9, 35.5, 35.3, 35.0, 30.9, 29.6, 29.5. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>40</sub>NO<sub>2</sub><sup>+</sup> 458.3054; found: 458.3066.

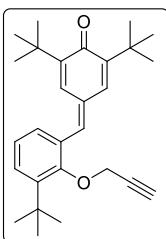
**4-(allyloxy)-3-(tert-butyl)benzylidene-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1w)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1w** as a light yellow solid (1.1 g, 54% yield), m.p.: 98.1-99.7 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 2.2 Hz, 1H), 7.44 – 7.36 (m, 1H), 7.25 (dd, *J* = 10.8, 2.2 Hz, 2H), 7.11 (t, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 2.3 Hz, 1H), 6.04 (ddt, *J* = 16.9, 10.5, 5.0 Hz, 1H), 5.43 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.28 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.38 (d, *J* = 4.9 Hz, 2H), 1.43 (s, 9H), 1.34 (s, 9H), 1.30 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 186.8, 158.2, 149.2, 147.8, 143.6, 139.9, 135.1, 133.6, 131.6, 130.8, 129.9, 128.6, 128.4, 123.6, 117.1, 75.5, 35.6, 35.3, 35.1, 30.8, 29.7, 29.7. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>39</sub>O<sub>2</sub><sup>+</sup> 407.2945; found: 407.2928.

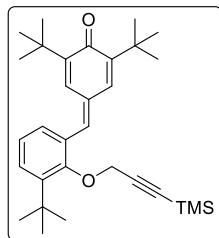
#### 2,6-di-tert-butyl-4-(3-(tert-butyl)-2-(prop-2-yn-1-yloxy)benzylidene)cyclohexa-2,5-dien-1-one (**1x**)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1x** as a reddish brown solid (728 mg, 36% yield), m.p.: 195.3-196.1 °C.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 7.7 Hz, 1H), 7.19 (s, 1H), 6.99 (d, *J* = 7.3 Hz, 1H), 6.91 (dd, *J* = 15.2, 7.5 Hz, 2H), 6.82 (s, 1H), 6.67 (s, 1H), 5.18 (s, 2H), 1.40 (s, 9H), 1.34 (s, 9H), 1.32 (s, 9H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 186.0, 152.2, 148.7, 147.9, 139.8, 137.9, 135.4, 133.3, 131.7, 131.2, 128.8, 127.1, 126.3, 123.6, 121.8, 66.8, 35.6, 35.2, 34.6, 29.8, 29.7, 29.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>37</sub>O<sub>2</sub><sup>+</sup> 405.2788; found: 405.2788.

#### 2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((3-(trimethylsilyl)prop-2-yn-1-yl)oxy)benzylidene)cyclohexa-2,5-dien-1-one (**1y**)

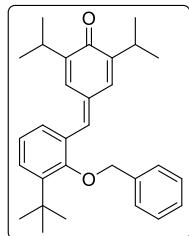


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1y** as a reddish brown solid (572 mg, 24% yield), m.p.: 123.2-124.9 °C.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.34 (s, 1H), 7.26 (s, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.0 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.11 (s, 1H), 4.61 (s, 2H), 1.40 (s, 9H), 1.34 (s, 9H), 1.25 (s, 9H), 0.41 (s, 9H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 186.5, 160.3, 151.6, 148.4, 148.0, 141.2, 137.8,

136.1, 131.7, 129.8, 126.7, 125.2, 123.6, 121.5, 121.4, 67.7, 35.6, 35.4, 34.6, 29.8, 29.6, 1.1. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>45</sub>O<sub>2</sub>Si<sup>+</sup> 477.3183; found: 477.3193.

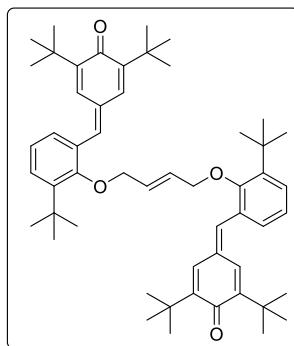
**4-(2-(benzyloxy)-3-(tert-butyl)benzylidene)-2,6-diisopropylcyclohexa-2,5-dien-1-one (1z)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1z** as a light yellow solid (622 mg, 29% yield), m.p.: 118.9–120.0 °C.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.46 – 7.39 (m, 2H), 7.35 (d, *J* = 3.9 Hz, 5H), 7.28 (s, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.84 (s, 1H), 4.87 (s, 2H), 3.15 (ddd, *J* = 10.7, 6.9, 3.5 Hz, 2H), 1.44 (s, 9H), 1.10 (t, *J* = 8.3 Hz, 12H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 185.5, 158.4, 147.3, 145.8, 143.7, 140.4, 137.3, 134.8, 131.7, 130.8, 129.9, 128.8, 128.6, 128.1, 128.1, 127.5, 123.7, 35.4, 30.9, 27.0, 26.6, 22.2. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>30</sub>H<sub>57</sub>O<sub>2</sub><sup>+</sup> 427.2788; found: 427.2799.

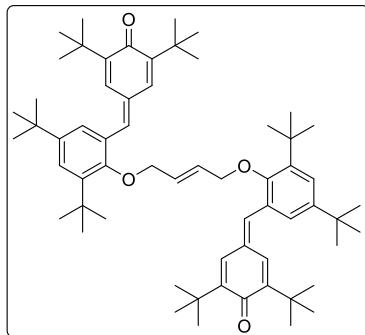
**(E)-4,4'-(((but-2-ene-1,4-diylbis(oxy))bis(3-(tert-butyl)-2,1-phenylene))bis(methaneylylidene))bis(2,6-di-tert-butylcyclohexa-2,5-dien-1-one) (1za)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1za** as a yellow solid (1.1 g, 28% yield), m.p.: 199.7–200.9 °C.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (s, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.29 (s, 2H), 7.25 (d, *J* = 6.5 Hz, 2H), 7.13 (t, *J* = 7.7 Hz, 2H), 7.03 (s, 2H), 6.10 (s, 2H), 4.45 (s, 4H), 1.44 (s, 18H), 1.31 (s, 18H), 1.30 (s, 18H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 186.7, 158.1, 149.3, 147.9, 143.6, 139.9, 135.0, 131.6, 130.9, 129.9, 128.7, 128.4, 128.2, 123.7, 74.5, 35.6, 35.3, 35.1, 30.9, 29.7, 29.7. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>54</sub>H<sub>73</sub>O<sub>4</sub><sup>+</sup> 785.5503; found: 785.5516.

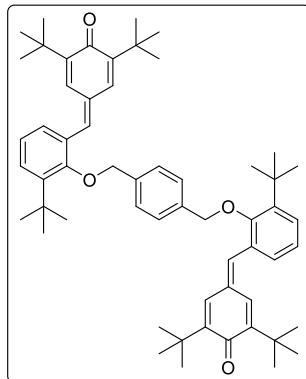
**(E)-4,4'-(((but-2-ene-1,4-diylbis(oxy))bis(3,5-di-tert-butyl-2,1-phenylene))bis(methaneylylidene))bis(2,6-di-tert-butylcyclohexa-2,5-dien-1-one) (1zb)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1zb** as a light yellow solid (1.66 g, 37% yield), m.p.: 216.6-217.8 °C.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.55 (s, 2H), 7.44 (d, *J* = 1.9 Hz, 2H), 7.34 (s, 2H), 7.26 (s, 2H), 7.05 (s, 2H), 6.11 (s, 2H), 4.44 (s, 4H), 1.45 (s, 18H), 1.35 (s, 18H), 1.32 (s, 36H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 186.8, 155.9, 149.2, 147.8, 145.9, 142.5, 140.8, 135.1, 131.4, 129.1, 128.6, 128.2, 128.1, 125.9, 74.6, 35.6, 35.5, 35.1, 34.8, 31.7, 30.9, 29.8, 29.7. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>62</sub>H<sub>89</sub>O<sub>4</sub><sup>+</sup> 897.6755; found: 897.6764.

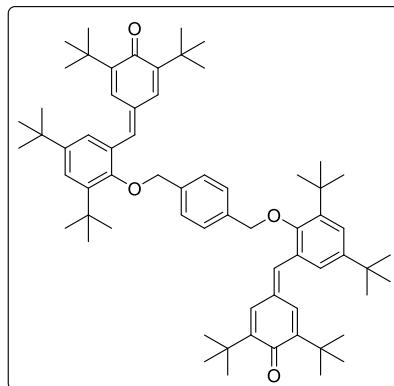
**4,4'-((((1,4-phenylenebis(methylene))bis(oxy))bis(3-(tert-butyl)-2,1-phenylene))bis(methaneylylidene))bis(2,6-di-tert-butylcyclohexa-2,5-dien-1-one) (1zc)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1zc** as a light yellow solid (1.42 g, 34% yield), m.p.: 225.4-226.8 °C.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (s, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.40 (s, 4H), 7.28 (s, 4H), 7.16 (t, *J* = 7.8 Hz, 2H), 6.94 (s, 2H), 4.92 (s, 4H), 1.47 (s, 18H), 1.31 (s, 18H), 1.28 (s, 18H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 186.7, 158.0, 149.2, 147.9, 143.7, 139.8, 137.1, 135.0, 131.8, 130.7, 130.0, 128.7, 128.6, 127.6, 123.8, 76.3, 35.6, 35.4, 35.1, 31.0, 29.7, 29.7. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>58</sub>H<sub>75</sub>O<sub>4</sub><sup>+</sup> 835.5660; found: 835.5666.

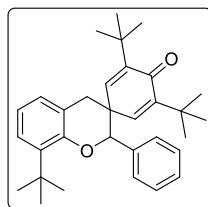
**4,4'-((((1,4-phenylenebis(methylene))bis(oxy))bis(3,5-di-tert-butyl-2,1-phenylene))bis(methaneylylidene))bis(2,6-di-tert-butylcyclohexa-2,5-dien-1-one) (1zd)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1zd** as a light yellow solid (1.99 g, 42% yield), m.p.: 234.2–235.4 °C.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.57 (s, 2H), 7.47 (d, *J* = 1.8 Hz, 2H), 7.44 (s, 4H), 7.31 (d, *J* = 13.1 Hz, 4H), 6.96 (s, 2H), 4.92 (s, 4H), 1.48 (s, 18H), 1.36 (s, 18H), 1.32 (s, 36H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 186.8, 155.9, 149.2, 147.7, 146.0, 142.7, 140.8, 137.2, 135.2, 131.5, 129.2, 128.7, 127.9, 127.6, 125.9, 76.4, 35.61, 35.57, 35.1, 34.9, 31.7, 31.0, 29.8, 29.7. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>66</sub>H<sub>91</sub>O<sub>4</sub><sup>+</sup> 947.6912; found: 947.6912.

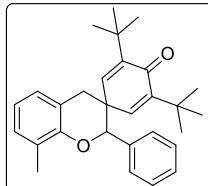
#### 3',5',8-tri-tert-butyl-2-phenylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2a** as a white solid (42.9 mg, 94% yield), m.p.: 194.5–195.7 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.23 (m, 6H), 7.02 (d, *J* = 6.9 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 2.6 Hz, 1H), 6.42 (d, *J* = 2.9 Hz, 1H), 5.10 (s, 1H), 3.40 (d, *J* = 16.2 Hz, 1H), 2.77 (d, *J* = 16.4 Hz, 1H), 1.40 (s, 9H), 1.13 (s, 9H), 1.07 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 185.8, 152.9, 149.1, 148.3, 142.0, 138.3, 137.9, 136.7, 128.4, 127.9, 127.5, 127.2, 125.1, 121.0, 119.6, 84.2, 41.5, 37.8, 35.1, 35.0, 34.8, 29.9, 29.3, 29.1. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>41</sub>O<sub>2</sub><sup>+</sup> 457.3101; found: 457.3113.

#### 3',5'-di-tert-butyl-8-methyl-2-phenylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2b)

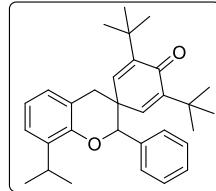


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2b** as a white solid (36.5 mg, 88% yield), m.p.: 172.7–173.3 °C.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.31 – 7.14 (m, 5H), 7.10 (d, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.70 (s, 1H), 6.45 (s, 1H), 5.11 (s, 1H), 3.36 (d, *J* = 16.4 Hz, 1H), 2.73 (d,

*J* = 16.4 Hz, 1H), 2.28 (s, 3H), 1.10 (s, 18H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  185.9, 152.1, 149.0, 148.3, 142.1, 137.7, 136.8, 129.2, 128.4, 127.4, 127.2, 127.1, 126.3, 120.9, 118.5, 83.8, 41.6, 37.2, 35.1, 34.8, 29.3, 29.2, 16.1. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>29</sub>H<sub>34</sub>O<sub>2</sub><sup>+</sup> 415.2632; found: 415.2638.

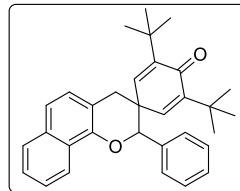
**3',5'-di-tert-butyl-8-isopropyl-2-phenylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2c)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2c** as a white solid (40.6 mg, 92% yield), m.p.: 164.3–164.8 °C.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.28 – 7.14 (m, 6H), 6.97 (q, *J* = 8.0, 7.4 Hz, 2H), 6.71 (s, 1H), 6.44 (s, 1H), 5.11 (s, 1H), 3.42 – 3.29 (m, 2H), 2.75 (d, *J* = 16.4 Hz, 1H), 1.26 (t, *J* = 6.8 Hz, 6H), 1.10 (s, 9H), 1.09 (s, 9H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  185.8, 151.2, 149.0, 148.3, 142.1, 137.7, 136.8, 136.7, 128.4, 127.4, 127.2, 124.6, 121.2, 118.7, 84.0, 41.5, 37.5, 35.1, 34.8, 29.2, 29.2, 27.0, 23.3, 22.1. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>38</sub>O<sub>2</sub><sup>+</sup> 443.2945; found: 443.2952.

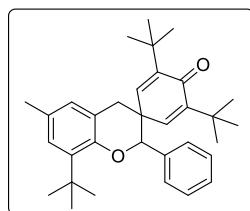
**3',5'-di-tert-butyl-2-phenyl-2H,4H-spiro[benzo[h]chromene-3,1'-cyclohexane]-2',5'-dien-4'-one (2d)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2d** as a yellow solid (41.1 mg, 91% yield), m.p.: 216.8–217.6 °C.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.25 (d, *J* = 7.7 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 3H), 7.24 (d, *J* = 13.0 Hz, 6H), 6.74 (s, 1H), 6.48 (s, 1H), 5.22 (s, 1H), 3.46 (d, *J* = 16.6 Hz, 1H), 2.82 (d, *J* = 16.6 Hz, 1H), 1.11 (s, 9H), 1.07 (s, 9H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  185.8, 149.1, 149.0, 148.5, 142.0, 137.6, 136.6, 133.6, 128.5, 127.6, 127.6, 127.4, 127.2, 126.3, 125.7, 125.0, 121.9, 121.0, 113.0, 84.0, 41.6, 37.1, 35.1, 34.9, 29.3, 29.2. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>34</sub>O<sub>2</sub><sup>+</sup> 451.2632; found: 451.2630.

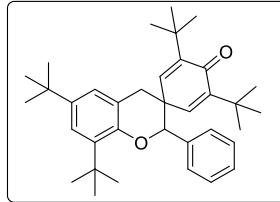
**3',5',8-tri-tert-butyl-6-methyl-2-phenylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2e)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2e** as a white solid (43.3 mg, 92% yield), m.p.: 190.9–191.5 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.31 – 7.13 (m, 5H), 7.04 (d, *J* = 2.2 Hz, 1H), 6.82 (s, 1H), 6.79 (d, *J* = 2.9 Hz, 1H), 6.42 (d, *J* = 2.9 Hz, 1H), 5.07 (s, 1H), 3.35 (d, *J* = 16.5 Hz, 1H), 2.72 (d, *J* = 16.5 Hz, 1H), 2.32 (s, 3H), 1.40 (s, 9H), 1.13 (s, 9H), 1.08 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 185.9, 150.7, 149.0, 148.2, 142.1, 138.1, 136.9, 129.9, 128.3, 128.0, 127.5, 127.2, 126.0, 119.3, 84.2, 41.6, 37.8, 35.1, 34.8, 34.8, 30.0, 29.3, 29.2, 21.1. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>43</sub>O<sub>2</sub><sup>+</sup> 471.3258; found: 471.3269.

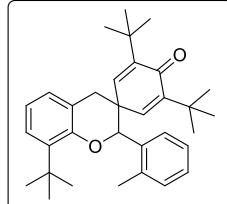
**3',5',6,8-tetra-tert-butyl-2-phenylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2f)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2f** as a light yellow solid (47.7 mg, 93% yield), m.p.: 194.6–195.8 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.28 – 7.25 (m, 1H), 7.22 (dd, *J* = 6.4, 3.4 Hz, 5H), 6.99 (d, *J* = 2.2 Hz, 1H), 6.81 (d, *J* = 2.8 Hz, 1H), 6.48 – 6.35 (m, 1H), 5.07 (s, 1H), 3.39 (d, *J* = 16.5 Hz, 1H), 2.75 (d, *J* = 16.5 Hz, 1H), 1.41 (s, 9H), 1.34 (s, 9H), 1.14 (s, 9H), 1.08 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 185.9, 150.6, 148.9, 148.1, 143.3, 142.2, 138.3, 137.5, 136.9, 128.3, 127.5, 127.1, 124.3, 122.4, 118.7, 84.2, 41.8, 38.0, 35.1, 34.8, 34.5, 31.7, 30.0, 29.3, 29.2. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>36</sub>H<sub>49</sub>O<sub>2</sub><sup>+</sup> 513.3727; found: 513.3737.

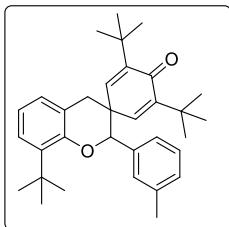
**3',5',8-tri-tert-butyl-2-(o-tolyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2g)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2g** as a white solid (43.8 mg, 93% yield), m.p.: 171.5–172.6 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 7.8 Hz, 2H), 7.10 (dt, *J* = 25.7, 7.7 Hz, 4H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 2.6 Hz, 1H), 6.43 (d, *J* = 2.7 Hz, 1H), 5.44 (s, 1H), 3.43 (d, *J* = 16.3 Hz, 1H), 2.84 (d, *J* = 16.4 Hz, 1H), 2.36 (s, 3H), 1.36 (s, 9H), 1.18 (s, 9H), 1.03 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 185.8, 153.4, 149.3, 148.8, 140.4, 138.4, 138.0, 134.8, 134.5, 129.9, 128.2, 128.0, 127.9, 125.1, 125.1, 120.9, 119.7, 79.9, 42.5, 38.4, 35.2, 34.9, 34.7, 30.4, 29.8, 29.3, 29.1, 20.4. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>43</sub>O<sub>2</sub><sup>+</sup> 471.3258; found: 471.3268.

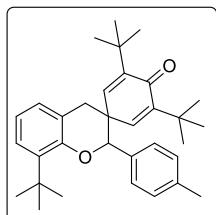
**3',5',8-tri-tert-butyl-2-(m-tolyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2h)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2h** as a white solid (42.8 mg, 91% yield), m.p.: 219.3–221.1 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.27 – 7.21 (m, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.08 – 6.96 (m, 4H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 2.9 Hz, 1H), 6.42 (d, *J* = 2.9 Hz, 1H), 5.07 (s, 1H), 3.39 (d, *J* = 16.4 Hz, 1H), 2.76 (d, *J* = 16.5 Hz, 1H), 2.29 (s, 3H), 1.41 (s, 9H), 1.12 (s, 9H), 1.08 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 185.9, 152.9, 149.0, 148.2, 142.1, 138.3, 138.0, 136.4, 129.1, 128.2, 127.9, 127.1, 125.1, 124.6, 121.0, 119.6, 84.3, 41.5, 37.8, 35.1, 35.0, 34.8, 29.9, 29.3, 29.2, 21.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>43</sub>O<sub>2</sub><sup>+</sup> 471.3258; found: 471.3267.

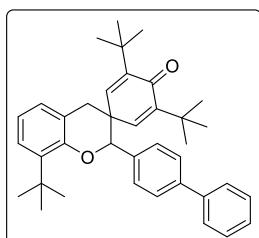
#### 3',5',8-tri-tert-butyl-2-(p-tolyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (**2i**)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2i** as a white solid (44.2 mg, 94% yield), m.p.: 180.8–181.4 °C.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 2H), 7.04 – 6.98 (m, 3H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 2.8 Hz, 1H), 6.41 (d, *J* = 2.8 Hz, 1H), 5.07 (s, 1H), 3.37 (d, *J* = 16.4 Hz, 1H), 2.75 (d, *J* = 16.5 Hz, 1H), 2.29 (s, 3H), 1.39 (s, 9H), 1.13 (s, 9H), 1.06 (s, 9H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 185.9, 153.0, 148.9, 148.1, 142.2, 138.3, 138.1, 138.0, 133.8, 127.9, 127.9, 127.4, 125.1, 120.9, 119.6, 84.1, 41.5, 37.8, 35.1, 35.0, 34.8, 29.9, 29.3, 29.1, 21.3. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>43</sub>O<sub>2</sub><sup>+</sup> 471.3258; found: 471.3264.

#### 2-([1,1'-biphenyl]-4-yl)-3',5',8-tri-tert-butylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (**2j**)

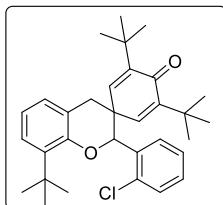


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2j** as a white solid (50.1 mg, 94% yield), m.p.: 212.5–213.9 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.56 – 7.50 (m, 2H), 7.49 – 7.39 (m, 4H), 7.35 (dt, *J* = 8.5, 2.0 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.04 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 2.9 Hz, 1H), 6.45 (d, *J* = 3.0 Hz, 1H), 5.16 (s, 1H), 3.42 (d, *J* = 16.4 Hz, 1H), 2.80 (d, *J* = 16.5 Hz, 1H), 1.43 (s, 9H), 1.15 (s, 9H), 1.09 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 185.8, 152.9, 149.2, 148.4,

141.9, 141.3, 141.0, 138.3, 137.9, 135.8, 128.9, 128.0, 127.9, 127.5, 127.3, 126.0, 125.2, 121.1, 119.6, 84.1, 41.6, 37.8, 35.2, 35.0, 34.9, 29.9, 29.3, 29.2. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>38</sub>H<sub>45</sub>O<sub>2</sub><sup>+</sup> 533.3414; found: 533.3422.

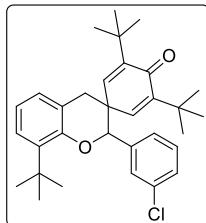
**3',5',8-tri-tert-butyl-2-(2-chlorophenyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2k)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2k** as a light yellow solid (45.2 mg, 92% yield), m.p.: 182.7–184.5 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 1H), 7.28 – 7.14 (m, 4H), 7.05 (d, *J* = 6.8 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 2.9 Hz, 1H), 6.66 (d, *J* = 2.9 Hz, 1H), 5.72 (s, 1H), 3.50 (d, *J* = 16.5 Hz, 1H), 2.84 (d, *J* = 16.5 Hz, 1H), 1.37 (s, 9H), 1.16 (s, 9H), 1.07 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 185.7, 153.1, 149.8, 148.7, 140.7, 138.3, 137.1, 134.1, 132.8, 129.5, 129.0, 128.1, 126.0, 125.1, 121.2, 119.7, 80.1, 42.5, 38.1, 35.2, 34.9, 34.8, 29.9, 29.4, 29.1. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>40</sub>ClO<sub>2</sub><sup>+</sup> 491.2711; found: 491.2720.

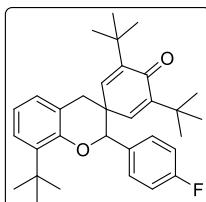
**3',5',8-tri-tert-butyl-2-(3-chlorophenyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2l)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2l** as a light yellow solid (46.2 mg, 94% yield), m.p.: 203.9–204.8 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.28 – 7.21 (m, 2H), 7.21 – 7.13 (m, 2H), 7.10 (dt, *J* = 7.5, 1.6 Hz, 1H), 7.02 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 2.9 Hz, 1H), 6.41 (d, *J* = 2.9 Hz, 1H), 5.07 (s, 1H), 3.39 (d, *J* = 16.5 Hz, 1H), 2.79 (d, *J* = 16.5 Hz, 1H), 1.40 (s, 9H), 1.13 (s, 9H), 1.10 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 185.7, 152.6, 149.6, 148.8, 141.4, 138.7, 138.4, 137.3, 133.1, 128.5, 128.5, 127.9, 127.8, 125.6, 125.3, 121.3, 119.5, 83.5, 41.4, 37.7, 35.2, 34.9, 34.9, 29.9, 29.3, 29.2. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>40</sub>ClO<sub>2</sub><sup>+</sup> 491.2711; found: 491.2719.

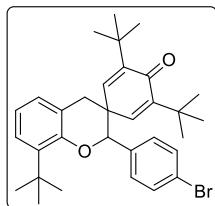
**3',5',8-tri-tert-butyl-2-(4-fluorophenyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2m)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2m** as a white solid (43.7 mg, 92% yield), m.p.: 194.2-195.8 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.26 – 7.21 (m, 1H), 7.21 – 7.14 (m, 2H), 7.01 (d, *J* = 6.6 Hz, 1H), 6.93 (td, *J* = 8.6, 8.0, 3.1 Hz, 3H), 6.75 (d, *J* = 2.9 Hz, 1H), 6.39 (d, *J* = 3.0 Hz, 1H), 5.09 (s, 1H), 3.38 (d, *J* = 16.5 Hz, 1H), 2.77 (d, *J* = 16.6 Hz, 1H), 1.39 (s, 9H), 1.13 (s, 9H), 1.08 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 185.7, 162.6 (d, *J* = 246.9 Hz), 152.8, 149.4, 148.7, 141.7, 138.3, 137.6, 132.7 (d, *J* = 3.0 Hz), 129.1 (d, *J* = 8.2 Hz), 127.9, 125.2, 121.2, 119.5, 114.2 (d, *J* = 21.6 Hz), 83.5, 41.5, 37.8, 35.2, 34.9, 34.9, 29.9, 29.3, 29.2. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>40</sub>FO<sub>2</sub><sup>+</sup> 475.3007; found: 475.3016.

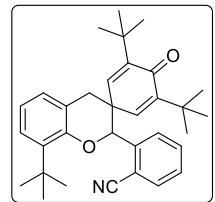
**2-(4-bromophenyl)-3',5',8-tri-tert-butylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2n)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2n** as a white solid (49.3 mg, 92% yield), m.p.: 225.8-226.9 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.41 – 7.32 (m, 2H), 7.28 – 7.20 (m, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 2.9 Hz, 1H), 6.39 (d, *J* = 2.9 Hz, 1H), 5.05 (s, 1H), 3.37 (d, *J* = 16.5 Hz, 1H), 2.76 (d, *J* = 16.6 Hz, 1H), 1.38 (s, 9H), 1.12 (s, 9H), 1.09 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 185.6, 152.6, 149.5, 148.8, 141.5, 138.3, 137.5, 135.9, 130.4, 129.1, 127.9, 125.2, 122.3, 121.2, 119.5, 83.6, 41.3, 37.8, 35.2, 34.9, 34.9, 29.9, 29.3, 29.2. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>40</sub>BrO<sub>2</sub><sup>+</sup> 535.2206; found: 535.2188.

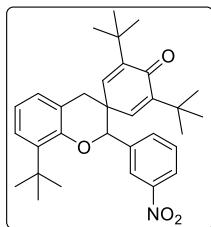
**2-(3',5',8-tri-tert-butyl-4'-oxospiro[chromane-3,1'-cyclohexane]-2',5'-dien-2-yl)benzonitrile (2o)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:50) afforded the product **2o** as a white solid (44.3 mg, 92% yield), m.p.: 193.9-195.2 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.58 – 7.52 (m, 1H), 7.52 – 7.43 (m, 2H), 7.37 (td, *J* = 7.6, 1.8 Hz, 1H), 7.27 – 7.21 (m, 1H), 7.10 – 7.01 (m, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 0.8 Hz, 2H), 5.62 (s, 1H), 3.54 (d, *J* = 16.6 Hz, 1H), 2.88 (d, *J* = 16.5 Hz, 1H), 1.36 (s, 9H), 1.13 (s, 9H), 1.09 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 185.6, 152.5, 150.2, 149.8, 140.4, 140.1, 138.3, 136.5, 132.0, 131.8, 128.9, 128.7, 128.1, 125.3, 121.6, 119.5, 118.1, 112.1, 81.4, 42.4, 37.8, 35.2, 35.0, 34.9, 29.9, 29.4, 29.1. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>40</sub>NO<sub>2</sub><sup>+</sup> 482.3054; found: 482.3065.

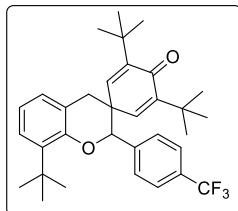
**3',5',8-tri-tert-butyl-2-(3-nitrophenyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2p)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:50) afforded the product **2p** as a light yellow solid (47.1 mg, 94% yield), m.p.: 212.6–213.7 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 8.13 (dt, *J* = 10.1, 1.6 Hz, 2H), 7.57 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.26 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.04 (dd, *J* = 7.5, 1.9 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 2.9 Hz, 1H), 6.46 (d, *J* = 2.9 Hz, 1H), 5.21 (s, 1H), 3.43 (d, *J* = 16.7 Hz, 1H), 2.83 (d, *J* = 16.6 Hz, 1H), 1.40 (s, 9H), 1.08 (s, 9H), 1.06 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 185.5, 152.3, 150.2, 149.6, 147.2, 140.9, 138.7, 138.4, 136.7, 133.3, 128.2, 128.0, 125.4, 123.4, 122.6, 121.6, 119.3, 83.0, 41.4, 37.5, 35.2, 34.9, 30.0, 29.3, 29.2. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>40</sub>NO<sub>4</sub><sup>+</sup> 502.2952; found: 502.2962.

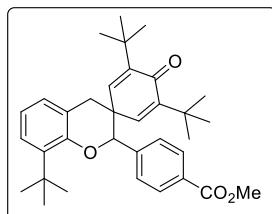
#### 3',5',8-tri-tert-butyl-2-(4-(trifluoromethyl)phenyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2q)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:80) afforded the product **2q** as a light yellow solid (44.6 mg, 85% yield), m.p.: 178.7–179.6 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.21 (m, 1H), 7.07 – 6.90 (m, 2H), 6.76 (d, *J* = 2.9 Hz, 1H), 6.42 (d, *J* = 2.9 Hz, 1H), 5.15 (s, 1H), 3.41 (d, *J* = 16.6 Hz, 1H), 2.80 (d, *J* = 16.6 Hz, 1H), 1.40 (s, 9H), 1.12 (s, 9H), 1.07 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 185.5, 152.5, 149.6, 149.0, 141.2, 140.7, 138.4, 137.2, 130.7 (q, *J* = 32.6 Hz), 128.0, 127.9, 125.3, 124.2 (q, *J* = 3.9 Hz), 124.1 (q, *J* = 270.7 Hz), 121.4, 119.5, 83.6, 41.4, 37.8, 35.2, 35.0, 34.9, 29.9, 29.3, 29.1. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>40</sub>F<sub>3</sub>O<sub>2</sub><sup>+</sup> 525.2975; found: 525.2983.

#### methyl 4-(3',5',8-tri-tert-butyl-4'-oxospiro[chromane-3,1'-cyclohexane]-2',5'-dien-2-yl)benzoate (2r)

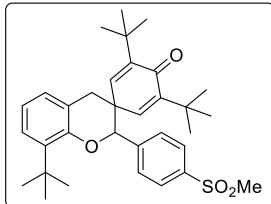


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:50) afforded the product **2r** as a light yellow solid (46.8 mg, 91% yield), m.p.: 201.8–202.6 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.96 – 7.89 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 1H), 7.05 – 6.98 (m, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 2.9 Hz, 1H), 6.43 (d, *J* = 2.9 Hz, 1H), 5.14 (s, 1H), 3.89 (s, 3H), 3.40 (d, *J* = 16.5 Hz, 1H), 2.78 (d, *J* = 16.5 Hz, 1H), 1.38 (s, 9H), 1.11 (s,

9H), 1.07 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*)  $\delta$  185.6, 166.8, 152.6, 149.4, 148.8, 141.7, 141.4, 138.4, 137.4, 130.1, 128.6, 127.9, 127.6, 125.3, 121.3, 119.5, 83.8, 52.2, 41.3, 37.8, 35.2, 34.9, 34.9, 29.9, 29.3, 29.2. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>43</sub>O<sub>4</sub><sup>+</sup> 515.3156; found: 515.3167.

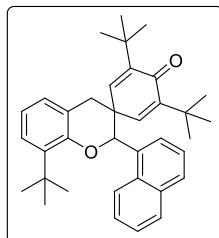
**3',5',8-tri-tert-butyl-2-(4-(methylsulfonyl)phenyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2s)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:30) afforded the product **2s** as a white solid (44.4 mg, 83% yield), m.p.: 257.2–258.6 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*)  $\delta$  7.82 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.03 (d, *J* = 7.0 Hz, 1H), 7.00 – 6.91 (m, 1H), 6.70 (d, *J* = 2.3 Hz, 1H), 6.40 (d, *J* = 2.2 Hz, 1H), 5.18 (s, 1H), 3.42 (d, *J* = 16.6 Hz, 1H), 2.94 (s, 3H), 2.85 (d, *J* = 16.7 Hz, 1H), 1.38 (s, 9H), 1.09 (s, 9H), 1.06 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*)  $\delta$  185.6, 152.3, 149.9, 149.3, 142.5, 141.0, 140.4, 138.4, 136.9, 128.7, 128.0, 126.3, 125.4, 121.6, 119.3, 83.3, 44.8, 41.4, 37.5, 35.2, 34.9, 29.9, 29.3, 29.1. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>43</sub>O<sub>4</sub>S<sup>+</sup> 535.2877; found: 535.2873.

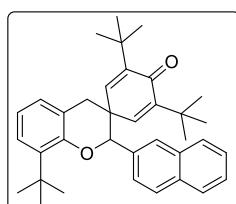
**3',5',8-tri-tert-butyl-2-(naphthalen-1-yl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2t)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2t** as a light yellow solid (47.6 mg, 94% yield), m.p.: 205.9–207.1 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*)  $\delta$  7.99 (d, *J* = 8.2 Hz, 1H), 7.88 – 7.79 (m, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.45 (m, 2H), 7.44 (ddd, *J* = 7.9, 6.8, 1.2 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 6.4 Hz, 1H), 7.10 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 2.9 Hz, 1H), 6.40 (d, *J* = 2.9 Hz, 1H), 6.13 (s, 1H), 3.57 (d, *J* = 16.5 Hz, 1H), 2.94 (d, *J* = 16.5 Hz, 1H), 1.40 (s, 10H), 1.15 (s, 9H), 0.60 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*)  $\delta$  185.4, 153.6, 149.6, 148.0, 141.9, 138.5, 137.6, 133.3, 132.1, 131.0, 129.5, 128.8, 128.1, 126.3, 126.1, 125.3, 125.1, 124.6, 122.8, 121.1, 119.9, 79.3, 42.6, 38.3, 35.1, 35.0, 34.3, 29.9, 29.4, 28.5. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>36</sub>H<sub>43</sub>O<sub>2</sub><sup>+</sup> 507.3258; found: 507.3267.

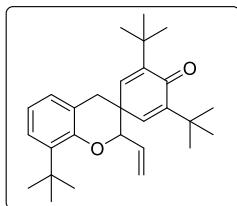
**3',5',8-tri-tert-butyl-2-(naphthalen-2-yl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2u)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2u** as a light yellow solid (48.1 mg, 95% yield), m.p.: 243.1–244.7 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.82 – 7.73 (m, 2H), 7.73 – 7.64 (m, 2H), 7.50 – 7.41 (m, 2H), 7.34 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 2.8 Hz, 1H), 6.51 (d, *J* = 2.9 Hz, 1H), 5.28 (s, 1H), 3.45 (d, *J* = 16.3 Hz, 1H), 2.81 (d, *J* = 16.5 Hz, 1H), 1.42 (s, 9H), 1.11 (s, 9H), 0.98 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 185.8, 153.0, 149.1, 148.4, 141.9, 138.4, 138.0, 134.5, 133.3, 132.3, 128.0, 128.0, 127.8, 126.8, 126.7, 126.2, 126.2, 125.4, 125.2, 121.1, 119.7, 84.4, 41.7, 37.9, 35.1, 35.0, 34.8, 29.9, 29.3, 29.1. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>36</sub>H<sub>43</sub>O<sub>2</sub><sup>+</sup> 507.3258; found: 507.3267.

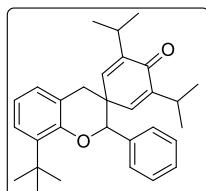
**3',5',8-tri-tert-butyl-2-vinylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2w)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2w** as a white solid (37.4 mg, 92% yield), m.p.: 131.7–133.9 °C.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*) δ 7.20 (dd, *J* = 7.5, 1.9 Hz, 1H), 6.98 – 6.83 (m, 2H), 6.62 (d, *J* = 2.9 Hz, 1H), 6.39 (d, *J* = 2.9 Hz, 1H), 5.67 (ddd, *J* = 16.9, 10.6, 6.2 Hz, 1H), 5.36 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.22 (dt, *J* = 10.6, 1.3 Hz, 1H), 4.49 (d, *J* = 6.2 Hz, 1H), 3.18 (d, *J* = 16.4 Hz, 1H), 2.67 (d, *J* = 16.4 Hz, 1H), 1.41 (s, 9H), 1.25 (s, 9H), 1.17 (s, 9H). **<sup>13</sup>C NMR** (75 MHz, Chloroform-*d*) δ 186.7, 152.1, 149.3, 149.0, 141.9, 138.9, 138.1, 133.1, 127.8, 125.2, 120.8, 119.5, 118.7, 81.6, 40.1, 37.1, 35.2, 35.1, 34.9, 29.8, 29.7, 29.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>39</sub>O<sub>2</sub><sup>+</sup> 407.2945; found: 407.2952.

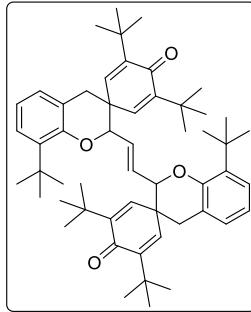
**8-(tert-butyl)-3',5'-diisopropyl-2-phenylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2z)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2z** as a white solid (39.4 mg, 92% yield), m.p.: 161.6–162.7 °C.

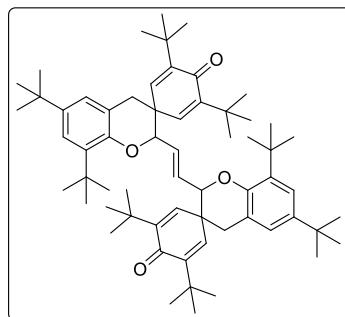
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 8.0 Hz, 1H), 7.21 (s, 5H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.83 – 6.78 (m, 1H), 6.47 – 6.42 (m, 1H), 5.13 (s, 1H), 3.41 (d, *J* = 16.5 Hz, 1H), 2.87 (dp, *J* = 28.3, 6.9 Hz, 2H), 2.72 (d, *J* = 16.5 Hz, 1H), 1.40 (s, 9H), 1.02 (d, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H), 0.83 (d, *J* = 6.9 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 184.8, 152.8, 147.0, 146.2, 142.4, 138.5, 138.3, 136.8, 128.4, 127.8, 127.3, 127.3, 125.2, 121.0, 119.5, 83.9, 41.8, 37.7, 35.0, 29.9, 26.8, 26.3, 22.8, 22.0, 21.7, 21.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>30</sub>H<sub>37</sub>O<sub>2</sub><sup>+</sup> 429.2788; found: 429.2798.

**(E)-2,2''-(ethene-1,2-diyl)bis(3',5',8-tri-tert-butylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one) (2za)**



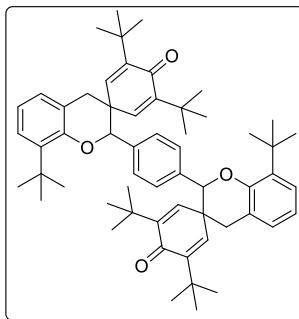
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2za** as inseparable diastereomers (*dr* = 1.3:1) as a white solid (62.8 mg, 80% yield), m.p.: 278.4–279.8 °C. **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.17 (dd, *J* = 7.1, 3.6 Hz, 2H), 6.87 (dq, *J* = 14.2, 7.5 Hz, 4H), 6.55 (d, *J* = 9.1 Hz, 2H), 6.41 (d, *J* = 32.9 Hz, 2H), 5.78 (d, *J* = 30.3 Hz, 2H), 4.48 (s, 2H), 2.95 (d, *J* = 16.3 Hz, 2H), 2.65 (d, *J* = 15.7 Hz, 2H), 1.37 (s, 18H), 1.20 (s, 18H), 1.16 (s, 18H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 186.3, 151.4, 149.5, 148.5, 141.7, 139.5, 137.8, 130.2, 127.8, 125.1, 120.8, 119.3, 80.2, 39.9, 36.4, 35.2, 35.0, 34.9, 29.8, 29.6, 29.5. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>54</sub>H<sub>73</sub>O<sub>4</sub><sup>+</sup> 785.5503; found: 785.5500.

(E)-2,2''-(ethene-1,2-diyl)bis(3',5',6,8-tetra-tert-butylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one) (2zb)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2zb** as inseparable diastereomers (*dr* = 10:1) as a white solid (70 mg, 78% yield), m.p.: 302.2–303.2 °C. **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.16 (d, *J* = 1.8 Hz, 2H), 6.86 – 6.82 (m, 2H), 6.57 (d, *J* = 2.5 Hz, 2H), 6.45 (d, *J* = 2.6 Hz, 2H), 5.86 – 5.74 (m, 2H), 4.47 – 4.42 (m, 2H), 2.95 (d, *J* = 16.4 Hz, 2H), 2.58 (d, *J* = 16.4 Hz, 2H), 1.34 (s, 18H), 1.28 (s, 18H), 1.20 (s, 18H), 1.18 (s, 18H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 186.5, 149.3, 149.1, 148.3, 143.0, 142.1, 139.9, 137.0, 130.1, 124.1, 122.3, 118.5, 80.0, 40.2, 36.8, 35.2, 35.0, 35.0, 34.4, 31.7, 29.9, 29.7, 29.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>62</sub>H<sub>89</sub>O<sub>4</sub><sup>+</sup> 897.6755; found: 897.6775.

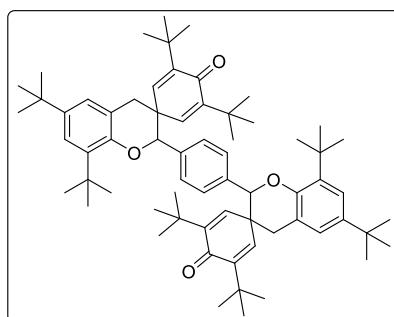
2,2''-(1,4-phenylene)bis(3',5',8-tri-tert-butylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one) (2zc)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2zc** as inseparable diastereomers (*dr* = 1.7:1) as a white solid (72.7 mg, 87% yield), m.p.: 298.8–299.4 °C.

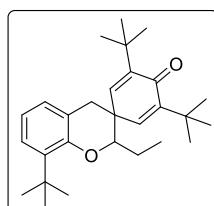
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 2.0 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 4H), 6.91 (t, *J* = 7.6 Hz, 2H), 6.77 (d, *J* = 2.5 Hz, 2H), 6.36 (d, *J* = 2.5 Hz, 2H), 5.02 (s, 2H), 3.36 (d, *J* = 16.5 Hz, 2H), 2.77 (d, *J* = 16.6 Hz, 2H), 1.30 (s, 18H), 1.14 (s, 18H), 1.01 (s, 18H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 185.5, 152.9, 148.9, 148.2, 141.8, 138.5, 137.9, 136.6, 127.8, 126.3, 125.1, 121.0, 119.5, 83.8, 41.5, 37.5, 35.2, 34.9, 34.8, 30.4, 29.8, 29.6, 29.4, 29.3, 29.2, 29.0. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>58</sub>H<sub>75</sub>O<sub>4</sub><sup>+</sup> 835.5660; found: 835.5675.

#### 2,2''-(1,4-phenylene)bis(3',5',6,8-tetra-tert-butylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one) (2zd)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **2zd** as inseparable diastereomers (*dr* = 7:1) as a white solid (77.7 mg, 82% yield), m.p.: 355.8–356.4 °C. **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.24 – 7.20 (m, 2H), 7.04 (s, 4H), 6.95 (s, 2H), 6.77 (d, *J* = 2.5 Hz, 2H), 6.39 (d, *J* = 2.5 Hz, 2H), 5.00 (s, 2H), 3.35 (d, *J* = 16.5 Hz, 2H), 2.73 (d, *J* = 16.6 Hz, 2H), 1.32 (s, 18H), 1.32 (s, 18H), 1.09 (s, 18H), 1.08 (s, 18H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 185.7, 150.5, 148.7, 148.1, 143.2, 142.3, 138.3, 136.7, 126.1, 124.2, 122.3, 118.6, 83.8, 41.8, 37.7, 35.1, 35.1, 34.8, 34.4, 31.7, 29.9, 29.4, 29.2. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>66</sub>H<sub>91</sub>O<sub>4</sub><sup>+</sup> 947.6912; found: 947.6923.

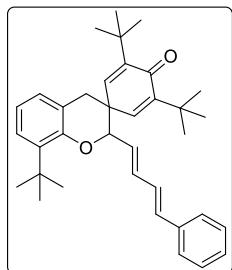
#### 3',5',8-tri-tert-butyl-2-ethylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (3w)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **3w** as a white solid (37.6 mg, 92% yield), m.p.: 146.9–147.8 °C.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 7.3 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 2.8 Hz, 1H), 6.35 (d, *J* = 2.8 Hz, 1H), 3.97 (dd, *J* = 8.9, 3.6 Hz, 1H), 3.22 (d, *J* = 16.2 Hz, 1H), 2.51 (d, *J* = 16.3 Hz, 1H), 1.49 (dt, *J* = 11.6, 4.5 Hz, 2H), 1.42 (s, 9H), 1.28 (s, 9H), 1.16 (s, 9H), 1.10 (t, *J* = 7.4 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 186.7, 152.6, 148.9, 148.6, 142.7, 139.4, 137.6, 127.7, 125.0, 120.4, 119.5, 82.6, 40.3, 38.3, 35.1, 35.1, 34.9, 29.7, 29.6, 29.5, 24.3, 11.6. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>41</sub>O<sub>2</sub><sup>+</sup> 409.3101; found: 409.3106.

**3',5',8-tri-tert-butyl-2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (4w)**



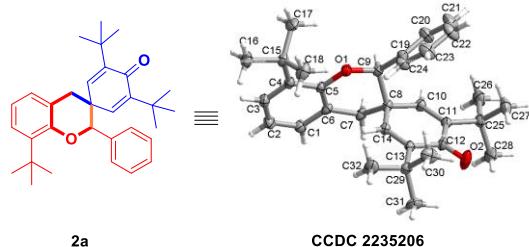
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **4w** as a light yellow solid (41.2 mg, 81% yield), m.p.: 154.3–155.8 °C.

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 2H), 7.19 (d, *J* = 5.6 Hz, 1H), 7.17 – 7.11 (m, 2H), 6.90 (d, *J* = 7.4 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.57 (q, *J* = 3.9, 2.7 Hz, 2H), 6.48 (d, *J* = 15.6 Hz, 1H), 6.41 – 6.31 (m, 2H), 5.53 (dd, *J* = 15.2, 7.0 Hz, 1H), 4.50 (d, *J* = 7.0 Hz, 1H), 3.12 (d, *J* = 16.5 Hz, 1H), 2.65 (d, *J* = 16.4 Hz, 1H), 1.36 (s, 9H), 1.16 (s, 9H), 1.11 (s, 9H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 186.5, 152.1, 149.3, 148.9, 142.0, 139.1, 138.1, 137.0, 134.4, 133.9, 128.7, 128.1, 127.9, 127.9, 127.7, 126.6, 125.1, 120.7, 119.4, 81.3, 40.5, 36.9, 35.2, 35.0, 34.9, 29.7, 29.6, 29.5. **HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>36</sub>H<sub>45</sub>O<sub>2</sub><sup>+</sup> 509.3414; found: 509.3420.

Reference:

1. X. Lv, F. Hu, K. Duan, S.-S. Li, Q. Liu and J. Xiao, *J. Org. Chem.*, 2019, **84**, 1833.

## 5. Crystal Structures and Data

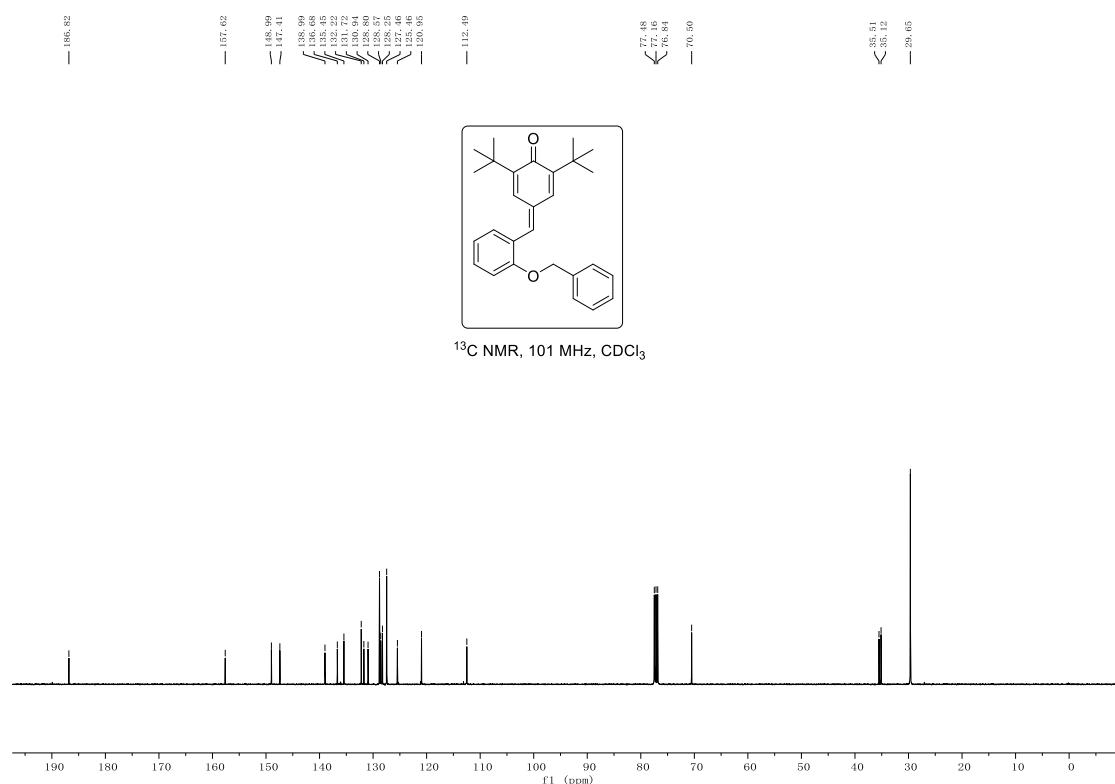
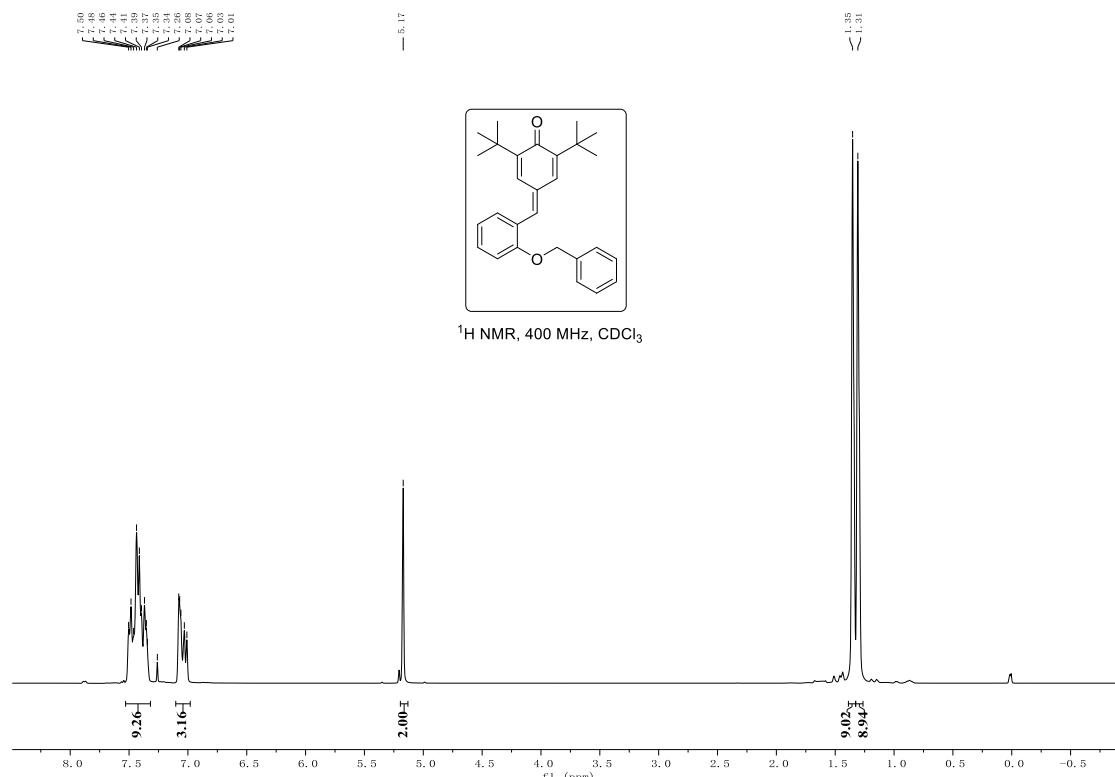


ORTEP diagram of compound **2a**, thermal ellipsoids are drawn on 50% probability level Crystal data and structure refinement for **2a**.

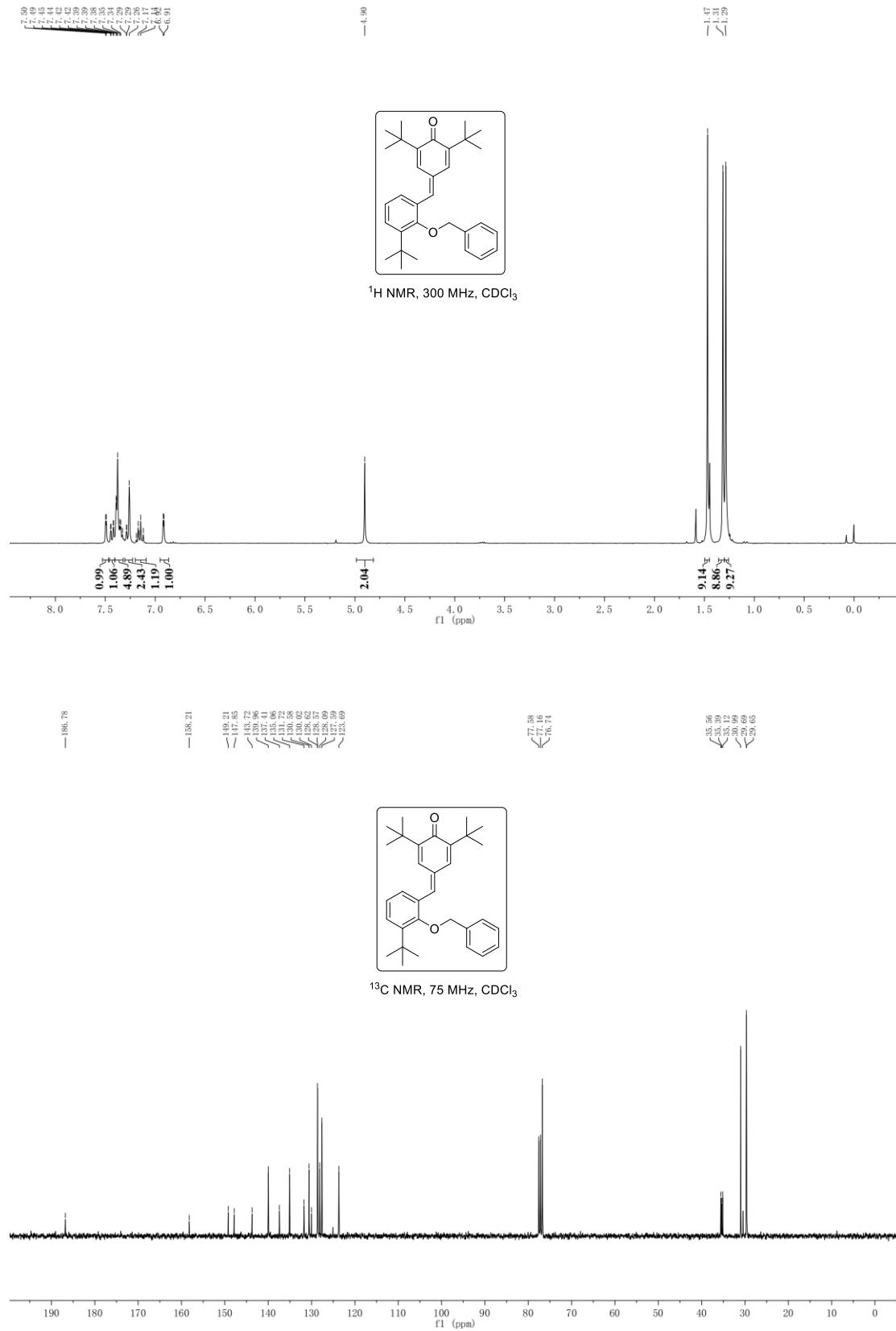
Identification code	<b>2a</b>
Empirical formula	C <sub>32</sub> H <sub>40</sub> O <sub>2</sub>
Formula weight	456.64
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.3055(7)
b/Å	11.0412(5)
c/Å	12.6071(9)
α/°	86.267(5)
β/°	81.047(6)
γ/°	77.001(5)
Volume/Å <sup>3</sup>	1380.02(16)
Z	2
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.099
μ/mm <sup>-1</sup>	0.509
F(000)	496.0
Crystal size/mm <sup>3</sup>	0.17 × 0.14 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.102 to 134.146
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 8, -14 ≤ l ≤ 15
Reflections collected	9919
Independent reflections	4916 [R <sub>int</sub> = 0.0294, R <sub>sigma</sub> = 0.0407]
Data/restraints/parameters	4916/0/316
Goodness-of-fit on F <sup>2</sup>	1.041
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0.0530, wR <sub>2</sub> = 0.1335
Final R indexes [all data]	R <sub>1</sub> = 0.0750, wR <sub>2</sub> = 0.1537
Largest diff. peak/hole / e Å <sup>-3</sup>	0.16/-0.18

## 6. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

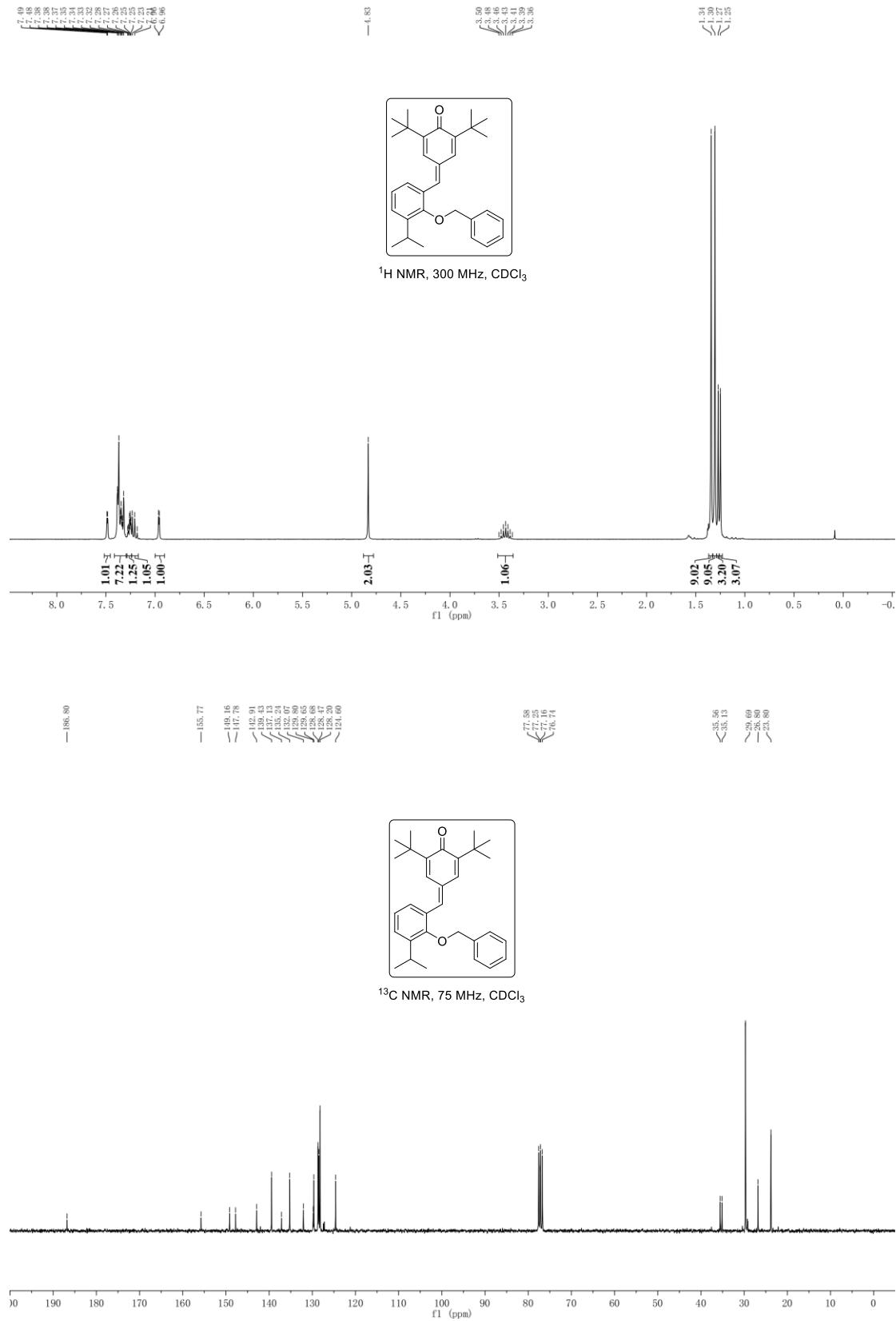
**4-(2-(benzyloxy)benzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1a')**



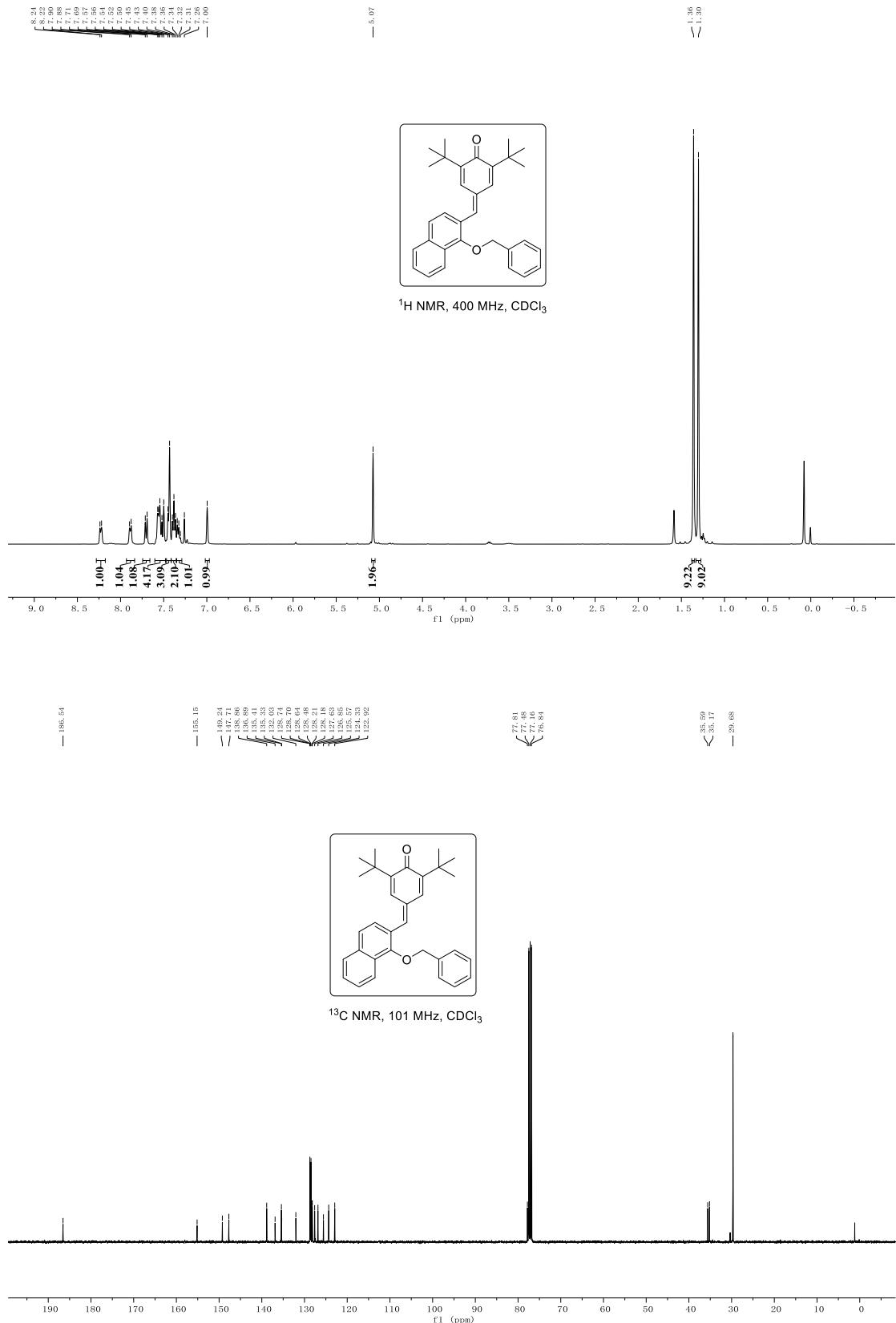
**4-(2-(benzyloxy)-3-(tert-butyl)benzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1a)**



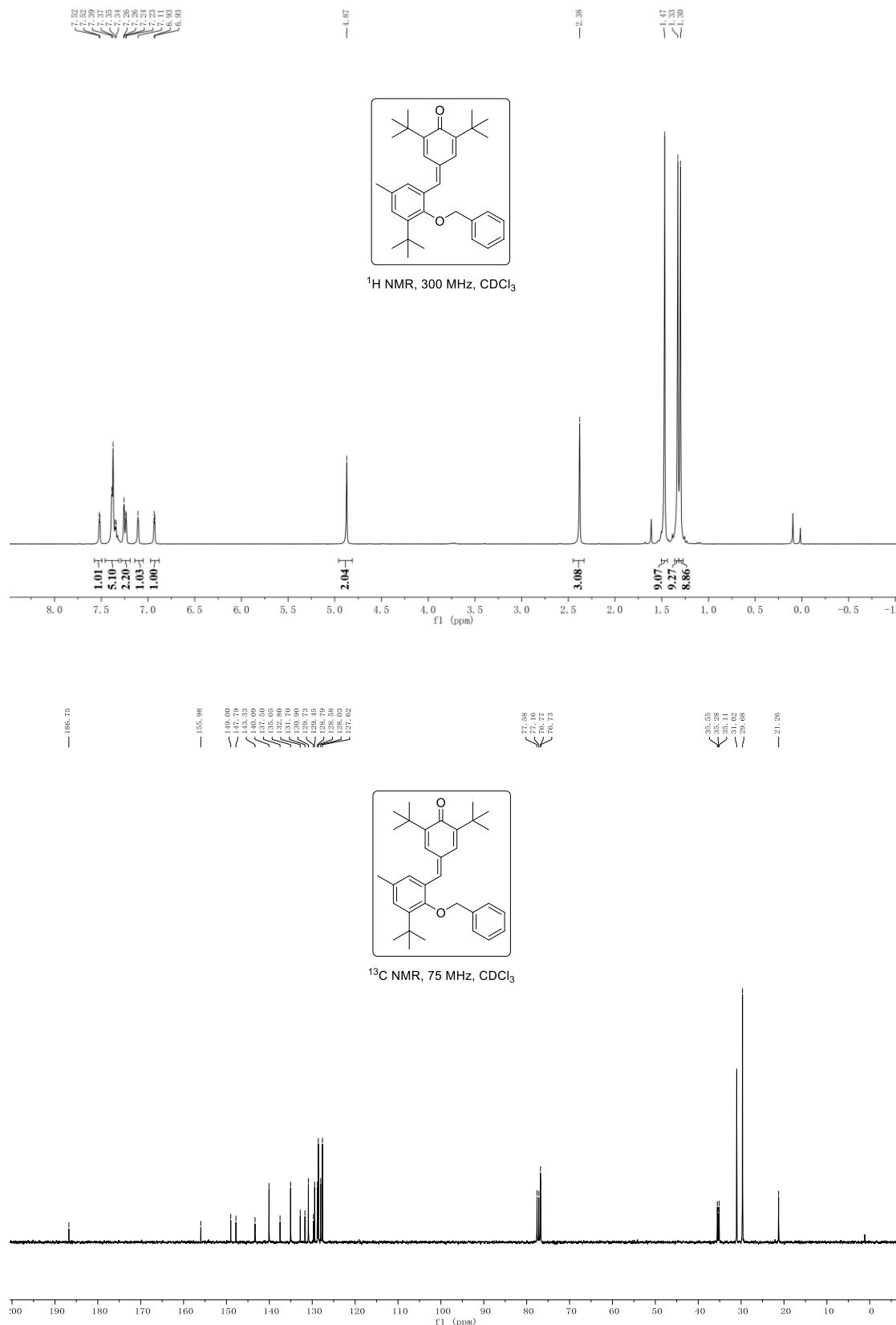
**4-(2-(benzyloxy)-3-isopropylbenzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1c)**



**4-((1-(benzyloxy)naphthalen-2-yl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1d)**



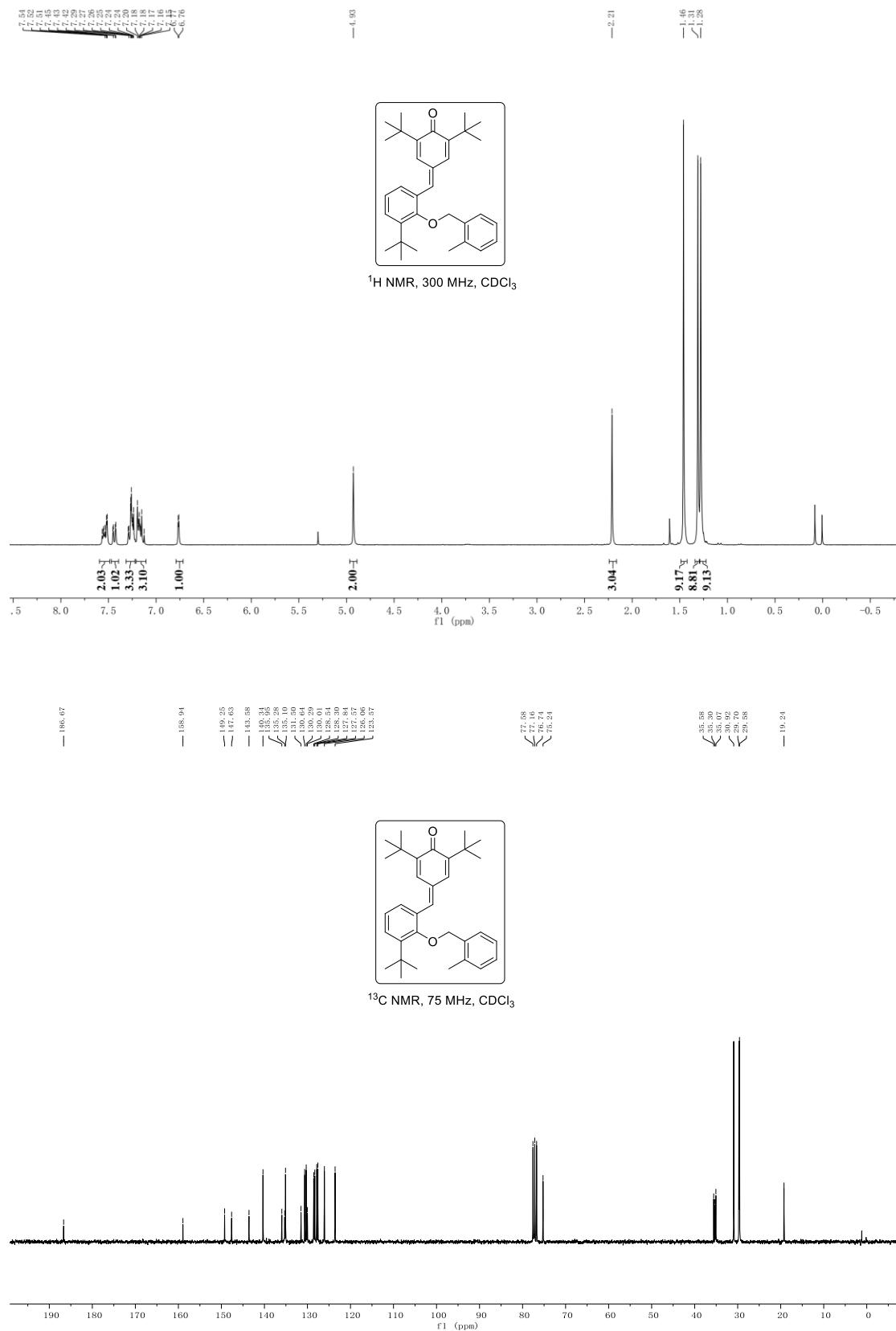
**4-(2-(benzyloxy)-3-(tert-butyl)-5-methylbenzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1e)**



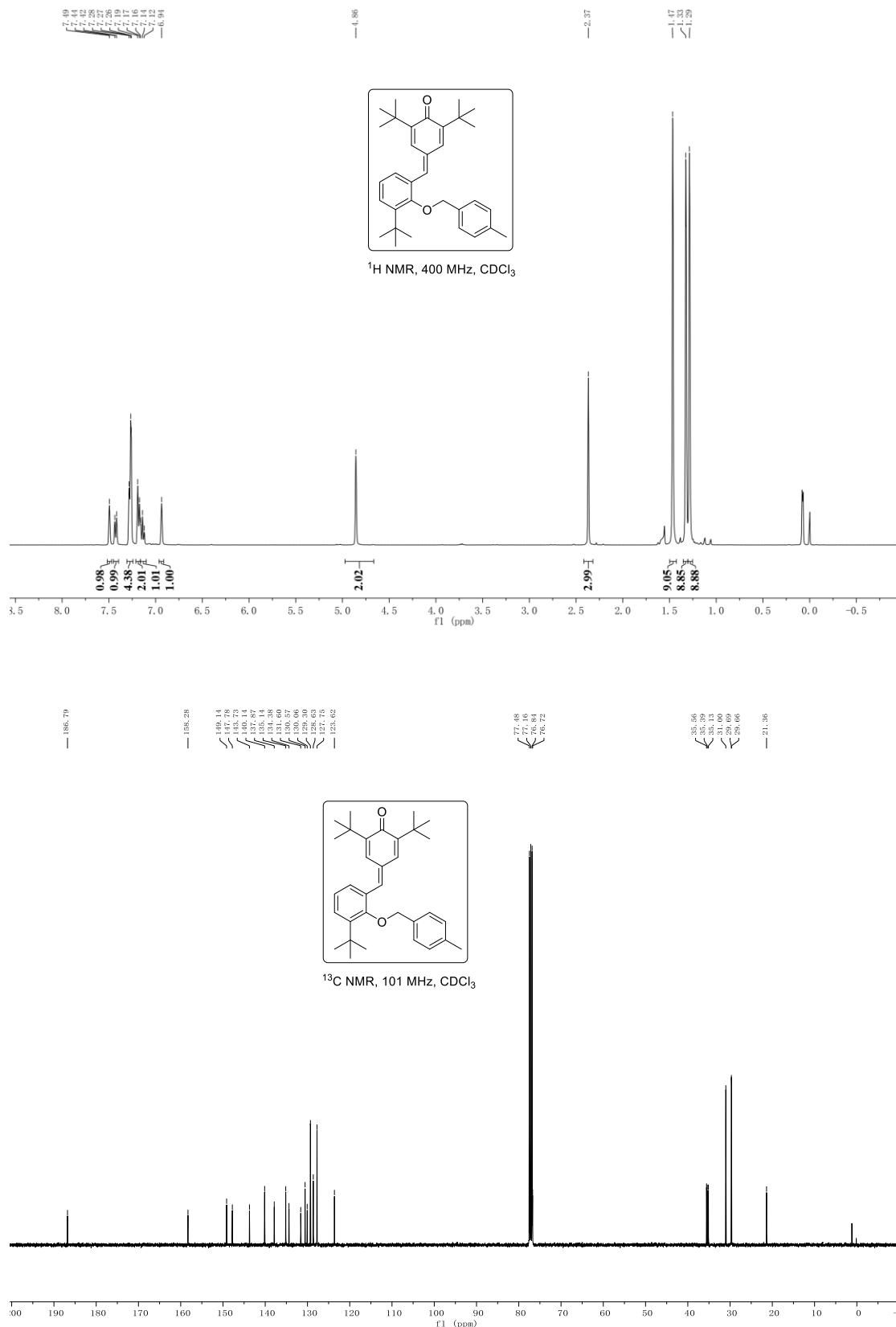
**4-(2-(benzyloxy)-3,5-di-tert-butylbenzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1f)**



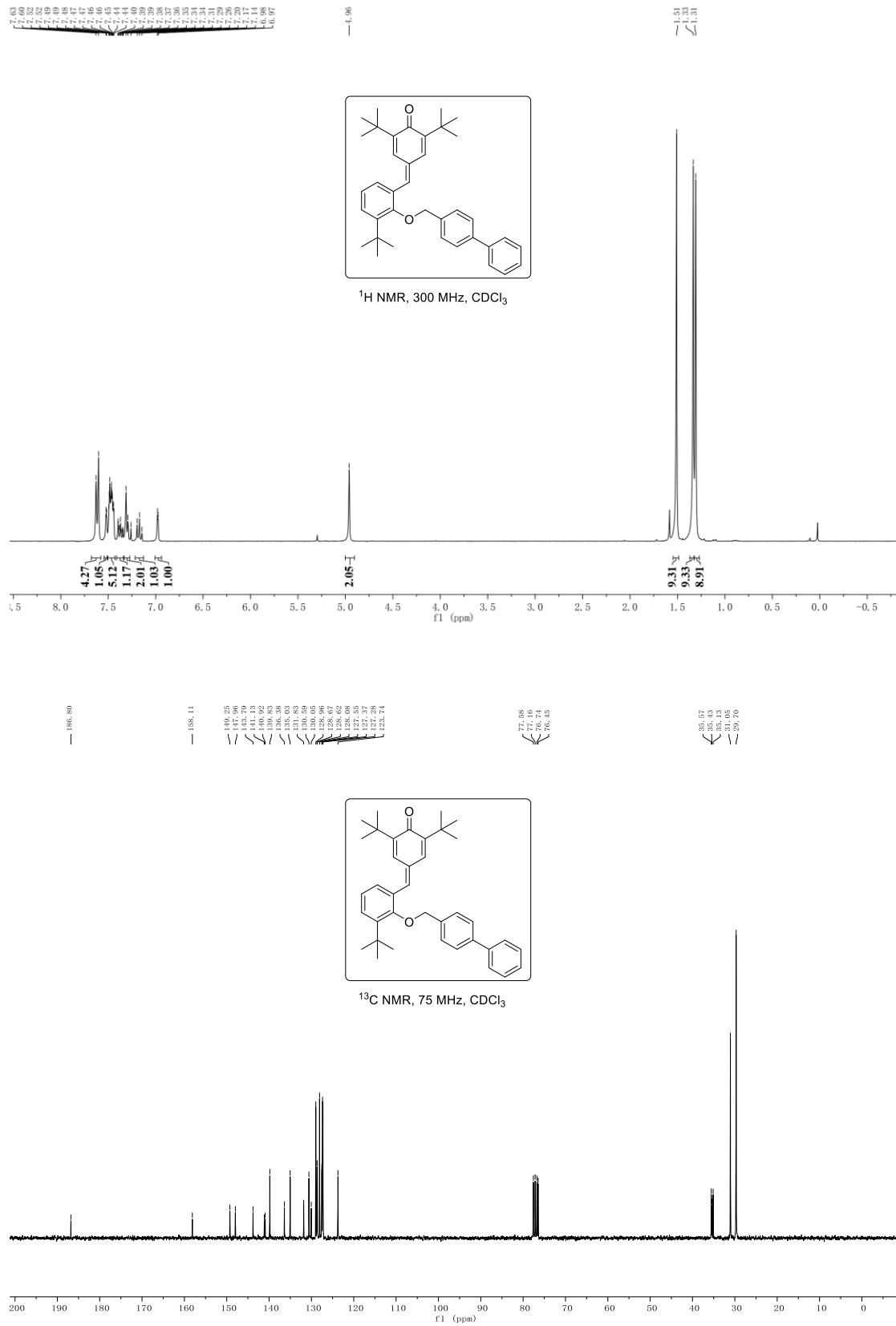
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((2-methylbenzyl)oxy)benzylidene)cyclohexa-2,5-dien-1-one (1g)**



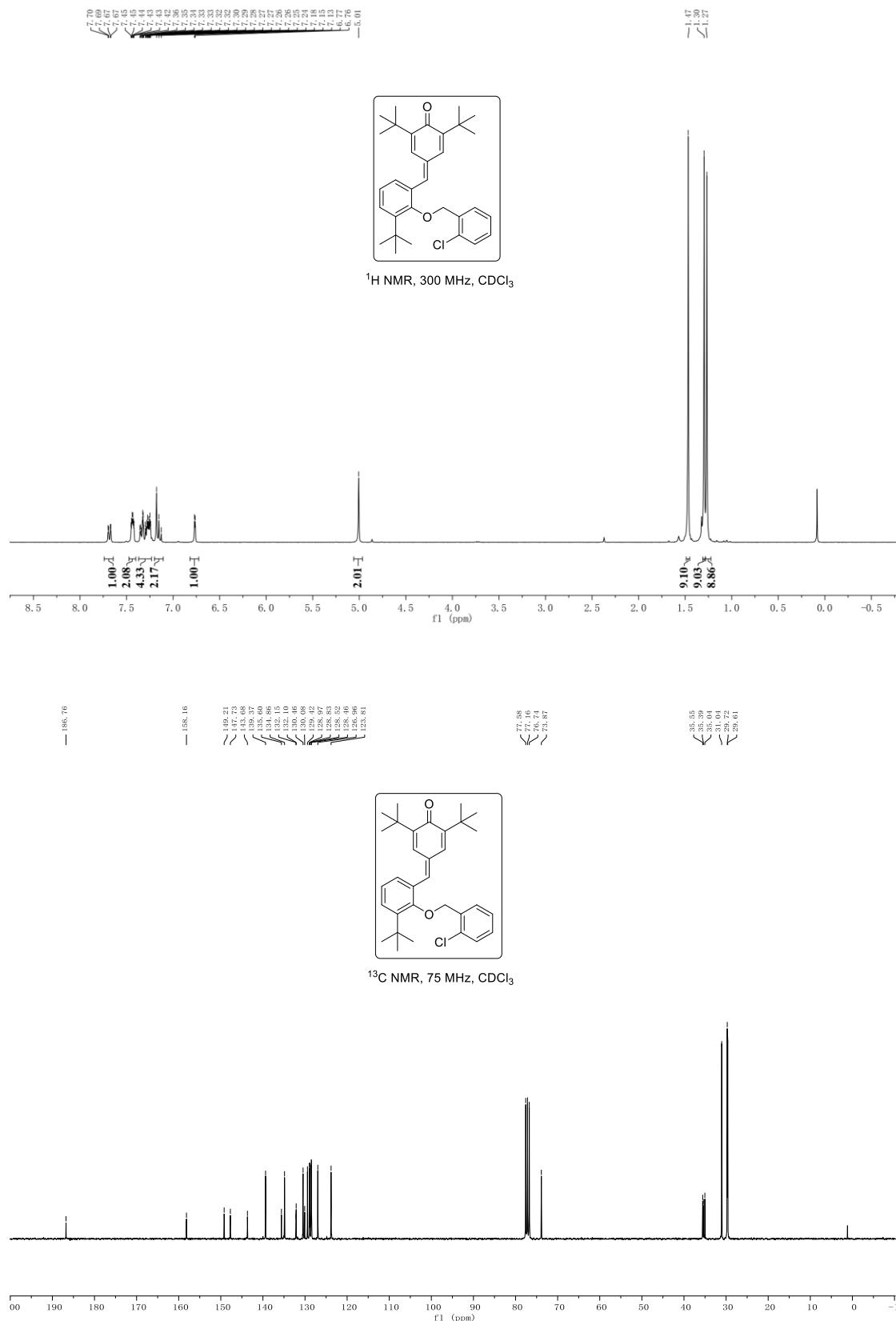
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((4-methylbenzyl)oxy)benzylidene)cyclohexa-2,5-dien-1-one (1i)**



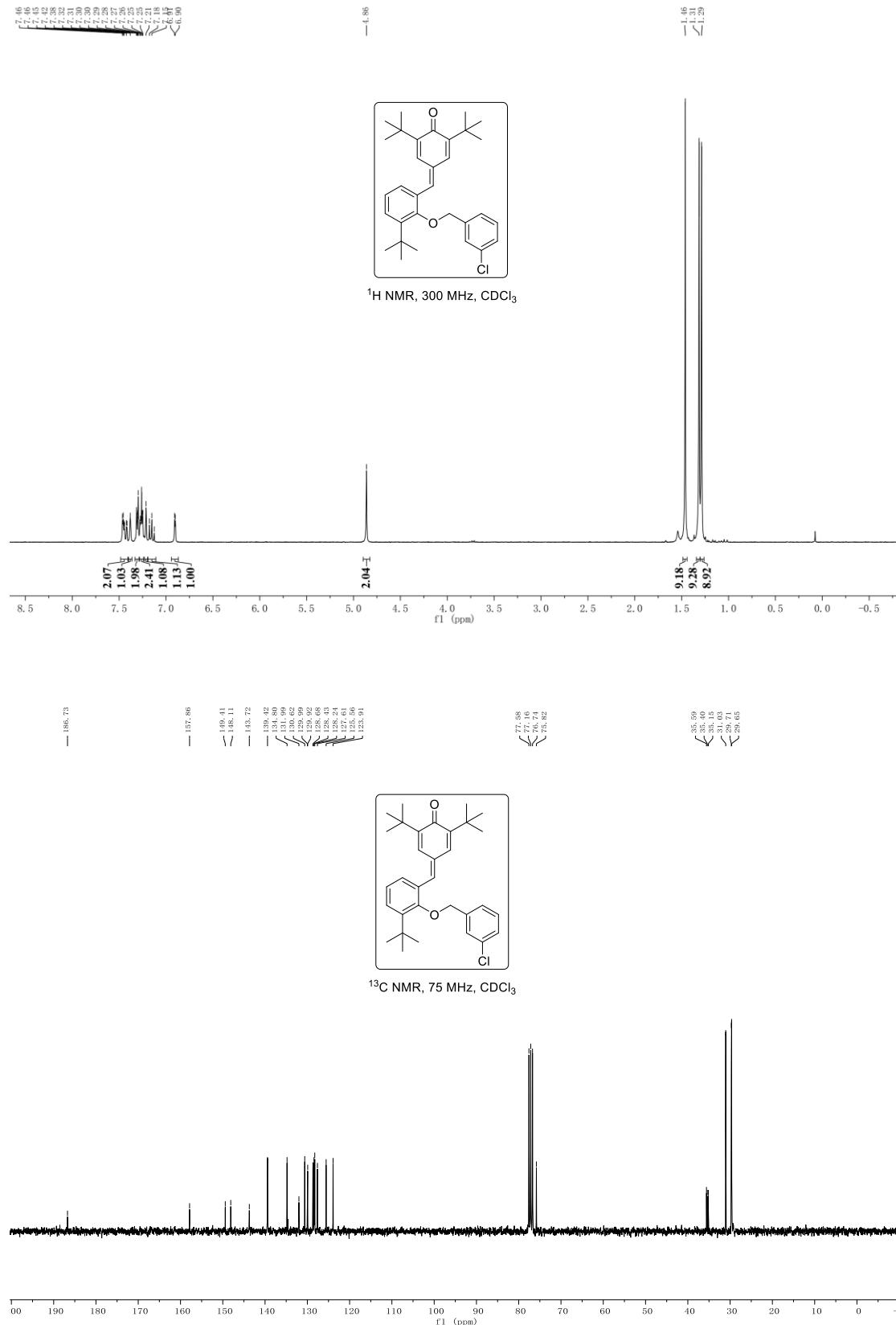
**4-(2-([1,1'-biphenyl]-4-ylmethoxy)-3-(tert-butyl)benzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1j)**



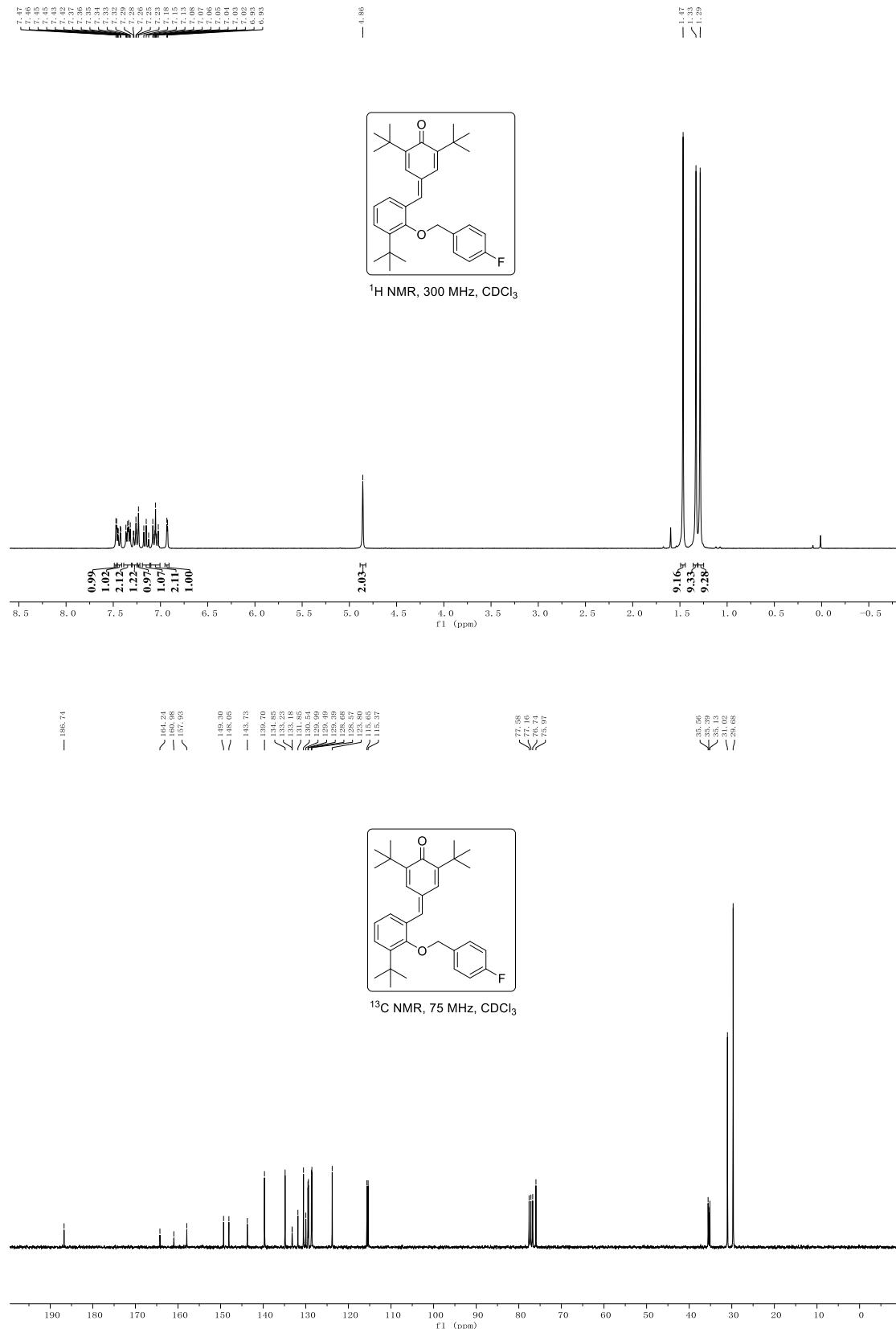
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((2-chlorobenzyl)oxy)benzylidene)cyclohexa-2,5-dien-1-one (1k)**



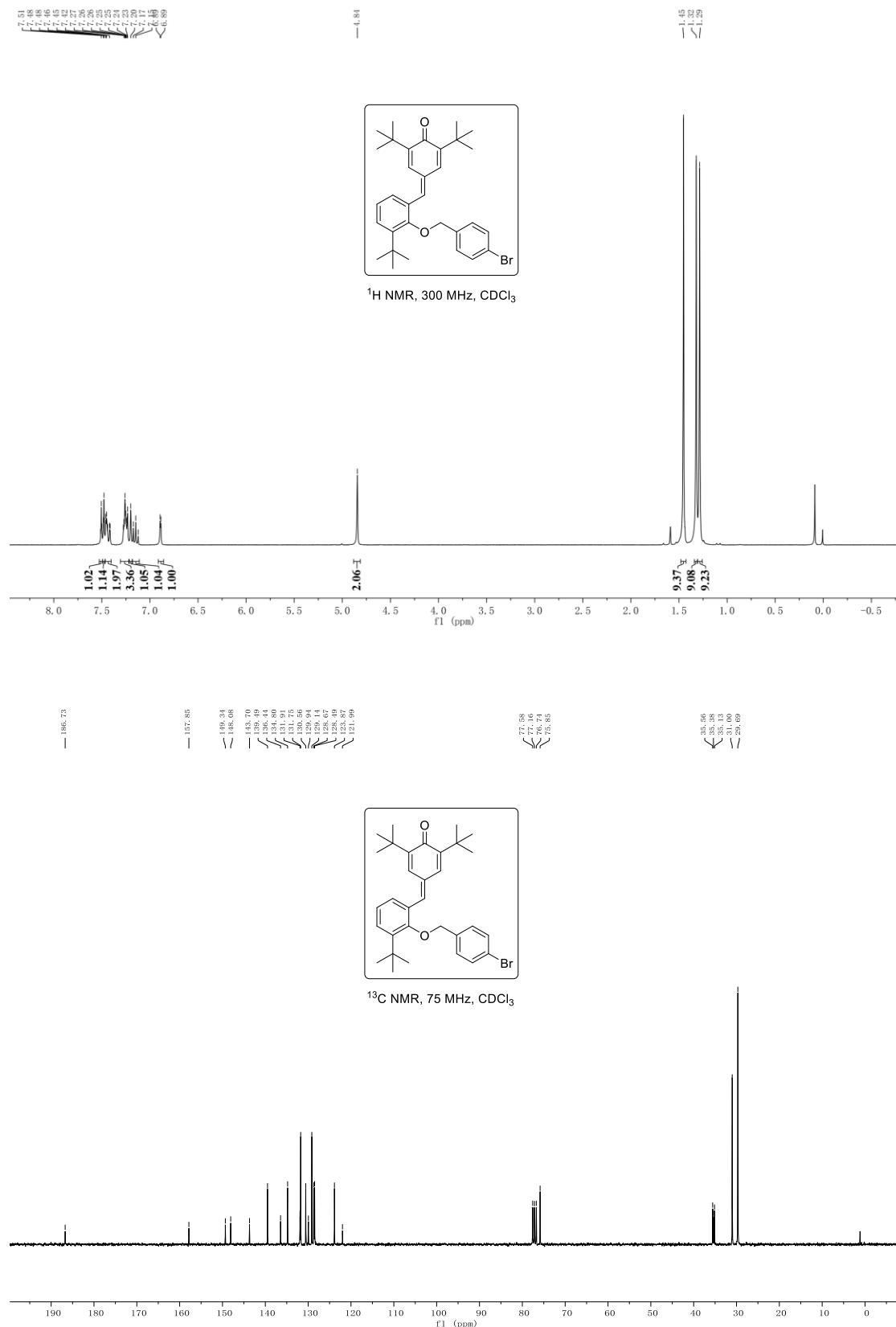
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((3-chlorobenzyl)oxy)benzylidene)cyclohexa-2,5-dien-1-one (1l)**



**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((4-fluorobenzyl)oxy)benzylidene)cyclohexa-2,5-dien-1-one (1m)**



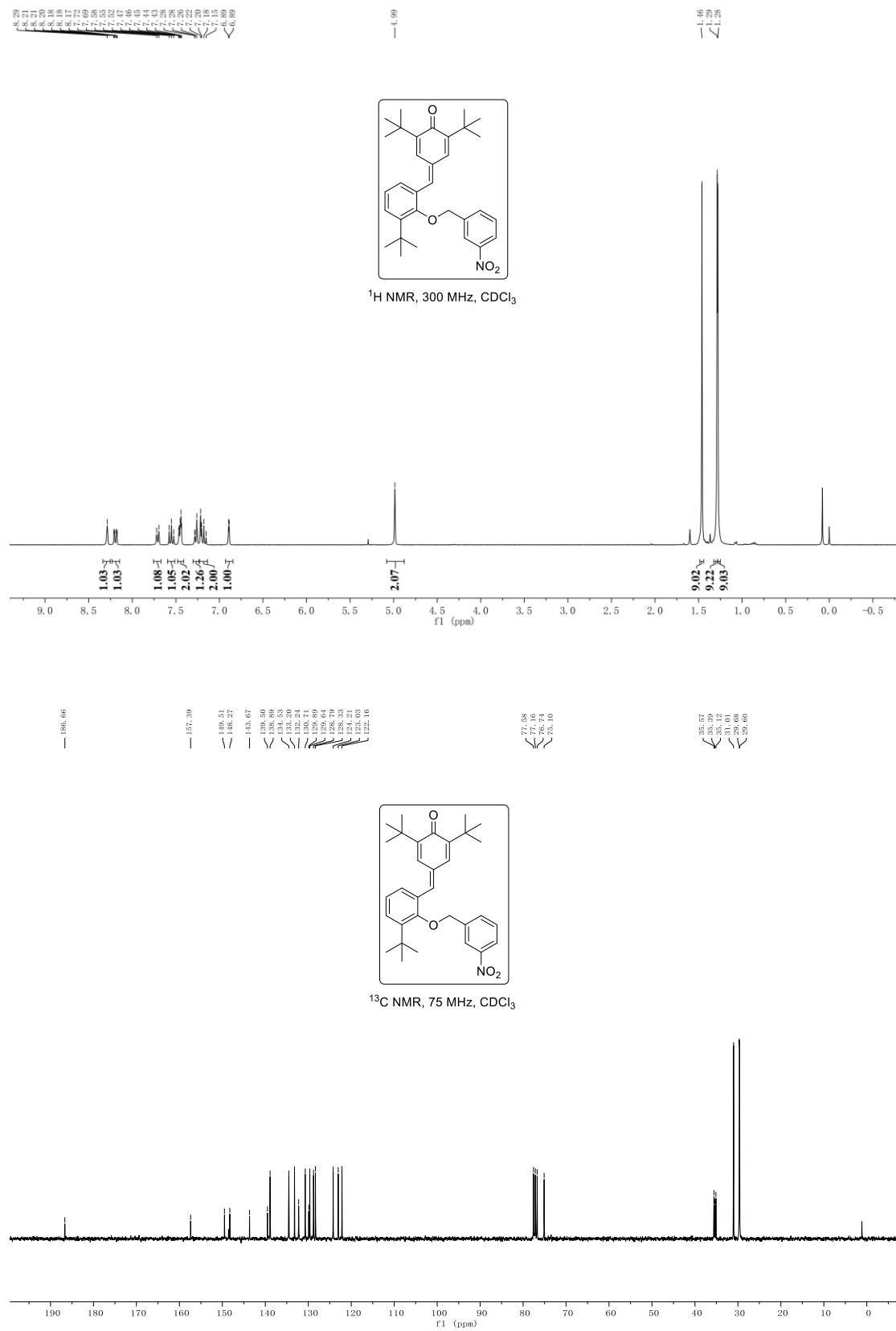
**4-((4-bromobenzyl)oxy)-3-(tert-butyl)benzylidene)-2,6-di-tert-butylecyclohexa-2,5-dien-1-one (**1n**)**



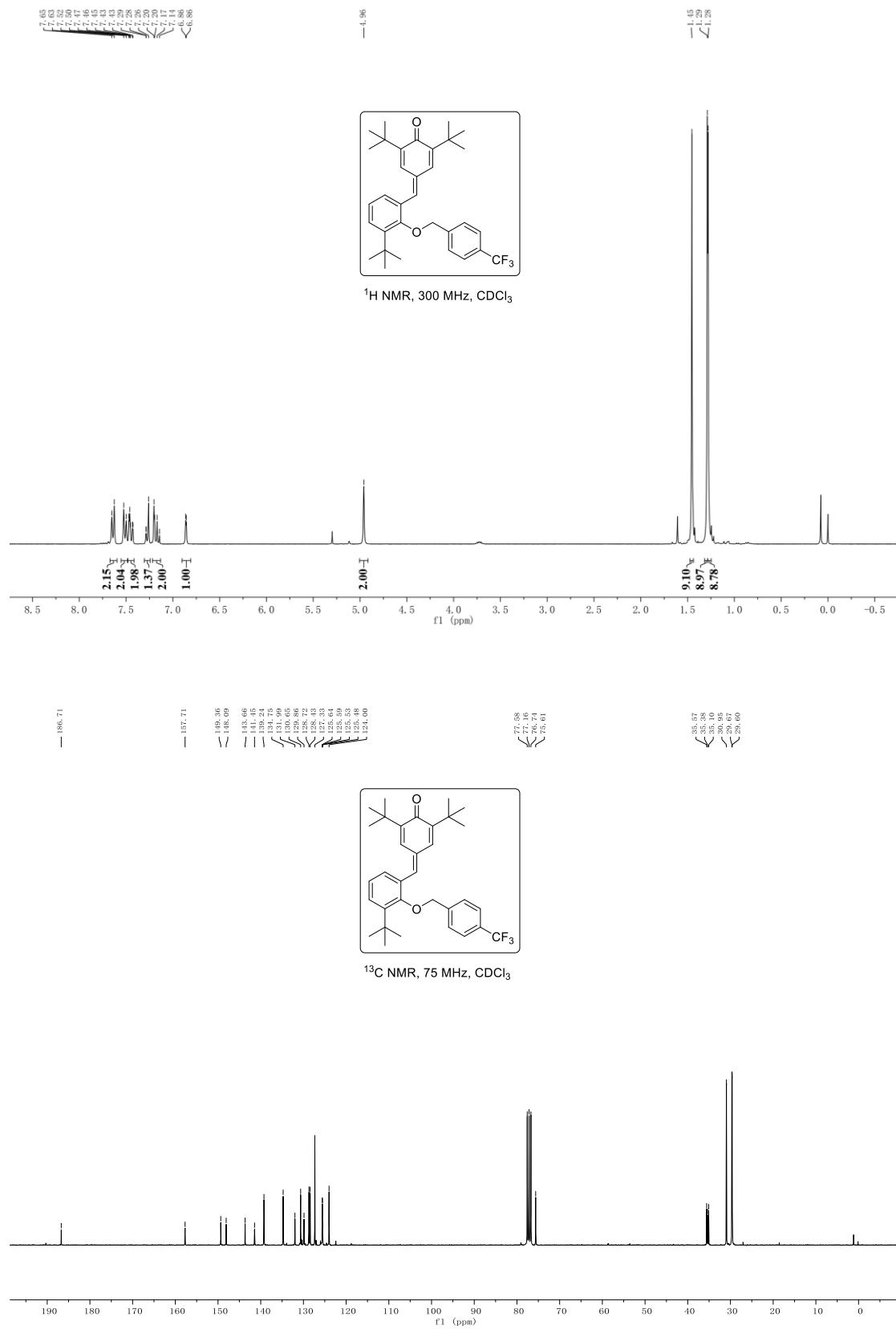
**2-((2-(tert-butyl)-6-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenoxy)methyl)benzonitrile (**1o**)**



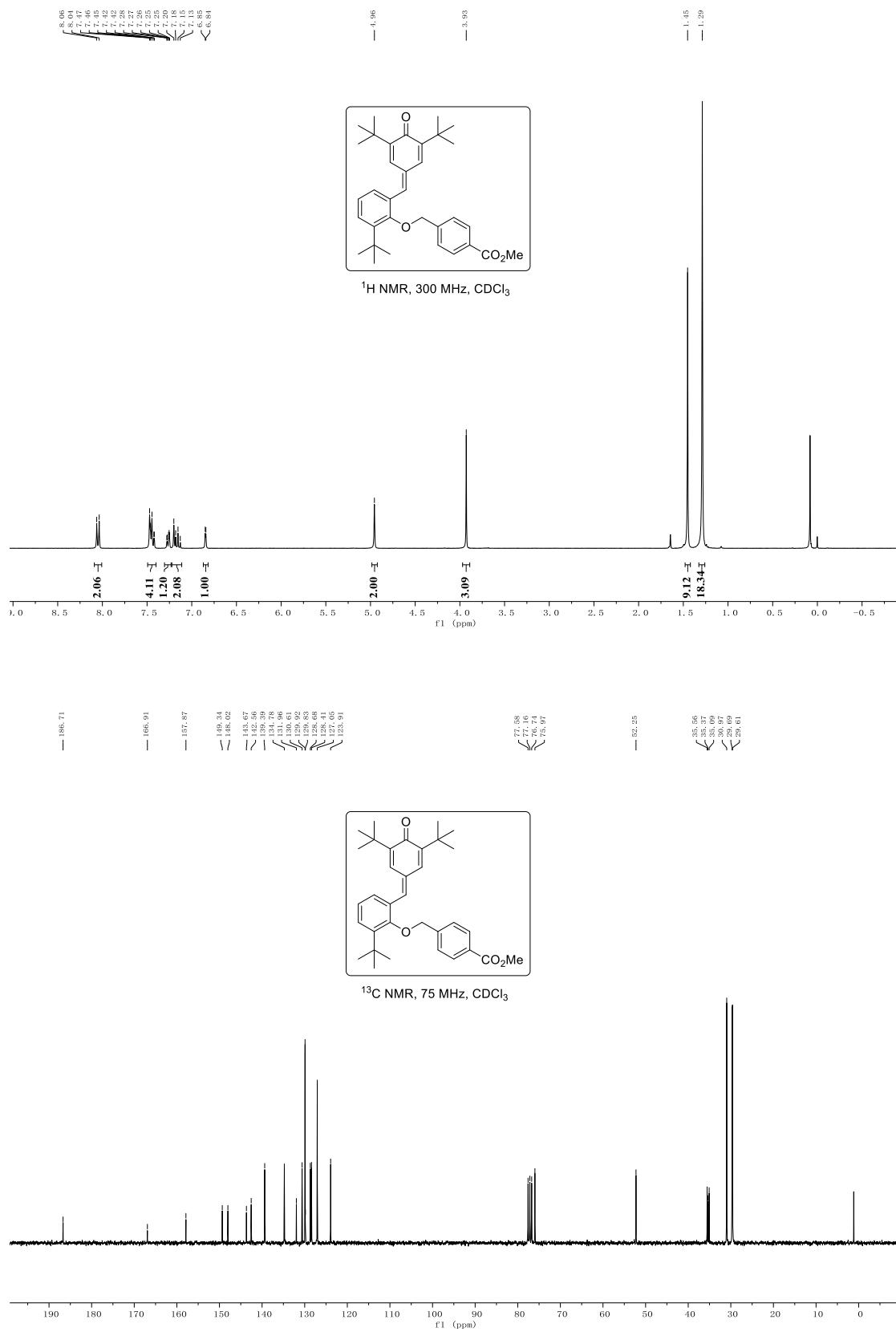
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((3-nitrobenzyl)oxy)benzylidene)cyclohexa-2,5-dien-1-one (1p)**



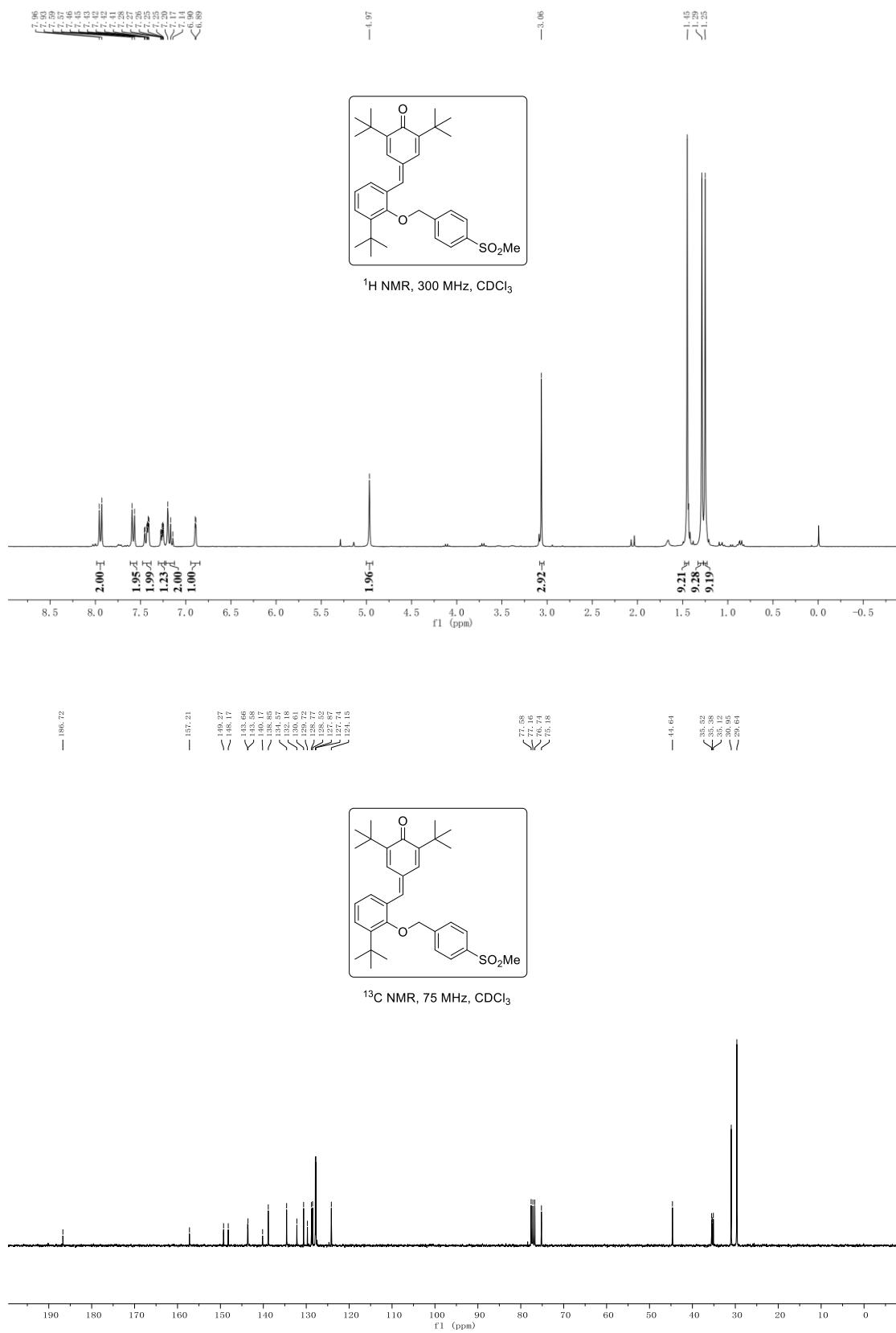
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((4-(trifluoromethyl)benzyl)oxy)benzylidene)cyclohexa-2,5-dien-1-one  
(1q)**



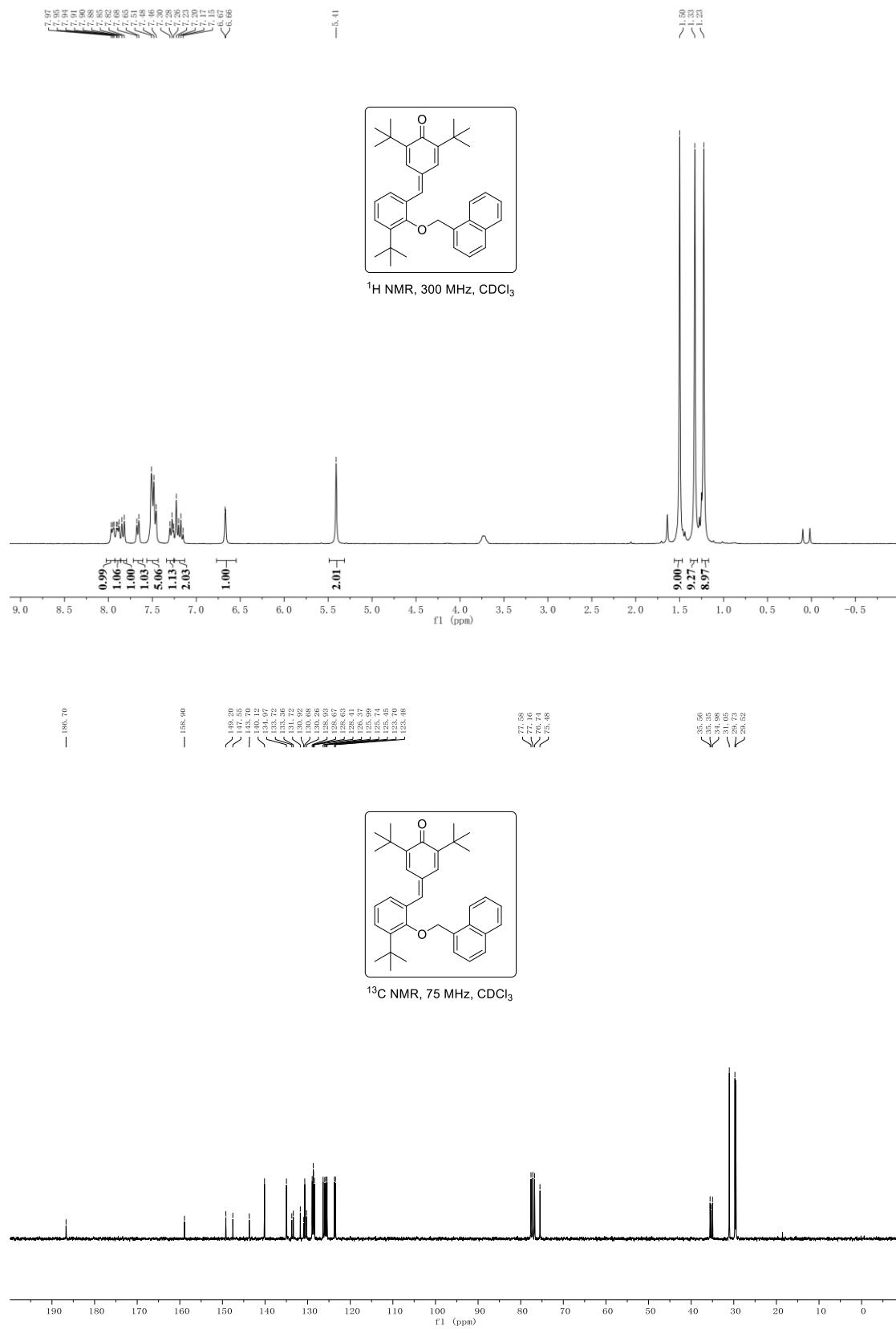
**methyl 4-((2-(tert-butyl)-6-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene) methyl) phenoxy) methyl) benzoate (1r)**



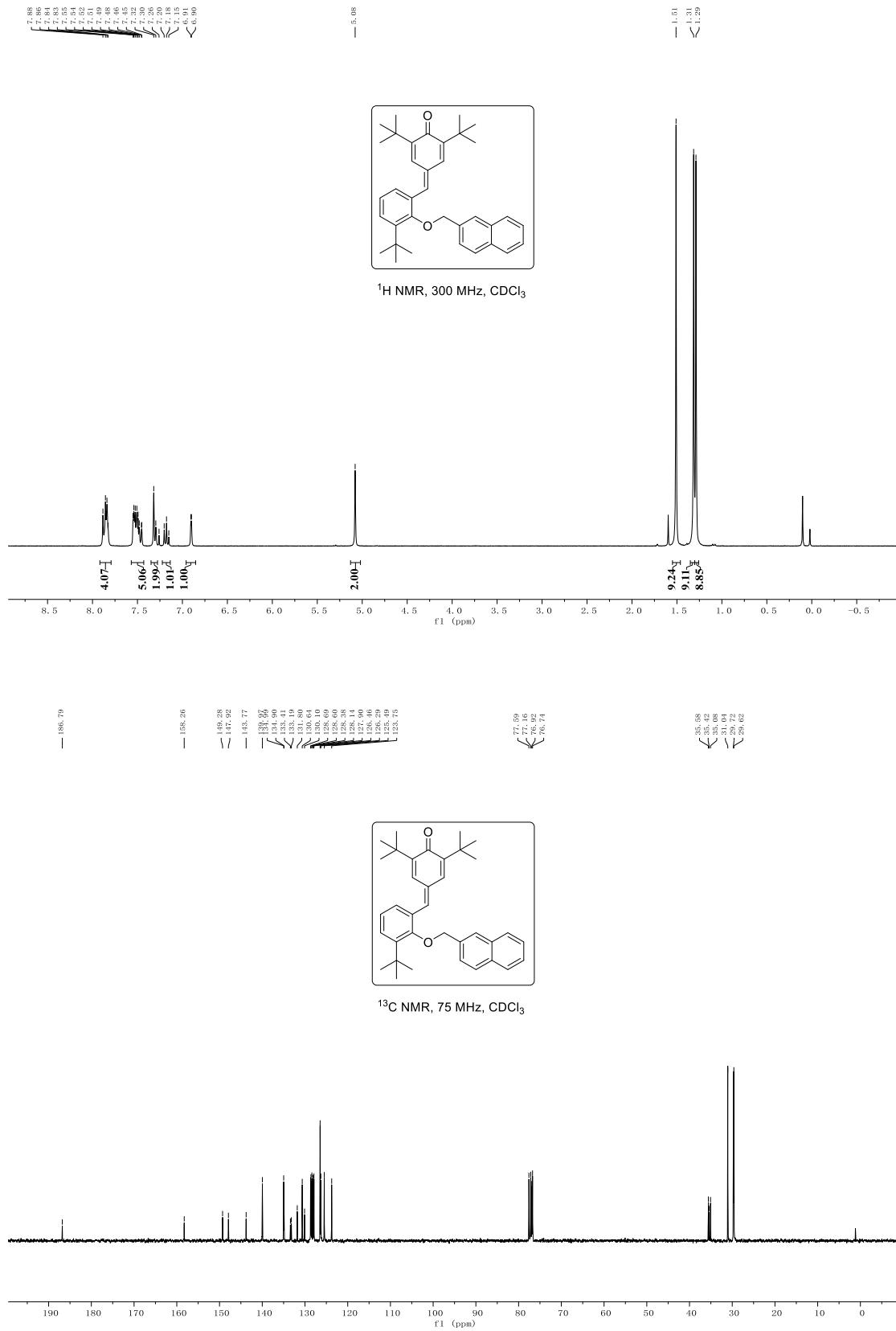
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((4-(methylsulfonyl)benzyl)oxy)benzylidene)cyclohexa-2,5-dien-1-one  
(1s)**



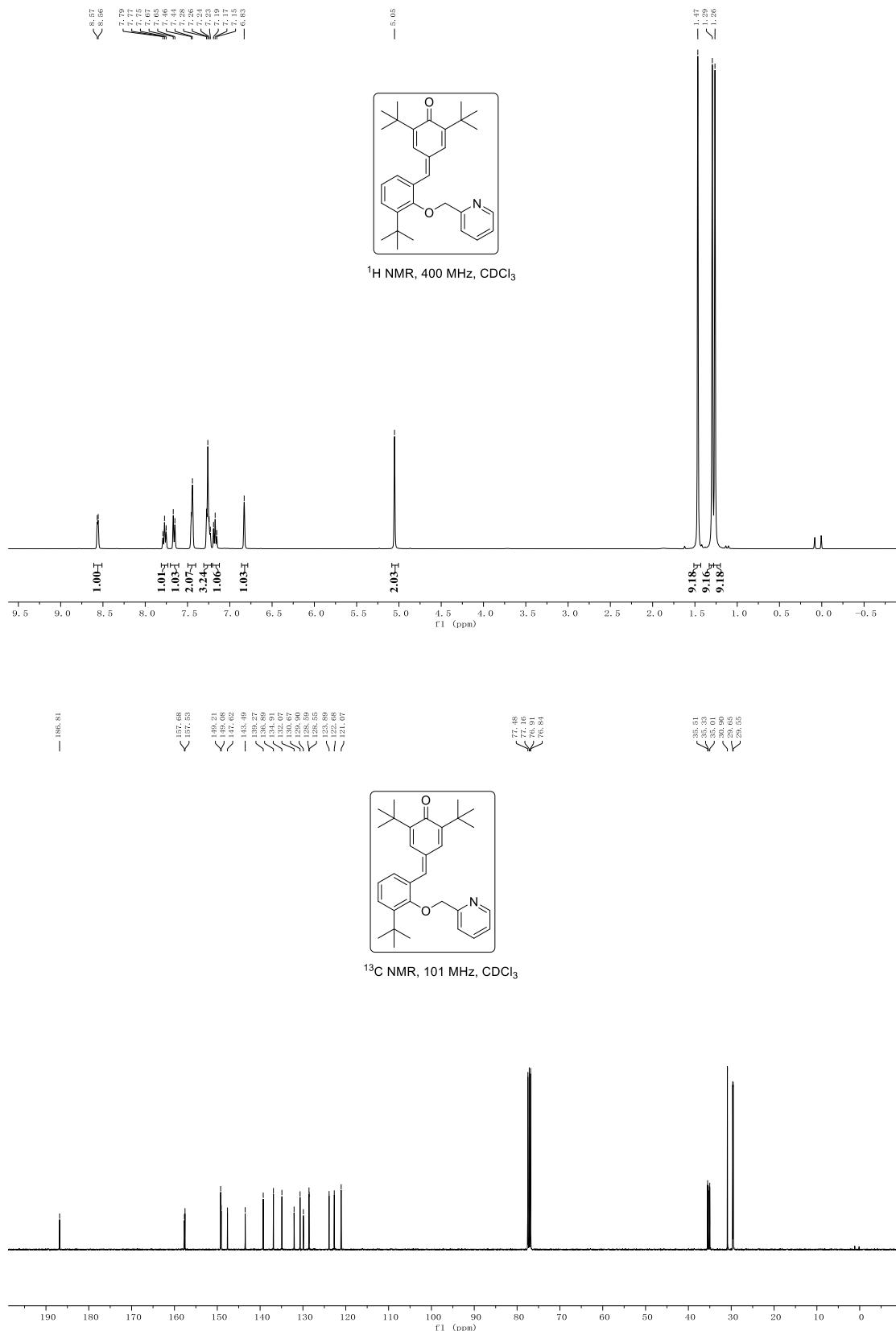
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-(naphthalen-1-ylmethoxy)benzylidene)cyclohexa-2,5-dien-1-one (1t)**



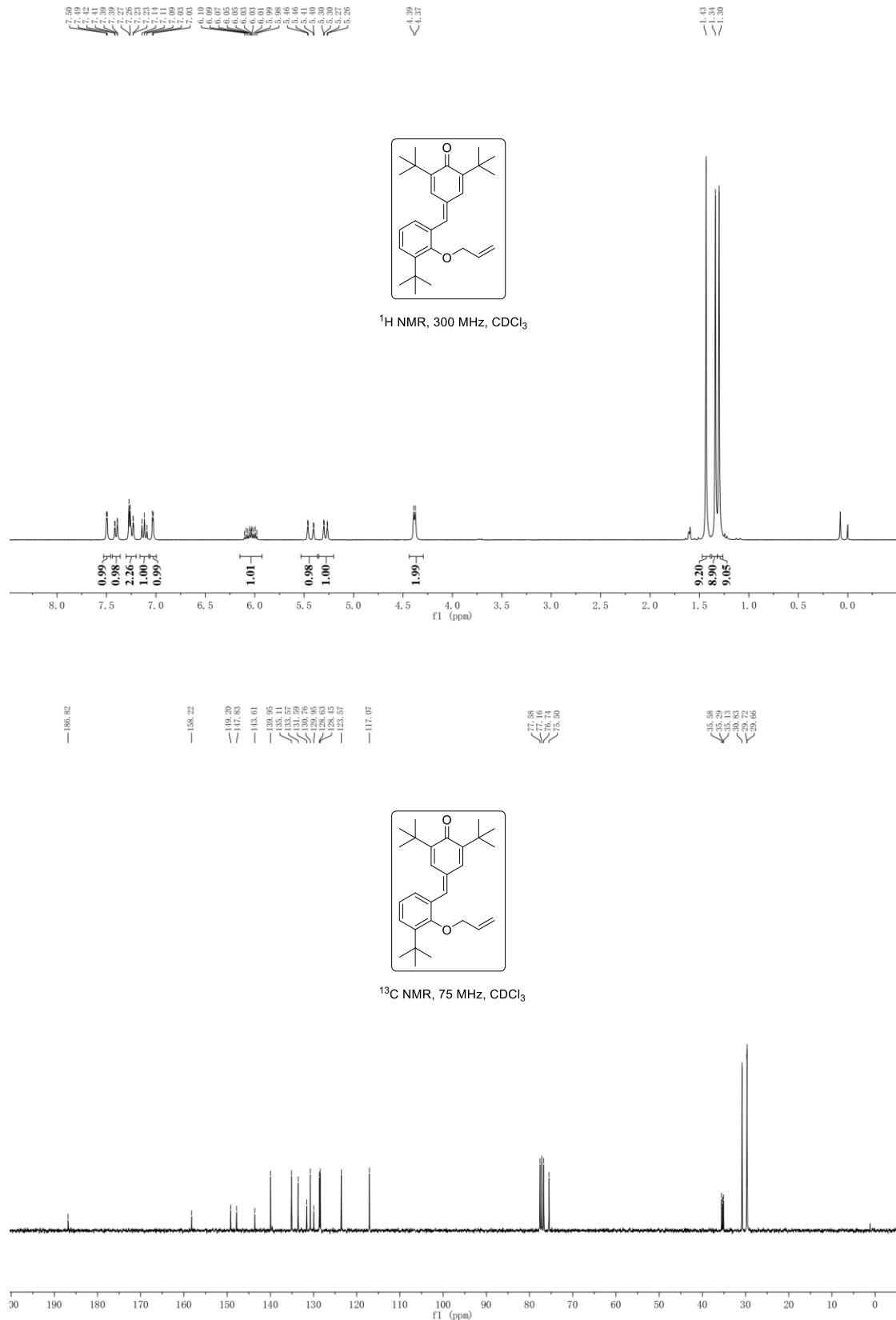
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-(naphthalen-2-ylmethoxy)benzylidene)cyclohexa-2,5-dien-1-one (1u)**



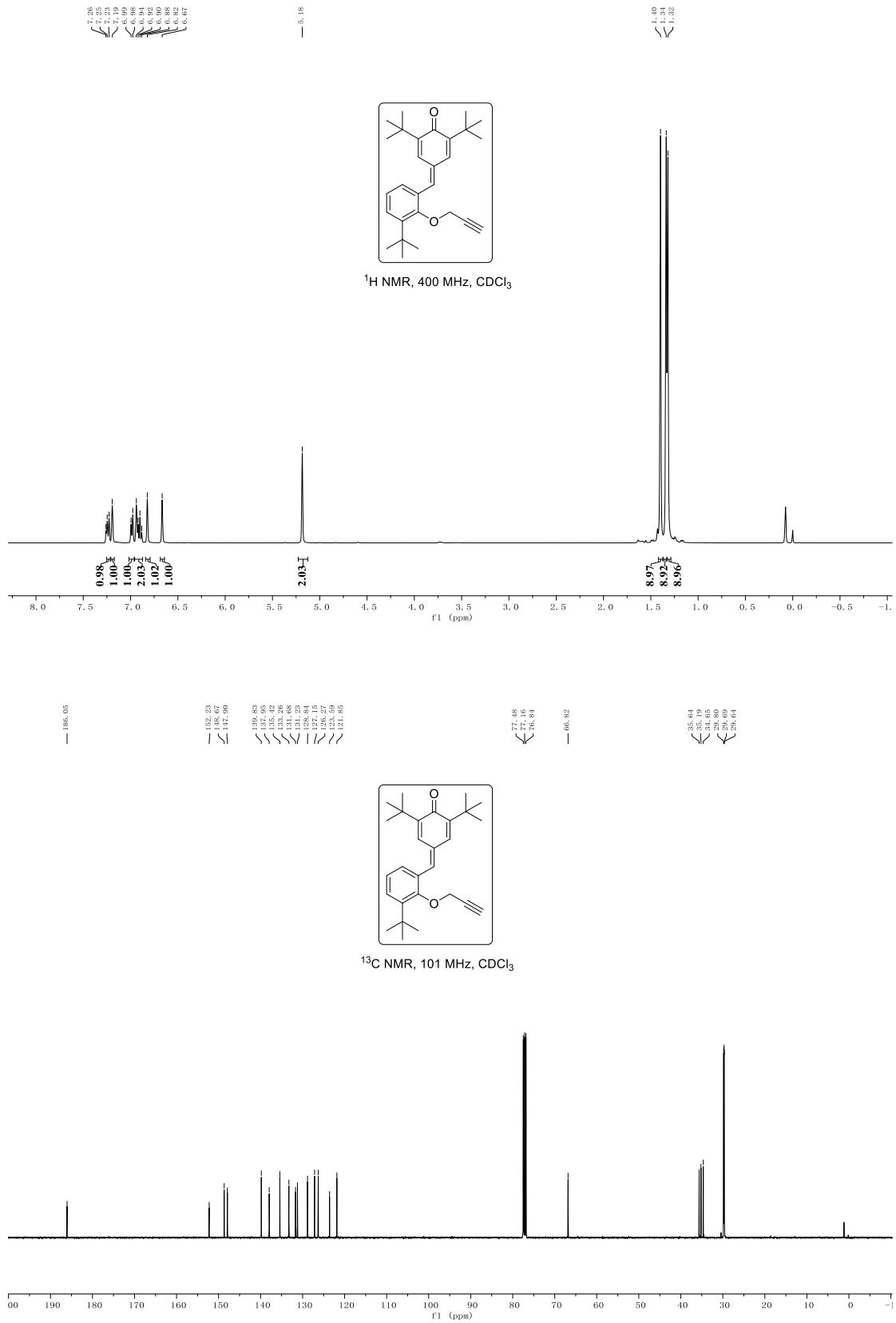
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-(pyridin-2-ylmethoxy)benzylidene)cyclohexa-2,5-dien-1-one (1v)**



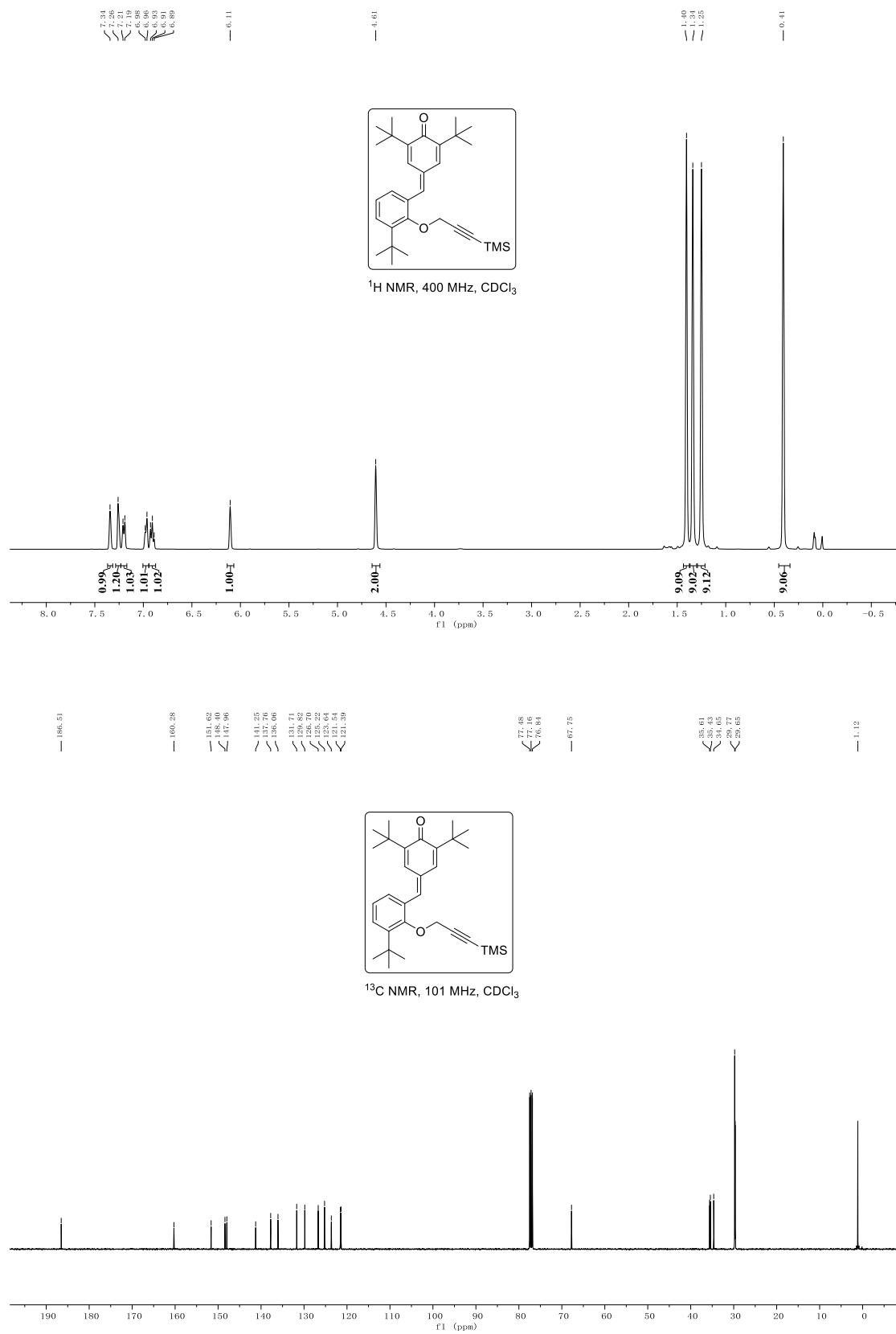
**4-(2-(allyloxy)-3-(tert-butyl)benzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1w)**



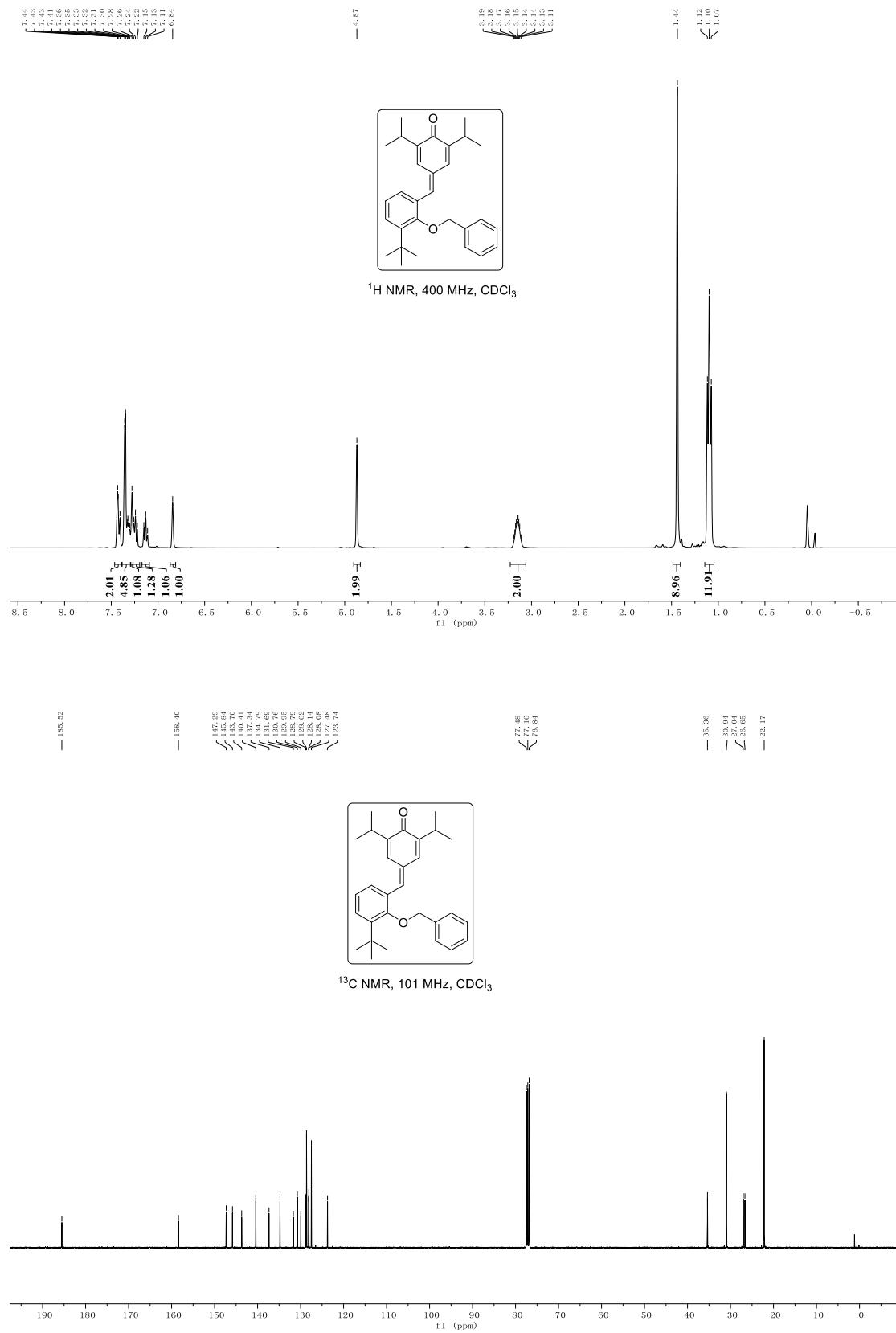
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-(prop-2-yn-1-yloxy)benzylidene)cyclohexa-2,5-dien-1-one (1x)**



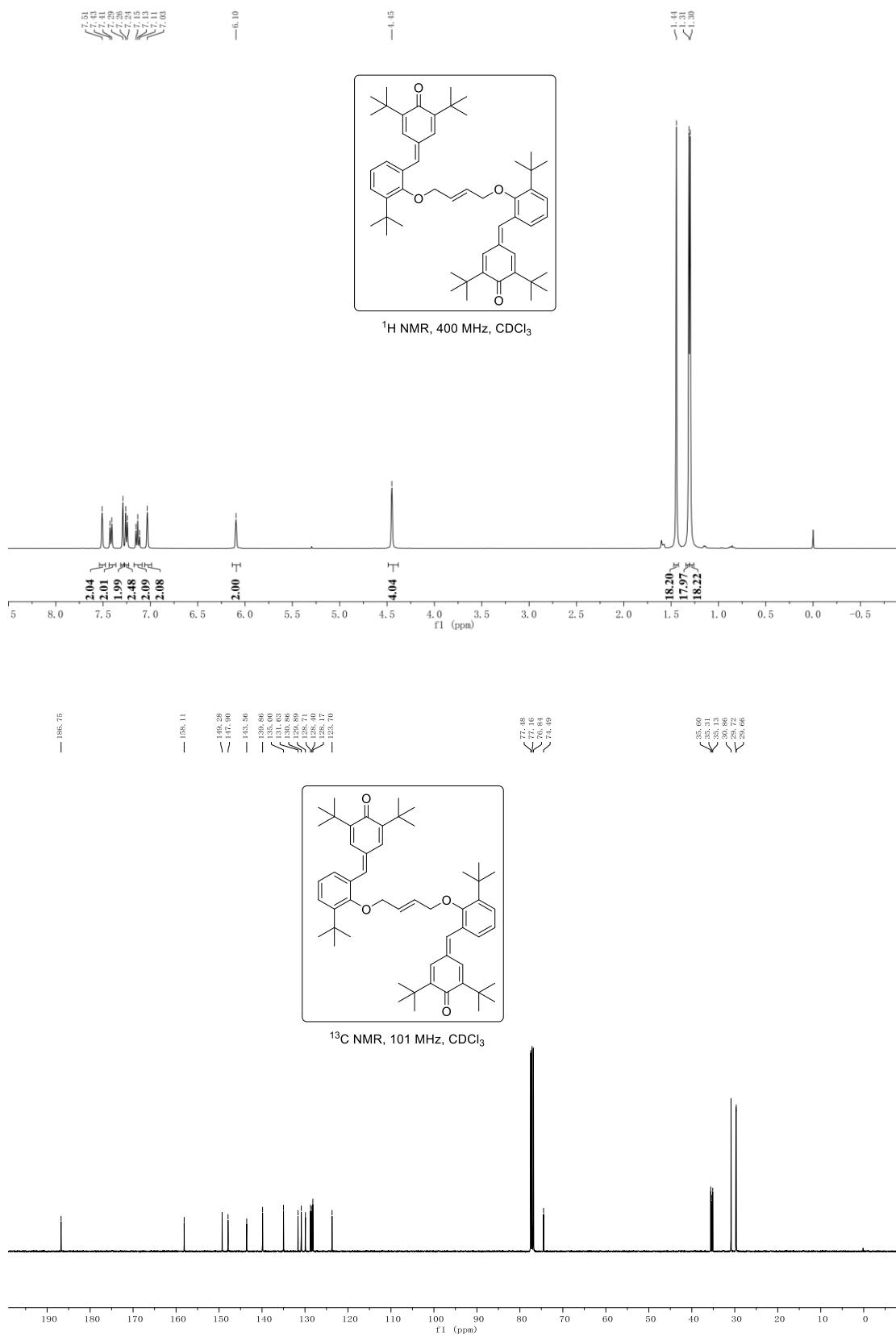
**2,6-di-tert-butyl-4-(3-(tert-butyl)-2-((3-(trimethylsilyl)prop-2-yn-1-yl)oxy)benzylidene)cyclohexa-2,5-dien-1-one (1y)**



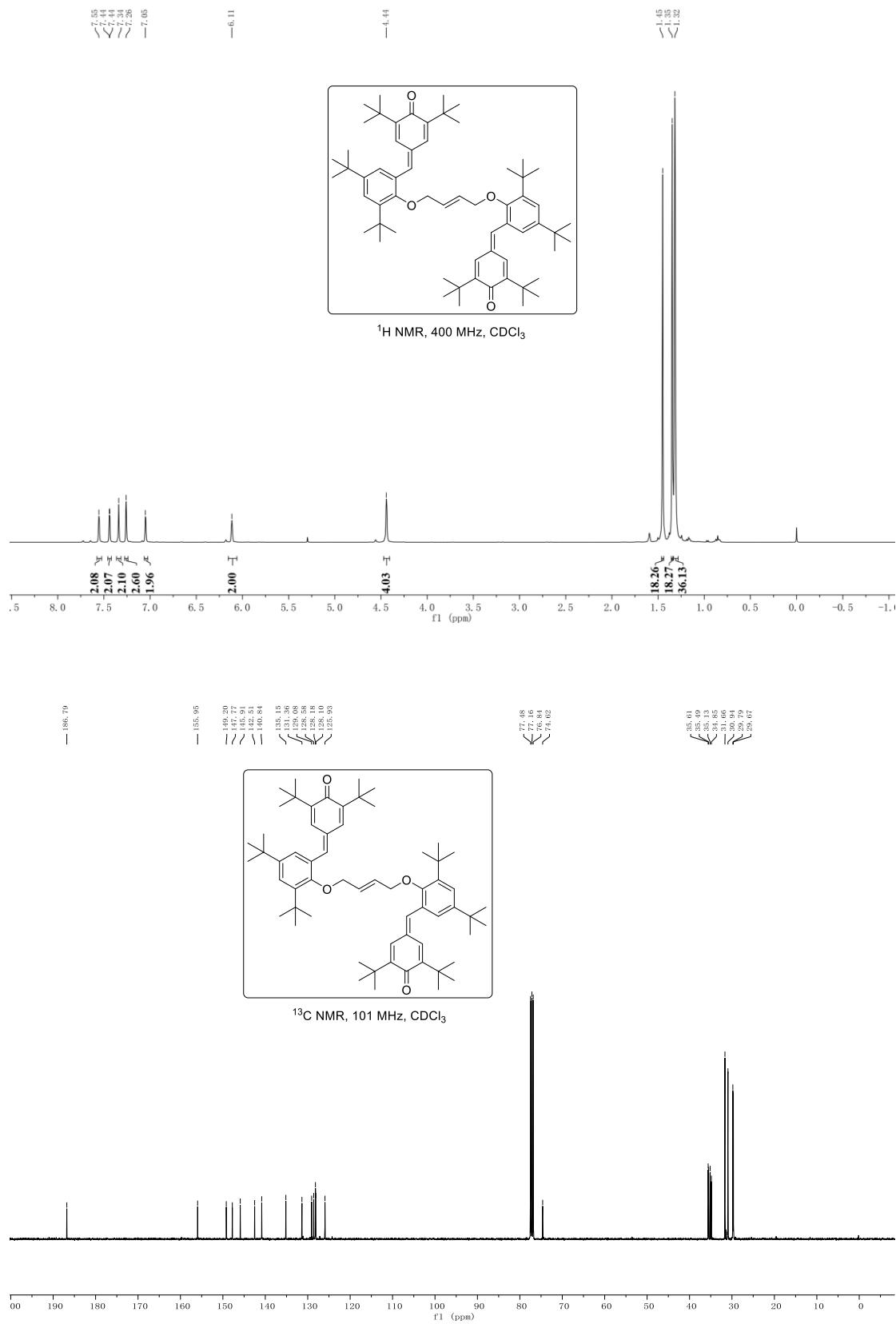
**4-(2-(benzyloxy)-3-(tert-butyl)benzylidene)-2,6-diisopropylcyclohexa-2,5-dien-1-one (1z)**



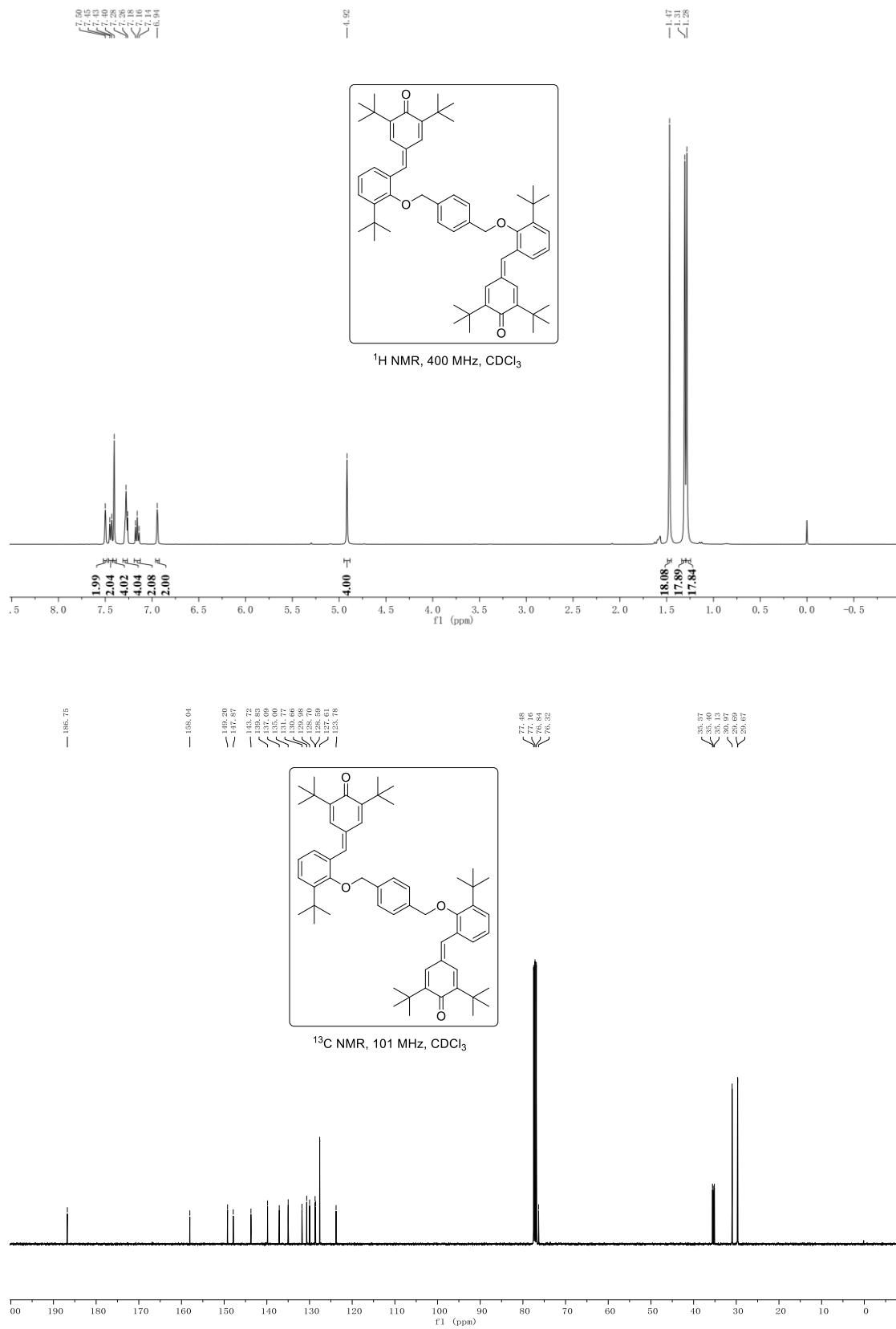
**(E)-4,4'-(((but-2-ene-1,4-diylbis(oxy))bis(3-(tert-butyl)-2,1-phenylene))bis(methaneylylidene))bis(2,6-di-tert-butylcyclohexa-2,5-dien-1-one) (1za)**



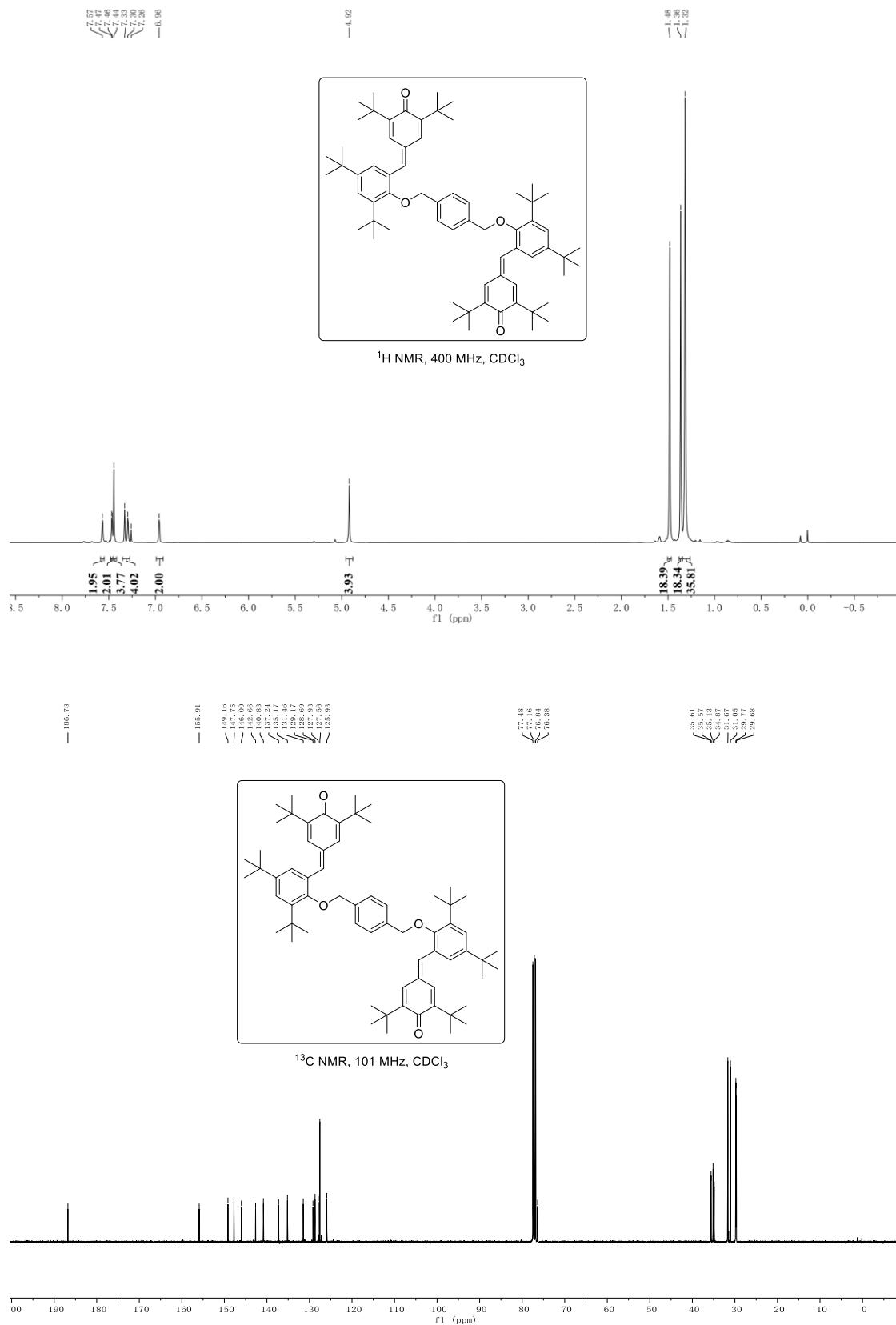
**(E)-4,4'-(((but-2-ene-1,4-diylbis(oxy))bis(3,5-di-tert-butyl-2,1-phenylene))bis(methanelylidene))bis(2,6-di-tert-butylcyclohexa-2,5-dien-1-one) (1zb)**



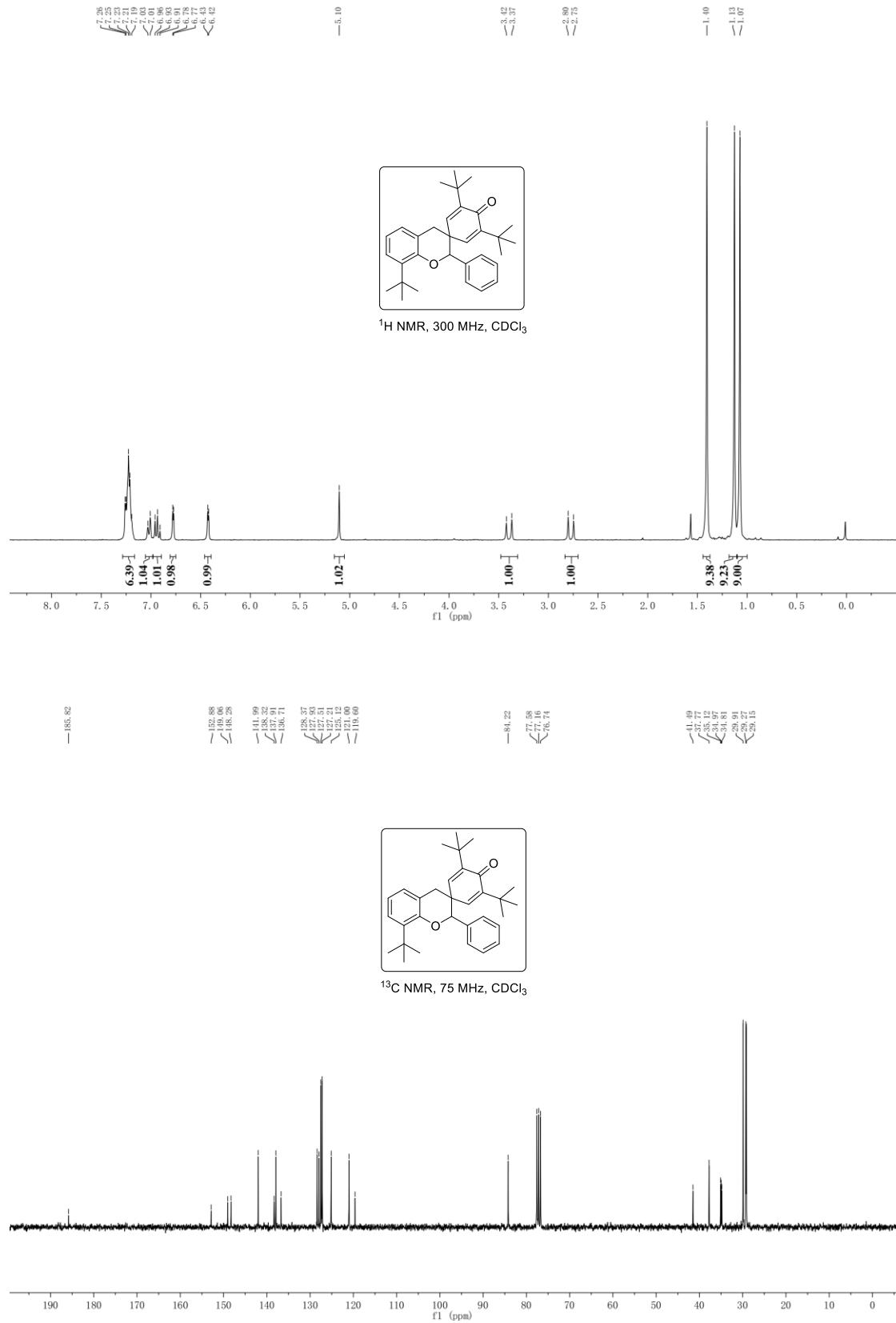
**4,4'-((((1,4-phenylenebis(methylene))bis(oxy))bis(3-(tert-butyl)-2,1-phenylene))bis(methaneylylidene))  
bis(2,6-di-tert-butylcyclohexa-2,5-dien-1-one) (1zc)**



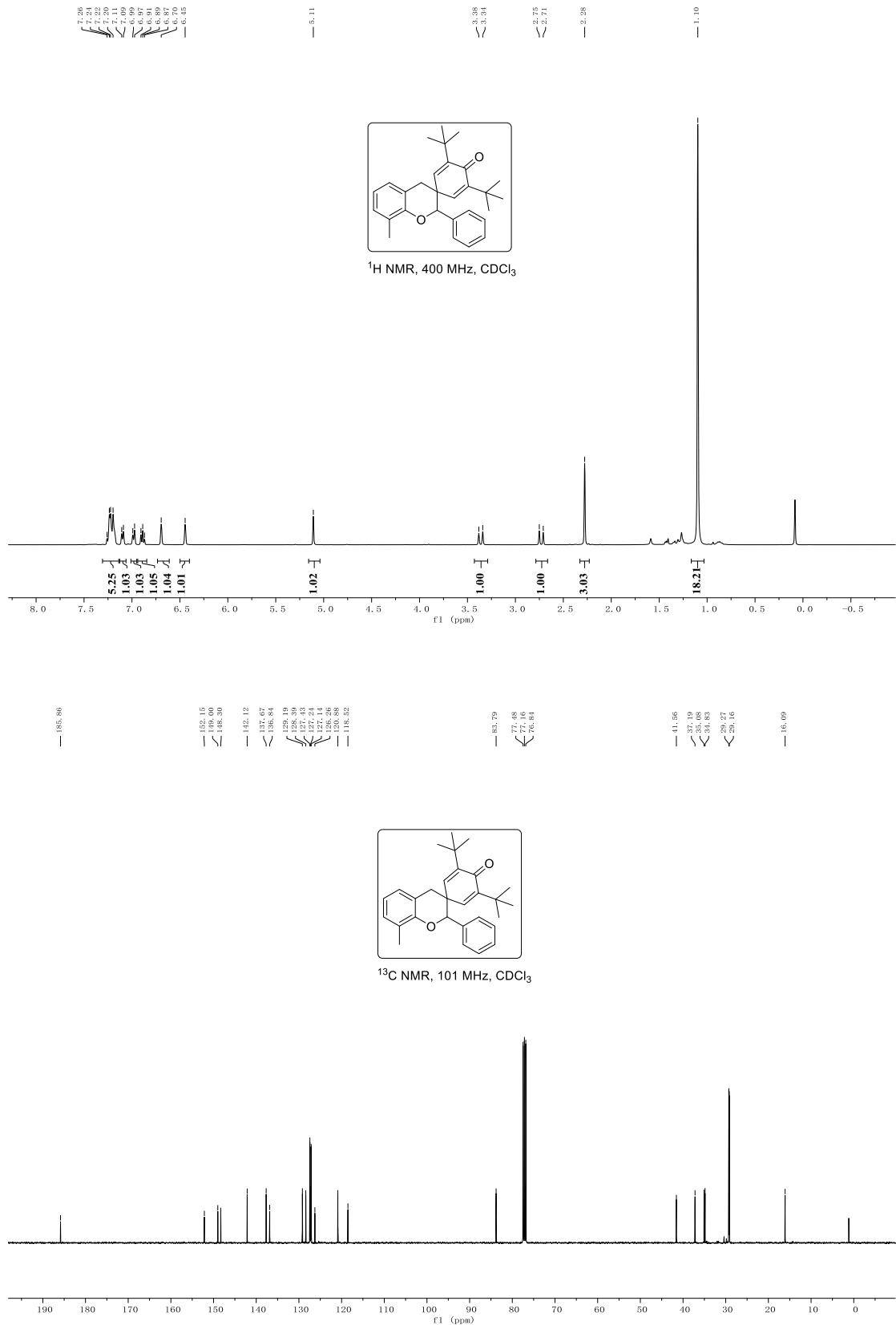
**4,4'-((((1,4-phenylenebis(methylene))bis(oxy))bis(3,5-di-tert-butyl-2,1-phenylene))bis(methaneylylidene))bis  
(2,6-di-tert-butylecyclohexa-2,5-dien-1-one) (1zd)**



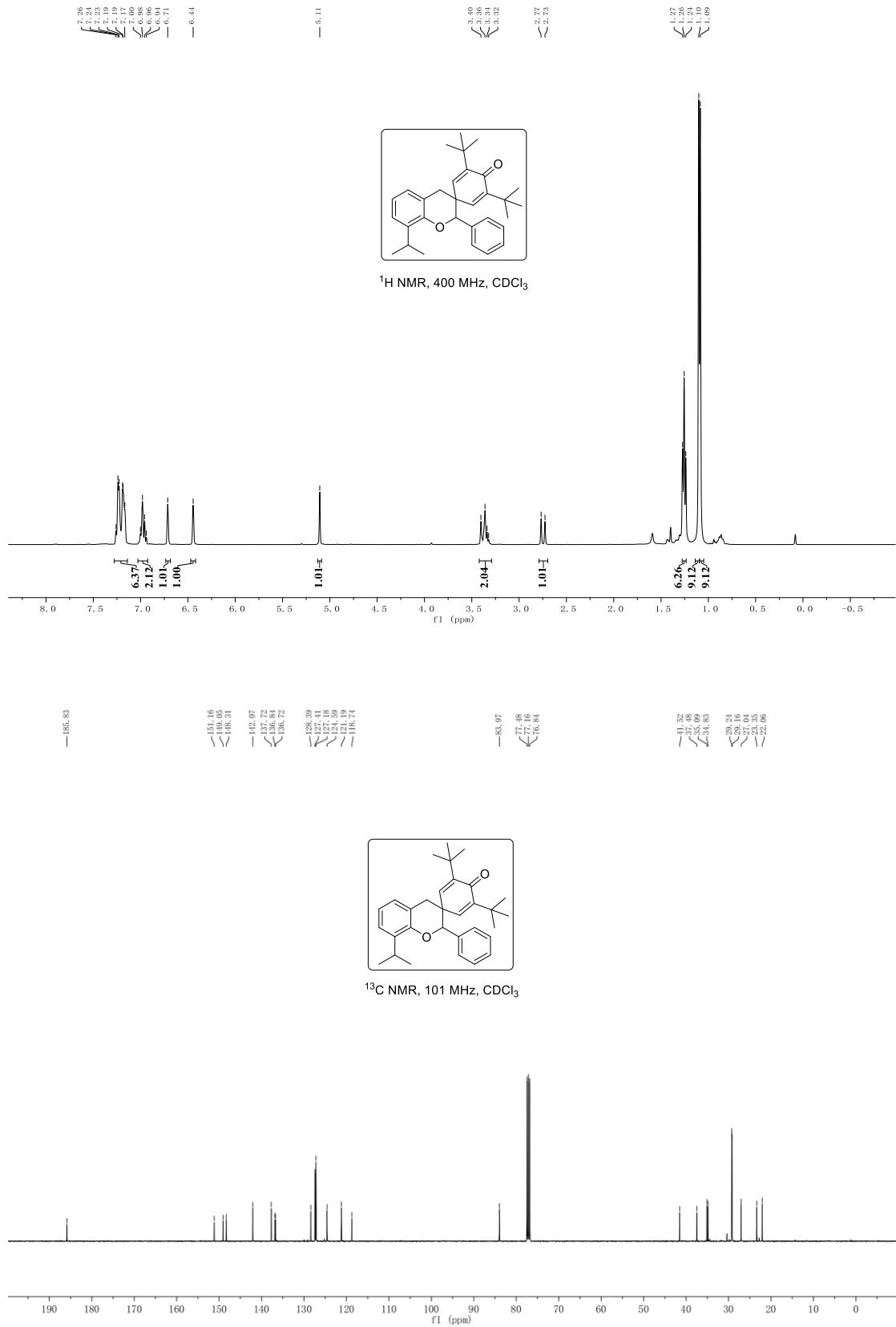
**3',5',8-tri-tert-butyl-2-phenylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2a)**



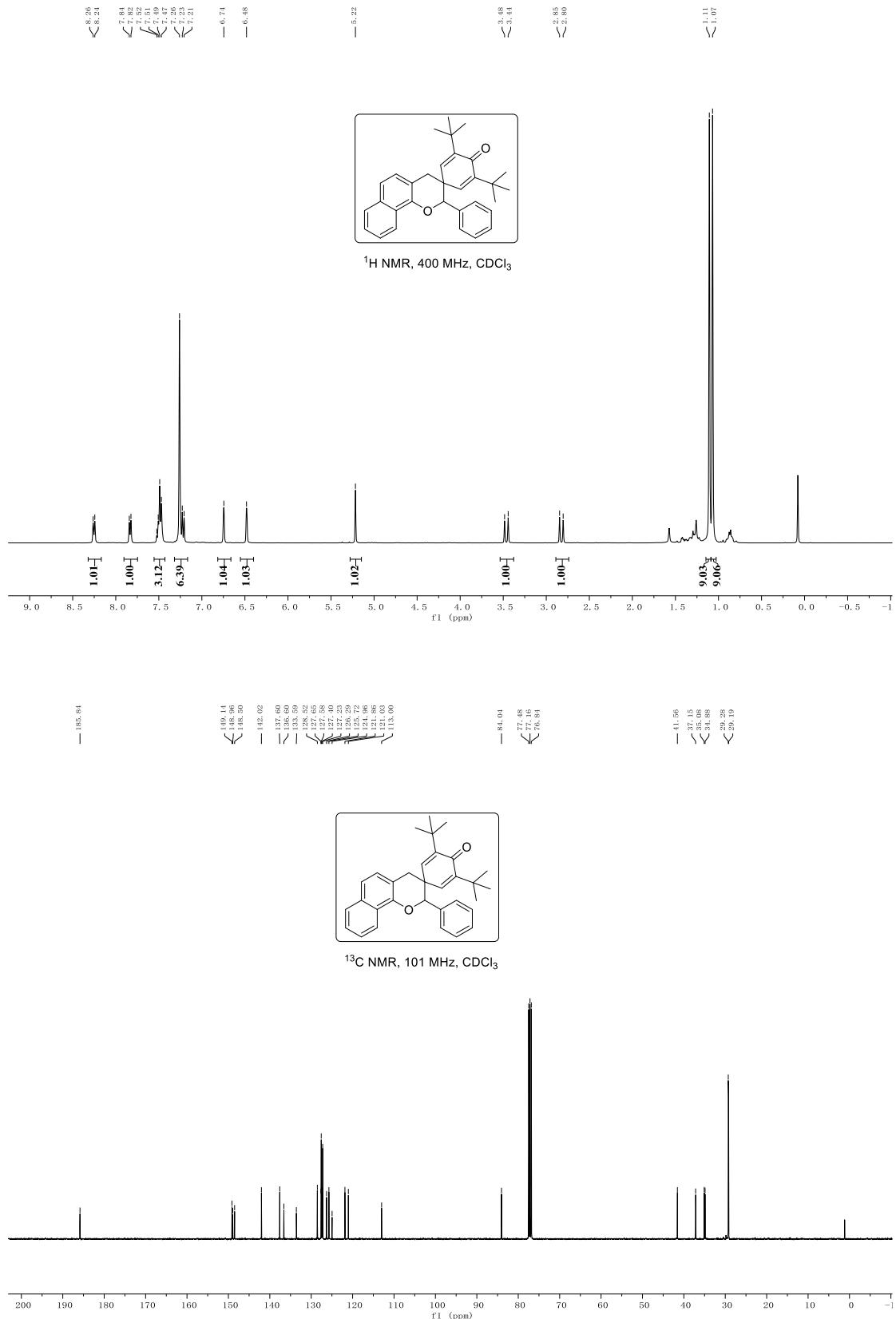
**3',5'-di-tert-butyl-8-methyl-2-phenylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2b)**



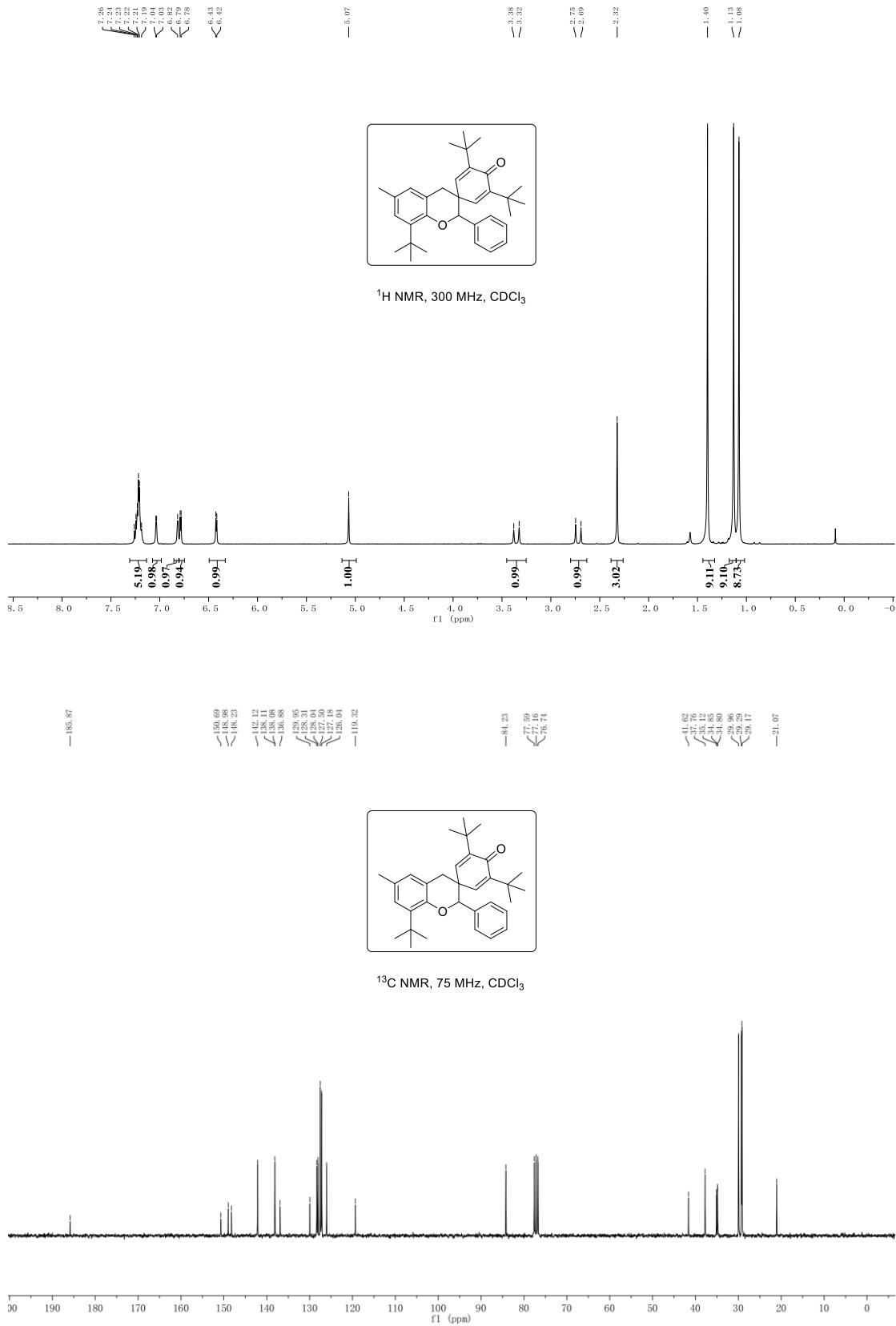
**3',5'-di-tert-butyl-8-isopropyl-2-phenylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2c)**



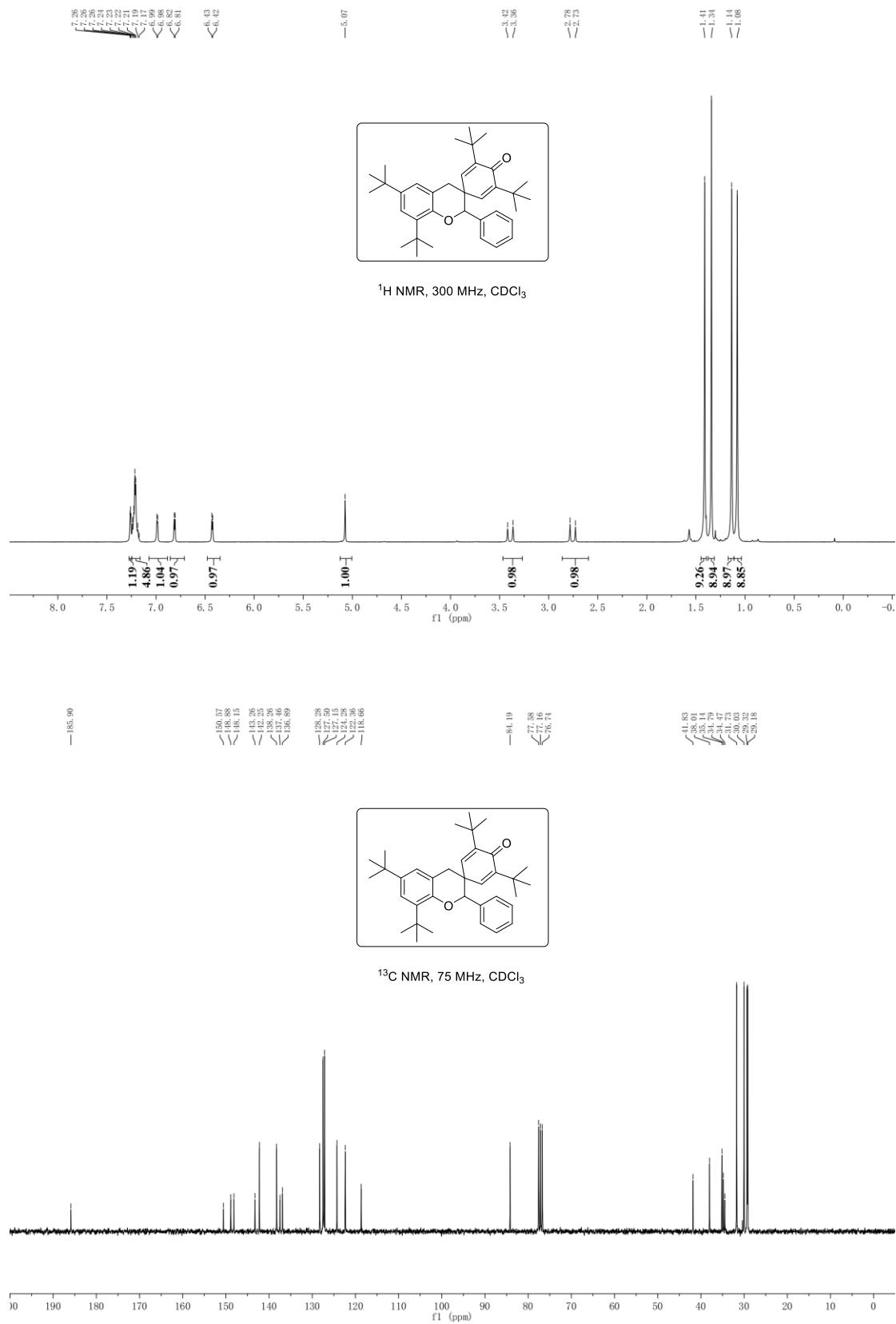
**3',5'-di-tert-butyl-2-phenyl-2H,4H-spiro[benzo[h]chromene-3,1'-cyclohexane]-2',5'-dien-4'-one (2d)**



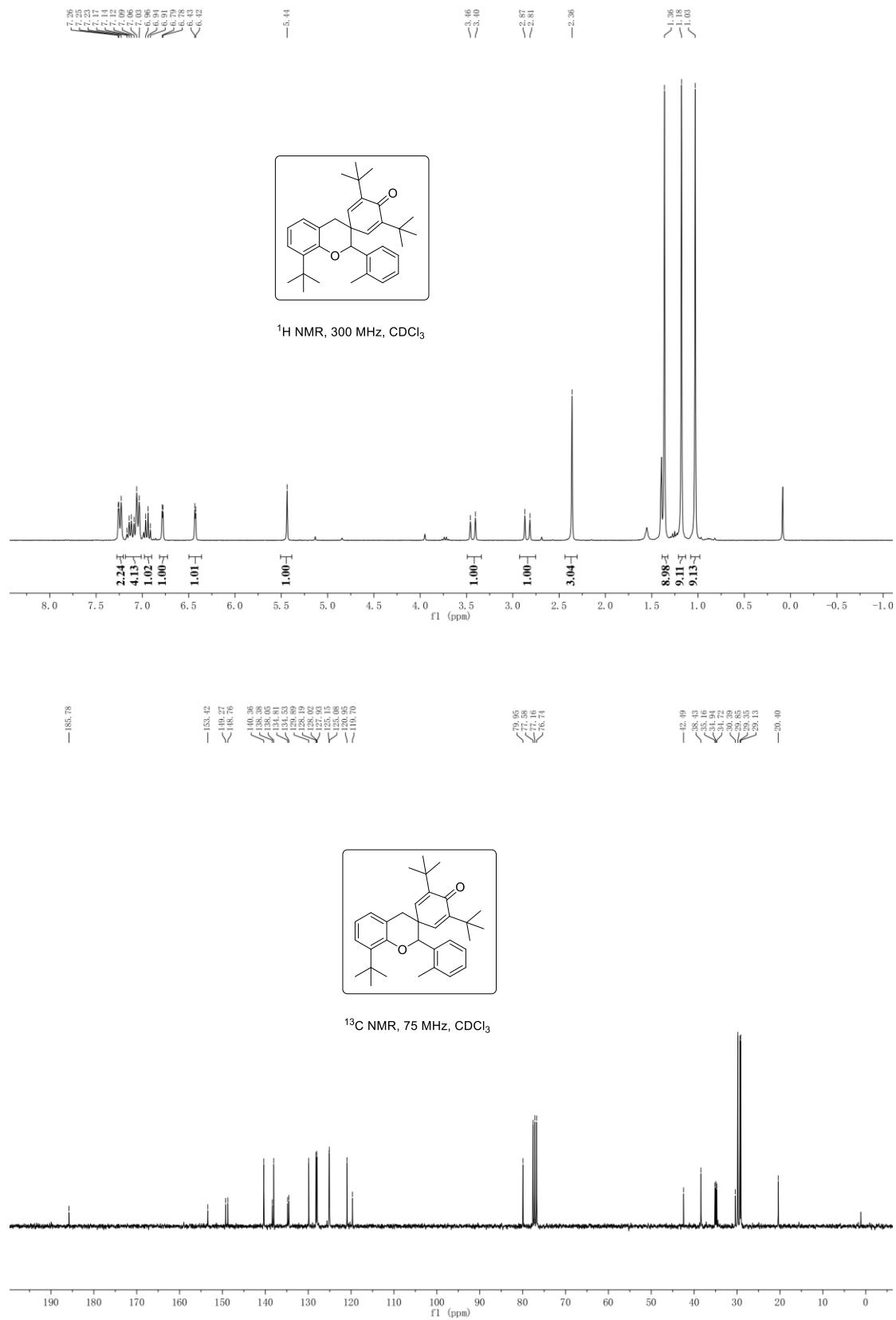
**3',5',8-tri-tert-butyl-6-methyl-2-phenylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2e)**



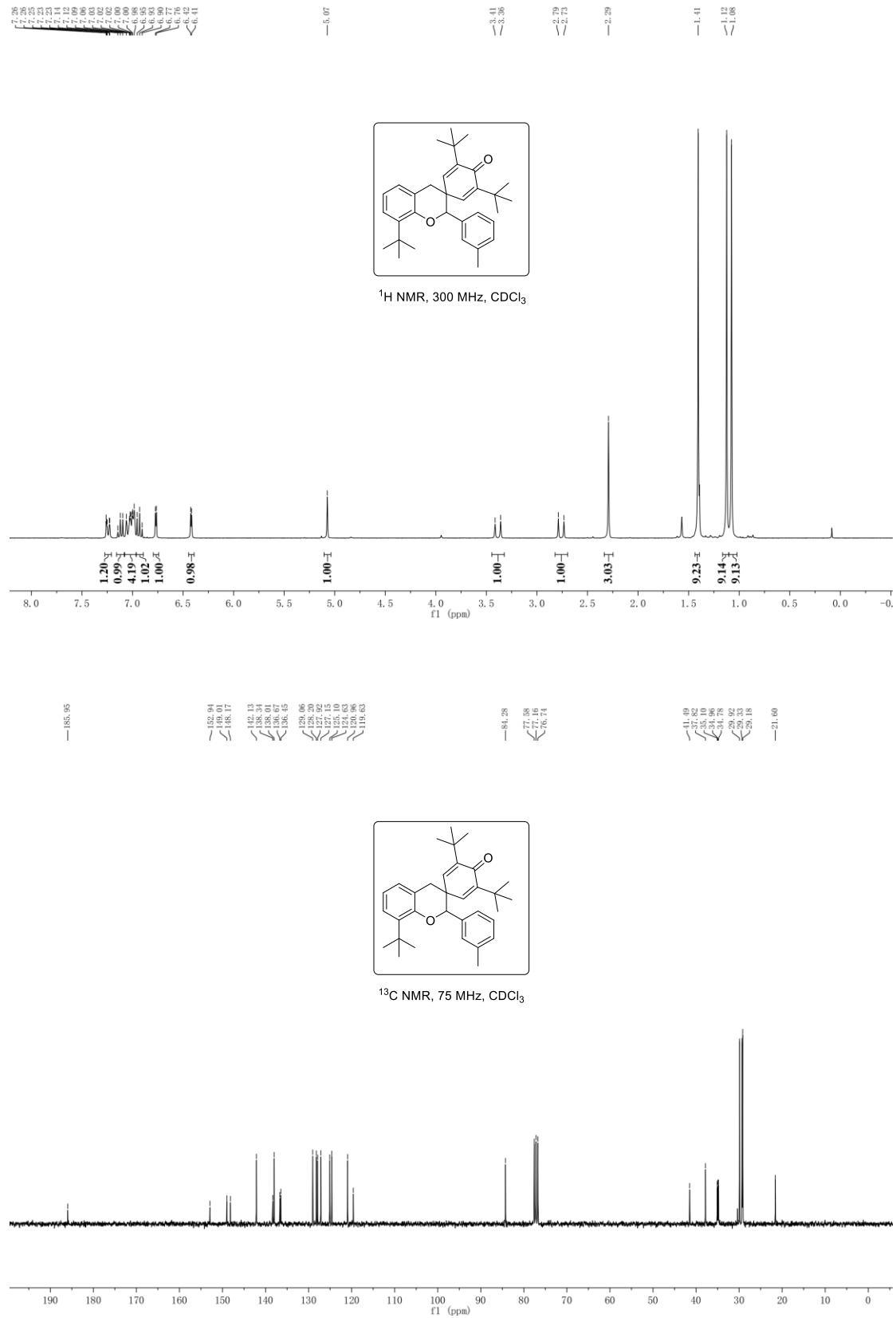
**3',5',6,8-tetra-tert-butyl-2-phenylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2f)**



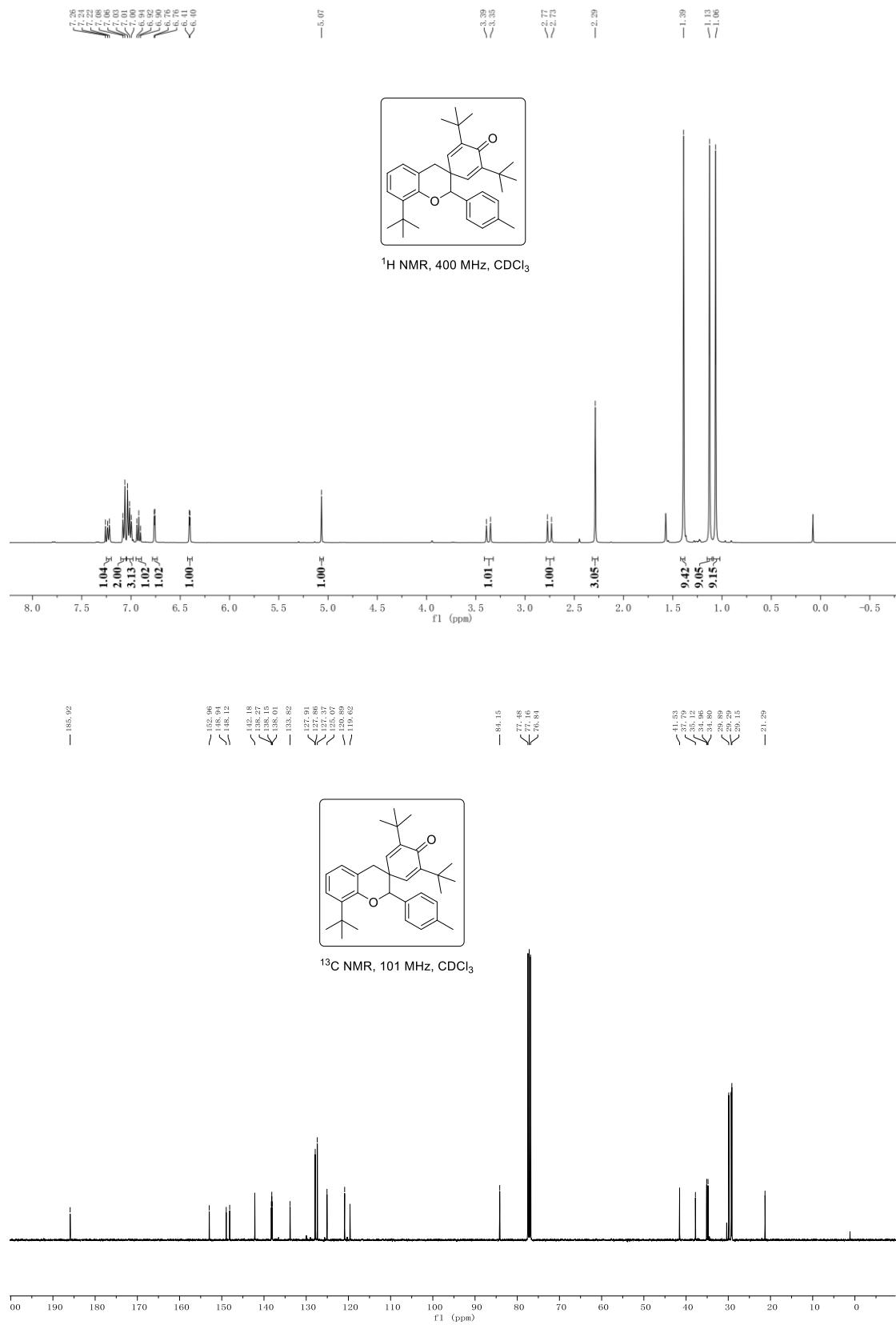
**3',5',8-tri-tert-butyl-2-(o-tolyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2g)**



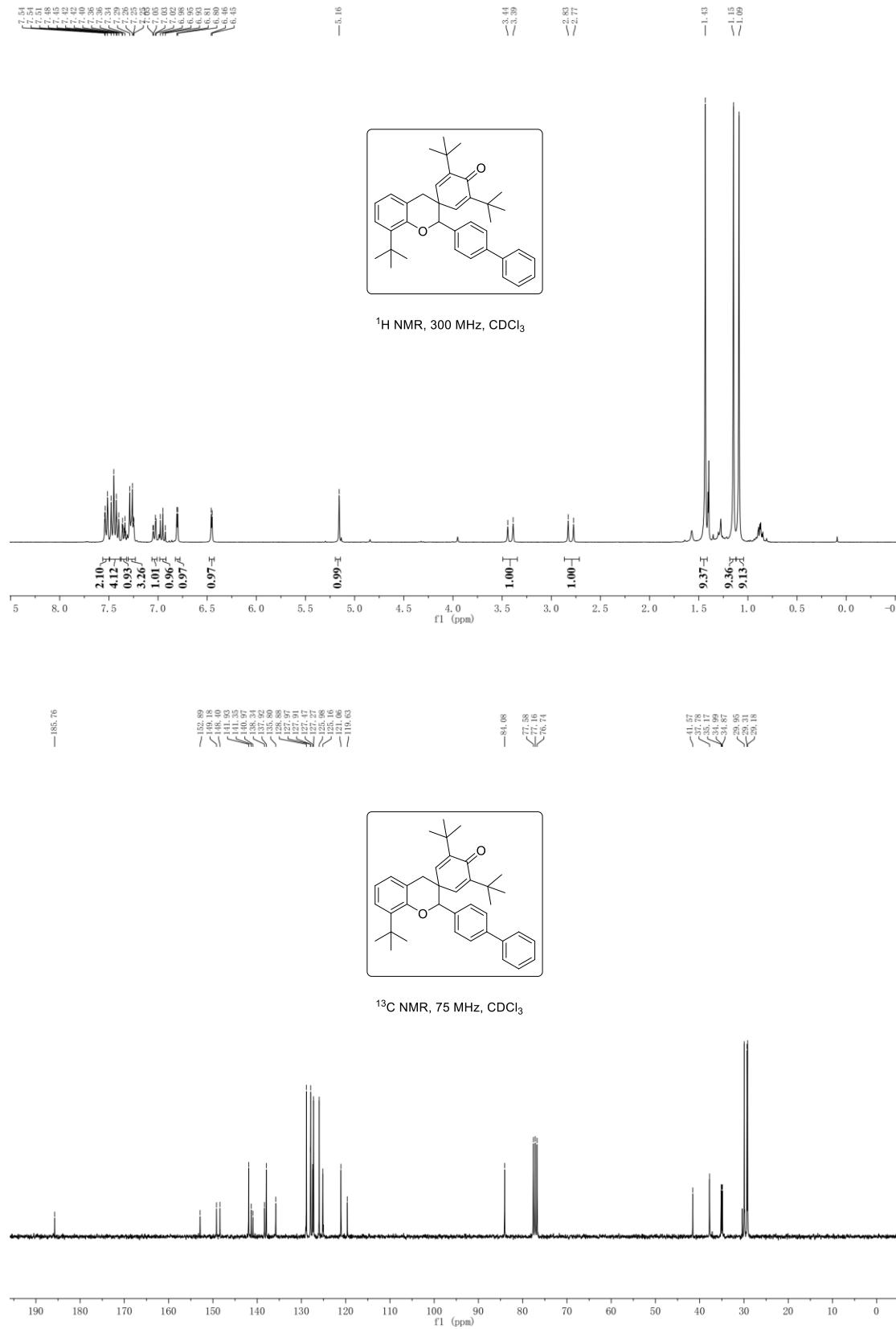
**3',5',8-tri-tert-butyl-2-(m-tolyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2h)**



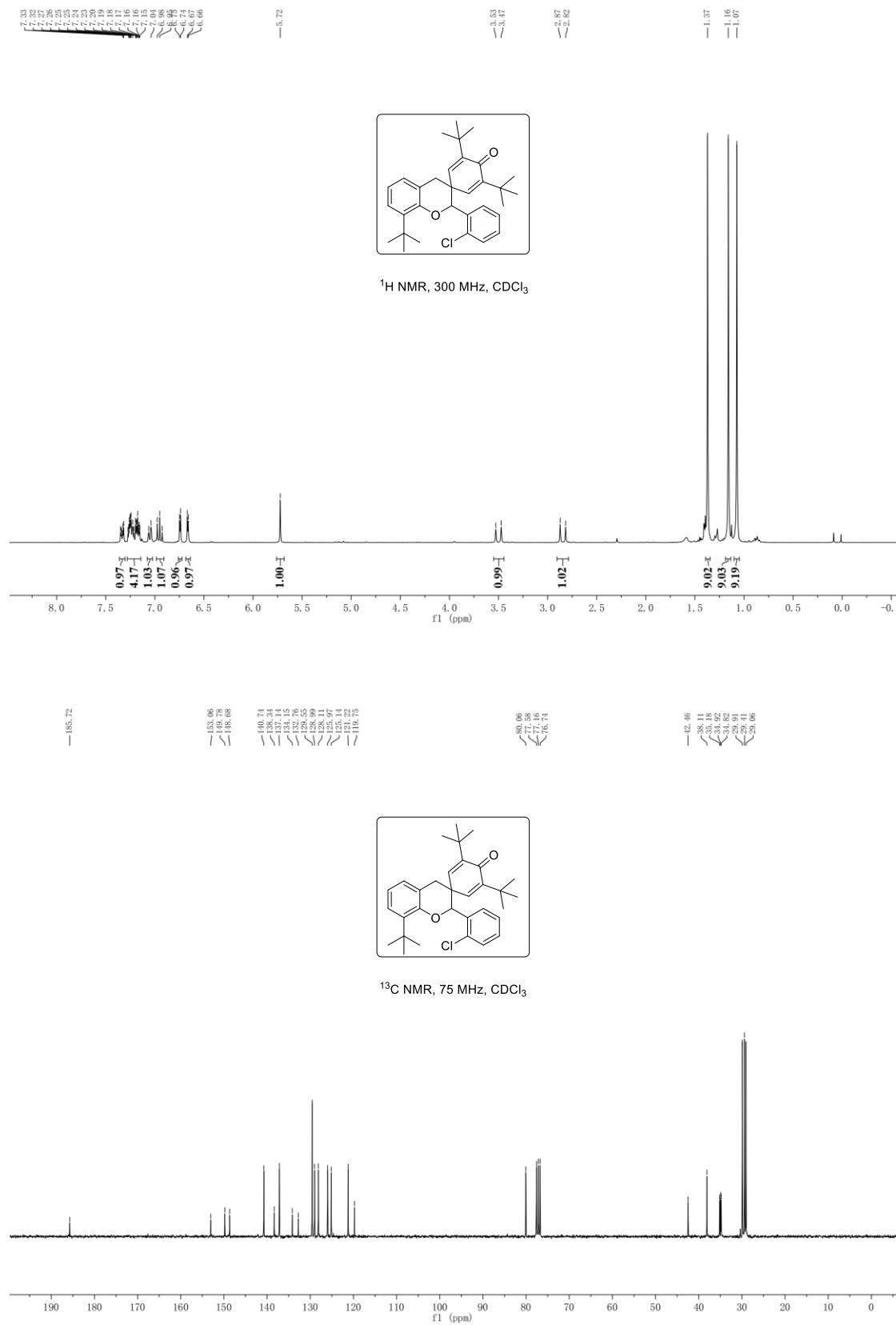
**3',5',8-tri-tert-butyl-2-(p-tolyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2i)**



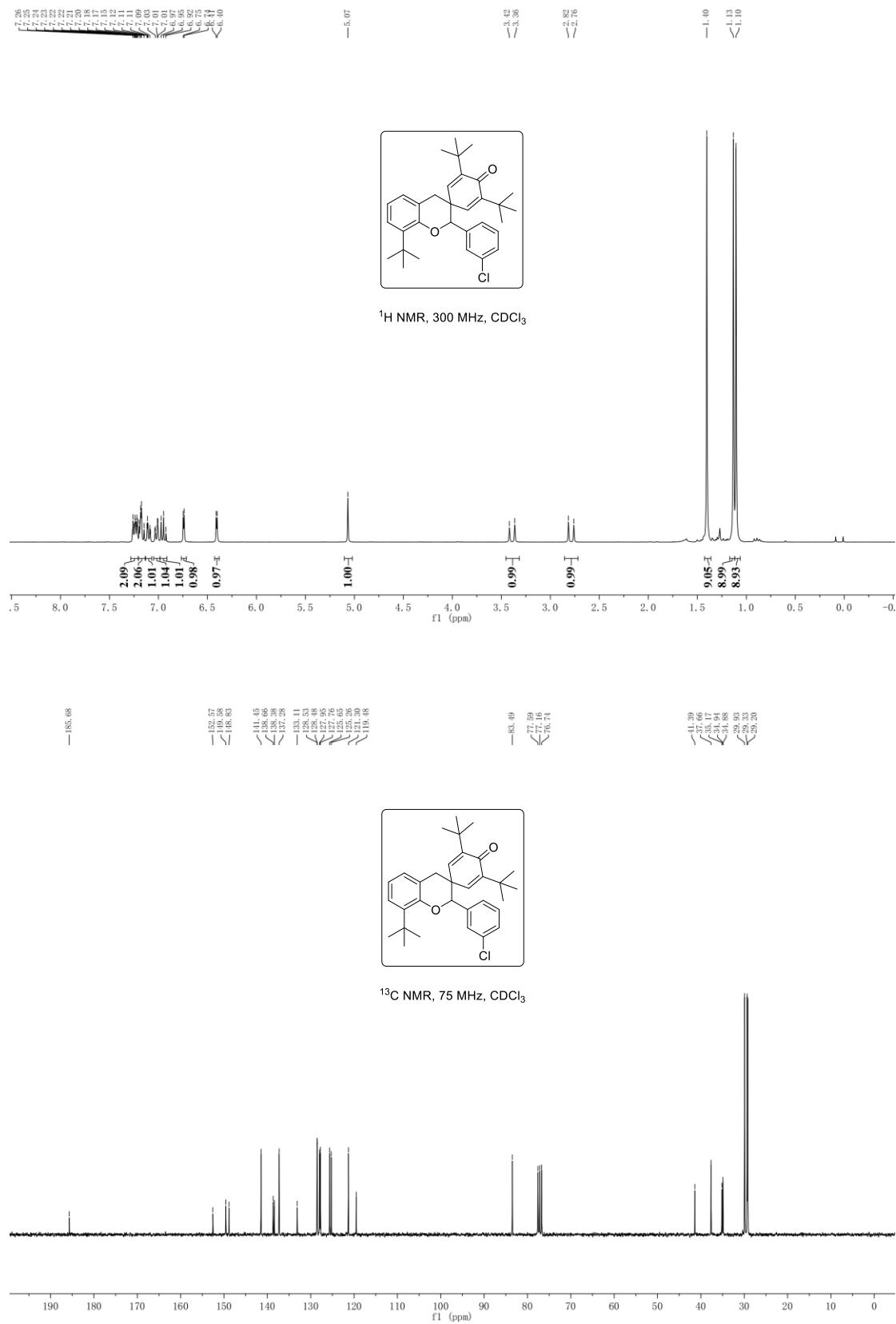
**2-([1,1'-biphenyl]-4-yl)-3',5',8-tri-tert-butylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2j)**



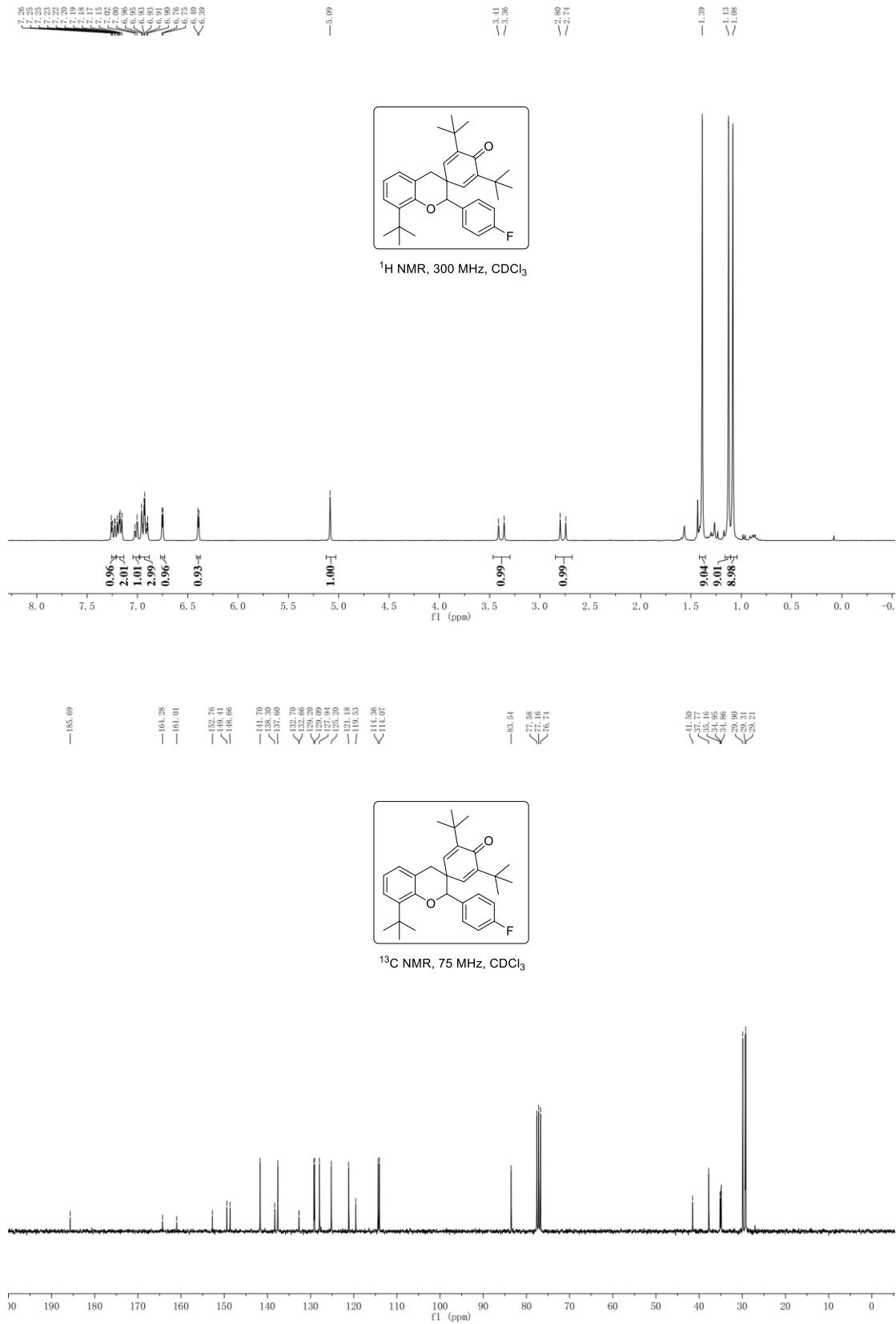
**3',5',8-tri-tert-butyl-2-(2-chlorophenyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2k)**



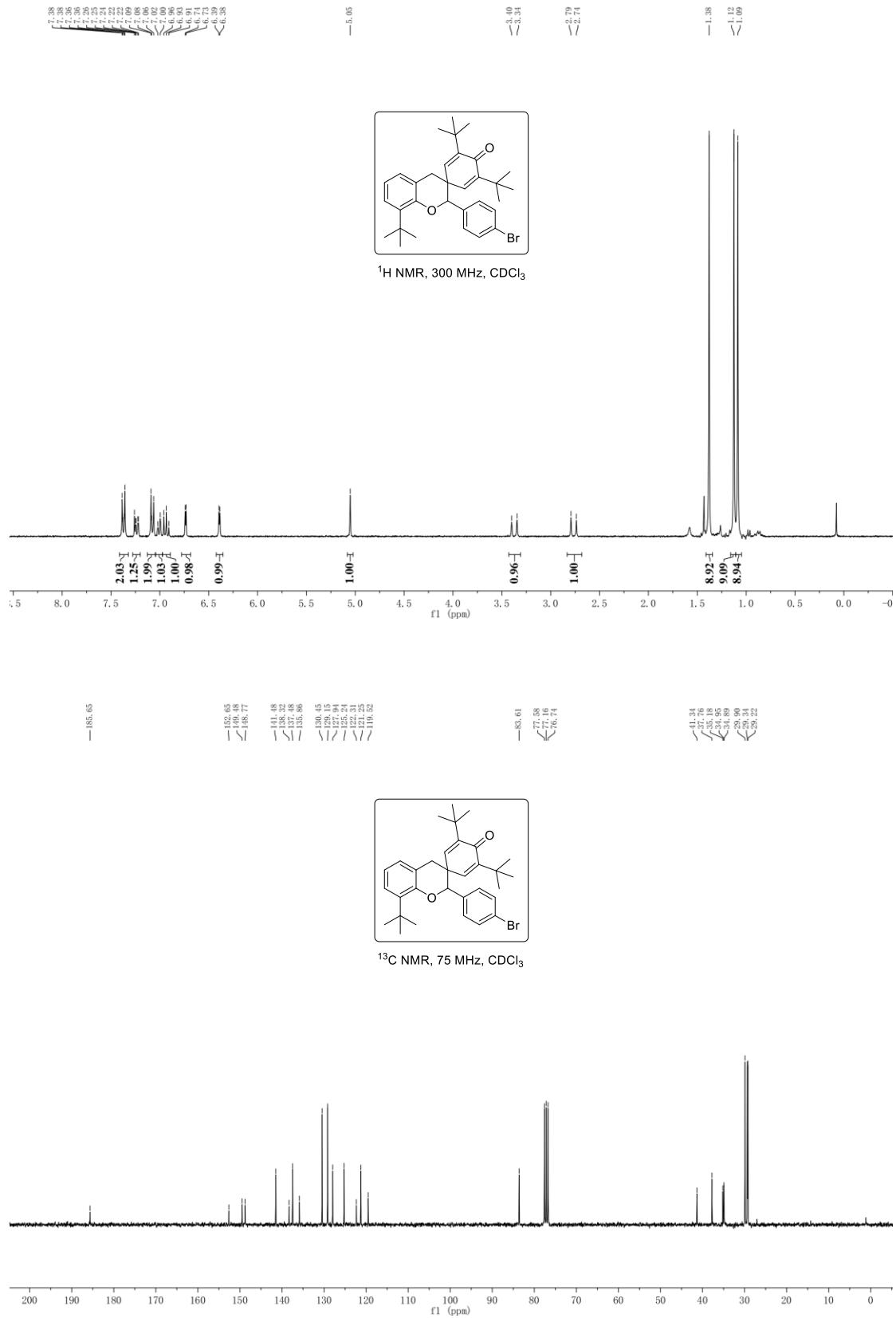
**3',5',8-tri-tert-butyl-2-(3-chlorophenyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2l)**



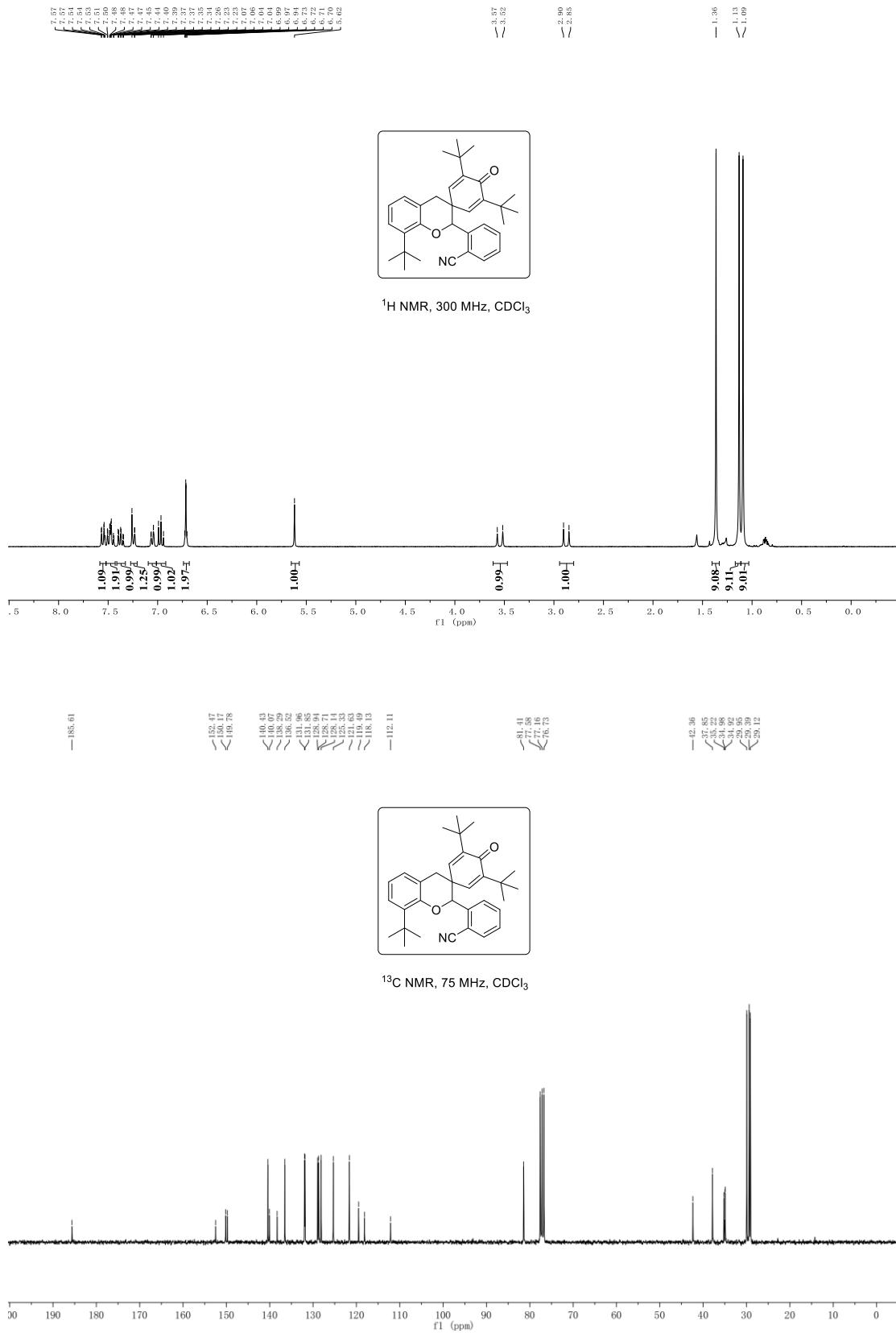
**3',5',8-tri-tert-butyl-2-(4-fluorophenyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2m)**



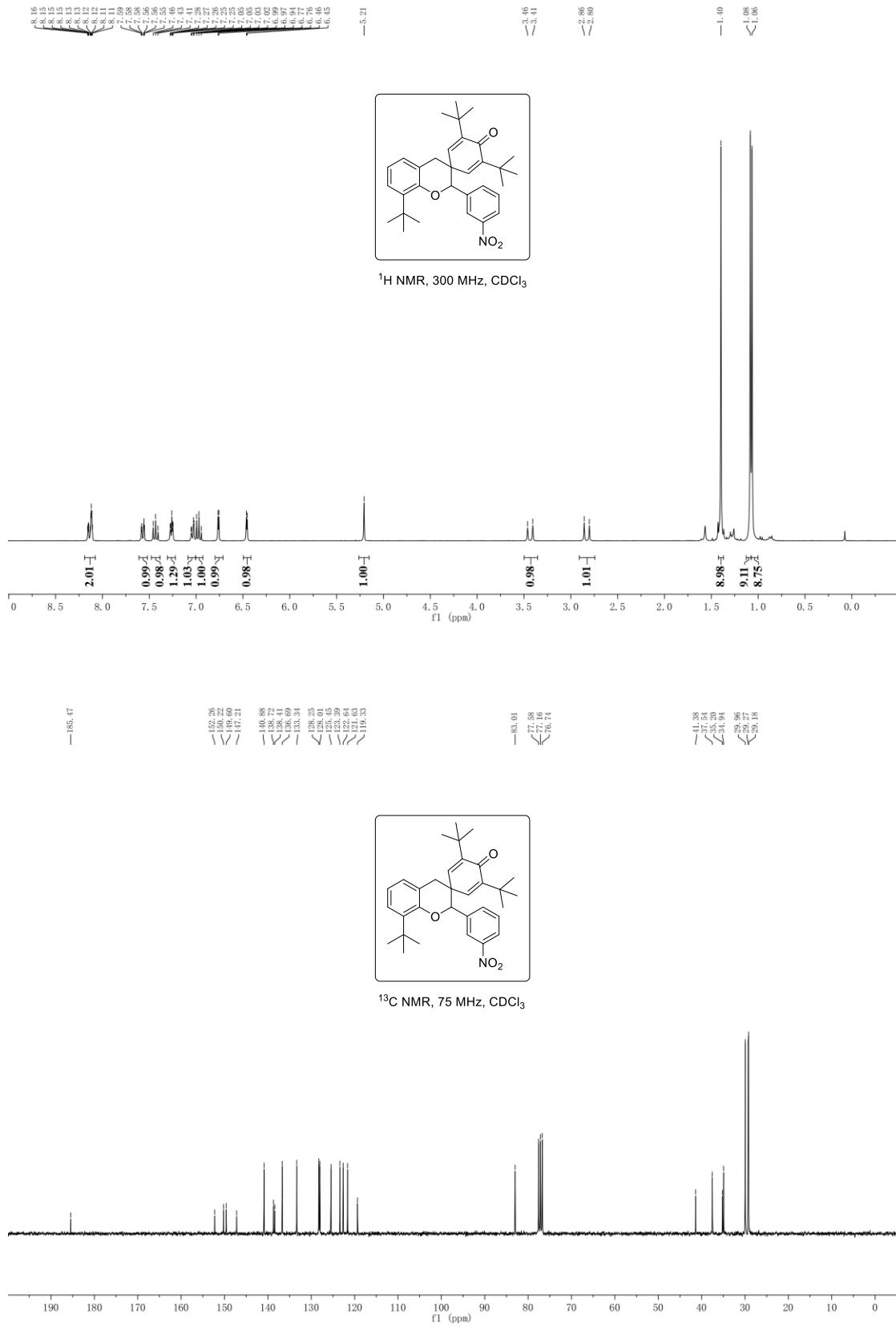
**2-(4-bromophenyl)-3',5',8-tri-tert-butylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2n)**



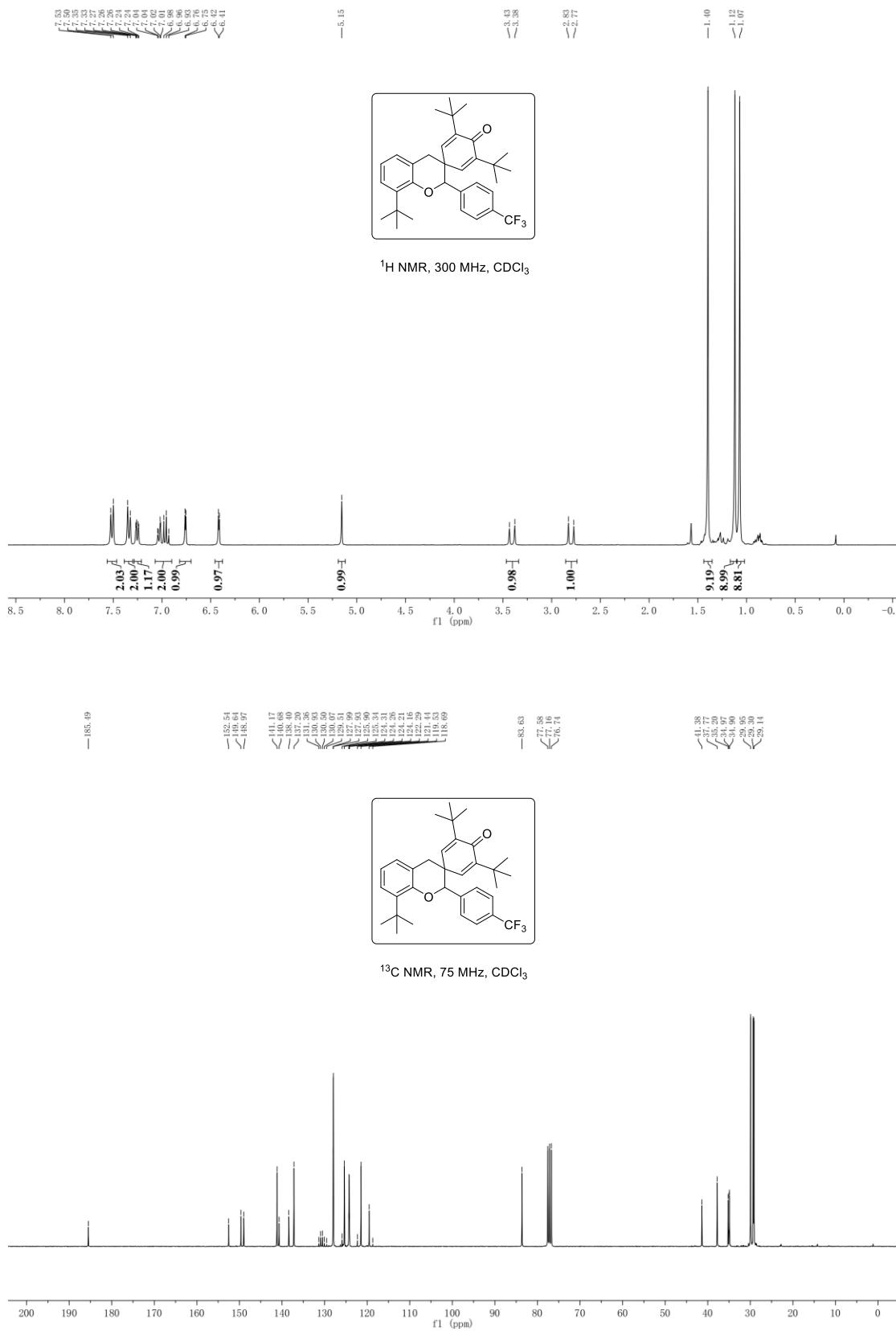
**2-(3',5',8-tri-tert-butyl-4'-oxospiro[chromane-3,1'-cyclohexane]-2',5'-dien-2-yl)benzonitrile (2o)**



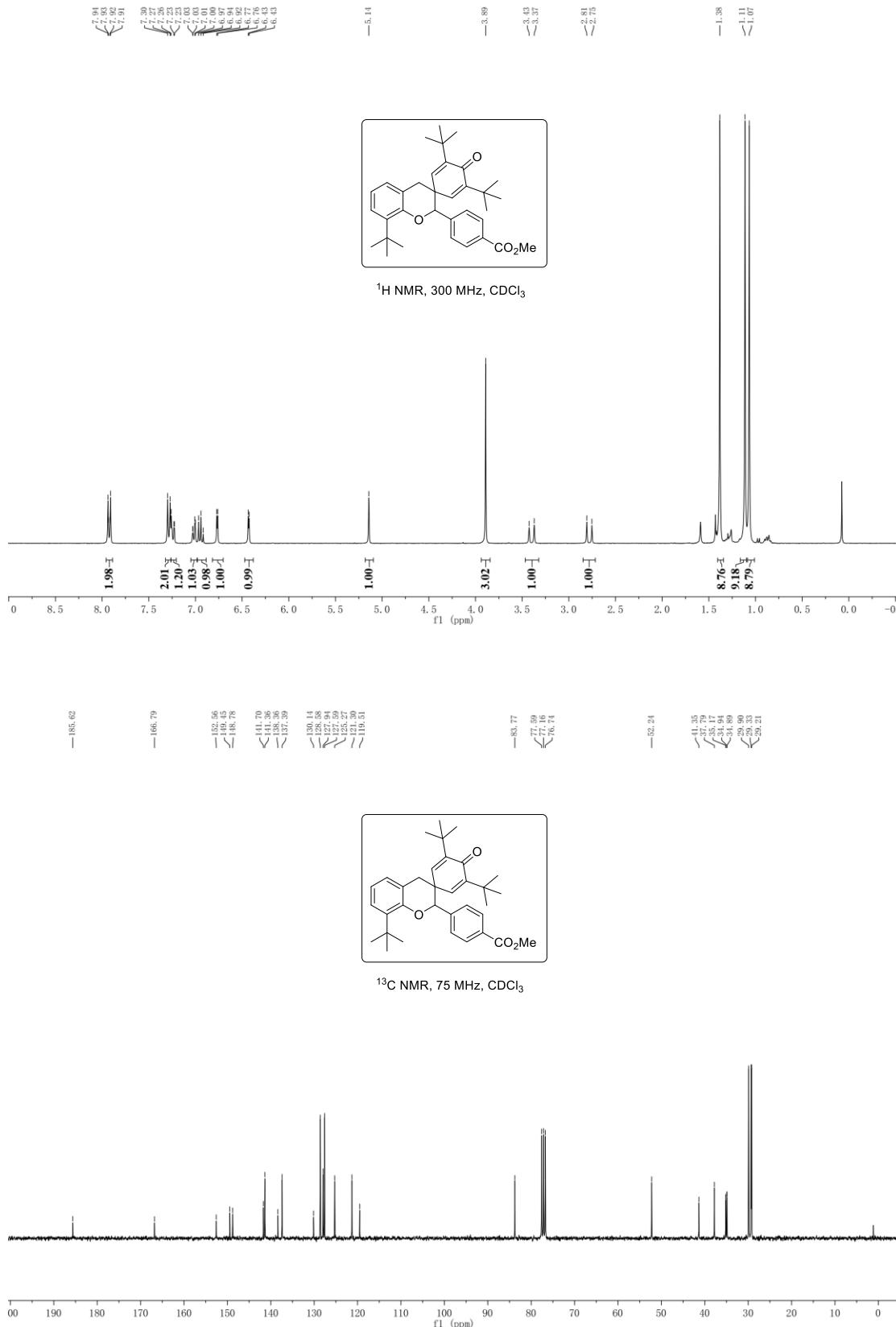
3',5',8-tri-tert-butyl-2-(3-nitrophenyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2p)



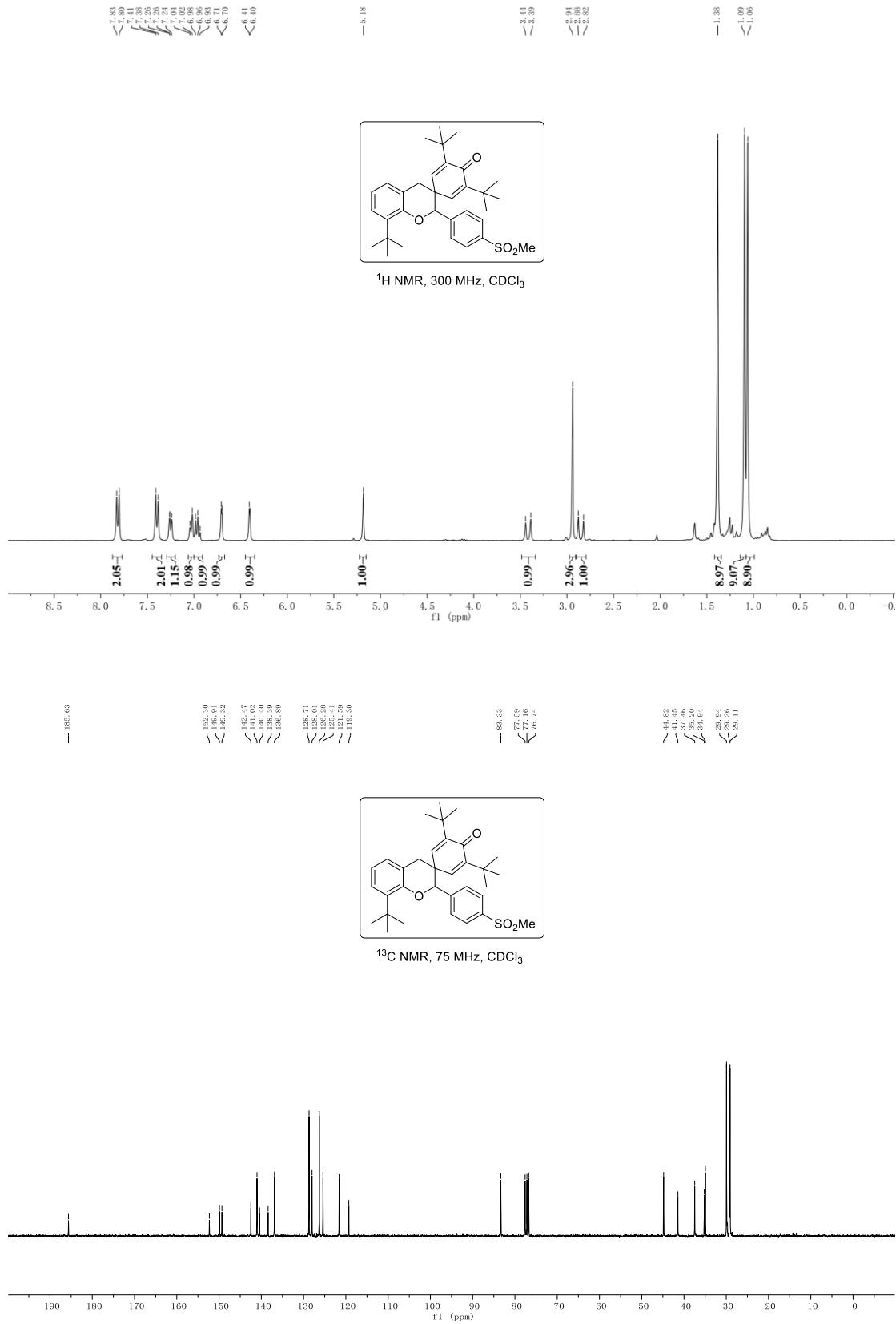
**3',5',8-tri-tert-butyl-2-(4-(trifluoromethyl)phenyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2q)**



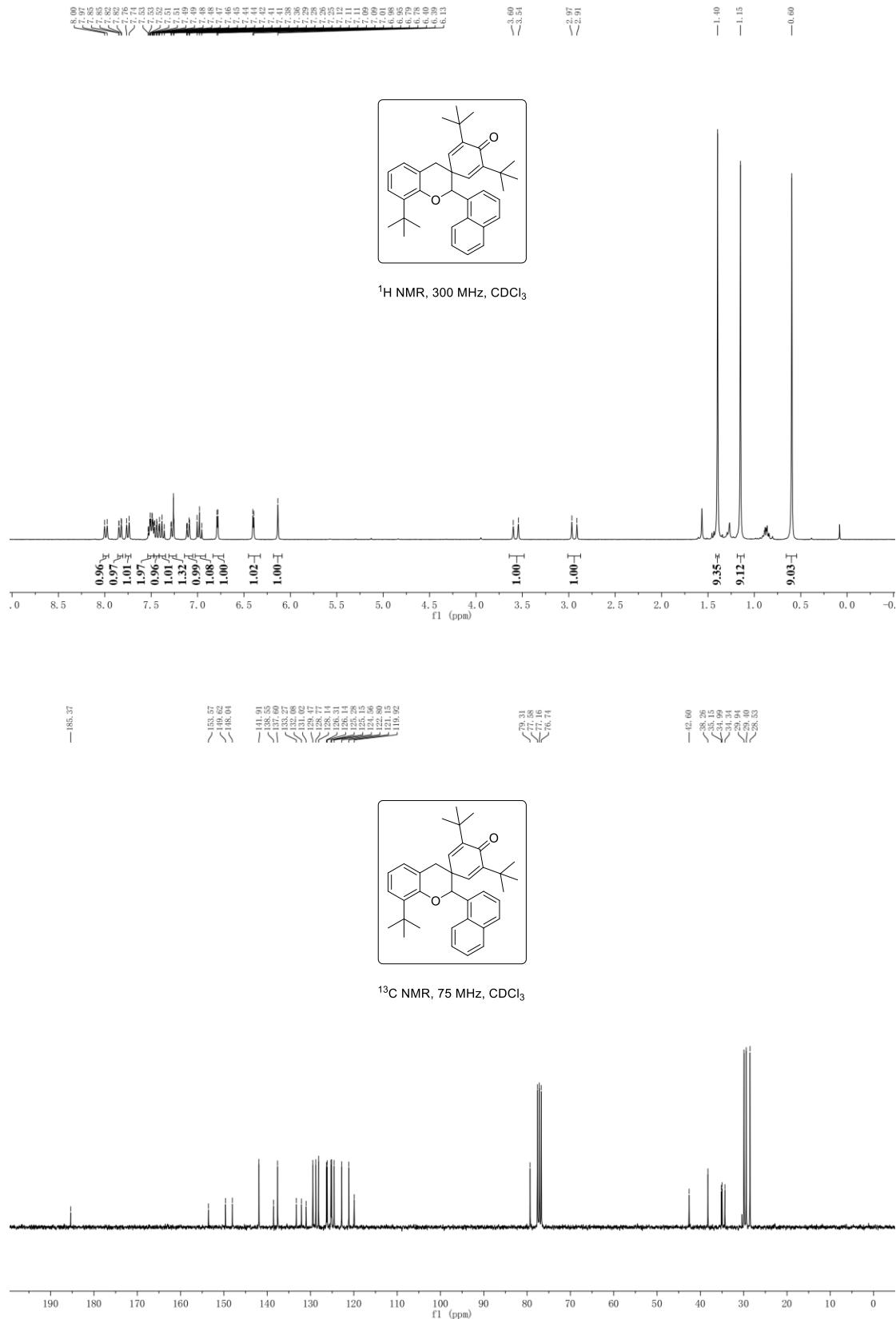
**methyl 4-(3',5',8-tri-tert-butyl-4'-oxospiro[chromane-3,1'-cyclohexane]-2',5'-dien-2-yl)benzoate (2r)**



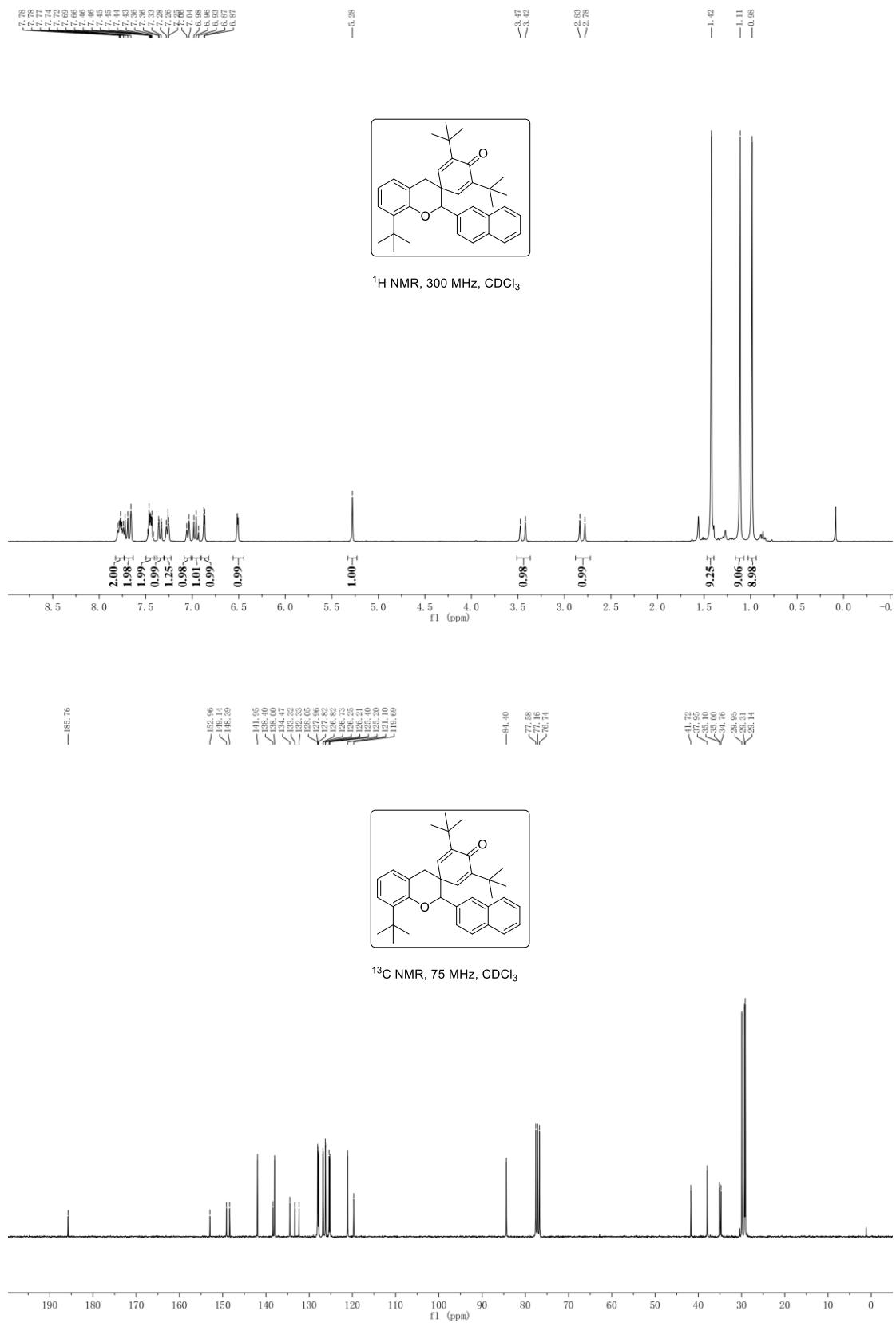
**3',5',8-tri-tert-butyl-2-(4-(methylsulfonyl)phenyl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2s)**



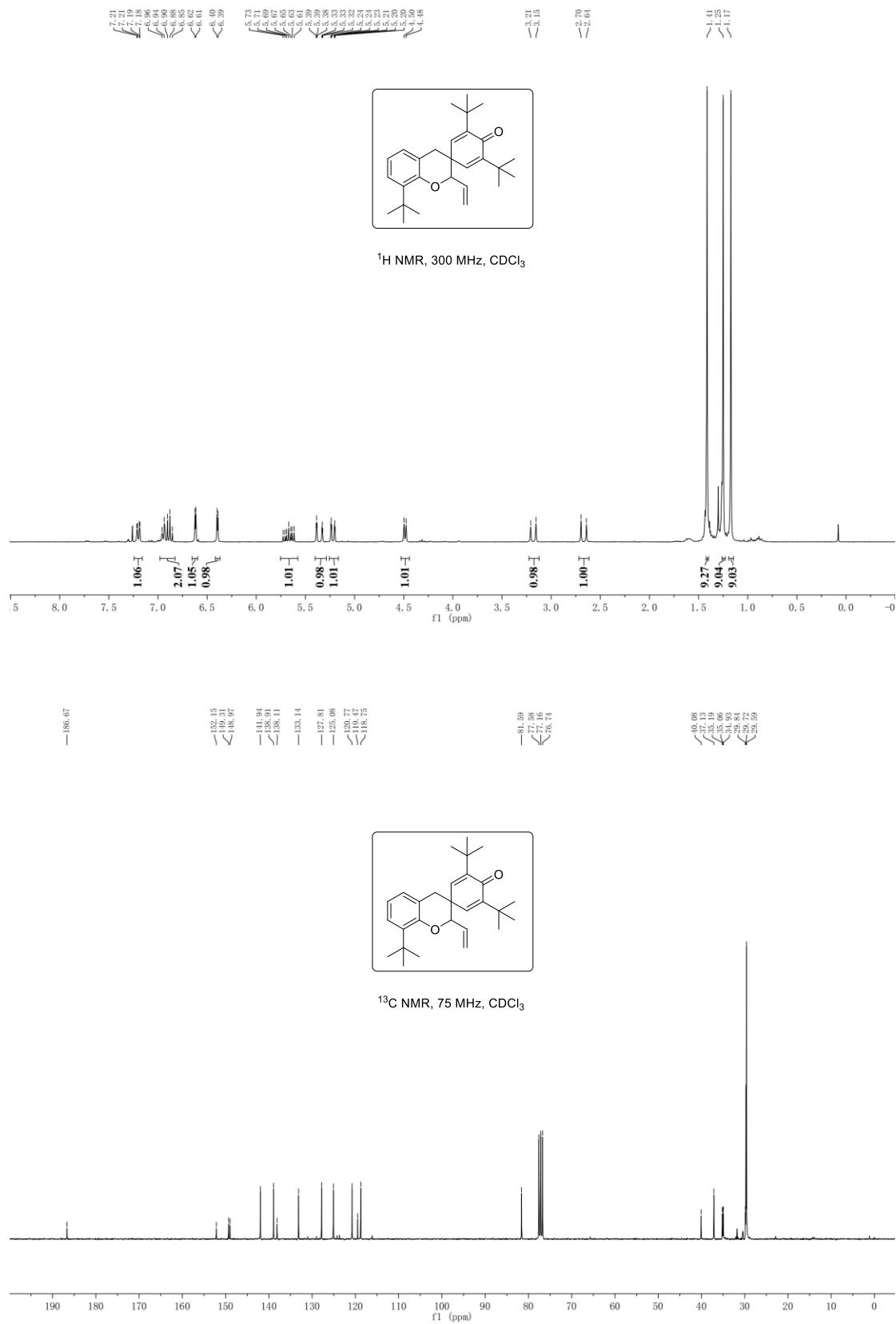
**3',5',8-tri-tert-butyl-2-(naphthalen-1-yl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2t)**



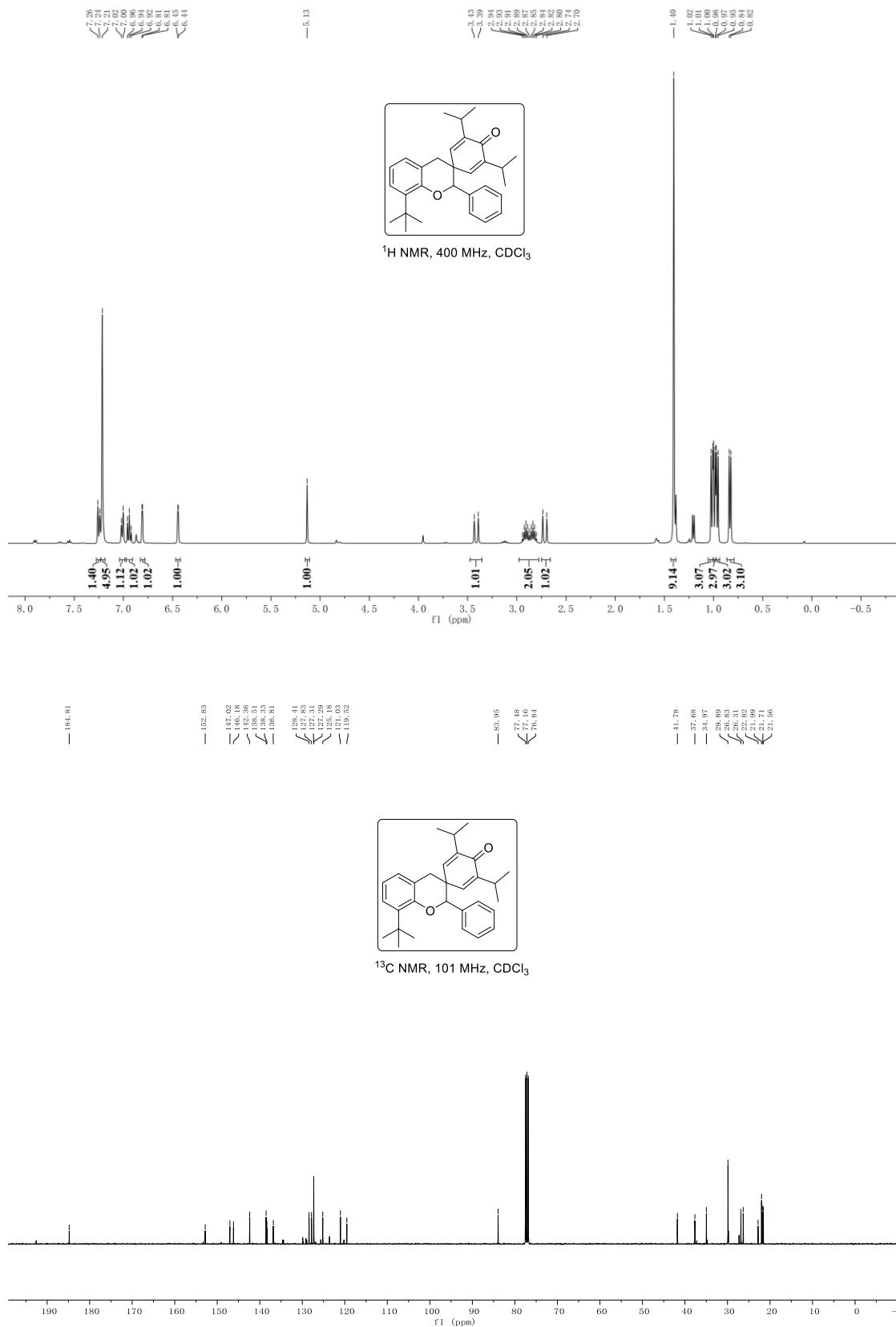
**3',5',8-tri-tert-butyl-2-(naphthalen-2-yl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2u)**



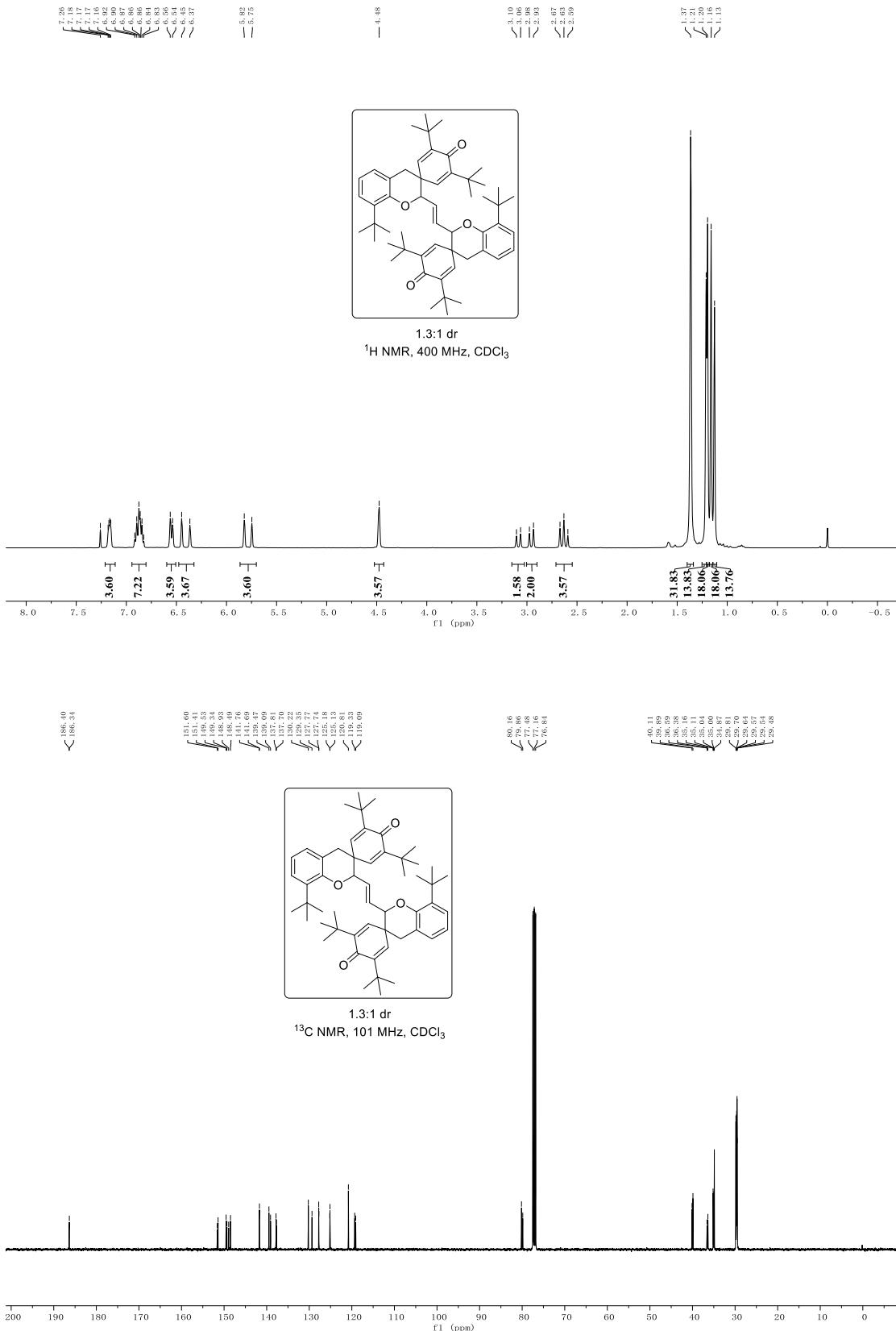
**3',5',8-tri-tert-butyl-2-vinylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2w)**



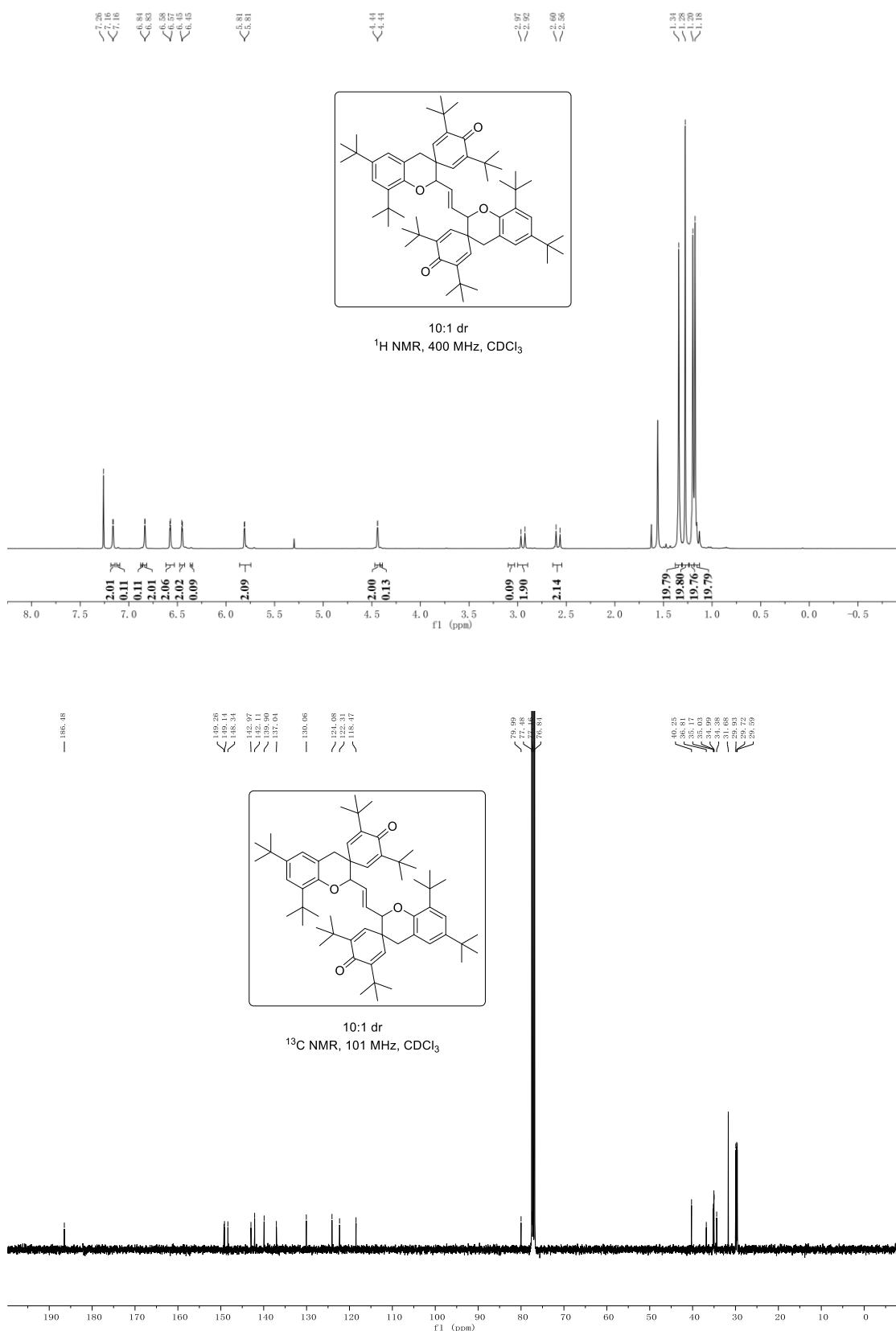
**8-(tert-butyl)-3',5'-diisopropyl-2-phenylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (2z)**



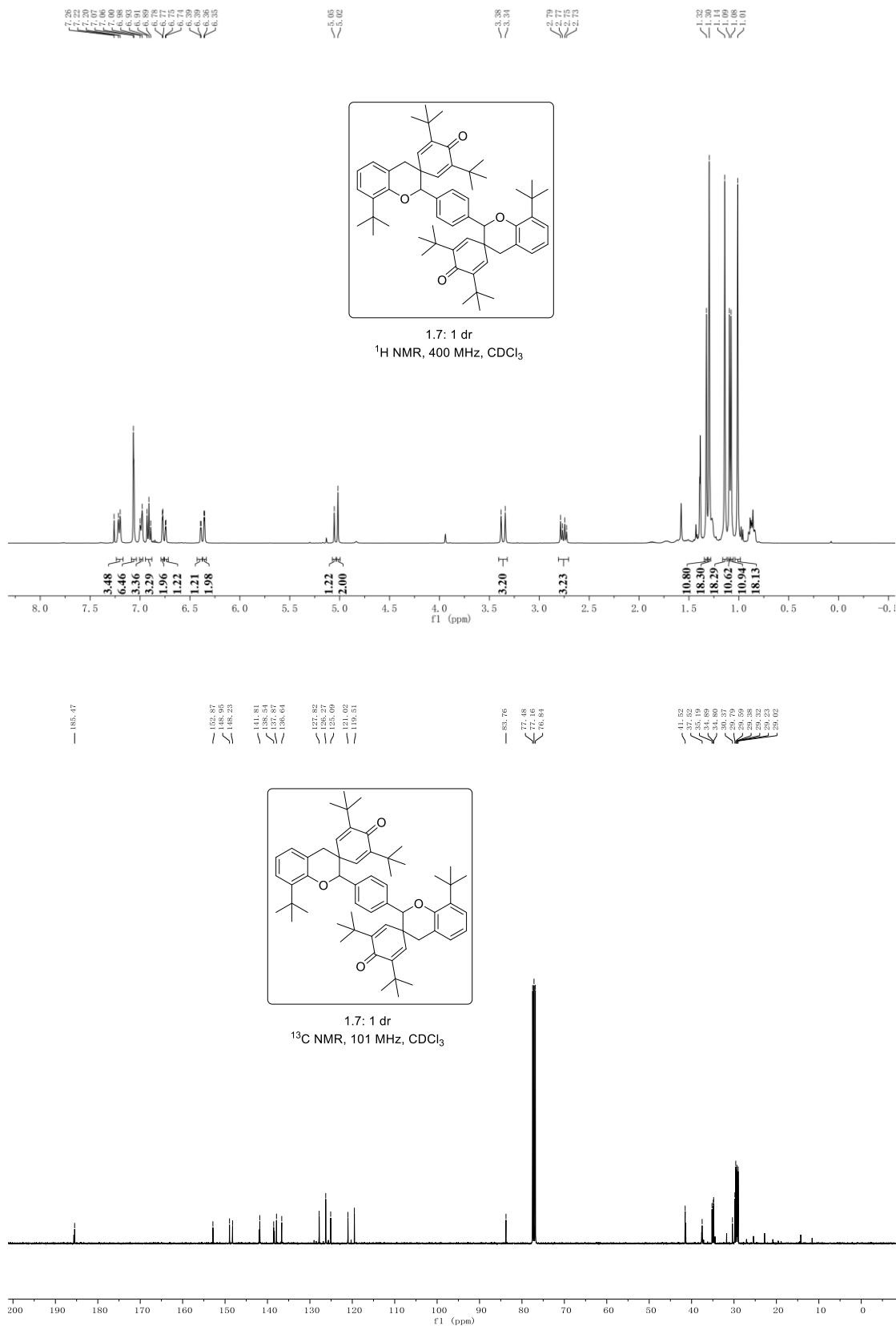
**(E)-2,2''-(ethene-1,2-diyl)bis(3',5'-tri-tert-butylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one) (2za)**



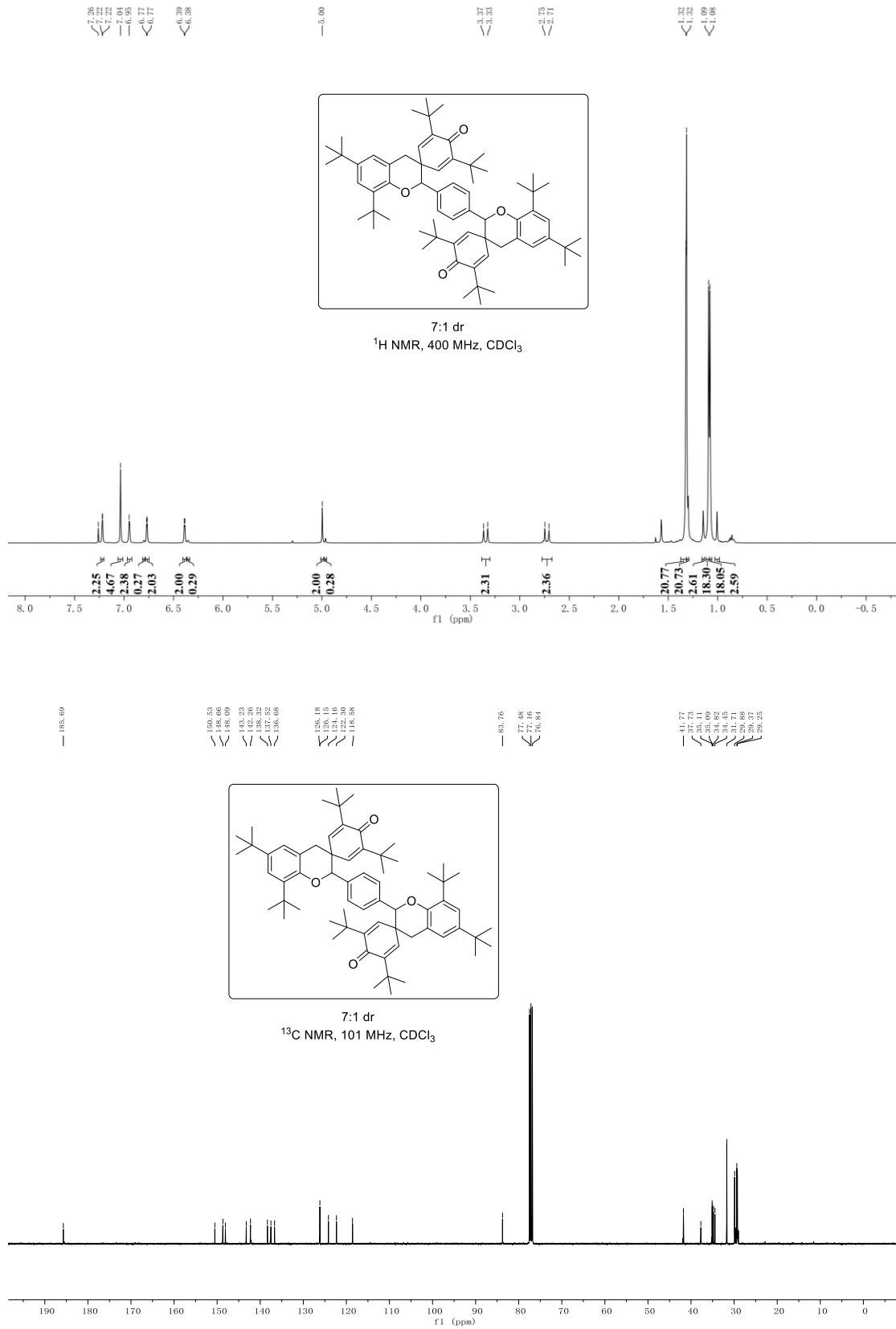
**(E)-2,2''-(ethene-1,2-diyl)bis(3',5',6,8-tetra-tert-butylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one)  
(2zb)**



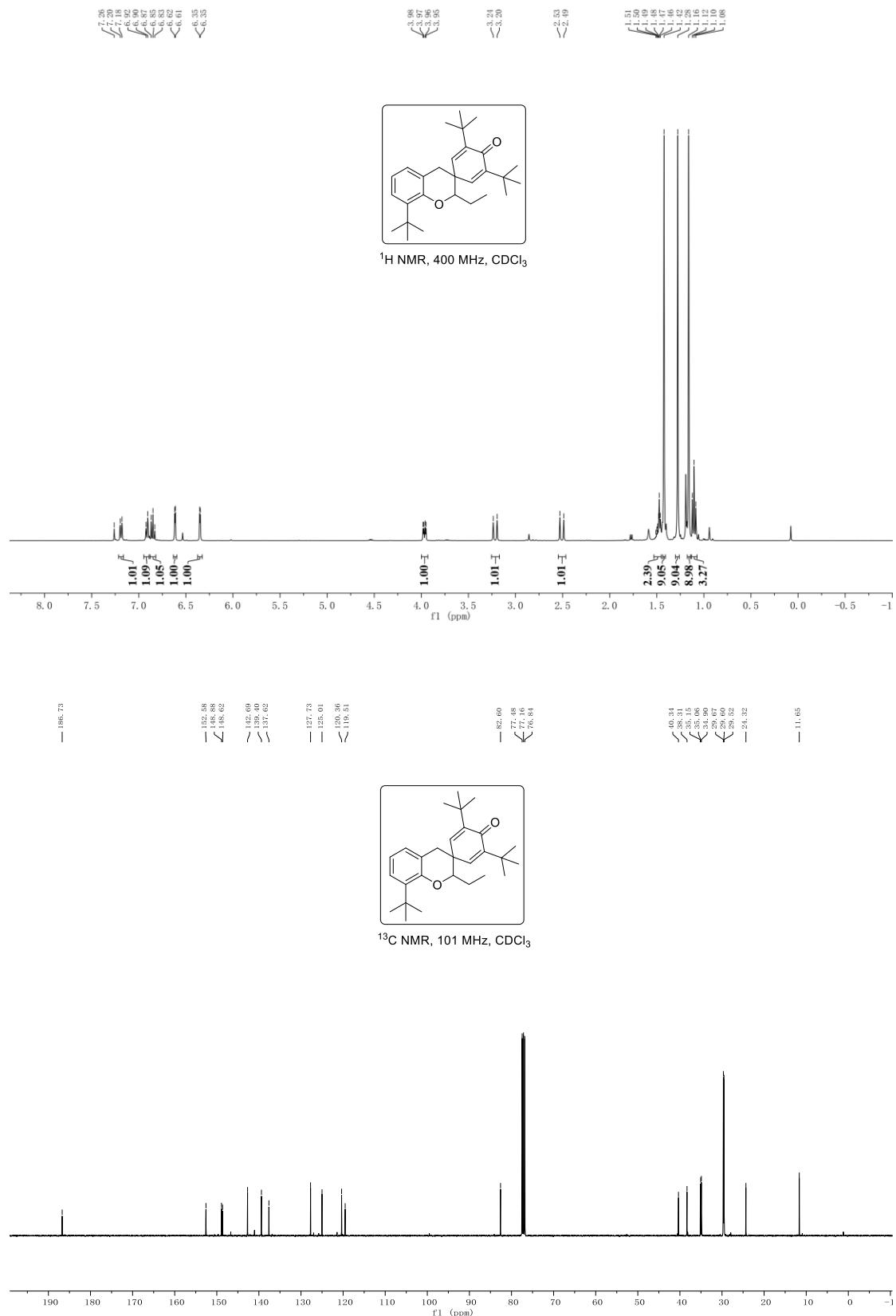
**2,2''-(1,4-phenylene)bis(3',5',8-tri-tert-butylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one) (2zc)**



**2,2''-(1,4-phenylene)bis(3',5',6,8-tetra-tert-butylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one) (2zd)**



**3',5',8-tri-tert-butyl-2-ethylspiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (3w)**



**3',5',8-tri-tert-butyl-2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)spiro[chromane-3,1'-cyclohexane]-2',5'-dien-4'-one (4w)**

