Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


# Supporting Information

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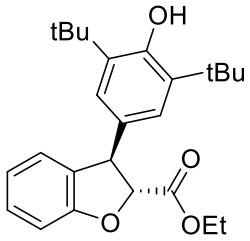
## 1. General information

- Chemicals were purchased from Acros or Aldrich and used without further purification unless otherwise noted. Solvents were predistilled according to standard laboratory methods.
- Chromatographic purification of the products was performed on Merck silica gel 60, particle size 0.040-0.063 mm (230-240 mesh, flash).
- Analytical TLC: SIL G-25 UV254 from MACHEREY&NAGEL. Visualization of the developed TLC plates was performed with ultraviolet irradiation (254 nm) or by staining with basic potassium permanganate solution.
- Melting points were determined using a Büchi 510 apparatus and are uncorrected.
- Mass spectra were acquired on a Finnigan SSQ7000 (EI/CI) spectrometer and high resolution mass spectra on a Finnigan MAT 95 (EI/CI) or on a ThermoFisher Scientific LTQOrbitrap XL (ESI). All signals over 10% relative intensity are listed.
- IR spectra were taken on a Perkin-Elmer FT-IR Spectrum 100 using a Diamant/KRS5 ATR. Evaluation was done using the supplementary software. The absorption bands are given in wave numbers ($cm^{-1}$).
- $^{1}H$- and $^{13}C$- NMR spectra were recorded at ambient temperature on Varian Mercury 300, VNMRS 600 and Inova 400 instruments. The chemical shifts are reported in ppm downfield of tetramethylsilane (TMS) and referenced to residual solvent peaks resonance as internal standard. The order of citation in parentheses is a) multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd= doublet of doublet, ddd= doublet of doublet of doublet, td = triplet of doublet, m = multiplet), b) coupling constants, c) number of protons. Coupling constants (*J*) are reported in Hertz (Hz).

## 2. Experimental Procedures and Characterization Data for 3a-3s:

A 10 mL glass tube equipped with a stirring bar was charged with *p*-QMs **1** (0.40 mmol, 1.0 equiv.), sulfonium bromides **2** (0.48 mmol, 1.2 equiv.), $Cs_2CO_3$ (0.48 mmol, 120 mol %) and $CH_3CN$ (4.0 mL). The resulting solution was stirred at room temperature for the indicated time. Then the solvent was evaporated under reduced pressure to give a residue, which was directly purified by flash column chromatography (pentane/$Et_2O$ from 30/1 to 10/1) to provide the desired product **3a-3s**.




**3a**

**Ethyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-carboxylate (3a)**

According to the general procedure, **3a** was obtained as a colorless solid (0.151 g, 95% yield) in 0.5 h.

**Melting Point:** 112-114 °C.

**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.22 – 7.19 (m, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 7.00 (s, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.93 – 6.90 (m, 1H), 5.18 (s, 1H), 5.00 (d, *J* = 6.6 Hz, 1H), 4.75 (d, *J* = 6.6 Hz, 1H), 4.36 – 4.24 (m, 2H), 1.41 (s, 18H), 1.33 (t, *J* = 7.2 Hz, 3H) ppm.

**$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 170.9, 159.2, 153.0, 136.1, 132.5, 128.7, 128.6, 125.4, 124.4 (2C), 121.4, 109.9, 87.4, 61.6, 52.6 (2C), 34.4 (2C), 30.2 (6C), 14.3 ppm.

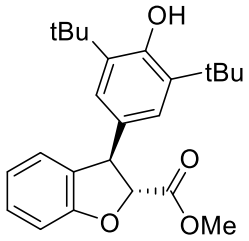
**IR (ATR):** 3771, 3634, 3460, 2967, 2645, 2334, 2084, 1900, 1740, 1594, 1437, 1366, 1217, 1103, 1042, 898, 672 $cm^{-1}$.

**MS (ESI):** *m/z* = 419.2 $[M+Na]^+$.

**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{25}H_{32}O_4Na^+$: 419.2193; found 419.2194.

The gram scale reaction for the synthesis of **3a** was carried out in a similar manner.

A round-bottom flask equipped with a stirring bar was charged with *p*-QMs **1a** (0.931 g, 3.0 mmol, 1.0 equiv), sulfonium bromide **2a** (0.825 g, 3.6 mmol, 1.2 equiv), $Cs_2CO_3$ (1.173 g, 3.6 mmol, 120 mol %) and $CH_3CN$ (30 mL). The resulting solution was stirred at room temperature for 1.5 h and then the solvent was evaporated under reduced pressure to give a residue which was directly purified by flash column chromatography (pentane/$Et_2O$ from 30/1 to 10/1) to provide the desired product **3a** (1.106 g, 93%). The analytical data of the gram scale reaction of **3a** are consistent with those of the 0.4 mmol scale experiment.




**3b**

**Methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-carboxylate (3b)**

According to the general procedure, **3b** was obtained as a colorless solid (0.120 g, 79% yield) in 1 h.

**Melting Point:** 126-128 ºC.

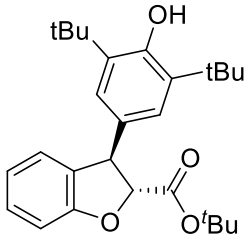
**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.22 – 7.19 (m, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.98 (s, 2H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.93 – 6.90 (m, 1H), 5.17 (s, 1H), 5.03 (d, *J* = 6.6 Hz, 1H), 4.75 (d, *J* = 6.6 Hz, 1H), 3.83 (s, 3H), 1.40 (s, 18H) ppm.

**$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 171.4, 159.0, 153.0, 136.1, 132.4, 128.7, 128.6, 125.4, 124.3 (2C), 121.5, 109.9, 87.3, 52.6, 52.5, 52.4, 34.4 (2C), 30.2 (6C) ppm.

**IR (ATR):** 3398, 2954, 2150, 1745, 1615, 1435, 1186, 1046, 746 $cm^{-1}$.

**MS (ESI):** *m/z* = 405.2 $[M+Na]^+$.

**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{24}H_{30}O_4Na^+$: 405.2036; found 405.2018.




**3c**

***tert*-Butyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-carboxylate (3c)**

According to the general procedure, **3c** was obtained as a colorless solid (0.139 g, 82% yield) in 0.5 h.

**Melting Point:** 146-148 ºC.

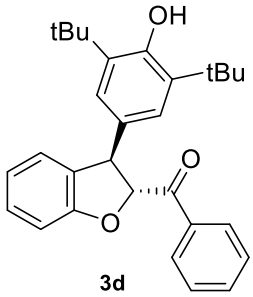
**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.22 – 7.18 (m, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.99 – 6.96 (m, 3H), 6.92 – 6.89 (m, 1H), 5.17 (s, 1H), 4.89 (d, *J* = 6.6 Hz, 1H), 4.67 (d, *J* = 6.6 Hz, 1H), 1.53 (s, 9H), 1.41 (s, 18H) ppm.

**$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 170.0, 159.5, 152.9, 136.1, 132.8, 128.7, 125.4, 124.3 (2C), 121.2, 109.9, 87.7, 82.2, 52.8 (2C), 34.4 (3C), 30.2 (6C), 28.1 (3C) ppm.

**IR (ATR):** 3602, 3463, 2962, 2322, 2099, 2990, 2905, 1742, 1598, 1475, 1436, 1366, 1313, 1227, 1152, 1036, 937, 823, 753 $cm^{-1}$.

**MS (ESI):** *m/z* = 447.2 $[M+Na]^+$.

**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{27}H_{36}O_4Na^+$: 447.2506; found 447.2493.




**3d**

**(3-(3,5-di-*tert*-Butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3d)**

According to the general procedure, **3d** was obtained as a colorless solid (0.144 g, 84% yield) in 12 h.

**Melting Point:** 145-147 ºC.

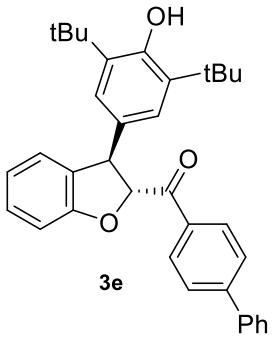
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.93 – 7.90 (m, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.22 – 7.16 (m, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.93 (s, 2H), 6.90 – 6.86 (m, 1H), 5.76 (d, *J* = 6.8 Hz, 1H), 5.16 (s, 1H), 4.84 (d, *J* = 6.8 Hz, 1H), 1.37 (s, 18H) ppm.

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 195.2, 159.2, 153.0, 136.2 (2C), 134.6, 133.6, 132.5, 129.3 (2C), 128.6, 128.5 (2C), 125.4, 124.7 (2C), 121.4, 109.8, 90.8, 51.2 (2C), 34.3 (2C), 30.2 (6C) ppm.

**IR (ATR):** 3758, 3626, 3458, 2957, 2287, 2190, 2104, 1973, 1899, 1739, 1688, 1595, 1445, 1366, 1302, 1220, 1153, 1007, 965, 861, 742, 705 $cm^{-1}$.

**MS (ESI):** *m/z* = 451.2 $[M+Na]^+$.

**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{29}H_{32}O_3Na^+$: 451.2249; found 451.2241.




**3e**

**[1,1'-Biphenyl]-4-yl(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl) methanone (3e)**

According to the general procedure, **3e** was obtained as a colorless solid (0.200 g, 99% yield) in 0.5 h.

**Melting Point:** 157-159 ºC.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.65 – 7.60 (m, 2H), 7.49 – 7.43 (m, 2H), 7.42 – 7.38 (m, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.02 – 6.97 (m, 3H), 6.92 (t, *J* = 7.2 Hz, 1H), 5.81 (d, *J* = 6.4 Hz, 1H), 5.19 (s, 1H), 4.93 (d, *J* = 6.4 Hz, 1H), 1.40 (s, 18H) ppm.

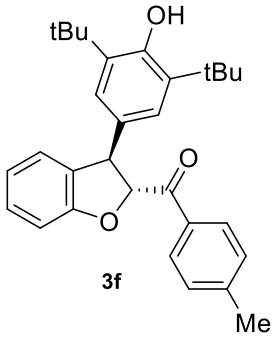
**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 194.8, 159.2, 153.0, 146.3, 139.8, 136.3, 133.3, 132.6, 129.9 (2C), 129.4, 129.0 (2C), 128.7, 128.4, 127.3 (2C), 127.2 (2C), 125.5, 124.8 (2C), 121.5, 109.8, 90.8, 51.2 (2C), 34.4 (2C), 30.3 (6C) ppm.

**IR (ATR):** 3930, 3782, 3581, 2953, 2316, 2081, 1911, 1739, 1684, 1597, 1446, 1366, 1223, 1299,

1223, 1113, 997, 953, 860, 744, 685 $cm^{-1}$.

**MS (ESI):** *m/z* = 505.1 $[M+H]^+$.

**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{35}H_{36}O_3Na^+$: 527.2557; found 527.2540.




**(3-(3,5-di-*tert*-Butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(p-tolyl)methanone (3f)**

According to the general procedure, **3f** was obtained as a colorless solid (0.160 g, 90% yield) in 0.5 h.

**Melting Point:** 159-161 ºC.

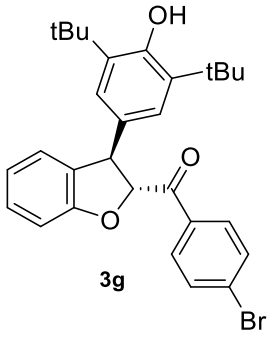
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 2H), 6.92 – 6.85 (m, 1H), 5.75 (d, *J* = 6.8 Hz, 1H), 5.17 (s, 1H), 4.84 (d, *J* = 6.8 Hz, 1H), 2.41 (s, 3H), 1.38 (s, 18H)ppm.

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 194.8, 159.2, 153.0, 140.7, 136.2, 132.6, 132.1, 129.4 (2C), 129.3, 129.2 (2C), 128.6, 125.4, 124.8 (2C), 121.4, 109.8, 90.7, 51.3 (2C), 34.3 (2C), 30.2 (6C), 21.7 ppm.

**IR (ATR):** 3924, 3784, 3710, 3596, 2959, 2324, 2108, 1920, 1744, 1677, 1599, 1442, 1368, 1306, 1229, 1114, 956, 863, 821, 750, 664 $cm^{-1}$.

**MS (EI):** *m/z* (%): 442.3 (72) $[M]^+ = [C_{30}H_{34}O_3]^+$, 425.3 (75) $[M - OH]^+ = [C_{30}H_{33}O_2]^+$, 119.1 (100) $[M - C_{22}H_{27}O_2]^+ = [C_8H_7O]^+$.

**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{30}H_{34}O_3Na^+$: 465.2400; found 465.2394.

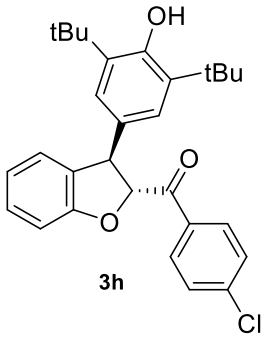



**(4-Bromophenyl)(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)methanone (3g)**

According to the general procedure, **3g** was obtained as an off-white solid (0.145 g, 72% yield) in 0.5 h.

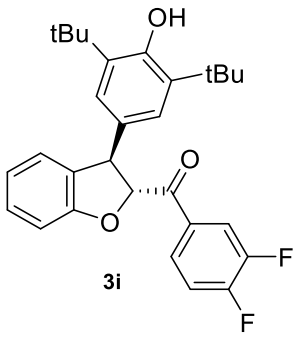
**Melting Point:** 175-177 ºC.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.21 – 7.17 (m, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.94 (s, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.91 – 6.88 (m, 1H), 5.68 (d, *J* = 7.2 Hz, 1H), 5.17 (s, 1H), 4.87 (d, *J* = 7.2 Hz, 1H), 1.37 (s, 18H) ppm.
$^{13}$C NMR (100 MHz, $CDCl_3$) δ 194.3, 158.9, 153.1, 136.3, 133.4, 132.3, 131.9 (2C), 130.8 (2C), 129.2, 128.9, 128.7, 125.4, 124.7 (2C), 121.6, 109.8, 90.8, 51.0 (2C), 34.3 (2C), 30.2 (6C) ppm.
**IR (ATR):** 3784, 3605, 2958, 2324, 2106, 1919, 1739, 1689, 1583, 1469, 1394, 1304, 1224, 1147, 1068, 1000, 960, 863, 820, 748 $cm^{-1}$.
**MS (ESI):** *m/z* = 529.3 $[M+Na]^+$.
**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{29}H_{31}O_3BrNa^+$: 529.1349; found 529.1346.



**3h**

**(4-Chlorophenyl)(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)methanone (3h)**
According to the general procedure, **3h** was obtained as an off-white solid (0.167 g, 90% yield) in 0.5 h.
**Melting Point:** 172-174ºC.
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.86 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.21 – 7.17 (m, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.93 (s, 2H), 6.91 – 6.87 (m, 1H), 5.68 (d, *J* = 6.8 Hz, 1H), 5.17 (s, 1H), 4.86 (d, *J* = 6.8 Hz, 1H), 1.37 (s, 18H) ppm.
**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 194.1, 158.9, 153.1, 140.1, 136.3, 133.0, 132.3, 130.7 (2C), 129.2, 128.9 (2C), 128.7, 125.4, 124.7 (2C), 121.6, 109.8, 90.8, 51.0 (2C), 34.3 (2C), 30.2 (6C) ppm.
**IR (ATR):** 3785, 3613, 2955, 2325, 2104, 1912, 1745, 1682, 1583, 1467, 1303, 1224, 1089, 958, 862, 824, 749 $cm^{-1}$.
**MS (EI):** *m/z* (%): 462.2 (73) $[M]^+ = [C_{29}H_{31}O_3Cl]^+$, 445.2 (77) $[M - OH]^+ = [C_{29}H_{30}O_2Cl]^+$, 139.0 (100) $[M - C_{22}H_{27}O_2]^+ = [C_7H_4OCl]^+$.
**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{29}H_{31}O_3ClNa^+$: 485.1854; found 485.1843.



**3i**

**(3-(3,5-di-*tert*-Butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(3,4-difluorophenyl) methanone (3i)**

According to the general procedure, **3i** was obtained as a colorless solid (0.183 g, 98% yield) in 0.5 h.

**Melting Point:** 164-166 °C.

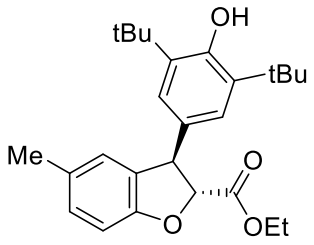
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.82 – 7.72 (m, 2H), 7.26 – 7.17 (m, 2H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.96 (s, 2H), 6.93 – 6.89 (m, 2H), 5.64 (d, *J* = 7.2 Hz, 1H), 5.19 (s, 1H), 4.90 (d, *J* = 7.2 Hz, 1H), 1.38 (s, 18H) ppm.

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 192.8, 158.8, 154.0 (dd, *J* = 256.6, 12.9 Hz), 153.1, 150.3 (dd, *J* = 249.6, 13.0 Hz), 136.4, 132.2, 131.7, 129.2, 128.7, 126.5 (dd, *J* = 7.4, 3.6 Hz), 125.5, 124.7 (2C), 121.7, 118.7 (d, *J* = 20.0 Hz), 117.4 (d, *J* = 17.7 Hz), 109.8, 90.8, 50.9 (2C), 34.3 (2C), 30.2 (6C) ppm.

**IR (ATR):** 3929, 3786, 3613, 3362, 2958, 2670, 2326, 2024, 1914, 1691, 1600, 1435, 1361, 1280, 1231, 1119, 972, 874, 825, 755, 663 $cm^{-1}$.

**MS (EI):** *m/z* (%): 464.2 (100) $[M]^+ = [C_{29}H_{30}O_3F_2]^+$, 447.2 (92) $[M - OH]^+ = [C_{29}H_{29}O_2F_2]^+$, 141.1 (100) $[M - C_{22}H_{27}O_2]^+ = [C_7H_3OF_2]^+$.

**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{29}H_{30}O_3F_2Na^+$: 487.2056; found 487.2049.




**3j**

**Ethyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5-methyl-2,3-dihydrobenzofuran-2-carboxylate (3j)**

According to the general procedure, **3j** was obtained as a colorless solid (0.113 g, 68% yield) in 0.5 h.

**Melting Point:** 127-129 °C.

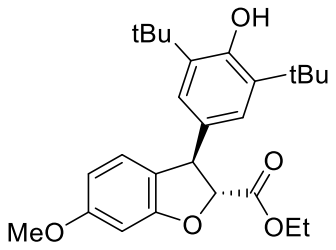
**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.01 – 6.98 (m, 3H), 6.87 – 6.84 (m, 2H), 5.17 (s, 1H), 4.98 (d, *J* = 6.6 Hz, 1H), 4.69 (d, *J* = 6.6 Hz, 1H), 4.34 – 4.21 (m, 2H), 2.25 (s, 3H), 1.41 (s, 18H), 1.32 (t, *J* = 7.2 Hz, 3H) ppm.

**$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 171.0, 157.1, 153.0, 136.1, 132.7, 130.7, 129.1, 128.7, 125.7, 124.4 (2C), 109.4, 87.5, 61.5, 52.7 (2C), 34.4 (2C), 30.2 (6C), 20.8, 14.2 ppm.

**IR (ATR):** 3593, 2951, 2305, 2076, 1750, 1619, 1454, 1194, 1044, 810 $cm^{-1}$.

**MS (ESI):** *m/z* = 433.2 $[M+Na]^+$.

**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{26}H_{34}O_4Na^+$: 433.2349; found 433.2329.




**3k**

**Ethyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6-methoxy-2,3-dihydrobenzofuran-2-carboxylate (3k)**

According to the general procedure, **3k** was obtained as a colorless solid (0.152 g, 89% yield) in 0.5 h.

**Melting Point:** 140-142 °C.

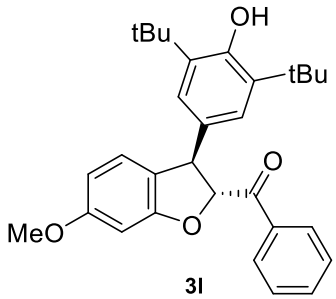
**$^1$H NMR (600 MHz, $CDCl_3$)** δ 6.99 (s, 2H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 2.4 Hz, 1H), 6.47 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.16 (s, 1H), 4.99 (d, *J* = 6.0 Hz, 1H), 4.67 (d, *J* = 6.0 Hz, 1H), 4.37 – 4.23 (m, 2H), 3.80 (s, 3H), 1.40 (s, 18H), 1.33 (t, *J* = 7.2 Hz, 3H) ppm.

**$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 170.9, 160.7, 160.5, 153.0, 136.1, 132.8, 125.5, 124.3 (2C), 120.5, 107.5, 96.2, 88.2, 61.5, 55.5, 55.4, 52.1, 34.4 (2C), 30.2 (6C), 14.3 ppm.

**IR (ATR):** 3779, 3550, 2949, 2174, 2092, 1986, 1904, 1739, 1619, 1487, 1442, 1365, 1329, 1269, 1154, 1052, 925, 834, 775 $cm^{-1}$.

**MS (ESI):** *m/z* = 449.2 $[M+Na]^+$.

**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{26}H_{34}O_5Na^+$: 449.2299; found 449.2292.




**3l**

**(3-(3,5-di-*tert*-Butyl-4-hydroxyphenyl)-6-methoxy-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3l)**

According to the general procedure, **3l** was obtained as a colorless solid (0.178 g, 97% yield) in 12 h.

**Melting Point:** 153-155 °C.

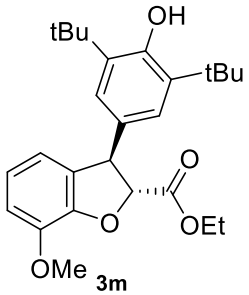
**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 6.94 (s, 2H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.59 (d, *J* = 2.4 Hz, 1H), 6.46 (dd, *J* = 7.8, 2.4 Hz, 1H), 5.79 (d, *J* = 6.6 Hz, 1H), 5.18 (s, 1H), 4.75 (d, *J* = 6.6 Hz, 1H), 3.80 (s, 3H), 1.39 (s, 18H) ppm.

**$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 195.2, 160.7, 160.5, 153.0, 136.2, 134.5, 133.6, 132.9, 129.3 (2C), 128.6 (2C), 125.6, 124.6 (2C), 121.2, 107.5, 96.0, 91.7, 55.5, 55.4, 50.9, 34.4 (2C), 30.3 (6C) ppm.

**IR (ATR):** 3753, 3572, 2959, 2640, 2288, 2096, 1952, 1737, 1610, 1493, 1441, 1362, 1285, 1225, 1106, 1045, 966, 882, 833, 770, 685 $cm^{-1}$.

**MS (ESI):** *m/z* = 481.2 $[M+Na]^+$.

**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{30}H_{34}O_4Na^+$: 481.2349; found 481.2338.



**3m**

**Ethyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-7-methoxy-2,3-dihydrobenzofuran-2-carboxylate (3m)**

According to the general procedure, **3m** was obtained as a colorless solid (0.156 g, 92% yield) in 0.5 h.

**Melting Point:** 139-141 ºC.

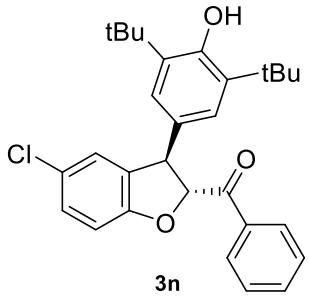
**$^1$H NMR (600 MHz, $CDCl_3$)** δ 6.99 (s, 2H), 6.88 – 6.85 (m, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 7.2 Hz, 1H), 5.17 (s, 1H), 5.04 (d, *J* = 6.6 Hz, 1H), 4.77 (d, *J* = 6.6 Hz, 1H), 4.35 – 4.23 (m, 2H), 3.93 (s, 3H), 1.40 (s, 18H), 1.32 (t, *J* = 7.2 Hz, 3H) ppm.

**$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 170.6, 153.0, 147.7, 144.5, 136.1, 132.2, 129.9, 124.4 (2C), 122.0, 117.4, 111.7, 87.9, 61.5, 56.2, 53.2 (2C), 34.5 (2C), 30.2 (6C), 14.2 ppm.

**IR (ATR):** 3598, 2956, 2629, 2302, 2166, 2065, 1925, 1742, 1613, 1441, 1362, 1281, 1192, 1089, 1035, 947, 882, 816, 742 $cm^{-1}$.

**MS (ESI):** *m/z* = 449.2 $[M+Na]^+$.

**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{26}H_{34}O_5Na^+$: 449.2299; found 449.2286.



**3n**

**(5-Chloro-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3n)**

According to the general procedure, **3n** was obtained as an off-white solid (0.175 g, 95% yield) in 12 h.

**Melting Point:** 139-141 ºC.

**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.94 – 7.90 (m, 2H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.16 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.94 (s, 2H), 6.91 (d, *J* = 8.4 Hz, 1H), 5.83 (d, *J* = 6.6 Hz, 1H), 5.22 (s, 1H), 4.82 (d, *J* = 6.6 Hz, 1H), 1.40 (s, 18H) ppm.

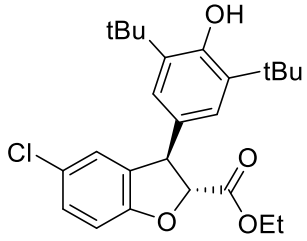
**$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 194.6, 157.8, 153.3, 136.4, 134.3, 133.8, 131.9, 131.5, 129.3 (2C), 128.7, 128.6 (2C), 126.2, 125.5, 124.7 (2C), 110.8, 91.2, 51.2, 51.1, 34.4 (2C), 30.2 (6C) ppm.

**IR (ATR):** 3812, 3590, 3463, 2956, 2642, 2293, 2072, 1953, 1738, 1590, 1461, 1364, 1223, 1113,

1054, 963, 875, 812, 685 $cm^{-1}$.

**MS (ESI):** *m/z* = 485.2 $[M+Na]^+$.

**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{29}H_{31}O_3ClNa^+$: 485.1854; found 485.1838.




**3o**

**Ethyl-5-chloro-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-carboxylate (3o)**

According to the general procedure, **3o** was obtained as a colorless solid (0.155 g, 90% yield) in 0.5 h.

**Melting Point:** 145-147 °C.

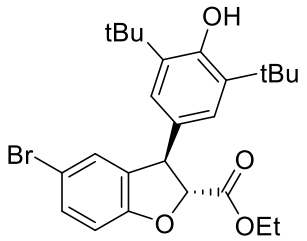
**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.16 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.97 (s, 2H), 6.90 (d, *J* = 9.0 Hz, 1H), 5.21 (s, 1H), 5.04 (d, *J* = 6.0 Hz, 1H), 4.70 (d, *J* = 6.0 Hz, 1H), 4.35 – 4.24 (m, 2H), 1.41 (s, 18H), 1.33 (t, *J* = 7.2 Hz, 3H) ppm.

**$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 170.4, 157.8, 153.2, 136.3, 131.8, 131.0, 128.7, 126.2, 125.4, 124.2 (2C), 110.9, 87.9, 61.7, 52.5 (2C), 34.4 (2C), 30.2 (6C), 14.2 ppm.

**IR (ATR):** 3784, 3541, 2953, 2326, 2113, 1741, 1591, 1466, 1368, 1213, 1157, 1115, 1044, 875, 811, 766, 685 $cm^{-1}$.

**MS (EI):** *m/z* (%): 430.0 (2) $[M]^+ = [C_{25}H_{31}O_4Cl]^+$, 57.2 (100) $[M - C_{21}H_{22}O_4Cl]^+ = [C_4H_9]^+$.

**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{25}H_{31}O_4ClNa^+$: 453.1803; found 453.1797.




**3p**

**Ethyl-5-bromo-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-carboxylate (3p)**

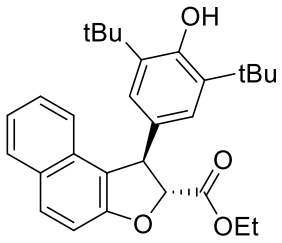
According to the general procedure, **3p** was obtained as a colorless solid (0.168 g, 89% yield) in 0.5 h.

**Melting Point:** 150-152 °C.

**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.30 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.15 (d, *J* = 1.8 Hz, 1H), 6.96 (s, 2H), 6.87 (d, *J* = 8.4 Hz, 1H), 5.21 (s, 1H), 5.03 (d, *J* = 6.0 Hz, 1H), 4.70 (d, *J* = 6.0 Hz, 1H), 4.35 – 4.23 (m, 2H), 1.41 (s, 18H), 1.32 (t, *J* = 7.2 Hz, 3H) ppm.

**$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 170.4, 158.3, 153.2, 136.3, 131.8, 131.6, 131.5, 128.3, 124.3 (2C), 113.3, 111.5, 87.9, 61.7, 52.5 (2C), 34.4 (2C), 30.2 (6C), 14.2 ppm.

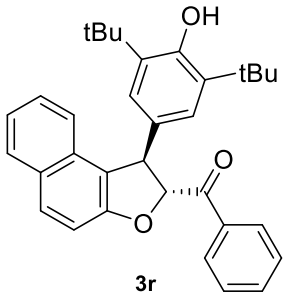
**IR (ATR):** 3852, 3637, 3074, 2958, 2324, 2174, 2063, 1986, 1934, 1749, 1587, 1470, 1435, 1369, 1300, 1199, 1153, 1112, 1047, 879, 807, 761, 726, 671 $cm^{-1}$.
**MS (ESI):** *m/z* = 499.1 $[M+Na]^+$.
**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{25}H_{31}O_4BrNa^+$: 497.1298; found 497.1294.




**3q**

**Ethyl-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,2-dihydronaphtho[2,1-b]furan-2-carboxylate (3q)**

According to the general procedure, **3q** was obtained as a colorless solid (0.151 g, 85% yield) in 1 h.
**Melting Point:** 143-145 ºC.
**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.33 – 7.25 (m, 3H), 7.02 (s, 2H), 5.16 (d, *J* = 5.4 Hz, 1H), 5.14 (s, 1H), 5.10 (d, *J* = 5.4 Hz, 1H), 4.38 – 4.24 (m, 2H), 1.36 – 1.33 (m, 21H) ppm.
**$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 171.1, 157.1, 152.9, 136.1, 132.6, 130.5, 130.3, 130.0, 128.7, 126.5, 124.2 (2C), 123.2, 123.1, 119.5, 112.2, 88.2, 61.6, 52.3 (2C), 34.3 (2C), 30.2 (6C), 14.3 ppm.
**IR (ATR):** 3586, 2939, 2326, 2078, 1913, 1747, 1615, 1427, 1195, 1047, 752 $cm^{-1}$.
**MS (ESI):** *m/z* = 469.2 $[M+Na]^+$.
**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{29}H_{34}O_4Na^+$: 469.2349; found 469.2332.




**3r**

**(1-(3,5-di-*tert*-Butyl-4-hydroxyphenyl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)(phenyl)methanone (3r)**

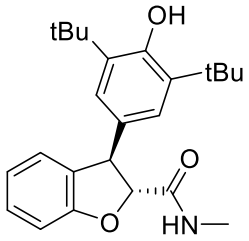
According to the general procedure, **3r** was obtained as a colorless solid (0.120 g, 63% yield) in 12 h.
**Melting Point:** 160-162 ºC.
**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.99 – 7.97 (m, 2H), 7.80 – 7.77 (m, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.33 – 7.30 (m, 2H), 7.29 – 7.22 (m, 2H), 7.00 (s, 2H), 5.94 (d, *J* = 5.4 Hz, 1H), 5.15 (s, 1H), 5.14 (d, *J* = 5.4 Hz, 1H), 1.35 (s, 18H) ppm.

**$^{13}$C NMR (150 MHz, $CDCl_3$)** δ 195.1, 157.1, 153.0, 136.3, 134.3, 133.7, 132.7, 130.5, 130.2, 130.0, 129.4 (2C), 128.7, 128.6 (2C), 126.5, 124.4 (2C), 123.1, 123.0, 120.1, 112.1, 91.8, 51.1 (2C), 34.3 (2C), 30.3 (6C) ppm.

**IR (ATR):** 3817, 3607, 3449, 2953, 2642, 2333, 2086, 1904, 1739, 1583, 1520, 1441, 1366, 1225, 1126, 1051, 965, 862, 811, 754, 690 $cm^{-1}$.

**MS (ESI):** *m/z* = 501.2 $[M+Na]^+$.

**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{33}H_{34}O_3Na^+$: 501.2400; found 501.2389.




**3s**

**3-(3,5-di-*tert*-Butyl-4-hydroxyphenyl)-N-methyl-2,3-dihydrobenzofuran-2-carboxamide (3s)**

According to the general procedure, **3s** was obtained as a wax (0.099 g, 65% yield) in 1 h.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.23 – 7.17 (m, 1H), 7.13 – 7.11 (m, 1H), 7.01 (s, 2H), 6.97 – 6.91 (m, 2H), 6.66 – 6.58 (m, 1H), 5.13 (s, 1H), 4.95 (d, *J* = 5.2 Hz, 1H), 4.80 (d, *J* = 5.2 Hz, 1H), 2.85 (d, *J* = 4.9 Hz, 3H), 1.38 (s, 18H) ppm.

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 172.0, 158.4, 152.9, 136.2, 133.7, 129.2, 128.7, 126.3, 124.3 (2C), 122.0, 109.8, 88.7, 52.2 (2C), 34.5 (2C), 30.3 (6C), 25.9 ppm.

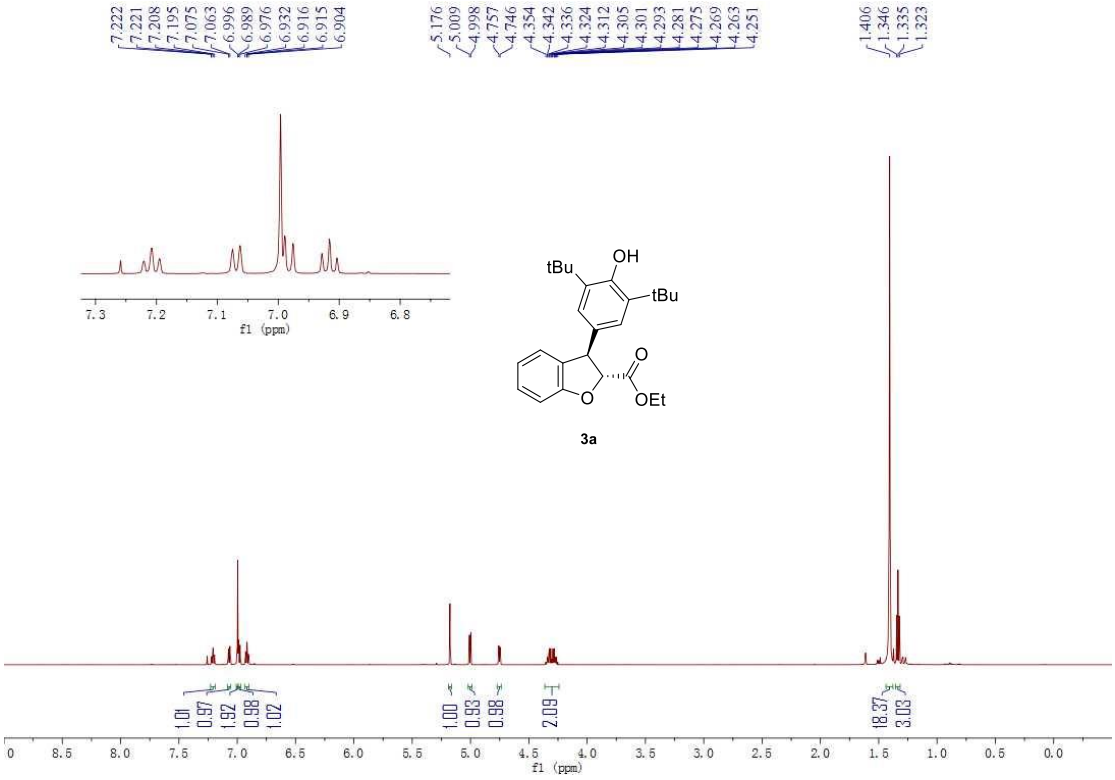
**IR (ATR):** 3634, 3440, 3334, 2955, 2913, 1664, 1597, 1537, 1476, 1460, 1434, 1318, 1265, 1229, 1154, 1119, 908. 861, 821, 732, 649 $cm^{-1}$.

**MS (ESI):** *m/z* = 382.0 $[M+H]^+$.

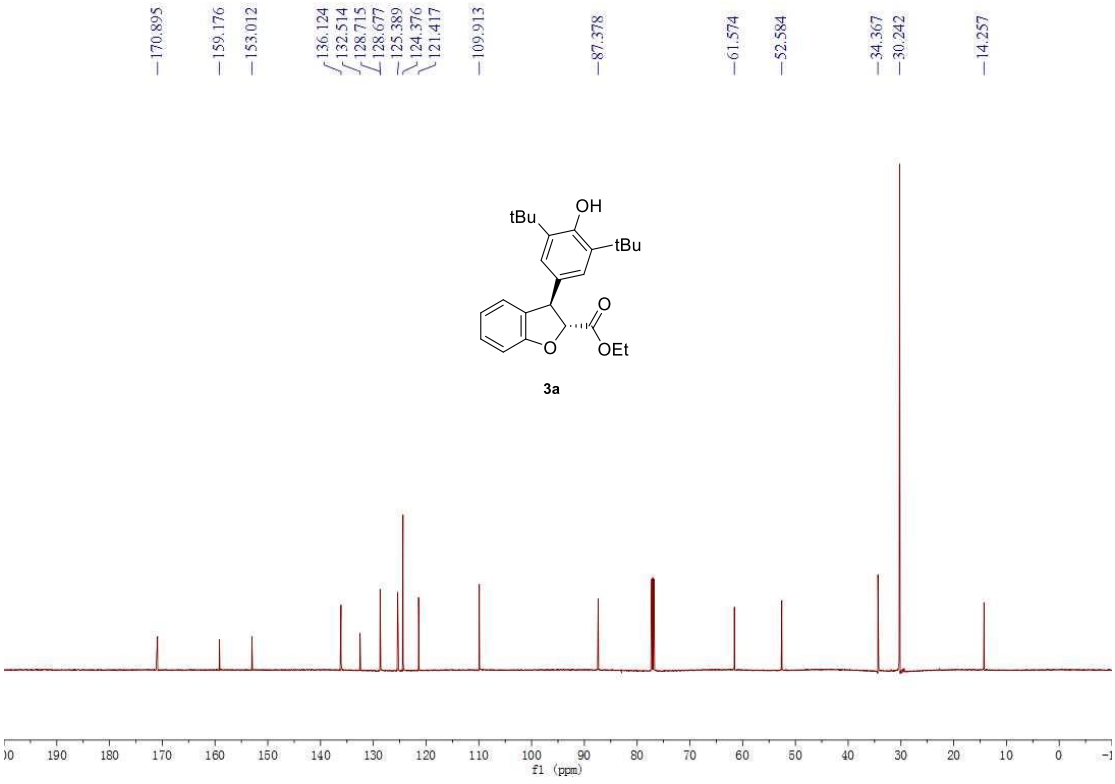
**HRMS (ESI):** *m/z* $[M+Na]^+$ calcd for $C_{24}H_{31}NO_3Na^+$: 404.2197; found 404.2191.

## 3. NMR Spectra:

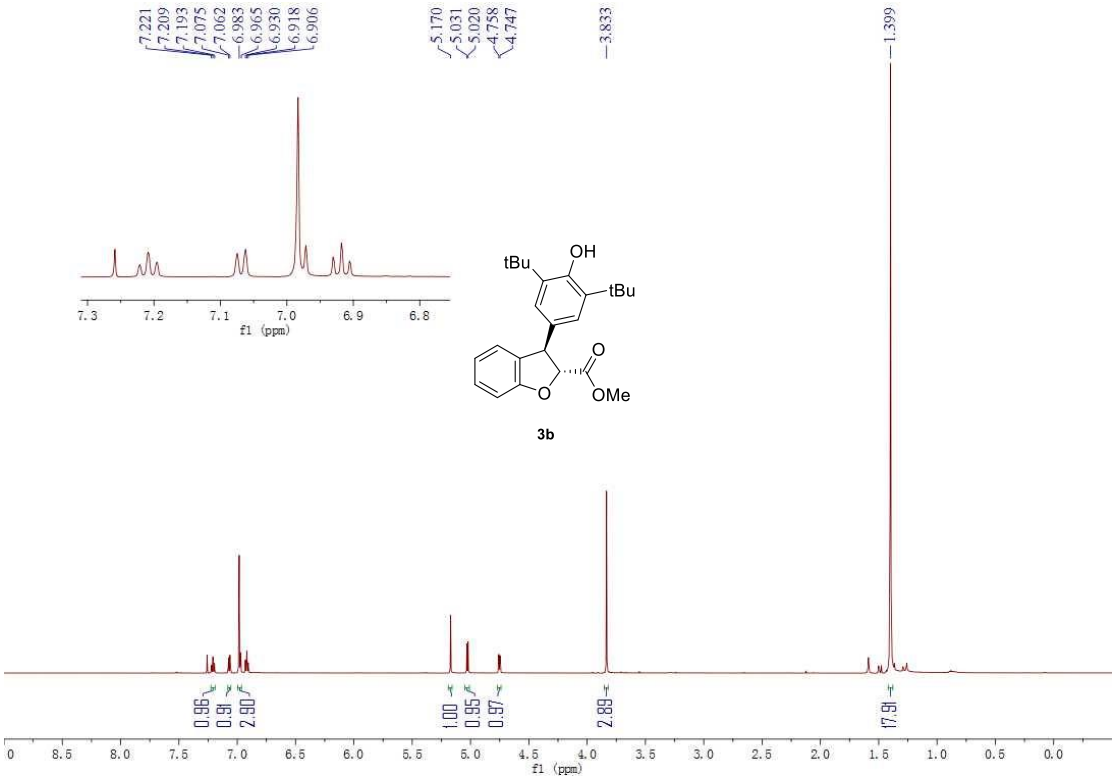
$^{1}$H NMR of **3a:**



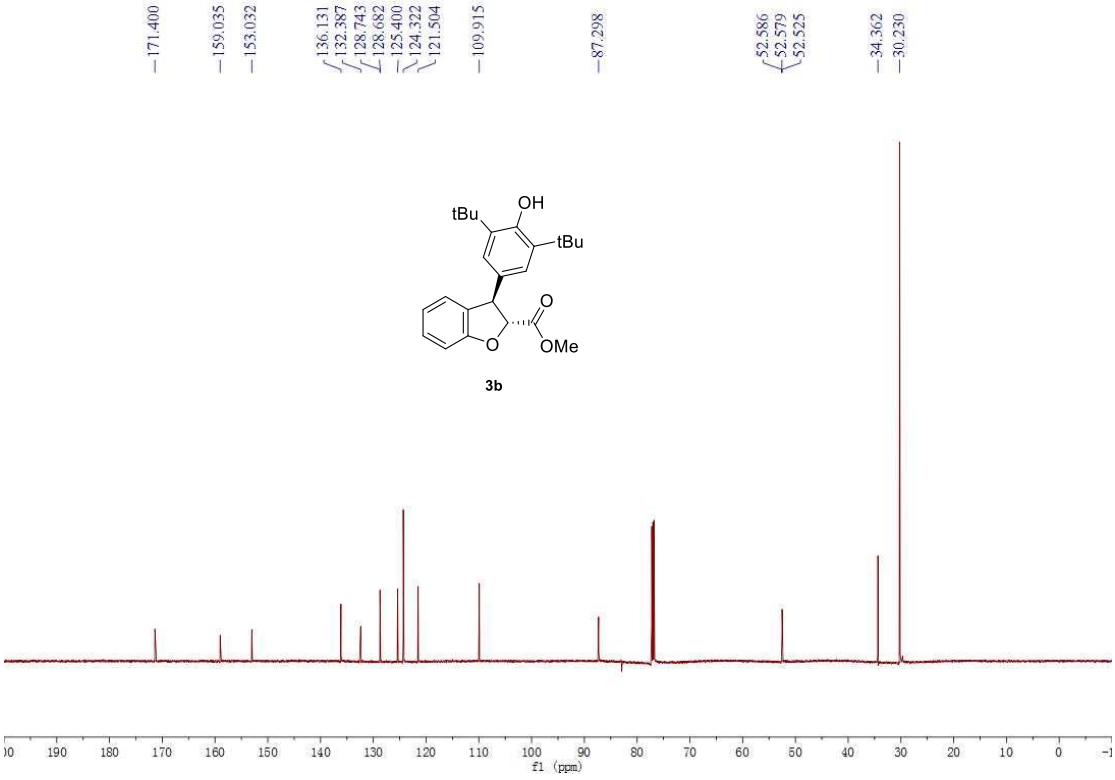

$^{13}$C NMR of **3a:**



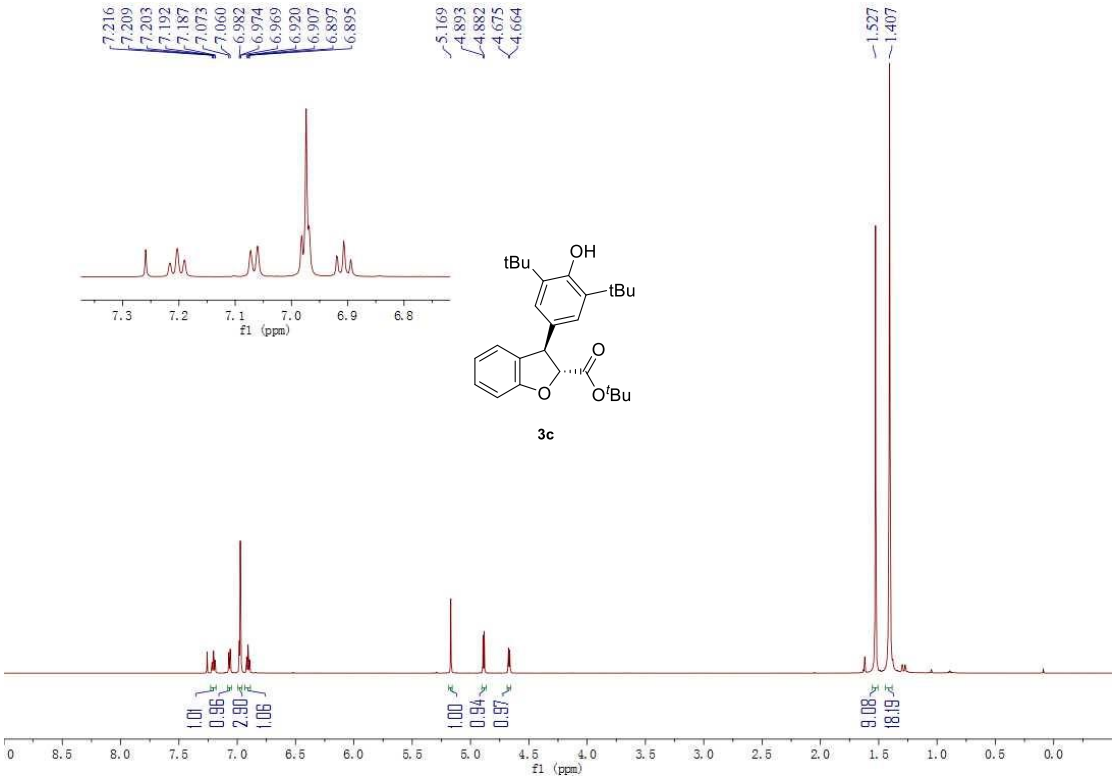
$^{1}$H NMR of **3b:**



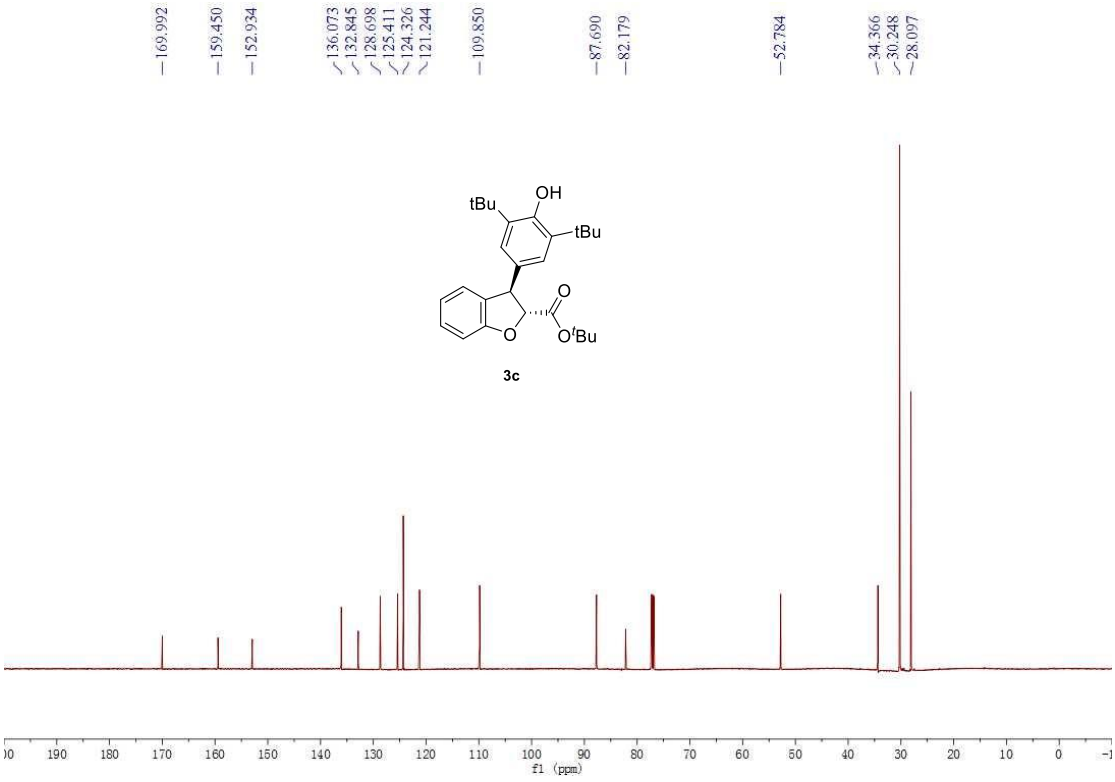

$^{13}$C NMR of **3b:**



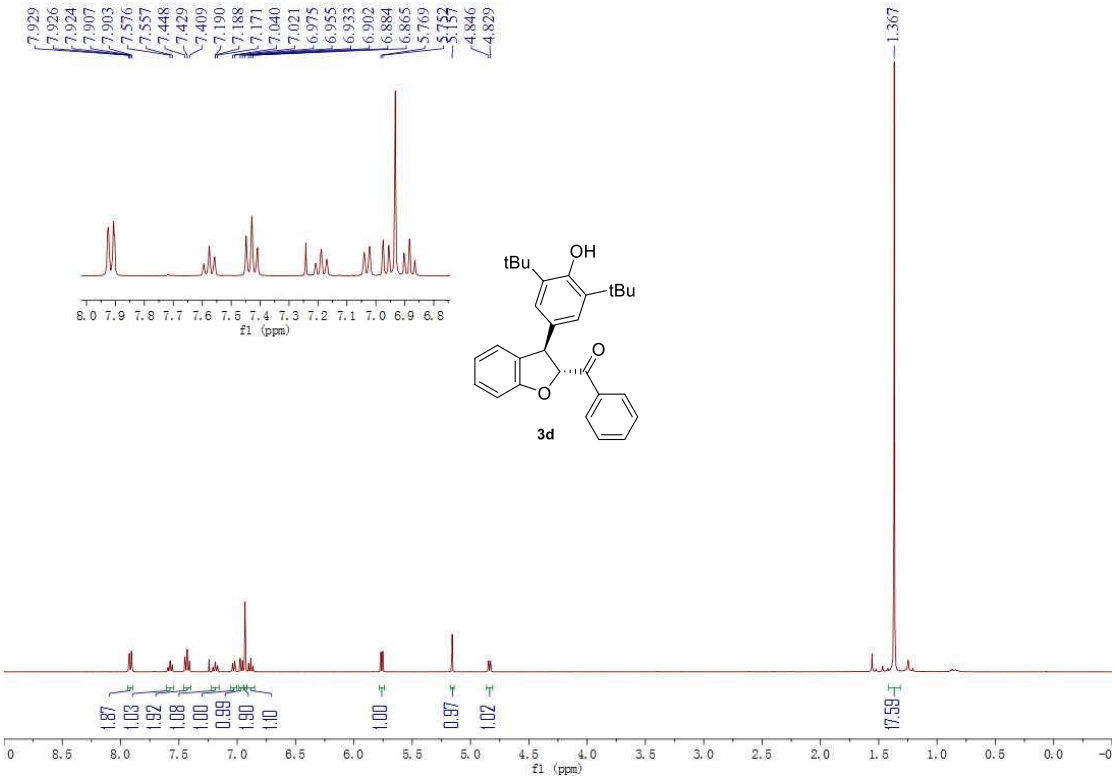
$^{1}$H NMR of **3c:**



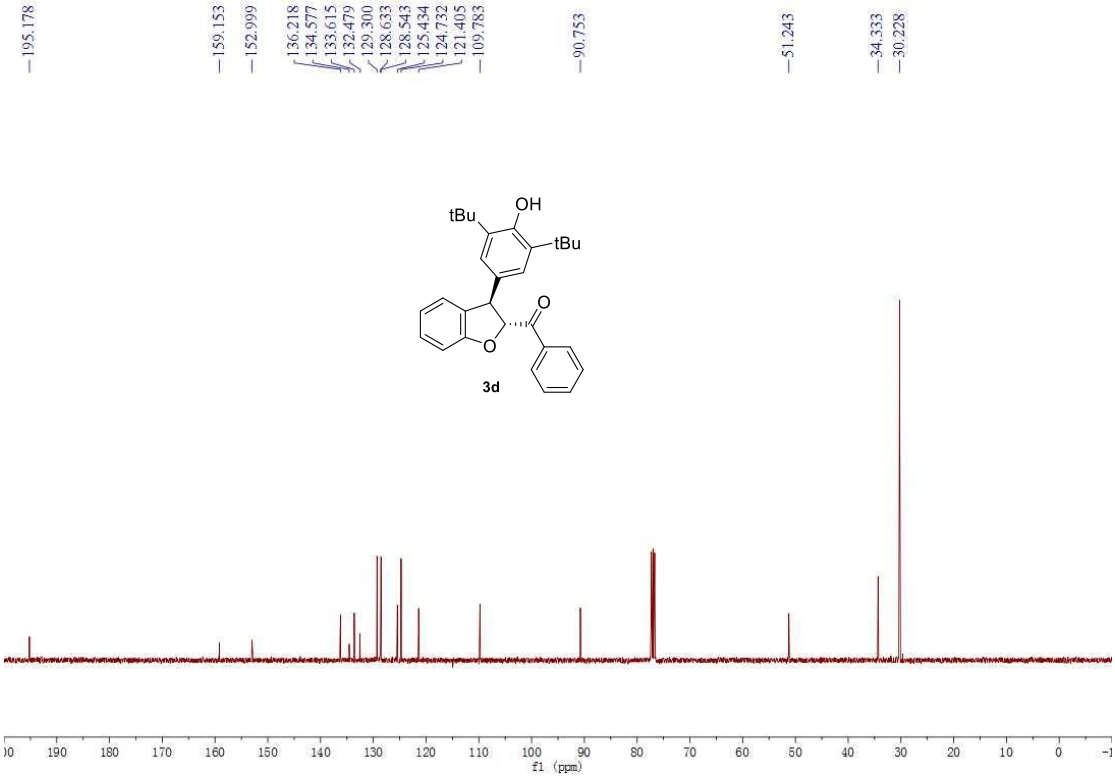

$^{13}$C NMR of **3c:**



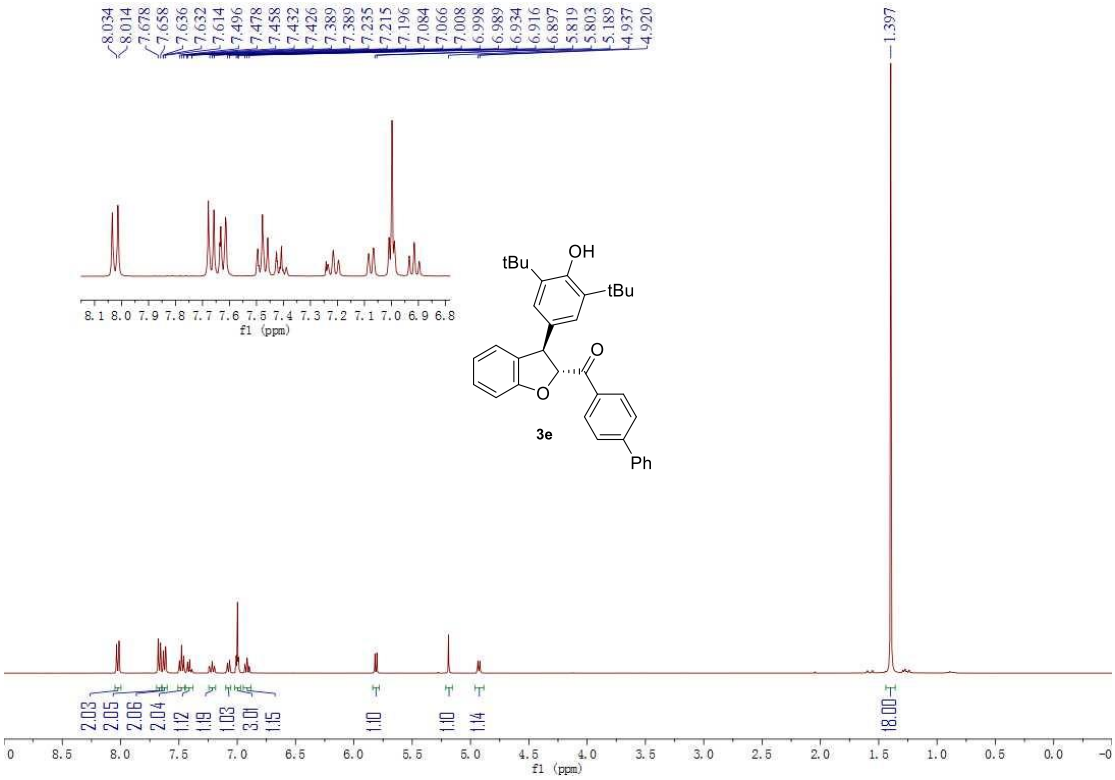
$^{1}$H NMR of **3d:**



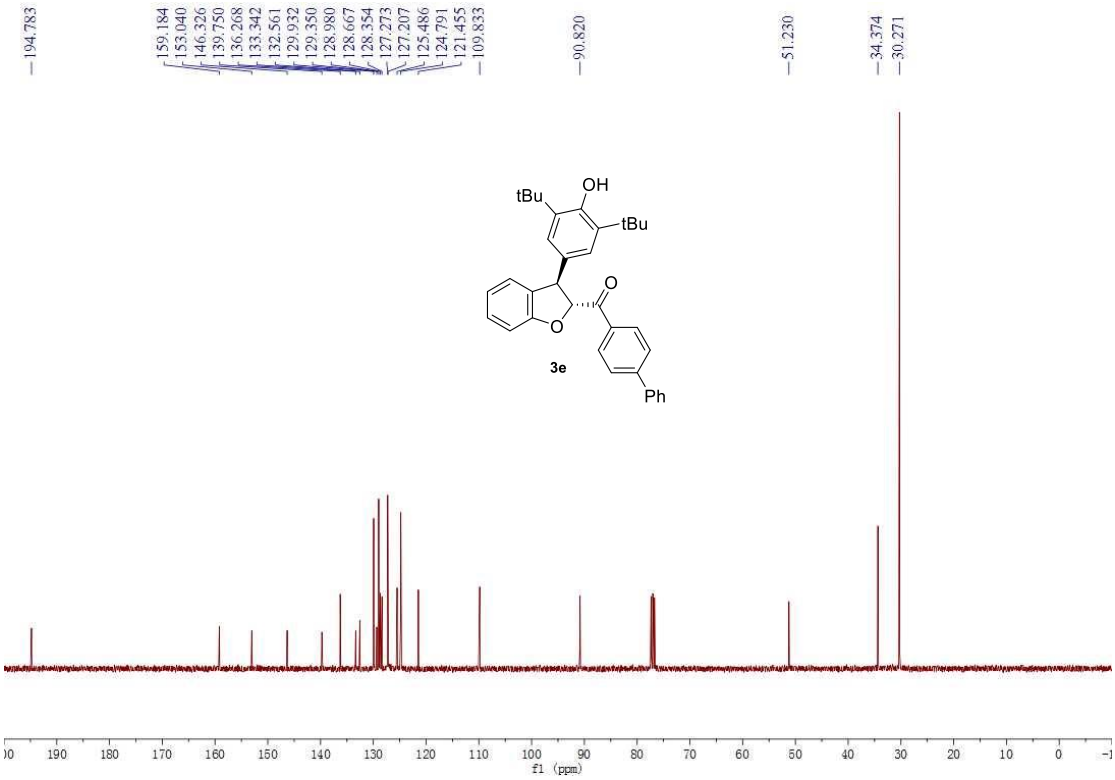

$^{13}$C NMR of **3d:**



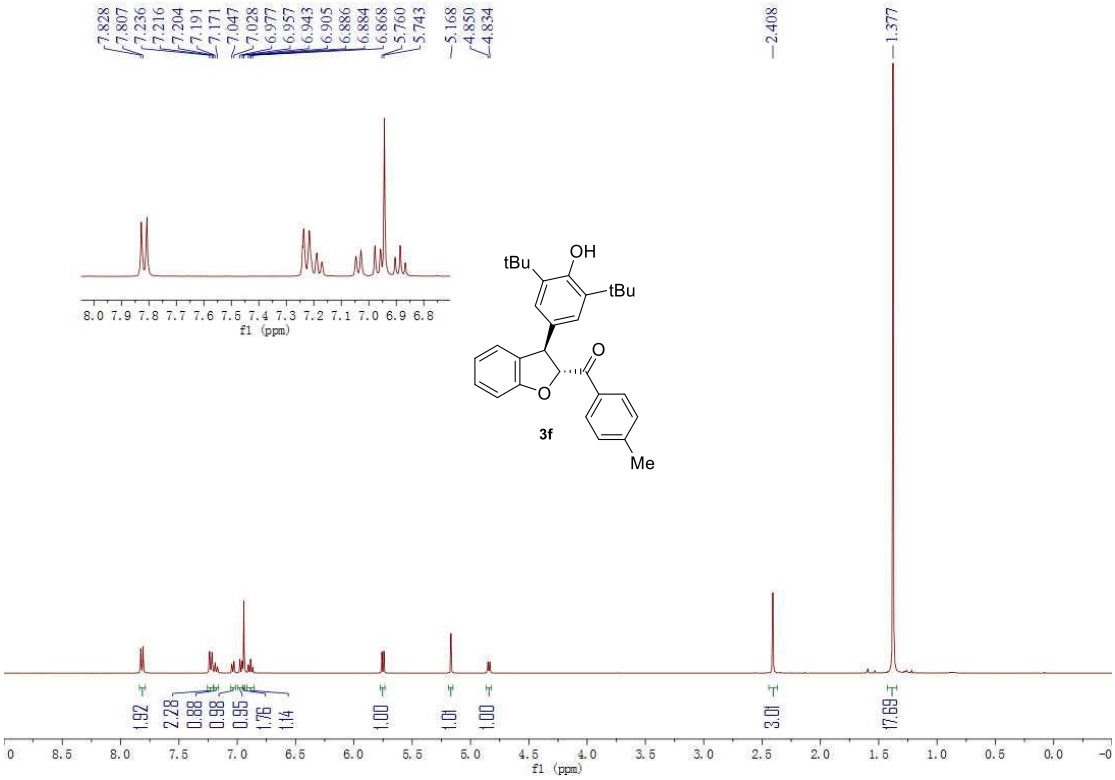
$^{1}$H NMR of **3e:**



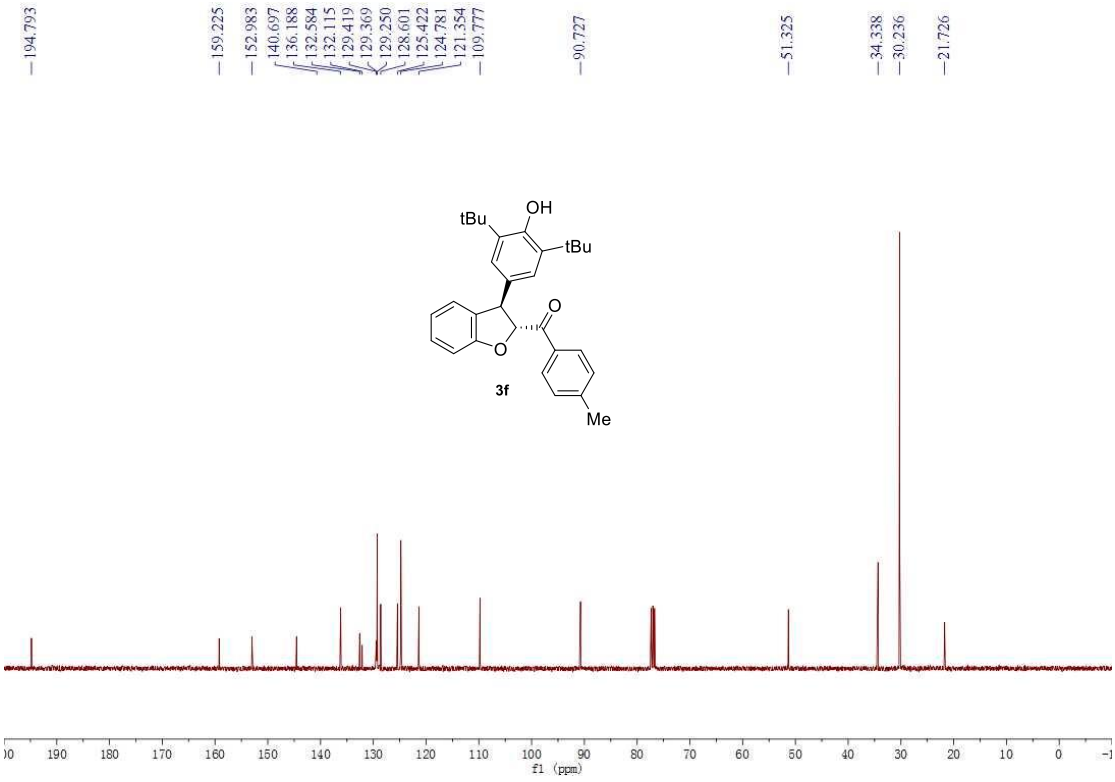

$^{13}$C NMR of **3e:**



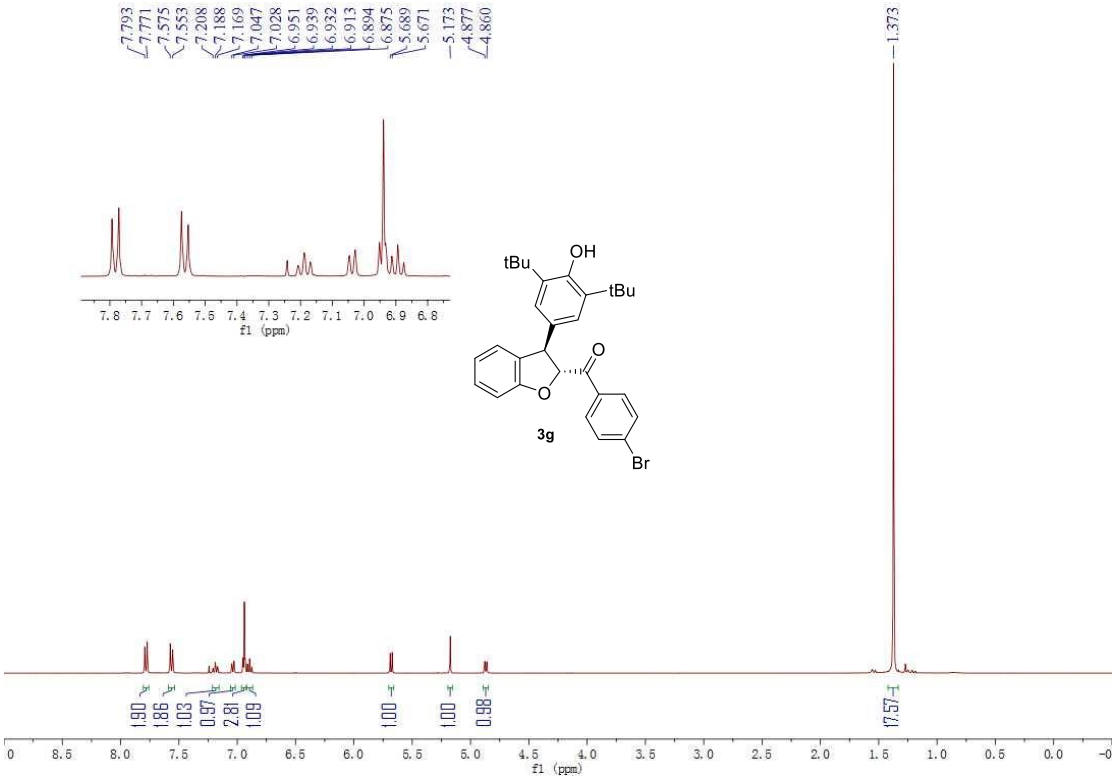
$^{1}$H NMR of **3f:**



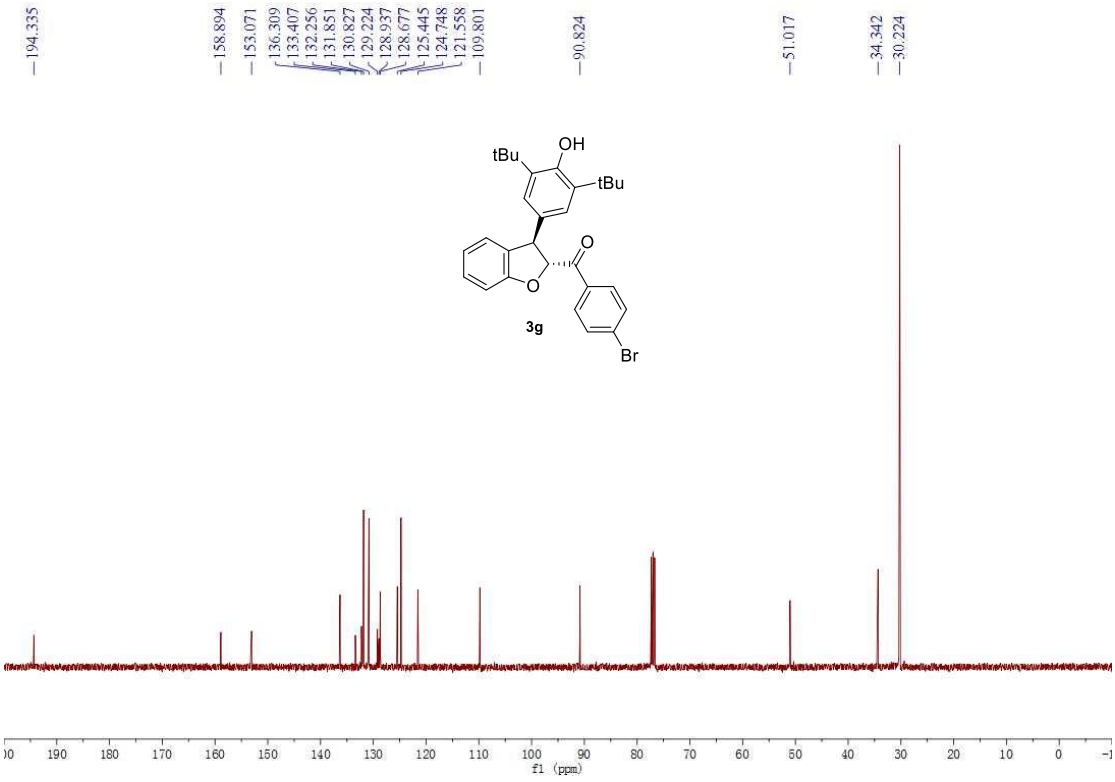

$^{13}$C NMR of **3f:**



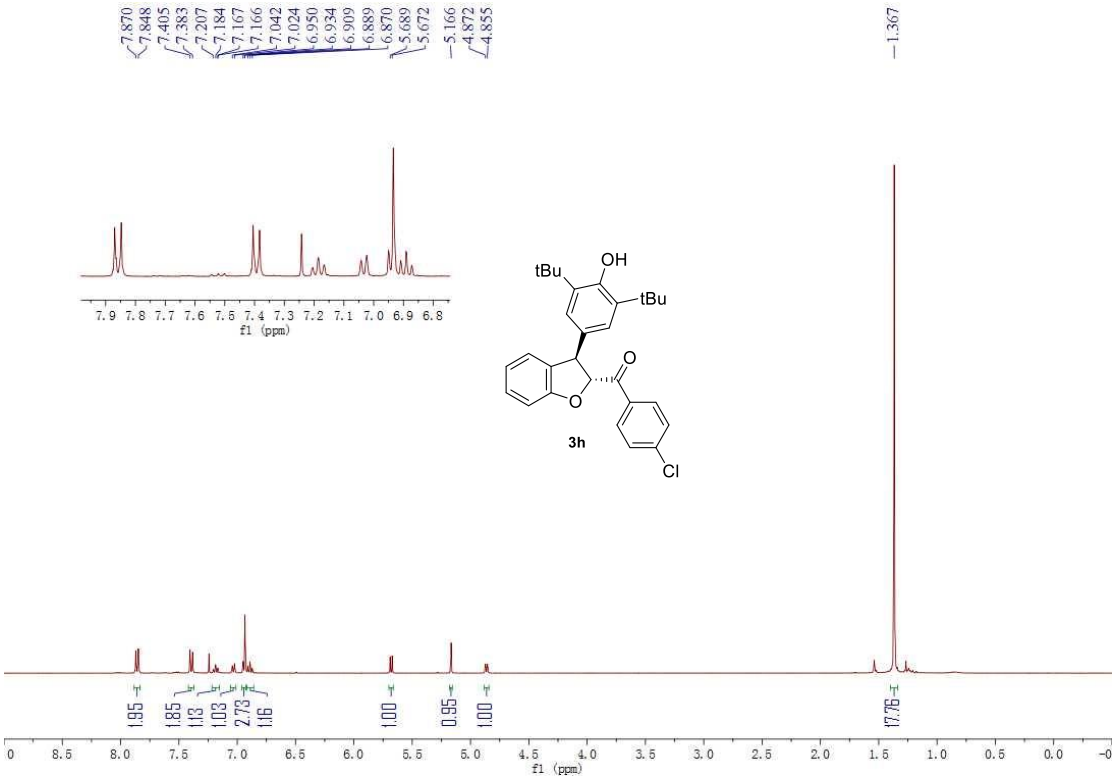
$^{1}$H NMR of **3g:**



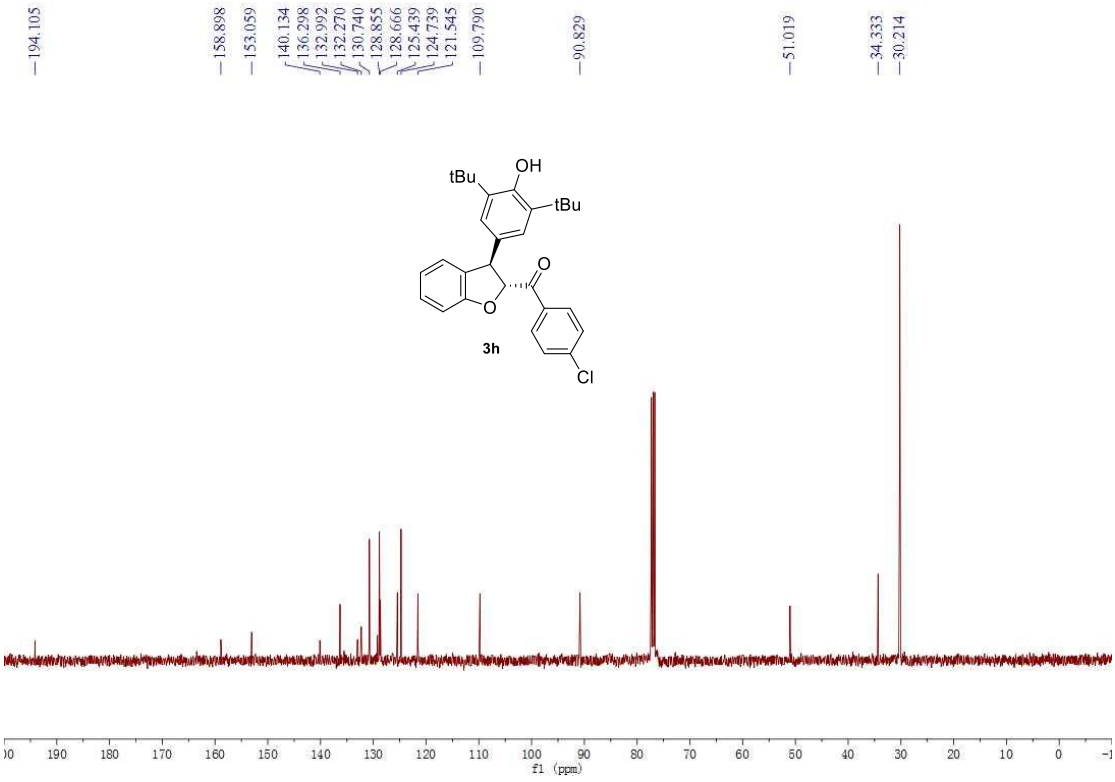

$^{13}$C NMR of **3g:**



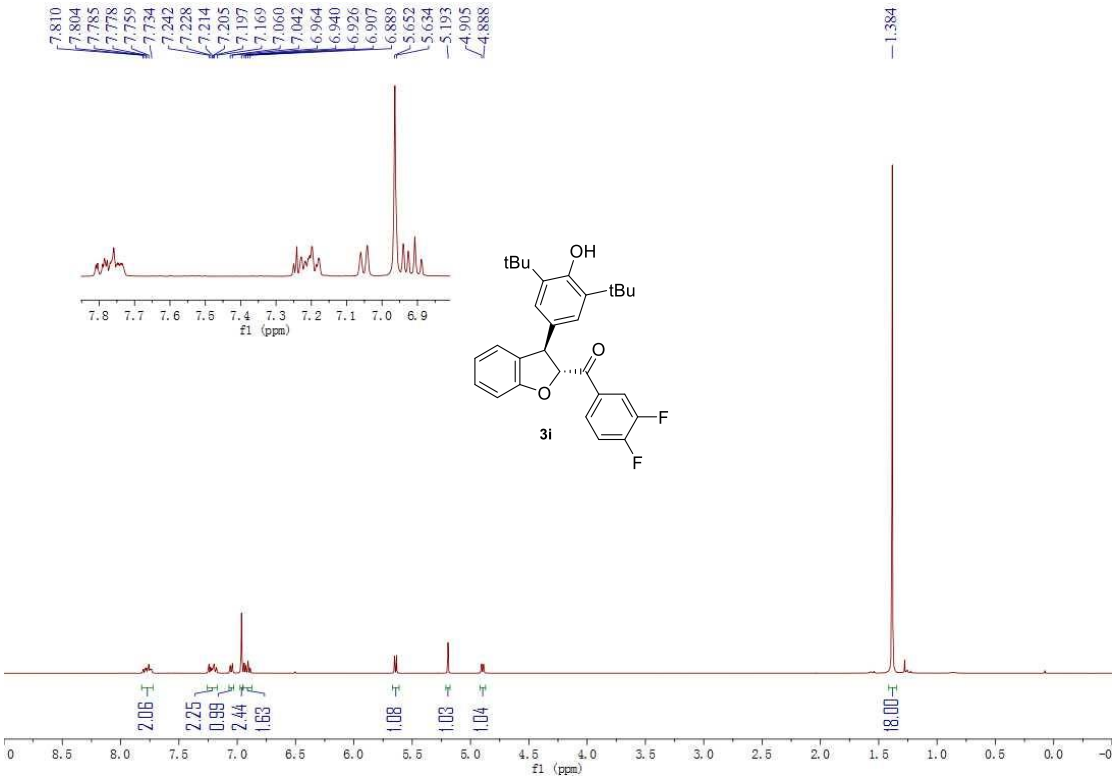
$^{1}$H NMR of **3h:**



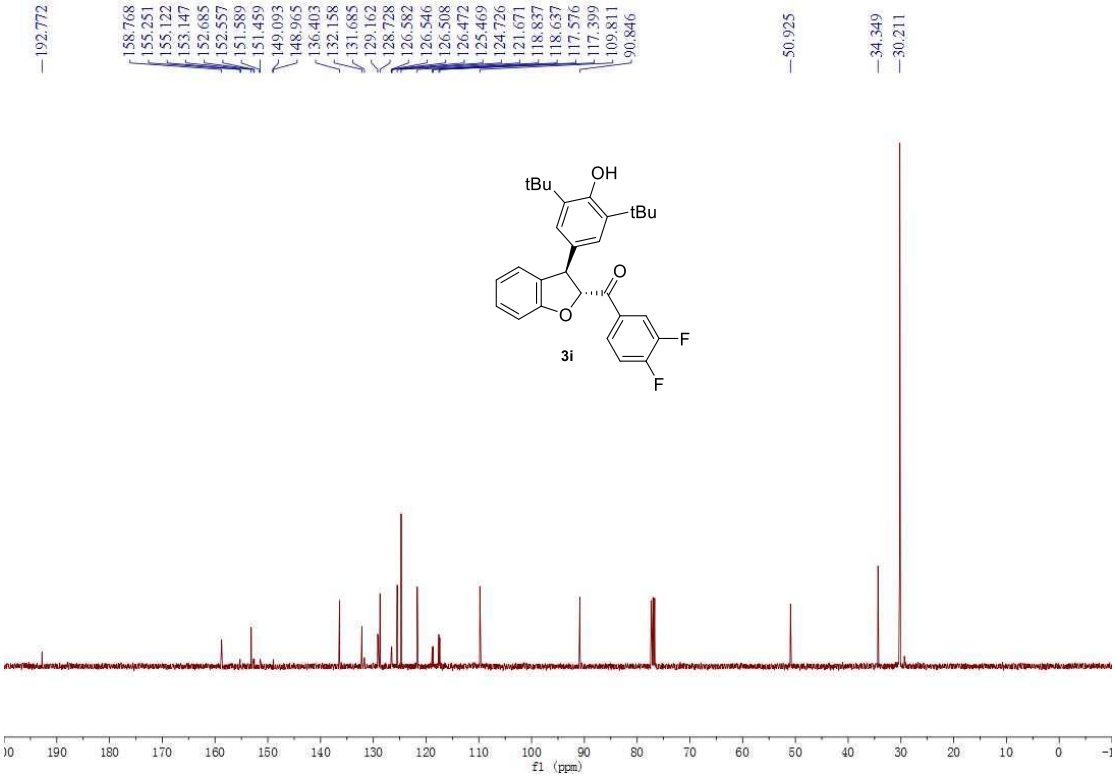

$^{13}$C NMR of **3h:**



$^{1}$H NMR of **3i:**




$^{13}$C NMR of **3i:**



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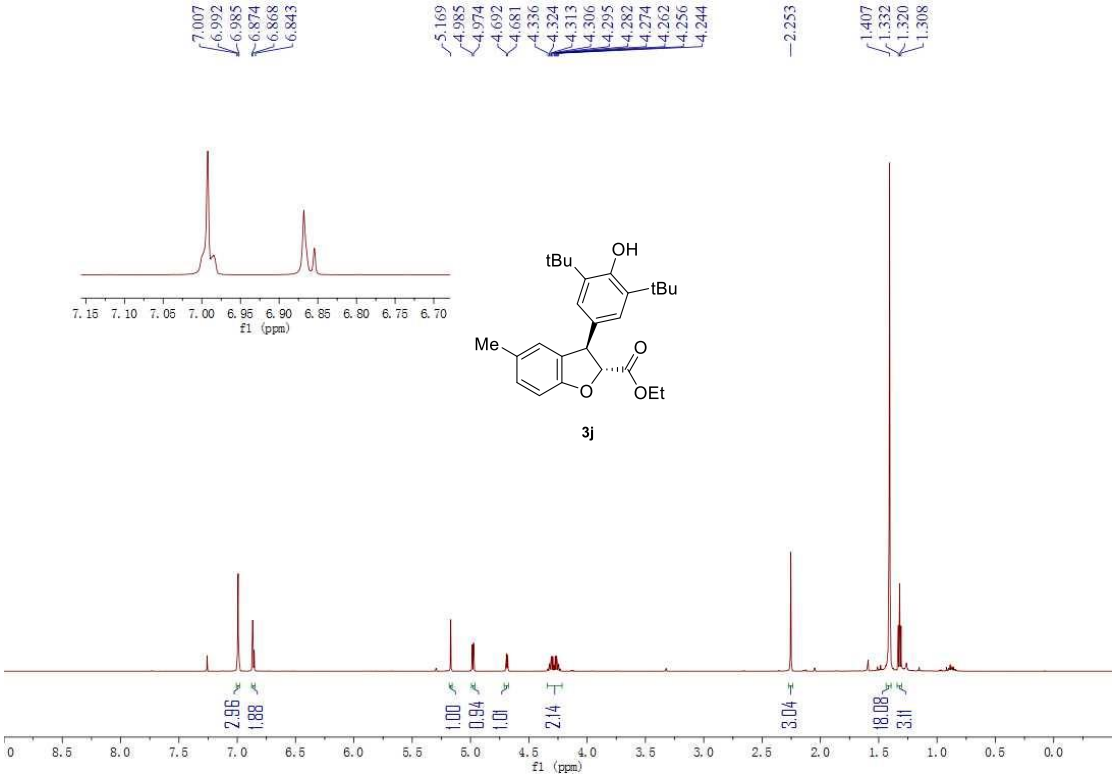


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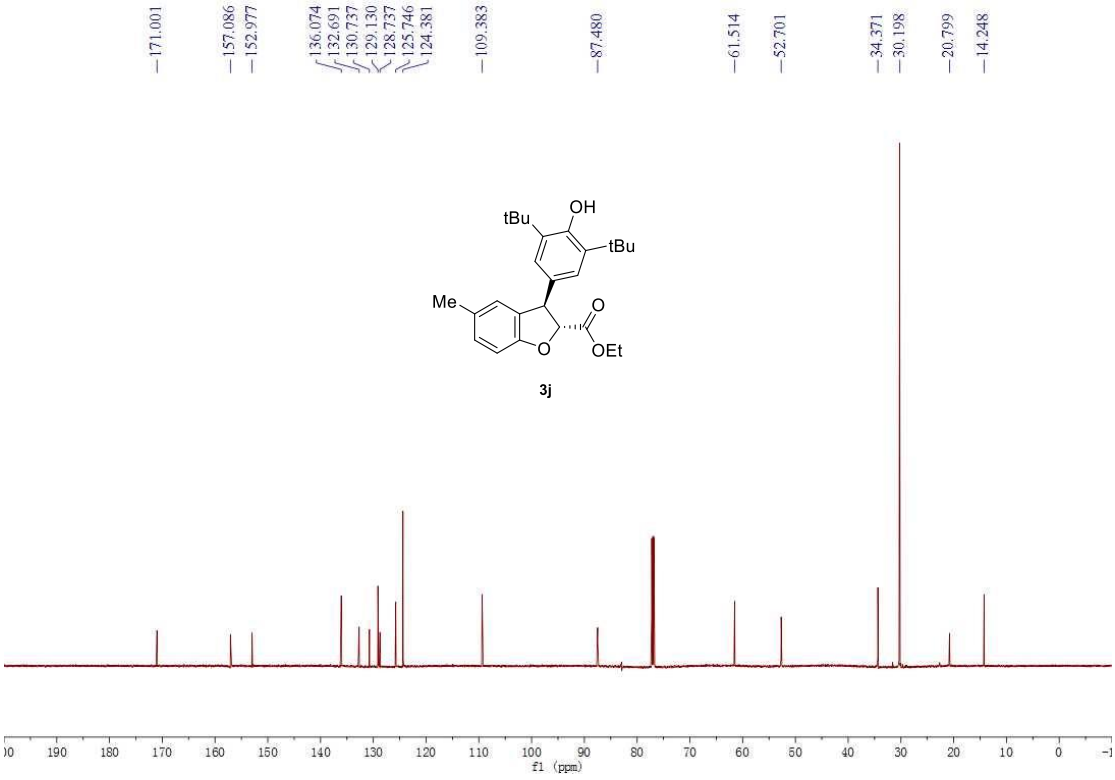
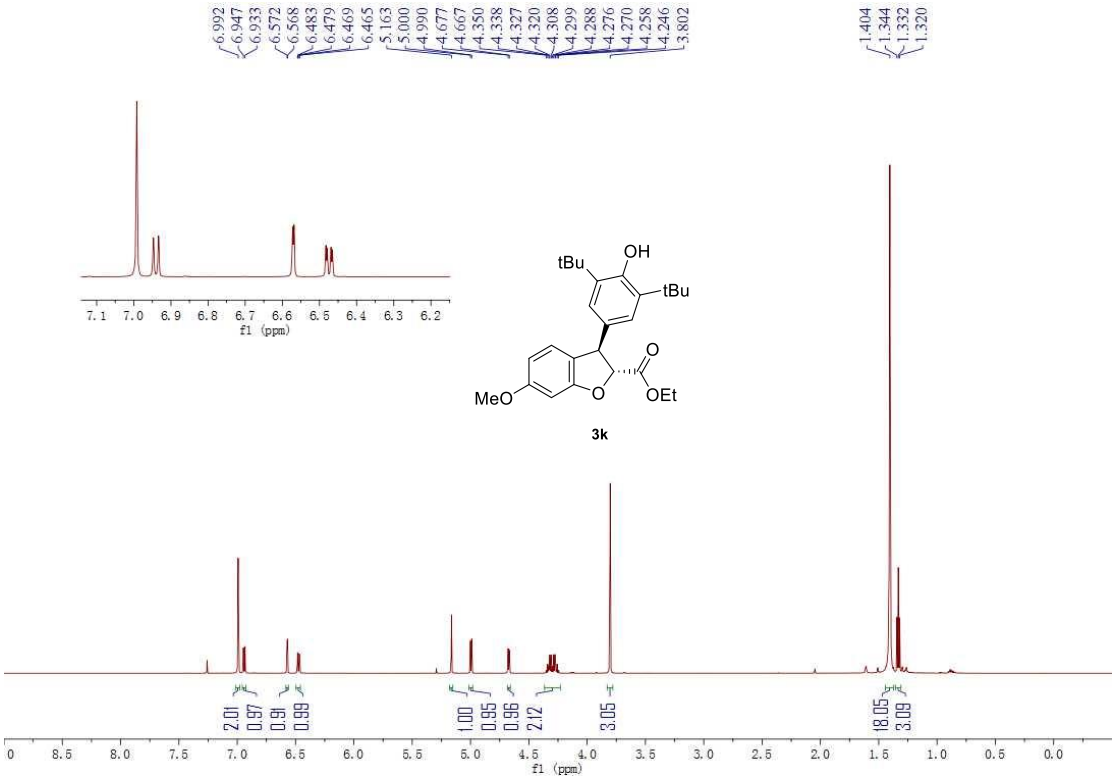
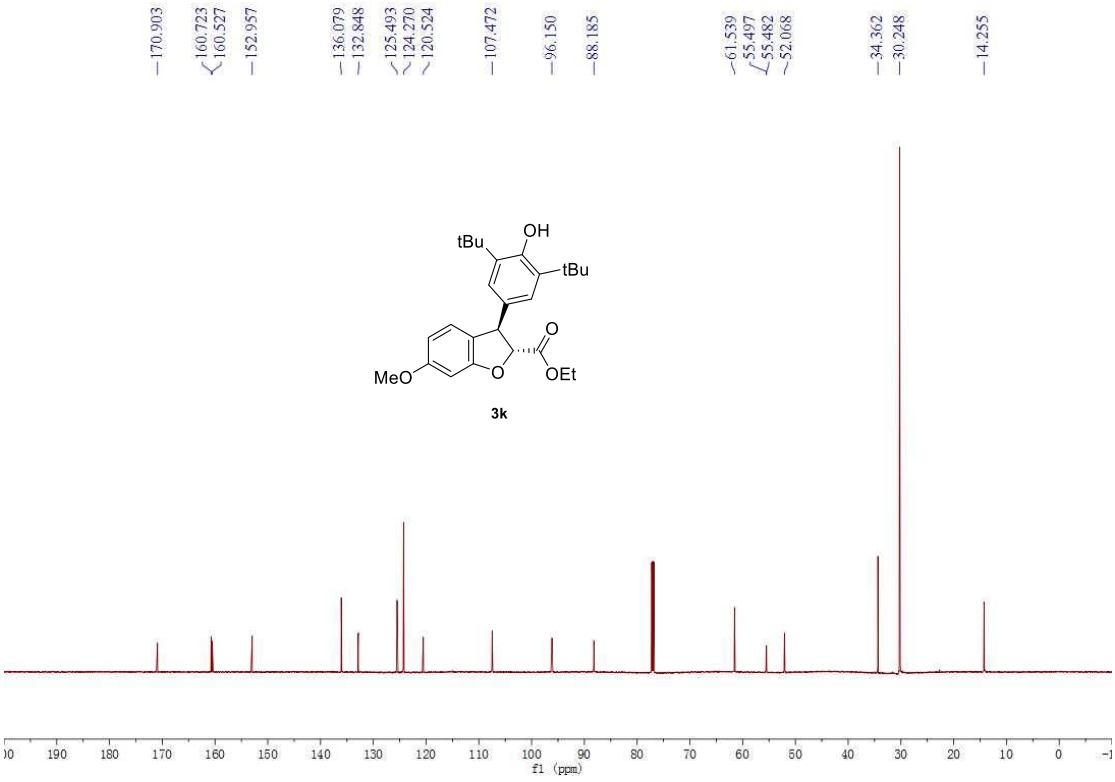


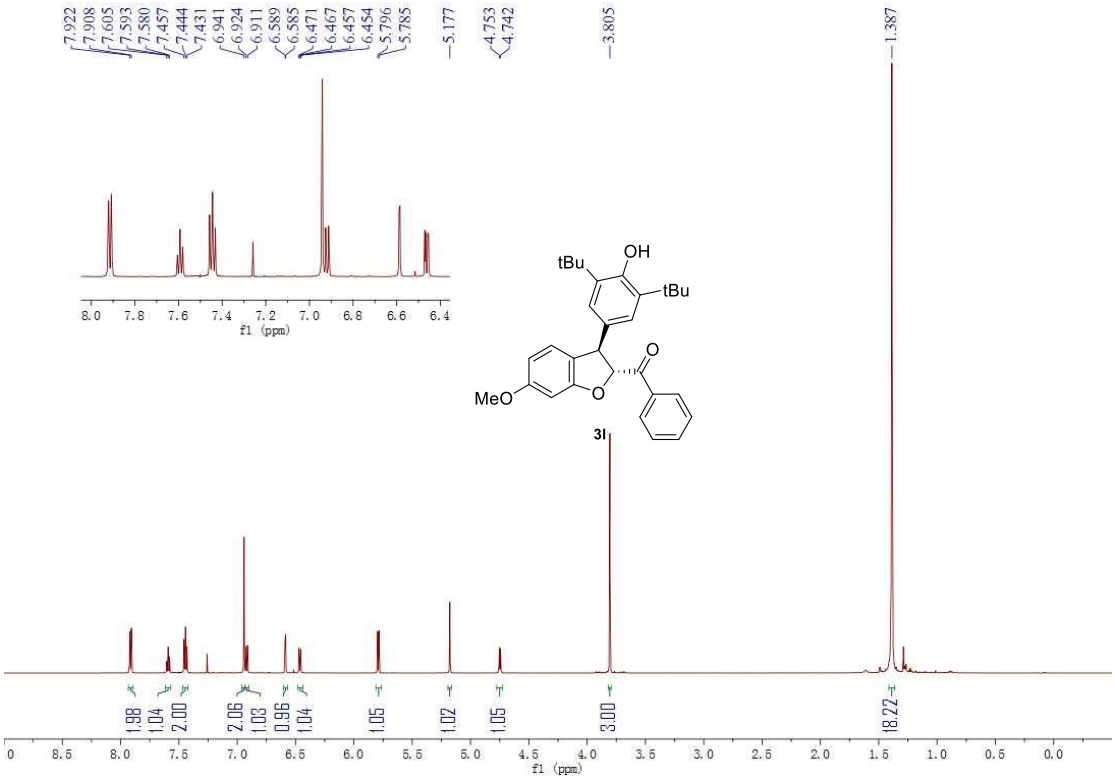
$^{1}$H NMR of **3k:**



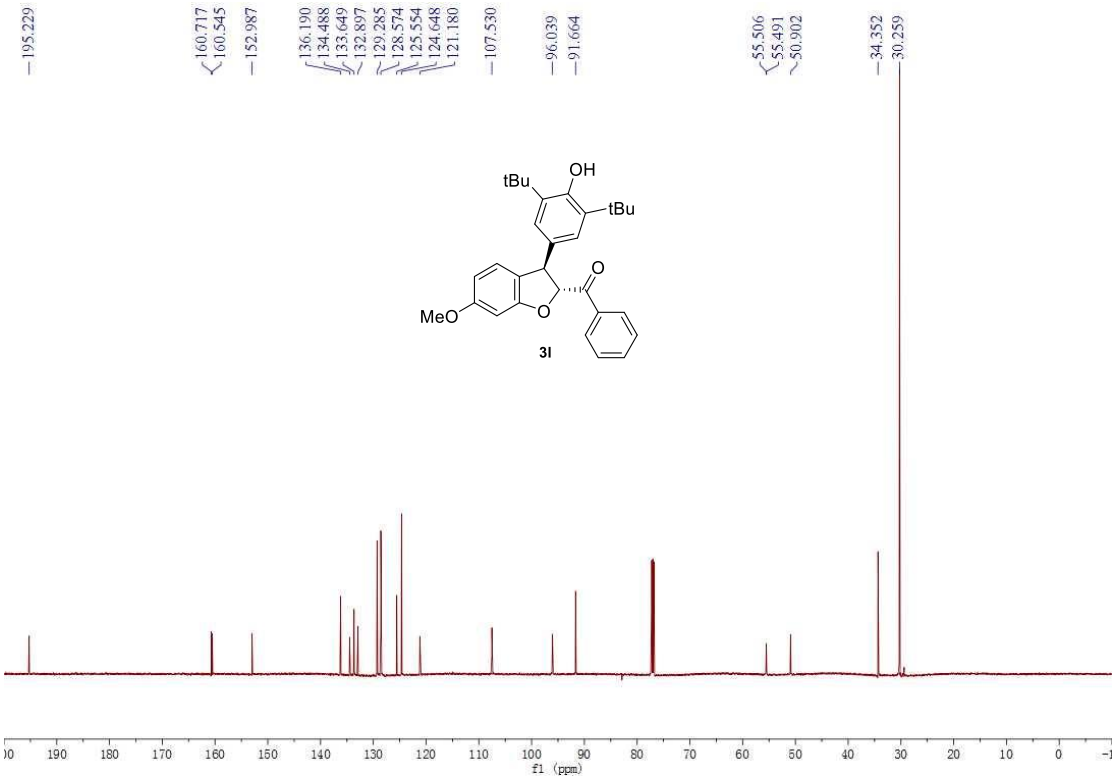

$^{13}$C NMR of **3k:**



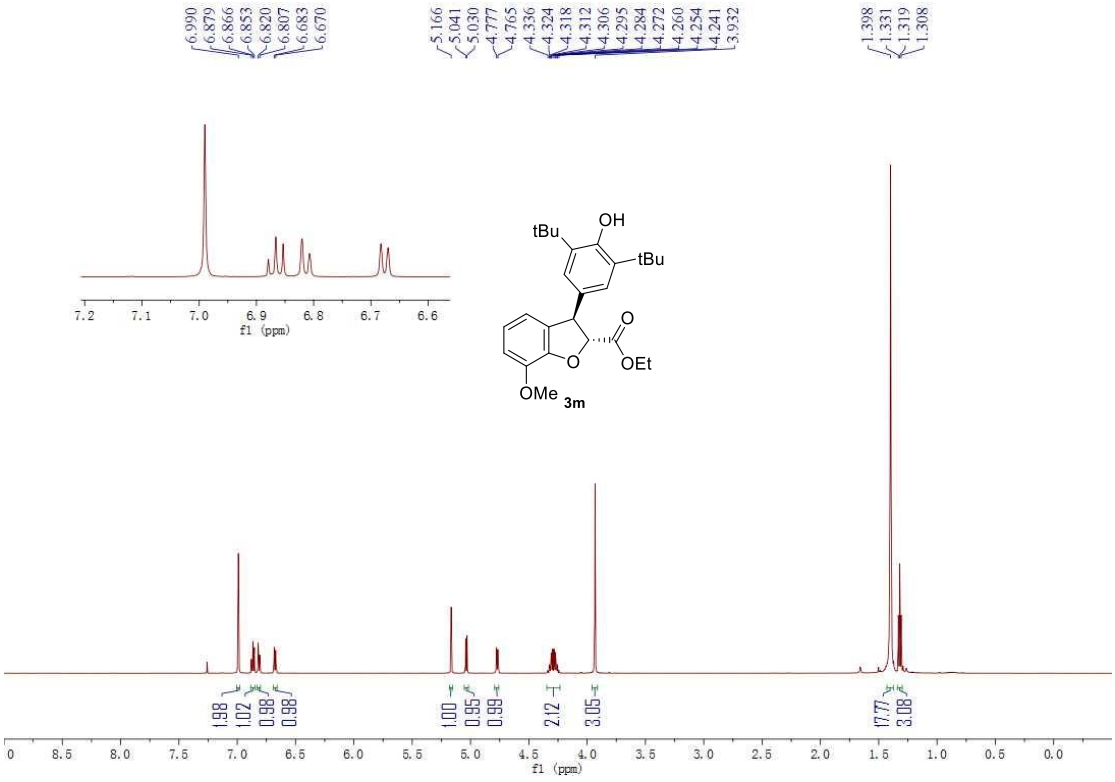
$^{1}$H NMR of **3l:**



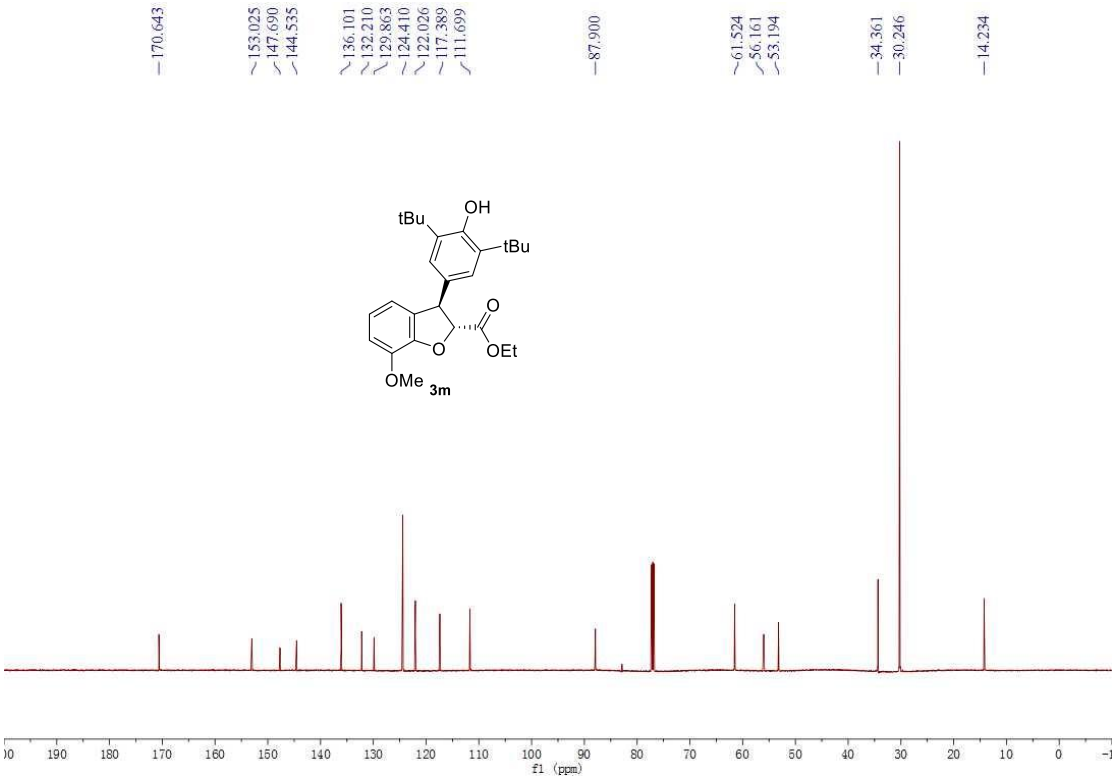

$^{13}$C NMR of **3l:**



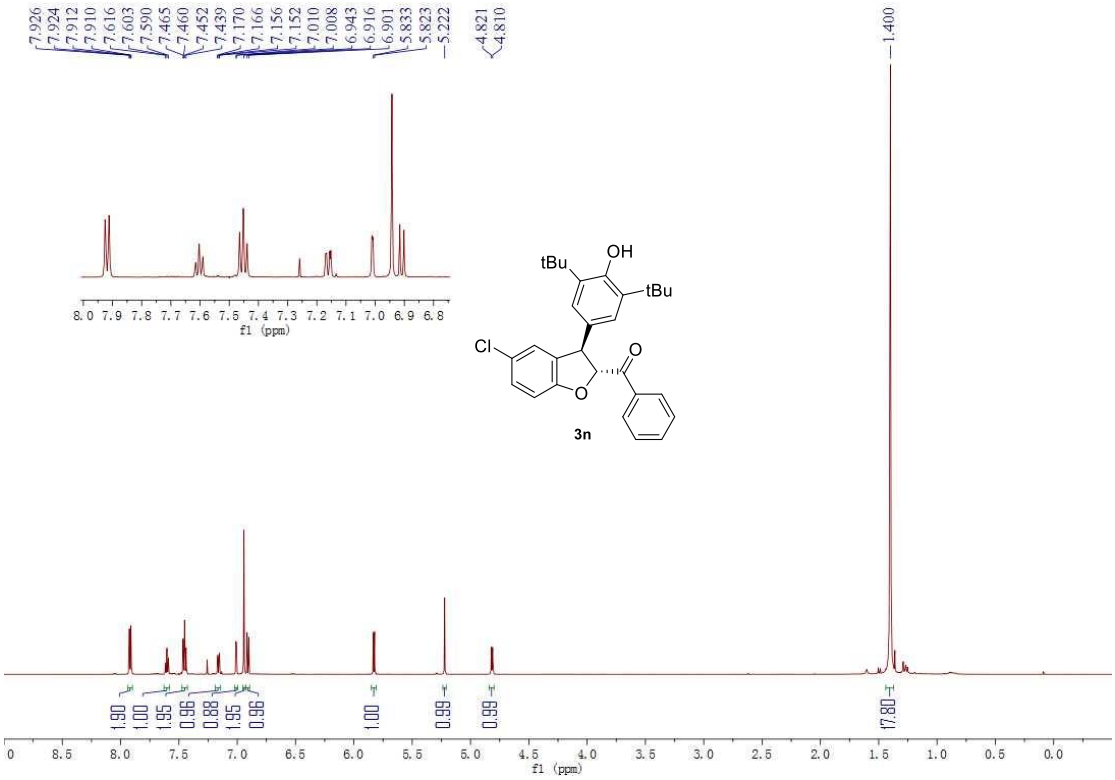
$^{1}$H NMR of **3m:**



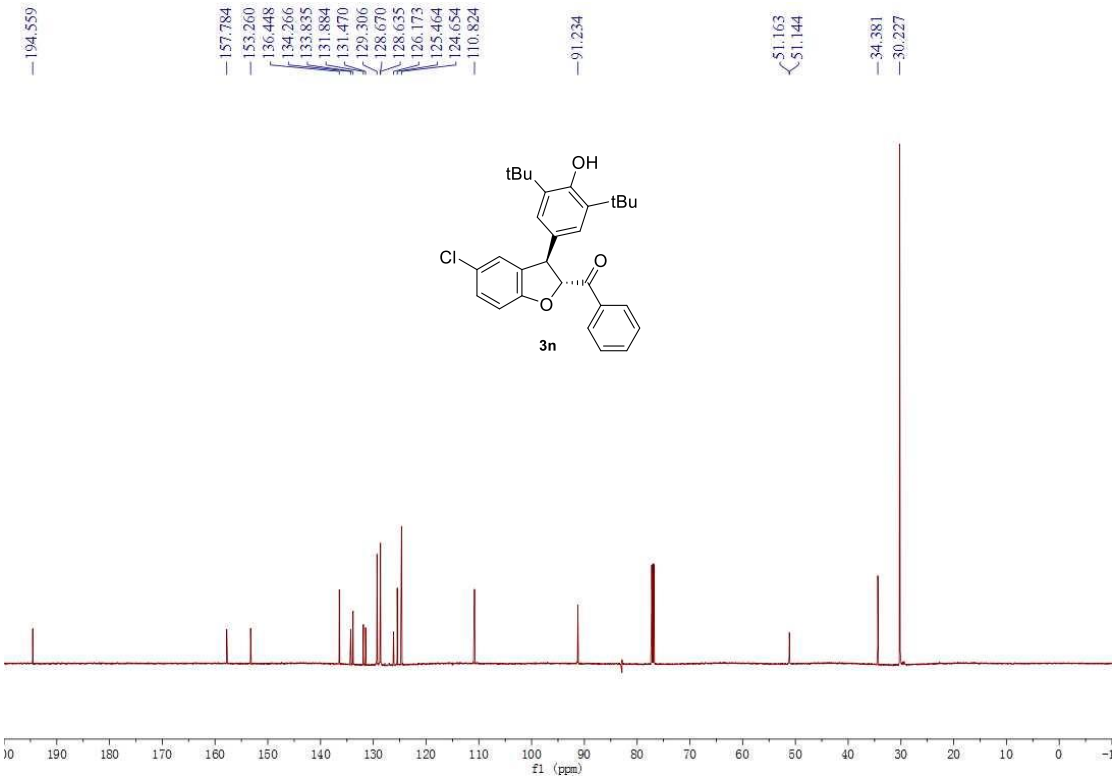

$^{13}$C NMR of **3m:**



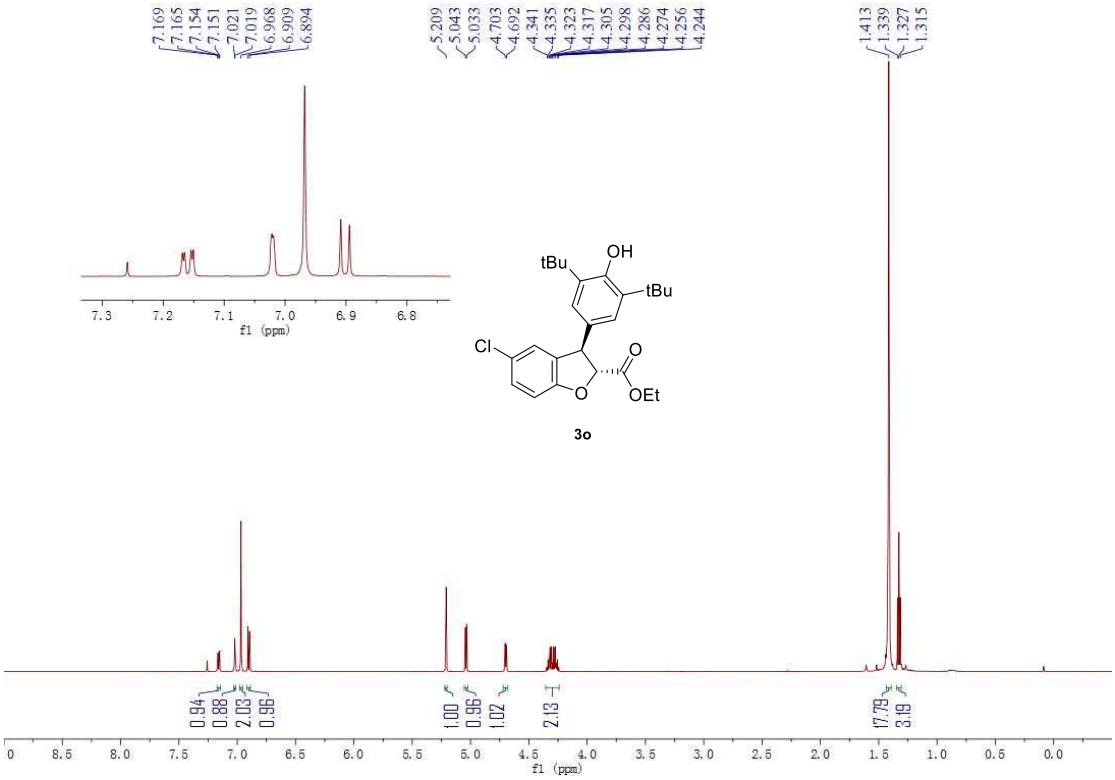
$^{1}$H NMR of **3n:**



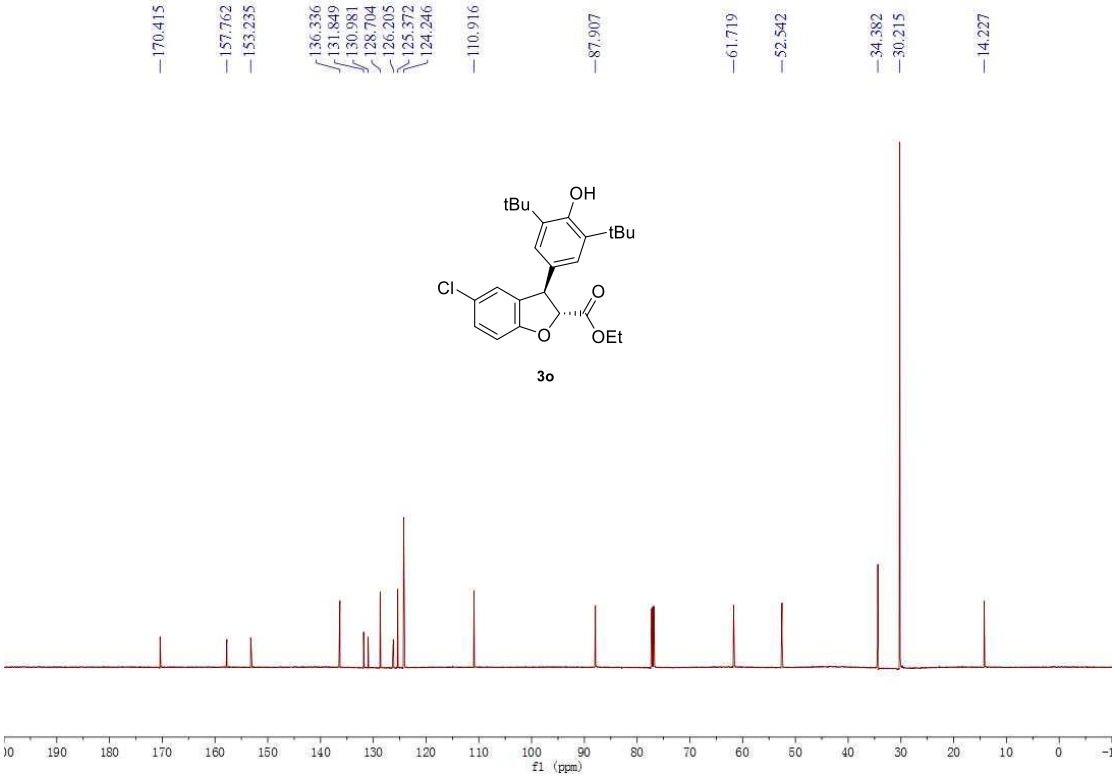

$^{13}$C NMR of **3n:**



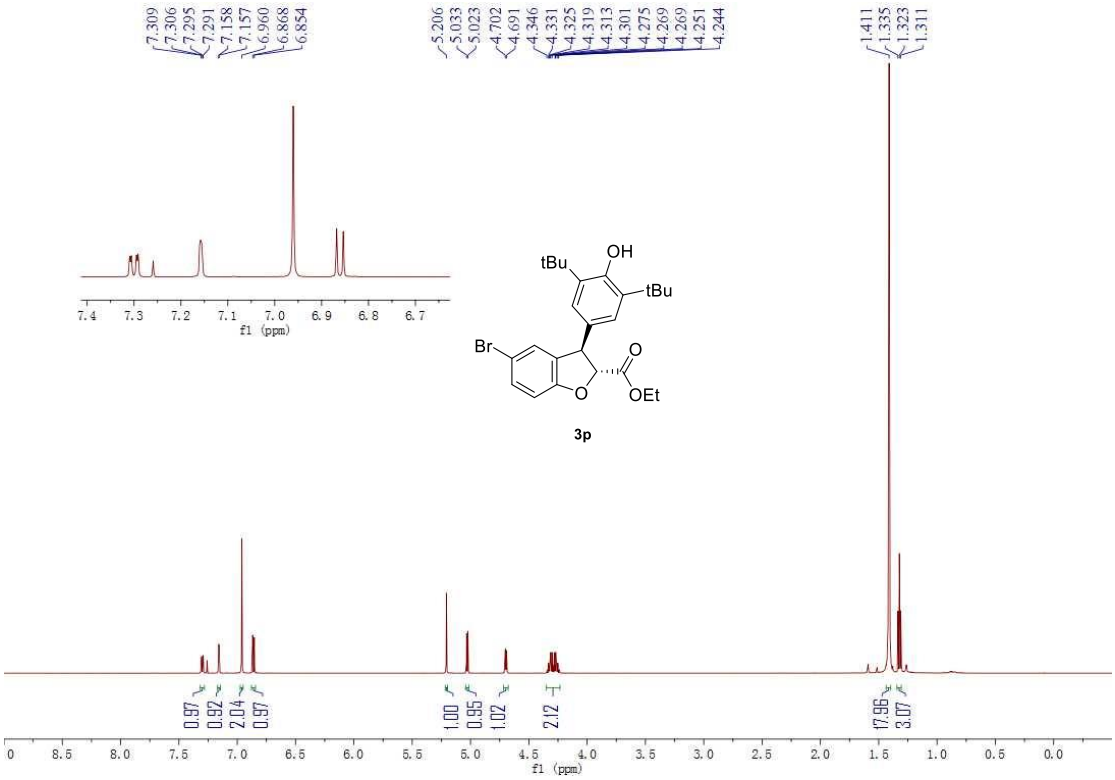
$^{1}$H NMR of **3o:**



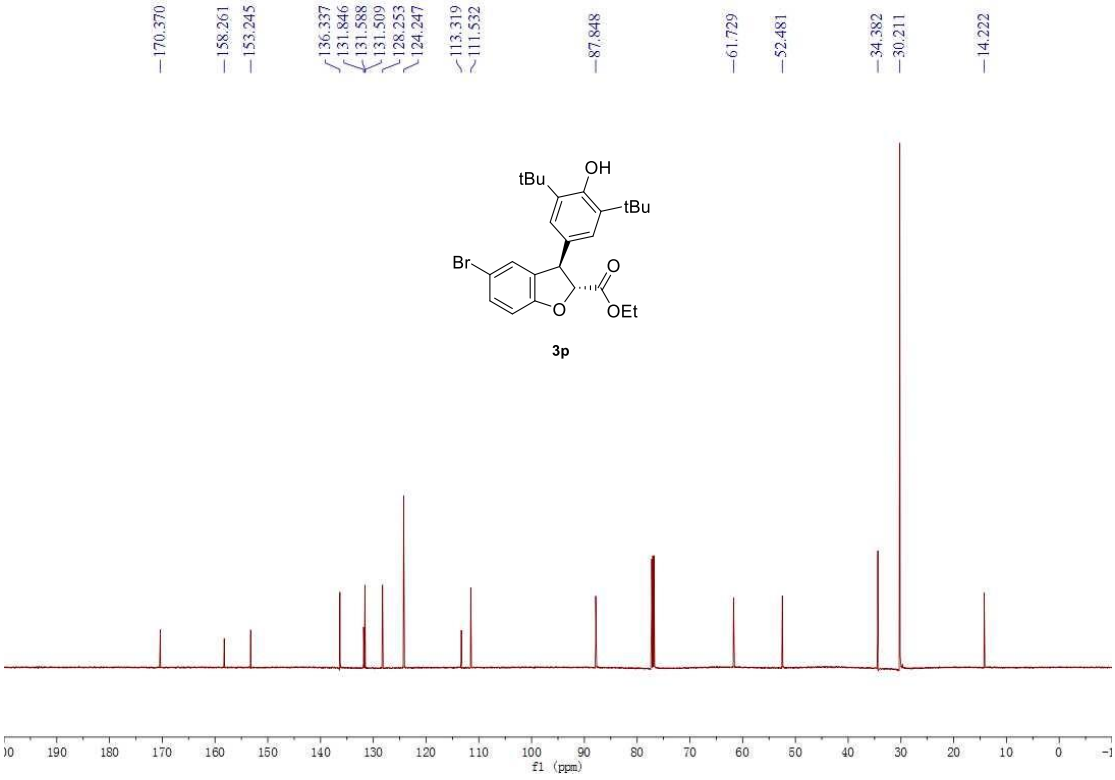

$^{13}$C NMR of **3o:**



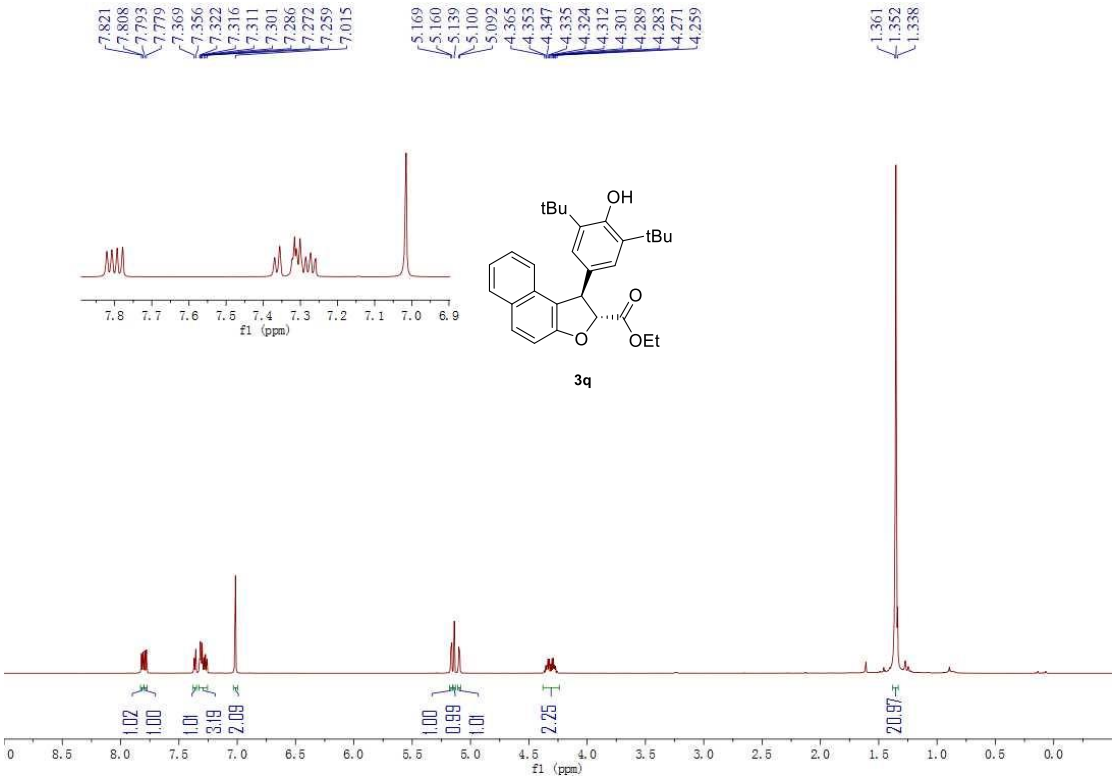
$^{1}$H NMR of **3p:**



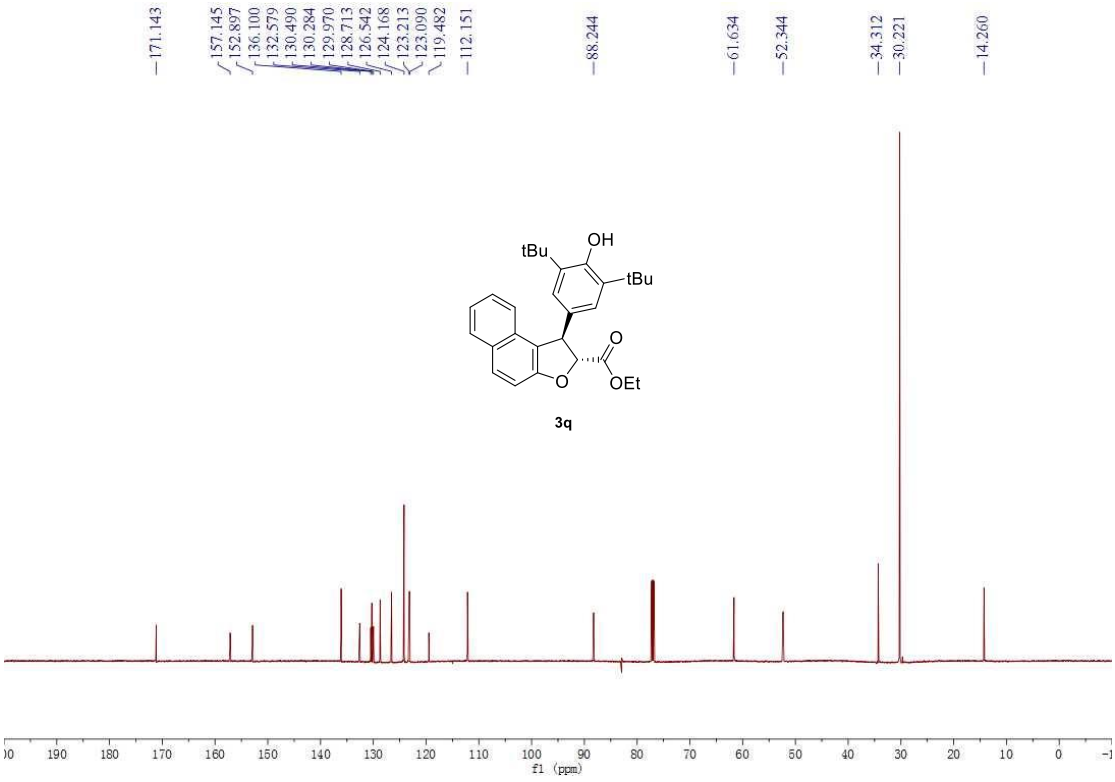

$^{13}$C NMR of **3p:**



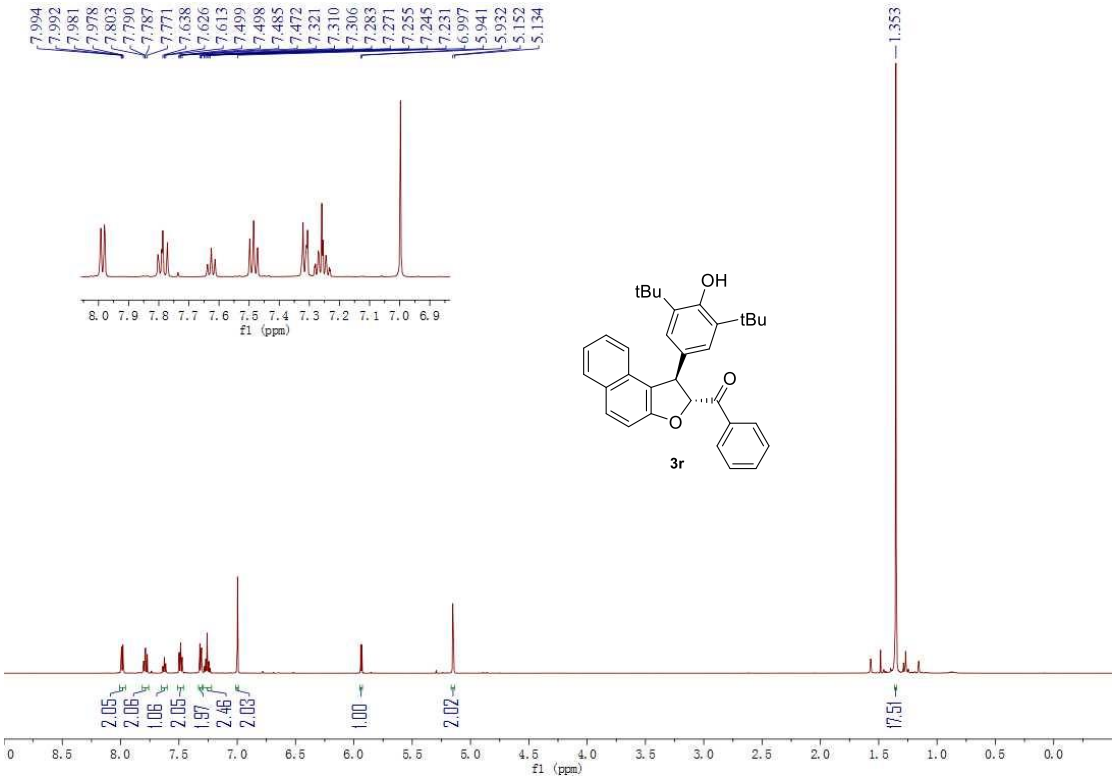
$^{1}$H NMR of **3q:**



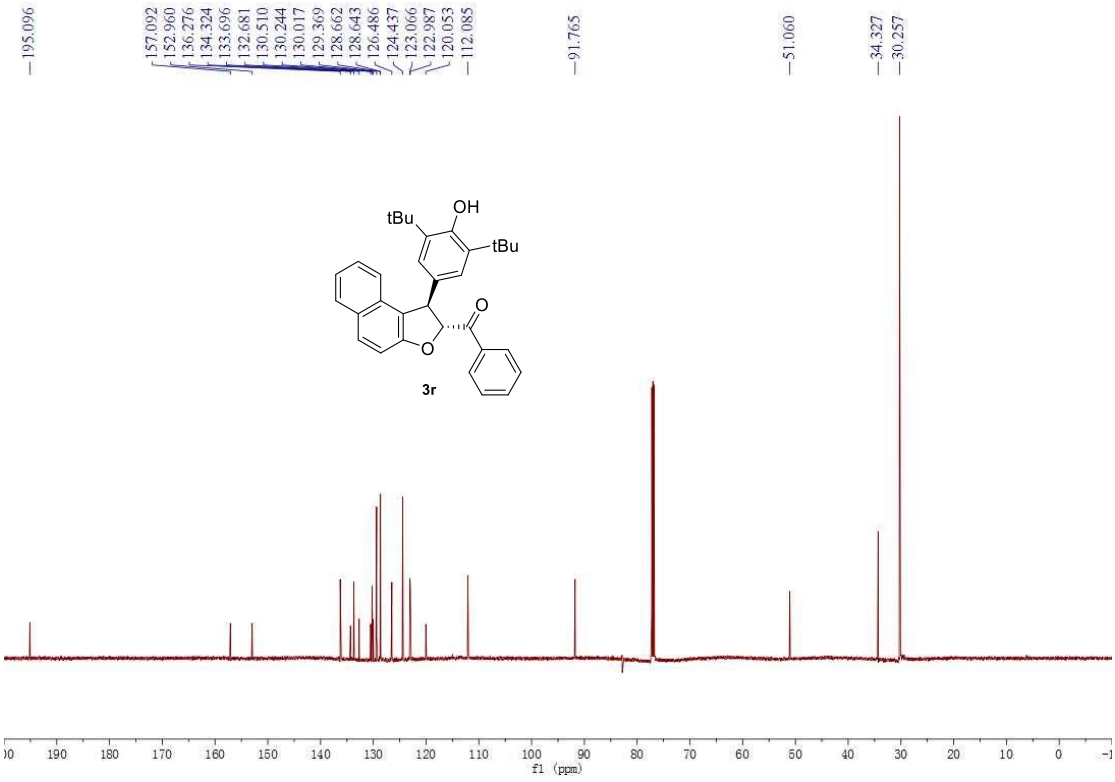

$^{13}$C NMR of **3q:**



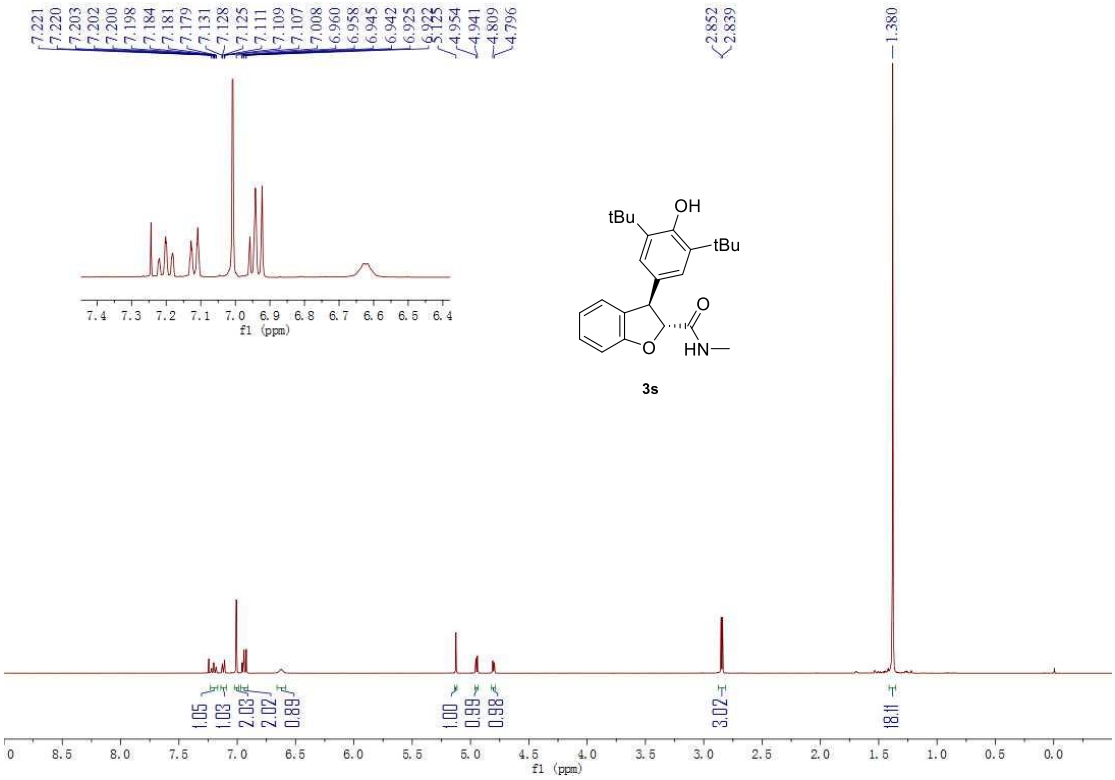
$^{1}$H NMR of **3r:**




$^{13}$C NMR of **3r:**



$^{1}$H NMR of **3s:**




$^{13}$C NMR of **3s:**