

## Supporting Information

### Photoinduced decarboxylative 1,6-addition of *para*-quinone methides with $\alpha$ -keto acids: an eco-friendly access to $\alpha,\alpha'$ -diarylated ketones

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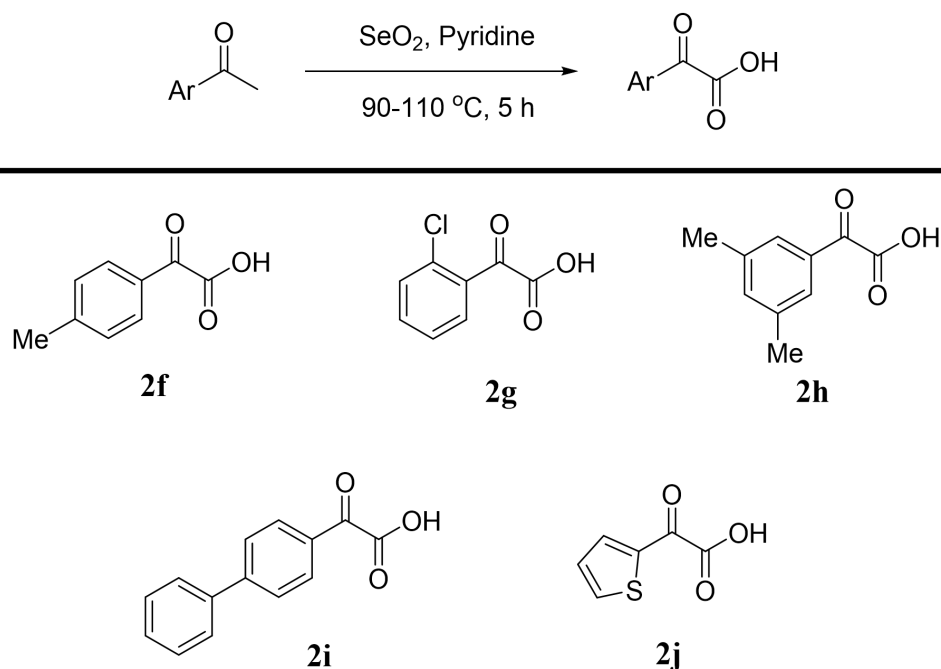
Liu,<sup>b\*</sup> Min Yang<sup>a\*</sup>

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## 1. General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63  $\mu\text{m}$ , standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at  $\sim 20$  Torr at 25-35  $^{\circ}\text{C}$ . Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the  $\delta$  scale.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument. The fluorescence spectra were recorded on ThermoFisher Varioskan LUX. *para*-Quinone methides (**1a-1p**) were prepared according the literature.<sup>1,2</sup>  $\alpha$ -keto acids (**2f-2j**) were prepared according the literature.<sup>3</sup>

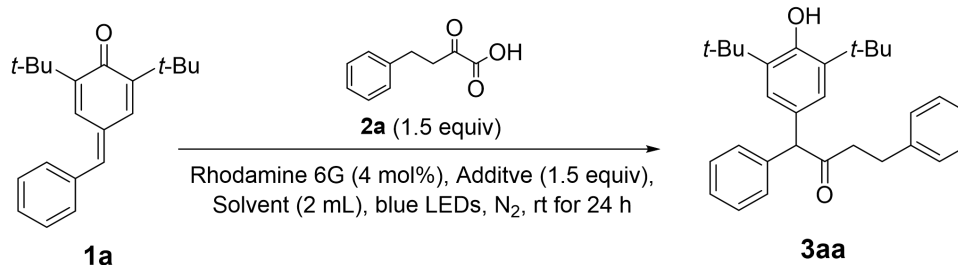
## 2. Synthesis of $\alpha$ -keto acids<sup>3</sup>



Methyl ketones (5 mmol),  $\text{SeO}_2$  (6 mmol), 20 mL of pyridine were added in a 50 mL round bottom flask. The reaction mixture was stirred at 110  $^{\circ}\text{C}$  for 1 h in an oil bath, then reduce the temperature to 90  $^{\circ}\text{C}$  for 4 h. The desired products were isolated by flash chromatography on silica

gel using (methanol / dichloromethane = 1: 10 ) to give  $\alpha$ -keto acids **2f-2j** in 60-86% yield. Other  $\alpha$ -keto acids are commercial.

### 3. Table S1. Optimization of the Reaction Conditions <sup>a</sup>



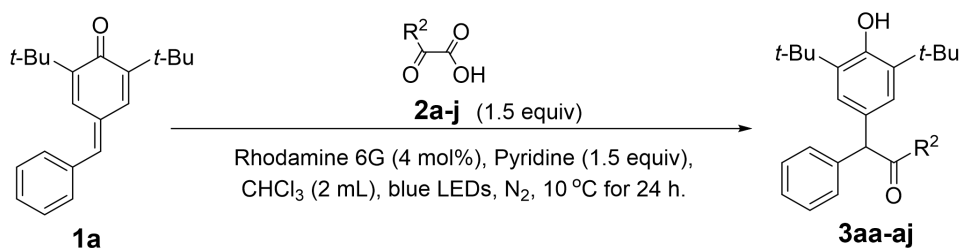
Entry	Additive	Solvent	Yield (%) <sup>b</sup>
1	DMAP	DCE	40
2	2,6-dimethoxypyridine	DCE	trace
3	2,6-bis(tert-butyl) pyridine	DCE	trace
4	2,6-pyridinedicarbonitrile	DCE	trace
5	2,4,6-trimethyl-pyridine	DCE	trace
6	Cs <sub>2</sub> CO <sub>3</sub>	DCE	trace
7	KOH	DCE	trace
8	t-BuOK	DCE	trace
9	t-BuOLi	DCE	n.d
10	CsF	DCE	trace
11	Pyridine	1,4-dioxane	trace
12	Pyridine	EA	53
13	Pyridine	MeOH	trace
14	Pyridine	DMF	trace
15	Pyridine	DMSO	trace
16	Pyridine	CF <sub>3</sub> CH <sub>2</sub> OH	trace
17	Pyridine	MeO- <i>t</i> -Bu	n.d
<sup>c,d</sup> 18	Pyridine	CHCl <sub>3</sub>	47
<sup>c,e</sup> 19	Pyridine	CHCl <sub>3</sub>	56
<sup>c,f</sup> 20	Pyridine	CHCl <sub>3</sub>	n.r

<sup>a</sup> Reaction conditions: 2,5-cyclohexadien-1-one,2,6-bis(1,1-dimethylethyl)-4-(phenylmethylene) **1a** (0.2 mmol),

2-oxo-4-phenylbutyric acid **2a** (0.3 mmol), Rhodamine 6G (4 mol%), additive (0.3 mmol), solvent (2.0 mL), N<sub>2</sub>, blue LEDs (10 W), rt for 24 h; rt = room temperature; n.d = no desired product; n.r = no reaction; <sup>b</sup> Isolated yield. <sup>c</sup> 10 °C was used instead of rt. <sup>d</sup> Pyridine (0.4 mmol) was used. <sup>e</sup> Rhodamine 6G (8 mol%) was used. <sup>f</sup> in the dark.

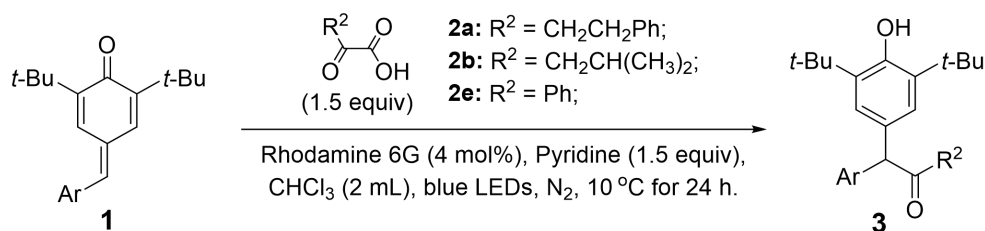
#### 4. General experimental procedure and characterization data

##### 4.1 General procedure for the synthesis of $\alpha,\alpha'$ -diaryl ketone **3aa-aj**



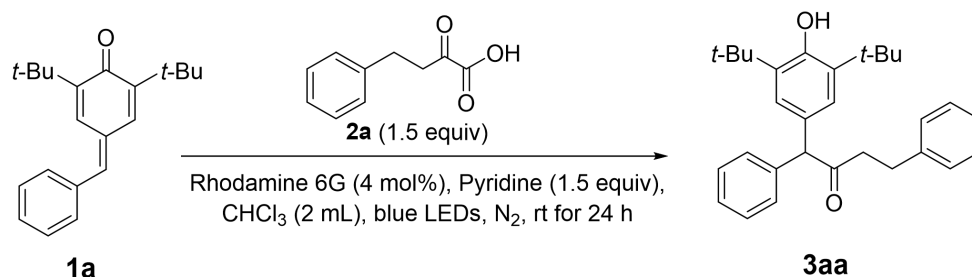
To a solution of 2,5-cyclohexadien-1-one,2,6-bis(1,1-dimethylethyl)-4-(phenylmethylene) **1a** (0.2 mmol),  $\alpha$ -keto acids **2a-j** (0.3 mmol), Rhodamine 6G (4 mol%) and pyridine (0.3 mmol) in CHCl<sub>3</sub> (2.0 mL) in 25 ml reaction tubes at N<sub>2</sub> atmosphere. The reaction was stirred under blue LEDs (10 W) for 24 h at 10 °C, After completion of reaction as indicated by TLC, the solvent was evaporated and the residue was purified directly by flash column chromatography (n-hexane/ethyl acetate = 15:1-10:1) to give  $\alpha,\alpha'$ -diaryl ketones **3aa-aj**.

##### 4.2 General procedure for the synthesis of $\alpha,\alpha'$ -diaryl ketone **3**



To a solution of *p*-QMs **1a-p** (0.2 mmol),  $\alpha$ -keto acids **2** (0.3 mmol), Rhodamine 6G (4 mol%) and pyridine (0.3 mmol) in CHCl<sub>3</sub> (2.0 mL) in 25 ml reaction tubes at N<sub>2</sub> atmosphere. The reaction was stirred under blue LEDs (10 W) for 24 h at 10 °C, After completion of reaction as indicated by TLC, the solvent was evaporated and the residue was purified directly by flash column chromatography (n-hexane/ethyl acetate = 15:1-10:1) to give  $\alpha,\alpha'$ -diaryl ketones **3**.

##### 4.3 A typical experimental procedure for the synthesis of **3aa**

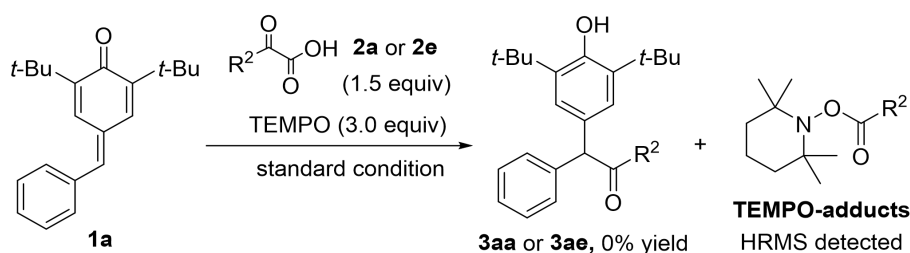


To a solution of 2,5-cyclohexadien-1-one,2,6-bis(1,1-dimethylethyl)-4-(phenylmethylene) **1a** (0.2 mmol), 2-oxo-4-phenylbutyric acid **2a** (0.3 mmol), Rhodamine 6G (4 mol%) and pyridine (0.3 mmol) in  $\text{CHCl}_3$  (2.0 mL) in 25 ml reaction tube at  $\text{N}_2$  atmosphere. The reaction was stirred under blue LEDs (10 W) for 24 h at 10 °C, After completion of reaction as indicated by TLC, the solvent was evaporated and the residue was purified directly by flash column chromatography (n-hexane/ethyl acetate = 15:1-10:1) to give  $\alpha,\alpha'$ -diaryl ketone **3aa** in 70% yield.

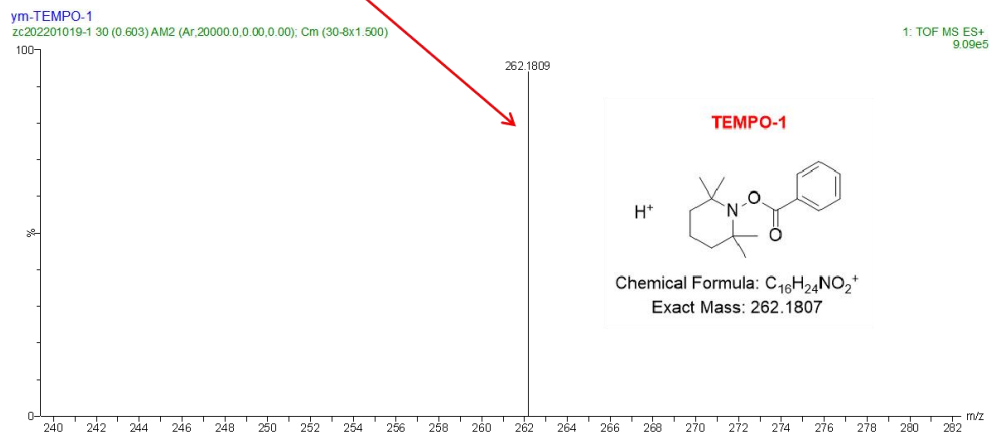
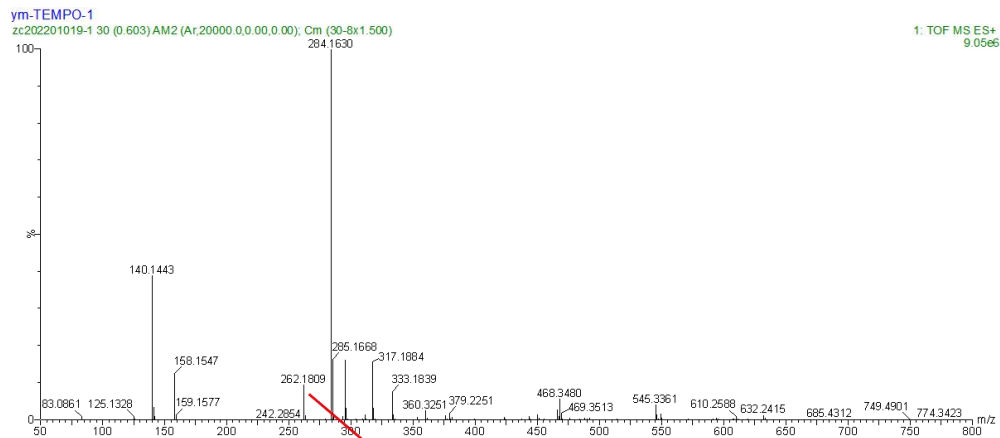
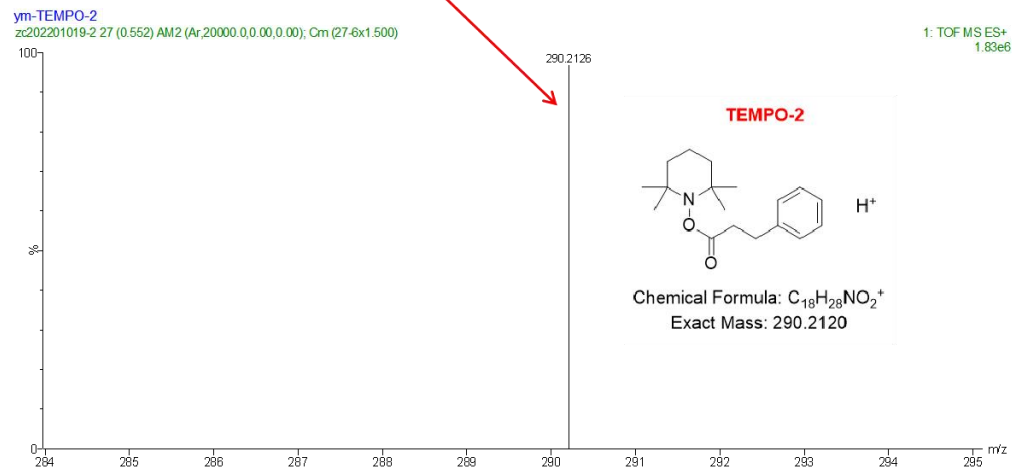
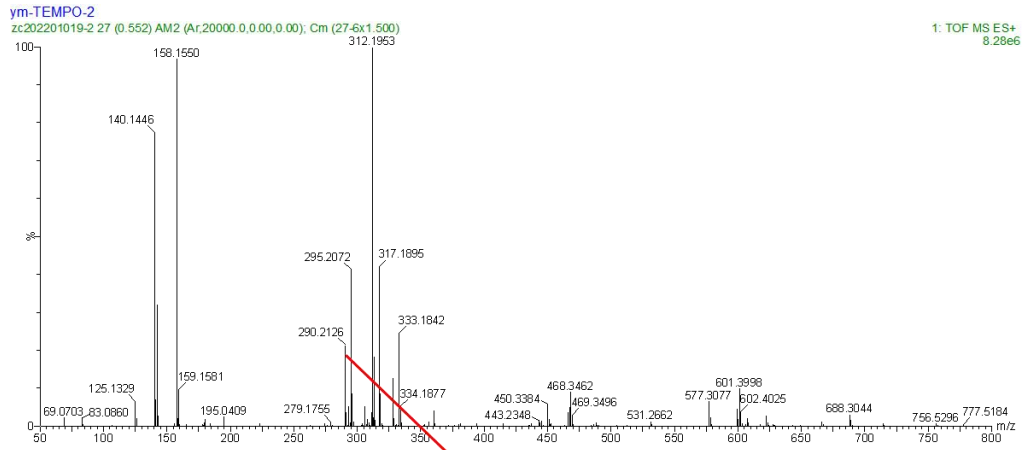
#### Experimental setup:



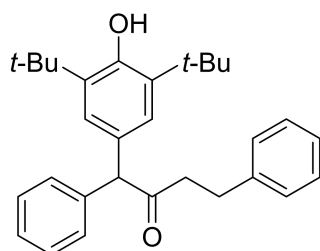
#### 4.4 TEMPO radical trapping reaction



To a solution of 2,5-cyclohexadien-1-one,2,6-bis(1,1-dimethylethyl)-4-(phenylmethylene) **1a** (0.2 mmol),  $\alpha$ -keto acid **2a** or **2e** (0.3 mmol), Rhodamine 6G (4 mol%), pyridine (0.3 mmol) and TEMPO (0.6 mmol) in  $\text{CHCl}_3$  (2.0 mL) in 25 ml reaction tube at  $\text{N}_2$  atmosphere. The reaction was stirred under blue LEDs (10 W) for 24 h at 10 °C. According to TLC, no desired product **3aa** was detected. And the TEMPO-adducts were detected by HRMS measurements of the crude reaction mixture.



#### 4.5 Characterization datas of $\alpha,\alpha'$ -diaryl ketones 3.

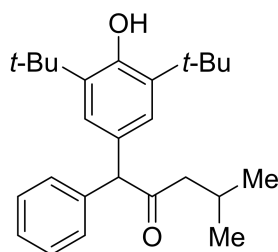


##### 1-(3,5-di-tert-butyl-4-hydroxyphenyl)-1,4-diphenylbutan-2-one (**3aa**)

yellow solid, m. p. = 100-102 °C

58.2 mg, 70%; n-hexane/ethyl acetate = 15/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 (t,  $J$  = 7.2 Hz, 2H), 7.24-7.18 (m, 3H), 7.18-7.12 (m, 3H), 7.11-7.06 (m, 2H), 6.95 (s, 2H), 5.12 (s, 1H), 4.93 (s, 1H), 2.90-2.79 (m, 4H), 1.36 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.4, 153.0, 141.0, 138.9, 136.0, 128.9, 128.7, 128.6, 128.5, 128.4, 127.0, 126.1, 125.6, 64.5, 44.1, 34.4, 30.3, 30.2. IR (neat): 3269.13, 2960.29, 1662.32, 1611.97, 1492.46, 1347.23, 1264.27, 1148.88, 1065.54, 732.98. HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{26}\text{NaO}_2^+$ : 451.2613 ( $\text{M}+\text{Na}^+$ ), found: 451.2617.

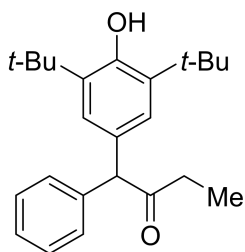


##### 1-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-methyl-1-phenylpentan-2-one (**3ab**)

light yellow solid, m. p. = 80-82 °C

50.1 mg, 66%; n-hexane/ethyl acetate = 10/1,  $R_f$  = 0.6

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34-7.28 (m, 2H), 7.24 (t,  $J$  = 7.6 Hz, 3H), 7.01 (s, 2H), 5.14 (s, 1H), 4.99 (s, 1H), 2.41 (d,  $J$  = 6.9 Hz, 2H), 2.20-2.13 (m, 1H), 1.40 (s, 18H), 0.90-0.83 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.7, 152.9, 139.1, 135.9, 129.0, 128.8, 128.5, 126.9, 125.7, 64.5, 51.6, 34.4, 30.3, 24.5, 22.5, 22.4. IR (neat): 3638.49, 2956.13, 1714.43, 1433.97, 1361.48, 1317.69, 1235.90, 1154.66, 1121.38, 1049.96, 894.04, 736.07, 700.22. HRMS (ESI) calcd for  $\text{C}_{26}\text{H}_{36}\text{NaO}_2^+$ : 403.2613 ( $\text{M}+\text{Na}^+$ ), found: 403.2616.

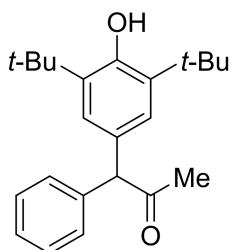


1-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-phenylbutan-2-one (**3ac**)

light yellow oil

35.9 mg, 51%; n-hexane/ethyl acetate = 15/1,  $R_f = 0.5$

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (t,  $J = 7.4$  Hz, 2H), 7.25 (d,  $J = 6.9$  Hz, 3H), 7.04 (s, 2H), 5.14 (s, 1H), 5.03 (s, 1H), 2.58-2.55 (m, 2H), 1.41 (s, 18H), 1.05 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.9, 152.9, 139.3, 135.9, 129.1, 128.9, 128.5, 126.9, 125.6, 64.0, 35.9, 34.4, 30.3, 8.2. IR (neat): 3638.15, 2957.33, 1715.70, 1434.24, 1360.25, 1317.98, 1236.78, 1155.10, 1107.27, 1033.33, 739.51. HRMS (ESI) calcd for  $\text{C}_{24}\text{H}_{33}\text{O}_2^+$ : 353.2480 ( $\text{M}+\text{H}^+$ ), found: 353.2470.



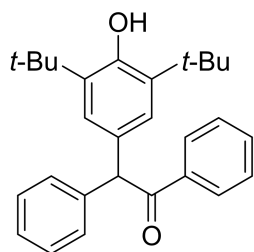
1-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-phenylpropan-2-one (**3ad**)

light yellow oil

27.1 mg, 40%; n-hexane/ethyl acetate = 20/1,  $R_f = 0.5$

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (t,  $J = 7.5$  Hz, 2H), 7.27-7.21 (m, 3H), 7.01 (s, 2H), 5.16 (s, 1H), 5.02 (s, 1H), 2.23 (s, 3H), 1.40 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  207.3, 153.0, 139.0, 136.0, 129.0, 128.7, 128.6, 127.0, 125.7, 65.1, 34.4, 30.3, 30.0. IR (neat): 3636.85, 2956.33, 1715.44, 1434.29, 1357.31, 1235.49, 1153.42, 1121.01, 1077.64, 1033.13, 733.33. HRMS (ESI) calcd for  $\text{C}_{23}\text{H}_{30}\text{NaO}_2^+$ : 361.2144 ( $\text{M}+\text{Na}^+$ ), found: 361.2135.



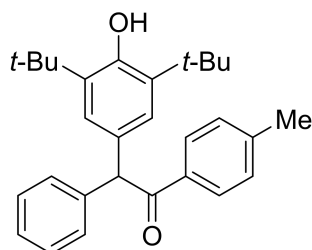


2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1,2-diphenylethan-1-one (**3ae**)

light yellow solid, m. p. = 91-93 °C

67.3 mg, 84%; n-hexane/ethyl acetate = 15/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (s, 2H), 7.52-7.15 (m, 8H), 7.03 (s, 2H), 5.91 (s, 1H), 5.09 (s, 1H), 1.35 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.9, 152.9, 139.7, 137.3, 135.9, 132.8, 129.5, 129.1, 128.9, 128.6, 128.6, 126.9, 125.9, 59.3, 34.4, 30.3. IR (neat): 3627.83, 2955.34, 1685.84, 1596.19, 1434.67, 1203.90, 1008.75, 806.96, 733.40, 696.14. HRMS (ESI) calcd for  $\text{C}_{28}\text{H}_{33}\text{O}_2^+$ : 401.2475 ( $\text{M}+\text{H}^+$ ), found: 401.2476. Spectral data match those previously reported.<sup>4</sup>

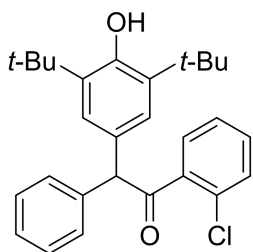


2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenyl-1-(p-tolyl)ethan-1-one (**3af**)

yellow solid, m. p. = 150-151 °C

41.5 mg, 50%; n-hexane/ethyl acetate = 10/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J$  = 8.0 Hz, 2H), 7.30 (d,  $J$  = 2.9 Hz, 4H), 7.20 (d,  $J$  = 8.0 Hz, 3H), 7.06 (s, 2H), 5.92 (s, 1H), 5.10 (s, 1H), 2.37 (s, 3H), 1.38 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.4, 152.8, 143.6, 139.9, 135.8, 129.6, 129.2, 129.1, 128.6, 126.8, 125.9, 59.1, 34.4, 30.3, 21.6. IR (neat): 3637.92, 2960.89, 1680.78, 1605.29, 1434.77, 1264.42, 1178.38, 894.49, 736.04, 702.37. HRMS (ESI) calcd for  $\text{C}_{29}\text{H}_{35}\text{O}_2^+$ : 415.2637 ( $\text{M}+\text{H}^+$ ), found: 415.2654. Spectral data match those previously reported.<sup>5</sup>

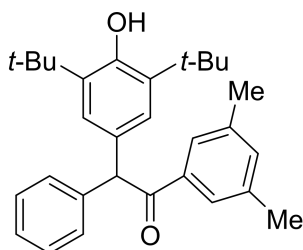


1-(2-chlorophenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylethan-1-one (**3ag**)

yellow solid, m. p. = 130-132 °C

30.4 mg, 35%; n-hexane/ethyl acetate = 10/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.26 (m, 7H), 7.22-7.15 (m, 2H), 7.07 (s, 2H), 5.78 (s, 1H), 5.14 (s, 1H), 1.38 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.9, 136.1, 135.9, 128.9, 128.5, 125.7, 125.3, 64.2, 51.5, 34.4, 34.4, 31.3, 30.3, 24.5, 22.5, 22.4. IR (neat): 3631.31, 2954.47, 1700.88, 1589.60, 1433.34, 1235.87, 1202.56, 1157.84, 1064.64, 737.56. HRMS (ESI) calcd for  $\text{C}_{28}\text{H}_{32}\text{ClO}_2^+$ : 435.2091 ( $\text{M}+\text{H}^+$ ), found: 435.2091.

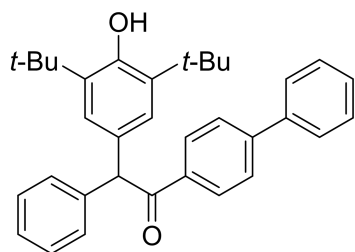


2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-(3,5-dimethylphenyl)-2-phenylethan-1-one (**3ah**)

yellow solid, m. p. = 118-119 °C

47.1 mg, 55%; n-hexane/ethyl acetate = 15/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (s, 2H), 7.32 (d,  $J$  = 4.2 Hz, 4H), 7.24 (d,  $J$  = 4.5 Hz, 1H), 7.15 (s, 1H), 7.09 (s, 2H), 5.94 (s, 1H), 5.12 (s, 1H), 2.33 (s, 6H), 1.39 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.2, 152.8, 139.9, 138.1, 137.5, 135.8, 134.5, 129.9, 129.6, 129.1, 129.0, 128.6, 127.6, 126.8, 126.7, 125.9, 59.2, 34.4, 30.3, 21.3. IR (neat): 3633.90, 2955.81, 1685.56, 1598.16, 1264.29, 1024.45, 859.79, 852.79, 734.38, 702.06. HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{37}\text{O}_2^+$ : 429.2793 ( $\text{M}+\text{H}^+$ ), found: 429.2791.

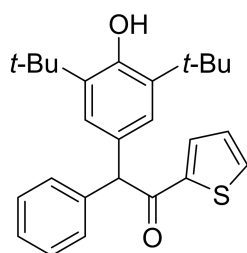


1-([1,1'-biphenyl]-4-yl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylethan-1-one (**3ai**)

light yellow solid, m. p. = 157-160 °C

49.6 mg, 52%; n-hexane/ethyl acetate = 15/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (d,  $J$  = 8.0 Hz, 2H), 7.67-7.58 (m, 4H), 7.50-7.38 (m, 4H), 7.34 (d,  $J$  = 4.2 Hz, 4H), 7.10 (s, 2H), 5.99 (s, 1H), 5.14 (s, 1H), 1.40 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.4, 152.9, 145.5, 139.9, 139.8, 135.9, 135.9, 129.5, 129.5, 129.1, 128.9, 128.7, 128.2, 127.3, 127.2, 127.0, 125.9, 59.4, 34.4, 30.3. IR (neat): 3624.93, 2955.82, 1678.62 1601.30, 1433.46, 1264.56, 1236.11, 1005.62, 735.24, 697.99. HRMS (ESI) calcd for  $\text{C}_{34}\text{H}_{36}\text{NaO}_2^+$ : 499.2613 ( $\text{M}+\text{Na}^+$ ), found: 499.2630.

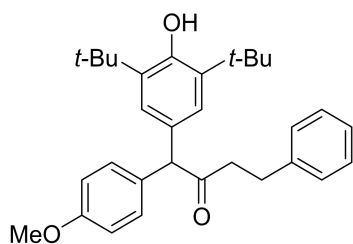


2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenyl-1-(thiophen-2-yl)ethan-1-one (**3aj**)

light yellow solid, m. p. = 110-112 °C

53.7 mg, 66%; n-hexane/ethyl acetate = 15/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J$  = 3.8 Hz, 1H), 7.59 (d,  $J$  = 5.0 Hz, 1H), 7.42-7.27 (m, 5H), 7.13 (s, 2H), 7.08 (t,  $J$  = 4.4 Hz, 1H), 5.76 (s, 1H), 5.14 (s, 1H), 1.40 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.6, 153.0, 144.5, 139.5, 135.9, 133.8, 132.6, 129.2, 128.9, 128.6, 128.1, 127.0, 125.8, 60.5, 34.4, 30.3. IR (neat): 3628.50, 2961.84, 1660.52, 1412.57, 1355.48, 1264.17, 1236.12, 1154.45, 1059.70, 894.65, 731.57. HRMS (ESI) calcd for  $\text{C}_{26}\text{H}_{30}\text{NaO}_2^+$ : 429.1865 ( $\text{M}+\text{Na}^+$ ), found: 429.1858. Spectral data match those previously reported.<sup>4</sup>

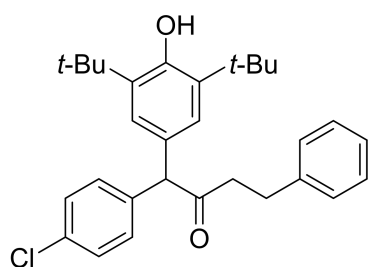


1-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-4-phenylbutan-2-one (**3ga**)

light yellow solid, m. p. = 150-153 °C

35.7 mg, 39%; n-hexane/dichloromethane = 2/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25-7.19 (m, 2H), 7.19-7.13 (m, 1H), 7.12-7.04 (m, 4H), 6.94 (d,  $J$  = 2.7 Hz, 2H), 6.85-6.78 (m, 2H), 5.12 (s, 1H), 4.88 (s, 1H), 3.76 (s, 3H), 2.90-2.77 (m, 4H), 1.37 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.6, 158.5, 152.9, 141.1, 135.9, 131.0, 130.0, 129.0, 128.5, 128.4, 126.1, 125.5, 113.9, 63.7, 55.3, 44.0, 34.4, 30.3, 30.3. IR (neat): 3627.96, 2953.78, 1713.81, 1608.04, 1508.20, 1433.75, 1248.12, 1154.16, 1032.19, 736.55. HRMS (ESI) calcd for  $\text{C}_{31}\text{H}_{38}\text{NaO}_3^+$ : 481.2719 ( $\text{M}+\text{Na}^+$ ), found: 481.2746.

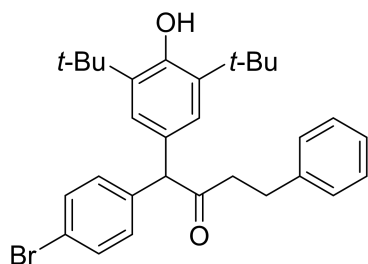


1-(4-chlorophenyl)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-phenylbutan-2-one (**3ha**)

light yellow oil

62.9 mg, 68%; n-hexane/dichloromethane = 2/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30-7.25 (m, 4H), 7.23-7.17 (m, 1H), 7.16-7.09 (m, 4H), 6.98 (s, 2H), 5.20 (s, 1H), 4.94 (s, 1H), 2.96-2.82 (m, 4H), 1.42 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  207.9, 153.2, 140.9, 137.5, 136.3, 132.8, 130.2, 128.6, 128.5, 128.4, 128.3, 126.1, 125.5, 63.7, 44.1, 34.4, 30.3, 30.2. IR (neat): 3638.13, 2956.08, 1715.44, 1490.13, 1433.97, 1235.33, 1154.50, 1090.32, 1015.35, 730.93. HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{36}\text{ClO}_2^+$ : 463.2398 ( $\text{M}+\text{H}^+$ ), found: 463.2400.

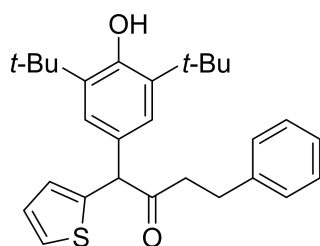


1-(4-bromophenyl)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-phenylbutan-2-one (**3ia**)

light yellow oil

53.6 mg, 53%; n-hexane/dichloromethane = 2/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48-7.39 (m, 2H), 7.30-7.25 (m, 2H), 7.24-7.18 (m, 1H), 7.17-7.10 (m, 2H), 7.06 (d,  $J$  = 8.5 Hz, 2H), 6.98 (s, 2H), 5.20 (s, 1H), 4.92 (s, 1H), 2.99-2.81 (m, 4H), 1.42 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  207.8, 153.2, 140.9, 138.1, 136.3, 131.5, 130.6, 128.5, 128.4, 128.2, 126.1, 125.4, 121.0, 63.8, 44.1, 34.4, 30.3, 30.2. IR (neat): 3633.88, 2953.72, 1714.05, 1486.71, 1433.09, 1235.52, 1153.55, 1120.54, 1010.56, 732.84. HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{36}\text{BrO}_2^+$ : 507.1893 ( $\text{M}+\text{H}^+$ ), found: 507.1899.

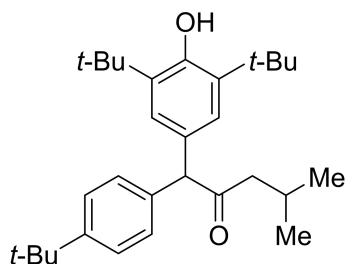


1-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-phenyl-1-(thiophen-2-yl)butan-2-one (**3pa**)

light yellow oil

36.4 mg, 42%; n-hexane/dichloromethane = 2/1,  $R_f$  = 0.4

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.20 (m, 3H), 7.19-7.14 (m, 1H), 7.09 (d,  $J$  = 11.3 Hz, 4H), 6.94-6.92 (m, 1H), 6.82 (d,  $J$  = 3.5 Hz, 1H), 5.18 (s, 1H), 5.13 (s, 1H), 2.88-2.86 (m, 4H), 1.40 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  206.1, 153.3, 140.9, 136.3, 128.4, 128.3, 126.4, 126.1, 126.0, 125.3, 125.0, 59.5, 43.2, 34.4, 30.3, 30.2. IR (neat): 3671.92, 2921.74, 1715.19, 1456.78, 1435.42, 1403.85, 1241.19, 1065.84, 897.54. HRMS (ESI) calcd for  $\text{C}_{28}\text{H}_{34}\text{NaO}_2\text{S}^+$ : 457.2177 ( $\text{M}+\text{H}^+$ ), found: 457.2176.

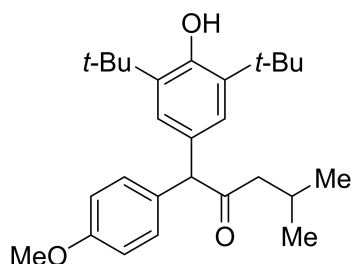


1-(4-(tert-butyl)phenyl)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-methylpentan-2-one (**3fb**)

light yellow oil

34.9 mg, 40%; n-hexane/dichloromethane = 2/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.29 (m, 2H), 7.15 (d,  $J$  = 8.4 Hz, 2H), 7.03 (s, 2H), 5.13 (s, 1H), 4.95 (s, 1H), 2.40 (d,  $J$  = 6.9 Hz, 2H), 2.17 (dq,  $J$  = 13.4, 6.6 Hz, 1H), 1.41 (s, 18H), 1.29 (s, 9H), 0.88-0.85 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.9, 136.1, 135.9, 128.9, 128.5, 125.7, 125.3, 64.2, 51.5, 34.4, 34.4, 31.3, 30.3, 24.5, 22.5, 22.4. IR (neat): 3645.65, 2954.57, 1712.96, 1434.13, 1362.48, 1234.66, 1155.01, 1121.11, 1048.22, 740.66. HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{45}\text{O}_2^+$ : 437.3420 ( $\text{M}+\text{H}^+$ ), found: 437.3425.

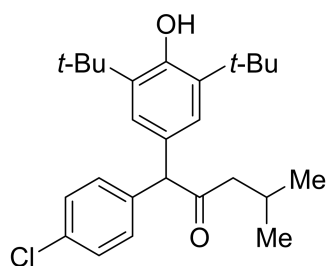


1-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-(4-methoxyphenyl)-4-methylpentan-2-one (**3gb**)

yellow oil

35.3 mg, 43%; n-hexane/dichloromethane = 2/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15 (d,  $J$  = 8.7 Hz, 2H), 7.00 (s, 2H), 6.86 (d,  $J$  = 8.7 Hz, 2H), 5.13 (s, 1H), 4.94 (s, 1H), 3.79 (s, 3H), 2.40 (d,  $J$  = 6.9 Hz, 2H), 2.22-2.12 (m, 1H), 1.41 (s, 18H), 0.88-0.86 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.0, 158.5, 152.8, 135.9, 131.2, 130.0, 129.2, 125.5, 113.9, 63.7, 55.2, 51.5, 34.4, 30.3, 24.6, 22.5, 22.4. IR (neat): 3637.44, 2956.04, 1714.18, 1610.38, 1509.67, 1434.61, 1361.36, 1249.20, 1034.87, 732.75. HRMS (ESI) calcd for  $\text{C}_{27}\text{H}_{39}\text{O}_3^+$ : 411.2899 ( $\text{M}+\text{H}^+$ ), found: 411.2900.

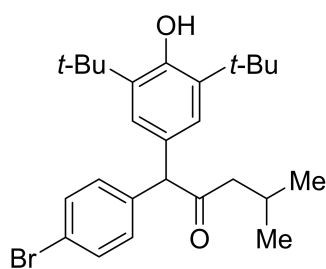


1-(4-chlorophenyl)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-methylpentan-2-one (**3hb**)

yellow oil

36.4 mg, 44%; n-hexane/dichloromethane = 2/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29-7.26 (m, 2H), 7.18-7.10 (m, 2H), 6.98 (s, 2H), 5.17 (s, 1H), 4.95 (s, 1H), 2.40 (d,  $J$  = 6.9 Hz, 2H), 2.21-2.11 (m, 1H), 1.40 (s, 18H), 0.89-0.84 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  207.0 153.1, 137.7, 136.2, 130.3, 128.5, 128.3, 125.5, 63.7, 51.6, 34.4, 30.3, 24.5, 22.5, 22.4. IR (neat): 3635.78, 2955.14, 1711.93, 1490.51, 1433.66, 1362.13, 1153.49, 1049.32, 1015.43, 738.22. HRMS (ESI) calcd for  $\text{C}_{26}\text{H}_{36}\text{ClO}_2^+$ : 415.2404 ( $\text{M}+\text{H}^+$ ), found: 415.2409.

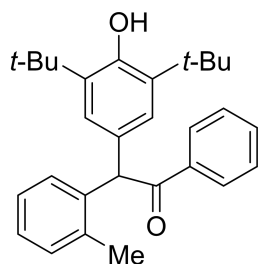


1-(4-bromophenyl)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-methylpentan-2-one (**3ib**)

yellow oil

37.6 mg, 41%; n-hexane/dichloromethane = 2/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49-7.42 (m, 2H), 7.16-7.10 (m, 2H), 7.01 (s, 2H), 5.20 (s, 1H), 4.97 (s, 1H), 2.44 (d,  $J$  = 6.9 Hz, 2H), 2.24-2.14 (m, 1H), 1.44 (s, 18H), 0.92-0.87 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.1, 153.1, 138.3, 136.2, 131.5, 130.7, 128.2, 125.5, 120.9, 63.8, 51.6, 34.4, 30.3, 24.5, 22.6, 22.4. IR (neat): 3634.62, 2954.87, 1713.24, 1434.57, 1362.95, 1263.81, 1236.54, 1155.34, 1049.48, 732.82. HRMS (ESI) calcd for  $\text{C}_{26}\text{H}_{36}\text{BrO}_2^+$ : 459.1893 ( $\text{M}+\text{H}^+$ ), found: 459.1882.

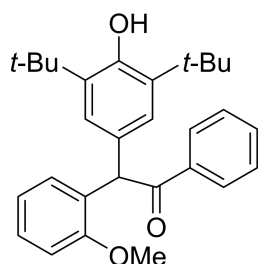


2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-phenyl-2-(o-tolyl)ethan-1-one (**3be**)

yellow oil

57.2 mg, 69%; n-hexane/ethyl acetate = 15/1,  $R_f = 0.5$

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 7.2$  Hz, 2H), 7.48 (d,  $J = 7.3$  Hz, 1H), 7.39 (t,  $J = 7.6$  Hz, 2H), 7.23-7.09 (m, 3H), 7.05 (d,  $J = 7.8$  Hz, 1H), 7.00 (s, 2H), 6.01 (s, 1H), 5.12 (s, 1H), 2.35 (s, 3H), 1.38 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.1, 152.8, 138.5, 137.2, 135.8, 132.7, 130.7, 128.7, 128.6, 128.6, 128.0, 127.0, 126.4, 126.2, 56.5, 34.4, 30.3, 30.1, 20.2. IR (neat): 3634.54, 2955.84, 1684.90, 1434.22, 1305.86, 1264.49, 1204.52, 1155.52, 1009.97, 734.70, 702.53. HRMS (ESI) calcd for  $\text{C}_{29}\text{H}_{35}\text{O}_2^+$ : 415.2637 ( $\text{M}+\text{H}^+$ ), found: 415.2633. Spectral data match those previously reported.<sup>4</sup>



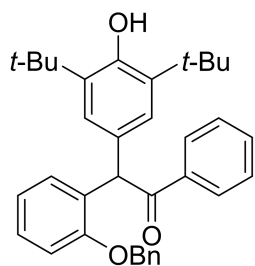
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-methoxyphenyl)-1-phenylethan-1-one (**3ce**)

light yellow solid, m. p. = 158-161 °C

64.5 mg, 75%; n-hexane/ethyl acetate = 15/1,  $R_f = 0.5$

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 7.1$  Hz, 2H), 7.47 (d,  $J = 7.5$  Hz, 1H), 7.40 (t,  $J = 7.6$  Hz, 2H), 7.23 (s, 1H), 7.11 (s, 2H), 6.94 (d,  $J = 7.6$  Hz, 1H), 6.88 (t,  $J = 8.6$  Hz, 2H), 6.21 (s, 1H), 5.13 (s, 1H), 3.76 (s, 3H), 1.39 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.5, 156.3, 152.9, 137.7, 135.9, 132.3, 129.7, 129.7, 128.6, 128.4, 128.1, 127.5, 126.5, 120.6, 110.3, 55.4, 53.0, 34.4, 30.4. IR (neat): 3631.26, 2956.96, 1685.24, 1598.21, 1489.12, 1434.46, 1240.31, 1159.01, 1207.96, 847.71, 752.55, 702.22. HRMS (ESI) calcd for  $\text{C}_{29}\text{H}_{35}\text{O}_3^+$ : 431.2581 ( $\text{M}+\text{H}^+$ ), found: 431.2569. Spectral data match those previously reported.<sup>6</sup>



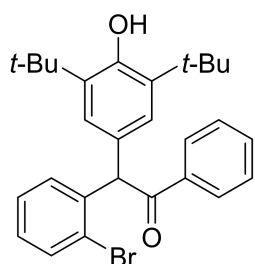


2-(2-(benzyloxy)phenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-phenylethan-1-one (**3de**)

light yellow solid, m. p. = 146-149 °C

64.9 mg, 64%; n-hexane/ethyl acetate = 15/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J$  = 7.7 Hz, 2H), 7.45 (t,  $J$  = 7.3 Hz, 1H), 7.32 (t,  $J$  = 7.6 Hz, 2H), 7.21 (d,  $J$  = 8.3 Hz, 5H), 7.12 (s, 2H), 6.98-6.91 (m, 4H), 6.29 (s, 1H), 5.14 (s, 1H), 5.03 (d,  $J$  = 4.5 Hz, 2H), 1.40 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.3, 155.4, 152.9, 137.5, 136.7, 136.0, 132.3, 130.0, 129.8, 128.8, 128.3, 128.3, 128.0, 127.7, 127.4, 127.2, 126.5, 120.8, 111.4, 70.0, 53.1, 34.4, 30.3. IR (neat): 3633.90, 2955.81, 1685.56, 1598.16, 1488.37, 1435.04, 1264.29, 1024.45, 859.79, 734.38. HRMS (ESI) calcd for  $\text{C}_{35}\text{H}_{38}\text{NaO}_3^+$ : 529.2719 ( $\text{M}+\text{Na}^+$ ), found: 529.2720.

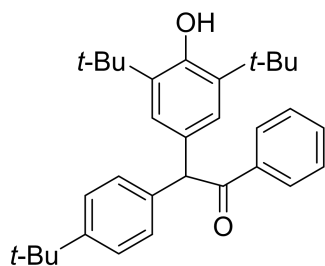


2-(2-bromophenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-phenylethan-1-one (**3ee**)

light yellow solid, m. p. = 122-124 °C

33.5 mg, 35%; n-hexane/ethyl acetate = 15/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J$  = 7.7 Hz, 2H), 7.58 (d,  $J$  = 7.9 Hz, 1H), 7.51 (t,  $J$  = 7.4 Hz, 1H), 7.42 (t,  $J$  = 7.6 Hz, 2H), 7.23 (d,  $J$  = 7.6 Hz, 1H), 7.10 (d,  $J$  = 10.2 Hz, 4H), 6.35 (s, 1H), 5.17 (s, 1H), 1.40 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.1, 153.1, 140.0, 137.1, 136.2, 132.8, 131.0, 128.8, 128.6, 128.5, 127.5, 127.3, 126.4, 124.9, 58.8, 34.4, 30.3. IR (neat): 3628.65, 2958.53, 1676.04, 1434.26, 1264.17, 1211.26, 1025.66, 895.50, 733.79, 702.72. HRMS (ESI) calcd for  $\text{C}_{28}\text{H}_{32}\text{BrO}_2^+$ : 479.1585 ( $\text{M}+\text{H}^+$ ), found: 479.1582.

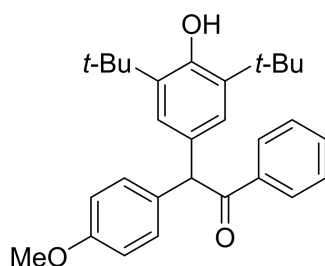


2-(4-(tert-butyl)phenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-phenylethan-1-one (**3fe**)

light yellow solid, m. p. = 142-144 °C

48.4 mg, 53%; n-hexane/ethyl acetate = 15/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J$  = 7.8 Hz, 2H), 7.50 (t,  $J$  = 7.3 Hz, 1H), 7.41 (t,  $J$  = 7.5 Hz, 2H), 7.33 (d,  $J$  = 8.1 Hz, 2H), 7.23 (d,  $J$  = 8.1 Hz, 2H), 7.10 (s, 2H), 5.91 (s, 1H), 5.11 (s, 1H), 1.39 (s, 18H), 1.28 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.0, 152.9, 149.6, 137.3, 136.7, 135.8, 132.7, 130.2, 129.5, 128.9, 128.6, 128.5, 125.8, 125.5, 58.8, 34.4, 31.3, 30.3, 29.7, 29.4. IR (neat): 3623.33, 2957.68, 2364.29, 1685.01, 1434.56, 1264.31, 1020.91, 896.25, 734.42, 702.71. HRMS (ESI) calcd for  $\text{C}_{32}\text{H}_{41}\text{O}_2^+$ : 457.3106 ( $\text{M}+\text{H}^+$ ), found: 457.3113.

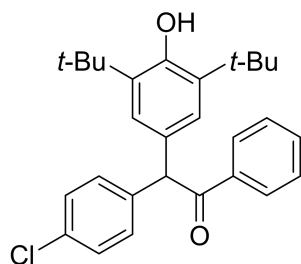


2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-methoxyphenyl)-1-phenylethan-1-one (**3ge**)

light yellow solid, m. p. = 128-131 °C

50.8 mg, 59%; n-hexane/ethyl acetate = 15/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J$  = 7.5 Hz, 2H), 7.50 (t,  $J$  = 7.3 Hz, 1H), 7.41 (t,  $J$  = 7.6 Hz, 2H), 7.22 (d,  $J$  = 8.6 Hz, 2H), 7.05 (s, 2H), 6.86 (d,  $J$  = 8.7 Hz, 2H), 5.89 (s, 1H), 5.12 (s, 1H), 3.78 (s, 3H), 1.39 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.1, 158.5, 152.8, 137.2, 135.8, 132.8, 131.8, 130.1, 129.8, 128.9, 128.5, 125.8, 114.1, 58.4, 55.2, 34.4, 30.3. IR (neat): 3634.21, 2953.62, 1681.70, 1509.16, 1433.58, 1248.56, 1176.74, 1033.87, 895.29, 736.16. HRMS (ESI) calcd for  $\text{C}_{29}\text{H}_{35}\text{O}_3^+$ : 431.2581 ( $\text{M}+\text{H}^+$ ), found: 431.2569. Spectral data match those previously reported.<sup>6</sup>



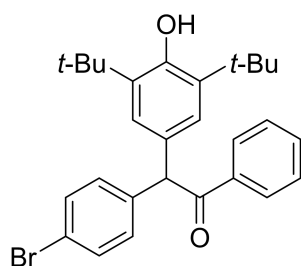
2-(4-chlorophenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-phenylethan-1-one (**3he**)

light yellow oil

63.5 mg, 73%; n-hexane/ethyl acetate = 15/1,  $R_f = 0.5$

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 7.1$  Hz, 2H), 7.52 (s, 1H), 7.47-7.37 (m, 4H), 7.26 (s, 1H), 7.17 (d,  $J = 8.4$  Hz, 2H), 7.05 (s, 2H), 5.90 (s, 1H), 5.16 (s, 1H), 1.39 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.4, 153.1, 138.9, 137.0, 136.1, 133.0, 131.7, 130.8, 128.9, 128.9, 128.6, 125.7, 121.0, 58.6, 34.4, 30.3. IR (neat): 3632.10, 2956.27, 1682.13, 1580.78, 1433.73, 1264.26, 1073.22, 1010.62, 895.99, 735.15. HRMS (ESI) calcd for  $\text{C}_{28}\text{H}_{31}\text{ClNaO}_2^+$ : 457.1911 ( $\text{M}+\text{Na}^+$ ), found: 457.1899.

Spectral data match those previously reported.<sup>6</sup>



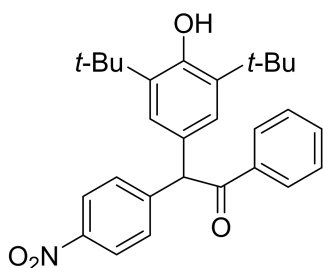
2-(4-bromophenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-phenylethan-1-one (**3ie**)

light yellow solid, m. p. = 86-89 °C

71.0 mg, 74%; n-hexane/ethyl acetate = 15/1,  $R_f = 0.5$

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 6.9$  Hz, 2H), 7.51 (t,  $J = 7.4$  Hz, 1H), 7.41 (t,  $J = 7.7$  Hz, 2H), 7.30-7.19 (m, 4H), 7.04 (s, 2H), 5.91 (s, 1H), 5.15 (s, 1H), 1.38 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.5, 153.0, 138.4, 137.0, 136.1, 133.0, 132.8, 130.5, 129.0, 128.9, 128.7, 128.6, 125.7, 58.5, 34.4, 30.3. IR (neat): 3633.11, 2956.94, 1681.76, 1595.36, 1489.75, 1433.96, 1236.77, 1003.34, 843.24, 738.39. HRMS (ESI) calcd for  $\text{C}_{28}\text{H}_{31}\text{NaBrO}_2^+$ : 501.1405 ( $\text{M}+\text{Na}^+$ ), found: 501.1419.

Spectral data match those previously reported.<sup>6</sup>

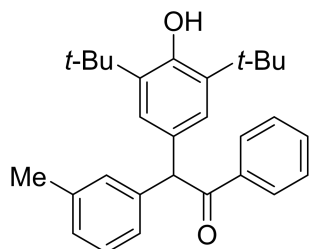


2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-nitrophenyl)-1-phenylethan-1-one (**3je**)

light yellow solid, m. p. = 164-166 °C

35.6 mg, 40%; n-hexane/ethyl acetate = 15/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (d,  $J$  = 8.3 Hz, 2H), 7.99 (d,  $J$  = 7.8 Hz, 2H), 7.55 (t,  $J$  = 7.3 Hz, 1H), 7.44 (t,  $J$  = 7.4 Hz, 4H), 7.06 (s, 2H), 6.03 (s, 1H), 5.21 (s, 1H), 1.38 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.5, 156.3, 152.9, 137.7, 135.9, 132.3, 129.7, 129.7, 128.6, 128.4, 128.1, 127.5, 126.5, 120.6, 110.3, 55.4, 53.0, 34.4, 30.3. IR (neat): 3636.50, 2961.09, 1685.84, 1596.48, 1521.95, 1434.42, 1346.62, 1264.55, 802.80, 737.98. HRMS (ESI) calcd for  $\text{C}_{28}\text{H}_{31}\text{NNaO}_4^+$ : 468.2151 ( $\text{M}+\text{Na}^+$ ), found: 468.2150. Spectral data match those previously reported.<sup>6</sup>

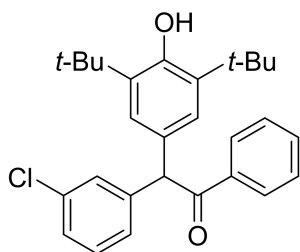


2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-phenyl-2-(m-tolyl)ethan-1-one (**3ke**)

red solid, m. p. = 108-111 °C

41.5 mg, 50%; n-hexane/ethyl acetate = 20/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J$  = 7.7 Hz, 2H), 7.54-7.47 (m, 1H), 7.41 (t,  $J$  = 7.6 Hz, 2H), 7.20 (t,  $J$  = 7.5 Hz, 1H), 7.08 (m, 5H), 5.90 (s, 1H), 5.11 (s, 1H), 2.31 (s, 3H), 1.38 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.9, 152.8, 139.5, 138.2, 137.3, 135.7, 132.7, 129.8, 129.5, 128.9, 128.5, 127.7, 126.1, 125.9, 59.3, 34.4, 30.3, 21.5. IR (neat): 3632.69, 2958.46, 1685.65, 1596.91, 1434.66, 1264.62, 1155.78, 1009.91, 897.02, 736.85. HRMS (ESI) calcd for  $\text{C}_{29}\text{H}_{35}\text{O}_2^+$ : 415.2637 ( $\text{M}+\text{H}^+$ ), found: 415.2633.

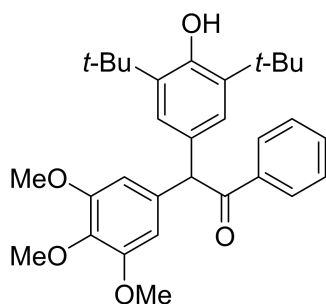


2-(3-chlorophenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-phenylethan-1-one (**3le**)

light yellow solid, m. p. = 130-133 °C

57.4 mg, 66%; n-hexane/ethyl acetate = 15/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J$  = 7.8 Hz, 2H), 7.51 (d,  $J$  = 6.8 Hz, 1H), 7.42 (t,  $J$  = 7.6 Hz, 2H), 7.30 (s, 1H), 7.21 (d,  $J$  = 15.7 Hz, 3H), 7.06 (s, 2H), 5.90 (s, 1H), 5.16 (s, 1H), 1.39 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.2, 153.1, 141.8, 137.0, 136.1, 134.4, 133.0, 129.7, 129.3, 128.9, 128.7, 128.6, 127.2, 127.1, 125.7, 58.8, 34.4, 30.3. IR (neat): 3634.13, 2962.00, 1683.47, 1595.05, 433.64, 1264.30, 1154.66, 1005.00, 896.07, 734.87. HRMS (ESI) calcd for  $\text{C}_{28}\text{H}_{32}\text{ClO}_2^+$ : 435.2091 ( $\text{M}+\text{H}^+$ ), found: 435.2091. Spectral data match those previously reported.<sup>6</sup>

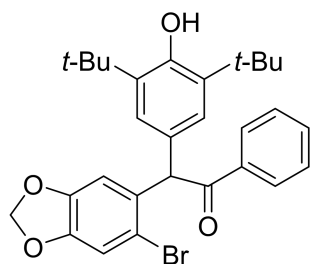


2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-phenyl-2-(3,4,5-trimethoxyphenyl)ethan-1-one (**3me**)

yellow oil

62.8 mg, 64%; n-hexane/ethyl acetate = 15/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J$  = 7.0 Hz, 2H), 7.53 (t,  $J$  = 7.4 Hz, 1H), 7.43 (t,  $J$  = 7.7 Hz, 2H), 7.11 (s, 2H), 6.54 (s, 2H), 5.86 (s, 1H), 5.15 (s, 1H), 3.81 (d,  $J$  = 2.0 Hz, 9H), 1.40 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.7, 153.3, 153.0, 137.2, 135.9, 135.1, 132.9, 129.1, 128.9, 128.6, 125.7, 106.1, 60.8, 59.3, 56.1, 34.4, 30.3. IR (neat): 3635.34, 2956.94, 1682.34, 1589.28, 1506.02, 1421.27, 1326.38, 1236.65, 1125.75, 1006.57, 812.81. HRMS (ESI) calcd for  $\text{C}_{31}\text{H}_{39}\text{O}_5^+$ : 491.2797 ( $\text{M}+\text{H}^+$ ), found: 491.2805.

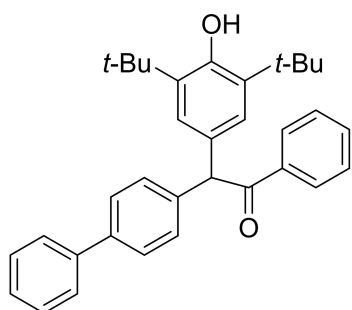


2-(6-bromobenzo[d][1,3]dioxol-5-yl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-phenylethan-1-one  
(**3ne**)

light yellow solid, m. p. = 150-153 °C

73.3 mg, 70%; n-hexane/ethyl acetate = 15/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J$  = 7.6 Hz, 2H), 7.56-47 (m, 1H), 7.42 (t,  $J$  = 7.5 Hz, 2H), 7.05 (d,  $J$  = 9.9 Hz, 3H), 6.59 (s, 1H), 6.27 (s, 1H), 5.93 (d,  $J$  = 8.5 Hz, 2H), 5.18 (s, 1H), 1.39 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.4, 153.2, 147.3, 147.3, 137.1, 136.3, 133.4, 132.8, 128.8, 128.6, 127.6, 126.1, 115.0, 112.6, 111.0, 101.7, 58.5, 34.4, 30.3. IR (neat): 3633.55, 2958.04, 1685.54, 1478.27, 1434.75, 1264.30, 1236.57, 1038.98, 932.80, 737.19. HRMS (ESI) calcd for  $\text{C}_{29}\text{H}_{31}\text{BrNaO}_4^+$ : 545.1304 ( $\text{M}+\text{Na}^+$ ), found: 545.1304.

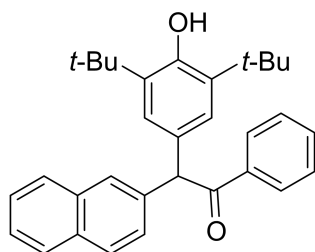


2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(naphthalen-2-yl)-1-phenylethan-1-one (**3oe**)

white solid, m. p. = 159-162 °C

68.5 mg, 72%; n-hexane/ethyl acetate = 15/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.0 (d,  $J$  = 7.9 Hz, 2H), 7.6 (q,  $J$  = 8.6, 7.9 Hz, 5H), 7.5-7.3 (m, 7H), 7.1 (s, 2H), 6.0 (s, 1H), 5.1 (s, 1H), 1.4 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.8, 153.0, 140.8, 139.8, 138.9, 137.2, 136.0, 132.9, 129.4, 129.3, 129.0, 128.7, 128.6, 127.3, 127.2, 127.1, 125.8, 59.0, 34.4, 30.3. IR (neat): 3627.98, 2963.20, 1685.50, 1435.02, 1264.21, 1233.19, 1206.88, 1075.58, 732.42. HRMS (ESI) calcd for  $\text{C}_{34}\text{H}_{37}\text{NaO}_2^+$ : 477.2788 ( $\text{M}+\text{H}^+$ ), found: 477.2787.



2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-phenyl-2-(thiophen-2-yl)ethan-1-one (**3pe**)

yellow solid, m. p. = 181-186 °C

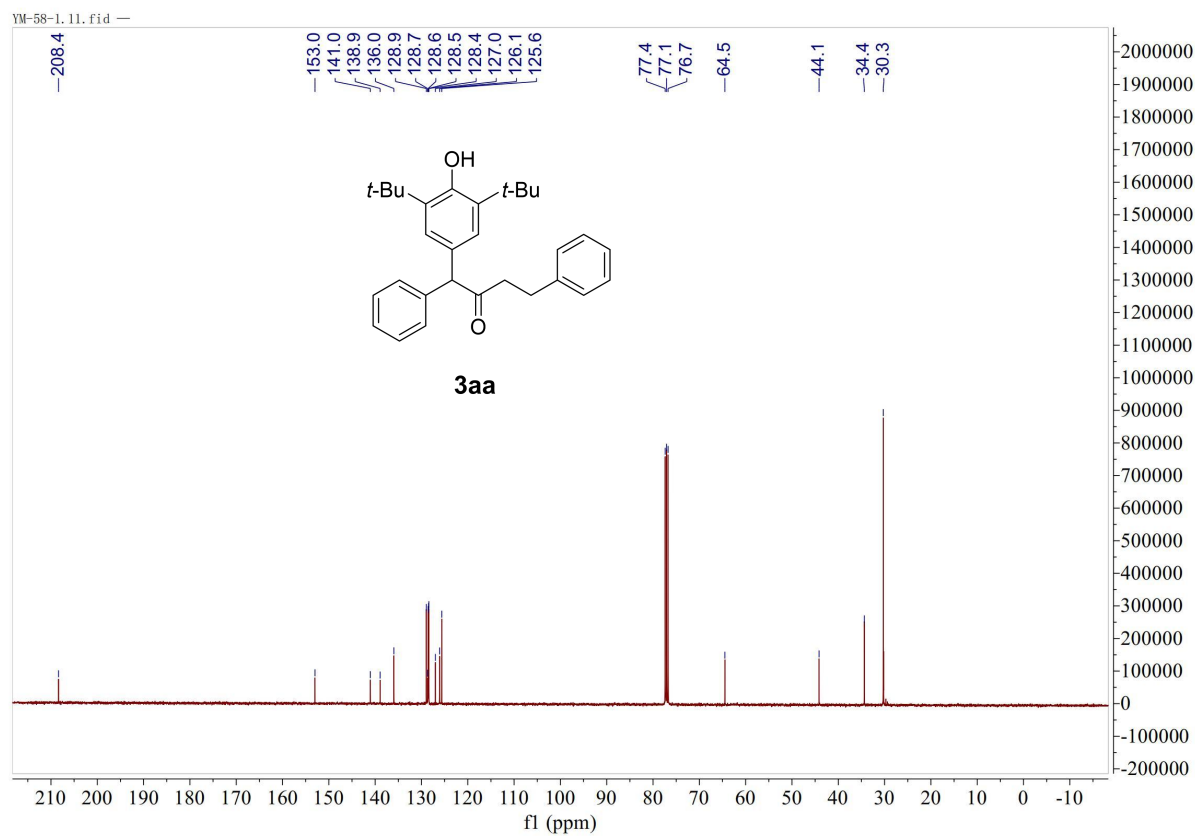
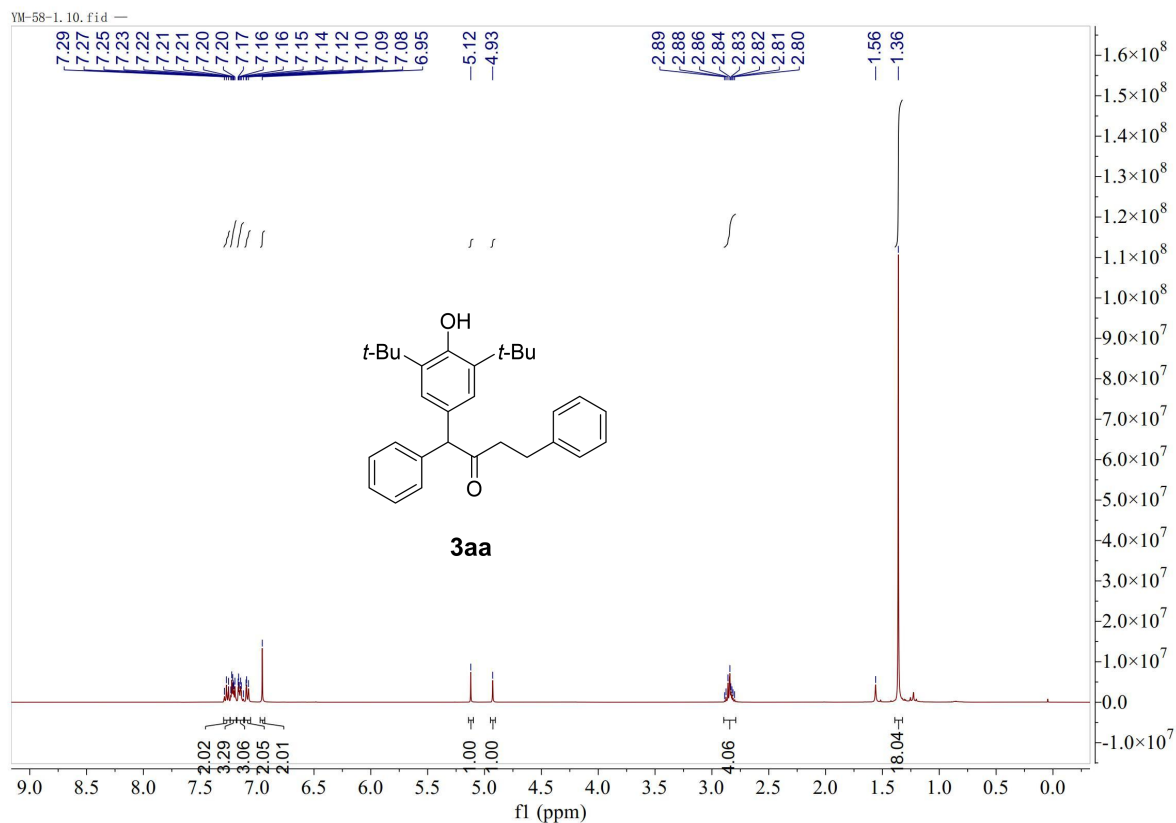
58.6 mg, 65%; n-hexane/ethyl acetate = 15/1,  $R_f$  = 0.5

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07-8.01 (m, 1H), 8.01-7.97 (m, 2H), 7.91-7.86 (m, 1H), 7.77 (d,  $J$  = 8.2 Hz, 1H), 7.53-7.46 (m, 3H), 7.39 (td,  $J$  = 7.4, 4.7 Hz, 3H), 7.21 (m, 1H), 7.09 (s, 2H), 6.64 (s, 1H), 5.13 (s, 1H), 1.38 (s, 18H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.8, 153.0, 137.0, 136.0, 135.9, 134.2, 132.8, 131.4, 129.1, 128.8, 128.6, 128.1, 127.8, 126.9, 126.5, 126.4, 125.6, 125.5, 123.3, 55.8, 34.4, 30.3. IR (neat): 3623.33, 3056.69, 2957.68, 2364.29, 1685.01, 1434.56, 1264.31, 1202.91, 896.25, 734.42. HRMS (ESI) calcd for  $\text{C}_{32}\text{H}_{35}\text{O}_2^+$ : 451.2637 ( $\text{M}+\text{H}^+$ ), found: 451.2635.

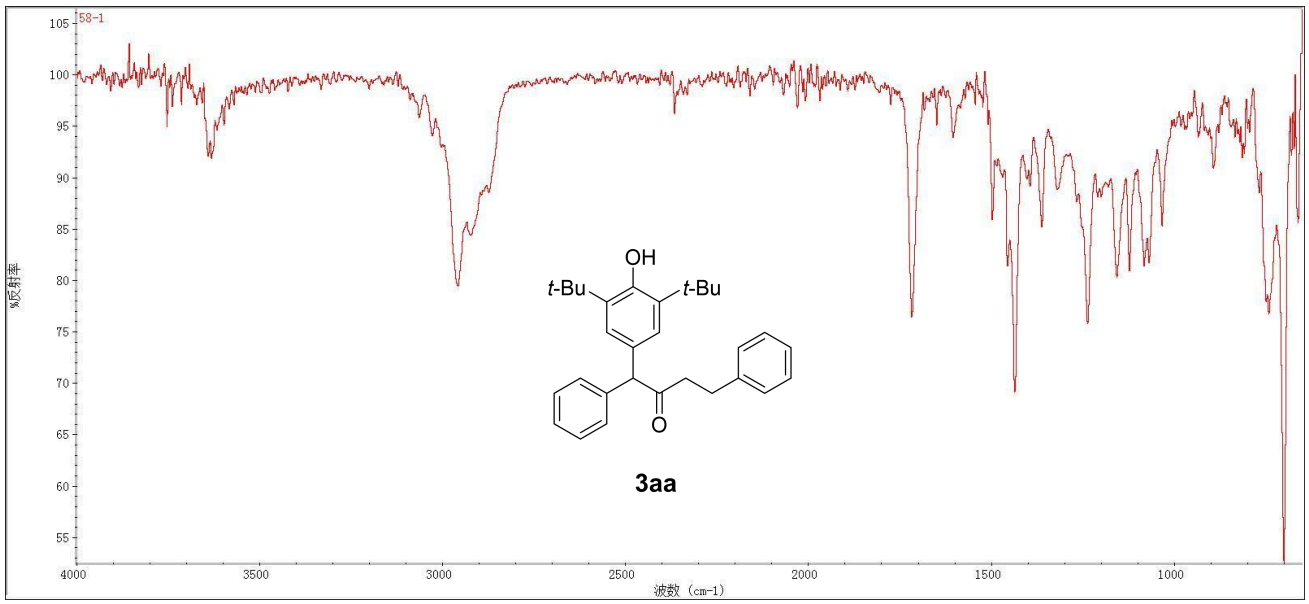
**References:**

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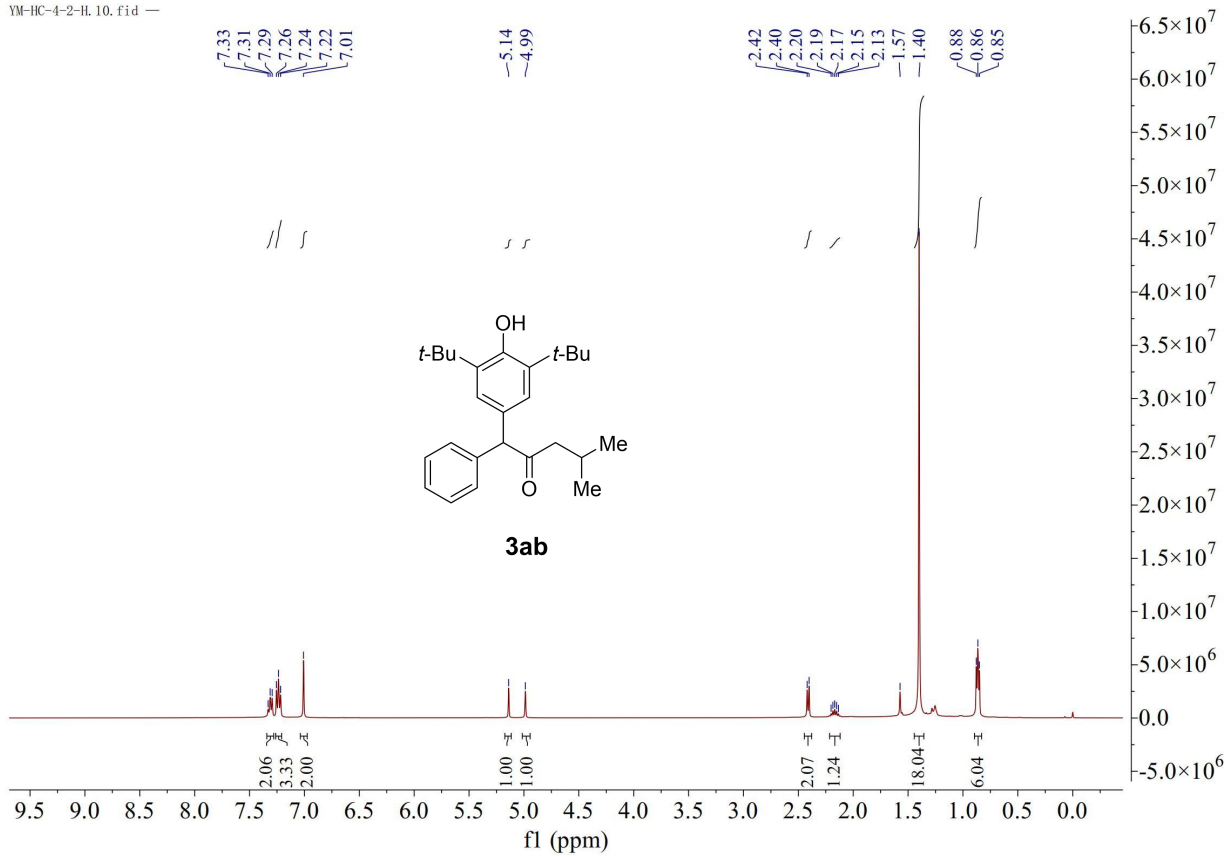
## 5. $^1\text{H}$ , $^{13}\text{C}$ NMR and IR spectra of $\alpha,\alpha'$ -diaryl ketones.



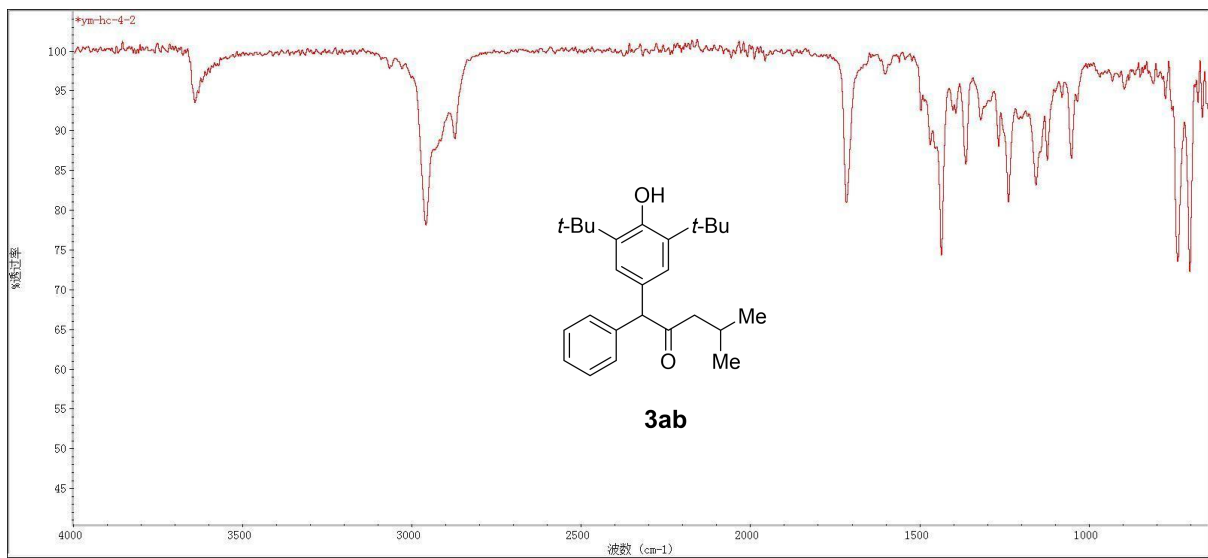
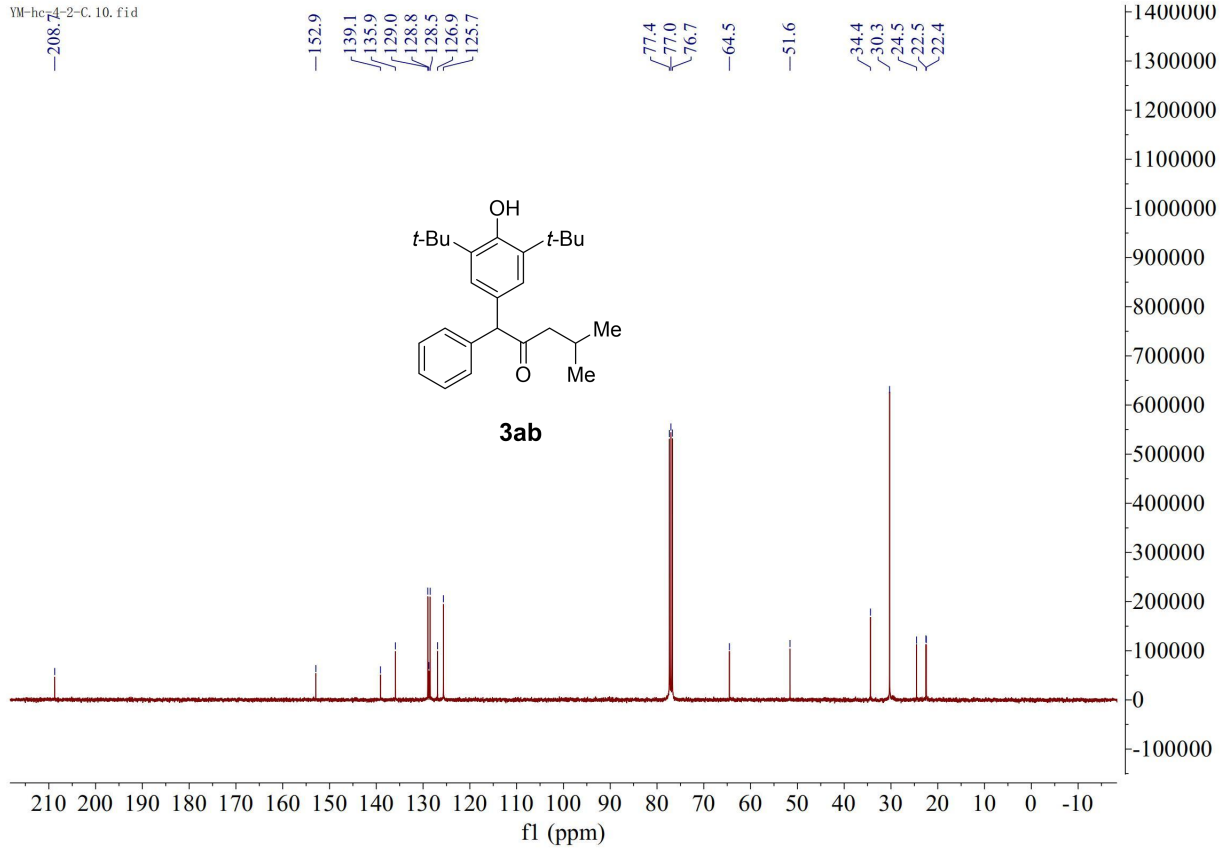




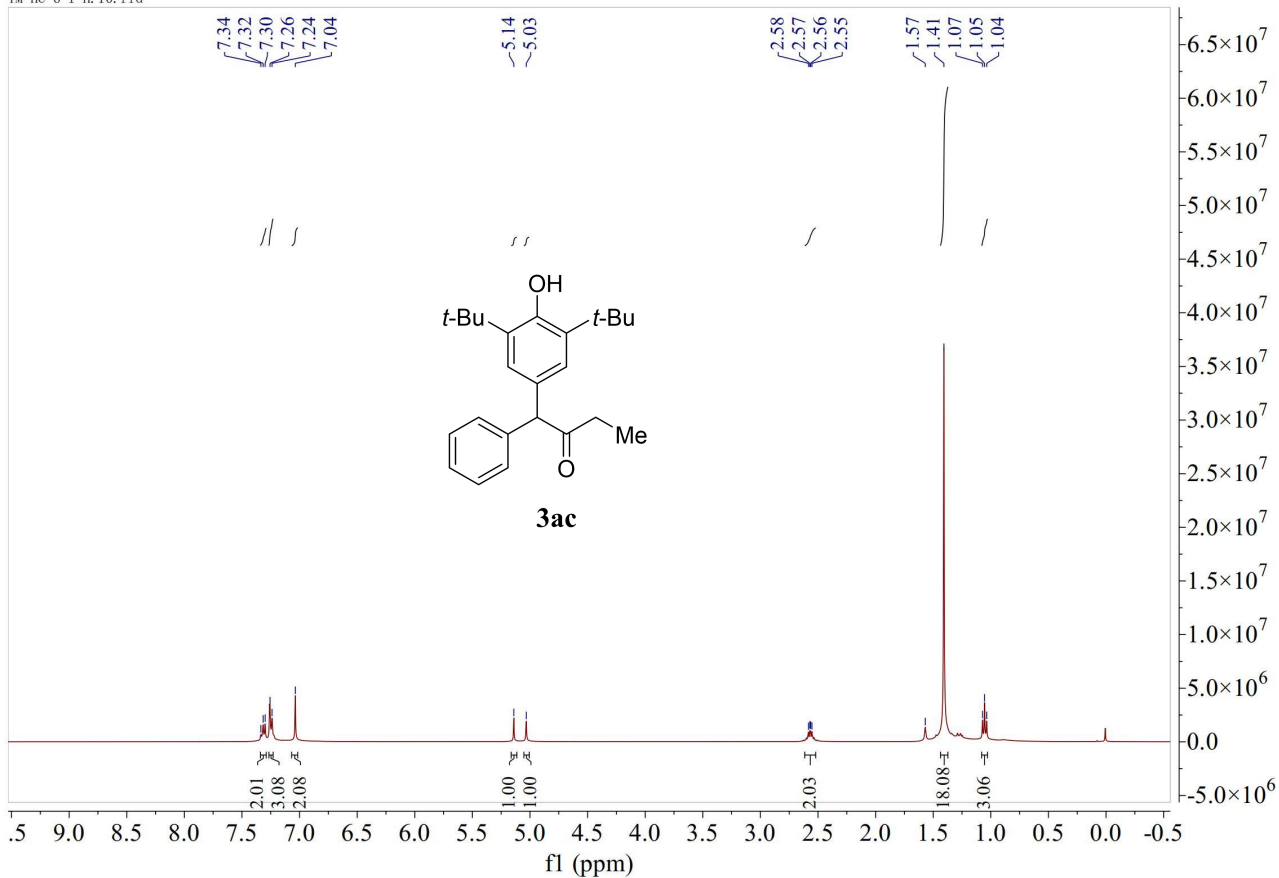
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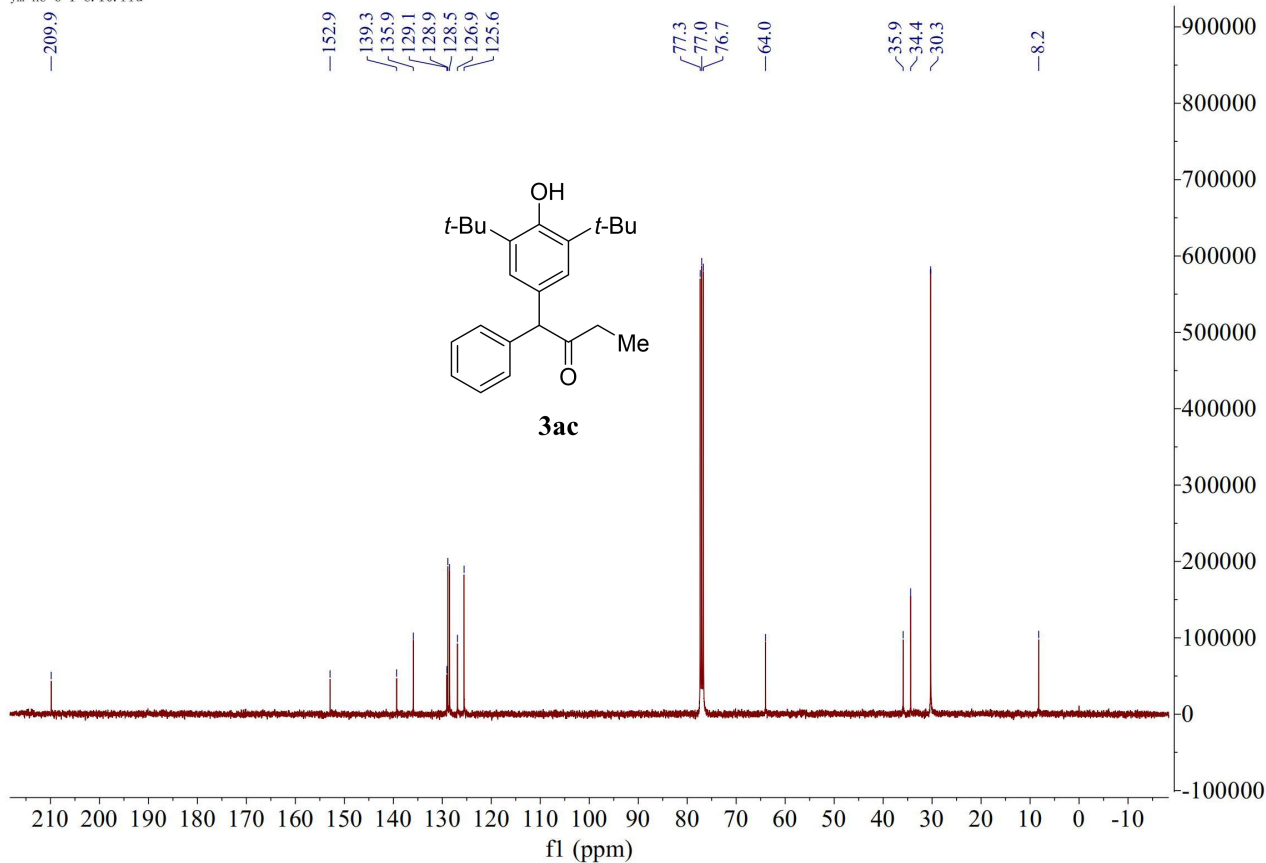
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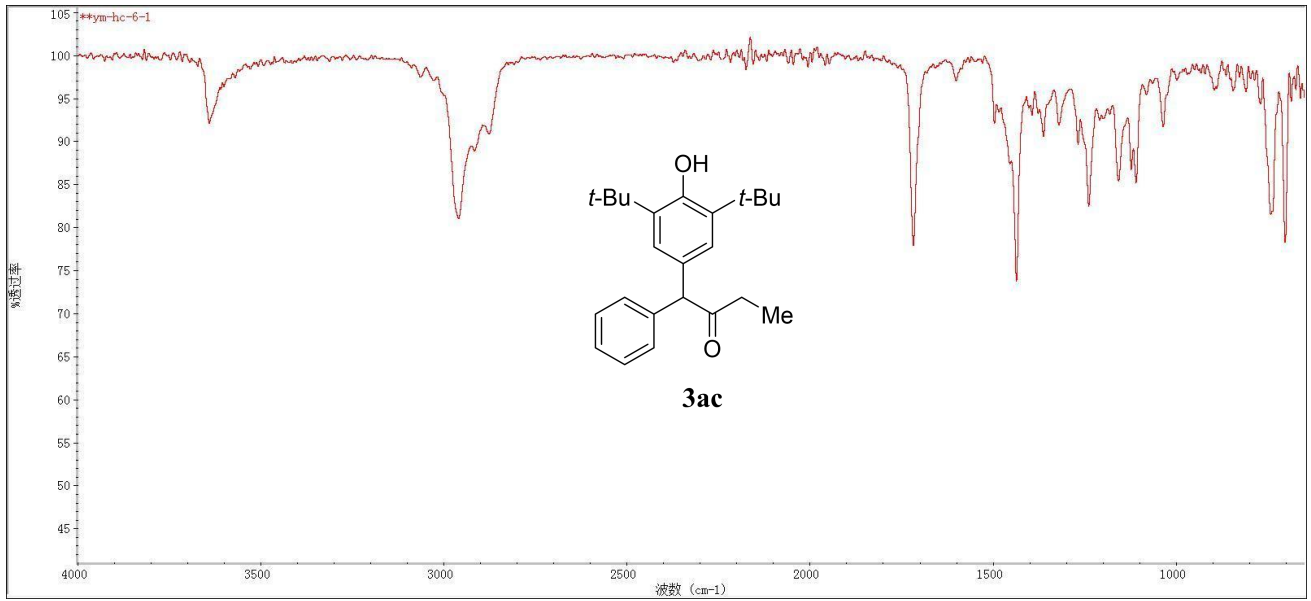


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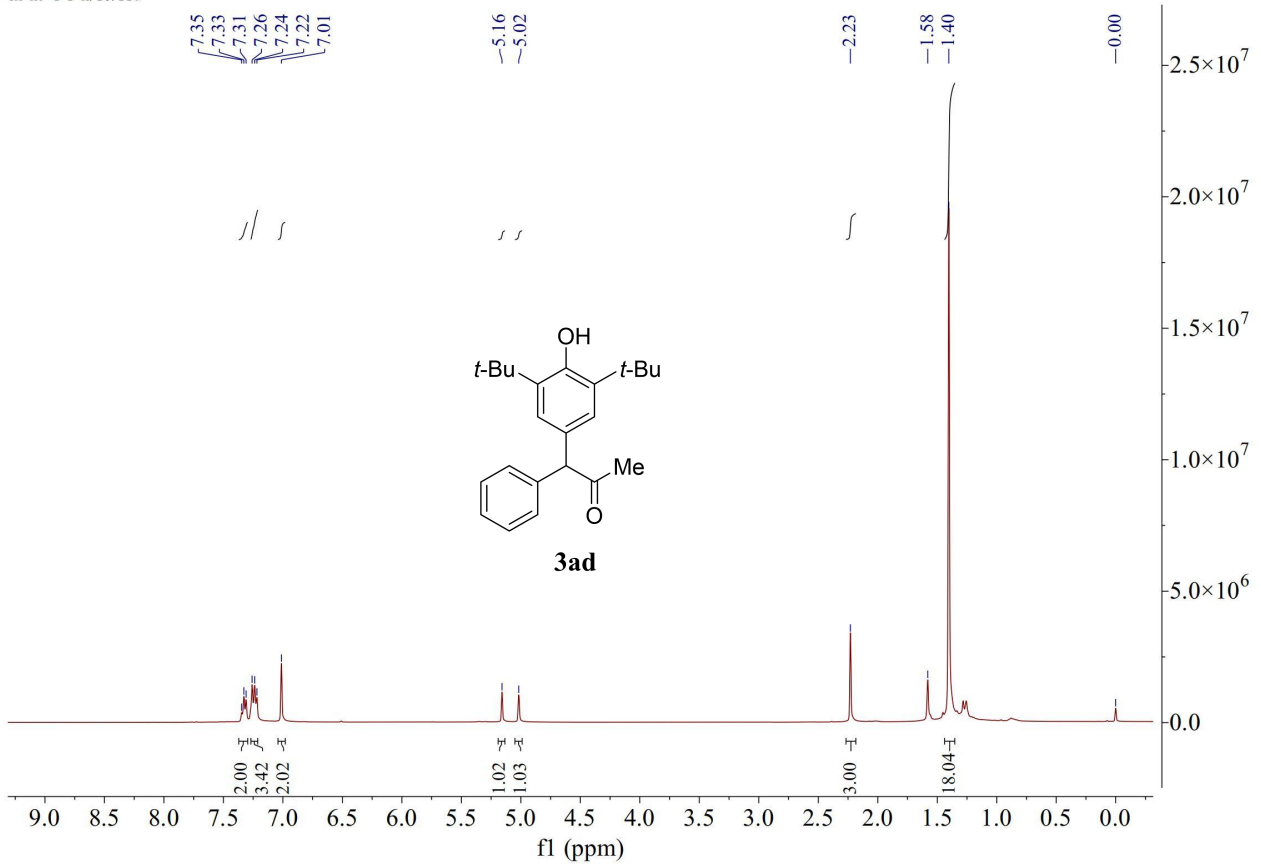


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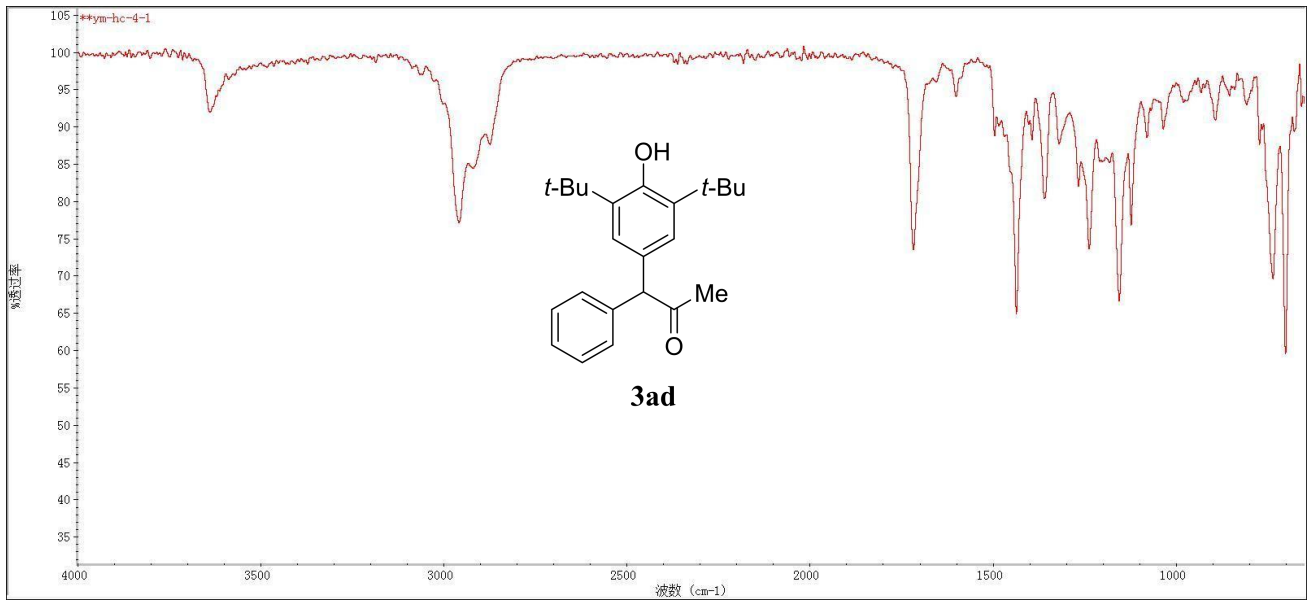
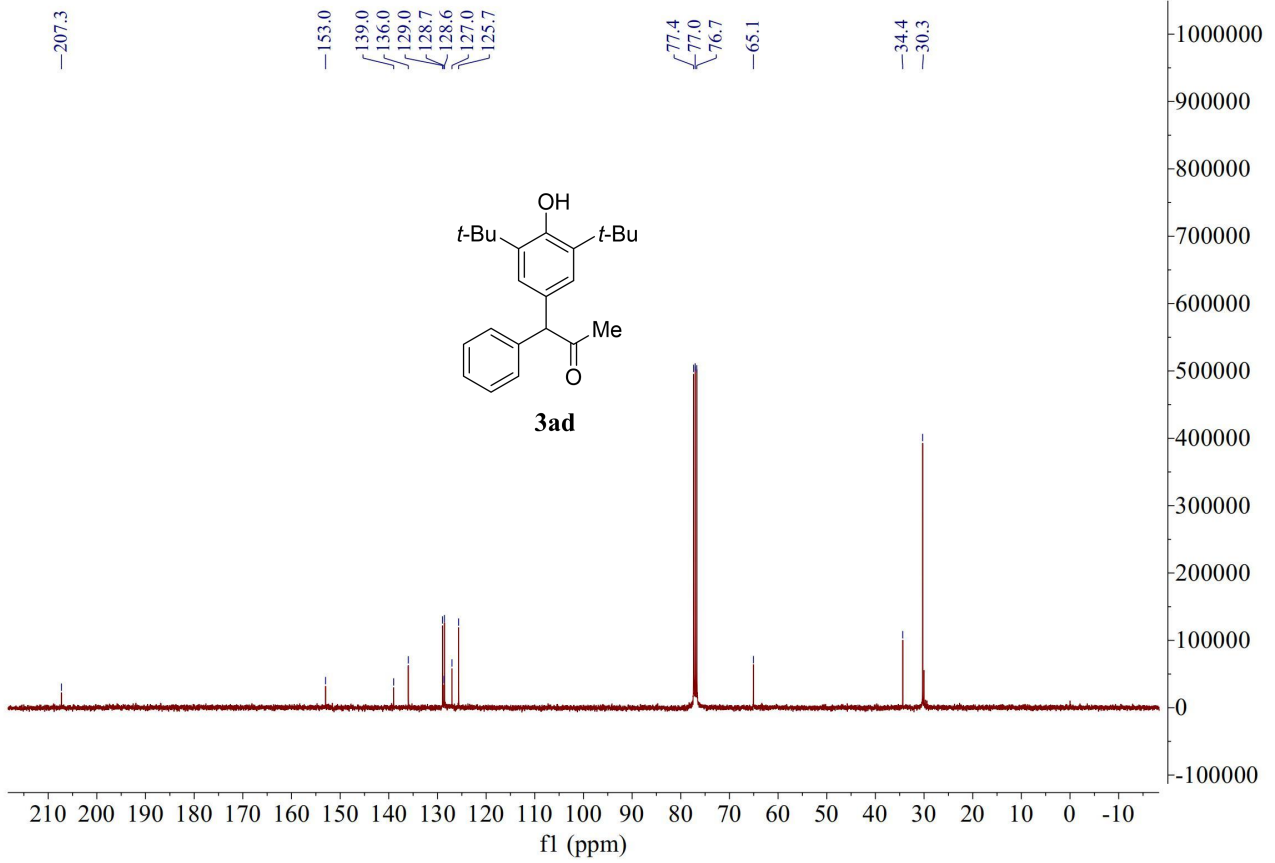




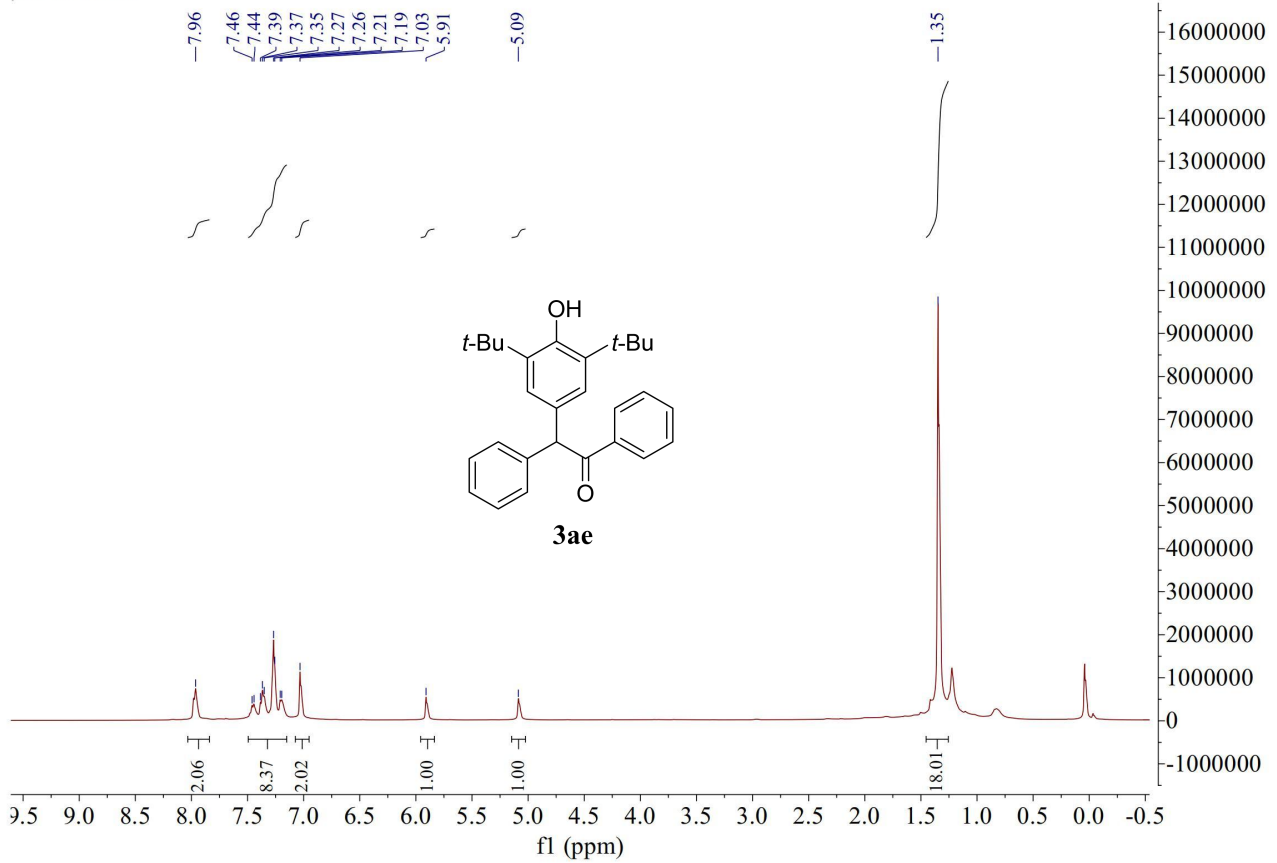
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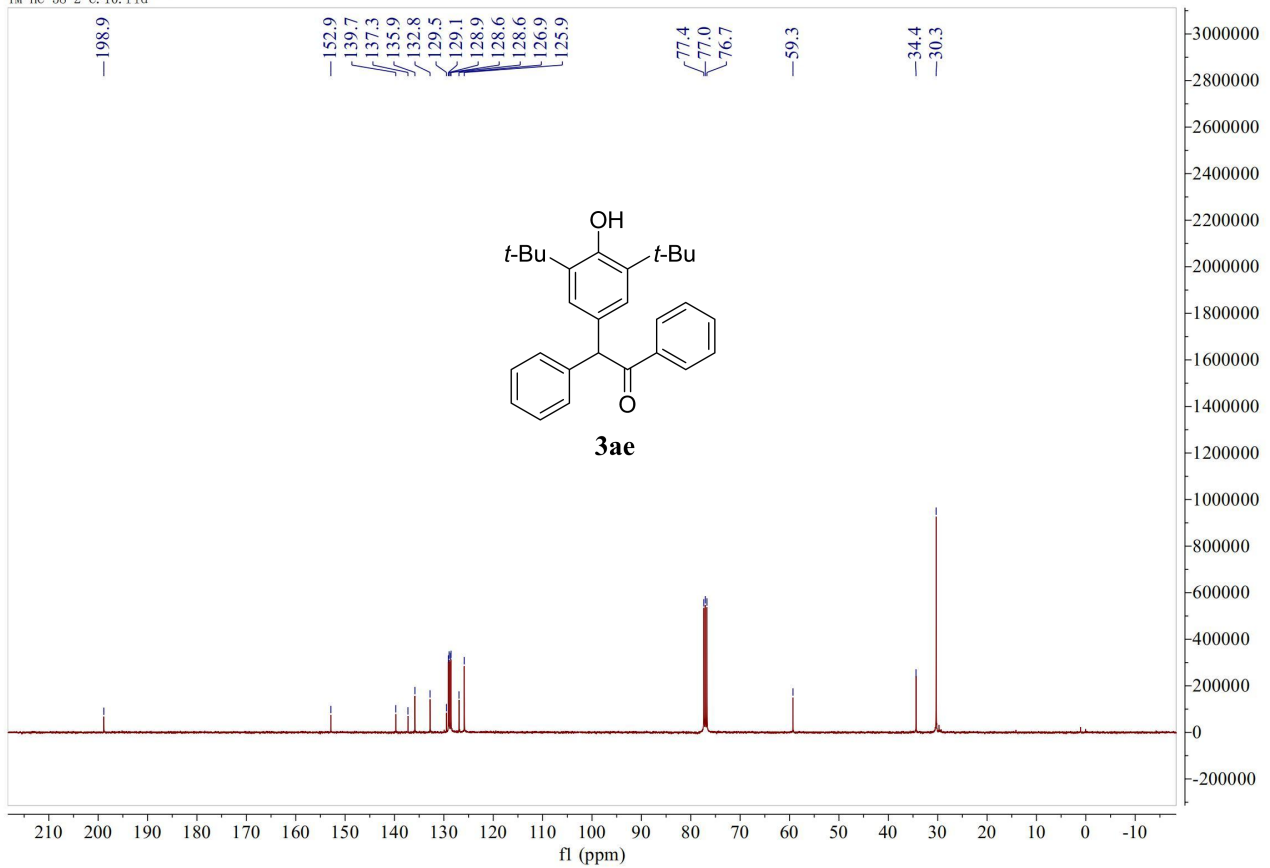
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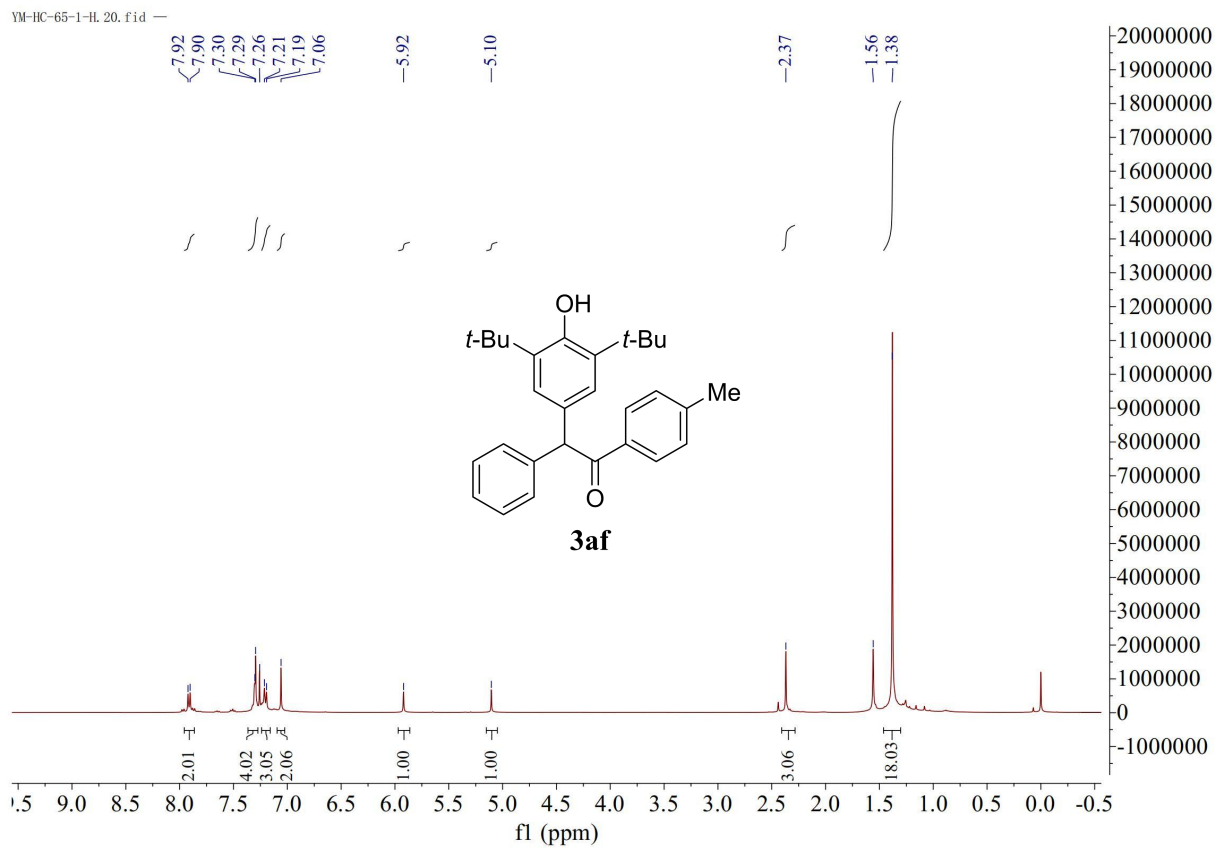
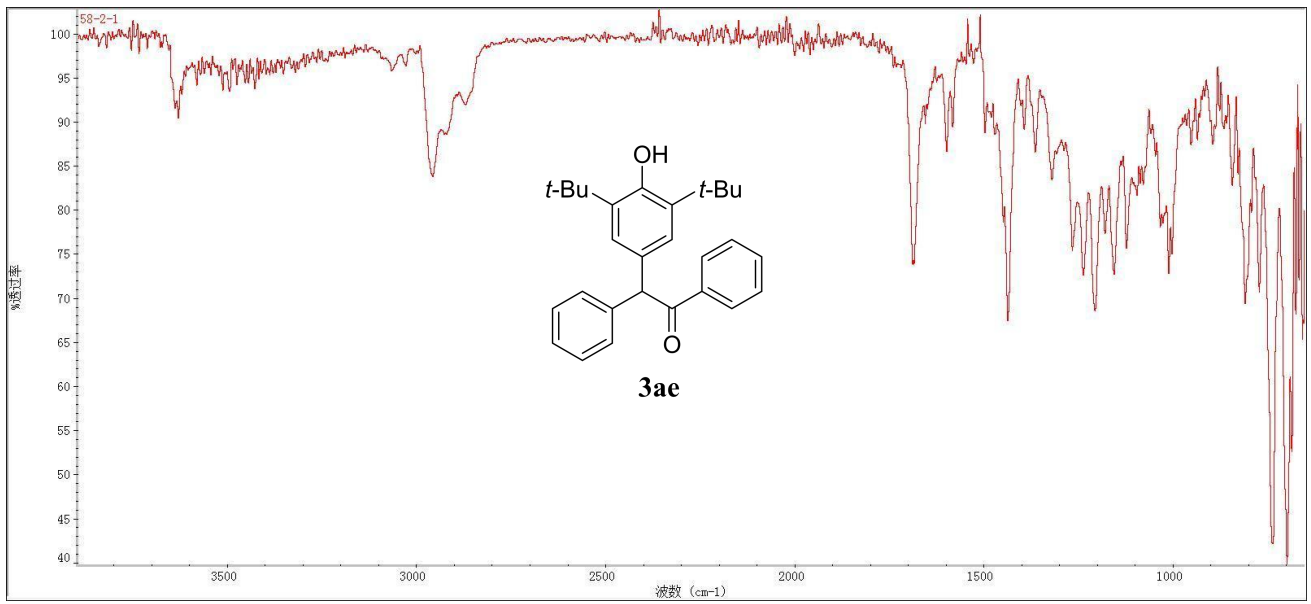


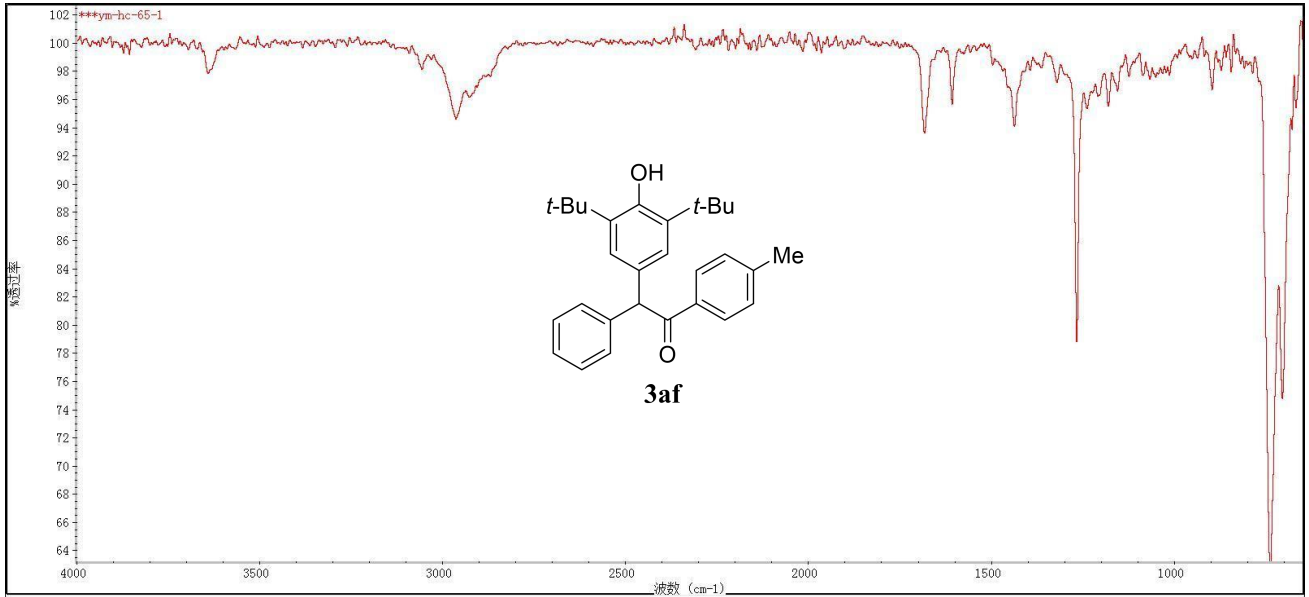
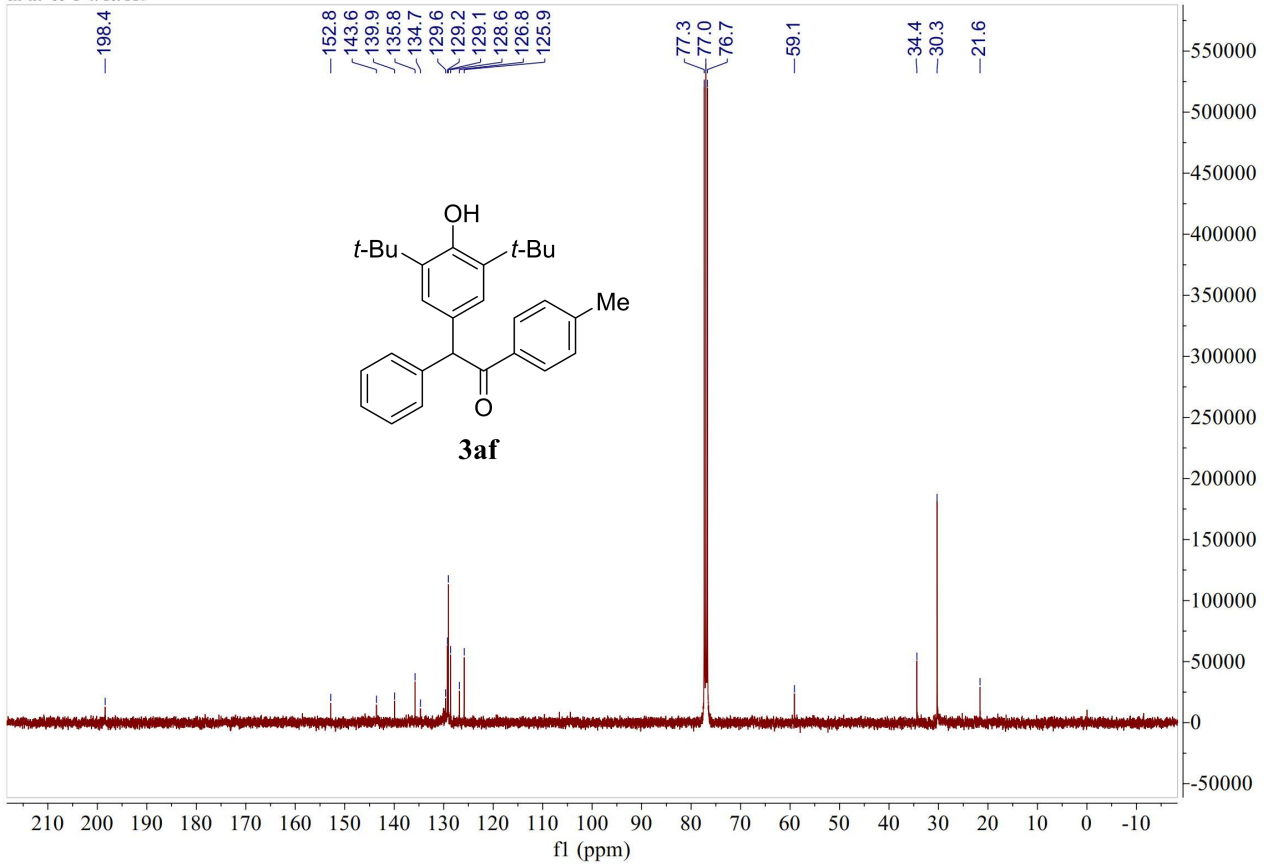
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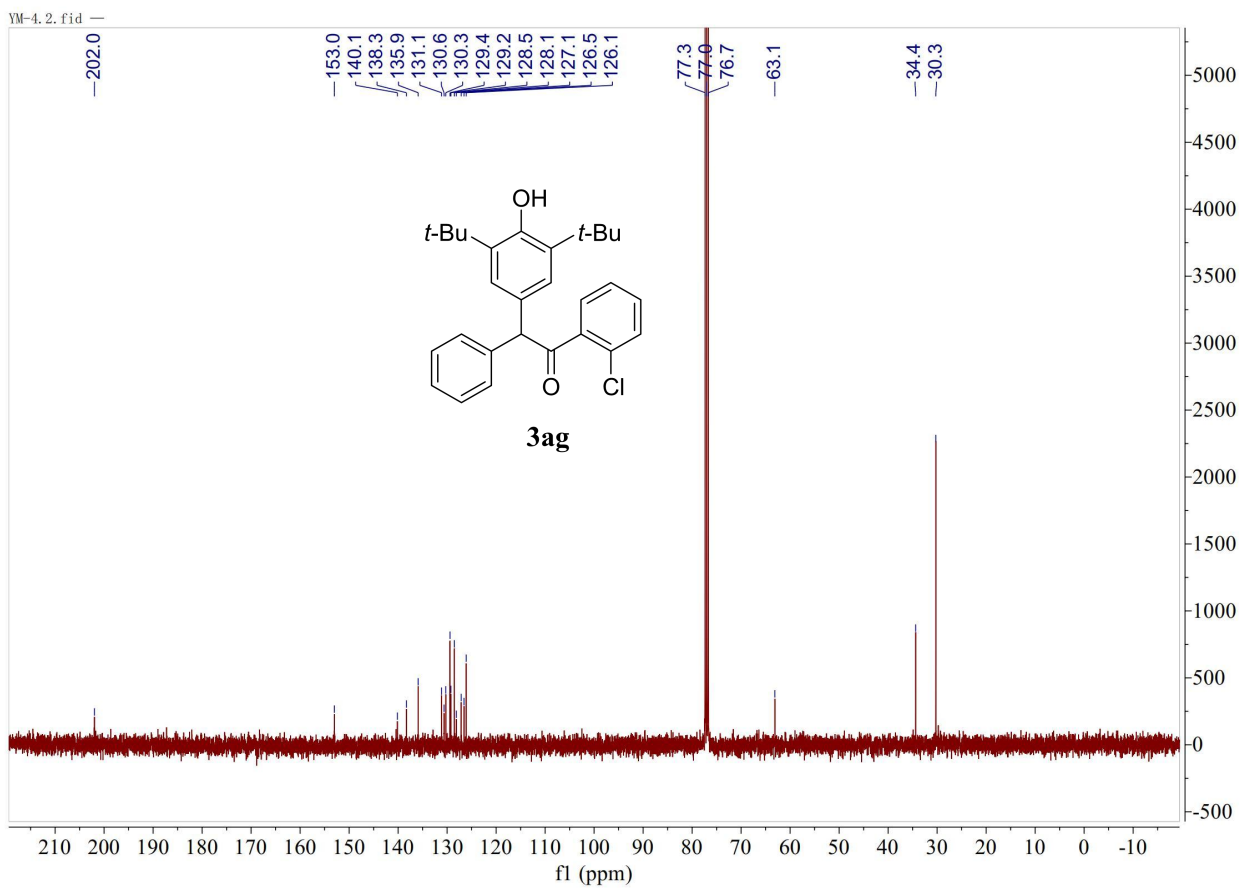
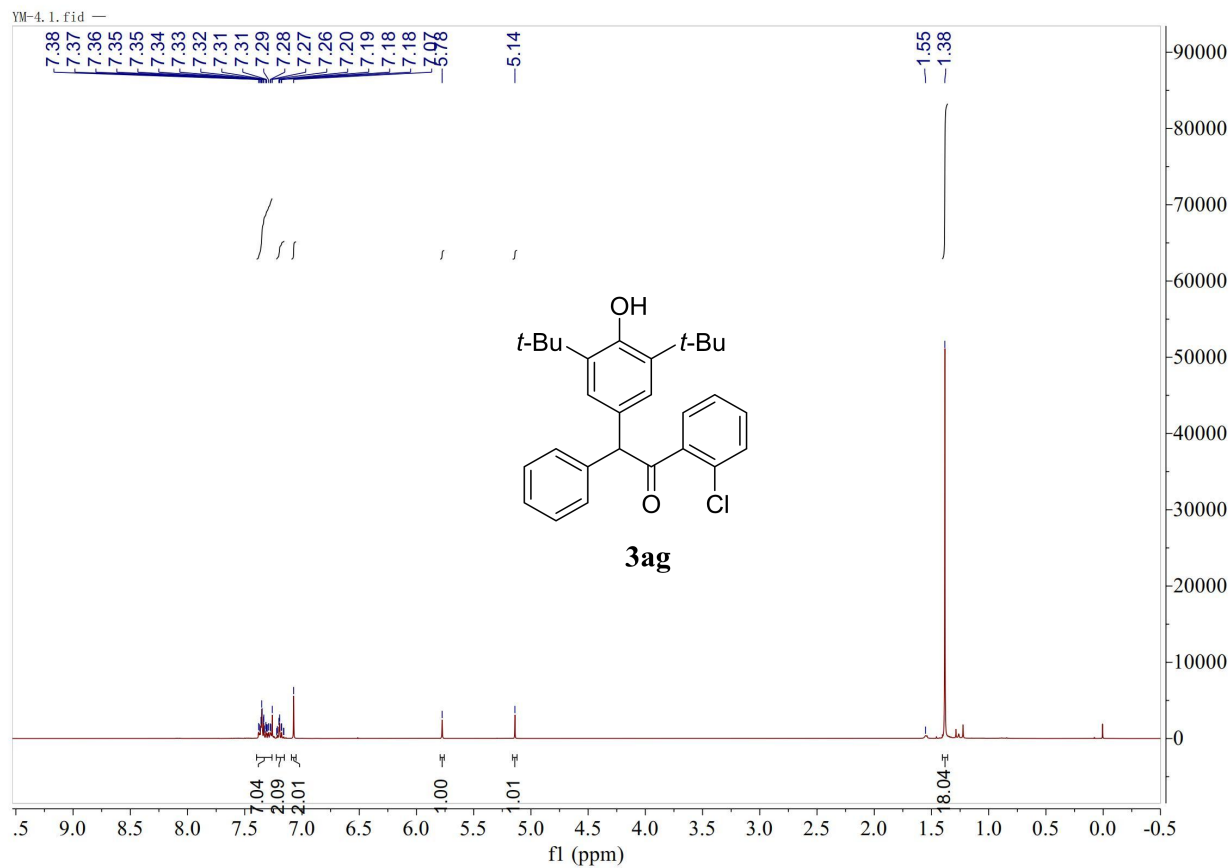
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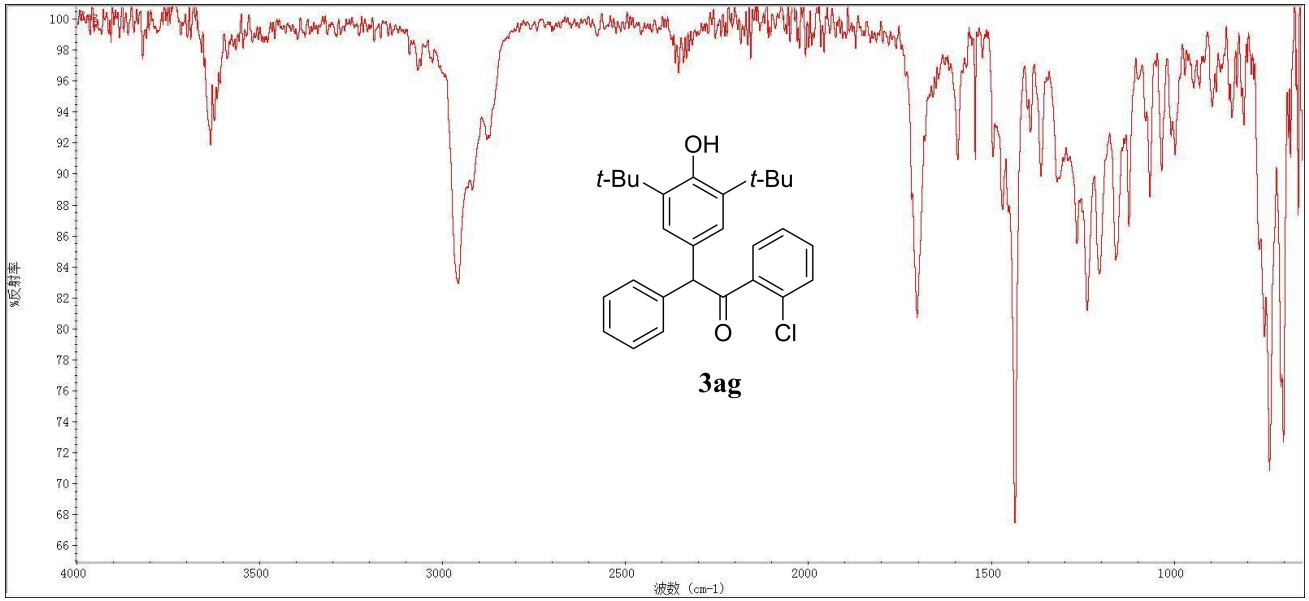




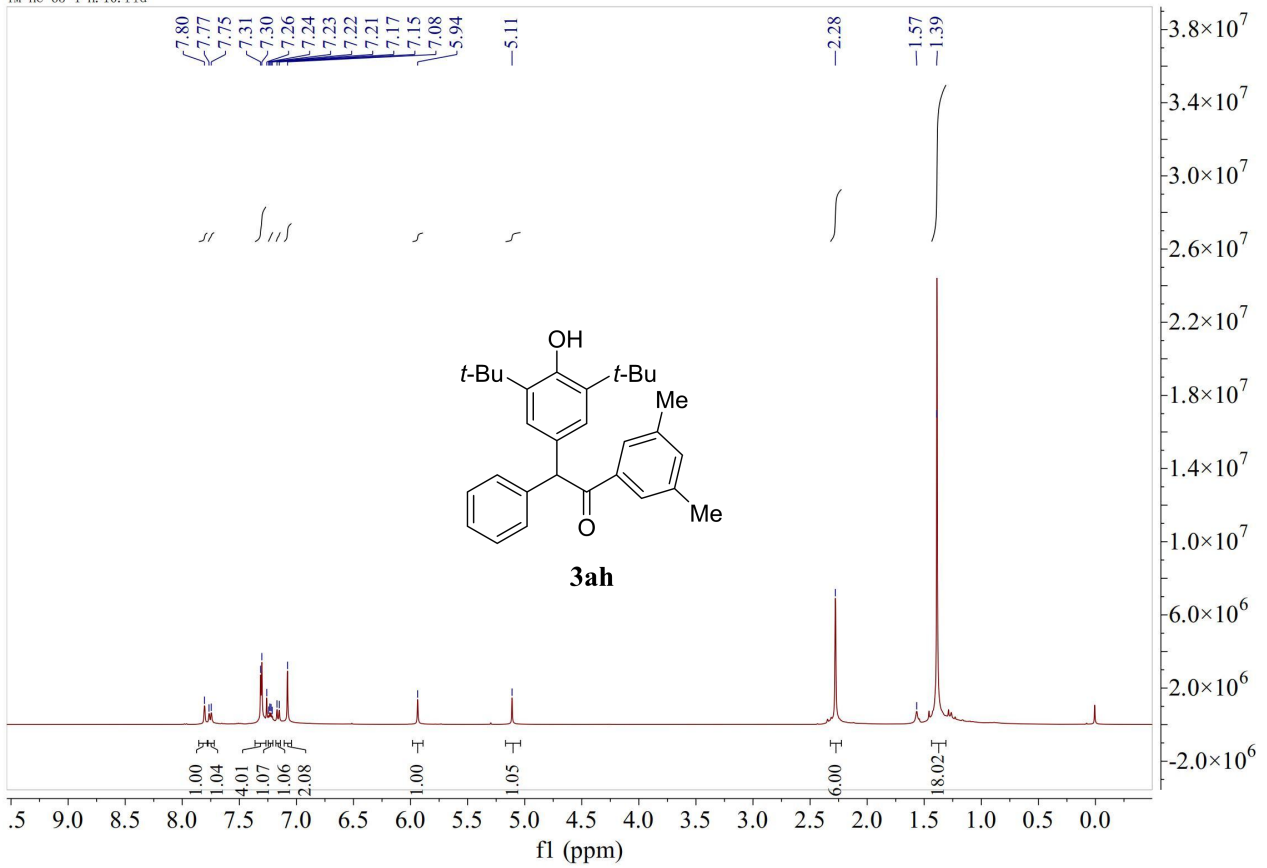




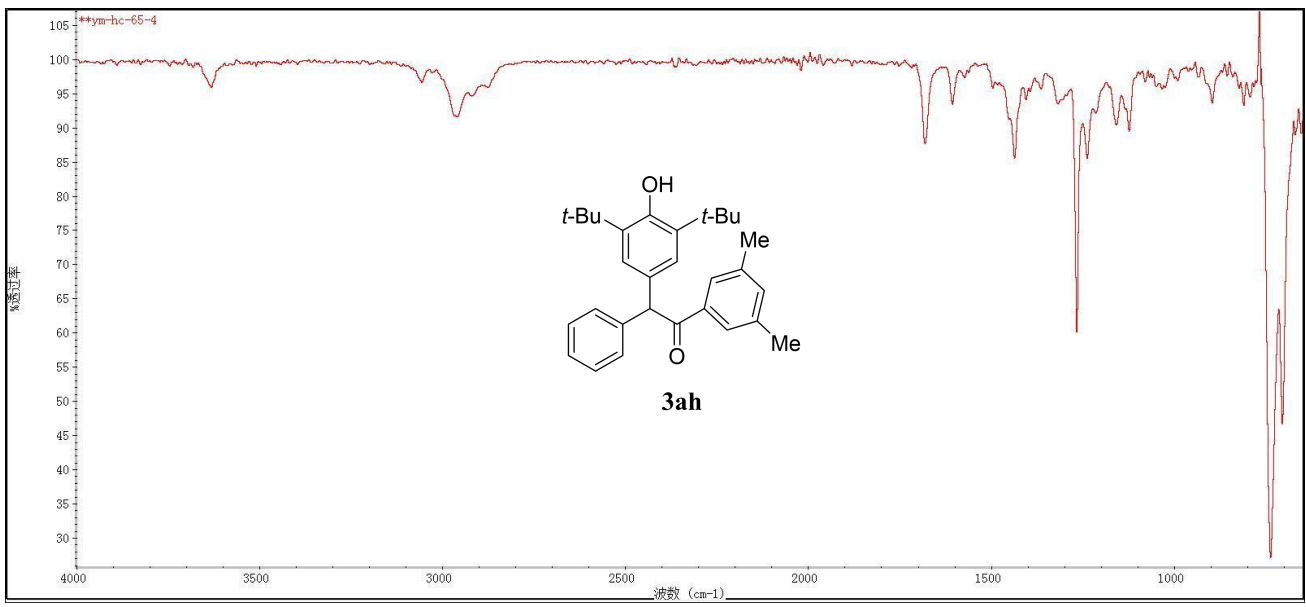
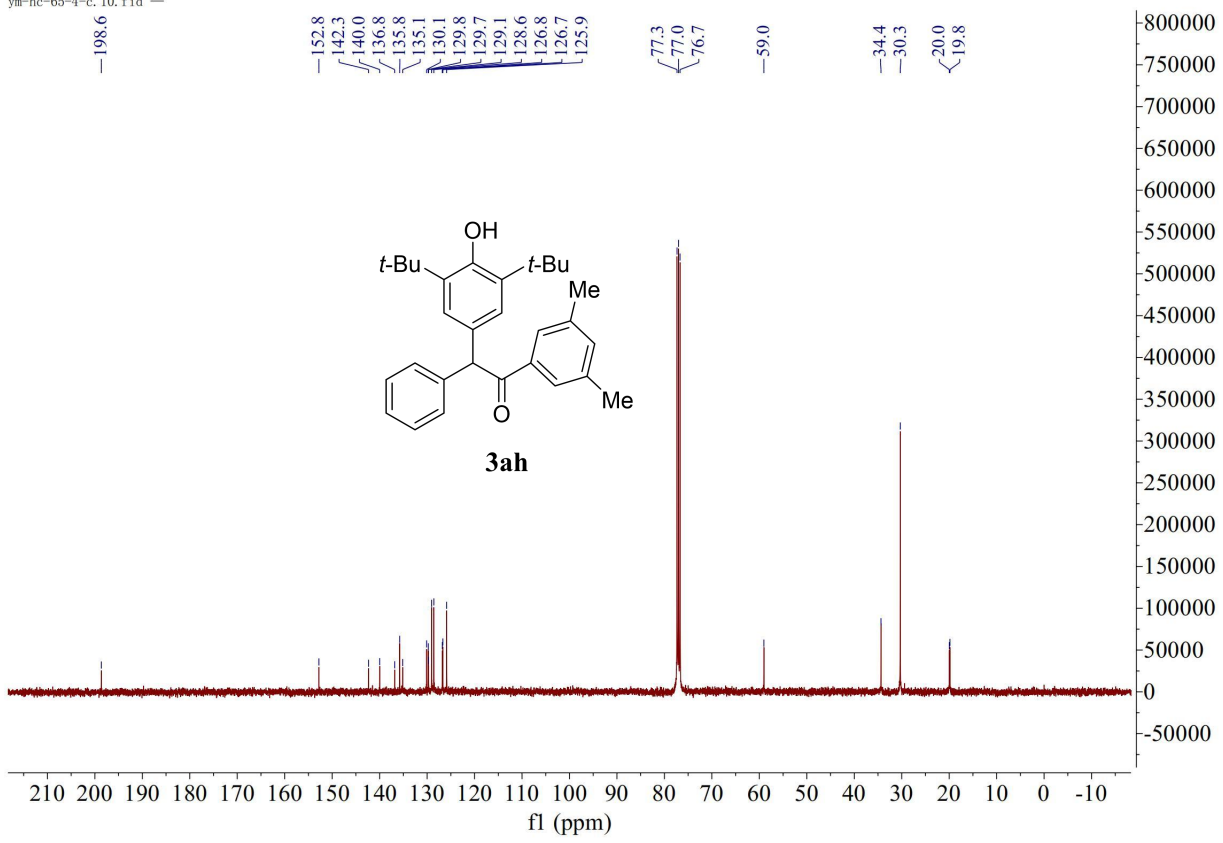


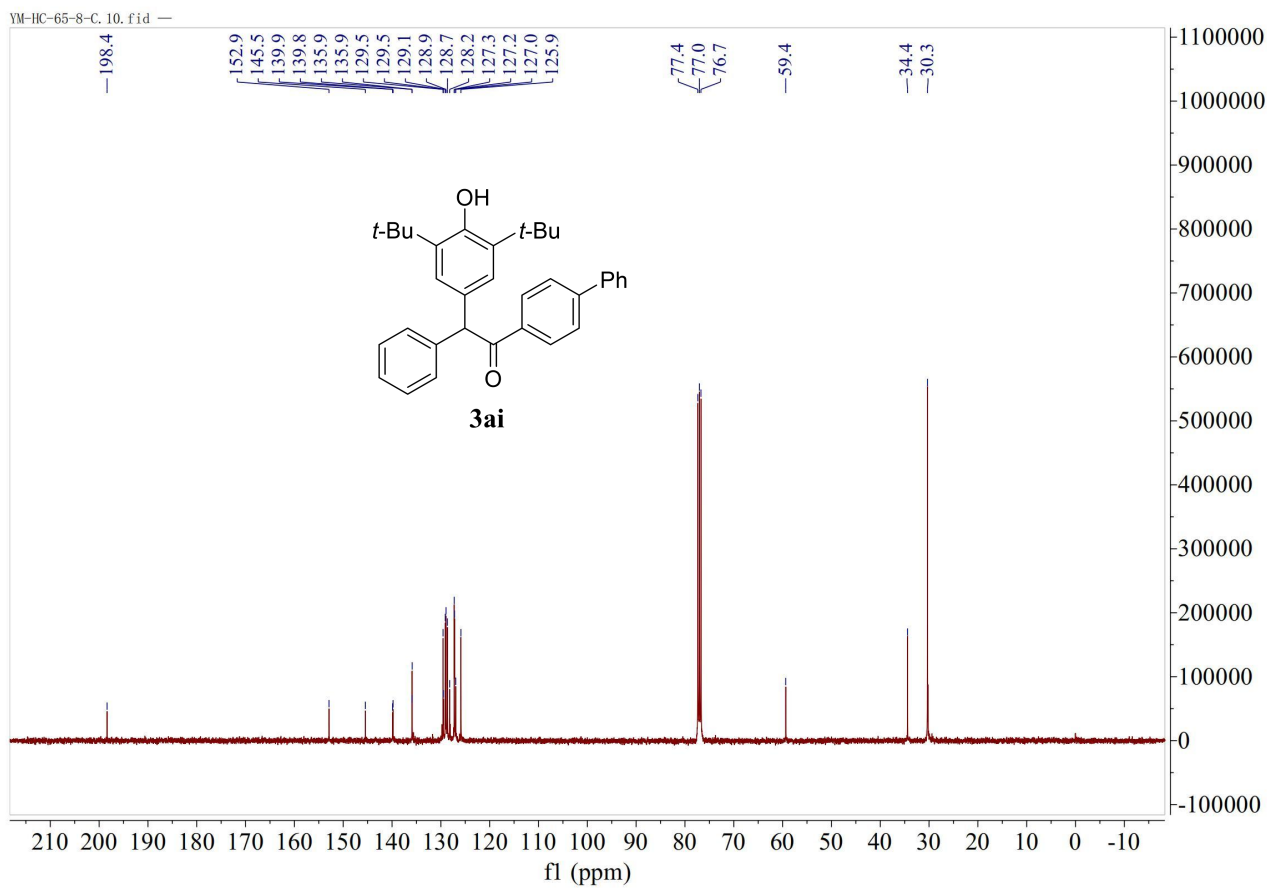
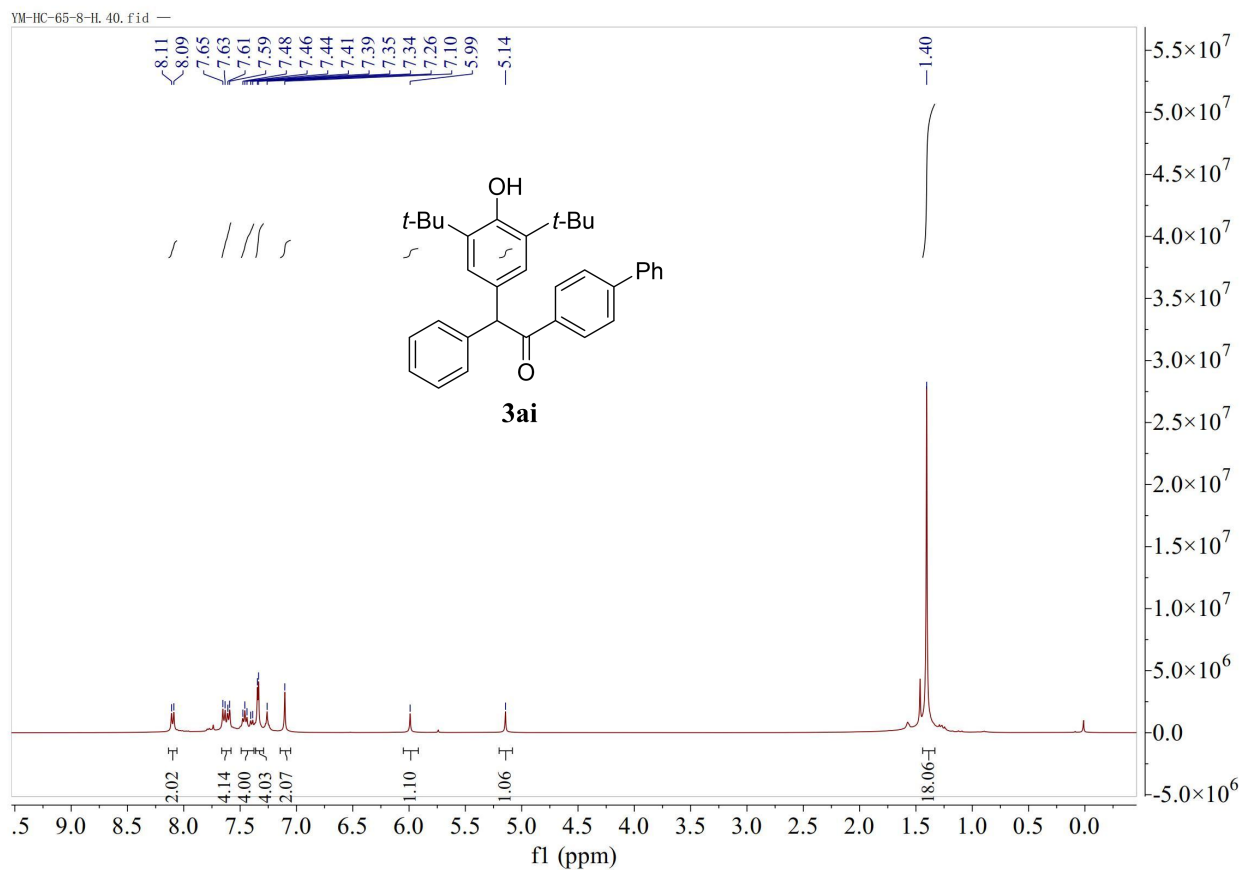


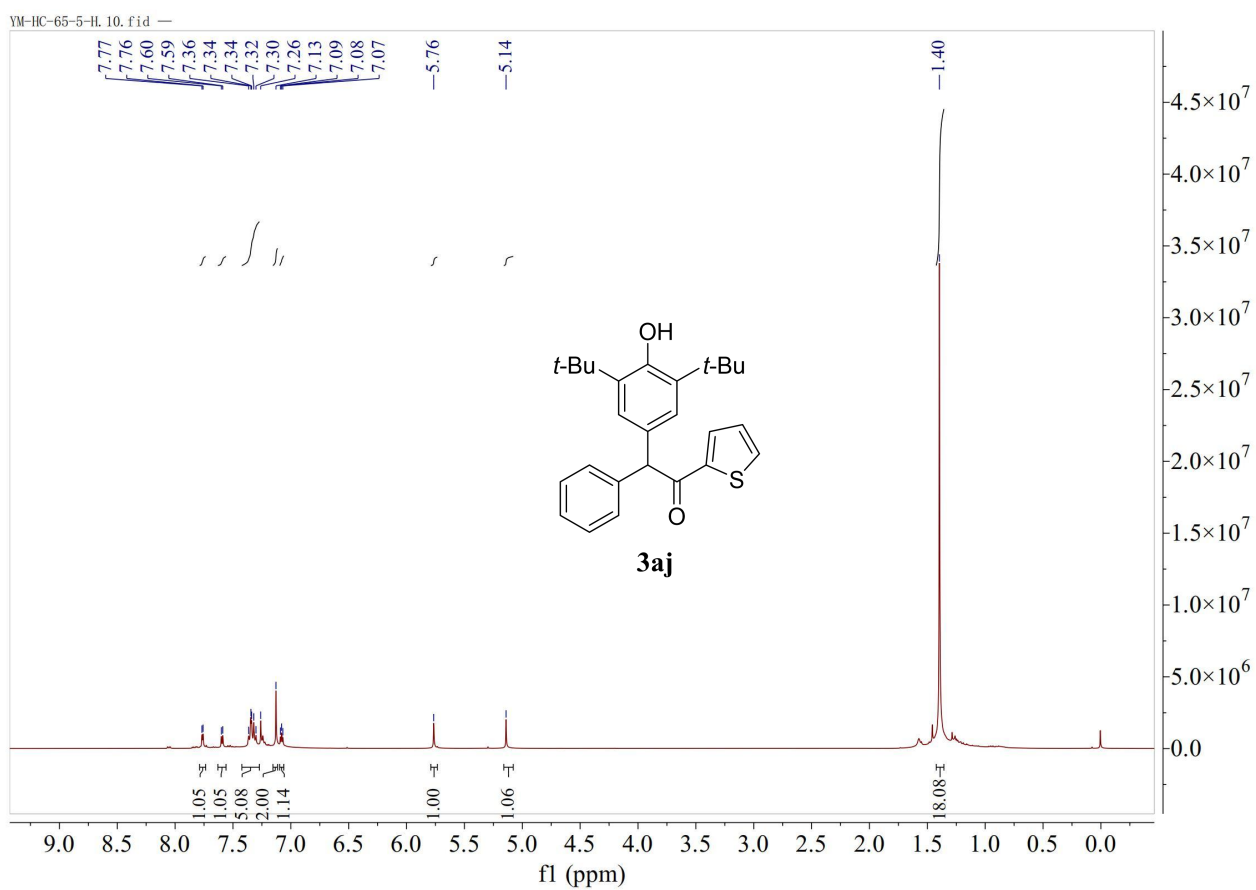
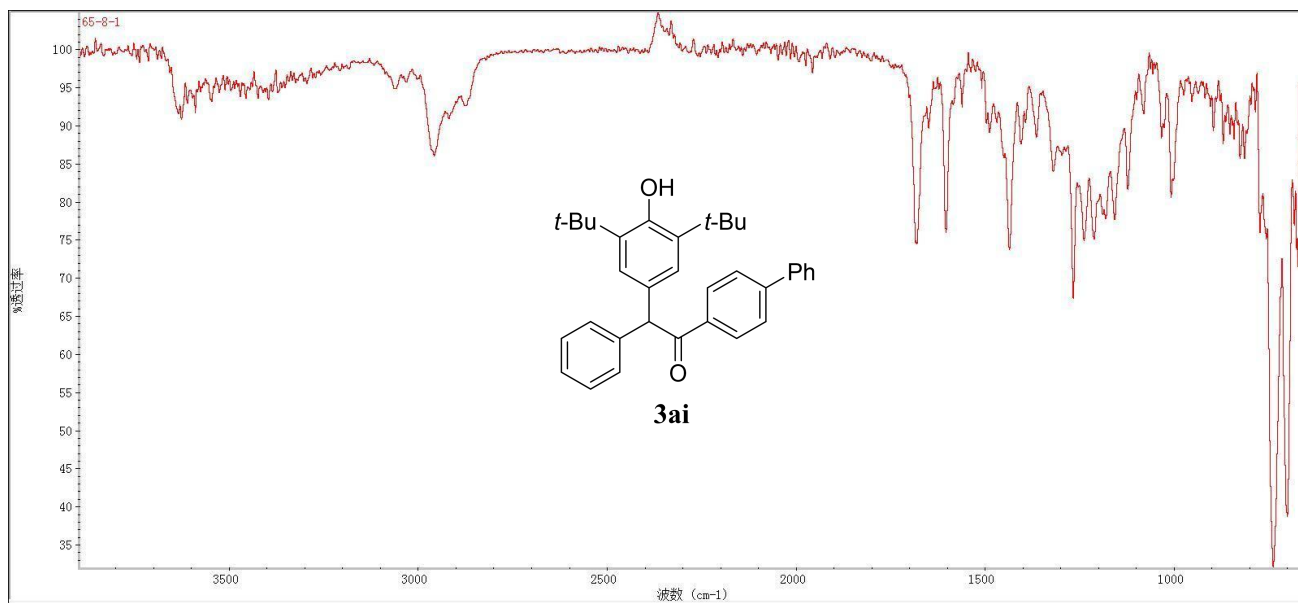
YM-HC-65-4-H. 10. fid -



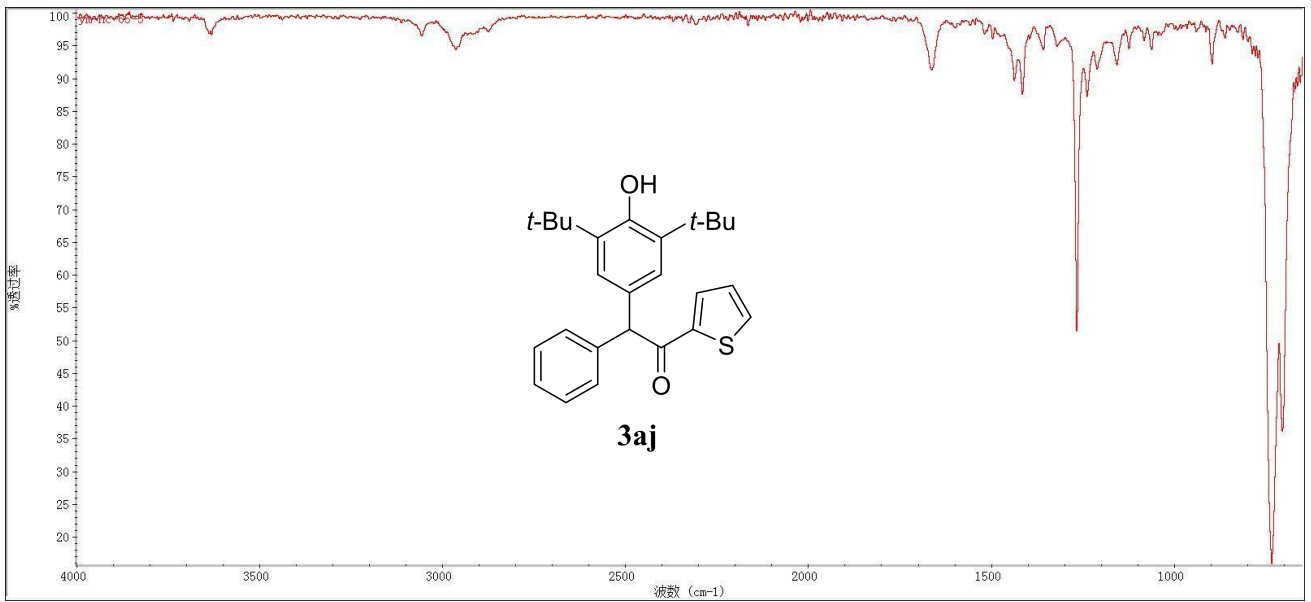
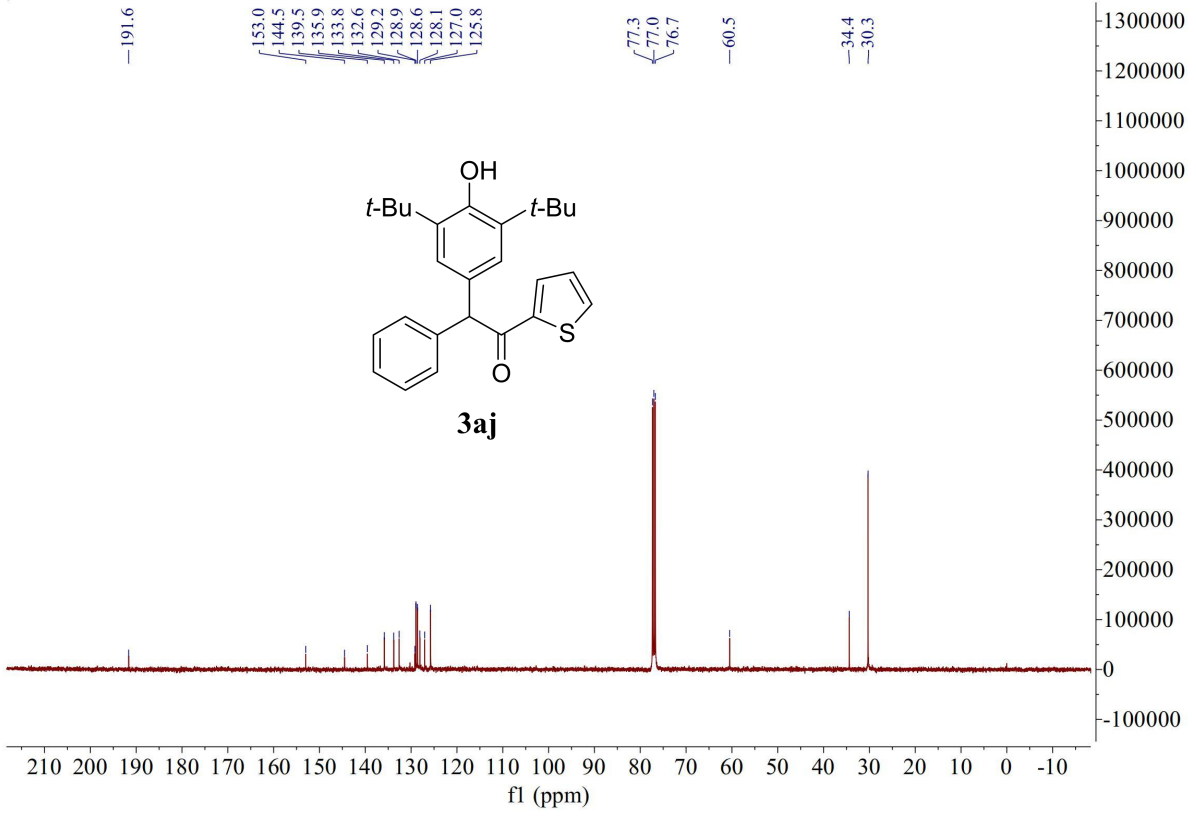
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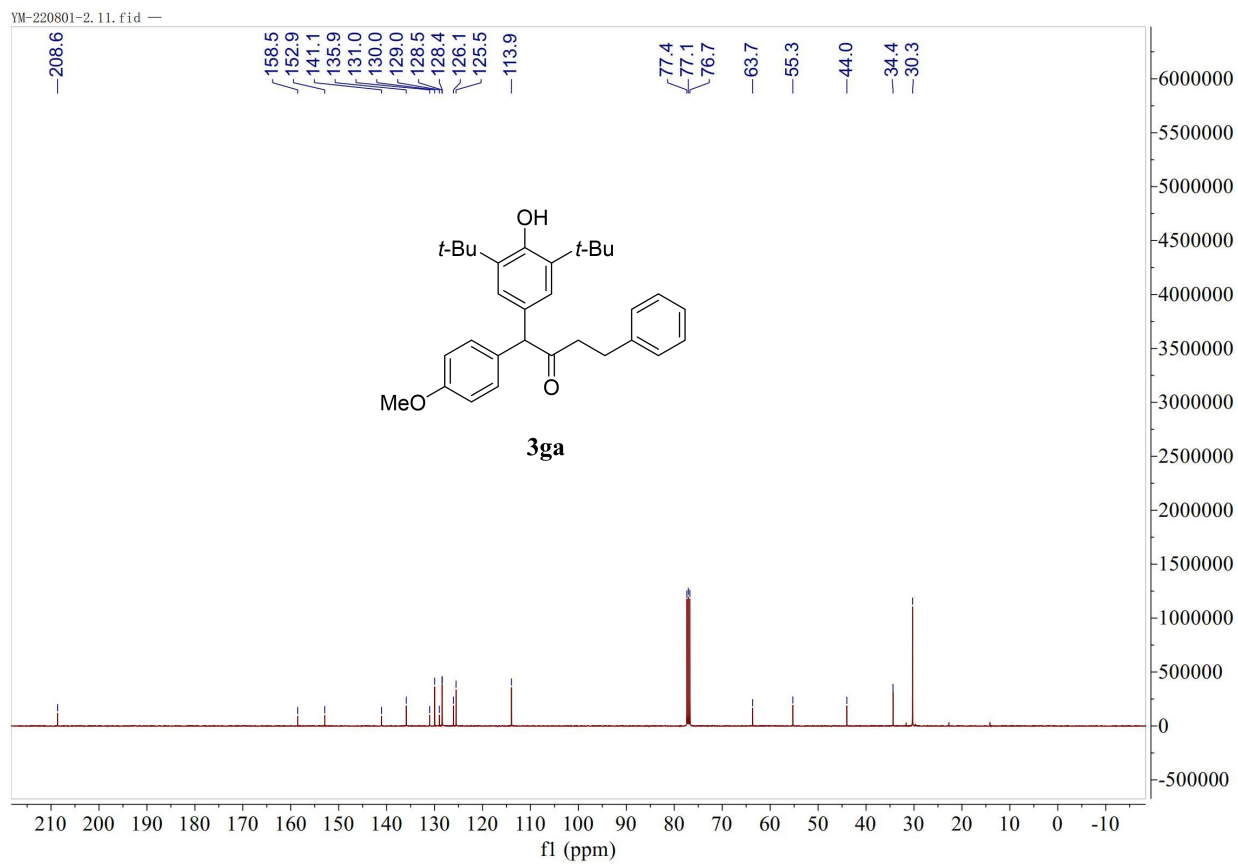
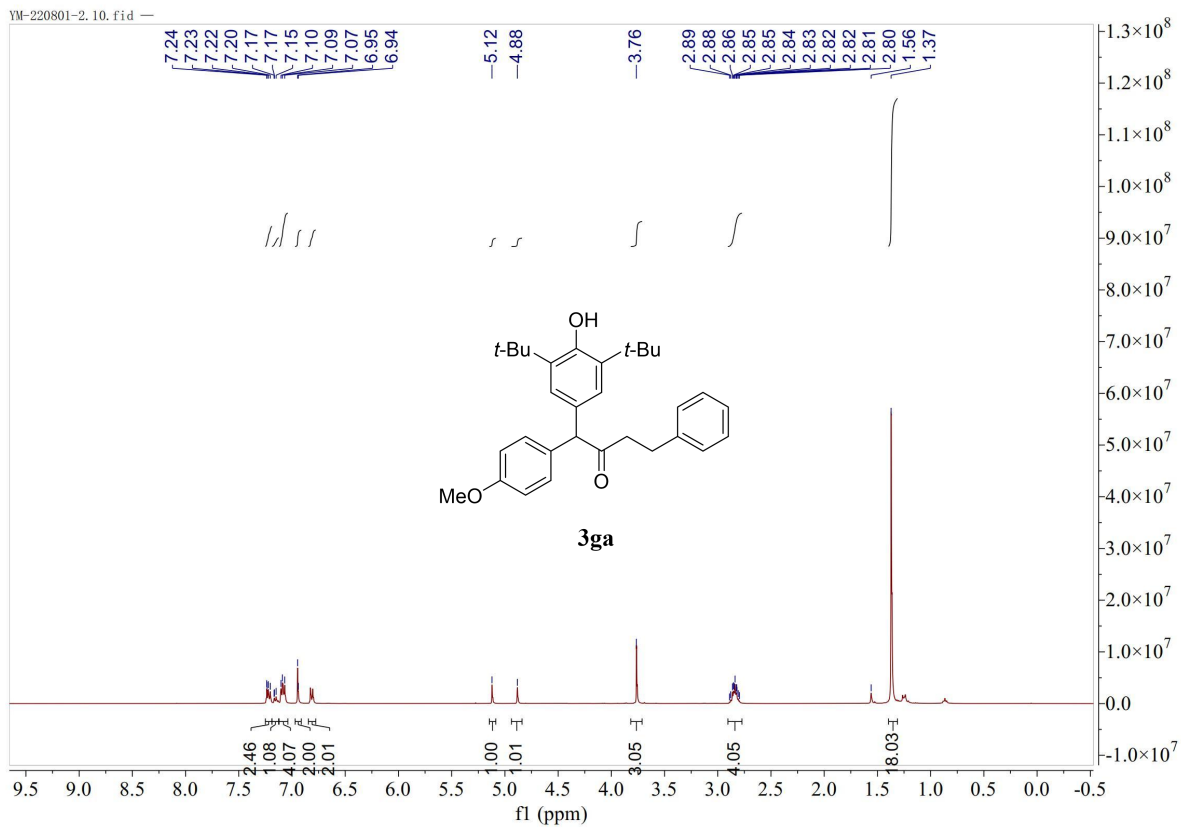


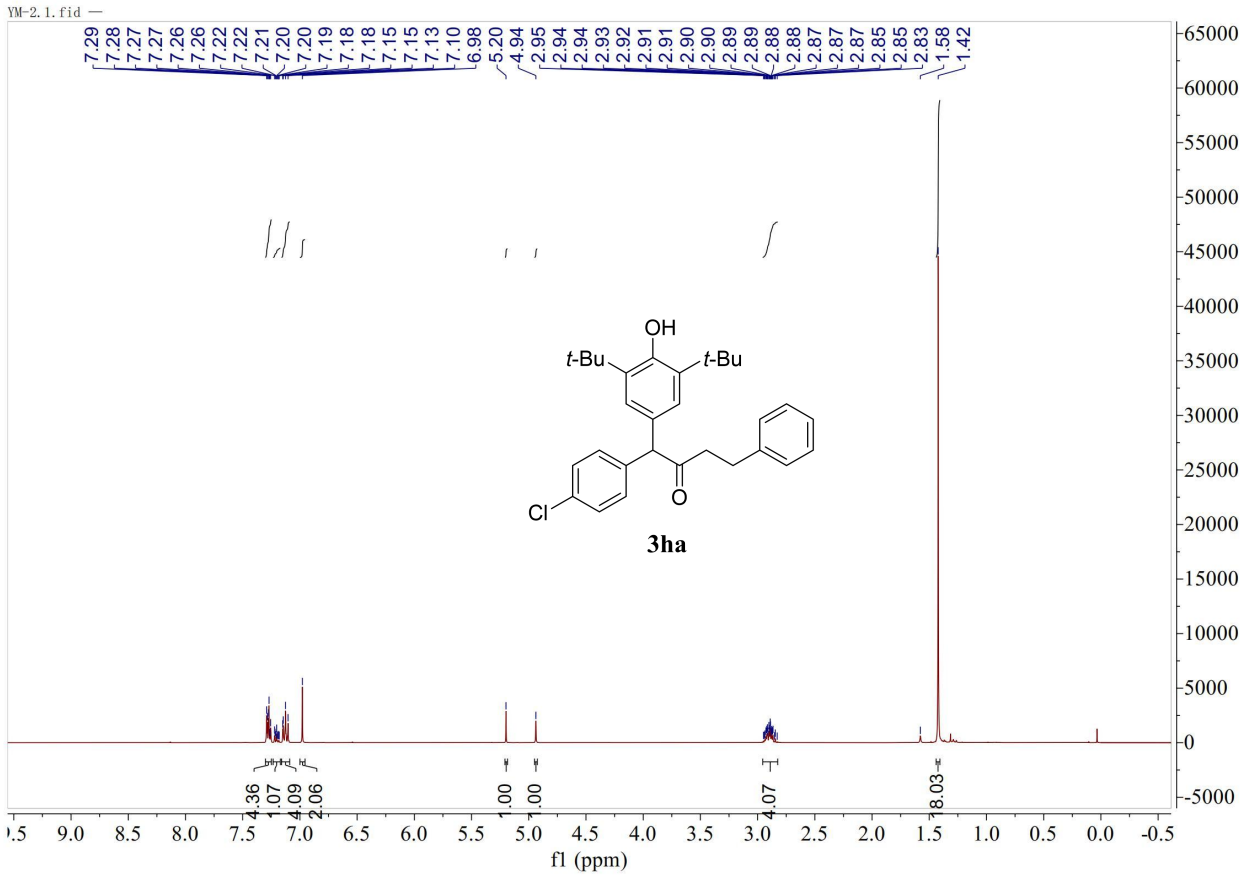
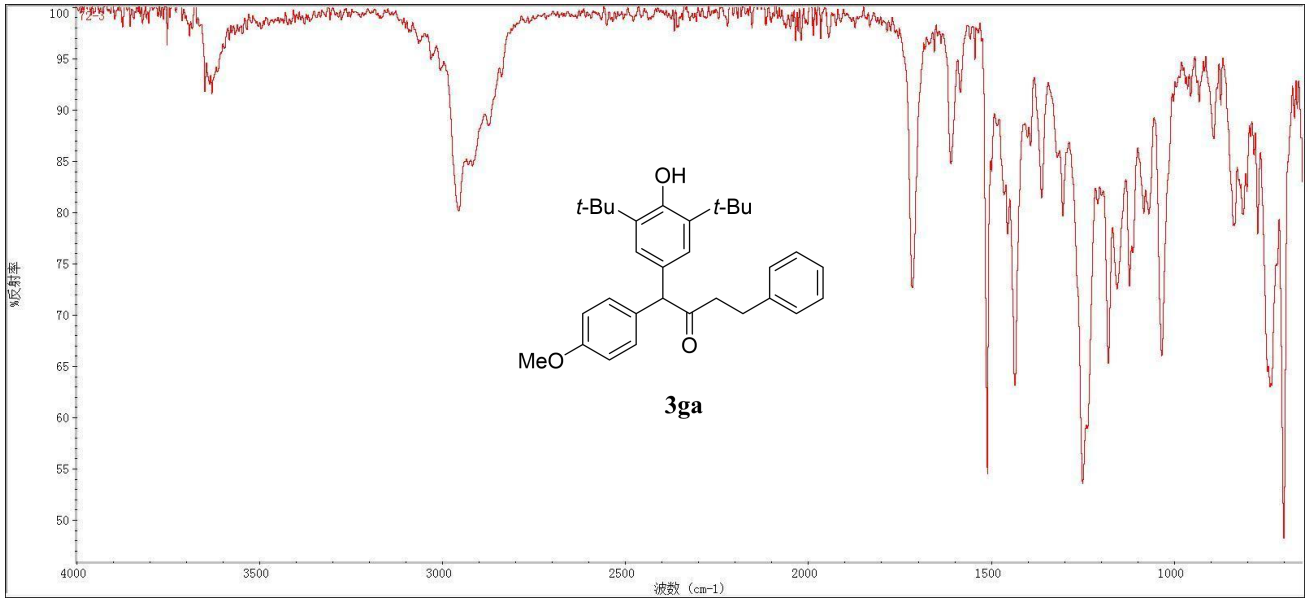




ym-hc-65-5-c. 10. fid

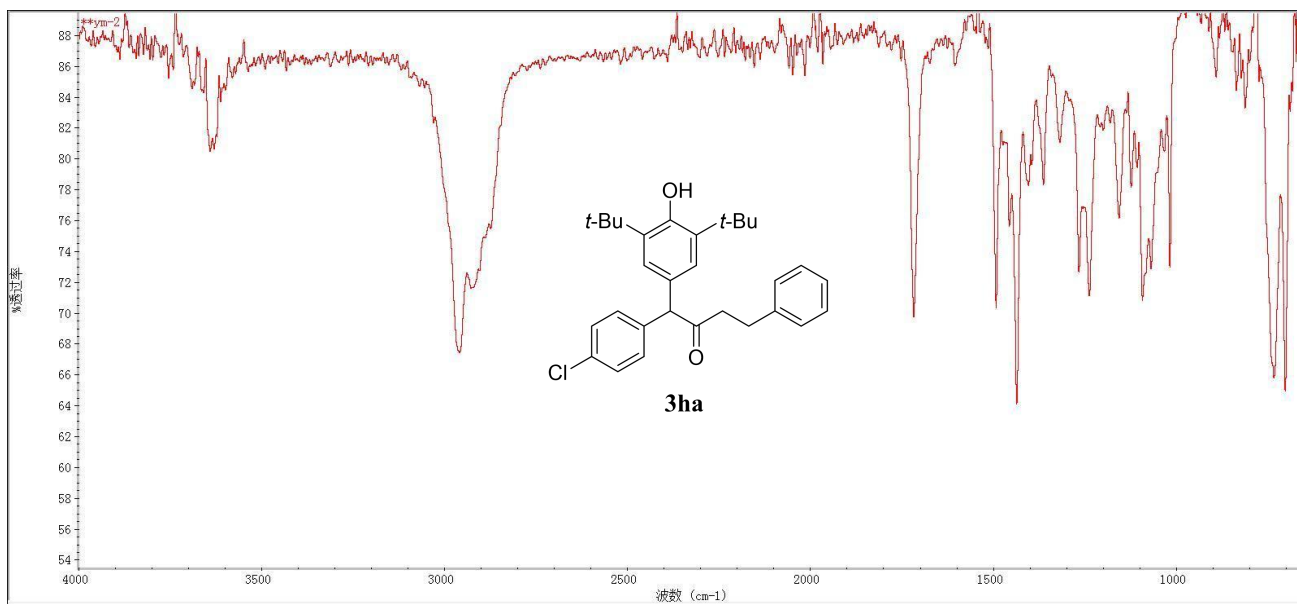
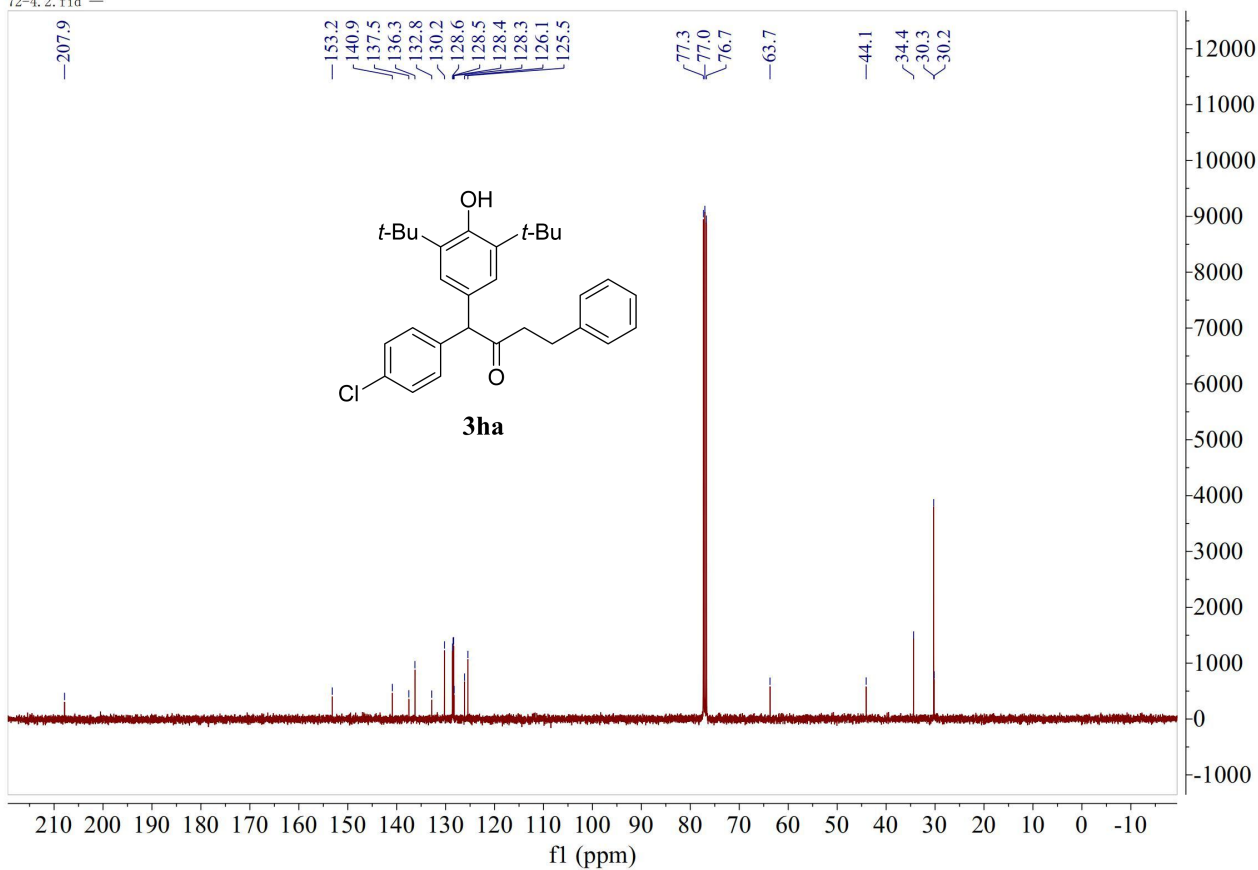


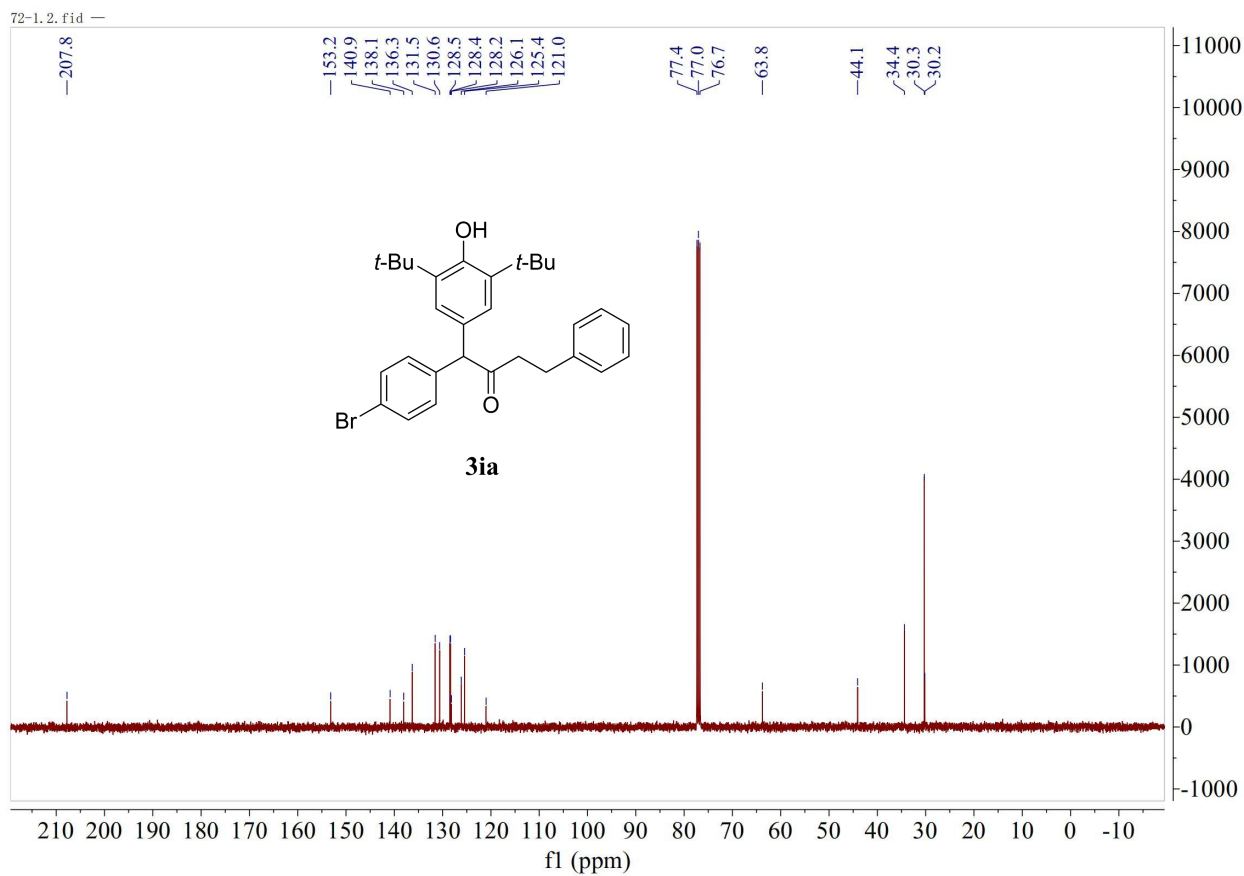
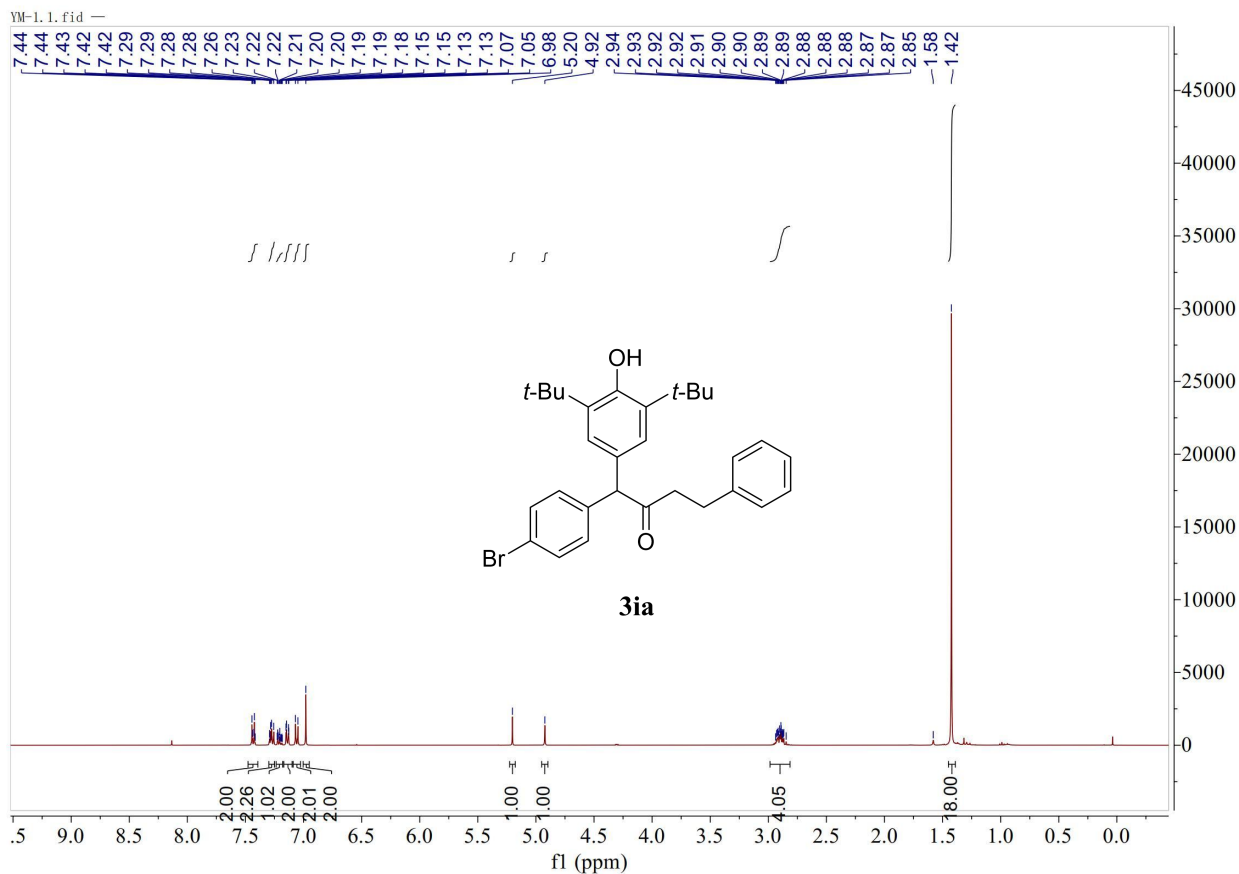


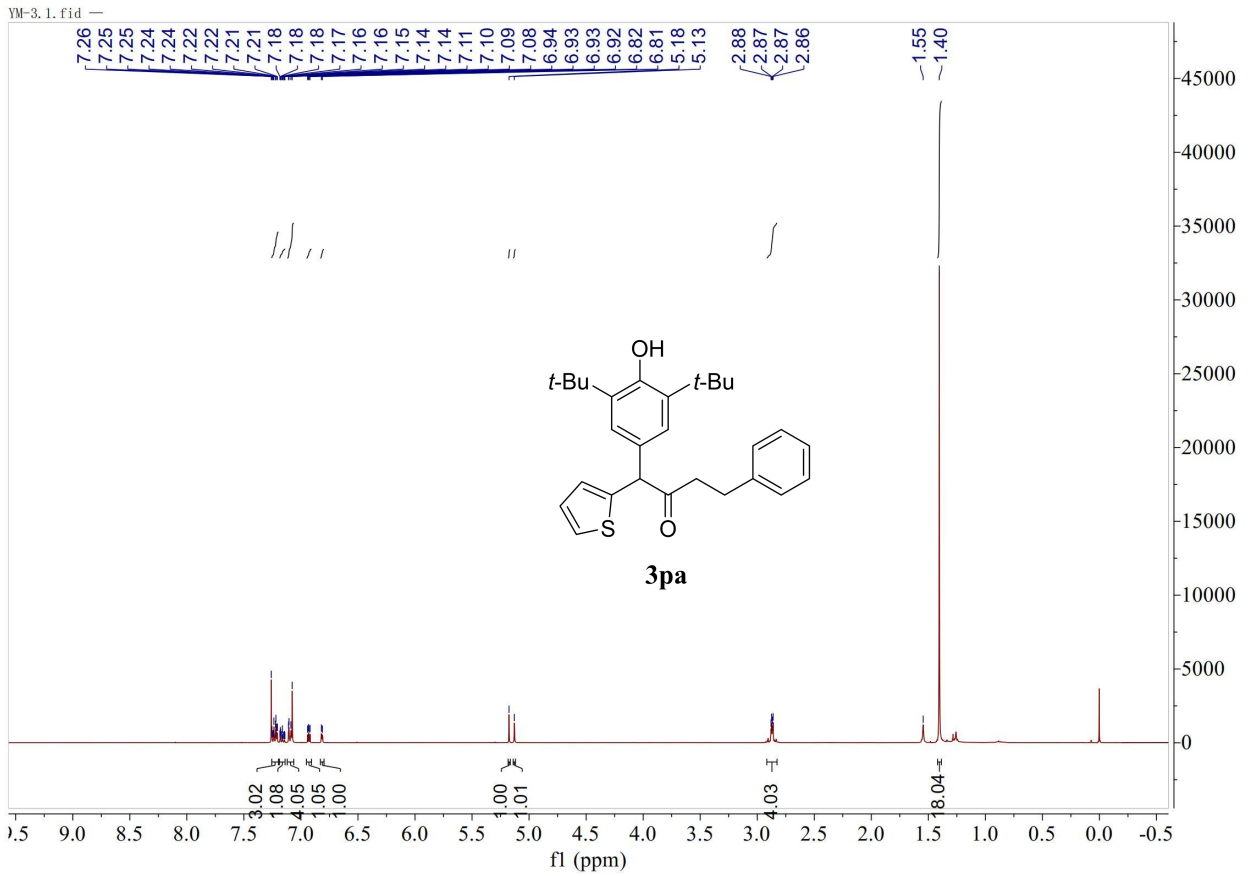
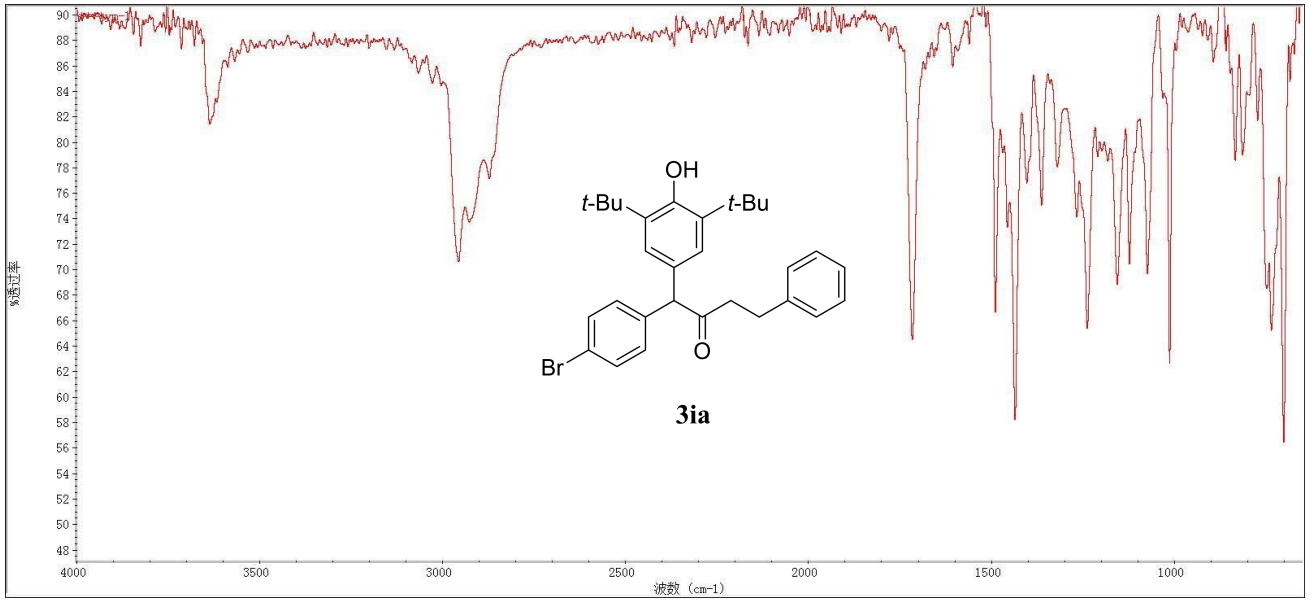




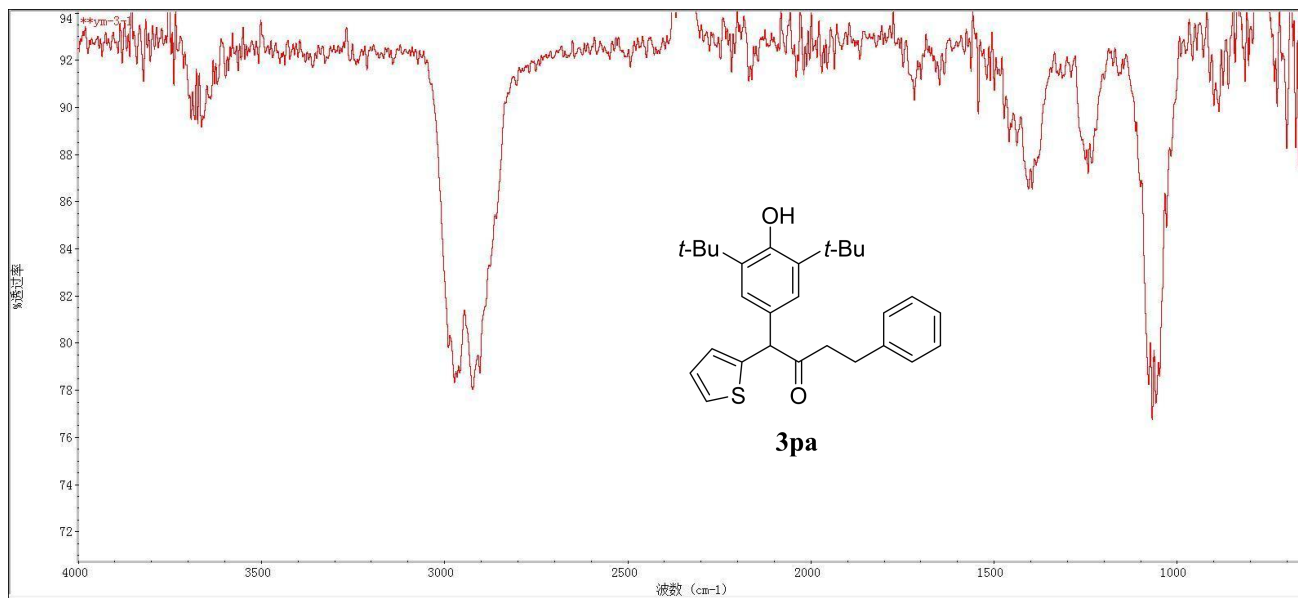
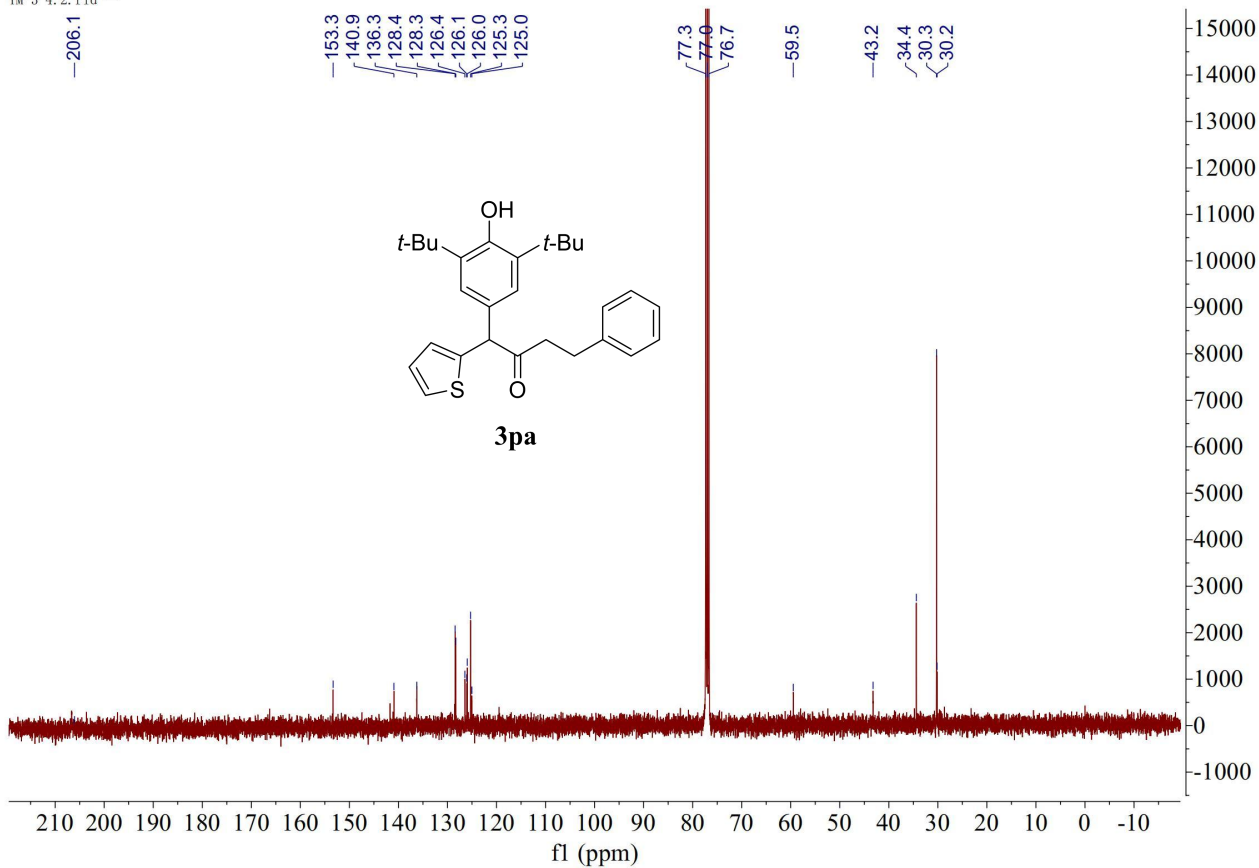
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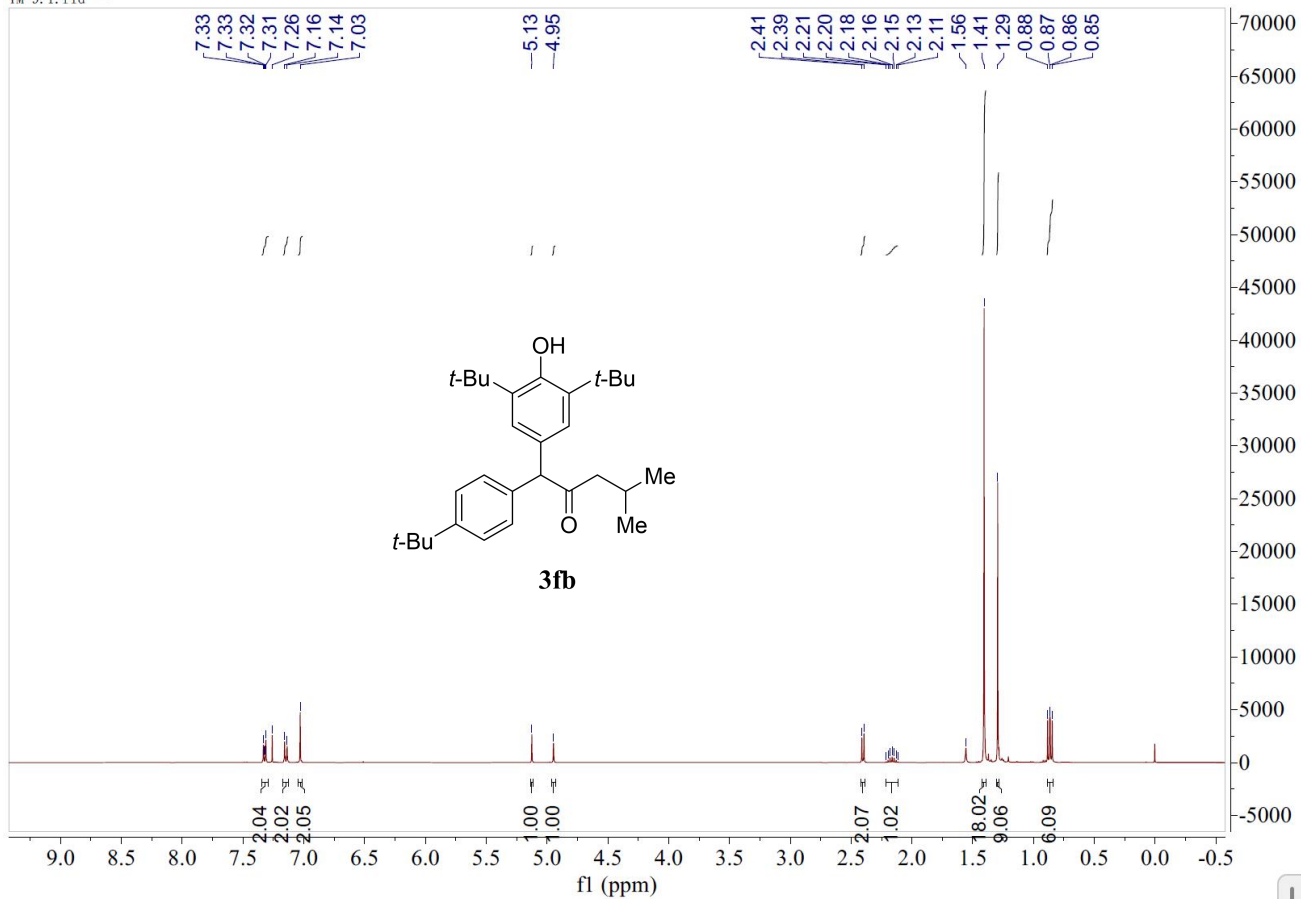




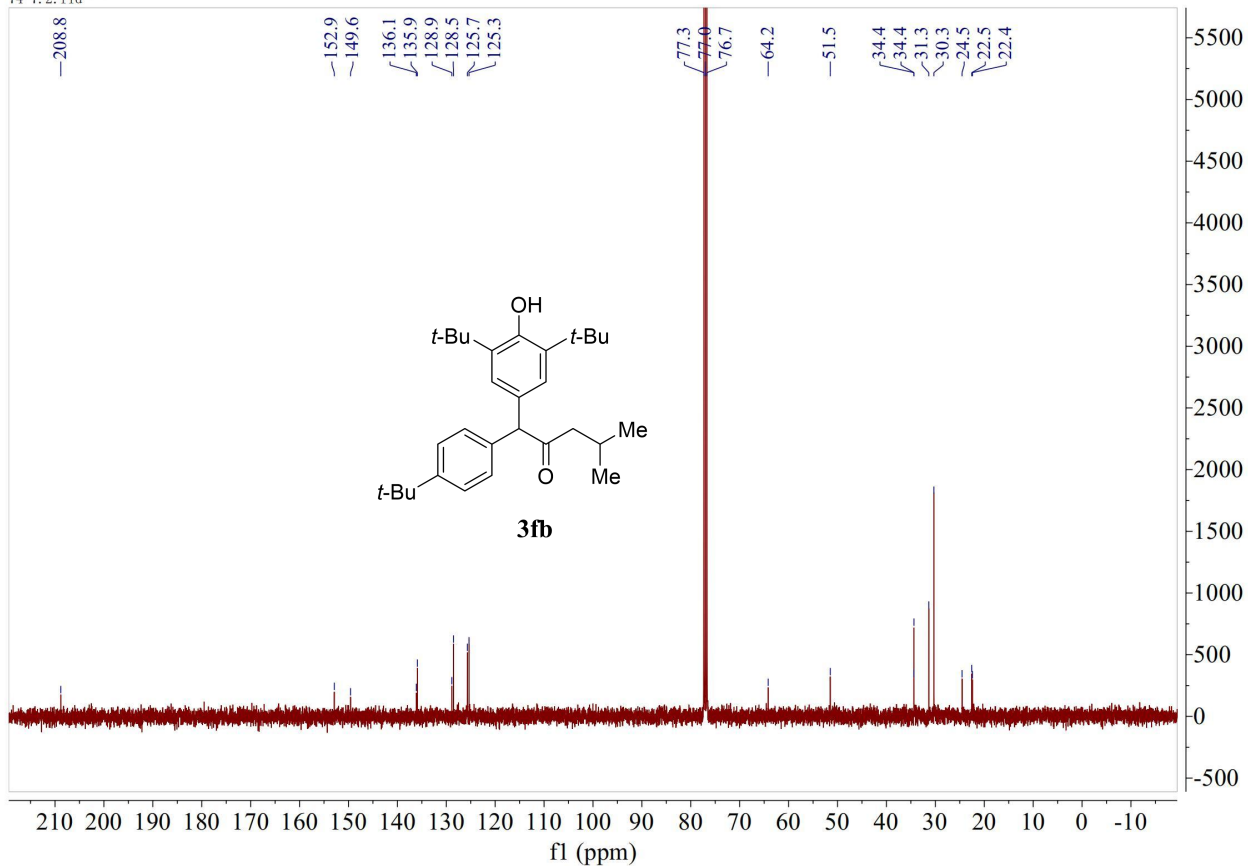
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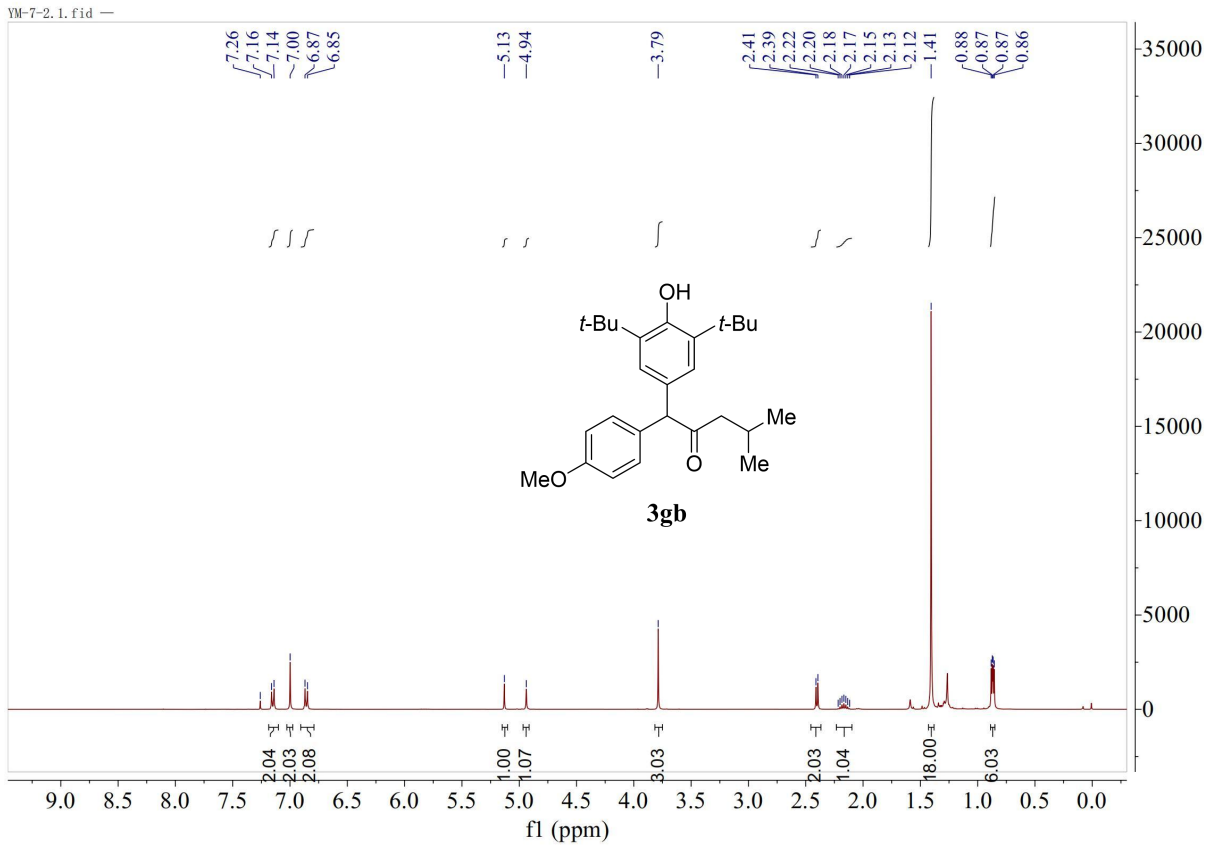
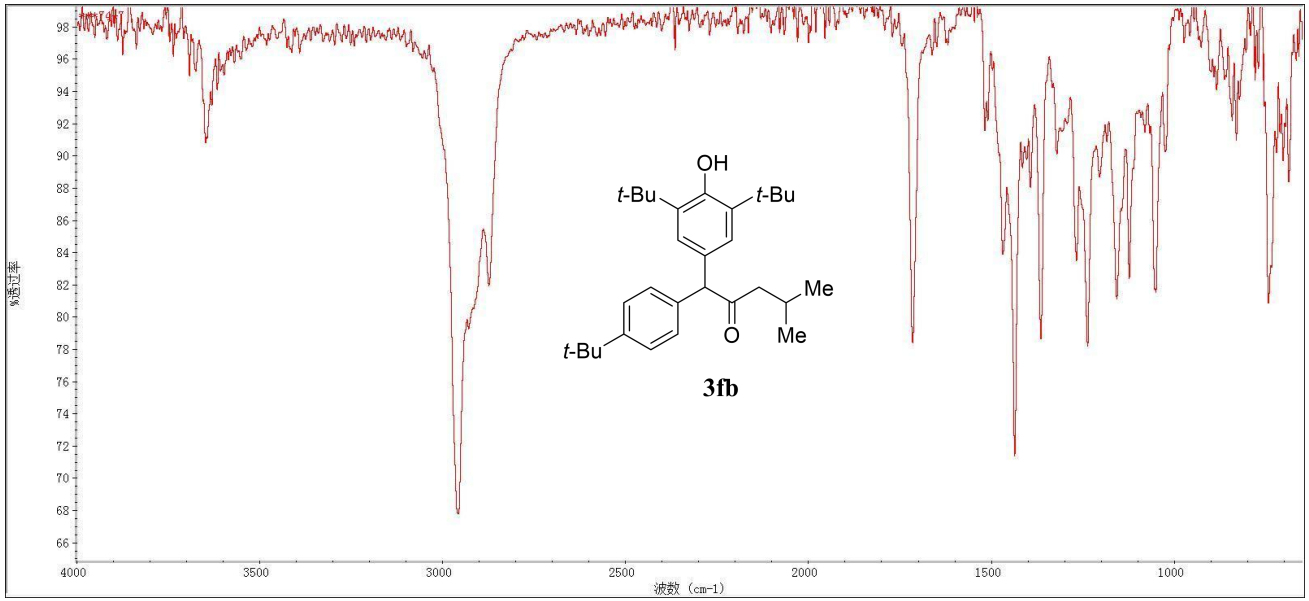


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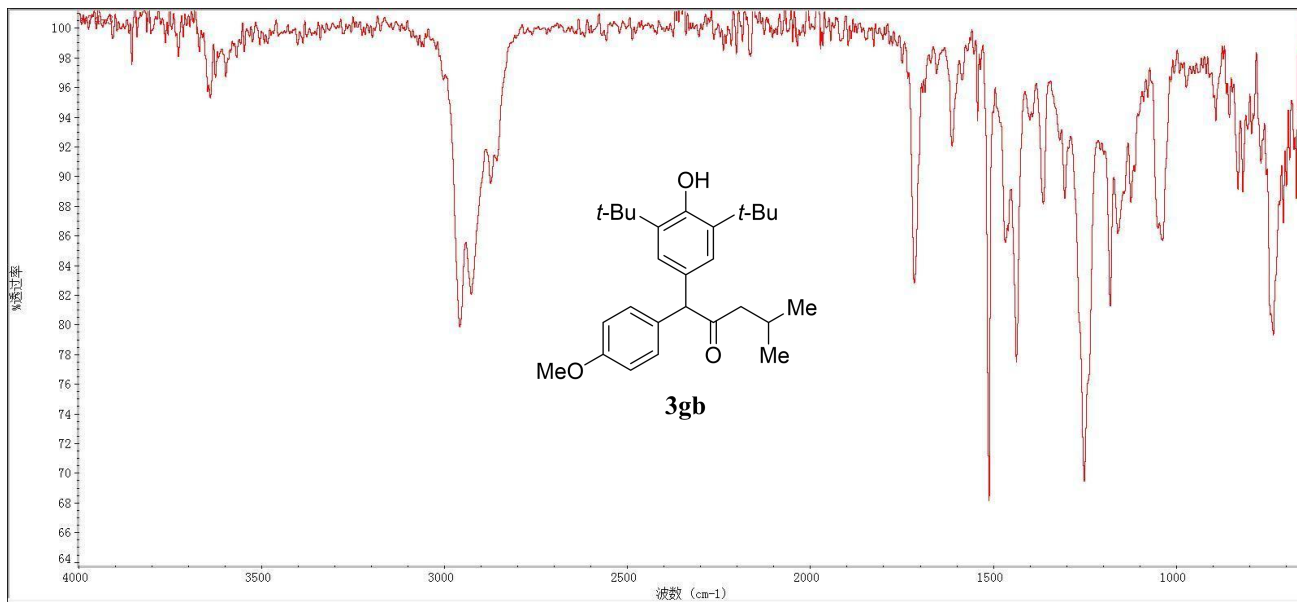
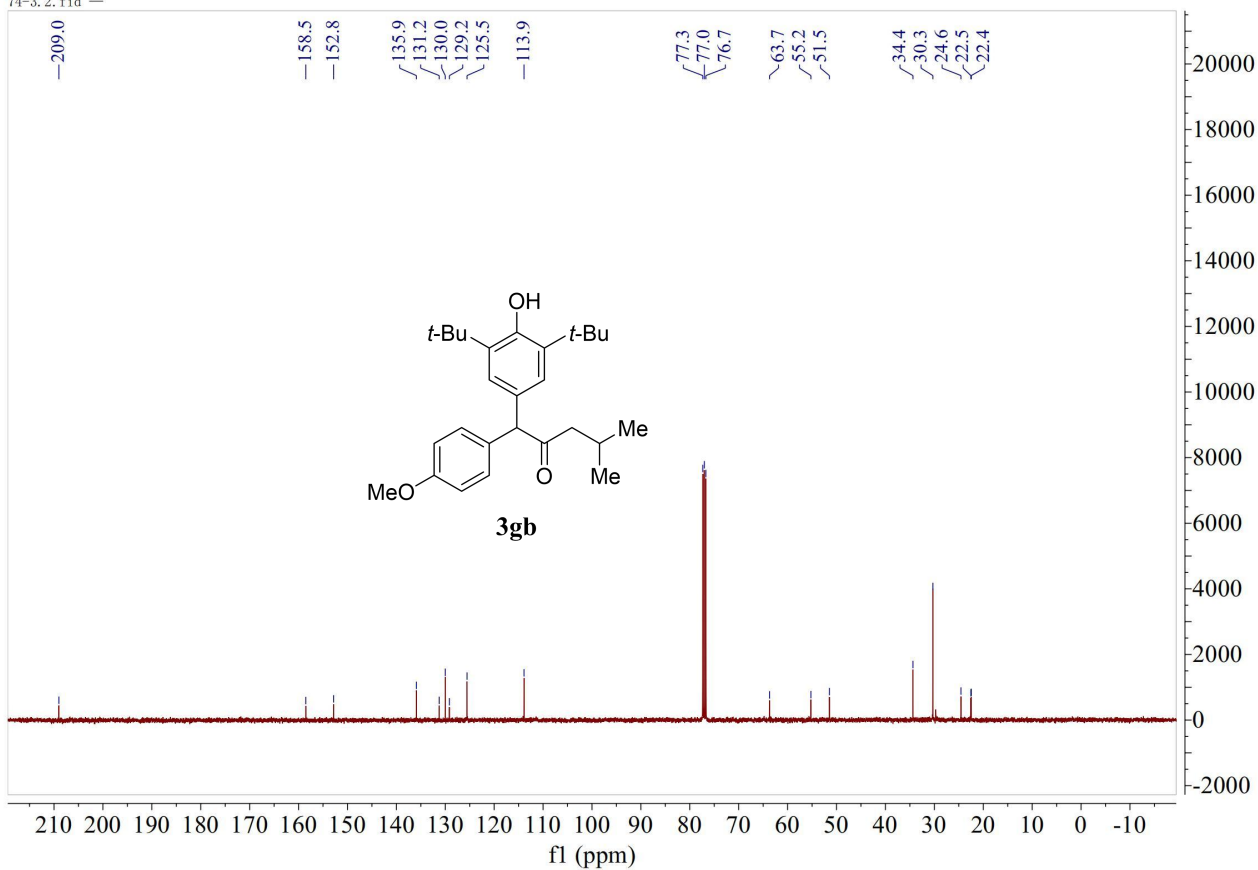


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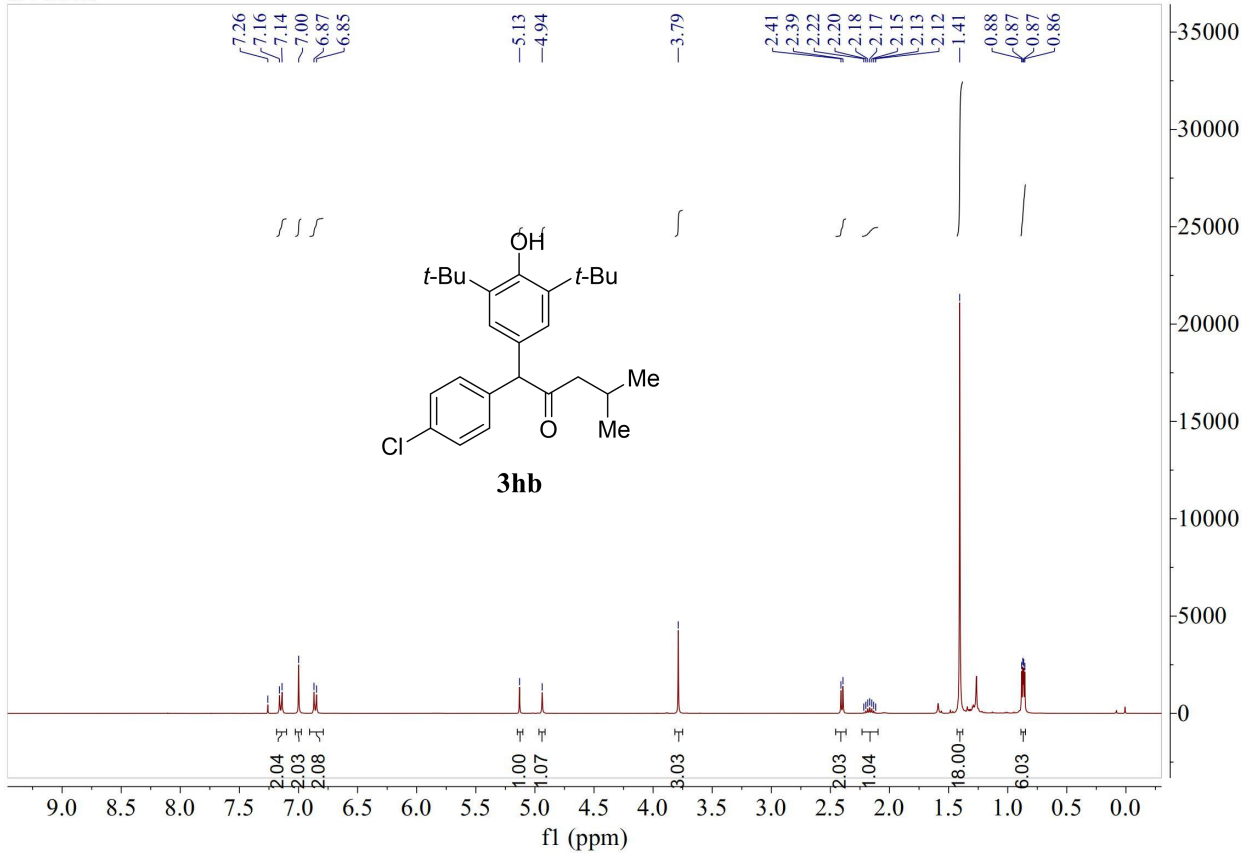




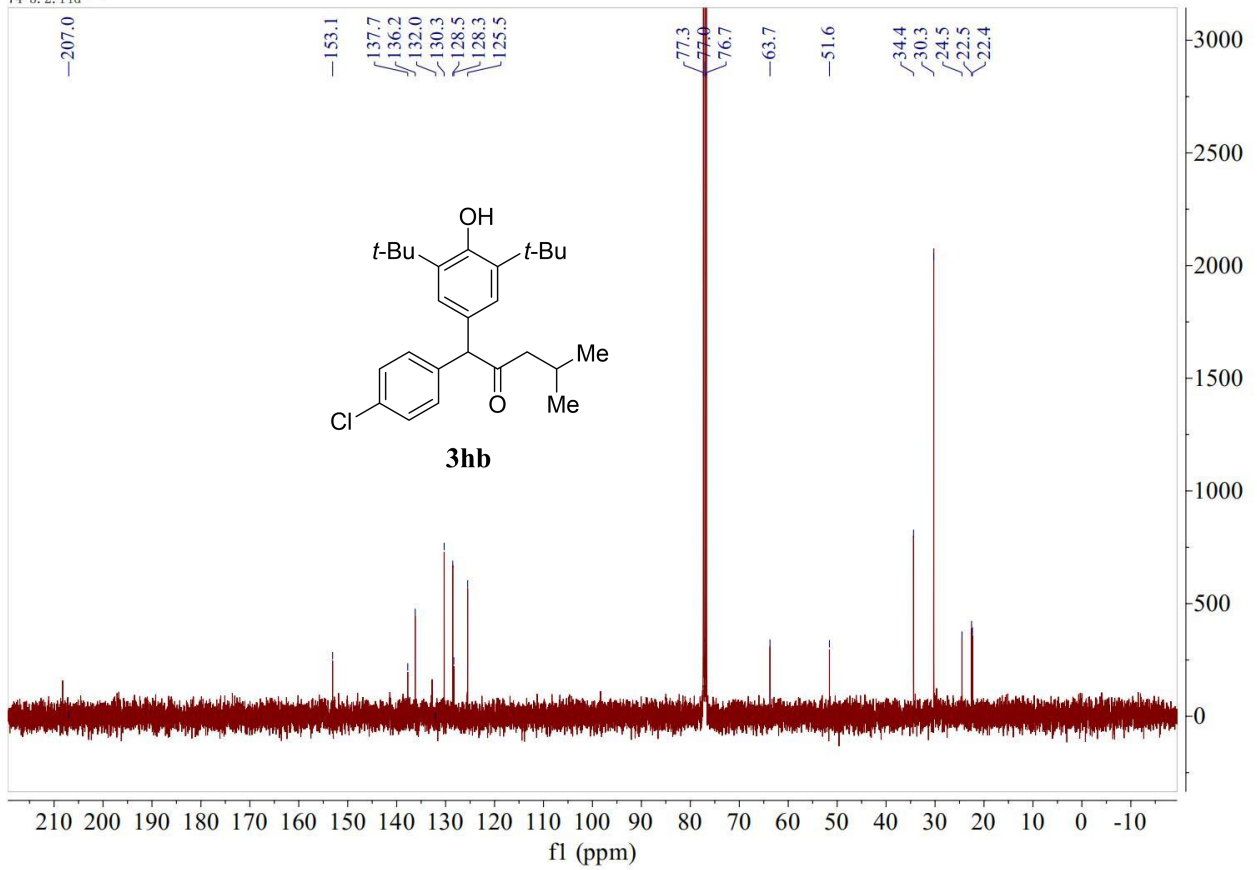
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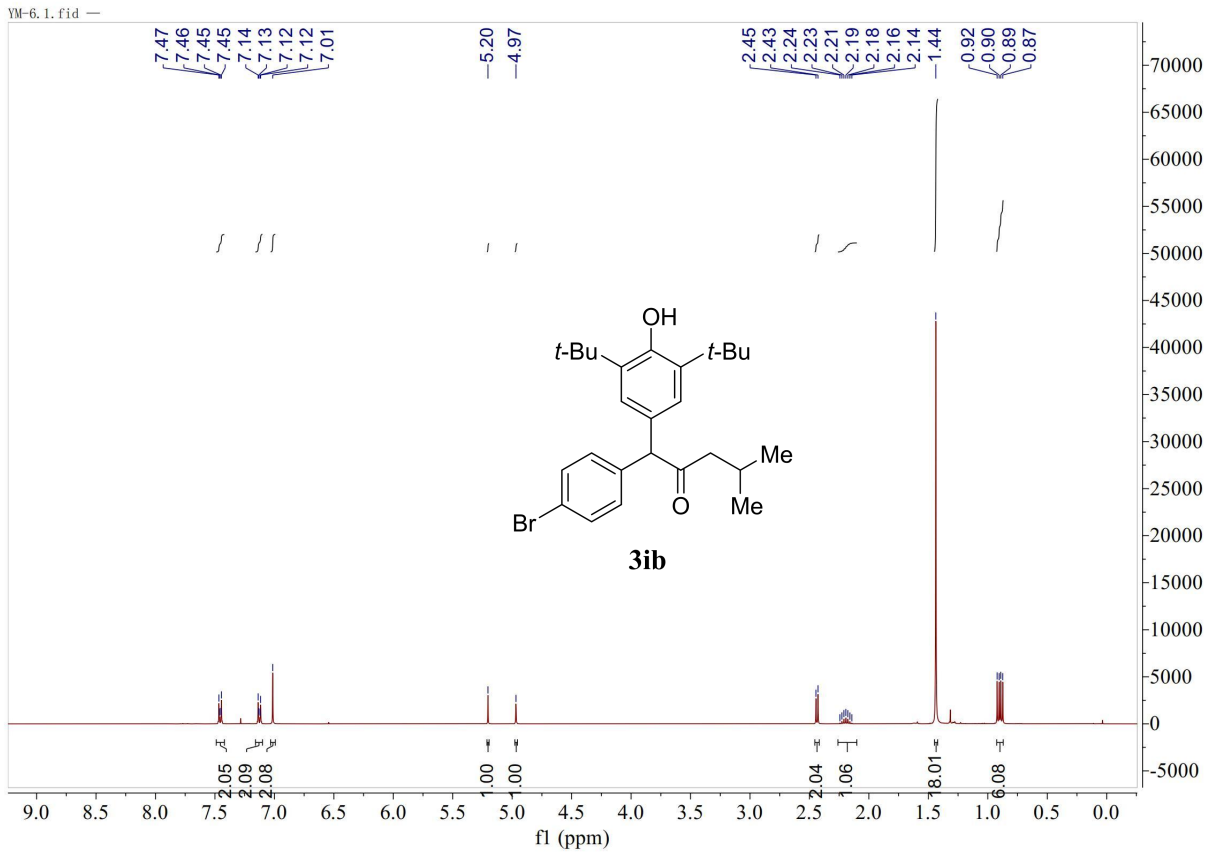
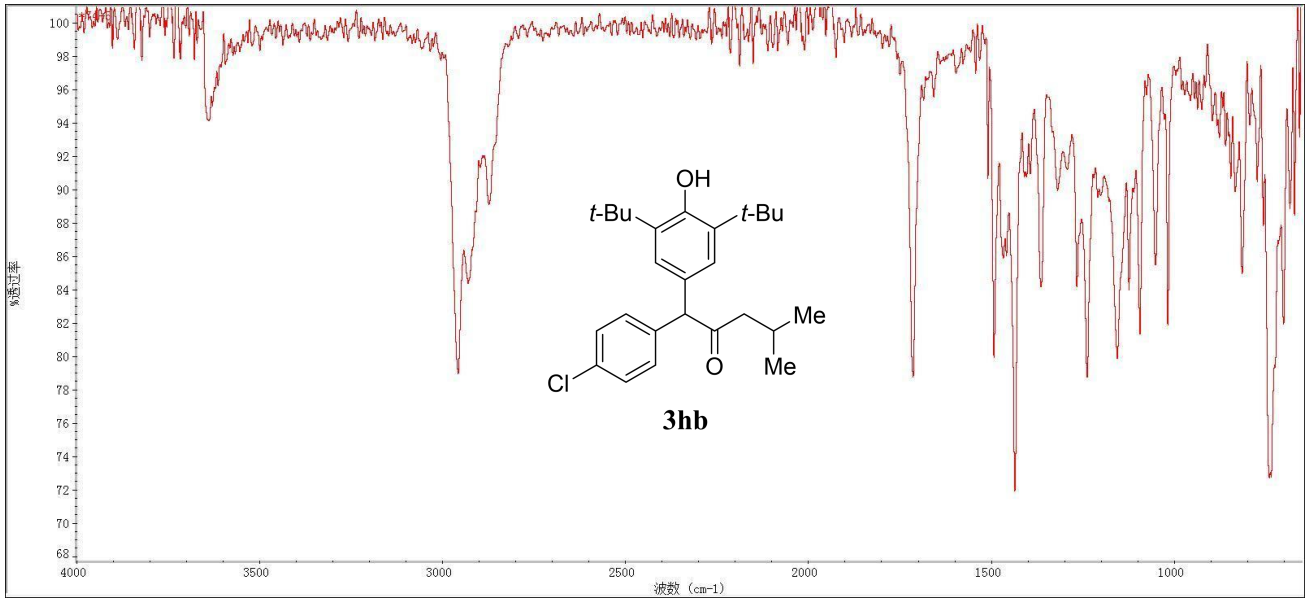
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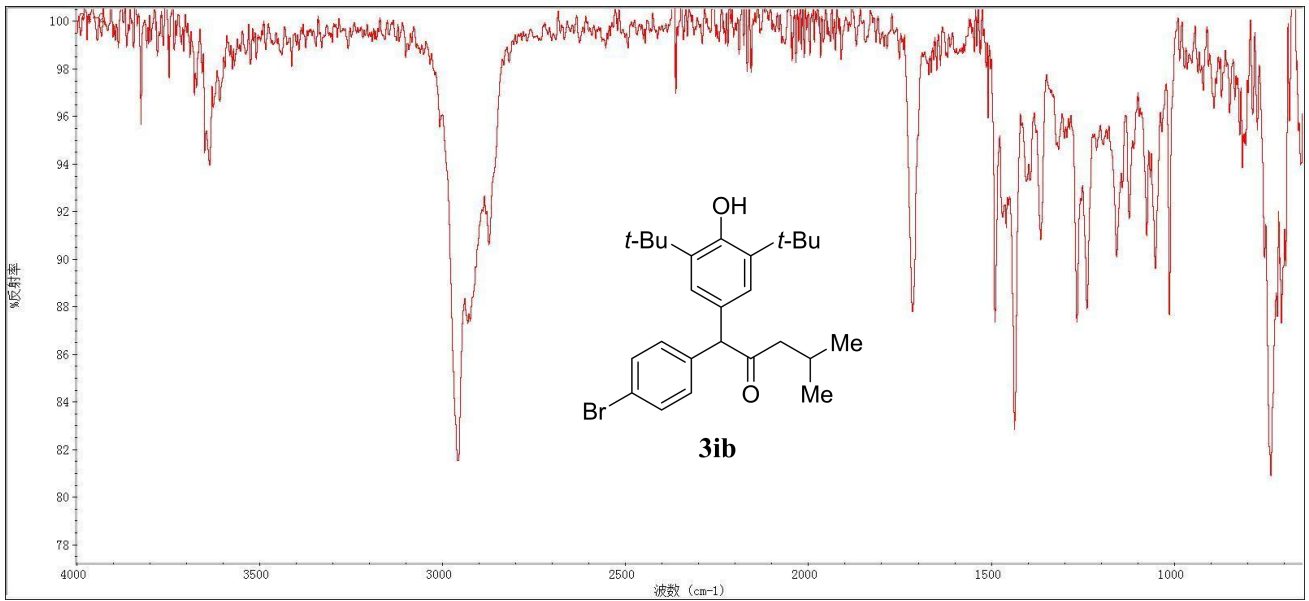
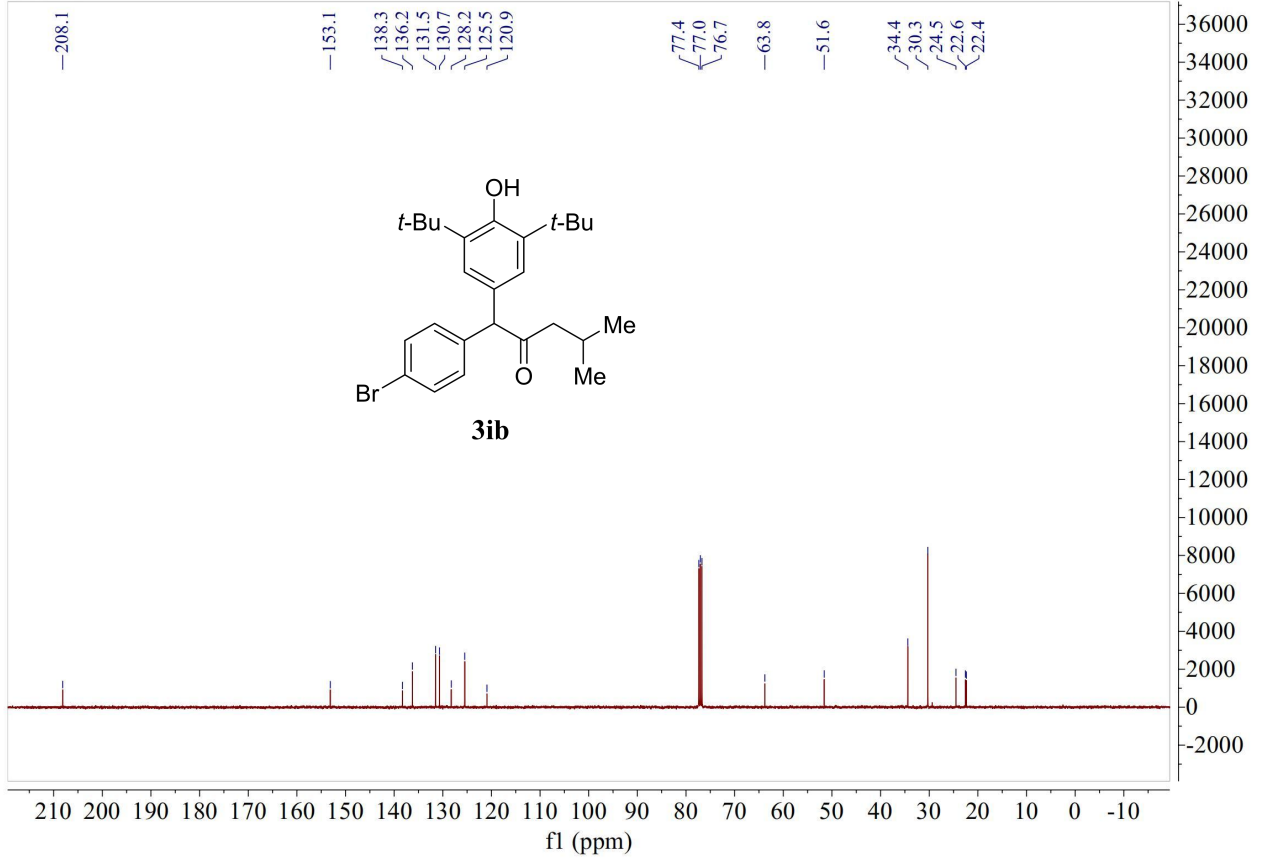
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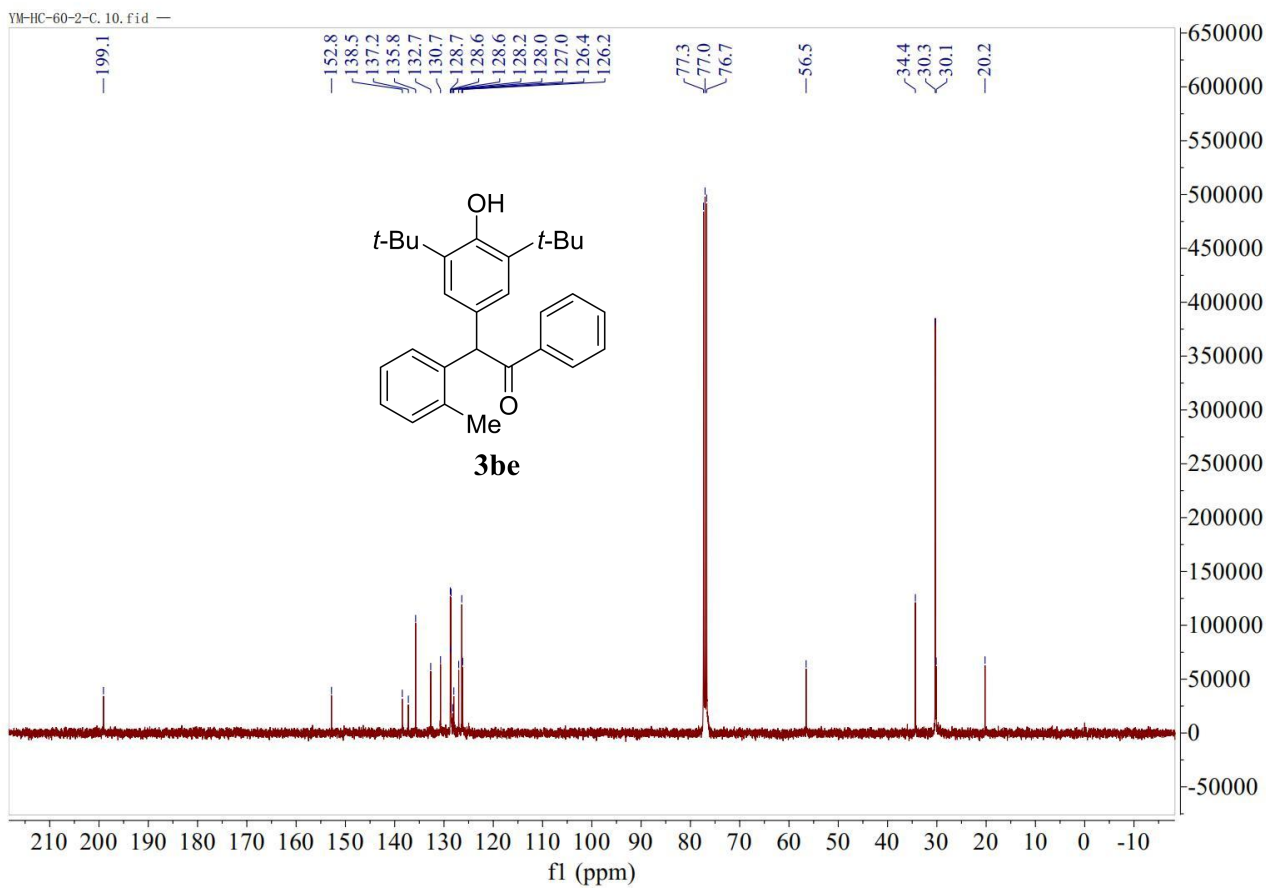
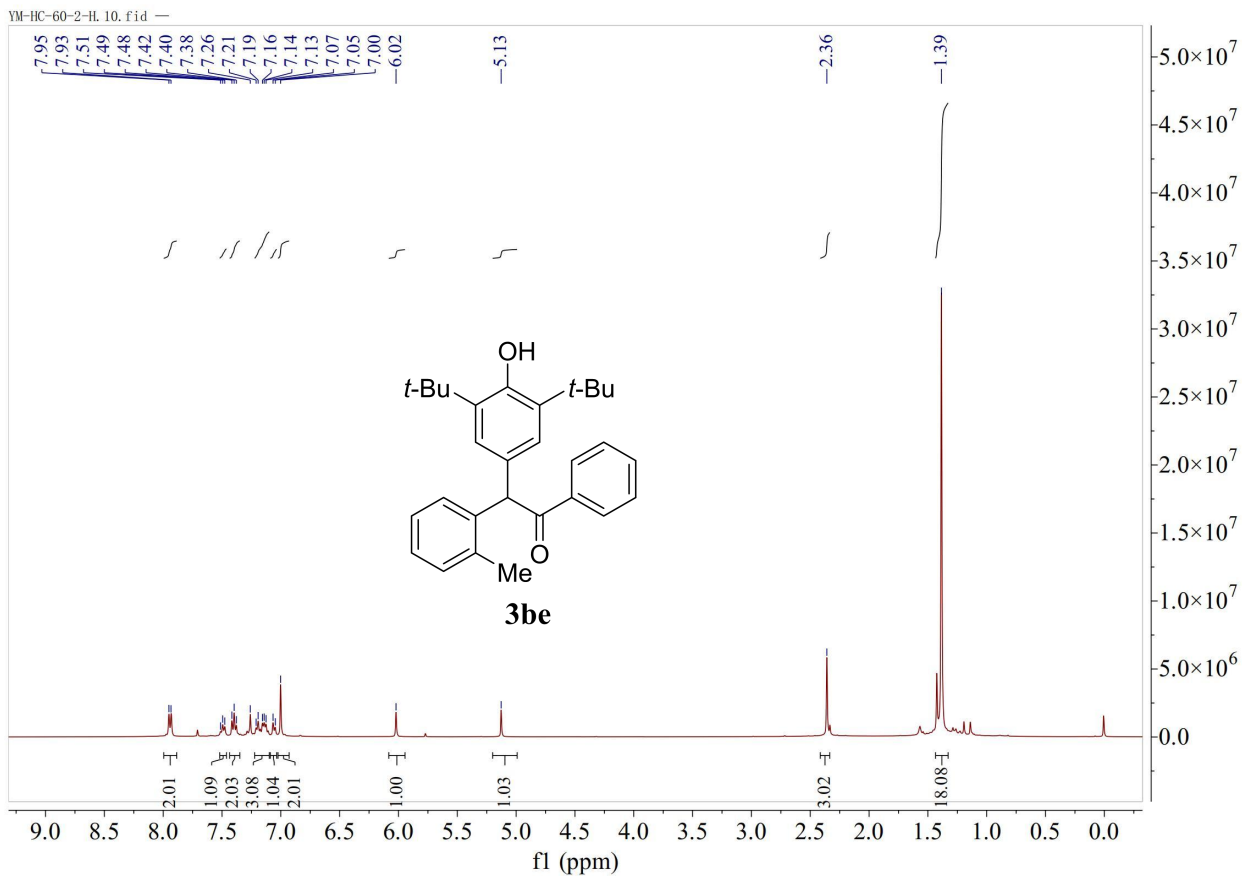


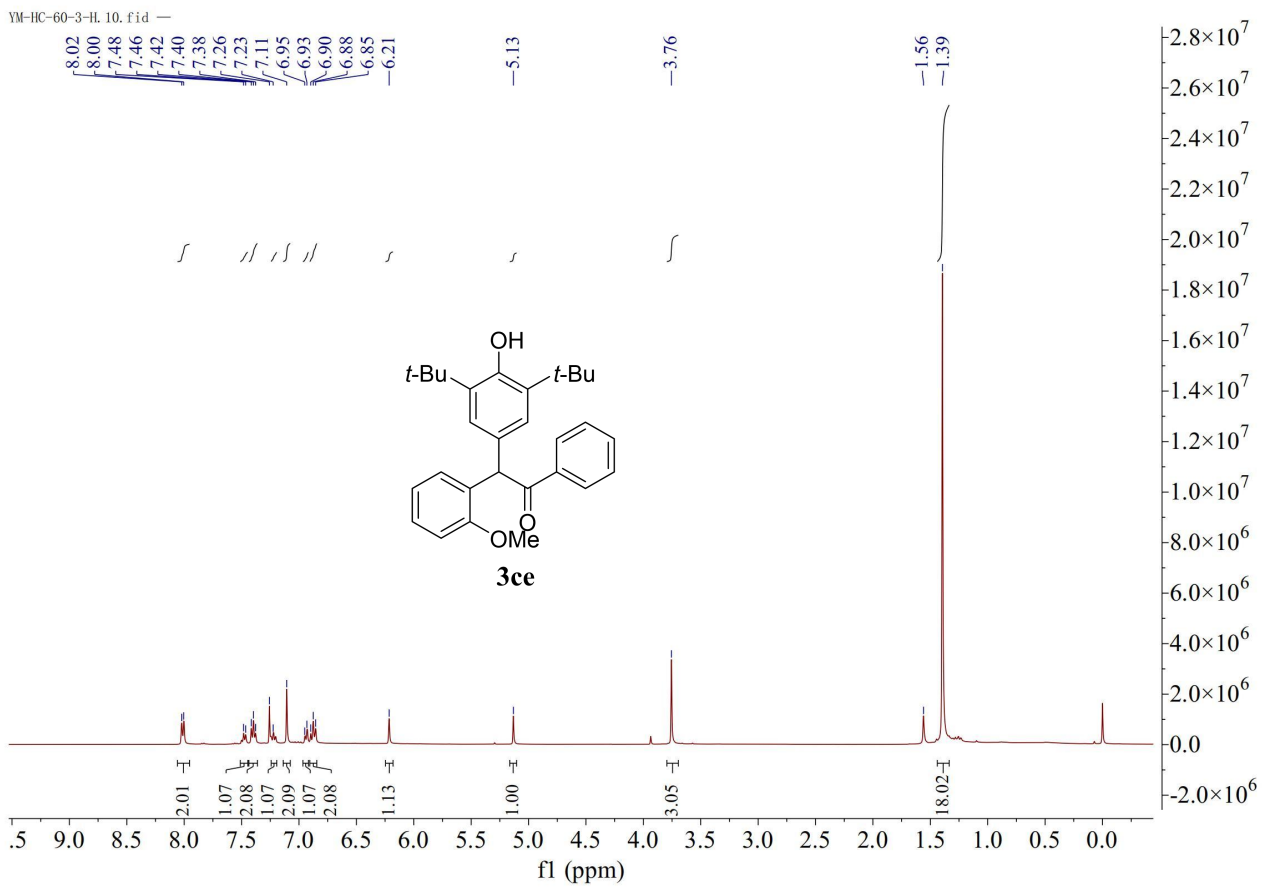
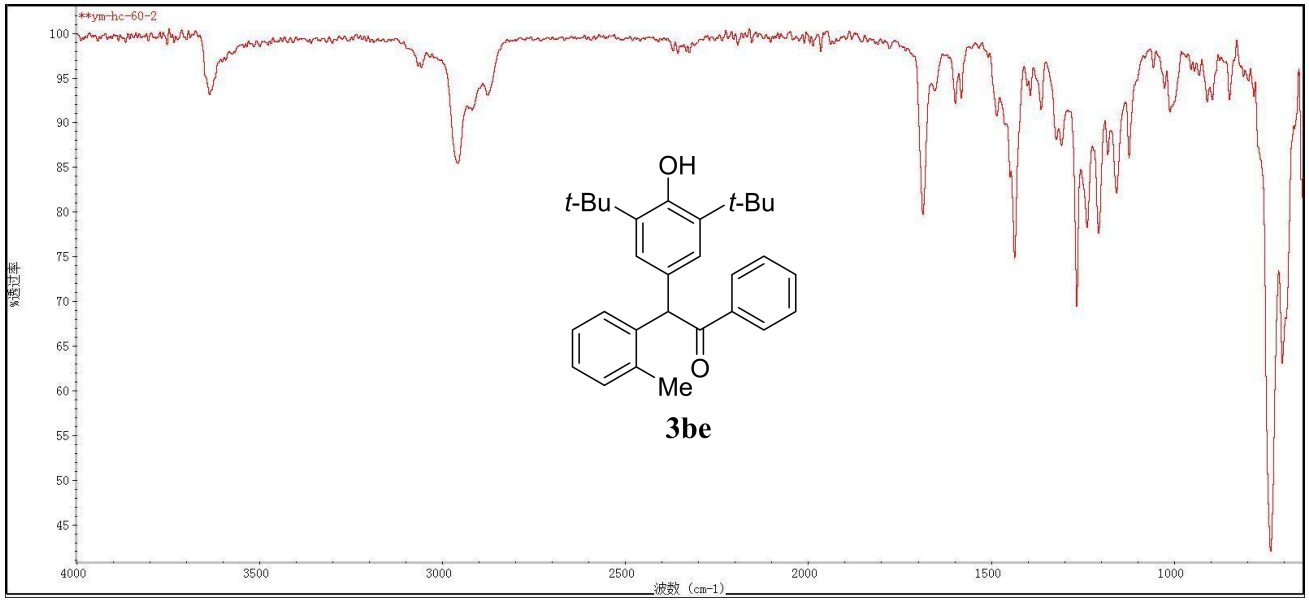




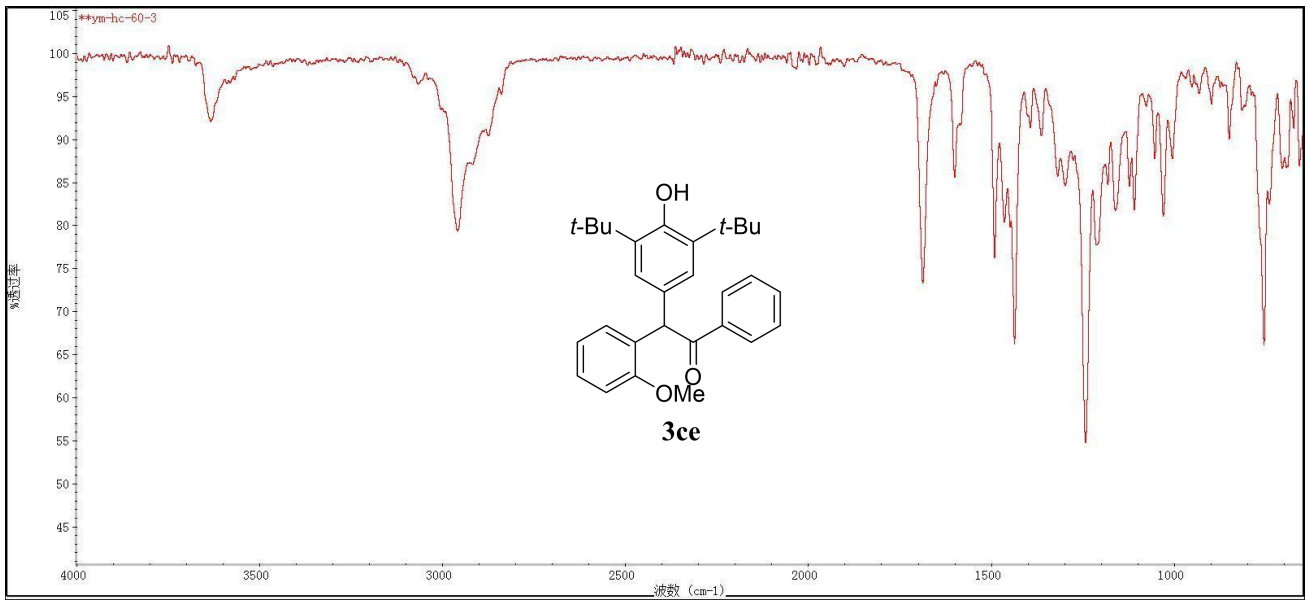
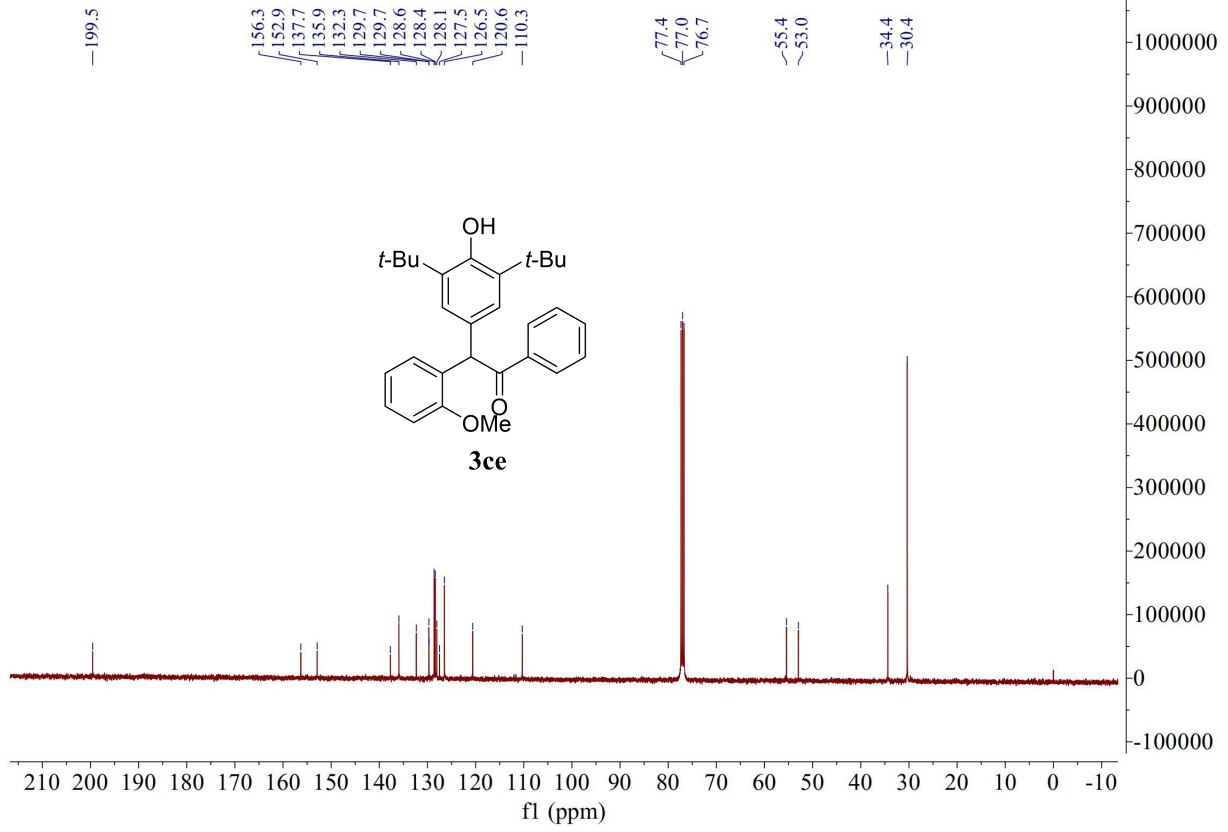
74-2.2.fid



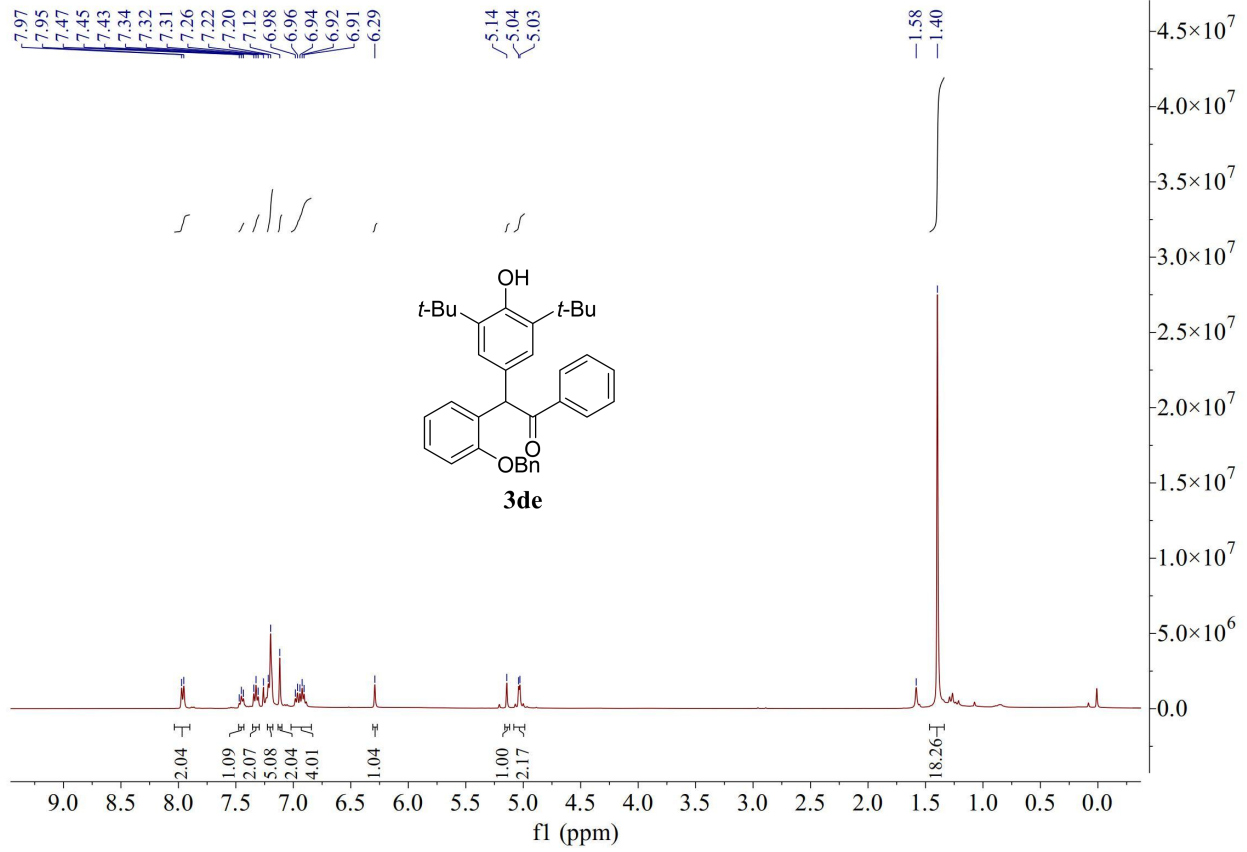




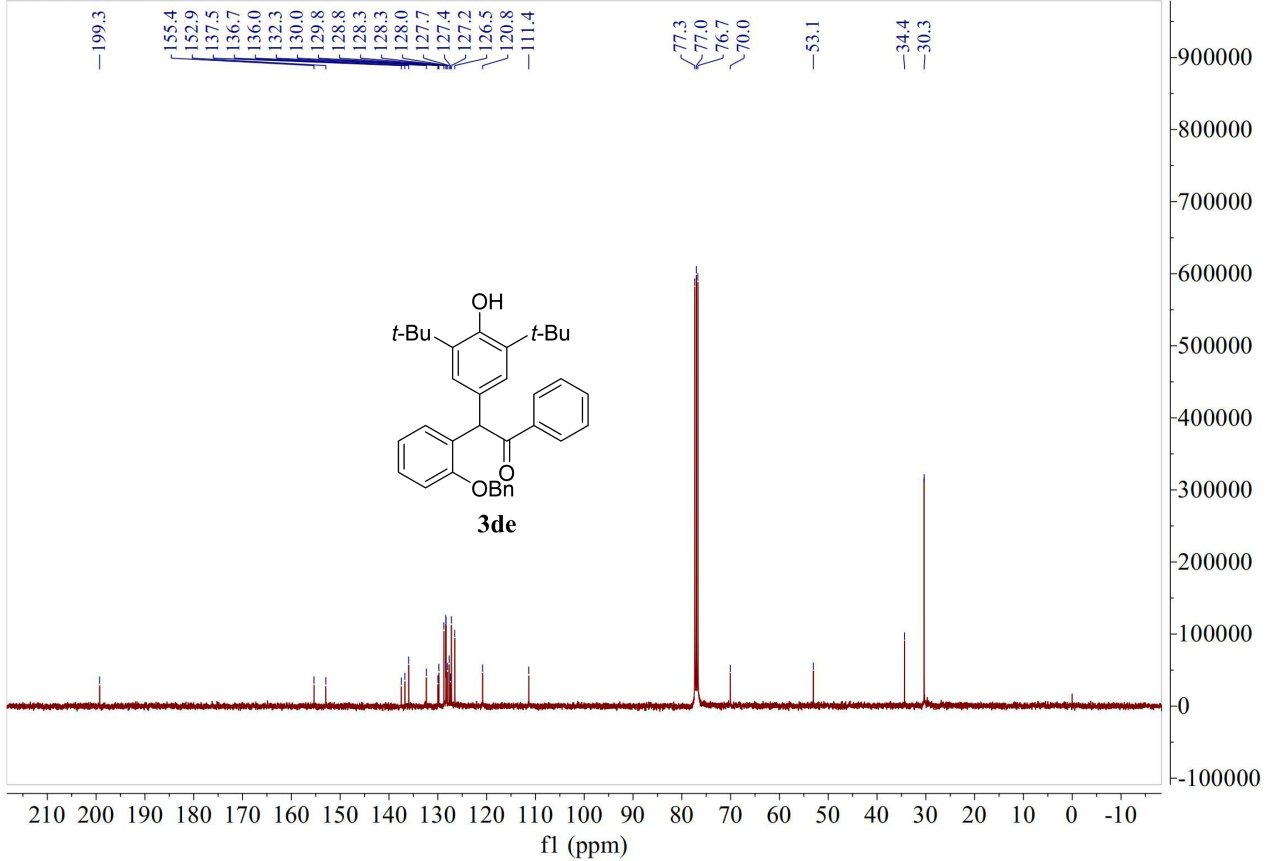
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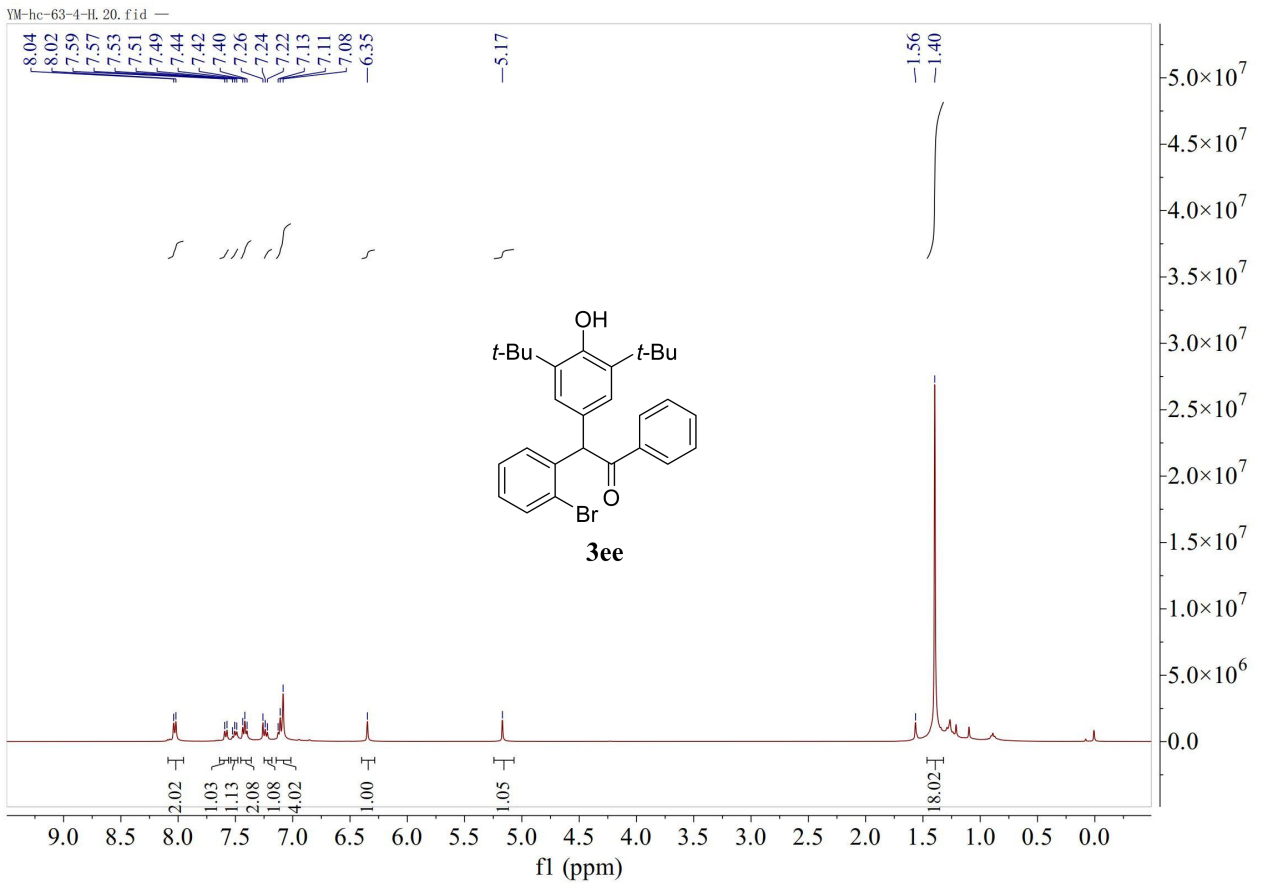
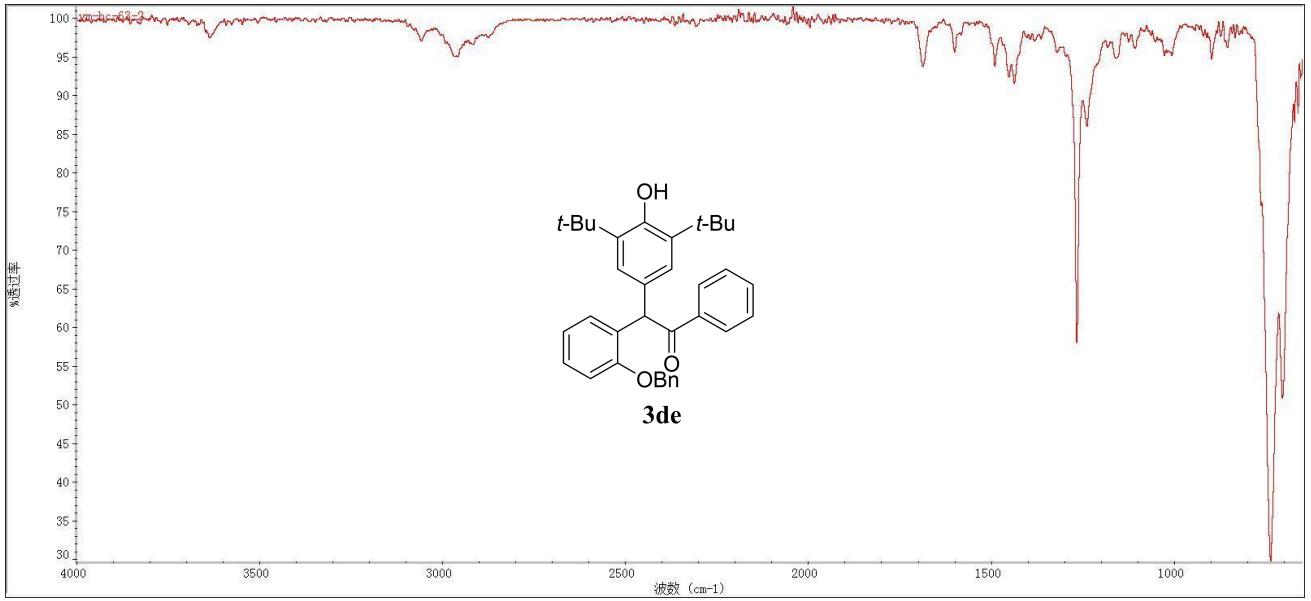


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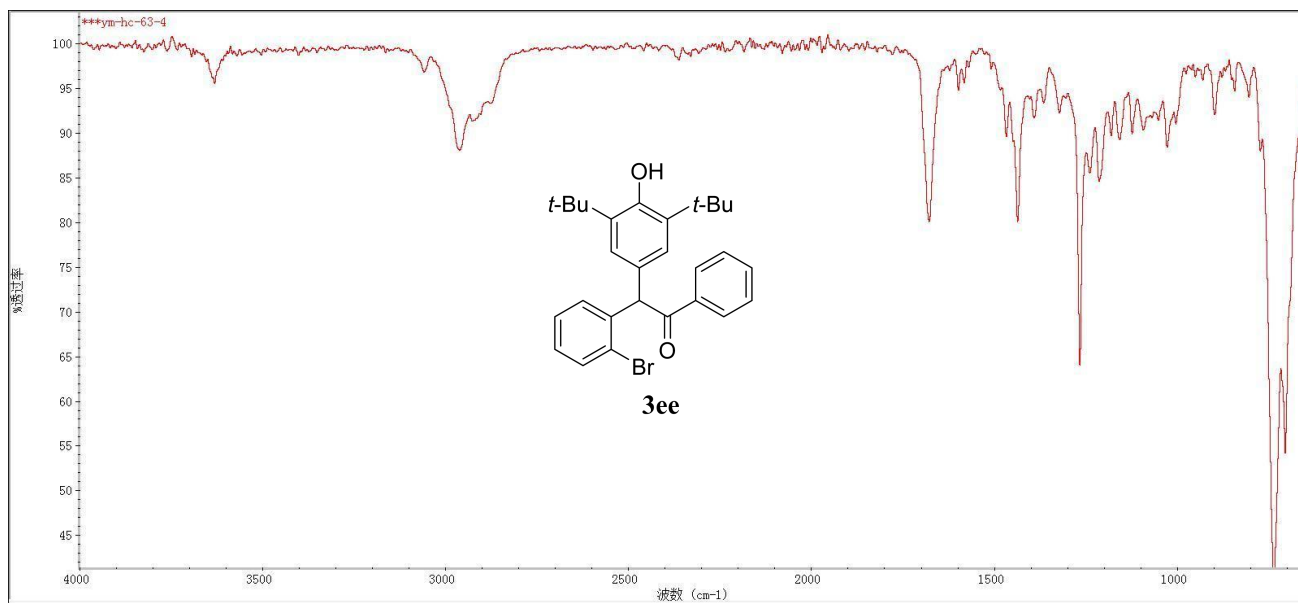
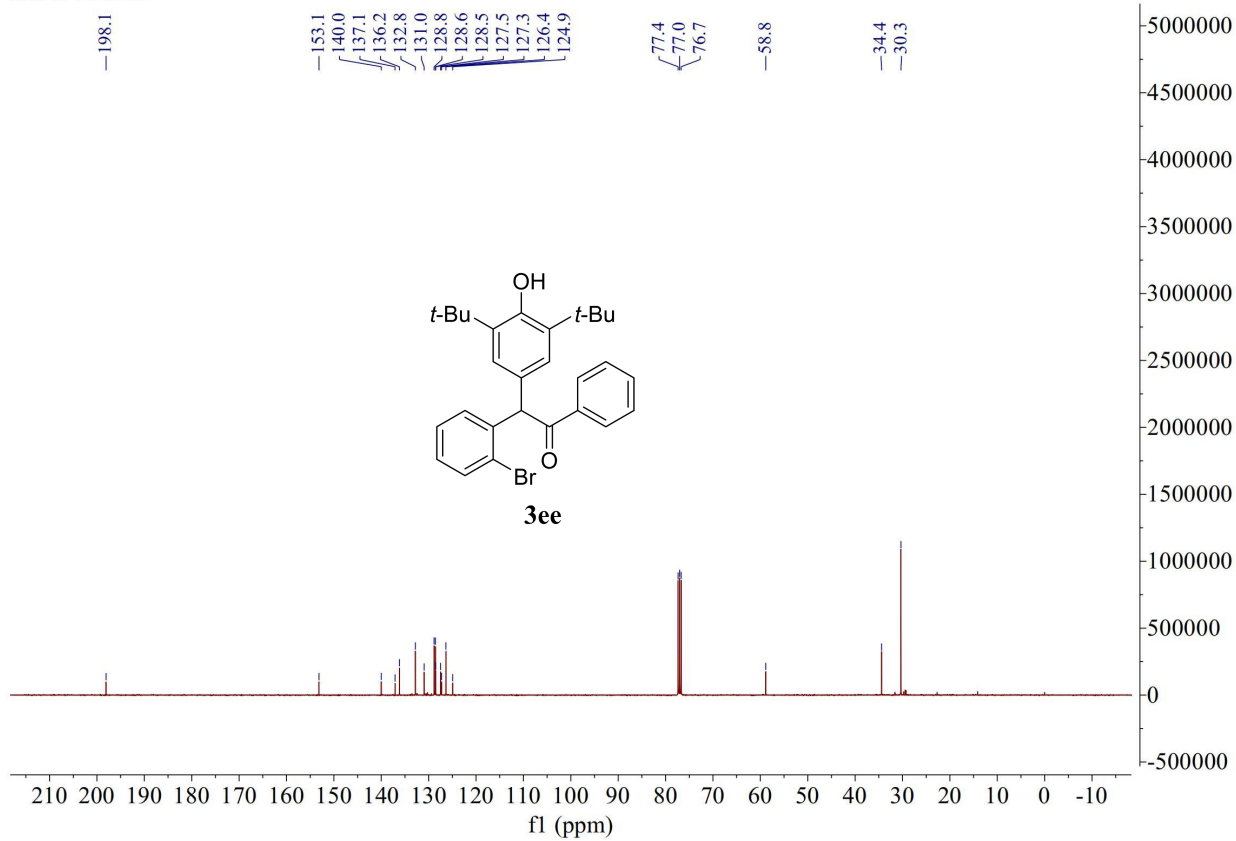


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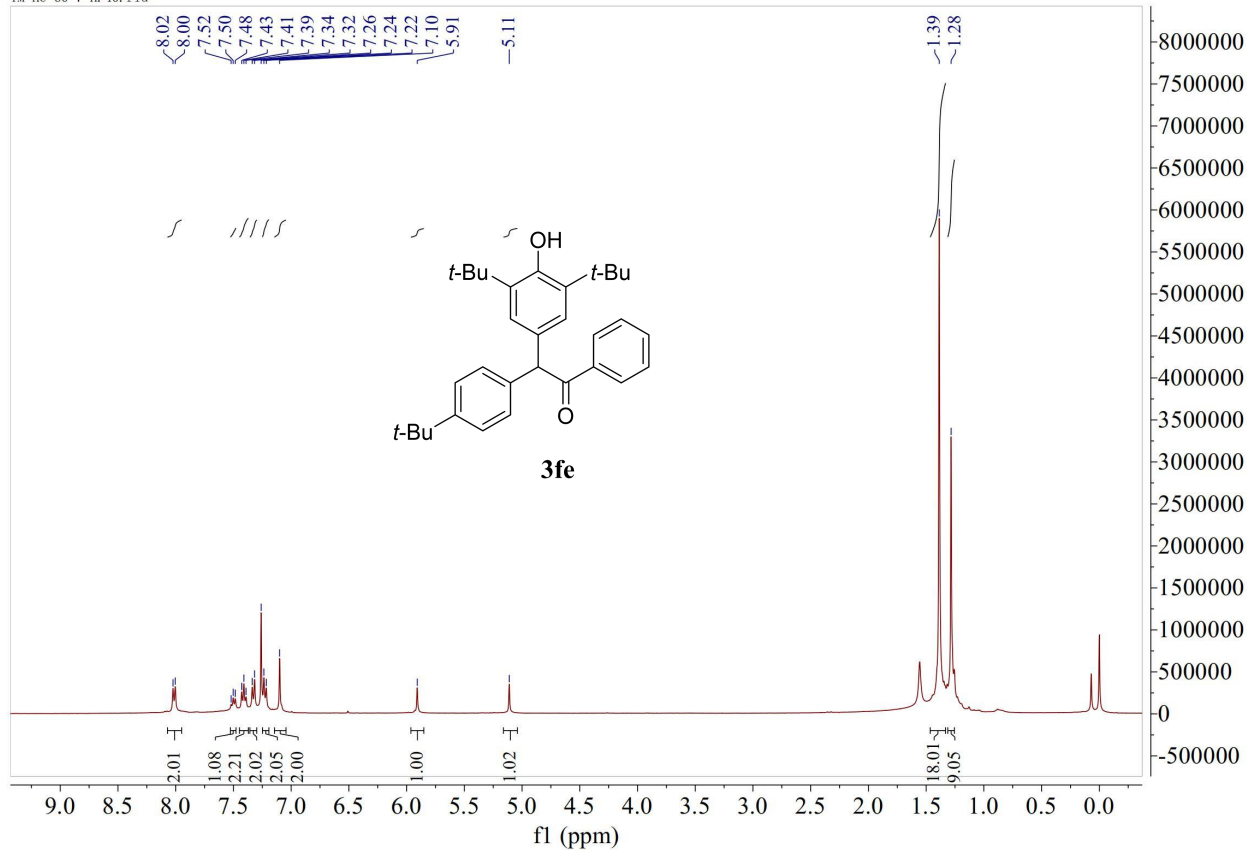


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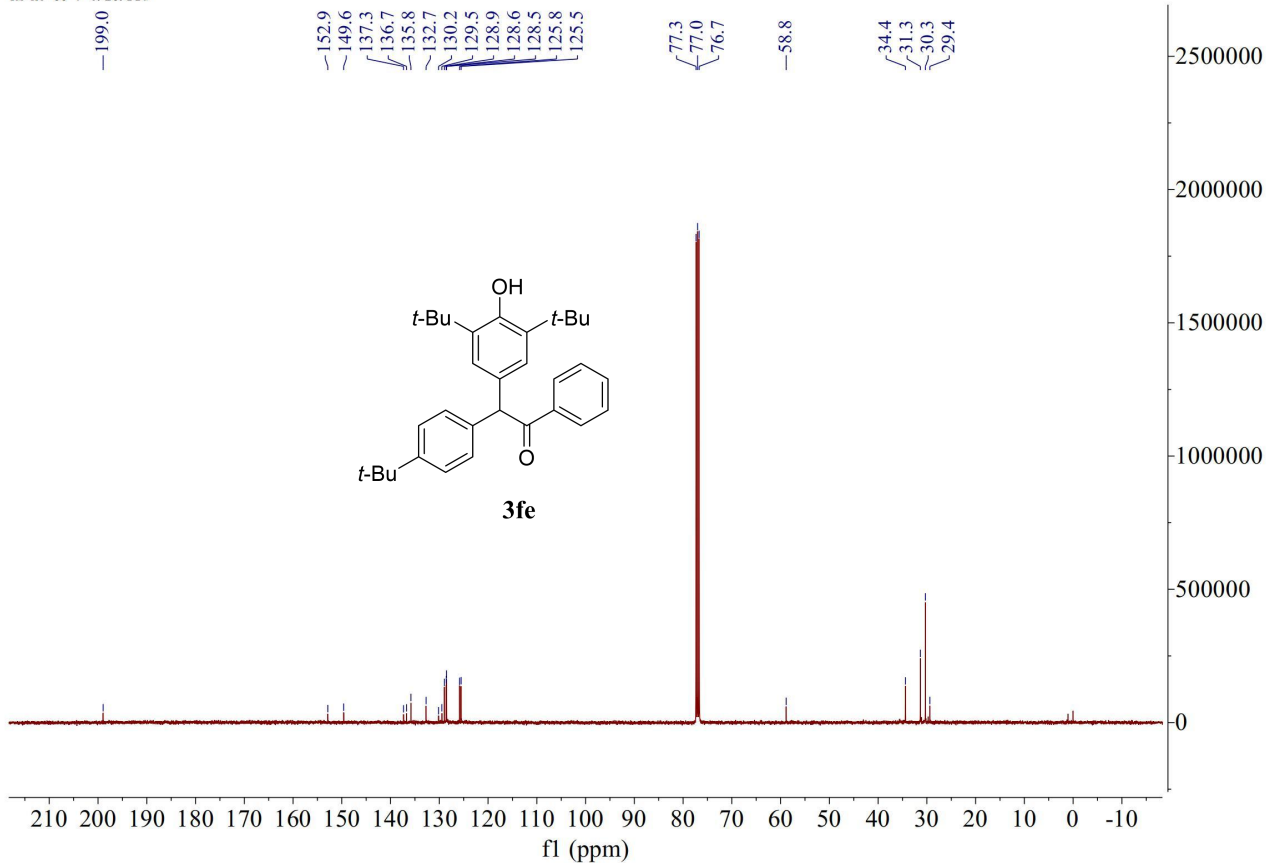


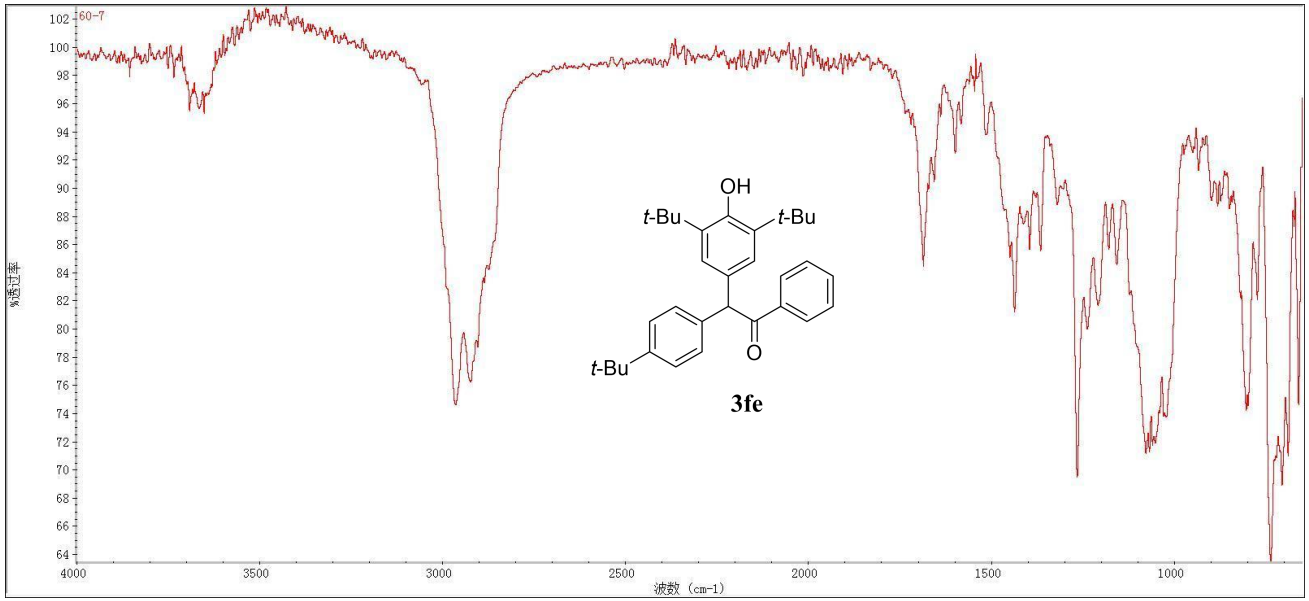


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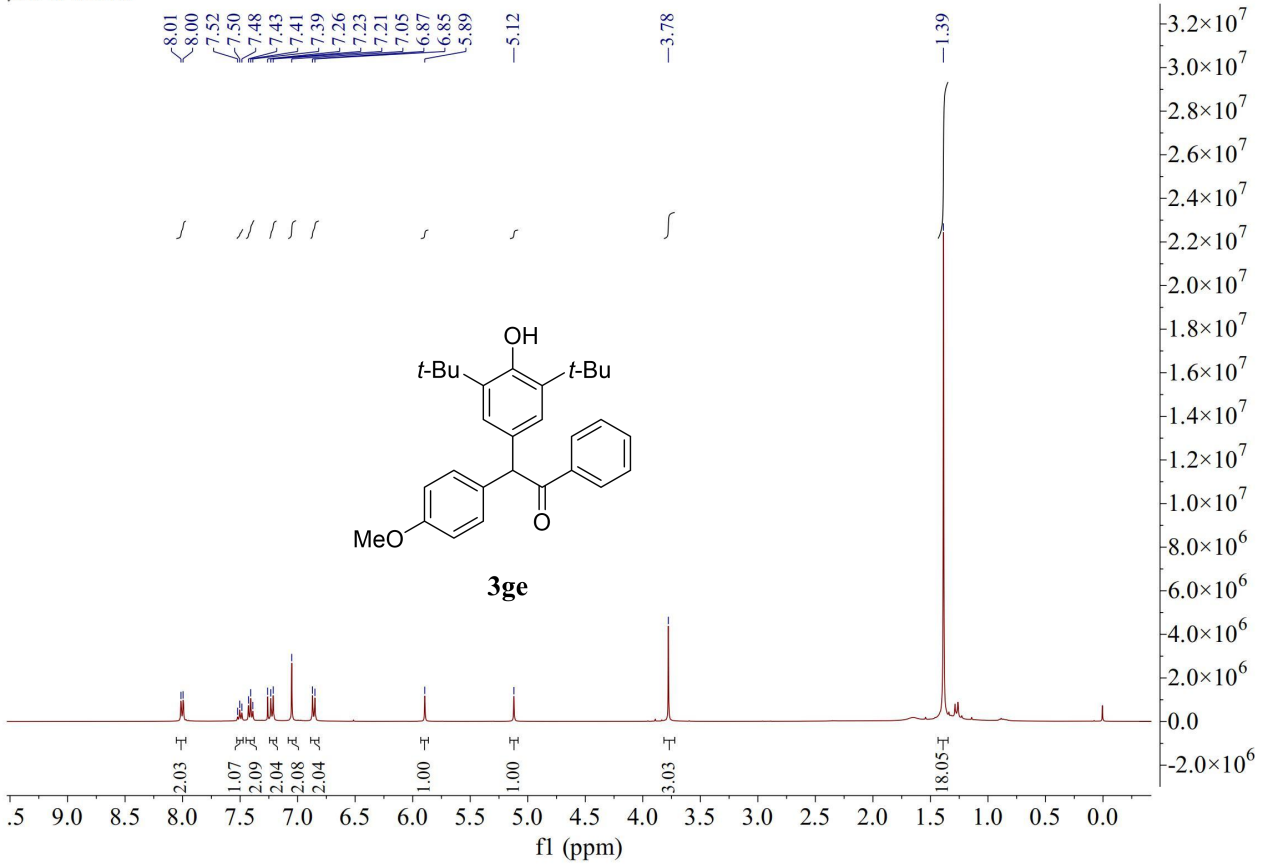


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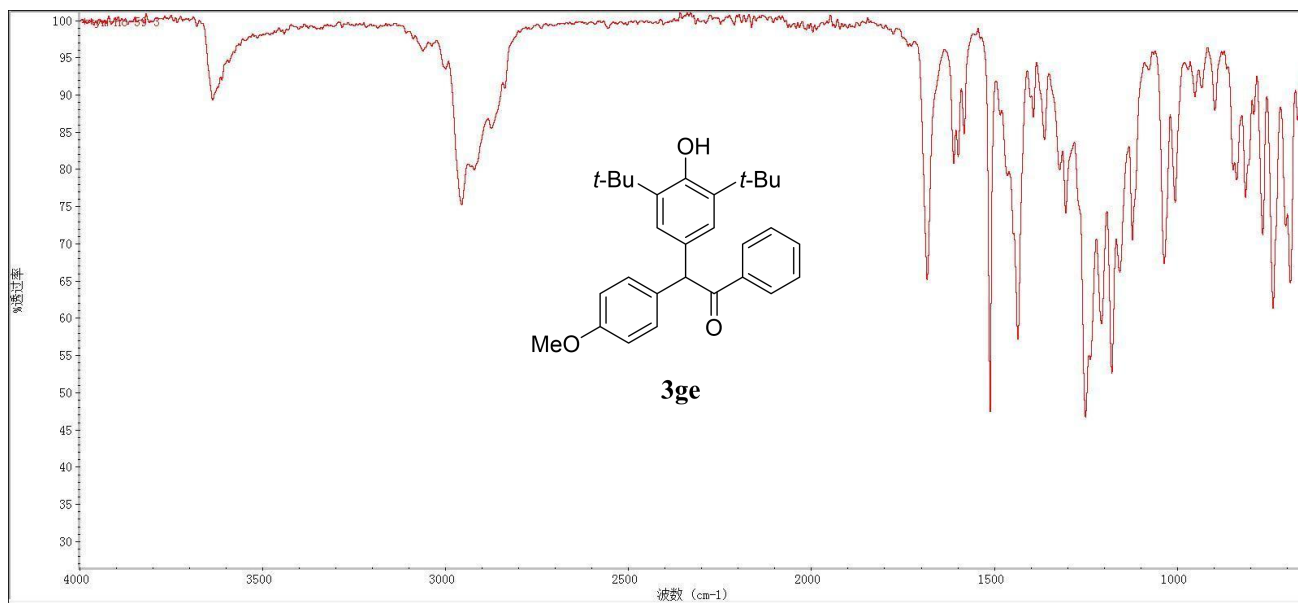
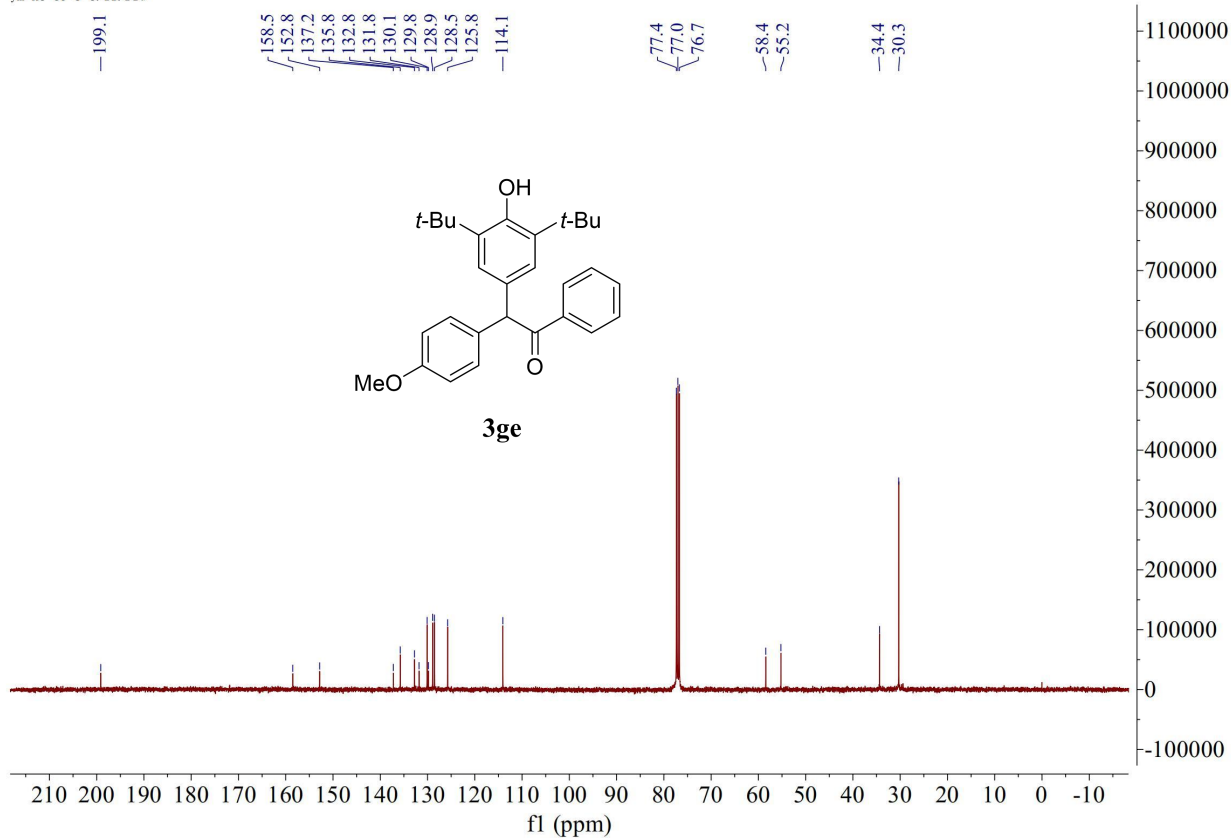




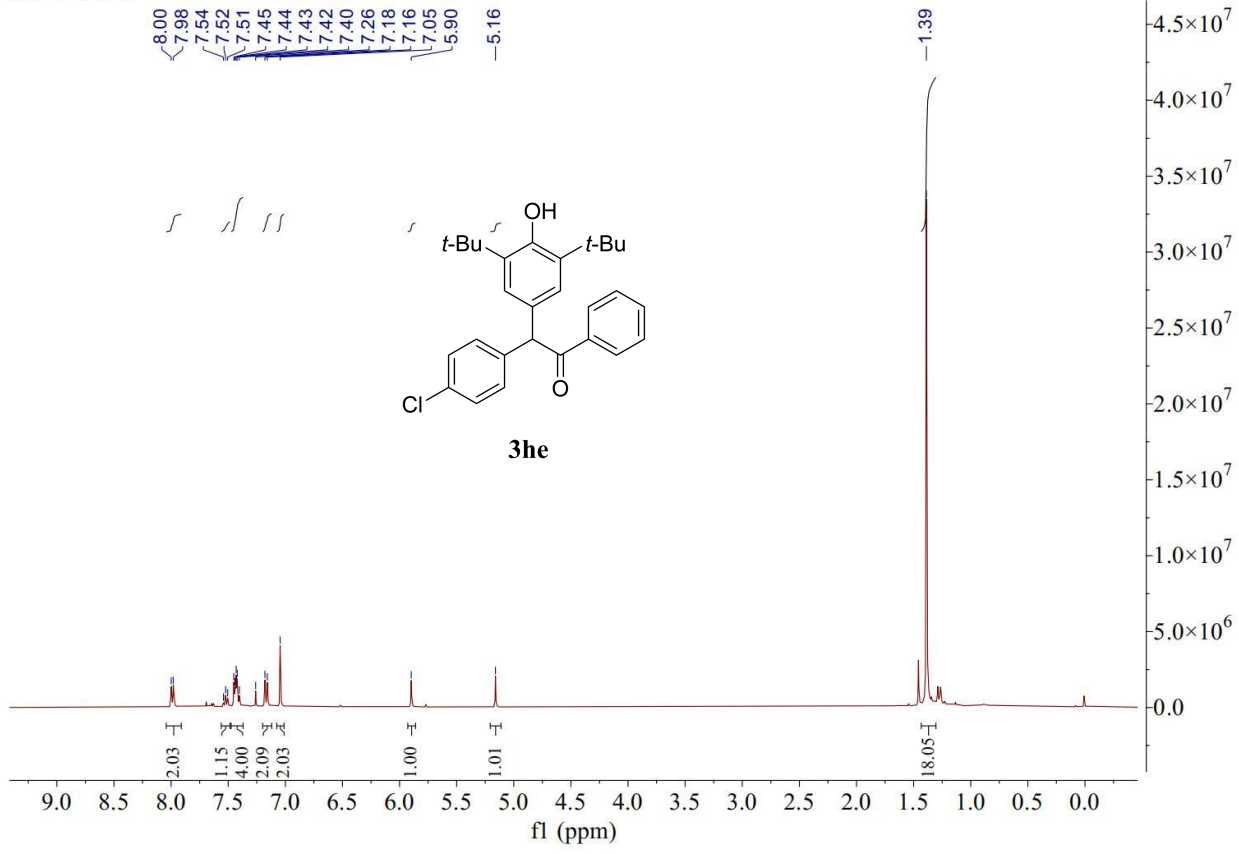
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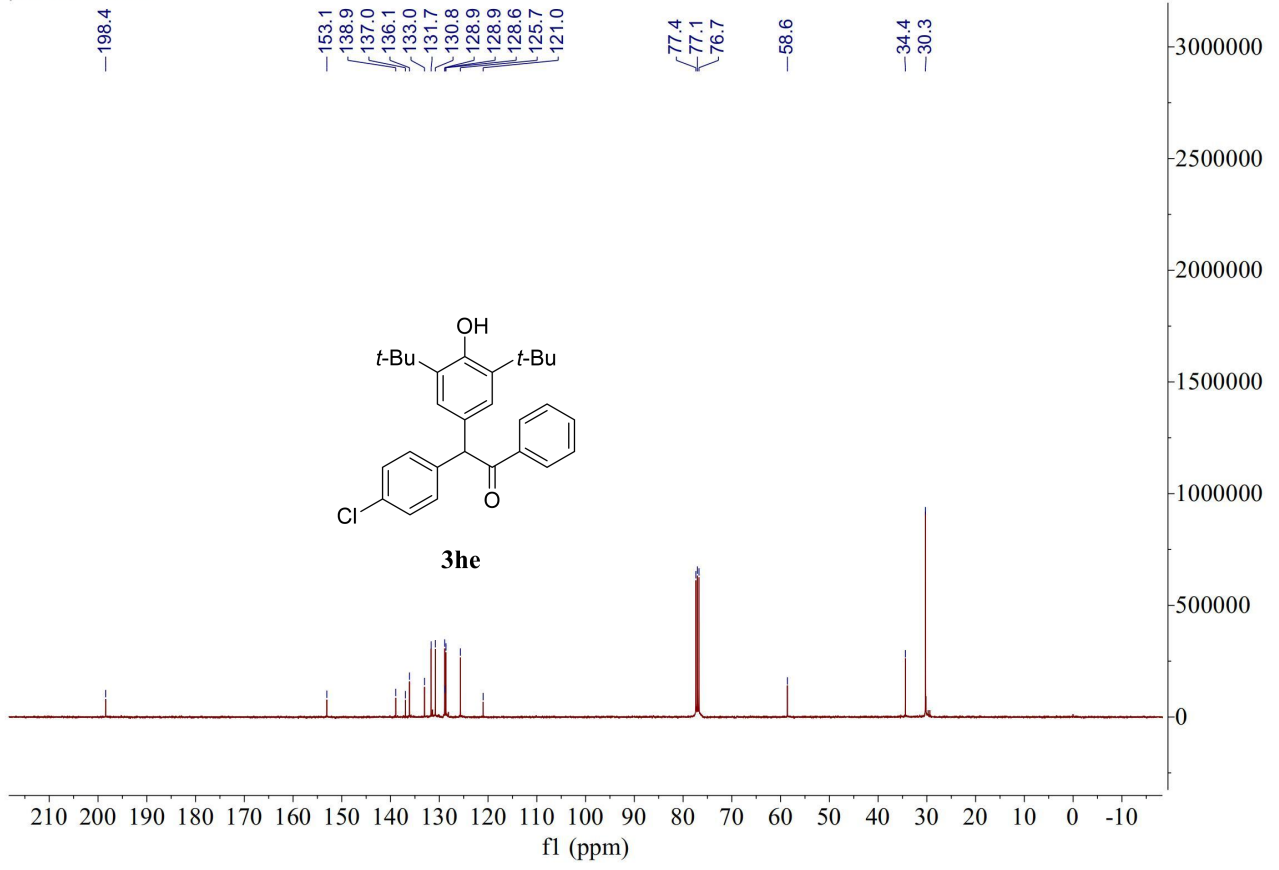
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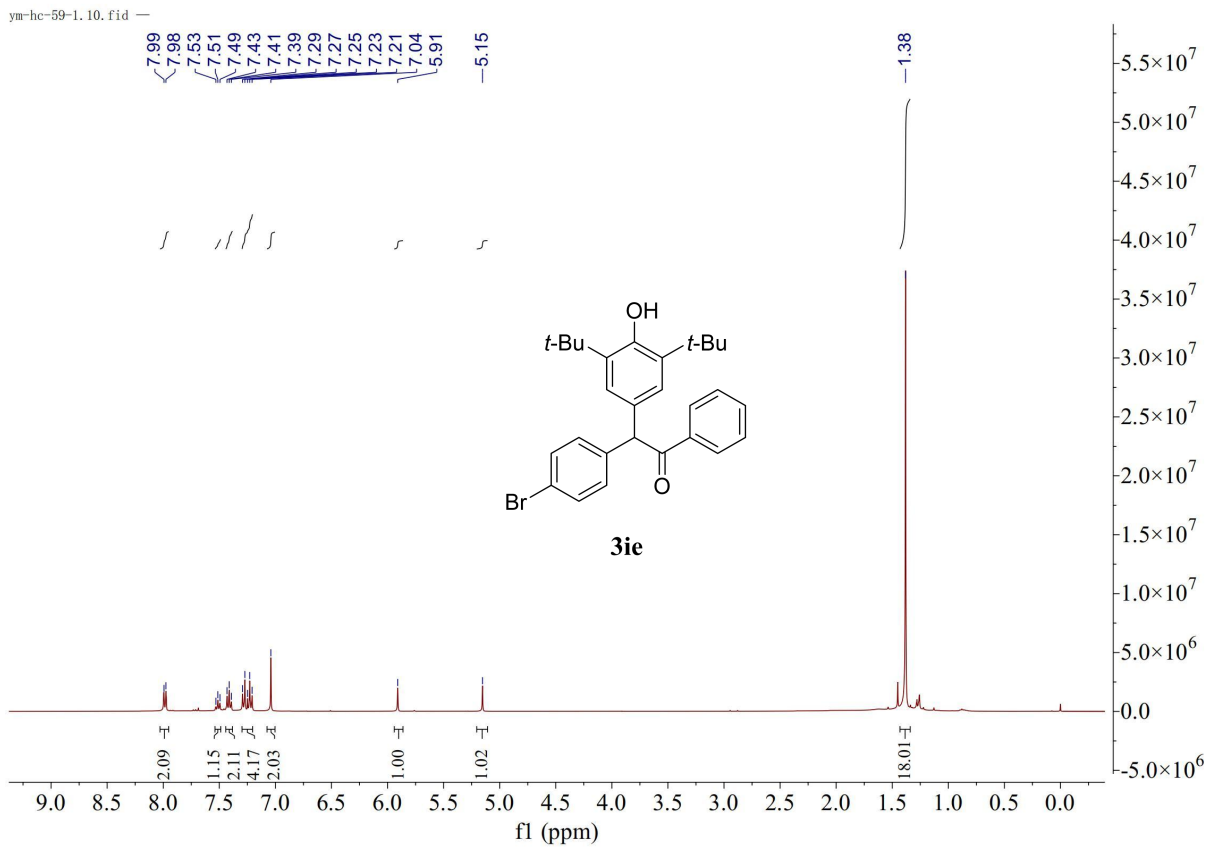
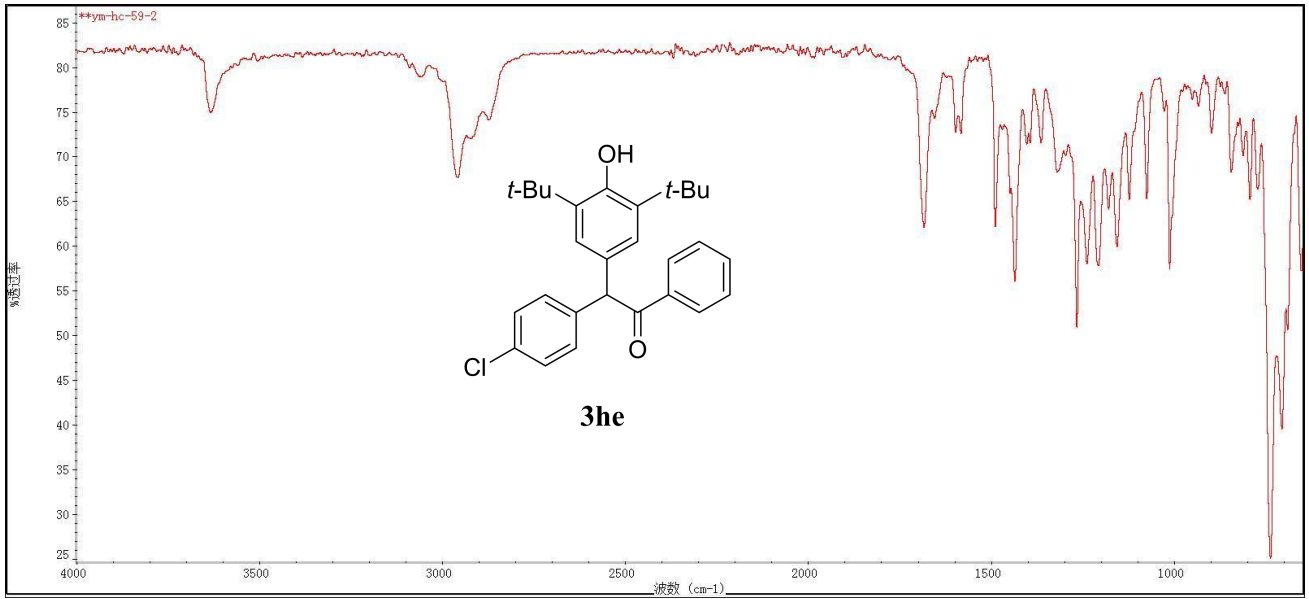


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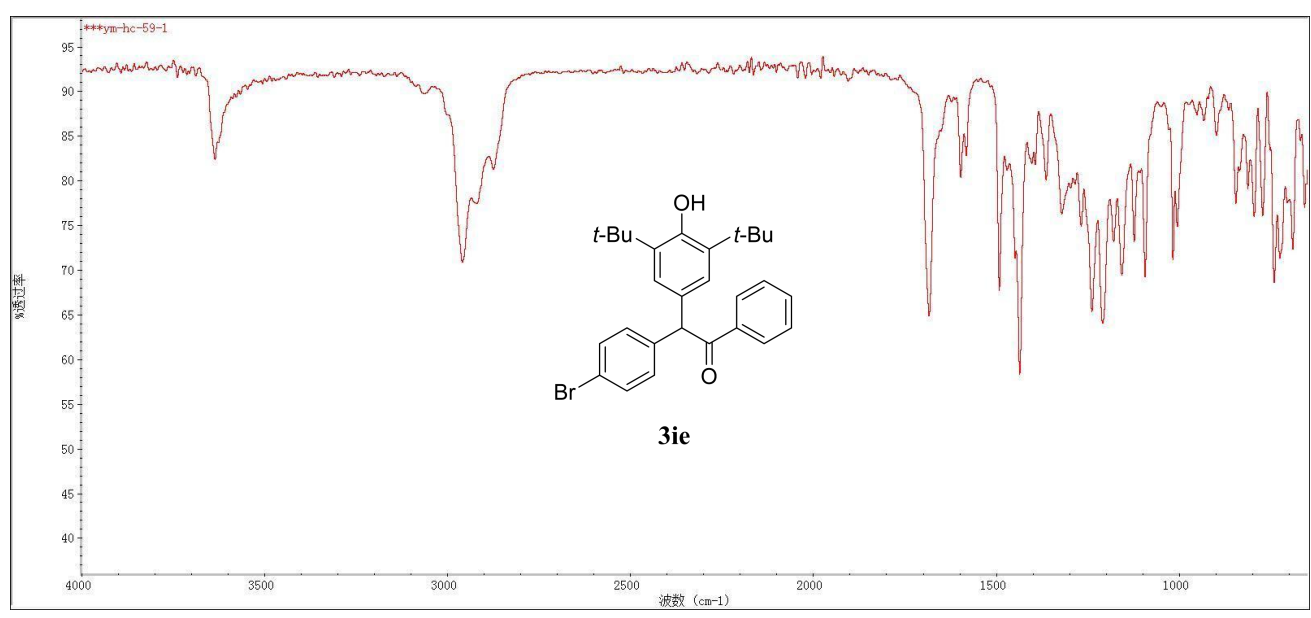
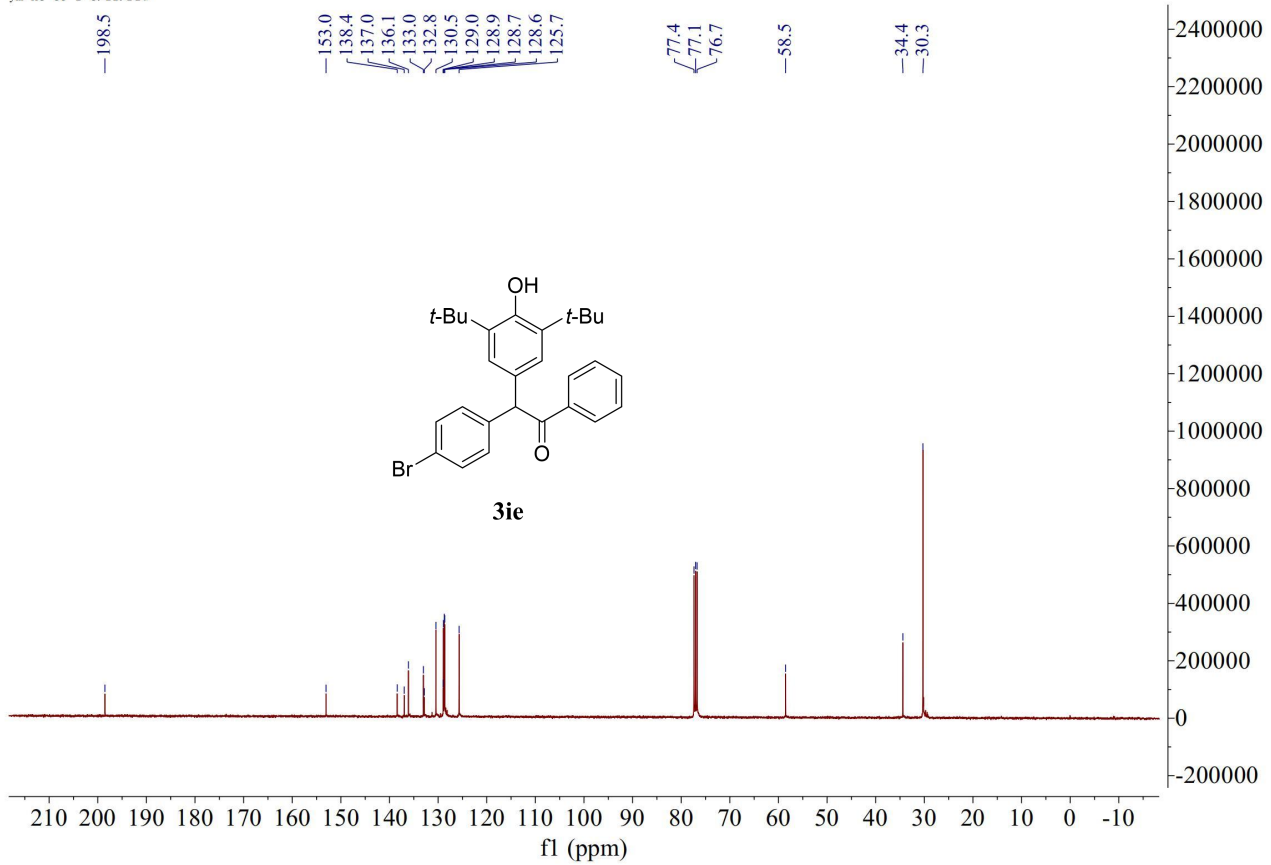


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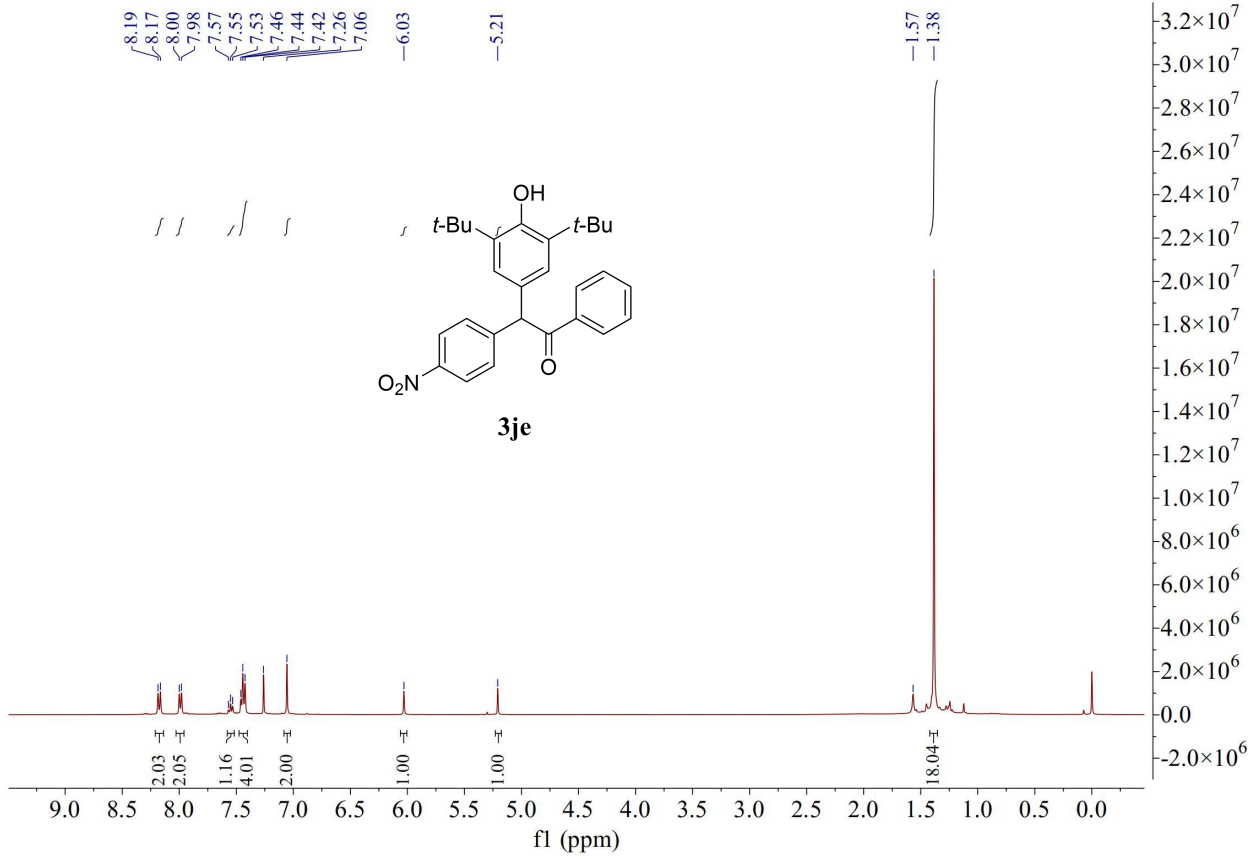




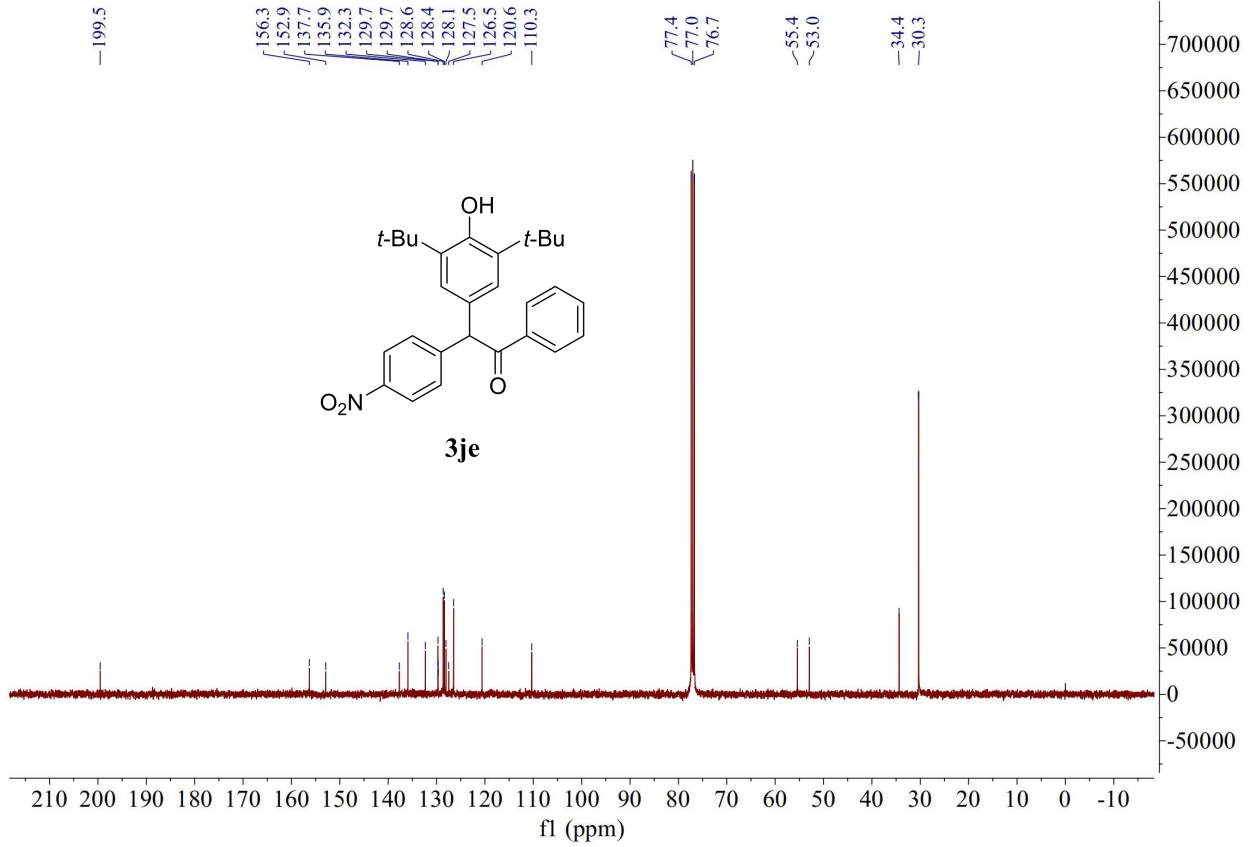
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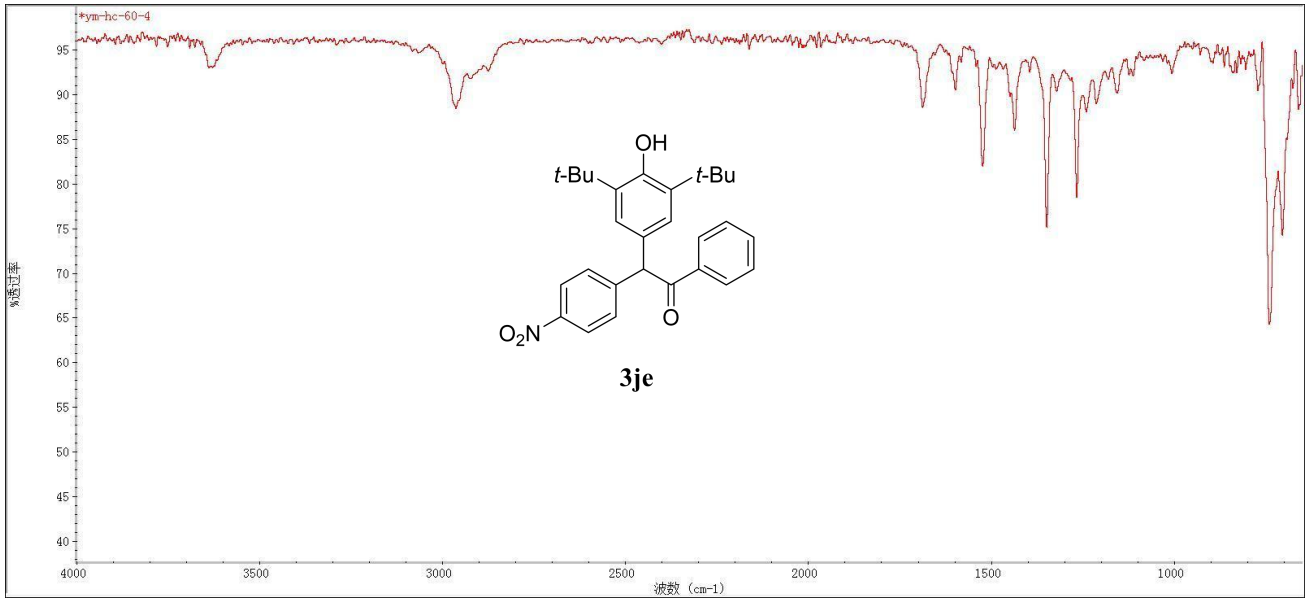


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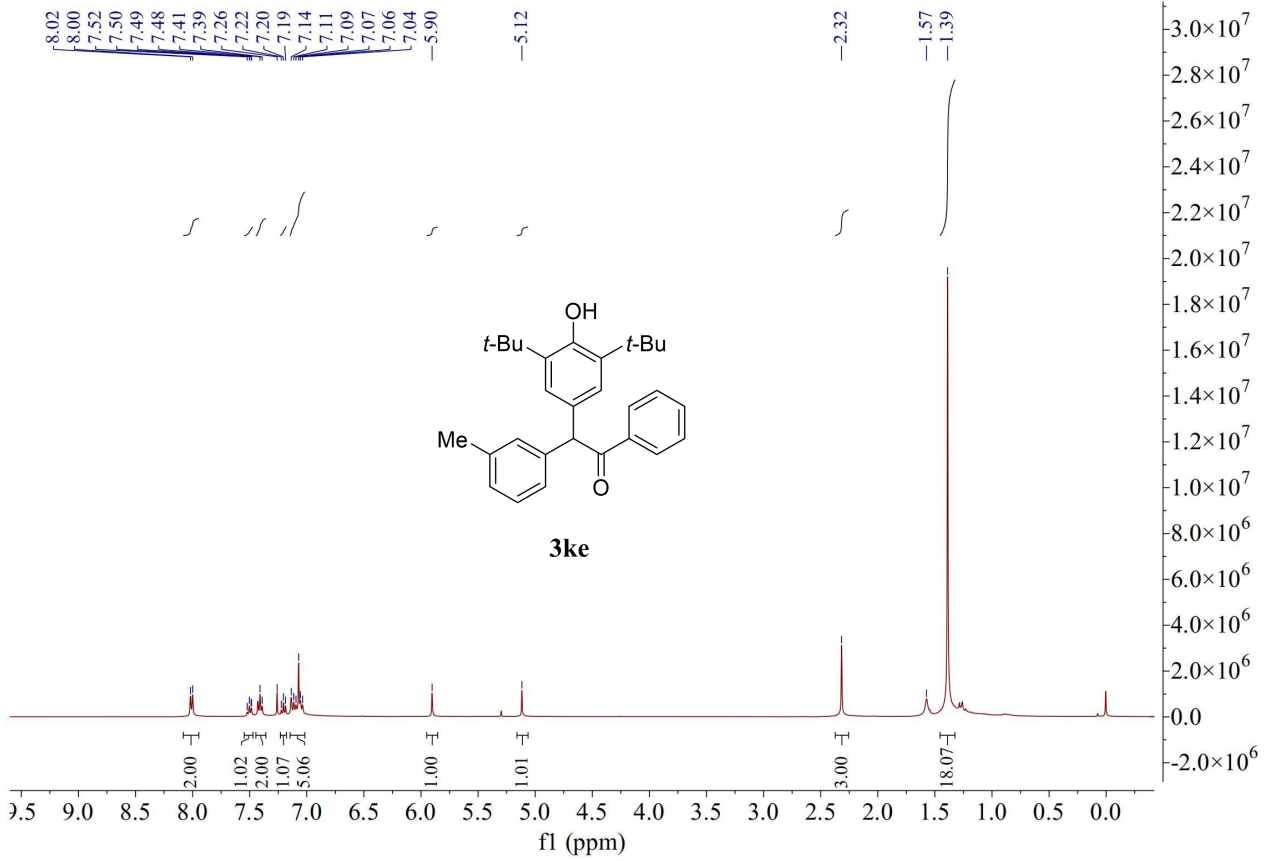


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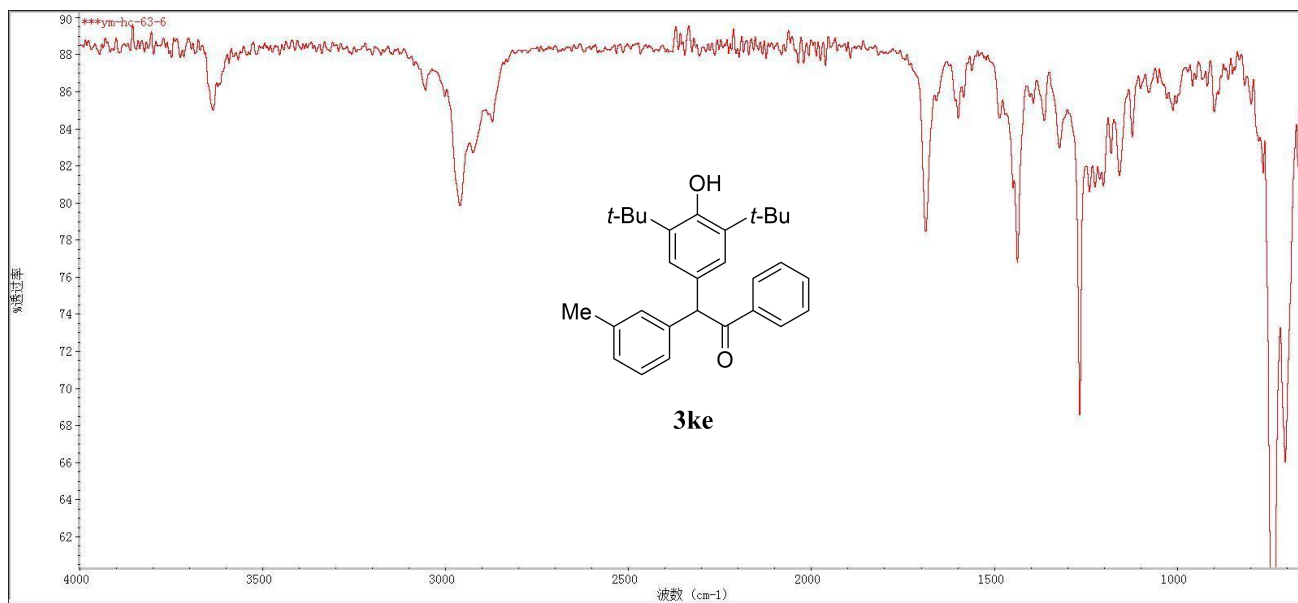
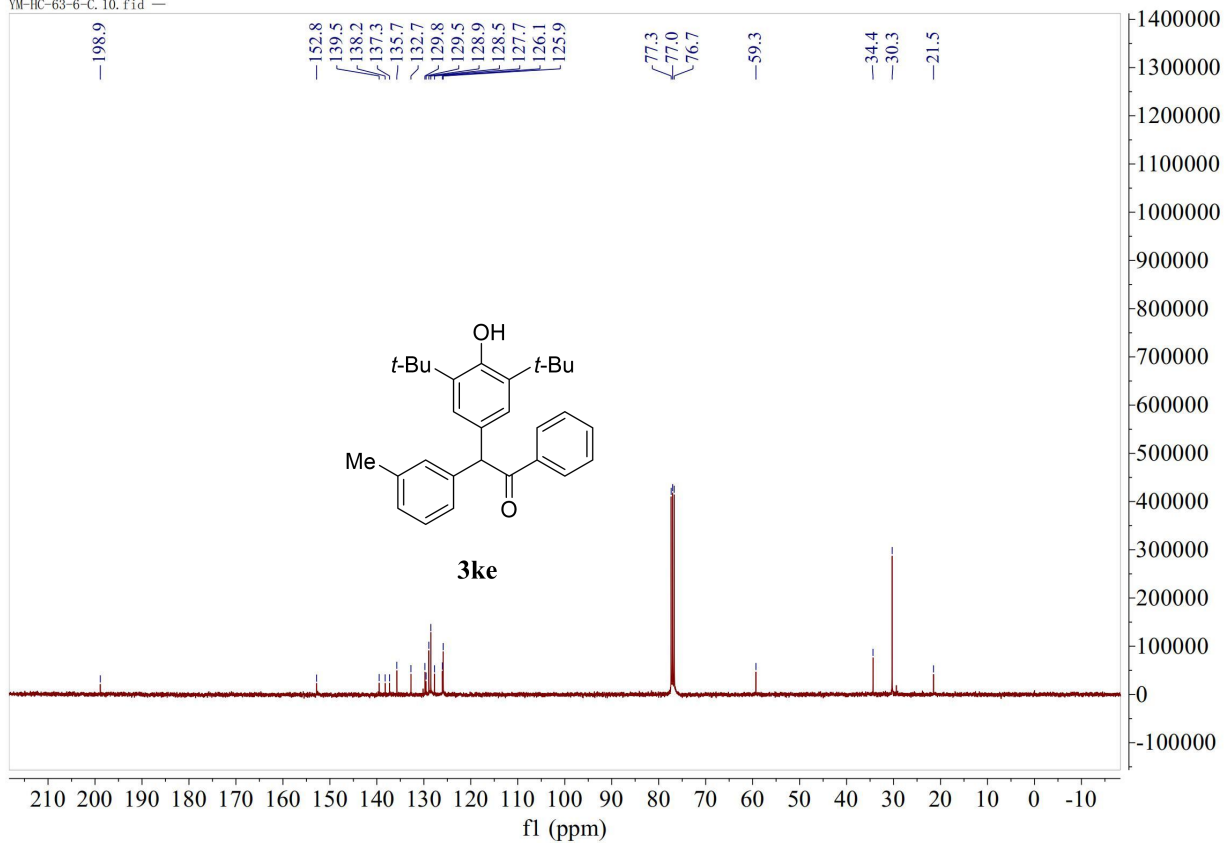




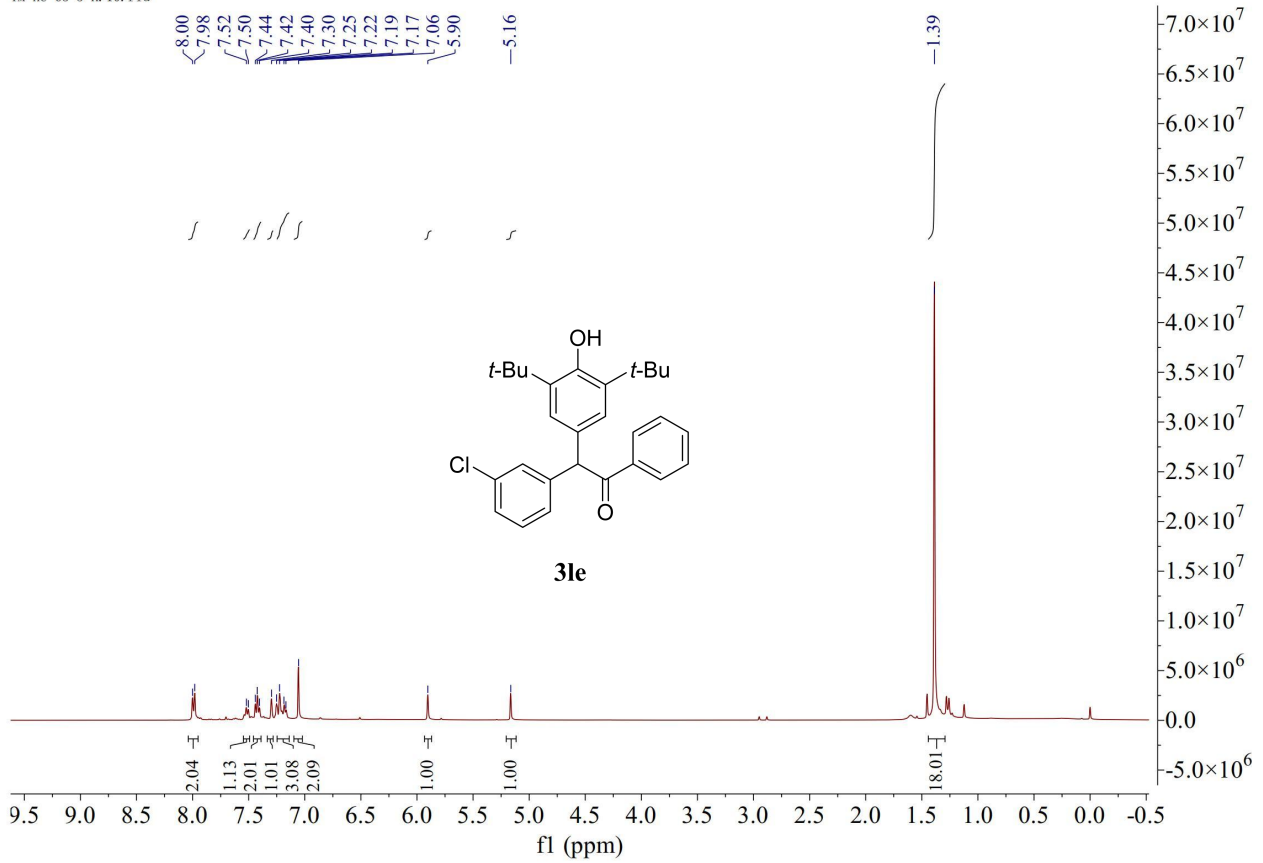
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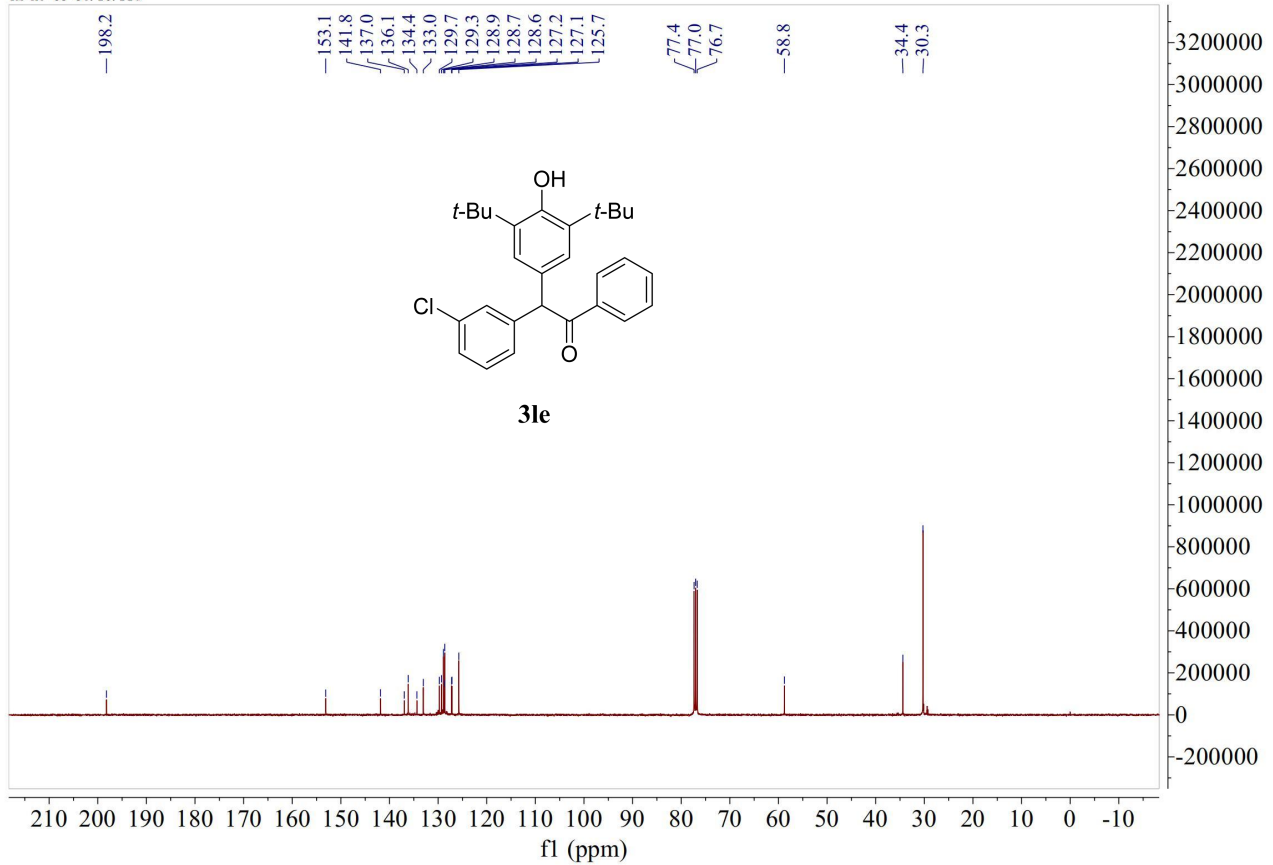


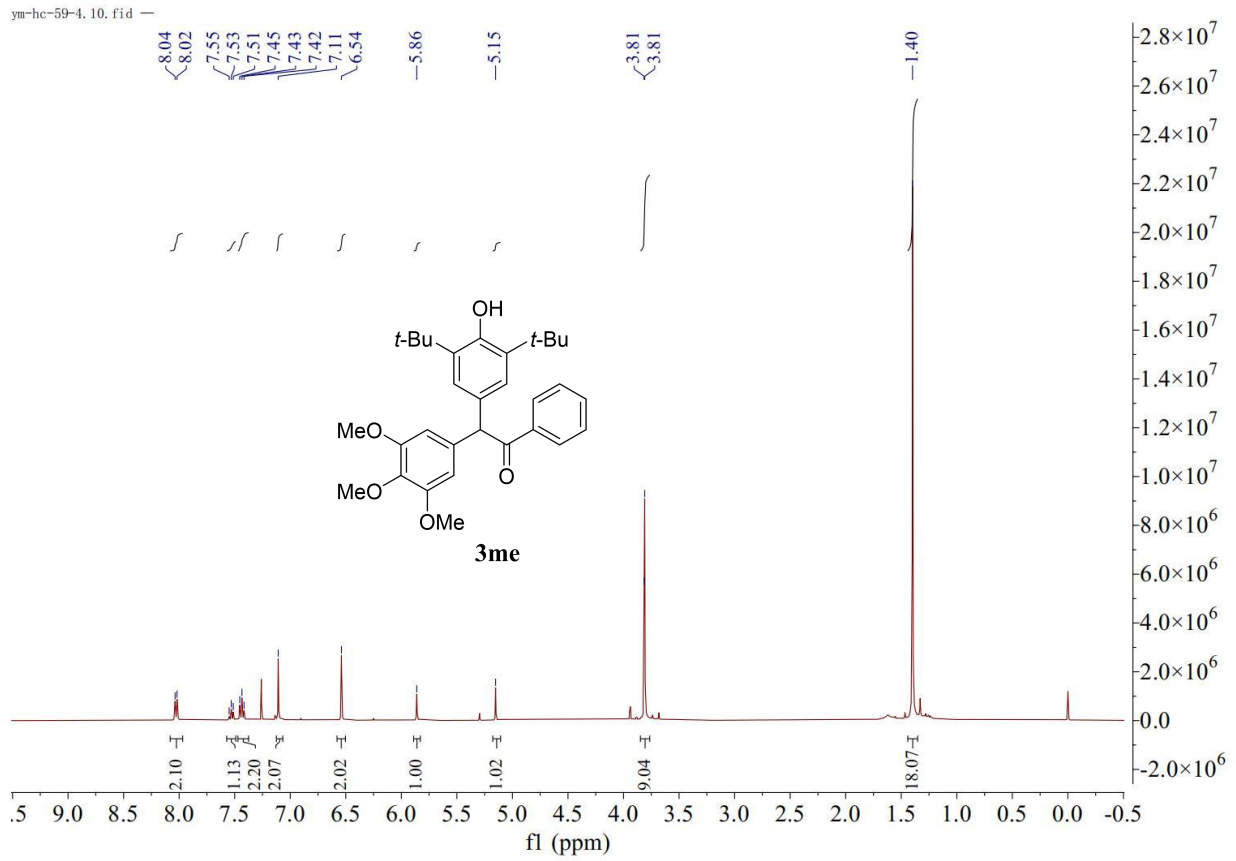
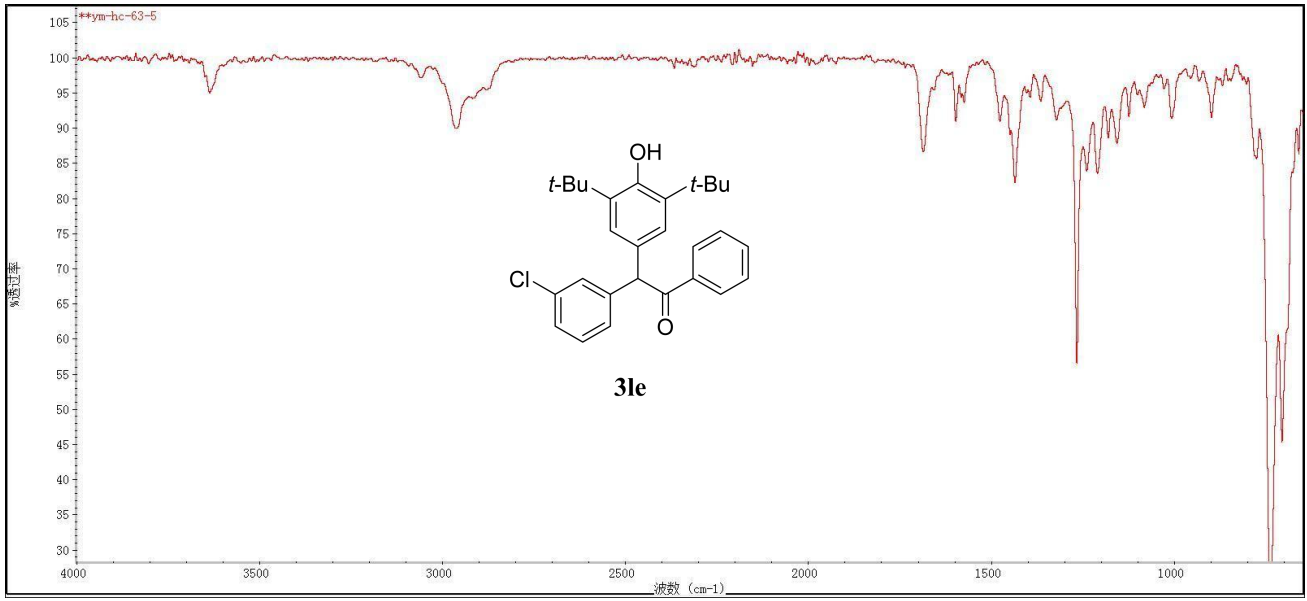


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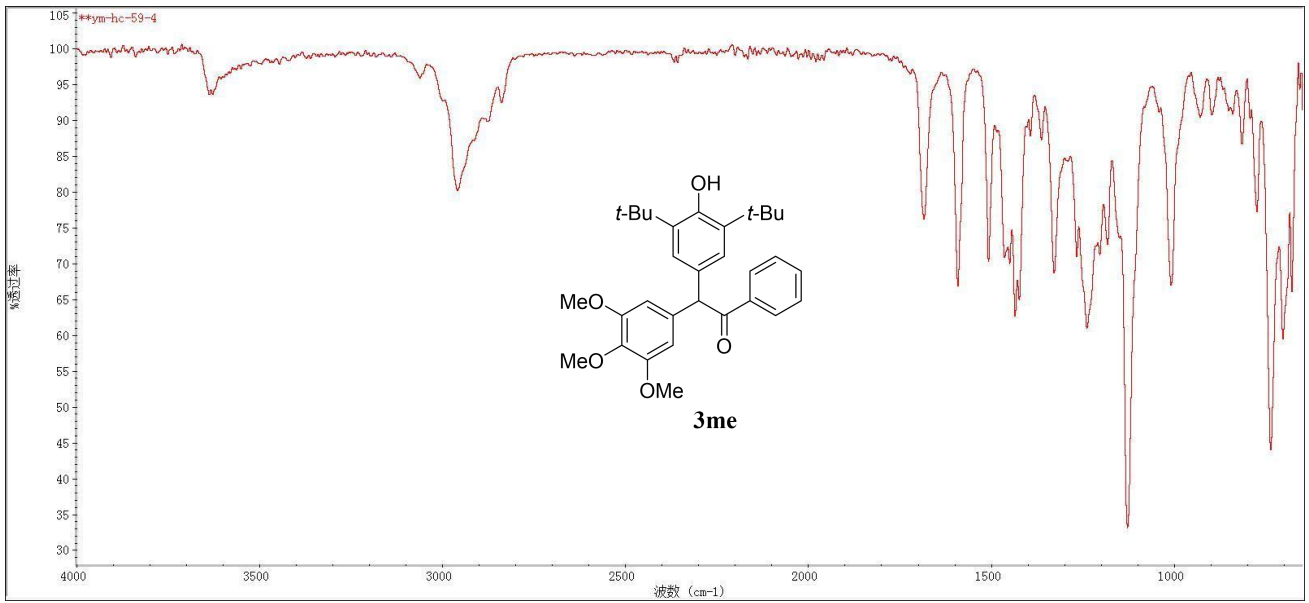
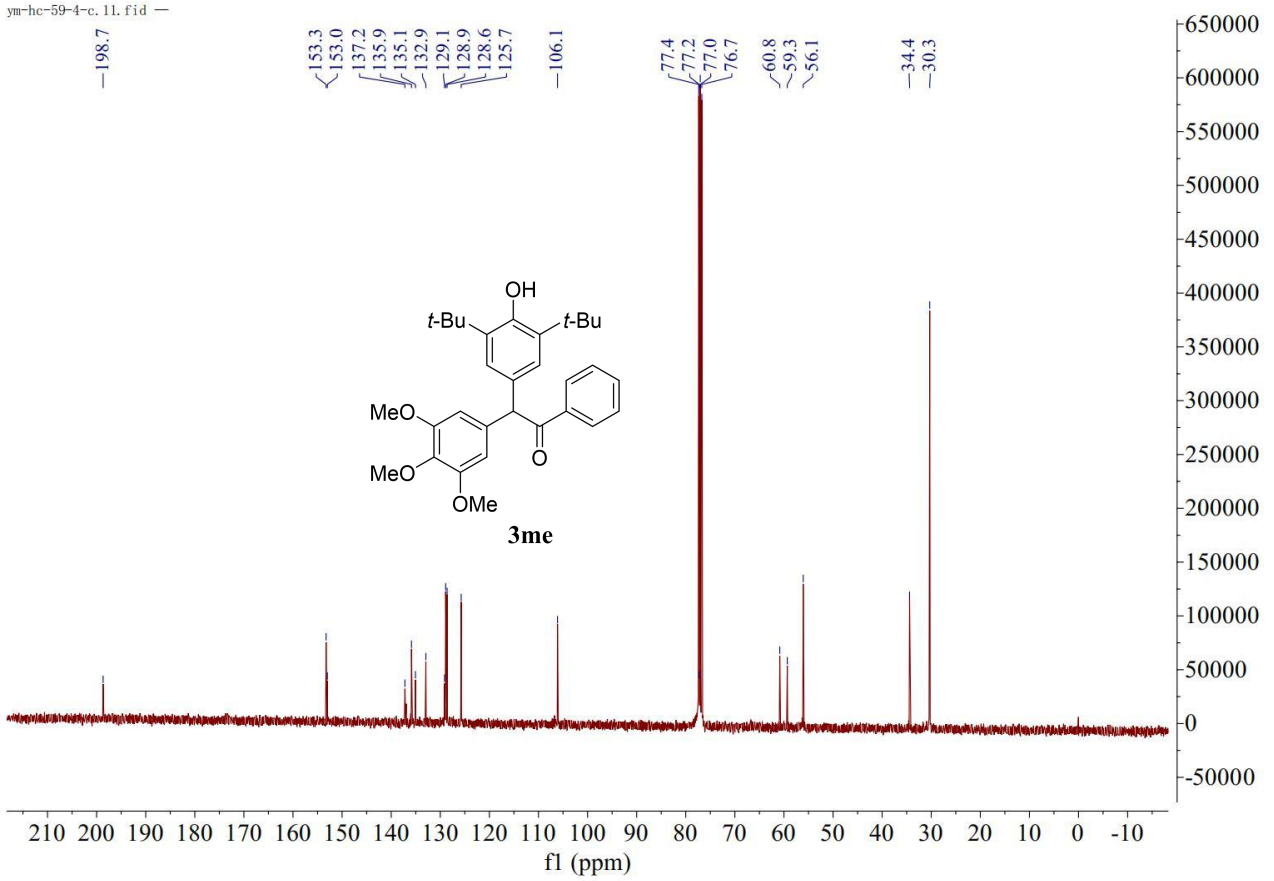


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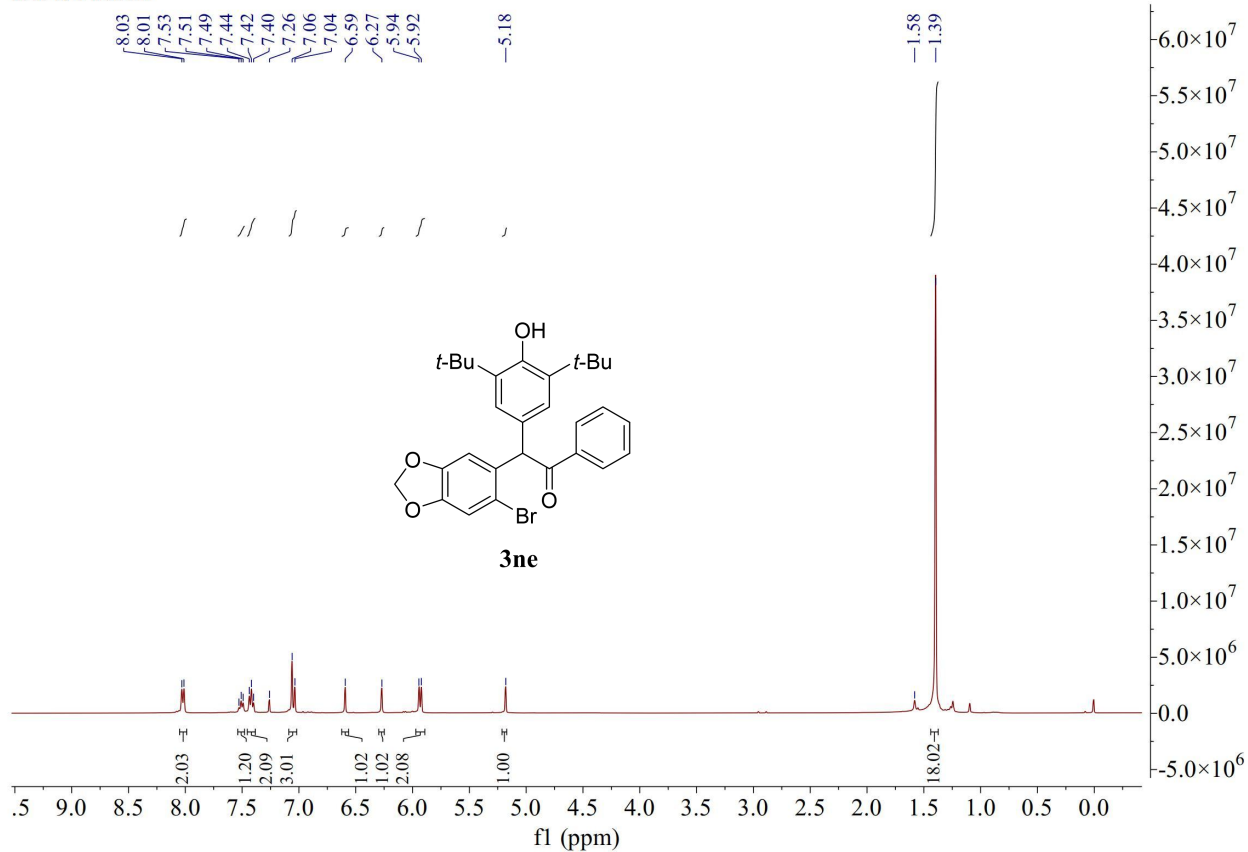




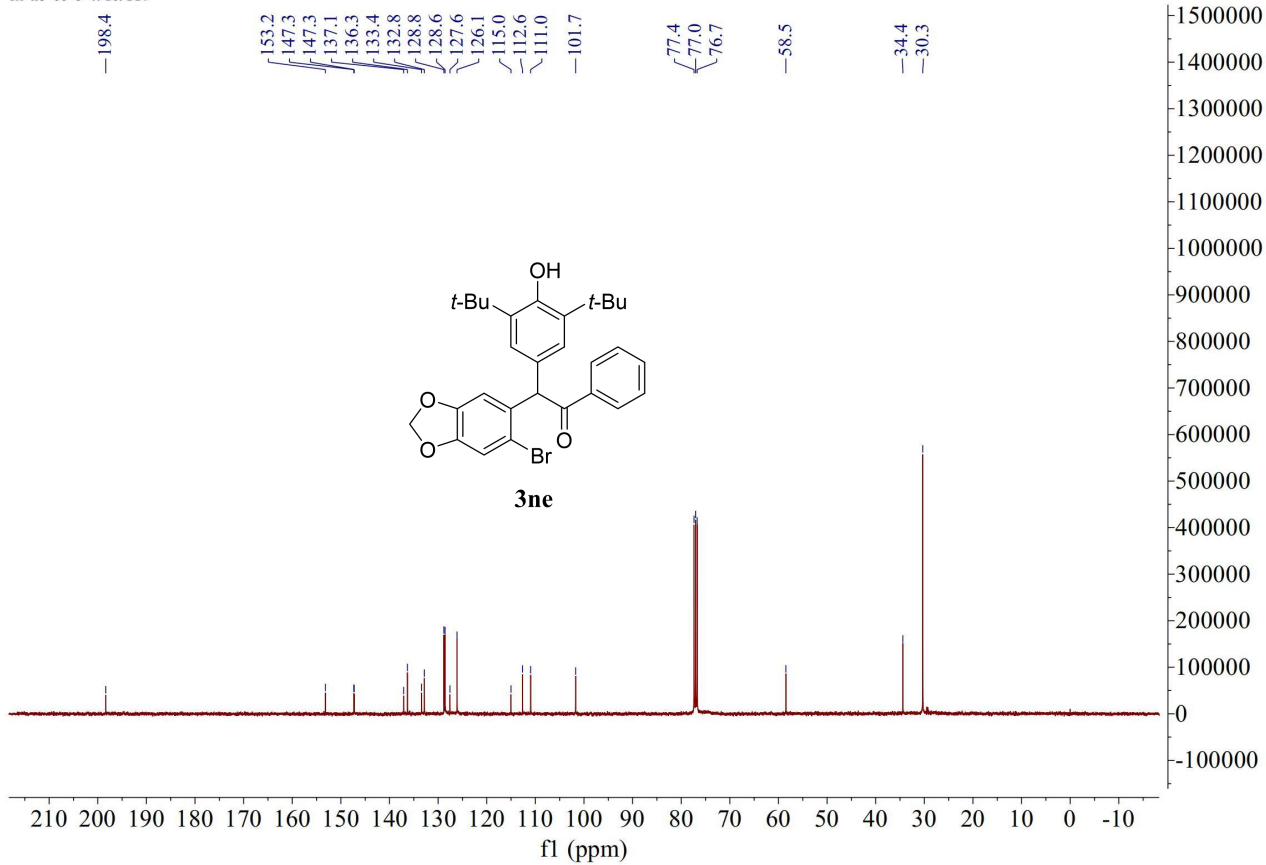
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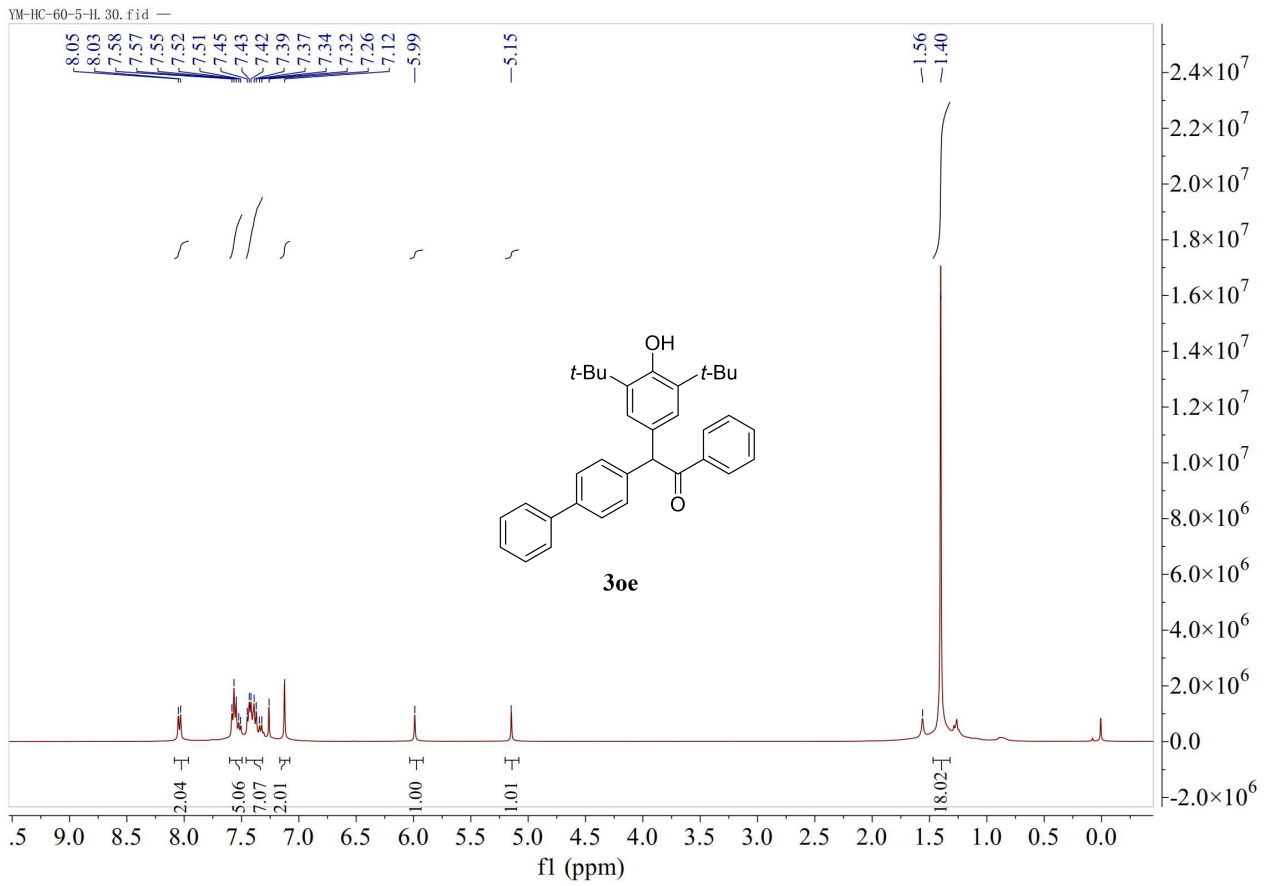
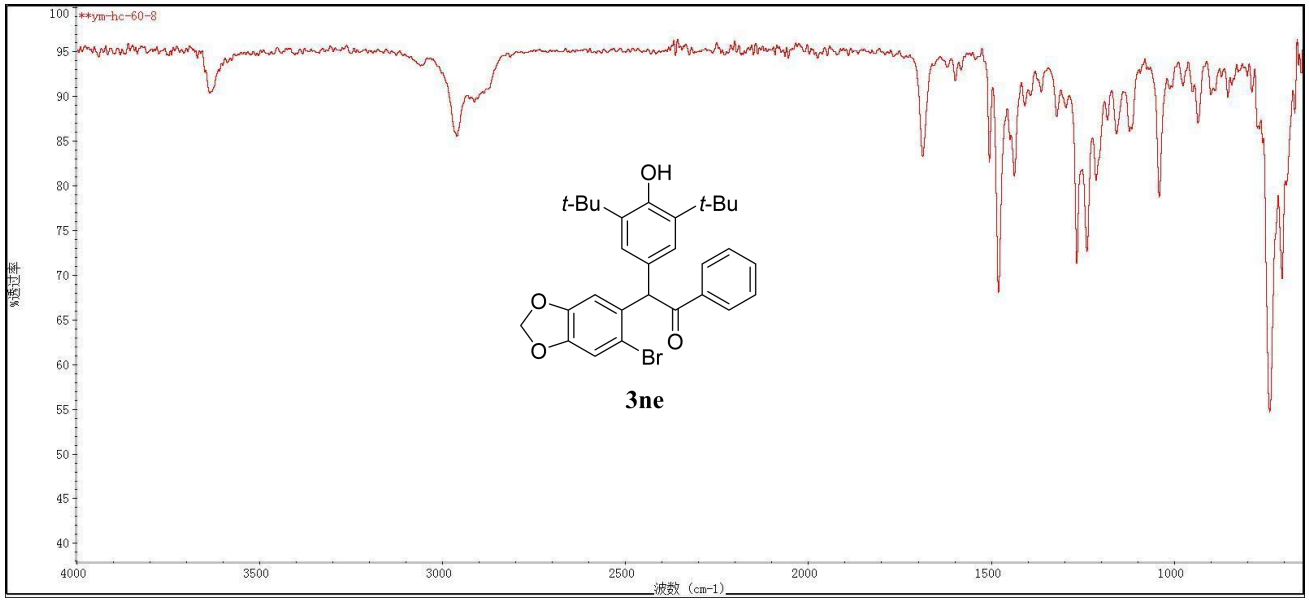


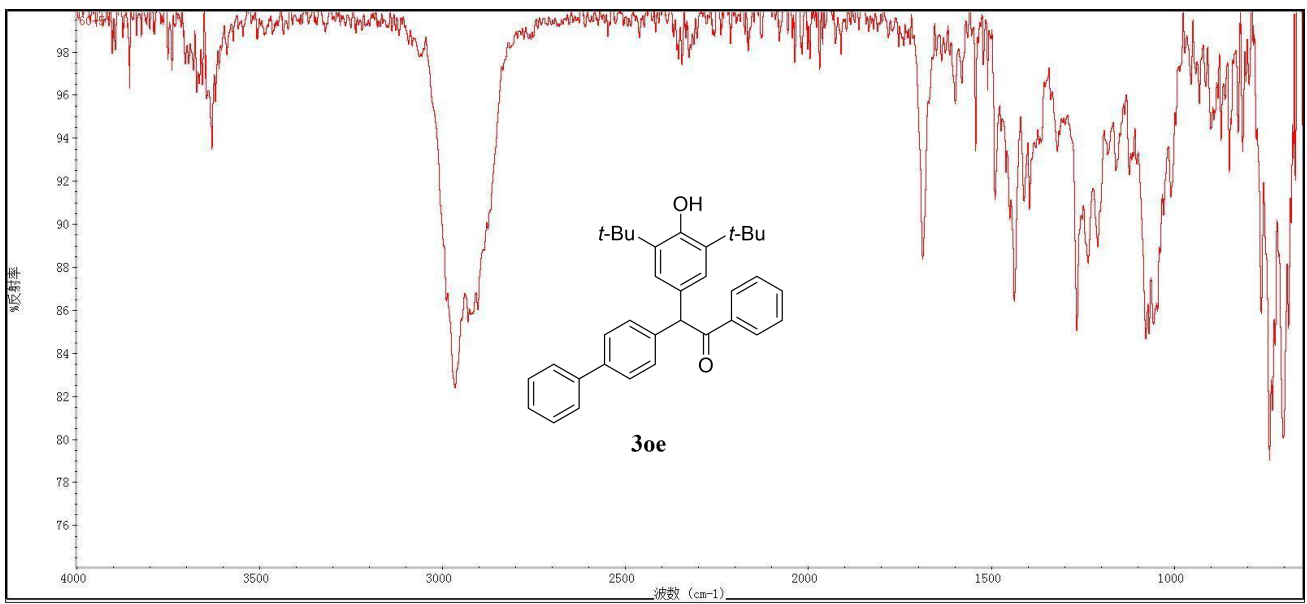
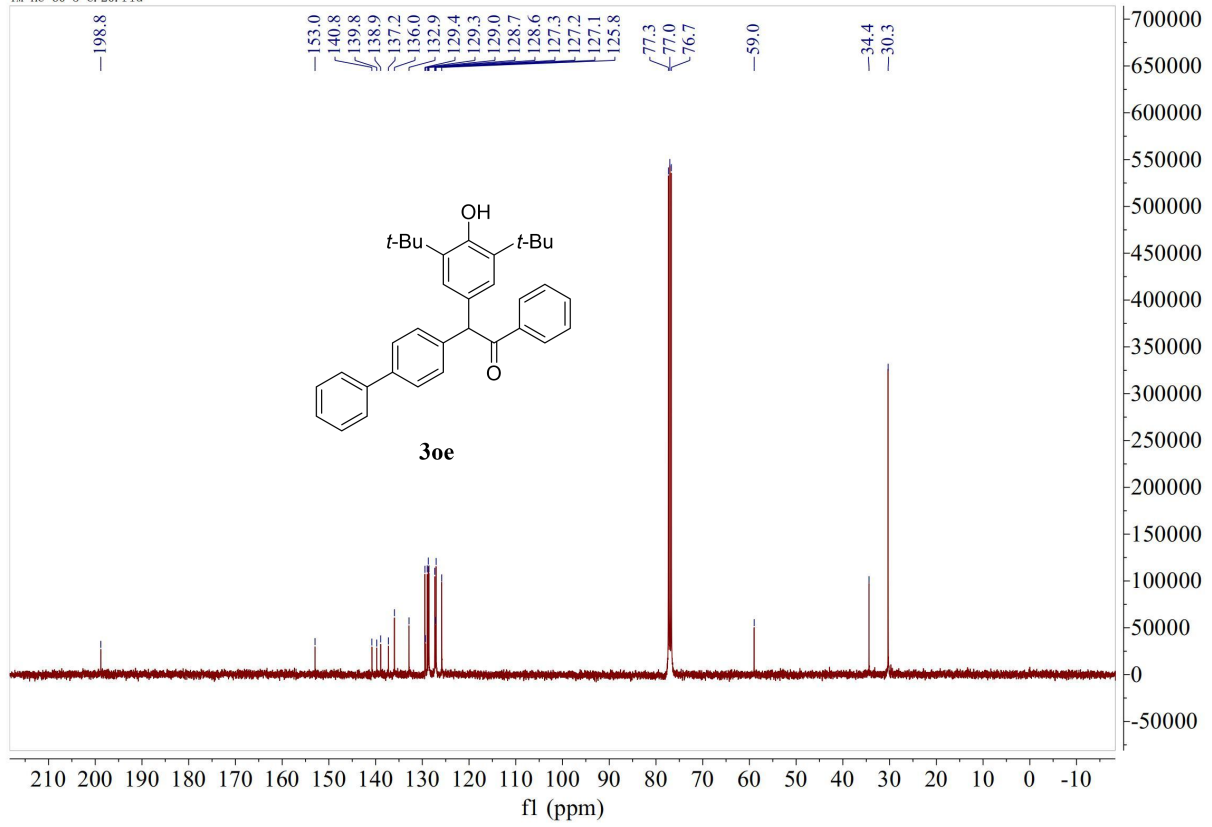
YM-HC-60-8-H. 20. fid

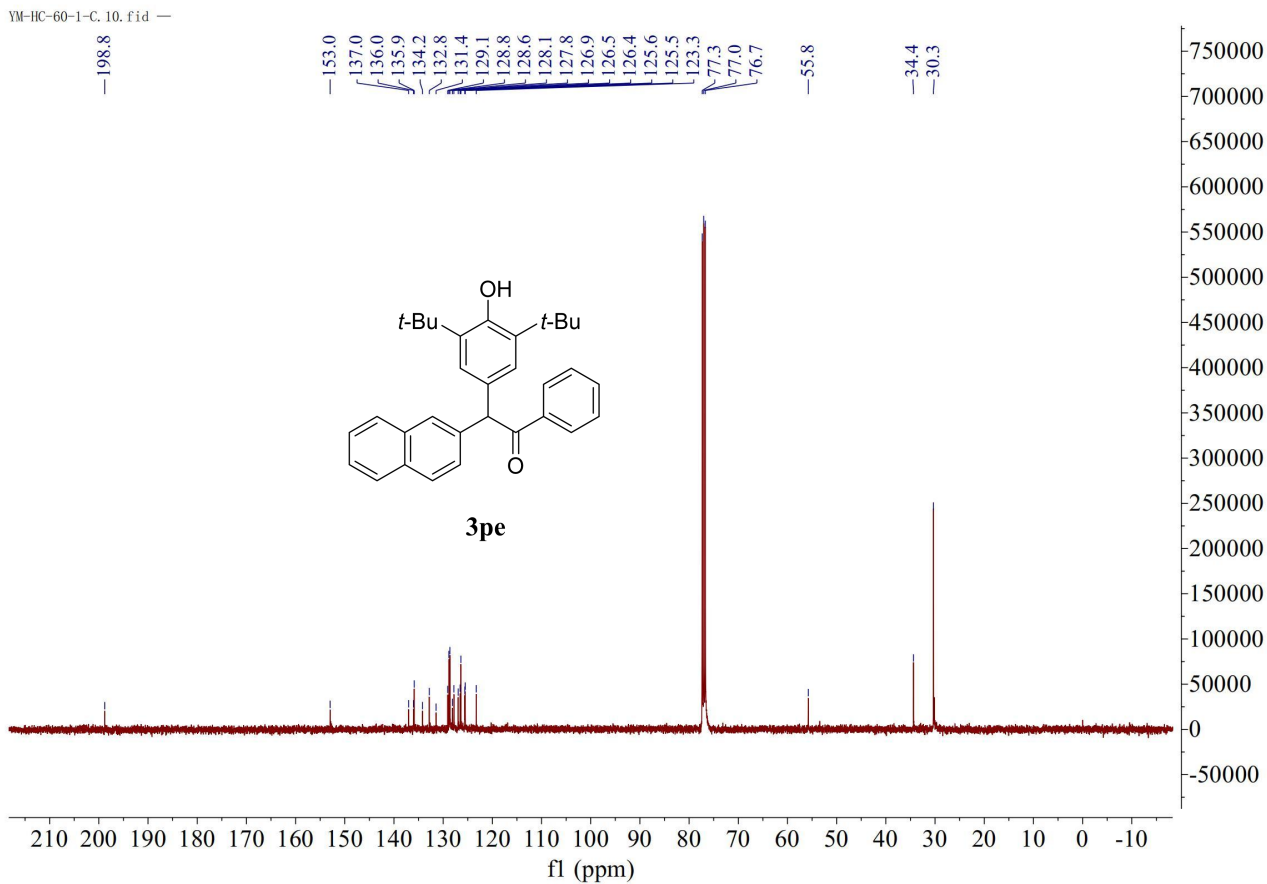
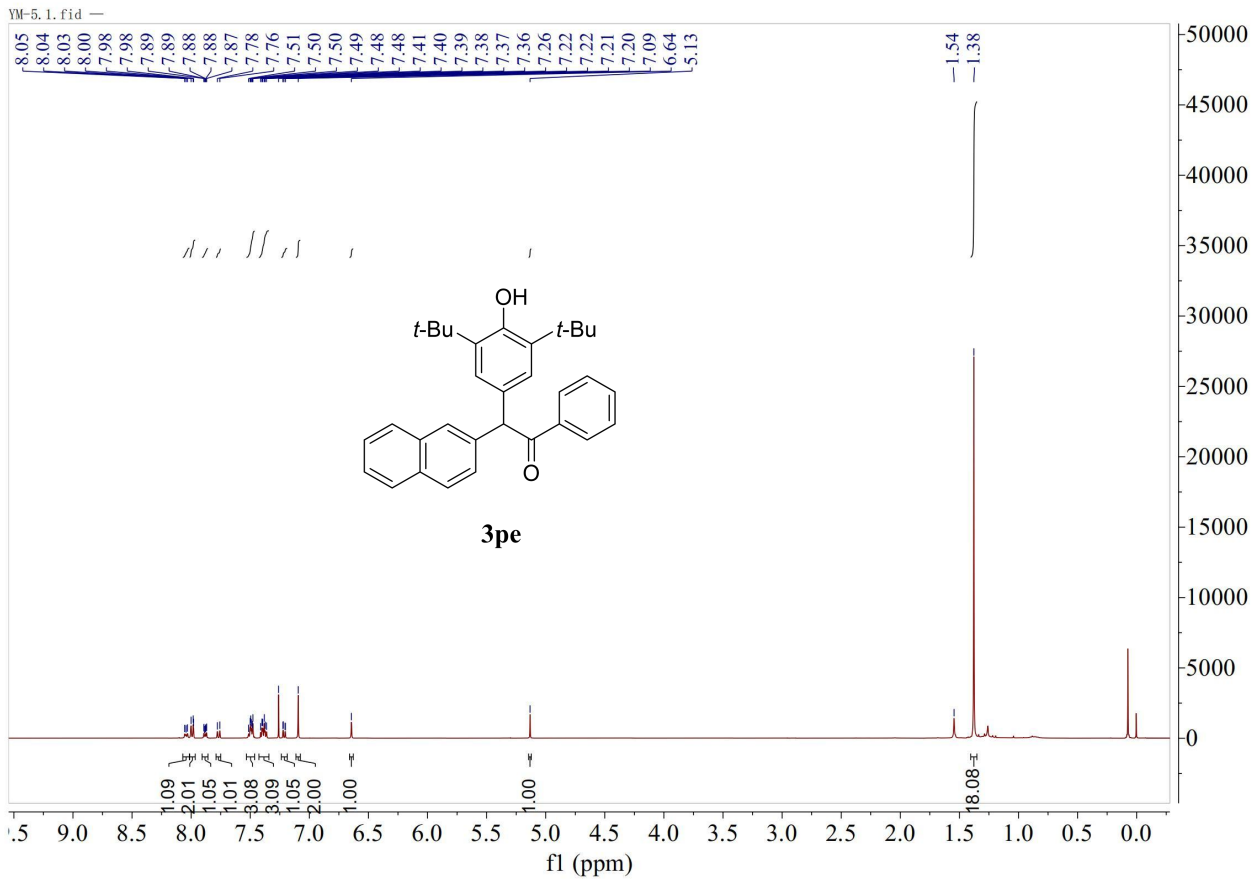


YM-hc-60-8-C. 10. fid

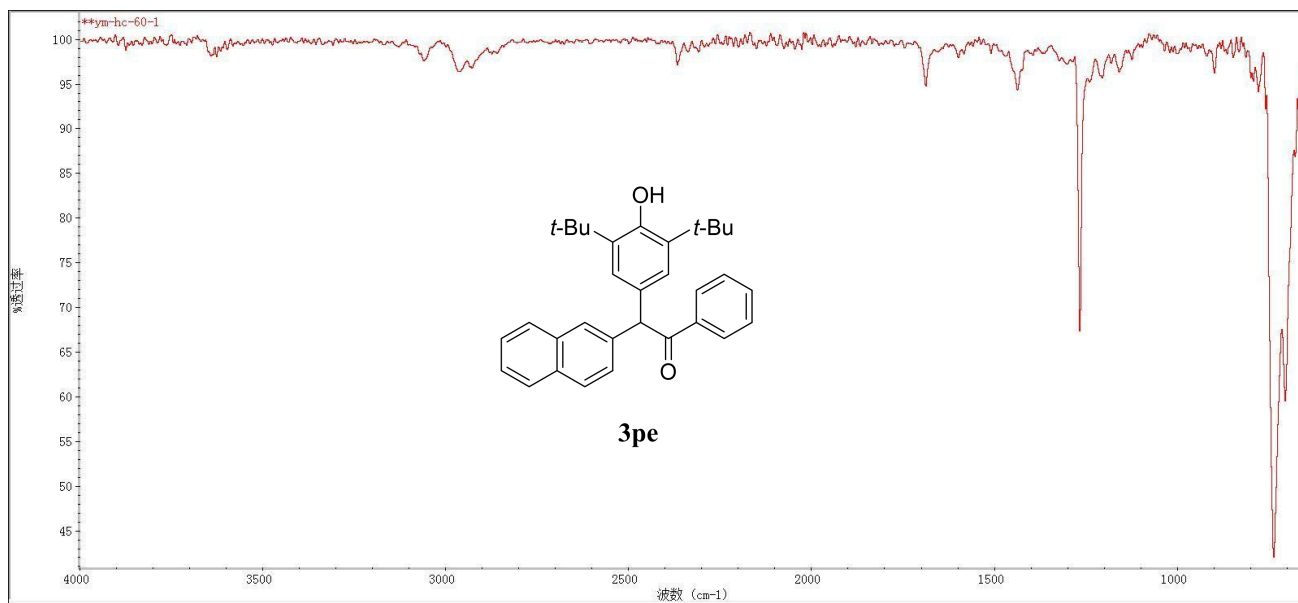








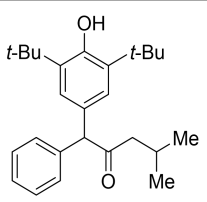
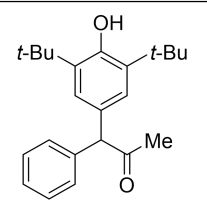




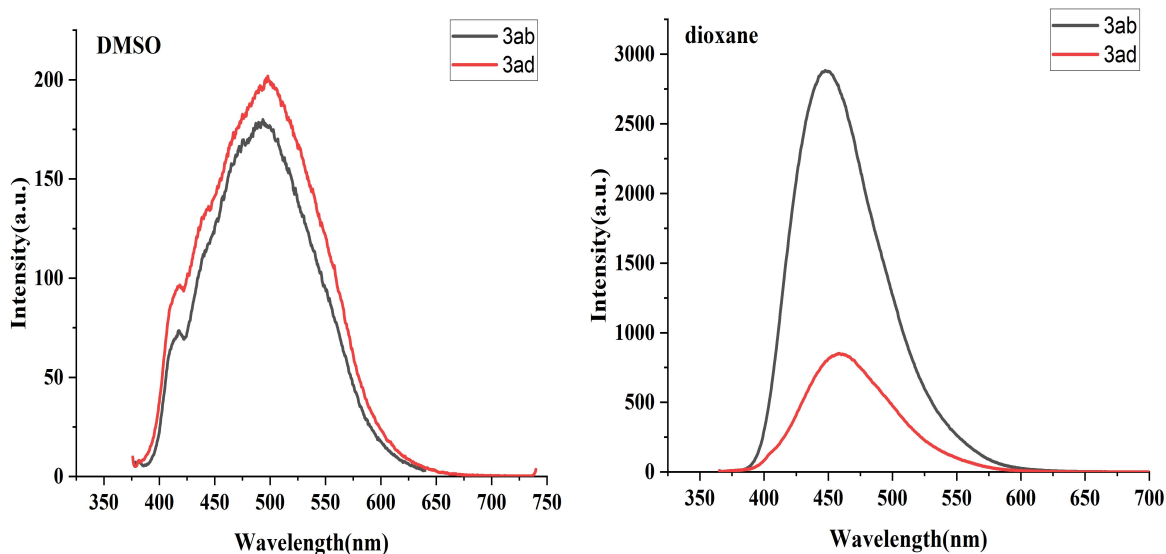
## 6. Fluorescence spectra analysis of pyridine compounds (3ab, 3ad).

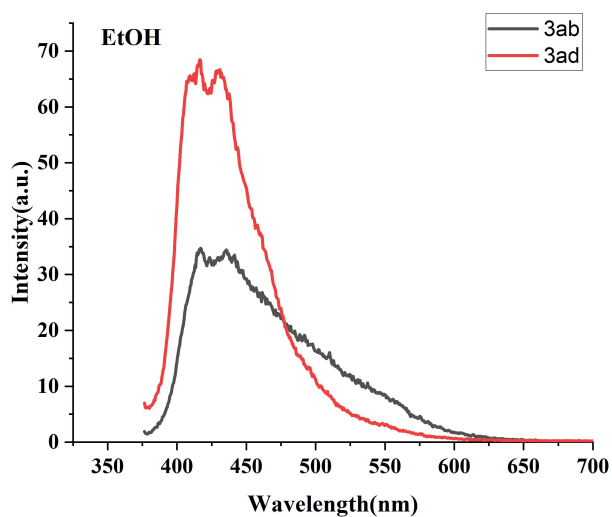
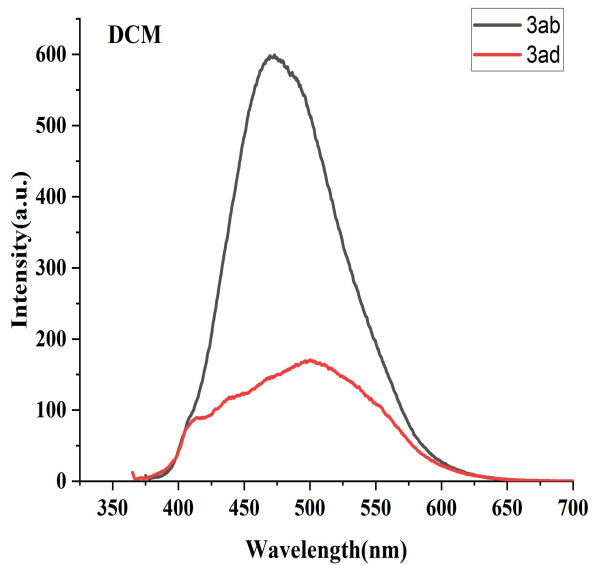
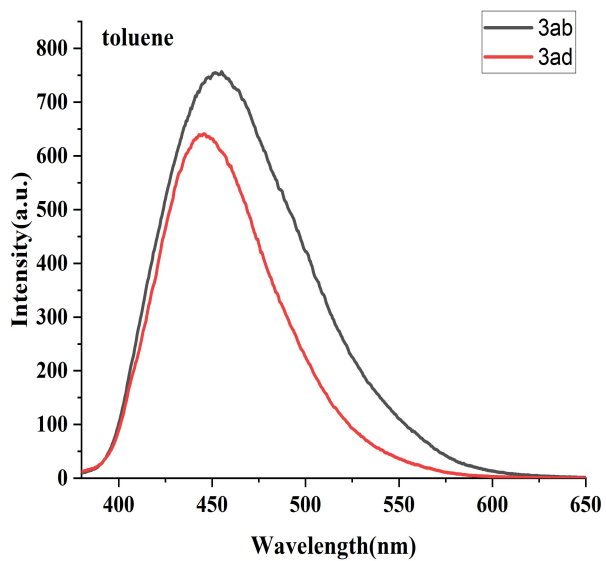
Experiments were set up using 96 well plates with black flat bottoms. 5 mM solution (3ab, 3ad,) in DMSO, dioxane, toluene, DCM and EtOH were separately placed in well plates and excited at range from 280 nm to 400 nm. The best results were chose to show as below.

### 6.1 Maximum intensity (I) of 3ab, 3ad and their emission wavelength ( $\lambda_{em}$ ) in organic solvents were obtained at the corresponding excitation wavelength.

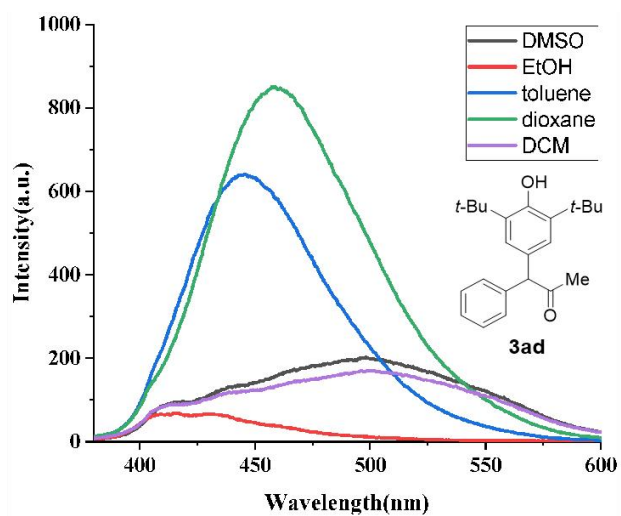
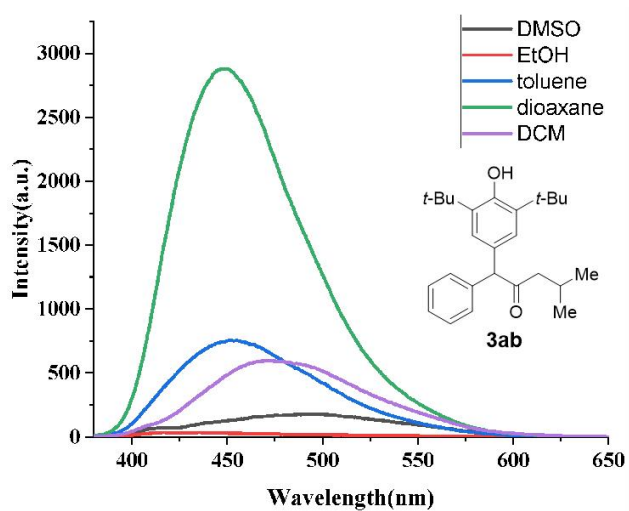
$\lambda_{em}$ I Compound	Solvent				
	DMSO	dioxane	toluene	DCM	EtOH
 <b>3ab</b>	494 nm 179	447 nm 2882	452 nm 754	473 nm 600	430 nm 33
 <b>3ad</b>	498 nm 201	458 nm 850	446 nm 640	500 nm 170	432 nm 66

### 6.2 Spectral characteristics of $\alpha,\alpha'$ -diarylated ketones in DMSO, dioxane, toluene, DCM and EtOH.

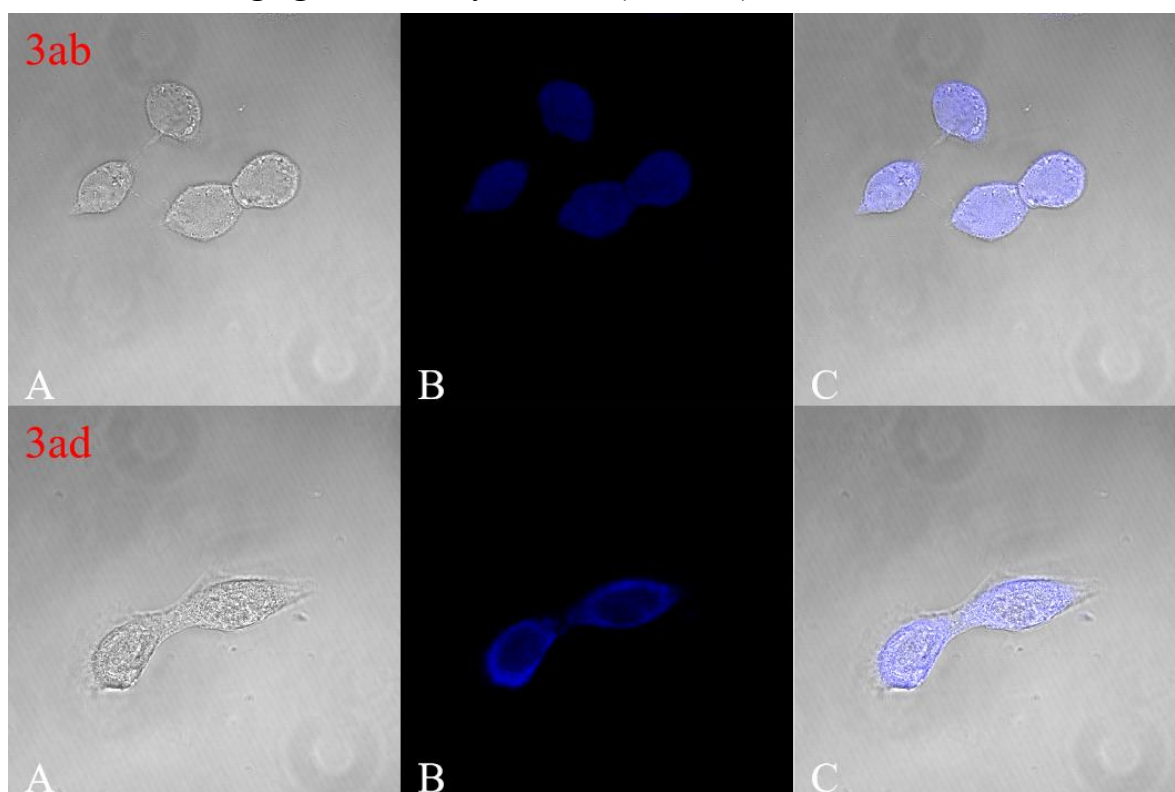




### 6.3 Hotophysical properties in five selected organic solvents.



7. Live HeLa cell Imaging of  $\alpha,\alpha'$ -diaryl ketones (3ab, 3ad).



Live HeLa cell imaging after 2 h incubation. (A) Bright field; (B) DAPI channel:  $\lambda_{\text{ex}}=405$  nm; (C) Merged image.