SUPPLEMENTARY INFORMATION

Uranyl-Catalyzed Hydrosilation of *para*-Quinone Methides: Access to Diarylmethane Derivatives

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1. General considerations

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a 500 MHz Bruker FT-NMR spectrometers (500 MHz or 125 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). Mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). GC-MS experiments were performed on an JEOL JMS-Q1050GC Master-Quad GC/MS. Commercial reagents and solvents were purchased from J&K Chemical and Beijing Ouhe Technology Company, and they were directly used without further purification. Organic solutions were concentrated under reduced pressure on a Heidolph rotary evaporator using an alcohol-ice bath. Chromatographic purification of products was accomplished by column chromatography on silica gel (Qingdao Haiyang, 200-300 mesh). Thin layer chromatography (TLC) was performed on Shandong Jiangyou 0.2 mm silica gel plates.

2. General procedure for synthesis of starting materials 1

In a Dean-Stark apparatus, a solution of phenols (10.0 mmol) and the corresponding aldehydes (10.0 mmol) in toluene (40 mL) was heated to reflux. Piperidine (20.0 mmol, 2.0 mL) was dropwise added over 0.5 h. The reaction mixture was continued to reflux for overnight. After cooling just below the boiling point of the reaction mixture, acetic anhydride (20.0 mmol, 2.0 mL) was added, and stirring was continued for 30 min. Then, the reaction mixture was poured on ice-water (200 mL) and extracted with EtOAc (4 × 50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, and the solvent of the filtrate was removed under reduced pressure. The crude products were purified by flash column chromatography, affording the desired substrate *p*-QMs[1].

3. Typical procedure for uranyl-catalyzed synthesis of diarylmethane and triarylmethane derivatives

To a 10 mL Schlenk tube, 2,6-di-alkyl-4-(arylidene)cyclohexa-2,5-dien-1-one (0.2 mmol), $UO_2(NO_3)_2 \cdot 6H_2O$ (5.0 mol %), CH_3CN (2 mL) and Et_3SiH (0.4 mmol, 2.0 equiv.) were added, then the system was sealed and stirred and the reaction mixture was stirring for 12 h. After the reaction was completed, the reaction solution was concentrated under reduced pressure to yield crude product, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate) to give the desired product **3**.

Caution, the silica gel used for column chromatography has been contaminated by uranium, which would be disposed as radioactive solid waste by government authorities.

4. In situ NMR and GC-MS experiments

To a 10 mL Schlenk tube, 4-benzylidene-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**1a**, 0.05 mmol), $UO_2(NO_3)_2 \cdot 6H_2O$ (1.3 mg, 5.0 mol %), CD_3CN (0.5 mL) and Et_3SiH (16 μL, 0.1 mmol, 2.0 equiv.) were added, then the system was sealed and stirred for 12 h. After the reaction was completed, the reaction mixture was detected by ^{1}H-NMR and subjected to GC-MS analysis. Through the GC-MS analysis, we can see that the main byproduct was $Et_3SiOSiEt_3$ (Comparing with the spectra in the GC-MS library, the similarity reached 97.9%), which has been further confirmed by ^{1}H-NMR.

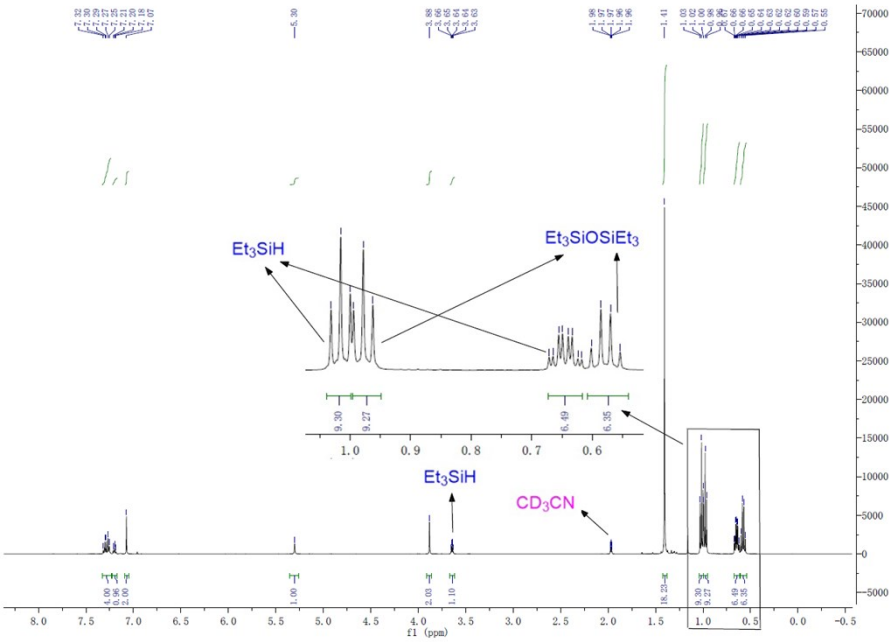


Figure S1. In situ NMR in CD_3CN

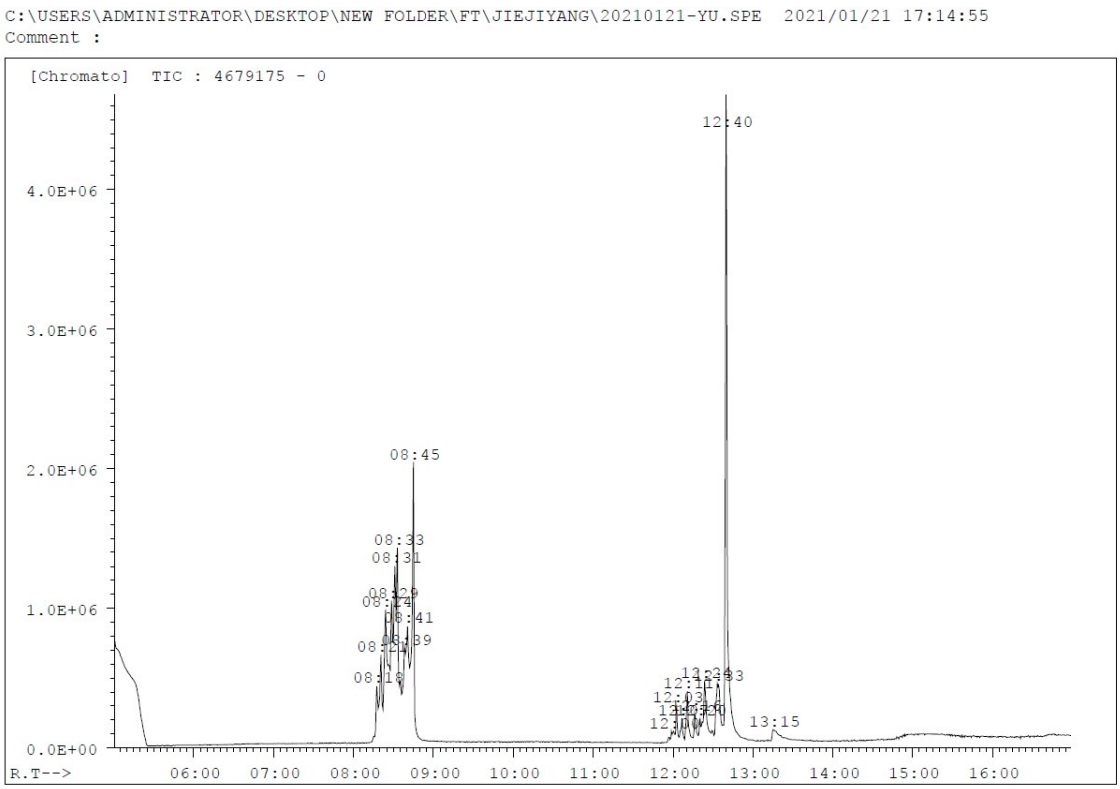


Figure S2. GC-MS analysis. Gradient conditions: 75 °C hold for 3 minutes, then heats up to 200 °C with a rate of 22 °C/min. Subsequently, the temperature rises to 300 °C with a rate of 30 °C/min and sustains for 5 minutes. The whole test time is 17 minutes

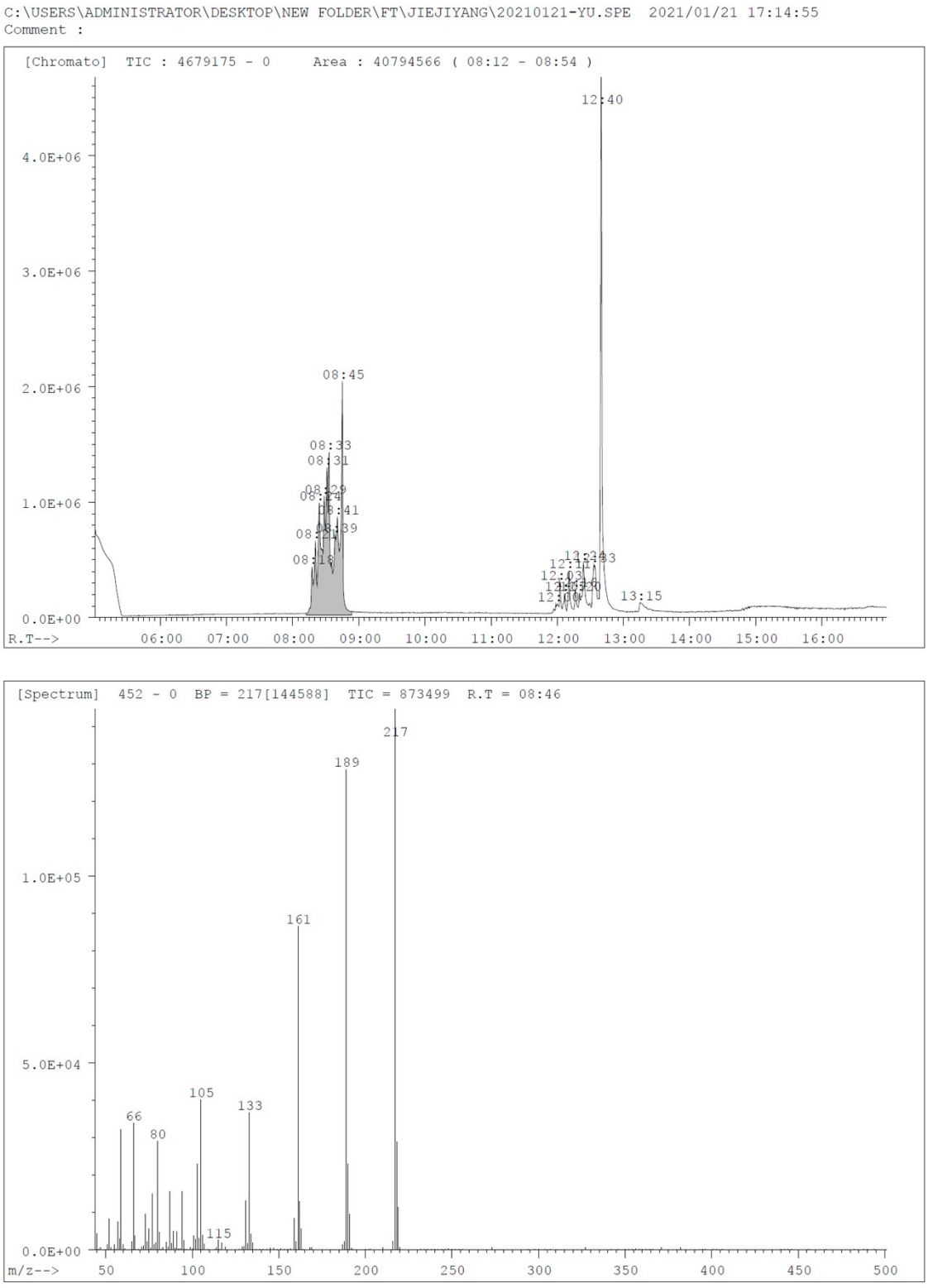


Figure S3. Fragment peaks of the component with retention time from 8:12 to 8:54

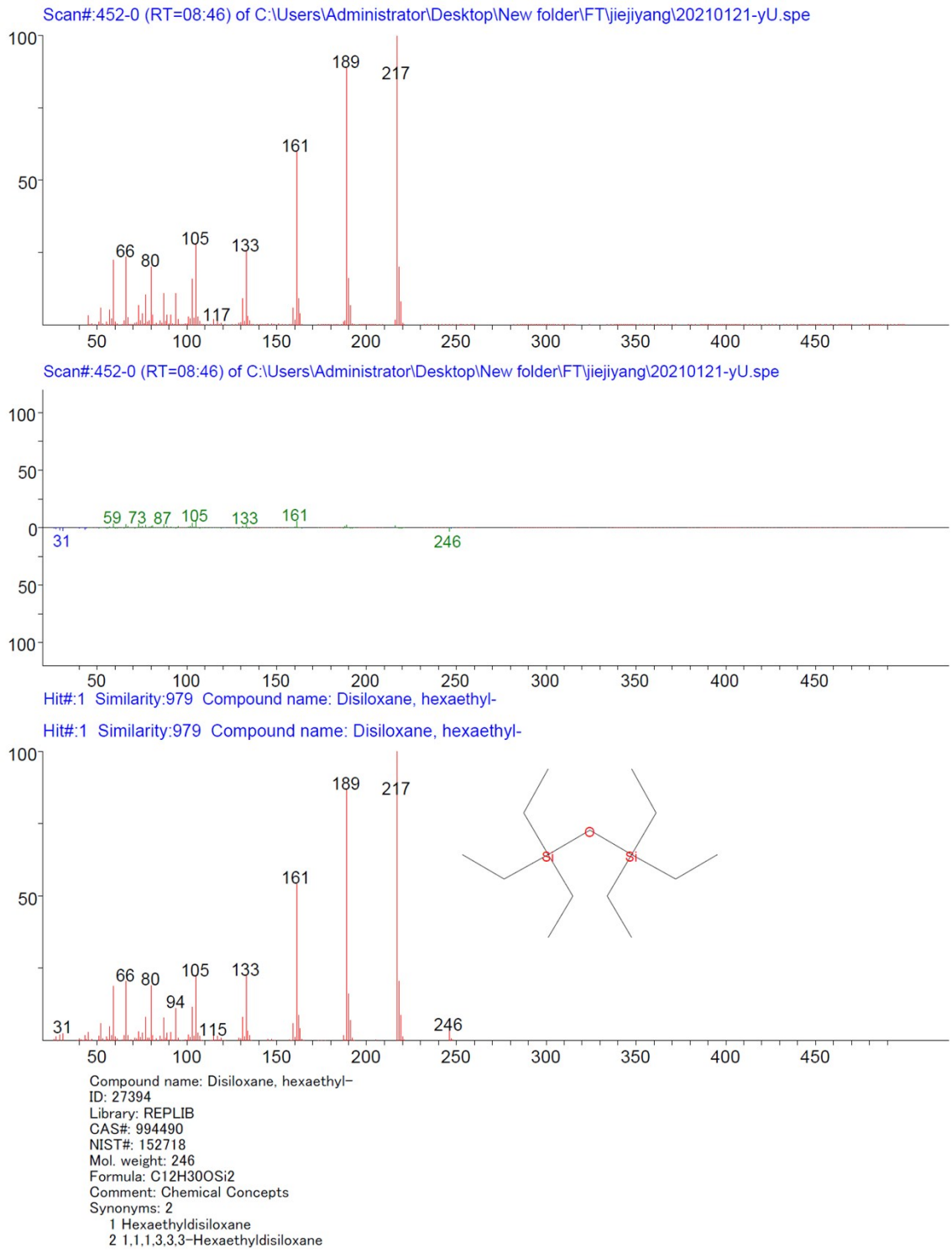


Figure S4. The component was identified as $Et_3SiOSiEt_3$ by comparing it with the spectra in standard library of GC-MS

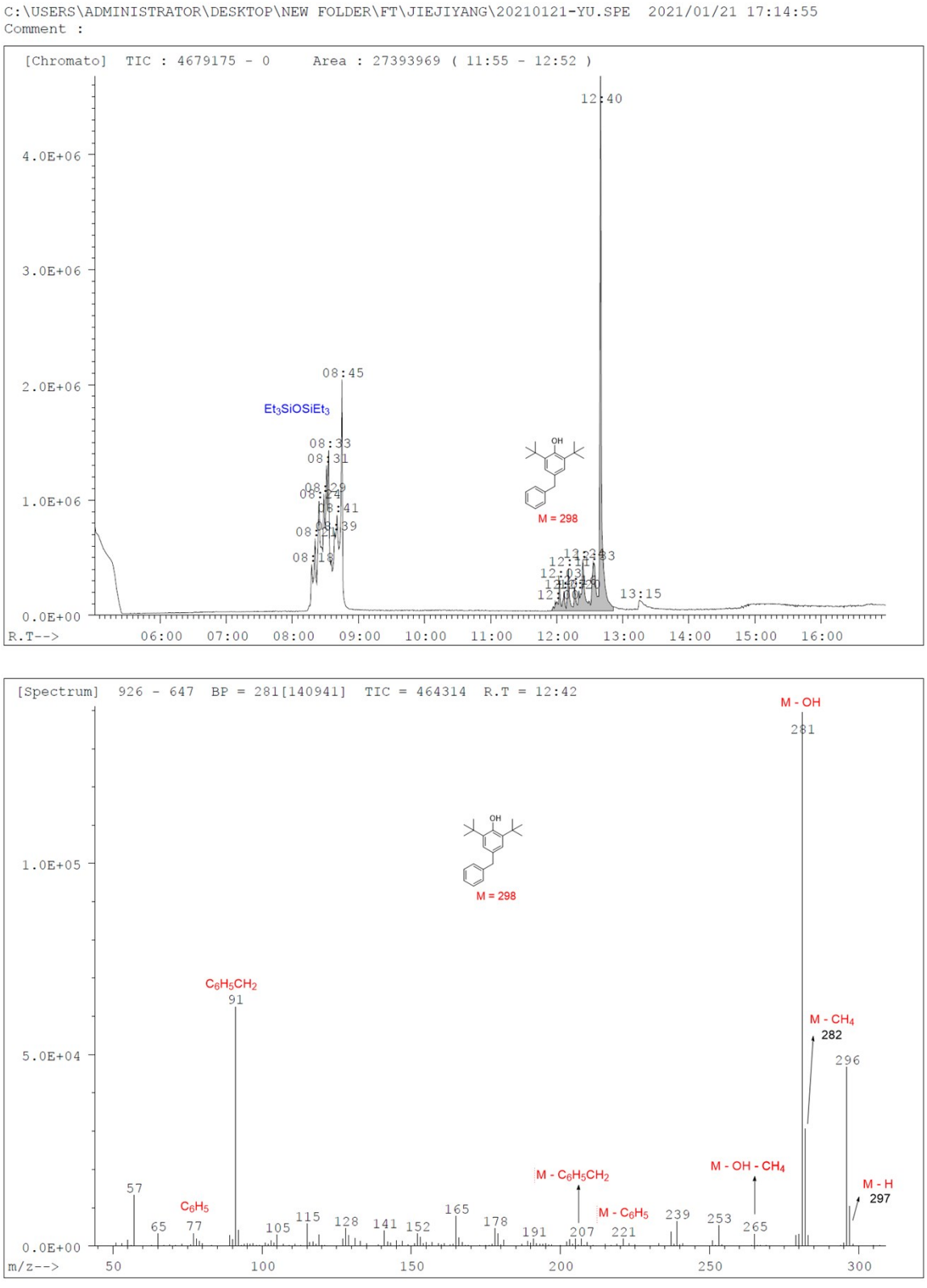
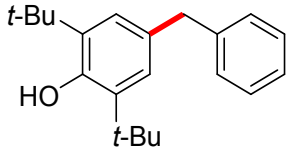


Figure S5. The component was identified as product 3a

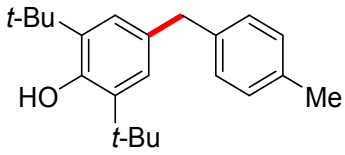
5. Characterization data of the compounds.

4-benzyl-2,6-di-tert-butylphenol (3a)



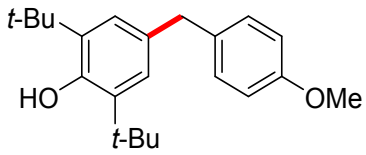
Light yellow gum; 29.4 mg; yield: 99%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28 (t, J = 7.5 Hz, 2H), 7.20-7.16 (m, 3H), 6.98 (s, 2H), 5.05 (s, 1H), 3.90 (s, 2H), 1.40 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 152.0; 141.8; 135.8; 131.5; 128.8; 128.3; 125.8; 125.4; 41.8; 34.3; 30.3. ESI-MS (m/z): Calcd for $C_{21}H_{29}O$, $[M+H]^+$: 297.2.

2,6-di-tert-butyl-4-(4-methylbenzyl)phenol (3b)



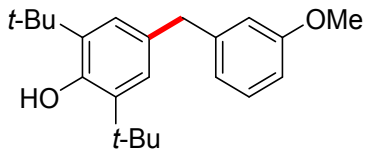
Light yellow solid; Mp 70-73 ^{o}C; 22.9 mg; yield: 74%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.08 (s, 4H), 6.98 (s, 2H), 5.03 (s, 1H), 3.85 (s, 2H), 2.31 (s, 3H), 1.40 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 151.9; 138.7; 135.7; 135.2; 131.8; 129.0; 128.6; 125.4; 41.4; 34.2; 30.3. ESI-MS (m/z): Calcd for $C_{22}H_{31}O$, $[M+H]^+$: 311.2.

2,6-di-tert-butyl-4-(4-methoxybenzyl)phenol（3c）



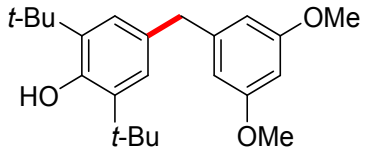
Light yellow solid; Mp 139-141 ^{o}C; 20.5 mg; yield: 63%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.11 (d, J = 8.4 Hz, 2H), 6.97 (s, 2H), 6.83 (d, J = 8.5 Hz, 2H), 5.04 (s, 1H), 3.84 (s, 2H), 3.78 (s, 3H), 1.40 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 157.8; 152.0; 135.8; 133.9; 132.0; 129.7; 125.3; 113.8; 55.2; 40.9; 34.3; 30.3. ESI-MS (m/z): Calcd for $C_{22}H_{31}O_2$, $[M+H]^+$: 327.2.

2,6-di-tert-butyl-4-(3-methoxybenzyl)phenol (3d)



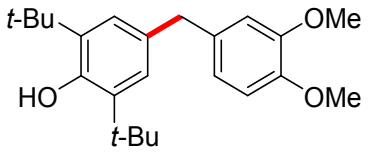
Light yellow solid; Mp 67-70 °C; 25.1 mg; yield: 77%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20 (t, J = 9.7 Hz, 1H), 6.99 (s, 2H), 6.81 and 6.79 (d, J = 7.5 Hz, 1H), 6.73 (t, J = 8.7 Hz, 2H), 5.05 (s, 1H), 3.87 (s, 2H), 3.77 (s, 3H), 1.41 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 159.6; 152.0; 143.4; 135.8; 131.3; 129.2; 125.4; 121.3; 114.6; 111.0; 55.1; 41.8; 34.2; 30.3. ESI-MS (m/z): Calcd for $C_{22}H_{30}O_2Na$, $[M+Na]^+$: 349.2.

2,6-di-tert-butyl-4-(3,5-dimethoxybenzyl)phenol (3e)



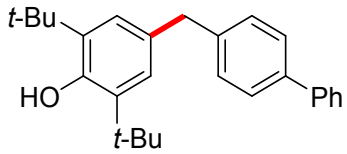
Light yellow gum; 10.3 mg; yield: 29%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.00 (s, 2H), 6.37 and 6.36 (d, J = 2.1 Hz, 2H), 6.30 (t, J = 2.1 Hz, 1H), 5.06 (s, 1H), 3.83 (s, 2H), 3.76 (s, 6H), 1.41 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 160.7; 152.1; 144.2; 135.8; 131.0; 125.4; 107.0; 97.8; 55.2; 42.0; 34.3; 30.3. ESI-MS (m/z): Calcd for $C_{23}H_{32}O_3Na$, $[M+Na]^+$: 379.2.

2,6-di-tert-butyl-4-(3,4-dimethoxybenzyl)phenol (3f)



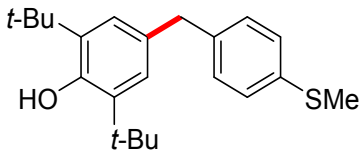
Light yellow solid; Mp 80-84 °C; 22.1 mg; yield: 62%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.98 (s, 2H), 6.80 (d, J = 7.8 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 5.05 (s, 1H), 3.86 (s, 6H), 3.84 (s, 2H), 1.41 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 152.0; 148.8; 147.2; 135.8; 134.3; 131.7; 125.2; 120.8; 112.2; 111.2; 55.9; 55.8; 41.2; 34.3; 30.3. ESI-MS (m/z): Calcd for $C_{23}H_{32}O_3Na$, $[M+Na]^+$: 379.2.

4-([1,1'-biphenyl]-4-ylmethyl)-2,6-di-tert-butylphenol (3g)



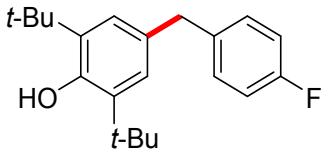
Light yellow gum; 16.0 mg; yield: 43%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 and 7.57 (d, J = 7.3 Hz, 2H), 7.53 and 7.51 (d, J = 8.1 Hz, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.28 and 7.26 (d, J = 8.0 Hz, 2H), 7.03 (s, 2H), 5.07 (s, 1H), 3.94 (s, 2H), 1.42 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 152.1; 141.1; 141.0; 138.7; 135.9; 131.4; 129.2; 128.7; 127.1; 126.9; 125.4; 41.5; 34.3; 30.3. ESI-MS (m/z): Calcd for $C_{27}H_{33}O_3$, $[M+H]^+$: 373.3.

2,6-di-tert-butyl-4-(4-(methylthio)benzyl)phenol (3h)



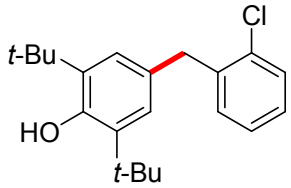
Light yellow solid; Mp 111-114 ^{o}C; 10.6 mg; yield: 31%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20 and 7.19 (d, J = 8.2 Hz, 1H), 7.13 and 7.11 (d, J = 5.2 Hz, 1H), 6.97 (s, 2H), 5.06 (s, 1H), 3.85 (s, 2H), 2.46 (s, 3H), 1.41 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 152.1; 139.0; 135.8; 135.3; 131.4; 129.3; 127.1; 125.3; 41.3; 34.3; 30.3. ESI-MS (m/z): Calcd for $C_{22}H_{31}OS$, $[M+H]^+$: 343.2.

2,6-di-tert-butyl-4-(4-fluorobenzyl)phenol (3i)



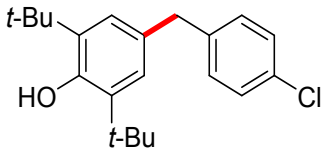
Light yellow solid; Mp 99-102 ^{o}C; 16.3 mg; yield: 52%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.24-7.13 (m, 2H), 6.98-6.96 (m, 4H), 5.06 (s, 1H), 3.86 (s, 2H), 1.40 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 162.3 (d, $^{1}J_{CF}$ = 243.4 Hz), 152.1; 135.9; 131.4; 130.2 (d, $^{3}J_{CF}$ = 7.8 Hz); 125.3; 115.0 (d, $^{2}J_{CF}$ = 21.1 Hz); 40.9; 34.3; 30.3. ^{19}F NMR (471 MHz, $CDCl_3$): δ = -117.83. ESI-MS (m/z): Calcd for $C_{21}H_{28}FO$, $[M+H]^+$: 315.2.

2,6-di-tert-butyl-4-(2-chlorobenzyl)phenol (3j)



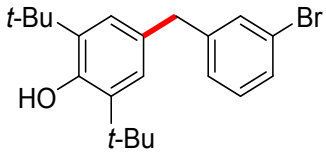
Light yellow solid; Mp 74-76 °C; 28.1 mg; yield: 85%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29 (dd, J = 1.7 Hz, J = 4.3 Hz, 1H), 7.10-7.04 (m, 3H), 6.95 (s, 2H), 4.99 (s, 1H), 3.93 (s, 2H), 1.33 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 151.1; 138.5; 134.8; 133.0; 129.7; 128.9; 128.3; 126.2; 125.7; 124.6; 37.9; 33.2; 29.3. ESI-MS (m/z): Calcd for $C_{21}H_{28}ClO$, $[M+H]^+$: 331.3.

2,6-di-tert-butyl-4-(4-chlorobenzyl)phenol (3k)



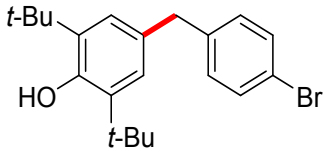
Light yellow solid; Mp 103-105 °C; 21.1 mg; yield: 64%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.24 (d, J = 8.3 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 6.95 (s, 2H), 5.07 (s, 1H), 3.86 (s, 2H), 1.40 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 152.1; 140.3; 135.9; 131.5; 131.0; 130.1; 128.4; 125.3; 41.1; 34.3; 30.3. ESI-MS (m/z): Calcd for $C_{21}H_{28}ClO$, $[M+H]^+$: 331.3.

4-(3-bromobenzyl)-2,6-di-tert-butylphenol (3l)



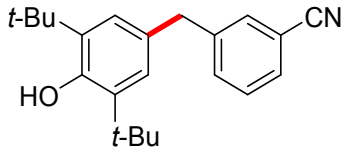
Light yellow gum; 33.4 mg; yield: 89%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28 (s, 1H), 7.25 and 7.24 (d, J = 7.5 Hz, 1H), 7.09-7.04 (m, 2H), 6.89 (s, 2H), 5.02 (s, 1H), 3.79 (s, 2H), 1.34 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 151.2; 143.1; 134.9; 130.8; 129.6; 128.8; 127.9; 126.4; 124.4; 121.4; 40.4; 33.3; 29.2. ESI-MS (m/z): Calcd for $C_{21}H_{28}BrO$, $[M+H]^+$: 375.3.

4-(4-bromobenzyl)-2,6-di-tert-butylphenol (3m)



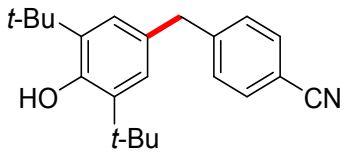
Light yellow solid; Mp 71-74 °C; 29.6 mg; yield: 79%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.3 Hz, 2H), 7.06 (d, J = 8.2 Hz, 2H), 6.95 (s, 2H), 5.07 (s, 1H), 3.84 (s, 2H), 1.40 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 152.2; 140.8; 135.9; 131.3; 130.9; 130.5; 125.3; 119.6; 41.2; 34.3; 30.2. ESI-MS (m/z): Calcd for $C_{21}H_{27}BrONa$, $[M+Na]^+$: 375.3.

3-(3,5-di-tert-butyl-4-hydroxybenzyl)benzonitrile (3n)



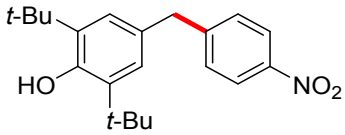
Light yellow solid; Mp 85-87 °C; 27.3 mg; yield: 85%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42-7.35 (m, 3H), 7.32-7.17 (m, 1H), 6.86 (s, 2H), 5.05 (s, 1H), 3.84 (s, 2H), 1.34 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 151.4; 142.3; 135.2; 132.3; 131.3; 128.9; 128.7; 128.0; 124.2; 118.0; 111.3; 40.3; 33.3; 29.2. ESI-MS (m/z): Calcd for $C_{22}H_{28}NO$, $[M+H]^+$: 322.1.

4-(3,5-di-tert-butyl-4-hydroxybenzyl)benzonitrile (3o)



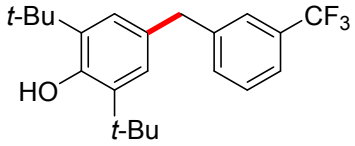
Light yellow solid; Mp 127-130 °C; 22.5 mg; yield: 70%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 6.93 (s, 2H), 5.12 (s, 1H), 3.94 (s, 2H), 1.41 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 152.4; 147.5; 136.2; 132.2; 129.8; 129.5; 125.4; 119.1; 109.7; 41.9; 34.3; 30.2. ESI-MS (m/z): Calcd for $C_{22}H_{28}NO$, $[M+H]^+$: 322.1.

2,6-di-tert-butyl-4-(4-nitrobenzyl)phenol (3p)



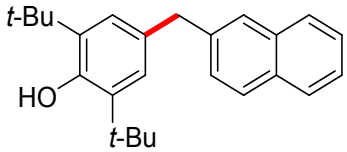
Light yellow solid; Mp 67-70 °C; 15.0 mg; yield: 44%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 6.95 (s, 2H), 5.13 (s, 1H), 3.99 (s, 2H), 1.41 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 152.5; 149.7; 136.2; 129.7; 129.5; 125.4; 123.6; 41.7; 34.3; 30.2. ESI-MS (m/z): Calcd for $C_{21}H_{27}NNaO_3$, $[M+Na]^+$: 364.2.

2,6-di-tert-butyl-4-(3-trifluoromethyl)phenol (3q)



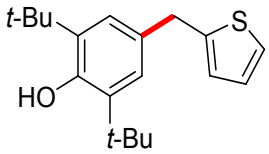
Light yellow gum; 24.4 mg; yield: 67%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40-7.37 (m, 2H), 7.33-7.17 (m, 2H), 6.89 (s, 2H), 5.02 (s, 1H), 3.88 (s, 2H), 1.33 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 152.3; 142.7; 136.1; 132.3 (q, $^{4}J_{CF}$ = 1.1 Hz); 130.6 (q, $^{2}J_{CF}$ = 30.6 Hz); 130.5; 128.8; 125.6 (q, $^{3}J_{CF}$ = 3.8 Hz); 125.4; 124.3 (q, $^{1}J_{CF}$ = 270.4 Hz); 122.8 (q, $^{3}J_{CF}$ = 3.8 Hz); 41.5; 34.3; 30.3. ^{19}F NMR (471 MHz, $CDCl_3$): δ = -62.52. ESI-MS (m/z): Calcd for $C_{22}H_{28}FO_3$, $[M+H]^+$: 365.2.

2,6-di-tert-butyl-4-(naphthalen-2-ylmethyl)phenol (3r)



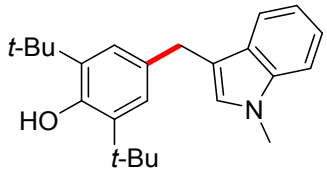
Light yellow solid; Mp 108-110 °C; 24.9 mg; yield: 72%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80-7.75 (m, 3H), 7.63 (s, 1H), 7.46-7.40 (m, 2H), 7.36 and 7.34 (dd, J = 1.3 Hz, J = 1.3 Hz, 1H), 7.04 (s, 2H), 5.07 (s, 1H), 4.06 (s, 2H), 1.40 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 152.1; 139.3; 135.8; 133.6; 132.0; 131.4; 127.8; 127.7; 127.6; 127.5; 126.8; 125.8; 125.5; 125.1; 42.0; 34.3; 30.3. ESI-MS (m/z): Calcd for $C_{25}H_{31}O$, $[M+H]^+$: 347.1.

2,6-di-tert-butyl-4-(thiophen-2-ylmethyl)phenol (3s)



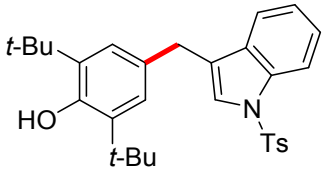
Light yellow gum; 17.8 mg; yield: 59%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.06 and 7.04 (dd, J = 0.8 Hz, J = 0.8 Hz, 1H), 6.98 (s, 2H), 6.85-6.83 (m, 1H), 6.71 (m, 1H), 5.01 (s, 1H), 4.00 (s, 2H), 1.35 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 152.3; 145.0; 135.9; 130.9; 126.7; 125.1; 124.7; 123.5; 35.9; 34.3; 30.3. ESI-MS (m/z): Calcd for $C_{19}H_{27}OS$, $[M+H]^+$: 303.2.

2,6-di-tert-butyl-4-((1-methyl-1H-indol-3-yl)methyl)phenol (3t)



Light yellow gum; 23.7 mg; yield: 68%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62 and 7.60 (d, J = 7.9 Hz, 1H), 7.28 and 7.26 (d, J = 8.1 Hz, 1H), 7.23-7.19 (m, 1H), 7.12 (s, 2H), 7.10-7.07 (m, 1H), 6.71 (s, 1H), 5.03 (s, 1H), 4.00 (s, 2H), 3.71 (s, 3H), 1.41 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 151.8; 137.1; 135.6; 131.8; 127.9; 126.8; 125.3; 121.4; 119.2; 118.6; 115.3; 109.0; 34.3; 32.5; 31.4; 30.3. ESI-MS (m/z): Calcd for $C_{24}H_{31}NNaO$, $[M+Na]^+$: 372.2.

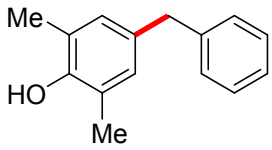
2,6-di-tert-butyl-4-((1-tosyl-1H-indol-3-yl)methyl)phenol (3u)



Light yellow solid; Mp 143-145 ^{o}C; 27.9 mg; yield: 57%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 and 7.99 (d, J = 8.3 Hz, 1H), 7.72 and 7.70 (d, J = 8.3 Hz, 2H), 7.44 and 7.43 (d, J = 7.8 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.26 (s, 1H), 7.22 and 7.20 (d, J = 7.7 Hz, 1H), 7.19 and 7.17 (d, J = 8.2 Hz, 2H), 6.99 (s, 2H), 5.08 (s, 1H), 3.90 (s, 2H), 2.33 (s, 3H), 1.38 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 152.2; 144.6; 135.8; 131.1; 129.7; 129.4; 126.7; 125.2; 124.6; 123.7; 123.6; 123.0; 119.7; 113.8; 34.2; 30.3; 29.7. ESI-MS (m/z):

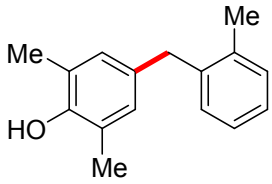
Calcd for $C_{30}H_{35}NNaO_3S$, $[M+Na]^+$: 512.2.

4-benzyl-2,6-dimethylphenol (3v)



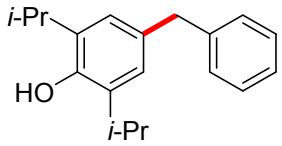
Light yellow solid; Mp 63-65 °C; 35.0 mg; yield: 83%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 (t, J = 7.6 Hz, 2H), 7.19-7.16 (m, 3H), 6.79 (s, 2H), 4.48 (s, 1H), 3.83 (s, 2H), 2.19 (s, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 150.5; 141.9; 132.8; 129.1; 128.8; 128.5; 126.0; 123.0; 41.2; 16.0. ESI-MS (m/z): Calcd for $C_{15}H_{16}NaO$, $[M+Na]^+$: 235.1.

2,6-dimethyl-4-(2-methylbenzyl)phenol (3w)



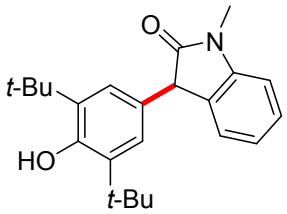
White solid; Mp 88-90 °C; 32.0 mg; yield: 71%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.14-7.12 (m, 3H), 7.08-7.07 (m, 1H), 6.73 (s, 2H), 4.01 (s, 1H), 3.84 (s, 2H), 2.25 (s, 3H), 2.18 (s, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 150.4; 139.6; 136.6; 131.9; 130.2; 129.8; 128.9; 126.2; 125.9; 122.9; 38.6; 19.7; 15.9. ESI-MS (m/z): Calcd for $C_{16}H_{18}NaO$, $[M+Na]^+$: 249.2.

4-benzyl-2,6-diisopropylphenol (3x)



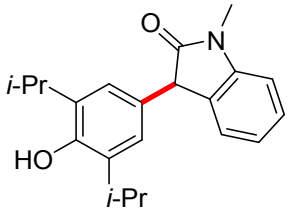
Light red solid; Mp 33-35 °C; 48.0 mg; yield: 90%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 (t, J = 7.6 Hz, 2H), 7.18-7.15 (m, 3H), 6.87 (s, 2H), 4.40 (s, 1H), 3.91 (s, 2H), 3.15-3.07 (m, 2H), 1.23 (d, J = 7.0 Hz, 12H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 148.3; 141.9; 133.7; 132.8; 128.8; 128.4; 125.9; 124.1; 41.7; 27.3; 22.8. ESI-MS (m/z): Calcd for $C_{19}H_{25}O$, $[M+H]^+$: 269.2.

3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methylindolin-2-one (3y)



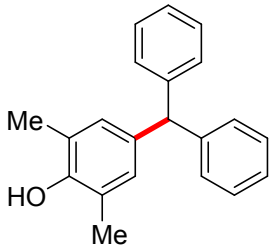
Light yellow gum; 16.0 mg; yield: 43%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 and 7.57 (d, J = 7.3 Hz, 2H), 7.53 and 7.51 (d, J = 8.1 Hz, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.28 and 7.26 (d, J = 8.0 Hz, 2H), 7.03 (s, 2H), 5.07 (s, 1H), 3.94 (s, 2H), 1.42 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 152.1; 141.1; 141.0; 138.7; 135.9; 131.4; 129.2; 128.7; 127.1; 126.9; 125.4; 41.5; 34.3; 30.3. ESI-MS (m/z): Calcd for $C_{23}H_{29}NNaO_2$, $[M+Na]^+$: 374.2.

3-(4-hydroxy-3,5-diisopropylphenyl)-1-methylindolin-2-one (3z)



Light yellow gum; 16.0 mg; yield: 43%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 and 7.57 (d, J = 7.3 Hz, 2H), 7.53 and 7.51 (d, J = 8.1 Hz, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.28 and 7.26 (d, J = 8.0 Hz, 2H), 7.03 (s, 2H), 5.07 (s, 1H), 3.94 (s, 2H), 1.42 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 152.1; 141.1; 141.0; 138.7; 135.9; 131.4; 129.2; 128.7; 127.1; 126.9; 125.4; 41.5; 34.3; 30.3. ESI-MS (m/z): Calcd for $C_{21}H_{25}NNaO_2$, $[M+Na]^+$: 336.1.

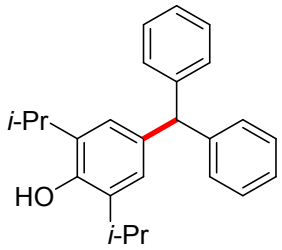
4-benzhydryl-2,6-dimethylphenol (3aa)



White solid; Mp 137-139 ^{o}C; 52.0 mg; yield: 91%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27 (t, J = 7.4 Hz, 4H), 7.19 (t, J = 7.2 Hz, 2H), 7.10 (d, J = 7.5 Hz, 4H), 6.72 (s, 2H), 5.42 (s,

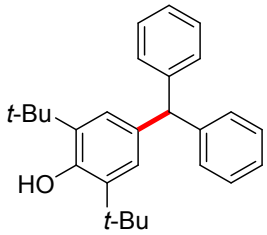
1H), 4.51 (s, 1H), 2.17 (s, 6H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 150.6; 144.4; 135.5; 129.6; 129.4; 128.3; 126.2; 122.8; 56.2; 16.0. ESI-MS (m/z): Calcd for $C_{21}H_{21}O$, $[M+H]^+$: 289.2.

4-benzhydryl-2,6-diisopropylphenol (3ab)



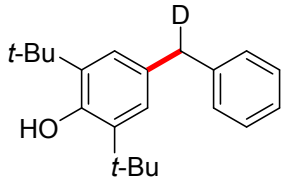
White solid; Mp 140-142 °C; 66.0 mg; yield: 96%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27 (t, J = 7.5 Hz, 4H), 7.19 (t, J = 7.3 Hz, 2H), 7.11 (d, J = 7.5 Hz, 4H), 6.79 (s, 2H), 5.47 (s, 1H), 4.67 (s, 1H), 3.13-3.05 (m, 2H), 1.18 (d, J = 6.9 Hz, 12H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 148.4; 144.7; 135.6; 133.3; 129.4; 128.2; 126.1; 124.6; 56.7; 27.4; 22.7. ESI-MS (m/z): Calcd for $C_{25}H_{29}O$, $[M+H]^+$: 345.2.

4-benzhydryl-2,6-di-tert-butylphenol (3ac)



Light yellow solid; Mp 143-145 °C; 72.0 mg; yield: 97%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 (t, J = 7.5 Hz, 4H), 7.18 (t, J = 7.3 Hz, 2H), 7.11 (d, J = 7.4 Hz, 4H), 6.90 (s, 2H), 5.44 (s, 1H), 5.07 (s, 1H), 1.35 (s, 18H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 152.1; 144.8; 135.4; 134.1; 129.4; 128.1; 126.1; 126.0; 56.8; 34.4; 30.3. ESI-MS (m/z): Calcd for $C_{27}H_{33}O$, $[M+H]^+$: 373.2.

2,6-di-tert-butyl-4-(phenylmethyl-*d*)phenol (3a-D)

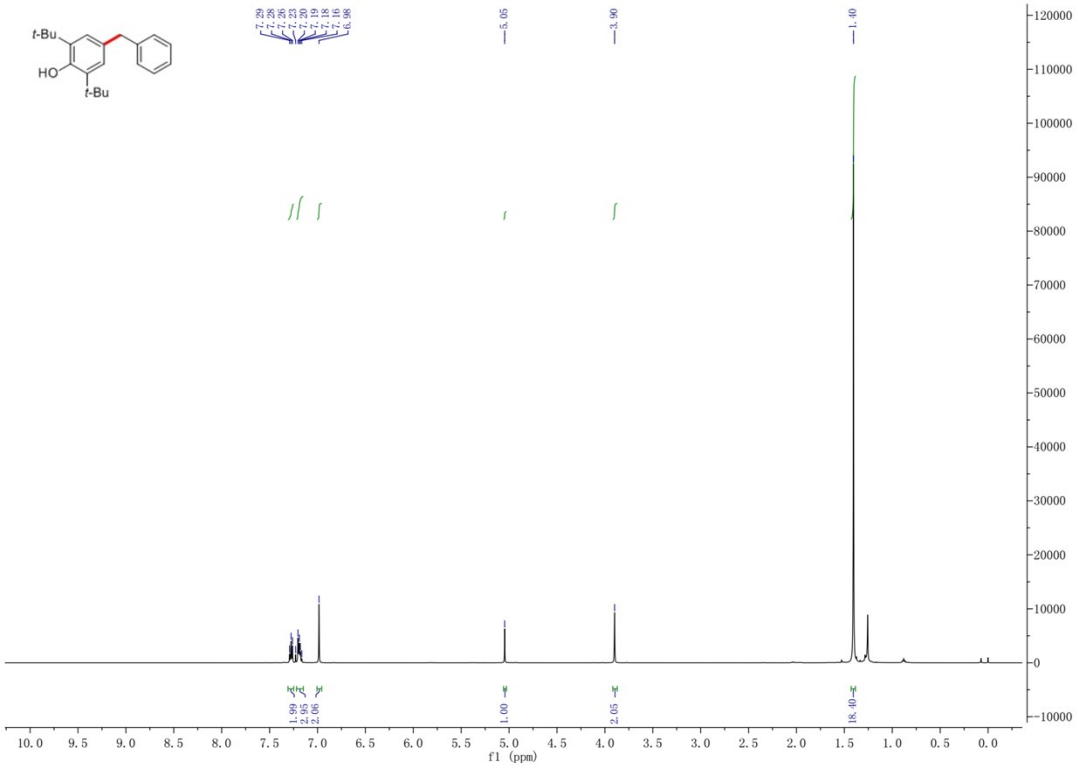


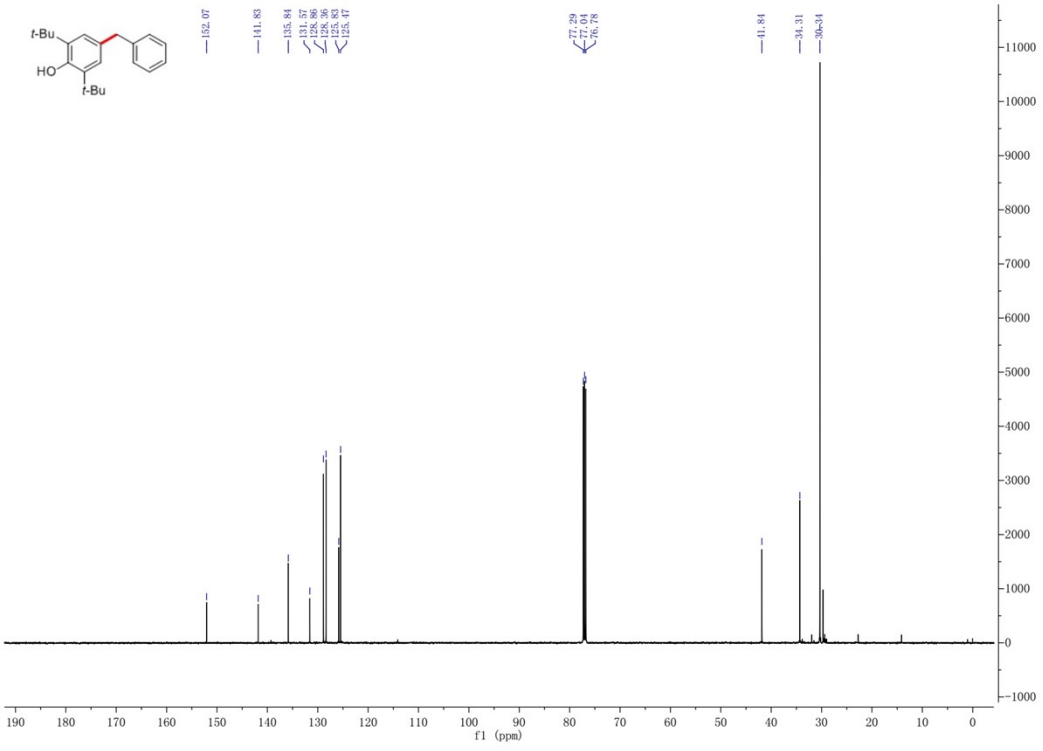
Light yellow gum; 29.4 mg; yield: 98%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20 (t, J = 7.5 Hz, 2H), 7.13-7.09 (m, 3H), 6.91 (s, 2H), 4.97 (s, 1H), 3.82 (s, 1H), 1.33 (s, 18H). ESI-MS (m/z): Calcd for $C_{21}H_{28}DO$, $[M+H]^+$: 298.2.

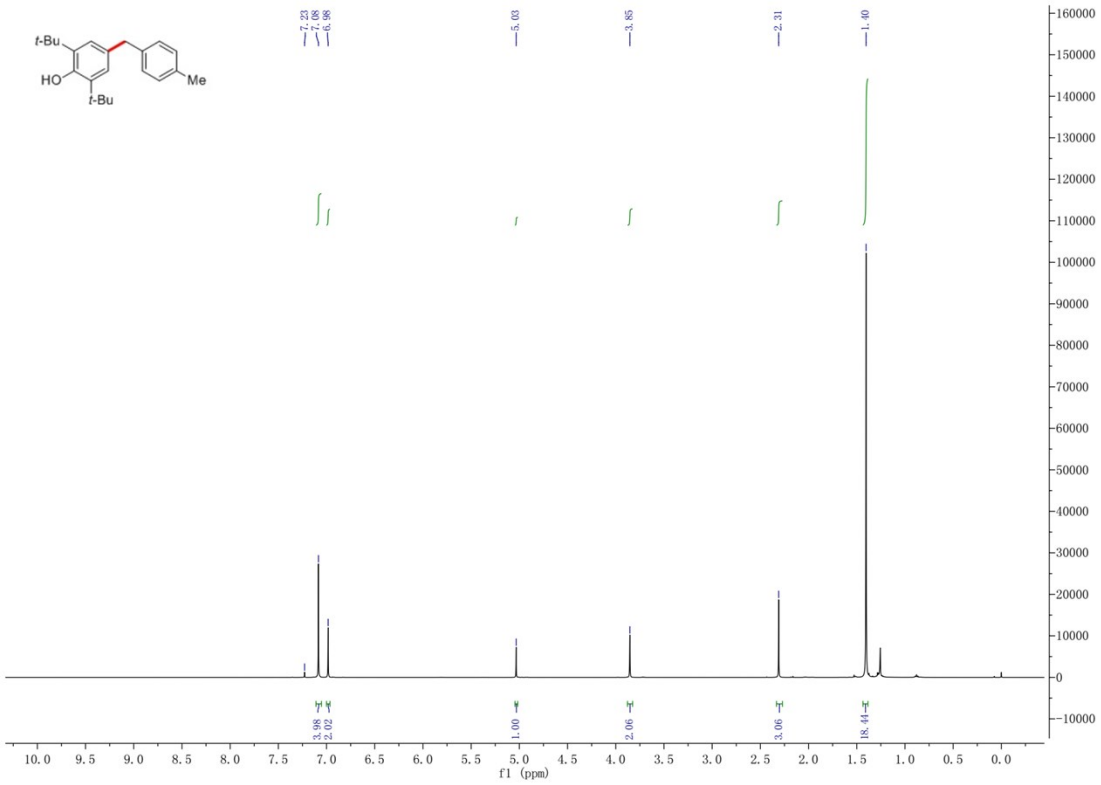
6. Reference

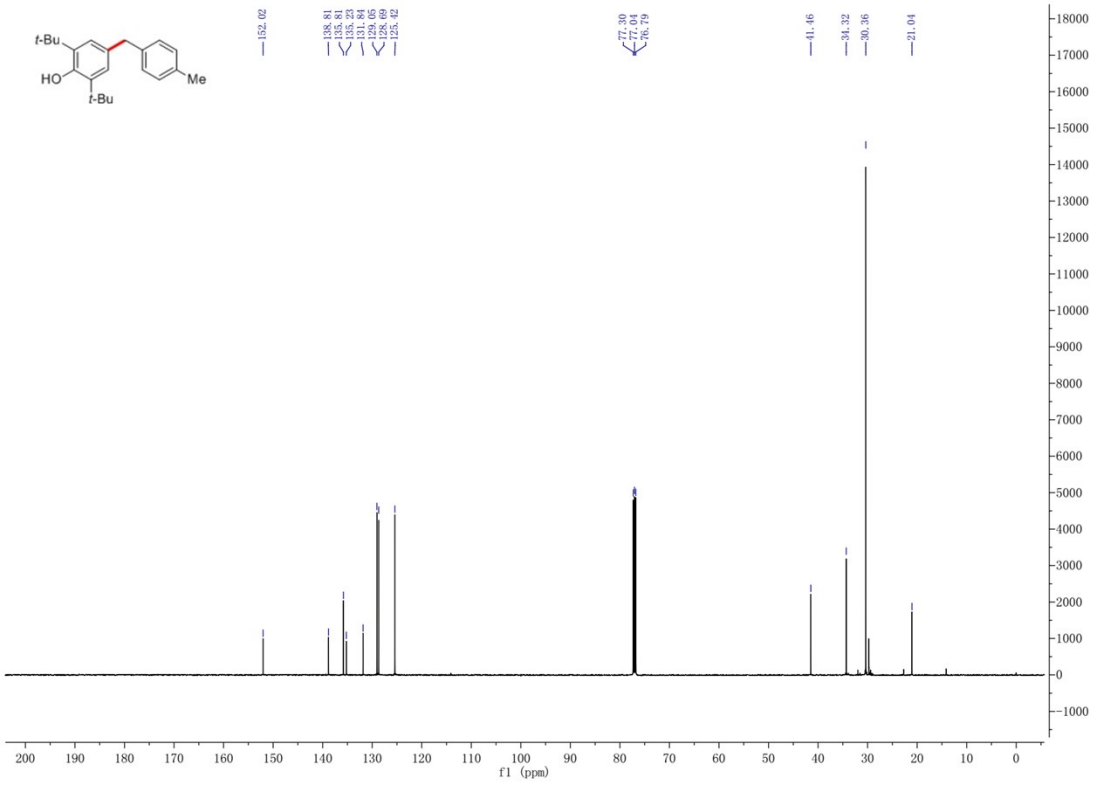
1. W. Chu, L. Zhang, X. Bao, X. Zhao, C. Zeng, J. Du, G. Zhang, F. Wang, X. Ma and C. Fan, *Angew. Chem. Int. Ed*. 2013, **52**, 9229-9233.

7. Supplementary Figures: ^{1}H、^{13}C and ^{19}F NMR spectra of the products






t-Bu
HO
t-Bu
Me
7.23
7.08
6.98
5.03
3.85
2.31
1.40
3.98
2.02
1.00
2.06
3.06
18.44
f1 (ppm)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Me
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135.81
135.23
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77.04
76.79
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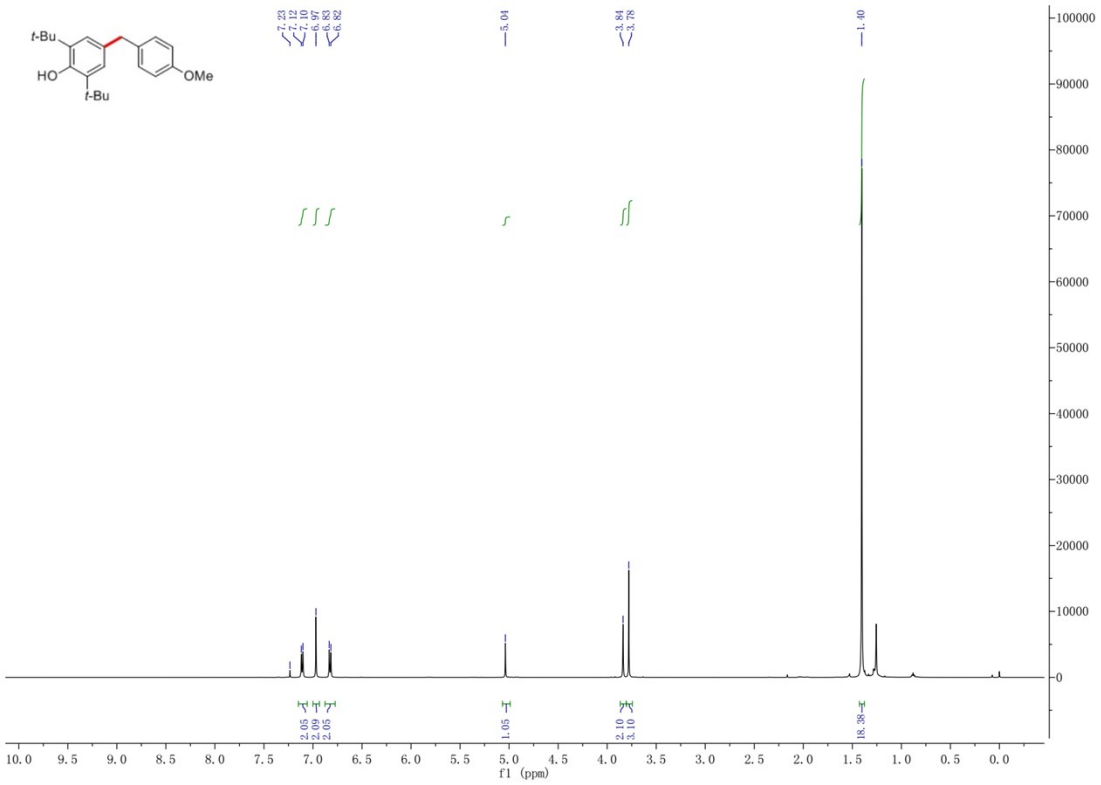
34.32
30.36
21.04
f1 (ppm)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HO
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OMe
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7.10
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6.83
6.82
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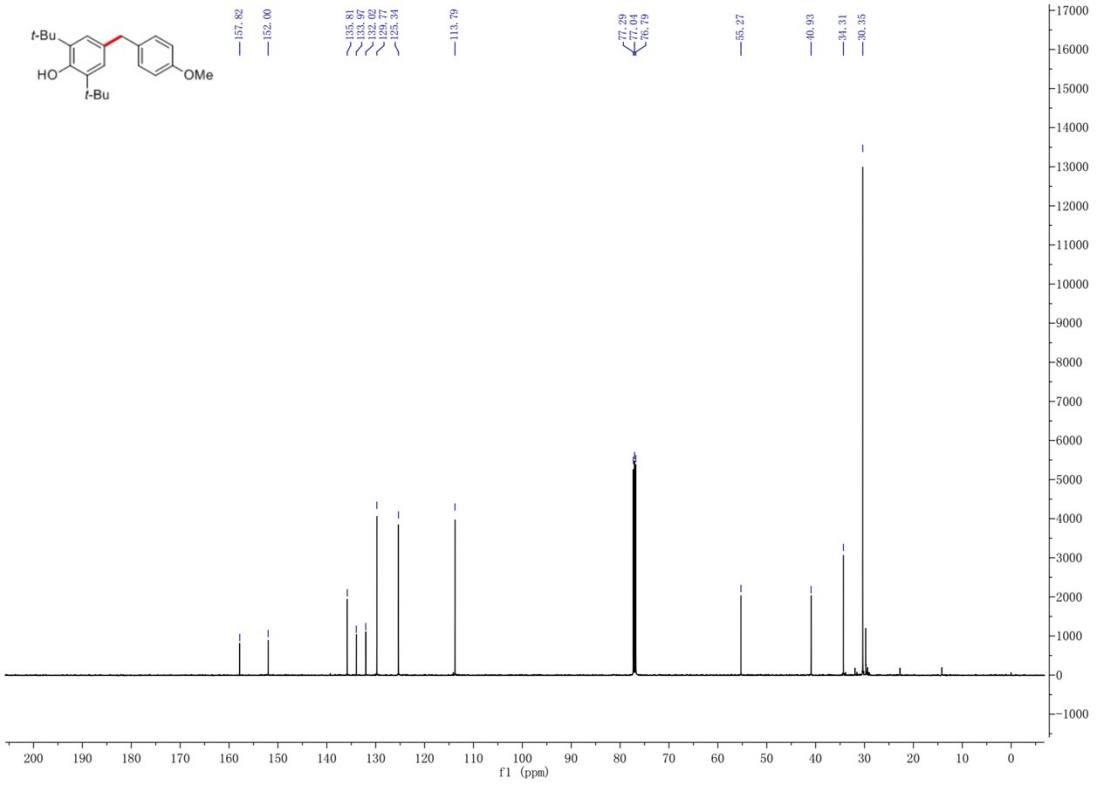
2.05
1.05
2.10
3.10
18.38
f1 (ppm)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OMe
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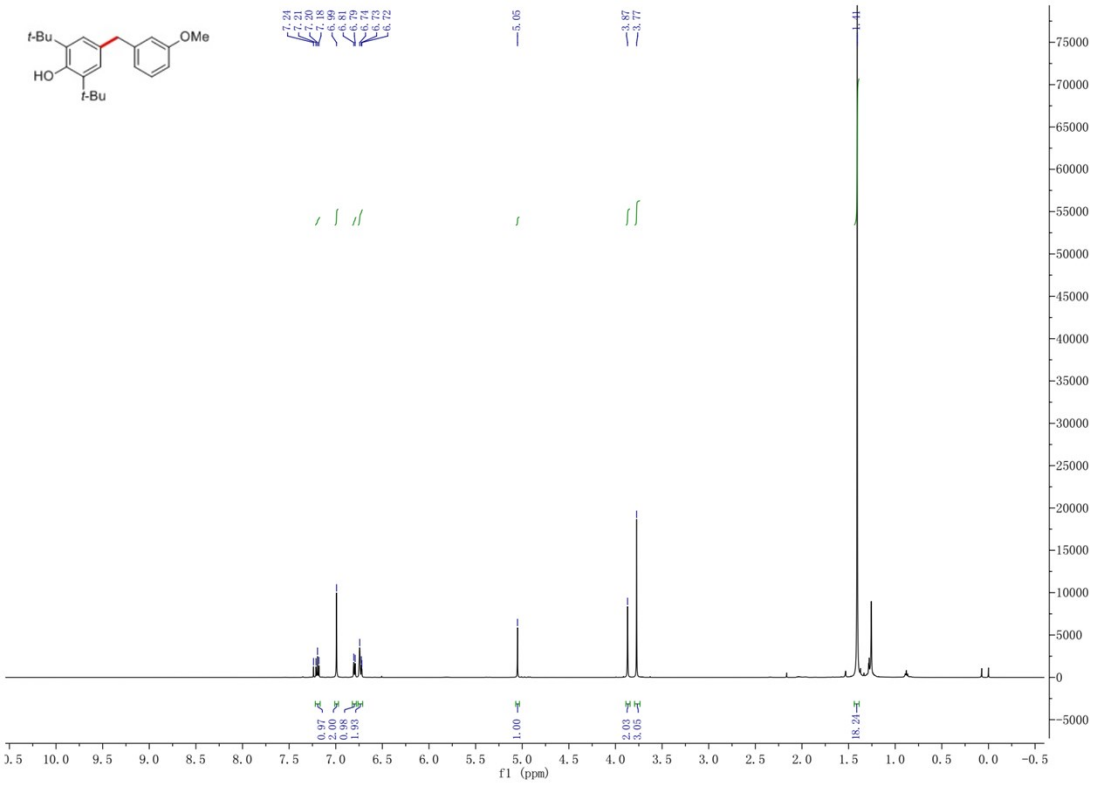
55.27
40.93
34.31
30.35
f1 (ppm)


t-Bu
HO
t-Bu
OMe
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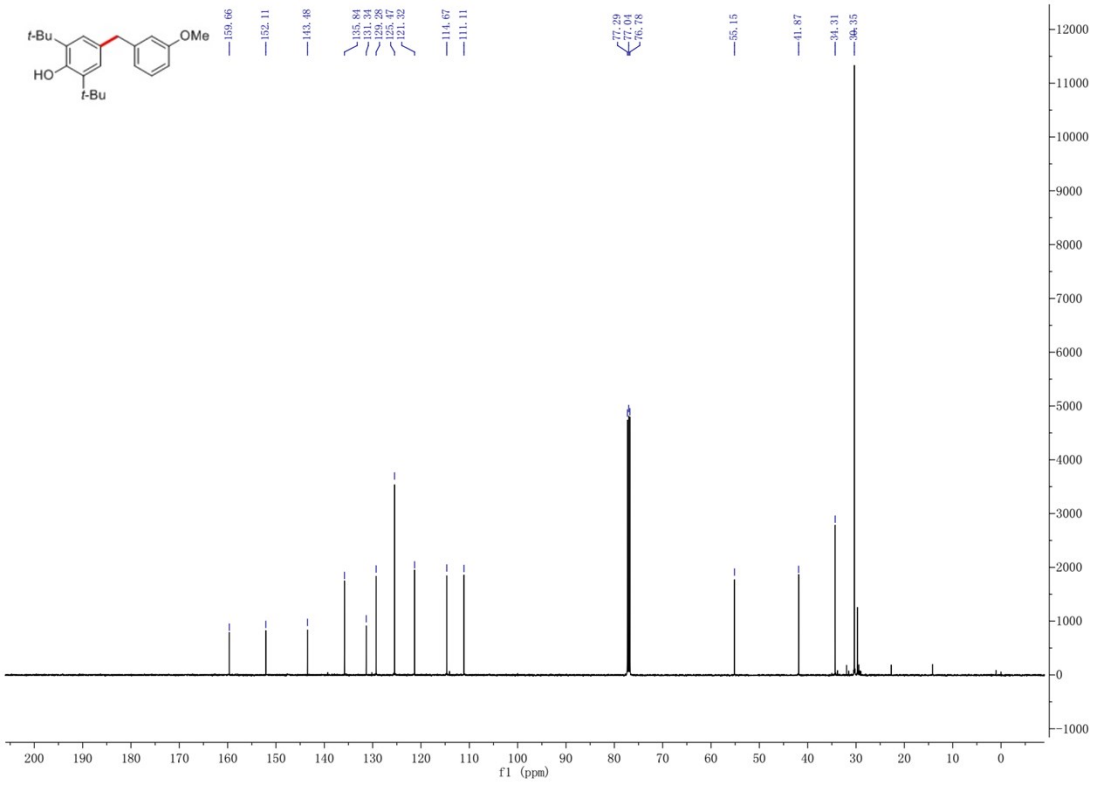
7.21
7.20
7.18
6.98
6.81
6.79
6.74
6.73
6.72
5.05
3.87
3.77
1.41
0.97
0.90
2.00
0.98
1.93
1.00
2.03
3.05
18.24
f1 (ppm)


t-Bu
HO
t-Bu
OMe
159.66
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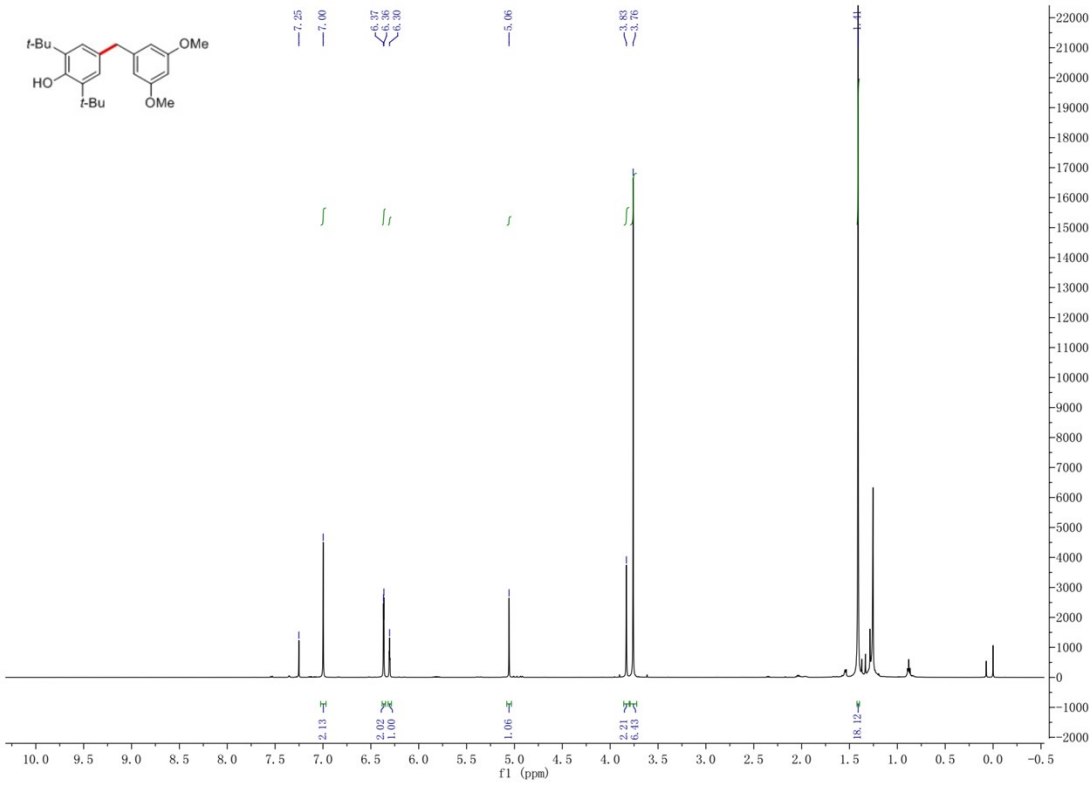
135.84
131.34
129.28
125.67
121.32
114.67
111.11
77.29
77.04
76.78
55.15
41.87
34.31
30.35
f1 (ppm)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HO
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OMe
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6.36
6.30
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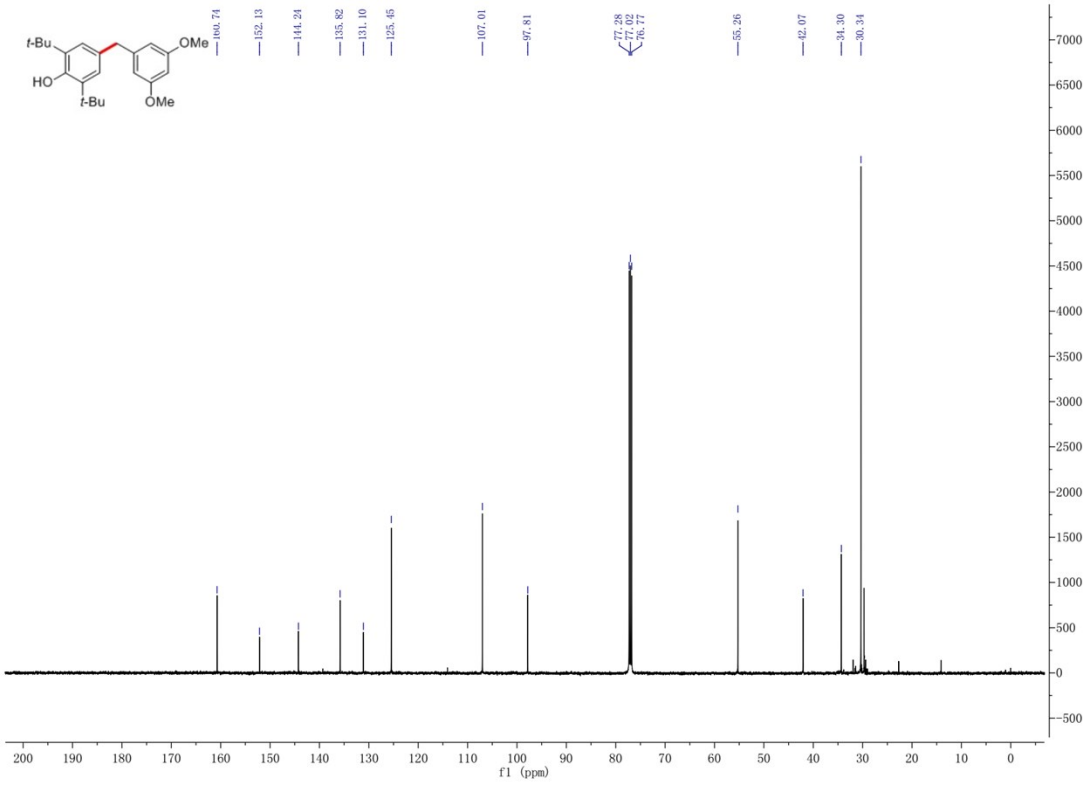
1.00
1.06
2.21
6.43
18.12
f1 (ppm)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HO
t-Bu
OMe
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144.24
135.82
131.10
125.45
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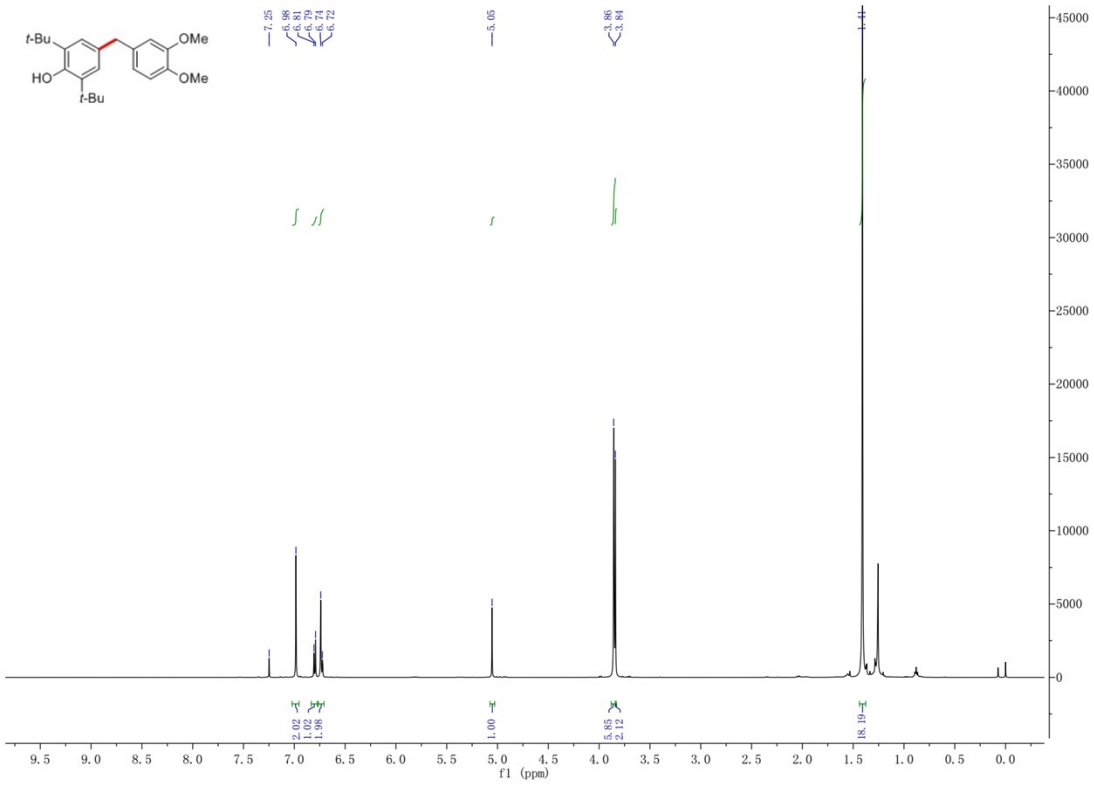
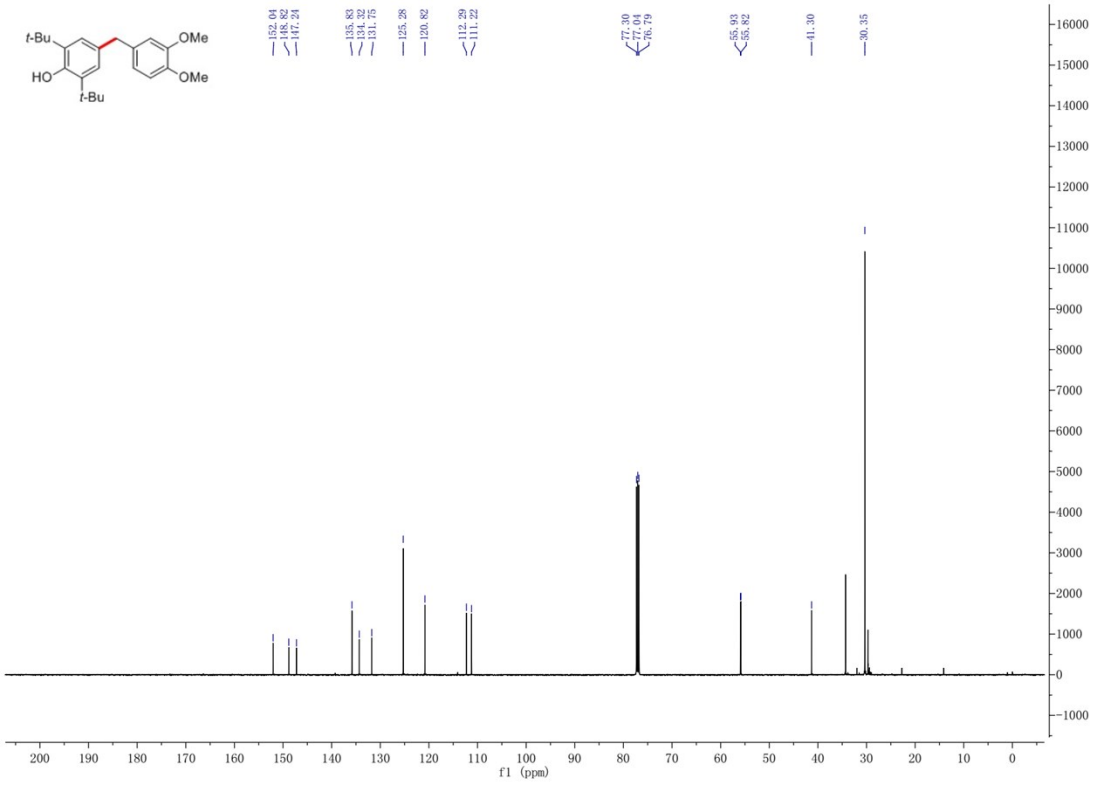
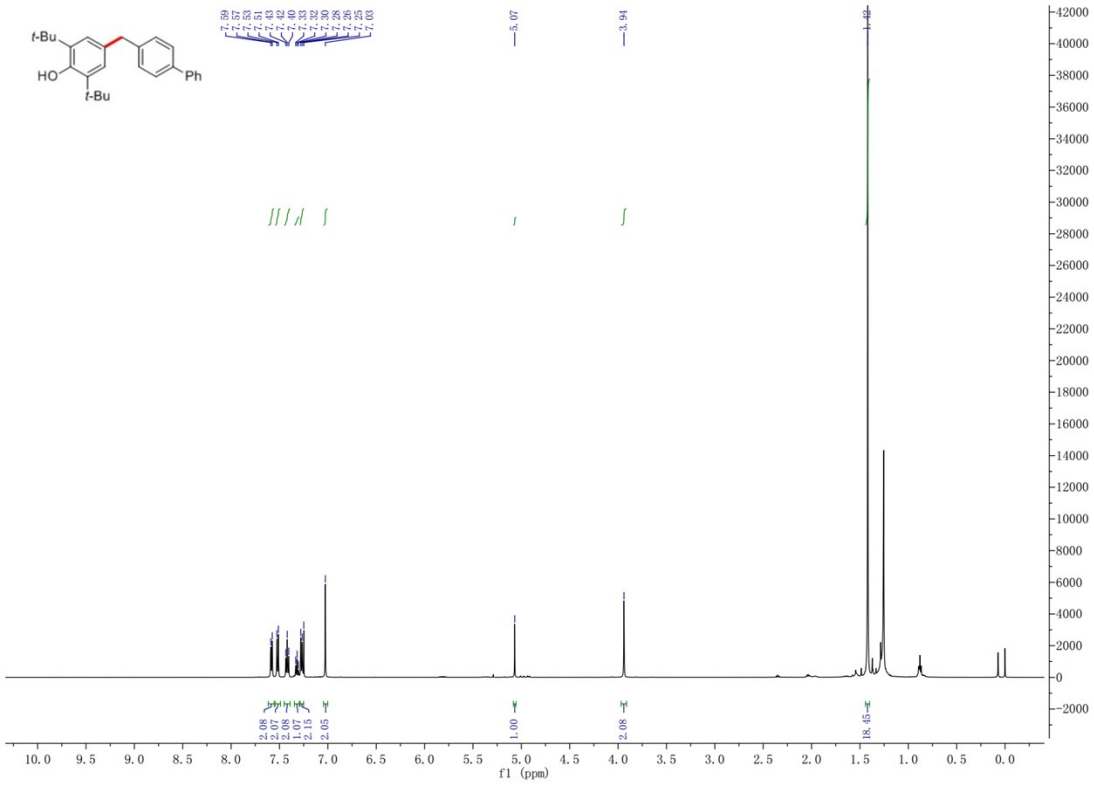
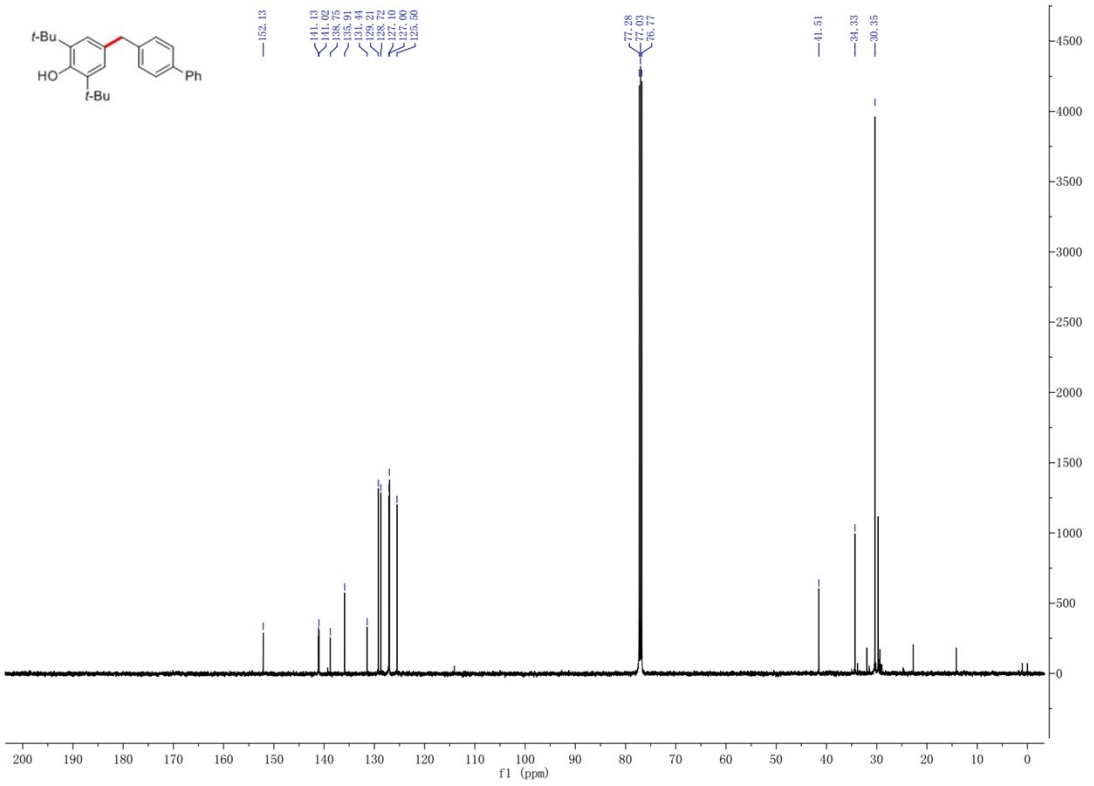
77.28
77.02
76.77
55.26
42.07
34.30
30.34
f1 (ppm)


t-Bu
HO
t-Bu
OMe
OMe
7.25
6.98
6.81
6.79
6.74
6.72
5.05
3.86
3.84
1.41
2.02
1.02
1.98
1.00
5.85
2.12
18.19
f1 (ppm)


t-Bu
HO
t-Bu
OMe
OMe
152.04
148.82
147.24
135.83
134.32
131.75
125.28
120.82
112.29
111.22
77.30
77.04
76.79
55.93
55.82
41.30
30.35
f1 (ppm)


t-Bu
HO
t-Bu
Ph
7.59
7.57
7.53
7.51
7.43
7.42
7.40
7.33
7.32
7.30
7.28
7.25
7.03
5.07
3.94
1.49
2.08
2.07
2.08
1.07
2.15
2.05
1.00
2.08
18.45
f1 (ppm)


t-Bu
HO
t-Bu
Ph
152.13
141.13
141.02
138.75
135.91
131.44
129.21
128.72
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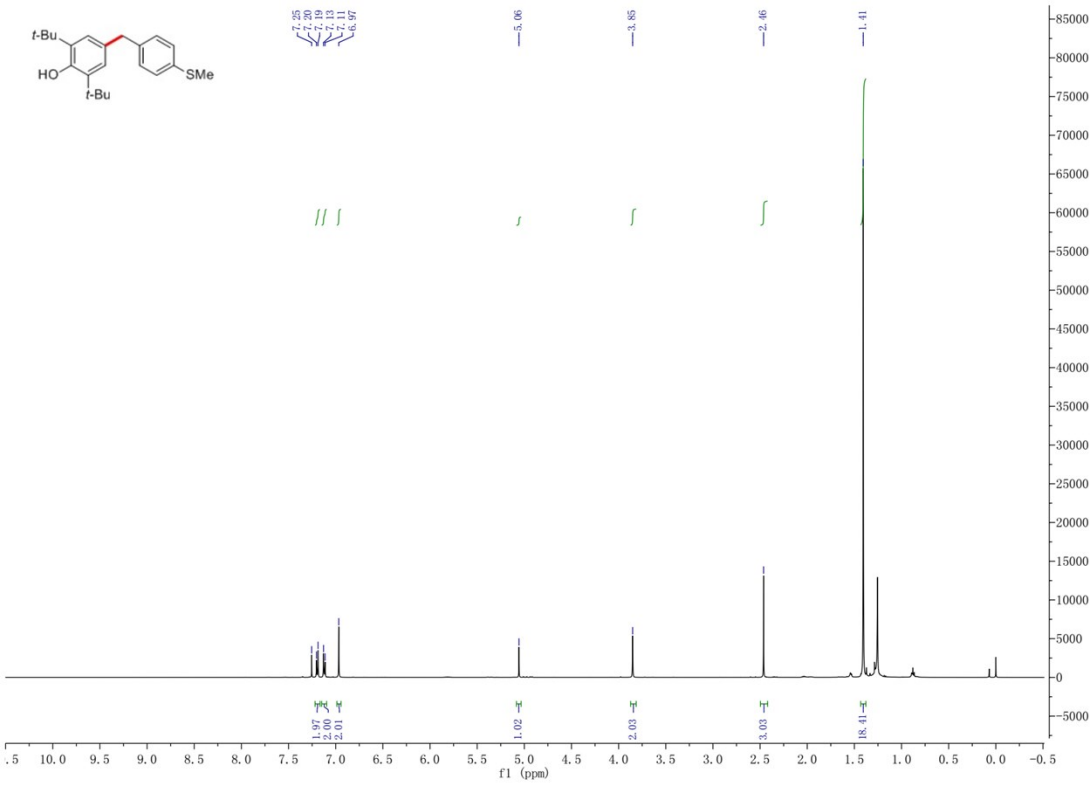
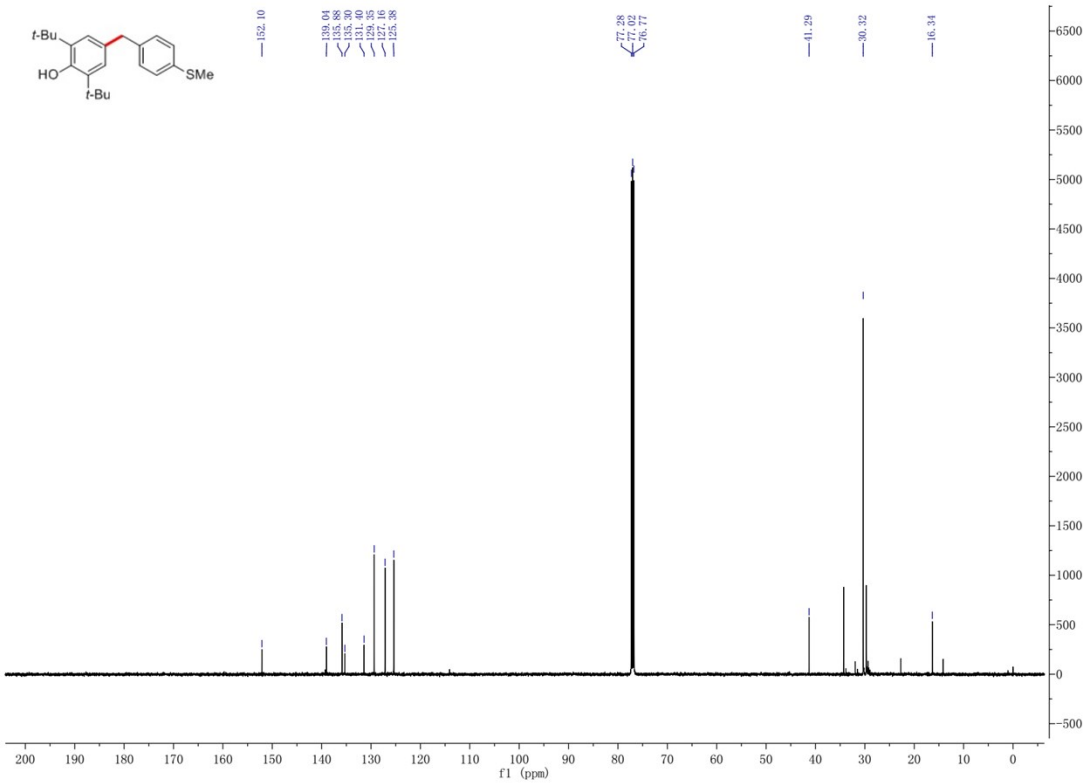
77.03
76.77
41.51
34.33
30.35
f1 (ppm)


t-Bu
HO
t-Bu
SMe
7.25
7.20
7.19
7.13
7.11
6.97
5.06
3.85
2.46
1.41
1.97
2.00
2.01
1.02
2.03
3.03
18.41
f1 (ppm)


t-Bu
HO
t-Bu
SMe
152.10
139.04
135.88
135.00
131.40
129.35
127.16
125.38
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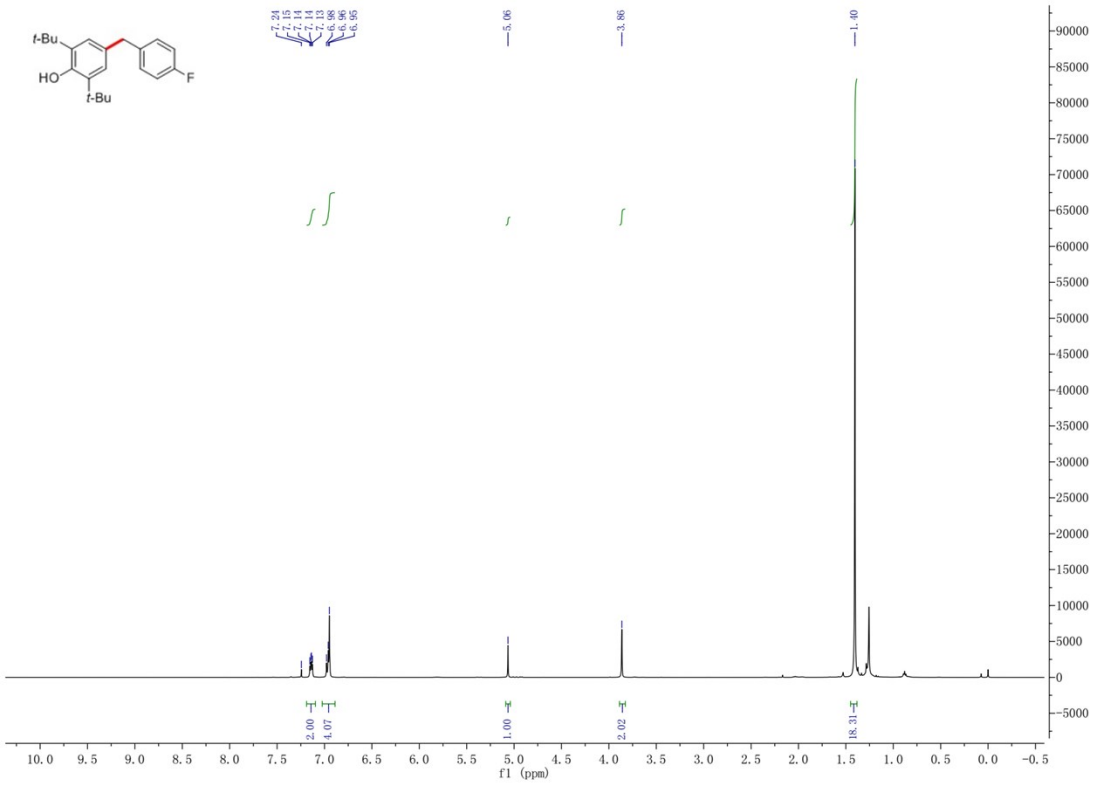
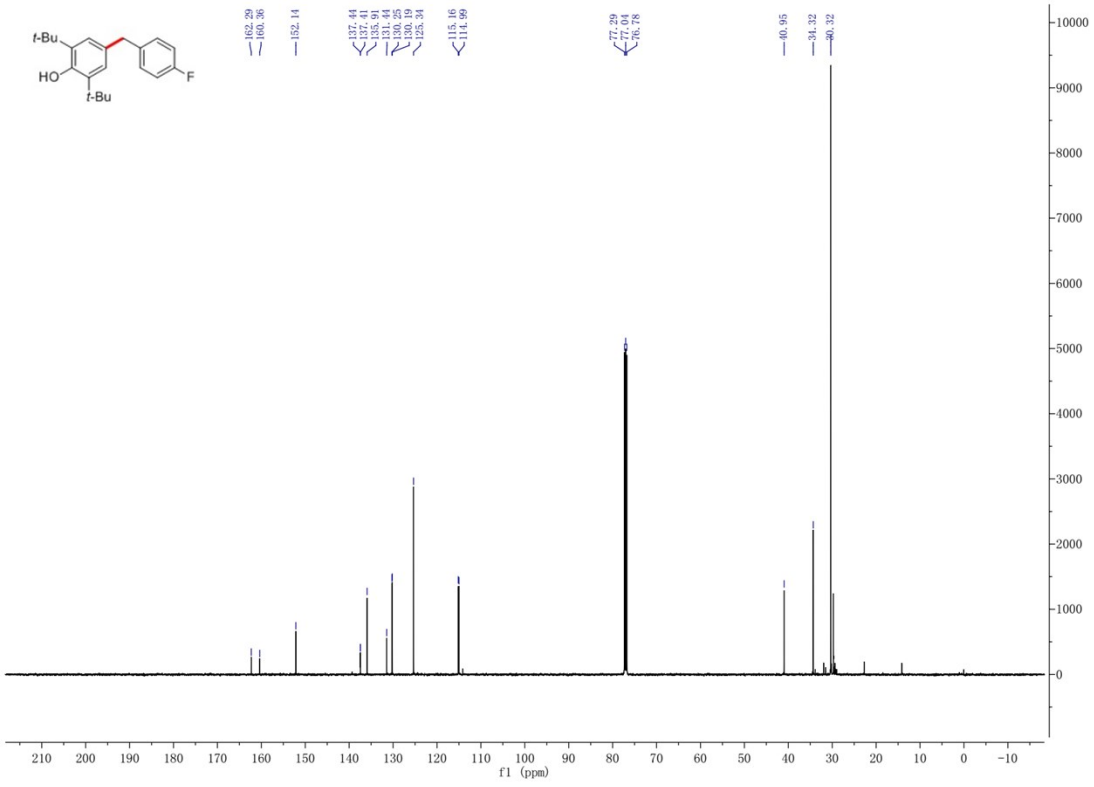
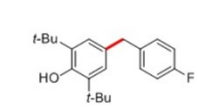
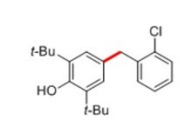
77.02
76.77
41.29
30.32
16.34
f1 (ppm)


t-Bu
HO
t-Bu
F
7.24
7.15
7.14
7.14
7.13
6.98
6.96
6.95
5.06
3.86
1.40
2.00
4.07
1.00
2.02
18.31
f1 (ppm)

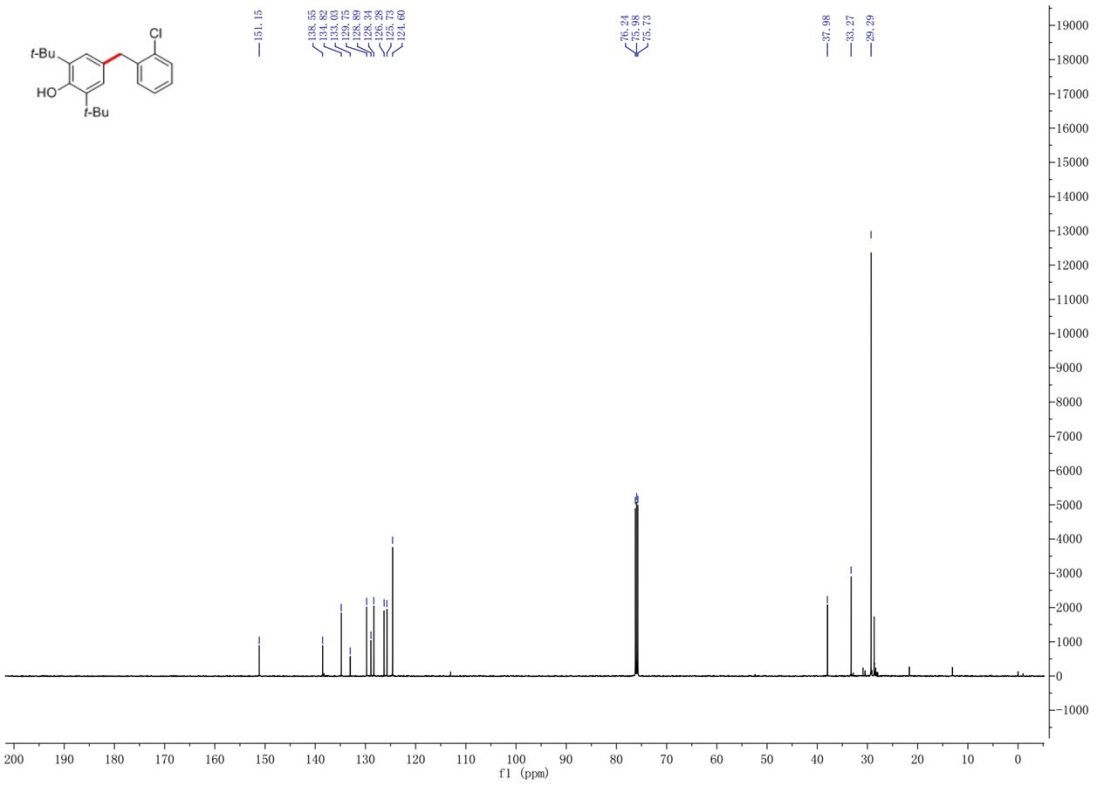

t-Bu
HO
t-Bu
F
162.29
160.36
152.14
137.44
137.41
135.91
131.44
130.25
130.19
125.34
115.16
114.99
77.29
77.04
76.78
40.95
34.32
30.32
f1 (ppm)

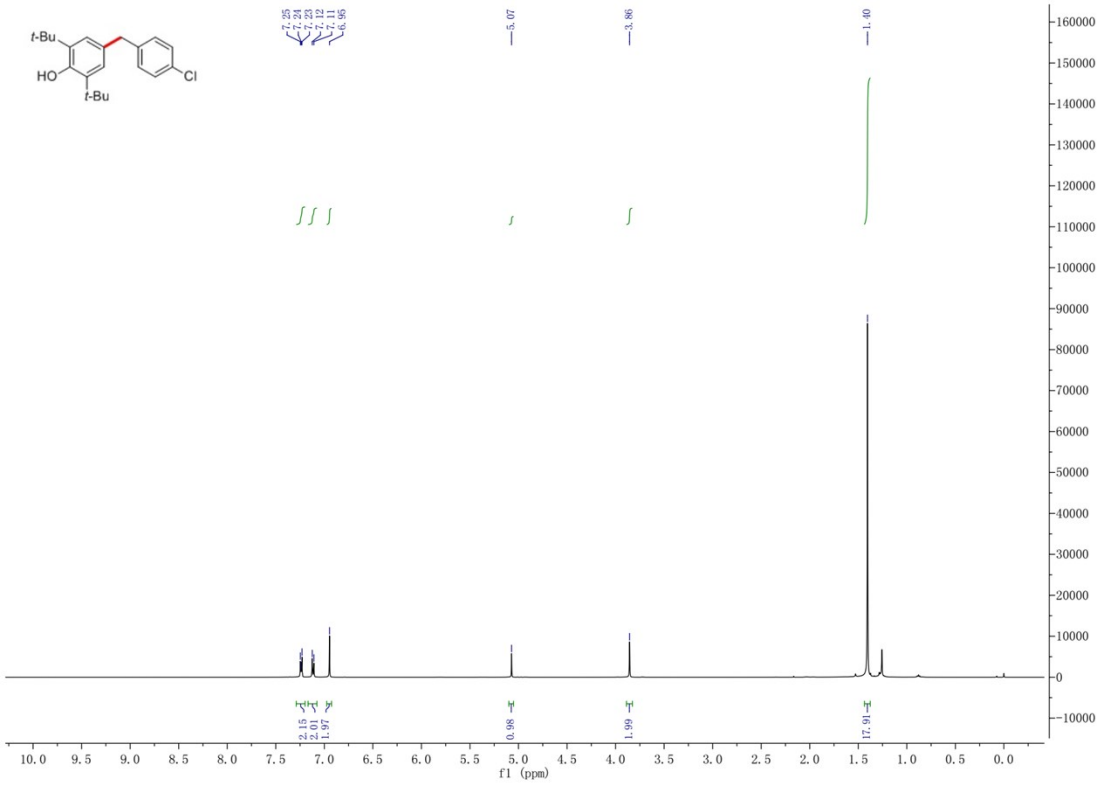

t-Bu
HO
t-Bu
F

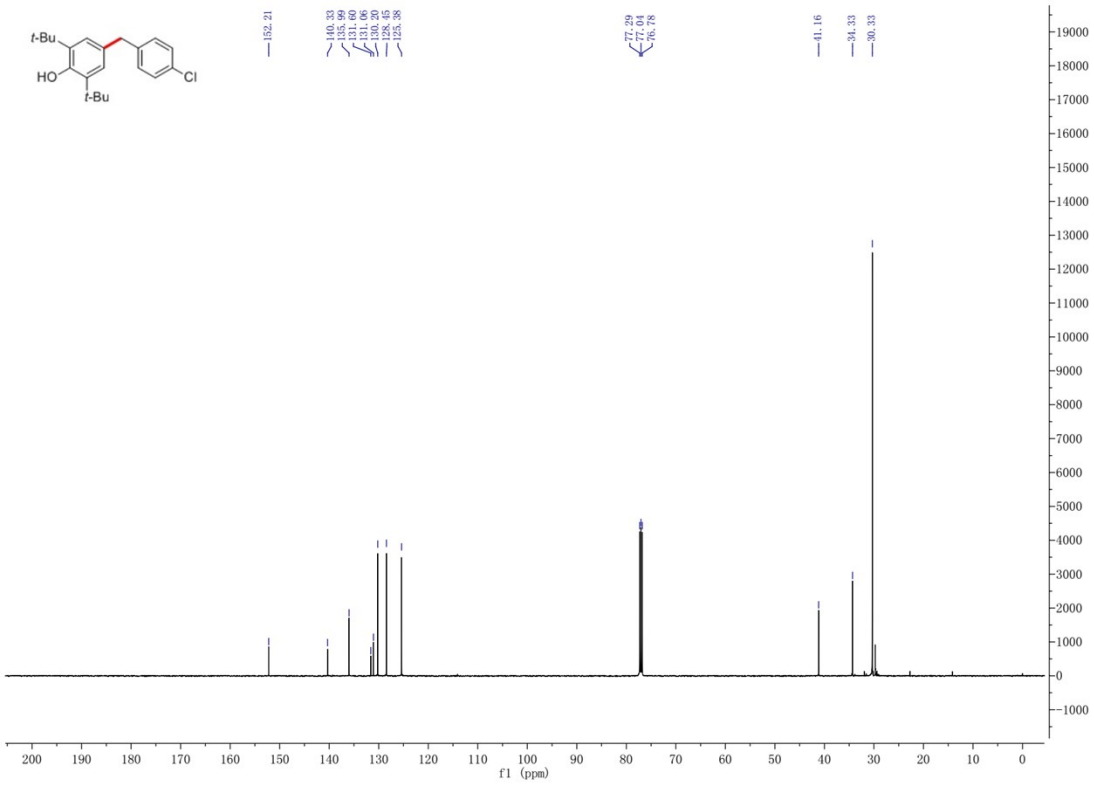
-117.83
f1 (ppm)

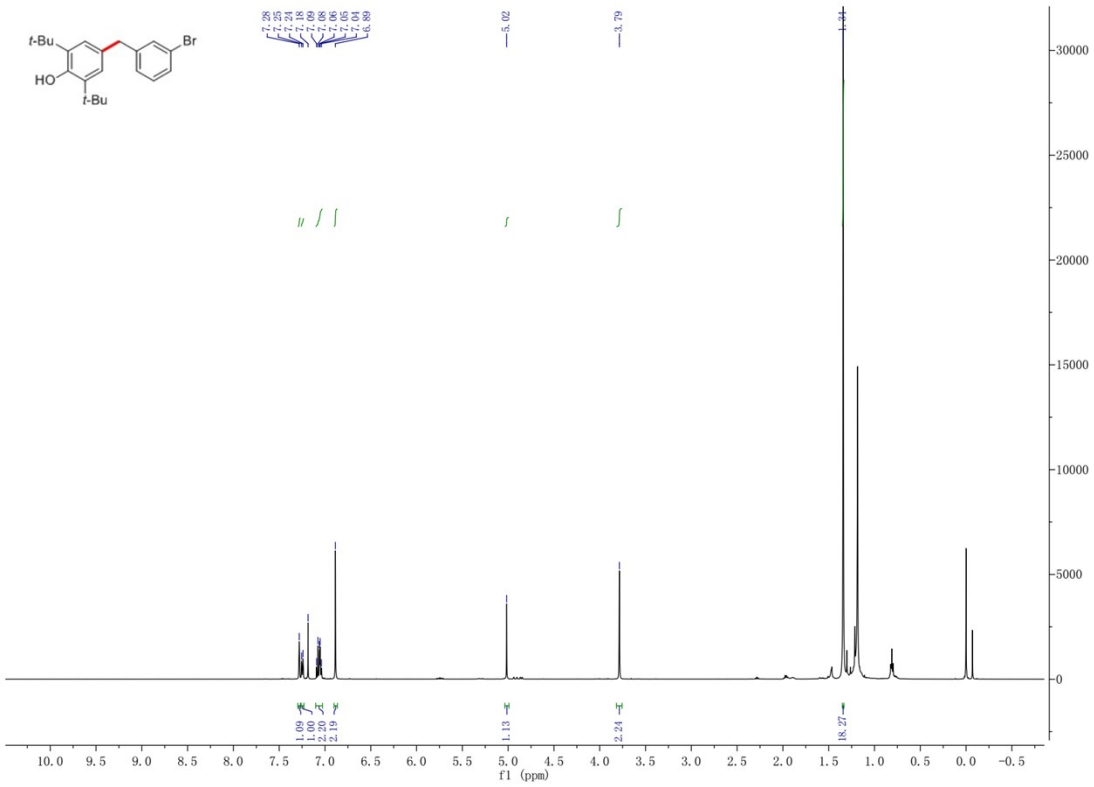

t-Bu
HO
t-Bu
Cl

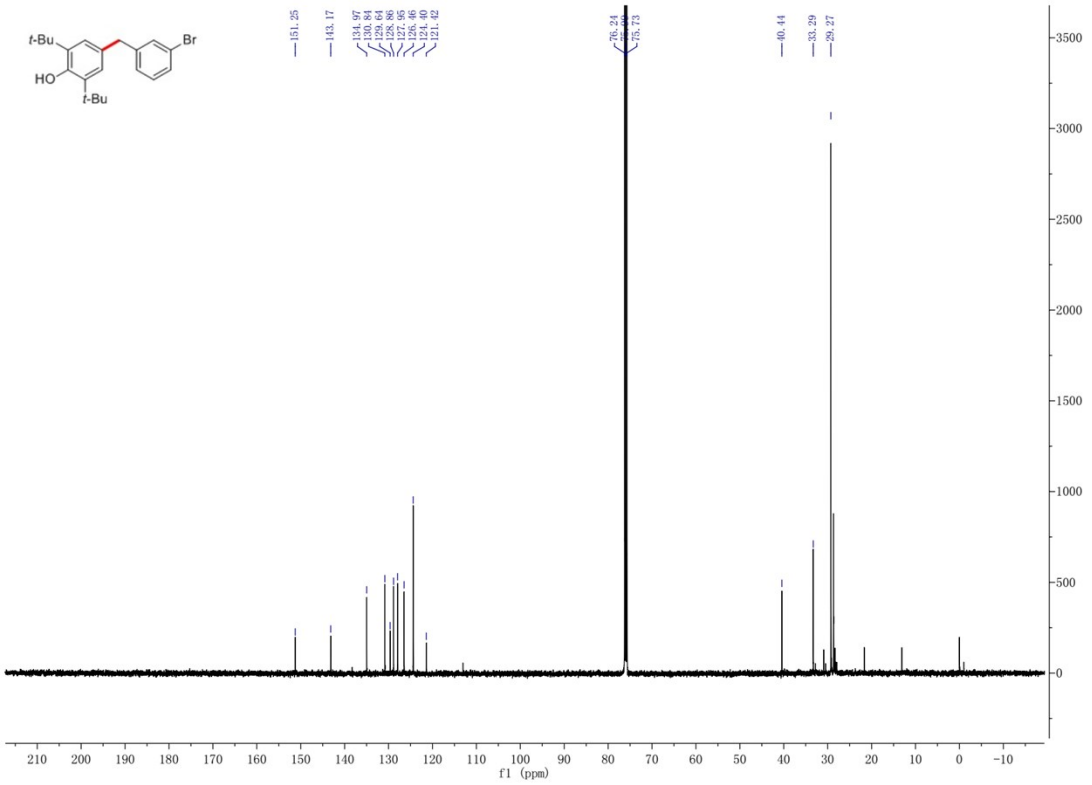
7.29
7.29
7.28
7.28
7.25
7.15
7.10
7.09
7.09
7.08
7.07
7.07
7.05
7.05
7.04
7.04
6.95
4.99
3.93
1.33
0.98
2.97
2.03
1.00
2.03
18.13
f1 (ppm)

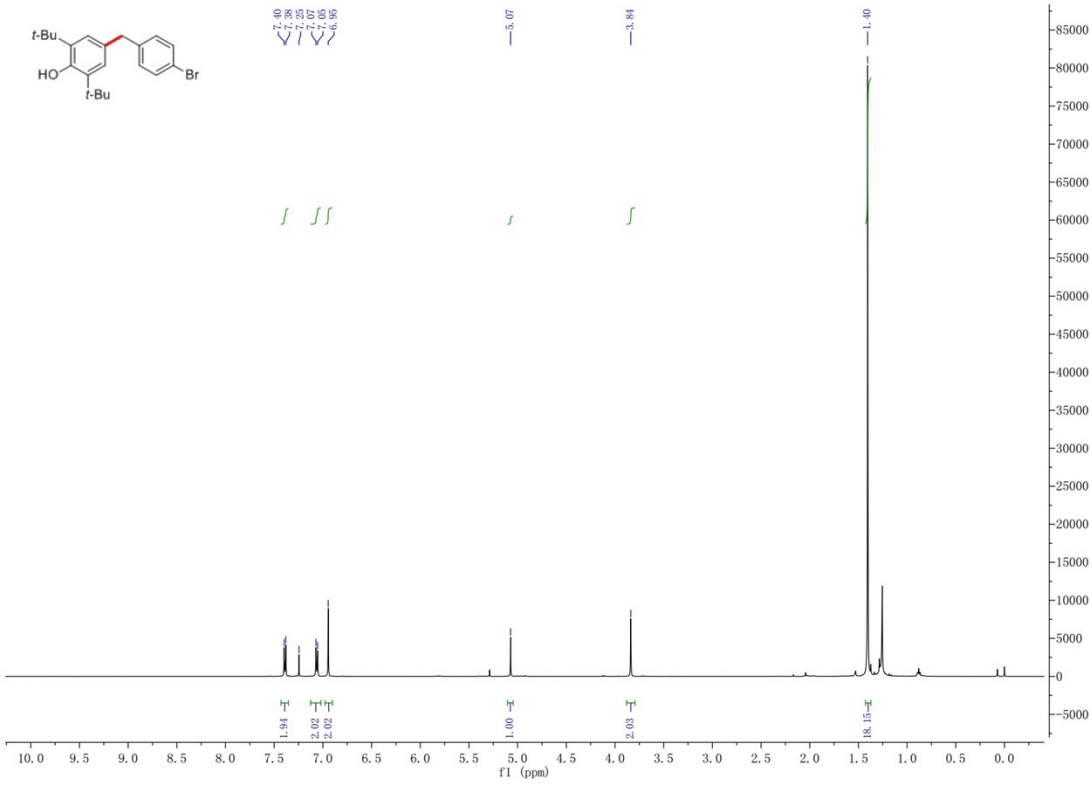

t-Bu
HO
t-Bu
Cl
151.15
138.55
134.62
133.03
129.15
128.89
128.34
126.28
125.73
124.60
76.24
75.98
75.73
37.98
33.27
29.29
f1 (ppm)

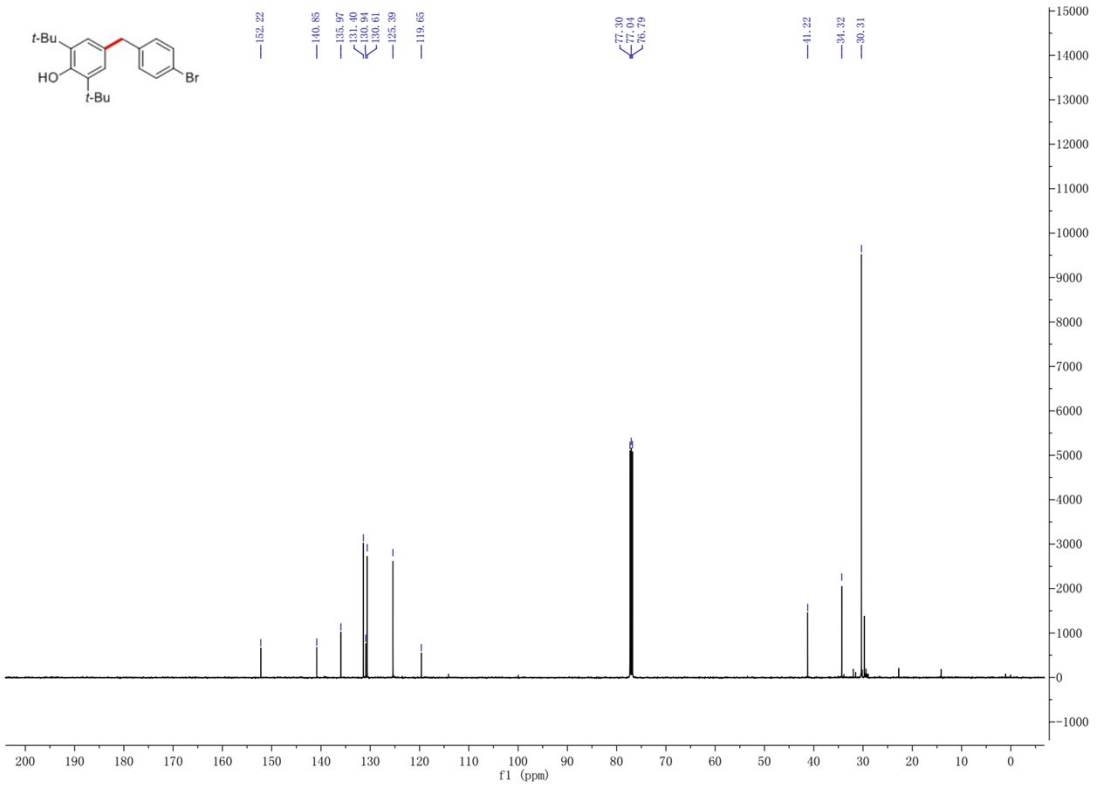

t-Bu
HO
t-Bu
Cl
7.25
7.24
7.23
7.22
7.11
6.95
5.07
3.86
1.40
2.15
2.01
1.97
0.98
1.99
17.91
f1 (ppm)


t-Bu
HO
t-Bu
Cl
152.21
140.33
135.99
131.60
131.06
130.30
128.45
125.38
77.29
77.04
76.78
41.16
34.33
30.33
f1 (ppm)


t-Bu
HO
t-Bu
Br
7.28
7.25
7.24
7.18
7.09
7.08
7.06
7.05
7.04
6.89
5.02
3.79
1.24
1.09
1.00
2.20
2.19
1.13
2.24
18.27
f1 (ppm)


t-Bu
HO
t-Bu
Br
151.25
143.17
134.97
130.84
129.64
128.96
127.95
126.46
124.40
121.42
76.24
75.73
40.44
33.29
29.27
f1 (ppm)


t-Bu
HO
t-Bu
Br
7.40
7.38
7.25
7.07
7.05
6.95
5.07
3.84
1.40
1.94
2.02
2.02
1.00
2.03
18.15
f1 (ppm)


t-Bu
HO
t-Bu
Br
152.22
140.85
135.97
131.40
130.94
130.61
125.39
119.65
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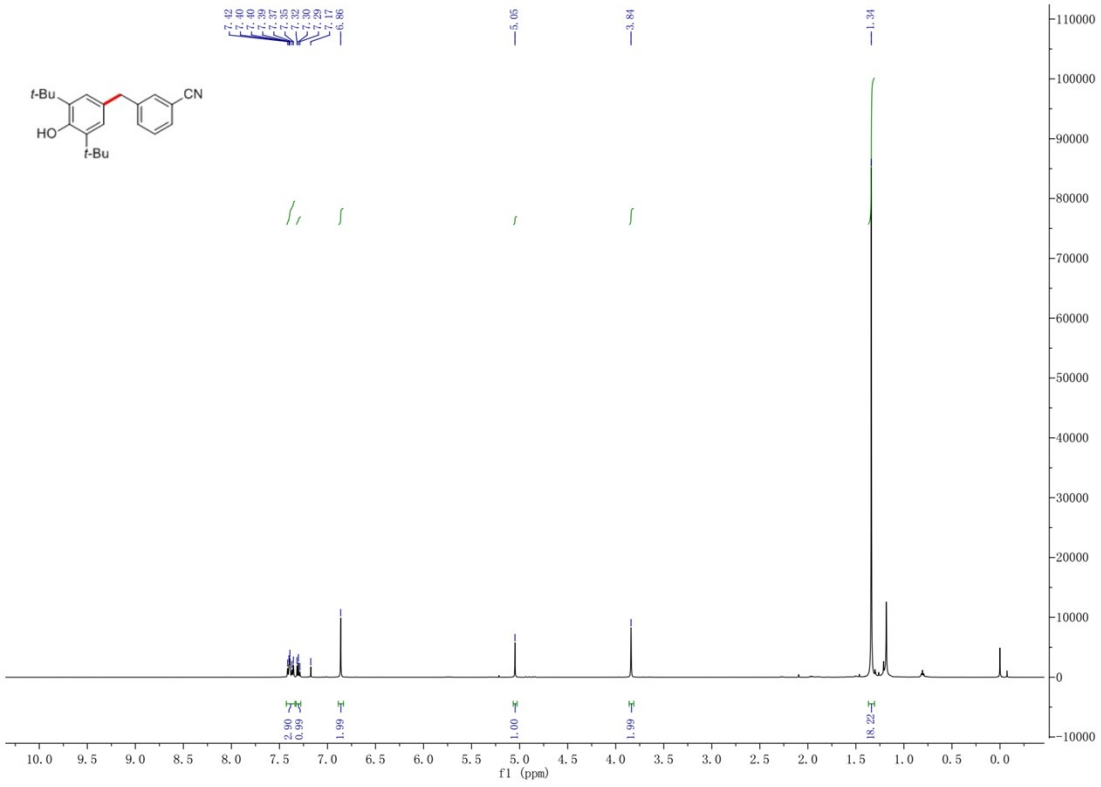
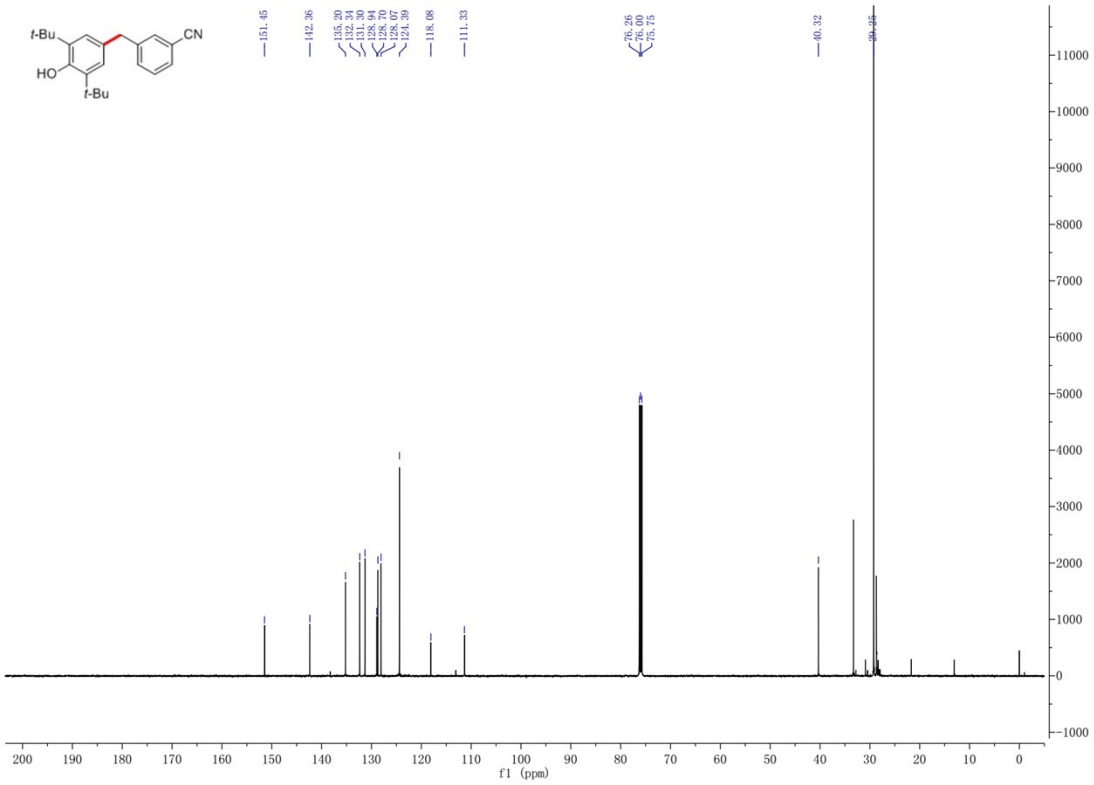
77.04
76.79
41.22
34.32
30.31
f1 (ppm)


t-Bu
HO
t-Bu
CN
7.42
7.40
7.40
7.39
7.37
7.35
7.32
7.30
7.29
7.17
6.86
5.05
3.84
1.34
2.90
0.99
1.99
1.00
1.99
18.22
f1 (ppm)


t-Bu
HO
t-Bu
CN
151.45
142.36
135.20
132.34
131.30
128.94
128.70
128.07
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118.08
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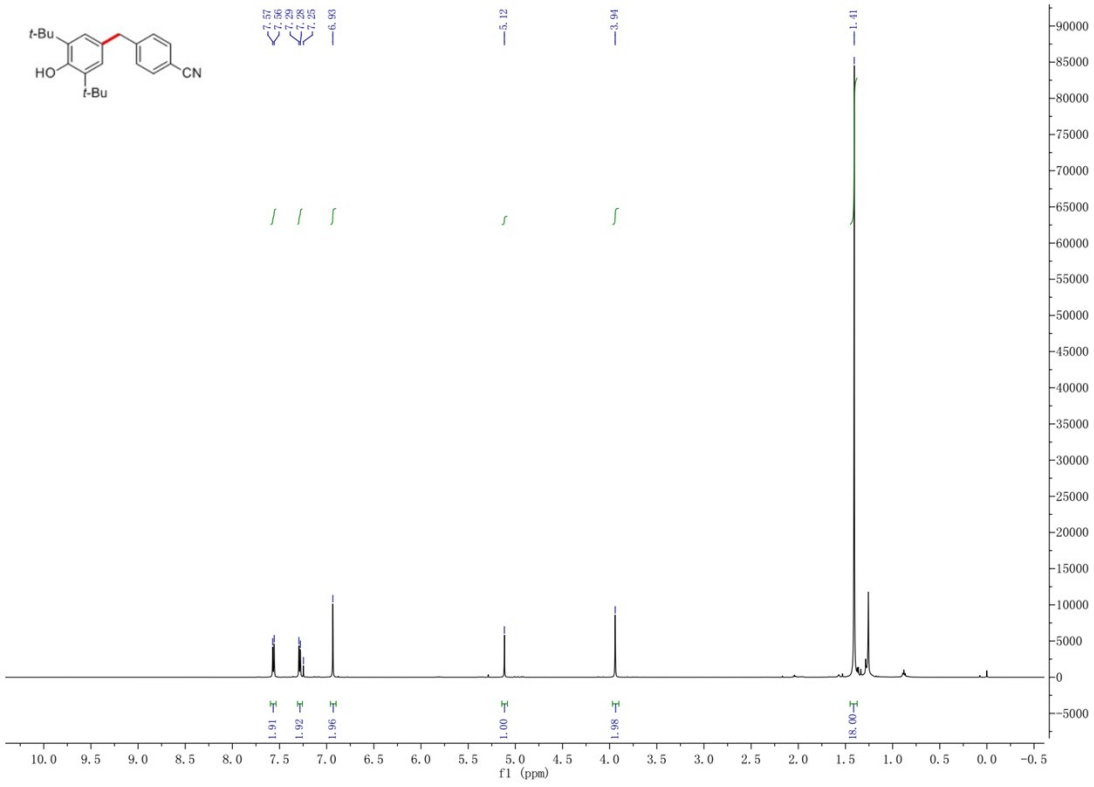
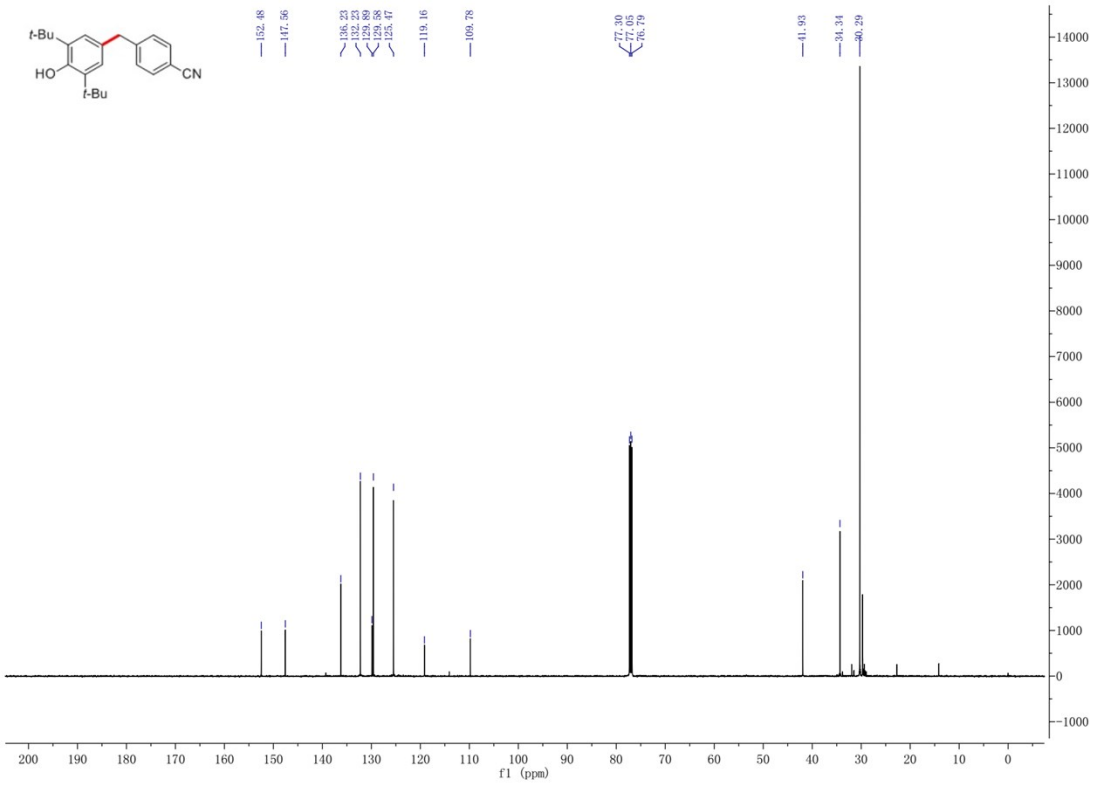
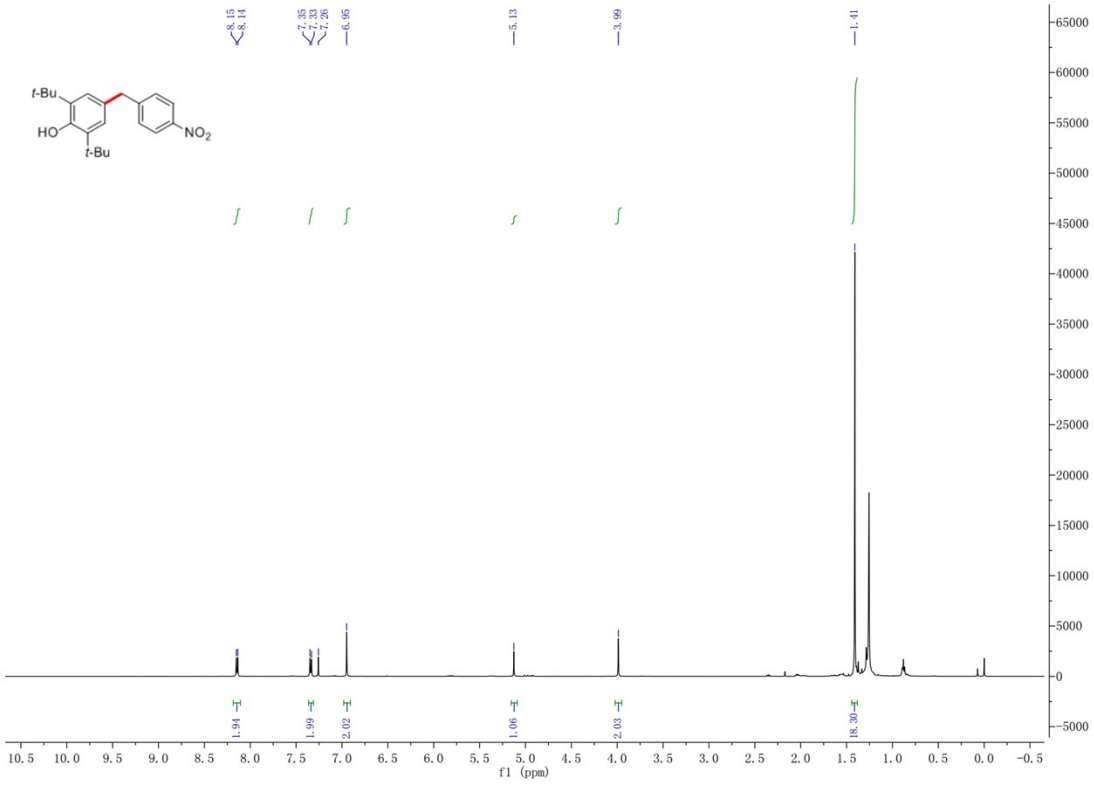
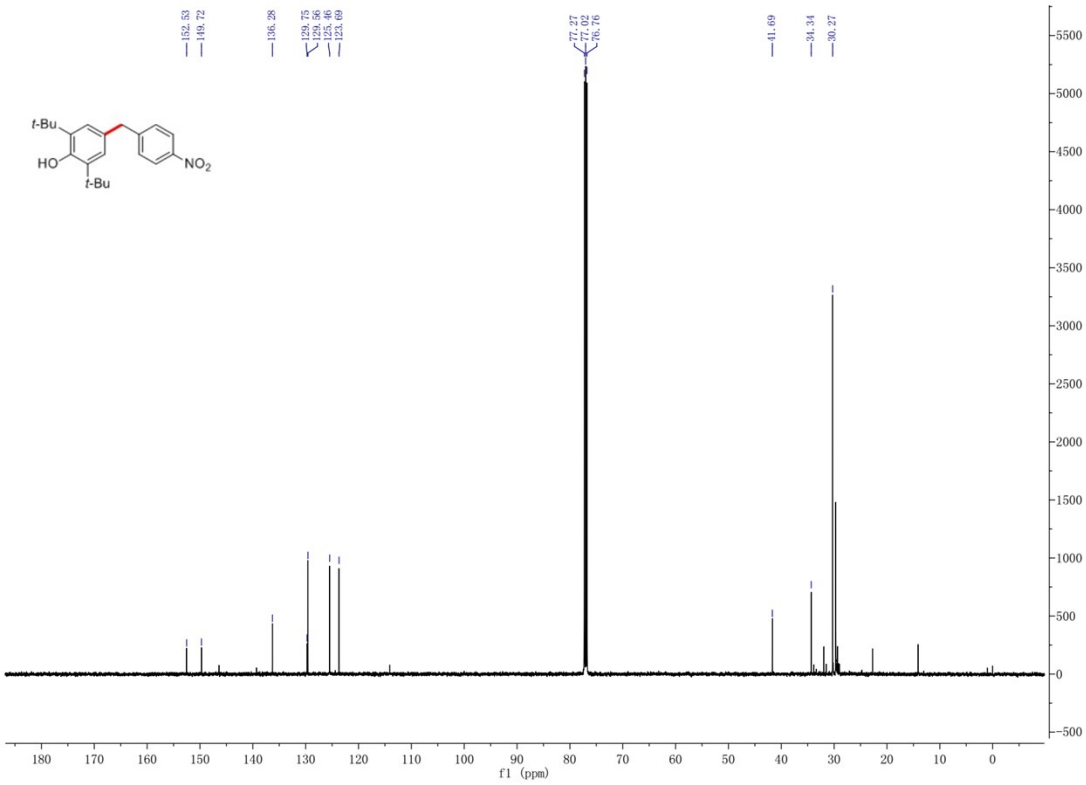
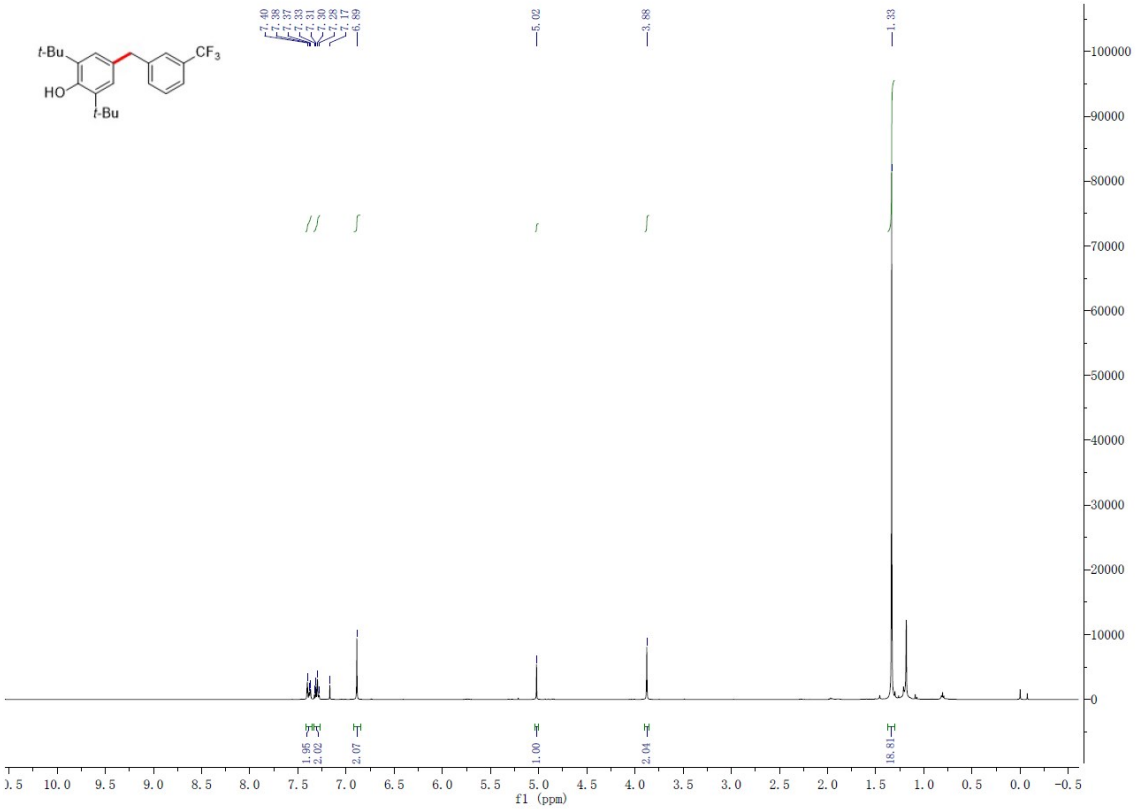
76.00
75.75
40.32
30.26
f1 (ppm)

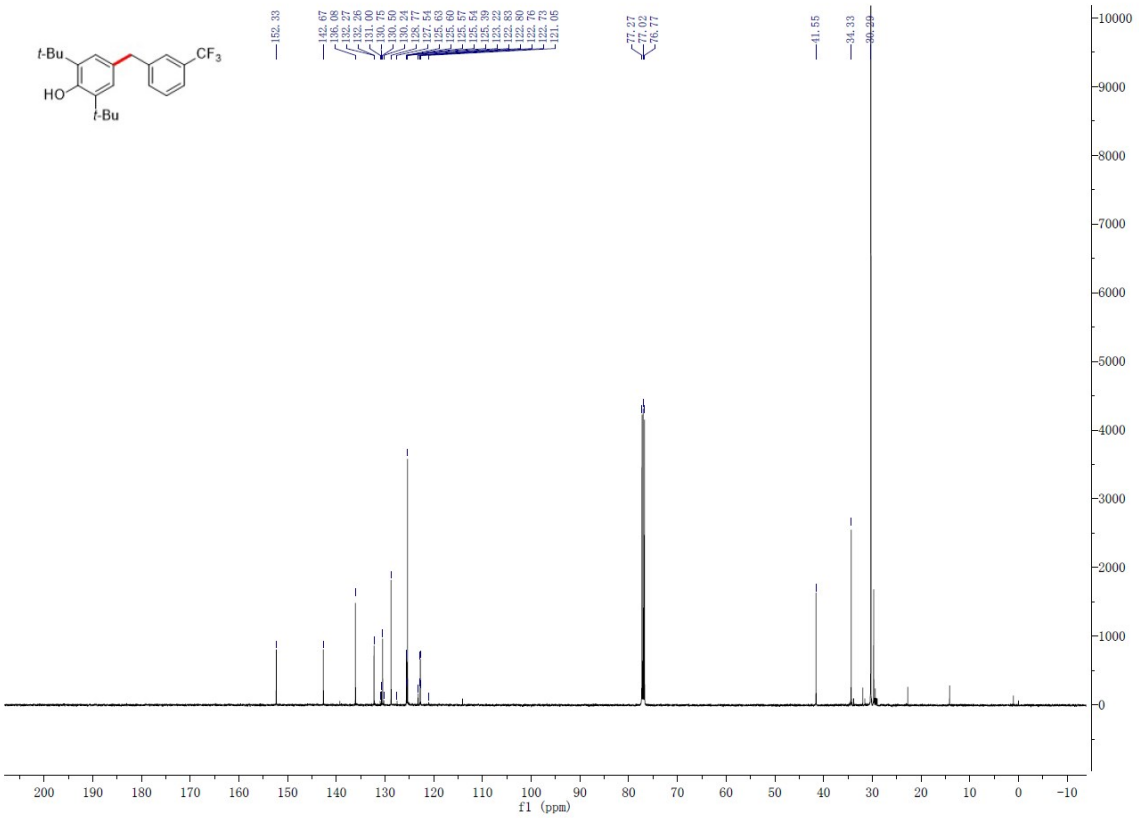

t-Bu
HO
t-Bu
CN
7.57
7.56
7.29
7.28
7.25
6.93
5.12
3.94
1.41
1.91
1.92
1.96
1.00
1.98
18.00
f1 (ppm)

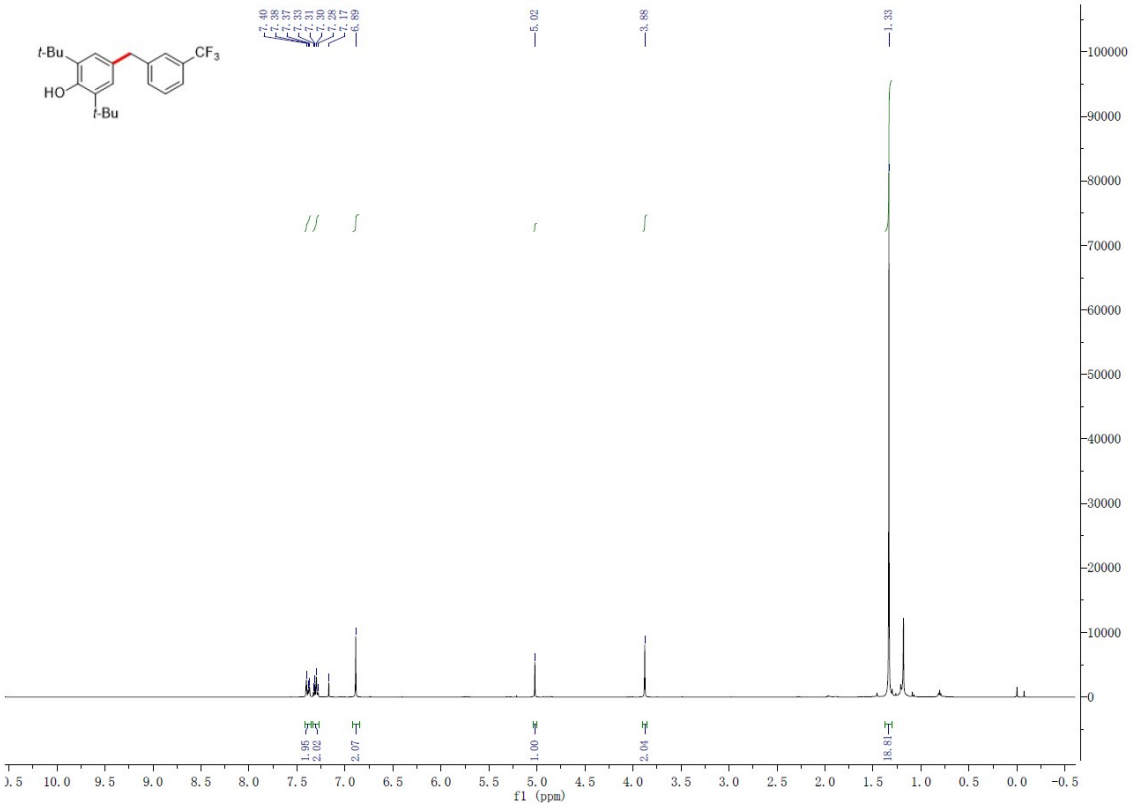

t-Bu
HO
t-Bu
CN
152.48
147.56
136.23
132.23
129.89
129.38
125.47
119.16
109.78
77.30
77.05
76.79
41.93
34.34
30.29
f1 (ppm)

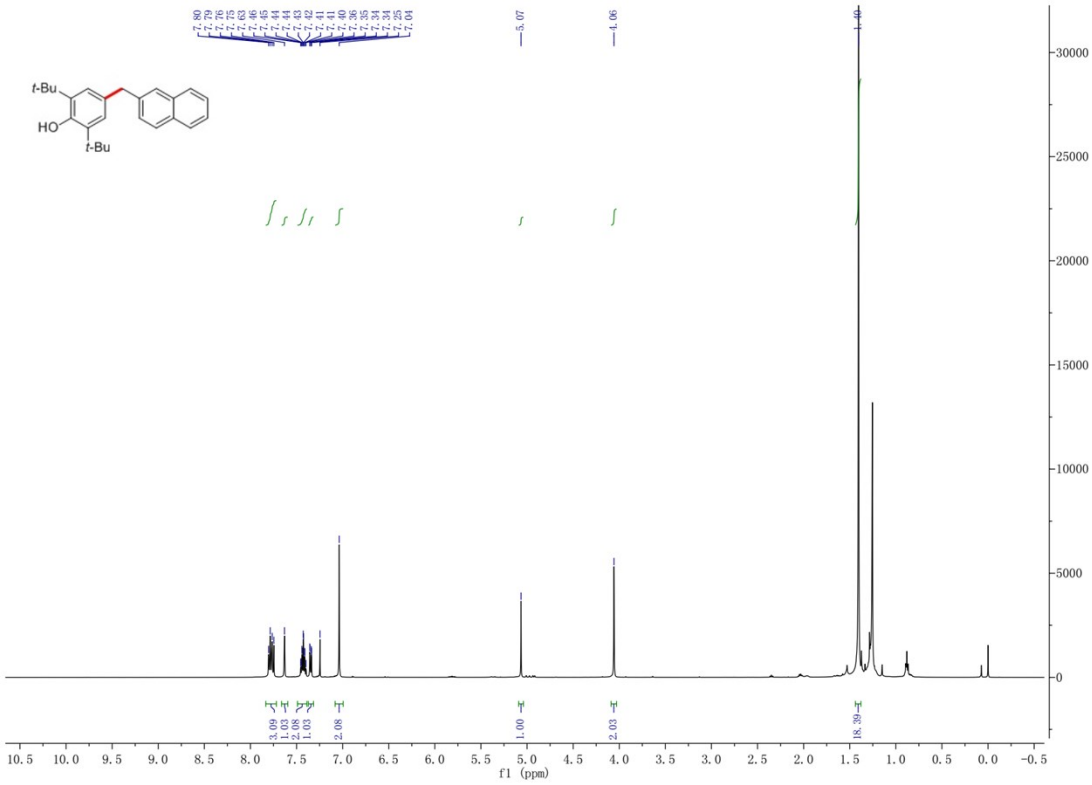

t-Bu
HO
t-Bu
NO2
8.15
8.14
7.35
7.33
7.26
6.95
5.13
3.99
1.41
1.94
1.99
2.02
1.06
2.03
18.30
f1 (ppm)


152.53
149.72
136.28
129.75
129.56
125.46
123.69
77.27
77.02
76.76
41.69
34.34
30.27
t-Bu
HO
t-Bu
NO2
f1 (ppm)


7.40
7.38
7.37
7.33
7.31
7.30
7.29
7.17
6.89
5.02
3.88
1.33
t-Bu
HO
t-Bu
CF3
1.95
2.02
2.07
1.00
2.04
18.81
f1 (ppm)


t-Bu
HO
t-Bu
CF3
152.33
142.67
136.08
132.27
132.26
131.00
130.75
130.59
130.24
128.77
127.54
125.63
125.60
125.57
125.54
125.39
123.22
122.83
122.80
122.76
122.73
121.05
77.27
77.02
76.77
41.55
34.33
30.29
f1 (ppm)


t-Bu
HO
t-Bu
CF3
7.40
7.38
7.37
7.33
7.31
7.30
7.28
7.17
6.89
5.02
3.88
1.33
1.95
2.02
2.07
1.00
2.04
18.81
f1 (ppm)


7.80
7.79
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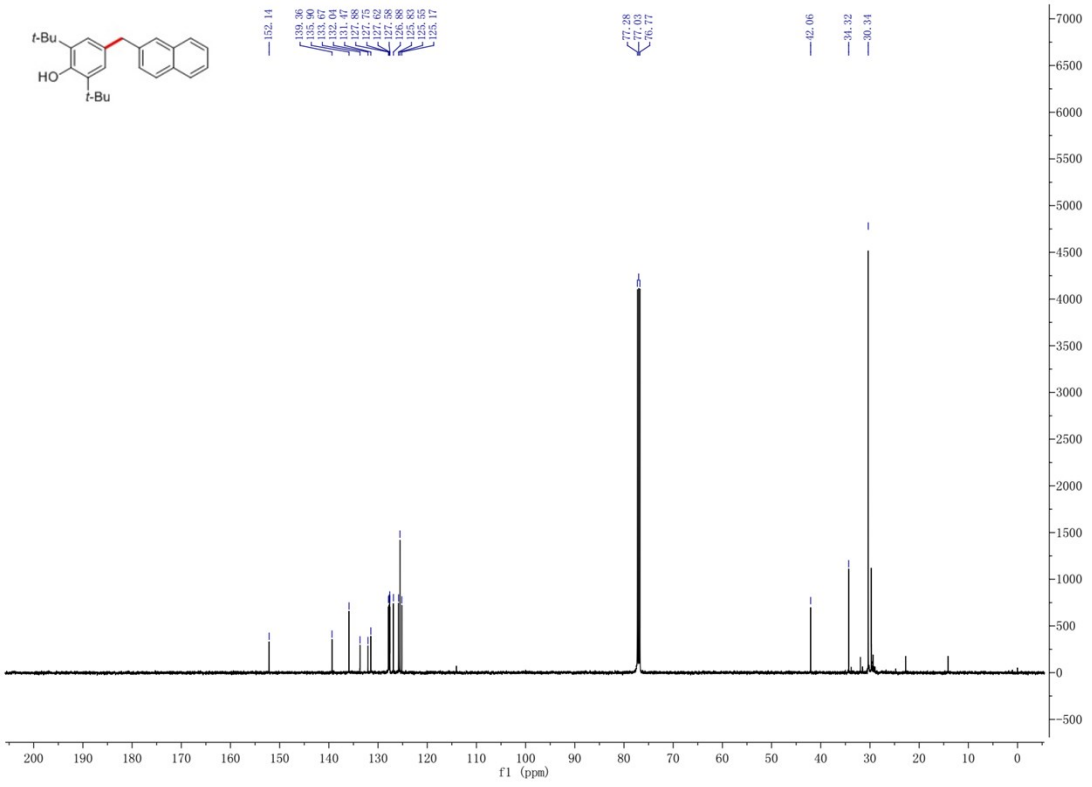
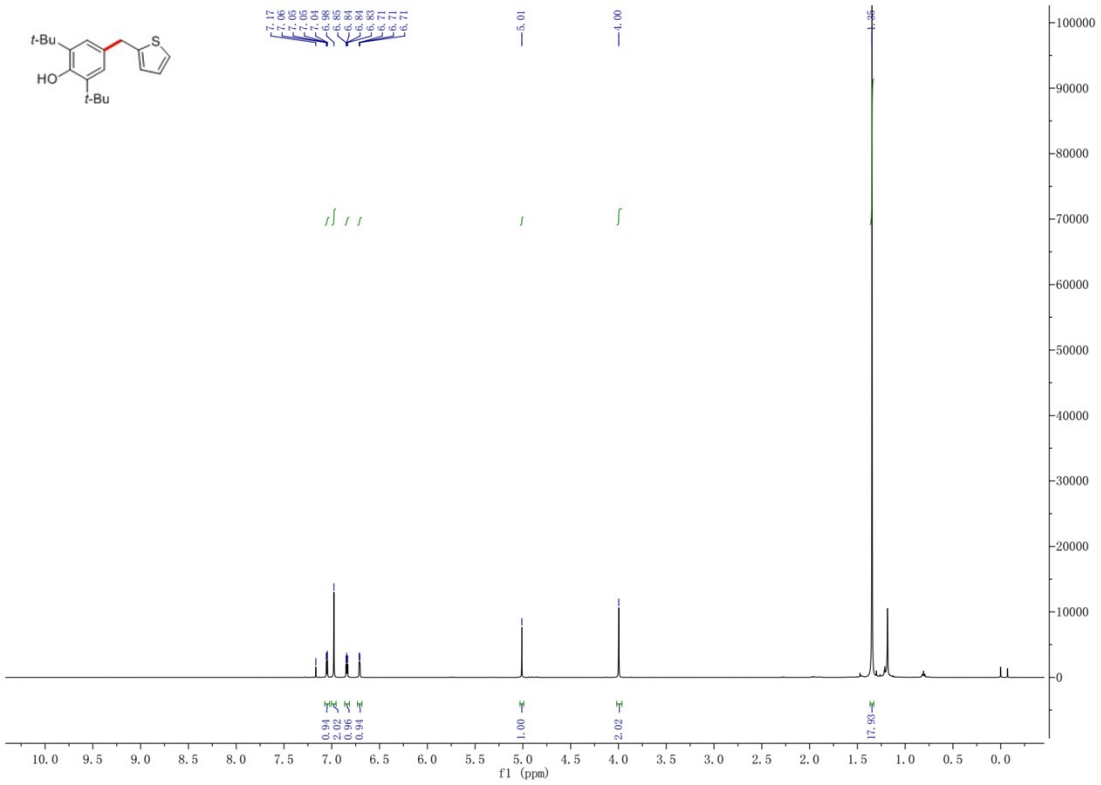
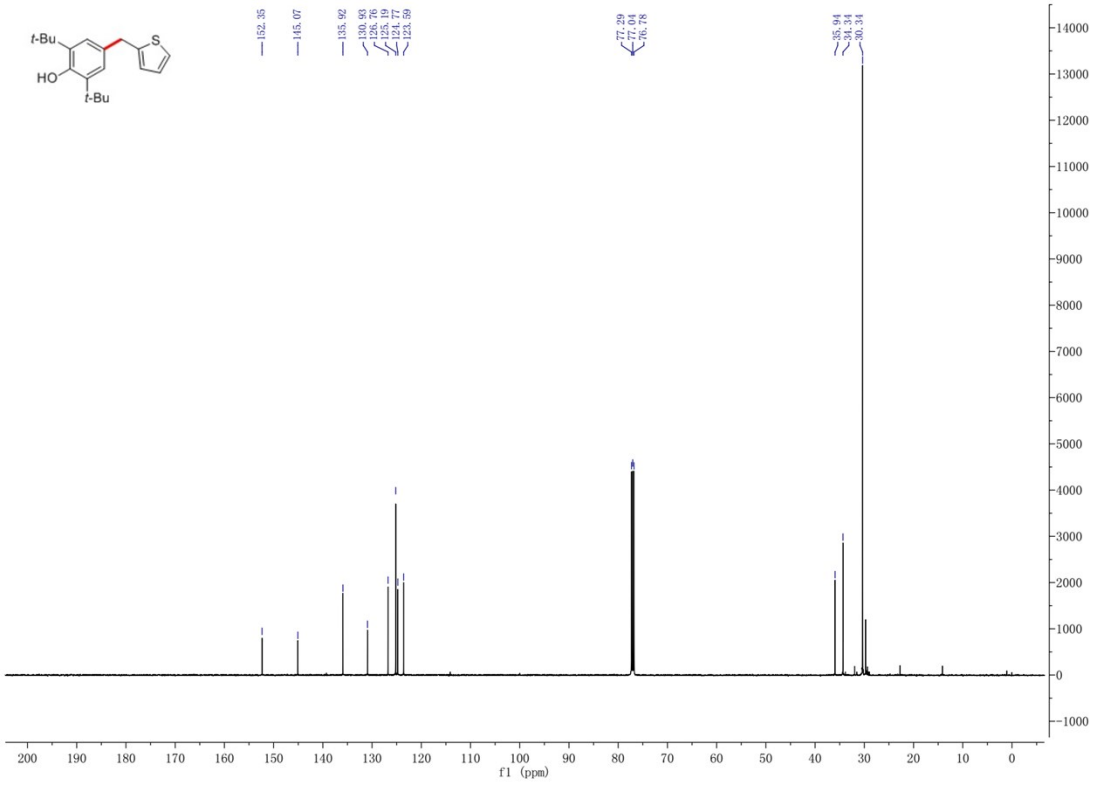
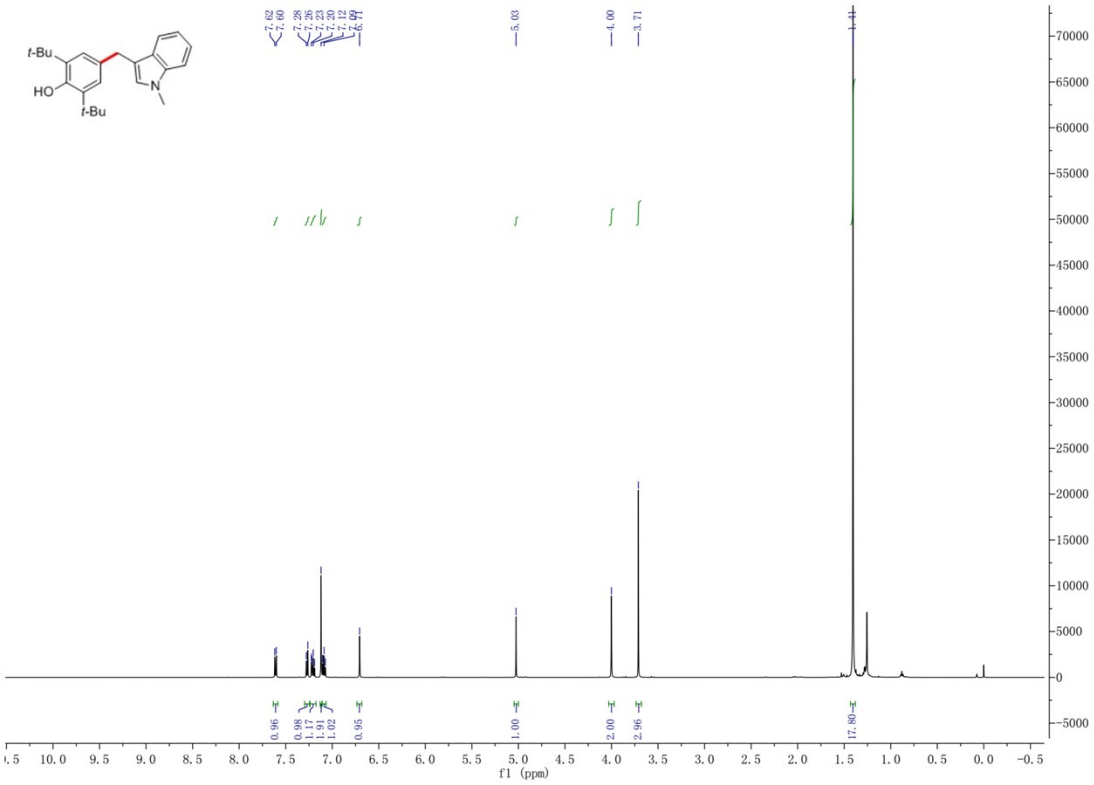
7.75
7.63
7.46
7.45
7.44
7.43
7.42
7.41
7.40
7.36
7.35
7.34
7.25
7.04
5.07
4.06
1.40
t-Bu
HO
t-Bu
3.09
1.03
2.08
1.03
2.08
1.00
2.03
18.39
f1 (ppm)


152.14
139.36
135.90
133.67
132.04
131.47
127.88
127.75
127.62
127.38
126.88
125.83
125.55
125.17
77.28
77.03
76.77
42.06
34.32
30.34
t-Bu
HO
t-Bu
f1 (ppm)


t-Bu
HO
t-Bu
S
7.17
7.06
7.05
7.05
7.04
6.98
6.85
6.84
6.84
6.83
6.71
6.71
6.71
5.01
4.00
1.45
0.94
2.02
0.96
0.94
1.00
2.02
17.93
f1 (ppm)


t-Bu
HO
t-Bu
S
152.35
145.07
135.92
130.93
129.76
125.19
124.77
123.59
77.29
77.04
76.78
35.94
34.34
30.34
f1 (ppm)


t-Bu
HO
t-Bu
N
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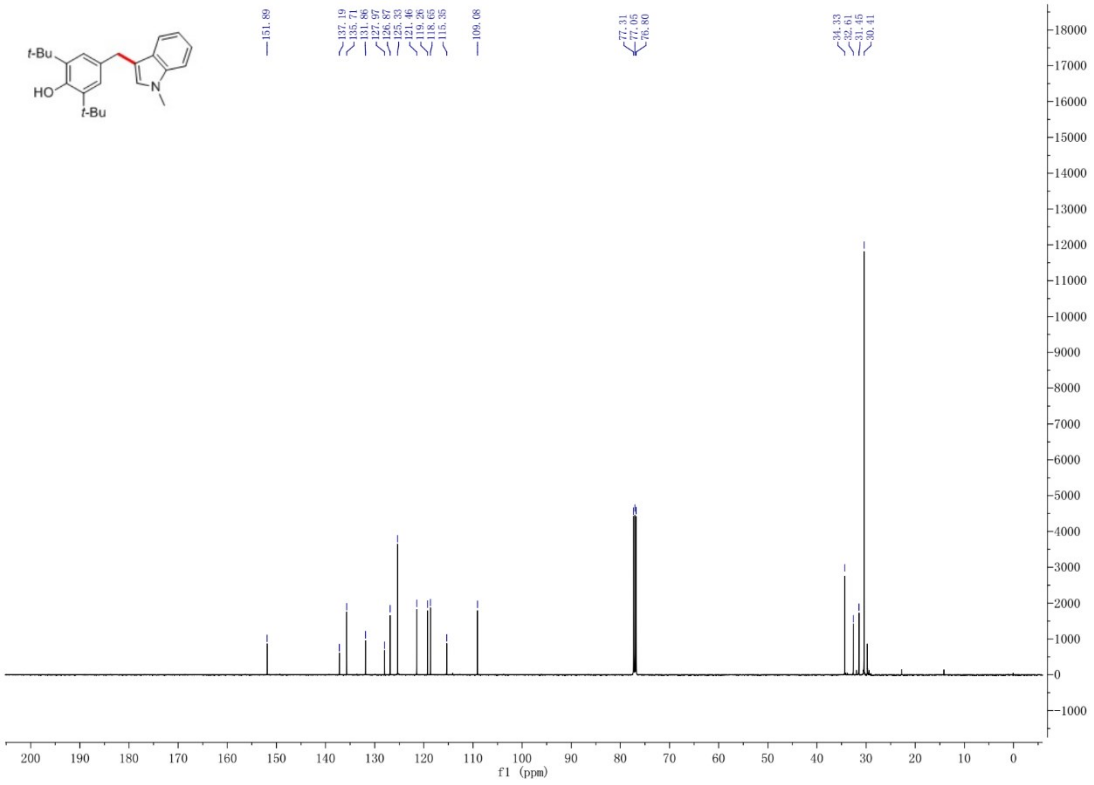
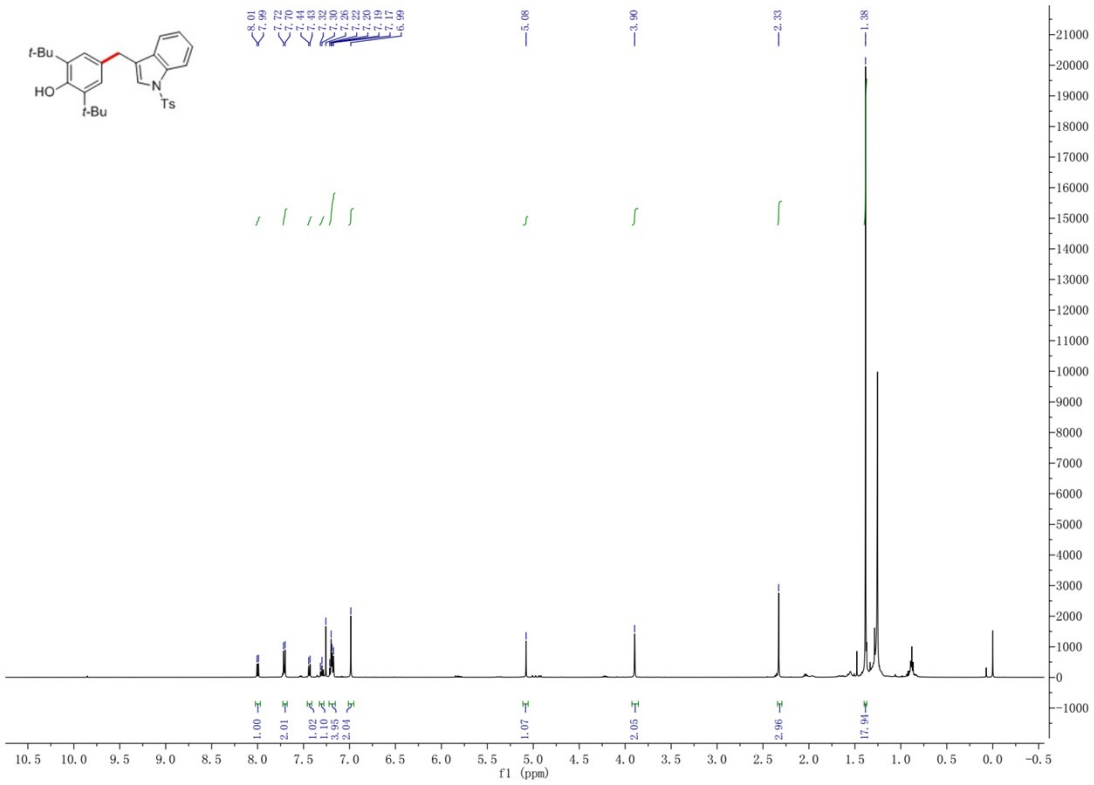
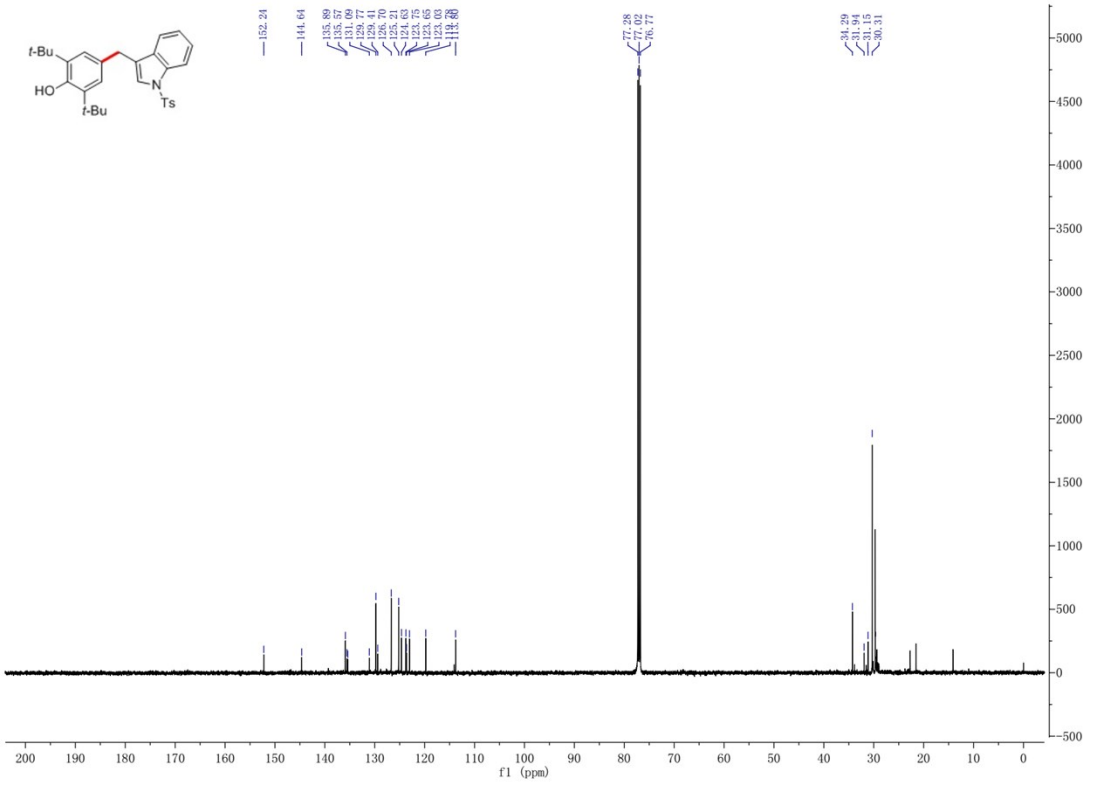
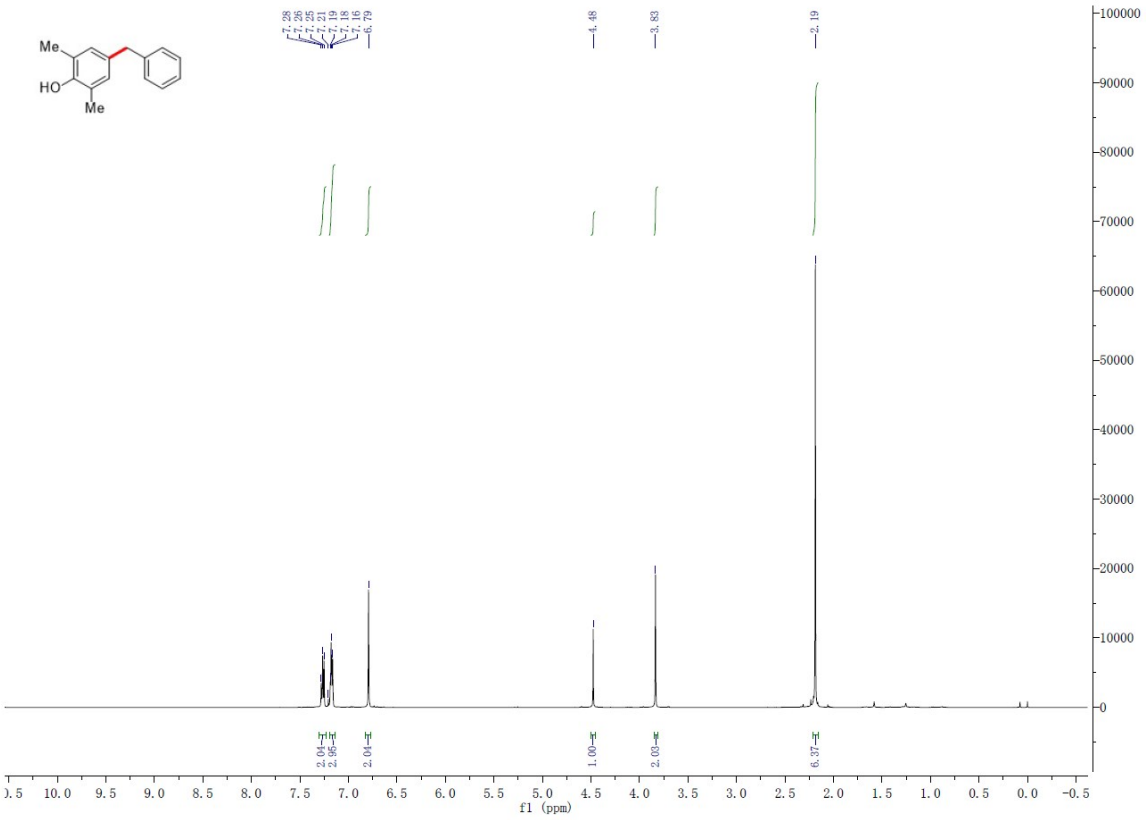
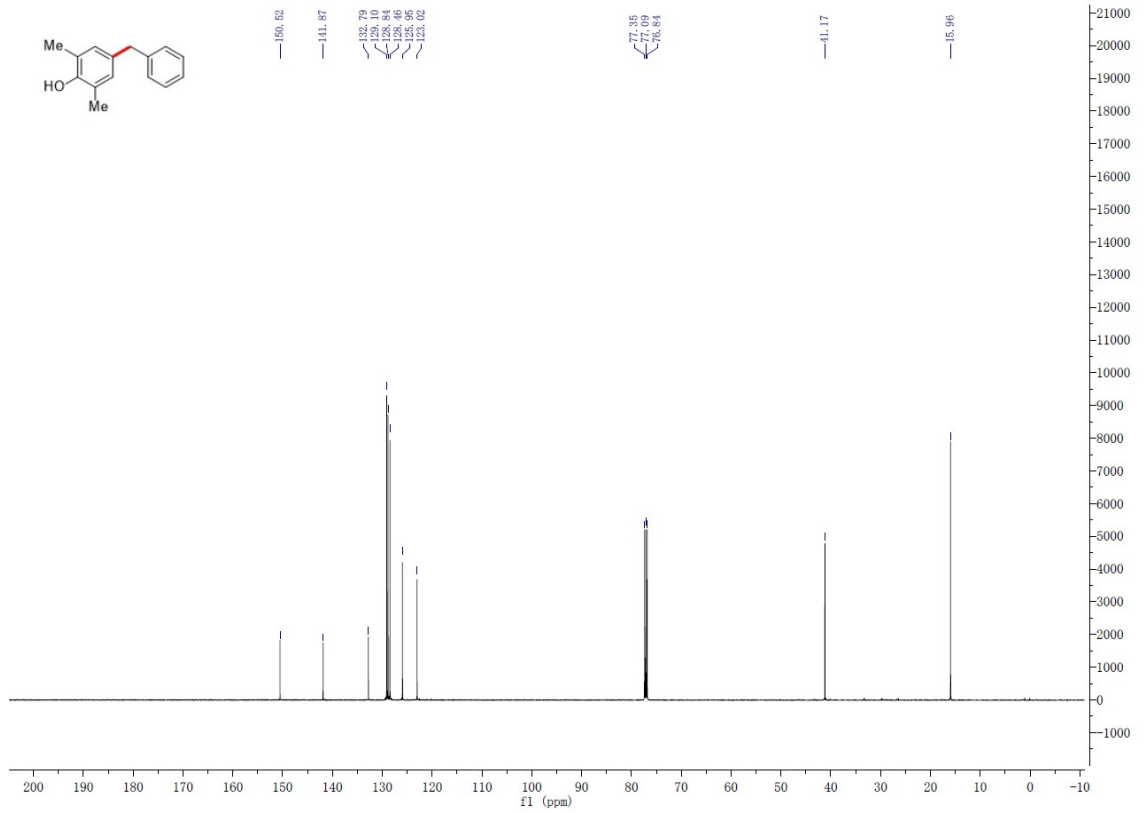
7.60
7.28
7.26
7.23
7.20
7.12
7.09
6.91
5.03
4.00
3.71
1.41
0.96
0.98
1.17
1.04
1.02
0.95
1.00
2.00
2.96
17.80
f1 (ppm)

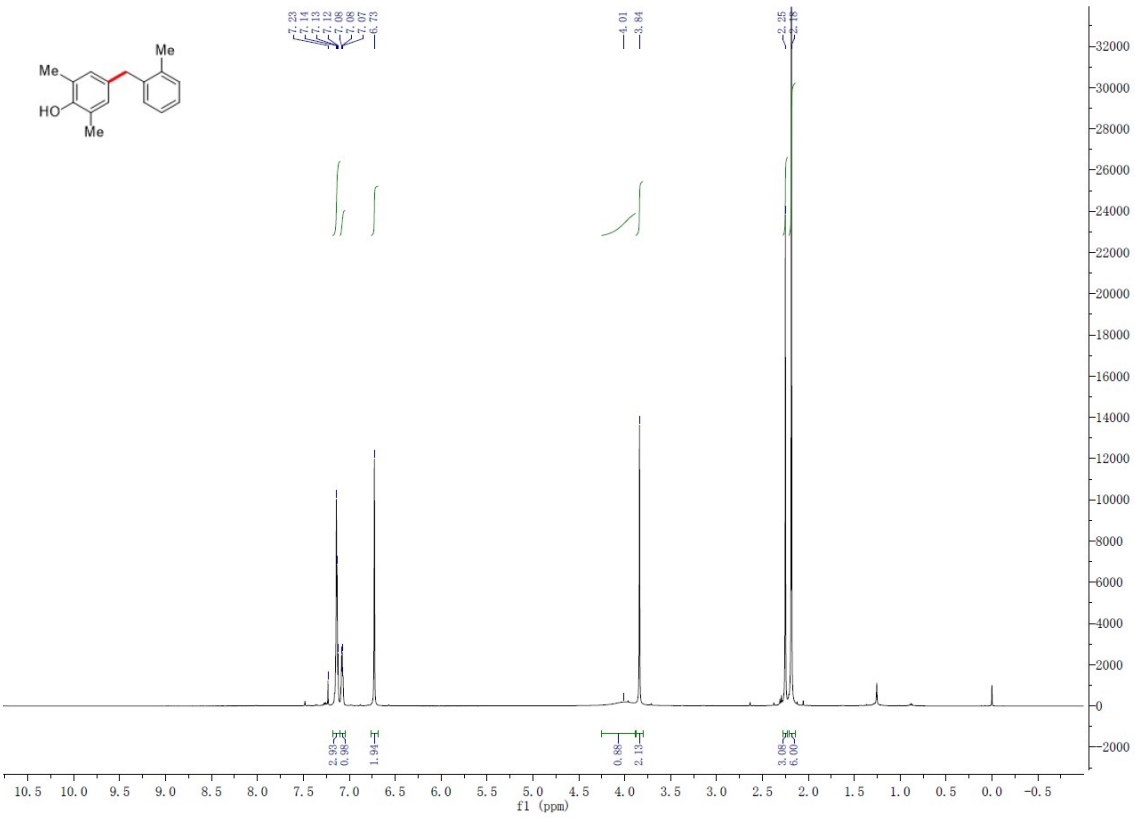

t-Bu
HO
t-Bu
N
151.89
137.19
135.71
131.86
127.57
126.87
125.33
121.46
119.25
118.65
115.35
109.08
77.31
77.05
76.80
34.33
32.61
31.45
30.41
f1 (ppm)

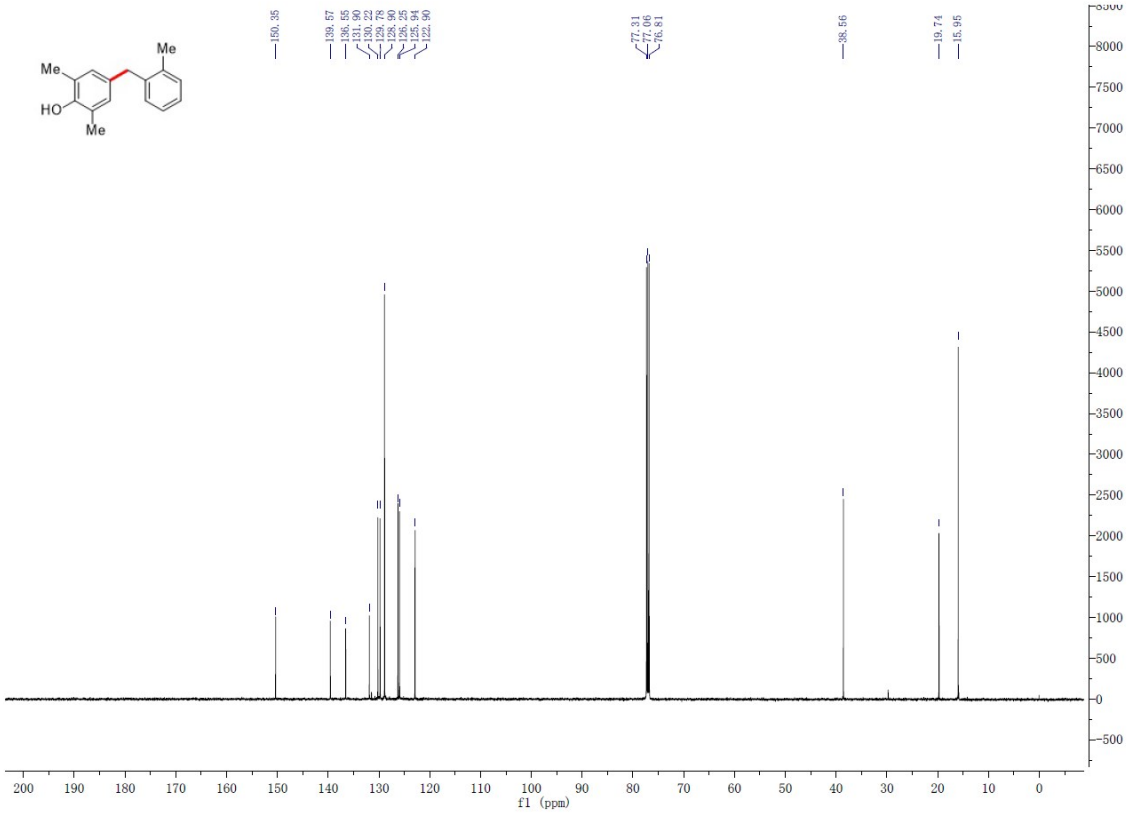

t-Bu
HO
t-Bu
N
Ts
8.01
7.99
7.72
7.70
7.44
7.43
7.32
7.30
7.26
7.22
7.20
7.19
7.17
6.99
5.08
3.90
2.33
1.38
1.00
2.01
1.02
1.10
3.95
2.04
1.07
2.05
2.96
17.94
f1 (ppm)

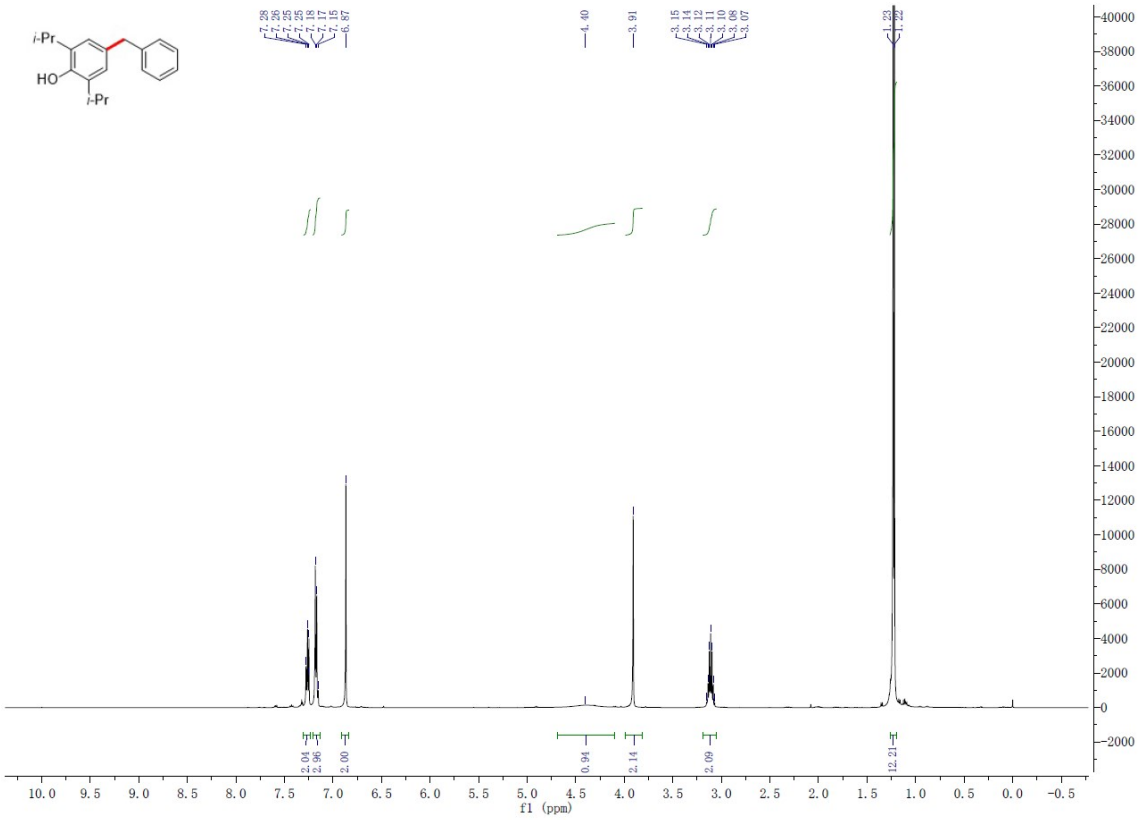

t-Bu
HO
t-Bu
N
Ts
152.24
144.64
135.89
135.57
131.09
130.77
129.41
126.70
125.21
124.63
123.75
123.65
123.03
77.28
77.02
76.77
34.29
31.94
31.15
30.31
f1 (ppm)

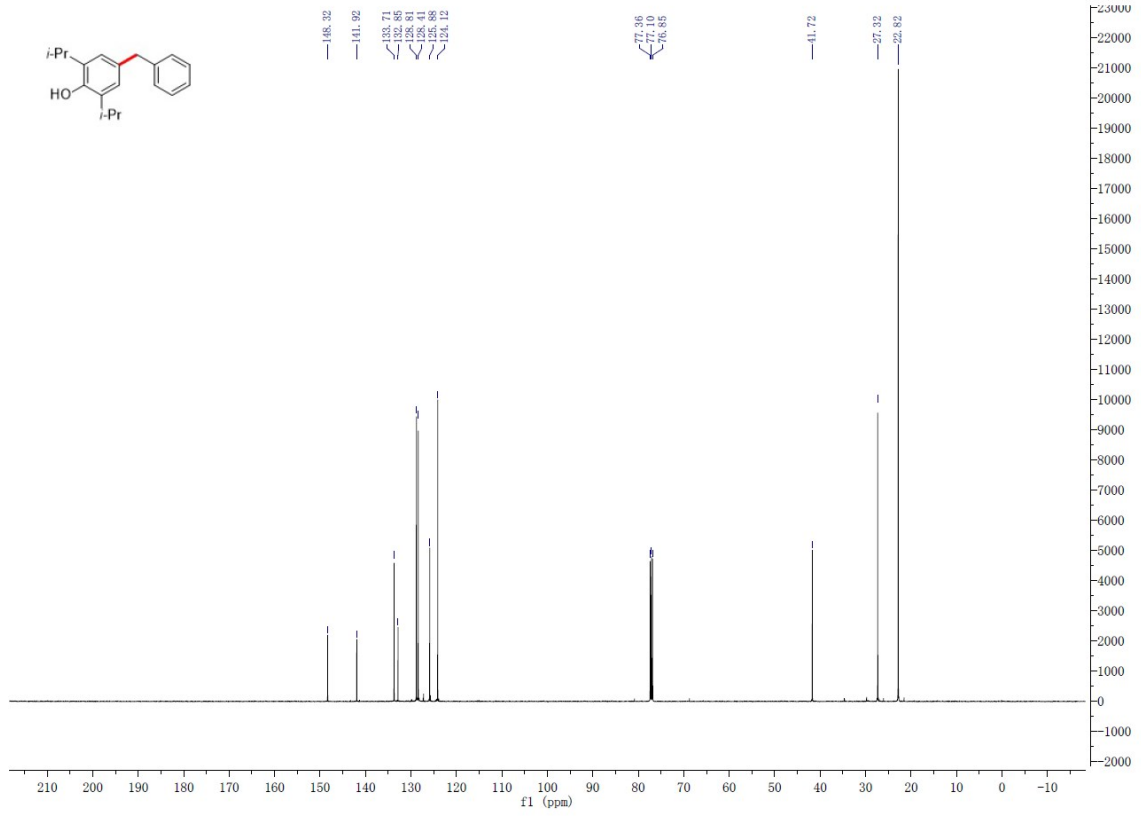

Me
HO
Me
7.28
7.25
7.21
7.19
7.18
7.15
6.79
4.48
3.83
2.19
2.04
2.05
2.04
1.00
2.03
6.37
f1 (ppm)

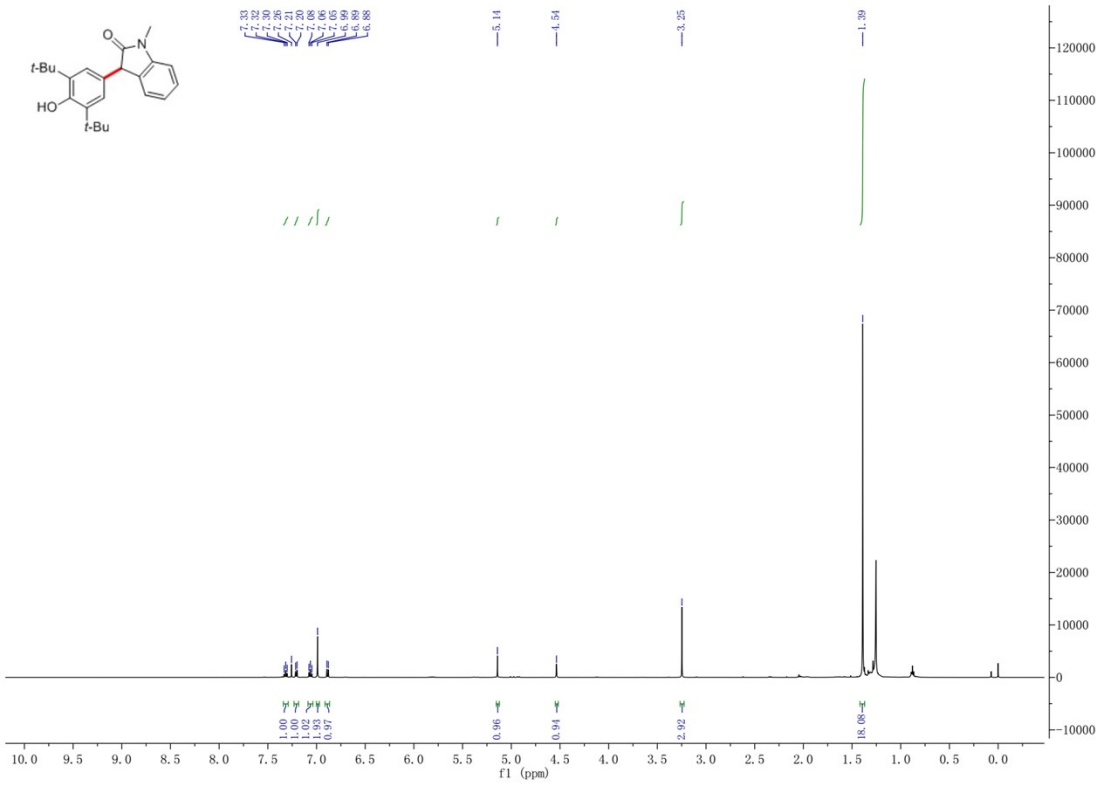

Me
HO
Me
150.52
141.87
132.79
129.10
128.84
126.46
125.95
123.02
77.35
77.09
76.84
41.17
15.96
f1 (ppm)

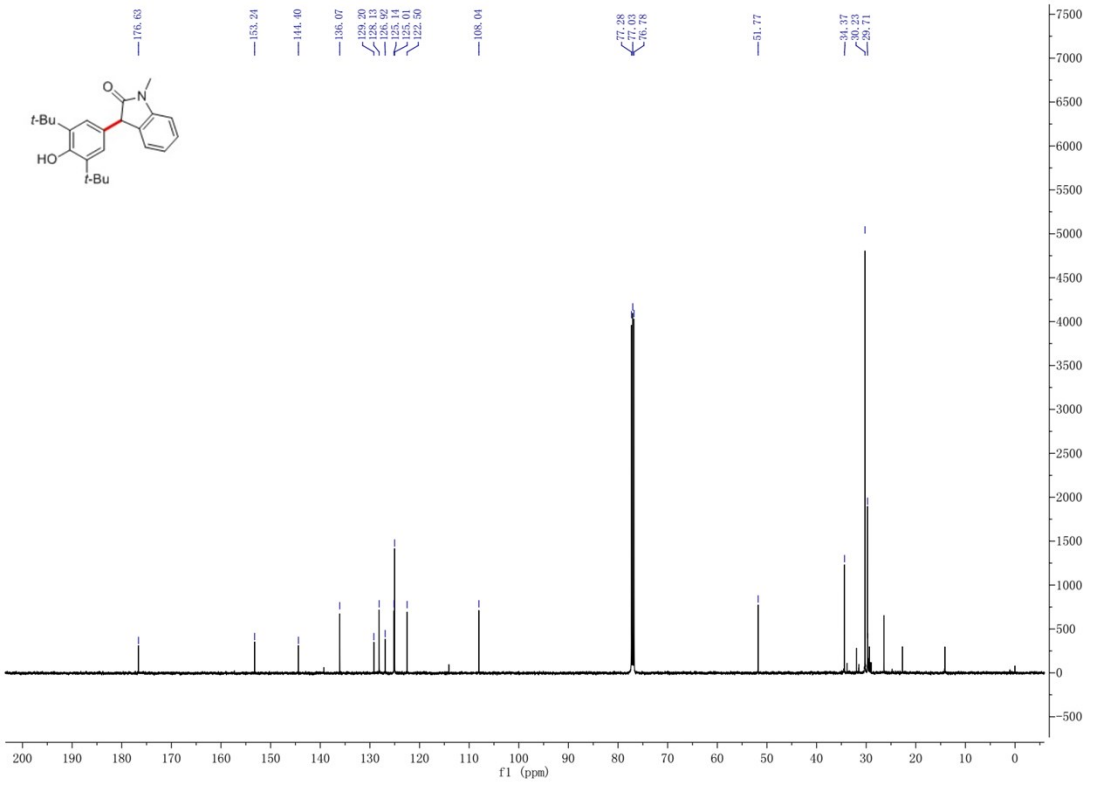

Me
Me
HO
Me
7.23
7.14
7.13
7.12
7.08
7.08
7.07
6.73
4.01
3.84
2.25
2.18
2.93
0.98
1.94
0.88
2.13
3.08
6.00
f1 (ppm)

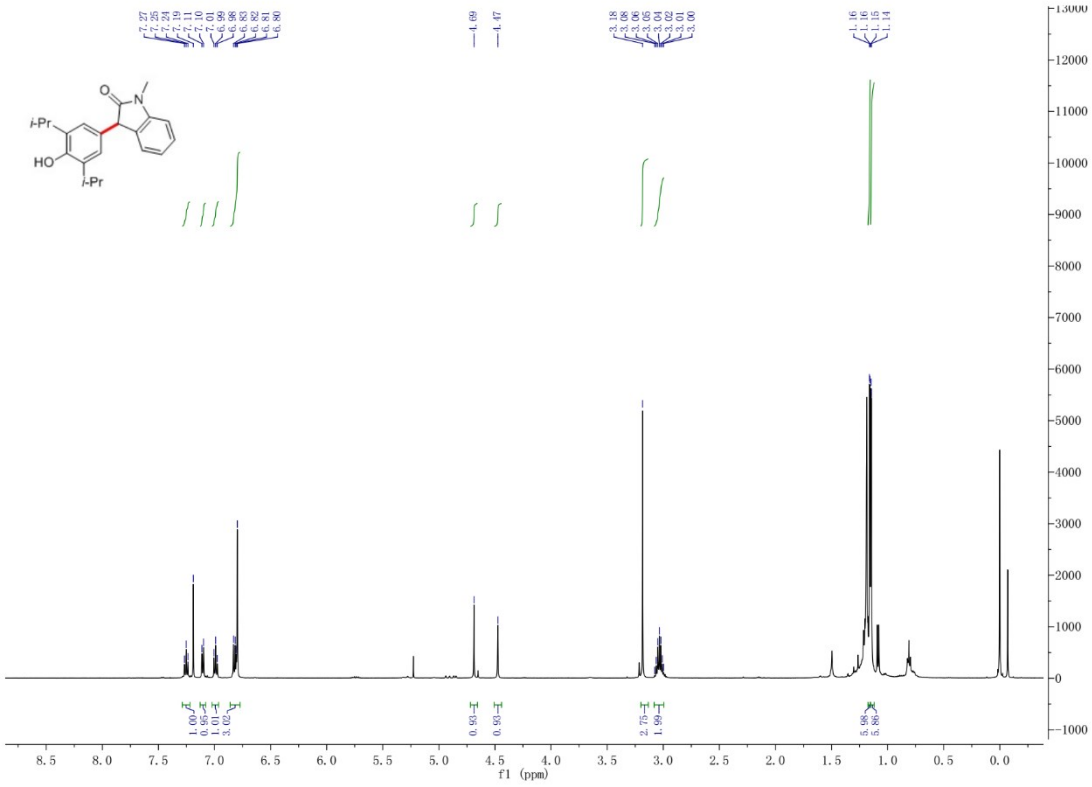

Me
Me
HO
Me
150.35
139.57
136.55
131.90
130.22
129.78
128.90
126.25
125.94
122.90
77.31
77.06
76.81
38.56
19.74
15.95
f1 (ppm)

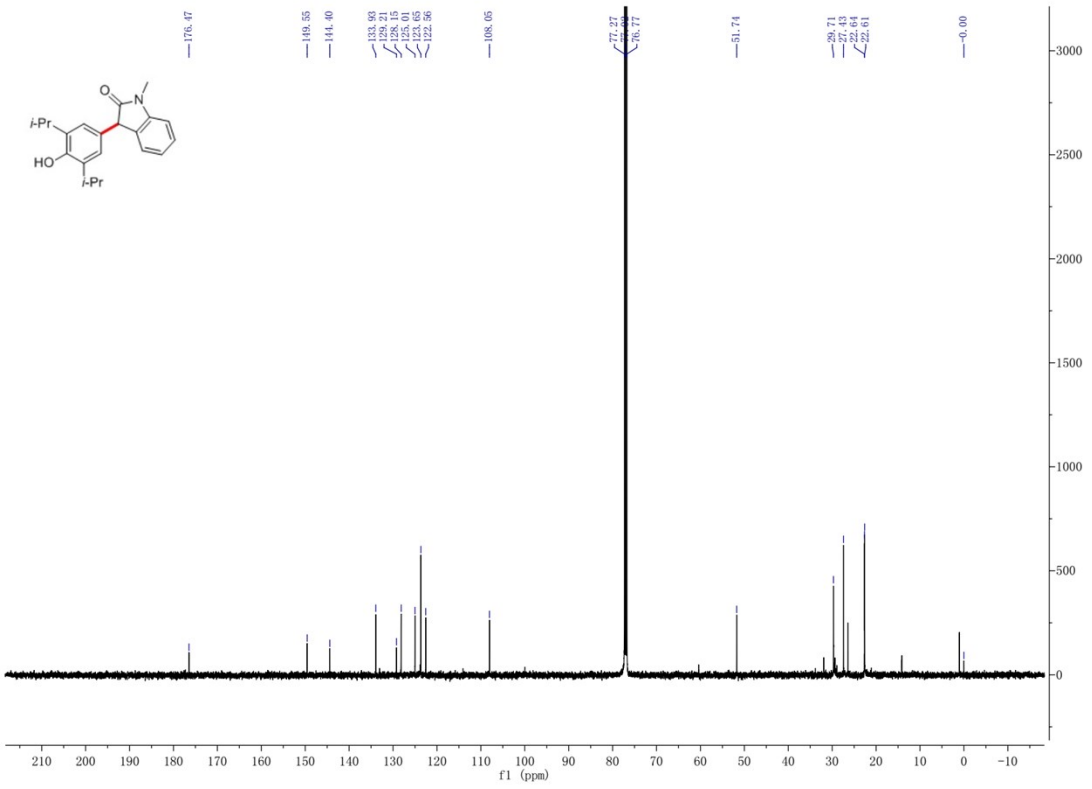

i-Pr
HO
i-Pr
7.28
7.26
7.25
7.25
7.18
7.17
7.15
6.87
4.40
3.91
3.15
3.14
3.12
3.11
3.10
3.08
3.07
1.23
1.22
2.04
2.96
2.00
0.94
2.14
2.09
12.21
f1 (ppm)

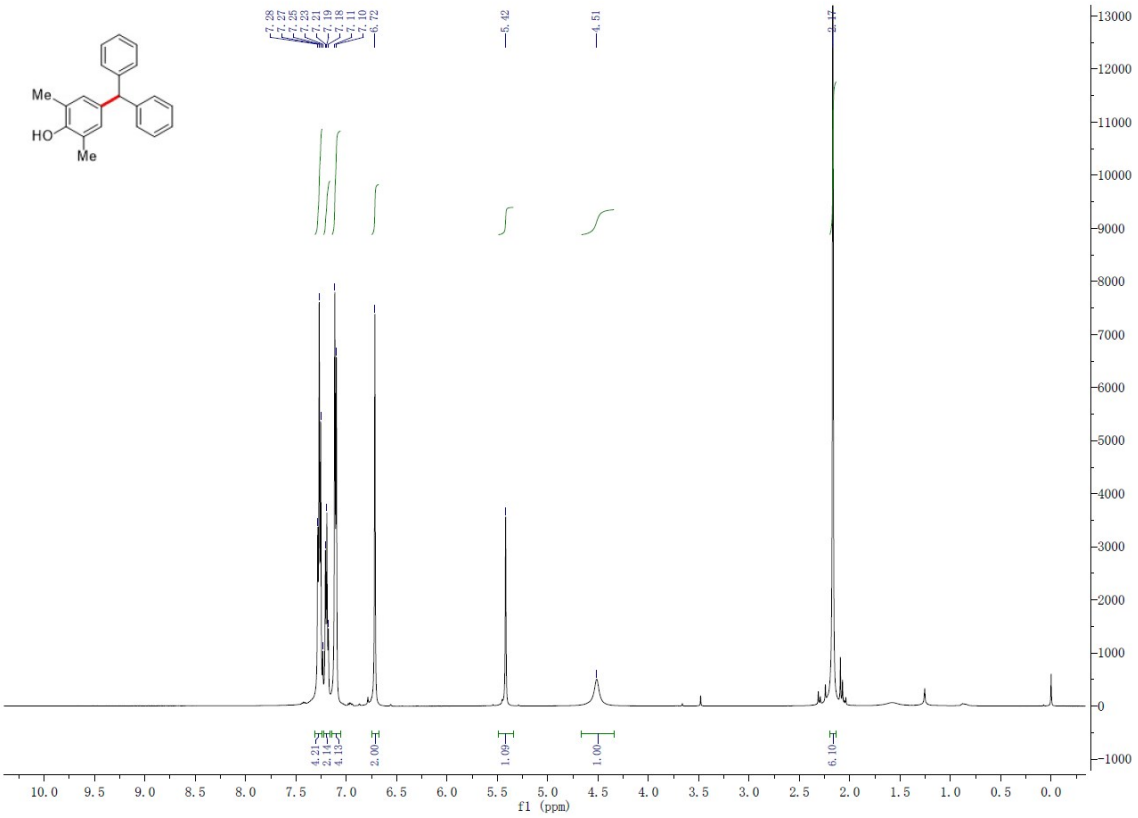

i-Pr
HO
i-Pr
148.32
141.92
133.71
132.85
129.81
128.41
125.88
124.12
77.36
77.10
76.85
41.72
27.32
22.82
f1 (ppm)

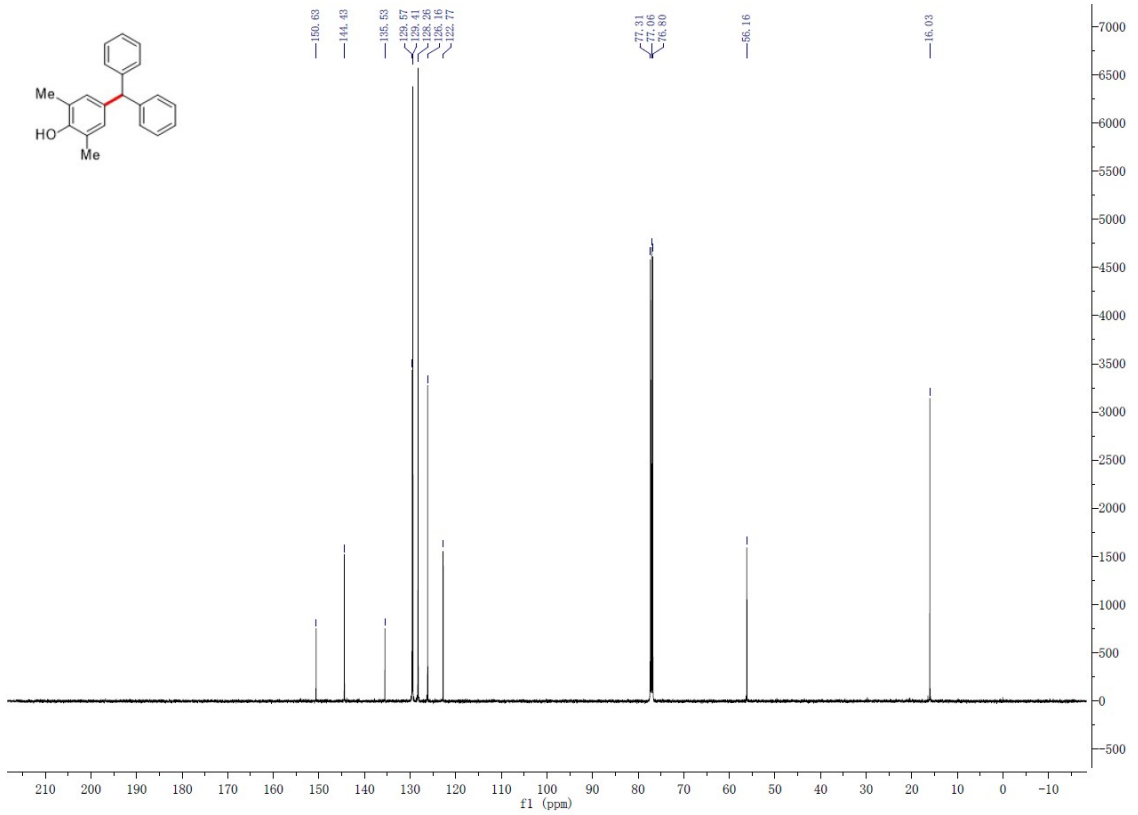

7.33
7.32
7.30
7.25
7.21
7.20
7.08
7.06
7.05
6.99
6.89
6.88
5.14
4.54
3.25
1.39
t-Bu
HO
t-Bu
O
N
1.00
1.00
1.02
1.93
0.97
0.96
0.94
2.92
18.08
f1 (ppm)

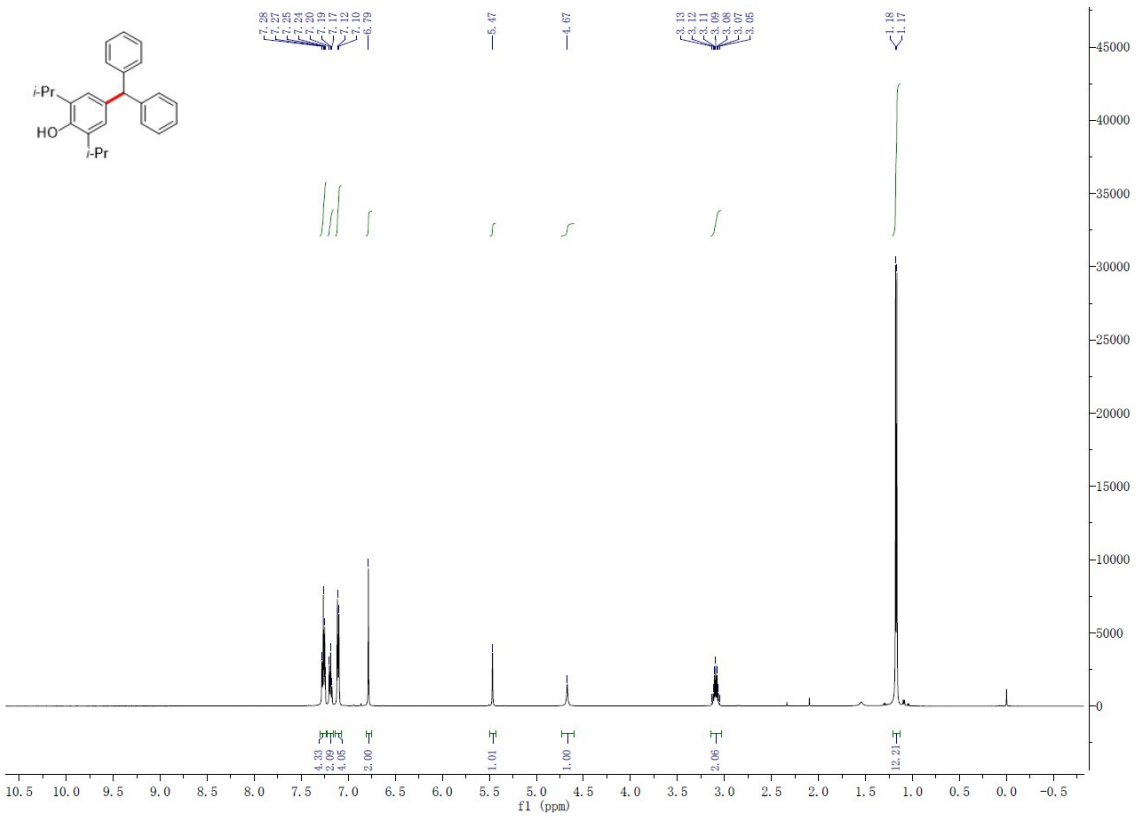

176.63
153.24
144.40
136.07
129.20
128.13
126.92
125.14
125.01
122.80
108.04
77.28
77.03
76.78
51.77
34.37
30.23
29.71
t-Bu
HO
t-Bu
O
N
f1 (ppm)

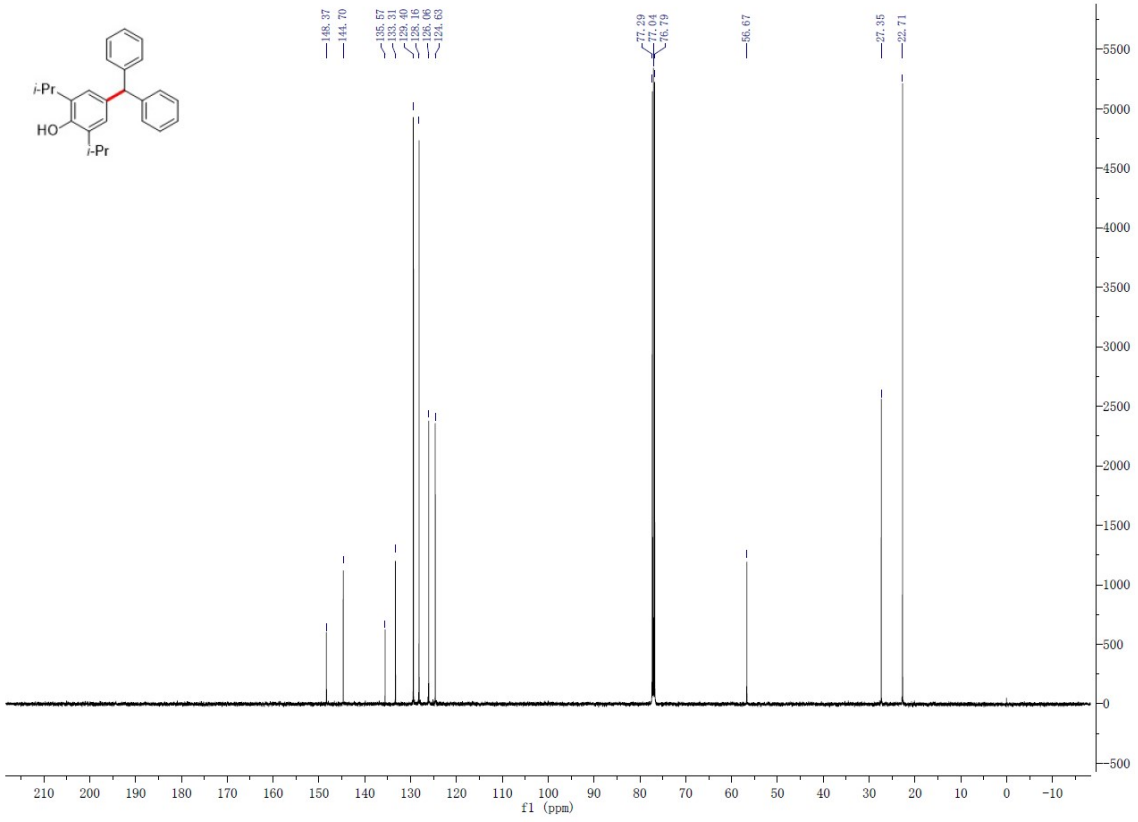

7.27
7.25
7.24
7.19
7.11
7.10
7.01
6.98
6.96
6.83
6.82
6.81
6.80
4.69
4.47
3.18
3.08
3.06
3.05
3.04
3.02
3.01
3.00
1.16
1.16
1.15
1.14
i-Pr
HO
i-Pr
1.00
0.95
1.01
3.02
0.93
0.93
2.75
1.99
5.98
5.88
f1 (ppm)

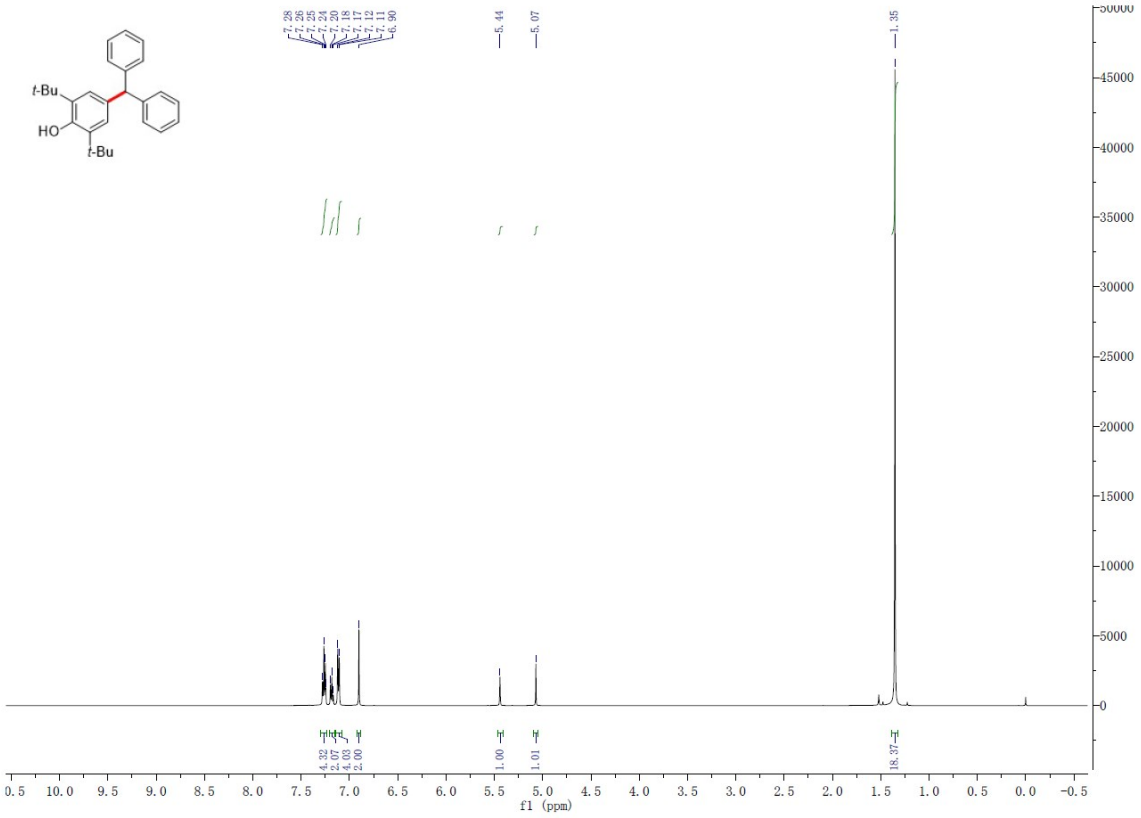

176.47
149.55
144.40
133.93
129.21
128.15
125.01
124.65
122.56
108.05
77.27
77.02
76.77
51.74
29.71
27.43
22.64
22.61
0.00
i-Pr
HO
i-Pr
f1 (ppm)


Me
HO
Me
7.28
7.27
7.25
7.23
7.21
7.19
7.18
7.11
7.10
6.72
5.42
4.51
2.17
4.21
2.13
4.15
2.00
1.09
1.00
6.10
f1 (ppm)


Me
HO
Me
150.63
144.43
135.53
129.67
129.41
128.26
126.16
122.77
77.31
77.06
76.80
56.16
16.03
f1 (ppm)


i-Pr
HO
i-Pr
7.28
7.27
7.25
7.24
7.20
7.19
7.17
7.12
7.10
6.79
5.47
4.67
3.13
3.12
3.11
3.09
3.08
3.07
3.05
1.18
1.17
4.33
2.09
4.06
2.00
1.01
1.00
2.06
12.21
f1 (ppm)


i-Pr
HO
i-Pr
148.37
144.70
135.57
133.31
129.40
128.16
126.06
124.63
77.29
77.04
76.79
56.67
27.35
22.71
f1 (ppm)


t-Bu
HO
t-Bu
7.28
7.26
7.25
7.24
7.20
7.18
7.17
7.12
7.11
6.90
5.44
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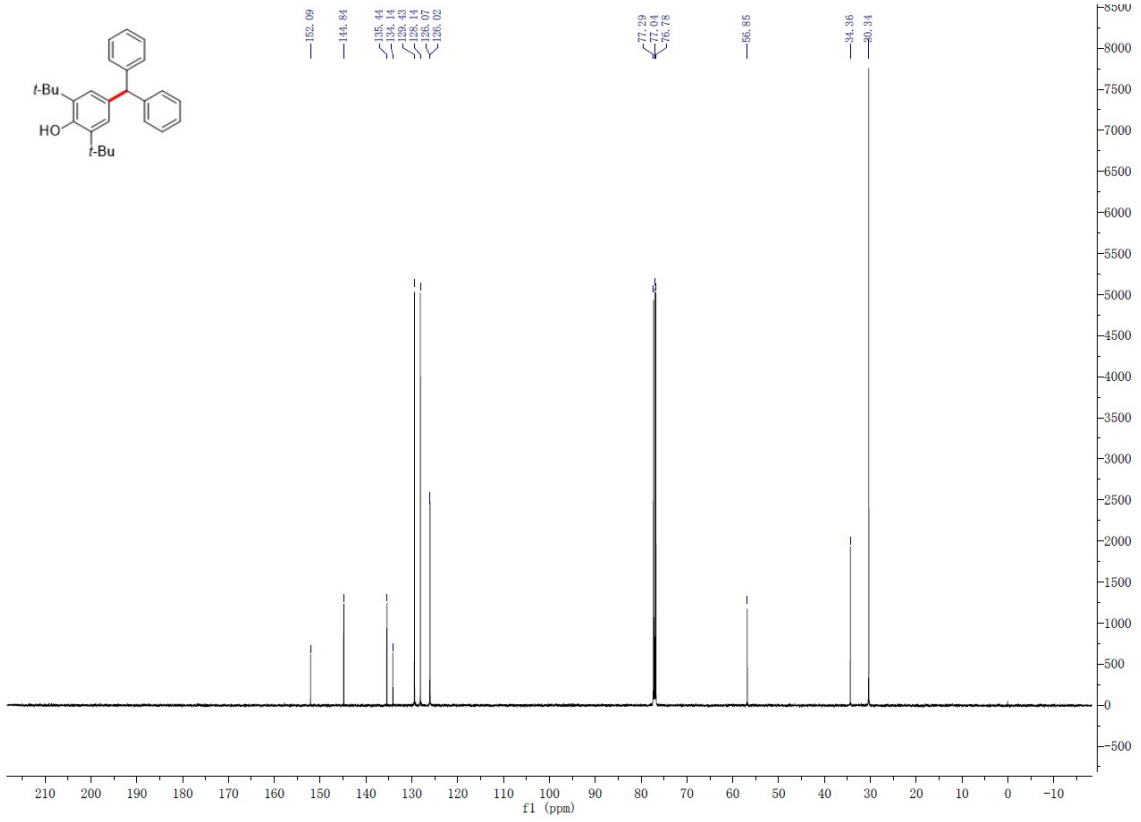
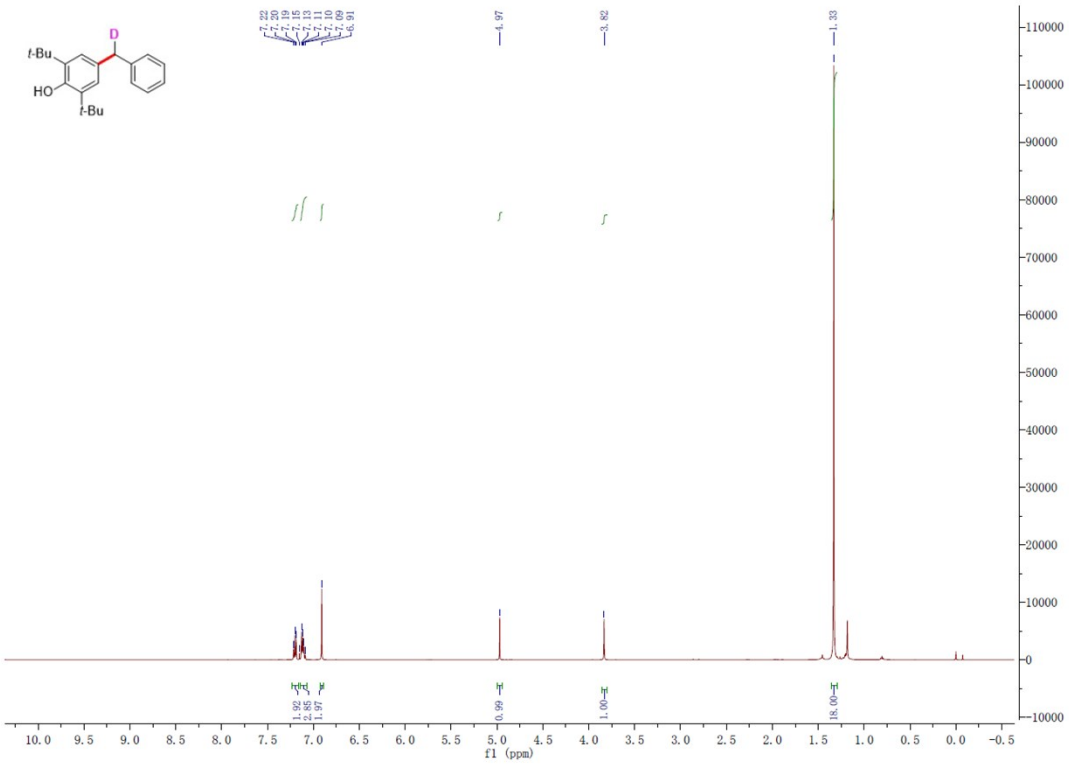
1.35
4.32
2.07
4.03
2.00
1.00
1.01
18.37
f1 (ppm)


t-Bu
HO
t-Bu
152.09
144.84
135.44
134.14
129.43
128.14
126.07
125.02
77.29
77.04
76.78
56.85
34.36
30.34
f1 (ppm)


D
t-Bu
HO
t-Bu
7.22
7.20
7.19
7.15
7.13
7.11
7.10
7.09
6.91
4.97
3.82
1.33
1.92
2.85
1.97
0.99
1.00
18.00
f1 (ppm)