Supporting Information

Visible-Light-Promoted Radical Cross-Coupling of *para*-Quinone Methides with *N*-Substituted Anilines: An Efficient Approch to 2,2-Diarylethylamines

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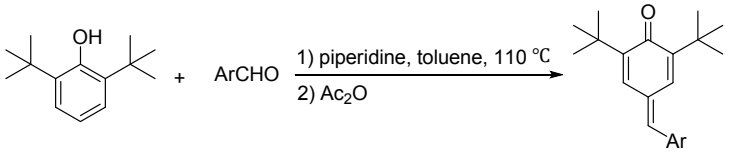
1. General Information

All the commercial reagents were used as such without further purification. All solvents were used as commercial anhydrous grade without further purification. The flash column chromatography was carried out over silica gel (230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 MHz spectrometer or Bruker Avance-500 MHz spectrometer. Chemical shifts in ^{1}H NMR spectra were reported in parts per million (ppm, δ) downfield from the internal standard Me_4Si (TMS, δ = 0 ppm). Chemical shifts in ^{13}C NMR spectra were reported relative to the central line of the chloroform signal (δ = 77.0 ppm). Peaks were labeled as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). High resolution mass spectra were obtained with a Shimadzu LCMS-IT-TOF mass spectrometer. Chemical yields refer to pure isolated substances.

2. General Procedure for the Synthesis of Substrates

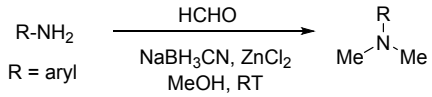
(a) General synthetic method of *p*-QMs derivatives[1]



1a-1m

In a dry 100 mL round-bottom flask, a solution of phenols (25.0 mmol) and the corresponding aldehydes (25.0 mmol) in toluene (100 mL) was heated to reflux. Piperidine (50.0 mmol, 4.95 mL) was dropwise added within 1 h. The reaction mixture was continued to reflux for 12-18 h. After cooling just below the boiling point of the reaction mixture, acetic anhydride (50.0 mmol, 2.55 g) was added and the stirring was continued for 15 min. Then the reaction mixture was cooled to room temperature, poured into water and extracted with CH_2Cl_2. The combined organic phases were dried over anhydrous Na_2SO_4 and solvents were removed under reduced pressure. The crude products were purified by flash column chromatography and further recrystallized from *n*-hexane, affording the desired *p*-QMs **1a**-**1m**.

(b) Experimental procedure for the preparation of tertiary amines (reductive methylation of amines)[2]



Amine (1.0 g) and aldehyde (8.0 equiv.) was stirred in methanol (15 mL) to which pre-prepared methanol (5 mL) solution of sodium cyanoborohydride (1.0 equiv.) and zinc chloride (0.5 equiv.) was added at room temperature. The resulted reaction mixture was stirred overnight at room temperature and basified with 0.1 N NaOH (20 mL). Methanol was evaporated and aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layer was washed with water and brine, dried over anhydrous sodium sulfate. Further, the organic layer was evaporated to

dryness and subjected for silica gel column chromatography using ethyl acetate/hexane as eluent. Yield of *tert*-amines were approx. 80-90%. **2n-2w.**

3. Mechanistic Experiments

(a) The Fluorescence Quenching Studies.

The Stern-Volmer fluorescence quenching studies were run with freshly prepared Eosin Y (0.16 μM solution in DMF) at room temperature. The solution was irradiated at 490 nm and fluorescence was measured from 500 nm to 655 nm. Control experiments showed that the excited EY* was quenched by *p*-QM **1a**.

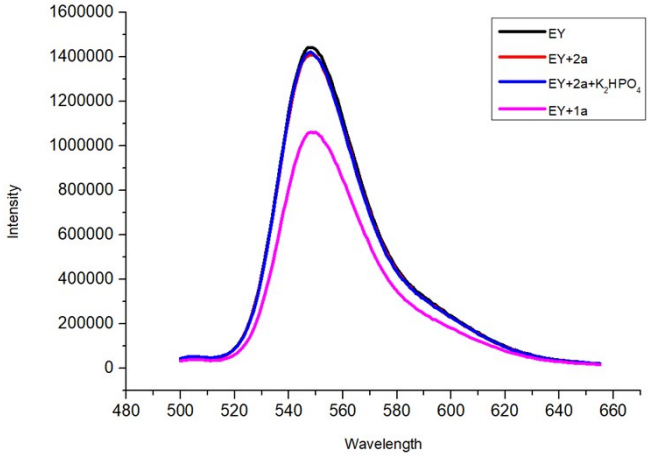


Figure S1. Fluorescence quenching of excited EY* with *p*-QM (**1a**), *N,N*-dimethylaniline (**2a**) or **2a**+K_2HPO_4 in DMF (excitation wavelength: 490 nm). EY (1.6 μM) in DMF (black line), EY (1.6 μM) with **2a** (0.72 mM) in DMF (red line), EY (1.6 μM) with **2a** (0.72 mM) and K_2HPO_4 (0.72 mM) in DMF (blue line), EY (1.6 μM) with **1a** (0.72 mM) in DMF (pink line).

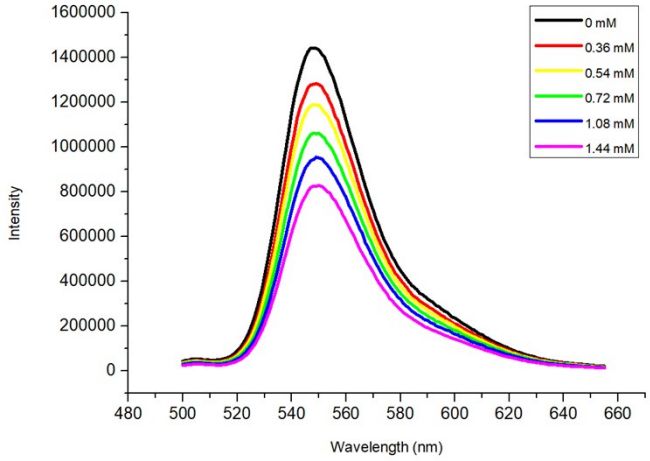


Figure S2. EY emission quenching by different concentrations of *p*-QM **1a** (excitation wavelength: 550 nm)

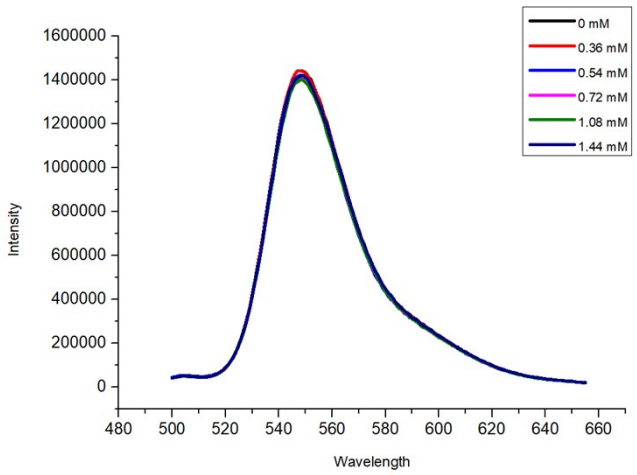


Figure S3. EY emission quenching by different concentrations of *N,N*-dimethylaniline **2a** (excitation wavelength: 550 nm)

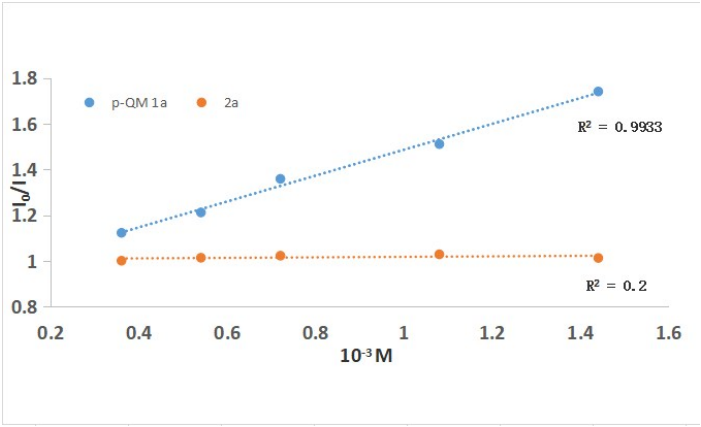
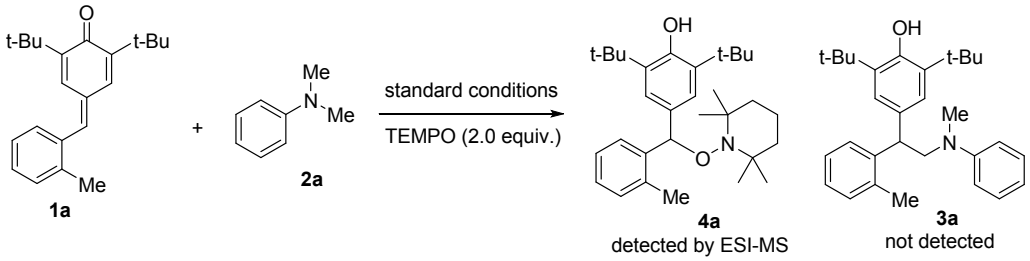
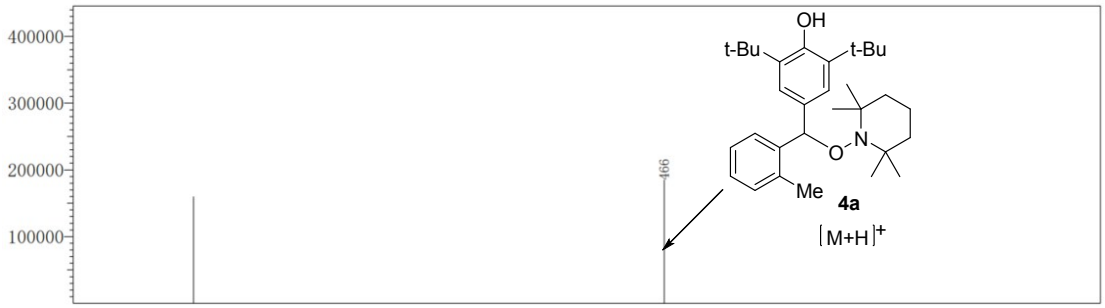


Figure S4. Stern-Volmer fluorescence quenching studies of EY by *p*-QM **1a** or *N,N*-dimethylaniline **2a**

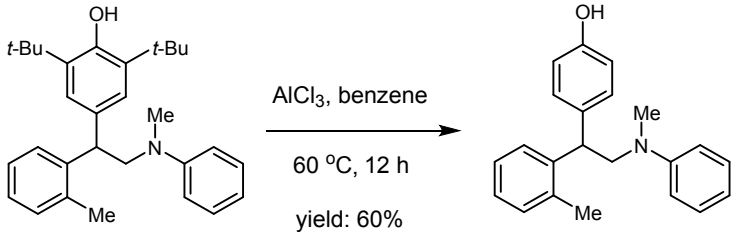
(b) Radical Trapping Experiments.



MS spectrum of product 4a



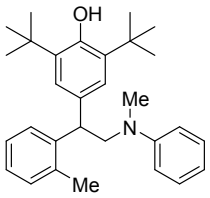
(c) De-*tert*-butylation of 2,2-diarylethylamine 3aa.[1b]



3a **3aa**

To a solution of **3a** (51.5 mg, 0.12 mmol) in dry benzene (3.0 mL) was added $AlCl_3$ (160 mg, 1.2 mmol) under nitrogen. The reaction mixture was then warmed to 60 °C and stirred for 1 h. Following addition of H_2O (10 mL), the resulting mixture was extracted with ethyl acetate (10 mL × 3), and the combined extracts were dried over anhydrous Na_2SO_4. The solvent of filtrate was concentrated under reduced pressure. The residue obtained was purified by flash column chromatography on silica gel eluting with petroleum ether/AcOEt (10/1 → 4/1) to afford the de-*tert*-butylation of 2,2-diarylethylamine **3aa** as a solid (22.8 mg, 60% yield).

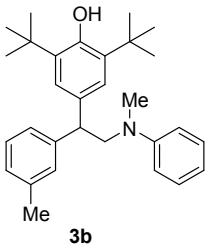
4. Characterization of Compounds 3a-3w and 3aa



3a

2,6-Di-*tert*-butyl-4-(2-(methyl(phenyl)amino)-1-(*o*-tolyl)ethyl)phenol (*3a*)

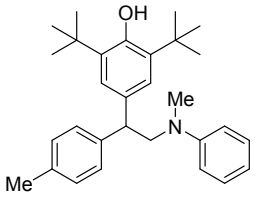
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 7.2 Hz, 1H), 7.26-7.23 (m, 1H), 7.22-7.18 (m, 2H), 7.13 (d, *J* = 4.4 Hz, 2H), 6.97 (s, 2H), 6.67 (t, *J* = 7.2 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 2H), 5.03 (s, 1H), 4.49 (t, *J* = 7.2 Hz, 1H), 3.97 (d, *J* = 7.6 Hz, 2H), 2.58 (s, 3H), 2.19 (s, 3H), 1.38 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 152.2, 148.8, 141.7, 136.7, 135.6, 135.6, 133.3, 130.5, 129.1, 129.1, 126.7, 126.1, 125.8, 124.7, 124.7, 115.6, 111.8, 111.8, 59.1, 43.7, 39.2, 34.3, 34.3, 30.3, 20.0. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{30}H_{40}NO]^+$: 430.3104, found: 430.3100.



3b

2,6-Di-*tert*-butyl-4-(2-(methyl(phenyl)amino)-1-(*m*-tolyl)ethyl)phenol (*3b*)

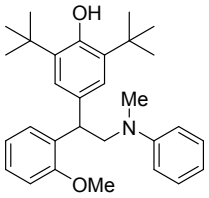
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26-7.15 (m, 3H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 5.6 Hz, 3H), 6.68 (t, *J* = 7.2 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 2H), 5.06 (s, 1H), 4.24 (t, *J* = 7.2 Hz, 1H), 3.93 (d, *J* = 7.2 Hz, 2H), 2.57 (s, 3H), 2.32 (s, 3H), 1.40 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.3, 148.7, 143.5, 137.9, 135.6, 135.6, 133.5, 129.3, 129.1, 129.1, 128.2, 127.0, 125.0, 124.7, 124.7, 115.6, 111.9, 119.9, 59.0, 48.6, 39.3, 34.3, 34.3, 30.3, 21.5. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{30}H_{40}NO]^+$: 430.3104, found: 430.3103.



3c

2,6-Di-*tert*-butyl-4-(2-(methyl(phenyl)amino)-1-(*p*-tolyl)ethyl)phenol (*3c*)

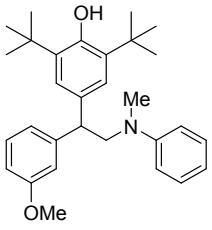
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26-7.21 (m, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.04 (s, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 5.07 (s, 1H), 4.26 (t, *J* = 7.2 Hz, 1H), 4.04-3.85 (m, 2H), 2.59 (s, 3H), 2.34 (s, 3H), 1.41(s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.3, 148.7, 140.6, 135.7, 135.6, 135.6, 133.6, 129.1, 129.1, 129.1, 129.1, 128.1, 128.1, 124.6, 124.6, 115.6, 111.9, 111.9, 59.1, 48.2, 39.3, 34.3, 34.3, 30.3, 21.0. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{30}H_{40}NO]^+$: 430.3104, found: 430.3098.



3d

2,6-Di-*tert*-butyl-4-(1-(2-methoxyphenyl)-2-(methyl(phenyl)amino)ethyl)phenol (*3d*)

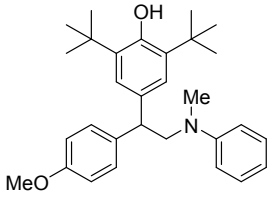
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29-7.24 (m, 1H), 7.24-7.14 (m, 3H), 7.08 (s, 2H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.67-6.64 (m, 3H), 5.02 (s, 1H), 4.70 (t, *J* = 7.2 Hz, 1H), 4.02-3.86 (m, 2H), 3.77 (s, 3H), 2.64 (s, 3H), 1.39 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.3, 152.1, 149.2, 135.3, 135.3, 133.1, 131.8, 128.9, 128.9, 128.7, 127.3, 125.2, 125.2, 120.4, 115.5, 112.1, 112.1, 110.8, 57.8, 55.4, 42.5, 39.0, 34.3, 34.3, 30.3. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{30}H_{40}NO_2]^+$: 446.3054, found: 446.3055.



3e

2,6-Di-*tert*-butyl-4-(1-(3-methoxyphenyl)-2-(methyl(phenyl)amino)ethyl)phenol (*3e*)

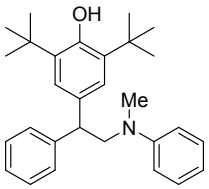
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26-7.12 (m, 3H), 7.03 (s, 2H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.81 (s, 1H), 6.76 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.68 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 5.07 (s, 1H), 4.25 (t, *J* = 7.2 Hz, 1H), 3.99-3.87 (m, 2H), 3.77 (s, 3H), 2.58 (s, 3H), 1.40 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.6, 152.4, 148.7, 145.3, 135.7, 135.7, 133.2, 129.2, 129.1, 129.1, 124.7, 124.7, 120.7, 115.7, 114.3, 111.9, 111.9, 111.5, 58.9, 55.1, 48.7, 39.3, 34.3, 34.3, 30.3. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{30}H_{40}NO_2]^+$: 446.3054, found: 446.3051.



3f

2,6-Di-*tert*-butyl-4-(1-(4-methoxyphenyl)-2-(methyl(phenyl)amino)ethyl)phenol (*3f*)

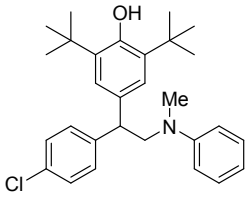
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28-7.22 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.03 (s, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 2H), 5.08 (s, 1H), 4.26 (t, *J* = 7.2 Hz, 1H), 3.93-3.86 (m, 2H), 3.81 (s, 3H), 2.59 (s, 3H), 1.42 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.0, 152.2, 148.7, 135.8, 135.7, 135.7, 133.7, 129.2, 129.2, 129.1, 129.1, 124.6, 124.6, 115.6, 113.7, 113.7, 111.9, 111.9, 59.1, 55.2, 47.7, 39.3, 34.3, 34.3, 30.3. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{30}H_{40}NO_2]^+$: 446.3054, found: 446.3053.



3g

2,6-Di-*tert*-butyl-4-(2-(methyl(phenyl)amino)-1-phenylethyl)phenol (*3g*)

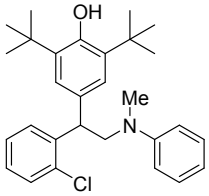
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24 (s, 1H), 7.23-7.19 (m, 3H), 7.18-7.14 (m, 3H), 6.97 (s, 2H), 6.62 (t, *J* = 7.2 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 2H), 5.01 (s, 1H), 4.24 (t, *J* = 7.2 Hz, 1H), 3.95-3.84 (m, 2H), 2.52 (s, 3H), 1.35 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.3, 148.7, 143.7, 135.7, 135.7, 133.4, 129.1, 129.1, 128.3, 128.3, 128.3, 128.3, 126.3, 124.7, 124.7, 115.7, 111.9, 111.9, 59.0, 48.6, 39.3, 34.3, 34.3, 30.3. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{29}H_{38}NO]^+$: 416.2948, found: 416.2944.



3h

2,6-Di-*tert*-butyl-4-(1-(4-chlorophenyl)-2-(methyl(phenyl)amino)ethyl)phenol (*3h*)

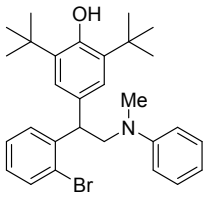
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.27 (d, *J* = 8.5 Hz, 2H), 7.23 (t, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.5Hz, 2H), 7.00 (s, 2H), 6.70 (t, *J* = 7.0 Hz, 1H), 6.62 (d, *J* = 8.5 Hz, 2H), 5.11 (s, 1H), 4.28 (t, *J* = 7.5 Hz, 1H), 4.00-3.85 (m, 2H), 2.59 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 152.5, 148.6, 142.3, 135.8, 135.8, 132.8, 132.0, 129.7, 129.7, 129.1, 129.1, 128.5, 128.5, 124.5, 124.5, 115.9, 112.0, 112.0, 58.9, 47.9, 39.4, 34.4, 34.4, 30.3. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{29}H_{37}NOCl]^+$: 450.2558, found: 450.2554.



3i

2,6-Di-*tert*-butyl-4-(1-(2-chlorophenyl)-2-(methyl(phenyl)amino)ethyl)phenol (*3i*)

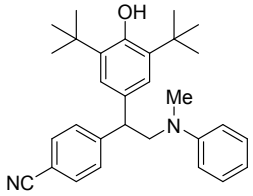
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.36 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.29-7.24 (m, 1H), 7.23-7.19 (m, 2H), 7.16 (td, *J* = 8.0, 1.6 Hz, 1H), 7.05 (s, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 5.08 (s, 1H), 4.88 (t, *J* = 7.2 Hz, 1H), 3.96 (d, *J* = 7.5 Hz, 2H), 2.68 (s, 3H), 1.40 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.3, 149.1, 141.0, 135.6, 135.6, 134.5, 132.2, 129.8, 129.0, 129.0, 128.7, 127.4, 126.7, 124.8, 124.8, 116.0, 112.3, 112.3, 58.2, 44.5, 38.8, 34.3, 34.3, 30.3. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{29}H_{37}NOCl]^+$: 450.2558, found: 450.2562.



3j

4-(1-(2-Bromophenyl)-2-(methyl(phenyl)amino)ethyl)-2,6-di-*tert*-butylphenol (*3j*)

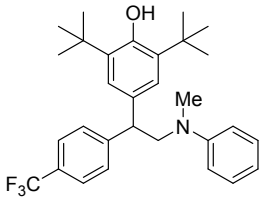
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 2H), 7.12-7.02 (m, 3H), 6.69 (t, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 5.07 (s, 1H), 4.86 (t, *J* = 7.0 Hz, 1H), 4.05-3.85 (m, 2H), 2.67 (s, 3H), 1.39 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.4, 149.2, 142.7, 135.7, 135.7, 133.2, 132.2, 129.0, 129.0, 128.9, 127.7, 127.4, 125.5, 124.8, 124.8, 116.1, 112.4, 112.4, 58.3, 47.2, 38.8, 34.3, 34.3, 30.3. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{29}H_{37}NOBr]^+$: 494.2053, found: 494.2051.



3K

4-(1-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-2-(methyl(phenyl)amino)ethyl)benzonitrile (*3k*)

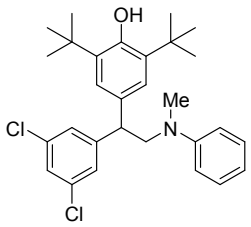
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.16-7.10 (m, 2H), 6.87 (s, 2H), 6.61 (t, *J* = 7.2 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 2H), 5.05 (s, 1H), 4.27 (t, *J* = 8.0 Hz, 1H), 3.93-3.77 (m, 2H), 2.49 (s, 3H), 1.31 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.7, 149.5, 148.5, 137.7, 136.1, 136.1, 132.1, 132.1, 131.8, 129.2, 129.1, 124.6, 124.6, 119.0, 116.3, 114.3, 112.1, 112.1, 110.1, 58.6, 48.6, 39.5, 34.4, 34.4, 30.2. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{30}H_{37}N_2O]^+$: 441.2900, found: 441.2900.



3l

2,6-Di-*tert*-butyl-4-(2-(methyl(phenyl)amino)-1-(4-(trifluoromethyl)phenyl)ethyl)phenol (*3l*)

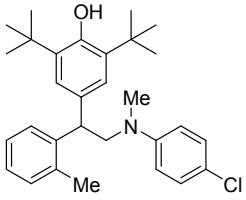
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.29-7.24 (m, 2H), 7.04 (s, 2H), 6.74 (t, *J* = 6.8 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 2H), 5.16 (s, 1H), 4.40 (t, *J* = 7.6 Hz, 1H), 4.07-3.92 (m, 2H), 2.62 (s, 3H), 1.44 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.6, 148.5, 148.0, 136.0, 136.0, 132.3, 129.2, 129.2, 128.6, 128.6, 128.8, 125.3 (d, *J* = 3.3 Hz), 125.2 (d, *J* = 3.7 Hz), 124.6, 124.6, 116.1, 112.1, 112.1, 58.8, 48.5, 39.5, 34.4, 34.4, 30.3. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{30}H_{37}NOF_3]^+$: 484.2822, found: 484.2824.



3m

2,6-Di-*tert*-butyl-4-(1-(3,5-dichlorophenyl)-2-(methyl(phenyl)amino)ethyl)phenol (*3m*)

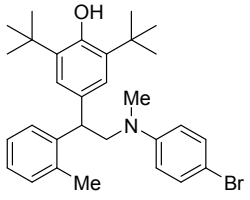
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (d, *J* = 3.2 Hz, 1H), 7.27 (d, *J* = 1.4 Hz, 1H), 7.26-7.24 (m, 1H), 7.18 (d, *J* = 1.6 Hz, 2H), 7.00 (s, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 2H), 5.18 (s, 1H), 4.27 (t, *J* = 7.2 Hz, 1H), 3.95 (qd, *J* = 14.5, 7.5 Hz, 2H), 2.65 (s, 3H), 1.45 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.8, 148.4, 147.3, 136.1, 136.1, 134.7, 134.7, 131.8, 129.2, 129.2, 126.9, 126.9, 126.5, 124.6, 124.6, 116.3, 112.1, 112.1, 58.6, 48.2, 39.6, 34.4, 34.4, 30.3. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{29}H_{36}NOCl_2]^+$: 484.2168, found: 484.2167.



3n

2,6-Di-*tert*-butyl-4-(2-((4-chlorophenyl)(methyl)amino)-1-(*o*-tolyl)ethyl)phenol (*3n*)

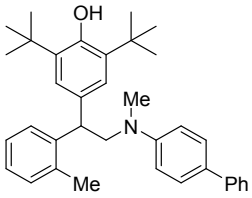
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 7.5 Hz, 1H), 7.24-7.21 (m, 1H), 7.13-7.11 (m, 3H), 7.10 (s, 1H), 6.92 (s, 2H), 6.45 (d, *J* = 9.0 Hz, 2H), 5.03 (s, 1H), 4.41 (t, *J* = 7.5 Hz, 1H), 3.98-3.87 (m, 2H), 2.54 (s, 3H), 2.17 (s, 3H), 1.35 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 152.3, 147.3, 141.4, 136.7, 135.7, 135.7, 133.0, 130.6, 128.8, 128.8, 126.5, 126.2, 125.9, 124.7, 124.7, 120.4, 112.8, 112.8, 59.1, 43.6, 39.3, 34.3, 34.3, 30.3, 20.0. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{30}H_{39}NOCl]^+$: 464.2715, found: 464.2716.



3o

4-(2-((4-Bromophenyl)(methyl)amino)-1-(*o*-tolyl)ethyl)-2,6-di-*tert*-butylphenol (*3o*)

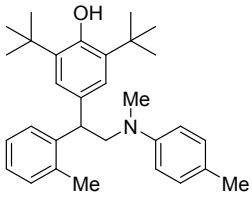
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 7.6 Hz, 1H), 7.27-7.22 (m, 3H), 7.16-7.09 (m, 2H), 6.92 (s, 2H), 6.41 (d, *J* =8.8 Hz, 2H), 5.04 (s, 1H), 4.41 (t, *J* = 7.2 Hz, 1H), 3.98-3.86 (m, 2H), 2.53 (s, 3H), 2.17 (s, 3H), 1.36 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.3, 147.7, 141.4, 136.7, 135.7, 135.7, 133.0, 131.7, 131.7, 130.6, 126.5, 126.2, 125.9, 124.7, 124.7, 113.3, 113.3, 107.5, 59.0, 43.5, 39.3, 34.3, 34.3, 30.3, 20.0. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{30}H_{39}NOBr]^+$: 508.2210, found: 508.2210.



3p

4-(2-([1,1'-Biphenyl]-4-yl(methyl)amino)-1-(*o*-tolyl)ethyl)-2,6-di-*tert*-butylphenol (*3p*)

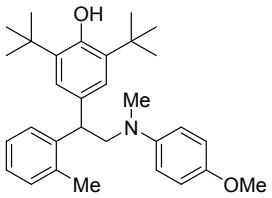
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.41-7.38 (m, 3H), 7.26-7.23 (m, 2H), 7.18-7.08 (m, 2H), 6.98 (s, 2H), 6.64 (d, *J* = 8.5 Hz, 2H), 5.04 (s, 1H), 4.50 (t, *J* = 7.0 Hz, 1H), 4.07-3.92 (m, 2H), 2.62 (s, 3H), 2.21 (s, 3H), 1.37 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 152.2, 148.2, 141.6, 141.3, 136.7, 135.6, 135.6, 133.2, 130.6, 128.6, 128.6, 128.6, 128.2, 127.7, 127.7, 126.6, 126.1, 126.2, 125.9, 125.8, 124.8, 124.7, 112.0, 111.9, 59.1, 43.9, 39.2, 34.3, 30.3, 30.3, 20.0. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{36}H_{44}NO]^+$: 506.3417, found: 506.3413.



3q

2,6-Di-*tert*-butyl-4-(2-(methyl(*p*-tolyl)amino)-1-(*o*-tolyl)ethyl)phenol (*3q*)

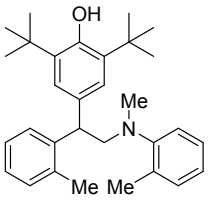
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (d, *J* = 7.6 Hz, 1H), 7.23 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.16-7.13 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.98 (s, 2H), 6.53 (d, *J* = 8.4 Hz, 2H), 5.04 (s, 1H), 4.47 (t, *J* = 7.2 Hz, 1H), 3.93 (d, *J* = 7.2 Hz, 2H), 2.56 (s, 3H), 2.26 (s, 3H), 2.20 (s, 3H), 1.38 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.1, 146.8, 141.9, 136.7, 135.5, 135.5, 133.5, 130.5, 129.6, 129.6, 129.6, 126.7, 126.0, 125.8, 124.8, 124.8, 112.1, 112.1, 59.5, 43.9, 39.3, 34.3, 34.3, 30.3, 20.1. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{31}H_{42}NO]^+$: 444.3261, found: 444.3262.



3r

2,6-Di-*tert*-butyl-4-(2-((4-methoxyphenyl)(methyl)amino)-1-(*o*-tolyl)ethyl)phenol (*3r*)

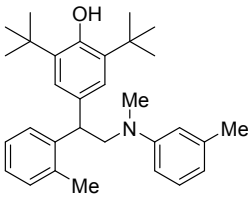
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 7.5 Hz, 1H), 7.26-7.24 (m, 1H), 7.14 (d, *J* = 3.5 Hz, 2H), 6.99 (s, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 2H), 5.05 (s, 1H), 4.46 (t, *J* = 7.0 Hz, 1H), 3.95-3.85 (m, 2H), 3.78 (s, 3H), 2.59 (s, 3H), 2.22 (s, 3H), 1.40 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 152.1, 151.1, 143.9, 141.9, 136.6, 135.5, 135.5, 133.5, 130.5, 126.7, 126.0, 125.8, 124.8, 124.8, 114.7, 114.7, 113.7, 113.7, 60.0, 55.9, 43.9, 39.6, 34.2, 34.2, 30.3, 20.0. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{31}H_{42}NO_2]^+$: 460.3210, found: 460.3211.



3s

2,6-Di-*tert*-butyl-4-(2-(methyl(*o*-tolyl)amino)-1-(*o*-tolyl)ethyl)phenol (*3s*)

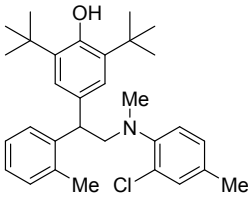
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29 (d, *J* = 7.6 Hz, 1H), 7.18-7.15 (m, 2H), 7.13-7.02 (m, 4H), 7.01-6.90 (m, 3H), 5.00 (s, 1H), 4.26 (t, *J* = 7.6 Hz, 1H), 3.61-3.47 (m, 2H), 2.62 (s, 3H), 2.17 (s, 3H), 1.87 (s, 3H), 1.37 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.9, 151.8, 141.8, 136.2, 135.2, 135.2, 134.4, 133.4, 130.9, 130.2, 127.1, 126.2, 125.7, 125.7, 124.9, 124.9, 123.1, 121.1, 60.8, 44.7, 43.2, 34.2, 30.3, 30.3, 19.8, 17.7. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{31}H_{42}NO]^+$: 444.3261, found: 444.3262.



3t

2,6-Di-*tert*-butyl-4-(2-(methyl(*m*-tolyl)amino)-1-(*o*-tolyl)ethyl)phenol (*3t*)

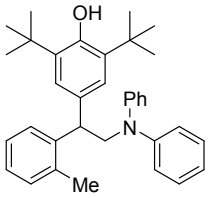
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 7.6 Hz, 1H), 7.27-7.23 (m, 1H), 7.18-7.12 (m, 2H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.98 (s, 2H), 6.51 (d, *J* = 7.4 Hz, 1H), 6.43 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.38 (s, 1H), 5.04 (s, 1H), 4.48 (t, *J* = 7.6 Hz, 1H), 3.94 (d, *J* = 7.2 Hz, 2H), 2.57 (s, 3H), 2.29 (s, 3H), 2.20 (s, 3H), 1.38 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.1, 148.9, 141.8, 138.6, 136.7, 135.5, 135.5, 133.4, 130.5, 128.9, 126.7, 126.1, 125.8, 124.8, 124.8, 116.7, 112.7, 109.1, 59.2, 43.9, 39.2, 34.3, 34.3, 30.3, 21.94, 20.0. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{31}H_{42}NO]^+$: 444.3261, found: 444.3257.



3u

2,6-Di-*tert*-butyl-4-(2-((2-chloro-4-methylphenyl)(methyl)amino)-1-(*o*-tolyl)ethyl)phenol (*3u*)

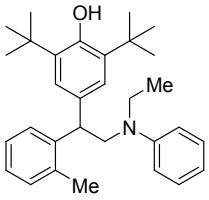
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31 (d, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 6.5 Hz, 1H), 7.10-7.07 (m, 3H), 6.96 (s, 2H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 4.97 (s, 1H), 4.34 (t, *J* = 7.5 Hz, 1H), 3.84 (dd, *J* = 13.5, 8.0 Hz, 1H), 3.63 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.74 (s, 3H), 2.25 (d, *J* = 4.0 Hz, 6H), 1.37 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 151.9, 146.7, 141.7, 136.0, 135.2, 135.2, 133.1, 132.9, 130.8, 130.3, 128.7, 127.6, 127.1, 125.8, 125.8, 125.0, 125.0, 122.3, 60.2, 44.6, 41.9, 34.2, 34.2, 30.2, 20.3, 19.9. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{31}H_{41}NOCl]^+$: 478.2871, found: 478.2873.



3v

2,6-Di-*tert*-butyl-4-(2-(diphenylamino)-1-(*o*-tolyl)ethyl)phenol (*3v*)

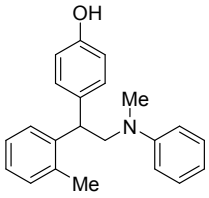
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 7.6 Hz, 1H), 7.25-7.20 (m, 1H), 7.19 (s, 1H), 7.17 (d, *J* = 0.8 Hz, 2H), 7.15 (s, 2H), 7.14 (s, 1H), 6.96 (s, 2H), 6.90 (t, *J* = 7.2 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 4H), 5.05 (s, 1H), 4.47 (dd, *J* = 8.8, 5.2 Hz, 1H), 4.38 (dd, *J* = 14.0, 5.2 Hz, 1H), 4.21 (dd, *J* = 14.0, 9.2 Hz, 1H) 2.16 (s, 3H), 1.36 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.2, 148.2, 141.3, 136.8, 135.6, 133.1, 130.5, 129.0, 126.5, 126.2, 125.9, 125.1, 121.2, 77.3, 77.0, 76.7, 58.8, 43.8, 34.3, 30.3, 19.9. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{35}H_{42}NO]^+$: 492.3261, found: 492.3255.



3w

2,6-Di-*tert*-butyl-4-(2-(ethyl(phenyl)amino)-1-(*o*-tolyl)ethyl)phenol (*3w*)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 7.6 Hz, 1H), 7.25-7.17 (m, 3H), 7.13 (d, *J* = 4.8 Hz, 2H), 6.98 (s, 2H), 6.73-6.44 (m, 3H), 5.02 (s, 1H), 4.44 (t, *J* = 7.1 Hz, 1H), 3.89 (d, *J* = 7.1 Hz, 2H), 3.14-2.84 (m, 2H), 2.20 (s, 3H), 1.37 (s, 18H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.7, 141.9, 136.8, 135.5, 133.4, 130.5, 129.2, 126.6, 126.1, 125.9, 124.8, 115.3, 111.9, 77.3, 77.0, 76.7, 57.2, 45.8, 43.8, 34.3, 30.3, 20.1, 11.7. HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{31}H_{42}NO]^+$: 444.3261, found: 444.3258.



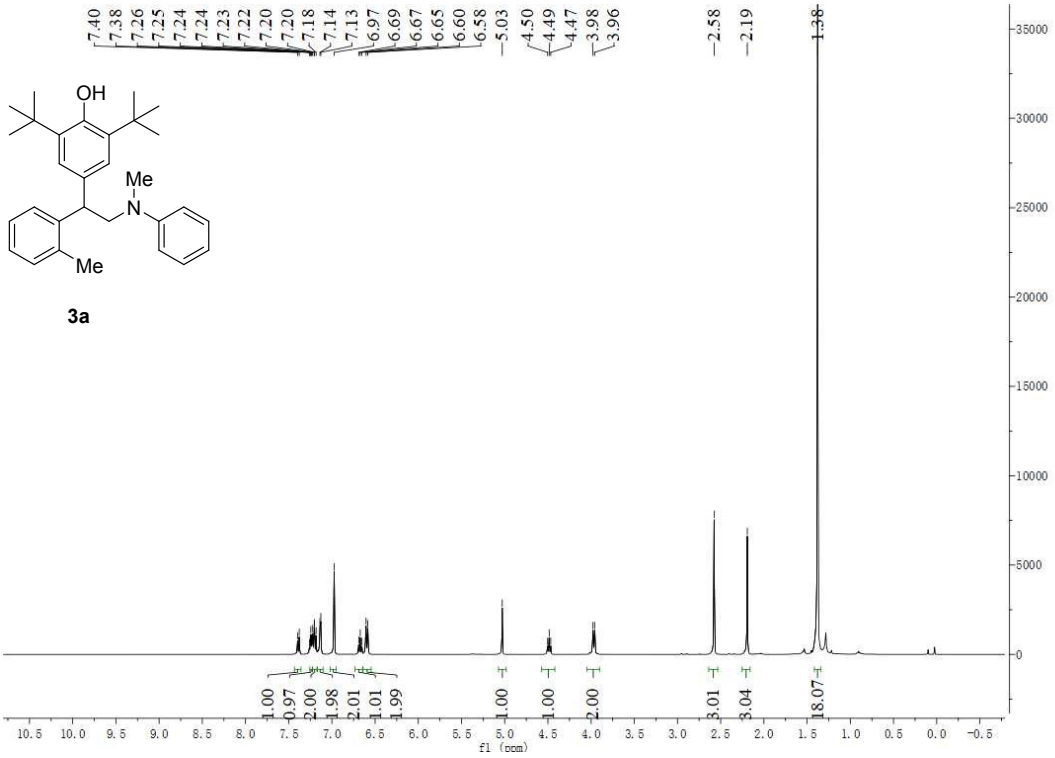
3aa

4-(2-(Ethyl(phenyl)amino)-1-(*o*-tolyl)ethyl)phenol (*3aa*)

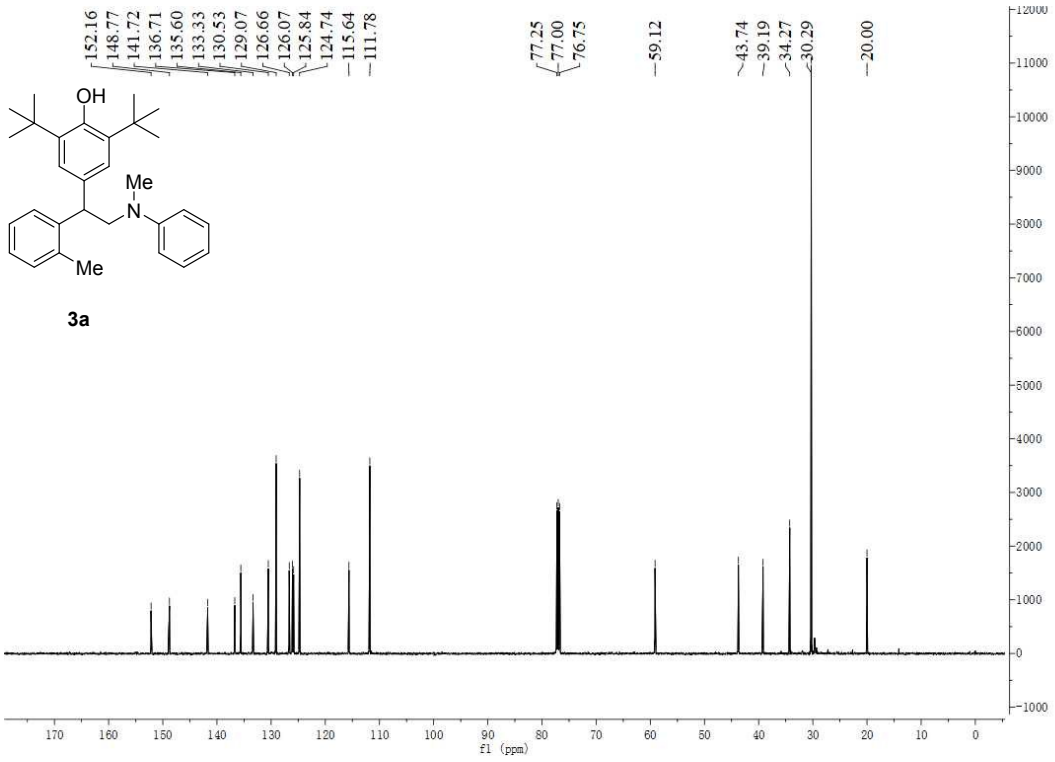
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 8.0 Hz, 1H), 7.29-7.24 (m, 3H), 7.21-7.13 (m, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.75-6.72 (m, 3H), 6.65 (d, *J* = 8.0 Hz, 2H), 4.93 (s, 1H), 4.52 (dd, *J* = 8.5, 6.0 Hz, 1H), 4.06 (dd, *J* = 8.5, 6.0 Hz, 1H), 3.93 (dd, *J* = 14.5, 9.0 Hz, 1H), 2.61 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 154.0, 148.7, 141.3, 136.9, 135.3, 130.7, 129.5, 129.5, 129.2, 129.2, 126.5, 126.4, 125.9, 115.9, 115.2, 115.2, 111.8, 59.1, 43.2, 39.5, 19.8. HRMS (ESI): *m/z* $[M+H]^+$: calcd. for $[C_{22}H_{24}NO]^+$: 318.1852, found: 318.1850.

5. Copies of ^{1}H and ^{13}C NMR Spectra of Compounds 3a-3w and 3aa

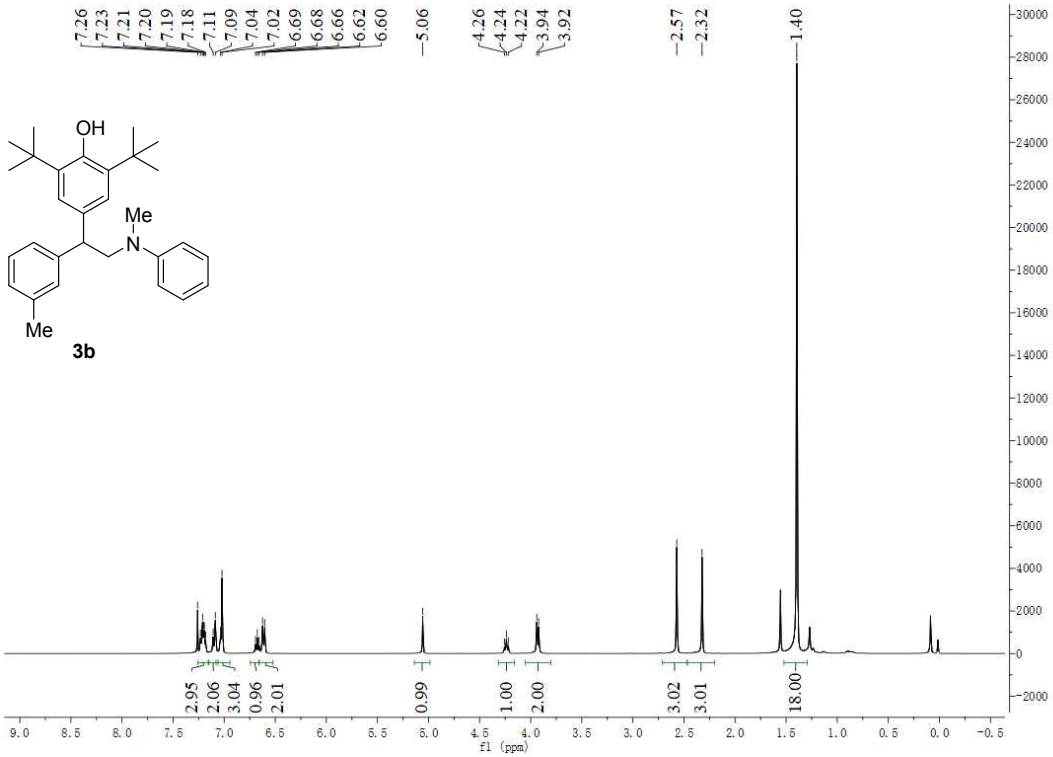
^{1}H NMR spectrum of 3a in $CDCl_3$



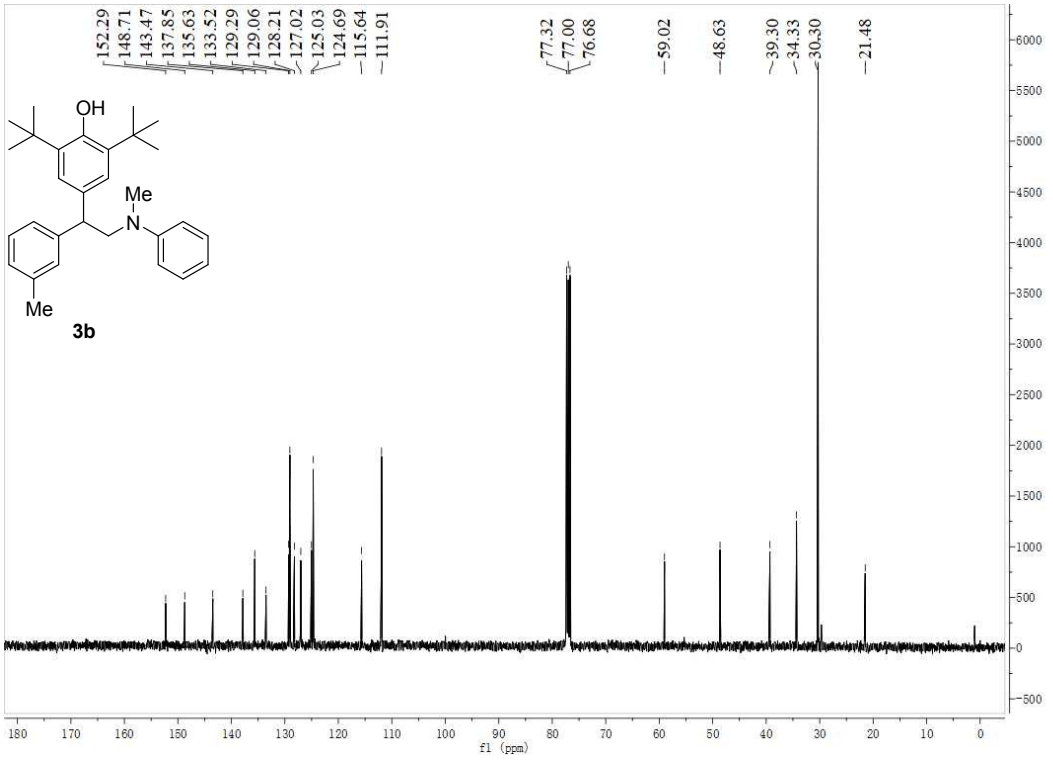
^{13}C NMR spectrum of 3a in $CDCl_3$



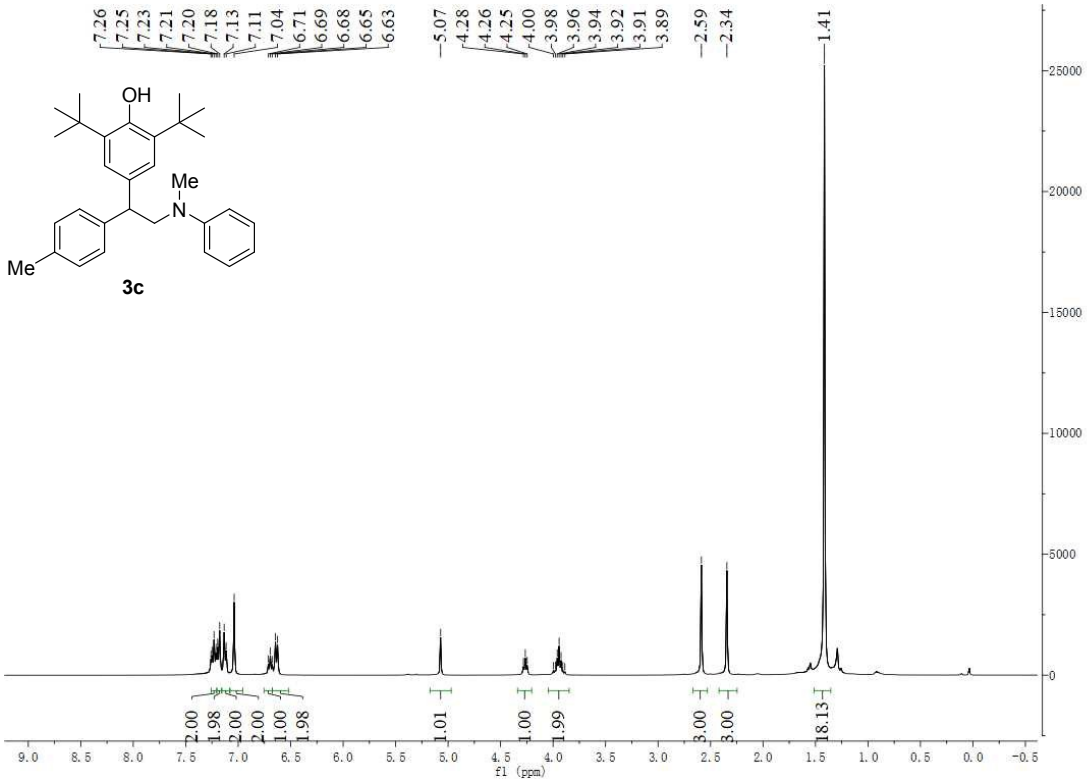
^{1}H NMR spectrum of 3b in $CDCl_3$



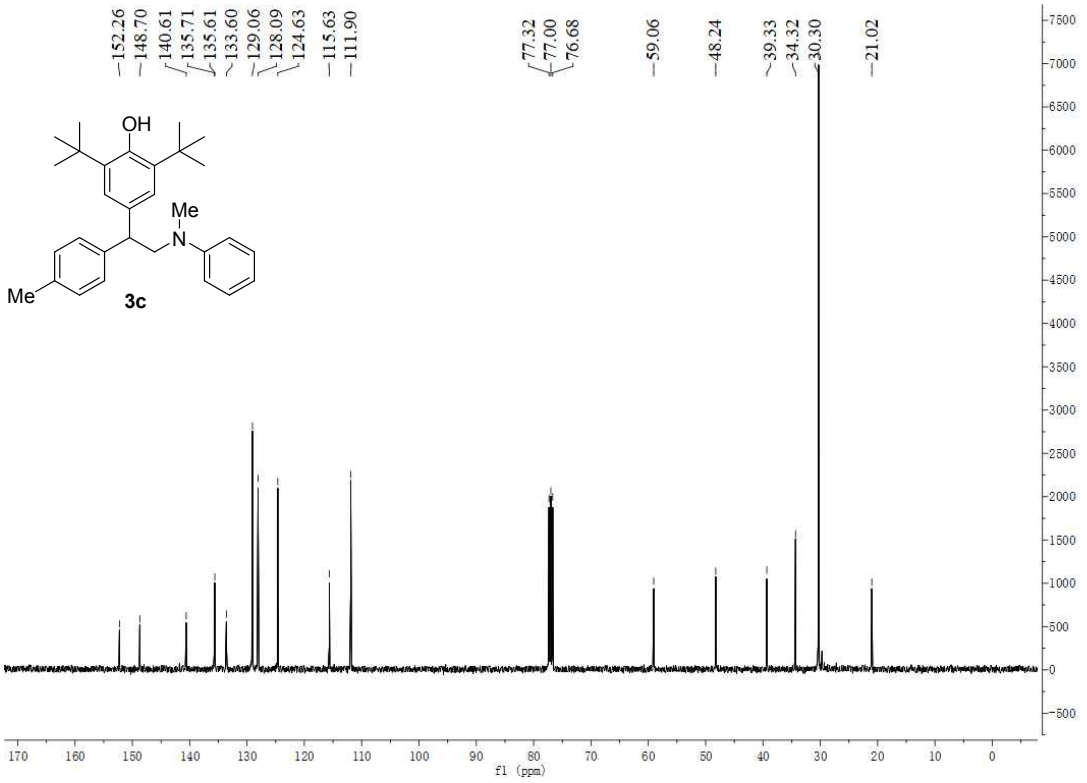
^{13}C NMR spectrum of 3b in $CDCl_3$



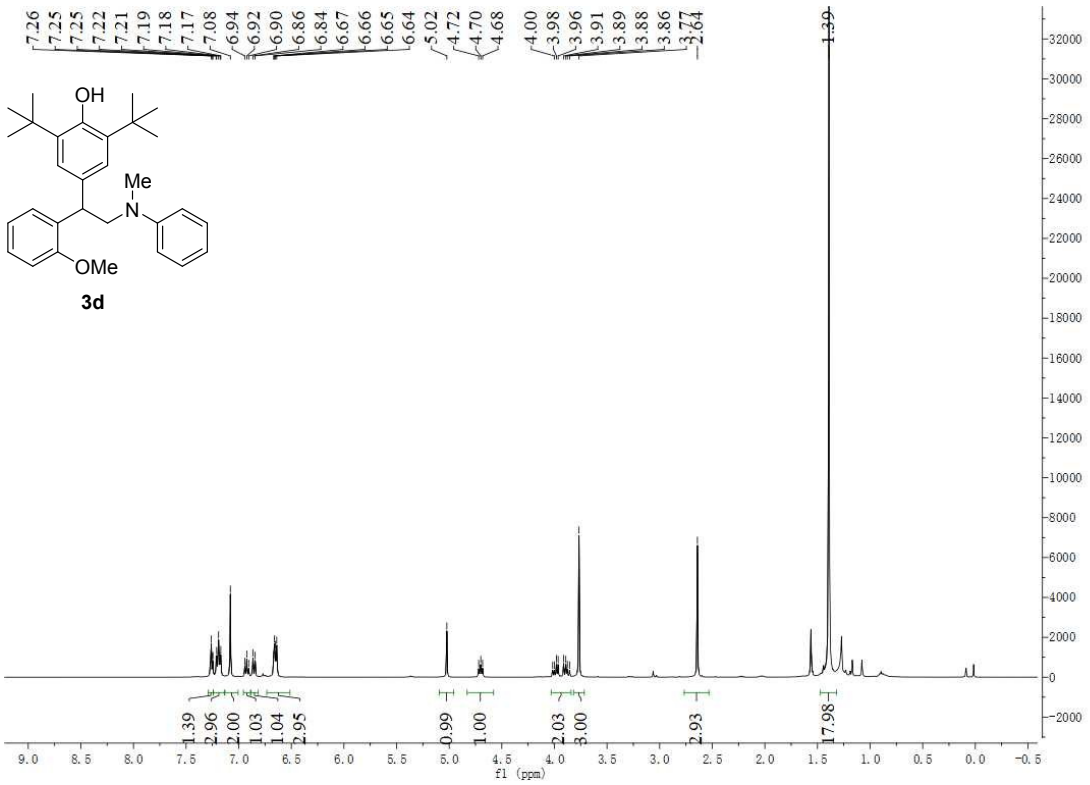
^{1}H NMR spectrum of 3c in $CDCl_3$



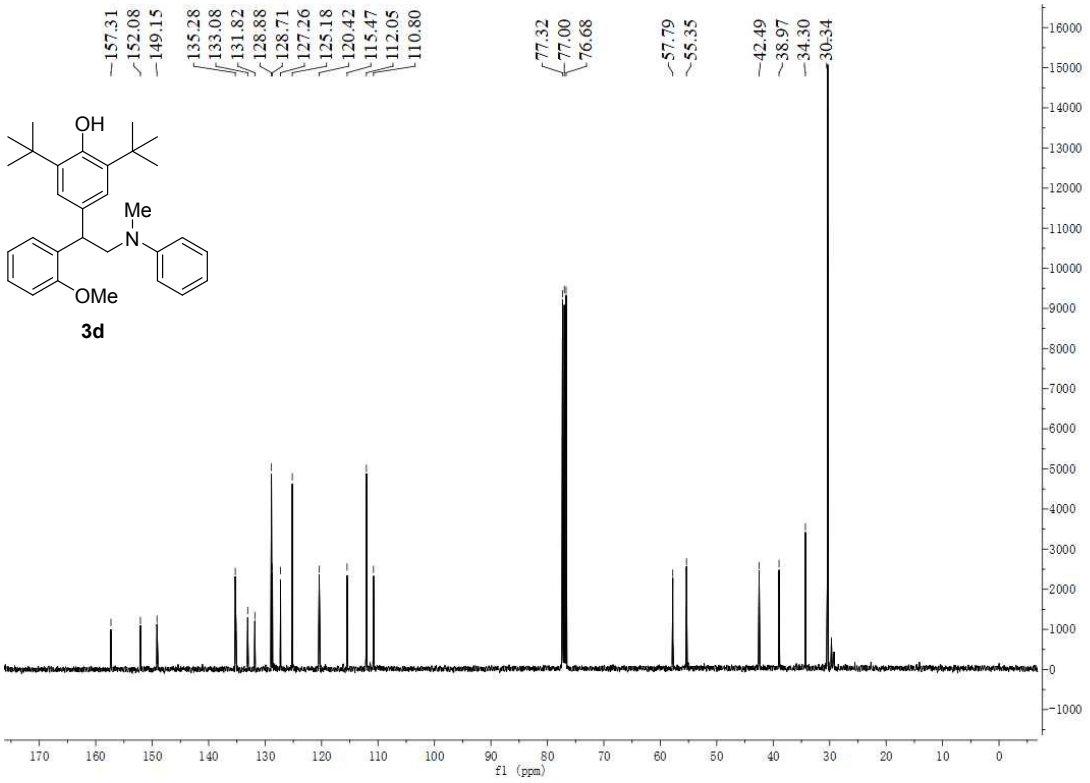
^{13}C NMR spectrum of 3c in $CDCl_3$



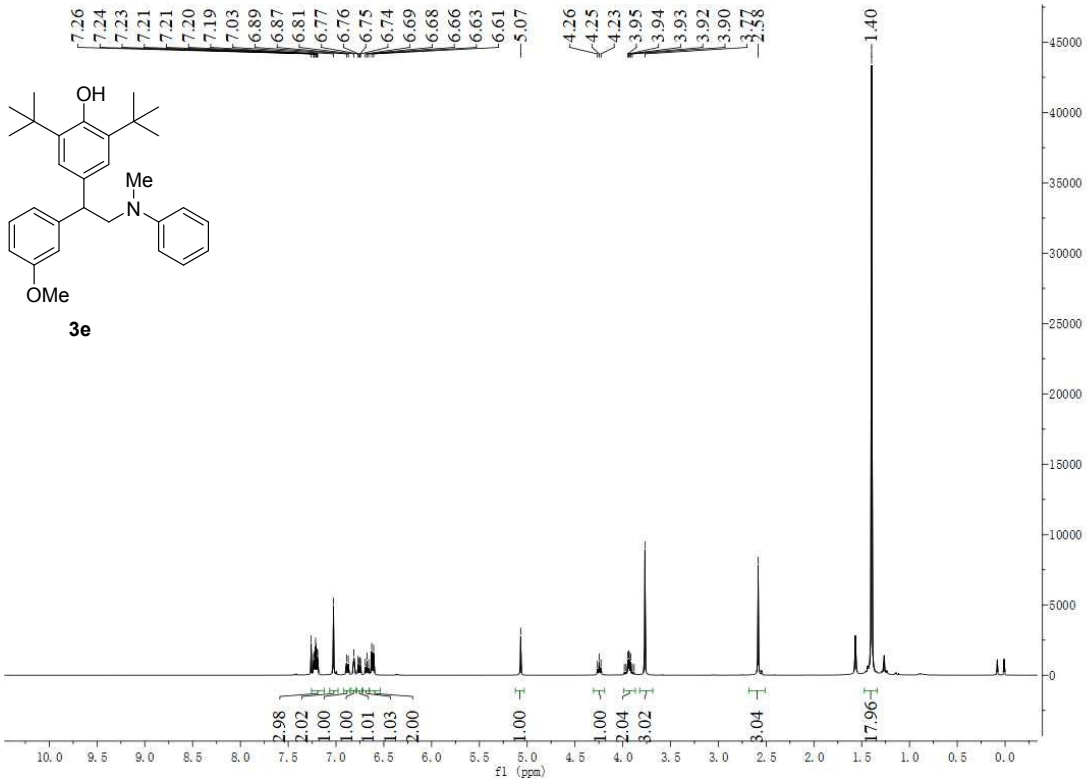
^{1}H NMR spectrum of 3d in $CDCl_3$



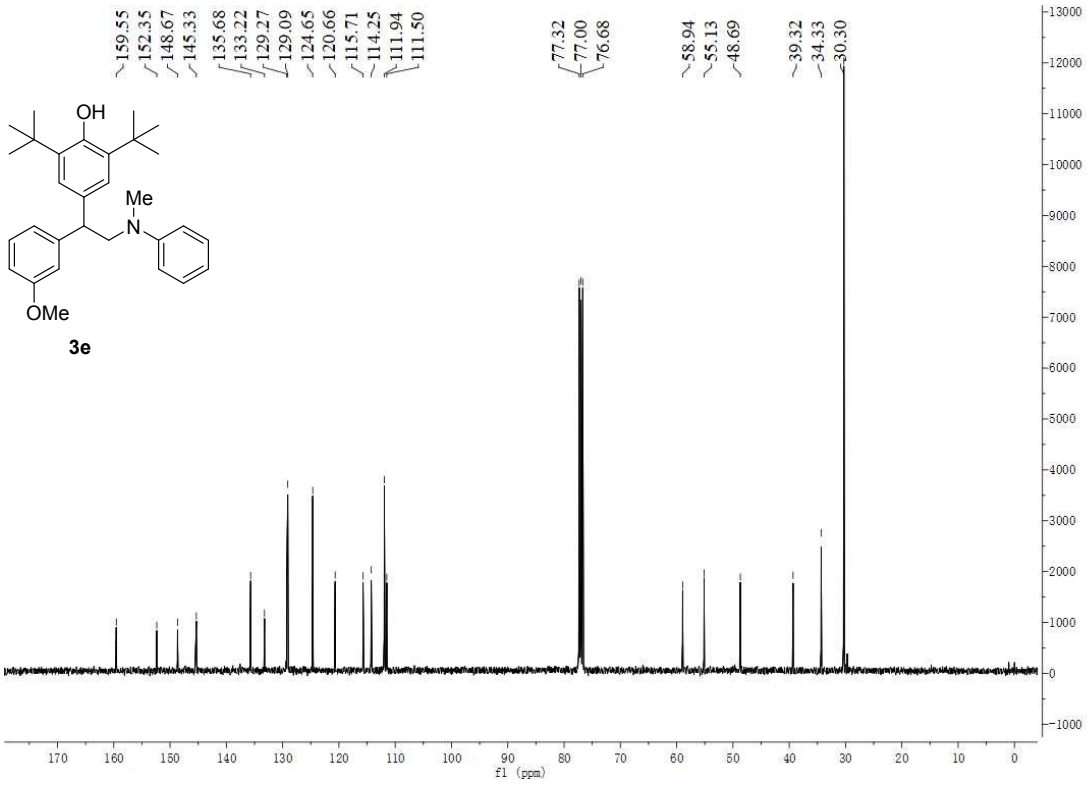
^{13}C NMR spectrum of 3d in $CDCl_3$



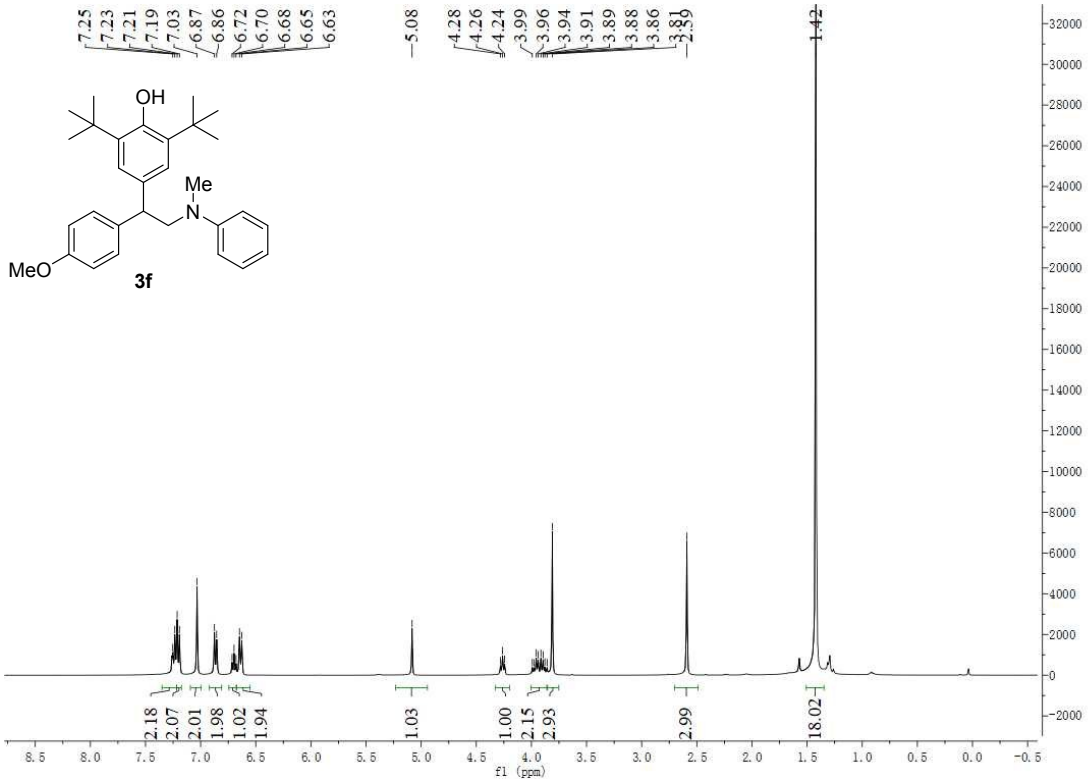
^{1}H NMR spectrum of 3e in $CDCl_3$



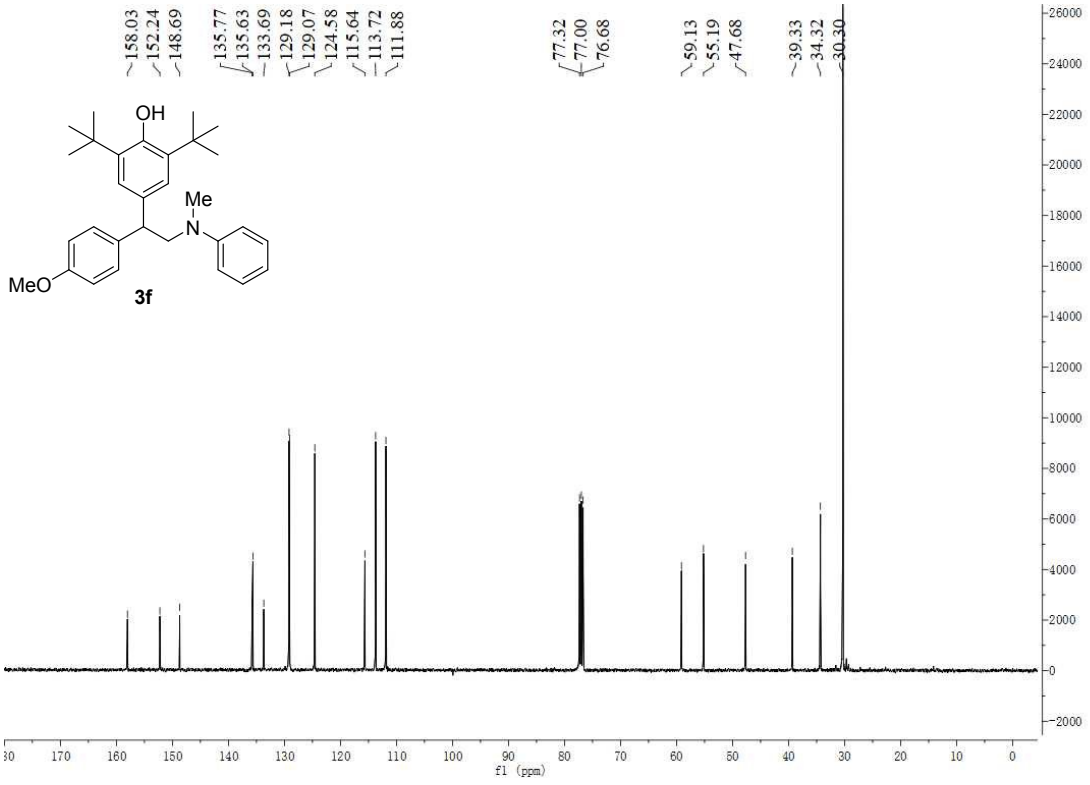
^{13}C NMR spectrum of 3e in $CDCl_3$



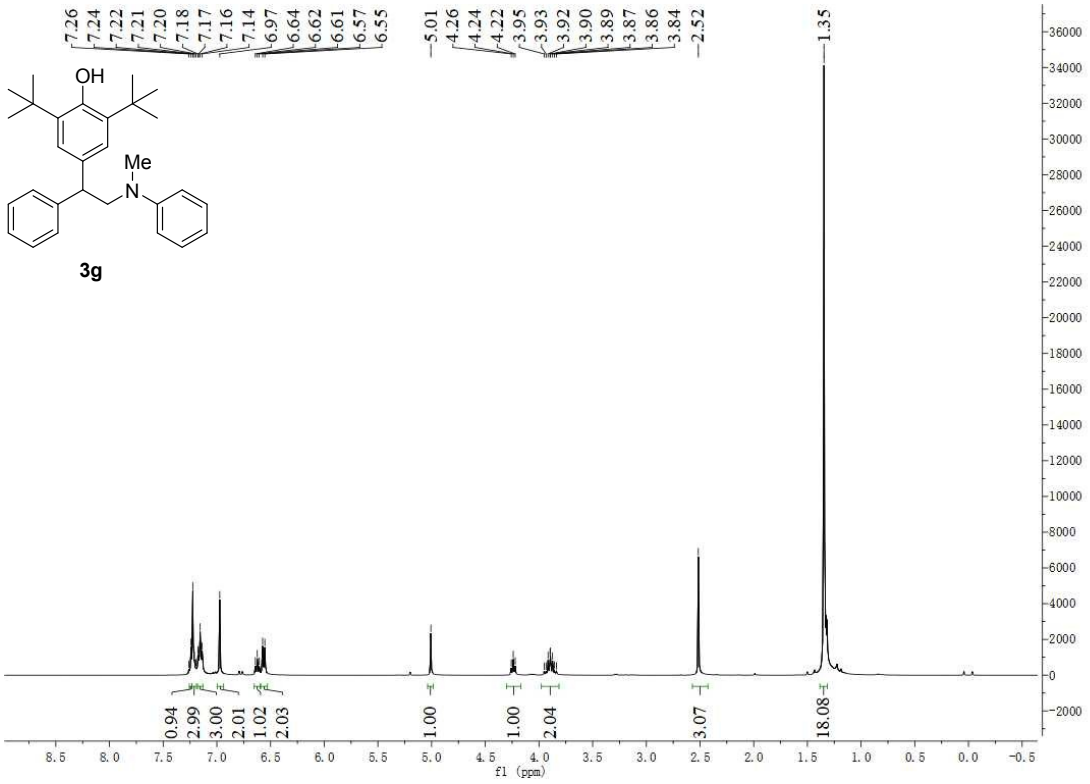
^{1}H NMR spectrum of 3f in $CDCl_3$



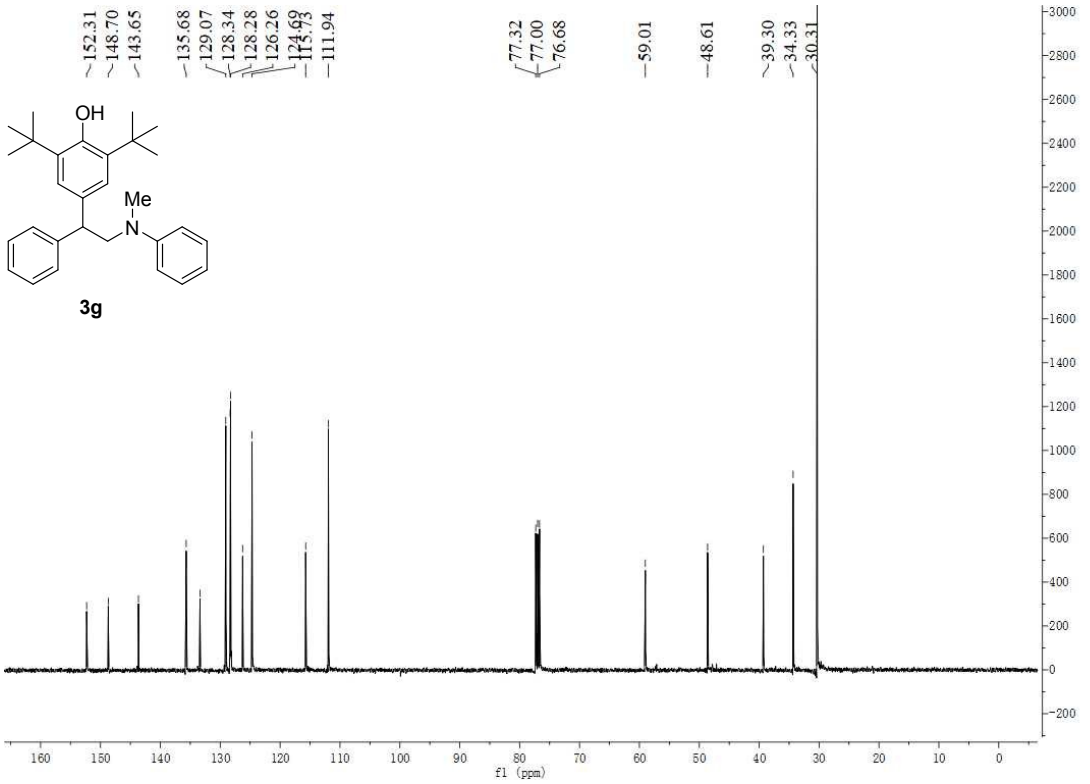
^{13}C NMR spectrum of 3f in $CDCl_3$



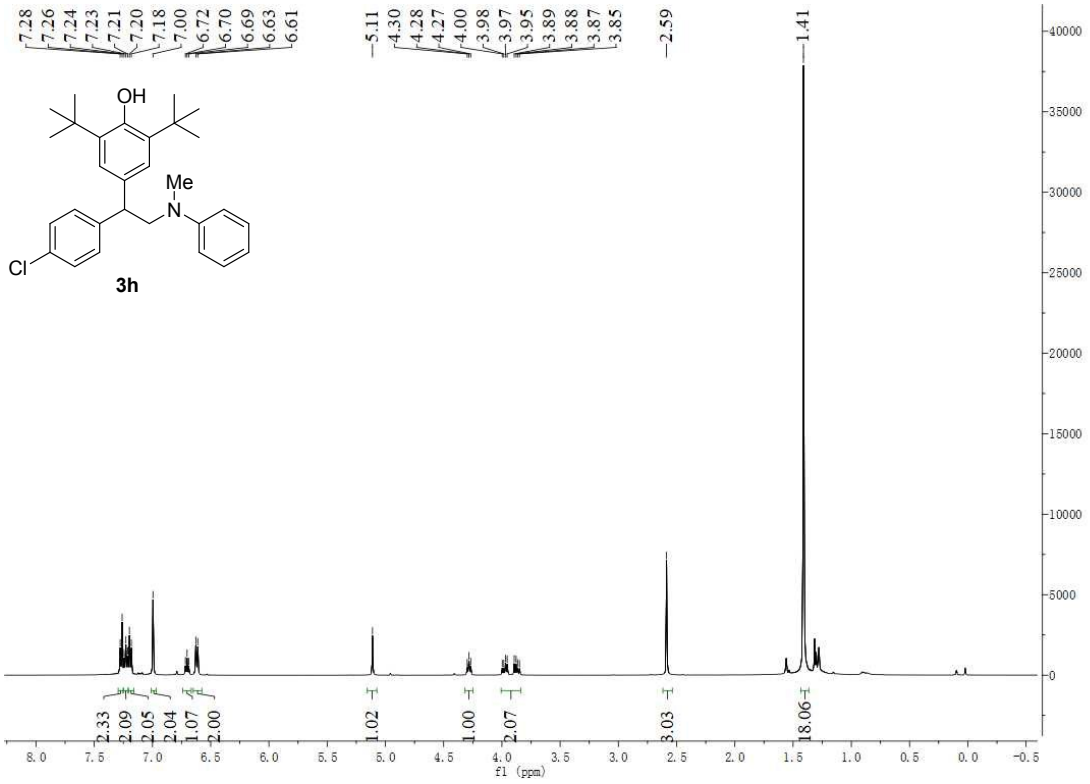
^{1}H NMR spectrum of 3g in $CDCl_3$



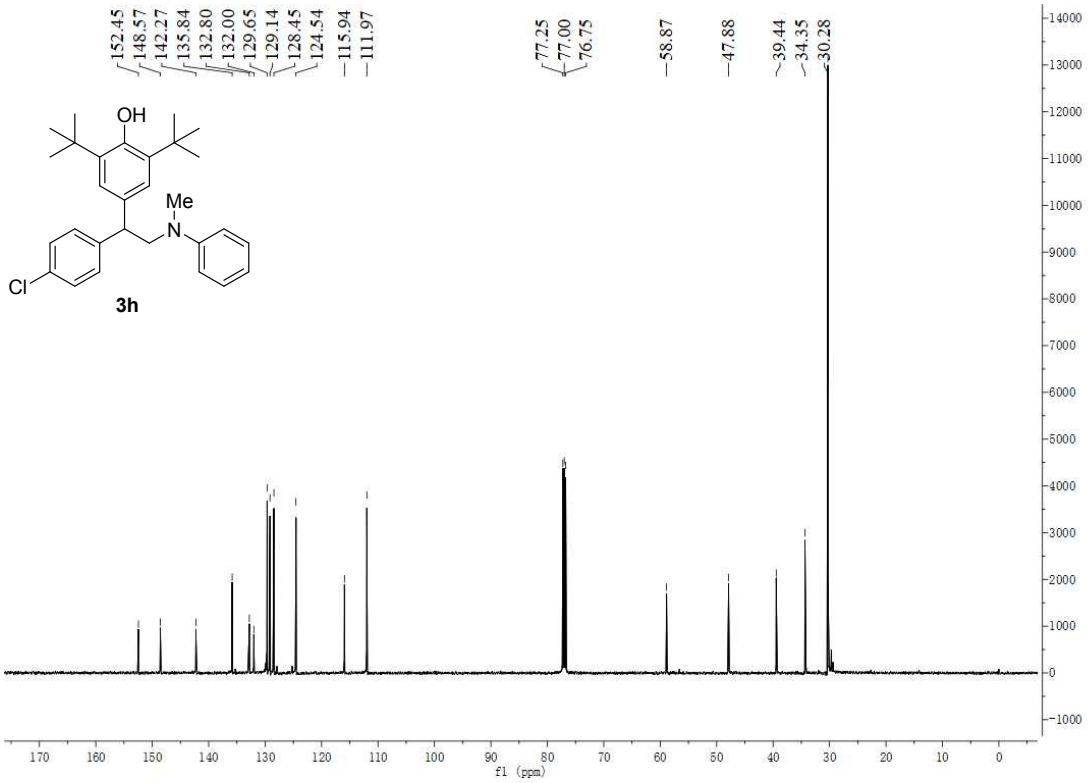
^{13}C NMR spectrum of 3g in $CDCl_3$



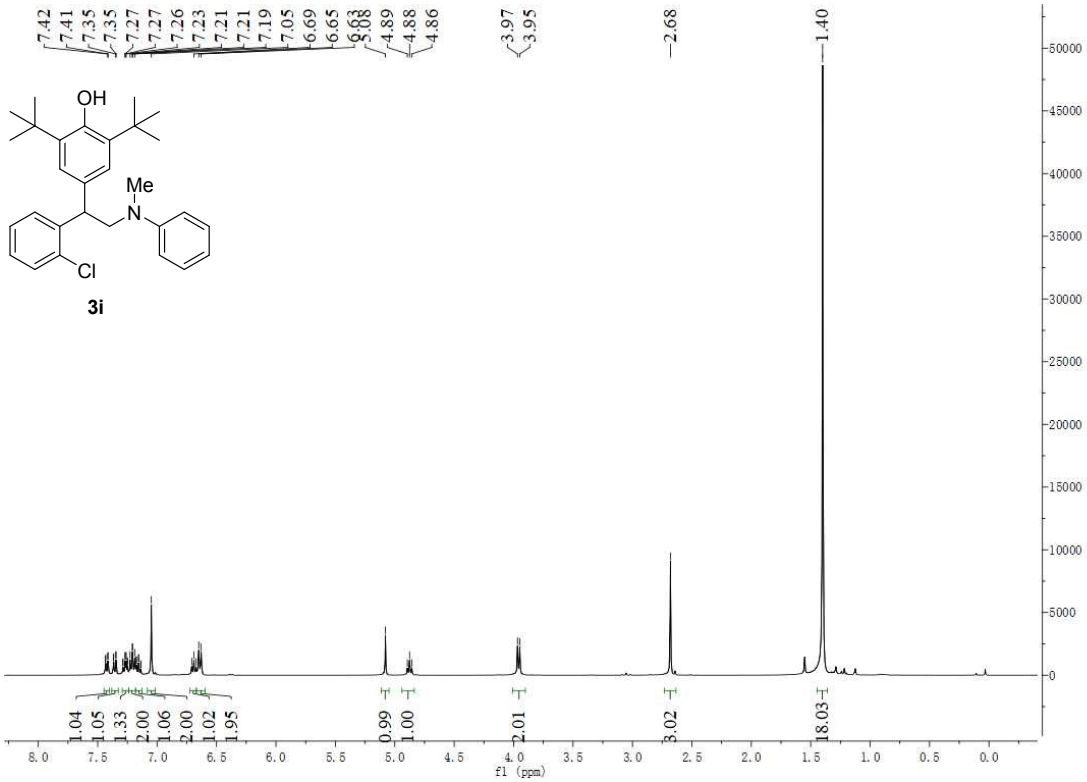
^{1}H NMR spectrum of 3h in $CDCl_3$



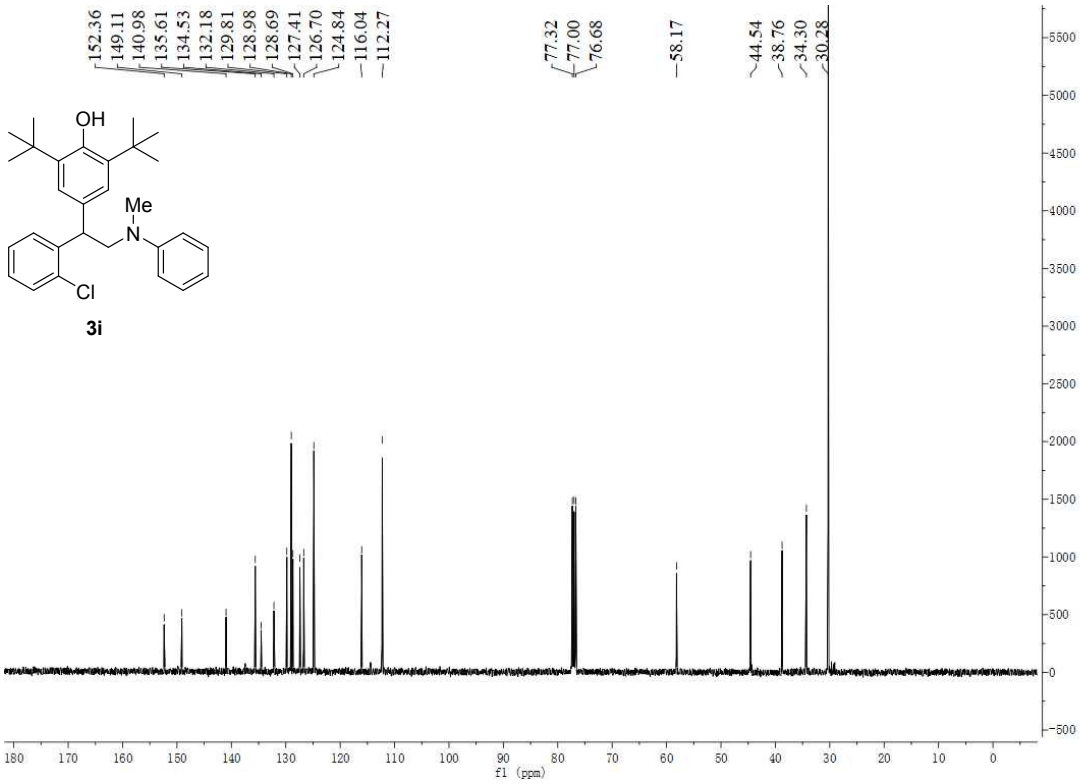
^{13}C NMR spectrum of 3h in $CDCl_3$



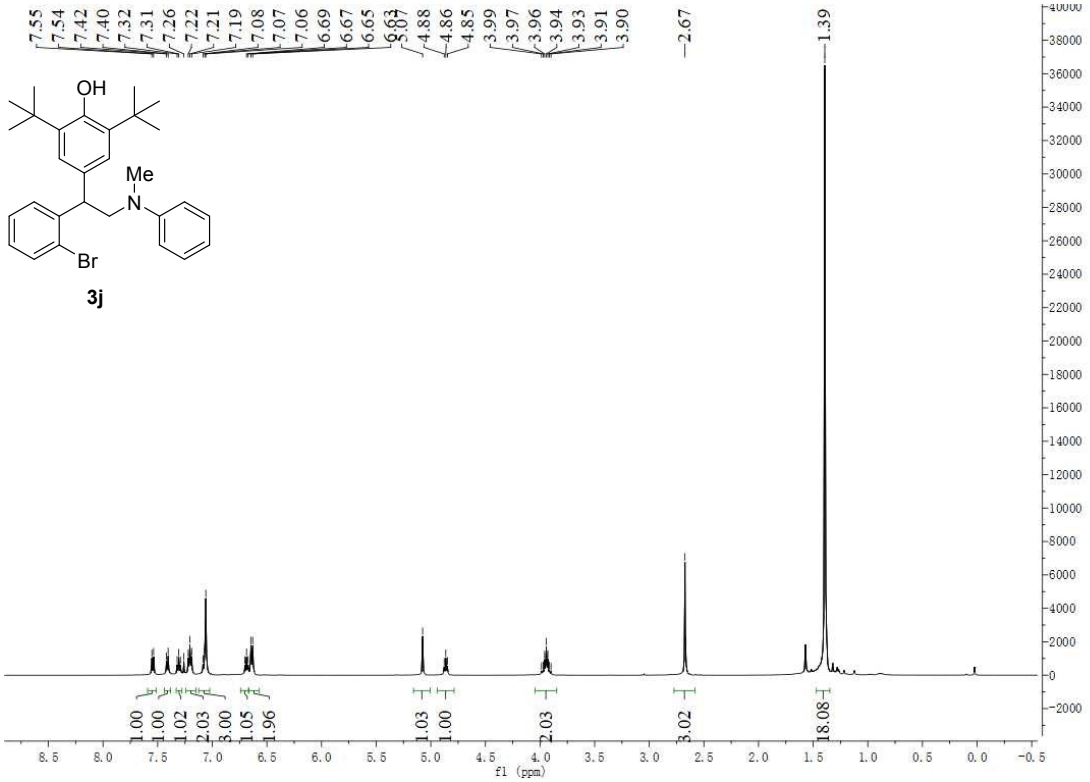
^{1}H NMR spectrum of 3i in $CDCl_3$



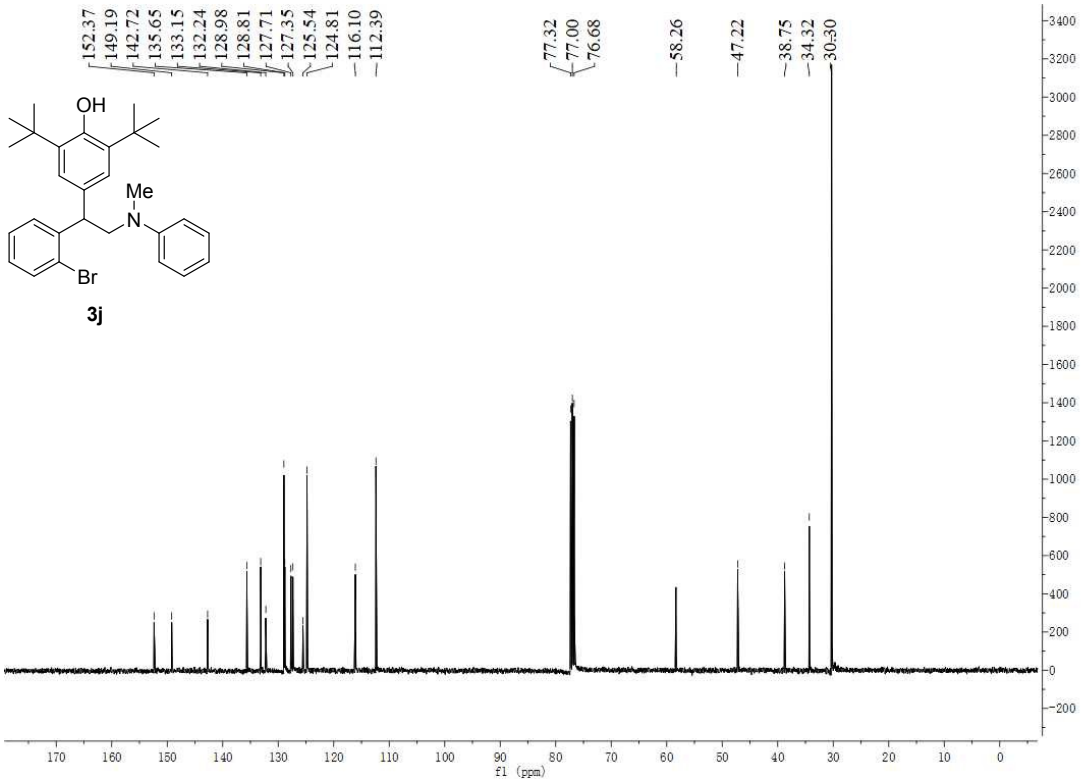
^{13}C NMR spectrum of 3i in $CDCl_3$



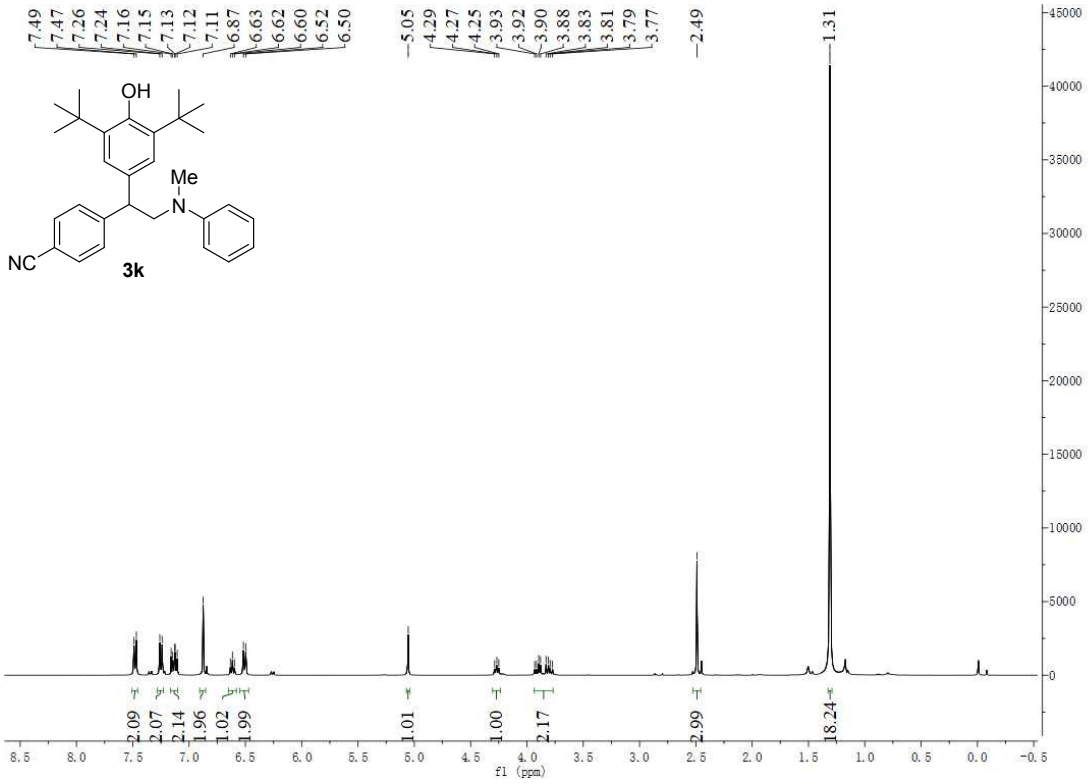
^{1}H NMR spectrum of 3j in $CDCl_3$



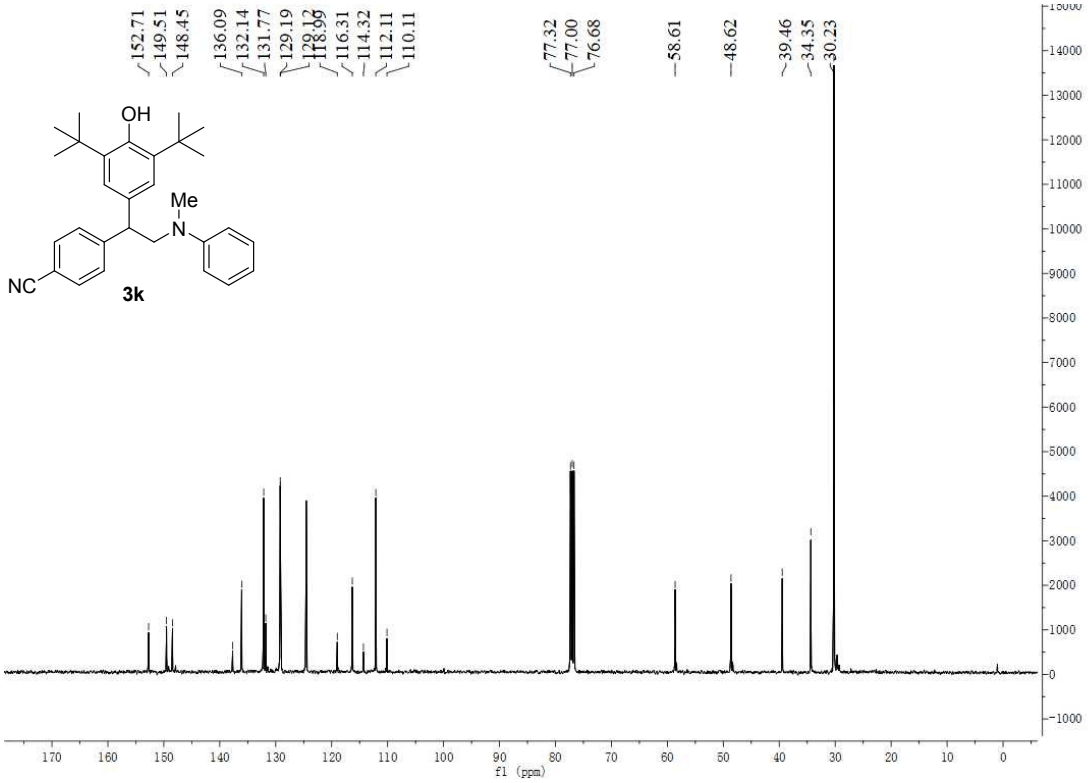
^{13}C NMR spectrum of 3j in $CDCl_3$



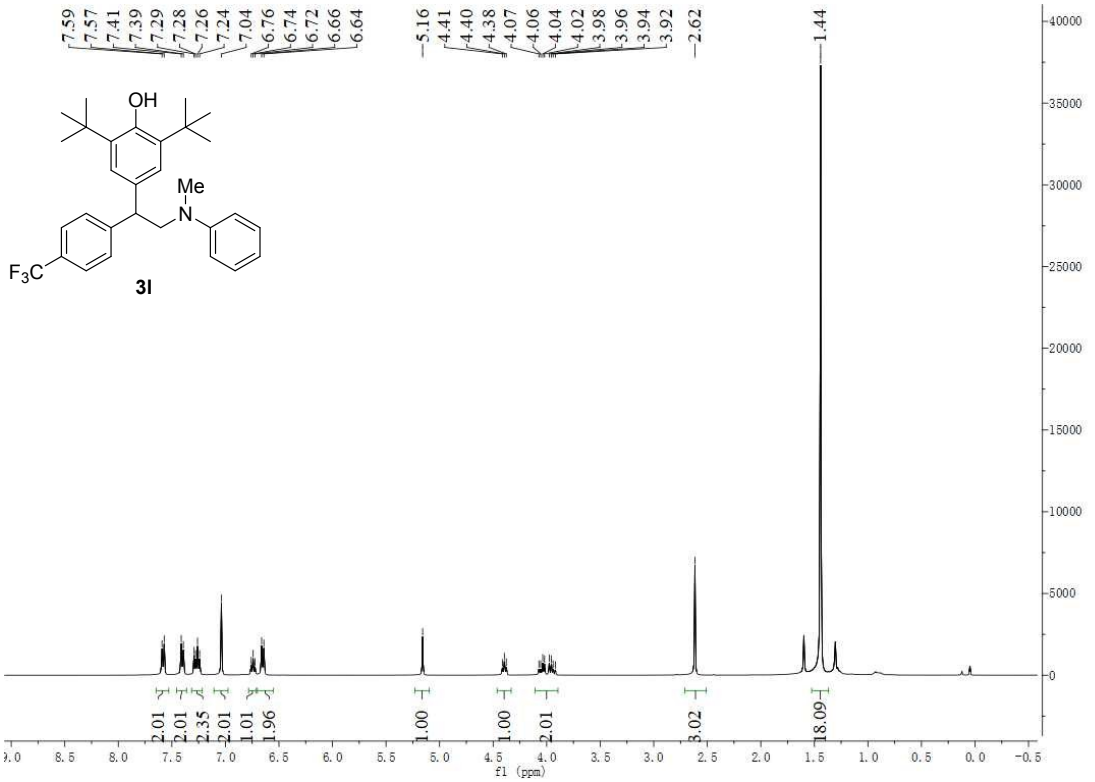
^{1}H NMR spectrum of 3k in $CDCl_3$



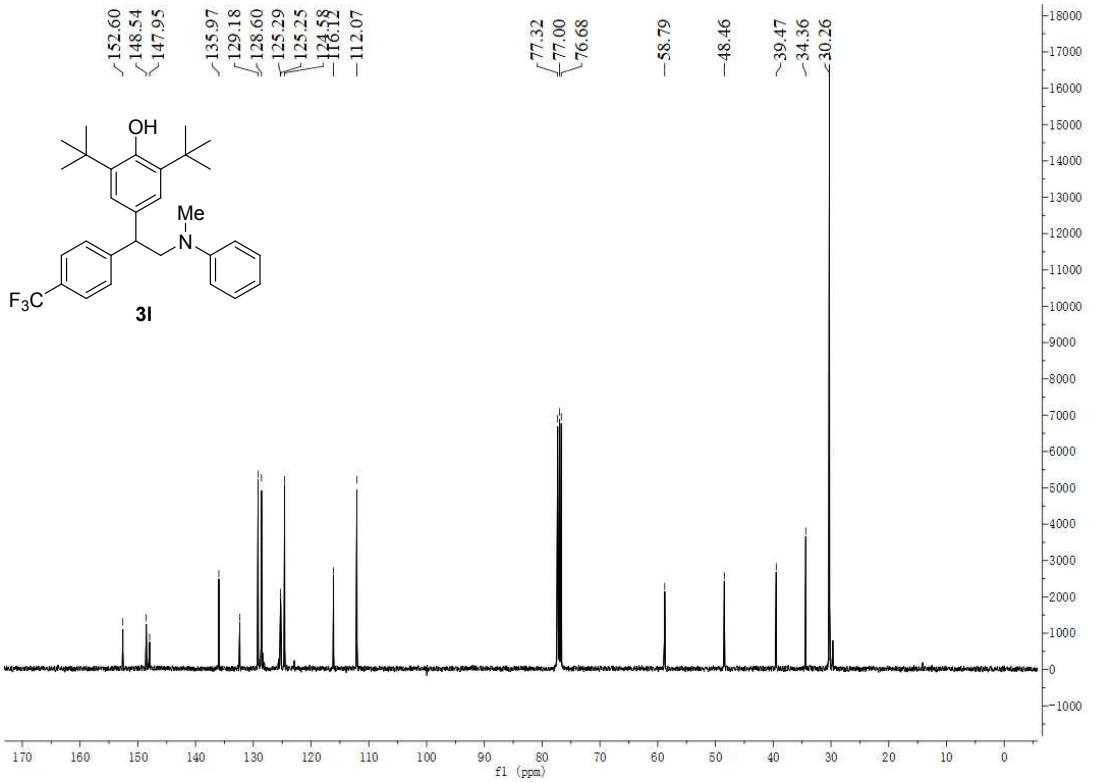
^{13}C NMR spectrum of 3k in $CDCl_3$



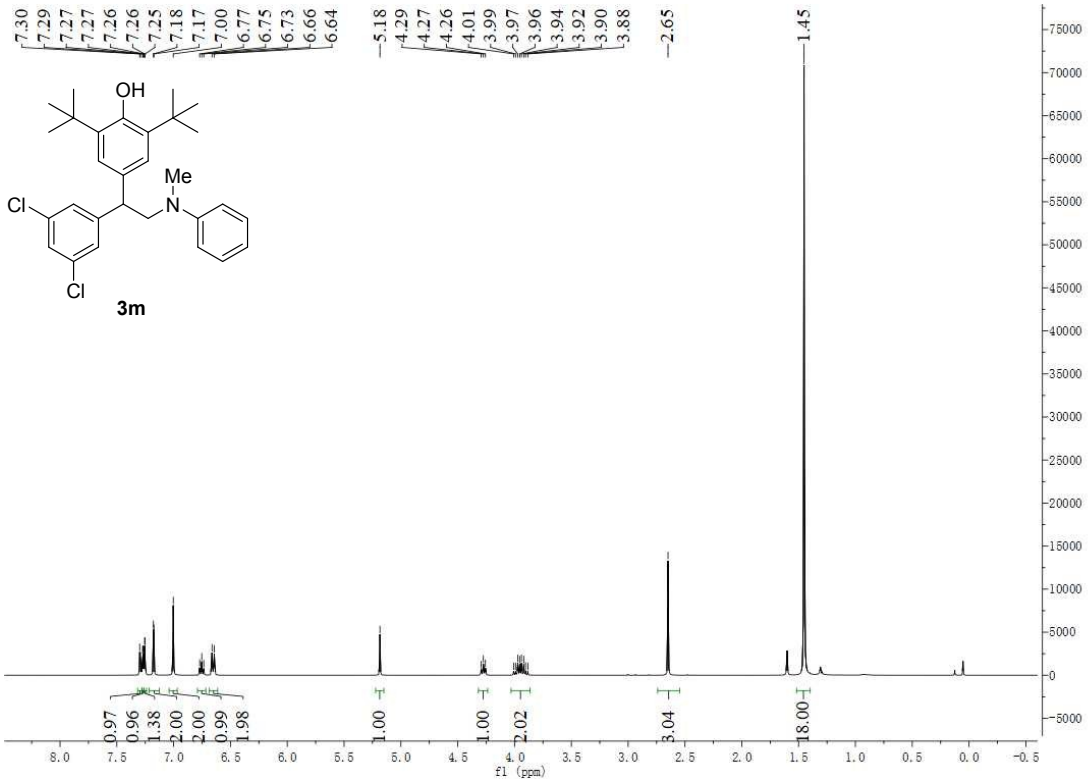
^{1}H NMR spectrum of 3l in $CDCl_3$



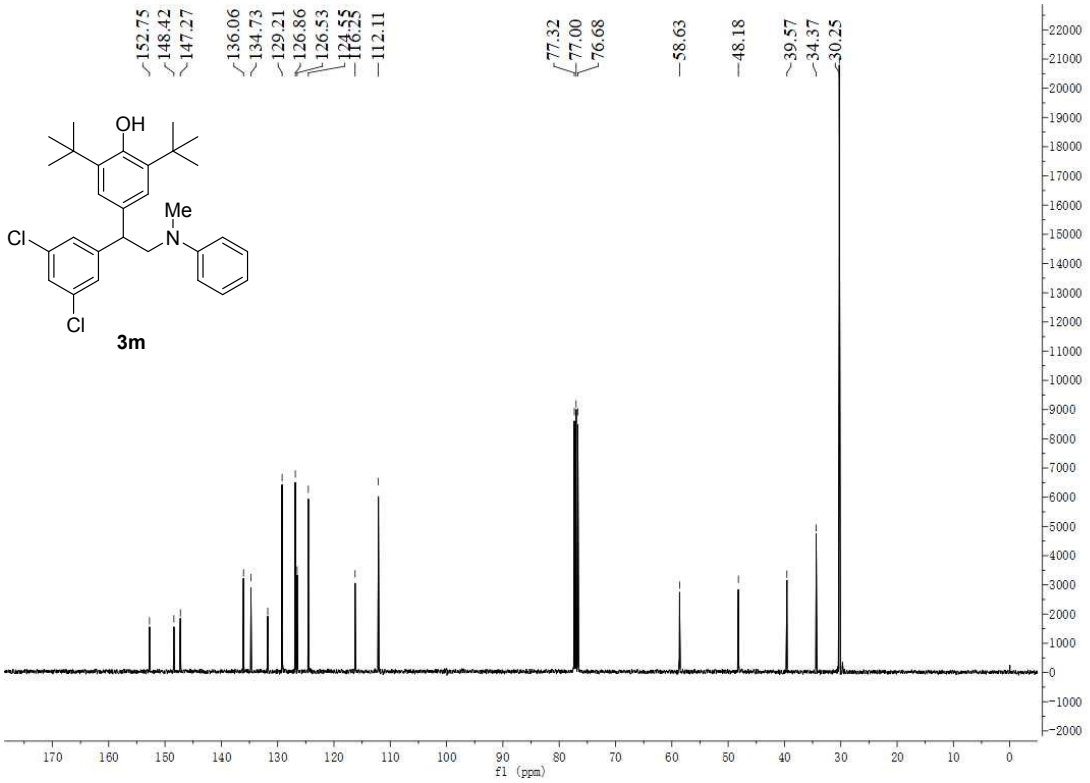
^{13}C NMR spectrum of 3l in $CDCl_3$



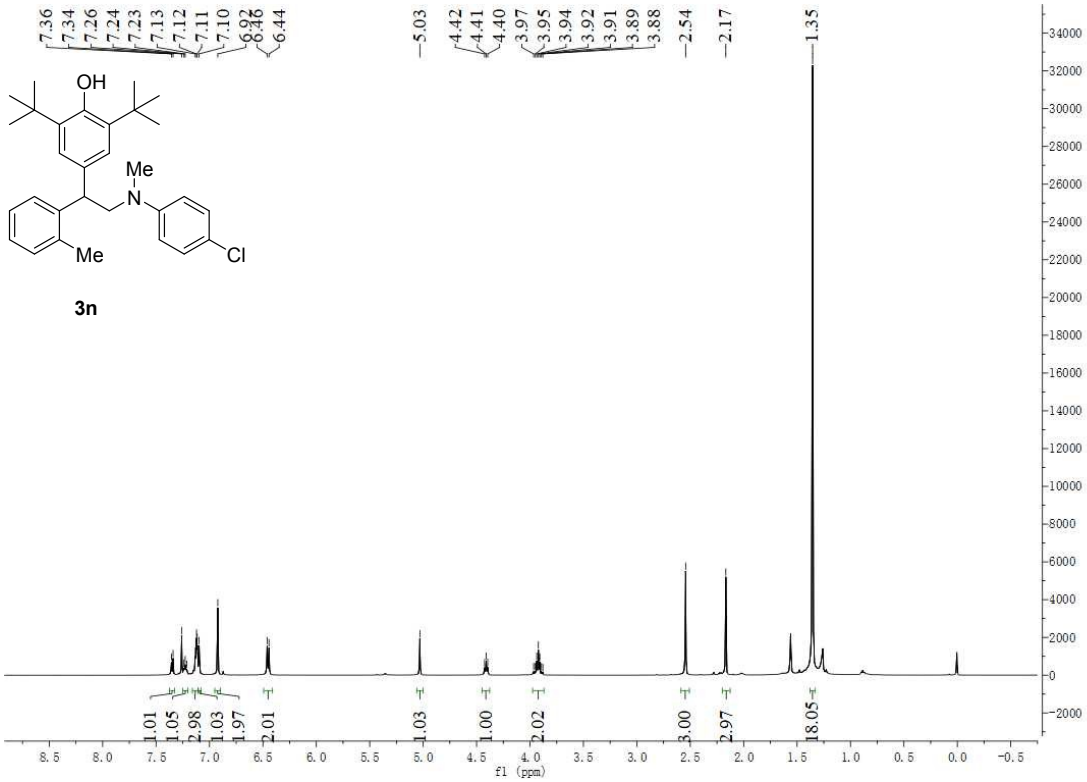
^{1}H NMR spectrum of 3m in $CDCl_3$



^{13}C NMR spectrum of 3m in $CDCl_3$

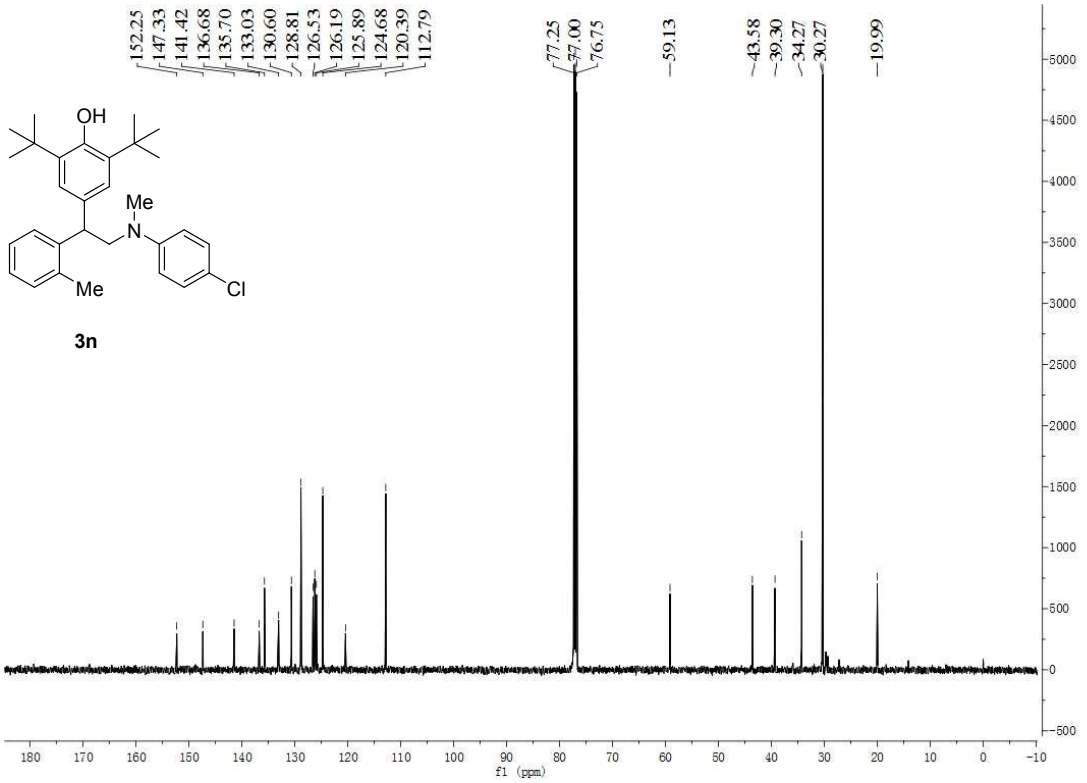


^{1}H NMR spectrum of 3n in $CDCl_3$



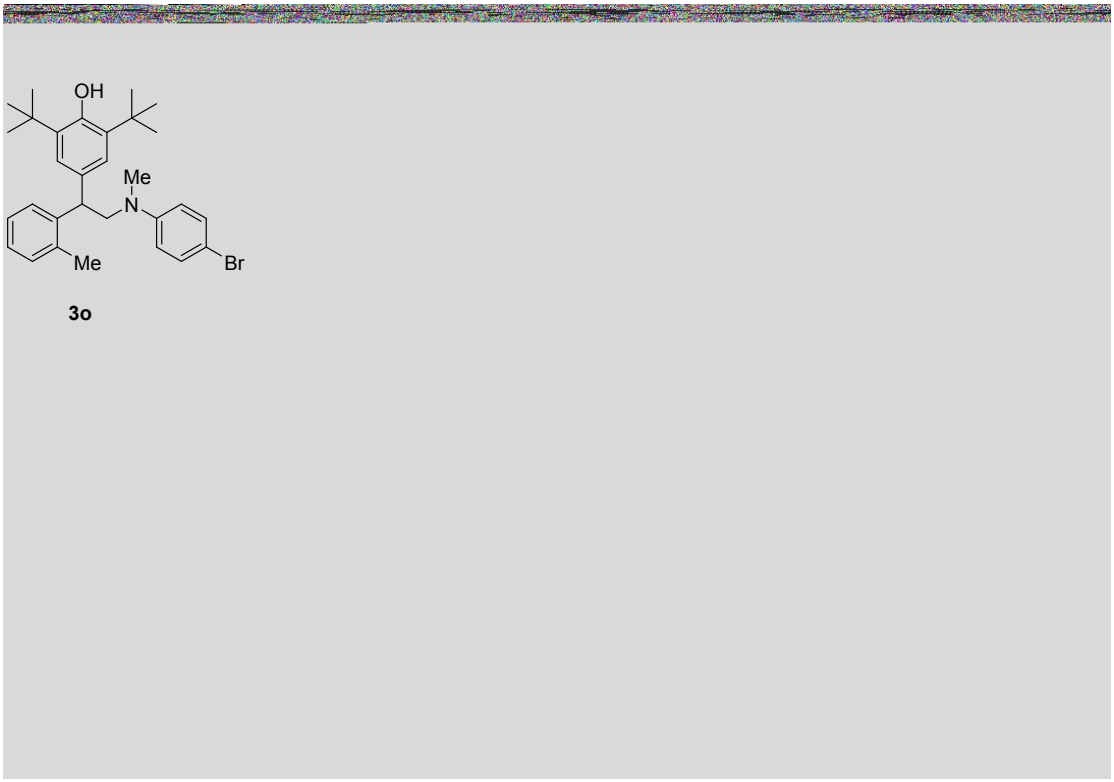
3n

^{13}C NMR spectrum of 3n in $CDCl_3$



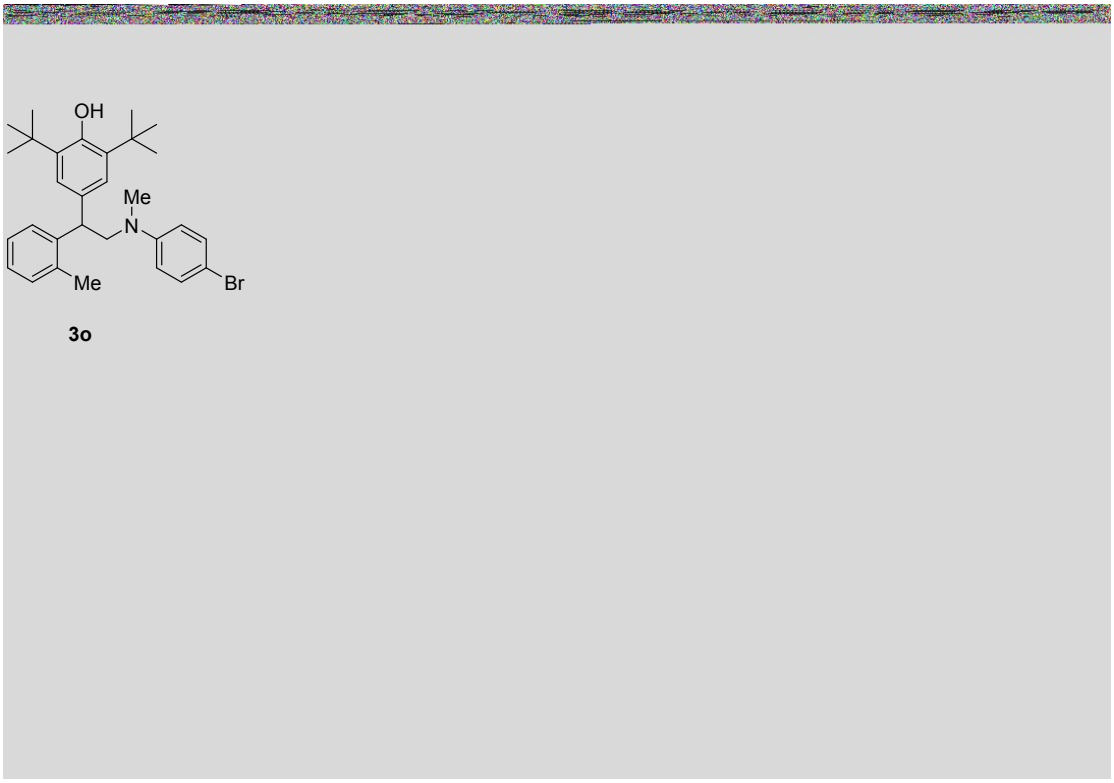
3n

^{1}H NMR spectrum of 3o in $CDCl_3$



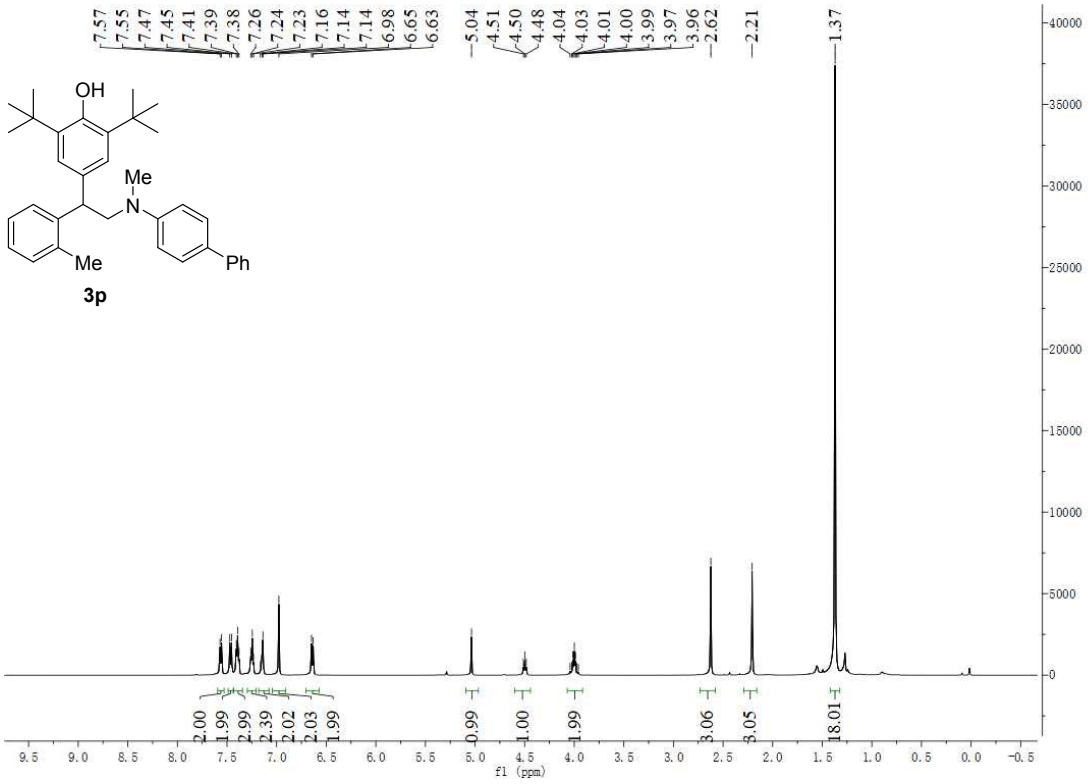
3o

^{13}C NMR spectrum of 3o in $CDCl_3$

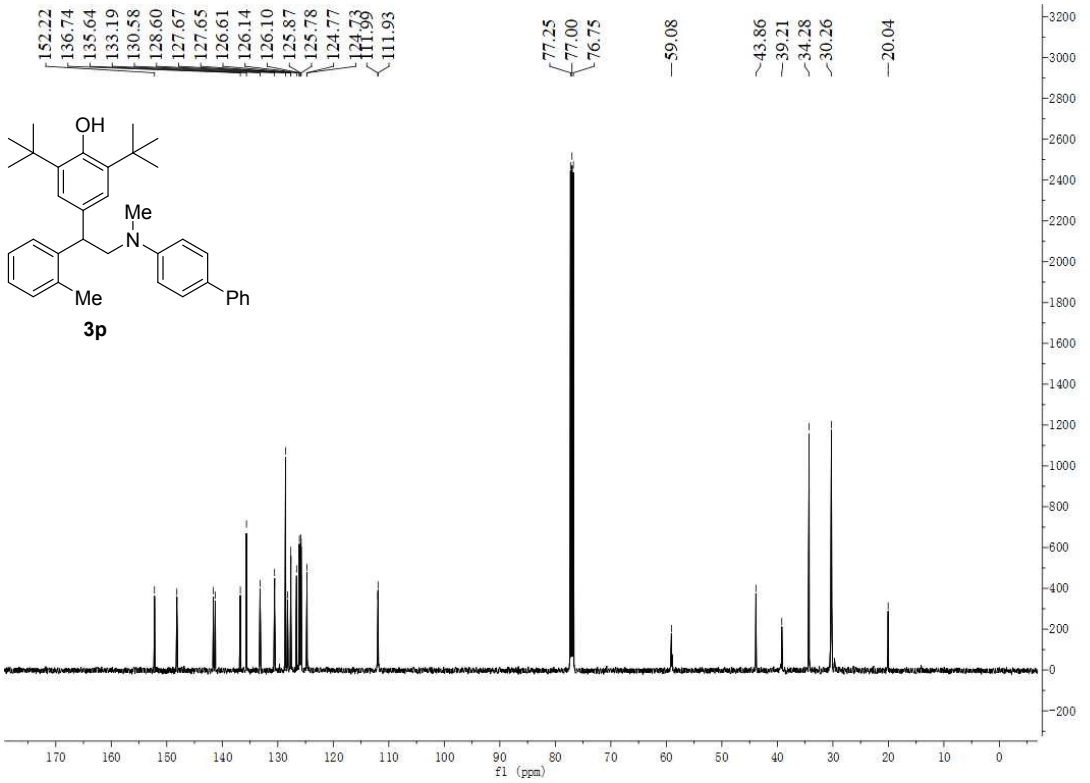


3o

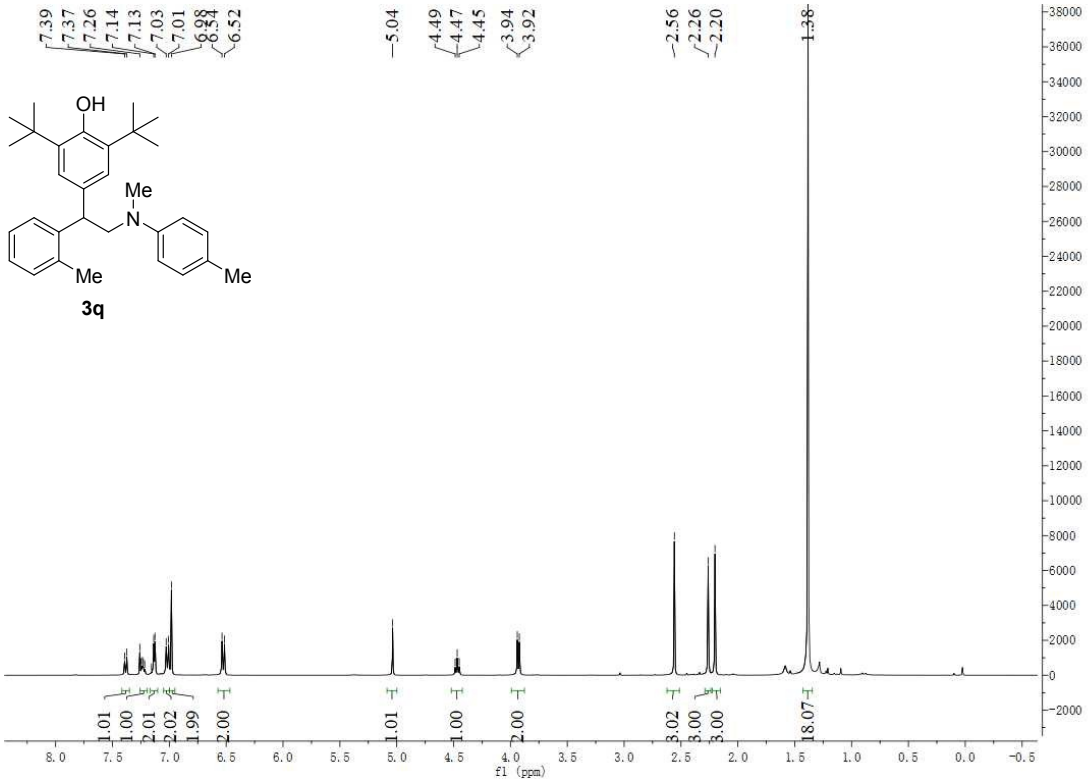
^{1}H NMR spectrum of 3p in $CDCl_3$



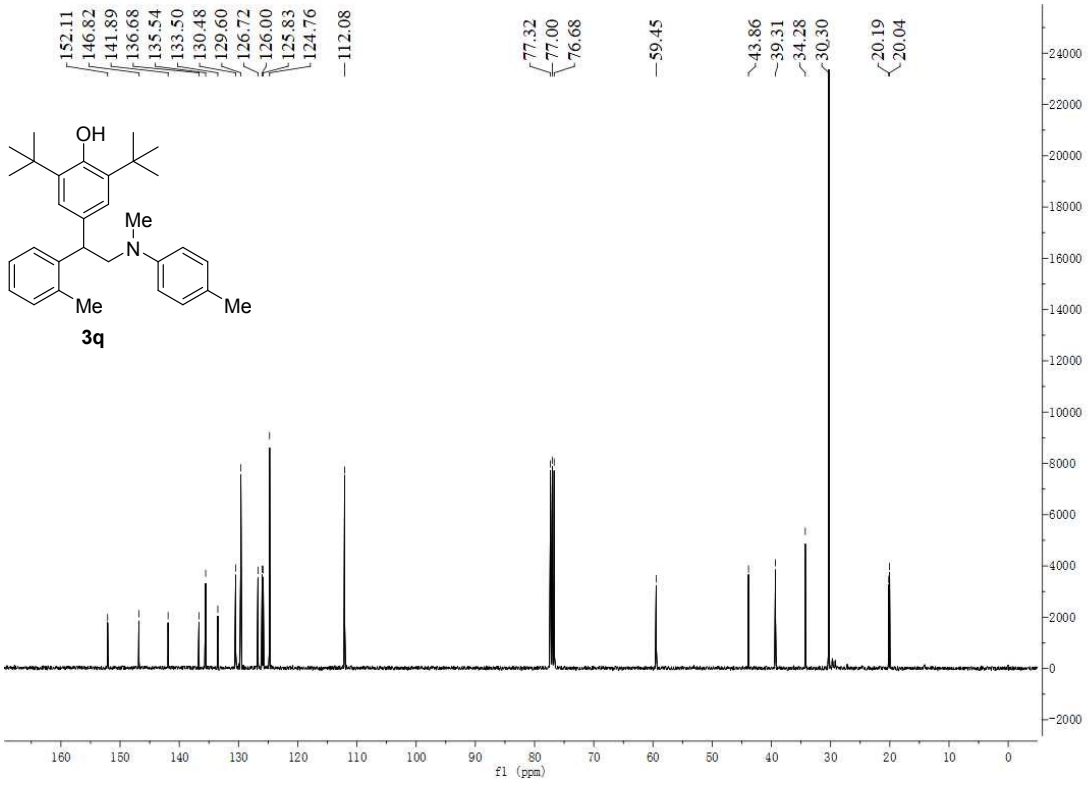
^{13}C NMR spectrum of 3p in $CDCl_3$



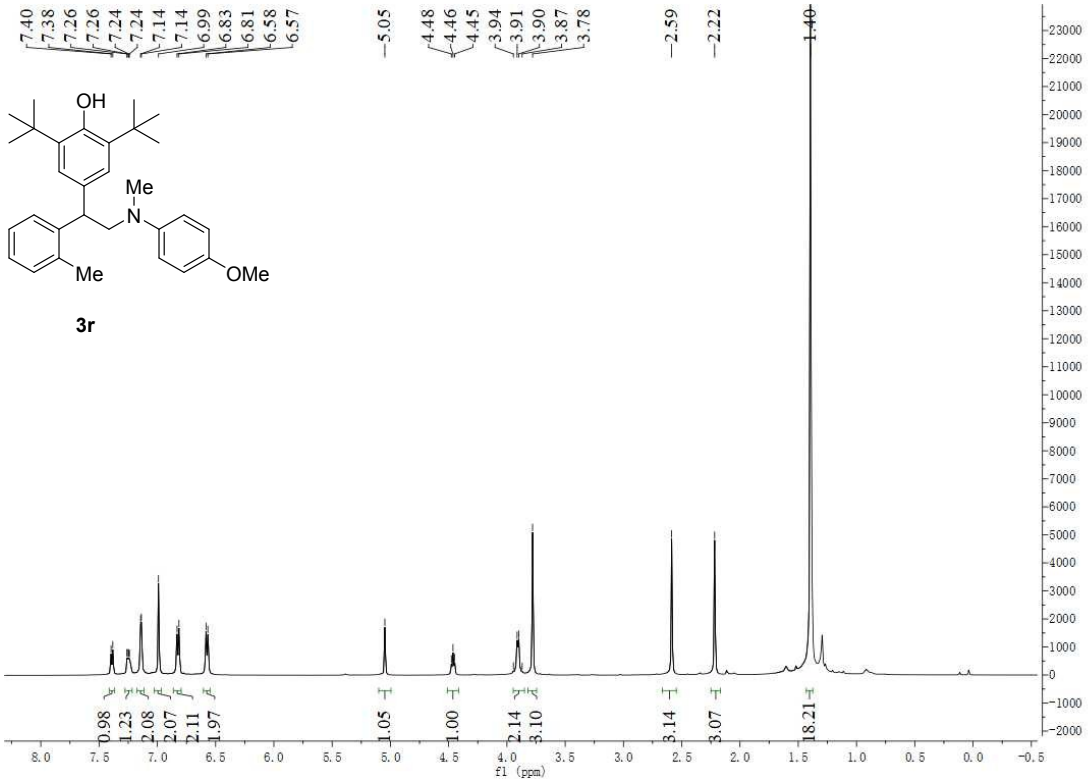
^{1}H NMR spectrum of 3q in $CDCl_3$



^{13}C NMR spectrum of 3q in $CDCl_3$

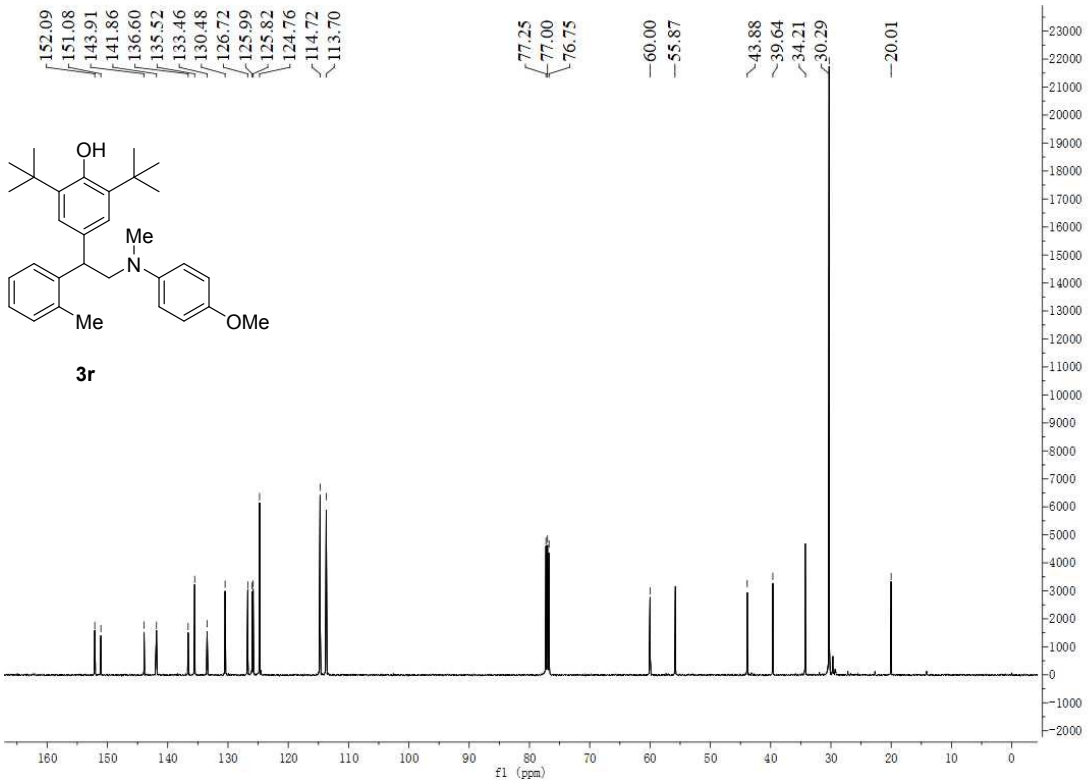


^{1}H NMR spectrum of 3r in $CDCl_3$



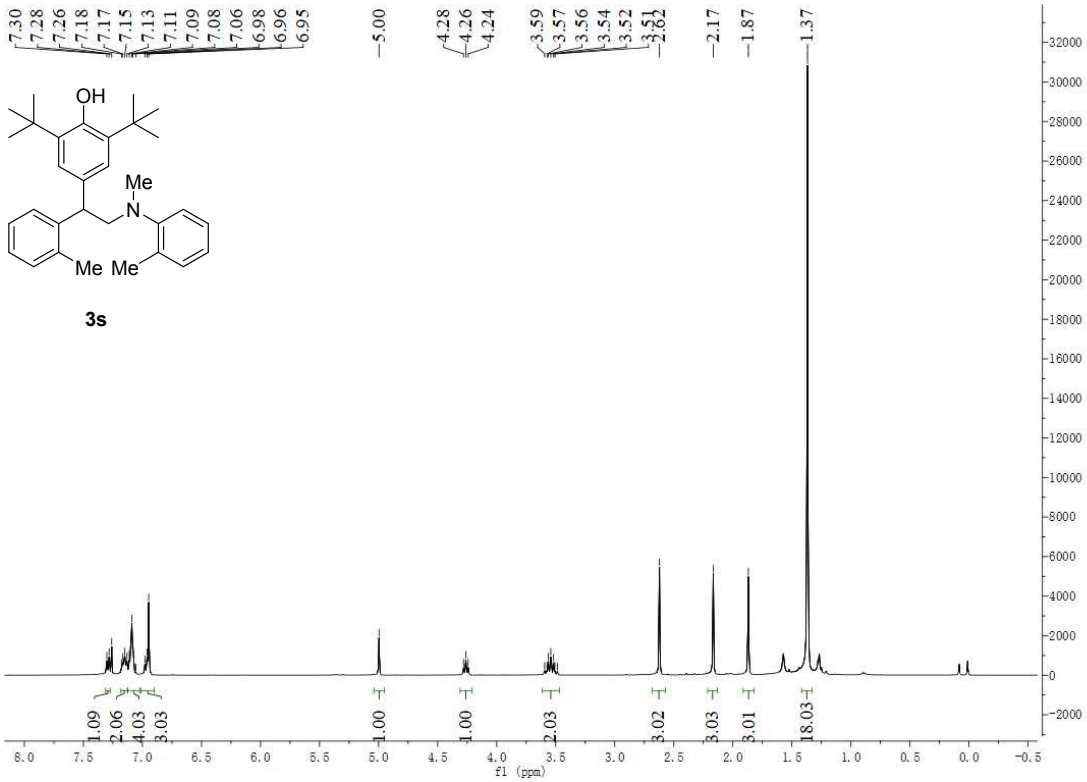
3r

^{13}C NMR spectrum of 3r in $CDCl_3$



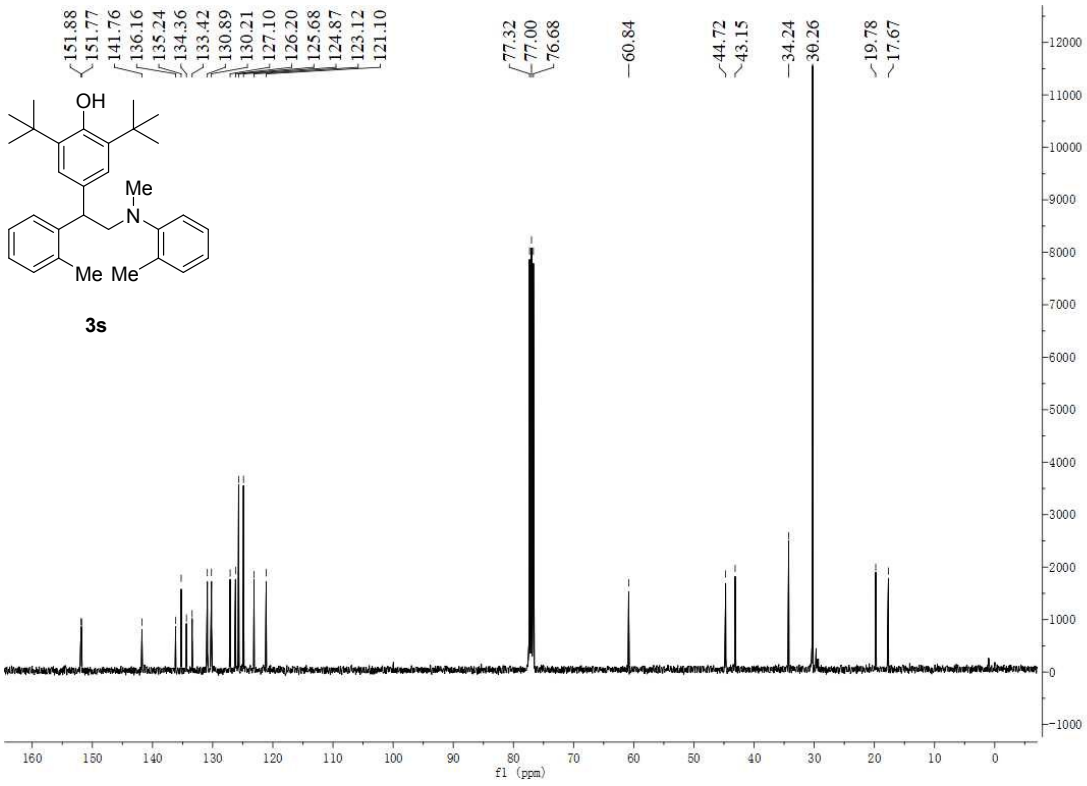
3r

^{1}H NMR spectrum of 3s in $CDCl_3$



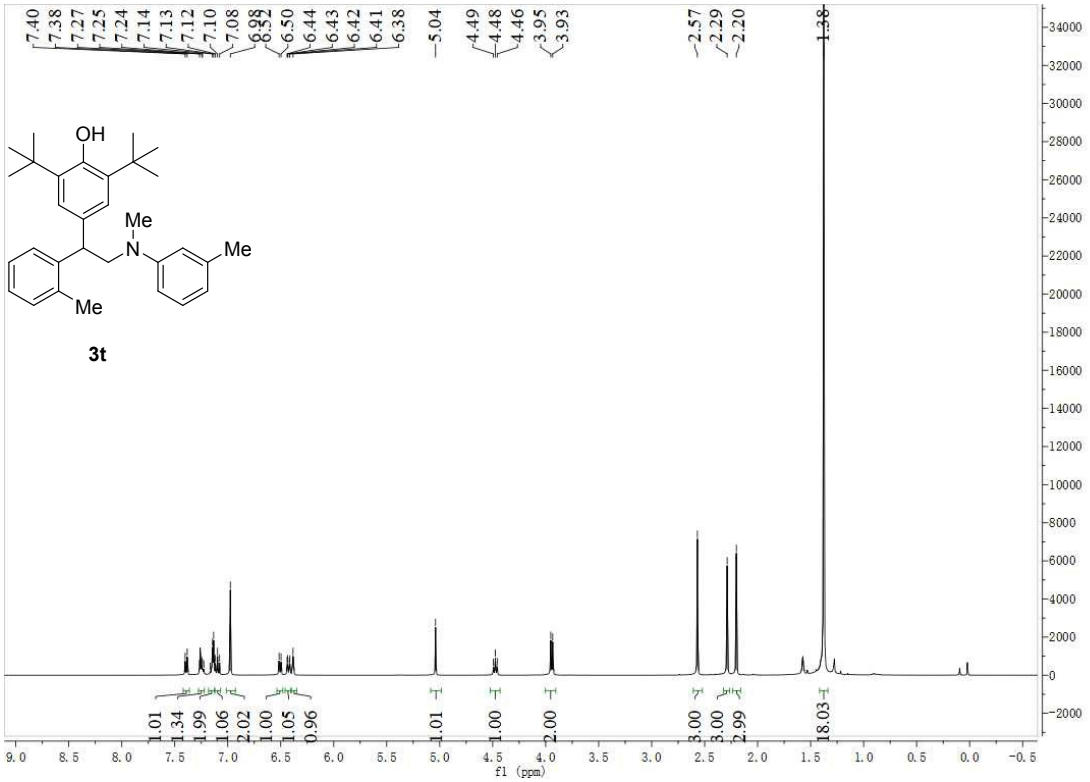
3s

^{13}C NMR spectrum of 3s in $CDCl_3$

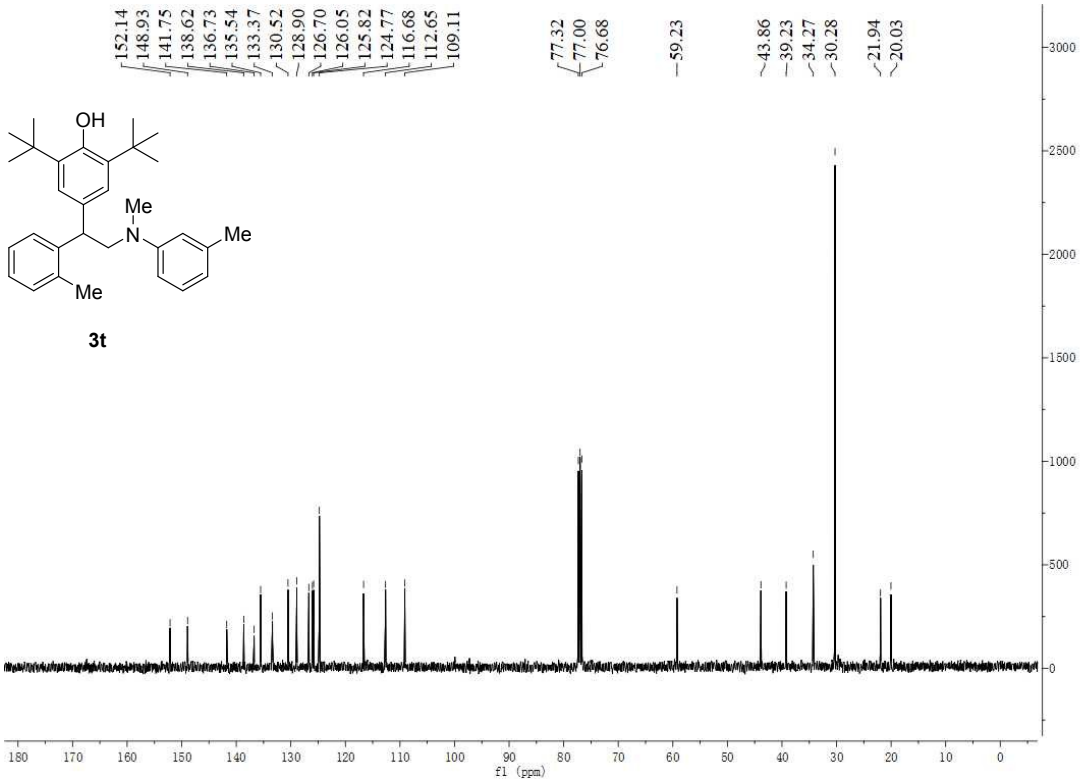


3s

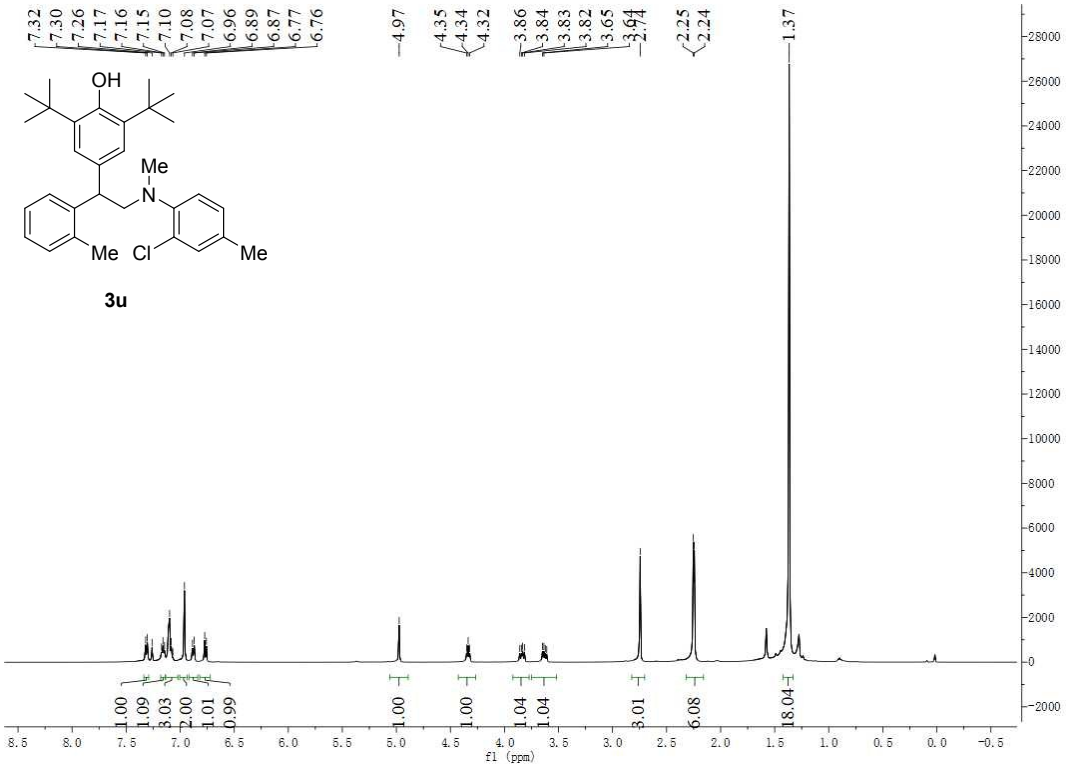
^{1}H NMR spectrum of 3t in $CDCl_3$



^{13}C NMR spectrum of 3t in $CDCl_3$

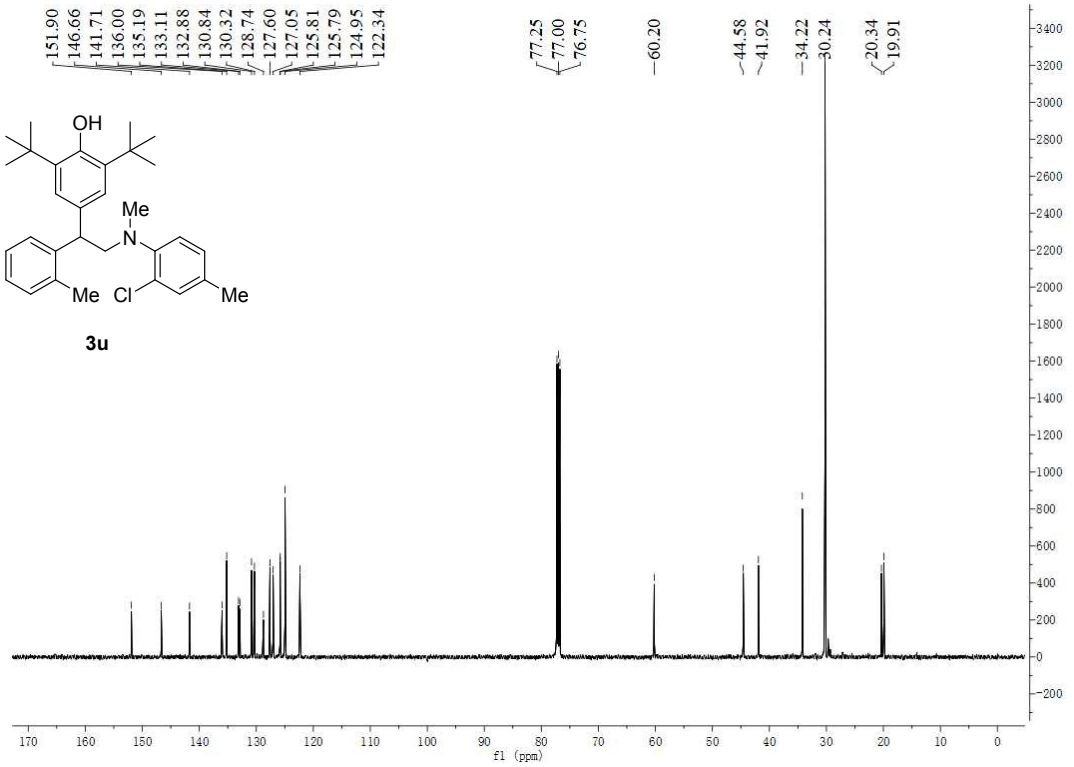


^{1}H NMR spectrum of 3u in $CDCl_3$



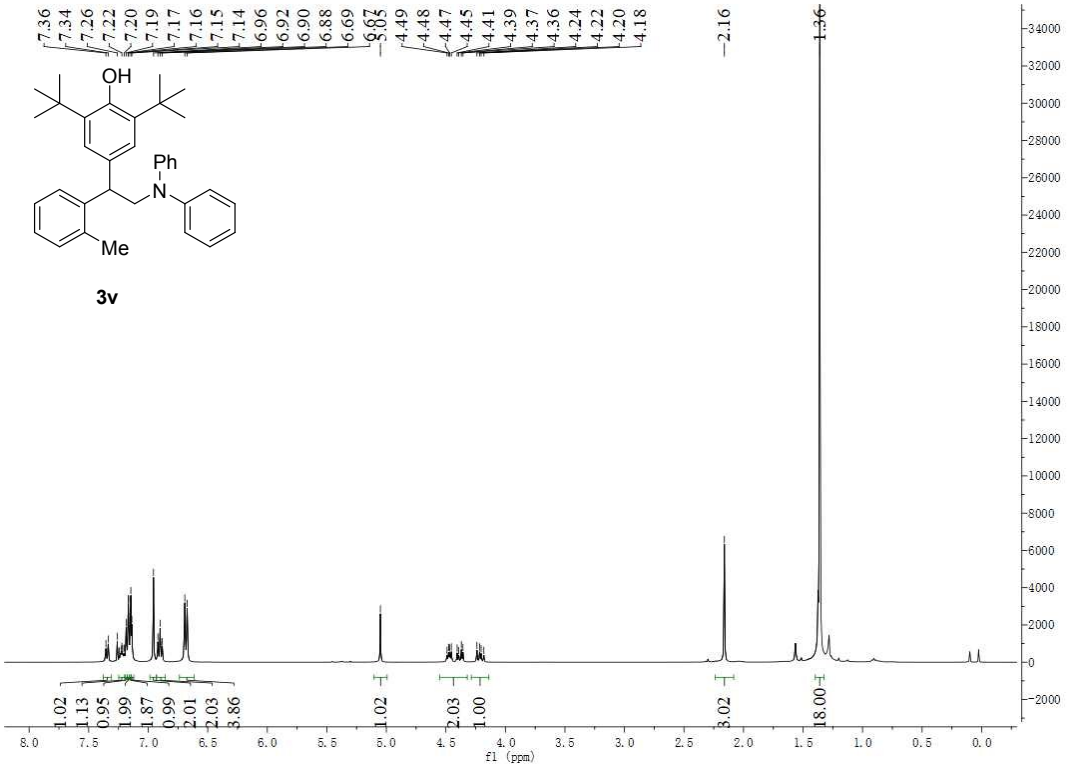
3u

^{13}C NMR spectrum of 3u in $CDCl_3$

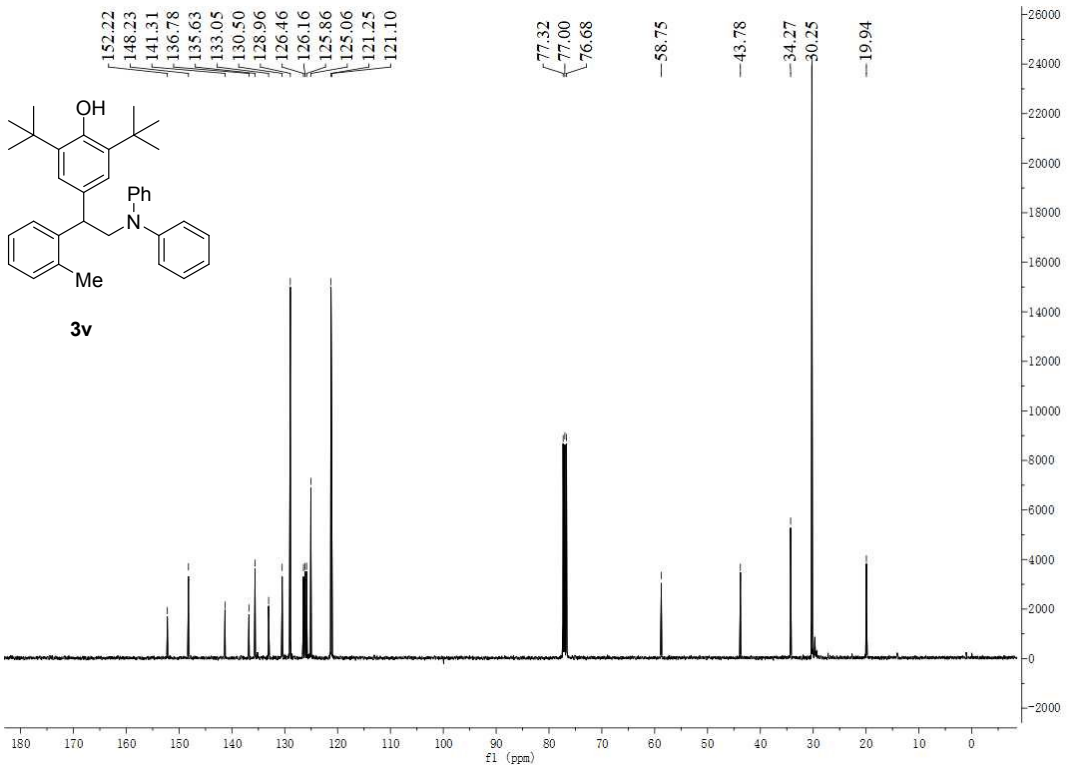


3u

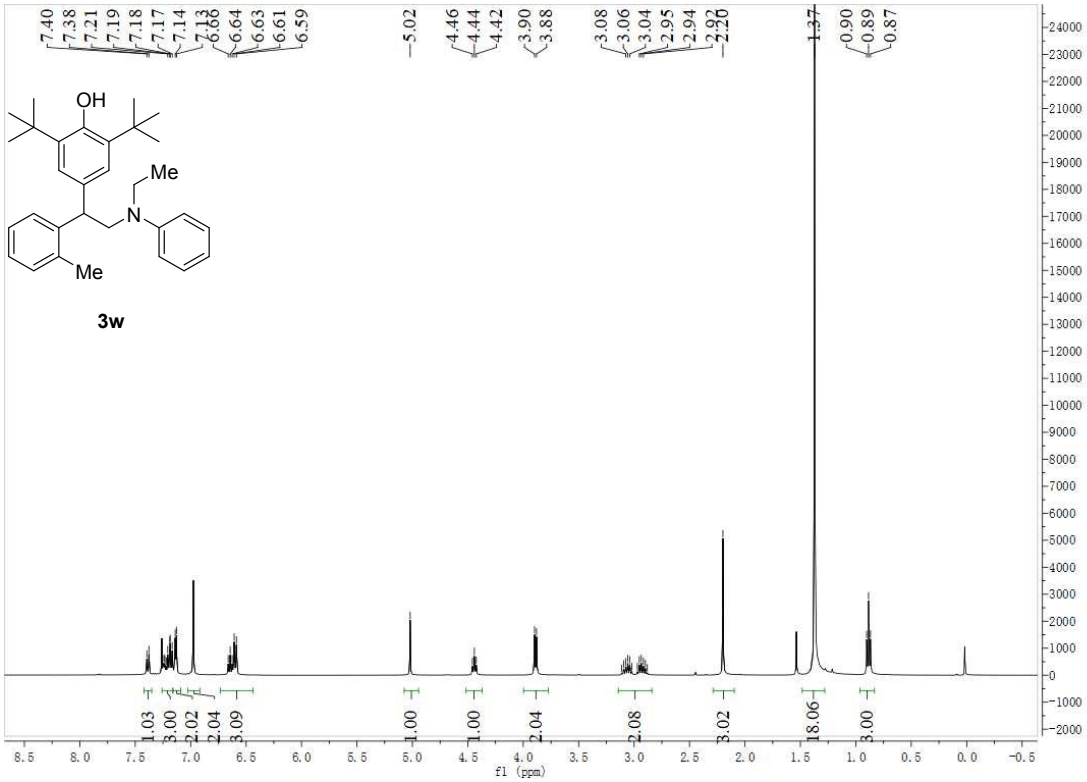
^{1}H NMR spectrum of 3v in $CDCl_3$



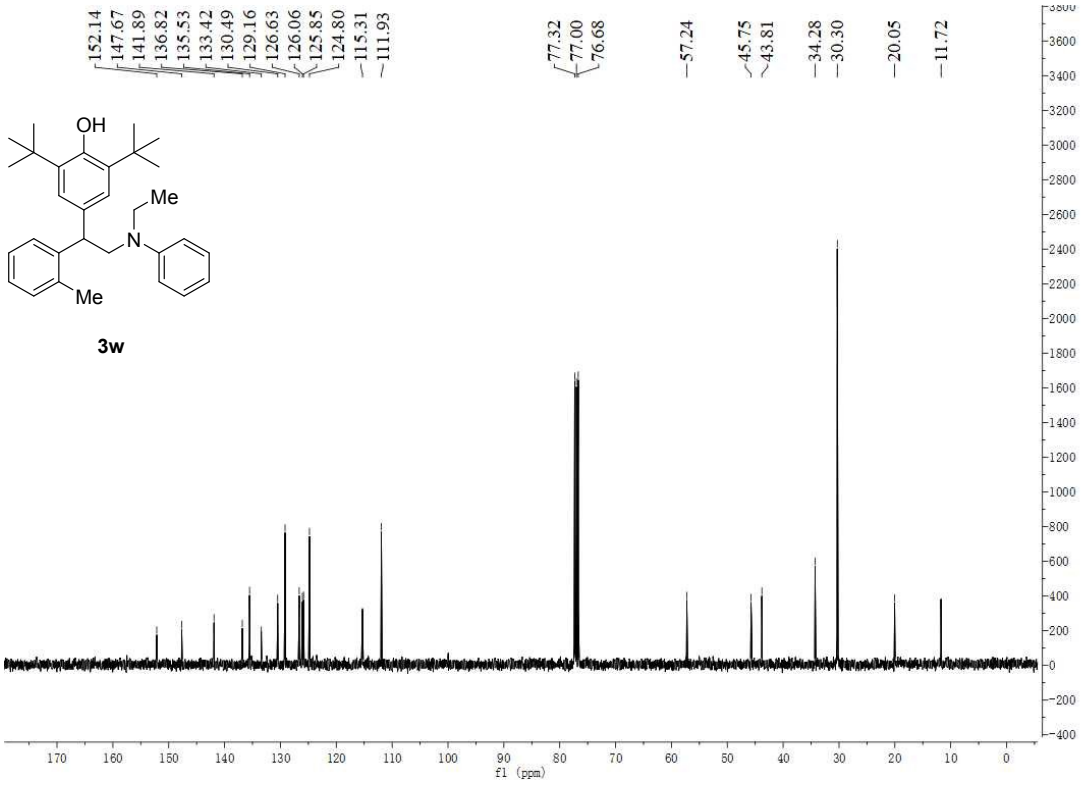
^{13}C NMR spectrum of 3v in $CDCl_3$



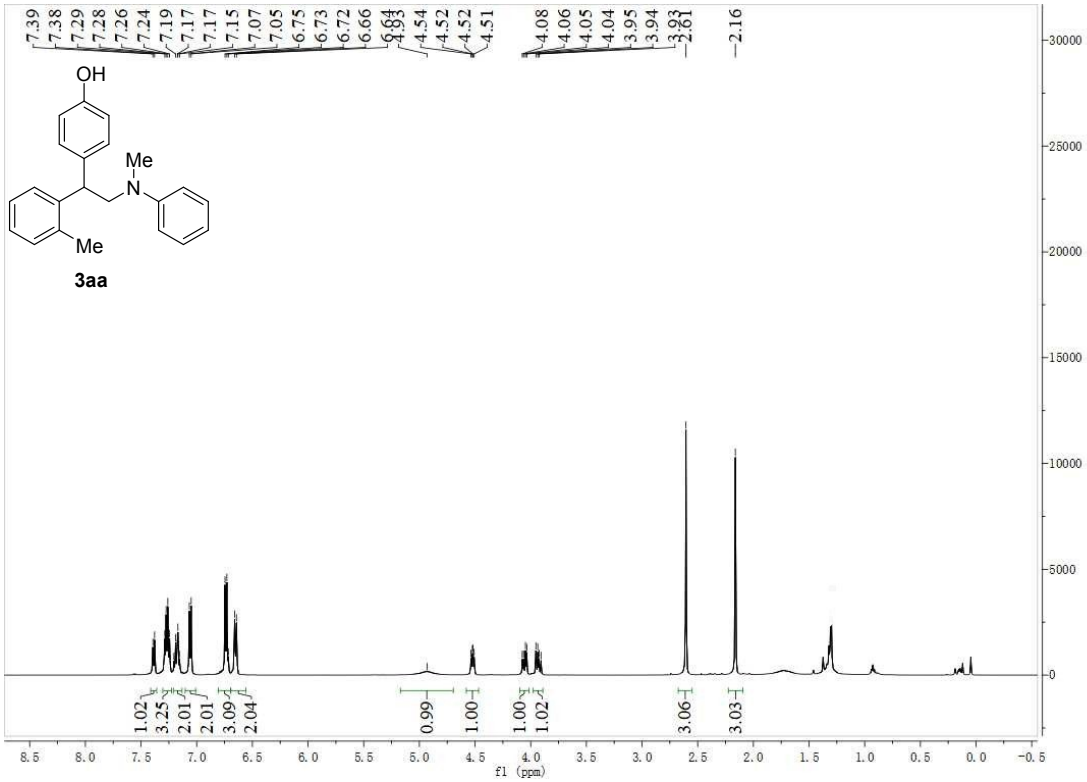
^{1}H NMR spectrum of 3w in $CDCl_3$



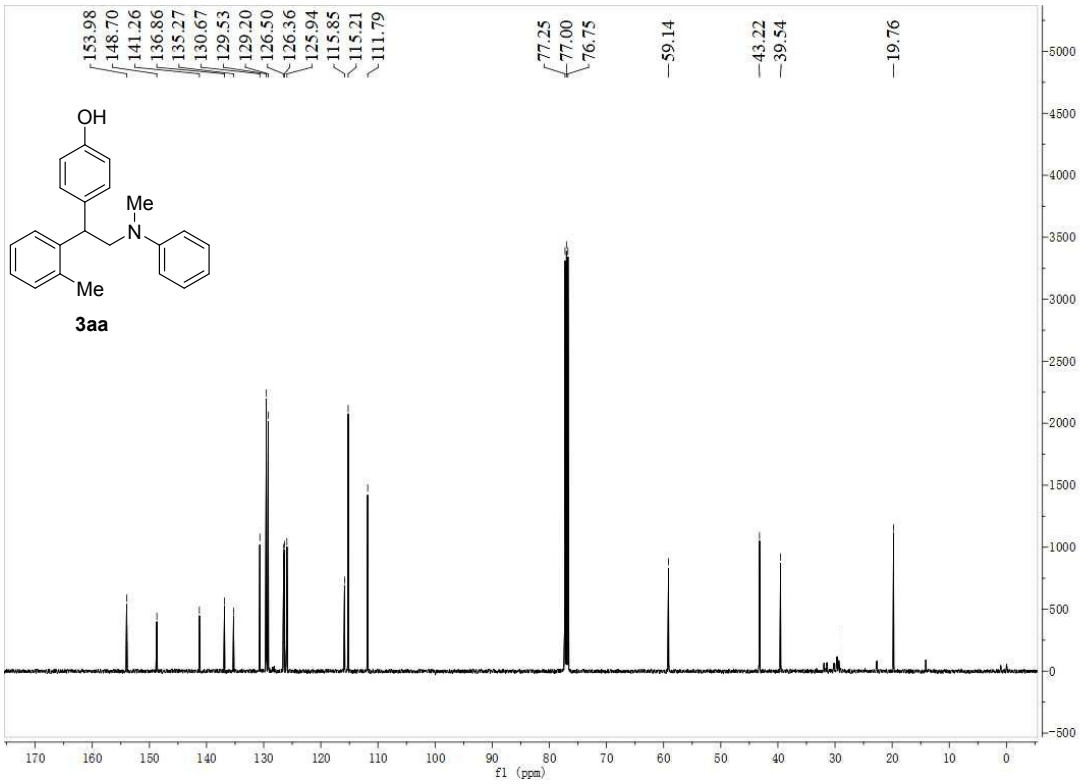
^{13}C NMR spectrum of 3w in $CDCl_3$



^{1}H NMR spectrum of 3aa in $CDCl_3$



^{13}C NMR spectrum of 3aa in $CDCl_3$



6. References.

(1) (a) J. Guo, G.-B. Huang, Q.-L. Wu, Y. Xie, J. Weng and G. Lu, *Org. Chem. Front*., 2019, **6**, 1955; (b) W.-D. Chu, L.-F. Zhang, X. Bao, X.-H. Zhao, C. Zeng, J.-Y. Du, G.-B. Zhang, F.-X. Wang, X.-Y. Ma, C.-A. Fan, *Angew. Chem., Int. Ed.* 2013, **52**, 9229; (c) L. Caruana, F. Kniep, T. K. Johansen, P. H. Poulsen, K. A. Jørgensen, *J. Am. Chem. Soc.* 2014, **136**, 15929; (d) D. Richter, N. Hampel, T. Singer, A. R. Ofial, H. Mayr, *Eur. J. Org. Chem.* 2009, **19**, 3203.

(2) S. Gupta, P. Sureshbabu, A. K. Singh, S. Sabiah, J. Kandasamy, *Tetrahedron Lett.* 2017, **58**, 909.