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Supporting Information

Cu-Catalyzed Cross-Dehydrogenative *ortho*-Aminomethylation of Phenols

*Congjun Yu and Frederic W. Patureau**

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Supporting Information

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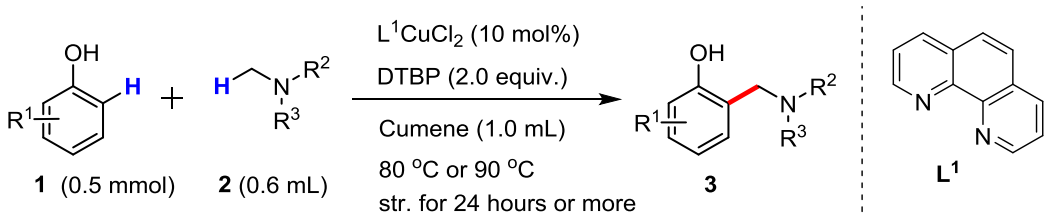
1. General Information

All reactions were carried out in dried reaction vials with sealed aluminous headspace caps under air, unless otherwise specified. NMR spectra were obtained on Bruker Avance 400 using $CDCl_3$ as solvents, with proton and carbon resonances at 400 MHz and 101 MHz, respectively. Chemical shifts are given in ppm and coupling constants (*J*) in Hz. ^1H spectra were calibrated in relation to the reference measurement of TMS (0.00 ppm). ^{13}C spectra were calibrated in relation to deuterated solvents, namely $CDCl_3$ (77.16 ppm). The following abbreviations were used for ^1H NMR spectra to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet) as well as combinations of them. Flash chromatography was performed on silica gel (40-63 mesh) by standard technique. Substrates were purchased either from Sigma Aldrich, Acros, TCI, or chemPUR. HRMS spectra were recorded on WATERS GCT-PremierTM mass spectrometer.

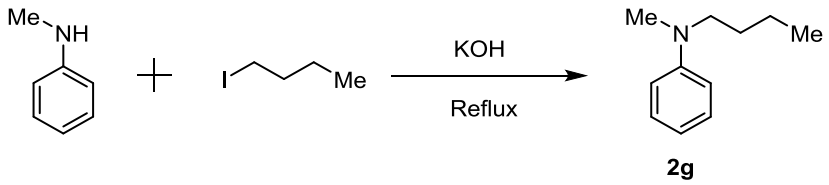
2. General Procedure for Cross-Dehydrogenative *ortho*-Aminomethylation of Phenols



Unless otherwise specified, the phenol **1** (0.5 mmol scale), the catalyst L^1CuCl_2 (10 mmol%), the methylamine derivative **2** (0.6 mL), cumene (1.0 mL), and DTBP (1.0 mmol) are united under air in a 20 mL reaction vial equipped with aluminous headspace cap. The reactor is sealed and exposed to 80 or 90°C (for same substrates) for 24 hours or more (for some substrates). Magnetic stirring set to approx. 240 turns/min. The reactor is then cooled to room temperature. The crude is directly engaged (unless otherwise specified) on SiO_2 gel column chromatography for purification. The expected cross-coupling products are generally (but not always) a little higher than the phenol starting material on the TLC plate in the given solvent systems.

3. Synthesis of Starting materials

(1) Synthesis of *N*-butyl-*N*-methylaniline **2g**



2g

According to a reported procedure[1], 5.4 mL (50 mmol, 1.0 equiv.) *N*-methylaniline and 10.0 mL (88 mmol, 1.8 equiv.) 1-iodobutane and 3.1 g (55 mmol, 1.1 equiv.) KOH were added into a 50 mL flask. After refluxing under 140℃ for 6 hours, the reaction was stopped and purified by SiO_2 gel column chromatography (hexane/EA = 70:1). 6.1 g product **2g** (colorless oil) was obtained with a

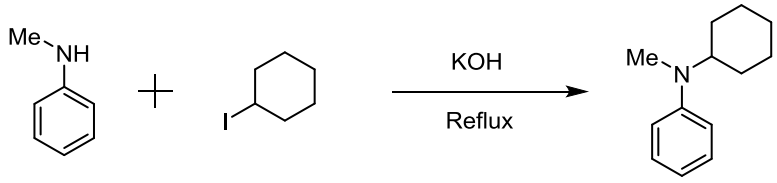
75% isolated yield.

The ^{1}H NMR and ^{13}C NMR are indentical to that reported in literature[2].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.0 Hz, 2H), 6.91–6.69 (m, 3H), 3.40 (t, *J* = 7.1 Hz, 2H), 3.01 (s, 3H), 1.73–1.57 (m, 2H), 1.54–1.38 (m, 2H), 1.13–0.97 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.45 (s, C_{quat}), 129.22 (s, CH), 115.87 (s, CH), 112.15 (s, CH), 52.62 (s, CH_2), 38.36 (s, CH_3), 28.94 (s, CH_2), 20.48 (s, CH_2), 14.13 (s, CH_3).

(2) Synthesis of *N*-cyclohexyl-*N*-methylaniline **2h**



2h

According to a reported procedure[1], 926 mg (8.66 mmol, 1.0 equiv.) *N*-methylaniline and 2.0 g (9.5 mmol, 1.1 equiv.) 1-iodobutane and 537 mg (9.5 mmol, 1.1 equiv.) KOH were added into a 25 mL flask. After refluxing under 120℃ for 24 hours, the reaction was stopped and purified by SiO_2 gel column chromatography (hexane/EA = 50:1). 800 mg product **2h** (yellow oil) was obtained with a 48% isolated yield.

The ^{1}H NMR and ^{13}C NMR are indentical to that reported in literature[3].

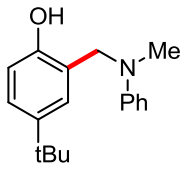
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.06 (m, 2H), 6.69 (d, *J* = 8.1 Hz, 2H), 6.59 (t, *J* = 7.2 Hz, 1H), 3.48 (tt, *J* = 11.3, 3.4 Hz, 1H), 2.68 (s, 3H), 1.82–1.64 (m, 4H), 1.64–1.52 (m, 1H), 1.44–1.19 (m, 4H), 1.12–0.95 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.27 (s, C_{quat}), 129.19 (s, CH), 116.32 (s, CH), 113.24 (s, CH), 58.22 (s, CH_3), 31.25 (s, CH), 30.15 (s, CH_2), 26.33 (s, CH_2), 26.06 (s, CH_2).

4. Preparation of *ortho*-Aminomethylation products from phenols

A series of variously substituted phenols (**1**) reacted with *N,N*-dimethylaniline (**2a**), providing the desired products (**3**) in moderate to good yields with 80 or 90 °C of reaction temperature (Table 2). With electron donating groups (i.e. methyl, methoxy) on the *para*-position of phenol, almost no coupling product could be obtained. However, groups with a large steric hindrance on the *para*-position are well tolerated (Table 2, **3a**, **3c**, **3d**). Interestingly, moderate to strong electron-withdrawing groups are also well tolerated on the *para*-position, such as fluorine and esters (Table 2, **3e-3g**). In contrast, *ortho*-substituted phenols generally perform poorly or not at all, with the noticeable exception of 2-methoxy- phenol which yielded an encouraging 52% yield of the expected product (Table 2, **3h**). Interestingly, when methoxy groups were installed on both *ortho* and *meta*-positions of the phenol, the reaction proceeded to the expected product in 81% yield (Table 2, **3i**). *Meta*-substitution is generally well tolerated (Table 2, **3j-3m**). For example, 3-phenyl-phenol is particularly efficient (80%, Table 2, **3l**). It should be noted that several poly-substituted phenols were also found very competent in the reaction (Table 2, **3n-3s**). The scope of methylamine derivatives (**2**) was thereafter investigated. *Para*-substituted *N,N*-dimethylanilines reacted smoothly and afforded the desired products in good yield (Table 3, **4a** and **4b**). An *ortho*-substituted *N,N*-dimethylanilines was also found effective, albeit in lower

yield (Table 3, **4d**). *Meta*-substituted *N,N*-dimethylanilines were found to be suitable substrates (64 and 73% yield, Table 3, **4c** and **4e**). Interestingly, *N*-methyldiphenylamine also converted to the expected coupling product, although only in moderate yield (Table 3, **4f**). Finally, unsymmetrically *N,N*-disubstituted anilines afforded high regioselectivity in favor of the least hindered alkyl chain (Table 3, **4g** and **4h**). Informatively, substrates **2i-2l** were found completely incompetent (Table 3, **2i**-**2l**).



Predicted: Chemical Formula: $C_{18}H_{23}NO$
Exact Mass: 269.1780
Molecular Weight: 269.3880
m/z: 269.1780 (100.0%), 270.1813 (19.5%), 271.1847 (1.8%)
Elemental Analysis: C, 80.26; H, 8.61; N, 5.20; O, 5.94

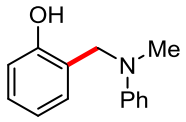
3a: Following the general procedure, the product was converted from 4-(*tert*-butyl)phenol and *N*,*N*-dimethylaniline at 80℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (25:1) and a second time with pentane/toluene (1:1). Isolated yield: 62% (yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (broad s, OH), 7.25 (d, *J* = 8.0 Hz, 2H), 7.18–7.12 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.00–6.92 (m, 2H), 6.73 (d, *J* = 8.4 Hz, 1H), 4.28 (s, 2H), 2.72 (s, 3H), 1.21 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.83 (s, C_{quat}), 151.11 (s, C_{quat}), 142.59 (s, C_{quat}), 129.39 (s, CH), 125.81 (s, CH), 125.59 (s, CH), 122.46 (s, CH), 121.28 (s, C_{quat}), 119.02 (s, CH), 115.88 (s, CH), 59.98 (s, CH_2), 40.21 (s, CH_3), 34.16 (s, C_{quat}), 31.73 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3215 (broad), 3028, 2960, 2902, 2867, 1658, 1599, 1496, 1460, 1363, 1245, 1233, 1122, 1103, 1091, 1030, 987, 972, 946, 904, 883, 821, 747, 730, 691, 674, 665, 653.

EI-HRMS: mass spectrometry: m/z calc. 269.1780 $[C_{18}H_{23}NO]^{\bullet+}$, measured 269.1773.



Chemical Formula: $C_{14}H_{15}NO$
Exact Mass: 213.1154
Molecular Weight: 213.2800
m/z: 213.1154 (100.0%), 214.1187 (15.1%), 215.1221 (1.1%)
Elemental Analysis: C, 78.84; H, 7.09; N, 6.57; O, 7.50

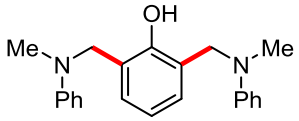
3b: Following the general procedure, the product was converted from phenol and *N*,*N*-dimethylaniline at 80℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (20:1) and a second time with DCM. Isolated yield: 47% (yellow solid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.77–8.23 (broad s, OH), 7.38 (t, *J* = 8.4Hz, 2H), 7.30–7.23 (m, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.15–7.06 (m, 2H), 6.97–6.87 (m, 2H), 4.41 (s, 2H), 2.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.22 (s, C_{quat}), 150.88 (s, C_{quat}), 129.38 (s, CH), 129.02 (s, CH), 128.75 (s, CH), 122.52 (s, CH), 122.15 (s, C_{quat}), 119.85 (s, CH), 119.01 (s, CH), 116.40 (s, CH), 59.44 (s, CH_2), 40.39 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3362 (broad), 3039, 2927, 2856, 2732, 1654, 1591, 1508, 1490, 1456, 1359, 1281, 1245, 1212, 1184, 1155, 1089, 1035, 983, 920, 901, 857, 838, 819, 809, 750, 710, 693, 657.

EI-HRMS: mass spectrometry: m/z calc. 213.1154 $[C_{14}H_{15}NO]^{\bullet+}$, measured 213.1143.



Chemical Formula: $C_{22}H_{24}N_2O$
Exact Mass: 332.1889
Molecular Weight: 332.4470
m/z: 332.1889 (100.0%), 333.1922 (23.8%), 334.1956 (2.7%)
Elemental Analysis: C, 79.48; H, 7.28; N, 8.43; O, 4.81

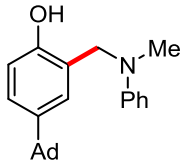
3b': Following the general procedure, the product was converted from phenol and *N*,*N*-dimethylaniline at 90℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (40:1) and a second time with pentane/EA (80/1). Isolated yield: 41% (yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (broad s, OH), 7.23–7.14 (m, 4H), 6.89 (t, *J* = 8.1 Hz, 6H), 6.78 (t, *J* = 7.3 Hz, 2H), 6.66 (t, *J* = 7.5 Hz, 1H), 4.37 (s, 4H), 2.84 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.21 (s, C_{quat}), 150.39 (s, C_{quat}), 129.31 (s, CH), 127.19 (s, CH), 123.52 (s, C_{quat}), 119.59 (s, CH), 119.44 (s, CH), 115.85 (s, CH), 55.80 (s, CH_2), 39.67 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3647, 3030, 2880, 1653, 1594, 1505, 1450, 1372, 1345, 1307, 1277, 1248, 1230, 1210, 1158, 1118, 1091, 1075, 1031, 1008, 986, 927, 860, 835, 816, 745, 689, 672.

EI-HRMS: mass spectrometry: m/z calc. 332.1889 $[C_{22}H_{24}N_2O]^{\bullet+}$, measured 332.1887.

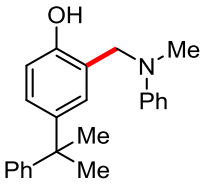


Chemical Formula: $C_{24}H_{29}NO$
Exact Mass: 347.2249
Molecular Weight: 347.5020
m/z: 347.2249 (100.0%), 348.2283 (26.0%), 349.2316 (2.7%)
Elemental Analysis: C, 82.95; H, 8.41; N, 4.03; O, 4.60

3c: Following the general procedure, the product was converted from 4-((3s)-adamantan-1-yl)phenol and *N*,*N*-dimethylaniline at 80℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (25:1). Isolated yield: 58% (white solid).

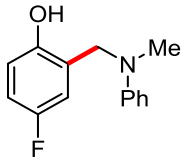
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (broad s, OH), 7.30–7.22 (m, 2H), 7.15–7.06 (m, 3H), 6.99–6.93 (m, 2H), 6.75 (d, *J* = 8.5 Hz, 1H), 4.28 (s, 2H), 2.72 (s, 3H), 2.07–1.94 (m, 3H), 1.81 (d, J = 2.7 Hz, 6H), 1.75–1.60 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.89 (s, C_{quat}), 151.08 (s, C_{quat}), 143.05 (s, C_{quat}), 129.39 (s, CH), 125.37 (s, CH), 125.20 (s, CH), 122.49 (s, CH), 121.29 (s, C_{quat}), 119.04 (s, CH), 115.94 (s, CH), 60.07 (s, CH_2), 43.57 (s, CH_2), 40.20 (s, CH), 36.94 (s, CH_2), 35.64 (s, C_{quat}), 29.13 (s, CH_3).
IR (neat, cm^{-1}): ṽ: 3242(broad), 3056, 3207, 2897, 2845, 2680, 1658, 1620, 1596, 1502, 1448, 1367, 1358, 1344, 1311, 1279, 1260, 1233, 1219, 1184, 1165, 1153, 1123, 1095, 1077, 1044, 1027, 995, 976, 934, 905, 884, 828, 809, 778, 762, 731, 711, 696, 681, 661.
EI-HRMS: mass spectrometry: m/z calc. 347.2249 $[C_{24}H_{29}NO]^{\bullet+}$, measured 347.2260.



Chemical Formula: $C_{23}H_{25}NO$
Exact Mass: 331.1936
Molecular Weight: 331.4590
m/z: 331.1936 (100.0%), 332.1970 (24.9%), 333.2003 (2.7%)
Elemental Analysis: C, 83.34; H, 7.60; N, 4.23; O, 4.83

3d: Following the general procedure, the product was converted from 4-(2-phenylpropan-2-yl)phenol and *N*,*N*-dimethylaniline at 80℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (20:1). Isolated yield: 56% (yellow oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (broad s, OH), 7.27–7.12 (m, 6H), 7.12–7.03 (m, 3H), 7.02–6.91 (m, 2H), 6.82 (d, *J* = 2.3 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 4.22 (s, 2H), 2.71 (s, 3H), 1.58 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) 155.03 (s, C_{quat}), 151.15 (s, C_{quat}), 150.90 (s, C_{quat}), 142.08 (s, C_{quat}), 129.37 (s, CH), 128.07 (s, CH), 127.38 (s, CH), 127.31 (s, CH), 126.86 (s, CH), 125.65 (s, CH), 122.60 (s, CH), 121.32 (s, C_{quat}), 119.16 (s, CH), 115.89 (s, CH), 59.81 (s, CH_2), 42.41 (s, C_{quat}), 40.47 (s, CH_3), 31.09 (s, CH_3).
IR (neat, cm^{-1}): ṽ: δ 3318 (broad), 3060, 3026, 2964, 2926, 2876, 1655, 1599, 1493, 1444, 1383, 1363, 1282, 1230, 1178, 1120, 1107, 1091, 1074, 1029, 972, 945, 885, 864, 823, 756, 697, 756.
EI-HRMS: mass spectrometry: m/z calc. 331.1936 $[C_{23}H_{25}NO]^{\bullet+}$, measured 331.1950.



Chemical Formula: $C_{14}H_{14}FNO$
Exact Mass: 231.1059
Molecular Weight: 231.2704
m/z: 231.1059 (100.0%), 232.1093 (15.1%), 233.1127 (1.1%)
Elemental Analysis: C, 72.71; H, 6.10; F, 8.21; N, 6.06; O, 6.92

3e: Following the general procedure, the product was converted from 4-fluorophenol and *N*,*N*-dimethylaniline at 90℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (15:1). Isolated yield: 45% (dark blue oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (broad s, OH), 7.30–7.22 (m, 2H), 7.09–7.02 (m, 2H), 7.00–6.94

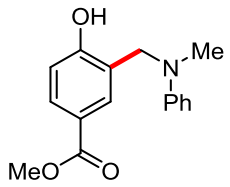
(m, 1H), 6.81 (td, *J* = 8.5, 3.0 Hz, 1H), 6.75–6.68 (m, 2H), 4.24 (s, 2H), 2.73 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.49 (d, *J* = 237.1 Hz, C_{quat}), 153.15 (d, *J* = 1.7 Hz, C_{quat}), 150.65 (s, C_{quat}), 129.47 (s, CH), 123.19 (d, *J* = 7.0 Hz, C_{quat}), 122.79 (s, CH), 119.07 (s, CH), 117.18 (d, *J* = 8.0 Hz, CH), 115.29 (d, *J* = 9.1 Hz, CH), 115.06 (d, *J* = 9.9 Hz, CH), 59.25 (s, CH_2), 40.64 (s, CH_3).

^{19}F NMR (376.5 MHz, $CDCl_3$) δ -124.93 (s, Ar-F)

IR (neat, cm^{-1}): ṽ: 3330 (broad), 3064, 3038, 2960, 2924, 2868, 1599, 1490, 1440, 1350, 1244, 1173, 1137, 1091, 1031, 997, 986, 954, 939, 916, 865, 810, 766, 746, 739, 713, 692, 668.

EI-HRMS: mass spectrometry: m/z calc. 231.1059 $[C_{14}H_{14}FNO]^{\bullet+}$, measured 231.1053.



Chemical Formula: $C_{16}H_{17}NO_3$
Exact Mass: 271.1208
Molecular Weight: 271.3160
m/z: 271.1208 (100.0%), 272.1242 (17.3%), 273.1276 (1.4%)
Elemental Analysis: C, 70.83; H, 6.32; N, 5.16; O, 17.69

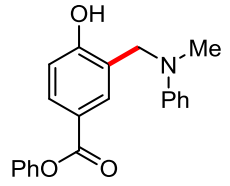
3f: Following the general procedure, the product was converted from methyl 4-hydroxybenzoate and *N*,*N*-dimethylaniline at 80℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with DCM. Isolated yield: 70% (green solid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (broad s, OH), 7.83 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.73 (d, *J* = 2.0 Hz, 1H), 7.31–7.23 (m, 2H), 7.10 (dd, *J* = 8.7, 1.0 Hz, 2H), 7.03–6.97 (m, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 4.31 (s, 2H), 3.81 (s, 3H), 2.73 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.06 (s, C_{quat}), 161.99 (s, C_{quat}), 150.47 (s, C_{quat}), 131.19 (s, CH), 130.74 (s, CH), 129.53 (s, CH), 123.45 (s, CH), 121.74 (s, C_{quat}), 119.70 (s, CH), 116.49 (s, CH), 59.74 (s, CH_2), 52.01 (s, CH_3), 41.05 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3242 (broad), 3027, 2952, 2893, 2872, 1676, 1598, 1506, 1443, 1429, 1359, 1308, 1283, 1256, 1212, 1191, 1115, 1033, 999, 988, 975, 948, 915, 903, 832, 770, 716, 747, 690, 683.

EI-HRMS: mass spectrometry: m/z calc. 271.1208 $[C_{16}H_{17}NO_3]^{\bullet+}$, measured 271.1219.



Chemical Formula: $C_{21}H_{19}NO_3$
Exact Mass: 333.1365
Molecular Weight: 333.3870
m/z: 333.1365 (100.0%), 334.1398 (22.7%), 335.1432 (2.5%)
Elemental Analysis: C, 75.66; H, 5.74; N, 4.20; O, 14.40

3g: Following the general procedure, the product was converted from phenyl 4-hydroxybenzoate and *N*,*N*-dimethylaniline at 90℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (15:1) and a second time with DCM. Isolated yield: 61% (yellow

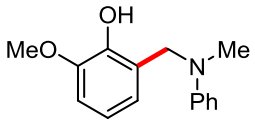
solid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (broad s, OH) 8.01 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.88 (d, *J* = 2.1 Hz, 1H), 7.40–7.25 (m, 4H), 7.21–7.16 (m, 1H), 7.15–7.09 (m, 4H), 7.07–6.99 (m, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 4.35 (s, 2H), 2.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.10 (s, C_{quat}), 162.68 (s, C_{quat}), 151.17 (s, C_{quat}), 150.32 (s, C_{quat}), 131.91 (s, CH), 131.39 (s, CH), 129.57 (s, CH), 125.86 (s, CH), 123.66 (s, CH), 121.93 (s, CH), 121.90 (s, C_{quat}), 120.96 (s, CH), 119.83 (s, CH), 116.73 (s, CH), 59.77 (s, CH_2), 41.23 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3392(broad), 2923, 2877, 2819, 1727, 1703, 1602, 1504, 1457, 1441, 1423, 1363, 1345, 1291, 1280, 1250, 1188, 1127, 1111, 1068, 1051, 1029, 952, 933, 828, 811, 799, 761, 746, 689, 672, 662.

EI-HRMS: mass spectrometry: m/z calc. 333.1365 $[C_{21}H_{19}NO_3]^{\bullet+}$, measured 333.1359.



Chemical Formula: $C_{15}H_{17}NO_2$
Exact Mass: 243.1259
Molecular Weight: 243.3060
m/z: 243.1259 (100.0%), 244.1293 (16.2%), 245.1326 (1.2%)
Elemental Analysis: C, 74.05; H, 7.04; N, 5.76; O, 13.15

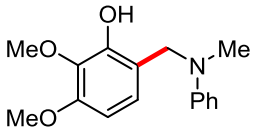
3h: Following the general procedure, the product was converted from 2-methoxyphenol and *N*,*N*-dimethylaniline at 90℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (20:1). Isolated yield: 52% (dark brown oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.12 (m, 2H), 7.00 (broad s, OH), 6.80 (d, *J* = 7.9 Hz, 2H), 6.76–6.65 (m, 3H), 6.65–6.59 (m, 1H), 4.41 (s, 2H), 3.80 (s, 3H), 2.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.12 (s, C_{quat}), 146.91 (s, C_{quat}), 144.32 (s, C_{quat}), 129.27 (s, CH), 123.87 (s, C_{quat}), 120.25 (s, CH), 119.49 (s, CH), 118.43 (s, CH), 114.55 (s, CH), 109.88 (s, CH), 56.11 (s, CH_3), 53.96 (s, CH_2), 39.36 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3513 (broad), 3061, 3037, 2937, 2903, 2840, 1598, 1506, 1478, 1440, 1353, 1259, 1207, 1160, 1117, 1068, 1032, 1001, 986, 940, 882, 827, 746, 729, 717, 689, 669.

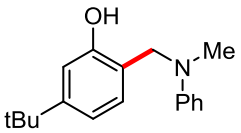
EI-HRMS: mass spectrometry: m/z calc. 243.1259 $[C_{15}H_{17}NO_2]^{\bullet+}$, measured 243.1273.



Chemical Formula: $C_{16}H_{19}NO_3$
Exact Mass: 273.1365
Molecular Weight: 273.3320
m/z: 273.1365 (100.0%), 274.1398 (17.3%), 275.1432 (1.4%)
Elemental Analysis: C, 70.31; H, 7.01; N, 5.12; O, 17.56

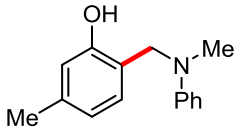
3i: Following the general procedure, the product was converted from 2,3-dimethoxyphenol and *N*,*N*-dimethylaniline at 90℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (15:1) and a second time with DCM. Isolated yield: 81% (yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.15 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 1H), 6.31 (d, *J* = 8.6 Hz, 1H), 4.35 (s, 2H), 3.84 (s, 3H), 3.76 (s, 3H), 2.87 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.02 (s, C_{quat}), 150.18 (s, C_{quat}), 148.54 (s, C_{quat}), 136.01 (s, C_{quat}), 129.28 (s, CH), 122.64 (s, CH), 118.72 (s, CH), 116.94 (s, C_{quat}), 114.90 (s, CH), 103.31 (s, CH), 61.01 (s, CH_3), 55.95 (s, CH_3), 54.15 (s, CH_2), 39.29 (s, CH_3).
IR (neat, cm^{-1}): ṽ: 3480 (broad), 3413, 3384, 2933, 2836, 1598, 1504, 1459, 1428, 1373, 1341, 1287, 1238, 1207, 1160, 1090, 1030, 999, 965, 944, 916, 881, 791, 746, 690, 667.
EI-HRMS: mass spectrometry: m/z calc. 273.1365 $[C_{16}H_{19}NO_3]^{\bullet+}$, measured 273.1366.



Chemical Formula: $C_{18}H_{23}NO$
Exact Mass: 269.1780
Molecular Weight: 269.3880
m/z: 269.1780 (100.0%), 270.1813 (19.5%), 271.1847 (1.8%)
Elemental Analysis: C, 80.26; H, 8.61; N, 5.20; O, 5.94

3j: Following the general procedure, the product was converted from 3-(*tert*-butyl)phenol and *N*,*N*-dimethylaniline at 90℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (30:1). Isolated yield: 66% (yellow oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (broad s, OH) 7.30–7.23 (m, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.84 (d, *J* = 1.8 Hz, 1H), 6.80 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.26 (s, 2H), 2.73 (s, 3H), 1.23 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.81 (s, C_{quat}), 152.67 (s, C_{quat}), 151.08 (s, C_{quat}), 129.39 (s, CH), 128.33 (s, CH), 122.41 (s, CH), 119.06 (s, C_{quat}), 118.98 (s, CH), 116.84 (s, CH), 113.71 (s, CH), 59.27 (s, CH_2), 40.23 (s, CH_3), 34.68 (s, C_{quat}), 31.45 (s, CH_3).
IR (neat, cm^{-1}): ṽ: 3343 (broad), 3055, 3028, 2962, 2903, 2865, 1656, 1574, 1505, 1478, 1450, 1412, 1362, 1283, 1216, 1199, 1119, 1090, 1030, 985, 942, 872, 827, 810, 795, 748, 717, 689.
EI-HRMS: mass spectrometry: m/z calc. 269.1780 $[C_{18}H_{23}NO]^{\bullet+}$, measured 269.1798.



Chemical Formula: $C_{15}H_{17}NO$
Exact Mass: 227.1310
Molecular Weight: 227.3070
m/z: 227.1310 (100.0%), 228.1344 (16.2%), 229.1377 (1.2%)
Elemental Analysis: C, 79.26; H, 7.54; N, 6.16; O, 7.04

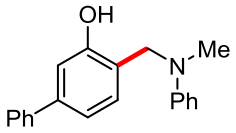
3k: Following the general procedure, the product was converted from m-cresol and *N*,*N*-dimethylaniline at 80℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (20:1) and a second time with DCM. Isolated yield: 51% (yellow oil).
^{1}H NMR (400 MHz, $CDCl_3$) 9.11 (broad s, OH) δ 7.42–7.32 (m, 2H), 7.25–7.16 (m, 2H), 7.12–7.04 (m, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.76 (s, 1H), 6.73–6.66 (m, 1H), 4.37 (s, 2H), 2.84 (s, 3H), 2.34 (s,

3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.02 (s, C_{quat}), 150.62 (s, C_{quat}), 139.28 (s, C_{quat}), 129.40 (s, CH), 128.76 (s, CH), 122.75 (s, CH), 120.66 (s, CH), 119.17 (s, CH), 118.91 (s, C_{quat}), 117.19 (s, CH), 59.23 (s, CH_2), 40.38 (s, CH_3), 21.33 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3034, 2916, 2865, 2137, 1598, 1505, 1495, 1449, 1417, 1373, 1352, 1318, 1283, 1263, 1212, 1190, 1152, 1115, 1091, 1032, 981, 947, 916, 863, 803, 748, 692, 668, 612, 602, 588.

EI-HRMS: mass spectrometry: m/z calc. 227.1310 $[C_{15}H_{17}NO]^{\bullet+}$, measured 227.1311.



Chemical Formula: $C_{20}H_{19}NO$
Exact Mass: 289.1467
Molecular Weight: 289.3780
m/z: 289.1467 (100.0%), 290.1500 (21.6%), 291.1534 (2.2%)
Elemental Analysis: C, 83.01; H, 6.62; N, 4.84; O, 5.53

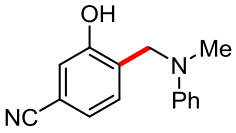
3l: Following the general procedure, the product was converted from [1,1'-biphenyl]-3-ol and *N*,*N*-dimethylaniline at 80℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (20:1). Isolated yield: 80% (yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (broad s, OH), 7.53–7.45 (m, 2H), 7.36–7.28 (m, 2H), 7.27–7.20 (m, 3H), 7.10–6.91 (m, 6H), 4.29 (s, 2H), 2.73 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.48 (s, C_{quat}), 150.84 (s, C_{quat}), 142.17 (s, C_{quat}), 140.78 (s, C_{quat}), 129.41 (s, CH), 129.12 (s, CH), 128.83 (s, CH), 127.45 (s, CH), 127.09 (s, CH), 122.61 (s, CH), 121.18 (s, C_{quat}), 119.06 (s, CH), 118.62 (s, CH), 115.07 (s, CH), 59.25 (s, CH_2), 40.49 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3295 (broad), 3059, 3029, 2918, 2850, 1598, 1565, 1505, 1494, 1485, 1455, 1409, 1352, 1304, 1271, 1246, 1202, 1157, 1119, 1091, 1076, 1026, 998, 900, 866, 818, 755, 690.

EI-HRMS: mass spectrometry: m/z calc. 289.1467 $[C_{20}H_{19}NO]^{\bullet+}$, measured 289.1450.



Chemical Formula: $C_{15}H_{14}N_2O$
Exact Mass: 238.1106
Molecular Weight: 238.2900
m/z: 238.1106 (100.0%), 239.1140 (16.2%), 240.1173 (1.2%)
Elemental Analysis: C, 75.61; H, 5.92; N, 11.76; O, 6.71

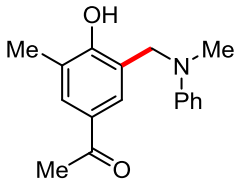
3m: Following the general procedure, the product was converted from 3-hydroxybenzonitrile and *N*,*N*-dimethylaniline at 90℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (6:1) and a second time with DCM. Isolated yield: 44% (brown solid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (broad s, OH), 7.33–7.26 (m, 2H), 7.23–7.10 (m, 4H), 7.09–7.00 (m, 2H), 4.54 (s, CH_2), 2.79 (s, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.42 (s, C_{quat}), 150.03 (s, C_{quat}), 129.67 (s, CH), 129.58 (s, CH), 124.47 (s, CH), 124.27 (s, CH), 121.66 (s, CH), 120.27 (s, CH), 118.66 (s, C_{quat}), 117.59 (s, C_{quat}), 111.99 (s, C_{quat}), 57.85 (s, CH_2), 42.07 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3258 (broad), 3077, 2922, 2898, 2875, 2852, 2692, 2235, 1736, 1671, 1649, 1608, 1583, 1505, 1475, 1458, 1446, 1376, 1350, 1340, 1288, 1271, 1249, 1215, 1194, 1177, 1165, 1155, 1119, 1100, 1071, 1035, 993, 914, 893, 853, 823, 788, 757, 742, 715, 684, 663.

EI-HRMS: mass spectrometry: m/z calc. 238.1106 $[C_{15}H_{14}N_2O]^{\bullet+}$, measured 238.1105.



Chemical Formula: $C_{17}H_{19}NO_2$
Exact Mass: 269.1416
Molecular Weight: 269.3440
m/z: 269.1416 (100.0%), 270.1449 (18.4%), 271.1483 (1.6%)
Elemental Analysis: C, 75.81; H, 7.11; N, 5.20; O, 11.88

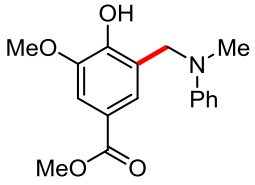
3n: Following the general procedure, the product was converted from 1-(4-hydroxy-3-methylphenyl)ethan-1-one and *N*,*N*-dimethylaniline at 80℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (5:1) and a second time with DCM. Isolated yield: 71% (yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.66 (broad s, OH), 7.65 (s, 1H), 7.52 (s, 1H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.03 (t, *J* = 7.1 Hz, 1H), 4.31 (s, 2H), 2.74 (s, 3H), 2.47 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.19 (s, C_{quat}), 160.58 (s, C_{quat}), 150.54 (s, C_{quat}), 131.32 (s, CH), 129.49 (s, CH), 129.00 (s, C_{quat}), 127.20 (s, CH), 125.34 (s, C_{quat}), 123.49 (s, CH), 121.02 (s, C_{quat}), 119.77 (s, CH), 59.98 (s, CH_2), 40.99 (s, CH_3), 26.38 (s, CH_3), 15.81 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3308 (broad), 3036, 2996, 2916, 2855, 1739, 1669, 1594, 1496, 1481, 1451, 1420, 1355, 1308, 1255, 1192, 1123, 1091, 1032, 977, 953, 927, 881, 823, 758, 748, 693, 672, 654.

EI-HRMS: mass spectrometry: m/z calc. 269.1416 $[C_{17}H_{19}NO_2]^{\bullet+}$, measured 269.1435.



Chemical Formula: $C_{17}H_{19}NO_4$
Exact Mass: 301.1314
Molecular Weight: 301.3420
m/z: 301.1314 (100.0%), 302.1348 (18.4%), 303.1381 (1.6%)
Elemental Analysis: C, 67.76; H, 6.36; N, 4.65; O, 21.24

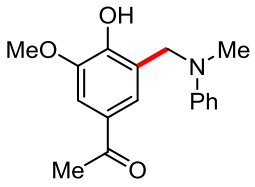
3o: Following the general procedure, the product was converted from methyl 4-hydroxy-3-methoxybenzoate and *N*,*N*-dimethylaniline at 80℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (6:1). Isolated yield: 82% (yellow solid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (broad s, OH), 7.46–7.38 (m, 2H), 7.25–7.11 (m, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 6.79 (t, *J* = 7.2 Hz, 1H), 4.38 (s, 2H), 3.85 (s, 3H), 3.77 (s, 3H), 2.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.09 (s, C_{quat}), 150.13 (s, C_{quat}), 149.30 (s, C_{quat}), 146.84 (s, C_{quat}), 129.34 (s, CH), 123.32 (s, C_{quat}), 122.81 (s CH), 121.54 (s, C_{quat}), 119.78 (s, CH), 115.81 (s, CH), 111.21 (s, CH), 56.27 (s, CH_3), 55.25 (s, CH_2), 52.07 (s, CH_3), 39.89 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3364 (broad), 3353, 3009, 2960, 2938, 2920, 2842, 1692, 1599, 1508, 1495, 1464, 1431, 1376, 1364, 1307, 1249, 1213, 1183, 1104, 1068, 1031, 997, 949, 917, 898, 874, 865, 813, 765, 748, 692.

EI-HRMS: mass spectrometry: m/z calc. 301.1314 $[C_{17}H_{19}NO_4]^{\bullet+}$, measured 301.1320.



Chemical Formula: $C_{17}H_{19}NO_3$
Exact Mass: 285.1365
Molecular Weight: 285.3430
m/z: 285.1365 (100.0%), 286.1398 (18.4%), 287.1432 (1.6%)
Elemental Analysis: C, 71.56; H, 6.71; N, 4.91; O, 16.82

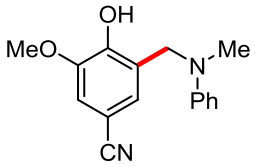
3p: Following the general procedure, the product was converted from 1-(4-hydroxy-3-methoxyphenyl)ethan-1-one and *N*,*N*-dimethylaniline at 80℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (8:1). Isolated yield: 73% (yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (broad s, OH), 7.38 (d, *J* = 1.8 Hz, 1H), 7.32 (s, 1H), 7.23–7.15 (m, 2H), 6.87 (d, *J* = 8.1 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 4.44 (s, 2H), 3.86 (s, 3H), 2.89 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.05 (s, C_{quat}), 149.89 (s, C_{quat}), 149.51 (s, C_{quat}), 147.13 (s, C_{quat}), 129.42 (s, C_{quat}), 129.37 (s, CH), 122.90 (s, C_{quat}), 122.66 (s, CH), 119.77 (s, CH), 115.64 (s, CH), 109.23 (s, CH), 56.27 (s, CH_3), 54.82 (s, CH_2), 39.89 (s, CH_3), 26.28 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3328 (broad), 3057, 3001, 2936, 1663, 1590, 1505, 1491, 1458, 1422, 1354, 1297, 1206, 1179, 1116, 1086, 1070, 1032, 1000, 978, 945, 912, 890, 870, 796, 746, 732, 691.

EI-HRMS: mass spectrometry: m/z calc. 285.1365 $[C_{17}H_{19}NO_3]^{\bullet+}$, measured 285.1363.



Chemical Formula: $C_{16}H_{16}N_2O_2$
Exact Mass: 268.1212
Molecular Weight: 268.3160
m/z: 268.1212 (100.0%), 269.1245 (17.3%), 270.1279 (1.4%)
Elemental Analysis: C, 71.62; H, 6.01; N, 10.44; O, 11.93

3q: Following the general procedure, the product was converted from 4-hydroxy-3-methoxybenzonitrile and *N*,*N*-dimethylaniline at 90℃ for 24 hours. The crude

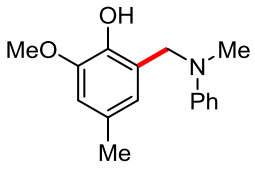
mixture is purified by SiO_2 gel column chromatography with hexane/EA (6:1). Isolated yield: 63% (yellow solid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (broad s, OH), 7.34–7.24 (m, 2H), 7.15–7.07 (m, 1H), 7.05 (d, J = 1.8 Hz, 1H), 6.94–6.81 (m, 3H), 4.49 (s, 2H), 3.94 (s, 3H), 3.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.45 (s, C_{quat}), 148.77 (s, C_{quat}), 147.04 (s, C_{quat}), 129.42 (s, CH), 125.22 (s, CH), 125.03 (s, C_{quat}), 119.55 (s, C_{quat}), 119.41 (s, CH), 114.90 (s, CH), 113.05 (s, CH), 102.69 (s, C_{quat}), 56.41 (s, CH_3), 53.98 (s, CH_2), 39.87 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3337 (broad), 2955, 2920, 2841, 2225, 1661, 1598, 1572, 1507, 1493, 1463, 1435, 1371, 1352, 1299, 1254, 1192, 1140, 1122, 1072, 1031, 1003, 985, 969, 945, 913, 868, 857, 796, 747, 726, 690.

EI-HRMS: mass spectrometry: m/z calc. 268.1212 $[C_{16}H_{16}N_2O_2]^{\bullet+}$, measured 268.1217.



Chemical Formula: $C_{16}H_{19}NO_2$
Exact Mass: 257.1416
Molecular Weight: 257.3330
m/z: 257.1416 (100.0%), 258.1449 (17.3%), 259.1483 (1.4%)
Elemental Analysis: C, 74.68; H, 7.44; N, 5.44; O, 12.43

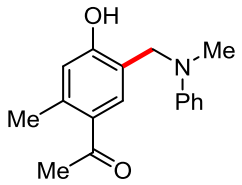
3r: Following the general procedure, the product was converted from 2-methoxy-4-methylphenol and *N*,*N*-dimethylaniline at 80℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (20:1) and a second time with DCM. Isolated yield: 41% (grass green oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.15 (m, 2H), 6.84 (d, *J* = 7.8 Hz, 2H), 6.75 (t, *J* = 7.1 Hz, 1H), 6.58–6.52 (m, 1H), 6.46 (s, 1H), 4.37 (s, 2H), 3.80 (s, 3H), 2.88 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.34 (s, C_{quat}), 146.74 (s, C_{quat}), 142.09 (s, C_{quat}), 129.30 (s, CH), 128.99 (s, C_{quat}), 123.45 (s, C_{quat}), 120.44 (s, CH), 118.60 (s, CH), 114.85 (s, CH), 110.96 (s, CH), 56.11 (s, CH_3), 54.39 (s, CH_2), 39.39 (s, CH_3), 21.36 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3518 (broad), 3441, 3421, 3030, 2918, 2858, 1598, 1574, 1493, 1463, 1448, 1352, 1295, 1252, 1229, 1208, 1186, 1146, 1114, 1073, 1033, 1001, 986, 941, 900, 834, 801, 745, 690, 666.

EI-HRMS: mass spectrometry: m/z calc. 257.1416 $[C_{16}H_{19}NO_2]^{\bullet+}$, measured 257.1422.



Chemical Formula: $C_{17}H_{19}NO_2$
Exact Mass: 269.1416
Molecular Weight: 269.3440
m/z: 269.1416 (100.0%), 270.1449 (18.4%), 271.1483 (1.6%)
Elemental Analysis: C, 75.81; H, 7.11; N, 5.20; O, 11.88

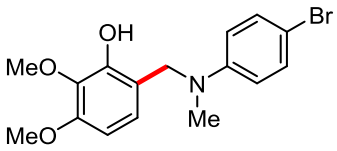
3s: Following the general procedure, the product was converted from 1-(4-hydroxy-2-methylphenyl)ethan-1-one and *N*,*N*-dimethylaniline at 90℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (6:1). Isolated yield: 72% (yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.31–7.24 (m, 2H), 7.14–7.07 (m, 2H), 7.04–6.97 (m, 1H), 6.65 (s, 1H), 4.30 (s, 2H), 2.74 (s, 3H), 2.50–2.43 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.48 (s, C_{quat}), 160.40 (s, C_{quat}), 150.57 (s, C_{quat}), 141.90 (s, C_{quat}), 131.62 (s, CH), 129.52 (s, CH), 129.32 (s, C_{quat}), 123.25 (s, CH), 120.07 (s, CH), 119.48 (s, CH), 118.84 (s, C_{quat}), 59.43 (s, CH_2), 40.86 (s, CH_3), 29.29 (s, CH_3), 22.36 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3137 (broad), 2962, 2925, 2855, 1648, 1598, 1570, 1504, 1449, 1411, 1352, 1302, 1247, 1191, 1156, 1128, 1093, 1032, 997, 943, 925, 890, 863, 812, 747, 691, 668, 661.

EI-HRMS: mass spectrometry: m/z calc. 269.1416 $[C_{17}H_{19}NO_2]^{\bullet+}$, measured 269.1403.



Chemical Formula: $C_{16}H_{18}BrNO_3$
Exact Mass: 351.0470
Molecular Weight: 352.2280
m/z: 351.0470 (100.0%), 353.0450 (97.3%), 352.0504 (17.3%), 354.0483 (16.8%), 355.0517 (1.2%), 353.0537 (1.1%)
Elemental Analysis: C, 54.56; H, 5.15; Br, 22.69; N, 3.98; O, 13.63

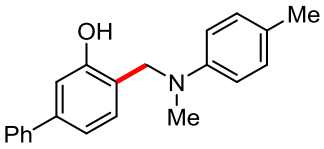
4a: Following the general procedure, the product was converted from 2,3-dimethoxyphenol and 4-bromo-*N,N*-dimethylaniline at 90℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (20:1). Isolated yield: 62% (yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.17 (m, 2H), 6.66–6.56 (m, 3H), 6.46 (s, OH), 6.31 (d, *J* = 8.6 Hz, 1H), 4.35 (s, 2H), 3.84 (s, 3H), 3.76 (s, 3H), 2.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.76 (s, C_{quat}), 148.97 (s, C_{quat}), 147.80 (s, C_{quat}), 135.78 (s, C_{quat}), 131.91 (s, CH), 122.36 (s, CH), 116.70 (s, C_{quat}), 115.17 (s, CH), 109.43 (s, C_{quat}), 103.44 (s, CH), 61.07 (s, CH_3), 55.94 (s, CH_3), 52.65 (s, CH_2), 39.07 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3487, 3435 (broad), 2997, 2935, 2834, 1663, 1642, 1615, 1588, 1497, 1460, 1428, 1374, 1315, 1287, 1266, 1244, 1207, 1162, 1091, 1033, 995, 966, 944, 917, 873, 805, 786, 767, 758, 742, 698, 672.

EI-HRMS: mass spectrometry: m/z calc. 351.0470 $[C_{16}H_{18}BrNO_3]^{\bullet+}$, measured 351.0467.



Chemical Formula: $C_{21}H_{21}NO$
Exact Mass: 303.1623
Molecular Weight: 303.4050
m/z: 303.1623 (100.0%), 304.1657 (22.7%), 305.1690 (2.5%)
Elemental Analysis: C, 83.13; H, 6.98; N, 4.62; O, 5.27

4b: Following the general procedure, the product was converted from [1,1'-biphenyl]-3-ol and

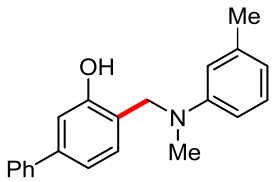
*N,N,*4-trimethylaniline at 80℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (25:1). Isolated yield: 77% (yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (broad s, OH), 7.55–7.47 (m, 2H), 7.37–7.31 (m, 2H), 7.24 (ddt, *J* = 6.1, 4.9, 2.5 Hz, 1H), 7.09–6.96 (m, 7H), 4.26 (s, 2H), 2.71 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.78 (s, C_{quat}), 148.59 (s, C_{quat}), 142.17 (s, C_{quat}), 140.87 (s, C_{quat}), 132.69 (s, C_{quat}), 129.98 (s, CH), 129.10 (s, CH), 128.83 (s, CH), 127.44 (s, CH), 127.12 (s, CH), 121.17 (s, C_{quat}), 119.68 (s, CH), 118.50 (s, CH), 115.09 (s, CH), 59.99 (s, CH_2), 41.13 (s, CH_3), 20.75 (s, CH_3).

IR (neat, cm^{-1}): ῡ: 3224, 3029, 3003, 2961, 2915, 2856, 1891, 1804, 1747, 1652, 1611, 1587, 1567, 1512, 1483, 1454, 1410, 1372, 1353, 1301, 1277, 1217, 1200, 1165, 1132, 1124, 1088, 1041, 1016, 983, 947, 925, 874, 827, 814, 780, 753, 733, 717, 708, 688, 655.

EI-HRMS: mass spectrometry: m/z calc. 303.1623 $[C_{21}H_{21}NO]^{\bullet+}$, measured 303.1626.



Chemical Formula: $C_{21}H_{21}NO$
Exact Mass: 303.1623
Molecular Weight: 303.4050
m/z: 303.1623 (100.0%), 304.1657 (22.7%), 305.1690 (2.5%)
Elemental Analysis: C, 83.13; H, 6.98; N, 4.62; O, 5.27

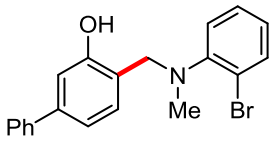
4c: Following the general procedure, the product was converted from [1,1'-biphenyl]-3-ol and *N,N,*3-trimethylaniline at 80℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (40:1). Isolated yield: 64% (yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (broad s, OH), 7.71–7.62 (m, 2H), 7.52–7.45 (m, 2H), 7.43–7.37 (m, 1H), 7.33–7.26 (m, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.18–7.12 (m, 2H), 7.11–7.04 (m, 2H), 6.96 (d, *J* = 7.5 Hz, 1H), 4.46 (s, 2H), 2.89 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.52 (s, C_{quat}), 150.33 (s, C_{quat}), 142.29 (s, C_{quat}), 140.76 (s, C_{quat}), 139.34 (s, C_{quat}), 129.37 (s, CH), 129.27 (s, CH), 128.82 (s, CH), 127.46 (s, CH), 127.09 (s, CH), 123.98 (s, CH), 120.86 (s, C_{quat}), 120.18 (s, CH), 118.61 (s, CH), 116.28 (s, CH), 115.19 (s, CH), 59.42 (s, CH_2), 40.53 (s, CH_3), 21.76 (s, CH_3).

IR (neat, cm^{-1}): ῡ: 3024, 2930, 2848, 1734, 1622, 1598, 1567, 1485, 1457, 1445, 1384, 1350, 1299, 1255, 1233, 1204, 1181, 1145, 1117, 1076, 1033, 998, 941, 904, 895, 879, 846, 815, 760, 745, 709, 689, 665, 652, 645 635, 621.

EI-HRMS: mass spectrometry: m/z calc. 303.1623 $[C_{21}H_{21}NO]^{\bullet+}$, measured 303.1622



Chemical Formula: $C_{20}H_{18}BrNO$
Exact Mass: 367.0572
Molecular Weight: 368.2740
m/z: 367.0572 (100.0%), 369.0551 (97.3%), 370.0585 (21.0%), 368.0605 (16.2%), 368.0605 (5.4%), 371.0618 (1.2%), 369.0639 (1.1%), 369.0639 (1.0%)
Elemental Analysis: C, 65.23; H, 4.93; Br, 21.70; N, 3.80; O, 4.34

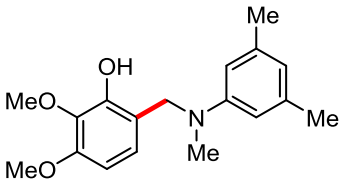
4d: Following the general procedure, the product was converted from [1,1'-biphenyl]-3-ol and 2-bromo-*N,N*-dimethylaniline at 90℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (25:1) and a second time with DCM. Isolated yield: 32% (white solid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (broad s, OH), 7.60–7.48 (m, 3H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.31–7.22 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.03–6.96 (m, 2H), 4.23 (s, 2H), 2.65 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.58 (s, C_{quat}), 149.96 (s, C_{quat}), 142.47 (s, C_{quat}), 140.84 (s, C_{quat}), 134.04 (s, CH), 129.63 (s, CH), 128.85 (s, CH), 128.73 (s, CH), 127.47 (s, CH), 127.13 (s, CH), 126.85 (s, CH), 122.50 (s, CH), 121.13 (s, C_{quat}), 120.15 (s, C_{quat}), 118.41 (s, CH), 115.23 (s, CH), 59.48 (s, CH_2), 42.87 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3058, 3029, 2957, 2855, 1737, 1624, 1586, 1562, 1513, 1483, 1475, 1450, 1437, 1305, 1270, 1202, 1161, 1121, 1089, 1043, 1027, 987, 929, 906, 871, 819, 755, 721, 693, 660.

EI-HRMS: mass spectrometry: m/z calc. 367.0572 $[C_{20}H_{18}BrNO]^{\bullet+}$, measured 367.0596.



Chemical Formula: $C_{18}H_{23}NO_3$
Exact Mass: 301.1678
Molecular Weight: 301.3860
m/z: 301.1678 (100.0%), 302.1711 (19.5%), 303.1745 (1.8%)
Elemental Analysis: C, 71.73; H, 7.69; N, 4.65; O, 15.93

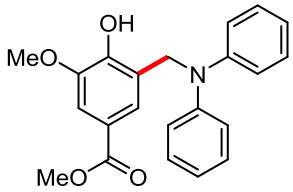
4e: Following the general procedure, the product was converted from 2,3-dimethoxyphenol and *N,N*,3,5-tetramethylaniline at 90℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (20:1). Isolated yield: 73% (yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (broad s, OH), 6.66 (d, *J* = 8.5 Hz, 1H), 6.50 (s, 2H), 6.44 (s, 1H), 6.30 (d, *J* = 8.5 Hz, 1H), 4.28 (s, 2H), 3.83 (s, 3H), 3.74 (s, 3H), 2.78 (s, 3H), 2.19 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.11 (s, C_{quat}), 150.51 (s, C_{quat}), 148.93 (s, C_{quat}), 138.81 (s, C_{quat}), 136.09 (s, C_{quat}), 122.64 (s, CH), 121.34 (s, CH), 117.00 (s, C_{quat}), 113.52 (s, CH), 103.18 (s, CH), 60.91 (s, CH_3), 55.89 (s, CH_3), 54.97 (s, CH_2), 39.30 (s, CH_3), 21.74 (s, CH_3).

IR (neat, cm^{-1}): ṽ: 3439 (broad), 2916, 2835, 1596, 1505, 1460, 1428, 1384, 1358, 1288, 1235, 1190, 1161, 1090, 1024, 986, 963, 859, 815, 787, 688.

EI-HRMS: mass spectrometry: m/z calc. 301.1678 $[C_{18}H_{23}NO_3]^{\bullet+}$, measured 301.1674.



Chemical Formula: $C_{22}H_{21}NO_4$
Exact Mass: 363.1471
Molecular Weight: 363.4130
m/z: 363.1471 (100.0%), 364.1504 (23.8%), 365.1538 (2.7%)
Elemental Analysis: C, 72.71; H, 5.82; N, 3.85; O, 17.61

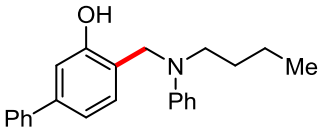
4f: Following the general procedure, the product was converted from methyl 4-hydroxy-3-methoxybenzoate and *N*-methyl-*N*-phenylaniline at 90℃ for 48 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (10:1). Isolated yield: 43% (green solid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.77 (m, 1H), 7.50 (d, *J* = 1.8 Hz, 1H), 7.34–7.25 (m, 4H), 7.20–7.11 (m, 4H), 7.04–6.95 (m, 2H), 6.69 (s, OH), 5.06 (s, 2H), 3.94 (s, 3H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.06 (s, C_{quat}), 148.13 (s, C_{quat}), 147.47 (s, C_{quat}), 146.08 (s, C_{quat}), 129.35 (s, CH), 124.48 (s, C_{quat}), 122.50 (s, CH), 121.76 (s, CH), 121.71 (s, C_{quat}), 120.99 (s, CH), 110.47 (s, CH), 56.26 (s, CH_3), 52.04 (s, CH_3), 51.55 (s, CH_2).

IR (neat, cm^{-1}): ῡ: 3488, 3404, 3387, 3067, 3011, 2947, 2922, 2850, 1714, 1699, 1662, 1590, 1488, 1459, 1434, 1401, 1368, 1357, 1302, 1275, 1242, 1216, 1181, 1118, 1103, 1085, 1077, 1058, 999, 961, 896, 854, 836, 809, 765, 750, 737, 694, 662.

EI-HRMS: mass spectrometry: m/z calc. 363.1471 $[C_{22}H_{21}NO_4]^{\bullet+}$, measured 363.1465.



Chemical Formula: $C_{23}H_{25}NO$
Exact Mass: 331.1936
Molecular Weight: 331.4590
m/z: 331.1936 (100.0%), 332.1970 (24.9%), 333.2003 (2.7%)
Elemental Analysis: C, 83.34; H, 7.60; N, 4.23; O, 4.83

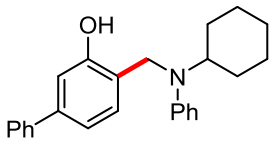
4g: Following the general procedure, the product was converted from [1,1'-biphenyl]-3-ol and *N*-butyl-*N*-methylaniline at 80℃ for 32 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (40:1) and a second time with DCM. Isolated yield: 49% (yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (broad s, OH), 7.54–7.47 (m, 2H), 7.38–7.30 (m, 2H), 7.24 (t, *J* = 8.0 Hz, 3H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.05–6.93 (m, 4H), 4.32 (s, 2H), 3.12 (t, *J* = 8.0 Hz, 2H), 1.48–1.34 (m, 2H), 1.25–1.14 (m, 2H), 0.78 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.61 (s, C_{quat}), 148.90 (s, C_{quat}), 142.05 (s, C_{quat}), 140.82 (s, C_{quat}), 129.38 (s, CH), 129.10 (s, CH), 128.80 (s, CH), 127.41 (s, CH), 127.08 (s, CH), 123.24 (s, CH), 121.23 (s, C_{quat}), 120.89 (s, CH), 118.54 (s, CH), 115.06 (s, CH), 56.91 (s, CH_2), 53.64 (s, CH_2), 28.02 (s, CH_2), 20.46 (s, CH_2), 14.00 (s, CH_3).

IR (neat, cm^{-1}): ῡ: 3061, 3027, 2955, 2929, 2872, 2333, 1654, 1598, 1566, 1485, 1453, 1410, 1364, 1305, 1220, 1202, 1158, 1100, 1076, 1039, 987, 925, 900, 863, 819, 756, 746, 691.

EI-HRMS: mass spectrometry: m/z calc. 331.1936 $[C_{23}H_{25}NO]^{\bullet+}$, measured 331.1956.



Chemical Formula: $C_{25}H_{27}NO$
Exact Mass: 357.2093
Molecular Weight: 357.4970
m/z: 357.2093 (100.0%), 358.2126 (27.0%), 359.2160 (2.7%)
Elemental Analysis: C, 83.99; H, 7.61; N, 3.92; O, 4.48

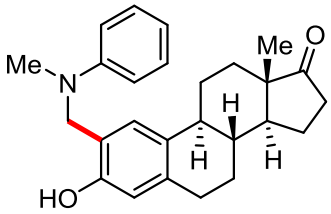
4h: Following the general procedure, the product was converted from [1,1'-biphenyl]-3-ol and *N*-cyclohexyl-*N*-methylaniline at 80℃ for 32 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (30:1) and a second time with DCM. Isolated yield: 50% (white solid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (broad s, OH), 7.51–7.42 (m, 2H), 7.35–7.27 (m, 2H), 7.25–7.15 (m, 3H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.03–6.96 (m, 2H), 6.96–6.88 (m, 2H), 4.38 (s, 2H), 3.14 (tt, *J* = 11.5, 3.3 Hz, 1H), 1.92 (d, *J* = 12.0 Hz, 2H), 1.73 (d, *J* = 12.9 Hz, 2H), 1.53 (d, *J* = 13.1 Hz, 1H), 1.33–1.12 (m, 4H), 1.05–0.88 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.85 (s, C_{quat}), 147.48 (s, C_{quat}), 141.64 (s, C_{quat}), 140.93 (s, C_{quat}), 129.01 (s, CH), 128.91 (s, CH), 128.75 (s, CH), 127.30 (s, CH), 127.05 (s, CH), 124.36 (s, CH), 124.06 (s, CH), 121.60 (s, C_{quat}), 118.21 (s, CH), 114.99 (s, CH), 63.62 (s, CH), 52.02 (s, CH_2), 29.84 (s, CH_2), 26.07 (s, CH_2), 25.88 (s, CH_2).

IR (neat, cm^{-1}): ṽ: 3022, 2984, 2957, 2860, 1603, 1584, 1563, 1485, 1455, 1426, 1329, 1303, 1271, 1222, 1206, 1176, 1162, 1119, 1090, 1077, 998, 972, 954, 932, 907, 876, 855, 825, 787, 771, 757, 730, 699, 691, 629, 613.

EI-HRMS: mass spectrometry: m/z calc. 357.2093 $[C_{25}H_{27}NO]^{\bullet+}$, measured 357.2097.



Chemical Formula: $C_{26}H_{31}NO_2$
Exact Mass: 389.2355
Molecular Weight: 389.5390
m/z: 389.2355 (100.0%), 390.2388 (28.1%), 391.2422 (2.7%), 391.2422 (1.1%)
Elemental Analysis: C, 80.17; H, 8.02; N, 3.60; O, 8.21

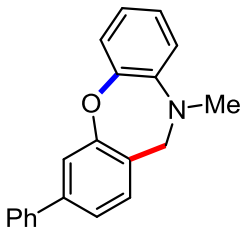
3u: Following the general procedure, the product was converted from estrone and *N*,*N*-dimethylaniline at 80℃ for 24 hours. The crude mixture is purified by SiO_2 gel column chromatography with hexane/EA (25:1) and a second time with DCM. Isolated yield: 55% (white solid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.30–7.22 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.89 (s, 1H), 6.55 (s, 1H), 4.25 (dd, *J* = 33.1, 14.4 Hz, 2H), 2.83–2.75 (m, 2H), 2.73 (s, 3H), 2.50–2.36 (m, 1H), 2.34–2.25 (m, 1H), 2.20–1.86 (m, 5H), 1.60–1.30 (m, 6H), 0.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 221.23 (s, C_{quat}), 155.01 (s, C_{quat}), 150.83 (s, C_{quat}), 137.45 (s, C_{quat}), 131.18 (s, C_{quat}), 129.41 (s, CH), 125.75 (s, CH), 122.61 (s, CH), 119.54 (s, C_{quat}), 119.06 (s, CH), 116.41 (s, CH), 59.58 (s, CH_2), 50.54 (s, CH_3), 48.15 (s, C_{quat}), 44.05 (s, CH), 40.35 (s, CH), 38.49 (s, CH), 36.01 (s, CH_2), 31.70 (s, CH_2), 29.37 (s, CH_2), 26.68 (s, CH_2), 26.15 (s, CH_2), 21.71 (s, CH_2), 14.01 (s, CH_3).

IR (neat, cm^{-1}): ν̃: 3186 (broad), 2931, 2866, 1735, 1652, 1597, 1496, 1453, 1428, 1372, 1250, 1208, 1190, 1164, 1085, 1052, 1034, 1005, 958, 907, 873, 829, 794, 725, 693, 671.

EI-HRMS: mass spectrometry: m/z calc. 389.2355 $[C_{26}H_{31}NO_2]^{\bullet+}$, measured 389.2372.



Chemical Formula: $C_{20}H_{17}NO$
Exact Mass: 287.1310
Molecular Weight: 287.3620
m/z: 287.1310 (100.0%), 288.1344 (21.6%), 289.1377 (2.2%)
Elemental Analysis: C, 83.59; H, 5.96; N, 4.87; O, 5.57

5: To a solution of **3l** (1.7g, 6.1 mmol, 1.0 equiv.) in HFIP solvent (25 mL) was added PIDA (3.9 g, 12.2 mmol, 2.0 equiv.) at room temperature. After string for 5 minutes, $NaBH_4$ (695 mg, 18.3 mmol, 3.0 equiv.) was added to the reaction mixture and stirring was continued at room temperature. After complete consumption in less than 5 minutes, as indicated by TLC, the reaction mixture was quenched with saturated $NaHCO_3$, extracted with DCM and dried over anhydrous Na_2SO_4. The organic layer was concentrated under reduced pressure, and the residue was purified by column chromatography (EtOAc/hexane 1:30) to afford 1.4 g **5** in 80% yield (yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.42 (m, 2H), 7.38–7.27 (m, 3H), 7.23 (ddt, *J* = 6.8, 5.6, 2.8 Hz, 1H), 7.17 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.10–7.02 (m, 2H), 6.95–6.87 (m, 1H), 6.81 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.78–6.68 (m, 1H), 4.27 (s, 2H), 2.85 (s, 3H).

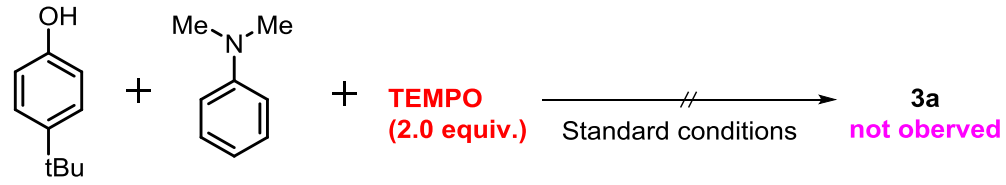
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.42 (s, C_{quat}), 149.06 (s, C_{quat}), 142.45 (s, C_{quat}), 142.04 (s, C_{quat}), 140.27 (s, C_{quat}), 129.03 (s, CH), 128.87 (s, CH), 128.05 (s, C_{quat}), 127.59 (s, CH), 127.08 (s, CH), 124.69 (s, CH), 122.27 (s, CH), 121.76 (s, CH), 121.35 (s, CH), 120.03 (s, CH), 119.03 (s, CH), 56.43 (s, CH_2), 43.00 (s, CH_3).

IR (neat, cm^{-1}): ν̃: 3030, 2853, 1601, 1563, 1484, 1449, 1404, 1312, 1227, 1195, 1134, 1108, 1075, 1040, 1023, 980, 927, 882, 846, 819, 757, 694, 671, 659.

EI-HRMS: mass spectrometry: m/z calc. 287.1310 $[C_{20}H_{17}NO]^{\bullet+}$, measured 287.1306.

5. Mechanistic experiments

(1) Addition of radical inhibitor



1a (0.5 mmol) **2a** (9.5 equiv.)

75 mg (0.5 mmol, 1.0 equiv.) **1a**, 15.7 mg (10 mol%) catalyst L^1CuCl_2, 0.6 mL (4.8 mmol, 9.5 equiv.) *N,N*-dimethylaniline **2a**, 156 mg (1.0 mmol, 2.0 equiv.) TEMPO, cumene (1.0 mL), and 0.2 mL DTBP (1.0 mmol, 2.0 equiv.) were united under air in a 20 mL reaction vial equipped with aluminous headspace cap. The reactor is sealed and exposed to 80 °C for 24 hours. The reaction mixture was analyzed by TLC and ^{1}H NMR. The results revealed that the reaction was completely suppressed.

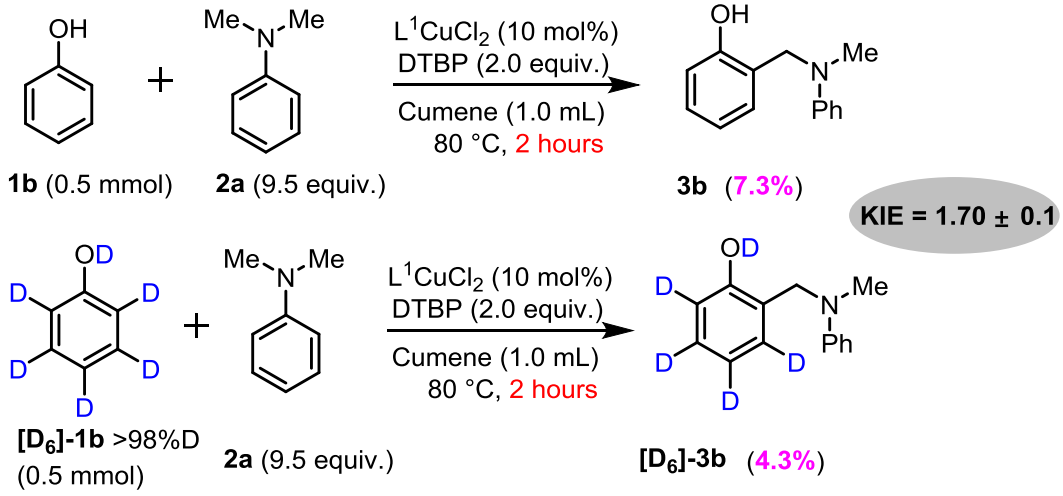
(2) Synthesis of **[D_6]-2a**

Chemical Formula: $C_8H_5D_6N$
Exact Mass: 127.1268
Molecular Weight: 127.2196
m/z: 127.1268 (100.0%), 128.1302 (8.7%)
Elemental Analysis: C, 75.53; H, 13.46; N, 11.01

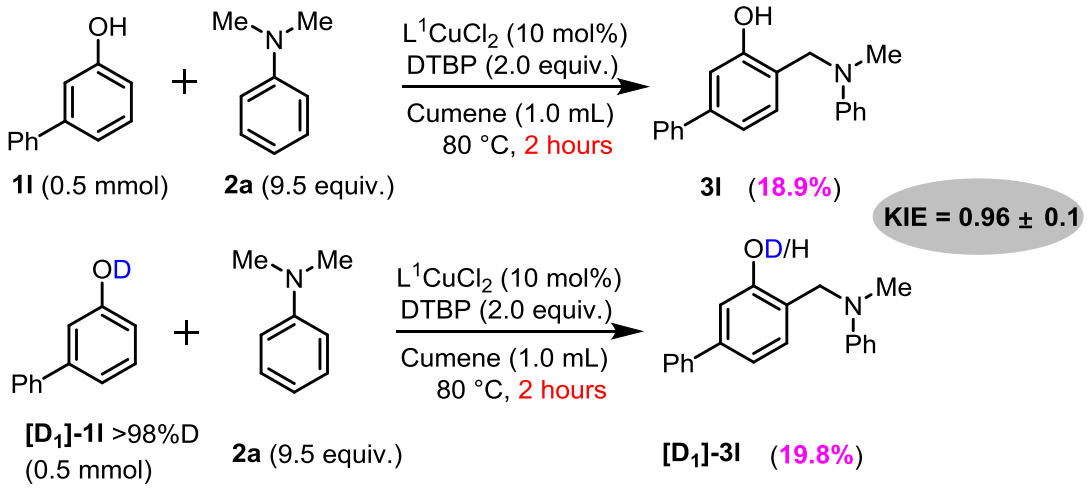
1.7 g (12.0 mmol, 2.0 equiv.) K_2CO_3 was added to 20 mL acetone in a 50 mL flask. Then 600 mg (6.0 mmol, 1.0 equiv.) aniline and 2.6 g (18.0 mmol, 3.0 equiv.) iodomethane-d_3 were added into the flask. After refluxing under 60℃ for 24 hours, the reaction was stopped and purified by SiO_2 gel column chromatography (hexane/EA = 50:1). 380 mg product **[D_6]-2a** (yellow liquid) was obtained with a 50% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.03 (m, 2H), 6.81 – 6.48 (m, 3H).

(3) KIE experiments of phenol

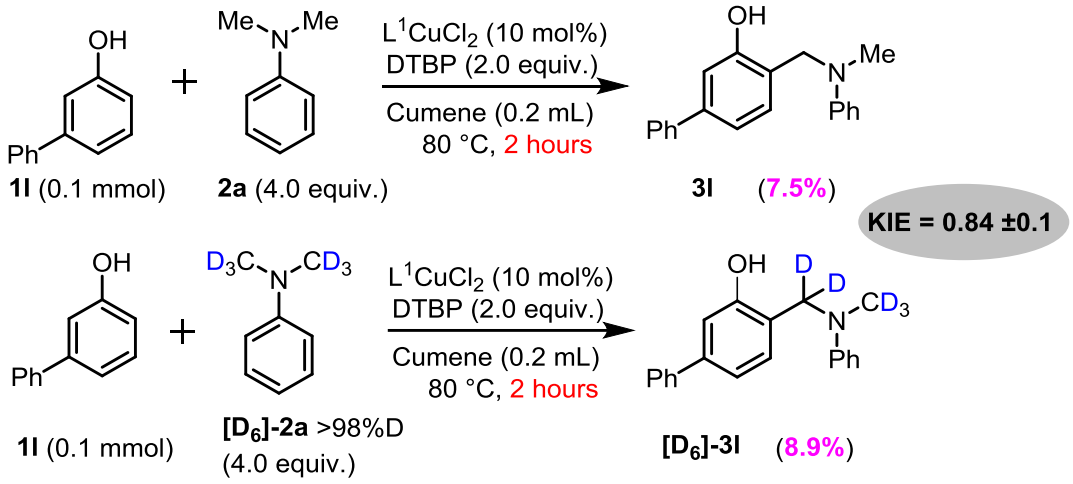


These two reactions were conducted at the same time in the same standard conditions for only two hours. The yields were determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.



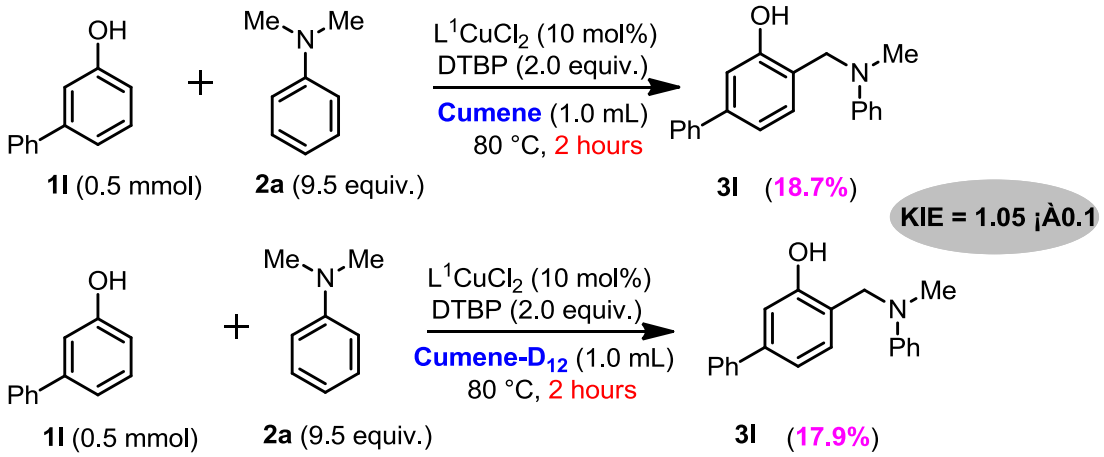
These two reactions were conducted at the same time in the same standard conditions for only two hours. The yields were determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

(4) KIE experiments of *N,N*-dimethylaniline



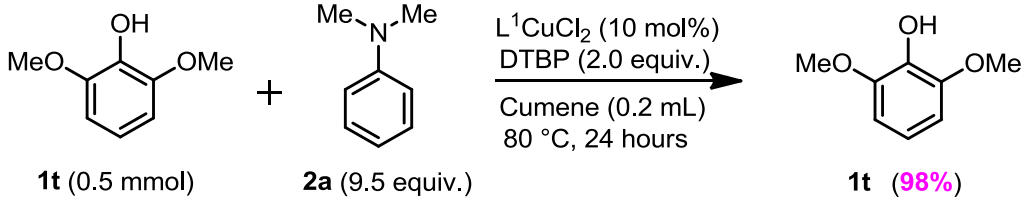
These two reactions were conducted at the same time in the same standard conditions for only two hours. The yields were determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

(5) KIE experiments of cumene



These two reactions were conducted at the same time in the same standard conditions for only two hours. The yields were determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

(6) Test of phenol with both *ortho*-positions blocked



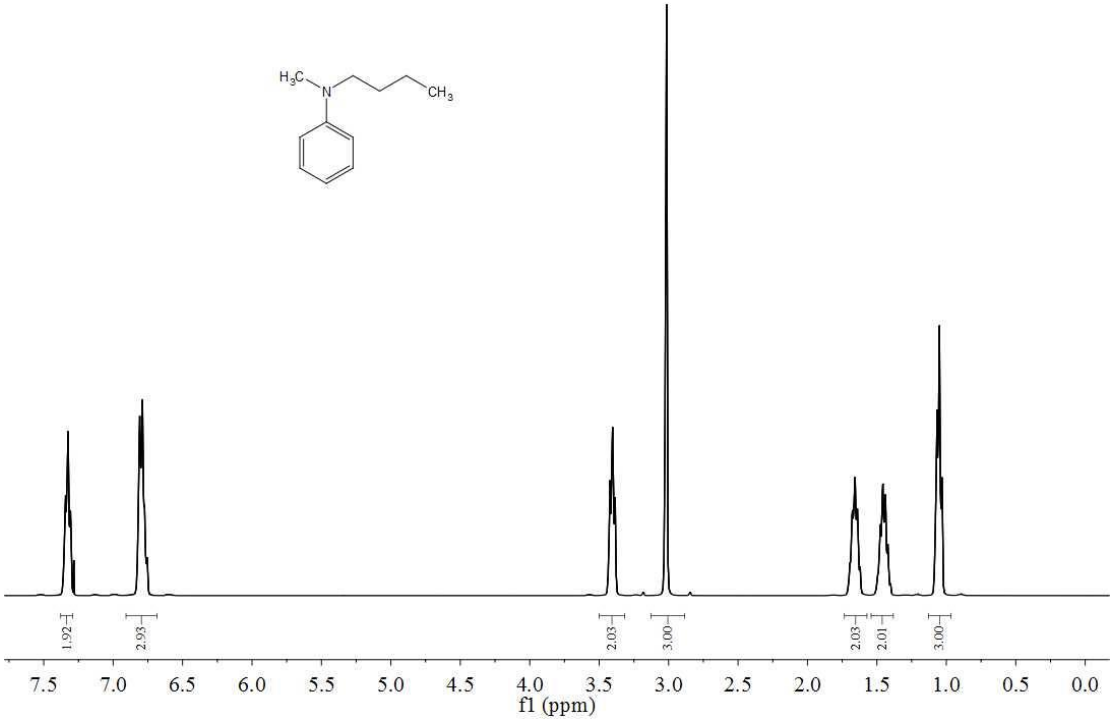
77 mg (0.5 mmol, 1.0 equiv.) **1t**, 15.7 mg (10 mol%) catalyst L^1CuCl_2, 0.6 mL (4.8 mmol, 9.5 equiv.) *N,N*-dimethylaniline **2a**, cumene (1.0 mL), and 0.2 mL DTBP (1.0 mmol, 2.0 equiv.) were united under air in a 20 mL reaction vial equipped with aluminous headspace cap. The reactor is sealed and exposed to 80 °C for 24 hours. The reaction mixture was measured by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. The results revealed that almost all the phenol remains unreacted.

6 References

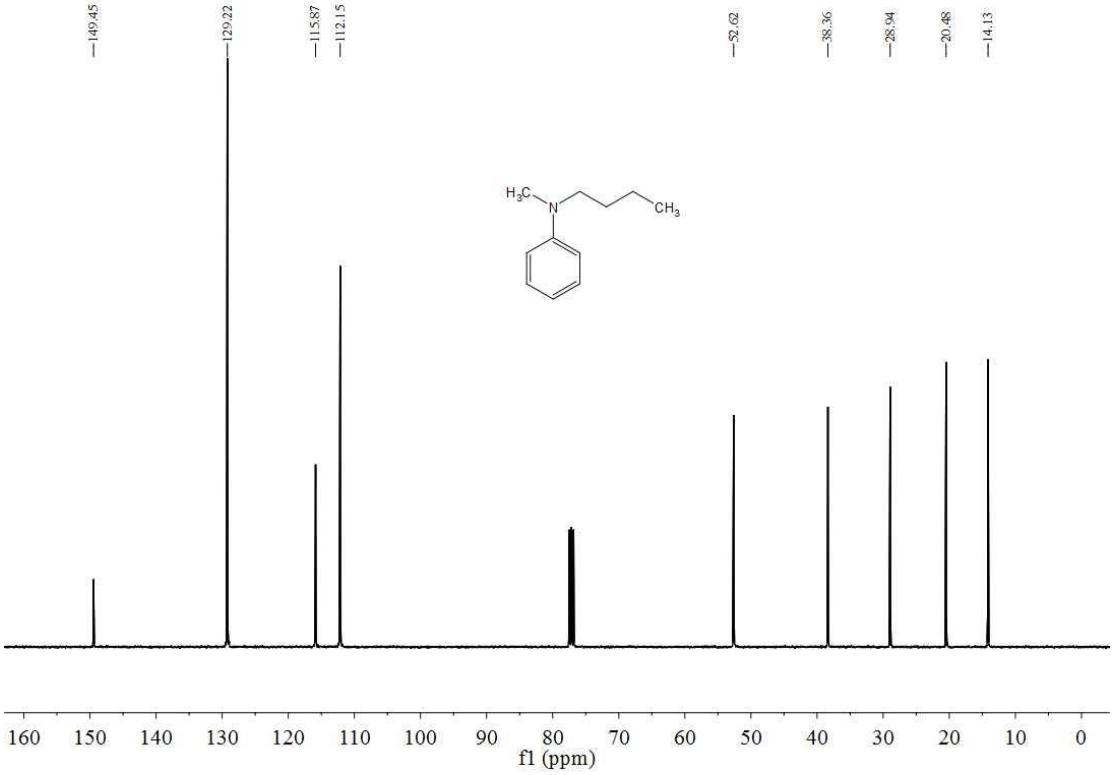
1. Elder P. J.W.; Landry J. C.; Cozzolino A. F.; Chapman A. E.A.; Vargas-Baca I. *J. Organomet. Chem.* **2012**, *716*, 11.
2. Barker T.; Jarvo E. R. *J. Am. Chem. Soc.* **2009**, *131*, 15598.
3. Liao W.; Chen Y.; Liu Y.; Duan H.; Petersen J. L.; Shi X. *Chem. Commun.* **2009**, *0*, 6436.

7 Copies of ^{1}H and ^{13}C Spectra

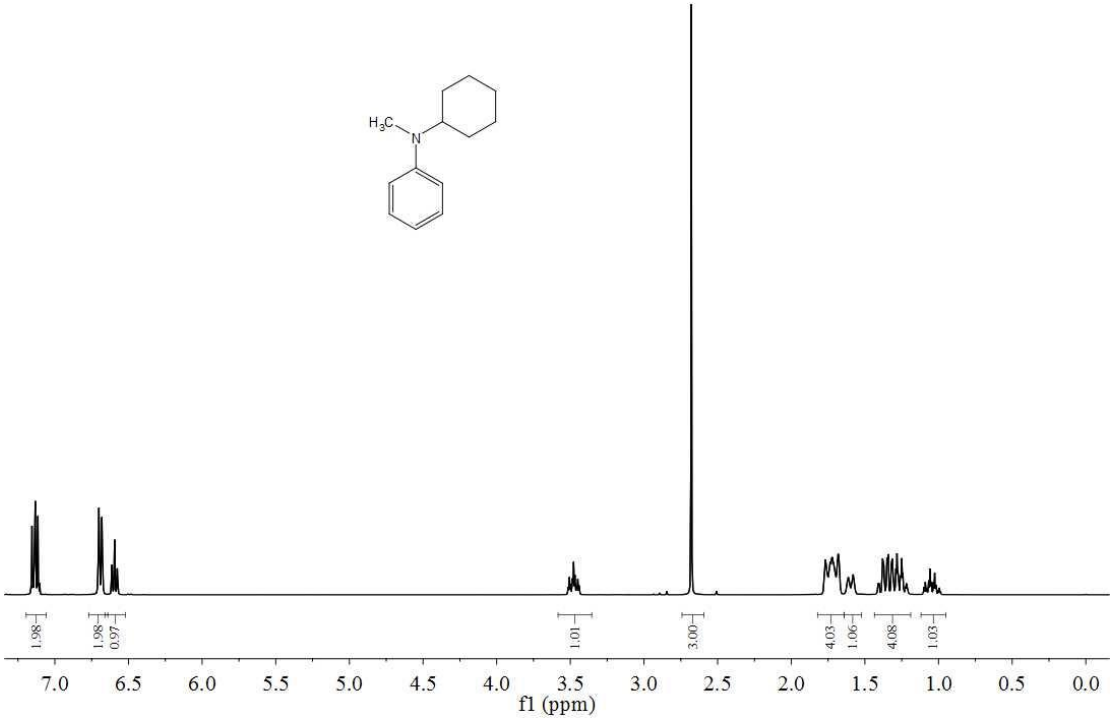
^{1}H NMR (**2g**)



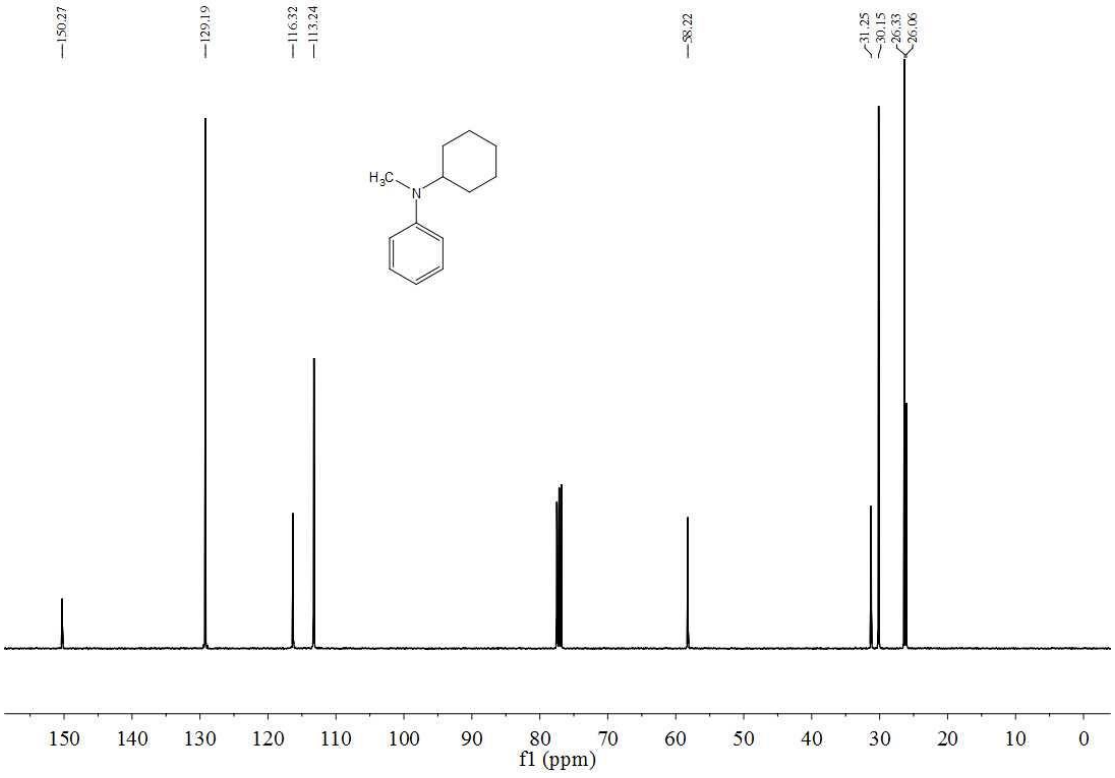
^{13}C NMR (**2g**)



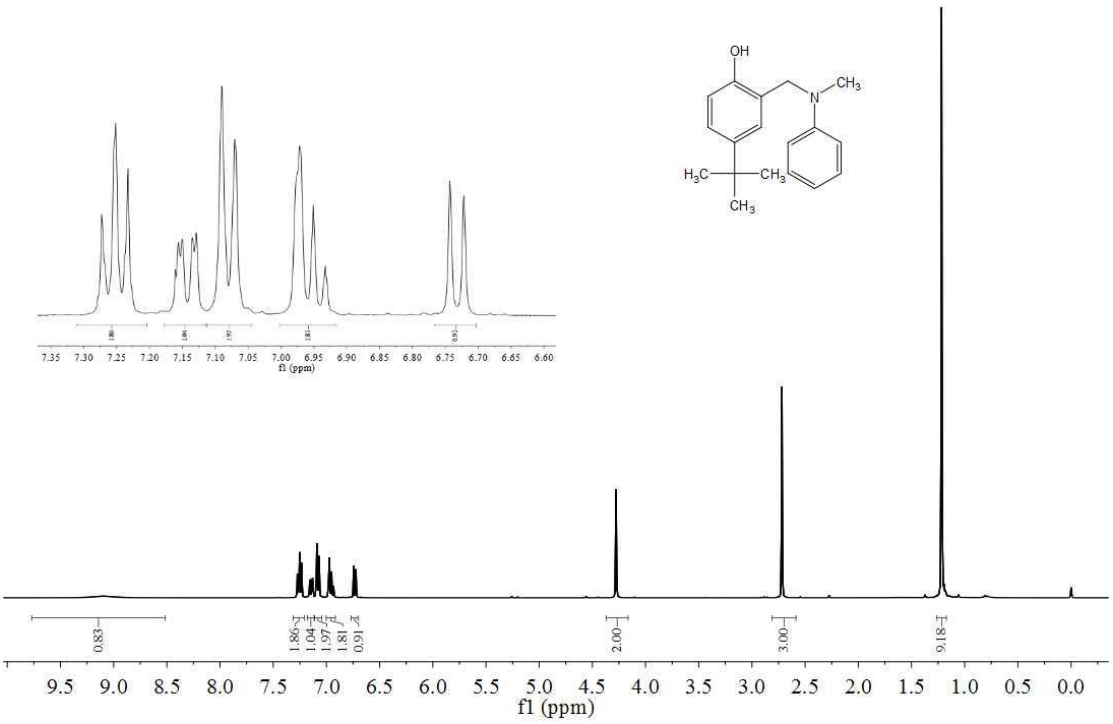
^{1}H NMR (**2h**)



^{13}C NMR (**2h**)



^{1}H NMR (**3a**)



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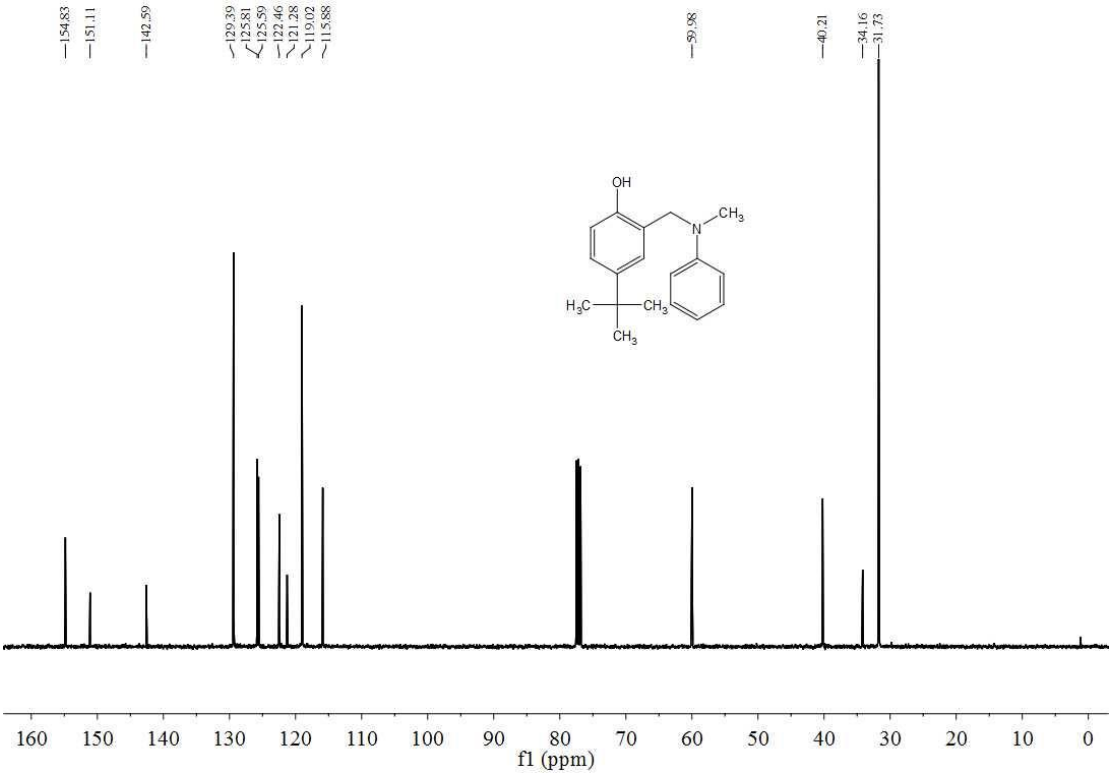
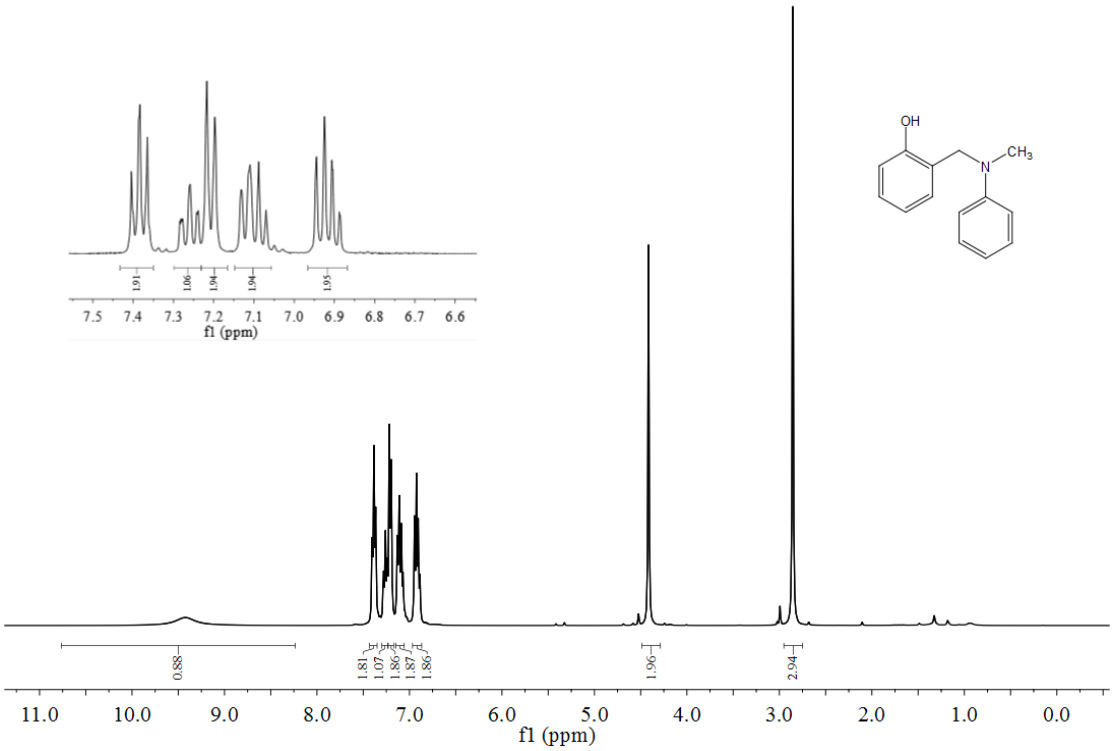
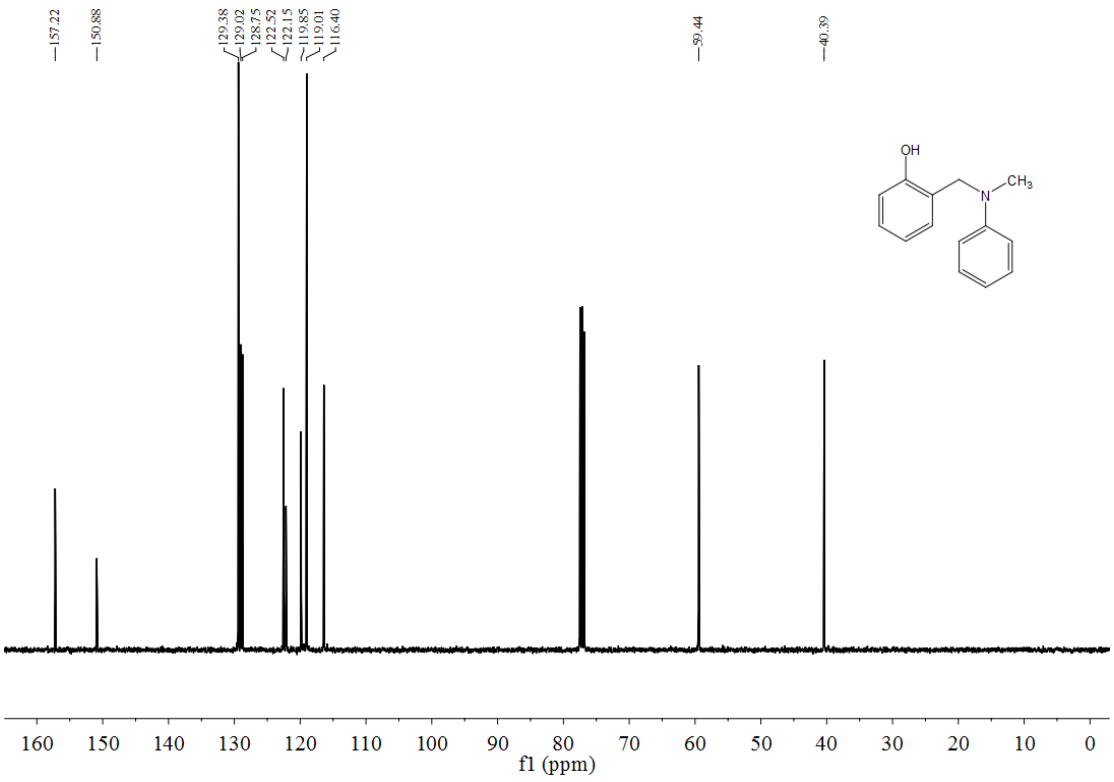


^{1}H NMR (**3b**)



^{13}C NMR (**3b**)



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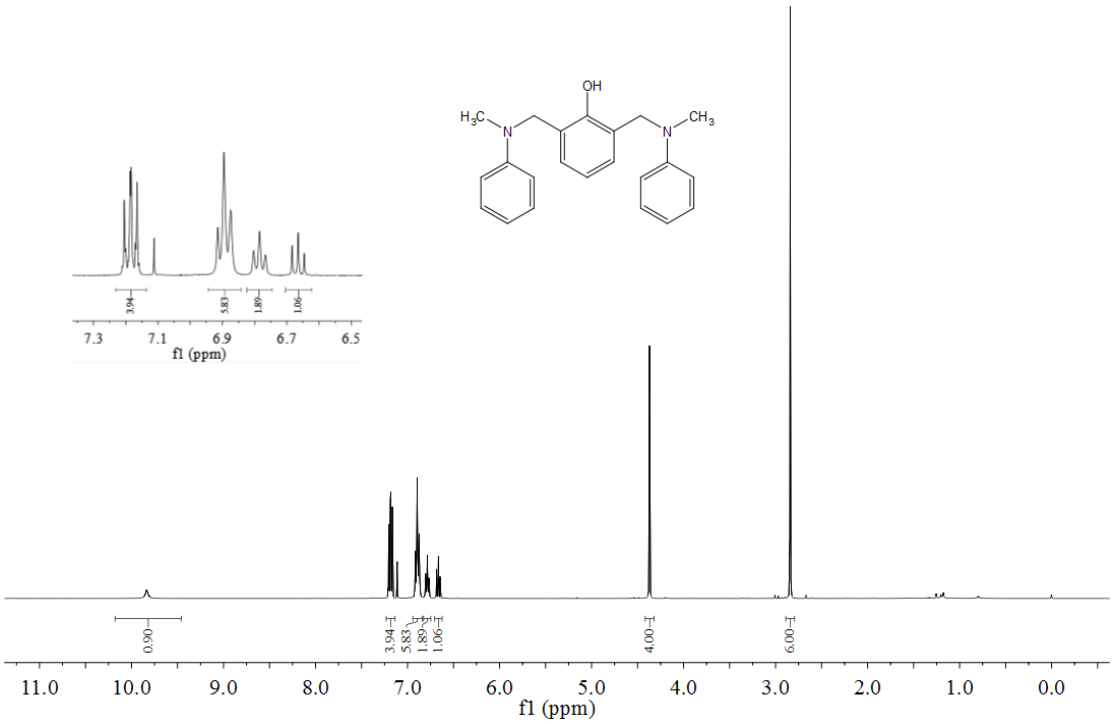

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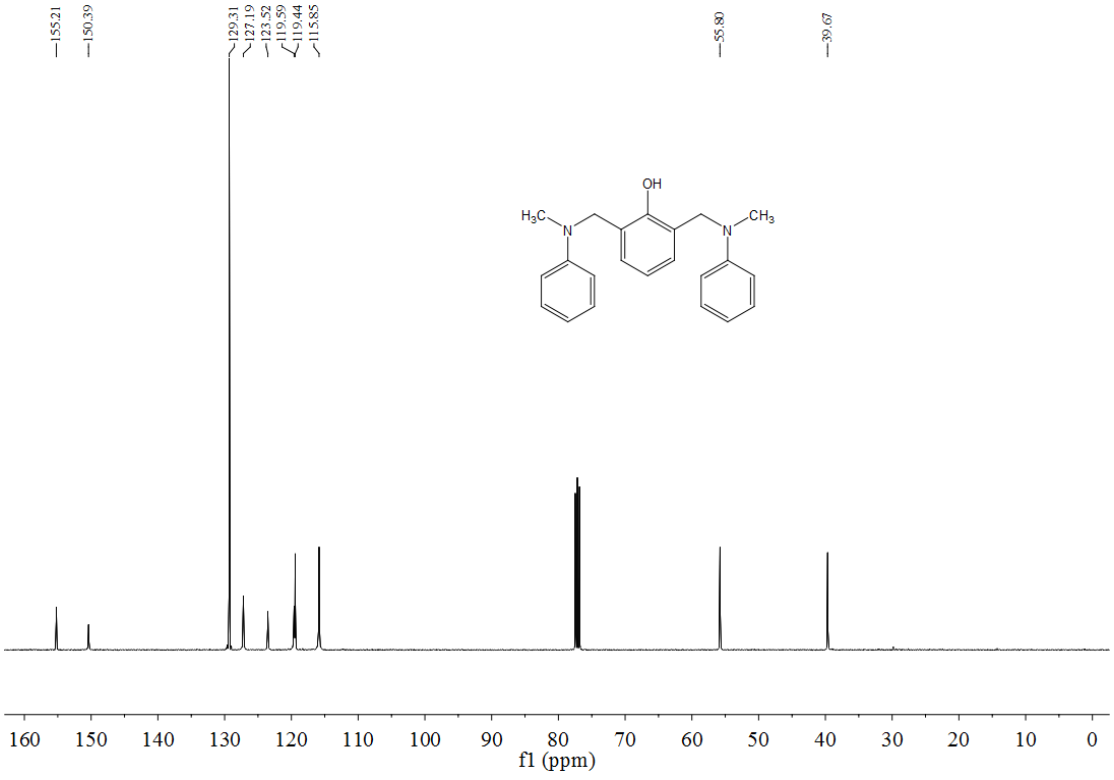
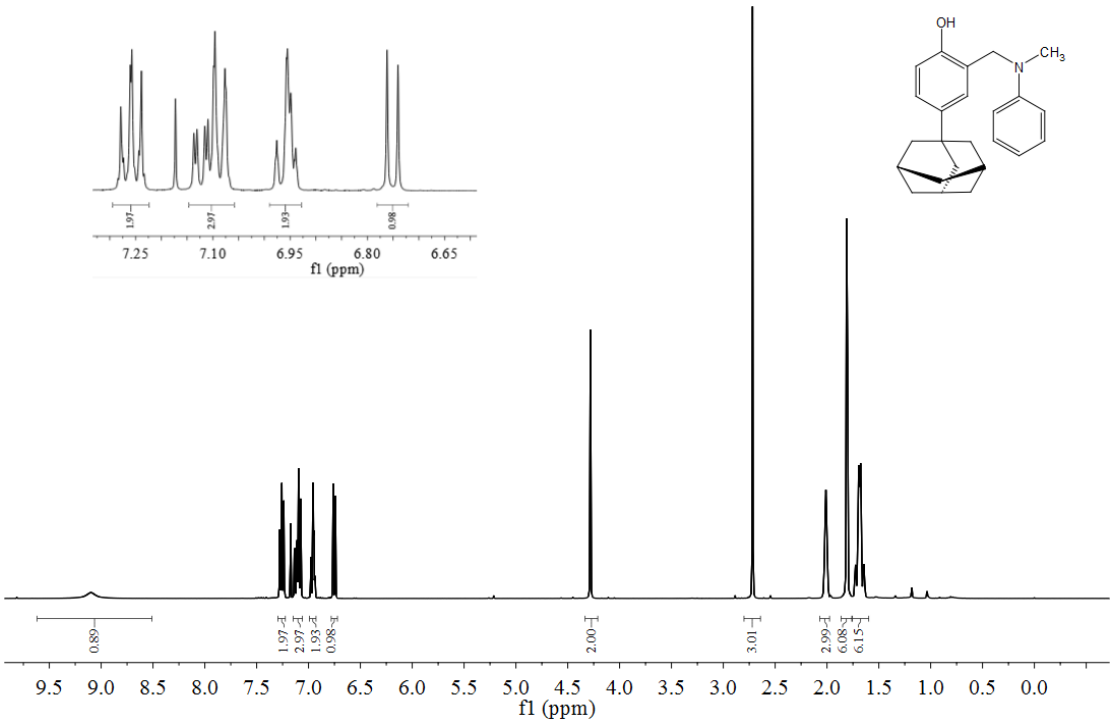
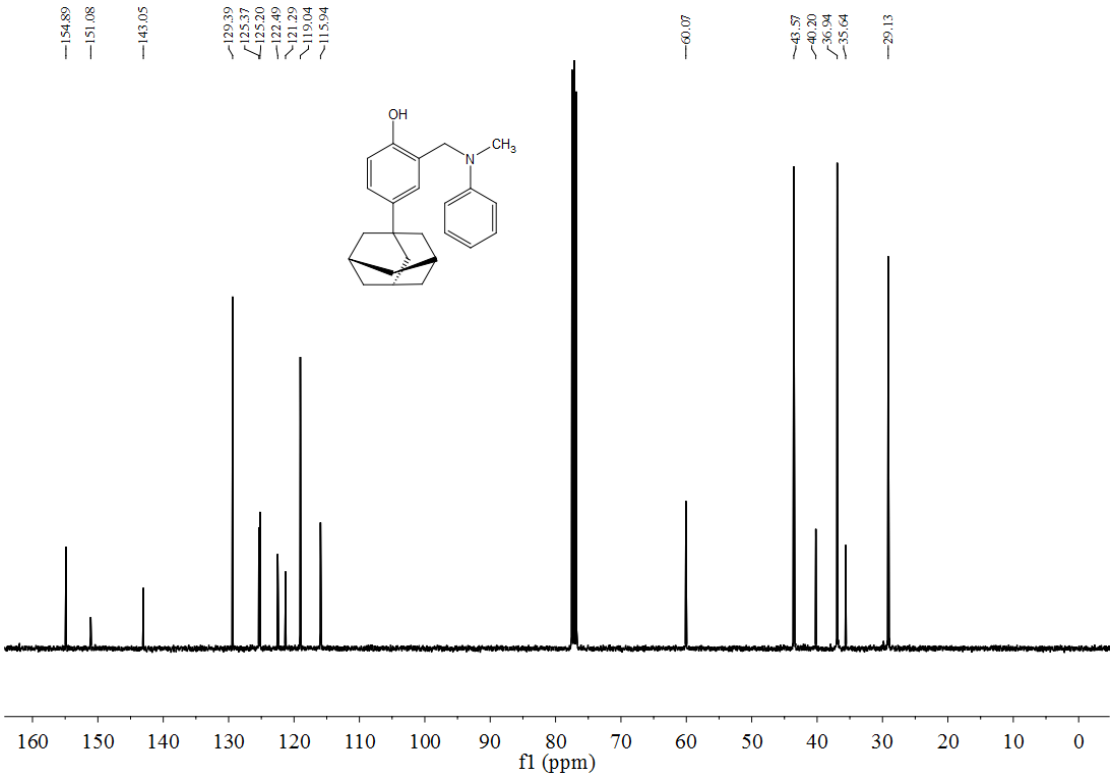


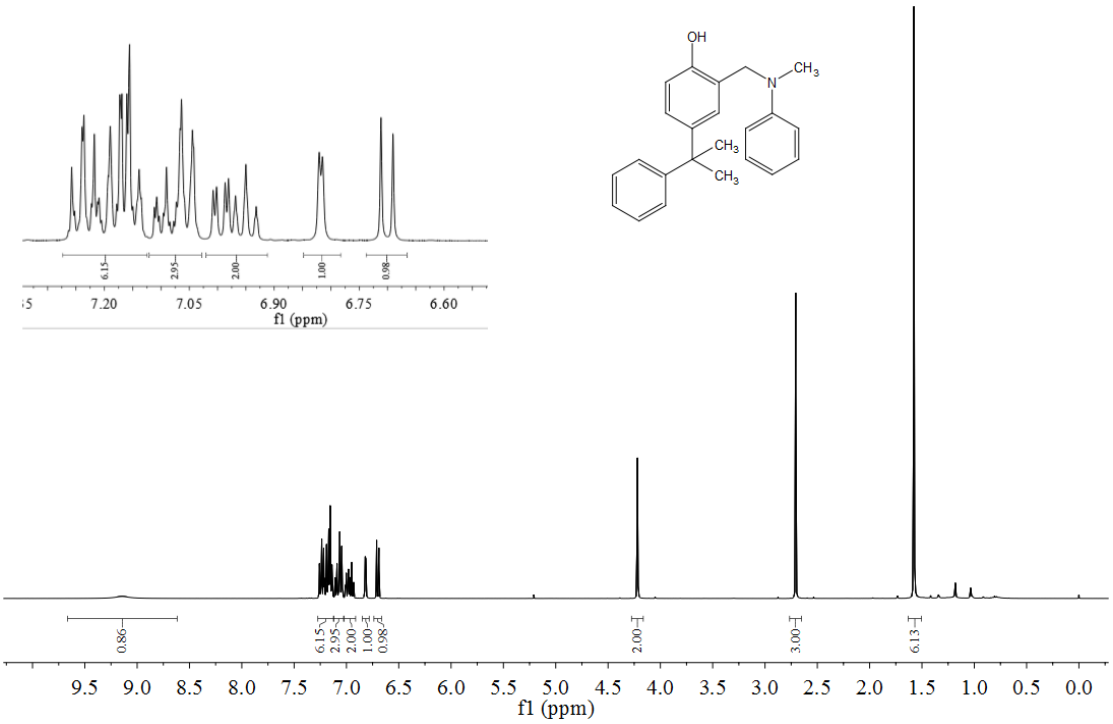
^{1}H NMR (**3c**)



^{13}C NMR (**3c**)



^{1}H NMR (**3d**)



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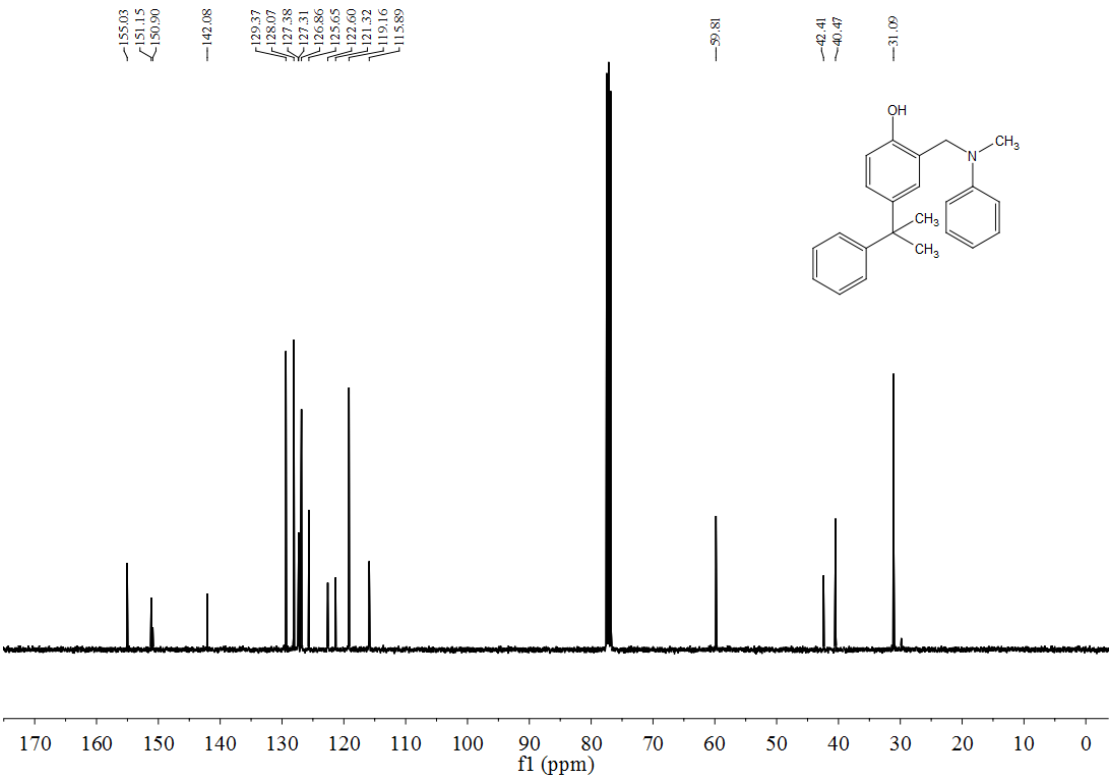

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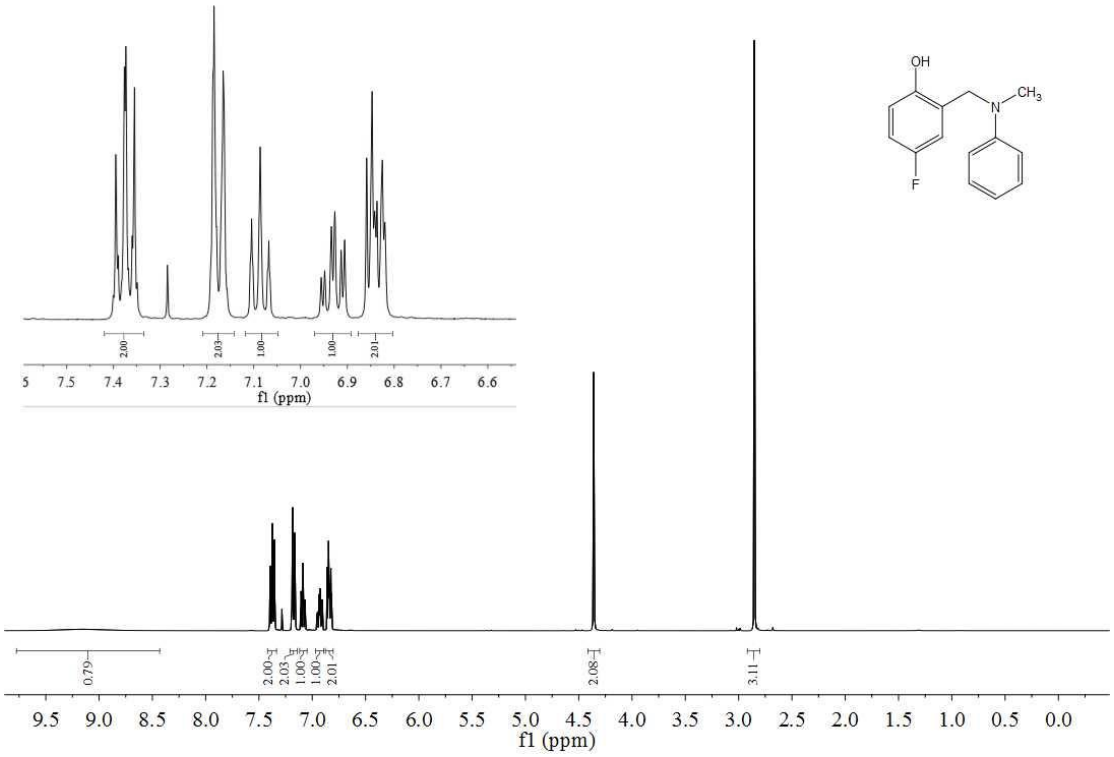
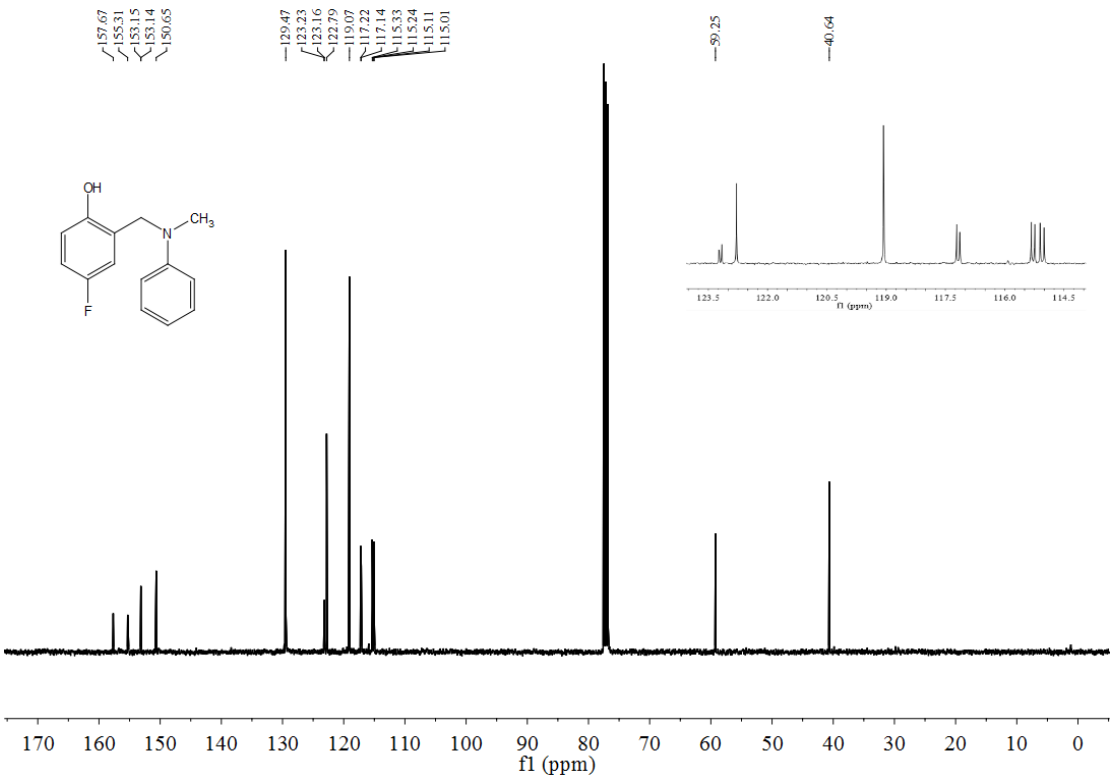
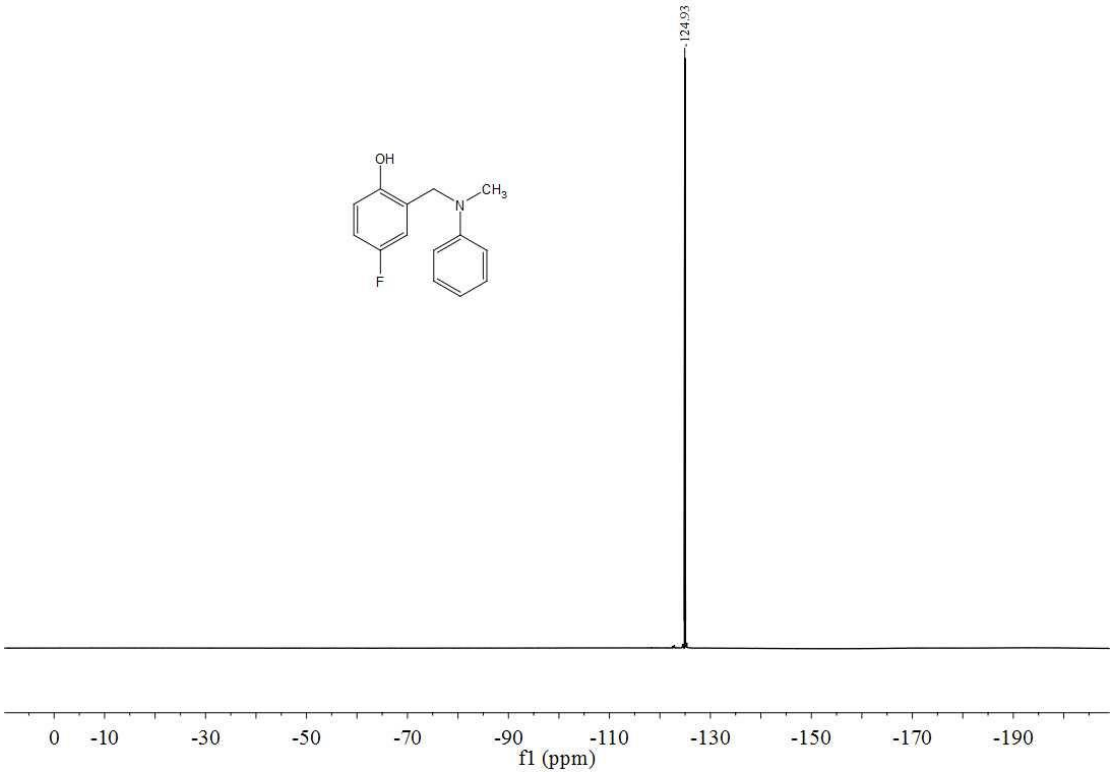


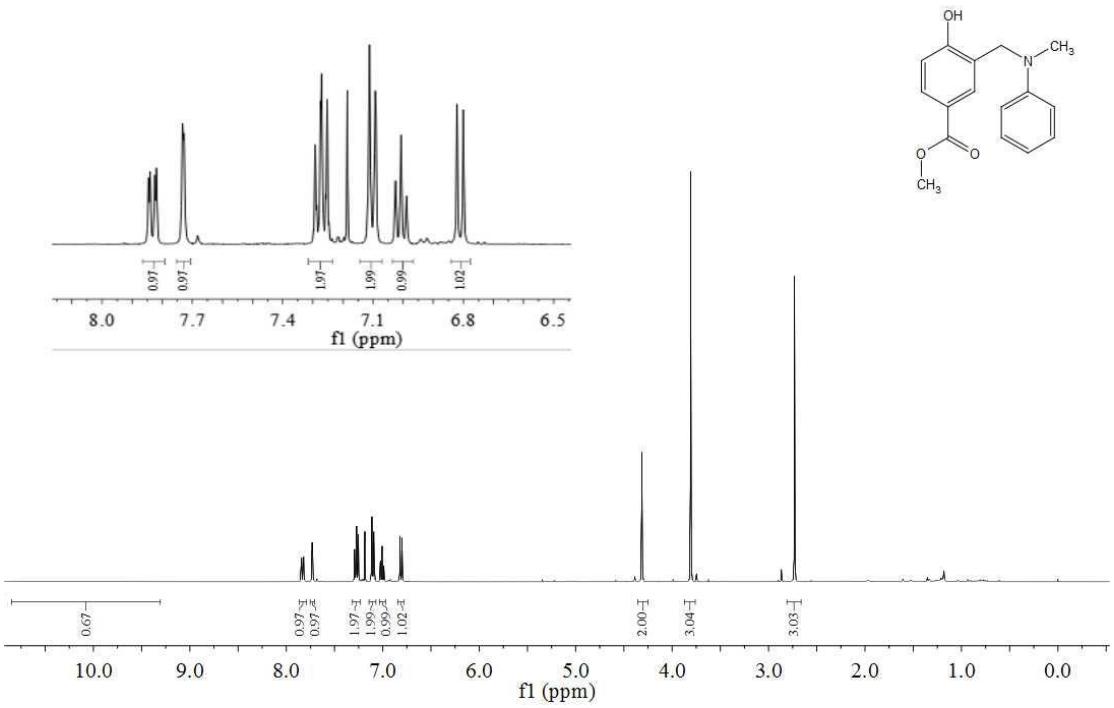
^{13}C NMR (**3e**)



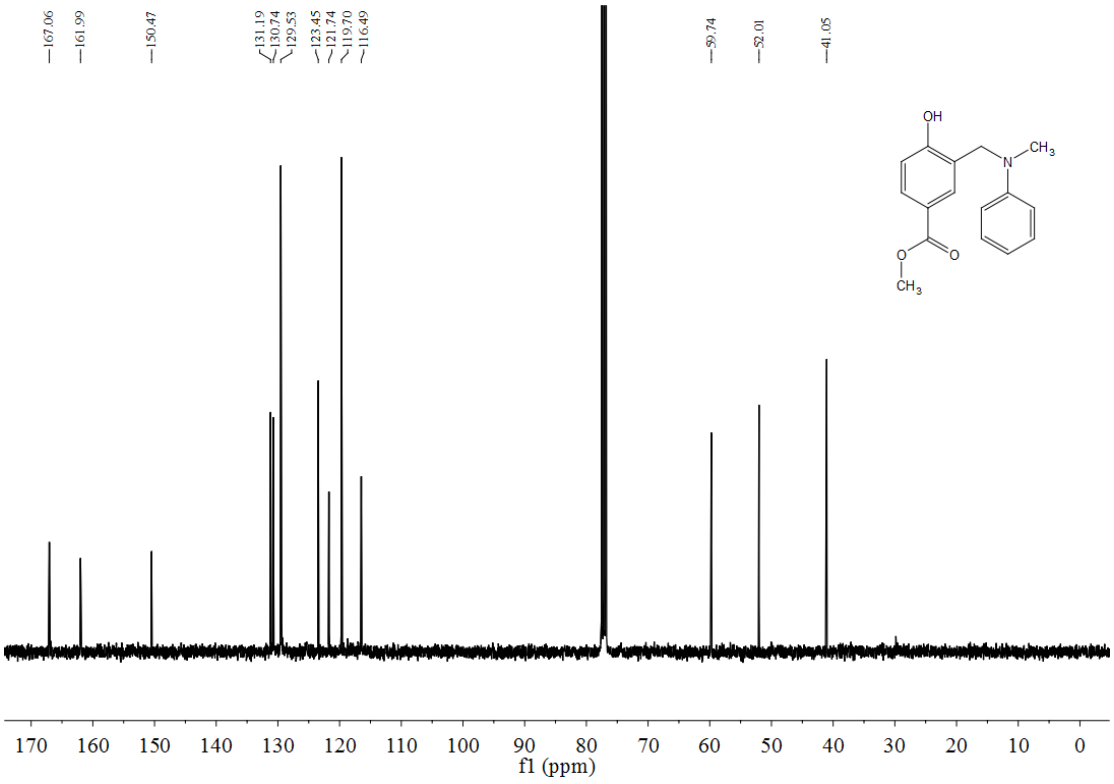
^{19}F NMR (**3e**)



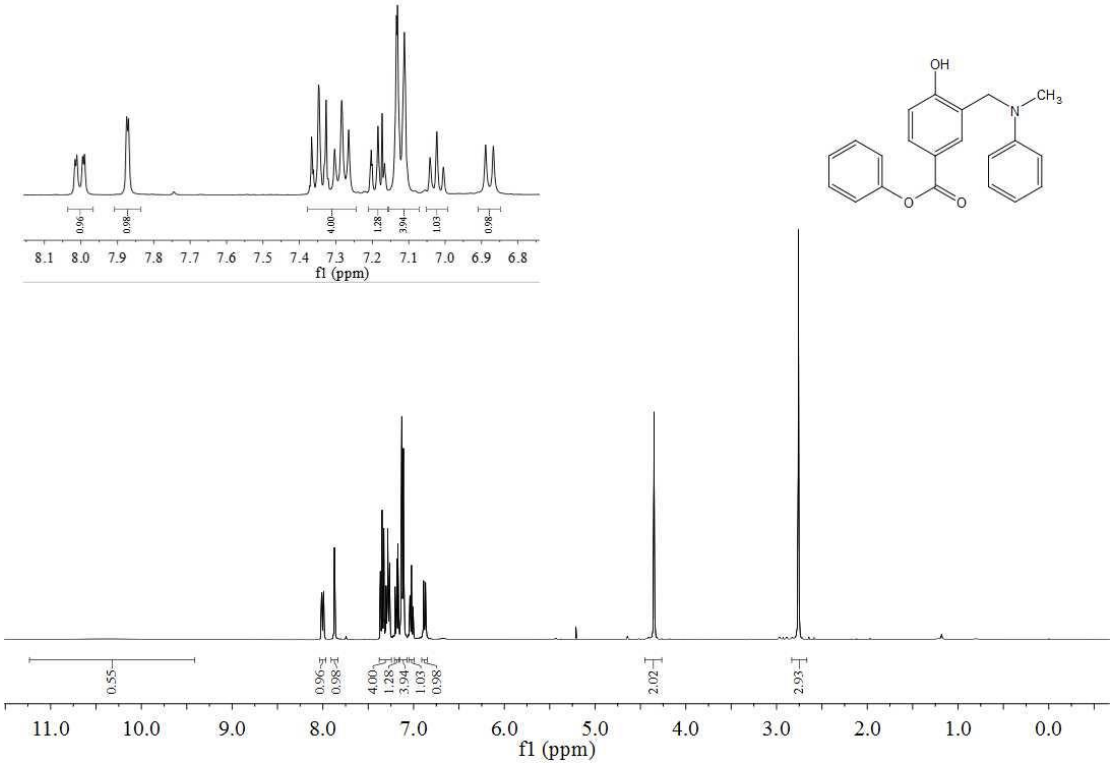
^{1}H NMR (**3f**)



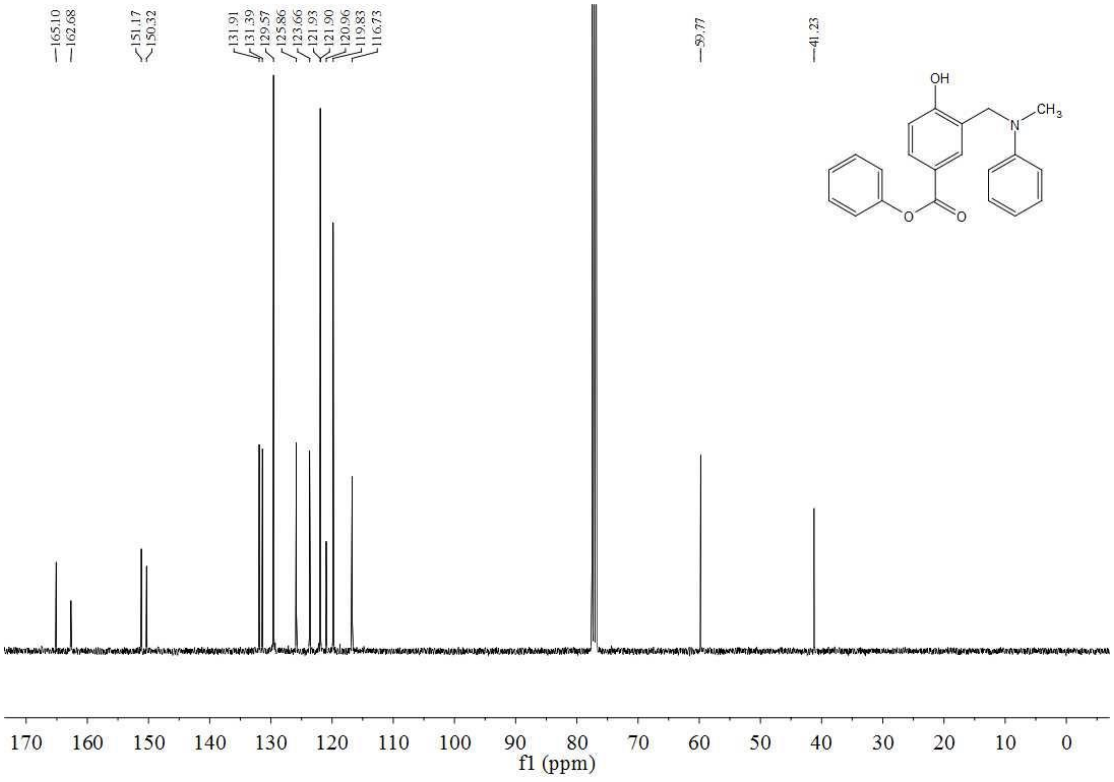
^{13}C NMR (**3f**)



^{1}H NMR (**3g**)



^{13}C NMR (**3g**)



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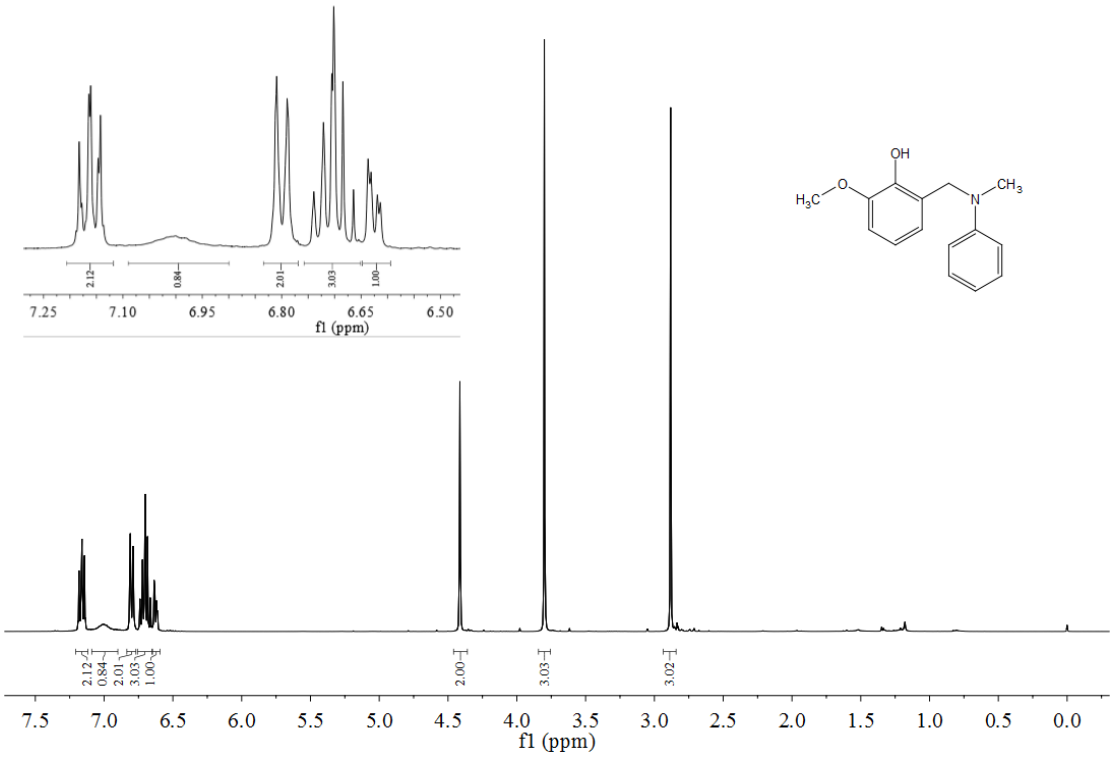
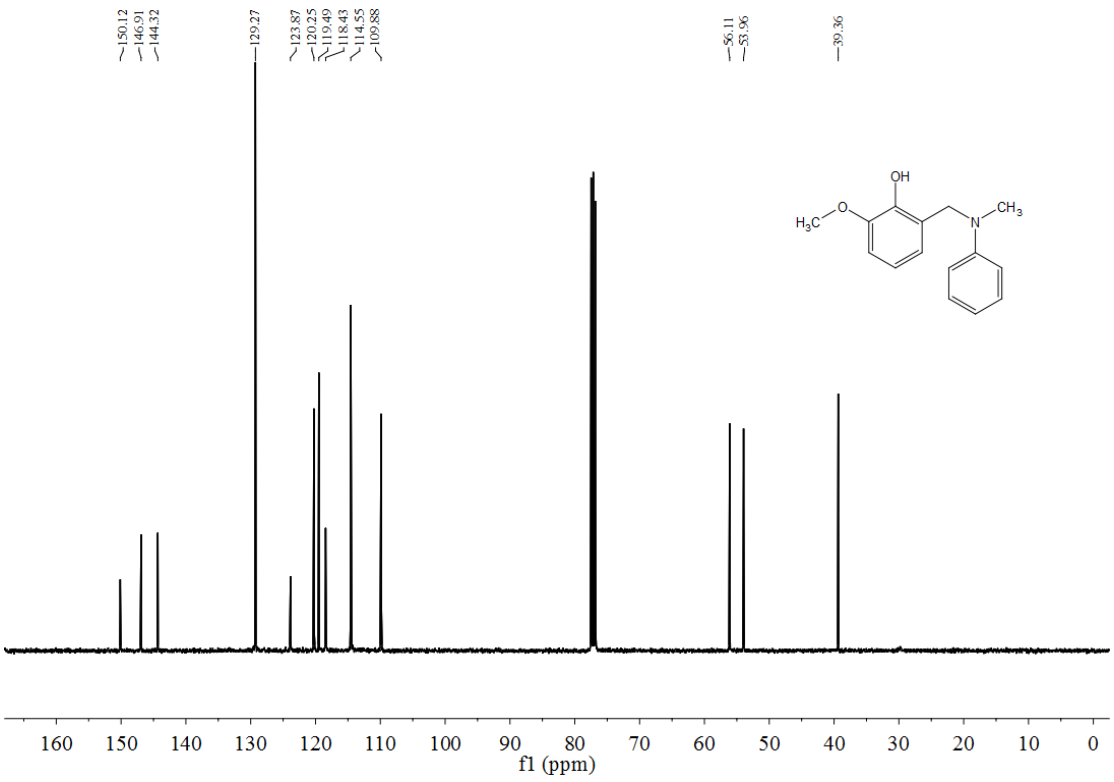


^{13}C NMR (**3h**)



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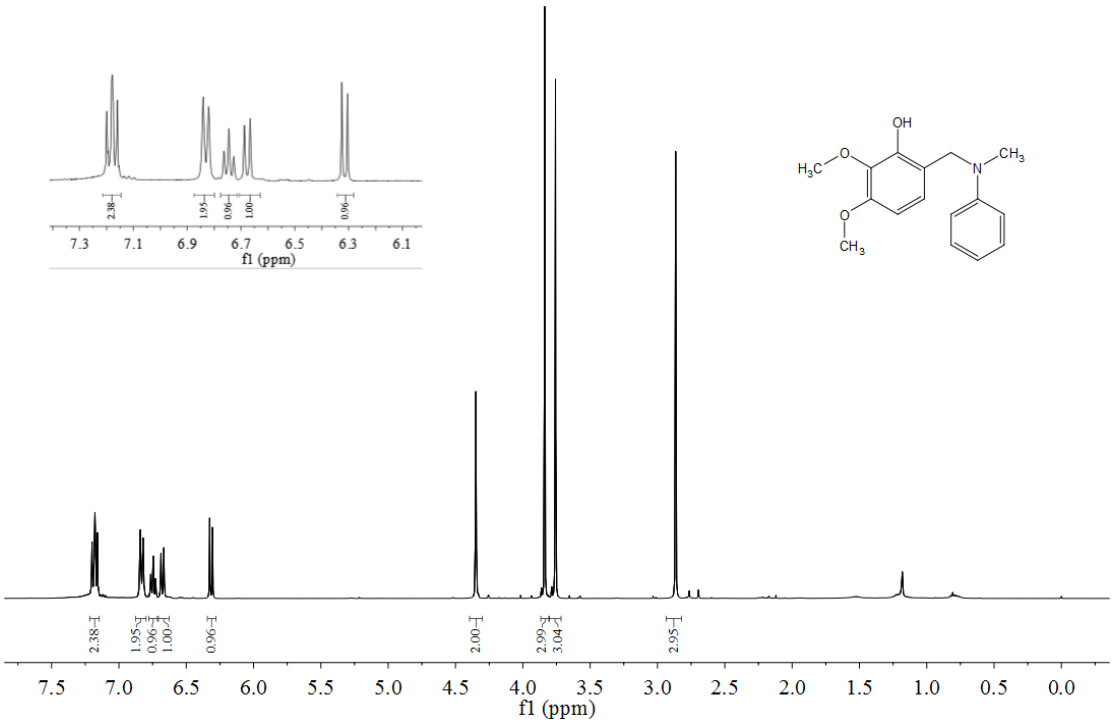

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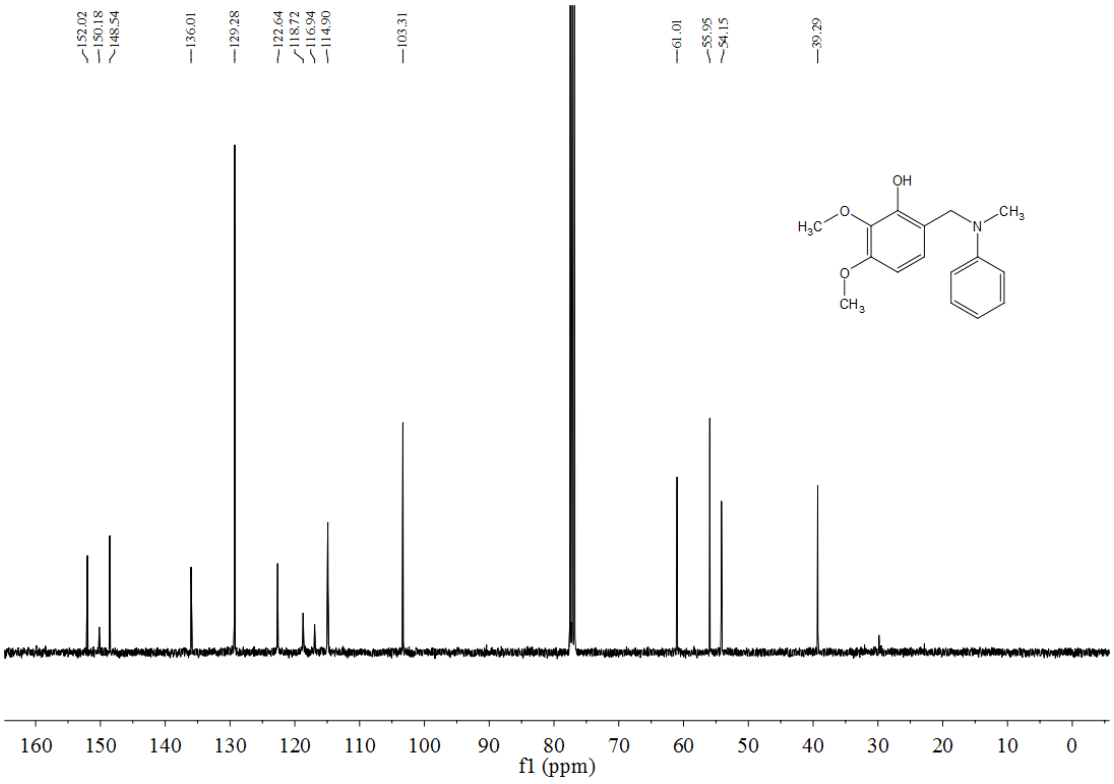

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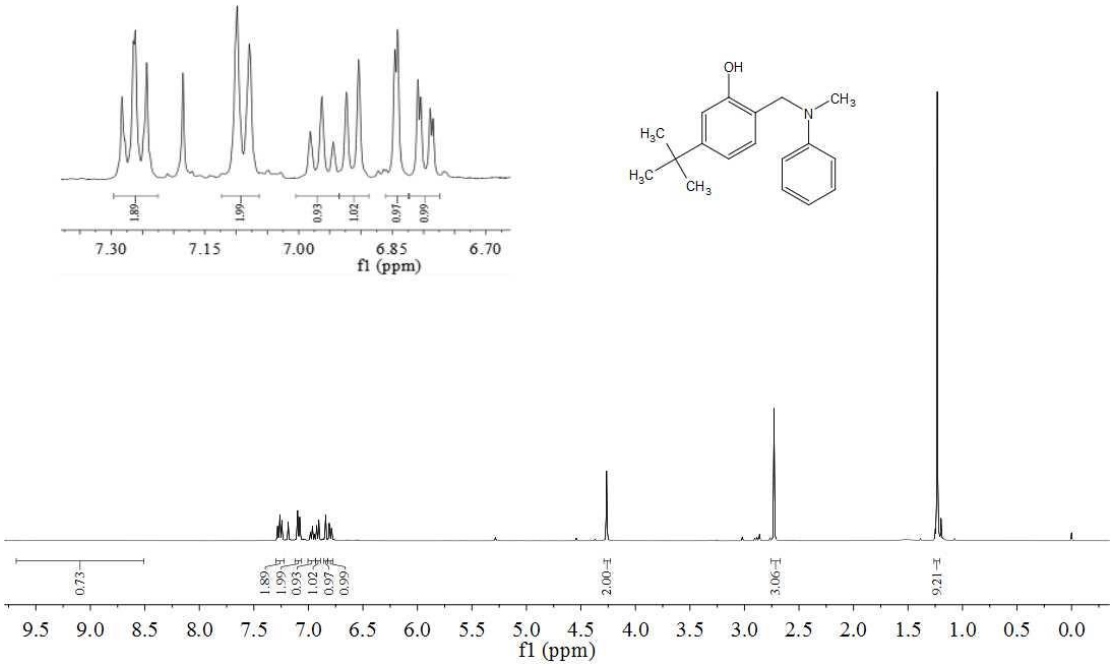

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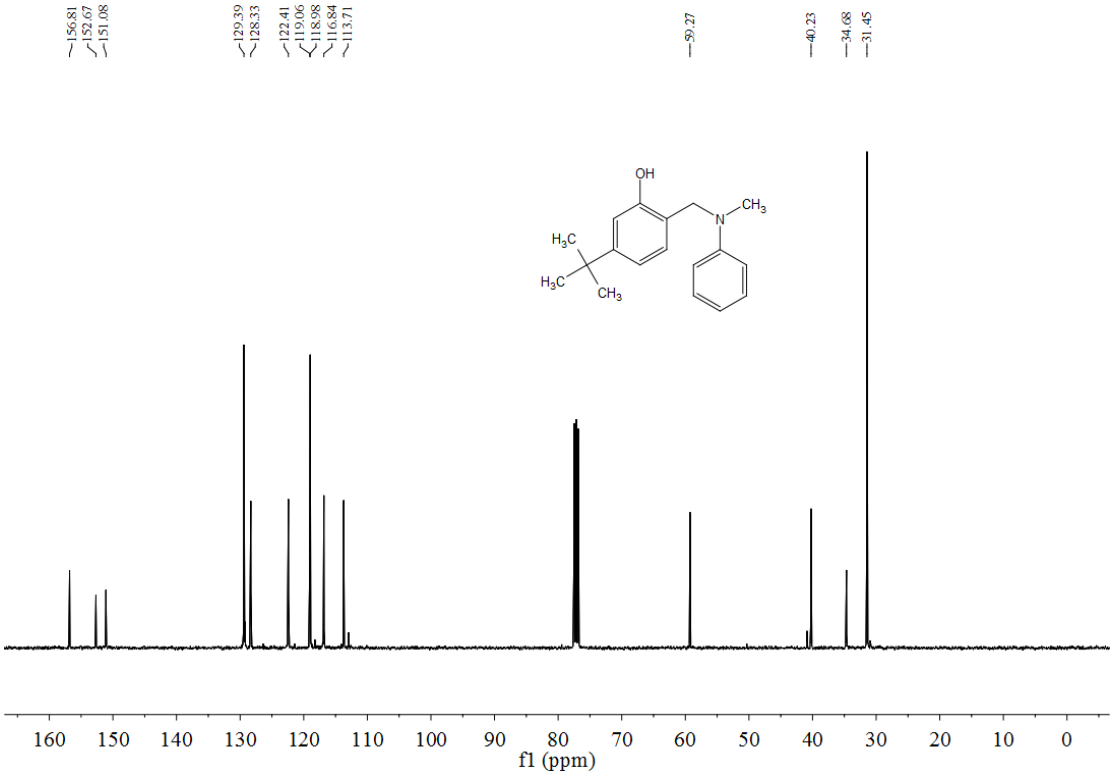

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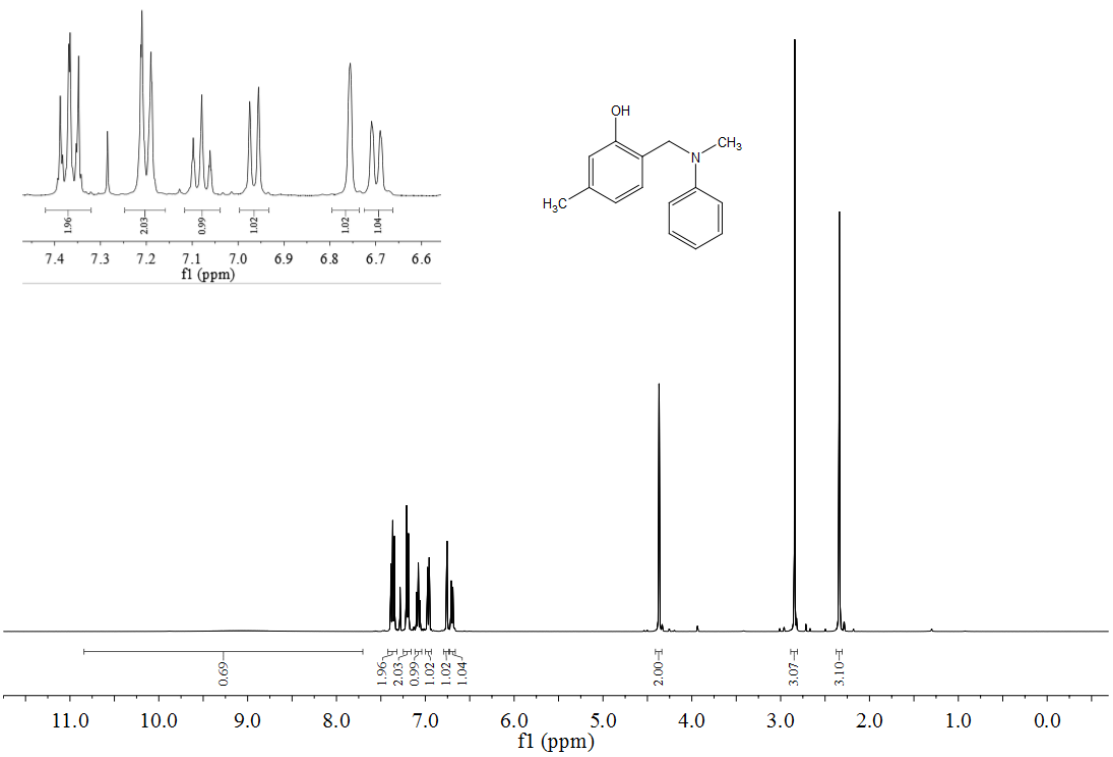
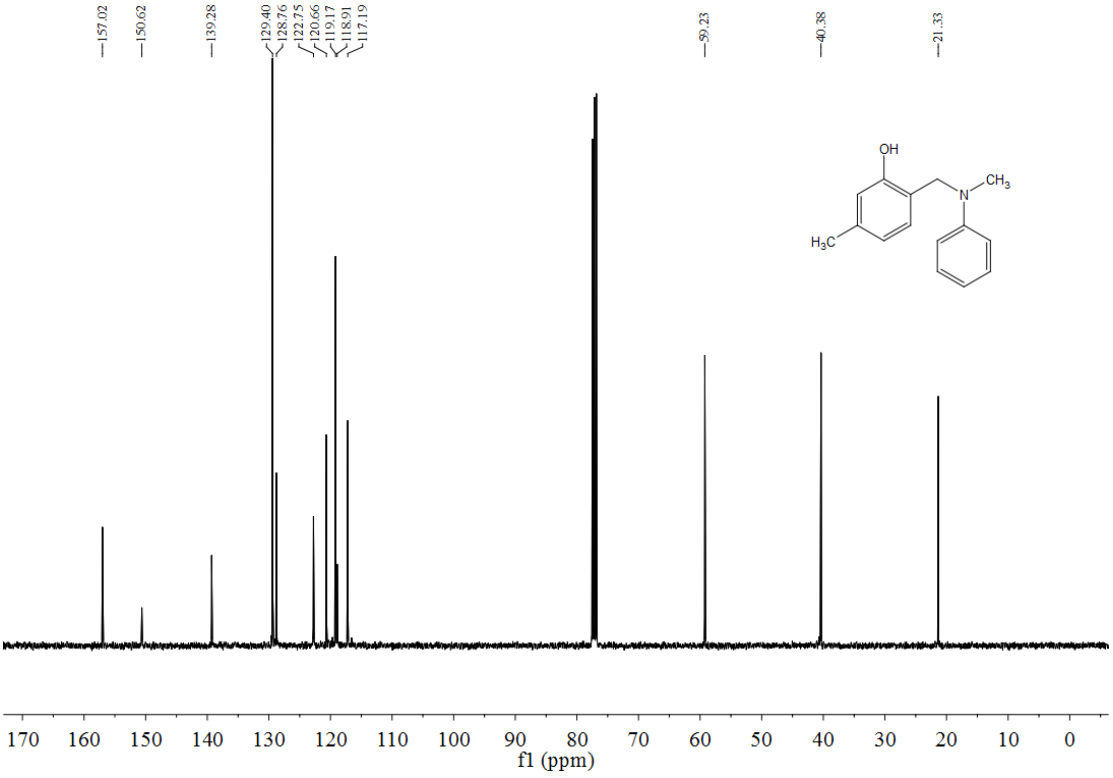
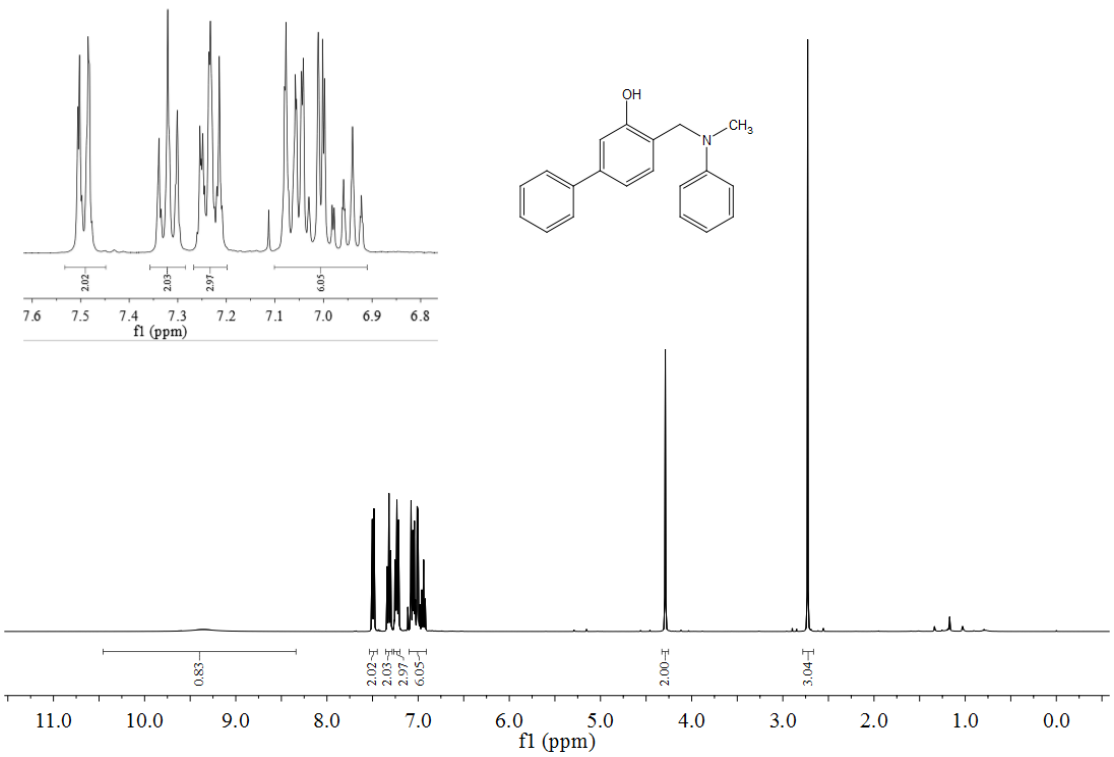


^{13}C NMR (**3k**)



^{1}H NMR (**3l**)



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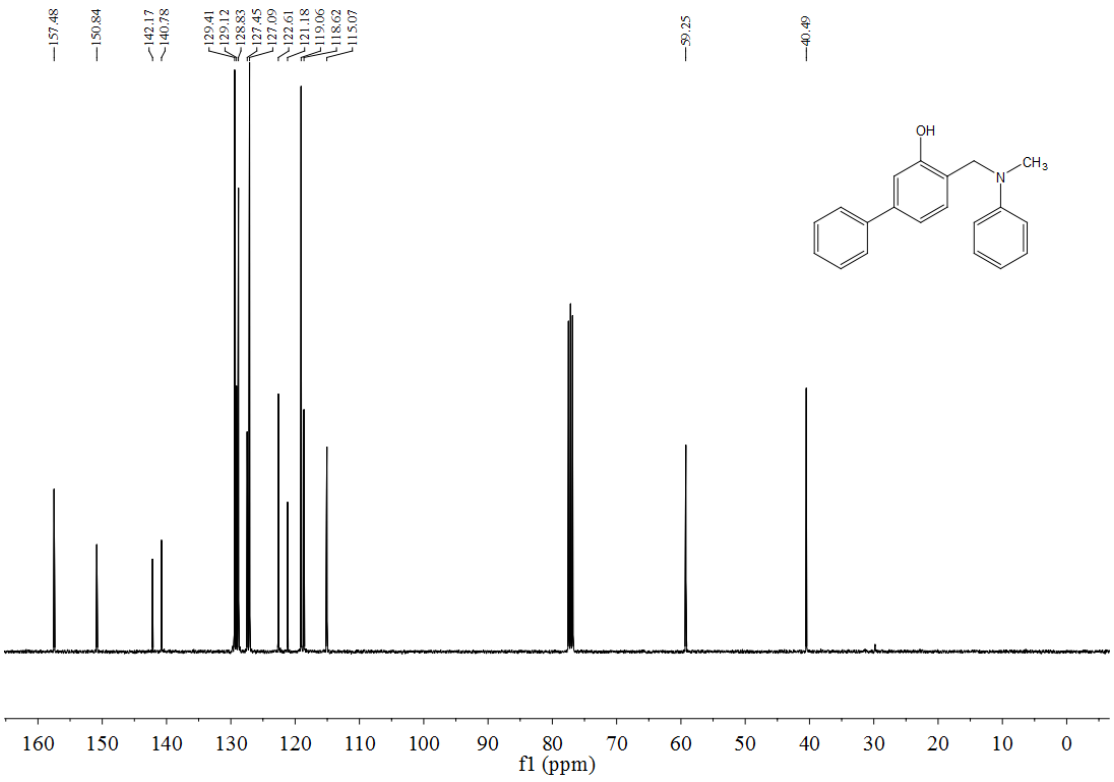

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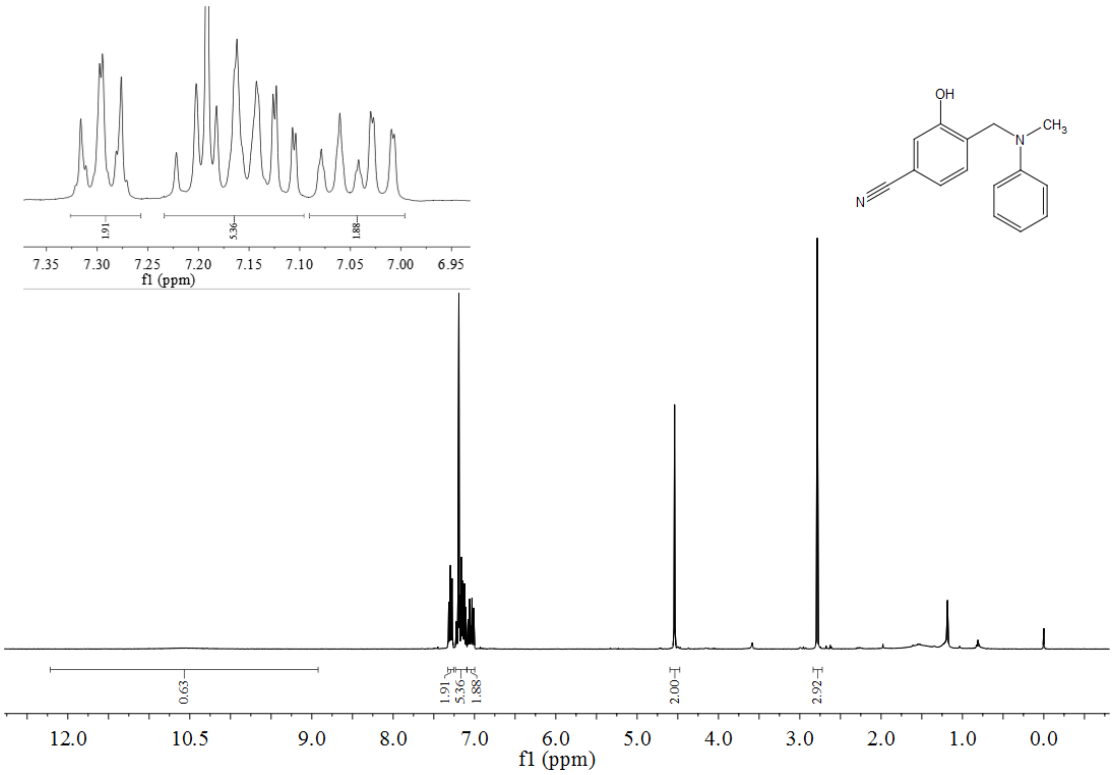

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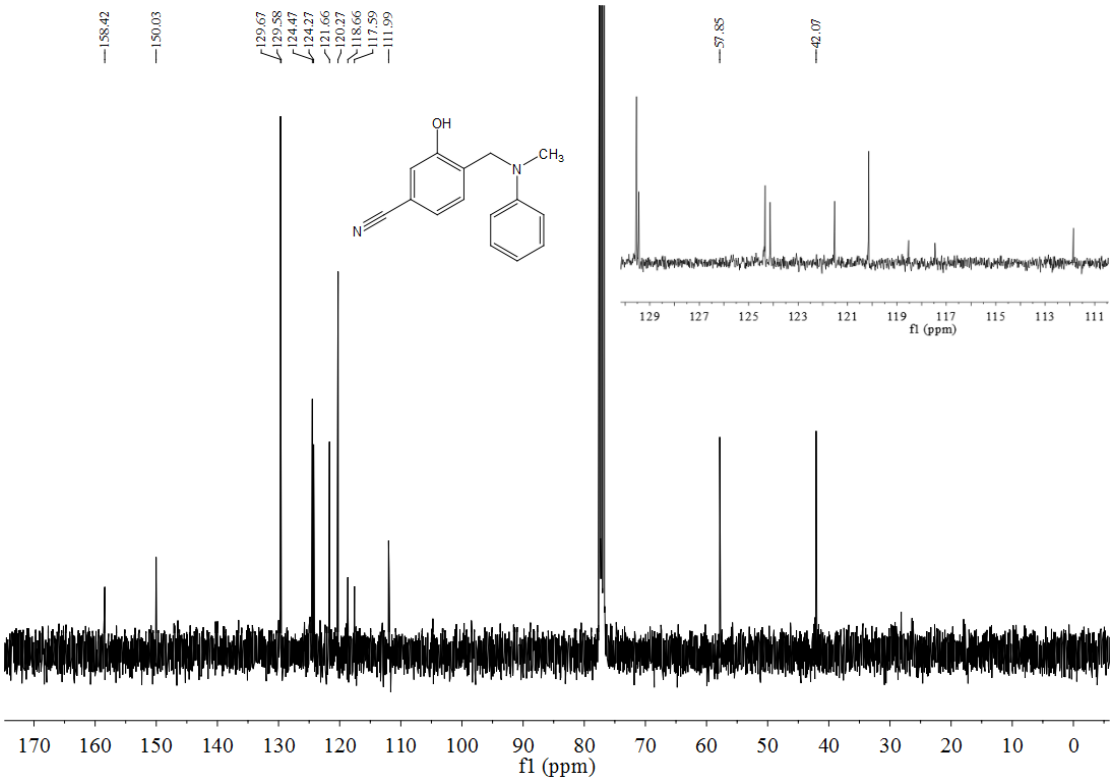
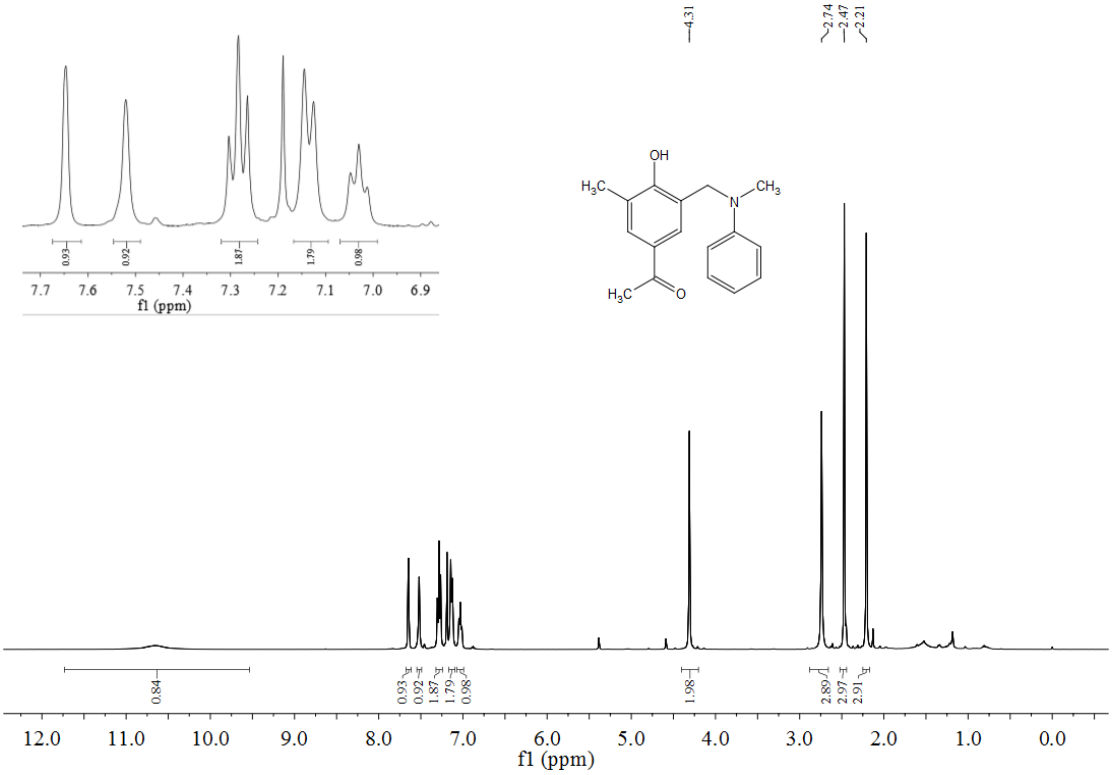
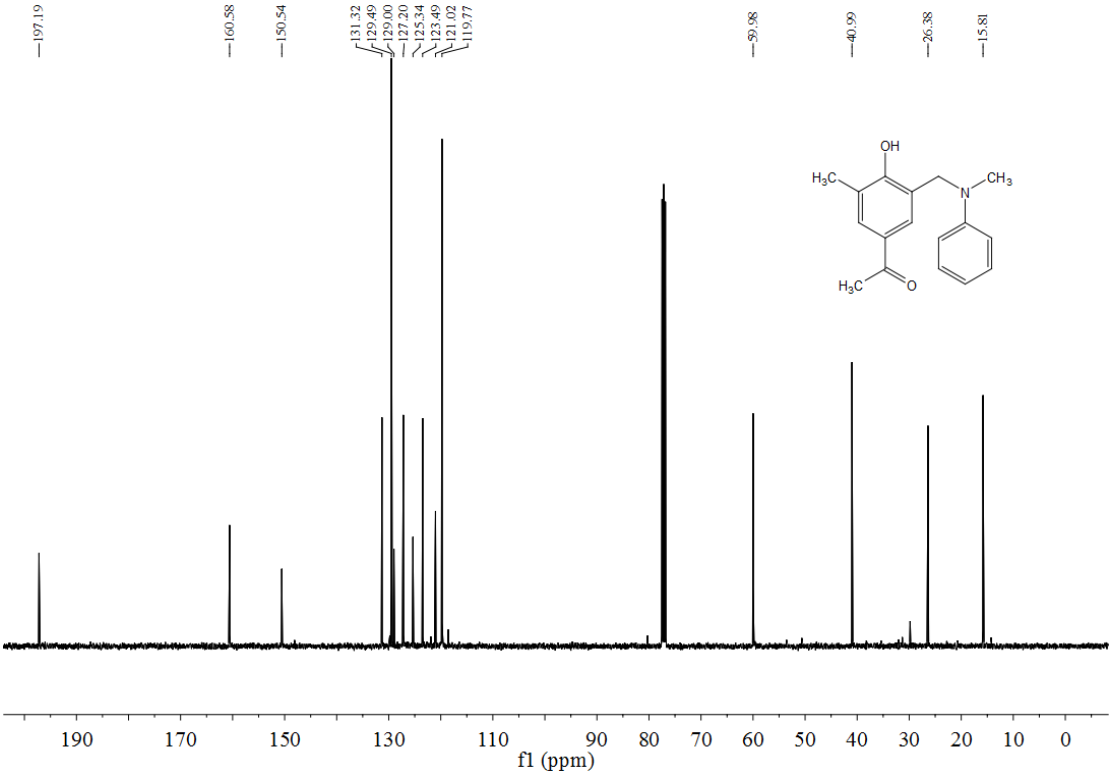


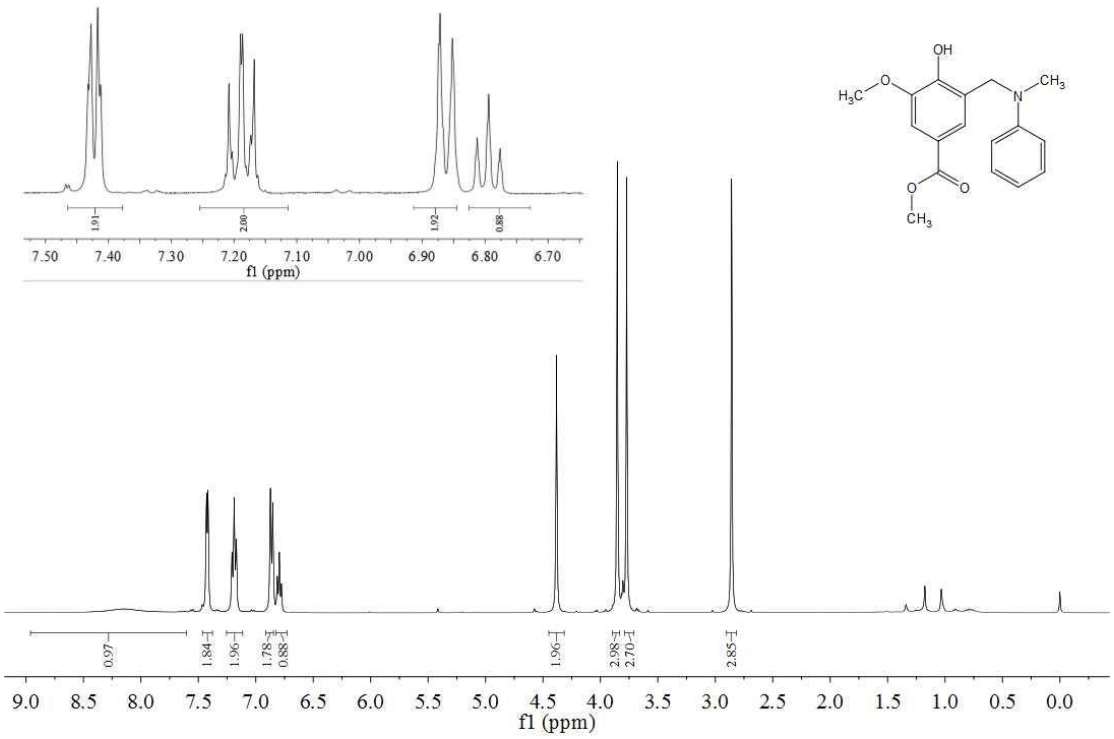
^{1}H NMR (**3n**)



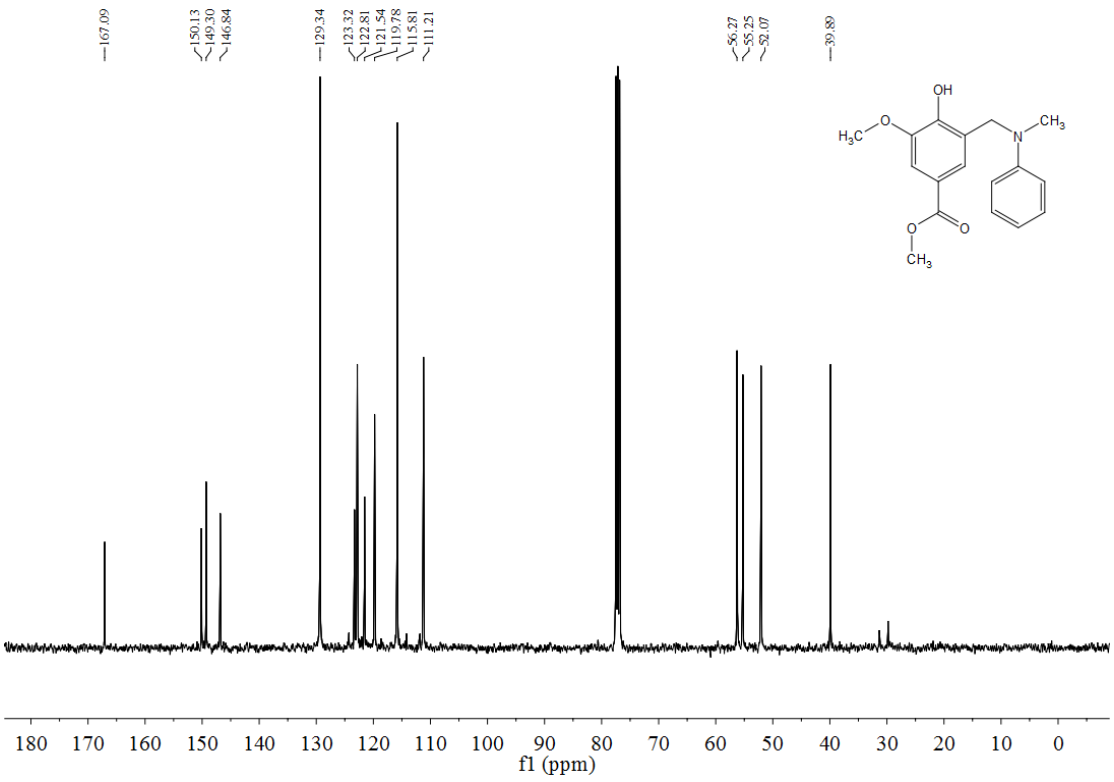
^{13}C NMR (**3n**)



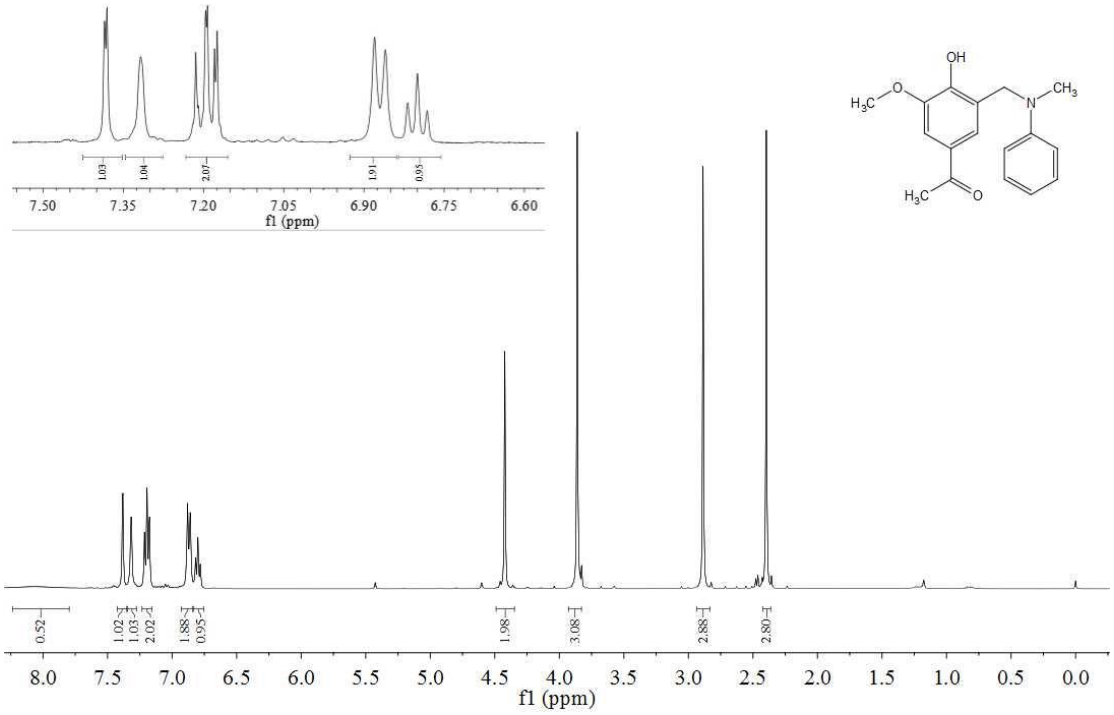
^{1}H NMR (**3o**)



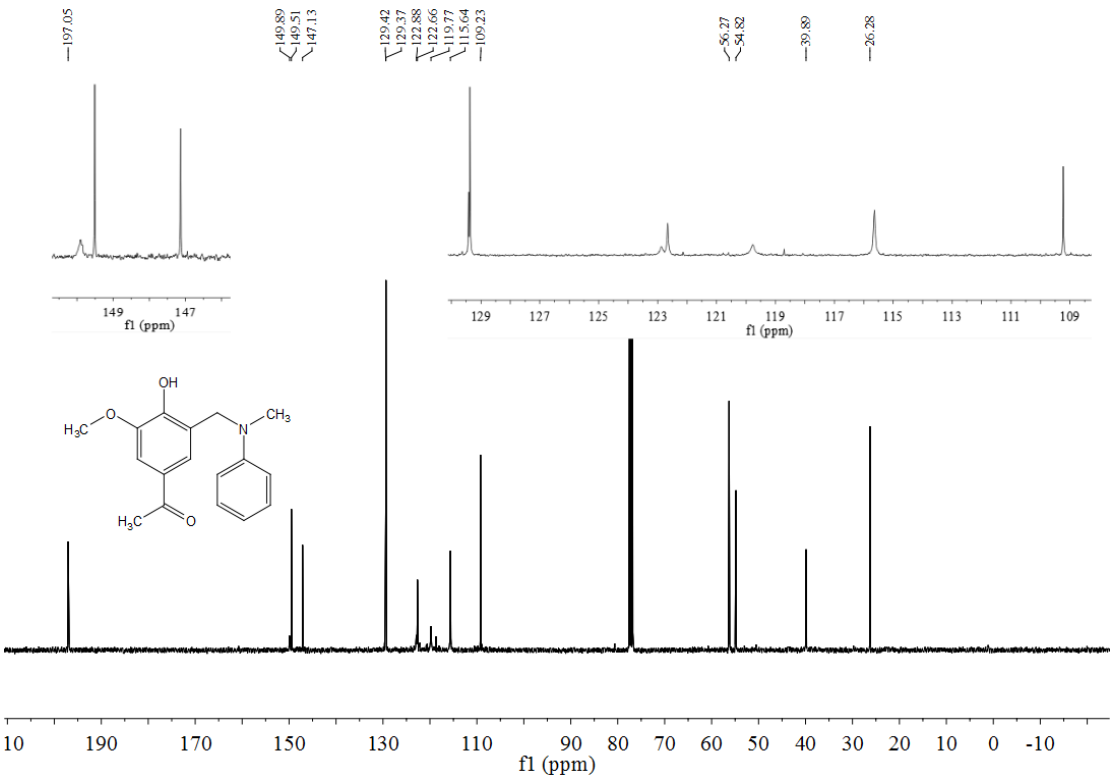
^{13}C NMR (**3o**)



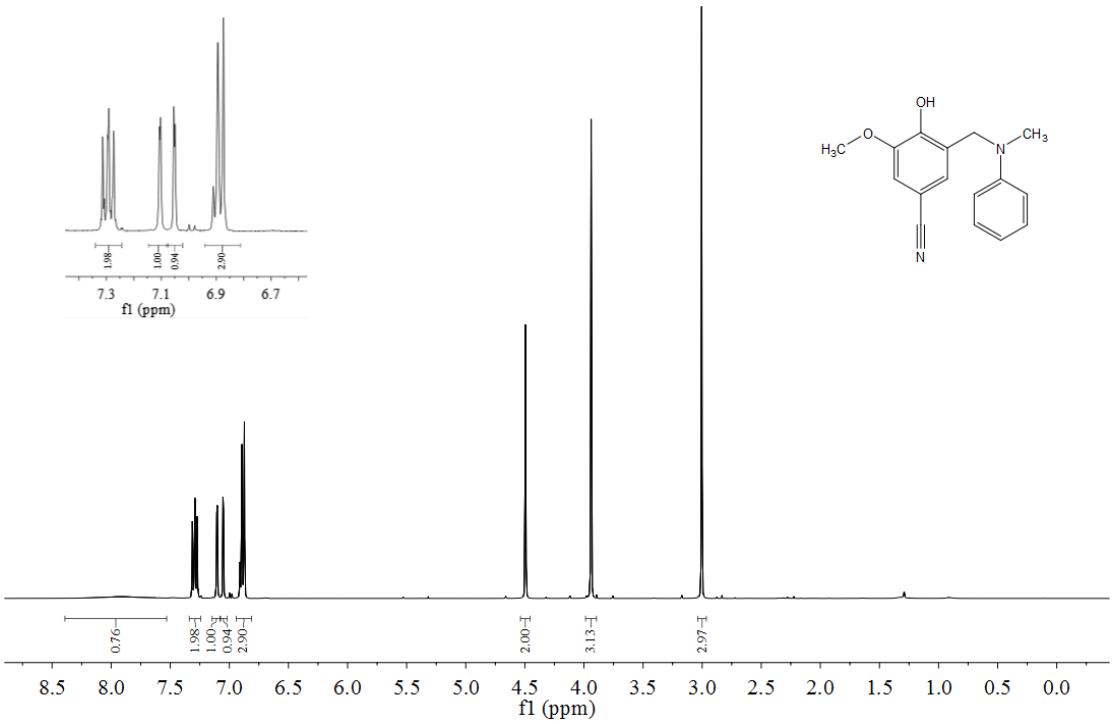
^{1}H NMR (**3p**)



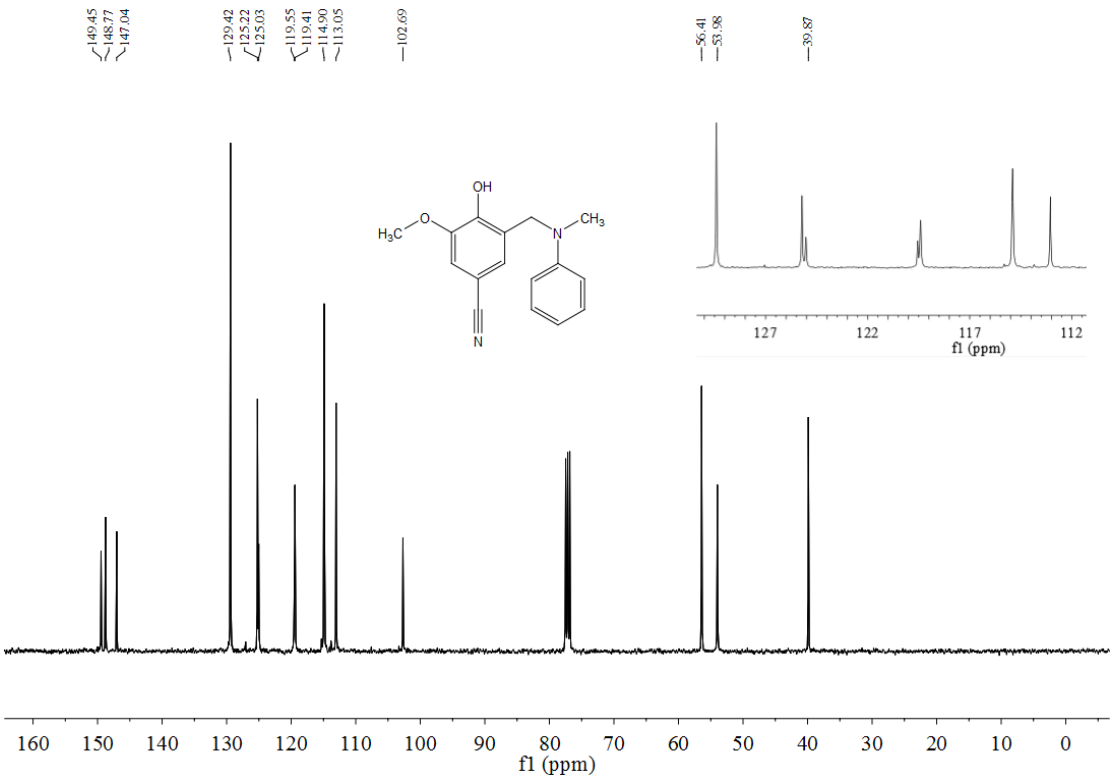
^{13}C NMR (**3p**)



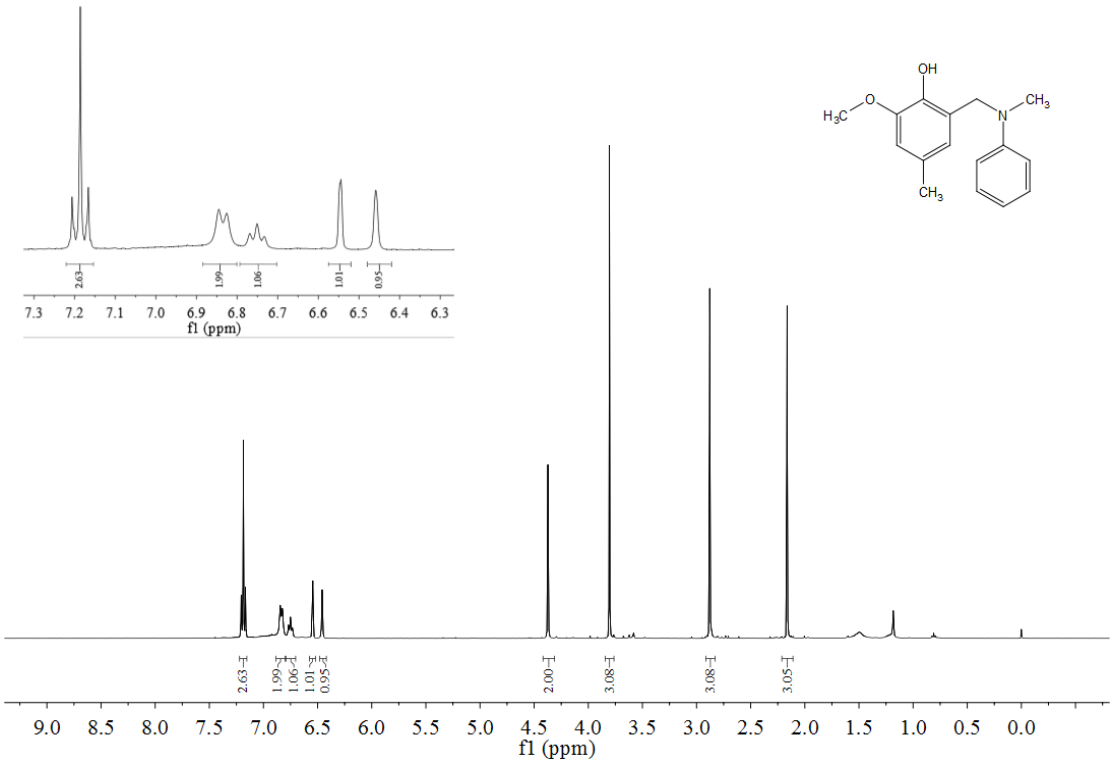
^{1}H NMR (**3q**)



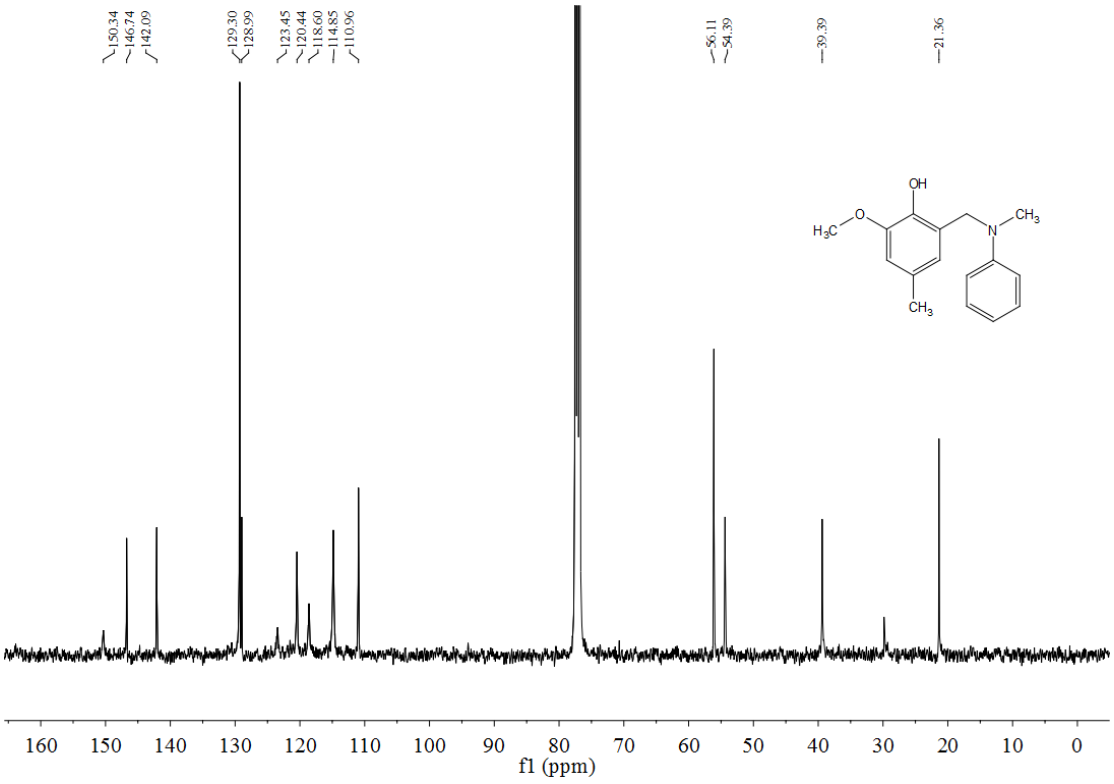
^{13}C NMR (**3q**)



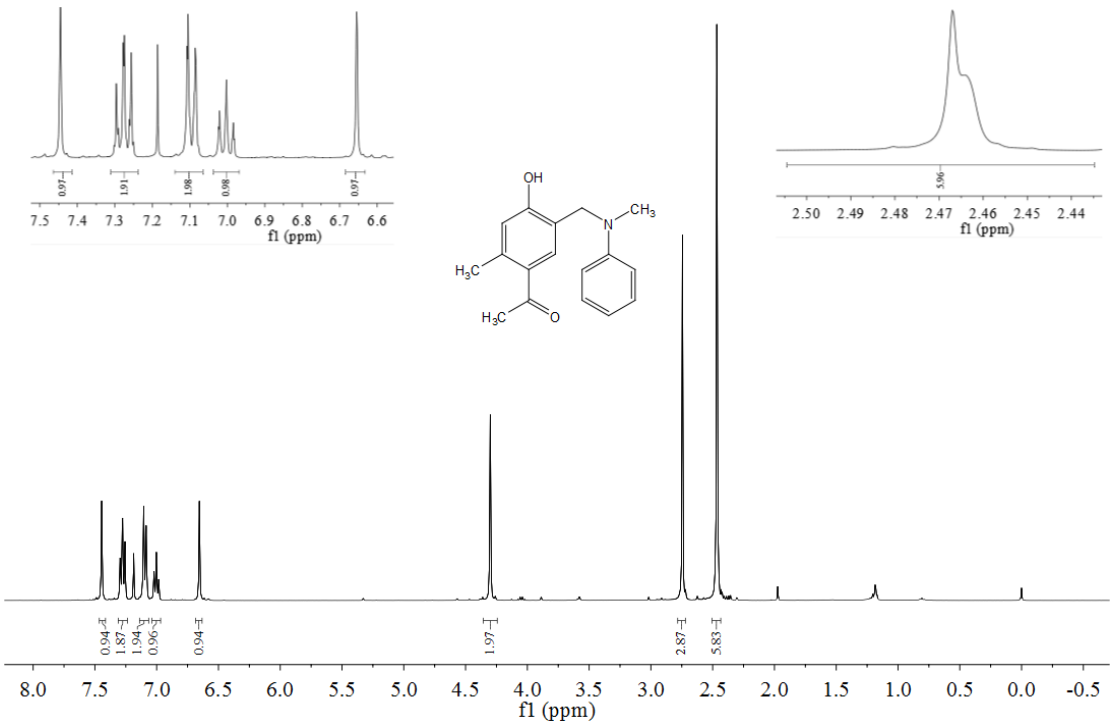
^{1}H NMR (**3r**)



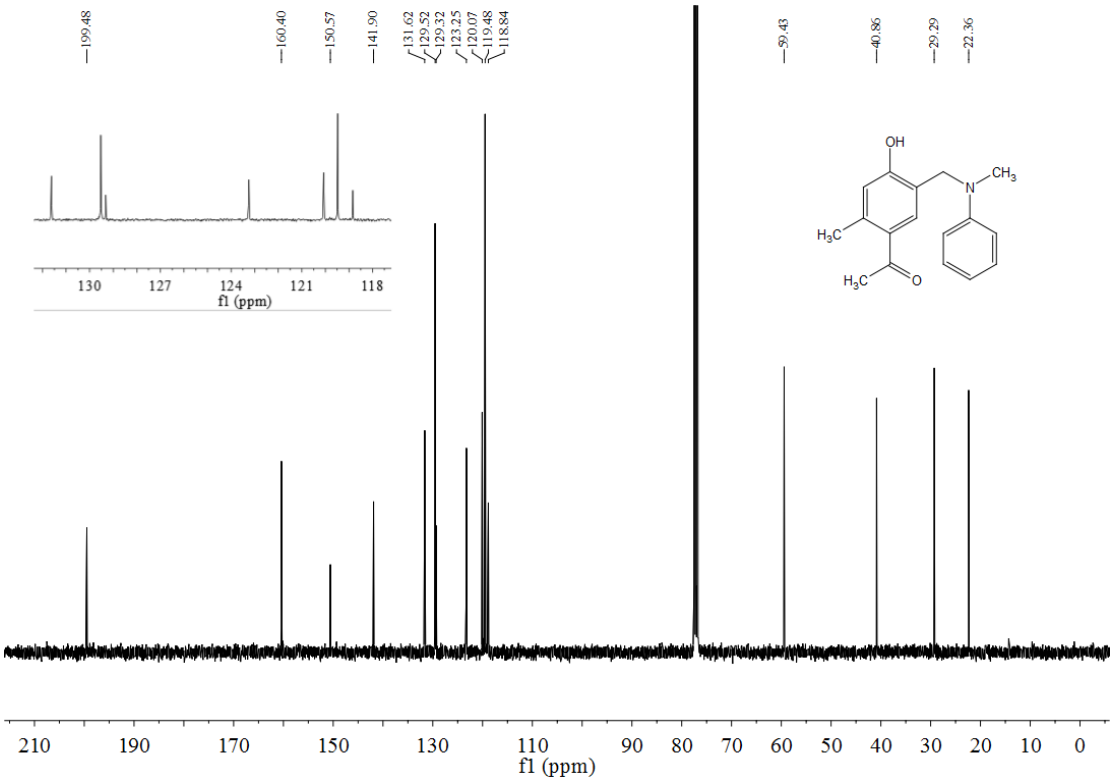
^{13}C NMR (**3r**)



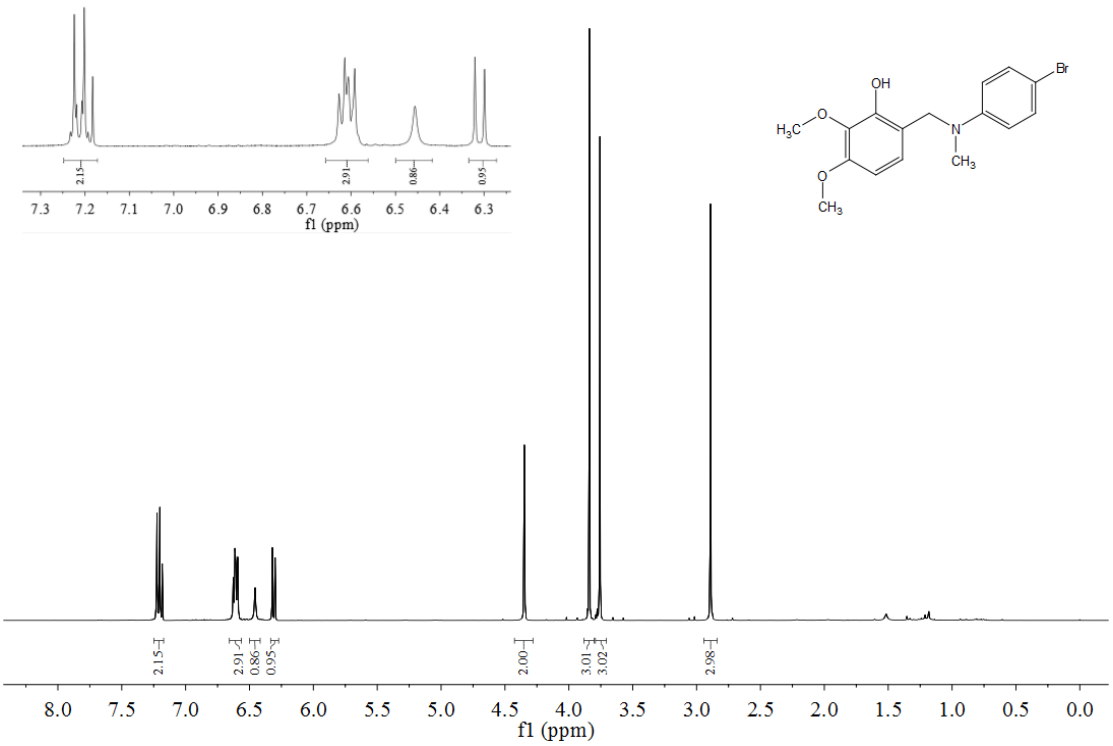
^{1}H NMR (**3s**)



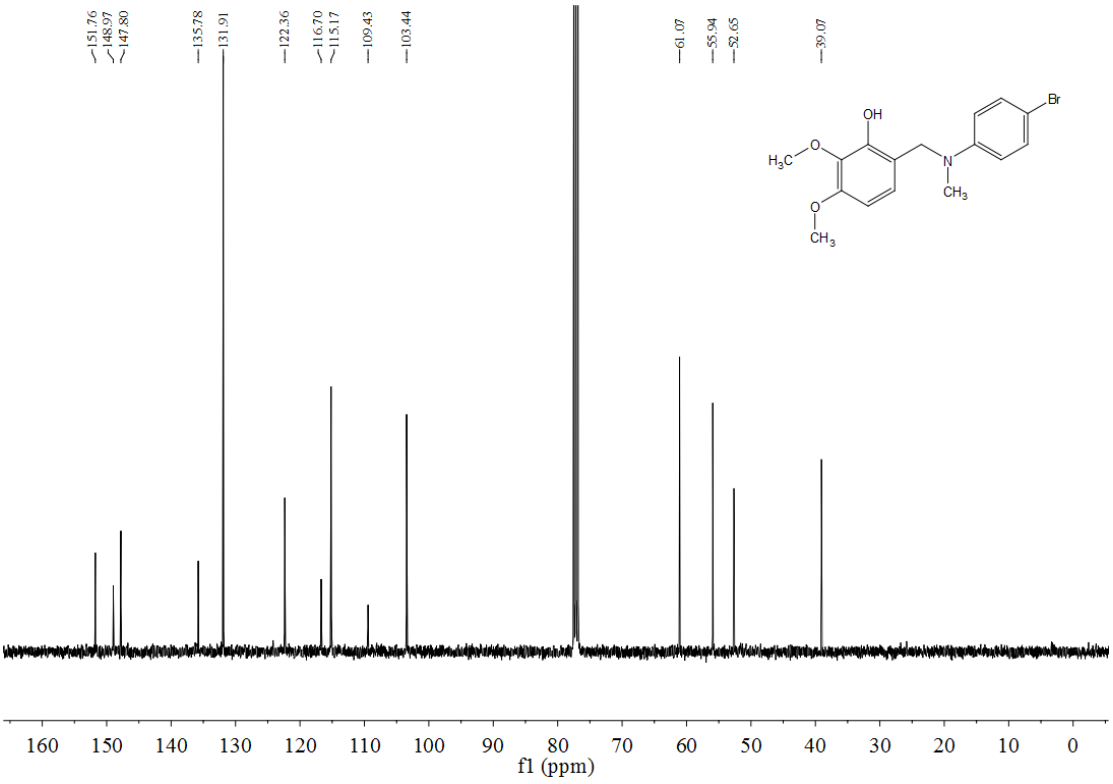
^{13}C NMR (**3s**)



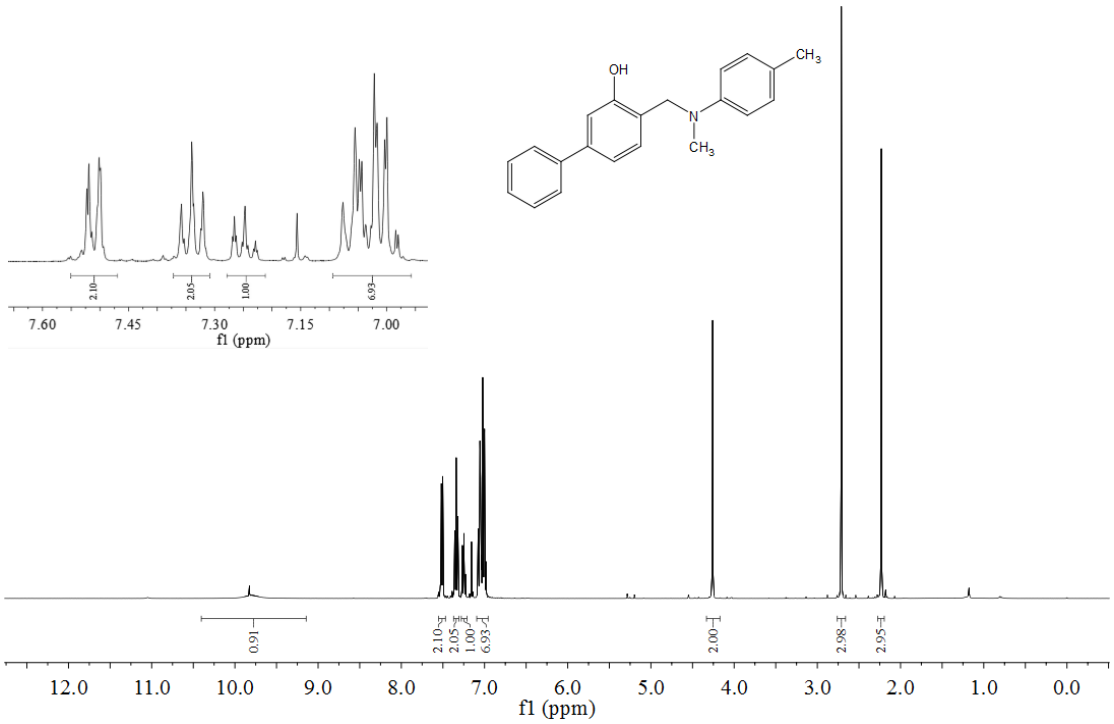
^{1}H NMR (**4a**)



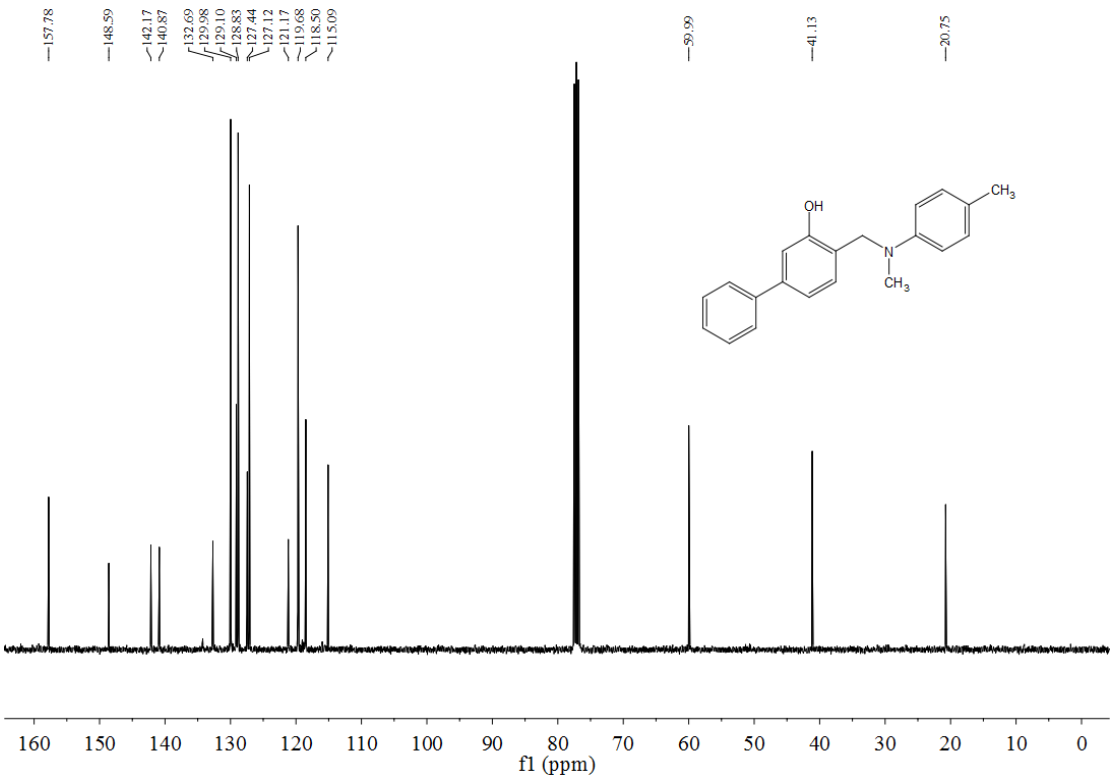
^{13}C NMR (**4a**)



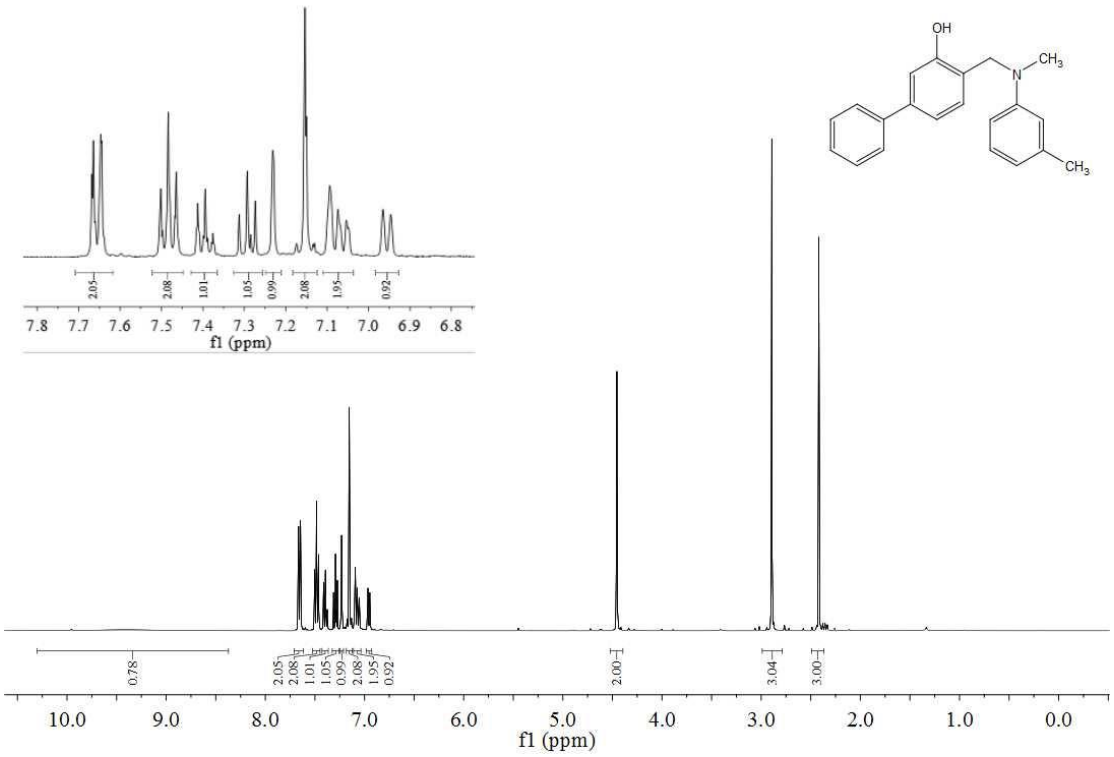
^{1}H NMR (**4b**)



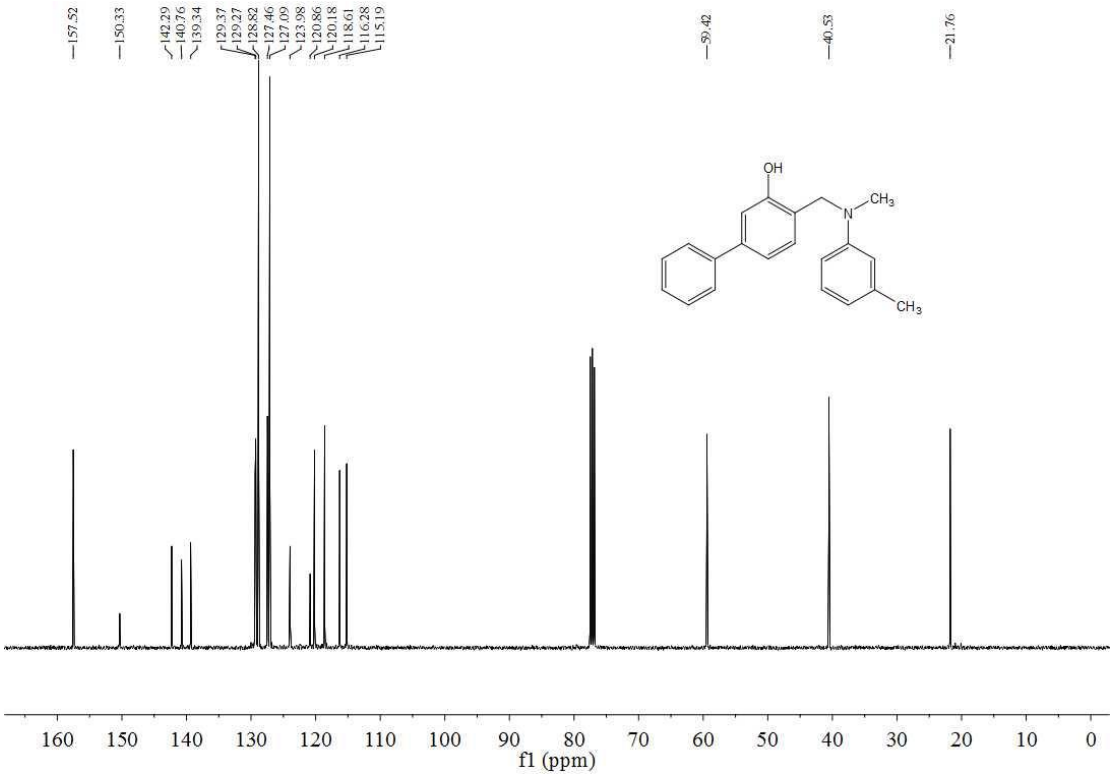
^{13}C NMR (**4b**)



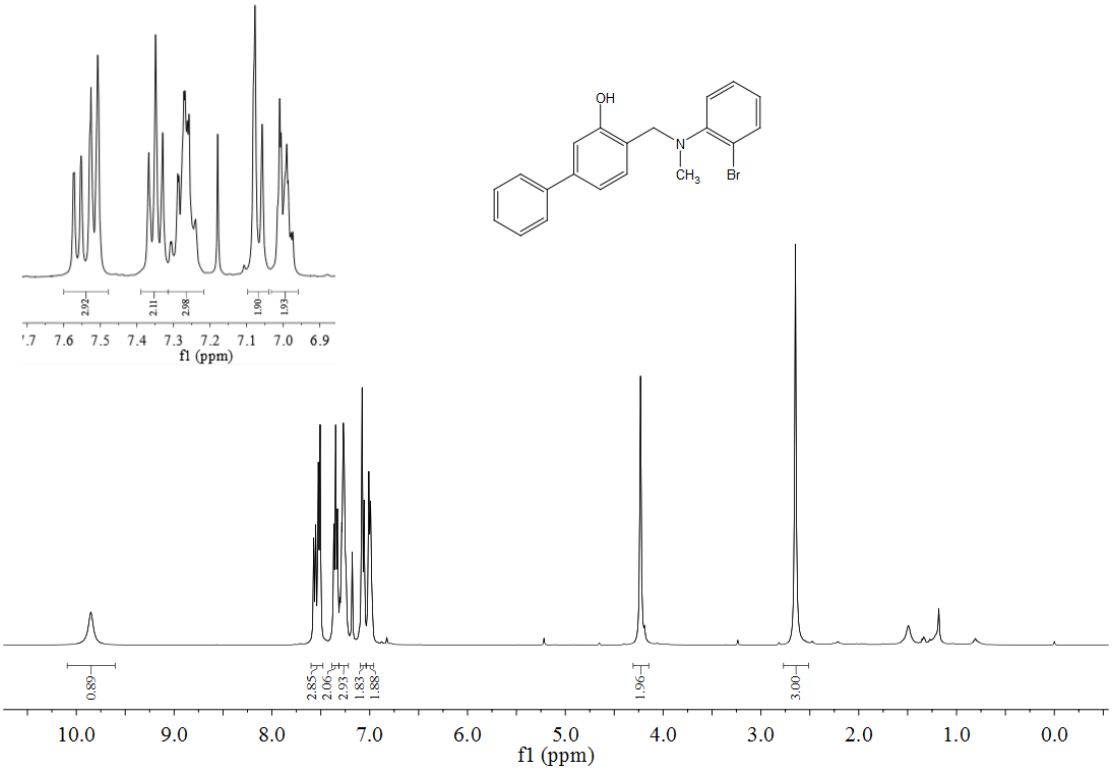
^{1}H NMR (**4c**)



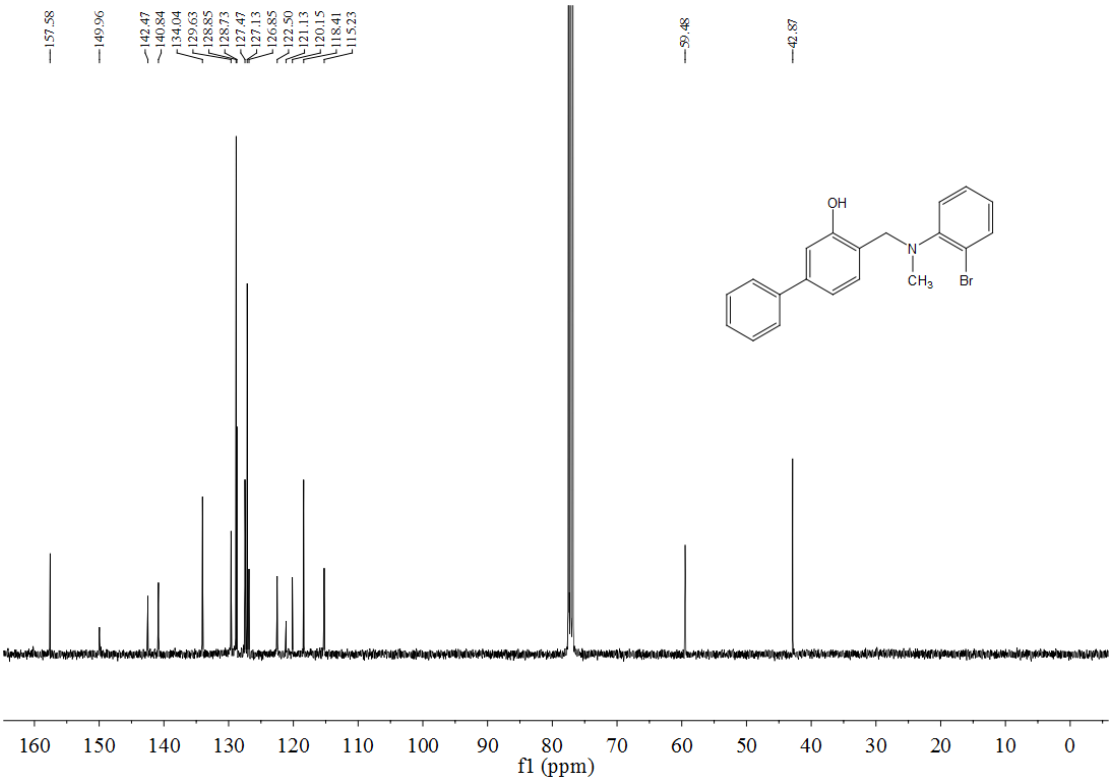
^{13}C NMR (**4c**)



^{1}H NMR (**4d**)



^{13}C NMR (**4d**)



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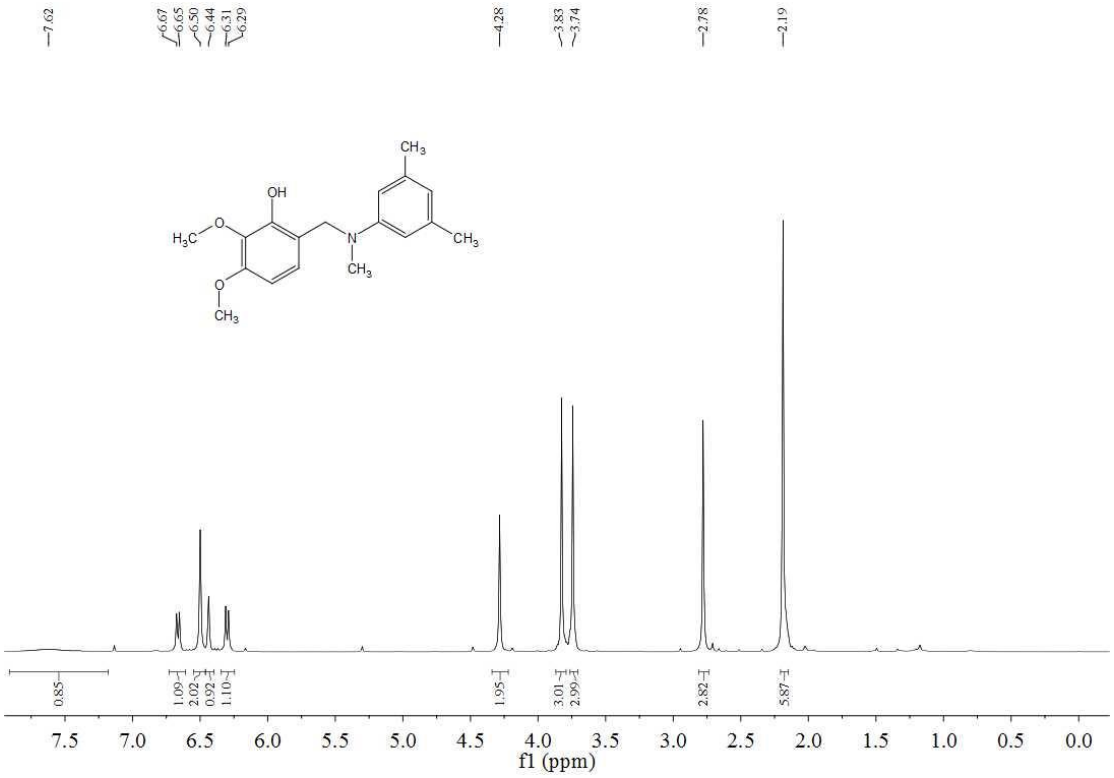
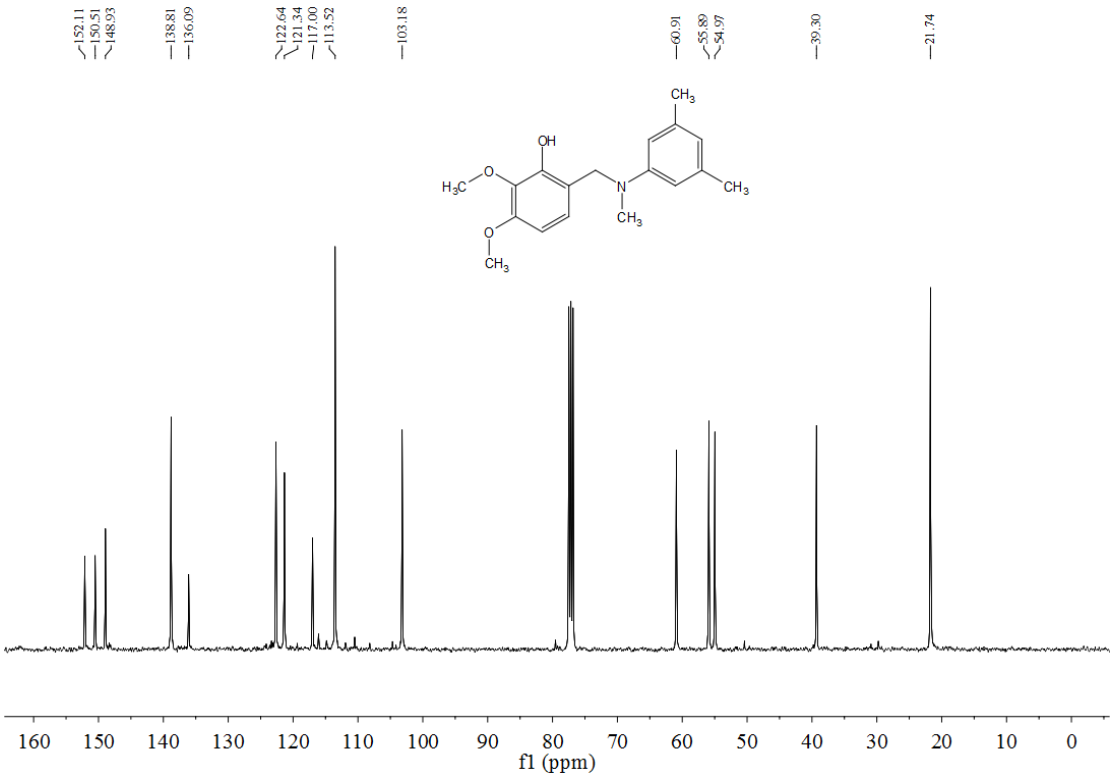
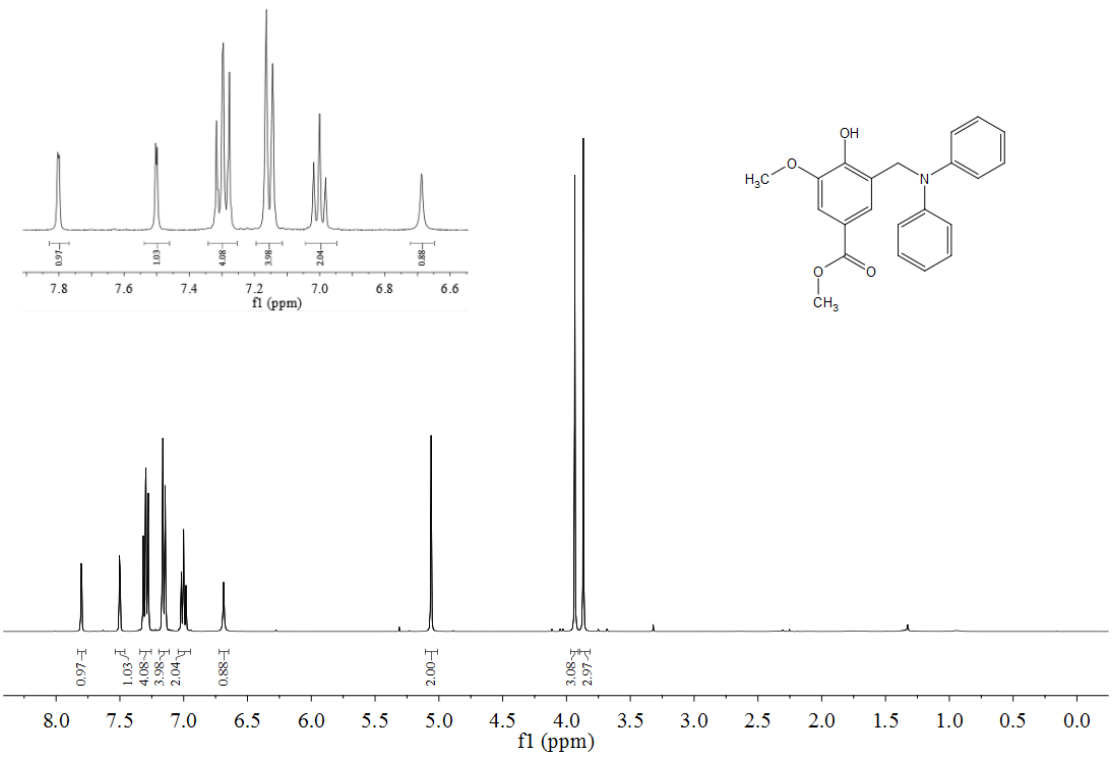


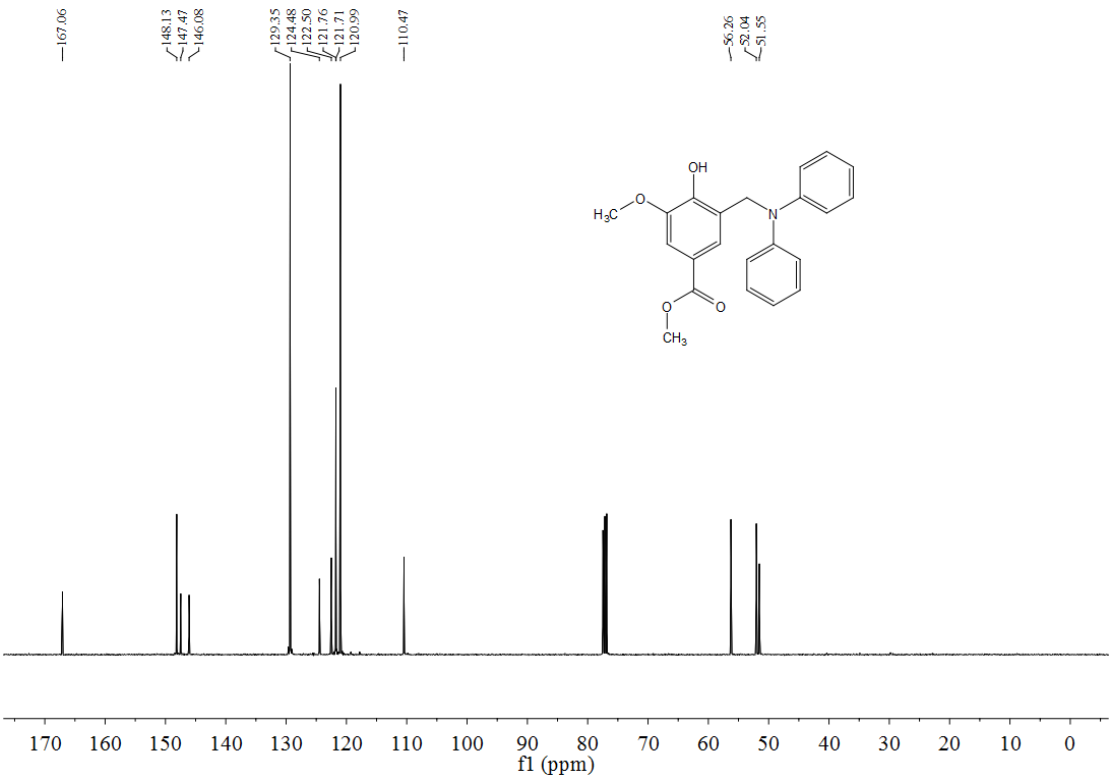
^{13}C NMR (**4e**)



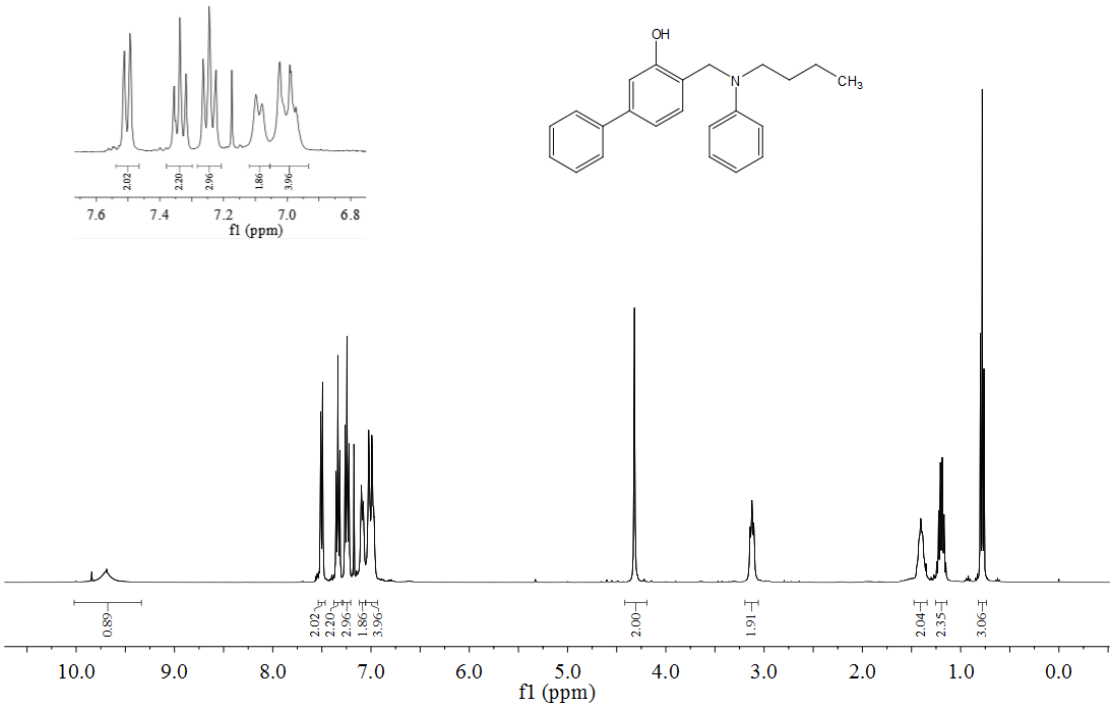
^{1}H NMR (**4f**)



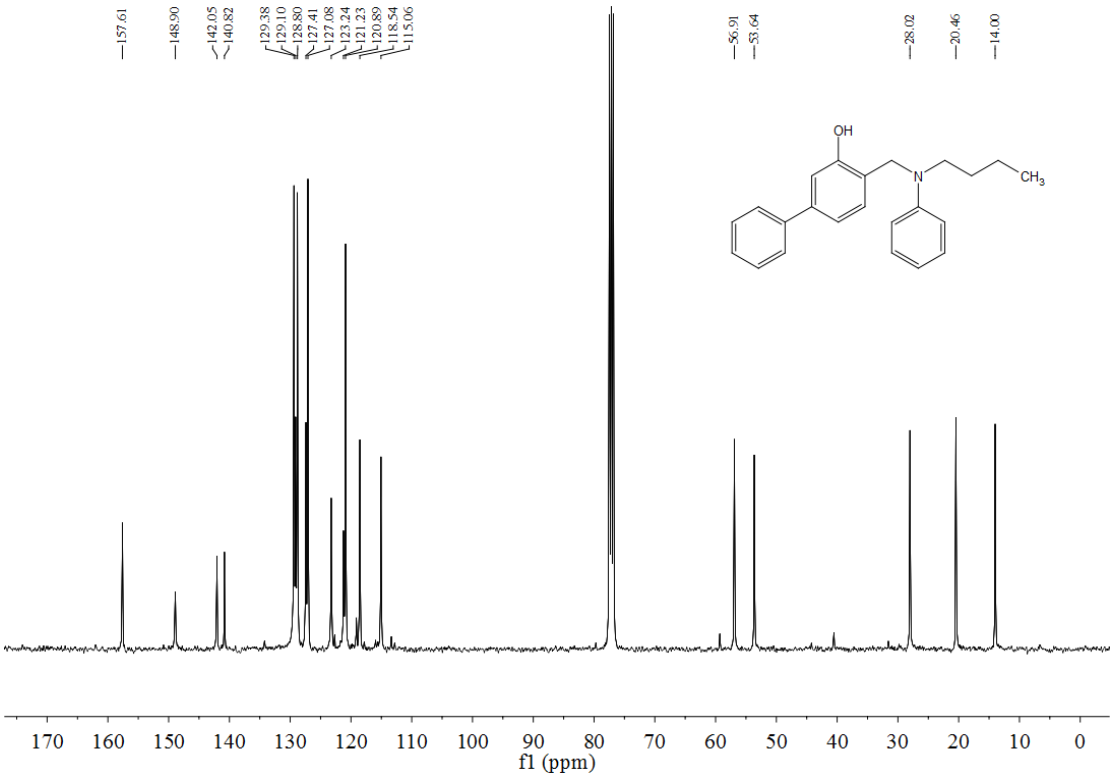
^{13}C NMR (**4f**)



^{1}H NMR (**4g**)



^{13}C NMR (**4g**)



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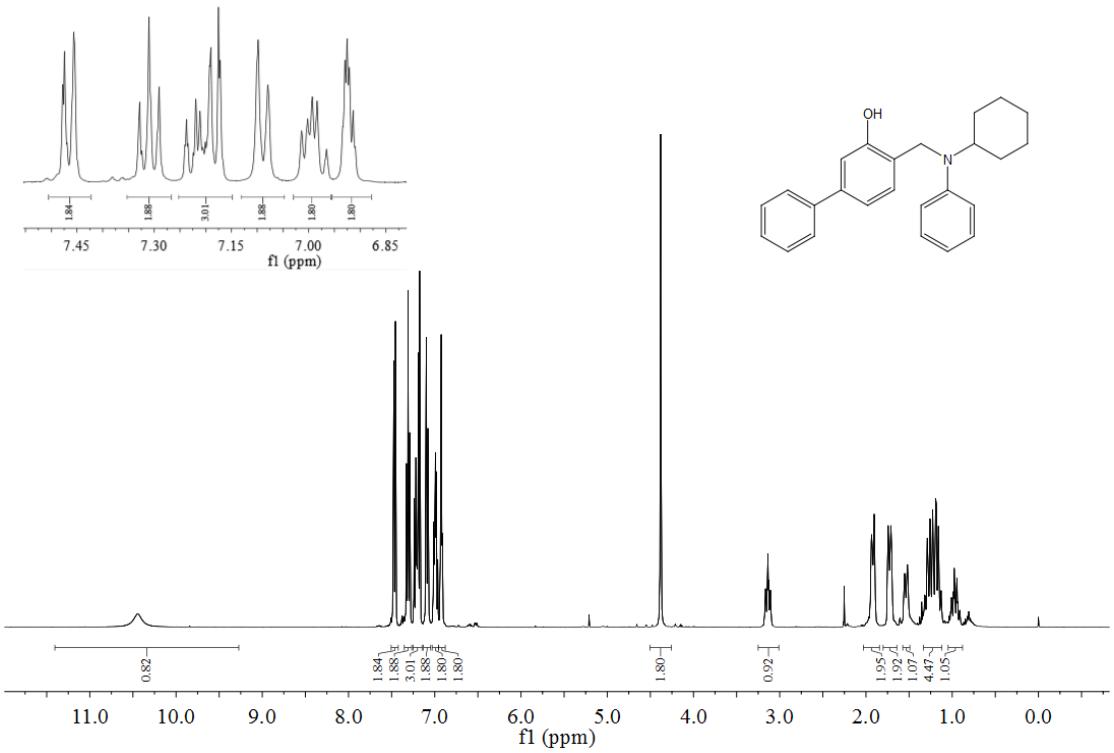
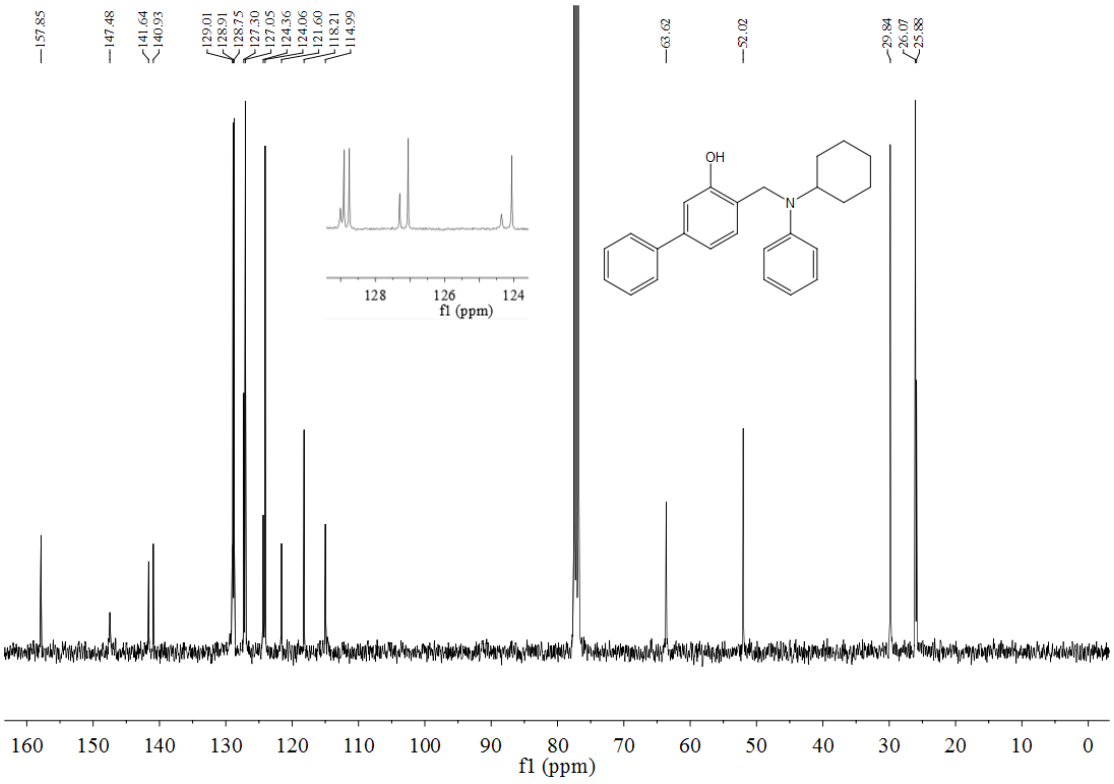
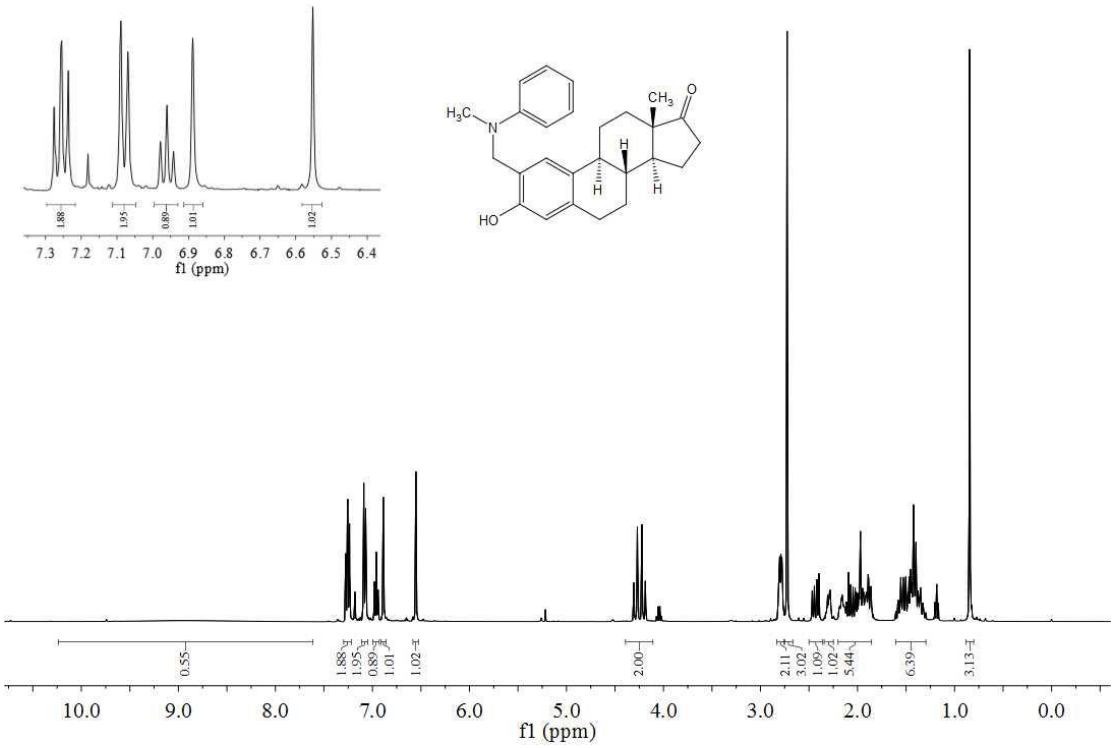


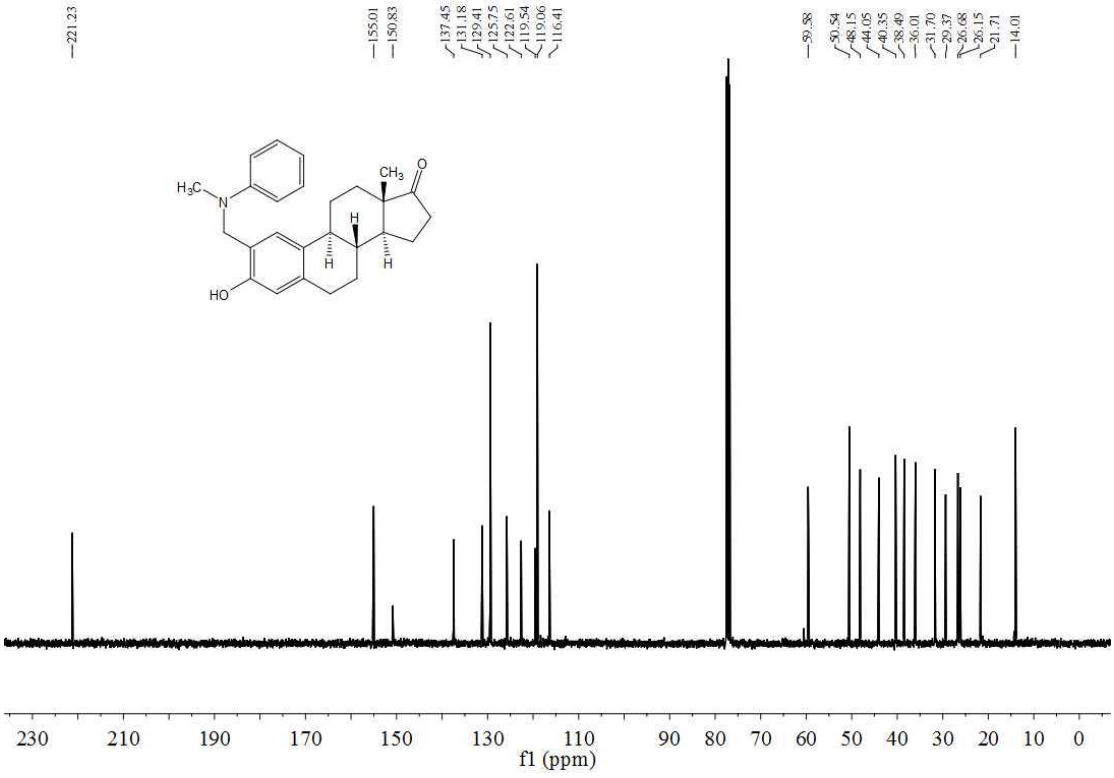
^{13}C NMR (**4h**)



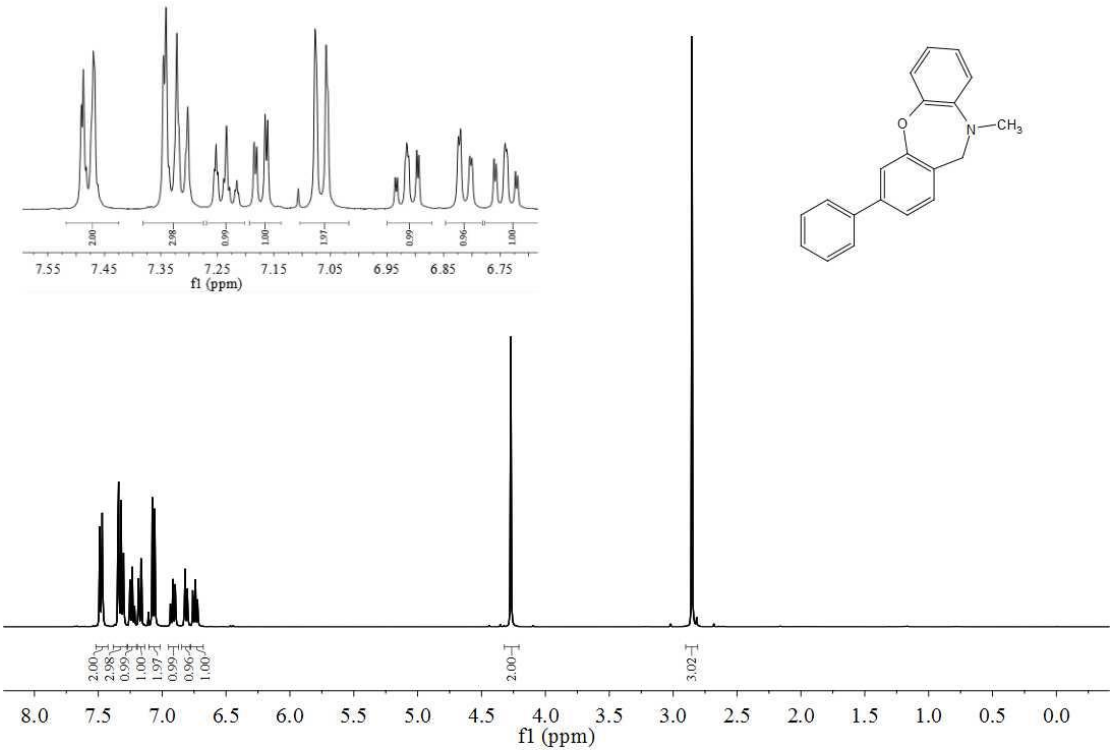
^{1}H NMR (**3u**)



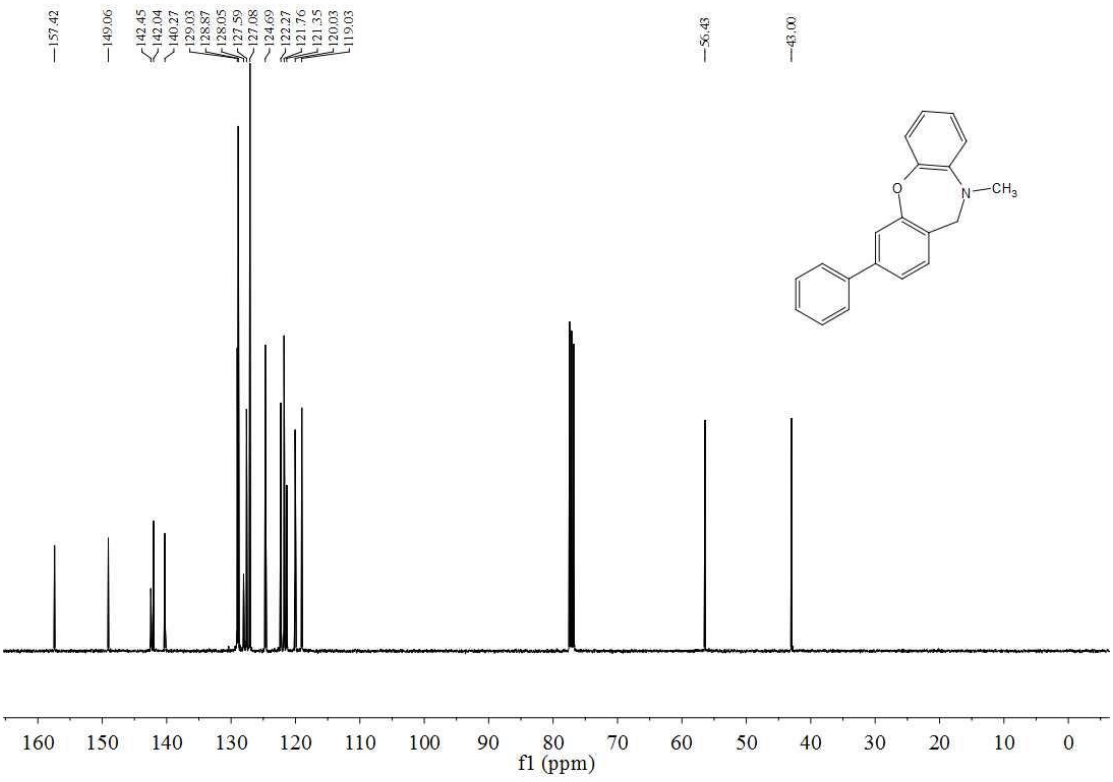
^{13}C NMR (**3u**)



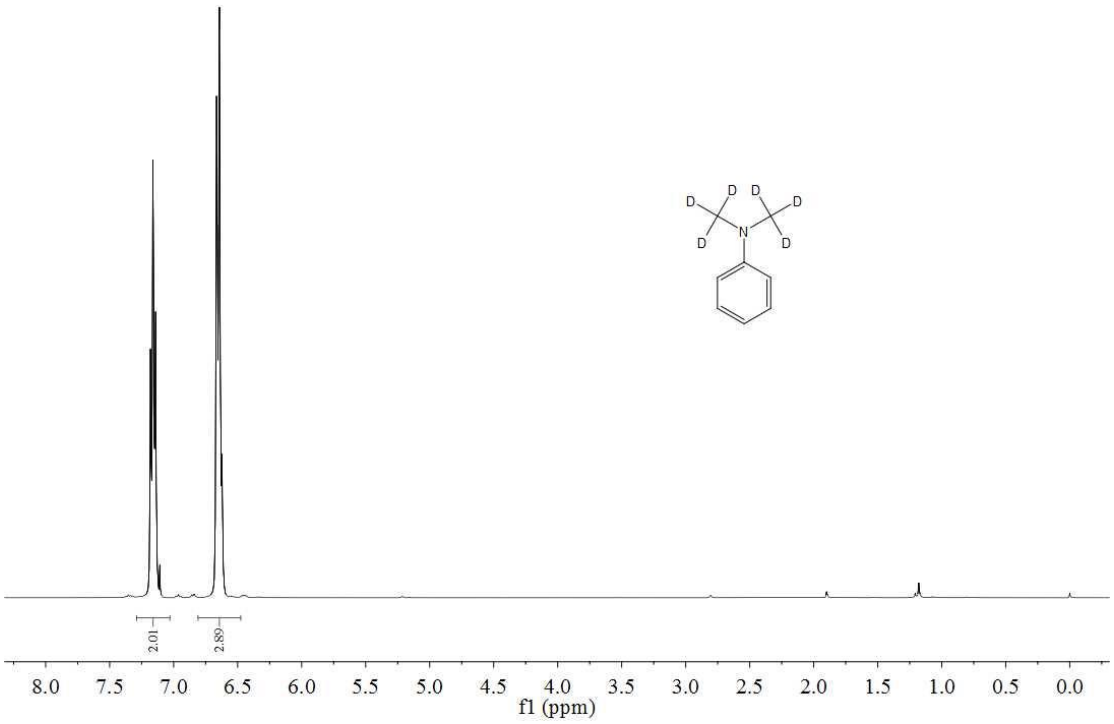
^{1}H NMR (**5**)



^{13}C NMR (**5**)



^{1}H NMR (**[D_6]-2a**)


D
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D
D
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4.5
4.0
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3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)