# Selective Oxidative Homo- and Cross-Coupling of Phenols with Aerobic Catalysts

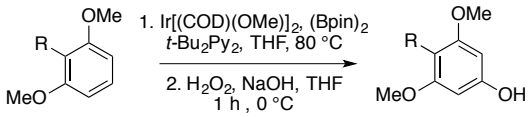
Young Eun Lee, Trung Cao, Carilyn Torruellas, Marisa C. Kozlowski*

Department of Chemistry, Roy and Diana Vagelos Laboratories, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States.
marisa@sas.upenn.edu

**General Considerations**: Unless otherwise noted, all non-aqueous reactions were carried out under an atmosphere of dry $N_2$ in dried glassware. When necessary, solvents and reagents were dried prior to use. THF was distilled from sodium benzophenone ketyl. $CH_3CN$, $CH_2Cl_2$, TMEDA, and toluene were distilled from $CaH_2$. 2-Ethyl-1,3-dimethoxybenzene was prepared following the literature protocols.[1] High throughput experimentation was performed at the Penn/Merck High Throughput Experimentation Laboratory at the University of Pennsylvania. The screens were analyzed by HPLC with addition of an internal standard.

Analytical thin layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica-gel 254-F plates. Visualization was accomplished with UV light. Chromatography was performed using a forced flow of the indicated solvent system on EM Reagents Silica Gel 60 (230-400 mesh). When necessary, the column was pre-washed with 1% $Et_3N$ in the eluent system. $^1H$ NMR spectra were recorded on Bruker AM-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane (0 ppm) or from the solvent resonance ($CDCl_3$ 7.26 ppm, THF-$d_8$ 3.58 ppm, acetone-$d_6$ 2.05 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants, and number of protons. Decoupled $^{13}C$ NMR spectra were recorded on Bruker AM-500 (125 MHz) spectrometer. IR spectra were taken on a Perkin-Elmer FT-IR spectrometer using a thin film on NaCl plate. Mass spectra were obtained on a low resolution Micromass Platform LC in electrospray mode and high resolution VG autospec with an ionization mode of either CI or ES. Melting points were obtained on Thomas Scientific Unimelt apparatus and are corrected.

**Preparation of Phenol Substrates**[2]



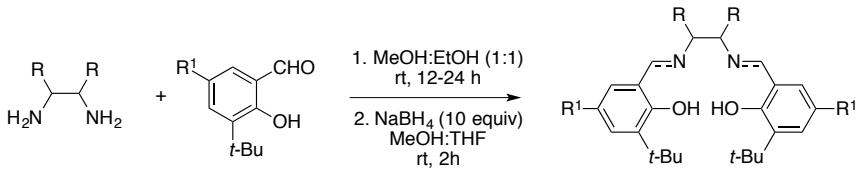

Dimethoxybenzene (3 mmol), $[Ir(COD)(OMe)]_2$ (2 mol% Ir), 4,4´-di-tert-butyl-2,2´-bipyridine (2 mol%), $B_2Pin_2$ (1 equiv), and THF (20 mL) were added to a reaction vessel equipped with a vacuum valve. The reaction vessel was sealed and stirred at 80 °C under Argon for 40 h. The reaction mixture was then cooled to room temperature, and the solvent was removed under vacuum. The arylboronate ester was dried under vacuum for 2 h.

The unpurified arylboronate ester was added to a solution of NaOH 10% (6 mL) in THF:MeOH (1:2, 30 mL). Hydrogen peroxide 30% (3 mL) was added dropwise at 0 °C and the mixture was stirred for 1 h. The reaction was quenched with saturated $NaHCO_3$, and extracted with $CH_2Cl_2$. The combined organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated under vacuum. The material was purified by column chromatography on silica gel using 30% ethyl acetate/hexane to afford the phenol product.

**4-Ethyl-3,5-dimethoxyphenol.** White solid, 85% yield over 2 steps. $^1H$ NMR matches the reported compound.[3]

**2,6-Dimethoxy-[1,1'-biphenyl]-4-ol**. White solid, 50% yield over 2 steps; mp 157-158 °C; $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.40-7.37 (m, 2H), 7.32-7.28 (m, 3H), 6.16 (s, 2H), 4.77 (bs, 1H), 3.69 (s, 6H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 158.6, 156.6, 134.2, 131.4, 127.9, 126.8, 112.5, 92.4, 56.1; IR (film) 3314, 2921, 2840, 1597, 1470, 1420, 1212, 1125 $cm^{-1}$; HRMS (ES) $m/z$ = 231.1021 calcd for $C_{14}H_{15}O_3$ $[MH]^+$, found 231.1023.

**Preparation of Salen/Salan Ligands**

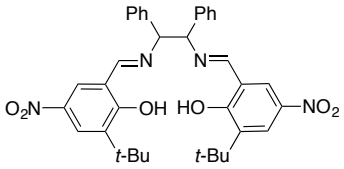



**General Procedure for the Preparation of Salen Ligands**

The substituted salicylaldehyde (4.5 mmol) and the diamine (2 mmol) were stirred at ambient temperature in MeOH:EtOH (1:1) (10–20 mL) for 12-24 h under an Ar atmosphere. The mixture was concentrated *in vacuo*. The resultant material was recrystallized using a 1:1 mixture of methanol and ethyl acetate to yield the salen ligand as a yellow solid.

**General Procedure for the Reduction of Salens to Salans**

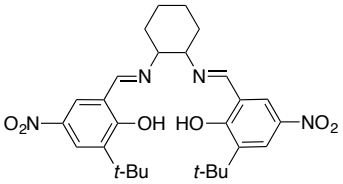
To a solution of the salen in THF:MeOH (1:1), sodium borohydride (10 equiv) was slowly added. The mixture was stirred at room temperature for 2 h (with a change of the solution color from yellow to colorless, except in the cases of nitro derivatives). The mixture was quenched with water and extracted with dichloromethane. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered and concentrated to yield the salan ligand as a solid.



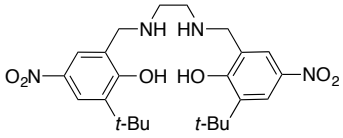

**6,6'-((1*E*,1'*E*)-((1,2-Diphenylethane-1,2-diyl)bis(azanylylidene))bis(methanylylidene))bis(2-(*tert*-butyl)-4-nitrophenol).**

Following the general procedure, the salen ligand was obtained as a yellow resin: $^1$H NMR (500 MHz, $CDCl_3$) δ 15.13 (s, 2H), 8.36 (s, 2H), 8.19 (d, $J$ = 2.5 Hz, 2H), 8.00 (d,

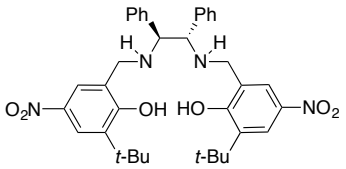
*J* = 2.5 Hz, 2H), 7.31-7.25 (m, 10H), 4.92 (s, 2H), 1.44 (s, 18H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 166.6, 166.0, 139,7, 139.1, 138.0, 128.9, 128.4, 127.9, 126.4, 125.4, 117.3, 79.2, 35.4, 29.0; IR (film) 2961, 1614, 1528, 1475, 1454, 1438, 1326, 1202, 1179, 1109, 1060 cm$^{-1}$; HRMS (ES) *m/z* = 623.2870 calcd for $C_{36}H_{39}N_4O_6$ $[M+H]^+$, found 623.2869.




**6,6'-((1*E*,1'*E*)-(Cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(2-(*tert*-butyl)-4-nitrophenol).** Following the general procedure, the salen ligand was obtained as a yellow resin: $^1$H NMR (500 MHz, $CDCl_3$) δ 15.13 (s, 2H), 8.35 (s, 2H), 8.14 (d, *J* = 3.0 Hz, 2H), 7.99 (d, *J* = 3.0 Hz, 2H), 3.48-3.47 (m, 2H), 2.10-2.07 (m, 2H), 1.97-19.6 (m, 2H), 1.81-1.79 (m, 2H), 1.60-1.55 (m, 2H), 1.40 (s, 18H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 167.4, 164.8, 139.8, 138.9, 126.4, 125.3, 117.1, 71.6, 35.4, 32.7, 29.1, 24.2; IR (film) 2942, 1614, 1474, 1327, 1284, 1202, 1108 cm$^{-1}$; HRMS (ES) *m/z* = 525.2713 calcd for $C_{27}H_{37}N_4O_6$ $[M+H]^+$, found 525.2709.

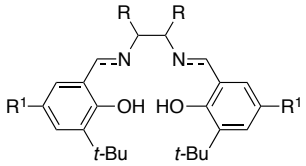



**6,6'-((Ethane-1,2-diylbis(azanediyl))bis(methylene))bis(2-(tert-butyl)-4-nitrophenol).** Following the general procedure, the salan ligand was obtained as a yellow resin: $^1$H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.5 Hz, 2H), 7.82 (d, *J* = 2.5 Hz, 2H), 4.09 (s, 4H), 2.99 (s, 4H), 1.40 (s, 18H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.8, 139.8, 138.2, 122.9, 122.8, 121.9, 52.7, 47.7, 35.2, 29.3; IR (film) 3289, 2951, 1588, 1483, 1334, 1262, 1100 cm$^{-1}$; HRMS (ES) m/z = 475.2557 calcd for $C_{24}H_{35}N_4O_6$ $[MH]^+$, found 475.2560.



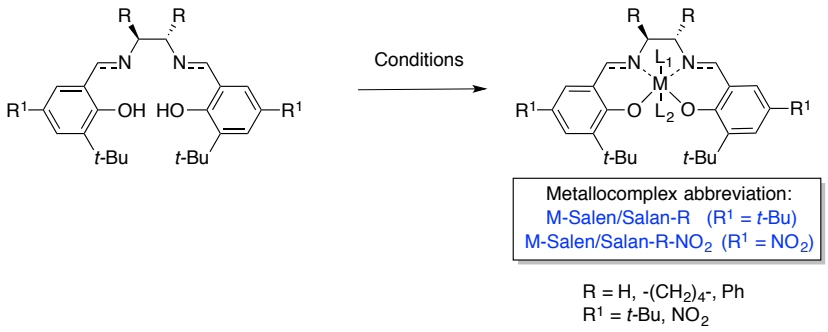

**6,6'-((((1*S*,2*S*)-1,2-Diphenylethane-1,2-diyl)bis(azanediyl))bis(methylene))bis(2-(*tert*-butyl)-4-nitrophenol).** Following the general procedure, the salan ligand was obtained as a yellow solid: mp 127-128 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, $J$ = 2.7 Hz, 2H), 7.59 (d, $J$ = 2.7 Hz, 2H), 7.27-7.25 (m, 6H), 6.97-6.95 (m, 4H), 3.98 (s, 2H), 3.95 (d, $J$ = 14.0 Hz, 2H), 3.69 (d, $J$ = 14.0 Hz, 2H), 1.41 (s, 18H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.6, 139.8, 138.2, 136.8, 129.1, 128.7, 128.0, 123.0(2), 122.4, 66.7, 50.3, 35.3, 29.3; IR (film) 3308, 2959, 2911, 1618, 1589, 1518, 1455, 1433, 1393, 1361, 1334, 1266, 1201, 1171, 1105 cm$^{-1}$; HRMS (ES) $m/z$ = 627.3183 calcd for $C_{36}H_{43}N_4O_6$ $[MH]^+$, found 627.3193.

**Table S1.** Other salen and salan ligands were prepared according to literature protocols.




| Ligand | R | $R^1$ | Reference Number |
|---|---|---|---|
| Salan | H | *t*-Bu | 4 |
| Salan | Ph | *t*-Bu | 5 |
| Salan | Cy | *t*-Bu | 6 |
| Salan | Cy | $NO_2$ | 7 |
| Salen | H | *t*-Bu | 8 |
| Salen | Ph | *t*-Bu | 9 |
| Salen | Cy | *t*-Bu | 9 |
| Salen | H | $NO_2$ | 10 |

## Preparation of Metallosalen/salan Complexes




## General Procedure for Preparation of Vanadium Catalysts[11]

To a suspension $VOF_3$ (1 equiv) in dichloromethane (0.14 M), a solution of the salen/salan ligand (1 equiv) in dichloromethane (0.16 M) was added. The reaction mixture was stirred for 2 h at room temperature under an argon atmostphere. The solvent was then evaporated to dryness and the residue was washed with water, small amounts of MeOH and *n*-hexane, and dried under vacuum to yield the vanadium complex.

V-Salen-Ph: Dark green solid; HRMS (ES) *m/z* = 709.3574 calcd for $C_{44}H_{54}N_2O_3V$ [M-F]$^+$, found 709.3582.

V-Salan-H: Dark green solid; HRMS (ES) *m/z* = 561.3261 calcd for $C_{32}H_{50}N_2O_3V$ [M-F]$^+$, found 561.3257.

V-Salan-Ph: Dark green solid; HRMS (ES) *m/z* = 713.3887 calcd for $C_{44}H_{58}N_2O_3V$ [M-F]$^+$, found 713.3874.

V-Salan-Cy: Dark green solid; HRMS (ES) *m/z* = 615.3731 calcd for $C_{36}H_{56}N_2O_3V$ [M-F]$^+$, found 615.3723.

V-Salan-Cy-$NO_2$: Dark green solid; HRMS (ES) *m/z* = 593.2180 calcd for $C_{28}H_{38}N_4O_7V$ [M-F]$^+$, found 593.2166.

## General Procedure for Preparation of Iron Catalysts[12]

To a suspension of NaH (2 equiv) at 0 ºC, a solution of the salen/salan ligand in THF (0.36 M) was added. The reaction mixture was heated to reflux for 2 h and cooled to room temperature. A solution of $FeCl_3$ (1.1 equiv) in THF (0.72 M) was added. This mixture was heated to reflux for an additional 4 h. The mixture was washed with water, filtered and concentrated *in vacuo*.

Fe-Salan-H: Purple solid; HRMS (ES) *m/z* = 550.3226 calcd for $C_{32}H_{50}N_2O_2Fe$ $[M\text{-}Cl]^+$, found 550.3222.

Fe-Salan-Ph: Voilet solid; HRMS (ES) *m/z* = 702.3851 calcd for $C_{44}H_{58}N_2O_2Fe$ $[M\text{-}Cl]^+$, found 702.3848.

Fe-Salan-Cy: Voilet solid; HRMS (ES) *m/z* = 604.3691 calcd for $C_{36}H_{56}N_2O_2Fe$ $[M\text{-}Cl]^+$, found 604.3688.

**General Procedure for Preparation of Ruthenium Catalysts**[13]

To a solution of the salen/salan ligand in dry DMF (0.01 M), NaH (2 equiv) was added. The resultant solution was stirred at room temperature for 1 h. Then a solution of $Ru(NO)(H_2O)Cl_3$ (1 equiv) in DMF (0.05 M) was added. This mixture was stirred for 18 h at 130 ºC. The solvent was evaporated under high vacuum upon cooling, and the residual material was chromatographed on silica ($CH_2Cl_2$/heptane/EtOAc).

Ru-Salen-H-$NO_2$: Brown-yellow solid; HRMS (ES) *m/z* = 640.0429 calcd for $C_{24}H_{28}N_4O_6Cl_2Ru$ $[M]^-$, found 640.0443.

Ru-Salan-Ph: Brown-red solid; HRMS (ES) *m/z* = 814.3288 calcd for $C_{44}H_{59}N_3O_3ClRu$ $[MH]^+$, found 814.3287.

Ru-Salan-Cy: Brown-red solid; HRMS (ES) *m/z* = 716.3132 calcd for $C_{36}H_{57}N_3O_3ClRu$ $[MH]^+$, found 716.3134.

**General Procedure for Preparation of Copper Salen Catalysts[14]**

To a solution of the salen ligand in toluene (0.12 M), a solution of $CuCl_2$ (1 equiv) in dry ethanol (0.12 M) was added. The reaction mixture was heated to reflux until a precipitate appeared. The precipitate was collected and dried over vacuum.

Cu-Salen-Ph: Orange solid; HRMS (ES) *m/z* = 706.3560 calcd for $C_{44}H_{55}N_2O_2Cu$ $[MH]^+$, found 716.3549.

**General Procedure for Preparation of Copper Salan Catalysts[14]**

To a solution of salan ligand in methanol (0.0312 M), $Cu(OAc)_2 \bullet H_2O$ (1 equiv) and powdered NaOH (2 equiv) were added. Once the salts had dissolved, the solvent was evaporated. The solid residue was dissolved in dichloromethane and washed with water. The solution was dried over $Na_2SO_4$, filtered and concentrated *in vacuo*.

Cu-Salan-Ph: Orange solid; HRMS (ES) *m/z* = 710.3873 calcd for $C_{44}H_{59}N_2O_2Cu$ $[MH]^+$, found 710.3840.

Cu-Salan-Cy-$NO_2$: Greenish yellow solid; HRMS (ES) *m/z* = 590.2166 calcd for $C_{28}H_{39}N_4O_6Cu$ $[MH]^+$, found 590.2168.

**General Procedure for Preparation of Chromium Catalysts[15]**

The salen/salan ligand and $CrCl_2$ (1.1 equiv) were dissolved in THF. The mixture was stirred under argon at ambient temperature for 24 h. Then the reaction mixture was exposed to air and stirred for an additional 24 h. The reaction mixture was poured into diethyl ether, washed with aqueous saturated $NH_4Cl$ and brine, followed by drying with $Na_2SO_4$. After filtration, the mixture was concentrated *in vacuo* to yield the chromium catalyst.

Cr-Salan-Ph: Green solid; HRMS (ES) *m/z* = 762.4428 calcd for $C_{46}H_{66}N_2O_4Cr$ $[M+2MeOH]^+$, found 762.4435.

Cr-Salan-Cy: Violet solid; HRMS (ES) *m/z* = 664.4271 calcd for $C_{38}H_{64}N_2O_4Cr$ $[M+2MeOH]^+$, found 664.4261.

**General Procedure for Preparation of Manganese Catalysts**[16]

To a solution of $Mn(OAc)_2 \bullet 4H_2O$ (3 equiv) in ethanol, a solution of the salen/salan ligand in toluene (0.36 M) was added. The mixture was heated at reflux under Ar atmosphere for 2 h and then air was bubbled for 1 h. Saturated aqueous sodium chloride wass added and the mixture was cooled to room temperature. The airflow was discontinued, followed by the addition of toluene. This mixture was washed with water and brine. The organic layer was dried over $Na_2SO_4$, filtered and concentrated *in vacuo*.

Mn-Salan-H: Brown solid; HRMS (ES) *m/z* = 545.2940 calcd for $C_{32}H_{46}N_2O_2Mn$ $[M-Cl]^+$, found 545.2924.

Mn-Salan-Ph: Brown solid; HRMS (ES) *m/z* = 697.3566 calcd for $C_{44}H_{54}N_2O_2Mn$ $[M-Cl]^+$, found 697.3542.

Mn-Salan-Cy: Brown solid; HRMS (ES) *m/z* = 601.3566 calcd for $C_{36}H_{54}N_2O_2Mn$ $[M-Cl]^+$, found 601.3575.

**Table S2.** Other metallocomplexes were prepared according to the literature protocols.

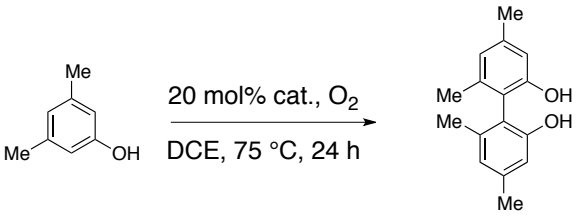
| Catalyst | Reference Number | Catalyst | Reference Number |
|---|---|---|---|
| Cr-Salan-H | 17 | V-Salan-Cy | 18 |
| Cr-Salen-H | 19 | V-Salen-H | 20 |
| Cr-Salen-Ph | 21 | V-Salen-Cy | 22 |
| Cr-Salen-Cy | 23 | Cu-Salan-H | 24 |
| Mn-Salen-H | 25 | Cu-Salan-Cy | 23 |
| Mn-Salan-Ph | 26 | Cu-Salen-H | 27 |

| | | | |
|---|---|---|---|
| Ru-Salen-H | 28 | Cu-Salen-Cy | 14 |
| Ru-Salen-Ph | 29 | Fe-Salen-H | 30 |
| Ru-Salen-Cy | 31 | Fe-Salen-Cy | 32 |

**General Procedure for High Throughput Experimentation (HTE)**

The following procedure is a representative of the HTE screening. The solutions of catalysts (2 μmol, 50 μL) in DCE and the solutions of phenol (10 μmol, 50 μL) in DCE were dosed into the 96-well plate reactor vials. The reaction plate was then purged and continuously back-filled with oxygen using a desiccator fixed with a T-valve for 3-5 min. The plate was sealed and stirred at 75 °C for 24 h. After cooling to ambient temperature, the vials were diluted with a solution of biphenyl (1 μmol, 500 μL) in MeCN and then sealed. The contents were shaken for 15 min. To a separate 96-well LC plate with 1 mL vials were added 700 μL of MeCN, and then 40 μL of the diluted reaction mixtures. The mixture was then analyzed using Agilent Chemstation on an HPLC modified with a 96-well plate auto-sampler.

**HTE of 3,5-Dimethylphenol (Figure 1 and Table 1, entry 3)**

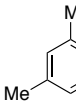
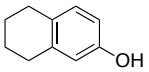
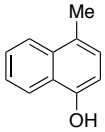
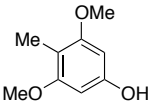
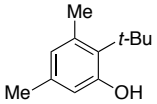



***ortho-ortho***

**Table S3. Complete HTE Results of 3,5-Dimethylphenol**

| Vial | M | Ligand | R | SM | *o-o* product | IS | Prod/IS |
|---|---|---|---|---|---|---|---|
| E1 | Cr | Salan | Cy | 1157 | 0 | 245 | 0.0 |
| E2 | Cr | Salan | H | 1017 | 0 | 213 | 0.0 |
| E3 | Cr | Salan | Ph | 1120 | 0 | 242 | 0.0 |
| E4 | Cr | Salen | Cy | 154 | 0 | 456 | 0.0 |
| G1 | Cr | Salen | H | 138 | 15 | 355 | 0.0 |
| E5 | Cr | Salen | Ph | 507 | 33 | 279 | 0.1 |
| G2 | Cu | Salan | Cy | 1182 | 0 | 242 | 0.0 |
| G3 | Cu | Salan | H | 1138 | 12 | 240 | 0.1 |
| E6 | Cu | Salan | Ph | 1139 | 0 | 239 | 0.0 |
| E7 | Cu | Salen | Cy | 1204 | 0 | 239 | 0.0 |
| E8 | Cu | Salen | H | 1195 | 9 | 237 | 0.0 |
| E9 | Cu | Salen | Ph | 1258 | 0 | 240 | 0.0 |
| G4 | Fe | Salan | Cy | 1185 | 9 | 247 | 0.0 |
| G5 | Fe | Salan | H | 1257 | 0 | 254 | 0.0 |
| E11 | Fe | Salan | Ph | 1212 | 9 | 252 | 0.0 |
| E12 | Fe | Salen | Cy | 1207 | 0 | 232 | 0.0 |
| F1 | Fe | Salen | H | 1169 | 0 | 235 | 0.0 |
| F2 | Fe | Salen | Ph | 1153 | 0 | 234 | 0.0 |
| G7 | Mn | Salan | Cy | 1095 | 34 | 246 | 0.1 |
| F3 | Mn | Salan | H | 1141 | 0 | 249 | 0.0 |
| G6 | Mn | Salan | Ph | 1162 | 16 | 246 | 0.1 |
| F4 | Mn | Salen | Cy | 1145 | 0 | 231 | 0.0 |
| F5 | Mn | Salen | H | 1172 | 0 | 234 | 0.0 |
| F6 | Mn | Salen | Ph | 1133 | 0 | 229 | 0.0 |
| F7 | Ru | Salan | Cy | 549 | 64 | 217 | 0.3 |
| G8 | Ru | Salan | H | 774 | 80 | 242 | 0.3 |
| F8 | Ru | Salen | Cy | 1022 | 40 | 230 | 0.2 |
| F9 | Ru | Salen | H | 957 | 69 | 239 | 0.3 |
| G9 | Ru | Salen | Ph | 950 | 54 | 241 | 0.2 |
| F10 | V | Salan | Cy | 726 | 327 | 234 | 1.4 |
| F11 | V | Salan | H | 1124 | 0 | 236 | 0.0 |
| G10 | V | Salan | Ph | 611 | 0 | 253 | 0.0 |
| G11 | V | Salen | Cy | 506 | 97 | 248 | 0.4 |
| F12 | V | Salen | H | 1110 | 26 | 237 | 0.1 |
| G12 | V | Salen | Ph | 833 | 197 | 239 | 0.8 |

**Table S4. Summary Initial HTE results (Figure 1).** values = product/internal standard)

| **Substrate** |  *ortho-ortho* |  *ortho-ortho* |  Pummerer ketone |  *ortho-ortho* | Pummerer ketone |  *ortho-ortho* |
|---|---|---|---|---|---|---|
| **Conditions** | 20 mol% cat., $O_2$, DCE, 75 °C, 24 h | 20 mol% cat., $O_2$, DCE, 40 °C, 24 h | 20 mol% cat., $O_2$, DCE, 80 °C, 24 h | 30 mol% cat, $O_2$, DCE, 40 °C, 24 h | | 20 mol% cat, $O_2$, DCE, 80 °C, 24 h |
| Cr-Salan-Cy | 0.00 | 0.00 | 0.00 | 0.18 | 0.45 | 2.46 |
| Cr-Salan-H | 0.00 | 0.00 | 0.00 | 0.81 | 0.24 | 1.11 |
| Cr-Salan-Ph | 0.00 | 0.00 | 0.00 | 0.64 | 0.35 | 1.59 |
| Cr-Salen-Cy | 0.00 | 0.99 | 0.00 | 1.39 | 0.98 | 5.92 |
| Cr-Salen-H | 0.04 | 1.82 | 0.00 | 1.28 | 0.76 | 6.08 |
| Cr-Salen-Ph | 0.12 | 0.00 | 0.00 | 0.46 | 0.23 | 3.43 |
| Cu-Salan-Cy | 0.00 | 0.00 | 0.70 | 2.32 | 0.38 | 7.32 |
| Cu-Salan-H | 0.05 | 0.02 | 0.55 | 2.06 | 0.20 | 5.61 |
| Cu-Salan-Ph | 0.00 | 0.16 | 0.37 | 0.77 | 0.45 | 6.87 |
| Cu-Salen-Cy | 0.00 | 0.12 | 0.00 | 1.22 | 0.25 | 3.12 |
| Cu-Salen-H | 0.04 | 0.04 | 0.00 | 1.15 | 0.40 | 0.91 |
| Cu-Salen-Ph | 0.00 | 0.00 | 0.00 | 1.43 | 0.34 | 0.00 |
| Fe-Salan-Cy | 0.04 | 0.08 | 0.00 | 0.00 | 0.38 | 4.32 |
| Fe-Salan-H | 0.00 | 0.00 | 0.00 | 0.32 | 0.45 | 2.51 |
| Fe-Salan-Ph | 0.04 | 0.04 | 0.00 | 0.53 | 0.36 | 6.34 |
| Fe-Salen-Cy | 0.00 | 0.00 | 0.00 | 0.27 | 0.42 | 0.38 |
| Fe-Salen-H | 0.00 | 0.00 | 0.00 | 0.72 | 0.09 | 0.82 |
| Fe-Salen-Ph | 0.00 | 0.00 | 0.13 | 0.22 | 0.05 | 1.20 |
| Mn-Salan-Cy | 0.14 | 0.46 | 0.00 | 0.41 | 0.05 | 7.45 |
| Mn-Salan-H | 0.00 | 0.00 | 0.25 | 0.96 | 0.75 | 7.31 |
| Mn-Salan-Ph | 0.07 | 0.31 | 0.29 | 1.17 | 0.48 | 7.63 |
| Mn-Salen-Cy | 0.00 | 0.03 | 0.00 | 0.11 | 0.71 | 4.29 |
| Mn-Salen-H | 0.00 | 0.00 | 0.00 | 0.98 | 0.50 | 0.00 |
| Mn-Salen-Ph | 0.00 | 0.03 | 0.00 | 2.14 | 0.40 | 3.14 |
| Ru-Salan-Cy | 0.29 | 0.21 | 1.28 | 0.09 | 0.88 | 7.52 |
| Ru-Salan-H | 0.33 | 0.66 | 0.89 | 0.12 | 1.35 | 7.69 |
| Ru-Salen-Cy | 0.17 | 0.57 | 0.19 | 2.53 | 0.45 | 4.42 |
| Ru-Salen-H | 0.29 | 0.71 | 0.31 | 1.04 | 0.56 | 8.05 |
| Ru-Salen-Ph | 0.22 | 0.71 | 0.00 | 2.68 | 0.55 | 2.94 |
| V-Salan-Cy | 1.40 | 1.35 | 0.00 | 2.32 | 1.52 | 7.55 |
| V-Salan-H | 0.00 | 0.00 | 0.00 | 0.69 | 0.14 | 4.35 |
| V-Salan-Ph | 0.00 | 0.16 | 0.00 | 2.27 | 0.58 | 5.61 |
| V-Salen-Cy | 0.39 | 0.66 | 0.00 | 2.14 | 0.60 | 5.99 |
| V-Salen-H | 0.11 | 0.15 | 0.00 | 0.46 | 0.38 | 4.53 |
| V-Salen-Ph | 0.82 | 0.46 | 0.00 | 3.72 | 1.24 | 6.45 |

## Additive Screening

Following the HTE general procedure, various solvents (PhCl, toluene, DCE) and additives [$Yb(OTf)_3$, molecular sieves, *i*-$Pr_2NEt$, tartaric acid, TBSOTf] were examined, using 24-or 96-well plates.

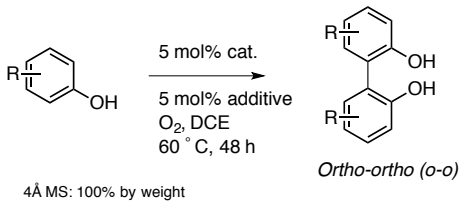
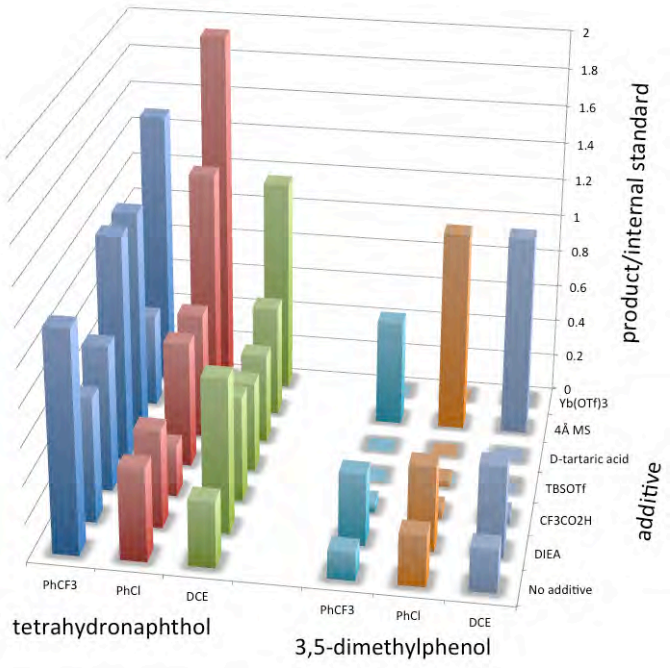



**Table S5. HTE Results of Additive Screening**

**(Value = Product/IS)**

| | 3,5-Dimethylphenol | | | Tetrahydro naphth-2-ol | | |
|---|---|---|---|---|---|---|
| | **$PhCF_3$** | **PhCl** | **DCE** | **$PhCF_3$** | **PhCl** | **DCE** |
| $CF_3CO_2H$ | 0.78 | 0.27 | 0.56 | 0.05 | 0.05 | 0.05 |
| $Yb(OTf)_3$ | 1.49 | 1.94 | 1.16 | 0.00 | 0.00 | 0.00 |
| DIEA | 0.66 | 0.52 | 0.82 | 0.38 | 0.45 | 0.48 |
| 4Å MS | 0.50 | 1.31 | 0.60 | 0.57 | 1.08 | 1.08 |
| D-tartaric acid | 1.21 | 0.68 | 0.48 | 0.00 | 0.00 | 0.00 |
| TBSOTf | 1.22 | 0.67 | 0.48 | 0.00 | 0.03 | 0.00 |
| No additive | 1.17 | 0.49 | 0.35 | 0.15 | 0.27 | 0.23 |

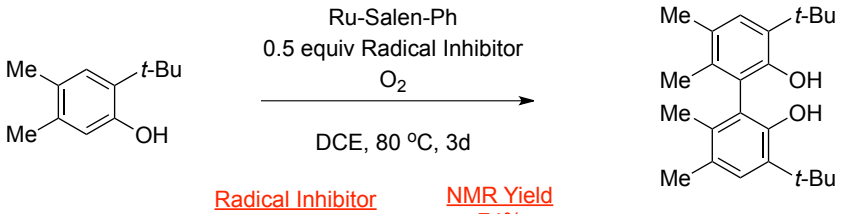
**Figure S1. HTE Results of Additive Screening**



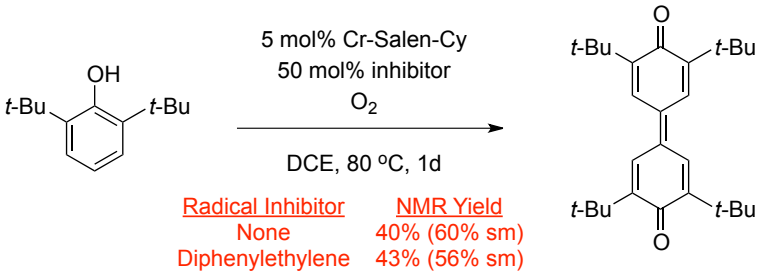
**anism Experiments.**

Overall, free radicals are not indicated (no change with diphenylethylene). With the Ru catalysts (ortho-ortho coupling, some radical character is evident from partial inhibition with TEMPO, which does not appear to alter the catalyst as judged by UV-Vis. TEMPO alters the Cr catalyst, shutting down the cross-coupling pathway and upregulating a catalyst mediated homo-coupling pathway.

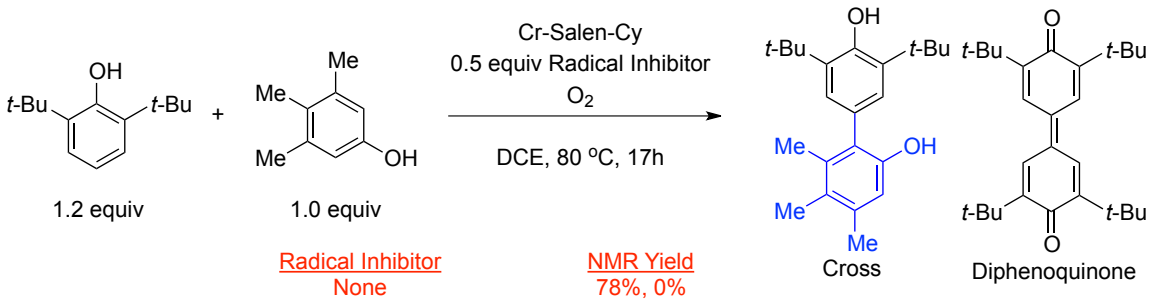
Radical Inhibitors:




| Radical Inhibitor | NMR Yield |
|---|---|
| None | 74% |
| Diphenylethylene | 76% |
| TEMPO | 43% |
| BHT | 37% |



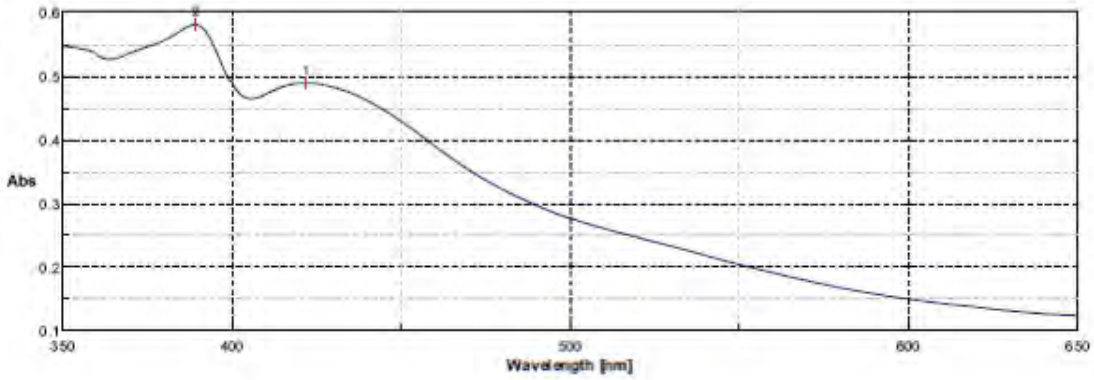

| Radical Inhibitor | NMR Yield |
|---|---|
| None | 40% (60% sm) |
| Diphenylethylene | 43% (56% sm) |
| TEMPO | 100% |
| BHT | 19% (51% sm) |



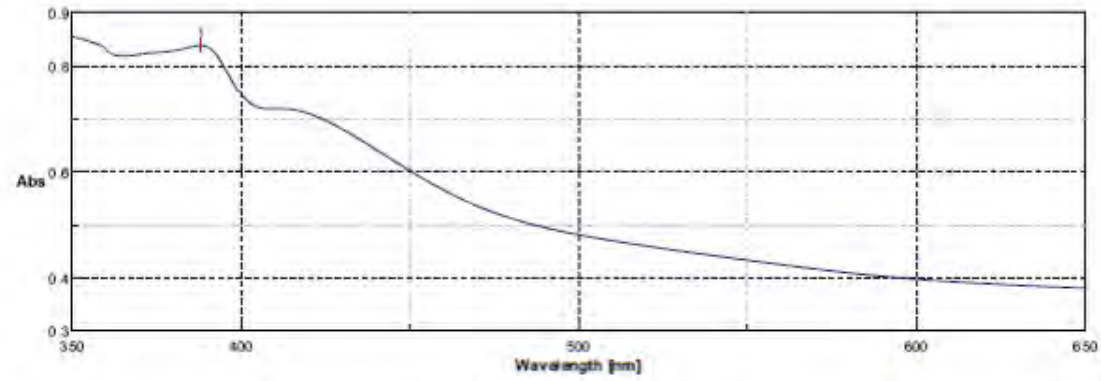

| Radical Inhibitor | NMR Yield |
|---|---|
| None | 78%, 0% |
| Diphenylethylene | 80%, 0% |
| TEMPO | 35%, 42% |
| 100 mol% TEMPO | 38%, 62% |
| BHT | 71%, 0% |
| 100 mol% TEMPO (no cat) | NR |

UV-Vis Spectra of Catalysts With and Without TEMPO:

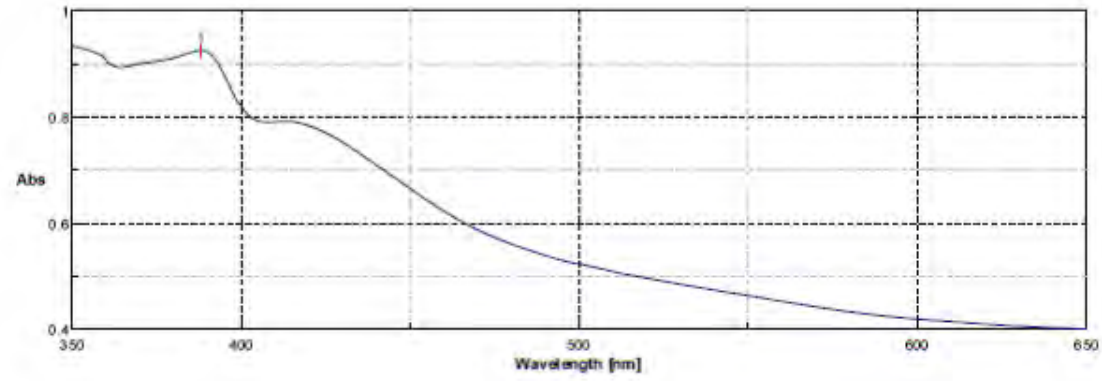
Ru-Salen-Ph, rt, $O_2$



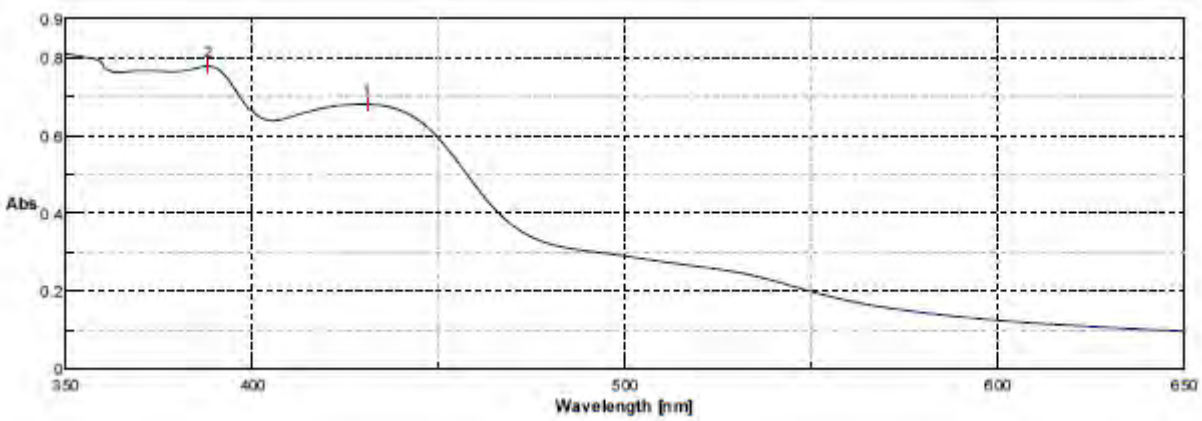

Ru-Salen-Ph, 80 °C, $O_2$



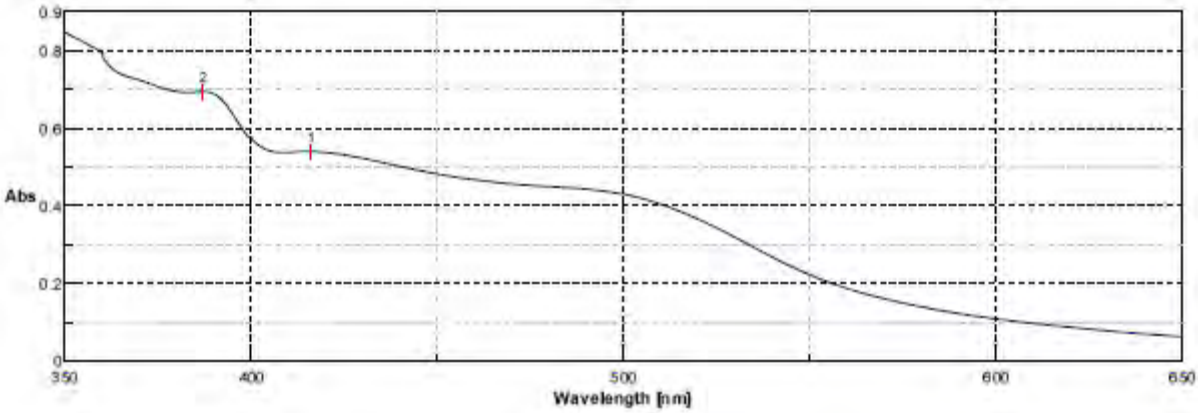

Ru-Salen-Ph, 80 °C, $O_2$, TEMPO



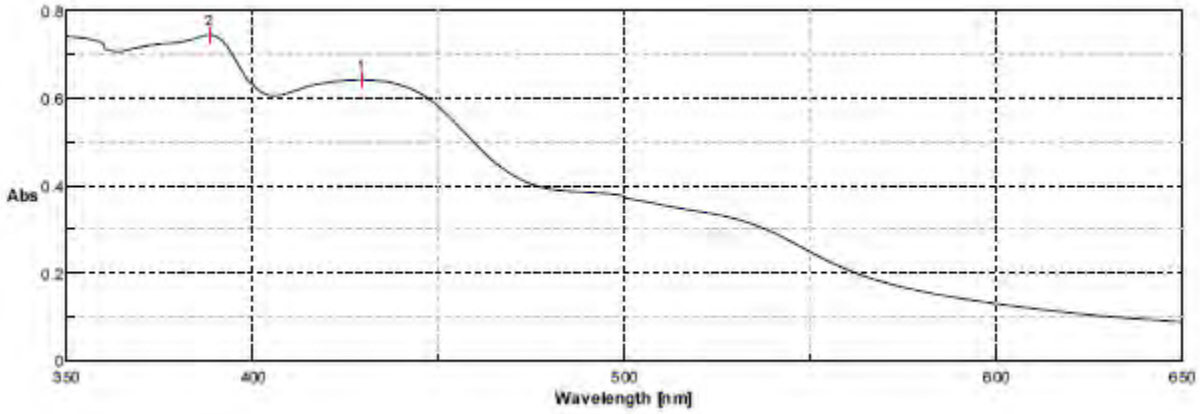
Cr-Salen-Cy, rt, $O_2$




Cr-Salen-Cy, 80 °C, $O_2$



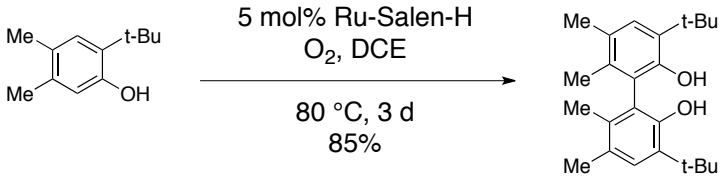

Cr-Salen-Cy, 80 °C, $O_2$, TEMPO



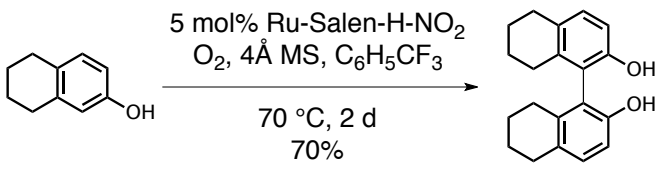
**General Procedure for the Regioselective Oxidative Coupling of Phenols**

To a 5 mL microwave vial was added phenol (0.1 mmol) and catalyst (0.005 mmol). The vial was sealed with a septum and solvent (1 mL) was added. Oxygen was added *via* active purge. The septum was replaced with a crimping cap and the vessel was sealed and stirred for the indicated time at the indicated temperature. After the reaction mixture was filtered through a plug of silica and concentrated *in* vacuo, the resultant mixture was chromatographed using ethyl acetate/hexane to afford the product.

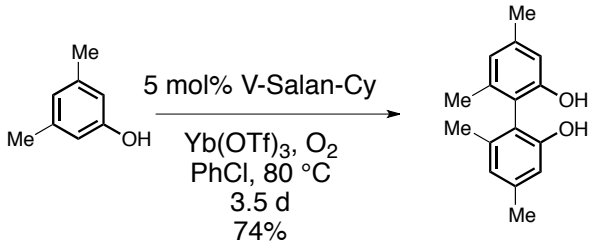
**Table 1 Data**



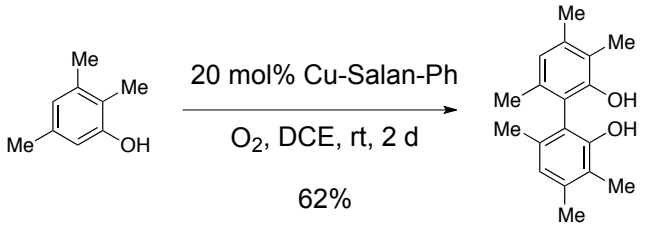

3,3'-Di-*tert*-butyl-5,5',6,6'-tetramethyl-[1,1'-biphenyl]-2,2'-diol **(Table 1, entry 1)**. Following the general procedure, using Ru-Salen-H catalyst in dichloroethane at 80 °C for 3 d, the *ortho-ortho* product was obtained as a colorless resin in 85% yield: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.14 (s, 2H), 4.80 (s, 2H), 2.27 (s, 6H), 1.83 (s, 6H), 1.41 (s, 18H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 150.4, 134.1, 133.4, 128.8, 128.1, 121.0, 34.5, 29.6, 20.0, 15.9; IR (film) 3493, 2959, 1388, 1277, 1183, 1041, 892 cm$^{-1}$; HRMS (ES) *m/z* = 354.2559 calcd for $C_{24}H_{34}O_2$ $[M]^+$, found 354.2559. $^{1}$H NMR spectrum matches the reported compound.[33]



**5,5',6,6',7,7',8,8'-Octahydro-[1,1'-binaphthalene]-2,2'-diol (Table 1, entry 2)**. Following the general procedure, using Ru-Salen-H-$NO_2$ catalyst with 4Å MS (2 equiv by weight) in $PhCF_3$ at 70 °C for 2 d, the *ortho-ortho* product was obtained as a colorless resin in 70% yield. $^1$H NMR spectrum matches the reported compound.[34]




**4,4',6,6'-Tetramethyl-[1,1'-biphenyl]-2,2'-diol (Table 1, entry 3)**. Following the general procedure, using V-Salan-Cy catalyst with $Yb(OTf)_3$ (0.5 equiv) in PhCl at 80 °C for 3.5 d, the *ortho-ortho* product was obtained as a colorless resin in 74% yield. $^1$H NMR spectrum matches the reported compound.[35,36]



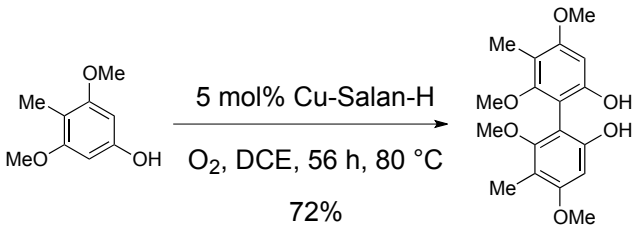

**2,2',3,3',5,5'-Hexamethyl-[1,1'-biphenyl]-2,2'-diol (Table 1, entry 4)**. Following the general procedure, using Cu-Salan-Ph catalyst (20 mol%) in dichloroethane as at ambient temperature for 2 d, the the *ortho-ortho* product was obtained as a colorless resin in 62% yield: $^1$H NMR (500 MHz, $CDCl_3$) δ 6.74 (s, 2H), 4.74 (s, 2H), 2.29 (s, 6H), 2.17 (s, 6H), 1.92 (s, 6H); $^{13}$C NMR (500 MHz, $CDCl_3$) δ 15.9, 138.6, 135.2, 123.9, 120.4, 117.0, 20.1, 19.3, 11.9; IR (film) 3509, 3460, 2922, 2359, 1560, 1458, 1298, 1079 $cm^{-1}$; HRMS (ES) *m/z* = 270.1620 calcd for $C_{18}H_{22}O_2$ $[M]^+$, found 270.1623.

$^1$H NMR matches the reported compound.[36]

**2',3,3',4,6,6'-Hexamethyl-[1,1'-biphenyl]-2,4'-diol (Table 1, entry 5)**. Following the general procedure, using Cr-Salen-Cy catalyst in dichloroethane at 50 °C for 2 d, starting material (40%) and the *para-para* product (8%) were obtained along with the *ortho-para* product in 52% yiel: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 6.68 (s, 1H), 6.65 (s, 1H), 4.65 (s, 1H), 4.53 (s, 1H), 2.82 (s, 3H), 2.19 (s, 3H), 2.17 (s, 3H), 1.90 (s, 3H), 1.89 (s, 3H), 1.83 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 153.3, 150.5, 138.4, 136.5, 136.3, 133.5, 126.4, 123.7, 123.0, 120.6 119.3, 114.7, 19.9, 19.8, 19.2, 16.6, 11.9, 11.8; IR (film) 3435, 2920, 1590, 1453, 1299, 1088, 910, 848 cm$^{-1}$; HRMS (ES) *m/z* = 271.1698 calcd for $C_{18}H_{23}O_2$ $[M+H]^+$, found 271.1700.

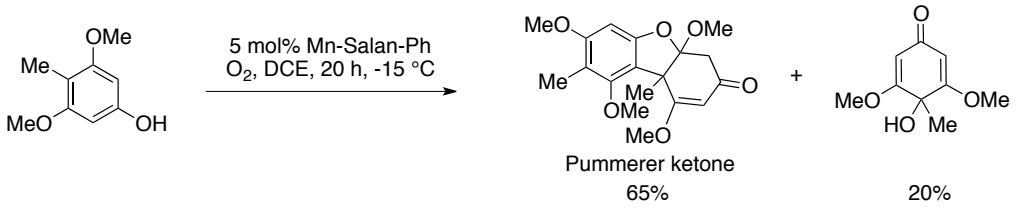
**2,2',3,3',6,6'-Hexamethyl-[1,1'-biphenyl]-4,4'-diol (Table 1, entry 6)**. Following the general procedure, using Cr-Salen-H catalyst (20 mol%) in dichloroethane at ambient temperature for 1 d, the *para-para* product was obtained in 34% yield (62% based on recovered starting material): $^{1}$H NMR (360 MHz, $CDCl_3$) δ 6.56 (s, 2H), 5.60 (s, 2H), 4.50 (s, 2H), 2.18 (s, 3H), 1.79 (d, *J* = 8.5 Hz, 6H); $^{13}$C NMR (500 MHz, CDCl3) δ 151.9, 136.2, 134.2, 133.3, 119.6, 113.9, 19.9, 16.5, 11.9; IR (film) 3434, 2916, 1633, 1285, 1280 12191, 12191, 1086 cm$^{-1}$; HRMS (ES) *m/z* = 269.1542 calcd for $C_{18}H_{21}O_2$ $[M-H]^-$, found 269.1549.

$^{1}$H Spectral data match those reported. [37]




**4,4',6,6'-Tetramethoxy-5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diol (Table 1, entry 7)**.

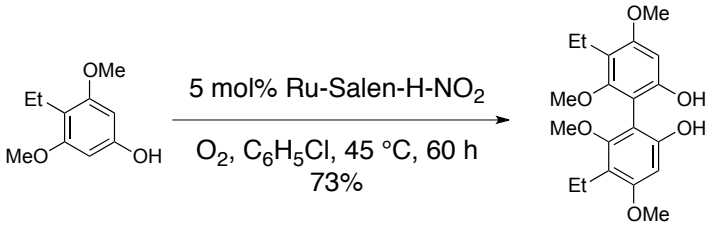
Following the general procedure, using Cu-Salan-H catalyst in dichlor0ethane at 80 °C for 2 d yielded the Pummerer ketone (white resin, 2.9 mg, 17% yield) and the *ortho-ortho* product (white resin, 12.1 mg, 72% yield): $^{1}$H NMR (500 MHz, $CDCl_3$) δ 6.48 (s, 2H), 5.92 (bs, 2H), 3.84 (s, 6H), 3.50 (s, 6H), 2.13 (s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 159.6, 156.7, 153.6, 112.5, 106.2, 97.3, 60.8, 55.9, 8.9; IR (film) 3389, 2936, 1609, 1465, 1402, 1190, 1154, 1117, 1061 cm$^{-1}$; HRMS (ES) *m/z* = 335.1495 calcd for $C_{18}H_{23}O_6$ $[MH]^+$, found 335.1491.



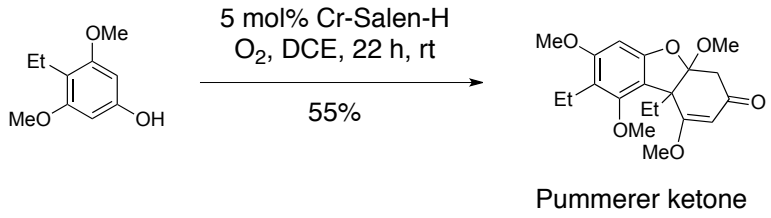

**1,4a,7,9-Tetramethoxy-8,9b-dimethyl-4a,9b-dihydrodibenzo[*b*,*d*]furan-3(4*H*)-one (Table 1, entry 8)**. Following the general procedure, using Mn-Salan-Ph catalyst in chlorobenzene at –15 °C for 20 h, the hydroxyl quinone was obtained in 20% yield along with the Pummerer ketone in 65% yield: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 6.24 (s, 1H), 5.36 (s, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.64 (s, 3H), 3.33 (s, 3H), 3.23 (d, *J* = 17.0 Hz, 1H), 2.62 (d, *J* = 17.0 Hz, 1H), 2.08 (s, 3H), 1.74 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 193.8, 178.0, 159.9, 158.2, 156.6, 114.1, 113.3, 111.4, 100.6, 91.1, 61.8, 56.7, 56.0, 54.6, 49.9, 39.5, 16.5, 9.7; IR (film) 2934, 2845, 1664, 1603, 1453, 1096 cm$^{-1}$; HRMS (ES) *m/z* = 335.1495 calcd for $C_{18}H_{23}O_6$ $[MH]^+$, found 335.1495.

4-Hydroxy-3,5-dimethoxy-4-methylcyclohexa-2,5-dien-1-one. mp 140-141 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 5.49 (s, 2H), 3.24 (s, 6H), 1.53 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 171.0, 102.2, 81.0, 77.5, 56.6, 21.6; IR (film) 3178, 2941, 2847, 1657, 1596,

1450, 1338, 1246, 1217, 1145 $cm^{-1}$; HRMS (ES) *m/z* = 185.0814 calcd for $C_9H_{13}O_4$ $[MH]^+$, found 185.0814.



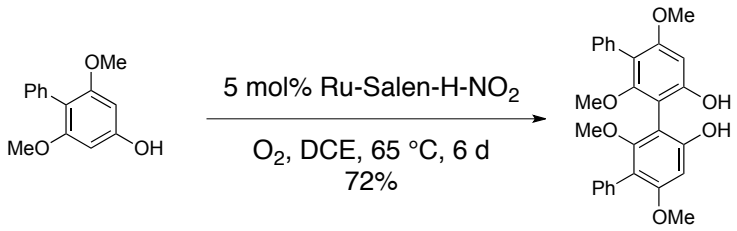

**5,5'-Diethyl-4,4',6,6'-tetramethoxy-[1,1'-biphenyl]-2,2'-diol (Table 1, entry 9)**. Following the general procedure, using Ru-Salen-H-$NO_2$ catalyst in PhCl at 45 °C for 2 d, the *ortho-ortho* product was obtained as a colorless resin in 73% yield: $^1$H NMR (500 MHz, $CDCl_3$) δ 6.48 (s, 2H), 6.08 (s, 2H), 3.84 (s, 6H), 3.51 (s, 6H), 2.69 (dq, *J* = 13.0, 7.4 Hz, 2H), 2.60 (dq, *J* = 13.0, 7.4 Hz, 2H), 1.14 (t, *J* = 7.4 Hz, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 159.5, 156.2, 153.7, 118.9, 106.5, 97.7, 61.4, 55.8, 17.3, 15.1; IR (film) 3376, 2937, 2872, 2836, 1606, 1454, 1409, 1319, 1233, 1190, 1154, 1121, 1021 $cm^{-1}$; HRMS (ES) *m/z* = 363.1808 calcd for $C_{20}H_{27}O_6$ $[MH]^+$, found 363.1818.



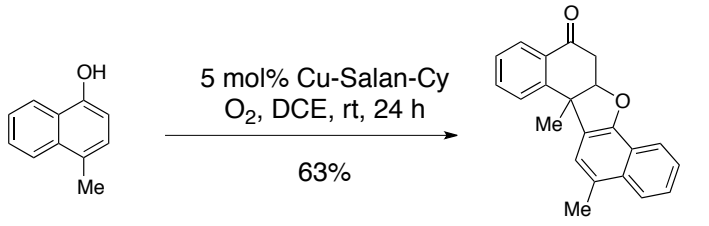

Pummerer ketone

**8,9b-Diethyl-1,4a,7,9-tetramethoxy-4a,9b-dihydrodibenzo[*b*,*d*]furan-3(4*H*)-one (Table 1, entry 10)**. Following the general procedure, using Cr-Salen-H catalyst in dichloroethane at ambient temperature for 22 h, the Pummerer ketone was obtained as a colorless resin in 55% yield: $^1$H NMR (500 MHz, $CDCl_3$) δ 6.22 (s, 1H), 5.51 (s, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 3.66 (s, 3H), 3.36 (s, 6H), 3.26 (d, *J* = 16.9 Hz, 1H), 2.83 (dq, *J*

= 14.2, 7.3 Hz, 1H), 2.62 (d, *J* = 16.9 Hz, 1H), 2.58 (q, *J* = 7.5 Hz, 2H), 2.15 (dq, *J* = 14.2, 7.3 Hz, 1H), 1.15 (t, *J* = 7.3 Hz, 3H), 0.93 (t, *J* = 7.5 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 194.2, 176.4, 160.2, 158.0, 156.6, 119.7, 114.1, 110.4, 102.9, 91.3, 63.2, 59.0, 56.6, 55.8, 49.8, 42.27, 22.9, 17.8, 14.5, 9.6; IR (film) 2965, 2939, 2875, 2837, 1663, 1603, 1466, 1416, 1356, 1339, 1288, 1233, 1198, 1126, 1078, 1050 cm$^{-1}$; HRMS (ES) *m/z* = 363.1808 calcd for $C_{20}H_{27}O_6$ $[MH]^+$, found 363.1816.




**2',2'',4'',6'-Tetramethoxy-[1,1':3',1'':3'',1'''-quaterphenyl]-4',6''-diol (Table 1, entry 11).** Following the general procedure, using Ru-Salen-H-$NO_2$ catalyst in PhCl at 65 °C for 6, the *ortho-ortho* product was obtained as a colorless resin in 72% yield: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.43-7.40 (m, 8H), 7.36-7.31 (m, 2H), 6.58 (s, 2H), 5.98 (s, 2H), 3.76 (s, 6H), 3.24 (s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 159.0, 156.5, 155.4, 134.1, 131.2, 128.1, 127.1, 117.9, 106.1, 97.5, 61.2, 56.1; IR (film) 3397, 2937, 2845, 1602, 1463, 1396, 1205, 1100, 1068 cm$^{-1}$; HRMS (ES) *m/z* = 459.1808 calcd for $C_{28}H_{27}O_6$ $[MH]^+$, found 459.1825.




Pummerer ketone

**12,13b-Dimethyl-6a,13b-dihydrodinaphtho[1,2-*b*:1',2'-*d*]furan-5(6*H*)-one (Table 1, entry 12)**. Following the general procedure, using Cu-Salan-Cy catalyst in dichloroethane at ambient temperature for 24 h, the Pummerer ketone was obtained as a purple resin in 63% yield: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.97 (dt, *J* = 7.9, 0.7 Hz, 1H), 7.94-7.92 (m, 1H), 7.89-7.88 (m, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.47-7.41 (m, 3H), 7.27-7.24 (m, 1H), 4.97 (t, *J* = 3.5 Hz, 1H), 3.44 (dd, *J* = 17.0, 3.5 Hz, 1H), 3.12 (dd, *J* = 17.0, 3.5 Hz, 1H), 2.67 (m, 1H), 1.91 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 194.9, 153.3, 145.4, 134.7, 133.0, 130.6, 128.1, 127.93, 127.89, 126.9, 126.5, 126.3, 125.7, 124.6, 122.4, 121.2, 121.0, 88.7, 47.4, 38.6, 29.9, 25.5; IR (film) 3065, 2963, 2924, 1692, 1599, 1454, 1408, 1382, 1329, 1290, 1261, 1077 cm$^{-1}$; HRMS (ES) *m*/*z* = 315.1385 calcd for $C_{22}H_{19}O_2$ $[MH]^+$, found 315.1383.

**5,5'-Diisopropyl-2,2'-dimethyl-[1,1'-biphenyl]-4,4'-diol (Table 1, entry 13)**. Following the general procedure, using Cr-Salen-Cy catalyst in dichloroethane at 50 °C for 2 d, the *para-para* product was obtained in 38% yield (balance of material is starting material, 55%): $^1$H NMR (500 MHz, $CDCl_3$) δ 6.93 (s, 2H), 6.66 (s, 2H), 4.61 (s, 2H), 3.18 (sept, *J*=6.9 Hz, 2H), 1.25 (d, *J*=6.9 Hz, 6H), 1.24 (d, *J*=6.9 Hz, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 151.4, 134.7, 134.1, 131.2, 128.0, 116.4, 26.8, 22.8, 22.7, 19.5; IR (film) 3328, 2920, 1616, 1405, 1335, 1097, 899, 735 cm$^{-1}$; HRMS (ES) *m*/*z* = 297.1855 calcd for $C_{20}H_{25}O_2$ $[M-H]^-$, found 297.1872.

**5,5'-Di-*tert*-butyl-2,2'-dimethyl-[1,1'-biphenyl]-4,4'-diol (Table 1, entry 14)**. Following the general procedure, using Cr-Salen-Cy catalyst in dichloroethane at 50 °C for 2 d, the *para-para* product was obtained in 44% yield (balance of material is starting material, 52%): $^1$H NMR (500 MHz, $CDCl_3$) δ 7.00 (s, 2H), 6.58 (s, 2H), 4.67 (s, 2H),

1.98 (s, 6H), 1.41 (s, 18H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 152.7, 134.9, 133.8, 133.0, 128.9, 117.7, 34.3, 29.9, 19.3; IR (film) 3324, 2917, 1611, 1383, 1093 $cm^{-1}$; HRMS (ES) *m/z* = 325.2168 calcd for $C_{22}H_{29}O_2$ $[M-H]^-$, found 325.2170.

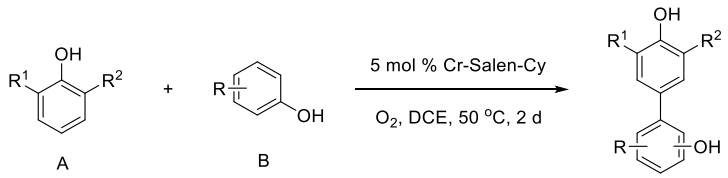
**3,3',5,5'-Tetramethyl-[1,1'-biphenyl]-4,4'-diol (Table 1, entry 15)**. Following the general procedure, using Cr-Salen-Cy catalyst in dichloroethane at 85 °C for 2 d, a mixture of the *para-para* bisphenol and the *para-para* diphenoquinone was obtained, which was concentrated *in vacuo* and directly subjected to sodium dithonite (0.3 mmol) in EtOH (0.2 M) heated to reflux for 5 h. The resultant precipitate was collected on a filter and the filtrate was concentrated *in vacuo* and chromatographed with EtOAc/hexanes to provide recovered starting material (35%) and the *para-para* product in 63% yield: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.15 (s, 4H), 4.56 (s, 2H), 2.30 (s, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 151.2, 133.4, 127.0, 123.1, 16.0; IR (film) 3339, 2919, 1650, 1385, 1094 $cm^{-1}$; HRMS (ES) *m/z* = 242.1307 calcd for $C_{16}H_{18}O_2$ $[M]^+$, found 242.1305.

**3,3',5,5'-Tetraisopropyl-[1,1'-biphenyl]-4,4'-diol (Table 1, entry 16)**. Following the general procedure, using Cr-Salen-Cy catalyst in dichloroethane at 85 °C for 1 d, a mixture of the *para-para* bisphenol and the *para-para* diphenoquinone was obtained, which was concentrated *in vacuo* and directly subjected to sodium dithonite (0.3 mmol) in EtOH (0.2 M) heated to reflux for 5 h. The resultant precipitate was collected on a filter and the filtrate was concentrated *in vacuo* and chromatographed with EtOAc/hexanes to provide the *para-para* product in 95% yield: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.20 (s, 4H), 4.78 (s, 2H), 3.22 (septet, *J*=6.5Hz, 4H), 1.34 (d, *J*=6.5Hz, 24H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 149.1, 134.7, 133.8, 122.4, 27.4, 22.8; IR (film) 3568,

2960, 1723, 1442, 13.4, 1197, 1147 $cm^{-1;}$ HRMS (ES) *m/z* = 353.2481 calcd for $C_{24}H_{33}O_2$ $[M-H]^-$, found 353.2481.

**3,3',5,5'-Tetra-*tert*-butyl-[1,1'-biphenyl]-4,4'-diol (Table 1, entry 17)**. Following the general procedure, using Cr-Salen-Cy catalyst in dichloroethane at 85 °C for 2 d, a mixture of the *para-para* bisphenol and the *para-para* diphenoquinone was obtained, which was concentrated *in vacuo* and directly subjected to sodium dithonite (0.3 mmol) in EtOH (0.2 M) heated to reflux for 5 h. The resultant precipitate was collected on a filter and the filtrate was concentrated *in vacuo* and chromatographed with EtOAc/hexanes to provide recovered starting material (23%) and the *para-para* product in 77% yield: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.31 (s, 4H), 5.18 (s, 2H), 1.50 (s, 36H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 152.8, 136.0, 133.9, 124.1, 34.4, 30.4; IR (film) 3622, 3304, 2917, 1649, 1424, 1098 $cm^{-1}$; HRMS (ES) *m/z* = 410.3185 calcd for $C_{28}H_{42}O_2$ $[M]^+$, found 410.3166.

**General Procedure for the Oxidative Cross-coupling Reaction of Phenols using Cr-Salen-Cy catalyst**




To a 5 mL microwave vial was added phenol A (0.1 mmol), phenol B (0.5 mmol) and Cr-Salen-Cy catalyst (0.005 mmol). The vial was sealed with a septum and 1,2-dichloroethane (2.5 mL) was added. Oxygen was added *via* active purge. The septum was replaced with a crimping cap and the vessel was sealed and stirred for 48 h at 50 °C. The

reaction mixture was filtered through a plug of silica and the resultant material was concentrated *in vacuo* and chromatographed using 20% ethyl acetate/hexane to afford the *ortho-para* or *para-para* biphenol.

**Table 2 Data**

3',5'-Di-*tert*-butyl-3,5-dimethyl-[1,1'-biphenyl]-2,4'-diol **(Table 2, entry 1)**. Following the general procedure, the *ortho-para* product was obtained in 75% yield: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.22 (s, 2H), 6.93 (s, 1H), 6.87 (s, 1H), 5.30 (s, 1H), 5.22 (s, 1H), 2.29 (s, 3H), 2.28 (s, 3H), 1.47 (s, 18H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 154.6, 148.5, 136.9, 130.6, 129.0, 128.3, 128.2, 128.1, 125.8, 124.1, 34.5, 30.3, 20.5, 16.1; IR (film) 3623, 2444, 2917, 1436, 1314, 1118 $cm^{-1}$; HRMS (ES) *m/z* = 325.2168 calcd for $C_{22}H_{29}O_2$ $[M-H]^-$, found 325.2154.

3',5'-Di-*tert*-butyl-4,5,6-trimethyl-[1,1'-biphenyl]-2,4'-diol **(Table 2, entry 2)**. Following the general procedure, the *ortho-para* product was obtained in 85% yield: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.04 (s, 2H), 6.73 (s, 1H), 5.29 (s, 1H), 4.75 (s, 1H), 2.31 (s, 3H), 2.17 (s, 3H), 2.02 (s, 3H), 1.45 (s, 18H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 153.5, 150.7, 136.9, 136.6, 135.6, 127.1, 126.9, 126.5, 113.6, 34.5, 30.4, 20.8, 17.9, 15.3; IR (film) 3538, 2959, 1576, 1431, 1301, 1142, 1040 $cm^{-1}$; HRMS (ES) *m/z* = 363.2300 calcd for $C_{23}H_{32}O_2$ Na $[M+Na]^+$, found 363.2310.

3',5'-Di-*tert*-butyl-4,6-dimethyl-[1,1'-biphenyl]-2,4'-diol **(Table 2, entry 3)**. Following the general procedure, the *ortho-para* product was obtained in 56% yield (91% based on recovered starting material): $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.05 (s, 2H), 6.69 (s, 2H), 5.29 (s, 1H), 4.92 (s, 1H), 2.32 (s, 3H), 2.06 (s, 3H), 1.45 (s, 18H); $^{13}$C NMR (125 MHz,

$CDCl_3$) δ 153.6, 153.1, 138.1, 137.3, 136.9, 126.9, 126.1, 125.6, 122.7, 112.9, 34.5, 30.4, 21.2, 20.4; IR (film) 3531, 2957, 1625, 1560, 1434, 1154 $cm^{-1}$; HRMS (ES) *m/z* = 325.2168 calcd for $C_{22}H_{29}O_2$ $[M-H]^-$, found 325.2167.

3',5'-Di-*tert*-butyl-3,4,6-trimethyl-[1,1'-biphenyl]-2,4'-diol **(Table 2, entry 4)**. Following the general procedure, the *ortho-para* product was obtained in 55% yield (89% based on recovered starting material): $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.05 (s, 2H), 6.69 (s, 1H), 5.29 (s, 1H), 5.03 (s, 1H), 2.29 (s, 3H), 2.19 (s, 3H), 2.03 (s, 3H), 1.45 (s, 18H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 153.5, 151.0, 37.0, 136.6, 133.8, 126.9, 126.2, 126.2, 122.9, 119.6, 34.5, 30.4, 20.1, 19.8, 11.7; IR (film) 3640, 3536, 2918, 1654, 1436, 1084, 890 $cm^{-1}$; HRMS (ES) *m/z* = 339.2324 calcd for $C_{23}H_{31}O_2$ $[M-H]^-$, found 339.2319.

3,3',4,5',6-Pentamethyl-[1,1'-biphenyl]-2,4'-diol **(Table 2, entry 5)**. Following the general procedure, the *ortho-para* product was obtained in 51% yield (89% based on recovered starting material): $^1H$ NMR (500 MHz, $CDCl_3$) δ 6.88 (s, 2H), 6.66 (s, 1H), 4.90 (s, 1H), 4.69 (s, 1H), 2.28 (s, 6H), 2.27 (s, 3H), 2.17 (s, 3H), 2.02 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 152.0, 150.9, 136.6, 133.6, 130.6, 127.2, 125.2, 124.1, 122.9, 119.5, 20.0, 19.9, 15.9, 11.7; IR (film) 3533, 2921, 1568, 1455, 1300, 1192, 1082 $cm^{-1}$; HRMS (ES) *m/z* = 255.1385 calcd for $C_{17}H_{19}O_2$ $[M-H]^-$, found 255.1392.

3',5'-Di-*tert*-butyl-[1-naphthyl-1'-phenyl]-2,4'-diol **(Table 2, entry 6)**. Following the general procedure, the *ortho-para* product was obtained in 83% yield: $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J*=8.0 Hz, 1H), 7.79 (d, *J*=8.5 Hz, 1H), 7.47 (d, *J*=8.0 Hz, 1H), 7.37-7.32 (m, 3H), 7.19 (s, 2H), 5.39 (s, 1H), 5.32 (s, 1H), 1.48 (s, 18H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 154.0, 150.4, 137.2, 133.7, 129.0, 128.9, 128.0, 127.6, 126.3, 124.9, 124.4, 123.1, 121.9, 117.2, 34.6, 30.4; IR (film) 3629, 3525, 2959, 1610, 1441, 1389,

1149, 889, 819, 742 $cm^{-1}$; HRMS (ES) *m/z* = 348.2089 calcd for $C_{24}H_{28}O_2$ $[M]^+$, found 348.2098.

3',5,5'-Tri-*tert*-butyl-2-methyl-[1,1'-biphenyl]-4,4'-diol **(Table 2, entry 7)**. Following the general procedure, the *para-para* product was obtained in 57% yield (90% based on recovered starting material): $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.16 (s, 1H), 7.12 (s, 2H), 6.59 (s, 1H), 5.18 (s, 1H), 4.71 (s, 1H), 2.21 (s, 3H), 1.47 (s, 18H), 1.42 (s, 9H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 152.8, 152.4, 135.2, 135.0, 134.2, 133.3, 132.9, 129.0, 126.1, 118.2, 34.4, 34.3, 30.4, 29.8, 20.0; IR (film) 3637, 3514, 2957, 1611, 1386, 1323, 1230, 1154 $cm^{-1}$; HRMS (ES) *m/z* = 367.2637 calcd for $C_{25}H_{35}O_2$ $[M-H]^-$, found 367.2639.

5-(*tert*-Butyl)-3',5'-diisopropyl-2-methyl-[1,1'-biphenyl]-4,4'-diol **(Table 2, entry 8)**. Following the general procedure, the *para-para* product was obtained in 47% yield (90% based on recovered starting material): $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.14 (s, 1H), 7.00 (s, 2H), 6.59 (s, 1H), 4.76 (s, 1H), 4.69 (s, 1H), 3.20 (septet, *J*=7.0 Hz, 2H), 2.19 (s, 3H), 1.42 (s, 9H), 1.29 (d, *J*=7.0 Hz, 12H,); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 152.8, 148.6, 134.8, 134.2, 133.4, 133.1, 128.8, 124.7, 118.2, 34.2, 29.8, 27.2, 22.8, 19.9; IR (film) 3409, 2919, 1611, 1466, 1385, 1096 $cm^{-1}$; HRMS (ES) *m/z* = 339.2324 calcd for $C_{23}H_{31}O_2$ $[M-H]^-$, found 339.2326.

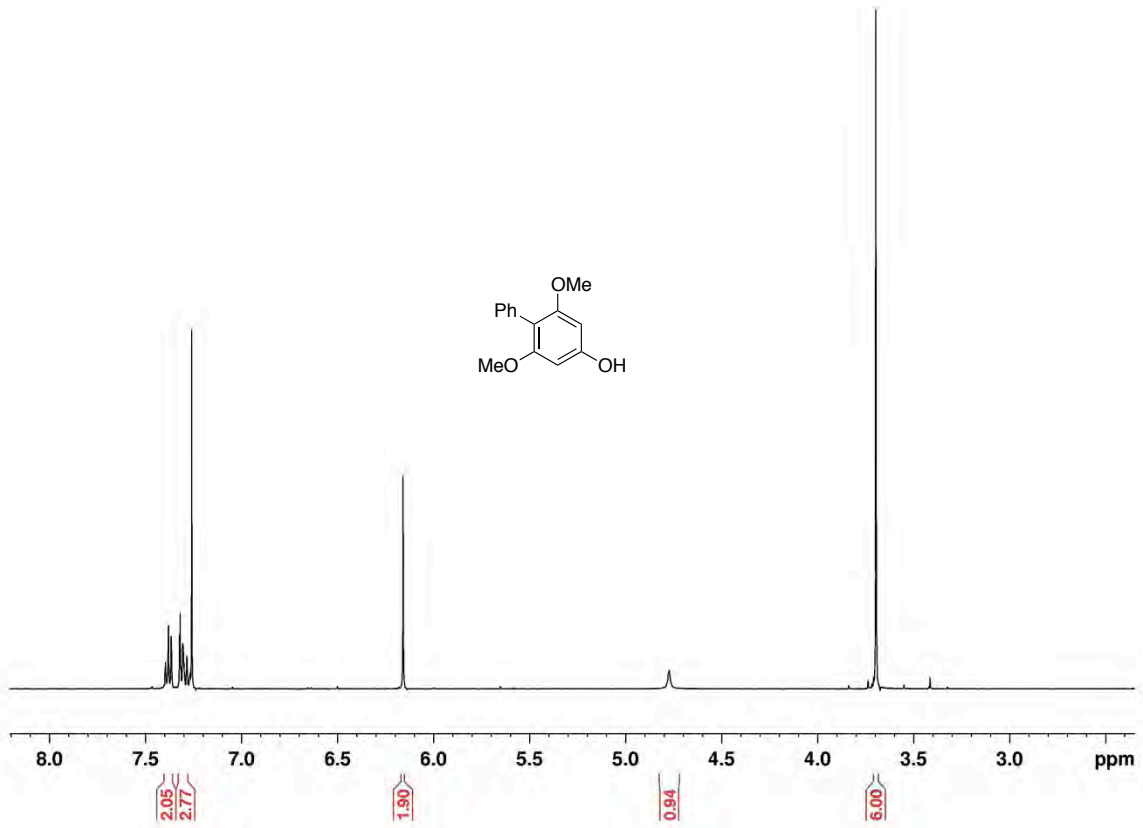
3',5-Di-*tert*-butyl-2,5'-dimethyl-[1,1'-biphenyl]-4,4'-diol **(Table 2, entry 9)**. Following the general procedure, the *para-para* product was obtained in 77% yield: $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.12 (s, 1H), 7.09 (d, *J*=2.0 Hz, 1H), 6.95 (d, *J*=2.0 Hz, 1H), 6.58 (s, 1H), 4.75 (s, 1H), 4.69 (s, 1H), 2.93 (s, 3H), 2.20 (s, 3H), 1.44 (s, 9H), 1.42 (s, 9H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 152.8, 151.3, 135.0, 134.5, 134.1, 133.6, 133.4, 129.4, 128.9, 126.5, 122.6, 118.2, 34.6, 34.2, 29.9, 29.8, 19.9, 16.1; IR (film) 3513, 2956, 1610, 1387, 1327,

1263, 1192, 1034 $cm^{-1}$; HRMS (ES) *m/z* = 325.2168 calcd for $C_{22}H_{29}O_2$ $[M-H]^-$, found 325.2168.

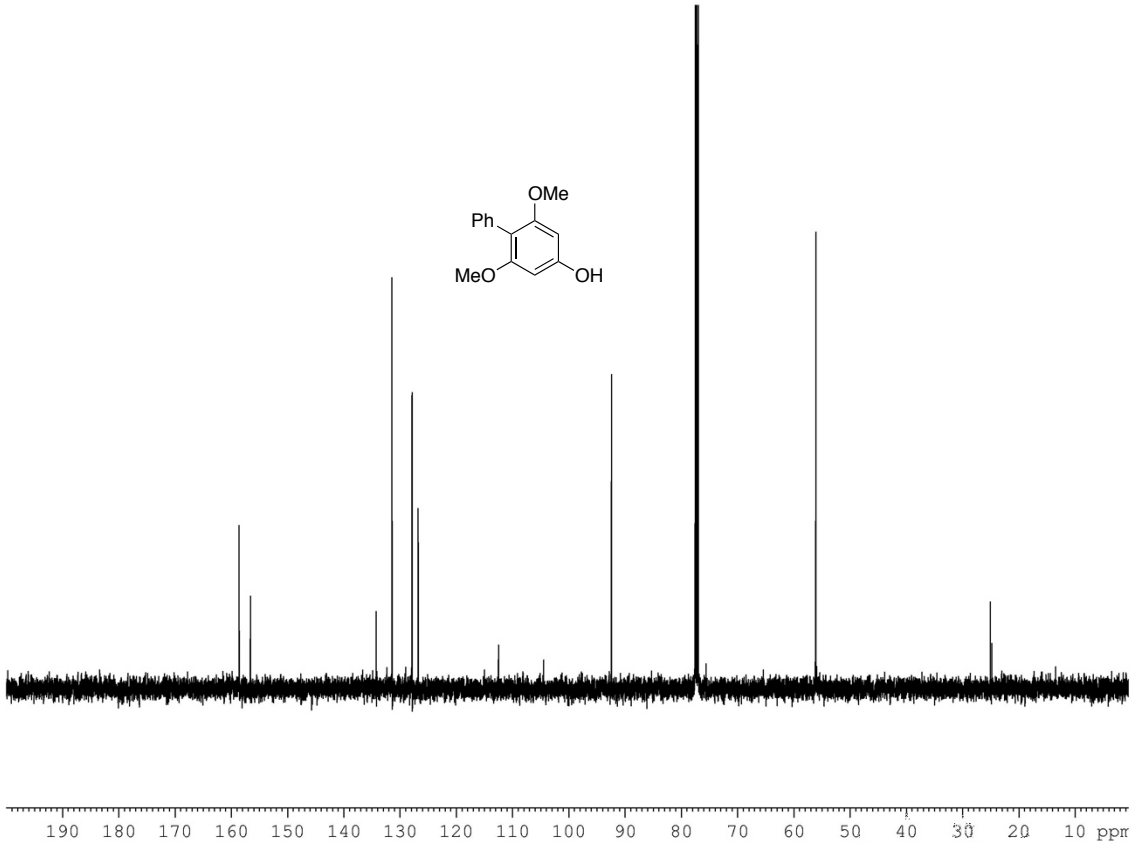
3'-(*tert*-Butyl)-2-isopropyl-5,5'-dimethyl-[1,1'-biphenyl]-4,4'-diol **(Table 2, entry 10)**. Following the general procedure, the *para-para* product was obtained in 74% yield: $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.04 (d, *J*=2.0 Hz, 1H), 6.95 (s, 1H), 6.91 (d, *J*=2.0 Hz, 1H), 6.78 (s, 1H), 4.76 (s, 1H), 4.70 (brs, 1H), 3.03 (ddd, *J*=7.0 Hz, 1H), 2.29 (s, 3H), 2.24 (s, 3H), 1.44 (s, 9H), 1.14 (d, 6H, *J*=7.0 Hz); IR (film) 3387, 2918, 1616, 1434, 1141 $cm^{-1}$; HRMS (ES) *m/z* = 311.2011 calcd for $C_{21}H_{27}O_2$ $[M-H]^-$, found 311.2011.

**Spectral Data**

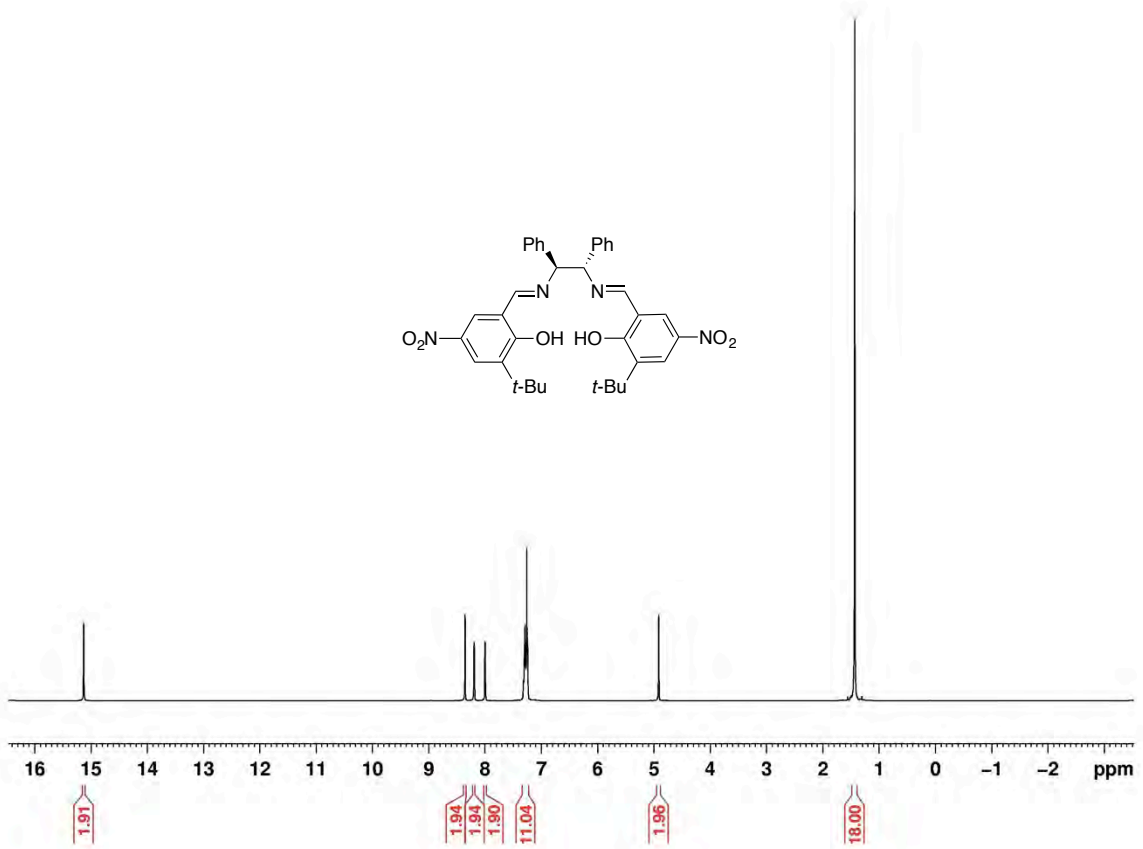
**500 MHz $^{1}$H NMR Spectrum of Substrate for Table 1, Entry 11 in $CDCl_3$**



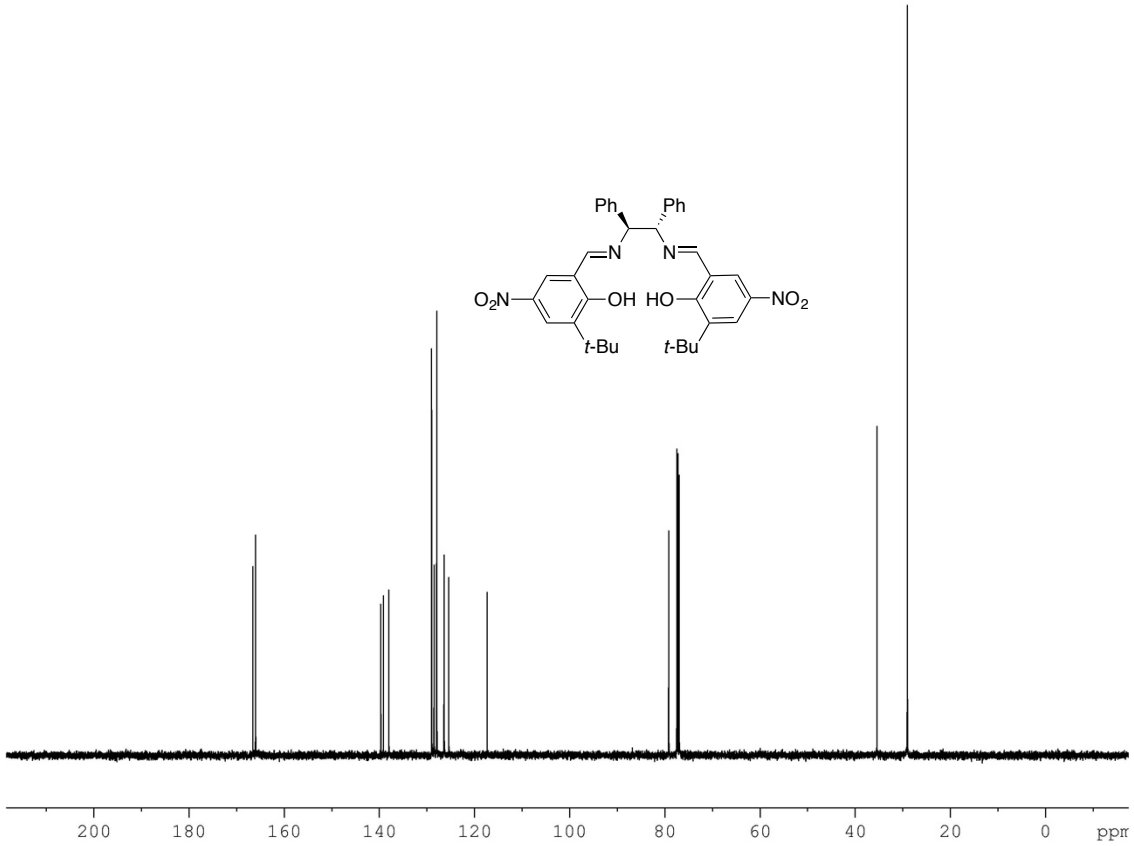
**125 MHz $^{13}C$ NMR Spectrum of Substrate for Table 1, Entry 11 in $CDCl_3$**



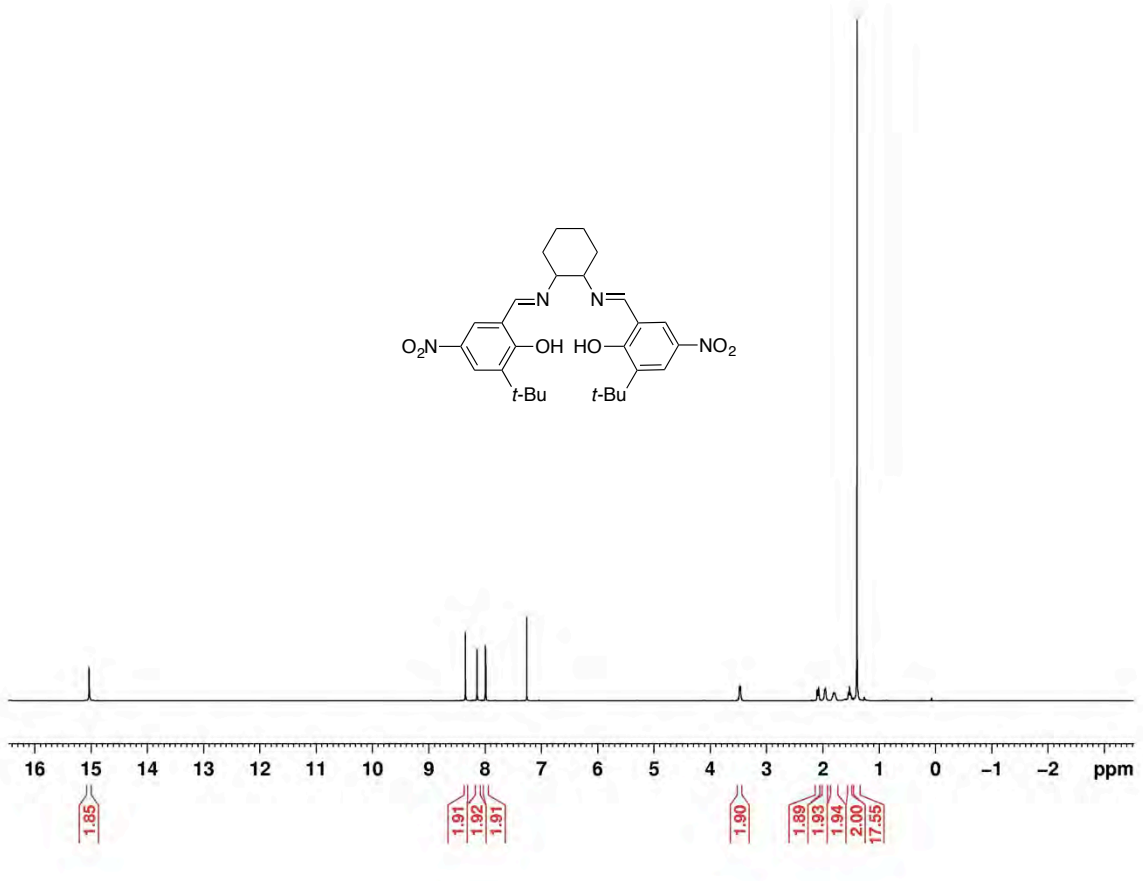
**500 MHz $^{1}$H NMR Spectrum of Compound 6,6'-((1*E*,1'*E*)-((1,2-Diphenylethane-1,2-diyl)bis(azanylylidene))bis(methanylylidene))bis(2-(*tert*-butyl)-4-nitrophenol) in $CDCl_3$**



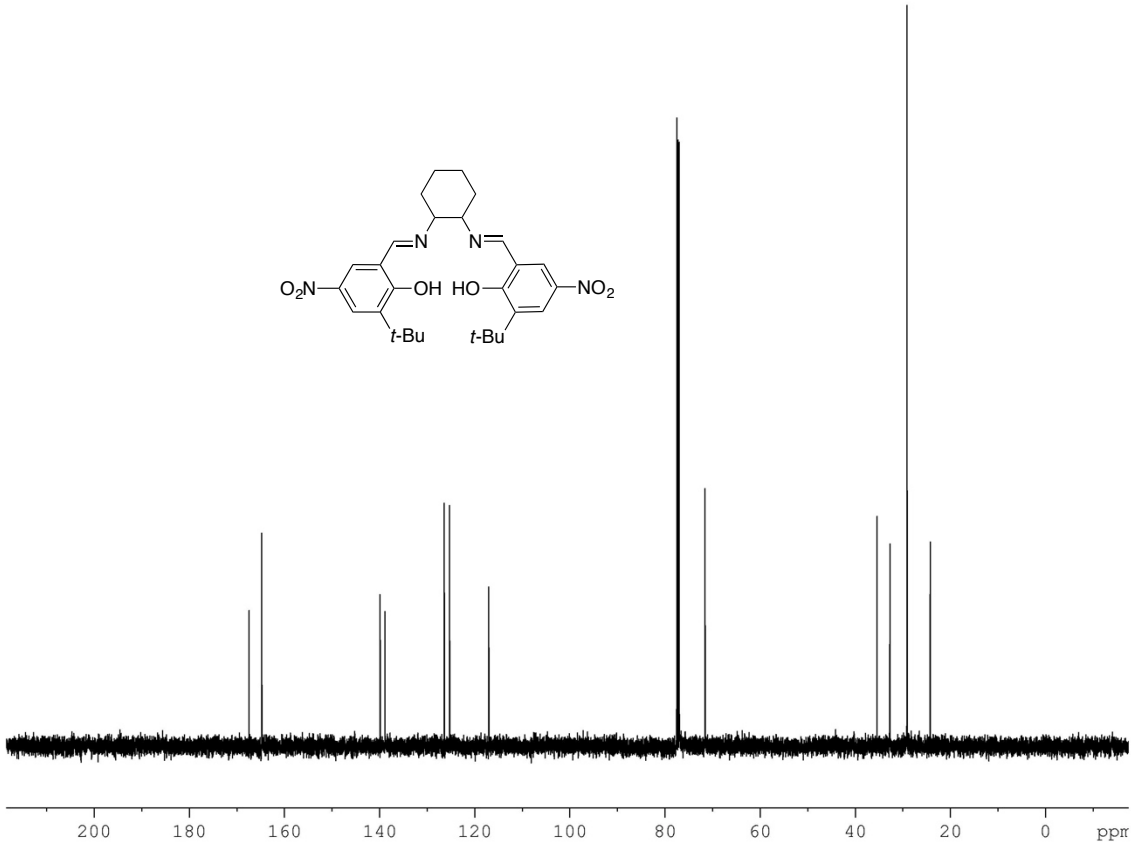
**125 MHz $^{13}$C NMR Spectrum of Compound 6,6'-((1*E*,1'*E*)-((1,2-Diphenylethane-1,2-diyl)bis(azanylylidene))bis(methanylylidene))bis(2-(*tert*-butyl)-4-nitrophenol) in $CDCl_3$**



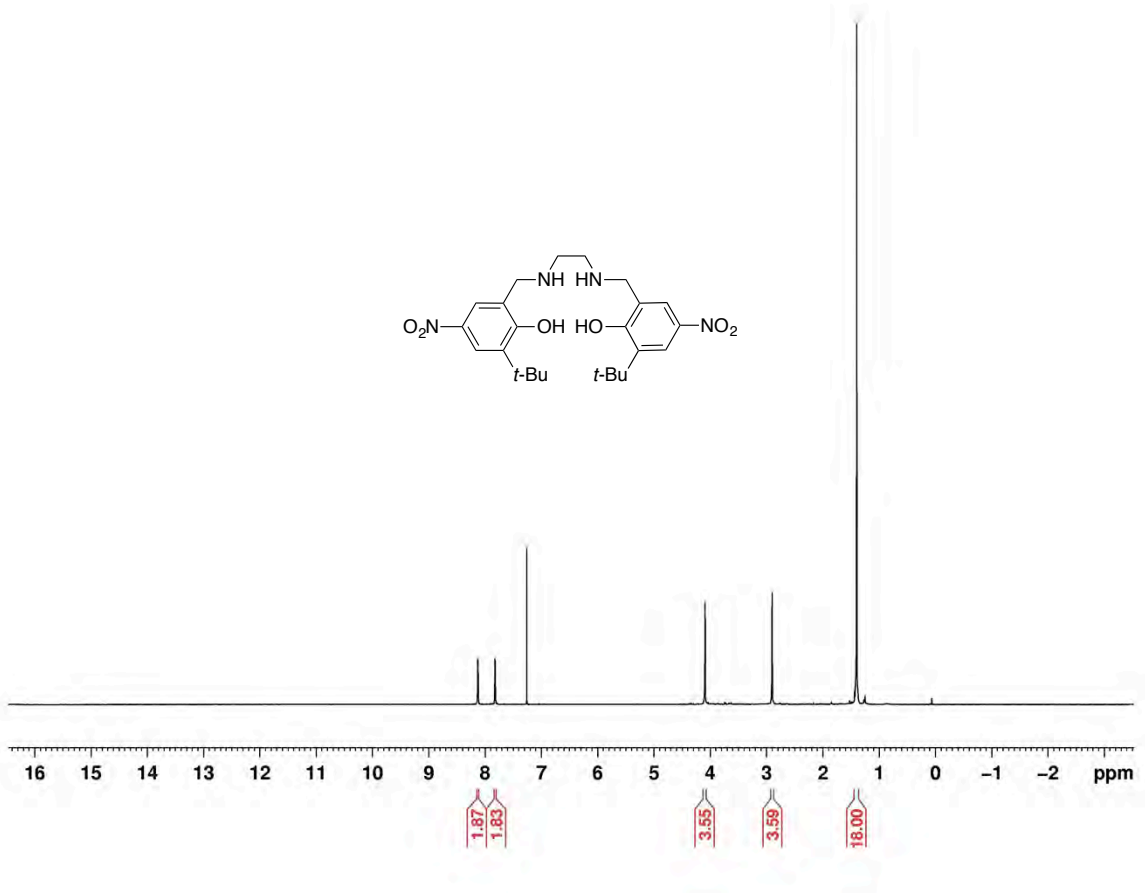
**500 MHz $^{1}$H NMR Spectrum of Compound 6,6'-((1*E*,1'*E*)-(Cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(2-(*tert*-butyl)-4-nitrophenol) in $CDCl_3$**



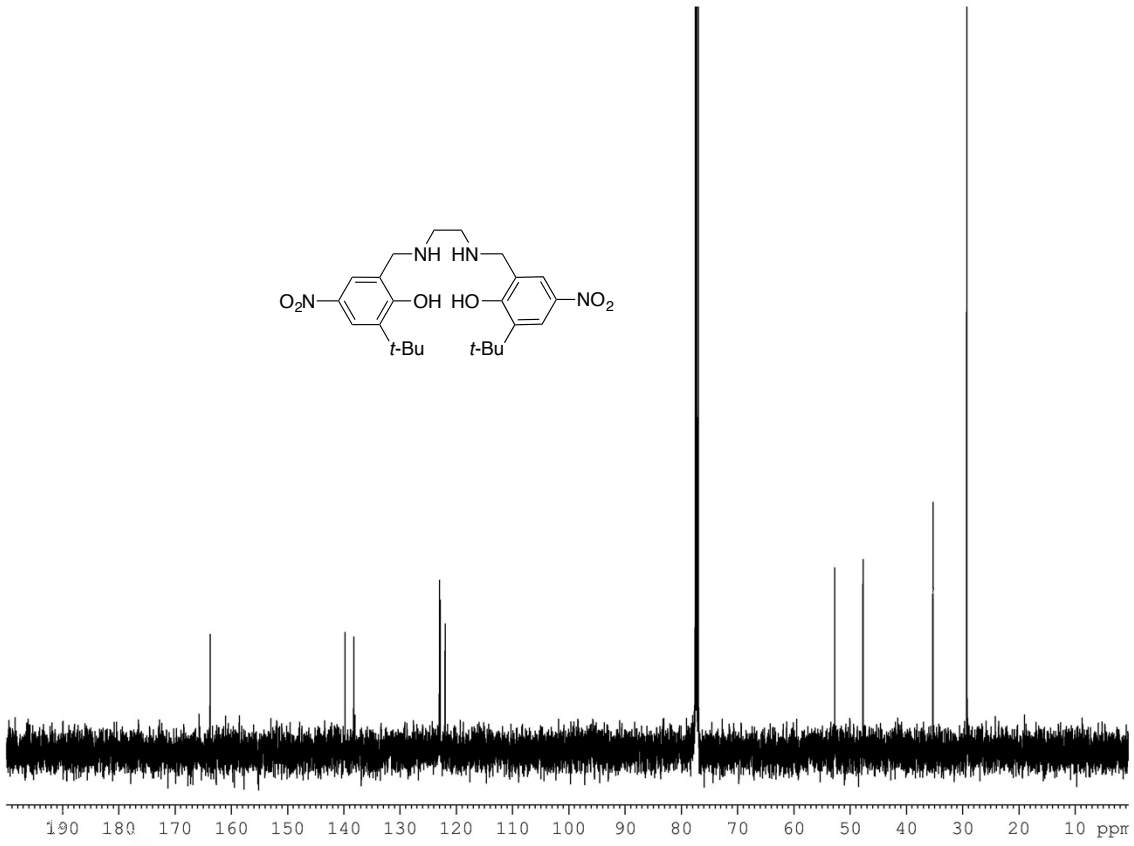
**125 MHz $^{13}$C NMR Spectrum of Compound 6,6'-((1*E*,1'*E*)-(Cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(2-(*tert*-butyl)-4-nitrophenol) in $CDCl_3$**



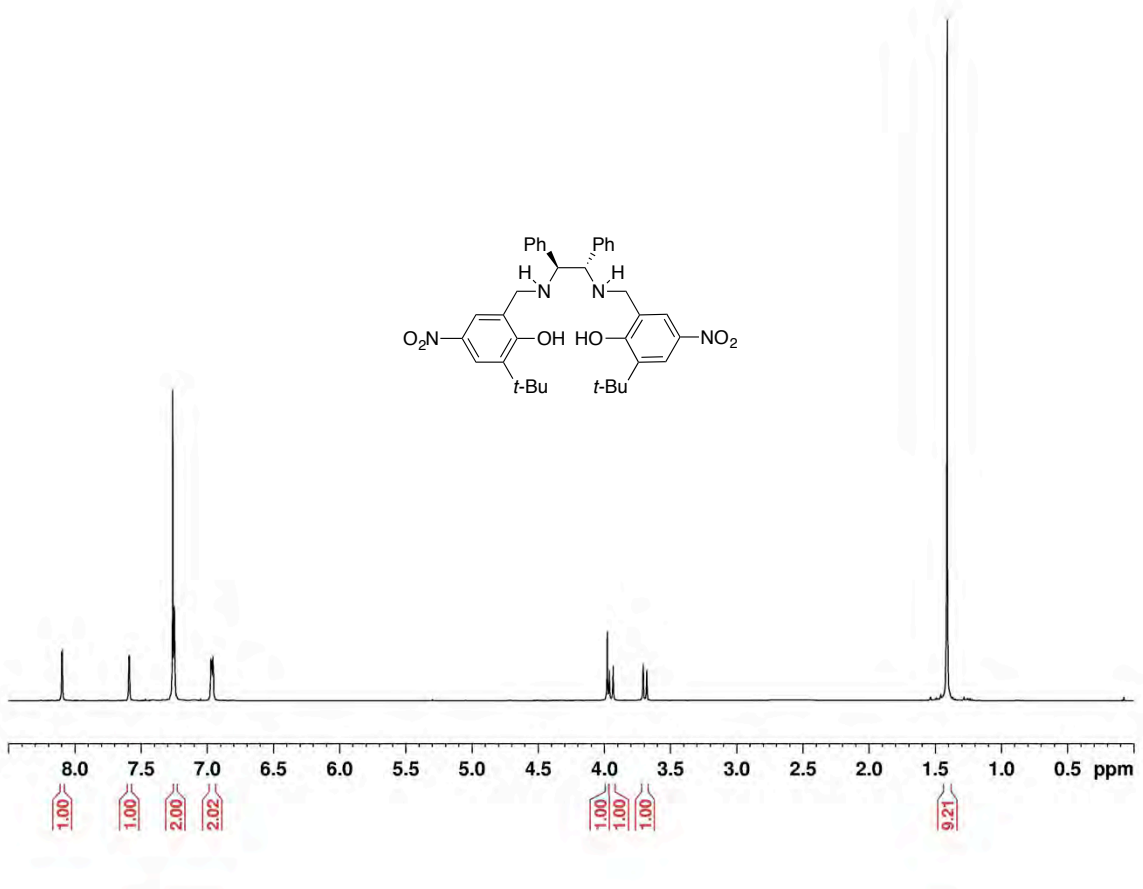
**500 MHz $^{1}$H NMR Spectrum of Compound 6,6'-((Ethane-1,2-diylbis(azanediyl))bis(methylene))bis(2-(tert-butyl)-4-nitrophenol) in $CDCl_3$**



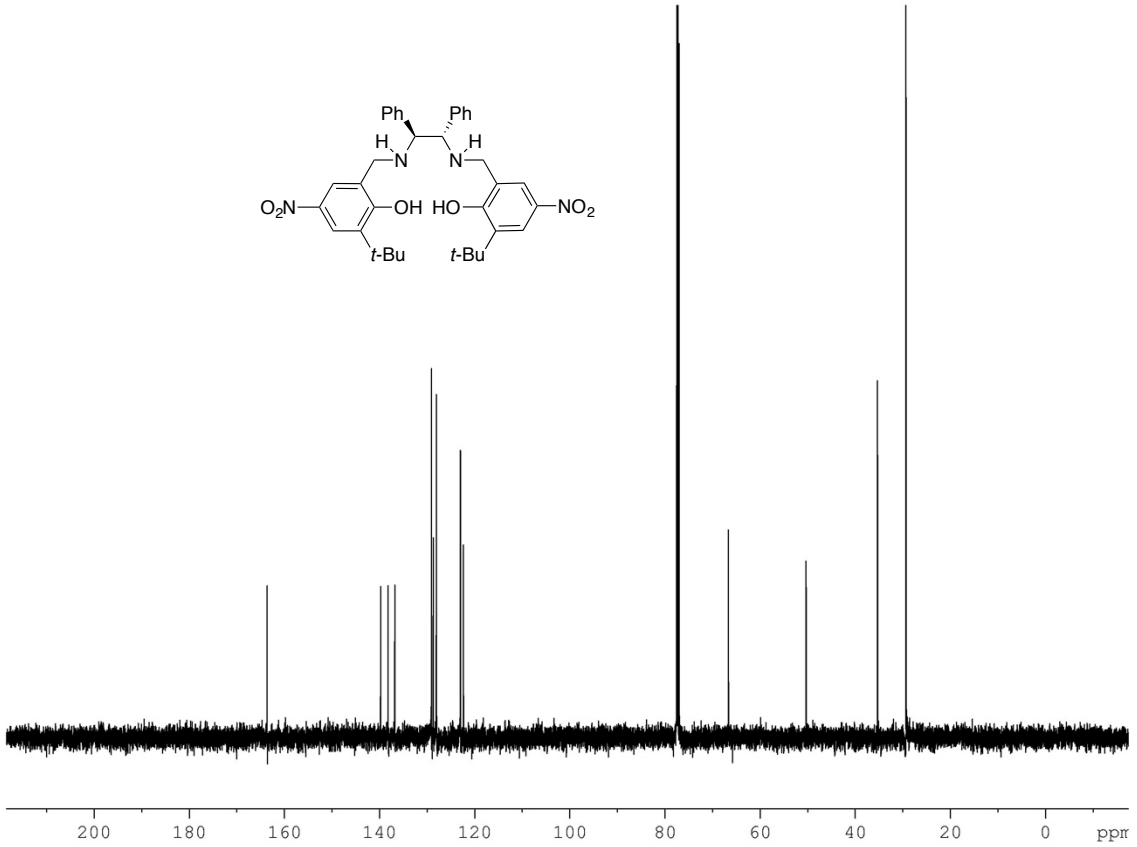
**125 MHz $^{13}$C NMR Spectrum of Compound 6,6'-((Ethane-1,2-diylbis(azanediyl))bis(methylene))bis(2-(tert-butyl)-4-nitrophenol) in $CDCl_3$**



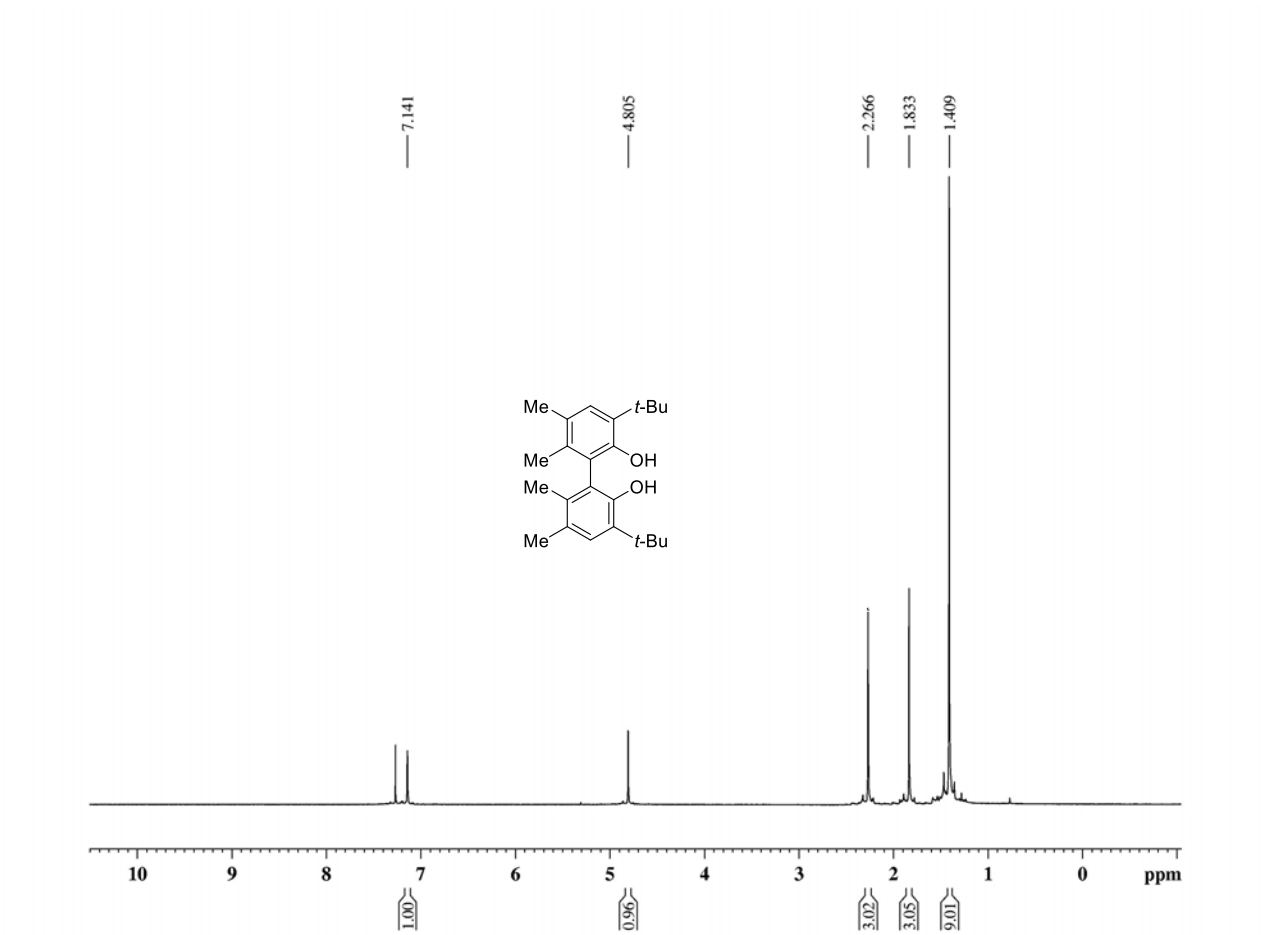
**500 MHz $^{1}$H NMR Spectrum of Compound 6,6'-((((1*S*,2*S*)-1,2-Diphenylethane-1,2-diyl)bis(azanediyl))bis(methylene))bis(2-(*tert*-butyl)-4-nitrophenol) in $CDCl_3$**



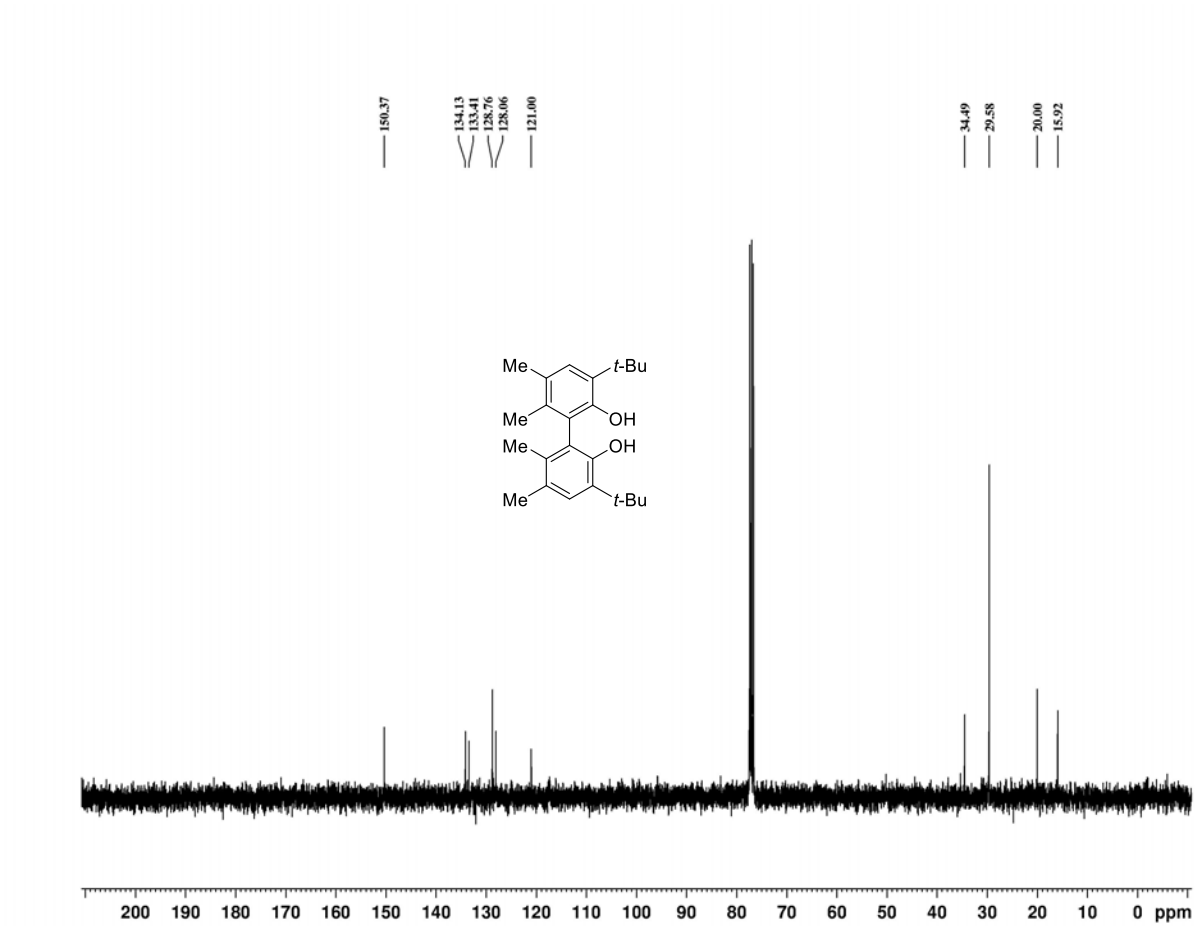
**125 MHz $^{13}$C NMR Spectrum of Compound 6,6'-((((1*S*,2*S*)-1,2-Diphenylethane-1,2-diyl)bis(azanediyl))bis(methylene))bis(2-(*tert*-butyl)-4-nitrophenol) in $CDCl_3$**



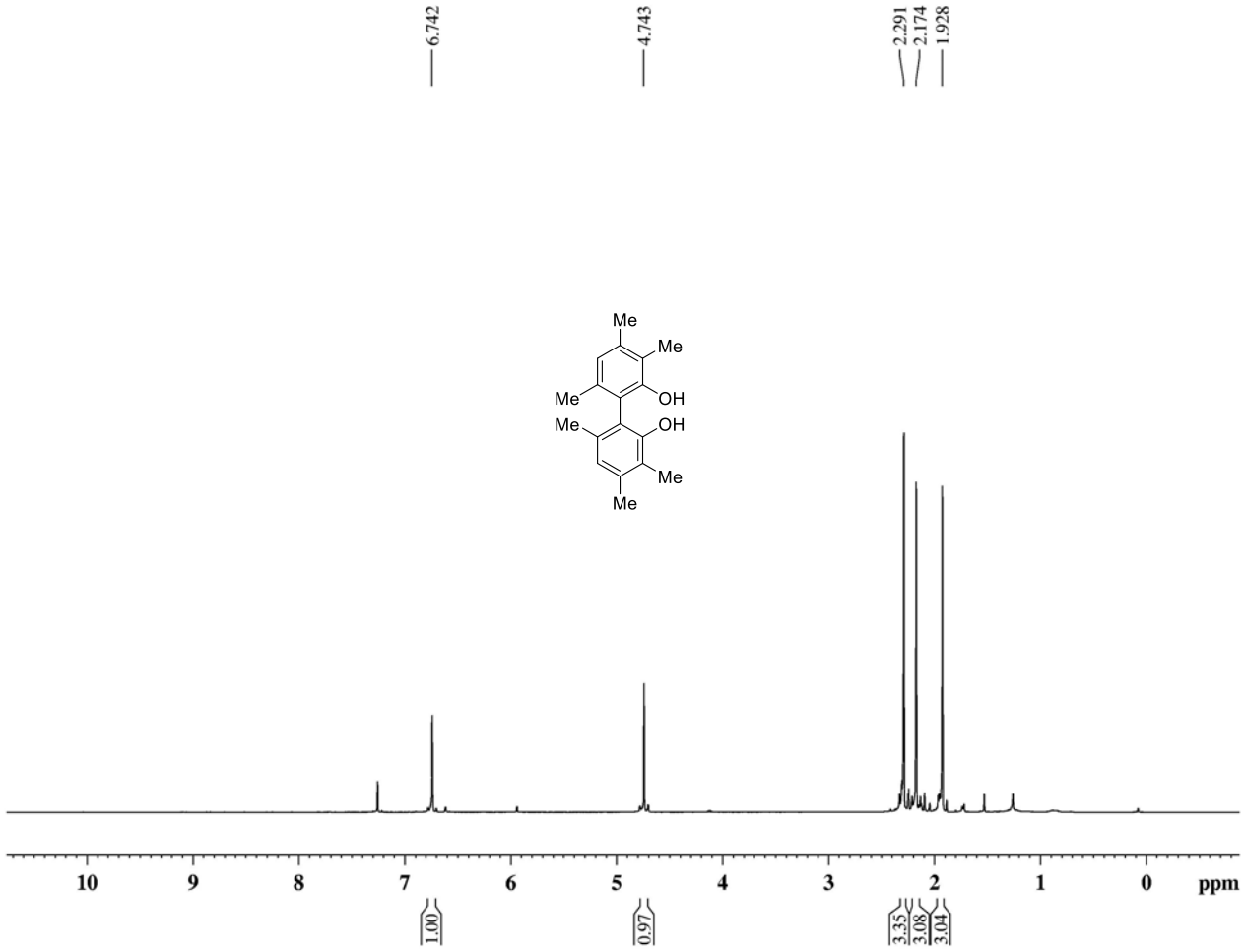
**500 MHz $^{1}$H NMR Spectrum of Table 1, Entry 1 Product in $CDCl_3$**



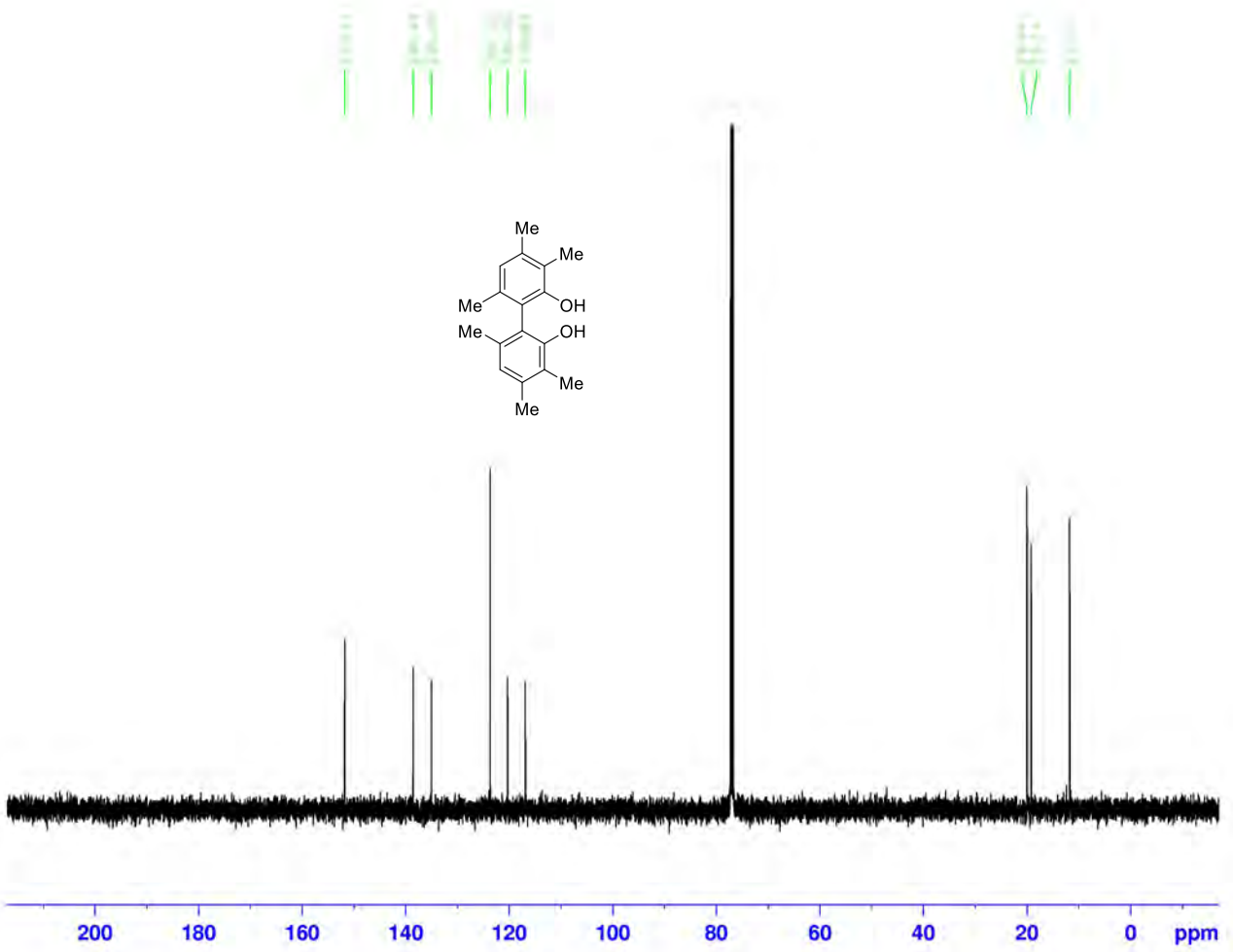
**125 MHz $^{13}C$ NMR Spectrum of Table 1, Entry 1 Product in $CDCl_3$**



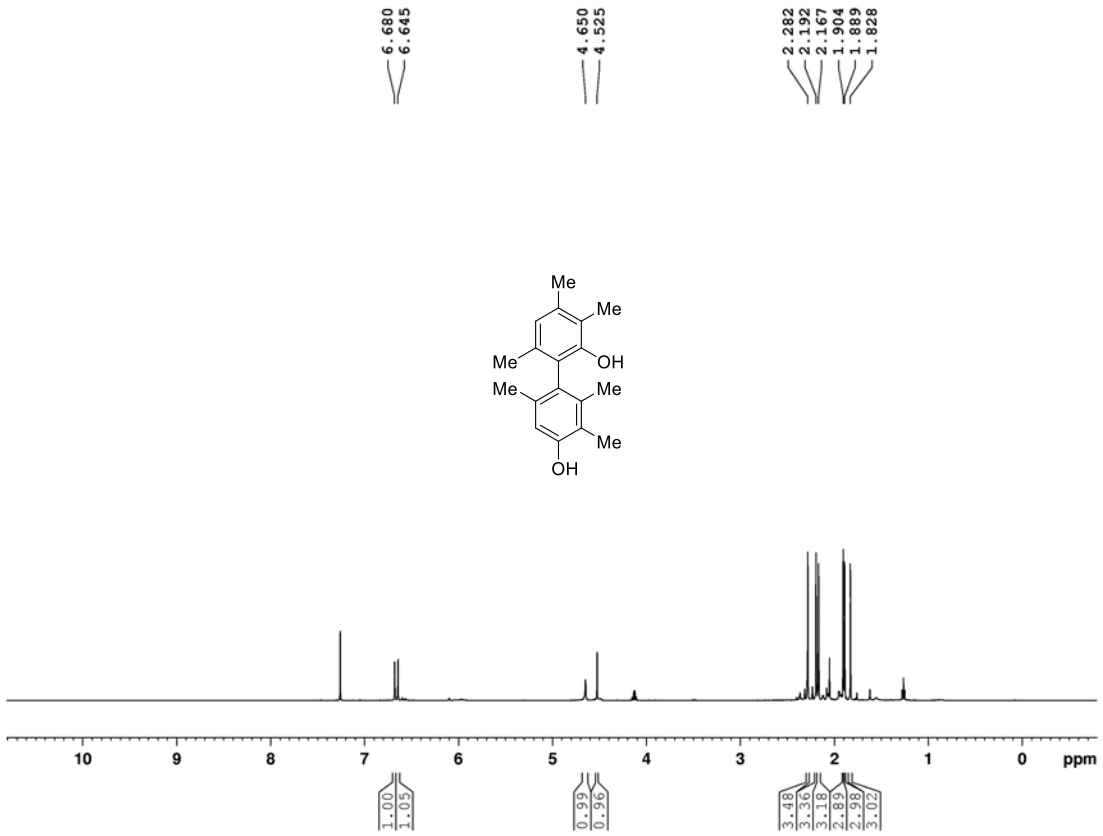
**500 MHz $^{1}$H NMR Spectrum of Table 1, Entry 4 Product in $CDCl_3$**



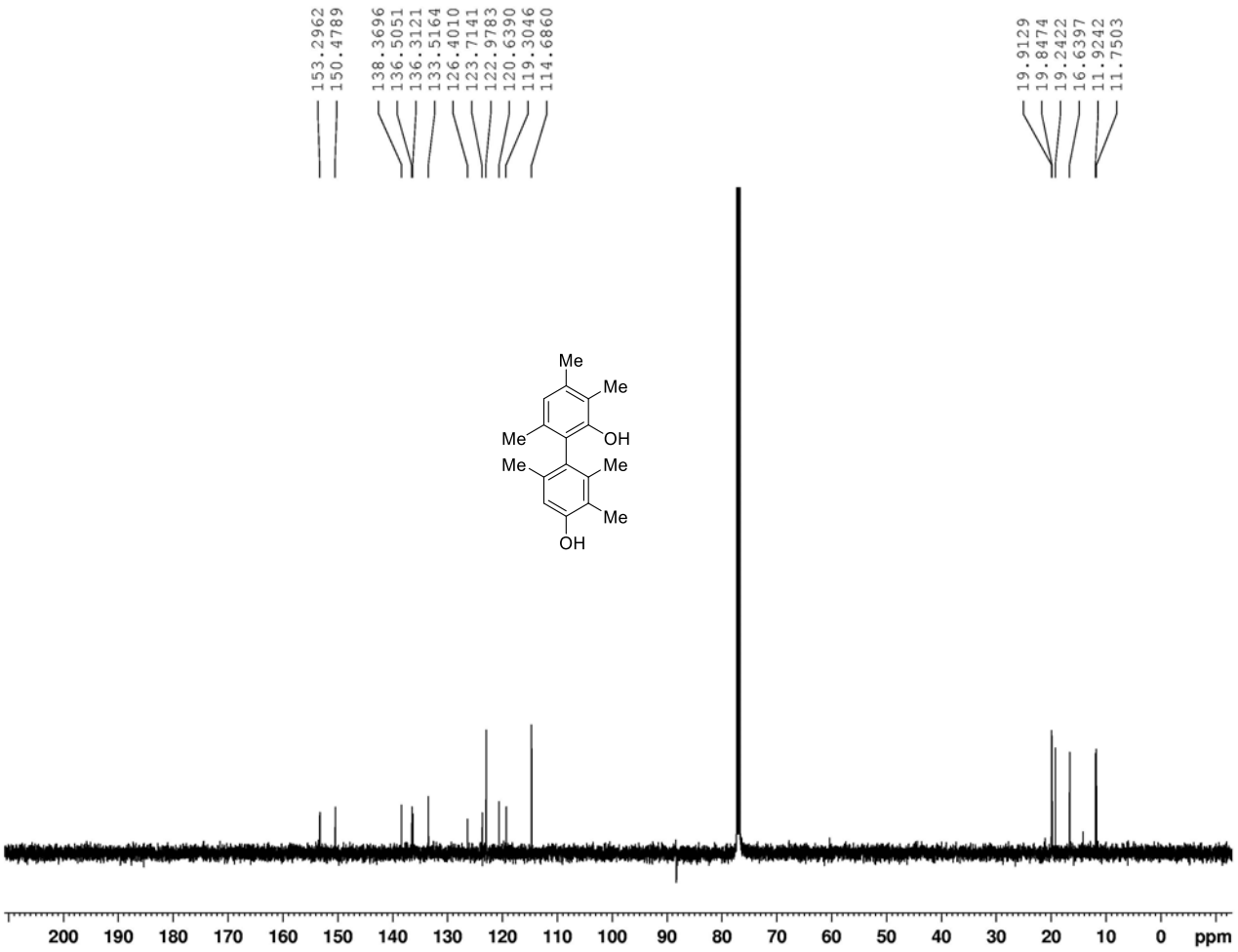
**125 MHz $^{13}C$ NMR Spectrum of Table 1, Entry 4 Product in $CDCl_3$**



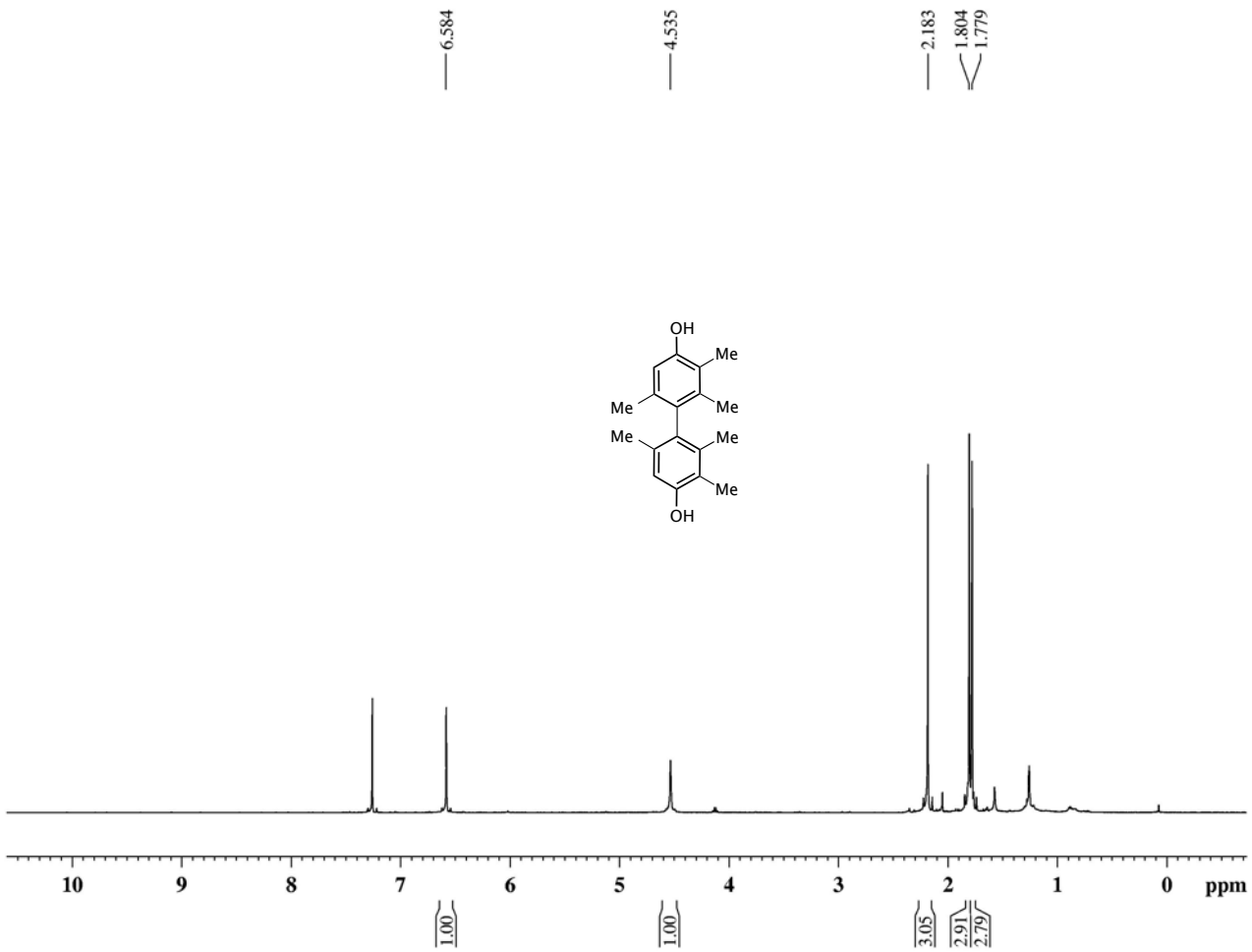
**500 MHz $^{1}$H NMR Spectrum Table 1, Entry 5 Product in $CDCl_3$**



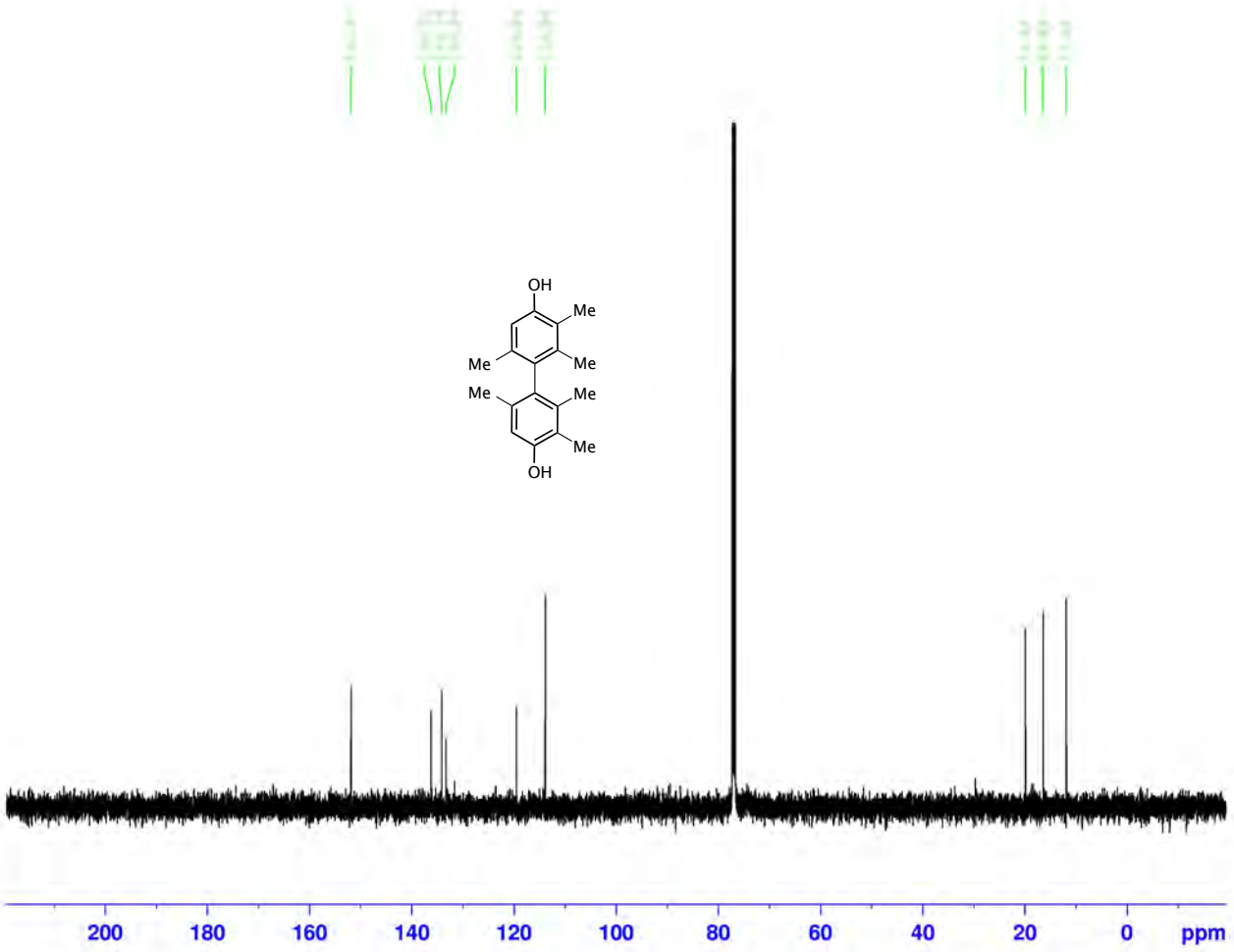
**125 MHz $^{13}$C NMR Spectrum of Table 1, Entry 5 Product in $CDCl_3$**



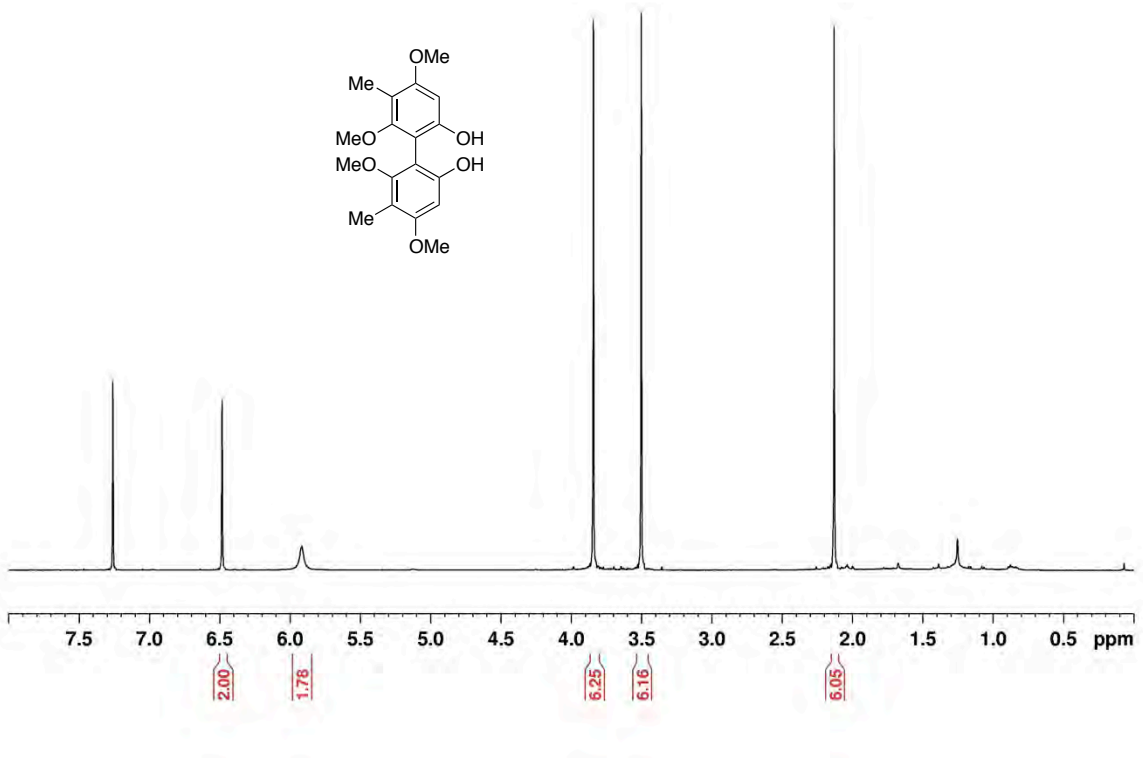
**500 MHz $^{1}$H NMR Spectrum of Table 1, Entry 6 Product in $CDCl_3$**



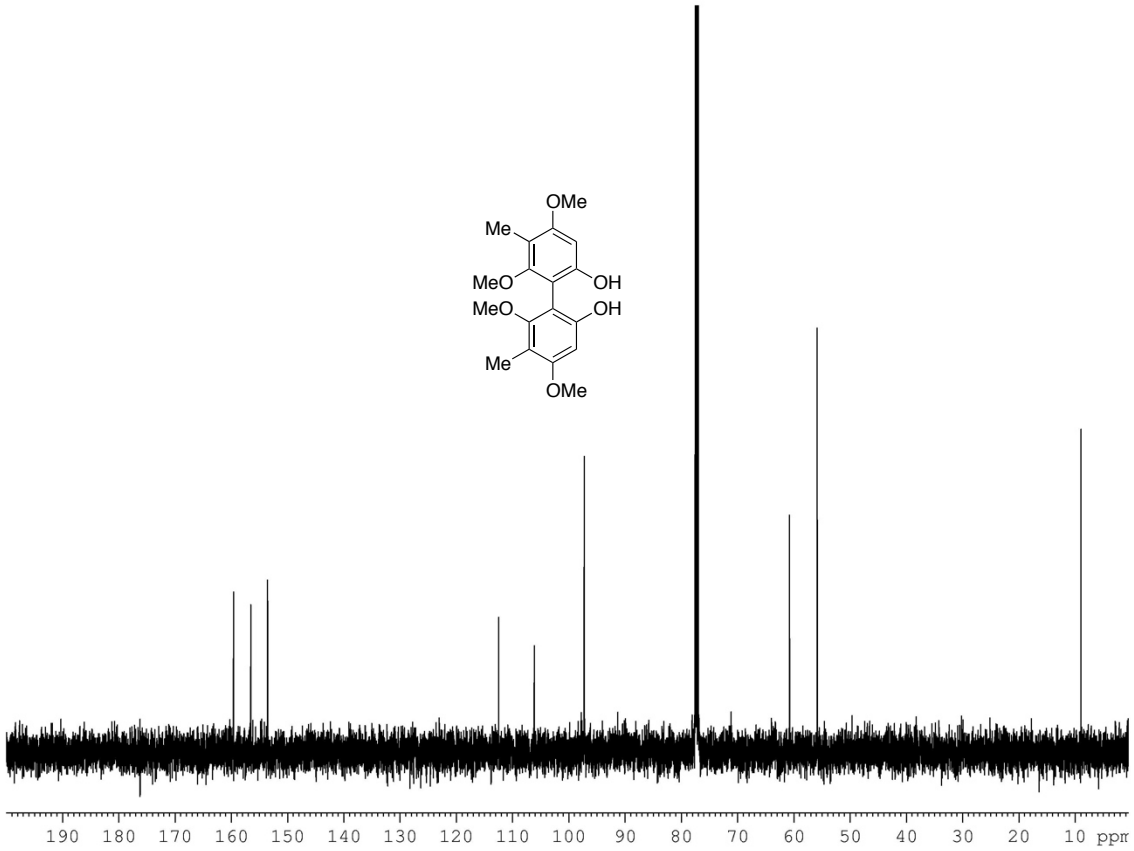
**125 MHz $^{13}C$ NMR Spectrum of Table 1, Entry 6 Product in $CDCl_3$**



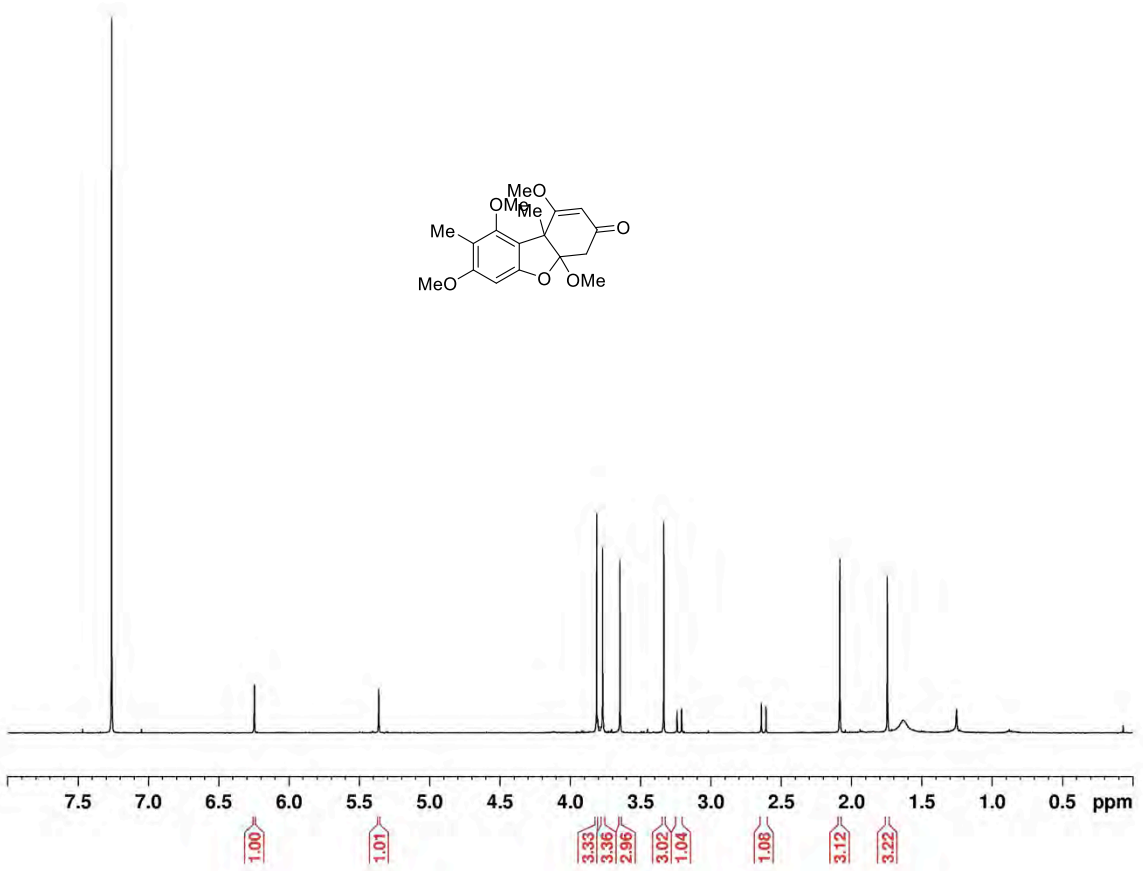
**500 MHz $^{1}$H NMR Spectrum of Table 1, Entry 7 Product in $CDCl_3$**



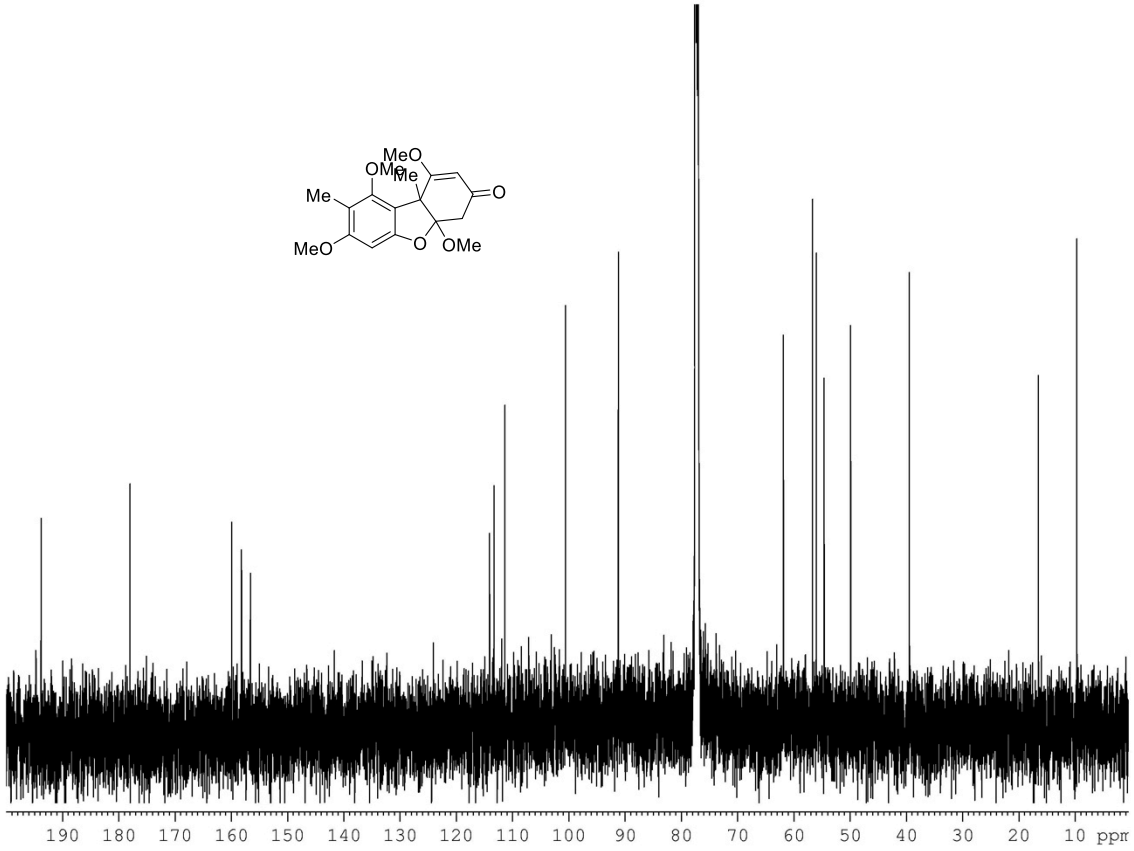
**125 MHz $^{13}C$ NMR Spectrum of Table 1, Entry 7 Product in $CDCl_3$**



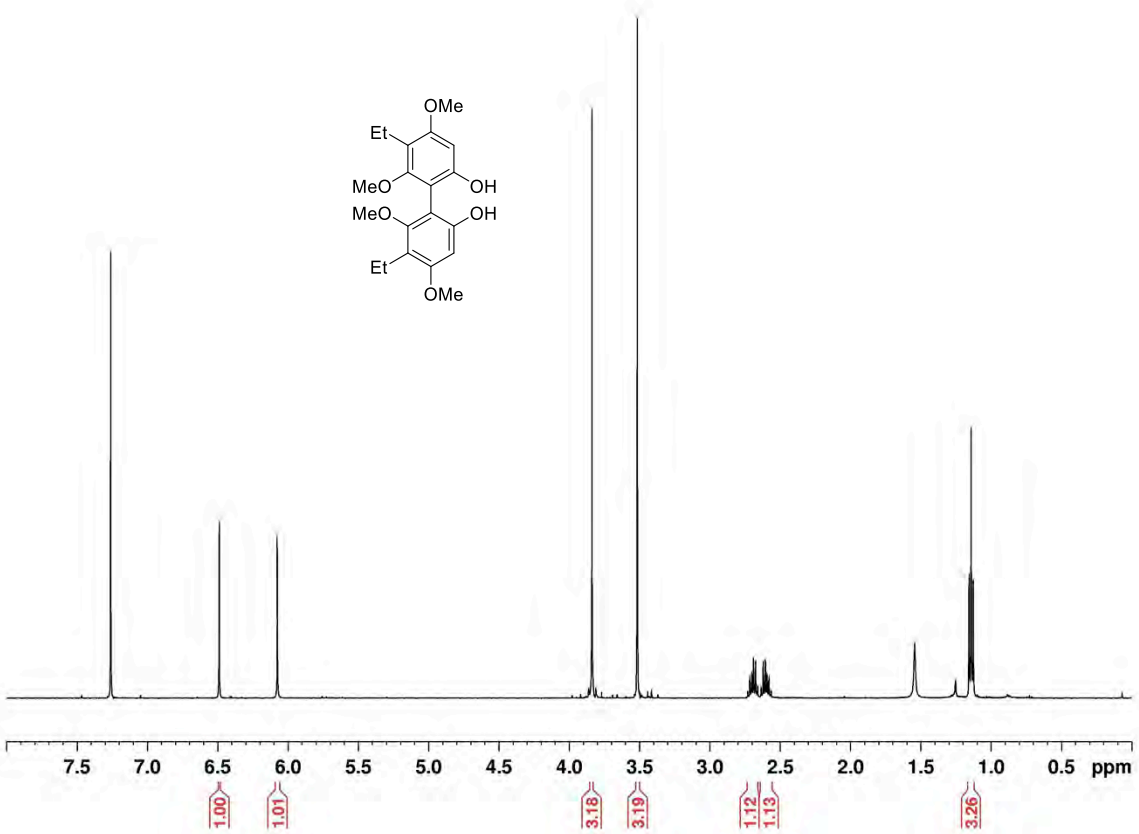
**500 MHz $^{1}$H NMR Spectrum of Table 2, Entry 1 Product in $CDCl_3$**



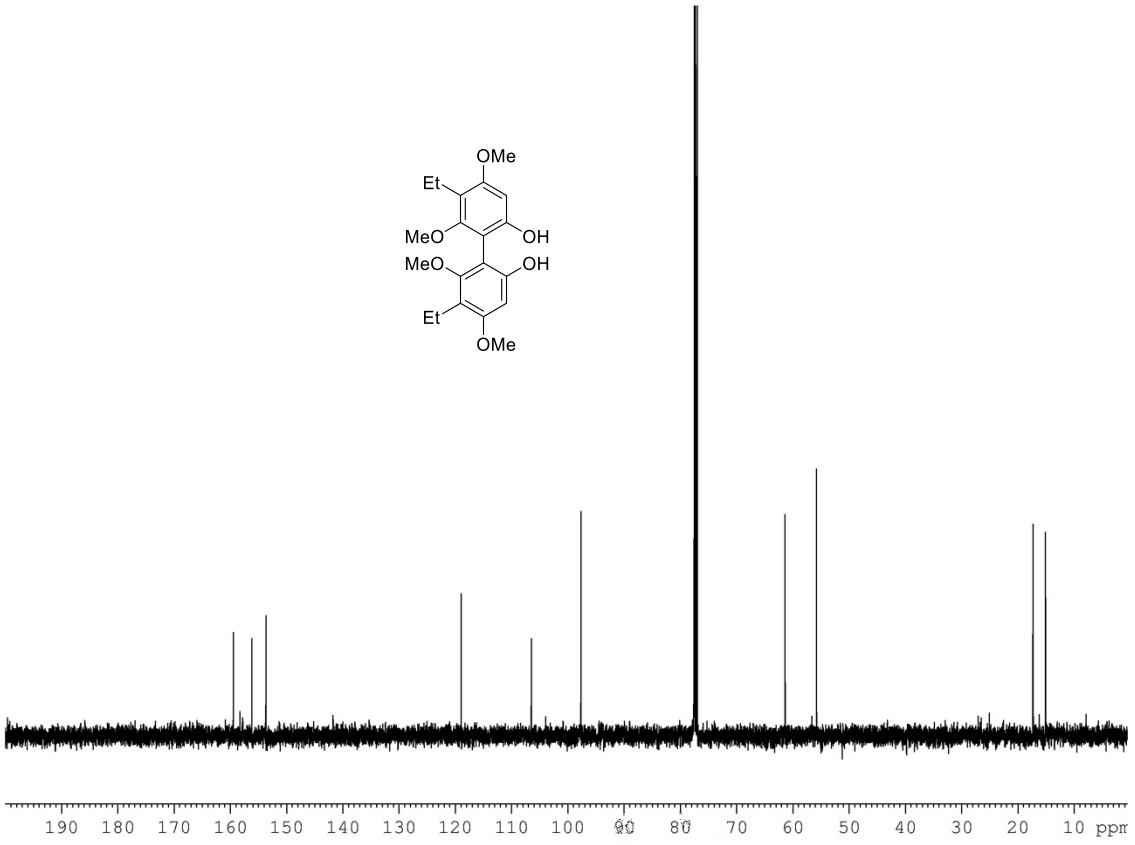
**125 MHz $^{13}$C NMR Spectrum of Table 1, Entry 8 Product in $CDCl_3$**



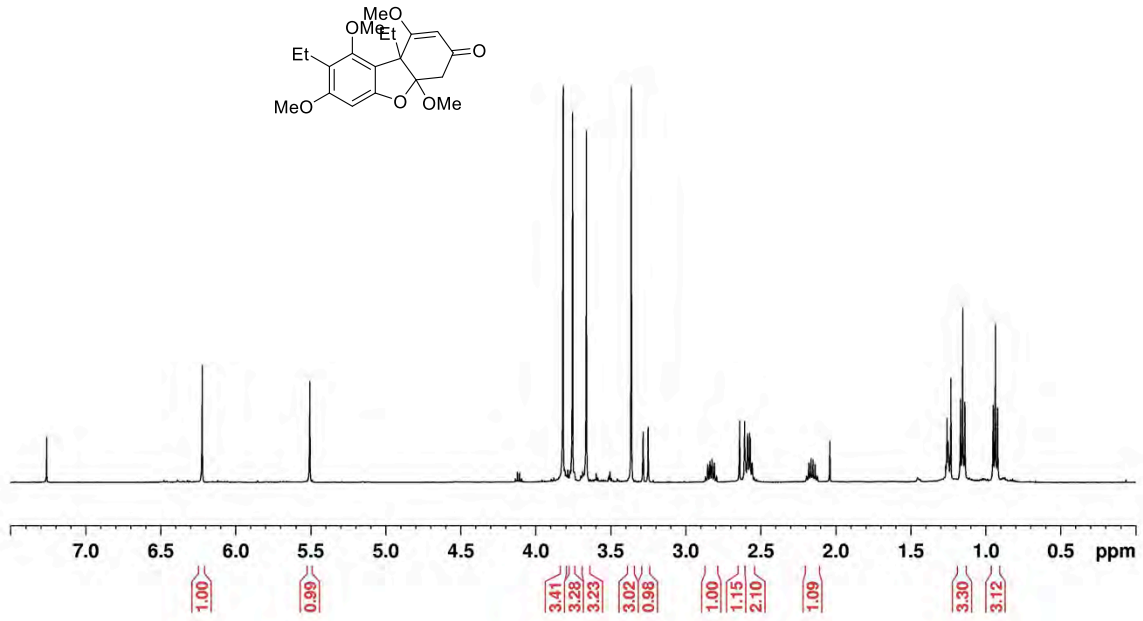
**500 MHz $^{1}$H NMR Spectrum of Table 1, Entry 9 Product in $CDCl_3$**



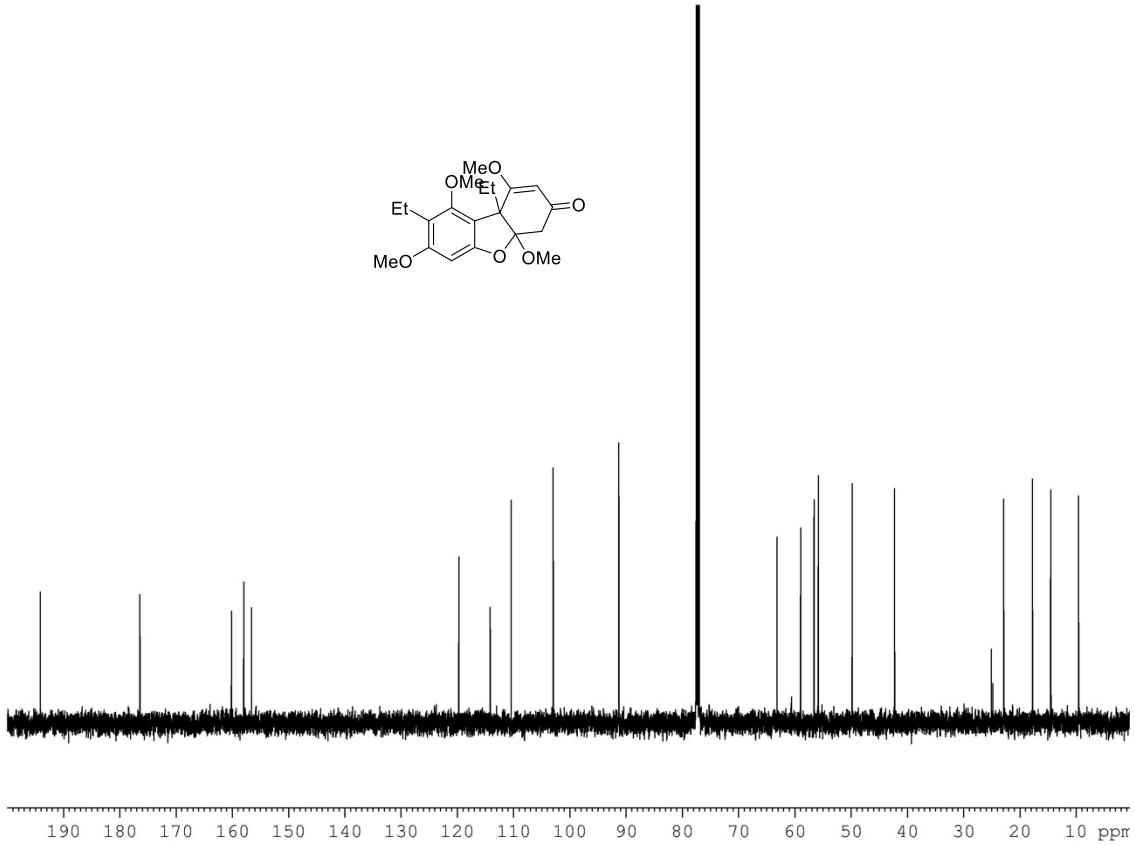
**125 MHz $^{13}C$ NMR Spectrum of Table 1, Entry 9 Product in $CDCl_3$**



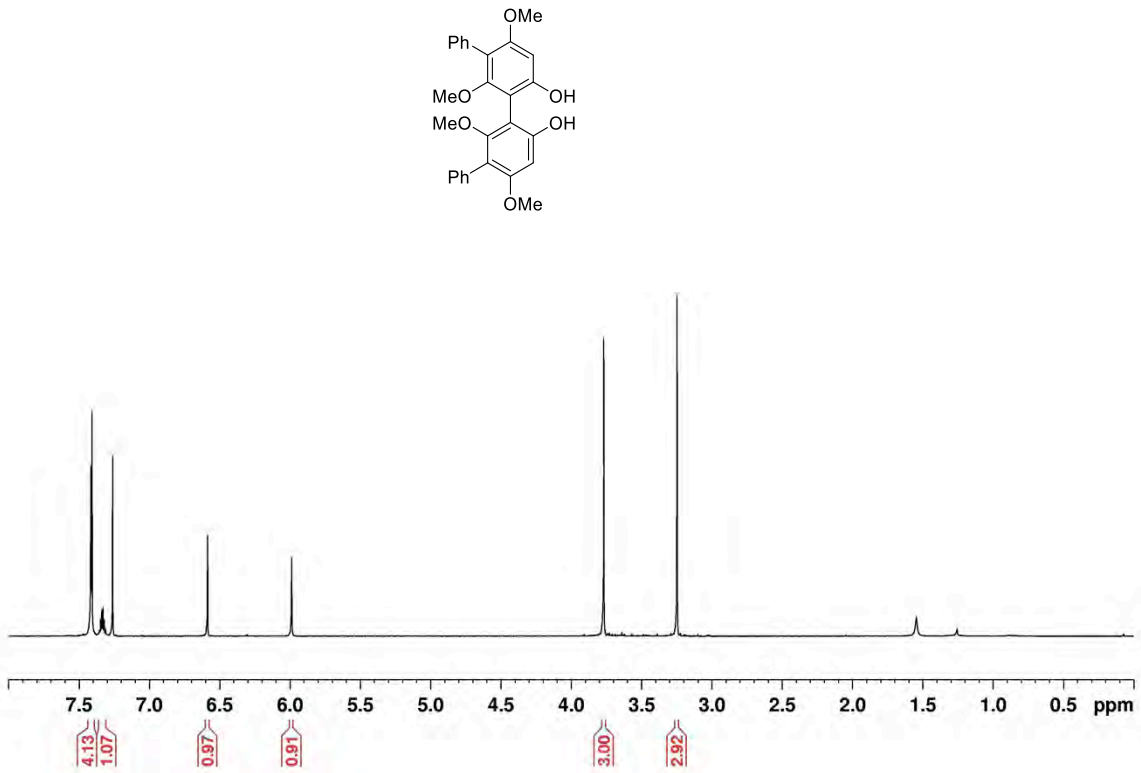
**500 MHz $^{1}$H NMR Spectrum of Table 2, Entry 2 Product in $CDCl_3$**



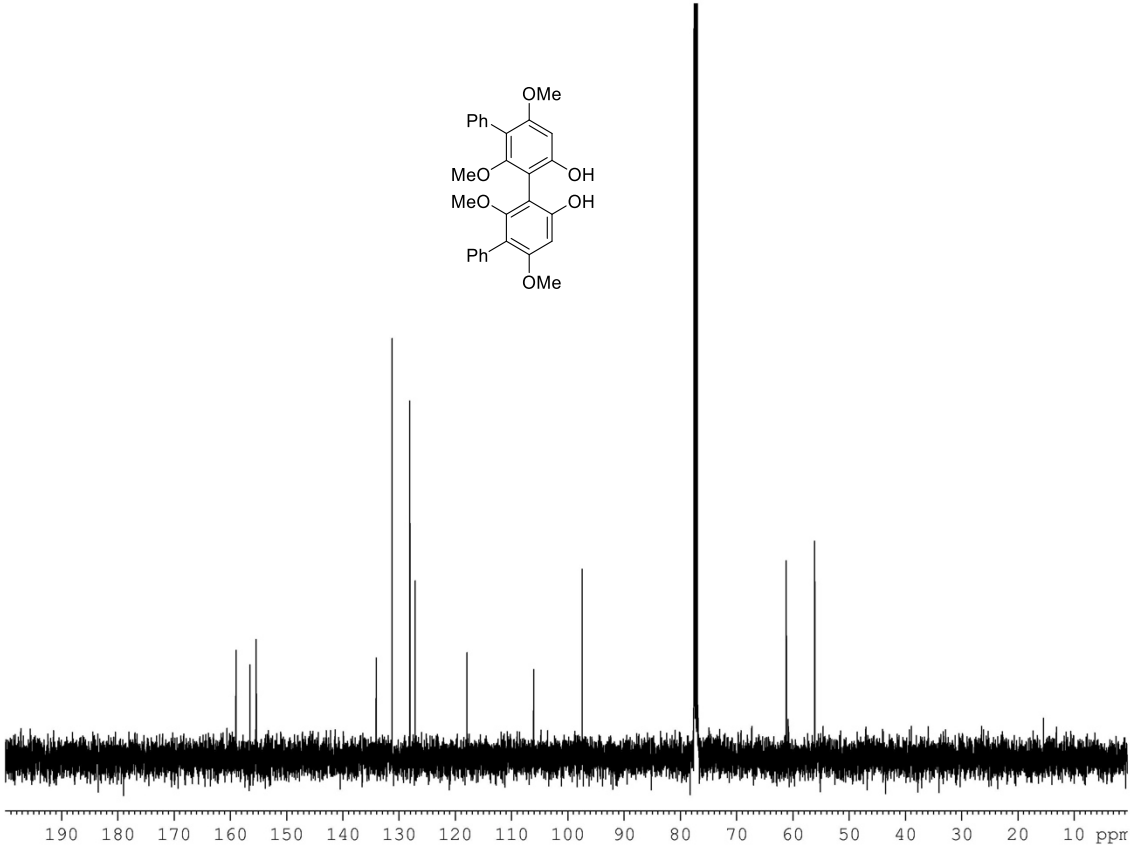
**125 MHz $^{13}$C NMR Spectrum of Table 2, Entry 2 Product in $CDCl_3$**



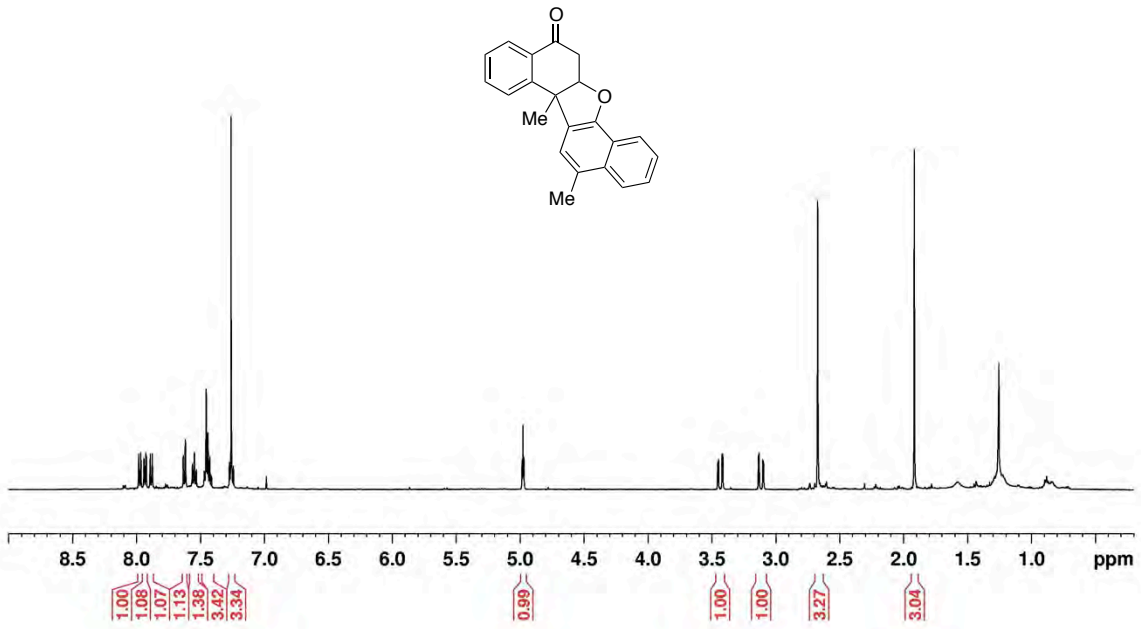
**500 MHz $^{1}$H NMR Spectrum of Table 1, Entry 11 Product in $CDCl_3$**



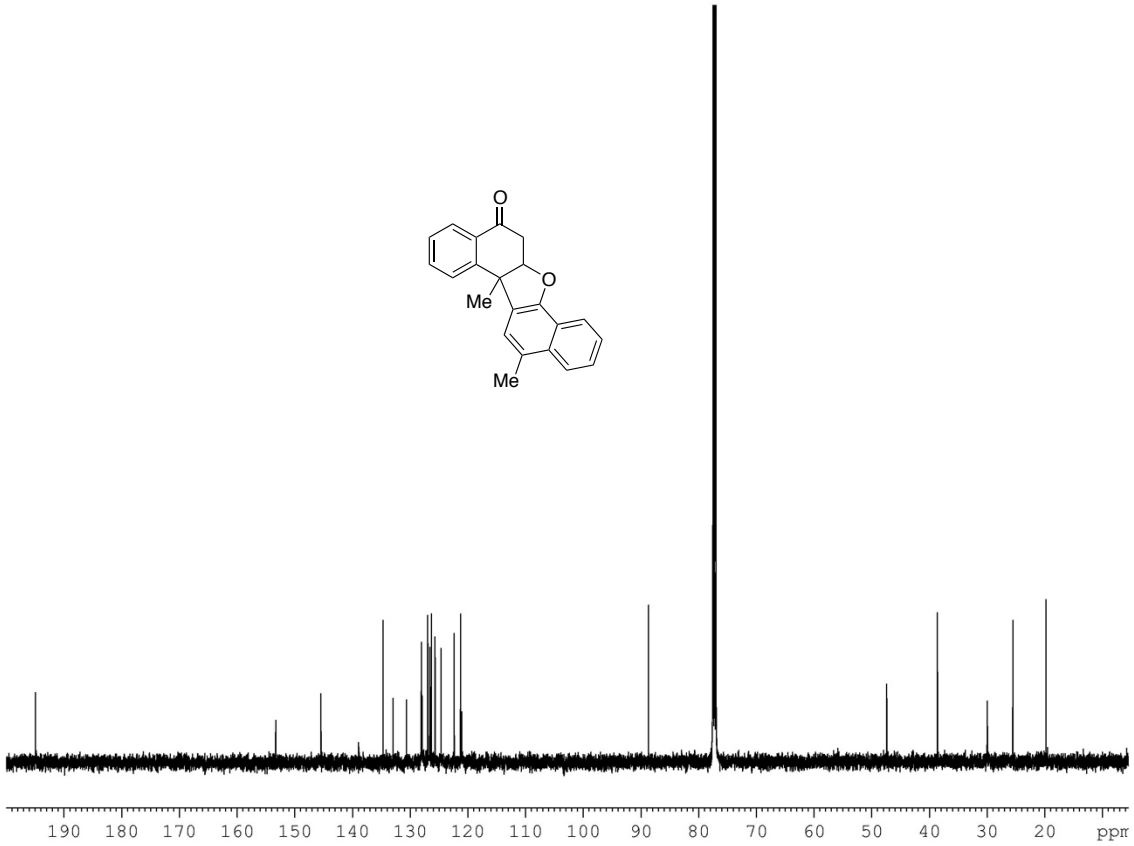
**125 MHz $^{13}C$ NMR Spectrum of Table 1, Entry 11 Product in $CDCl_3$**



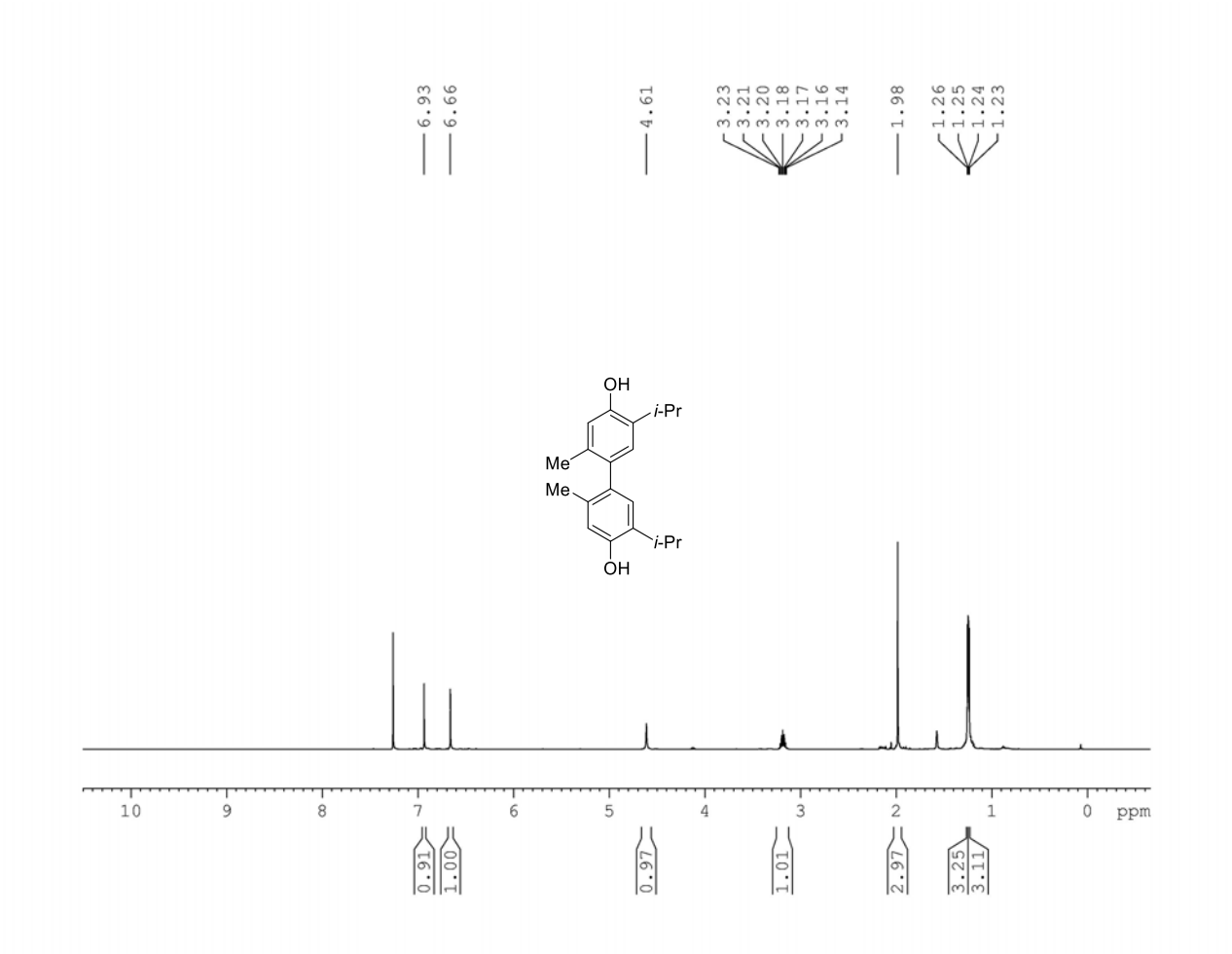
**500 MHz $^{1}$H NMR Spectrum of Table 1, Entry 12 Product in $CDCl_3$**



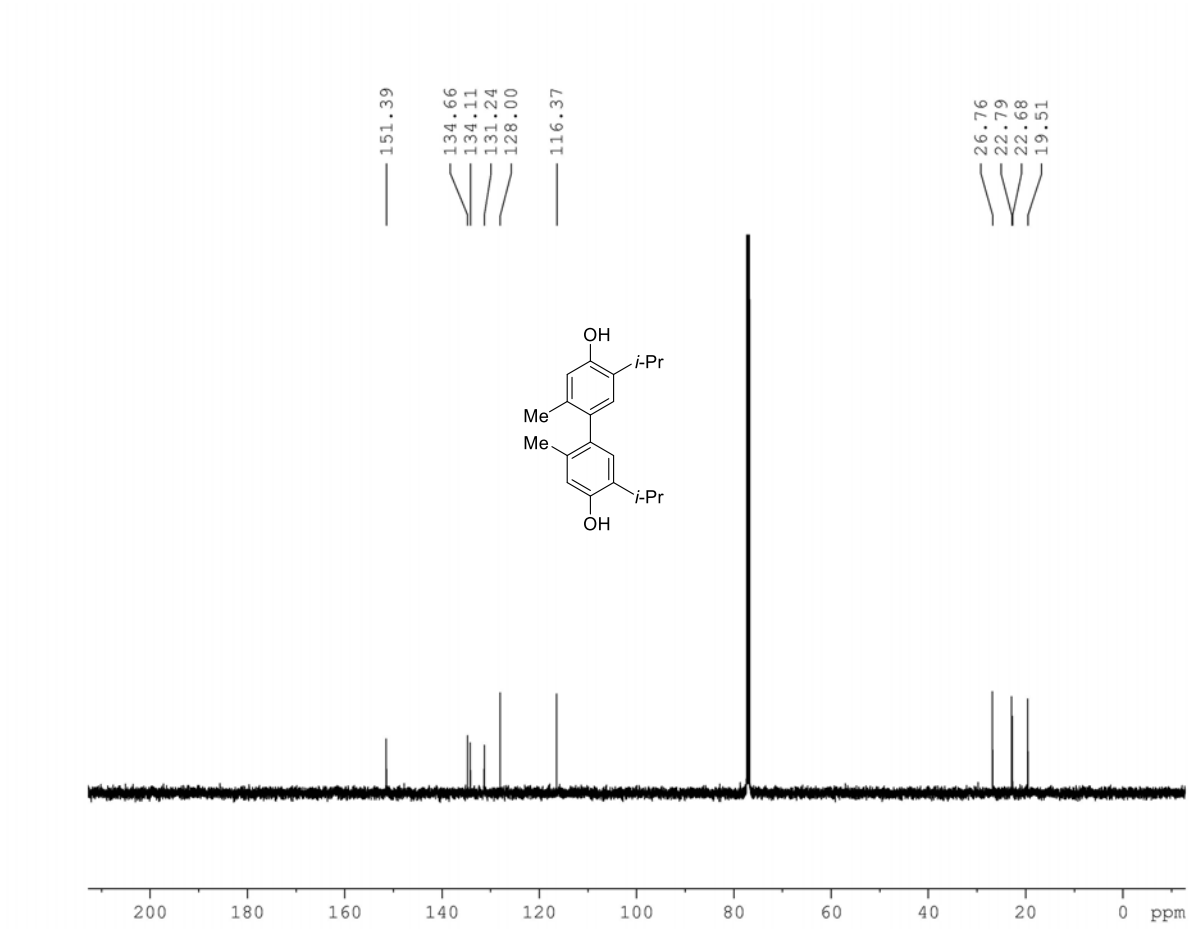
**125 MHz $^{13}$C NMR Spectrum of Table 1, Entry 12 Product in $CDCl_3$**



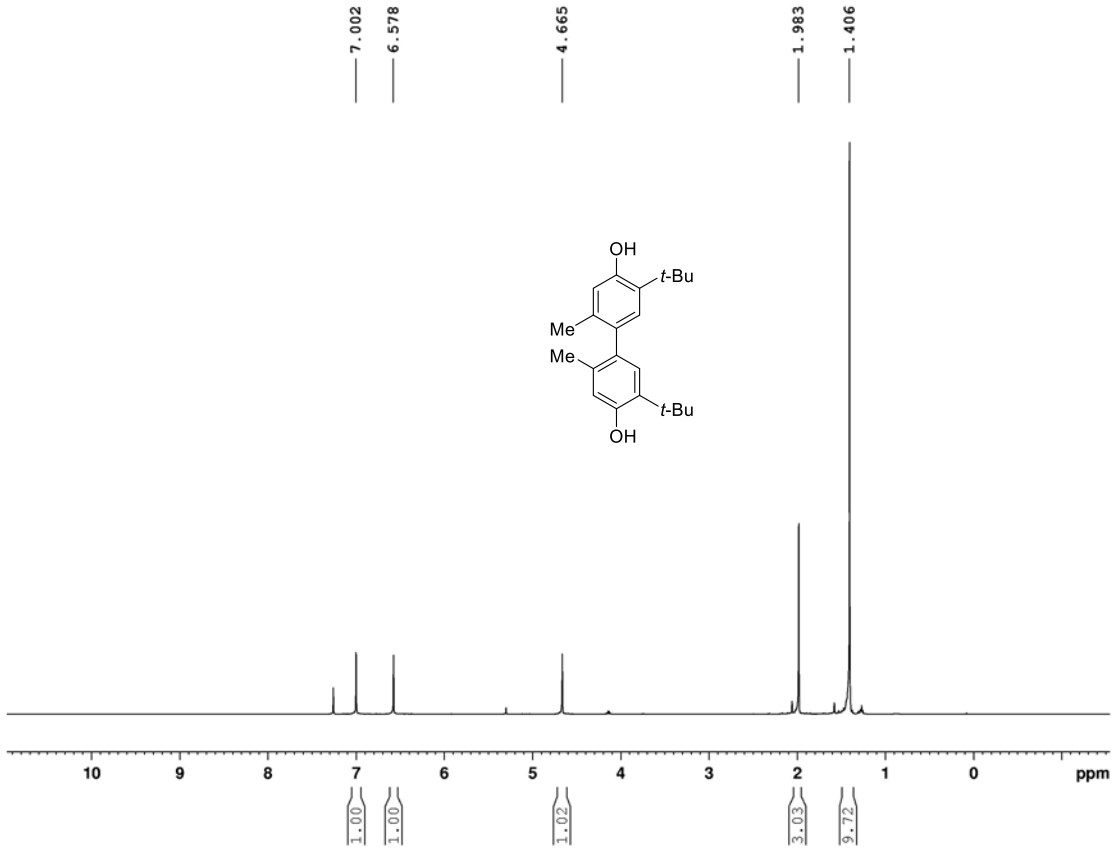
**500 MHz $^{1}$H NMR Spectrum of Table 1, Entry 13 Product in $CDCl_3$**



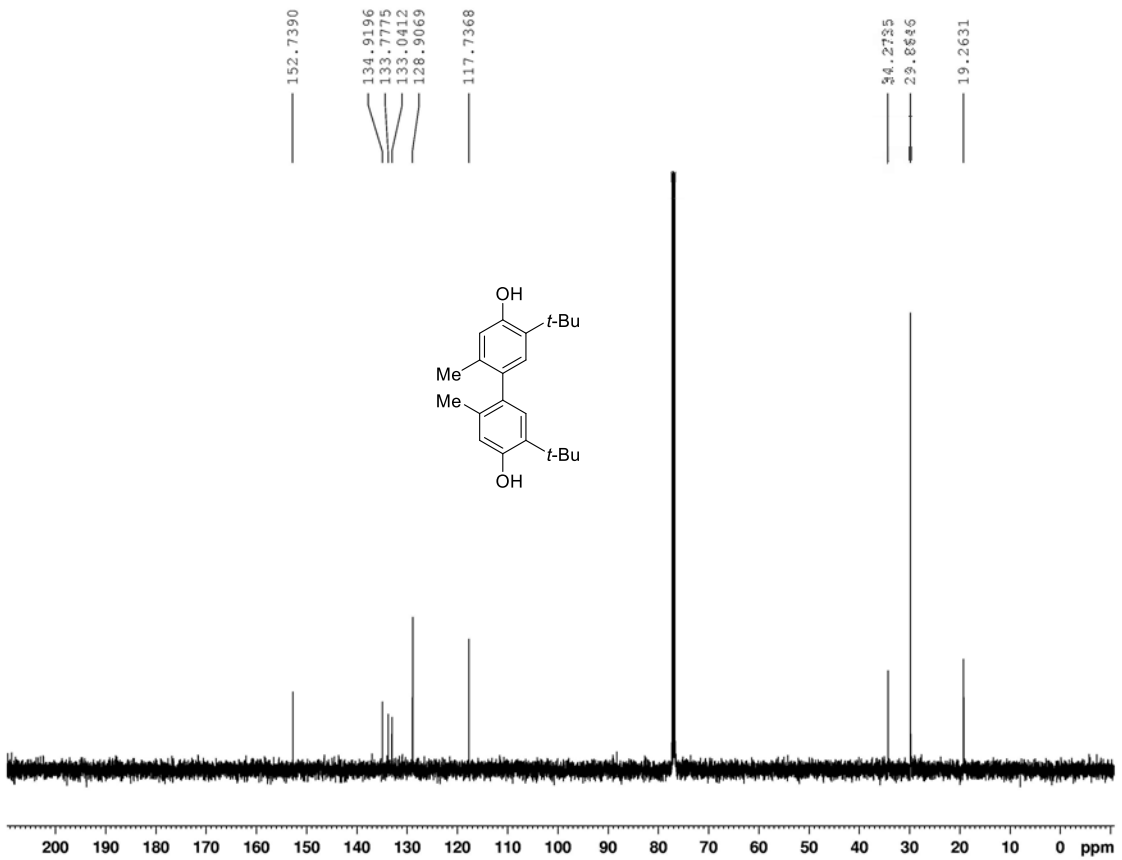
**125 MHz $^{13}$C NMR Spectrum of Table 1, Entry 13 Product in $CDCl_3$**



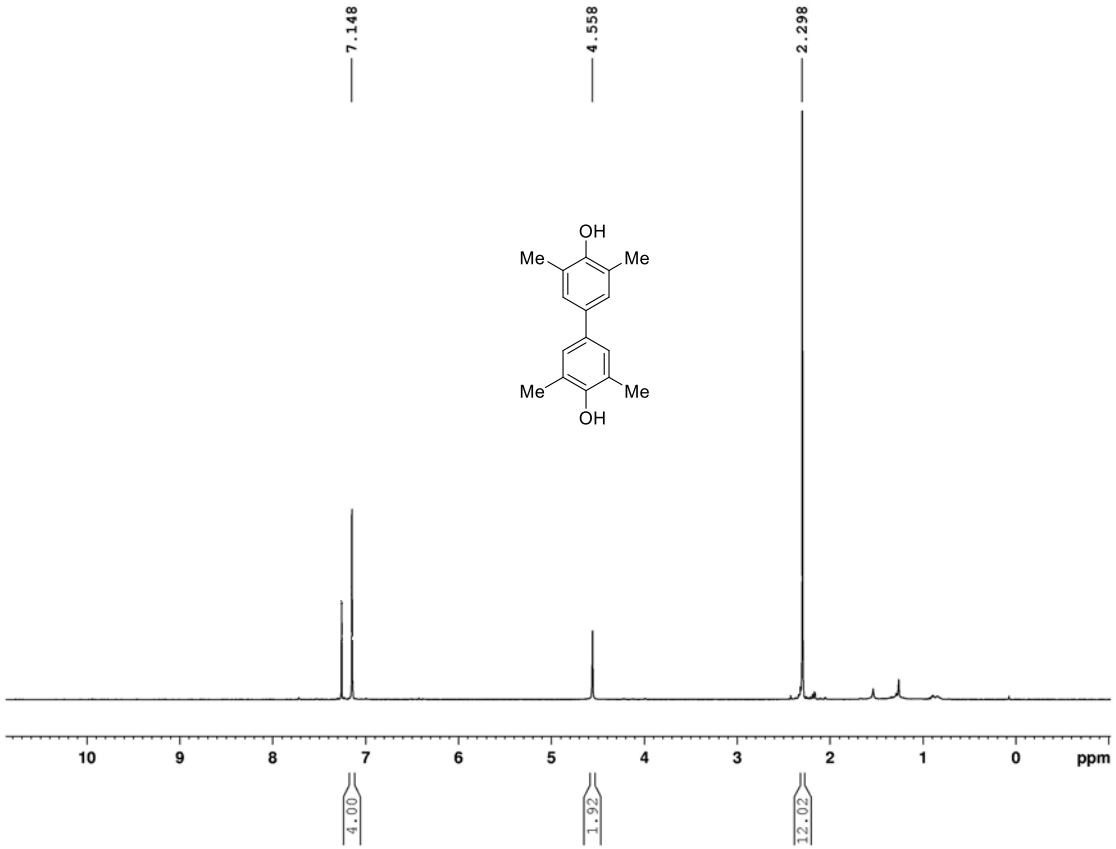
**500 MHz $^{1}$H NMR Spectrum of Table 1, Entry 14 Product in $CDCl_3$**



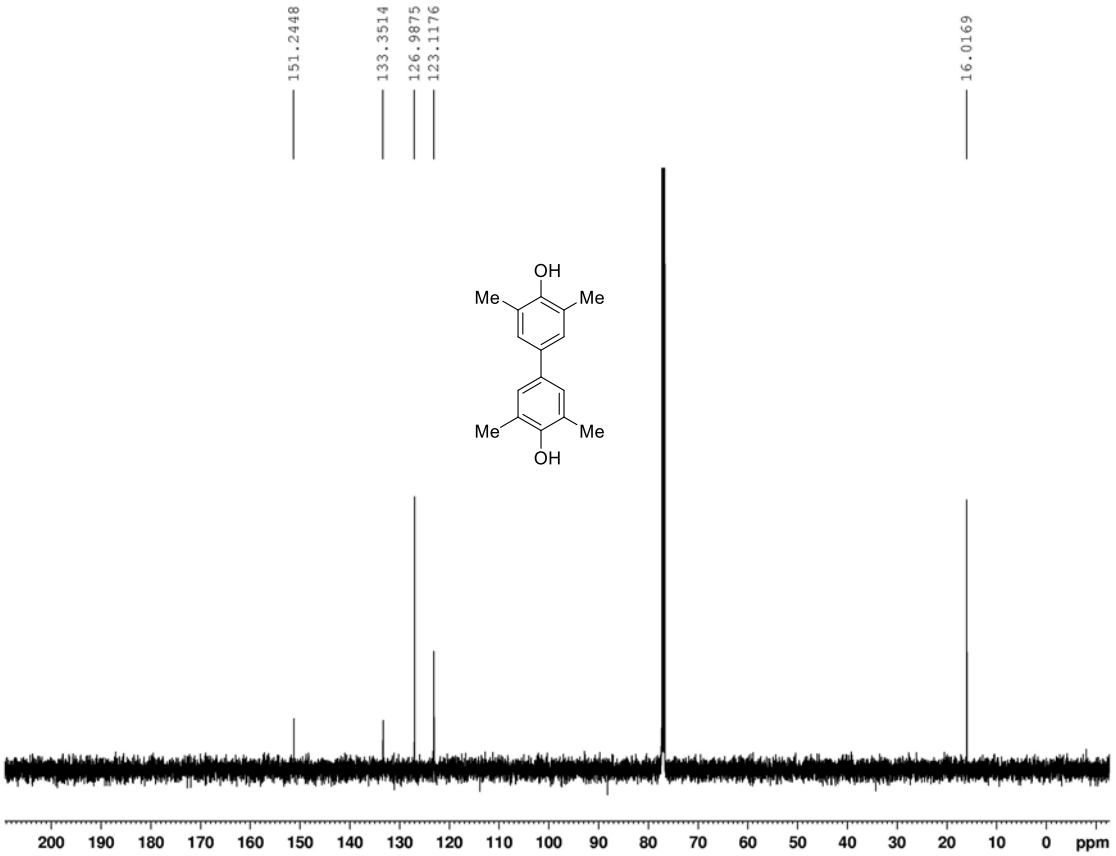
**125 MHz $^{13}$C NMR Spectrum of Table 1, Entry 14 Product in $CDCl_3$**



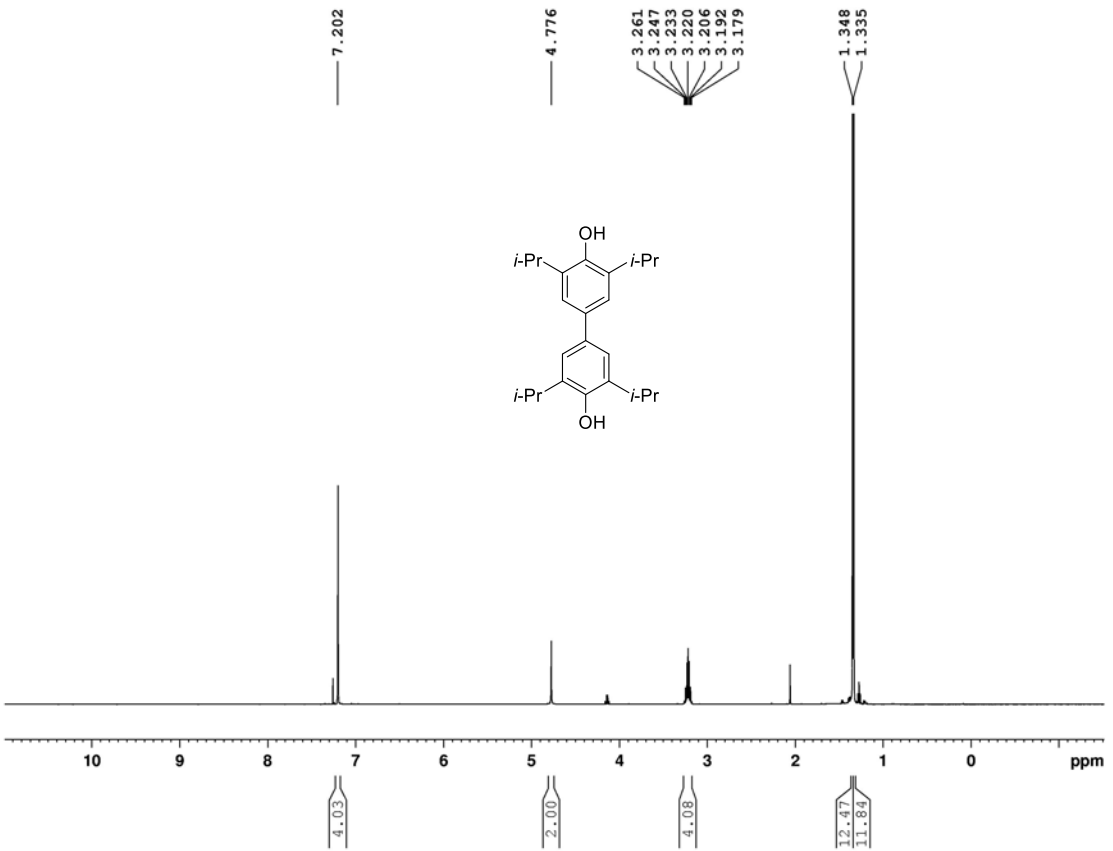
**500 MHz $^{1}$H NMR Spectrum of Table 1, Entry 15 Product in $CDCl_3$**



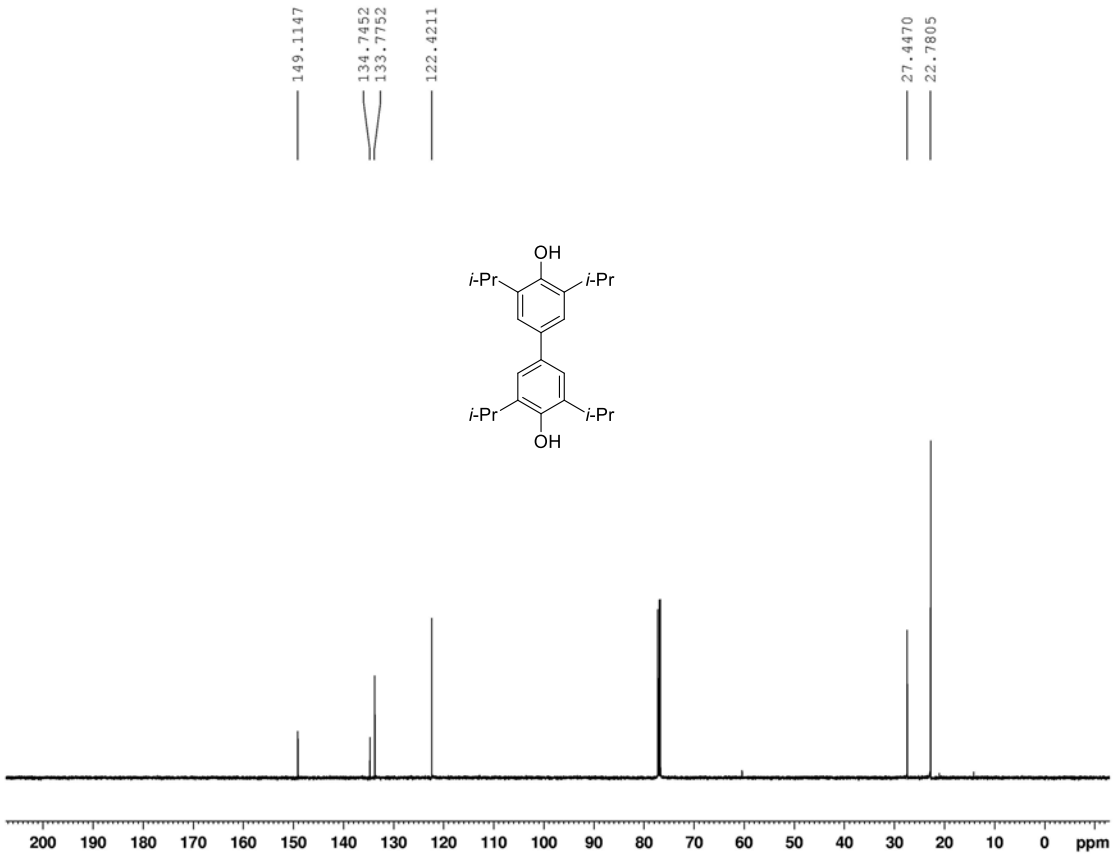
**125 MHz $^{13}C$ NMR Spectrum of Table 1, Entry 15 Product in $CDCl_3$**



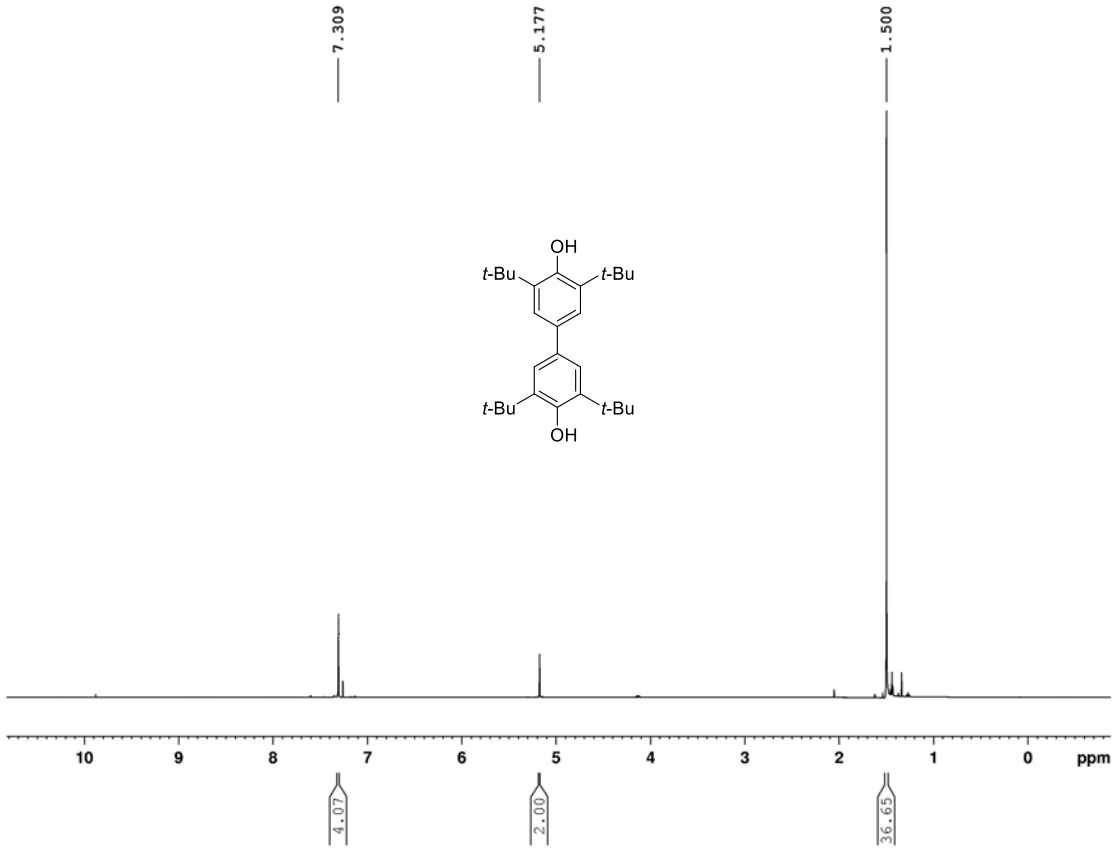
**500 MHz $^{1}$H NMR Spectrum of Table 1, Entry 16 Product in $CDCl_3$**



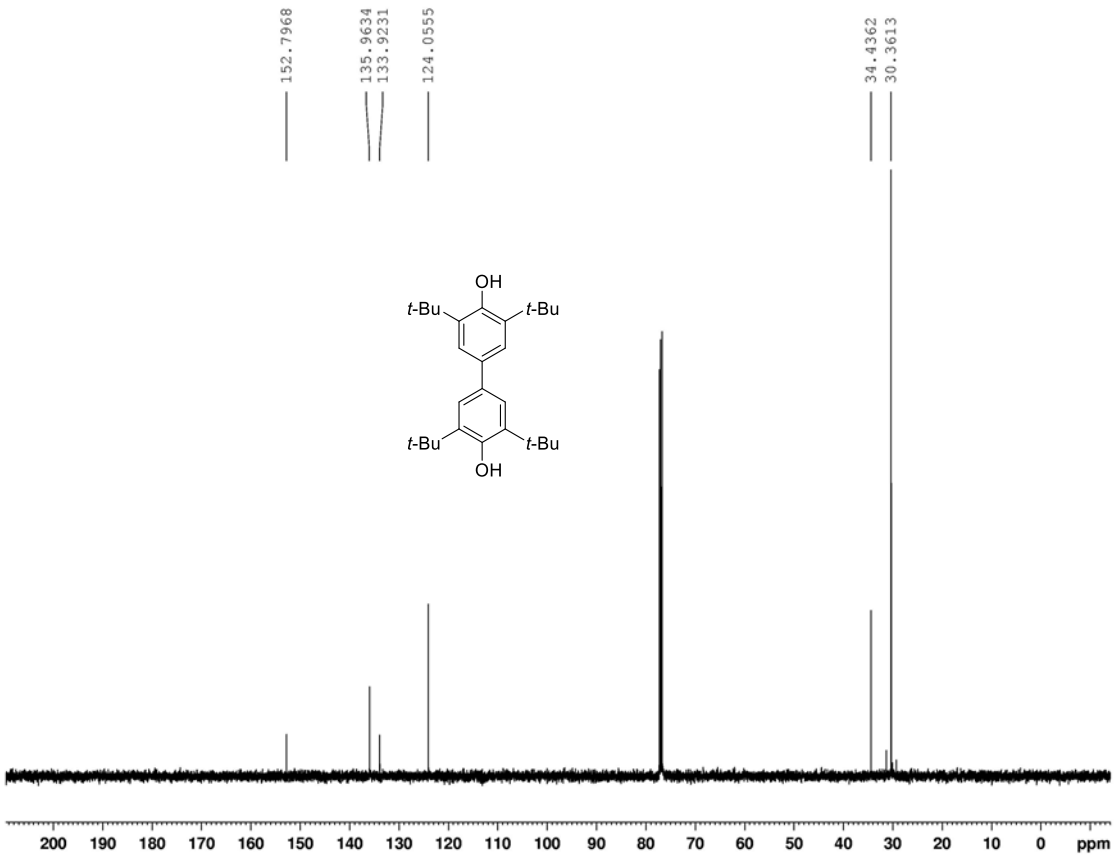
**125 MHz $^{13}C$ NMR Spectrum of Table 1, Entry 16 Product in $CDCl_3$**



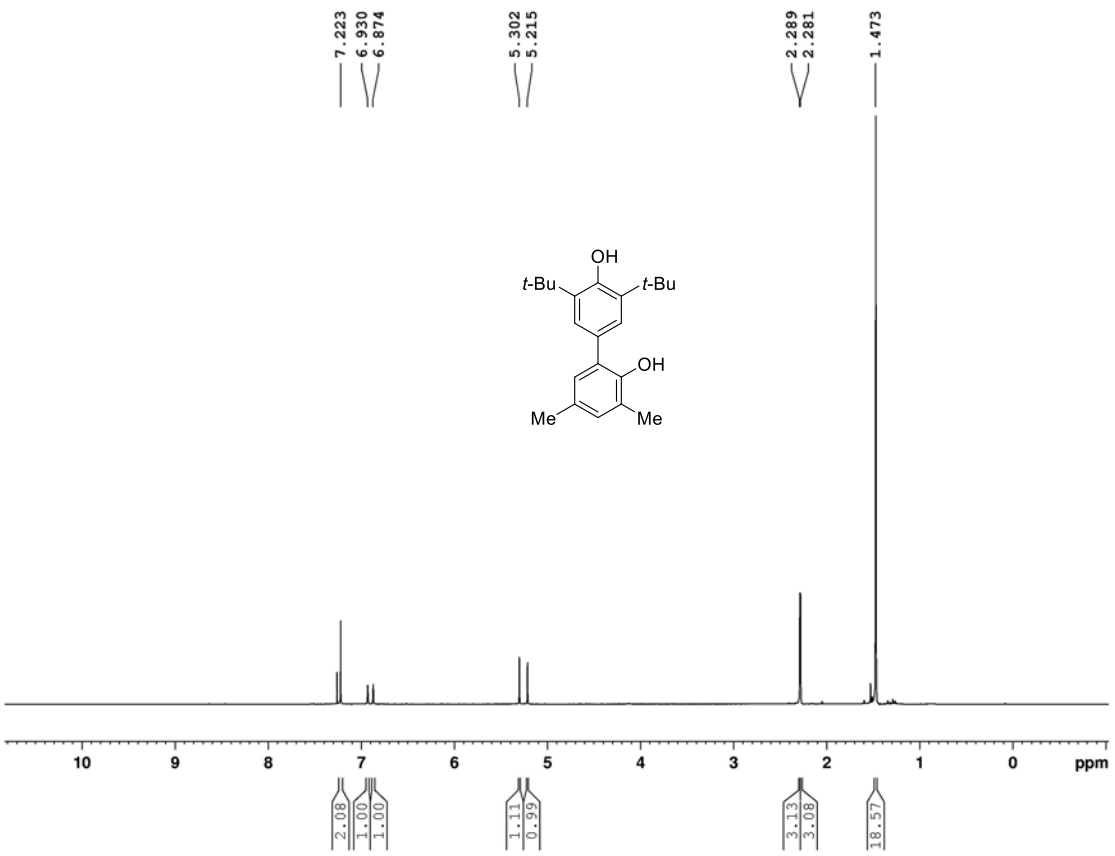
**500 MHz $^{1}$H NMR Spectrum of Table 1, Entry 17 Product in $CDCl_3$**



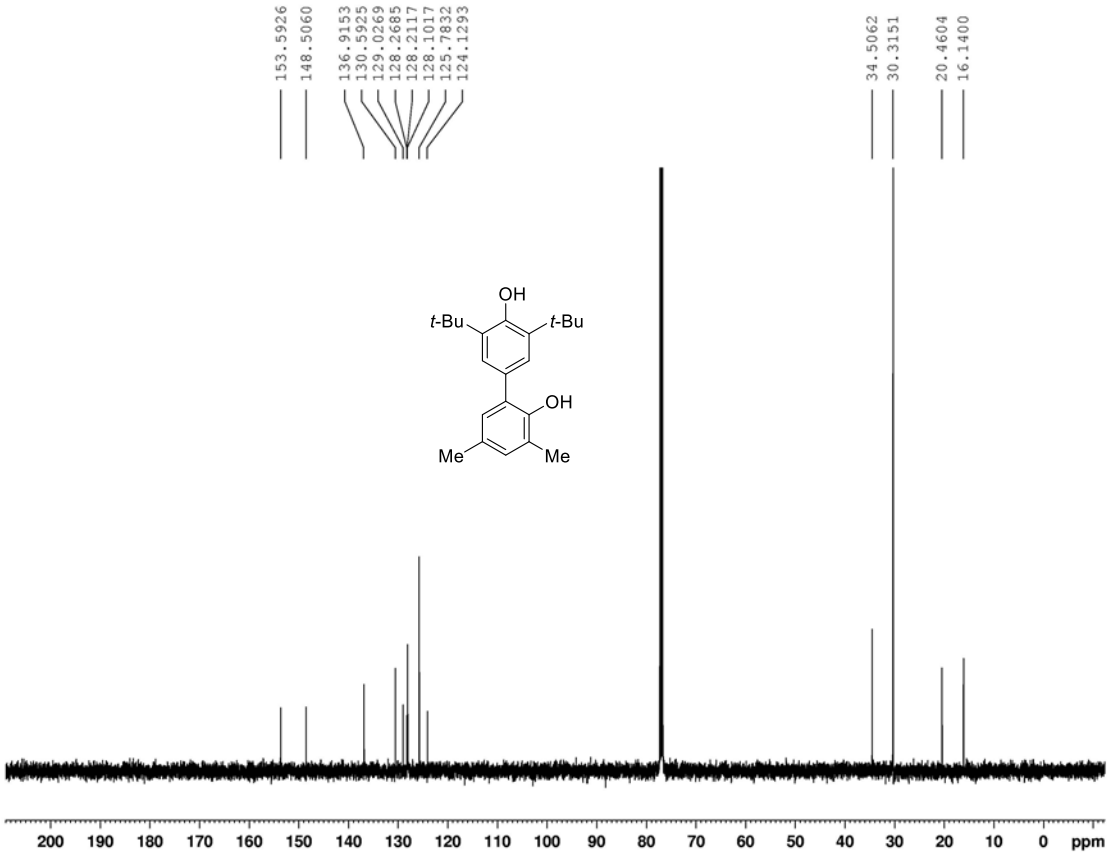
**125 MHz $^{13}C$ NMR Spectrum of Table 1, Entry 17 Product in $CDCl_3$**



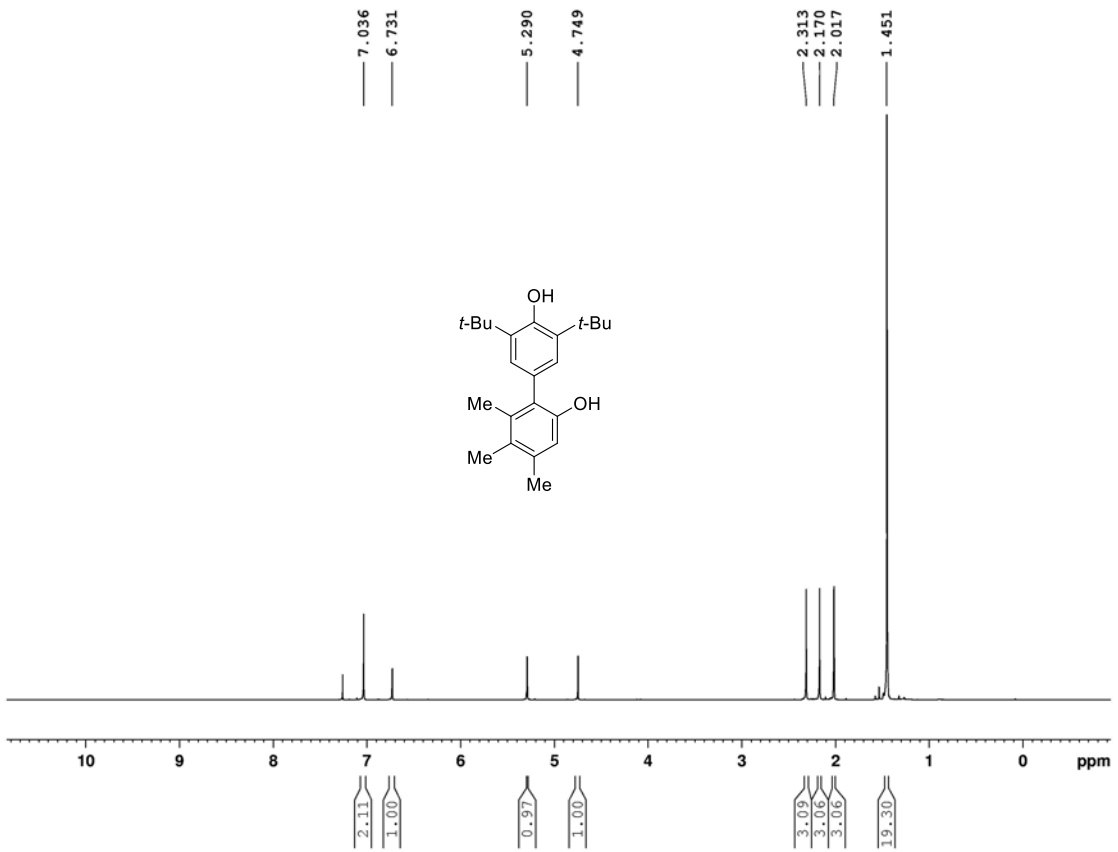
**500 MHz $^{1}$H NMR Spectrum of Table 2, Entry 1 Product in $CDCl_3$**



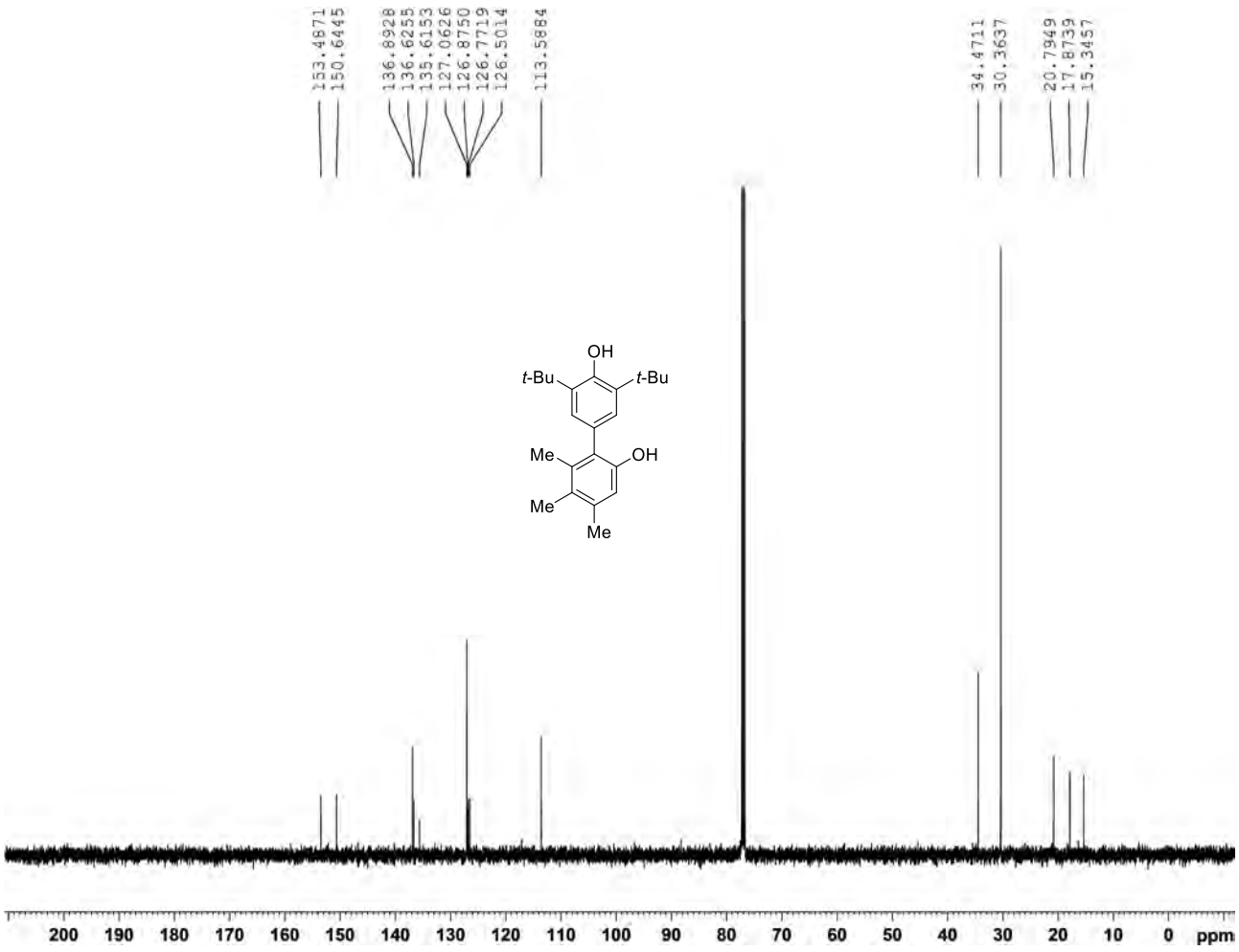
**125 MHz $^{13}$C NMR Spectrum of Table 2, Entry 1 Product in $CDCl_3$**



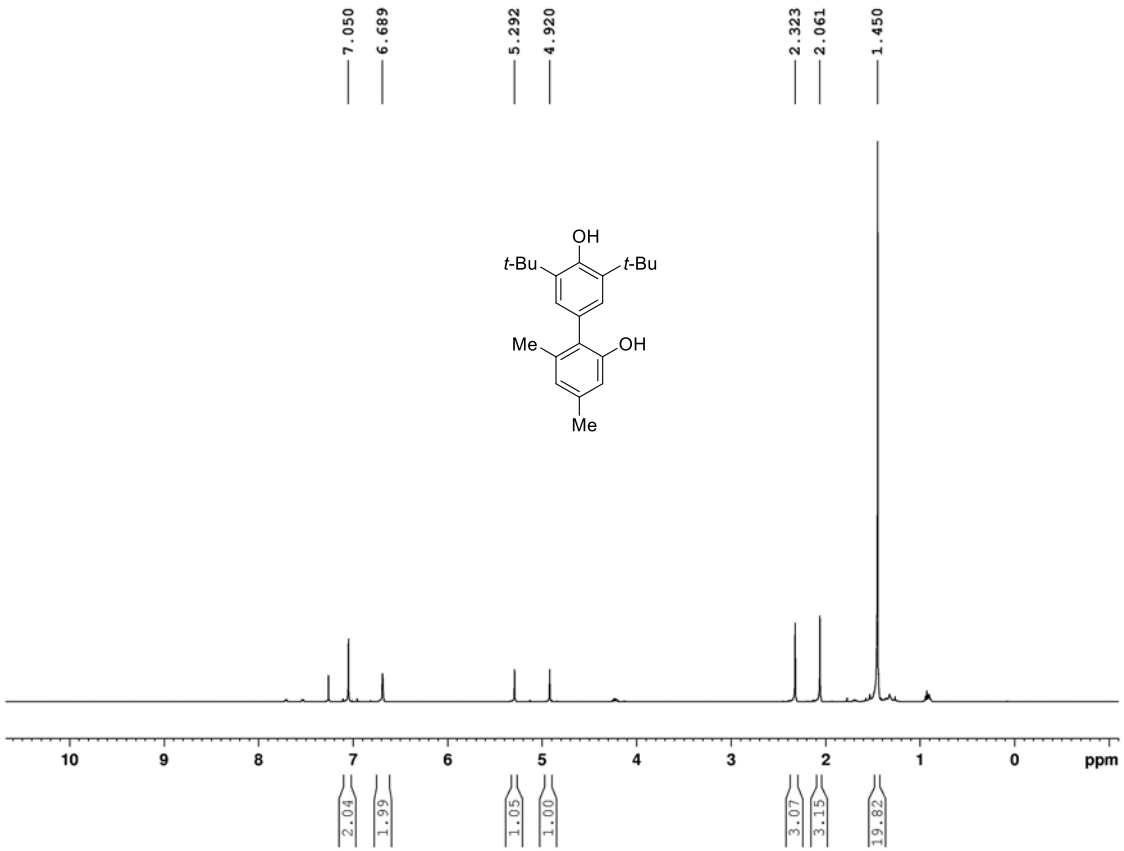
**500 MHz $^{1}$H NMR Spectrum of Table 2, Entry 2 Product in $CDCl_3$**



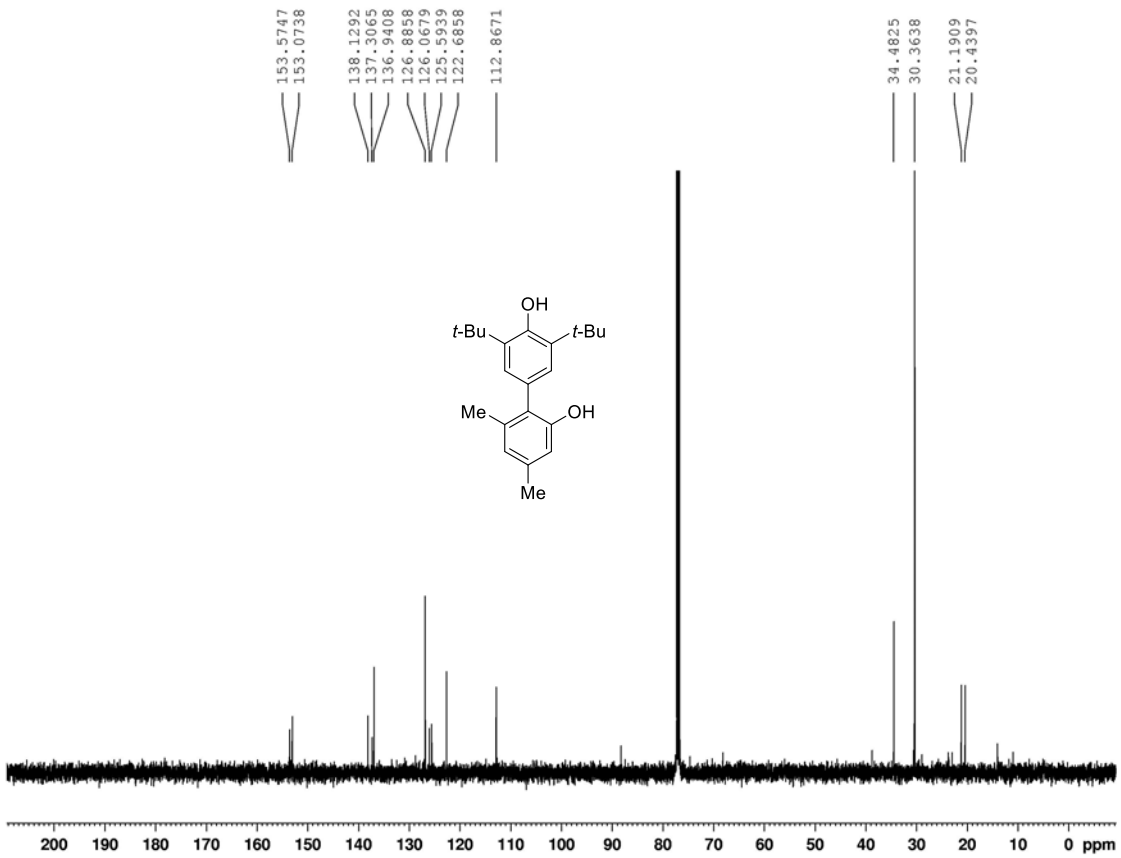
**125 MHz $^{13}C$ NMR Spectrum of Table 2, Entry 2 Product in $CDCl_3$**



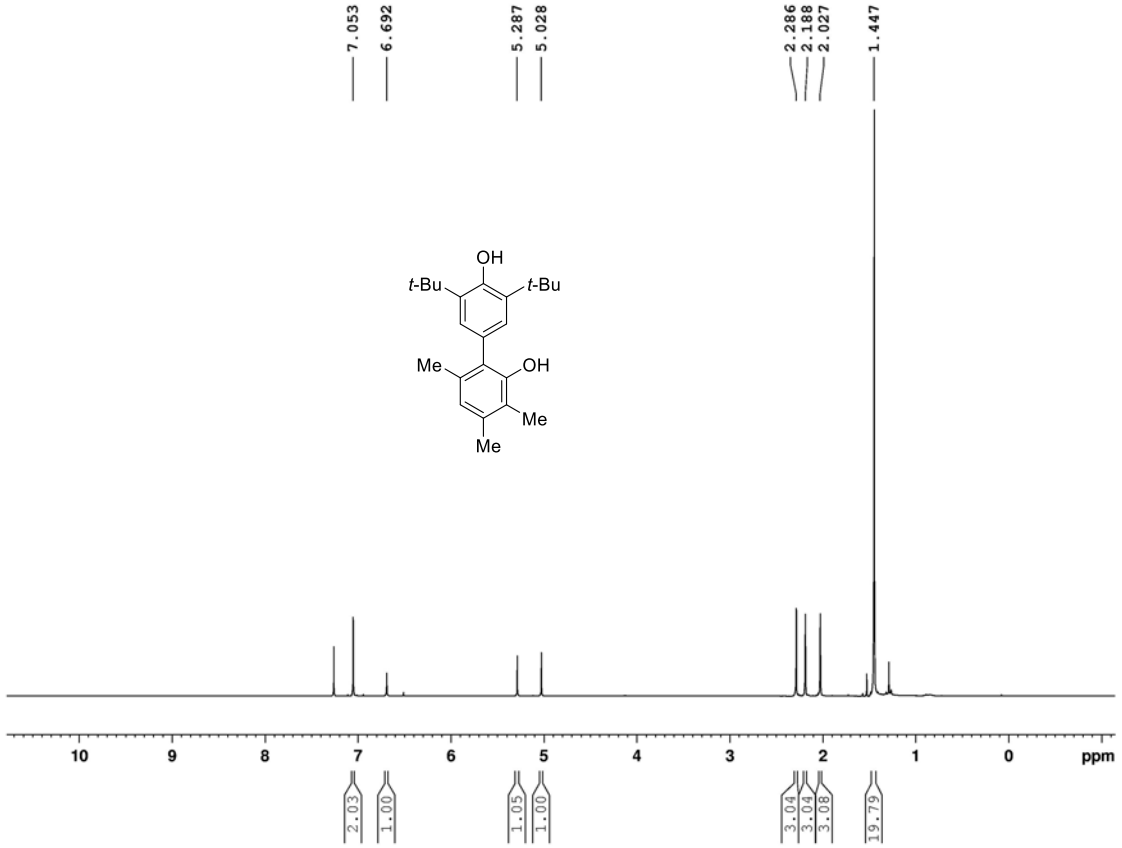
**500 MHz $^{1}$H NMR Spectrum of Table 2, Entry 3 Product in $CDCl_3$**



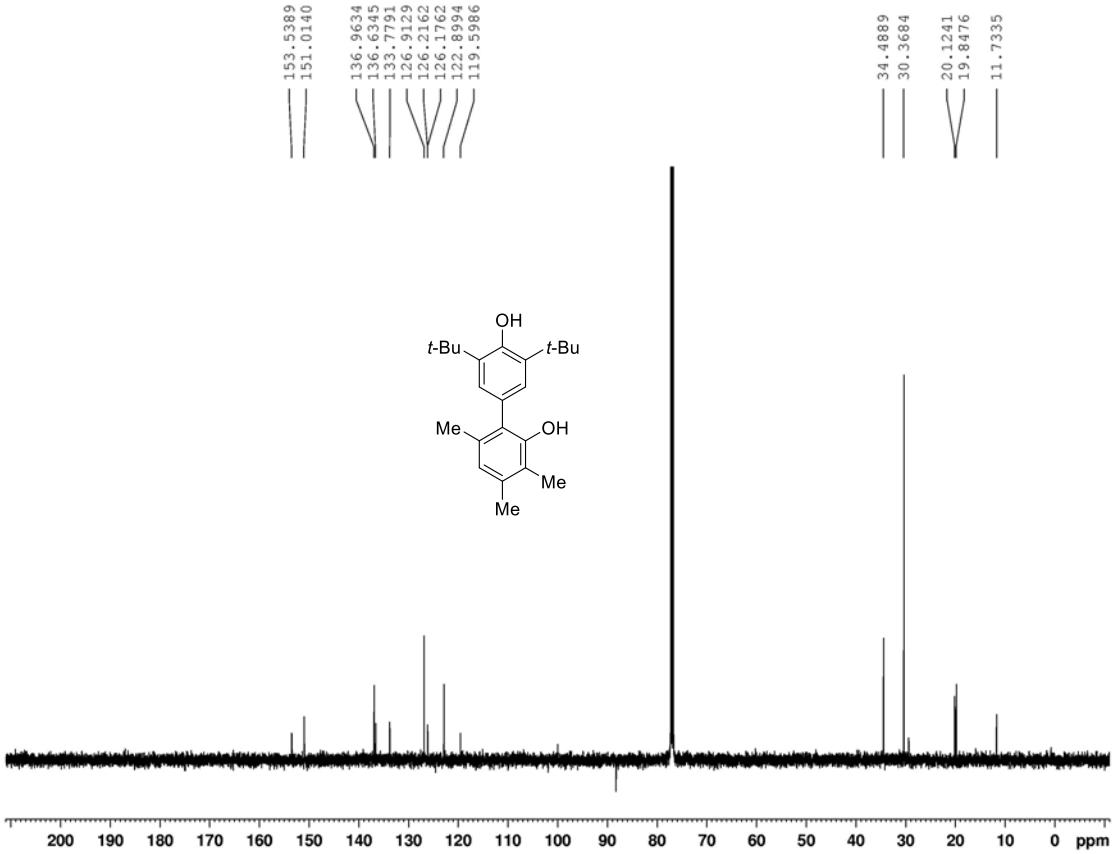
**125 MHz $^{13}C$ NMR Spectrum of Table 2, Entry 3 Product in $CDCl_3$**



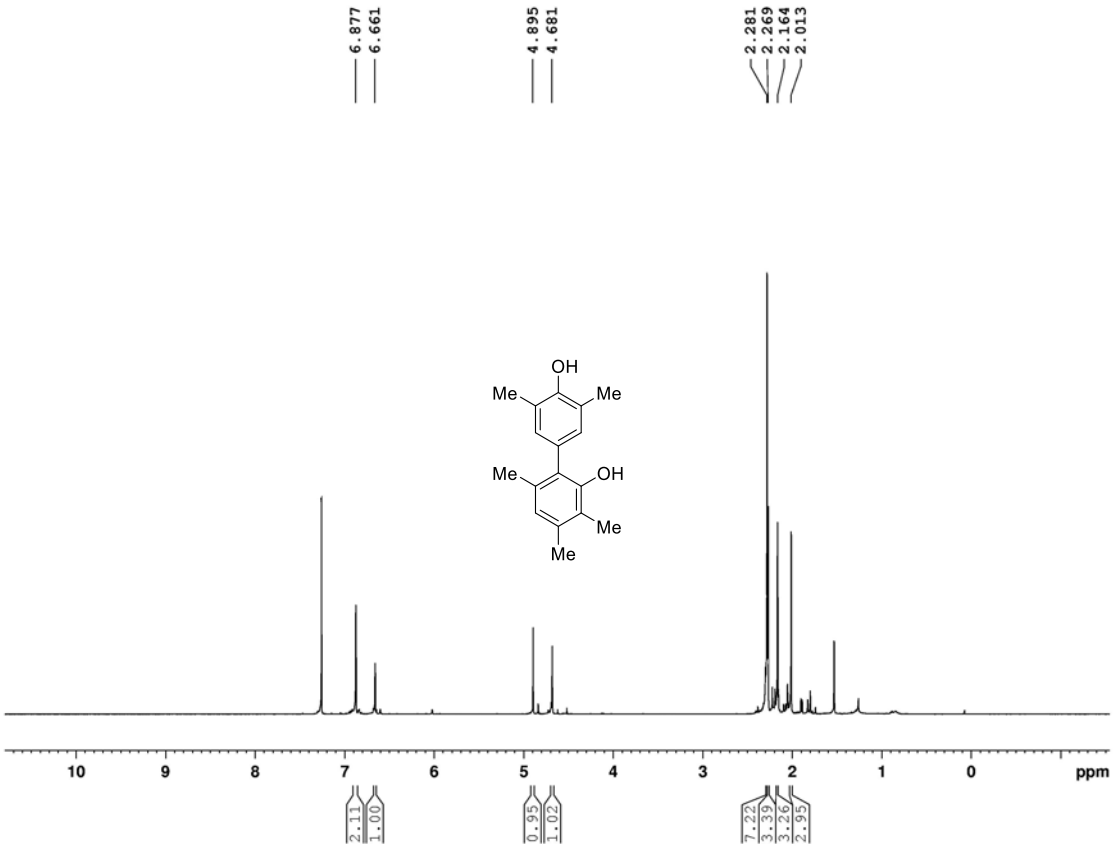
**500 MHz $^{1}$H NMR Spectrum of Table 2, Entry 4 Product in $CDCl_3$**



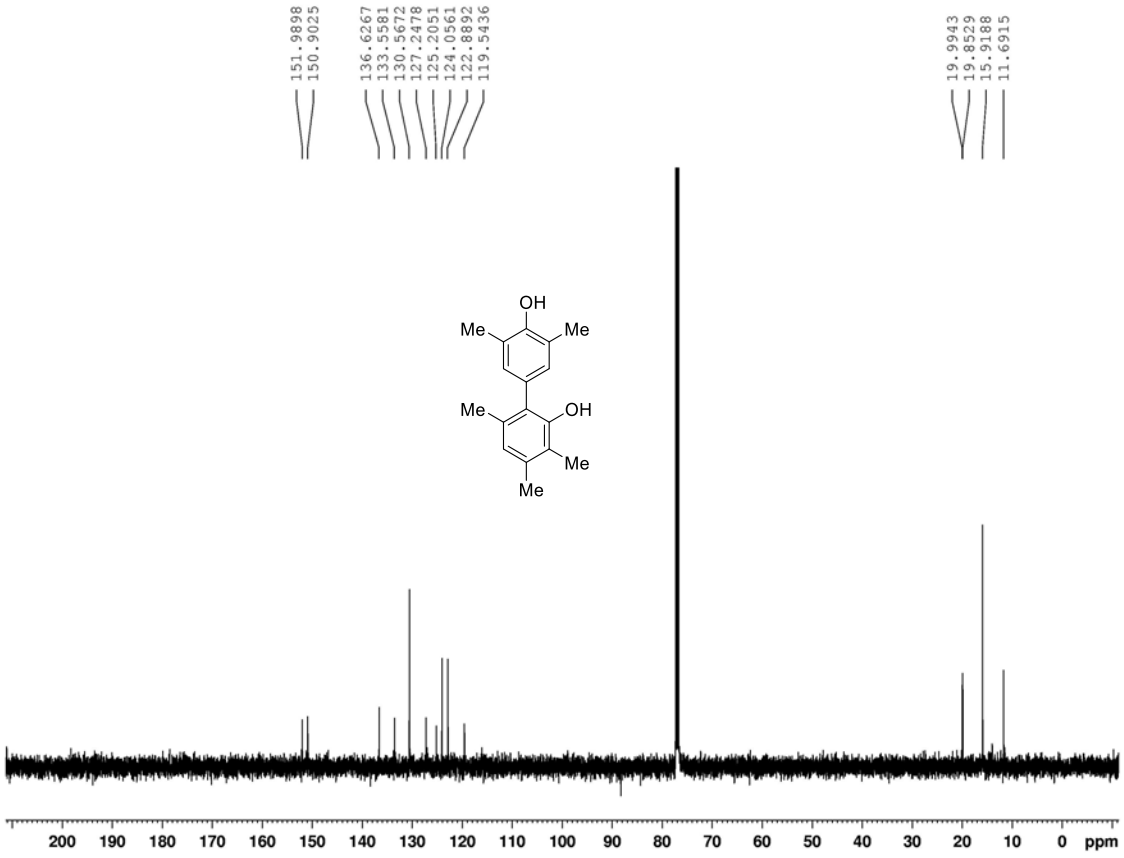
**125 MHz $^{13}$C NMR Spectrum of Table 2, Entry 4 Product in $CDCl_3$**



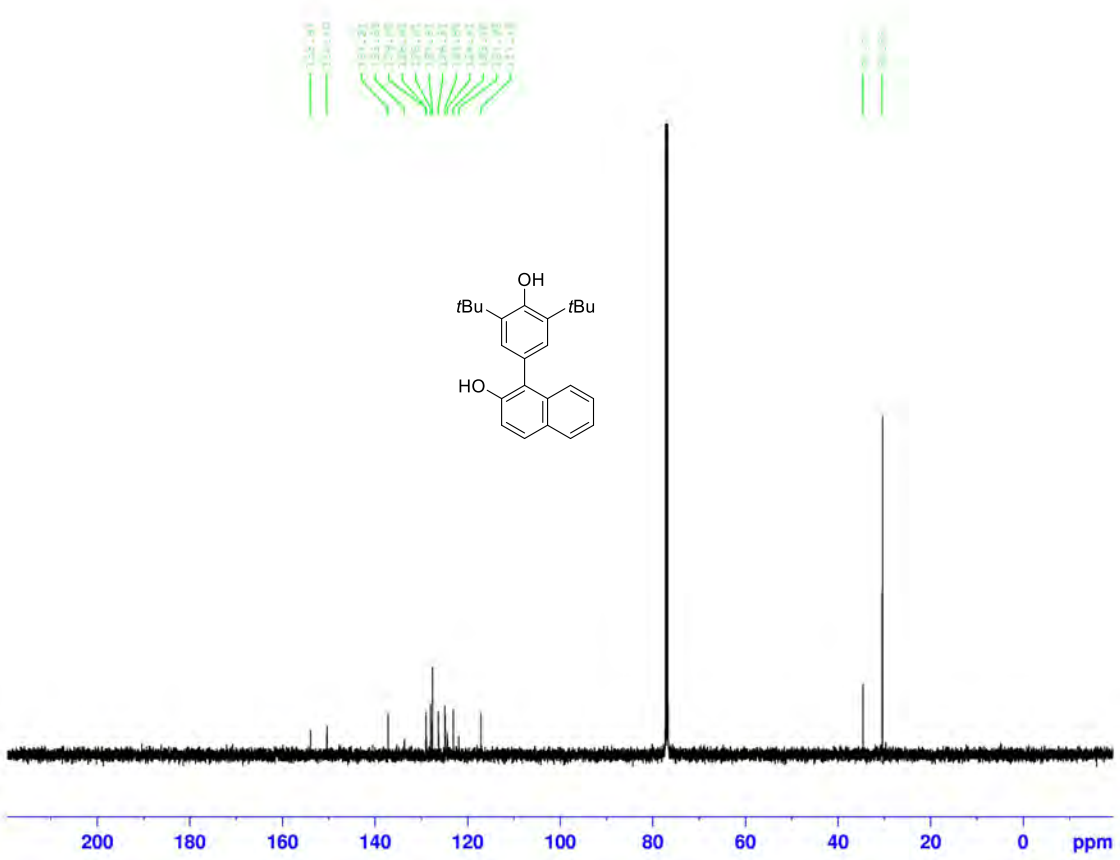
**500 MHz $^{1}$H NMR Spectrum of Table 2, Entry 5 Product in $CDCl_3$**



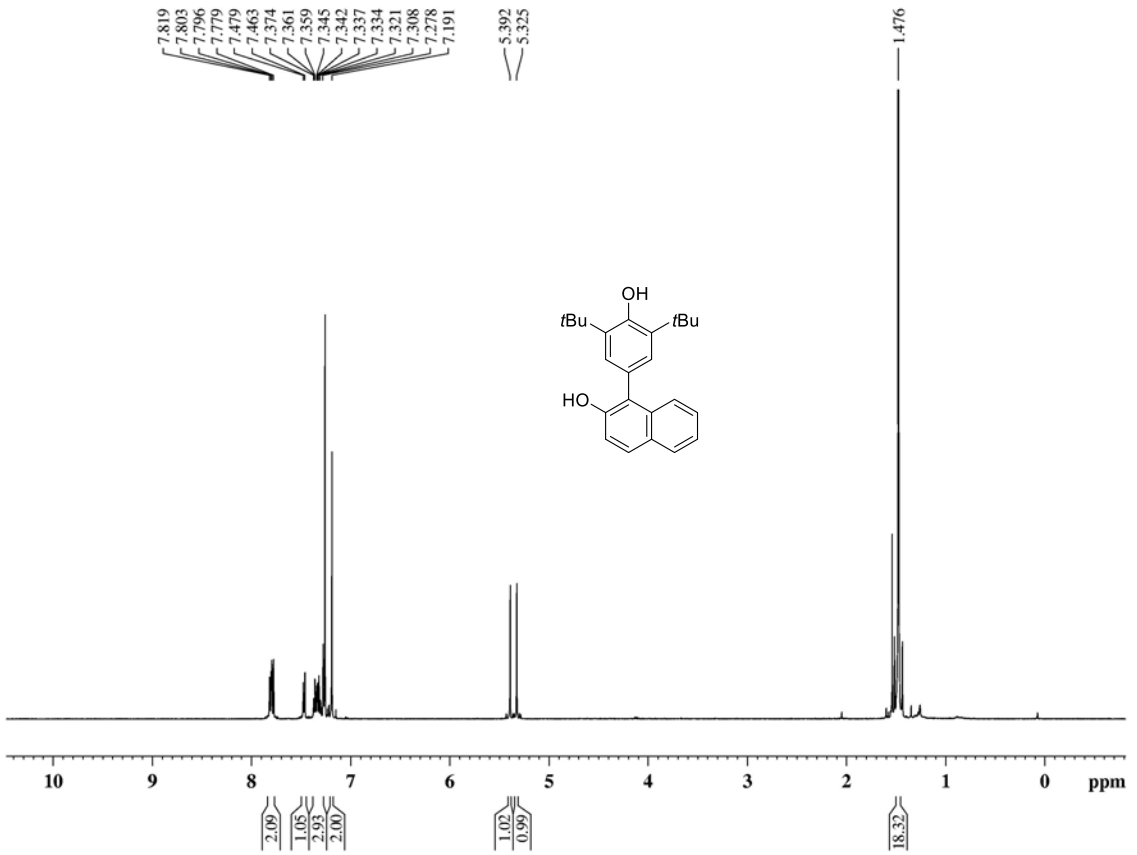
**125 MHz $^{13}C$ NMR Spectrum of Table 2, Entry 5 Product in $CDCl_3$**



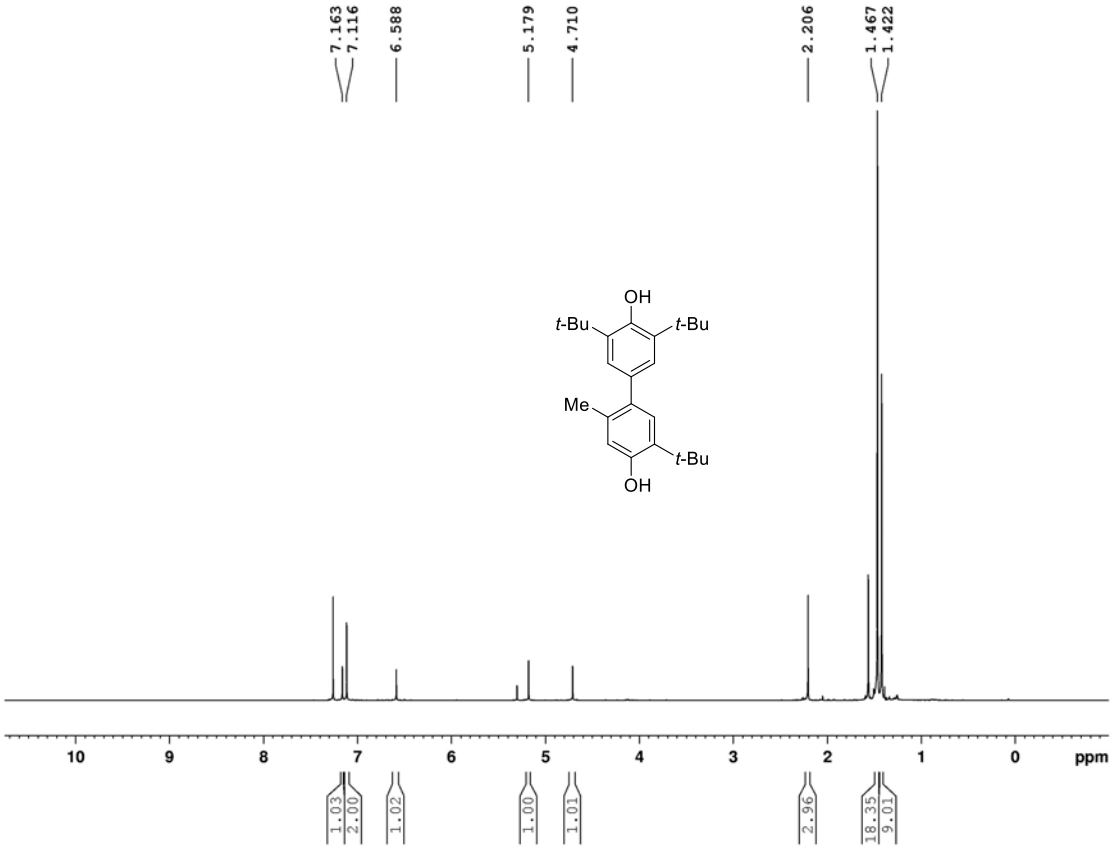
**125 MHz $^{13}C$ NMR Spectrum of Table 2, Entry 6 Product in $CDCl_3$**



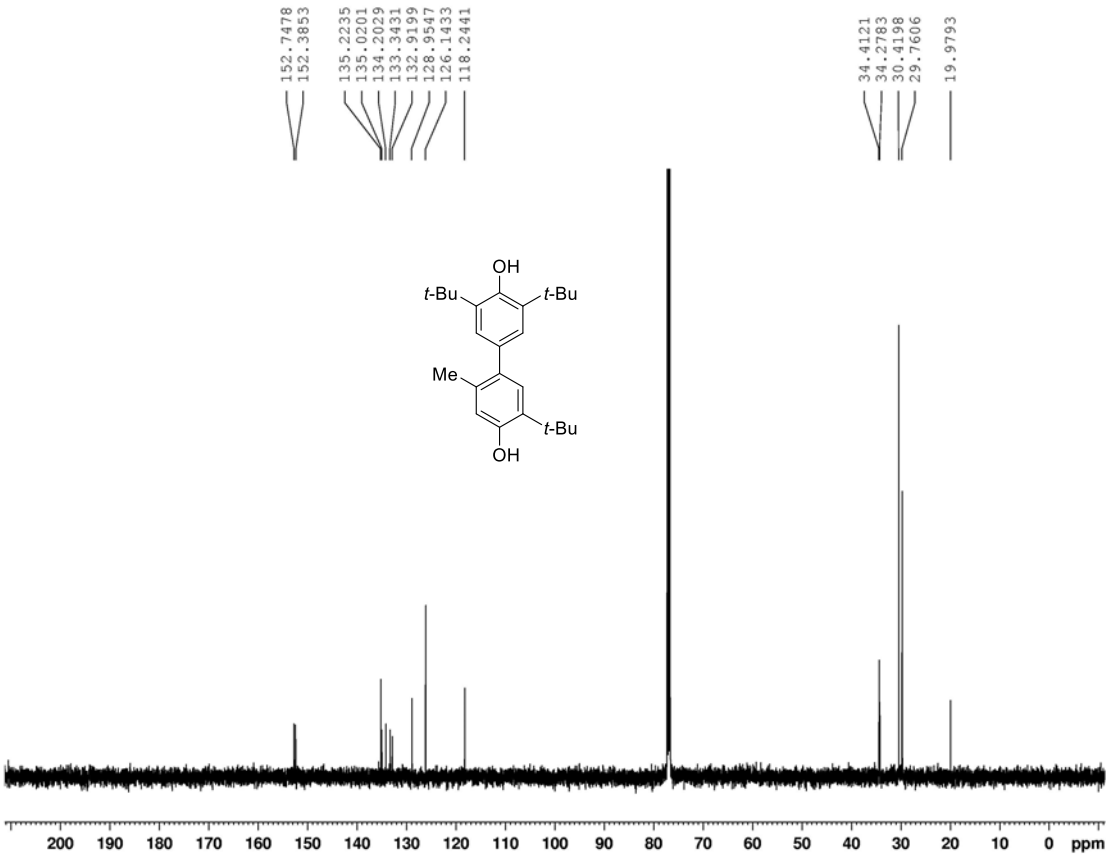
**500 MHz $^{1}$H NMR Spectrum of Table 2, Entry 6 Product in $CDCl_3$**



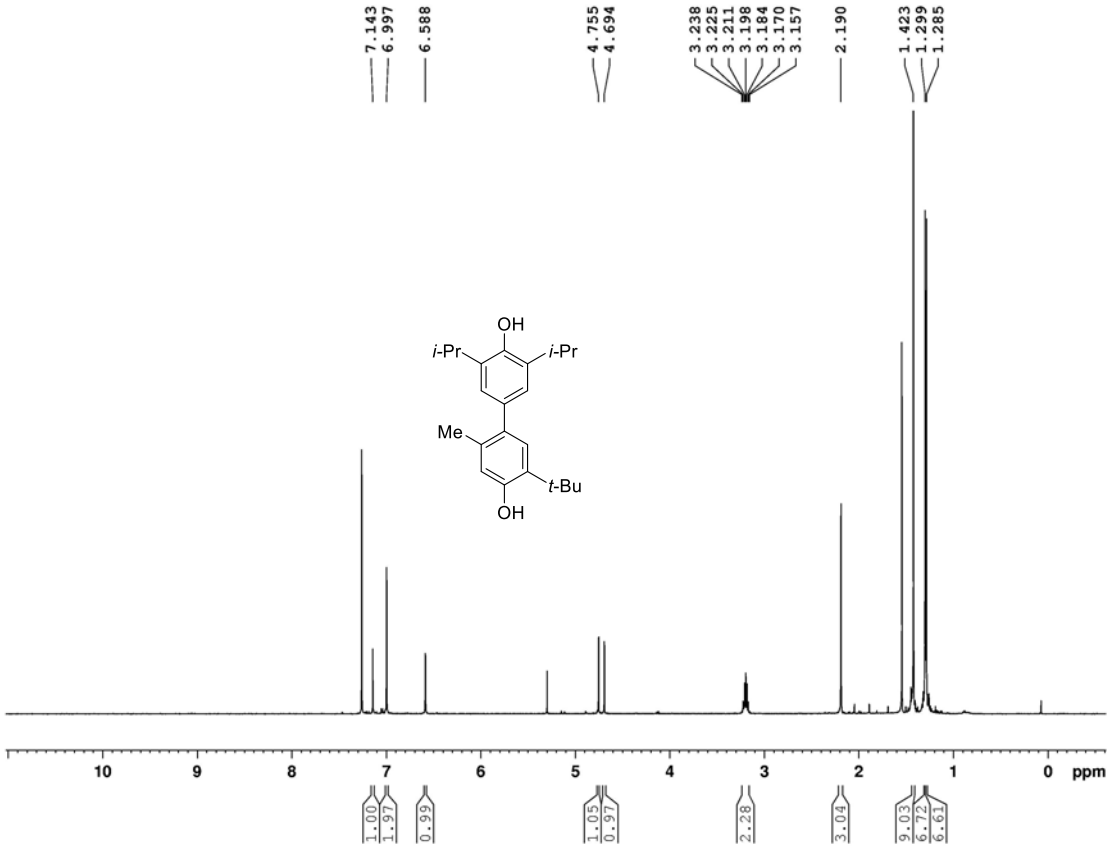
**500 MHz $^{1}$H NMR Spectrum of Table 2, Entry 7 Product in $CDCl_3$**



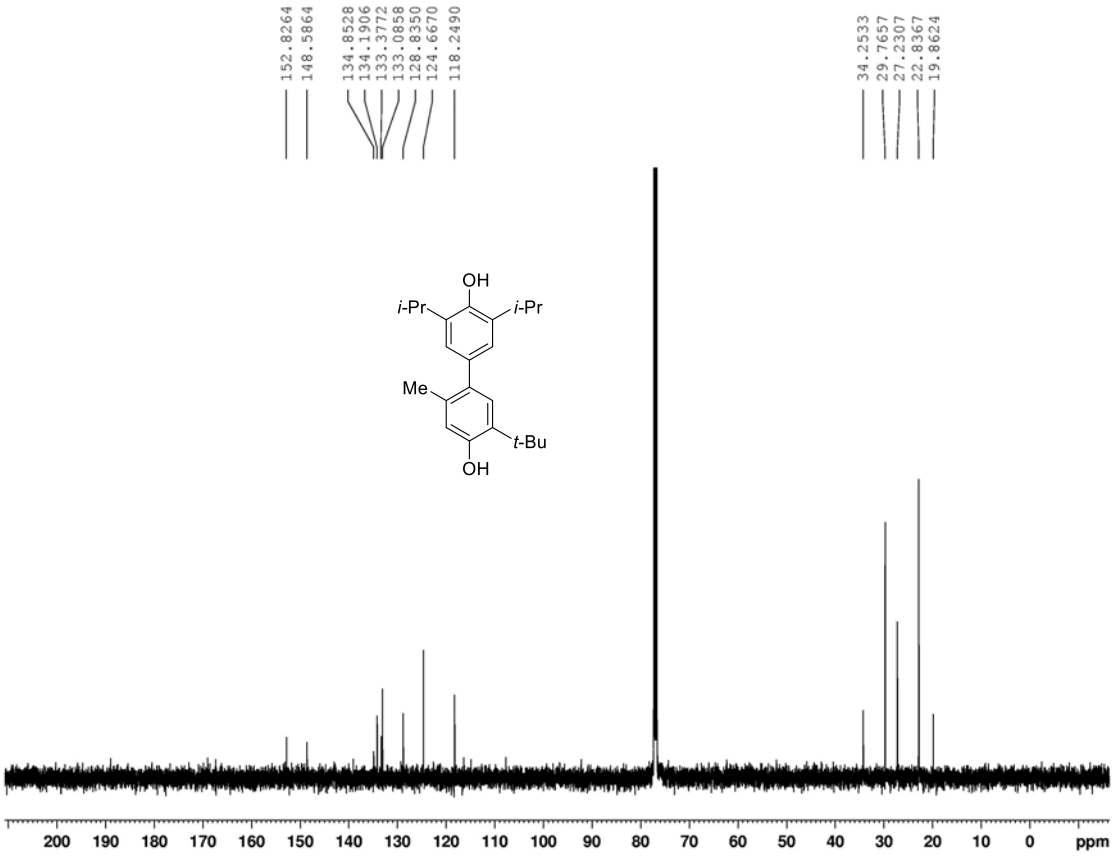
**125 MHz $^{13}$C NMR Spectrum of Table 2, Entry 7 Product in $CDCl_3$**



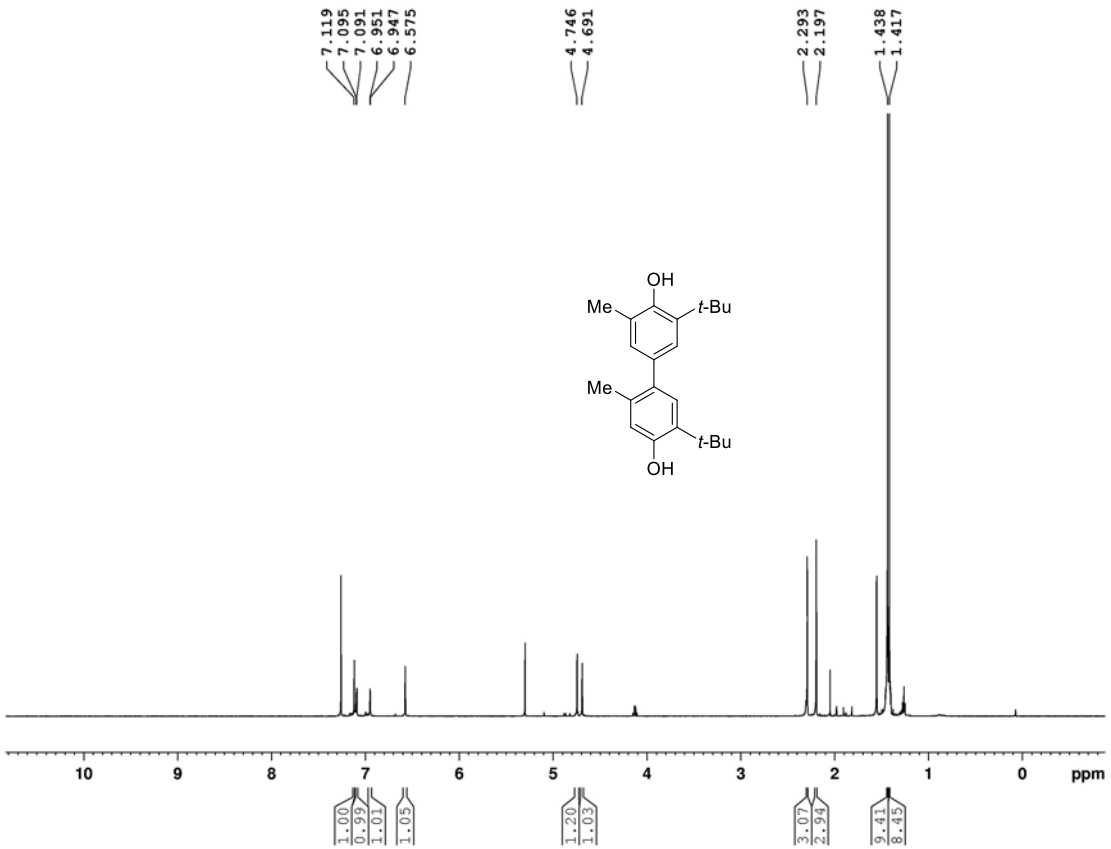
**500 MHz $^{1}$H NMR Spectrum of Table 2, Entry 8 Product in $CDCl_3$**



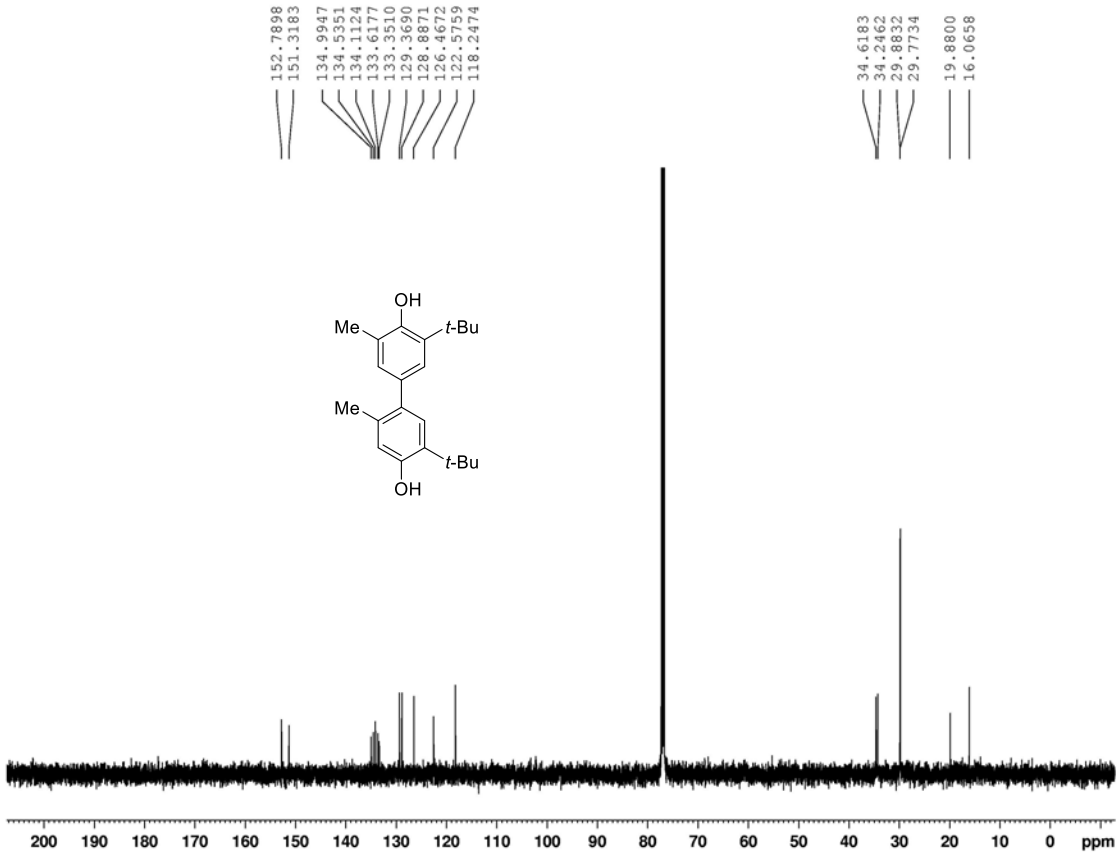
**125 MHz $^{13}$C NMR Spectrum of Table 2, Entry 8 Product in $CDCl_3$**



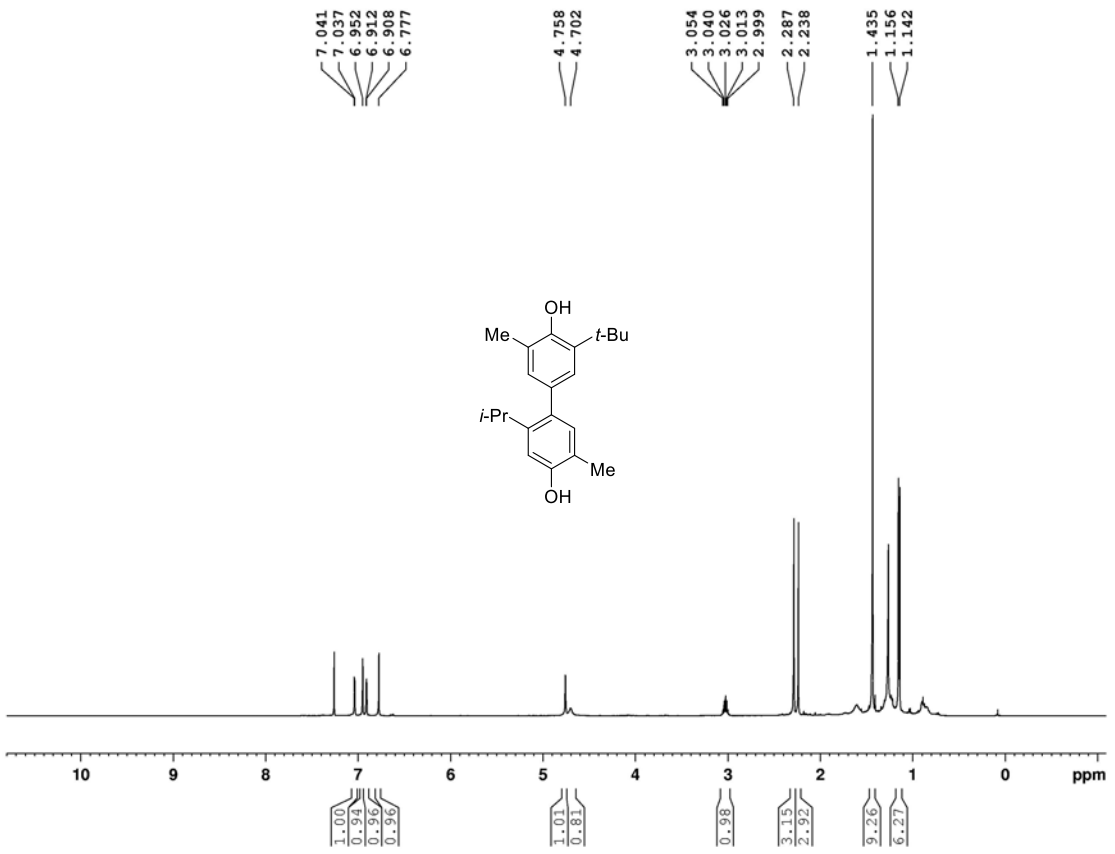
**500 MHz $^{1}$H NMR Spectrum of Table 2, Entry 9 Product in $CDCl_3$**



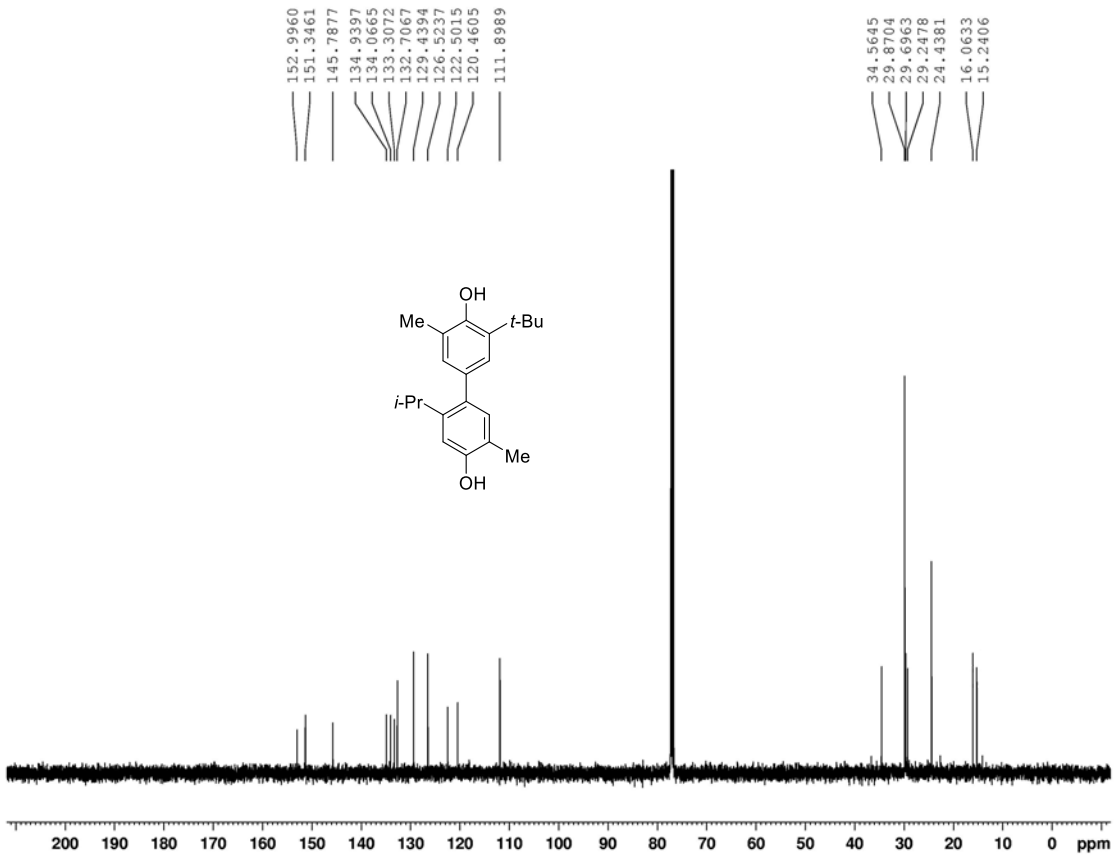
**125 MHz $^{13}C$ NMR Spectrum of Table 2, Entry 9 Product in $CDCl_3$**



**500 MHz $^{1}$H NMR Spectrum of Table 2, Entry 10 Product in $CDCl_3$**



**125 MHz $^{13}$C NMR Spectrum of Table 2, Entry 10 Product in $CDCl_3$**



## References


(1) Krow, G. R.; Miles, W. H.; Smiley, P. M.; Lester, W. S.; Kim, Y. J. *J. Org. Chem.* **1992**, *57*, 4040-4043.

(2) Liao, X.; Stanley, L. M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2011**, *133*, 2088-2091.

(3) Lal, K.; Ghosh, S.; Salomon, R. G. *J. Org. Chem.* **1987**, *52*, 1072-1078.

(4) Nielson, A. J.; Waters, J. M. *Polyhedron*, *29*, 1715-1726.

(5) Sun, J.; Zhu, C.; Dai, Z.; Yang, M.; Pan, Y.; Hu, H. *J. Org. Chem.* **2004**, *69*, 8500-8503.

(6) Kurahashi, T.; Hada, M.; Fujii, H. *J. Am. Chem. Soc.* **2009**, *131*, 12394-12405.

(7) Bryliakov, K. P.; Talsi, E. P. *Eur. J. Org. Chem.* **2008**, *2008*, 3369-3376.

(8) Fallis, I. A.; Murphy, D. M.; Willock, D. J.; Tucker, R. J.; Farley, R. D.; Jenkins, R.; Strevens, R. R. *J. Am. Ch* *Soc.* **2004**, *126*, 15660-15661.

(9) He, B.; Chen, F.-X.; Li, Y.; Feng, X.; Zhang, G. *Eur. J. Org. Chem.* **2004**, *2004*, 4657-4666.

(10) Darensbourg, D. J.; Billodeaux, D. R. *Inorg. Chem.* **2005**, *44*, 1433-1442.

(11) Adano P.; Costa Pessoa, J.; Henriques J.T.; Kuznetsov M. L.; Avecilla F.; Maurya M.R; Kumar U.; Correi *Inorg. Chem.* **2009,** *48*, 3542-3561.

(12) Bryliakov, K. P.; Talsi, E. P. *Angew. Chem. Int. Ed.* **2004**, 43, 5228-5230.

(13) Sauve A.A.; Grove J. T. *J. Am. Chem. Soc.* **2002**, *126*, 4770-4778.

(14) Pratt R. C.; Stack T. D. P. *J. Am. Chem. Soc.* **2003**, 1*25*, 8716–8717.

(15) Li B.; Wu G. P.; Ren W. M.; Wang Y. M.; Rao D. Y.; Lu X. B.; *J. Polym. Sci.: Polym. Chem.* **2008,** *46*, 61 6113.

(16) Larrow, J. F.; Jacobsen, E. N.; Gao, Y.; Hong, Y. P.; Nie, X. Y.; Zepp, C. M. *J. Org. Chem.* **1994**, *59*, 19 1942.

(17) Sanzenbacher, R.; Bottcher, A.; Elias, H.; Huber, M.; Haase, W.; Glerup, J.; Jensen, T. B.; Neuburger, Zehnder, M.; Springborg, J.; Olsen, C. E. *Inorg. Chem.* **1996**, *35*, 7493-7499.

(18) Adao, P.; Pessoa, J. C.; Henriques, R. T.; Kuznetsov, M. L.; Avecilla, F.; Maurya, M. R.; Kumar, U.; Correia *Inorg. Chem.* **2009**, *48*, 3542-3561.

(19) Darensbourg, D. J.; Ganguly, P.; Choi, W. *Inorg. Chem.* **2006**, *45*, 3831-3833.

(20) Liu, Z.; Anson, F. C. *J. Mol. Cat. A – Chem.* **2002**, *186*, 43-51.

(21) Chaladaj, W.; Jurczak, J. *Chem. Commun.* **2009**, 6747-6749.

(22) Baleizao, C.; Gigante, B.; Garcia, H.; Corma, A. *J. Cat.* **2003**, *215*, 199-207.

(23) Kozmin, S. A.; Iwama, T.; Huang, Y.; Rawal, V. H. *J. Am. Chem. Soc.* **2002**, *124*, 4628-4641.

(24) Kasumov, V. T.; Koksal, F. *Spectrochim. Acta. A. – Mol. Biomol. Spectrosc.* **2005**, *61*, 225-231.

(25) Petersen, N.; Raebiger, J. W.; Miller, J. S. *J. Therm. Anal. Calorim.* **2001**, *159*, 403-406.

(26) Sun, W.; Wang, H.; Xia, C.; Li, J.; Zhao, P. *Angew. Chem. Int. Ed.* 2003, *42*, 1042-1044.

(27) Niu, S.; Lu, C.; Han, K.; Zhao, J. *J. Therm. Anal. Calorim.* **2009**, *98*, 267-274.

(28) Works, C. F.; Jocher, C. J.; Bart, G. D.; Bu, X.; Ford, P. C. *Inorg. Chem.* **2002**, *41*, 3728-3739.

(29) Masutani, K.; Irie, R.; Katsuki, T. *Chem. Lett.* **2002**, *31*, 36-37.

(30) Jayaseeli, A. M. I.; Rajagopal, S. *J. Mol. Cat. A – Chem.* **2009**, *309*, 103-110.

(31) Nagano, H.; Katsuki, T. *Chem. Lett.* **2002**, *31*, 782-783.

(32) Tong, S.; Wang, D.-X.; Zhao, L.; Zhu, J.; Wang, M.-X. *Angew. Chem. Int. Ed.* **2012**, *51*, 4417-4420.

(33)Malkowsky, I. M.; Rommel, C. E.; Fröhlich, R.; Griesbach, U.; Pütter, H.; Waldvogel, S. R. *Chem. Eur. J.* **2006**, *12*, 7482-7488.

(34) Li, X. S.; Ding, Q. C.; Ge, J. F.; Xie, J. W.; Xu, D. C. *J. Org. Chem.* **2009**, *74*, 1785-1787.

(35) Coleman, R. S.; Guernon, J. M.; Roland, J. T. *Org. Lett.* **2000**, *2*, 277-280.

(36) Armstrong, D. R.; Cameron, C.; Nonhebel, D. C.; Perkins, P. G. *J. Chem. Soc.-Perkin Trans. 2* **1983**, 581-585.

(37) Toda, F.; Tanaka, K.; Miyamoto, H.; Koshima, H.; Miyahara, I.; Hirotsu, K. *J. Chem. Soc.-Perkin Trans. 2* **1997**, 1877-1885.