Supporting Information

Synthesis of 2,2′-biphenols through direct C(sp^2)–H hydroxylation of [1,1'-biphenyl]-2-ols

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I. General Experimental Information

All the commercial reagents were used without further purification. 2-Phenylphenol (**1a**) is commercially available and used as received. Other 2-arylphenol substrates were prepared based on literature procedures. Melting points were recorded with a micro melting point apparatus and uncorrected. The ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), quint (quintuplet), dd (doublet of doublet), m (multiplet), etc. The coupling constants J were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental Procedures and Spectroscopic Data

1. Preparation of 2-arylphenols (1)

(1) General procedure for the preparation of 2-arylphenols 1b-1w [1]

To a tube were added 2-bromophenol or substituted 2-bromophenol (1 mmol), arylboronic acid (1.5 mmol), $^{i}Pr_2NH$ (202 mg, 2 mmol), $Pd(OAc)_2$ (0.6 mg, 0.0025 mmol) and H_2O (2 mL). The tube was then sealed, and stirred at 100 ºC for 10 min-2 h. Upon completion, it was quenched with brine (10 mL), and extracted with EtOAc (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as eluent to afford 2-arylphenols **1b-1w**.

4'-Fluoro-[1,1'-biphenyl]-2-ol (1b)

White solid (169 mg, 90%), mp 44-45 ºC (lit.[2] 45-46 ºC); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.13-5.16 (m, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.97 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.11-7.15 (m, 2H), 7.20 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.23 (td, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.41-7.43 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 116.1 (d, $^2J_{C\text{-}F}$ = 20.7 Hz), 121.1, 127.3, 129.3, 130.5, 131.0 (d, $^3J_{C\text{-}F}$ = 7.65 Hz), 133.2, 152.4, 162.5 (d, $^1J_{C\text{-}F}$ = 244.95 Hz). MS: m/z 187 $[M\text{-}H]^-$.

4'-Chloro-[1,1'-biphenyl]-2-ol (1c)

White solid (182 mg, 89%), mp 52-53 ºC (lit.[2] 51-53 ºC); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.84 (br s, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.98 (t, J = 7.8 Hz, 1H), 7.20-7.25 (m, 2H), 7.40-7.43 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 116.1, 121.1, 127.1, 129.3, 129.4, 130.4, 130.6, 133.8, 135.8, 152.4. MS: m/z 203 $[M\text{-}H]^-$.

4'-Methyl-[1,1'-biphenyl]-2-ol (1d) [2]

Colorless syrup (152 mg, 86%); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.40 (s, 3H), 5.24 (s, 1H), 6.96-6.98 (m, 2H), 7.21-7.25 (m, 2H), 7.28 (d, J = 7.8 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 21.2, 115.8, 120.8, 128.1, 128.99, 129.0, 130.1, 130.3, 134.1, 137.8, 152.5. MS: m/z 183 $[M-H]^-$.

4'-Ethyl-[1,1'-biphenyl]-2-ol (1e)

Colorless syrup (174 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.28 (t, J = 7.6 Hz, 3H), 2.70 (q, J = 7.6 Hz, 2H), 5.27 (br s, 1H), 6.96-7.00 (m, 2H), 7.22-7.26 (m, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.37-7.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 15.6, 28.6, 115.7, 120.8, 128.1, 128.9, 129.0, 129.1, 130.3, 134.3, 144.1, 152.5. HRMS calcd for $C_{14}H_{13}O$: 197.0972 $[M-H]^-$, found: 197.0961.

4'-Pentyl-[1,1'-biphenyl]-2-ol (1f)

Colorless syrup (211 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.91 (t, J = 6.8 Hz, 3H), 1.33-1.36 (m, 4H), 1.61-1.68 (m, 2H), 2.63 (t, J = 7.6 Hz, 2H), 4.98 (br s, 1H), 6.93-6.97 (m, 2H), 7.19-7.22 (m, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.35 (dd, J_1 = 6.4 Hz, J_2 = 1.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 22.7, 31.3, 31.7, 35.8, 115.8, 120.9, 128.2, 129.01, 129.04, 129.4, 130.3, 134.4, 142.8, 152.6. HRMS calcd for $C_{17}H_{19}O$: 239.1441 $[M-H]^-$, found: 239.1432.

4'-(*tert*-Butyl)-[1,1'-biphenyl]-2-ol (1g)

Colorless syrup (208 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.36 (s, 9H), 4.87 (br s, 1H), 6.96-7.00 (m, 2H), 7.22-7.26 (m, 2H), 7.38-7.42 (m, 2H), 7.50-7.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 31.4, 34.7, 115.8, 120.8, 126.3, 128.1, 128.8, 129.0, 130.3, 134.1, 150.9, 152.6. HRMS calcd for $C_{16}H_{17}O$: 225.1285 $[M-H]^-$, found: 225.1272.

4'-(Trifluoromethyl)-[1,1'-biphenyl]-2-ol (1h)

White solid (202 mg, 85%), mp 112-113 ºC (lit.[2] 112-114 ºC); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.94 (s, 1H), 6.89 (d, J = 7.8 Hz, 1H), 6.95 (t, J = 7.8 Hz, 1H), 7.17-7.23 (m, 2H), 7.55 (d, J = 7.8 Hz, 2H), 7.65 (d, J = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 116.3, 121.3, 124.2 (q, $^{1}J_{C-F}$ = 271.35 Hz), 125.9 (q,

$^{3}J_{C\text{-}F}$ = 3.3 Hz), 127.0, 129.6, 129.79 (q, $^{2}J_{C\text{-}F}$ = 32.7 Hz), 129.83, 130.4, 141.2, 152.3. MS: m/z 237 [M-H]$^{-}$.

[1,1':4',1''-Terphenyl]-2-ol (1i)

White solid (197 mg, 80%), mp 175-176 ºC (lit.[3] 176-177 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.28 (br s, 1H), 6.99-7.03 (m, 2H), 7.25-7.31 (m, 2H), 7.35-7.39 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.54-7.56 (m, 2H), 7.63-7.65 (m, 2H), 7.70-7.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 116.0, 121.0, 127.2, 127.6, 127.8, 128.0, 128.9, 129.3, 129.5, 130.3, 136.1, 140.5, 140.8, 152.5. MS: m/z 245 [M-H]$^{-}$.

4'-Methoxy-[1,1'-biphenyl]-2-ol (1j)

White solid (180 mg, 90%), mp 67-68 ºC (lit.[2] 66-67 ^{o}C); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 3.81 (s, 3H), 5.35 (s, 1H), 6.93-6.95 (m, 2H), 6.96-6.98 (m, 2H), 7.19-7.22 (m, 2H), 7.36-7.38 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 55.4, 114.7, 115.8, 120.9, 128.0, 128.8, 129.4, 130.4, 152.6, 159.3. MS: m/z 199 [M-H]$^{-}$.

4'-Ethoxy-[1,1'-biphenyl]-2-ol (1k)

White solid (184 mg, 86%), mp 55-56 ºC (lit.[4] 53.5-54.5 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.44 (t, *J* = 6.8 Hz, 3H), 4.06 (q, *J* = 7.2 Hz, 2H), 5.29 (br s, 1H), 6.94-7.01 (m, 4H), 7.20-7.24 (m, 2H), 7.35-7.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.9, 63.6, 115.3, 115.7, 120.8, 127.9, 128.8, 129.1, 130.3, 152.6, 158.7. MS: m/z 213 [M-H]$^{-}$.

4'-(Trifluoromethoxy)-[1,1'-biphenyl]-2-ol (1l)

White solid (229 mg, 90%), mp 88-89 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.85 (br s, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 7.21-7.25 (m, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 116.2, 120.6 (q, $J_{C\text{-}F}$ = 254.85 Hz), 121.2, 121.5, 127.0, 129.5, 130.5, 130.7, 136.1, 148.8, 152.4. HRMS calcd for $C_{13}H_8F_3O_2$: 253.0482 [M-H]$^{-}$, found: 253.0473.

4'-Phenoxy-[1,1'-biphenyl]-2-ol (1m) [5]

White solid (225 mg, 86%), mp 102-103 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.17 (br s, 1H), 6.96-7.00 (m, 2H), 7.09 (t, *J* = 8.0 Hz, 4H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.23-7.27 (m, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 115.8, 119.2, 119.4, 120.9, 123.8, 127.6, 129.1, 129.9, 130.3, 130.6, 131.7, 152.5, 156.7, 157.3. MS: m/z 261 $[M-H]^-$.

1-(2'-Hydroxy-[1,1'-biphenyl]-4-yl)ethan-1-one (1n)

White solid (182 mg, 86%), mp 145-146 ºC (lit.[6] 145-148 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.65 (s, 3H), 5.35 (br s, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 7.26-7.30 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 8.06 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.7, 116.3, 121.2, 127.2, 129.0, 129.4, 129.8, 130.4, 136.1, 142.5, 152.5, 198.0. MS: m/z 211 $[M-H]^-$.

3'-Fluoro-[1,1'-biphenyl]-2-ol (1o) [7]

Colorless syrup (162 mg, 86%); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.15 (br s, 1H), 6.96 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 6.98-7.01 (m, 1H), 7.06-7.10 (m, 1H), 7.19-7.21 (m, 1H), 7.24 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.25-7.28 (m, 2H), 7.42-7.45 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 114.7 (d, $^{2}J_{C-F}$ = 20.85 Hz), 116.1, 116.3 (d, $^{2}J_{C-F}$ = 20.85 Hz), 121.1, 124.7 (d, $^{4}J_{C-F}$ = 3.3 Hz), 127.0, 129.6, 130.3, 130.7 (d, $^{3}J_{C-F}$ = 8.85 Hz), 139.5 (d, $^{3}J_{C-F}$ = 7.65 Hz), 152.3, 163.2 (d, $^{1}J_{C-F}$ = 246.15 Hz). MS: m/z 187 $[M-H]^-$.

3'-Chloro-[1,1'-biphenyl]-2-ol (1p) [8]

White solid (189 mg, 92%), mp 142-143 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.21 (br s, 1H), 6.94 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 6.99 (td, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 7.21-7.28 (m, 2H), 7.33-7.39 (m, 3H), 7.48 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 116.1, 121.1, 126.9, 127.3, 127.9, 129.4, 129.6, 130.3, 130.4, 134.9, 139.2, 152.3. MS: m/z 203 $[M-H]^-$.

3'-Methyl-[1,1'-biphenyl]-2-ol (1q) [2]

Colorless syrup (158 mg, 86%); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.41 (s, 3H), 5.27 (br s, 1H), 6.96-6.99 (m, 2H), 7.20-7.27 (m, 5H), 7.37 (t, J = 7.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 21.5, 115.8, 120.8, 126.1, 128.3, 128.7, 129.1, 129.3, 129.8, 130.2, 137.0, 139.2, 152.5. MS: m/z 183 $[M-H]^-$.

2'-Fluoro-[1,1'-biphenyl]-2-ol (1r)

Colorless syrup (165 mg, 88%); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.06 (br s, 1H), 6.97-7.02 (m, 2H), 7.19 (t, J = 9.0 Hz, 1H), 7.23-7.25 (m, 2H), 7.29 (t, J = 7.8 Hz, 1H), 7.37-7.38 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 116.2, 116.3 (d, $^{2}J_{C-F}$ = 21.9 Hz), 120.9, 122.4, 124.6 (d, $^{2}J_{C-F}$ = 15.3 Hz), 124.8 (d, $^{4}J_{C-F}$ = 3.3 Hz), 129.8, 130.0 (d, $^{3}J_{C-F}$ = 7.65 Hz), 131.2, 132.0 (d, $^{4}J_{C-F}$ = 3.3 Hz), 152.9, 160.0 (d, $^{1}J_{C-F}$ = 244.95 Hz). HRMS calcd for $C_{12}H_8FO$: 187.0565 $[M-H]^-$, found: 187.0558.

2'-Chloro-[1,1'-biphenyl]-2-ol (1s)

White solid (176 mg, 86%), mp 144-145 ºC (lit.[9] 145.1-146.4 ºC); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.82 (br s, 1H), 6.98-7.01 (m, 2H), 7.16 (d, J = 7.2 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 7.34-7.35 (m, 3H), 7.51-7.52 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 115.9, 120.6, 126.0, 127.4, 129.7, 129.9, 130.2, 130.7, 132.2, 134.1, 135.7, 152.6. MS: m/z 203 $[M-H]^-$.

2'-Methyl-[1,1'-biphenyl]-2-ol (1t) [2]

Colorless syrup (140 mg, 76%); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.15 (s, 3H), 4.80 (s, 1H), 6.94-6.97 (m, 2H), 7.09 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.20-7.22 (m, 1H), 7.24-7.28 (m, 2H), 7.29-7.31 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 19.8, 115.4, 120.5, 126.5, 127.8, 128.6, 129.2, 130.2, 130.6, 130.7, 135.8, 137.5, 152.6. MS: m/z 183 $[M-H]^-$.

4-Fluoro-[1,1'-biphenyl]-2-ol (1b') [10]

Colorless syrup (147 mg, 78%); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.46 (br s, 1H), 6.66-6.69 (m, 2H), 7.13-7.15 (m, 1H), 7.34-7.38 (m, 3H), 7.44 (t, J = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 103.4 (d, $^{2}J_{C-F}$

= 25.05 Hz), 107.9 (d, $^{2}J_{C\text{-}F}$ = 20.85 Hz), 124.4 (d, $^{4}J_{C\text{-}F}$ = 2.1 Hz), 128.1, 129.2, 129.5, 131.1 (d, $^{3}J_{C\text{-}F}$ = 9.75 Hz), 136.4, 153.6 (d, $^{3}J_{C\text{-}F}$ = 12.15 Hz), 163.2 (d, $^{1}J_{C\text{-}F}$ = 243.9 Hz). MS: m/z 187 $[M\text{-}H]^{-}$.

4-Chloro-[1,1'-biphenyl]-2-ol (1c')

White solid (176 mg, 86%), mp 39-40 ºC (lit.[11] 38.5-39 ºC); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.37 (br s, 1H), 6.95-6.98 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.37-7.41 (m, 3H), 7.47 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 116.3, 121.2, 126.8, 128.3, 129.0, 129.5, 131.1, 134.3, 136.1, 153.1. MS: m/z 203 $[M\text{-}H]^{-}$.

4-Methoxy-[1,1'-biphenyl]-2-ol (1j')

White solid (178 mg, 89%), mp 68-69 ºC (lit.[10] 66-67 ºC); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 3.78 (s, 3H), 5.39 (br s, 1H), 6.54-6.56 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.40-7.45 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 55.4, 101.5, 107.0, 121.0, 127.5, 129.2, 129.3, 130.9, 137.1, 153.5, 160.6. MS: m/z 199 $[M\text{-}H]^{-}$.

5-Chloro-[1,1'-biphenyl]-2-ol (1p') [12]

Colorless syrup (160 mg, 78%); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.07 (br s, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 7.17 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.20 (d, *J* = 2.4 Hz, 1H), 7.36-7.41 (m, 3H), 7.44-7.46 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 117.3, 125.6, 128.4, 128.9, 129.0, 129.4, 129.6, 129.9, 136.0, 151.1. MS: m/z 203 $[M\text{-}H]^{-}$.

5-Methyl-[1,1'-biphenyl]-2-ol (1q')

White solid (156 mg, 85%), mp 70-71 ºC (lit.[13] 68-69 ºC); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.28 (s, 3H), 5.15 (s, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 7.01-7.02 (m, 2H), 7.32-7.33 (m, 1H), 7.40-7.42 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 20.6, 115.8, 127.8, 128.0, 129.22, 129.25, 129.7, 130.1, 130.8, 137.5, 150.3. MS: m/z 183 $[M\text{-}H]^{-}$.

5-Methoxy-[1,1'-biphenyl]-2-ol (1u) [2]

Colorless syrup (152 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.77 (s, 3H), 4.58 (br s, 1H), 6.80-6.83 (m, 2H), 6.90 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.36-7.41 (m, 1H), 7.46-7.47 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.9, 114.6, 115.3, 116.7, 128.0, 128.7, 129.1, 129.2, 137.3, 146.5, 153.6. MS: m/z 199 $[M-H]^-$.

2-(Naphthalen-2-yl)phenol (1v)

White solid (176 mg, 80%), mp 95-96 ºC (lit.[14] 96.2-96.8 ºC); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.73 (br s, 1H), 7.00-7.03 (m, 2H), 7.27 (t, J = 7.8 Hz, 1H), 7.33 (d, J = 7.2 Hz, 1H), 7.50-7.51 (m, 2H), 7.56 (d, J = 8.4 Hz, 1H), 7.84-7.85 (m, 2H), 7.92-7.93 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 116.0, 121.0, 126.5, 126.7, 127.2, 127.86, 127.93, 128.1, 128.2, 129.2, 129.3, 130.6, 132.8, 133.7, 134.6, 152.7. MS: m/z 219 $[M-H]^-$.

4-Fluoro-4'-methoxy-[1,1'-biphenyl]-2-ol (1w)

White solid (185 mg, 85%), mp 65-66 ºC (lit.[10] 63-65 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.85 (s, 3H), 5.38 (br s, 1H), 6.66-6.72 (m, 2H), 6.99-7.03 (m, 2H), 7.12-7.16 (m, 1H), 7.31-7.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.4, 103.1 (d, $^2J_{C-F}$ = 24.8 Hz), 107.7 (d, $^2J_{C-F}$ = 21.1 Hz), 114.9, 124.0 (d, $^4J_{C-F}$ = 3.7 Hz), 128.3, 130.3, 131.0 (d, $^3J_{C-F}$ = 9.5 Hz), 153.7 (d, $^3J_{C-F}$ = 12.4 Hz), 159.5, 162.9 (d, $^1J_{C-F}$ = 243.6 Hz). MS: m/z 217 $[M-H]^-$.

(2) Procedure for the preparation of [1,1'-binaphthalen]-2-ol (1x) [15]

To a Schlenk flask were added $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), Na_2CO_3 (223 mg, 2.1 mmol), 1-bromonaphthalen-2-ol (223 mg, 1.0 mmol), naphthalen-1-ylboronic acid (344 mg, 2.0 mmol), toluene (5 mL), ethanol (1 mL) and water (1 mL). After the flask was evacuated and flushed with nitrogen, the mixture was stirred at 80 °C for 20 h. Upon completion, it was quenched with saturated NH_4Cl (10 mL), and extracted with EtOAc (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4,

and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as eluent to afford **1x**.

[1,1'-Binaphthalen]-2-ol (1x)

White solid (232 mg, 86%), mp 95-96 ºC (lit. [16] 90-93 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.93 (s, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.17-7.21 (m, 1H), 7.27-7.32 (m, 3H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.45-7.50 (m, 2H), 7.56-7.60 (m, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.91-7.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 117.6, 118.8, 123.5, 125.1, 125.9, 126.1, 126.7, 127.0, 128.1, 128.6, 129.0, 129.3, 129.7, 130.0, 131.6, 132.9, 134.0, 134.3, 151.1. MS: m/z 269 $[M-H]^-$.

(3) Procedure for the preparation of [1,1'-biphenyl]-2',3',4',5',6'-*d*$_5$-2-ol (1a-*d*$_5$) [1]

To a tube were added 1-bromobenzene-2,3,4,5,6-d_5 (162 mg, 1 mmol), (2-hydroxyphenyl)boronic acid (207 mg, 1.5 mmol), ^{i}Pr$_2$NH (202 mg, 2 mmol), $Pd(OAc)_2$ (0.56 mg, 0.0025 mmol) and H_2O (2 mL). The tube was then sealed, and the mixture was stirred at 100 ºC for 30 min. Upon completion, it was quenched with brine (10 mL), and extracted with EtOAc (10 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as eluent to afford **1a-*d*$_5$**.

[1,1'-Biphenyl]-2',3',4',5',6'-*d*$_5$-2-ol (1a-*d*$_5$) [6]

White solid (168 mg, 96%), mp 85-86 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.28 (br s, 1H), 6.95-6.98 (m, 2H), 7.22-7.24 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 116.0, 121.0, 127.4 (t, *J* = 24.0 Hz, 1C), 128.2, 128.77 (t, *J* = 24.0 Hz, 2C), 128.80 (t, *J* = 24.0 Hz, 2C), 129.2, 130.4, 137.0, 152.5. MS: m/z 174 $[M-H]^-$.

(4) Procedure for the preparation of [1,1'-biphenyl]-2'-*d*-2-ol (1a-*d*$_1$) [6]

To a Schlenk tube were added 2'-bromo-[1,1'-biphenyl]-2-ol (249 mg, 1 mmol) and Et_2O (6 mL). The solution was cooled to –78 ^{o}C, followed by dropwise addition of *n*-BuLi (1.6 M in hexane, 3 mL) under nitrogen. The resulting mixture was stirred at –78 ^{o}C for 15 min, then at 0 ^{o}C for additional 2 h. The

reaction was quenched with careful addition of D_2O (1 mL), followed by vigorous stirring at room temperature for 1 h. Then, the reaction mixture was diluted with EtOAc (30 mL), and the organic phase was dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as eluent to afford **1a-*d*$_1$**.

[1,1'-Biphenyl]-2'-*d*-2-ol (1a-*d*$_1$)

White solid (164 mg, 96%), mp 58-59 ºC (lit.[6] 56-57 ºC); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.16 (s, 1H), 6.87-6.90 (m, 2H), 7.13-7.16 (m, 2H), 7.28 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.35-7.38 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 115.9, 120.9, 127.9, 128.2, 128.9 (t, J = 24.0 Hz, 1C), 129.18, 129.21, 129.23, 129.3, 130.3, 137.1, 152.5. MS: m/z 170 $[M-H]^-$.

2. Preparation of 2,2′-biphenols (2)

A typical procedure for the preparation of [1,1'-biphenyl]-2,2'-diol (2a)

To a tube containing 2-phenylphenol (**1a**, 85 mg, 0.5 mmol) were added $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol), PivOH (51 mg, 0.5 mmol), CH_3CN (2 mL) and TBHP (0.27 mL, 70% aqueous solution, 2 mmol) under air. The tube was then sealed, and stirred at 80 ºC for 18 h. Afterwards, the reaction was quenched with saturated NH_4Cl (10 mL), and extracted with EtOAc (6 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as eluent to afford **2a** (71 mg, 76%) and recover **1a** (5 mg, 6%). **2b**-**2w** were obtained in a similar manner.

[1,1'-Biphenyl]-2,2'-diol (2a) [17]

Colorless syrup (71 mg, 76%); ^{1}H NMR (600 MHz, DMSO-d_6) δ: 6.79 (t, J = 7.8 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 7.09-7.13 (m, 4H), 9.16 (br s, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 116.2, 119.4, 126.4,

128.6, 132.0, 154.9. FT-IR (KBr) ν (cm^{-1}): 744, 840, 1094, 1224, 1440, 1483, 3150. HRMS calcd for $C_{12}H_{10}NaO_2$: 209.0573 $[M+Na]^+$, found: 209.0578.

4-Fluoro-[1,1'-biphenyl]-2,2'-diol (2b) [17]

Colorless solid (82 mg, 80%), mp 80-81 ºC. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 6.65 (td, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.72 (dd, J_1 = 10.8 Hz, J_2 = 2.4 Hz, 1H), 6.83 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 6.92 (dd, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 7.12-7.17 (m, 3H), 9.47 (br s, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 103.0 (d, $^2J_{C\text{-}F}$ = 24.0 Hz), 105.7 (d, $^2J_{C\text{-}F}$ = 20.85 Hz), 116.1, 119.2, 122.9 (d, $^4J_{C\text{-}F}$ = 3.15 Hz), 125.4, 128.6, 132.0, 133.0 (d, $^3J_{C\text{-}F}$ = 9.9 Hz), 155.1, 156.5 (d, $^3J_{C\text{-}F}$ = 10.95 Hz), 162.3 (d, $^1J_{C\text{-}F}$ = 240.6 Hz). FT-IR (KBr) ν (cm^{-1}): 743, 831, 970, 1089, 1139, 1278, 1482, 1604, 3277. HRMS calcd for $C_{12}H_8FO_2$: 203.0514 $[M-H]^-$, found: 203.0508.

4-Chloro-[1,1'-biphenyl]-2,2'-diol (2c) [18]

Colorless solid (85 mg, 77%), mp 119-120 ºC. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 6.83 (t, J = 7.2 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.97 (s, 1H), 7.13-7.17 (m, 3H), 9.49 (br s, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 115.8, 116.1, 119.0, 119.2, 125.1, 125.5, 128.8, 131.8, 132.2, 133.2, 155.0, 156.2. FT-IR (KBr) ν (cm^{-1}): 757, 900, 1005, 1191, 1290, 1481, 1599, 3280. HRMS calcd for $C_{12}H_8ClO_2$: 219.0218 $[M-H]^-$, found: 219.0219.

4-Methyl-[1,1'-biphenyl]-2,2'-diol (2d)

Colorless solid (77 mg, 77%), mp 78-79 ºC. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 2.25 (s, 3H), 6.64 (d, J = 7.2 Hz, 1H), 6.71 (s, 1H), 6.81 (t, J = 7.2 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 7.02 (d, J = 7.2 Hz, 1H), 7.10-7.13(m, 2H), 9.10 (br s, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 21.3, 116.2, 116.8, 119.3, 120.2, 123.4, 126.4, 128.3, 131.8, 132.0, 137.8, 154.7, 154.9. FT-IR (KBr) ν (cm^{-1}): 750, 941, 1043, 1225, 1279, 1483, 1703, 3203. HRMS calcd for $C_{13}H_{11}O_2$: 199.0765 $[M-H]^-$, found: 199.0766.

4-Ethyl-[1,1'-biphenyl]-2,2'-diol (2e)

Colorless syrup (83 mg, 78%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.15 (t, J = 7.6 Hz, 3H), 2.51 (q, J = 7.6 Hz, 2H), 6.65 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 6.73 (d, J = 1.6 Hz, 1H), 6.78 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 6.87 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 7.06-7.12 (m, 2H), 9.13 (br s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 15.5, 27.9, 115.1, 115.7, 118.5, 118.9, 123.2, 125.9, 127.9, 131.3, 131.5, 143.8, 154.2, 154.4. FT-IR (KBr) ν (cm^{-1}): 752, 935, 1039, 1226, 1289, 1491, 1723, 3233. HRMS calcd for $C_{14}H_{13}O_2$: 213.0921 [M-H]$^-$, found: 213.0923.

4-Pentyl-[1,1'-biphenyl]-2,2'-diol (2f)

Colorless syrup (96 mg, 75%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.91 (t, J = 6.8 Hz, 3H), 1.29-1.38 (m, 4H), 1.61 (quint, J = 7.2 Hz, 2H), 2.54 (t, J = 7.6 Hz, 2H), 6.69 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 6.78 (d, J = 1.2 Hz, 1H), 6.84 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 6.93-6.95 (m, 1H), 7.09 (d, J = 8.0 Hz, 1H), 7.14 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.18 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 9.20 (br s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 13.9, 22.1, 30.6, 31.0, 34.9, 115.6, 115.8, 118.9, 119.1, 123.2, 126.0, 127.8, 131.3, 131.5, 142.4, 154.1, 154.4. FT-IR (KBr) ν (cm^{-1}): 755, 945, 1049, 1228, 1288,1412, 1493, 1705, 3212. HRMS calcd for $C_{17}H_{19}O_2$: 255.1391 [M-H]$^-$, found: 255.1403.

4-(*tert*-Butyl)-[1,1'-biphenyl]-2,2'-diol (2g)

Colorless solid (91 mg, 75%), mp 116-117 ºC. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 1.30 (s, 9H), 6.84 (t, J = 7.8 Hz, 1H), 6.89 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.95 (d, J = 1.8 Hz, 1H), 7.11 (d, J = 7.8 Hz, 1H), 7.12-7.15 (m, 1H), 7.17 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 9.07 (br s, 1H), 9.19 (br s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 31.6, 34.6, 113.3, 116.2, 116.4, 119.4, 123.4, 126.3, 128.4, 131.5, 132.0, 151.3, 154.4, 154.9. FT-IR (KBr) ν (cm^{-1}): 748, 863, 930, 1099, 1223, 1408, 1483, 2961, 3198. HRMS calcd for $C_{16}H_{17}O_2$: 241.1234 [M-H]$^-$, found: 241.1251.

4-(Trifluoromethyl)-[1,1'-biphenyl]-2,2'-diol (2h)

Colorless solid (102 mg, 80%), mp 101-102 ºC. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 6.84 (td, J_1 = 7.2 Hz, J_2 = 0.6 Hz, 1H), 6.94 (d, J = 7.2 Hz, 1H), 7.15-7.19 (m, 3H), 7.21 (d, J = 1.2 Hz, 1H), 7.36 (d, J = 7.8 Hz, 1H), 9.65 (br s, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 112.3 (q, $^{3}J_{C-F}$ = 3.3 Hz), 115.5 (q, $^{3}J_{C-F}$ = 3.15 Hz), 116.2, 119.2, 124.7 (q, $^{1}J_{C-F}$ = 270.15 Hz), 124.9, 129.0 (q, $^{2}J_{C-F}$ = 31.65 Hz), 129.2, 130.7, 131.7, 132.9, 155.1, 155.7. FT-IR (KBr) ν(cm^{-1}): 754, 822, 914, 1004, 1119, 1331, 1422, 3071. HRMS calcd for $C_{13}H_8F_3O_2$: 253.0482 [M-H]$^-$, found: 253.0502.

[1,1':4',1''-Terphenyl]-2,2'-diol (2i)

Colorless solid (101 mg, 77%), mp 139-140 ºC. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 6.88 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 7.15-7.20(m, 2H), 7.24-7.25(m, 2H), 7.29 (d, J = 7.2 Hz, 1H), 7.37 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.2 Hz, 2H), 7.65(d, J = 7.8 Hz, 2H), 9.41 (br s, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 114.4, 116.3, 117.9, 119.4, 125.7, 126.0, 127.0, 127.8, 128.7, 129.4, 132.0, 132.6, 140.72, 140.74, 155.0, 155.4. FT-IR (KBr) ν (cm^{-1}): 759, 820, 895, 1172, 1404, 1476, 2922, 3515. HRMS calcd for $C_{18}H_{13}O_2$: 261.0921 [M-H]$^-$, found: 261.0919.

4-Methoxy-[1,1'-biphenyl]-2,2'-diol (2j) [17]

Colorless syrup (81 mg, 75%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 3.72 (s, 3H), 6.45 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.49 (d, J = 2.8 Hz, 1H), 6.81 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 6.89 (dd, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H), 7.09-7.14 (m, 2H), 9.24 (br s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 54.9, 101.5, 104.5, 115.6, 118.5, 118.8, 125.7, 127.7, 131.6, 132.0, 154.4, 155.3, 159.3. FT-IR (KBr) ν (cm^{-1}): 755, 829, 1037, 1157, 1284, 1484, 1573, 1619, 2928, 3280. HRMS calcd for $C_{13}H_{11}O_3$: 215.0714 [M-H]$^-$, found: 215.0709.

4-Ethoxy-[1,1'-biphenyl]-2,2'-diol (2k)

Colorless solid (86 mg, 75%), mp 99-100 ºC. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 1.32 (t, J = 7.2 Hz, 3H), 3.98 (q, J = 7.2 Hz, 2H), 6.41 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.45 (d, J = 2.4 Hz, 1H), 6.80 (t, J = 7.2

Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 7.08-7.11(m, 2H), 9.15 (br s, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 15.2, 63.3, 102.5, 105.5, 116.1, 118.8, 119.3, 126.2, 128.1, 132.1, 132.4, 154.9, 155.8, 159.1. FT-IR (KBr) ν (cm^{-1}): 759, 843, 982, 1103, 1176, 1293, 1480, 1618, 2925, 2983, 3156. HRMS calcd for $C_{14}H_{13}O_3$: 229.0870 $[M-H]^-$, found: 229.0872.

4-(Trifluoromethoxy)-[1,1'-biphenyl]-2,2'-diol (2l)

Colorless solid (101 mg, 75%), mp 75-76 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.78-6.84(m, 2H), 6.86 (d, J = 1.2 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 7.13-7.17 (m, 2H), 7.24 (d, J = 8.4 Hz, 1H), 9.60 (br s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 107.8, 110.6, 115.6, 118.6, 120.1 (q, J_{C-F} = 254.6 Hz), 124.4, 125.3, 128.4, 131.4, 132.6, 147.8, 154.6, 155.8. FT-IR (KBr) ν (cm^{-1}): 752, 868, 986, 1095, 1147, 1208, 1482, 1610, 3280. HRMS calcd for $C_{13}H_8F_3O_3$: 269.0431 $[M-H]^-$, found: 269.0429.

4-Phenoxy-[1,1'-biphenyl]-2,2'-diol (2m)

Colorless syrup (106 mg, 76%). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 6.47 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.52 (d, J = 2.4 Hz, 1H), 6.81(t, J = 7.8 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 7.08 (d, J = 8.4 Hz, 2H), 7.10-7.17(m, 4H), 7.42 (t, J = 8.4 Hz, 2H), 9.14(br s, 1H) , 9.40(br s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 105.9, 109.1, 116.1, 119.2, 119.6, 121.5, 124.0, 125.7, 128.4, 130.5, 132.1, 132.9, 155.0, 156.2, 156.9, 157.2. FT-IR (KBr) ν (cm^{-1}): 753, 829, 974, 1097, 1211, 1483, 1589, 2853, 2923, 3288. HRMS calcd for $C_{18}H_{13}O_3$: 277.0870 $[M-H]^-$, found: 277.0863.

1-(2,2'-Dihydroxy-[1,1'-biphenyl]-4-yl)ethan-1-one (2n)

Colorless solid (88 mg, 77%), mp 149-150 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.54 (s, 3H), 6.83 (td, J_1 = 7.2 Hz, J_2 = 0.8 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 7.14-7.18 (m, 2H), 7.28 (dd, J_1 = 6.8 Hz, J_2 = 1.6 Hz, 1H), 7.44-7.46 (m, 2H), 9.50 (br s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 26.7, 114.4, 115.6, 118.6, 119.1, 124.8, 128.6, 131.10, 131.15, 131.8, 136.6, 154.5, 154.8, 197.5. FT-IR (KBr) ν (cm^{-1}): 757, 825,

1005, 1154, 1291, 1415, 1483, 1571, 1652, 2923, 3327. HRMS calcd for $C_{14}H_{11}O_3$: 227.0714 $[M-H]^-$, found: 227.0720.

5-Fluoro-[1,1'-biphenyl]-2,2'-diol (2o)

Colorless solid (77 mg, 75%), mp 76-77 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.83 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 6.86-6.92 (m, 2H), 6.95-6.98 (m, 2H), 7.13-7.19 (m, 2H), 9.30 (br s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 114.1 (d, $^2J_{C-F}$ = 22.5 Hz), 115.7, 116.3 (d, $^3J_{C-F}$ = 8.0 Hz), 117.4 (d, $^2J_{C-F}$ = 22.5 Hz), 118.7, 124.6, 126.8 (d, $^3J_{C-F}$ = 8.0 Hz), 128.5, 131.4, 150.8 (d, $^4J_{C-F}$ = 1.4 Hz), 154.4, 155.1 (d, $^1J_{C-F}$ = 232.0 Hz). FT-IR (KBr) ν (cm^{-1}): 753, 822, 877, 1170, 1219, 1419, 1488, 1592, 3166. HRMS calcd for $C_{12}H_8FO_2$: 203.0514 $[M-H]^-$, found: 203.0496.

5-Chloro-[1,1'-biphenyl]-2,2'-diol (2p)

Colorless solid (80 mg, 73%), mp 105-106 ºC (lit.[19] 109.2-109.7 ºC). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.80-6.84 (m, 1H), 6.91 (d, J = 8.0 Hz, 2H), 7.13-7.18 (m, 4H), 9.46 (br s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 115.6, 117.1, 118.7, 121.9, 124.3, 127.5, 127.6, 128.5, 130.8, 131.3, 153.6, 154.4. FT-IR (KBr) ν (cm^{-1}): 755, 905, 1021, 1201, 1285, 1483, 1601, 3273. HRMS calcd for $C_{12}H_8ClO_2$: 219.0218 $[M-H]^-$, found: 219.0223.

5-Methyl-[1,1'-biphenyl]-2,2'-diol (2q)

Colorless solid (71 mg, 71%), mp 83-84 ºC (lit.[20] 81-83 ºC). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 2.23 (s, 3H), 6.81 (d, J = 7.8 Hz, 1H), 6.84 (t, J = 7.8 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 6.95-6.96 (m, 2H), 7.13-7.16(m, 2H), 9.07 (br s, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 20.6, 116.1, 116.2, 119.3, 126.2, 126.6, 127.7, 128.5, 128.9, 132.0, 132.4, 152.6, 154.9. FT-IR (KBr) ν (cm^{-1}): 756, 943, 1055, 1216, 1285, 1476, 1711, 3205. HRMS calcd for $C_{13}H_{11}O_2$: 199.0765 $[M-H]^-$, found: 199.0767.

6-Fluoro-[1,1'-biphenyl]-2,2'-diol (2r)

Colorless solid (59 mg, 58%), mp 75-76 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.60-6.65 (m, 1H), 6.72 (d, J = 8.0 Hz, 1H), 6.80 (td, J_1 = 7.2 Hz, J_2 = 0.8 Hz, 1H), 6.87-6.89 (m, 1H), 7.05 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.10-7.17 (m, 2H), 9.43 (br s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 105.4 (d, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 111.2 (d, $^{4}J_{C\text{-}F}$ = 2.2 Hz), 114.0 (d, $^{2}J_{C\text{-}F}$ = 19.7 Hz), 115.3, 118.4, 119.1, 128.4 (d, $^{3}J_{C\text{-}F}$ = 10.9 Hz), 128.6, 131.9, 155.2, 156.5 (d, $^{3}J_{C\text{-}F}$ = 7.3 Hz), 160.6 (d, $^{1}J_{C\text{-}F}$ = 240.0 Hz). FT-IR (KBr) ν (cm^{-1}): 756, 831, 1003, 1111, 1260, 1449, 1465, 1607, 3359, 3561. HRMS calcd for $C_{12}H_8FO_2$: 203.0514 [M-H]$^{-}$, found: 203.0497.

6-Chloro-[1,1'-biphenyl]-2,2'-diol (2s)

Colorless solid (61 mg, 55%), mp 115-116 ºC (lit.[19] 117.2-117.7 ºC). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 6.80 (t, J = 7.8 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 6.95 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.11-7.16 (m, 2H), 9.16 (br s, 1H) , 9.49 (br s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 114.4, 115.8, 118.9, 119.7, 123.4, 125.8, 129.0, 129.2, 131.9, 134.6, 155.4, 157.0. FT-IR (KBr) ν (cm^{-1}): 750, 941, 1043, 1225, 1279, 1483, 1703, 3203. HRMS calcd for $C_{12}H_8ClO_2$: 219.0218 [M-H]$^{-}$, found: 219.0197.

6-Methyl-[1,1'-biphenyl]-2,2'-diol (2t)

Colorless solid (50 mg, 50%), mp 99-100 ºC (lit.[21] 101-102 ºC). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 1.95 (s, 3H), 6.68 (d, J = 7.8 Hz, 1H), 6.70 (d, J = 7.8 Hz, 1H), 6.80 (t, J = 7.8 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 6.93 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.00 (t, J = 7.8 Hz, 1H), 7.11-7.13 (m, 1H), 8.84 (br s, 1H), 9.02 (br s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 20.4, 113.1, 115.8, 119.1, 120.5, 125.1, 126.3, 127.8, 128.3, 131.9, 138.2, 155.2, 155.3. FT-IR (KBr) ν (cm^{-1}): 750, 941, 1043, 1225, 1279, 1483, 1703, 3203. HRMS calcd for $C_{13}H_{11}O_2$: 199.0765 [M-H]$^{-}$, found: 199.0767.

5-Methoxy-[1,1'-biphenyl]-2,2'-diol (2u)

Colorless syrup (81 mg, 75%). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 3.70 (s, 3H), 6.77-6.78 (m, 2H), 6.86 (d, J = 7.2 Hz, 2H), 6.94 (d, J = 7.8 Hz, 1H), 7.17 (t, J = 7.8 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 9.02 (br s, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 55.8, 114.0, 116.4, 116.9, 117.1, 119.5, 126.3, 127.0, 128.7, 132.0, 148.7, 152.5, 154.8. FT-IR (KBr) ν (cm^{-1}): 756, 835, 1039, 1163, 1292, 1492, 1575, 1622, 2925, 3285. HRMS calcd for $C_{13}H_{11}O_3$: 215.0714 [M-H]$^-$, found: 215.0694.

3-(2-Hydroxyphenyl)naphthalen-2-ol (2v) [22]

Colorless syrup (68 mg, 58%). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 6.85 (t, J = 7.8 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 7.17-7.21 (m, 3H), 7.26 (t, J = 7.8 Hz, 1H), 7.38 (t, J = 8.4 Hz, 1H), 7.67-7.69 (m, 2H), 7.76 (d, J = 7.8 Hz, 1H), 9.22 (br s, 1H), 9.61 (br s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 109.3, 116.0, 119.1, 123.2, 125.9, 126.2, 126.3, 128.0, 128.1, 128.8, 129.6, 130.8, 132.0, 134.3, 154.2, 155.3. FT-IR (KBr) ν (cm^{-1}): 745, 839, 1102, 1167, 1279, 1443, 1632, 1703, 2923, 3281. HRMS calcd for $C_{16}H_{11}O_2$: 235.0765 [M-H]$^-$, found: 235.0761.

4-Fluoro-4'-methoxy-[1,1'-biphenyl]-2,2'-diol (2w)

Colorless solid (90 mg, 77%), mp 89-90 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 3.68 (s, 3H), 6.39 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.45 (d, J = 2.4 Hz, 1H), 6.59 (td, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.65 (dd, J_1 = 10.8 Hz, J_2 = 2.4 Hz, 1H), 7.00 (d, J = 8.4 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 9.41 (br s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 54.8, 101.4, 102.4 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 104.3, 105.1 (d, $^{2}J_{C\text{-}F}$ = 20.3 Hz), 117.5, 122.1 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz), 132.0, 132.6 (d, $^{3}J_{C\text{-}F}$ = 9.5 Hz), 155.5, 156.0 (d, $^{3}J_{C\text{-}F}$ = 10.9 Hz), 159.4, 161.6 (d, $^{1}J_{C\text{-}F}$ = 240.8 Hz). FT-IR (KBr) ν (cm^{-1}): 730, 832, 971, 1151, 1264, 1418, 1496, 1606, 2923, 3335. HRMS calcd for $C_{13}H_{10}FO_3$: 233.0619 [M-H]$^-$, found: 233.0609.

3. Preparation of 1-hydroxy-[1,1'-binaphthalen]-2(1*H*)-one (3)

To a tube containing [1,1'-binaphthalen]-2-ol (**1x**, 135 mg, 0.5 mmol) were added $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol), PivOH (51 mg, 0.5 mmol), CH_3CN (2 mL) and TBHP (0.27

mL, 70% aqueous solution, 2 mmol) under air. The tube was then sealed, and stirred at 80 ºC for 18 h. Afterwards, the reaction was quenched with saturated NH_4Cl (10 mL), and extracted with EtOAc (6 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was separated by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as eluent to afford 1-hydroxy-[1,1'-binaphthalen]-2(1*H*)-one (**3**, 64 mg, 45%) and recover **1x** (62 mg, 46%).

1-Hydroxy-[1,1'-binaphthalen]-2(1*H*)-one (3)

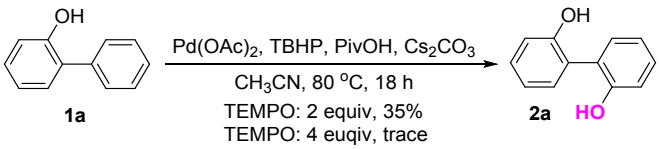
White solid (64 mg, 45%), mp 196-197 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 3.32 (s, 1H), 6.35 (d, J = 10.2 Hz, 1H), 7.18-7.19 (m, 1H), 7.22-7.25 (m, 2H), 7.32-7.38 (m, 3H), 7.43 (d, J = 6.6 Hz, 1H), 7.53 (t, J = 7.2 Hz, 1H), 7.60 (d, J = 10.2 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 8.00 (dd, J_1 = 7.2 Hz, J_2 = 0.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 77.4, 123.9, 124.45, 124.51, 125.0, 125.5, 126.4, 129.03, 129.05, 129.3, 129.37, 129.43, 129.8, 130.0, 130.9, 134.2, 138.0, 142.9, 145.2, 200.4. HRMS calcd for $C_{20}H_{14}O_2Na$: 309.0886 $[M+Na]^+$, found: 309.0882.

III. Mechanism studies

1. Control experiment 1

To a tube containing 2-phenylphenol (**1a**, 85 mg, 0.5 mmol) were added $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol), PivOH (51 mg, 0.5 mmol), CH_3CN (2 mL), TBHP (0.27 mL, 70% aqueous solution, 2 mmol) and TEMPO (156.3 mg, 1 mmol) under air (Scheme 1). The tube was then sealed, and stirred at 80 ºC for 18 h. Afterwards, the reaction was quenched with saturated NH_4Cl (10 mL), and extracted with EtOAc (6 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as eluent to afford **2a** (33 mg, 35%).

To a tube containing 2-phenylphenol (**1a**, 85 mg, 0.5 mmol) were added $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol), PivOH (51 mg, 0.5 mmol), CH_3CN (2 mL), TBHP (0.27 mL, 70% aqueous solution, 2 mmol) and TEMPO (312.6 mg, 2 mmol) under air (Scheme 1). The tube was then sealed, and stirred at 80 ºC for 18 h. Afterwards, the reaction was quenched with saturated NH_4Cl (10 mL), and extracted with EtOAc (6 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was separated by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as eluent to give trace amount of **2a** and 72 mg of **1a**.

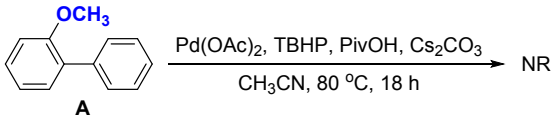


Scheme 1. Control experiment 1

2. Control experiment 2

To a tube containing 2-methoxy-1,1'-biphenyl (**A**, 92 mg, 0.5 mmol) were added $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol), PivOH (51 mg, 0.5 mmol), CH_3CN (2 mL) and TBHP (0.27 mL, 70% aqueous solution, 2 mmol) under air (Scheme 2). The tube was then sealed, and stirred at 80 ºC for 18 h. Afterwards, the reaction was quenched with saturated NH_4Cl (10 mL), and extracted with

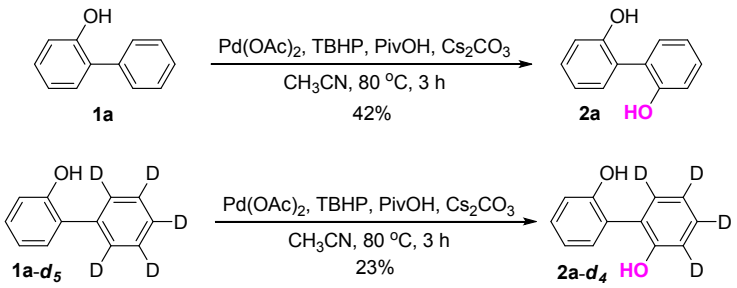
EtOAc (6 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was separated by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as eluent to give 86 mg of **A**.



Scheme 2. Control experiment 2

3. The intermolecular KIE experiments

To two tubes, one containing 2-phenylphenol (**1a**, 85.1 mg, 0.5 mmol) and another one containing 2-phenylphenol-d_5 (**1a-*d*$_5$**, 87.6 mg, 0.5 mmol), were respectively added $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol), PivOH (51 mg, 0.5 mmol), CH_3CN (2 mL) and TBHP (0.27 mL, 70% aqueous solution, 2 mmol) under air. After being sealed, the two tubes were stirred side-by-side in an oil bath at 80 ºC for 3 h. Then, the reactions were quenched with saturated NH_4Cl (10 mL), and extracted with EtOAc (6 mL × 3). The following purifications *via* column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as eluent afforded **2a** (39 mg, 42%) and **2a-*d*$_4$** (22 mg, 23%), respectively. From these results, an intermolecular KIE (k_H/k_D) value of 1.8 is obtained.

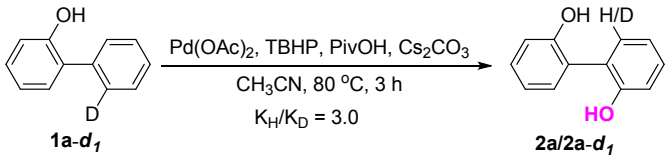


Scheme 3. Intermolecular KIE experiments

4. The intramolecular KIE experiments

To a tube containing 2'-deuterio-biphenyl-2-ol (**1a-*d*$_1$**, 85.6 mg, 0.5 mmol) were added $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol), PivOH (51 mg, 0.5 mmol), CH_3CN (2 mL) and

TBHP (0.27 mL, 70% aqueous solution, 2 mmol) under air. After being sealed, the tube was stirred at 80 ºC for 3 h. Then, the reaction was quenched with saturated NH_4Cl (10 mL), and extracted with EtOAc (6 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as eluent to afford a mixture of **2a** and **2a-*d*$_1$**. Upon analyzing the corresponding ^{1}H NMR spectrum as shown in Fig 1, the ratio of **2a** and **2a-*d*$_1$** in the resulting mixture was determined as 0.75:0.25. Accordingly, the intramolecular KIE (k_H/k_D) was calculated as 3.0.



Scheme 4. The intramolecular KIE experiment

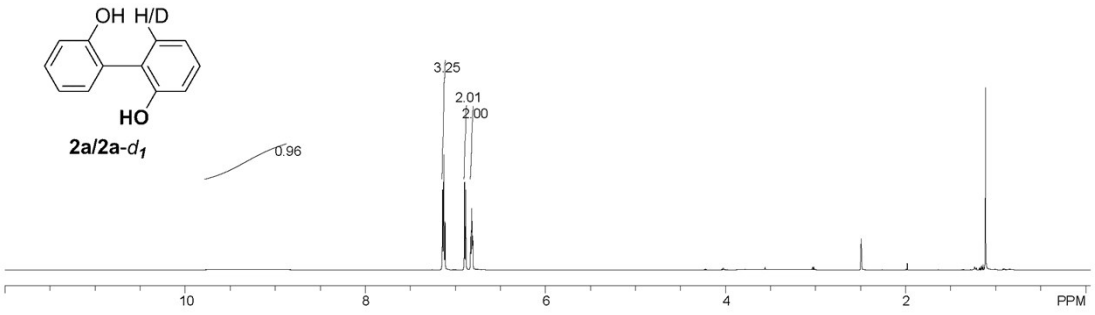
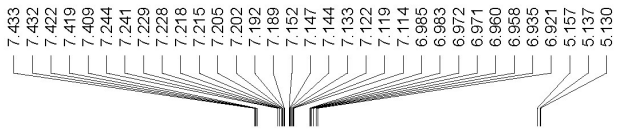
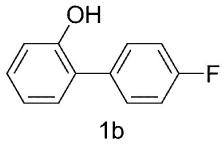


Fig 1 The ^{1}H NMR spectrum of the products obtained from the intramolecular KIE experiment

IV. Copies of ^{1}H and ^{13}C NMR Spectra of 1b-1x





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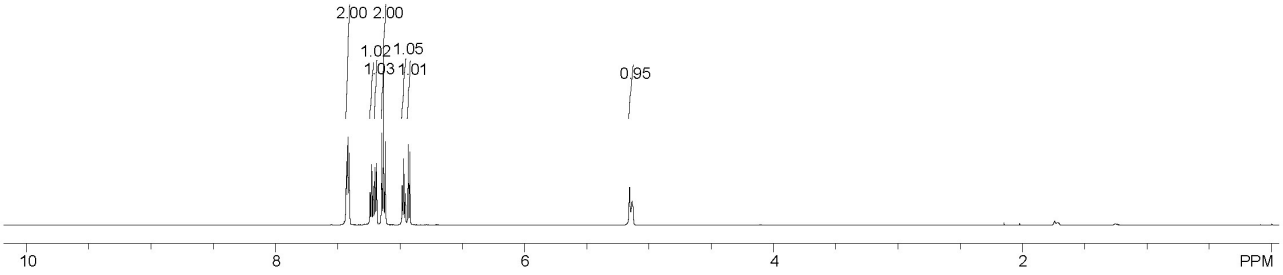

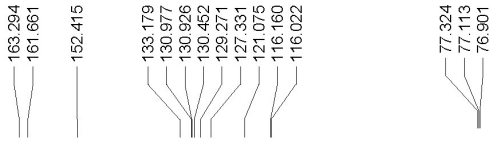

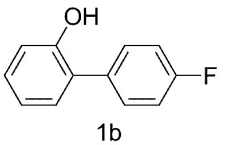

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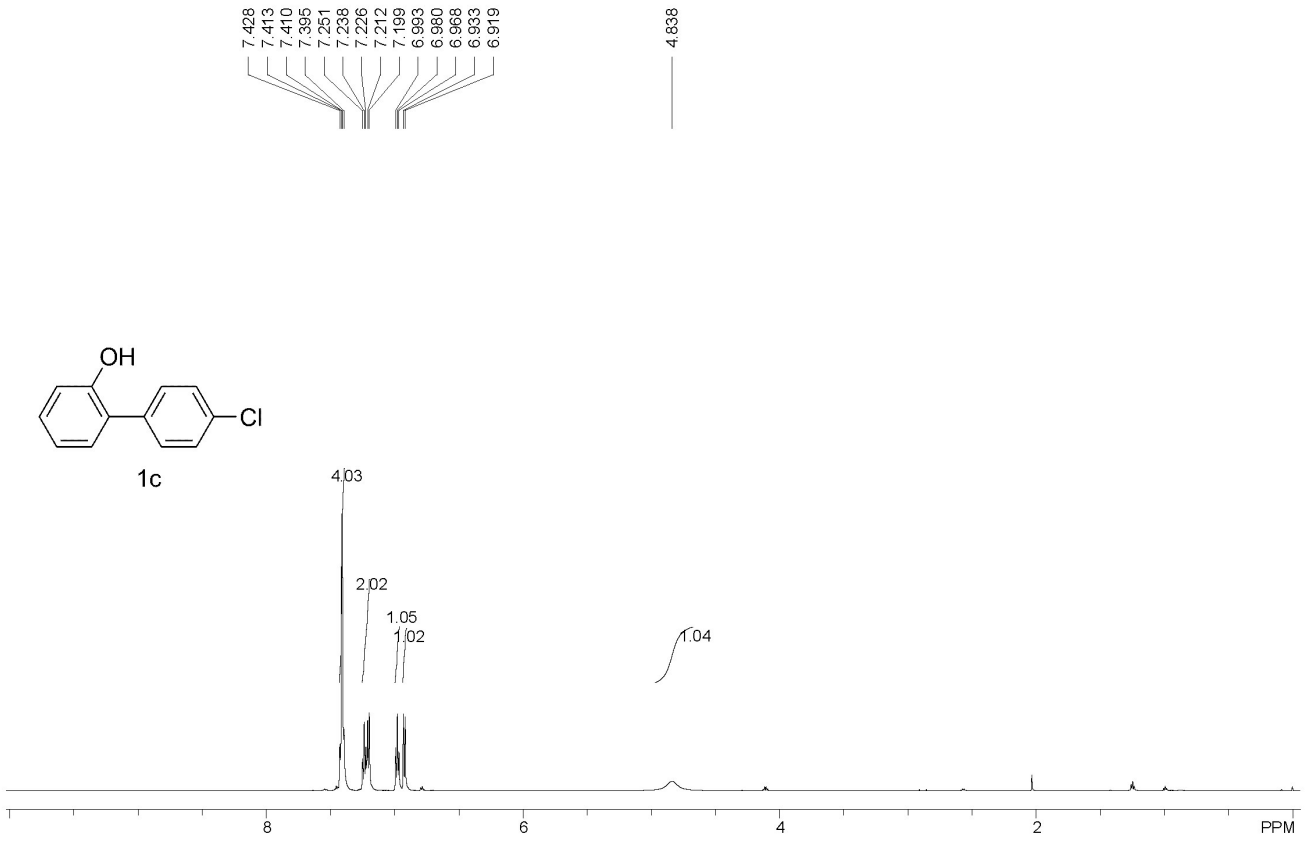
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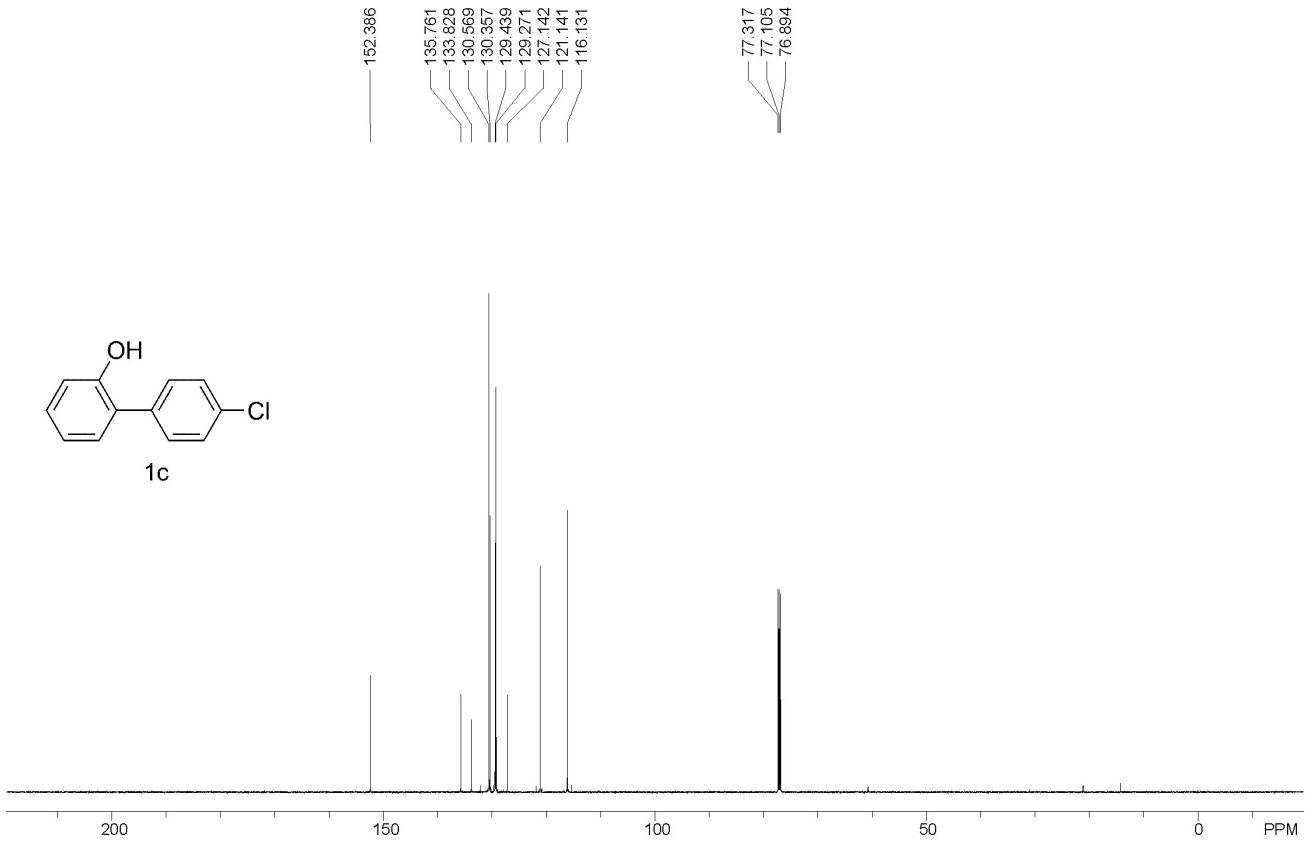
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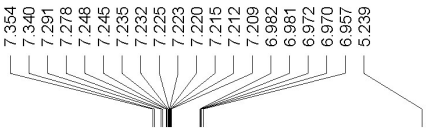
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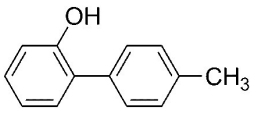
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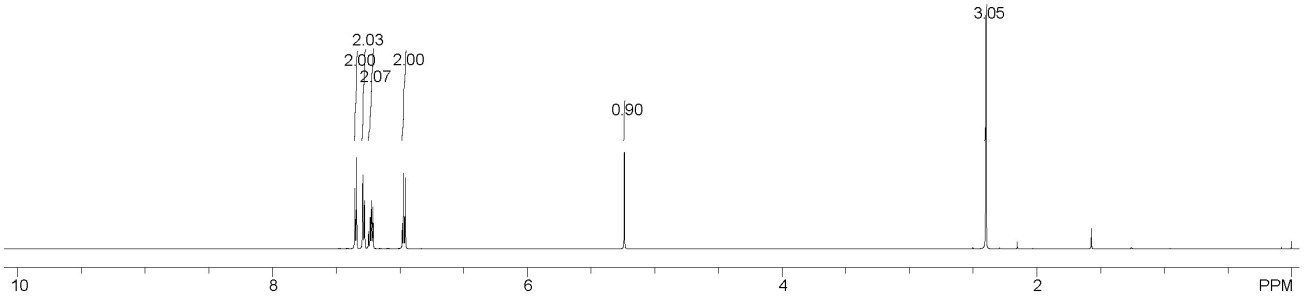
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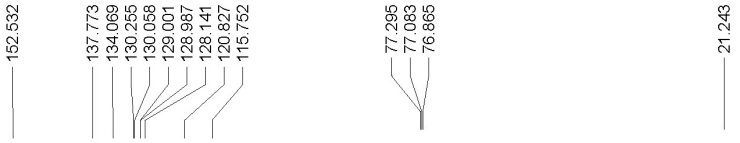
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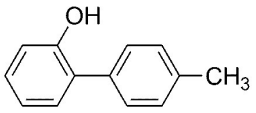
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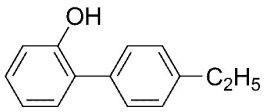
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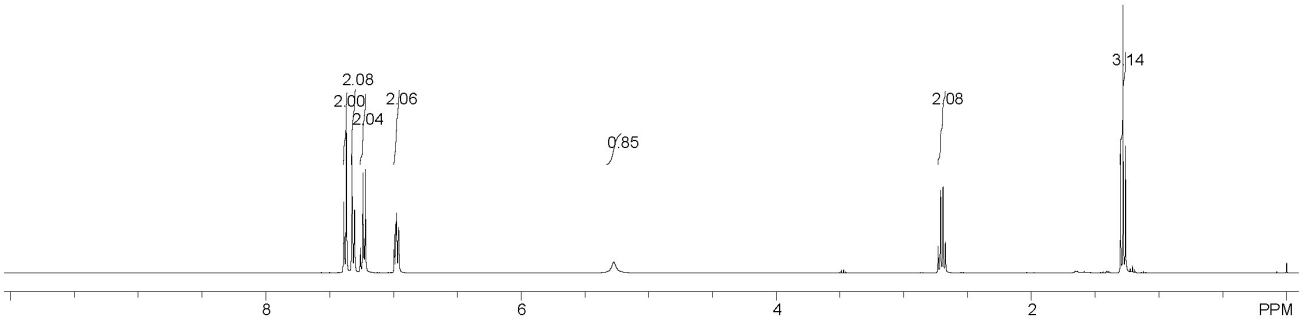
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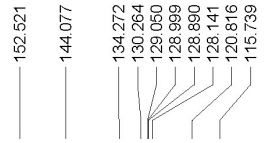
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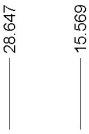
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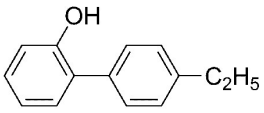
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C2H5

1e

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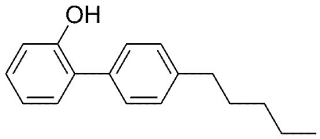
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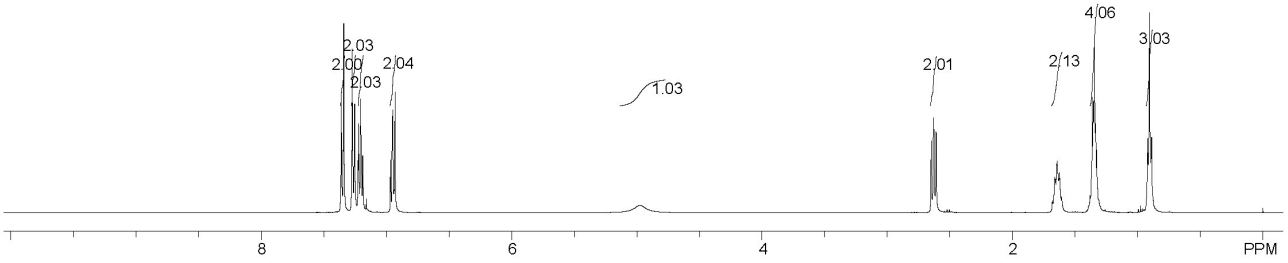
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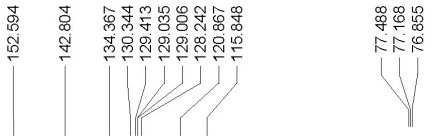
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76.855
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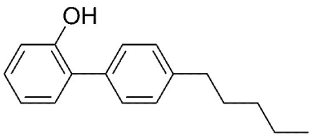
31.251
22.683
14.173


OH

1f

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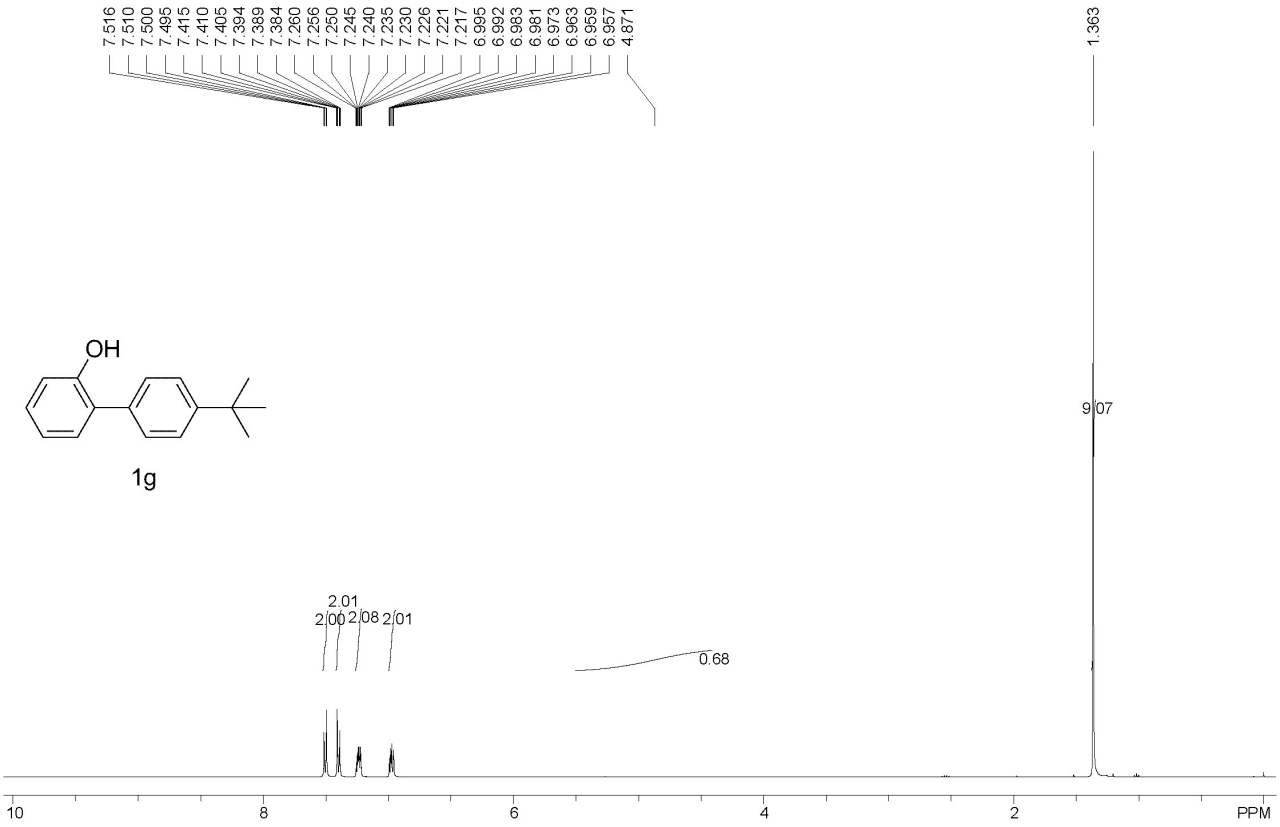
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7.256
7.250
7.245
7.240
7.235
7.230
7.226
7.221
7.217
6.995
6.992
6.983
6.981
6.973
6.963
6.959
6.957
4.871
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OH
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2.00
2.08
2.01
0.68
10
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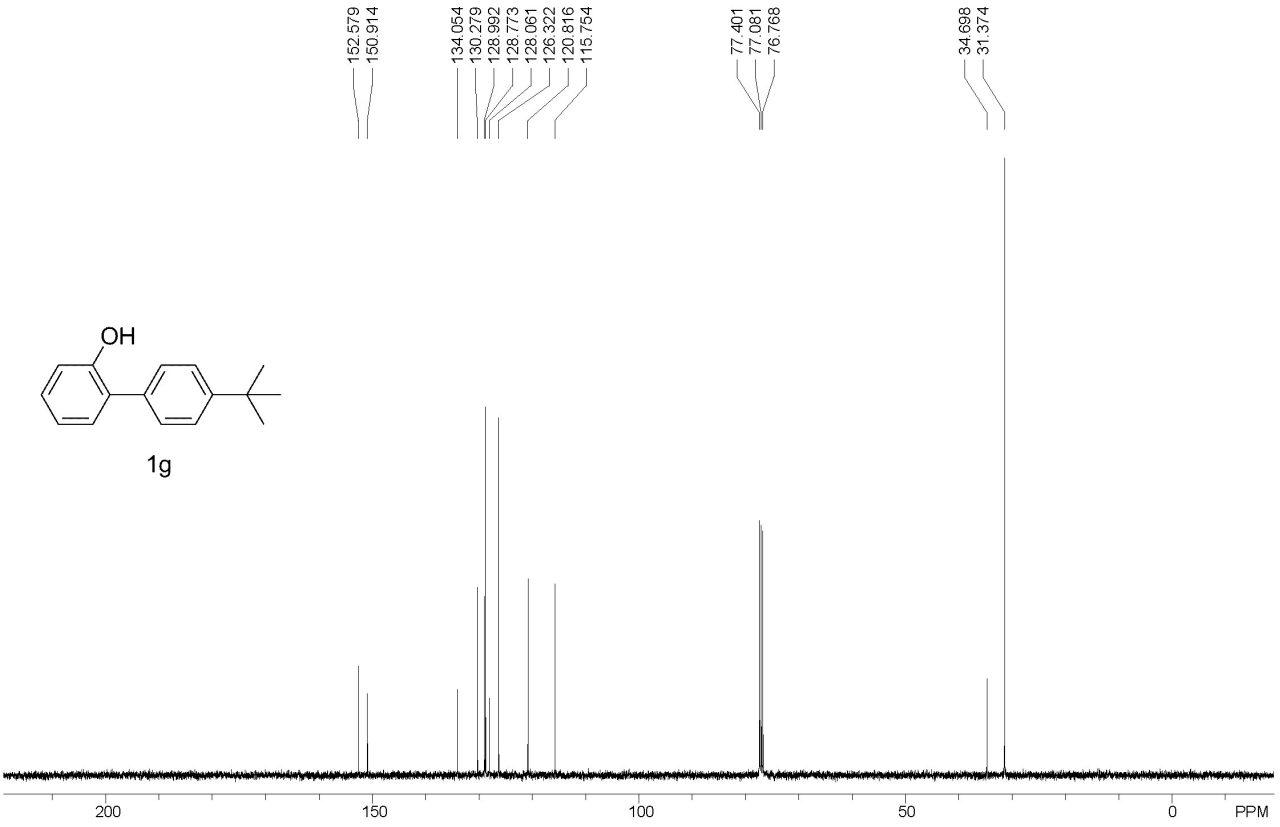
2
PPM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34.698
31.374
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1g
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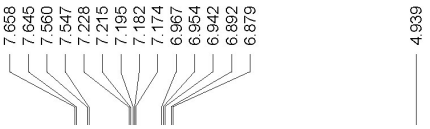
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6.942
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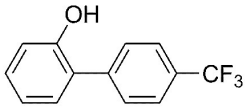
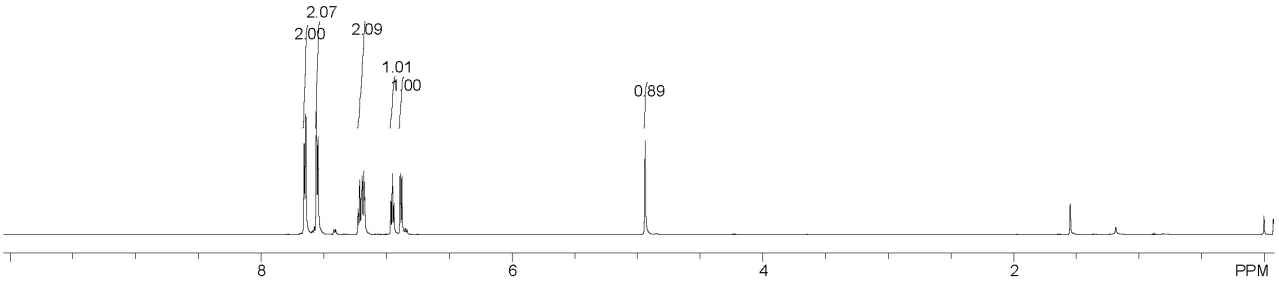
6.879
4.939


OH
CF3

1h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6
4
2
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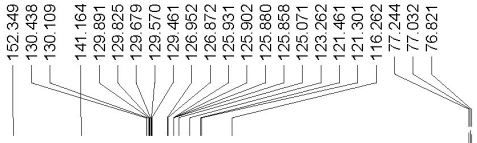
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129.570
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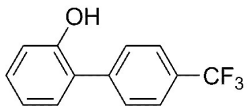
77.032
76.821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CF3

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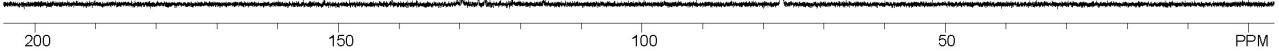
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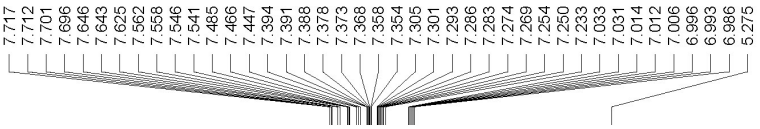
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7.546
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7.485
7.466
7.447
7.394
7.391
7.388
7.378
7.373
7.368
7.358
7.354
7.305
7.301
7.293
7.286
7.283
7.274
7.269
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6.986
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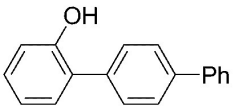
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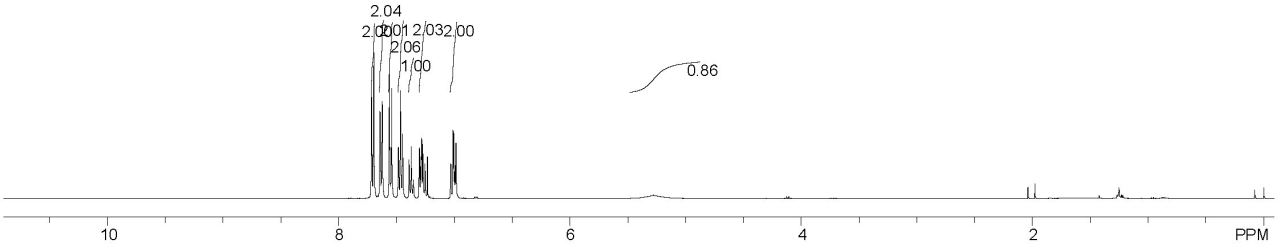
Ph

1i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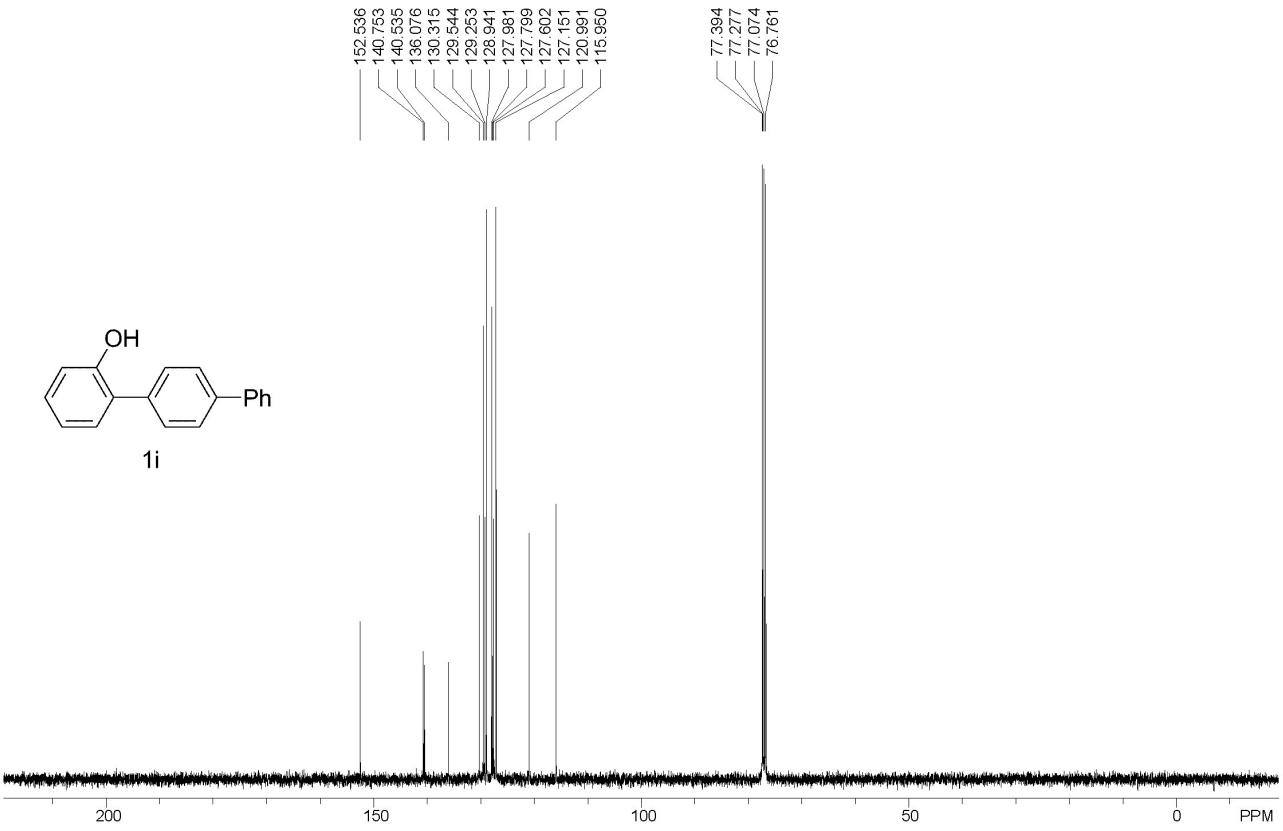
8
6
4
2
PPM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129.544
129.253
128.941
127.981
127.799
127.602
127.151
120.991
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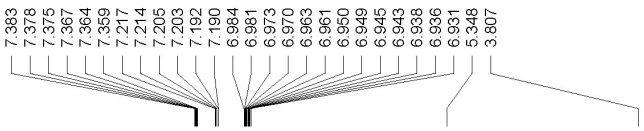
77.394
77.277
77.074
76.761
200
150
100
50
0
PPM

OH
Ph

1i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7.359
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7.214
7.205
7.203
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7.190
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6.981
6.973
6.970
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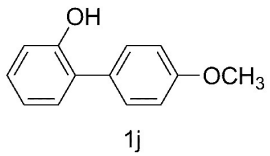
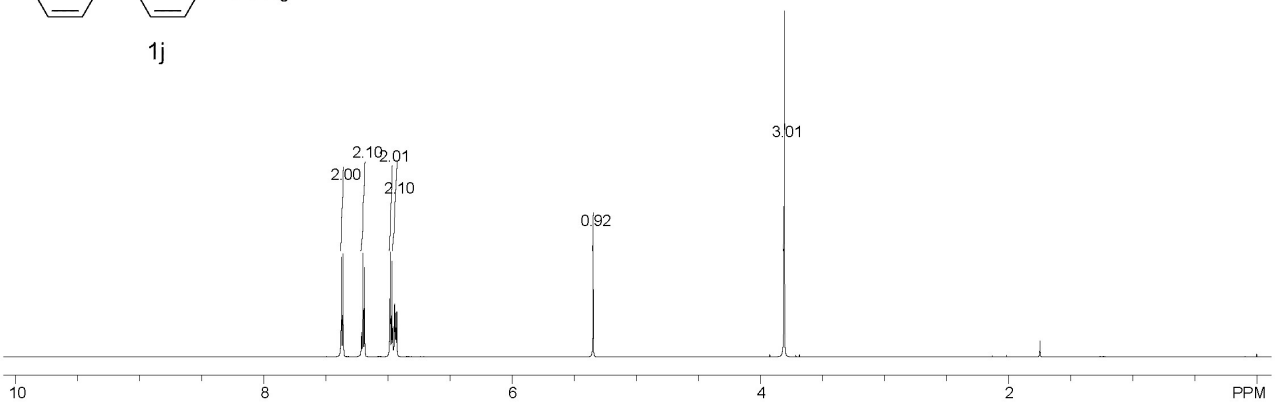
6.936
6.931
5.348
3.807


OH
OCH3

1j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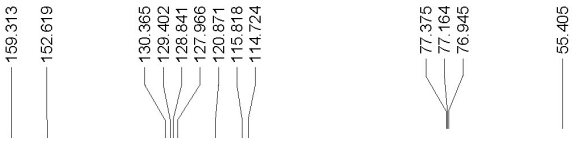
0.92
3.01
10
8
6
4
2
PPM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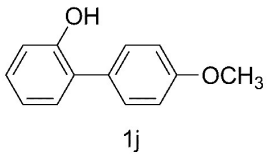
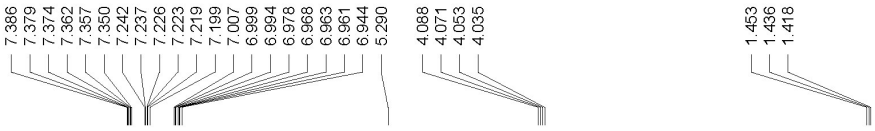
77.375
77.164
76.945
55.405


OH
OCH3

1j

200
150
100
50
0
PPM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7.242
7.237
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7.223
7.219
7.199
7.007
6.999
6.994
6.978
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4.053
4.035
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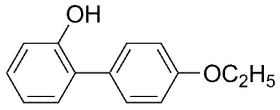
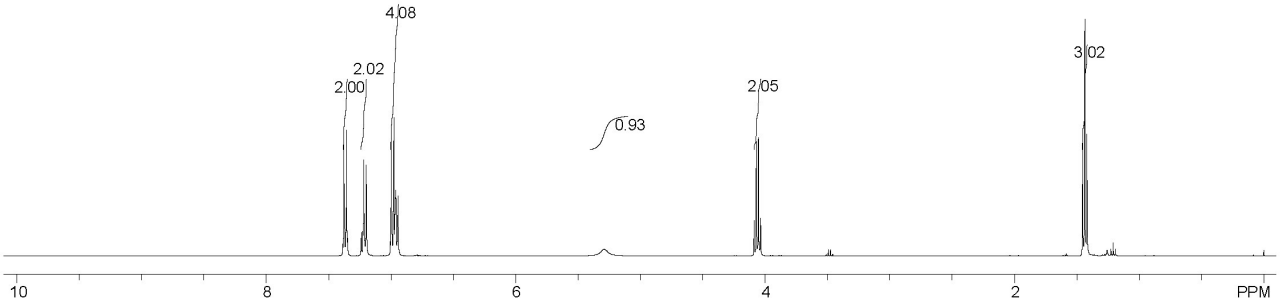
1.436
1.418


OH
OC2H5

1k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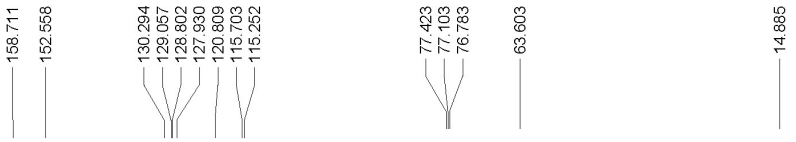
10
8
6
4
2
PPM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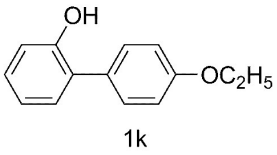
14.885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OC2H5

1k

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50
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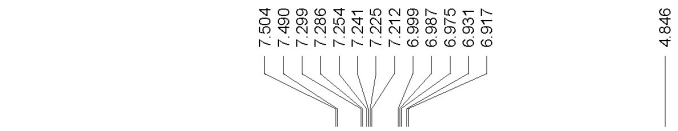
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7.241
7.225
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6.975
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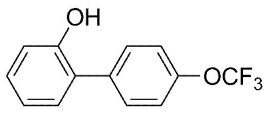
6.917
4.846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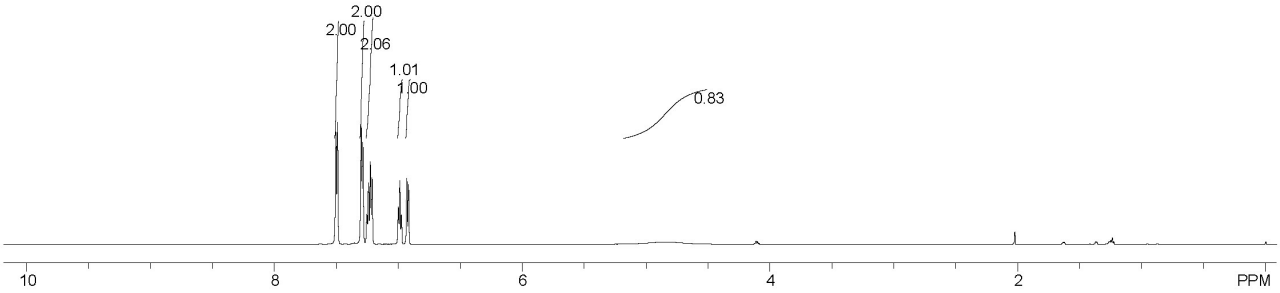
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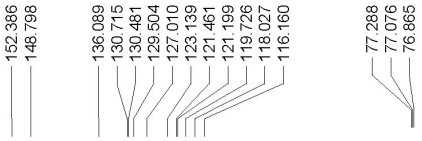
1.00
0.83
10
8
6
4
2
PPM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123.139
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118.027
116.160
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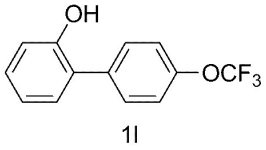
77.076
76.865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OCF3

1l

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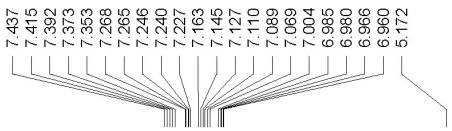
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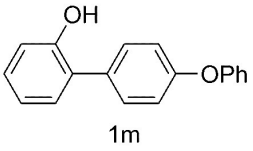
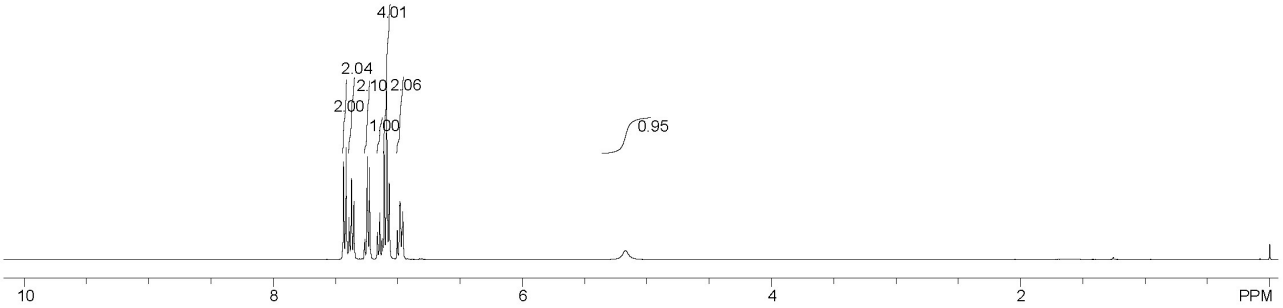
6.960
5.172


OH
OPh

1m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6
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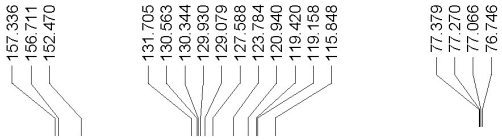
2
PPM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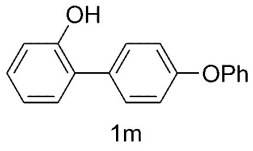
OH
OPh

1m

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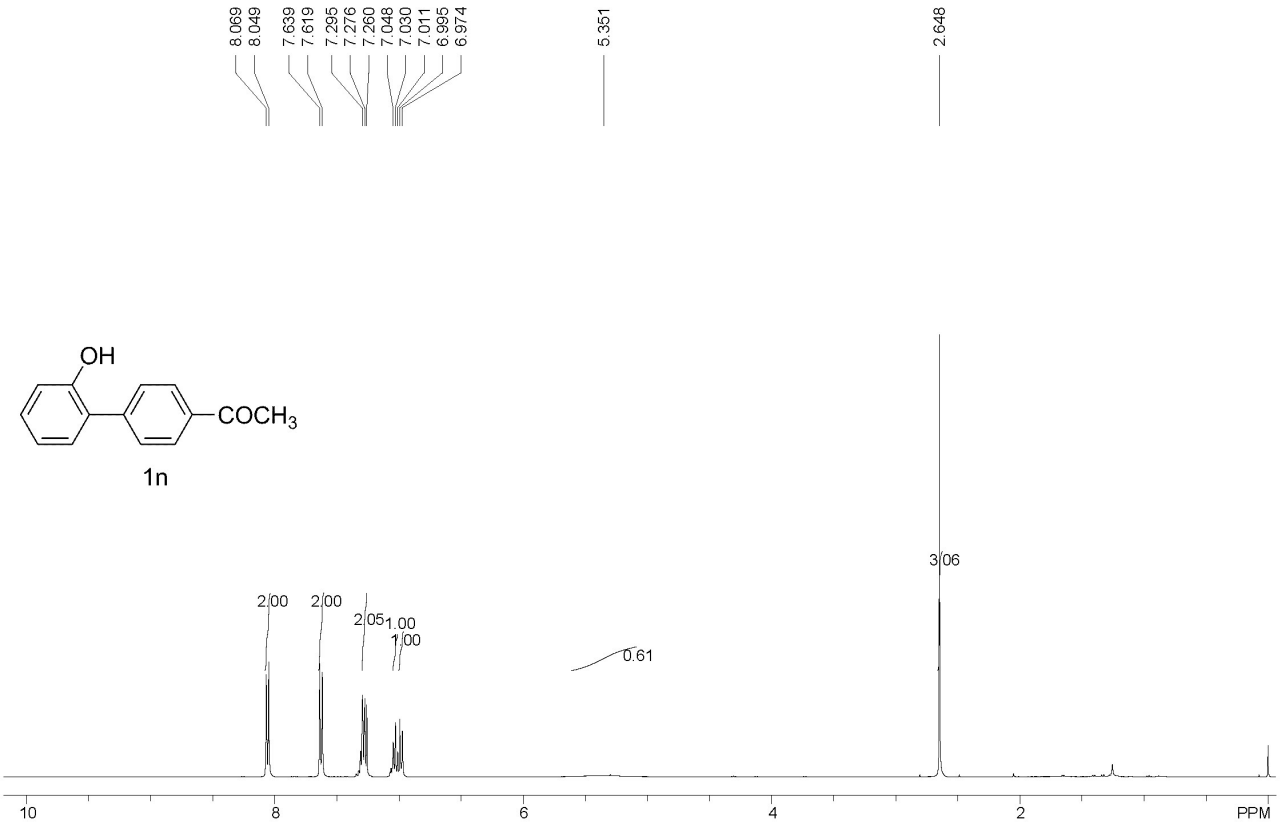
100
50
0
PPM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7.011
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6.974
5.351
2.648
OH
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2.00
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1.00
1.00
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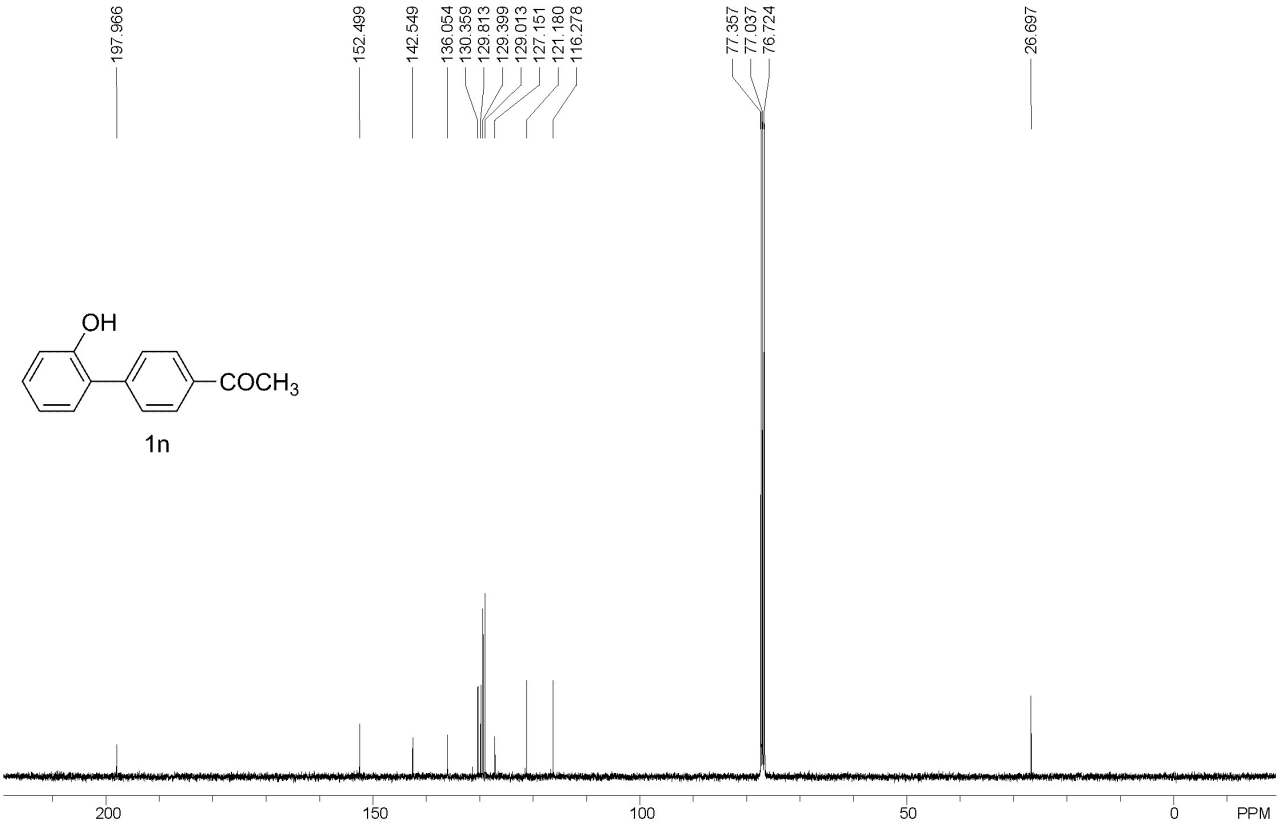
3.06
10
8
6
4
2
PPM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77.037
76.724
26.697
OH
COCH3
1n
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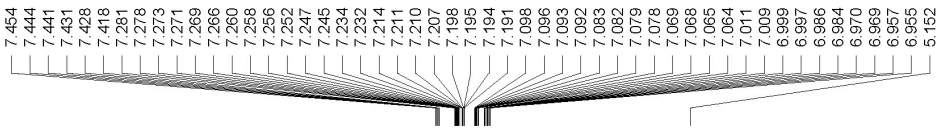
100
50
0
PPM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6.955
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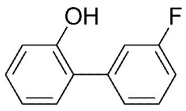
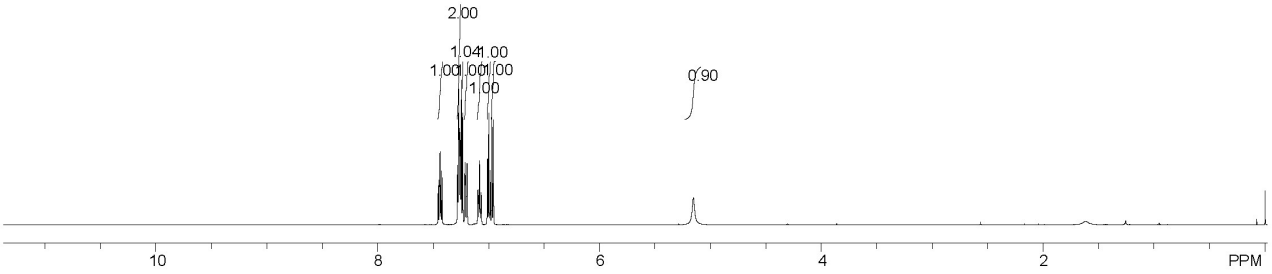

OH
F

1o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1.00
1.00
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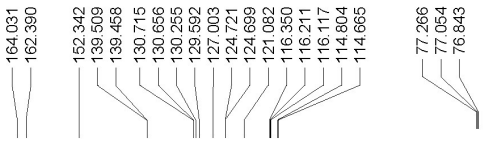
0.90
10
8
6
4
2
PPM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121.082
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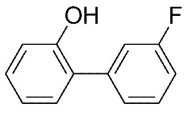
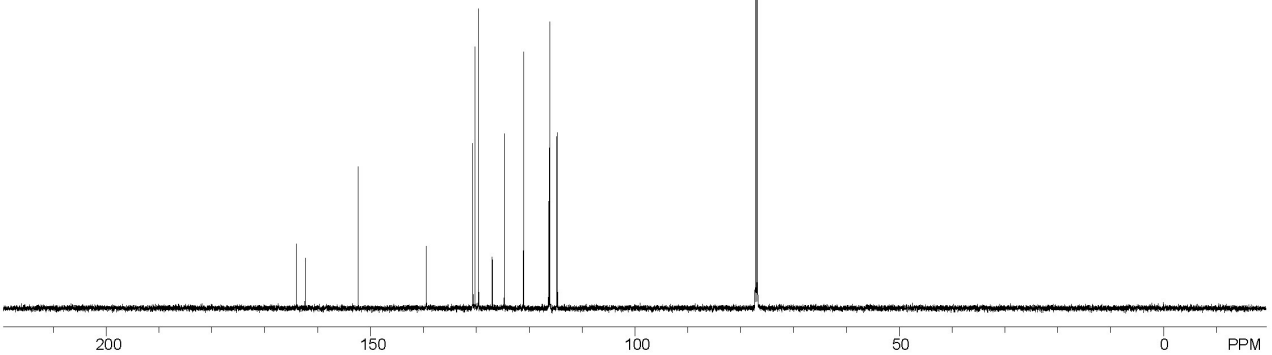
77.054
76.843


OH
F

1o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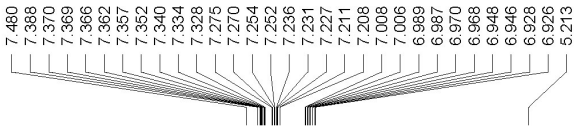
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7.270
7.254
7.252
7.236
7.231
7.227
7.211
7.208
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6.987
6.970
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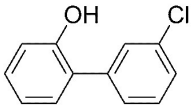
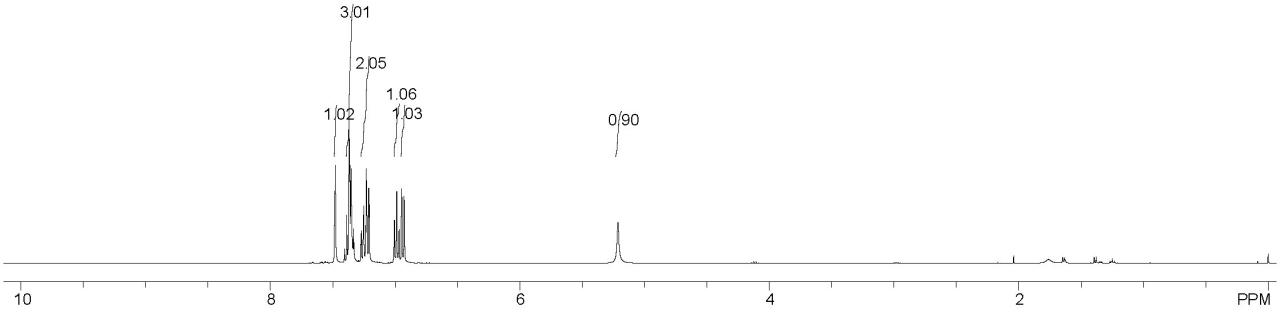
6.946
6.928
6.926
5.213


OH
Cl

1p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1.03
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6
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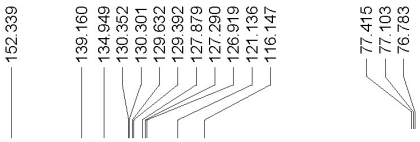
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121.136
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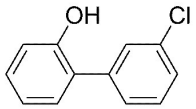
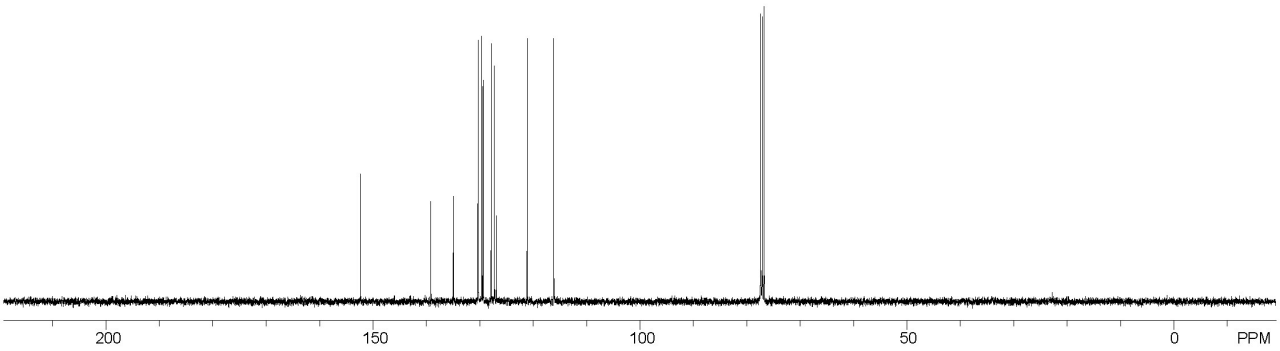
77.103
76.783


OH
Cl

1p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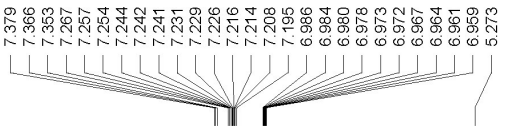
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7.254
7.244
7.242
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7.231
7.229
7.226
7.216
7.214
7.208
7.195
6.986
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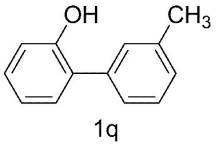
6.978
6.973
6.972
6.967
6.964
6.961
6.959
5.273


2.406


OH
CH3

1q

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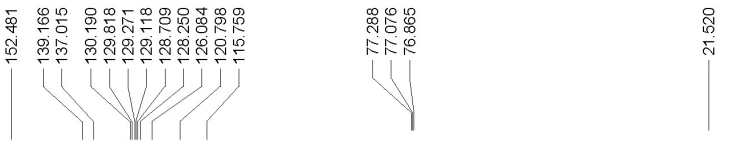
3.03
2.00
1.00
0.91
10
8
6
4
2
PPM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137.015
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129.271
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128.709
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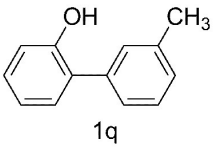
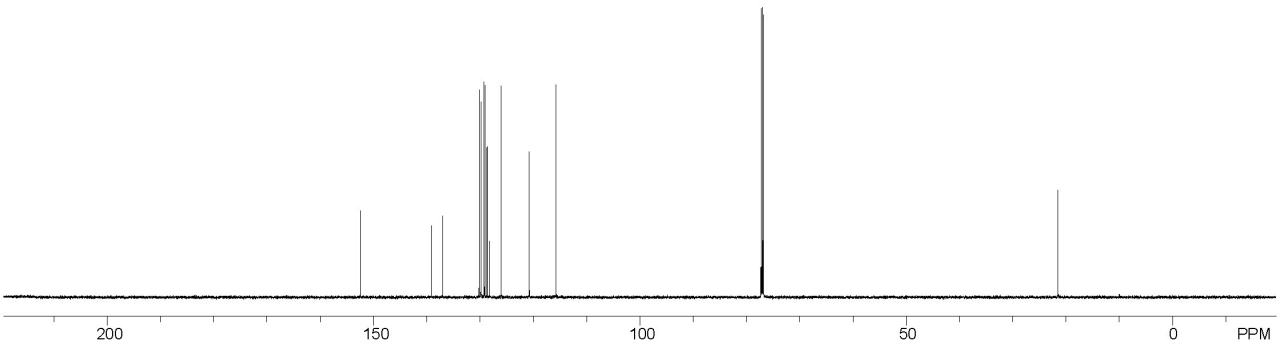
126.084
120.798
115.759
77.288
77.076
76.865
21.520


OH
CH3

1q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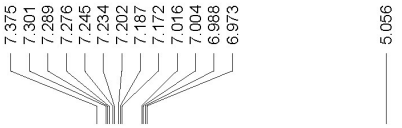
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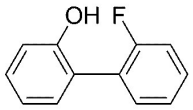
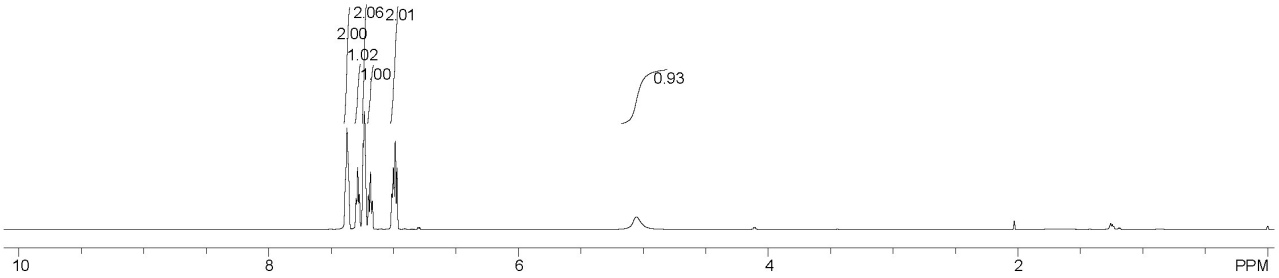
7.234
7.202
7.187
7.172
7.016
7.004
6.988
6.973
5.056


OH F

1r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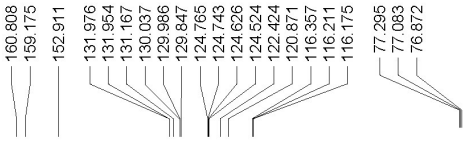
2.00
1.02
1.00
0.93
10
8
6
4
2
PPM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130.037
129.986
129.847
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124.743
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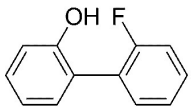
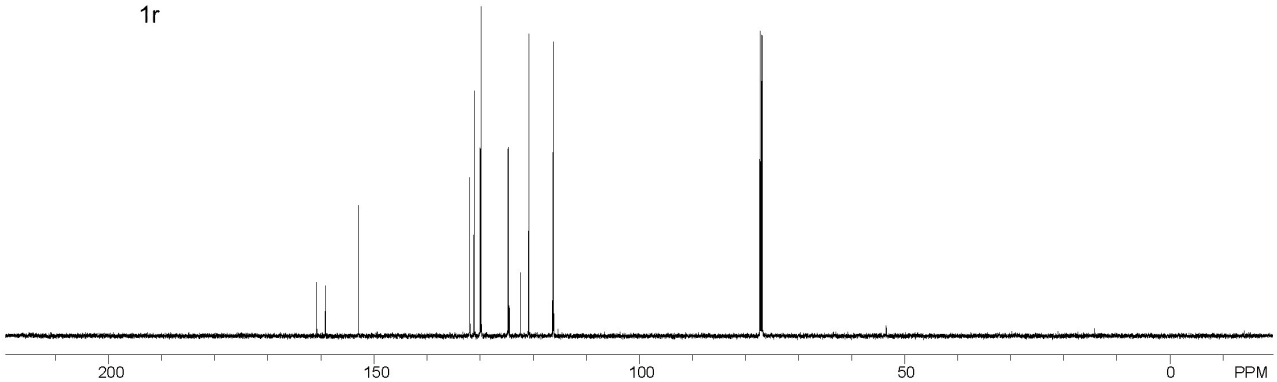
124.524
122.424
120.871
116.357
116.211
116.175
77.295
77.083
76.872


OH F

1r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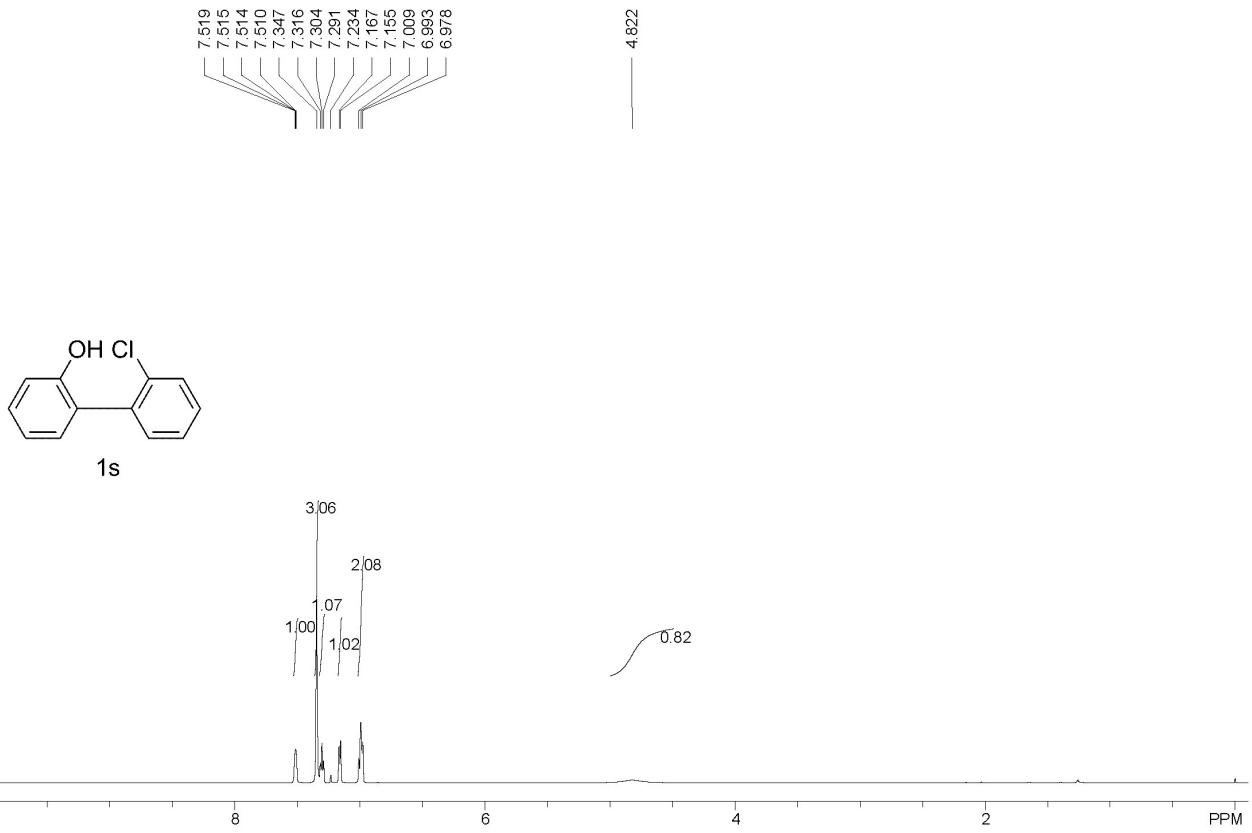
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7.514
7.510
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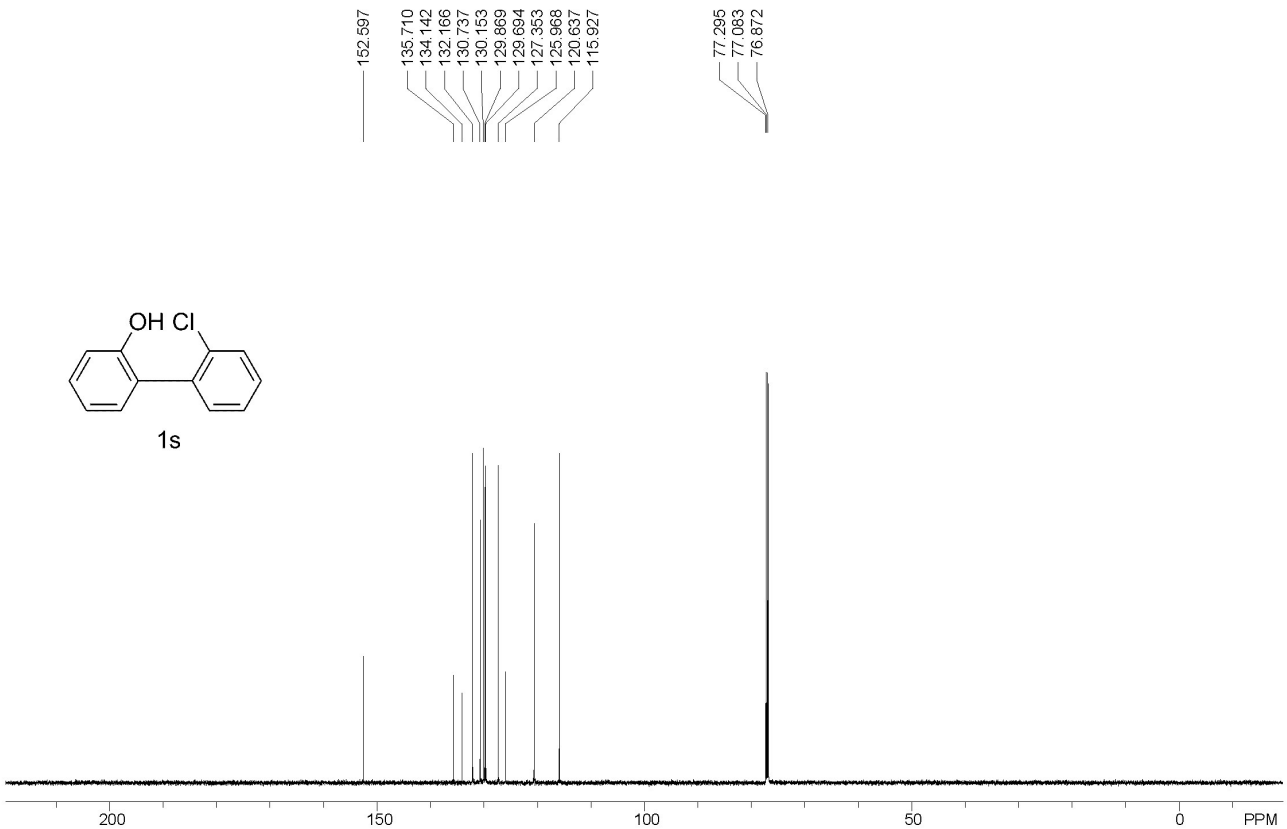
7.316
7.304
7.291
7.234
7.167
7.155
7.009
6.993
6.978
4.822
OH Cl
1s
3.06
2.08
1.07
1.00
1.02
0.82
10
8
6
4
2
PPM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130.153
129.869
129.694
127.353
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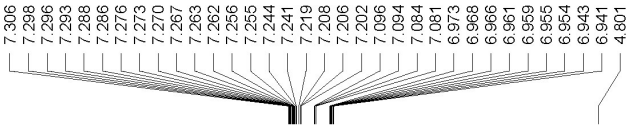
115.927
77.295
77.083
76.872
OH Cl
1s
200
150
100
50
0
PPM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7.273
7.270
7.267
7.263
7.262
7.256
7.255
7.244
7.241
7.219
7.208
7.206
7.202
7.096
7.094
7.084
7.081
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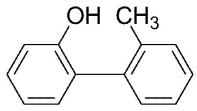
6.966
6.961
6.959
6.955
6.954
6.943
6.941
4.801
2.152


OH
CH3

1t

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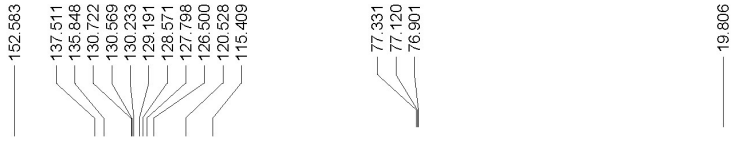
2.02
2.07
2.06
1.00
1.00
0.93
10
8
6
4
2
PPM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130.722
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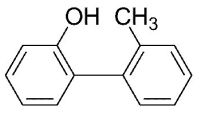
127.798
126.500
120.528
115.409
77.331
77.120
76.901
19.806


OH
CH3

1t

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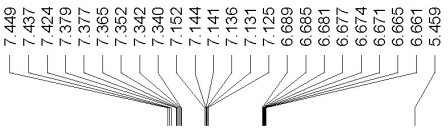
150
100
50
0
PPM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7.377
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7.342
7.340
7.152
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7.141
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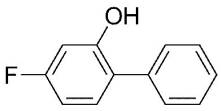
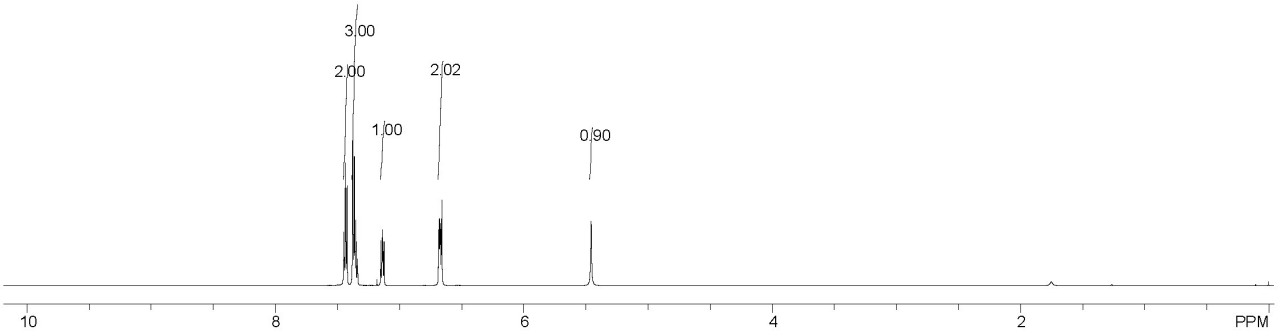
6.661
5.459


OH
F

1b'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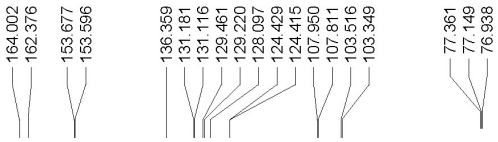
2.02
1.00
0.90
10
8
6
4
2
PPM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131.116
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124.429
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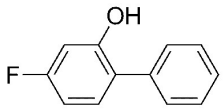
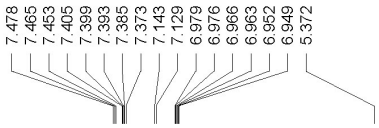
103.516
103.349
77.361
77.149
76.938


OH
F

1b'

200
150
100
50
0
PPM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7.393
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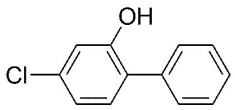
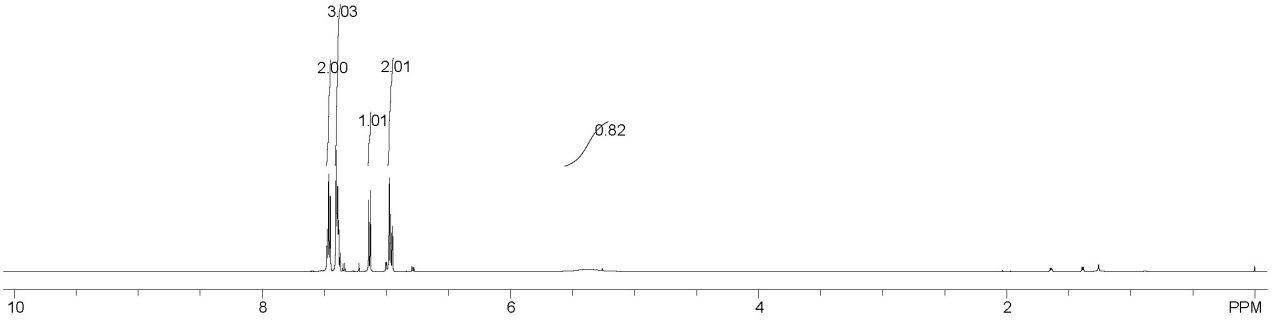
6.966
6.963
6.952
6.949
5.372


OH
Cl

1c'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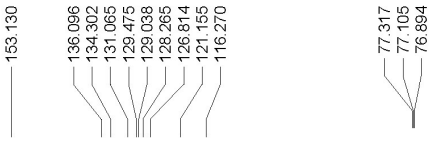
2.01
1.01
0.82
10
8
6
4
2
PPM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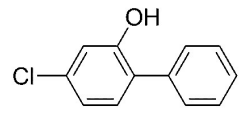
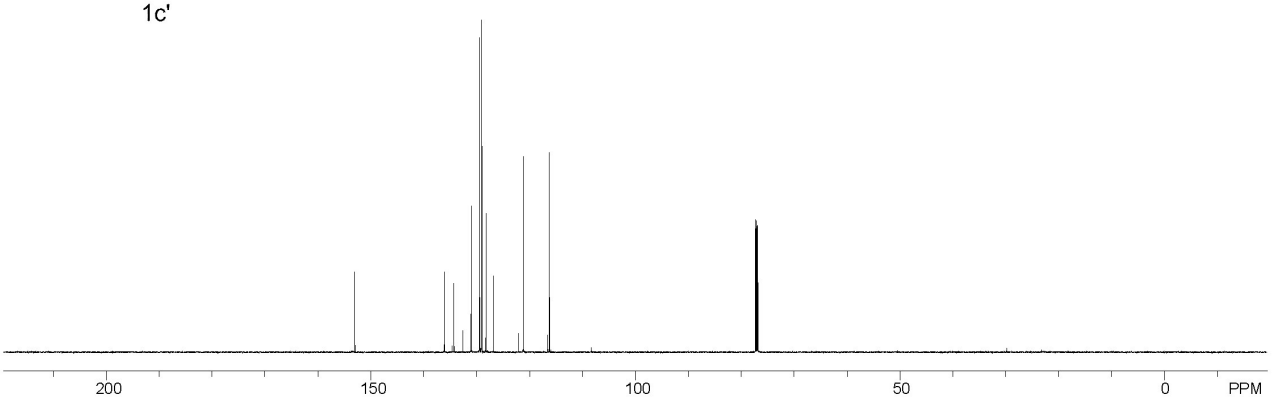
76.894


OH
Cl

1c'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100
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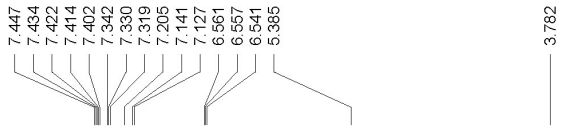
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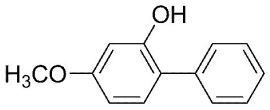
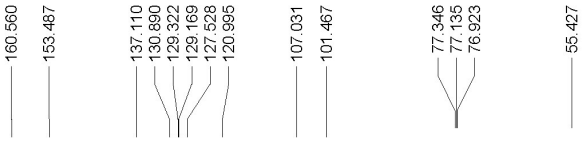
7.141
7.127
6.561
6.557
6.541
5.385
3.782


OH
H3CO

1j'

4.00
3.00
2.04
1.01
1.03
0.89
10
8
6
4
2
PPM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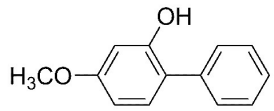
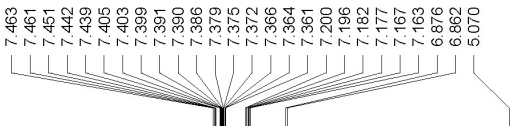
120.995
107.031
101.467
77.346
77.135
76.923
55.427


OH
H3CO

1j'

200
150
100
50
0
PPM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7.390
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7.375
7.372
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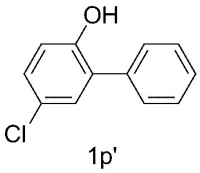
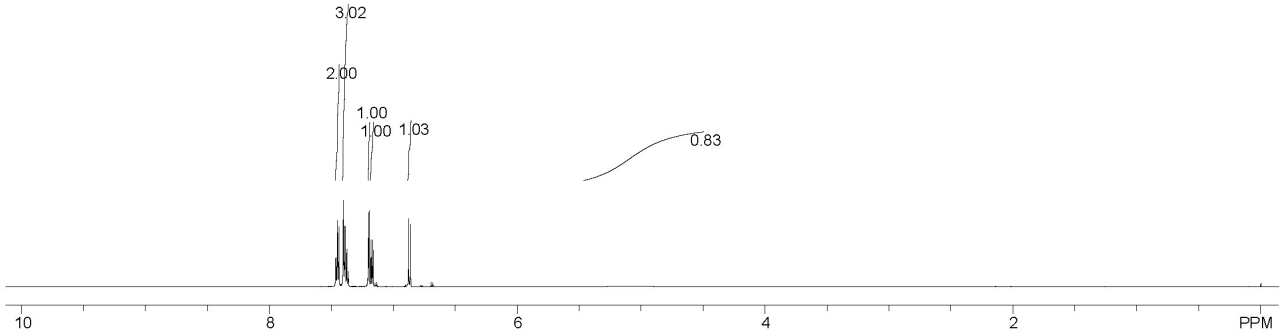

OH
Cl

1p'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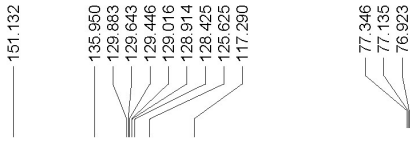
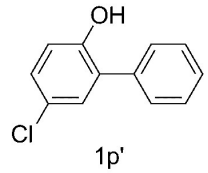
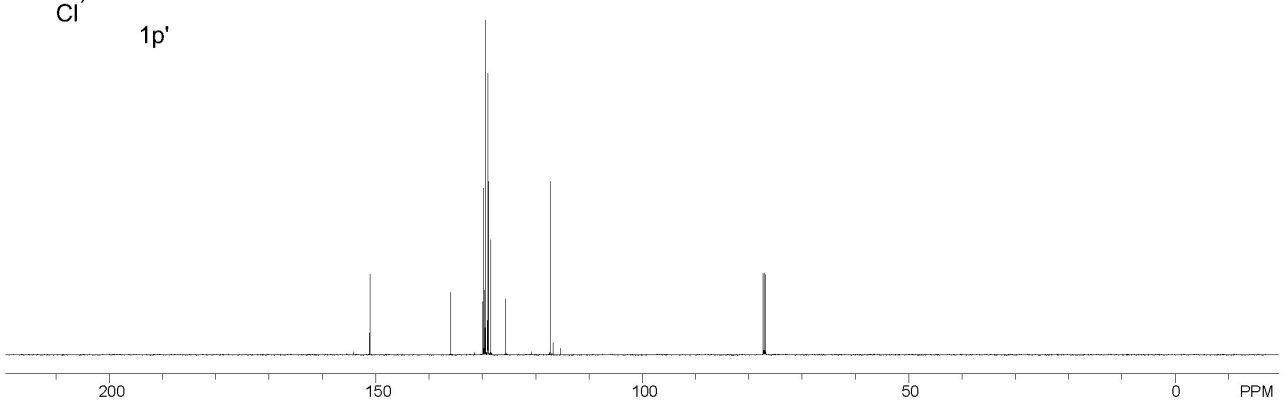
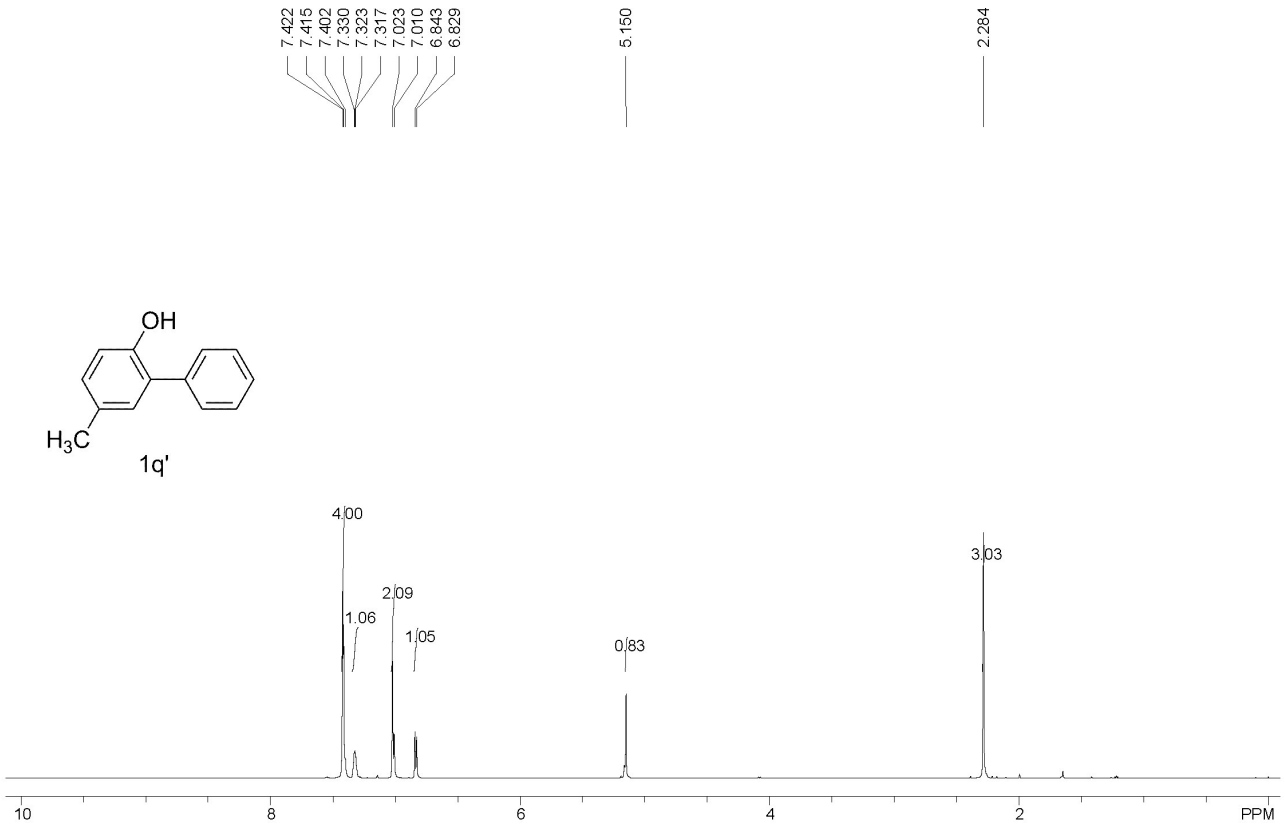
2.00
1.00
1.00
1.03
0.83
10
8
6
4
2
PPM

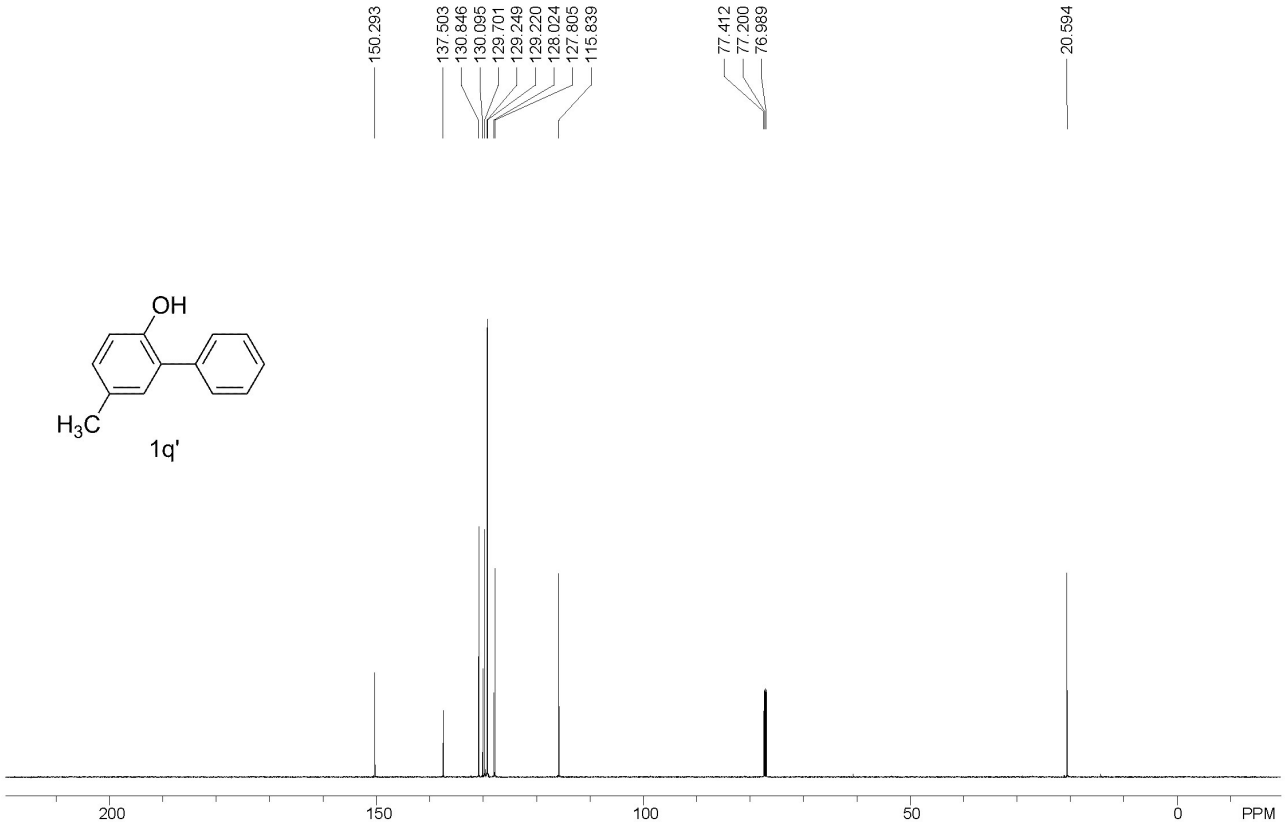

151.132
135.950
129.883
129.643
129.446
129.016
128.914
128.425
125.625
117.290
77.346
77.135
76.923

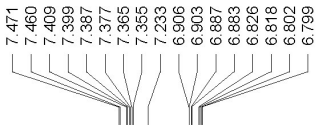

OH
Cl

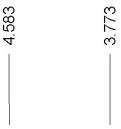
1p'

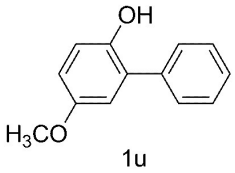

200
150
100
50
0
PPM


7.422
7.415
7.402
7.330
7.323
7.317
7.023
7.010
6.843
6.829
5.150
2.284
OH
H3C
1q'
4.00
2.09
1.06
1.05
0.83
3.03
10
8
6
4
2
PPM

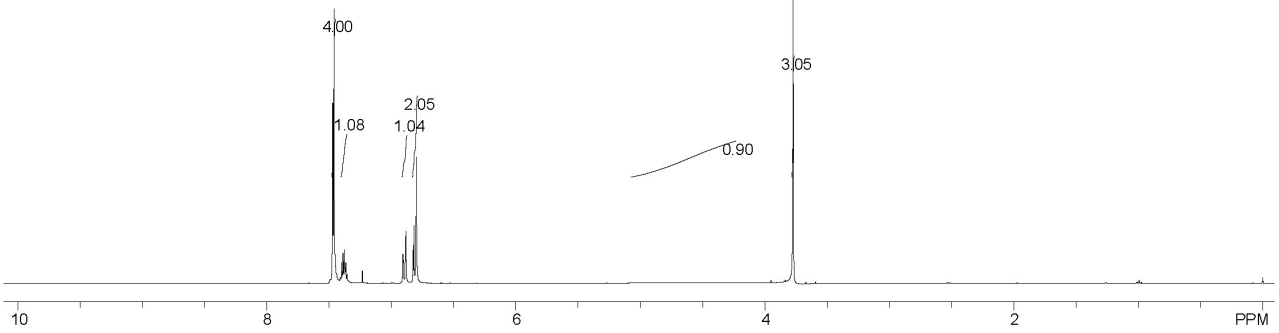

150.293
137.503
130.846
130.095
129.701
129.249
129.220
128.024
127.805
115.839
77.412
77.200
76.989
20.594
OH
H3C
1q'
200
150
100
50
0
PPM

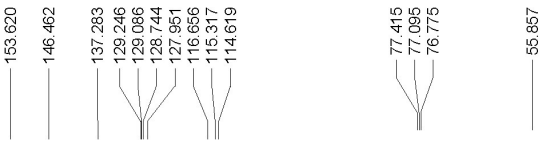

7.471
7.460
7.409
7.399
7.387
7.377
7.365
7.355
7.233
6.906
6.903
6.887
6.883
6.826
6.818
6.802
6.799


4.583
3.773

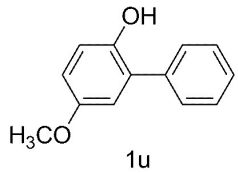

OH
H3CO

1u


4.00
1.08
2.05
1.04
0.90
3.05
10
8
6
4
2
PPM

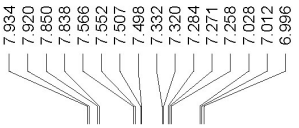

153.620
146.462
137.283
129.246
129.086
128.744
127.951
116.656
115.317
114.619

77.415
77.095
76.775
55.857

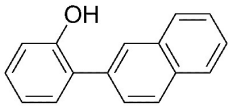

OH
H3CO

1u

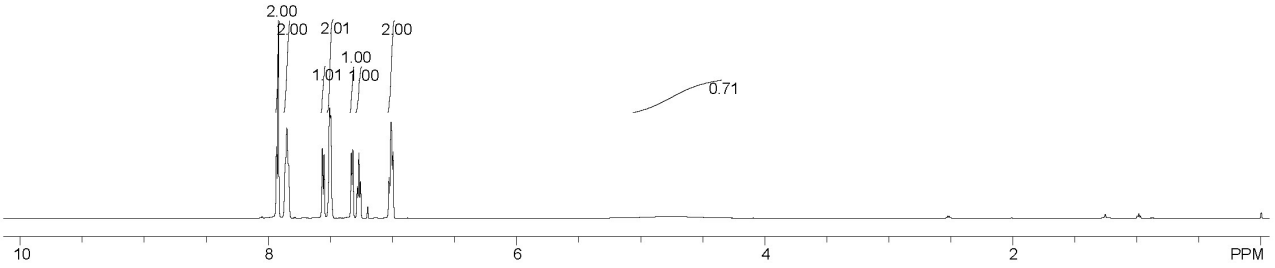
200
150
100
50
0
PPM

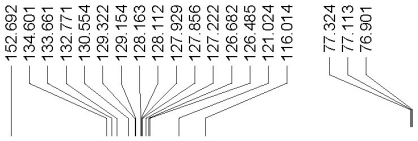

7.934
7.920
7.850
7.838
7.566
7.552
7.507
7.498
7.332
7.320
7.284
7.271
7.258
7.028
7.012
6.996

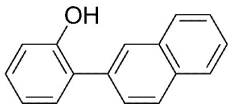

4.725


OH

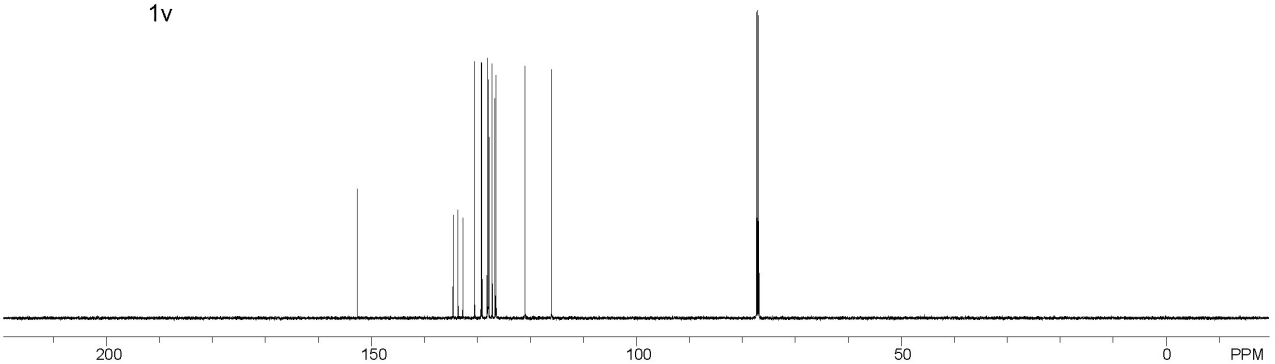
1v

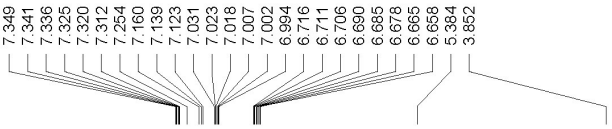

2.00
2.00
2.01
2.00
1.00
1.01
1.00
0.71
10
8
6
4
2
PPM


152.692
134.601
133.661
132.771
130.554
129.322
129.154
128.163
128.112
127.929
127.856
127.222
126.682
126.485
121.024
116.014
77.324
77.113
76.901


OH

1v


200
150
100
50
0
PPM


7.349
7.341
7.336
7.325
7.320
7.312
7.254
7.160
7.139
7.123
7.031
7.023
7.018
7.007
7.002
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6.711
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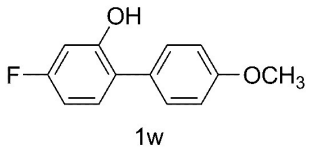
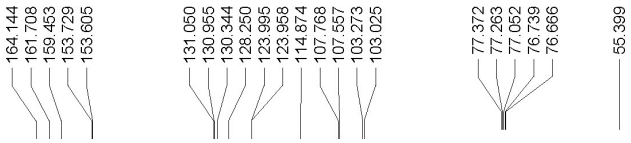
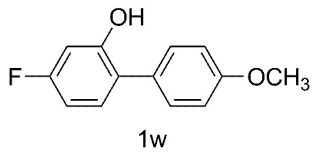
6.685
6.678
6.665
6.658
5.384
3.852


OH
F
OCH3

1w

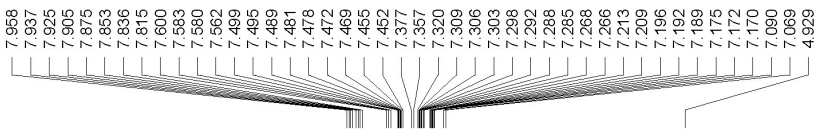
3.07
2.00
2.05
2.02
1.01
0.89
10
8
6
4
2
PPM

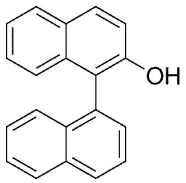

164.144
161.708
159.453
153.729
153.605
131.050
130.955
130.344
128.250
123.995
123.958
114.874
107.768
107.557
103.273
103.025
77.372
77.263
77.052
76.739
76.666
55.399


OH
F
OCH3

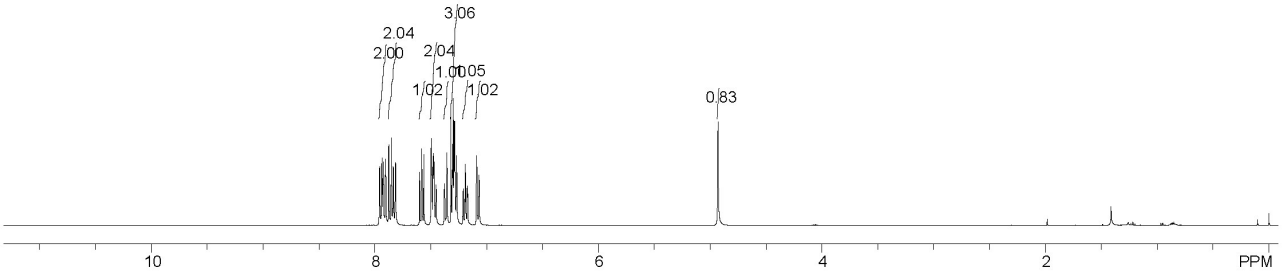
1w

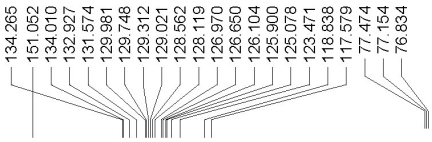
200
150
100
50
0
PPM

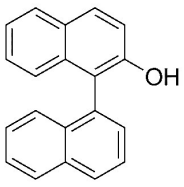

7.958
7.937
7.925
7.905
7.875
7.853
7.836
7.815
7.600
7.583
7.580
7.562
7.499
7.495
7.489
7.481
7.478
7.472
7.469
7.455
7.452
7.377
7.357
7.320
7.309
7.306
7.303
7.298
7.292
7.288
7.285
7.268
7.266
7.213
7.209
7.196
7.192
7.189
7.175
7.172
7.170
7.090
7.069
4.929


OH

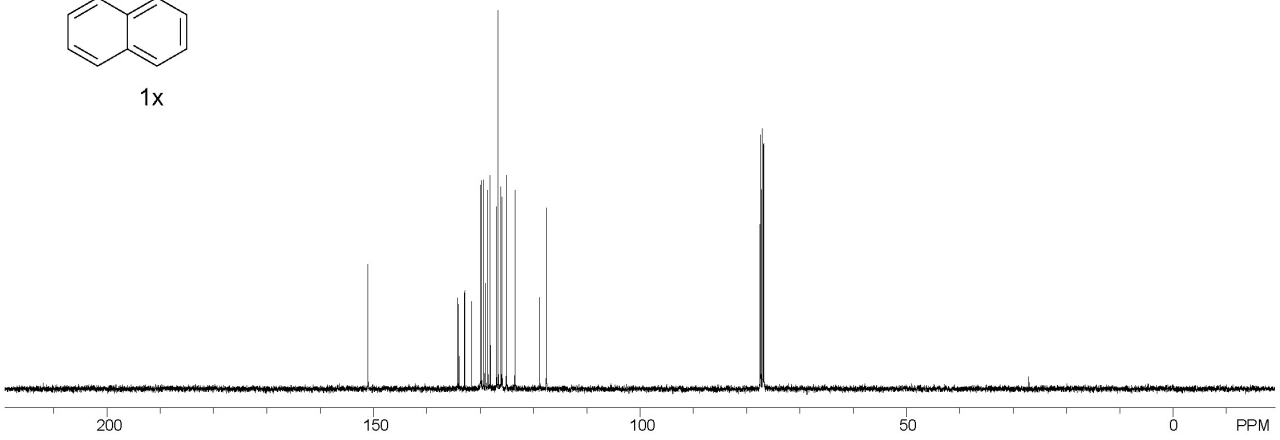
1x


3.06
2.04
2.00
2.04
1.00
1.05
1.02
1.02
0.83
10
8
6
4
2
PPM

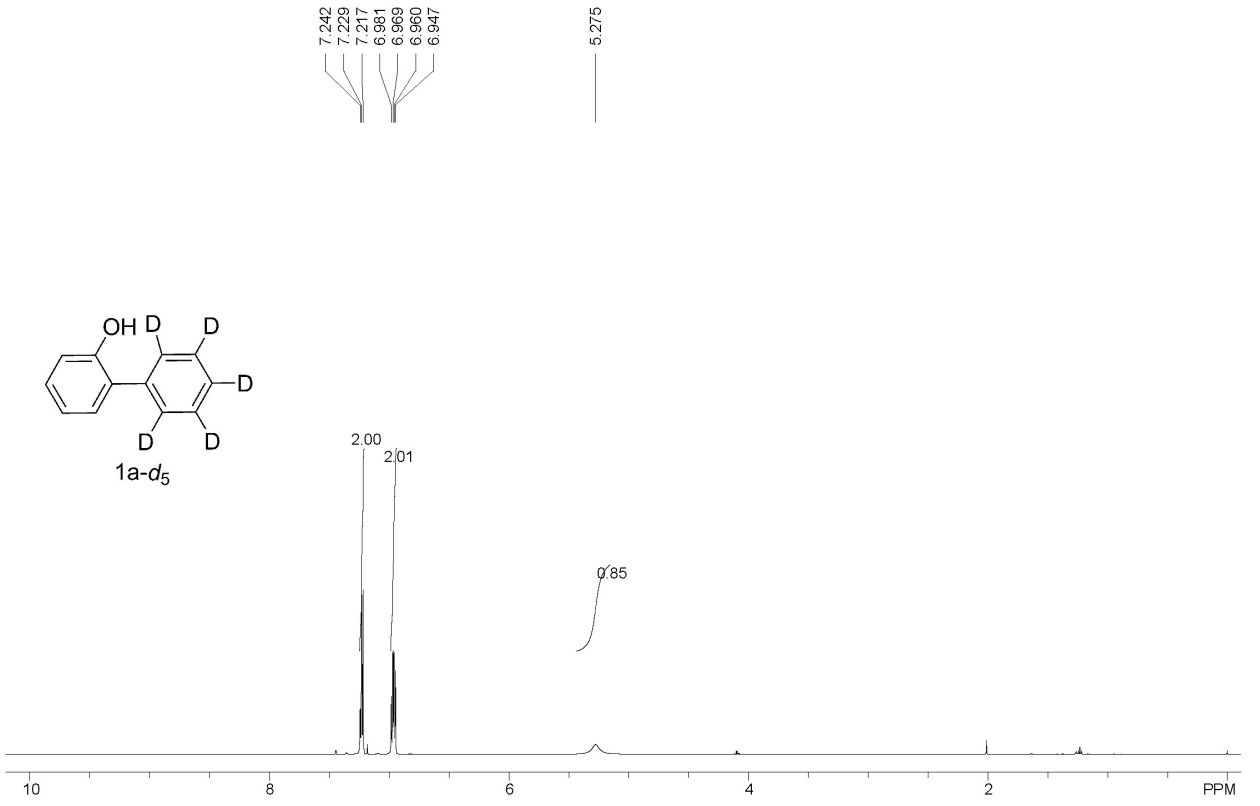

134.265
151.052
134.010
132.927
131.574
129.981
129.748
129.312
129.021
128.562
128.119
126.970
126.650
126.104
125.900
125.078
123.471
118.838
117.579
77.474
77.154
76.834

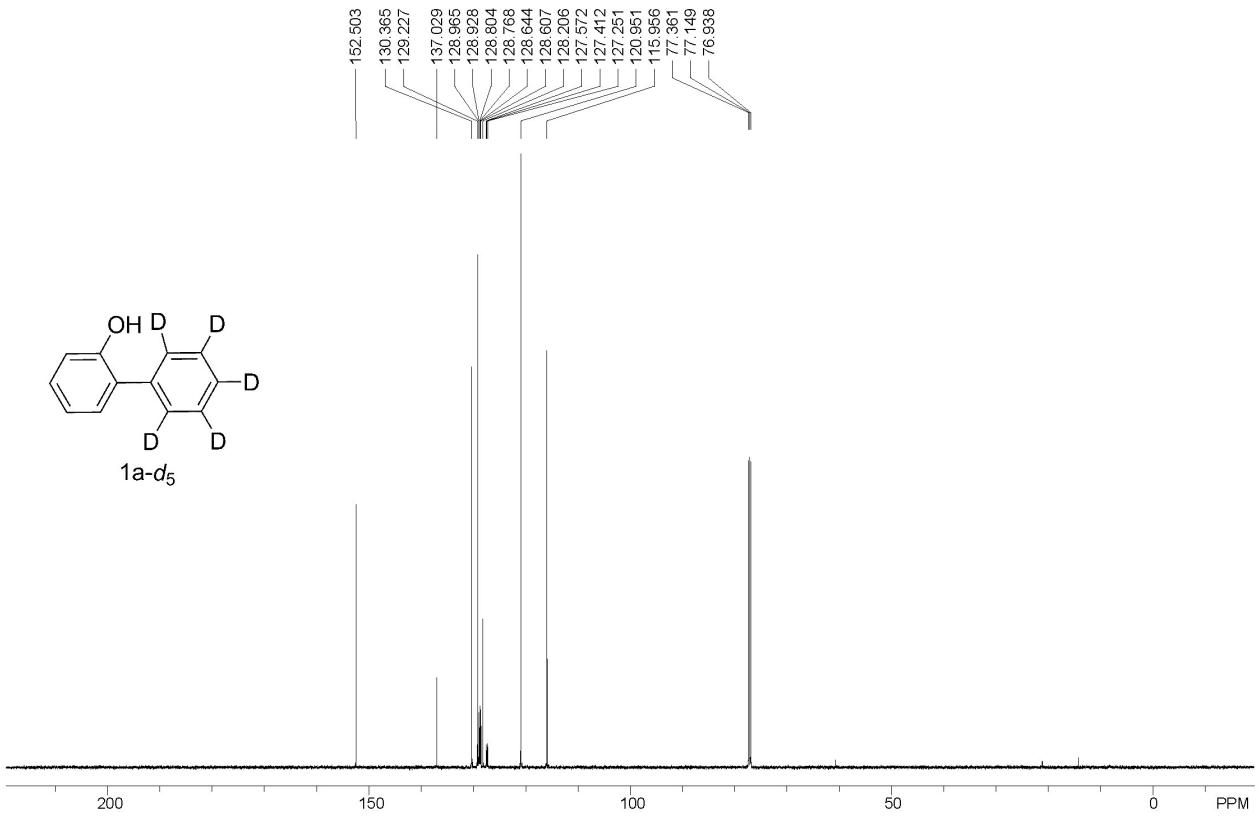

OH

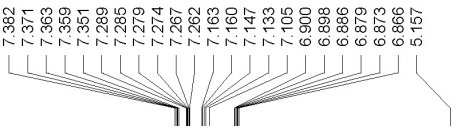
1x

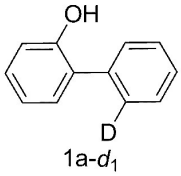

200
150
100
50
0
PPM

V. Copies of ^{1}H and ^{13}C NMR Spectra of 1a-d_5 and 1a-d_1

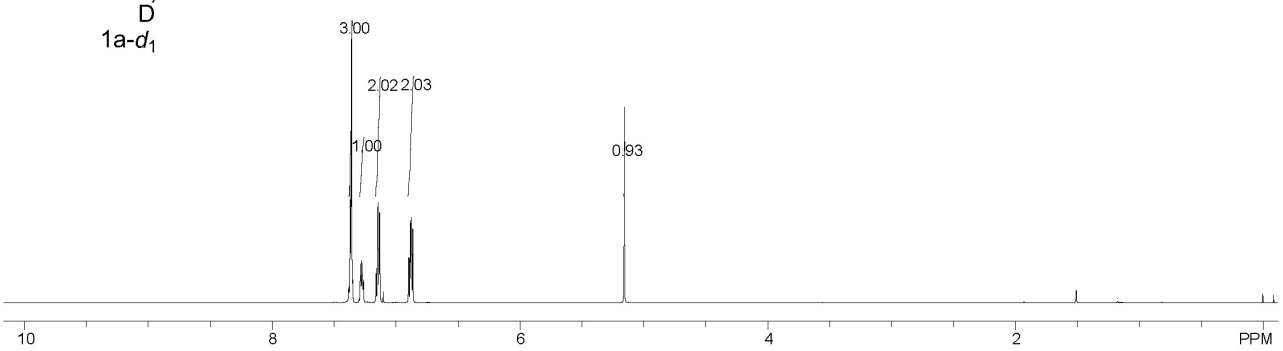


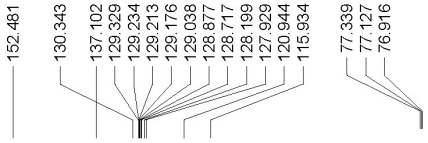


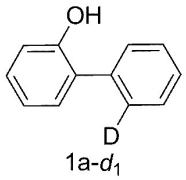

7.382
7.371
7.363
7.359
7.351
7.289
7.285
7.279
7.274
7.267
7.262
7.163
7.160
7.147
7.133
7.105
6.900
6.898
6.886
6.879
6.873
6.866
5.157


OH
D

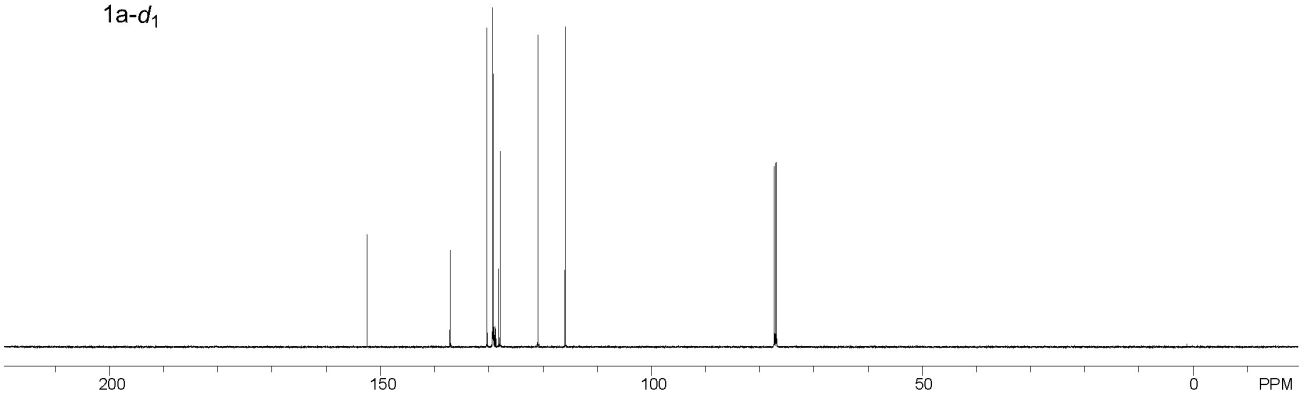
1a-d_1


3.00
2.02
2.03
1.00
0.93
10
8
6
4
2
PPM

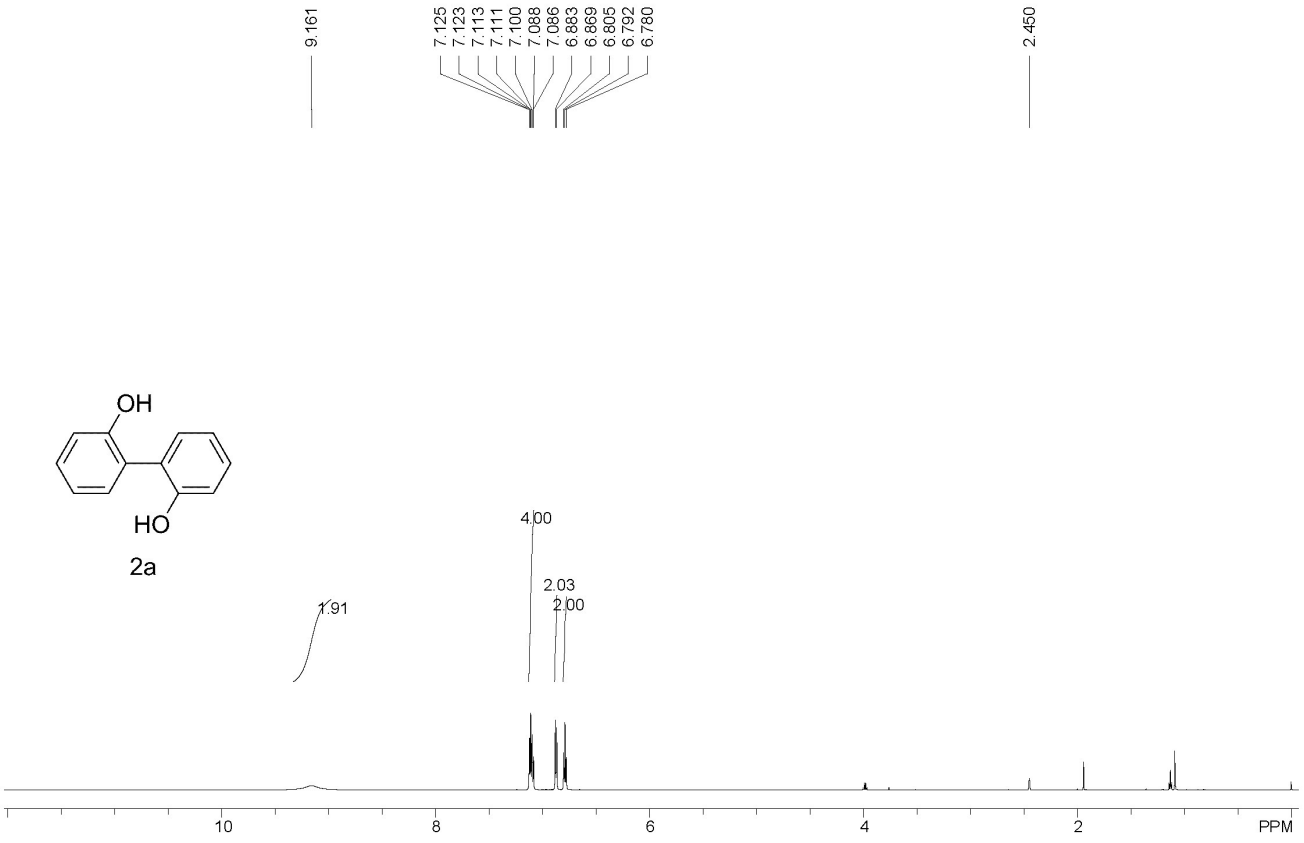

152.481
130.343
137.102
129.329
129.234
129.213
129.176
129.038
128.877
128.717
128.199
127.929
120.944
115.934
77.339
77.127
76.916

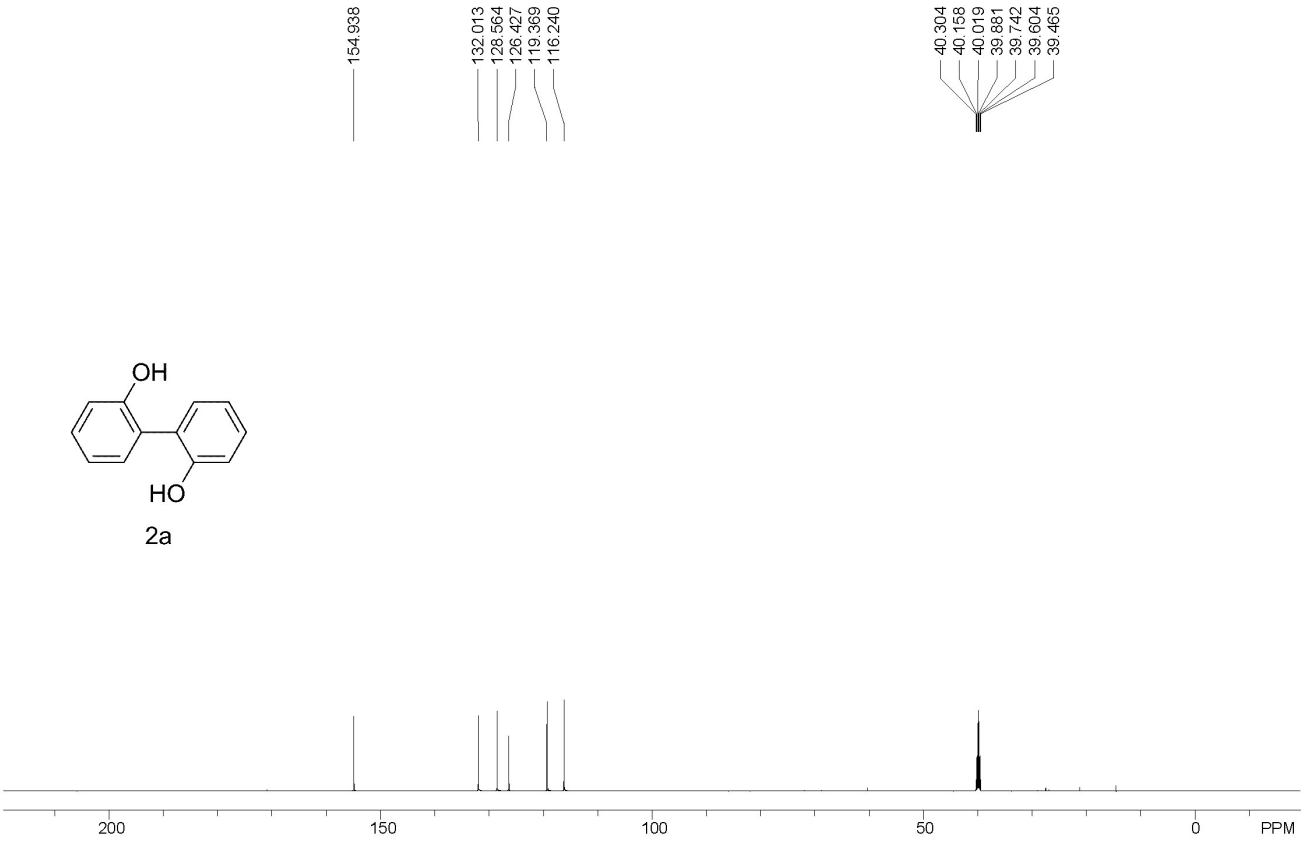

OH
D

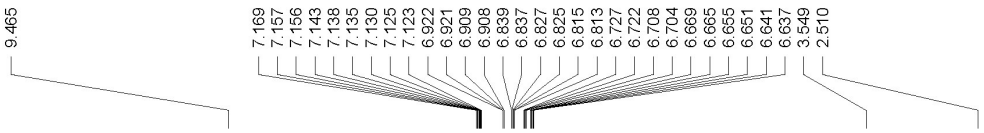
1a-d_1

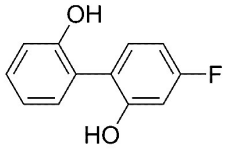

200
150
100
50
0
PPM

VI. Copies of ^{1}H and ^{13}C NMR spectra of 2a-2w

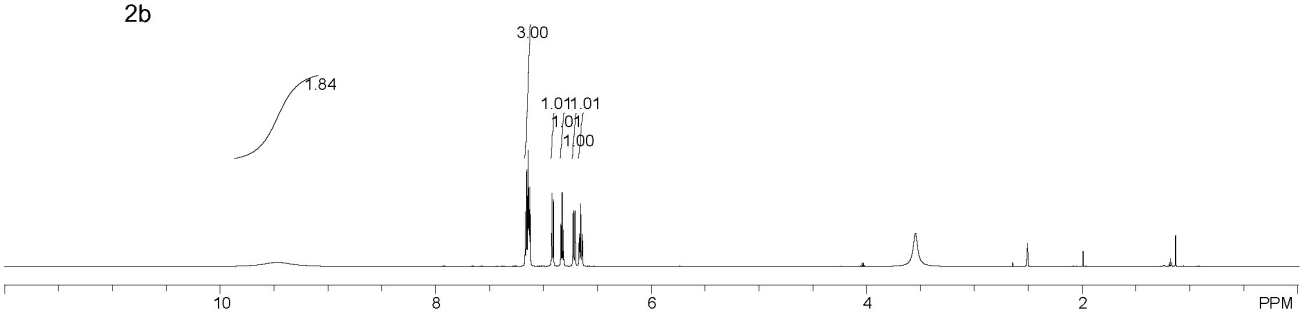


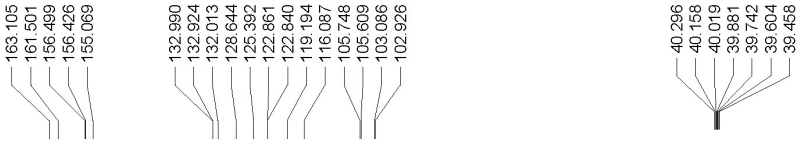


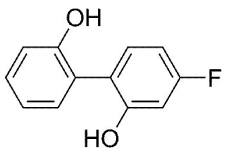

9.465
7.169
7.157
7.156
7.143
7.138
7.135
7.130
7.125
7.123
6.922
6.921
6.909
6.908
6.839
6.837
6.827
6.825
6.815
6.813
6.727
6.722
6.708
6.704
6.669
6.665
6.655
6.651
6.641
6.637
3.549
2.510


OH
F
HO

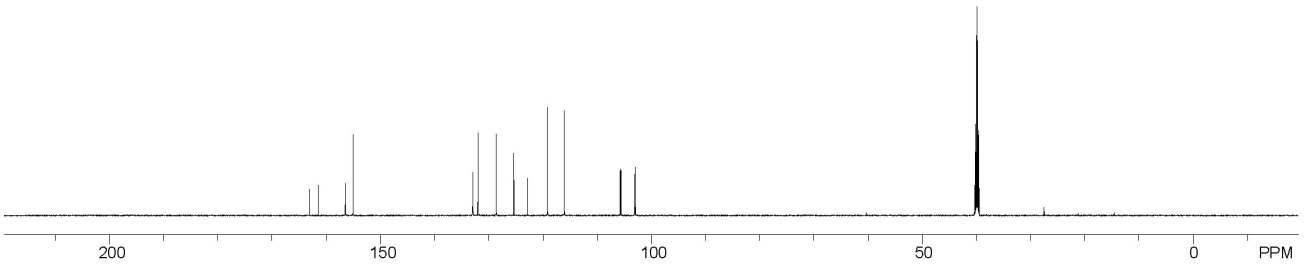
2b

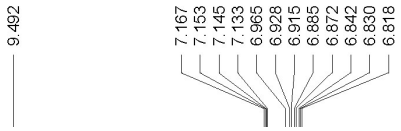

3.00
1.84
1.01
1.01
1.01
1.00
10
8
6
4
2
PPM


163.105
161.501
156.499
156.426
155.069
132.990
132.924
132.013
128.644
125.392
122.861
122.840
119.194
116.087
105.748
105.609
103.086
102.926
40.296
40.158
40.019
39.881
39.742
39.604
39.458


OH
F
HO

2b


200
150
100
50
0
PPM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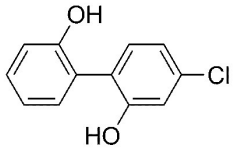
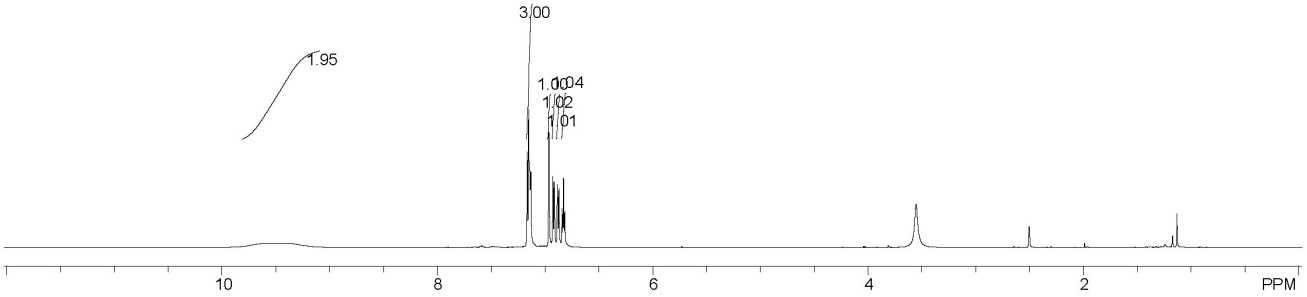
3.557
2.507


OH
Cl
HO

2c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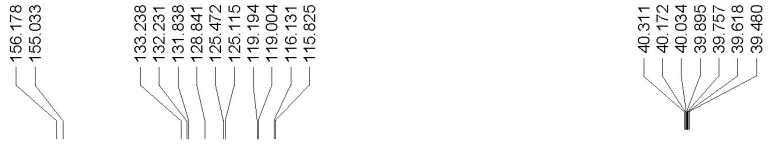
2
PPM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115.825
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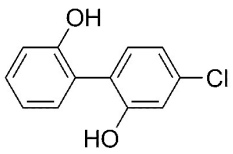
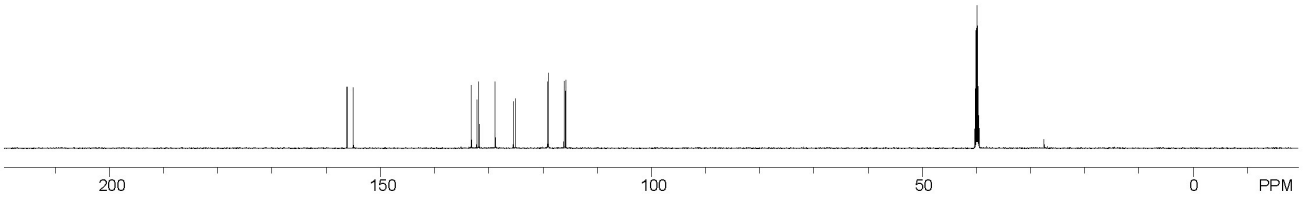
39.895
39.757
39.618
39.480


OH
Cl
HO

2c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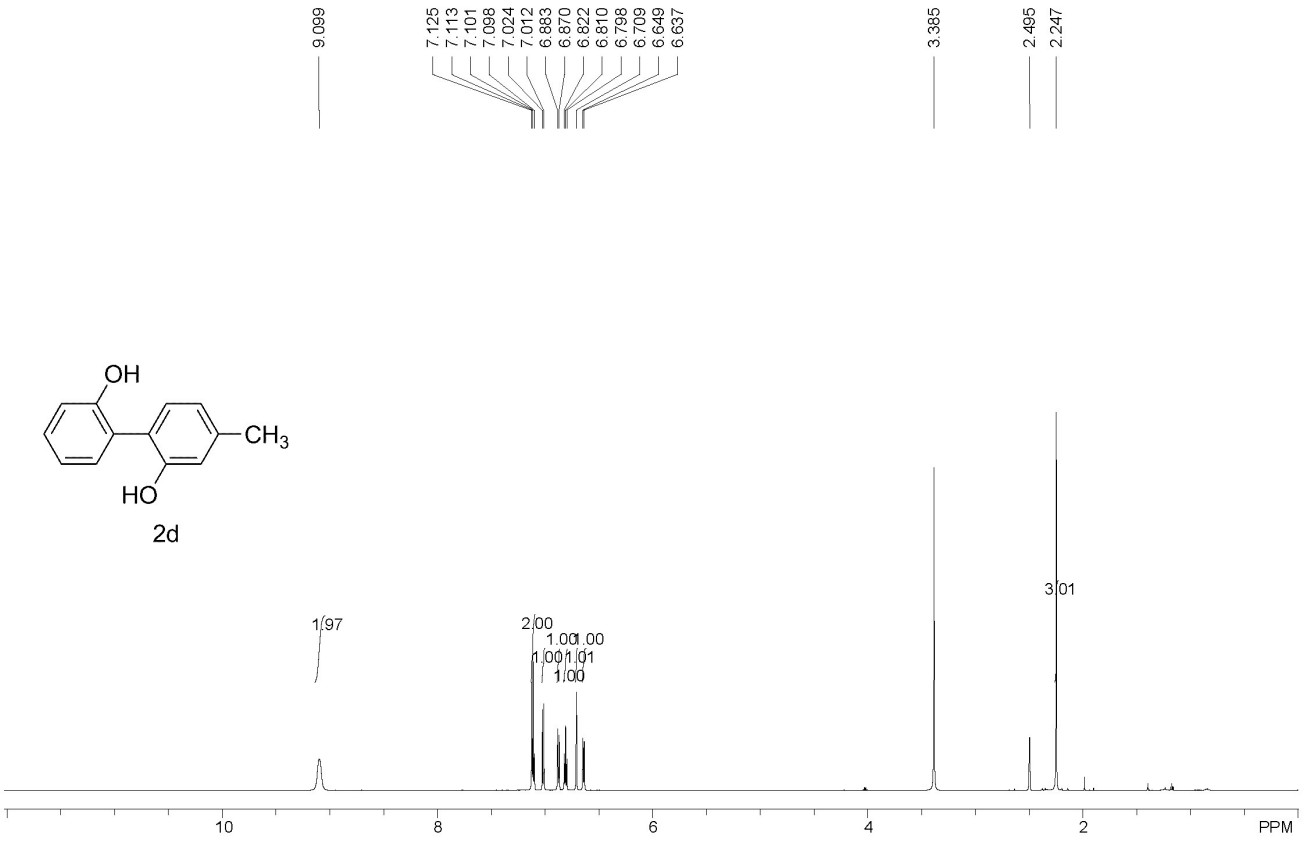
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6.798
6.709
6.649
6.637
3.385
2.495
2.247
OH
CH3
HO
2d
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1.00
1.00
1.00
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3.01
10
8
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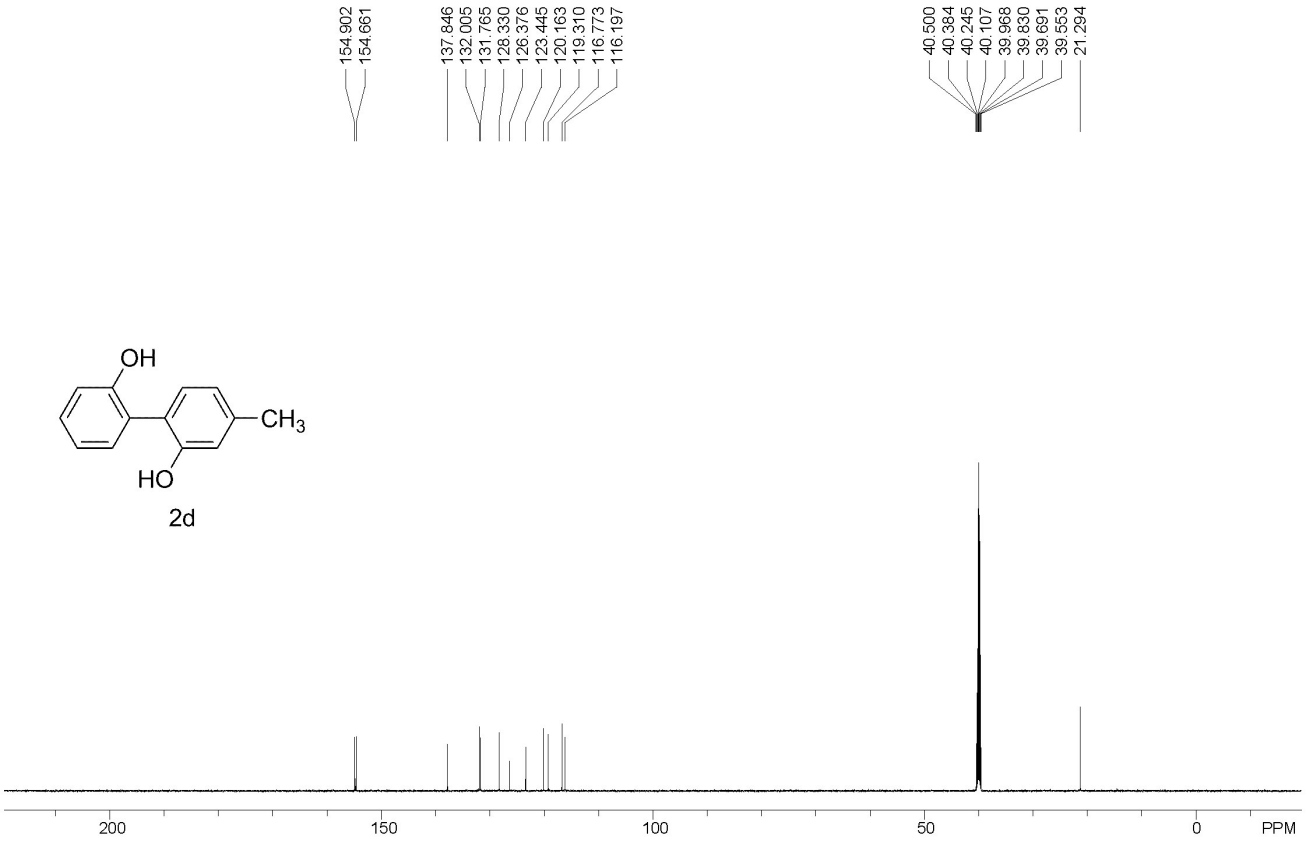
4
2
PPM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123.445
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116.197
40.500
40.384
40.245
40.107
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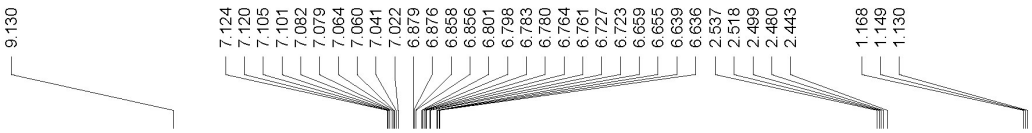
39.691
39.553
21.294
OH
CH3
HO
2d
200
150
100
50
0
PPM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6.876
6.858
6.856
6.801
6.798
6.783
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6.723
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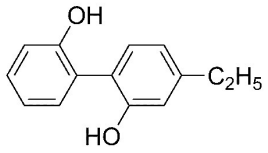
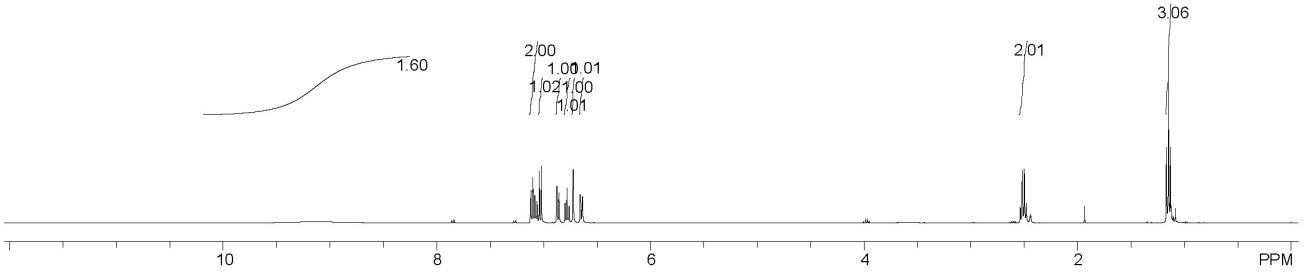
1.149
1.130


OH
C_2H_5
HO

2e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1.00
1.01
2.01
3.06
10
8
6
4
2
PPM


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131.524
131.343
127.859
125.946
123.247
118.869
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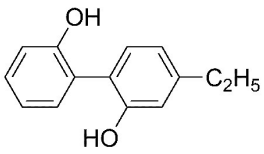
38.744
27.943
15.513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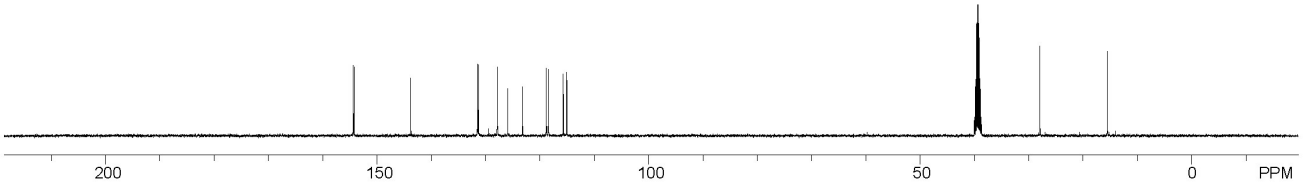
C_2H_5
HO

2e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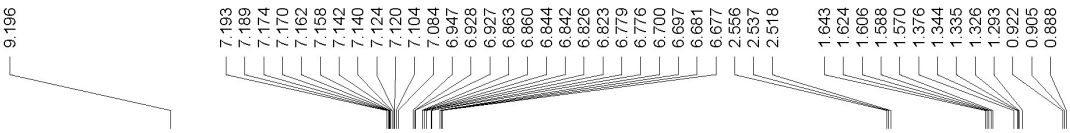
PPM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7.142
7.140
7.124
7.120
7.104
7.084
6.947
6.928
6.927
6.863
6.860
6.844
6.842
6.826
6.823
6.779
6.776
6.700
6.697
6.681
6.677
2.556
2.537
2.518
1.643
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1.326
1.293
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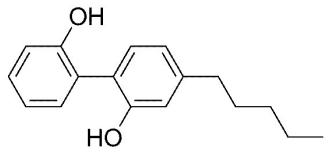
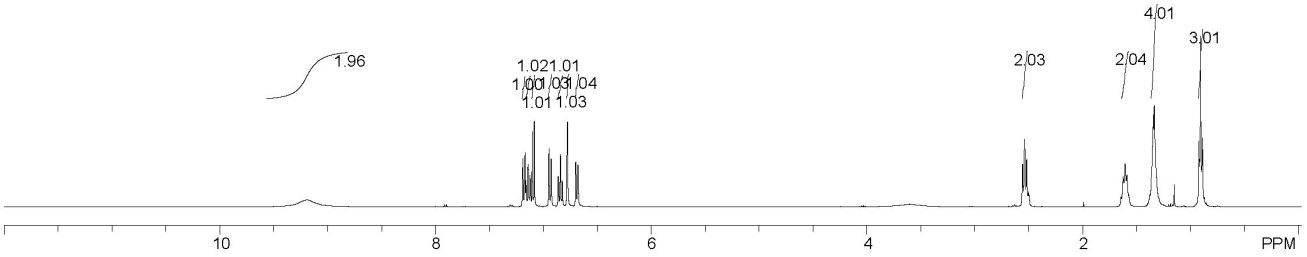
0.905
0.888


OH
HO

2f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1.04
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1.03
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2.04
4.01
3.01
10
8
6
4
2
PPM


154.399
154.145
142.420
131.524
131.263
127.837
125.953
123.240
119.050
118.898
115.777
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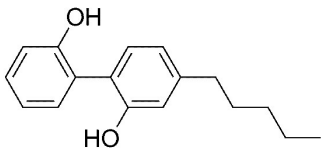
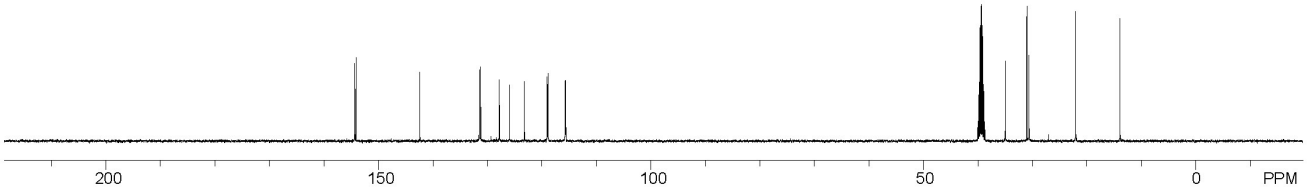
13.905


OH
HO

2f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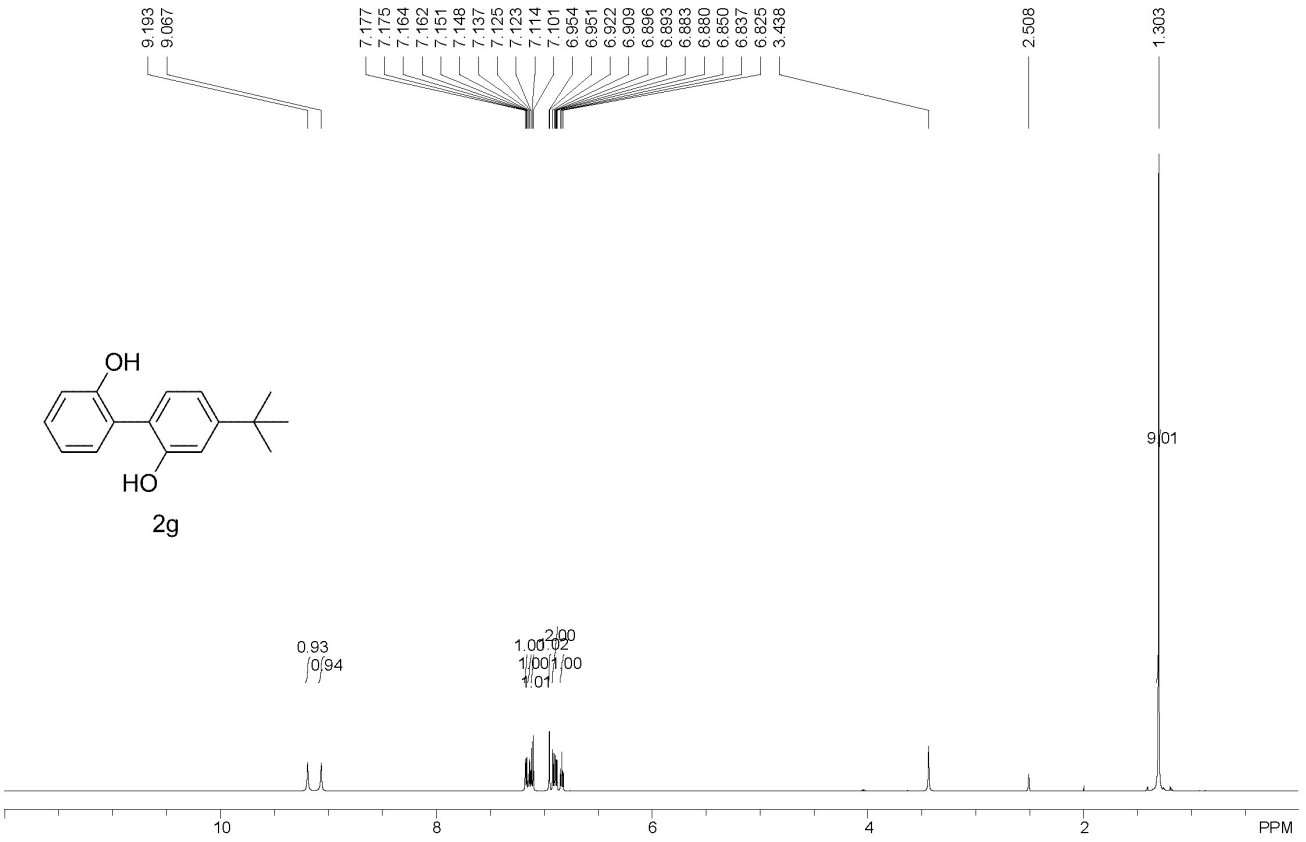
150
100
50
0
PPM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7.162
7.151
7.148
7.137
7.125
7.123
7.114
7.101
6.954
6.951
6.922
6.909
6.896
6.893
6.883
6.880
6.850
6.837
6.825
3.438
2.508
1.303
OH
HO
2g
9.01
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1.02
2.00
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1.01
10
8
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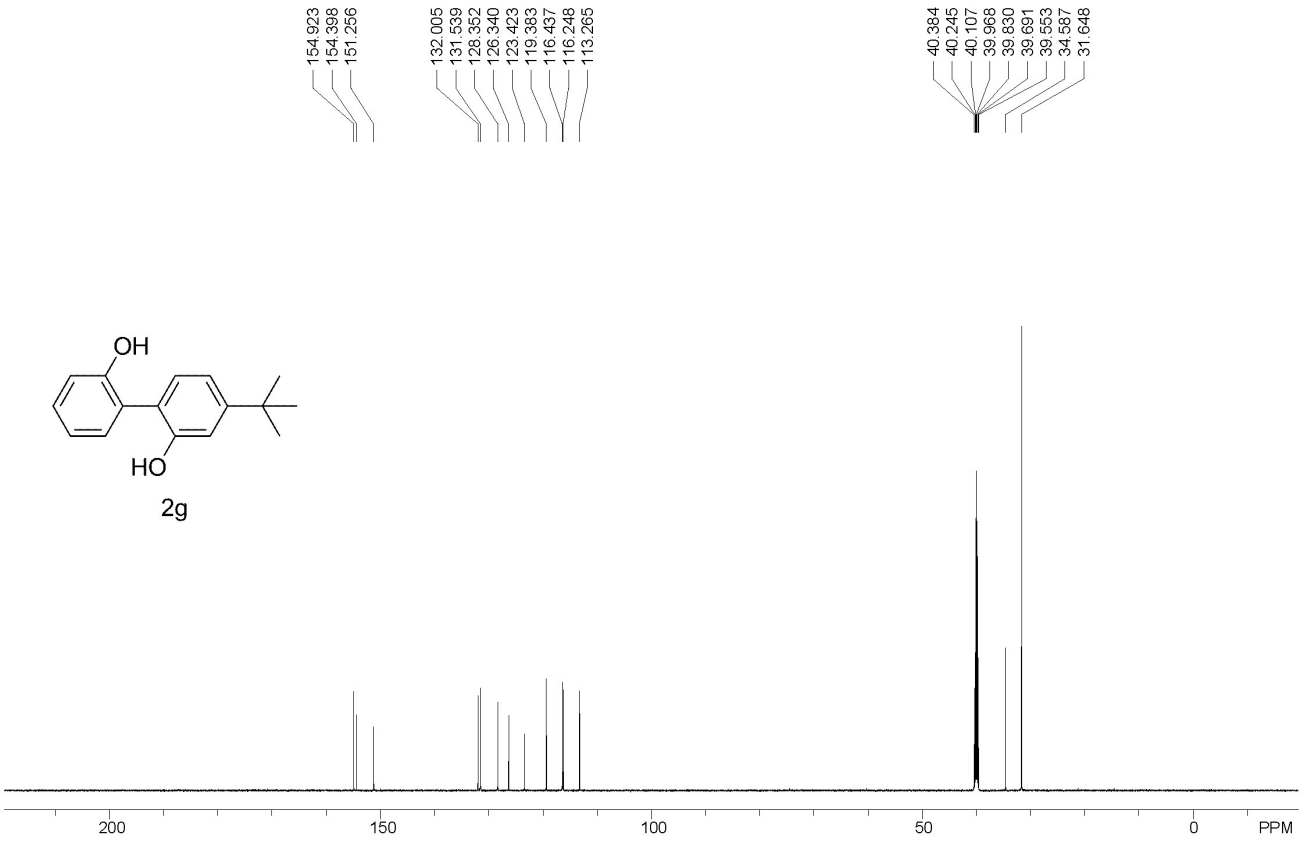
4
2
PPM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116.248
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40.384
40.245
40.107
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39.553
34.587
31.648
OH
HO
2g
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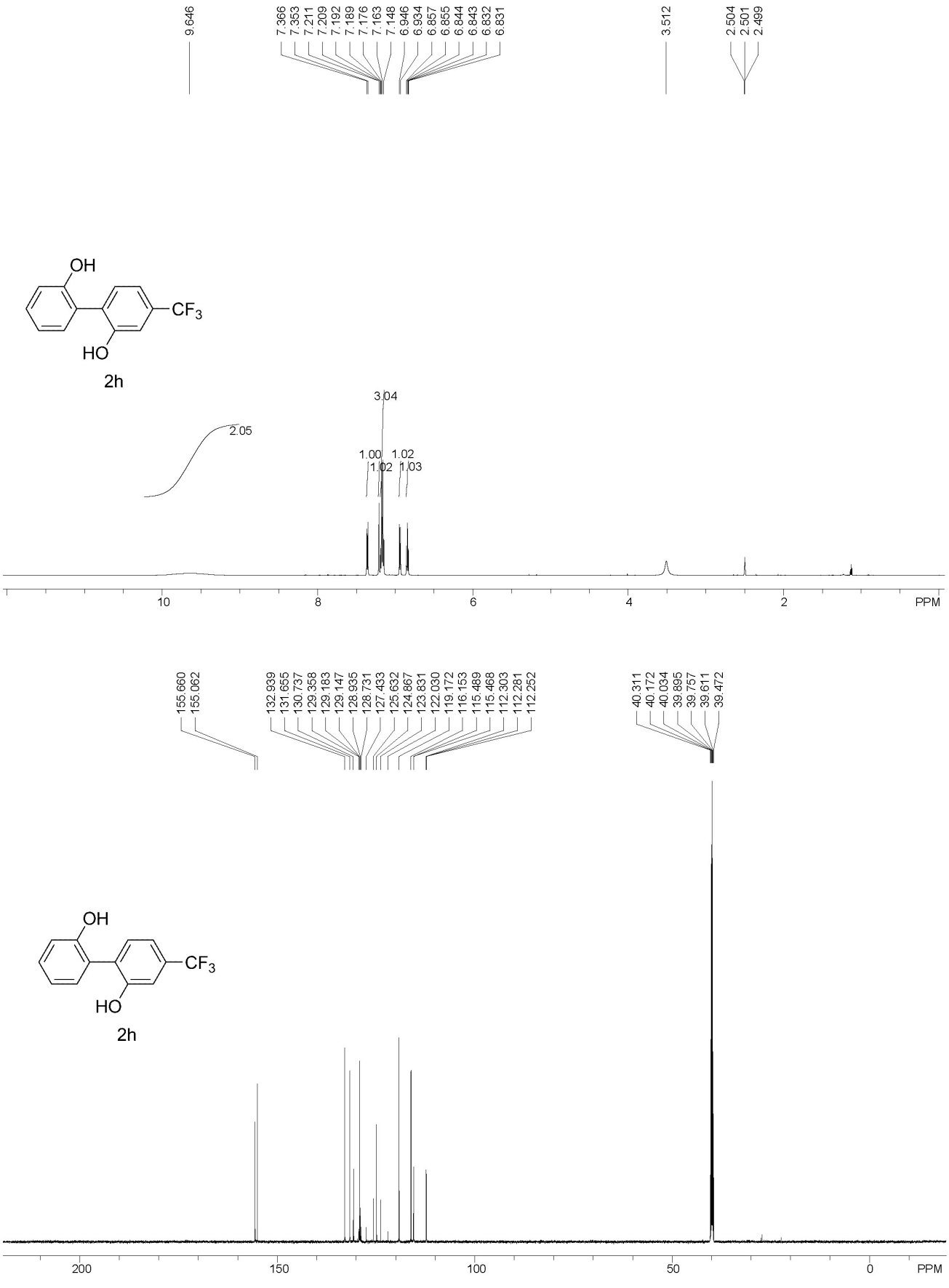
100
50
0
PPM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7.163
7.148
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6.934
6.857
6.855
6.844
6.843
6.832
6.831
3.512
2.504
2.501
2.499
OH
CF3
HO
2h
2.05
3.04
1.00
1.02
1.02
1.03
10
8
6
4
2
PPM
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155.062
132.939
131.655
130.737
129.358
129.183
129.147
128.935
128.731
127.433
125.632
124.867
123.831
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119.172
116.153
115.489
115.468
112.303
112.281
112.252
40.311
40.172
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39.757
39.611
39.472
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CF3
HO
2h
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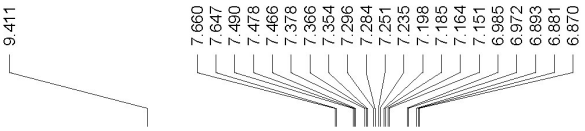
150
100
50
0
PPM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7.251
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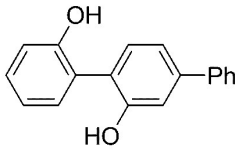
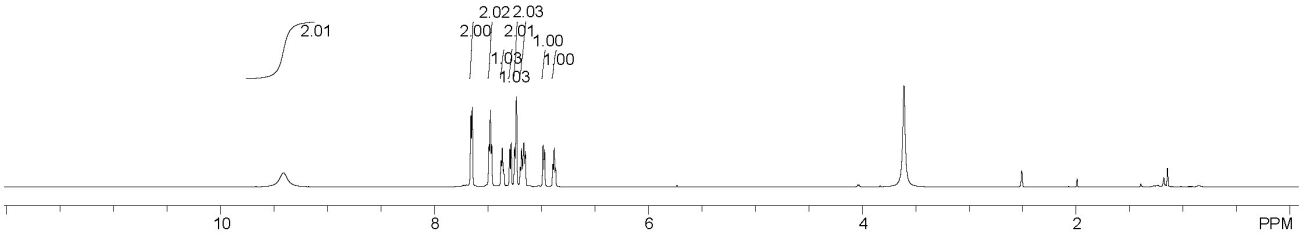
2.509


OH
Ph
HO

2i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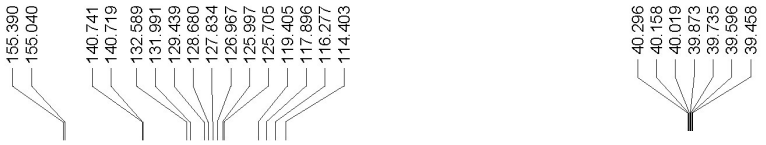
2.01
2.03
1.08
1.03
1.00
1.00
10
8
6
4
2
PPM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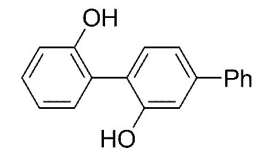
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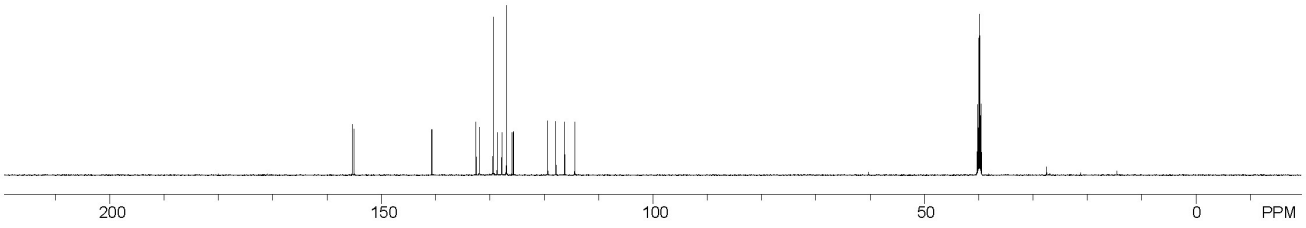
Ph
HO

2i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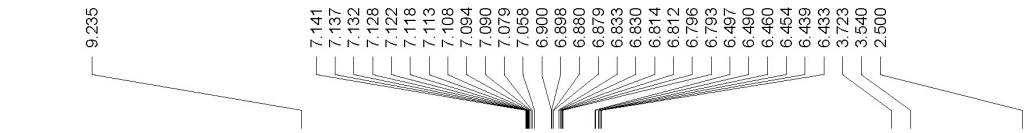
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6.433
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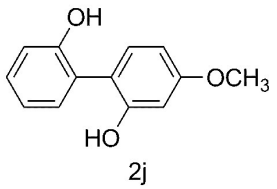
2.500


OH
OCH3
HO

2j

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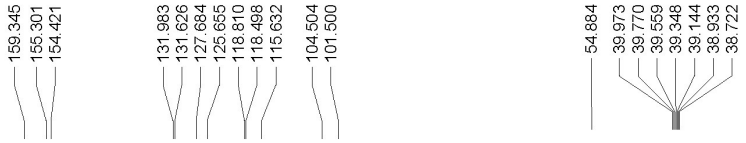
10
8
6
4
2
PPM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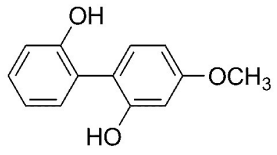
38.722


OH
OCH3
HO

2j

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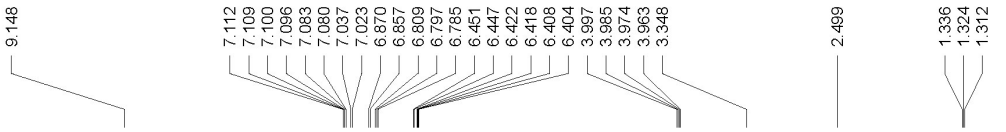
PPM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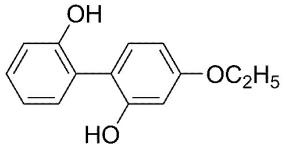
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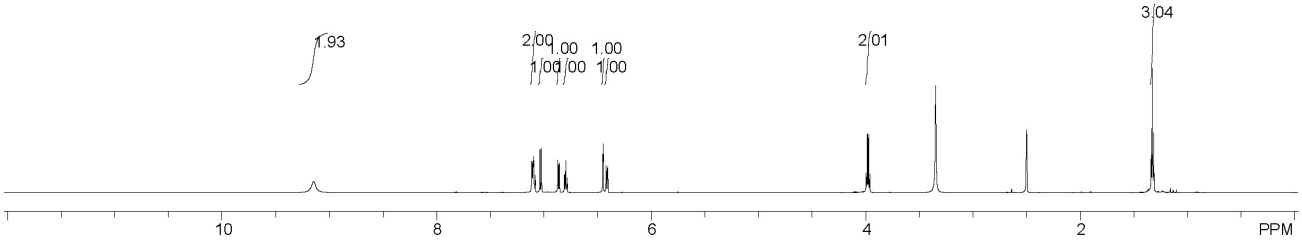
OC2H5
HO

2k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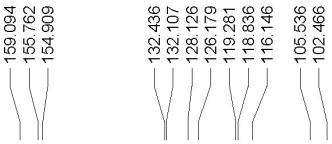
8
6
4
2
PPM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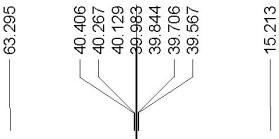
102.466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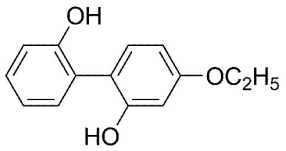
15.213


OH
OC2H5
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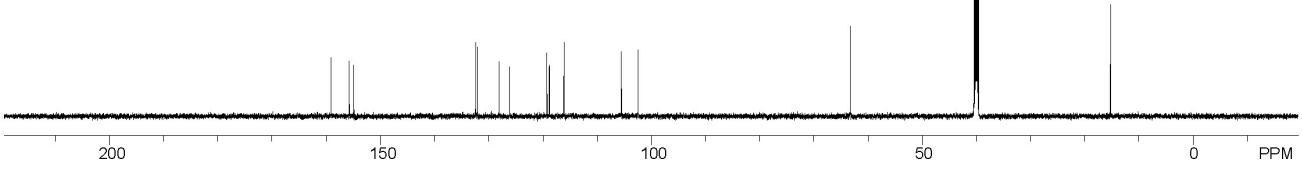
2k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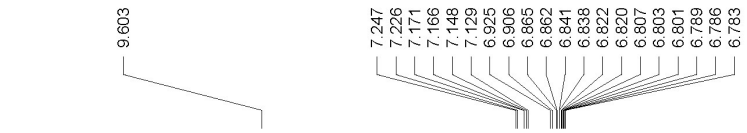
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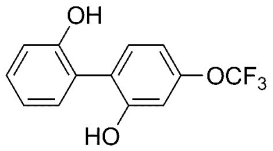
2.500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OCF3
HO

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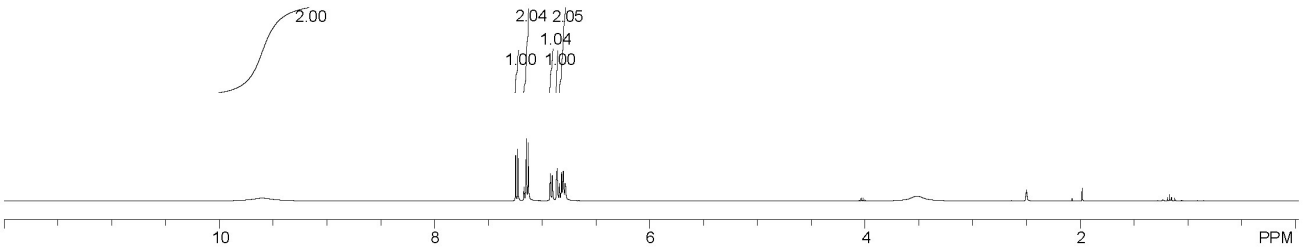
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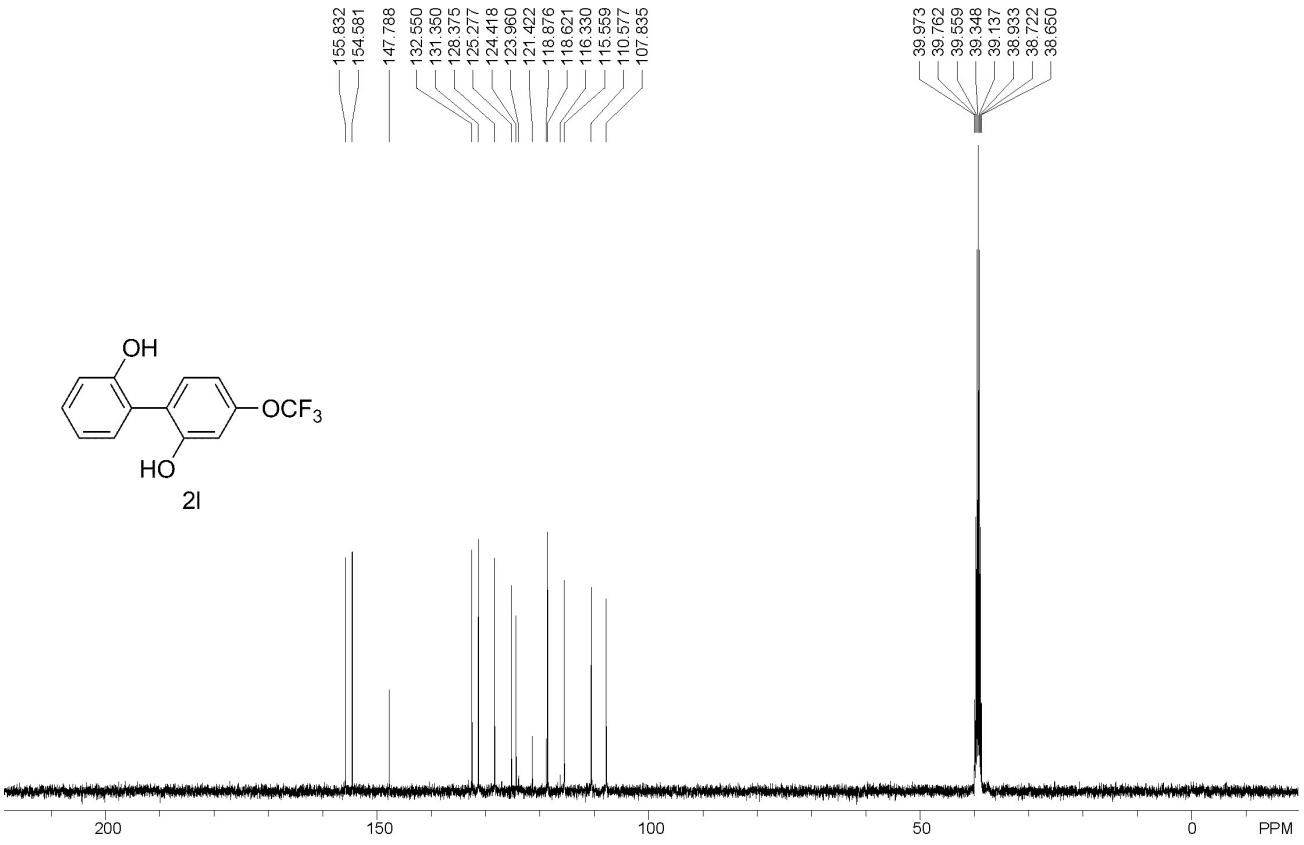
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OCF3
HO
200
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100
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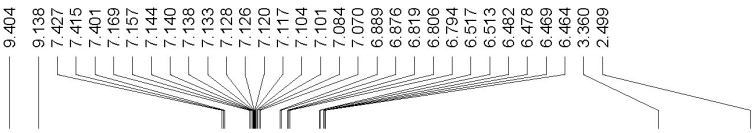
0
PPM

2l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7.126
7.120
7.117
7.104
7.101
7.084
7.070
6.889
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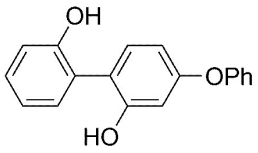
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HO

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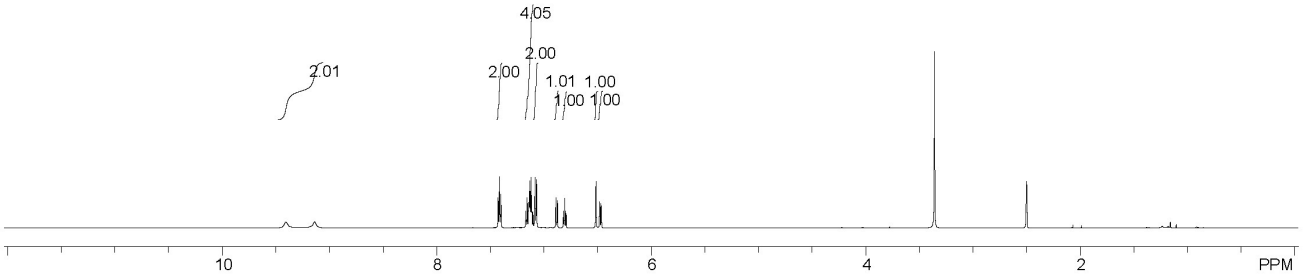
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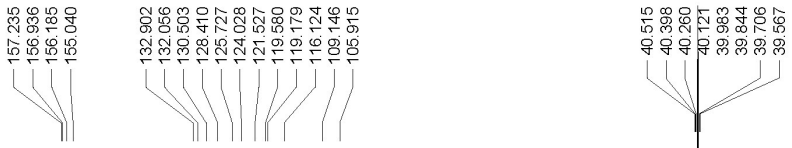
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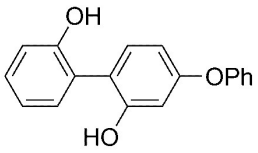
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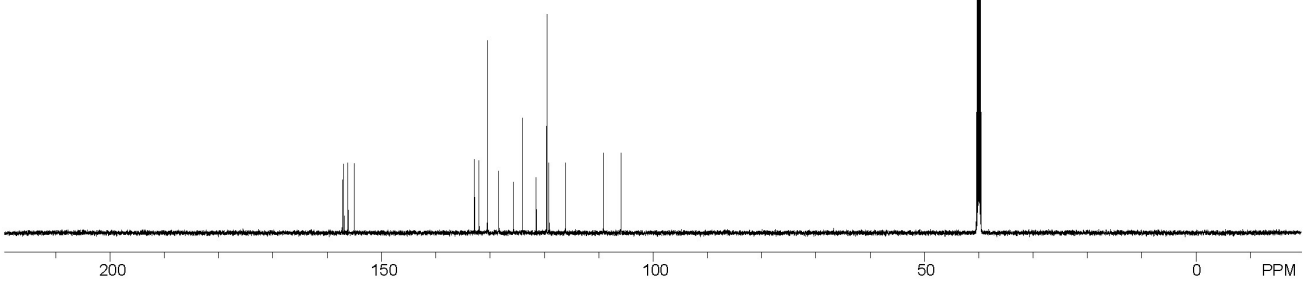
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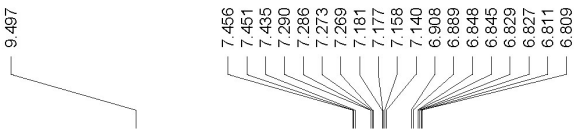
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7.269
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7.177
7.158
7.140
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6.848
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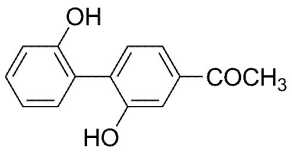
2.500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HO

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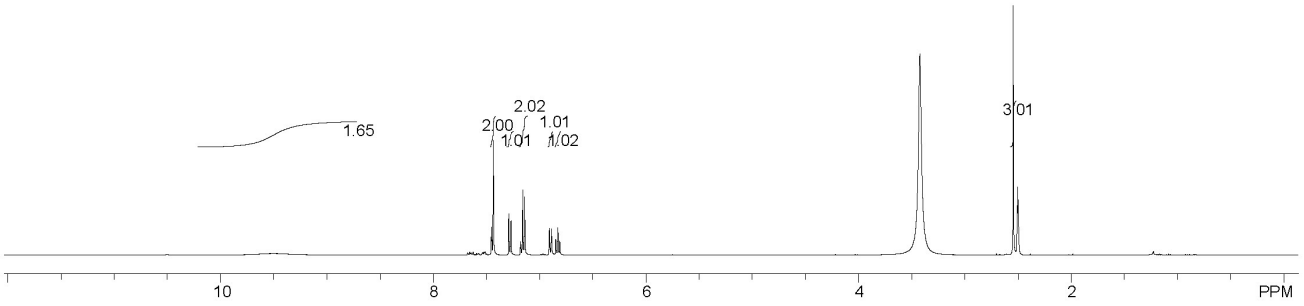
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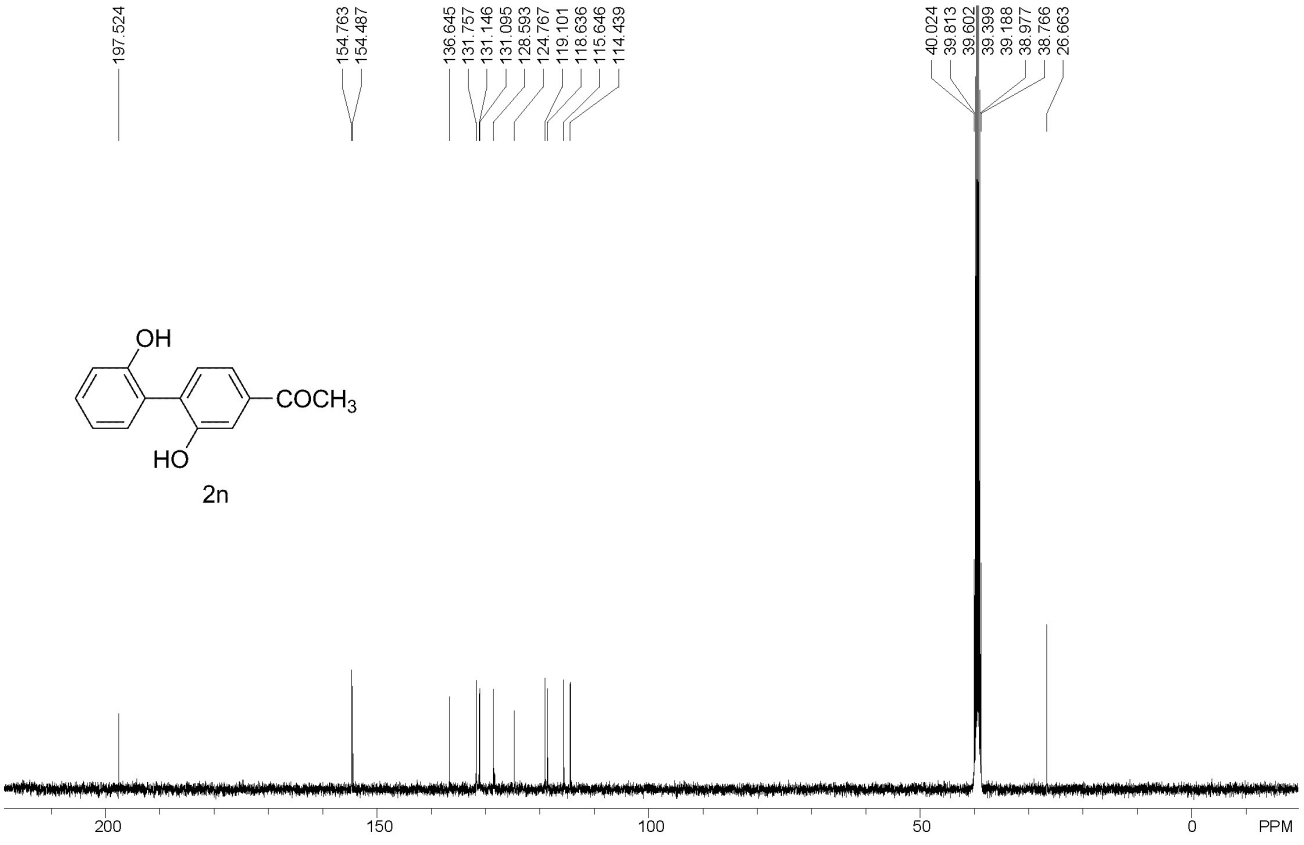
8
6
4
2
PPM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39.813
39.602
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150
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50
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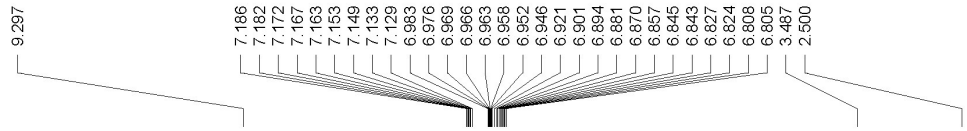
PPM

OH
COCH3
HO

2n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7.129
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6.963
6.958
6.952
6.946
6.921
6.901
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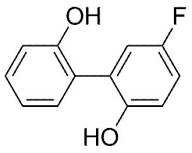
2.500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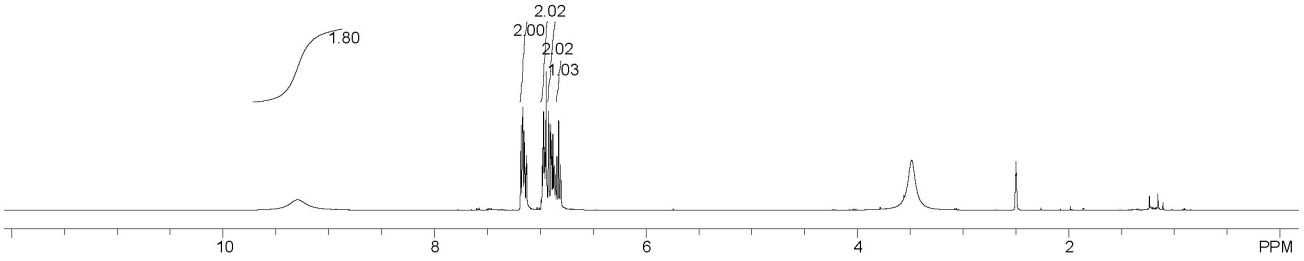
F
HO

2o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10
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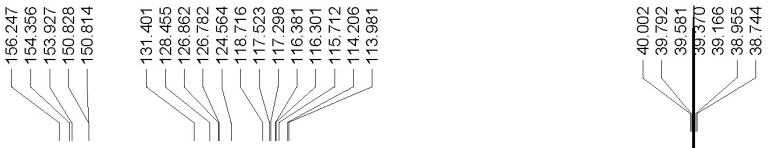
4
2
PPM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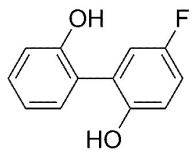
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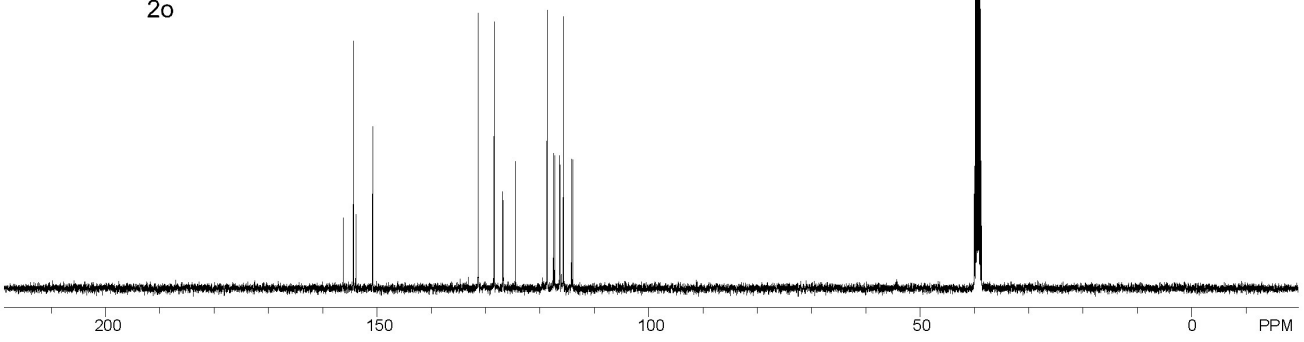
2o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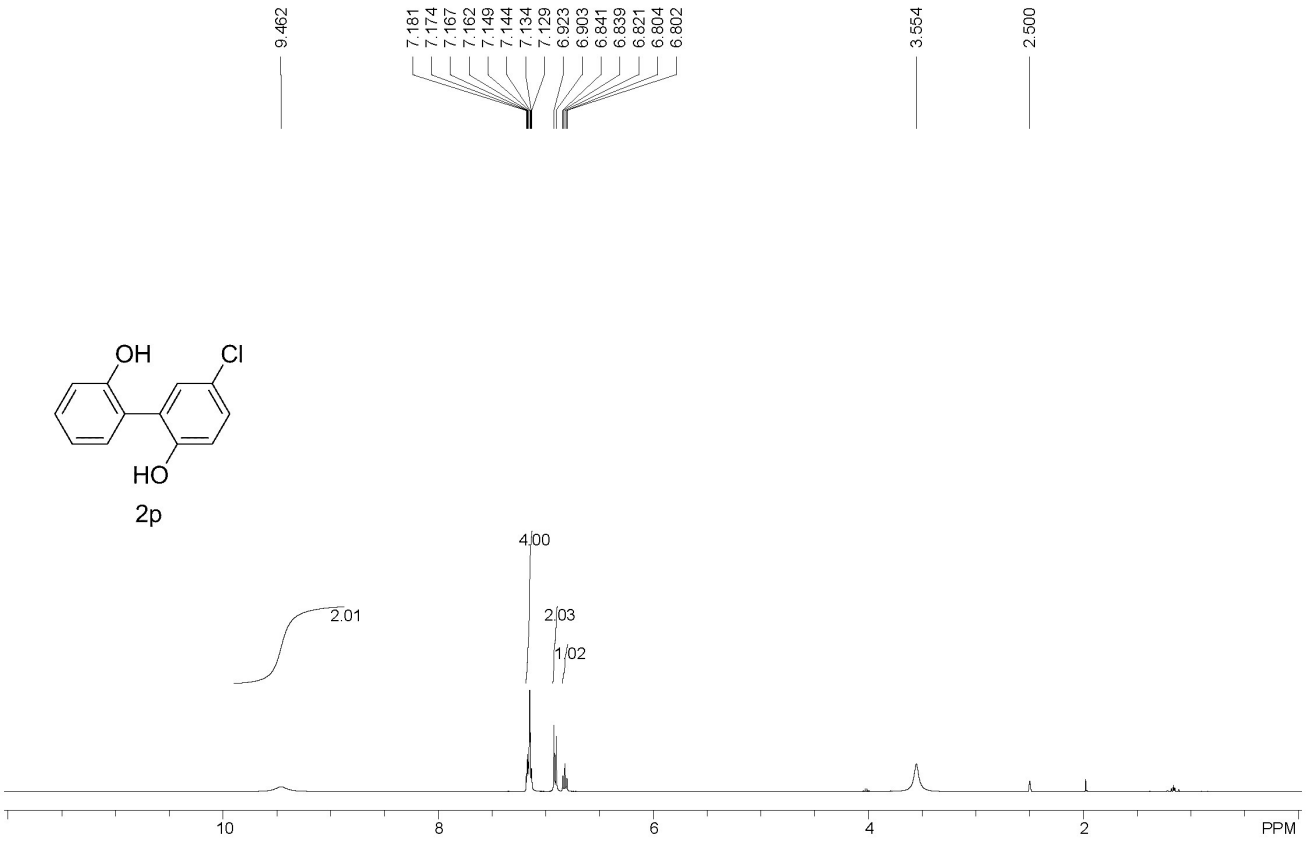
100
50
0
PPM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7.129
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6.903
6.841
6.839
6.821
6.804
6.802
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Cl
HO
2p
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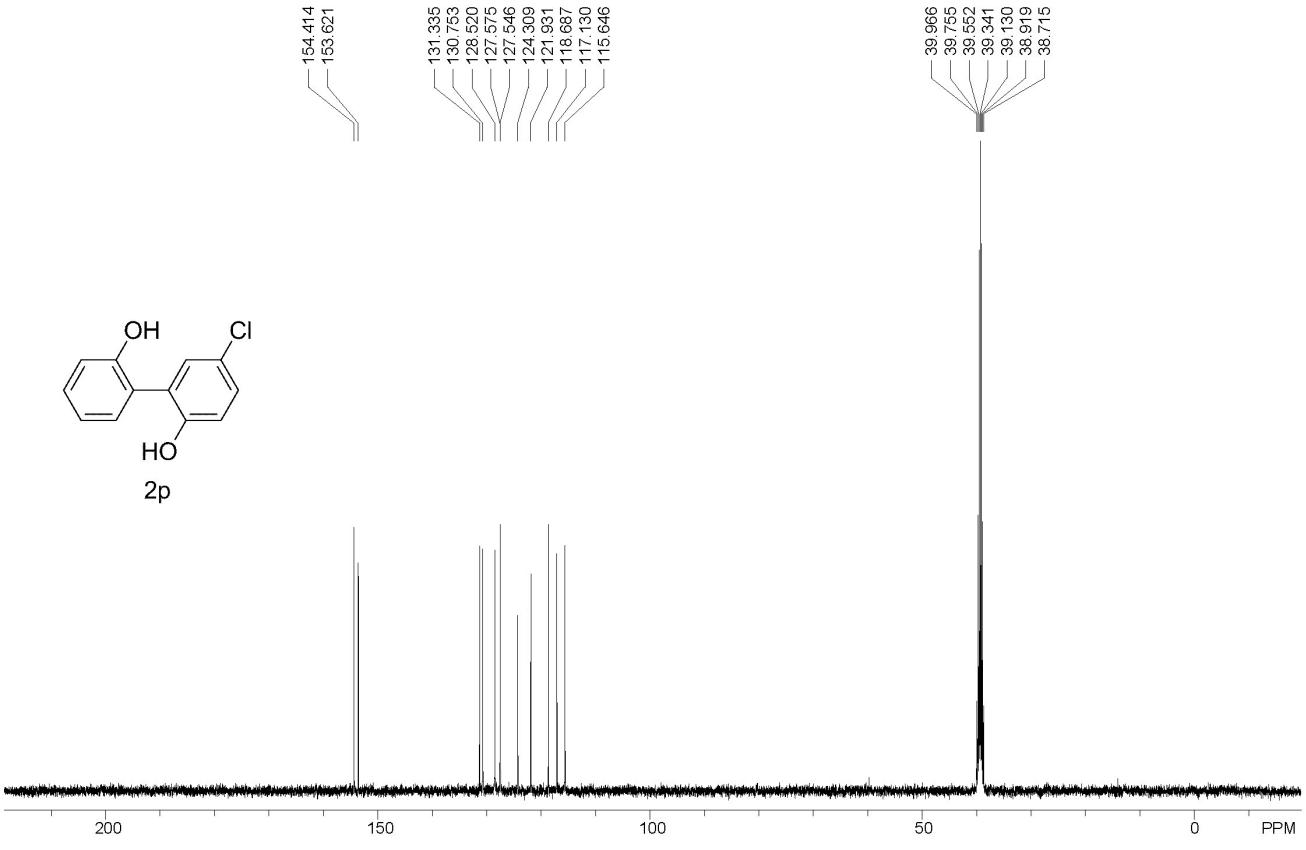
2.03
1.02
10
8
6
4
2
PPM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Cl
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2p
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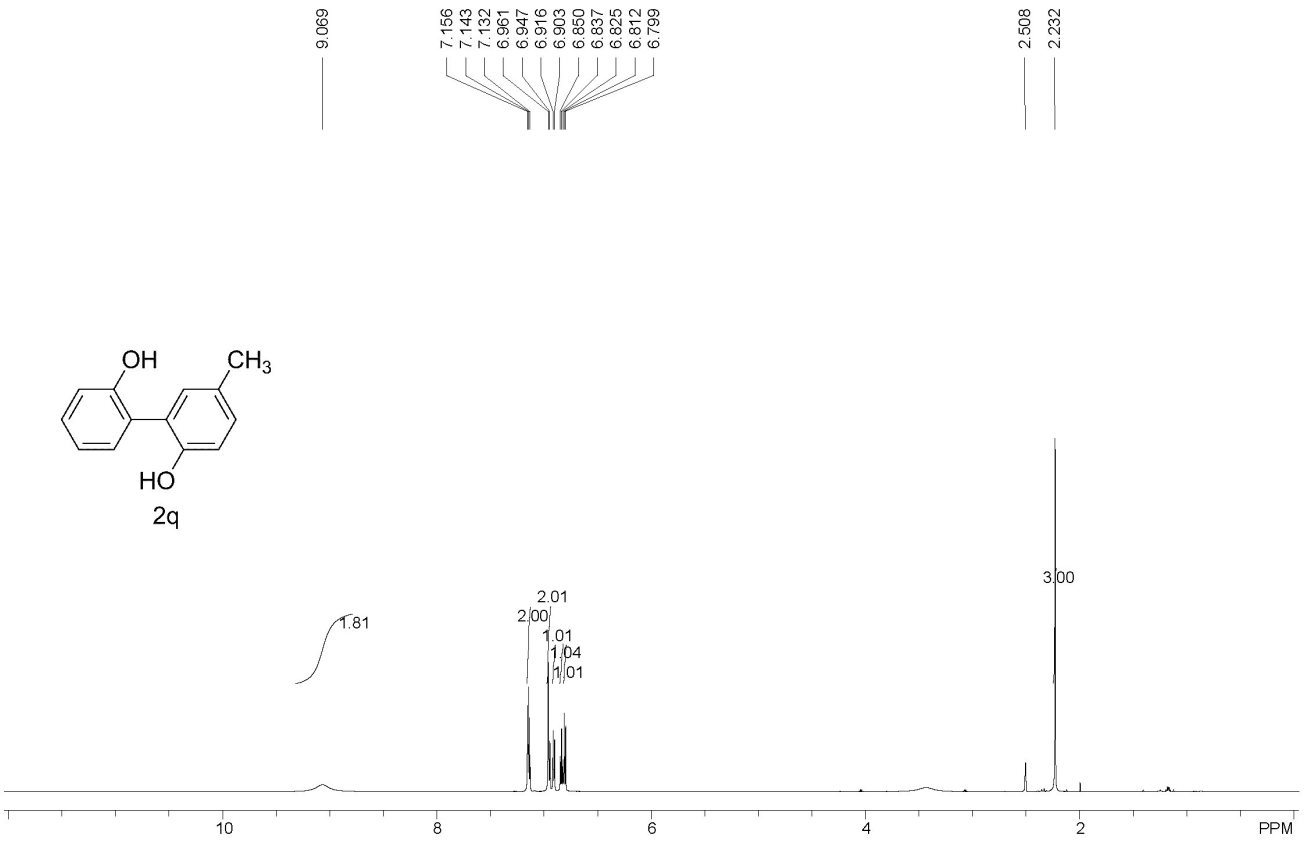
0
PPM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6.825
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OH
CH3
HO
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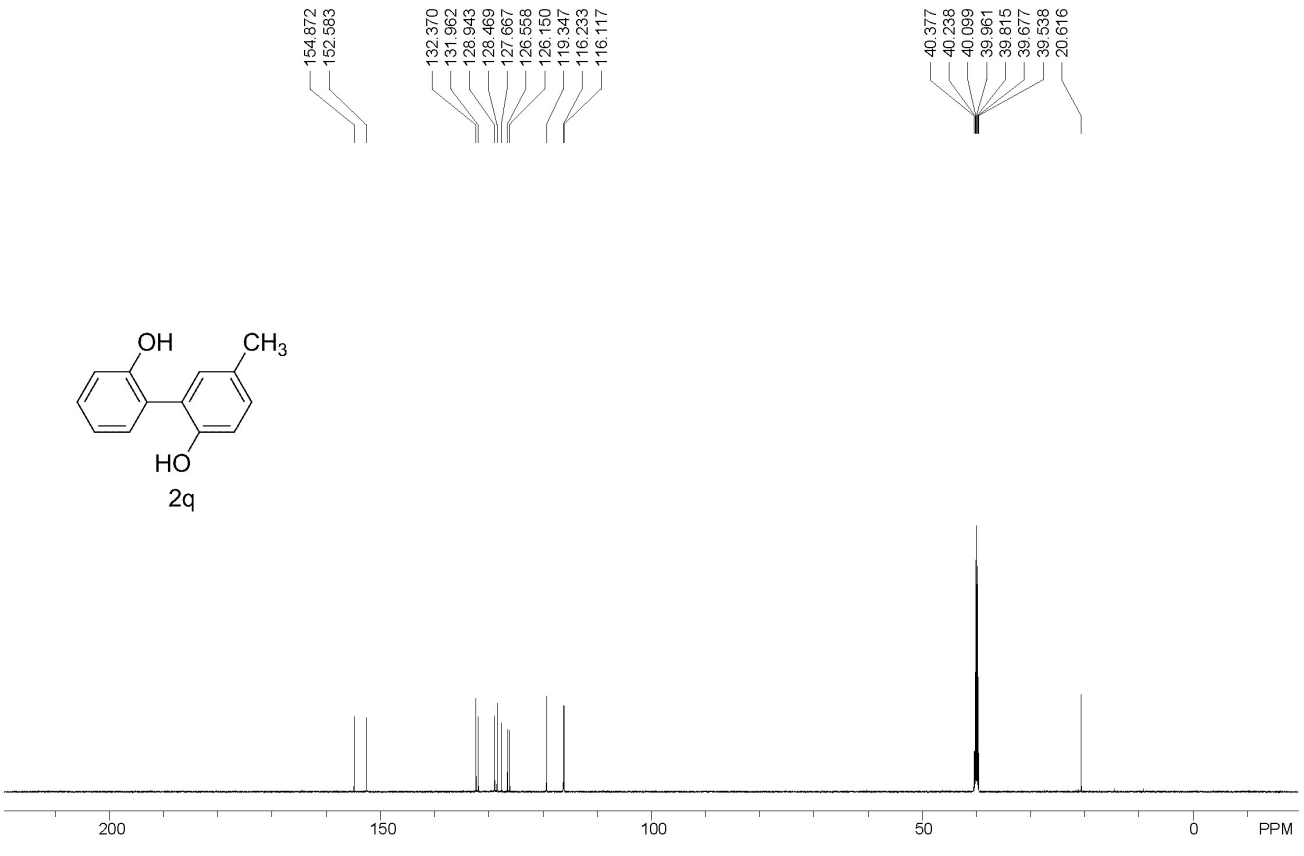
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2q
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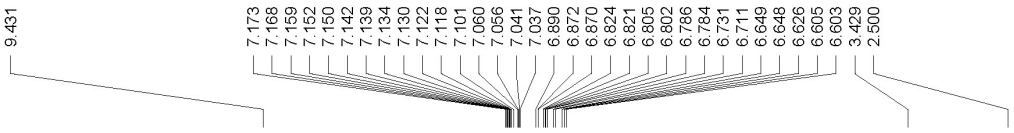
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7.037
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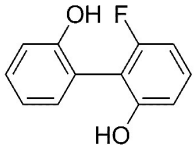
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HO

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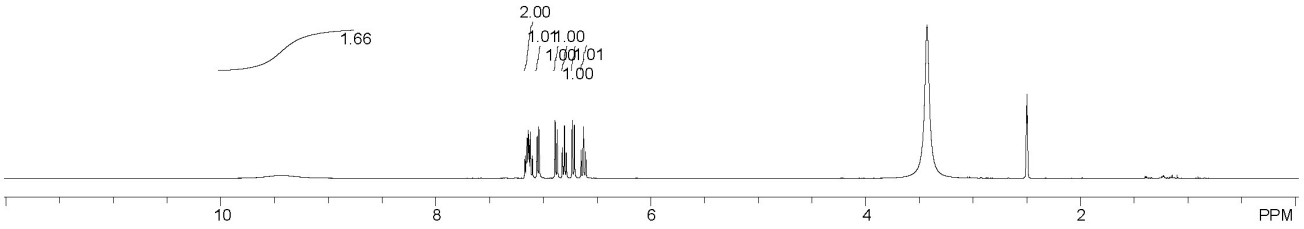
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10
8
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2
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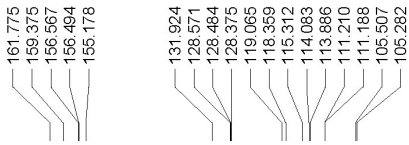
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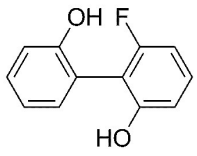
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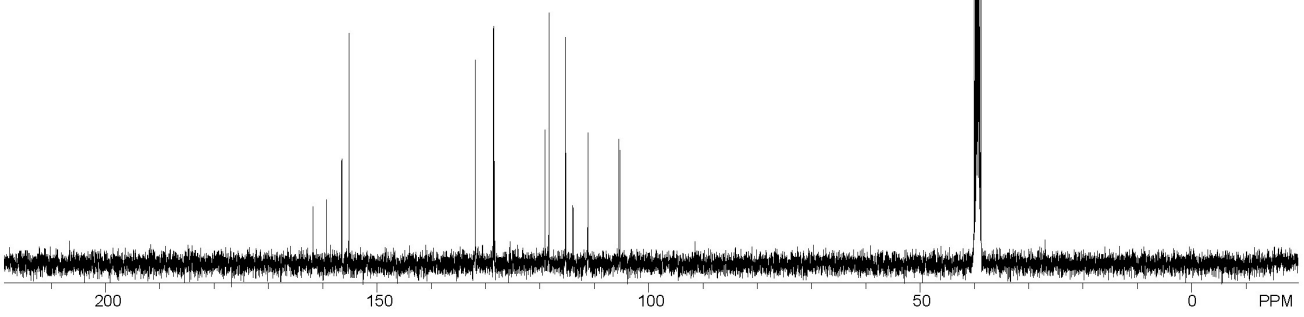
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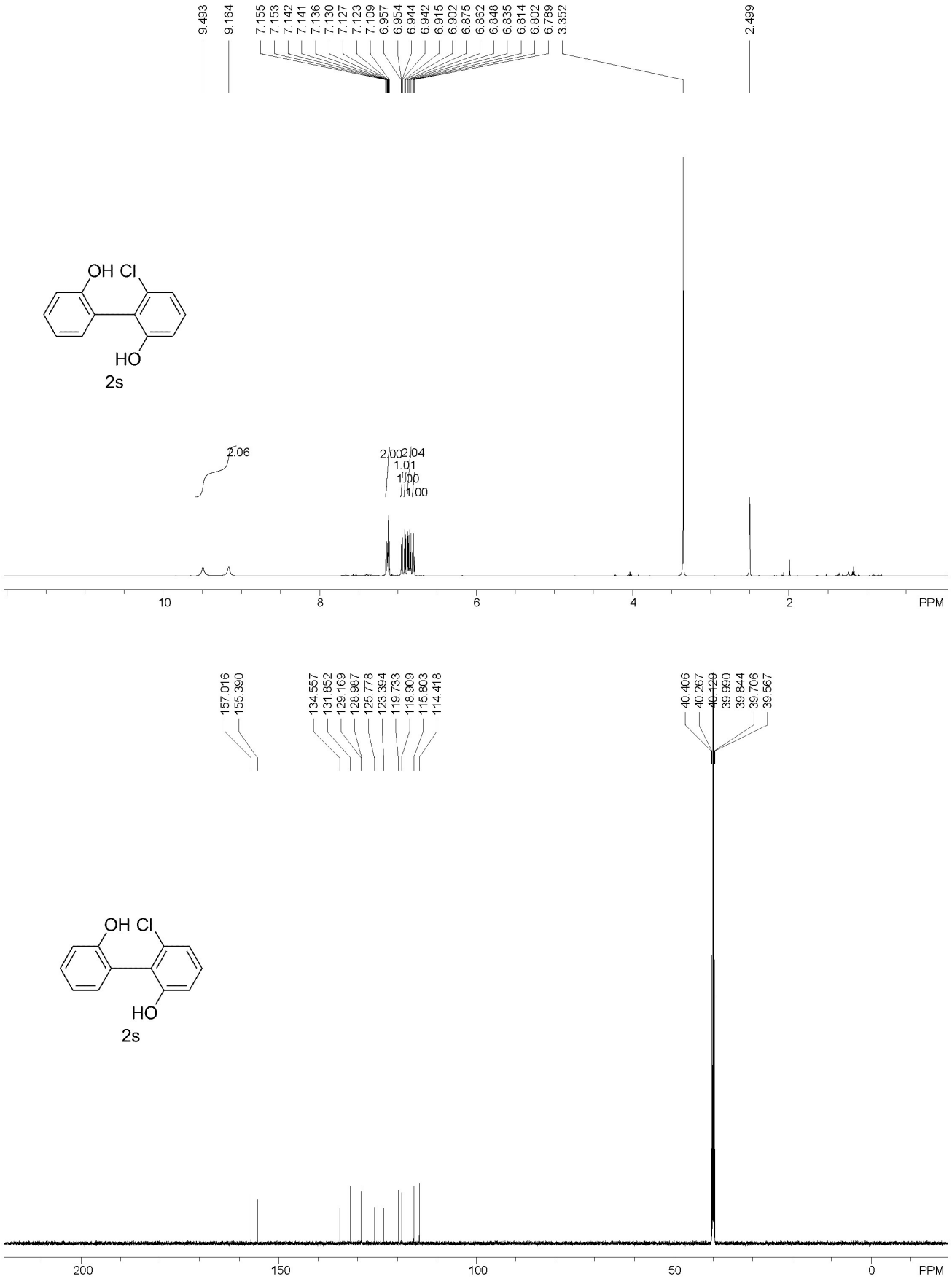
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6.848
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6.814
6.802
6.789
3.352
2.499
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HO
2s
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2.00
2.04
1.01
1.00
1.00
10
8
6
4
2
PPM
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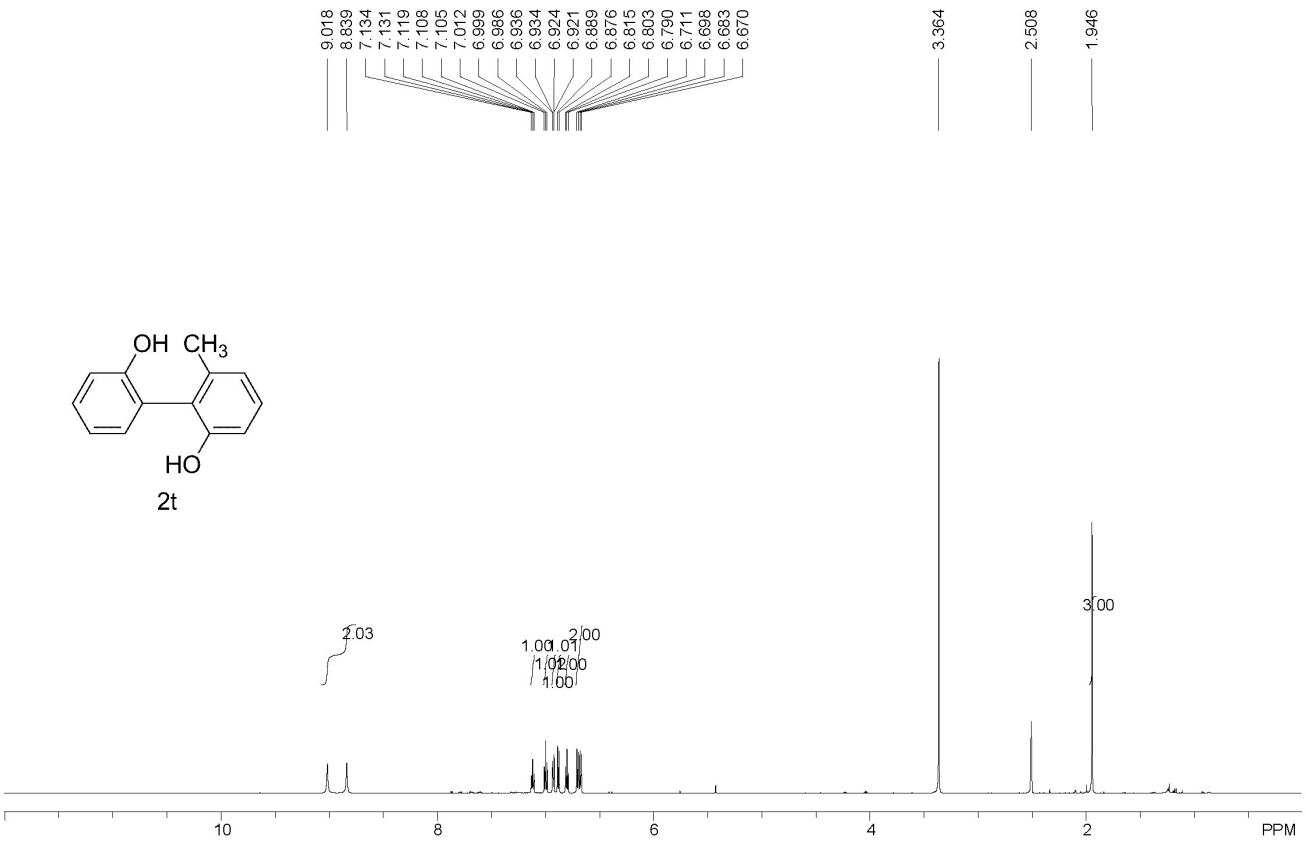
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CH3
HO
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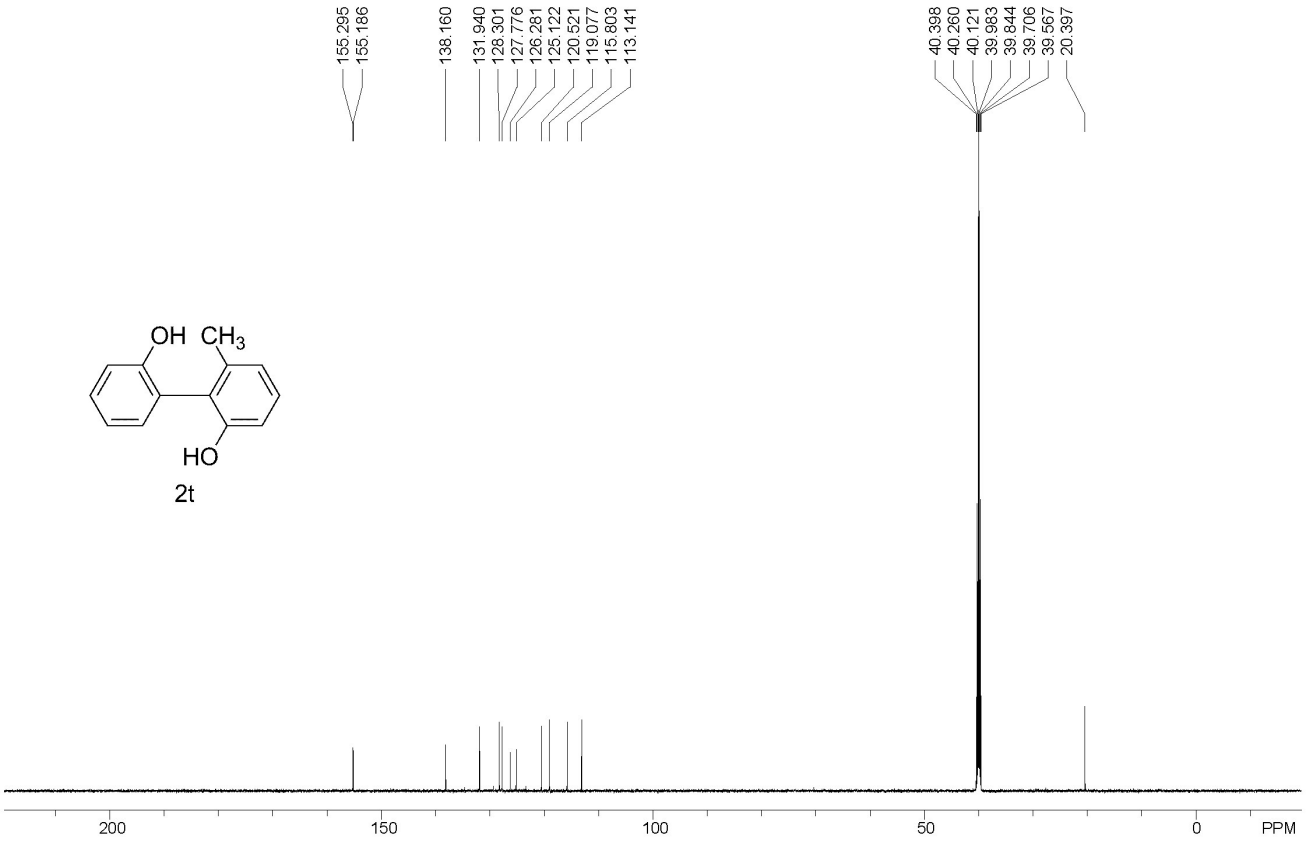
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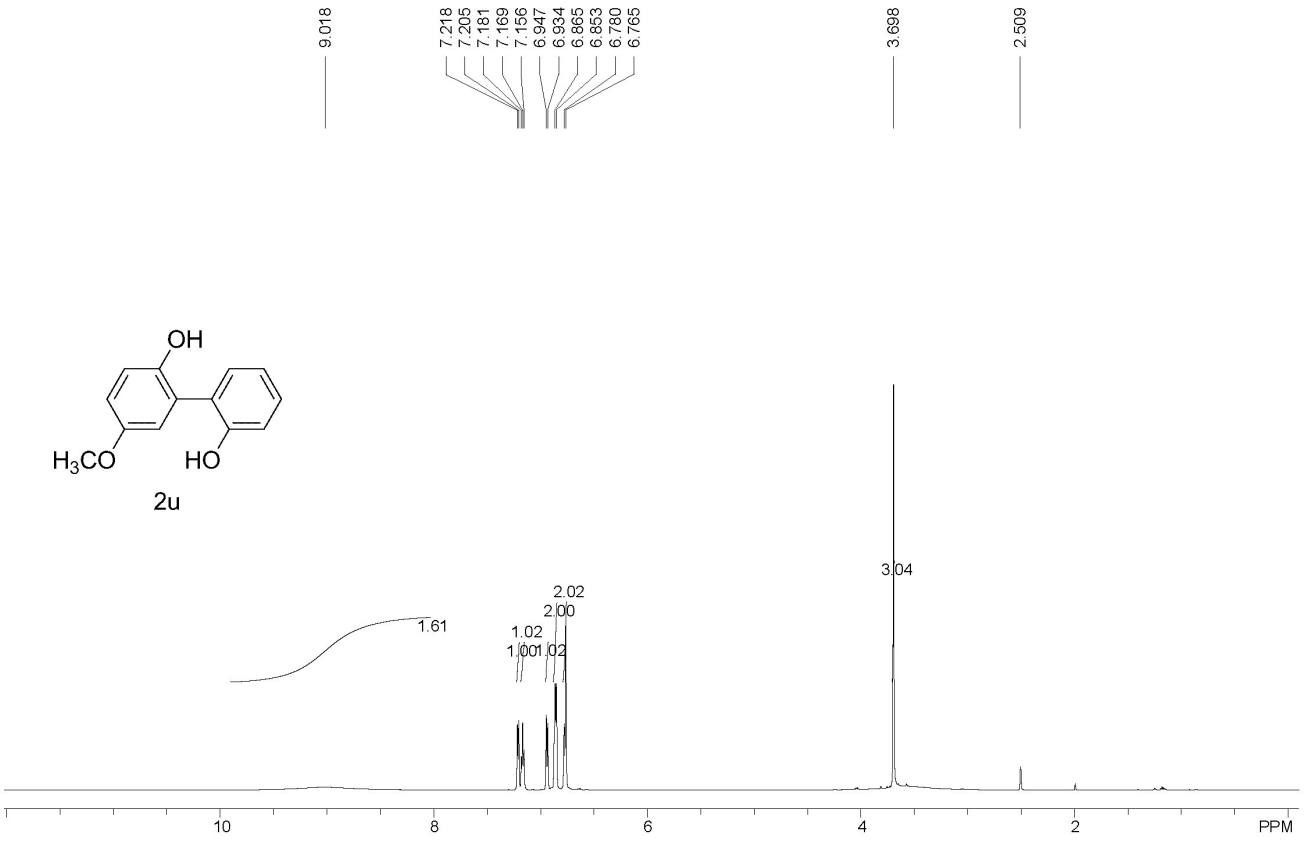
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3.698
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OH
H3CO
HO
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1.02
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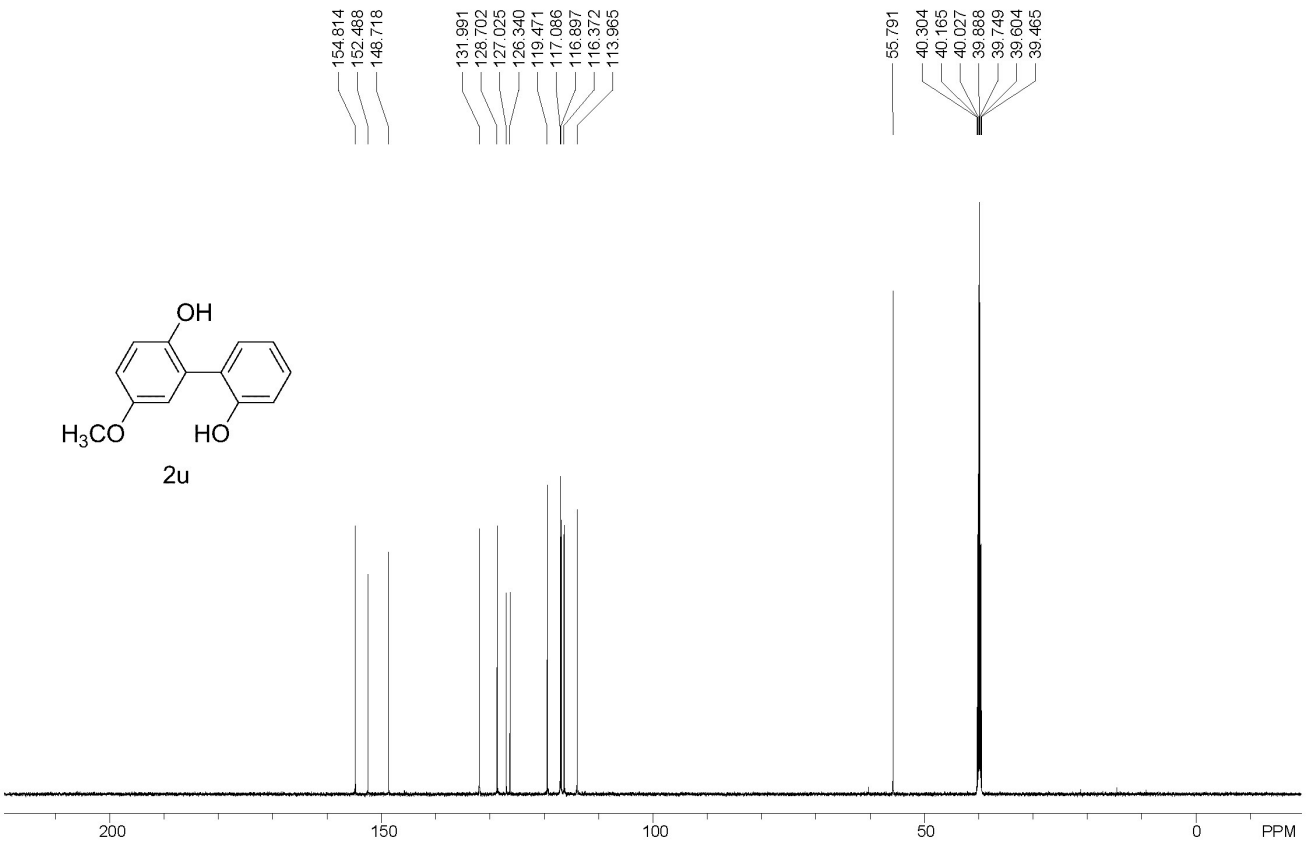
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40.027
39.888
39.749
39.604
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OH
H3CO
HO
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200
150
100
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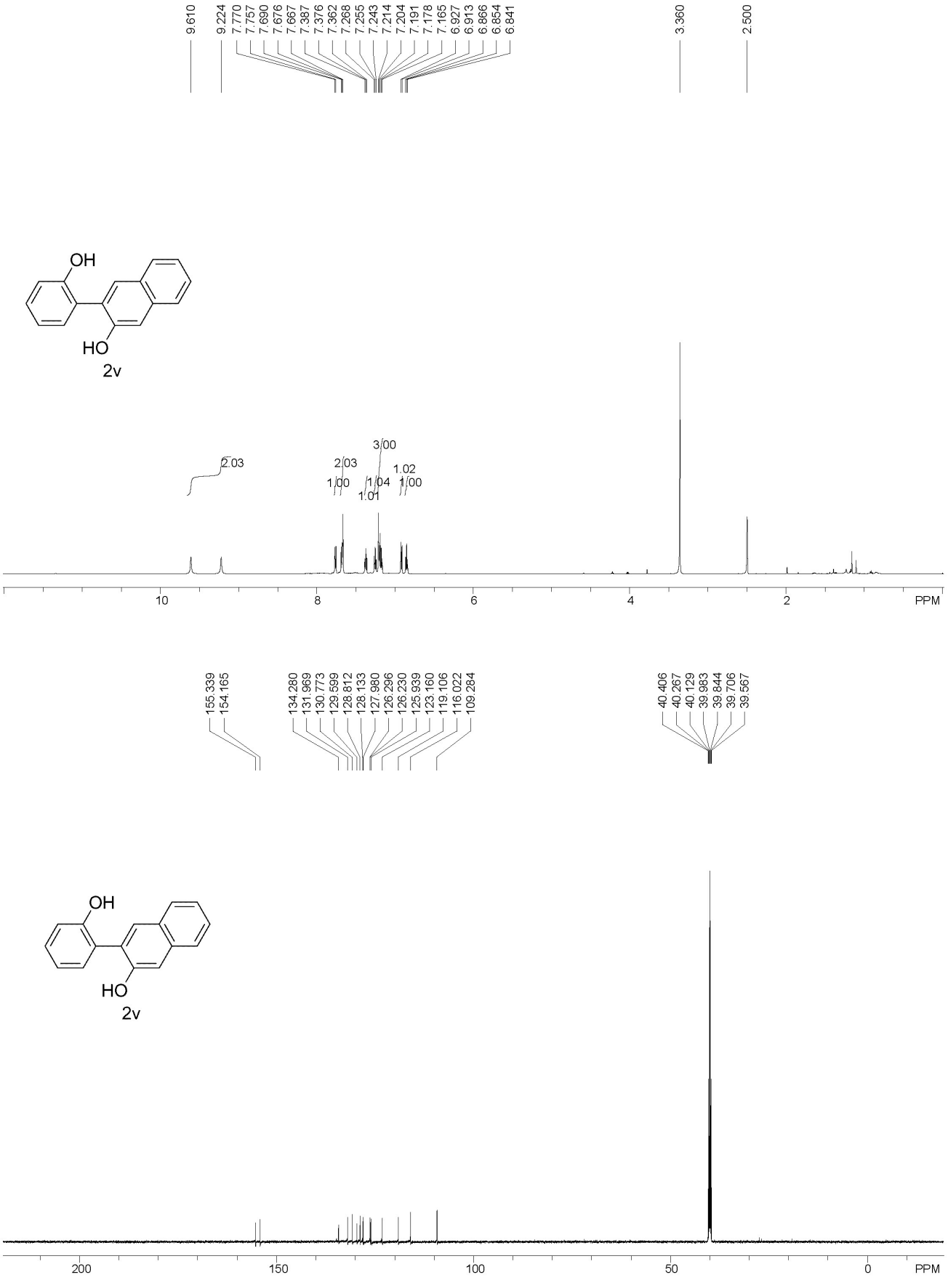
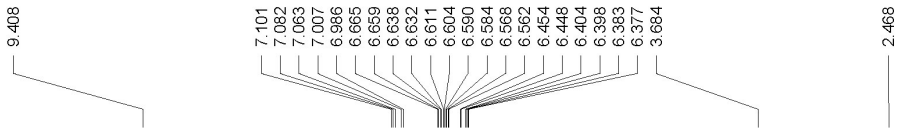
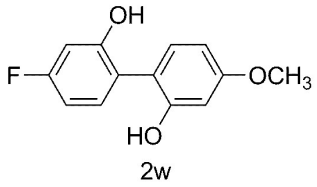
0
PPM

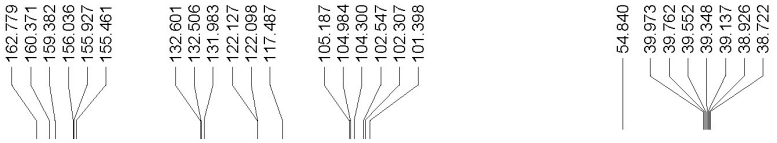

9.610
9.224
7.770
7.757
7.690
7.676
7.667
7.387
7.376
7.362
7.268
7.255
7.243
7.214
7.204
7.191
7.178
7.165
6.927
6.913
6.866
6.854
6.841
3.360
2.500
OH
HO
2v
2.03
2.03
1.00
3.00
1.04
1.01
1.02
1.00
10
8
6
4
2
PPM
155.339
154.165
134.280
131.969
130.773
129.599
128.812
128.133
127.980
126.296
126.230
125.939
123.160
119.106
116.022
109.284
40.406
40.267
40.129
39.983
39.844
39.706
39.567
OH
HO
2v
200
150
100
50
0
PPM


9.408
7.101
7.082
7.063
7.007
6.986
6.665
6.659
6.638
6.632
6.611
6.604
6.590
6.584
6.568
6.562
6.454
6.448
6.404
6.398
6.383
6.377
3.684
2.468


OH
F
OCH3
HO

2w

3.05
1.60
1.02
1.00
1.02
1.00
1.01
1.00
10
8
6
4
2
PPM


162.779
160.371
159.382
156.036
155.927
155.461
132.601
132.506
131.983
122.127
122.098
117.487
105.187
104.984
104.300
102.547
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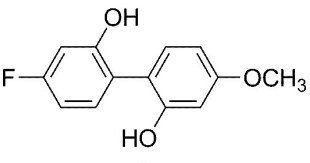
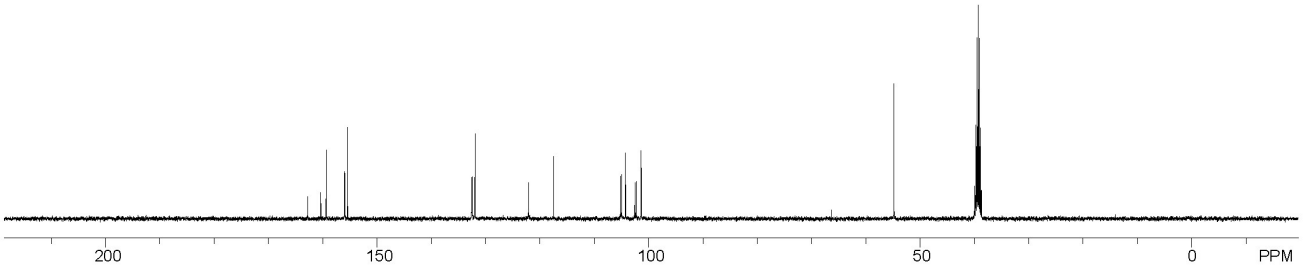
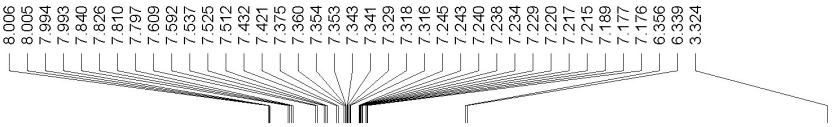
101.398
54.840
39.973
39.762
39.552
39.348
39.137
38.926
38.722

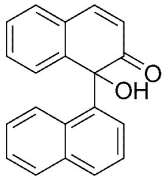

OH
F
OCH3
HO

2w

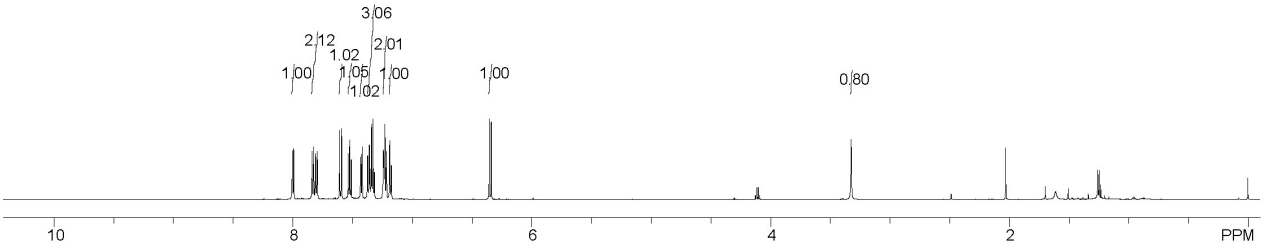

200
150
100
50
0
PPM

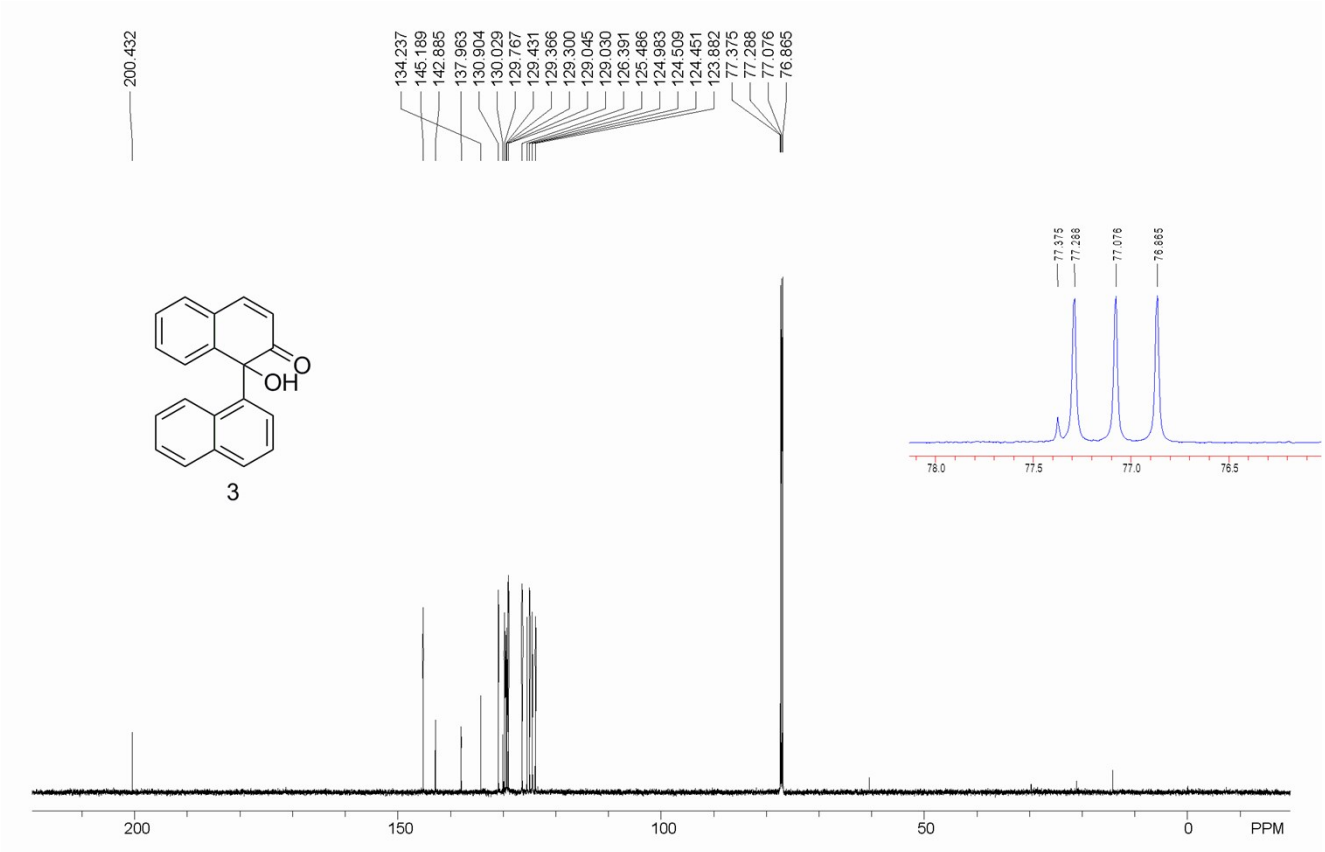
VII. Copies of ^{1}H and ^{13}C NMR Spectra of 3





3





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