

Supporting Information

Hydrobromic Acid-Catalyzed Friedel-Crafts Type Reactions of Naphthols

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A. General Information

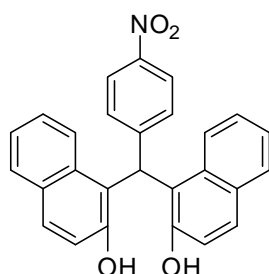
All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. ^1H NMR and ^{13}C NMR spectra were recorded at 25°C on a Varian 500 MHz and 125 MHz, respectively, and TMS as internal standard. IR spectra (KBr) were recorded on a Magna-560 FTIR spectrophotometer in the range of 400–4000 cm^{-1} . Melting points were obtained with a micro melting point XT4A Beijing Keyi electrooptic apparatus and are uncorrected. Elemental analyses were measured on a VarioEL analyzer. Mass spectra were recorded on Agilent 1100 LCMsD mass spectrometer. All reactions were monitored by TLC with Taizhou GF254 silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure. Compound **4b** with dimension 0.15 × 0.13 × 0.11 mm, was glued on a glass fiber. Data were collected on a Rigaku R-axis RAPID IP diffractometer at 293 K using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069\text{\AA}$) and Bruker APEX CCD area-detector in the range $2.50^\circ < \theta < 25.95^\circ$. Empirical absorption correction was applied. The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXS 97 crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps.

B. HBr-catalyzed hydroxyalkylation reaction of **1** with **2**

General procedure for the HBr-catalyzed hydroxyalkylation of naphthols with aldehydes: To a solution of β -naphthol **1a** (288 mg, 2.0 mmol) and 4-nitrobenzaldehyde **2a** (166 mg, 1.1 mmol) in acetonitrile (9.0 mL) was added HBr (47% aqueous)-MeCN solution (1.0 mL, prediluted with MeCN, $M = 0.1 \text{ mol}\cdot\text{L}^{-1}$, 0.1 mmol) at room temperature. After stirring for 7.0 h monitored by TLC, the reaction mixture was poured into water (20 mL) and extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were dried over anhydrous MgSO_4 , filtered, and concentrated. The residue was purified by flash silica gel chromatography (petroleum ether/ether: 5/1, V/V) to give compound **3a** (320 mg, 76%) as a white solid.

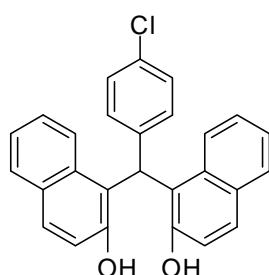
Procedure for the HBr-catalyzed hydroxyalkylation of *p*-cresol with 4-nitrobenzaldehyde: To a solution of *p*-cresol **1e** (216 mg, 2.0 mmol) and 4-nitrobenzaldehyde **2a** (166 mg, 1.1 mmol) in acetonitrile (10 mL) was added HBr (47% aqueous, 0.11 mL, 1.0 mmol) at room temperature. After refluxing for 15 h monitored by TLC, the reaction mixture was poured into water (20 mL) and extracted with CH₂Cl₂ (2 × 20 mL). The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated. The residue was purified by flash silica gel chromatography (petroleum ether/ethyl acetate: 1/4, V/V) to give compound **3k'** (210 mg, 70%) as a white solid.

1,1'-((4-Nitrophenyl)methylene)dinaphthalen-2-ol (3a**)**



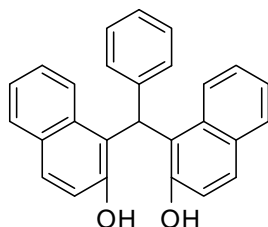
White solid (76%). M.p. 137–139 °C; ¹H NMR (500 MHz, CDCl₃): δ 6.78 (s, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 7.14 (s, 1H), 7.28 (d, *J* = 9.0 Hz, 2H), 7.36 (t, *J* = 7.0 Hz, 2H), 7.41 (t, *J* = 7.0 Hz, 2H), 7.68 (d, *J* = 9.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.5 Hz, 2H), 8.08 (d, *J* = 8.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 42.0, 118.0 (2C), 119.0 (2C), 122.1 (2C), 123.7 (2C), 123.8 (2C), 127.7 (2C), 128.5 (2C), 129.2 (2C), 129.8 (2C), 130.3 (2C), 133.7 (2C), 146.4, 150.1, 151.8 (2C); *v*_{max}/cm⁻¹ (KBr): 3280, 3060, 2955, 1622, 1515, 1344, 813; ES-MS calcd *m/z* 421.1, Found 422.1 [(*M* + 1)]⁺; Anal. Calcd for C₂₇H₁₉NO₄: C, 76.95; H, 4.54; N, 3.32. Found: C, 76.71; H, 4.69; N, 3.22.

1,1'-((4-Chlorophenyl)methylene)dinaphthalen-2-ol (3b**)**¹



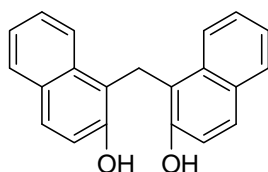
Prepared according to the general procedure from β -naphthol and 4-chlorobenzaldehyde. White solid (79%). M.p. 192–194 °C (lit. 189–190 °C); ^1H NMR (500 MHz, CDCl_3): δ 6.39 (s, 2H), 6.96 (d, $J = 9.0$ Hz, 2H), 7.03 (s, 1H), 7.12 (d, $J = 8.5$ Hz, 2H), 7.25 (d, $J = 7.0$ Hz, 2H), 7.33–7.41 (m, 4H), 7.67 (d, $J = 9.0$ Hz, 2H), 7.79 (d, $J = 7.5$ Hz, 2H), 7.88 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (125 MHz, DMSO): δ 41.5, 119.5 (2C), 120.5 (2C), 122.8 (2C), 124.4 (2C), 126.5 (2C), 128.1 (2C), 129.0 (2C), 129.2 (2C), 129.3 (2C), 129.9, 130.6 (2C), 134.7 (2C), 144.1, 153.2 (2C); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3206, 3061, 2921, 1485, 1357, 1143, 783; ES-MS calcd m/z 410.1, Found 411.1 $[(\text{M} + 1)]^+$; Anal. Calcd for $\text{C}_{27}\text{H}_{19}\text{ClO}_2$: C, 78.92; H, 4.66. Found: C, 79.02; H, 4.52.

1,1'-(Phenylmethylene)dinaphthalen-2-ol (**3c**)²



Prepared according to the general procedure from β -naphthol and benzaldehyde. White solid (39%). M.p. 196–198 °C (lit. 187 °C); ^1H NMR (500 MHz, CDCl_3): δ 5.99 (s, 2H), 6.99 (d, $J = 8.5$ Hz, 2H), 7.07 (s, 1H), 7.24–7.38 (m, 9H), 7.68 (d, $J = 9.0$ Hz, 2H), 7.78 (d, $J = 1.5, 8.0$ Hz, 2H), 7.87 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 42.7, 118.4 (2C), 119.9 (2C), 122.5 (2C), 123.5 (2C), 127.4 (2C), 127.7, 128.4 (2C), 128.9 (2C), 129.7 (2C), 129.9 (2C), 130.1 (2C), 133.5 (2C), 140.4, 152.9 (2C); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3473, 3055, 2922, 1491, 1217, 825, 781; ES-MS calcd m/z 376.2, Found 377.1 $[(\text{M} + 1)]^+$; Anal. Calcd for $\text{C}_{27}\text{H}_{20}\text{O}_2$: C, 86.14; H, 5.36. Found: C, 86.38; H, 5.50.

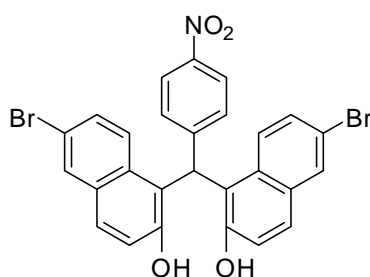
1,1'-Methylenedinaphthalen-2-ol (**3d**)³



Prepared according to the general procedure from β -naphthol and formaldehyde. White solid (99%). M.p. 197–198 °C (lit. 207 °C); ^1H NMR (500 MHz, CDCl_3): δ 4.81 (s, 2H),

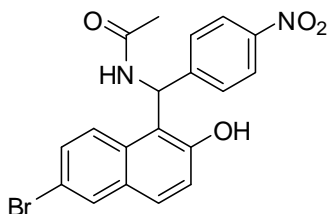
6.49 (s, 2H), 7.03 (d, $J = 8.5$ Hz, 2H), 7.32 (t, $J = 7.0$ Hz, 2H), 7.43 (t, $J = 7.0$ Hz, 2H), 7.63 (d, $J = 9.0$ Hz, 2H), 7.76 (d, $J = 8.0$ Hz, 2H), 8.21 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 21.8, 117.2 (2C), 118.0 (2C), 123.1 (2C), 123.3 (2C), 126.9 (2C), 128.9 (2C), 129.8 (4C), 133.5 (2C), 151.6 (2C); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3323, 3055, 2952, 1621, 1514, 1215, 805; ES-MS calcd m/z 300.1, Found 301.0 $[(M + 1)]^+$; Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{O}_2$: C, 83.98; H, 5.37. Found: C, 83.69; H, 5.29.

1,1'-((4-Nitrophenyl)methylene)bis(6-bromonaphthalen-2-ol) (3e)



Prepared according to the general procedure from 6-bromo- β -naphthol and 4-nitrobenzaldehyde. Light yellow solid (52%). M.p. 128–130 °C; ^1H NMR (500 MHz, CDCl_3): δ 6.80 (s, 2H), 6.98 (s, 1H), 7.06 (d, $J = 9.0$ Hz, 2H), 7.27 (d, $J = 8.5$ Hz, 2H), 7.47 (dd, $J = 2.0, 9.5$ Hz, 2H), 7.66 (d, $J = 8.5$ Hz, 2H), 7.71 (d, $J = 9.5$ Hz, 2H), 7.98 (d, $J = 2.0$ Hz, 2H), 8.11 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 42.2, 117.5 (2C), 118.1 (2C), 120.4 (2C), 123.8 (2C), 123.9 (2C), 128.5 (2C), 129.5 (2C), 130.9 (4C), 131.1 (2C), 132.2 (2C), 146.7, 149.2, 152.3 (2C); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3387, 3069, 2928, 1616, 1501, 1343, 855; ES-MS calcd m/z 579.0, Found 580.0 $[(M + 1)]^+$. Anal. Calcd for $\text{C}_{27}\text{H}_{17}\text{Br}_2\text{NO}_4$: C, 55.99; H, 2.96; N, 2.42. Found: C, 55.61; H, 2.80; N, 2.32.

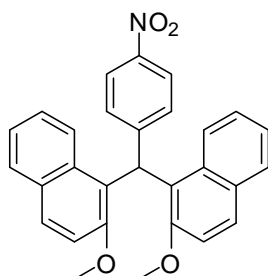
N-((6-Bromo-2-hydroxynaphthalen-1-yl)(4-nitrophenyl)methyl)acetamide (3e')



Prepared according to the general procedure from 6-bromo- β -naphthol and 4-nitrobenzaldehyde. White solid (21%). M.p. 250–252 °C; ^1H NMR (500 MHz, DMSO):

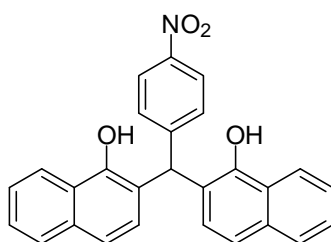
δ 2.01 (s, 3H), 7.12 (d, $J = 7.0$ Hz, 1H), 7.25 (d, $J = 9.0$ Hz, 1H), 7.36 (d, $J = 8.5$ Hz, 2H), 7.49 (d, $J = 8.5$ Hz, 1H), 7.73 (s, 1H), 7.80 (d, $J = 9.0$ Hz, 1H), 8.11 (s, 1H), 8.13 (d, $J = 9.0$ Hz, 2H), 8.62 (d, $J = 7.5$ Hz, 1H), 10.3 (s, 1H); ^{13}C NMR (125 MHz, DMSO): δ 23.0, 48.3, 115.9, 118.7, 120.1, 123.8 (2C), 127.7 (2C), 129.7, 129.9 (2C), 130.3, 130.8, 131.4, 146.5, 151.3, 154.4, 170.3; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3418, 3193, 1645, 1513, 1342, 760; ES-MS calcd m/z 414.0, Found 415.0 $[(M + 1)]^+$; Anal. Calcd for $\text{C}_{19}\text{H}_{15}\text{BrN}_2\text{O}_4$: C, 54.96; H, 3.64; N, 6.75. Found: C, 55.20; H, 3.45; N, 6.62.

1,1'-((4-Nitrophenyl)methylene)bis(2-methoxynaphthalene) (3f)



Prepared according to the general procedure from 2-methoxynaphthalene and 4-nitrobenzaldehyde. White solid (71%). M.p. 213–215 °C; ^1H NMR (500 MHz, DMSO): δ 3.92 (s, 6H), 6.67 (d, $J = 8.0$ Hz, 2H), 6.83 (d, $J = 8.0$ Hz, 2H), 7.07 (s, 1H), 7.44–7.49 (m, 6H), 7.92 (d, $J = 8.0$ Hz, 2H), 8.18–8.22 (m, 4H); ^{13}C NMR (125 MHz, DMSO): δ 47.7, 56.0 (2C), 104.2 (2C), 122.7 (2C), 124.2 (2C), 124.5 (2C), 125.8 (2C), 125.9 (2C), 127.5 (2C), 127.9 (2C), 131.2 (2C), 131.3 (2C), 132.4 (2C), 146.7, 152.4, 154.5 (2C); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3397, 3069, 2957, 1620, 1513, 1341, 1106, 813; ES-MS calcd m/z 449.2, Found 450.3 $[(M + 1)]^+$. Anal. Calcd for $\text{C}_{29}\text{H}_{23}\text{NO}_4$: C, 77.49; H, 5.16; N, 3.12. Found: C, 76.68; H, 5.30; N, 3.02.

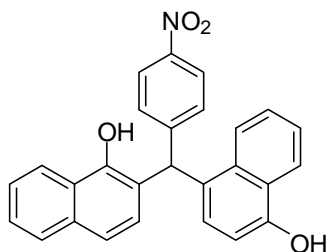
2,2'-((4-Nitrophenyl)methylene)dinaphthalen-1-ol (3g)



Prepared according to the general procedure from α -naphthol and 4-nitrobenzaldehyde.

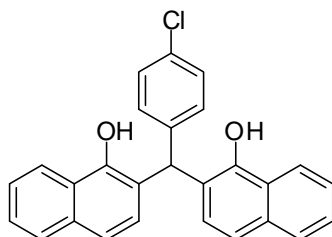
White solid (58%). M.p. 142–144 °C; ^1H NMR (500 MHz, DMSO): δ 6.57 (d, J = 8.0 Hz, 2H), 6.72 (d, J = 8.0 Hz, 2H), 6.97 (s, 1H), 7.39–7.44 (m, 6H), 7.88 (d, J = 8.0 Hz, 2H), 8.15–8.19 (m, 4H), 10.2 (s, 2H); ^{13}C NMR (125 MHz, DMSO): δ 47.7, 107.7 (2C), 123.2 (2C), 124.1 (2C), 124.3 (2C), 125.0 (2C), 125.7 (2C), 127.1 (2C), 128.1 (2C), 129.6 (2C), 131.3 (3C), 132.7 (2C), 146.6, 152.9 (2C); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3406, 3069, 2957, 1514, 1344, 1268, 842; ES-MS calcd m/z 421.1, Found 422.1 $[(M + 1)]^+$; Anal. Calcd for $\text{C}_{27}\text{H}_{19}\text{NO}_4$: C, 76.95; H, 4.54; N, 3.32. Found: C, 76.63; H, 4.42; N, 3.25.

2,4'-((4-Nitrophenyl)methylene)dinaphthalen-1-ol (3g')



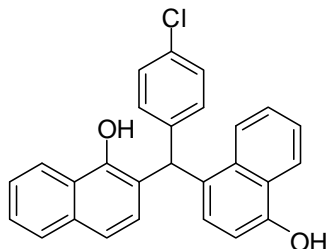
Prepared according to the general procedure from α -naphthol and 4-nitrobenzaldehyde. Yellow solid (23%). M.p. 178–180 °C; ^1H NMR (500 MHz, CDCl_3): δ 5.26 (s, 1H), 5.37 (s, 1H), 6.59 (s, 1H), 6.71 (d, J = 8.0 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 6.89 (d, J = 9.0 Hz, 1H), 7.34 (d, J = 9.0 Hz, 2H), 7.37 (d, J = 8.5 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.49–7.52 (m, 3H), 7.79 (t, J = 7.0 Hz, 1H), 7.85 (d, J = 8.5 Hz, 1H), 8.04 (t, J = 7.0 Hz, 1H), 8.16 (d, J = 9.0 Hz, 2H), 8.28 (d, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 47.2, 107.8, 120.8, 120.9, 122.5, 122.6, 123.7 (2C), 123.8, 124.7, 125.1, 125.5, 125.8, 126.3, 127.2, 127.3, 127.4, 127.9, 129.2, 130.5 (2C), 132.7, 133.7, 146.8, 148.5, 150.8, 151.5; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3391, 3062, 1693, 1510, 1339, 676; ES-MS calcd m/z 421.1, Found 422.1 $[(M + 1)]^+$; Anal. Calcd for $\text{C}_{27}\text{H}_{19}\text{NO}_4$: C, 76.95; H, 4.54; N, 3.32. Found: C, 76.69; H, 4.53; N, 3.28.

2,2'-((4-Chlorophenyl)methylene)dinaphthalen-1-ol (3h)



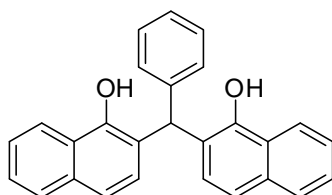
Prepared according to the general procedure from α -naphthol and 4-chlorobenzaldehyde. White solid (51%). M.p. 100–102 °C; ^1H NMR (500 MHz, DMSO): δ 6.57 (d, J = 8.0 Hz, 2H), 6.72 (d, J = 8.0 Hz, 2H), 6.79 (s, 1H), 7.16 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 7.38–7.41 (m, 4H), 7.87 (d, J = 8.0 Hz, 2H), 8.17 (t, J = 8.0 Hz, 2H), 10.1 (s, 2H); ^{13}C NMR (125 MHz, DMSO): δ 47.3, 107.7 (2C), 123.2 (2C), 124.3 (2C), 124.9 (2C), 125.7 (2C), 126.9 (2C), 127.9 (2C), 128.8 (2C), 130.4 (2C), 131.3, 131.9 (2C), 132.7 (2C), 143.7, 152.7 (2C); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3359, 3066, 2973, 1584, 1299, 1049, 761; ES-MS calcd m/z 410.1, Found 411.1 [(M + 1)] $^+$; Anal. Calcd for $\text{C}_{27}\text{H}_{19}\text{ClO}_2$: C, 78.92; H, 4.66. Found: C, 78.75; H, 4.54.

2,4'-((4-Chlorophenyl)methylene)dinaphthalen-1-ol (3h')



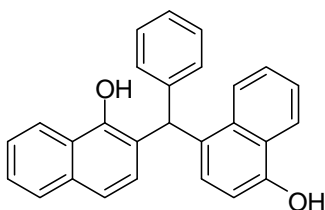
Prepared according to the general procedure from α -naphthol and 4-chlorobenzaldehyde. Light yellow oil (17%). ^1H NMR (500 MHz, CDCl_3): δ 5.22 (s, 1H), 5.35 (s, 1H), 6.39 (s, 1H), 6.69 (d, J = 7.5 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 8.5 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.5 Hz, 1H), 7.41 (t, J = 7.0 Hz, 1H), 7.47 (t, J = 8.5 Hz, 3H), 7.77 (t, J = 5.0 Hz, 1H), 7.86 (d, J = 8.5 Hz, 1H), 8.09 (d, J = 5.5 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 47.1, 107.8, 120.6, 121.3, 122.5, 123.1, 123.9, 124.9, 125.0, 125.3, 125.5, 126.1, 127.1, 127.2, 127.6, 127.7, 128.9 (2C), 129.8, 130.9 (2C), 132.7, 132.8, 133.6, 140.9, 148.6, 151.3; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3448, 3062, 2952, 1655, 1587, 1302, 845; ES-MS calcd m/z 410.1, Found 411.0 [(M + 1)] $^+$; Anal. Calcd for $\text{C}_{27}\text{H}_{19}\text{ClO}_2$: C, 78.92; H, 4.66. Found: C, 78.79; H, 4.58.

2,2'-(Phenylmethylene)dinaphthalen-1-ol (3i)



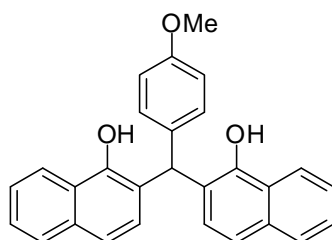
Prepared according to the general procedure from α -naphthol and benzaldehyde. White solid (45%). M.p. 72–74 °C; ^1H NMR (500 MHz, CDCl_3): δ 5.16 (s, 2H), 6.63 (d, $J = 8.0$ Hz, 2H), 6.69 (d, $J = 8.0$ Hz, 2H), 6.73 (s, 1H), 7.14 (d, $J = 7.0$ Hz, 2H), 7.22 (d, $J = 7.5$ Hz, 3H), 7.37 (t, $J = 7.5$ Hz, 2H), 7.45 (t, $J = 7.5$ Hz, 2H), 7.88 (d, $J = 8.5$ Hz, 2H), 8.23 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 48.7, 107.8 (2C), 122.3 (2C), 124.1 (2C), 124.7 (2C), 125.0, 126.2 (2C), 126.6 (2C), 127.7 (2C), 128.3 (2C), 129.8 (2C), 132.2 (2C), 132.8 (2C), 144.0, 150.7 (2C); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3391, 3061, 2978, 1625, 1582, 1377, 759; ES-MS calcd m/z 376.2, Found 377.1 $[(M + 1)]^+$; Anal. Calcd for $\text{C}_{27}\text{H}_{20}\text{O}_2$: C, 86.14; H, 5.36. Found: C, 86.01; H, 5.27.

2,4'-(Phenylmethylene)dinaphthalen-1-ol (3i')



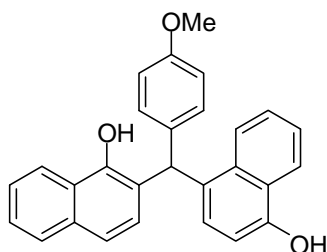
Prepared according to the general procedure from α -naphthol and benzaldehyde. White solid (32%). M.p. 100–102 °C; ^1H NMR (500 MHz, DMSO): δ 6.72–6.76 (m, 4H), 6.90 (s, 1H), 7.11–7.44 (m, 9H), 7.76 (s, 1H), 7.91 (s, 1H), 8.17–8.22 (m, 2H), 9.50 (s, 1H), 10.1 (s, 1H); ^{13}C NMR (125 MHz, DMSO): δ 45.5, 107.6, 119.5, 122.7, 123.1, 124.4, 124.7, 125.4, 125.6, 125.7, 125.8, 126.1, 126.5, 126.7, 127.6, 128.1, 128.3, 128.7 (2C), 129.9 (2C), 130.8, 133.0, 133.6, 144.6, 149.4, 152.5; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3392, 3059, 2979, 1656, 1586, 1378, 698; ES-MS calcd m/z 376.2, Found 377.2 $[(M + 1)]^+$. Anal. Calcd for $\text{C}_{27}\text{H}_{20}\text{O}_2$: C, 86.14; H, 5.36. Found: C, 85.98; H, 5.29.

2,2'-((4-Methoxyphenyl)methylene)dinaphthalen-1-ol (3j)



Prepared according to the general procedure from α -naphthol and 4-methoxybenzaldehyde. White solid (27%). M.p. 148–150 °C; ^1H NMR (500 MHz, CDCl_3): δ 3.77 (s, 3H), 5.26 (s, 2H), 6.61 (d, $J = 7.5$ Hz, 2H), 6.68 (d, $J = 5.5$ Hz, 2H), 6.70 (s, 1H), 6.80 (d, $J = 8.5$ Hz, 2H), 7.03 (d, $J = 8.5$ Hz, 2H), 7.36 (t, $J = 7.0$ Hz, 2H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.88 (d, $J = 8.5$ Hz, 2H), 8.23 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 47.9, 55.2, 107.8 (2C), 113.8 (2C), 122.2 (2C), 124.2 (2C), 124.8 (4C), 126.7 (2C), 127.5 (2C), 130.7 (2C), 132.8 (2C), 132.9 (2C), 135.9, 150.3 (2C), 157.9; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3386, 3065, 2954, 1509, 1242, 759, 416; ES-MS calcd m/z 406.2, Found 407.2 $[(M + 1)]^+$. Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{O}_3$: C, 82.74; H, 5.46. Found: C, 82.55; H, 5.32.

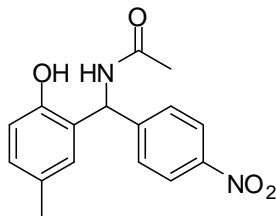
2,4'-((4-Methoxyphenyl)methylene)dinaphthalen-1-ol (3j')



Prepared according to the general procedure from α -naphthol and 4-methoxybenzaldehyde. White solid (31%). M.p. 62–63 °C; ^1H NMR (500 MHz, CDCl_3): δ 3.79 (s, 3H), 5.29 (s, 2H), 6.32 (s, 1H), 6.69 (d, $J = 8.0$ Hz, 1H), 6.85–6.87 (m, 3H), 6.93 (d, $J = 8.5$ Hz, 1H), 7.09 (d, $J = 8.5$ Hz, 2H), 7.32 (d, $J = 8.5$ Hz, 1H), 7.41 (d, $J = 7.5$ Hz, 1H), 7.46–7.49 (m, 3H), 7.75 (t, $J = 6.0$ Hz, 1H), 7.88 (d, $J = 8.5$ Hz, 1H), 8.13 (t, $J = 6.0$ Hz, 1H), 8.25 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 47.3, 55.2, 107.9, 114.3 (2C), 120.3, 121.6, 122.4, 123.7, 124.2, 124.9, 125.1, 125.2, 125.3, 125.9, 127.0, 127.2, 127.5, 128.0, 130.5 (2C), 130.6, 132.9, 133.6, 133.9, 148.8, 151.1, 158.6; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3402, 3064, 2955, 1659, 1508, 1247, 765; ES-MS calcd m/z 406.2, Found 407.2 $[(M + 1)]^+$. Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{O}_3$: C, 82.74; H, 5.46. Found: C, 82.61; H,

5.34.

N-((2-Hydroxy-5-methylphenyl)(4-nitrophenyl)methyl)acetamide (3k')

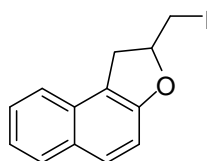


Prepared according to the general procedure from *p*-cresol and 4-nitrobenzaldehyde. White solid (70%). M.p. 217–218 °C; ¹H NMR (500 MHz, DMSO): δ 1.94 (s, 3H), 2.17 (s, 3H), 6.44 (d, *J* = 8.5 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 7.01 (s, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 8.16 (d, *J* = 9.0 Hz, 2H), 8.66 (d, *J* = 8.5 Hz, 1H), 9.49 (s, 1H); ¹³C NMR (125 MHz, DMSO): δ 20.8, 23.1, 50.5, 115.8, 123.9 (2C), 127.5, 128.1, 128.5 (2C), 128.8, 129.4, 146.7, 151.5, 152.5, 169.3; $\nu_{\max}/\text{cm}^{-1}$ (KBr): 3319, 3076, 2946, 1512, 1374, 1350, 887; ES-MS calcd *m/z* 300.1, Found 301.1 [(*M* + 1)]⁺. Anal. Calcd for C₁₆H₁₆N₂O₄: C, 63.99; H, 5.37; N, 9.33. Found: C, 64.20; H, 5.22; N, 9.21.

C. HBr -catalyzed hydroxyalkylation-iodocyclization of 1 with allyl iodide

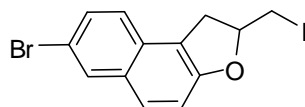
General procedure for the hydrobromic acid-catalyzed alkylation-cyclization of β-naphthols 1 with allyl iodide: To a solution of β-naphthol **1a** (144 mg, 1.0 mmol) and allyl iodide (0.92 mL, 10 mmol) in acetonitrile (10 mL) was added HBr (47% aqueous, 0.11 mL, 1.0 mmol) at room temperature. The reaction was allowed to proceed at 60 °C and complete in 8.0 h. The above mixture was quenched with water (20 mL), then extracted with CH₂Cl₂ (3 × 20 mL). The combined organic extracts were washed with water, dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether) to give coupling product 2-(iodomethyl)-1,2-dihydronaphtho[2,1-*b*]furan **4a** (217 mg, 70%) as a light yellow oil.

2-(Iodomethyl)-1,2-dihydronaphtho[2,1-*b*]furan (4a)⁴



White solid (70%). M.p. 58–60 °C (lit. 58–60 °C); ^1H NMR (500 MHz, CDCl_3): δ 3.29 (dd, $J = 6.5, 16.5$ Hz, 1H), 3.40 (dd, $J = 7.5, 10.0$ Hz, 1H), 3.51 (dd, $J = 5.0, 10.0$ Hz, 1H), 3.65 (dd, $J = 9.0, 16.0$ Hz, 1H), 5.08–5.11 (m, 1H), 7.09 (d, $J = 8.5$ Hz, 1H), 7.31 (q, $J = 7.0$ Hz, 1H), 7.47–7.50 (m, 1H), 7.59 (d, $J = 8.5$ Hz, 1H), 7.69 (d, $J = 9.0$ Hz, 1H), 7.80 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 9.33, 34.9, 82.3, 111.9, 117.3, 122.6, 123.0, 126.7, 128.7, 129.1, 129.2, 130.5, 156.5. $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3056, 2951, 1628, 1516, 1242, 957, 808; ES-MS calcd m/z 310.0, Found 311.0 $[(M + 1)]^+$.

7-Bromo-2-(iodomethyl)-1,2-dihydronaphtho[2,1-b]furan (4b)



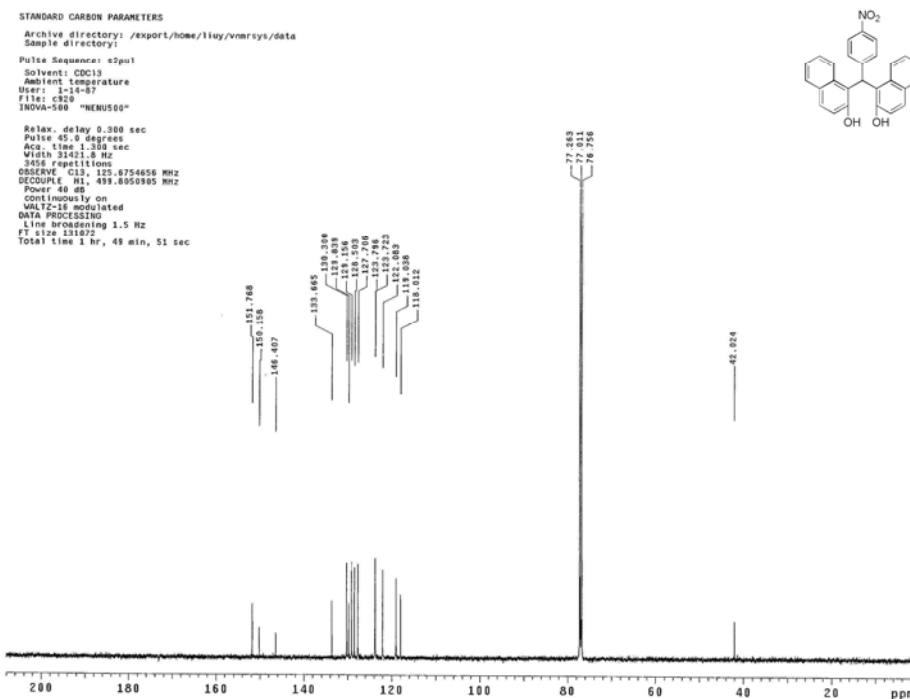
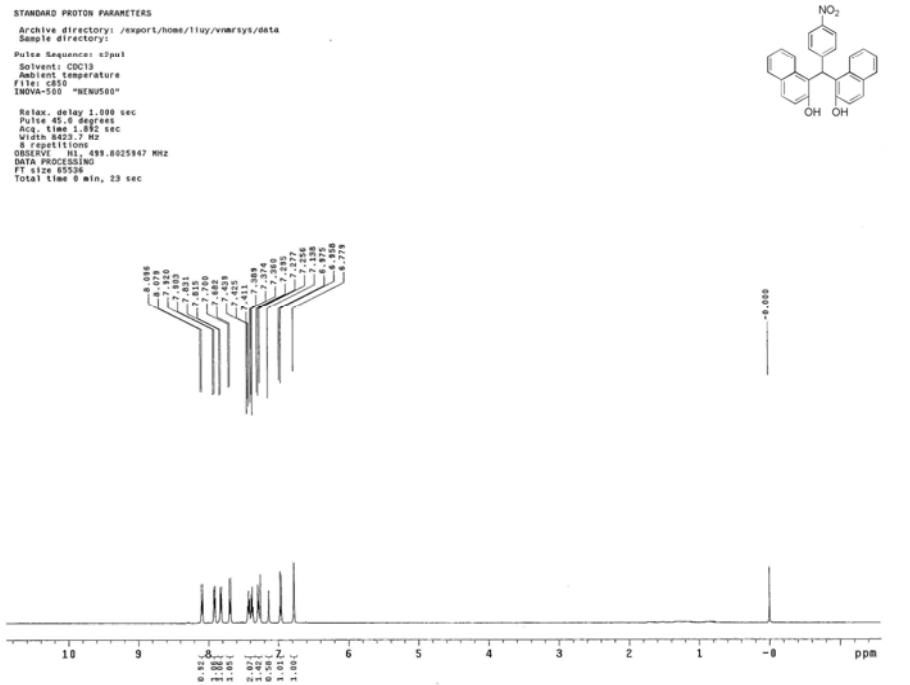
Prepared according to the general procedure from 6-bromo β -naphthol. Colorless solid (52%). M.p. 135–137 °C; ^1H NMR (500 MHz, CDCl_3): δ 3.26 (dd, $J = 6.5, 16.0$ Hz, 1H), 3.39 (dd, $J = 7.5, 10.0$ Hz, 1H), 3.50 (dd, $J = 5.0, 10.0$ Hz, 1H), 3.63 (dd, $J = 9.5, 15.5$ Hz, 1H), 5.07–5.09 (m, 1H), 7.10 (d, $J = 8.5$ Hz, 1H), 7.45 (d, $J = 9.0$ Hz, 1H), 7.53 (dd, $J = 2.0, 2.0$ Hz, 1H), 7.59 (d, $J = 9.0$ Hz, 1H), 7.95 (d, $J = 2.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 8.8, 34.8, 82.3, 112.9, 116.5, 117.6, 124.3, 128.3, 129.0, 129.9, 130.3, 130.5, 156.9; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3038, 2936, 1652, 1502, 1233, 957, 803; ES-MS calcd m/z 389.0, Found 390.0 $[(M + 1)]^+$. Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{BrIO}$: C, 40.14; H, 2.59. Found: C, 40.01; H, 2.48.

D. References

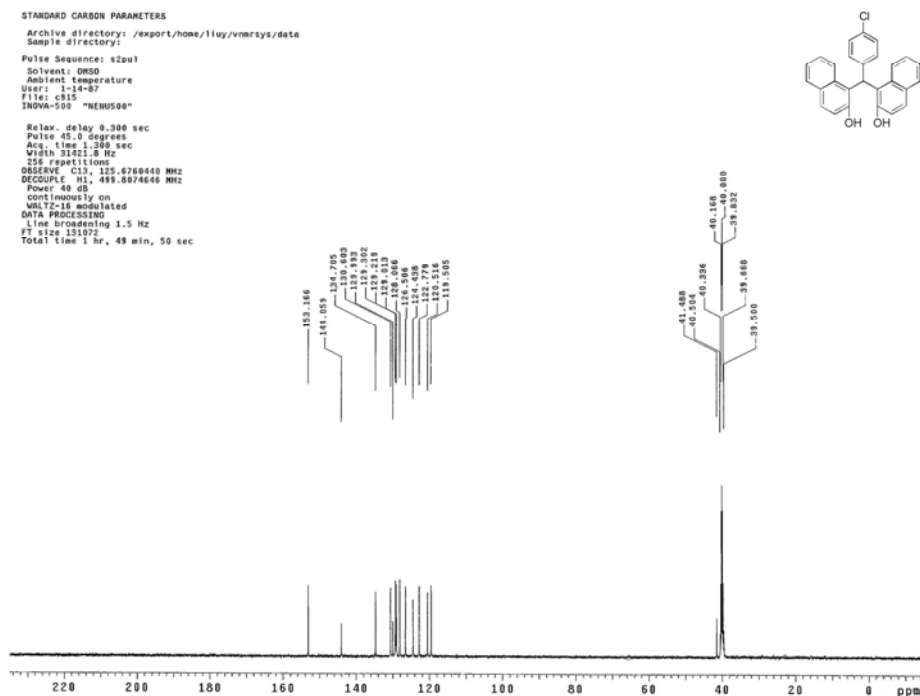
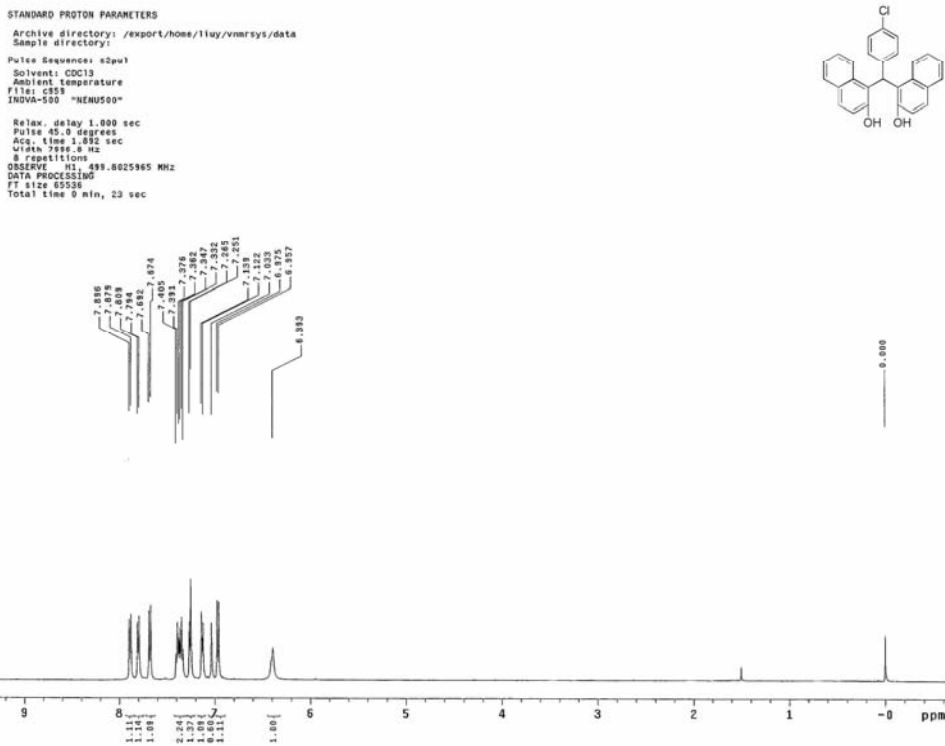
1. O. Dischendorfer, E. Fransevic, *Monatshefte Fuer Chem.*, 1932, **59**, 93.
2. T. Kito, K. Yoshinaga, S. Ohkami, K. Ikeda, M. Yamaye, *J. Org. Chem.*, 1985, **50**, 628.
3. T. Kito, K. Yoshinaga, M. Yamaye, H. Mizobe, *J. Org. Chem.*, 1991, **56**, 3336.
4. Q. Z. Zhou, C. L. He, Z. C. Chen, *Chin. Chem. Lett.*, 2008, **19**, 661.

E. Copies of ^1H NMR and ^{13}C NMR spectra of compounds 3 and 4

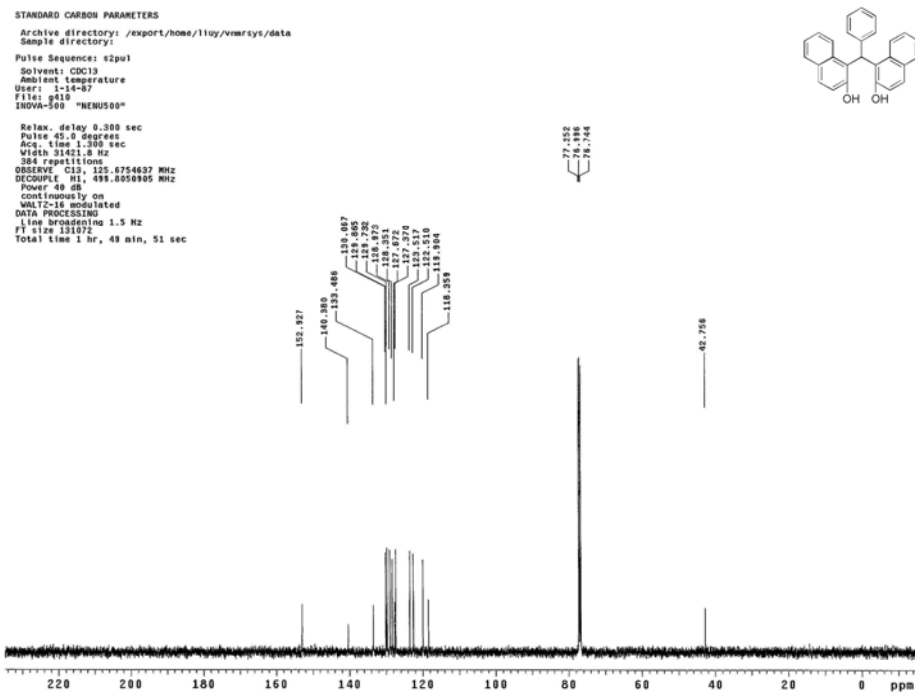
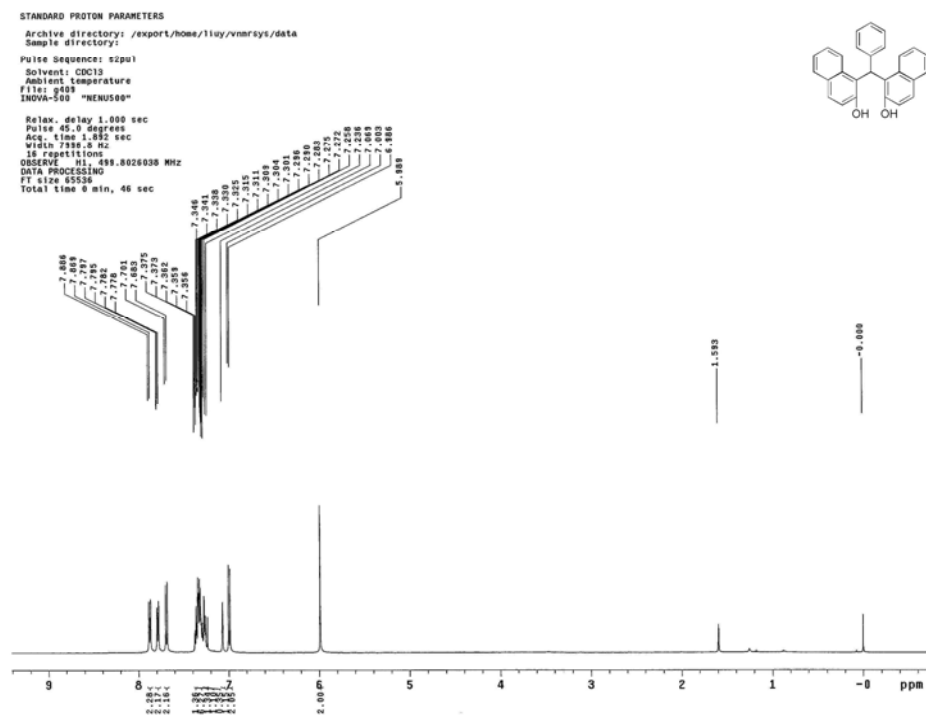
3a



3b

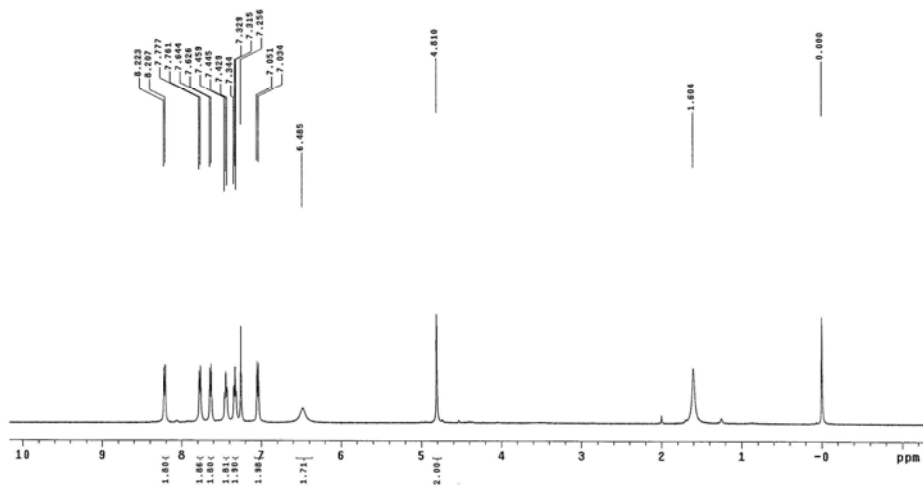
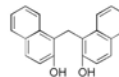


3c

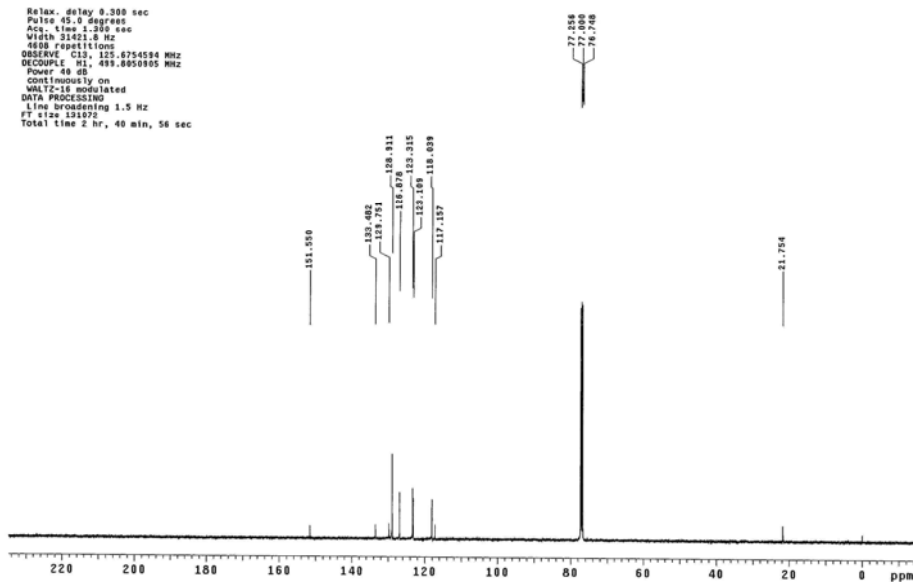
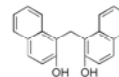


3d

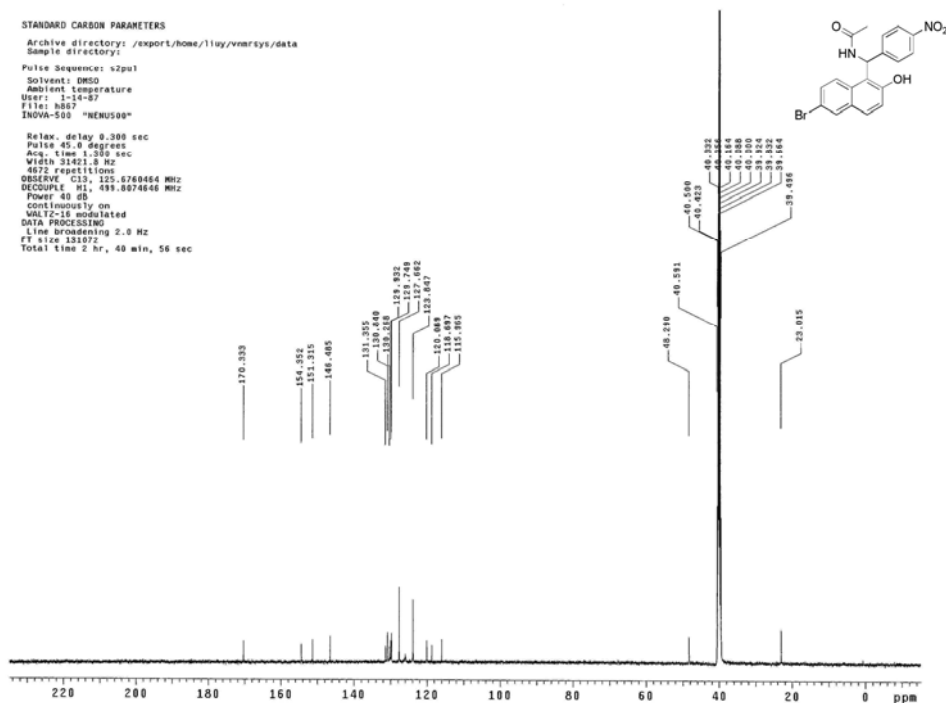
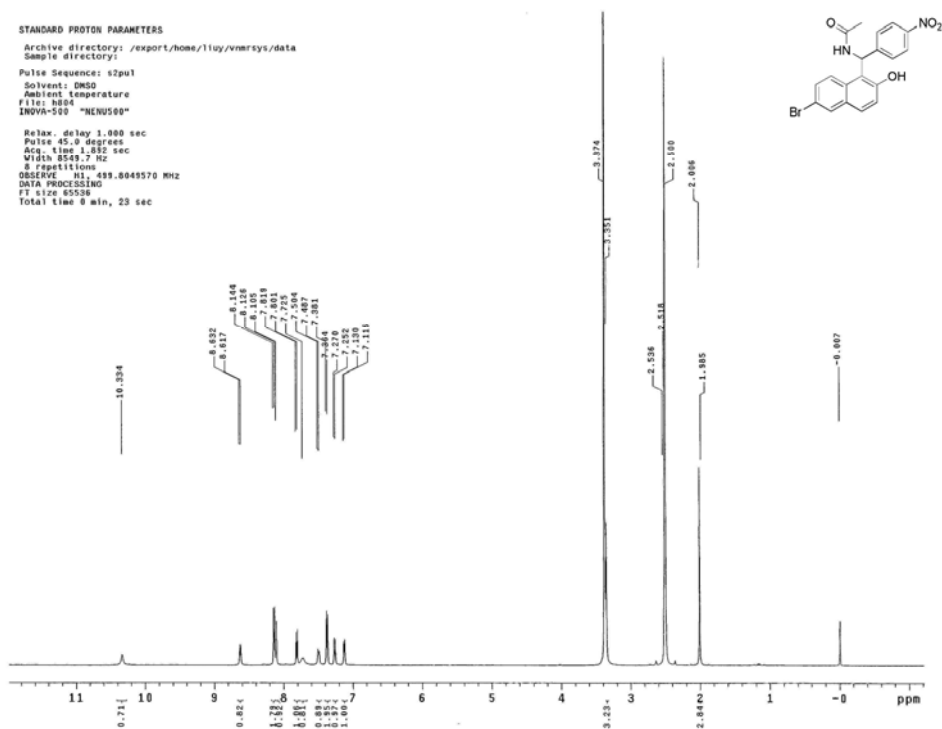
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DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec



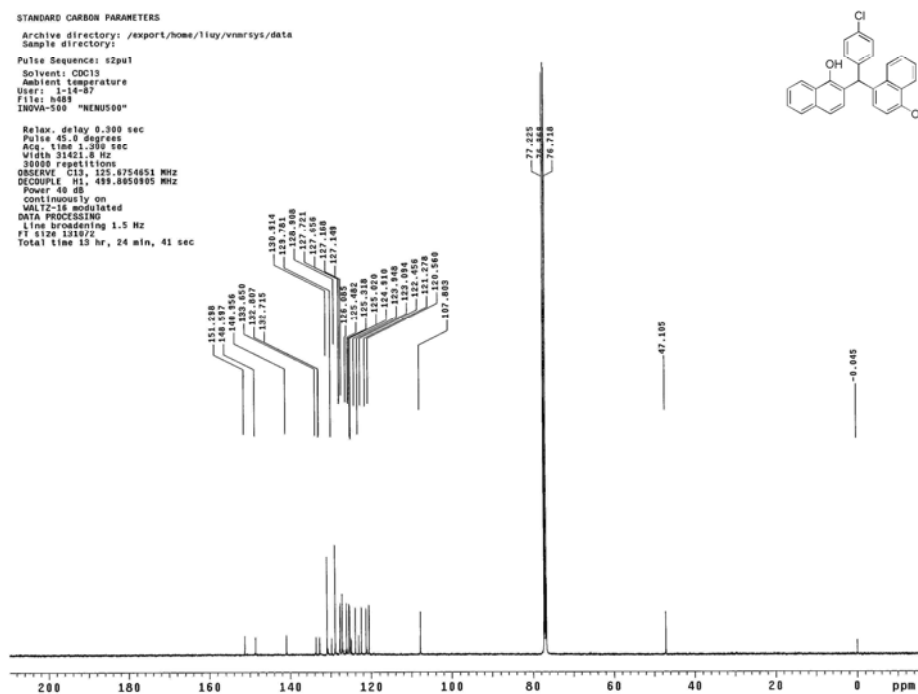
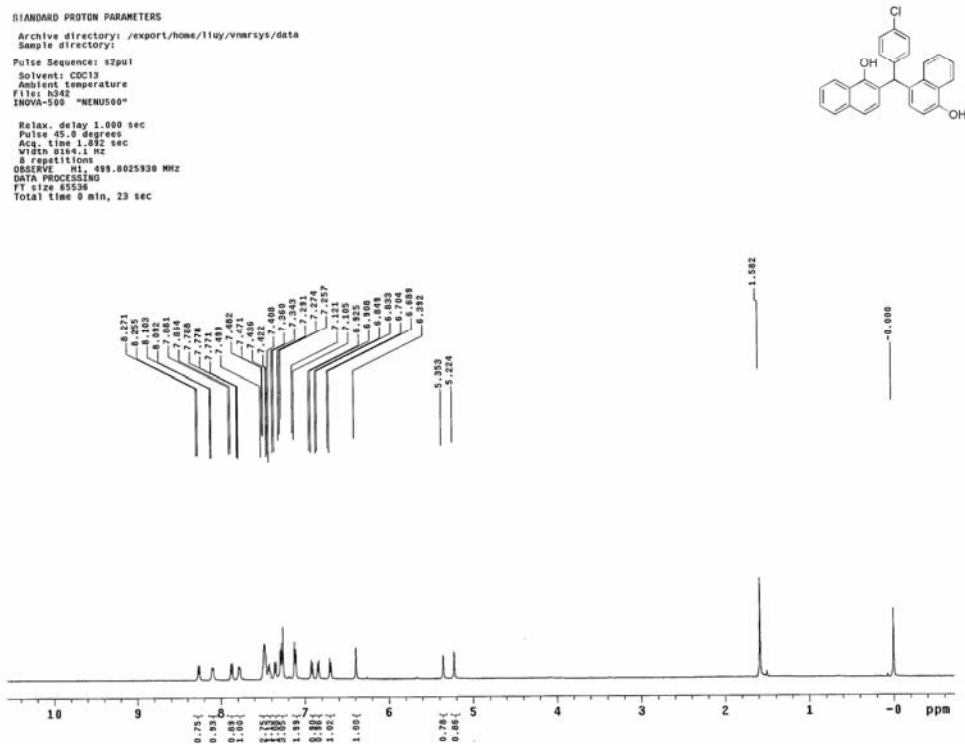
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User: 114-07
File: h32
INOVA-500 "NENU500"
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Pulse 45.0 degrees
Acq. time 1.200 sec
Width 21421.0 Hz
400 repetitions
OBSERVE C15, 125.6754584 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
Continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 191976
Total time 2 hr, 40 min, 56 sec



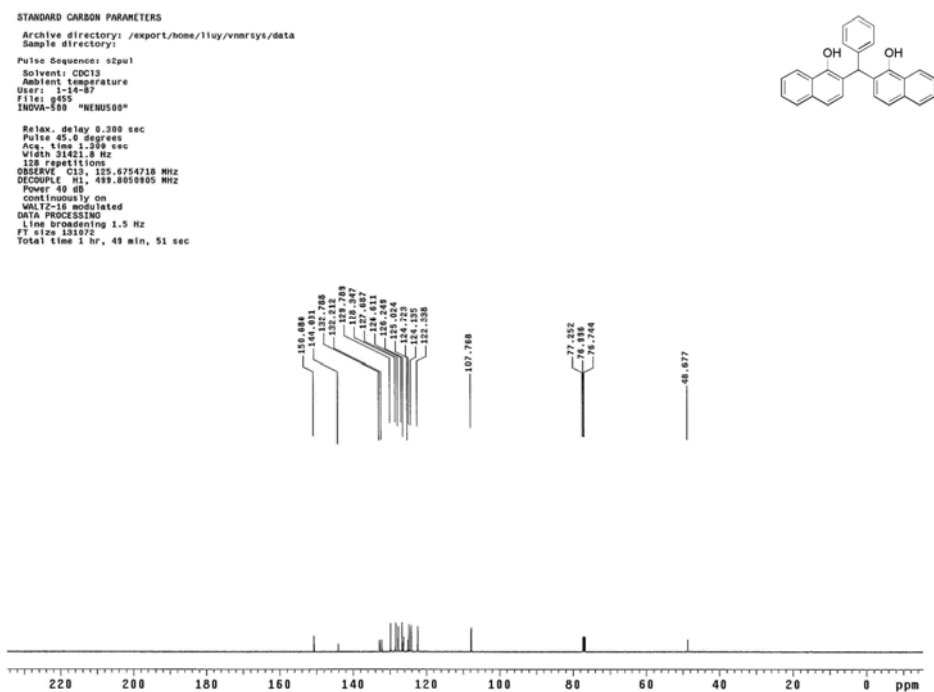
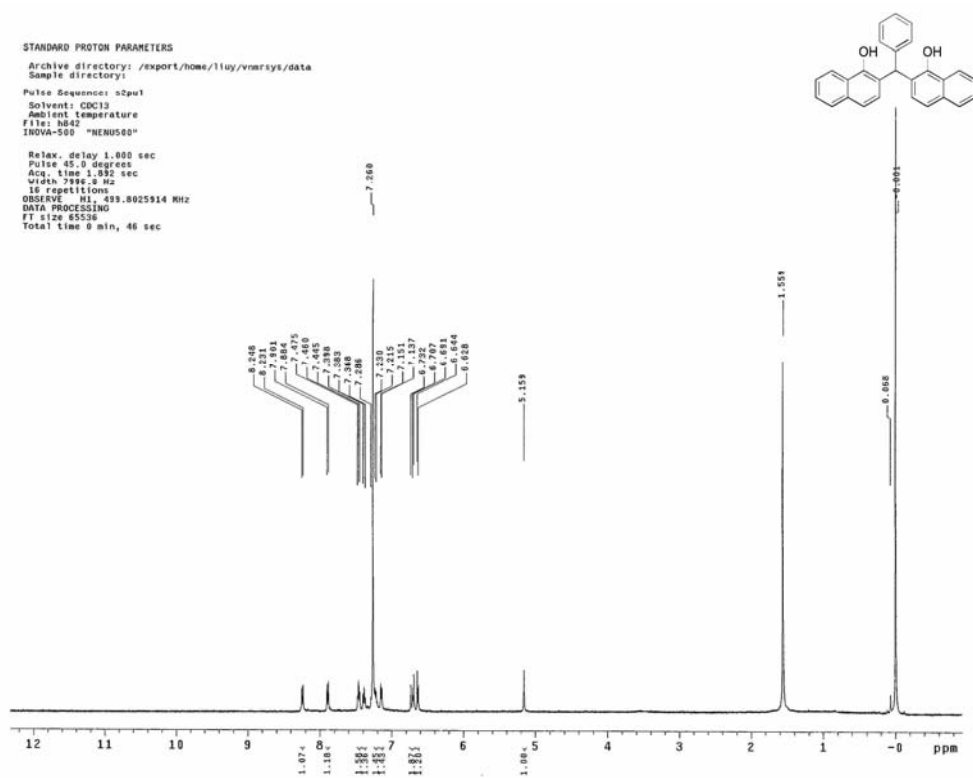
3e'



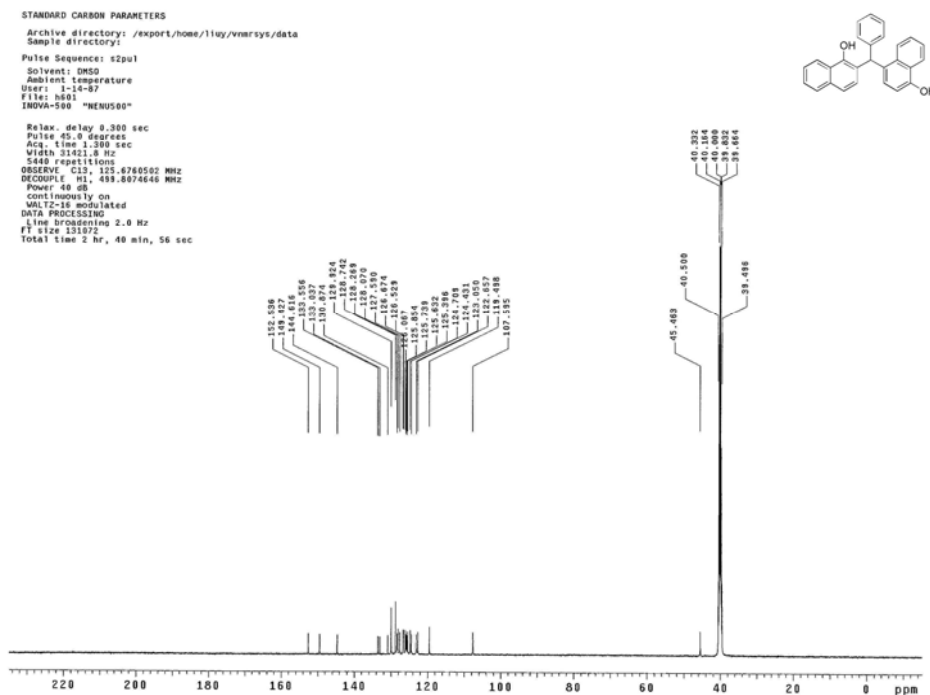
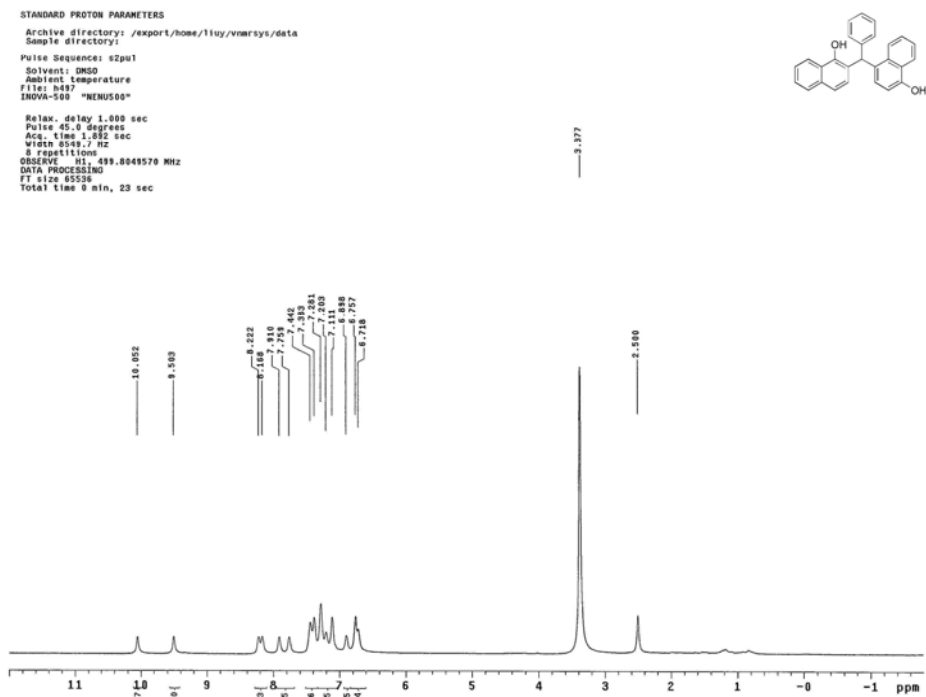
3h'



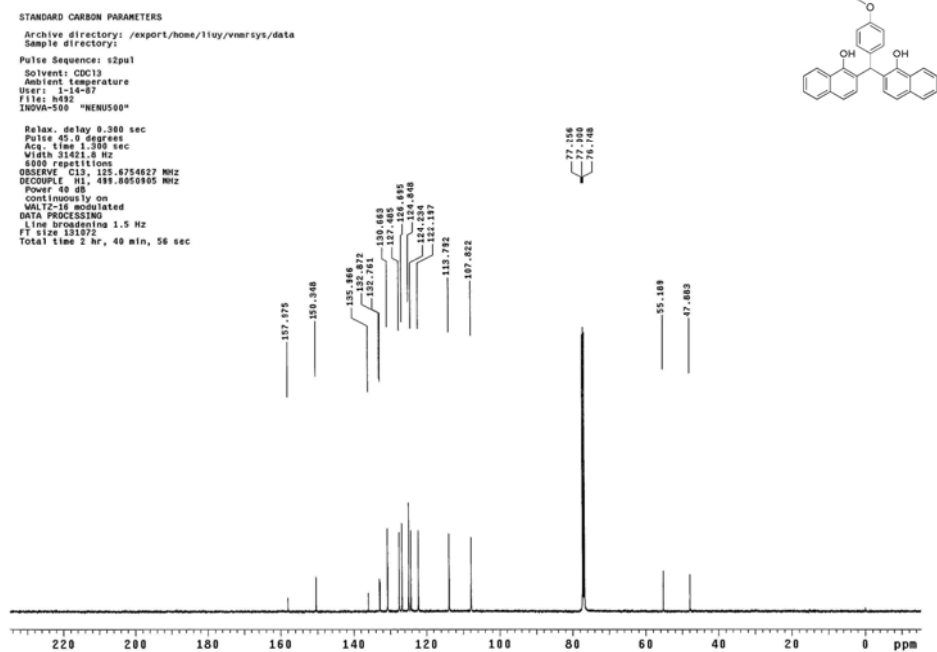
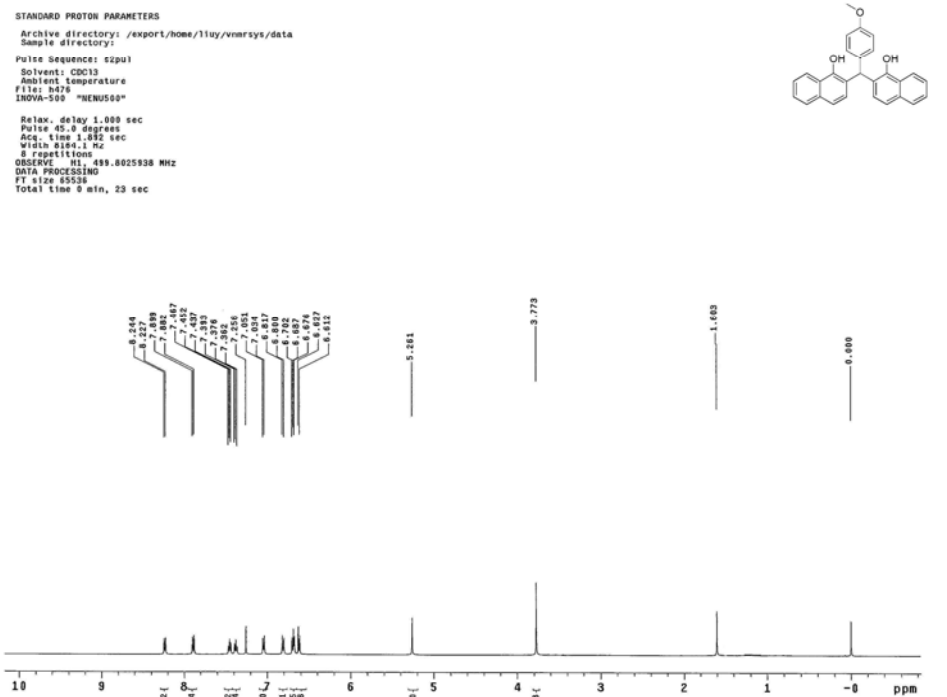
3i



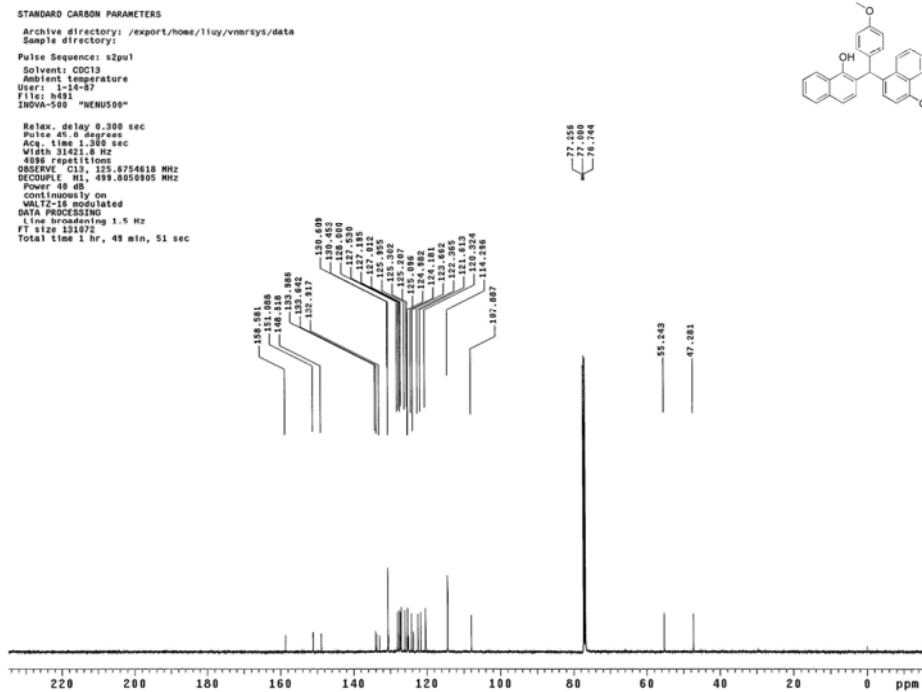
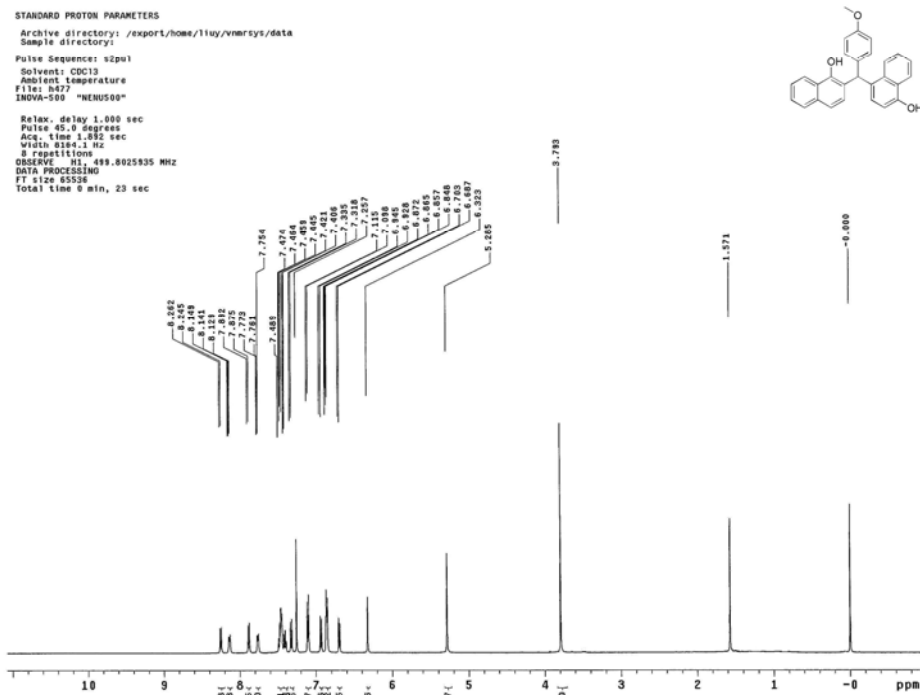
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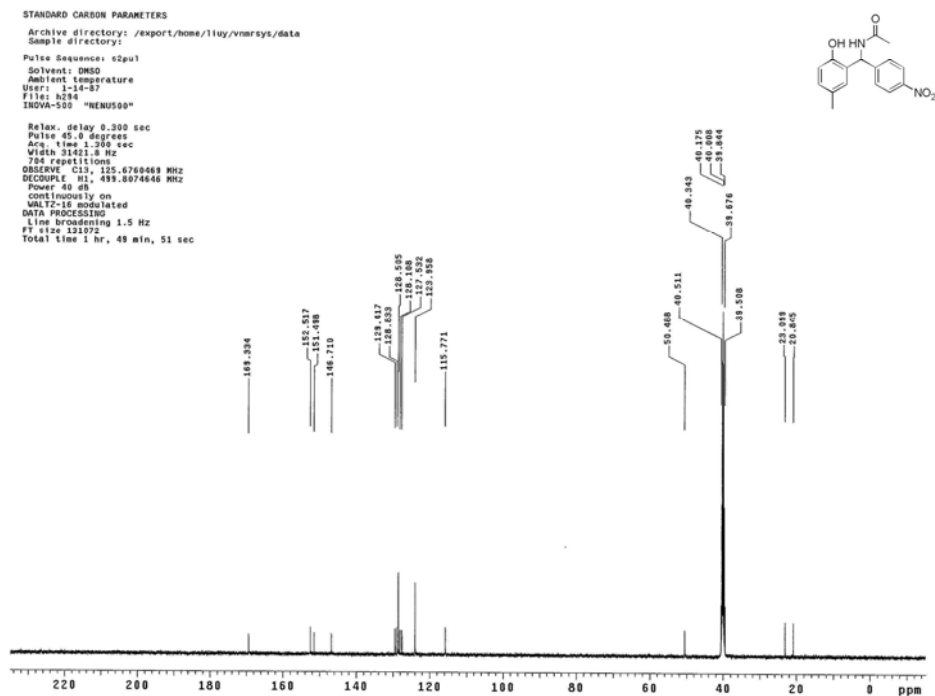
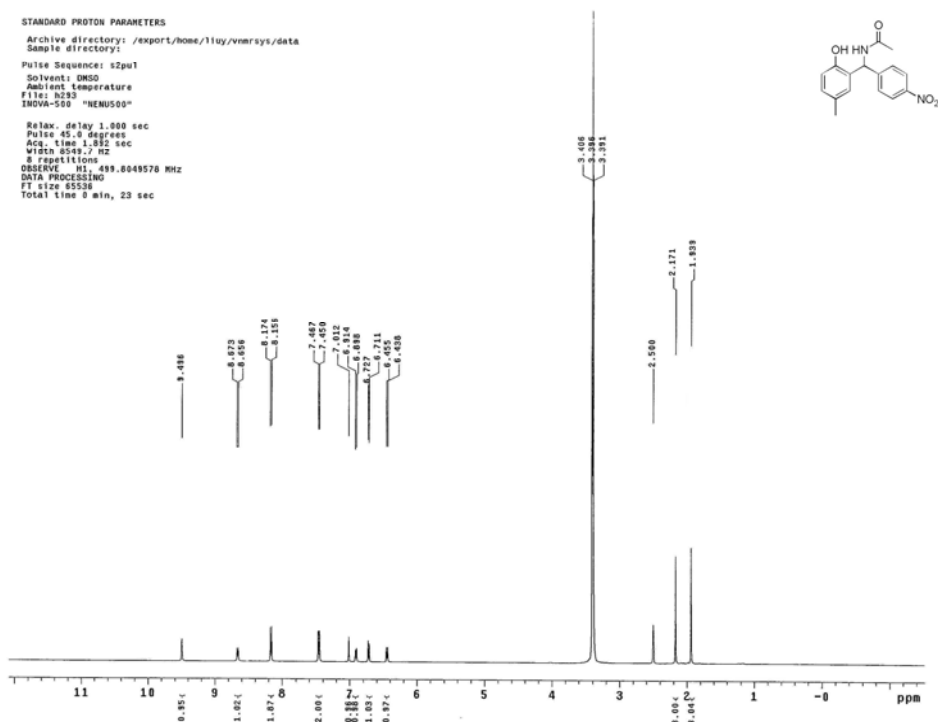
3j



3j'

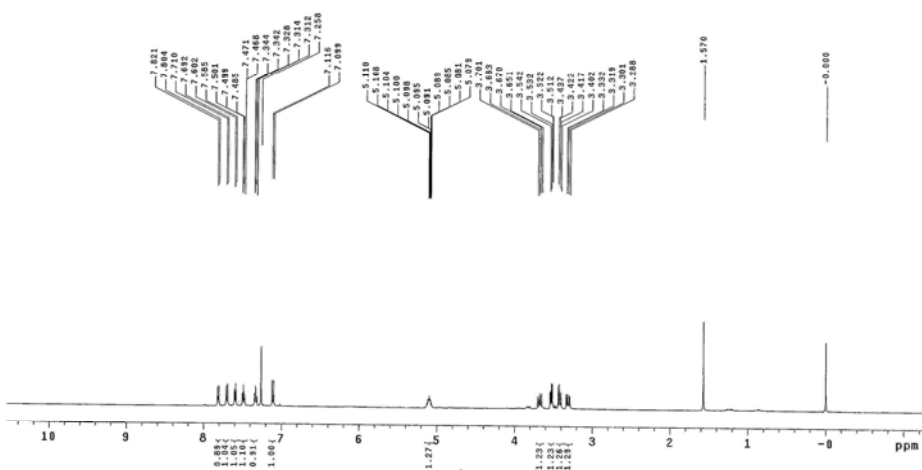


3k'

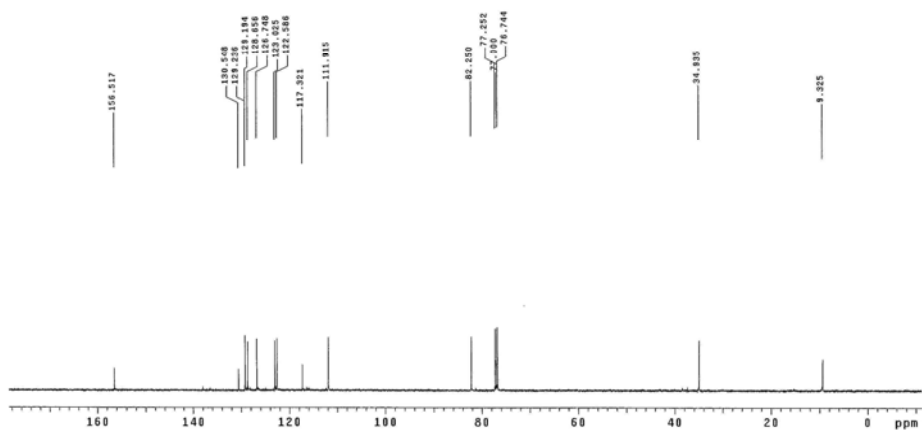


4a

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DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS
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File: 4372
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Power 40 dB
continuously on
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DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 40 min, 56 sec



4b

