Supporting Information for

Highly Efficient Synthesis of Optically Pure 5,5',6,6',7,7',8,8'-Octahydro-1,1'-bi-2-naphthol and -naphthylamine Derivatives by Partial Hydrogenation of 1,1'-Binaphthyls with Carbon Nanofiber-Supported Ruthenium Nanoparticles

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1. General Methods.

Chemical shifts for ^{1}H NMR are described in parts per million downfield from tetramethylsilane as an internal standard ($\delta = 0$) in $CDCl_3$ unless otherwise noted. Chemical shifts for ^{13}C NMR are expressed in parts per million in $CDCl_3$ as an internal standard ($\delta = 77.1$) unless otherwise noted. (*R*)-1,1'-Bi-2-naphthol (BINOL) and 2,2'-diamino-1,1'-binaphthyl (DABN) were purchased from commercially sources. Ru/CNF-P catalyst was prepared by the method reported previously.[1]

2. Preparation of 1,1'-Binaphthyls.

(*R*)-1,1'-Bi-2-naphthol (BINOL) (1a). Optically pure (*R*)-BINOL (>99.9% ee) was obtained by recrystallization of commercially available (*R*)-BINOL (99.1% ee) from ether/*n*-hexane. HPLC (DAICEL CHIRALCEL OD-H, UV Detector 254 nm, hexane/*i*-PrOH = 3:1, Flow Rate 0.5 mL/min), t_R = 14.1 min (*S*), 15.8 min (*R*); (Daicel CHIRALPAK AD-H, UV Detector 254 nm, hexane/*i*-PrOH = 3:1, Flow Rate 0.5 mL/min), t_R = 28.4 min (*R*), 34.2 min (*S*); (Daicel CHIRALPAK AS, UV Detector 254 nm, hexane/*i*-PrOH = 3:1, Flow Rate 0.5 mL/min), t_R = 13.8 min (*R*), 18.0 min (*S*).

(*R*)-2,2'-Dimethoxy-1,1'-binaphthyl (BINOL-Me_2) (1b). (*R*)-1,1-Bi-2-naphthol (2.86 g, 10 mmol, >99.9% ee) was suspended with 50% NaOH solution (10 mL). The resultant mixture was added MeI (10 mL) and a catalytic amount of Bu_4NI (ca. 20 mg) at room temperature. After stirring for 10 h at that temperature, the reaction mixture was poured into water (100 mL). Aqueous layer was acidified with conc. HCl and extracted three times with dichloromethane (totally 400 mL). The combined organic layer was washed with brine (100 mL), dried over $MgSO_4$ and evaporated under reduced pressure. Recrystallization from dichloromethane/ether to gave (*R*)-2,2'-dimethoxy-1,1'-binaphthyl **1b** in 98% yield (colorless solid); Mp 225-227 °C; $[\alpha]_D^{23}$ +75.8° (c 1.03, THF: >99.9% ee, *R*); IR (KBr) ν 3050, 2362, 1624, 1247, 1064, 1004, 808, 775 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 3.77 (s, 6H), 7.10 (dm, *J* = 8.7 Hz, 2H), 7.21 (ddd, *J* = 8.3, 6.8, 1.5 Hz, 2H), 7.31 (ddd, *J* = 8.3, 6.8, 1.5 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.98 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 57.0, 114.3, 119.7, 123.6, 125.3, 126.4, 128.0, 129.3, 129.5, 134.1, 155.1; HPLC (DAICEL CHIRALCEL OD-H, UV Detector 254 nm, hexane/*i*-PrOH = 40:1, Flow Rate 0.5 mL/min), t_R = 15.2 min (*R*), 17.1 min (*S*); or (Daicel CHIRALPAC AS, UV Detector 254 nm, hexane/*i*-PrOH = 3:1, Flow Rate 0.5 mL/min), t_R = 13.8 min (*S*), 18.0 min (*R*). This compound was identified by spectral comparison with literature data.[2]

(*R*)-2,2'-Di[(methoxymethyl)oxy]-1,1'-binaphthyl (BINOL-MOM_2) (1c). This compound was prepared from (*R*)-BINOL (>99.9% ee) and MOMCl according to the literature method[3] in 98% yield (colorless solid); Mp 95-96 °C; IR (KBr) ν 2958, 2818, 1591, 1507, 1479, 1247, 1153, 1023, 921, 809 cm^{-1}; ^{1}H NMR (396 MHz, $CDCl_3$) δ 3.14 (s, 6H), 4.97 (d, *J* = 6.8 Hz, 2H), 5.08 (d, *J* = 6.8 Hz, 2H), 7.15 (bd, *J* = 8.2 Hz, 2H), 7.22 (ddd, *J* = 8.2, 6.8, 1.5 Hz, 2H), 7.34 (ddd, *J* = 7.7, 6.8, 1.5 Hz, 2H), 7.57 (d, *J* = 9.2 Hz, 2H), 7.87 (bd, *J* = 7.7 Hz, 2H), 7.95 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 55.9, 95.3, 117.4, 121.4, 124.2, 125.6, 126.3, 127.9, 129.5, 130.0, 134.1, 152.7; HPLC (DAICEL CHIRALCEL OD-H, UV Detector 254 nm, hexane/*i*-PrOH = 40:1, Flow Rate 0.5 mL/min), t_R = 14.3 min (*R*), 15.9 min (*S*). This compound was identified by spectral comparison with literature data.[3]

(*R*)-2-Hydroxy-2'-methoxy-1,1'-binaphthyl (BINOL-Me) (1d). To a stirred solution of (*R*)-BINOL-Me_2 **1b** (1.114 g, 3.54 mmol, >99.9% ee) in dichloromethane (50 mL) was added a 1 *N* solution of BBr_3 in dichloromethane (3.6 mL) at -78 °C. After it was stirred for 30 min at that temperature, the reaction mixture was quenched by the addition of 1 *N* HCl and extracted twice with ether (totally 100 mL). The combined organic layer was washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. Purification by silica gel chromatography (benzene) gave (*R*)-2-hydroxy-2'-methoxy-1,1'-binaphthyl **1d** in 98% yield (colorless solid); Mp 107-109 °C; $[\alpha]_D^{25}$ +47.2° (c 0.70, $CDCl_3$: >99.9% ee, *R*); IR (KBr) ν 3491, 3060, 1622, 1595, 1508, 1266, 1083, 814, 750 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$) δ 3.81 (s, 3H), 4.90 (bs, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 1H), 7.22 (ddd, *J* = 8.2, 6.8, 1.0 Hz, 1H), 7.28 (ddd, *J* = 8.7, 7.3, 1.0 Hz, 1H), 7.31 (ddd, *J* = 7.7, 6.8, 1.0 Hz, 1H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.37 (ddd, *J* = 8.2, 6.8, 1.0 Hz, 1H), 7.49 (d, *J* = 9.2 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.88~7.93 (m, 2H), 8.06 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 56.8, 113.9, 115.1, 115.4, 117.5, 123.3, 124.2, 124.9, 125.0, 126.5, 127.4, 128.21, 128.23, 129.2, 129.5, 129.9, 131.2, 133.8, 134.1, 151.3, 156.1; HPLC (DAICEL CHIRALPAK AD-H, UV Detector 254 nm, hexane/*i*-PrOH = 3:1, Flow Rate 0.5 mL / min), t_R = 14.6 min (*S*), 18.3 min (*R*); (DAICEL CHIRALPAK AS, UV Detector 254 nm, hexane/*i*-PrOH = 3:1, Flow Rate 0.5 mL / min), t_R = 13.5 min (*S*), 22.5 min (*R*). This compound was identified by spectral comparison with literature data.[4]

(*R*)-2-Hydroxy-2'-(pivaloyl)oxy-1,1'-binaphthyl (BINOL-Piv) (1e). This compound was prepared from (*R*)-BINOL (>99.9% ee) and pivaloly chloride according to the literature method[5] in 92% yield (colorless solid); Mp 128-130 °C; IR (KBr) ν 3386, 3050, 2967,1729, 1627, 1507, 1209, 1153, 809 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.78 (s, 9H), 5.13 (s, 1H), 7.06 (dm, *J* = 8.3 Hz, 1H), 7.25 (ddd, *J* = 8.3, 6.8, 1.5 Hz, 1H), 7.29–7.40 (m, 5H), 7.51 (ddd, *J* = 8.3, 6.3, 1.7 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 26.5, 38.8, 114.3, 118.3, 121.9, 123.0, 123.6, 124.6, 125.7, 126.3, 126.7, 127.5, 128.0, 128.4, 129.1, 130.4, 130.8, 132.3, 133.6, 133.7, 148.4, 151.8, 177.9. HPLC (DAICEL CHIRALCEL OD-H, UV Detector 254 nm, hexane/*i*-PrOH = 40:1, Flow Rate 0.5 mL/min), t_R = 14.8 min (*R*), 16.7 min (*S*). This compound was identified by spectral comparison with literature data.[5]

3. Gram-Scale Reaction of (*R*)-BINOL 1a to (*R*)-H_8-BINOL 2a. Hydrogenation of (*R*)-BINOL **1a** (>99.9% ee) was performed in a 100 mL stainless autoclave fitted with a glass inner tube, in the presence of (*R*)-BINOL **1a** (1.0 g, 3.5 mmol), EtOH (15 mL) and Ru/CNF-P (1.7 wt % Ru, 15 mg; S/C = 1,390) at 50 °C for 48 h under H_2 (initial pressure = 40 atm). After the reaction mixture was cooled to ambient temperature, the insoluble Ru/CNF-P was removed by filtration, and the filtrate was concentrated under reduced pressure. Purification by silica gel chromatography (hexane/ether = 2:1) gave (*R*)-H_8-BINOL **2a** in 99% yield (1.02 g).

4. Spectral Data of H_8-Binaphthyls.

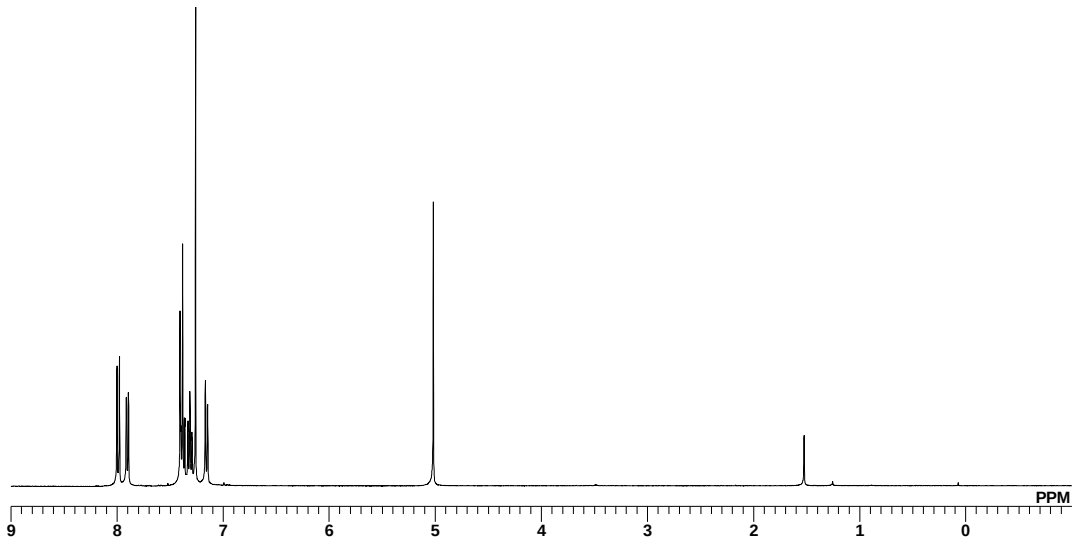
(*R*)-2,2'-Dihydroxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (H_8-BINOL) (2a). Colorless solid; Mp 156-157 °C; $[\alpha]_D^{27}$ +48.6° (c 1.00, $CHCl_3$: >99.9% ee, *R*); lit.[6a] $[\alpha]_{589}^{25}$ +52.8° (c 1.1, $CHCl_3$: >99.9% ee, *R*); IR (KBr) ν 3479, 2930, 2856, 1600, 1479, 1301, 1247, 1191, 1163, 819 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$) δ 1.62–1.84 (m, 8H), 2.16 (dt, *J* = 17.4, 6.3 Hz, 2H), 2.30 (dt, *J* = 17.4, 6.3 Hz, 2H), 2.75 (t, *J* = 6.3 Hz, 4H), 4.54 (s, 2H), 6.83 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 23.0, 23.1, 27.2, 29.3, 113.0, 118.9, 130.2, 131.1, 137.2, 151.5; HPLC (DAICEL CHIRALCEL OD-H, UV Detector 254 nm, hexane/*i*-PrOH = 20:1, Flow Rate 0.5 mL/min), t_R = 15.1 min (*R*), 17.9 min (*S*); (DAICEL CHIRALPAK AD-H, UV Detector 254 nm, hexane/*i*-PrOH = 3:1, Flow Rate 0.5 mL/min), t_R = 12.8 min (*S*), 39.9 min (*R*); (DAICEL CHIRALPAK AS, UV Detector 254 nm, hexane/*i*-PrOH = 40:1, Flow Rate 0.5 mL/min), t_R = 32.7 min (*S*), 35.9 min (*R*). This compound was identified by spectral comparison with literature data.[6]

(*R*)-2,2'-Dimethoxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (H_8-BINOL-Me_2) (2b). Colorless solid; Mp 193-195 °C; $[\alpha]_D^{29}$ +37.1° (c 1.00, $CHCl_3$: >99.9% ee, *R*); IR (KBr) ν 2930, 2836, 1590, 1487, 1265, 1097, 809 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$) δ 1.56–1.81 (m, 8H), 2.08 (dt, *J* = 17.4, 6.3 Hz, 2H), 2.27 (dt, *J* = 17.4, 6.3 Hz, 2H), 2.66–2.87 (m, 4H), 3.67 (s, 6H), 6.78 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 23.2, 23.3, 27.2, 29.5, 56.1, 108.9, 126.0, 128.8, 129.6, 136.8, 154.8. The optical purity was determined by HPLC analysis after converting to the H_8-BINOL. This compound was identified by spectral comparison with literature data.[7]

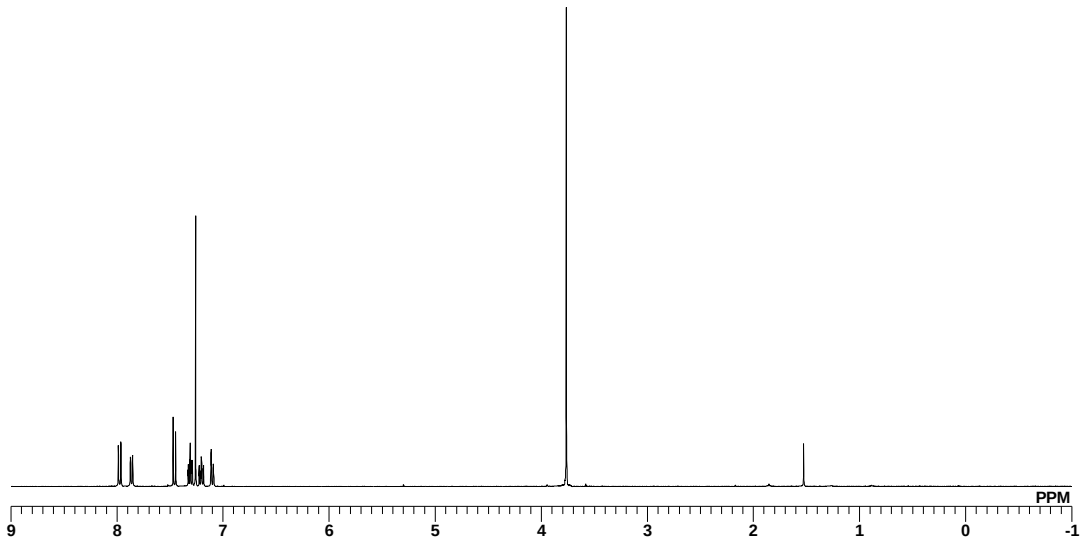
(*R*)-2-Hydroxy-2'-methoxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (H_8-BINOL-Me) (2d). Colorless solid; Mp 137 °C; $[\alpha]_D^{28}$ +21.7° (c 1.00, $CHCl_3$: >99.9% ee, *R*); lit.[8] $[\alpha]_D^{21}$ +22.0° (c 1.01, $CHCl_3$: >99.9% ee, *R*); IR (KBr) ν 3466, 2923, 2851, 1539, 1485, 1277, 1196, 1087, 816 cm^{-1}; ^1H NMR (396 MHz, $CDCl_3$) δ 1.61-1.81 (m, 8H), 2.04-2.21 (m, 2H), 2.21-2.35 (m, 2H), 2.70-2.83 (m, 4H), 3.69 (s, 3H), 4.38 (bs, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 7.13(d, *J* = 8.2 Hz, 1H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 23.06, 23.15, 23.19, 23.24, 27.1, 27.3, 29.37, 29.38, 55.8, 109.0, 112.1, 122.0, 122.8, 129.1, 129.5, 130.3, 130.5, 136.2, 138.1, 150.2, 155.6; HPLC (DAICEL CHIRALCEL OD-H, UV Detector 254 nm, hexane/*i*-PrOH = 100:1, Flow Rate 0.5 mL/min), t_R = 18.0 min (*R*), 19.3 min (*S*);(DAICEL CHIRALPAK AD-H, UV Detector 254 nm, hexane/*i*-PrOH = 3:1, Flow Rate 0.5 mL/min), t_R = 8.6 min (*S*), 14.0 min (*R*). This compound was identified by spectral comparison with literature data.[7]

5. ^{1}H NMR Spectra of 1a-f

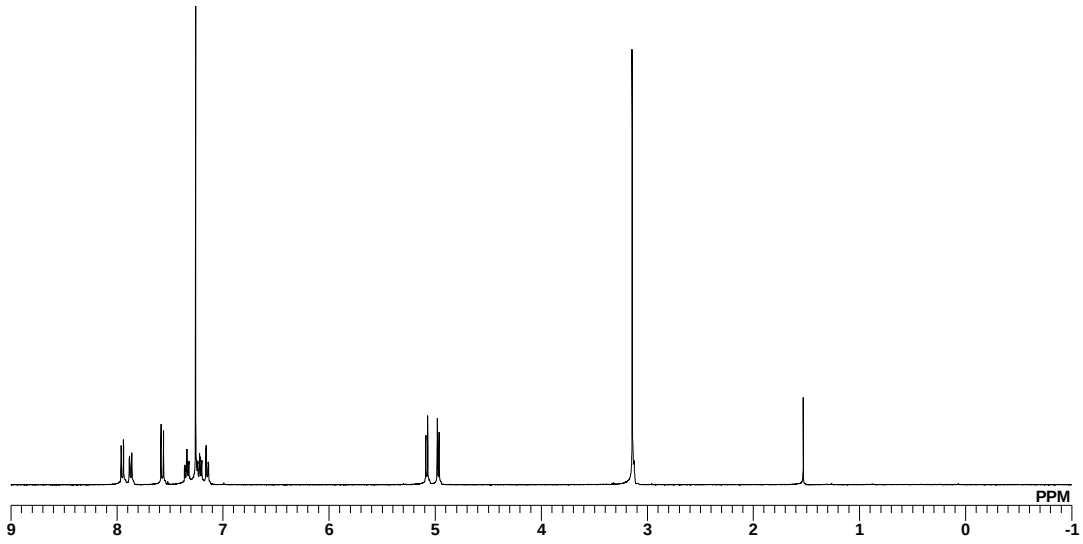
BINOL (1 a)



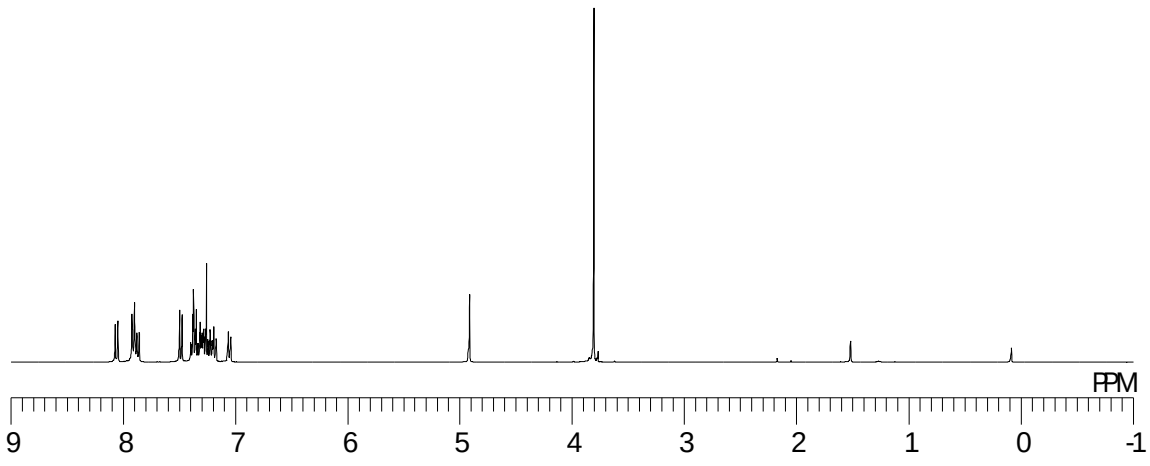
BINOL-Me_2 (1b)



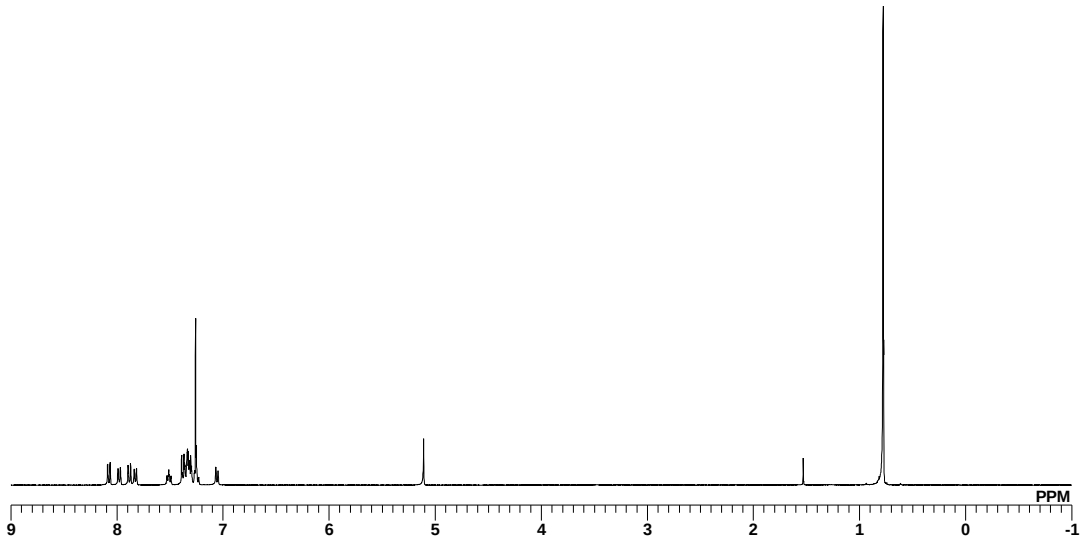
BINOL-MOM$_2$ (1c)



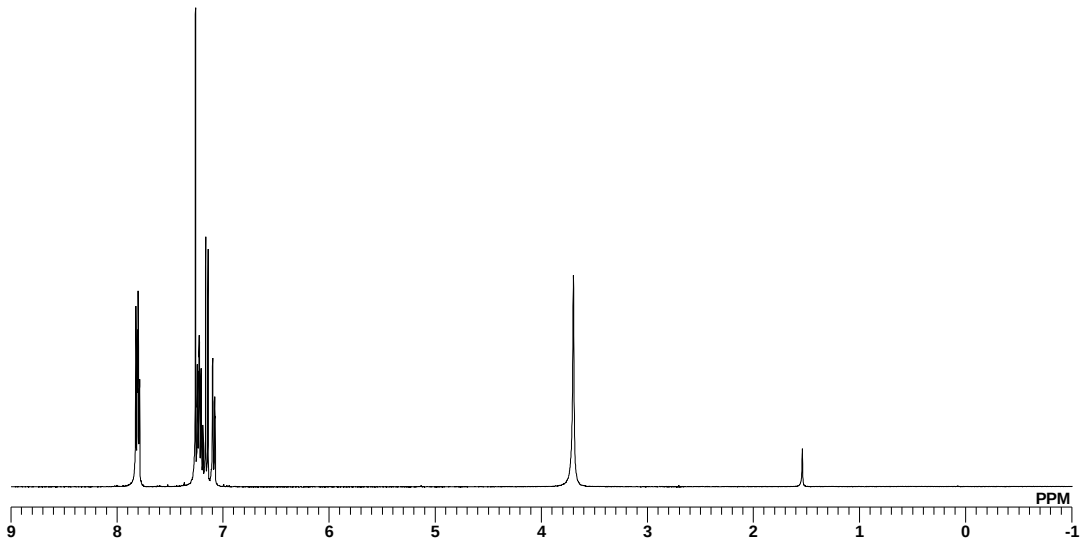
BINOL-Me (1d)



BINOL-Piv (1e)

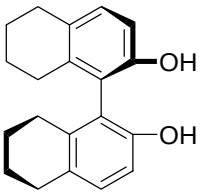


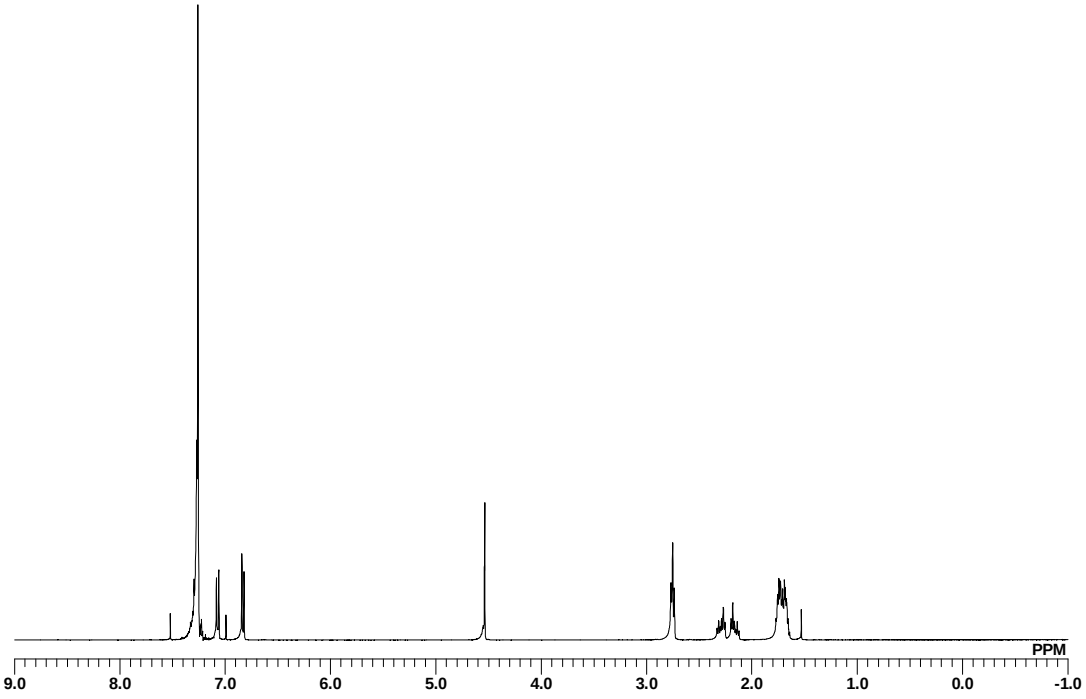
DABN (1f)

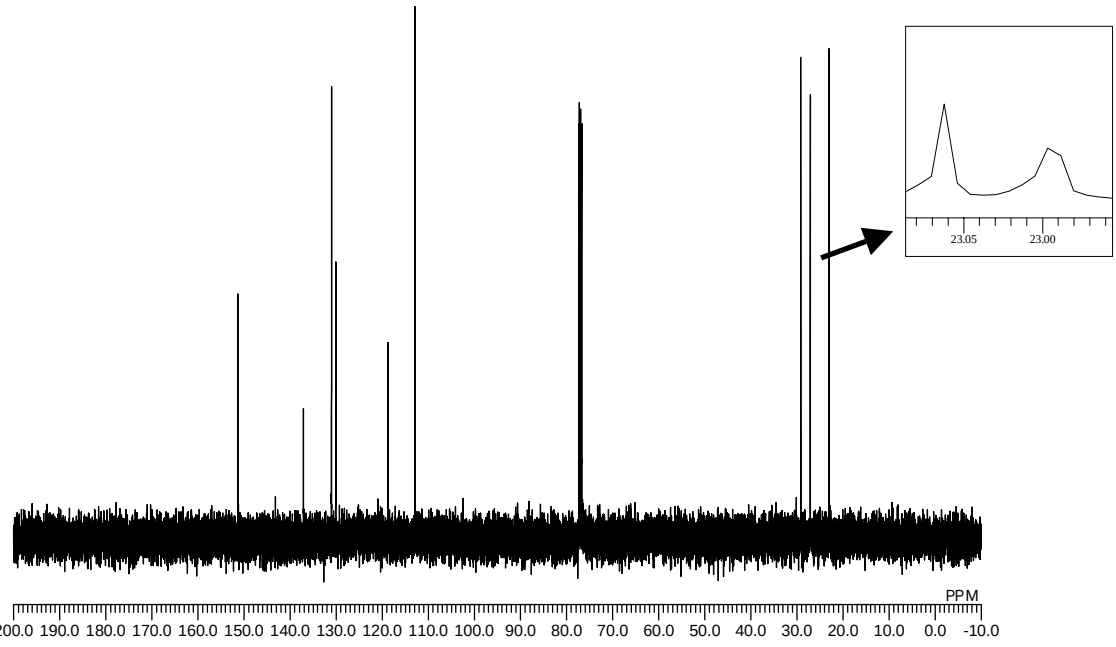


6. ^{1}H and ^{13}C NMR Spectra of 2a-f

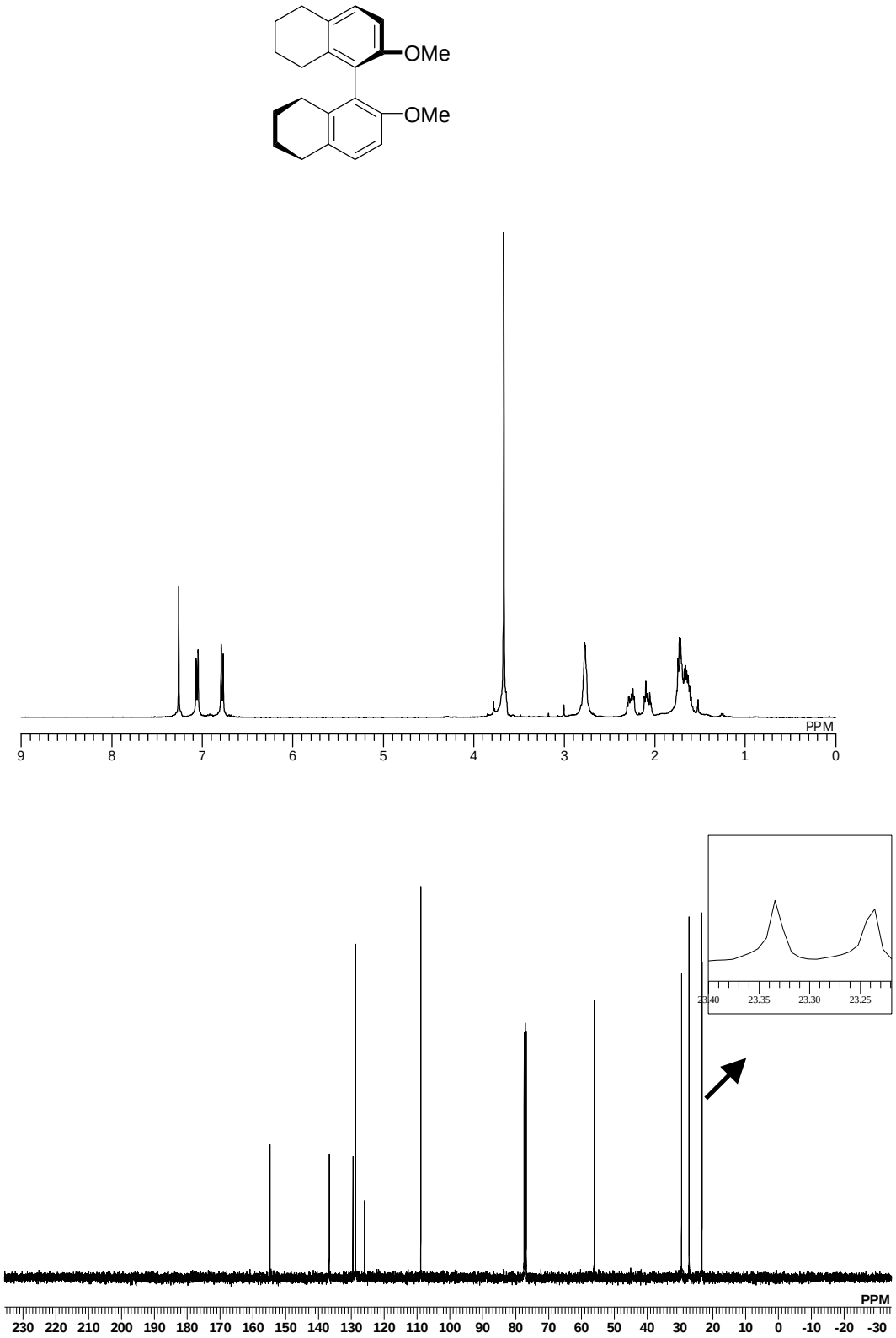
H_8-BINOL (2a)



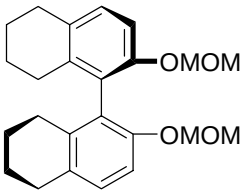


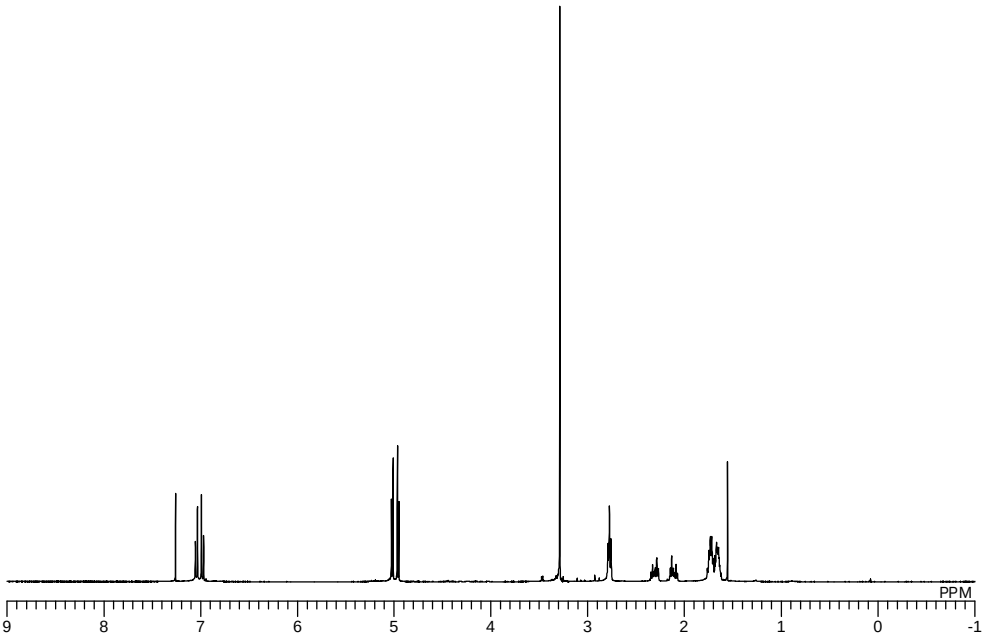


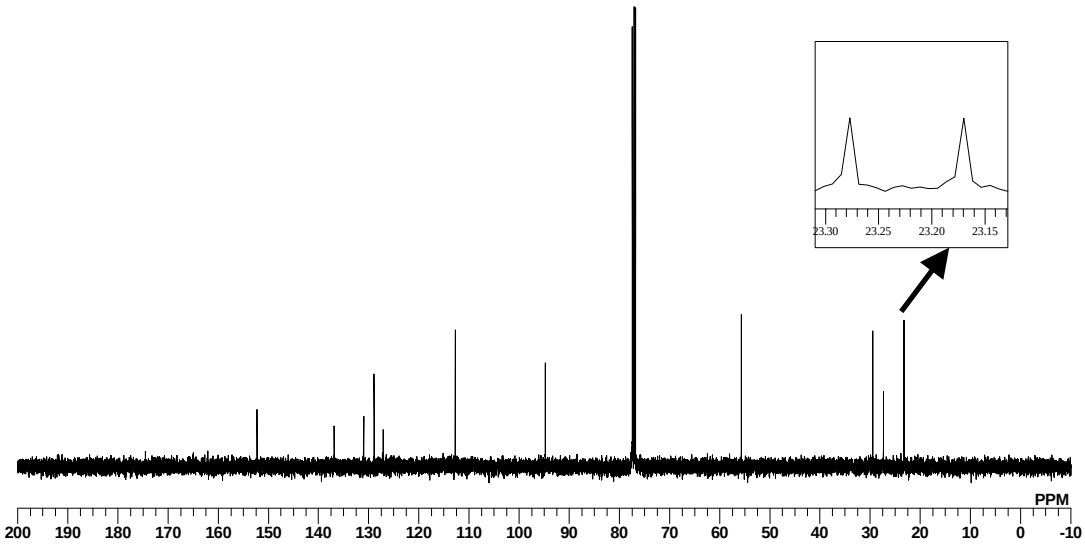
H_8-BINOL-Me_2 (2b)



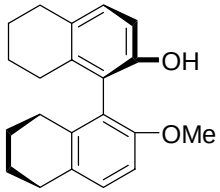
H_8-BINOL-MOM_2 (2c)

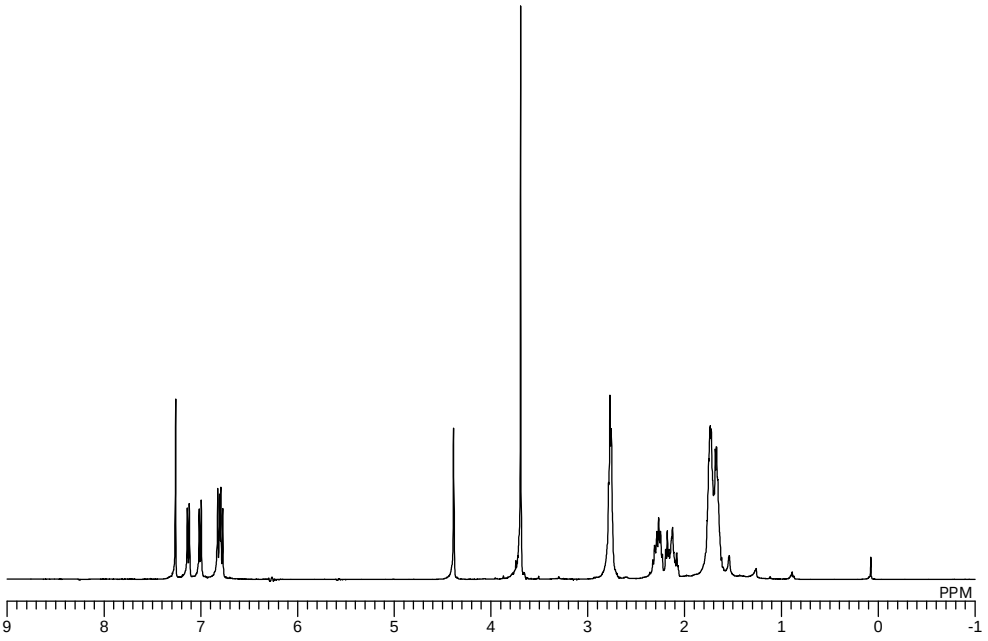


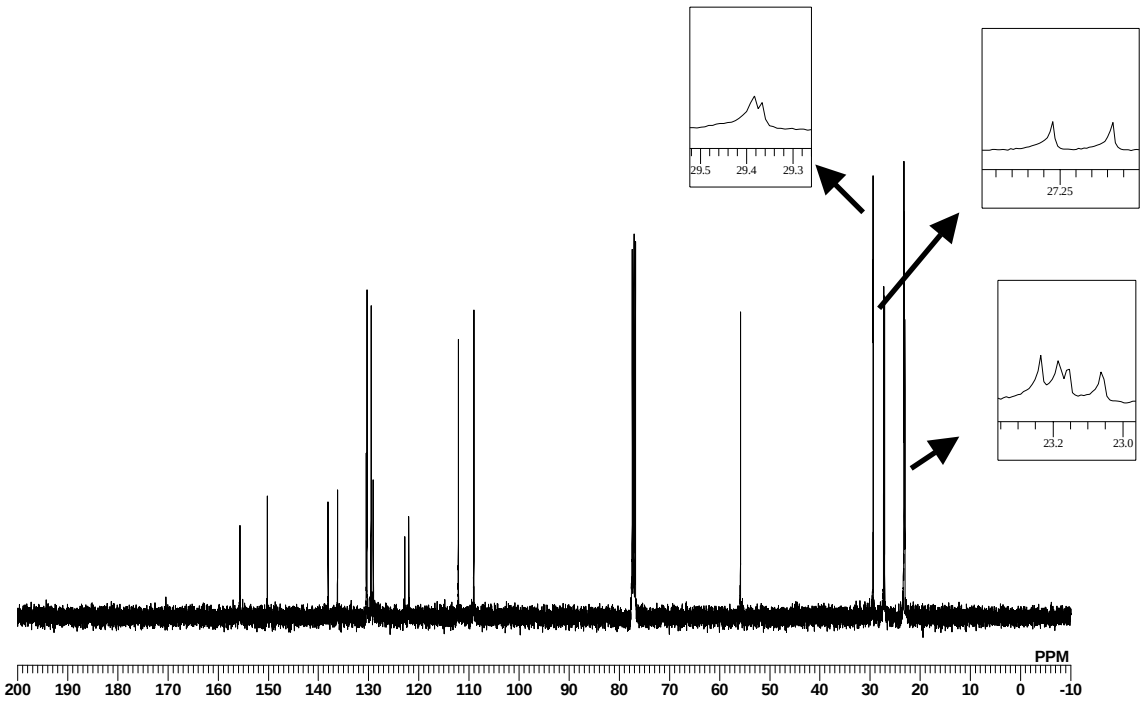




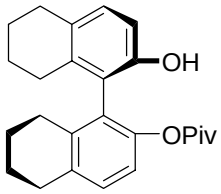
H_8-BINOL-Me (2d)

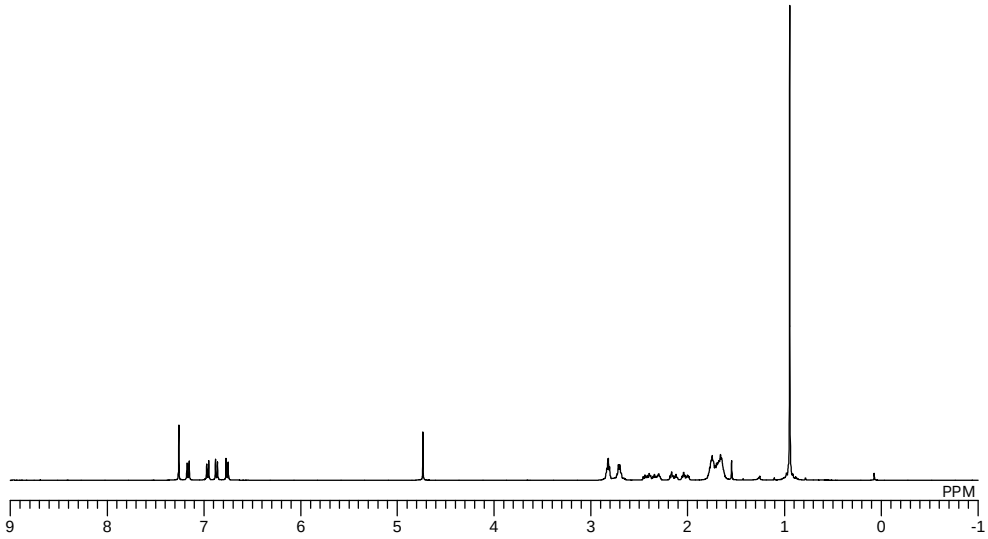


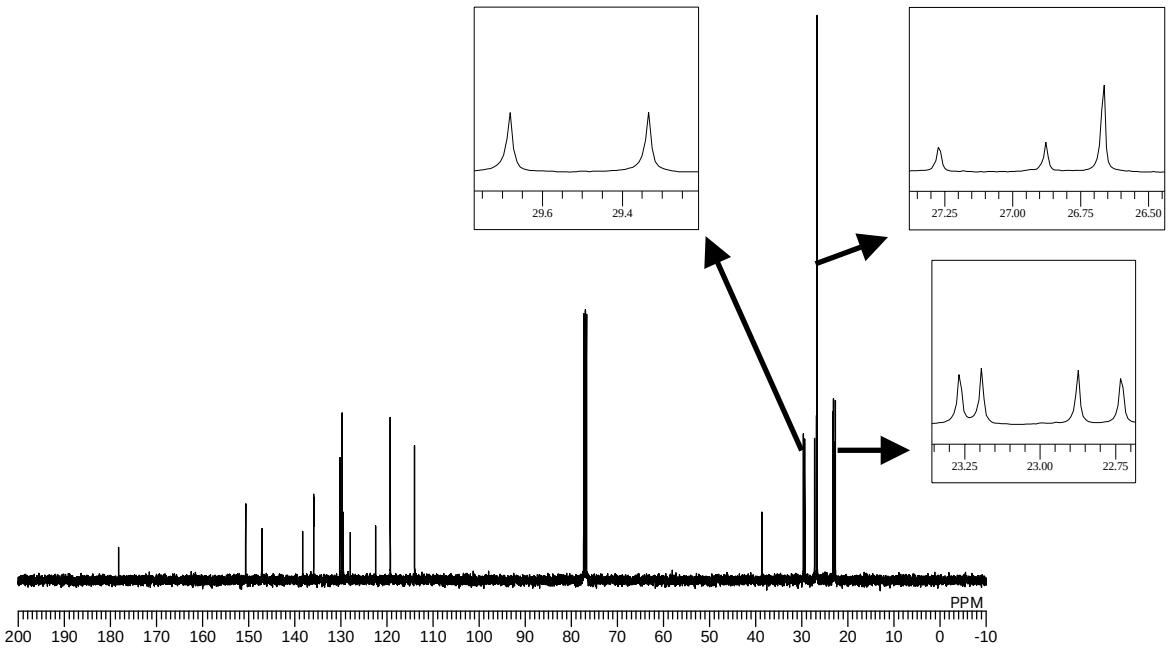




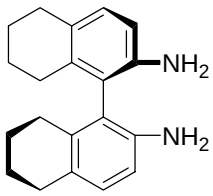
H_8-BINOL-Piv (2e)

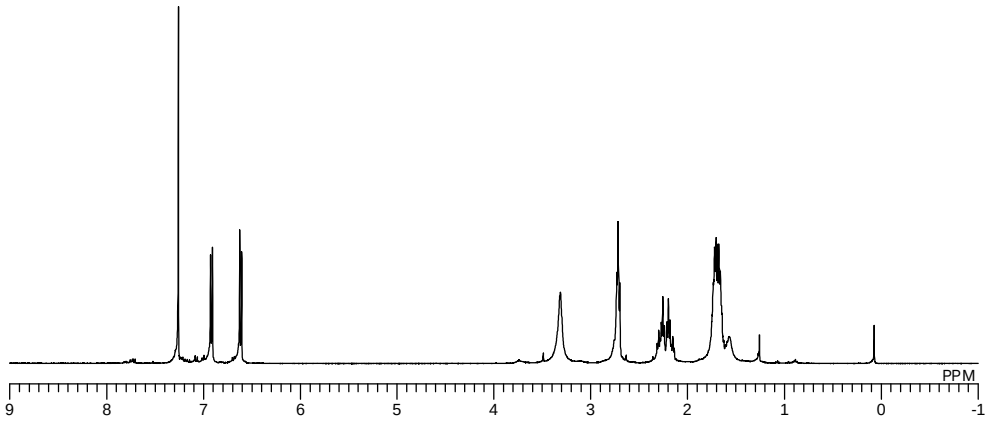






H_8-DABN (2f)


NH2
NH2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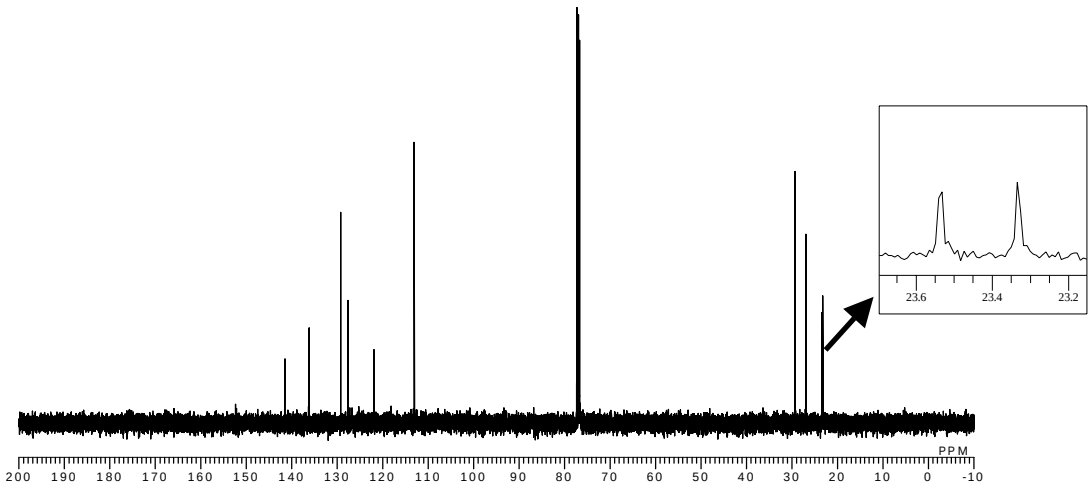
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180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

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