Rhodium-Catalyzed Asymmetric Arylative Ring-Opening Reactions of Heterobicyclic Alkenes with Anilines

Jingchao Chen,*[†] Lingling Zou,[†] Chaoyuan Zeng,[†] Yongyun Zhou,[†] and Baomin Fan*[†‡]

Supporting Information

Table of Contents

A: General Information

The reactions and manipulations were performed under an atmosphere of argon by using standard Schlenk techniques and Drybox (Mikrouna, Supper 1220/750). Common substrates and reagents were obtained from commercial suppliers and used without further purification. Anhydrous toluene and 1,4-dioxane were distilled from sodium benzophenone ketyl prior to use. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-Avance 400 MHz spectrometer. $CDCl_3$ was used as solvent. Chemical shifts (δ) were reported in ppm with tetramethylsilane as internal standard, and *J* values were given in Hz. The enantiomeric excesses were determined by Agilent 1260 Series HPLC using Daicel AD-H、AS-H、and OD-H chiral columns eluted with a mixture of isopropyl alcohol and hexane. Melting points were measured on X-4 melting point apparatus and uncorrected. High resolution mass spectra (HRMS) were obtained on a double-focusing high resolution magnetic-sector mass-analyzed instrument, operating in an electron impact (EI) mode. Column chromatography was performed with silica gel (200 - 300 mesh) with petroleum ether and ethyl acetate as eluents.

B: Procedure for the reactions

Typical procedure for the asymmetric ring opening reactions: $Rh(COD)_2SbF_6$ (28 mg, 0.05 mmol), (*R*)-DifluroPHOS (41 mg, 0.06 mmol) and 1,4-dioxane (5.0 mL) were added to a Schlenk tube under argon atmosphere. The resulting solution was stirred at room temperature for 30 min, then a solution of azabenzonorbornadiene **1a** (243 mg, 1.0 mmol) in 1,4-dioxane (5 mL) was added, and the mixture was stirred for additional 10 min. Then *N*,*N*-dimethylaniline **2a** (0.65 mL, 5 mmol) was added, and the mixture was stirred at 80 °C under argon atmosphere with TLC monitoring until the complete consumption of **1a**. The solvent was removed by reduced pressure and the residue was purified by silica gel column chromatography to provide the desired product **3aa** (280 mg, 77% yield). The enantiomeric excess value of the product was determined by HPLC on a chiral stationary phase (92% *ee*).

C: Characterization Data of Products

***tert-butyl ((1R,2R)-2-(4-(dimethylamino)phenyl)-1,2-dihydronaphthalen-1-yl) carbamate* (3aa):**

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1⁄15), 56 mg, 77% yield, 92% *ee*. Mp 136 - 139 ^{o}C. $[\alpha]_D^{21}$ = +368.8 (c= 1.02, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 - 7.06 (m, 6H), 6.67 - 6.59 (m, 3H), 6.05 (dd, *J* = 8.9 Hz, 4.8 Hz, 1H), 4.85 (s, 2H), 3.76 (s, 1H), 2.86 (s, 6H), 1.41 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.1, 149.7, 133.7, 133.1, 130.3, 128.9, 128.7, 128.3, 128.0, 127.6, 127.5, 126.4, 112.9, 79.4, 55.2, 46.5, 40.8, 28.5. HRMS calcd for $C_{23}H_{28}N_2O_2$ $[M]^+$: 364.2151. Found: 364.2152. The *ee* of **3aa** was determined by HPLC analysis using a Daicel Chiralcel AS-H columns (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 0.5 mL/min, 254 nm; t_{major} = 11.5 min, t_{minor} = 15.0 min.

tert-butyl ((1R,2R)-2-(4-(dimethylamino)-2-methylphenyl)-1,2-dihydronaphthalen-1-yl)carbamate

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1⁄15), 51 mg, 68% yield, 87% *ee*. Mp 99 – 102 ^{o}C. $[\alpha]_D^{21}$ = +451.2 (c = 0.93, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 - 7.12 (m, 4H), 6.76 (d, *J* = 8.5 Hz, 1H), 6.68 (d, *J* = 9.6 Hz, 1H), 6.57 - 6.56 (m, 1H), 6.35 (d, *J* = 8.2 Hz, 1H), 5.99 (dd, *J*= 9.3, 5.1 Hz, 1H), 4.92 - 4.82 (m, 2H), 3.93 (s, 1H), 2.84 (s, 6H), 2.50 (s, 3H), 1.40 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.0, 149.6, 137.4, 134.2, 133.0, 130.6, 128.7, 128.2, 128.0, 127.6, 126.4, 125.1, 115.3, 110.4, 79.3, 53.7, 43.2, 40.8, 28.5, 20.5. HRMS calcd for $C_{24}H_{30}N_2O_2$ $[M]^+$: 378.2307. Found: 378.2310. The *ee* of **3ab** was determined by HPLC analysis using a Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 0.5 mL/min, 254 nm; t_{major} = 12.4 min, t_{minor} = 14.0 min.

***tert-butyl ((1R,2R)-2-(4-(dimethylamino)-2-methoxyphenyl)-1,2-dihydronaphthalen-1-yl)carbamate* (3ac):**

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1⁄15), 65 mg, 83% yield, 93% *ee*. Mp 98 – 101 ^{o}C. $[\alpha]_D^{21}$ = +270.8 (c = 1.31, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.2 Hz, 1H), 7.24 - 7.17 (m, 2H), 7.12-7.10 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.62 (d, *J* = 9.5 Hz, 1H), 6.28 - 6.27 (m, 1H), 6.23 (d, J = 8.4 Hz, 1H), 6.02 (dd, *J* = 9.3, 3.6 Hz, 1H), 5.04 - 4.92 (m, 2H), 4.12 - 4.10 (m, 1H), 3.87 (s, 3H), 2.91 (s, 6H), 1.36 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.1, 155.6, 151.2, 135.9, 133.2, 131.3, 128.9, 127.8, 127.7, 126.9, 126.3, 117.0, 105.1, 96.4, 79.0, 55.4, 54.6, 40.9, 39.8, 28.5. HRMS calcd for $C_{24}H_{30}N_2O_3$ $[M]^+$: 394.2256. Found: 394.2248. The *ee* of **3ac** was determined by HPLC analysis using a Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1mL/min, 254 nm; t_{minor} = 13.6 min, t_{major} = 11.4 min.

***tert-butyl ((1R,2R)-2-(4-(dimethylamino)-3-methoxyphenyl)-1,2-dihydronaphthalen-1-yl)carbamate* (3ad):**

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1⁄15), 21 mg, 27% yield, 88% *ee*. Mp 44 – 47 ^{o}C. $[\alpha]_D^{22}$ = +274.9 (c = 0.43, CH_2Cl_2). ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.27 - 7.13 (m, 4H), 6.80 - 6.66 (m, 4H), 6.06 (dd, *J* = 9.5, 4.8 Hz, 1H), 4.92 - 4.84 (m, 2H), 3.76 (s, 4H), 2.71 (s, 6H), 1.40 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.1, 152.3, 141.3, 134.3, 134.0, 133.1, 130.2, 128.3, 128.2, 127.7, 126.4, 120.3, 118.1, 111.0, 79.5, 55.3, 55.0, 47.3, 43.5, 28.5. HRMS calcd for $C_{24}H_{30}N_2O_3$ $[M]^+$: 394.2256. Found: 394.2252. The *ee* of **3ad** was determined by HPLC analysis using a Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 0.5 mL/min, 254 nm; t_{major} = 11.5 min, t_{minor} = 14.4 min.

***tert-butyl ((1R,2R)-2-(2-chloro-4-(dimethylamino)phenyl)-1,2-dihydronaphthalen-1-yl)carbamate* (3ae):**

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/15), 32 mg, 40% yield, 77% *ee*. Mp 134 - 137 °C. $[\alpha]_D^{22}$ = +222.9 (c = 0.62, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 - 7.30 (m,1H), 7.25 - 7.18 (m, 2H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.71 - 6.70 (m, 1H), 6.64 (dd, *J* = 9.6, 1.6 Hz, 1H), 6.49 (dd, *J* = 8.6, 2.0 Hz, 1H), 5.98 (dd, *J* = 9.5, 3.9 Hz, 1H), 5.05 - 4.92 (m, 2H), 4.19 (s, 1H), 2.88 (s, 6H), 1.36 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.3, 150.4, 135.2, 135.0, 133.0, 130.3, 129.4, 128.1, 128.0, 127.0, 126.5, 125.0, 113.1, 111.5, 79.35, 54.2, 43.4, 40.5, 28.5. HRMS calcd for $C_{23}H_{27}ClN_2O_2$ $[M]^+$: 398.1761. Found: 398.1756. The *ee* of **3ae** was determined by HPLC analysis using a Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 10.2 min, t_{minor} = 7.7 min.

***tert-butyl ((1'R,2'R)-4-(dimethylamino)-1',2'-dihydro-[1,2'-binaphthalen]-1'-yl) carbamate* (3af):**

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/15), 50 mg, 60% yield, 91% *ee*. Mp 144 – 146 °C. $[\alpha]_D^{22}$ = +104.5 (c = 0.77, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.5 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 7.65 - 7.50 (m, 2H), 7.29 - 7.15 (m, 5H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 9.6 Hz, 1H), 6.12 (dd, *J* = 9.6, 4.8 Hz, 1H), 5.11 (dd, *J* = 8.3, 4.6 Hz, 1H), 4.96 - 4.94 (m, 1H), 4.61 (s, 1H), 2.82 (s, 6H), 1.39 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.2, 150.2, 134.5, 133.1, 132.8, 130.3, 129.5, 128.9, 128.5, 128.3, 128.2, 126.6, 126.3, 125.2, 125.0, 124.9, 124.3, 113.6, 79.4, 53.8, 45.4, 42.8, 28.5. HRMS calcd for $C_{27}H_{30}N_2O_2$ $[M]^+$: 414.2307. Found: 414.2314. The *ee* of **3af** was determined by HPLC analysis using two Daicel Chiralcel OD-H columns (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, 254 nm; t_{major} = 25.0 min, t_{minor} = 28.1 min.

***tert-butyl ((1R,2R)-2-(4-(diethylamino)phenyl)-1,2-dihydronaphthalen-1-yl) carbamate* (3ag):**

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/15), 67 mg, 85% yield, 92% *ee*. Mp 126 - 128 °C. $[\alpha]_D^{21}$ = +449.5 (c = 1.38, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 - 7.11 (m, 4H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.65 (d, *J* = 9.5 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 2H), 6.05 (dd, *J* = 9.2, 4.9 Hz, 1H), 4.85 (s, 2H), 3.73 (s, 1H), 3.27 (dd, *J* = 13.4, 6.6 Hz, 4H), 1.41 (s, 9H), 1.09 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.1, 146.9, 133.9, 133.2, 130.5, 129.1, 128.7, 128.2, 128.0, 127.3, 126.4, 112.0, 79.4, 55.2, 46.6, 44.4, 28.5, 12.7. HRMS calcd for$C_{25}H_{32}N_2O_2$ $[M]^+$+H:

393.2542. Found: 393.2538. The *ee* of **3ag** was determined by HPLC analysis using a Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 0.5mL/min, 254 nm; t_{major} = 13.7 min, t_{minor} = 11.4 min.

***tert-butyl ((1R,2R)-2-(4-(diethylamino)-2-methylphenyl)-1,2-dihydronaphthalen-1-yl) carbamate* (3ah):**

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/15), 67 mg, 83% yield, 91% *ee*. Mp 104 – 107 °C. $[\alpha]_D^{21}$ = +463.0 (c = 1.24, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 - 7.12 (m, 4H), 6.73 (d, *J* = 8.6 Hz, 1H), 6.67 (d, *J* = 9.6 Hz, 1H), 6.49 (s, 1H), 6.28 (d, *J* = 8.1 Hz, 1H), 6.00 (dd, *J* = 9.3, 5.1 Hz, 1H), 4.92 - 4.83 (m, 2H), 3.91 (s, 1H), 3.25 (dd, *J* = 13.8, 6.8 Hz, 4H), 2.49 (s, 3H), 1.40 (s, 9H), 1.09 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.0, 146.7, 137.5, 134.3, 133.0, 130.8, 128.7, 128.5, 128.1, 128.0, 127.4, 126.3, 123.7, 114.1, 109.4, 79.2, 53.7, 44.3, 43.2, 28.5, 20.6, 12.7. HRMS calcd for $C_{26}H_{34}N_2O_2$ $[M]^+$: 406.2620. Found: 406.2616. The *ee* of **3ah** was determined by HPLC analysis using a Daicel Chiralcel AS-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, 254 nm; t_{major} = 12.3 min, t_{minor} = 14.3 min.

***((1R,2R)-2-(4-(piperidin-1-yl)phenyl)-1,2-dihydronaphthalen-1-yl)carbamate* (3ai):**

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/15), 39 mg, 48% yield, 85% *ee*. Mp 50 – 53 °C. $[\alpha]_D^{22}$ = +184.1 (c = 1.02, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 - 7.07 (m, 6H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 9.6, 1H), 6.04 (dd, *J* = 9.5, 5.0 Hz, 1H), 4.84 (s, 2H), 3.77 (s, 1H), 3.6 (t, *J* = 5.2 Hz, 4H), 1.69 - 1.63 (m, 4H), 1.55 - 1.41 (m, 2H), 1.41 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.1, 151.2, 133.7, 133.0, 130.0, 130.1, 128.8, 128.5, 128.2, 128.0, 127.5, 126.3, 116.6, 79.3, 55.1, 50.7, 46.5, 28.4, 26.0, 24.3. HRMS calcd for $C_{26}H_{32}N_2O_2$ $[M]^+$: 404.2464. Found: 404.2462. The *ee* of **3ai** was determined by HPLC analysis using a Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH= 90/10, 0.5 mL/min, 254 nm; t_{major} = 11.7 min, t_{minor} = 10.4 min.

***tert-butyl ((1R,2R)-2-(4-((2-hydroxyethyl)(methyl)amino)phenyl)-1,2-dihydronaphthalen-1-yl)carbamate* (3aj):**

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/10), 55 mg, 70% yield, 92% *ee*. Mp 120 – 123 °C. $[\alpha]_D^{22}$ = +197.6 (c = 1.01, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 - 7.20 (m, 3H), 7.13 (d, *J* = 7.3 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.55 (dd, *J* = 9.6, 1H), 6.21 - 6.06 (m, 4H), 5.09 - 5.05 (m, 1H), 4.70 (d, *J* = 8.7 Hz, 1H), 4.30 - 4.27 (m, 1H), 3.75 (s, 1H), 2.92 (s, 6H), 1.45 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.1, 149.2, 133.7, 133.1, 130.2, 129.1, 128.7, 128.5, 128.3, 128.1, 127.6, 126.4, 113.4, 79.5, 60.1, 55.7, 55.2, 46.5, 39.0, 28.5. HRMS calcd for $C_{24}H_{30}N_2O_3$ $[M]^+$: 394.2256. Found: 394.2251. The *ee* of **3ak** was determined by HPLC analysis using a Daicel Chiralcel AS-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH= 90/10, 1 mL/min, 254 nm; t_{major} = 11.0 min, t_{minor} = 14.8 min.

***tert-butyl ((1R,2R)-2-(1H-indol-3-yl)-1,2-dihydronaphthalen-1-yl)carbamate* (3ak)[1]:**

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/15), 60 mg, 83% yield, 94% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 - 7.97 (m, 2H), 7.28 - 7.30 (m, 1H), 7.13 - 7.26 (m, 7H), 6.78 (s, 1H), 6.67 (d, *J* = 9.5 Hz, 1H), 6.17 - 6.20 (m, 1H), 5.08 - 5.11 (m, 1H), 4.92 (d, *J* = 8.1 Hz, 1H), 4.22 (s, 1H), 1.43 (s, 9H). The *ee* of **3ak** was determined by HPLC analysis using two Daicel Chiralcel OJ-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 17.1 min, t_{minor} = 28.4 min.

***tert-butyl ((1R,2R)-6,7-dibromo-2-(4-(diethylamino)-2-methylphenyl)-1,2-dihydronaphthalen-1-yl)carbamate* (3bh):**

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/15), 73 mg, 65% yield, 91% *ee*. Mp 110 - 113 ^{o}C. $[\alpha]_D^{22}$ = +278.4 (c = 1.01, $CHCl_2$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.39 (s, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 9.5 Hz, 1H), 6.49 (s, 1H), 6.30 (d, *J* = 7.8 Hz, 1H), 6.08 (dd, *J* = 9.0, 4.8 Hz, 1H), 4.88 - 4.77 (m, 2H), 3.90 (s, 1H), 3.28 (q, *J* = 6.9 Hz, 4H), 2.45 (s, 3H), 1.40 (s, 9H), 1.11 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100MHz): δ 154.7, 146.8, 137.5, 135.1, 133.7, 133.5, 132.8, 130.8, 128.3, 125.6, 124.0, 123.1, 122.4, 114.0, 109.3, 79.7, 52.9, 44.2, 43.0, 28.4, 20.5, 12.7. HRMS calcd for $C_{26}H_{32}Br_2N_2O_2$ $[M]^+$: 562.0831. Found: 562.0825. The *ee* of **3bh** was determined by HPLC analysis using a Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, 254 nm; t_{major} = 10.0 min, t_{minor}= 13.2 min.

tert-butyl ((1R,2R)-2-(4-(diethylamino)-2-methylphenyl)-6,7-dimethyl-1,2-dihydronaphthalen-1-yl)carbamate (3ch):

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/15), 70 mg, 81% yield, 92% *ee*. Mp 99 – 102 ^{o}C. $[\alpha]_D^{22}$ = +304.5 (c = 1.02, $CHCl_2$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 - 6.91 (m, 2H), 6.71 (d, *J* = 8.6 Hz, 1H), 6.62 (d, *J* = 9.5 Hz, 1H), 6.49 (s, 1H), 6.28 - 6.26 (m, 1H), 5.92 (dd, *J* = 9.3, 5.3 Hz, 1H), 4.88 - 4.75 (m, 2H), 3.87 (s, 1H), 3.25 (q, *J* = 6.4 Hz, 4H), 2.49 (s, 3H), 2.23 - 2.18 (m, 6H), 1.40 (s, 9H), 1.10 - 1.07 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.8, 146.5, 137.5, 136.2, 136.2, 131.5, 130.6, 130.2, 129.4, 128.5, 127.6, 127.2, 123.8, 114.0, 109.3, 79.0, 53.3, 44.2, 43.3, 28.4, 20.5, 19.6, 19.5, 12.7. HRMS calcd for $C_{28}H_{38}N_2O_2$ $[M]^+$: 434.2933. Found: 434.2938. The *ee* of **3ch** was determined by HPLC analysis using a Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 0.5mL/min, 254 nm; t_{major} = 8.1 min, t_{minor}= 10.5 min.

***N*-((1R,2R)-2-(4-(diethylamino)-2-methylphenyl)-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide* (3dh):**

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/15), 82 mg, 89% yield, 75% *ee*. Mp 88 – 91 ^{o}C. $[\alpha]_D^{22}$ = +347.6 (c = 1.05, $CHCl_2$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.24 - 7.18 (m, 2H), 7.11 - 7.10 (m, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 9.6 Hz, 1H), 6.51 -6.49 (m, 2H), 6.43 (d, *J* = 2.6 Hz, 1H), 6.14 (dd, *J* = 8.7, 2.7 Hz, 1H), 5.98 (dd, *J* = 9.5, 5.7 Hz, 1H), 4.88 (d, *J* = 8.1 Hz, 1H), 4.32 (d, *J* = 8.5 Hz, 1H), 4.05 (d, *J* = 4.2, Hz, 1H), 3.23 (q, *J* = 7.0 Hz, 4H), 2.42 (s,

3H), 2.38 (s, 3H), 1.07 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.7, 143.2, 138.1, 137.5, 132.9, 132.2, 130.1, 129.6, 128.8, 128.7, 128.4, 127.8, 127.2, 126.5, 122.1, 113.7, 109.1, 56.6, 44.1, 43.1, 21.6, 20.5, 12.7. HRMS calcd for $C_{28}H_{32}N_2O_2S$ $[M]^+$: 460.2184. Found: 460.2189. The *ee* of **3dh** was determined by HPLC analysis using a Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1 mL/min, 254 nm; t_{major} = 11.2 min, t_{minor} = 13.6 min.

***benzyl ((1R,2R)-2-(4-(diethylamino)-2-methylphenyl)-1,2-dihydronaphthalen-1-yl) carbamate* (3eh):**

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/15), 62 mg, 70% yield, 84% *ee*. Mp 106 - 109 °C. $[\alpha]_D^{22}$ = +254.3 (c = 0.99, $CHCl_2$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.26 (m, 6H), 7.21 - 7.16 (m, 3H), 6.71 (dd, *J* = 9.4, 5.1 Hz, 2H), 6.53 (s, 1H), 6.28 - 6.26 (m, 1H), 6.02 (dd, *J* = 9.4, 5.4 Hz, 1H), 5.20 (d, *J* = 8.7 Hz, 1H), 5.11 (s, 2H), 4.91 - 4.89 (m, 1H), 4.00 (s, 1H), 3.28 (q, *J* = 6.9 Hz, 4H), 2.54 (s, 3H), 1.11 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.5, 146.7, 137.6, 136.5, 133.5, 132.9, 130.3, 129.2, 128.6, 128.5, 128.4, 128.2, 128.1, 127.5, 126.5, 122.9, 114.1, 109.3, 66.8, 54.1, 44.2, 42.8, 20.6, 12.8. HRMS calcd for $C_{29}H_{32}N_2O_2$ $[M]^+$: 440.2464. Found: 440.2467. The *ee* of **3eh** was determined by HPLC analysis using a Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH =90/10, 1mL/min, 254 nm; t_{major} = 8.1 min, t_{minor} = 10.1 min.

***(1R,2R)-2-(4-(diethylamino)-2-methylphenyl)-1,2-dihydronaphthalen-1-ol* (3fh):**

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/15), 47 mg, 77% yield, 93% *ee*. Mp 85 – 88 °C. $[\alpha]_D^{22}$ = -374.8 (c = 0.92, $CHCl_2$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.2 Hz, 1H), 7.29 - 7.20 (m, 2H), 7.14 (d, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.62 (d, *J* = 9.6 Hz, 1H), 6.51 (s, 1H), 6.40 (d, *J* = 8.3 Hz, 1H), 5.97 (dd, *J* = 9.6, 3.8 Hz, 1H), 4.80 (d, *J* = 7.0 Hz, 1H), 3.99 (s, 1H), 3.29 (q, *J* = 6.9 Hz, 4H), 2.41 (s, 3H), 2.03 (s, 1H), 1.12 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.7, 137.8, 135.9, 132.9, 131.3, 128.7, 128.2, 127.9, 127.1, 126.8, 126.3, 124.7, 113.8, 109.8, 74.0, 44.9, 44.3, 20.7, 12.8. HRMS calcd for $C_{21}H_{25}NO$ $[M]^+$: 307.1936. Found: 307.1933. The *ee* of **3fh** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 0.5 mL/min, 254 nm; t_{major} = 15.5 min, t_{minor} = 14.4 min.

***(1R,2R)-6,7-dibromo-2-(4-(diethylamino)-2-methylphenyl)-1,2-dihydronaphthalen-1-ol* (3gh):**

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/20), 78 mg, 84% yield, 83% *ee*. Mp 135 – 138 °C. $[\alpha]_D^{22}$ = -365.9 (c = 1.05, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.39 (s, 1H), 6.93 (d, *J* = 8.6 Hz, 1H), 6.52 - 6.45 (m, 3H), 6.04 (dd, *J* = 9.6, 3.5 Hz, 1H), 4.75 (d, *J* = 8.6 Hz, 1H), 3.94 (d, *J* = 6.1 Hz, 1H), 3.32 (q, *J* = 7.0 Hz, 4H), 2.39 (s, 3H), 2.09 (s, 1H), 1.15 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR

($CDCl_3$, 100MHz): δ 146.9, 137.9, 136.9, 133.7, 133.7, 131.4, 130.7, 128.6, 125.4, 123.9, 123.2, 113.8, 109.8, 73.4, 44.7, 44.2, 20.6, 12.7. HRMS calcd for $C_{21}H_{23}Br_2NO$ $[M]^+$: 463.0146. Found: 463.0154. The *ee* of **3gh** was determined by HPLC analysis using a Daicel Chiralcel AS-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 0.5mL/min, 254 nm; t_{major} = 10.0 min, t_{minor} = 12.1 min.

***(1R,2R)-2-(4-(diethylamino)-2-methylphenyl)-6,7-dimethyl-1,2-dihydronaphthalen-1-ol* (3hh):**

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/15), 54 mg, 80% yield, 94% *ee*. Mp 128 – 131 °C. $[\alpha]_D^{22}$ = -395.0 (c = 1.06, $CHCl_2$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 1H), 6.97 (s, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.62 (dd, *J* = 9.6, 1.7 Hz, 1H), 6.54 (d, *J* = 2.6 Hz, 1H), 6.42 (dd, *J* = 8.6, 2.7 Hz, 1H), 5.94 (dd, *J* = 9.6, 4.2 Hz, 1H), 4.76 (d, *J* = 6.1 Hz, 1H), 4.00 - 3.97 (m, 1H), 3.32 (q, *J* = 7.1 Hz, 4H), 2.45 (s, 3H), 2.27 (d, *J* = 8.5 Hz, 6H), 1.99 (s, 1H), 1.15 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.7, 137.6, 136.3, 136.2, 133.2, 130.5, 130.0, 128.6, 128.6, 127.8, 126.8, 124.8, 113.8, 109.7, 73.8, 45.0, 44.3, 20.7, 19.7, 19.6, 12.8. HRMS calcd for $C_{23}H_{29}NO$ $[M]^+$: 335.2249. Found: 335.2244. The *ee* of **3hh** was determined by HPLC analysis using a Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1mL/min, 254 nm; t_{major} = 6.0 min, t_{minor} = 5.3 min.

***(5R,6R)-6-(4-(diethylamino)-2-methylphenyl)-5,6-dihydronaphtho[2,3-d][1,3]dioxol-5-ol* (3ih):**

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/15), 55 mg, 78% yield, 93% *ee*. Mp 125 – 128 °C. $[\alpha]_D^{22}$ = -306.8 (c = 1.07, $CHCl_2$). ^1H NMR (400 MHz, $CDCl_3$) δ 6.91 - 6.89 (m, 2H), 6.68 (s, 1H), 6.54 - 6.51 (m, 2H), 6.41 (dd, *J* = 8.6, 2.5 Hz, 1H), 5.94 - 5.89 (m, 3H), 4.69 - 4.68 (m, 1H), 3.97 - 3.94 (m, 1H), 3.32 (q, *J* = 7.0 Hz, 4H), 2.43 (s, 3H), 2.07 - 2.06 (m, 1H), 1.14 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.2, 146.9, 146.7, 137.6, 129.9, 129.2, 128.5, 127.1, 126.6, 124.4, 113.8, 109.7, 108.3, 107.0, 101.0, 74.0, 44.7, 44.2, 20.6, 12.7. HRMS calcd for $C_{22}H_{25}NO_3$ $[M]^+$: 351.1834. Found: 351.1838. The *ee* of **3ih** was determined by HPLC analysis using a Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1 mL/min, 254 nm; t_{major} = 8.8min, t_{minor} = 9.7min .

***(1R,2R)-2-(4-(diethylamino)-2-methylphenyl)-6,7-dimethoxy-1,2-dihydronaphthalen-1-ol* (3jh):**

Colourless oil, purified by silica gel column chromatography (ethyl acetate/hexane, 1/10), 53 mg, 72% yield, 97% *ee*. $[\alpha]_D^{22}$ = -372.7 (c = 1.01, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 1H), 6.89 (d, *J* = 8.6 Hz, 1H), 6.71 (s, 1H), 6.56 (dd, *J* = 9.6, 1.7 Hz, 1H), 6.52 (d, *J* = 2.5 Hz, 1H), 6.40 (dd, *J* = 8.6, 2.7 Hz, 1H), 5.90 (dd, *J* = 9.6, 4.2 Hz, 1H), 4.74 (d, *J* = 6.5 Hz, 1H), 3.98 - 3.95 (m, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.31 (q, *J* = 7.1 Hz, 4H), 2.44 (s, 3H), 1.99 (s, 1H), 1.13 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.6, 148.4, 146.7, 137.7, 129.2, 128.7, 128.4, 126.5, 125.8, 124.6, 113.8, 110.8, 109.8, 109.7, 74.0, 56.1, 56.0, 45.0, 44.3, 20.7, 12.8. HRMS calcd for $C_{23}H_{29}NO_3$ $[M]^+$:

367.2147. Found: 367.2139. The *ee* of **3jh** was determined by HPLC analysis using a Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1 mL/min, 254 nm; t_{major} = 12.4 min, t_{minor} = 20.2 min.

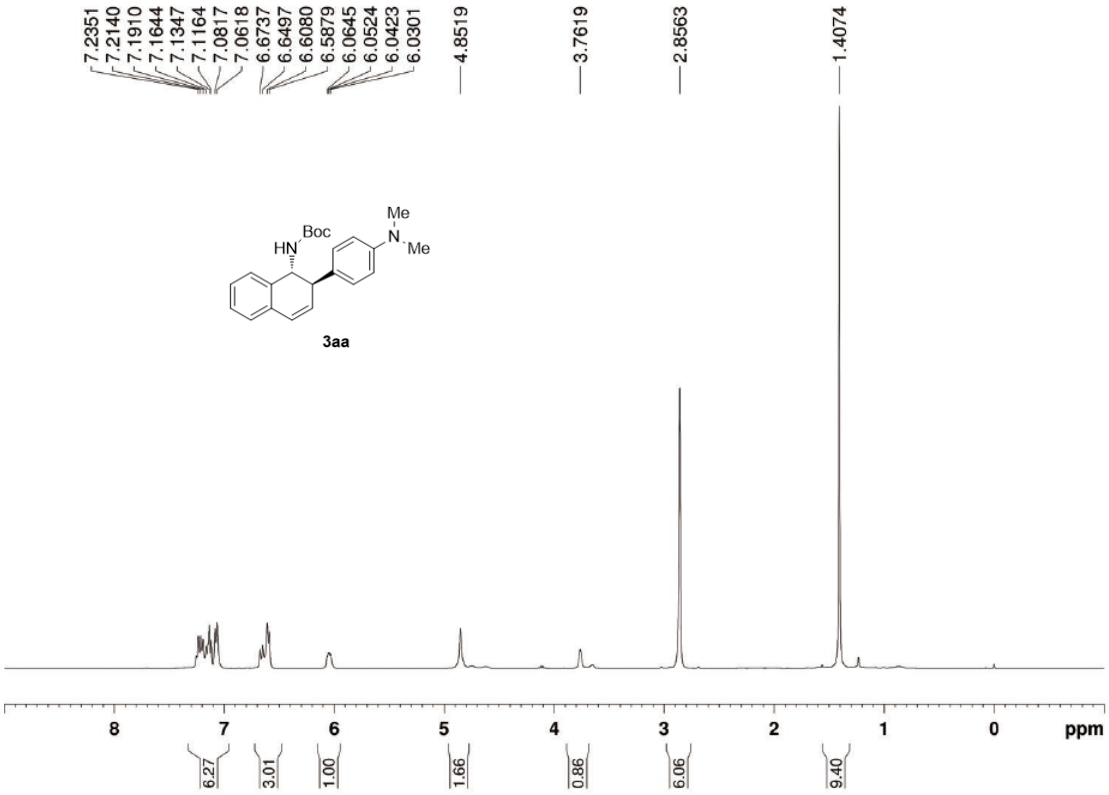
***(1R,2R)-2-(4-(diethylamino)-2-methylphenyl)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol* (3kh):**

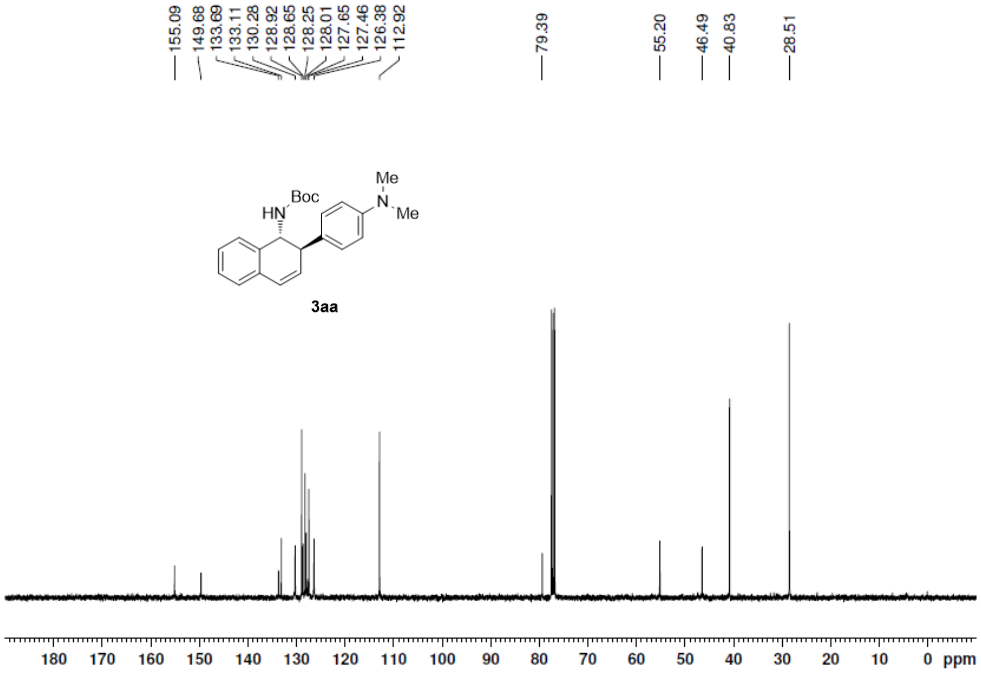
White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/10), 51 mg, 70% yield, 90% *ee*. Mp 126 – 129 ^{o}C. $[\alpha]_D^{22}$ = -363.7 (c = 1.01, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 9.8 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 1H), 6.71 (d, *J* = 8.9 Hz, 2H), 6.53 (s, 1H), 6.30 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.08 (dd, *J* = 9.8, 5.6 Hz, 1H), 5.11 (s, 1H), 4.05 (d, *J* = 5.3 Hz, 1H), 3.85 (s, 3H), 3.74 (s, 3H), 3.28 (q, *J* = 7.0 Hz, 4H), 2.51 (s, 3H), 2.30 (s, 1H), 1.11 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.5, 149.5, 146.6, 137.2, 129.2, 128.2, 124.2, 123.5, 122.7, 120.0, 114.0, 111.2, 110.1, 109.4, 66.5, 56.3, 55.8, 44.3, 43.3, 20.5, 12.8. HRMS calcd for $C_{23}H_{29}NO_3$ $[M]^+$: 367.2147. Found: 367.2145. The *ee* of **3kh** was determined by HPLC analysis using a Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 85/15, 1 mL/min, 254 nm; t_{major} = 14.1 min, t_{minor} = 11.0 min.

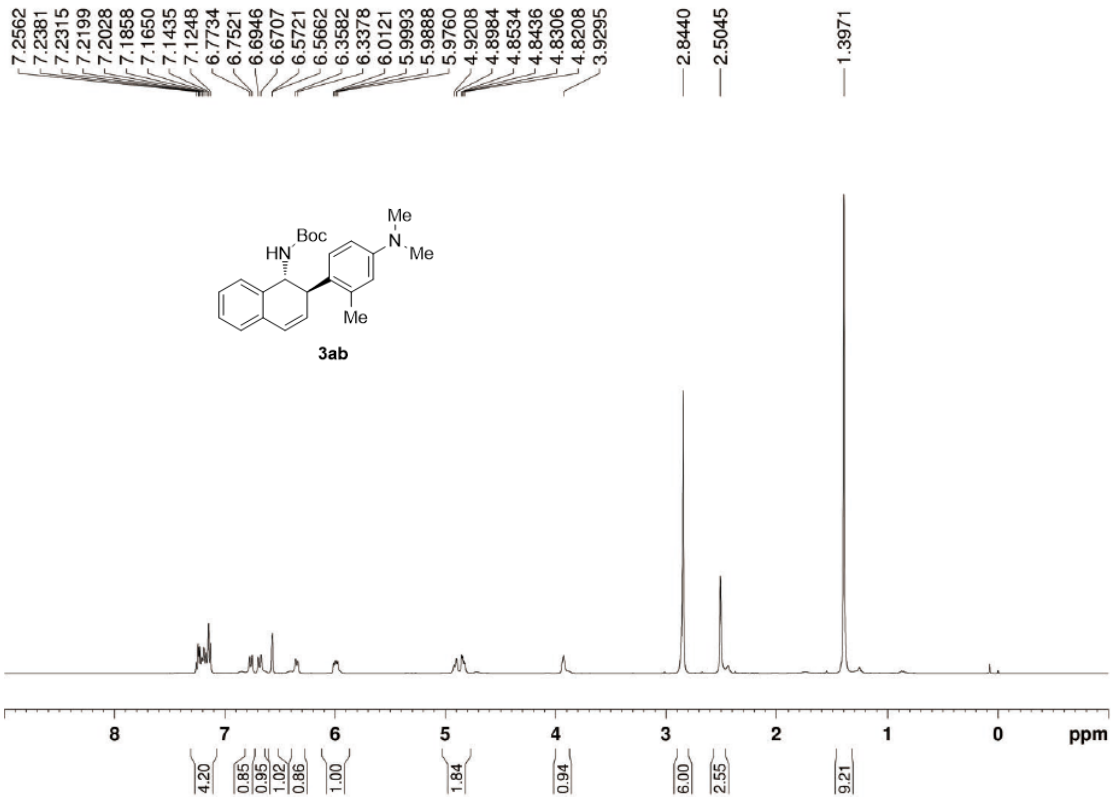
References:

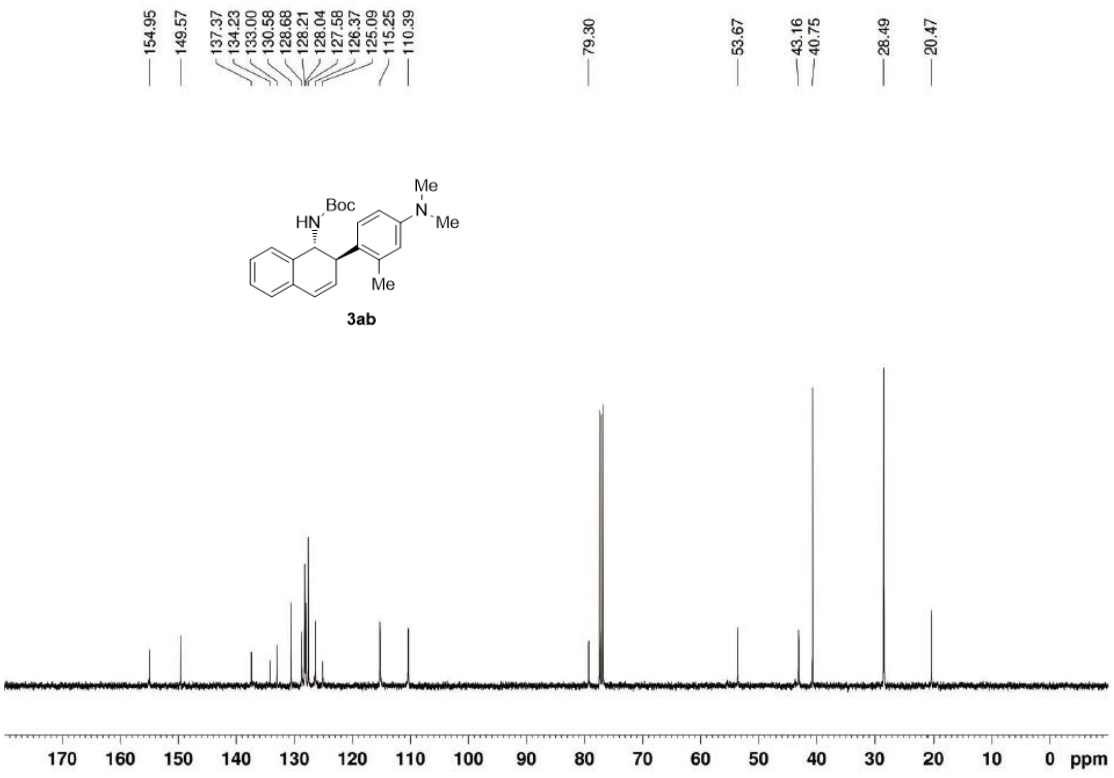
(1) Cho, Y.-h.; Zunic, V.; Senboku, H.; Olsen, M.; Lautens, M. *J. Am. Chem. Soc.* **2006**, *128*, 6837-6846.

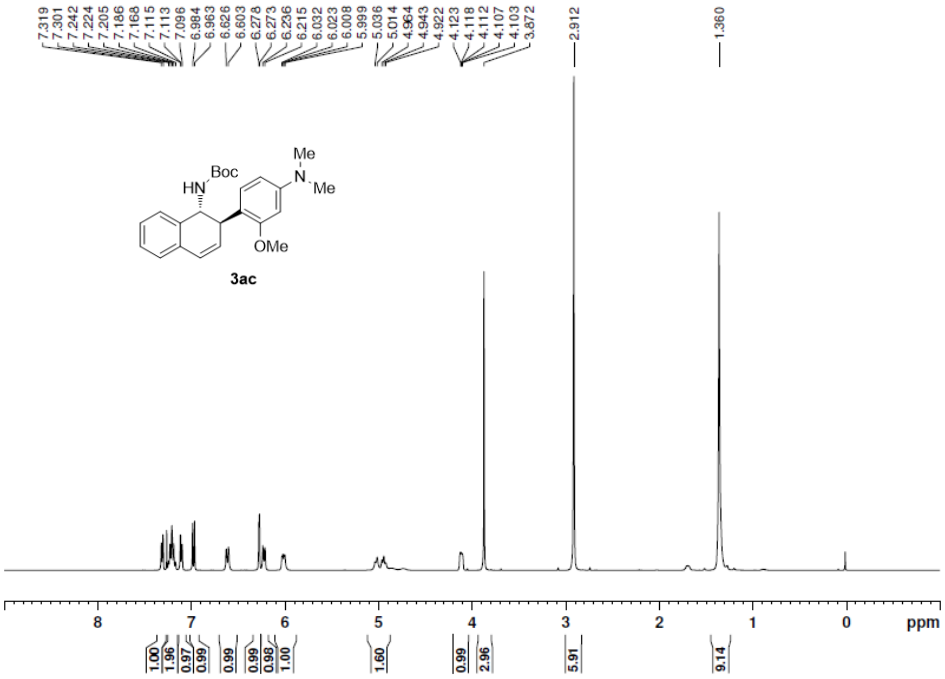
D: NMR Spectra of Products

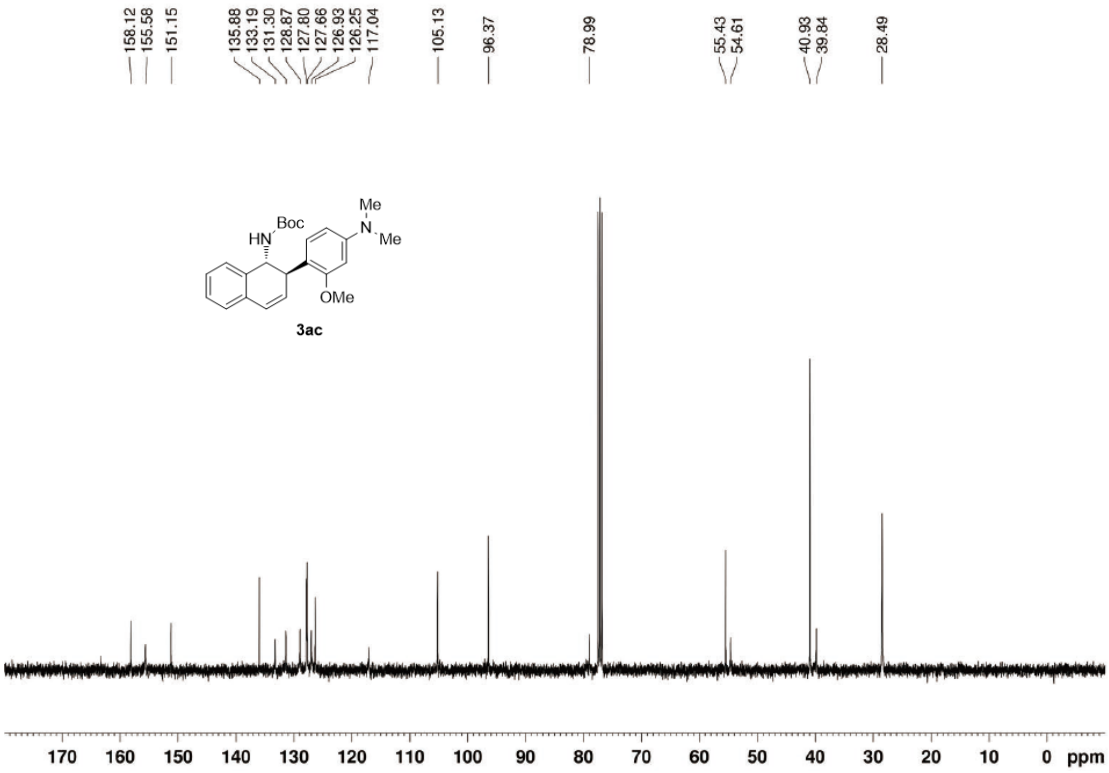


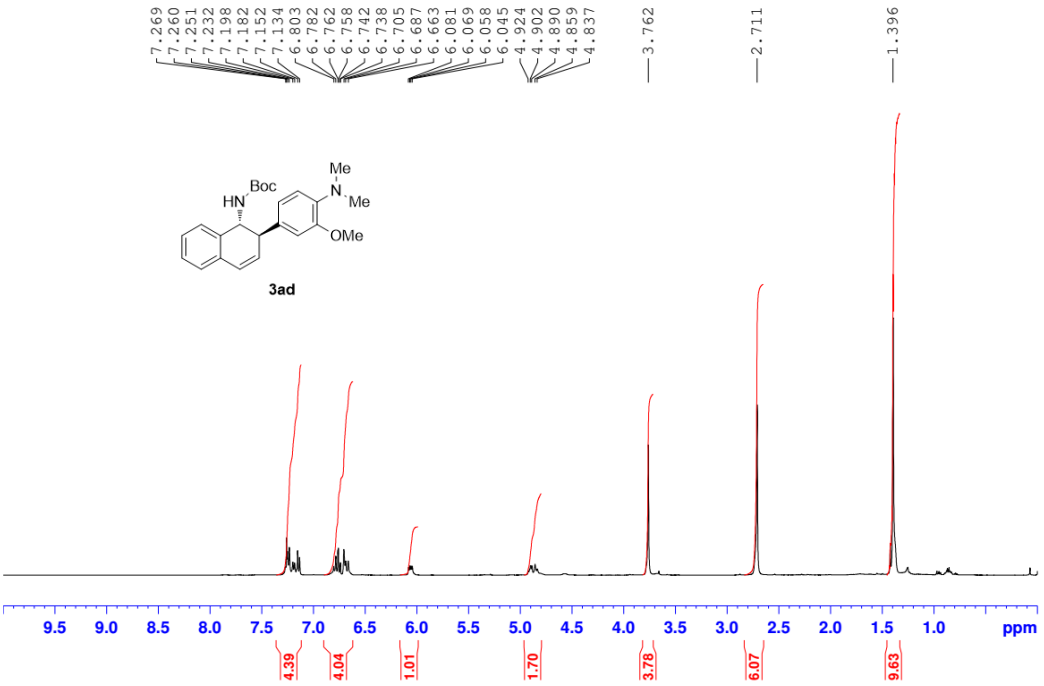


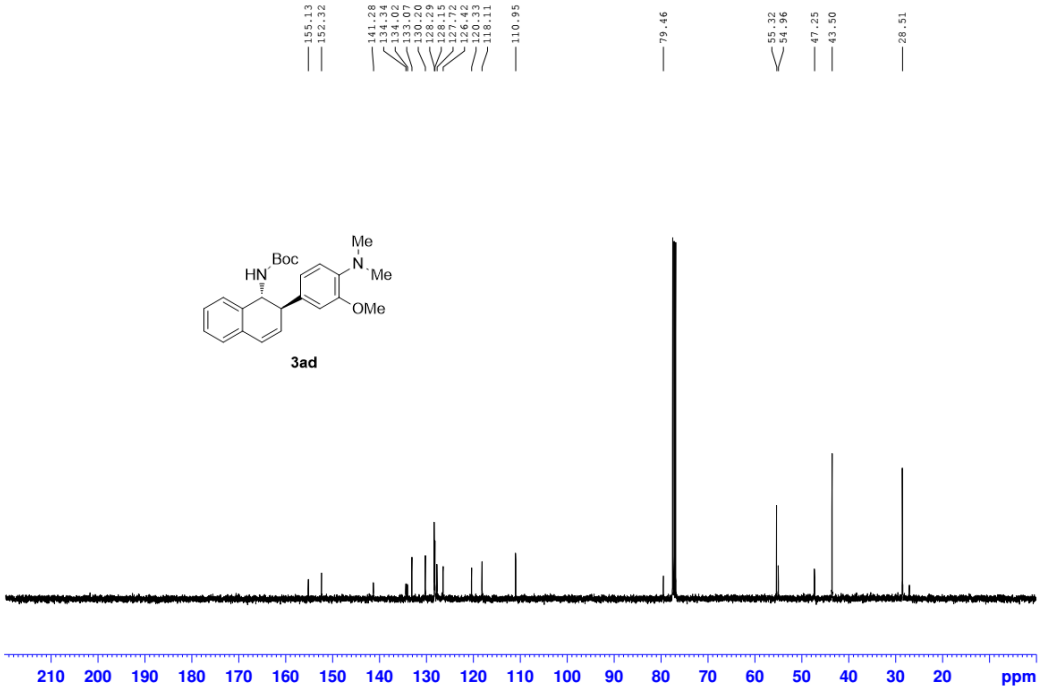

7.2562
7.2381
7.2315
7.2199
7.2028
7.1858
7.1650
7.1435
7.1248
6.7734
6.7521
6.6946
6.6707
6.5721
6.5662
6.3582
6.3378
6.0121
5.9993
5.9888
5.9760
4.9208
4.8984
4.8534
4.8436
4.8306
4.8208
3.9295
2.8440
2.5045
1.3971
Boc
HN
Me
N
Me
Me
3ab
8
7
6
5
4
3
2
1
0
ppm
4.20
0.85
0.95
1.02
0.86
1.00
1.84
0.94
6.00
2.55
9.21

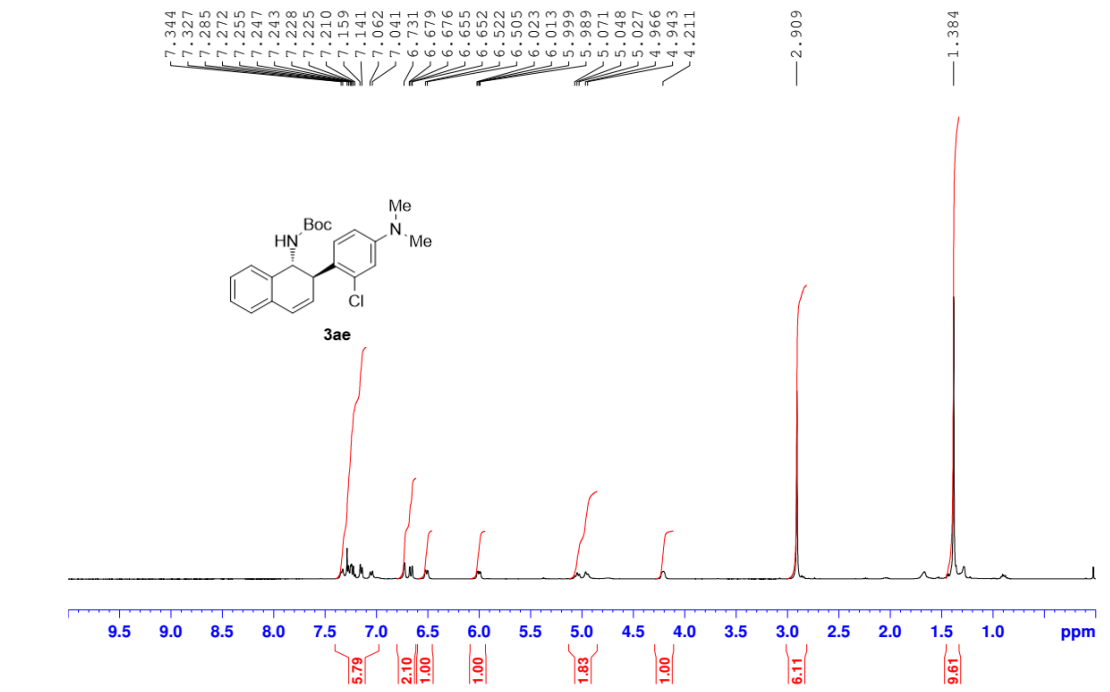

154.95
149.57
137.37
134.23
133.00
130.58
128.68
128.21
128.04
127.58
126.37
125.09
115.25
110.39
79.30
53.67
43.16
40.75
28.49
20.47
Boc
HN
Me
N
Me
Me
3ab
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

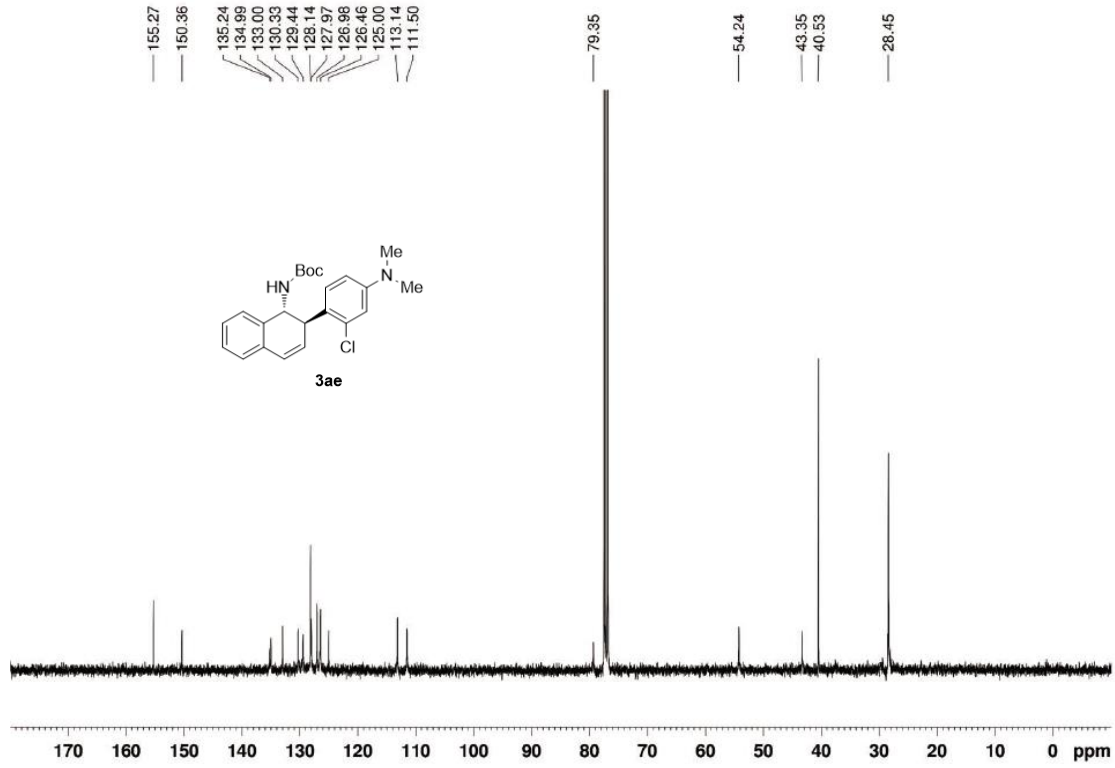

7.319
7.301
7.242
7.224
7.205
7.186
7.168
7.115
7.113
7.096
6.984
6.963
6.626
6.603
6.278
6.273
6.236
6.215
6.032
6.023
6.008
5.999
5.036
5.014
4.964
4.943
4.922
4.123
4.118
4.112
4.107
4.103
3.872
2.912
1.360
Me
N
Me
Boc
HN
OMe
3ac
8
7
6
5
4
3
2
1
0
ppm
1.00
1.96
0.97
0.99
0.99
0.99
0.98
1.00
1.60
0.99
2.96
5.91
9.14

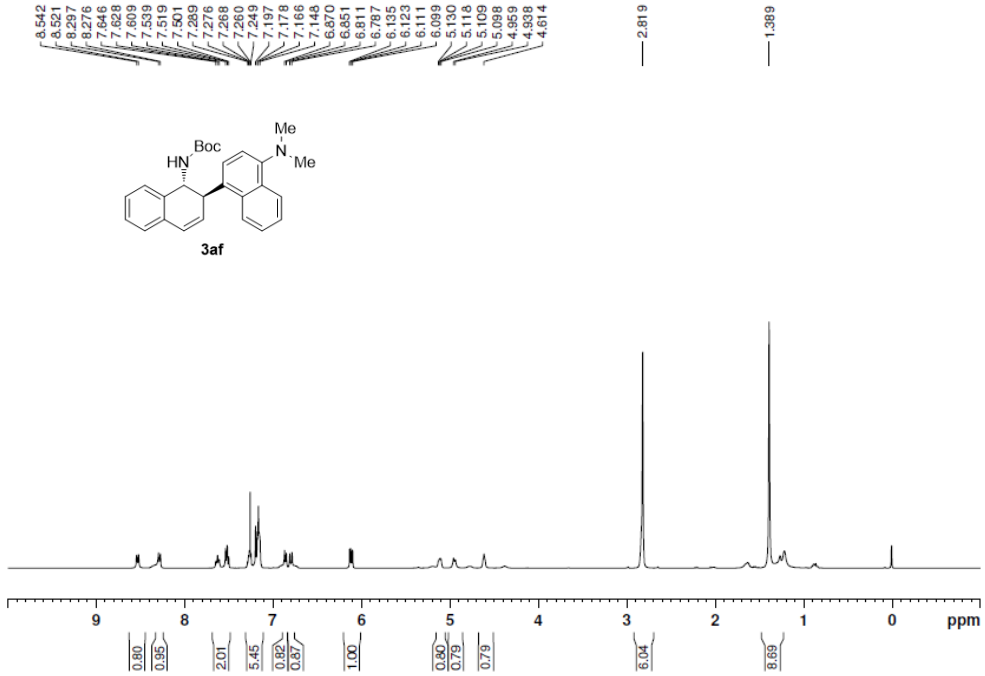

158.12
155.58
151.15
135.88
133.19
131.30
128.87
127.80
127.66
126.93
126.25
117.04
105.13
96.37
78.99
55.43
54.61
40.93
39.84
28.49
Me
N
Me
Boc
HN
OMe
3ac
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

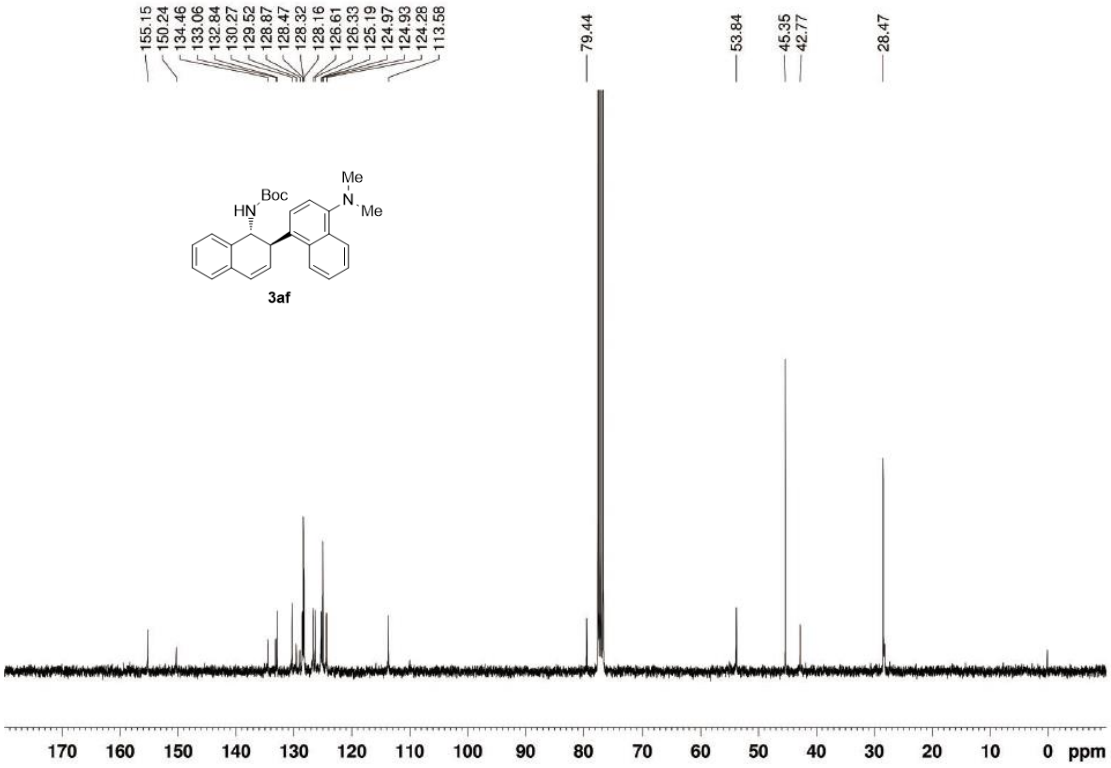

7.269
7.260
7.251
7.232
7.198
7.182
7.152
7.134
6.803
6.782
6.762
6.758
6.742
6.738
6.705
6.687
6.663
6.081
6.069
6.058
6.045
4.924
4.902
4.890
4.859
4.837
3.762
2.711
1.396
Boc
HN
Me
N
Me
OMe
3ad
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
4.39
4.04
1.01
1.70
3.78
6.07
9.63

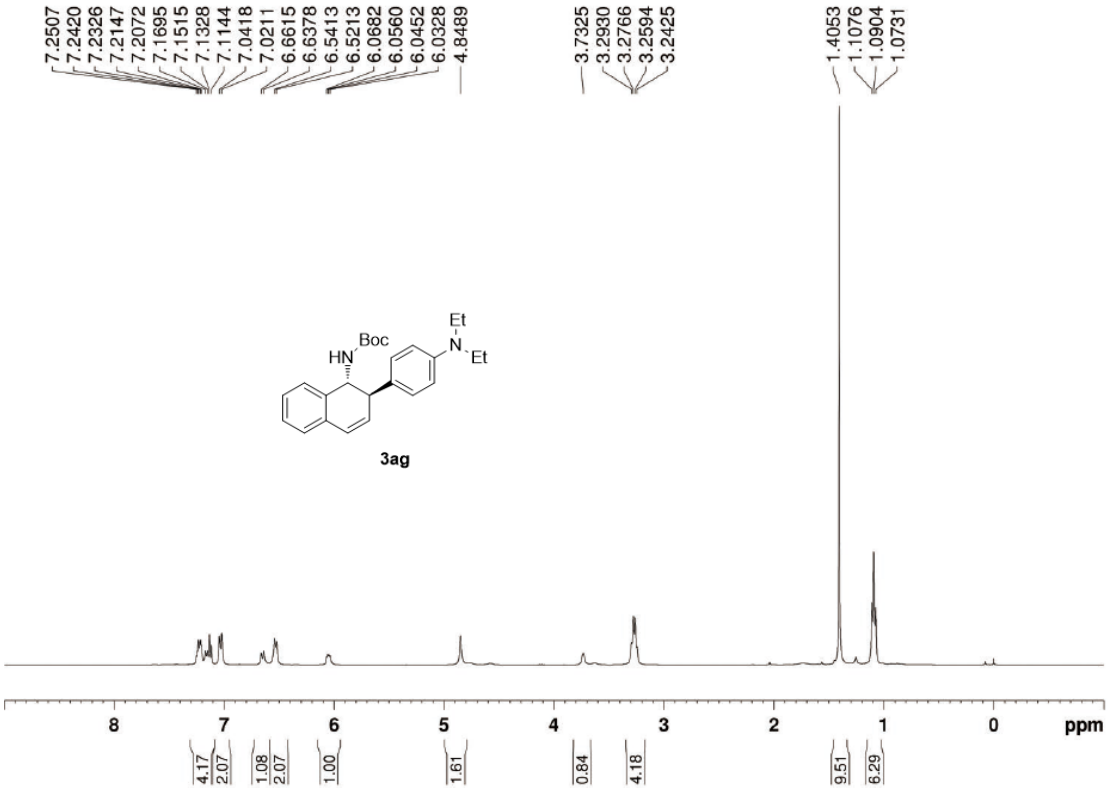

155.13
152.32
141.28
134.34
134.02
133.07
130.00
128.29
128.15
127.72
126.42
120.33
118.11
110.95
79.46
55.32
54.96
47.25
43.50
28.51
Boc
HN
Me
N
Me
OMe
3ad
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

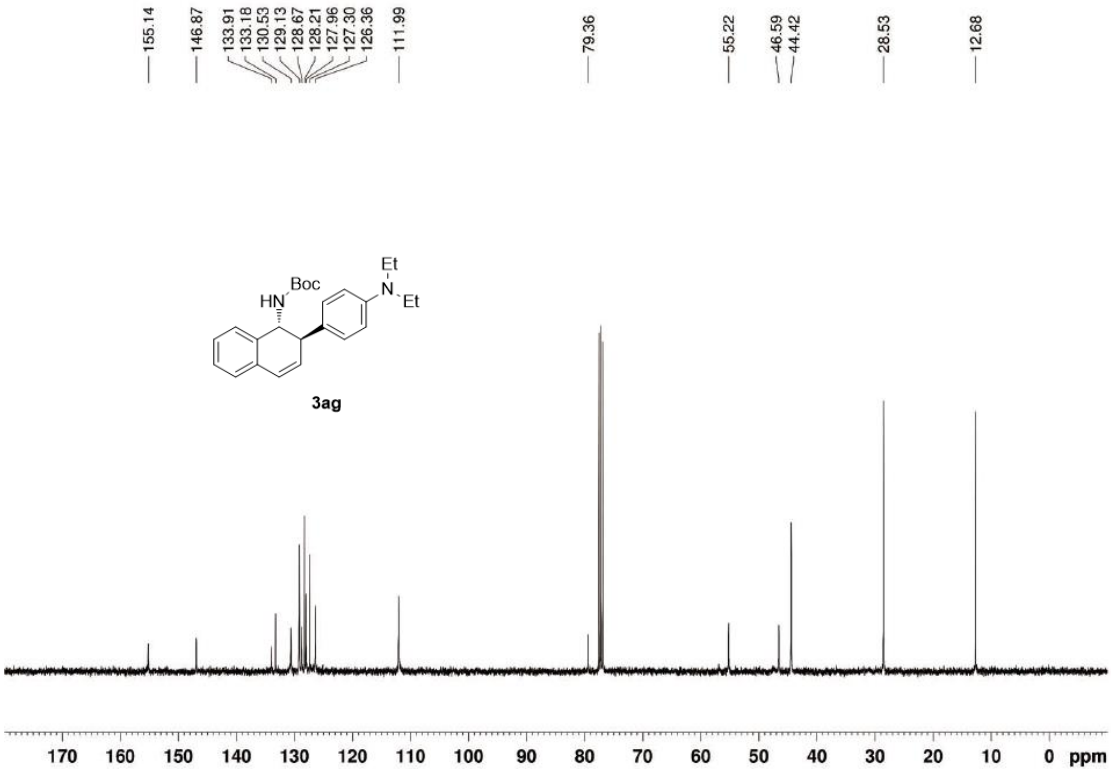

7.344
7.327
7.285
7.272
7.255
7.247
7.243
7.228
7.225
7.210
7.159
7.141
7.062
7.041
6.731
6.679
6.676
6.655
6.652
6.522
6.505
6.023
6.013
5.999
5.989
5.071
5.048
5.027
4.966
4.943
4.211
2.909
1.384
Boc
HN
Me
N
Me
Cl
3ae
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
5.79
2.10
1.00
1.00
1.83
1.00
6.11
9.61

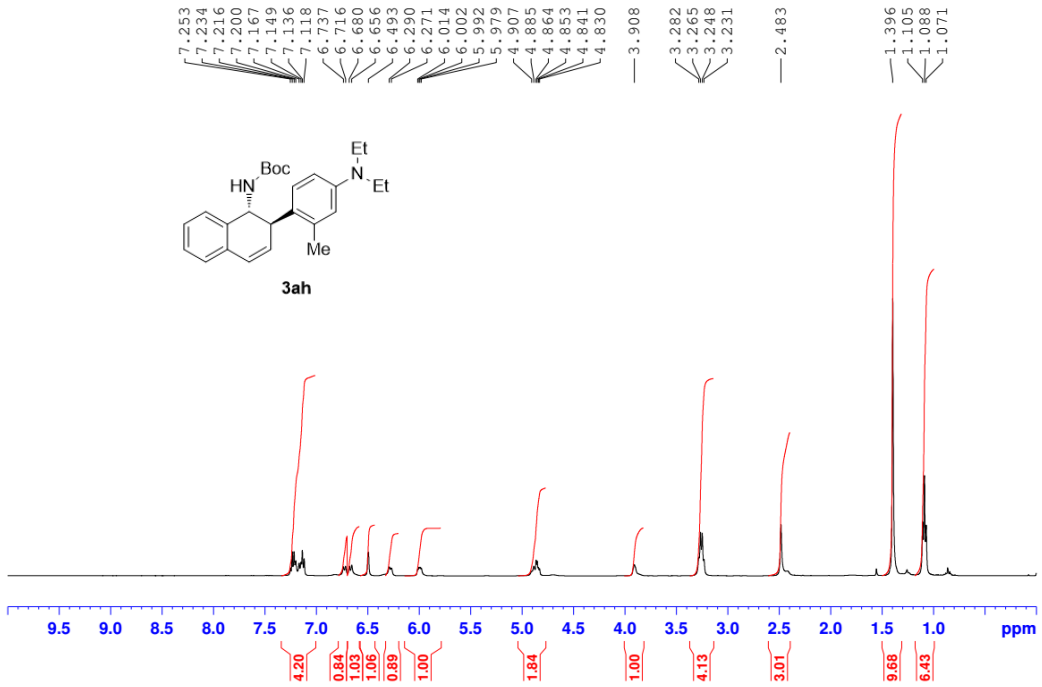

155.27
150.36
135.24
134.99
133.00
130.33
129.44
128.14
127.97
126.98
126.46
125.00
113.14
111.50
79.35
54.24
43.35
40.53
28.45
Boc
HN
Me
N
Me
Cl
3ae
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

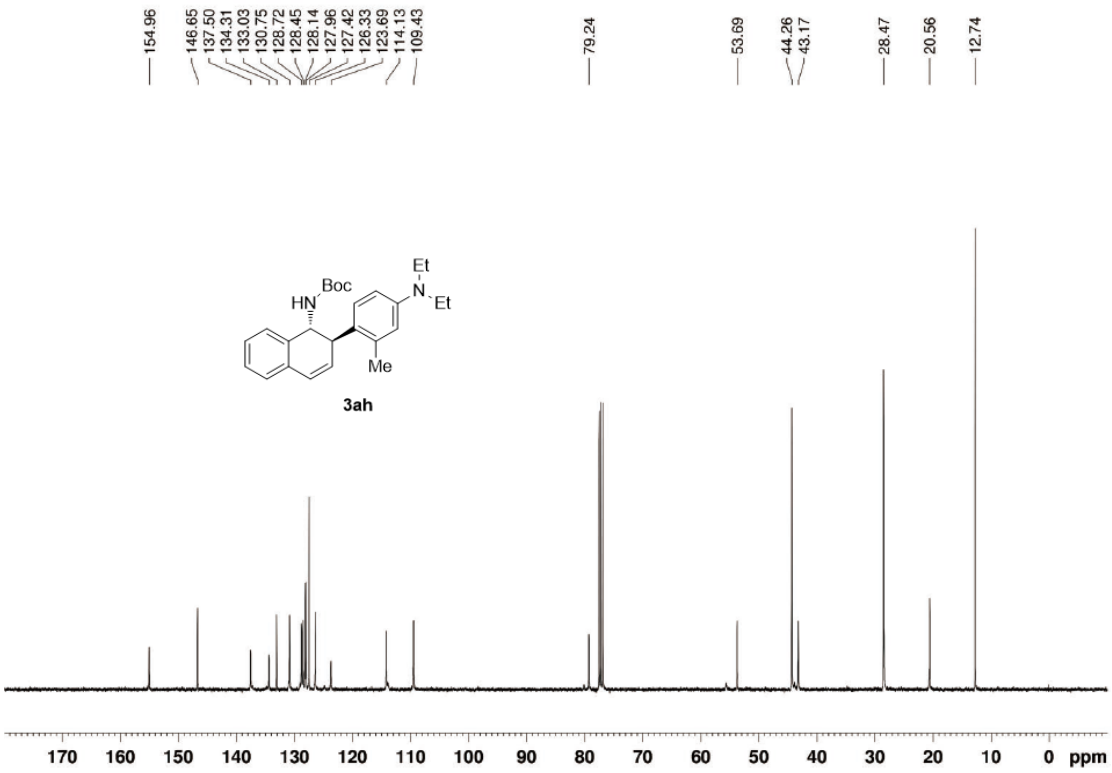

8.542
8.521
8.297
8.276
7.646
7.628
7.609
7.539
7.519
7.501
7.289
7.276
7.268
7.260
7.249
7.197
7.178
7.166
7.148
6.870
6.851
6.811
6.787
6.135
6.123
6.111
6.099
5.130
5.118
5.109
5.098
4.959
4.938
4.614
2.819
1.389
Me
N
Me
Boc
HN
3af
9
8
7
6
5
4
3
2
1
0
ppm
0.80
0.95
2.01
5.45
0.82
0.87
1.00
0.80
0.79
0.79
6.04
8.69

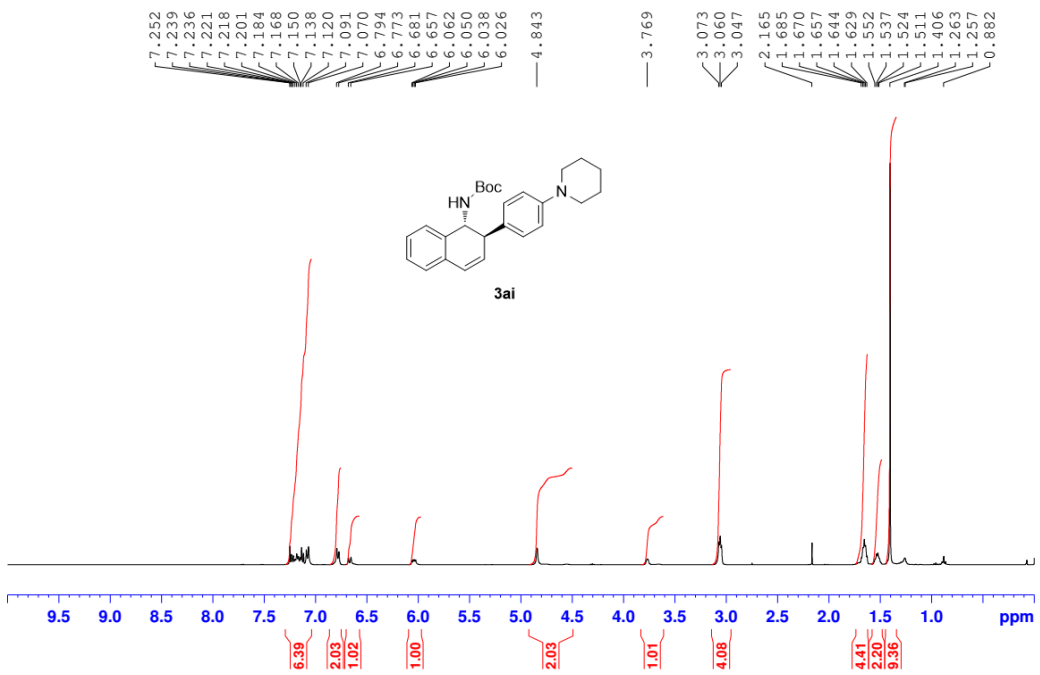

155.15
150.24
134.46
133.06
132.84
130.27
129.52
128.87
128.47
128.32
128.16
126.61
126.33
125.19
124.97
124.93
124.28
113.58
79.44
53.84
45.35
42.77
28.47
Me
N
Me
Boc
HN
3af
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

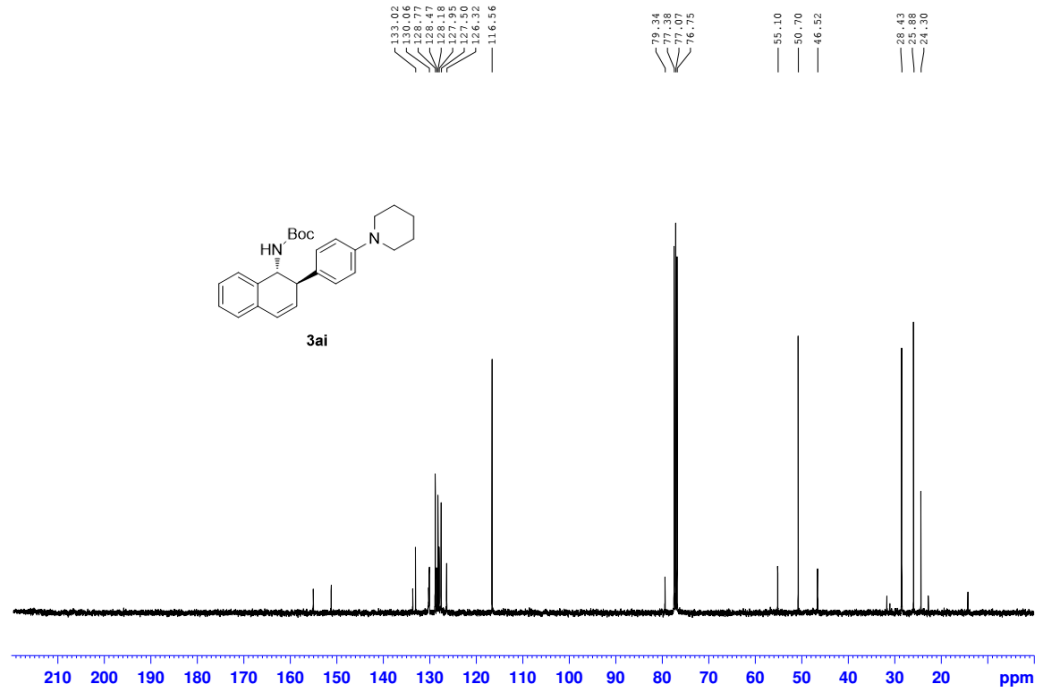

7.2507
7.2420
7.2326
7.2147
7.2072
7.1695
7.1515
7.1328
7.1144
7.0418
7.0211
6.6615
6.6378
6.5413
6.5213
6.0682
6.0560
6.0452
6.0328
4.8489
3.7325
3.2930
3.2766
3.2594
3.2425
1.4053
1.1076
1.0904
1.0731
Boc
HN
Et
N
Et
3ag
8
7
6
5
4
3
2
1
0
ppm
4.17
2.07
1.08
2.07
1.00
1.61
0.84
4.18
9.51
6.29

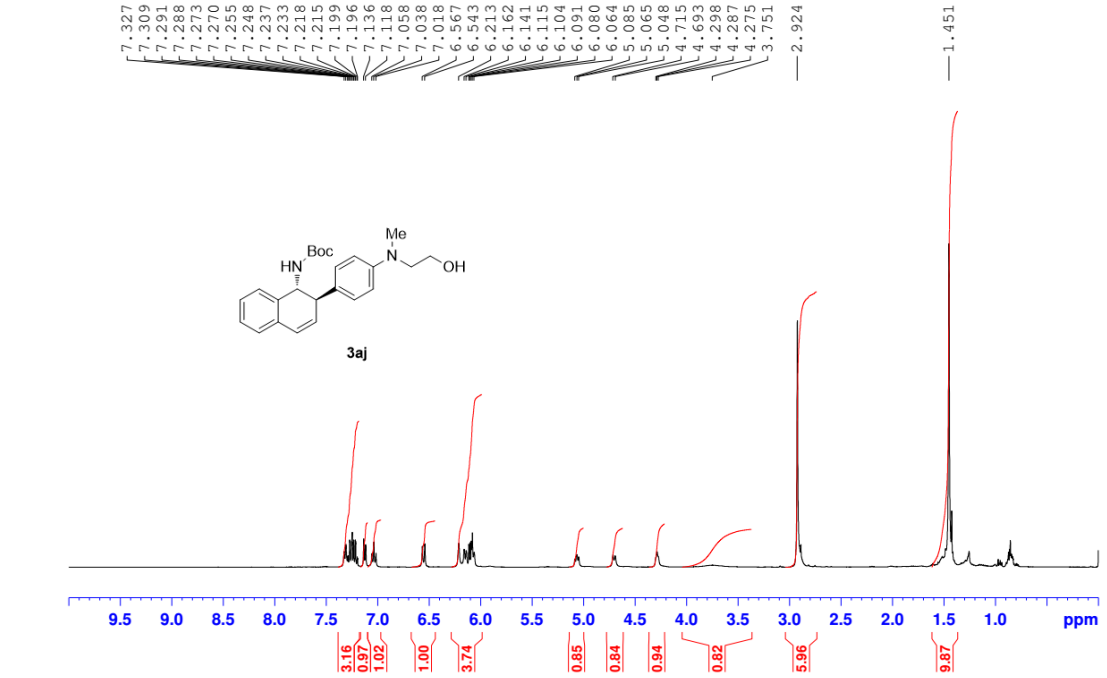

155.14
146.87
133.91
133.18
130.53
129.13
128.67
128.21
127.96
127.30
126.36
111.99
79.36
55.22
46.59
44.42
28.53
12.68
Boc
HN
Et
N
Et
3ag
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

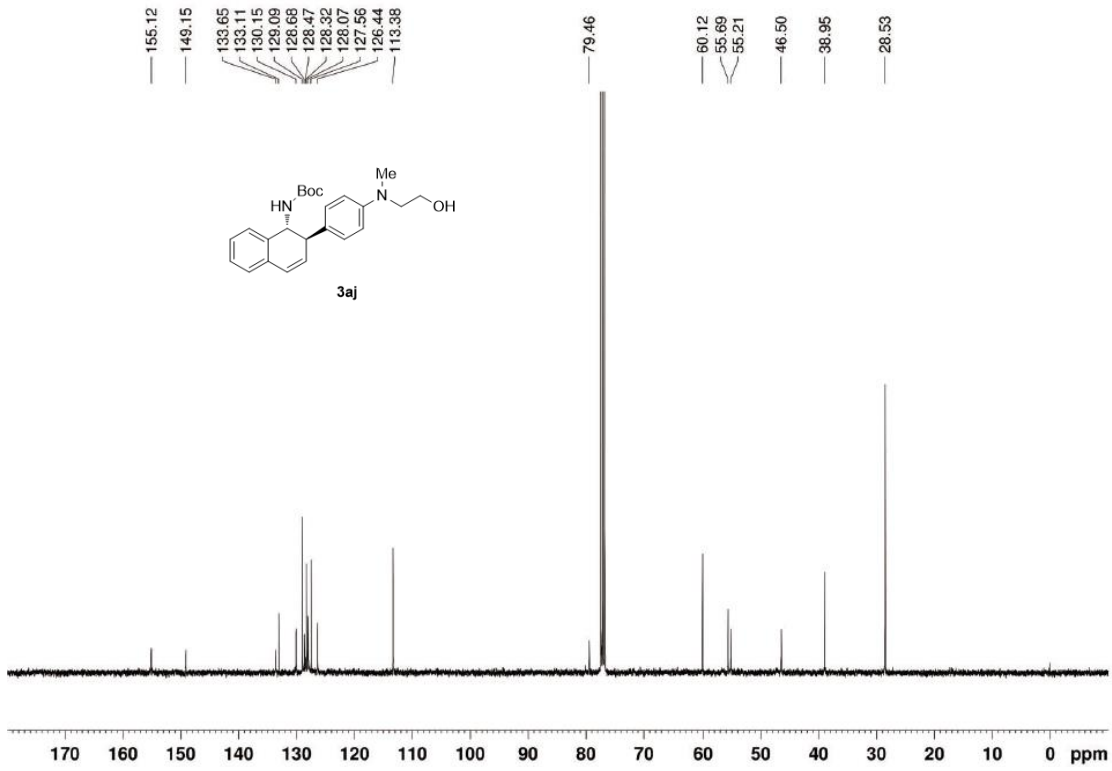

7.253
7.234
7.216
7.200
7.167
7.149
7.136
7.118
6.737
6.716
6.680
6.656
6.493
6.290
6.271
6.014
6.002
5.992
5.979
4.907
4.885
4.864
4.853
4.841
4.830
3.908
3.282
3.265
3.248
3.231
2.483
1.396
1.105
1.088
1.071
Et
Boc
HN
N
Et
Me
3ah
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
4.20
0.84
1.03
1.06
0.89
1.00
1.84
1.00
4.13
3.01
9.68
6.43

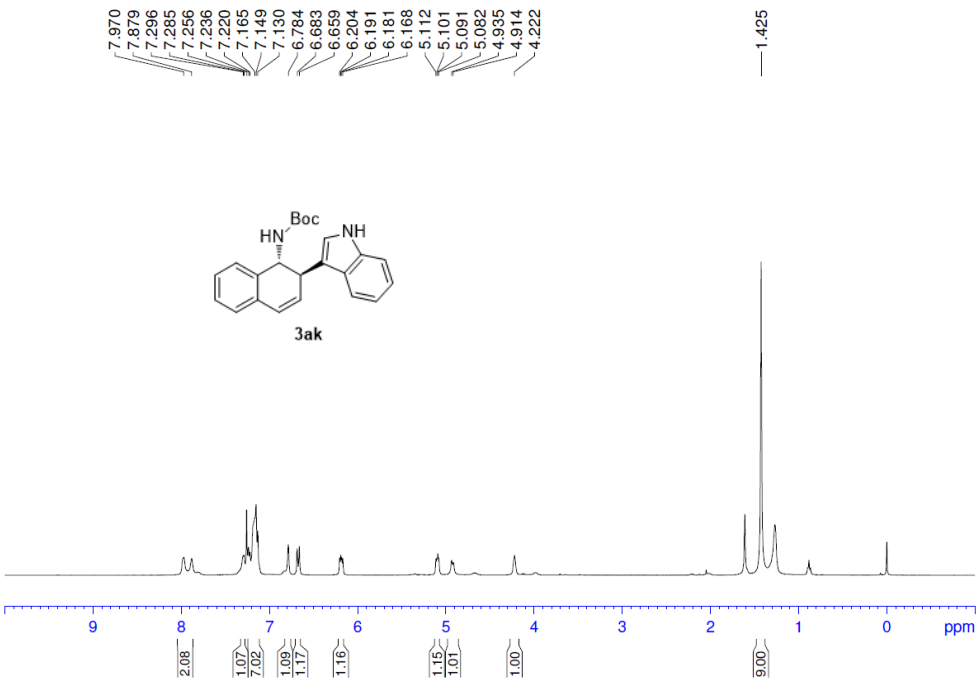

154.96
146.65
137.50
134.31
133.03
130.75
128.72
128.45
128.14
127.96
127.42
126.33
123.69
114.13
109.43
79.24
53.69
44.26
43.17
28.47
20.56
12.74
Et
Boc
HN
N
Et
Me
3ah
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

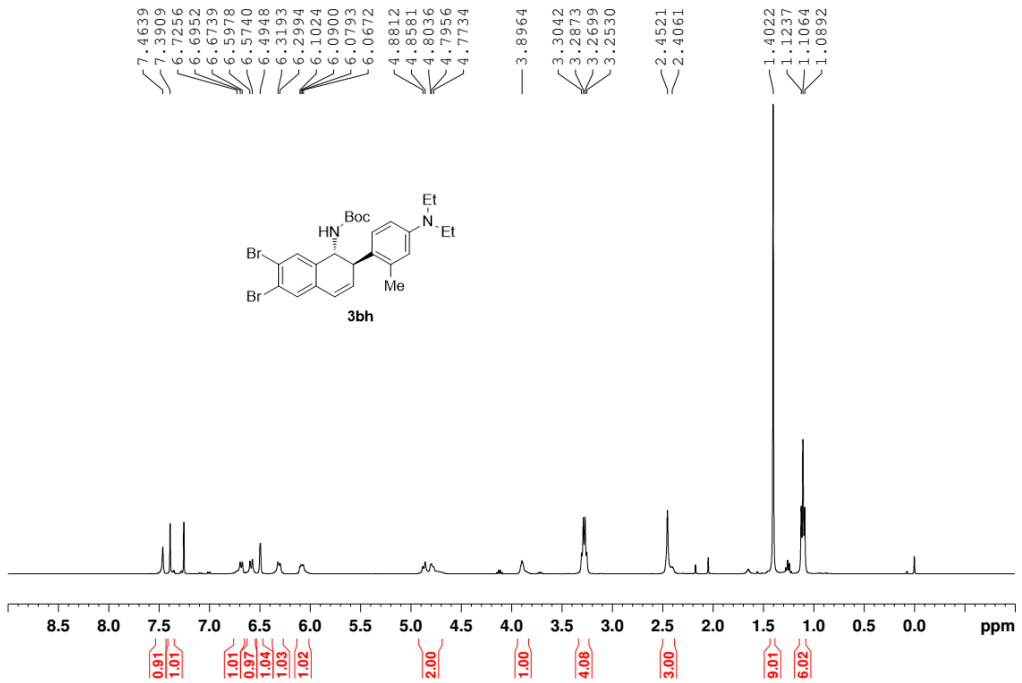

7.252
7.239
7.236
7.221
7.218
7.201
7.184
7.168
7.150
7.138
7.120
7.091
7.070
6.794
6.773
6.681
6.657
6.062
6.050
6.038
6.026
4.843
3.769
3.073
3.060
3.047
2.165
1.685
1.670
1.657
1.644
1.629
1.552
1.537
1.524
1.511
1.406
1.263
1.257
0.882
Boc
HN
N
3ai
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
6.39
2.03
1.02
1.00
2.03
1.01
4.08
4.41
2.20
9.36

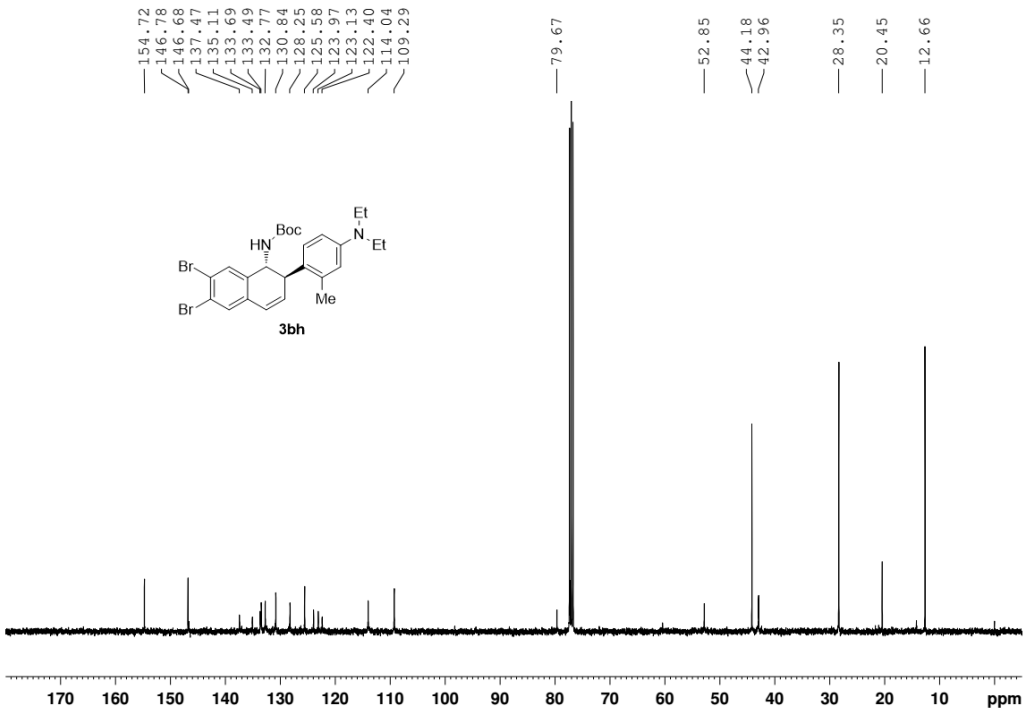

133.02
130.06
128.77
128.47
128.18
127.95
127.50
126.32
116.56
79.34
77.38
77.07
76.75
55.10
50.70
46.52
28.43
25.88
24.30
Boc
HN
N
3ai
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

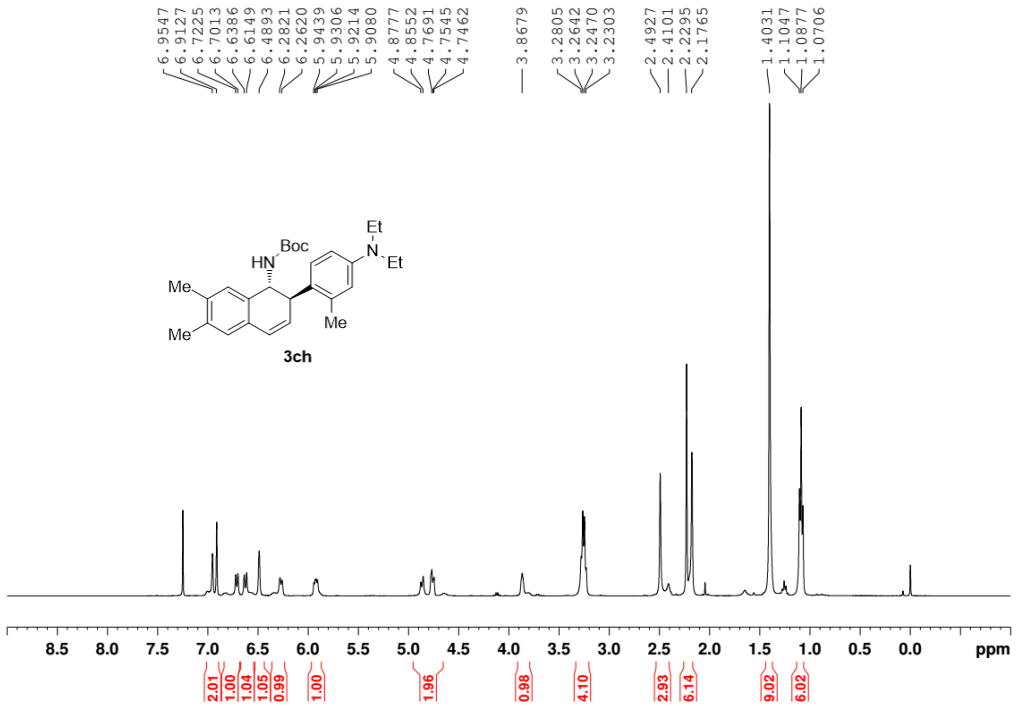

7.327
7.309
7.291
7.288
7.273
7.270
7.255
7.248
7.237
7.233
7.218
7.215
7.199
7.196
7.136
7.118
7.058
7.038
7.018
6.567
6.543
6.213
6.162
6.141
6.115
6.104
6.091
6.080
6.064
5.085
5.065
5.048
4.715
4.693
4.298
4.287
4.275
3.751
2.924
1.451
Me
Boc
HN
N
OH
3aj
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
3.16
0.97
1.02
1.00
3.74
0.85
0.84
0.94
0.82
5.96
9.87

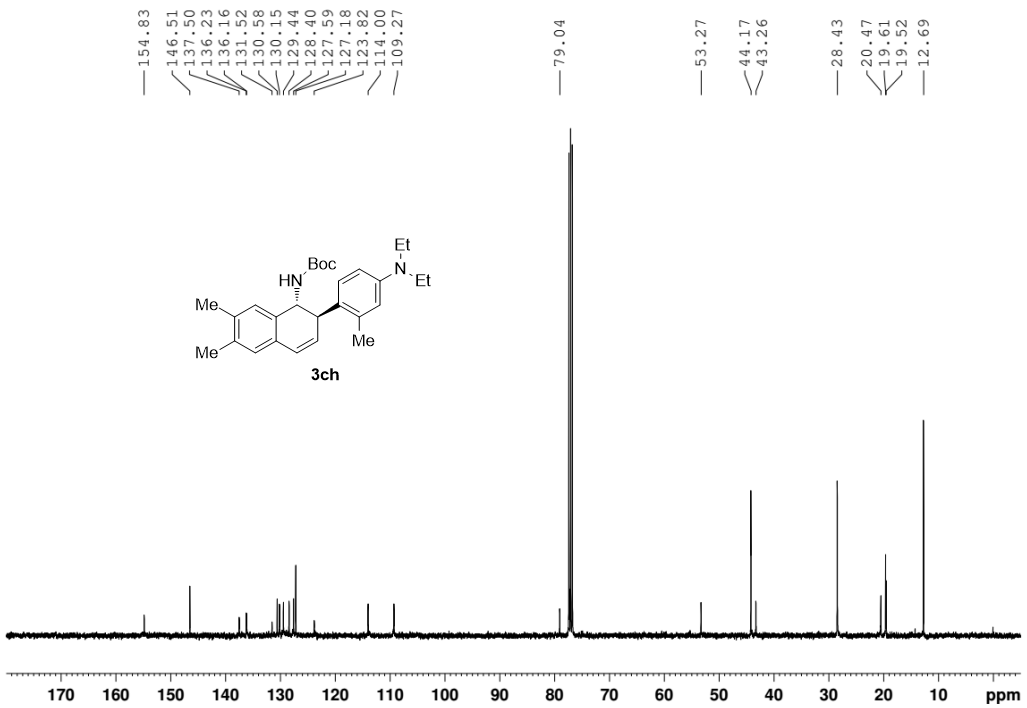

155.12
149.15
133.65
133.11
130.15
129.09
128.68
128.47
128.32
128.07
127.56
126.44
113.38
79.46
60.12
55.69
55.21
46.50
38.95
28.53
Me
Boc
HN
N
OH
3aj
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

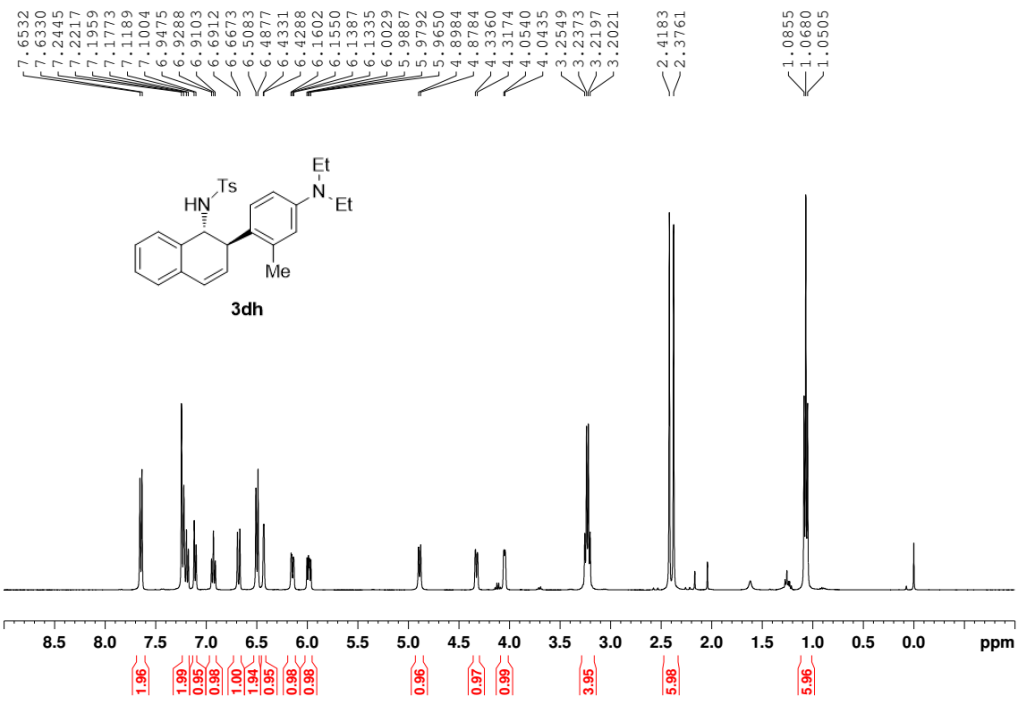

7.970
7.879
7.296
7.285
7.256
7.236
7.220
7.165
7.149
7.130
6.784
6.683
6.659
6.204
6.191
6.181
6.168
5.112
5.101
5.091
5.082
4.935
4.914
4.222
1.425
Boc
HN
NH
3ak
9
8
7
6
5
4
3
2
1
0
ppm
2.08
1.07
7.02
1.09
1.17
1.16
1.15
1.01
1.00
9.00

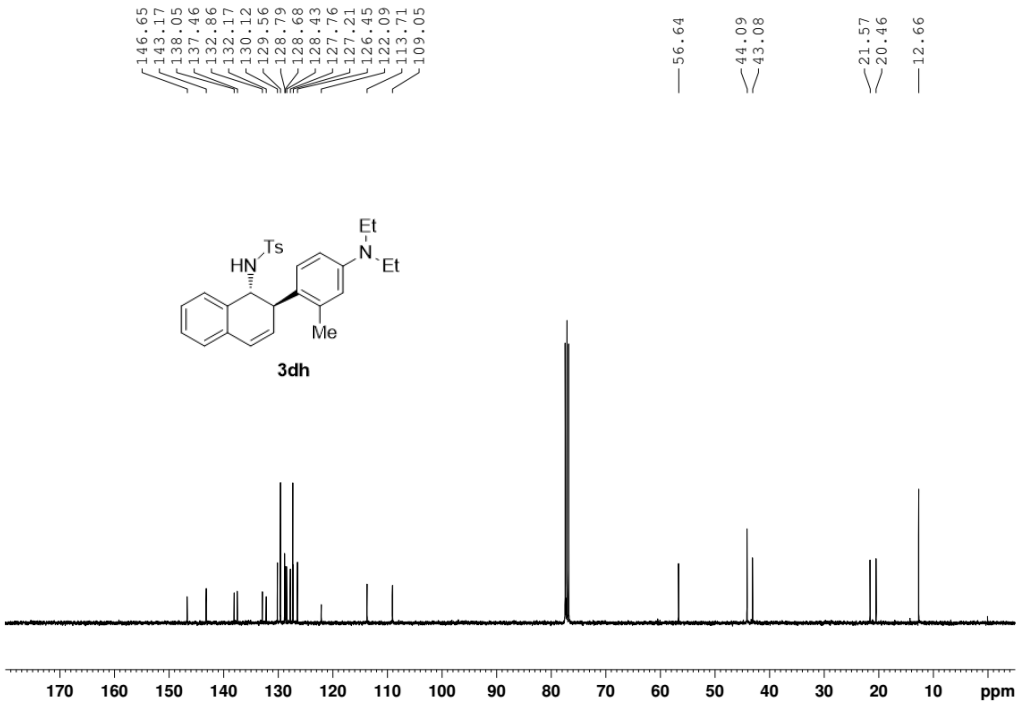

7.4639
7.3909
6.7256
6.6952
6.6739
6.5978
6.5740
6.4948
6.3193
6.2994
6.1024
6.0900
6.0793
6.0672
4.8812
4.8581
4.8036
4.7956
4.7734
3.8964
3.3042
3.2873
3.2699
3.2530
2.4521
2.4061
1.4022
1.1237
1.1064
1.0892
Boc
HN
Et
N
Et
Br
Br
Me
3bh
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.91 1.01 1.01 0.97 1.04 1.03 1.02 2.00 1.00 4.08 3.00 9.01 6.02

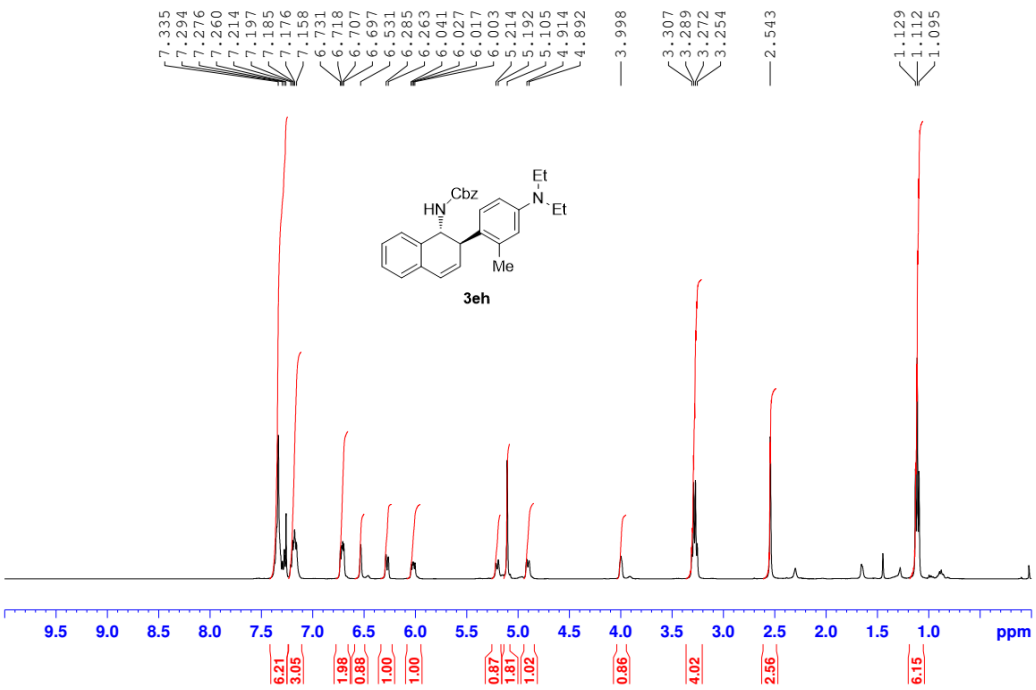

154.72
146.78
146.68
137.47
135.11
133.69
133.49
132.77
130.84
128.25
125.58
123.97
123.13
122.40
114.04
109.29
79.67
52.85
44.18
42.96
28.35
20.45
12.66
Boc
HN
Et
N
Et
Br
Br
Me
3bh
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

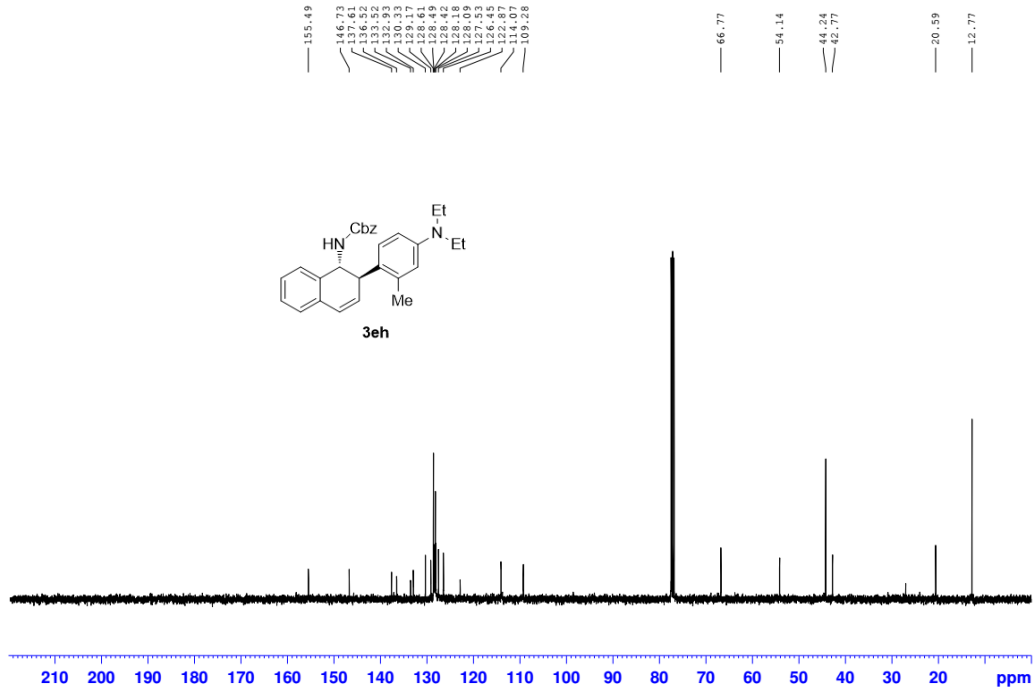

6.9547
6.9127
6.7225
6.7013
6.6386
6.6149
6.4893
6.2821
6.2620
5.9439
5.9306
5.9214
5.9080
4.8777
4.8552
4.7691
4.7545
4.7462
3.8679
3.2805
3.2642
3.2470
3.2303
2.4927
2.4101
2.2295
2.1765
1.4031
1.1047
1.0877
1.0706
Et
N
Et
Boc
HN
Me
Me
Me
3ch
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.01
1.00
1.04
1.05
0.99
1.00
1.96
0.98
4.10
2.93
6.14
9.02
6.02

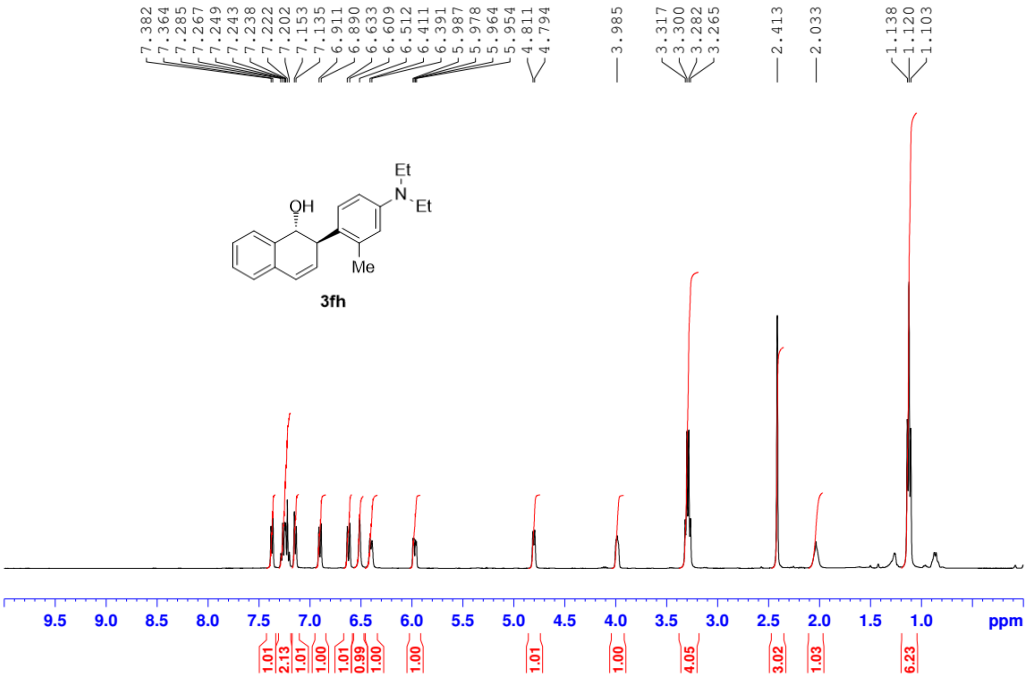

154.83
146.51
137.50
136.23
136.16
131.52
130.58
130.15
129.44
128.40
127.59
127.18
123.82
114.00
109.27
79.04
53.27
44.17
43.26
28.43
20.47
19.61
19.52
12.69
Et
N
Et
Boc
HN
Me
Me
Me
3ch
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

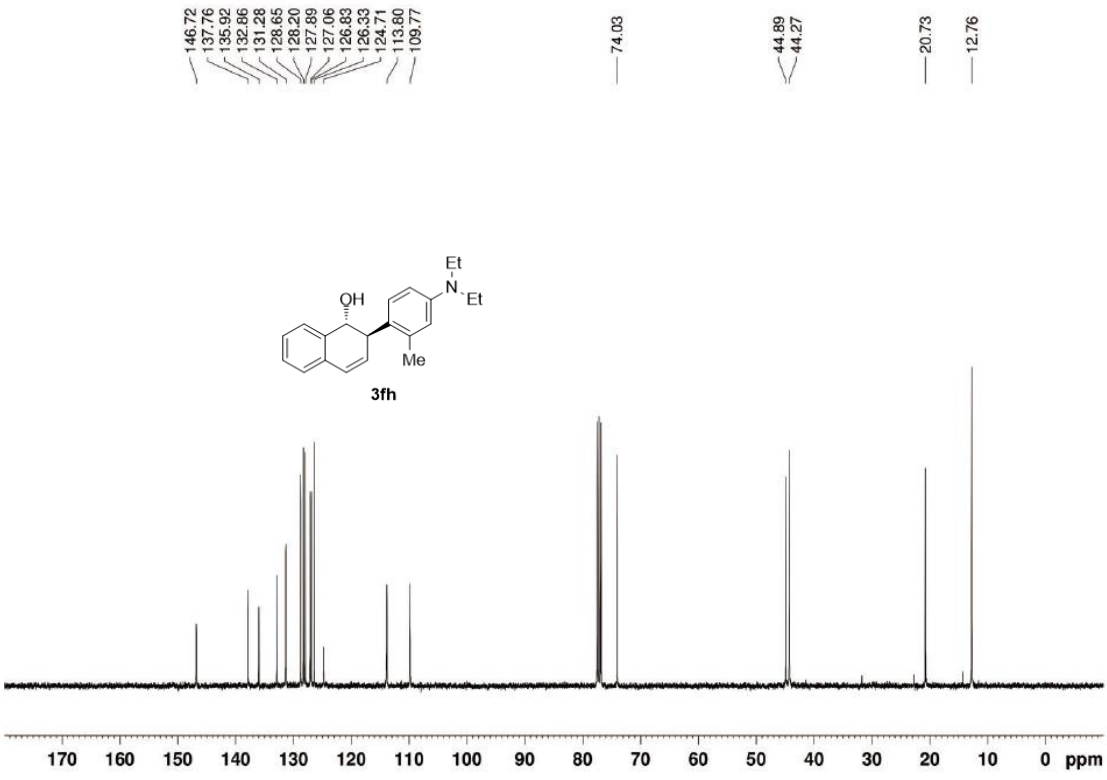

7.6532
7.6330
7.2445
7.2217
7.1959
7.1773
7.1189
7.1004
6.9475
6.9288
6.9103
6.6912
6.6673
6.5083
6.4877
6.4331
6.4288
6.1602
6.1550
6.1387
6.1335
6.0029
5.9887
5.9792
5.9650
4.8984
4.8784
4.3360
4.3174
4.0540
4.0435
3.2549
3.2373
3.2197
3.2021
2.4183
2.3761
1.0855
1.0680
1.0505
Et
N
Et
HN
Ts
Me
3dh
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.96
1.99
0.95
0.98
1.00
1.94
0.95
0.98
0.98
0.96
0.97
0.99
3.95
5.98
5.96

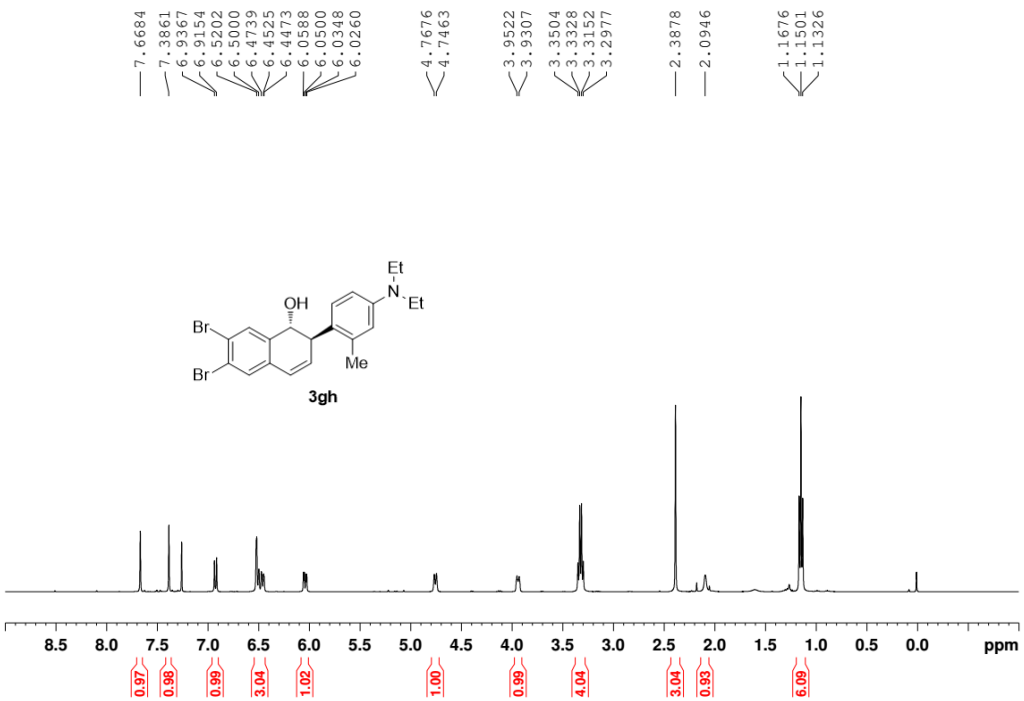

146.65
143.17
138.05
137.46
132.86
132.17
130.12
129.56
128.79
128.68
128.43
127.76
127.21
126.45
122.09
113.71
109.05
56.64
44.09
43.08
21.57
20.46
12.66
Et
N
Et
HN
Ts
Me
3dh
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

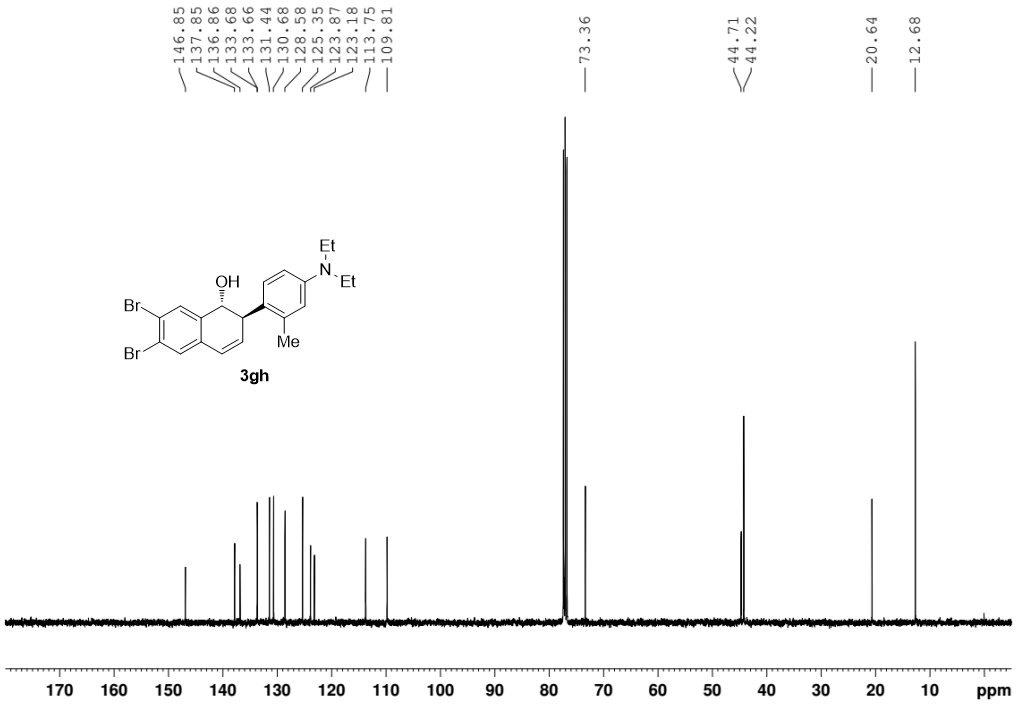

7.335
7.294
7.276
7.260
7.214
7.197
7.185
7.176
7.158
6.731
6.718
6.707
6.697
6.531
6.285
6.263
6.041
6.027
6.017
6.003
5.214
5.192
5.105
4.914
4.892
3.998
3.307
3.289
3.272
3.254
2.543
1.129
1.112
1.095
Et
N
Et
Cbz
HN
Me
3eh
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
6.21
3.05
1.98
0.88
1.00
1.00
0.87
1.81
1.02
0.86
4.02
2.56
6.15

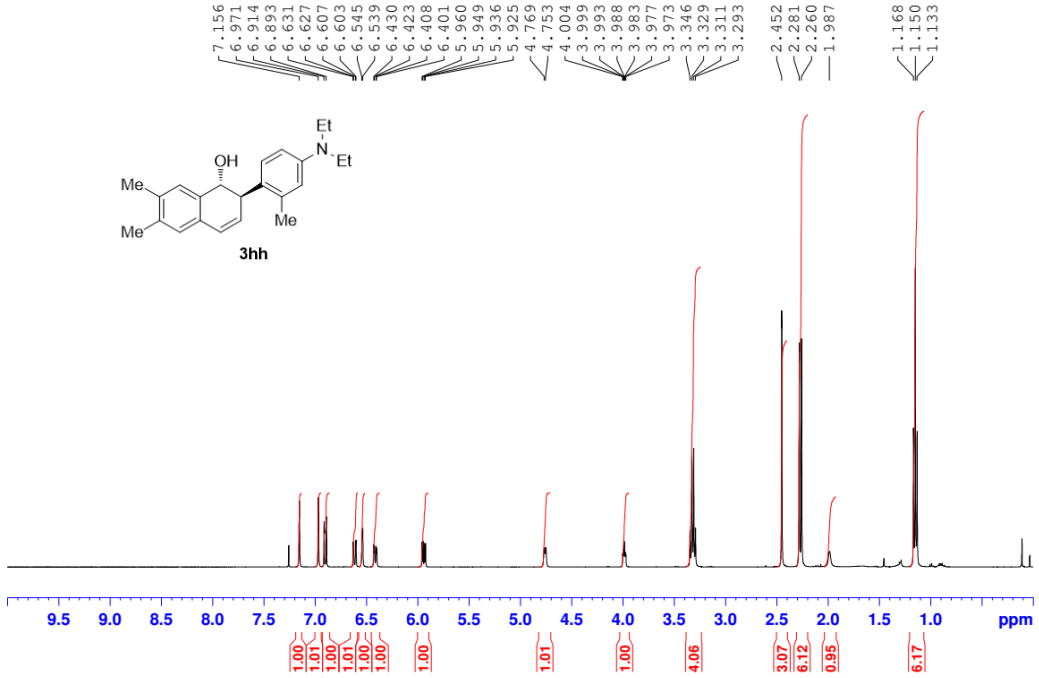

155.49
146.73
137.61
136.52
133.52
132.33
130.33
129.17
128.61
128.49
128.42
128.18
128.09
127.53
126.45
122.87
114.07
109.28
66.77
54.14
44.24
42.77
20.59
12.77
Et
N
Et
Cbz
HN
Me
3eh
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

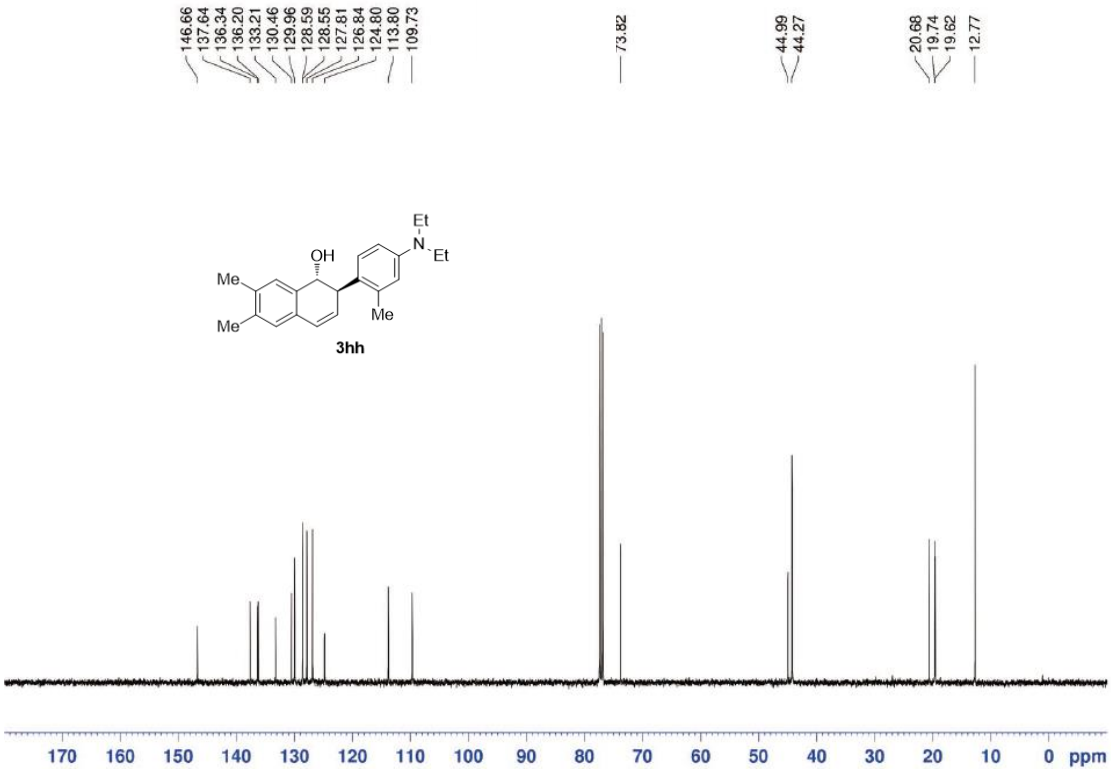

7.382
7.364
7.285
7.267
7.249
7.243
7.238
7.222
7.202
7.153
7.135
6.911
6.890
6.633
6.609
6.512
6.411
6.391
5.987
5.978
5.964
5.954
4.811
4.794
3.985
3.317
3.300
3.282
3.265
2.413
2.033
1.138
1.120
1.103
Et
N
Et
OH
Me
3fh
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.01 2.13 1.01 1.00 1.01 0.99 1.00 1.00 1.01 1.00 4.05 3.02 1.03 6.23

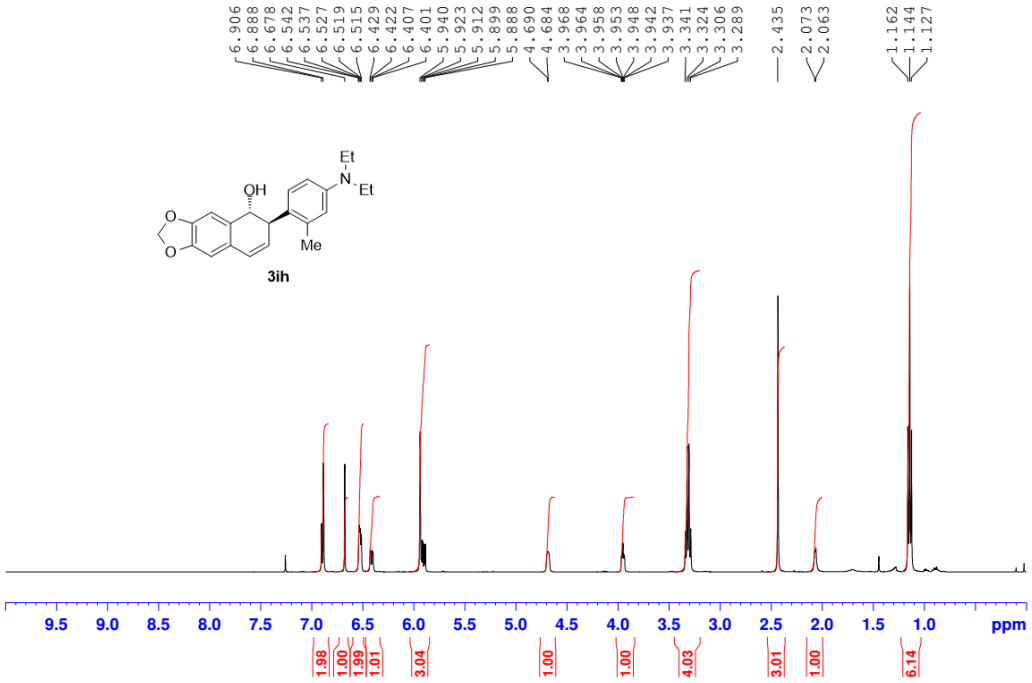

146.72
137.76
135.92
132.86
131.28
128.65
128.20
127.89
127.06
126.83
126.33
124.71
113.80
109.77
74.03
44.89
44.27
20.73
12.76
Et
N
Et
OH
Me
3fh
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

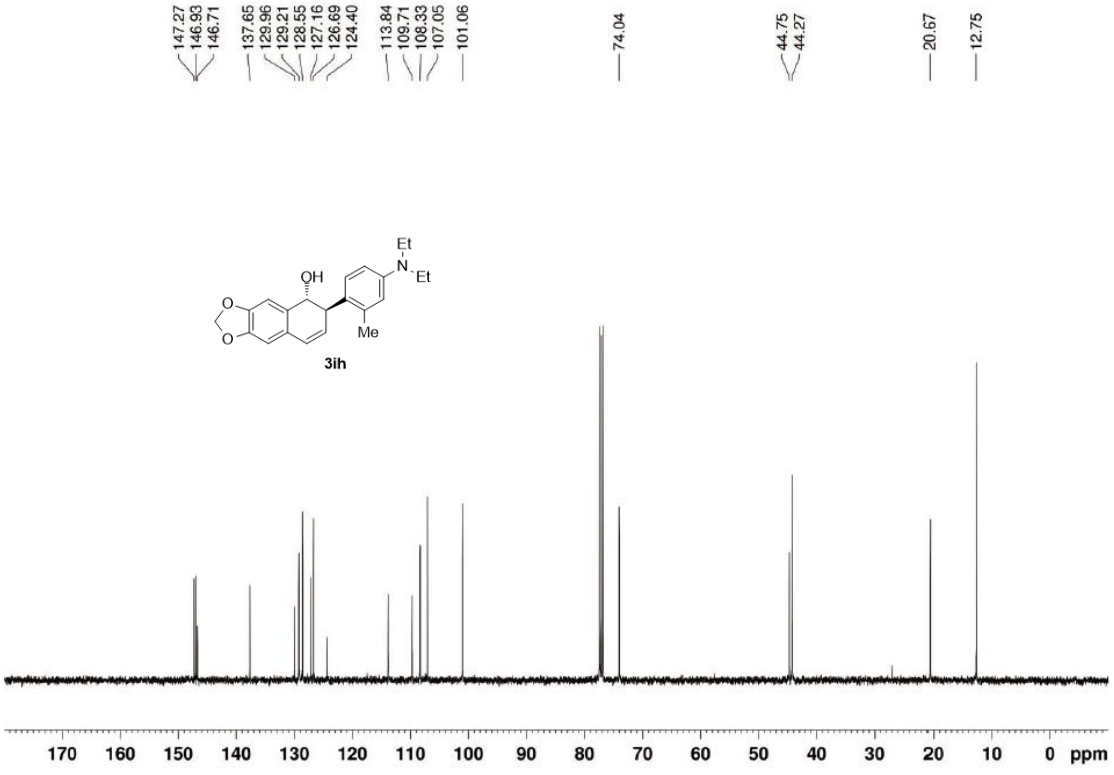

7.6684
7.3861
6.9367
6.9154
6.5202
6.5000
6.4739
6.4525
6.4473
6.0588
6.0500
6.0348
6.0260
4.7676
4.7463
3.9522
3.9307
3.3504
3.3328
3.3152
3.2977
2.3878
2.0946
1.1676
1.1501
1.1326
Et
N
Et
OH
Br
Br
Me
3gh
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.97
0.98
0.99
3.04
1.02
1.00
0.99
4.04
3.04
0.93
6.09

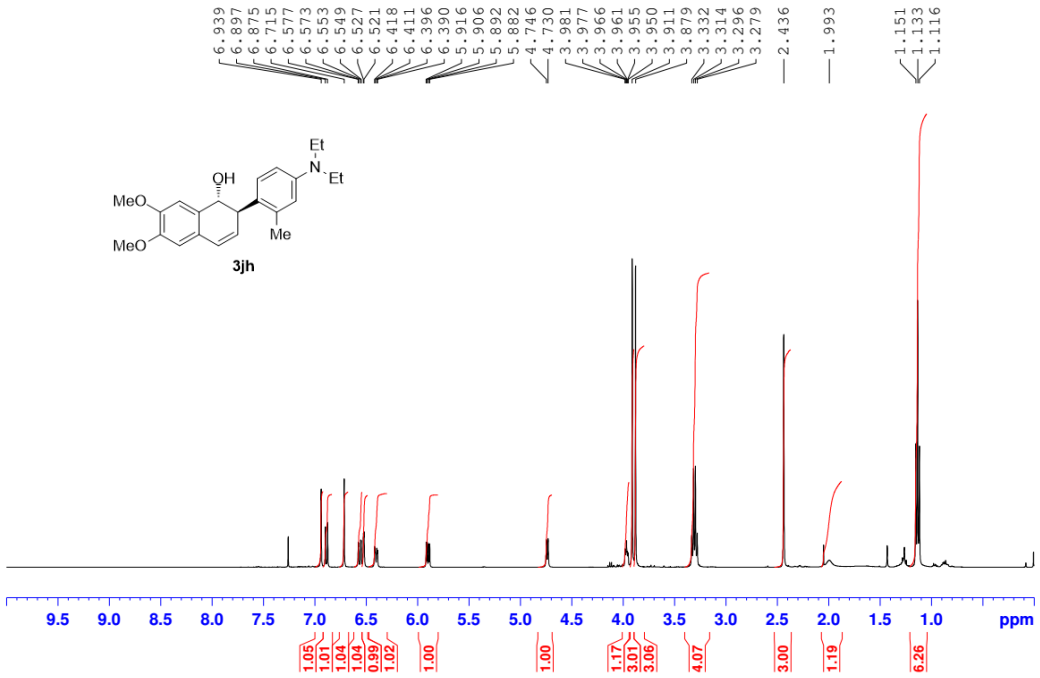

146.85
137.85
136.86
133.68
133.66
131.44
130.68
128.58
125.35
123.87
123.18
113.75
109.81
73.36
44.71
44.22
20.64
12.68
Et
N
Et
OH
Br
Br
Me
3gh
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

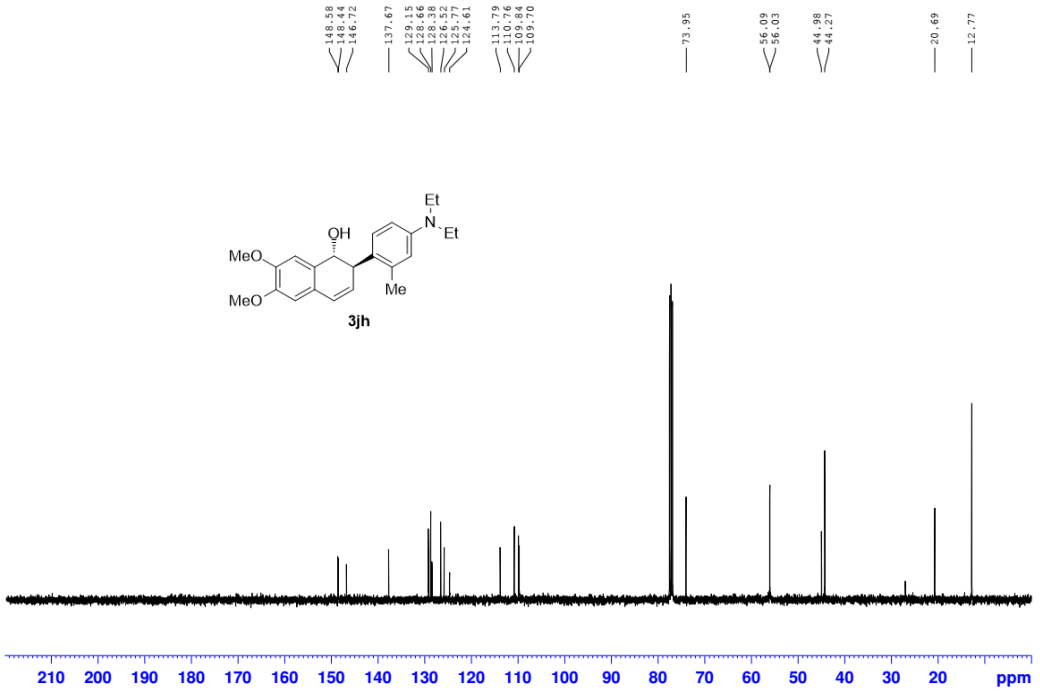

7.156
6.971
6.914
6.893
6.631
6.627
6.607
6.603
6.545
6.539
6.430
6.423
6.408
6.401
5.960
5.949
5.936
5.925
4.769
4.753
4.004
3.999
3.993
3.988
3.983
3.977
3.973
3.346
3.329
3.311
3.293
2.452
2.281
2.260
1.987
1.168
1.150
1.133
Et
N
Et
OH
Me
Me
Me
3hh
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00 1.01 1.00 1.01 1.00 1.00 1.00 1.01 1.00 4.06 3.07 6.12 0.95 6.17

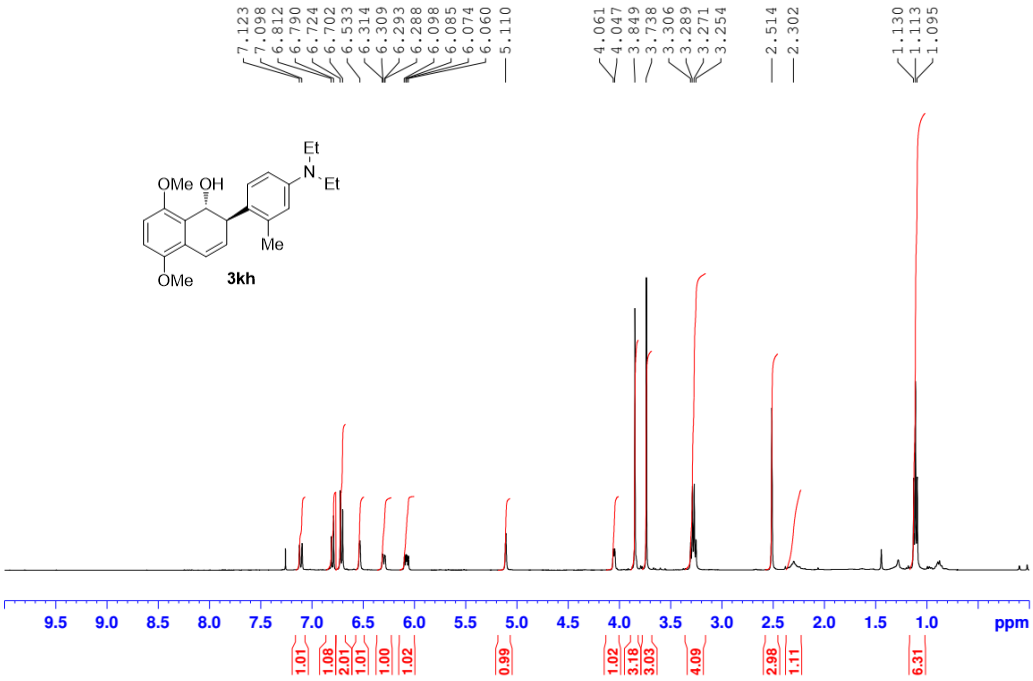

146.66
137.64
136.34
136.20
133.21
130.46
129.96
128.59
128.55
127.81
126.84
124.80
113.80
109.73
73.82
44.99
44.27
20.68
19.74
19.62
12.77
Et
N
Et
OH
Me
Me
Me
3hh
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

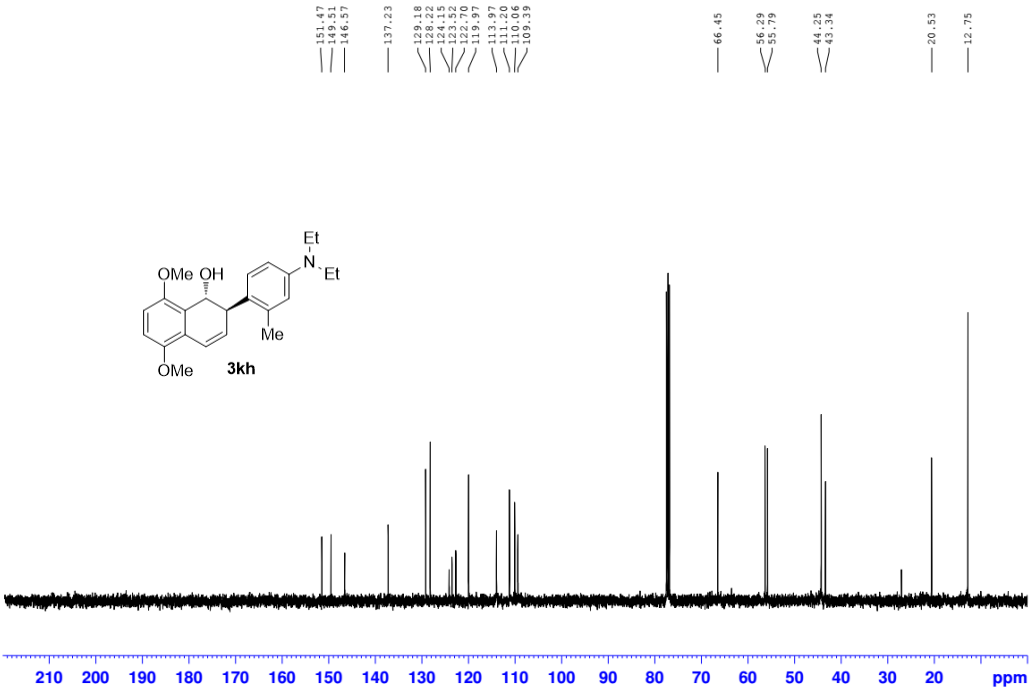

6.906
6.888
6.678
6.542
6.537
6.527
6.519
6.515
6.429
6.422
6.407
6.401
5.940
5.923
5.912
5.899
5.888
4.690
4.684
3.968
3.964
3.958
3.953
3.948
3.942
3.937
3.341
3.324
3.306
3.289
2.435
2.073
2.063
1.162
1.144
1.127
Et
N
Et
OH
O
O
Me
3ih
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.98
1.00
1.99
1.01
3.04
1.00
1.00
4.03
3.01
1.00
6.14


147.27
146.93
146.71
137.65
129.96
129.21
128.55
127.16
126.69
124.40
113.84
109.71
108.33
107.05
101.06
74.04
44.75
44.27
20.67
12.75
Et
N
Et
OH
O
O
Me
3ih
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


6.939
6.897
6.875
6.715
6.577
6.573
6.553
6.549
6.527
6.521
6.418
6.411
6.396
6.390
5.916
5.906
5.892
5.882
4.746
4.730
3.981
3.977
3.966
3.961
3.955
3.950
3.911
3.879
3.332
3.314
3.296
3.279
2.436
1.993
1.151
1.133
1.116
Et
N
Et
OH
MeO
MeO
Me
3jh
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.05
1.01
1.04
1.04
0.99
1.02
1.00
1.00
1.17
3.01
3.06
4.07
3.00
1.19
6.26

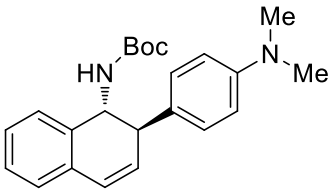

148.58
148.44
146.72
137.67
129.15
128.66
128.38
126.52
125.77
124.61
113.79
110.76
109.84
109.70
73.95
56.09
56.03
44.98
44.27
20.69
12.77
Et
N
Et
OH
MeO
MeO
Me
3jh
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.123
7.098
6.812
6.790
6.724
6.702
6.533
6.314
6.309
6.293
6.288
6.098
6.085
6.074
6.060
5.110
4.061
4.047
3.849
3.738
3.306
3.289
3.271
3.254
2.514
2.302
1.130
1.113
1.095
Et
N
Et
OMe OH
Me
OMe
3kh
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.01 1.08 2.01 1.01 1.00 1.02 0.99 1.02 3.18 3.03 4.09 2.98 1.11 6.31


151.47
149.51
146.57
137.23
129.18
128.22
124.15
123.52
122.70
119.97
113.97
111.20
110.06
109.39
66.45
56.29
55.79
44.25
43.34
20.53
12.75
Et
N
Et
OMe OH
Me
OMe
3kh
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

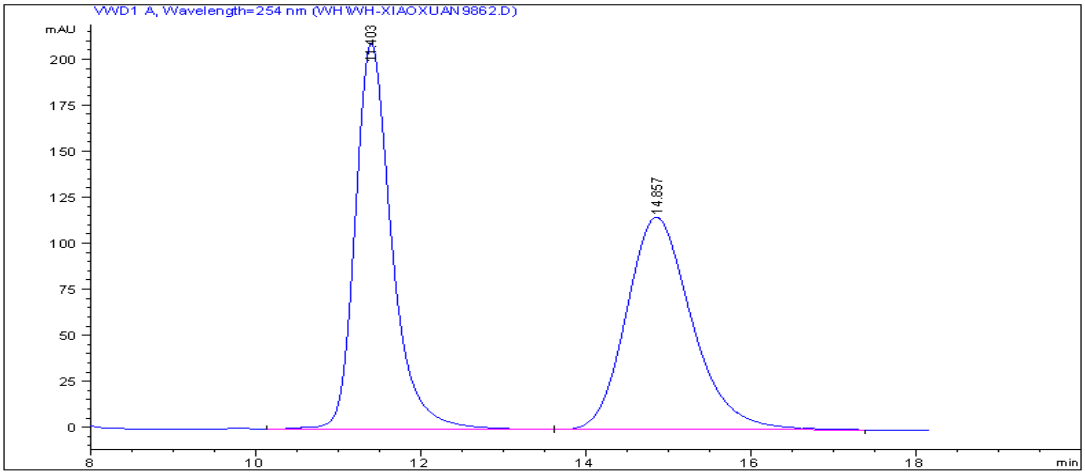
E: HPLC Spectra of Products

Note: The racemic ring opening products were prepared by using (±)-binap (for azabenzonorbornadienes) or (±)- difluroPHOS (for oxabenzonorbornadienes) as ligand.



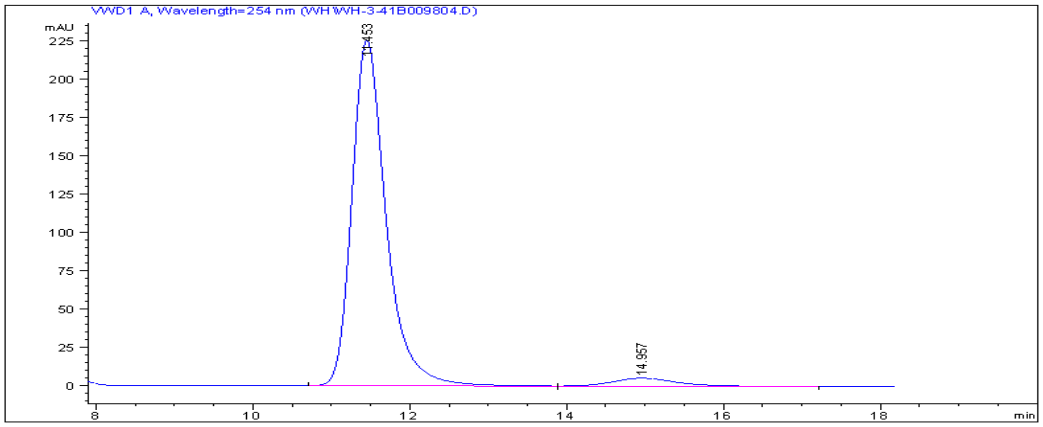
3aa

Racemic:

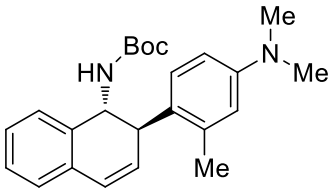


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.403	BB	0.4682	6448.13867	209.43990	50.4616
2	14.857	BB	0.8443	6330.16357	115.34850	49.5384

Enantioenriched:

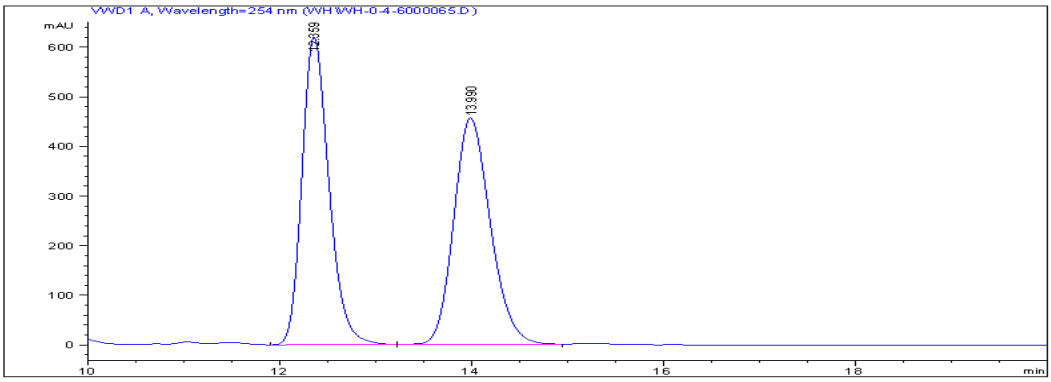


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.453	BB	0.4596	6819.66699	225.62206	96.0530
2	14.957	BB	0.8159	280.23526	5.11745	3.9470



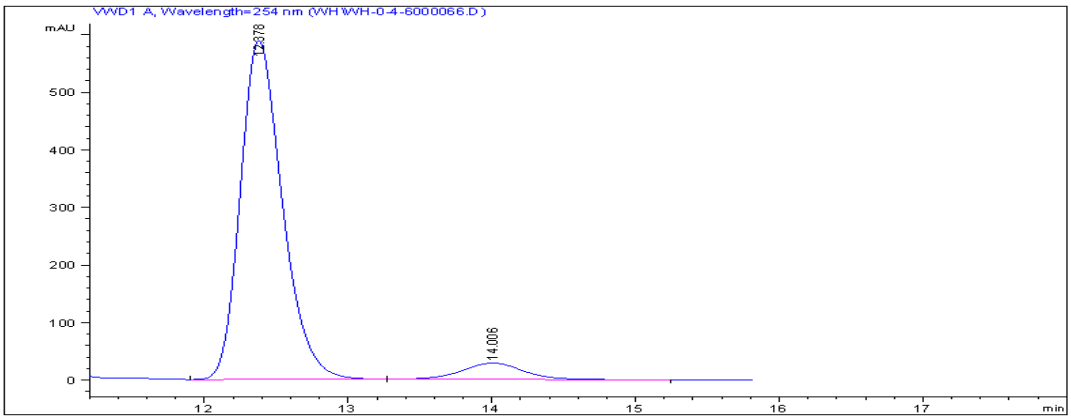
3ab

Racemic:

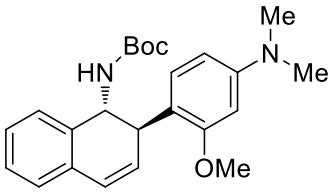


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.359	BB	0.2998	1.21066e4	620.05365	50.0561
2	13.990	BB	0.4081	1.20794e4	455.91898	49.9439

Enantioenriched:

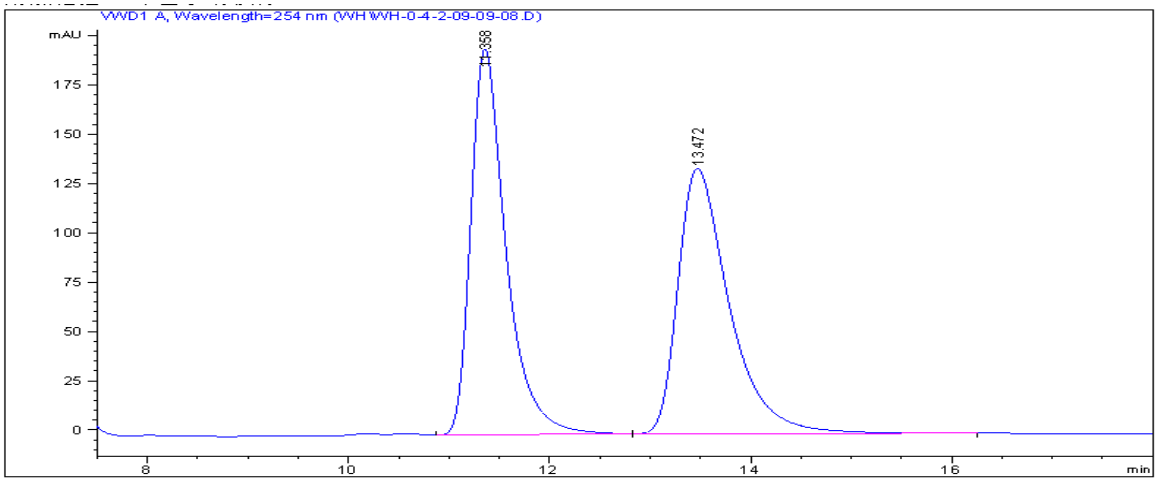


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.378	BB	0.3117	1.19532e4	589.08289	93.4703
2	14.006	BB	0.4443	835.03137	28.54070	6.5297



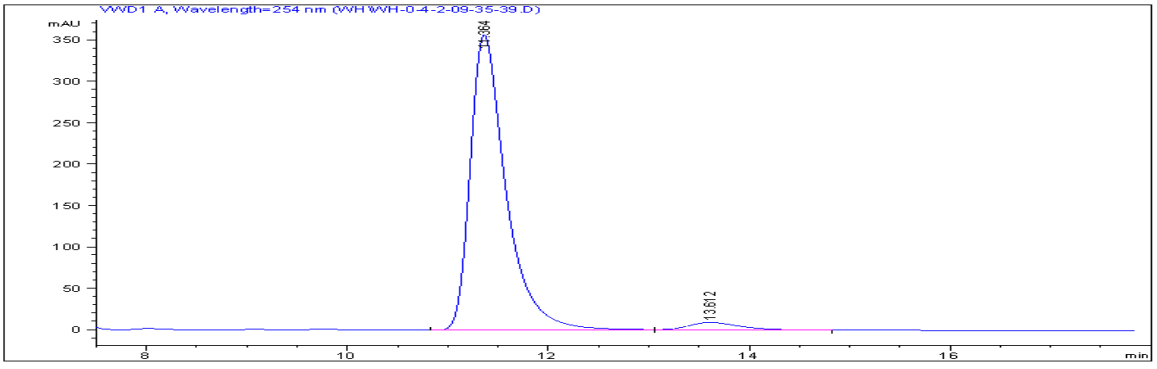
3ac

Racemic:

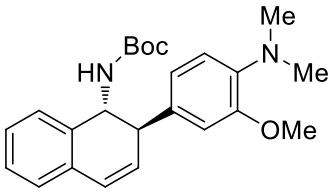


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.358	BB	0.3653	4748.64307	195.52371	49.9457
2	13.472	BB	0.5332	4758.96191	134.36363	50.0543

Enantioenriched:

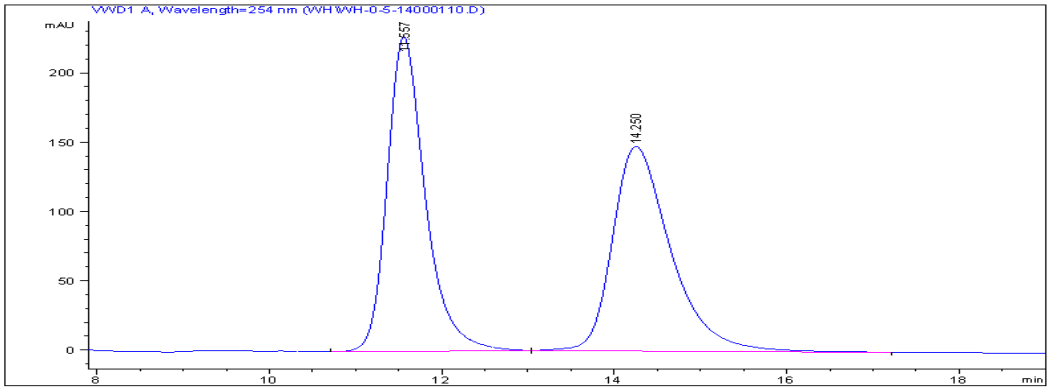


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.364	BB	0.3693	8789.68066	356.93051	96.6429
2	13.612	BB	0.5306	305.32745	8.82618	3.3571



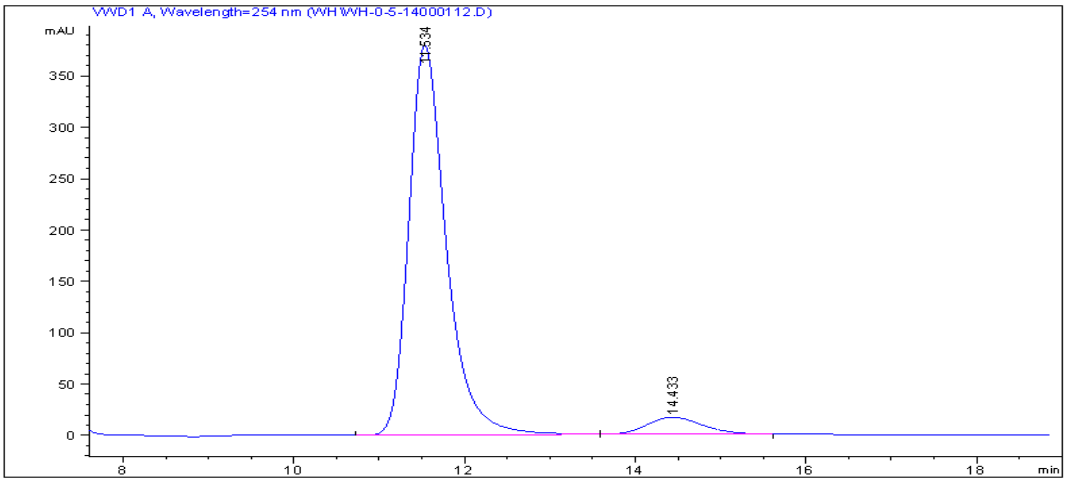
3ad

Racemic:

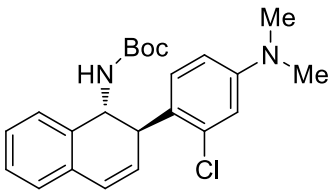


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.557	BB	0.4662	6969.95996	227.02475	50.1789
2	14.250	BB	0.7107	6920.26855	147.68405	49.8211

Enantioenriched:

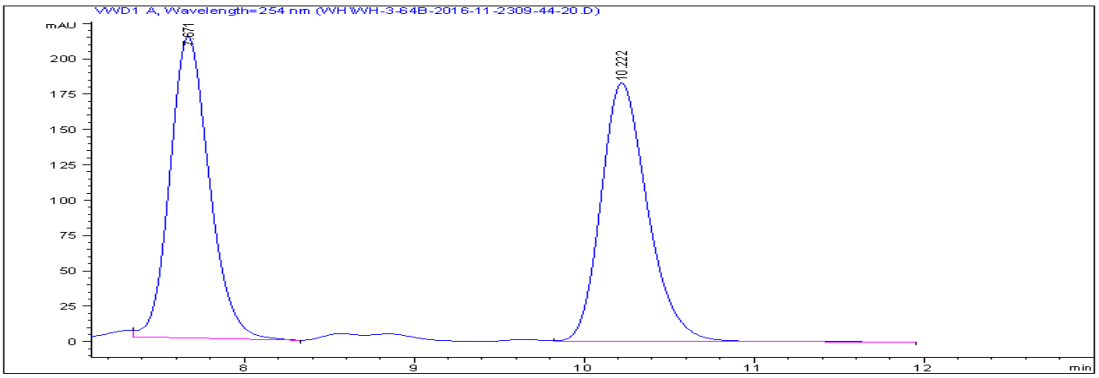


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.534	BB	0.4615	1.15651e4	379.51715	93.9790
2	14.433	BB	0.6907	740.93921	16.56828	6.0210



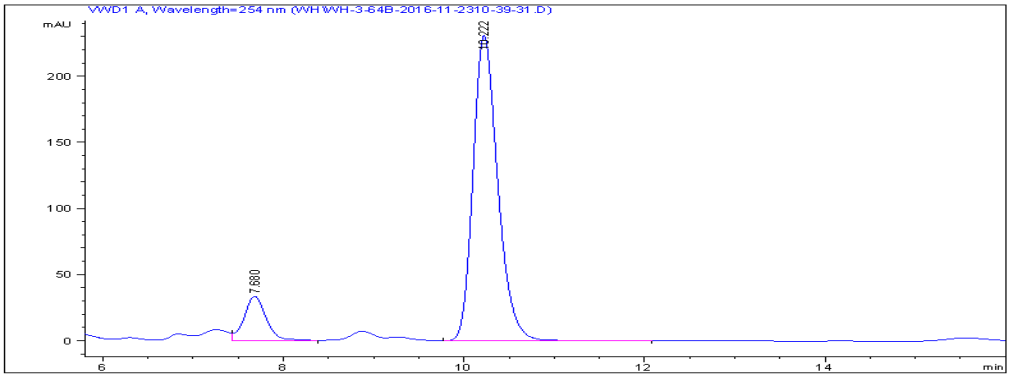
3ae

Racemic:

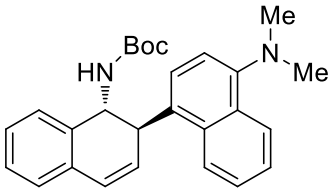


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.671	VB	0.2477	3427.18921	213.00208	49.5714
2	10.222	VBA	0.2924	3486.45166	182.88257	50.4286

Enantioenriched:

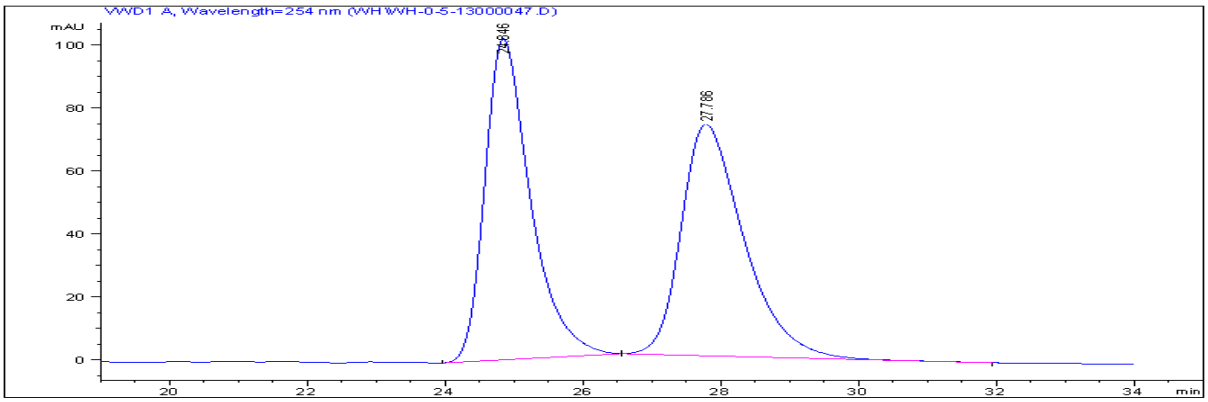


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.680	VB	0.2558	562.90820	33.36375	11.3409
2	10.222	VB	0.2913	4400.60107	230.91512	88.6591



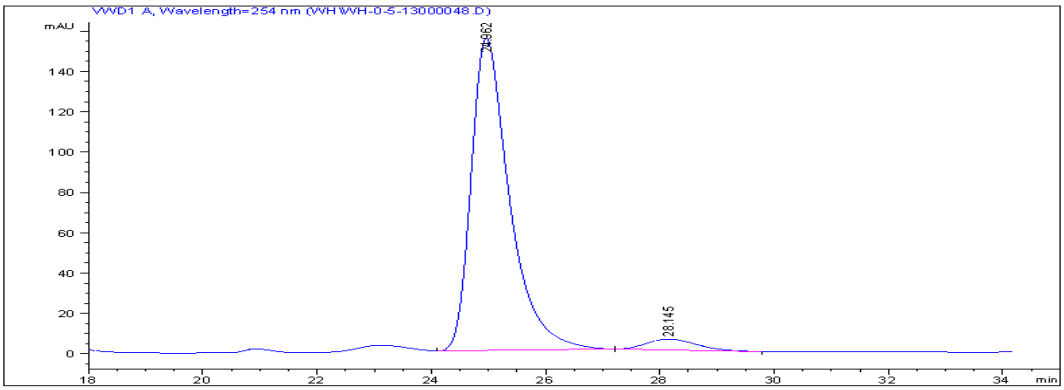
3af

Racemic:

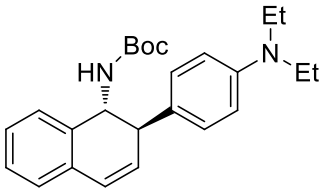


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.846	BB	0.6919	4690.51611	101.93227	50.2748
2	27.786	BB	0.9534	4639.23291	73.49626	49.7252

Enantioenriched:

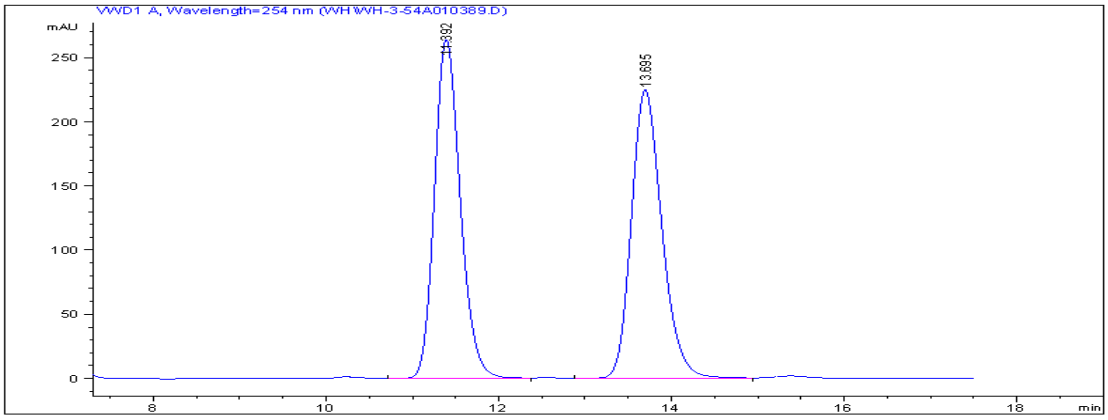


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.962	BB	0.6995	7218.24170	154.95103	95.6992
2	28.145	BB	0.9052	324.39166	5.35117	4.3008



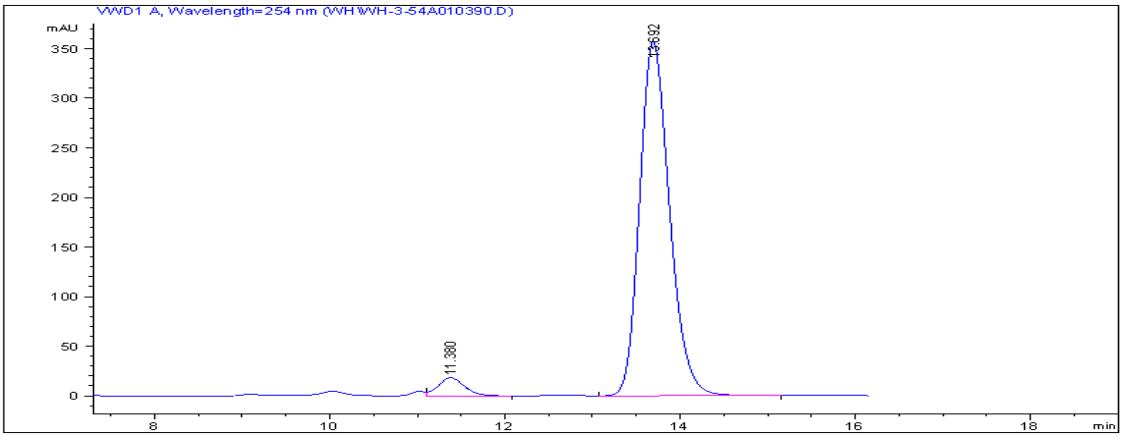
3ag

Racemic:

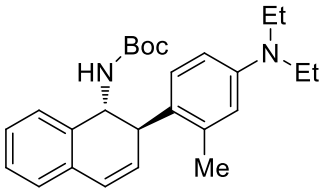


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.392	BB	0.3198	5468.45801	263.89978	49.8710
2	13.695	BB	0.3774	5496.74414	224.72650	50.1290

Enantioenriched:

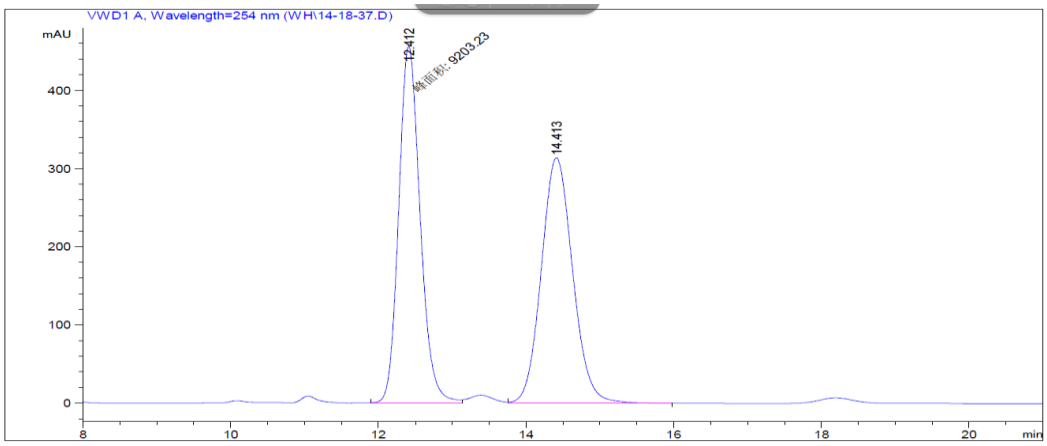


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.380	VB	0.3149	374.57260	18.14152	4.2385
2	13.692	BB	0.3642	8462.90918	357.43201	95.7615



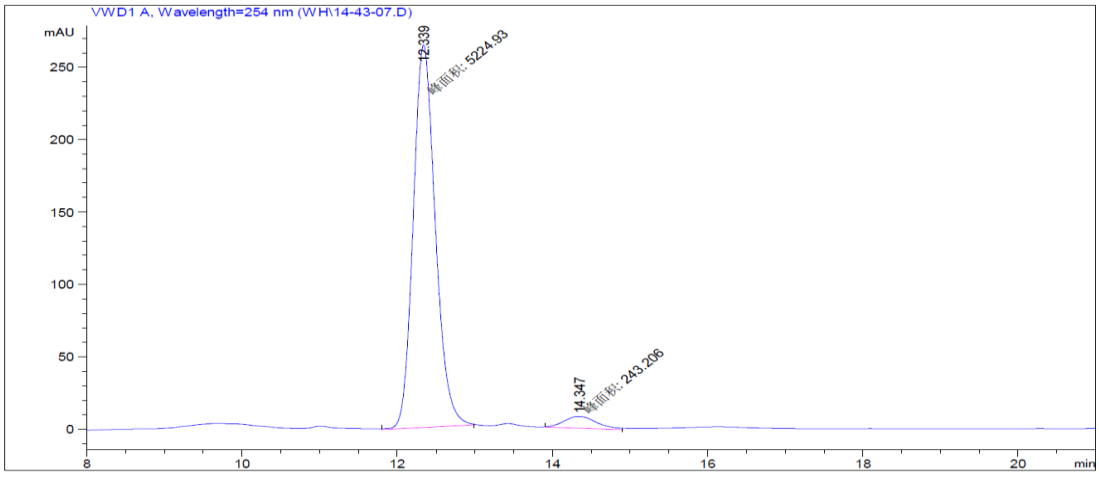
3ah

Racemic:

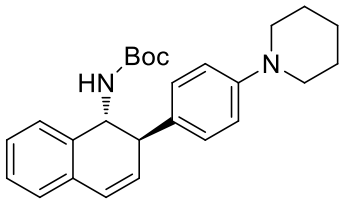


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.412	MM	0.3360	9203.23047	456.51758	49.8753
2	14.413	VB	0.4569	9249.24707	313.78311	50.1247

Enantioenriched:

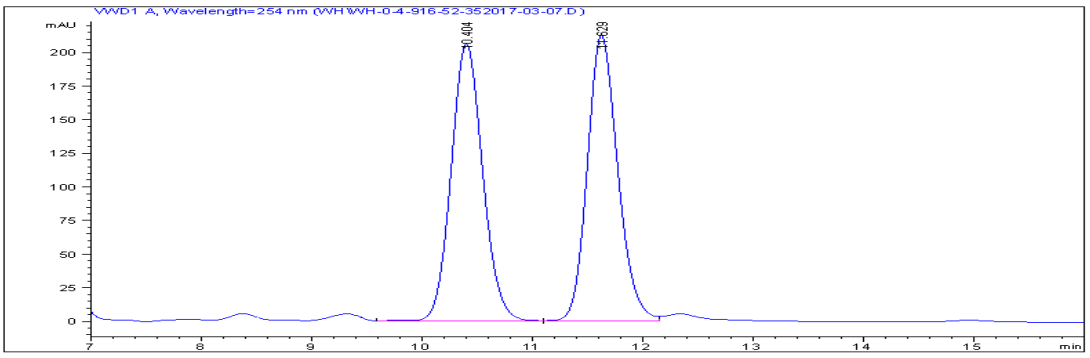


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.339	MM	0.3297	5224.93262	264.14651	95.5523
2	14.347	MM	0.4888	243.20610	8.29210	4.4477



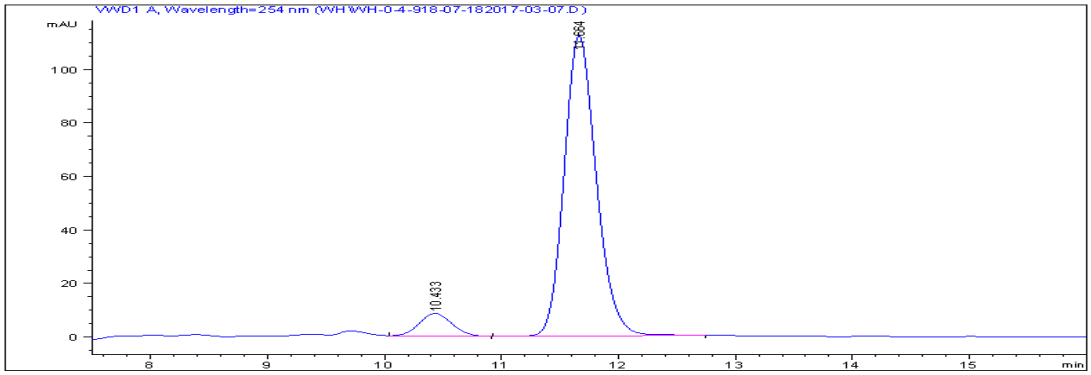
3ai

Racemic:

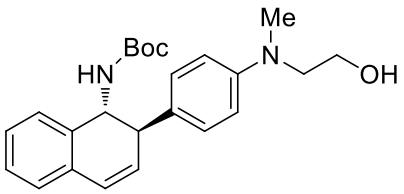


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.404	BB	0.3052	4075.79419	205.68428	50.0871
2	11.629	BV	0.2945	4061.61353	211.99188	49.9129

Enantioenriched:

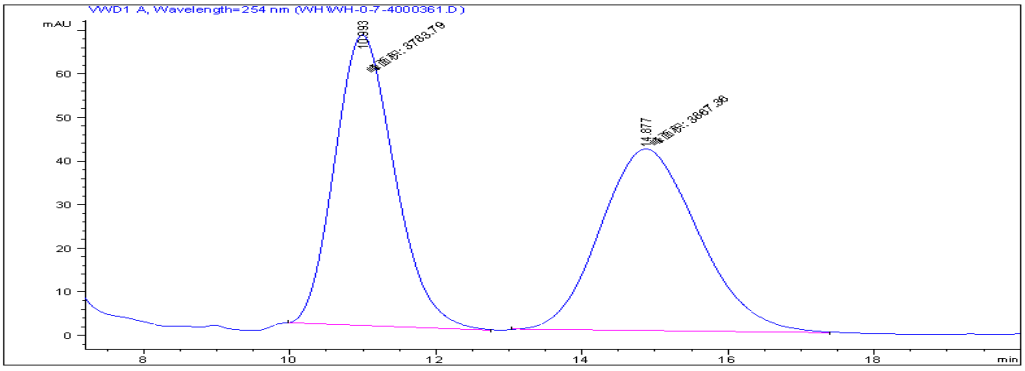


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.433	VB	0.3043	169.04805	8.56326	7.3080
2	11.664	BB	0.2928	2144.13745	112.28082	92.6920



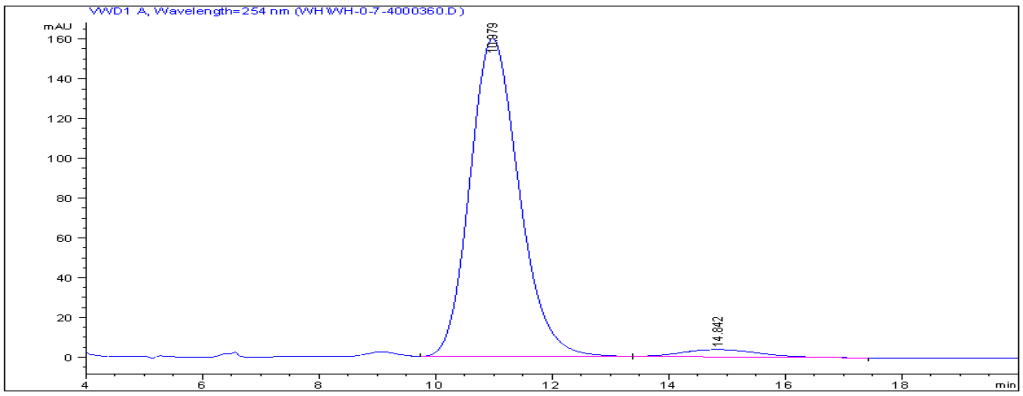
3aj

Racemic:

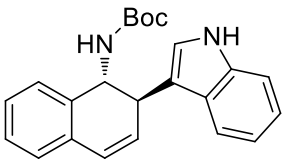


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.993	MM	0.9468	3783.79395	66.61001	49.4539
2	14.877	MM	1.5477	3867.36108	41.64698	50.5461

Enantioenriched:

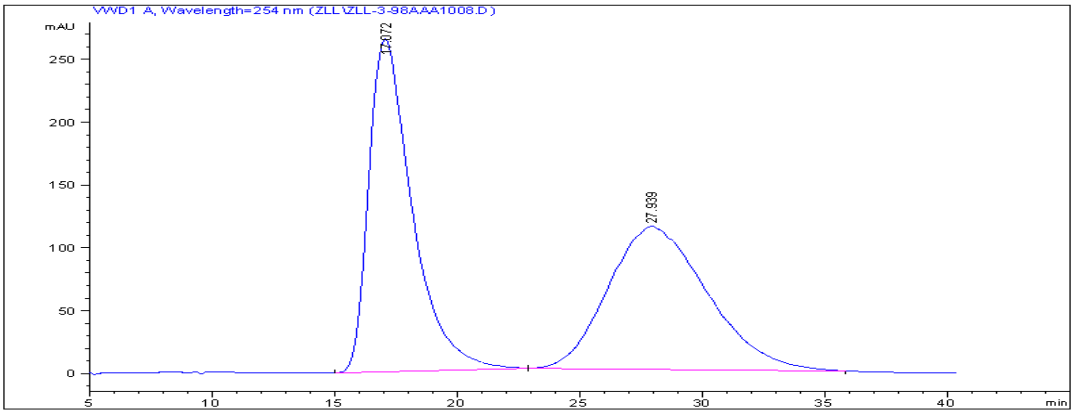


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.979	VV	0.9092	9421.43750	160.41411	95.9682
2	14.842	VB	1.4610	395.81256	4.01884	4.0318



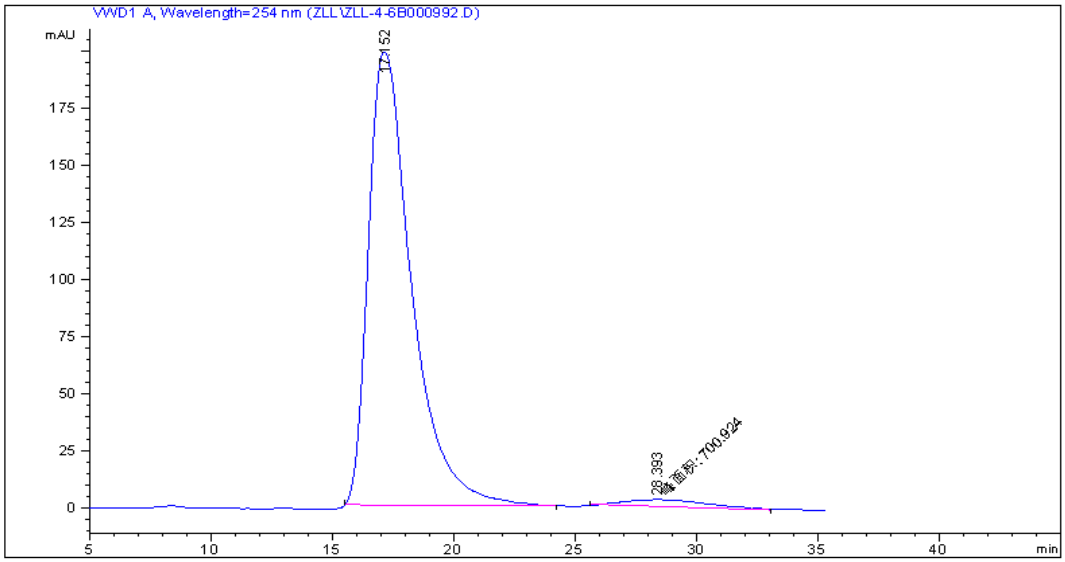
3ak

Racemic:

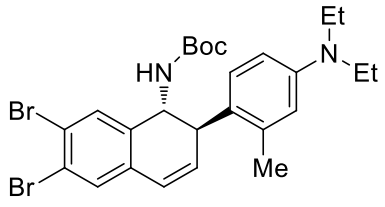


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.072	BB	1.6876	3.25991e4	264.91742	50.5313
2	27.939	BB	3.4587	3.19136e4	113.76646	49.4687

Enantioenriched:

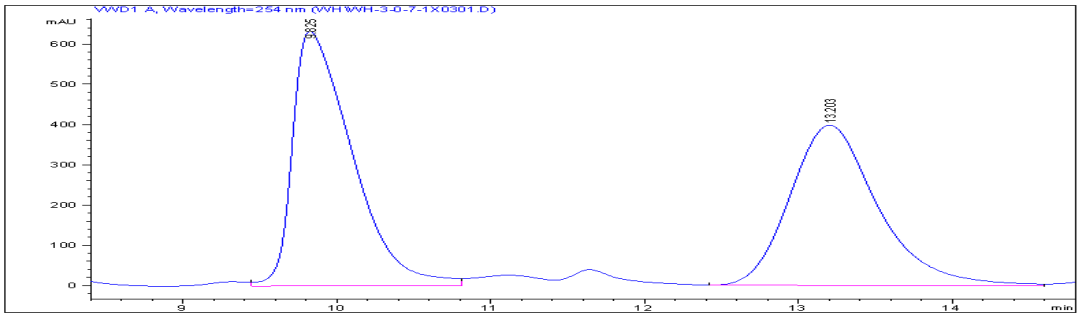


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.152	BB	1.7152	2.45903e4	198.37186	97.2286
2	28.393	MM	3.7632	700.92371	3.10432	2.7714



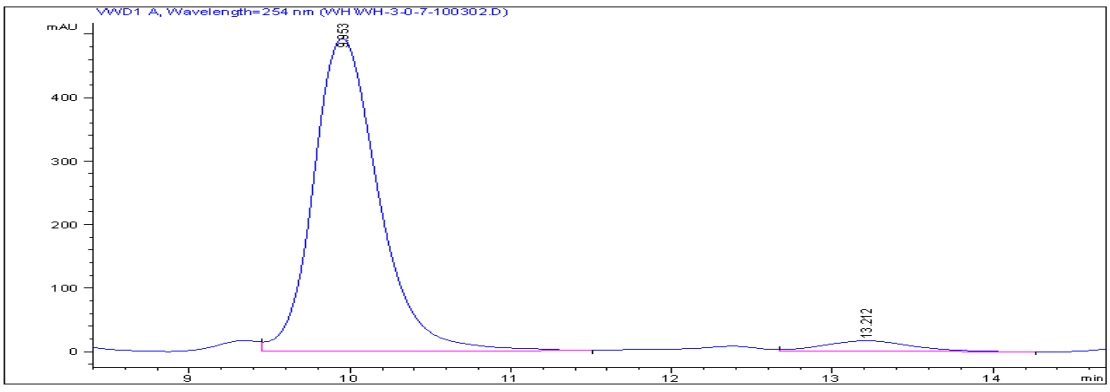
3bh

Racemic:

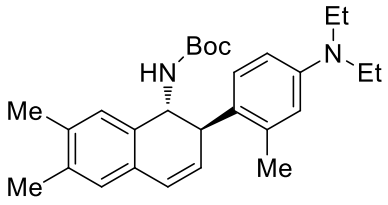


Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.825	VV	0.4244	1.69996e4	632.77795	51.8011
2	13.203	BV	0.6016	1.58174e4	398.06970	48.1989

Enantioenriched:

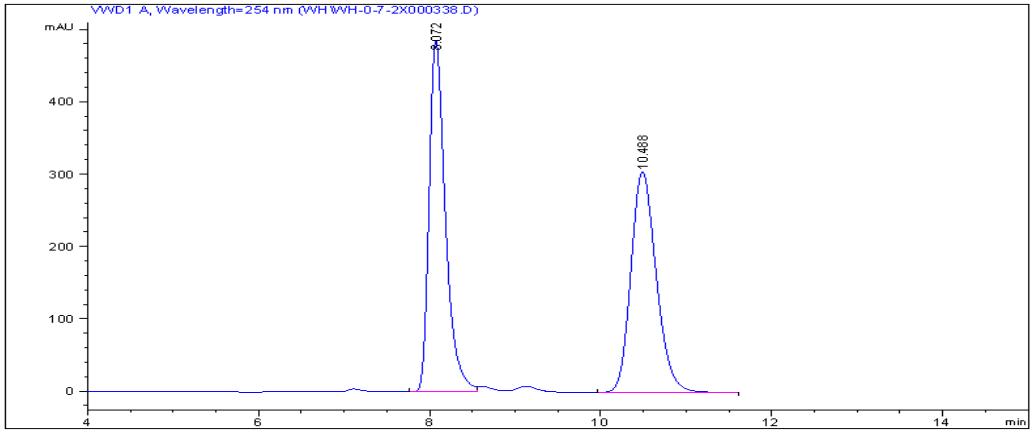


Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.953	VB	0.4287	1.37722e4	491.74847	95.6941
2	13.212	VB	0.5740	619.70782	16.46855	4.3059



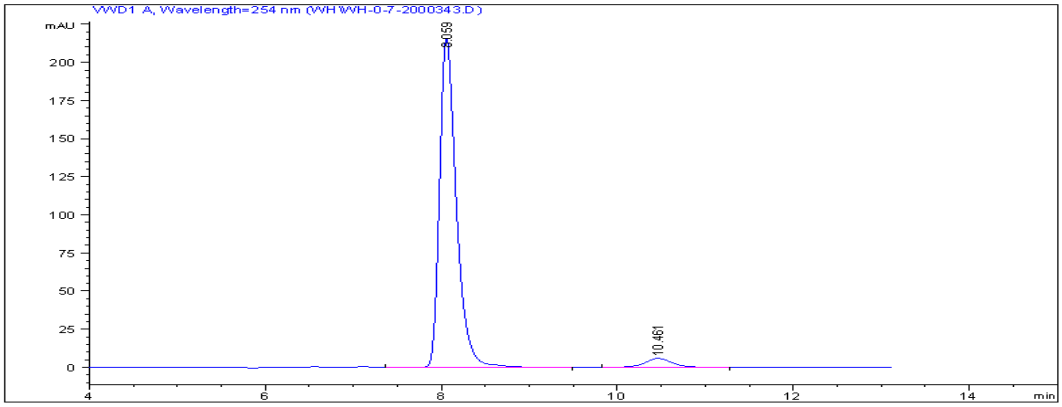
3ch

Racemic:

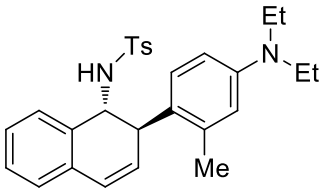


Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.072	BV	0.2009	6457.71680	486.36526	50.8169
2	10.488	BBA	0.3165	6250.10059	304.48669	49.1831

Enantioenriched:

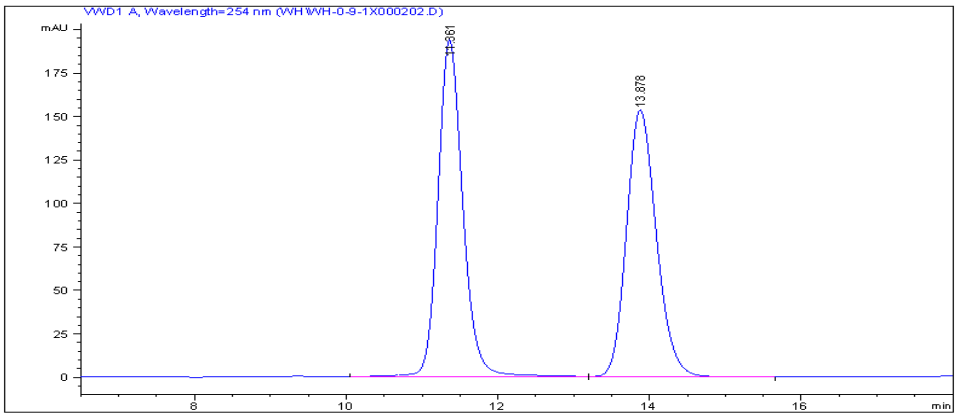


Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.059	BB	0.2002	2856.17236	216.03543	95.7903
2	10.461	BB	0.3272	125.51980	5.80604	4.2097



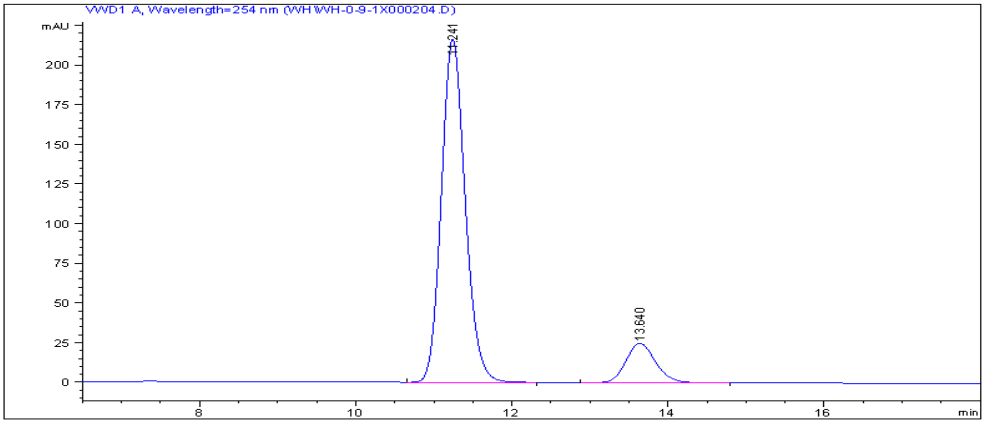
3dh

Racemic:

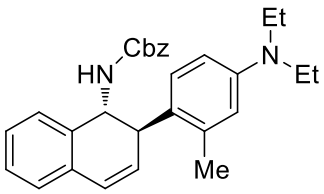


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.361	BB	0.3483	4400.12500	193.48698	51.2677
2	13.878	BB	0.4223	4182.52148	153.31763	48.7323

Enantioenriched:

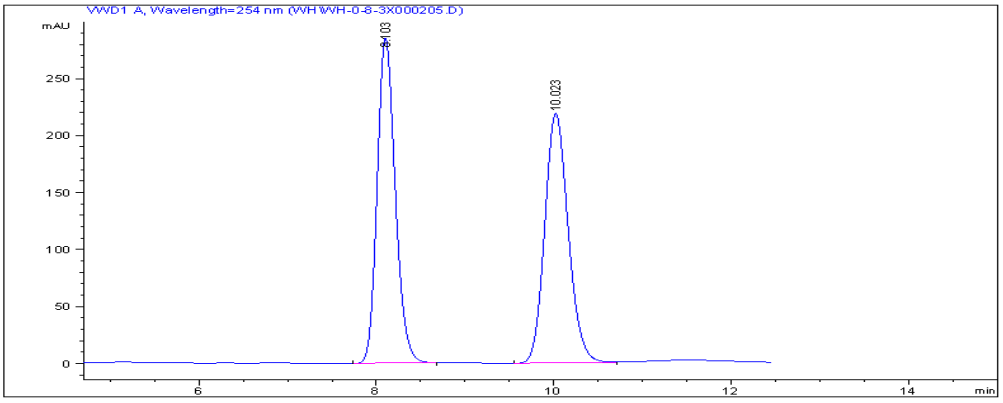


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.241	BB	0.3262	4588.01221	216.49797	87.4862
2	13.640	BB	0.4072	656.25555	24.83994	12.5138



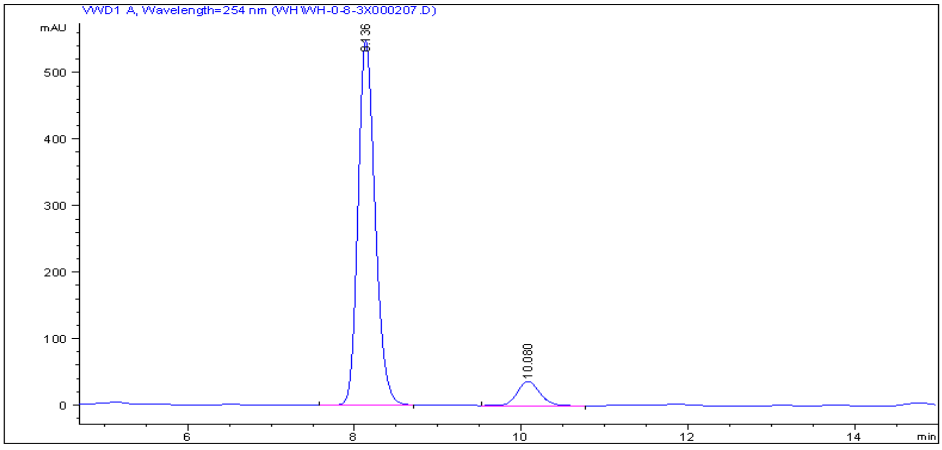
3eh

Racemic:

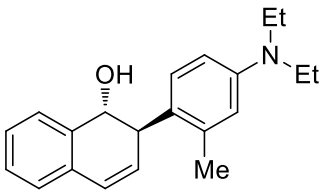


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.103	BB	0.2179	4031.57886	285.19574	50.1223
2	10.023	BB	0.2840	4011.90088	218.67828	49.8777

Enantioenriched:

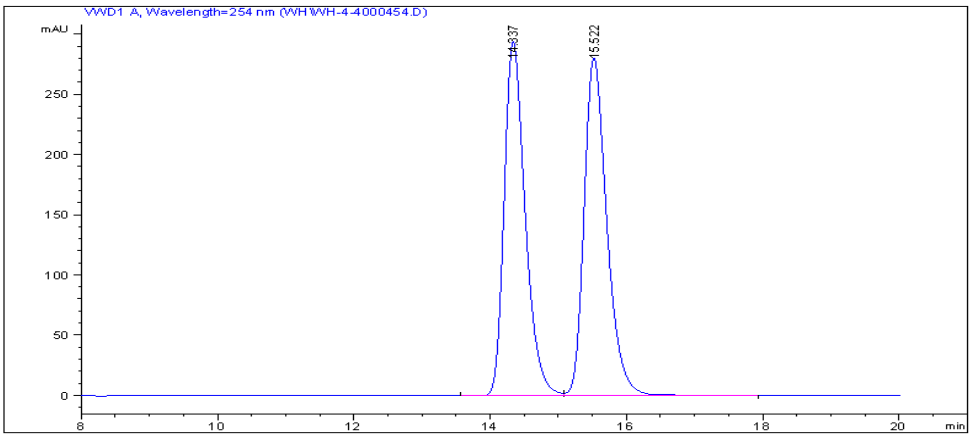


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.136	BV	0.2198	7831.02246	547.61230	92.0850
2	10.080	BB	0.2864	673.10333	36.29638	7.9150



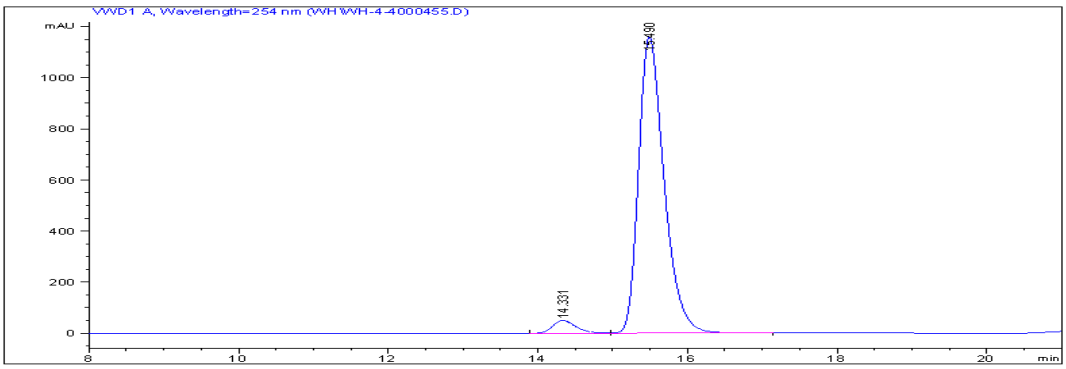
3fh

Racemic:

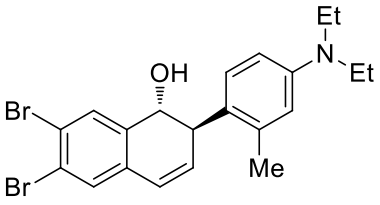


Peak	RetTime	Type	Width	Area	Height	Area
1	14.337	BV	0.3266	6281.48926	293.59662	49.2060
2	15.522	VB	0.3529	6484.20557	280.29282	50.7940

Enantioenriched:

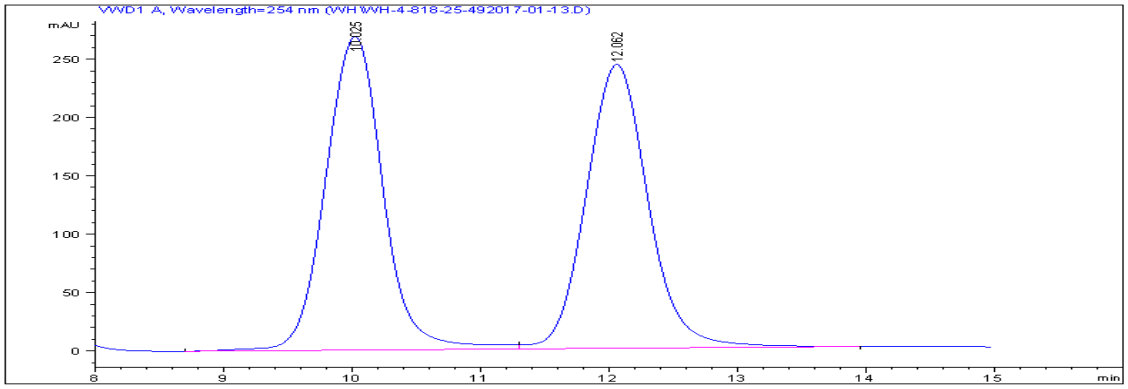


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.331	BV	0.3266	1068.44165	50.14924	3.7485
2	15.490	VB	0.3620	2.74344e4	1159.78369	96.2515



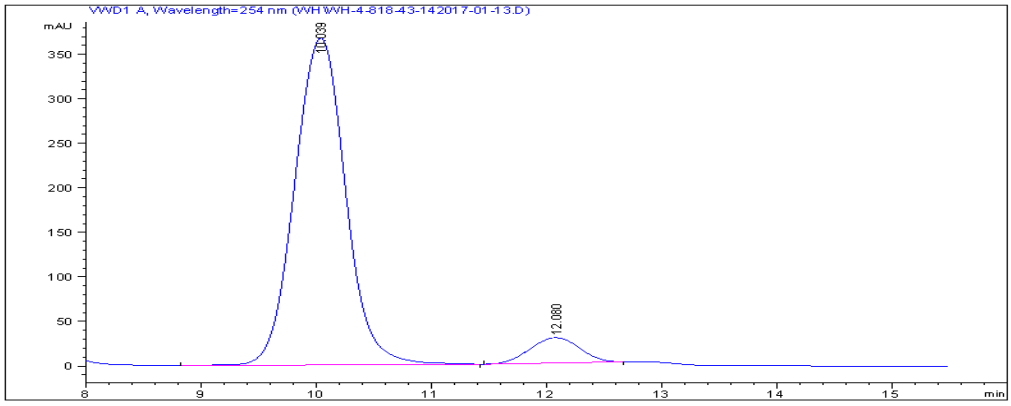
3gh

Racemic:

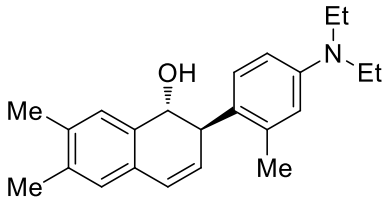


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.025	BV	0.4858	8349.97852	268.51184	50.6795
2	12.062	VB	0.5181	8126.07715	242.99557	49.3205

Enantioenriched:

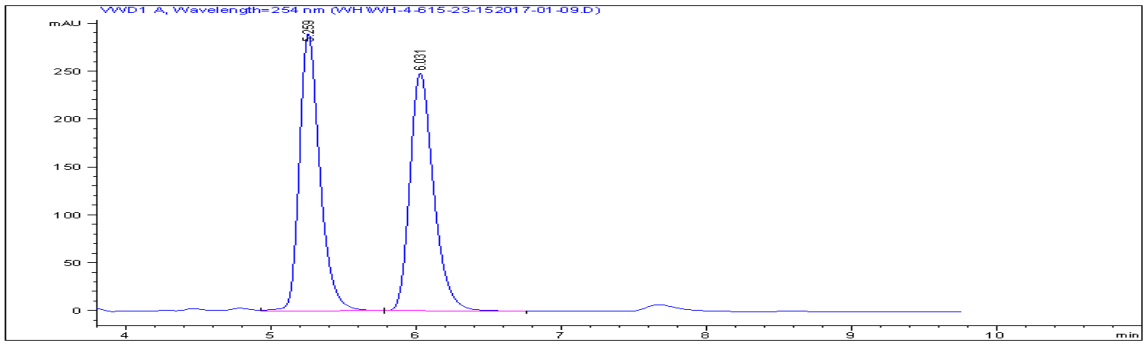


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.039	BV	0.4857	1.13993e4	367.68768	91.3039
2	12.080	VV	0.5272	1085.70605	31.72812	8.6961



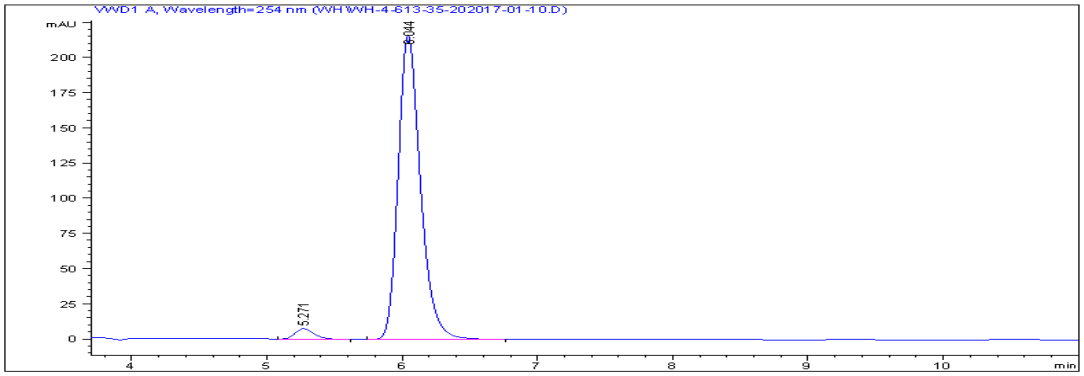
3hh

Racemic:

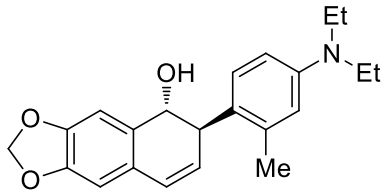


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.259	VB	0.1504	2832.49951	288.90894	50.1551
2	6.031	BB	0.1765	2814.98608	247.81114	49.8449

Enantioenriched:

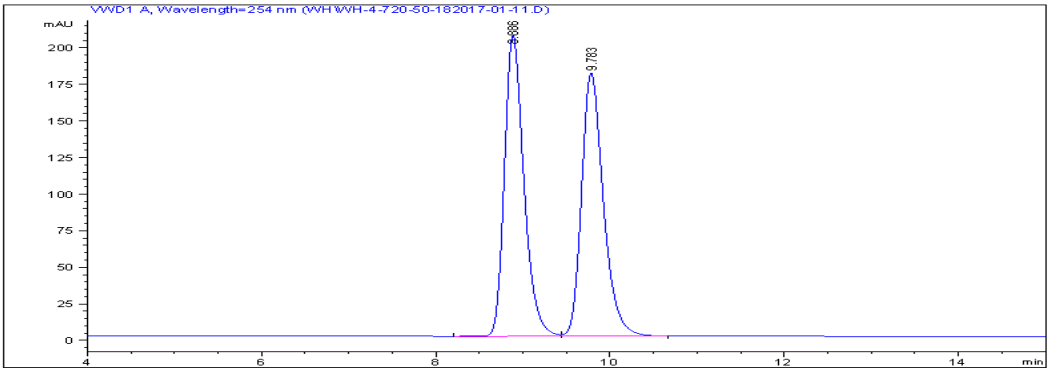


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.271	VB	0.1536	77.33765	7.67277	3.0291
2	6.045	BV	0.1780	2475.78906	215.61607	96.9709



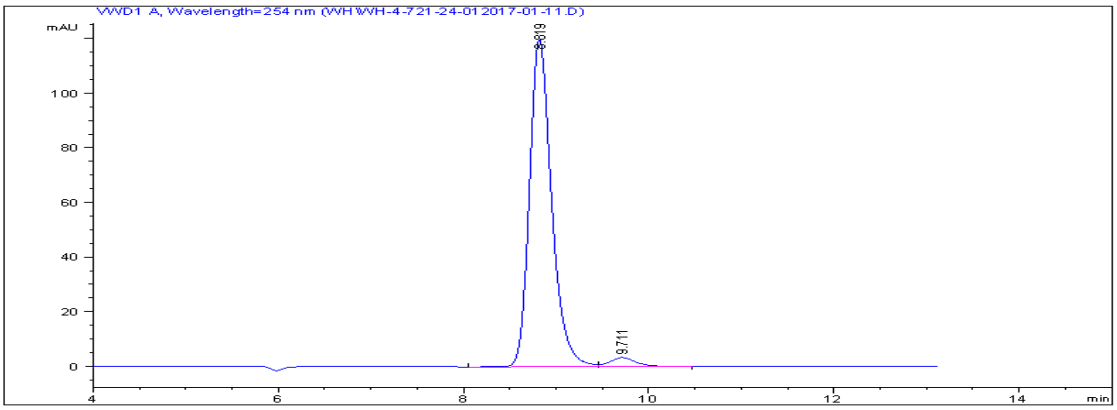
3ih

Racemic:

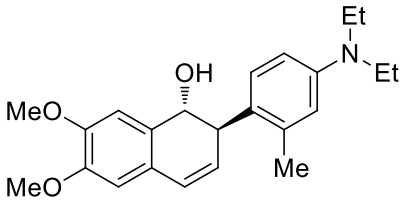


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.886	BV	0.2367	3186.72119	205.74065	50.5112
2	9.783	VB	0.2647	3122.21411	179.71478	49.4888

Enantioenriched:

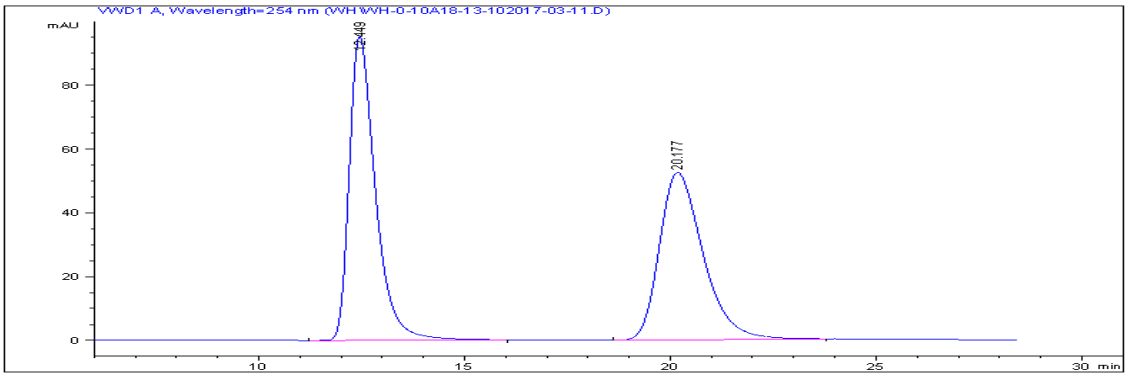


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.819	BV	0.2527	1989.19861	119.78371	96.7649
2	9.711	VB	0.2957	66.50419	3.33363	3.2351



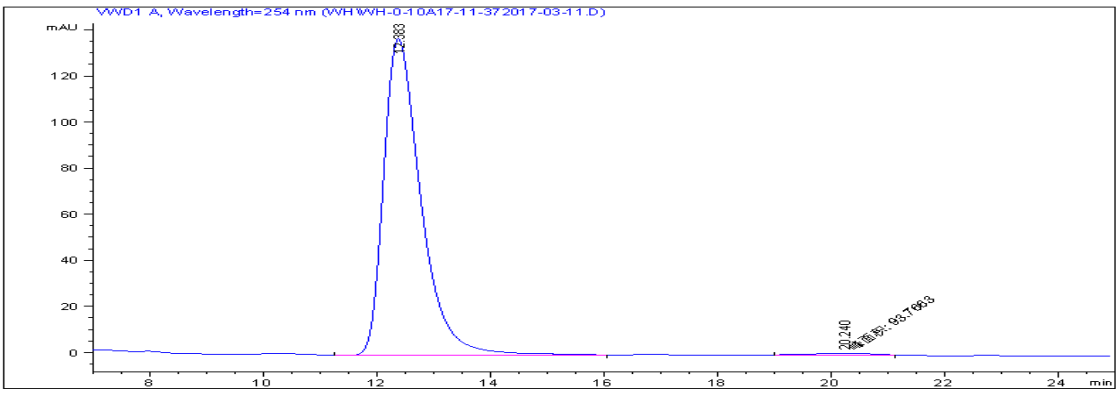
3jh

Racemic:

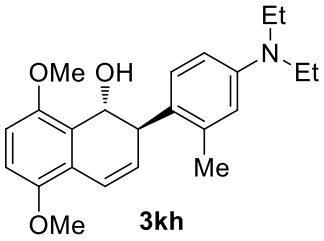


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.449	BB	0.6704	4212.83301	95.17267	50.6680
2	20.177	BB	1.2812	4101.75293	53.36025	49.3320

Enantioenriched:

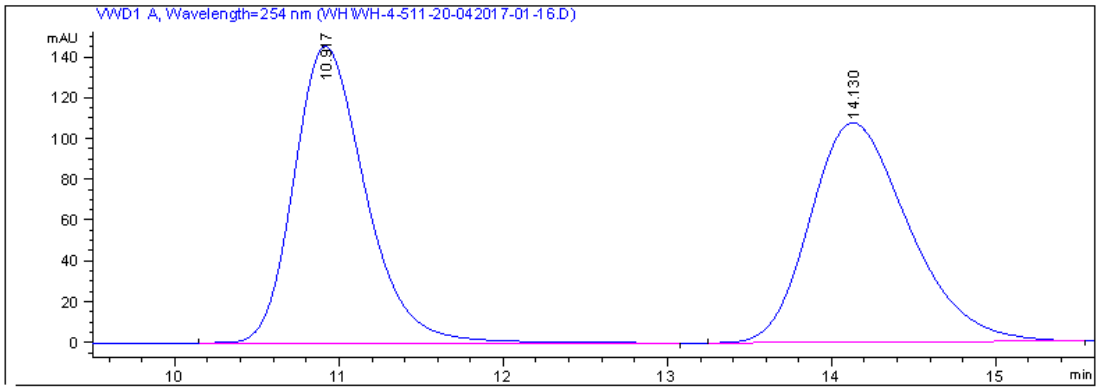


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.383	BB	0.6909	6247.09570	137.27184	98.5212
2	20.240	MM	1.4008	93.76634	1.11561	1.4788



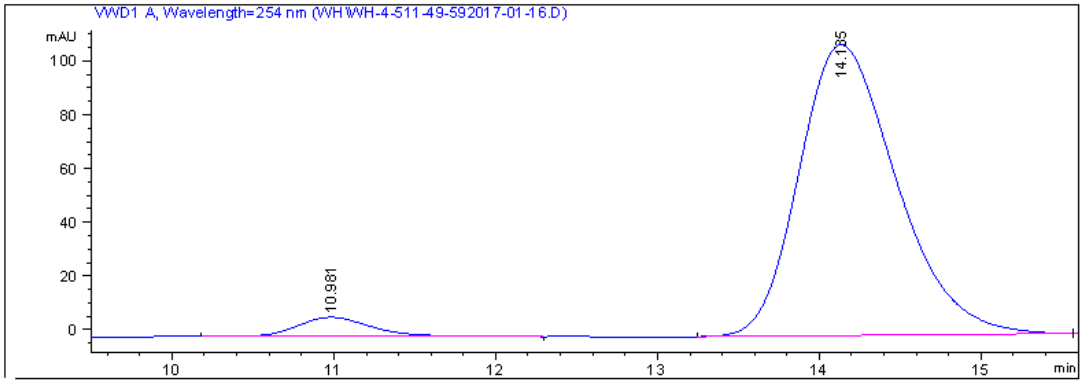
3kh

Racemic:



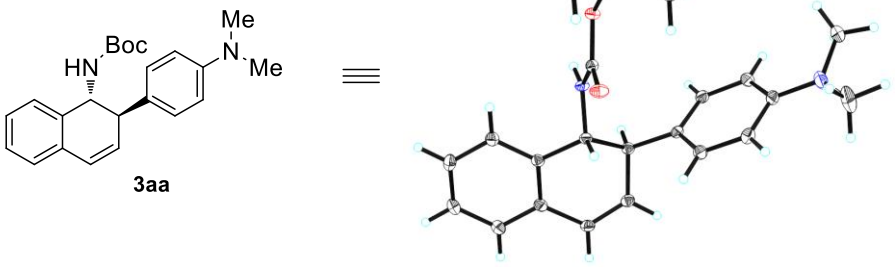
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.917	BB	0.4653	4408.11914	145.58290	49.0684
2	14.130	BV	0.6544	4575.50684	107.98198	50.9316

Enantioenriched:



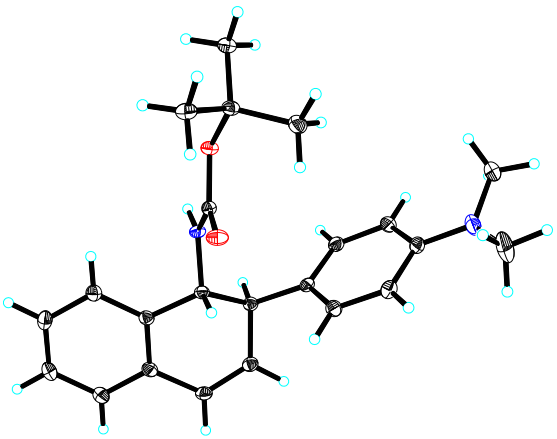
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.981	BB	0.5151	252.06400	7.29581	5.1862
2	14.135	BV	0.6509	4608.18896	108.62795	94.8138

F: X-ray Crystallography of Compound 3aa



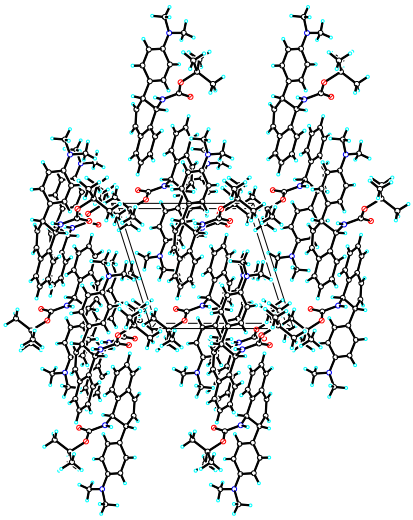
CCDC 1571052

Crystal data for cu_qwh418a_0m: $C_{23}H_{28}N_2O_2$, M = 364.47, a = 9.9707(2) Å, b = 9.7555(2) Å, c = 10.8203(2) Å, α = 90 °, β = 107.7860(10) °, γ = 90 °, V = 1002.18(3) Å^3, T = 100(2) K, space group $P21$, Z = 2, μ(CuKα) = 0.607 mm^{-1}, 10190 reflections measured, 3044 independent reflections (R_{int} = 0.0323). The final R_1 values were 0.0301 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0777 ($I > 2\sigma(I)$). The final R_1 values were 0.0302 (all data). The final $wR(F^2)$ values were 0.0778 (all data). The goodness of fit on F^2 was 1.050. Flack parameter = -0.03(7).



View of a molecule of qwh418a with the atom-labelling scheme.

Displacement ellipsoids are drawn at the 30% probability level.



View of the pack drawing of qwh418a.

Hydrogen-bonds are shown as dashed lines.

Table 1. Crystal data and structure refinement for cu_qwh418a_0m.

Identification code	cu_qwh418a_0m	
Empirical formula	C23 H28 N2 O2	
Formula weight	364.47	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.9707(2) Å	α= 90 °.
	b = 9.7555(2) Å	β= 107.7860(10) °.
	c = 10.8203(2) Å	γ = 90 °.
Volume	1002.18(3) $Å^3$	
Z	2	
Density (calculated)	1.208 Mg/m^3	
Absorption coefficient	0.607 mm^{-1}	
F(000)	392	
Crystal size	1.000 x 0.520 x 0.130 mm^3	
Theta range for data collection	4.291 to 70.246 °.	
Index ranges	-12<=h<=11, -10<=k<=11, -12<=l<=12	
Reflections collected	10190	
Independent reflections	3044 [R(int) = 0.0323]	
Completeness to theta = 67.679 °	98.0 %	
Absorption correction	Semi-empirical from equivalents	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3044 / 1 / 250
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0301, wR2 = 0.0777
R indices (all data)	R1 = 0.0302, wR2 = 0.0778
Absolute structure parameter	-0.03(7)
Extinction coefficient	0.0242(17)
Largest diff. peak and hole	0.172 and -0.171 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for cu_qwh418a_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	9510(1)	11121(1)	7569(1)	22(1)
O(2)	8619(1)	9073(2)	7983(1)	27(1)
N(1)	14166(2)	6706(2)	7986(2)	36(1)
N(2)	8322(2)	9820(2)	5927(1)	20(1)
C(1)	14323(2)	5803(4)	9075(2)	54(1)
C(2)	12826(2)	6983(2)	7156(2)	26(1)
C(3)	11625(2)	6343(2)	7312(2)	26(1)
C(4)	10294(2)	6632(2)	6481(2)	24(1)
C(5)	10082(2)	7553(2)	5458(2)	21(1)
C(6)	8625(2)	7889(2)	4562(2)	20(1)
C(7)	7693(2)	8566(2)	5295(2)	20(1)
C(8)	8808(2)	9923(2)	7237(2)	19(1)
C(9)	10316(2)	11388(2)	8939(2)	22(1)
C(10)	9334(2)	11478(2)	9766(2)	28(1)
C(11)	15312(2)	7625(3)	8007(3)	44(1)
C(12)	12621(2)	7890(2)	6110(2)	28(1)
C(13)	11277(2)	8155(2)	5287(2)	24(1)
C(14)	7877(2)	6641(2)	3836(2)	23(1)
C(15)	6481(2)	6579(2)	3371(2)	25(1)
C(16)	5587(2)	7705(2)	3539(2)	23(1)
C(17)	6177(2)	8751(2)	4431(2)	21(1)
C(18)	5350(2)	9840(2)	4573(2)	26(1)
C(19)	3930(2)	9908(3)	3827(2)	30(1)

C(20)	3342(2)	8873(3)	2964(2)	30(1)
C(21)	4162(2)	7777(2)	2819(2)	28(1)
C(22)	10983(2)	12777(2)	8872(2)	26(1)
C(23)	11437(2)	10292(2)	9409(2)	30(1)

Table 3. Bond lengths [Å] and angles [°] for cu_qwh418a_0m.

O(1)-C(8)	1.353(2)
O(1)-C(9)	1.478(2)
O(2)-C(8)	1.211(2)
N(1)-C(2)	1.390(2)
N(1)-C(1)	1.441(3)
N(1)-C(11)	1.447(3)
N(2)-C(8)	1.354(2)
N(2)-C(7)	1.447(3)
N(2)-H(4)	0.8800
C(1)-H(6)	0.9800
C(1)-H(5)	0.9800
C(1)-H(1)	0.9800
C(2)-C(12)	1.401(3)
C(2)-C(3)	1.405(3)
C(3)-C(4)	1.386(3)
C(3)-H(12)	0.9500
C(4)-C(5)	1.391(3)
C(4)-H(13)	0.9500
C(5)-C(13)	1.390(3)
C(5)-C(6)	1.515(2)
C(6)-C(14)	1.516(3)
C(6)-C(7)	1.542(3)
C(6)-H(14)	1.0000
C(7)-C(17)	1.526(2)
C(7)-H(21)	1.0000
C(9)-C(23)	1.518(3)
C(9)-C(10)	1.518(3)
C(9)-C(22)	1.520(3)
C(10)-H(2)	0.9800
C(10)-H(28)	0.9800

C(10)-H(3)	0.9800
C(11)-H(9)	0.9800
C(11)-H(7)	0.9800
C(11)-H(8)	0.9800
C(12)-C(13)	1.388(3)
C(12)-H(11)	0.9500
C(13)-H(10)	0.9500
C(14)-C(15)	1.329(3)
C(14)-H(20)	0.9500
C(15)-C(16)	1.460(3)
C(15)-H(19)	0.9500
C(16)-C(21)	1.399(3)
C(16)-C(17)	1.404(3)
C(17)-C(18)	1.382(3)
C(18)-C(19)	1.401(3)
C(18)-H(15)	0.9500
C(19)-C(20)	1.379(3)
C(19)-H(16)	0.9500
C(20)-C(21)	1.383(3)
C(20)-H(17)	0.9500
C(21)-H(18)	0.9500
C(22)-H(23)	0.9800
C(22)-H(24)	0.9800
C(22)-H(22)	0.9800
C(23)-H(26)	0.9800
C(23)-H(25)	0.9800
C(23)-H(27)	0.9800

C(8)-O(1)-C(9)	119.83(14)
C(2)-N(1)-C(1)	119.35(19)
C(2)-N(1)-C(11)	119.3(2)
C(1)-N(1)-C(11)	118.52(19)
C(8)-N(2)-C(7)	121.49(16)
C(8)-N(2)-H(4)	119.3
C(7)-N(2)-H(4)	119.3
N(1)-C(1)-H(6)	109.5
N(1)-C(1)-H(5)	109.5
H(6)-C(1)-H(5)	109.5

N(1)-C(1)-H(1)	109.5
H(6)-C(1)-H(1)	109.5
H(5)-C(1)-H(1)	109.5
N(1)-C(2)-C(12)	121.24(19)
N(1)-C(2)-C(3)	121.48(19)
C(12)-C(2)-C(3)	117.27(17)
C(4)-C(3)-C(2)	120.93(19)
C(4)-C(3)-H(12)	119.5
C(2)-C(3)-H(12)	119.5
C(3)-C(4)-C(5)	122.03(18)
C(3)-C(4)-H(13)	119.0
C(5)-C(4)-H(13)	119.0
C(13)-C(5)-C(4)	116.76(17)
C(13)-C(5)-C(6)	121.11(17)
C(4)-C(5)-C(6)	122.13(17)
C(5)-C(6)-C(14)	112.40(16)
C(5)-C(6)-C(7)	111.98(14)
C(14)-C(6)-C(7)	109.40(15)
C(5)-C(6)-H(14)	107.6
C(14)-C(6)-H(14)	107.6
C(7)-C(6)-H(14)	107.6
N(2)-C(7)-C(17)	113.25(16)
N(2)-C(7)-C(6)	111.29(14)
C(17)-C(7)-C(6)	112.03(14)
N(2)-C(7)-H(21)	106.6
C(17)-C(7)-H(21)	106.6
C(6)-C(7)-H(21)	106.6
O(2)-C(8)-O(1)	125.98(16)
O(2)-C(8)-N(2)	124.58(18)
O(1)-C(8)-N(2)	109.43(15)
O(1)-C(9)-C(23)	109.33(16)
O(1)-C(9)-C(10)	110.53(15)
C(23)-C(9)-C(10)	112.62(17)
O(1)-C(9)-C(22)	102.79(14)
C(23)-C(9)-C(22)	110.87(16)
C(10)-C(9)-C(22)	110.27(17)
C(9)-C(10)-H(2)	109.5
C(9)-C(10)-H(28)	109.5

H(2)-C(10)-H(28)	109.5
C(9)-C(10)-H(3)	109.5
H(2)-C(10)-H(3)	109.5
H(28)-C(10)-H(3)	109.5
N(1)-C(11)-H(9)	109.5
N(1)-C(11)-H(7)	109.5
H(9)-C(11)-H(7)	109.5
N(1)-C(11)-H(8)	109.5
H(9)-C(11)-H(8)	109.5
H(7)-C(11)-H(8)	109.5
C(13)-C(12)-C(2)	120.62(18)
C(13)-C(12)-H(11)	119.7
C(2)-C(12)-H(11)	119.7
C(12)-C(13)-C(5)	122.35(19)
C(12)-C(13)-H(10)	118.8
C(5)-C(13)-H(10)	118.8
C(15)-C(14)-C(6)	121.66(18)
C(15)-C(14)-H(20)	119.2
C(6)-C(14)-H(20)	119.2
C(14)-C(15)-C(16)	121.83(18)
C(14)-C(15)-H(19)	119.1
C(16)-C(15)-H(19)	119.1
C(21)-C(16)-C(17)	119.14(18)
C(21)-C(16)-C(15)	121.61(18)
C(17)-C(16)-C(15)	119.25(16)
C(18)-C(17)-C(16)	119.75(17)
C(18)-C(17)-C(7)	122.38(17)
C(16)-C(17)-C(7)	117.65(17)
C(17)-C(18)-C(19)	120.31(19)
C(17)-C(18)-H(15)	119.8
C(19)-C(18)-H(15)	119.8
C(20)-C(19)-C(18)	120.1(2)
C(20)-C(19)-H(16)	120.0
C(18)-C(19)-H(16)	120.0
C(19)-C(20)-C(21)	119.94(17)
C(19)-C(20)-H(17)	120.0
C(21)-C(20)-H(17)	120.0
C(20)-C(21)-C(16)	120.75(19)

C(20)-C(21)-H(18)	119.6
C(16)-C(21)-H(18)	119.6
C(9)-C(22)-H(23)	109.5
C(9)-C(22)-H(24)	109.5
H(23)-C(22)-H(24)	109.5
C(9)-C(22)-H(22)	109.5
H(23)-C(22)-H(22)	109.5
H(24)-C(22)-H(22)	109.5
C(9)-C(23)-H(26)	109.5
C(9)-C(23)-H(25)	109.5
H(26)-C(23)-H(25)	109.5
C(9)-C(23)-H(27)	109.5
H(26)-C(23)-H(27)	109.5
H(25)-C(23)-H(27)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for cu_qwh418a_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	24(1)	19(1)	19(1)	-2(1)	4(1)	-5(1)
O(2)	36(1)	24(1)	23(1)	0(1)	10(1)	-9(1)
N(1)	21(1)	41(1)	42(1)	5(1)	3(1)	2(1)
N(2)	24(1)	15(1)	21(1)	1(1)	6(1)	-3(1)
C(1)	28(1)	81(2)	47(1)	21(2)	3(1)	12(1)
C(2)	23(1)	25(1)	30(1)	-6(1)	7(1)	4(1)
C(3)	28(1)	25(1)	26(1)	2(1)	10(1)	4(1)
C(4)	23(1)	25(1)	27(1)	0(1)	12(1)	-1(1)
C(5)	23(1)	17(1)	23(1)	-4(1)	8(1)	1(1)
C(6)	21(1)	20(1)	21(1)	0(1)	8(1)	-1(1)
C(7)	20(1)	17(1)	21(1)	0(1)	6(1)	-2(1)
C(8)	19(1)	18(1)	21(1)	-2(1)	6(1)	-1(1)
C(9)	24(1)	21(1)	19(1)	-2(1)	2(1)	-4(1)
C(10)	34(1)	25(1)	26(1)	-5(1)	10(1)	-6(1)
C(11)	24(1)	38(2)	60(2)	-1(1)	-2(1)	1(1)
C(12)	21(1)	27(1)	38(1)	-1(1)	11(1)	-3(1)

C(13)	26(1)	20(1)	28(1)	2(1)	10(1)	0(1)
C(14)	26(1)	21(1)	23(1)	-2(1)	10(1)	0(1)
C(15)	27(1)	21(1)	26(1)	-5(1)	8(1)	-5(1)
C(16)	22(1)	24(1)	24(1)	2(1)	8(1)	-3(1)
C(17)	21(1)	21(1)	22(1)	2(1)	8(1)	-2(1)
C(18)	24(1)	26(1)	28(1)	-2(1)	9(1)	0(1)
C(19)	27(1)	31(1)	34(1)	4(1)	12(1)	8(1)
C(20)	19(1)	38(1)	31(1)	2(1)	6(1)	1(1)
C(21)	24(1)	32(1)	27(1)	-2(1)	7(1)	-3(1)
C(22)	27(1)	24(1)	25(1)	-2(1)	6(1)	-6(1)
C(23)	26(1)	29(1)	31(1)	2(1)	2(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{3}) for cu_qwh418a_0m.

	x	y	z	U(eq)
H(4)	8389	10532	5450	24
H(6)	13868	6212	9672	81
H(5)	15326	5663	9528	81
H(1)	13880	4919	8765	81
H(12)	11728	5703	7996	31
H(13)	9502	6188	6615	29
H(14)	8739	8562	3904	24
H(21)	7661	7916	6000	24
H(2)	8568	12120	9367	42
H(28)	9860	11803	10637	42
H(3)	8940	10570	9830	42
H(9)	15391	7710	7130	66
H(7)	16194	7259	8591	66
H(8)	15127	8529	8316	66
H(11)	13410	8327	5963	34
H(10)	11170	8769	4582	29
H(20)	8420	5883	3710	27
H(19)	6053	5780	2917	30
H(15)	5746	10546	5179	31
H(16)	3371	10667	3917	36

H(17)	2376	8913	2468	36
H(18)	3751	7066	2224	33
H(23)	11642	12697	8365	39
H(24)	11490	13088	9752	39
H(22)	10245	13441	8456	39
H(26)	10984	9400	9410	45
H(25)	12026	10512	10292	45
H(27)	12023	10255	8830	45

Table 6. Torsion angles [°] for cu_qwh418a_0m.

C(1)-N(1)-C(2)-C(12)	177.9(2)
C(11)-N(1)-C(2)-C(12)	17.3(3)
C(1)-N(1)-C(2)-C(3)	-3.6(3)
C(11)-N(1)-C(2)-C(3)	-164.1(2)
N(1)-C(2)-C(3)-C(4)	179.7(2)
C(12)-C(2)-C(3)-C(4)	-1.7(3)
C(2)-C(3)-C(4)-C(5)	0.4(3)
C(3)-C(4)-C(5)-C(13)	1.3(3)
C(3)-C(4)-C(5)-C(6)	-178.93(18)
C(13)-C(5)-C(6)-C(14)	118.65(19)
C(4)-C(5)-C(6)-C(14)	-61.1(2)
C(13)-C(5)-C(6)-C(7)	-117.7(2)
C(4)-C(5)-C(6)-C(7)	62.5(2)
C(8)-N(2)-C(7)-C(17)	120.48(17)
C(8)-N(2)-C(7)-C(6)	-112.24(17)
C(5)-C(6)-C(7)-N(2)	58.8(2)
C(14)-C(6)-C(7)-N(2)	-175.88(15)
C(5)-C(6)-C(7)-C(17)	-173.23(16)
C(14)-C(6)-C(7)-C(17)	-47.9(2)
C(9)-O(1)-C(8)-O(2)	9.6(3)
C(9)-O(1)-C(8)-N(2)	-171.28(14)
C(7)-N(2)-C(8)-O(2)	-9.2(3)
C(7)-N(2)-C(8)-O(1)	171.65(15)
C(8)-O(1)-C(9)-C(23)	59.5(2)
C(8)-O(1)-C(9)-C(10)	-65.1(2)
C(8)-O(1)-C(9)-C(22)	177.28(15)

N(1)-C(2)-C(12)-C(13)	179.89(19)
C(3)-C(2)-C(12)-C(13)	1.3(3)
C(2)-C(12)-C(13)-C(5)	0.4(3)
C(4)-C(5)-C(13)-C(12)	-1.7(3)
C(6)-C(5)-C(13)-C(12)	178.51(18)
C(5)-C(6)-C(14)-C(15)	156.31(17)
C(7)-C(6)-C(14)-C(15)	31.3(2)
C(6)-C(14)-C(15)-C(16)	-0.4(3)
C(14)-C(15)-C(16)-C(21)	165.63(19)
C(14)-C(15)-C(16)-C(17)	-13.5(3)
C(21)-C(16)-C(17)-C(18)	-0.8(3)
C(15)-C(16)-C(17)-C(18)	178.31(17)
C(21)-C(16)-C(17)-C(7)	173.99(16)
C(15)-C(16)-C(17)-C(7)	-6.9(3)
N(2)-C(7)-C(17)-C(18)	-20.5(2)
C(6)-C(7)-C(17)-C(18)	-147.35(19)
N(2)-C(7)-C(17)-C(16)	164.88(16)
C(6)-C(7)-C(17)-C(16)	38.0(2)
C(16)-C(17)-C(18)-C(19)	-0.3(3)
C(7)-C(17)-C(18)-C(19)	-174.84(18)
C(17)-C(18)-C(19)-C(20)	1.2(3)
C(18)-C(19)-C(20)-C(21)	-1.0(3)
C(19)-C(20)-C(21)-C(16)	-0.2(3)
C(17)-C(16)-C(21)-C(20)	1.1(3)
C(15)-C(16)-C(21)-C(20)	-178.06(19)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cu_qwh418a_0m [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(23)-H(26)...O(2)	0.98	2.41	3.007(2)	118.5
C(10)-H(3)...O(2)	0.98	2.42	2.983(3)	116.3
C(23)-H(26)...O(2)	0.98	2.41	3.007(2)	118.5
C(10)-H(3)...O(2)	0.98	2.42	2.983(3)	116.3
C(23)-H(26)...O(2)	0.98	2.41	3.007(2)	118.5
C(10)-H(3)...O(2)	0.98	2.42	2.983(3)	116.3

C(23)-H(26)...O(2)	0.98	2.41	3.007(2)	118.5
C(10)-H(3)...O(2)	0.98	2.42	2.983(3)	116.3
C(23)-H(26)...O(2)	0.98	2.41	3.007(2)	118.5
C(10)-H(3)...O(2)	0.98	2.42	2.983(3)	116.3
C(23)-H(26)...O(2)	0.98	2.41	3.007(2)	118.5
C(10)-H(3)...O(2)	0.98	2.42	2.983(3)	116.3
C(23)-H(26)...O(2)	0.98	2.41	3.007(2)	118.5
C(10)-H(3)...O(2)	0.98	2.42	2.983(3)	116.3
C(23)-H(26)...O(2)	0.98	2.41	3.007(2)	118.5
C(10)-H(3)...O(2)	0.98	2.42	2.983(3)	116.3
C(10)-H(3)...O(2)	0.98	2.42	2.983(3)	116.3
C(23)-H(26)...O(2)	0.98	2.41	3.007(2)	118.5
C(10)-H(3)...O(2)	0.98	2.42	2.983(3)	116.3
C(23)-H(26)...O(2)	0.98	2.41	3.007(2)	118.5
C(10)-H(3)...O(2)	0.98	2.42	2.983(3)	116.3
C(23)-H(26)...O(2)	0.98	2.41	3.007(2)	118.5
C(10)-H(3)...O(2)	0.98	2.42	2.983(3)	116.3
C(23)-H(26)...O(2)	0.98	2.41	3.007(2)	118.5
C(10)-H(3)...O(2)	0.98	2.42	2.983(3)	116.3
C(23)-H(26)...O(2)	0.98	2.41	3.007(2)	118.5