Iridium/Copper-Cocatalyzed Asymmetric Ring Opening Reaction of Azabenzonorbornadienes with Amines

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Supporting Information

Contents

A: General method

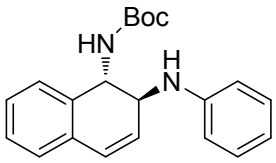
The reactions and manipulations were performed under an atmosphere of argon by using standard Schlenk techniques and Drybox (Mikrouna, Supper 1220/750). Anhydrous toluene, DME (Dimethoxyethane), THF (Tetrahydrofuran), MTBE (Methyl *tert*-butyl ether), ether and dioxane were distilled from sodium benzophenone ketyl prior to use. Anhydrous DCE (sym-Dichloroethane), CH_3CN (acetonitrile) and DMAc (Dimethylacetamide) were distilled from calcium hydride and stored under argon. ^1H 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 enantioselective excesses were determined by Agilent 1260 Series HPLC using Daicel AD-H、OD-H chiral columns eluted with a mixture of isopropyl alcohol and hexane.. Column chromatography was performed with silica gel (200-300 mesh).

B: Typical procedure for the reaction

$[Ir(COD)Cl]_2$ (3.4 mg, 0.005 mmol), (*R*)-Difluorphos (8.2 mg, 0.012 mmol) and 1.0 mL toluene were added to a Schlenk tube in argon atmosphere. The resulting solution was stirred at room temperature for 30 min, then CuBr (5.8 mg, 0.04mmol) was added and stirred for additional 10 min, then a solution of *N*-Boc-azabenzonorbornadiene **1a** (48.6 mg, 0.2mmol) in toluene(1 mL) was added, and the mixture was stirred for additional 10 min. After the addition of aminobenzene **2a** (55.8 mg, 0.6mmol) and 1.0mL toluene, the mixture was stirred at 70 °C under argon atmosphere with TLC monitoring until the complete consumption of **1a**. The reaction mixture was concentrated. The residue was purified by chromatography on a silica gel column to afford the desired product **3aa** (65.2mg, 97% yield). The enantioselective excess value of the product was determined by HPLC on a chiral stationary phase (95% ee).

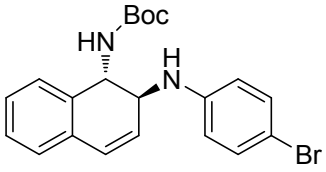
C: Characterization Data of Products

2-(Phenylamino)-1,2-dihydronaphthalen-1-yl-carbamic acid *tert*-butyl ester (3aa)



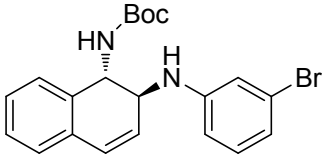
White solid, 97% yield, 95% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.04 (m, 6H), 6.64-6.62 (d, *J* = 7.2Hz, 3H), 6.49-6.47 (d, *J* = 9.6Hz, 1H), 6.20-5.98 (dd, *J* = 9.6,4.4Hz, 1H), 4.98-4.96 (t, *J* = 8Hz, 1H), 4.67-4.65 (d, *J* = 8.4Hz, 1H), 4.19 (s, 1H), 3.78 (s, 1H), 1.38 (s, 9H). The *ee* of **3aa** was determined by HPLC analysis using 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_{minor} = 7.1 min, t_{major} = 11.5 min.

2-(4-Bromophenylamino)-1,2-dihydro-naphthalen-1-yl-carbamic acid *tert*-butyl ester (3ac)



White solid,96% yield, 95% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.21 (m, 5H), 7.15-7.13 (d, *J* = 7.2Hz, 1H), 6.64-6.57 (dd, *J* = 17.6,8.4Hz, 3H), 6.07-6.04 (dd, *J* = 14.0,4.4Hz, 1H), 5.01-4.97 (t, *J* = 14.4Hz, 1H), 4.72-4.69 (d, *J* = 9.2Hz, 1H), 4.24 (s, 1H), 3.67 (s, 1H), 1.45 (s, 9H). The *ee* of **3ab** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{minor} = 6.3 min, t_{major} = 11.5 min.

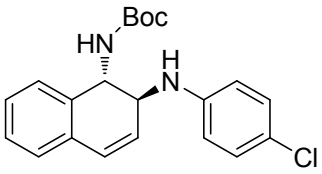
2-(3-Bromophenylamino)-1,2-dihydro-naphthalen-1-yl-carbamic acid *tert*-butyl ester (3ab)



White solid, 95% yield, 91% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.21 (m, 3H), 7.15-7.13 (d, *J* = 7.2Hz, 1H), 7.05-7.01 (t, *J* = 8Hz, 1H), 6.82-6.80 (d, *J* = 8Hz, 2H),

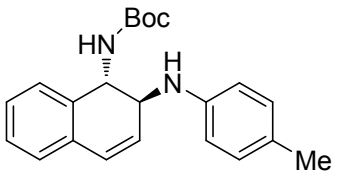
6.70-6.68 (d,*J* = 7.6Hz, 1H), 6.58-6.56 (d, *J* = 9.6Hz, 1H), 6.06-6.02 (dd, *J*= 9.6,4.0Hz, 1H), 5.03-5.00 (t, *J* = 8Hz, 1H), 4.73 (d, *J* = 8.8Hz, 1H), 4.24 (d, *J* = 5.2Hz, 1H), 3.95 (s, 1H), 1.46 (s, 9H). ^{13}C NMR ($CDCl_3$, 100MHz): δ 156.02, 148.11, 133.63, 132.41, 130.74, 128.94, 128.61, 128.39, 127.89, 127.76, 127.03, 123.33, 120.27, 115.86, 111.68, 80.06, 53.63, 52.33, 28.39. HRMS (EI^+): calcd for $C_{21}H_{23}BrN_2O_2$ $[M]^+$: 414.0943, Found: 414.0938. The *ee* of **3ac** was determined by HPLC analysis using 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_{minor} = 6.5 min, t_{major} = 13.8 min.

2-(4-Chlorophenylamino)-1,2-dihydro-naphthalen-1-yl-carbamic acid *tert*-butyl ester (3ad)



White solid, 96% yield, 94% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.21 (m, 3H), 7.15-7.11 (t, *J* = 14.0Hz, 3H), 6.67-6.56 (dd,*J* = 32.0,8.0Hz, 3H), 6.07-6.04 (dd, *J* = 9.6,4.4Hz, 1H), 5.01-4.97 (t, *J* = 14.4Hz, 1H), 4.71 (d, *J* = 8.8Hz, 1H), 4.23 (s, 1H), 3.85 (s,1H), 1.45 (s, 9H), The *ee* of **3ad** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{major} = 6.4 min, t_{minor} = 11.6 min.

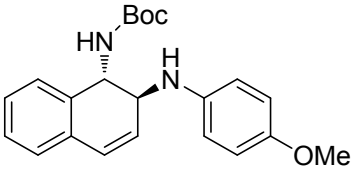
2-(*p*-Tolylamino)-1,2-dihydro-naphthalen-1-yl-carbamic acid *tert*-butyl ester (3ae)



White solid,97% yield, 93% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.17 (m, 3H), 7.11-7.10 (d, *J* = 7.2Hz, 1H), 7.00-6.98 (d, *J* = 6.8Hz, 2H), 6.63-6.61 (d, *J* = 7.2Hz, 2H), 6.54-6.51 (d, *J* = 9.6Hz, 1H), 6.08-6.04 (dd, *J* = 9.2,3.2Hz, 1H), 5.01-5.00 (d, *J* = 6.4Hz, 1H), 4.78-4.76 (d, *J* = 8.8Hz, 1H), 4.22 (s, 1H), 3.64 (s, 1H), 2.22 (s, 3H), 1.44(s, 9H). The *ee* of **3ae** was determined by HPLC analysis using Daicel Chiralcel

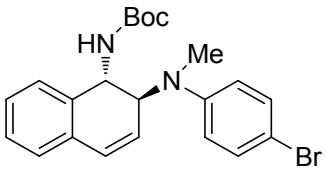
AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 7.9min, t_{major} = 10.1 min.

2-(4-Methoxyphenylamino)-1,2-dihydro-naphthalen-1-yl-carbamic acid *tert*-butyl ester (3af)



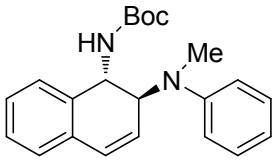
White solid, 97% yield, 94% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.11 (m, 3H), 7.05 (d, *J* = 7.6Hz, 1H), 6.71-6.69 (d,*J* = 8.8Hz, 2H), 6.61-6.59 (d, *J* = 8.8, 2H), 6.47-6.45 (d, *J* = 9.6Hz, 1H), 6.01-5.98 (dd, *J* = 9.6,4.8Hz, 1H), 4.94-4.91 (t, *J* = 14.8Hz, 1H), 4.69-4.67(d, *J* = 8.8 Hz, 1H), 4.12-4.10 (t, *J* = 4.8Hz, 1H), 3.65 (s, 3H), 3.55 （s，1H）, 1.37 (s, 9H). The *ee* of **3ai** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 85/15, 1 mL/min, 254 nm; t_{minor} = 8.3 min, t_{major} =10.8 min.

2-[(4-Bromophenyl)methylamino]-1,2-dihydronaphthalen-1-yl-carbamic acid tert-butyl ester (3ai)



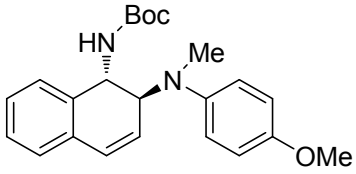
White solid, 83% yield, 94% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.21 (m, 5H), 7.11-7.09 (d, 1H), 6.73-6.71 (d,*J*=9.2Hz, 2H), 6.63-6.60 (dd,*J*=2.0, 8.0Hz, 1H), 5.90-5.86 (dd,*J*=2.8, 10.0Hz, 1H),5.18-5.13 (t, *J* = 10.0Hz, 1H), 4.74-4.72 (d, *J* = 10.0Hz, 1H), 4.51-4.49 (d, *J*=9.6, 1H), 2.79(s, 3H), 1.34(s, 9H). The *ee* of **3ag** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 95/5, 1.0 mL/min, 254 nm; t_{minor} = 7.9 min, t_{major} = 8.8 min.

2-(Methylphenylamino)-1,2-dihydronaphthalen-1-yl-carbamic acid tert-butyl ester (3ah)



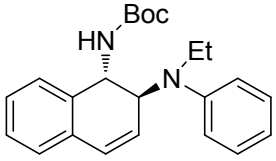
White solid,94% yield, 95% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 6.4Hz, 1H), 7.33-7.20 (m, 4H), 7.11 (d, *J* =7.2Hz, 1H), 6.86-6.84 (d, *J* = 8.0Hz, 2H), 6.74-6.70 (t, *J* = 14.4Hz, 1H), 6.62-6.60 (d, *J* = 7.6Hz, 1H), 5.95-5.91 (dd, *J* = 9.6,2.4Hz, 1H), 5.23-5.18 (t, *J* = 10.4Hz, 1H), 4.81-4.78 (d, *J* = 10.8Hz, 1H), 4.50-4.48 (d, *J* = 9.2Hz, 1H), 2.84 (s, 1H), 1.34(s,9H). The *ee* of **3ah** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 95/5, 1mL/min, 254 nm; t_{minor} = 7.8 min, t_{major} = 9.1 min.

2-[(4-Methoxyphenyl)methylamino]-1,2-dihydronaphthalen-1-yl-carbamic acid tert-butyl ester (3aj)



White solid, 96% yield, 95% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.30 (d, *J* = 6.8Hz, 1H), 7.24-7.18 (m, 2H), 7.09-7.07 (d, *J* = 7.2Hz, 1H), 6.81 (s, 4H), 6.60-6.57 (dd, *J* =10.0,2.0Hz, 1H), 5.94-5.91 (dd, *J* = 10.0,2.8Hz, 1H), 5.19-5.14 (t, *J* = 10.0Hz, 1H), 4.61-4.58 (d, *J* =10.0Hz, 2H), 4.53 (s, 1H),3.75 (s, *3*H), 2.75 (s, 3H), 1.38 (s, 9H). The *ee* of **3af** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 254 nm; t_{major} = 17.0 min, t_{minor} = 19.0 min.

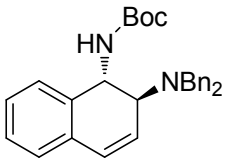
2-(Ethylphenylamino)-1,2-dihydronaphthalen-1-yl-carbamic acid tert-butyl ester (3ak)



White solid,96% yield, 94% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.30 (d, *J* = 6.4Hz, 1H), 7.24-7.20 (m, 4H), 7.11-7.09 (d, *J* = 6.4, 1H), 6.88-6.86 (d, *J* = 8.0Hz, 2H), 6.73-6.69 (t, *J* = 7.2Hz, 1H), 6.62-6.60 (d, *J* = 10.0Hz, 1H), 5.97-5.94 (t, *J* = 1.6Hz, 1H), 5.18-5.13 (t, *J* = 8.8Hz, 1H), 4.72-4.70 (d, *J* = 8.8HZ, 1H), 4.60 (s, 1H)

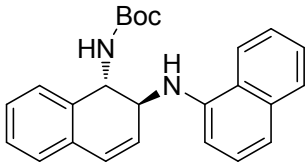
3.29-3.28 (d, *J* = 6.8Hz, 2H) 1.39 (s, 9H), 1.09-1.06 (t, *J* = 12.8Hz, 3H). The *ee* of **3aj** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 95/5,1mL/min, 254 nm; t_{minor} = 6.9 min, t $_{major}$ =10.1min.

2-Dibenzylamino-1,2-dihydro-naphthalen-1-yl-carbamic acid *tert*-butyl ester (3al)



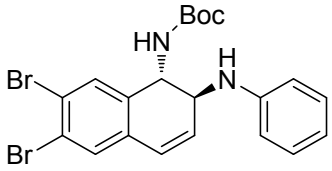
White solid, 90% yield, 93% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.37 (d, *J* = 7.2Hz, 4H), 7.29-7.25 (m, 4H), 7.22-7.19 (m, 4H), 7.05-7.03 (t, *J* = 4.8Hz, 1H), 6.61-6.58 (dd, *J* = 10.0, 1.6Hz, 1H), 6.07-6.04 (dd, *J* = 10.0, 3.6Hz, 1H), 5.27-5.23 (t, *J* = 8.4Hz, 1H), 4.50-4.48 (d, *J* = 8.8Hz, 1H),3.76-3.73 (d, *J* = 13.6Hz, 1H), 3.56-3.53 (d, *J* = 13.6Hz, 1H), 3.47 (s, 1H), 1.53 (s, 9H). The *ee* of **3ak** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 95/5, 1mL/min, 254 nm; t_{minor} = 7.7 min, t_{major} = 10.7 min.

2-(Naphthalen-1-yl-amino)-1,2-dihydro-naphthalen-1-yl-carbamic acid *tert*-butyl ester (3ag)



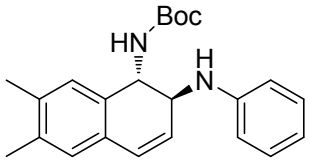
White solid,80% yield, 93% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.75 (t, *J* = 16Hz, 2H), 7.44-7.34(m, 4H), 7.31-7.21 (m, 3H),7.17-7.15 (d, *J* = 7.2Hz, 1H), 6.75-6.73 (d, *J* = 7.6Hz, 1H), 6.59-6.57(d, *J* = 9.6Hz, 1H), 6.20-6.17 (dd, *J* = 9.6,3.2Hz, 1H), 5.34-5.29 (t, *J* = 9.6Hz, 1H), 5.00 (s, 1H), 4.86-4.84 (d, *J* = 9.6Hz, 1H),4.45-4.43 (d, *J.*= 8.8Hz, 1H), 1.44 (s, 9Hz). The *ee* of **3al** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 90/10, 1 mL/min, 254 nm; t_{minor} = 6.4 min, t_{major} = 10.5 min.

2-(Naphthalen-1-yl-amino)-6,7-dibromo-1,2-dihydro-naphthalen-1-yl-carbamic acid *tert*-butyl ester (3ga)



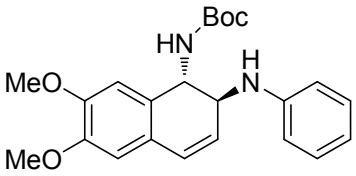
White solid, 93% yield, 94% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.38 (s, 1H), 7.22-7.18 (t, *J* = 8.0Hz, 2H), 6.75-6.71 (t, *J* = 7.2Hz, 1H), 6.69-6.67 (d, *J* = 7.6Hz, 1H), 6.48-6.46 (d, *J* = 9.6Hz, 1H),6.18-6.15 (dd, *J* = 9.6,4.0Hz, 1H), 5.02-4.98 (t, *J* = 8.4Hz, 1H), 4.71-4.69 (d, *J* = 9.2Hz, 1H), 4.25 (s, 1H), 3.83 (s, 1H), 1.46 (s, 9H). ^{13}C NMR ($CDCl_3$, 100MHz): δ 155.88, 146.35, 134.94, 133.20, 132.71, 131.46, 130.63, 129.53, 126.76, 124.54, 123.79,117.89, 113.13, 80.39, 53.45, 51.76, 28.35). HRMS (EI$^+$): calcd for $C_{21}H_{22}Br_2N_2O_2$ $[M]^+$: 492.0048; Found: 492.0074. The *ee* of **3ea** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 95/5, 1 mL/min, 254 nm; t_{minor} = 10.6min, t_{major} = 12.6 min.

2-(Naphthalen-1-yl-amino)-6,7-dimethyl-1,2-dihydro-naphthalen-1-yl-carbamic acid *tert*-butyl ester (3ea)



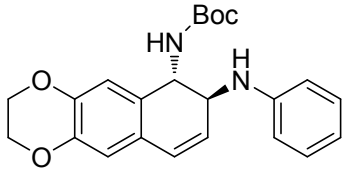
White solid, 93% yield, 93% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.17 (t, *J* = 15.6Hz, 2H), 7.07(s, 1H), 6.92 (s, 1H), 6.74-6.68 (m, 3H), 6.53-6.51 (d, *J* = 9.6Hz, 1H), 6.04-6.00 (dd, *J* = 9.6,4.4Hz, 1H), 4.98-4.95 (t, *J* = 8.0Hz, 1H), 4.68-4.66 (d, *J* = 8.8Hz, 1H), 4.25-4.22 (t, *J* = 4.8Hz, 1H), 3.82 (s, 1H), 2.24-2.23 (s, 6H), 1.46(s, 9H). ^{13}C NMR ($CDCl_3$, 100MHz): δ 155.86, 146.50, 136.85, 136.76, 131.17, 129.96, 129.67, 129.43, 128.66, 128.35, 126.90, 117.68, 113.44, 79.72, 53.45, 51.71, 28.44, 19.69, 19.48. HRMS (EI$^+$): calcd for $C_{23}H_{28}N_2O_2$ $[M]^+$: 364.2151, Found: 364.2159. The *ee* of **3fa** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm; t_{minor} = 31.8 min, t_{major} = 34.4 min.

2-(Naphthalen-1-yl-amino)-6,7-dimethoxy-1,2-dihydro-naphthalen-1-yl-carbamic acid *tert*-butyl ester (3fa)



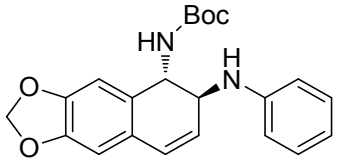
White solid, 94% yield, 93% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.19 (t, *J* = 17.2Hz, 2H), 6.83 (s, 1H), 6.77-6.75 (d, *J* = 8.0Hz, 2H), 6.72-6.68 (t, *J* = 7.2Hz,1H), 6.66(s, 1H), 6.51-6.48 (d, *J* = 9.6Hz, 1H), 6.00-5.96 (dd, *J* = 8.0,4.0Hz, 1H), 4.95-4.93 (dd, *J* =8.0,4.0Hz, 1H), 4.75-4.73 (d, *J* = 8.8Hz, 1H), 4.24 (s, 1H), 3.98-3.97 (d, *J* = 2.4Hz, 1H), 3.87 (s, 1H), 3.83 (s, 3H), 1.46 (s, 9H). ^{13}C NMR ($CDCl_3$, 100MHz): δ 155.72, 148.72, 148.70, 146.65, 129.45, 128.48, 126.29, 125.53, 124.94, 117.50, 113.22, 112.23, 110.15, 79.75, 56.06, 56.03, 52.48, 51.47, 28.42. HRMS (EI$^+$): calcd for $C_{23}H_{28}N_2O_4$ $[M]^+$: 396.2049; Found: 396.2039. The *ee* of **3ga** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 95/5, 1 mL/min, 254 nm; t_{major} = 26.9 min, t_{minor} = 29.1 min.

2-(Naphthalen-1-yl-amino)-1,2-dihydro-naphthalen[2,3-*b*][1,4]dioxin-1-yl-carbamic acid *tert*-butyl ester (3ha)



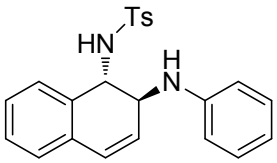
White solid, 95% yield, 94% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.17 (t, *J* = 8.0Hz, 2H), 6.84 (s, 1H), 6.75-6.69 (m, 3H), 6.67 (s, 1H), 6.45-6.43 (d, *J* = 9.2Hz, 1H), 6.00-5.96 (dd, *J* = 9.6,4.4Hz, 1H), 4.93-4.89 (t, *J* = 8.4Hz, 1H), 4.69-4.67 (d, *J* = 8.8Hz, 1H), 4.35-4.33 (t, *J* = 2.8Hz, 1H), 4.24 (s, 5H), 1.45 (s, 9H), ^{13}C NMR ($CDCl_3$, 100MHz): δ 155.74, 143.23,129.38, 129.28, 128.24, 127.23, 126.03, 125.92, 118.30, 117.28, 115.83,114.03, 113.35, 79.77, 64.40, 64.35, 53.83, 51.56, 28.35. HRMS (EI$^+$): calcd for $C_{23}H_{26}N_2O_4$ $[M]^+$: 394.1893; Found: 394.1909. The *ee* of **3fa** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 85/15, 1 mL/min, 254 nm; t_{minor} = 11.3 min, t_{major} = 14.3min.

2-(Naphthalen-1-yl-amino)-1,2-dihydro-naphthalen[2,3-*d*][1,3]dioxol-1-yl-carbamic acid *tert*-butyl ester (3ia)



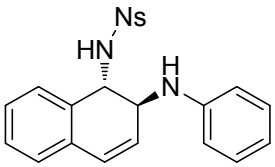
White solid, 95% yield, 94% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.17 (t, *J* = 8.0Hz, 2H), 6.82 (s, 1H), 6.74-6.68 (m, 3H), 6.63 (s, 1H), 6.46-6.44 (d, *J* = 9.6Hz, 1H), 6.01-5.97 (dd, *J* = 9.6,4.8Hz, 1H), 5.94-5.93 (d, *J* = 3.2Hz, 1H), 4.93-4.90 (m, 1H), 4.70-4.68 (d, *J* = 8.8Hz, 1H), 4.21 (s, 1H), 3.74 (s, 1H), 1.45 (s, 9H), ^{13}C NMR ($CDCl_3$, 100MHz): δ 155.71, 143.53,147.29, 146.56, 129.45, 128.53, 127.98, 126.46, 125.91, 117.68, 113.32,109.44,107.49,101.23, 79.83, 52.91, 52.03, 28.41. HRMS (EI^+): calcd for $C_{22}H_{24}N_2O_4$ $[M]^+$: 380.1736, Found: 380.1748. The *ee* of **3fa** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 90/10, 1 mL/min, 254 nm; t_{minor} = 12.1 min, t_{major} = 14.7min.

_N_-[2-(Phenylamino)-1,2-dihydro-naphthalen-1-yl]-4-methyl-benzenesulfonamide (3ba)



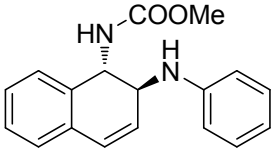
White solid, 90% yield, 88% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.74 (d, *J* = 8.0Hz, 2H), 7.32-7.30 (d, *J* = 8.0Hz, 1H), 7.24 (d, *J* = 1.2Hz, 1H), 7.18-7.11 (m, 3H), 7.04-7.00 (dt, *J* = 7.6, 0.8Hz, 1H), 6.74-6.71 (t, *J* = 14.4Hz, 1H), 6.62-6.54 (m, 4H), 6.10-6.06 (dd, *J* = 9.6,5.6Hz, 1H), 4.80-4.78 (d, *J* = 8.0Hz, 1H), 4.45-4.43 (dd, *J* = 7.6, 3.2Hz, 1H), 4.36 (s, 1H), 3.47 (s, 1H), 2.46 (s, 3H). The *ee* of **3fa** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 70/30, 1 mL/min, 254 nm; t_{minor} = 8.4 min, t_{major} = 10.2min.

4-nitro-_N_-[2-(Phenylamino)-1,2-dihydro-naphthalen-1-yl]-4-methyl-benzenesulfonamide (3ca)



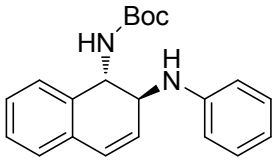
White solid, 86% yield, 84% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29-8.27 (d, *J* = 8.4Hz, 2H), 7.98-7.96(d, *J* = 8.4Hz, 2H), 7.28-7.24 (t, *J* = 6.8Hz, 2H), 7.19-7.13(m, 3H), 7.05-7.01 (t, *J* = 7.6Hz, 1H), 6.77-6.73(t, *J* = 7.2Hz, 1H), 6.64-6.59 (dd, *J* = 14.0, 6.4Hz, 4H), 6.10=6.06 (dd, *J* = 9.2, 5.2Hz, 1H), 5.12-5.10 (d, *J* = 8.0Hz, 1H), 4.58-4.55 (dd, *J* = 8.0,3.2Hz, 1H), 4.36 (s, 1H), 3.47 (s,1H). ^{13}C NMR ($CDCl_3$, 100MHz): δ 149.84, 146.37, 145.52 , 131.66, 131.32, 129.51, 129.46, 129.35, 128.88, 128.49, 128.33, 127.49 , 126.38, 124.29, 118.22 , 113.23, 54.13, 52.39. HRMS (EI^+): calcd for $C_{22}H_{19}N_3O_4S$ $[M]^+$: 421.1096, Found: 421.1103. The *ee* of **3fa** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 60/40, 1 mL/min, 254 nm; t_{minor} = 12.8 min, t_{major} = 17.7min.

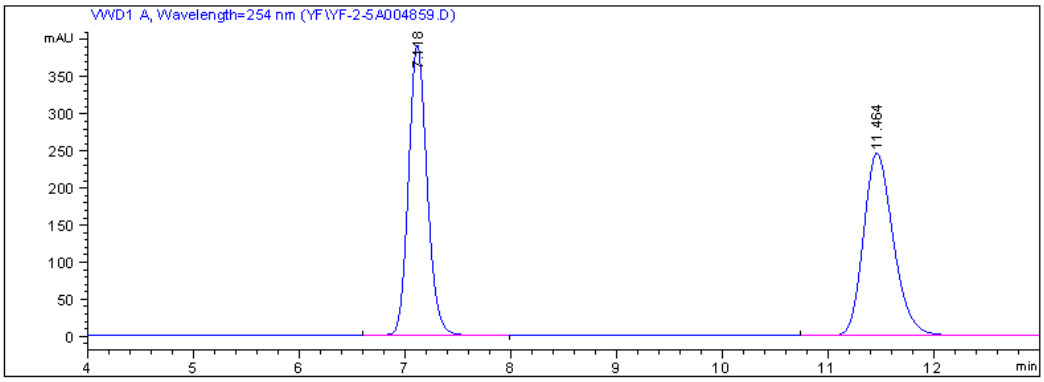
2-(Phenylamino)-1,2-dihydronaphthalen-1-yl-carbamic acid methyl ester (3da)



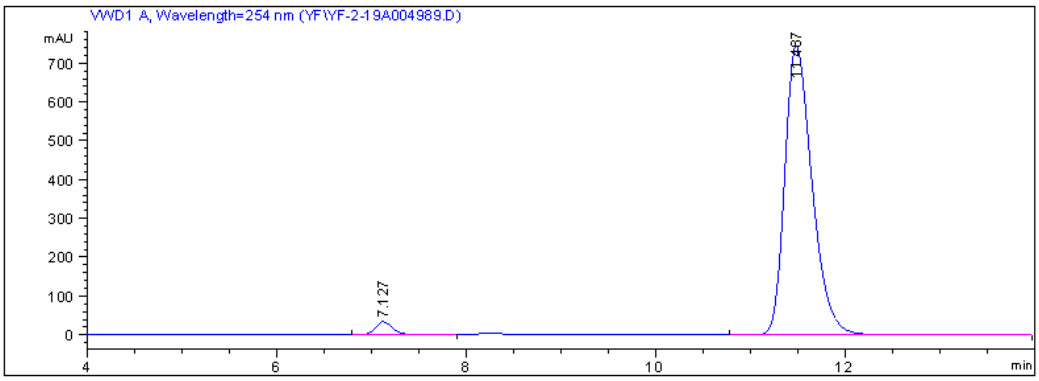
White solid, 88% yield, 83% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.28 (d, *J* = 7.2Hz, 2H), 7.22-7.13(m, 4H), 6.76-6.69(m, 3H), 6.59-6.56(d, *J* = 9.6, 1H), 6.08-6.04 (dd, *J* = 9.6,5.2Hz, 1H), 5.05-5.02(t, *J* = 5.6Hz, 1H), 4.96-4.94(d, *J* = 8.4Hz, 1H),4.32-4.30 (t, *J* = 4.8, 1H), 3.79 (s, 1H), 3.65(s, 1H), ^{13}C NMR ($CDCl_3$, 100MHz): δ 156.88, 146.35, 133.27 , 132.13, 129.40, 129.34, 128.85, 128.73, 128.39, 127.50, 127.04, 117.75 , 113.34, 52.50, 52.27. HRMS (EI^+): calcd for $C_{18}H_{18}N_2O_2$ $[M]^+$: 294.1368, Found:294.1367. The *ee* of **3fa** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/*i*-PrOH = 90/10, 1 mL/min, 254 nm; t_{minor} = 8.7min, t_{major} = 13.1min.

D. HPLC Spectra

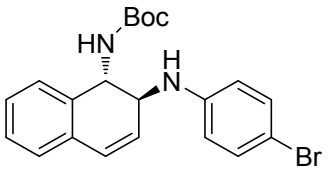


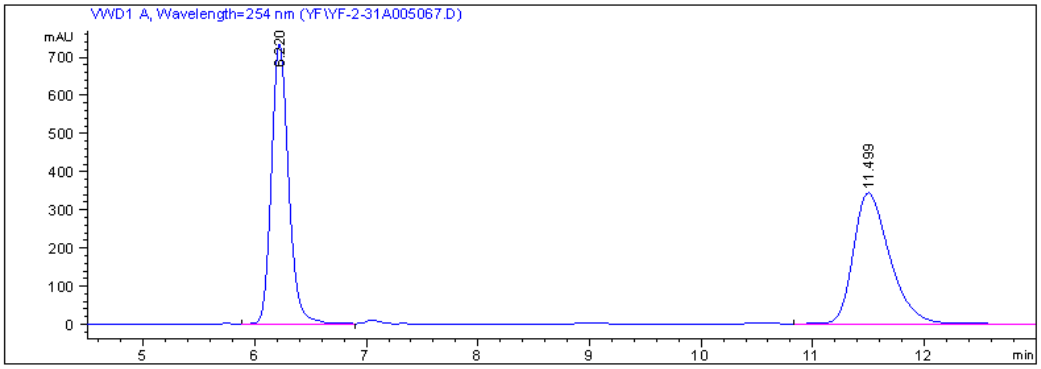


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.118	BB	0.1888	4795.83789	391.80380	49.7952
2	11.464	BBA	0.3033	4835.27930	246.00044	50.2048

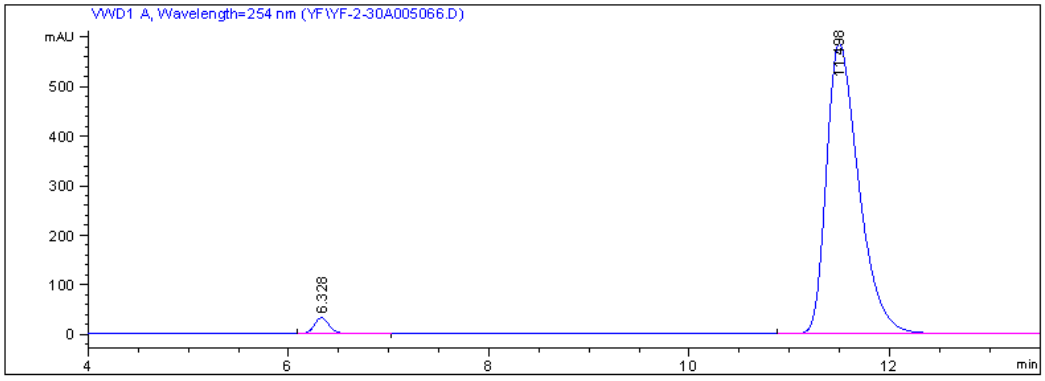


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.127	BB	0.1939	419.46729	33.30483	2.7346
2	11.487	BBA	0.3065	1.49200e4	745.52228	97.2654

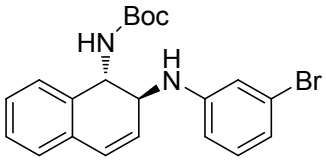


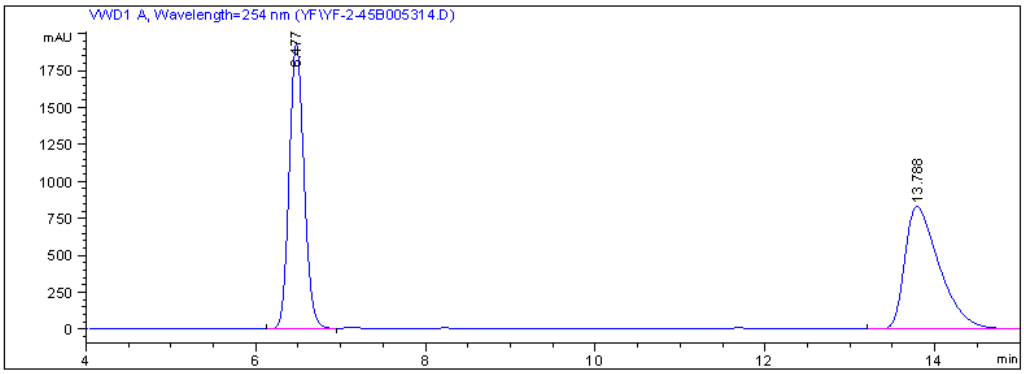


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.220	VV	0.1647	7854.50732	734.91833	49.7783
2	11.499	VB	0.3483	7924.46631	344.57745	50.2217

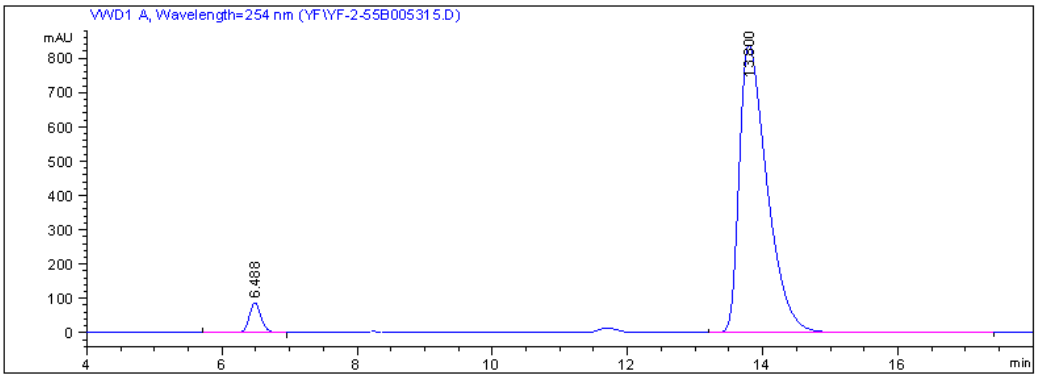


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.328	BB	0.1607	339.55743	32.28323	2.5069
2	11.498	BBA	0.3448	1.32054e4	586.16656	97.4931

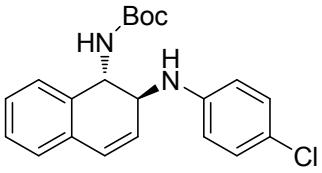


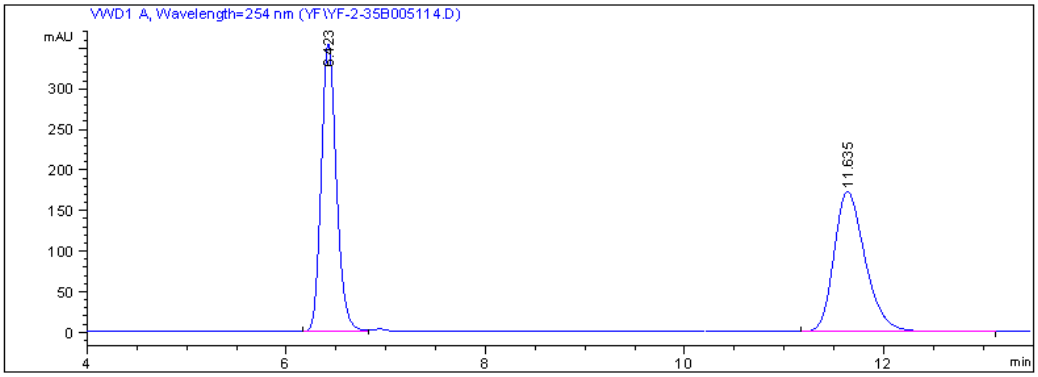


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.477	BV	0.1889	2.34417e4	1927.71423	49.8774
2	13.788	BBA	0.4276	2.35569e4	831.43274	50.1226

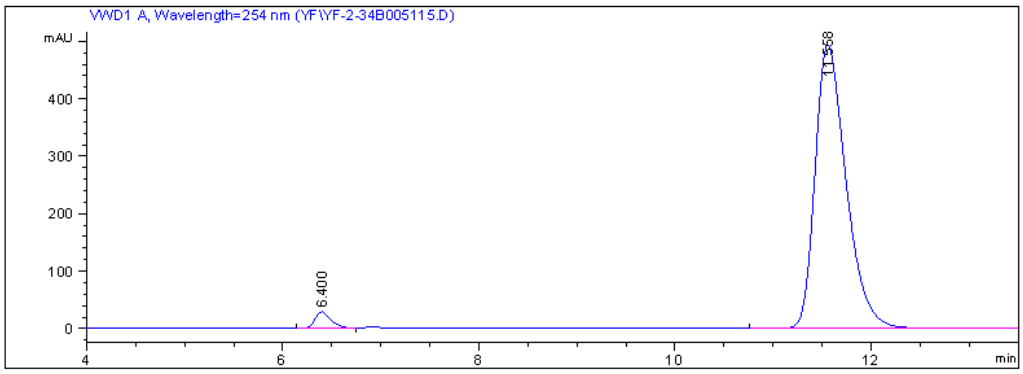


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.488	BV	0.1878	1067.16528	87.81960	4.2769
2	13.800	BB	0.4290	2.38844e4	839.23438	95.7231

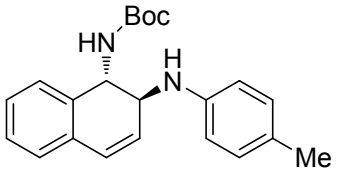


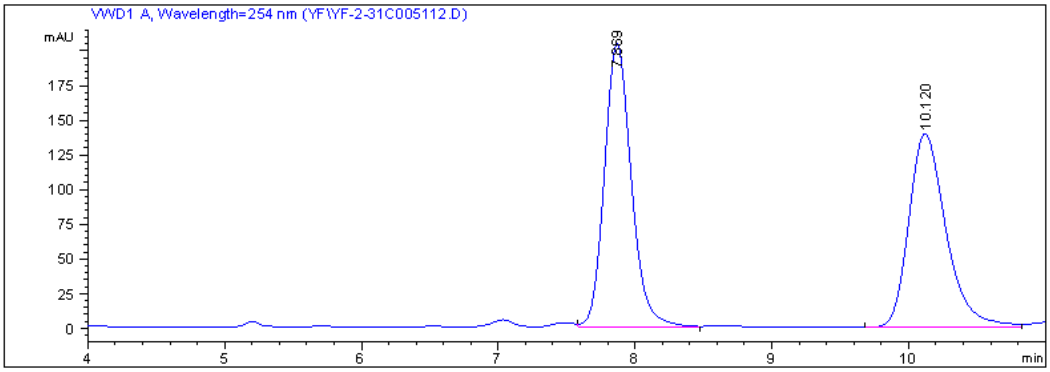


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.423	BV	0.1661	3770.54053	354.52911	50.3218
2	11.635	BB	0.3320	3722.31470	172.30028	49.6782

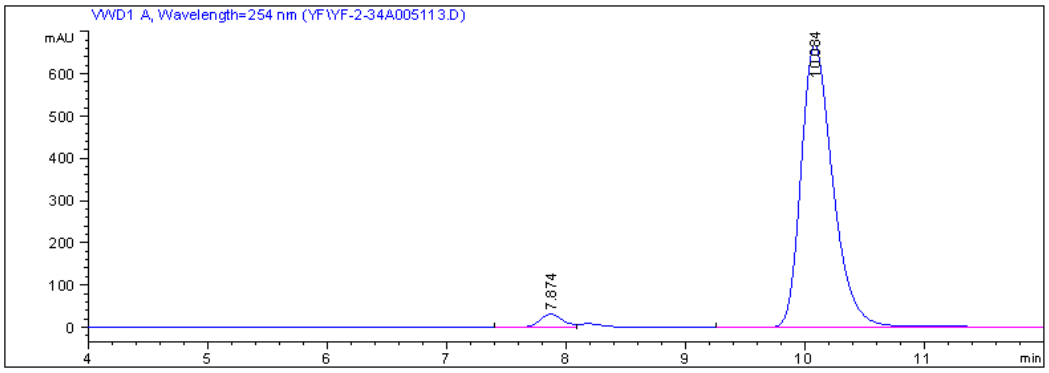


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.400	BV	0.1759	341.29016	29.28971	3.0422
2	11.558	BBA	0.3389	1.08773e4	493.98364	96.9578

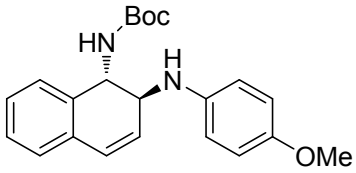


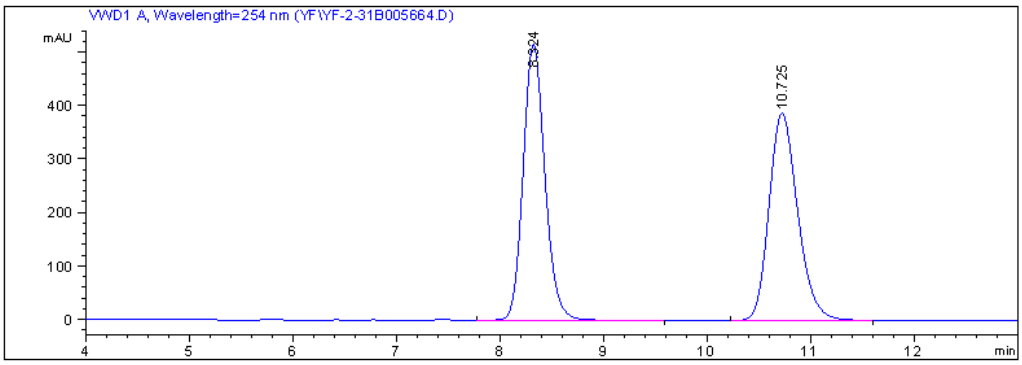


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.869	VB	0.2089	2776.30347	203.88681	51.2753
2	10.120	BV	0.2887	2638.20459	139.46426	48.7247

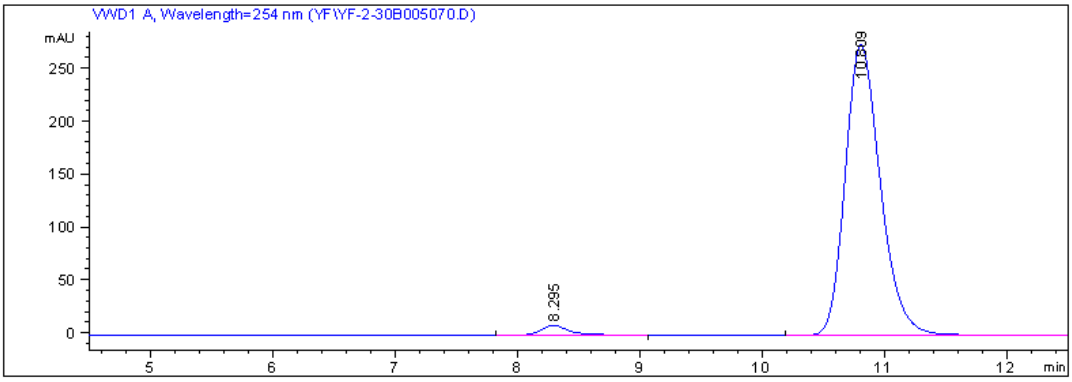


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.874	BV	0.2063	420.42468	30.98948	3.2688
2	10.084	BBA	0.2850	1.24412e4	669.03516	96.7312

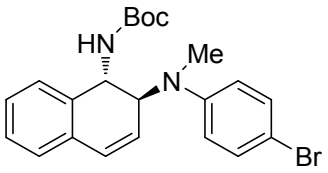


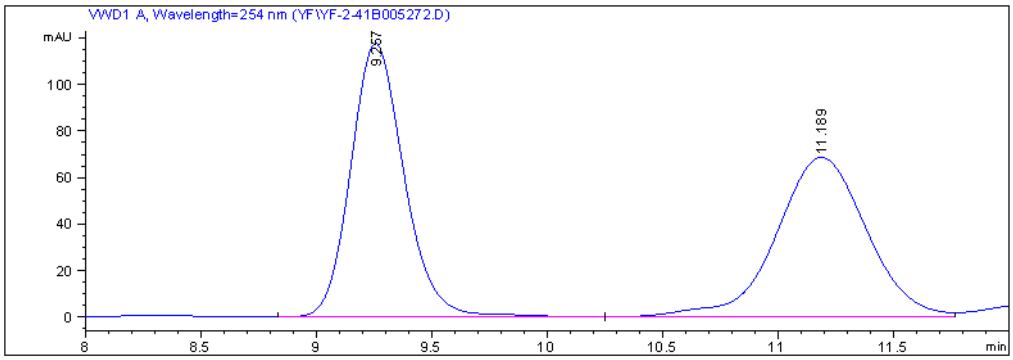


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.324	BB	0.2254	7540.50293	516.28625	50.3038
2	10.725	BB	0.2963	7449.41846	387.38812	49.6962

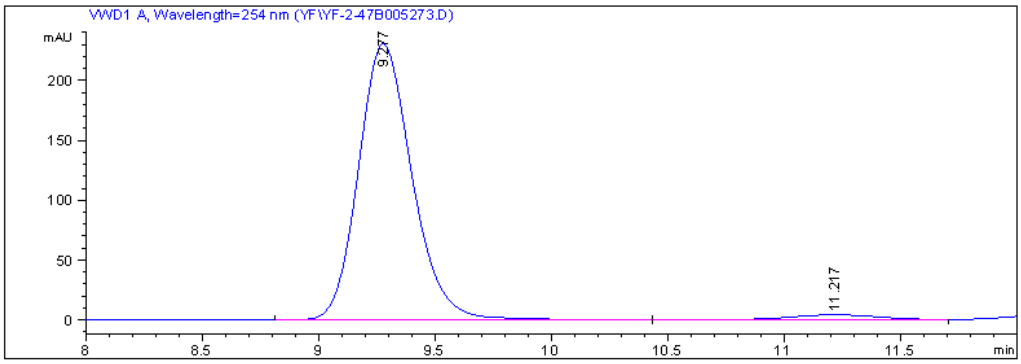


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.295	BB	0.2512	156.64738	9.31397	2.7733
2	10.809	BB	0.3074	5491.80029	274.45465	97.2267

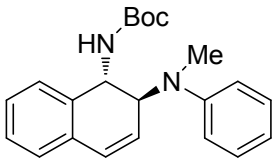


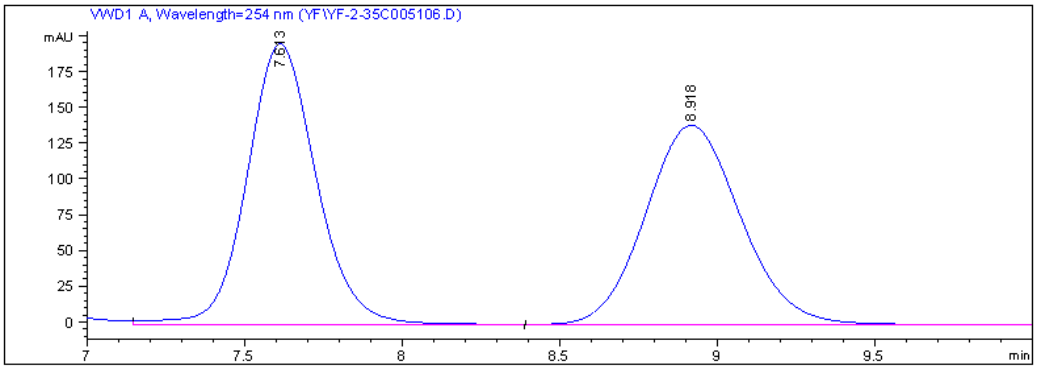


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.257	BB	0.2468	1883.45215	117.64974	50.2377
2	11.189	BV	0.4205	1865.63000	68.56197	49.7623

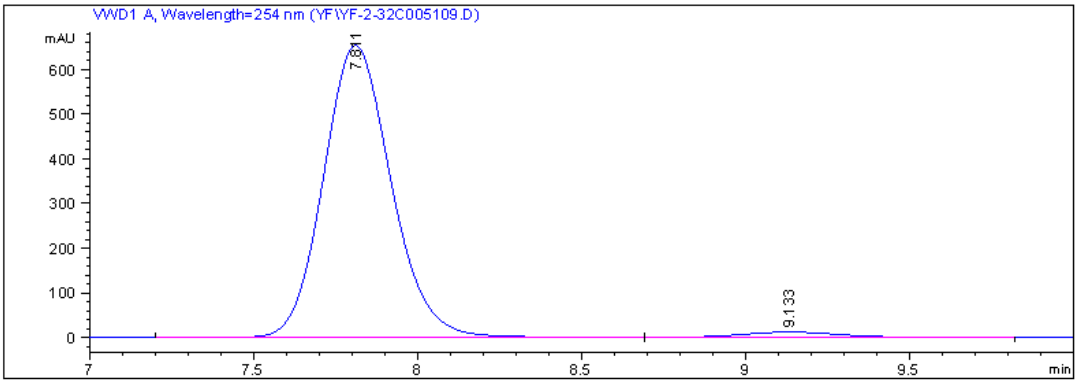


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.277	BB	0.2454	3682.23413	230.45601	97.0462
2	11.217	BV	0.4157	112.07603	4.20805	2.9538

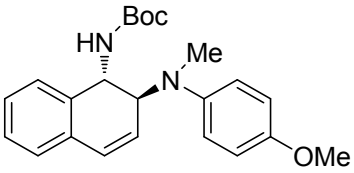


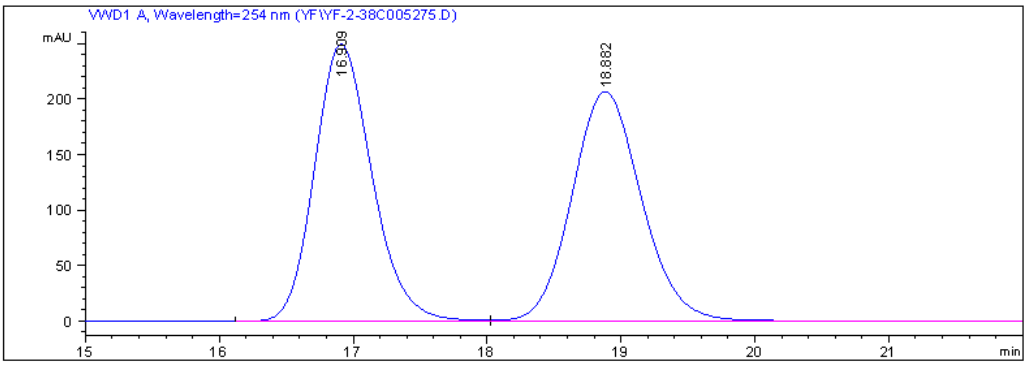


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.613	VB	0.2342	2994.43335	196.09740	50.5089
2	8.918	BB	0.3266	2934.09644	139.37543	49.4911

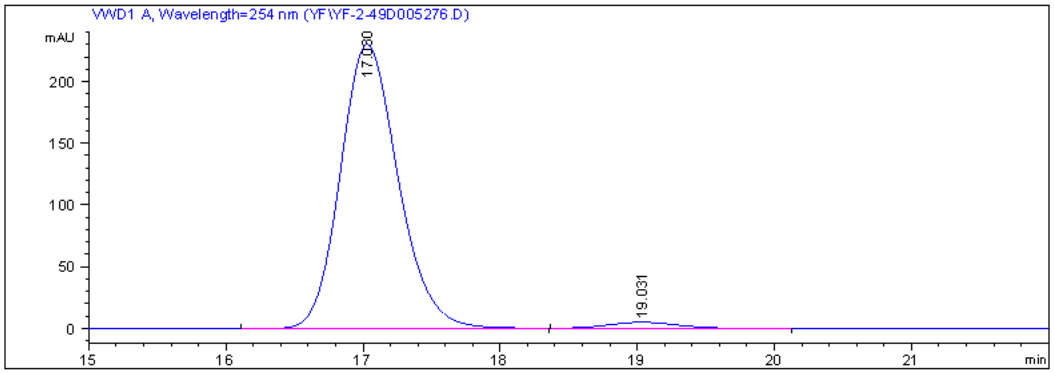


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.811	BB	0.2223	9376.73242	653.78461	97.5175
2	9.133	BB	0.3137	238.70103	11.86453	2.4825

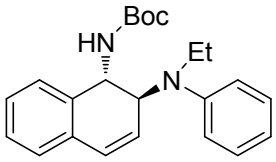


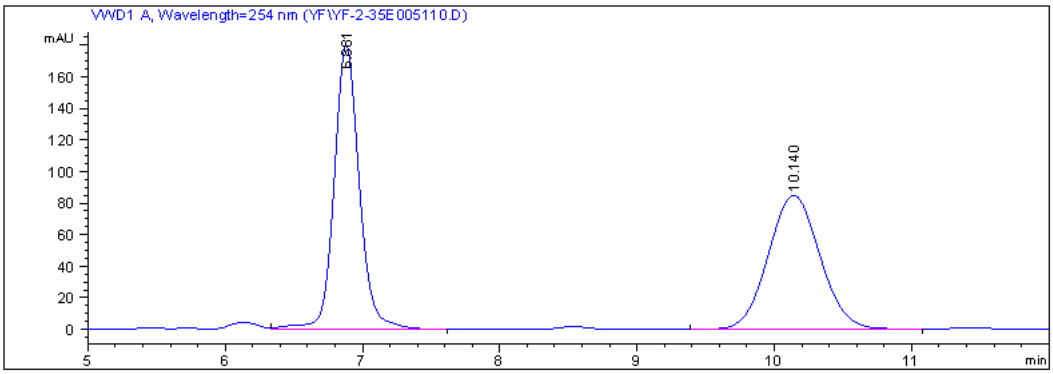


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.909	BV	0.4599	7445.46924	249.66118	49.8226
2	18.882	VBA	0.5587	7498.50488	206.95987	50.1774

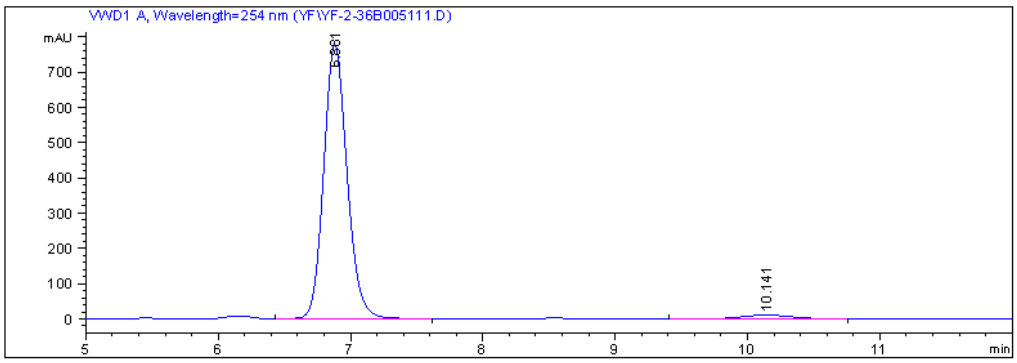


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.030	BB	0.4496	6736.91260	230.08426	97.5035
2	19.031	BB	0.5620	172.49542	4.86123	2.4965

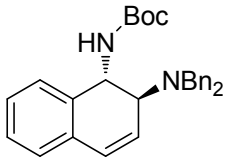


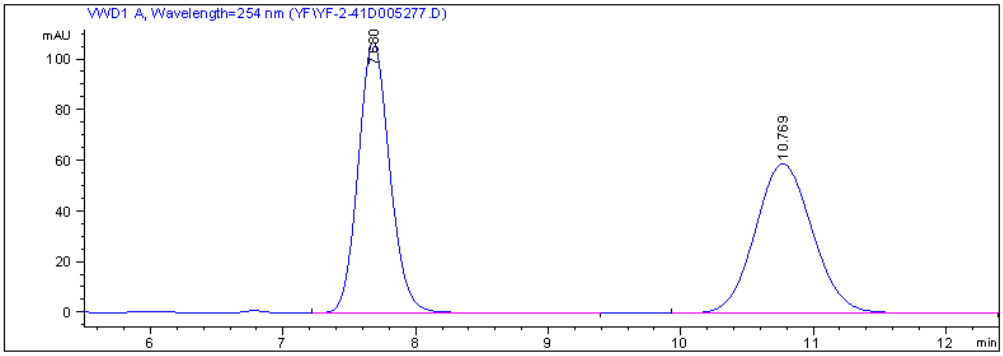


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.881	VB	0.1973	2300.47705	179.81374	50.9302
2	10.140	BB	0.4088	2216.43994	84.84193	49.0698

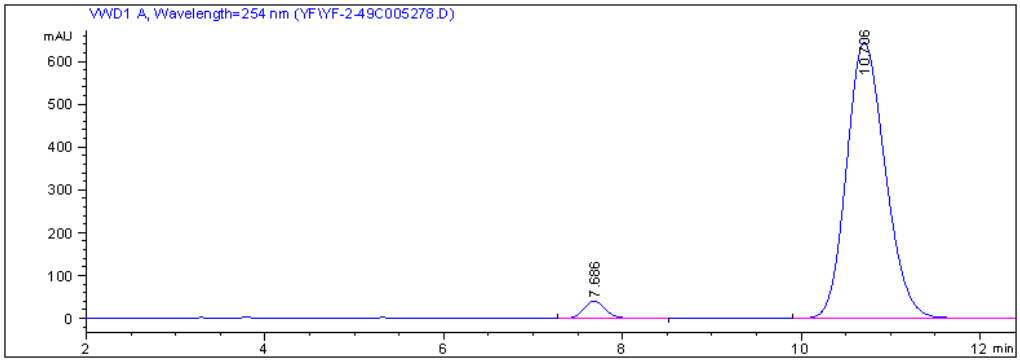


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.881	VB	0.1898	9587.42383	777.81891	97.1087
2	10.141	BB	0.3999	285.45468	11.10435	2.8913

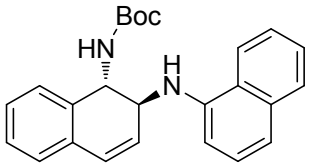


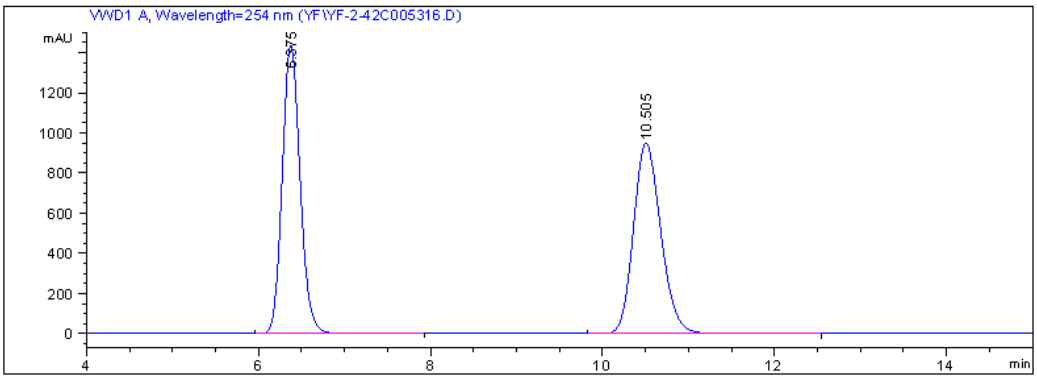


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.680	BB	0.2553	1764.58057	107.06245	49.9669
2	10.769	BB	0.4662	1766.91980	59.04038	50.0331

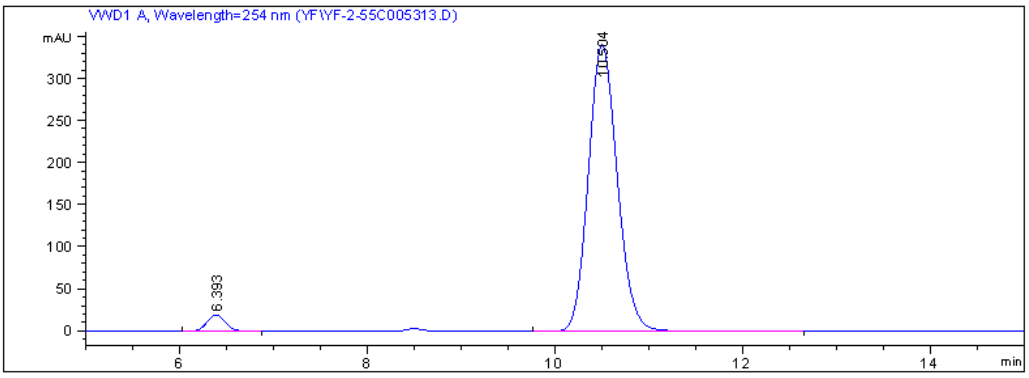


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.686	BB	0.2593	666.73627	40.02446	3.3348
2	10.706	BBA	0.4663	1.93263e4	643.59265	96.6652

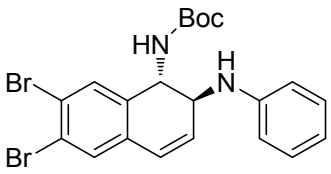


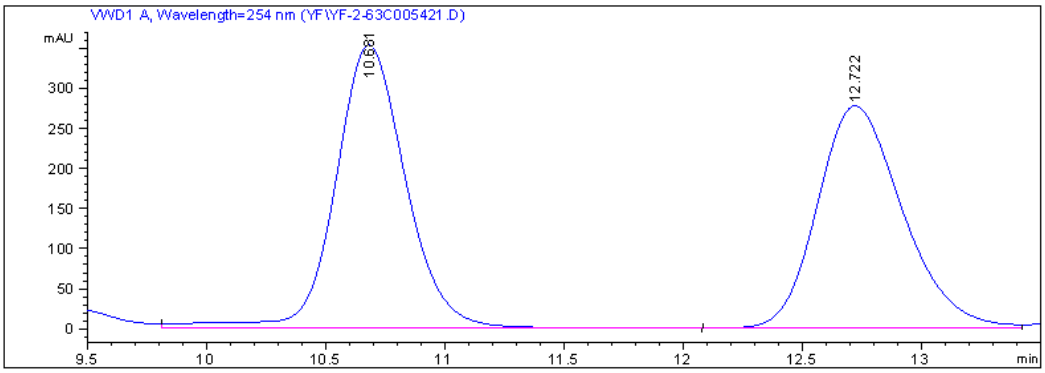


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.375	BB	0.2237	2.07629e4	1436.11926	49.8100
2	10.505	BB	0.3428	2.09213e4	946.82690	50.1900

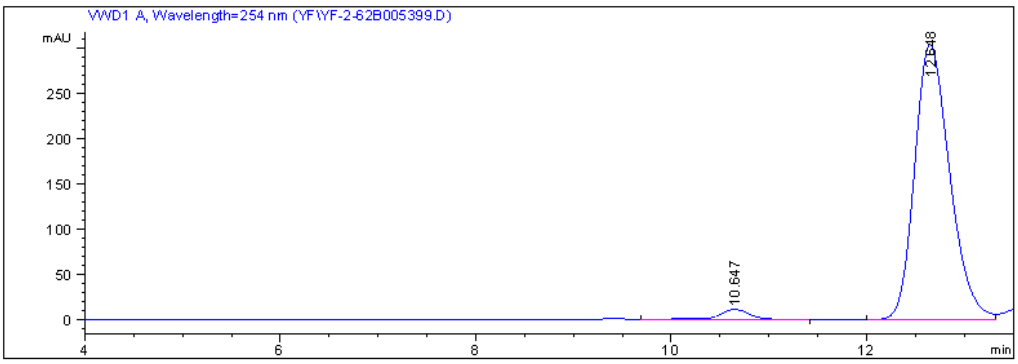


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.393	BB	0.2177	267.24817	19.28623	3.5220
2	10.504	BB	0.3330	7320.75684	340.32135	96.4780

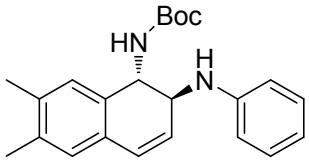


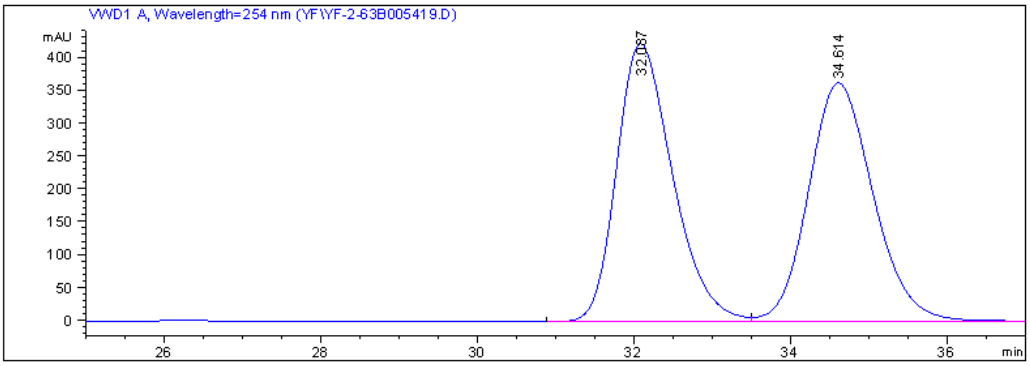


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.681	VB	0.3132	7240.88379	353.17575	51.3230
2	12.722	BV	0.3811	6867.57715	277.16641	48.6770

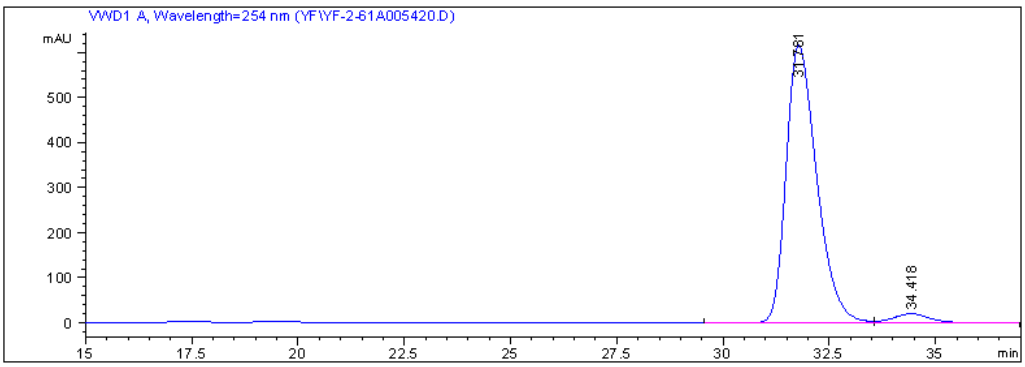


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.647	BB	0.3201	234.78267	11.17488	3.0072
2	12.648	BV	0.3837	7572.55127	303.94971	96.9928

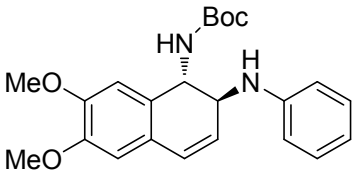


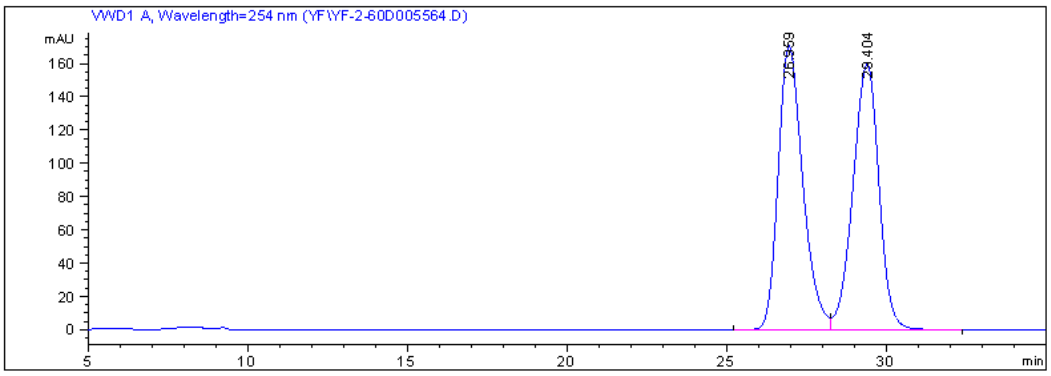


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.087	BV	0.7610	2.09800e4	422.72424	50.3079
2	34.614	VBA	0.8825	2.07232e4	362.74377	49.6921

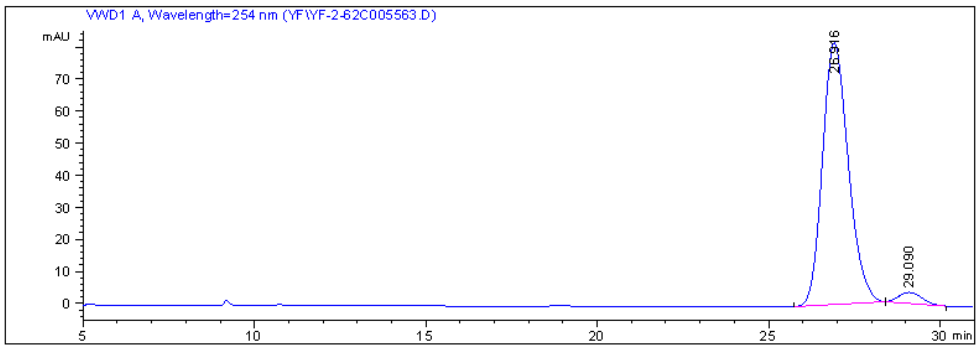


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.781	BV	0.7693	3.08527e4	616.03589	96.3048
2	34.418	VB	0.9000	1183.80273	20.07495	3.6952

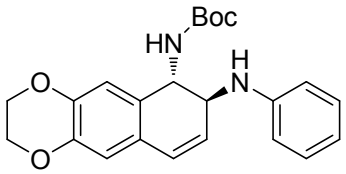


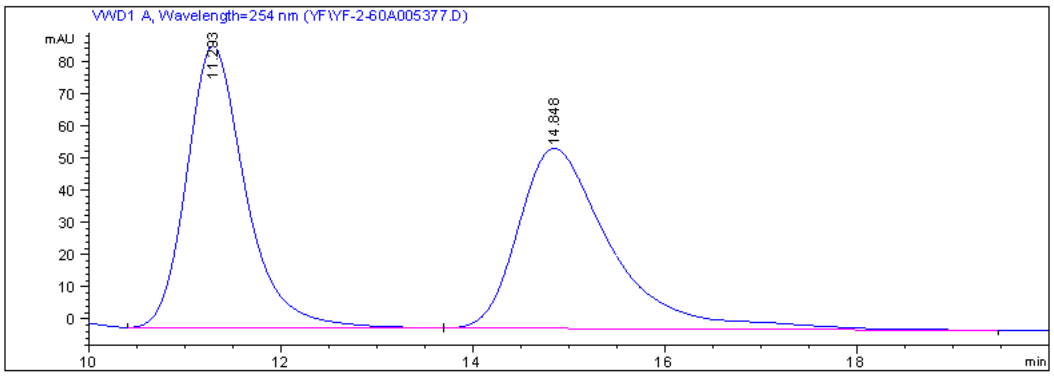


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.959	BV	0.8206	9176.57520	170.86055	50.3042
2	29.404	VB	0.8804	9065.57813	159.67296	49.6958

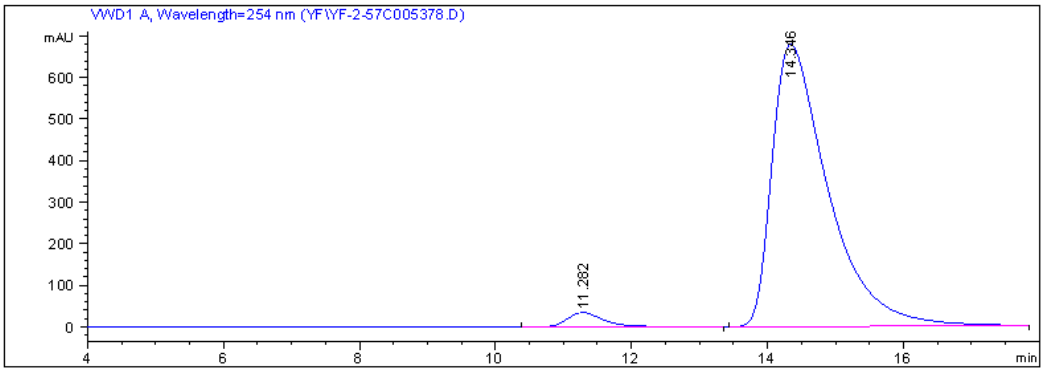


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.916	BB	0.8127	4279.49756	81.61860	96.3328
2	29.090	BB	0.7043	162.91208	3.44143	3.6672

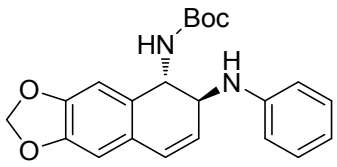


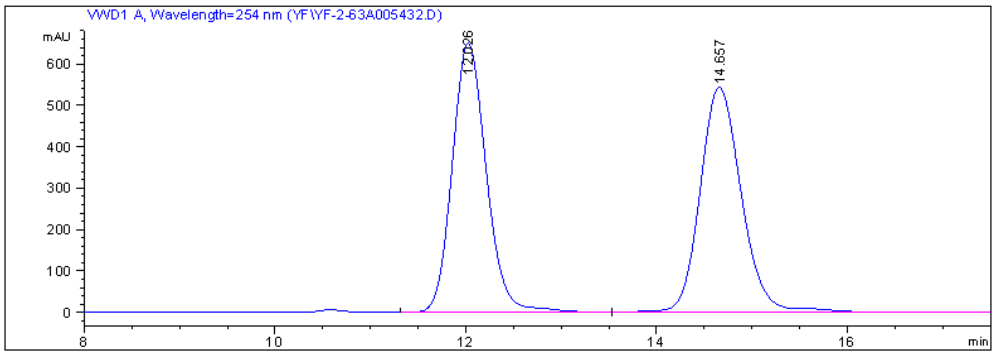


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.293	BB	0.6401	3714.93018	87.53896	49.8053
2	14.848	BB	0.9935	3743.97510	55.89447	50.1947

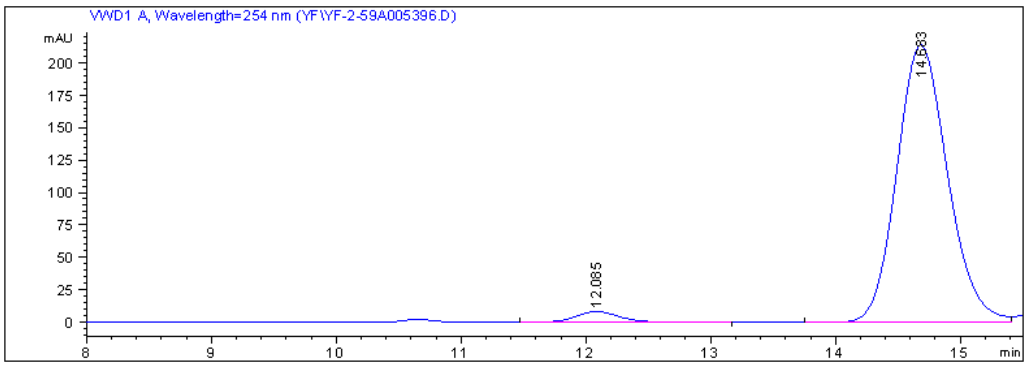


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.282	BB	0.5656	1295.53955	34.69836	3.2179
2	14.346	BBA	0.8576	3.89655e4	678.94775	96.7821

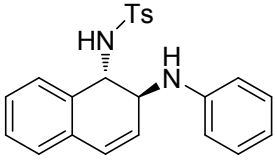


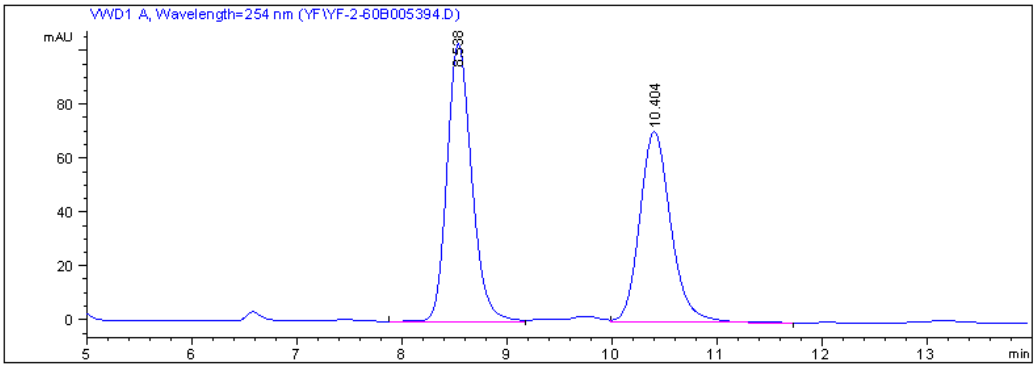


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.026	BB	0.3827	1.60808e4	649.78937	49.7183
2	14.657	BBA	0.4632	1.62630e4	543.33582	50.2817

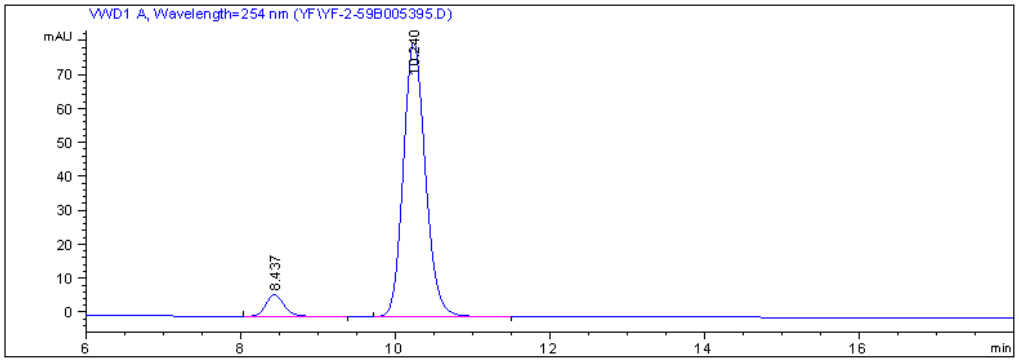


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.085	BB	0.3707	194.87715	8.15831	3.1259
2	14.683	BV	0.4362	6039.41992	214.00836	96.8741

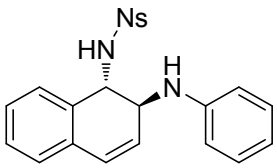


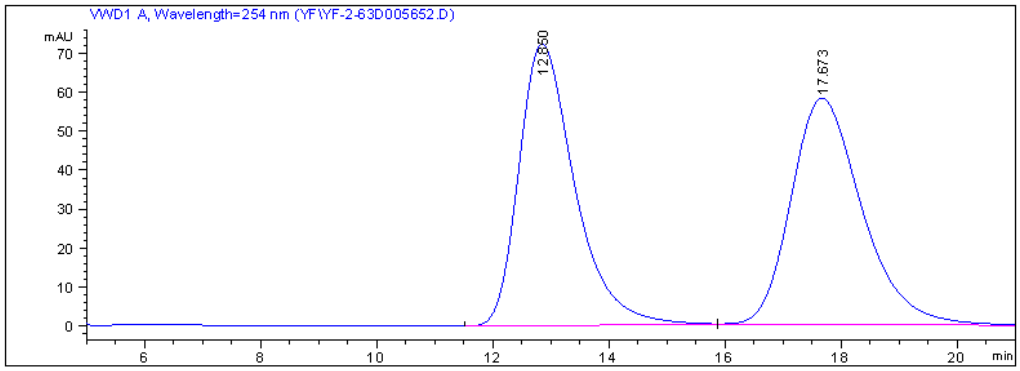


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.538	BV	0.2513	1693.56653	103.29844	53.7654
2	10.404	VB	0.3160	1456.35425	70.80702	46.2346

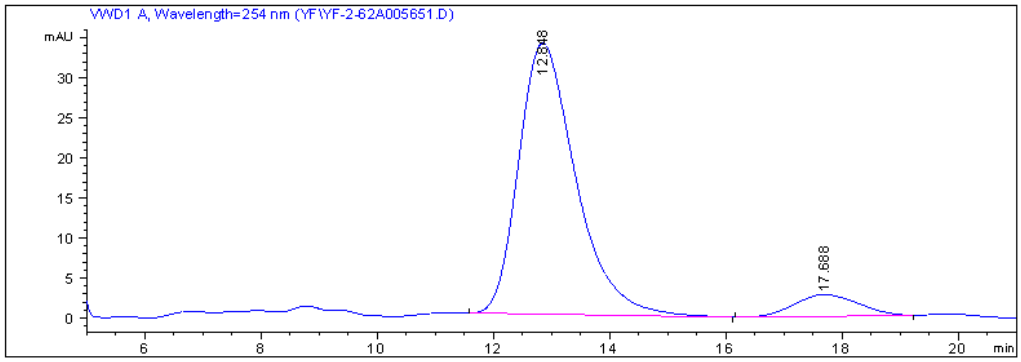


#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.437	BB	0.2506	102.68209	6.31761	6.0303
2	10.240	BB	0.3067	1600.09607	80.58021	93.9697

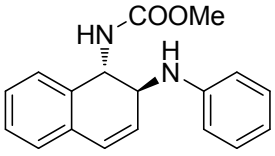


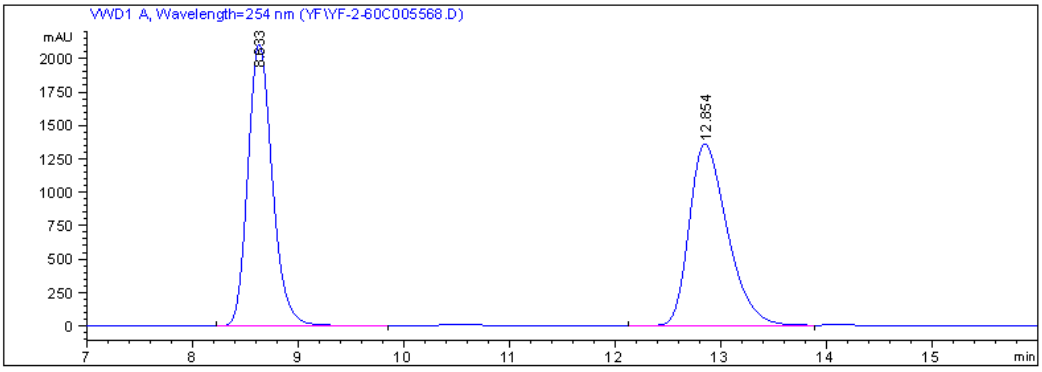


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.850	BB	1.0121	4814.90283	72.28268	49.4112
2	17.673	BBA	1.2917	4929.65332	57.99320	50.5888

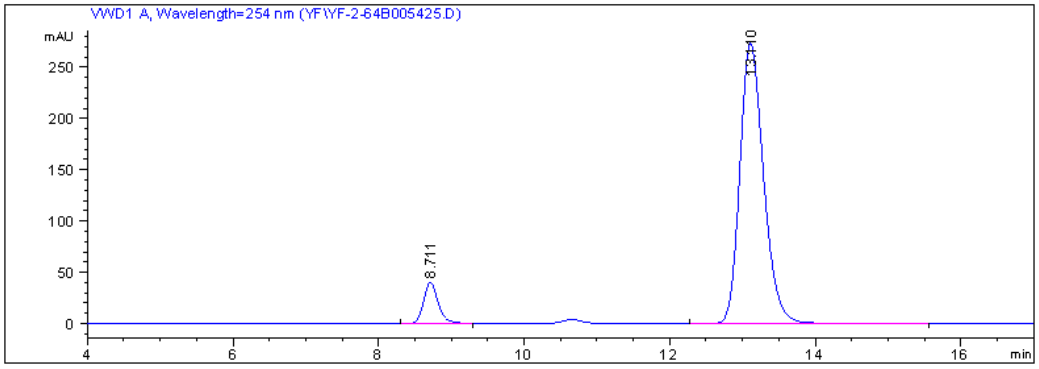


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.848	BB	1.0272	2311.25781	33.82497	91.8013
2	17.688	BB	0.8936	206.41635	2.70096	8.1987



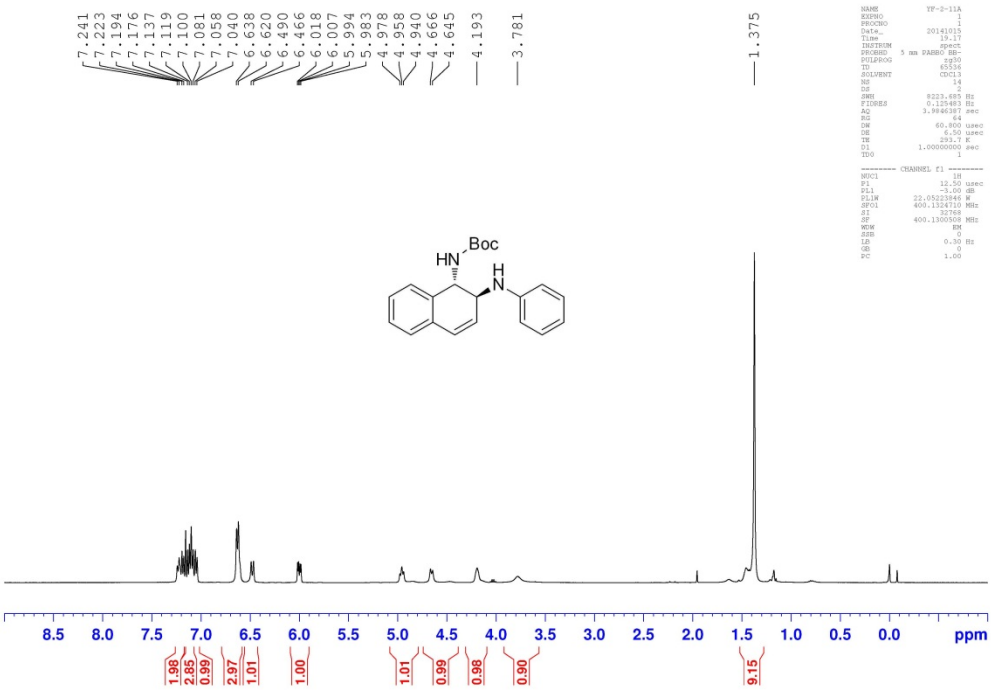


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.633	BB	0.2474	3.38764e4	2108.69263	49.7333
2	12.854	BV	0.3901	3.42398e4	1358.12964	50.2667



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.711	BV	0.2155	560.50543	39.98707	8.3019
2	13.110	BB	0.3481	6191.01465	273.51895	91.6981

E: Copies of NMR spectra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6.490
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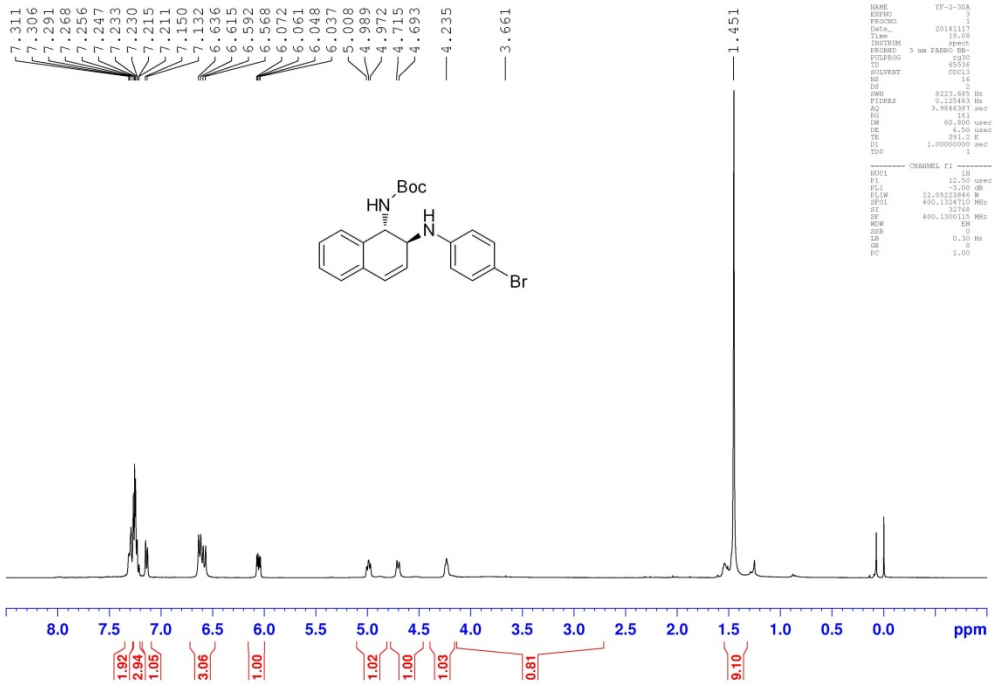
6.018
6.007
5.994
5.983
4.978
4.958
4.940
4.666
4.645
4.193
3.781
1.375
Boc
HN
H
N
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.98
2.85
0.99
2.97
1.01
1.00
1.01
0.99
0.98
0.90
9.15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7.211
7.150
7.132
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6.615
6.592
6.568
6.072
6.061
6.048
6.037
5.008
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4.972
4.715
4.693
4.235
3.661
1.451
Boc
HN
H
N
Br
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
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2.94
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1.02
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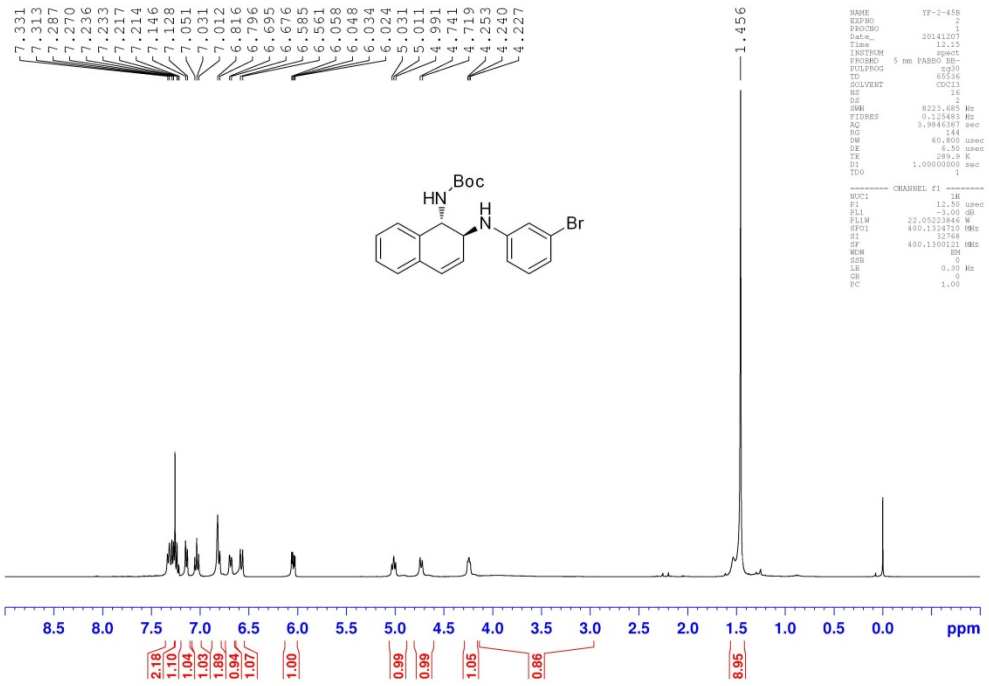
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6.796
6.695
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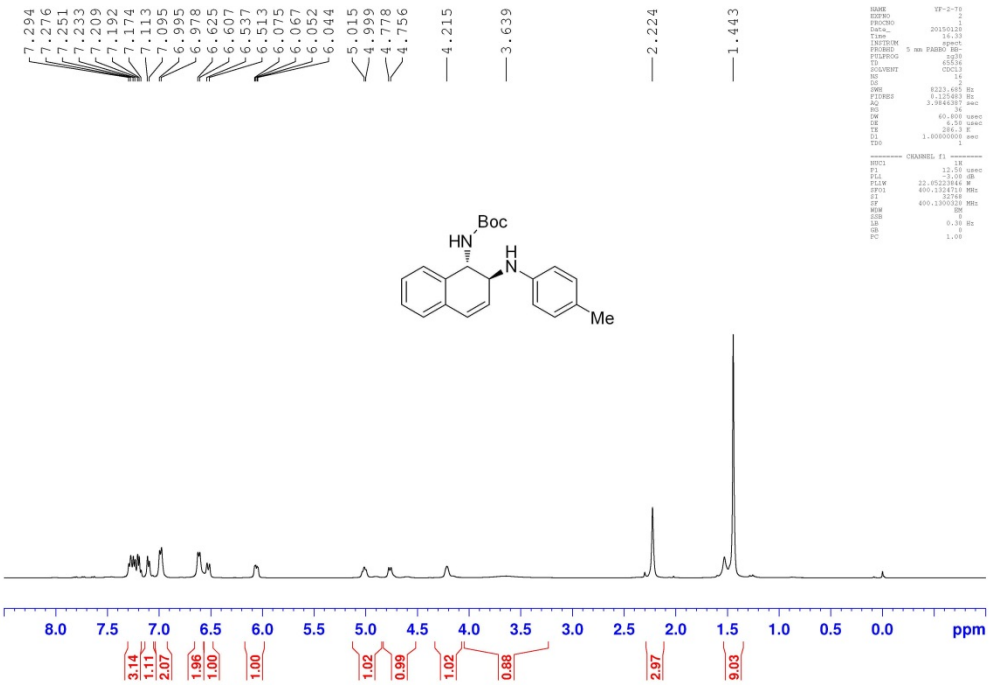
6.561
6.058
6.048
6.034
6.024
5.031
5.011
4.991
4.741
4.719
4.253
4.240
4.227
1.456
Boc
HN
H
N
Br
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.18
1.10
1.04
1.03
1.89
0.94
1.07
1.00
0.99
0.99
1.05
0.86
8.95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7.276
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7.233
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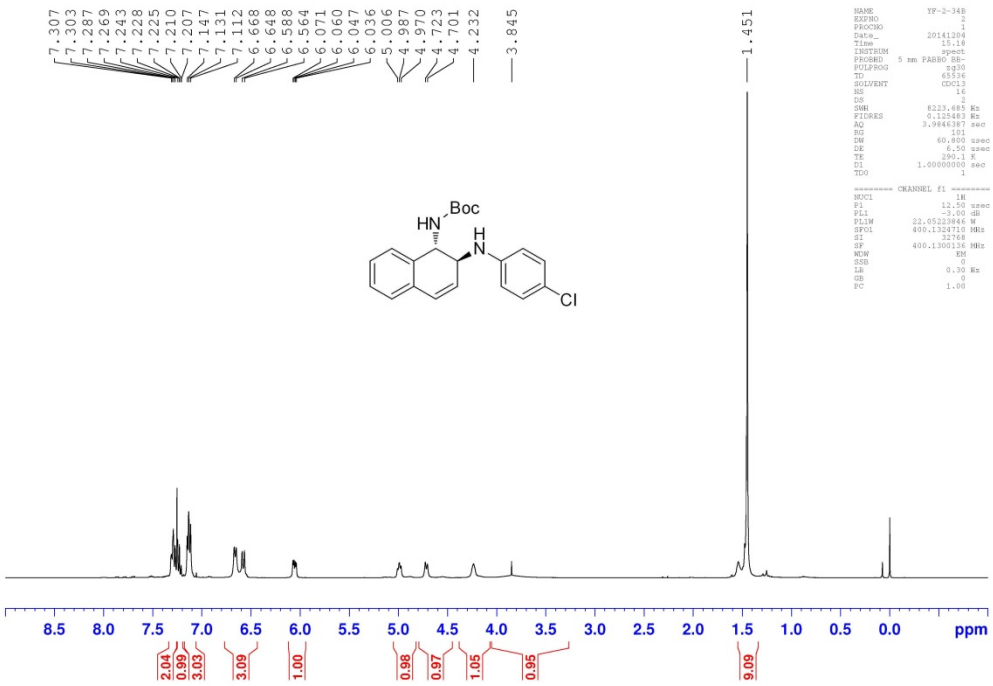
7.113
7.095
6.995
6.978
6.625
6.607
6.537
6.513
6.075
6.067
6.052
6.044
5.015
4.999
4.778
4.756
4.215
3.639
2.224
1.443
Boc
HN
H
N
Me
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.14
1.11
2.07
1.96
1.00
1.00
1.02
0.99
1.02
0.88
2.97
9.03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7.287
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7.225
7.210
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7.147
7.131
7.112
6.668
6.648
6.588
6.564
6.071
6.060
6.047
6.036
5.006
4.987
4.970
4.723
4.701
4.232
3.845
1.451
Boc
HN
H
N
Cl
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
2.04
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3.03
3.09
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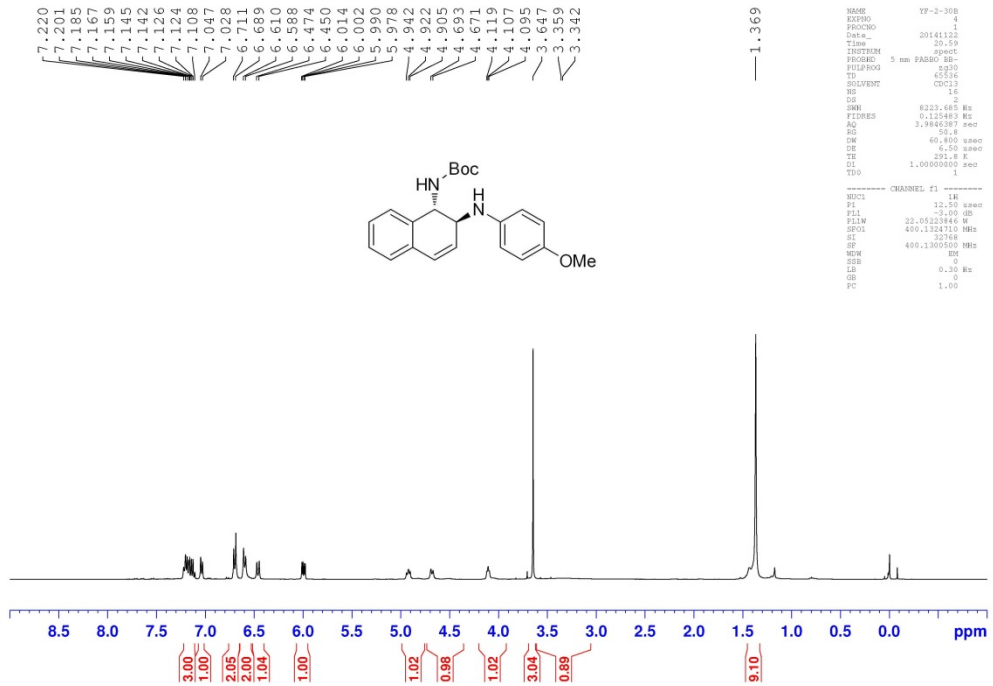
0.98
0.97
1.05
0.95
9.09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7.185
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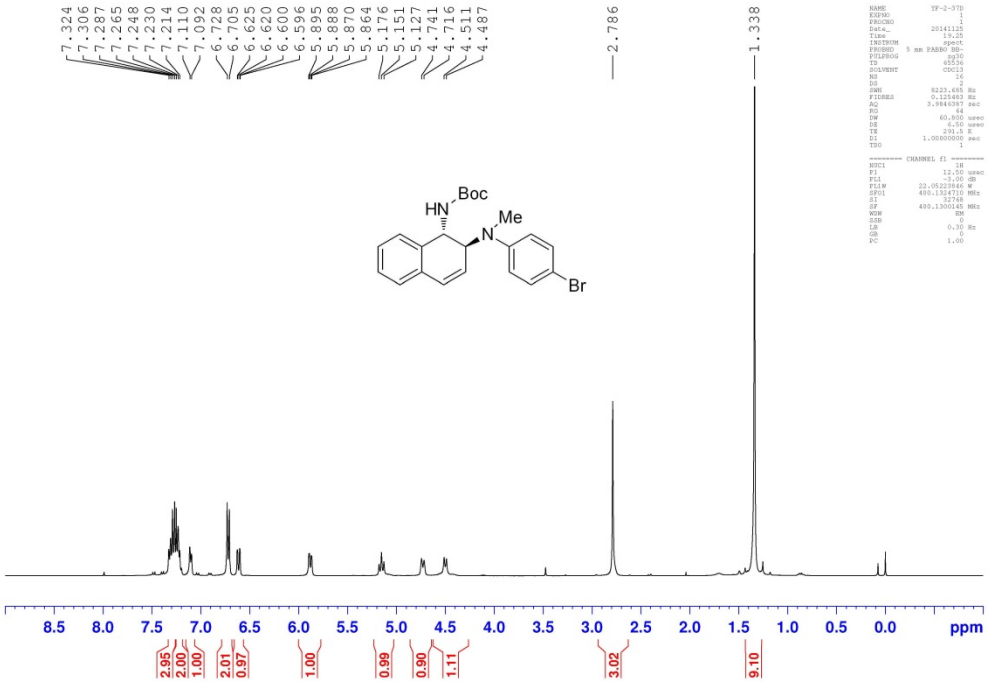
7.142
7.126
7.124
7.108
7.047
7.028
6.711
6.689
6.610
6.598
6.474
6.450
6.014
6.002
5.990
5.978
4.942
4.922
4.905
4.693
4.671
4.119
4.107
4.095
3.647
3.359
3.342
1.369
Boc
HN
H
N
OMe
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.00
1.00
2.05
2.00
1.04
1.00
1.02
0.98
1.02
3.04
0.89
9.10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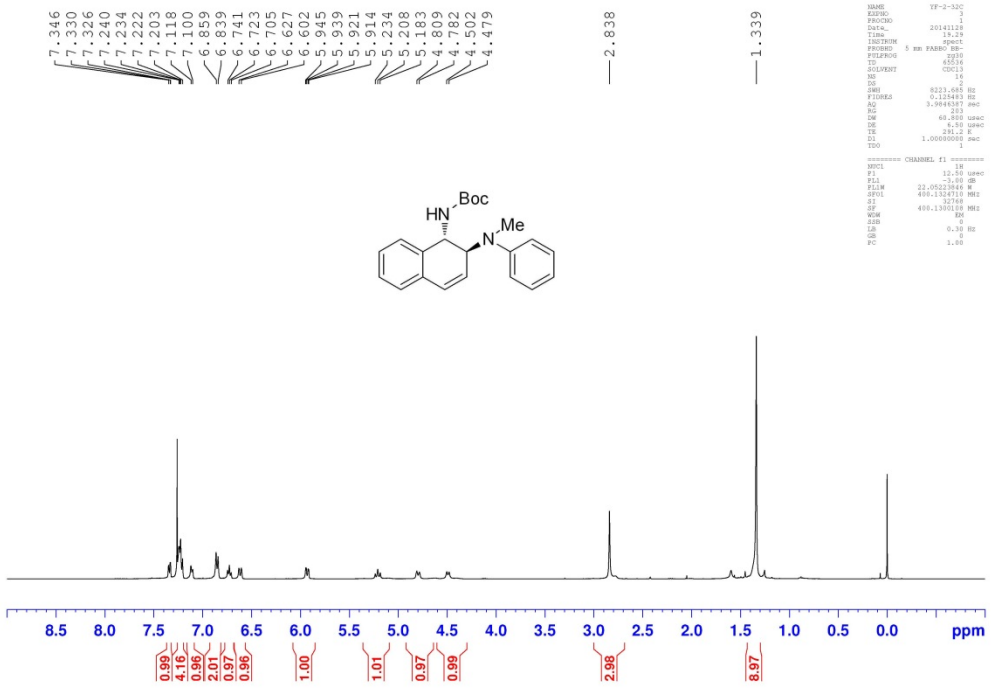
7.287
7.265
7.248
7.230
7.214
7.110
7.092
6.728
6.705
6.625
6.620
6.600
6.596
5.895
5.888
5.870
5.864
5.176
5.151
5.127
4.741
4.716
4.511
4.487
2.786
1.338
Boc
HN
Me
N
Br
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.95 2.00 1.00 2.01 0.97 1.00 0.99 0.90 1.11 3.02 9.10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7.326
7.240
7.234
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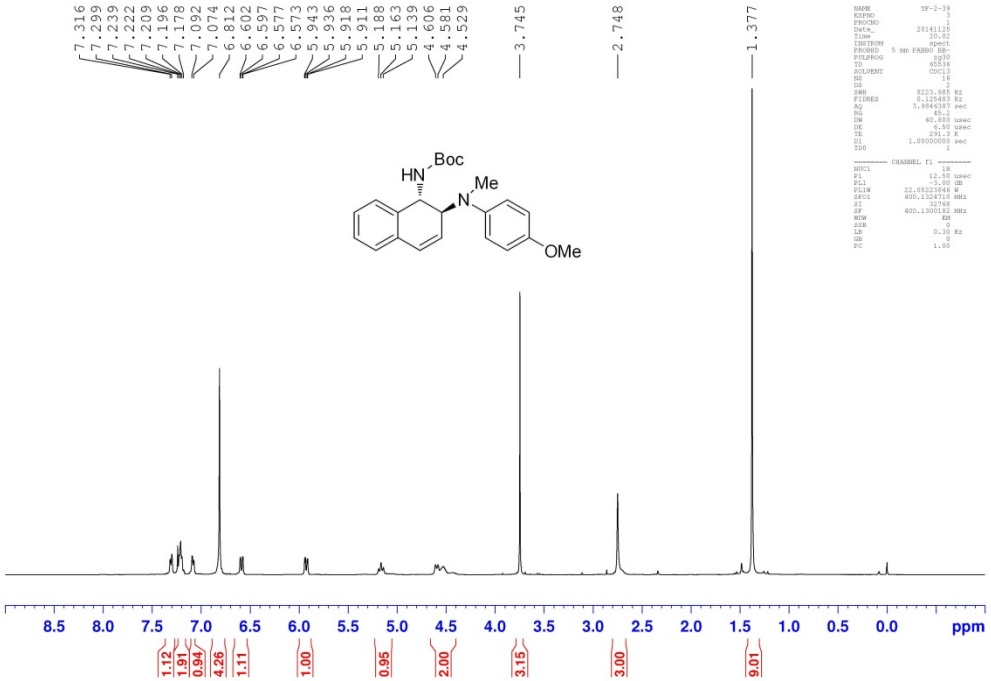
7.118
7.100
6.859
6.839
6.741
6.723
6.705
6.627
6.602
5.945
5.939
5.921
5.914
5.234
5.208
5.183
4.809
4.782
4.502
4.479
2.838
1.339
Boc
HN
Me
N
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.99 4.16 0.96 2.01 0.97 0.96 1.00 1.01 0.97 0.99 2.98 8.97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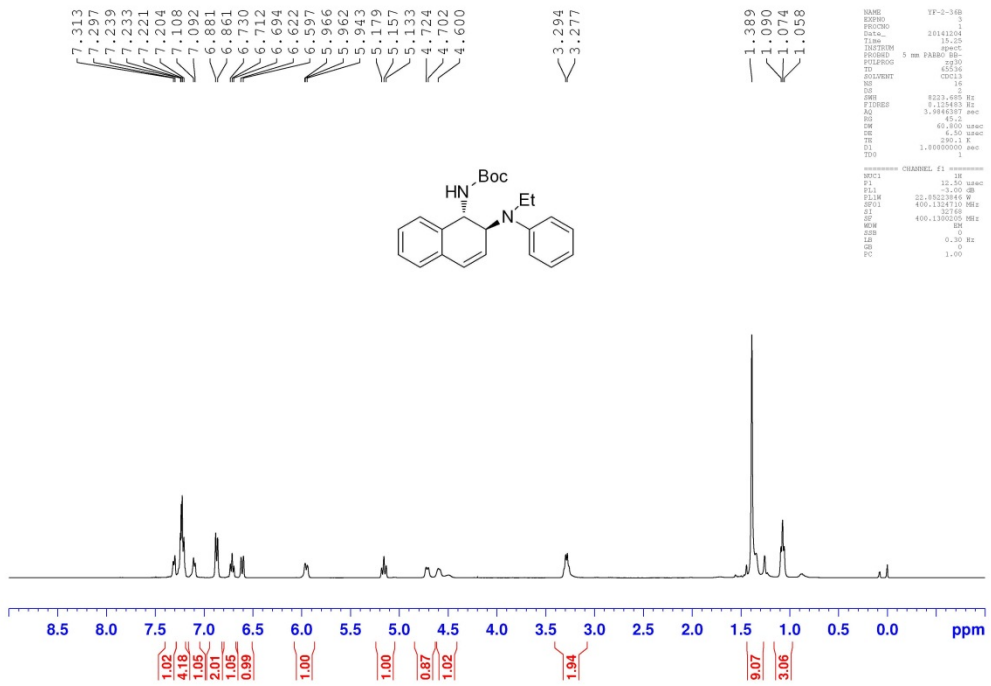
7.299
7.239
7.222
7.209
7.196
7.178
7.092
7.074
6.812
6.602
6.597
6.577
6.573
5.943
5.936
5.918
5.911
5.188
5.163
5.139
4.606
4.581
4.529
3.745
2.748
1.377
Boc
HN
Me
N
OMe
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.12 1.91 0.94 4.26 1.11 1.00 0.95 2.00 3.15 3.00 9.01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7.239
7.233
7.221
7.204
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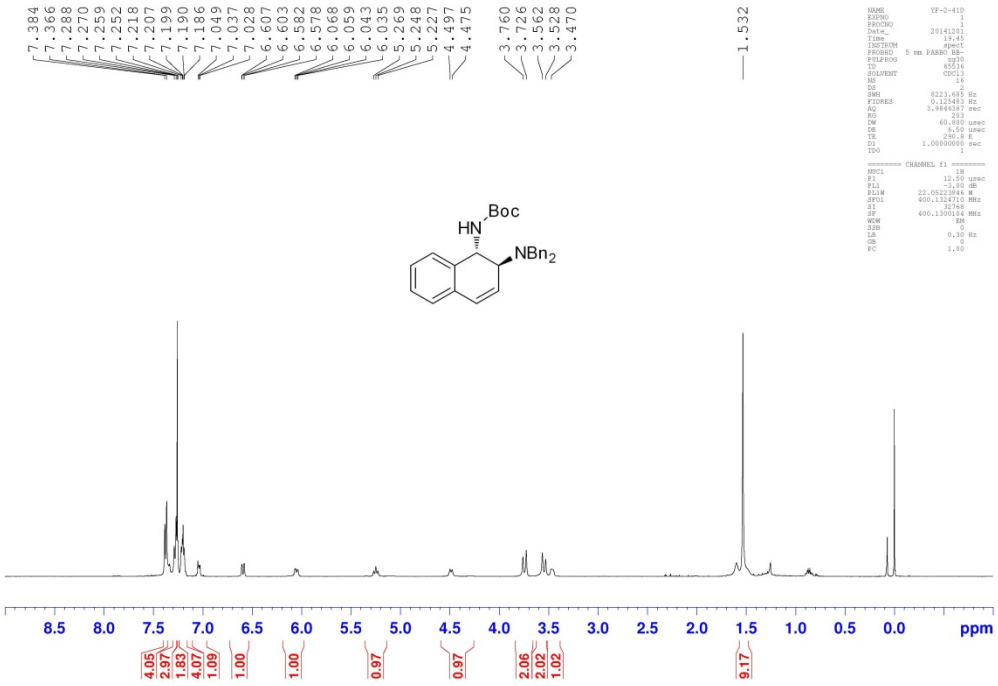
7.092
6.881
6.861
6.730
6.712
6.694
6.622
6.597
5.966
5.962
5.943
5.179
5.157
5.133
4.724
4.702
4.600
3.294
3.277
1.389
1.090
1.074
1.058
Boc
HN
Et
N
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.02 4.18 1.05 2.01 1.05 0.99 1.00 1.00 0.87 1.02 1.94 9.07 3.06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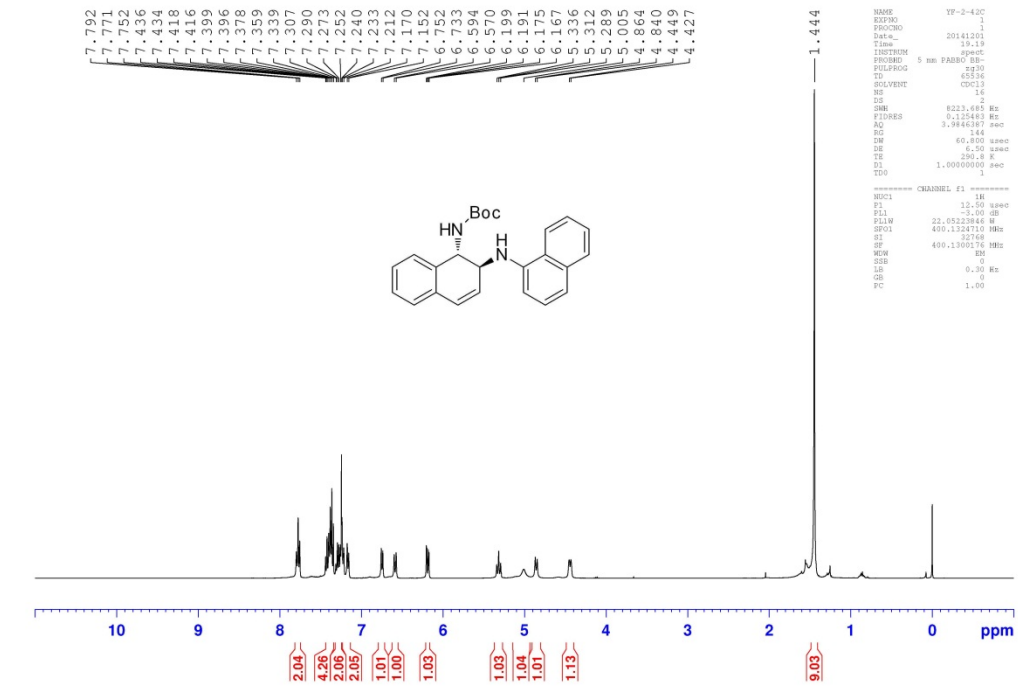
7.366
7.288
7.270
7.259
7.252
7.218
7.207
7.199
7.190
7.186
7.049
7.037
7.028
6.607
6.603
6.582
6.578
6.068
6.059
6.043
6.035
5.269
5.248
5.227
4.497
4.475
3.760
3.726
3.562
3.528
3.470
1.532
Boc
HN
NBn2
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.05 2.97 1.83 4.07 1.09 1.00 1.00 0.97 0.97 2.06 2.02 1.02 9.17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7.771
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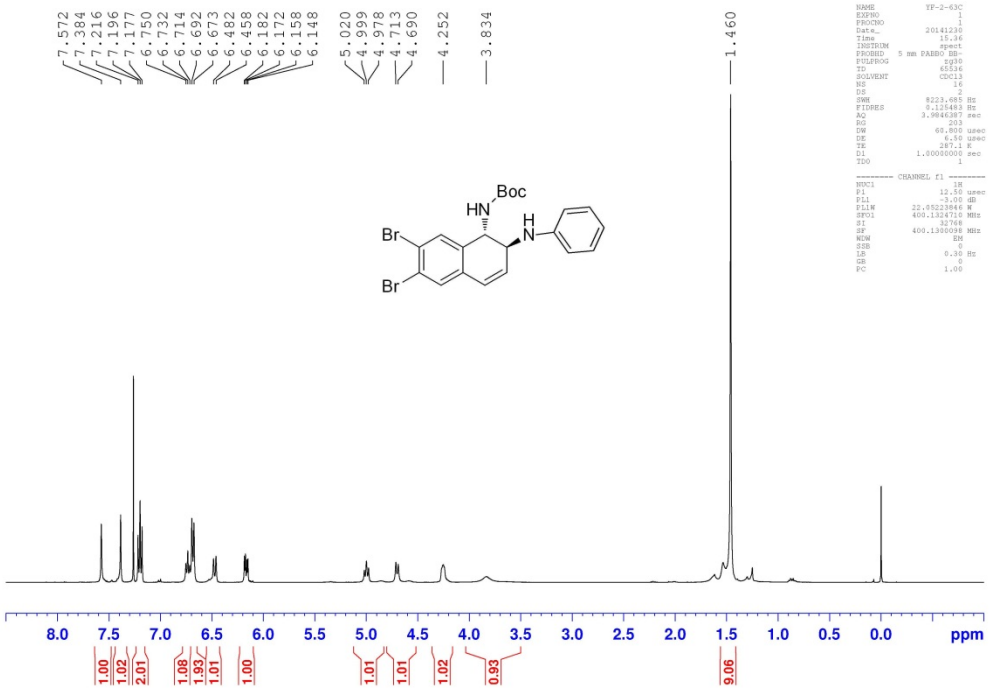
7.436
7.434
7.418
7.416
7.399
7.396
7.378
7.359
7.339
7.307
7.290
7.273
7.252
7.240
7.233
7.212
7.170
7.152
6.752
6.733
6.594
6.570
6.199
6.191
6.175
6.167
5.336
5.312
5.289
5.005
4.864
4.840
4.449
4.427
1.444
Boc
HN
H
N
10 9 8 7 6 5 4 3 2 1 0 ppm
2.04 4.26 2.06 2.05 1.01 1.00 1.03 1.03 1.04 1.01 1.13 9.03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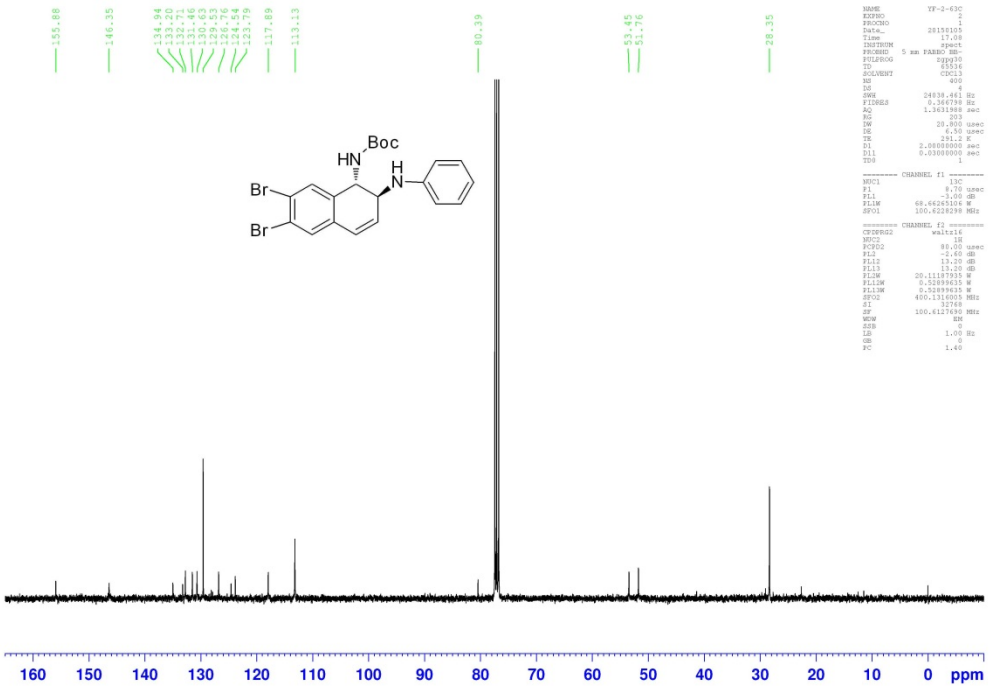
7.196
7.177
6.750
6.732
6.714
6.692
6.673
6.482
6.458
6.182
6.172
6.158
6.148
5.020
4.999
4.978
4.713
4.690
4.252
3.834
1.460
Boc
HN
H
N
Br
Br
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.02
2.01
1.08
1.93
1.01
1.00
1.01
1.01
1.02
0.93
9.06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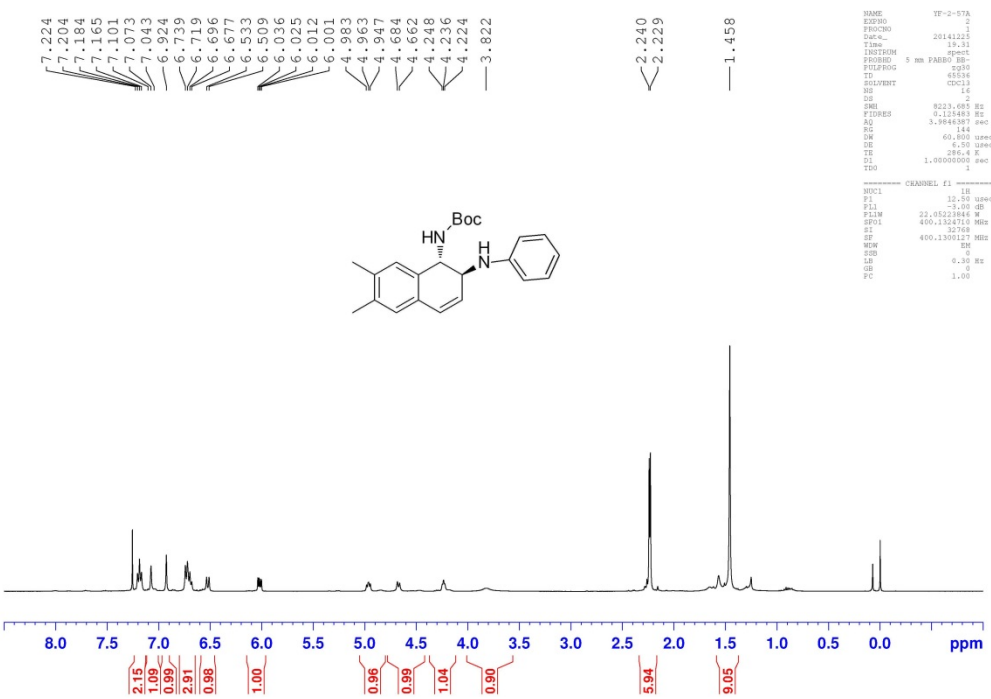
146.35
134.94
133.20
132.71
130.46
130.45
129.53
126.76
124.54
123.79
117.89
113.13
80.39
53.45
51.76
28.35
Boc
HN
H
N
Br
Br
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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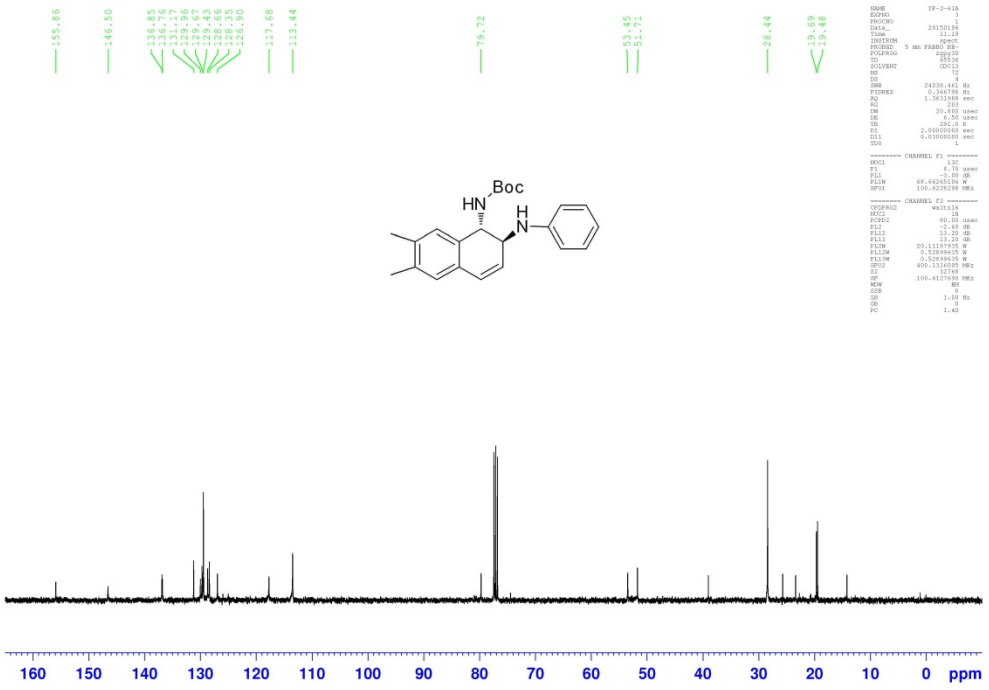
7.204
7.184
7.165
7.101
7.073
7.043
6.924
6.739
6.719
6.696
6.677
6.533
6.509
6.036
6.025
6.012
6.001
4.983
4.963
4.947
4.684
4.662
4.248
4.236
4.224
3.822
2.240
2.229
1.458
Boc
HN
H
N
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.15
1.09
0.99
2.91
0.98
1.00
0.96
0.99
1.04
0.90
5.94
9.05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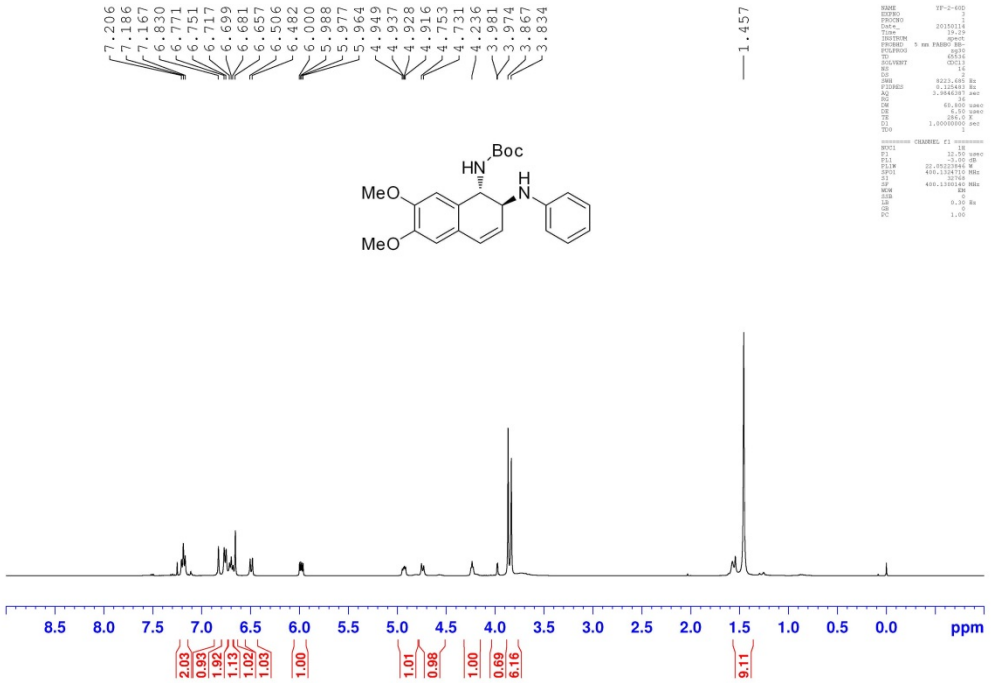
146.50
136.85
136.46
131.17
129.96
129.67
129.43
128.46
128.35
126.90
117.68
113.44
79.72
53.45
52.72
28.44
19.69
19.48
Boc
HN
H
N
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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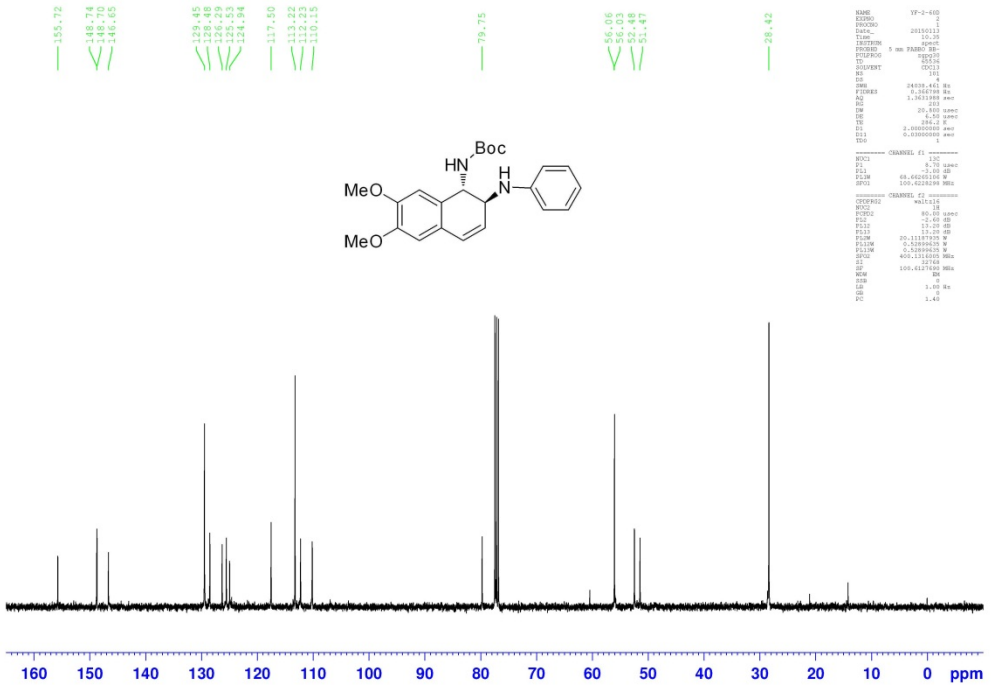
6.699
6.681
6.657
6.506
6.482
6.000
5.988
5.977
5.964
4.949
4.937
4.928
4.916
4.753
4.731
4.236
3.981
3.974
3.867
3.834
1.457
Boc
HN
H
N
MeO
MeO
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.03
0.93
1.92
1.13
1.02
1.03
1.00
1.01
0.98
1.00
0.69
6.16
9.11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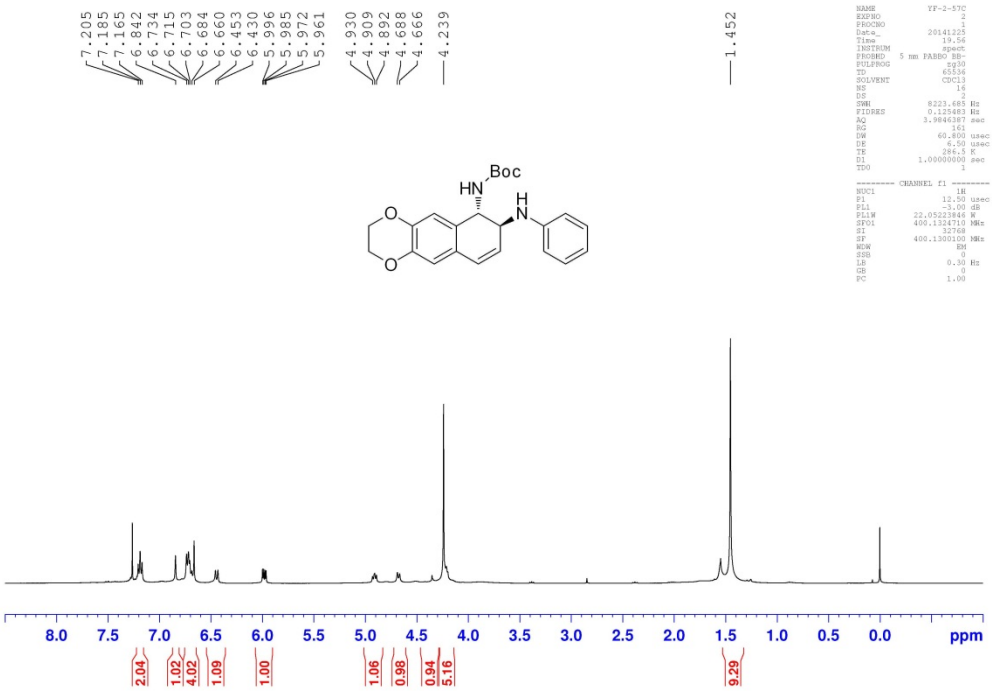
148.74
148.70
146.65
129.45
128.48
128.09
125.53
124.94
117.50
113.22
113.03
110.15
79.75
56.06
56.03
52.48
51.47
28.42
Boc
HN
H
N
MeO
MeO
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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6.715
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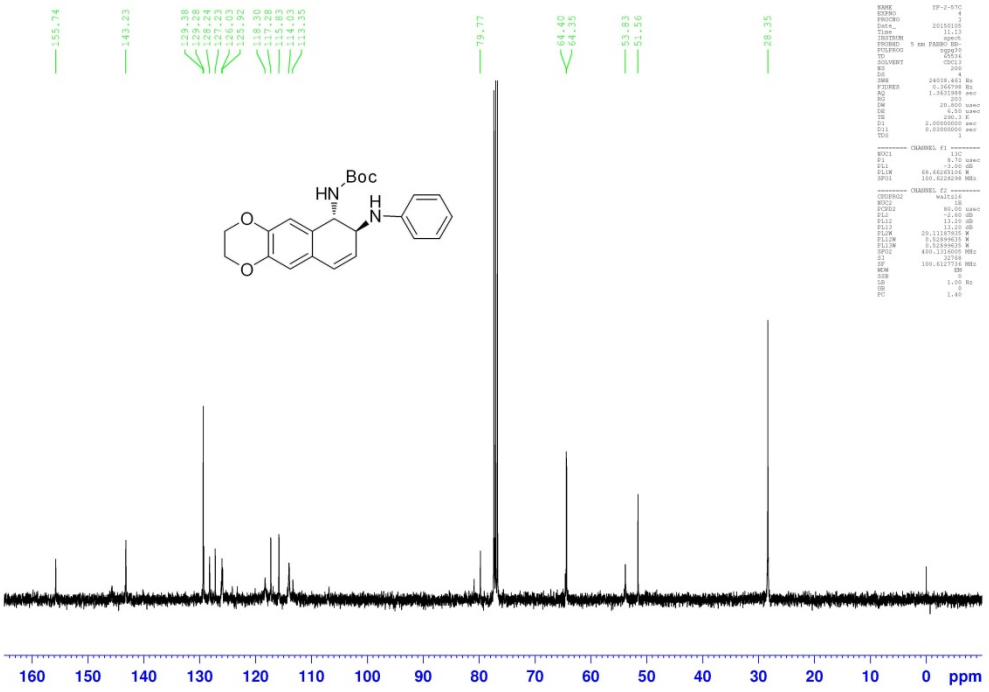
6.684
6.660
6.453
6.430
5.996
5.985
5.972
5.961
4.930
4.909
4.892
4.688
4.666
4.239
1.452
Boc
HN
H
N
O
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.04
1.02
4.02
1.09
1.00
1.06
0.98
0.94
5.16
9.29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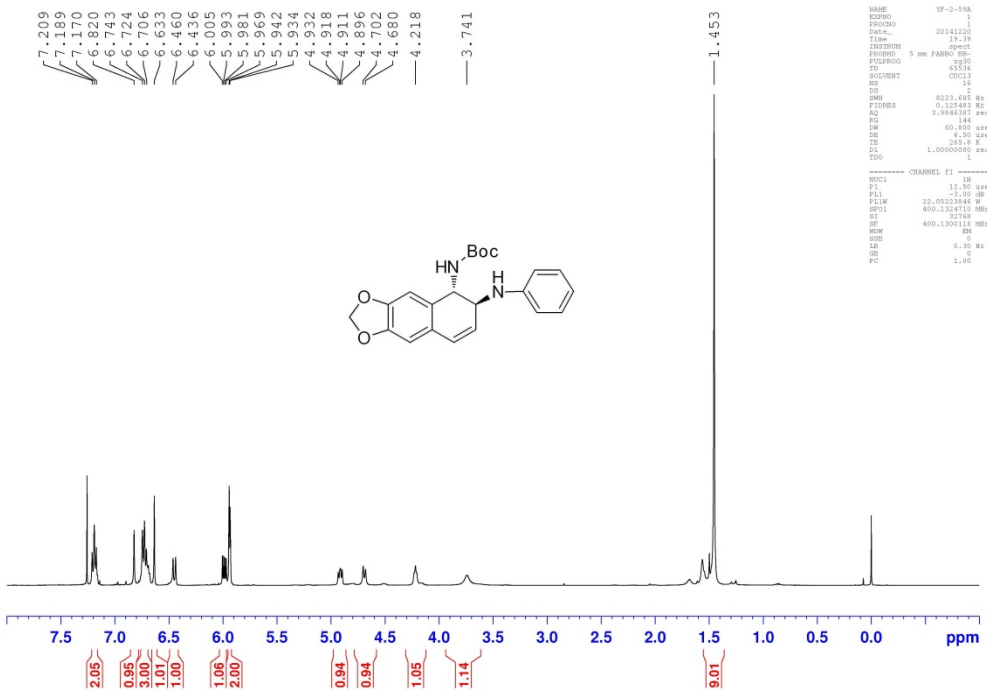
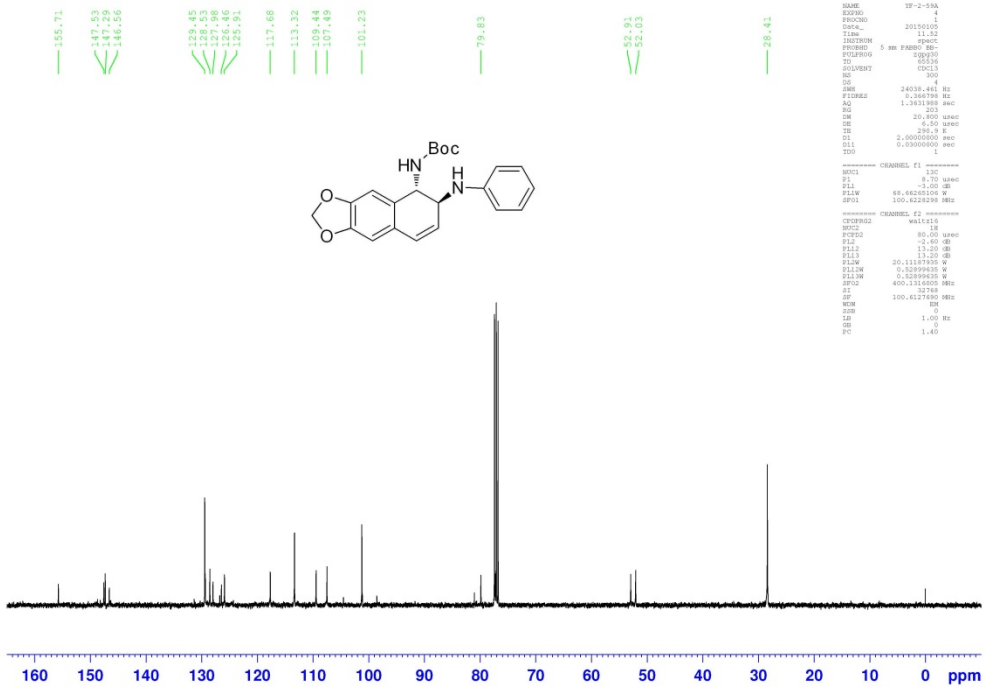
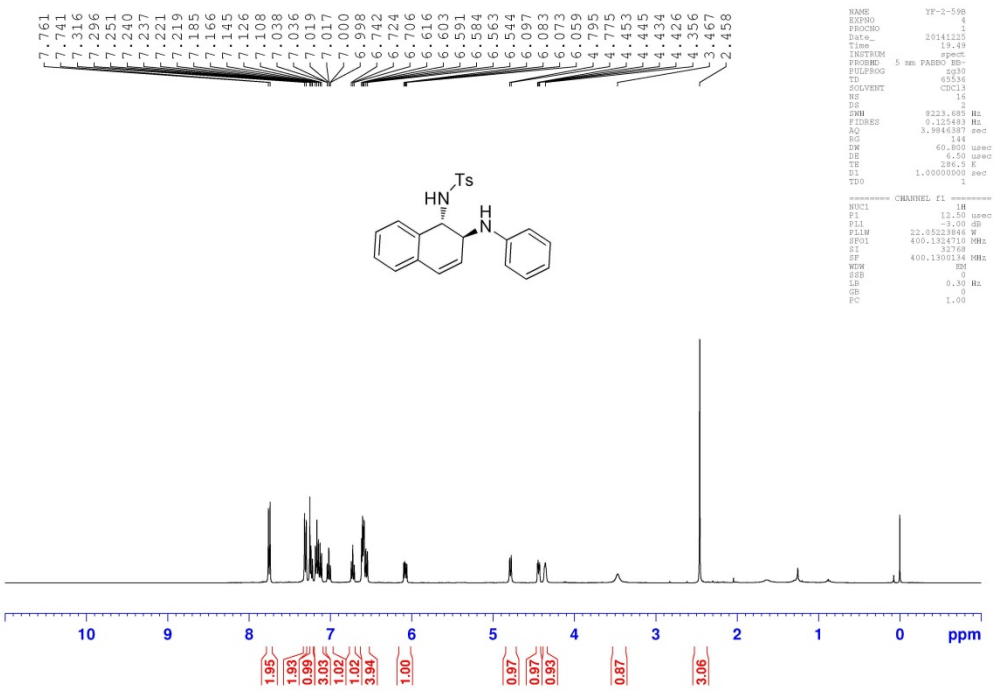
143.23
129.38
129.28
128.24
127.23
126.03
125.92
118.30
117.28
115.83
114.03
113.35
79.77
64.40
64.35
53.83
53.56
28.35
Boc
HN
H
N
O
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

6-(methyl(phenyl)amino)-5,6-dihydronaphtho[2,3-d][1,3]dioxol-5-ol (3ia)



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7.221
7.219
7.185
7.166
7.145
7.126
7.108
7.038
7.036
7.019
7.017
7.000
6.998
6.742
6.724
6.706
6.616
6.603
6.591
6.584
6.563
6.544
6.097
6.083
6.073
6.059
4.795
4.775
4.453
4.445
4.434
4.426
4.356
3.467
2.458
Ts
HN
H
N
10
9
8
7
6
5
4
3
2
1
0
ppm
1.95
1.93
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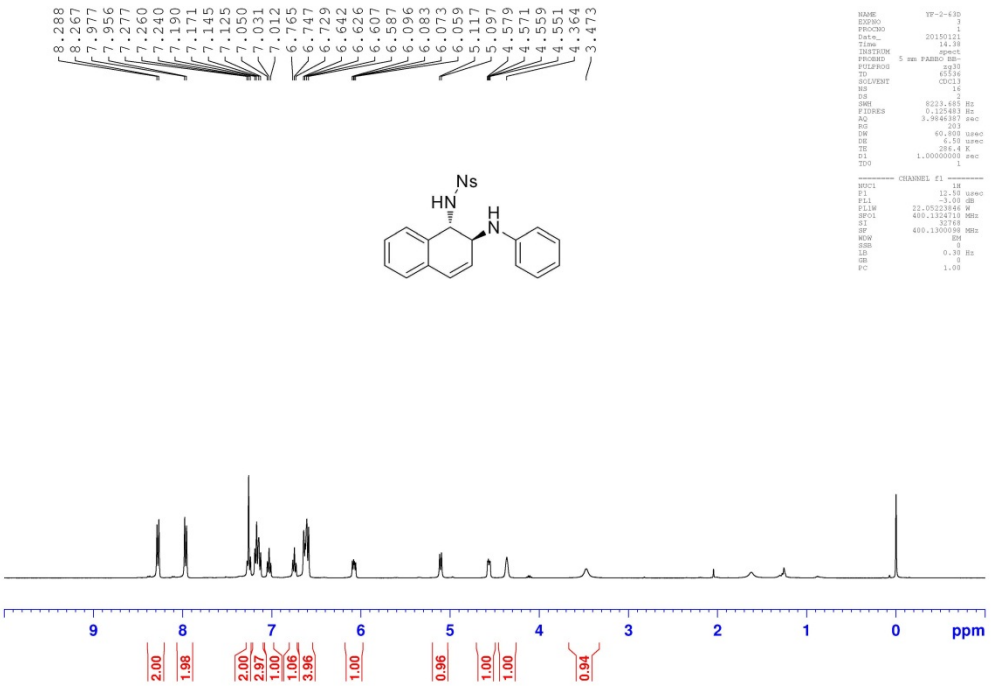
1.02
1.02
3.94
1.00
0.97
0.97
0.93
0.87
3.06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7.260
7.240
7.190
7.171
7.145
7.125
7.050
7.031
7.012
6.765
6.747
6.729
6.642
6.626
6.607
6.587
6.096
6.083
6.073
6.059
5.117
5.097
4.579
4.571
4.559
4.551
4.364
3.473
Ns
HN
H
N
9
8
7
6
5
4
3
2
1
0
ppm
2.00
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2.00
2.97
1.00
1.06
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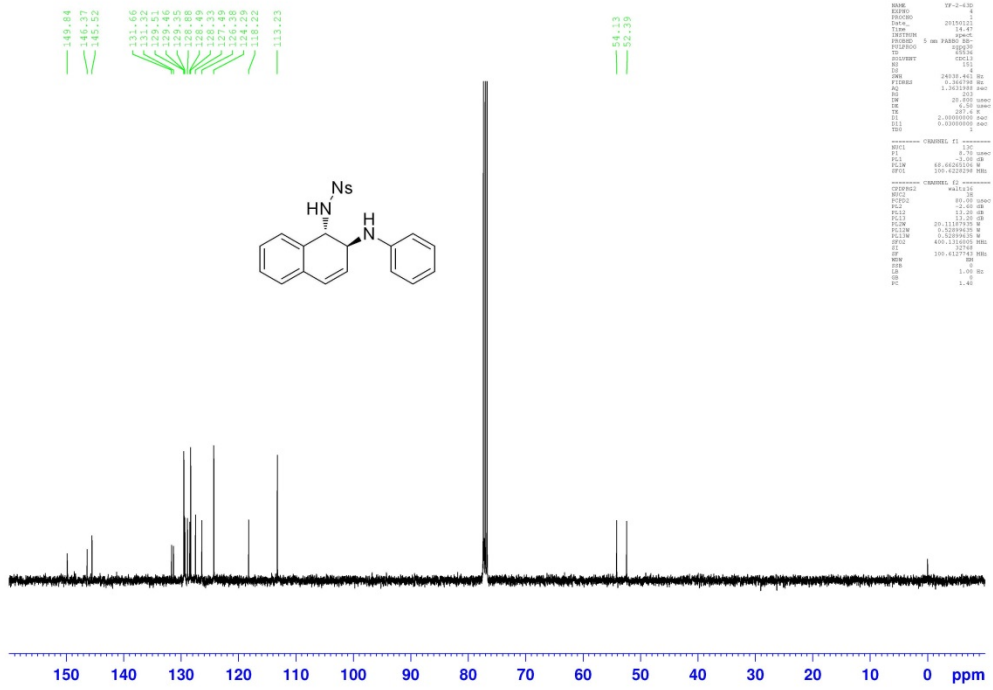
1.00
0.96
1.00
1.00
0.94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146.37
145.52
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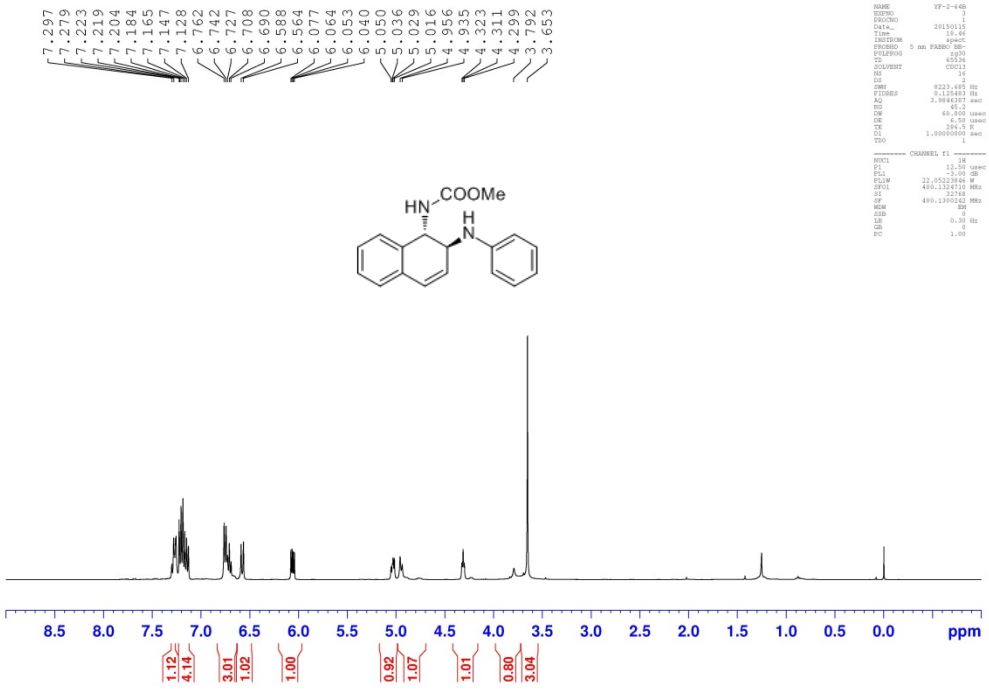
131.32
129.51
129.46
128.95
128.88
128.49
128.33
127.49
127.38
124.29
118.22
113.23
54.13
53.93
52.39
Ns
HN
H
N
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.279
7.223
7.219
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7.184
7.165
7.147
7.128
6.762
6.742
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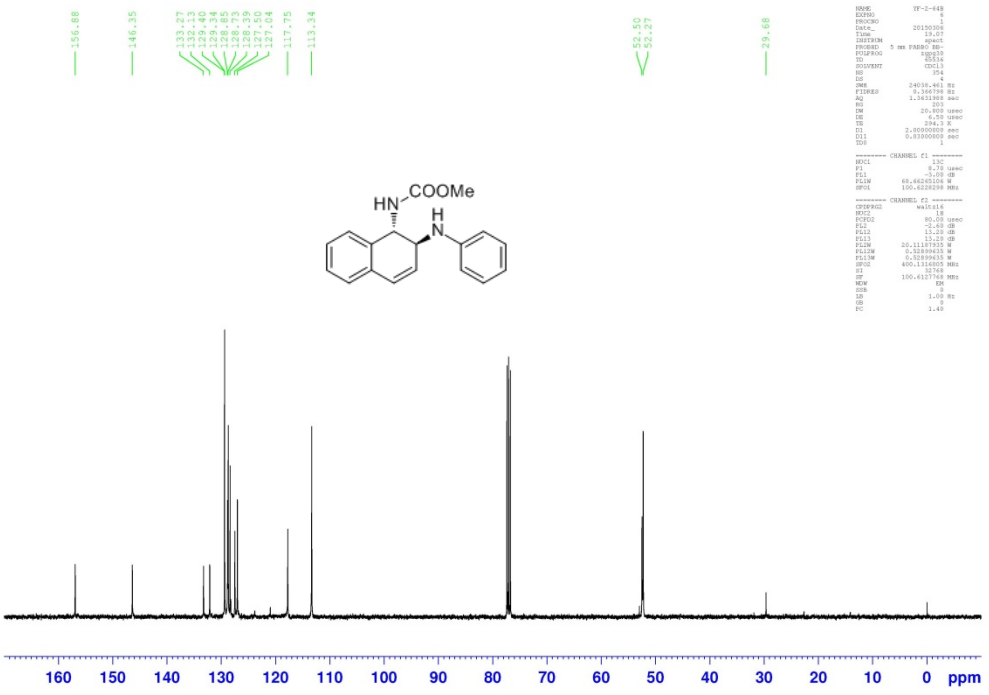
6.708
6.690
6.588
6.564
6.077
6.064
6.053
6.040
5.050
5.036
5.029
5.016
4.956
4.935
4.323
4.311
4.299
3.792
3.653
COOMe
HN
H
N
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.12
4.14
3.01
1.02
1.00
0.92
1.07
1.01
0.80
3.04


156.88
146.35
133.27
132.13
129.40
129.34
128.85
128.73
127.29
127.20
127.04
117.75
113.34
52.50
52.27
29.68
COOMe
HN
H
N
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm