Supporting Information

Palladium/Lewis Acid Co-catalyzed Divergent Asymmetric Ring Opening Reactions of Azabenzonorbornadienes with Alcohols

Fan Yang,[†] Jingchao Chen,[†] Jianbin Xu, Fujie Ma, Yongyun Zhou, Madhuri Vikas Shinde, and Baomin Fan[*]

YMU-HKBU Joint Laboratory of Traditional Natural Medicine, Yunnan Minzu University, 650500 (Kunming) China.

E-mail: adams.bmf@hotmail.com

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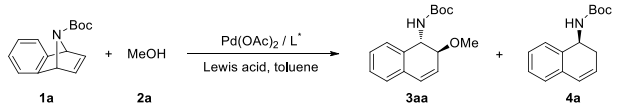
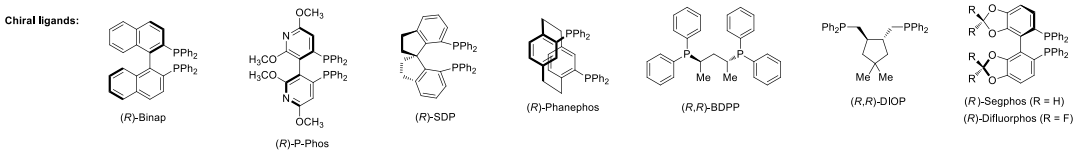
A: General Information

The reactions and manipulations were performed under an atmosphere of argon by using standard Schlenk techniques and Drybox (Mikrouna, Supper 1220/750). Anhydrous toluene was distilled from sodium benzophenone ketyl prior to use. Anhydrous DCM (Dichloromethane) was distilled from calcium hydride and stored under argon. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-Avance 400 MHz spectrometer. $CDCl_3$ or CH_3OD 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、AS-H、OJ-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 performed on a VG Autospec-3000 spectrometer. Column chromatography was performed with silica gel (200-300 mesh) with petroleum ether and ethyl acetate as eluents.

B: Table S1. Reaction condition optimizations



Chiral ligands:



Entry	Ligand	Lewis acid	Methanol amount (eq.)	Time (h)	**3aa** Yield (%)[b]	**3aa** Ee(%)[c]	**4a** Yield (%)[b]	**4a** Ee(%)[c]
1	(*R*)-Binap	$AgBF_4$	3	8	89	92	5	---
2	(*R*)-P-Phos	$AgBF_4$	3	7	95	72	2	---
3	(*R*)-Segphos	$AgBF_4$	3	48	8	95	0	---
4	(*R*)-SDP	$AgBF_4$	3	3	63	70	29	59
5	(*R,R*)-BDPP	$AgBF_4$	3	48	68	75	13	46
6	(*R,R*)-DIOP	$AgBF_4$	3	1.5	60	0	36	4
7	(*R*)-Phanephos	$AgBF_4$	3	1	34	79	65	60
8	(*R*)-Difluorphos	$AgBF_4$	3	5	96	97	trace	---
9	(*R*)-Difluorphos	AgOTf	3	15	61	98	32	69
10	(*R*)-Difluorphos	CuOTf	3	48	20	97	76	68
11	(*R*)-Difluorphos	$Cu(OTf)_2$	3	8	83	97	16	70

12	(*R*)-Difluorphos	$Zn(OTf)_2$	3	26	42	96	55	71
13	(*R*)-Binap	$Zn(OTf)_2$	3	48	30	90	38	38
14	(*R)*-Segphos	$Zn(OTf)_2$	3	48	25	94	18	63
15	(*R*,*R*)-DIOP	$Zn(OTf)_2$	3	3	45	8	61	3
16	(*R)*-SDP	$Zn(OTf)_2$	3	1.5	67	81	trace	---
17	(*R,R*)-BDPP	$Zn(OTf)_2$	3	48	76	85	8	81
18	(*R*)-P-Phos	$Zn(OTf)_2$	3	9	20	90	79	68
19	(*R*)-Phanephos	$Zn(OTf)_2$	3	0.6	trace	---	94	93
20[d]	(*R*)-Phanephos	$Zn(OTf)_2$	3	1.5	trace	---	94	96
21[e]	(*R*)-Phanephos	$Zn(OTf)_2$	3	5.5	7	97	89	94
22[d]	(*R*)-Phanephos	$Zn(OTf)_2$	5	0.7	trace	---	94	96
23[d]	(*R*)-Phanephos	$Zn(OTf)_2$	10	0.5	trace	---	94	96
24[d]	(*R*)-Phanephos	$Zn(OTf)_2$	20	0.5	trace	---	94	95
25[d]	(*R*)-Phanephos	$Zn(OTf)_2$	2 ml	3	trace	---	94	90

[a]Reaction conditions: $Pd(OAc)_2$ (0.01 mmol), $AgBF_4$ (0.02 mol), and chiral ligand (0.012 mol) in toluene (1 mL) was stirred at room temperature for 30 min under Ar. **1a** (0.2 mmol) and **2a** (0.6 mmol) were added, and the reaction mixture was stirred at 60 ^{o}C for indicated period of time. [b]Yields were calculated based on ^{1}H-NMR using 1,3-benzodioxole as internal standard. [c]Determined by HPLC analysis. [d]The reaction was performed at 40 ^{o}C. [e]The reaction was performed at room temperature.

C: Proposed mechanism for the divergent ARO reactions

On the basis of the deuterium labeling experiments, a proposed mechanism is outlined in figure S1. The additional ARO catalytic cycle for the ring opening reaction is initiated by the coordination of $Pd(OAc)_2$ with (*R*)-difluorphos to generate the chiral complex **A**, which coordinates with azabenzonorbornadiene (**1a**), CD_3OH and silver ion to yield the complex **B**. The subsequently intramolecular addition of **B** affords **C**, and the following rearrangement gives **D**, which then disassociates to yield the additional ring opening product **3-D**. And the reductive ARO catalytic cycle is initiated by the coordination of $Pd(OAc)_2$ with (*R*)-Phanephos to generate the chiral palladium complex **E**, the following addition of **E** into the C-D bond of CD_3OH affords the intermediate **F**. Subsequently, the additionreaction between **F** and azabenzonorbornadiene (**1a**) generates intermediate **G**, which then undergoes β-elimination to give the ring-opened species **H**. Finally, the product **4-D** is formed by disassociation. And the relative configuration of **4-D** was confirmed by two-dimensional NMR experiments.

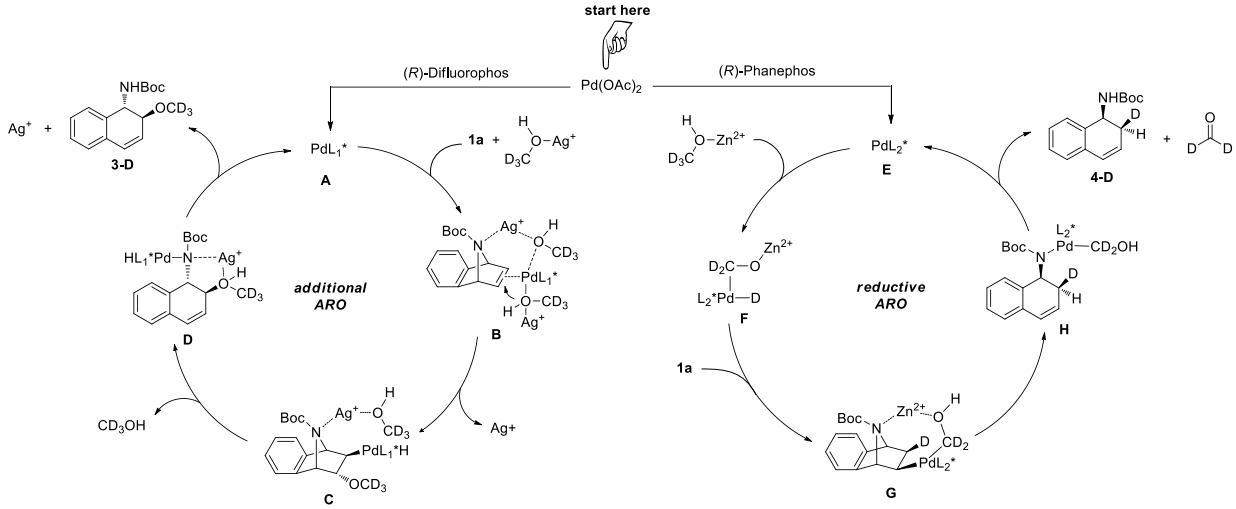


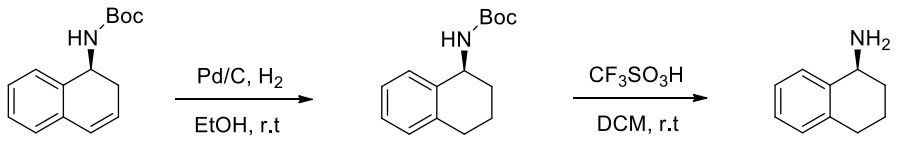
Figure S1. Proposed mechanism for the ARO reactions of azabenzonorbornadiene 1a with CD_3OH.

D: Procedure for the reactions

D_1: Typical procedure for the asymmetric ring opening reaction of azabenzonorbornadienes: $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), (*R*)-Difluorphos (8.2 mg, 0.012 mmol) and 1.0 mL toluene were added to a Schlenk tube under argon atmosphere. The resulting solution was stirred at room temperature for 30 min, then $AgBF_4$ (3.9 mg, 0.02mmol) was added and stirred for additional 10 min, then a solution of *N*-Boc-azabenzonorbornadiene **1a** (48.6 mg, 0.2 mmol) in toluene (1.0 mL) was added, and the mixture was stirred for additional 10 min. After the addition of methanol **2a** (24 μL, 0.6 mmol), the mixture was stirred at 40 °C under argon atmosphere with TLC monitoring until the complete consumption of **1a**. The residue was purified by chromatography on a silica gel column to afford the desired product **3aa** (53 mg, 96% yield).

D_2: Typical procedure for the asymmetric transfer hydrogenation reaction of azabenzonorbornadienes: $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), (*R*)-Phanephos (6.9 mg, 0.012 mmol) and 1.0 mL toluene were added to a Schlenk tube under argon atmosphere. The resulting solution was stirred at room temperature for 30 min, then $Zn(OTf)_2$ (7.3 mg, 0.02mmol) was added and stirred for an additional 10 min, then a solution of *N*-Boc-azabenzonorbornadiene **1a** (48.6 mg, 0.2 mmol) in toluene (1.0 mL) was added, and the mixture was stirred for additional 10 min. After the addition of methanol **2a** (40μL, 0.6 mmol), the mixture was stirred at 40 °C under argon atmosphere with TLC monitoring until the complete consumption of **1a**. The residue was purified by chromatography on a silica gel column to afford the desired product **4** (46 mg, 95% yield).

D_3: Preparing of (*S*)-1,2,3,4-Tetrahydro-1-naphthylamine (5)

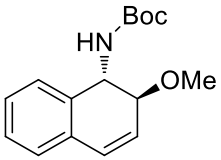


4a **5-Boc** **5**

Compound **4a** (98mg, 0.4mmol), 10% palladium on carbon (22 mg, 0.02mmol) and ethanol (3 mL) were added into a Schlenk tube. After degassing and H_2-filling procedures, the reaction mixture was stirred at room temperature for 17 hours. The resultant suspension was diluted with 10 mL ethanol, and filtered through a Celite cake. The residues on Celite were washed with ethanol. The combined ethanol solution was concentrated under reduced pressure to give compound **5-Boc** (98mg, 99% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, 1H), 7.08 (d, 2H), 7.00 (s, 1H), 4.76 (s, 1H), 2.73 - 2.62 (m, 2H), 1.95 (s, 1H), 1.73 (s, 3H), 1.40 (s, 9H).

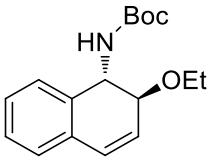
To a solution of compound **5-Boc** (98mg, 0.4 mmol) in DCM (2 mL) at room temperature was added dropwise a solution of CF_3SO_3H (400 mg, 1.7 mmol) in DCM (3 mL). The resulting mixture was then stirred at room temperature for 2 hours. A solution of 5% NaOH was added and the mixture was stirred for an additional 5 minutes. After separation of the organic phase, the aqueous phase was back-extracted with dichloromethane (2×5 mL) and the combined organic phases were dried over anhydrous sodium sulfate. After filtration, the solvents were removed under reduced pressure and the residue was chromatographed on silica gel (petroleum ether : Ethyl acetate = 1 : 2) to afford (*S*)-1,2,3,4-Tetrahydro-1-naphthylamine (51 mg , 88% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.32 (d, *J* = 2.8 Hz, 1H), 7.15 (d, 2H), 7.07 (s, 1H), 4.22 (s, 1H), 4.04 (s, 1H), 2.77 - 2.66 (m, 2H), 2.04 - 1.66 (m, 4H). The ee of **5** was determined by HPLC analysis using Daicel Chiralcel AS-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 82/18, 1 mL/min, 254 nm; t_{major} = 8.7 min, t_{minor} = 9.9 min. $[\alpha]_D^{22}$ = +5.3 (c = 0.72, EtOH).

E: Characterization Data of Products



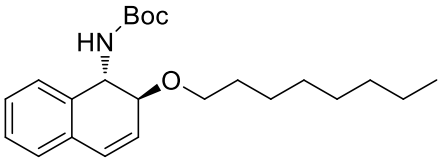
***tert*-butyl ((1*S*,2*S*)-2-methoxy-1,2-dihydronaphthalen-1-yl)carbamate (3aa)**

White solid, 52.8 mg, 96% yield, 97% *ee*. $[\alpha]_D^{22}$ = -212.1 (c = 1.02, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 6.8 Hz, 1H), 7.18-7.13 (m, 2H), 7.01 (d, *J* = 6.8 Hz, 1H), 6.50 (d, *J* = 9.6 Hz, 1H), 5.99 (dd, *J* = 9.6, 4 Hz, 1H), 4.91 (s, 1 Hz, 1H), 4.59 (d, *J* = 7.2 Hz, 1H), 3.93 (s, 1H), 3.36 (s, 3H), 1.37 (s, 9H). The *ee* of **3aa** was determined by HPLC analysis using two Daicel Chiralcel OD-H columns (2 × 25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, 254 nm; t_{major} = 19.0 min, t_{minor} = 20.2 min.



***tert*-butyl ((1*S*,2*S*)-2-ethoxy-1,2-dihydronaphthalen-1-yl)carbamate (3ab)**

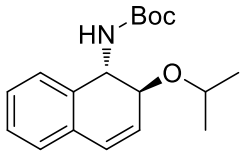
Colorness oil, 53.8 mg, 93% yield, 97% *ee*. $[\alpha]_D^{22}$ = 252.7 (c = 0.86, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 6.4 Hz, 1H), 7.19 - 7.14 (m, 2H), 7.02 (d, *J* = 6.8 Hz, 1H), 6.49 (d, *J* = 9.6 Hz, 1H), 5.98 (dd, *J* = 9.2, 3.6 Hz, 1H), 4.90 (s, 1H), 4.54 (d, *J* = 6.8 Hz, 2H), 4.03 (s, 1H), 3.63 (q, *J* = 7.2 Hz, 2H), 1.38 (s, 9H), 1.12 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100MHz): δ 155.41, 134.17, 132.07, 129.64, 128.23, 127.05, 126.67, 79.63, 75.65, 64.28, 51.74, 28.41, 15.62. HRMS calcd for $C_{17}H_{23}NO_3$ $[M]^+$: 289.1678. Found: 289.1682. The *ee* of **3ab** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, 254 nm; t_{major} = 5.3 min, t_{minor} = 5.8 min.



***tert*-butyl ((1*S*,2*S*)-2-(heptyloxy)-1,2-dihydronaphthalen-1-yl)carbamate (3ac)**

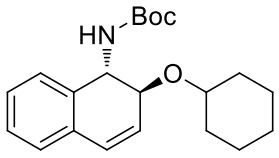
White solid, 62.7 mg, 84% yield, 97% *ee*. Mp 62-64 °C. $[\alpha]_D^{22}$ = 148.3 (c = 0.325, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.2 Hz, 1H), 7.18 - 7.12 (m, 2H), 7.02 (d, *J* = 6.0 Hz, 1H), 6.48 (d, *J* = 10.0 Hz, 1H), 5.98 (dd, *J* = 9.6, 4.0 Hz, 1H), 4.92 (t, *J* = 6.4 Hz, 1H), 4.53 (d, *J* = 8.0 Hz, 1H), 4.01(s, 1H), 3.53 (t, *J* = 6.4 Hz, 2H), 1.47 (t, *J* = 4.4 Hz, 2H), 1.38 (s, 9H), 1.17 (s, 10H), 0.80 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.43, 134.35, 132.12, 129.54, 128.16, 128.04，126.99, 126.87, 79.59, 175.92, 68.97, 51.83, 31.83, 30.09, 29.44, 29.25, 28.41, 26.10, 22.66, 14.10. HRMS calcd for

$C_{23}H_{35}NO_3$ $[M]^+$: 373.2617. Found: 373.2613. 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 = 95/5, 0.5 mL/min, 254 nm; t_{major} = 12.9 min, t_{minor} = 17.3 min.



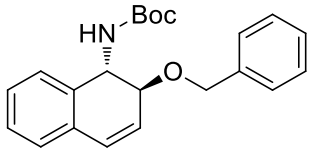
***tert*-butyl ((1*S*,2*S*)-2-isopropoxy-1,2-dihydronaphthalen-1-yl)carbamate (3ad)**

White solid, 50.9 mg, 84% yield, 97% *ee*. Mp 117-119 °C. $[\alpha]_D^{22}$ = 161.9 (c = 1.22, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 6.8 Hz, 1H), 7.15 - 7.14 (m, 2H), 7.01 (d, *J* = 6.8 Hz, 1H), 6.45 (d, *J* = 9.6 Hz, 1H), 5.93 (dd, *J* = 9.6, 4.0 Hz, 1H), 4.81 (t, *J* = 6.8 Hz, 1H), 4.52 (d, *J* = 7.6 Hz, 1H), 4.06 (t, *J* = 4.8 Hz, 1H), 3.85 (t, *J* = 6.0 Hz, 1H), 1.38 (s, 9H), 1.10 (t, *J* = 6.4 Hz, 6H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.36, 134.13, 132.16, 129.15, 128.24, 128.17, 128.10, 127.56, 127.01, 79.55, 73.72, 70.82, 52.81, 28.42, 23.03, 22.71. HRMS calcd for $C_{18}H_{25}NO_3$ $[M]^+$: 303.1834. Found: 303.1845. 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 = 95/5, 1.0 mL/min, 254 nm; t_{major} = 6.9 min, t_{minor} = 9.1 min.



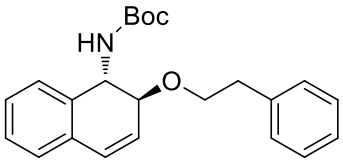
***tert*-butyl ((1*S*,2*S*)-2-(cyclohexyloxy)-1,2-dihydronaphthalen-1-yl)carbamate (3ae)**

White solid, 50.8 mg, 74% yield, ＞99% *ee*. Mp 102-104 °C. $[\alpha]_D^{22}$ = 212.6 (c = 0.94, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 6.8 Hz, 1H), 7.17 - 7.11 (m, 2H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 9.6, 1H), 5.93 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.82 (t, *J* = 6.8 Hz, 1H), 4.54 (d, *J* = 8.0 Hz, 1H), 4.12 (t, *J* = 4.4 Hz, 1H), 3.46 (s, 1H), 1.83 (t, *J* = 9.6 Hz, 2H), 1.65 (s, 2H), 1.46 (s, 1H), 1.38(s, 9H), 1.27-1.08 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.34, 133.42, 131.19, 127.88, 126.00, 126.79, 125.87, 78.44, 72.75, 52.16, 32.03, 31.94, 27.38, 24.65, 23.25, 23.19. HRMS calcd for $C_{21}H_{29}NO_3$ $[M]^+$: 343.2147. Found: 343.2152. 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 = 95/5, 1.0 mL/min, 254 nm; t_{major} = 6.3 min.



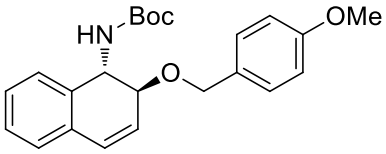
***tert*-butyl ((1*S*,2*S*)-2-(benzyloxy)-1,2-dihydronaphthalen-1-yl)carbamate (3af)**

Transparent solid, 51.3 mg, 73% yield, 96% *ee*. Mp 88-90 °C. $[\alpha]_D^{22}$ = 215.2 (c = 1.06, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 - 7.11 (m, 8H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.48 (d, *J* = 9.6 Hz, 1H), 5.95 (dd, *J* = 9.6, 3.6 Hz, 1H), 5.02 (t, *J* = 7.2 Hz, 1H), 4.65-4.53 (m, 3H), 4.11 (t, 1H), 1.38 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.37, 137.34, 133.11, 131.03, 128.75, 127.24, 126.96, 126.86, 126.51, 125.94, 125.43, 78.58, 74.22, 69.33, 50.90, 27.35. HRMS calcd for $C_{22}H_{25}NO_3$ $[M]^+$: 351.1834. Found: 351.1837. The *ee* of **3af** 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} = 12.3 min, t_{major} = 14.3min.



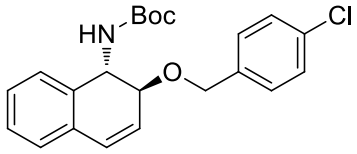
***tert*-butyl ((1*S*,2*S*)-2-phenethoxy-1,2-dihydronaphthalen-1-yl)carbamate (3ag)**

White solid, 60 mg, 82% yield, 96% *ee*. Mp 80-82 °C. $[\alpha]_D^{22}$ = 197.5 (c = 1.18, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 6.8 Hz, 1H), 7.19 - 7.09 (m, 7H), 7.01 (d, *J* = 6.8 Hz, 1H), 6.47 (d, *J* = 9.6 Hz, 1H), 5.92 (dd, *J* = 9.6, 4.0 Hz, 1H), 4.90 (t, *J* = 6.8 Hz, 1H), 4.51 (d, *J* = 8.0 Hz, 1H), 4.03 (s, 1H), 3.76 (t, *J* = 7.2 Hz, 2H), 2.79 (t, *J* = 6.8 Hz, 2H), 1.38 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.33, 137.78, 133.12, 130.98, 128.68, 127.93, 127.24, 127.15, 127.04, 125.94, 125.48, 125.09, 78.58, 74.92, 68.65, 50.80, 35.64, 27.35. HRMS calcd for $C_{23}H_{27}NO_3$ $[M]^+$: 365.1991. Found: 365.1982. The *ee* of **3ag** was determined by HPLC analysis using Daicel Chiralcel AS-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 98/2, 0.5 mL/min, 254 nm; t_{major} = 22.6 min, t_{minor} = 26.8 min.



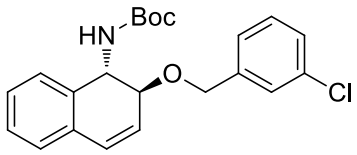
***tert*-butyl (1*S*,2*S*)-2-((4-methoxybenzyl)oxy)-1,2-dihydronaphthalen-1-yl)carbamate (3ah)**

White solid, 51.1 mg, 67% yield, 98% *ee*. Mp 85-87 °C. $[\alpha]_D^{22}$ = 223.5 (c = 0.78, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 5.2 Hz, 1H), 7.21 - 7.11 (m, 4H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.47 (d, *J* = 9.6 Hz, 1H), 5.93 (dd, *J* = 9.6, 3.6 Hz, 1H), 5.00 (t, *J* = 7.2 Hz, 1H), 4.49-4.51 (m, 3H), 4.09 (t, *J* = 4.4 Hz, 1H), 3.70 (s, 3H), 1.39 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.21, 155.47, 134.21, 132.14, 130.50, 129.75, 129.62, 128.23, 128.09, 127.02, 126.67, 113.75, 79.64, 74.84, 70.07, 55.27, 51.94, 28.45. HRMS calcd for $C_{23}H_{27}NO_4$ $[M]^+$: 381.1940. Found: 381.1953. 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, 1.0 mL/min, 254 nm; t_{minor} =10.8 min, t_{major} = 11.7 min.



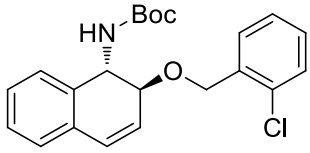
***tert*-butyl ((1*S*,2*S*)-2-((4-chlorobenzyl)oxy)-1,2-dihydronaphthalen-1-yl)carbamate (3ai)**

White solid, 44.7 mg, 58% yield, 98% *ee*. Mp 96-98 ^{o}C. $[\alpha]_D^{22}$ = 203.2 (c = 0.9, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 5.6Hz, 1H), 7.28 - 7.23 (m, 6H), 7.12 - 7.10 (m, 1H), 6.60 (d, *J* = 10.0 Hz, 1H), 6.03 (dd, *J* = 9.6, 4.0 Hz, 1H), 5.08 (dd, *J* = 8.4, 6.0 Hz, 1H), 4.71 - 4.59 (m, 3H), 4.17 (t, *J* = 5.2Hz, 1H), 1.46 (s, 9H). ^{13}C NMR ($CDCl_3$, 100MHz): δ 155.39, 136.95, 133.86, 133.31, 132.01, 130.12, 129.24, 128.45, 128.38, 128.25, 127.12, 126.02, 79.79, 75.25, 69.60, 51.72, 28.41. HRMS calcd for $C_{22}H_{24}ClNO_3$ $[M]^+$: 385.1445. Found: 385.1460. The *ee* of **3ai** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 98/2, 0.5 mL/min, 254 nm; t_{minor} = 16.7 min, t_{major} = 17.7 min.



***tert*-butyl ((1*S*,2*S*)-2-((3-chlorobenzyl)oxy)-1,2-dihydronaphthalen-1-yl)carbamate (3aj)**

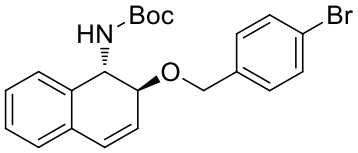
White solid, 47.0 mg, 61% yield, 99% *ee*. Mp 71-73 ^{o}C. $[\alpha]_D^{22}$ = 249.7 (c = 6.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.19 - 7.14 (m, 5H), 7.03 - 7.01 (m, 1H), 6.51 (d, *J* = 9.6 Hz, 1H), 5.95 (dd, *J* = 9.6, 4.0 Hz, 1H), 5.00 (dd, *J* = 8.4, 6.0 Hz, 1H), 4.63 - 4.55 (m, 3H), 4.11 (t, *J* = 5.2 Hz, 1H), 1.38 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.33, 139.48, 133.14, 132.84, 130.94, 129.04, 128.50, 127.28, 127.08, 126.78, 126.62, 126.03, 124.93, 124.77, 78.72, 74.42, 68.46, 50.72, 27.34. HRMS calcd for $C_{22}H_{24}ClNO_3$ $[M]^+$: 385.1445. Found: 385.1449. The *ee* of **3aj** was determined by HPLC analysis using two Daicel Chiralcel OD-H columns (2 × 25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 98/2, 0.5 mL/min, 254 nm; t_{minor} = 24.0 min, t_{major} = 25.2 min.



***tert*-butyl ((1*S*,2*S*)-2-((2-chlorobenzyl)oxy)-1,2-dihydronaphthalen-1-yl)carbamate (3ak)**

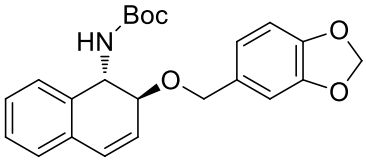
Colorless oil, 28.5 mg, 37% yield, ＞99% *ee*. $[\alpha]_D^{22}$ = 250.2 (c = 0.84, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 1.6 Hz, 1H), 7.29 (t, *J* = 4.8 Hz, 1H), 7.23 (d, *J* = 1.6 Hz, 1H), 7.18-7.09 (m, 4H), 7.03 (t, *J* = 3.6 Hz, 1H), 6.51 (d, *J* = 10.0 Hz, 1H), 6.04 (dd, *J* =

10.0, 4.0 Hz, 1H), 5.06 (t, *J* = 8.0 Hz, 1H), 4.74 - 4.67 (m, 2H), 4.59 (d, *J* = 8.4 Hz, 1H), 4.20 (t, *J* = 5.6 Hz, 1H), 1.38 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.42, 135.01, 133.20, 131.87, 131.05, 128.10, 127.61, 127.22, 127.19, 126.73, 125.99, 125.67, 125.22, 78.65, 75.27, 66.70, 51.19, 27.36. HRMS calcd for $C_{22}H_{24}ClNO_3$ $[M]^+$: 385.1445. Found: 385.1434. The *ee* of **3ak** was determined by HPLC analysis using Daicel Chiralcel AS-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 98/2, 0.8 mL/min, 254 nm; t_{major} = 16.8 min.



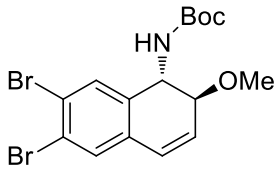
***tert*-butyl ((1*S*,2*S*)-2-((4-bromobenzyl)oxy)-1,2-dihydronaphthalen-1-yl)carbamate (3al)**

White solid, 58.4 mg, 68% yield, 99% *ee*. $[\alpha]_D^{22}$ = 188.5 (c = 1.14, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 5.6 Hz, 1H), 7.25 - 7.12 (m, 4H), 7.03 - 7.01 (m, 1H), 6.50 (d, *J* = 9.6 Hz, 1H), 5.93 (dd, *J* = 9.6, 4.4 Hz, 1H), 4.99 (dd, *J* = 8.4, 6.0 Hz, 1H), 4.61-4.53 (m, 3H), 4.09 (t, *J* = 4.8 Hz, 1H), 1.38 (s, 9H). 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 = 95/5, 0.5 mL/min, 254 nm; t_{minor} = 30.2 min, t_{major} = 30.9 min.



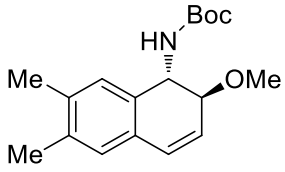
***tert*-butyl ((1*S*,2*S*)-2-(benzo[*d*][1,3]dioxol-5-ylmethoxy)-1,2-dihydronaphthalen-1-yl) carbamate (3am)**

White solid, 56.1 mg, 71% yield, >99% *ee*. Mp 77-79 °C. $[\alpha]_D^{22}$ = 196.5 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 5.6 Hz, 1H), 7.17 - 7.13 (m, 2H), 7.05 (d, *J* = 6.8 Hz, 1H), 6.77 (s, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 9.6 Hz, 1H), 5.93 (dd, *J* = 9.6, 4.0 Hz, 1H), 5.82 (s, 2H), 4.99 (t, *J* = 7.2 Hz, 1H), 4.55 - 4.47 (m, 2H), 4.08 (t, 1H), 1.39 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.36, 146.62, 146.03, 133.02, 131.14, 131.01, 128.72, 127.16, 126.97, 125.94, 125.41, 120.53, 107.70, 106.89, 99.84, 78.61, 73.84, 69.16, 50.81, 27.34. HRMS calcd for $C_{23}H_{25}NO_5$ $[M]^+$: 395.1733. Found: 395.1735. The *ee* of **3am** 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_{major} = 16.4 min.



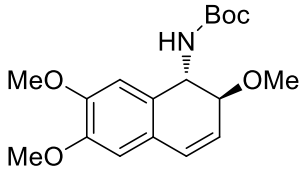
***tert*-butyl ((1*S*,2*S*)-6,7-dibromo-2-methoxy-1,2-dihydronaphthalen-1-yl)carbamate (3ba)**

White solid, 76.1 mg, 88% yield, 84% *ee*. Mp 50-52 °C. $[\alpha]_D^{22}$ = 75.5 (c = 0.74, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.34 (s, 1H), 6.47 (d, *J* = 9.6 Hz, 1H), 6.16 (dd, *J* = 9.2, 2.8 Hz, 2H), 4.91 (t, 1H), 4.70 (d, *J* = 8.0 Hz, 1H), 4.02 (s, 1H), 3.44 (s, 3H), 1.47 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.27, 135.05, 133.00, 132.69, 131.53, 128.40, 127.93, 124.26, 123.79, 80.18, 56.54, 51.01, 28.36. HRMS calcd for $C_{16}H_{19}Br_2NO_3$ $[M]^+$: 430.9732. Found: 430.9728. The *ee* of **3ba** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 0.3 mL/min, 254 nm; t_{minor} = 26.8min, t_{major} = 30.9 min.



***tert*-butyl ((1*S*,2*S*)-2-methoxy-6,7-dimethyl-1,2-dihydronaphthalen-1-yl)carbamate (3ca)**

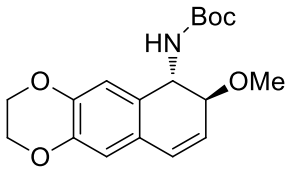
White solid, 54.6 mg, 90% yield, 95% *ee*. Mp 43-45 °C. $[\alpha]_D^{22}$ = 197.1 (c = 0.86, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 1H), 6.81 (s, 1H), 6.48 (d, *J* = 9.6 Hz, 1H), 5.94 (dd, *J* = 9.2, 4.0 Hz, 1H), 4.83 (t, 1H), 4.51 (d, *J* = 7.2 Hz, 1H), 3.88 (s, 1H), 3.36 (s, 3H), 2.15 (d, *J* = 8.8 Hz, 6H), 1.37 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.34, 136.84, 136.54, 131.26, 130.21, 129.98, 129.52, 128.46, 124.67, 79.57, 76.53, 56.36, 50.75, 28.42, 19.63, 19.38. HRMS calcd for $C_{18}H_{25}NO_3$ $[M]^+$: 303.1834. Found: 303.1839. The *ee* of **3ca** 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_{major} = 7.1 min t_{minor} = 7.9 min.



***tert*-butyl ((1*S*,2*S*)-2,6,7-trimethoxy-1,2-dihydronaphthalen-1-yl)carbamate (3da)**

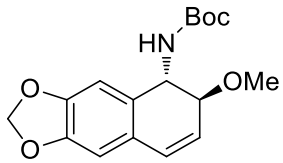
White solid, 62.3 mg, 93% yield, 99% *ee*. Mp 40-42 °C. $[\alpha]_D^{22}$ = 202.1 (c = 1.22, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 1H), 6.57 (s, 1H), 6.46 (d, *J* = 9.6 Hz, 1H), 5.93 (dd,

J = 8.4, 3.6 Hz, 1H), 4.81 (s, 1H), 4.55 (d, *J* = 7.6 Hz, 1H), 3.86 (t, 1H), 3.80 (d, *J* = 11.6 Hz, 6H), 3.38 (s, 3H), 1.38 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.30, 147.85, 147.68, 128.98, 125.44, 123.65, 122.30, 111.17, 109.47, 78.66, 75.13, 55.40, 55.01, 54.98, 49.74, 27.34. HRMS calcd for $C_{18}H_{25}NO_5$ $[M]^+$: 335.1733. Found: 335.1754. The *ee* of **3da** was determined by HPLC analysis using 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} = 10.5 min, t_{minor} = 12.2 min.



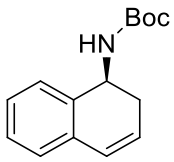
***tert*-butyl ((6*S*,7*S*)-7-methoxy-2,3,6,7-tetrahydronaphtho[2,3-*b*][1,4]dioxin-6-yl) carbamate (3ea)**

White solid, 58.6 mg, 88% yield, >99% *ee*. Mp 58-60 °C. $[\alpha]_D^{22}$ = 165.6 (c = 1.04, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.62 (s, 1H), 6.47 (d, *J* = 9.6 Hz, 1H), 5.97 (dd, *J* = 9.2, 4.0 Hz, 1H), 4.86 (t, 1H), 4.62 (d, *J* = 7.6 Hz, 1H), 4.22 (s, 4H), 3.94 (s, 1H), 3.44 (s, 3H), 1.45 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.28, 143.30, 143.18, 129.53, 127.44, 125.70, 124.14, 117.72, 115.98, 79.60, 76.51, 64.43, 64.35, 56.35, 50.74, 28.41. HRMS calcd for $C_{18}H_{23}NO_5$ $[M]^+$: 333.1576. Found: 333.1585. 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 =80/20, 1 mL/min, 254 nm; t_{major} = 13.5 min.



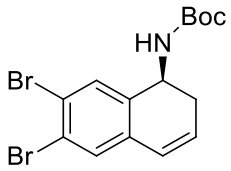
***tert*-butyl ((5*S*,6*S*)-6-methoxy-5,6-dihydronaphtho[2,3-*d*][1,3]dioxol-5-yl)carbamate (3fa)**

White solid, 57.4 mg, 90% yield, 98% *ee*. Mp 55-57 °C. $[\alpha]_D^{22}$ = 181.7 (c = 1.08, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 1H), 6.52 (s, 1H), 6.40 (d, *J* = 9.6 Hz, 1H), 5.90 (dd, *J* = 8.8, 3.6 Hz, 1H), 5.84 (d, *J* = 8.4 Hz, 2H), 4.79 (t, 1H), 4.58 (d, 1H), 3.86 (s, 1H), 3.36 (s, 3H), 1.37 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.27, 147.39, 147.30, 129.97, 126.09, 123.65, 109.46, 107.61, 101.14, 79.72, 76.33, 56.38, 51.15, 28.39. HRMS calcd for $C_{17}H_{21}NO_5$ $[M]^+$: 319.1420. Found: 319.1413. The *ee* of **3fa** was determined by HPLC analysis using 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} = 7.4 min, t_{minor} = 9.6 min.



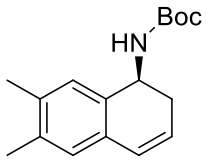
(*S*)-*tert*-butyl (1,2-dihydronaphthalen-1-yl)carbamate (4a)

Prepared following typical procedure **B_2** using methanol as reductant. Colorless oil, 46.1 mg, 94% yield, 95% *ee*. $[\alpha]_D^{22}$ = -38.7 (c = 0.86, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 6.8 Hz, 1H), 7.22 (m, 2H), 7.08 (dd, *J* = 7.2, 1.6 Hz, 1H), 6.52 (d, *J* = 9.6 Hz, 1H), 5.99 - 4.95 (m, 1H), 4.89 (t, 2H), 2.60 - 2.46 (m, 2H), 1.44 (s, 9H). The *ee* of **4a** was determined by HPLC analysis using Daicel Chiralcel OJ-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm; t_{minor} = 6.4 min, t_{major} = 7.4 min.



(*S*)-*tert*-butyl (6,7-dibromo-1,2-dihydronaphthalen-1-yl)carbamate (4b)

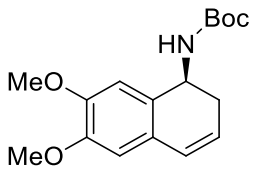
Prepared following typical procedure **B_2** using methanol as reductant. Colorless oil, 60.4 mg, 75% yield, 90% *ee*. $[\alpha]_D^{22}$ = -21.7 (c = 1.14, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.33 (s, 1H), 6.43 (d, *J* = 10.0 Hz, 1H), 6.08 - 6.04 (m, 1H), 4.84 (s, 2H), 2.58 - 2.40 (m, 2H), 1.45 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.02, 135.93, 133.87, 131.77, 131.04, 127.95, 126.12, 123.85, 122.92, 79.96, 46.87, 30.31, 28.38. HRMS calcd for $C_{15}H_{17}Br_2NO_2$ $[M]^+$: 400.9626. Found: 400.9624. The *ee* of **4c** was determined by HPLC analysis using Daicel Chiralcel AS-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 98/2, 0.5 mL/min, 254 nm; t_{minor} = 17.4 min, t_{major} = 19.3 min .



(*S*)-*tert*-butyl (6,7-dimethyl-1,2-dihydronaphthalen-1-yl)carbamate (4c)

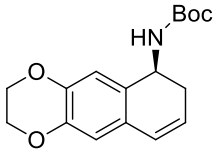
Prepared following typical procedure **B_2** using methanol as reductant. Colorless oil, 51.9 mg, 95% yield, 96% *ee*. $[\alpha]_D^{22}$ = -26.7 (c = 1.02, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 1H), 6.87 (s, 1H), 6.48 (d, *J* = 9.6 Hz, 1H), 5.90 (t, *J* = 4.8 Hz, 1H), 4.83 (d, *J* = 9.6 Hz, 2H), 2.57 - 2.42 (m, 2H), 2.24 (d, *J* = 9.6 Hz, 6H), 1.44(s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.12, 136.16, 136.05, 132.46, 130.83, 128.50, 127.80, 127.54, 124.81, 79.30, 47.25, 30.79, 28.45, 19.64, 19.43. HRMS calcd for $C_{17}H_{23}NO_2$ $[M]^+$: 273.1729. Found: 273.1729. The *ee* of **4b** 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} = 11.2 min, t_{major} = 12.6 min .



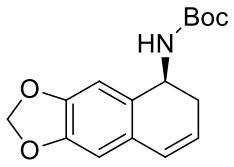
(*S*)-*tert*-butyl (6,7-dimethoxy-1,2-dihydronaphthalen-1-yl)carbamate (4d)

Prepared following typical procedure **B_2** using methanol as reductant. Colorless oil, 50.1 mg, 82% yield, 95% *ee*. $[\alpha]_D^{22}$ = -57.8 (c = 0.82, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 1H), 6.55 (s, 1H), 6.36 (d, *J* = 9.6 Hz, 1H), 5.81 - 5.76 (m, 1H), 4.84 (d, *J* = 8.8 Hz, 1H), 4.74 - 4.69 (m, 1H), 3.80 (d, *J* = 6.8 Hz, 6H), 2.51 - 2.37 (m, 2H), 1.36 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.20, 148.53, 148.24, 127.67, 127.25, 126.07, 123.62, 111.04, 109.87, 79.40, 56.13, 56.02, 47.30, 30.55, 28.45. HRMS calcd for $C_{17}H_{23}NO_4$ $[M]^+$: 305.1627. Found: 305.1627. The *ee* of **4d** was determined by HPLC analysis using Daicel Chiralcel AS-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1 mL/min, 254 nm; t_{minor} = 13.7 min, t_{major} = 14.7 min .



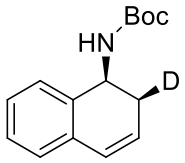
(*S*)-tert-butyl (2,3,6,7-tetrahydronaphtho[2,3-*b*][1,4]dioxin-6-yl)carbamate (4e)

Prepared following typical procedure **B_2** using methanol as reductant. Colorless oil, 50.3 mg, 83% yield, 96% *ee*. $[\alpha]_D^{22}$ = -22.3 (c = 1.04, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.60 (s, 1H), 6.39 (d, *J* = 9.6 Hz, 1H), 5.87 - 5.83 (m, 1H), 4.85 (m, 2H), 4.23 (s, 4H), 2.55 - 2.37 (m, 2H), 1.44 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.08, 142.91, 142.70, 128.78, 127.06, 124.11, 116.06, 115.78, 79.33, 64.45, 64.40, 47.26, 30.58, 28.44. HRMS calcd for $C_{17}H_{21}NO_4$ $[M]^+$: 303.1471. Found: 303.1472. The *ee* of **4e** was determined by HPLC analysis using Daicel Chiralcel AS-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 0.5 mL/min, 254 nm; t_{major} = 21.6 min, t_{minor} = 24.3 min.



(*S*)-*tert*-butyl (5,6-dihydronaphtho[2,3-*d*][1,3]dioxol-5-yl)carbamate (4f)

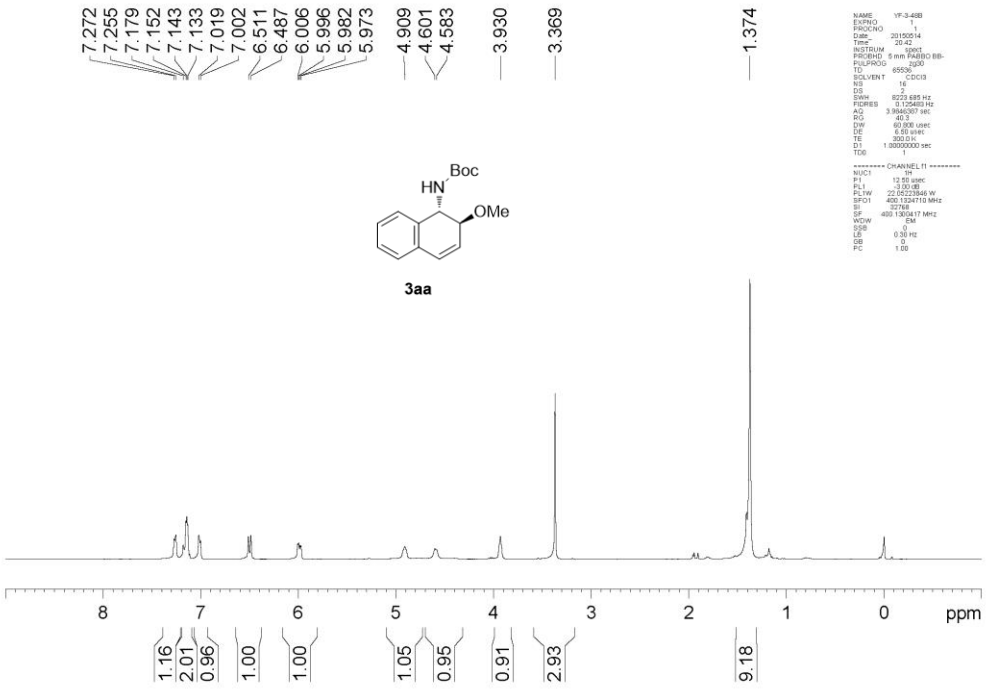
Prepared following typical procedure **B_2** using methanol as reductant. Colorless oil, 46.3 mg, 80% yield, 94% *ee*. $[\alpha]_D^{22}$ = -49.5 (c = 0.56, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.57 (s, 1H), 6.39 (d, *J* = 9.6 Hz, 1H), 5.92 (s, 2H), 5.85 (t, *J* = 4.8 Hz, 1H), 4.93 (d, *J* = 6.4 Hz, 1H), 4.75 (d, *J* = 6.8 Hz, 1H), 2.54 - 2.41 (m, 2H), 1.43 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.06, 147.07, 146.63, 129.16, 127.47, 127.40, 123.71, 108.17, 106.98, 100.96, 79.40, 47.40, 47.60, 30.45, 28.42. HRMS calcd for $C_{16}H_{19}NO_4$ $[M]^+$: 289.1314. Found: 289.1316. The *ee* of **4f** was determined by HPLC analysis using Daicel Chiralcel AS-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 0.5 mL/min, 254 nm; t_{major} = 15.0 min, t_{minor} = 20.2 min.

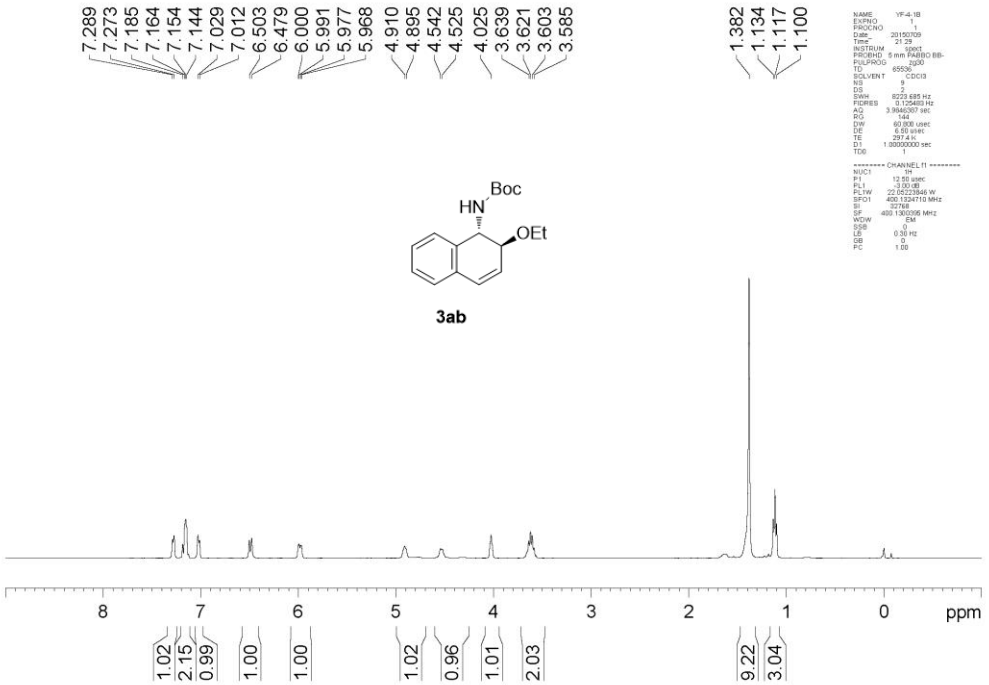


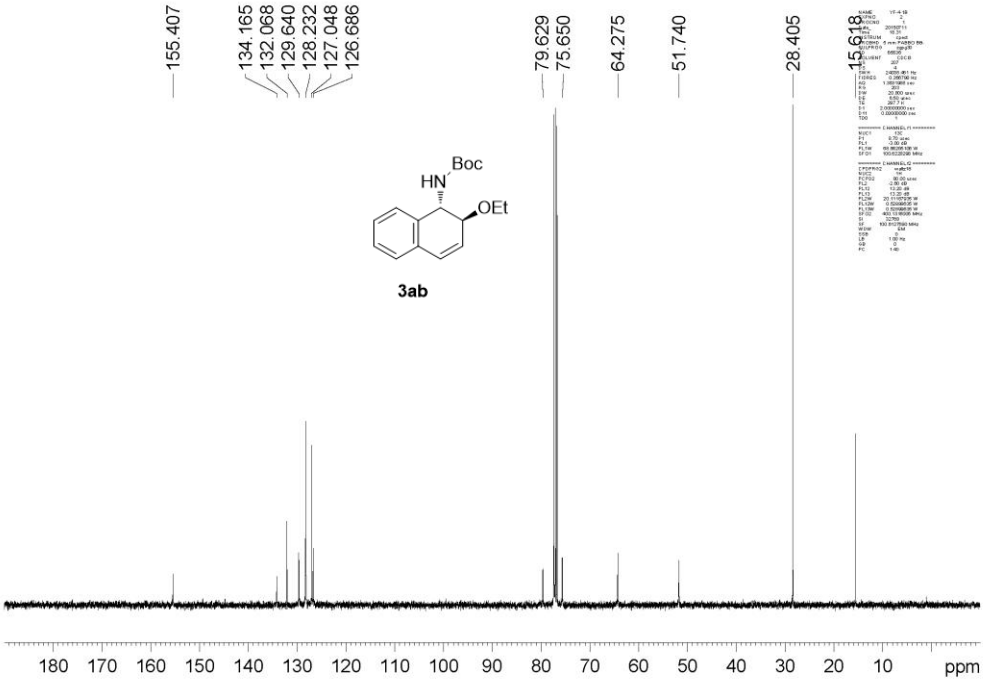
***tert-butyl* ((1*R*,2*S*)-2-deuterium-1,2-dihydronaphthalen-1-yl)carbamate (4-D^3)**

Prepared following typical procedure **B_2** using CD_3OH as reductant. The relative stereochemistry of 4-D^3 was determined by 2D NMR spectrums (page S42-43). Colorless oil, 45.3 mg, 92% yield, 95% *ee*. $[\alpha]_D^{22}$ = -70.4 (c = 0.72, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.33 (d, *J* = 6.8 Hz, 1H), 7.26 - 7.19 (m, 2H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.52 (d, *J* = 9.6 Hz, 1H), 5.97 (d, *J* = 9.2 Hz, 1H), 4.89 (t, 2H), 2.55 (s, 1H), 1.44 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.14, 134.00, 133.16, 128.03, 127.81, 127.69, 127.14, 126.47, 125.86, 79.43, 79.40, 47.43, 30.38, 30.18, 29.97, 28.44. HRMS calcd for $C_{16}H_{18}DNO_4$ $[M]^+$: 246.1479. Found $[M]^+$+Na: 269.1370. The *ee* of **4-D^3** was determined by HPLC analysis using Daicel Chiralcel OJ-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm; t_{minor} = 6.3 min, t_{major} = 7.3 min.

F: NMR Spectra of Products



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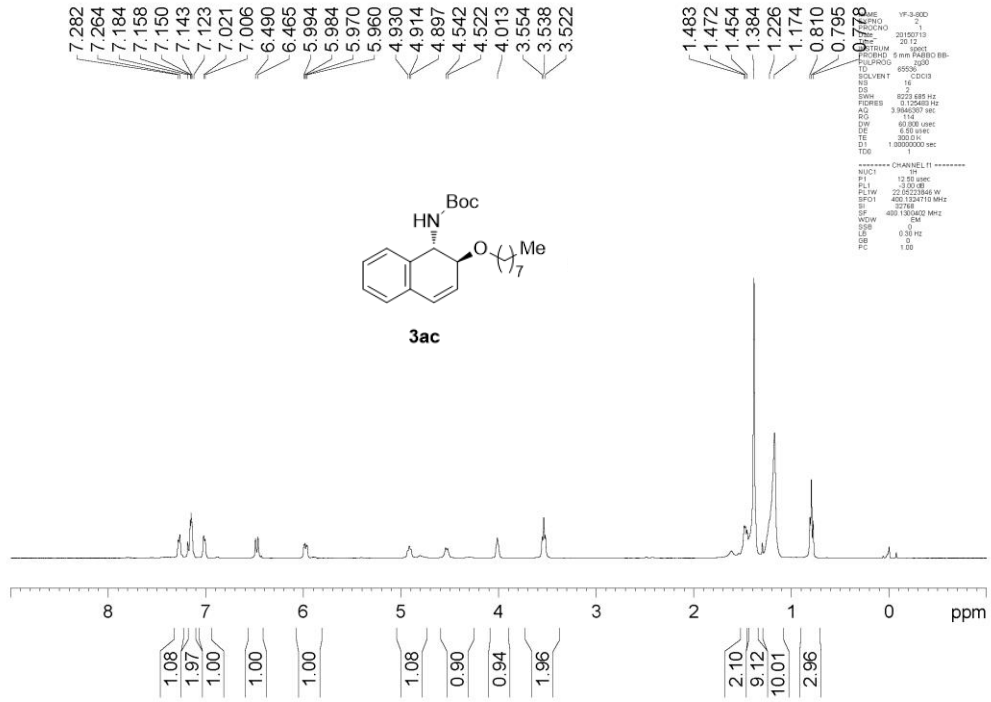
134.165
132.068
129.640
128.232
127.048
126.686
79.629
75.650
64.275
51.740
28.405
15.618
Boc
HN
OEt
3ab
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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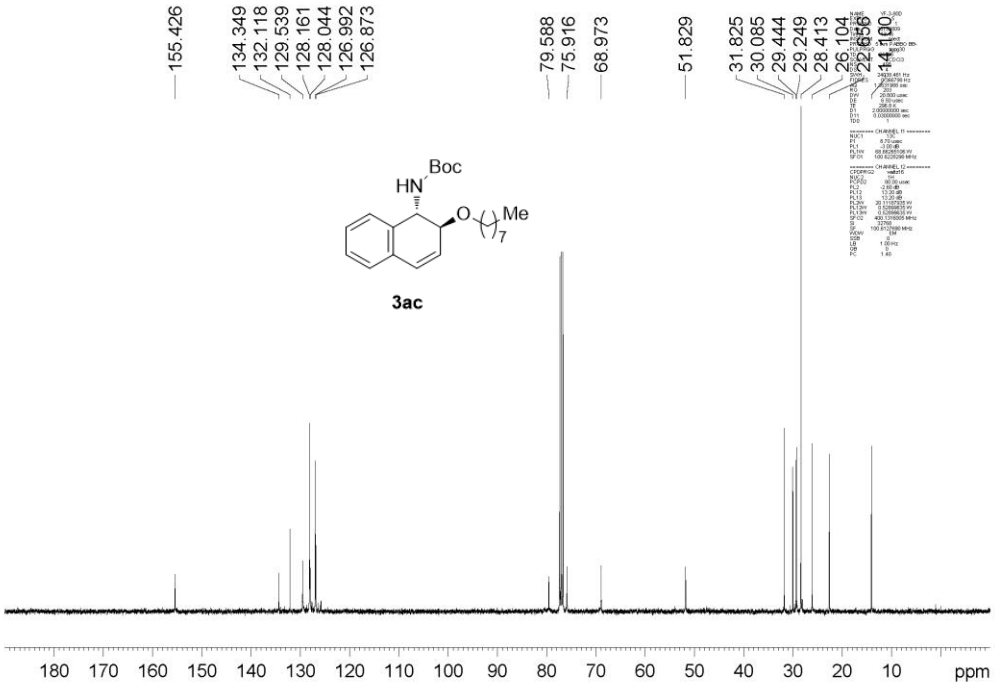
7.264
7.184
7.158
7.150
7.143
7.123
7.021
7.006
6.490
6.465
5.994
5.984
5.970
5.960
4.930
4.914
4.897
4.542
4.522
4.013
3.554
3.538
3.522
1.483
1.472
1.454
1.384
1.226
1.174
0.810
0.795
Boc
HN
O
Me
7
3ac
8 7 6 5 4 3 2 1 0 ppm
1.08
1.97
1.00
1.00
1.00
1.08
0.90
0.94
1.96
2.10
9.12
10.01
2.96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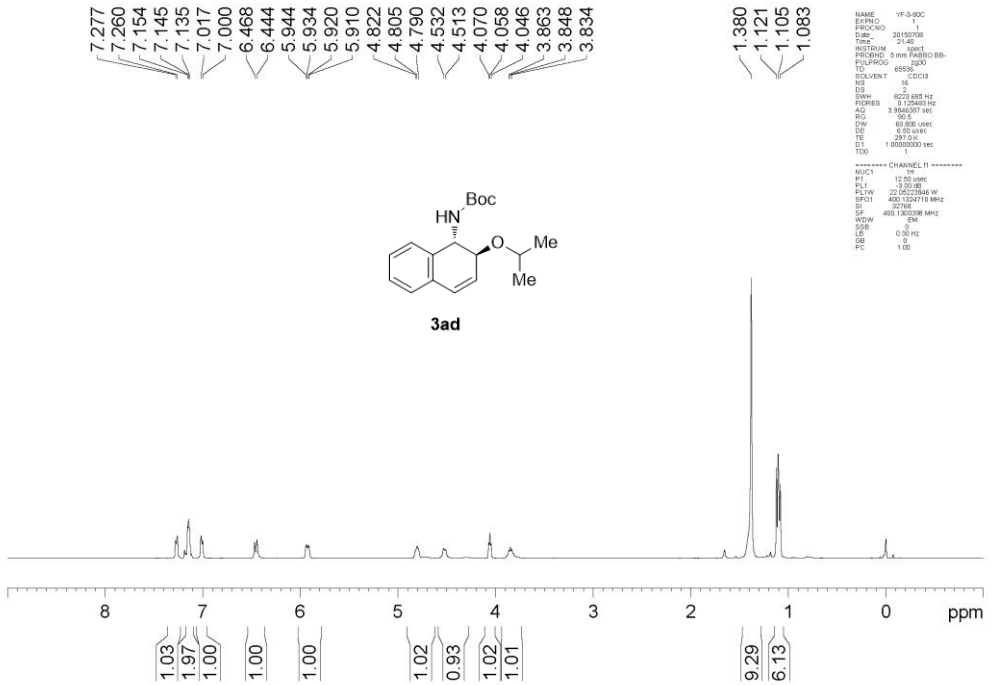
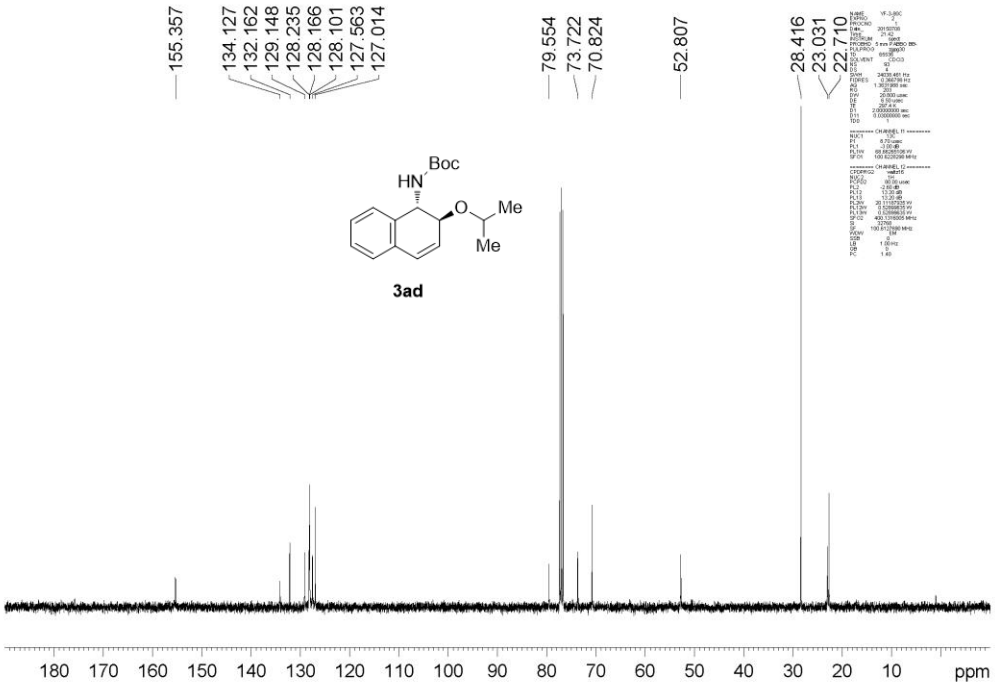
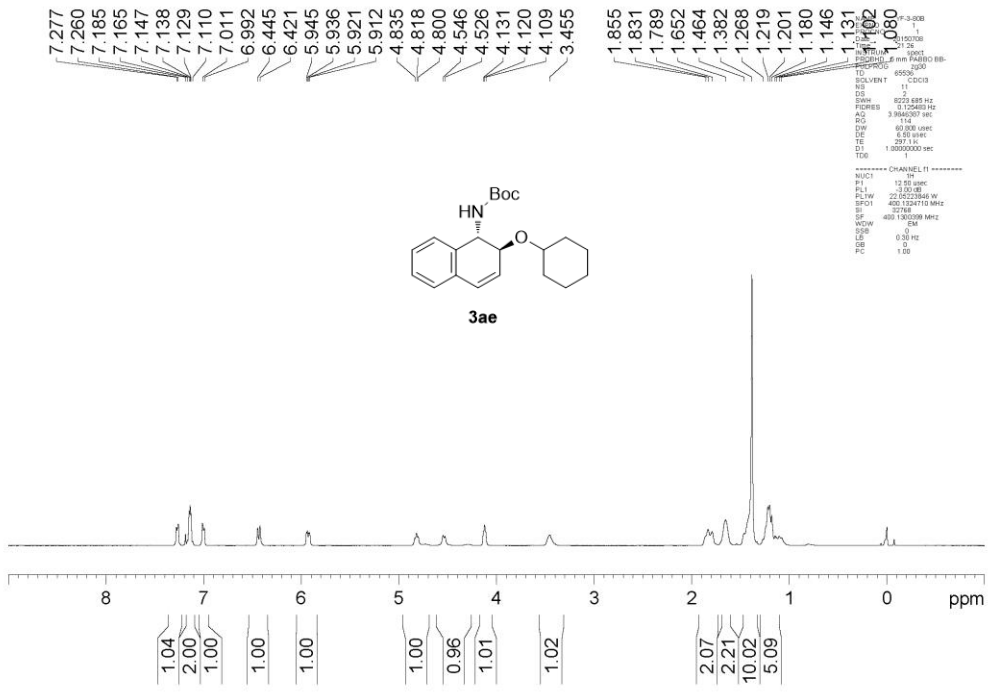
134.349
132.118
129.539
128.161
128.044
126.992
126.873
79.588
75.916
68.973
51.829
31.825
30.085
29.444
29.249
28.413
26.104
22.556
14.100
Boc
HN
O
Me
7
3ac
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

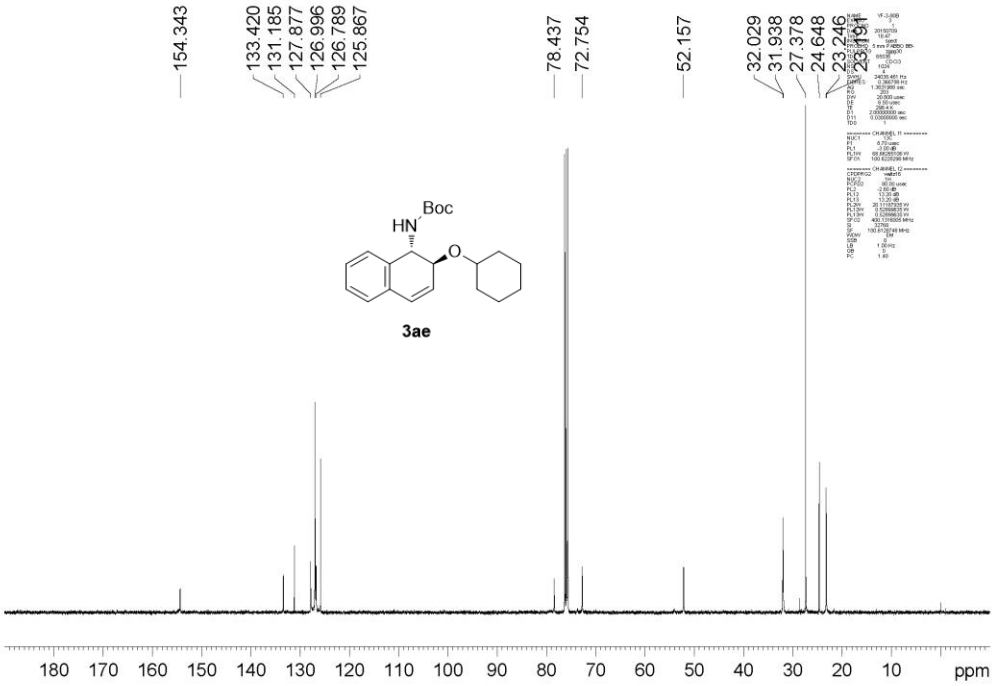

7.277
7.260
7.154
7.145
7.135
7.017
7.000
6.468
6.444
5.944
5.934
5.920
5.910
4.822
4.805
4.790
4.532
4.513
4.070
4.058
4.046
3.863
3.848
3.834
1.380
1.121
1.105
1.083
Boc
HN
O
Me
Me
3ad
8 7 6 5 4 3 2 1 0 ppm
1.03
1.97
1.00
1.00
1.00
1.02
0.93
1.02
1.01
9.29
6.13

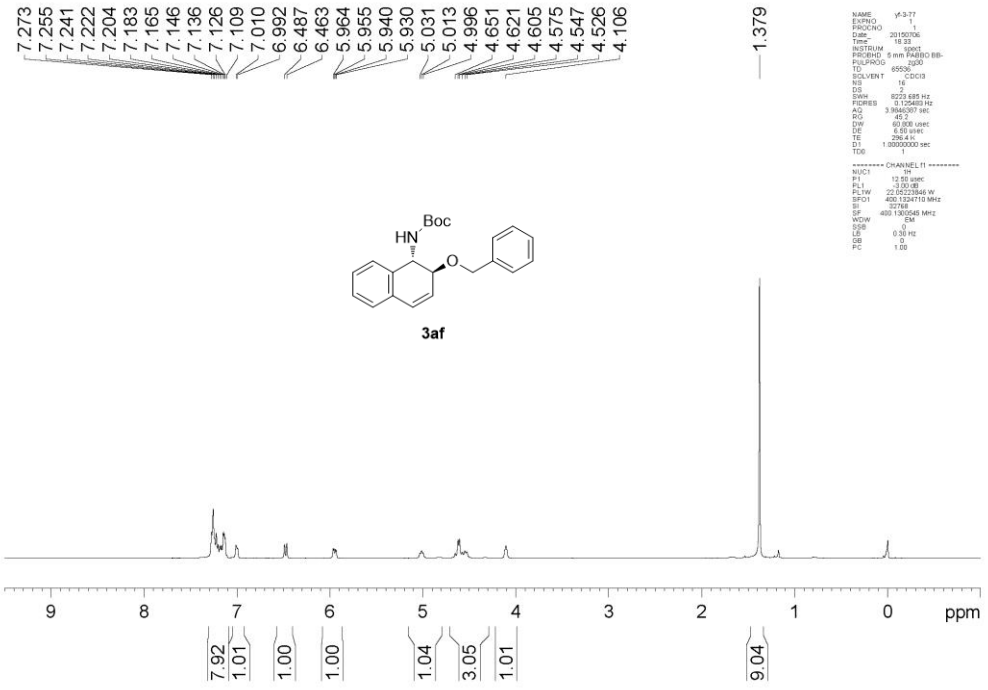

155.357
134.127
132.162
129.148
128.235
128.166
128.101
127.563
127.014
79.554
73.722
70.824
52.807
28.416
23.031
22.710
Boc
HN
O
Me
Me
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

3ad


7.277
7.260
7.185
7.165
7.147
7.138
7.129
7.110
7.011
6.992
6.445
6.421
5.945
5.936
5.921
5.912
4.835
4.818
4.800
4.546
4.526
4.131
4.120
4.109
3.455
1.855
1.831
1.789
1.652
1.464
1.382
1.268
1.219
1.201
1.180
1.146
1.131
Boc
HN
O
8 7 6 5 4 3 2 1 0 ppm
1.04
2.00
1.00
1.00
1.00
1.00
0.96
1.01
1.02
2.07
2.21
10.02
5.09

3ae


154.343
133.420
131.185
127.877
126.996
126.789
125.867
78.437
72.754
52.157
32.029
31.938
27.378
24.648
23.246
Boc
HN
O
3ae
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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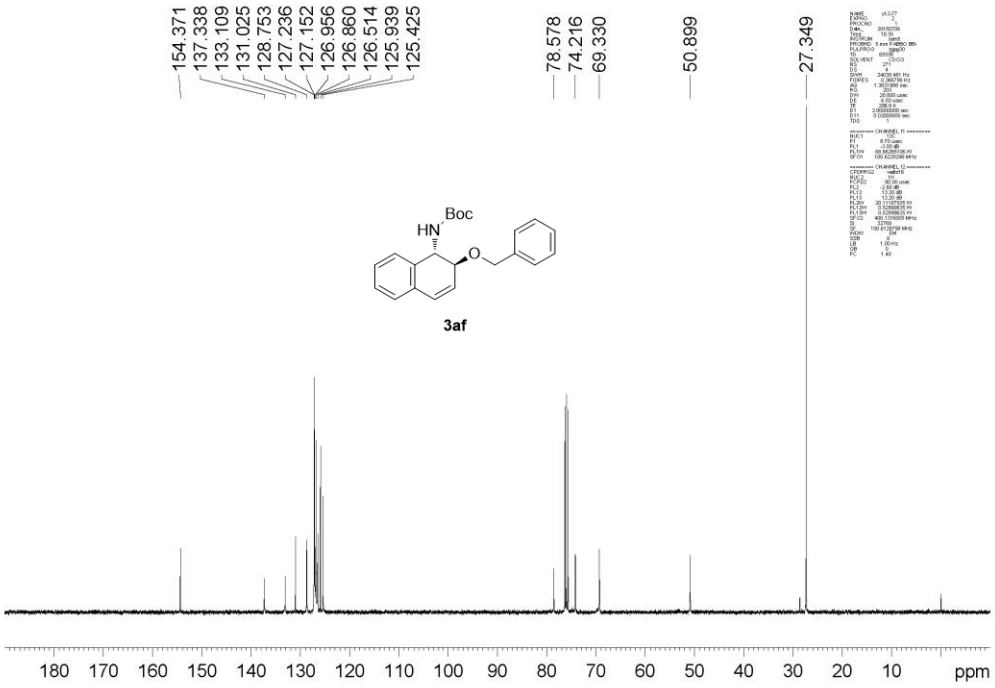
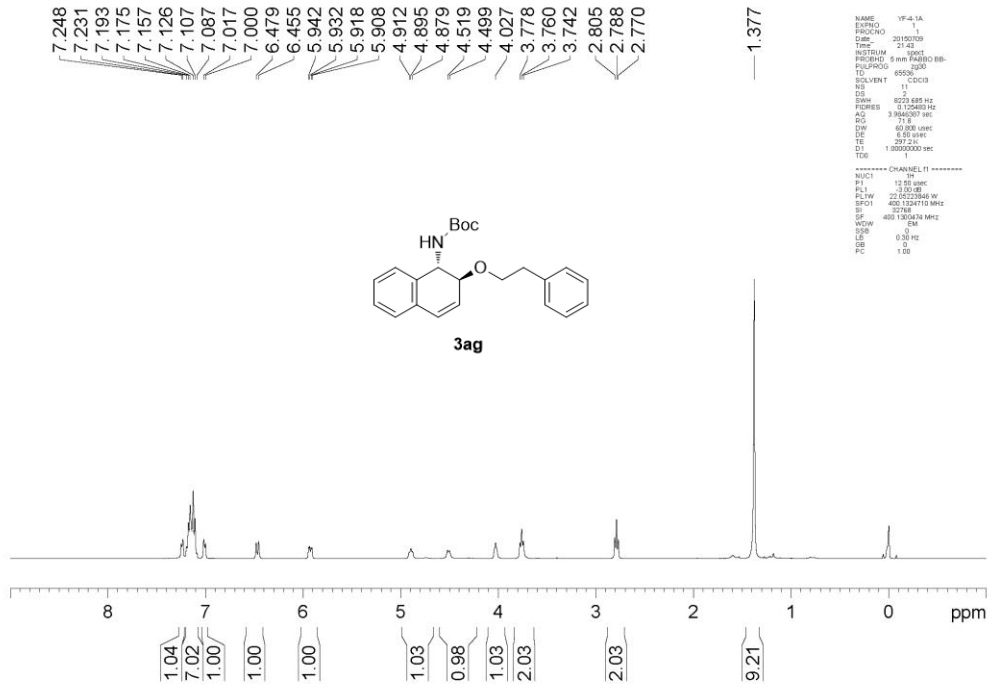
7.255
7.241
7.222
7.204
7.183
7.165
7.146
7.136
7.126
7.109
7.010
6.992
6.487
6.463
5.964
5.955
5.940
5.930
5.031
5.013
4.996
4.651
4.621
4.605
4.575
4.547
4.526
4.106
1.379
Boc
HN
O
3af
9 8 7 6 5 4 3 2 1 0 ppm
7.92
1.01
1.00
1.00
1.04
3.05
1.01
9.04


154.371
137.338
133.109
131.025
128.753
127.236
127.152
126.956
126.860
126.514
125.939
125.425
78.578
74.216
69.330
50.899
27.349
Boc
HN
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

3af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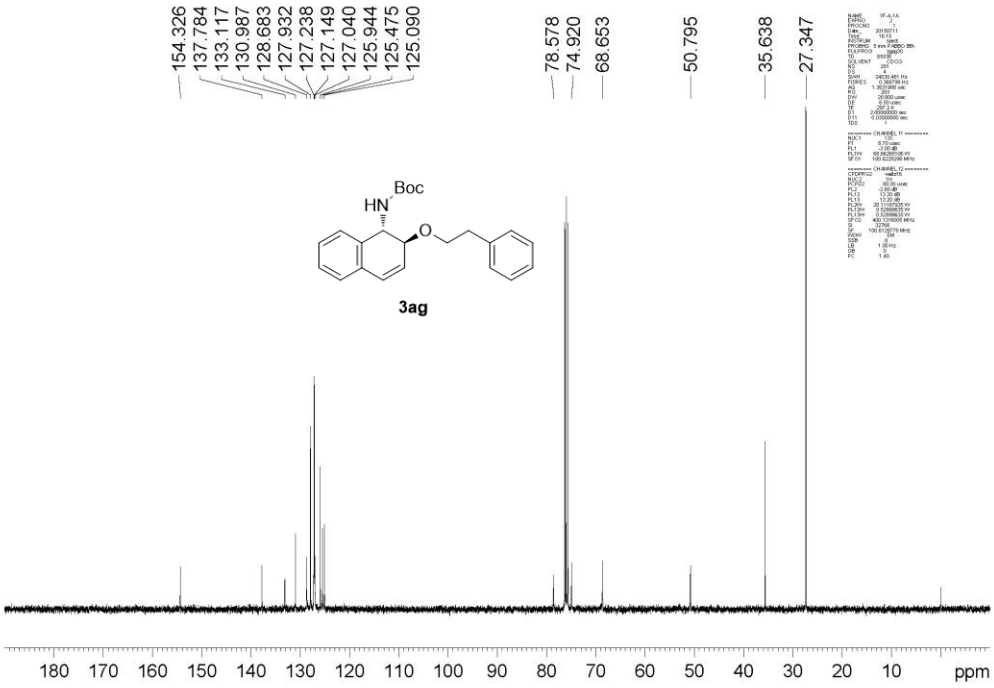
7.231
7.193
7.175
7.157
7.126
7.107
7.087
7.017
7.000
6.479
6.455
5.942
5.932
5.918
5.908
4.912
4.895
4.879
4.519
4.499
4.027
3.778
3.760
3.742
2.805
2.788
2.770
1.377
Boc
HN
O
8 7 6 5 4 3 2 1 0 ppm
1.04
7.02
1.00
1.00
1.00
1.03
0.98
1.03
2.03
2.03
9.21

3ag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130.987
128.683
127.932
127.238
127.149
127.040
125.944
125.475
125.090
78.578
74.920
68.653
50.795
35.638
27.347
Boc
HN
O
3ag
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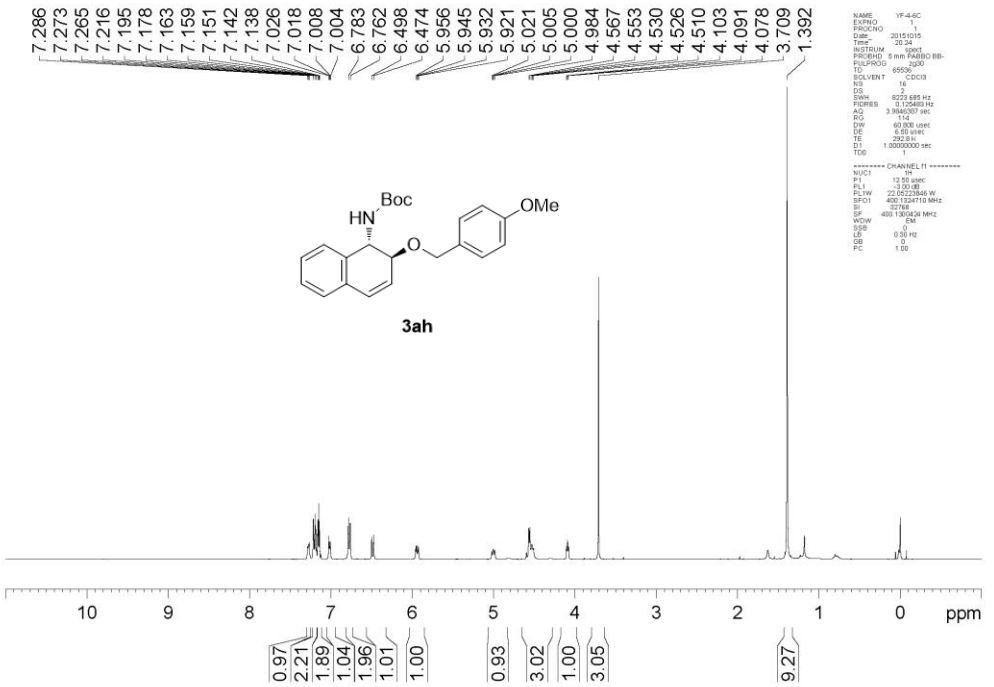
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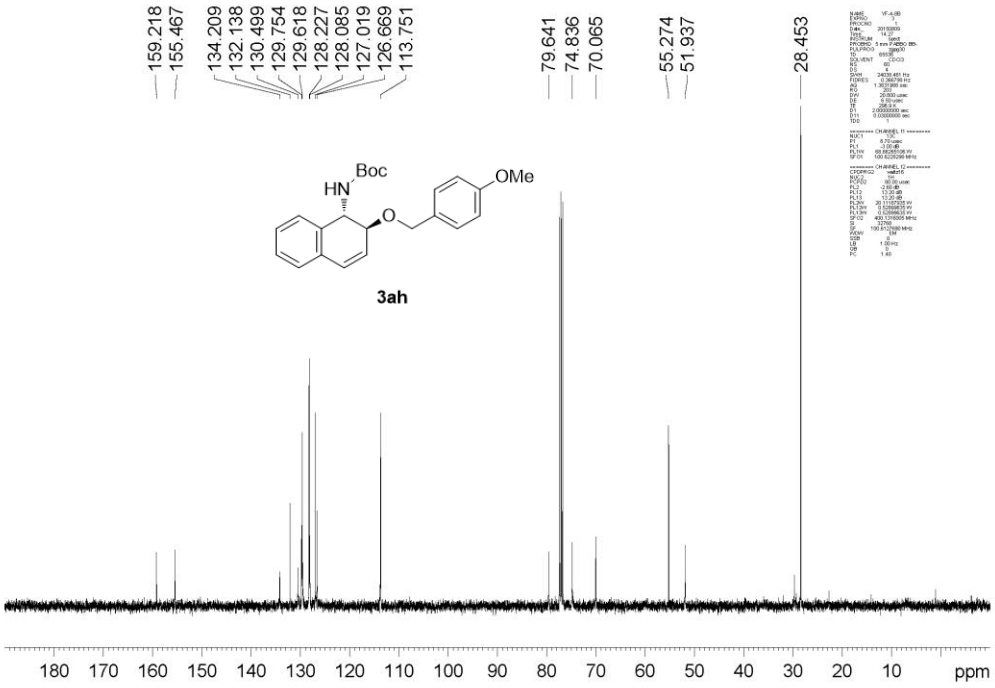
7.273
7.265
7.216
7.195
7.178
7.163
7.159
7.151
7.142
7.138
7.026
7.018
7.008
7.004
6.783
6.762
6.498
6.474
5.956
5.945
5.932
5.921
5.021
5.005
5.000
4.984
4.567
4.553
4.530
4.526
4.510
4.103
4.091
4.078
3.709
1.392
Boc
HN
O
OMe
3ah
10 9 8 7 6 5 4 3 2 1 0 ppm
0.97
2.21
1.89
1.04
1.96
1.01
1.00
0.93
3.02
1.00
3.05
9.27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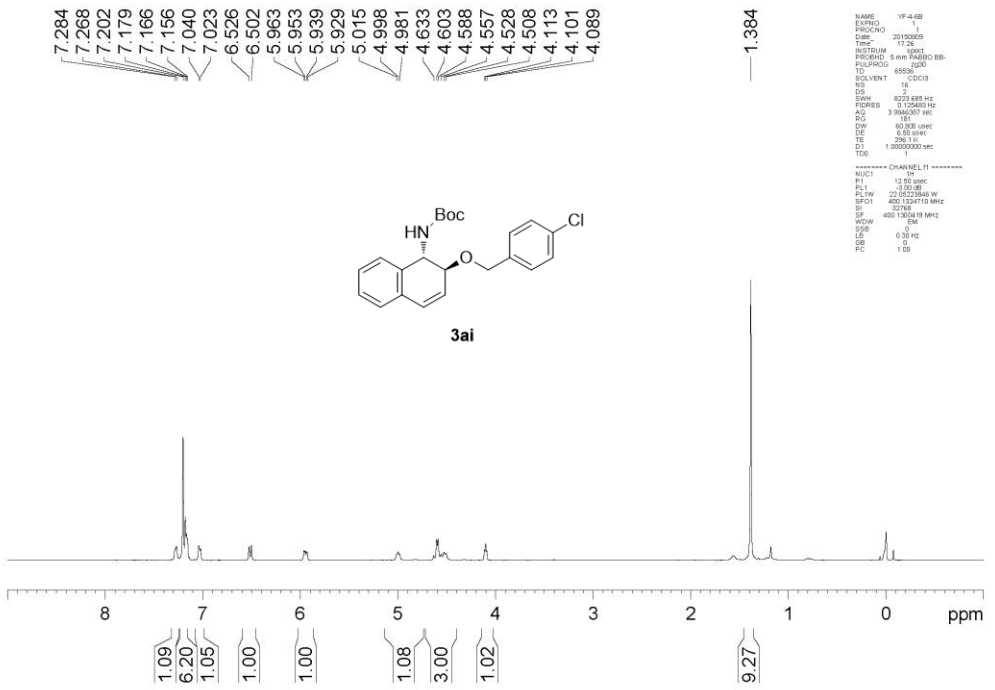
132.138
130.499
129.754
129.618
128.227
128.085
127.019
126.669
113.751
79.641
74.836
70.065
55.274
51.937
28.453
Boc
HN
O
OMe
3ah
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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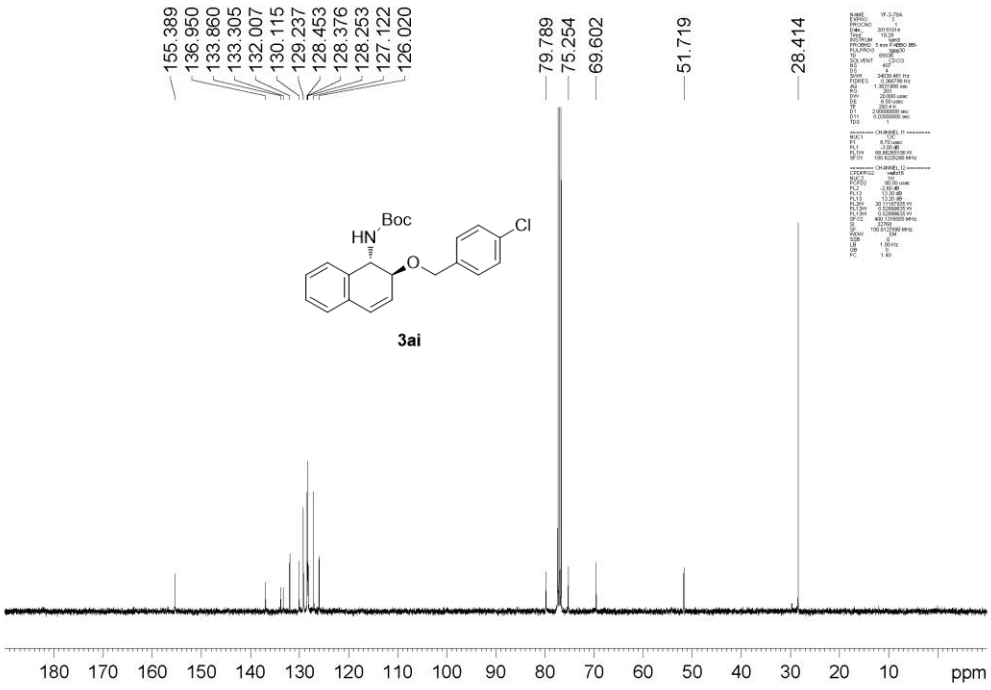
7.179
7.166
7.156
7.040
7.023
6.526
6.502
5.963
5.953
5.939
5.929
5.015
4.998
4.981
4.633
4.603
4.588
4.557
4.528
4.508
4.113
4.101
4.089
1.384
Boc
HN
O
Cl
3ai
8 7 6 5 4 3 2 1 0 ppm
1.09
6.20
1.05
1.00
1.00
1.08
3.00
1.02
9.27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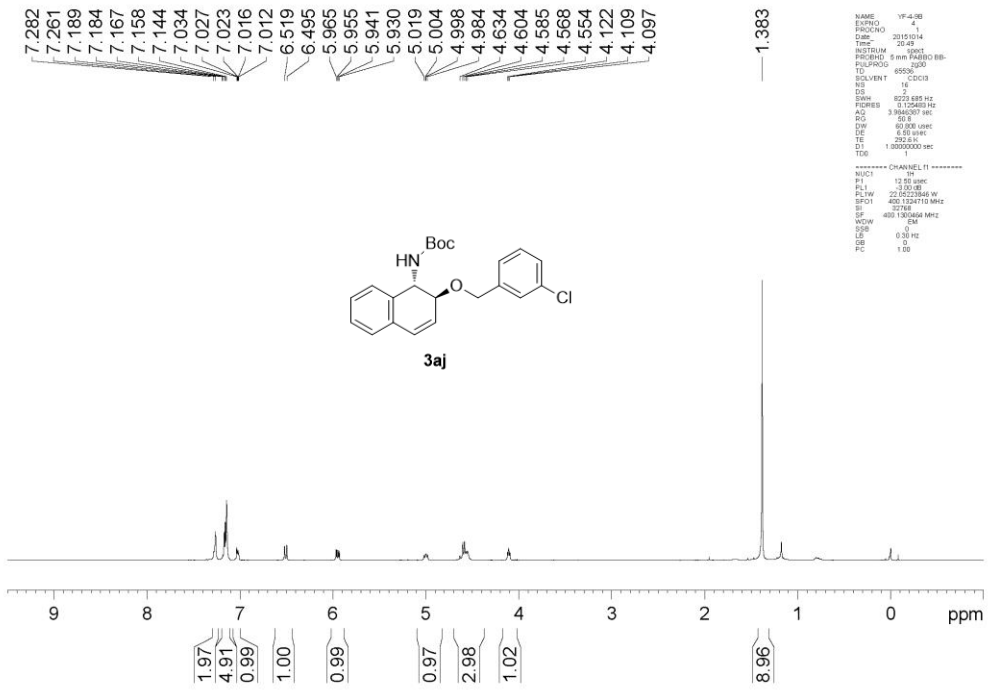
133.305
132.007
130.115
129.237
128.453
128.376
128.253
127.122
126.020
79.789
75.254
69.602
51.719
28.414
Boc
HN
O
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

3ai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7.184
7.167
7.158
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7.027
7.023
7.016
7.012
6.519
6.495
5.965
5.955
5.941
5.930
5.019
5.004
4.998
4.984
4.634
4.604
4.585
4.568
4.554
4.122
4.109
4.097
1.383
Boc
HN
O
Cl
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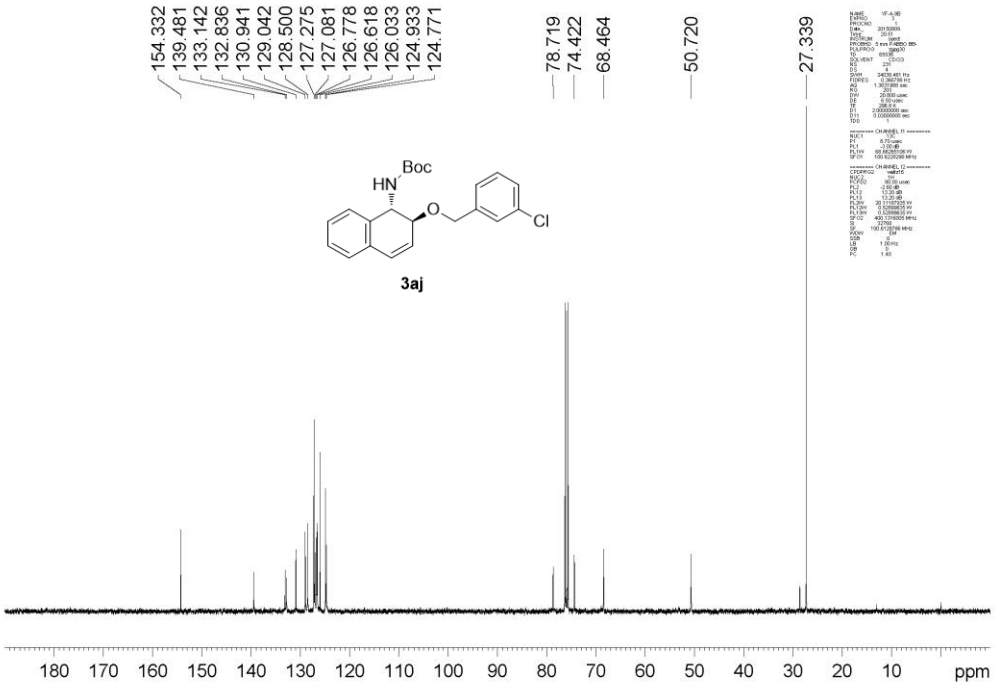
4.91
0.99
1.00
0.99
0.97
2.98
1.02
8.96

3aj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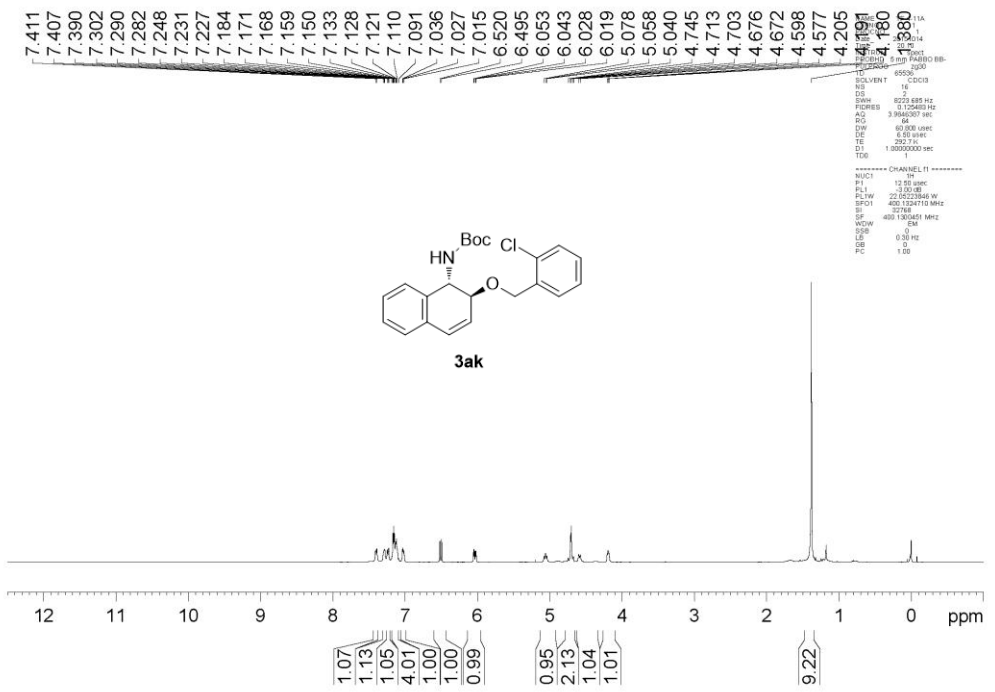
127.275
127.081
126.778
126.618
126.033
124.933
124.771
78.719
74.422
68.464
50.720
27.339
Boc
HN
O
Cl
3aj
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.227
7.184
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7.168
7.159
7.150
7.133
7.128
7.121
7.110
7.091
7.036
7.027
7.015
6.520
6.495
6.053
6.043
6.028
6.019
5.078
5.058
5.040
4.745
4.713
4.703
4.676
4.672
4.598
4.577
4.205
4.191
4.180
Boc
HN
Cl
O
3ak
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.07
1.13
1.05
4.01
1.00
1.00
0.99
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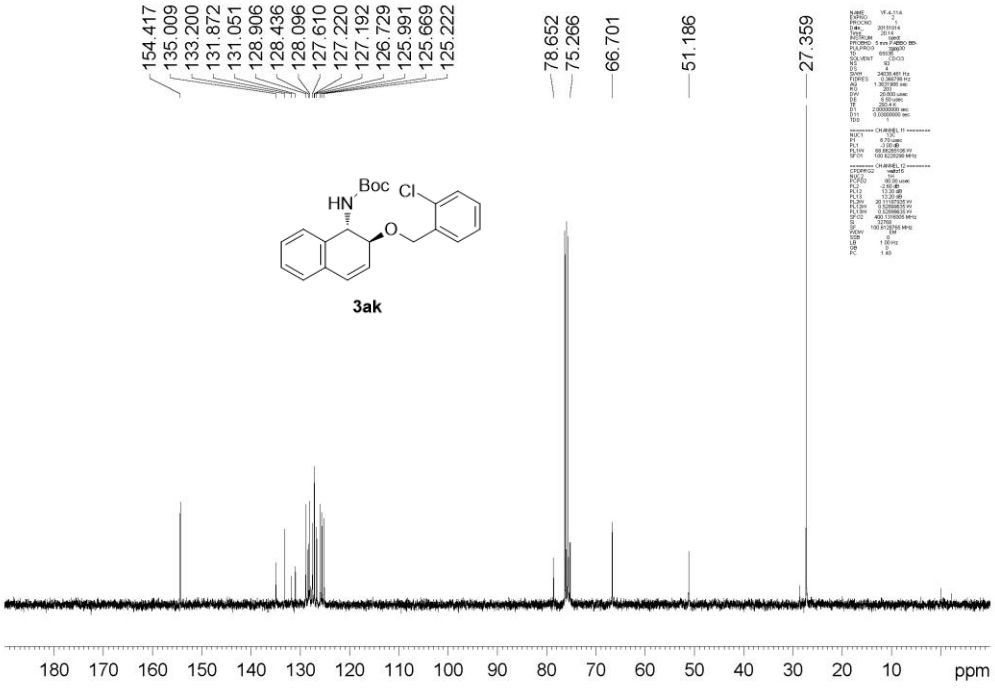
1.01
9.22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128.436
128.096
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127.192
126.729
125.991
125.669
125.222
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51.186
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Boc
HN
Cl
O
3ak
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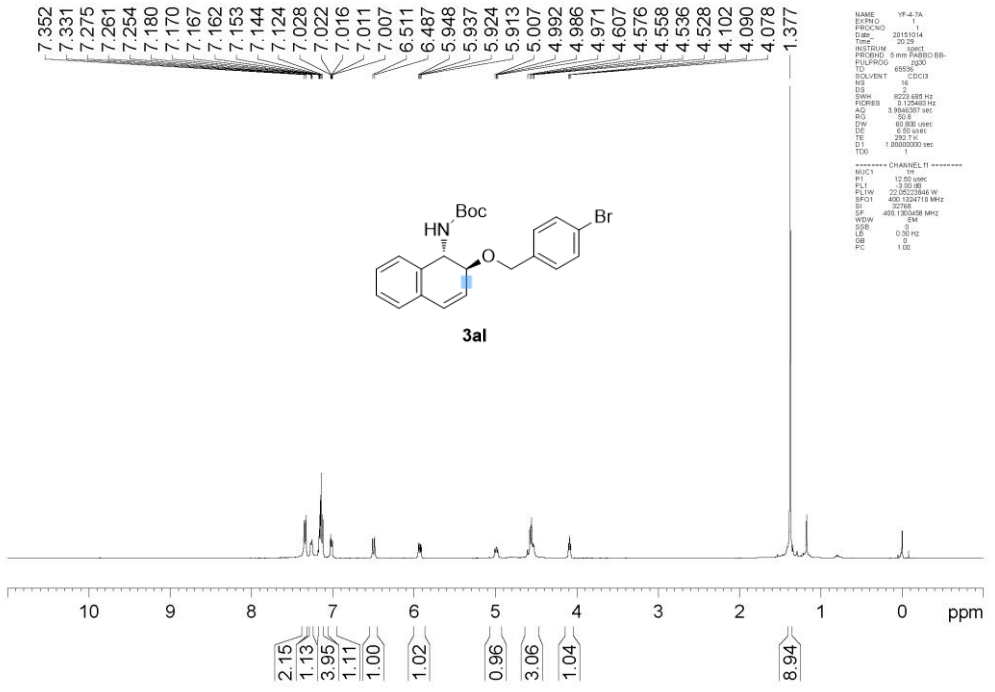
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7.167
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7.028
7.022
7.016
7.011
7.007
6.511
6.487
5.948
5.937
5.924
5.913
5.007
4.992
4.986
4.971
4.607
4.576
4.558
4.536
4.528
4.102
4.090
4.078
1.377
Boc
HN
O
Br
3al
10 9 8 7 6 5 4 3 2 1 0 ppm
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1.13
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1.00
1.02
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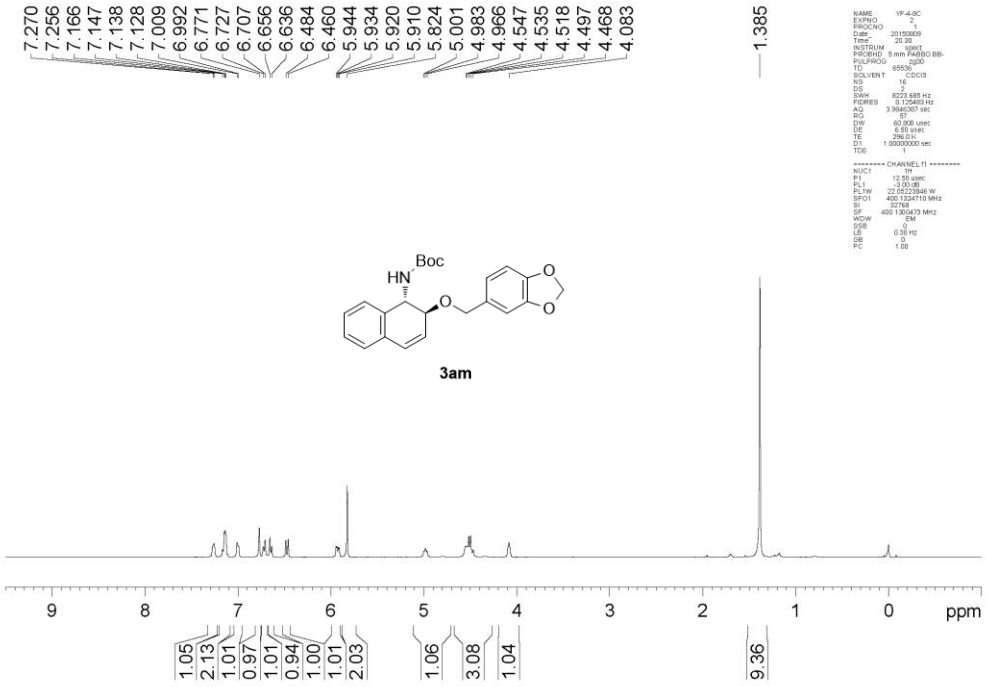
1.04
8.94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6.992
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6.707
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6.636
6.484
6.460
5.944
5.934
5.920
5.910
5.824
5.001
4.983
4.966
4.547
4.535
4.518
4.497
4.468
4.083
1.385
Boc
HN
O
O
O
3am
9
8
7
6
5
4
3
2
1
0
ppm
1.05
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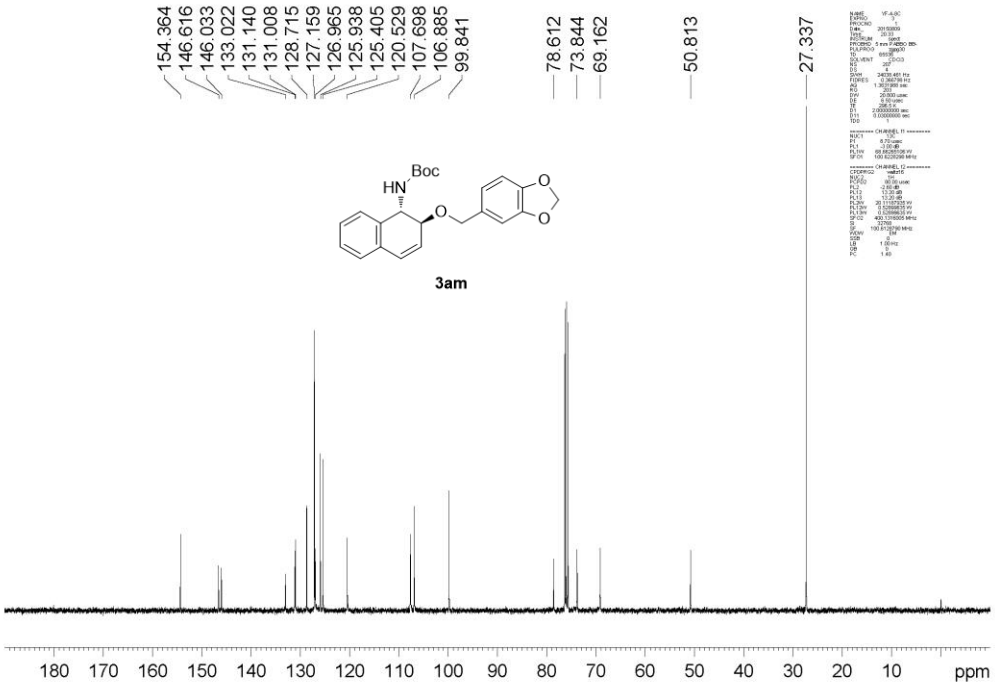
1.04
9.36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146.033
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128.715
127.159
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125.405
120.529
107.698
106.885
99.841
78.612
73.844
69.162
50.813
27.337
Boc
HN
O
O
O
3am
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150
140
130
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110
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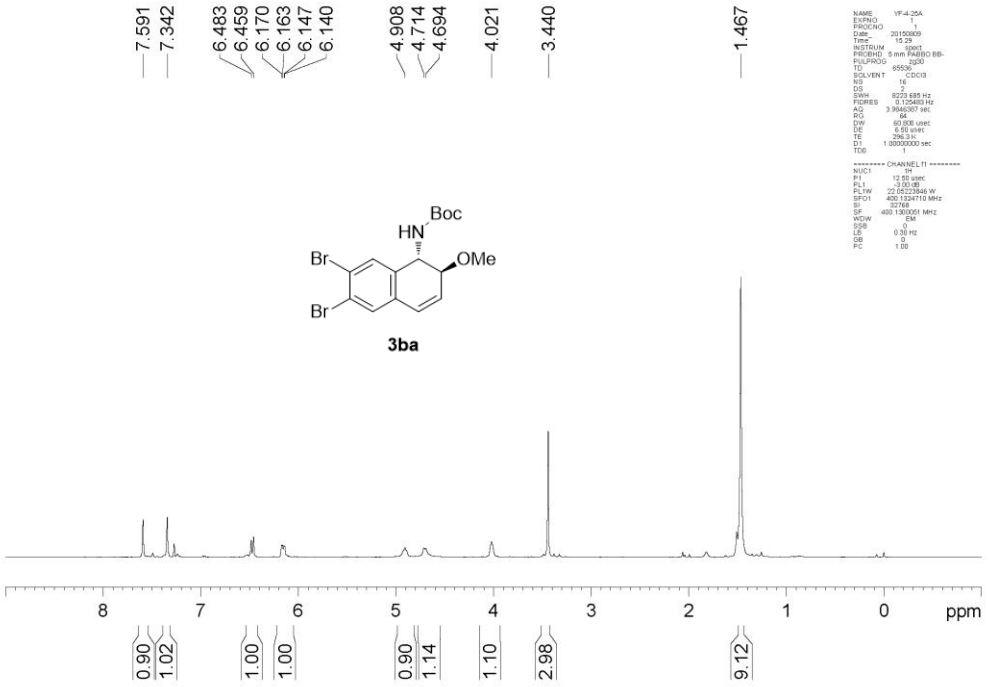
90
80
70
60
50
40
30
20
10
ppm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6.163
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6.140
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4.694
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3.440
1.467
Boc
HN
Br
Br
OMe
3ba
8
7
6
5
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ppm
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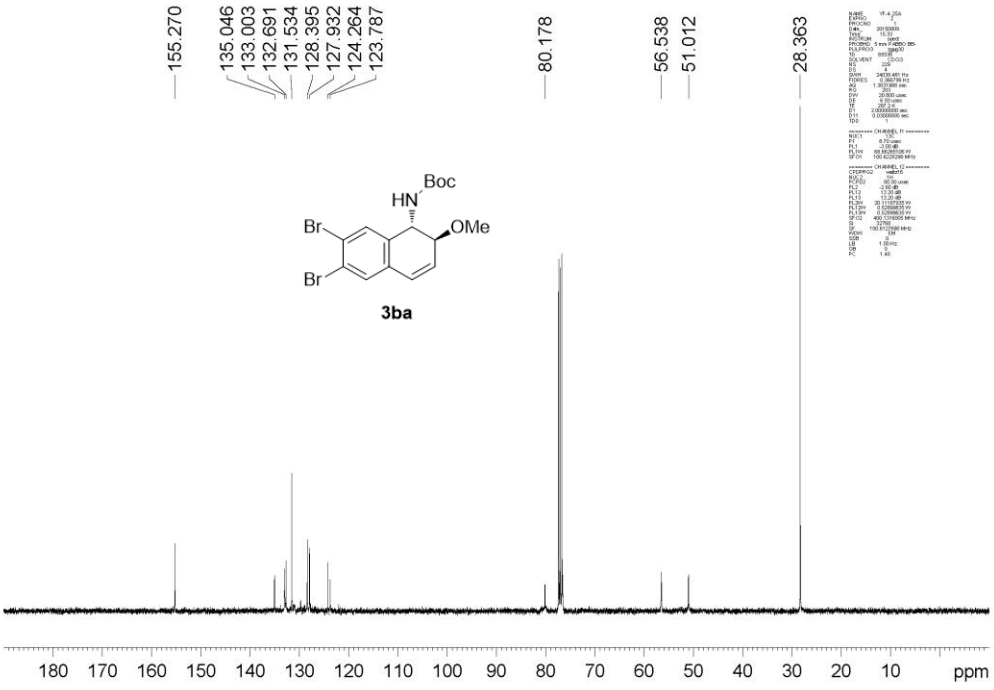
9.12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124.264
123.787
80.178
56.538
51.012
28.363
Boc
HN
Br
Br
OMe
3ba
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150
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70
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50
40
30
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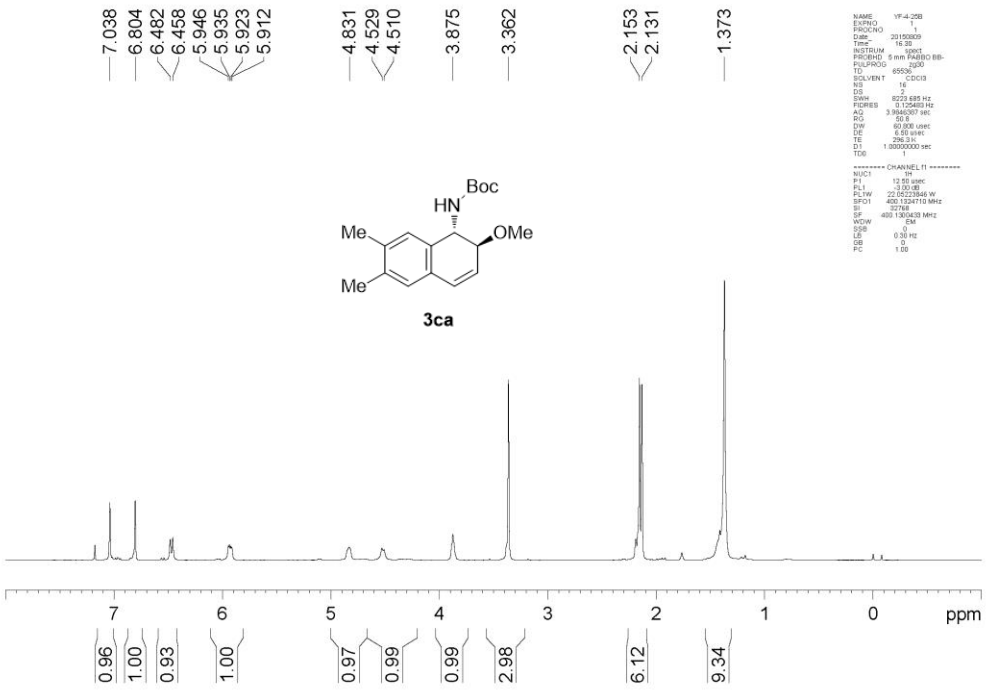
ppm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6.482
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5.935
5.923
5.912
4.831
4.529
4.510
3.875
3.362
2.153
2.131
1.373
Boc
HN
Me
OMe
Me
3ca
7
6
5
4
3
2
1
0
ppm
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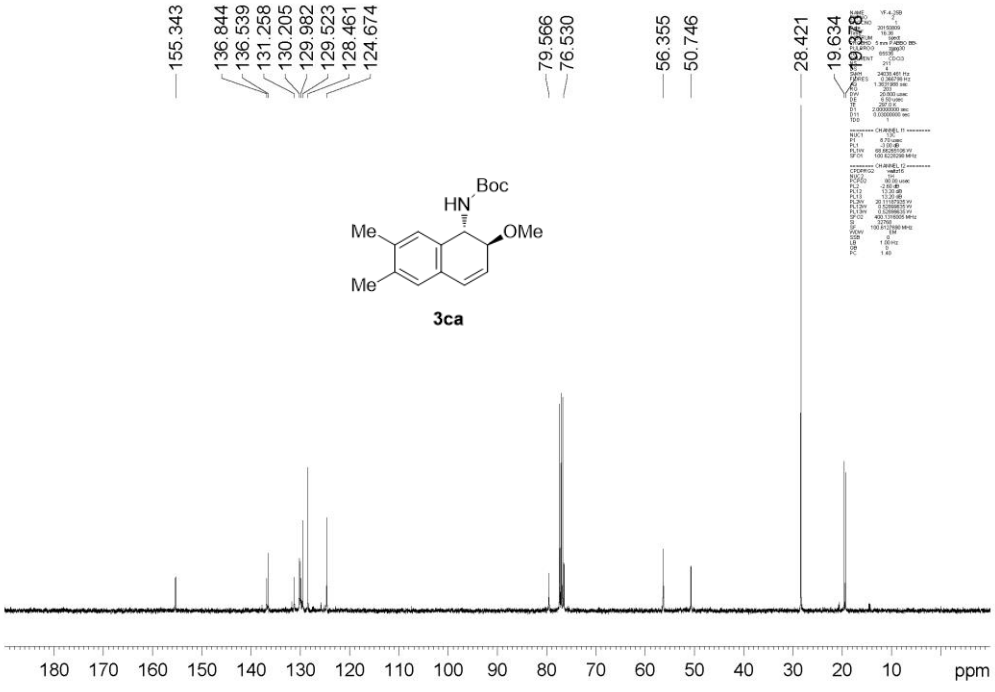
1.00
0.93
1.00
0.97
0.99
0.99
2.98
6.12
9.34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136.539
131.258
130.205
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129.523
128.461
124.674
79.566
76.530
56.355
50.746
28.421
19.634
Boc
HN
Me
OMe
Me
3ca
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150
140
130
120
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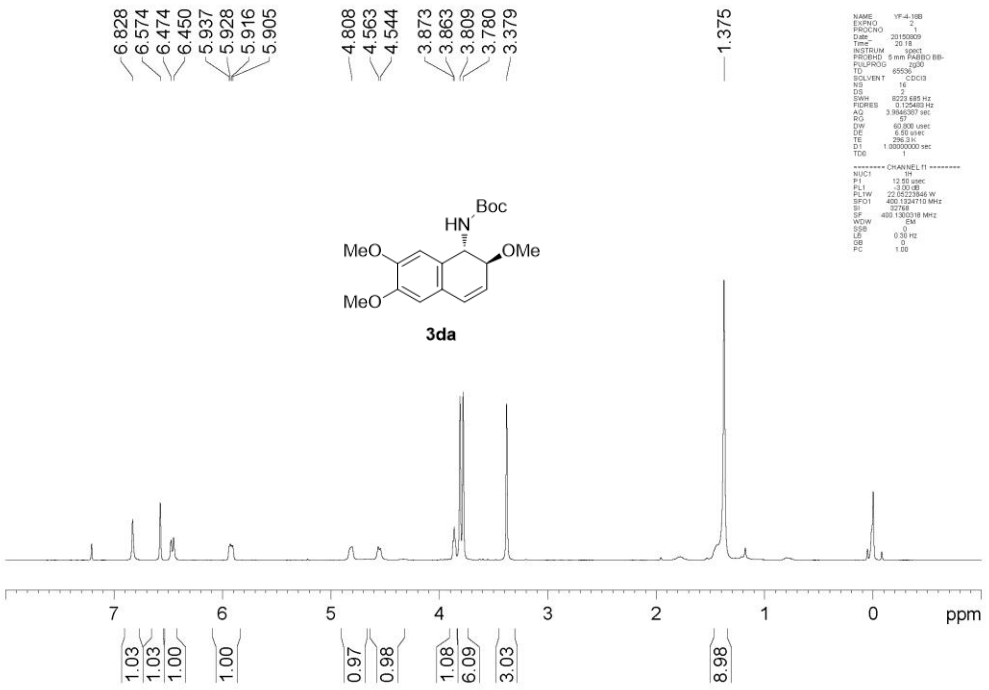
100
90
80
70
60
50
40
30
20
10
ppm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6.574
6.474
6.450
5.937
5.928
5.916
5.905
4.808
4.563
4.544
3.873
3.863
3.809
3.780
3.379
1.375
Boc
HN
MeO
OMe
MeO
3da
7
6
5
4
3
2
1
0
ppm
1.03
1.03
1.00
1.00
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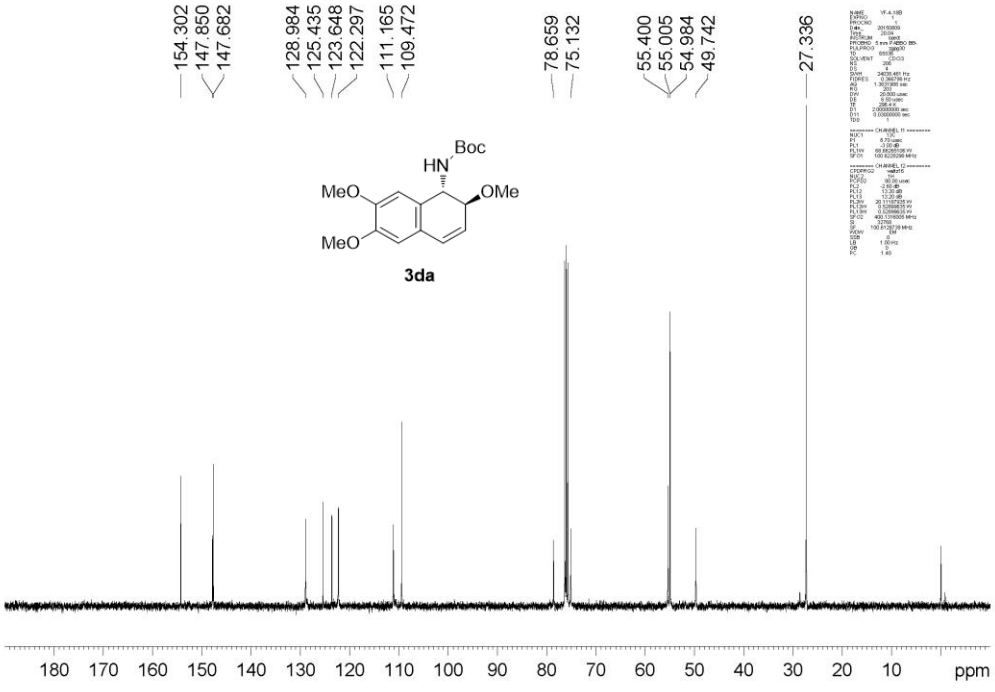
0.98
1.08
6.09
3.03
8.98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123.648
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111.165
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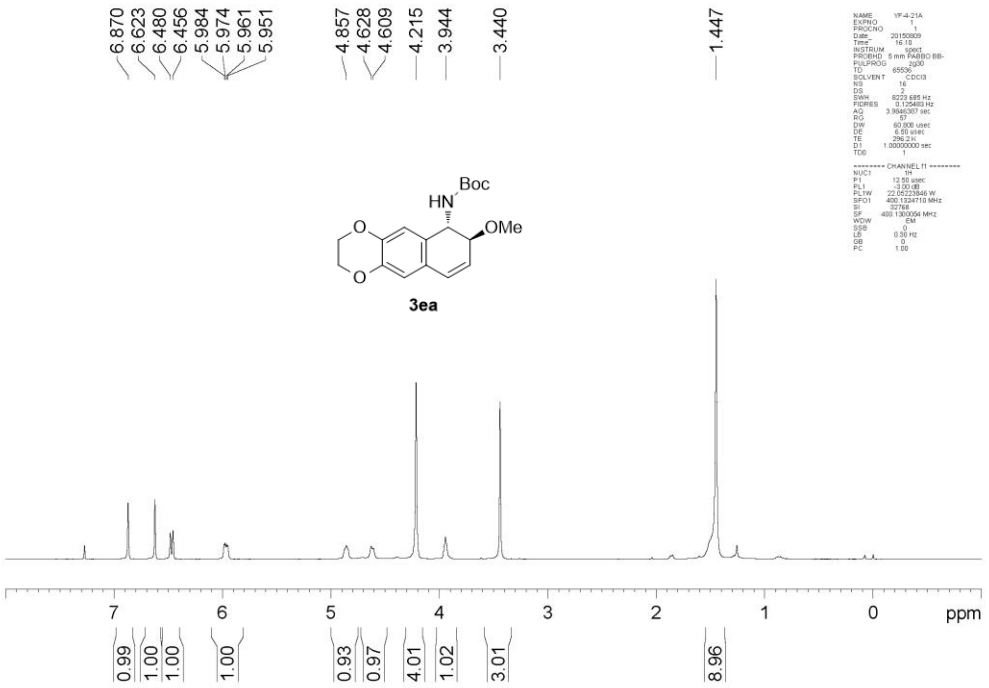
78.659
75.132
55.400
55.005
54.984
49.742
27.336
Boc
HN
MeO
OMe
MeO
3da
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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6.623
6.480
6.456
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5.974
5.961
5.951
4.857
4.628
4.609
4.215
3.944
3.440
1.447
Boc
HN
OMe
O
O
3ea
7
6
5
4
3
2
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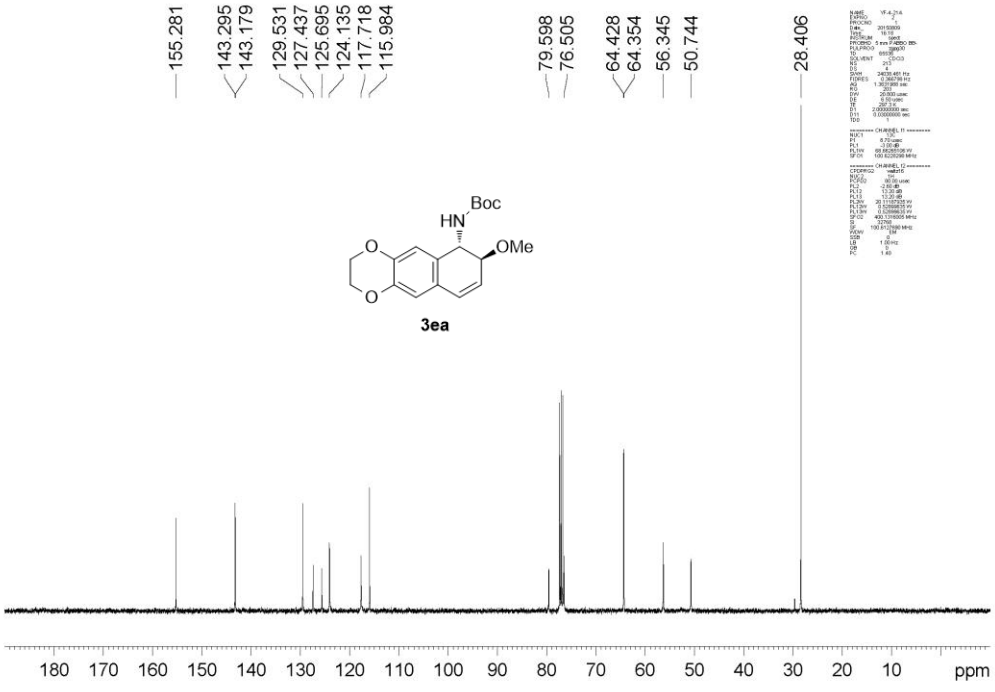
0
ppm
0.99
1.00
1.00
1.00
0.93
0.97
4.01
1.02
3.01
8.96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117.718
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79.598
76.505
64.428
64.354
56.345
50.744
28.406
Boc
HN
OMe
O
O
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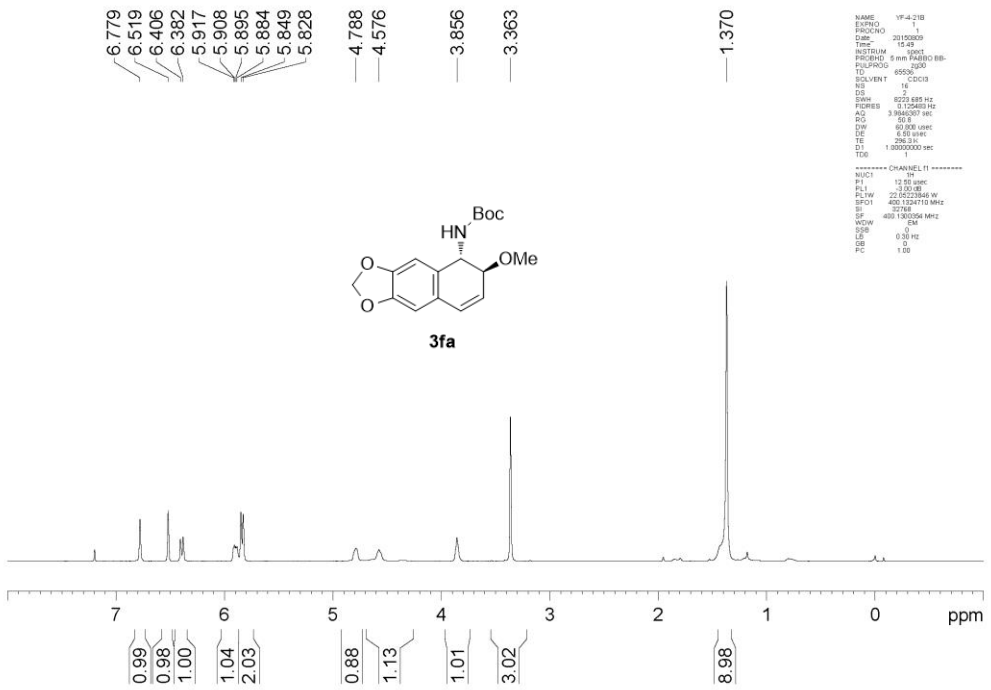
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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5.884
5.849
5.828
4.788
4.576
3.856
3.363
1.370
Boc
HN
OMe
O
O
3fa
7
6
5
4
3
2
1
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ppm
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0.98
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1.04
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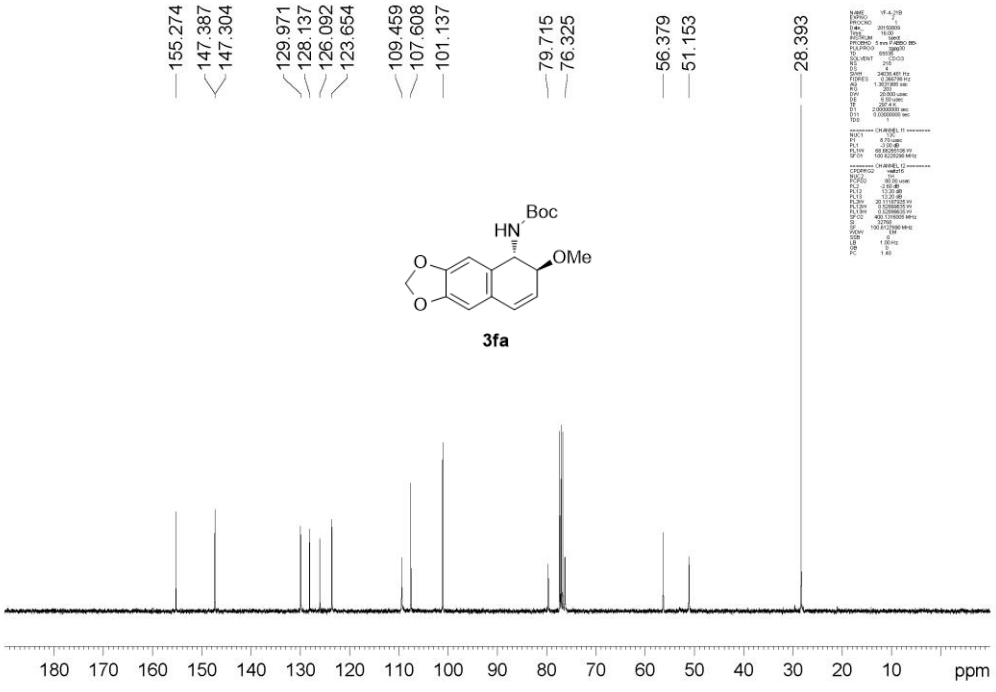
1.01
3.02
8.98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101.137
79.715
76.325
56.379
51.153
28.393
Boc
HN
OMe
O
O
3fa
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150
140
130
120
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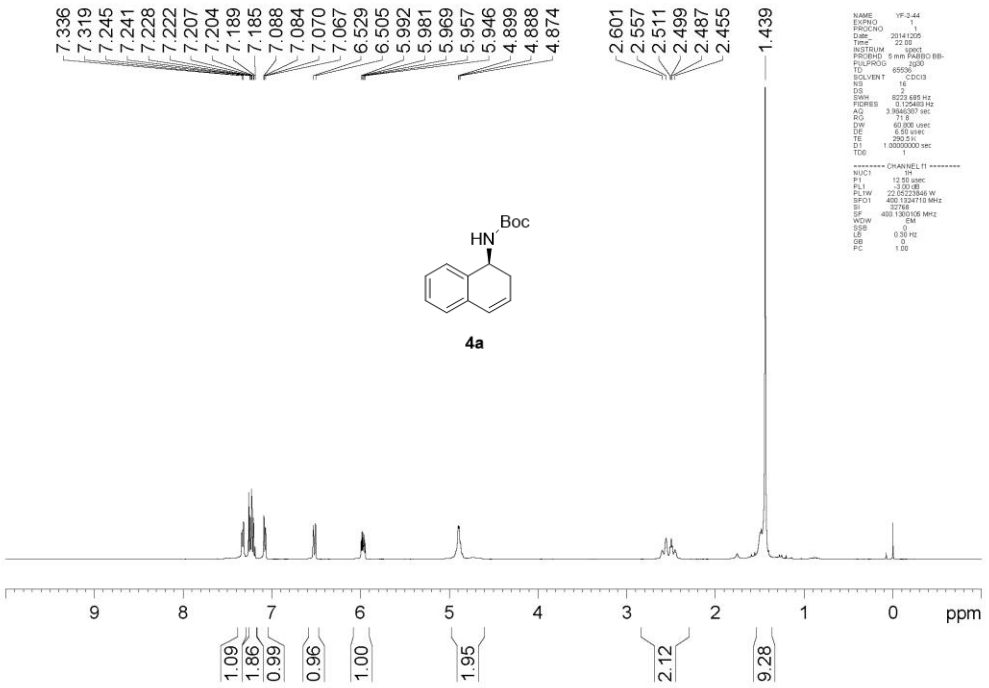
90
80
70
60
50
40
30
20
10
ppm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7.204
7.189
7.185
7.088
7.084
7.070
7.067
6.529
6.505
5.992
5.981
5.969
5.957
5.946
4.899
4.888
4.874
2.601
2.557
2.511
2.499
2.487
2.455
1.439
Boc
HN
4a
9
8
7
6
5
4
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1
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ppm
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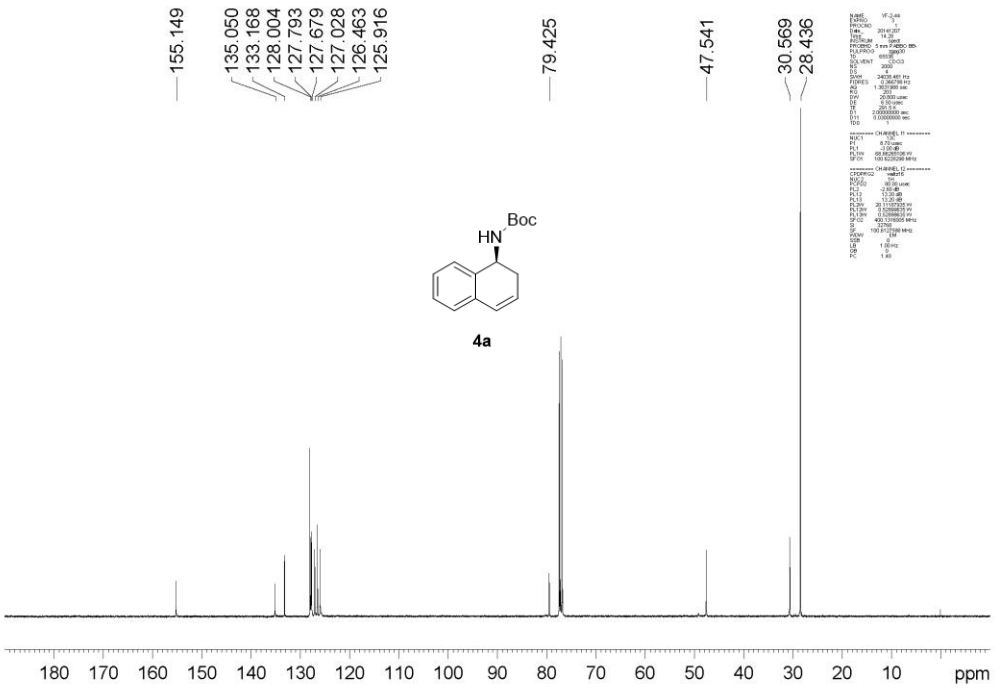
9.28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30.569
28.436
Boc
HN
4a
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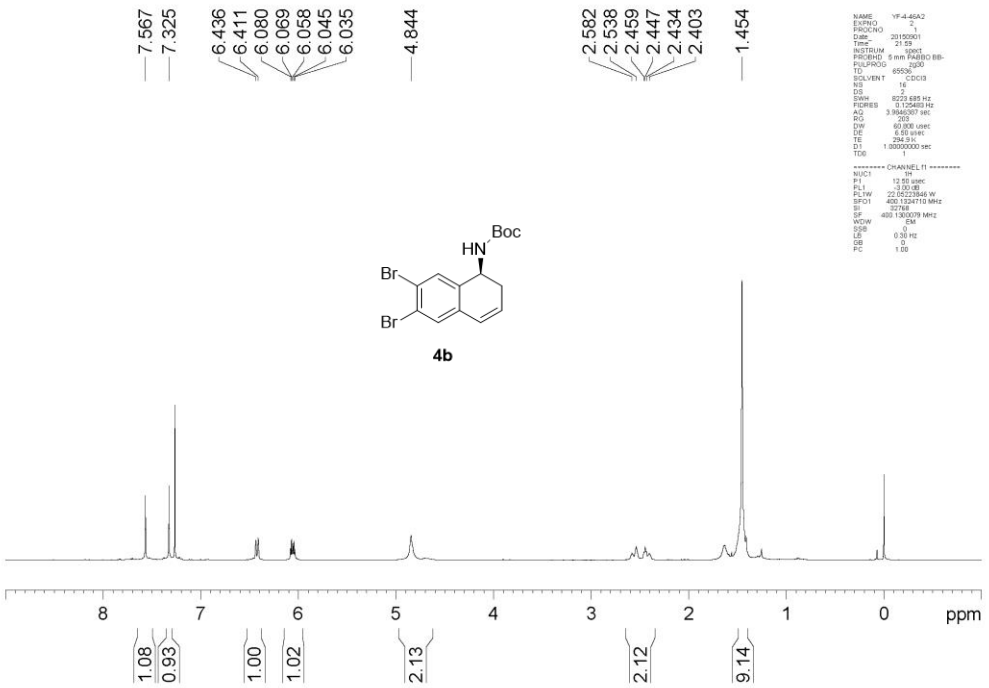
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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6.035
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2.459
2.447
2.434
2.403
1.454
Boc
HN
Br
Br
4b
8
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1
0
ppm
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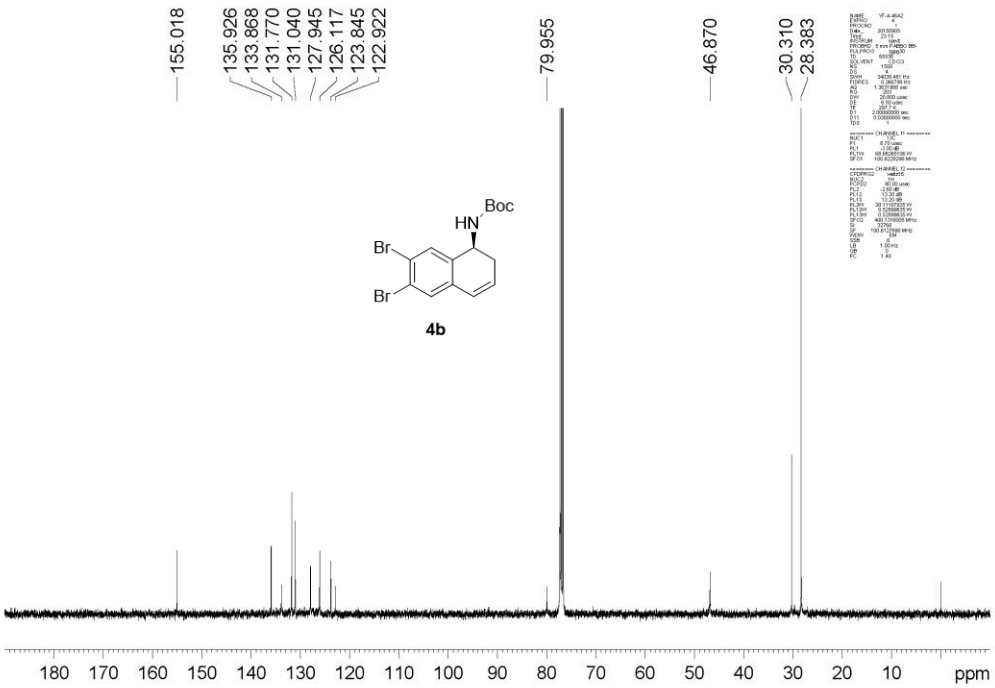
1.00
1.02
2.13
2.12
9.14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123.845
122.922
79.955
46.870
30.310
28.383
Boc
HN
Br
Br
4b
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150
140
130
120
110
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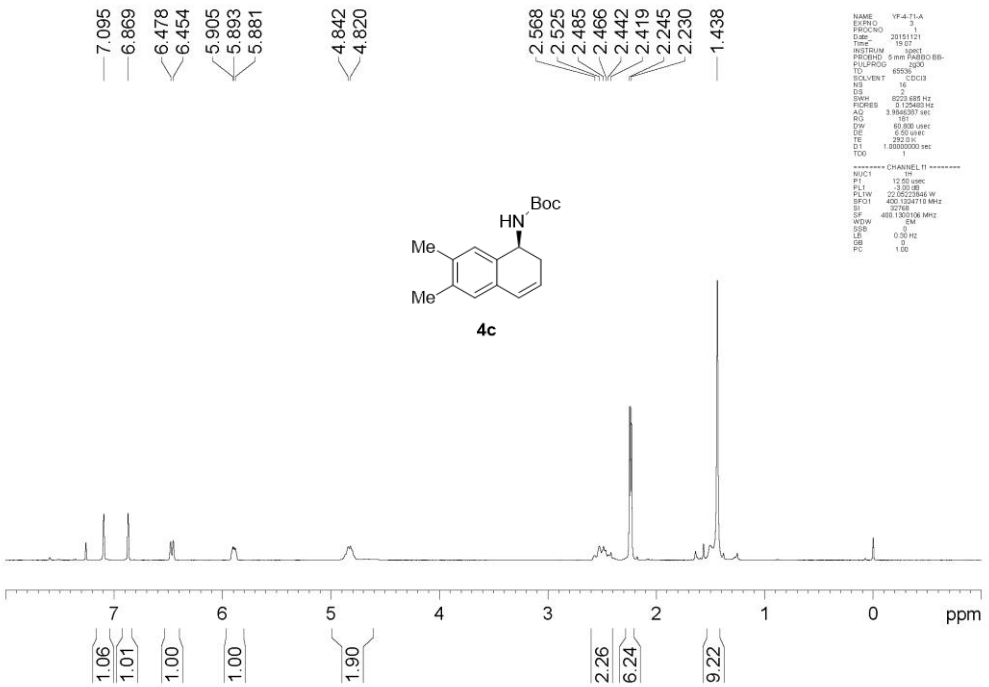
70
60
50
40
30
20
10
ppm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4.820
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2.525
2.485
2.466
2.442
2.419
2.245
2.230
1.438
Boc
HN
Me
Me
4c
7
6
5
4
3
2
1
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ppm
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1.00
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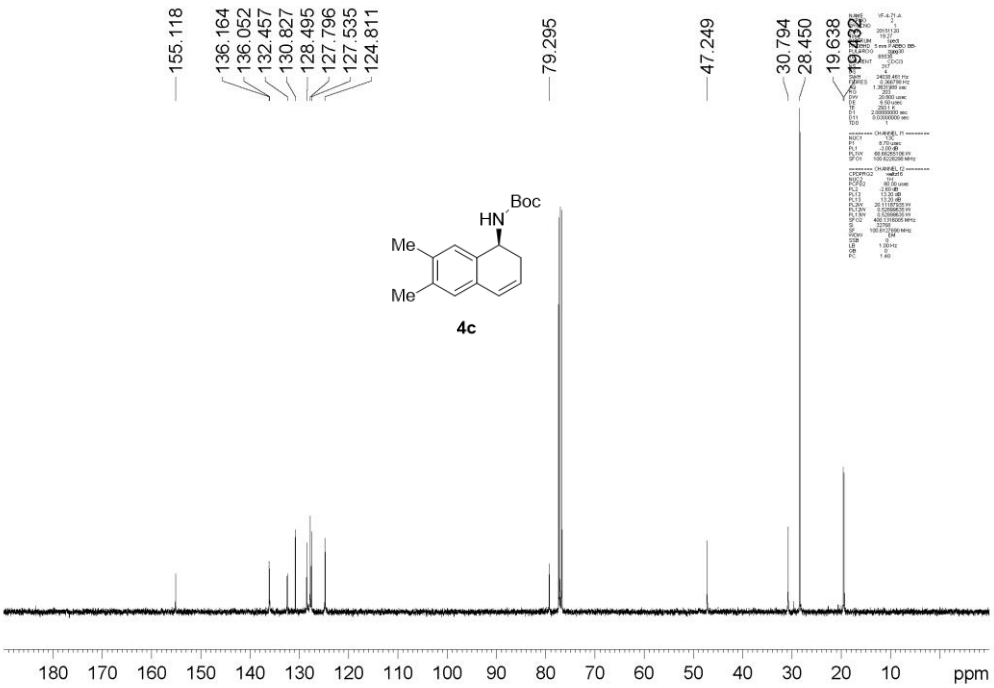
9.22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127.535
124.811
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47.249
30.794
28.450
19.638
19.432
Boc
HN
Me
Me
4c
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150
140
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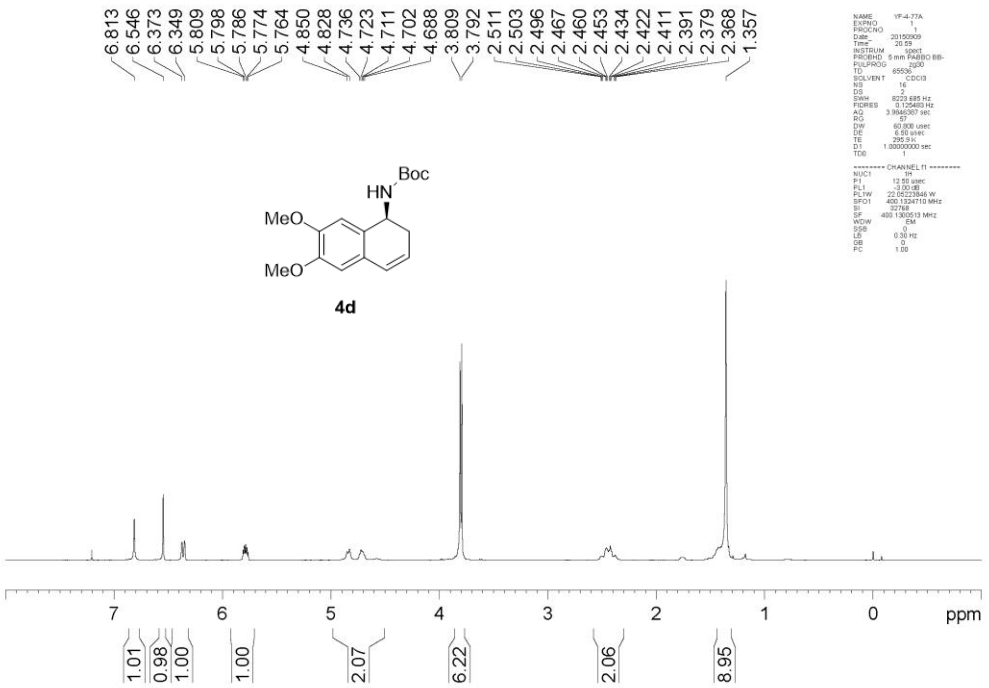
30
20
10
ppm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5.774
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4.723
4.711
4.702
4.688
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3.792
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2.503
2.496
2.467
2.460
2.453
2.434
2.422
2.411
2.391
2.379
2.368
1.357
Boc
HN
MeO
MeO
4d
7
6
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ppm
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1.00
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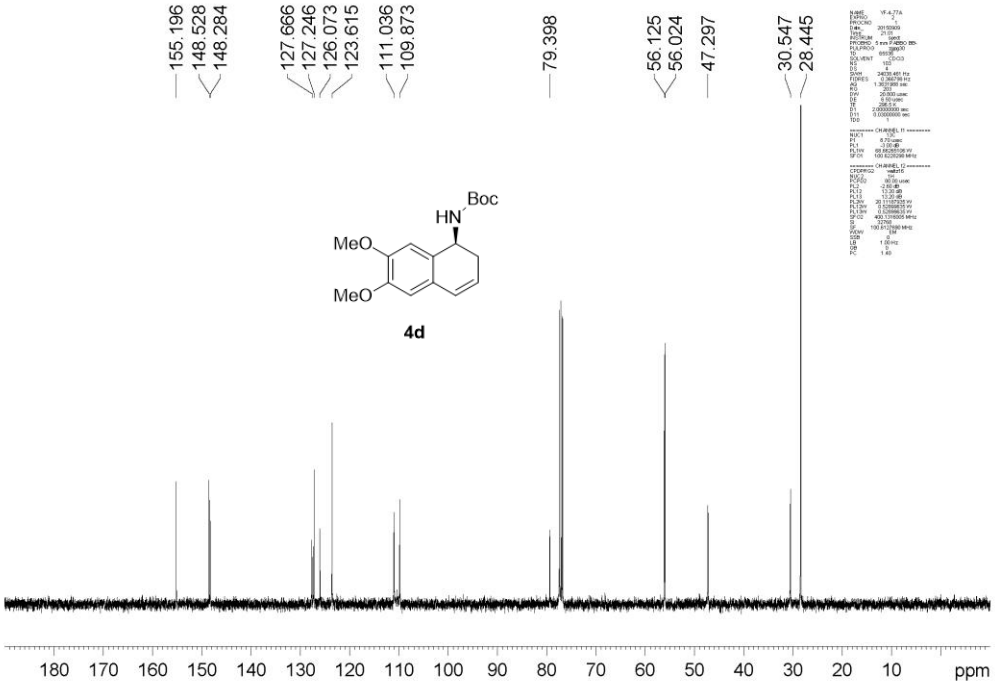
2.06
8.95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111.036
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79.398
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56.024
47.297
30.547
28.445
Boc
HN
MeO
MeO
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150
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70
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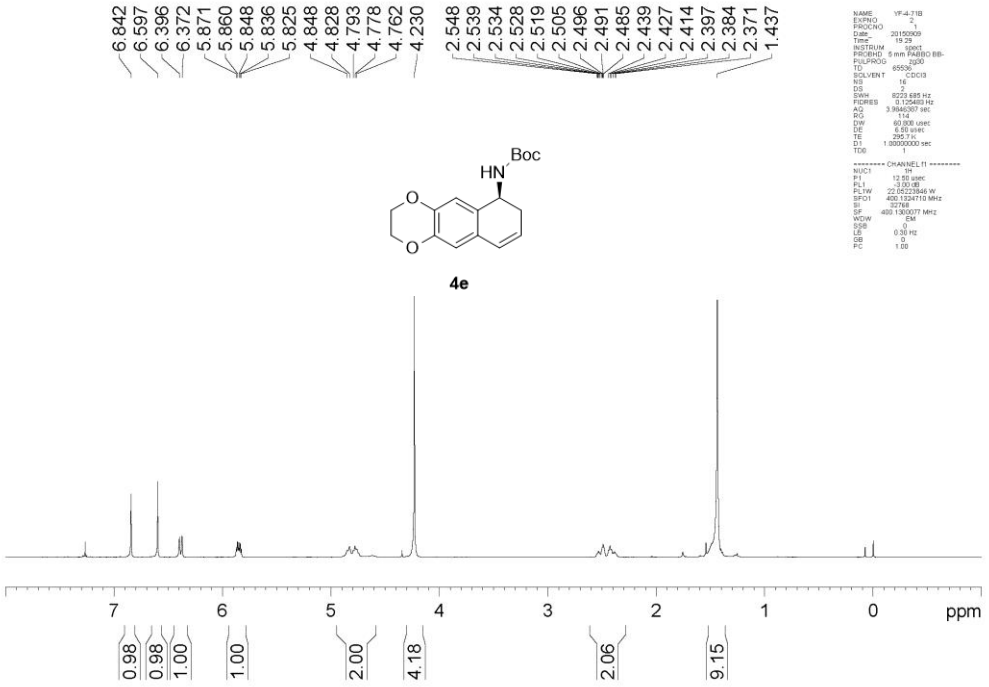
30
20
10
ppm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5.836
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4.793
4.778
4.762
4.230
2.548
2.539
2.534
2.528
2.519
2.505
2.496
2.491
2.485
2.439
2.427
2.414
2.397
2.384
2.371
1.437
Boc
HN
O
O
4e
7
6
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1.00
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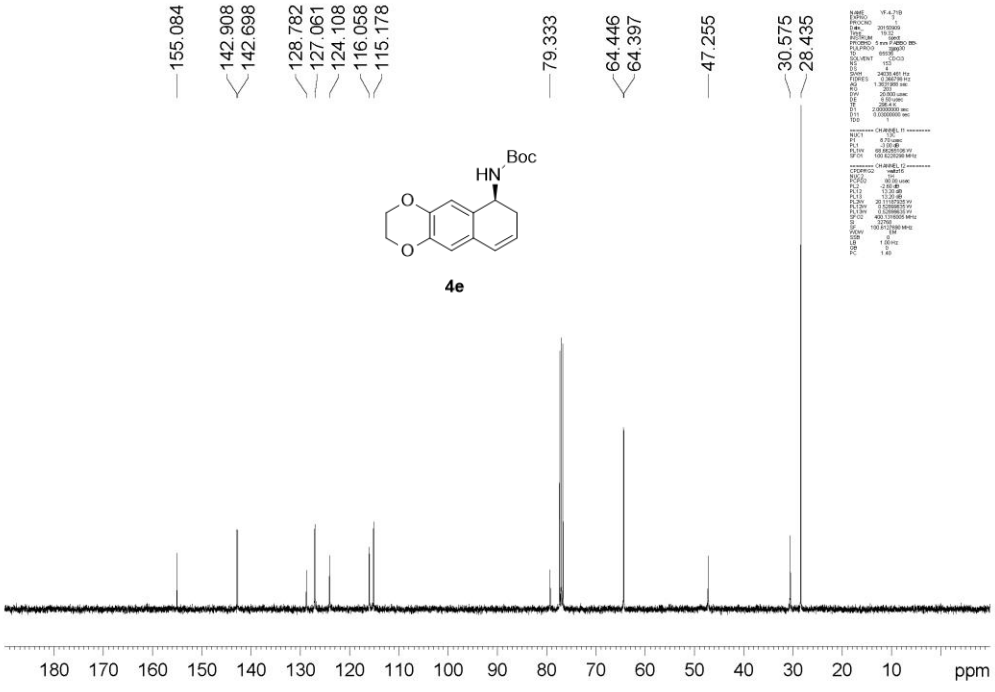
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64.397
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28.435
Boc
HN
O
O
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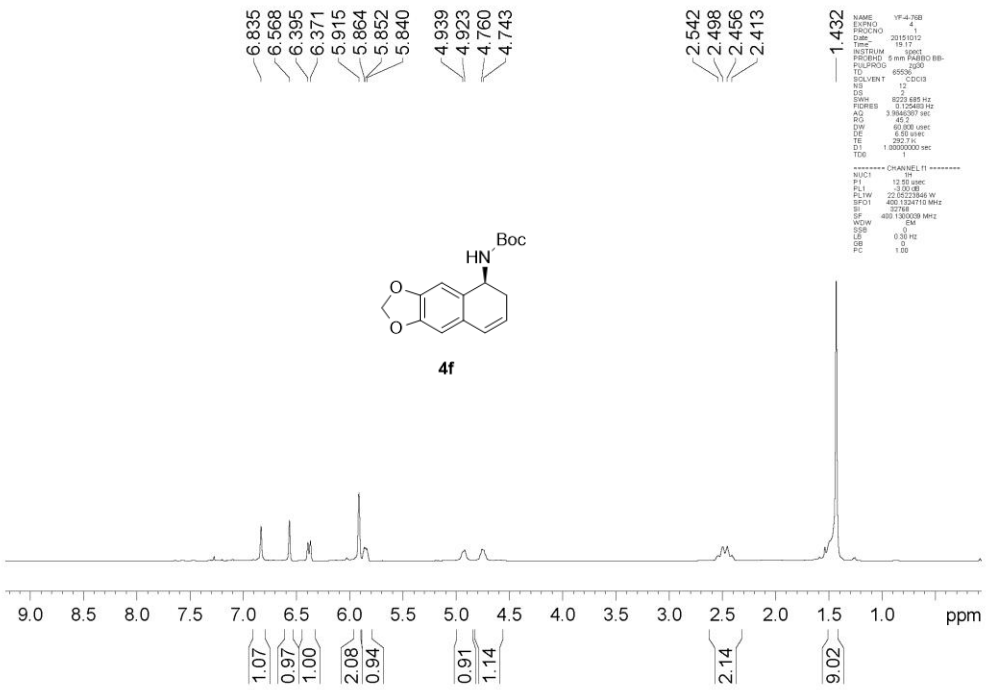
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5.864
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5.840
4.939
4.923
4.760
4.743
2.542
2.498
2.456
2.413
1.432
Boc
HN
O
O
4f
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
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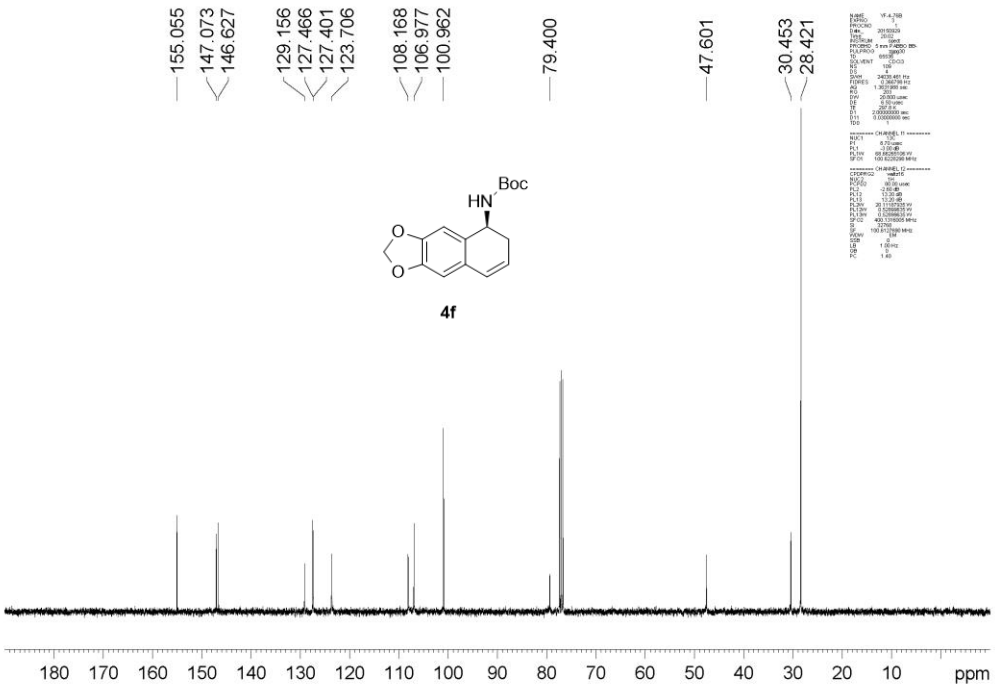
1.00
2.08
0.94
0.91
1.14
2.14
9.02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127.401
123.706
108.168
106.977
100.962
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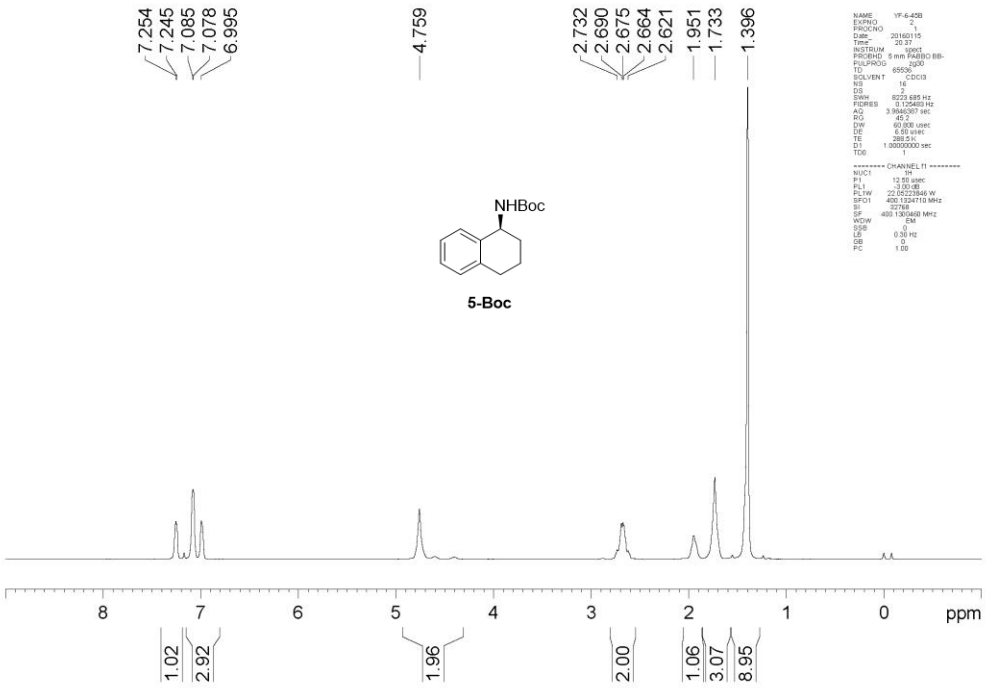
30.453
28.421
Boc
HN
O
O
4f
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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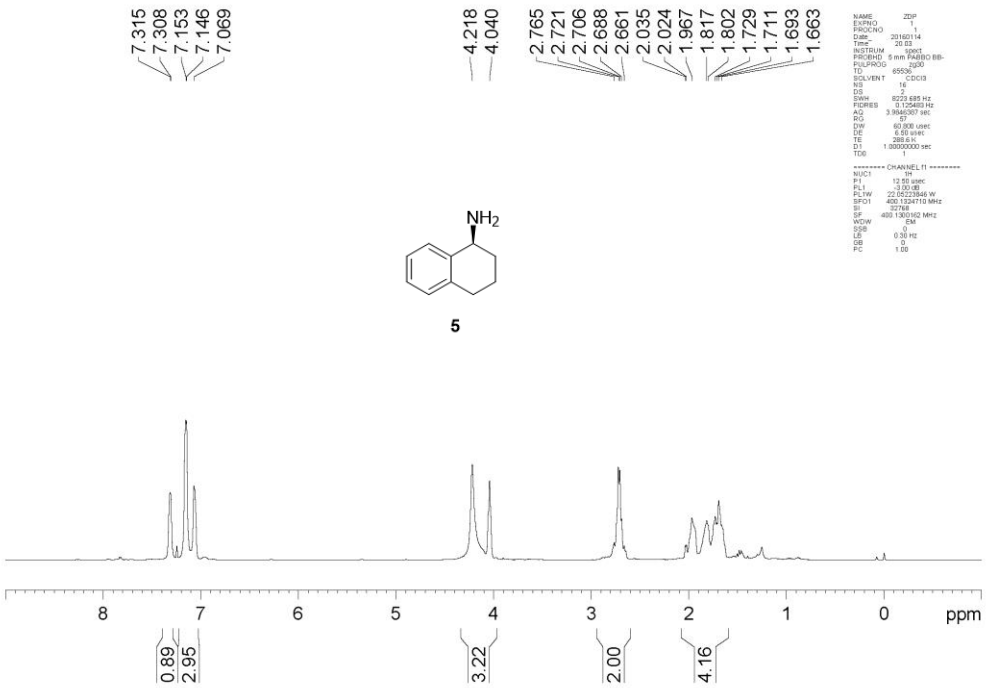
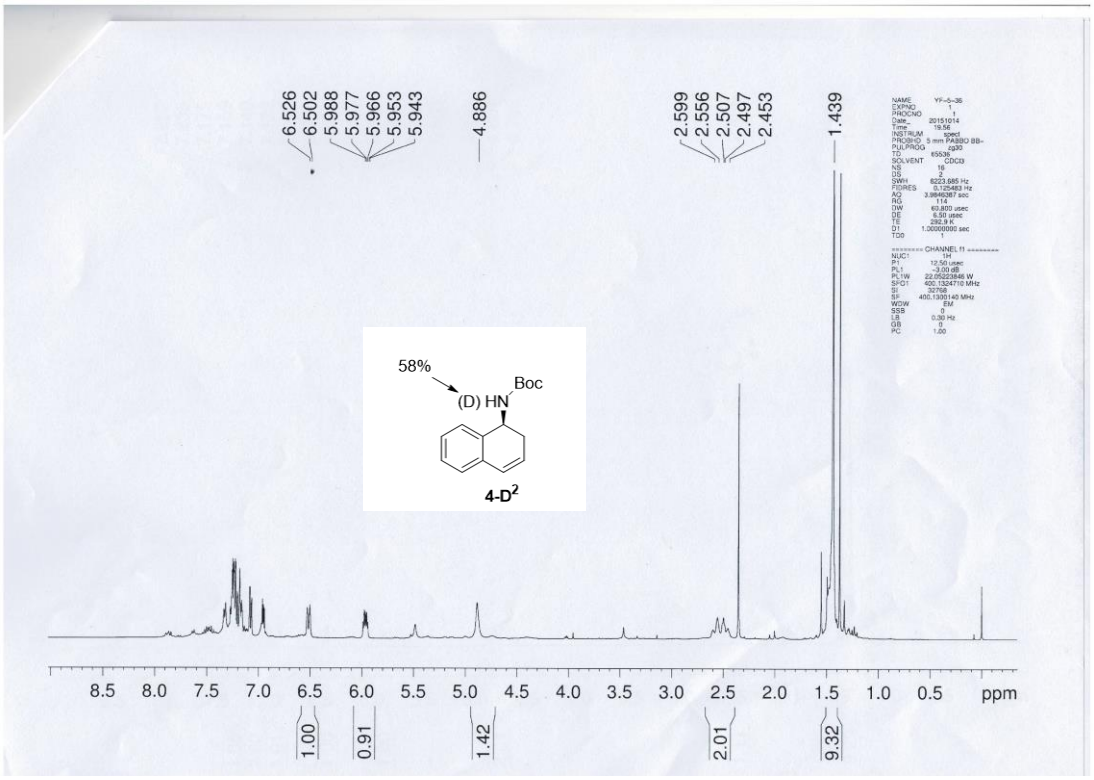
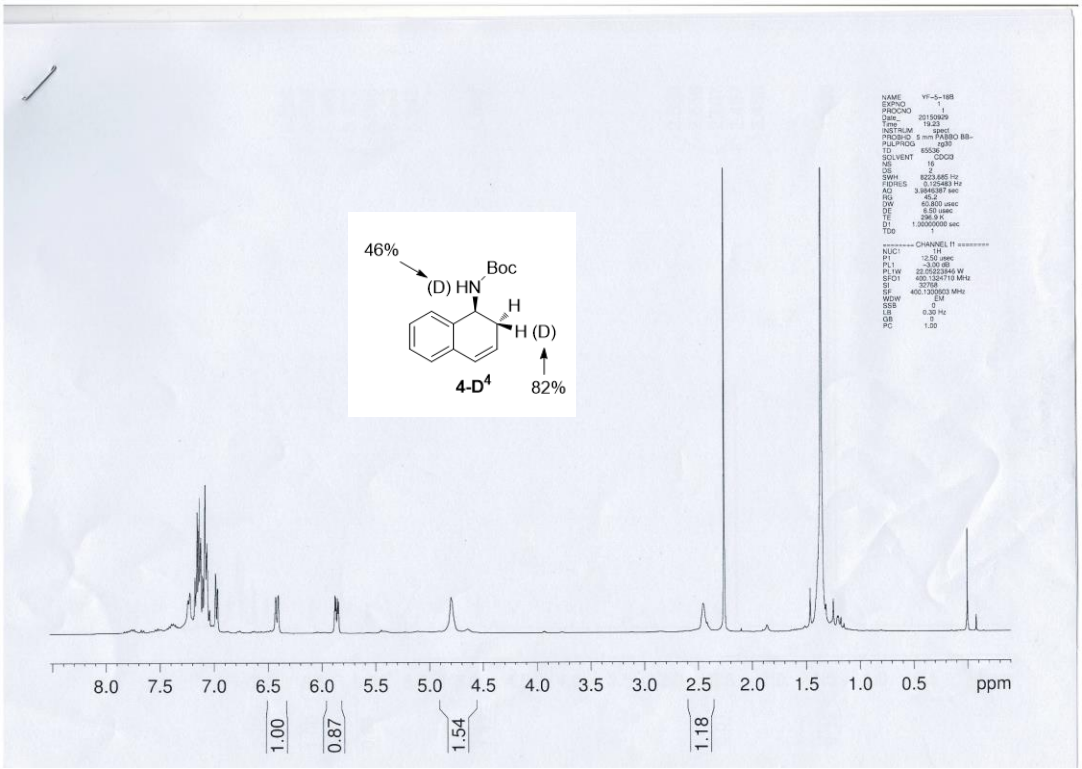
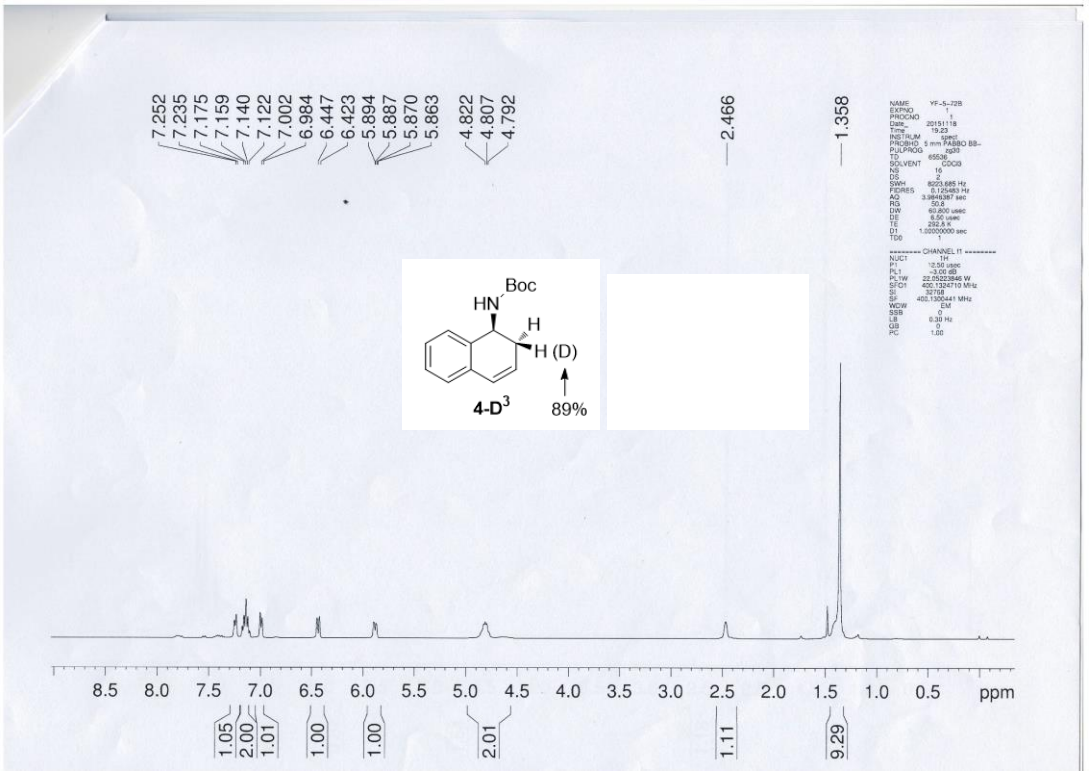
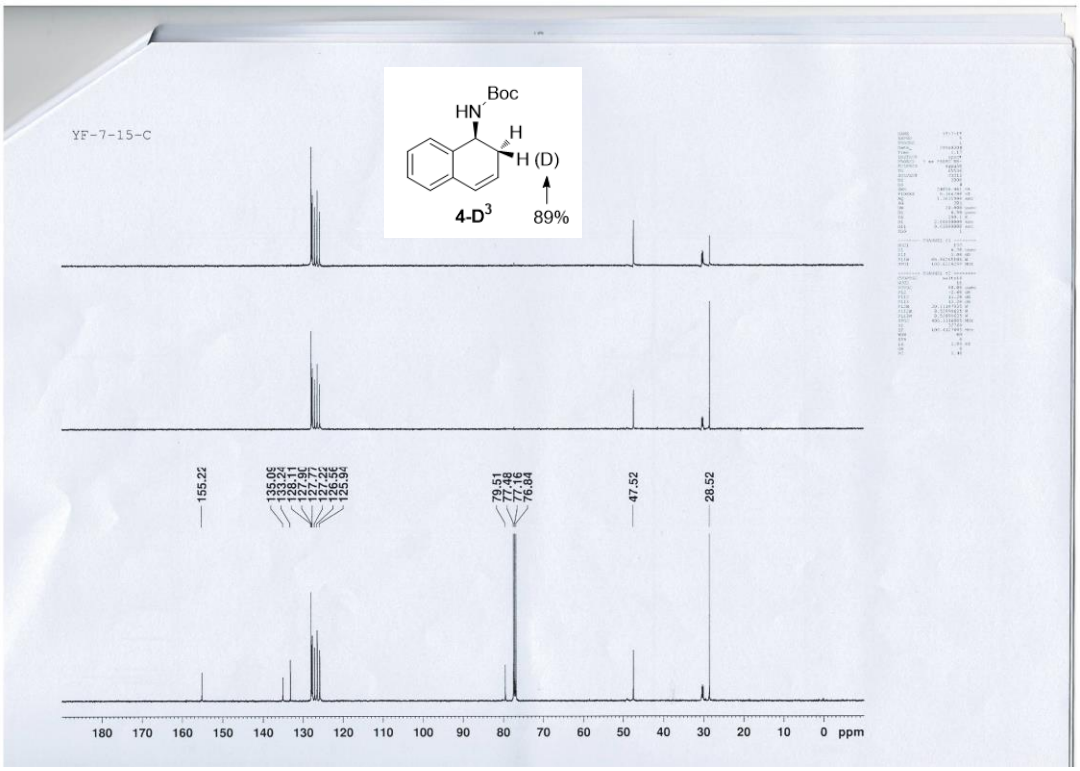
7.085
7.078
6.995
4.759
2.732
2.690
2.675
2.664
2.621
1.951
1.733
1.396
NHBoc
5-Boc
8
7
6
5
4
3
2
1
0
ppm
1.02
2.92
1.96
2.00
1.06
3.07
8.95


7.315
7.308
7.153
7.146
7.069
4.218
4.040
2.765
2.721
2.706
2.688
2.661
2.035
2.024
1.967
1.817
1.802
1.729
1.711
1.693
1.663
NH2
5
8
7
6
5
4
3
2
1
0
ppm
0.89
2.95
3.22
2.00
4.16

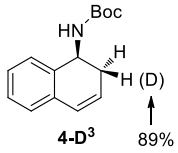

6.526
6.502
5.988
5.977
5.966
5.953
5.943
4.886
2.599
2.556
2.507
2.497
2.453
1.439
58%
(D) HN
Boc
4-D2
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
0.91
1.42
2.01
9.32


46%
(D) HN
Boc
H
H (D)
4-D4
82%
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 ppm
1.00
0.87
1.54
1.18

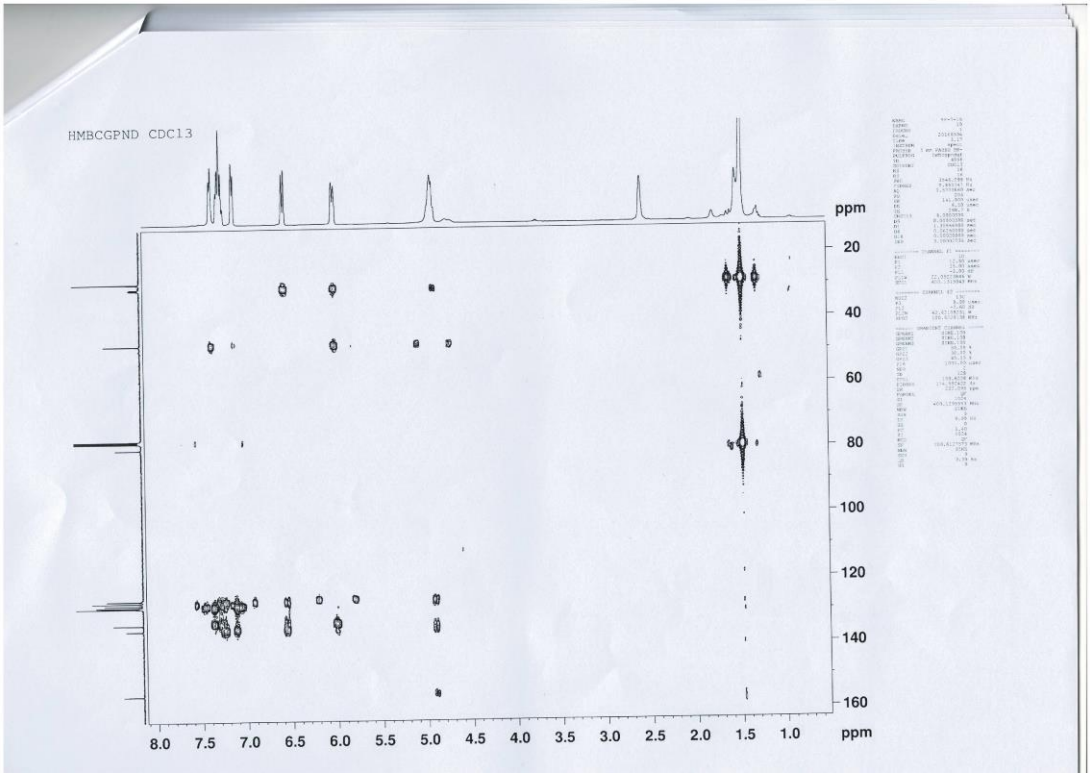

7.252
7.235
7.175
7.159
7.140
7.122
7.002
6.984
6.447
6.423
5.894
5.887
5.870
5.863
4.822
4.807
4.792
2.466
1.358
Boc
HN
H
H (D)
4-D3
89%
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.05
2.00
1.01
1.00
1.00
2.01
1.11
9.29

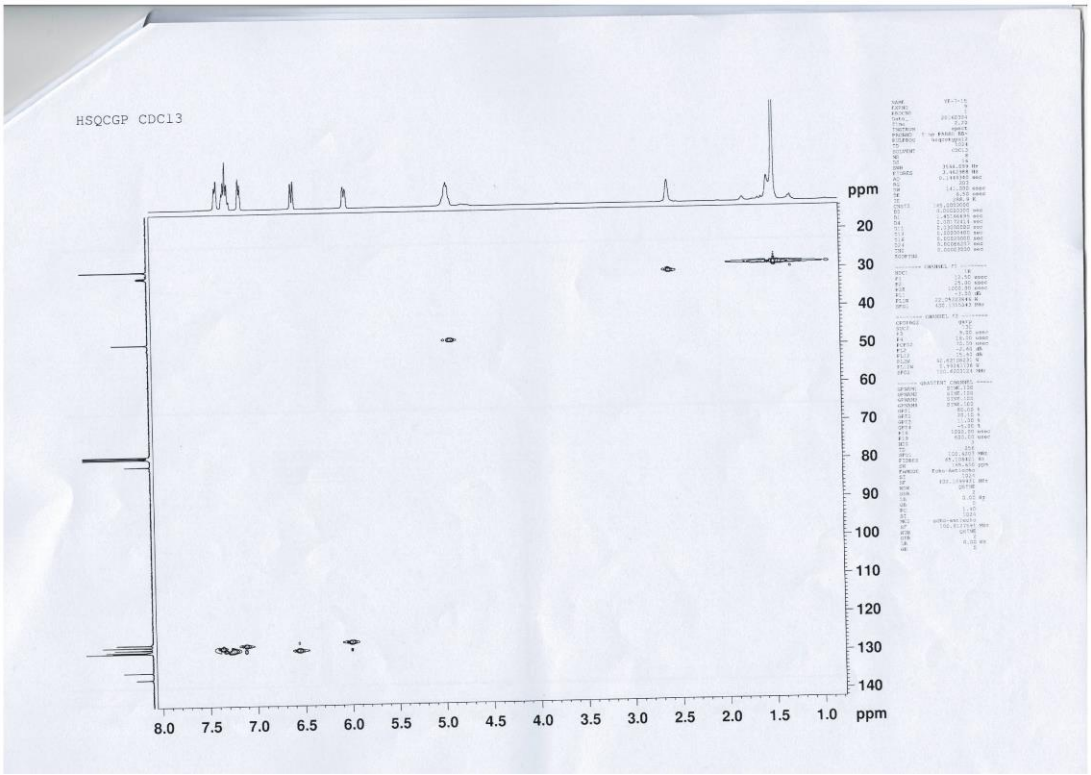

YF-7-15-C
Boc
HN
H
H (D)
4-D3
89%
155.22
135.05
133.24
128.11
127.85
127.77
127.22
126.54
125.94
79.51
77.48
77.16
76.84
47.52
28.52
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

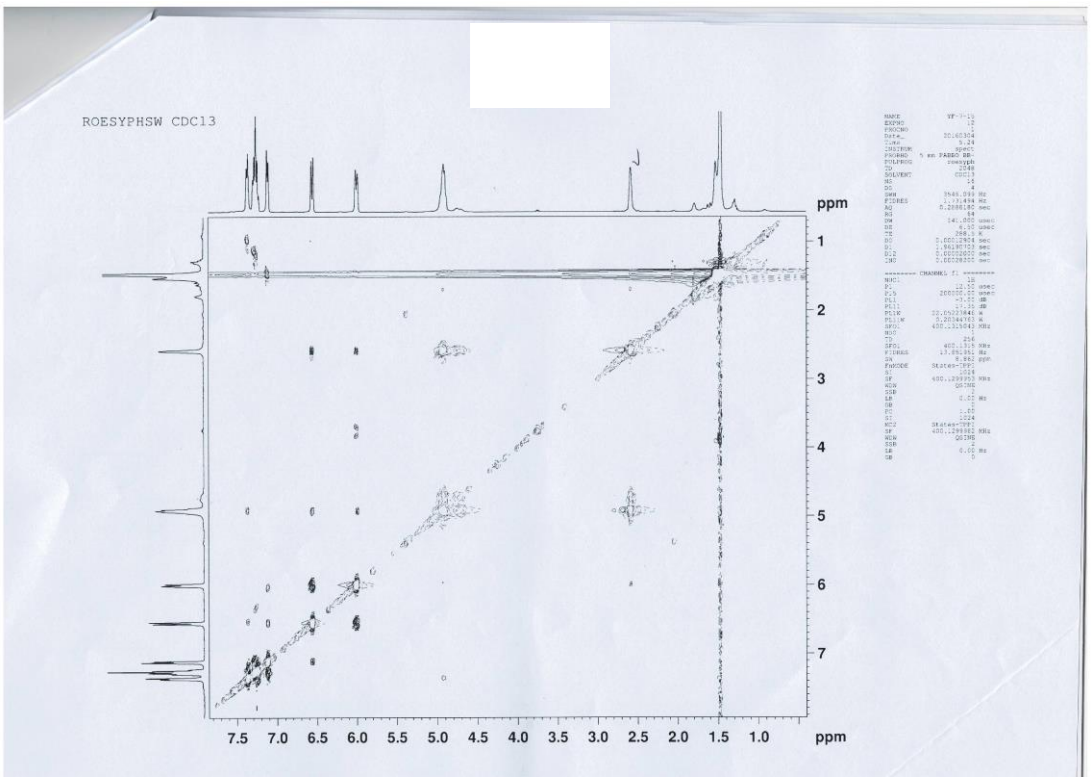
2D NMR spectrums of 4-D^3

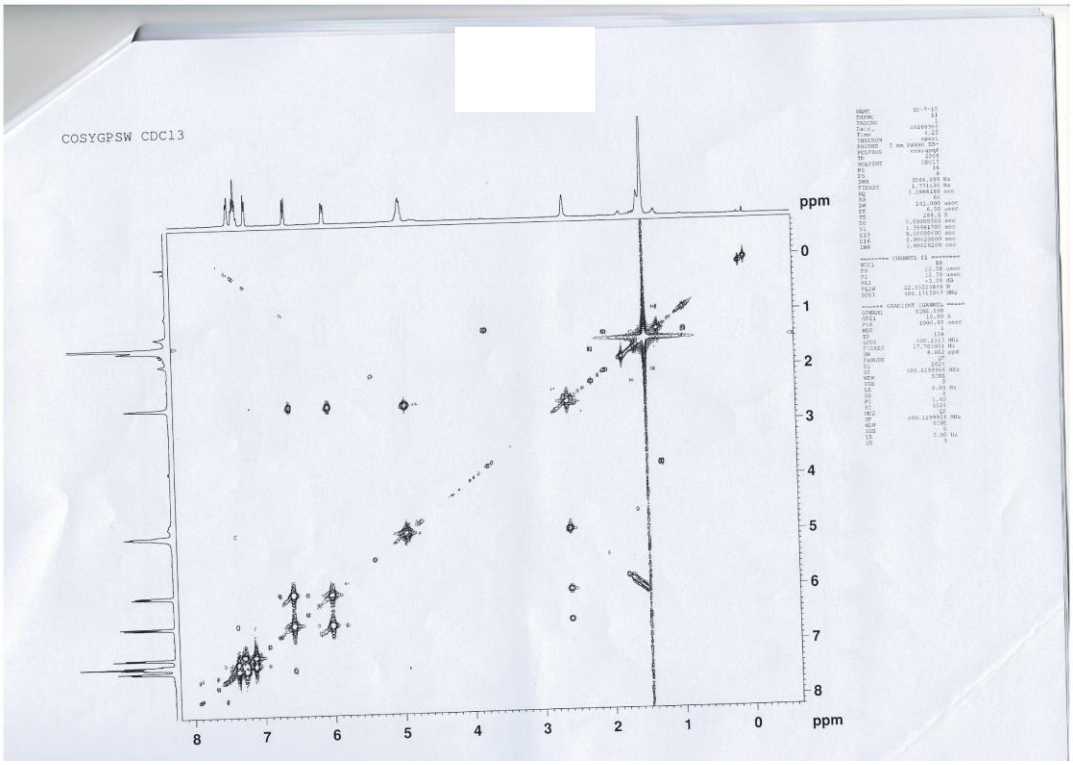


4-D^3



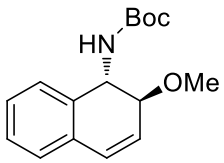



ROESYPHSW CDCl3
ppm
1
2
3
4
5
6
7
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm


COSYGPSW CDCl3
ppm
0
1
2
3
4
5
6
7
8
8 7 6 5 4 3 2 1 0
ppm

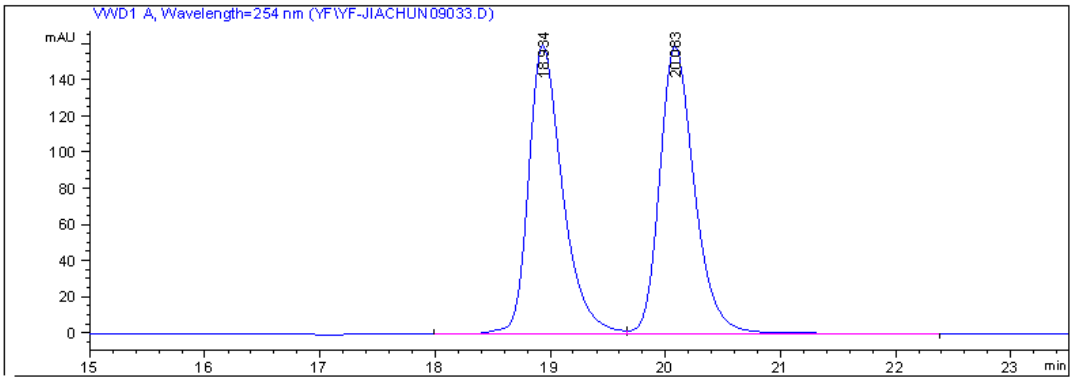
G: HPLC Spectra of Products

Note: All of the racemic products were prepared by using (±)-binap as ligand.



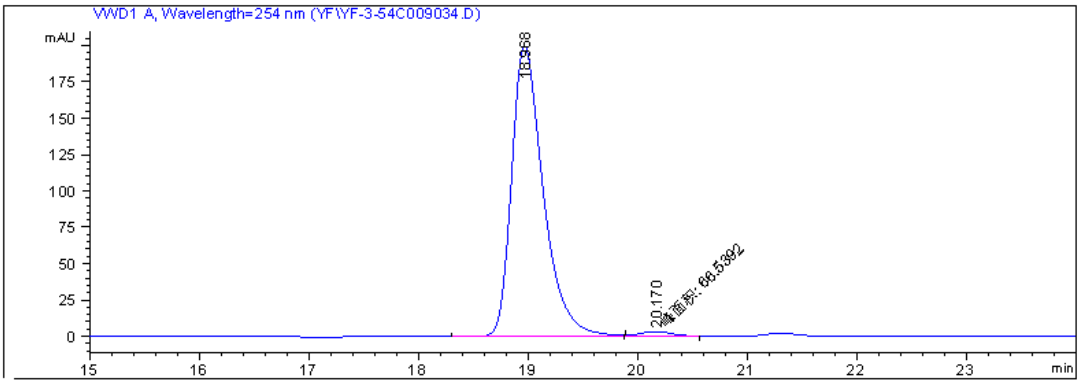
3aa

Racemic:

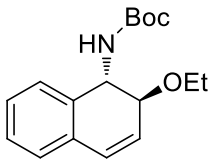


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.934	BV	0.3101	3291.27246	159.94156	49.5230
2	20.083	VB	0.3209	3354.67334	159.14153	50.4770

Enantioenriched:

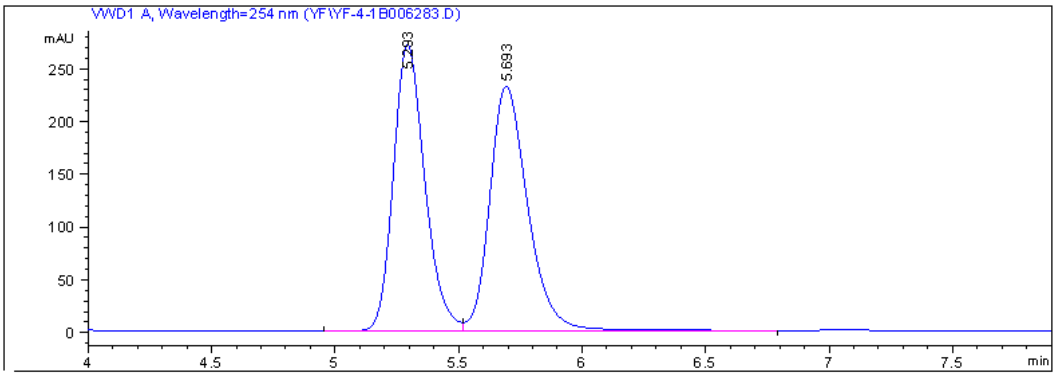


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.968	BV	0.3046	4025.25488	200.13960	98.3738
2	20.170	MM	0.3583	66.53922	3.09507	1.6262



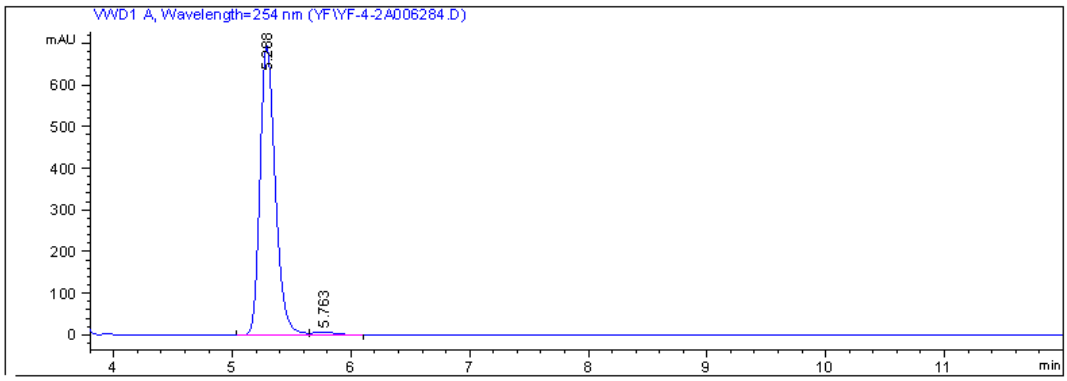
3ab

Racemic:

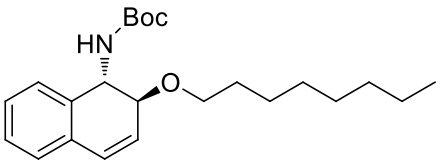


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.293	BV	0.1363	2397.55029	270.77722	49.2032
2	5.693	VB	0.1636	2475.19897	231.81474	50.7968

Enantioenriched:

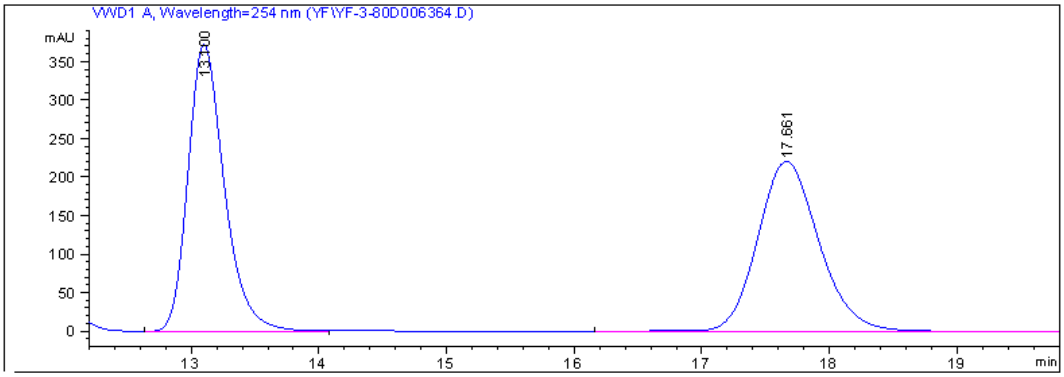


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.288	BV	0.1386	6217.96094	693.28442	98.7454
2	5.763	VB	0.1742	79.00145	6.76842	1.2546



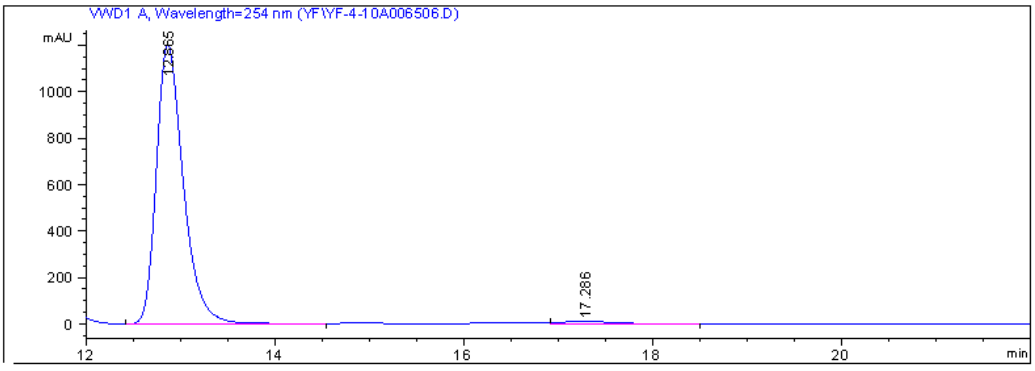
3ac

Racemic:

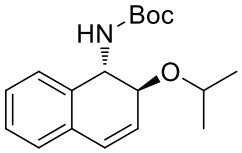


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.100	BB	0.3010	7347.11133	372.65503	49.8612
2	17.661	BBA	0.5164	7388.00342	220.75735	50.1388

Enantioenriched:

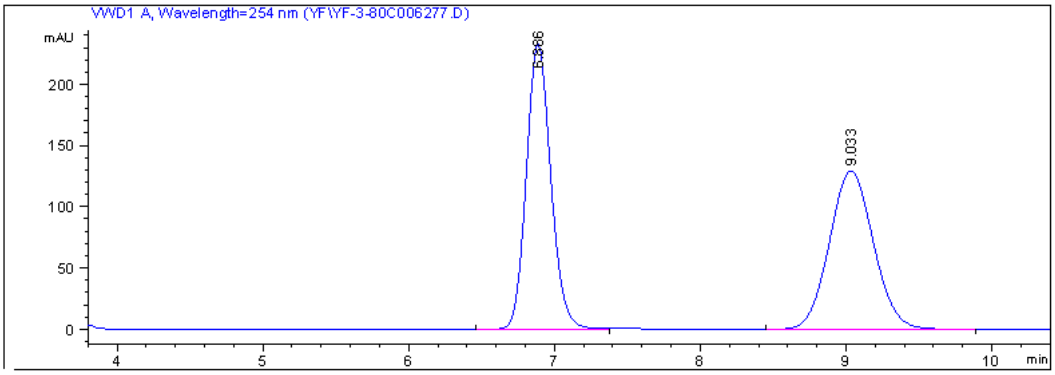


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.865	BB	0.3014	2.37874e4	1204.26758	98.5200
2	17.286	VB	0.5046	357.34863	10.64645	1.4800



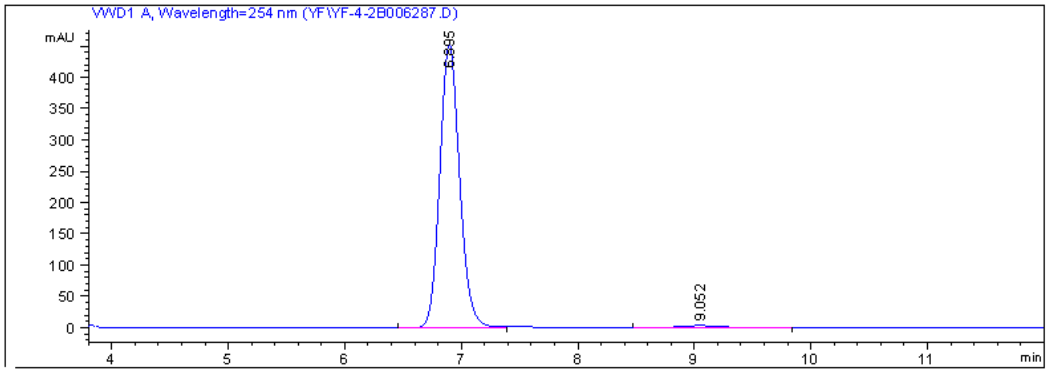
3ad

Racemic:

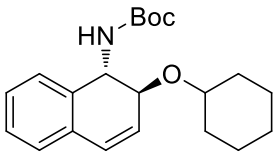


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.886	BV	0.1803	2719.03369	232.70789	50.0522
2	9.033	BB	0.3254	2713.36401	129.50873	49.9478

Enantioenriched:

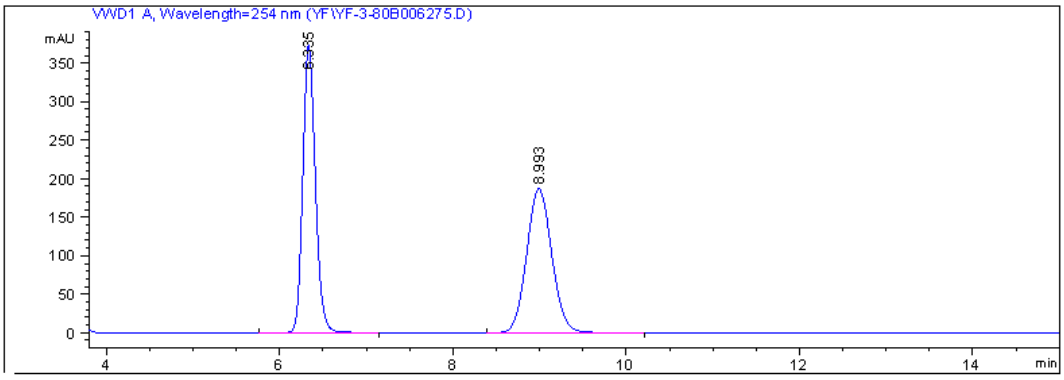


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.895	BV	0.1819	5357.93262	453.42059	98.7482
2	9.052	BB	0.3382	67.91901	3.09307	1.2518



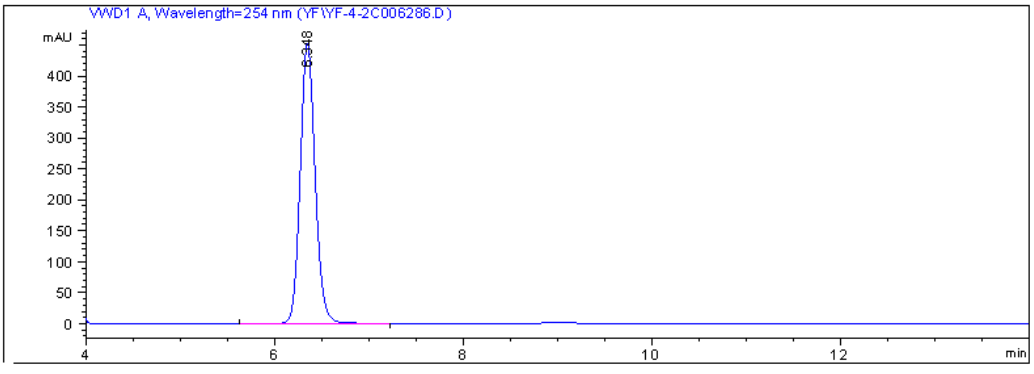
3ae

Racemic:

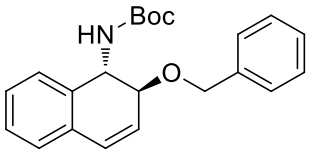


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.335	BB	0.1555	3755.31445	372.92151	49.9308
2	8.993	BB	0.3130	3765.72363	186.96271	50.0692

Enantioenriched:

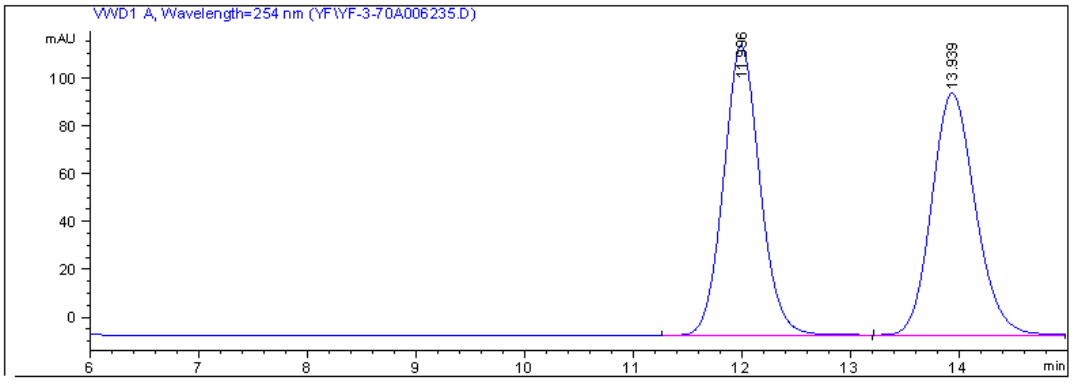


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.348	BB	0.1690	4959.19678	451.91028	100.0000



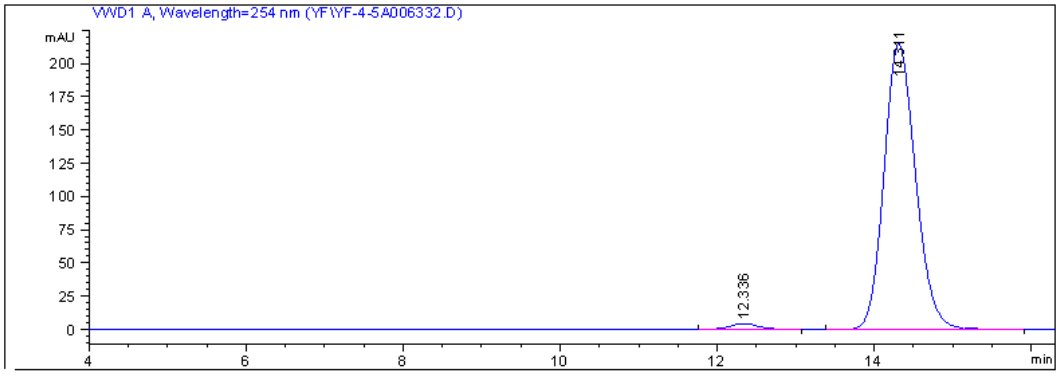
3af

Racemic:

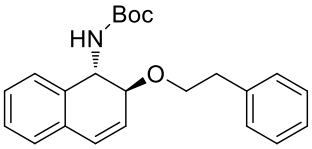


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.996	BB	0.3569	2819.96606	120.98866	50.0766
2	13.939	BBA	0.4310	2811.34009	100.91968	49.9234

Enantioenriched:

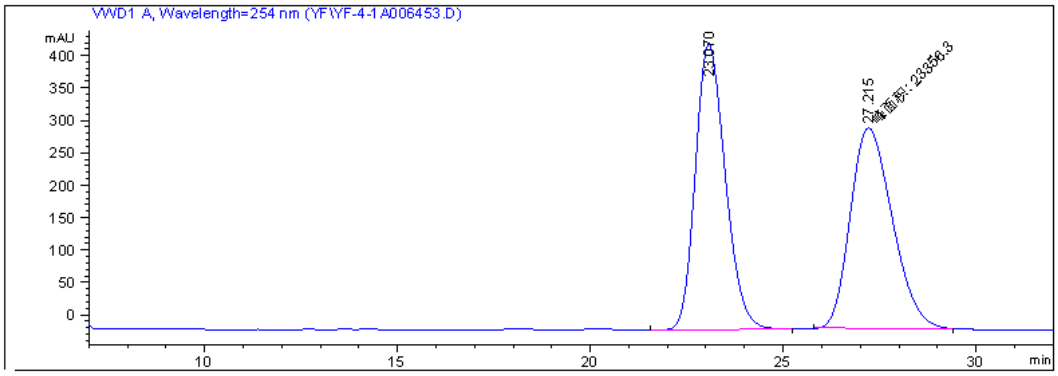


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.336	BB	0.3676	104.26031	4.36565	1.7056
2	14.311	BB	0.4320	6008.53955	215.02243	98.2944



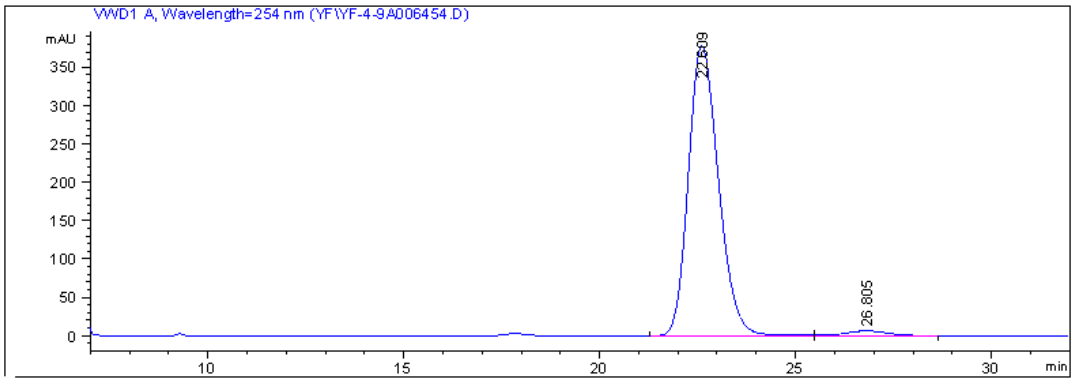
3ag

Racemic:

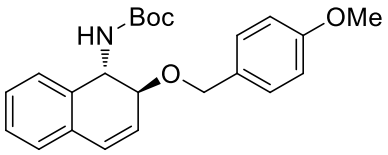


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.070	BB	0.8406	2.37662e4	439.71295	50.4350
2	27.215	MM	1.2591	2.33563e4	309.15561	49.5650

Enantioenriched:

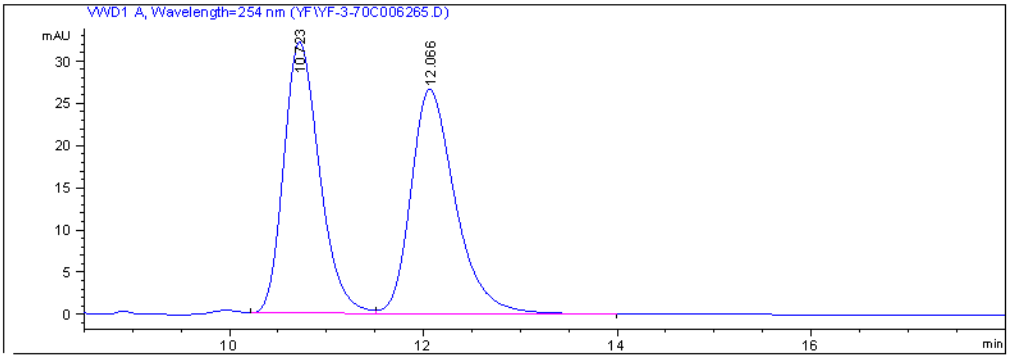


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.609	BB	0.8302	2.01705e4	378.18042	97.9452
2	26.805	BB	1.0164	423.16547	6.10692	2.0548



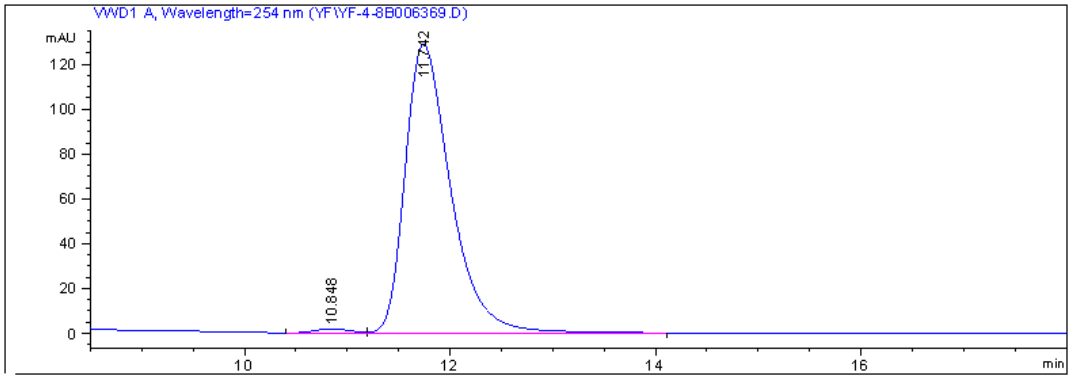
3ah

Racemic:

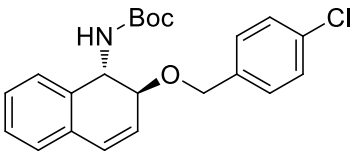


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.723	BV	0.3959	822.36383	32.10005	49.3133
2	12.066	VB	0.4852	845.26660	26.56570	50.6867

Enantioenriched:

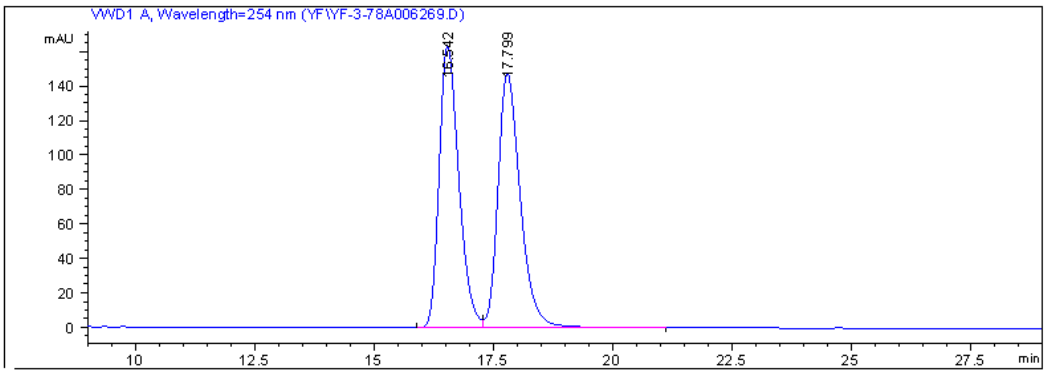


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.848	BV	0.3598	43.48345	1.90174	1.0809
2	11.742	VB	0.4703	3979.35303	128.84181	98.9191



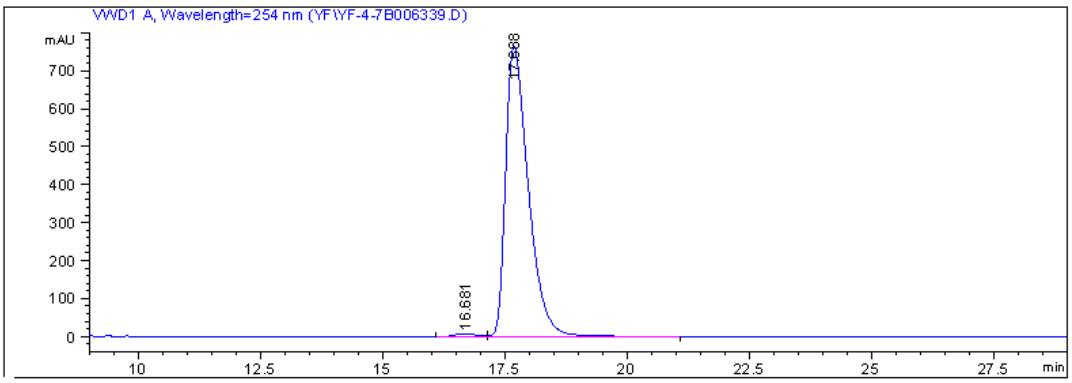
3ai

Racemic:

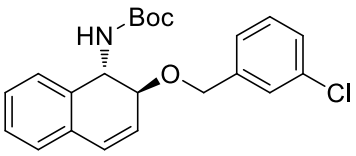


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.542	BV	0.4386	4688.32715	163.95755	49.3300
2	17.799	VB	0.5010	4815.67139	147.47113	50.6700

Enantioenriched:

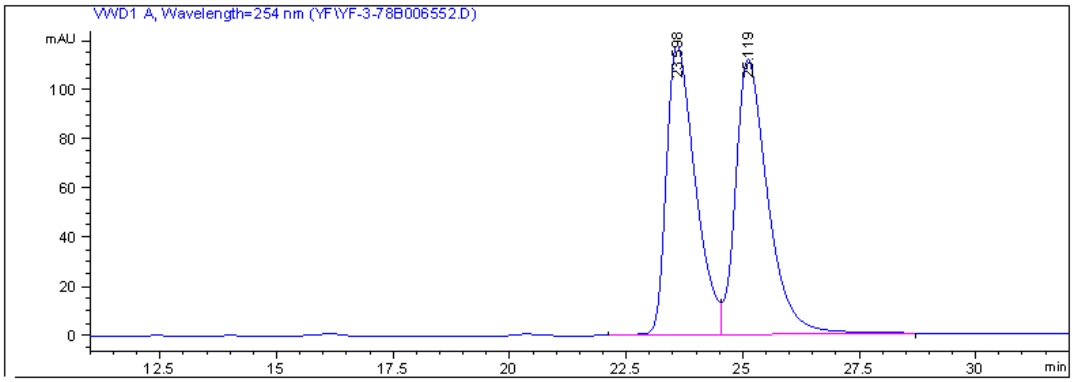


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.681	BV	0.4297	224.38802	8.06283	0.9002
2	17.688	VB	0.4932	2.47012e4	763.96924	99.0998



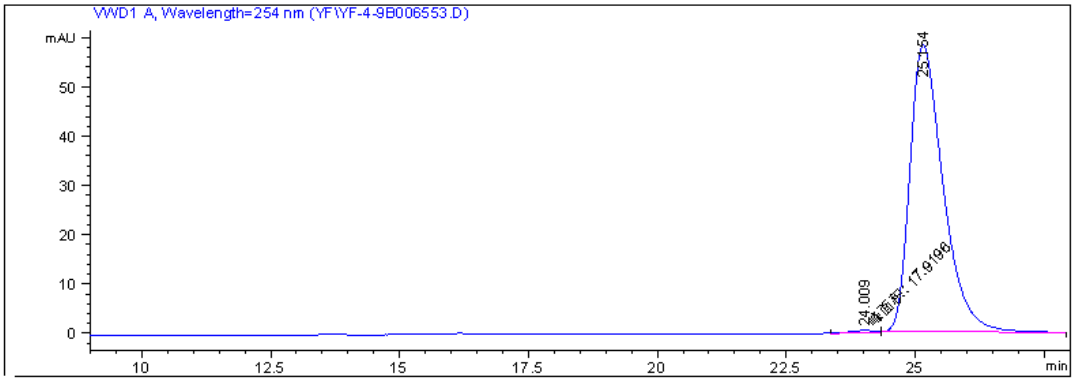
3aj

Racemic:

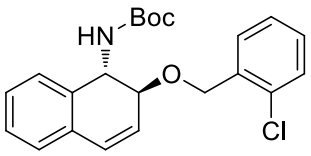


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.598	BV	0.6560	5066.55811	117.75548	48.5301
2	25.119	VB	0.7247	5373.46680	112.00275	51.4699

Enantioenriched:

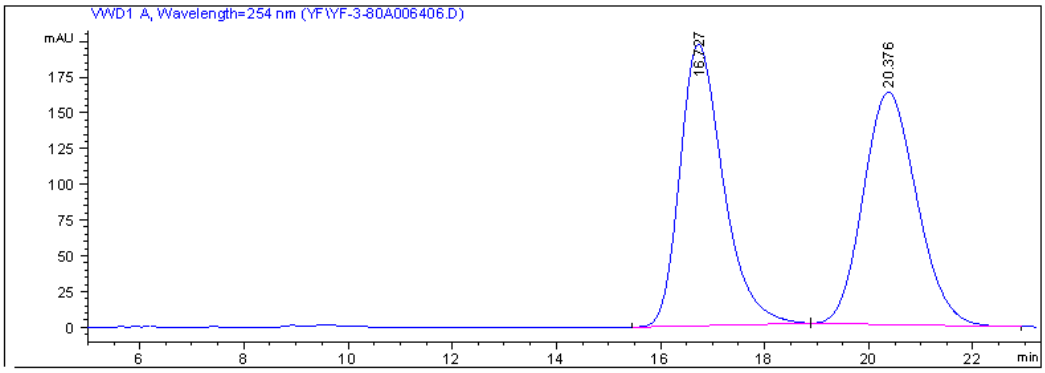


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.009	MM	0.5846	17.91962	5.10874e-1	0.6822
2	25.154	BBA	0.6799	2608.79150	58.20523	99.3178



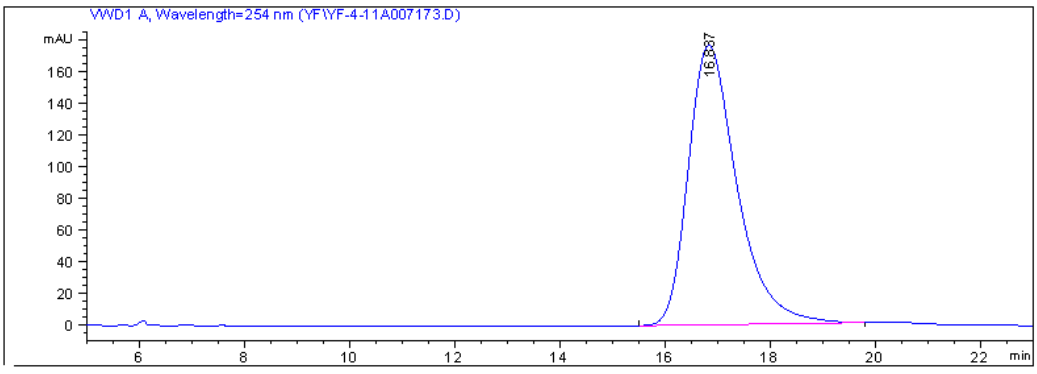
3ak

Racemic:

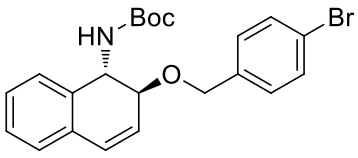


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.727	BB	0.8829	1.13702e4	196.54770	49.5226
2	20.376	BBA	1.1189	1.15894e4	162.53705	50.4774

Enantioenriched:

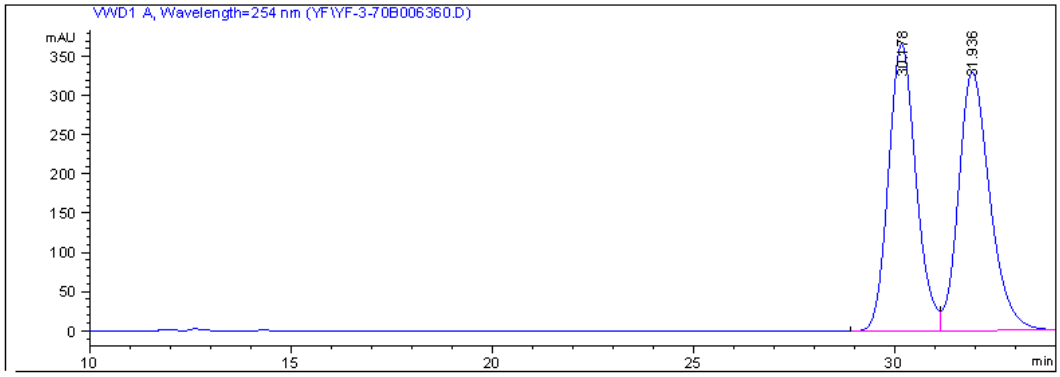


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.837	BB	0.9760	1.13769e4	176.50842	100.0000



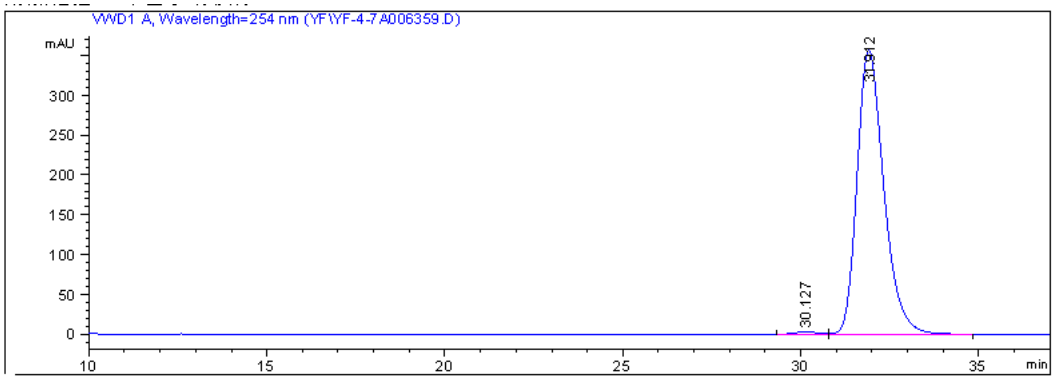
3al

Racemic:

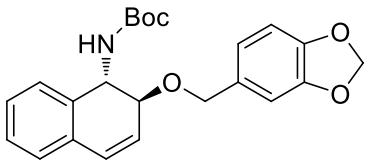


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.178	BV	0.7320	1.73659e4	365.69983	49.3331
2	31.936	VBA	0.8286	1.78354e4	329.96570	50.6669

Enantioenriched:

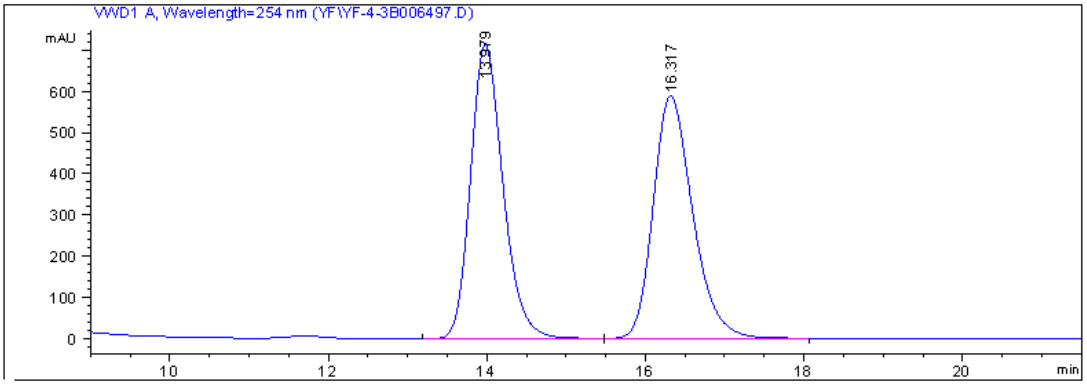


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.127	BB	0.6064	114.14535	2.85553	0.6092
2	31.912	BB	0.7968	1.86223e4	356.89352	99.3908



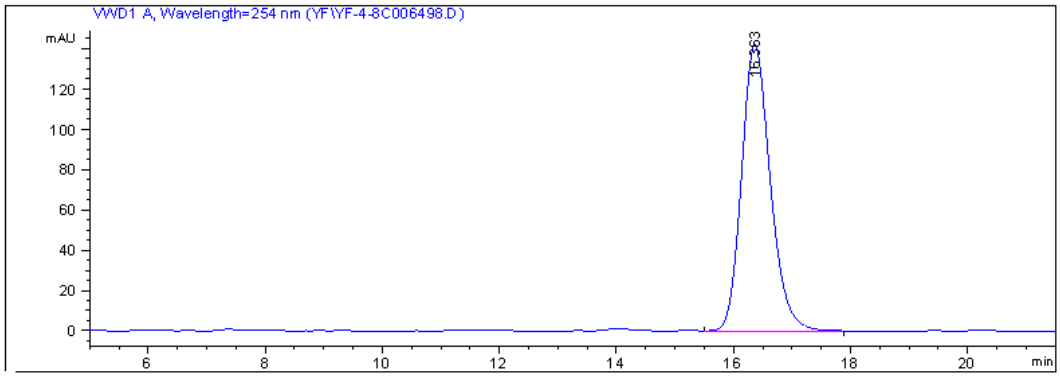
3am

Racemic:

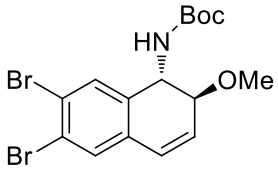


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.979	BB	0.4372	2.02983e4	712.93085	49.9932
2	16.317	BB	0.5281	2.03039e4	589.06305	50.0068

Enantioenriched:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.363	BB	0.5240	4847.18994	142.08702	100.0000



3ba

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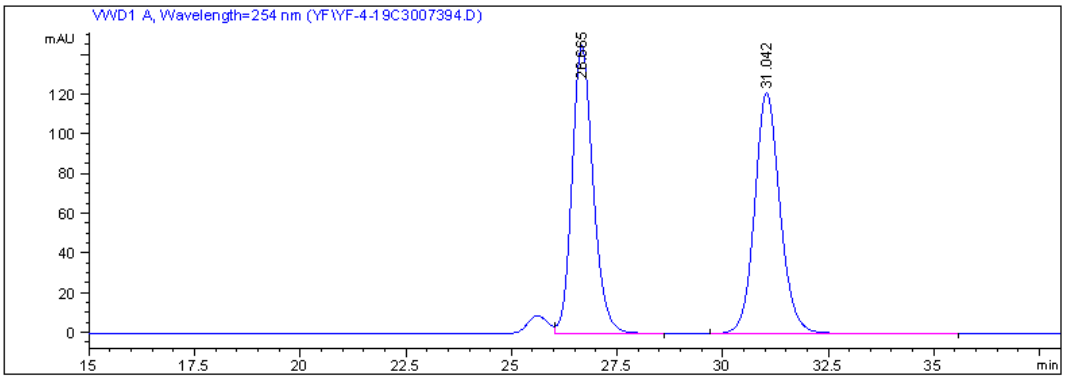
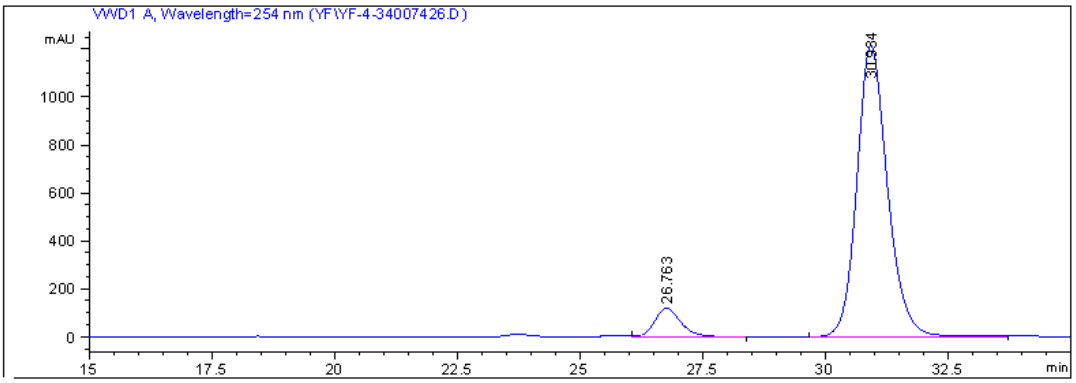
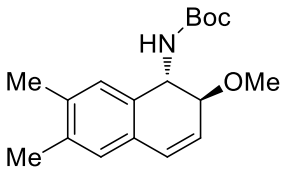


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.665	VB	0.5311	5031.12207	144.90996	49.8253
2	31.042	BB	0.6360	5066.39990	121.11738	50.1747

Enantioenriched:

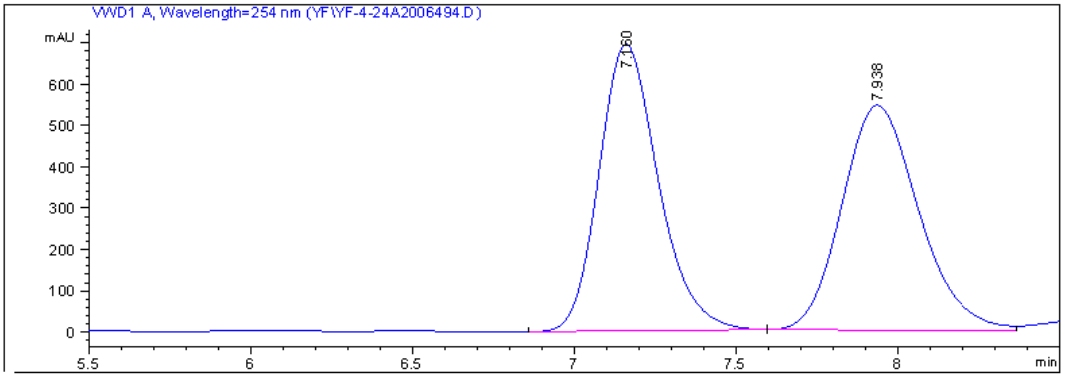


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.763	VB	0.5642	4436.21875	119.74636	7.7935
2	30.934	BB	0.6597	5.24860e4	1213.20178	92.2065



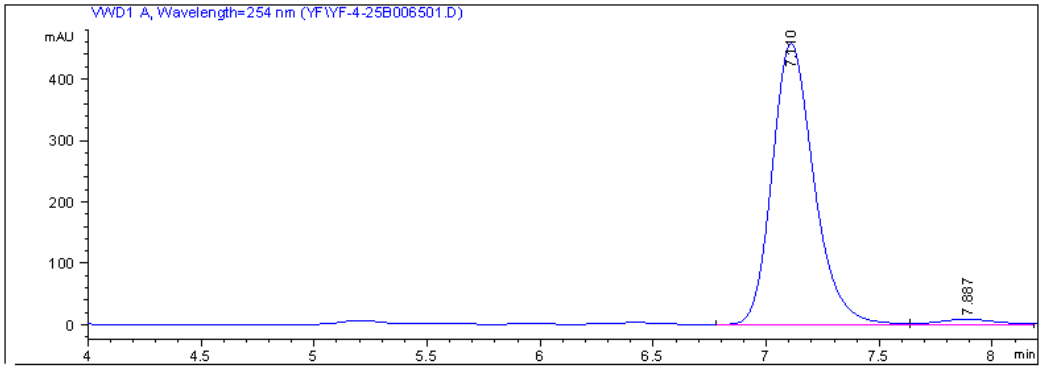
3ca

Racemic:

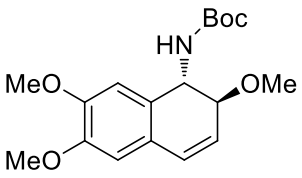


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.160	BB	0.1956	8852.20605	695.02826	49.6356
2	7.938	BV	0.2555	8982.17480	544.38635	50.3644

Enantioenriched:

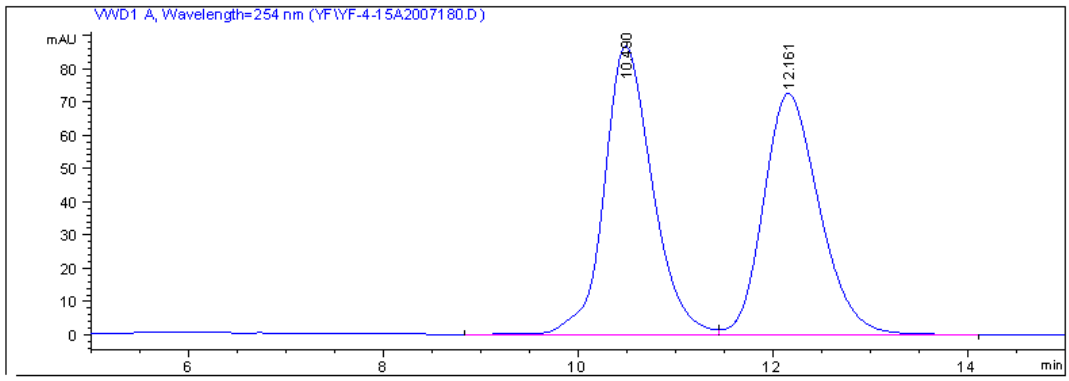


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.110	BV	0.1965	5862.82666	457.53226	97.5592
2	7.887	VV	0.2618	146.68231	8.56527	2.4408



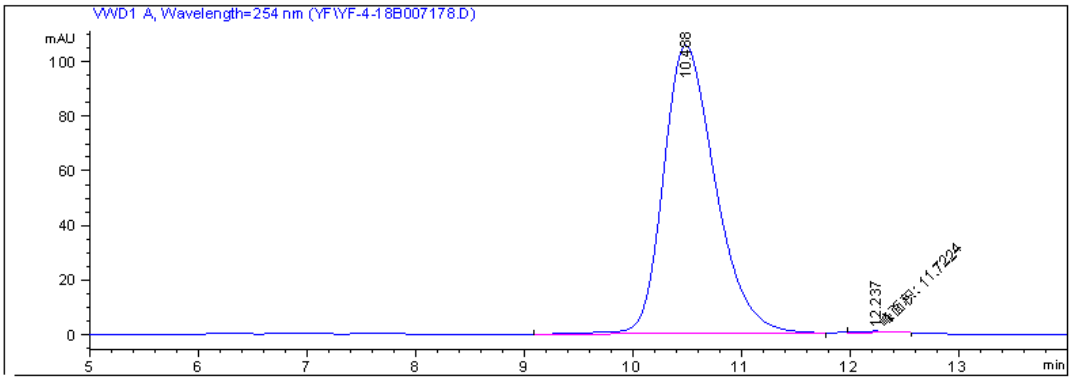
3da

Racemic:

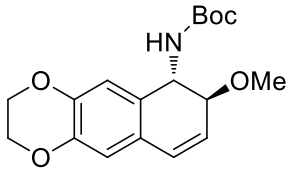


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.490	BV	0.5208	2980.07275	86.73942	50.8818
2	12.161	VB	0.6127	2876.78247	72.53736	49.1182

Enantioenriched:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.488	BB	0.5105	3503.63208	105.77065	99.6665
2	12.237	MM	0.3801	11.72240	5.13997e-1	0.3335



3ea

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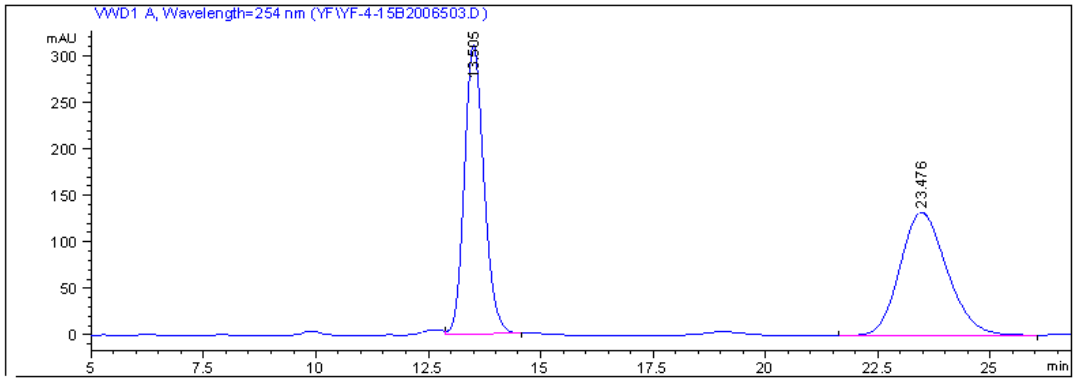
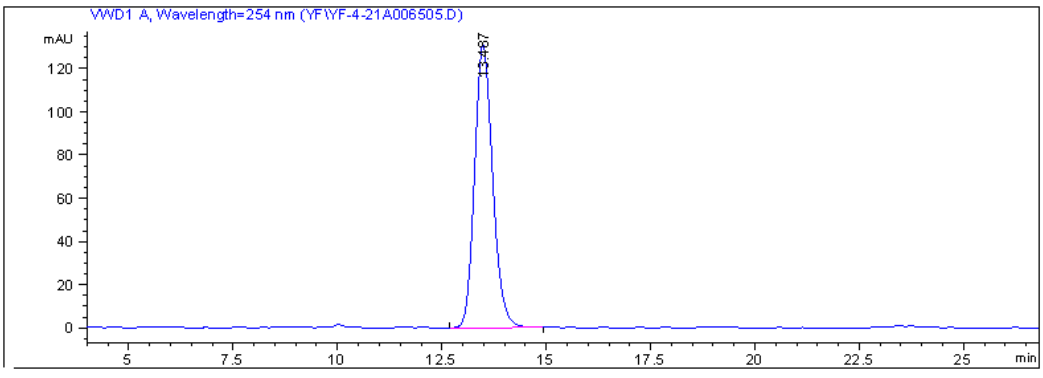
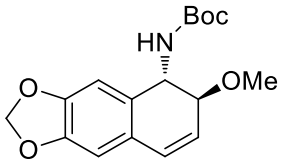


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.505	VB	0.4696	9434.62207	310.39920	49.6452
2	23.476	BB	1.1221	9569.46777	131.94962	50.3548

Enantioenriched:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.487	BB	0.4678	3960.16431	130.57002	100.0000



3fa

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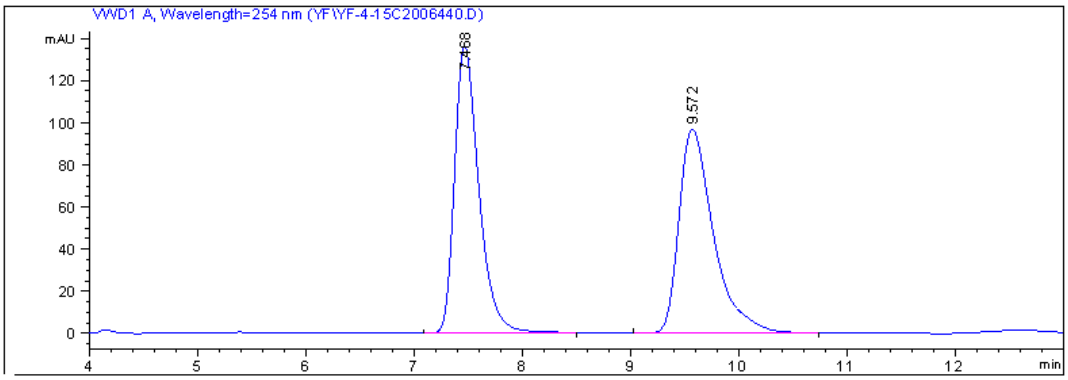
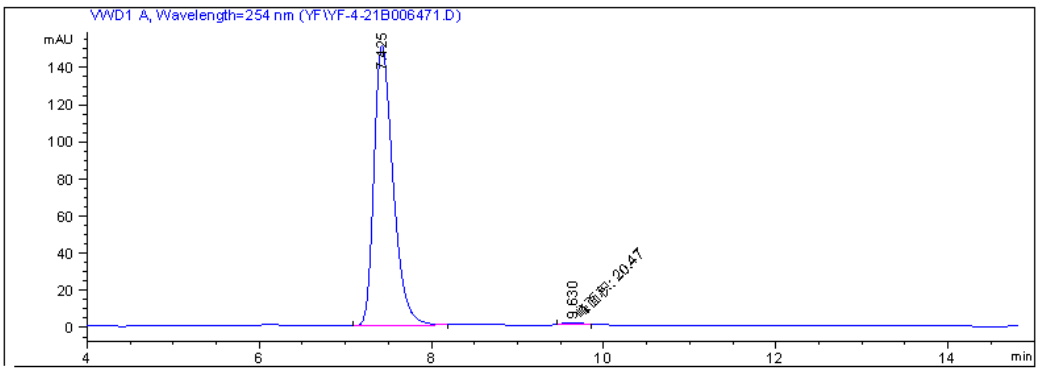
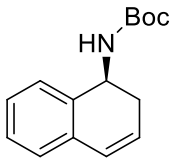


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.468	BB	0.2393	2133.60889	136.53616	49.8366
2	9.572	BB	0.3378	2147.60254	96.82796	50.1634

Enantioenriched:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.425	BB	0.2370	2321.18042	150.41811	99.1258
2	9.630	MM	0.2719	20.47004	1.25488	0.8742



4a

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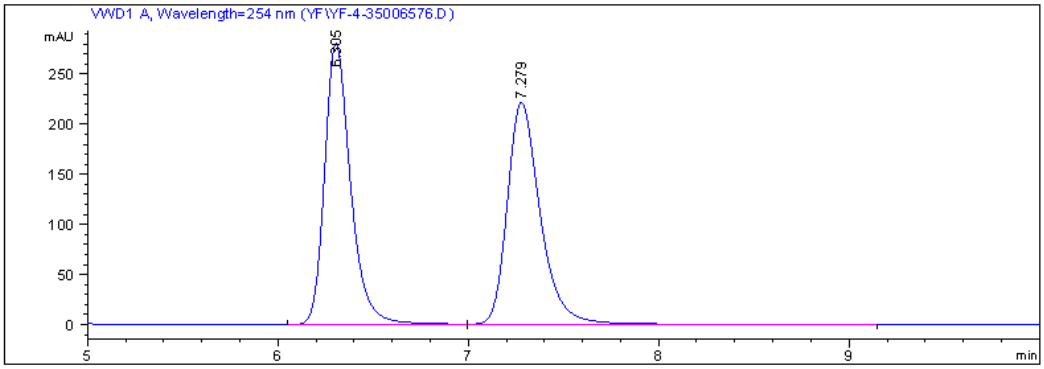
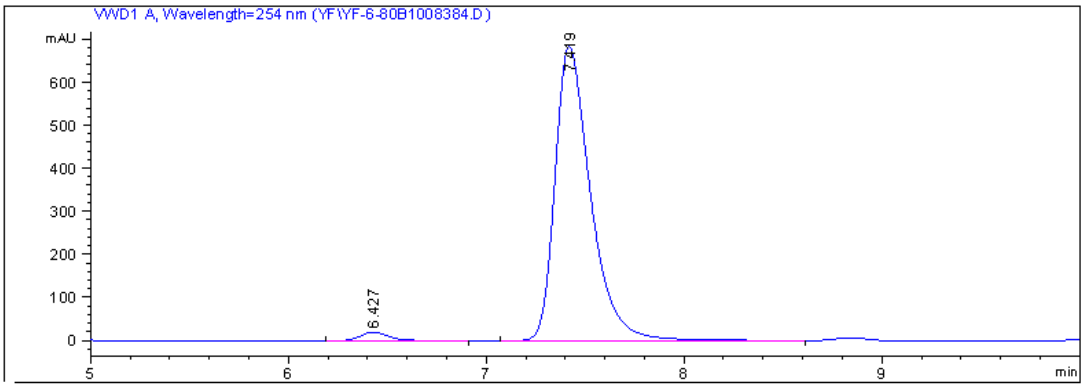
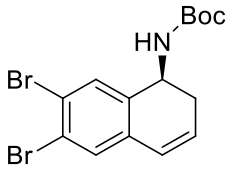


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.305	BB	0.1467	2661.73340	280.64432	49.9734
2	7.279	BB	0.1844	2664.57227	221.38438	50.0266

Enantioenriched:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.427	BB	0.1523	199.81676	19.87626	2.2822
2	7.419	BV	0.1890	8555.73730	683.70776	97.7178



4b

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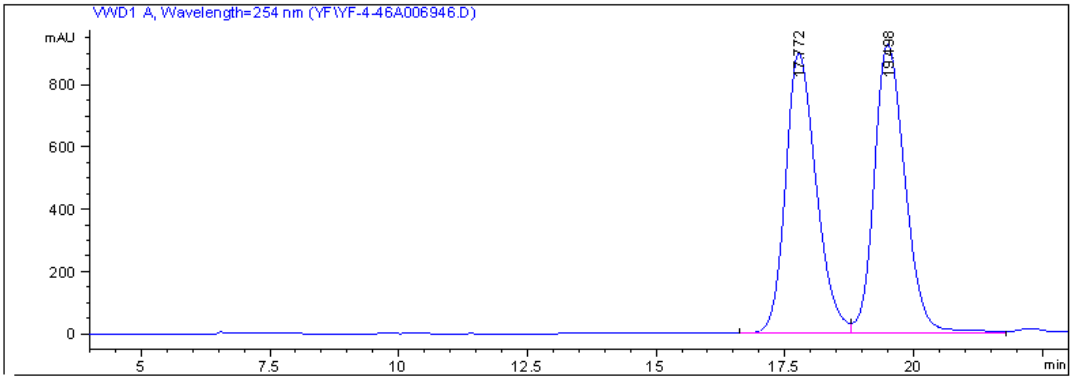
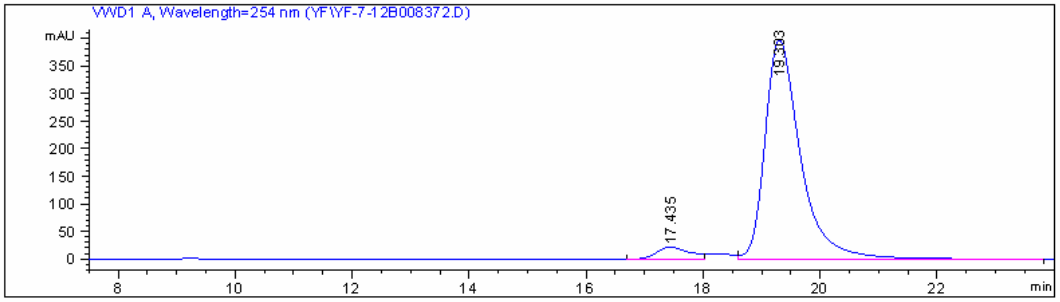
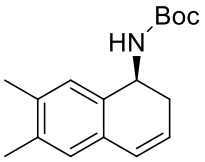


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.772	BV	0.6320	3.71309e4	896.95837	49.1831
2	19.498	VV	0.6413	3.83643e4	926.13885	50.8169

Enantioenriched:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.435	BV	0.5844	859.58087	21.78228	4.8874
2	19.303	VB	0.6369	1.67281e4	396.75577	95.1126



4c

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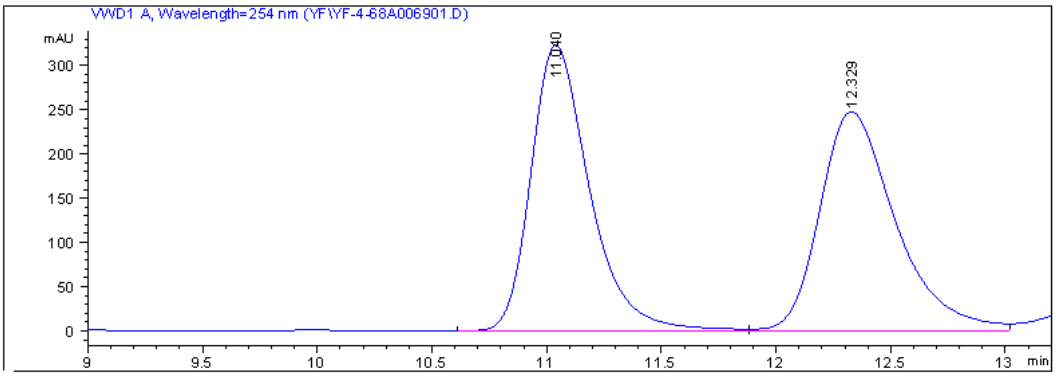
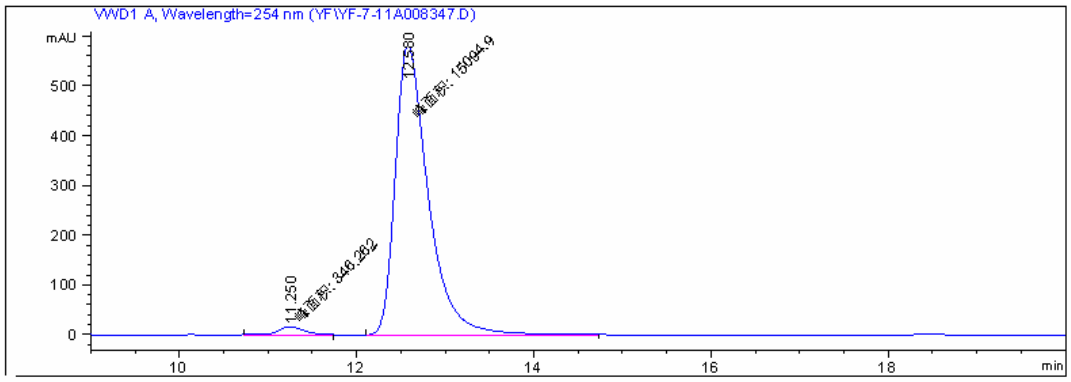
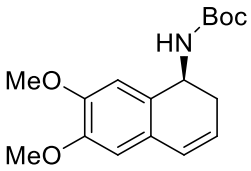


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.040	BV	0.2698	5727.09229	323.10321	50.2005
2	12.329	VV	0.3477	5681.33594	247.63959	49.7995

Enantioenriched:

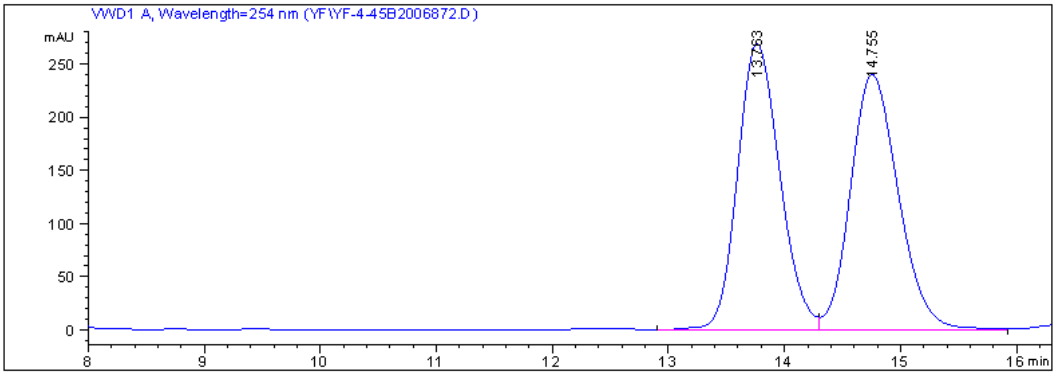


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.250	MM	0.3490	346.26215	16.53514	2.2425
2	12.580	MM	0.4327	1.50949e4	581.45178	97.7575



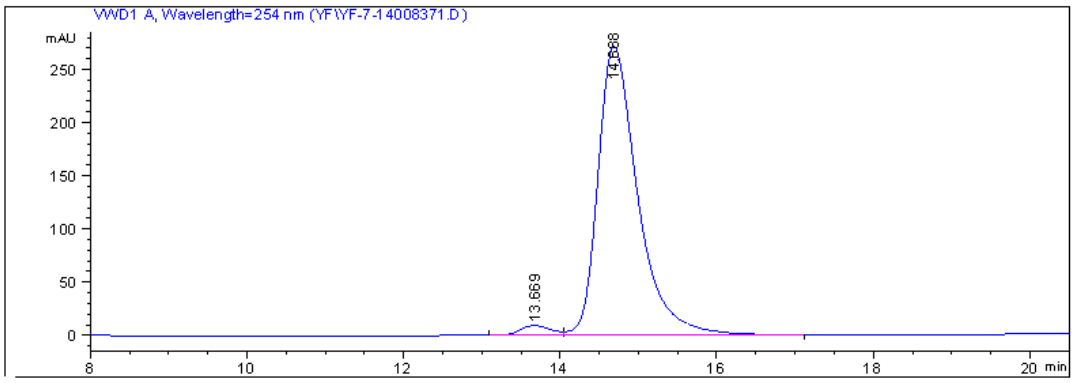
4d

Racemic:

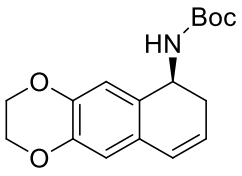


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.763	BV	0.3953	6797.96143	268.60135	49.7624
2	14.755	VV	0.4456	6862.87598	240.00993	50.2376

Enantioenriched:

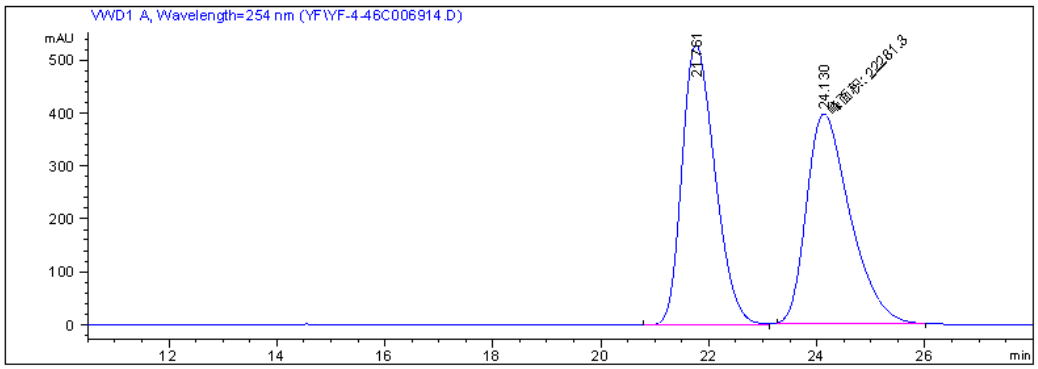


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.669	BV	0.4141	252.32999	9.37283	2.5622
2	14.688	VB	0.5348	9595.91309	271.87543	97.4378



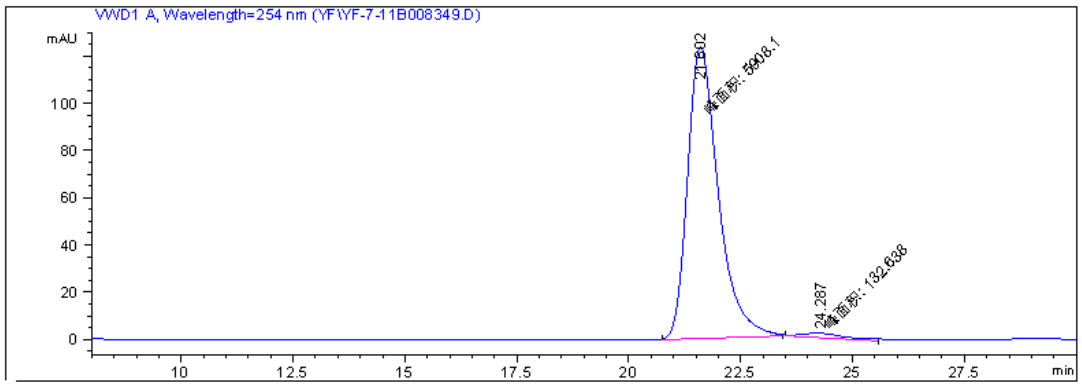
4e

Racemic:

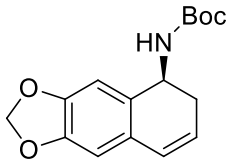


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.761	BV	0.6631	2.24345e4	528.68958	50.1713
2	24.130	MM	0.9356	2.22812e4	396.91205	49.8287

Enantioenriched:

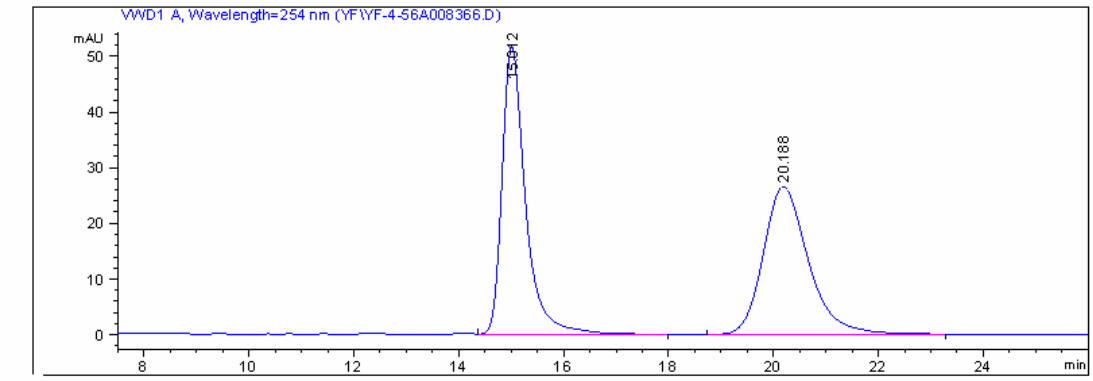


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.602	MM	0.7971	5908.09521	123.52825	97.8043
2	24.287	MM	1.1759	132.63789	1.87988	2.1957



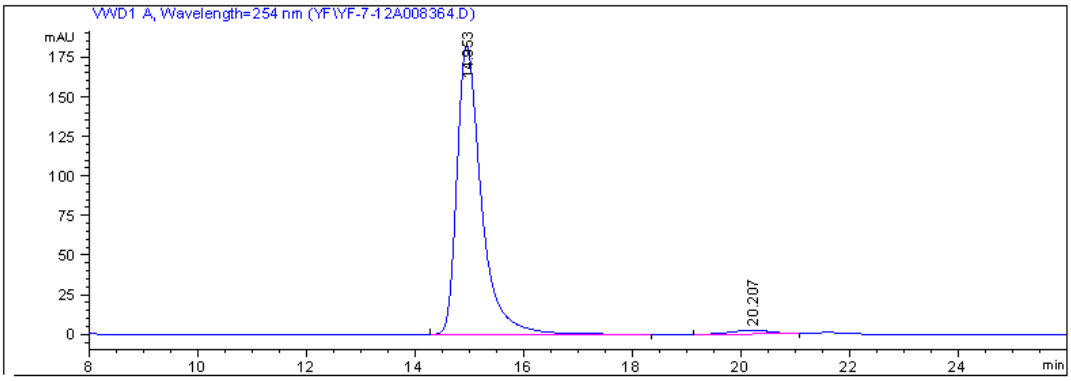
4f

Racemic:

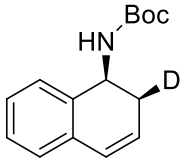


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.012	BB	0.4625	1594.50757	51.74400	50.3654
2	20.188	BB	0.8914	1571.37048	26.51523	49.6346

Enantioenriched:

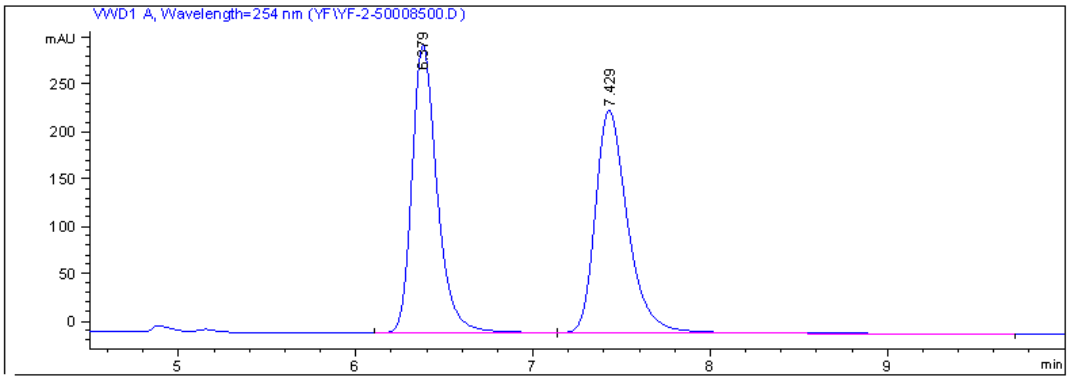


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.953	BB	0.4708	5689.81104	182.46301	97.9674
2	20.207	BB	0.7113	118.04913	2.38574	2.0326



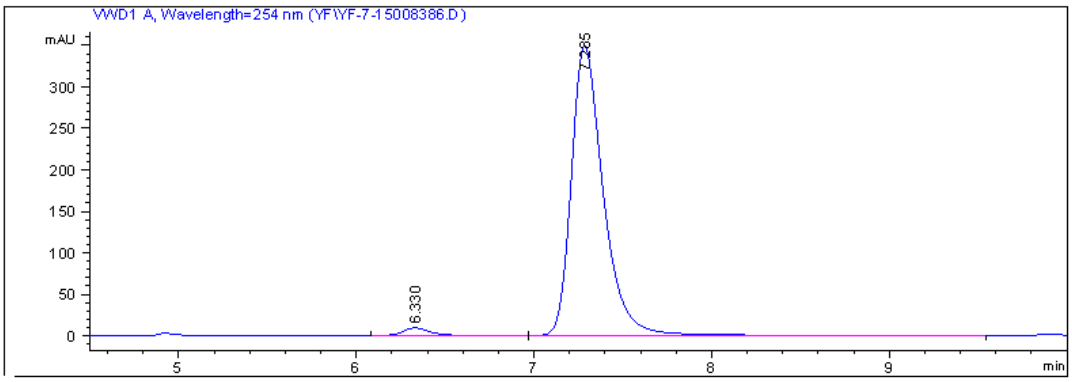
4-D^3

Racemic:

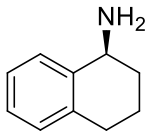


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.379	BV	0.1500	2987.78003	303.02585	49.8479
2	7.429	VBA	0.1931	3006.00781	235.25735	50.1521

Enantioenriched:



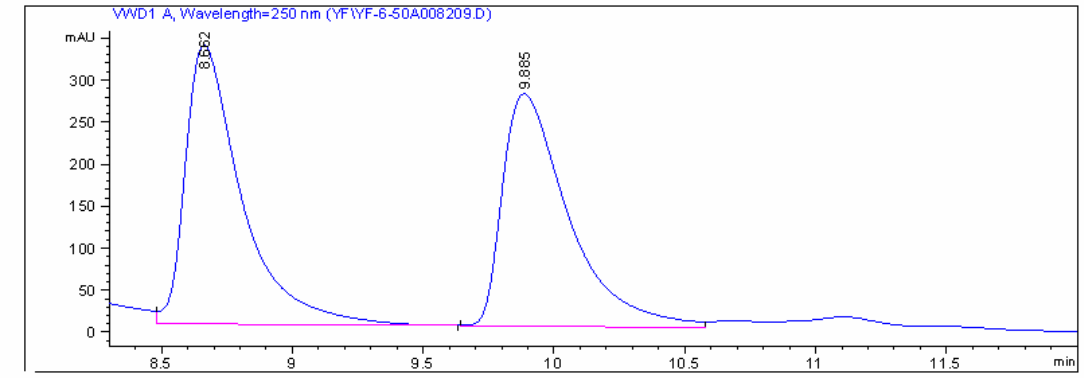
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.330	BB	0.1615	95.16880	8.98788	2.1302
2	7.285	BB	0.1891	4372.47168	349.07401	97.8698



5 (derived from **4a**)

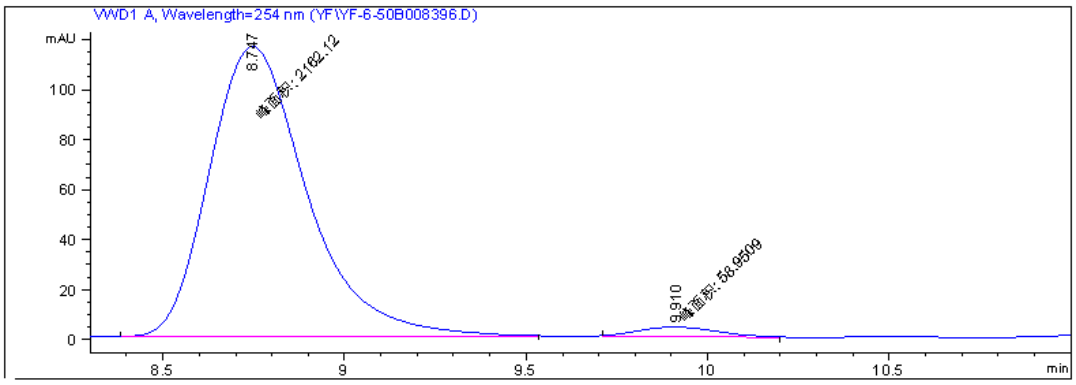
Racemic:

*Note: Racemic **5** was derived from the racemic **4a**, which was prepared by following the typical procedure **B₂** using (±)-Binap as ligand.*

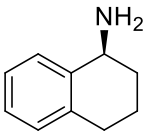


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.662	VB	0.2215	4963.88086	331.85876	50.5641
2	9.885	BV	0.2649	4853.12646	276.26273	49.4359

Enantioenriched:

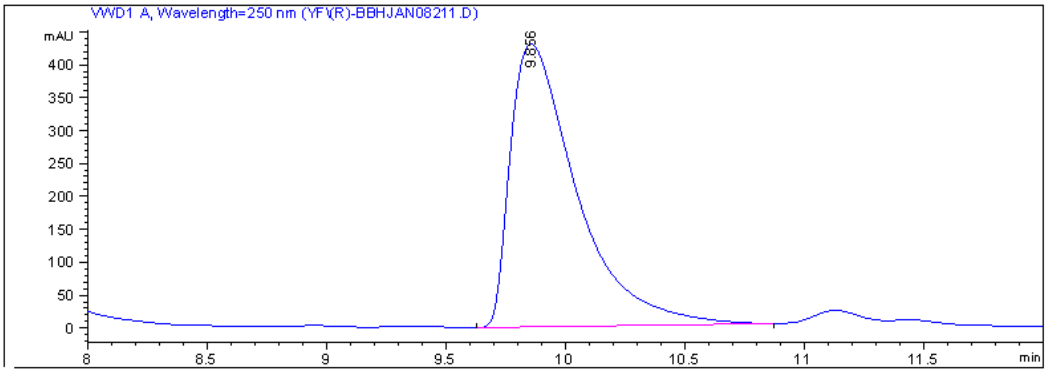


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.747	MM	0.3110	2162.11938	115.88654	97.3458
2	9.910	MM	0.2519	58.95088	3.89969	2.6542



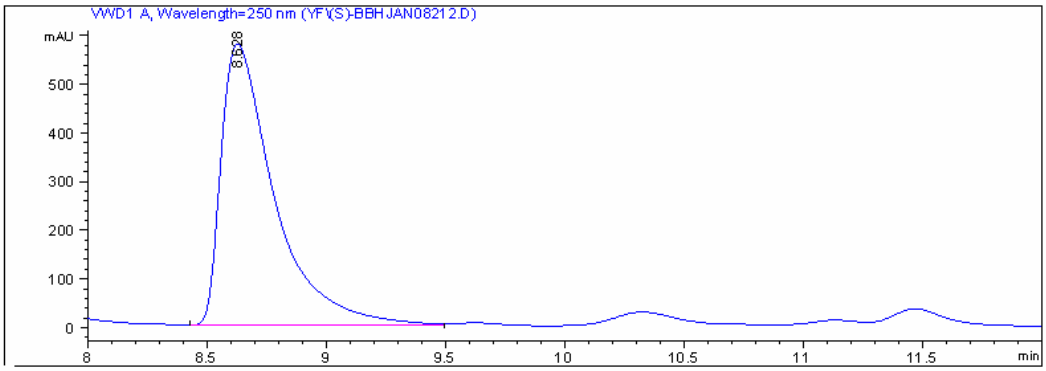
5 (purchased)

(*R*)-1,2,3,4-tetrahydronaphthalen-1-amine (purchased from J&K corporation):



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.856	BB	0.2913	8299.33887	429.69809	100.0000

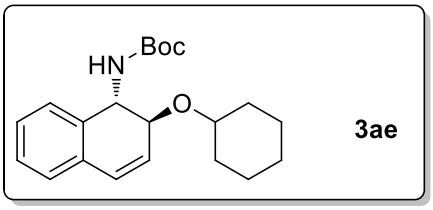
(*S*)-1,2,3,4-tetrahydronaphthalen-1-amine (purchased from J&K corporation):

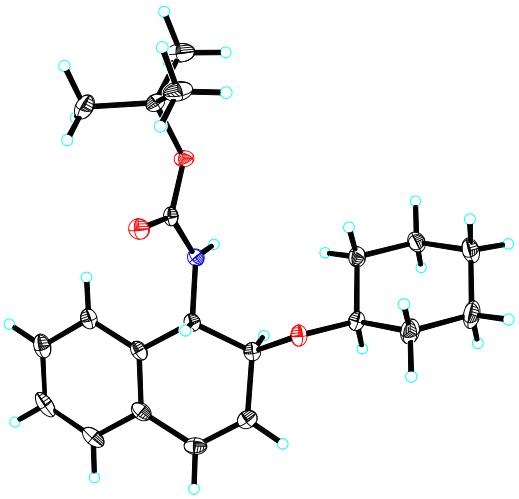


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.628	BV	0.2328	8991.78418	577.07391	100.0000

H: X-Ray Crystallography of Compound 3ae

The absolute configuration of the ring opening products was determined by crystallization of **3ae**.





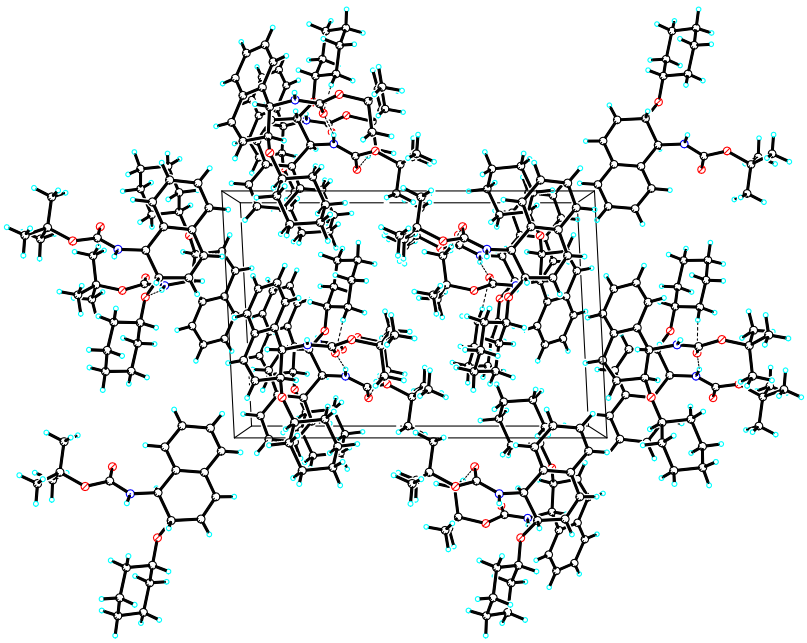


Table 1. Crystal data and structure refinement for yf412.

Identification code	cu_yf412_0m
Empirical formula	C21 H29 N O3
Formula weight	343.45
Temperature	100(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P 21
Unit cell dimensions	a = 12.0136(3) A alpha = 90 deg. b = 8.8743(2) A beta = 92.8950(10) deg. c = 18.0879(4) A gamma = 90 deg.
Volume	1925.93(8) A^3
Z, Calculated density	4, 1.184 Mg/m^3
Absorption coefficient	0.621 mm^-1
F(000)	744
Crystal size	1.35 x 0.58 x 0.38 mm
Theta range for data collection	2.45 to 69.45 deg.
Limiting indices	-14<=h<=14, -10<=k<=10, -21<=l<=21
Reflections collected / unique	18477 / 6242 [R(int) = 0.0403]
Completeness to theta = 69.45	96.5 %

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7981 and 0.4876
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6242 / 1 / 457
Goodness-of-fit on F^2	1.118
Final R indices [I>2sigma(I)]	R1 = 0.0422, wR2 = 0.1102
R indices (all data)	R1 = 0.0423, wR2 = 0.1104
Absolute structure parameter	0.13(14)
Largest diff. peak and hole	0.260 and -0.440 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for yf412.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	2010(1)	4428(2)	4123(1)	28(1)
O(2)	4280(1)	2558(1)	2383(1)	26(1)
O(3)	1346(1)	2295(2)	3548(1)	31(1)
O(4)	1610(1)	9082(1)	1302(1)	27(1)
O(5)	3971(1)	9364(2)	3271(1)	26(1)
O(6)	3391(1)	7131(1)	2762(1)	23(1)

N(1)	2338(1)	4050(2)	2945(1)	23(1)
N(2)	3762(1)	9200(2)	2066(1)	21(1)
C(1)	1872(2)	2709(3)	5172(1)	43(1)
C(2)	1449(1)	4149(2)	4814(1)	27(1)
C(3)	1853(1)	3477(2)	3538(1)	23(1)
C(4)	2353(1)	3224(2)	2256(1)	23(1)
C(5)	3491(1)	3383(2)	1922(1)	24(1)
C(6)	5342(1)	3283(2)	2504(1)	26(1)
C(7)	6206(2)	2078(2)	2698(1)	40(1)
C(8)	7351(2)	2802(3)	2855(2)	51(1)
C(9)	7338(2)	3978(3)	3457(1)	43(1)
C(10)	203(2)	4152(4)	4659(1)	52(1)
C(11)	1398(1)	3662(2)	1704(1)	25(1)
C(12)	411(1)	4252(2)	1929(1)	30(1)
C(13)	-470(2)	4551(2)	1417(1)	39(1)
C(14)	-358(2)	4243(3)	675(1)	41(1)
C(15)	616(2)	3624(2)	445(1)	36(1)
C(16)	1510(2)	3340(2)	952(1)	29(1)
C(17)	2562(2)	2746(2)	708(1)	32(1)
C(18)	3482(2)	2772(2)	1145(1)	29(1)
C(19)	6457(2)	5163(3)	3277(1)	36(1)
C(20)	5315(2)	4436(2)	3122(1)	33(1)
C(21)	1816(2)	5487(3)	5288(1)	48(1)
C(22)	-1247(2)	9291(3)	2584(1)	43(1)
C(23)	-1344(2)	9715(2)	1769(1)	34(1)
C(24)	-198(1)	10035(2)	1470(1)	28(1)
C(25)	565(1)	8677(2)	1590(1)	25(1)
C(26)	2371(1)	7862(2)	1235(1)	23(1)
C(27)	3543(1)	8541(2)	1342(1)	22(1)
C(28)	3676(1)	8440(2)	2707(1)	20(1)
C(29)	3723(1)	9009(2)	4040(1)	26(1)
C(30)	2473(1)	8863(2)	4100(1)	27(1)
C(31)	4342(2)	7609(3)	4312(1)	35(1)
C(32)	4170(2)	10394(3)	4442(1)	35(1)
C(33)	4442(1)	7424(2)	1125(1)	22(1)

C(34)	5508(1)	7440(2)	1459(1)	26(1)
C(35)	6327(2)	6464(2)	1224(1)	32(1)
C(36)	6088(2)	5475(2)	646(1)	33(1)
C(37)	5027(2)	5467(2)	300(1)	31(1)
C(38)	4205(2)	6439(2)	531(1)	26(1)
C(39)	3074(2)	6427(2)	179(1)	29(1)
C(40)	2229(1)	7087(2)	500(1)	28(1)
C(41)	680(2)	8286(3)	2410(1)	33(1)
C(42)	-462(2)	7949(3)	2714(1)	42(1)

Table 3. Bond lengths [A] and angles [deg] for yf412.

O(1)-C(3)	1.359(2)
O(1)-C(2)	1.470(2)
O(2)-C(5)	1.432(2)
O(2)-C(6)	1.435(2)
O(3)-C(3)	1.214(2)
O(4)-C(26)	1.426(2)
O(4)-C(25)	1.428(2)
O(5)-C(28)	1.343(2)
O(5)-C(29)	1.470(2)
O(6)-C(28)	1.216(2)
N(1)-C(3)	1.346(2)
N(1)-C(4)	1.447(2)
N(1)-H(1)	0.8800
N(2)-C(28)	1.350(2)
N(2)-C(27)	1.447(2)
N(2)-H(2)	0.8800
C(1)-C(2)	1.510(3)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(10)	1.509(3)

C(2)-C(21)	1.518(3)
C(4)-C(5)	1.528(2)
C(4)-C(11)	1.533(2)
C(4)-H(4)	1.0000
C(5)-C(18)	1.507(2)
C(5)-H(5)	1.0000
C(6)-C(20)	1.517(3)
C(6)-C(7)	1.520(2)
C(6)-H(6A)	1.0000
C(7)-C(8)	1.531(3)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.510(4)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(19)	1.515(3)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(12)	1.377(3)
C(11)-C(16)	1.402(3)
C(12)-C(13)	1.397(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.383(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.376(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.399(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.459(3)
C(17)-C(18)	1.325(3)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500

C(19)-C(20)	1.529(3)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-C(23)	1.521(3)
C(22)-C(42)	1.530(3)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-C(24)	1.531(2)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-C(25)	1.523(2)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(25)-C(41)	1.523(3)
C(25)-H(25)	1.0000
C(26)-C(40)	1.499(3)
C(26)-C(27)	1.534(2)
C(26)-H(26)	1.0000
C(27)-C(33)	1.532(2)
C(27)-H(27)	1.0000
C(29)-C(32)	1.513(3)
C(29)-C(31)	1.516(3)
C(29)-C(30)	1.517(2)
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800

C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-C(34)	1.389(2)
C(33)-C(38)	1.403(3)
C(34)-C(35)	1.394(3)
C(34)-H(34)	0.9500
C(35)-C(36)	1.383(3)
C(35)-H(35)	0.9500
C(36)-C(37)	1.392(3)
C(36)-H(36)	0.9500
C(37)-C(38)	1.391(3)
C(37)-H(37)	0.9500
C(38)-C(39)	1.471(3)
C(39)-C(40)	1.330(3)
C(39)-H(39)	0.9500
C(40)-H(40)	0.9500
C(41)-C(42)	1.533(3)
C(41)-H(41A)	0.9900
C(41)-H(41B)	0.9900
C(42)-H(42A)	0.9900
C(42)-H(42B)	0.9900

C(3)-O(1)-C(2)	120.35(13)
C(5)-O(2)-C(6)	114.57(13)
C(26)-O(4)-C(25)	114.77(13)
C(28)-O(5)-C(29)	121.90(13)
C(3)-N(1)-C(4)	121.33(14)
C(3)-N(1)-H(1)	119.3
C(4)-N(1)-H(1)	119.3
C(28)-N(2)-C(27)	123.88(14)
C(28)-N(2)-H(2)	118.1
C(27)-N(2)-H(2)	118.1
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5

C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(1)-C(2)-C(10)	109.66(15)
O(1)-C(2)-C(1)	110.42(15)
C(10)-C(2)-C(1)	112.94(19)
O(1)-C(2)-C(21)	102.50(15)
C(10)-C(2)-C(21)	111.13(19)
C(1)-C(2)-C(21)	109.70(17)
O(3)-C(3)-N(1)	125.15(17)
O(3)-C(3)-O(1)	125.14(16)
N(1)-C(3)-O(1)	109.70(14)
N(1)-C(4)-C(5)	110.12(13)
N(1)-C(4)-C(11)	113.05(14)
C(5)-C(4)-C(11)	111.99(14)
N(1)-C(4)-H(4)	107.1
C(5)-C(4)-H(4)	107.1
C(11)-C(4)-H(4)	107.1
O(2)-C(5)-C(18)	109.43(14)
O(2)-C(5)-C(4)	107.59(13)
C(18)-C(5)-C(4)	111.76(14)
O(2)-C(5)-H(5)	109.3
C(18)-C(5)-H(5)	109.3
C(4)-C(5)-H(5)	109.3
O(2)-C(6)-C(20)	111.27(13)
O(2)-C(6)-C(7)	108.15(15)
C(20)-C(6)-C(7)	110.06(16)
O(2)-C(6)-H(6A)	109.1
C(20)-C(6)-H(6A)	109.1
C(7)-C(6)-H(6A)	109.1
C(6)-C(7)-C(8)	110.16(18)
C(6)-C(7)-H(7A)	109.6
C(8)-C(7)-H(7A)	109.6
C(6)-C(7)-H(7B)	109.6
C(8)-C(7)-H(7B)	109.6

H(7A)-C(7)-H(7B)	108.1
C(9)-C(8)-C(7)	112.42(18)
C(9)-C(8)-H(8A)	109.1
C(7)-C(8)-H(8A)	109.1
C(9)-C(8)-H(8B)	109.1
C(7)-C(8)-H(8B)	109.1
H(8A)-C(8)-H(8B)	107.9
C(8)-C(9)-C(19)	110.91(18)
C(8)-C(9)-H(9A)	109.5
C(19)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
C(19)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	108.0
C(2)-C(10)-H(10A)	109.5
C(2)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(2)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(12)-C(11)-C(16)	119.37(16)
C(12)-C(11)-C(4)	122.06(16)
C(16)-C(11)-C(4)	118.39(16)
C(11)-C(12)-C(13)	120.68(19)
C(11)-C(12)-H(12)	119.7
C(13)-C(12)-H(12)	119.7
C(14)-C(13)-C(12)	119.96(19)
C(14)-C(13)-H(13)	120.0
C(12)-C(13)-H(13)	120.0
C(15)-C(14)-C(13)	119.86(18)
C(15)-C(14)-H(14)	120.1
C(13)-C(14)-H(14)	120.1
C(14)-C(15)-C(16)	120.65(19)
C(14)-C(15)-H(15)	119.7
C(16)-C(15)-H(15)	119.7
C(15)-C(16)-C(11)	119.44(18)

C(15)-C(16)-C(17)	120.99(18)
C(11)-C(16)-C(17)	119.56(16)
C(18)-C(17)-C(16)	121.53(17)
C(18)-C(17)-H(17)	119.2
C(16)-C(17)-H(17)	119.2
C(17)-C(18)-C(5)	121.93(16)
C(17)-C(18)-H(18)	119.0
C(5)-C(18)-H(18)	119.0
C(9)-C(19)-C(20)	110.93(18)
C(9)-C(19)-H(19A)	109.5
C(20)-C(19)-H(19A)	109.5
C(9)-C(19)-H(19B)	109.5
C(20)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	108.0
C(6)-C(20)-C(19)	111.59(15)
C(6)-C(20)-H(20A)	109.3
C(19)-C(20)-H(20A)	109.3
C(6)-C(20)-H(20B)	109.3
C(19)-C(20)-H(20B)	109.3
H(20A)-C(20)-H(20B)	108.0
C(2)-C(21)-H(21A)	109.5
C(2)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(2)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(23)-C(22)-C(42)	110.95(17)
C(23)-C(22)-H(22A)	109.4
C(42)-C(22)-H(22A)	109.4
C(23)-C(22)-H(22B)	109.4
C(42)-C(22)-H(22B)	109.4
H(22A)-C(22)-H(22B)	108.0
C(22)-C(23)-C(24)	111.20(16)
C(22)-C(23)-H(23A)	109.4
C(24)-C(23)-H(23A)	109.4

C(22)-C(23)-H(23B)	109.4
C(24)-C(23)-H(23B)	109.4
H(23A)-C(23)-H(23B)	108.0
C(25)-C(24)-C(23)	110.43(16)
C(25)-C(24)-H(24A)	109.6
C(23)-C(24)-H(24A)	109.6
C(25)-C(24)-H(24B)	109.6
C(23)-C(24)-H(24B)	109.6
H(24A)-C(24)-H(24B)	108.1
O(4)-C(25)-C(24)	106.44(14)
O(4)-C(25)-C(41)	111.93(14)
C(24)-C(25)-C(41)	110.03(15)
O(4)-C(25)-H(25)	109.5
C(24)-C(25)-H(25)	109.5
C(41)-C(25)-H(25)	109.5
O(4)-C(26)-C(40)	112.26(14)
O(4)-C(26)-C(27)	106.23(13)
C(40)-C(26)-C(27)	110.75(14)
O(4)-C(26)-H(26)	109.2
C(40)-C(26)-H(26)	109.2
C(27)-C(26)-H(26)	109.2
N(2)-C(27)-C(33)	113.30(13)
N(2)-C(27)-C(26)	113.36(13)
C(33)-C(27)-C(26)	111.57(14)
N(2)-C(27)-H(27)	106.0
C(33)-C(27)-H(27)	106.0
C(26)-C(27)-H(27)	106.0
O(6)-C(28)-O(5)	125.93(16)
O(6)-C(28)-N(2)	125.49(16)
O(5)-C(28)-N(2)	108.57(14)
O(5)-C(29)-C(32)	101.34(14)
O(5)-C(29)-C(31)	111.32(14)
C(32)-C(29)-C(31)	110.69(15)
O(5)-C(29)-C(30)	109.58(13)
C(32)-C(29)-C(30)	111.25(15)

C(31)-C(29)-C(30)	112.16(16)
C(29)-C(30)-H(30A)	109.5
C(29)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(29)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(29)-C(31)-H(31A)	109.5
C(29)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(29)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(29)-C(32)-H(32A)	109.5
C(29)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(29)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(34)-C(33)-C(38)	119.13(16)
C(34)-C(33)-C(27)	121.91(15)
C(38)-C(33)-C(27)	118.76(15)
C(33)-C(34)-C(35)	120.68(17)
C(33)-C(34)-H(34)	119.7
C(35)-C(34)-H(34)	119.7
C(36)-C(35)-C(34)	120.20(17)
C(36)-C(35)-H(35)	119.9
C(34)-C(35)-H(35)	119.9
C(35)-C(36)-C(37)	119.53(17)
C(35)-C(36)-H(36)	120.2
C(37)-C(36)-H(36)	120.2
C(38)-C(37)-C(36)	120.64(18)
C(38)-C(37)-H(37)	119.7
C(36)-C(37)-H(37)	119.7
C(37)-C(38)-C(33)	119.79(17)

C(37)-C(38)-C(39)	121.30(17)
C(33)-C(38)-C(39)	118.88(16)
C(40)-C(39)-C(38)	121.12(17)
C(40)-C(39)-H(39)	119.4
C(38)-C(39)-H(39)	119.4
C(39)-C(40)-C(26)	122.25(16)
C(39)-C(40)-H(40)	118.9
C(26)-C(40)-H(40)	118.9
C(25)-C(41)-C(42)	110.78(15)
C(25)-C(41)-H(41A)	109.5
C(42)-C(41)-H(41A)	109.5
C(25)-C(41)-H(41B)	109.5
C(42)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	108.1
C(22)-C(42)-C(41)	110.43(19)
C(22)-C(42)-H(42A)	109.6
C(41)-C(42)-H(42A)	109.6
C(22)-C(42)-H(42B)	109.6
C(41)-C(42)-H(42B)	109.6
H(42A)-C(42)-H(42B)	108.1

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for yf412.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	32(1)	30(1)	23(1)	-2(1)	6(1)	-8(1)
O(2)	22(1)	21(1)	35(1)	5(1)	-1(1)	1(1)

O(3)	34(1)	25(1)	33(1)	-1(1)	4(1)	-8(1)
O(4)	19(1)	22(1)	39(1)	4(1)	0(1)	1(1)
O(5)	30(1)	25(1)	24(1)	-2(1)	0(1)	-6(1)
O(6)	23(1)	19(1)	26(1)	2(1)	-2(1)	0(1)
N(1)	24(1)	19(1)	25(1)	0(1)	1(1)	-3(1)
N(2)	21(1)	16(1)	26(1)	0(1)	0(1)	-1(1)
C(1)	61(1)	40(1)	27(1)	5(1)	9(1)	15(1)
C(2)	28(1)	29(1)	25(1)	2(1)	7(1)	0(1)
C(3)	17(1)	22(1)	28(1)	1(1)	-1(1)	2(1)
C(4)	23(1)	18(1)	27(1)	0(1)	-1(1)	0(1)
C(5)	24(1)	18(1)	30(1)	2(1)	0(1)	0(1)
C(6)	22(1)	25(1)	30(1)	2(1)	3(1)	1(1)
C(7)	30(1)	32(1)	59(1)	-5(1)	0(1)	8(1)
C(8)	24(1)	48(1)	79(2)	-14(1)	-2(1)	11(1)
C(9)	30(1)	48(1)	50(1)	1(1)	-12(1)	5(1)
C(10)	28(1)	79(2)	50(1)	-4(1)	10(1)	11(1)
C(11)	26(1)	18(1)	31(1)	2(1)	-5(1)	-5(1)
C(12)	25(1)	27(1)	37(1)	0(1)	-3(1)	-2(1)
C(13)	27(1)	32(1)	56(1)	-1(1)	-8(1)	2(1)
C(14)	39(1)	31(1)	51(1)	3(1)	-24(1)	-6(1)
C(15)	45(1)	31(1)	32(1)	2(1)	-14(1)	-7(1)
C(16)	36(1)	20(1)	31(1)	0(1)	-5(1)	-6(1)
C(17)	45(1)	25(1)	26(1)	-2(1)	5(1)	-4(1)
C(18)	33(1)	22(1)	32(1)	0(1)	7(1)	0(1)
C(19)	30(1)	37(1)	40(1)	-7(1)	-8(1)	4(1)
C(20)	26(1)	34(1)	39(1)	-3(1)	-3(1)	9(1)
C(21)	70(2)	41(1)	33(1)	-6(1)	14(1)	-14(1)
C(22)	37(1)	51(1)	44(1)	-1(1)	11(1)	16(1)
C(23)	24(1)	37(1)	43(1)	-3(1)	1(1)	8(1)
C(24)	24(1)	26(1)	35(1)	-2(1)	-6(1)	2(1)
C(25)	19(1)	25(1)	30(1)	-3(1)	-3(1)	0(1)
C(26)	20(1)	21(1)	28(1)	2(1)	-1(1)	1(1)
C(27)	22(1)	20(1)	23(1)	3(1)	0(1)	0(1)
C(28)	15(1)	20(1)	25(1)	-2(1)	0(1)	1(1)
C(29)	26(1)	28(1)	22(1)	0(1)	-2(1)	0(1)

C(30)	26(1)	27(1)	27(1)	-2(1)	-1(1)	1(1)
C(31)	35(1)	41(1)	30(1)	-1(1)	-6(1)	13(1)
C(32)	33(1)	40(1)	32(1)	-8(1)	0(1)	-5(1)
C(33)	24(1)	20(1)	24(1)	5(1)	5(1)	-1(1)
C(34)	22(1)	27(1)	29(1)	1(1)	4(1)	-3(1)
C(35)	23(1)	34(1)	40(1)	8(1)	5(1)	1(1)
C(36)	31(1)	28(1)	41(1)	3(1)	16(1)	6(1)
C(37)	38(1)	25(1)	31(1)	-2(1)	12(1)	-3(1)
C(38)	30(1)	23(1)	24(1)	4(1)	6(1)	-3(1)
C(39)	37(1)	28(1)	23(1)	-2(1)	-2(1)	-5(1)
C(40)	28(1)	26(1)	29(1)	4(1)	-7(1)	-4(1)
C(41)	29(1)	40(1)	30(1)	2(1)	-2(1)	9(1)
C(42)	40(1)	50(1)	38(1)	8(1)	12(1)	15(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for yf412.

	x	y	z	U(eq)
H(1)	2652	4945	2977	27
H(2)	3962	10153	2091	25
H(1A)	1630	1847	4866	64
H(1B)	1571	2611	5664	64
H(1C)	2687	2733	5221	64
H(4)	2254	2135	2377	27
H(5)	3709	4470	1919	29
H(6A)	5542	3799	2037	31
H(7A)	6245	1357	2283	48
H(7B)	5987	1515	3141	48
H(8A)	7896	2008	3003	61
H(8B)	7598	3275	2395	61

H(9A)	8078	4466	3513	52
H(9B)	7184	3488	3933	52
H(10A)	-16	5064	4384	78
H(10B)	-171	4131	5129	78
H(10C)	-14	3261	4366	78
H(12)	328	4458	2439	36
H(13)	-1146	4965	1577	47
H(14)	-952	4458	324	50
H(15)	683	3387	-63	44
H(17)	2589	2330	226	38
H(18)	4155	2395	962	35
H(19A)	6665	5745	2838	43
H(19B)	6419	5870	3698	43
H(20A)	5076	3940	3577	40
H(20B)	4763	5228	2983	40
H(21A)	2630	5486	5359	71
H(21B)	1483	5416	5771	71
H(21C)	1572	6422	5042	71
H(22A)	-1994	9032	2754	52
H(22B)	-962	10164	2877	52
H(23A)	-1820	10621	1703	41
H(23B)	-1705	8882	1482	41
H(24A)	-282	10268	935	34
H(24B)	138	10922	1727	34
H(25)	245	7796	1307	30
H(26)	2256	7115	1638	28
H(27)	3570	9392	981	26
H(30A)	2100	9728	3859	40
H(30B)	2298	8836	4624	40
H(30C)	2214	7931	3858	40
H(31A)	4013	6719	4066	53
H(31B)	4283	7515	4849	53
H(31C)	5128	7689	4197	53
H(32A)	4973	10477	4381	52
H(32B)	4031	10310	4970	52

H(32C)	3794	11292	4237	52
H(34)	5681	8123	1853	31
H(35)	7051	6478	1461	39
H(36)	6645	4805	488	40
H(37)	4862	4793	-98	38
H(39)	2945	5939	-285	35
H(40)	1511	7067	254	33
H(41A)	1030	9140	2686	40
H(41B)	1170	7395	2481	40
H(42A)	-787	7045	2465	51
H(42B)	-373	7735	3251	51

Table 6. Torsion angles [deg] for yf412.

C(3)-O(1)-C(2)-C(10)	-59.6(2)
C(3)-O(1)-C(2)-C(1)	65.4(2)
C(3)-O(1)-C(2)-C(21)	-177.76(17)
C(4)-N(1)-C(3)-O(3)	-4.0(2)
C(4)-N(1)-C(3)-O(1)	176.38(13)
C(2)-O(1)-C(3)-O(3)	-6.9(2)
C(2)-O(1)-C(3)-N(1)	172.74(14)
C(3)-N(1)-C(4)-C(5)	-138.70(15)
C(3)-N(1)-C(4)-C(11)	95.20(18)
C(6)-O(2)-C(5)-C(18)	98.66(16)
C(6)-O(2)-C(5)-C(4)	-139.72(14)
N(1)-C(4)-C(5)-O(2)	69.77(17)
C(11)-C(4)-C(5)-O(2)	-163.53(14)
N(1)-C(4)-C(5)-C(18)	-170.07(14)
C(11)-C(4)-C(5)-C(18)	-43.37(19)
C(5)-O(2)-C(6)-C(20)	82.87(18)
C(5)-O(2)-C(6)-C(7)	-156.13(15)
O(2)-C(6)-C(7)-C(8)	-178.36(17)
C(20)-C(6)-C(7)-C(8)	-56.6(2)

C(6)-C(7)-C(8)-C(9)	56.2(3)
C(7)-C(8)-C(9)-C(19)	-55.0(3)
N(1)-C(4)-C(11)-C(12)	-25.4(2)
C(5)-C(4)-C(11)-C(12)	-150.54(17)
N(1)-C(4)-C(11)-C(16)	159.52(15)
C(5)-C(4)-C(11)-C(16)	34.4(2)
C(16)-C(11)-C(12)-C(13)	-0.9(3)
C(4)-C(11)-C(12)-C(13)	-175.93(17)
C(11)-C(12)-C(13)-C(14)	0.5(3)
C(12)-C(13)-C(14)-C(15)	0.9(3)
C(13)-C(14)-C(15)-C(16)	-1.8(3)
C(14)-C(15)-C(16)-C(11)	1.4(3)
C(14)-C(15)-C(16)-C(17)	-177.31(19)
C(12)-C(11)-C(16)-C(15)	0.0(3)
C(4)-C(11)-C(16)-C(15)	175.19(16)
C(12)-C(11)-C(16)-C(17)	178.70(17)
C(4)-C(11)-C(16)-C(17)	-6.1(2)
C(15)-C(16)-C(17)-C(18)	165.36(18)
C(11)-C(16)-C(17)-C(18)	-13.3(3)
C(16)-C(17)-C(18)-C(5)	1.4(3)
O(2)-C(5)-C(18)-C(17)	146.74(17)
C(4)-C(5)-C(18)-C(17)	27.7(2)
C(8)-C(9)-C(19)-C(20)	54.2(3)
O(2)-C(6)-C(20)-C(19)	177.42(16)
C(7)-C(6)-C(20)-C(19)	57.5(2)
C(9)-C(19)-C(20)-C(6)	-56.3(2)
C(42)-C(22)-C(23)-C(24)	-55.8(3)
C(22)-C(23)-C(24)-C(25)	57.0(2)
C(26)-O(4)-C(25)-C(24)	-168.71(14)
C(26)-O(4)-C(25)-C(41)	71.04(19)
C(23)-C(24)-C(25)-O(4)	-179.50(15)
C(23)-C(24)-C(25)-C(41)	-58.0(2)
C(25)-O(4)-C(26)-C(40)	89.06(17)
C(25)-O(4)-C(26)-C(27)	-149.76(14)
C(28)-N(2)-C(27)-C(33)	-71.75(18)

C(28)-N(2)-C(27)-C(26)	56.71(19)
O(4)-C(26)-C(27)-N(2)	62.53(17)
C(40)-C(26)-C(27)-N(2)	-175.31(14)
O(4)-C(26)-C(27)-C(33)	-168.12(13)
C(40)-C(26)-C(27)-C(33)	-45.97(19)
C(29)-O(5)-C(28)-O(6)	-15.4(2)
C(29)-O(5)-C(28)-N(2)	165.41(13)
C(27)-N(2)-C(28)-O(6)	-1.3(2)
C(27)-N(2)-C(28)-O(5)	177.93(13)
C(28)-O(5)-C(29)-C(32)	-177.69(14)
C(28)-O(5)-C(29)-C(31)	64.59(19)
C(28)-O(5)-C(29)-C(30)	-60.1(2)
N(2)-C(27)-C(33)-C(34)	-20.8(2)
C(26)-C(27)-C(33)-C(34)	-150.16(15)
N(2)-C(27)-C(33)-C(38)	164.43(14)
C(26)-C(27)-C(33)-C(38)	35.1(2)
C(38)-C(33)-C(34)-C(35)	-1.8(3)
C(27)-C(33)-C(34)-C(35)	-176.53(16)
C(33)-C(34)-C(35)-C(36)	0.7(3)
C(34)-C(35)-C(36)-C(37)	0.3(3)
C(35)-C(36)-C(37)-C(38)	-0.3(3)
C(36)-C(37)-C(38)-C(33)	-0.8(3)
C(36)-C(37)-C(38)-C(39)	-178.94(17)
C(34)-C(33)-C(38)-C(37)	1.8(2)
C(27)-C(33)-C(38)-C(37)	176.71(15)
C(34)-C(33)-C(38)-C(39)	-179.99(16)
C(27)-C(33)-C(38)-C(39)	-5.1(2)
C(37)-C(38)-C(39)-C(40)	164.41(18)
C(33)-C(38)-C(39)-C(40)	-13.8(3)
C(38)-C(39)-C(40)-C(26)	-0.7(3)
O(4)-C(26)-C(40)-C(39)	149.73(17)
C(27)-C(26)-C(40)-C(39)	31.2(2)
O(4)-C(25)-C(41)-C(42)	176.60(16)
C(24)-C(25)-C(41)-C(42)	58.5(2)
C(23)-C(22)-C(42)-C(41)	55.6(3)

C(25)-C(41)-C(42)-C(22)	-57.2(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for yf412 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(6)	0.88	2.18	3.0382(18)	165.9
N(2)-H(2)...O(2)#1	0.88	2.23	3.0915(19)	167.4

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z