Supporting Information

Rhodium Catalyzed Asymmetric Cyclization/Addition Reactions of 1, 6-Enynes and Oxa/Azabenzonorbornadienes

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A: General method

The reactions and manipulations were performed under an atmosphere of argon by using standard Schlenk techniques and Drybox (Mikrouna, Supper 1220/750). Anhydrous toluene, DME (Dimethoxyethane), THF (Tetrahydrofuran), MTBE (Methyl *tert*-butyl ether) and 1,4- dioxane were distilled from sodium benzophenone ketyl prior to use. Anhydrous DCE (1, 2-Dichloroethane) were distilled from calcium hydride and stored under argon. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-Avance 400 MHz spectrometer. $CDCl_3$ 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 AS-H, AD-H or 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).

B: Typical procedure for the Cyclization/Addition Reactions

$Rh(COD)_2BF_4$ (20.5 mg, 0.05 mmol), (*R*)-An-SDP (37.0 mg, 0.065 mmol) and 5.0 mL DCE were added to a Schlenk tube under argon atmosphere. The resulting solution was stirred at room temperature for 30 min, then a solution of 1,6-enynes **1a** (250 mg, 1.0 mmol) and azabenzonorbornadienes **2a** (365 mg, 1.5 mmol) in DCE (5.0 mL) was added, the resulting mixture was stirred at 40 ℃ under argon atmosphere with TLC monitoring until the complete consumption of **1a**. The solvent was removed by reduced pressure and the residue was purified by silica gel column chromatography to provide the desired product **3aa** (415 mg, 84% yield). The enantioselective excess of the product was determined to be 99% by chiral HPLC.

C: Characterization data of products

(1*R*,2*S*,4*S*)-*tert*-butyl 2-((*E*)-(4-methylene-1-tosylpyrrolidin-3-ylidene)methyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (3aa)

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/5), 83mg, 84% yield, mp 71-73℃, 99% *ee*. $[\alpha]_D^{20}$ = -10.0 (c = 1.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.05 (m, 6H), 5.61 (d, *J* = 9.0 Hz, 1H), 5.07 – 5.00 (m, 3H), 4.74 (s, 1H), 3.87 (s, 4H), 2.59 (td, *J* = 8.6, 3.8 Hz, 1H), 2.58 (s, 3H), 1.73 – 1.62 (m, 2H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 140.4, 132.2, 132.1, 130.5, 129.7, 128.0, 126.6, 126.5, 110.6, 80.3, 54.5, 54.4, 28.2, 21.6. HRMS calcd for C28H32N2O4S [M]+: 492.2083. Found: 492.2057. The *ee* of **3aa** was determined by HPLC analysis using Daicel Chiralcel AS-H column (25 cm × 0.46 cm ID), conditions: n-hexane/i-PrOH = 90/10, 0.8 mL/min, 215 nm; t_{major} = 52.6 min, t_{minor} = 70.7 min.

(1*R*,2*S*,4*S*)-*tert*-butyl 2-((*E*)-(4-methylene-1-((4-nitrophenyl)sulfonyl)pyrrolidin-3-ylidene) methyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (3ba)

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/5), 49 mg, 76% yield, mp 87-88℃, 99% *ee*. $[\alpha]_D^{20}$ = -18.3 (c = 1.2, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 8.7 Hz, 2H), 7.27 – 7.18 (m, 2H), 7.14 (dd, *J* = 5.9, 2.3 Hz, 2H), 5.72 (d, *J* = 9.1 Hz, 1H), 5.12 (d, *J* = 5.2 Hz, 3H), 4.82 (s, 1H), 4.03 (s, 4H), 2.65 (td, *J* = 8.6, 3.7 Hz, 1H), 1.89 – 1.58 (m, 2H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 141.8, 139.6, 131.34, 131.2, 128.9, 126.8, 126.7, 124.4, 111.2, 80.4, 54.3, 54.2, 28.2. HRMS calcd for C27H29N3O6S [M]+: 523.1777. Found: 523.1773. 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 = 80/20, 1 mL/min, 254 nm; t_{major} = 18.2 min.

(1*R*,2*S*,4*S*)-*tert*-butyl 2-((*E*)-(4-methylene-1-(phenylsulfonyl)pyrrolidin-3-ylidene)methyl) -1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (3ca)

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/5), 77 mg, 81% yield, mp 68 - 70℃, 98% *ee*. $[\alpha]_D^{20}$= -5.7 (c = 13.6, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 14.8 Hz, 2H), 7.13 (t, *J* = 4.0 Hz, 2H), 5.67 (d, *J* = 8.8 Hz, 1H), 5.13 (s, 1H), 5.07 (d, *J* = 6.0 Hz, 2H), 4.80 (s, 1H), 3.96 (s, 4H), 2.64 (s, 1H), 1.79 (d, *J* = 12.0 Hz, 1H), 1.74 – 1.69 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 135.5, 133.0, 132.1, 130.6, 129.1, 127.9, 126.7, 126.6, 110.7, 80.3, 54.5, 54.4, 28.2. HRMS calcd for $C_{27}H_{30}N_2O_4S$ $[M]^+$: 478.1926. Found: 478.1913. 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 = 80/20, 1 mL/min, 254 nm; t_{major} = 9.9 min, t_{minor} = 15.1 min.

(1*R*,2*S*,4*S*)-*tert*-butyl 2-((*E*)-(1-(tert-butoxycarbonyl)-4-methylenepyrrolidin-3-ylidene) methyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (3da)

Colorless oil, purified by silica gel column chromatography (ethyl acetate/hexane, 1/5), 65 mg, 74% yield, 98% *ee*. $[\alpha]_D^{20}$= -3.00 (c = 6.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 4.0 Hz, 2H), 7.15 (d, *J* = 3.2 Hz, 2H), 5.72 (s, 1H), 5.12 (s, 3H), 4.89 (s, 1H), 4.12 (d, *J* = 7.2 Hz, 4H), 2.77 (s, 1H), 1.86 (d, *J* = 2.8 Hz, 1H), 1.78 (t, *J* = 20.0 Hz, 2H), 1.47 (s, 9H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2, 145.5, 126.7, 126.5, 110.2, 80.2, 79.6, 52.9, 52.6, 28.5, 28.2. HRMS calcd for $C_{26}H_{34}N_2O_4$ $[M]^+$: 438.2519. Found: 438.2527. The *ee* of **3da** 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} = 6.1 min, t_{minor} = 8.4 min.

(*Z*)-diethyl 3-(((1*R*,2*S*,4*S*)-9-(*tert*-butoxycarbonyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalen-2-yl)methylene)-4-methylenecyclopentane-1,1-dicarboxylate (3ea)

Colorless oil, purified by silica gel column chromatography (ethyl acetate/hexane, 1/10), 57 mg, 59% yield, 97% *ee*, $[\alpha]_D^{20}$ = -6.0 (c = 1.1, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.25 (m, 2H), 7.16 – 7.13 (m, 2H), 5.69 – 5.67 (m, 1H), 5.16 – 5.05 (m, 3H), 4.86 (s, 1H), 4.24 – 4.15 (m, 4H), 3.05 (s, 4H), 2.78 – 2.73 (m, 1H), 1.89 – 1.73 (m, 2H), 1.37 (s, 9H), 1.28 – 1.22 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 145.5, 144.0, 135.5, 130.0, 126.5, 126.4, 110.6, 80.1, 61.6, 61.5, 57.3, 42.7, 42.4, 28.2, 14.0, 14.0. HRMS calcd for $C_{28}H_{35}NO_6$ $[M]^+$: 481.2464. Found: 481.2462. The *ee* of **3ea** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/i-PrOH = 95/5, 1 mL/min, 254 nm; t_{major} = 10.3 min, t_{minor} = 12.5 min.

(*Z*)-dimethyl 3-(((1*R*,2*S*,4*S*)-9-(*tert*-butoxycarbonyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalen-2-yl)methylene)-4-methylenecyclopentane-1,1-dicarboxylate (3fa)

Colorless oil, purified by silica gel column chromatography (ethyl acetate/hexane, 1/10), 61 mg, 67% yield, 97% *ee*. $[\alpha]_D^{20}$ = -3.7 (c = 10.6, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.4 Hz, 2H), 7.07 (dd, *J* = 5.0, 3.2 Hz, 2H), 5.62 (s, 1H), 5.03 (dd, *J* = 27.7, 16.5 Hz, 3H), 4.80 (s, 1H), 3.69 (s, 3H), 3.65 (s, 3H), 3.09 – 2.78 (m, 4H), 2.75 – 2.60 (m, 1H), 1.82 – 1.67 (m, 2H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 145.5, 143.9, 135.3, 130.2, 126.5, 126.4, 110.7, 80.1, 57.3, 52.9, 52.8, 42.9, 42.5, 28.2. HRMS calcd for $C_{26}H_{31}NO_6$ $[M]^+$: 453.2151. Found: 453.2150. The *ee* of **3fa** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/i-PrOH = 96/4, 1 mL/min, 254 nm; t_{major} = 14.2 min, t_{minor} = 17.5 min.

(1*R*,2*S*,4*S*)-*tert*-butyl 2-((*E*)-(4-methylenedihydrofuran-3(2H)-ylidene)methyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (3ga)

Colorless oil, purified by silica gel column chromatography (ethyl acetate/hexane, 1/10), 26 mg, 38% yield, 98% *ee*, $[\alpha]_D^{20}$ = 6.8 (c = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.26 (m, 2H), 7.18 – 7.15 (m, 2H), 5.72 (d, *J* = 7.4 Hz, 1H), 5.17 – 5.11 (m, 3H), 4.92 (s, 1H), 4.50 – 4.42 (m, 4H), 2.84 – 2.79 (m, 1H), 1.93 – 1.88 (m, 1H), 1.84 – 1.79 (m, 1H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 143.9, 135.2, 127.8, 126.7, 126.6, 107.5, 80.3, 74.4, 74.2, 28.3. HRMS calcd for $C_{21}H_{25}NO_3$ $[M]^+$: 339.1834. Found: 339.1840. The *ee* of **3ga** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/i-PrOH = 95/5, 1 mL/min, 254 nm; t_{major} = 7.6 min, t_{minor} = 8.3 min.

(1*R*,2*S*,4*S*)-2-((*E*)-(4-methylene-1-tosylpyrrolidin-3-ylidene)methyl)-9-tosyl-1,2,3,4-tetrahydro-1,4-epiminonaphthalene (3ab)

Light yellow solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/5), 48 mg, 44% yield, mp 87 - 89℃, 99% *ee*. $[\alpha]_D^{20}$ = -6.8 (c = 9.1, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.19 -7.17 (m, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.76 (s, 4H), 5.75 (d, *J* = 9.1 Hz, 1H), 4.97 (d, *J* = 3.2 Hz, 2H), 4.89 (m, 1H), 4.59 (m, 1H), 3.87 – 3.86 (m, 4H), 2.57 – 2.52 (m, 1H), 2.38 (s, 3H), 2.15 (s, 3H), 1.90 – 1.85 (m, 1H), 1.66 – 1.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 143.4, 142.9, 141.8, 140.5, 134.5, 132.6, 132.2, 129.8, 129.7, 128.9, 128.0, 127.9, 126.7, 126.6, 120.1, 120.0, 110.5, 68.8, 63.6, 54.5, 54.3, 40.3, 37.2, 21.6, 21.3. HRMS calcd for $C_{30}H_{30}N_2O_4S_2$ $[M]^+$: 546.1647. Found: 546.1632. The *ee* of **3ab** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/i-PrOH = 60/40, 1 mL/min, 254 nm; t_{major} = 14.6 min, t_{minor} = 26.1 min.

(1*R*,2*S*,4*S*)-*tert*-butyl 6,7-dimethyl-2-((*E*)-(4-methylene-1-tosylpyrrolidin-3-ylidene)methyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (3ac)

Colorless oil, purified by silica gel column chromatography (ethyl acetate/hexane, 1/10), 84 mg, 80% yield, 98% *ee*, $[\alpha]_D^{20}$= -8.1 (c = 1.8, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 6.4 Hz, 2H), 5.68 (d, *J* = 8.8 Hz, 1H), 5.32 (s, 3H), 4.76 (s, 1H), 3.94 (s, 4H), 2.64 (s, 1H), 2.47 (s, 3H), 2.24 (s, 6H),1.79 (d, *J* = 11.6 Hz, 1H), 1.72(d, *J* = 8.4 Hz, 1H) 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 140.4, 134.7, 134.5, 132.4, 131.9, 130.9, 129.7, 128.0, 110.6, 80.2, 54.6, 54.4, 28.3, 21.6, 19.9. HRMS calcd for $C_{30}H_{36}N_2O_4S$ $[M]^+$: 520.2396. Found: 520.2427. 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 = 85/15, 1 mL/min, 254 nm; t_{major} = 14.2 min, t_{minor} = 17.0 min.

(1*R*,2*S*,4*S*)-*tert*-butyl 6,7-dimethoxy-2-((*E*)-(4-methylene-1-tosylpyrrolidin-3-ylidene) methyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (3ad)

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/5), 82 mg, 74% yield, mp 57 - 59℃, 99% *ee*, $[\alpha]_D^{20}$ = -25.8 (c = 1.7, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 7.6 Hz, 2H), 5.69 (d, *J* = 7.6 Hz, 1H), 5.08 (d, *J* = 7.6 Hz, 3H), 4.77(s, 1H), 3.92 – 3.87 (m, 10H), 2.62 (s, 1H), 2.46 (s, 3H), 1.77 – 1.68 (m, 2H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 147.7, 143.8, 140.5, 132.3, 131.9, 130.7, 129.7, 128.0, 110.4, 80.4, 56.2, 54.5, 54.3, 28.2, 21.6. HRMS calcd for $C_{30}H_{36}N_2O_6S$ $[M]^+$: 552.2294. Found: 552.2301. 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 = 70/30, 1 mL/min, 254 nm; t_{major} = 13.8 min, t_{minor} = 16.2 min.

(5*R*,6*S*,8*S*)-*tert*-butyl 6-((*E*)-(4-methylene-1-tosylpyrrolidin-3-ylidene)methyl)-5,6,7,8-tetrahydro-5,8-epiminonaphtho[2,3-*d*][1,3]dioxole-10-carboxylate (3ae)

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/5), 86 mg, 80% yield, mp 76 - 79℃, 98% *ee*, $[\alpha]_D^{20}$ = -17.0 (c = 0.90, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 6.77 (d, *J* = 7.2 Hz, 2H), 5.95 (s, 2H), 5.65 (d, *J* = 8.8 Hz, 2H), 5.08 (d, *J* = 13.2 Hz, 3H), 4.72(s, 1H), 3.94 (s, 4H), 2.61 (s,1H), 2.44 (s, 3H), 1.76 – 1.64 (m, 2H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 146.1, 143.8, 140.5, 132.3, 132.1, 130.5, 129.7, 128.0, 110.5, 101.1, 80.4, 54.5, 54.3, 28.2, 21.6. HRMS calcd for $C_{29}H_{32}N_2O_6S$ [M]+: 536.1981. Found: 536.2014. 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 = 70/30, 1 mL/min, 254 nm; t_{major} = 11.2 min, t_{minor} = 17.1 min.

(6*R*,7*S*,9*S*)-*tert*-butyl 7-((*E*)-(4-methylene-1-tosylpyrrolidin-3-ylidene)methyl)-2,3,6,7,8,9-hexahydro-6,9-epiminonaphtho[2,3-*b*][1,4]dioxine-11-carboxylate (3af)

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/5), 79 mg, 72% yield, mp 99 - 101℃, 98% *ee*, $[\alpha]_D^{20}$ = -14.0 (c = 1.8, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 6.0 Hz, 2H), 5.65 (d, *J* = 8.8 Hz, 1H), 5.09 (d, *J* = 6.4 Hz, 3H), 4.71 (s, 1H), 4.23 (s, 4H), 3.94 (s, 4H), 2.62 (s, 1H), 2.46 (s, 3H), 1.75 – 1.69 (m, 2H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 141.9, 141.7, 140.4, 132.3, 132.0, 130.7, 129.7, 128.0, 110.5, 80.3, 64.2, 54.5, 54.3, 28.2, 21.5. HRMS calcd for $C_{30}H_{34}N_2O_6S$ [M]+: 550.2138. Found: 550.2153. 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 = 70/30, 1 mL/min, 254 nm; t_{major} = 12.5 min, t_{minor} = 18.9 min.

(1*R*,2*S*,4*S*)-*tert*-butyl 6,7-dibromo-2-((*E*)-(4-methylene-1-tosylpyrrolidin-3-ylidene)methyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (3ag)

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/15), 115 mg, 89% yield, mp 95 - 97℃, 99% *ee*, $[\alpha]_D^{20}$ = -12.3 (c = 1.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 9.6 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.62 (d, *J* = 8.8 Hz, 1H), 5.10 – 5.06 (m, 2H), 5.01 – 4.96 (m, 1H), 4.75 (s, 1H), 3.92 (s, 4H), 2.64 – 2.61 (m, 1H), 2.44 (s, 3H), 1.82 – 1.68 (m, 2H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 140.4, 132.7, 132.3, 129.8, 129.5, 128.0, 122.8, 122.6, 110.8, 81.0, 54.5, 54.3, 28.2, 21.6. HRMS calcd for $C_{28}H_{30}Br_2N_2O_4S$ $[M]^+$: 648.0293. Found: 648.0280. The *ee* of **3ag** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/i-PrOH = 90/10, 1 mL/min, 254 nm; t_{major} = 28.6 min, t_{minor} = 34.6 min.

(*E*)-3-methylene-4-(((1*R*,2*S*,4*S*)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)methylene)-1-tosylpyrrolidine (3ah)

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/4), 61 mg, 78% yield, mp 64 - 67℃, 93% *ee*. $[\alpha]_D^{20}$= 4.9 (c = 1.2, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 2H), 7.37 – 7.31 (m, 2H), 7.26 – 7.20 (m, 2H), 7.19 – 7.15 (m, 2H), 5.68 (d, *J* = 9.3 Hz, 1H), 5.44 (d, *J* = 4.7 Hz, 1H), 5.14 – 5.07 (m, 2H), 5.02 (s, 1H), 4.01 – 3.91 (m, 4H), 2.78– 2.70 (m, 1H), 2.44 (s, 3H), 1.85 – 1.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 144.5, 143.8, 140.6, 132.5, 132.1, 131.1, 129.7, 128.0, 126.9, 126.7, 119.0, 118.8, 110.5, 84.3, 79.3, 54.6, 54.4, 39.8, 36.4, 21.5. HRMS calcd for $C_{23}H_{23}NO_3S$ $[M]^+$: 393.1399. Found: 393.1402. 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 = 70/30, 1 mL/min, 254 nm; t_{minor} = 14.7 min, t_{major} = 17.7 min.

(*E*)-3-(((1*R*,2*S*,4*S*)-5,8-dimethoxy-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)methylene)-4-methylene-1-tosylpyrrolidine (3ai)

White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/4), 79 mg, 87% yield, mp 71 - 73℃, 96% *ee*. $[\alpha]_D^{22}$ = 11.5 (c = 1.6, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.58 (s, 2H), 5.58 – 5.52 (m, 2H), 5.20 (s, 1H), 5.07 (d, *J* = 23.7 Hz, 1H), 3.93 – 3.70 (m, 4H), 3.71 (d, *J* = 4.5 Hz, 3H), 2.77 – 2.69 – 2.63 (m, 1H), 2.37 (s, 3H), 1.78 – 1.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 146.5, 143.8, 140.3, 135.0, 133.7, 132.4, 132.2, 131.1, 129.7, 128.0, 111.2, 111.1, 110.8, 82.3, 56.0, 55.8, 54.6, 54.4, 39.4, 36.2, 21.5. HRMS calcd for $C_{25}H_{27}NO_5S$ $[M]^+$: 453.1610. Found: 453.1603. The *ee* of **3ai** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/i-PrOH = 80/20, 1 mL/min, 254 nm; t_{major} = 41.0 min, t_{minor} = 43.6 min.

(*E*)-3-methylene-4-(((1*R*,2*S*,4*S*)-1,2,3,4-tetrahydro-1,4-epoxytriphenylen-2-yl)methylene)-1-tosylpyrrolidine (3aj)

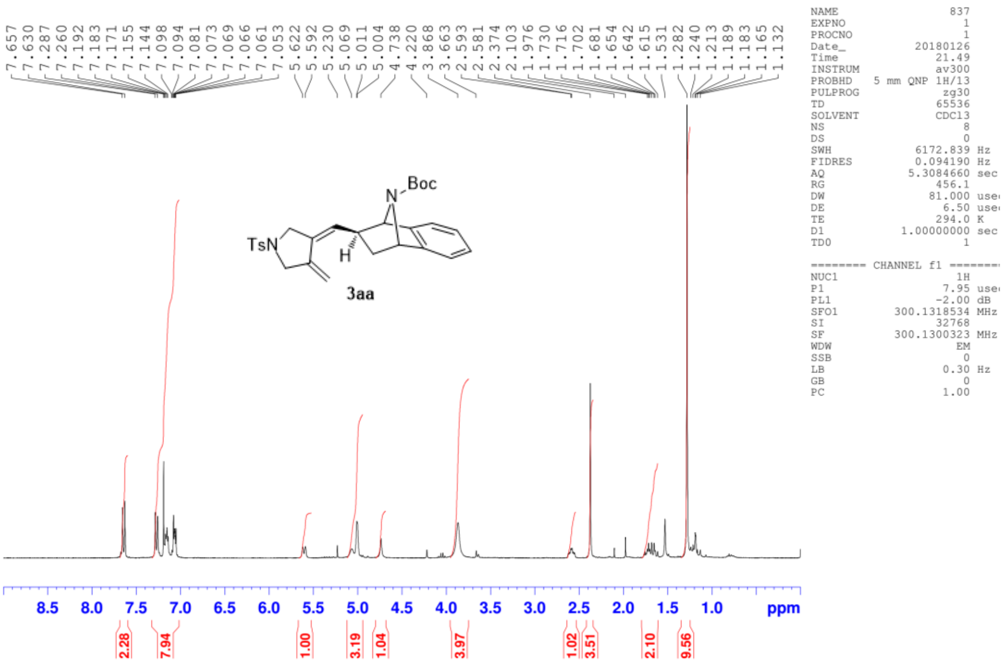
White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/5), 81 mg, 82% yield, mp 119 - 120℃, 82% *ee*. $[\alpha]_D^{21}$ = +10.3 (c = 1.6, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 – 8.66 (m, 2H), 7.85 – 7.78 (m, 2H), 7.68 – 7.66 (m, 2H), 7.62 – 7.57 (m, 4H), 7.30 – 7.28 (m, 2H), 5.98 (d, *J* = 4.4 Hz, 1H), 5.74 (d, *J* = 9.6 Hz, 1H), 5.55 (s, 1H), 4.99 (s, 1H), 4.92 (s, 1H), 3.98 – 3.83 (m, 4H), 2.74 – 2.70 (m, 1H), 2.38 (s, 3H), 1.96 – 1.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 141.4, 140.7, 139.5, 132.7, 132.3, 131.2, 130.3, 130.3, 129.9, 128.2, 127.9, 127.2, 126.6, 126.5, 125.7, 125.7, 124.3, 124.1, 123.8, 123.8, 110.9, 84.0, 78.9, 54.8, 54.7, 40.1, 36.5, 21.7. HRMS calcd for $C_{31}H_{27}NO_3S$ $[M]^+$: 493.1712. Found: 493.1702. The *ee* of **3aj** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/i-PrOH = 60/40, 1 mL/min, 254 nm; t_{minor} = 45.5 min, t_{major} = 54.5 min.

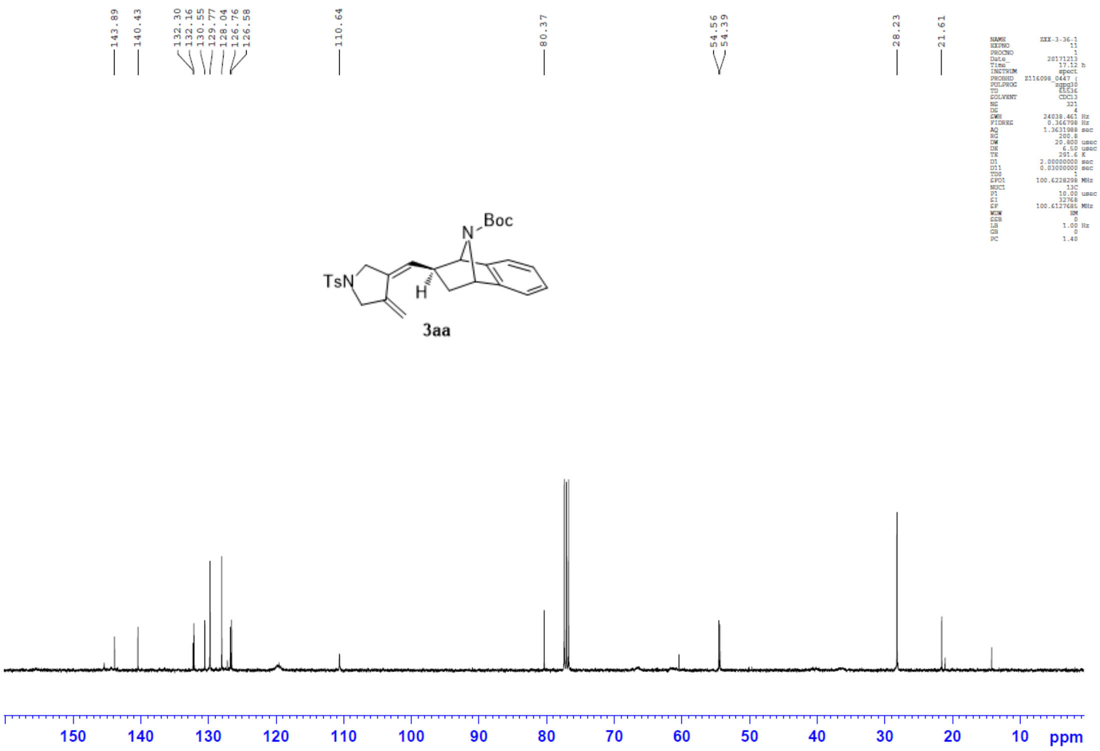
(*E*)-3-(((6*R*,7*S*,9*S*)-2,3,6,7,8,9-hexahydro-6,9-epoxynaphtho[2,3-*b*][1,4]dioxin-7-yl)methylene)-4-methylene-1-tosylpyrrolidine (3ak)

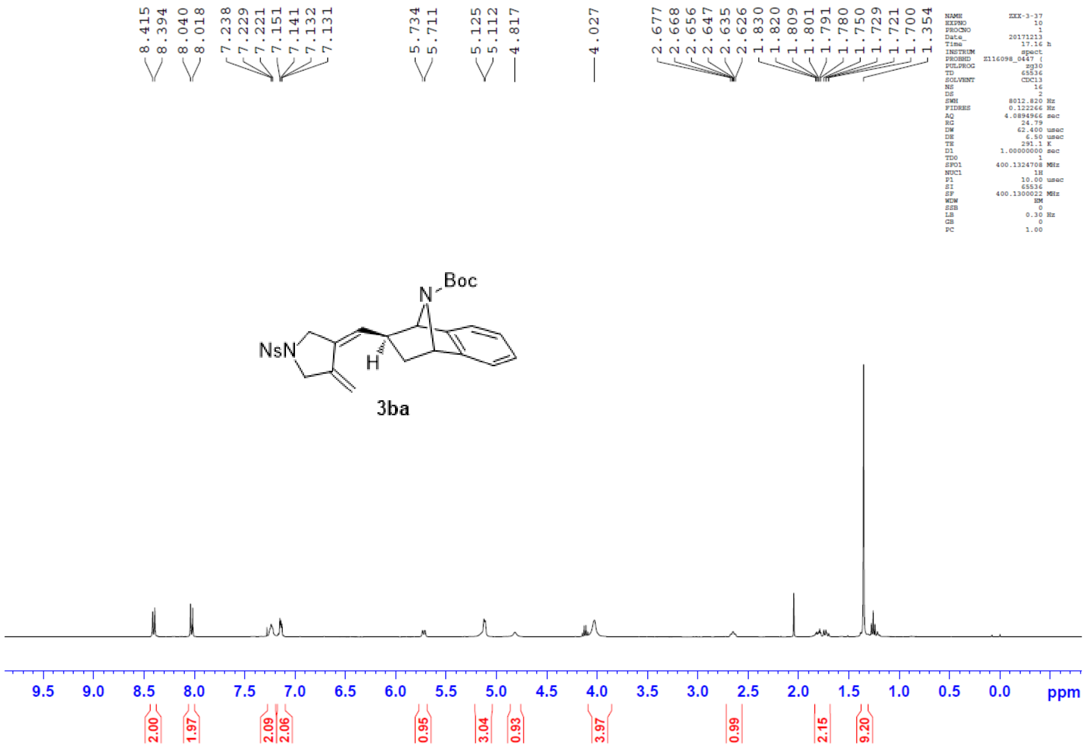
White solid, purified by silica gel column chromatography (ethyl acetate/hexane, 1/5), 61 mg, 68% yield, mp 104 - 105℃, 87% *ee*. $[\alpha]_D^{21}$ = -6.1 (c = 0.7, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.71 (m, 2H), 7.36 – 7.34 (m, 2H), 6.77 – 6.75 (m, 2H), 5.65 (d, *J* = 9.2 Hz, 1H), 5.36 (d, *J* = 4.4 Hz, 1H), 5.13 – 5.11 (m, 2H), 4.93 (s, 1H), 4.22 (s, 4H), 3.97 – 3.94 (m, 4H), 2.73 – 2.68 (m, 1H), 2.45 (s, 3H), 1.82 – 1.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 142.1, 142.0, 140.6, 138.9, 137.5, 132.4, 131.9, 131.3, 129.7, 128.0, 110.6, 109.0, 108.7, 84.2, 79.2, 64.3, 54.6, 54.4, 40.4, 37.0, 21.6. HRMS calcd for $C_{25}H_{25}NO_5S$ $[M]^+$: 451.1453. Found: 451.1475. The *ee* of

3ak was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/i-PrOH = 60/40, 1 mL/min, 254 nm; t_{major} = 37.4 min, t_{minor} = 52.2 min.

D: NMR Spectra of Products



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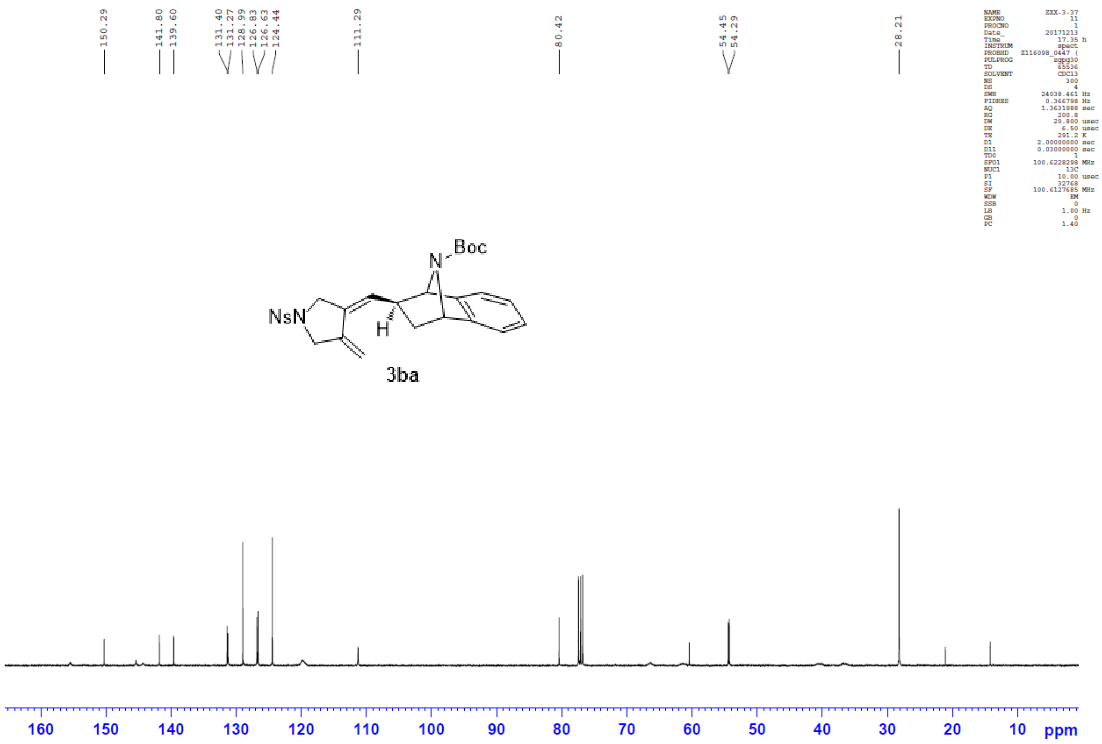
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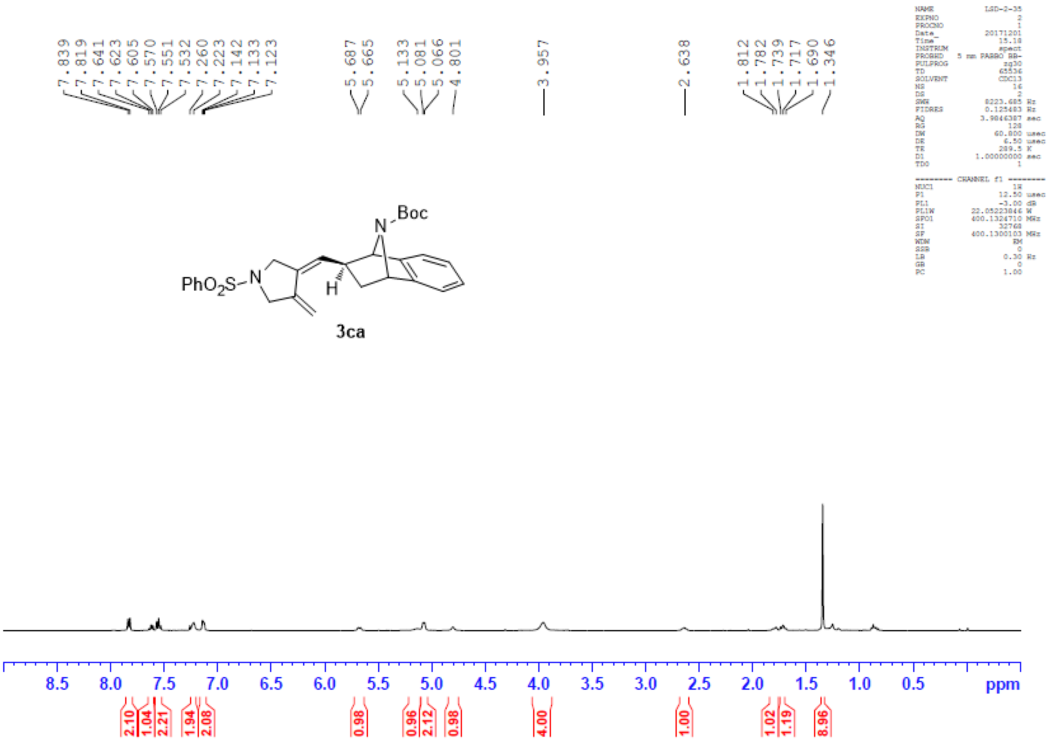
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7.123
5.687
5.665
5.133
5.081
5.066
4.801
3.957
2.638
1.812
1.782
1.739
1.717
1.690
1.346
Boc
N
PhO2S–N
H
3ca
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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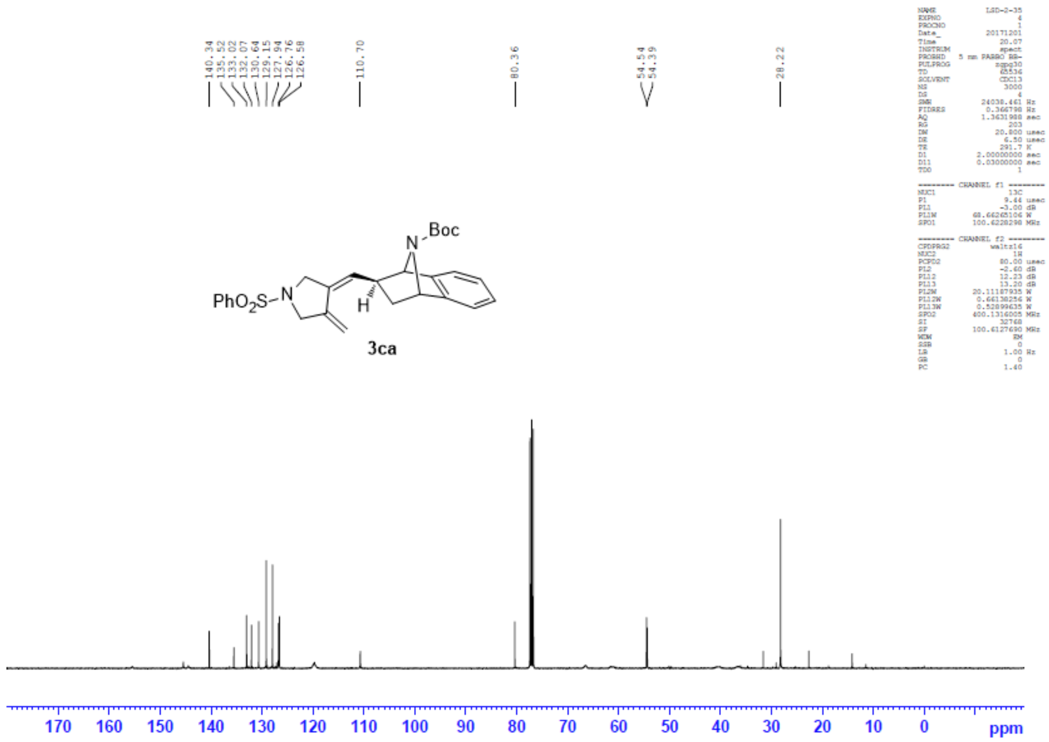
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Boc
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H
3ca
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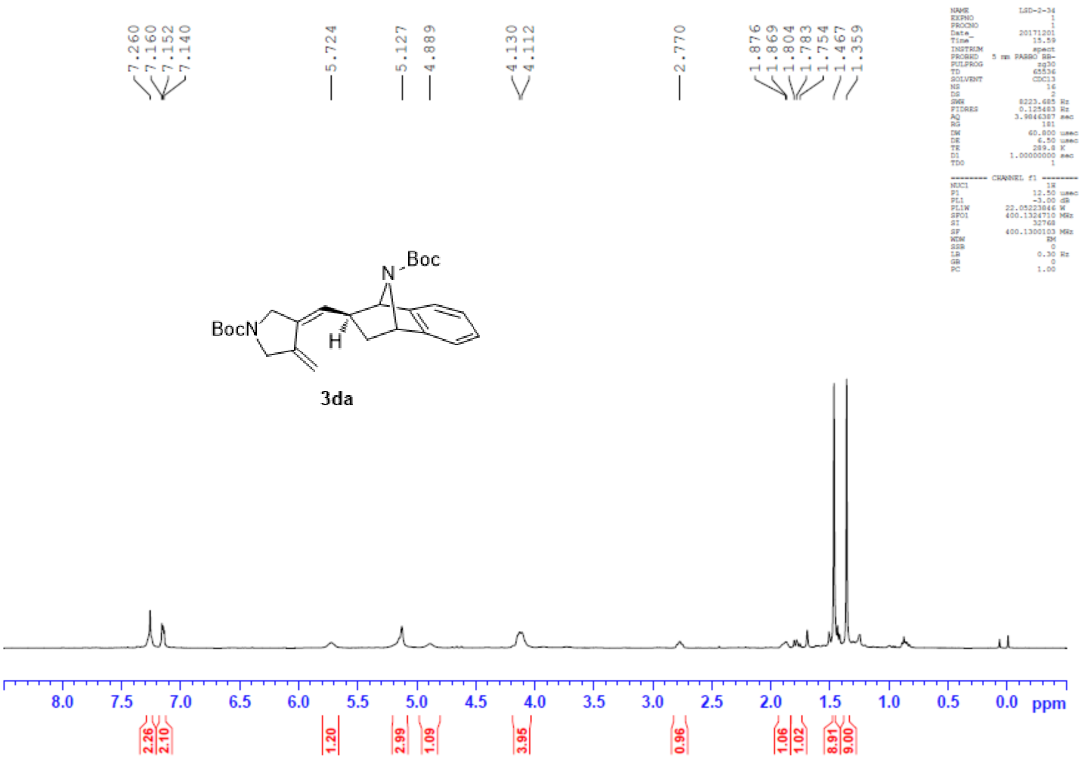
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1.783
1.754
1.467
1.359
Boc
BocN
H
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0.96
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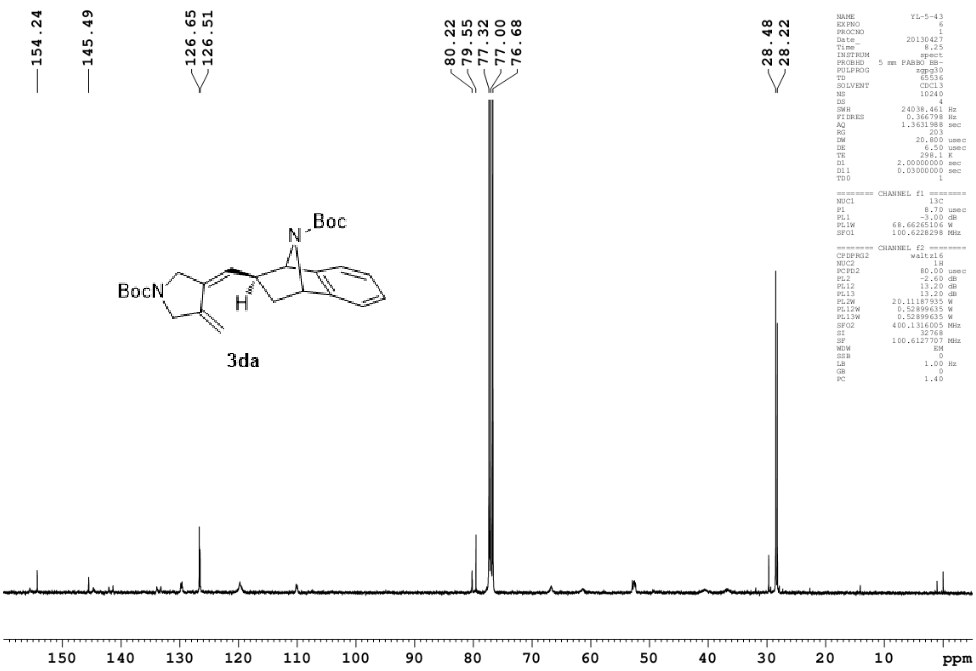
1.02
8.91
9.00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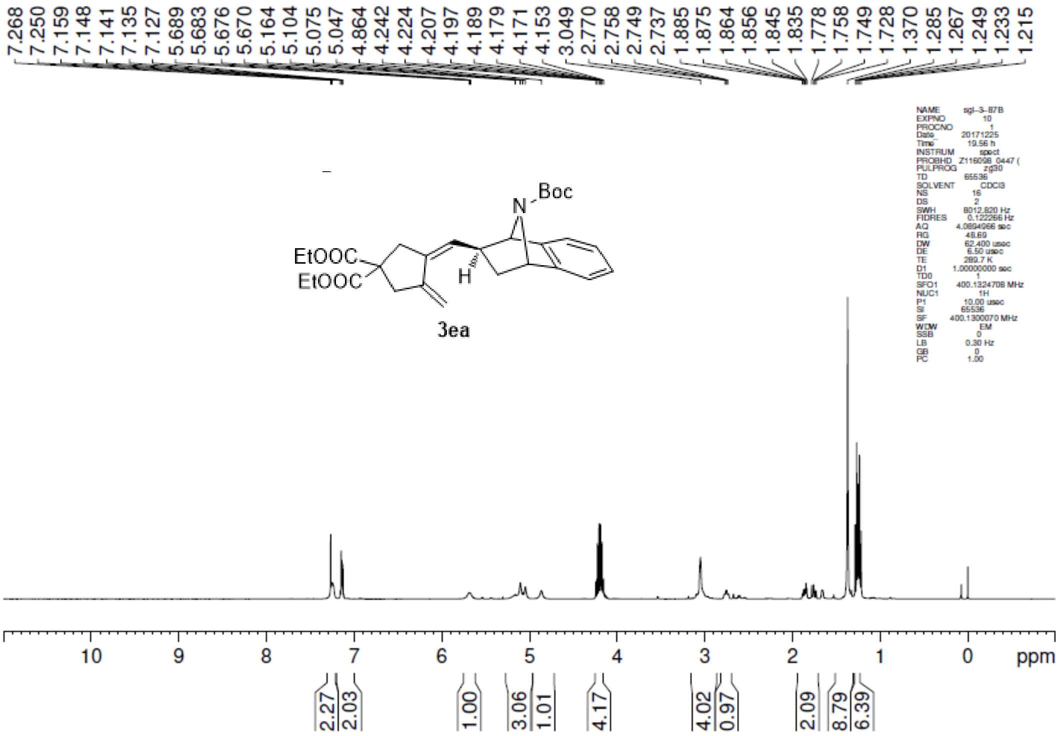
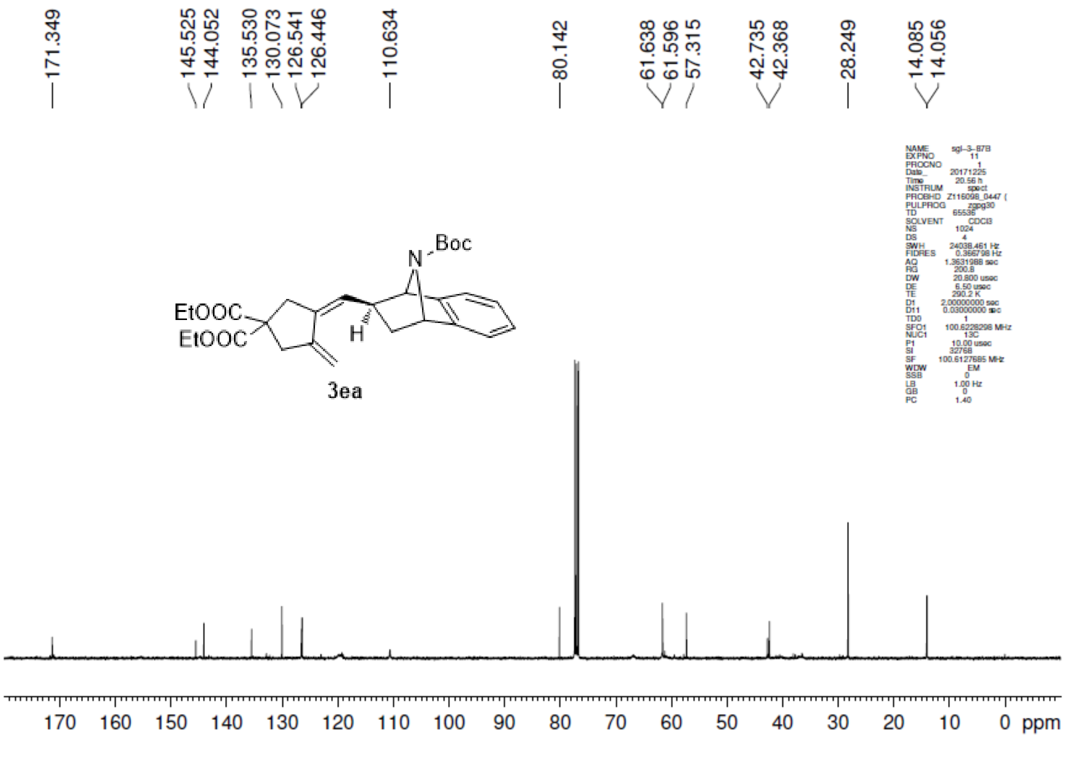
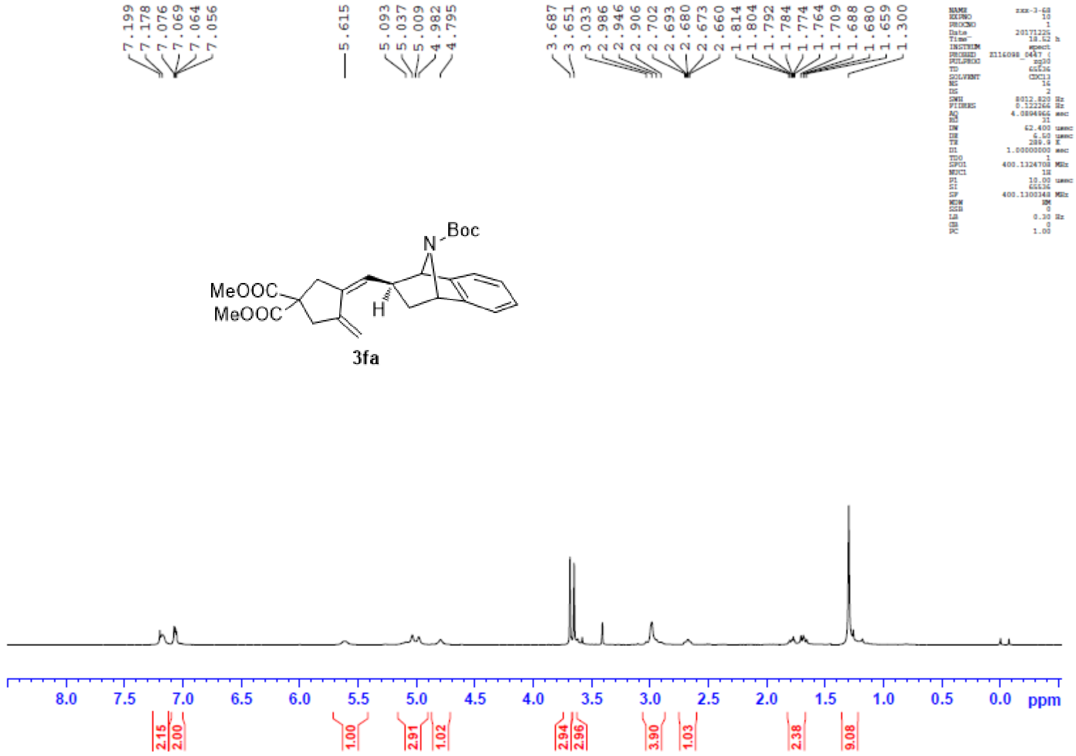
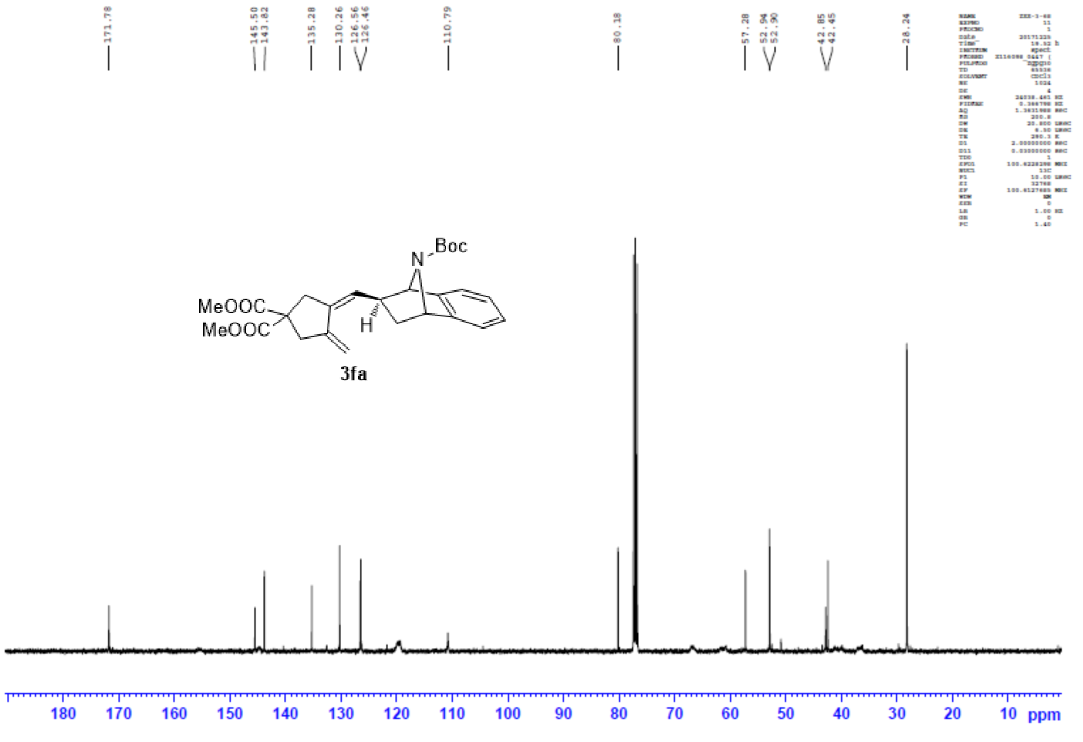
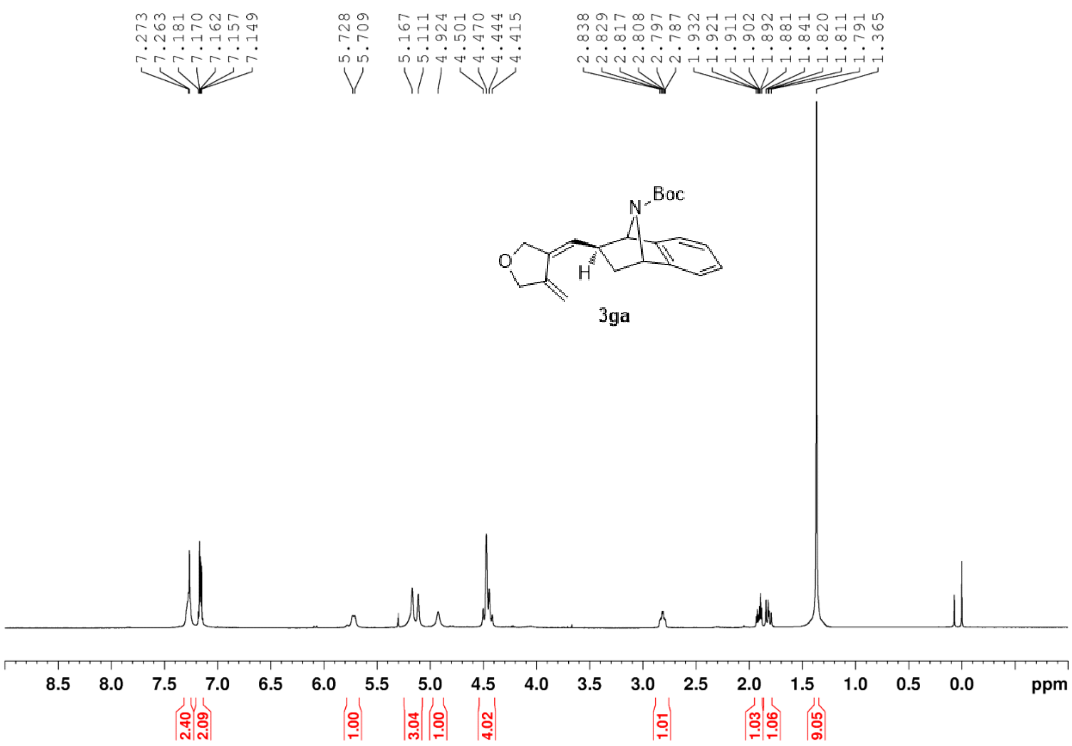
BocN
H
3da
ppm







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4.470
4.444
4.415
2.838
2.829
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2.797
2.787
1.932
1.921
1.911
1.902
1.892
1.881
1.841
1.820
1.811
1.791
1.365
Boc
N
O
H
3ga
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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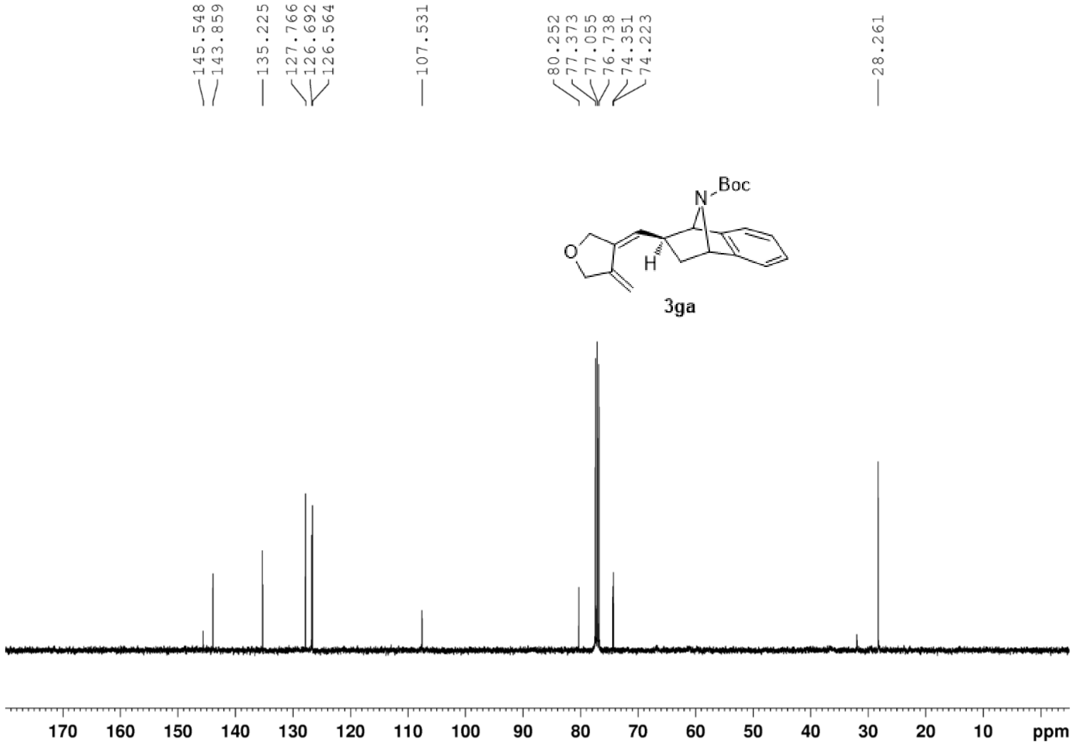
1.03
1.06
9.05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Boc
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O
H
3ga
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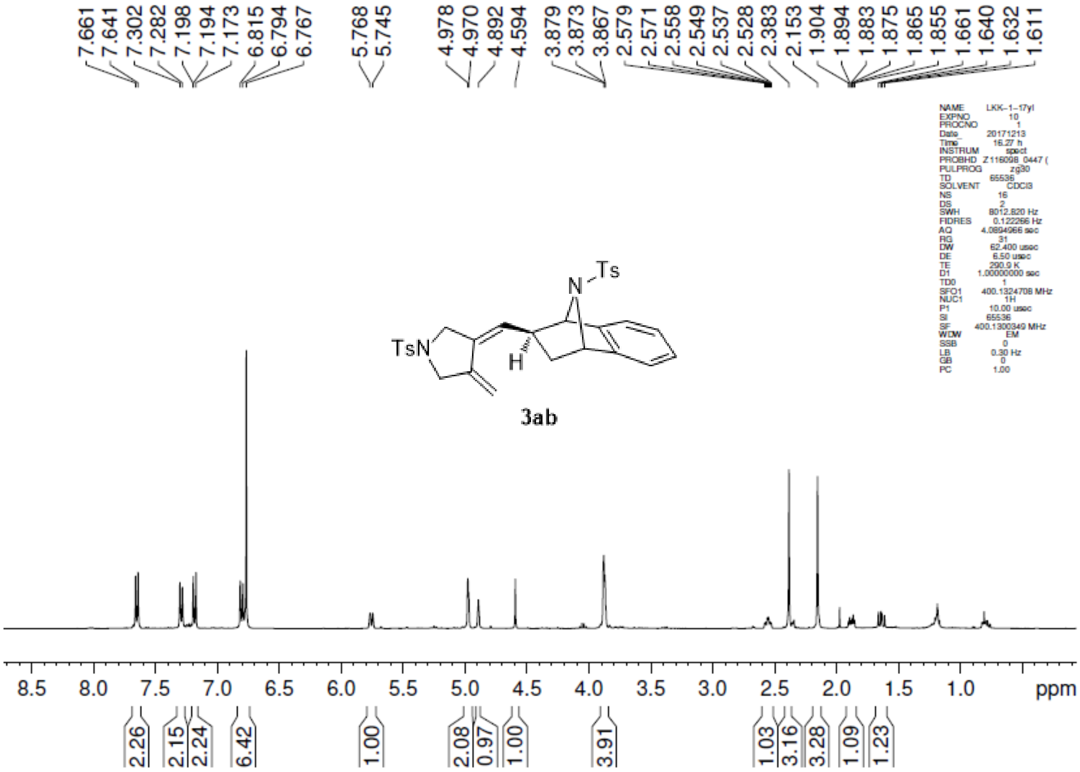
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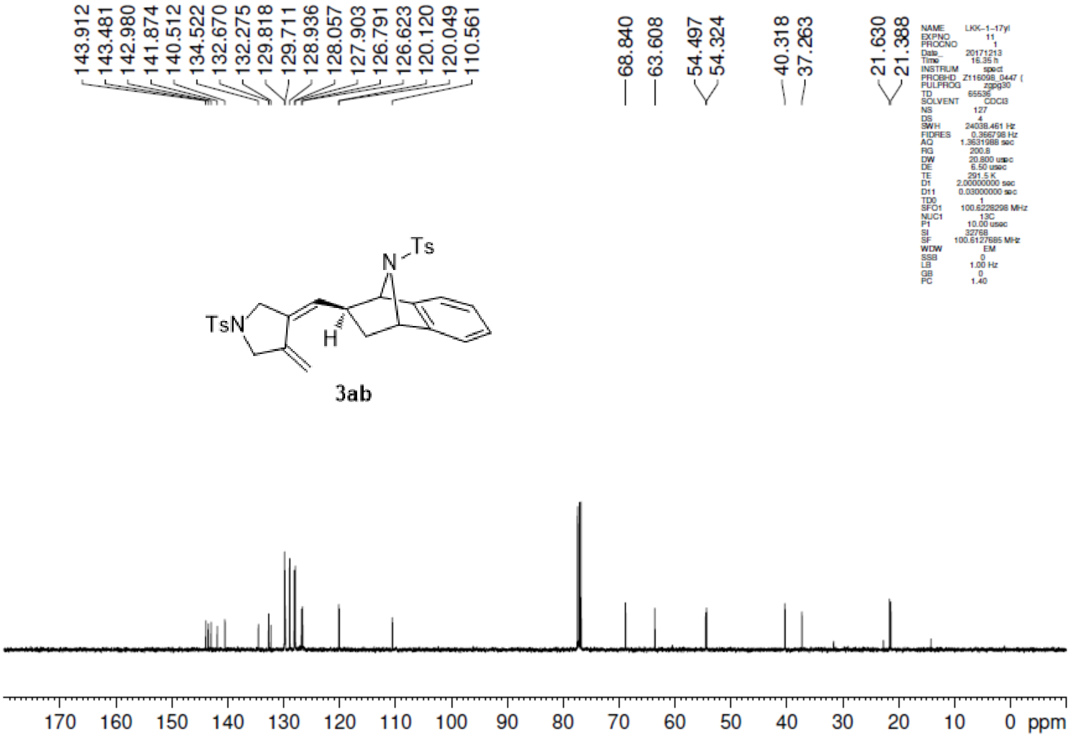
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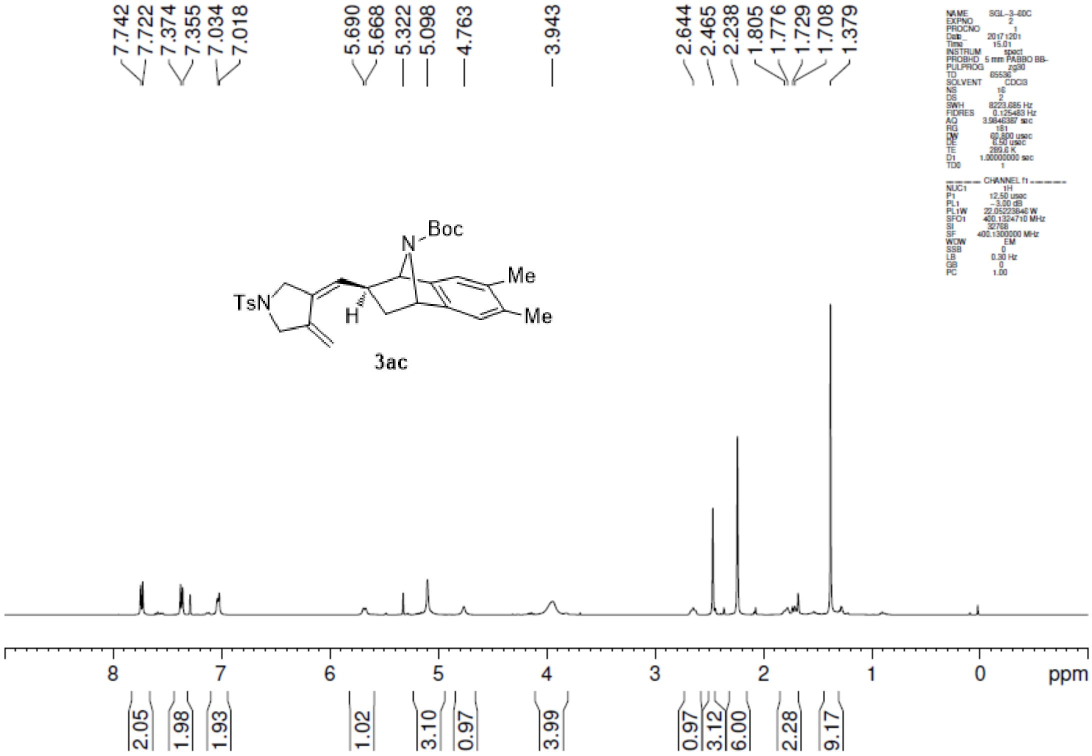
ppm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2.465
2.238
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1.776
1.729
1.708
1.379
Boc
N
TsN
H
Me
Me
3ac
8
7
6
5
4
3
2
1
0
ppm
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1.02
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0.97
3.99
0.97
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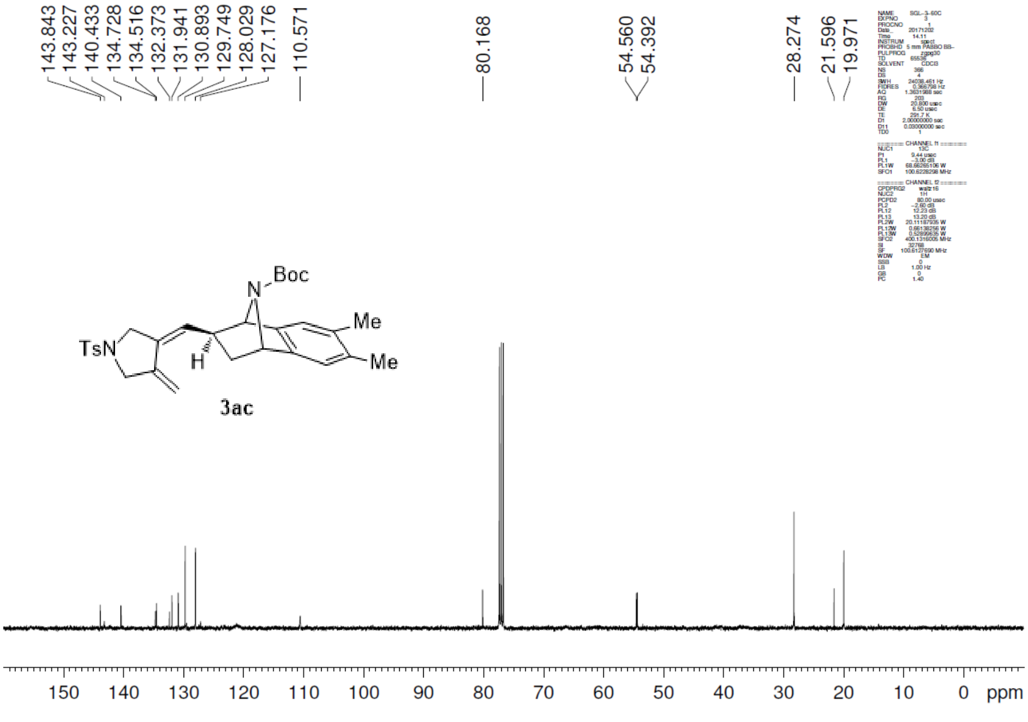
2.28
9.17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80.168
54.560
54.392
28.274
21.596
19.971
Boc
N
TsN
H
Me
Me
3ac
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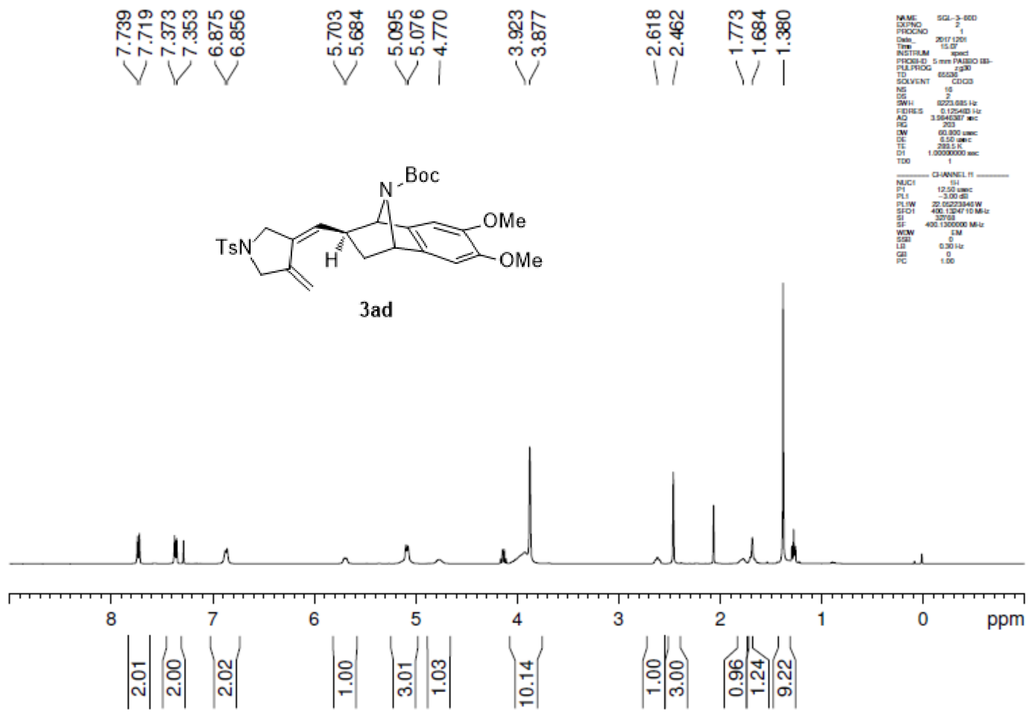
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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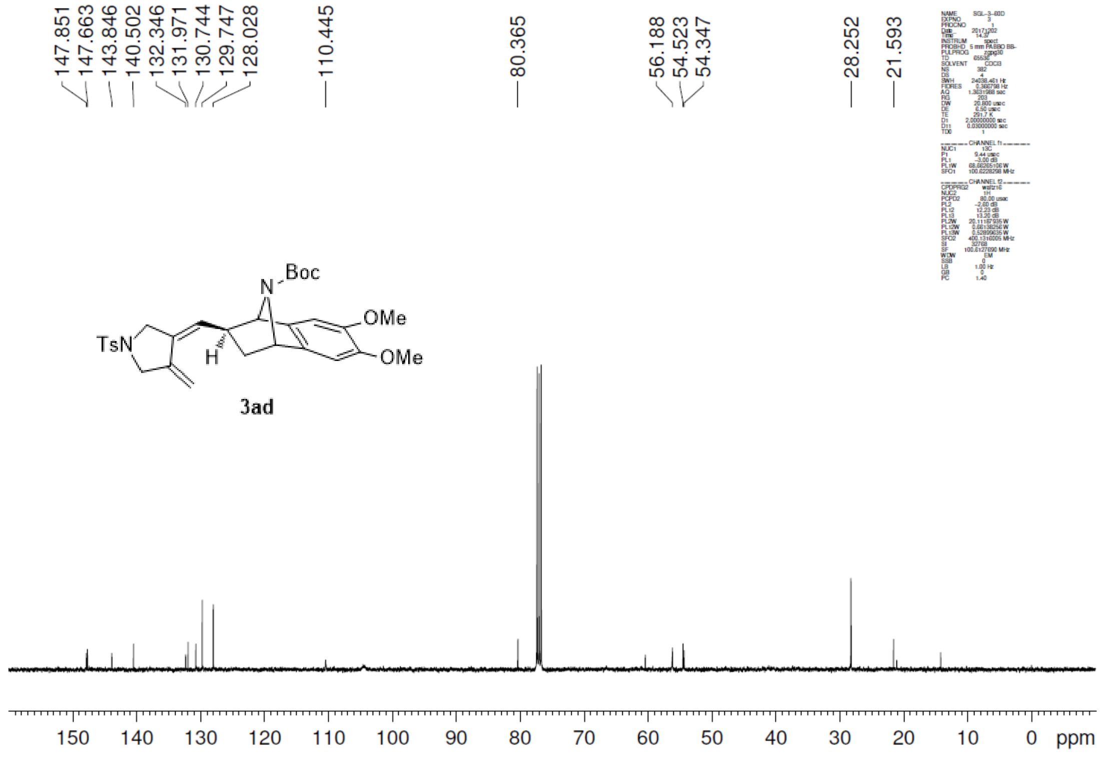
H
OMe
3ad
ppm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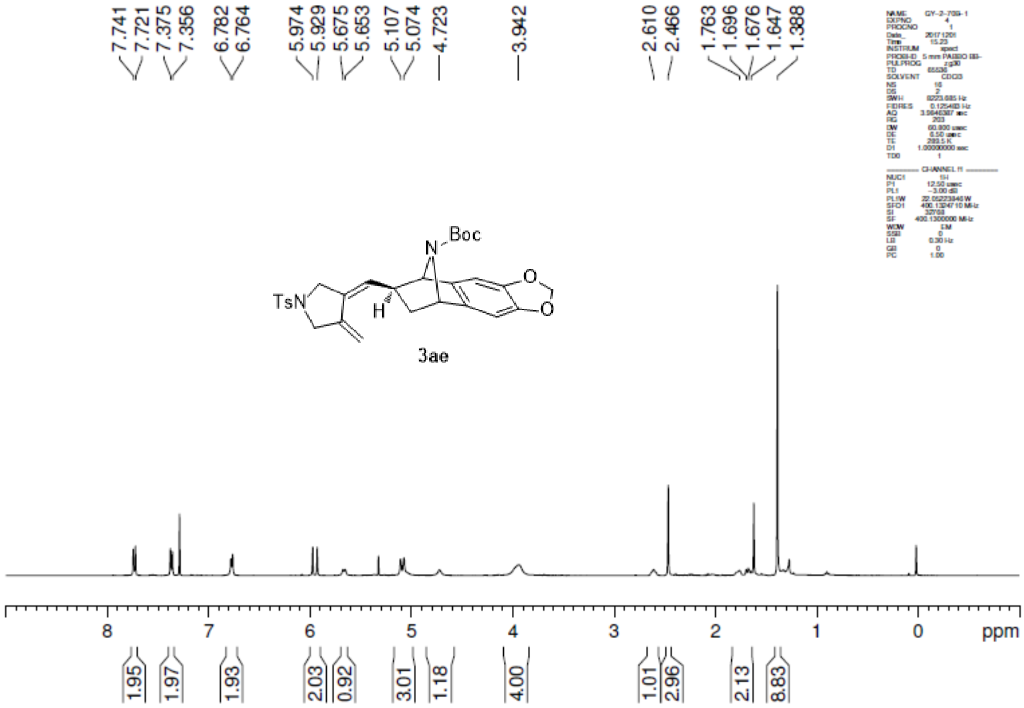
ppm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4.723
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2.610
2.466
1.763
1.696
1.676
1.647
1.388
Boc
N
TsN
H
O
O
3ae
8 7 6 5 4 3 2 1 0 ppm
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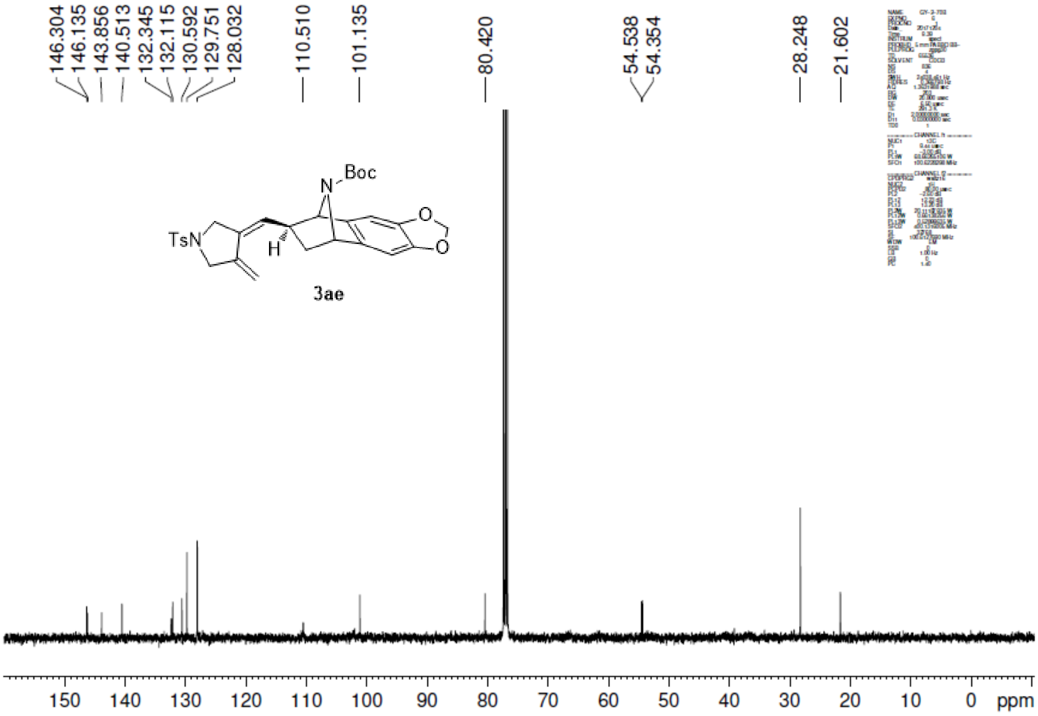
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TsN
H
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O
3ae
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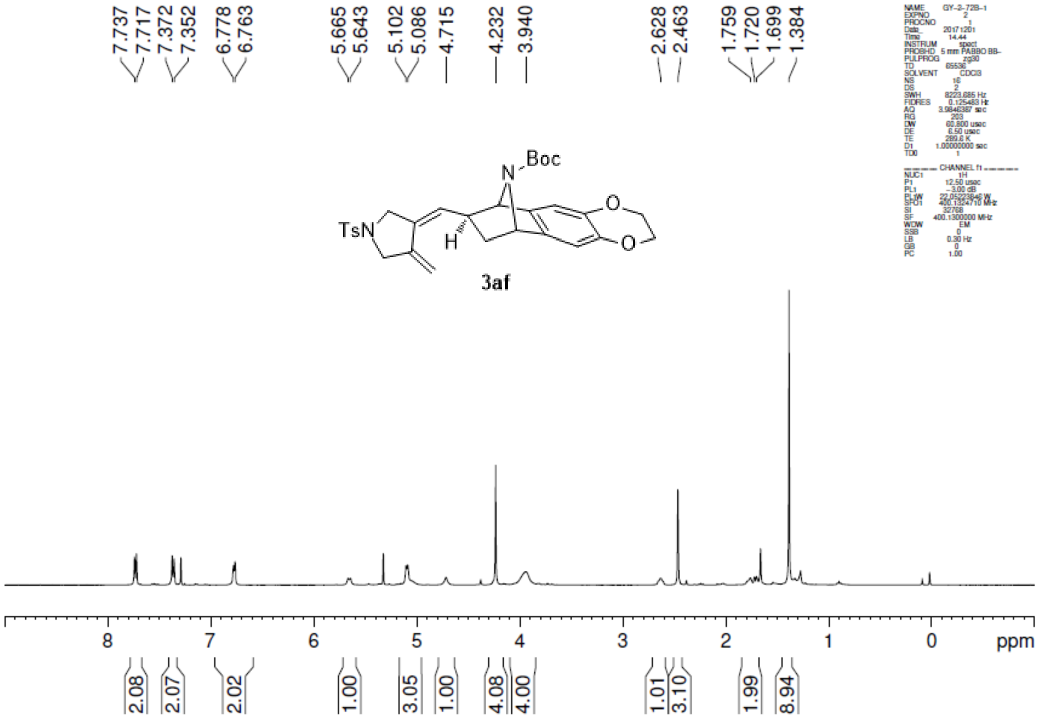
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2.463
1.759
1.720
1.699
1.384
N
Boc
TsN
H
O
O
3af
8
7
6
5
4
3
2
1
0
ppm
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1.00
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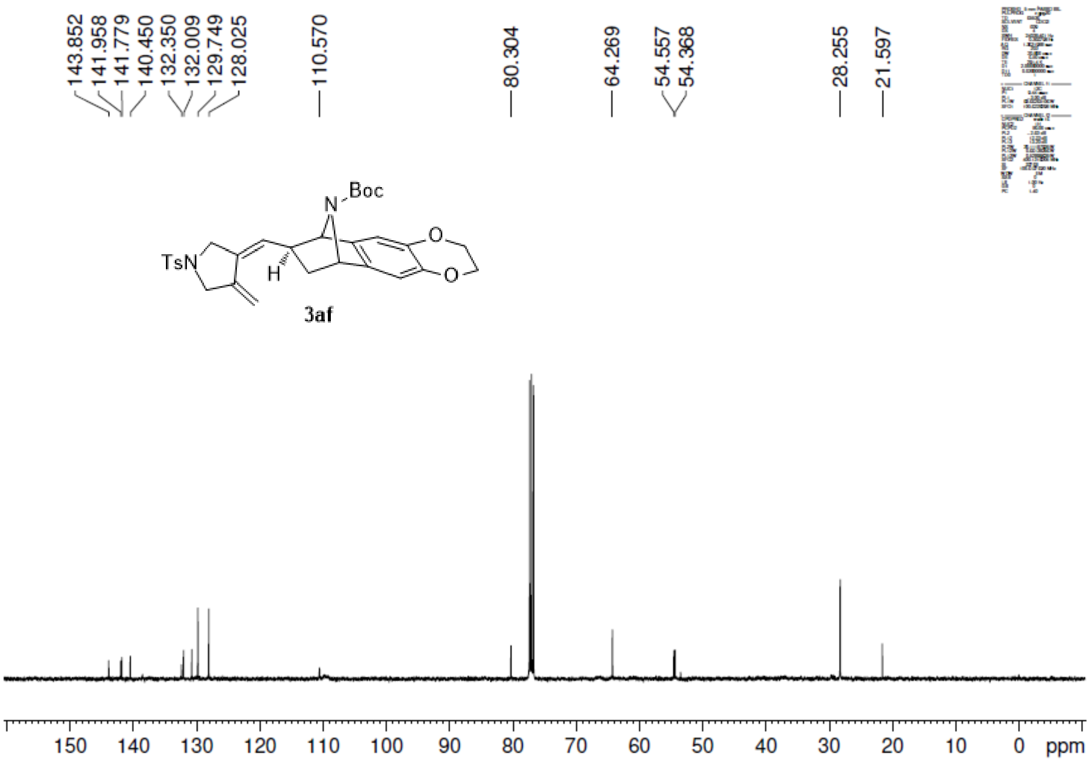
1.00
4.08
4.00
1.01
3.10
1.99
8.94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28.255
21.597
N
Boc
TsN
H
O
O
3af
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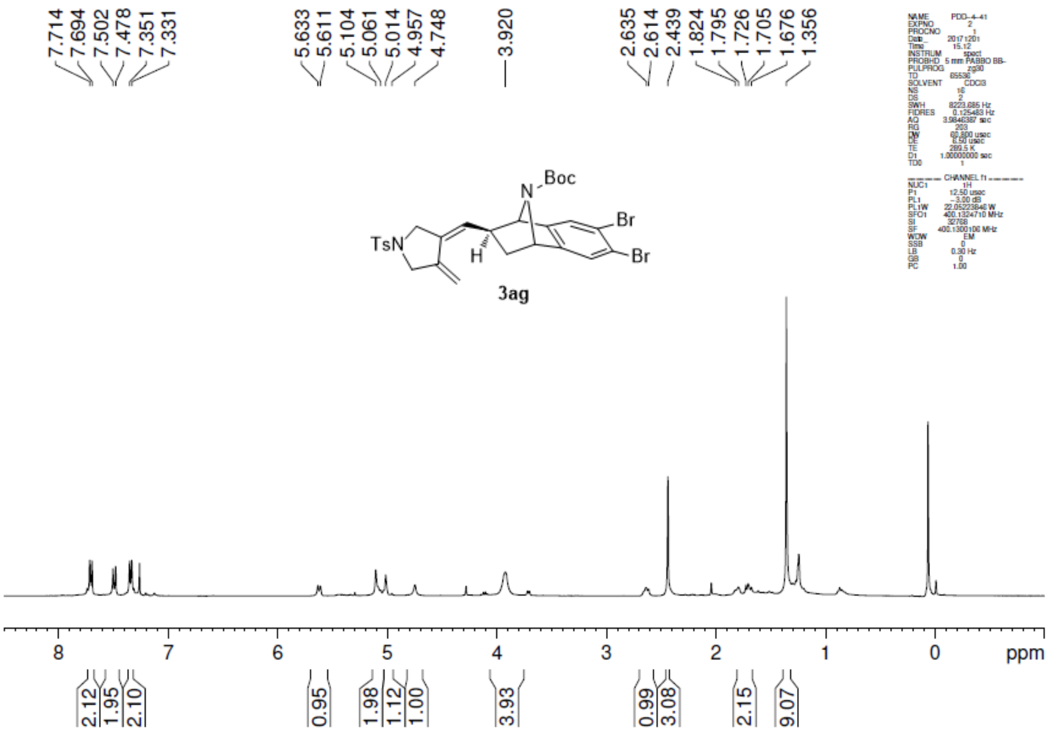
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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4.748
3.920
2.635
2.614
2.439
1.824
1.795
1.726
1.705
1.676
1.356
N Boc
TsN
H
Br
Br
3ag
8 7 6 5 4 3 2 1 0 ppm
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1.00
3.93
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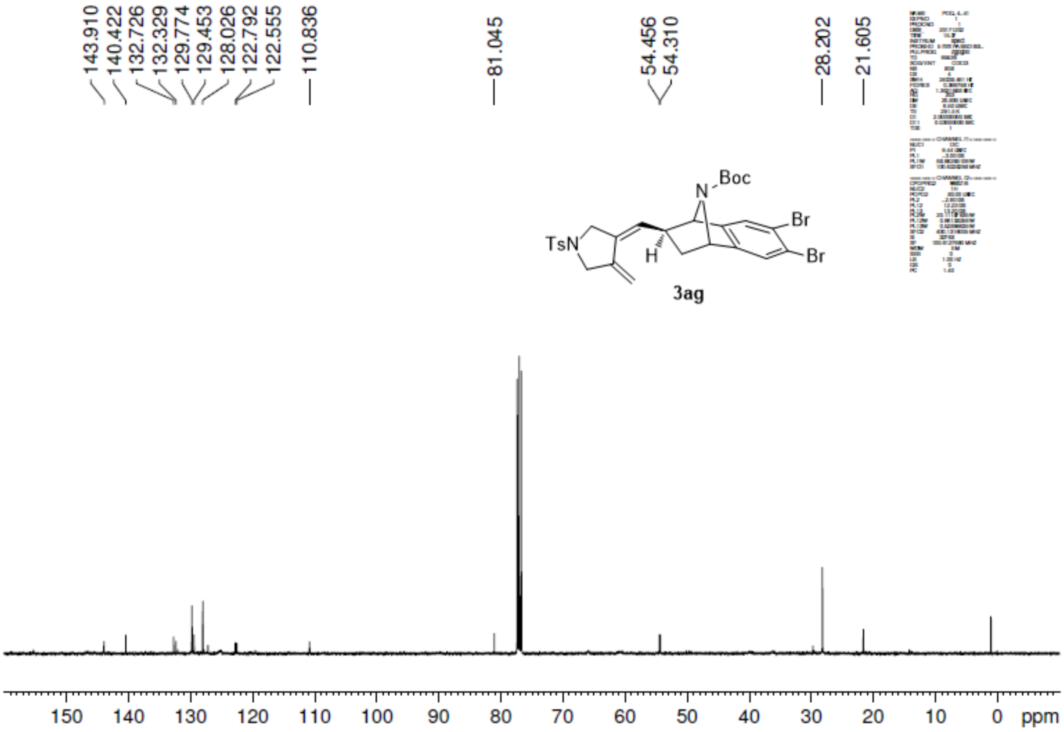
2.15
9.07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TsN
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Br
Br
3ag
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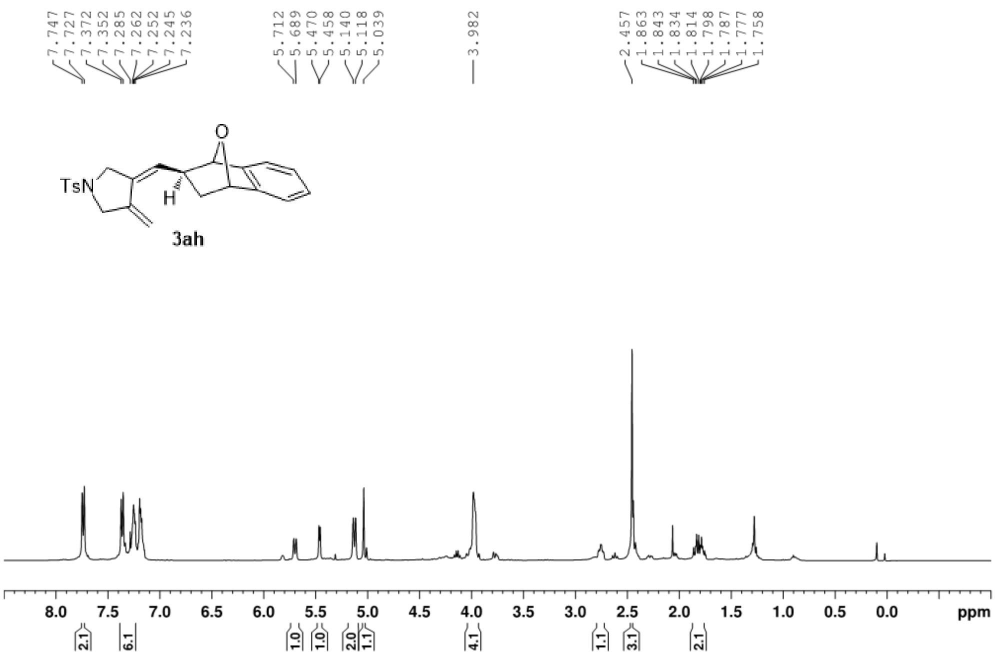
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O
TsN
H
3ah
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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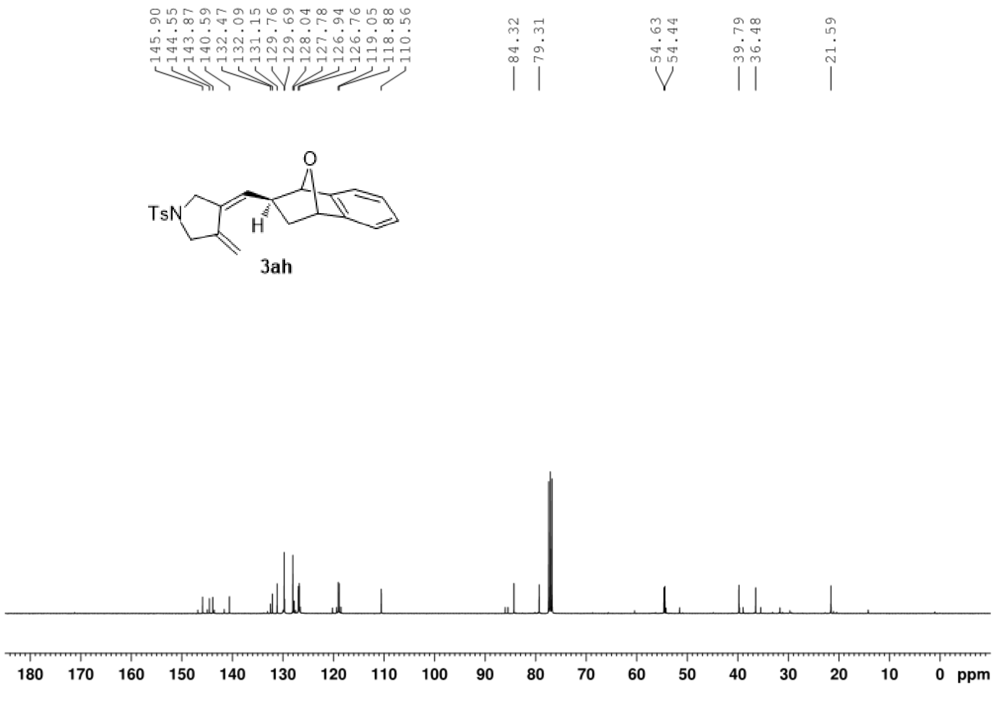
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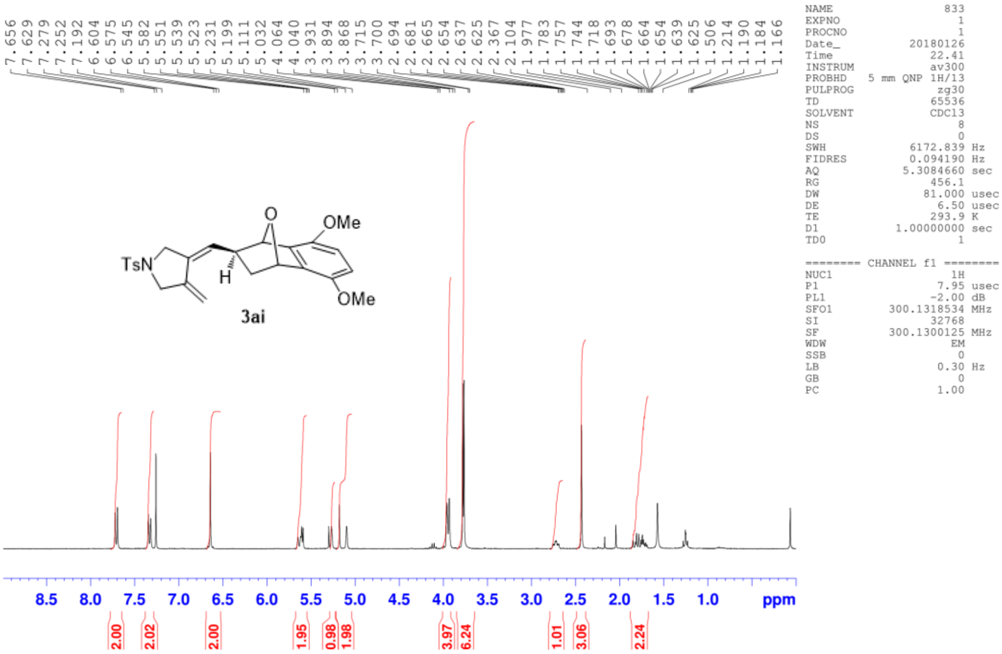
84.32 79.31
54.63 54.44
39.79 36.48
21.59
O
TsN
H
3ah
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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6.545
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5.199
5.111
5.032
4.064
4.040
3.931
3.894
3.868
3.715
3.700
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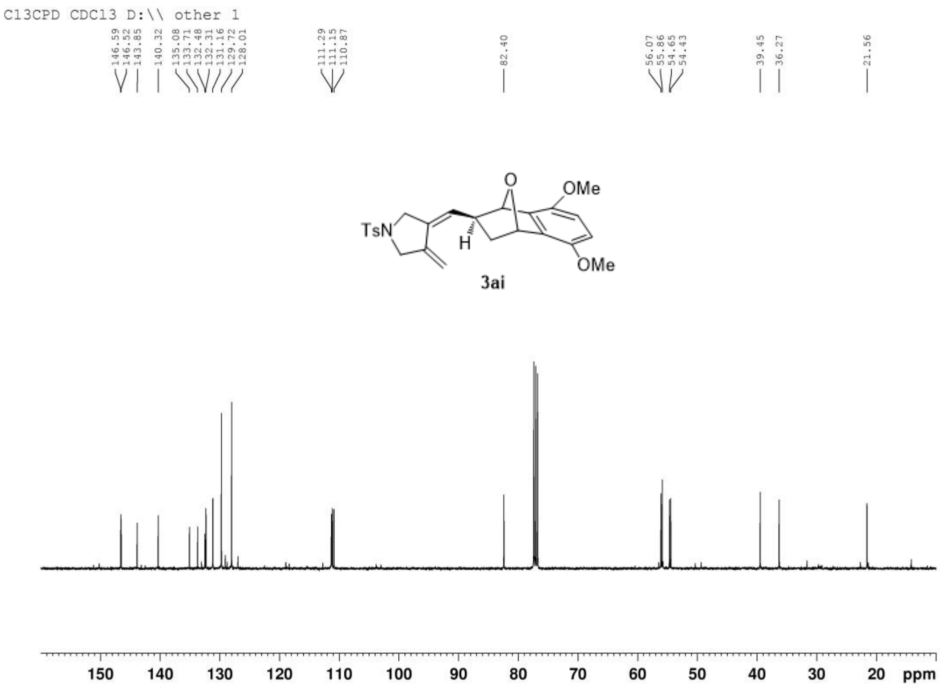
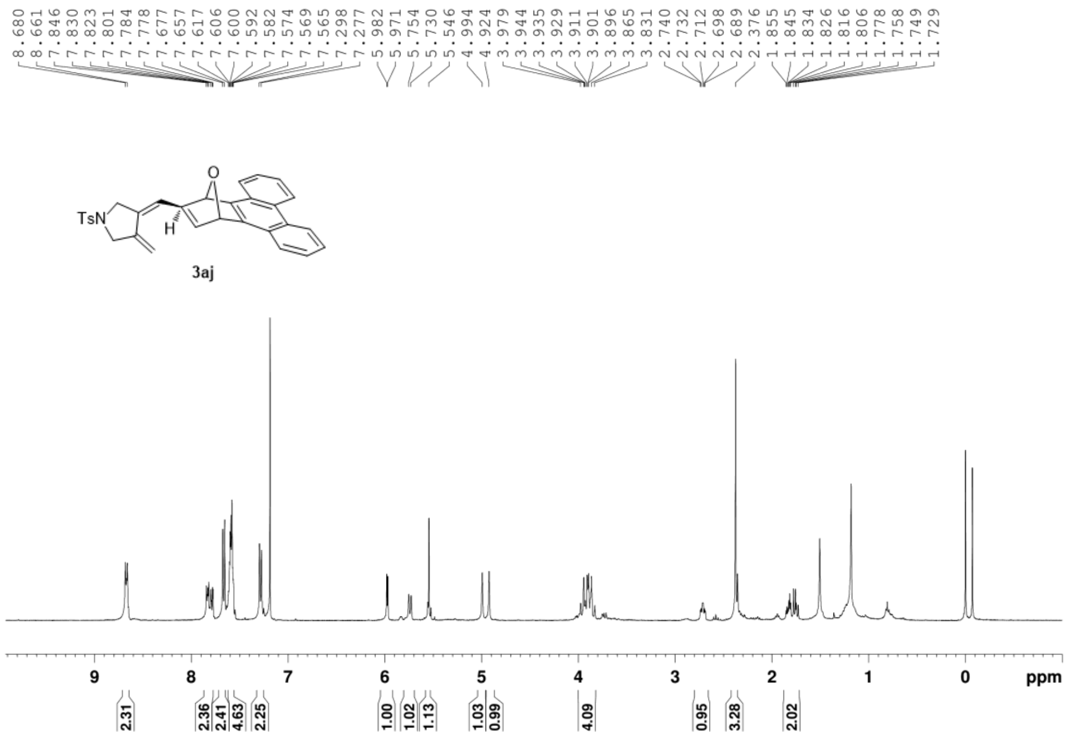
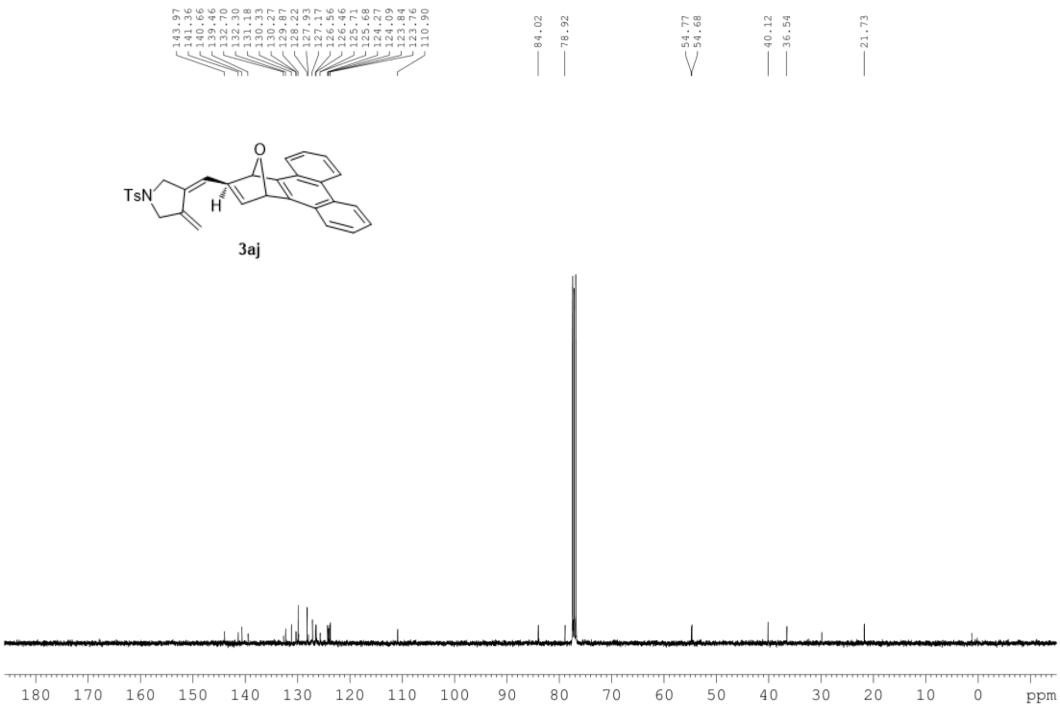
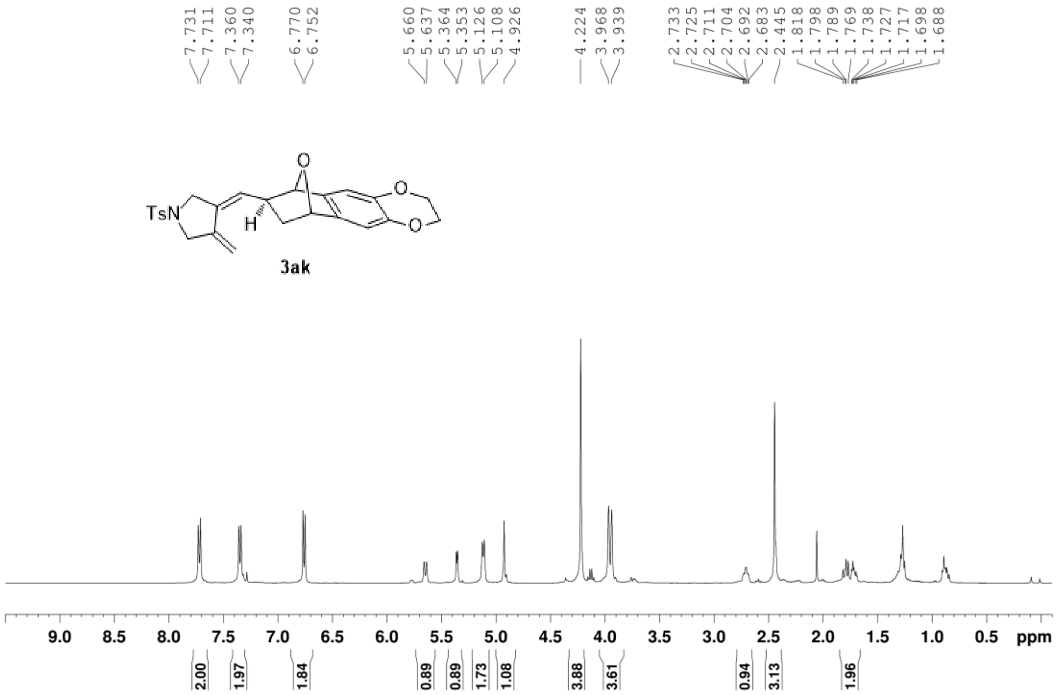
1.625
1.506
1.214
1.190
1.184
1.166
NAME 833
EXPNO 1
PROCNO 1
Date_ 20180126
Time 22.41
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 456.1
DW 81.000 usec
DE 6.50 usec
TE 293.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.95 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300125 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OMe
O
TsN
H
OMe
3ai
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
2.00 2.02 2.00 1.95 0.98 1.98 3.97 6.24 1.01 3.06 2.24


C13CPD CDCl3 D:\\ other 1
146.59
146.52
143.85
140.32
135.08
133.71
132.48
132.31
131.16
129.72
128.01
111.29
111.15
110.87
82.40
56.07
55.86
54.65
54.43
39.45
36.27
21.56
O
OMe
TsN
H
OMe
3ai
150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.680 8.661 7.846 7.830 7.823 7.801 7.784 7.778 7.677 7.657 7.617 7.606 7.600 7.592 7.582 7.574 7.569 7.565 7.298 7.277 5.982 5.971 5.754 5.730 5.546 4.994 4.924 3.979 3.944 3.935 3.929 3.911 3.901 3.896 3.865 3.831 2.740 2.732 2.712 2.698 2.689 2.376 1.855 1.845 1.834 1.826 1.816 1.806 1.778 1.758 1.749 1.729
TsN
O
H
3aj
9 8 7 6 5 4 3 2 1 0 ppm
2.31 2.36 2.41 4.63 2.25 1.00 1.02 1.13 1.03 0.99 4.09 0.95 3.28 2.02


143.97 141.36 140.66 139.46 132.70 132.30 131.18 130.33 130.27 129.87 128.22 127.93 127.17 126.56 126.46 125.71 125.68 124.27 124.09 123.84 123.76 110.90
84.02 78.92
54.77 54.68
40.12 36.54
21.73
TsN
O
H
3aj
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.731
7.711
7.360
7.340
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5.637
5.364
5.353
5.126
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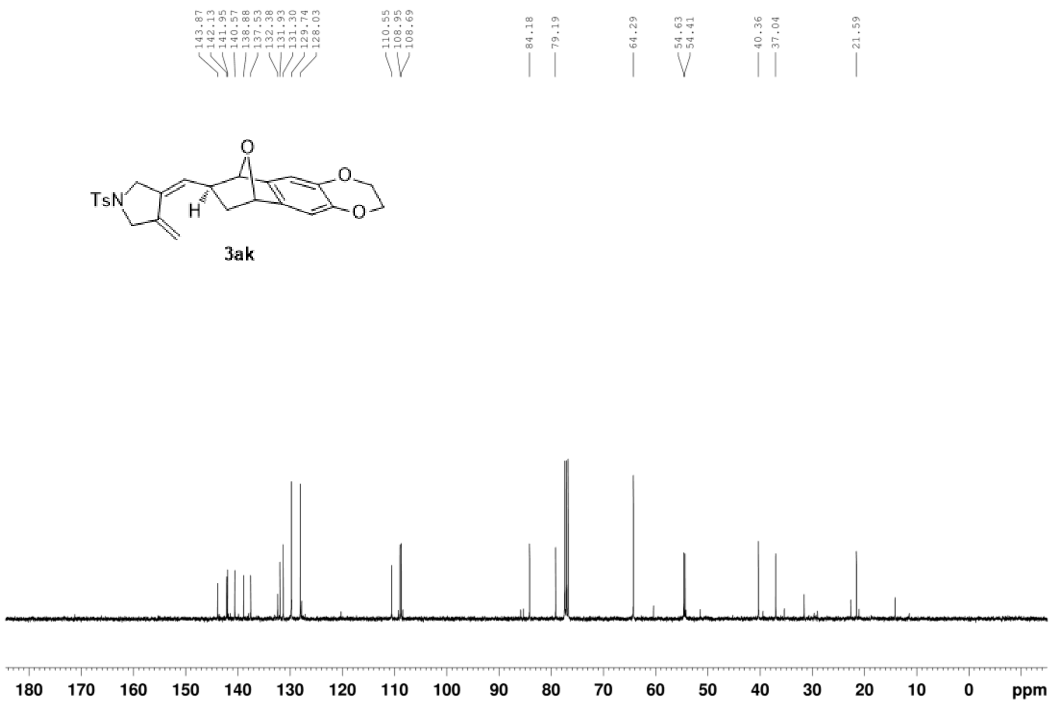
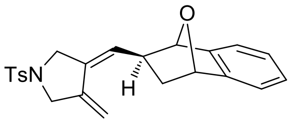
4.224
3.968
3.939
2.733
2.725
2.711
2.704
2.692
2.683
2.445
1.818
1.798
1.789
1.769
1.738
1.727
1.717
1.698
1.688
TsN
O
H
3ak
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
1.97
1.84
0.89
0.89
1.73
1.08
3.88
3.61
0.94
3.13
1.96

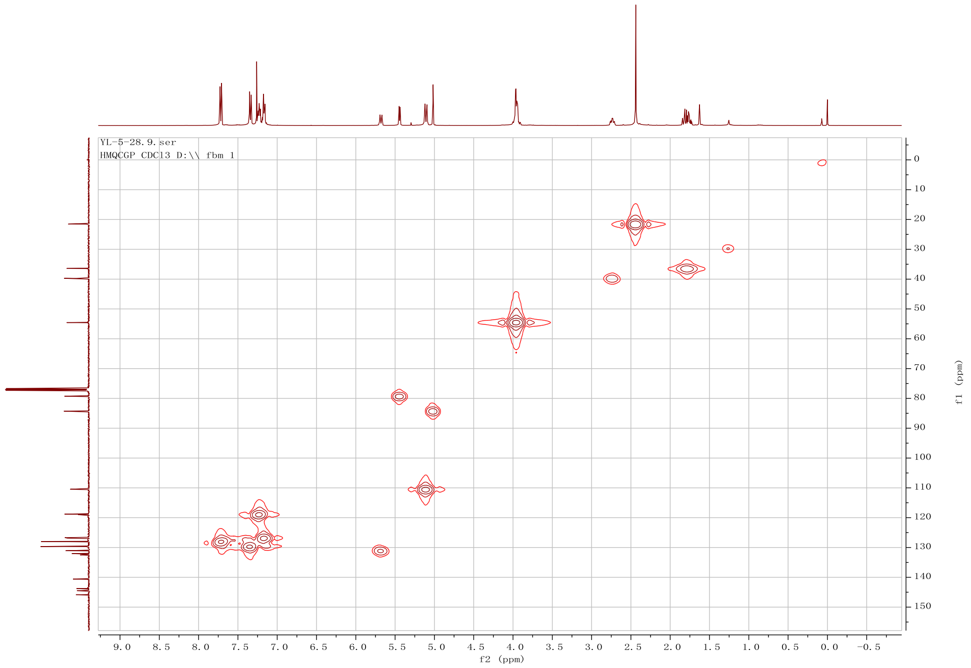

143.87
142.13
141.95
140.57
138.88
137.53
132.38
131.93
131.30
129.74
128.03
110.55
108.95
108.69
84.18
79.19
64.29
54.63
54.41
40.36
37.04
21.59
TsN
O
H
3ak
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

2D-NMR of **3ah**:

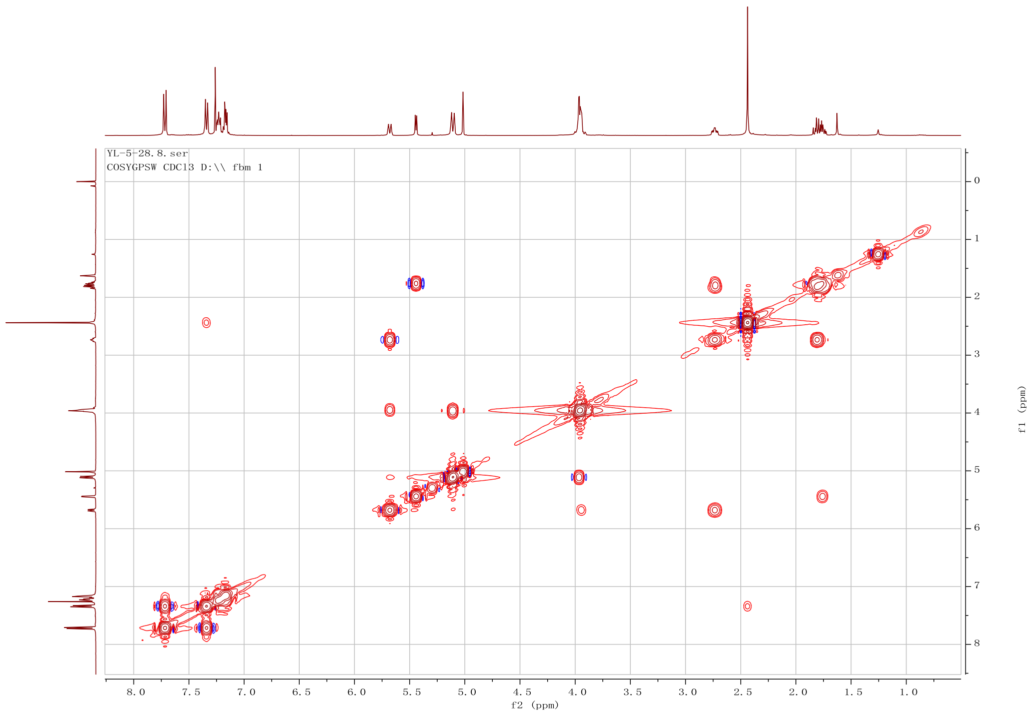


3ah

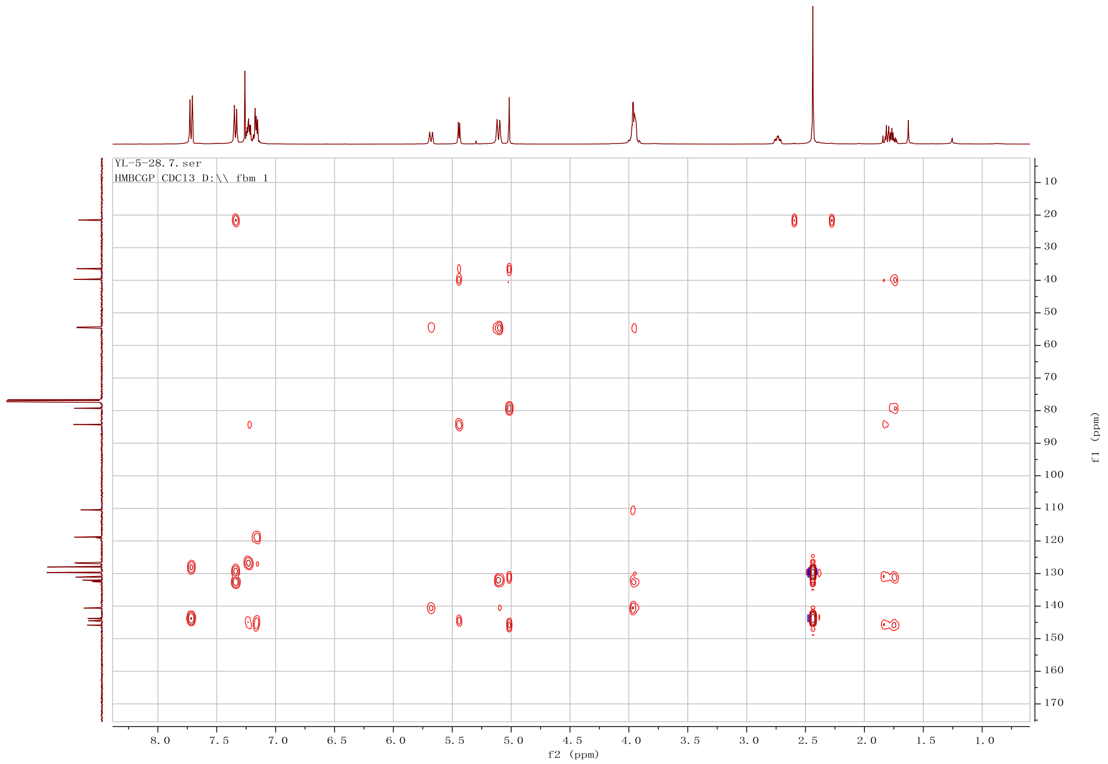
HMQC



H-H COSY



HMBC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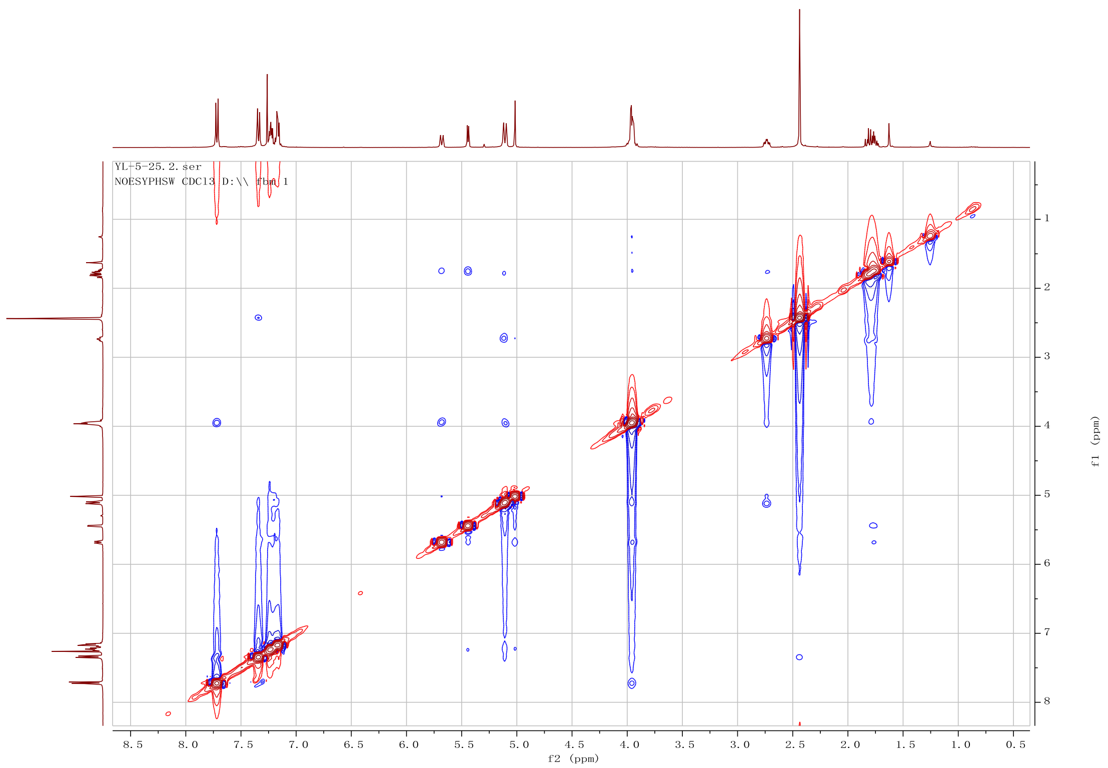
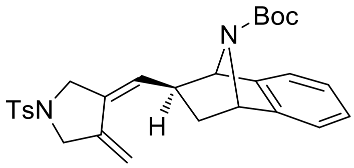
f1 (ppm)
f2 (ppm)

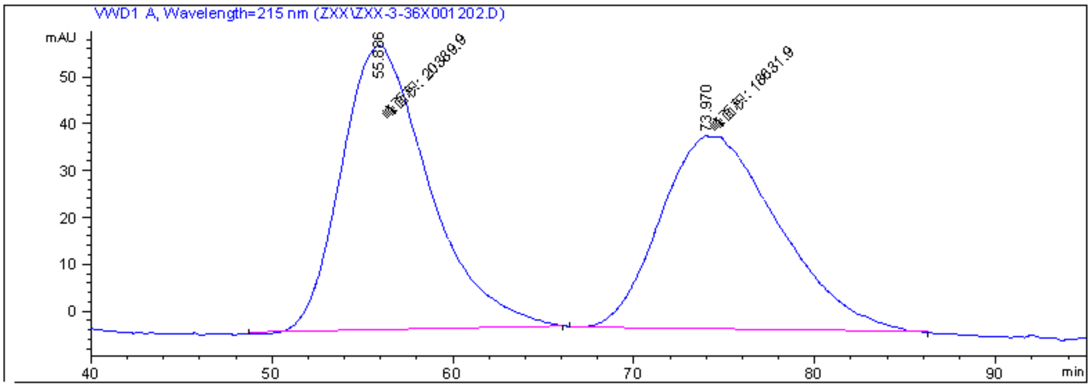
NOE


YL-5-25.2.ser
NOESYPHSW CDCl3 D:\\ fbm 1
f1 (ppm)
f2 (ppm)

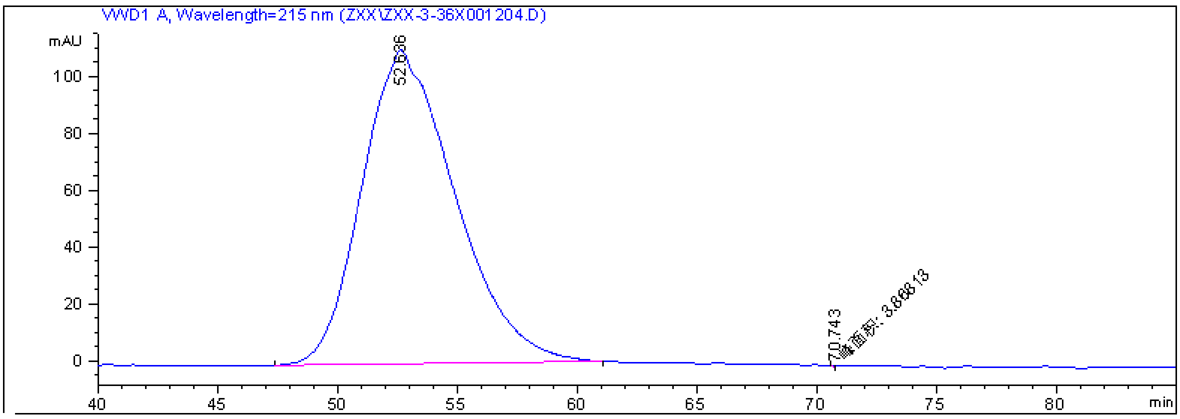
E: HPLC Spectra of Products



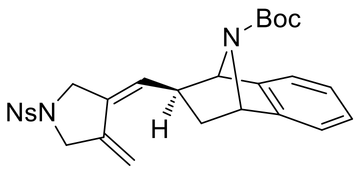
3aa



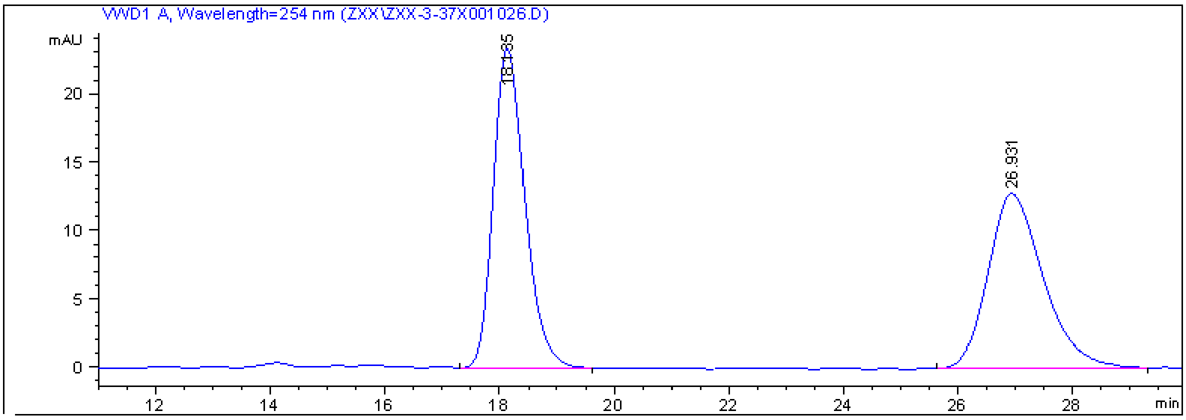
#	[min]		[min]	[mAU*s]	[mAU]	%
1	55.886	MM	5.6030	2.03899e4	60.65144	52.2525
2	73.970	MM	7.5555	1.86319e4	41.09994	47.7475



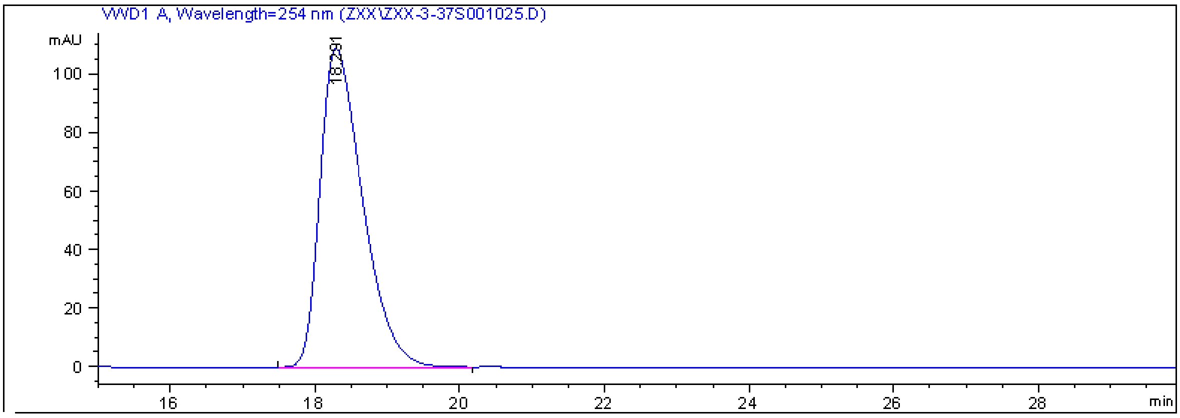
#	[min]		[min]	[mAU*s]	[mAU]	%
1	52.636	BB	3.3195	2.98015e4	110.46326	99.9870
2	70.743	MM	0.0771	3.86813	8.36429e-1	0.0130



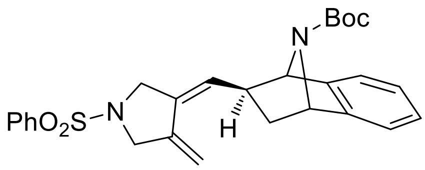
3ba



#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.135	BB	0.5881	891.06128	23.35622	51.0078
2	26.931	BB	1.0073	855.85107	12.76362	48.9922



#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.291	BB	0.6323	4466.94971	108.73255	100.0000



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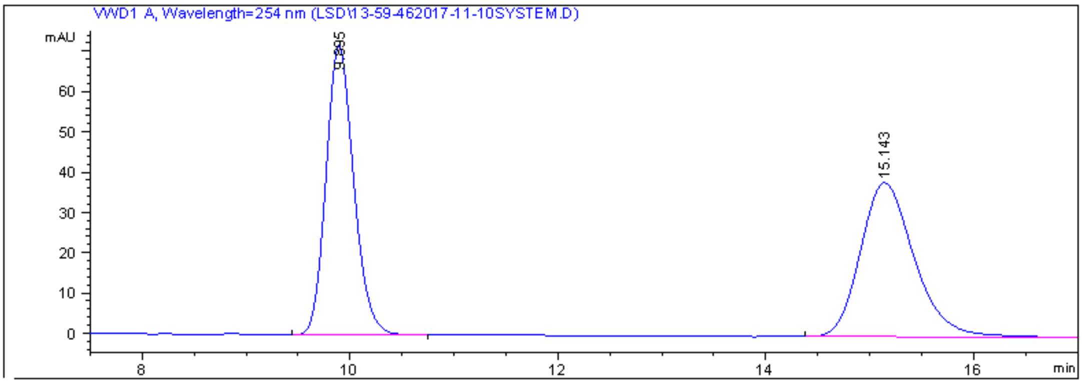
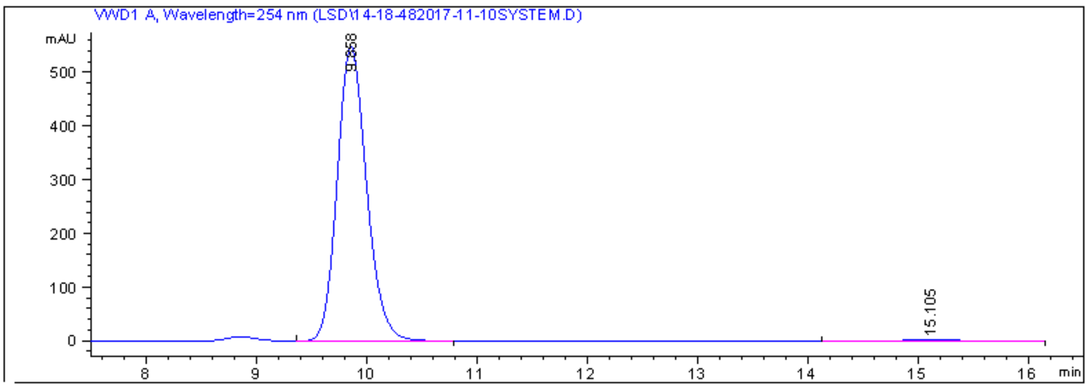
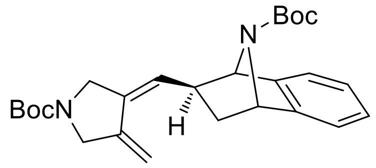


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.895	BB	0.2849	1331.02429	71.92025	49.2326
2	15.143	BBA	0.5507	1372.51624	38.24609	50.7674



#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.858	BB	0.2845	1.01242e4	548.05841	99.3693
2	15.105	BBA	0.5313	64.25330	1.74203	0.6307



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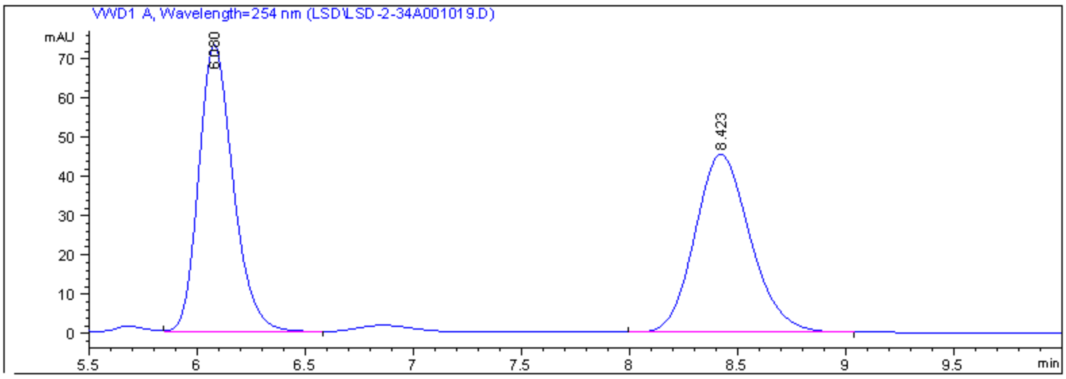
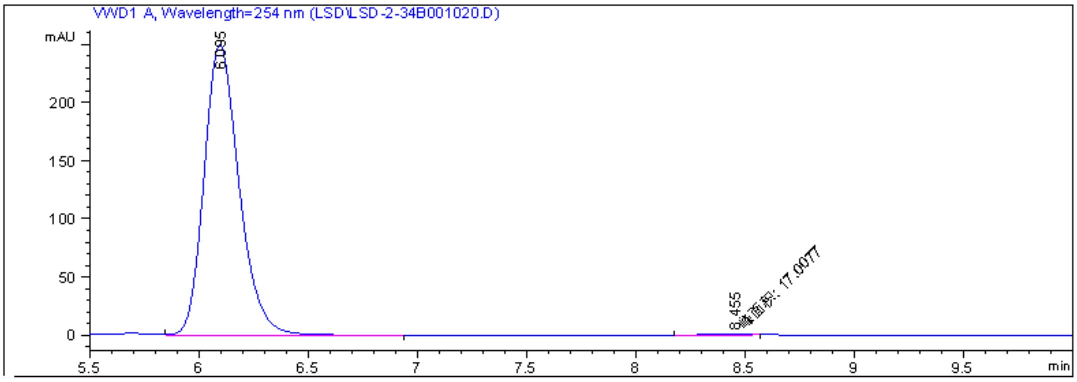
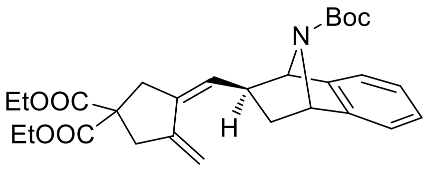


#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.080	VB	0.1691	808.24799	73.05535	50.0583
2	8.423	BB	0.2732	806.36615	45.40971	49.9417



#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.095	VB	0.1699	2776.06665	249.32176	99.3911
2	8.455	MM	0.2653	17.00774	1.06842	0.6089



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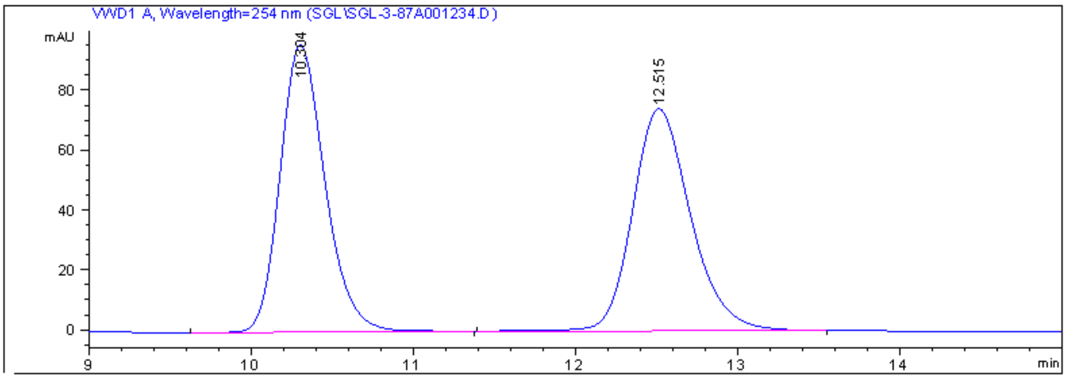
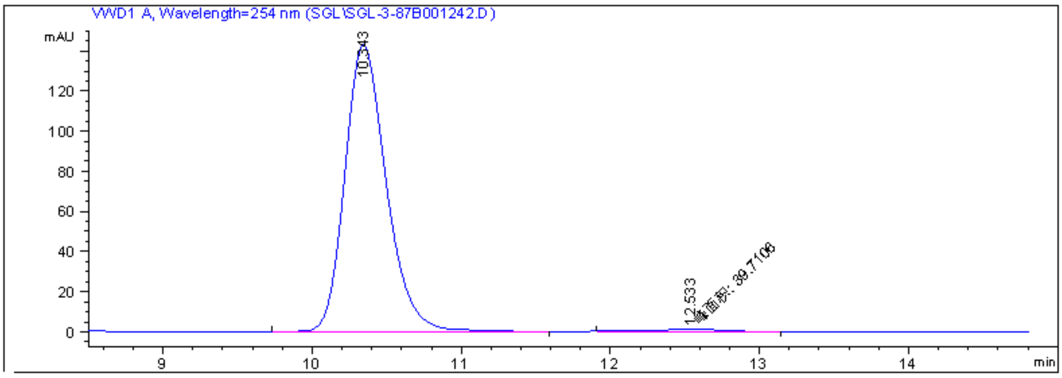
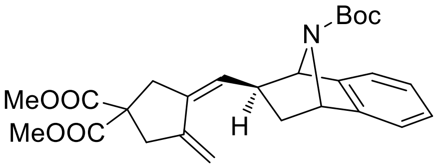


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.304	BB	0.2957	1848.33289	95.97860	50.0798
2	12.515	BB	0.3817	1842.44568	74.18967	49.9202



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.343	BB	0.2961	2759.11328	142.97041	98.5812
2	12.533	MM	0.4584	39.71064	1.44379	1.4188



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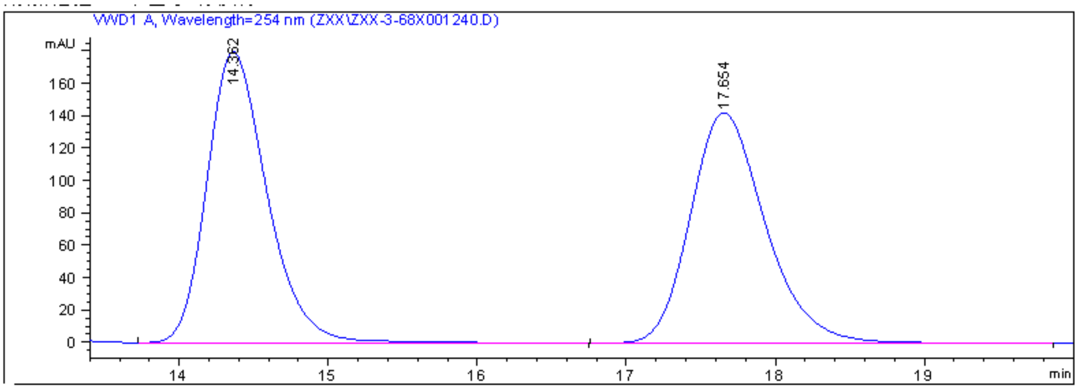
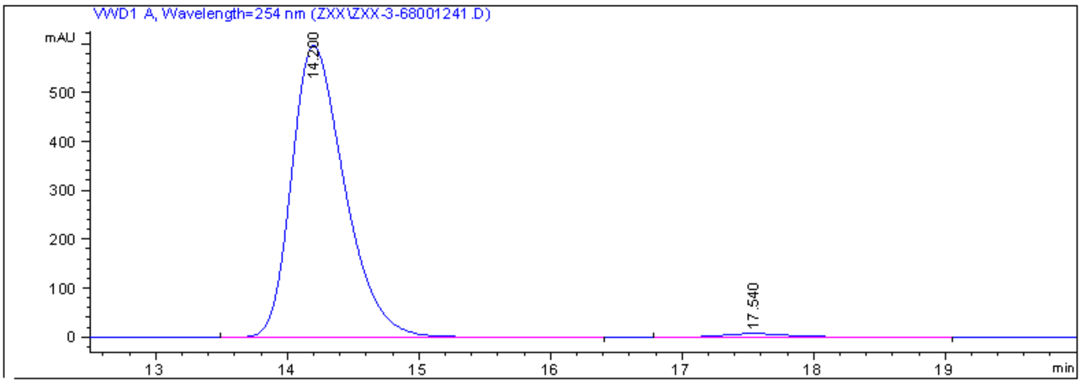
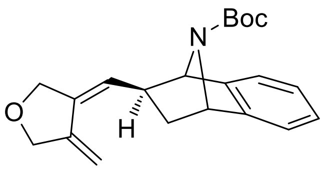


#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.362	BB	0.4290	5039.65771	179.80377	50.3758
2	17.654	BB	0.5366	4964.46143	142.10913	49.6242



#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.200	BB	0.4262	1.66155e4	596.05499	98.4727
2	17.540	BB	0.5355	257.70432	7.30581	1.5273



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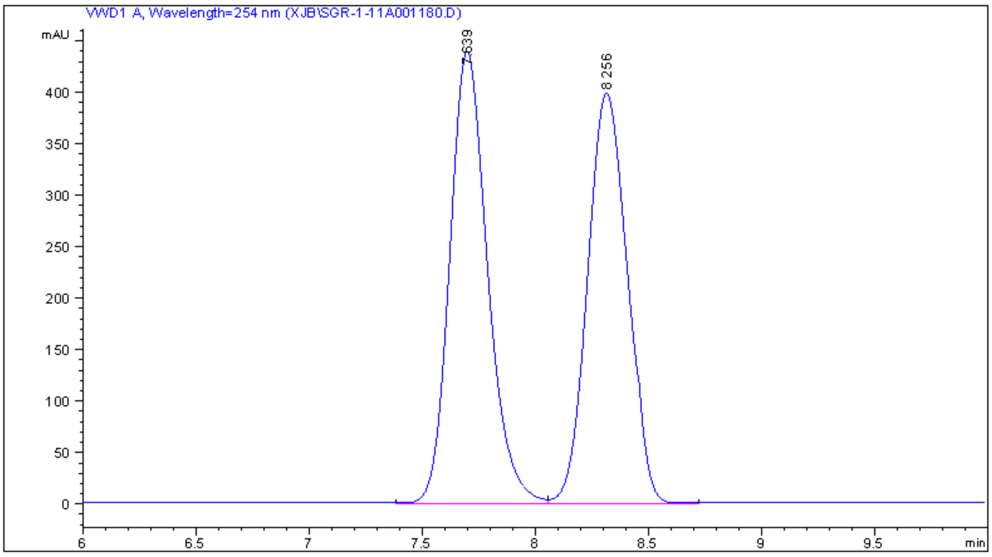
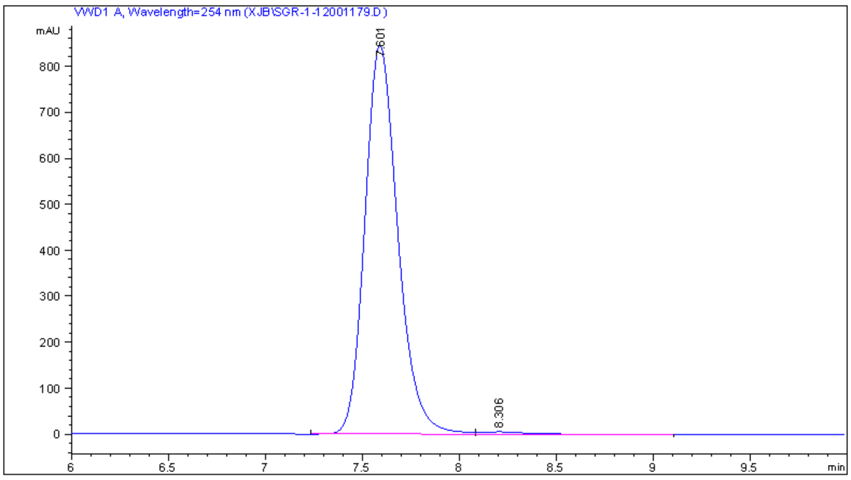
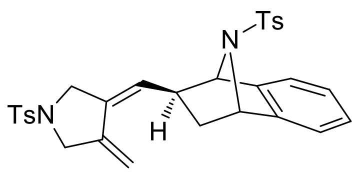


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.639	VV	0.1774	5099.32715	439.43433	49.3073
2	8.256	VB	0.1991	5242.61328	399.42438	50.6927



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.601	BV	0.1809	1.00026e4	846.03778	99.2447
2	8.306	VB	0.2274	76.55753	4.86886	0.7553



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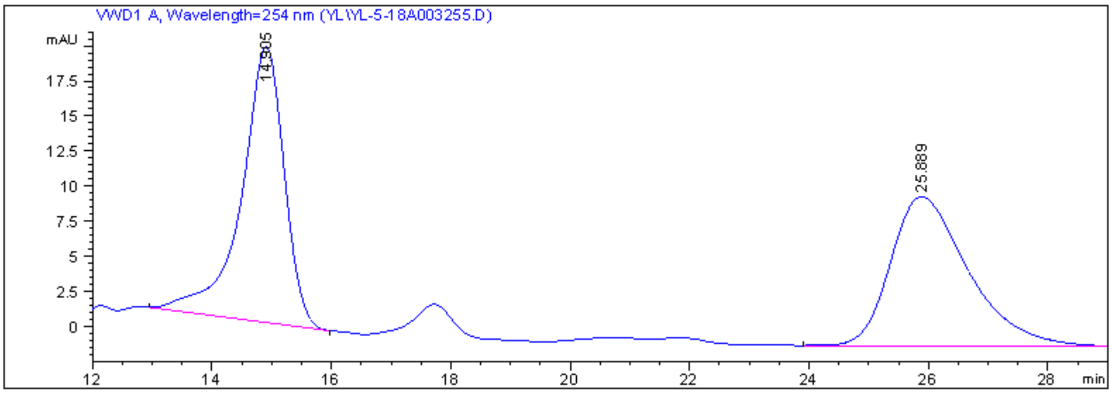
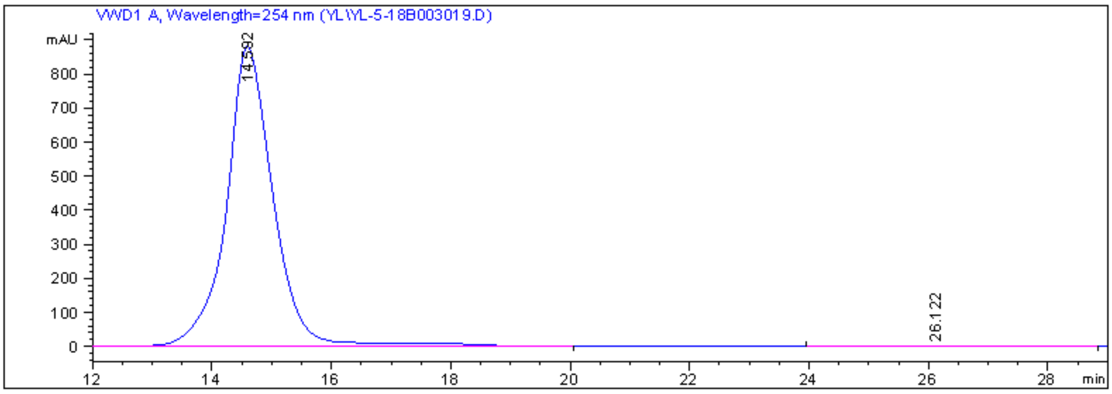
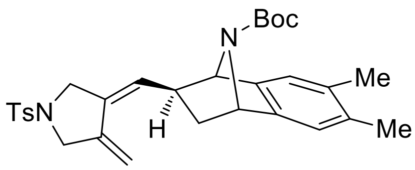


PEAK #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.905	BB	0.7420	979.87946	19.64277	50.3469
2	25.889	BB	1.3622	966.37750	10.65449	49.6531



PEAK #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.593	VB	0.8073	4.82301e4	880.12854	99.6353
2	26.117	BB	1.3884	176.55431	1.90653	0.3647



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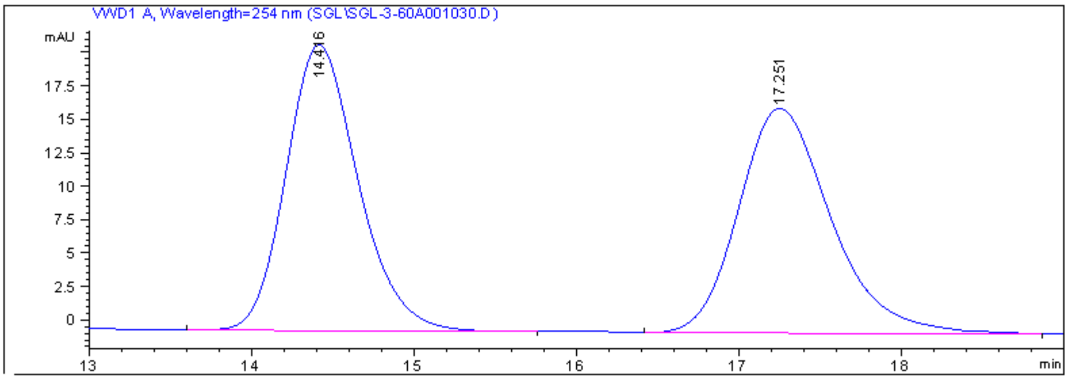
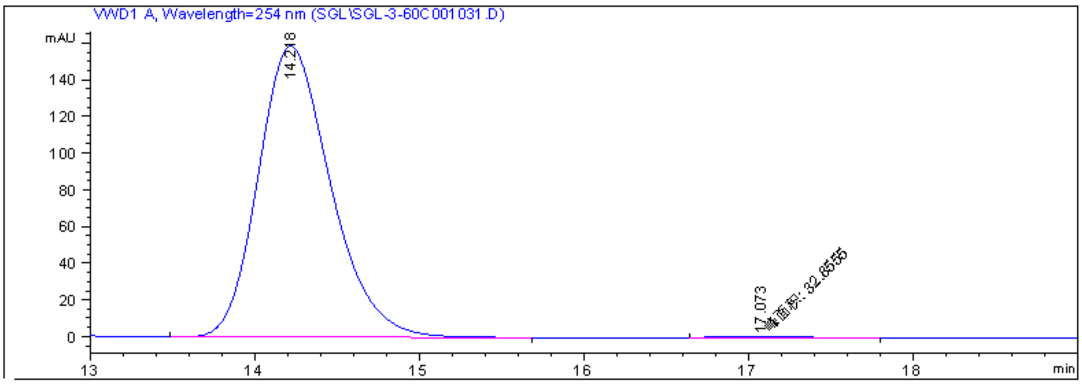
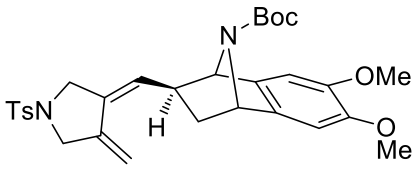


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.416	BB	0.4753	659.42017	21.35457	49.8147
2	17.251	BB	0.6040	664.32623	16.81349	50.1853



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.218	BB	0.4695	4853.78027	158.84305	99.3276
2	17.073	MM	0.7924	32.85547	6.91095e-1	0.6724



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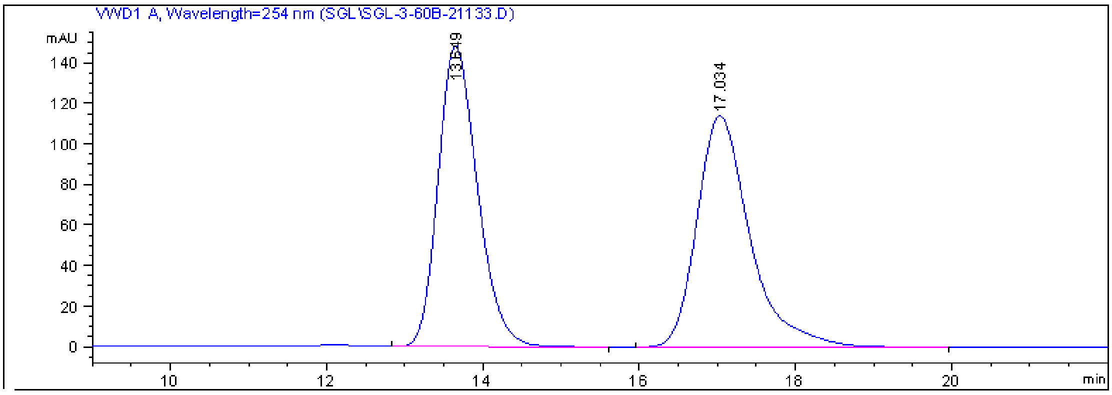
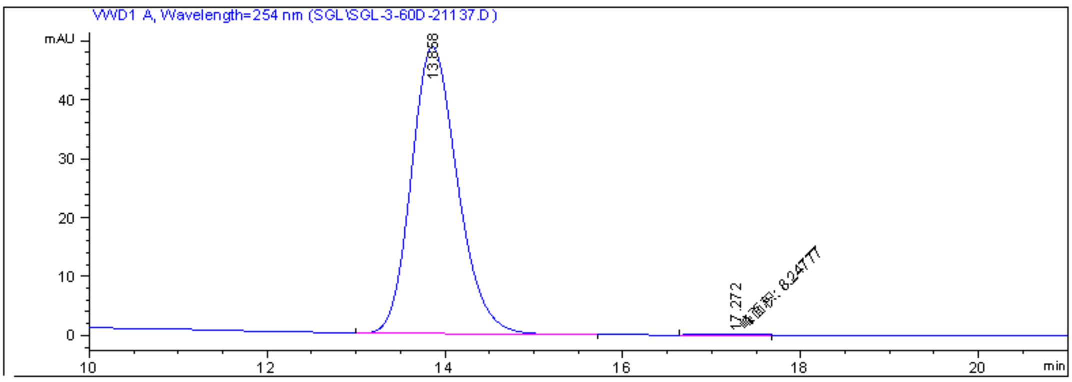
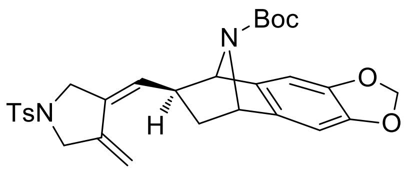


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.649	BB	0.5405	5185.15088	148.08440	49.1716
2	17.034	BB	0.7139	5359.86914	114.12704	50.8284



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.858	BB	0.5563	1755.54150	48.72659	99.5324
2	17.272	MM	0.6912	8.24777	1.98887e-1	0.4676



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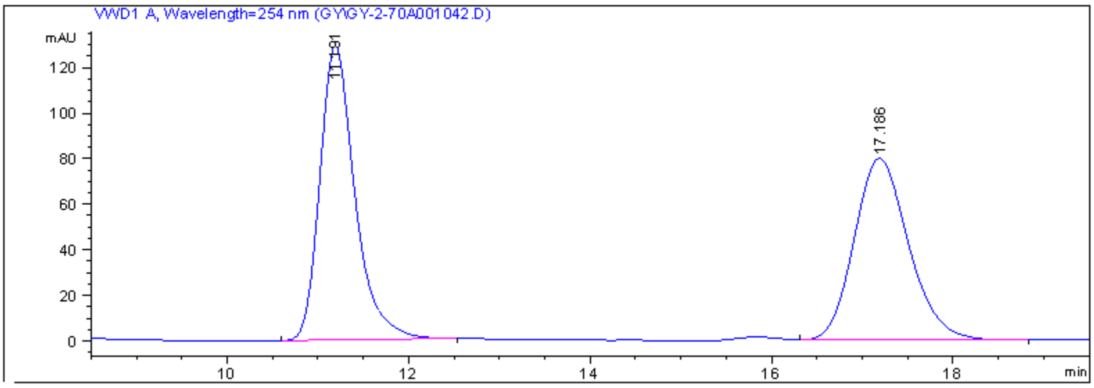
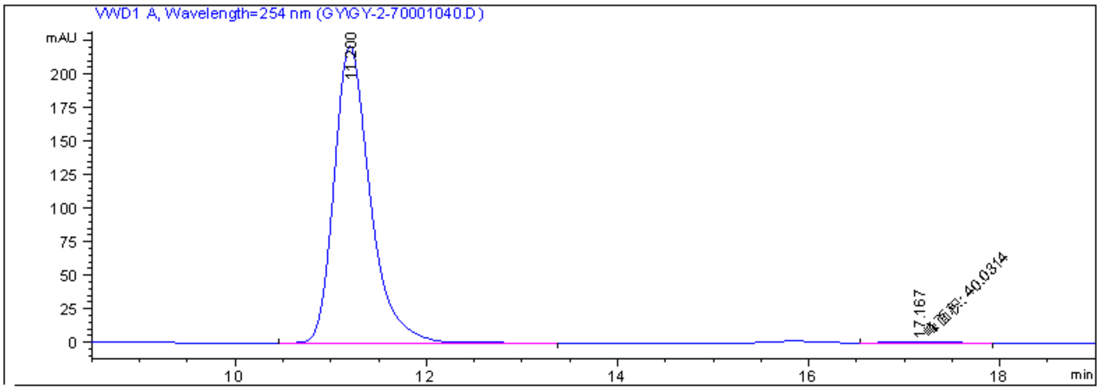
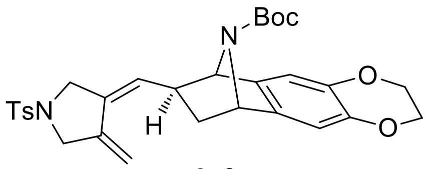


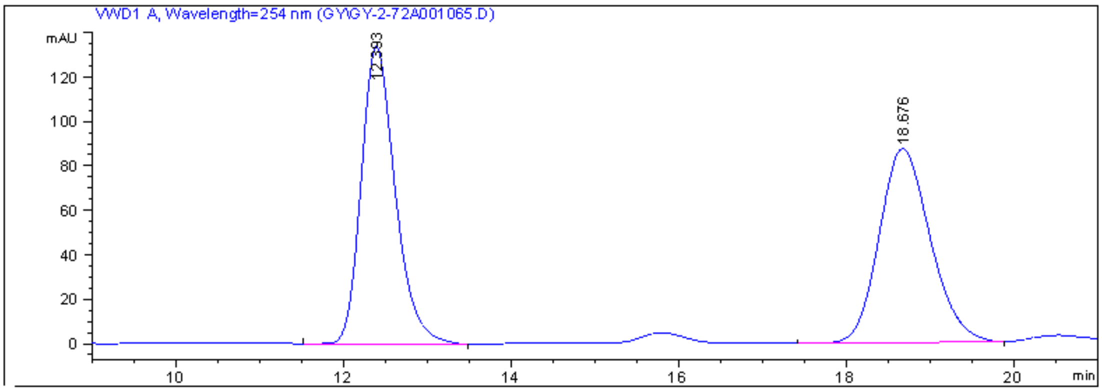
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.191	BB	0.4085	3459.42017	129.13417	51.0885
2	17.186	BB	0.6406	3312.00122	79.72854	48.9115



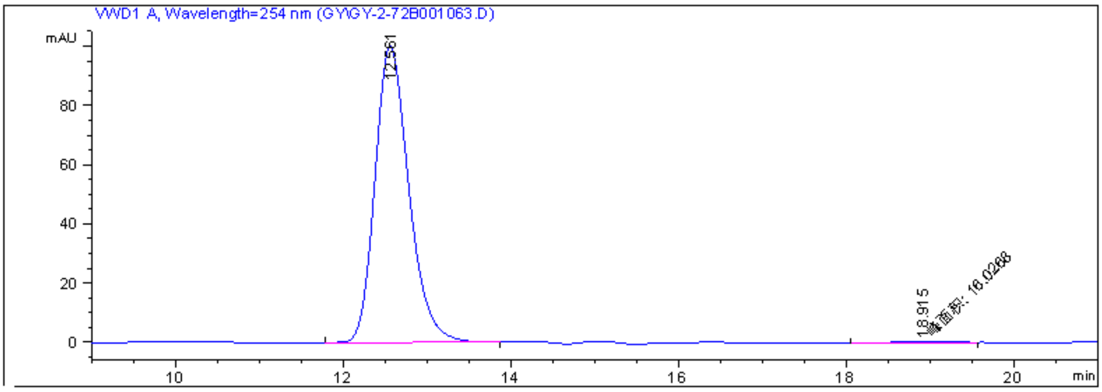
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.200	BB	0.3984	5794.44678	221.37781	99.3139
2	17.167	MM	0.6461	40.03141	1.03260	0.6861



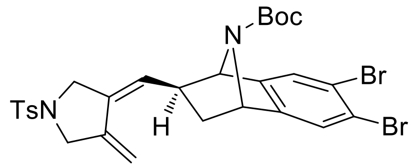
3af



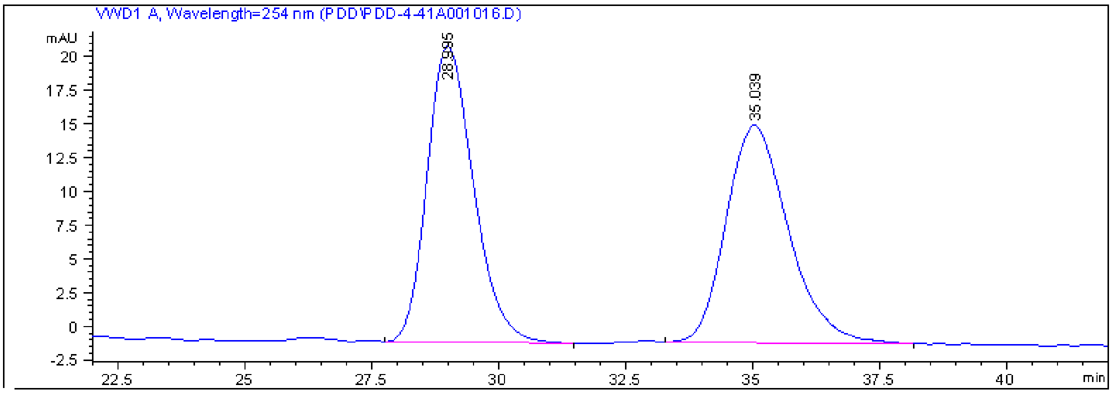
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.393	BB	0.4331	3776.29199	133.89012	50.5665
2	18.676	BB	0.6548	3691.68066	87.21271	49.4335



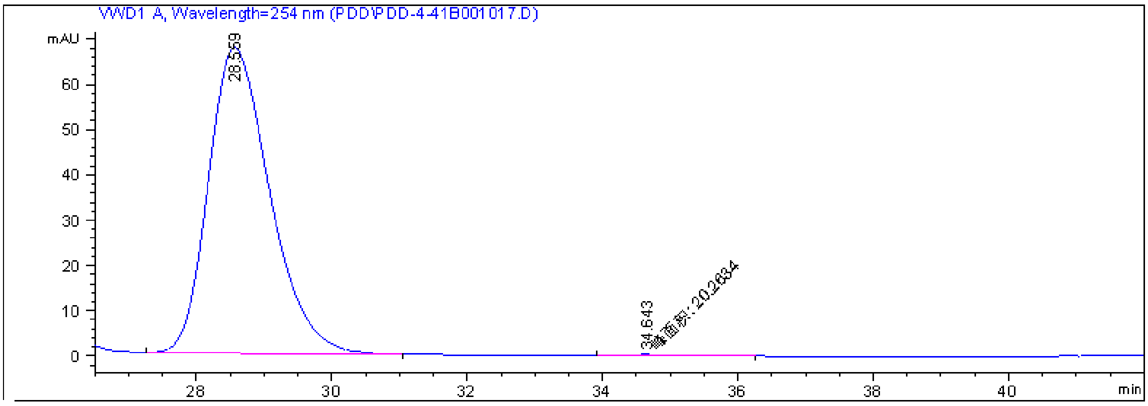
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.561	BB	0.4299	2803.77954	100.06040	99.4316
2	18.915	MM	0.6045	16.02683	4.41880e-1	0.5684



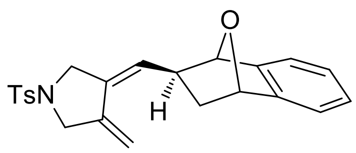
3ag



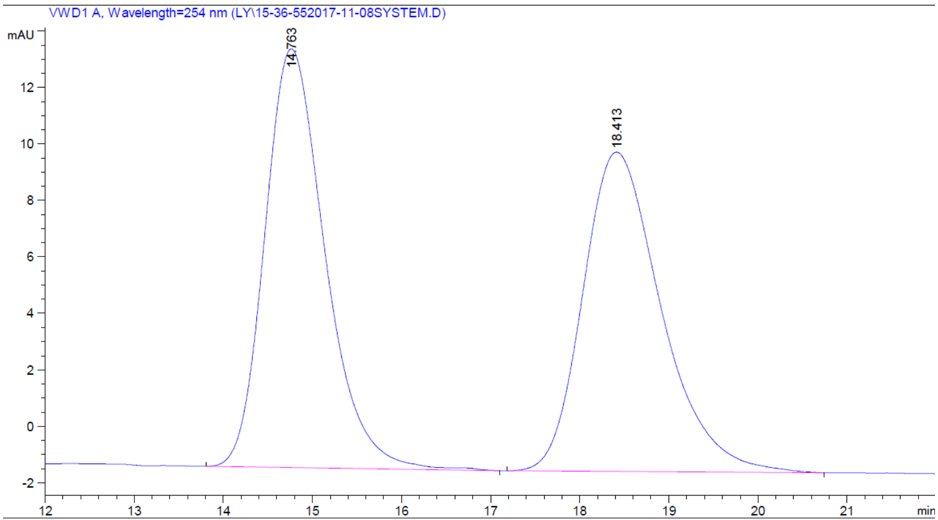
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.995	BB	0.9646	1399.26514	21.95238	50.4314
2	35.039	BB	1.3096	1375.32446	16.13187	49.5686



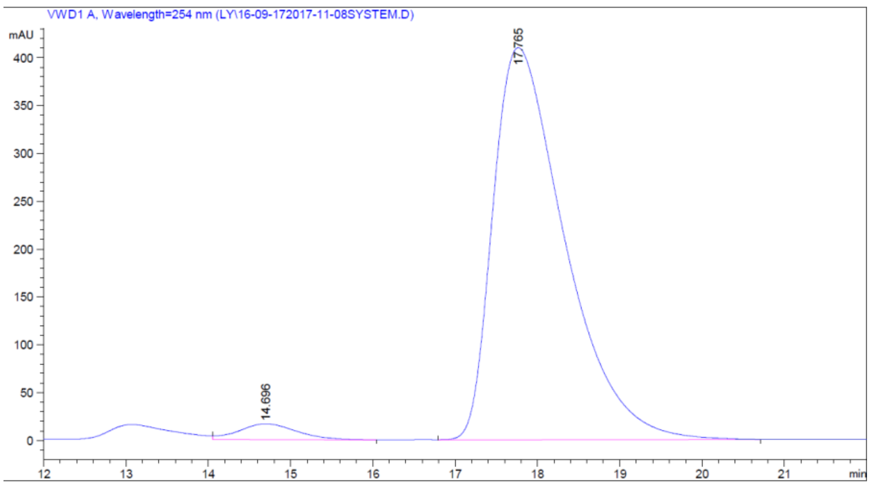
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.559	BB	0.9665	4258.01221	67.53703	99.5264
2	34.643	PM	1.2546	20.26337	2.69191e-1	0.4736



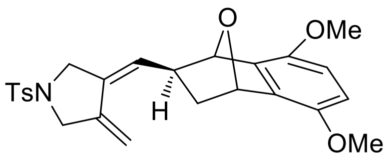
3ah



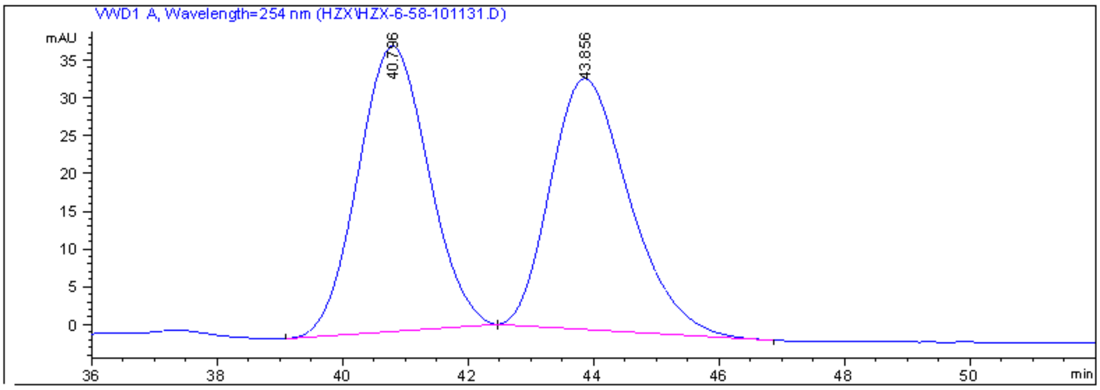
Peak #	Ret Time [min]	Type	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.763	BB	0.7147	696.08923	14.82765	50.2332
2	18.413	BB	0.9124	689.62738	11.31003	49.7668



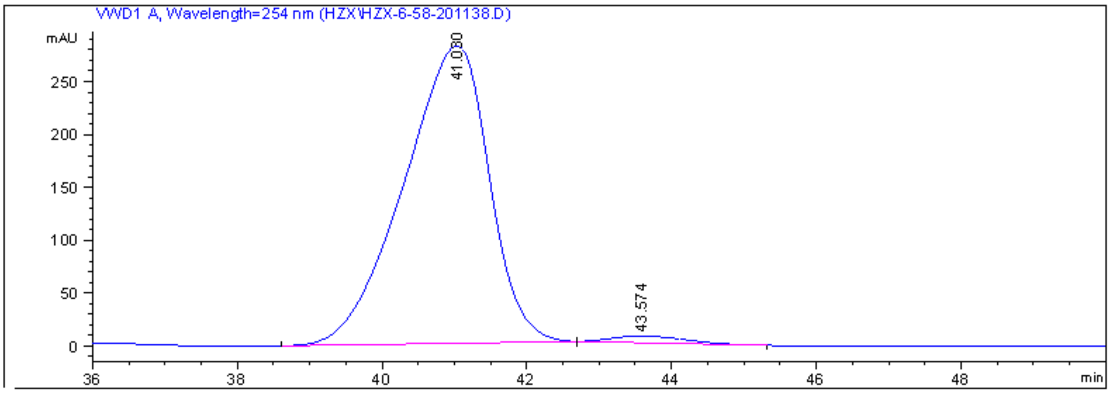
Peak #	Ret Time [min]	Type	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.696	VB	0.7388	808.38062	16.58085	3.1525
2	17.765	BBA	0.9216	2.48340e4	409.48303	96.8475



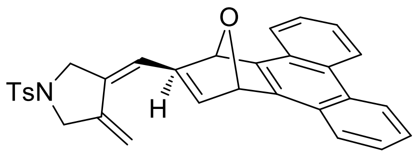
3ai



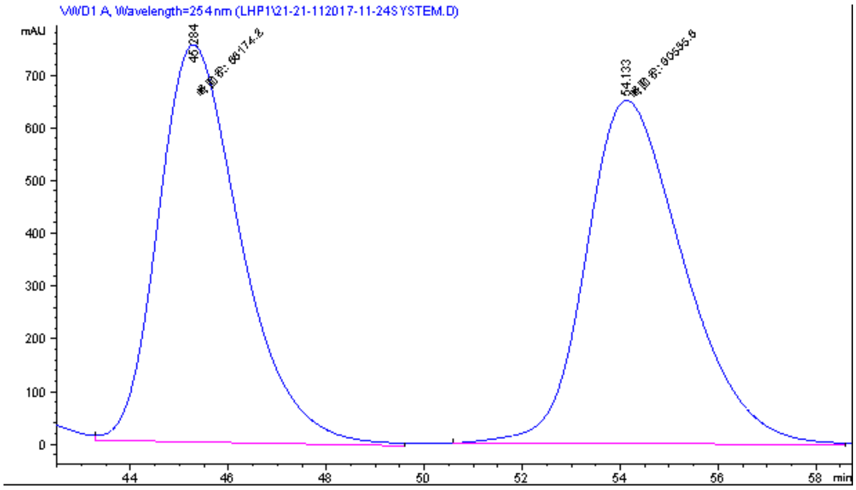
#	[min]		[min]	[mAU*s]	[mAU]	%
1	40.796	BB	1.1944	2944.82031	37.77810	50.3766
2	43.856	BB	1.3423	2900.78857	33.20038	49.6234



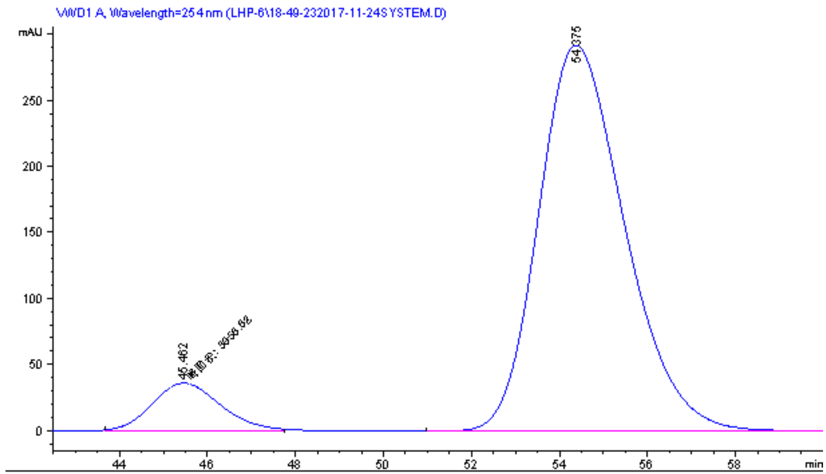
#	[min]		[min]	[mAU*s]	[mAU]	%
1	41.030	BB	1.2400	2.30450e4	280.65765	98.1023
2	43.574	BB	1.0351	445.78168	6.34972	1.8977



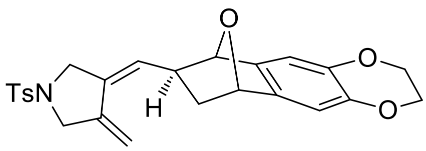
3aj



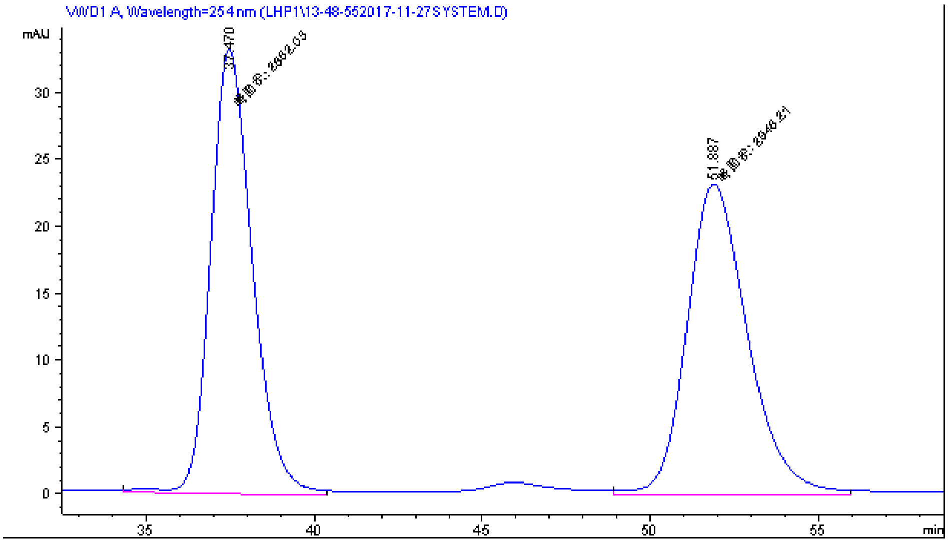
#	[min]		[min]	[mAU*s]	[mAU]	%
1	45.284	MM	1.9515	8.81742e4	753.04718	49.3393
2	54.133	MM	2.3180	9.05356e4	650.94720	50.6607



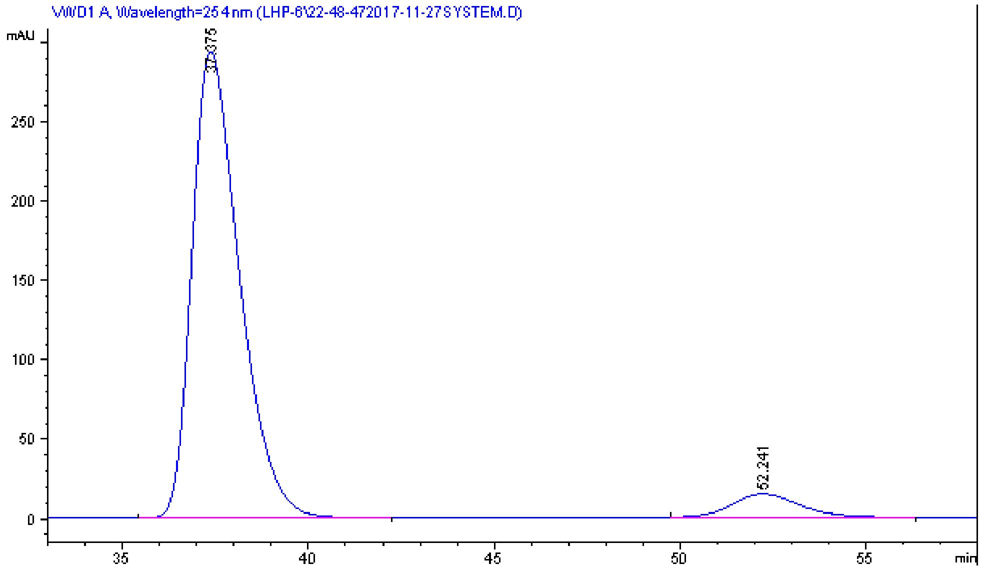
#	[min]		[min]	[mAU*s]	[mAU]	%
1	45.462	MM	1.8170	3958.82178	36.31369	9.0633
2	54.375	BB	2.0955	3.97209e4	291.91678	90.9367



3ak

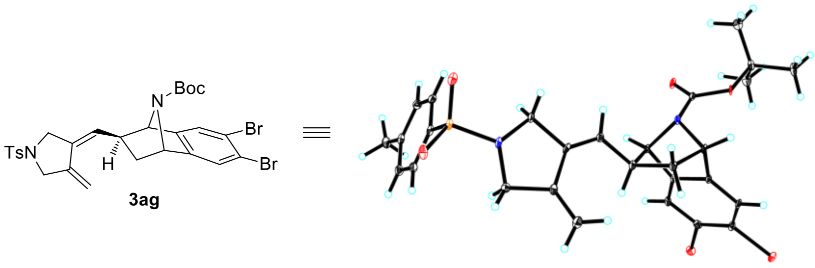


#	[min]		[min]	[mAU*s]	[mAU]	%
1	37.470	MM	1.4452	2882.02881	33.23609	49.4494
2	51.887	MM	2.1107	2946.21313	23.26379	50.5506



#	[min]		[min]	[mAU*s]	[mAU]	%
1	37.375	BB	1.3581	2.60904e4	294.07516	93.3062
2	52.241	BB	1.7556	1871.72974	14.78863	6.6938

F: Crystal structure data



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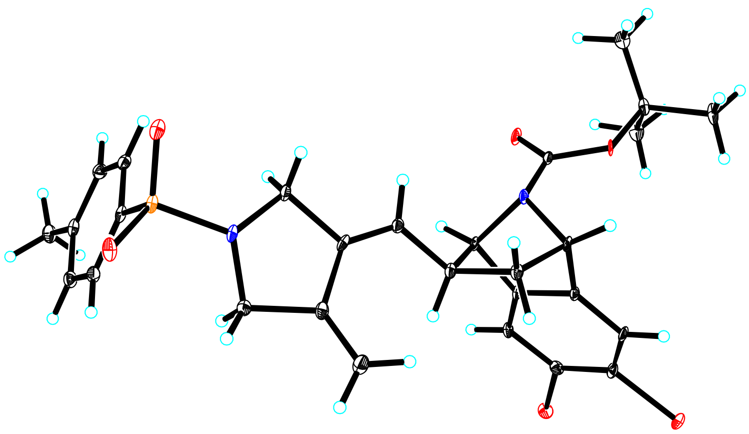
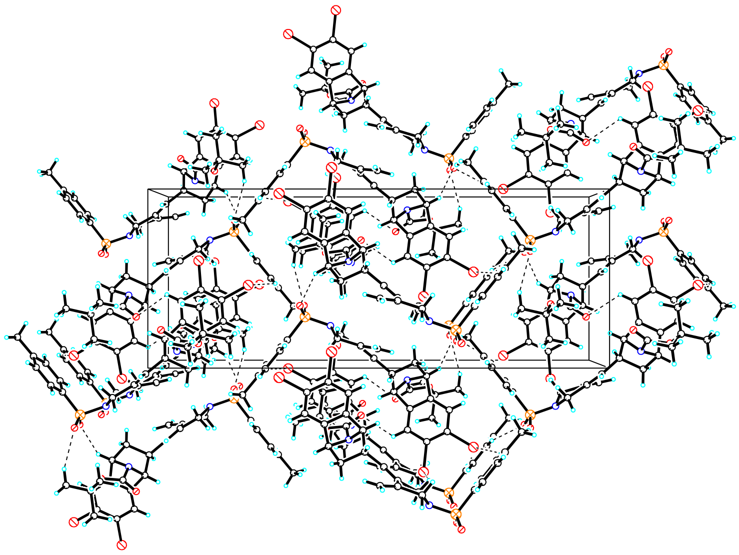
Crystal data for cu_qxjb_0m: $C_{28}H_{30}Br_2N_2O_4S$, M = 650.42, a = 9.5643(2) Å, b = 10.6107(3) Å, c = 27.3279(7) Å, α = 90 °, β = 90 °, γ = 90 °, V = 2773.34(12) Å^3, T = 100(2) K, space group P212121, Z = 4, μ(CuKα) = 4.712 mm^{-1}, 16557 reflections measured, 5044 independent reflections (R_{int} = 0.0436). The final R_1 values were 0.0317 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0827 ($I > 2\sigma(I)$). The final R_1 values were 0.0317 (all data). The final $wR(F^2)$ values were 0.0827 (all data). The goodness of fit on F^2 was 1.116. Flack parameter = 0.097(8).



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

Displacement ellipsoids are drawn at the 30% probability level.



View of the pack drawing of qxjb.

Hydrogen-bonds are shown as dashed lines.

Table 1. Crystal data and structure refinement for cu_qxjb_0m.

Identification code	cu_qxjb_0m	
Empirical formula	C28 H30 Br2 N2 O4 S	
Formula weight	650.42	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.5643(2) Å	α= 90 °.
	b = 10.6107(3) Å	β= 90 °.
	c = 27.3279(7) Å	γ = 90 °.
Volume	2773.34(12) Å^3	
Z	4	
Density (calculated)	1.558 Mg/m^3	
Absorption coefficient	4.712 mm^{-1}	
F(000)	1320	
Crystal size	0.840 x 0.320 x 0.130 mm^3	
Theta range for data collection	3.234 to 70.168 °.	
Index ranges	-11<=h<=11, -12<=k<=12, -30<=l<=33	
Reflections collected	16557	
Independent reflections	5044 [R(int) = 0.0436]	

Completeness to theta = 67.679 °	99.8 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5044 / 0 / 338
Goodness-of-fit on F^2	1.116
Final R indices [I>2sigma(I)]	R1 = 0.0317, wR2 = 0.0827
R indices (all data)	R1 = 0.0317, wR2 = 0.0827
Absolute structure parameter	0.097(8)
Extinction coefficient	n/a
Largest diff. peak and hole	0.391 and -0.917 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)
for cu_qxjb_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	7702(1)	4623(1)	7100(1)	21(1)
Br(2)	7871(1)	6020(1)	5992(1)	20(1)
S(1)	7662(1)	-2815(1)	3369(1)	13(1)
O(1)	2794(3)	1462(3)	6174(1)	14(1)
O(2)	2697(3)	2196(3)	5391(1)	18(1)
O(3)	6340(3)	-3447(3)	3326(1)	18(1)
O(4)	8952(4)	-3469(3)	3276(1)	20(1)
N(1)	4512(4)	968(3)	5653(1)	13(1)
N(2)	7748(4)	-2312(3)	3932(1)	14(1)
C(1)	1431(5)	1702(4)	6866(2)	23(1)
C(2)	1441(5)	2019(4)	6324(1)	16(1)
C(3)	3274(4)	1613(4)	5716(1)	14(1)
C(4)	5601(4)	1583(3)	5342(1)	11(1)
C(5)	6662(4)	481(4)	5297(1)	14(1)
C(6)	6213(4)	-392(4)	4890(1)	14(1)
C(7)	7051(5)	-1052(4)	4597(1)	14(1)
C(8)	6483(4)	-1746(4)	4149(1)	14(1)
C(9)	7631(5)	-1493(3)	2975(1)	14(1)
C(10)	8889(4)	-926(4)	2837(2)	16(1)
C(11)	8862(5)	94(4)	2518(2)	18(1)
C(12)	7596(5)	553(3)	2334(1)	16(1)
C(13)	7563(5)	1648(4)	1980(1)	21(1)
C(14)	9008(4)	-1620(4)	4096(2)	16(1)
C(15)	8587(5)	-1194(4)	4604(1)	15(1)
C(16)	259(5)	1360(4)	6055(2)	24(1)
C(17)	1453(6)	3438(4)	6253(2)	25(1)
C(18)	5444(4)	682(4)	6080(1)	12(1)
C(19)	6094(4)	1965(4)	6166(1)	13(1)
C(20)	6569(5)	2579(4)	6580(1)	15(1)
C(21)	7111(5)	3784(4)	6525(1)	15(1)
C(22)	7205(4)	4353(3)	6068(1)	15(1)
C(23)	6762(4)	3713(4)	5644(1)	14(1)

C(24)	6198(4)	2532(4)	5700(1)	12(1)
C(25)	6548(4)	-134(4)	5816(1)	15(1)
C(26)	9457(5)	-1066(4)	4973(2)	21(1)
C(27)	6369(4)	-1044(4)	2803(1)	16(1)
C(28)	6363(5)	-18(4)	2481(2)	17(1)

Table 3. Bond lengths [Å] and angles [°] for cu_qxjb_0m.

Br(1)-C(21)	1.892(4)
Br(2)-C(22)	1.892(4)
S(1)-O(3)	1.436(3)
S(1)-O(4)	1.438(3)
S(1)-N(2)	1.632(3)
S(1)-C(9)	1.768(4)
O(1)-C(3)	1.342(4)
O(1)-C(2)	1.480(5)
O(2)-C(3)	1.216(5)
N(1)-C(3)	1.378(5)
N(1)-C(4)	1.495(5)
N(1)-C(18)	1.500(5)
N(2)-C(8)	1.475(5)
N(2)-C(14)	1.480(5)
C(1)-C(2)	1.521(5)
C(1)-H(1)	0.9800
C(1)-H(8)	0.9800
C(1)-H(7)	0.9800
C(2)-C(16)	1.518(6)
C(2)-C(17)	1.519(6)
C(4)-C(24)	1.517(5)
C(4)-C(5)	1.553(5)
C(4)-H(17)	1.0000
C(5)-C(6)	1.508(5)
C(5)-C(25)	1.566(5)
C(5)-H(18)	1.0000
C(6)-C(7)	1.332(6)
C(6)-H(19)	0.9500
C(7)-C(15)	1.477(6)
C(7)-C(8)	1.528(5)
C(8)-H(21)	0.9900
C(8)-H(20)	0.9900
C(9)-C(27)	1.380(6)
C(9)-C(10)	1.397(6)
C(10)-C(11)	1.389(6)
C(10)-H(28)	0.9500

C(11)-C(12)	1.399(6)
C(11)-H(29)	0.9500
C(12)-C(28)	1.386(6)
C(12)-C(13)	1.511(5)
C(13)-H(2)	0.9800
C(13)-H(3)	0.9800
C(13)-H(30)	0.9800
C(14)-C(15)	1.515(5)
C(14)-H(24)	0.9900
C(14)-H(25)	0.9900
C(15)-C(26)	1.315(6)
C(16)-H(6)	0.9800
C(16)-H(4)	0.9800
C(16)-H(5)	0.9800
C(17)-H(10)	0.9800
C(17)-H(9)	0.9800
C(17)-H(11)	0.9800
C(18)-C(19)	1.514(5)
C(18)-C(25)	1.544(5)
C(18)-H(14)	1.0000
C(19)-C(20)	1.381(6)
C(19)-C(24)	1.413(5)
C(20)-C(21)	1.388(6)
C(20)-H(13)	0.9500
C(21)-C(22)	1.390(5)
C(22)-C(23)	1.408(5)
C(23)-C(24)	1.373(6)
C(23)-H(12)	0.9500
C(25)-H(16)	0.9900
C(25)-H(15)	0.9900
C(26)-H(22)	0.9500
C(26)-H(23)	0.9500
C(27)-C(28)	1.400(6)
C(27)-H(27)	0.9500
C(28)-H(26)	0.9500
O(3)-S(1)-O(4)	121.05(17)
O(3)-S(1)-N(2)	105.89(18)

O(4)-S(1)-N(2)	106.35(19)
O(3)-S(1)-C(9)	107.83(19)
O(4)-S(1)-C(9)	106.83(19)
N(2)-S(1)-C(9)	108.41(16)
C(3)-O(1)-C(2)	120.6(3)
C(3)-N(1)-C(4)	117.0(3)
C(3)-N(1)-C(18)	120.9(3)
C(4)-N(1)-C(18)	96.7(3)
C(8)-N(2)-C(14)	110.2(3)
C(8)-N(2)-S(1)	118.1(3)
C(14)-N(2)-S(1)	119.2(3)
C(2)-C(1)-H(1)	109.5
C(2)-C(1)-H(8)	109.5
H(1)-C(1)-H(8)	109.5
C(2)-C(1)-H(7)	109.5
H(1)-C(1)-H(7)	109.5
H(8)-C(1)-H(7)	109.5
O(1)-C(2)-C(16)	109.5(3)
O(1)-C(2)-C(17)	110.7(3)
C(16)-C(2)-C(17)	113.6(4)
O(1)-C(2)-C(1)	100.8(3)
C(16)-C(2)-C(1)	111.4(4)
C(17)-C(2)-C(1)	110.1(4)
O(2)-C(3)-O(1)	126.0(4)
O(2)-C(3)-N(1)	123.4(4)
O(1)-C(3)-N(1)	110.6(3)
N(1)-C(4)-C(24)	100.6(3)
N(1)-C(4)-C(5)	99.9(3)
C(24)-C(4)-C(5)	107.8(3)
N(1)-C(4)-H(17)	115.5
C(24)-C(4)-H(17)	115.5
C(5)-C(4)-H(17)	115.5
C(6)-C(5)-C(4)	109.5(3)
C(6)-C(5)-C(25)	113.1(3)
C(4)-C(5)-C(25)	101.3(3)
C(6)-C(5)-H(18)	110.9
C(4)-C(5)-H(18)	110.9
C(25)-C(5)-H(18)	110.9

C(7)-C(6)-C(5)	126.5(4)
C(7)-C(6)-H(19)	116.8
C(5)-C(6)-H(19)	116.8
C(6)-C(7)-C(15)	130.2(4)
C(6)-C(7)-C(8)	121.4(4)
C(15)-C(7)-C(8)	108.3(3)
N(2)-C(8)-C(7)	103.1(3)
N(2)-C(8)-H(21)	111.1
C(7)-C(8)-H(21)	111.1
N(2)-C(8)-H(20)	111.1
C(7)-C(8)-H(20)	111.1
H(21)-C(8)-H(20)	109.1
C(27)-C(9)-C(10)	120.8(3)
C(27)-C(9)-S(1)	119.7(3)
C(10)-C(9)-S(1)	119.5(3)
C(11)-C(10)-C(9)	119.3(4)
C(11)-C(10)-H(28)	120.3
C(9)-C(10)-H(28)	120.3
C(10)-C(11)-C(12)	120.9(4)
C(10)-C(11)-H(29)	119.6
C(12)-C(11)-H(29)	119.6
C(28)-C(12)-C(11)	118.7(3)
C(28)-C(12)-C(13)	120.3(4)
C(11)-C(12)-C(13)	121.1(4)
C(12)-C(13)-H(2)	109.5
C(12)-C(13)-H(3)	109.5
H(2)-C(13)-H(3)	109.5
C(12)-C(13)-H(30)	109.5
H(2)-C(13)-H(30)	109.5
H(3)-C(13)-H(30)	109.5
N(2)-C(14)-C(15)	102.0(3)
N(2)-C(14)-H(24)	111.4
C(15)-C(14)-H(24)	111.4
N(2)-C(14)-H(25)	111.4
C(15)-C(14)-H(25)	111.4
H(24)-C(14)-H(25)	109.2
C(26)-C(15)-C(7)	128.9(4)
C(26)-C(15)-C(14)	124.5(4)

C(7)-C(15)-C(14)	106.5(3)
C(2)-C(16)-H(6)	109.5
C(2)-C(16)-H(4)	109.5
H(6)-C(16)-H(4)	109.5
C(2)-C(16)-H(5)	109.5
H(6)-C(16)-H(5)	109.5
H(4)-C(16)-H(5)	109.5
C(2)-C(17)-H(10)	109.5
C(2)-C(17)-H(9)	109.5
H(10)-C(17)-H(9)	109.5
C(2)-C(17)-H(11)	109.5
H(10)-C(17)-H(11)	109.5
H(9)-C(17)-H(11)	109.5
N(1)-C(18)-C(19)	100.6(3)
N(1)-C(18)-C(25)	99.0(3)
C(19)-C(18)-C(25)	107.2(3)
N(1)-C(18)-H(14)	115.9
C(19)-C(18)-H(14)	115.9
C(25)-C(18)-H(14)	115.9
C(20)-C(19)-C(24)	120.9(4)
C(20)-C(19)-C(18)	133.3(4)
C(24)-C(19)-C(18)	105.8(3)
C(19)-C(20)-C(21)	118.0(4)
C(19)-C(20)-H(13)	121.0
C(21)-C(20)-H(13)	121.0
C(20)-C(21)-C(22)	121.3(3)
C(20)-C(21)-Br(1)	117.1(3)
C(22)-C(21)-Br(1)	121.5(3)
C(21)-C(22)-C(23)	120.8(3)
C(21)-C(22)-Br(2)	121.7(3)
C(23)-C(22)-Br(2)	117.5(3)
C(24)-C(23)-C(22)	117.7(3)
C(24)-C(23)-H(12)	121.1
C(22)-C(23)-H(12)	121.1
C(23)-C(24)-C(19)	121.2(3)
C(23)-C(24)-C(4)	133.0(3)
C(19)-C(24)-C(4)	105.8(3)
C(18)-C(25)-C(5)	103.8(3)

C(18)-C(25)-H(16)	111.0
C(5)-C(25)-H(16)	111.0
C(18)-C(25)-H(15)	111.0
C(5)-C(25)-H(15)	111.0
H(16)-C(25)-H(15)	109.0
C(15)-C(26)-H(22)	120.0
C(15)-C(26)-H(23)	120.0
H(22)-C(26)-H(23)	120.0
C(9)-C(27)-C(28)	119.1(4)
C(9)-C(27)-H(27)	120.5
C(28)-C(27)-H(27)	120.5
C(12)-C(28)-C(27)	121.3(4)
C(12)-C(28)-H(26)	119.4
C(27)-C(28)-H(26)	119.4

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for cu_qxjb_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	24(1)	26(1)	12(1)	-7(1)	-4(1)	-3(1)
Br(2)	23(1)	14(1)	22(1)	-3(1)	4(1)	-5(1)
S(1)	22(1)	10(1)	8(1)	0(1)	1(1)	2(1)
O(1)	19(1)	20(1)	2(1)	2(1)	4(1)	1(1)
O(2)	23(2)	26(1)	5(1)	3(1)	-3(1)	2(1)
O(3)	31(2)	11(1)	13(1)	0(1)	1(1)	-2(1)
O(4)	29(2)	17(2)	14(1)	1(1)	4(1)	8(1)
N(1)	18(2)	17(2)	6(1)	3(1)	1(1)	-2(1)
N(2)	21(2)	16(1)	6(1)	-1(1)	0(1)	0(1)
C(1)	37(3)	21(2)	11(2)	2(2)	10(2)	0(2)
C(2)	22(2)	15(2)	11(2)	0(2)	6(2)	1(2)
C(3)	18(2)	18(2)	7(2)	-1(2)	1(2)	-6(2)
C(4)	18(2)	11(2)	4(2)	2(1)	0(2)	-3(2)
C(5)	19(2)	13(2)	9(2)	0(2)	1(2)	-1(2)
C(6)	18(2)	16(2)	9(2)	0(2)	1(2)	-5(2)
C(7)	23(2)	14(2)	6(2)	0(1)	-4(2)	-1(2)
C(8)	18(2)	18(2)	7(2)	-3(2)	0(2)	2(2)
C(9)	22(2)	12(2)	8(2)	-2(1)	1(2)	1(2)
C(10)	18(2)	19(2)	12(2)	-1(2)	1(2)	4(2)
C(11)	21(2)	20(2)	13(2)	1(2)	3(2)	-2(2)
C(12)	27(2)	13(2)	9(2)	-1(1)	2(2)	2(2)
C(13)	27(2)	20(2)	14(2)	4(2)	4(2)	0(2)
C(14)	16(2)	21(2)	13(2)	-1(2)	0(2)	1(2)
C(15)	21(2)	14(2)	10(2)	2(2)	1(2)	0(2)
C(16)	23(2)	27(2)	20(2)	-1(2)	3(2)	-1(2)
C(17)	38(3)	15(2)	21(2)	1(2)	8(2)	3(2)
C(18)	19(2)	14(2)	4(2)	2(1)	-2(2)	-1(1)
C(19)	17(2)	15(2)	6(2)	1(1)	1(2)	-2(2)
C(20)	19(2)	22(2)	5(2)	1(2)	-3(2)	2(2)
C(21)	20(2)	17(2)	9(2)	-6(1)	0(2)	3(2)
C(22)	16(2)	12(2)	18(2)	-1(1)	4(2)	-3(1)
C(23)	20(2)	14(2)	9(2)	2(1)	3(2)	0(2)
C(24)	18(2)	13(2)	5(2)	0(1)	1(2)	1(2)

C(25)	20(2)	13(2)	11(2)	1(1)	1(2)	0(2)
C(26)	24(2)	23(2)	15(2)	-2(2)	-2(2)	6(2)
C(27)	20(2)	16(2)	11(2)	-1(2)	-1(2)	-3(2)
C(28)	18(2)	19(2)	14(2)	1(2)	-2(2)	0(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for cu_qxjb_0m.

	x	y	z	U(eq)
H(1)	1438	785	6908	35
H(8)	588	2053	7018	35
H(7)	2261	2065	7023	35
H(17)	5259	1940	5025	13
H(18)	7628	808	5237	16
H(19)	5236	-479	4838	17
H(21)	5800	-2402	4245	17
H(20)	6031	-1154	3918	17
H(28)	9753	-1235	2959	19
H(29)	9715	484	2424	21
H(2)	6663	1661	1810	31
H(3)	8320	1555	1741	31
H(30)	7686	2438	2161	31
H(24)	9208	-893	3880	20
H(25)	9837	-2178	4106	20
H(6)	326	1541	5704	35
H(4)	-640	1665	6180	35
H(5)	328	449	6108	35
H(10)	2306	3790	6396	37
H(9)	634	3807	6413	37
H(11)	1426	3633	5902	37
H(14)	4981	286	6370	15
H(13)	6526	2188	6892	18
H(12)	6851	4086	5329	17
H(16)	6237	-1021	5793	18
H(15)	7457	-103	5989	18
H(22)	9111	-853	5288	25
H(23)	10431	-1186	4924	25
H(27)	5516	-1427	2902	19
H(26)	5497	292	2361	20

Table 6. Torsion angles [°] for cu_qxjb_0m.

O(3)-S(1)-N(2)-C(8)	-42.2(3)
O(4)-S(1)-N(2)-C(8)	-172.2(3)
C(9)-S(1)-N(2)-C(8)	73.3(3)
O(3)-S(1)-N(2)-C(14)	179.5(3)
O(4)-S(1)-N(2)-C(14)	49.6(3)
C(9)-S(1)-N(2)-C(14)	-65.0(3)
C(3)-O(1)-C(2)-C(16)	67.5(4)
C(3)-O(1)-C(2)-C(17)	-58.6(5)
C(3)-O(1)-C(2)-C(1)	-175.0(3)
C(2)-O(1)-C(3)-O(2)	0.6(6)
C(2)-O(1)-C(3)-N(1)	-177.2(3)
C(4)-N(1)-C(3)-O(2)	39.7(5)
C(18)-N(1)-C(3)-O(2)	157.0(4)
C(4)-N(1)-C(3)-O(1)	-142.4(3)
C(18)-N(1)-C(3)-O(1)	-25.2(5)
C(3)-N(1)-C(4)-C(24)	78.7(4)
C(18)-N(1)-C(4)-C(24)	-51.0(3)
C(3)-N(1)-C(4)-C(5)	-170.9(3)
C(18)-N(1)-C(4)-C(5)	59.3(3)
N(1)-C(4)-C(5)-C(6)	83.5(3)
C(24)-C(4)-C(5)-C(6)	-171.8(3)
N(1)-C(4)-C(5)-C(25)	-36.1(3)
C(24)-C(4)-C(5)-C(25)	68.5(4)
C(4)-C(5)-C(6)-C(7)	147.3(4)
C(25)-C(5)-C(6)-C(7)	-100.5(5)
C(5)-C(6)-C(7)-C(15)	4.7(7)
C(5)-C(6)-C(7)-C(8)	-170.5(4)
C(14)-N(2)-C(8)-C(7)	-22.0(4)
S(1)-N(2)-C(8)-C(7)	-163.7(3)
C(6)-C(7)-C(8)-N(2)	178.9(4)
C(15)-C(7)-C(8)-N(2)	2.8(4)
O(3)-S(1)-C(9)-C(27)	17.5(4)
O(4)-S(1)-C(9)-C(27)	149.0(3)
N(2)-S(1)-C(9)-C(27)	-96.7(3)
O(3)-S(1)-C(9)-C(10)	-161.6(3)
O(4)-S(1)-C(9)-C(10)	-30.0(4)

N(2)-S(1)-C(9)-C(10)	84.2(3)
C(27)-C(9)-C(10)-C(11)	-0.6(6)
S(1)-C(9)-C(10)-C(11)	178.5(3)
C(9)-C(10)-C(11)-C(12)	-0.3(6)
C(10)-C(11)-C(12)-C(28)	0.9(6)
C(10)-C(11)-C(12)-C(13)	-178.9(4)
C(8)-N(2)-C(14)-C(15)	31.9(4)
S(1)-N(2)-C(14)-C(15)	173.1(3)
C(6)-C(7)-C(15)-C(26)	24.8(8)
C(8)-C(7)-C(15)-C(26)	-159.6(4)
C(6)-C(7)-C(15)-C(14)	-159.1(4)
C(8)-C(7)-C(15)-C(14)	16.5(5)
N(2)-C(14)-C(15)-C(26)	147.5(4)
N(2)-C(14)-C(15)-C(7)	-28.8(4)
C(3)-N(1)-C(18)-C(19)	-75.8(4)
C(4)-N(1)-C(18)-C(19)	51.2(3)
C(3)-N(1)-C(18)-C(25)	174.7(3)
C(4)-N(1)-C(18)-C(25)	-58.3(3)
N(1)-C(18)-C(19)-C(20)	148.7(5)
C(25)-C(18)-C(19)-C(20)	-108.4(5)
N(1)-C(18)-C(19)-C(24)	-32.7(4)
C(25)-C(18)-C(19)-C(24)	70.2(4)
C(24)-C(19)-C(20)-C(21)	1.9(6)
C(18)-C(19)-C(20)-C(21)	-179.6(4)
C(19)-C(20)-C(21)-C(22)	-1.4(6)
C(19)-C(20)-C(21)-Br(1)	178.1(3)
C(20)-C(21)-C(22)-C(23)	-0.6(6)
Br(1)-C(21)-C(22)-C(23)	179.9(3)
C(20)-C(21)-C(22)-Br(2)	177.4(3)
Br(1)-C(21)-C(22)-Br(2)	-2.1(5)
C(21)-C(22)-C(23)-C(24)	2.0(6)
Br(2)-C(22)-C(23)-C(24)	-176.1(3)
C(22)-C(23)-C(24)-C(19)	-1.5(6)
C(22)-C(23)-C(24)-C(4)	179.0(4)
C(20)-C(19)-C(24)-C(23)	-0.5(6)
C(18)-C(19)-C(24)-C(23)	-179.3(4)
C(20)-C(19)-C(24)-C(4)	179.1(4)
C(18)-C(19)-C(24)-C(4)	0.3(4)

N(1)-C(4)-C(24)-C(23)	-148.1(4)
C(5)-C(4)-C(24)-C(23)	107.8(5)
N(1)-C(4)-C(24)-C(19)	32.4(4)
C(5)-C(4)-C(24)-C(19)	-71.8(4)
N(1)-C(18)-C(25)-C(5)	35.1(4)
C(19)-C(18)-C(25)-C(5)	-69.0(4)
C(6)-C(5)-C(25)-C(18)	-116.6(4)
C(4)-C(5)-C(25)-C(18)	0.5(4)
C(10)-C(9)-C(27)-C(28)	0.8(5)
S(1)-C(9)-C(27)-C(28)	-178.3(3)
C(11)-C(12)-C(28)-C(27)	-0.7(6)
C(13)-C(12)-C(28)-C(27)	179.1(4)
C(9)-C(27)-C(28)-C(12)	-0.1(6)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cu_qxjb_0m [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(23)-H(12)...O(2)#1	0.95	2.53	3.118(5)	120.6
C(18)-H(14)...O(4)#2	1.00	2.37	3.263(5)	148.1
C(17)-H(11)...O(2)	0.98	2.40	2.949(5)	115.0
C(16)-H(6)...O(2)	0.98	2.52	3.086(6)	116.4
C(8)-H(20)...Br(2)#3	0.99	3.04	3.560(4)	114.4
C(1)-H(1)...O(3)#2	0.98	2.56	3.495(6)	158.6
C(1)-H(1)...Br(1)#4	0.98	3.09	3.678(4)	120.1
C(23)-H(12)...O(2)#1	0.95	2.53	3.118(5)	120.6
C(18)-H(14)...O(4)#2	1.00	2.37	3.263(5)	148.1
C(17)-H(11)...O(2)	0.98	2.40	2.949(5)	115.0
C(16)-H(6)...O(2)	0.98	2.52	3.086(6)	116.4
C(8)-H(20)...Br(2)#3	0.99	3.04	3.560(4)	114.4
C(1)-H(1)...O(3)#2	0.98	2.56	3.495(6)	158.6
C(1)-H(1)...Br(1)#4	0.98	3.09	3.678(4)	120.1
C(23)-H(12)...O(2)#1	0.95	2.53	3.118(5)	120.6
C(18)-H(14)...O(4)#2	1.00	2.37	3.263(5)	148.1
C(17)-H(11)...O(2)	0.98	2.40	2.949(5)	115.0
C(16)-H(6)...O(2)	0.98	2.52	3.086(6)	116.4
C(8)-H(20)...Br(2)#3	0.99	3.04	3.560(4)	114.4
C(1)-H(1)...O(3)#2	0.98	2.56	3.495(6)	158.6
C(1)-H(1)...Br(1)#4	0.98	3.09	3.678(4)	120.1
C(23)-H(12)...O(2)#1	0.95	2.53	3.118(5)	120.6
C(18)-H(14)...O(4)#2	1.00	2.37	3.263(5)	148.1
C(17)-H(11)...O(2)	0.98	2.40	2.949(5)	115.0
C(16)-H(6)...O(2)	0.98	2.52	3.086(6)	116.4
C(8)-H(20)...Br(2)#3	0.99	3.04	3.560(4)	114.4
C(1)-H(1)...O(3)#2	0.98	2.56	3.495(6)	158.6
C(1)-H(1)...Br(1)#4	0.98	3.09	3.678(4)	120.1
C(1)-H(1)...Br(1)#4	0.98	3.09	3.678(4)	120.1
C(1)-H(1)...O(3)#2	0.98	2.56	3.495(6)	158.6
C(8)-H(20)...Br(2)#3	0.99	3.04	3.560(4)	114.4
C(16)-H(6)...O(2)	0.98	2.52	3.086(6)	116.4
C(17)-H(11)...O(2)	0.98	2.40	2.949(5)	115.0
C(18)-H(14)...O(4)#2	1.00	2.37	3.263(5)	148.1

C(23)-H(12)...O(2)#1	0.95	2.53	3.118(5)	120.6
C(1)-H(1)...Br(1)#4	0.98	3.09	3.678(4)	120.1
C(1)-H(1)...O(3)#2	0.98	2.56	3.495(6)	158.6
C(8)-H(20)...Br(2)#3	0.99	3.04	3.560(4)	114.4
C(16)-H(6)...O(2)	0.98	2.52	3.086(6)	116.4
C(17)-H(11)...O(2)	0.98	2.40	2.949(5)	115.0
C(18)-H(14)...O(4)#2	1.00	2.37	3.263(5)	148.1
C(23)-H(12)...O(2)#1	0.95	2.53	3.118(5)	120.6
C(1)-H(1)...Br(1)#4	0.98	3.09	3.678(4)	120.1
C(1)-H(1)...O(3)#2	0.98	2.56	3.495(6)	158.6
C(8)-H(20)...Br(2)#3	0.99	3.04	3.560(4)	114.4
C(16)-H(6)...O(2)	0.98	2.52	3.086(6)	116.4
C(17)-H(11)...O(2)	0.98	2.40	2.949(5)	115.0
C(18)-H(14)...O(4)#2	1.00	2.37	3.263(5)	148.1
C(23)-H(12)...O(2)#1	0.95	2.53	3.118(5)	120.6

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1/2,-z+1   #2 x-1/2,-y-1/2,-z+1   #3 x-1/2,-y+1/2,-z+1

#4 -x+1,y-1/2,-z+3/2