Supporting Information:

Construction of Chiral 1,3-Diamines through Rhodium-Catalyzed Asymmetric Arylation of Cyclic *N*-Sulfonyl Imines

Chun-Yan Wu,[†] and Ming-Hua Xu*[†‡]

[†]*State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Chinese Academy of Sciences,555 Zuchongzhi Road, Shanghai 201203, China.*

[‡]*Shenzhen Grubbs Institute and Department of Chemistry, Southern University of Science and Technology, 1088 Xueyuan Blvd., Shenzhen 518055, China.*

E-mail: xumh@simm.ac.cn; xumh@sustech.edu.cn

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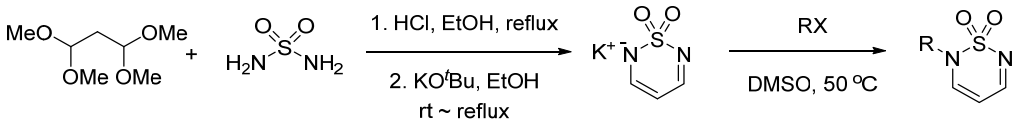
1. General

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or argon. Solvents were dried and distilled by standard procedures. NMR spectra were recorded on a Mercury 300 spectrometer (300 MHz for ^{1}H), Variant EM 390 (400 MHz for 1H), and Varian spectrometer (300 MHz for ^{1}H, 125 MHz, 150 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H NMR and chloroform-*d* (δ 77.36) for ^{13}C NMR. HRMS were recorded on a Q-TOF mass spectrometer with ESI resource or Magnetic Sector for EI. Optical rotations were measured on a Perkin-Elmer 241 MC polarimeter. HPLC was performed on a JASCO 2000 instrument by using Daicel columns with 2-propanol/hexane as the eluent.

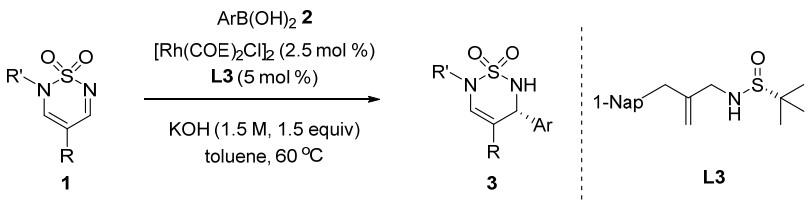
2. General procedure for synthesis of substrate



Dry hydrogen chloride was bubbled through a solution of sulfamide (1 equiv.) and 1,1,3,3-tetramethoxypropane (1 equiv.) in ethanol at room temperature for 15 min, and the mixture was heated under reflux for 6 h. Then, the solvent was evaporated and the residue redissolved in ethanol. Potassium *t*-butoxide (1 equiv.) was added at room temperature in small portions, and the reaction was heated at 80 °C for 10 min, cooled and filtered to afford the intermediate residue. Dissolved the intermediate in DMSO and added 1 equiv. halide, the reaction was stirred at 50 °C for 3 h. Cooled the mixture to room temperature and extracted with EA, washed with water, dried on anhydrous Na_2SO_4 and removed the solvent under vacuum, the residue was purified by silica gel column chromatography to afford the substrate as white solid.

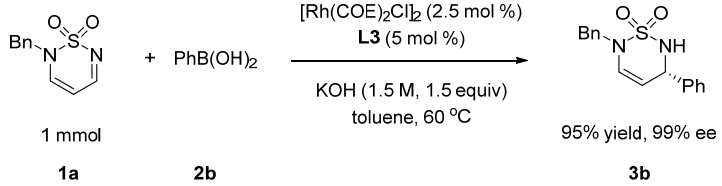
The substrate was chlorinated by *N*-chlorosuccinimide (1.2 equiv.) and brominated by *N*-bromosuccinimide (1.2 equiv.) in DCM to afford the 4-position halide substrates. The 4-vinyl and 4-phenyl subatrates could be obtained through $Pd(PPh_3)_2Cl_2$ (5 mol %) catalyzed coupling reactions with tributyl(vinyl)tin (1 equiv.) and tributyl(phenyl)tin (1 equiv.) in DCE at 50 °C.

3. General procedure for Rh-catalyzed 1,2-arylation of cyclic *N*-sulfonyl imines



Under Ar atmosphere, a solution of cyclic *N*-sulfonyl imine (0.20 mmol), $[Rh(COE)_2Cl]_2$ (2.5 mol %, 3.6 mg, 0.01 mmol of Rh), **L3** (3.0 mg, 5 mol %, 0.01 mmol), and arylboronic acid **2** (0.40 mmol) in 2.0 mL of toluene was stirred at room temperature for 30 min. To this mixture was added aqueous KOH (0.2 mL, 1.5 M, 0.30 mmol) and then the resulting mixture was stirred at 60 °C for 2 ~ 15 hours. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate to afford the corresponding addition product **3**.

Representative example at 1 mmol scale:



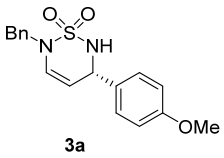
1 mmol — 95% yield, 99% ee

1a **2b** **3b**

Under Ar atmosphere, a solution of cyclic *N*-sulfonyl imine **1a** (1.0 mmol), $[Rh(COE)_2Cl]_2$ (2.5 mol %, 18 mg, 0.05 mmol of Rh), **L3** (15 mg, 5 mol %, 0.05 mmol), and phenylboronic acid **2b** in 10 mL of toluene was stirred at room temperature for 30 min. To this mixture was added aqueous KOH (1 mL, 1.5 M, 1.5 mmol) and then the resulting mixture was stirred at 60 °C for 3 hours. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate to afford the addition product **3b** (95% yield, 99% ee).

4. Characterization data and HPLC of addition products

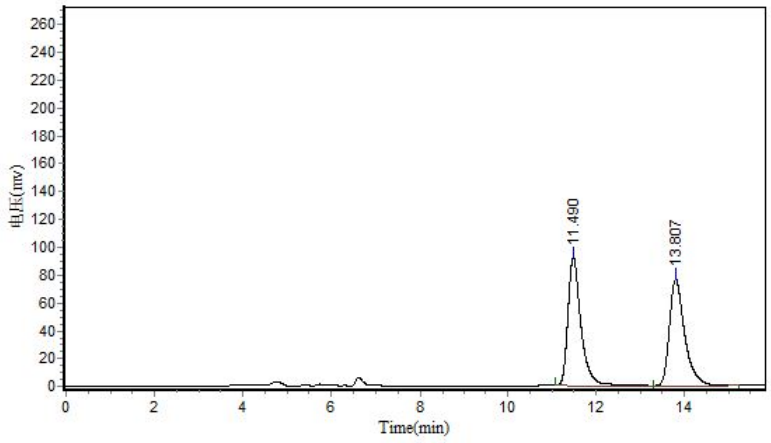
(*S*)-6-benzyl-3-(4-methoxyphenyl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3a)



3a

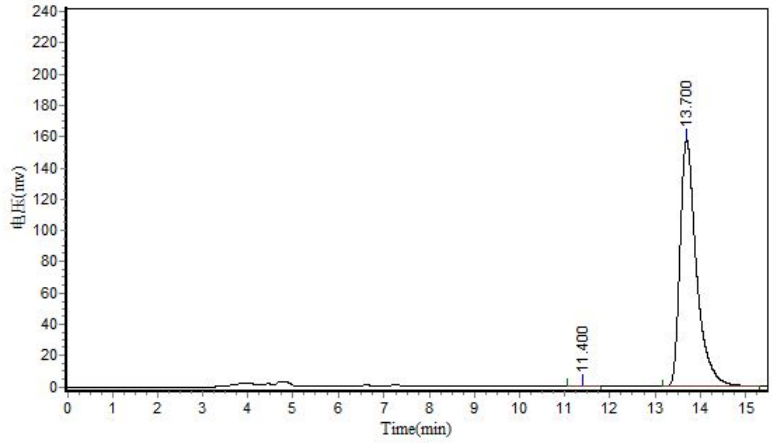
White solid, 58 mg, 88% yield, 99% ee. $[\alpha]^{20}_{D}$ = -47.3, (c 0.38, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 - 7.34 (m, 5H), 7.21 - 7.17 (m, 2H), 6.89 - 6.84 (m, 2H), 6.10 (dd, *J* = 8.5, 2.1 Hz, 1H), 5.29 (d, *J* = 9.8 Hz, 1H), 5.09 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.60 (dd, *J* = 96.2, 14.9 Hz, 2H), 3.80 (s, 3H), 3.77 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 135.6, 130.7, 130.1, 129.3, 129.2, 129.1, 128.6, 114.7, 108.2, 60.0, 55.7, 52.5. HRMS (ESI) for $C_{17}H_{18}N_2NaO_3S$ $[M+Na]^+$: calcd 353.0930, found 353.0925.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 11.4 min, 13.7 min (major).



Results

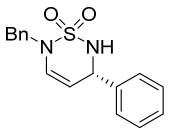
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.490	92013.602	1891363.375	50.5937
2		13.807	76493.484	1846973.625	49.4063
Total			168507.086	3738337.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.400	111.329	2183.901	0.0548
2		13.700	157477.625	3983325.500	99.9452
Total			157588.954	3985509.401	100.0000

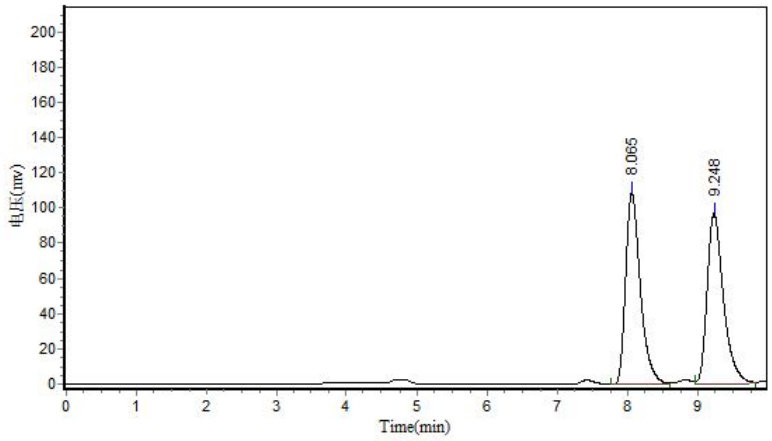
(*S*)-6-benzyl-3-phenyl-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3b)



3b

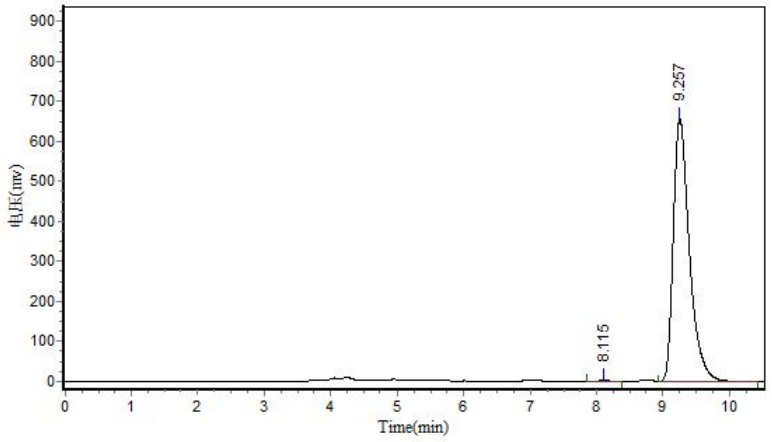
White solid, 59.4 mg, 99% yield, 99% ee. $[\alpha]^{20}_{D}$ = -40.0, (c 1.14, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 - 7.34 (m, 8H), 7.27 (dd, *J* = 6.7, 2.5 Hz, 2H), 6.11 (dd, *J* = 8.5, 2.1 Hz, 1H), 5.36 - 5.32 (m, 1H), 5.11 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.60 (dd, *J* = 90.7, 15.0 Hz, 2H), 3.87 (d, *J* = 9.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 135.6, 130.9, 129.4, 129.3, 129.2, 129.1, 128.6, 128.0, 107.9, 60.5, 52.6. HRMS (ESI) for $C_{16}H_{16}N_2NaO_2S$ $[M+Na]^+$: calcd 323.0825, found 323.0824.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 8.1 min, 9.3 min (major).



Results

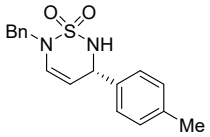
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.065	108656.445	1597885.750	49.8376
2		9.248	97008.125	1608302.375	50.1624
Total			205664.570	3206188.125	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.115	2142.436	32279.057	0.2899
2		9.257	656104.625	11104065.000	99.7101
Total			658247.061	11136344.057	100.0000

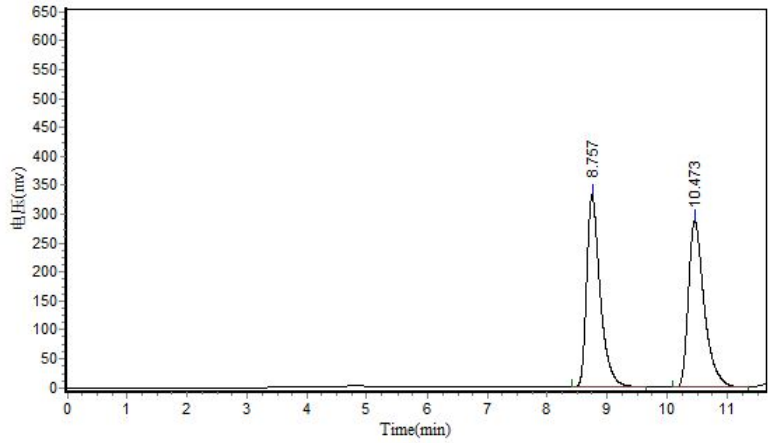
(*S*)-6-benzyl-3-(*p*-tolyl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3c)



3c

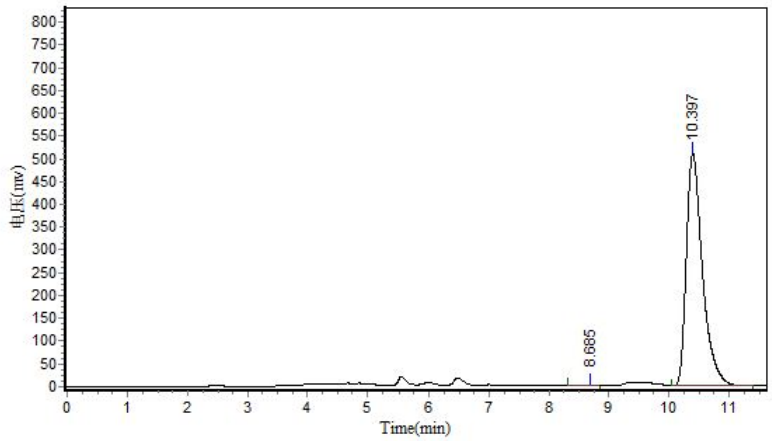
White solid, 60.2 mg, 96% yield, 99% ee. $[\alpha]^{20}_{D}$ = -42.3 (c 0.62, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 - 7.34 (m, 5H), 7.17 - 7.12 (m, 4H), 6.10 (dd, *J* = 8.5, 2.1 Hz, 1H), 5.30 (dt, *J* = 10.0, 1.9 Hz, 1H), 5.09 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.60 (dd, *J* = 95.1, 14.9 Hz, 2H), 3.81 (d, *J* = 10.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 135.6, 135.1, 130.7, 130.1, 129.2, 129.1, 128.6, 127.9, 108.2, 60.3, 52.6, 21.5. HRMS (ESI) for $C_{17}H_{18}N_2NaO_2S$ $[M+Na]^+$: calcd 337.0981, found 337.0988.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 8.7 min, 10.4 min (major).



Results

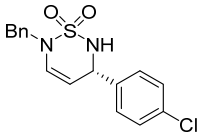
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.757	331933.781	5266562.000	49.6491
2		10.473	287834.750	5341001.500	50.3509
Total			619768.531	10607563.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.685	1055.293	19031.516	0.1986
2		10.397	510926.406	9565654.000	99.8014
Total			511981.699	9584685.516	100.0000

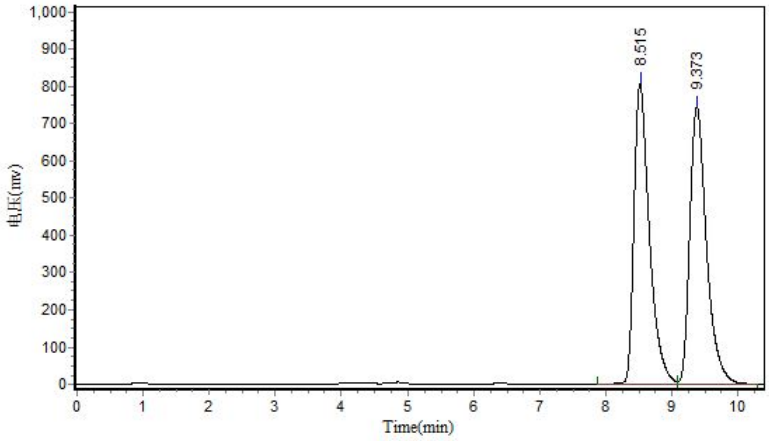
(*S*)-6-benzyl-3-(4-chlorophenyl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3d)



3d

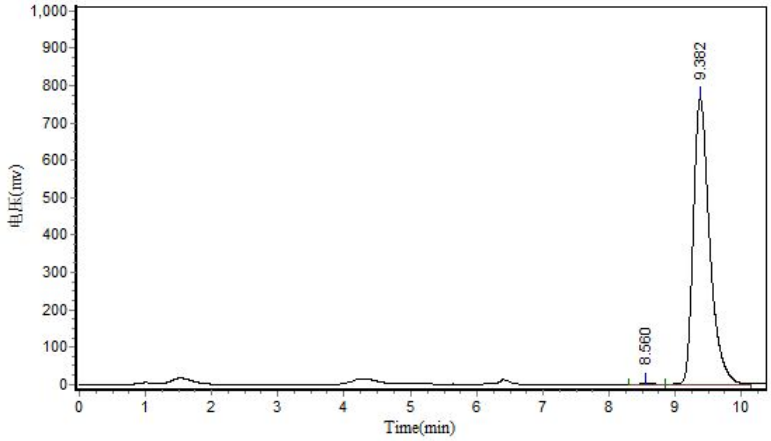
White solid, 66.1 mg, 99% yield, 99% ee. $[\alpha]^{20}_{D}$ = -39.4 (c 0.98, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 - 7.31 (m, 7H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.13 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.31 (d, *J* = 9.9 Hz, 1H), 5.08 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.60 (dd, *J* = 87.2, 15.0 Hz, 2H), 3.84 (d, *J* = 9.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.5, 135.4, 135.2, 131.2, 129.6, 129.4, 129.3, 129.1, 128.7, 107.4, 59.8, 52.6. HRMS (ESI) for $C_{16}H_{15}ClN_2NaO_2S$ $[M+Na]^+$: calcd 357.0435, found 357.0434.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 8.6 min, 9.4 min (major).



Results

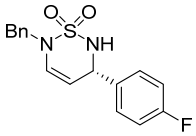
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.515	805317.625	13093558.000	49.8983
2		9.373	743444.438	13146919.000	50.1017
Total			1548762.063	26240477.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.560	5408.985	93361.156	0.6966
2		9.382	764623.688	13309231.000	99.3034
Total			770032.673	13402592.156	100.0000

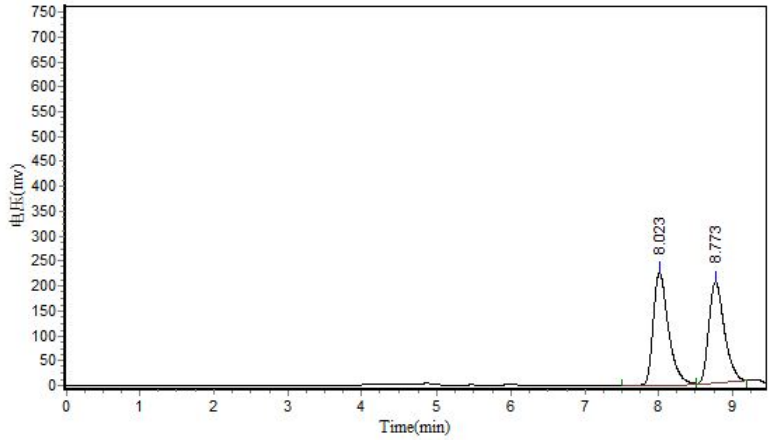
(*S*)-6-benzyl-3-(4-fluorophenyl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3e)



3e

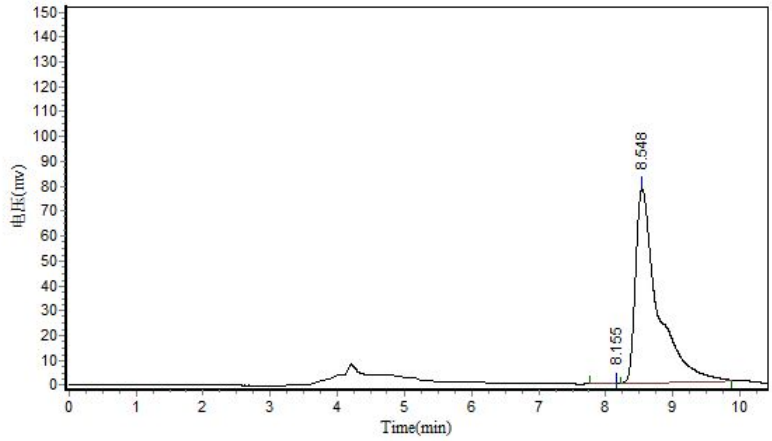
White solid, 63 mg, 99% yield, 99% ee. $[\alpha]^{20}_{D}$ = 1.7 (c 0.44, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 - 7.35 (m, 5H), 7.28 - 7.23 (m, 2H), 7.06 - 7.01 (m, 2H), 6.14 - 6.10 (m, 1H), 5.32 (d, *J* = 9.8 Hz, 1H), 5.09 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.60 (dd, *J* = 88.6, 15.0 Hz, 2H), 3.84 (d, *J* = 9.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2 (d, J_{CF} = 247 Hz), 135.5, 133.9 (d, J_{CF} = 3.1 Hz), 131.1, 129.9 (d, J_{CF} = 8.4 Hz), 129.2, 129.1, 128.7, 116.3 (d, J_{CF} = 21.6 Hz), 107.6, 59.8, 52.6. HRMS (ESI) for $C_{16}H_{15}FN_2NaO_2S$ $[M+Na]^+$: calcd 341.0730, found 341.0730.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 8.2 min, 8.5 min (major).



Results

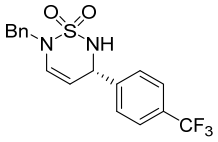
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.023	225993.141	3294043.250	50.3092
2		8.773	209000.578	3253549.500	49.6908
Total			434993.719	6547592.750	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.155	1.000	655.950	0.0370
2		8.548	77720.430	1773899.875	99.9630
Total			77721.430	1774555.825	100.0000

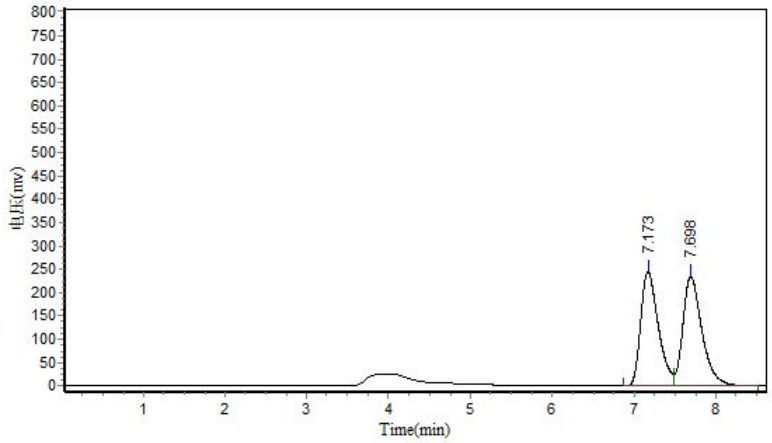
(*S*)-6-benzyl-3-(4-(trifluoromethyl)phenyl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3f)



3f

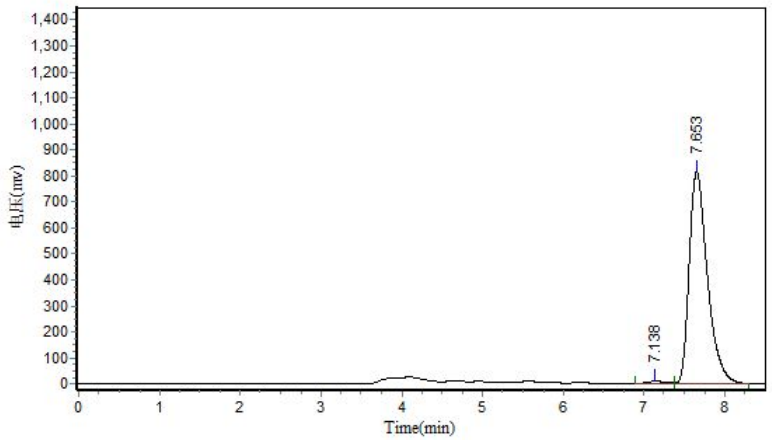
White solid, 44.2 mg, 60% yield, 98% ee. $[\alpha]^{20}_{D}$ = -23.4 (c 0.71, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.42 - 7.36 (m, 7H), 6.16 (d, *J* = 8.5 Hz, 1H), 5.38 (d, *J* = 7.3 Hz, 1H), 5.11 (d, *J* = 8.5 Hz, 1H), 4.62 (dd, *J* = 78.3, 15.0 Hz, 2H), 3.96 (d, *J* = 9.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 135.4, 131.5 (q, J_{CF} = 32.5 Hz), 131.4, 129.3, 129.1, 128.8, 128.4, 126.3 (d, J_{CF} = 3.6 Hz), 124.1 (q, J_{CF} = 270 Hz), 106.9, 59.9, 52.7. HRMS (ESI) for $C_{17}H_{15}F_3N_2NaO_2S$ $[M+Na]^+$: calcd 391.0699, found 391.0701.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 7.1 min, 7.7 min (major).



Results

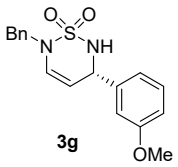
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.173	244267.984	3666652.250	48.9232
2		7.698	233733.203	3828054.250	51.0768
Total			478001.188	7494706.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.138	8911.578	126654.203	0.9850
2		7.653	812722.688	12731264.000	99.0150
Total			821634.266	12857918.203	100.0000

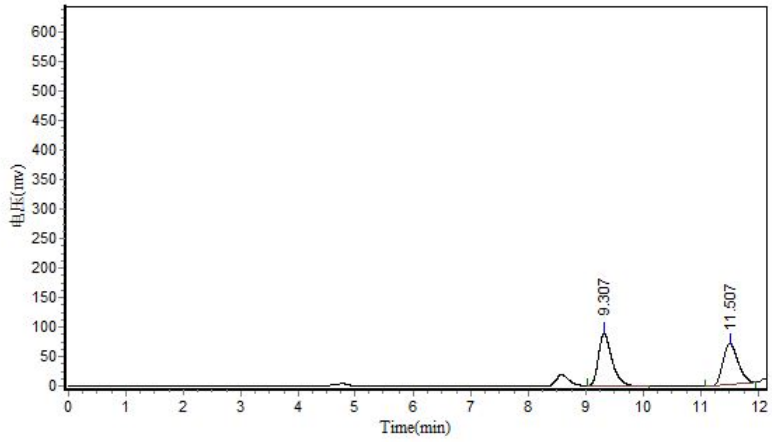
(*S*)-6-benzyl-3-(3-methoxyphenyl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3g)



3g

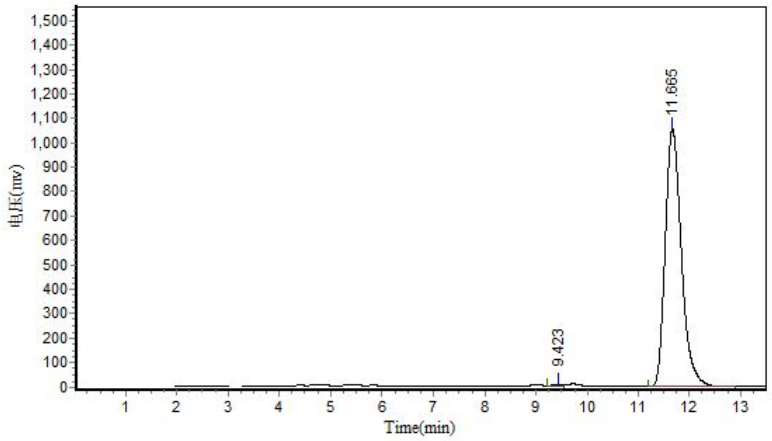
White solid, 60.0 mg, 91% yield, 99% ee. $[\alpha]^{20}_{D}$ = -52.6 (c 1.19, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 - 7.24 (m, 6H), 6.89 - 6.84 (m, 3H), 6.10 (dt, *J* = 8.5, 1.9 Hz, 1H), 5.33 - 5.29 (m, 1H), 5.10 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.60 (ddd, *J* = 87.1, 15.0, 1.7 Hz, 2H), 3.92 (d, *J* = 9.9 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 139.5 135.6, 130.8, 130.5, 129.2, 129.0, 128.6, 120.1, 114.8, 113.7, 107.7, 60.4, 55.7, 52.5. HRMS (ESI) for $C_{17}H_{18}N_2NaO_3S$ $[M+Na]^+$: calcd 353.0930, found 353.0932.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 9.4 min, 11.7 min (major).



Results

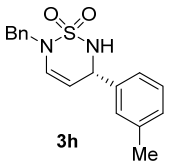
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.307	88981.250	1478861.125	50.2107
2		11.507	73488.523	1466447.000	49.7893
Total			162469.773	2945308.125	100.0000



Results

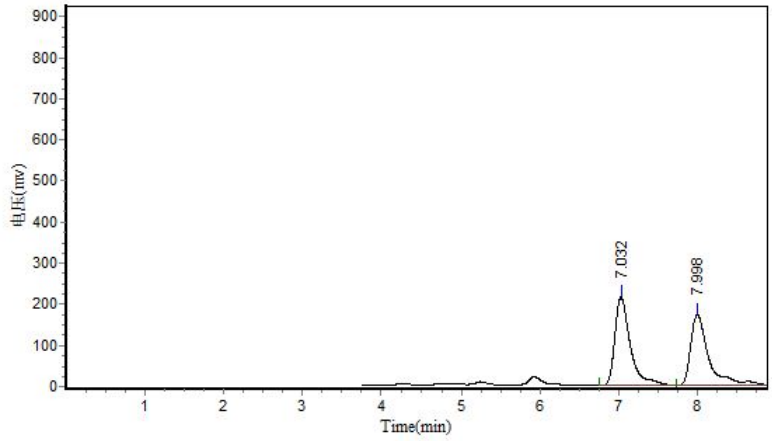
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.423	6466.544	95291.180	0.4087
2		11.665	1056651.250	23220936.000	99.5913
Total			1063117.794	23316227.180	100.0000

(*S*)-6-benzyl-3-(*m*-tolyl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3h)



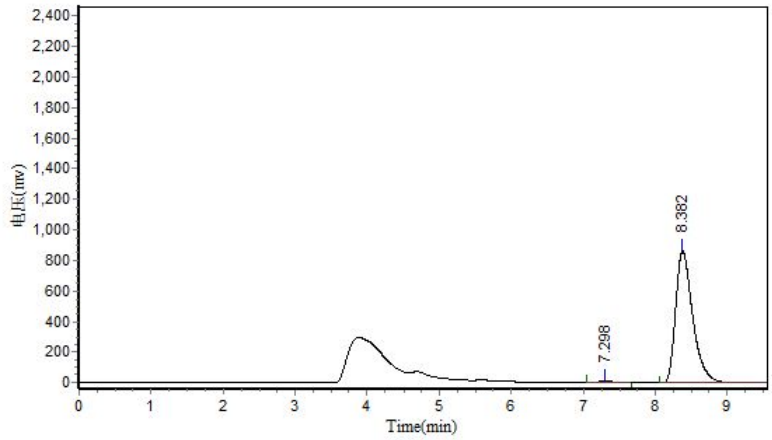
White solid, 59 mg, 94% yield, 98% ee. $[\alpha]^{20}_{D}$ = -19.0 (c 0.47, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 - 7.33 (m, 5H), 7.27 - 7.22 (m, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.08 - 7.07 (m, 2H), 6.11 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.30 (d, *J* = 9.9 Hz, 1H), 5.10 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.79 - 4.43 (m, 2H), 3.92 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 137.9, 135.5, 130.6, 130.0, 129.2, 129.1, 129.0, 128.6, 125.0, 108.2, 60.5, 52.5, 21.7. HRMS (ESI) for $C_{17}H_{18}N_2NaO_2S$ $[M+Na]^+$: calcd 337.0981, found 337.0984.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 7.3 min, 8.4 min (major).



Results

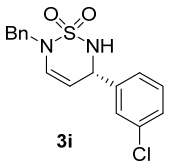
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.032	215037.953	2961570.000	48.9697
2		7.998	174580.656	3086194.750	51.0303
Total			389618.609	6047764.750	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.298	9552.199	140959.453	0.9801
2		8.382	861864.063	14241176.000	99.0199
Total			871416.262	14382135.453	100.0000

(*S*)-6-benzyl-3-(3-chlorophenyl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3i)

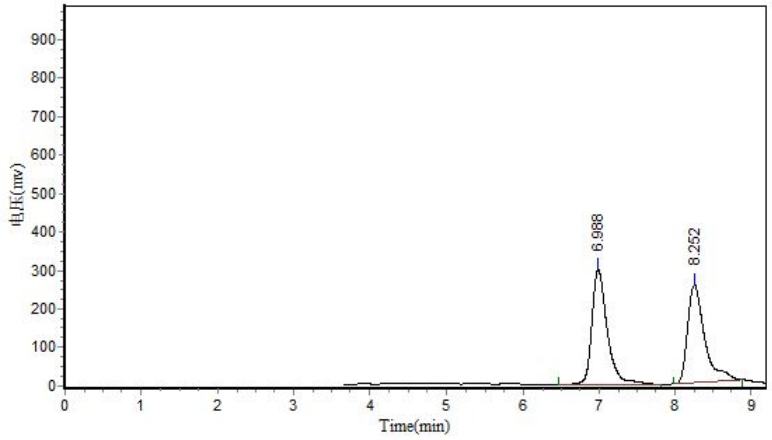


3i

White solid, 60.1 mg, 90% yield, 99% ee. $[\alpha]^{20}_{D}$ = -23.2 (c 0.45, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 - 7.17 (m, 9H), 6.14 - 6.11 (m, 1H), 5.29 (d, *J* = 9.8 Hz, 1H), 5.08 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.59 (dd, *J* = 82.9, 15.0 Hz, 2H), 3.94 (d, *J* = 9.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.9, 135.32, 135.26, 131.3, 130.7, 129.5, 129.3, 129.1, 128.8, 128.1, 126.3, 107.3, 59.9, 52.7.

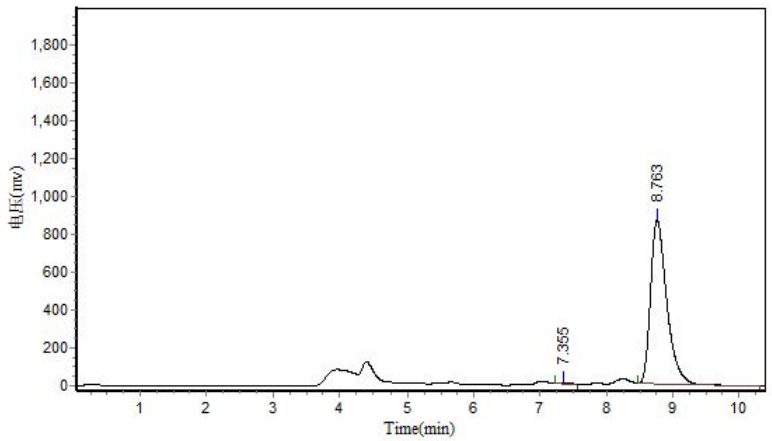
HRMS (ESI) for $C_{16}H_{15}ClN_2NaO_2S$ $[M+Na]^+$: calcd 357.0435, found 357.0437.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 7.4 min, 8.8 min (major).



Results

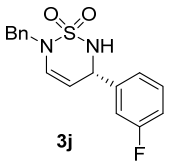
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.988	297950.719	4170252.750	51.1892
2		8.252	255261.609	3976484.000	48.8108
Total			553212.328	8146736.750	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.355	7718.971	85773.391	0.5882
2		8.763	864571.313	14497296.000	99.4118
Total			872290.284	14583069.391	100.0000

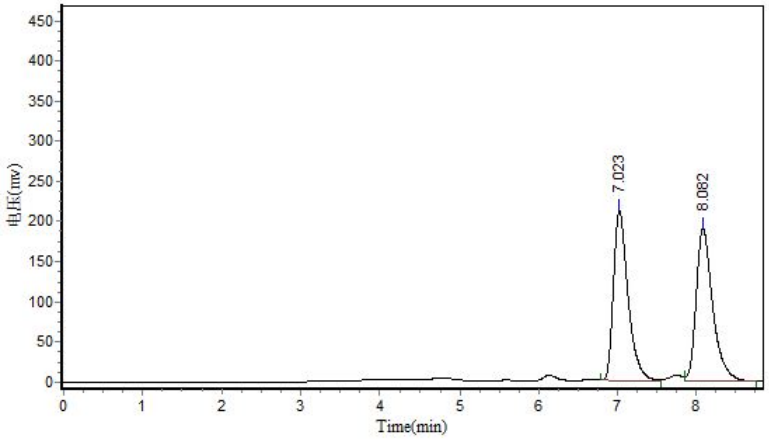
(*S*)-6-benzyl-3-(3-fluorophenyl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3j)



3j

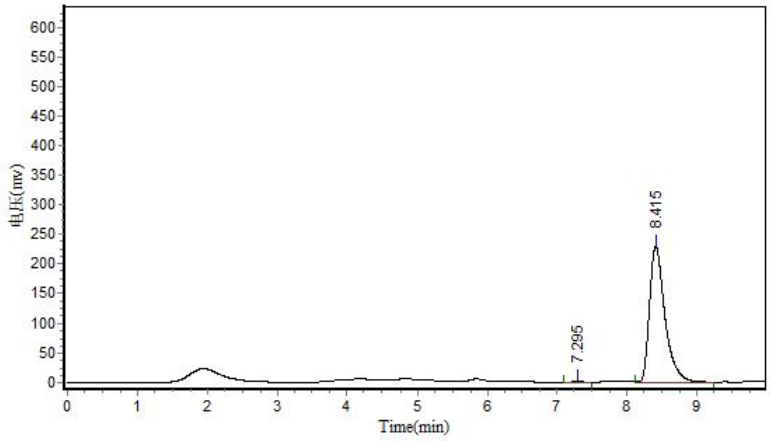
White solid, 63 mg, 99% yield, 99% ee. $[\alpha]^{20}_{D}$ = -20.1 (c 0.82, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 - 7.29 (m, 6H), 7.09 - 6.95 (m, 3H), 6.12 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.32 (d, *J* = 9.9 Hz, 1H), 5.09 (dd, *J* = 8.5, 1.9 Hz, 1H), 4.60 (dd, *J* = 83.8, 15.0 Hz, 2H), 3.92 (d, *J* = 9.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3 (d, J_{CF} = 246.1 Hz), 140.4 (d, J_{CF} = 7.0 Hz), 135.4, 131.2, 131.0 (d, J_{CF} = 8.1 Hz), 129.3, 129.0, 128.7, 123.7 (d, J_{CF} = 2.9 Hz), 116.3 (d, J_{CF} = 21.0 Hz), 115.0 (d, J_{CF}= 22.3 Hz), 107.3, 59.9, 52.6. HRMS (ESI) for $C_{16}H_{16}FN_2O_2S$ $[M+H]^+$: calcd 319.0911, found 319.0912.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 7.3 min, 8.4 min (major).



Results

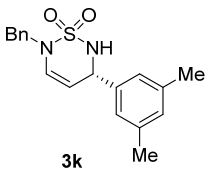
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.023	212759.813	2785286.500	49.6578
2		8.082	190890.234	2823669.750	50.3422
Total			403650.047	5608956.250	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.295	288.761	3866.619	0.1087
2		8.415	230421.016	3552008.750	99.8913
Total			230709.776	3555875.369	100.0000

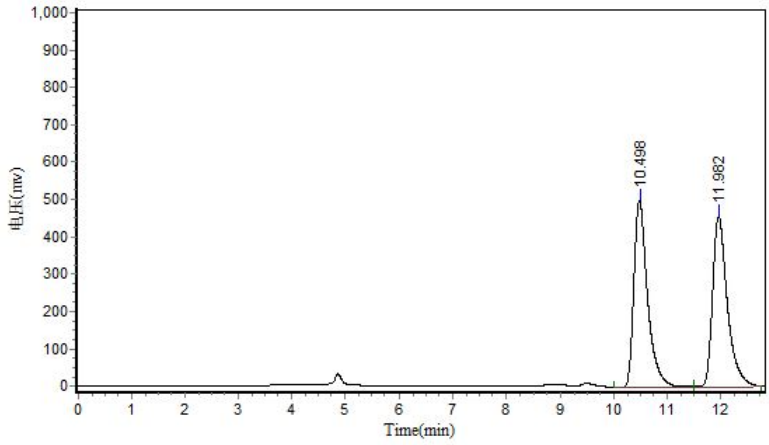
(*S*)-6-benzyl-3-(3,5-dimethylphenyl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3k)



3k

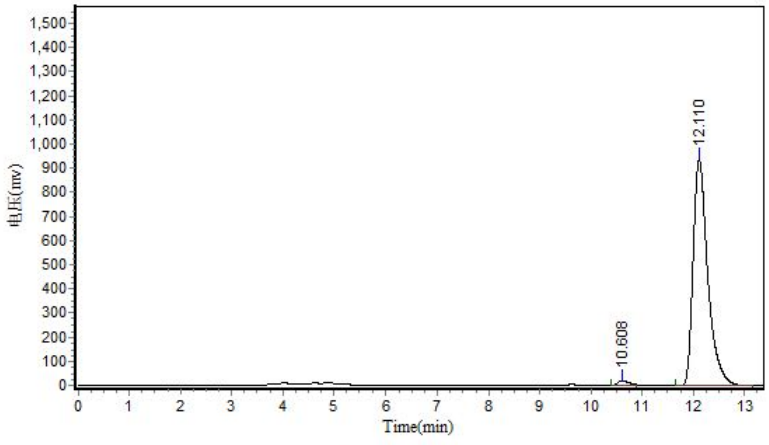
White solid, 57.1 mg, 87% yield, 97% ee. $[\alpha]^{19}_{D}$ = -64.8 (c 0.55, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 - 7.26 (m, 5H), 6.97 (d, *J* = 5.6 Hz, 1H), 6.85 (d, *J* = 6.1 Hz, 2H), 6.09 (dd, *J* = 8.4, 1.9 Hz, 1H), 5.24 (d, *J* = 9.8 Hz, 1H), 5.11 - 5.07 (m, 1H), 4.79 - 4.41 (m, 2H), 3.77 (d, *J* = 9.8 Hz, 1H), 2.30 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.1, 137.9, 135.5, 130.9, 130.6, 129.20, 129.15, 128.7, 125.6, 108.7, 60.5, 52.7, 21.6. HRMS (ESI) for $C_{18}H_{20}N_2NaO_2S$ $[M+Na]^+$: calcd 351.1138, found 351.1146.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 10.6 min, 12.1 min (major).



Results

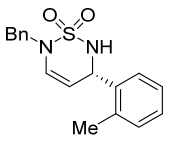
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.498	500146.000	8946450.000	50.2470
2		11.982	458758.938	8858508.000	49.7530
Total			958904.938	17804958.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.608	19348.076	283570.906	1.4928
2		12.110	937999.875	18712018.000	98.5072
Total			957347.951	18995588.906	100.0000

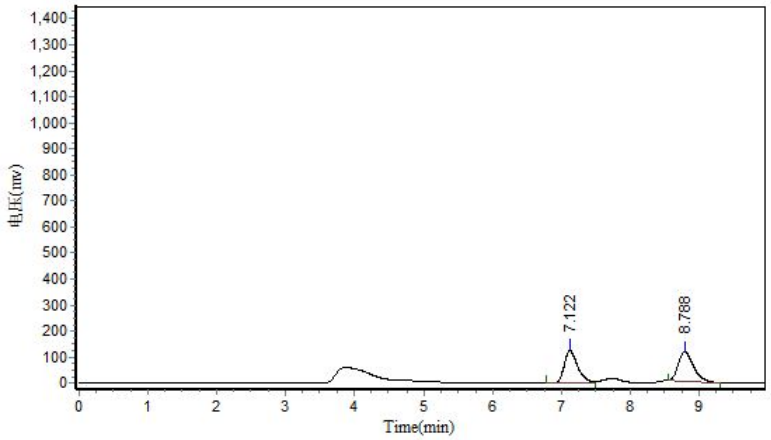
(*S*)-6-benzyl-3-(*o*-tolyl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3l)



3l

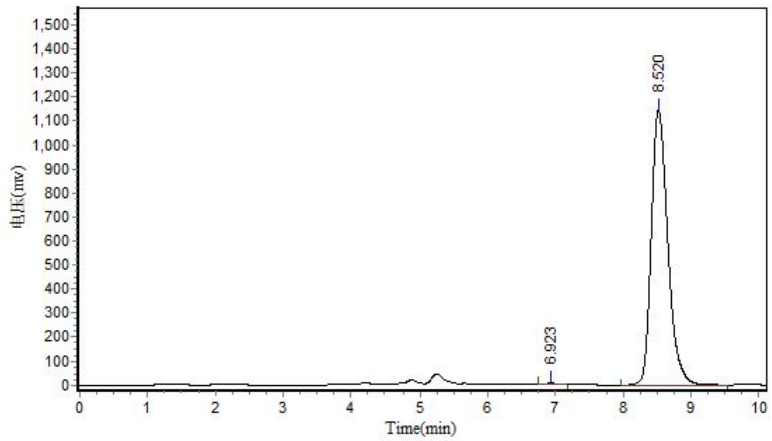
White solid, 55.9 mg, 89% yield, 99% ee. $[\alpha]^{20}_{D}$ = -4.4 (c 0.50, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 - 7.33 (m, 5H), 7.26 - 7.16 (m, 4H), 6.16 (dd, *J* = 8.6, 2.1 Hz, 1H), 5.57 (dt, *J* = 10.3, 1.9 Hz, 1H), 5.13 (dd, *J* = 8.6, 1.7 Hz, 1H), 4.61 (dd, *J* = 91.7, 15.0 Hz, 2H), 3.74 (d, *J* = 10.2 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7, 136.0, 135.6, 131.3, 131,2, 129.3, 129.2, 129.0, 128.6, 127.3, 126.8, 107.9, 57.1, 52.5, 19.1. HRMS (ESI) for $C_{17}H_{18}N_2NaO_2S$ $[M+Na]^+$: calcd 337.0981, found 337.0985.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 6.9 min, 8.5 min (major).



Results

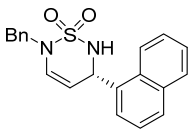
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.122	123737.898	1696104.375	49.4714
2		8.788	113575.313	1732346.750	50.5286
Total			237313.211	3428451.125	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.923	5997.568	70364.297	0.3617
2		8.520	1143820.250	19385820.000	99.6383
Total			1149817.818	19456184.297	100.0000

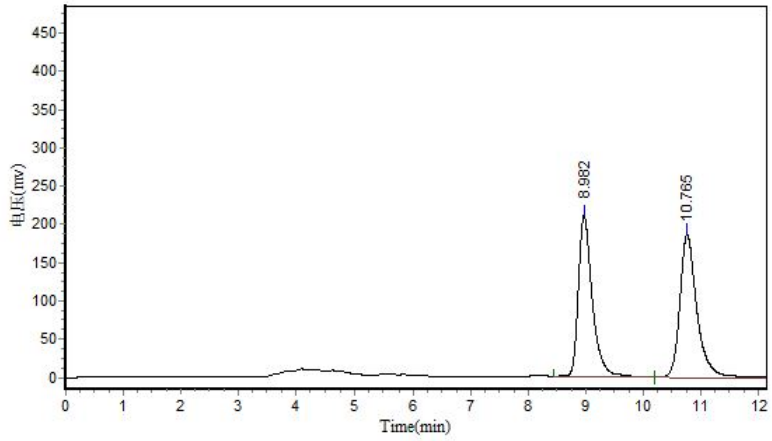
(*S*)-6-benzyl-3-(naphthalen-1-yl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3m)



3m

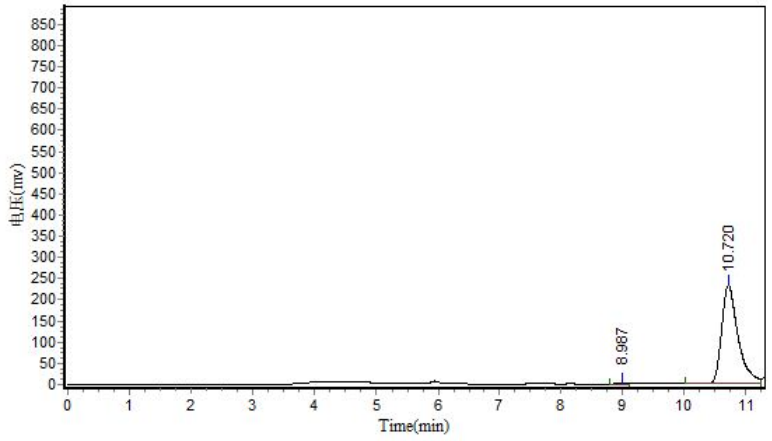
White solid, 60.2 mg, 86% yield, 99% ee. $[\alpha]^{20}_{D}$ = 60.0 (c 0.52, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 1H), 7.82 (t, *J* = 8.4 Hz, 2H), 7.56 - 7.29 (m, 9H), 6.19 - 6.08 (m, 2H), 5.23 (d, *J* = 8.5 Hz, 1H), 4.58 (dd, *J* = 89.1, 15.0 Hz, 2H), 4.01 (d, *J* = 10.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.6, 134.2, 133.4, 131.32, 131.28, 130.1, 129.2, 129.1, 128.9, 128.5, 127.3, 126.6, 125.8, 125.4, 123.6, 107.5, 56.7, 52.4. HRMS (ESI) for $C_{20}H_{18}N_2NaO_2S$ $[M+Na]^+$: calcd 373.0981, found 373.0988.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 9.0 min, 10.7 min (major).



Results

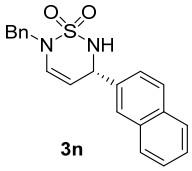
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.982	210984.000	3625896.500	48.5217
2		10.765	185814.719	3846840.000	51.4783
Total			396798.719	7472736.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.987	254.311	2967.807	0.0686
2		10.720	233837.250	4323261.500	99.9314
Total			234091.561	4326229.307	100.0000

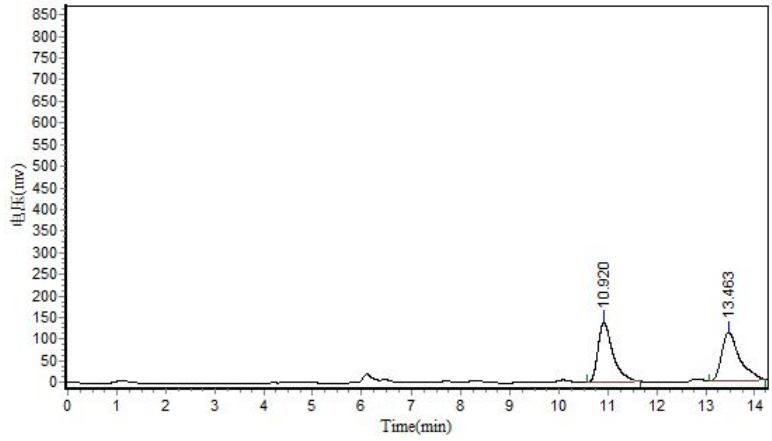
(*S*)-6-benzyl-3-(naphthalen-2-yl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3n)



3n

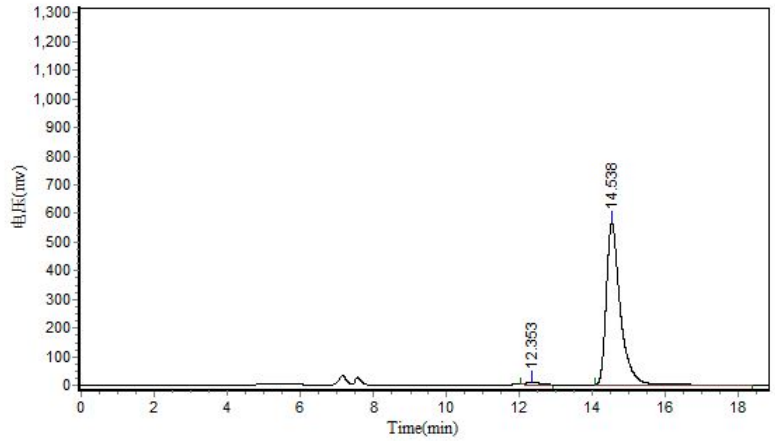
White solid, 64.4 mg, 92% yield, 98% ee. $[\alpha]^{20}_{D}$ = -80.0 (c 0.47, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 - 7.73 (m, 4H), 7.52 - 7.34 (m, 8H), 6.17 (dd, *J* = 8.5, 1.5 Hz, 1H), 5.50 (d, *J* = 9.9 Hz, 1H), 5.22 (dd, *J* = 8.5, 1.2 Hz, 1H), 4.64 (dd, *J* = 95.3, 14.9 Hz, 2H), 3.94 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.5, 135.3, 133.7, 133.6, 131.0, 129.4, 129.3, 129.1, 128.7, 128.4, 128.1, 127.10, 127.07, 127.0, 125.5, 108.0, 60.6, 52.7. HRMS (ESI) for $C_{20}H_{18}N_2NaO_2S$ $[M+Na]^+$: calcd 373.0981, found 373.0984.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 12.4 min, 14.5 min (major).



Results

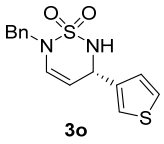
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.920	138711.031	2909647.000	50.9542
2		13.463	111955.664	2800675.000	49.0458
Total			250666.695	5710322.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.353	7804.929	155406.813	1.0155
2		14.538	563977.438	15148515.000	98.9845
Total			571782.366	15303921.813	100.0000

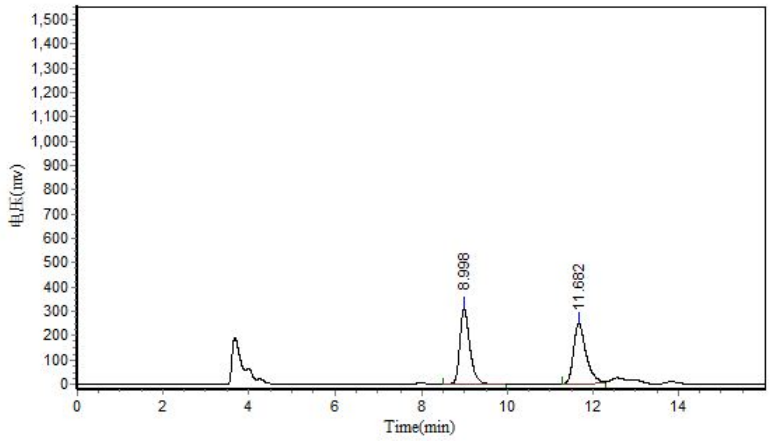
(*S*)-6-benzyl-3-(thiophen-3-yl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3o)



3o

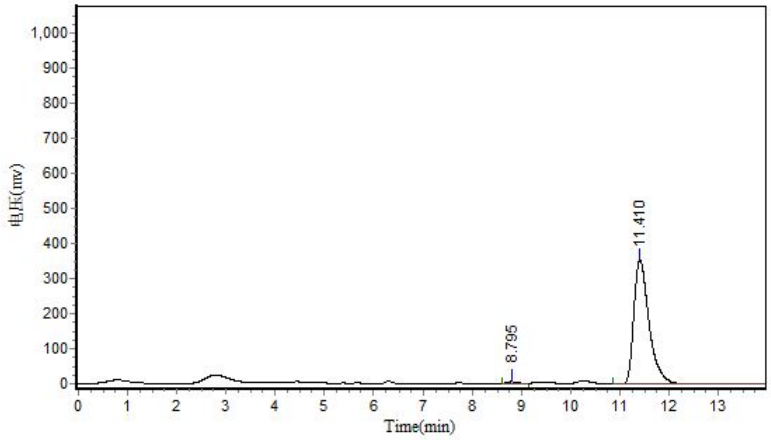
White solid, 30 mg, 49% yield, 98% ee. $[\alpha]^{20}_{D}$ = -45.2 (c 0.91, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 - 7.31 (m, 6H), 7.22 (s, 1H), 7.01 (d, *J* = 5.0 Hz, 1H), 6.06 (dd, *J* = 8.5, 2.1 Hz, 1H), 5.42 (d, *J* = 10.2 Hz, 1H), 5.14 (d, *J* = 8.5 Hz, 1H), 4.58 (dd, *J* = 78.6, 15.0 Hz, 2H), 3.92 (d, *J* = 10.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 135.6, 130.6, 129.2, 128.9, 128.6, 127.4, 126.9, 123.8, 107.1, 55.8, 52.4. HRMS (ESI) for $C_{14}H_{15}N_2O_2S_2$ $[M+H]^+$: calcd 307.0569, found 307.0570.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 8.8 min, 11.4 min (major).



Results

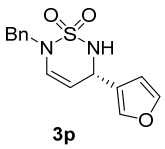
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.998	309673.094	5046558.000	49.0619
2		11.682	249672.594	5239544.500	50.9381
Total			559345.688	10286102.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.795	5446.750	73411.203	0.9495
2		11.410	354957.906	7658441.500	99.0505
Total			360404.656	7731852.703	100.0000

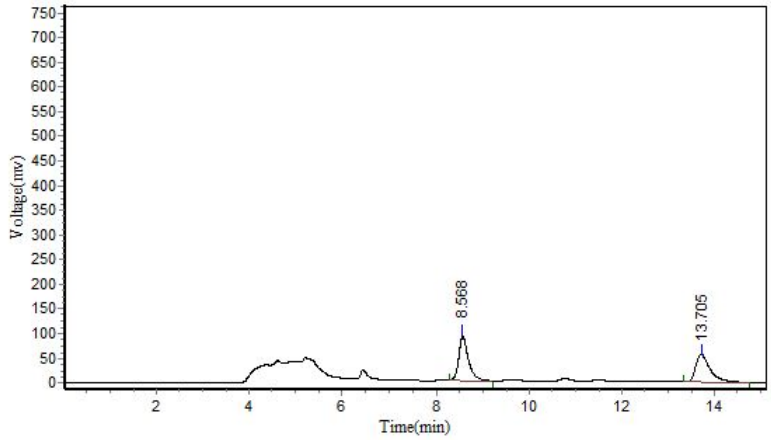
(*S*)-6-benzyl-3-(furan-3-yl)-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3p)



3p

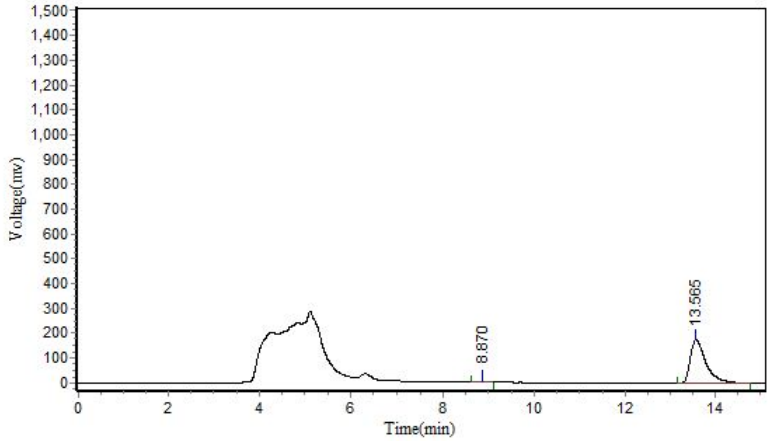
Oil liquid, 45.2 mg, 76% yield, 99% ee. $[\alpha]^{19}_{D}$ = -39.8 (0.25, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.32 (m, 7H), 6.36 (s, 1H), 6.05 (dd, *J* = 8.5, 2.1 Hz, 1H), 5.32 (d, *J* = 10.3 Hz, 1H), 5.06 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.58 (dd, *J* = 98.4, 15.0 Hz, 2H), 3.88 (d, *J* = 10.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 140.7, 135.5, 130.7, 129.2, 128.9, 128.6, 123.3, 109.6, 106.5, 52.7, 52.4. HRMS (ESI) for $C_{14}H_{14}N_2NaO_3S$ $[M+Na]^+$: calcd 313.0617, found 313.0618.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 8.9 min, 13.6 min (major).



Results

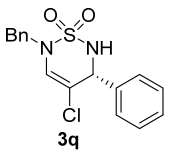
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.568	89575.039	1298799.625	51.5183
2		13.705	55987.918	1222246.875	48.4817
Total			145562.957	2521046.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.870	2039.944	24519.352	0.5911
2		13.565	175071.297	4123502.750	99.4089
Total			177111.241	4148022.102	100.0000

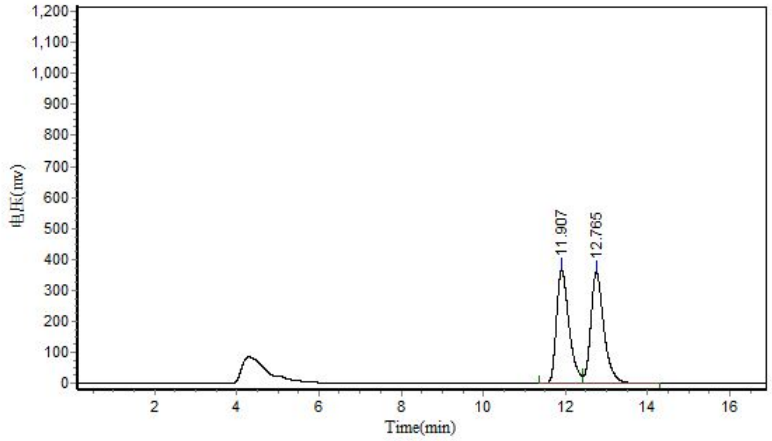
(*R*)-6-benzyl-4-chloro-3-phenyl-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3q)



3q

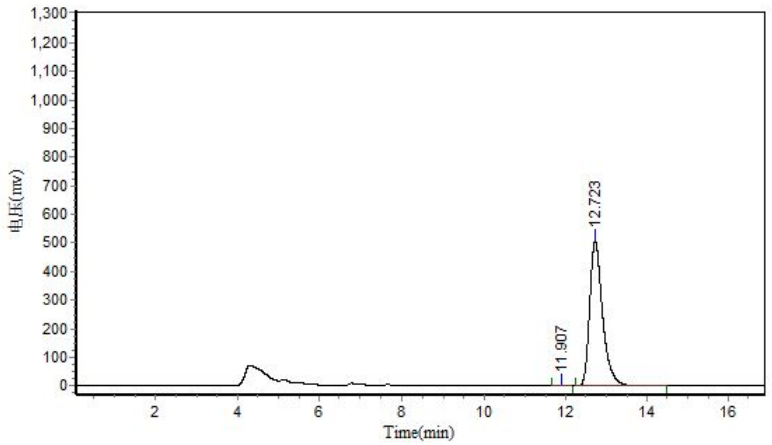
White solid, 63.5 mg, 95% yield, 99% ee. $[\alpha]^{20}_{D}$ = -39.6 (c 0.90, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 - 7.26 (m, 8H), 7.07 - 7.04 (m, 2H), 6.32 (s, 1H), 5.15 (s, 1H), 4.59 (dd, *J* = 129.4, 14.7 Hz, 2H), 4.03 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.6, 134.6, 129.8, 129.5, 129.4, 129.2, 129.1, 128.5, 116.9, 64.3, 53.8. HRMS (ESI) for $C_{16}H_{15}ClN_2NaO_2S$ $[M+Na]^+$: calcd 357.0435, found 357.0442.

HPLC: Chiralcel AD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 80/20; flow =0.7 mL/min; Retention time: 11.9 min, 12.7 min (major).



Results

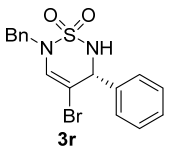
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.907	367755.906	7860545.500	49.3954
2		12.765	358201.250	8052961.500	50.6046
Total			725957.156	15913507.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.907	1998.136	32004.951	0.2878
2		12.723	506555.250	11088934.000	99.7122
Total			508553.386	11120938.951	100.0000

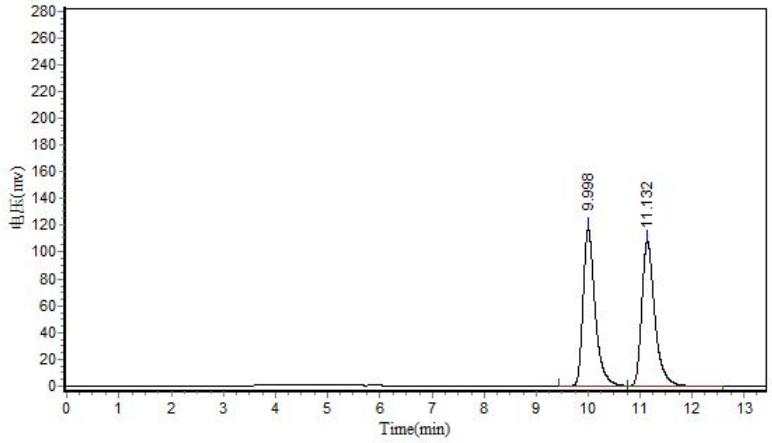
(*R*)-6-benzyl-4-bromo-3-phenyl-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3r)



3r

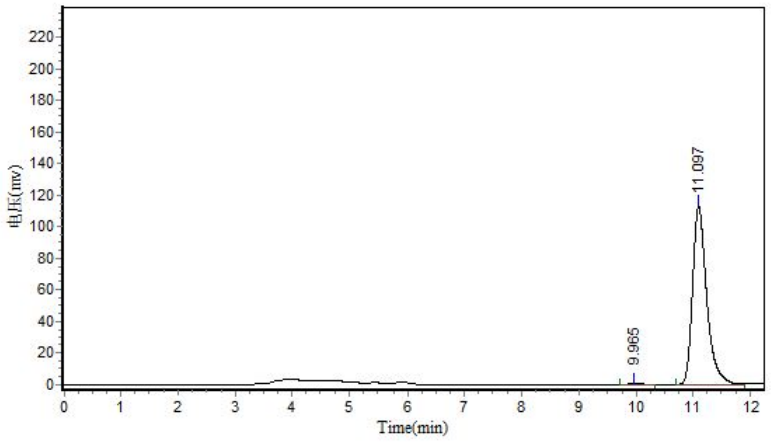
White solid, 59.7 mg, 79% yield, 99% ee. $[\alpha]^{20}_{D}$ = -37.4 (c 0.85, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 - 7.32 (m, 8H), 7.09 - 7.06 (m, 2H), 6.44 (s, 1H), 5.20 (d, *J* = 9.0 Hz, 1H), 4.60 (dd, *J* = 125.4, 14.8 Hz, 2H), 4.12 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.4, 134.7, 131.8, 129.8, 129.5, 129.3, 129.0, 128.5, 105.8, 65.3, 53.5. HRMS (ESI) for $C_{16}H_{15}BrN_2NaO_2S$ $[M+Na]^+$: calcd 400.9930, found 400.9936.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 80/20; flow =0.7 mL/min; Retention time: 10.0 min, 11.1 min (major).



Results

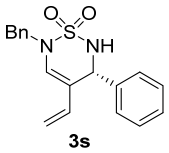
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.998	117332.180	1885400.750	49.9924
2		11.132	108019.406	1885971.625	50.0076
Total			225351.586	3771372.375	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.965	325.027	4894.700	0.2516
2		11.097	112431.328	1940426.375	99.7484
Total			112756.355	1945321.075	100.0000

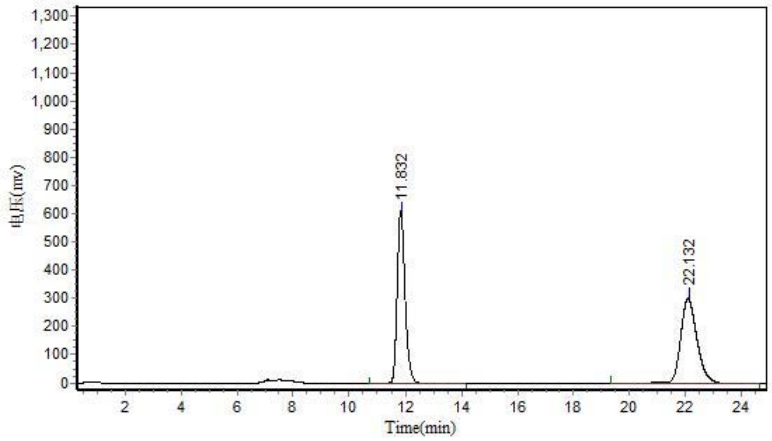
(*R*)-6-benzyl-3-phenyl-4-vinyl-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3s)



3s

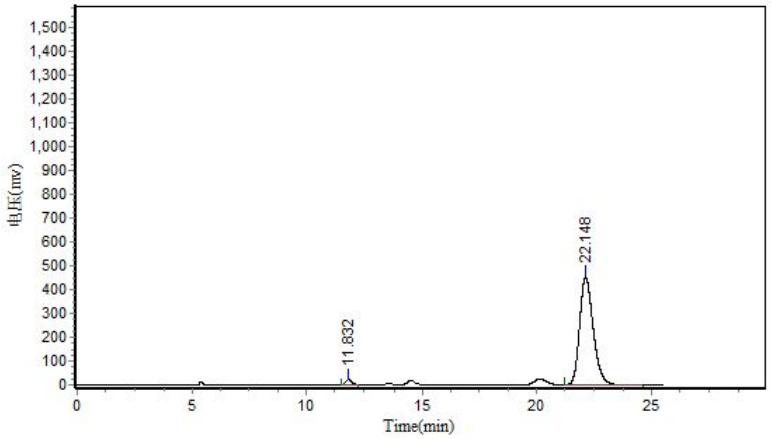
White solid, 35.9 mg, 55% yield, 95% ee. $[\alpha]^{20}_{D}$ = -6.4 (c 0.42, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 - 7.32 (m, 9H), 7.25 - 7.23 (m, 1H), 6.23 (s, 1H), 6.00 (dd, *J* = 17.7, 11.3 Hz, 1H), 5.39 (d, *J* = 8.3 Hz, 1H), 4.78 (s, 1H), 4.62 (dd, *J* = 65.6, 4.0 Hz, 2H), 4.46 (d, *J* = 7.6 Hz, 1H), 4.14 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7, 135.5, 133.3, 132.1, 129.32, 129.28, 129.1, 129.0, 128.7, 128.6, 118.3, 113.7, 61.2, 52.5. HRMS (ESI) for $C_{18}H_{19}N_2O_2S$ $[M+H]^+$: calcd 327.1162, found 327.1170.

HPLC: Chiralcel IC column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 11.8 min, 22.1 min (major).



Results

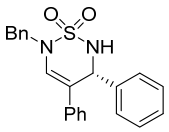
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.832	613105.313	12431924.000	49.4345
2		22.132	302834.563	12716350.000	50.5655
Total			915939.875	25148274.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.832	25394.301	466965.781	2.4286
2		22.148	453456.781	18760680.000	97.5714
Total			478851.082	19227645.781	100.0000

(*R*)-6-benzyl-3,4-diphenyl-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3t)

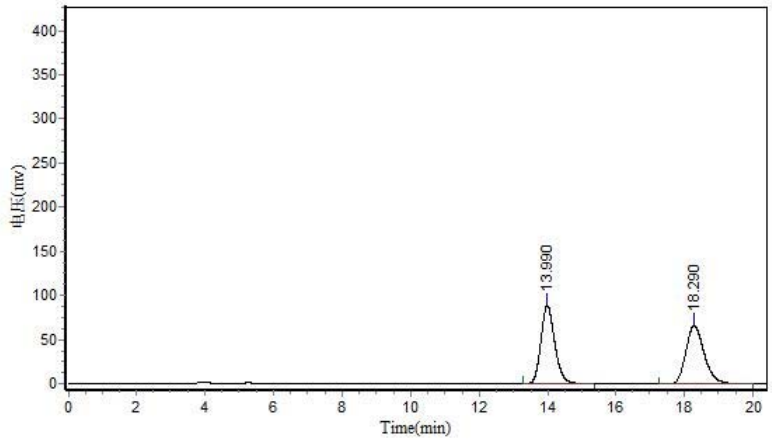


3t

White solid, 69.2 mg, 92% yield, 99% ee. $[\alpha]^{20}_{D}$ = -160.5 (c 0.45, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 - 7.36 (m, 5H), 7.21 - 7.05 (m, 8H), 7.00 - 6.97 (m, 2H), 6.34 (d, *J* = 1.2 Hz, 1H), 5.74 (d, *J* = 8.4 Hz, 1H), 4.67 (dd, *J* = 102.8, 15.0 Hz, 2H), 4.17 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 137.4, 135.5, 129.9, 129.3, 129.2, 129.1, 128.93, 128.87, 128.7, 127.2, 126.4, 120.2, 62.7, 52.7.

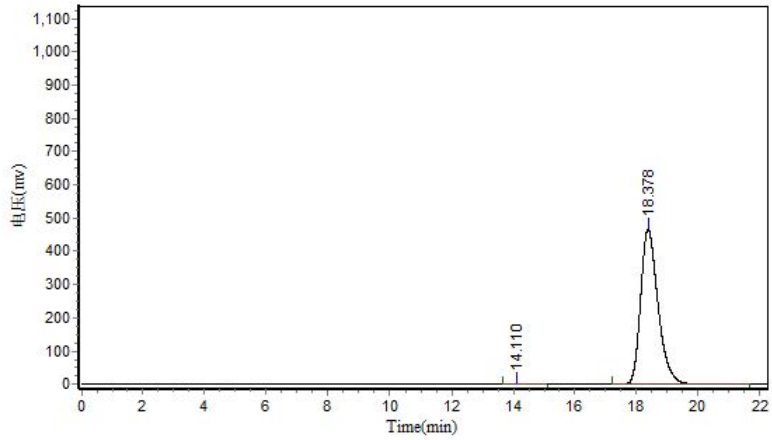
HRMS (ESI) for $C_{22}H_{20}N_2NaO_2S$ $[M+Na]^+$: calcd 399.1138, found 399.1142.

HPLC: Chiralcel IC column (250 mm); detected at 224 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 14.1 min, 18.4 min (major).



Results

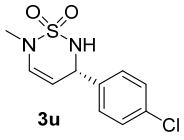
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.990	88374.742	2479551.000	50.2070
2		18.290	66068.406	2459101.500	49.7930
Total			154443.148	4938652.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.110	2703.977	78659.000	0.4272
2		18.378	466852.063	18335080.000	99.5728
Total			469556.040	18413739.000	100.0000

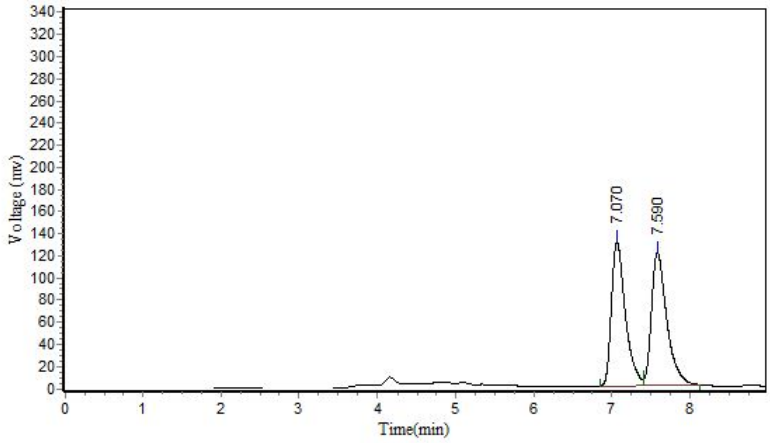
(*S*)-3-(4-chlorophenyl)-6-methyl-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3u)



3u

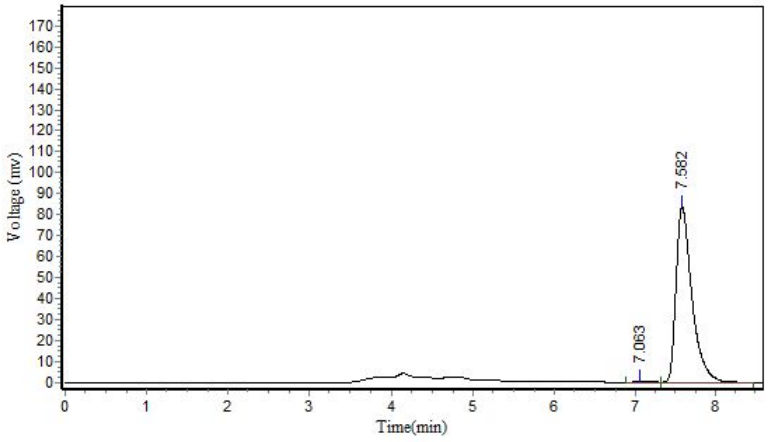
White solid, 35.1 mg, 68% yield, 99% ee. $[\alpha]^{20}_{D}$ = -130.5 (c 1.05, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.30 (m, 4H), 6.09 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.33 (d, *J* = 9.8 Hz, 1H), 5.07 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.13 (d, *J* = 9.8 Hz, 1H), 3.10 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.6, 135.2, 133.7, 129.6, 129.4, 105.7, 59.7, 36.0. HRMS (ESI) for $C_{10}H_{10}ClN_2O_2S$ $[M-H]^-$: calcd 257.0157, found 257.0166.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 7.1 min, 7.6 min (major).



Results

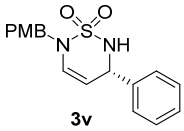
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.070	130222.109	1628372.875	49.8222
2		7.590	120024.328	1639992.625	50.1778
Total			250246.438	3268365.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.063	546.857	6348.032	0.5550
2		7.582	83510.445	1137384.875	99.4450
Total			84057.303	1143732.907	100.0000

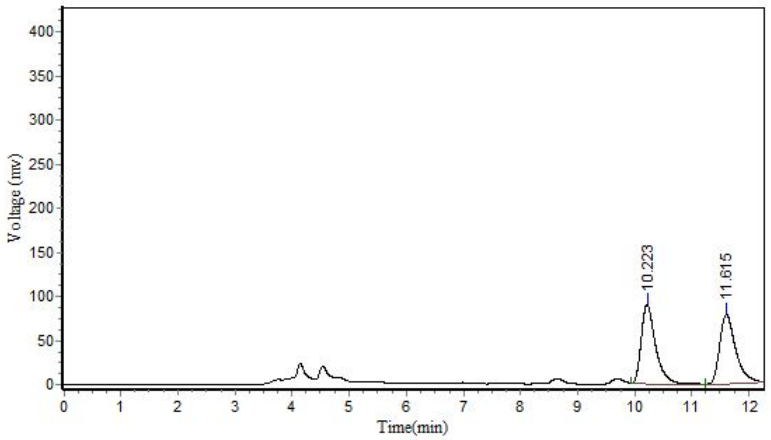
(*S*)-6-(4-methoxybenzyl)-3-phenyl-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (3v)



3v

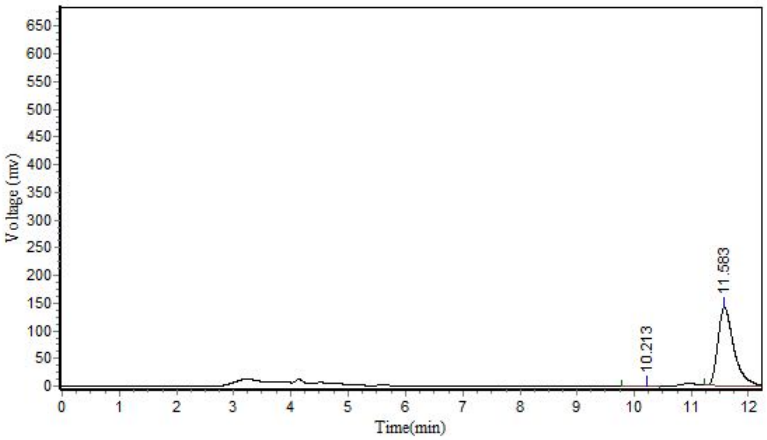
White solid, 64.7 mg, 98% yield, 99% ee. $[\alpha]^{20}_{D}$ = -34.1 (c 1.23, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 - 7.32 (m, 5H), 7.25 (dd, *J* = 6.1, 2.0 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.11 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.33 - 5.30 (m, 1H), 5.11 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.54 (dd, *J* = 131.6, 14.7 Hz, 2H), 3.84 - 3.77 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 138.1, 130.7, 130.6, 129.4, 129.3, 128.0, 127.4, 114.6, 108.2, 60.5, 55.7, 52.2. HRMS (ESI) for $C_{17}H_{19}N_2O_3S$ $[M+H]^+$: calcd 331.1111, found 331.1117.

HPLC: Chiralcel AD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 70/30; flow =0.7 mL/min; Retention time: 10.2 min, 11.6 min (major).



Results

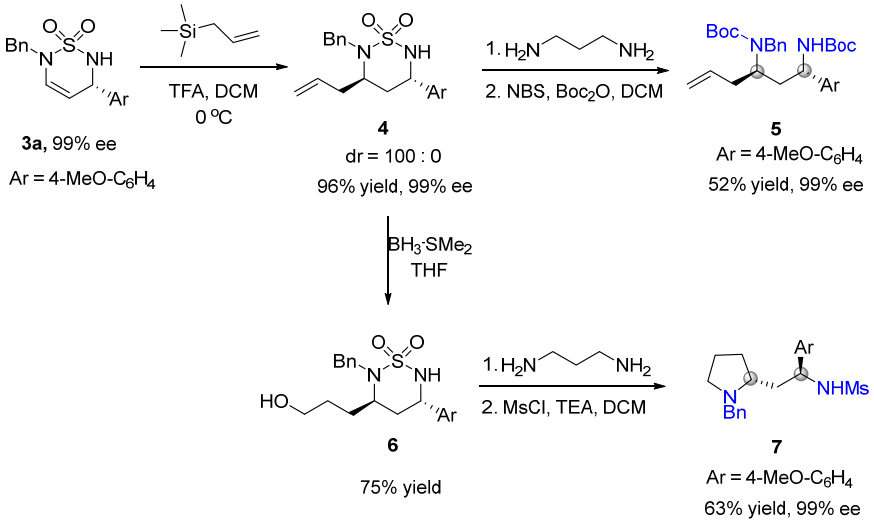
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.223	90088.586	1591037.500	49.9260
2		11.615	79551.281	1595752.125	50.0740
Total			169639.867	3186789.625	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.213	520.599	4044.999	0.1462
2		11.583	141346.484	2761970.750	99.8538
Total			141867.083	2766015.749	100.0000

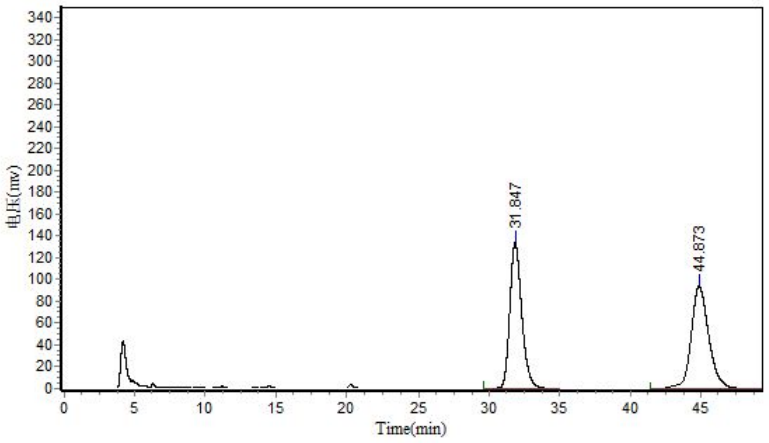
5. Construction of Chiral 1,3-diamines



Synthesis of (3*R*,5*S*)-3-allyl-2-benzyl-5-(4-methoxyphenyl)-1,2,6-thiadiazinane 1,1-dioxide (4): A 10 mL vessel was charged with the 1,2-adduct **3a** (66 mg, 0.20 mmol, 99% ee) in 2 mL DCM, then TFA (90 μL, 1.2 mmol, 6 equiv.) and allyltrimethylsilane (127 μL, 0.8 mmol, 4 equiv.) was added at 0 °C and the reaction stirred at 0 °C for 30 minutes. The reaction was diluted with $NaHCO_3$ (aq.), extracted with DCM, dried on anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by silica gel column chromatography to afford the chiral allyl product **4** as white solid (71.4 mg, 96% yield, dr = 100: 0, 99% ee). $[\alpha]^{19}_D$ = 59.3 (c 0.22, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.23 (m, 7H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.65 - 5.54 (m, 1H), 5.09 - 5.01 (m, 2H), 4.85 (dd, *J* = 13.6, 7.9 Hz, 1H), 4.45 (dd, *J* = 62.9, 14.4 Hz, 2H), 4.12 (d, *J* = 7.0 Hz, 1H), 3.80 (s, 3H), 3.42 - 3.36 (m, 1H), 2.89 - 2.61 (m, 2H), 1.91 - 1.83 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.9, 136.24, 135.5, 131.9, 129.08, 129.05, 128.4, 127.9, 118.3, 114.6, 57.5, 55.7, 55.2, 52.4, 35.4, 31.7.

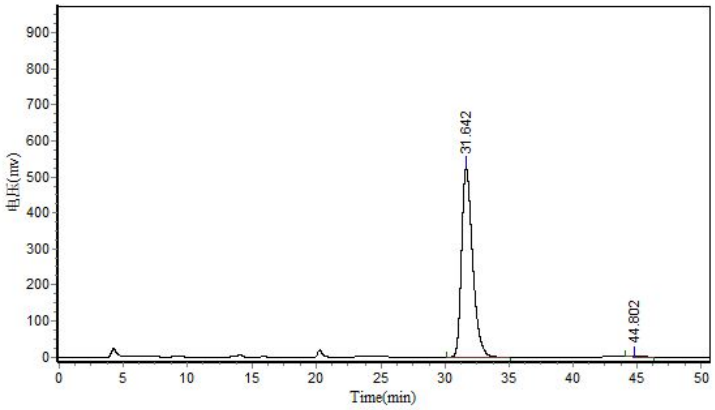
HRMS (ESI) for $C_{20}H_{24}N_2NaO_3S$ $[M+Na]^+$: calcd 395.1400, found 395.1397.

HPLC: Chiralcel IC column (250 mm); detected at 224 nm; hexane/*i*-propanol = 80/20; flow =0.7 mL/min; Retention time: 31.6 min (major), 44.8 min.



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		31.847	133609.953	7847705.000	49.2933
2		44.873	93801.688	8072727.500	50.7067
Total			227411.641	15920432.500	100.0000

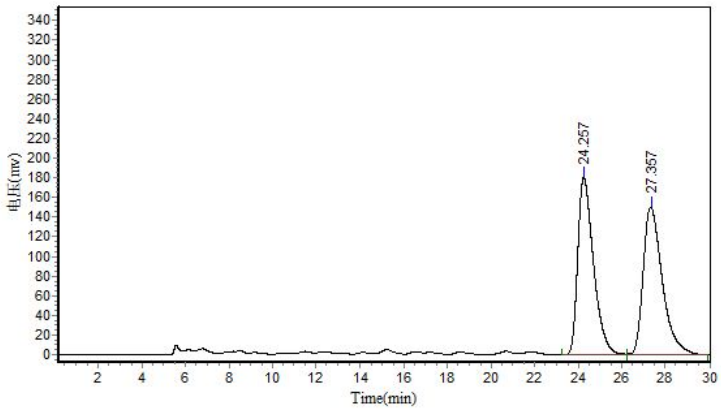


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		31.642	525973.625	31465080.000	99.5695
2		44.802	2219.774	136053.781	0.4305
Total			528193.399	31601133.781	100.0000

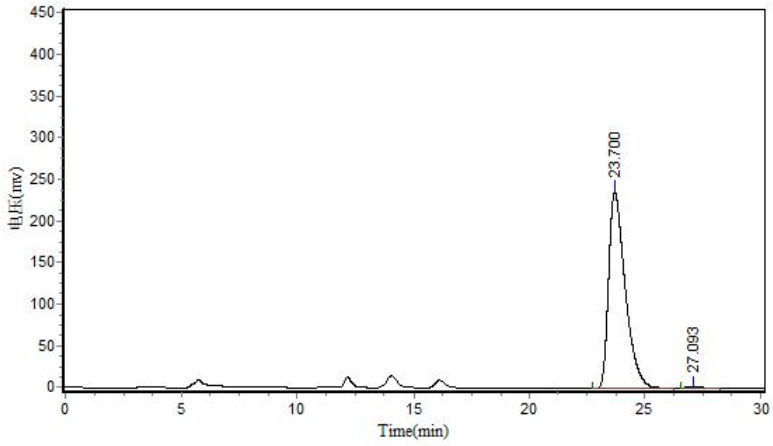
***Tert*-butyl-benzyl((1*S*,3*R*)-1-((*tert*-butoxycarbonyl)amino)-1-(4-methoxyphenyl)hex-5-en-3-yl)carbamate (5):** A N_2 protected solution of **4** (37.2 mg, 0.1 mmol) in 1,3-propanediamine solvent was heated to reflux for 3 hours. The reaction was naturally cooled to room temperature, extracted with DCM, washed with water, dried on anhydrous Na_2SO_4 and removed the solvent under vacuum. The residue was dissolved in 2 mL DCM, NBS (2 mg, 0.01 mmol, 0.1 equiv.) and Boc_2O (44 mg, 0.2 mmol, 2 equiv.) was added and the reaction was stirred for 0.5 hour and purified by silica gel column chromatography to afford product **5** as colorless solid (26.5 mg, 52% yield, 99% ee). $[\alpha]^{19}_D$ = -48.1 (c 0.12, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.27 (m, 5H), 7.09 - 6.80 (m, 4H), 5.54 (d, *J* = 7.1 Hz, 1H), 4.94 (d, *J* = 12.7 Hz, 2H), 4.67 - 4.31 (m, 3H), 4.15 - 4.11 (m, 1H), 3.97 - 3.80 (m, 4H), 2.26 (dd, *J* = 25.1, 17.8 Hz, 2H), 2.07 - 1.86 (m, 2H), 1.50 - 1.43 (m, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.9, 139.8, 135.6, 128.7, 128.5, 127.9, 127.5, 127.3, 117.5, 114.2, 80.3, 79.7, 55.6, 52.0, 38.4, 30.0, 28.8, 28.7, 28.4. HRMS (ESI) for $C_{30}H_{42}N_2NaO_5$ $[M+Na]^+$: calcd 533.2986, found 533.2989.

HPLC: Chiralcel AD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 95/5; flow =0.5 mL/min; Retention time: 23.7 min (major), 27.1 min.



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		24.257	180213.422	9075610.000	49.5399
2		27.357	150794.688	9244190.000	50.4601
Total			331008.109	18319800.000	100.0000



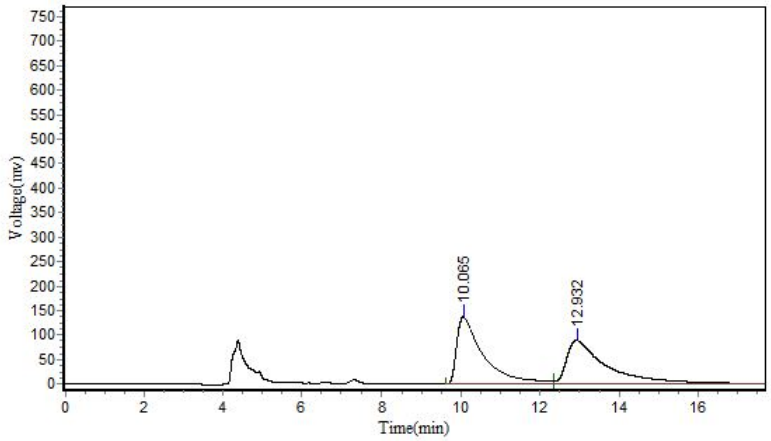
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.700	235937.969	11774225.000	99.5265
2		27.093	1491.029	56020.602	0.4735
Total			237428.997	11830245.602	100.0000

(3*R*,5*S*)-2-benzyl-3-(3-hydroxypropyl)-5-(4-methoxyphenyl)-1,2,6-thiadiazinane 1,1-dioxide (6): Compound **5** (110 mg, 0.3 mmol) was dissolved in 4 mL THF, borane-methyl sulfide complex (54 μL, 0.9 mmol, 3 equiv., 94%) was added at 0 °C and the reaction was stirred at room temperature for 3 hours. After reaction completion, diluted the reaction with NaOH (2M aq.) and H_2O_2 (30% aq.), extracted the reaction with EtOAc and dried on anhydrous Na_2SO_4, removed the solvent under vacuum and the residue was purified by silica gel column chromatography to afford alcohol **6** as white solid (86.5 mg, 75% yield). $[\alpha]^{19}_D$ = 47.2 (c 0.26, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 - 7.36 (m, 5H), 7.30 - 7.27 (m, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 4.87 - 4.84 (m, 1H), 4.47 (dd, *J* = 125.2, 14.1 Hz, 2H), 4.17 (t, *J* = 6.1 Hz, 1H), 3.85 (s, 3H), 3.58 - 3.53 (m, 2H), 3.44 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.44 - 2.33 (m, 1H), 2.08 - 1.99 (m, 1H), 1.74 - 1.60 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 136.5, 132.2, 129.4, 129.1, 128.5, 128.0, 114.6, 62.7, 58.3, 55.73, 55.69, 54.1, 32.1, 30.1, 28.5. HRMS (ESI) for $C_{20}H_{26}N_2NaO_4S$ $[M+Na]^+$: calcd 413.1505, found 413.1500.

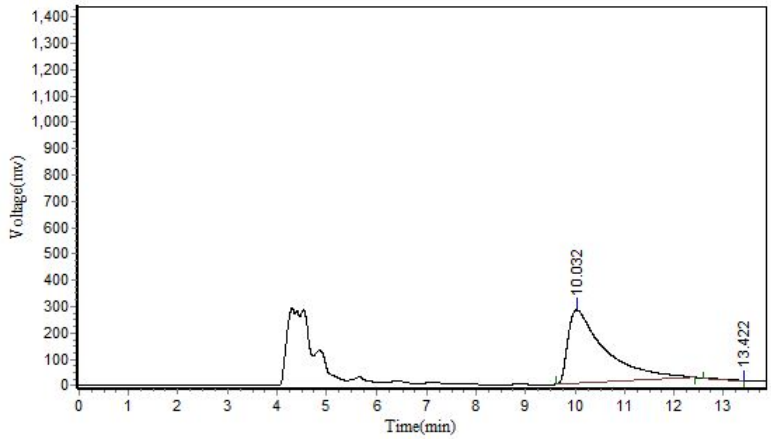
***N*-((*S*)-2-((*R*)-1-benzylpyrrolidin-2-yl)-1-(4-methoxyphenyl)ethyl)methanesulfonamide (7):** The lcohol intermediate **6** (39 mg, 0.1 mmol) was refluxed in 0.3 mL 1,3-propanediamine under N_2 atmosphere for 3 hours. Cooled the mixture to room temperature and extracted with DCM, washed with water, dried on anhydrous Na_2SO_4 and removed the solvent under vacuum. The ring-opening residue was dissolved in 1 mL DCM under N_2 atmosphere, TEA (28 μL, 0.2 mmol, 2 equiv.) and MsCl (16 μL, 0.2 mmol, 2 equiv.) were added at 0 °C. The mixture was stirred at room temperature for 3 h and diluted with water, extracted with DCM, washed with brine and dried on anhydrous Na_2SO_4. The solvent was removed and the residue was purified by silica gel column chromatography to afford the pyrrolidine product **7** as colorless solid (24.4 mg, 63% yield, 99% ee). $[\alpha]^{17}_D$ = -28.1 (c 0.44, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 9.7, 3.3 Hz, 4H), 7.30 - 7.24 (m, 3H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.75 (dd, *J* = 10.8, 4.0 Hz, 1H), 4.12 (d, *J* = 13.1 Hz, 1H), 3.80 (s, 3H), 3.33 (d, *J* = 13.1 Hz, 1H), 3.13 - 3.09 (m, 1H), 2.89 - 2.85 (m, 1H), 2.39 (s, 3H), 2.25 - 2.19 (m, 1H), 2.03 - 1.96 (m, 4H), 1.80 - 1.74 (m, 1H), 1.67 (dt, *J* = 14.9, 3.9 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 138.8, 134.3, 129.2, 128.8, 128.7, 127.6, 114.4, 63.4, 59.5, 55.6, 55.5, 54.3, 42.7, 36.6, 28.3, 23.7. HRMS (ESI) for $C_{21}H_{29}N_2O_3S$ $[M+H]^+$: calcd 389.1893, found 389.1885.

HPLC: Chiralcel OZ-H column (250 mm); detected at 210 nm; hexane/*i*-propanol = 60/40; flow =0.7 mL/min; Retention time: 10.0 min (major), 13.4 min.



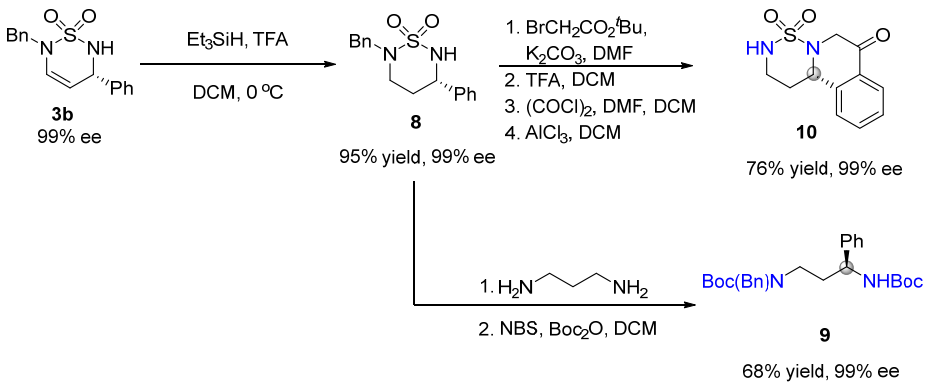
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.065	137601.672	6652506.500	49.0658
2		12.932	89661.984	6905818.500	50.9342
Total			227263.656	13558325.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.032	278574.063	14537189.000	99.9626
2		13.422	18.466	5439.146	0.0374
Total			278592.529	14542628.146	100.0000



3b
99% ee

8
95% yield, 99% ee

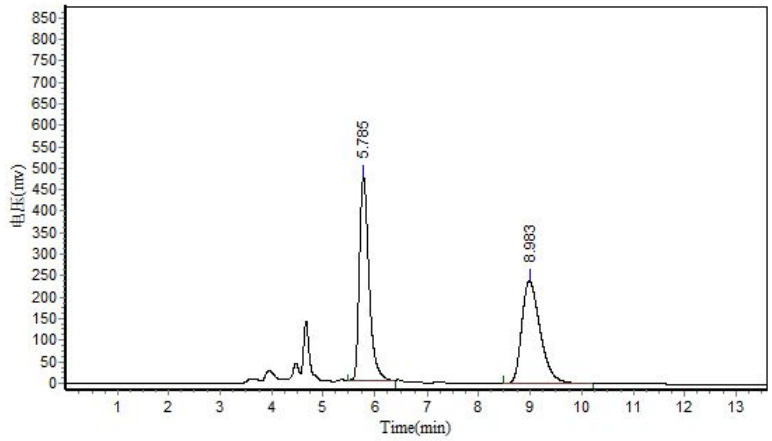
10
76% yield, 99% ee

9
68% yield, 99% ee

(*S*)-2-benzyl-5-phenyl-1,2,6-thiadiazinane 1,1-dioxide (8): A 10 mL vessel was charged with the **3b** (60 mg, 0.20 mmol, 99% ee) in 2 mL DCM, then TFA (90 μL, 1.2 mmol, 6 equiv.) and triethylsilane (127 μL, 0.8 mmol, 4 equiv.) was added at 0 °C and the reaction stirred for another 30 minutes. The reaction was diluted with $NaHCO_3$ (aq.), extracted with DCM, dried on anhydrous Na_2SO_4. The solvent was removed and the residue was purified by silica gel column chromatography to afford product **8** as white solid (57.4 mg, 95% yield). $[\alpha]^{19}_D$ = 30.8 (c 0.29, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.32 (m, 10H), 4.80 - 4.76 (m, 1H), 4.56 - 4.11 (m, 3H), 3.52 (td, *J* = 13.2, 2.7 Hz, 1H), 3.21 (ddd, *J* = 13.4, 4.2, 2.3 Hz, 1H), 2.04 - 1.93 (m, 1H), 1.85 (dd, *J* = 14.1, 2.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.5, 135.7, 129.3, 129.2, 129.1, 128.9, 128.4, 126.6, 60.0, 52.2, 47.8, 29.6. HRMS (ESI) for $C_{16}H_{18}N_2NaO_2S$ $[M+Na]^+$: calcd 325.0981, found 325.0990.

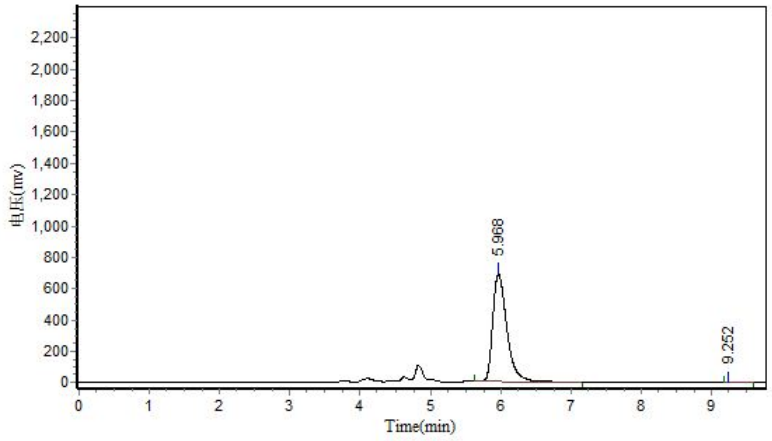
***Tert*-butyl (*S*)-benzyl(3-((*tert*-butoxycarbonyl)amino)-3-phenylpropyl)carbamate (9):** The reaction procedure was the same as the synthesis of product **5**. The reaction was purified by silica gel column chromatography to afford the chiral 1,3-diamine product **9** as colorless solid (49.5 mg, 68% yield, 99% ee). $[\alpha]^{19}_D$ = 0.2 (c 0.62, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 - 7.16 (m, 10H), 5.08 - 4.34 (m, 4H), 3.34 - 3.31 (m, 2H), 2.04 - 1.95 (m, 2H), 1.45 - 1.40 (s, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.6, 138.7, 128.9, 128.8, 128.2, 127.6, 126.5, 80.2, 79.8, 53.1, 50.5, 44.5, 35.6, 28.8, 28.7. HRMS (ESI) for $C_{26}H_{36}N_2NaO_4$ $[M+Na]^+$: calcd 463.2567, found 463.2579.

HPLC: Chiralcel OD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 90/10; flow =0.7 mL/min; Retention time: 6.0 min (major), 9.3 min.



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.785	472033.969	6103729.000	50.6404
2		8.983	238680.938	5949355.000	49.3596
Total			710714.906	12053084.000	100.0000

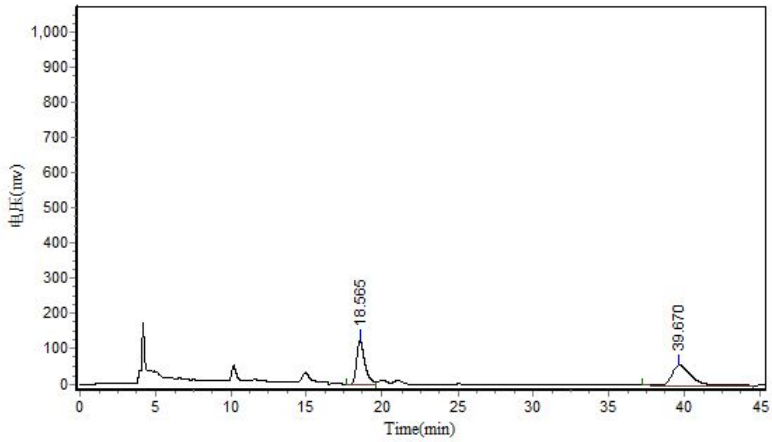


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.968	684285.688	9641137.000	99.8251
2		9.252	1403.485	16891.992	0.1749
Total			685689.172	9658028.992	100.0000

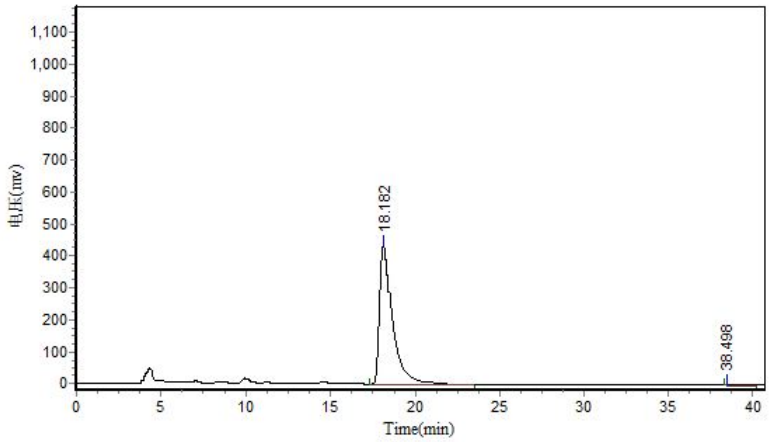
(*S*)-1,2,3,11b-tetrahydro-[1,2,6]thiadiazino[3,2-*a*]isoquinolin-7(6*H*)-one 4,4-dioxide (10): To a solution of product **8** (60 mg, 0.2 mmol) in 2 mL dry DMF was added K_2CO_3 (41.5 mg, 0.3 mmol, 1.5 equiv.) and *tert*-butyl bromoacetate (59 μL, 0.4 mmol, 2 equiv.) and the mixture was stirred at 60 °C for 2 hours. The reaction was diluted with water and extracted with EtOAc, washed with brine and dried on anhydrous Na_2SO_4. The solvent was removed and the residue was dissolved in 2 mL DCM, 0.4 mL TFA was added and the reaction was stirred for 3 hours. After reaction completion, diluted with $NaHCO_3$ (aq.), extracted with DCM, dried on anhydrous Na_2SO_4. The solvent was removed and the residue was dissolved in 2 mL dry DCM, a drop dry DMF was added, followed with oxalyl chloride (82 μL, 0.6 mmol, 3 equiv.) at 0 °C. The reaction was stirred at room temperature for 0.5 hour. Then the solvent was removed and the residue was dissolved in 2 mL dry DCM, $AlCl_3$ (54 mg, 0.4 mmol, 2 equiv.) was added and the reaction stirred at room temperature for 3 hours and purified by silica gel column chromatography to afford the cyclic product **10** as yellow solid (38.2 mg, 76% yield for 4 steps, 99% ee). $[\alpha]^{19}_D$ = 30.6 (c 0.15, $CHCl_3$). ^{1}H NMR (400 MHz, DMSO) δ 7.95 (d, *J* = 7.7 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.28 (s, 1H), 5.20 - 5.17 (m, 1H), 4.00 (dd, *J* = 107.9, 17.0 Hz, 2H), 3.54 (t, *J* = 12.7 Hz, 1H), 3.36 - 3.33 (m, 1H), 1.88 (qd, *J* = 12.9, 4.6 Hz, 1H), 1.66 (d, *J* = 14.1 Hz, 1H). ^{13}C NMR (125 MHz, DMSO) δ 190.9, 143.3, 134.8, 128.5, 128.1, 127.1, 126.1, 58.0, 50.2, 43.2, 24.0. HRMS (ESI) for $C_{11}H_{12}N_2NaO_3S$ $[M+Na]^+$: calcd 275.0461, found 275.0464.

HPLC: Chiralcel IC column (250 mm); detected at 224 nm; hexane/*i*-propanol = 60/40; flow =0.7 L/min; Retention time: 18.2 min (major), 38.5 min.



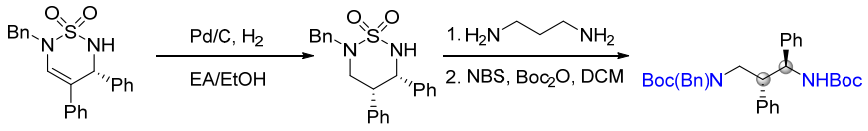
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.565	125564.672	4808399.500	49.1619
2		39.670	58581.031	4972352.000	50.8381
Total			184145.703	9780751.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.182	434232.594	22352638.000	99.8307
2		38.498	432.802	37918.398	0.1693
Total			434665.396	22390556.398	100.0000



3t 99% ee

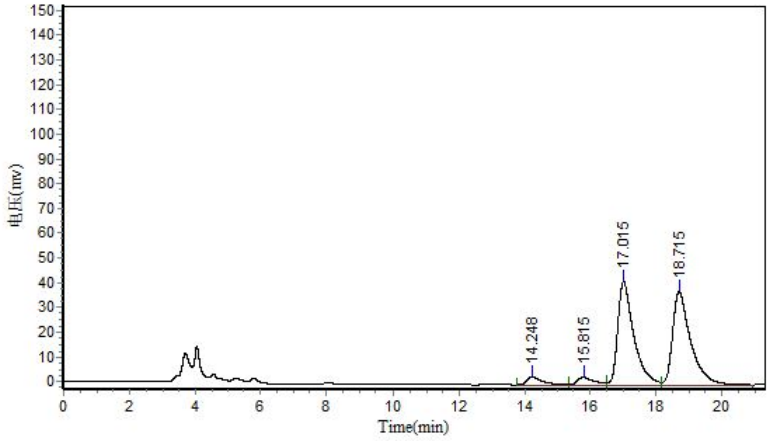
11 dr = 98:2, 99% ee

12 64% yield, 99% ee

(4*R*,5*S*)-2-benzyl-4,5-diphenyl-1,2,6-thiadiazinane 1,1-dioxide (11): To a solution of 1,2-adduct **3t** (20 mg, mmol) in 2 mL EA and 2 mL EtOH was added Pd/C (palladium 10% on Carbon)(10 mol%, 2 mg) under H_2 atmosphere. And the reaction was stirred at 40 °C for 6 h. The mixture was filtered and the solvent was removed, the residue was purified by silica gel column chromatography to afford the product **11** as white solid (82% yield, 16.4 mg, dr = 98:2, 99% ee). $[\alpha]^{17}_D$ = -27.7 (c 0.39, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 6.99 (m, 13H), 6.77 (dd, *J* = 6.5, 2.5 Hz, 2H), 5.35 (dd, *J* = 12.1, 3.3

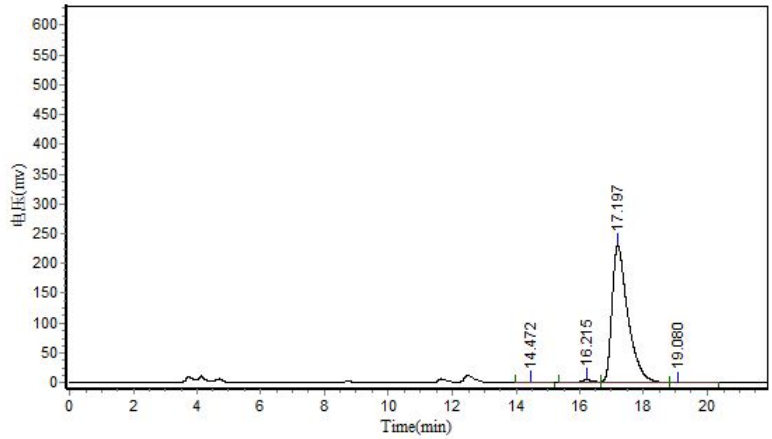
Hz, 1H), 4.89 (t, *J* = 12.8 Hz, 2H), 3.77 (d, *J* = 13.6 Hz, 1H), 3.65 (dd, *J* = 12.4, 3.9 Hz, 1H), 3.40 (dd, *J* = 12.4, 1.6 Hz, 1H), 3.15 - 3.14 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.3, 137.0, 134.7, 130.0, 129.9, 129.7, 128.9, 128.6, 128.5, 128.4, 128.0, 127.7, 126.2, 62.6, 53.9, 52.7, 45.0. HRMS (ESI) for $C_{22}H_{22}N_2NaO_2S$ $[M+Na]^+$: calcd 401.1294, found 401.1295.

HPLC: Chiralcel AD-3 column (250 mm); detected at 224 nm; hexane/*i*-propanol = 80/20; flow =0.7 mL/min; Retention time: 14.5 min, 16.2 min, 17.2 min (major), 19.1 min.



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.248	3436.578	110234.172	3.5594
2		15.815	3059.270	109137.156	3.5240
3		17.015	41603.355	1422392.375	45.9288
4		18.715	37605.723	1455189.375	46.9878
Total			85704.926	3096953.078	100.0000



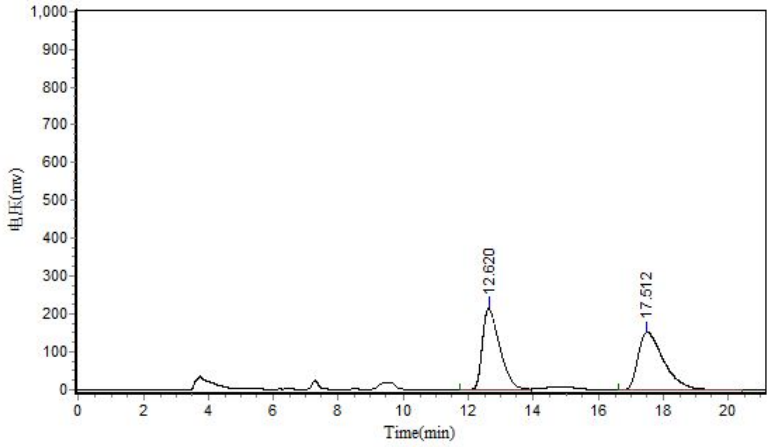
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.472	574.718	18740.299	0.2271
2		16.215	4678.342	144585.188	1.7518
3		17.197	230585.063	8040162.000	97.4153
4		19.080	1142.977	49998.285	0.6058
Total			236981.099	8253485.771	100.0000

***Tert*-butyl benzyl((2*R*,3*S*)-3-((*tert*-butoxycarbonyl)amino)-2,3-diphenylpropyl)carbamate (12):** The reaction procedure was the same as the synthesis of product **5**. The reaction was purified by silica gel column chromatography to afford the chiral 1,3-diamine product **12** as colorless solid (14.3 mg, 64% yield, 99% ee). $[\alpha]^{19}_D$ = 18.8 (c 0.33, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 - 7.23 (m, 10H),

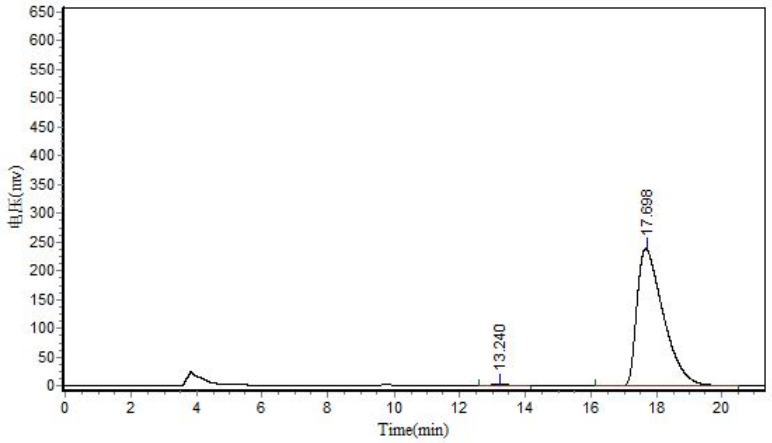
7.10 - 7.00 (m, 5H), 4.96 - 4.69 (m, 2H), 4.25 - 3.76 (m, 2H), 3.52 - 3.27 (m, 3H), 1.37 (s, 9H), 1.27 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0, 155.4, 142.1, 138.4, 129.3, 128.8, 128.2, 127.64, 127.58, 127.53, 127.4, 127.1, 80.1, 79.9, 56.8, 51.4, 50.3, 49.4, 28.7, 28.6. HRMS (ESI) for $C_{32}H_{40}N_2NaO_4$ $[M+Na]^+$: calcd 539.2880, found 539.2894.

HPLC: Chiralcel AD-H column (250 mm); detected at 224 nm; hexane/*i*-propanol = 95/5; flow =0.7 mL/min; Retention time: 13.2 min, 17.7 min (major).



Results

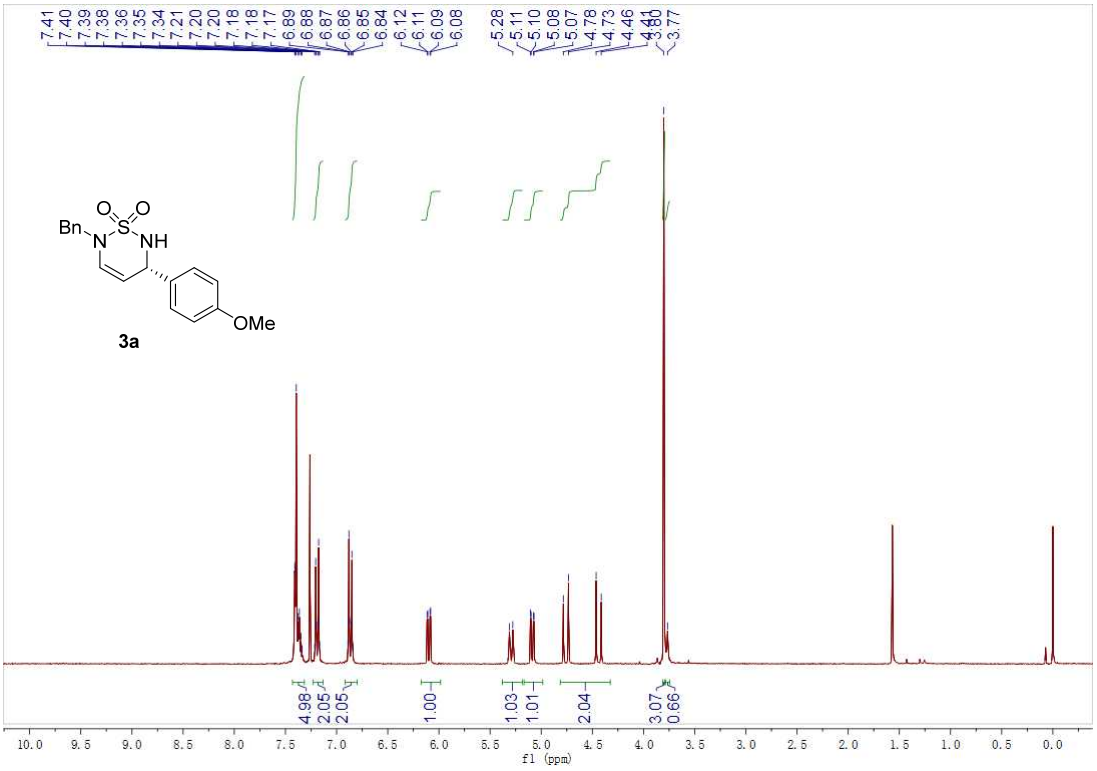
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.620	214189.031	8027909.500	49.0673
2		17.512	151688.422	8333095.500	50.9327
Total			365877.453	16361005.000	100.0000

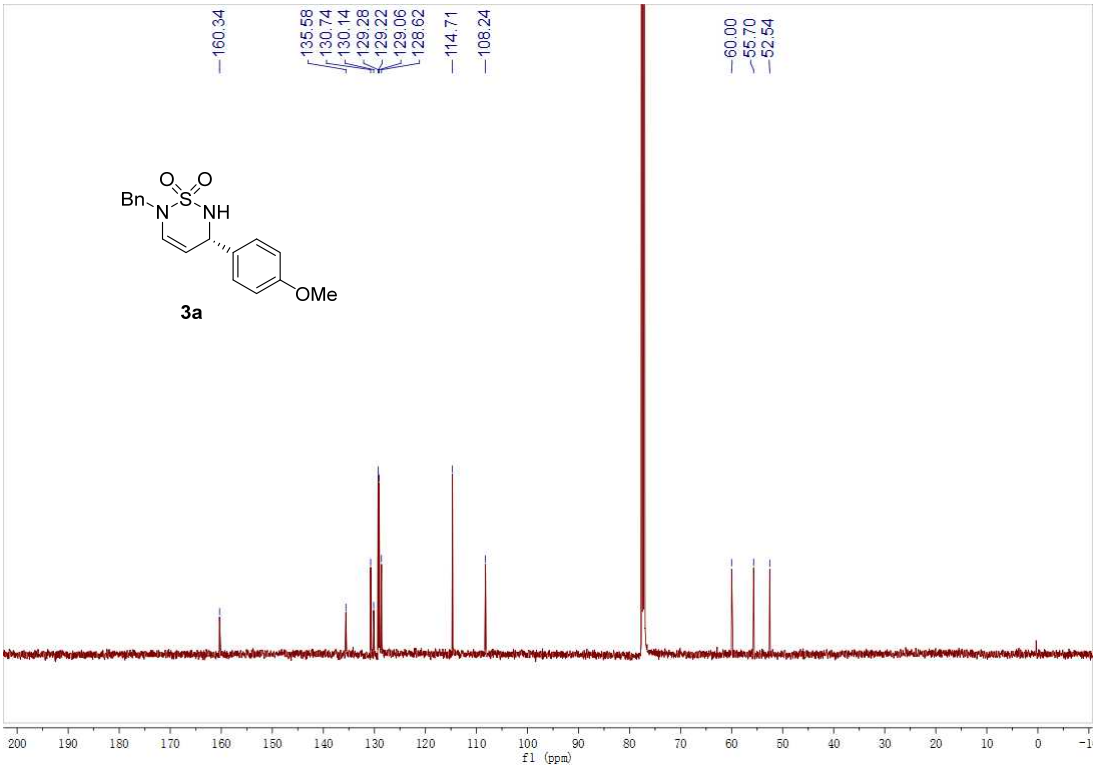


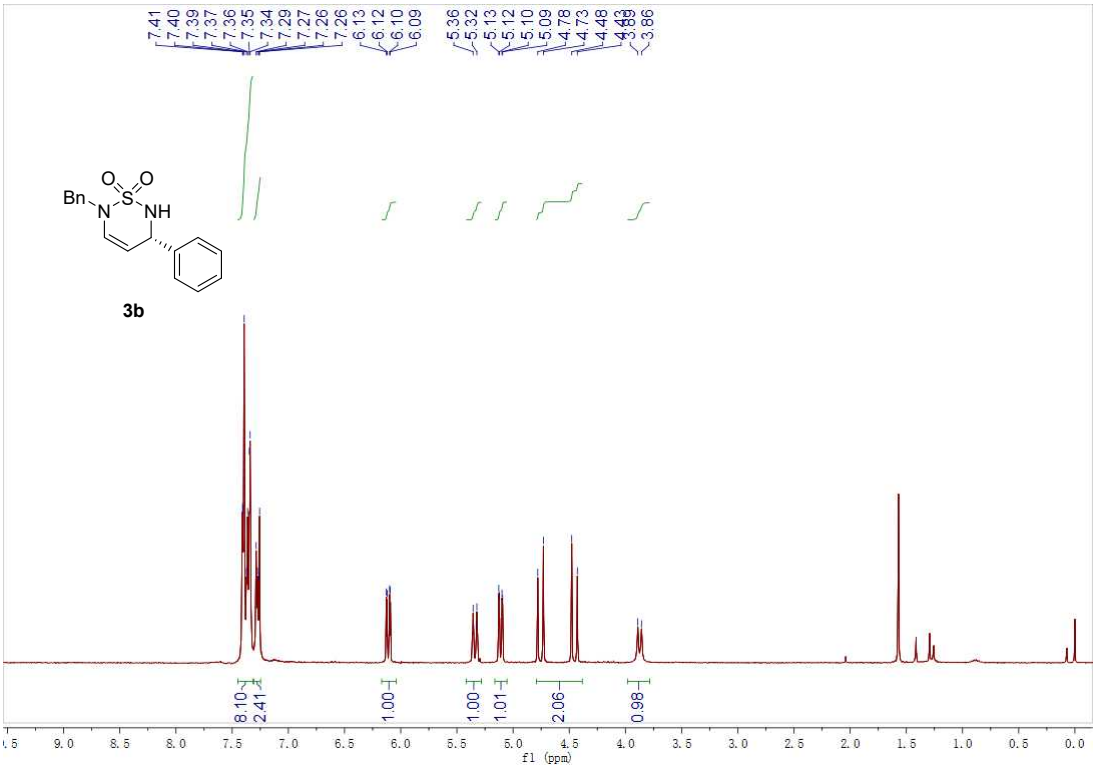
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.240	2481.470	87683.328	0.6525
2		17.698	238258.750	13349384.000	99.3475
Total			240740.220	13437067.328	100.0000

6. Copies of ^{1}H NMR and ^{13}C NMR spectra



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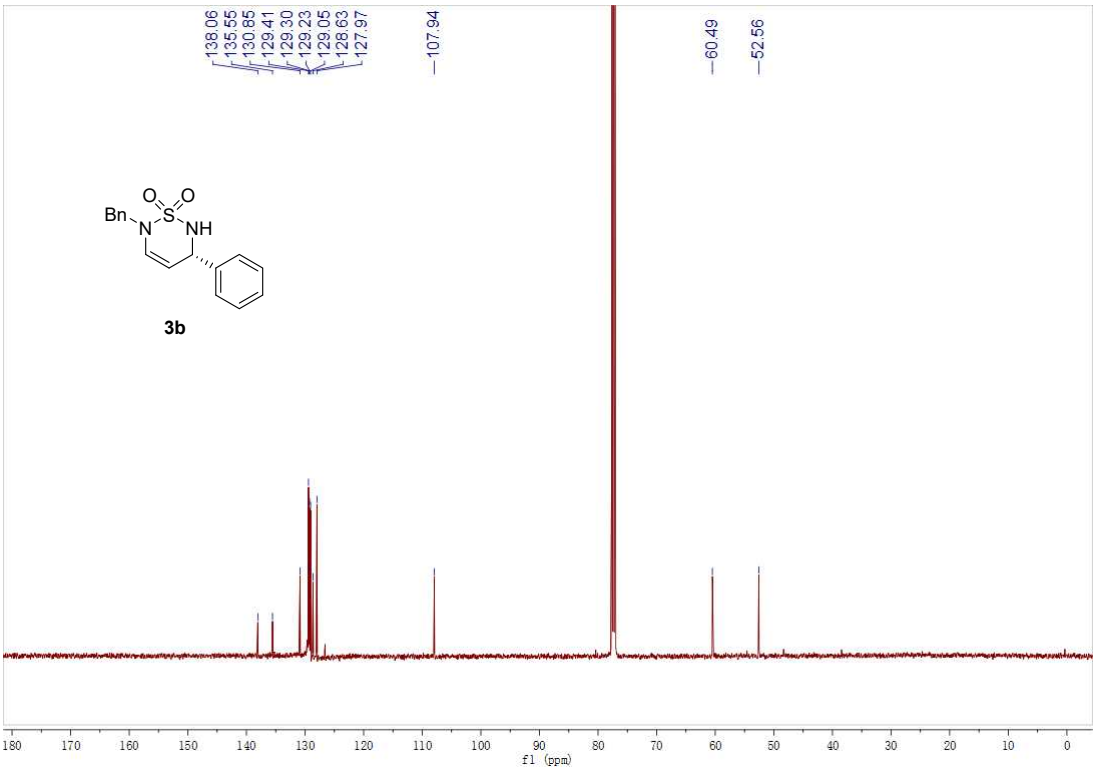
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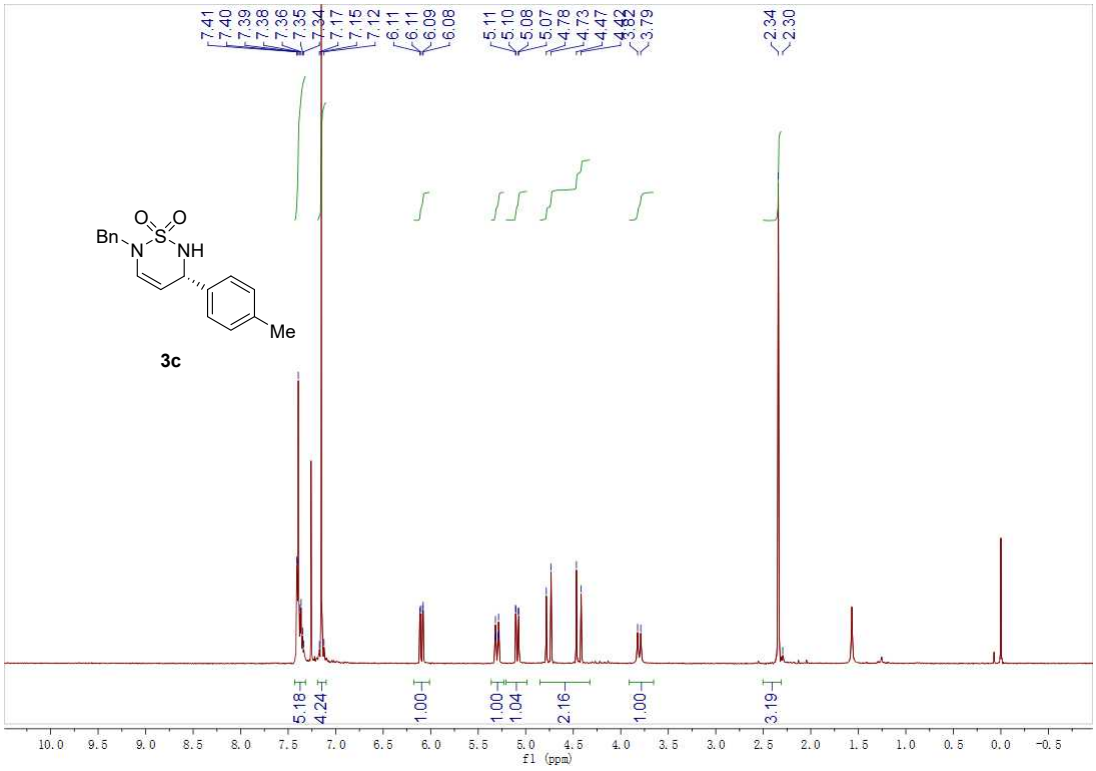
3b
f1 (ppm)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5.10
5.08
5.07
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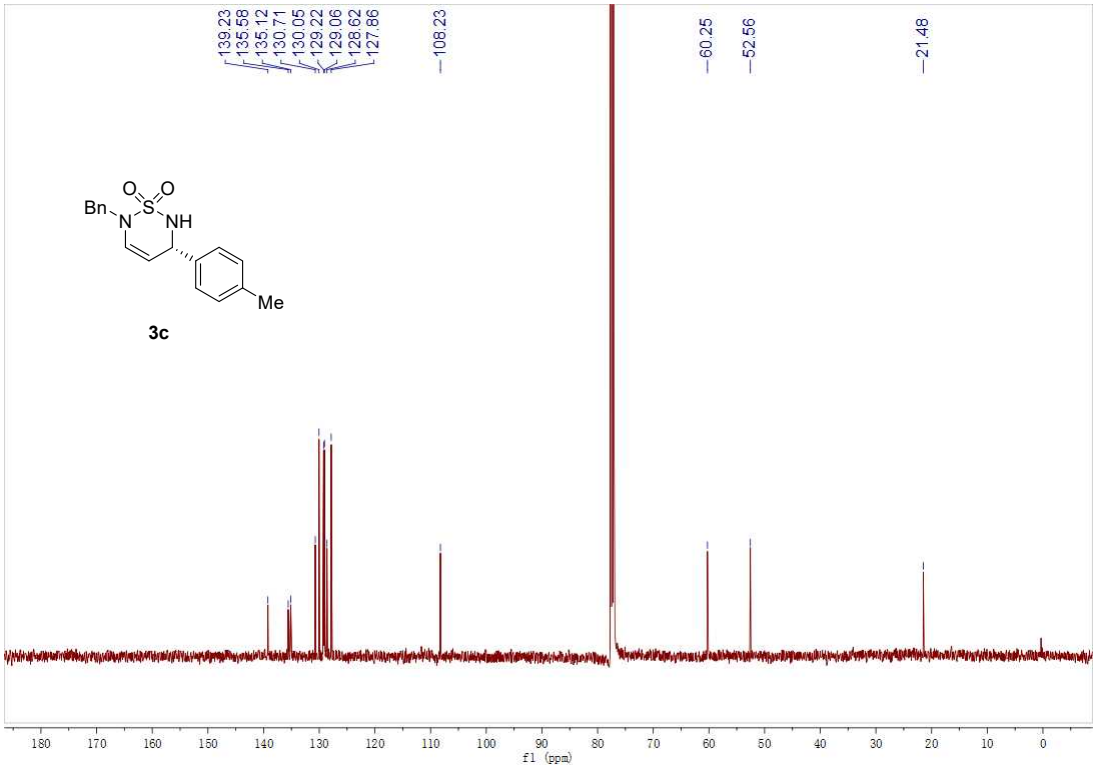
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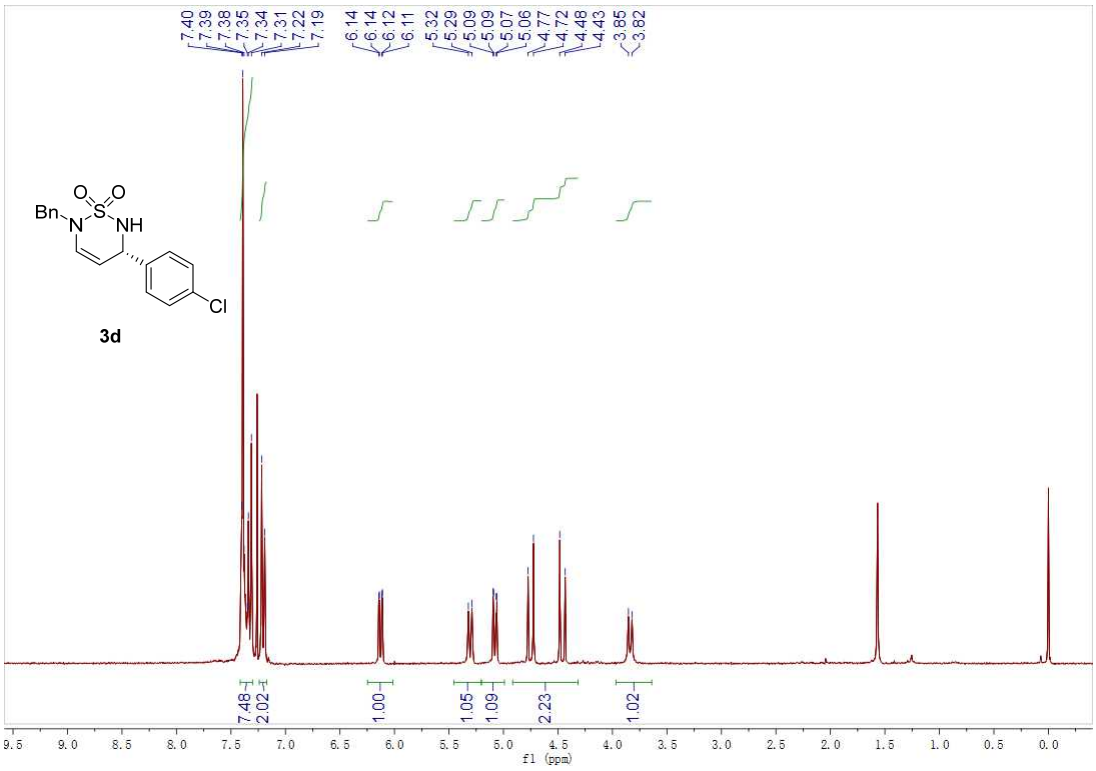
Me
3c
f1 (ppm)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5.07
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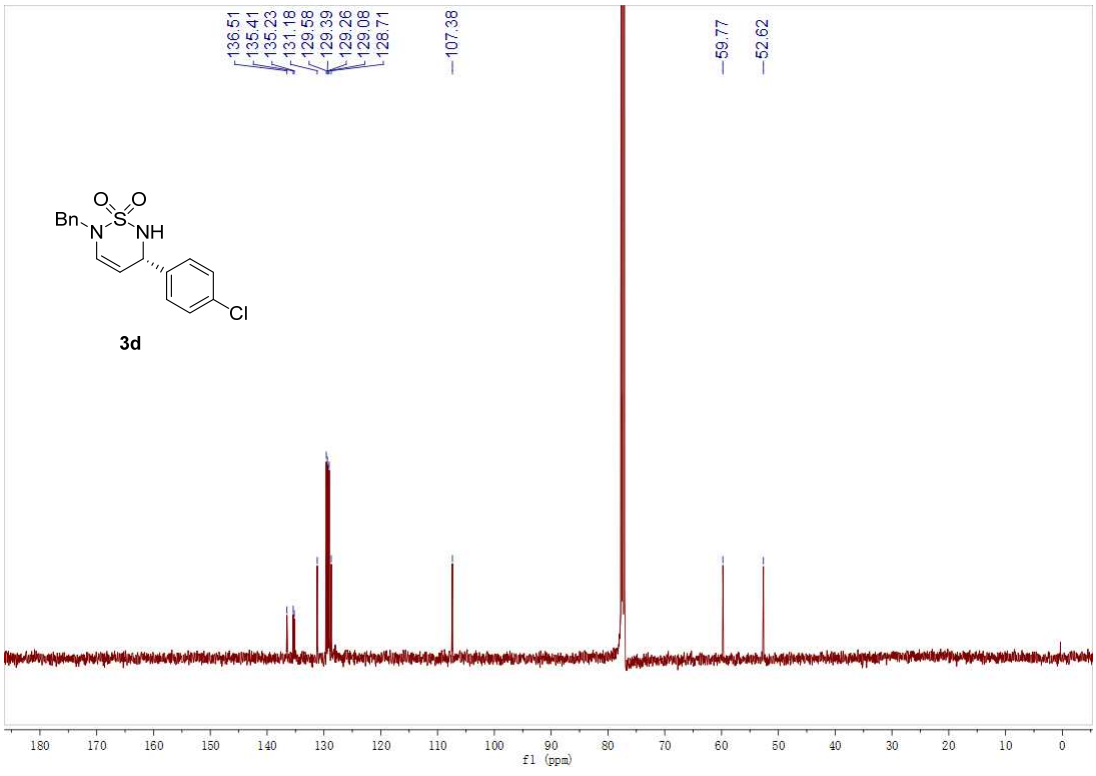
f1 (ppm)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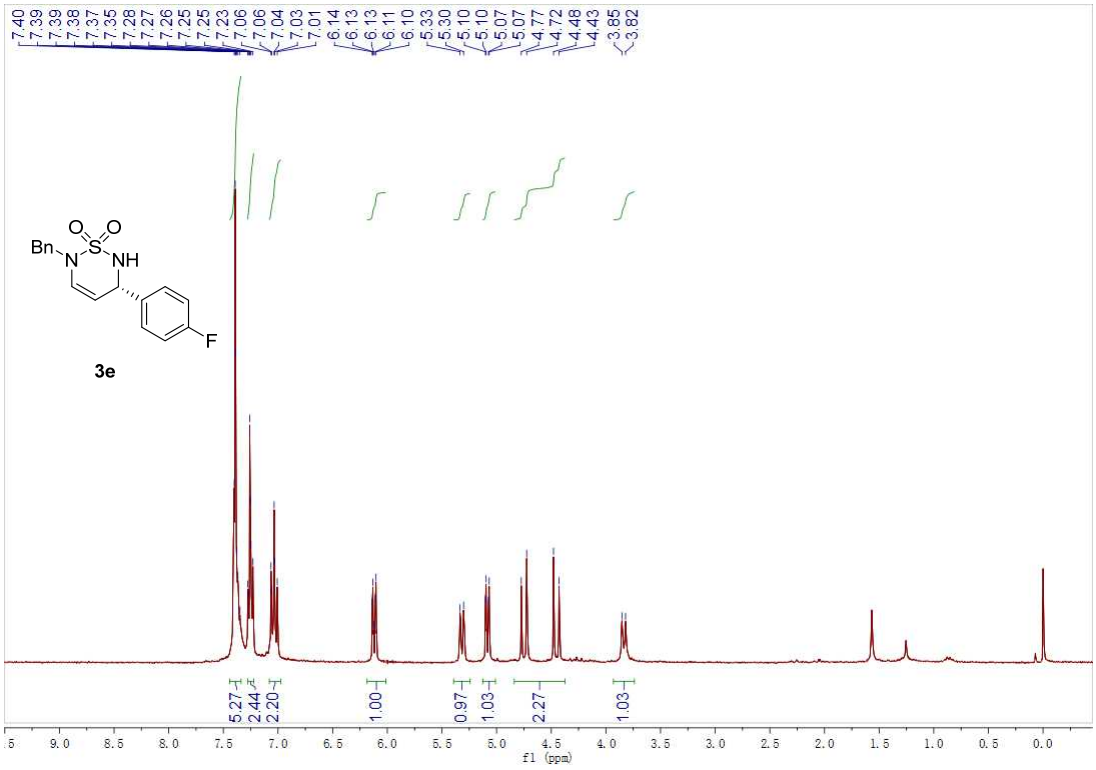
3d
f1 (ppm)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7.06
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7.03
7.01
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6.11
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5.30
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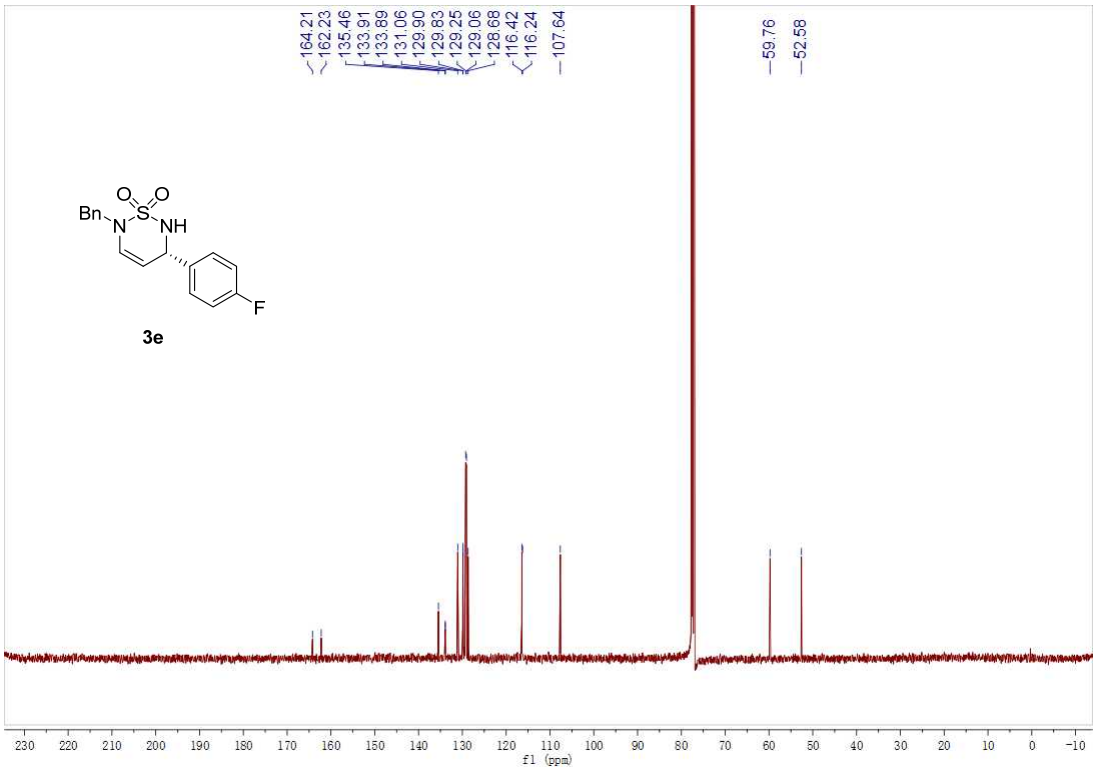
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O
O
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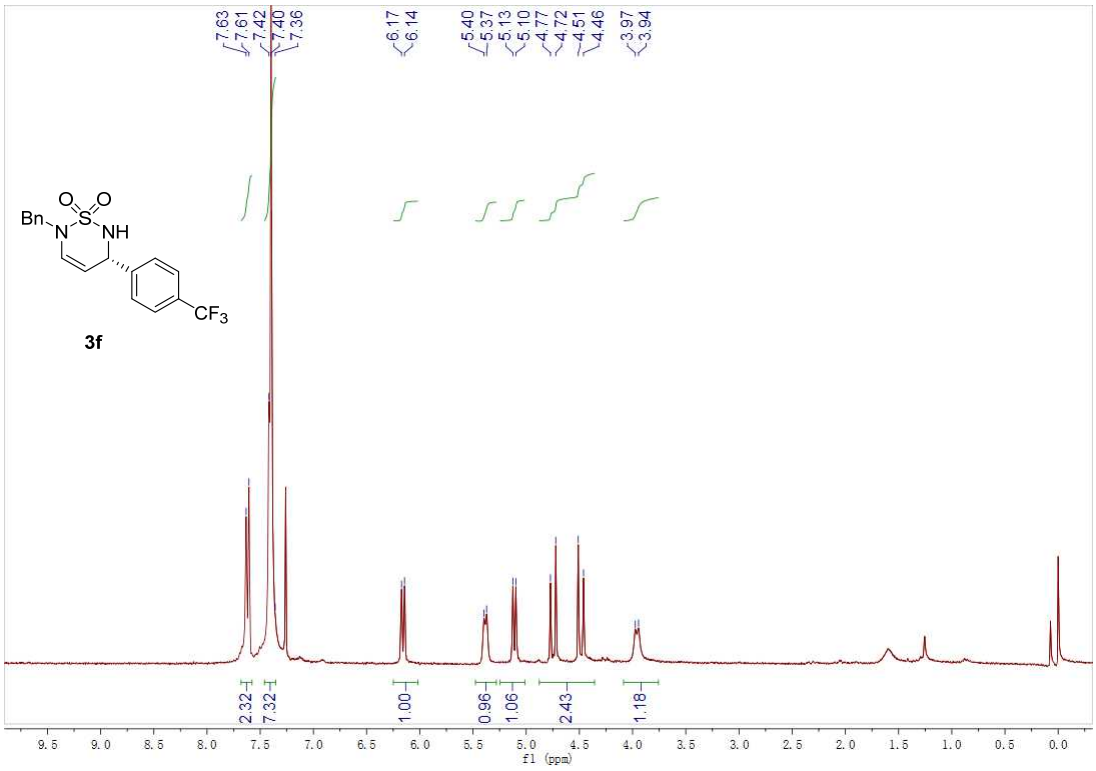
F
3e
f1 (ppm)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5.13
5.10
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4.51
4.46
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3.94
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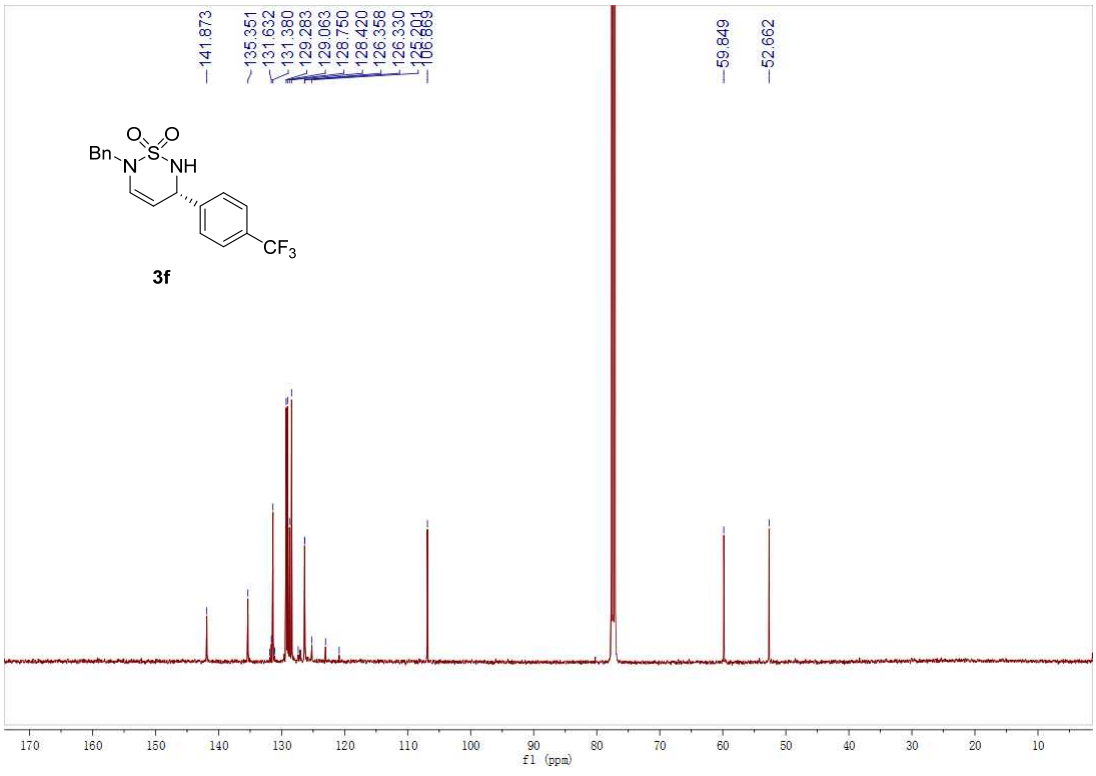
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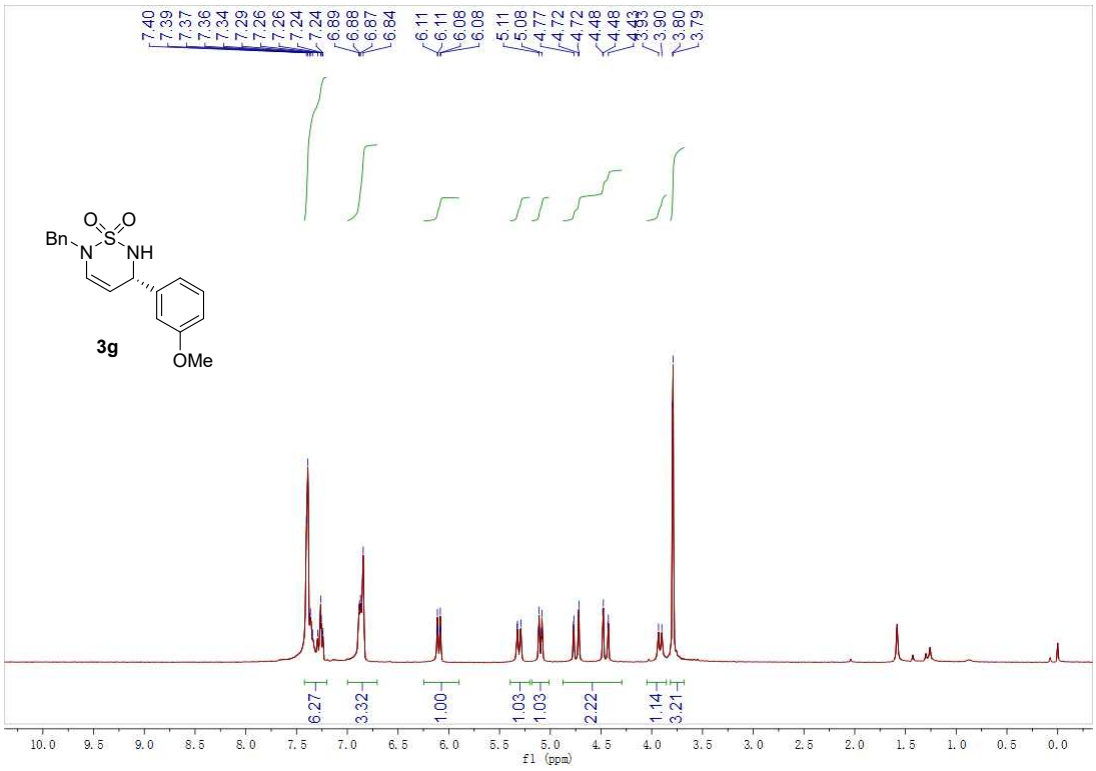
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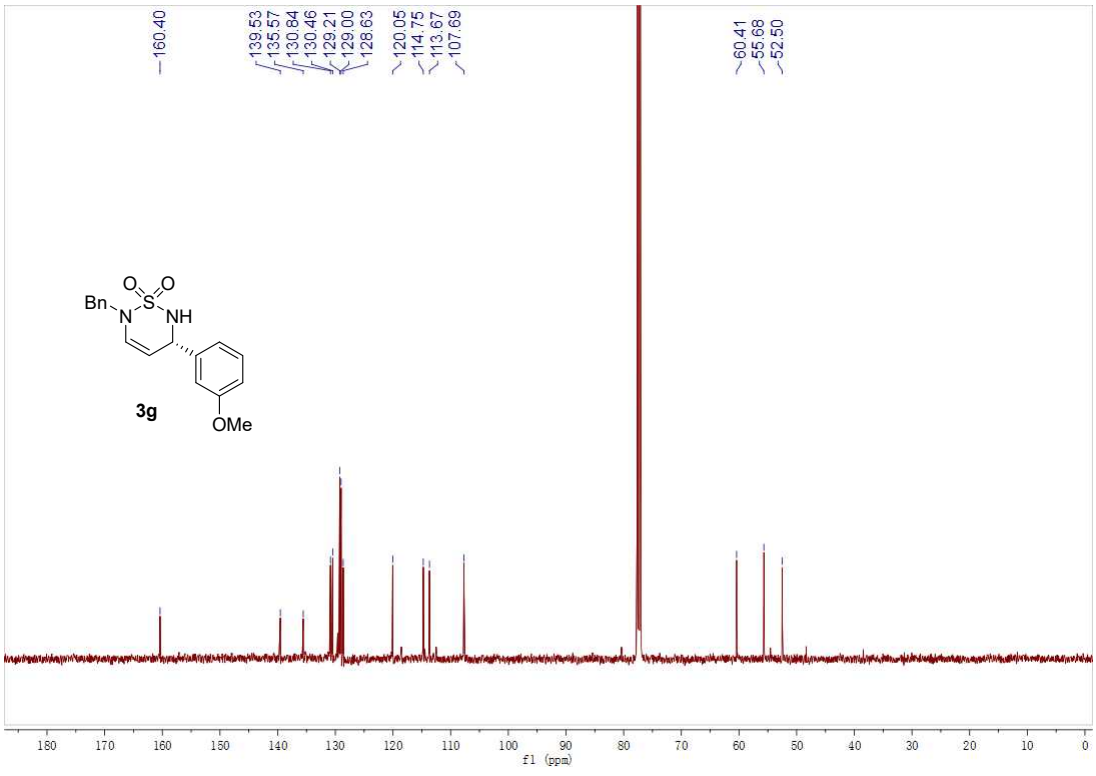
f1 (ppm)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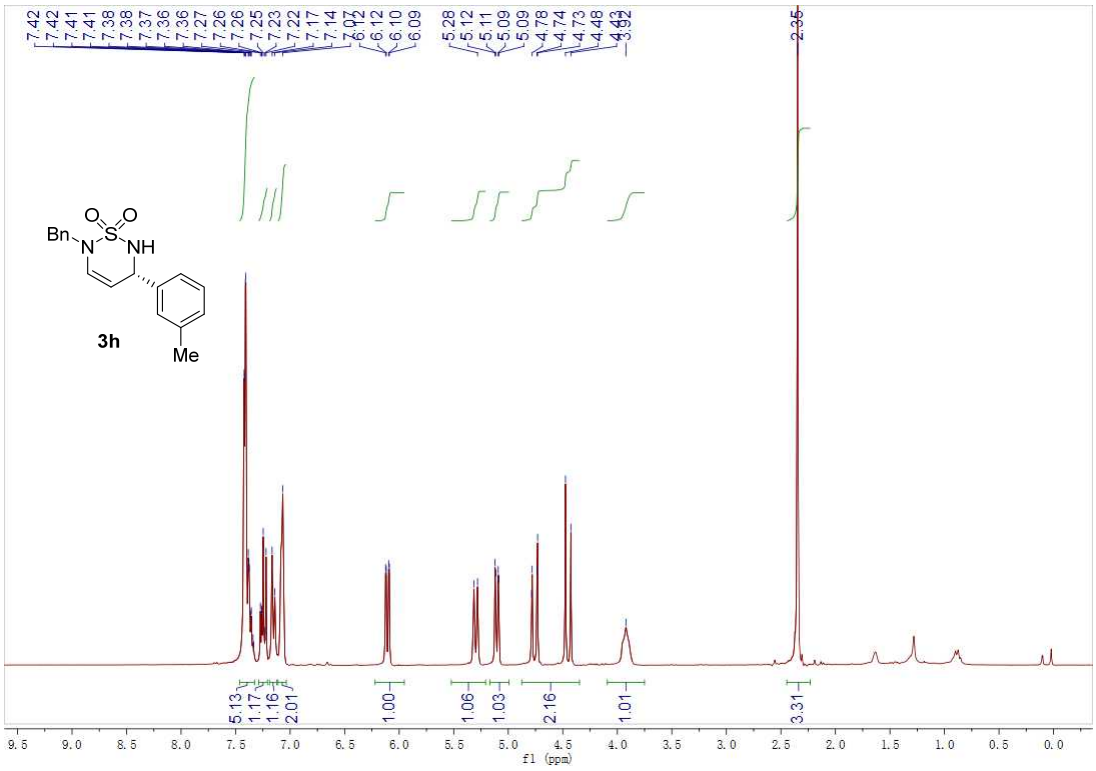
OMe
f1 (ppm)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7.14
7.07
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6.10
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5.09
5.09
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O
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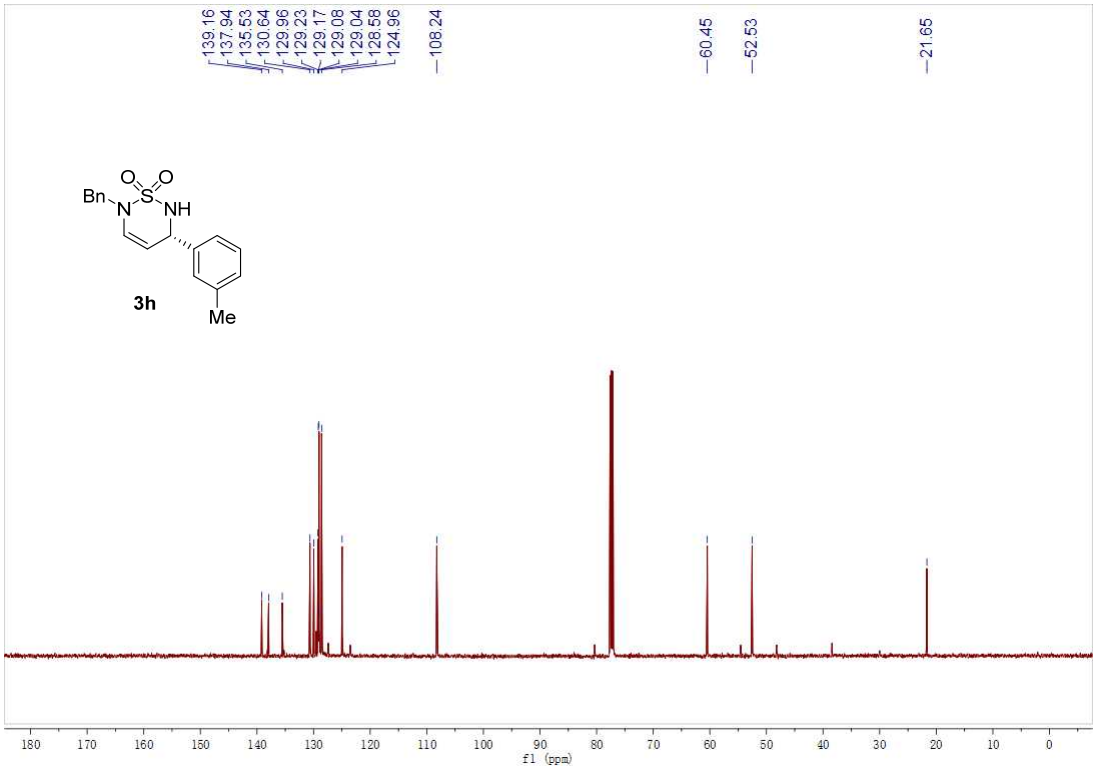
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O
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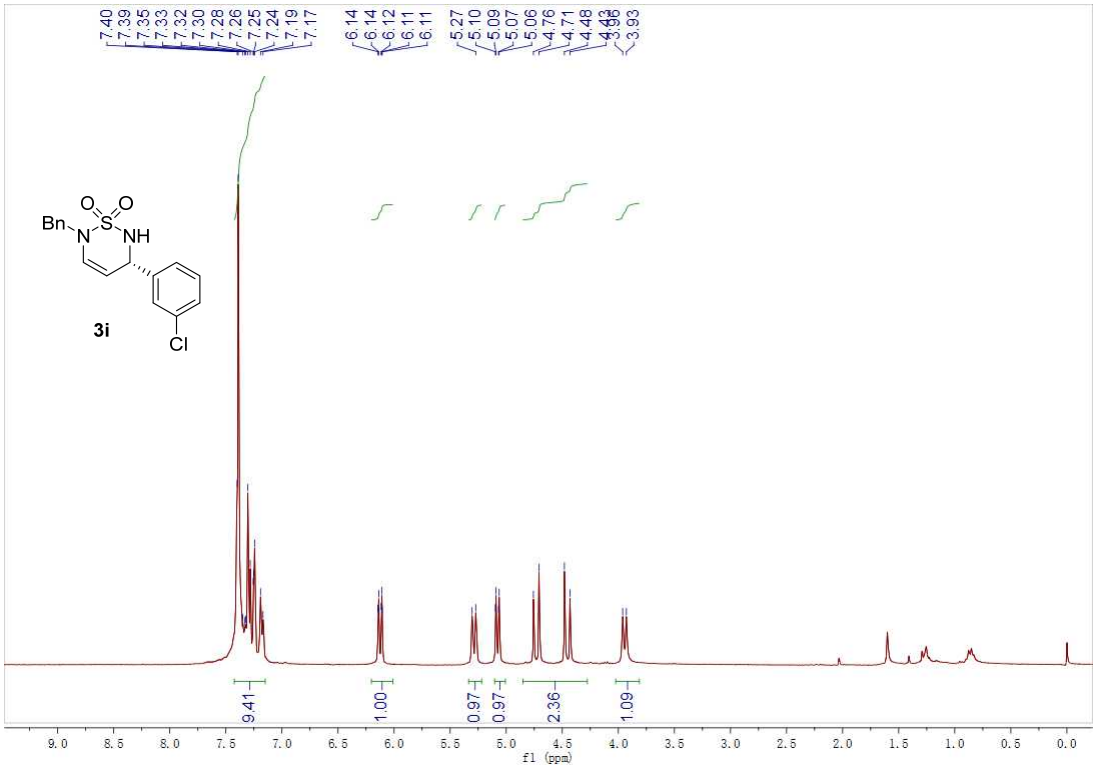
f1 (ppm)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5.10
5.09
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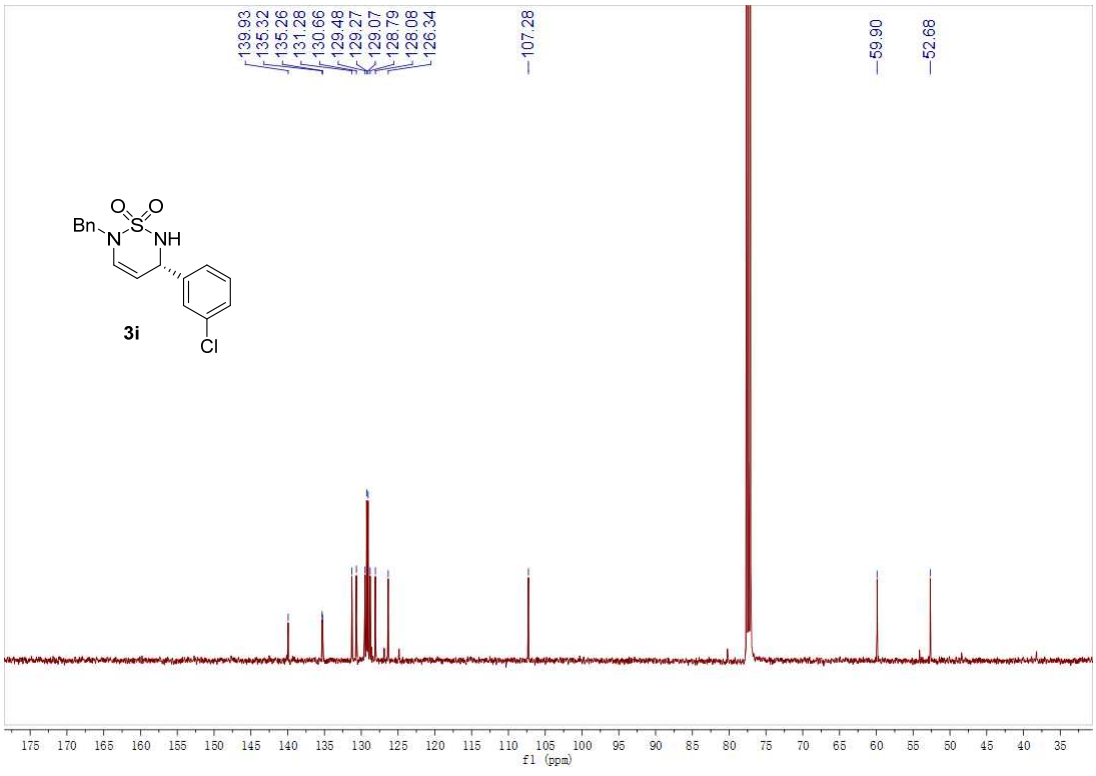
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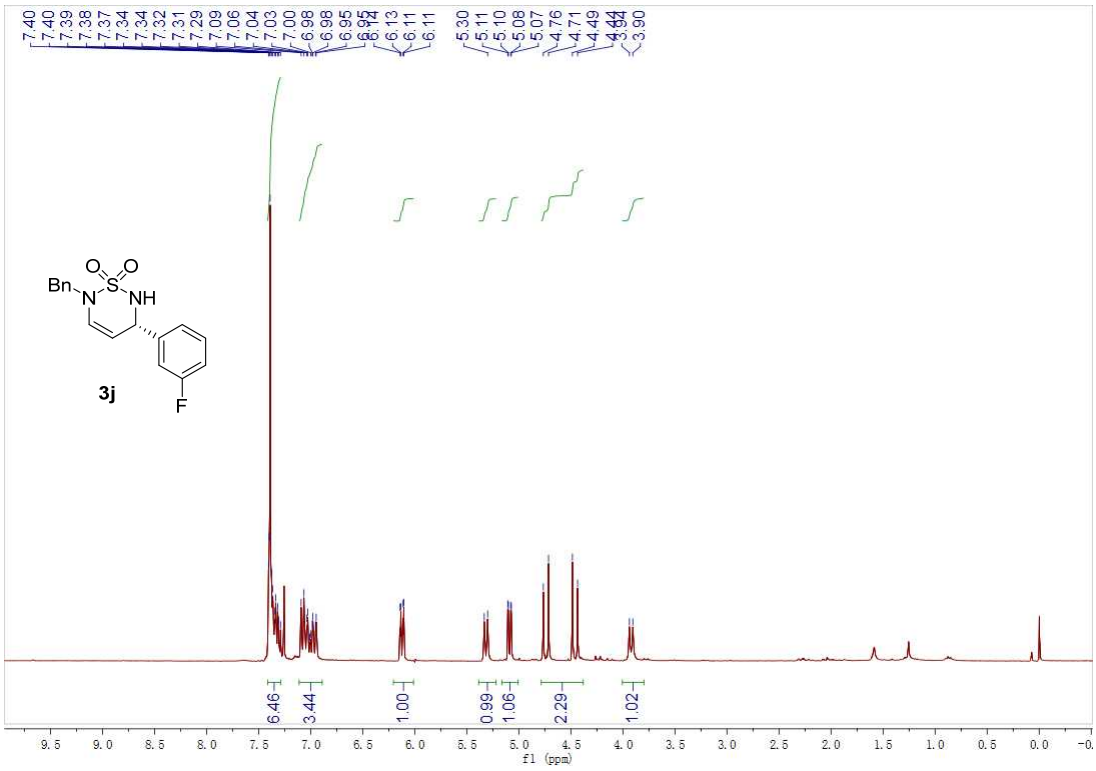
f1 (ppm)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4.71
4.49
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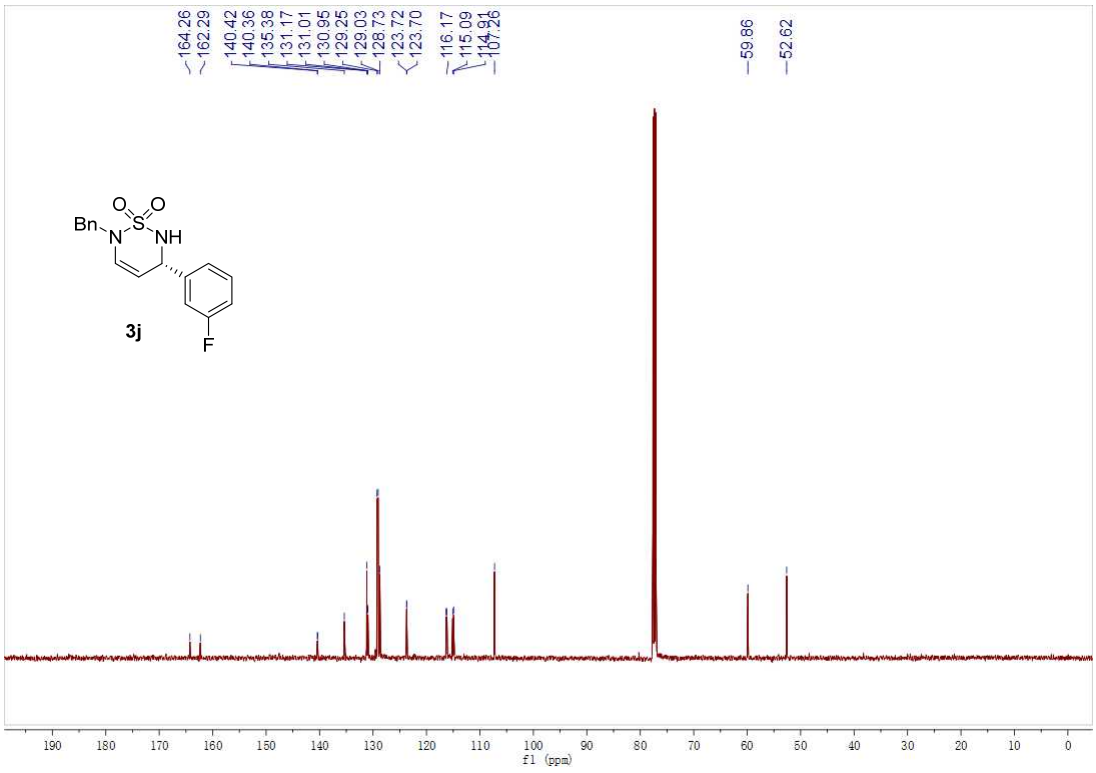
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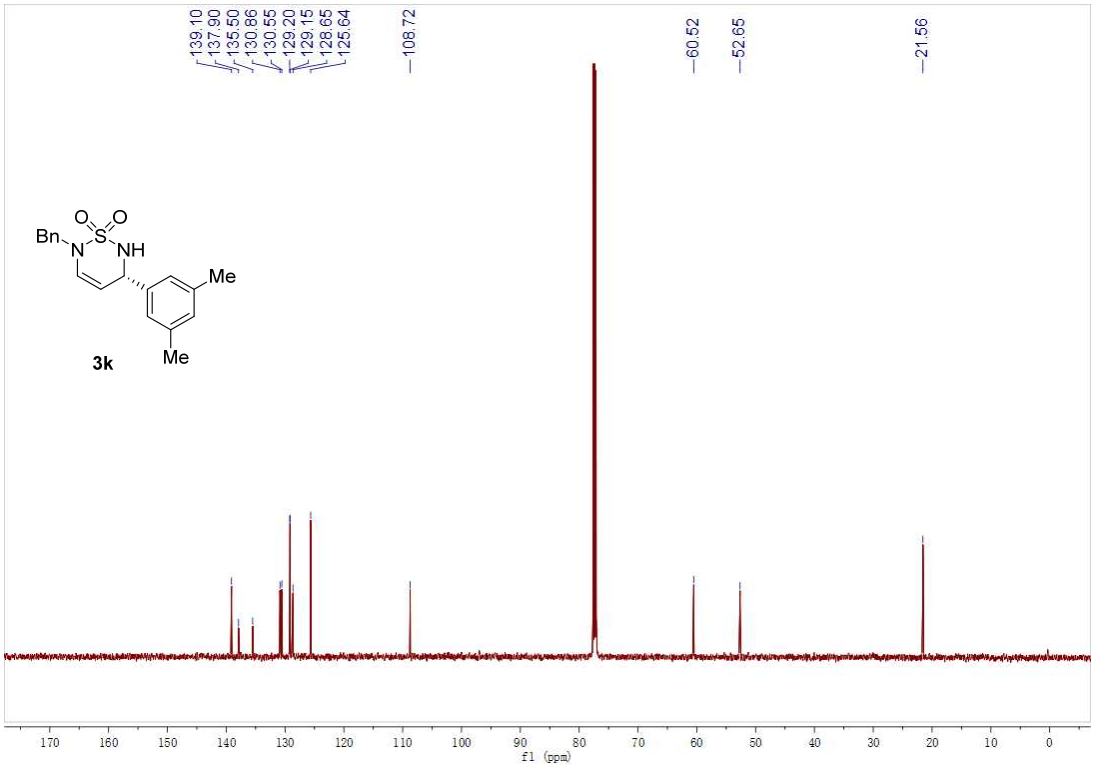
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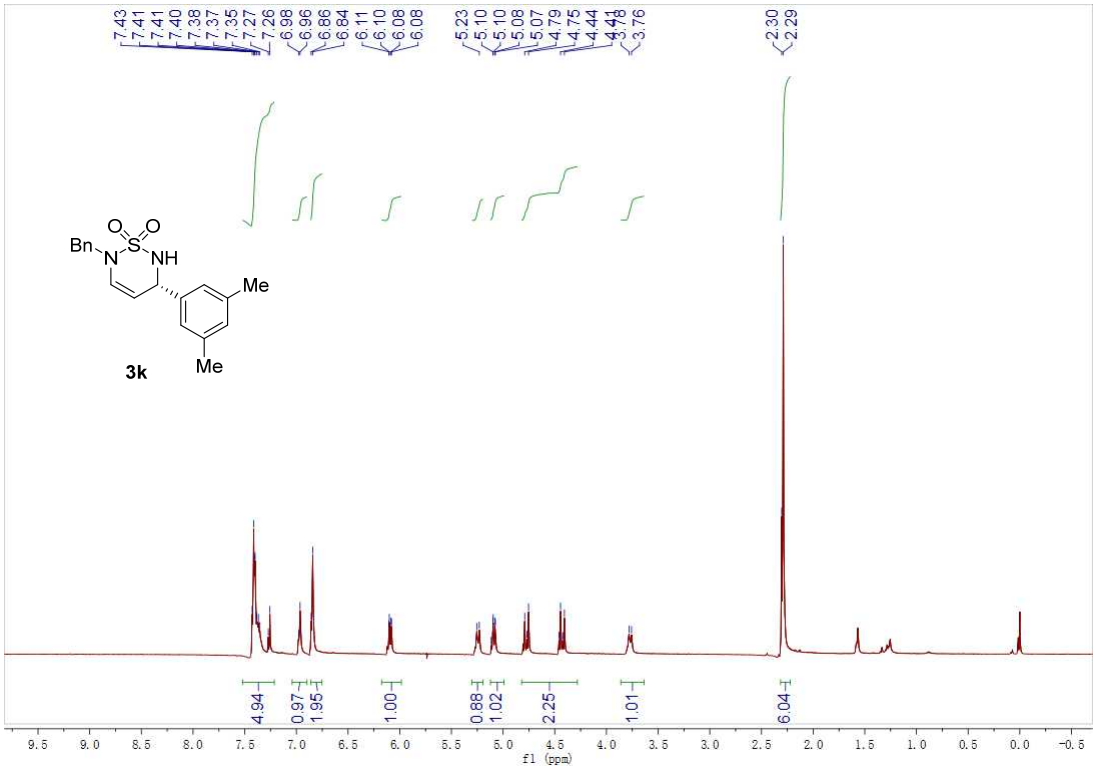
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2.29
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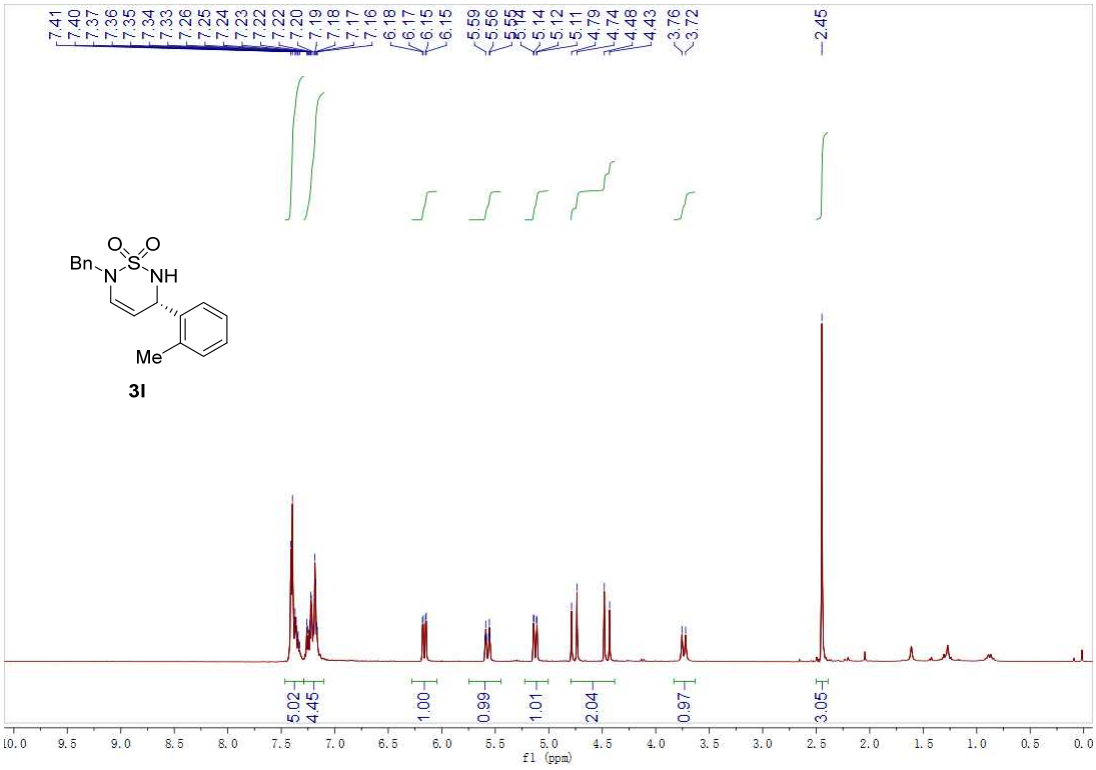
f1 (ppm)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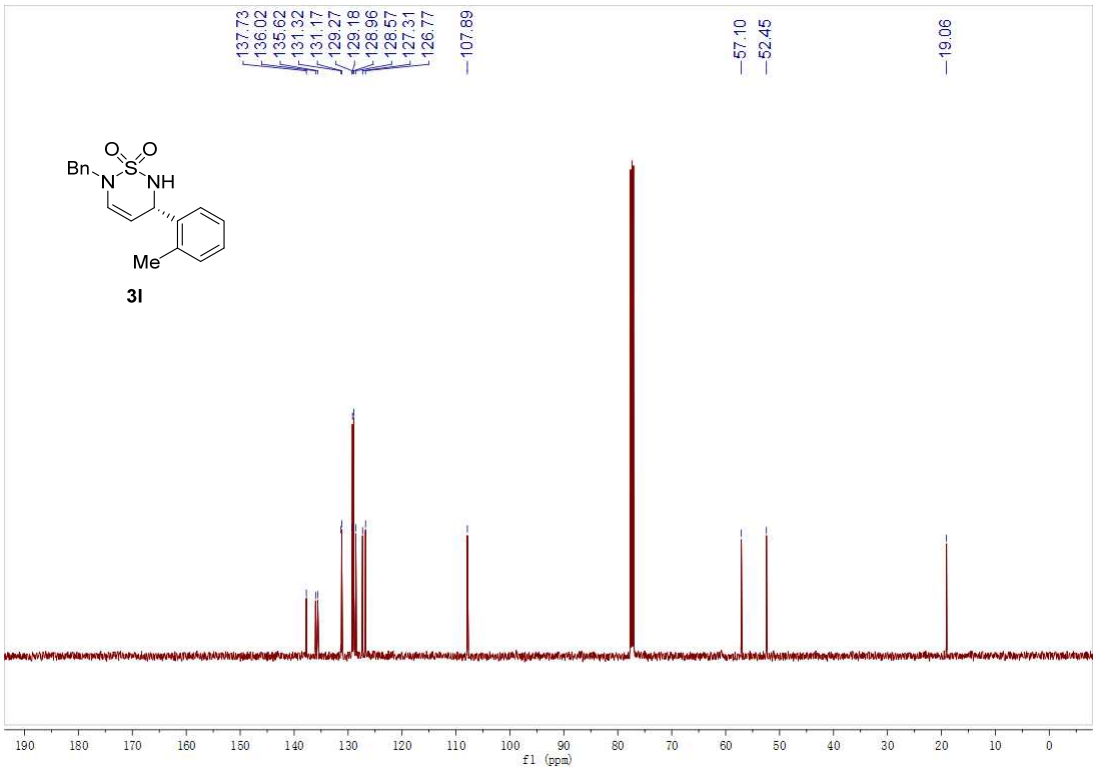
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Bn
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O
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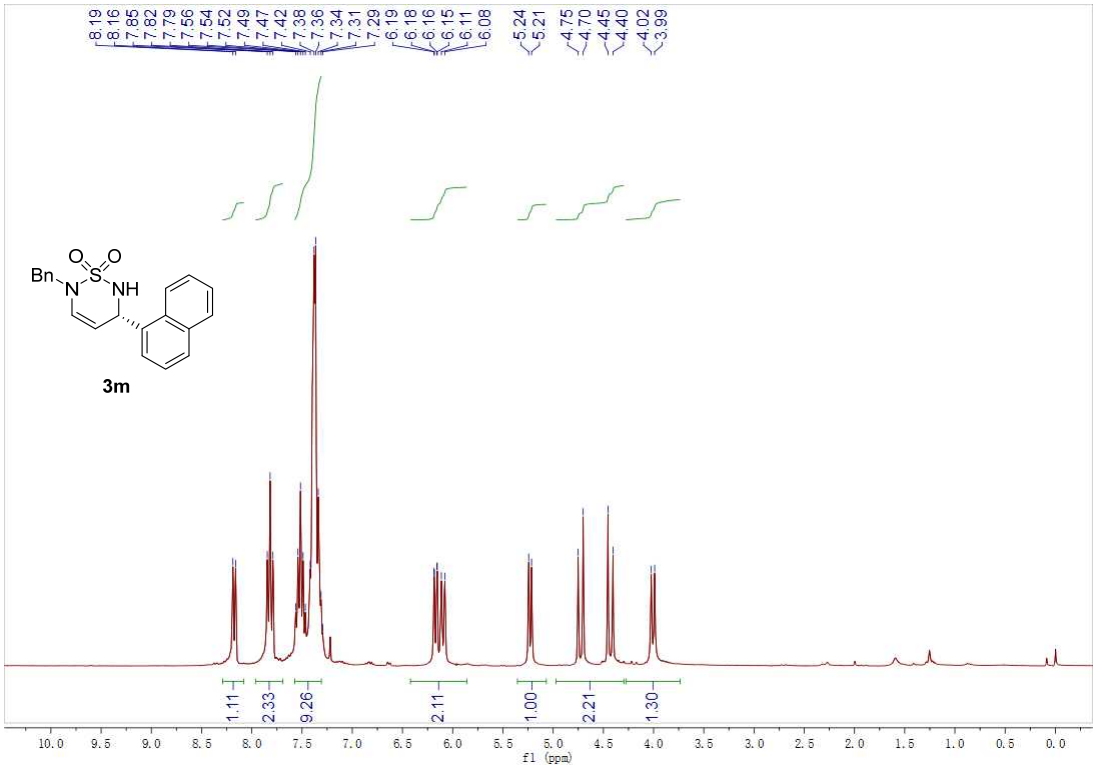
3l
f1 (ppm)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6.19
6.18
6.16
6.15
6.11
6.08
5.24
5.21
4.75
4.70
4.45
4.40
4.02
3.99
Bn
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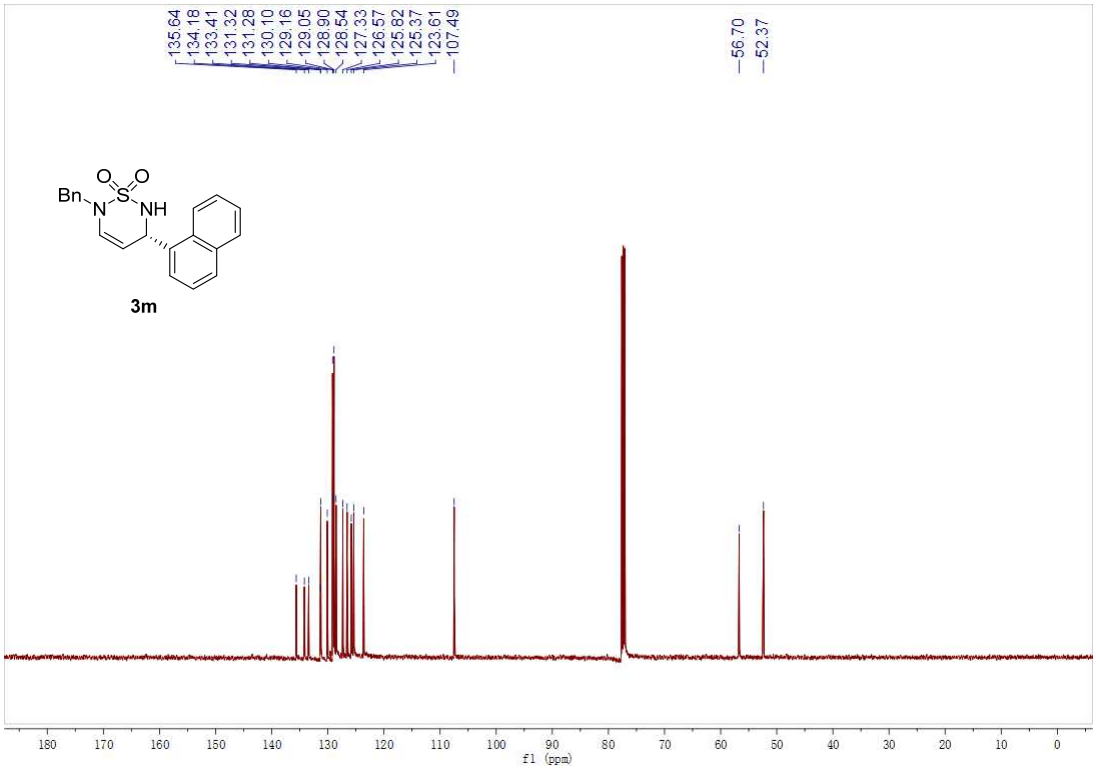
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123.61
107.49
56.70
52.37
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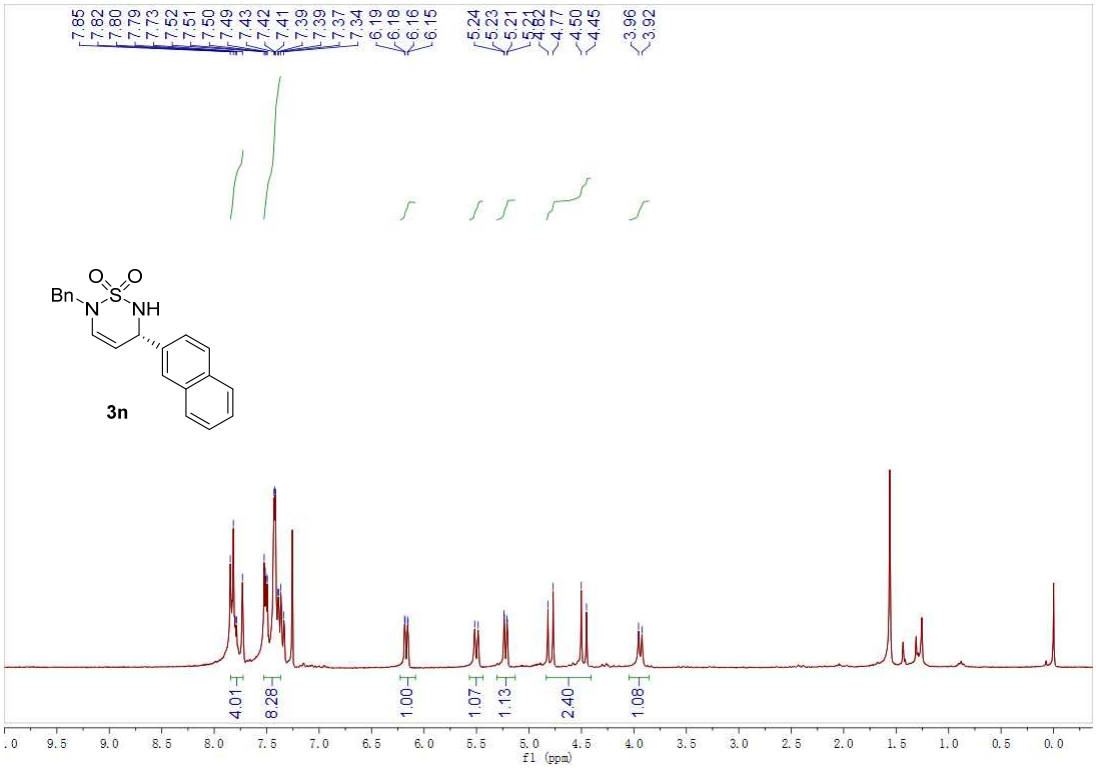
S
O
O
NH
3m
f1 (ppm)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7.39
7.39
7.37
7.34
6.19
6.18
6.16
6.15
5.24
5.23
5.21
5.21
4.82
4.77
4.50
4.45
3.96
3.92
Bn
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O
NH
3n
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1.07
1.13
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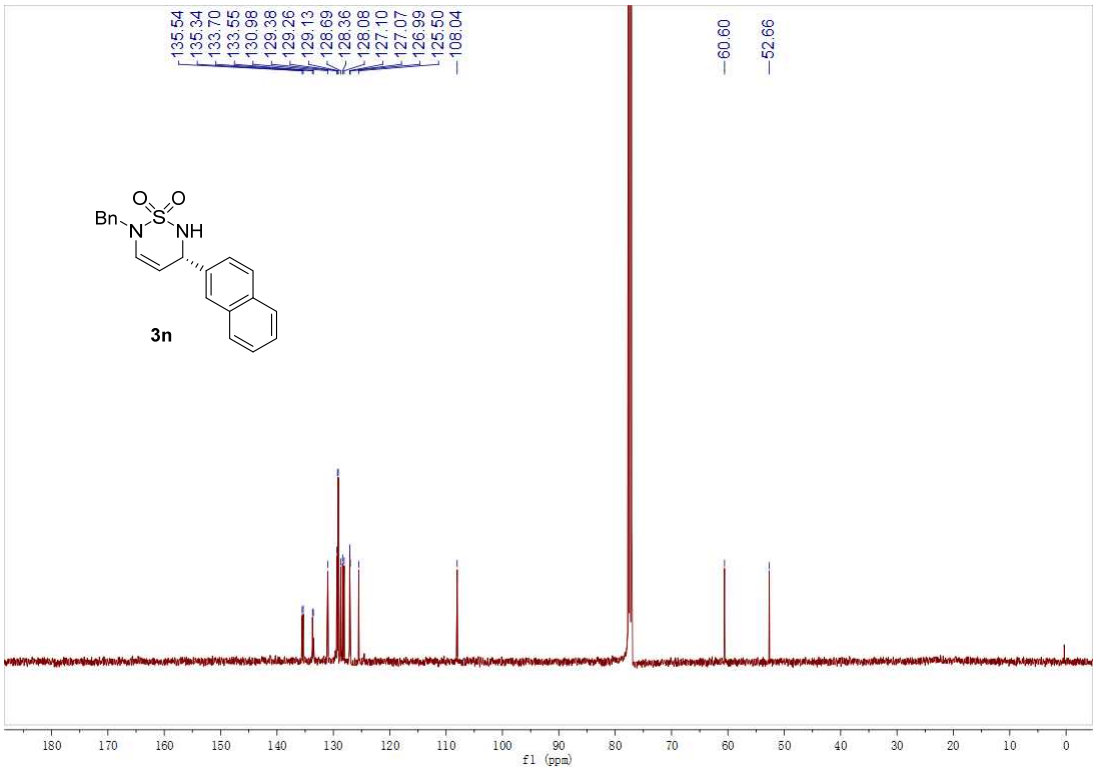
1.08
f1 (ppm)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108.04
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52.66
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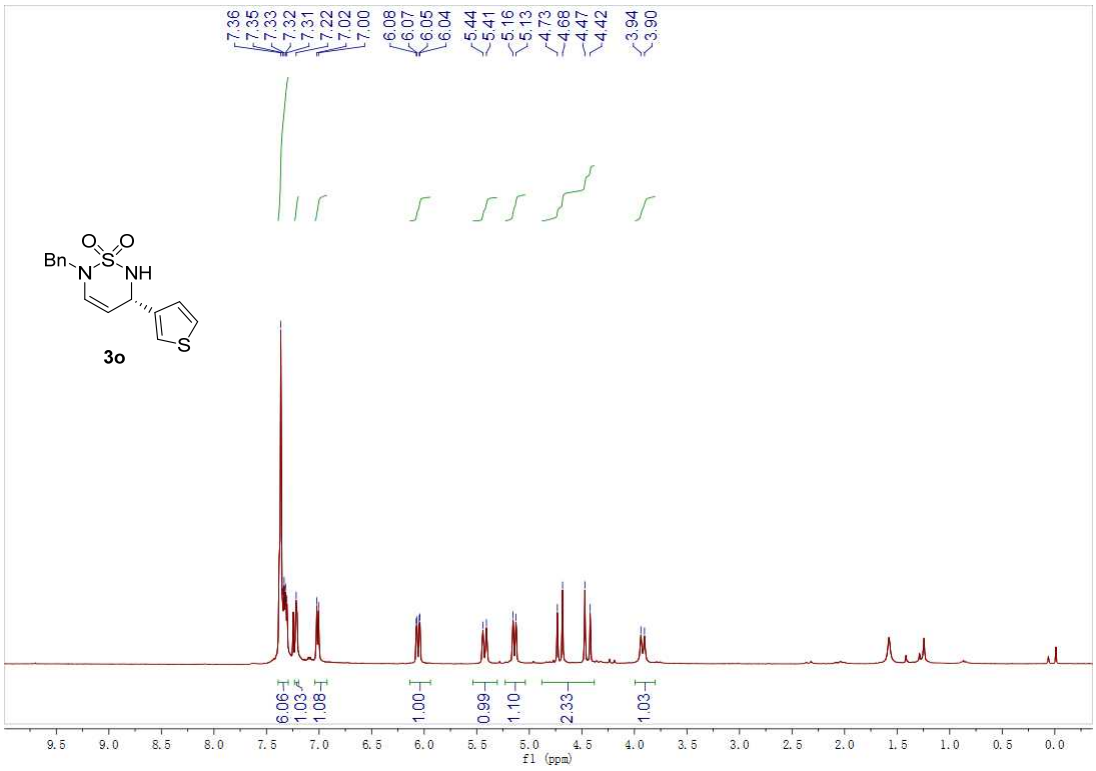
S
O
O
NH
3n
f1 (ppm)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6.07
6.05
6.04
5.44
5.41
5.16
5.13
4.73
4.68
4.47
4.42
3.94
3.90
Bn
N
S
O
O
NH
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1.08
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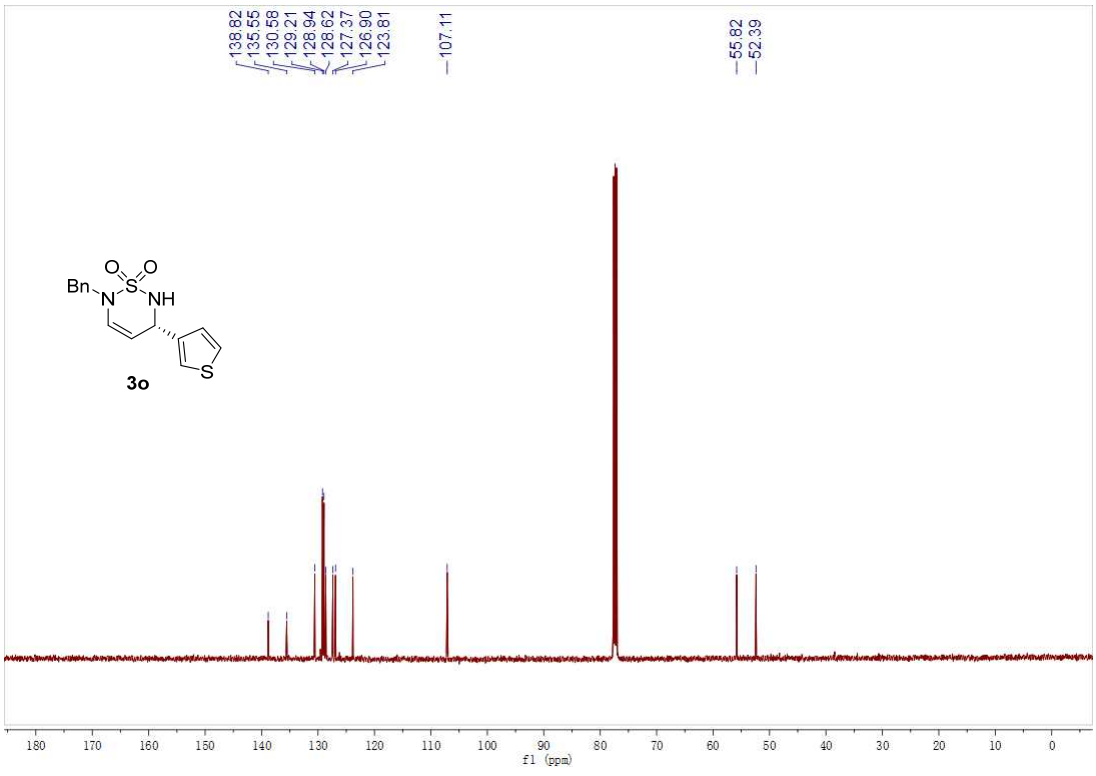
1.03
f1 (ppm)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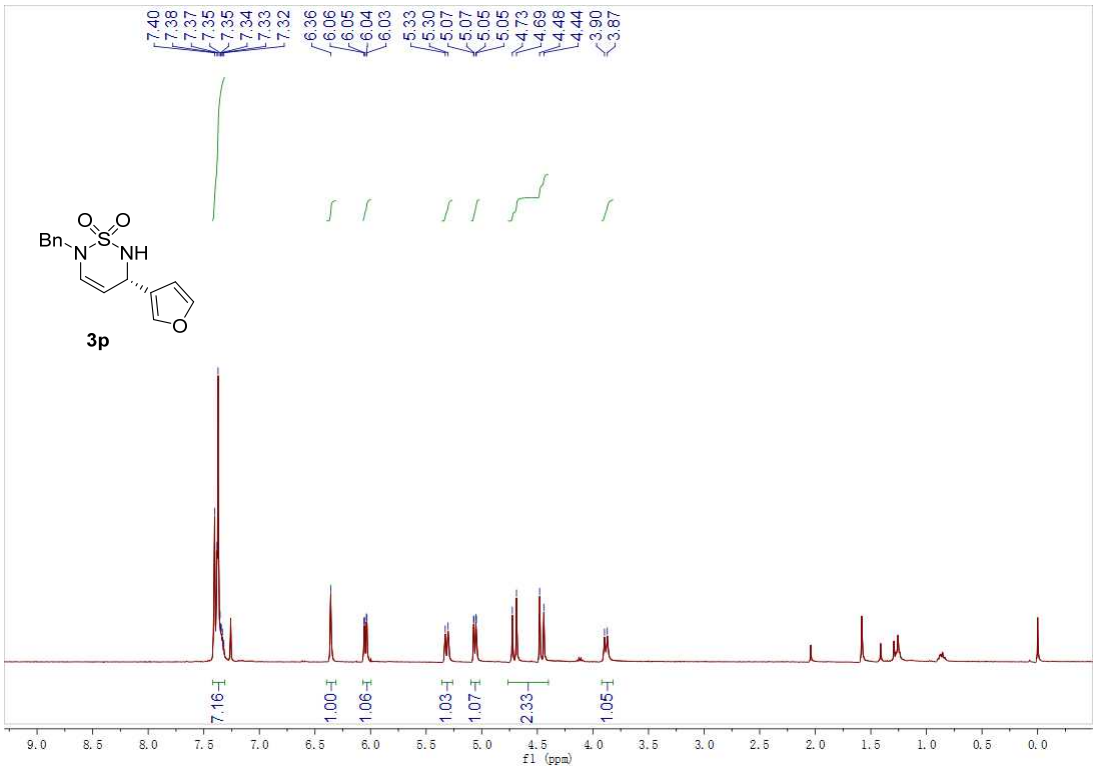
S
O
O
NH
S
3o
f1 (ppm)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6.05
6.04
6.03
5.33
5.30
5.07
5.07
5.05
5.05
4.73
4.69
4.48
4.44
3.90
3.87
Bn
N
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O
3p
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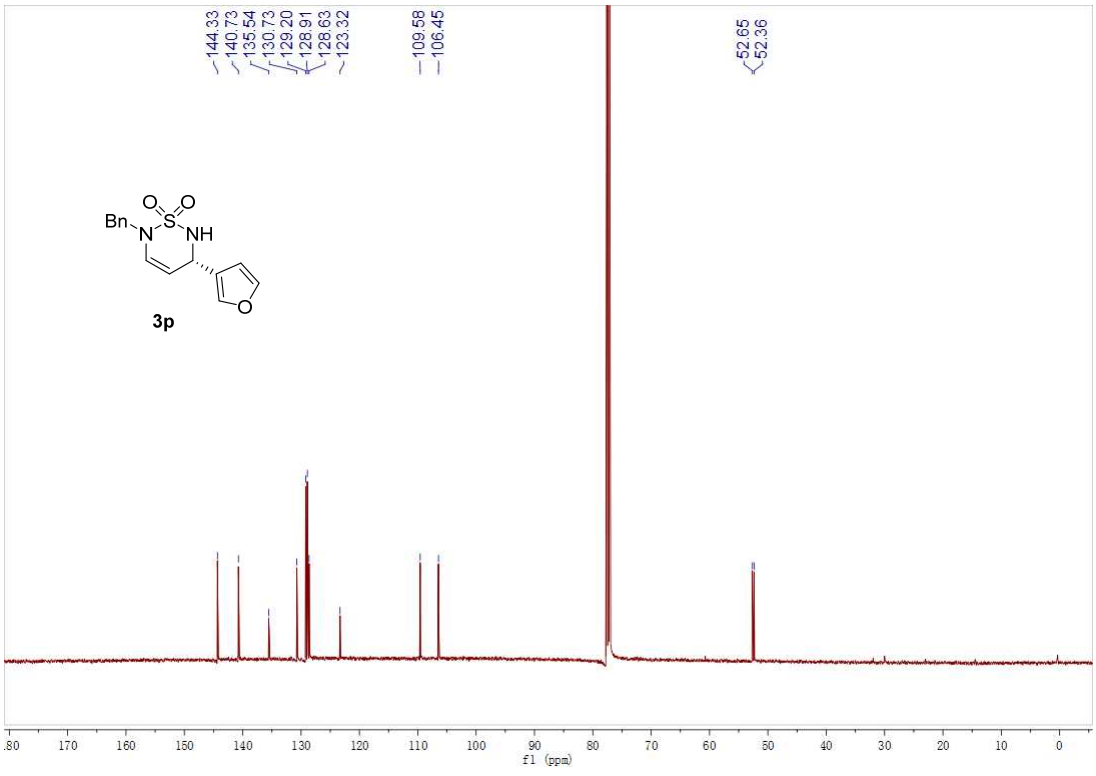
1.03
1.07
2.33
1.05
f1 (ppm)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52.36
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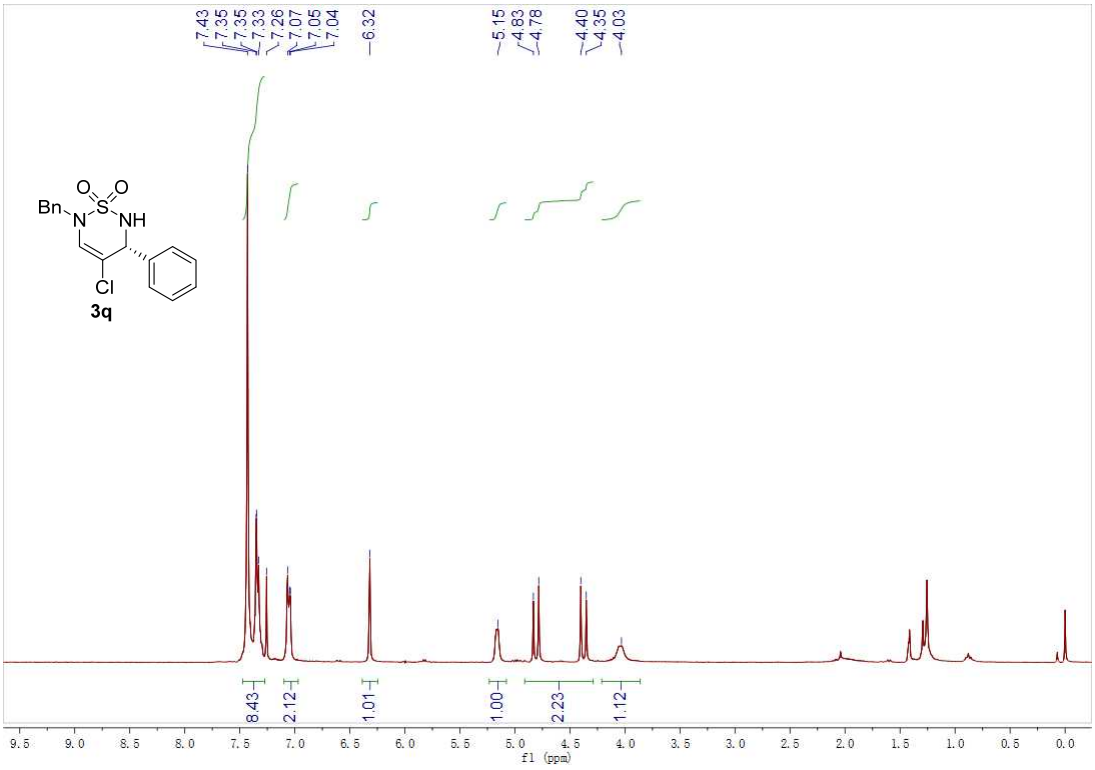
S
O
O
NH
O
3p
f1 (ppm)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7.07
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7.04
6.32
5.15
4.83
4.78
4.40
4.35
4.03
Bn
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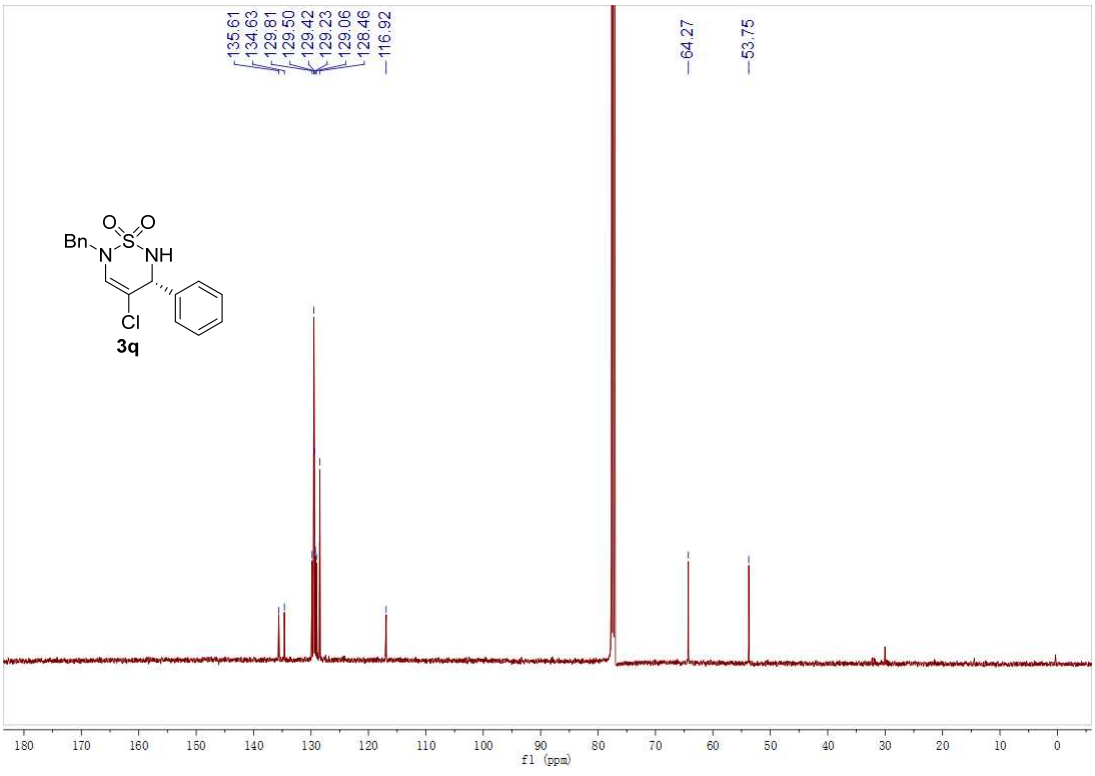
S
O
O
NH
Cl
3q
8.43
2.12
1.01
1.00
2.23
1.12
f1 (ppm)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64.27
53.75
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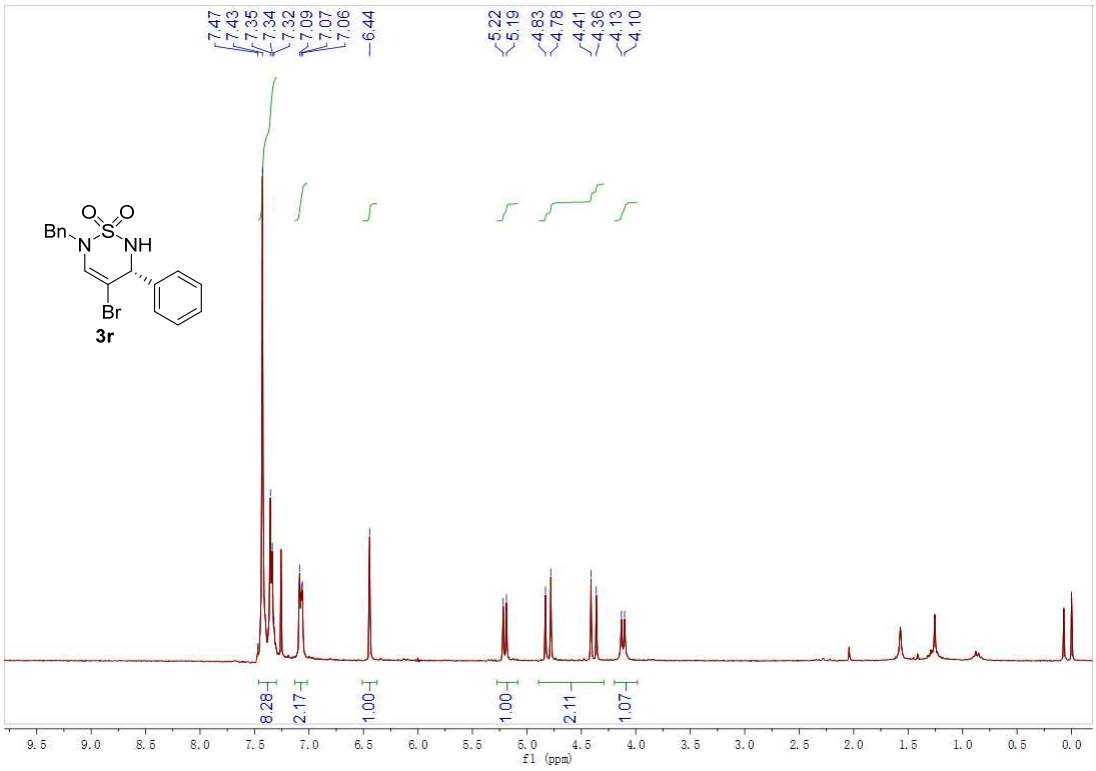
S
O
O
NH
Cl
3q
f1 (ppm)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7.07
7.06
6.44
5.22
5.19
4.83
4.78
4.41
4.36
4.13
4.10
Bn
N
O
O
S
NH
Br
3r
8.28
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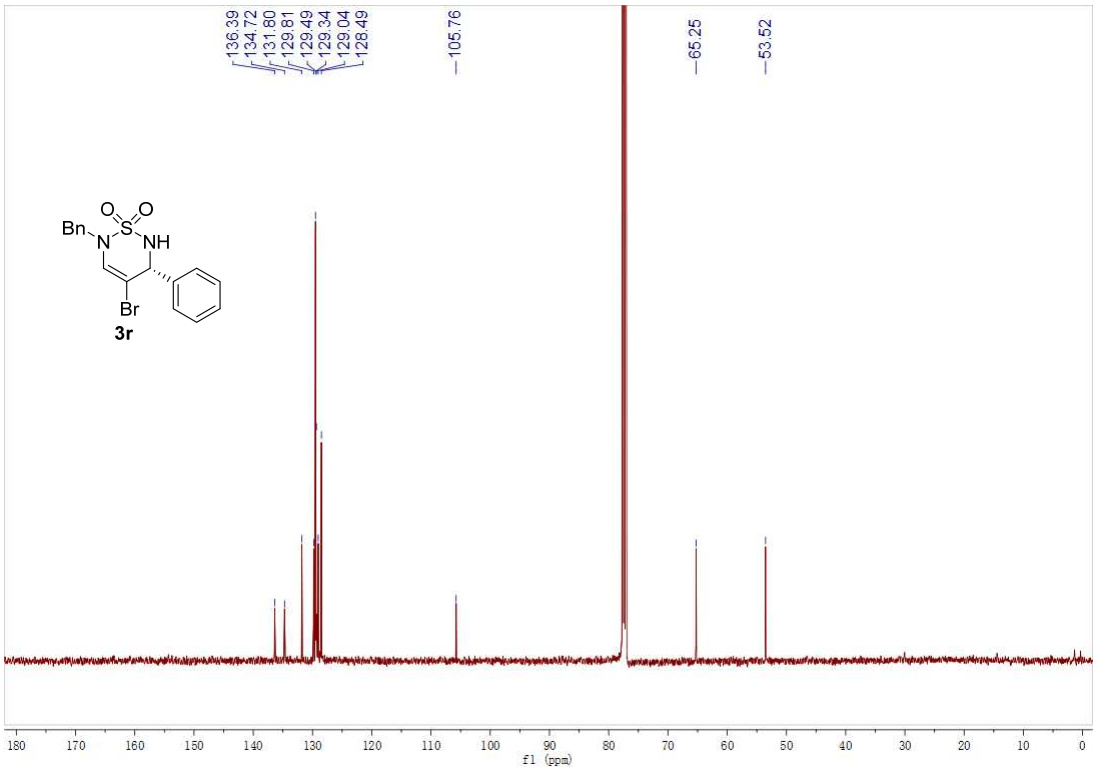
1.00
1.00
2.11
1.07
f1 (ppm)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105.76
65.25
53.52
Bn
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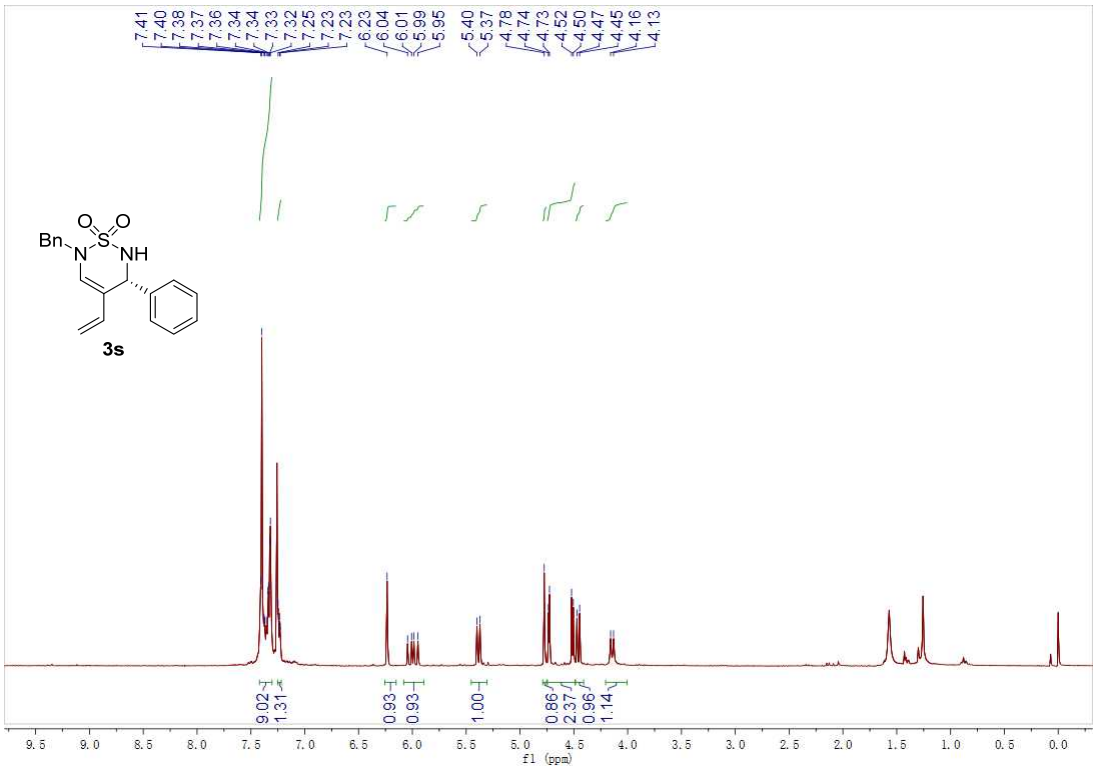
O
O
S
NH
Br
3r
f1 (ppm)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7.33
7.32
7.25
7.23
7.23
6.23
6.04
6.01
5.99
5.95
5.40
5.37
4.78
4.74
4.73
4.52
4.50
4.47
4.45
4.16
4.13
Bn
N
S
O
O
NH
3s
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0.93
0.93
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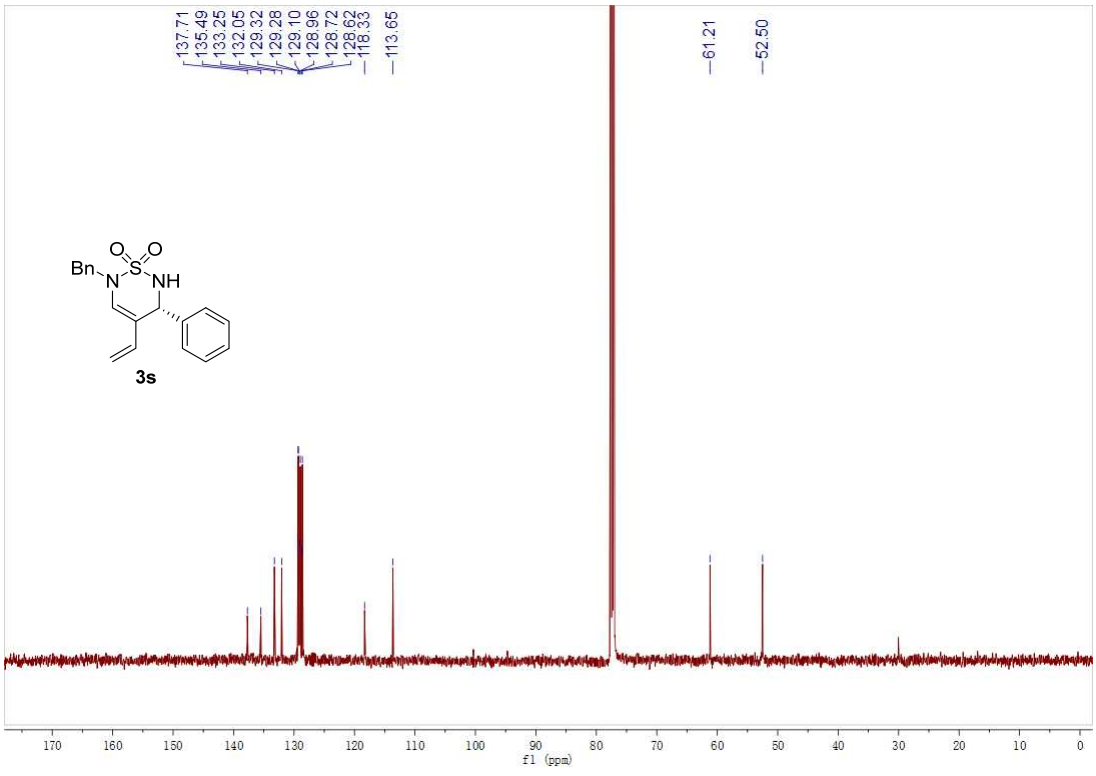
2.37
0.96
1.14
f1 (ppm)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113.65
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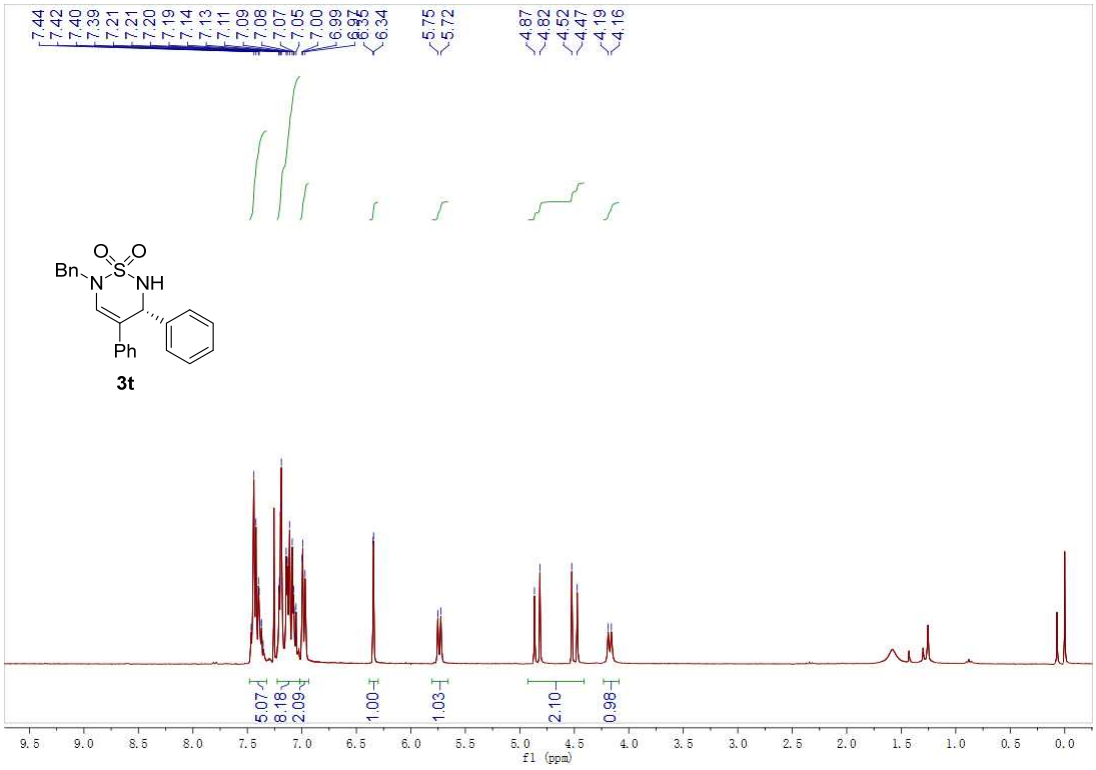
52.50
Bn
N
S
O
O
NH
3s
f1 (ppm)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7.13
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7.08
7.07
7.05
7.00
6.99
6.97
6.95
6.34
5.75
5.72
4.87
4.82
4.52
4.47
4.19
4.16
Bn
N
S
O
O
NH
Ph
3t
5.07
8.18
2.09
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1.03
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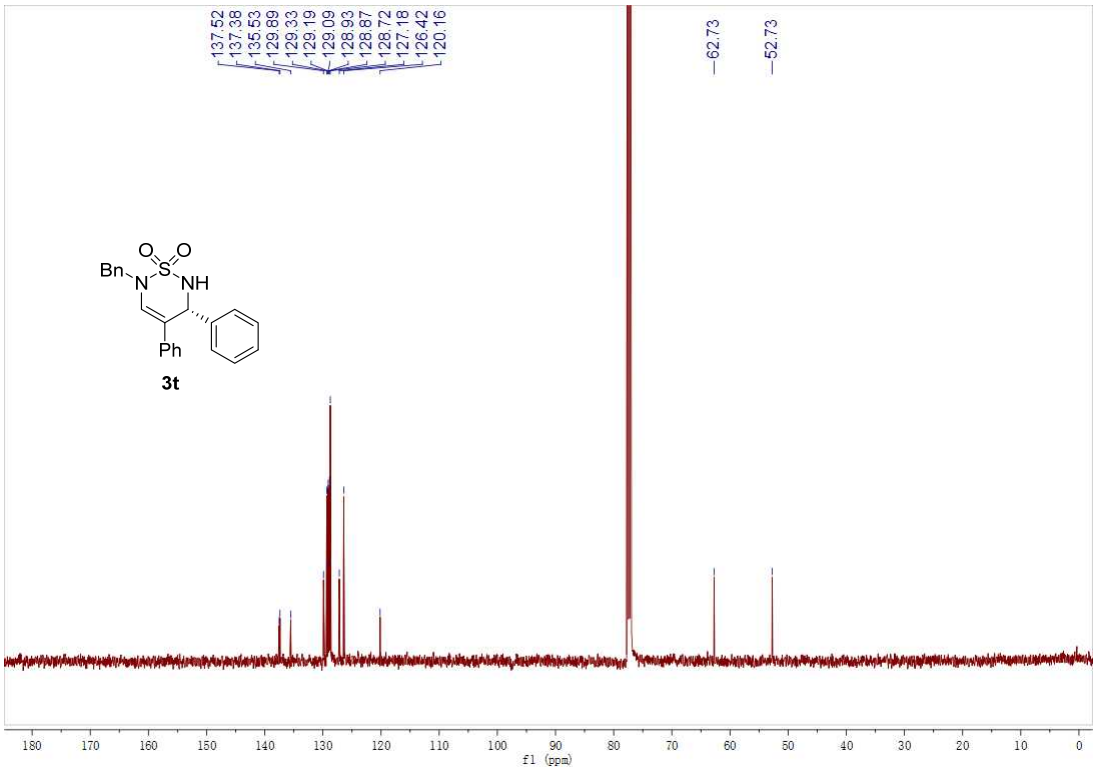
0.98
f1 (ppm)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128.93
128.87
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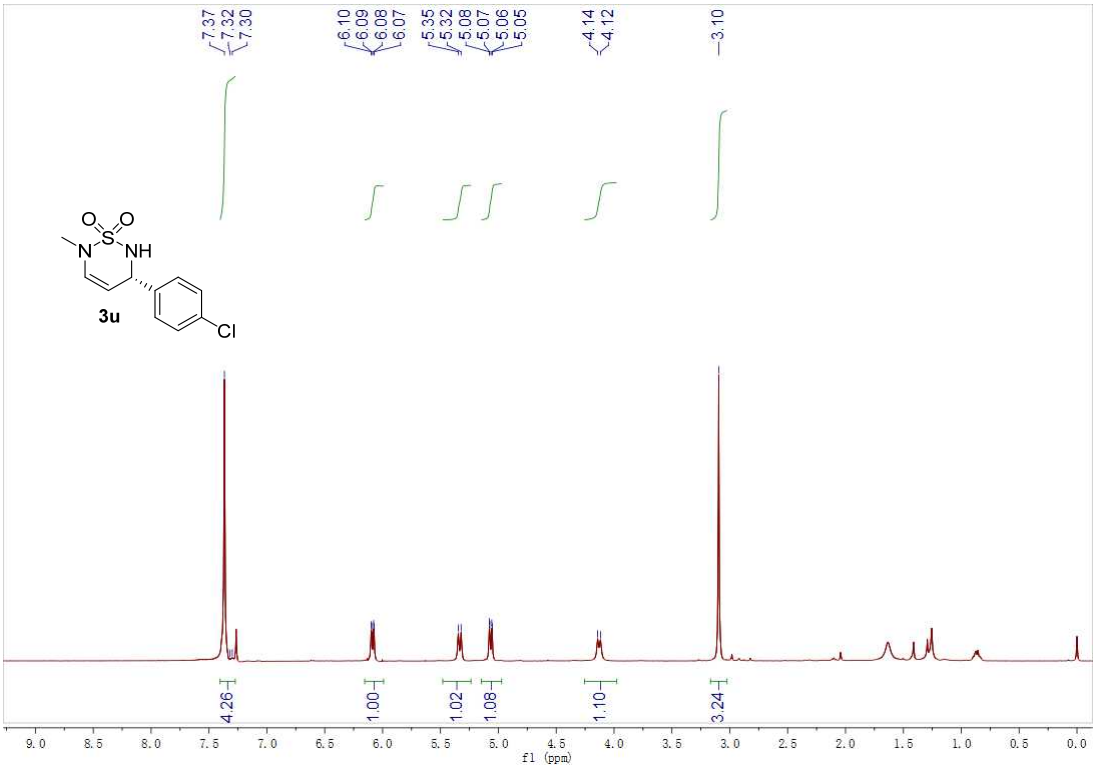
126.42
120.16
62.73
52.73
Bn
N
S
O
O
NH
Ph
3t
f1 (ppm)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6.07
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5.08
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5.06
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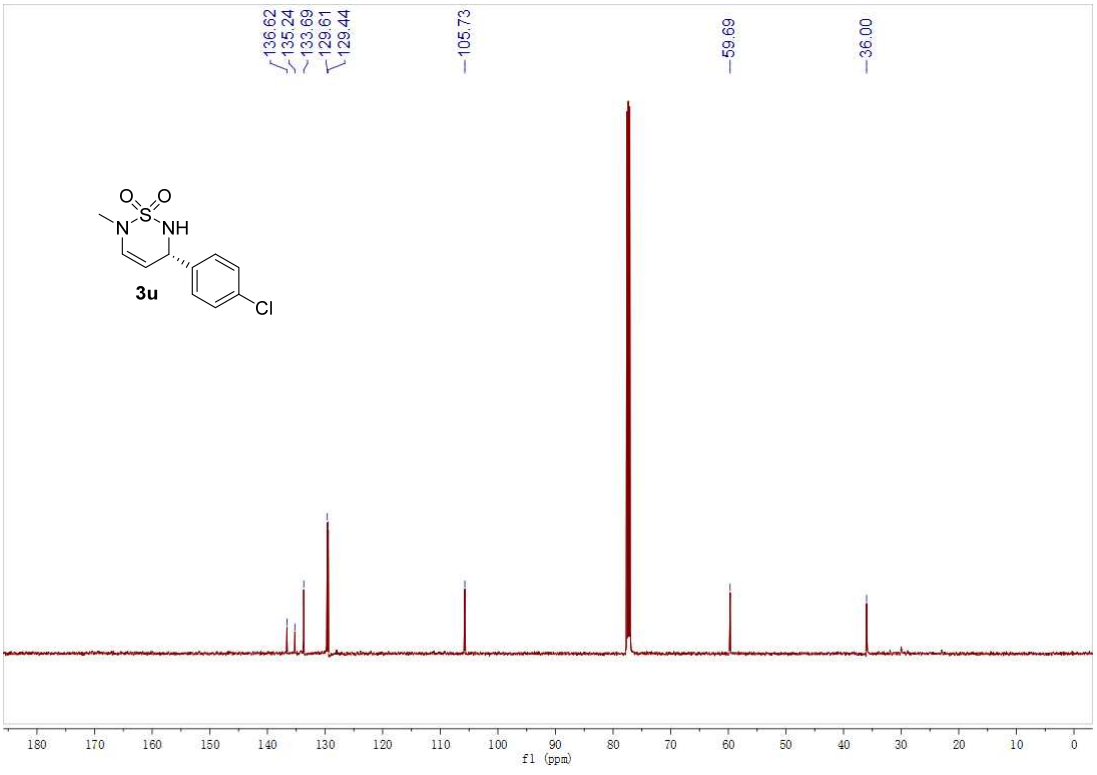
4.12
3.10
3u
4.26
1.00
1.02
1.08
1.10
3.24
f1 (ppm)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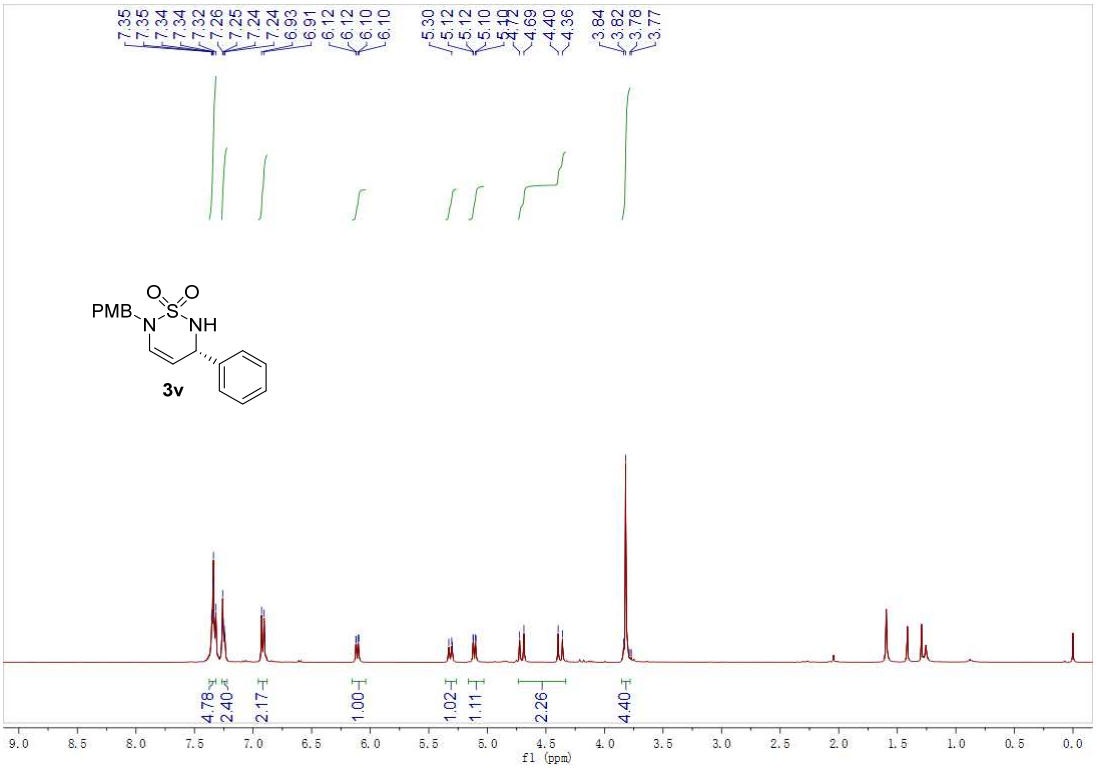
3u
f1 (ppm)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6.91
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6.12
6.10
6.10
5.30
5.12
5.12
5.10
5.10
4.72
4.69
4.40
4.36
3.84
3.82
3.78
3.77
PMB
N
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O
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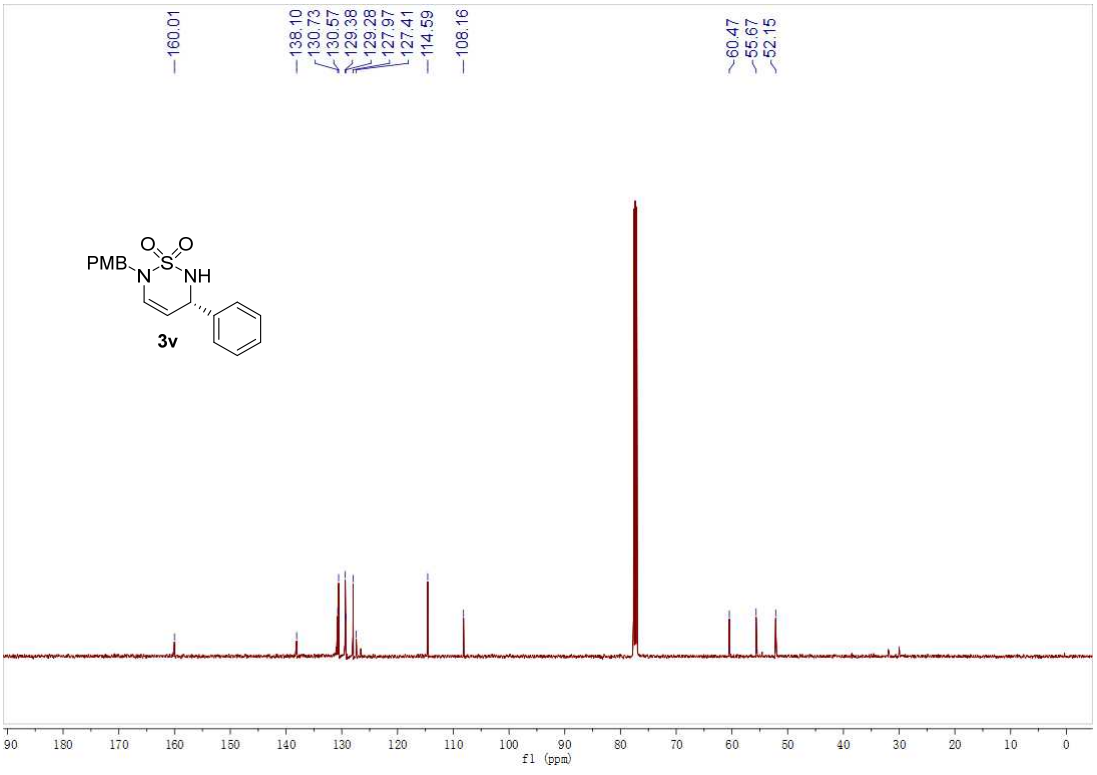
2.40
2.17
1.00
1.02
1.11
2.26
4.40
f1 (ppm)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127.97
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60.47
55.67
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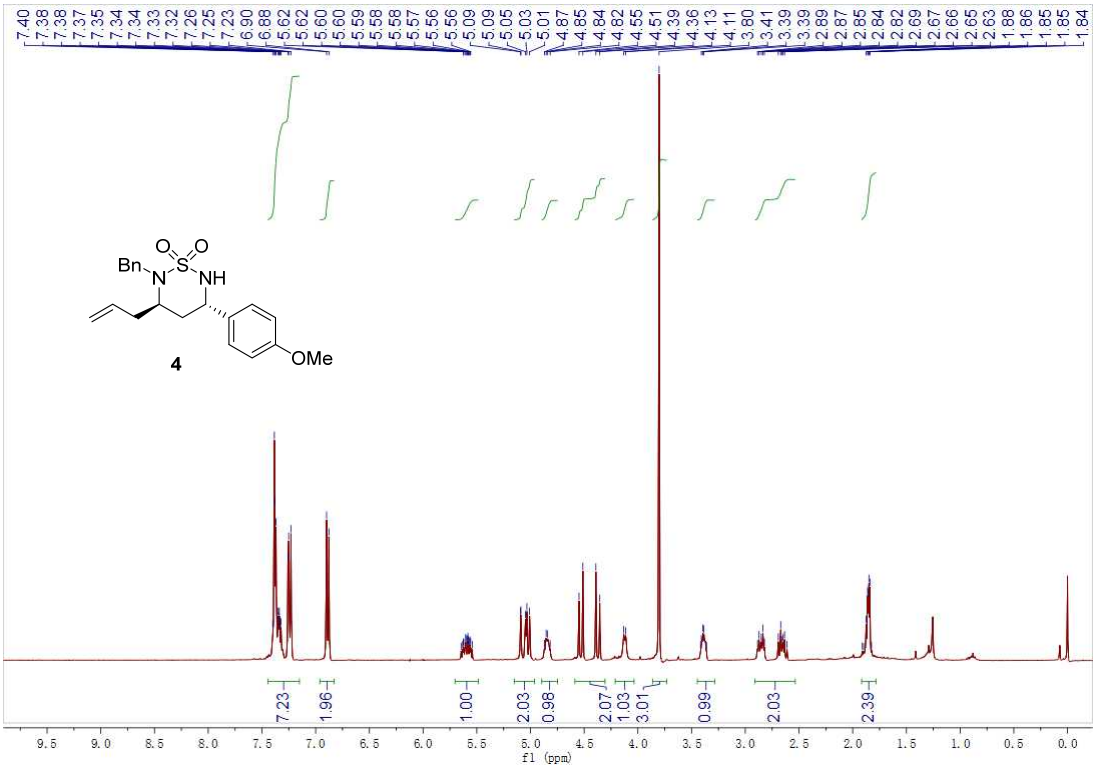
PMB
N
S
O
O
NH
3v
f1 (ppm)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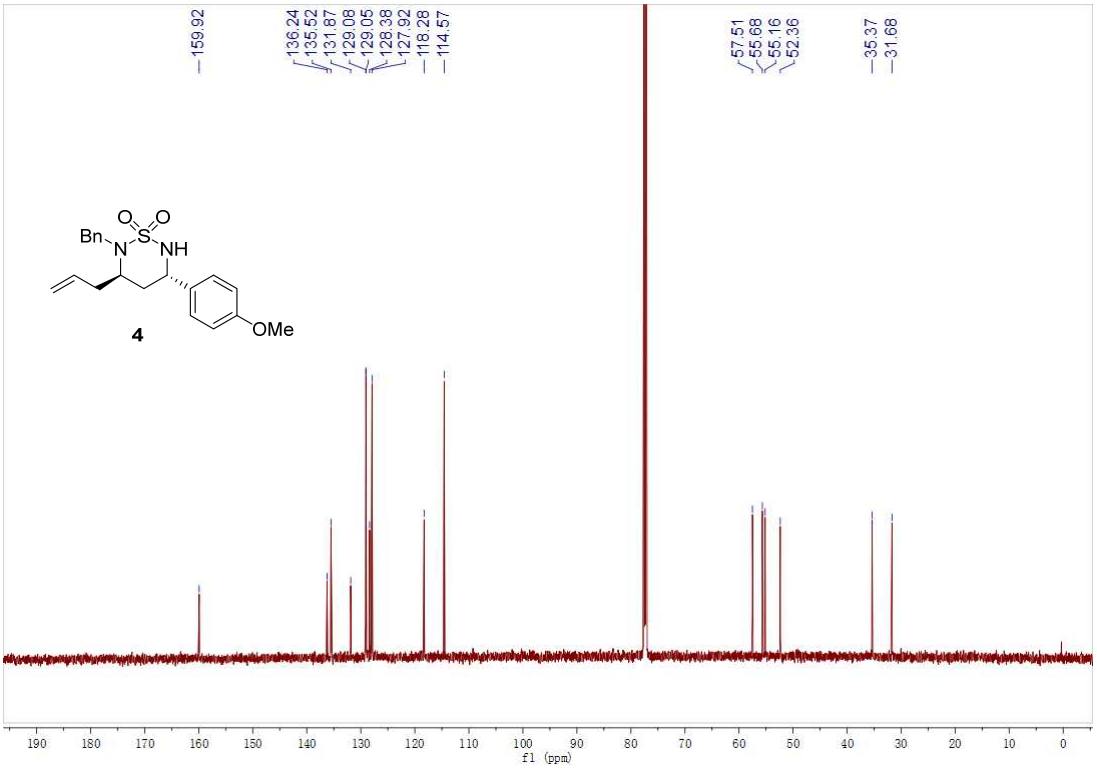
Bn
N
S
O
O
NH
OMe
4
7.23
1.96
1.00
2.03
0.98
2.07
1.03
3.01
0.99
2.03
2.39
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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55.68
55.16
52.36
35.37
31.68
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S
O
O
NH
OMe
4
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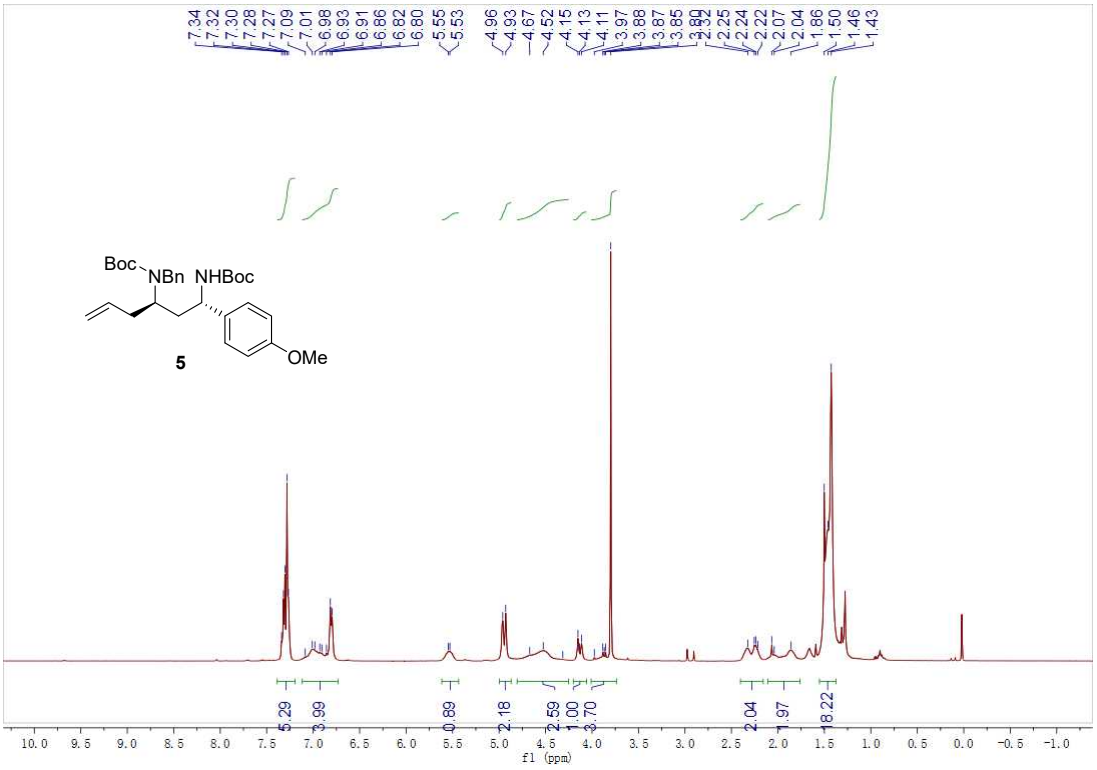
f1 (ppm)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6.98
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6.91
6.86
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6.80
5.55
5.53
4.96
4.93
4.67
4.52
4.15
4.13
4.11
3.97
3.88
3.87
3.85
2.25
2.24
2.22
2.07
2.04
1.86
1.50
1.46
1.43
Boc
NBn
NHBoc
OMe
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1.00
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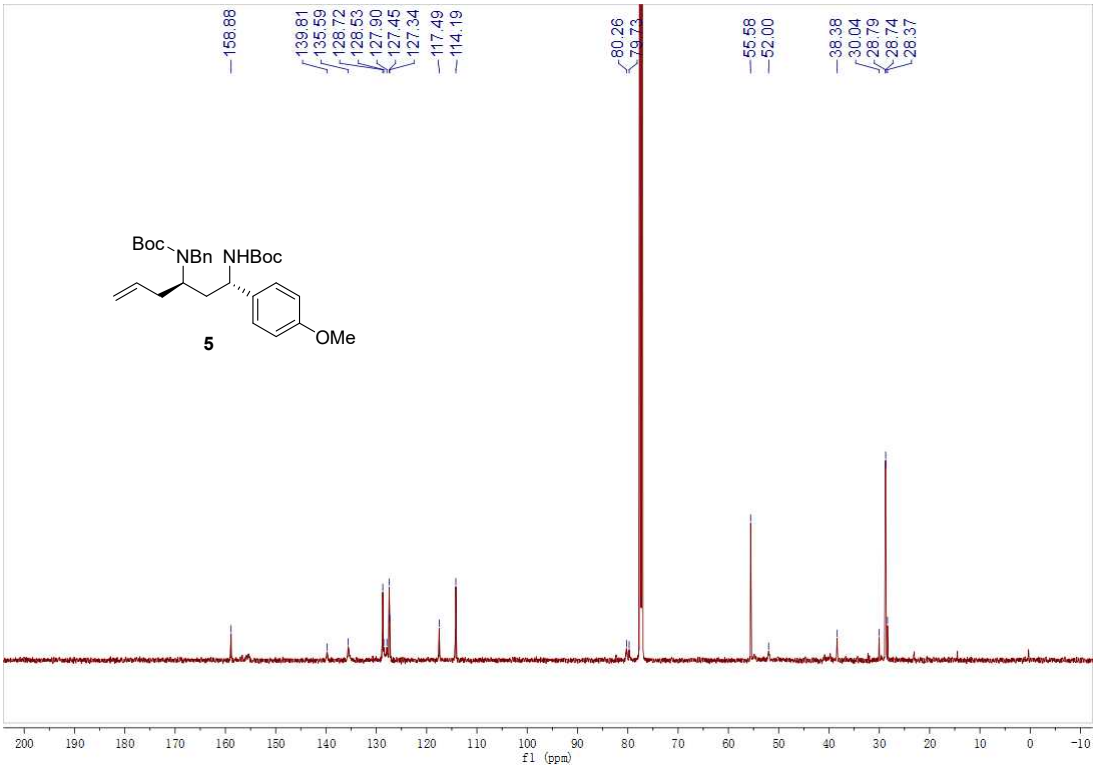
2.04
1.97
18.22
f1 (ppm)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114.19
80.26
79.73
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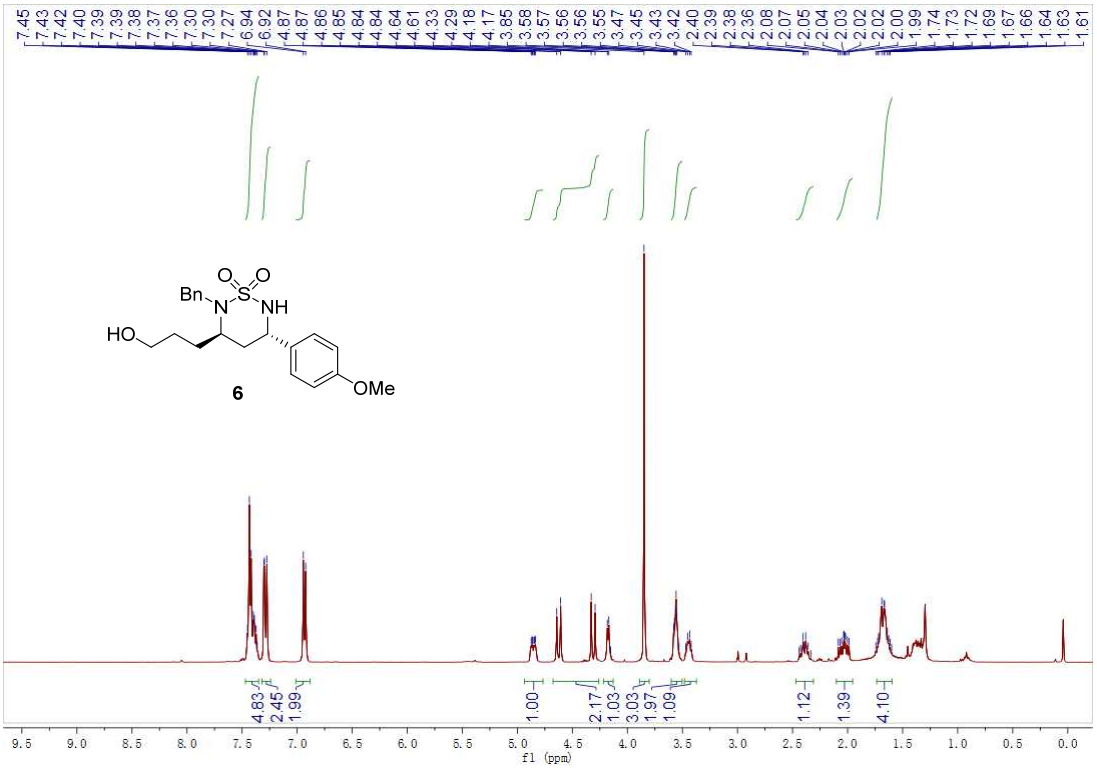
30.04
28.79
28.74
28.37
Boc
NBn
NHBoc
OMe
5
f1 (ppm)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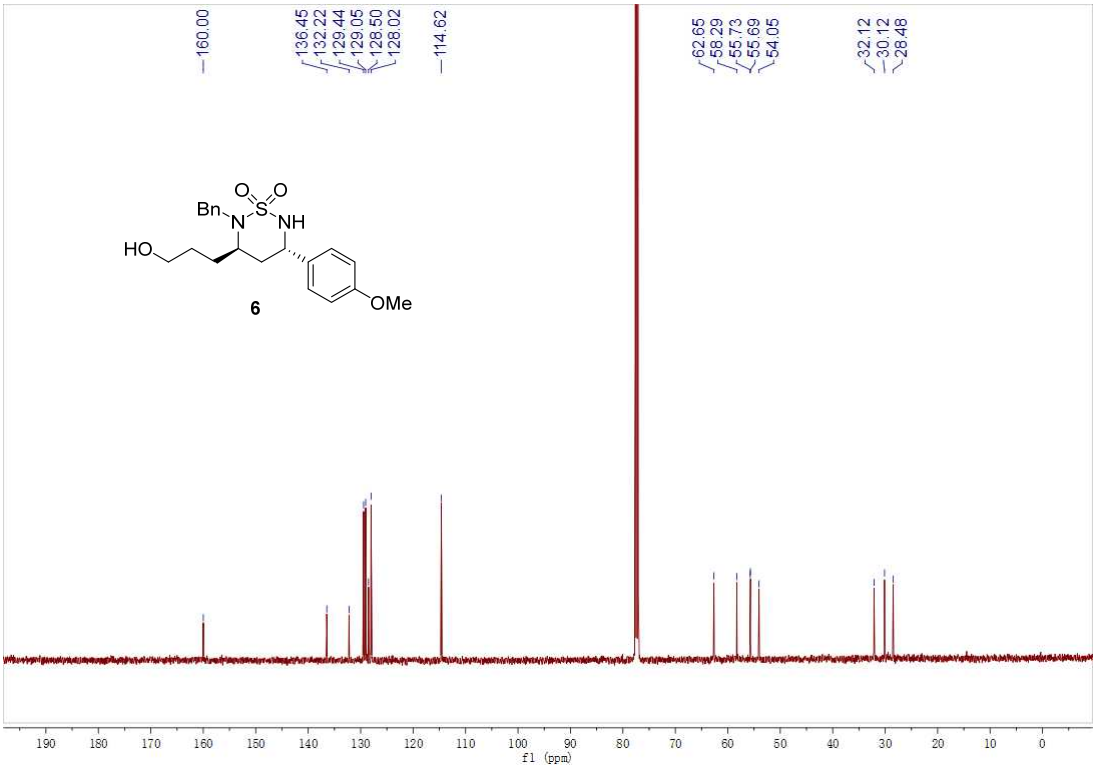
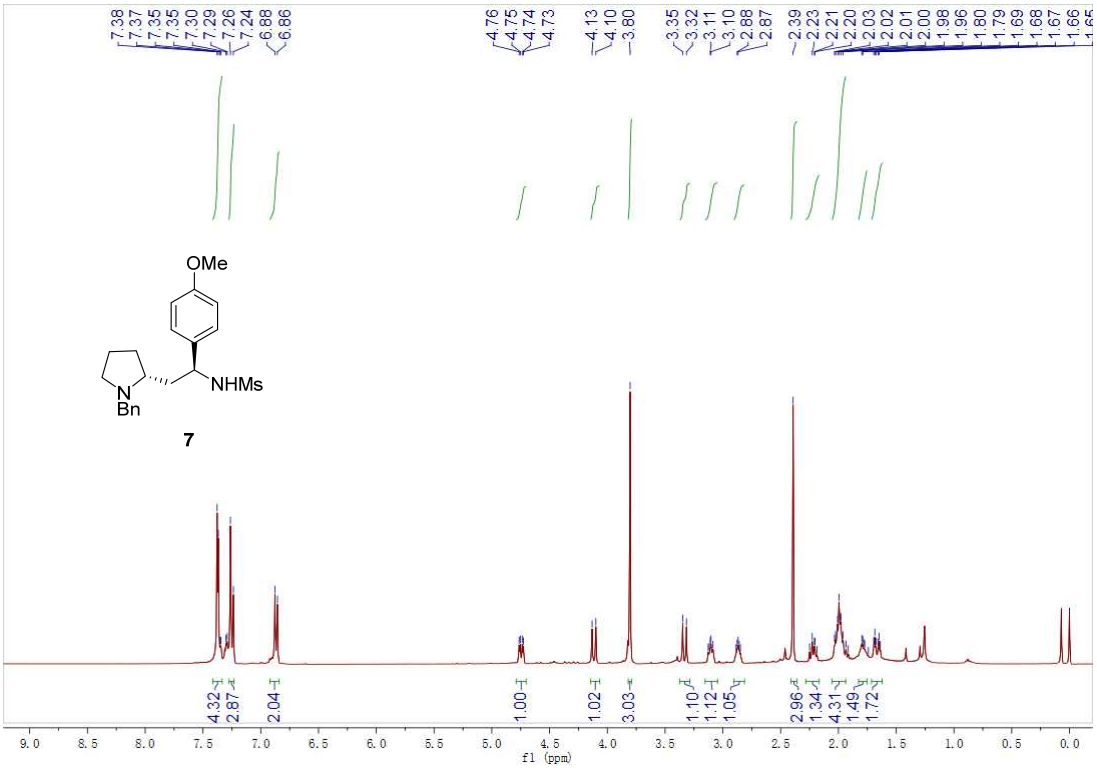
Bn
N
S
O
O
NH
HO
OMe
6
4.83 2.45 1.99 1.00 2.17 1.03 3.03 1.97 1.09 1.12 1.39 4.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


160.00 136.45 132.22 129.44 129.05 128.50 128.02 114.62 62.65 58.29 55.73 55.69 54.05 32.12 30.12 28.48
Bn
N
S
O
O
NH
HO
OMe
6
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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4.73
4.13
4.10
3.80
3.35
3.32
3.11
3.10
2.88
2.87
2.39
2.23
2.21
2.20
2.03
2.02
2.01
2.00
1.98
1.96
1.80
1.79
1.69
1.68
1.67
1.66
OMe
NHMs
N
Bn
7
4.32
2.87
2.04
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1.10
1.12
1.05
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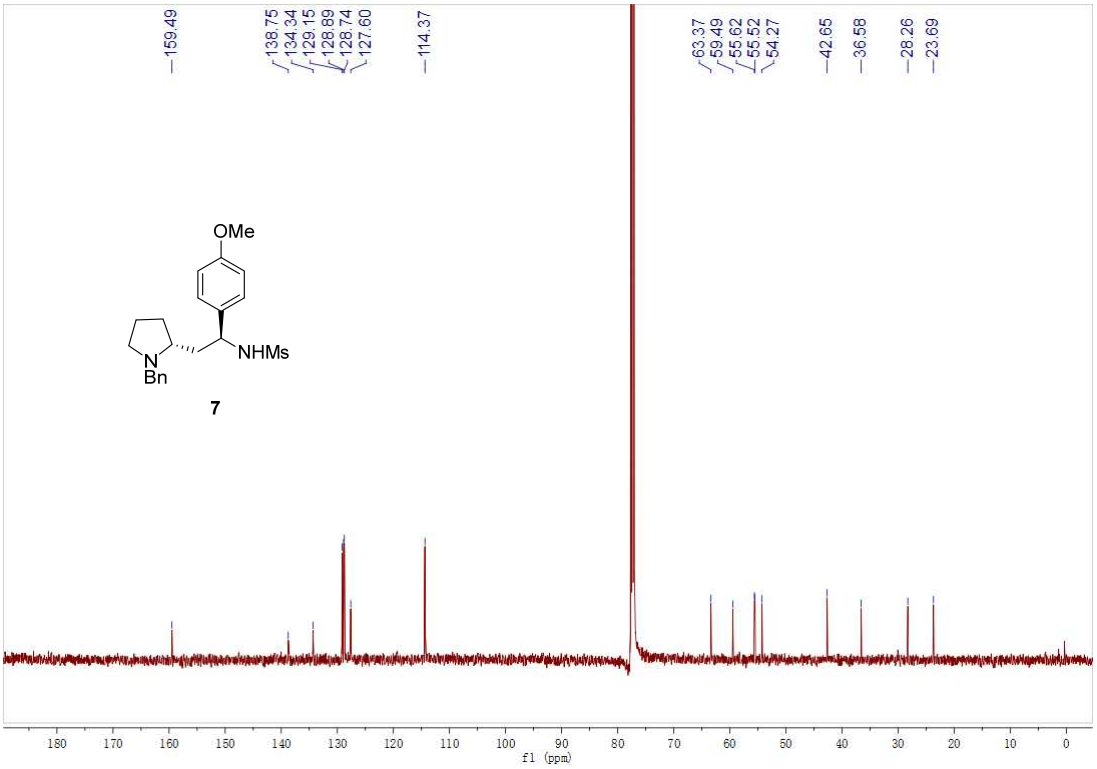
1.72
f1 (ppm)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42.65
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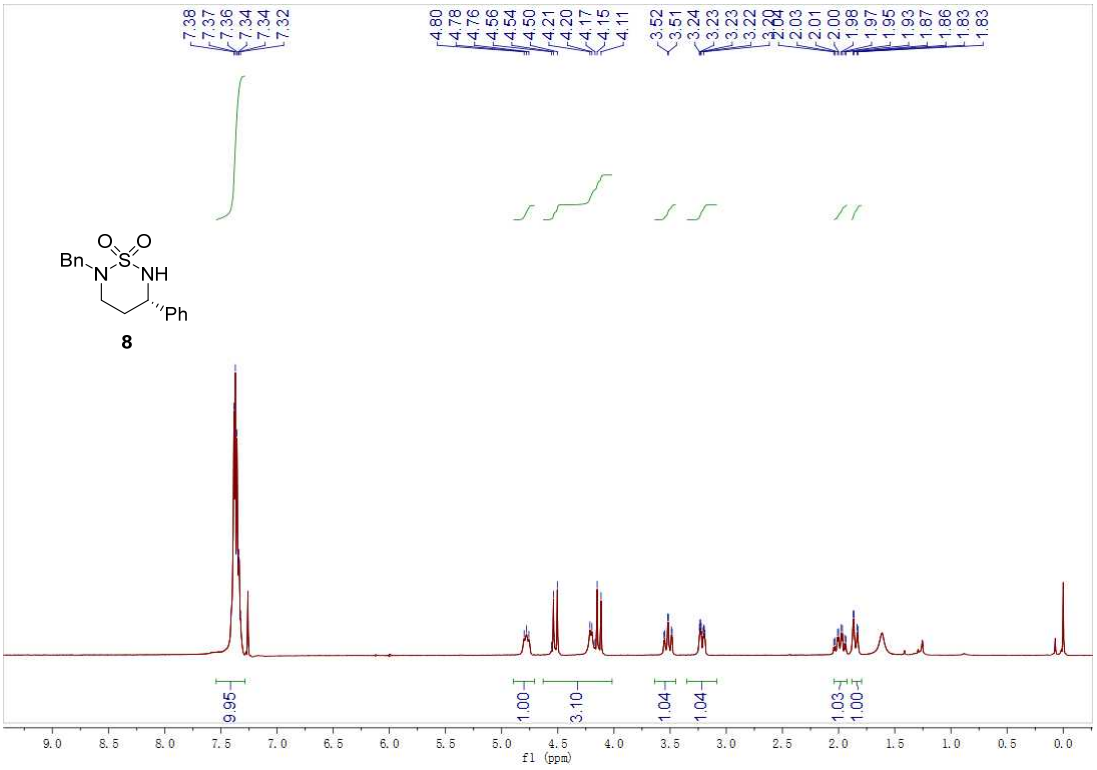
28.26
23.69
OMe
NHMs
N
Bn
7
f1 (ppm)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4.20
4.17
4.15
4.11
3.52
3.51
3.24
3.23
3.23
3.22
2.03
2.01
2.00
1.98
1.97
1.95
1.93
1.87
1.86
1.83
1.83
Bn
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O
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Ph
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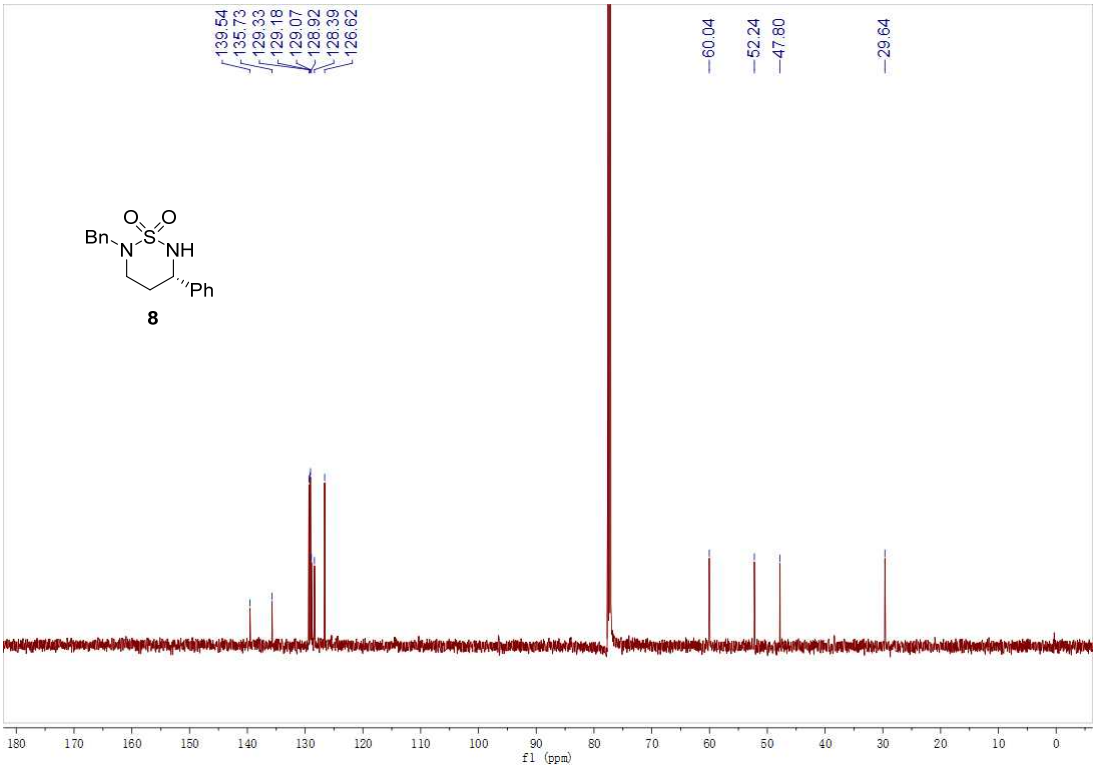
1.04
1.03
1.00
f1 (ppm)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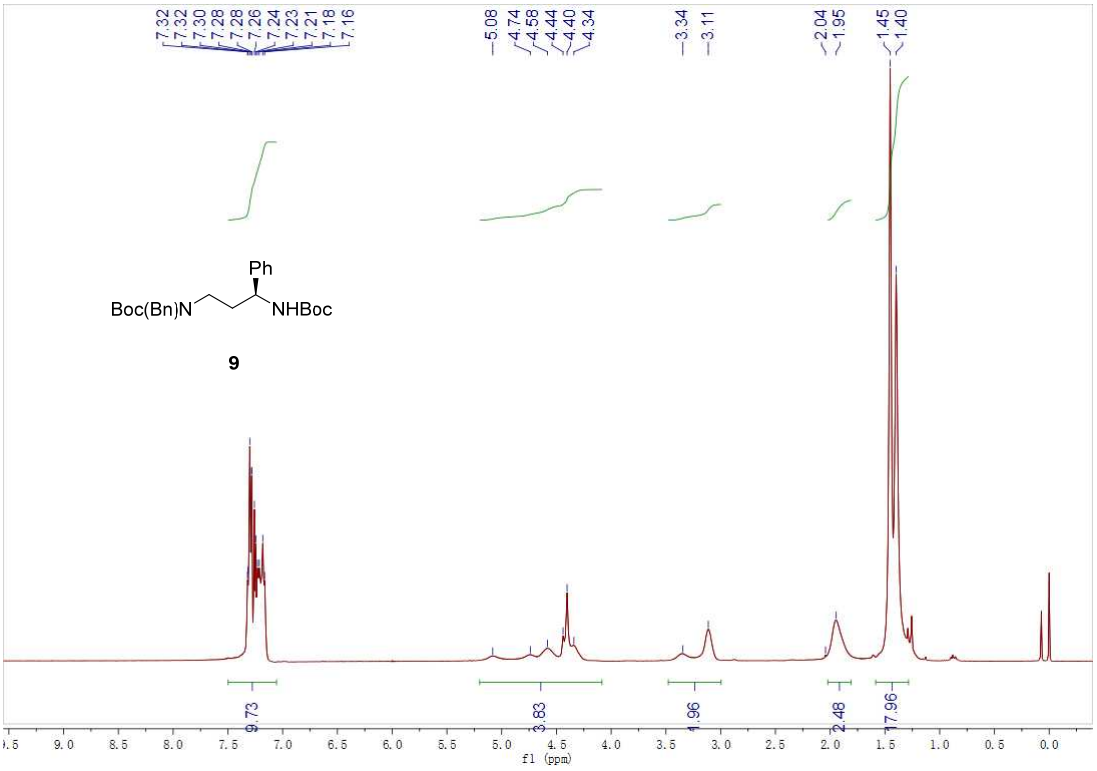
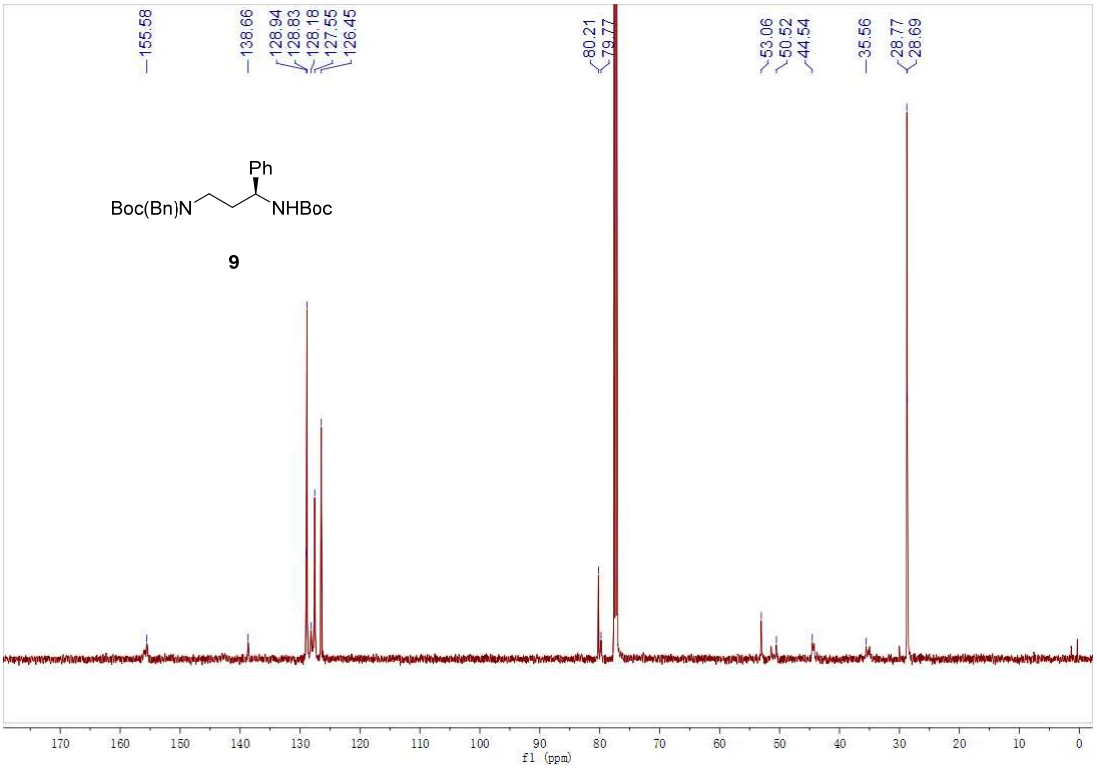
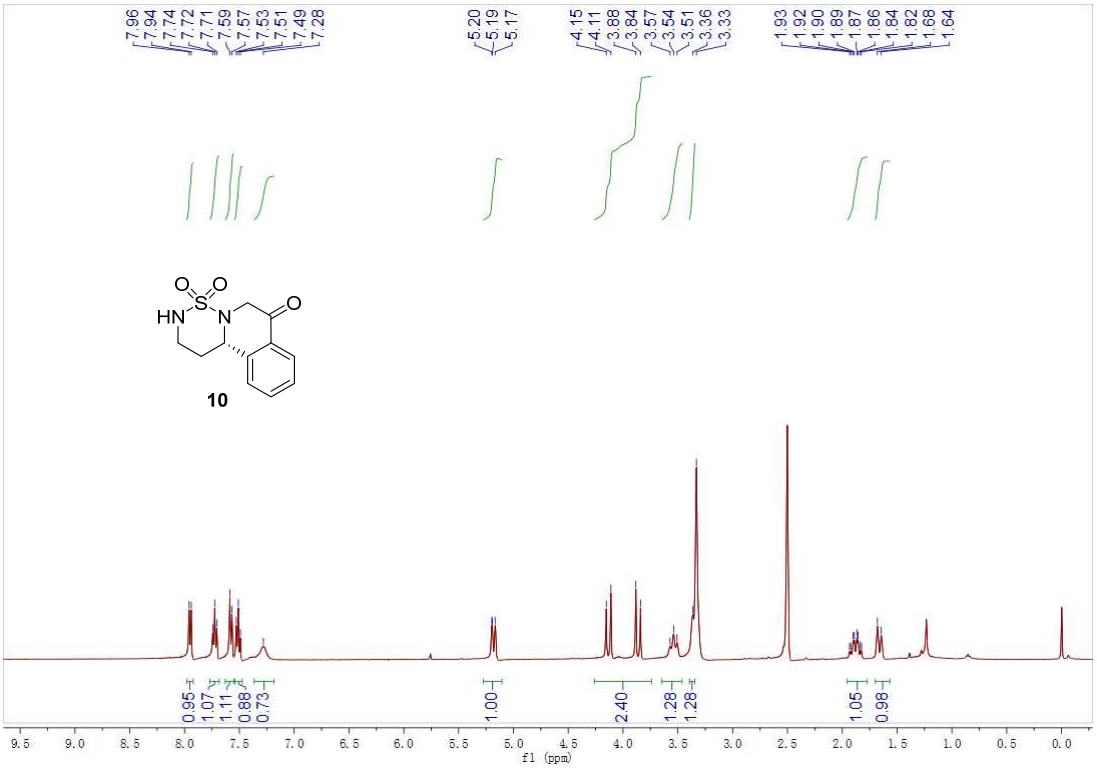
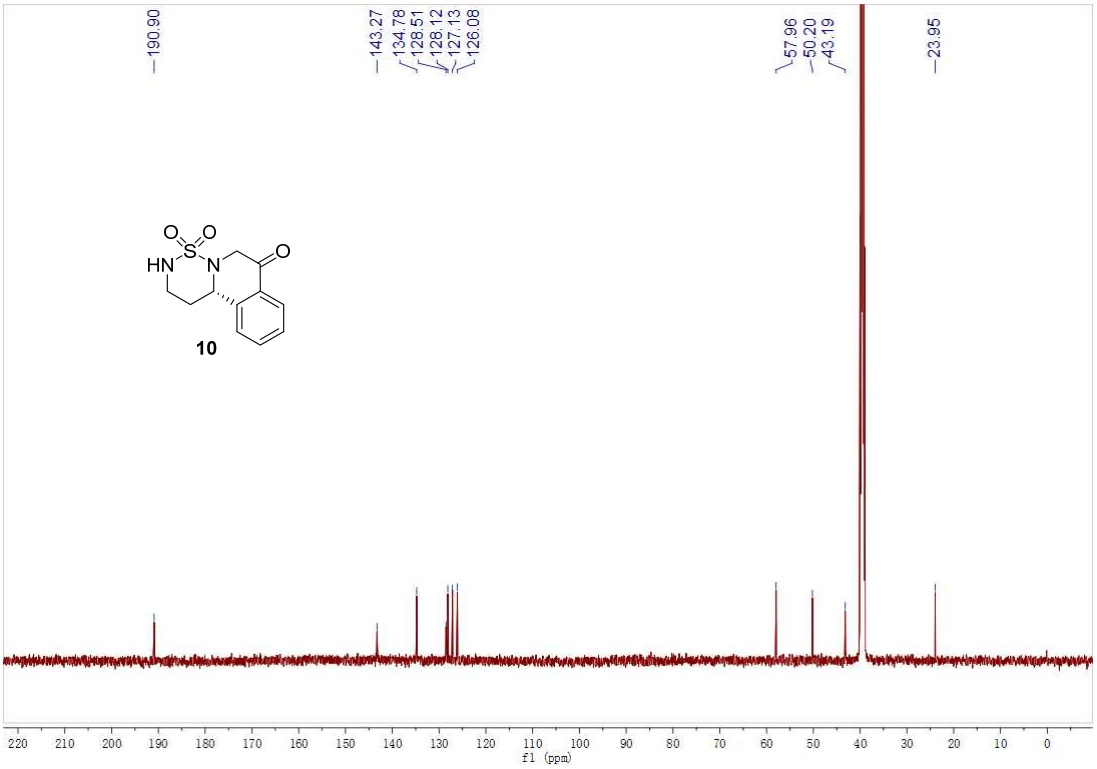
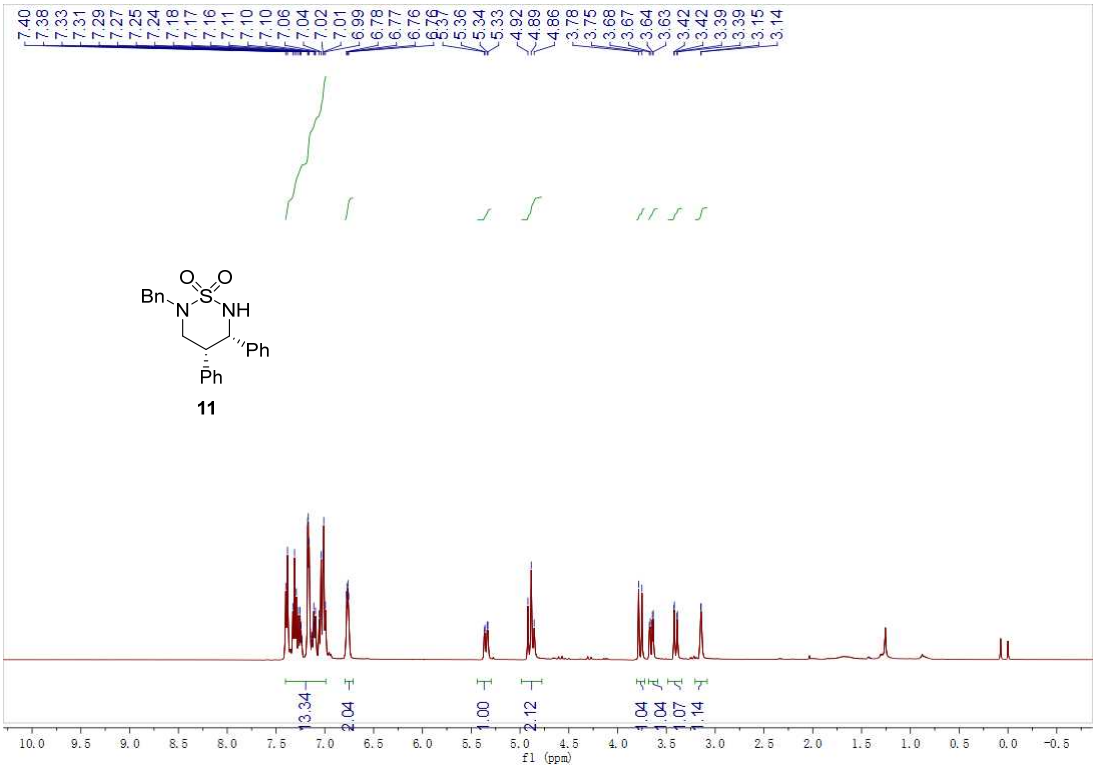
129.18
129.07
128.92
128.39
126.62
60.04
52.24
47.80
29.64
Bn
N
S
O
O
NH
Ph
8
f1 (ppm)

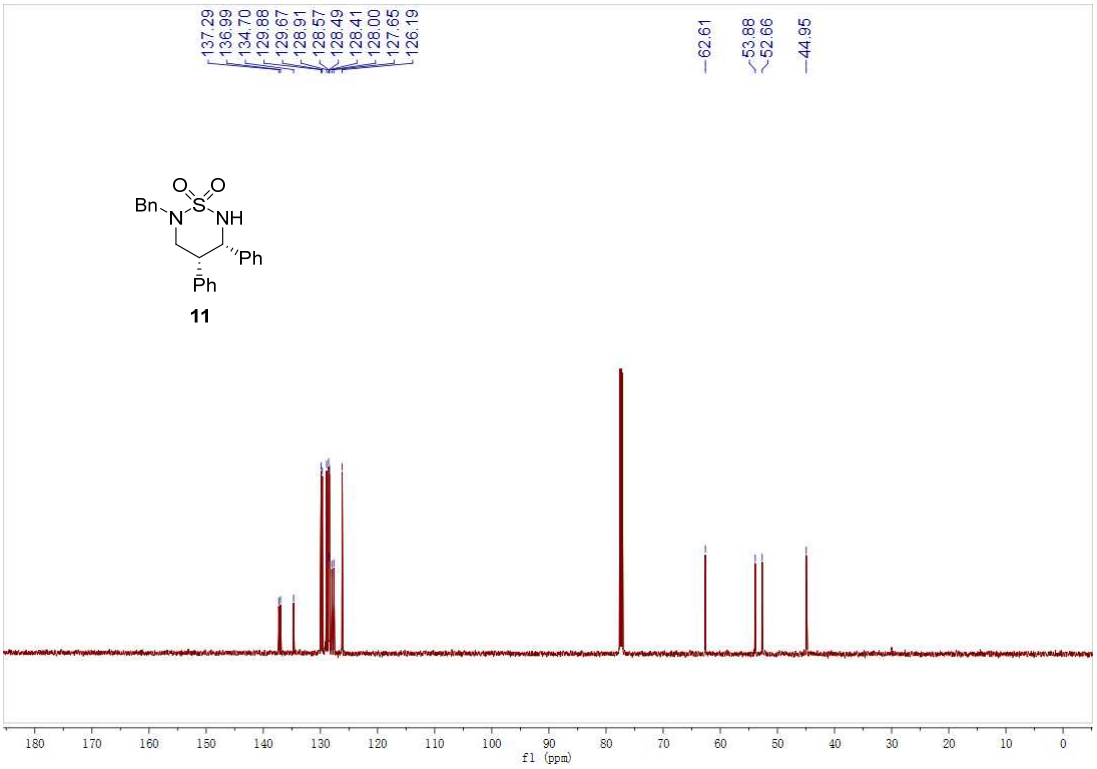

7.32
7.32
7.30
7.28
7.28
7.26
7.24
7.23
7.21
7.18
7.16
5.08
4.74
4.58
4.44
4.40
4.34
3.34
3.11
2.04
1.95
1.45
1.40
Ph
Boc(Bn)N
NHBoc
9
9.73
3.83
4.96
2.48
17.96
f1 (ppm)

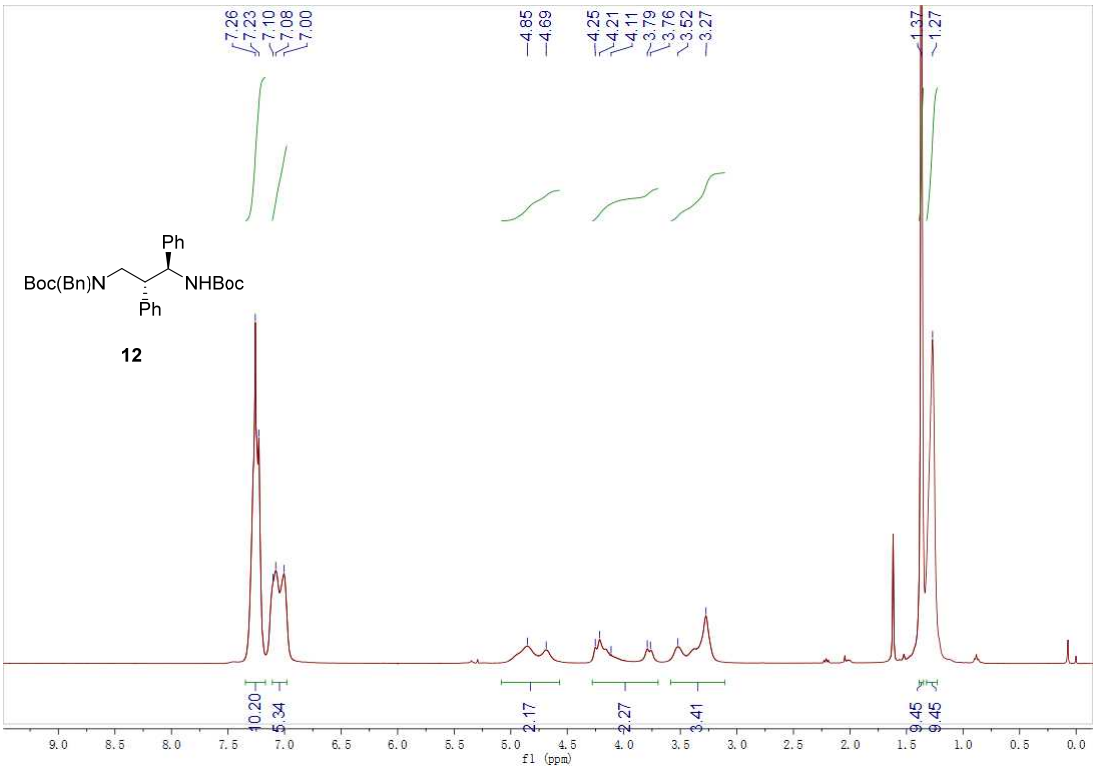

155.58
138.66
128.94
128.83
128.18
127.55
126.45
80.21
79.77
53.06
50.52
44.54
35.56
28.77
28.69
Ph
Boc(Bn)N
NHBoc
9
f1 (ppm)

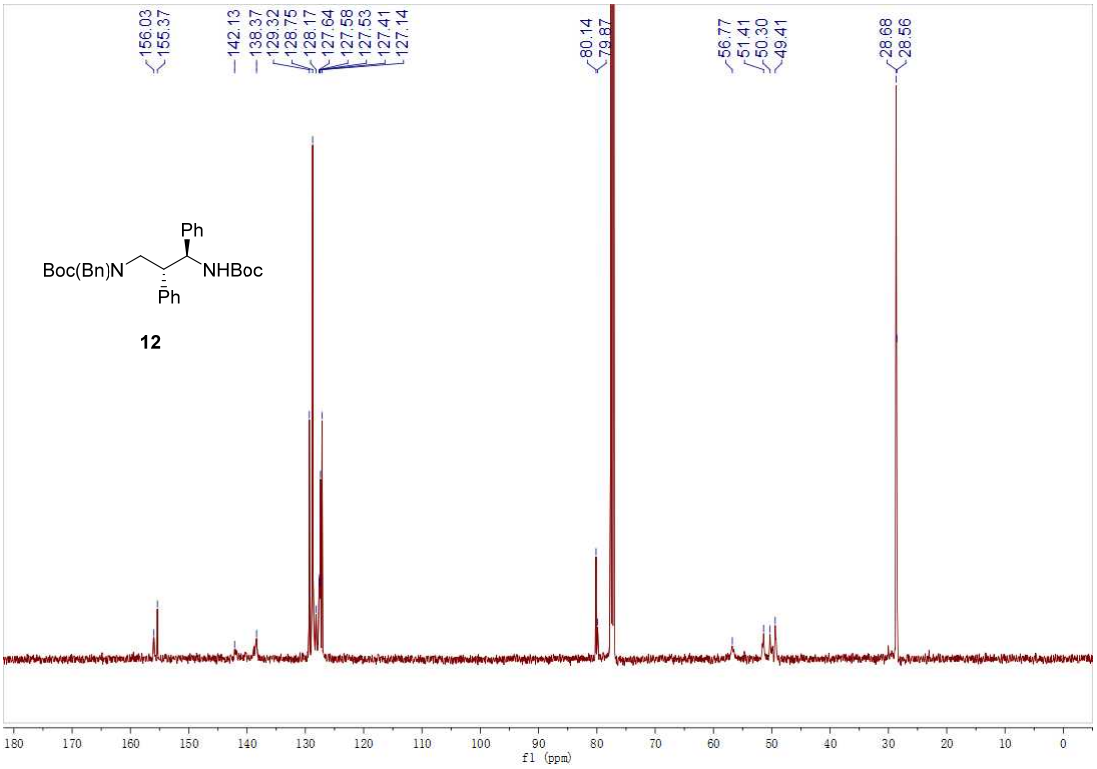

7.96
7.94
7.74
7.72
7.71
7.59
7.57
7.53
7.51
7.49
7.28
5.20
5.19
5.17
4.15
4.11
3.88
3.84
3.57
3.54
3.51
3.36
3.33
1.93
1.92
1.90
1.89
1.87
1.86
1.84
1.82
1.68
1.64
HN
S
N
O
O
O
10
0.95
1.07
1.11
0.88
0.73
1.00
2.40
1.28
1.28
1.05
0.98
f1 (ppm)


190.90
143.27
134.78
128.51
128.12
127.13
126.08
57.96
50.20
43.19
23.95
HN
S
N
O
O
O
10
f1 (ppm)


7.40
7.38
7.33
7.31
7.29
7.27
7.25
7.24
7.18
7.17
7.16
7.11
7.10
7.06
7.04
7.02
7.01
6.99
6.78
6.77
6.76
5.37
5.36
5.34
5.33
4.92
4.89
4.86
3.78
3.75
3.68
3.67
3.64
3.63
3.42
3.42
3.39
3.39
3.15
3.14
Bn
N
S
O
O
NH
Ph
Ph
11
13.34
2.04
1.00
2.12
1.04
1.04
1.07
1.14
f1 (ppm)


137.29
136.99
134.70
129.88
129.67
128.91
128.57
128.49
128.41
128.00
127.65
126.19
62.61
53.88
52.66
44.95
Bn
N
S
O
O
NH
Ph
Ph
11
f1 (ppm)


7.26
7.23
7.10
7.08
7.00
4.85
4.69
4.25
4.21
4.11
3.79
3.76
3.52
3.27
1.37
1.27
Ph
Boc(Bn)N
NHBoc
Ph
12
10.20
5.34
2.17
2.27
3.41
9.45
9.45
f1 (ppm)


156.03
155.37
142.13
138.37
129.32
128.75
128.17
127.64
127.58
127.53
127.41
127.14
80.14
79.87
56.77
51.41
50.30
49.41
28.68
28.56
Ph
Boc(Bn)N
NHBoc
Ph
12
f1 (ppm)