Supporting Information

Chiral Pentacarboxycyclopentadiene-based Brønsted Acid Catalyzed Enantioselective Desymmetrization of *meso*-Epoxides by 2-Mercaptobenzothiazoles

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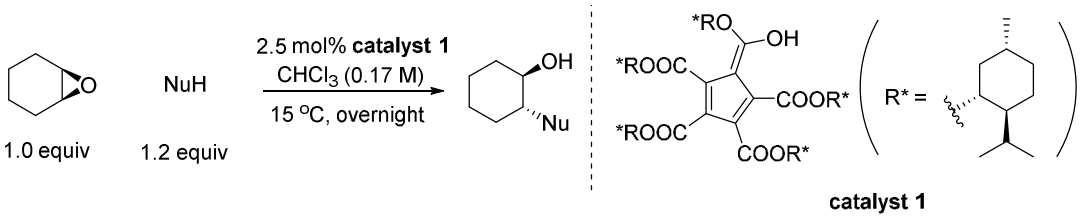
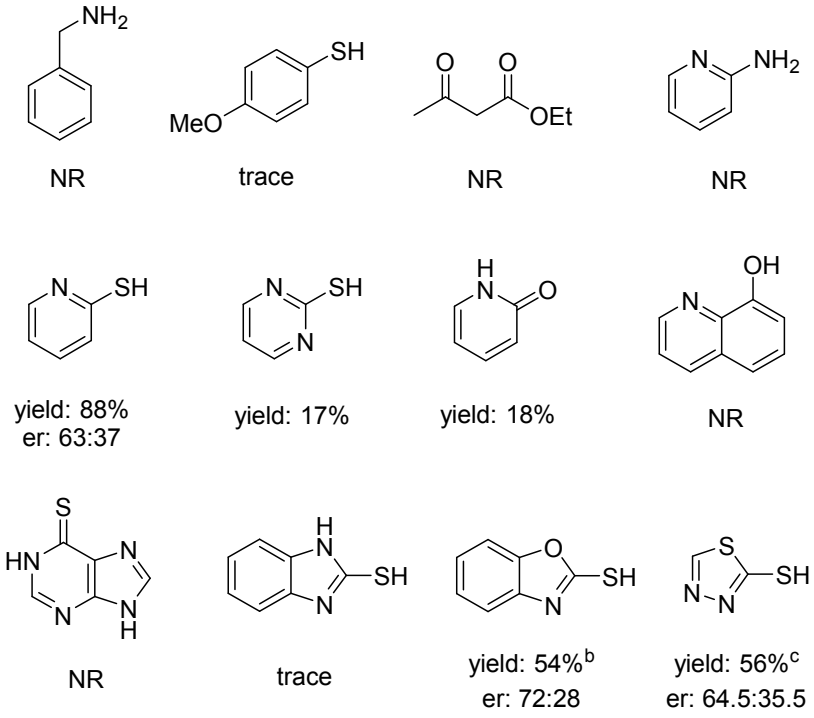
Contents:

1. Experimental details of the condition optimization

Table S1. Nucleophiles optimization[a]

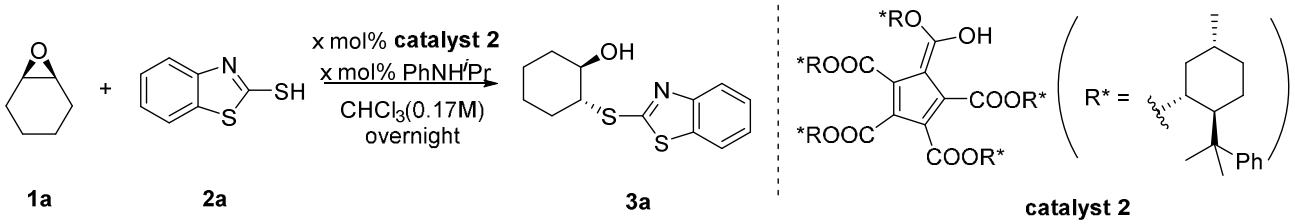


NuH:



[a] Isolated yield. [b] Run at 22 °C. [c] 2.5 mol% **catalyst 2** was used.

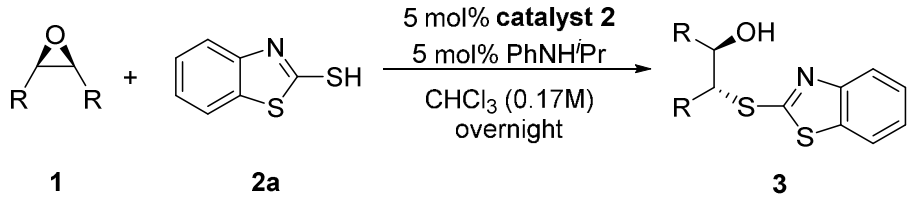
Table S2. Temperature optimization[a]



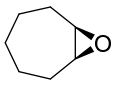
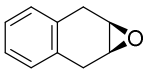
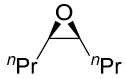
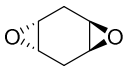
entry	temp (^{o}C)	x	yield (%)	er
1[b]	25	2.5	99	82.5: 17.5
2	0	2	57	69.5:30.5
3	10	2	88	85.5:14.5
4	15	2	93	86.5:13.5
5	20	2	94	86:14
6	25	2	99	85.5:14.5
7	15	5	99	89.5:10.5

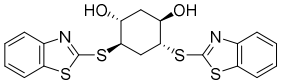
[a] Isolated yield. [b] PhNH^{i}Pr was not added.

Table S3. Epoxides and temperature optimization[a]



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

entry	epoxide	temp (^{o}C)	yield (%)	er
1		15	trace	/
		30	54, 73[b]	80:20, 81.5:18.5[b]
		40	72	74:26
		55	98	70.5:29.5
2		15	74[c]	87:13[c]
		30	94[b]	84:16[b]
3		15	42	74.5:25.5
		30	84, 80[b]	85:15, 86.5:13.5[b]
		40	67	82.5:17.5
		55	58	73.5:26.5
4		15	32	65:35
		30	93[b]	81.5:18.5[b]
		40	76	77:23
5		15	7	70:30
		30	62[b, d]	68:32[b, d]
		55	62	59:41
6[e, f]		15	1	74:26
		30	49	89:11
		40	58	81.5:18.5
		55	53	78:22

[a] Isolated yield. [b] 10 mol % catalyst loading. [c] 15 mol % catalyst loading. [d] Reaction time: 24 h. [e] 2.2 eq of thiol was used. [f] Structure of product: 

2. NMR copies of all compounds

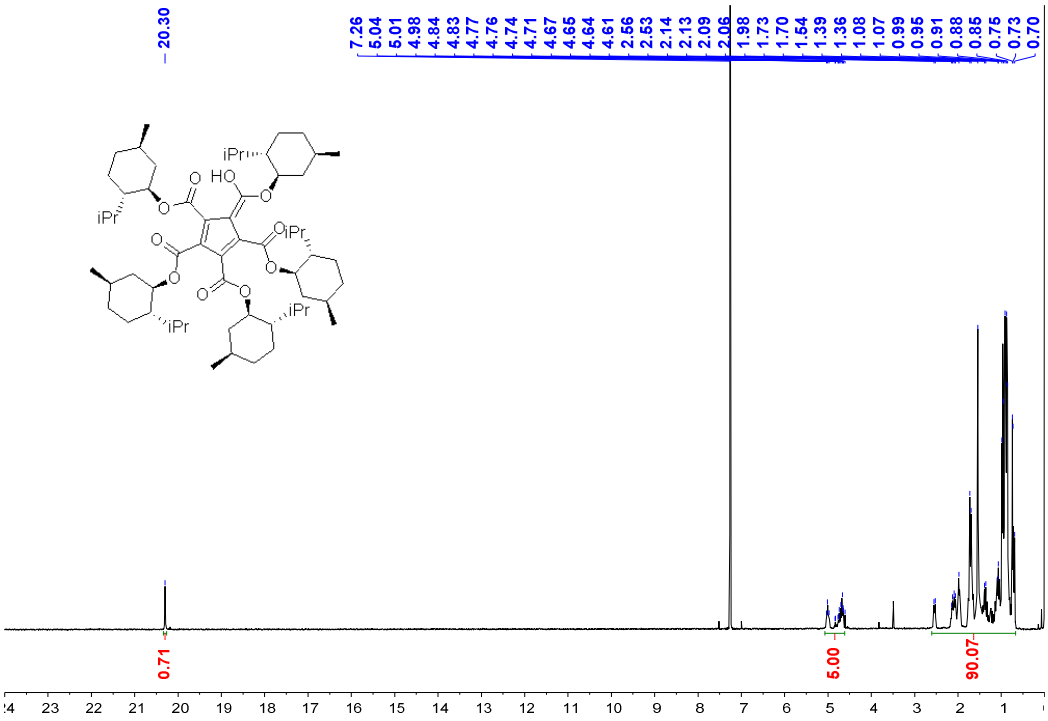


Figure S1. ^{1}H NMR spectrum of **Catalyst 1** in $CDCl_3$

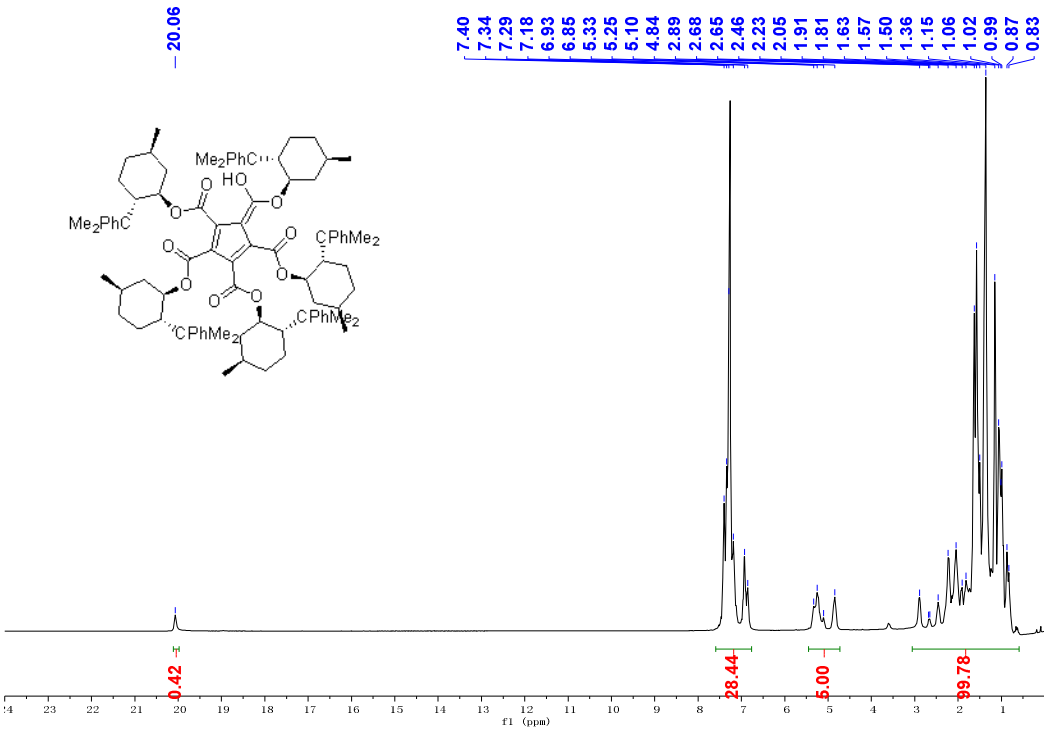


Figure S2. ^{1}H NMR spectrum of **Catalyst 2** in $CDCl_3$

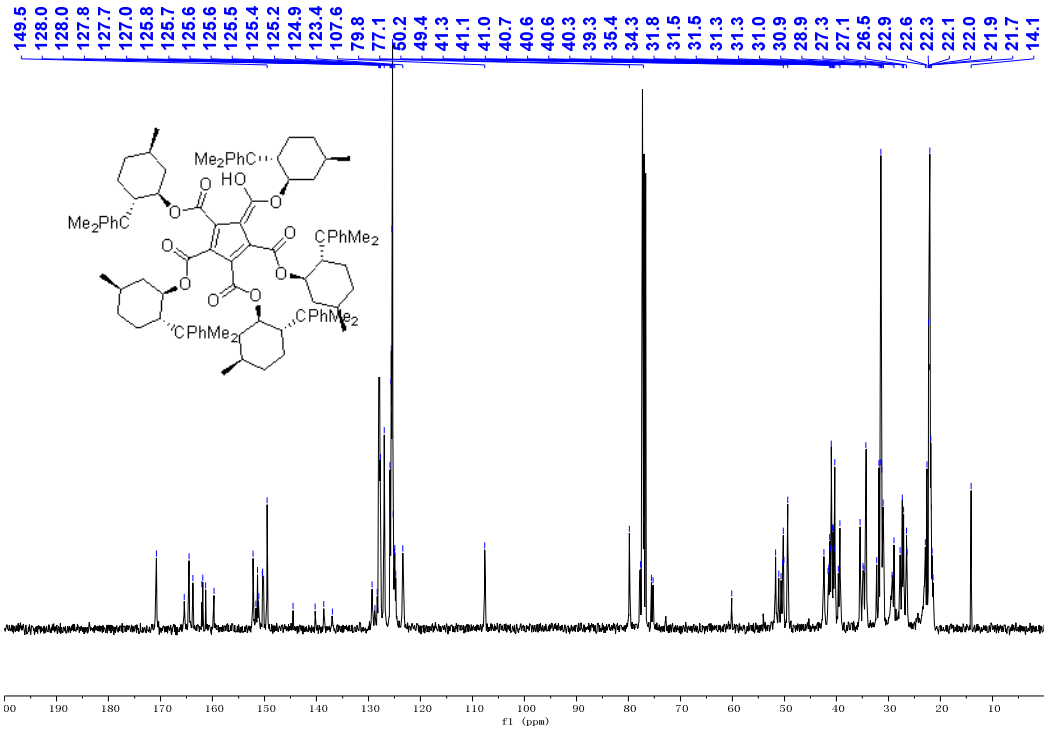


Figure S3. ^{13}C NMR spectrum of **Catalyst 2** in $CDCl_3$

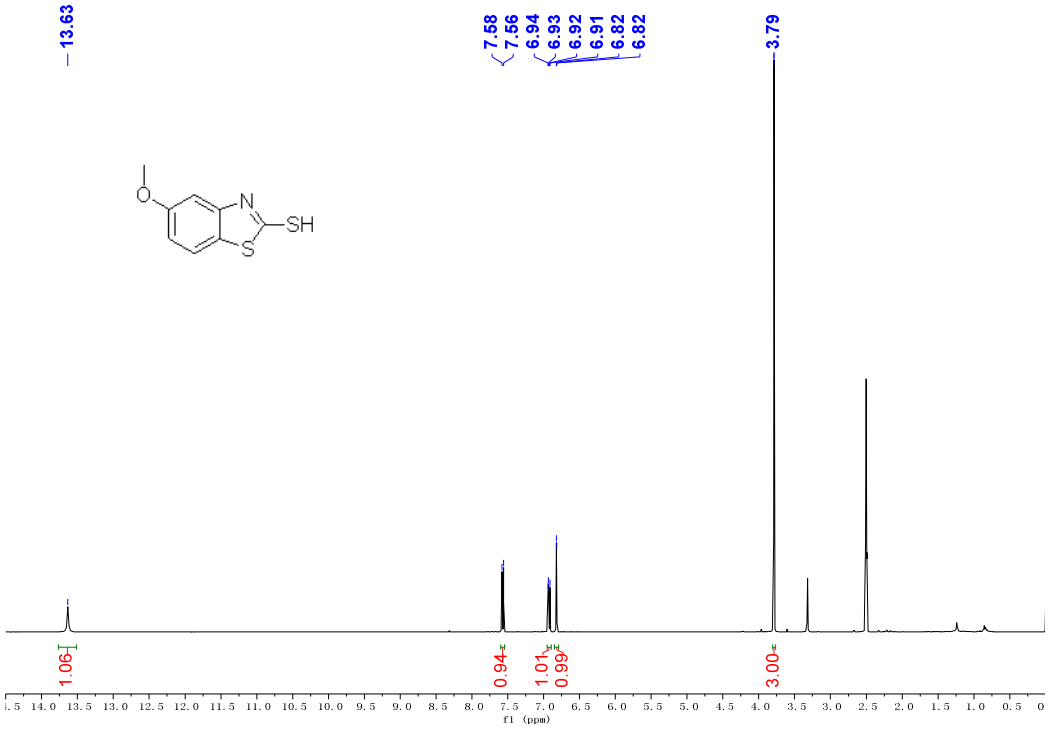


Figure S4. ^{1}H NMR spectrum of **2b** in DMSO-d_6

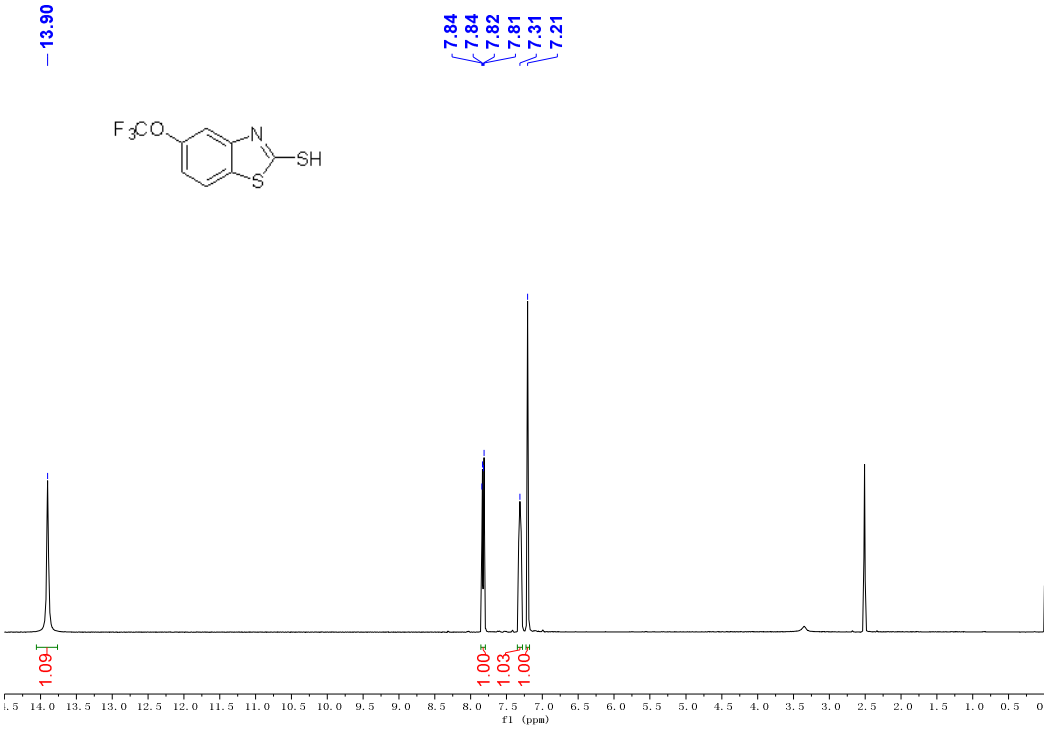


Figure S5. ^{1}H NMR spectrum of **2c** in DMSO-d_6

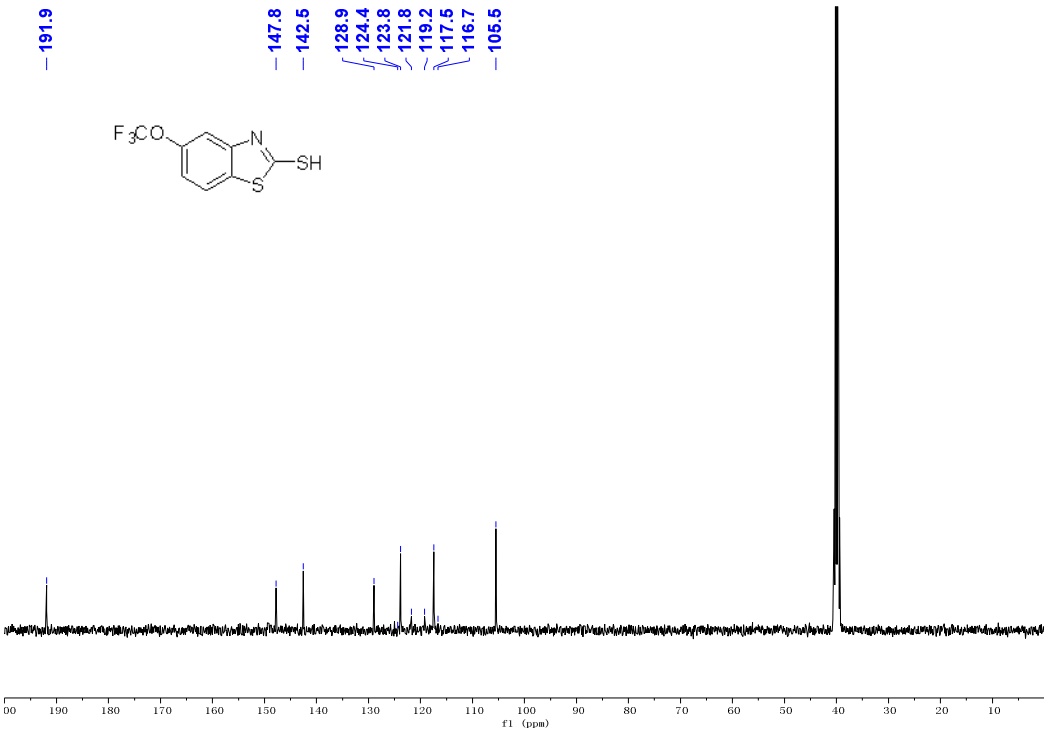


Figure S6. ^{13}C NMR spectrum of **2c** in DMSO-d_6

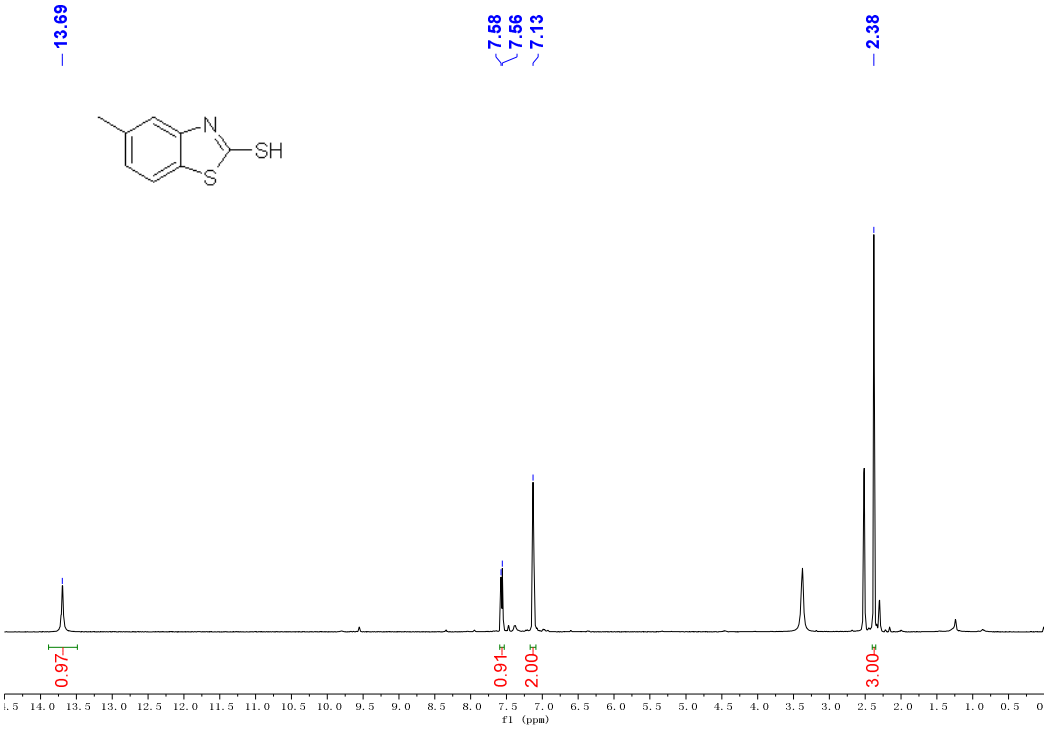


Figure S7. ^{1}H NMR spectrum of **2d** in DMSO-d_6

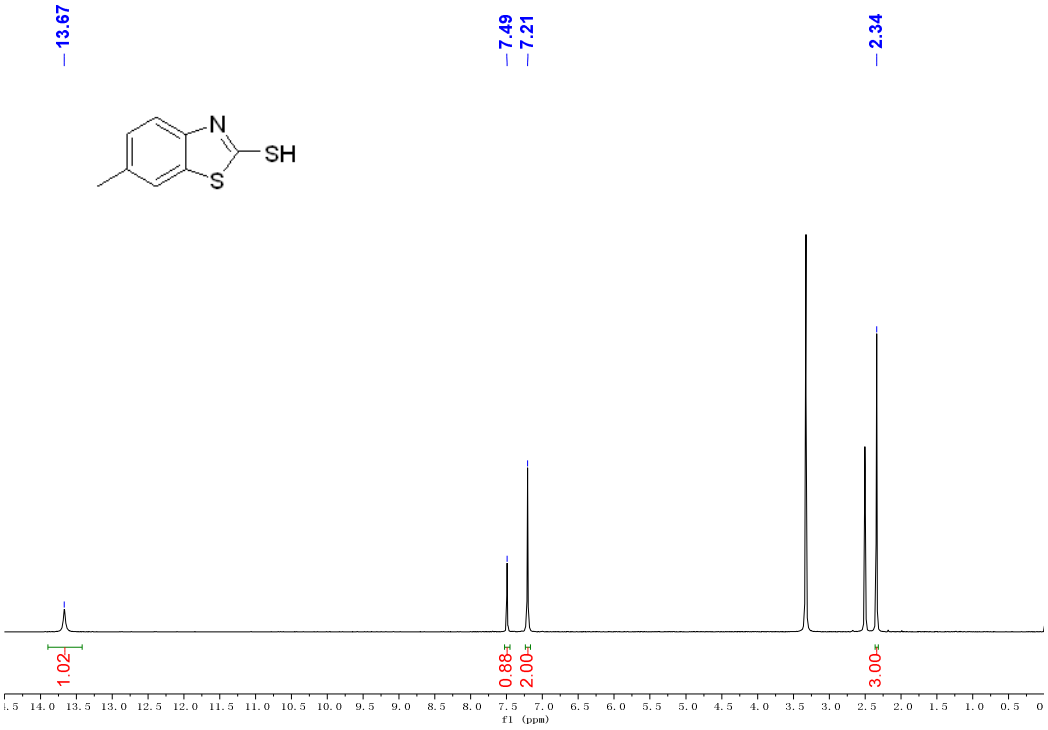


Figure S8. ^{1}H NMR spectrum of **2e** in DMSO-d_6

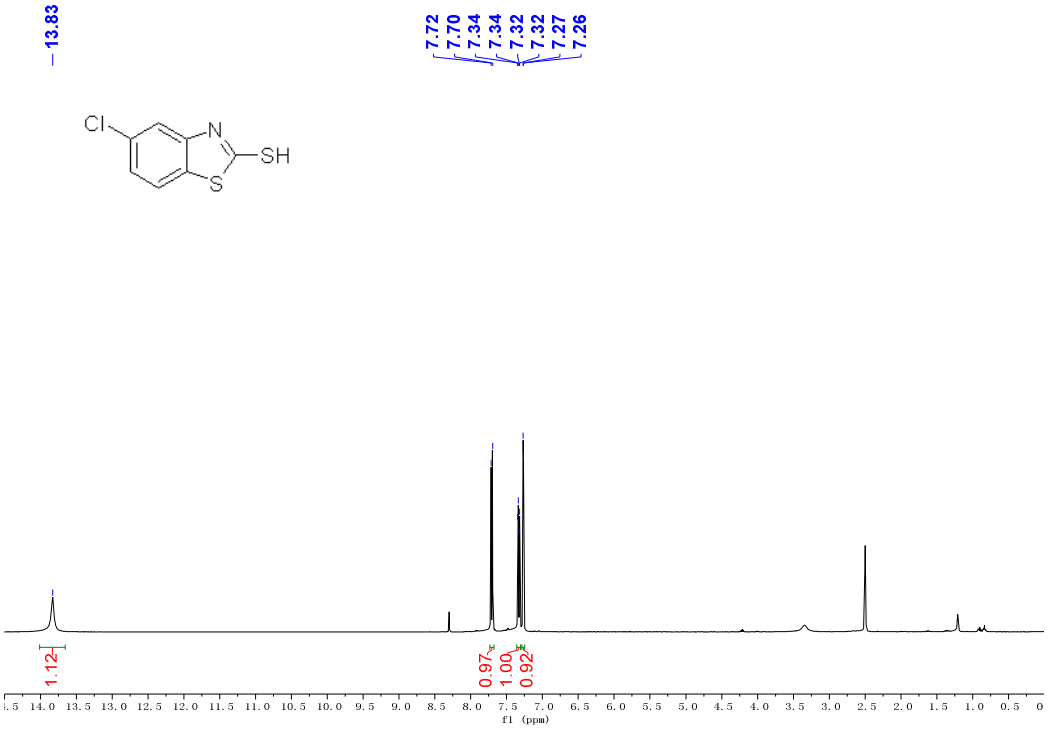


Figure S9. ^{1}H NMR spectrum of **2f** in DMSO-d_6

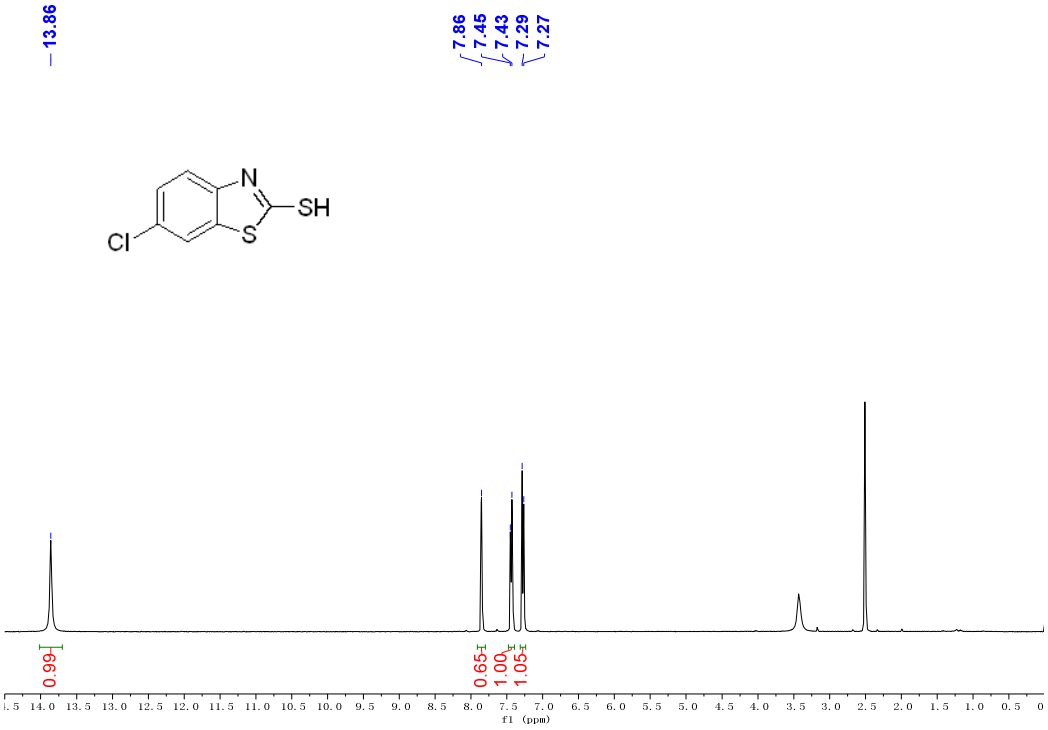


Figure S10. ^{1}H NMR spectrum of **2g** in DMSO-d_6

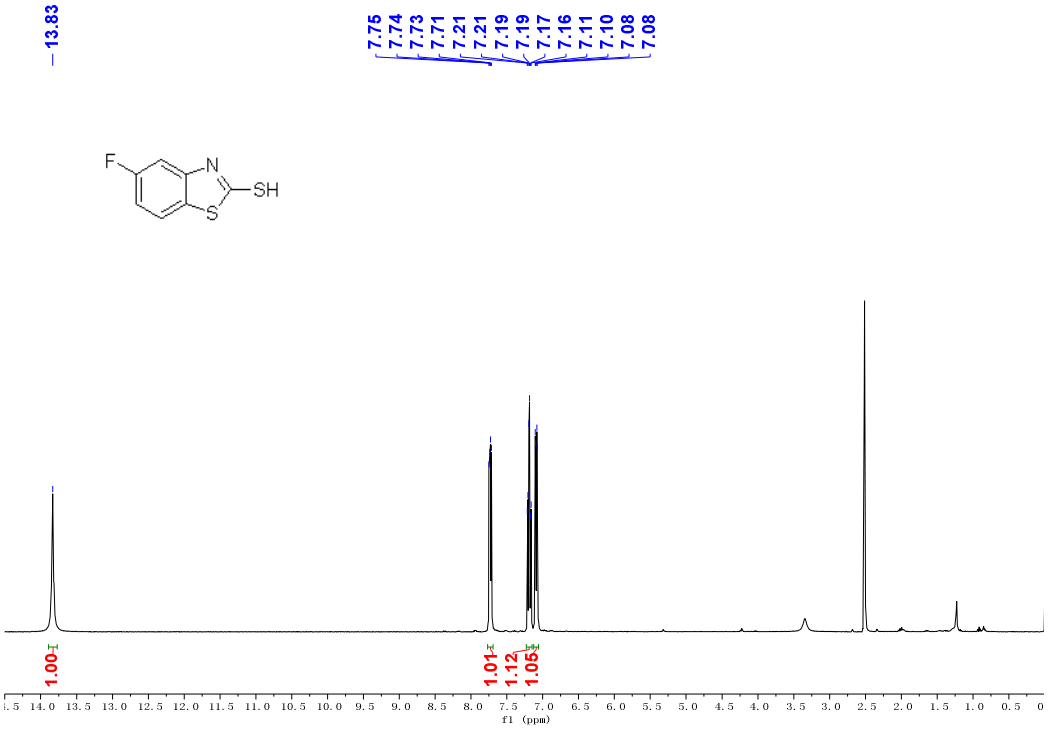


Figure S11. ^{1}H NMR spectrum of **2h** in DMSO-d_6

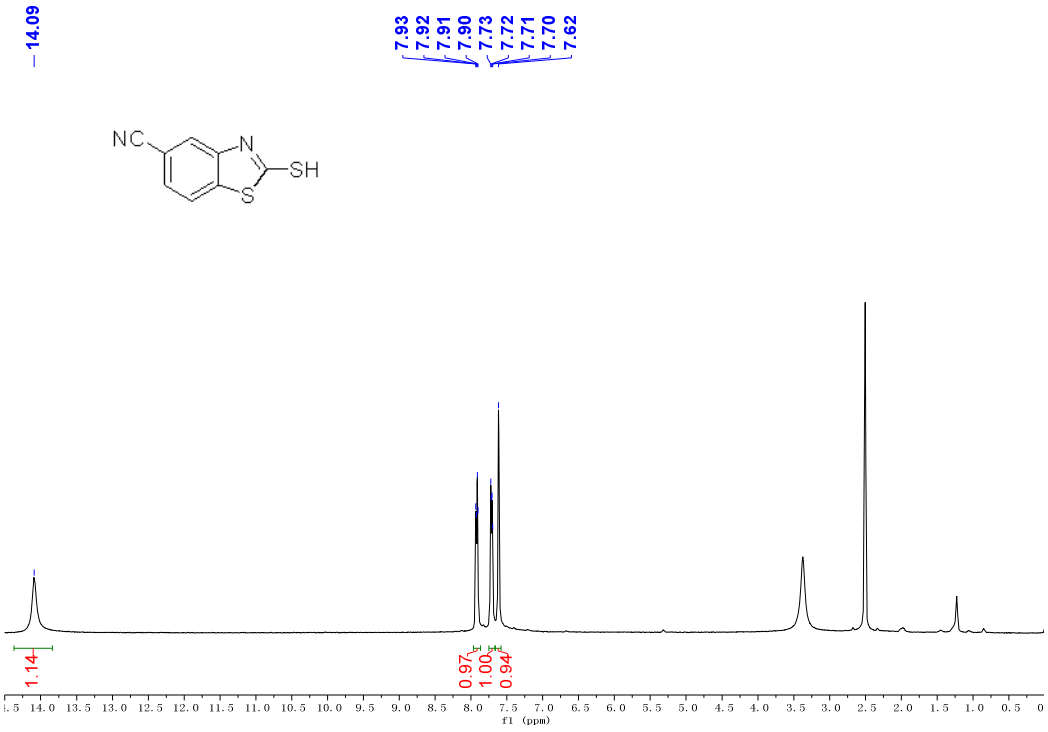


Figure S12. ^{1}H NMR spectrum of **2i** in DMSO-d_6

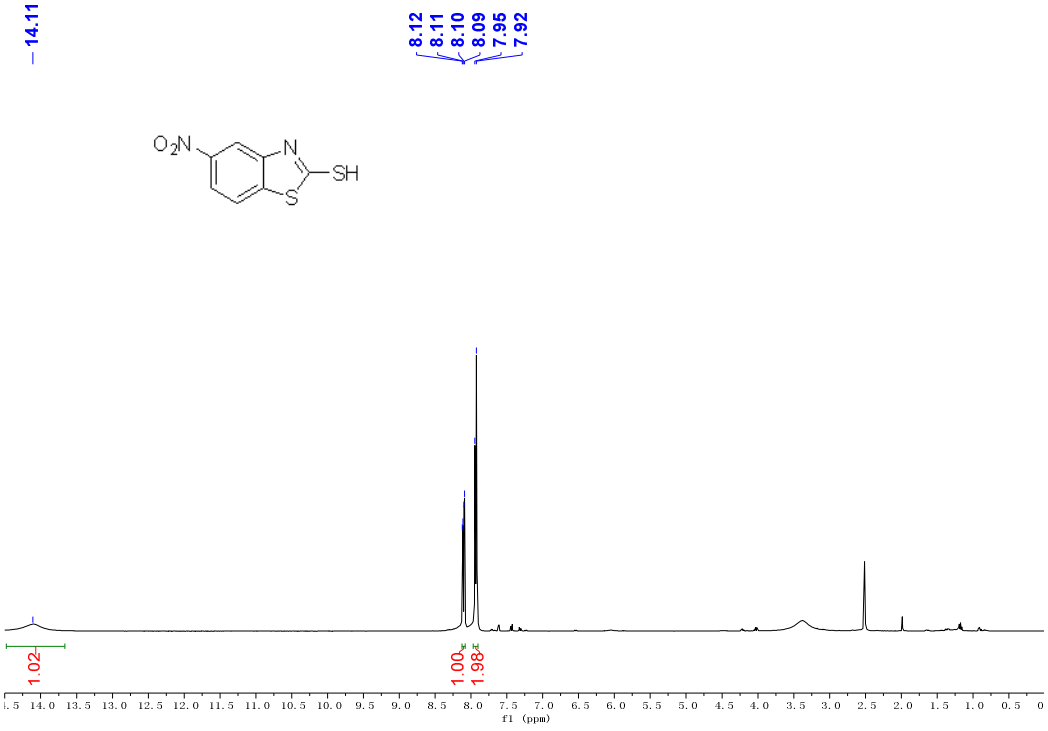


Figure S13. ^{1}H NMR spectrum of **2j** in DMSO-d_6

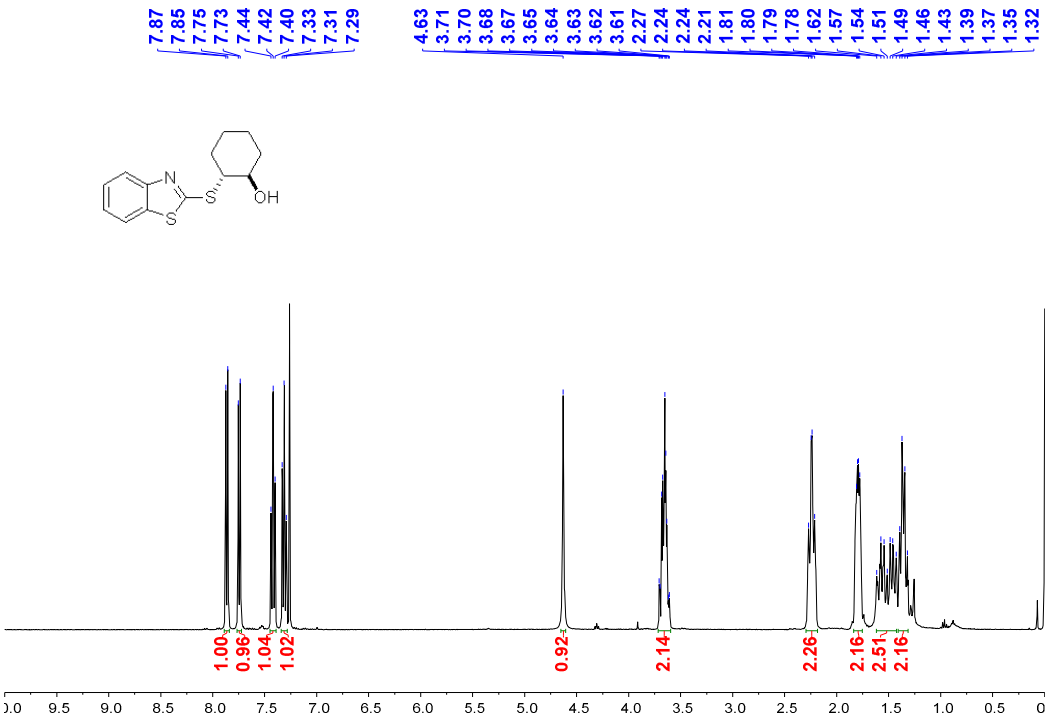


Figure S14. ^{1}H NMR spectrum of **3a** in $CDCl_3$

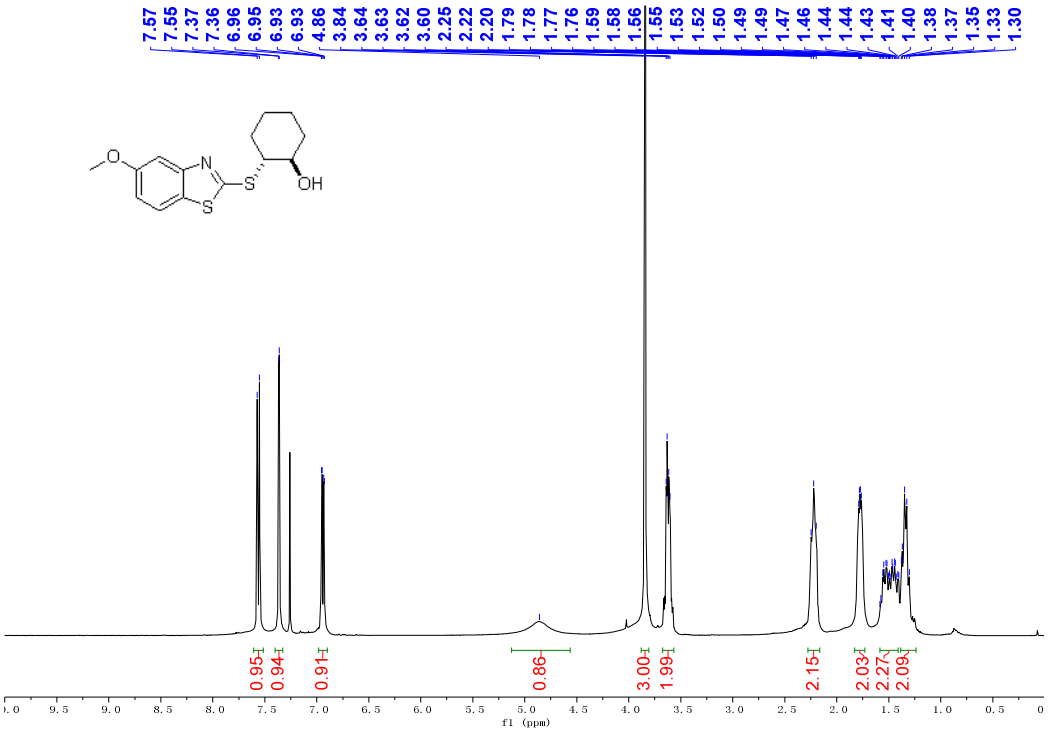


Figure S15. ^{1}H NMR spectrum of **3b** in $CDCl_3$

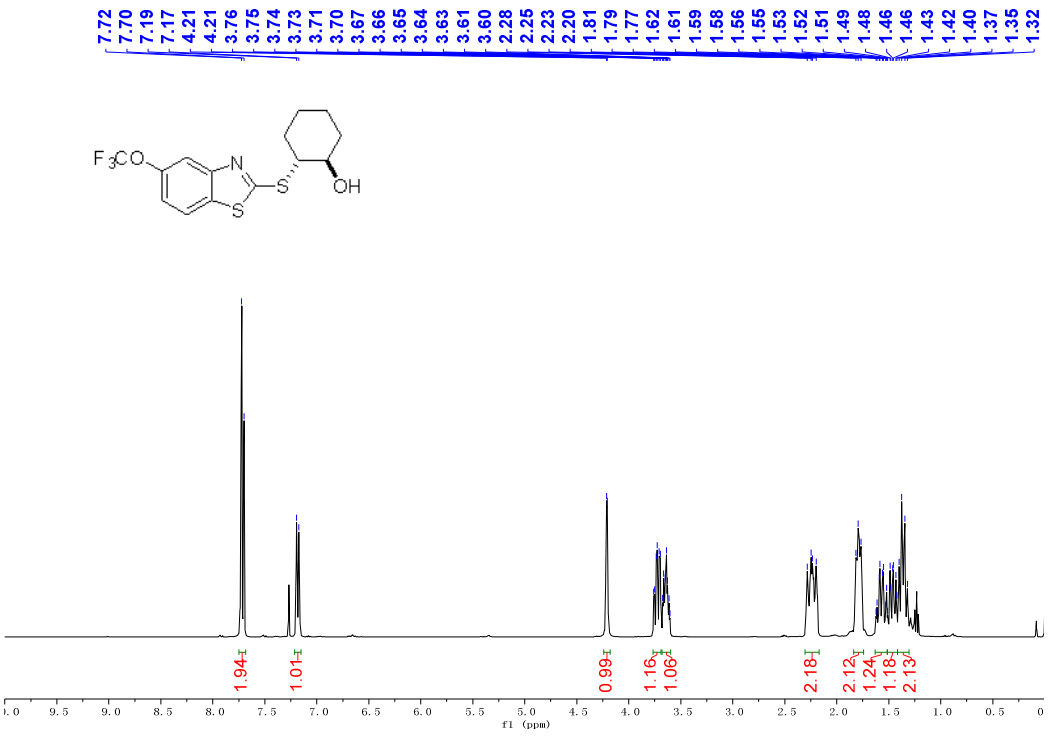


Figure S16. ^{1}H NMR spectrum of **3c** in $CDCl_3$

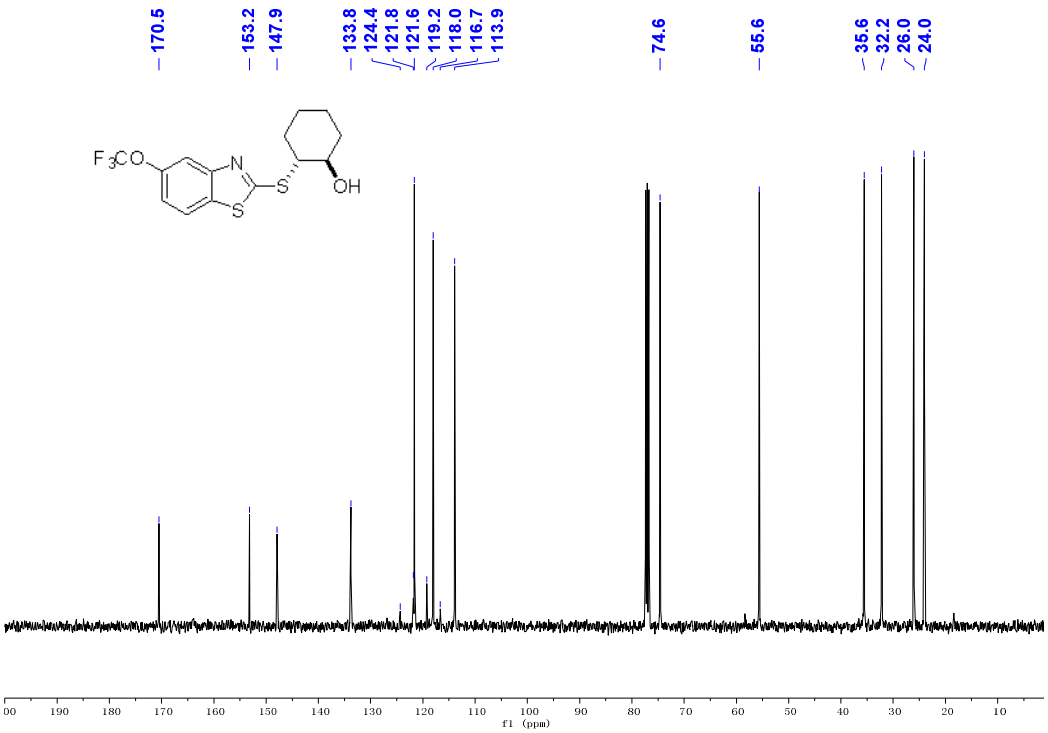


Figure S17. ^{13}C NMR spectrum of **3c** in $CDCl_3$

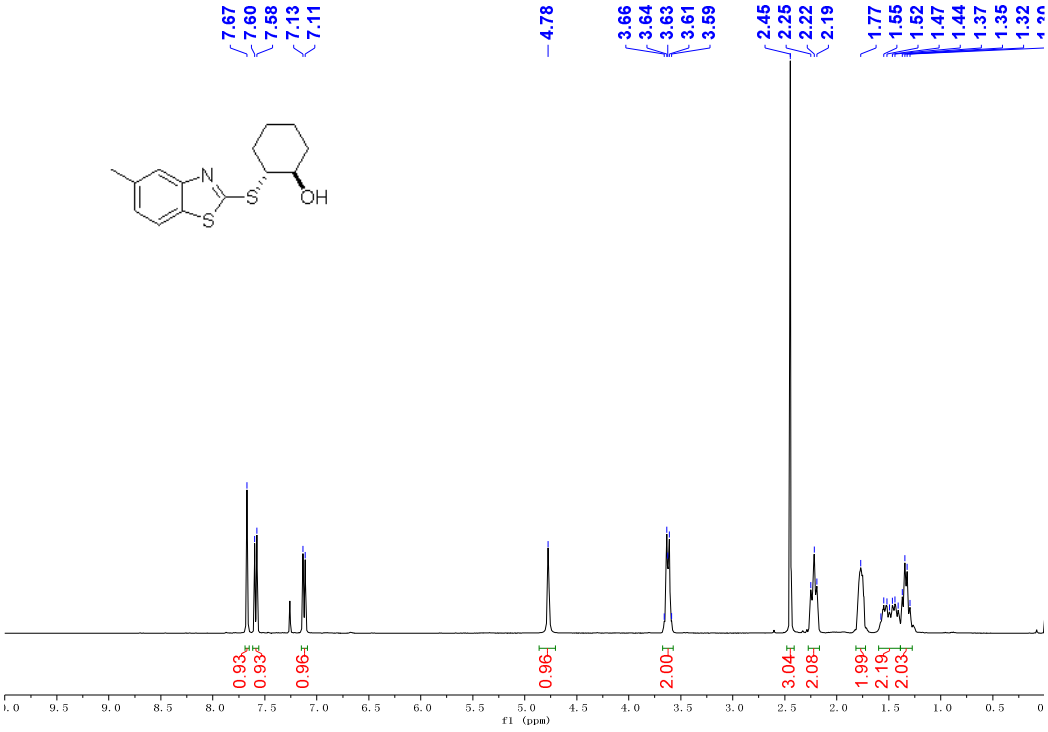


Figure S18. ^{1}H NMR spectrum of **3d** in $CDCl_3$

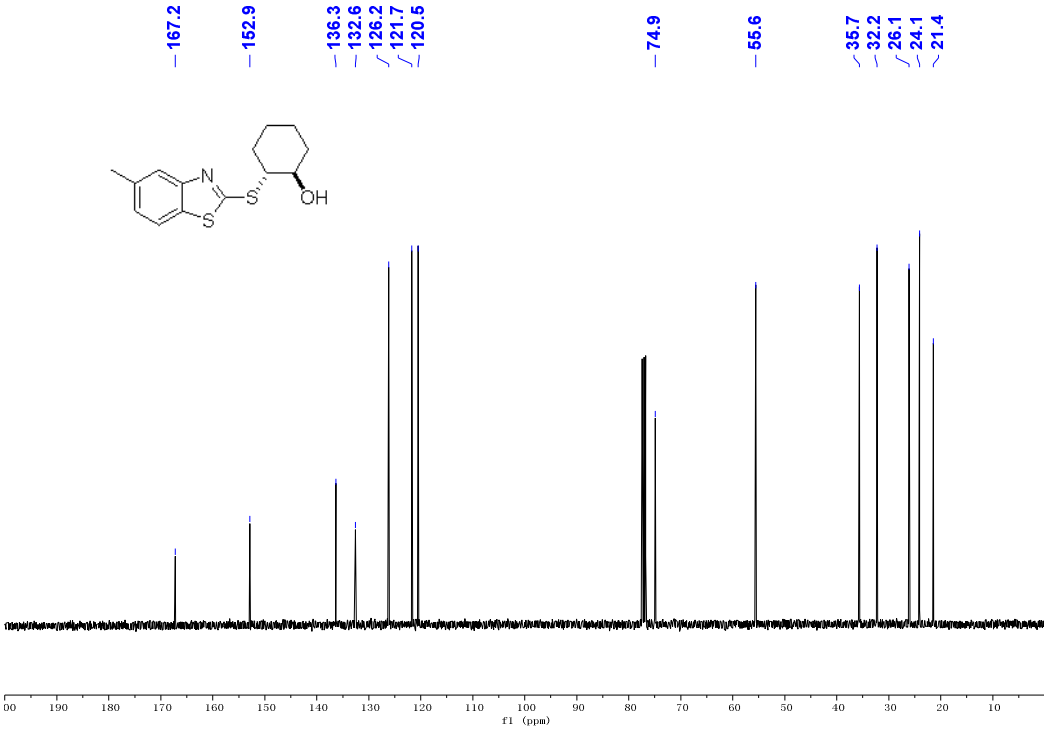


Figure S19. ^{13}C NMR spectrum of **3d** in $CDCl_3$

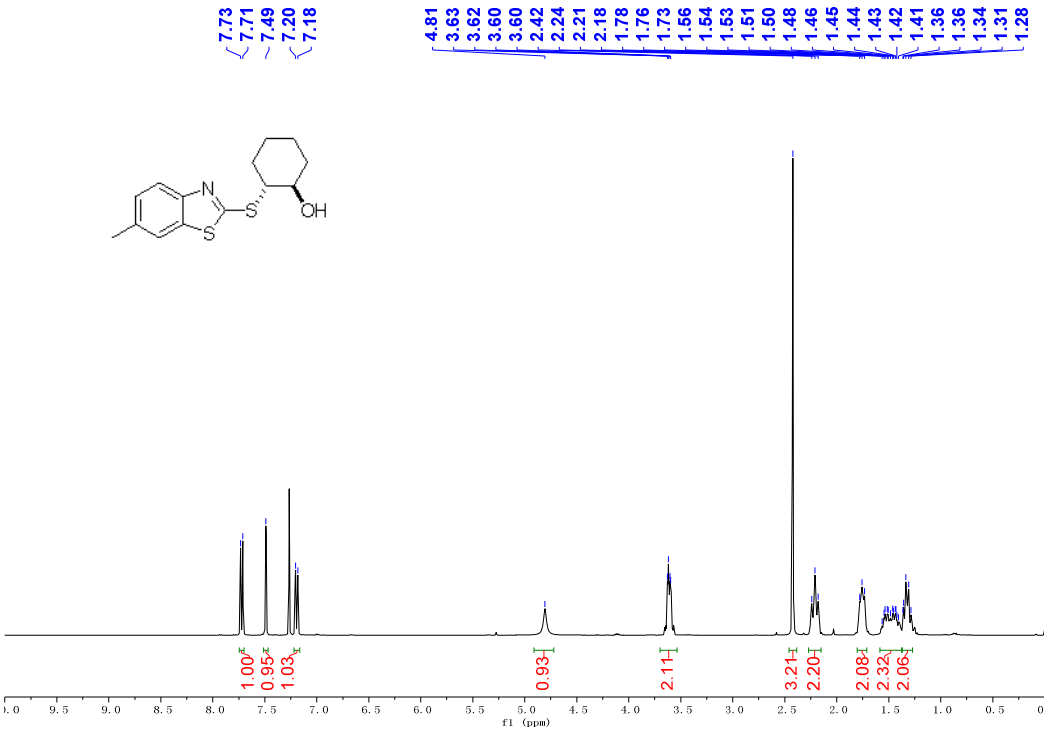


Figure S20. ^{1}H NMR spectrum of **3e** in $CDCl_3$

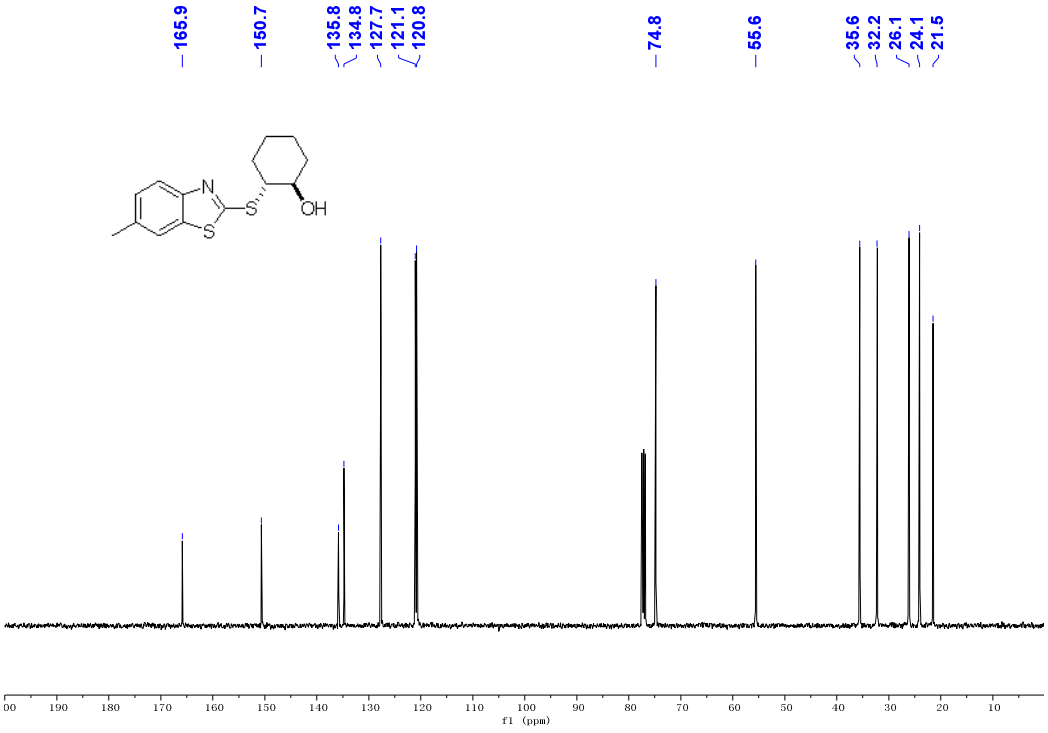


Figure S21. ^{13}C NMR spectrum of **3e** in $CDCl_3$

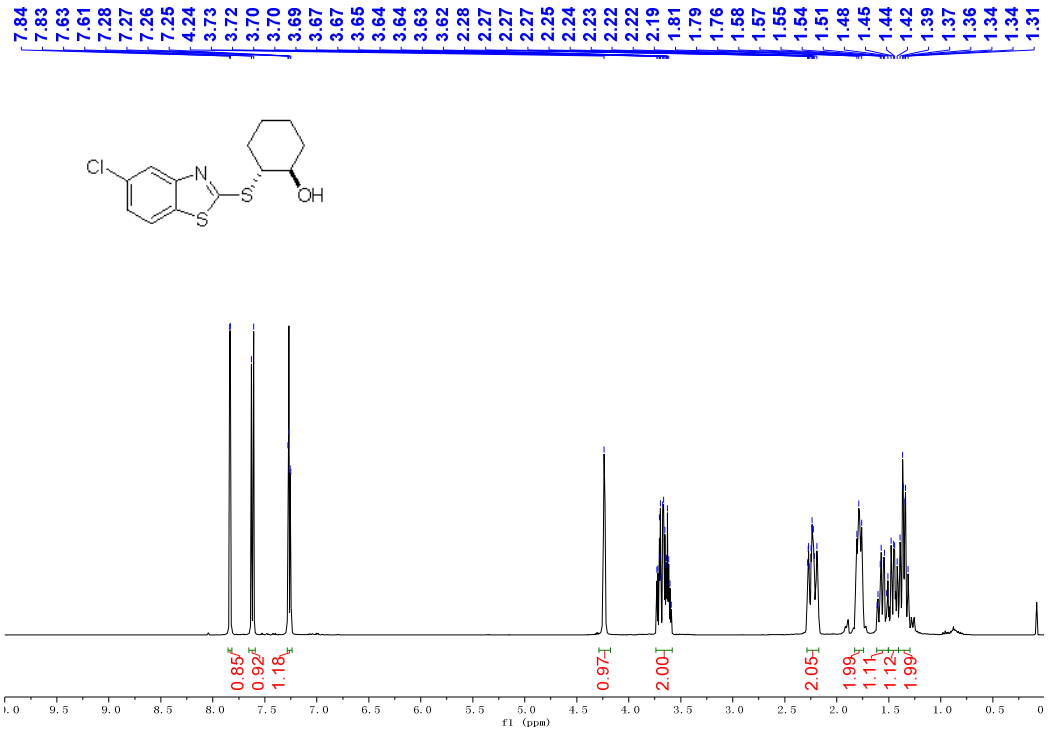


Figure S22. ^{1}H NMR spectrum of **3f** in $CDCl_3$

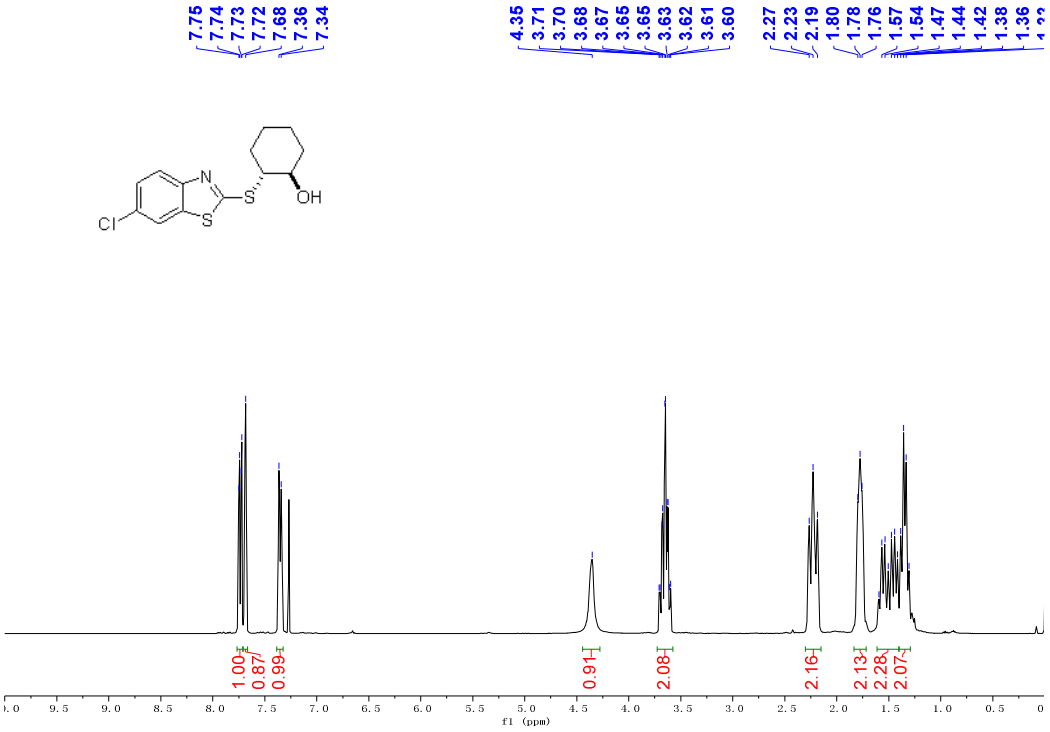


Figure S23. ^{1}H NMR spectrum of **3g** in $CDCl_3$

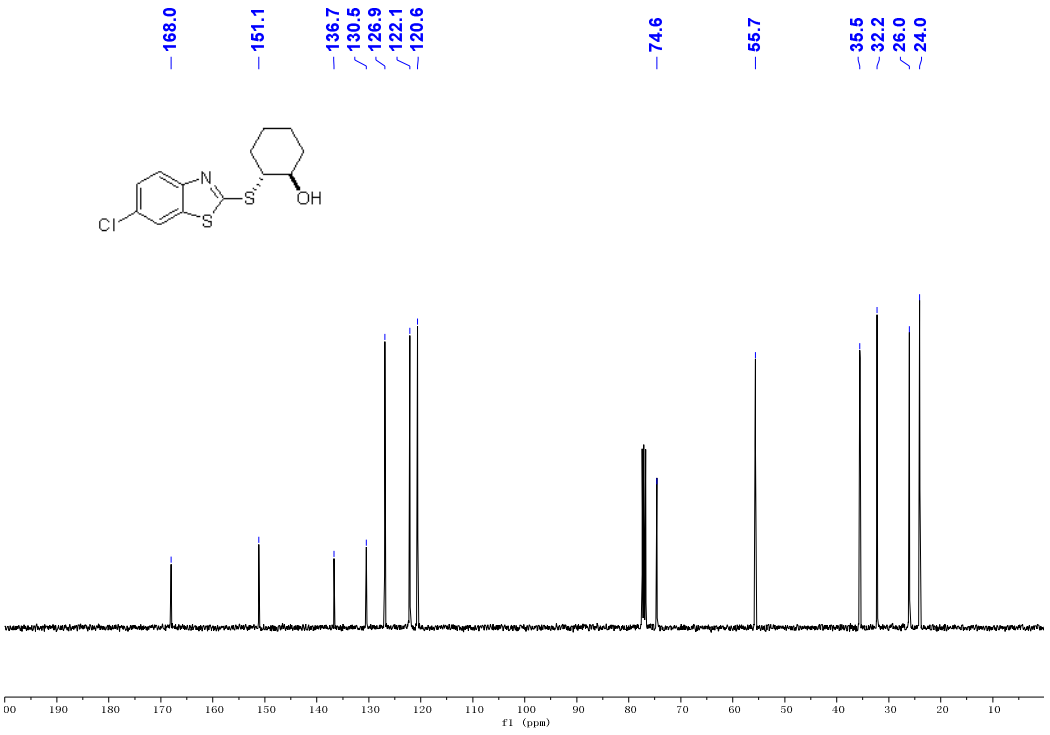


Figure S24. ^{13}C NMR spectrum of **3g** in $CDCl_3$

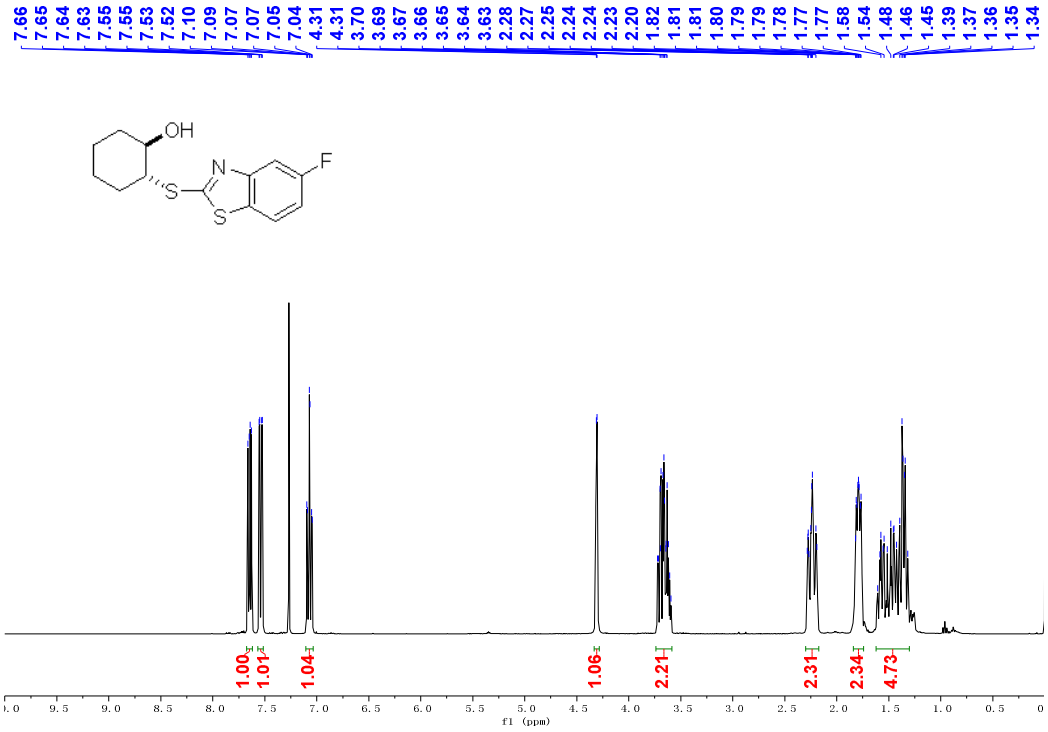


Figure S25. ^{1}H NMR spectrum of **3h** in $CDCl_3$

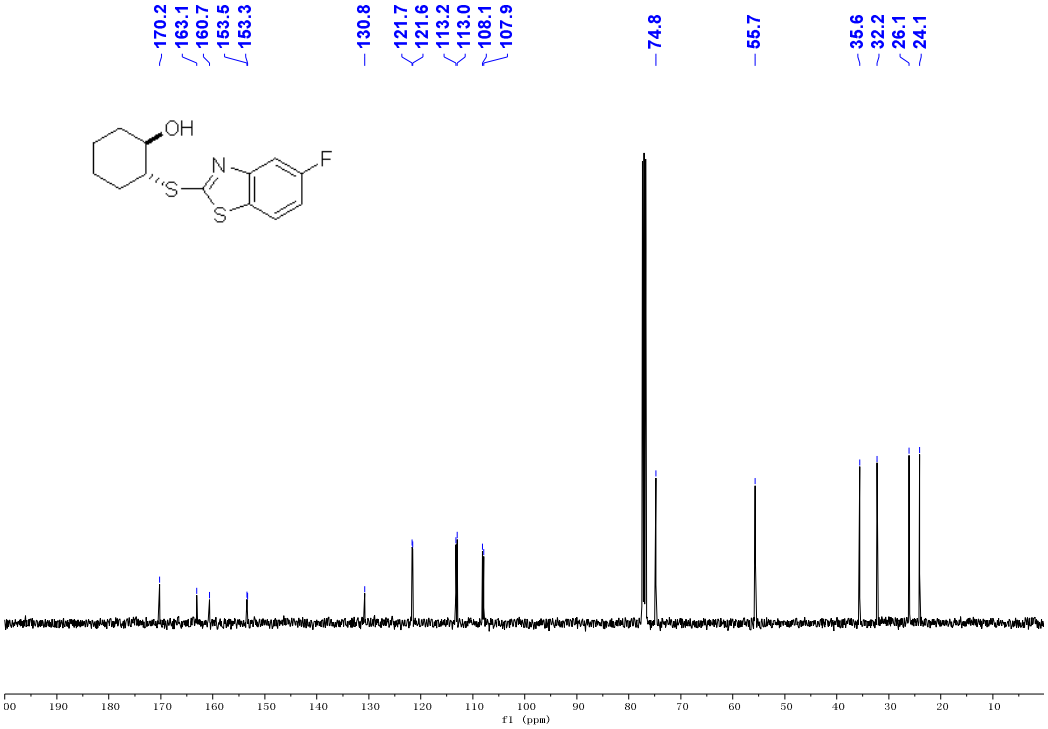


Figure S26. ^{13}C NMR spectrum of **3h** in $CDCl_3$

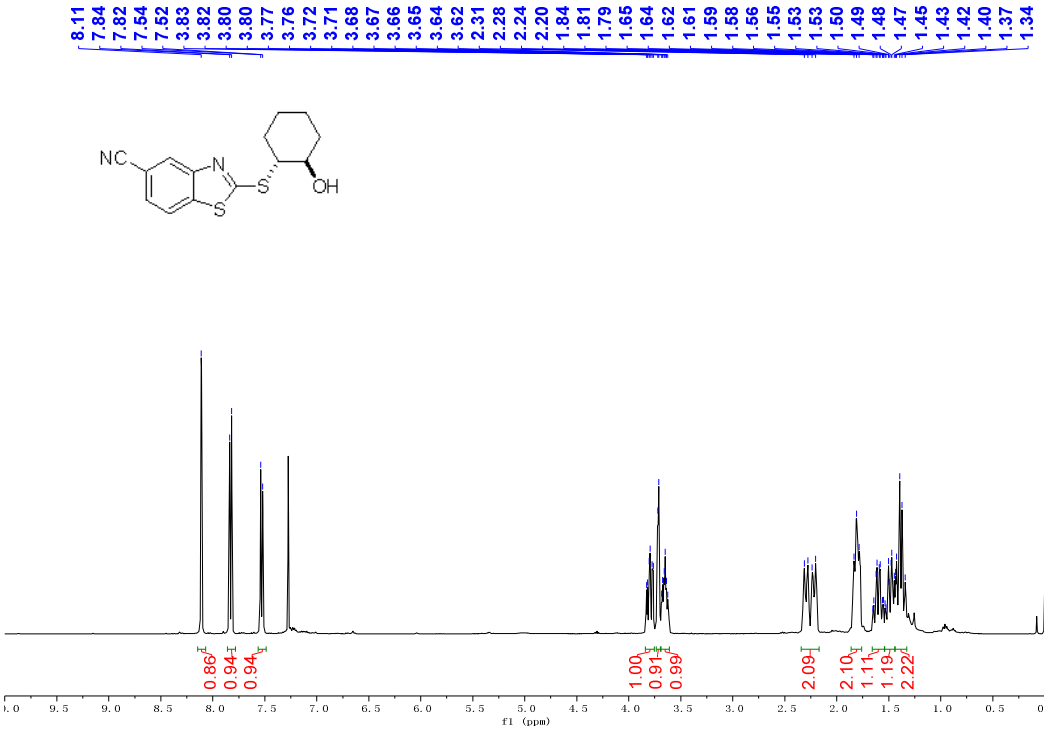


Figure S27. ^{1}H NMR spectrum of **3i** in $CDCl_3$

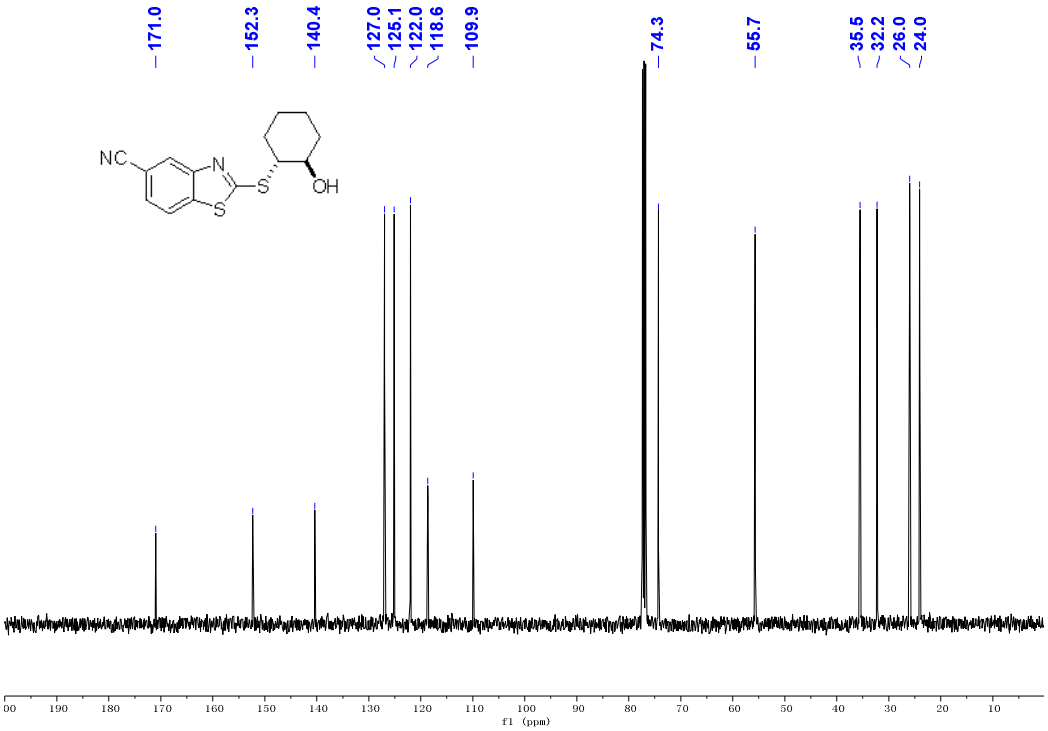


Figure S28. ^{13}C NMR spectrum of **3i** in $CDCl_3$

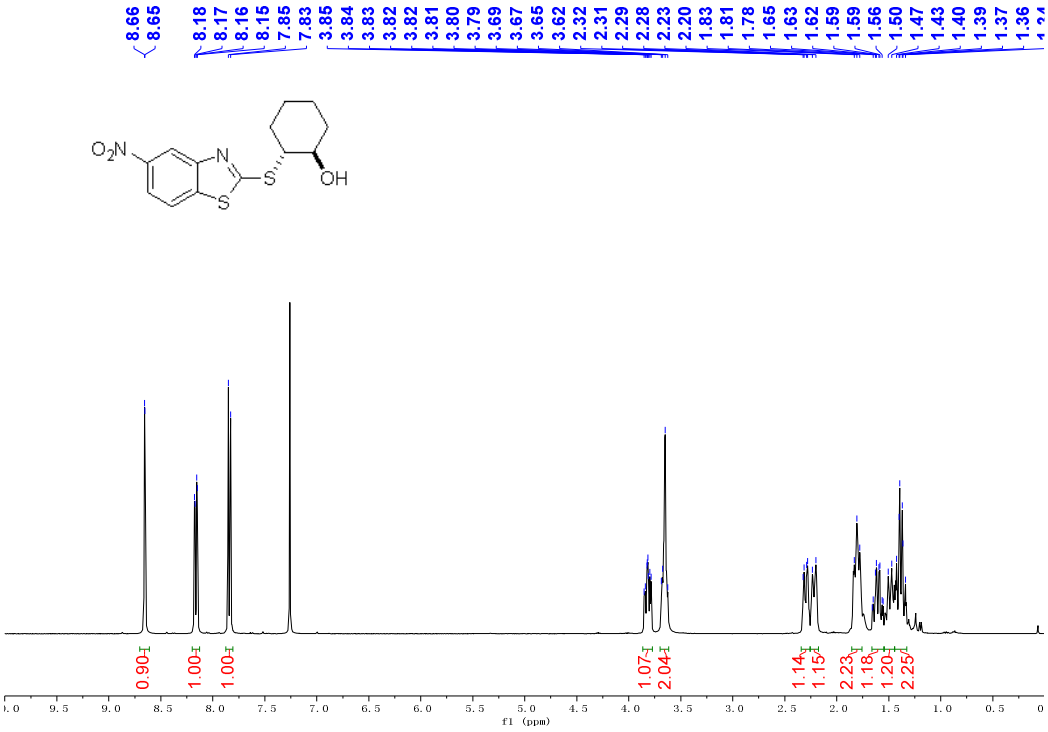


Figure S29. ^{1}H NMR spectrum of **3j** in $CDCl_3$

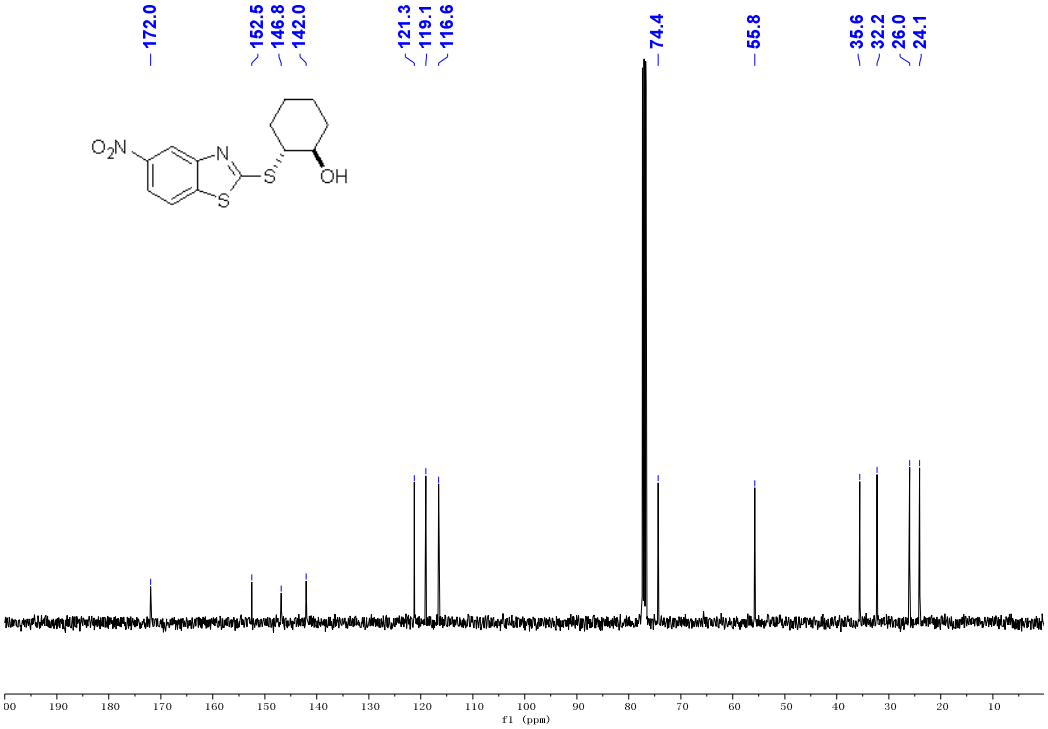


Figure S30. ^{13}C NMR spectrum of **3j** in $CDCl_3$

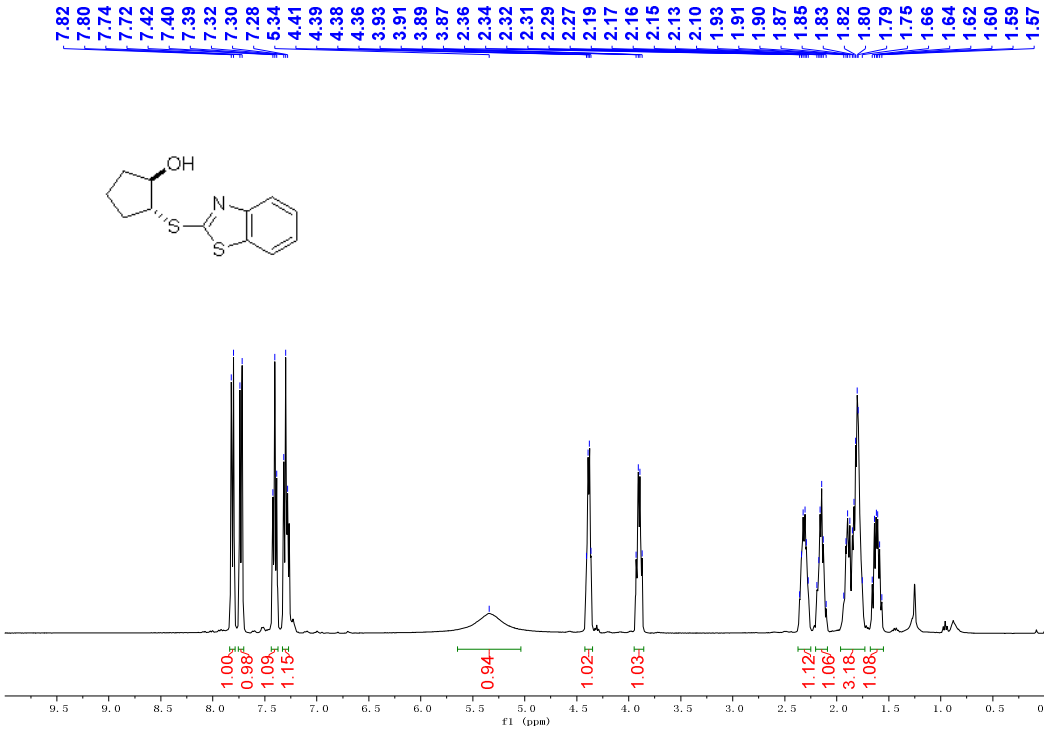


Figure S31. ^{1}H NMR spectrum of **3k** in $CDCl_3$

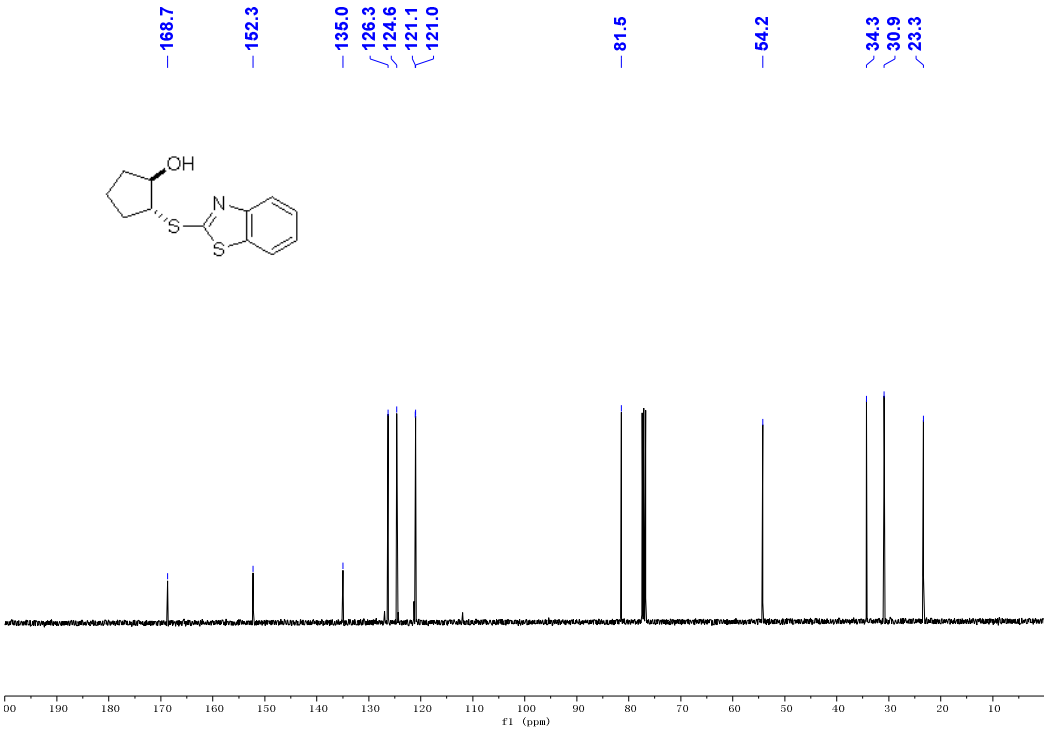


Figure S32. ^{13}C NMR spectrum of **3k** in $CDCl_3$

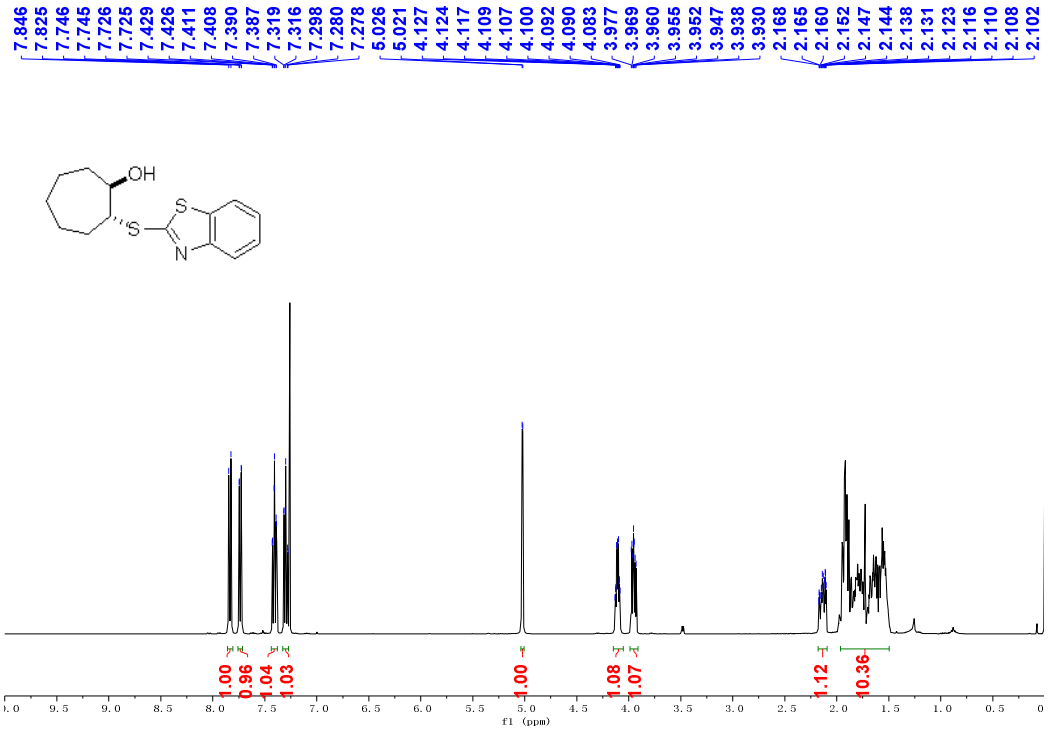


Figure S33. ^{1}H NMR spectrum of **3l** in $CDCl_3$

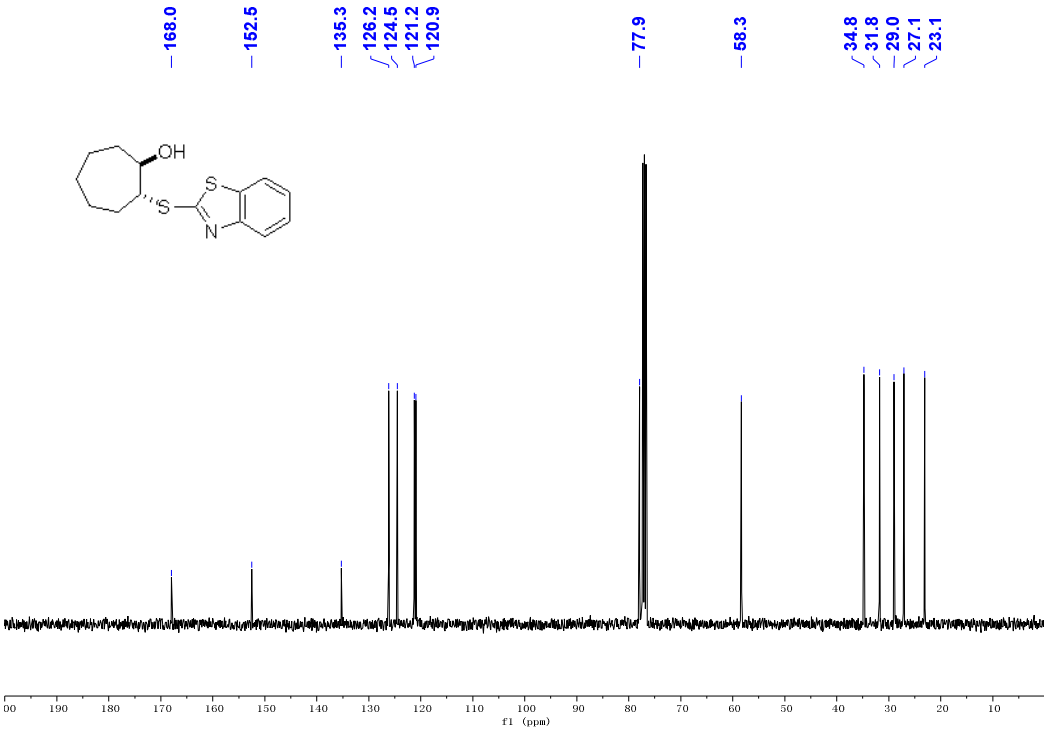


Figure S34. ^{13}C NMR spectrum of **3l** in $CDCl_3$

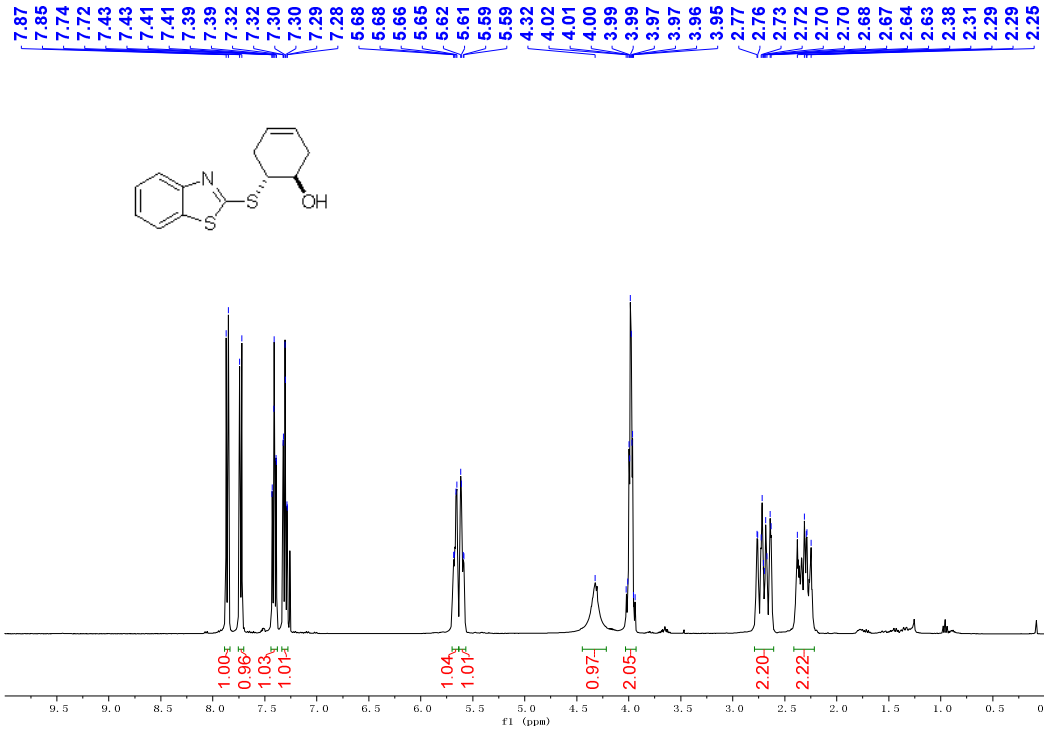


Figure S35. ^{1}H NMR spectrum of **3m** in $CDCl_3$

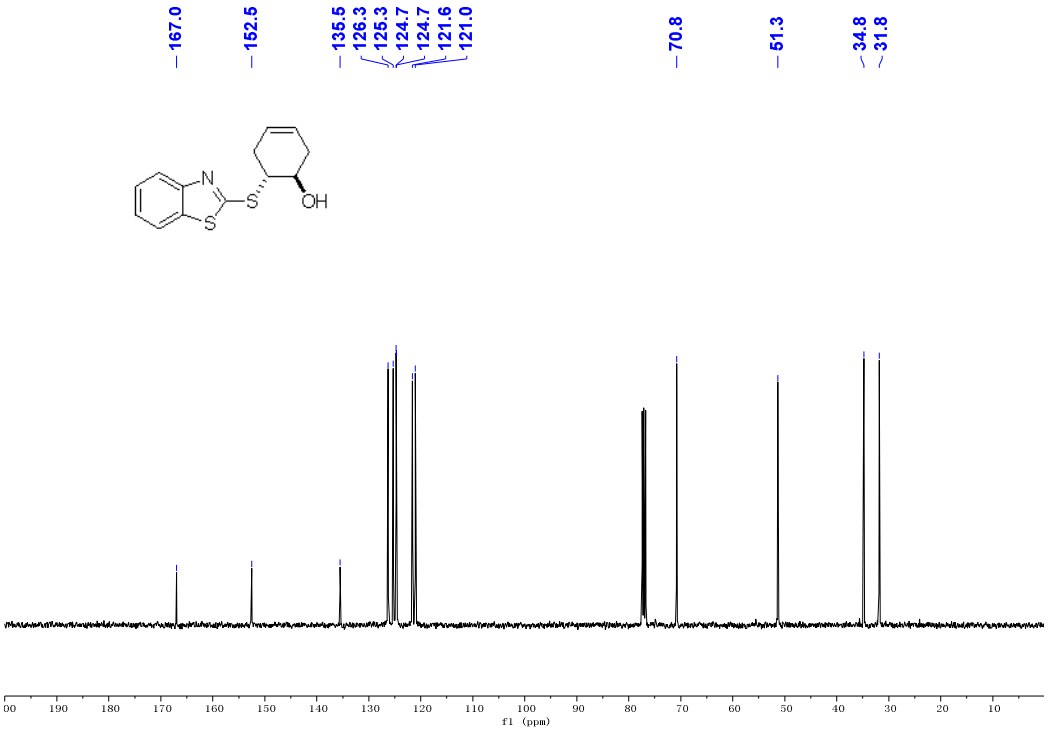


Figure S36. ^{13}C NMR spectrum of **3m** in $CDCl_3$

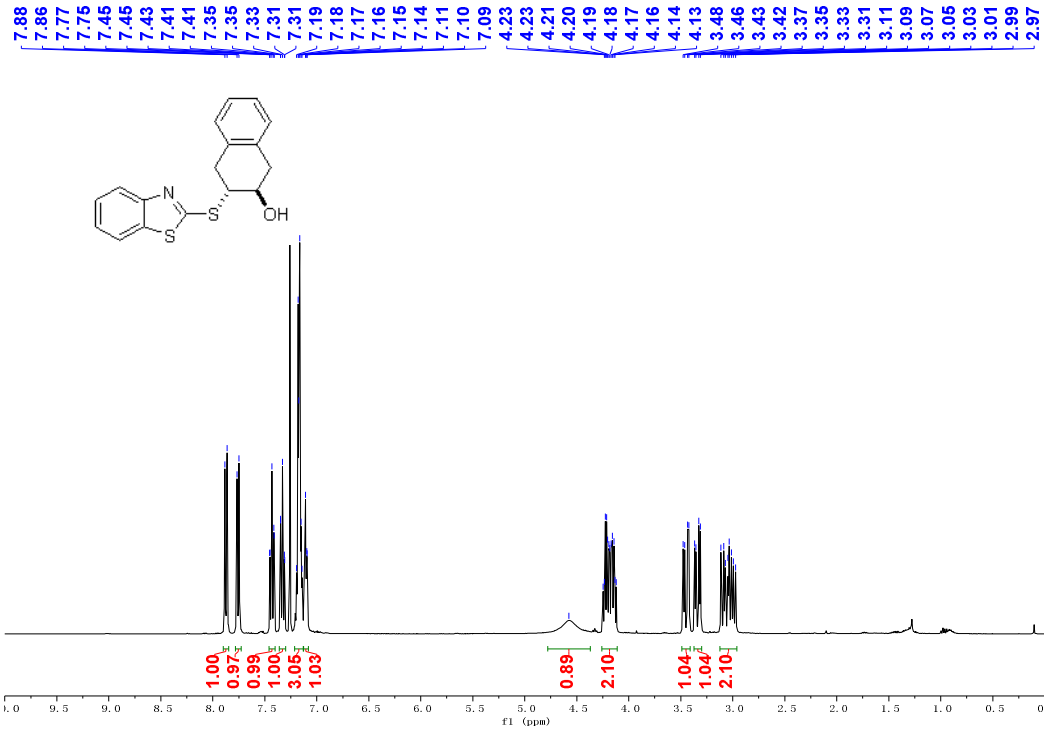


Figure S37. ^{1}H NMR spectrum of **3n** in $CDCl_3$

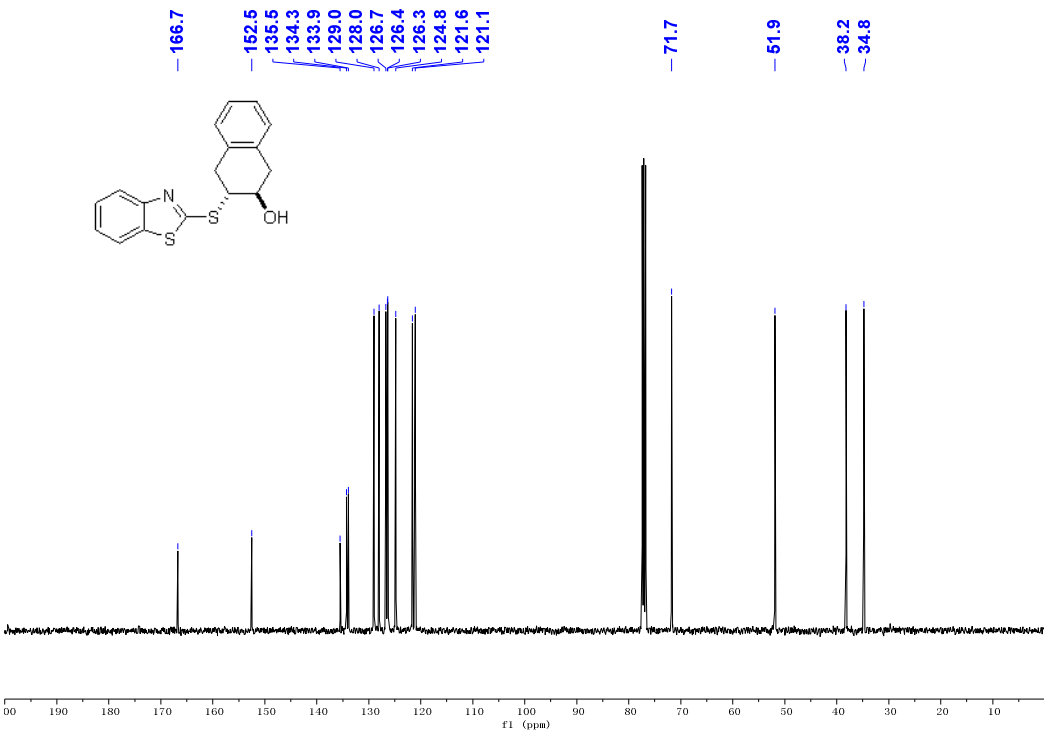


Figure S38. ^{13}C NMR spectrum of **3n** in $CDCl_3$

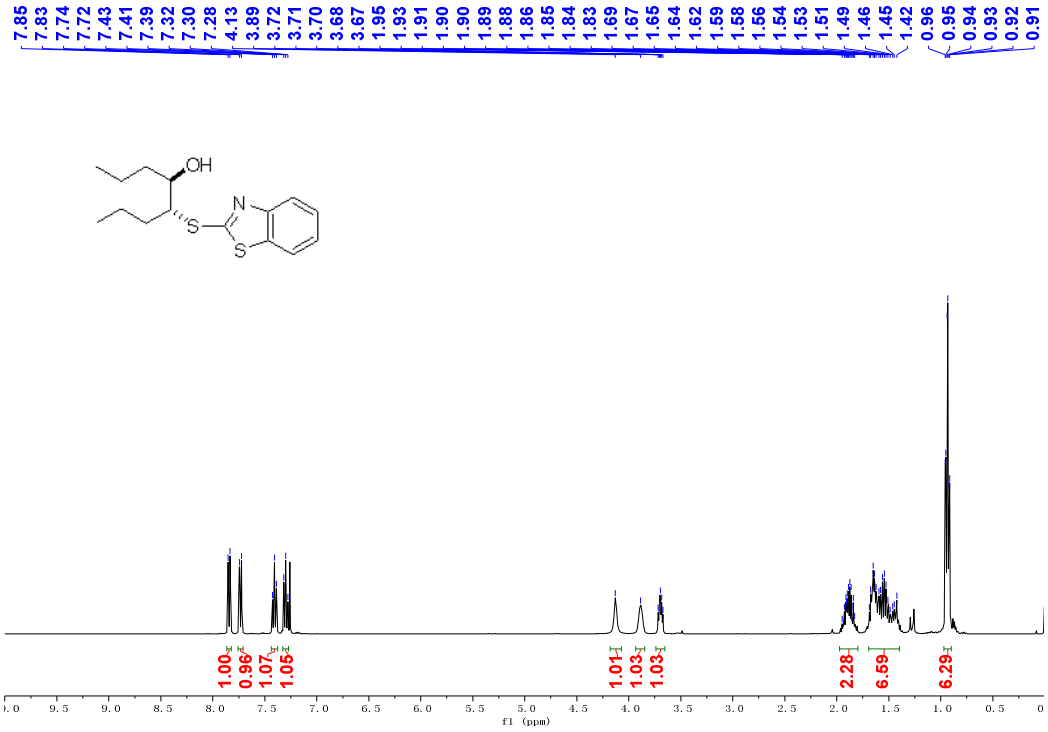


Figure S39. ^{1}H NMR spectrum of **3o** in $CDCl_3$

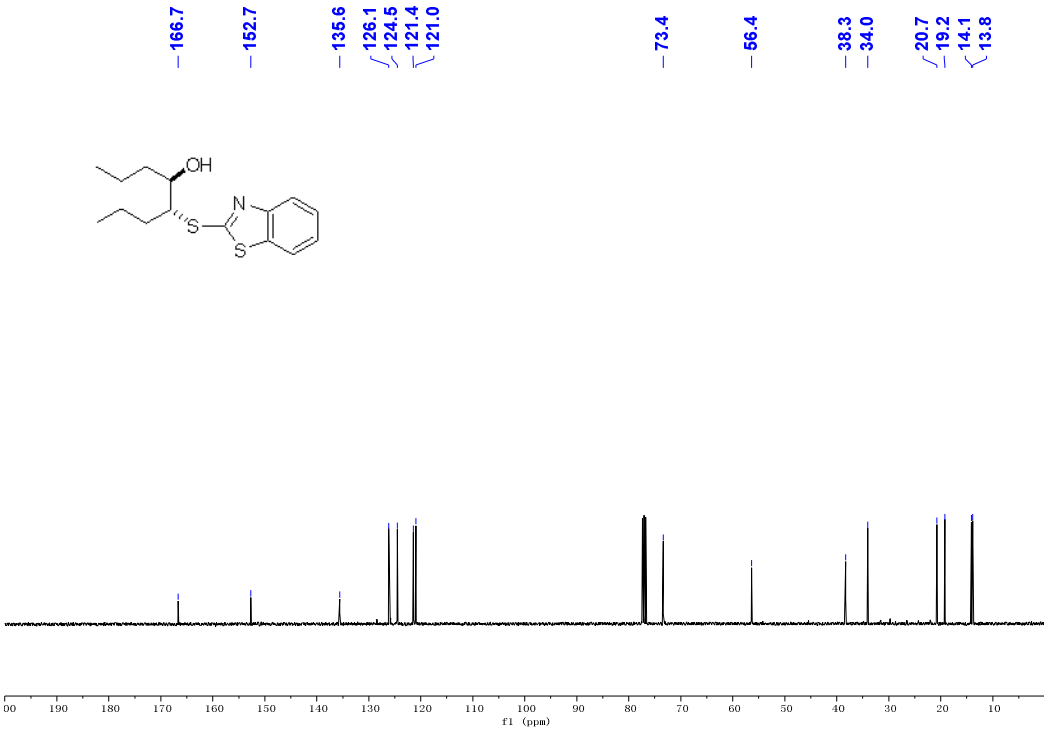


Figure S40. ^{13}C NMR spectrum of **3o** in $CDCl_3$

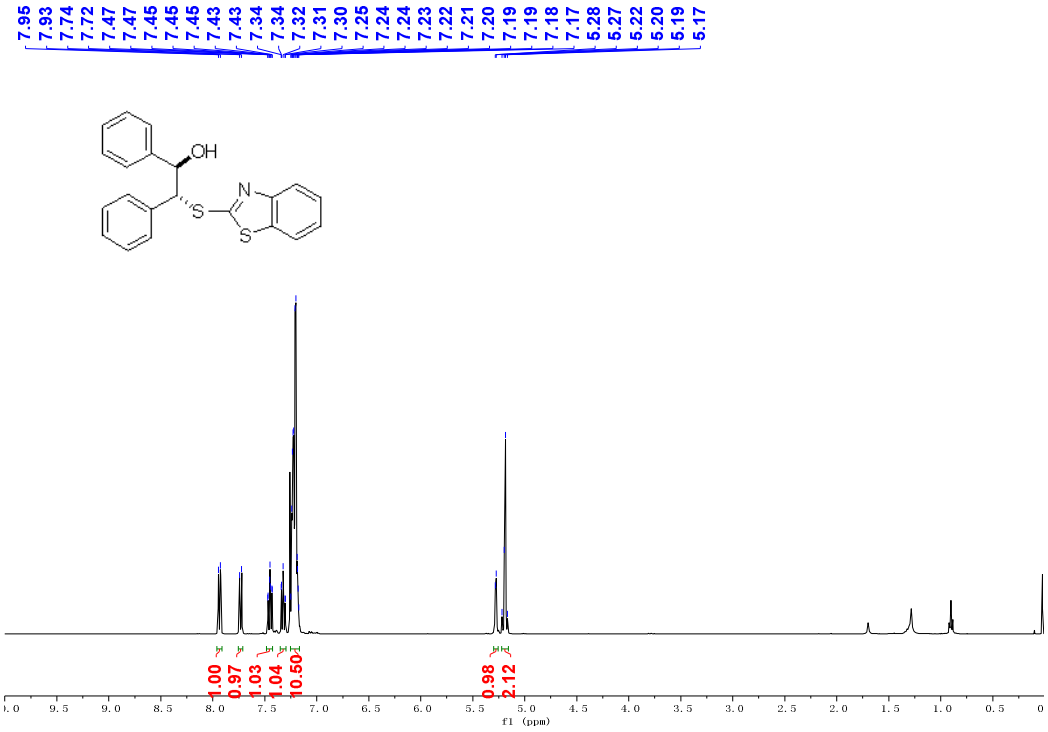


Figure S41. ^{1}H NMR spectrum of **3p** in $CDCl_3$

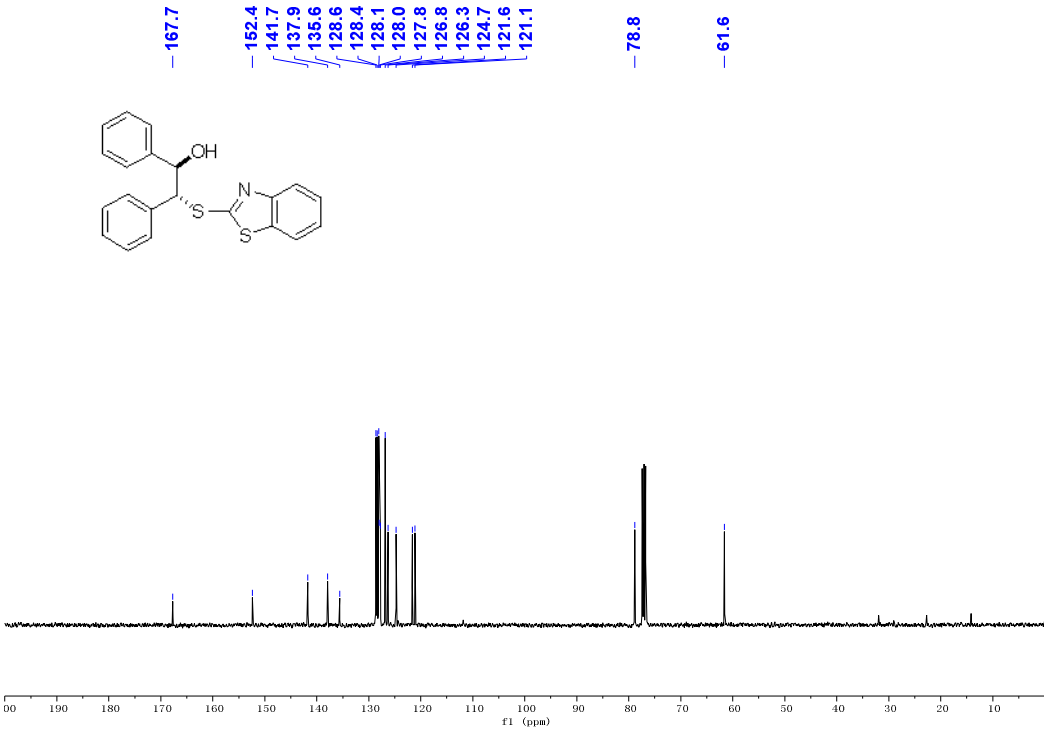


Figure S42. ^{13}C NMR spectrum of **3p** in $CDCl_3$

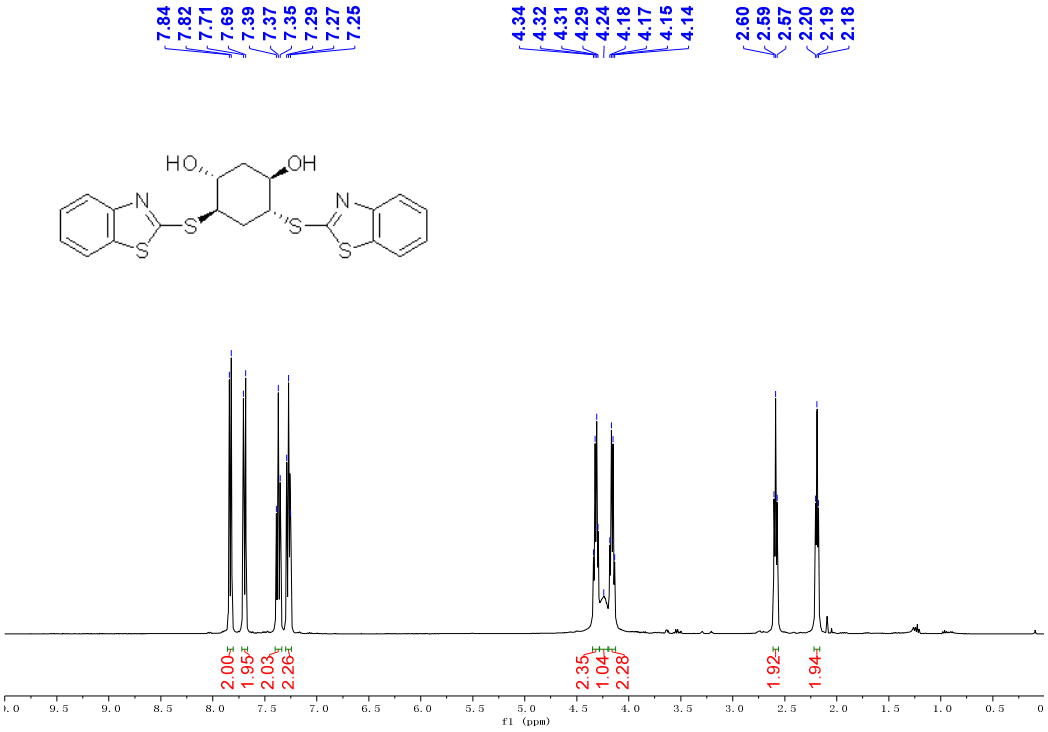


Figure S43. ^{1}H NMR spectrum of **3q** in $CDCl_3$

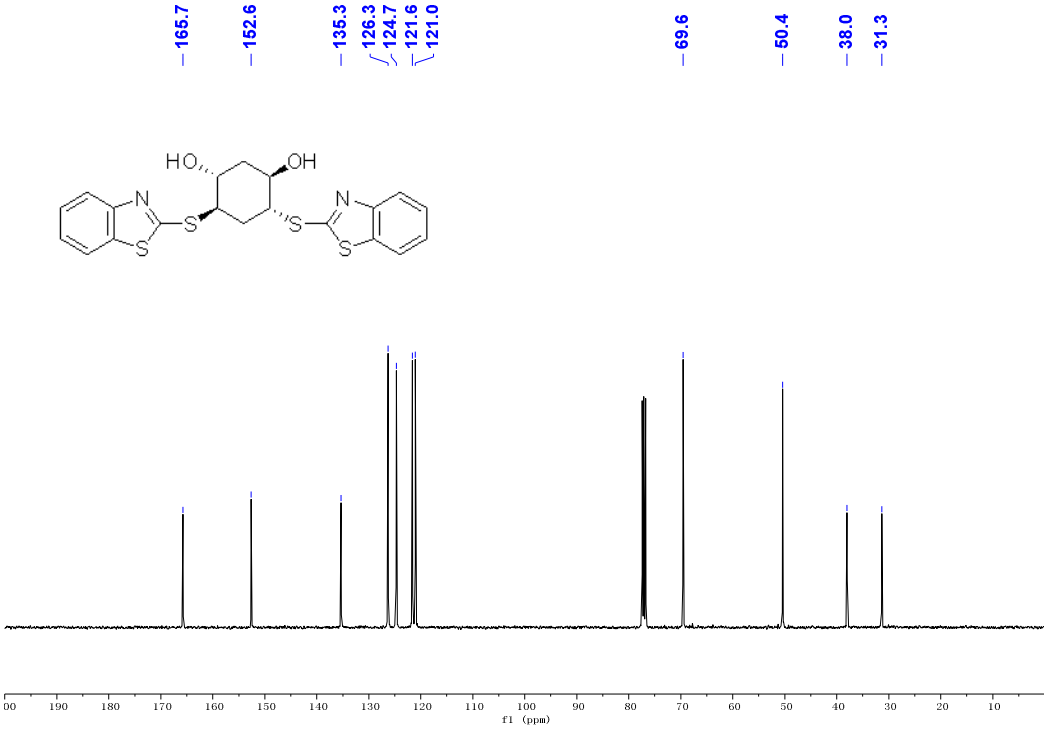
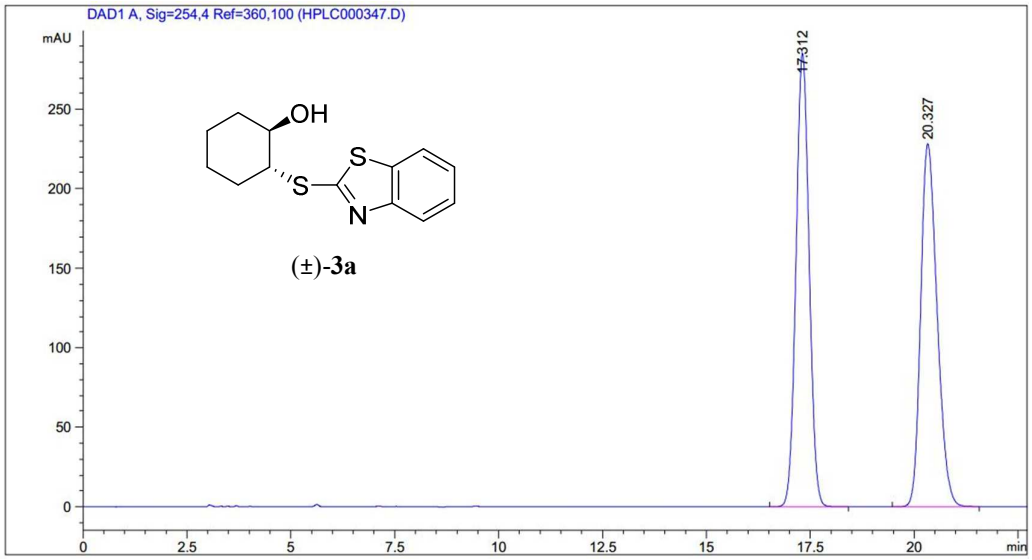


Figure S44. ^{13}C NMR spectrum of **3q** in $CDCl_3$

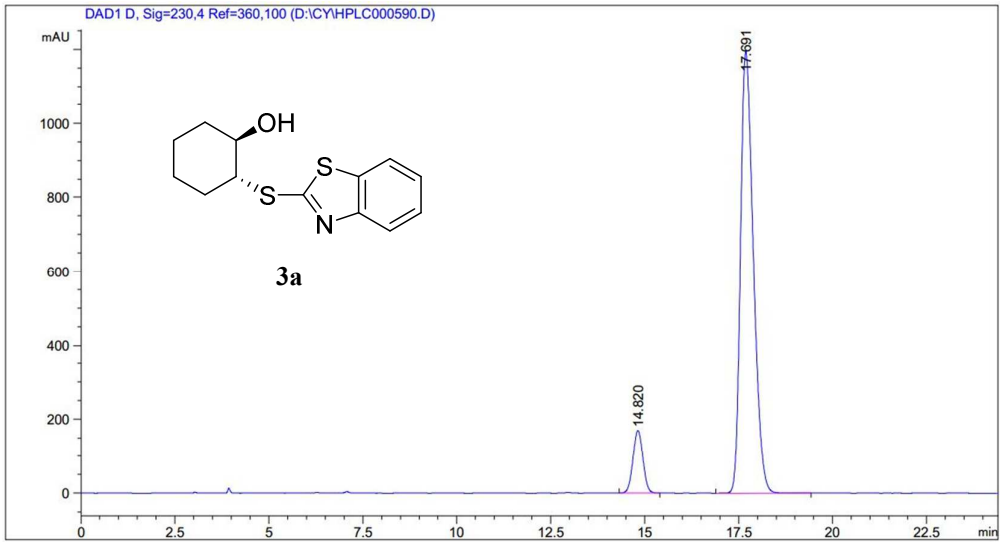
3. HPLC copies of products

AD-H, iPrOH/Hex 10/90, flow rate = 1.0 mL/min



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.312	BB	0.3419	6258.04102	285.29044	50.0153
2	20.327	BB	0.4236	6254.21533	228.28448	49.9847

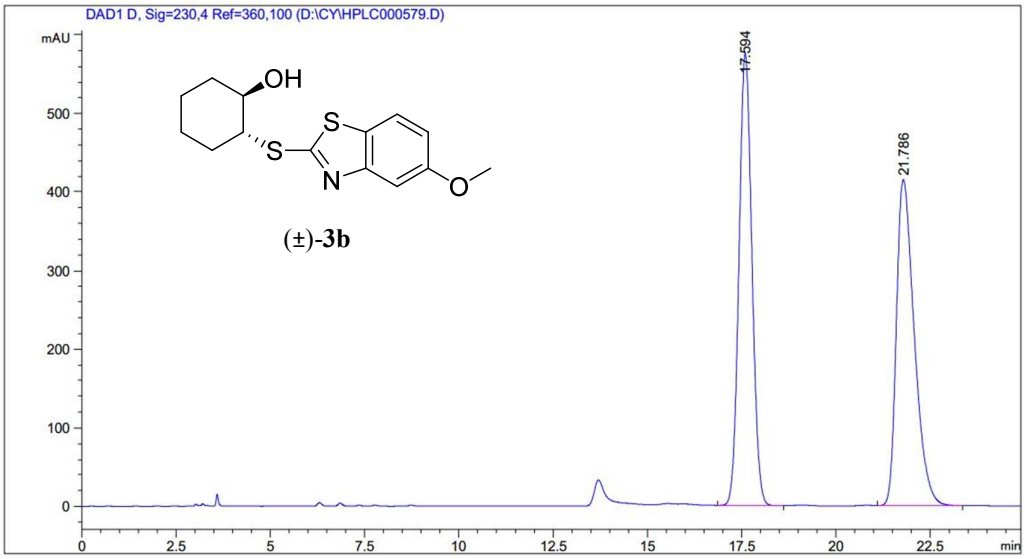
Figure S45. HPLC copies of compound **rac-3a**



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.820	BB	0.2833	3103.90820	169.76711	9.8689
2	17.691	BB	0.3670	2.83476e4	1193.94897	90.1311

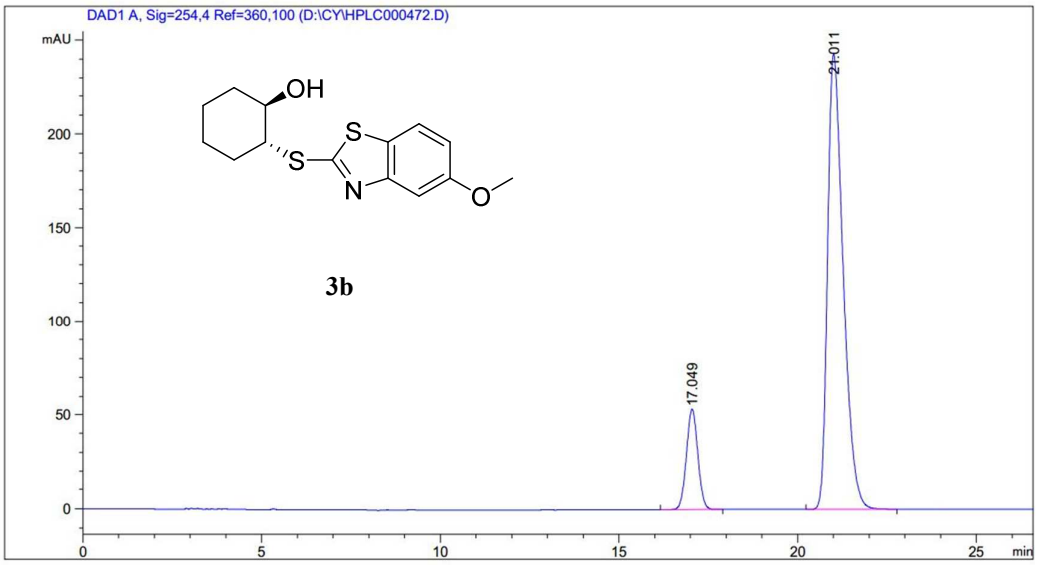
Figure S46. HPLC copies of compound **3a**

AD-H, iPrOH/Hex 10/90, flow rate = 1.0 mL/min



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.594	BB	0.3699	1.37086e4	575.56250	50.0758
2	21.786	BB	0.5039	1.36671e4	415.29184	49.9242

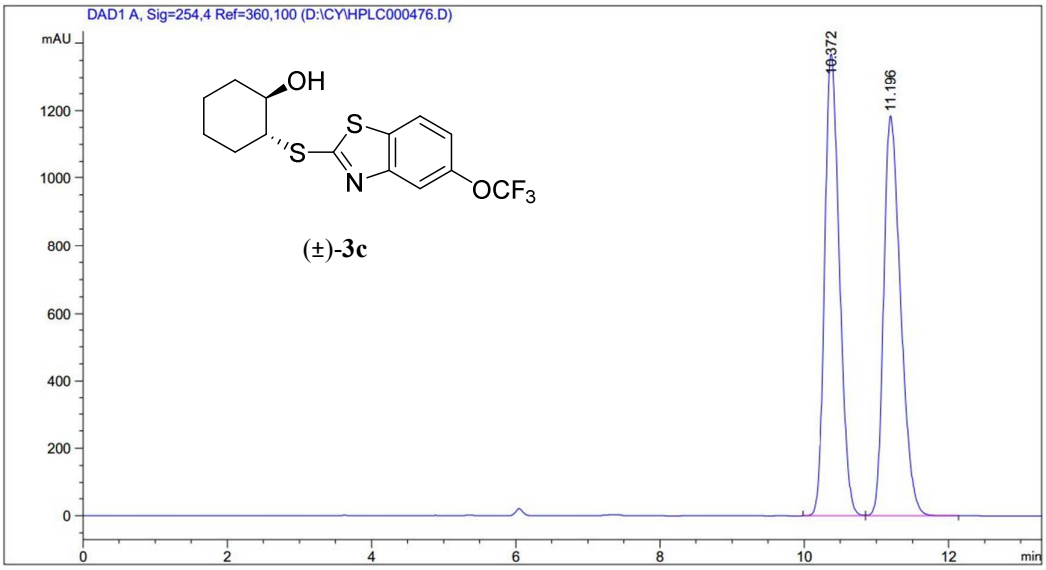
Figure S47. HPLC copies of compound **rac-3b**



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.049	BB	0.3453	1181.88489	53.18024	13.8119
2	21.011	BB	0.4621	7375.13281	242.99344	86.1881

Figure S48. HPLC copies of compound **3b**

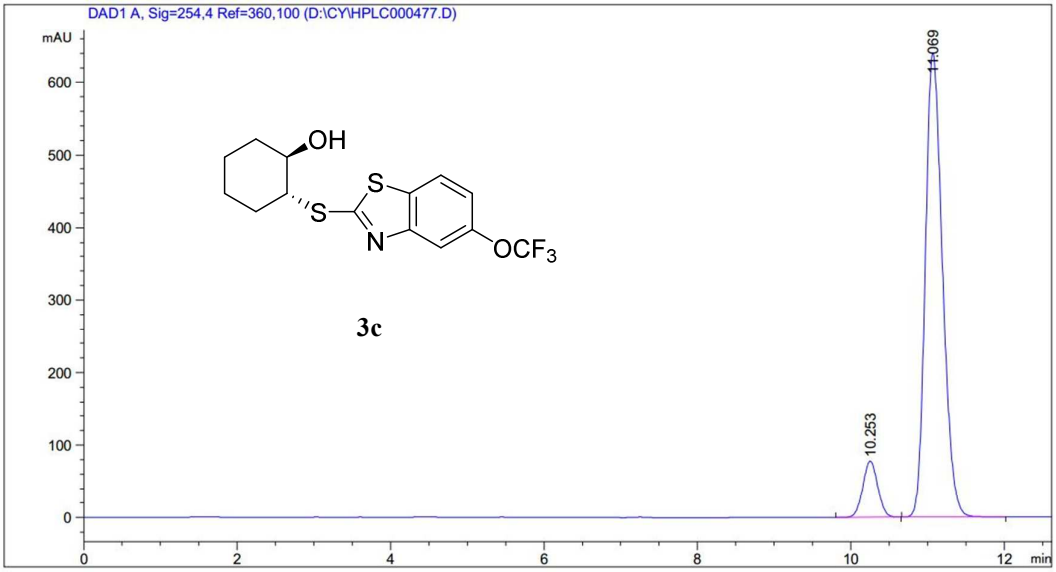
AD-H, iPrOH/Hex 10/90, flow rate = 1.0 mL/min



(±)-**3c**

Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.372	BB	0.2189	1.93252e4	1367.35132	49.9911
2	11.196	BB	0.2506	1.93321e4	1183.27747	50.0089

Figure S49. HPLC copies of compound **rac-3c**

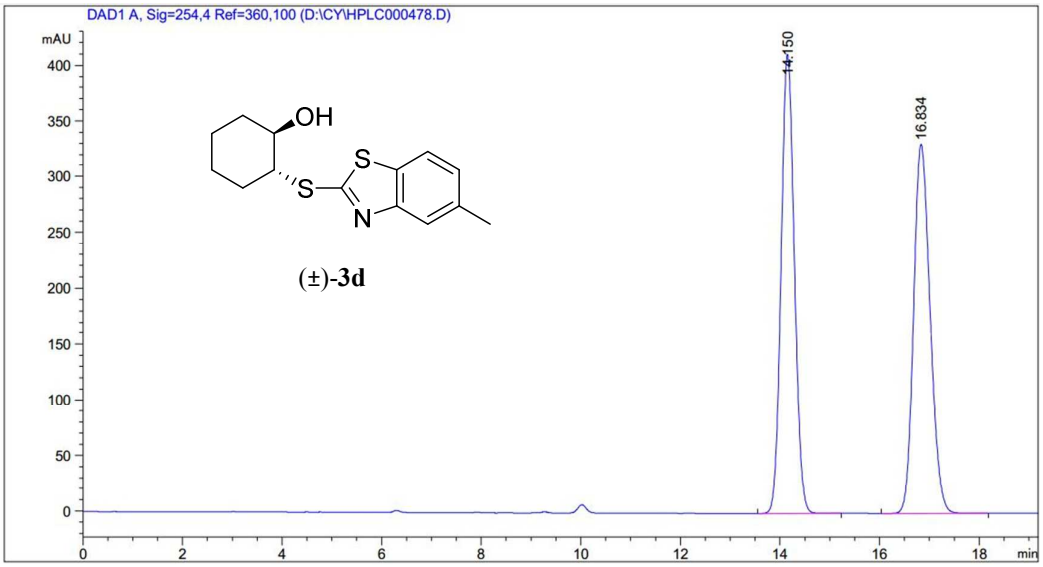


3c

Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.253	BB	0.2118	1054.36487	77.95897	9.5906
2	11.069	BB	0.2392	9939.40820	640.03607	90.4094

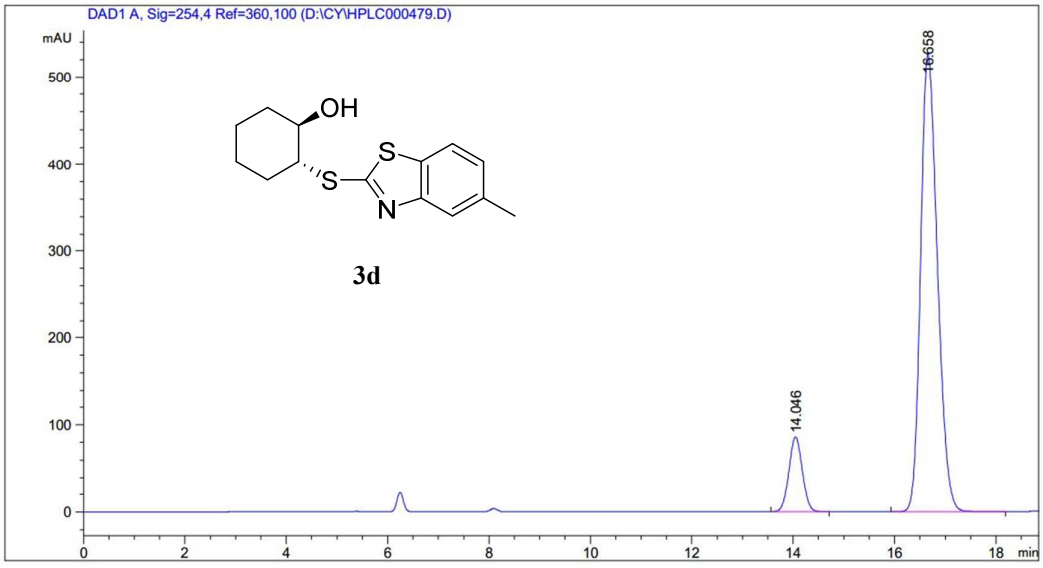
Figure S50. HPLC copies of compound **3c**

AD-H, iPrOH/Hex 10/90, flow rate = 1.0 mL/min



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.150	BB	0.2899	7620.70605	411.86768	49.9649
2	16.834	BB	0.3564	7631.40186	331.68381	50.0351

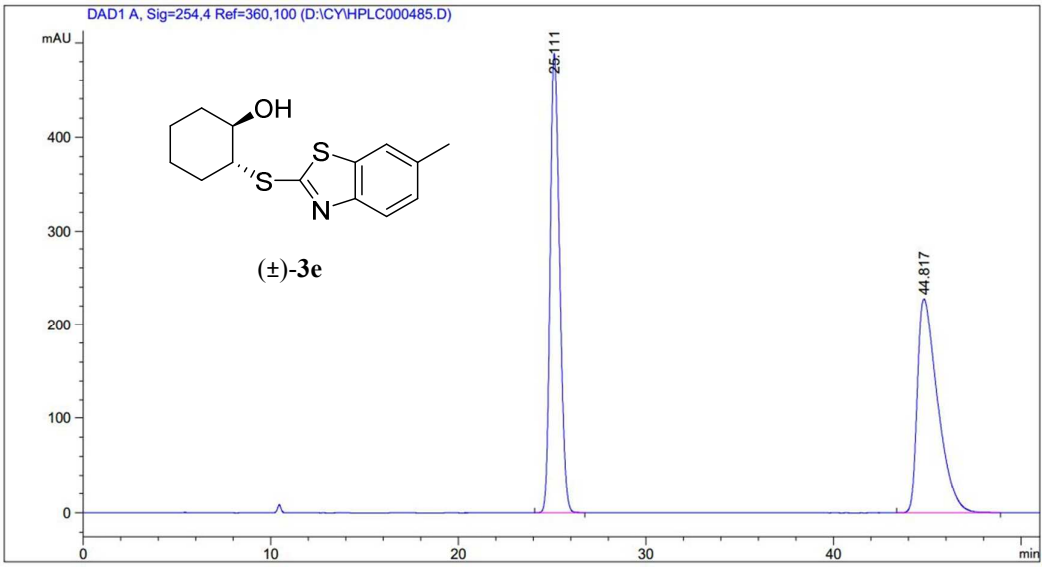
Figure S51. HPLC copies of compound **rac-3d**



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.046	BB	0.2859	1575.76318	85.95020	11.5195
2	16.658	BB	0.3579	1.21033e4	527.17896	88.4805

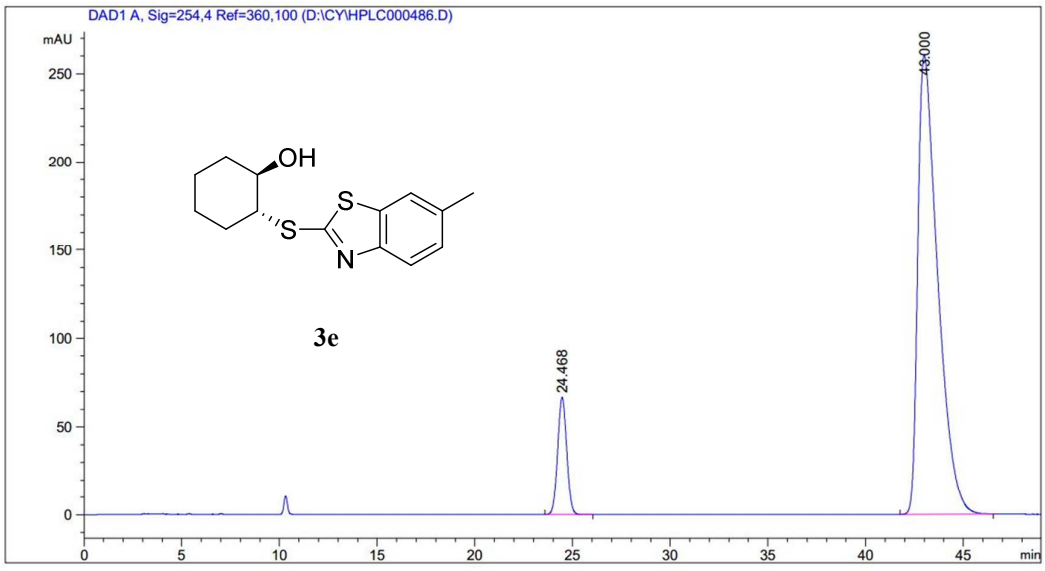
Figure S52. HPLC copies of compound **3d**

AD-H, iPrOH/Hex 10/90, flow rate = 1.0 mL/min



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.111	BB	0.5450	1.70377e4	488.33844	49.9729
2	44.817	BB	1.1393	1.70562e4	227.33032	50.0271

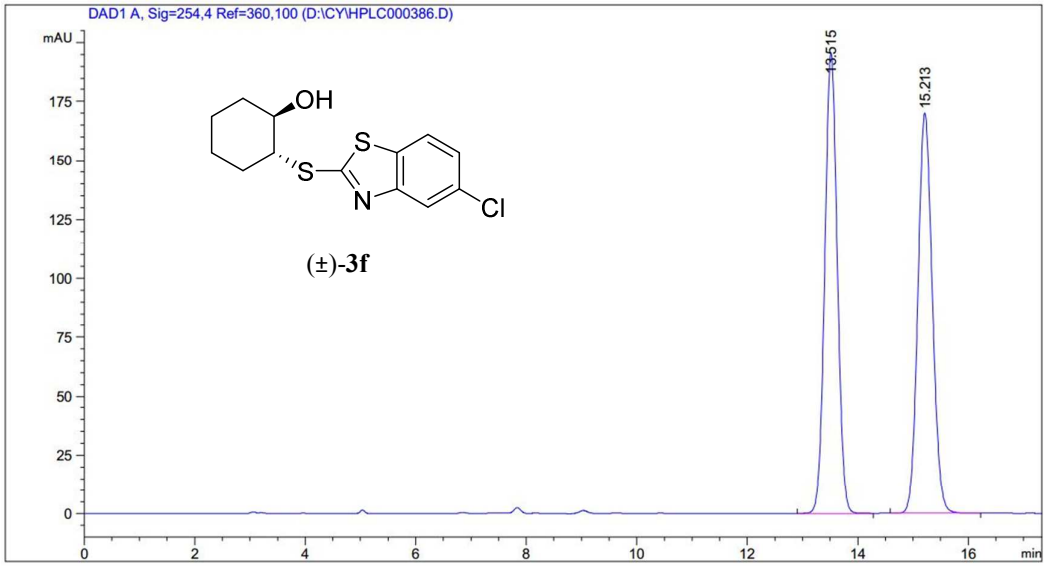
Figure S53. HPLC copies of compound **rac-3e**



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.468	BB	0.5022	2145.77100	66.54942	10.4290
2	43.000	BB	1.0736	1.84293e4	260.43127	89.5710

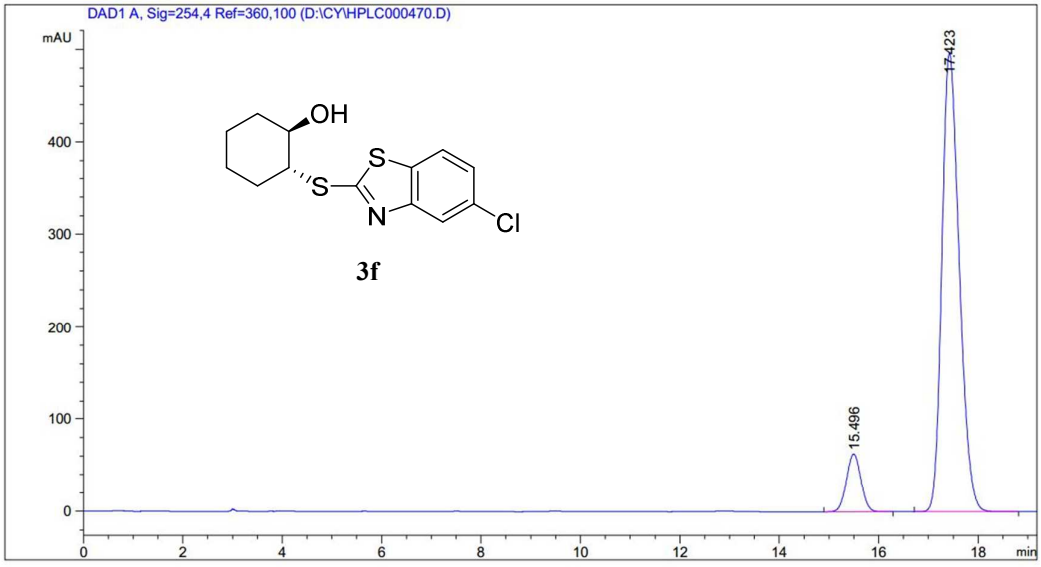
Figure S54. HPLC copies of compound **3e**

AD-H, iPrOH/Hex 10/90, flow rate = 1.0 mL/min



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.515	BB	0.2452	3068.63403	195.43034	49.9232
2	15.213	BB	0.2814	3078.07739	169.85976	50.0768

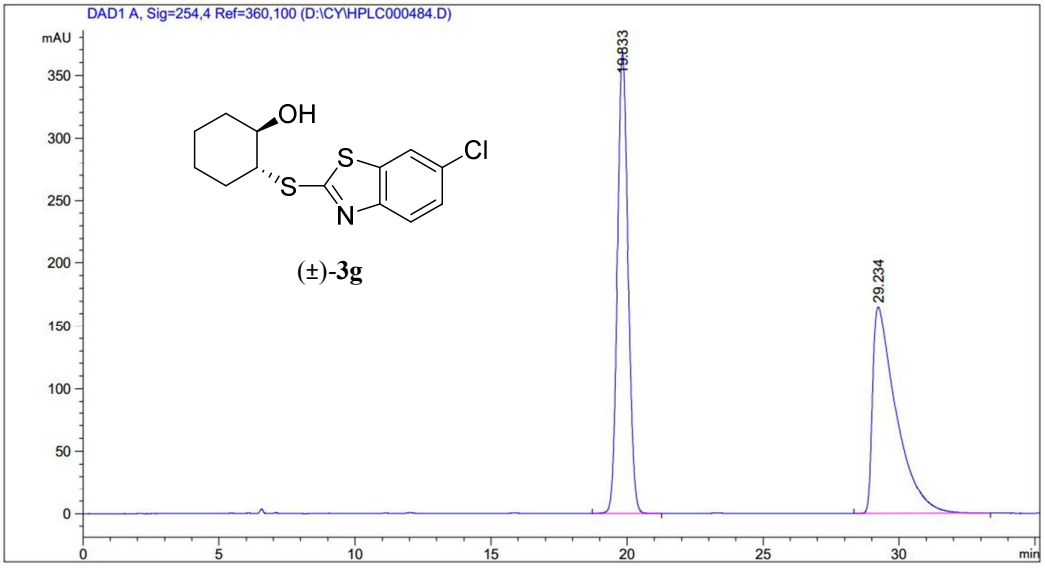
Figure S55. HPLC copies of compound **rac-3f**



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.496	BB	0.3170	1276.31934	62.83426	9.5569
2	17.423	BB	0.3757	1.20786e4	496.67197	90.4431

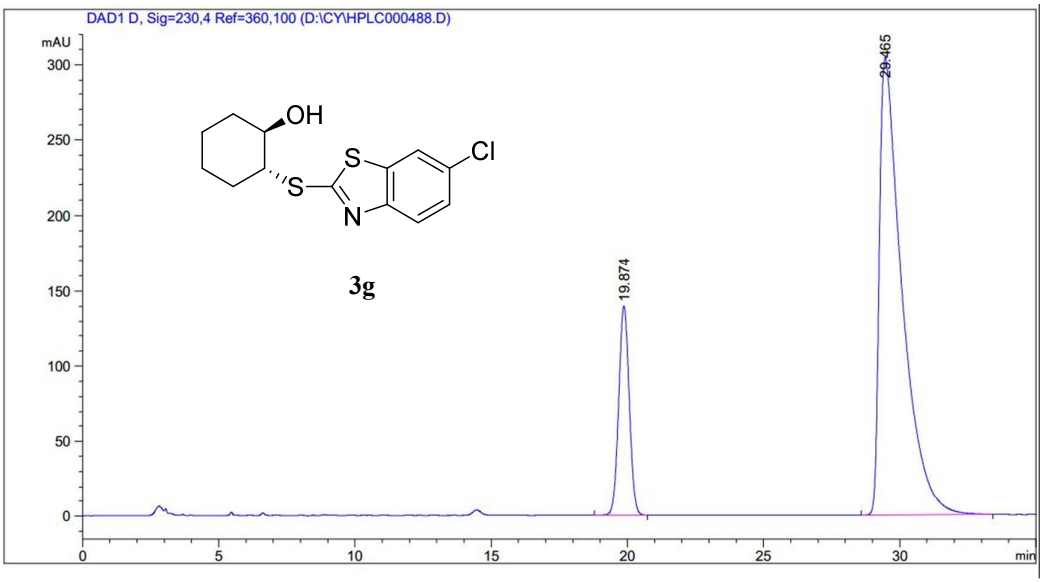
Figure S56. HPLC copies of compound **3f**

AD-H, iPrOH/Hex 10/90, flow rate = 1.0 mL/min



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.833	BB	0.4243	1.00166e4	367.08221	50.0915
2	29.234	BB	0.8489	9980.04004	165.18932	49.9085

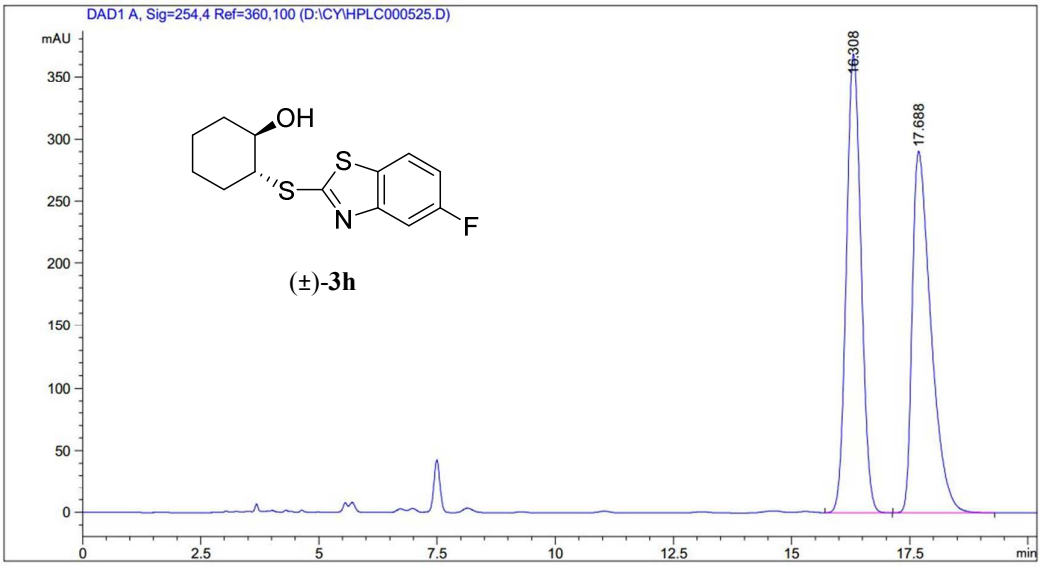
Figure S57. HPLC copies of compound **rac-3g**



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.874	BB	0.4204	3764.62622	139.71402	17.5971
2	29.465	BB	0.8344	1.76288e4	304.08557	82.4029

Figure S58. HPLC copies of compound **3g**

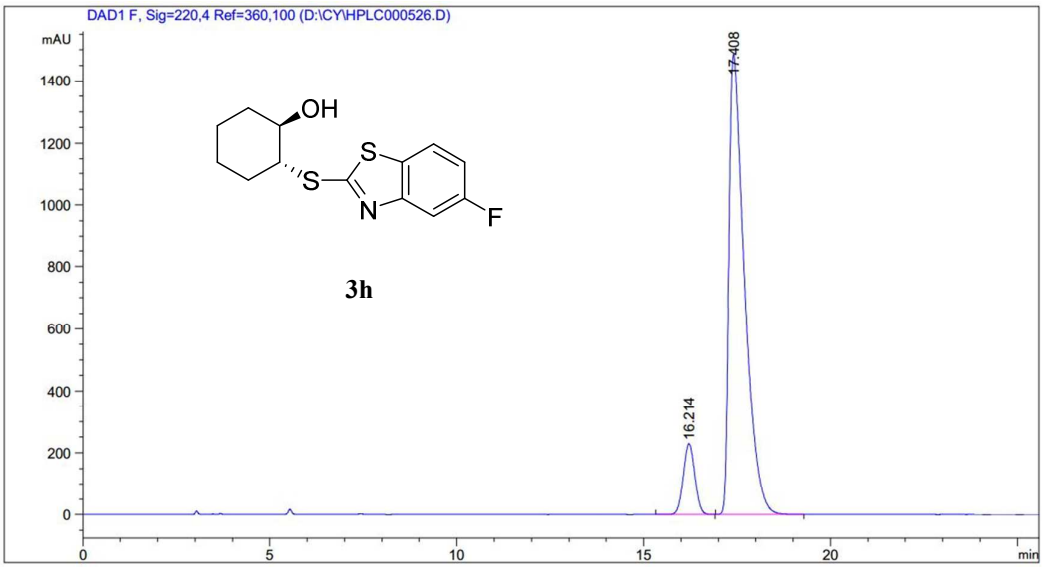
AD-H, iPrOH/Hex 10/90, flow rate = 1.0 mL/min



(±)-**3h**

Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.308	BB	0.3389	7987.84863	368.47336	49.9782
2	17.688	BB	0.4169	7994.81592	290.64139	50.0218

Figure S59. HPLC copies of compound **rac-3h**

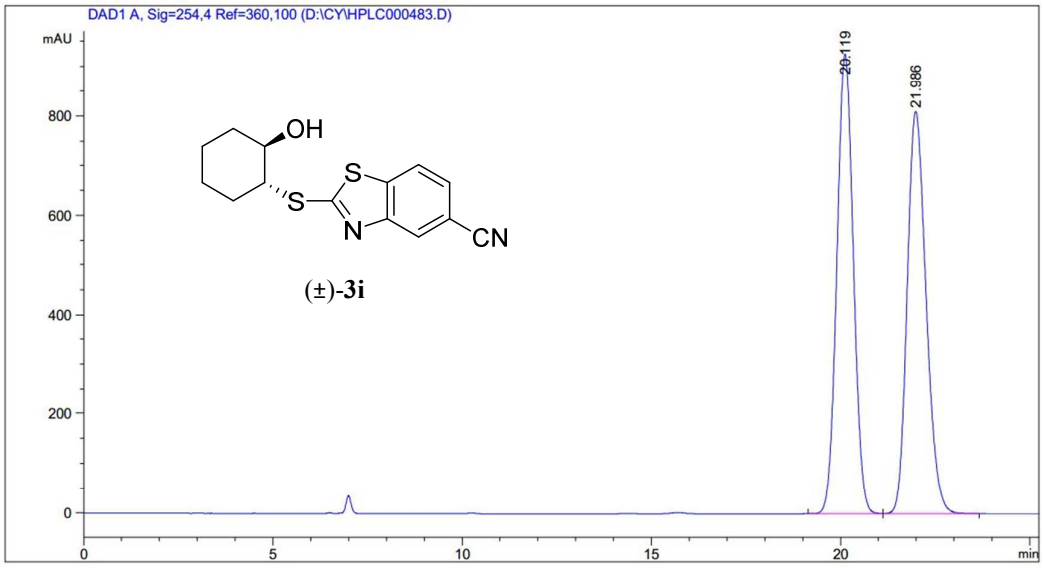


3h

Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.214	BB	0.3382	4953.45361	229.10614	10.3511
2	17.408	BB	0.4311	4.29010e4	1484.92041	89.6489

Figure S60. HPLC copies of compound **3h**

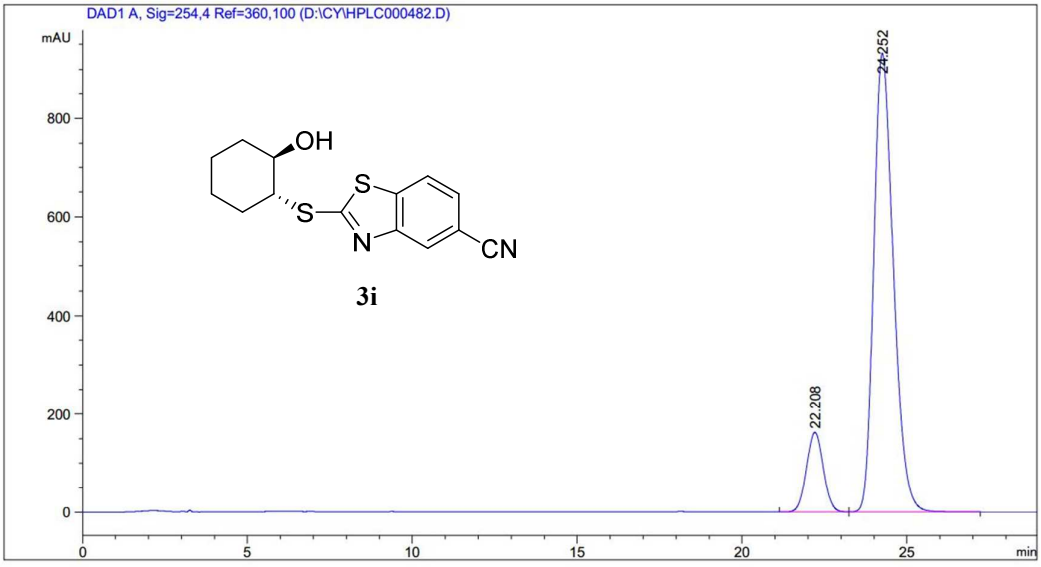
AD-H, iPrOH/Hex 20/80, flow rate = 1.0 mL/min



(±)-**3i**

Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.119	BB	0.4740	2.80851e4	925.62012	49.9842
2	21.986	BB	0.5387	2.81029e4	810.22986	50.0158

Figure S61. HPLC copies of compound **rac-3i**

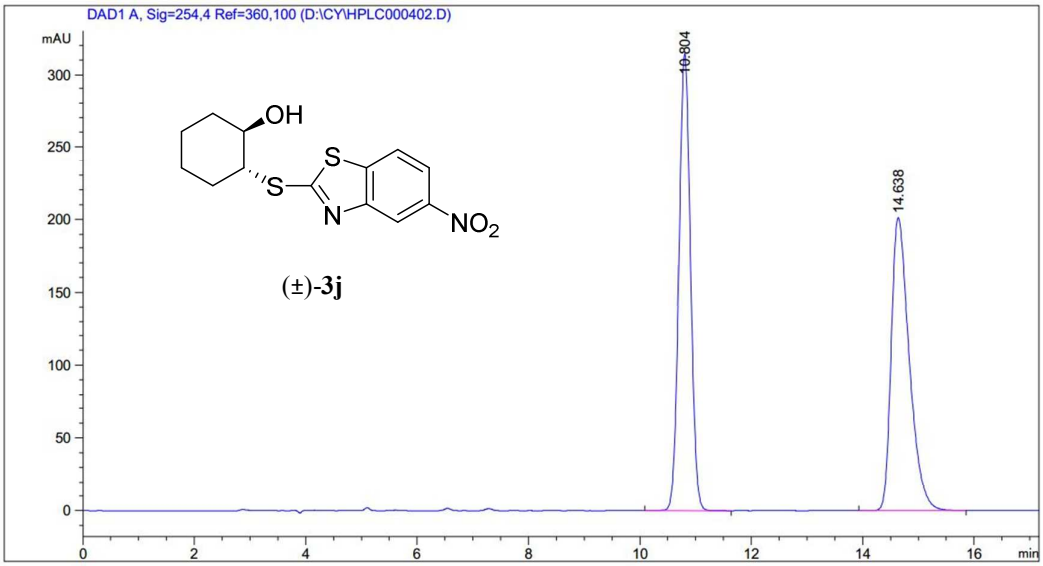


3i

Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.208	BB	0.5540	5759.89111	162.31488	12.9925
2	24.252	BB	0.6389	3.85724e4	931.86798	87.0075

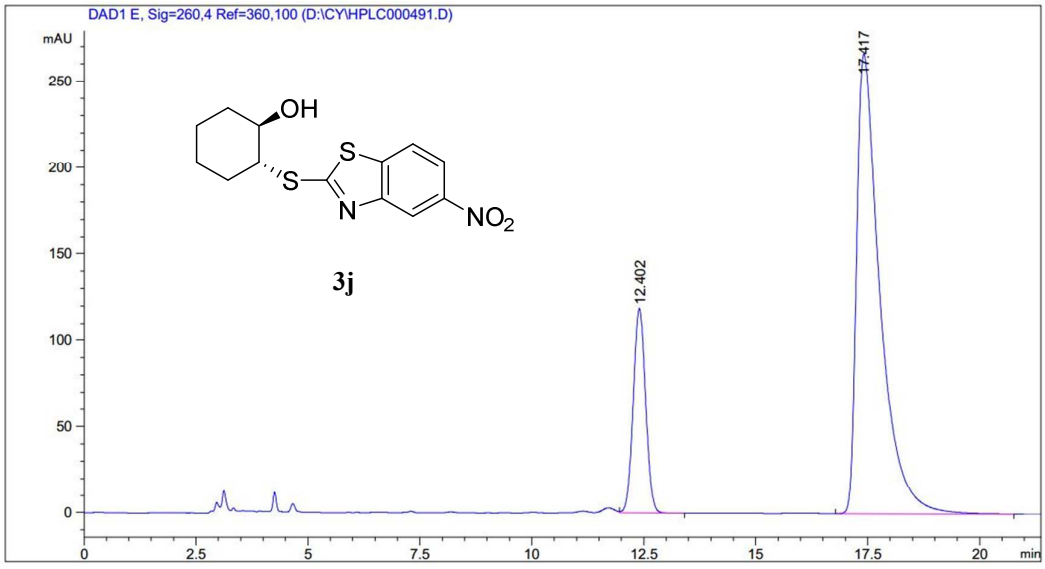
Figure S62. HPLC copies of compound **3i**

AD-H, iPrOH/Hex 30/70, flow rate = 1.0 mL/min



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.804	BB	0.2239	4522.75537	314.26477	49.9981
2	14.638	BB	0.3421	4523.10254	201.34048	50.0019

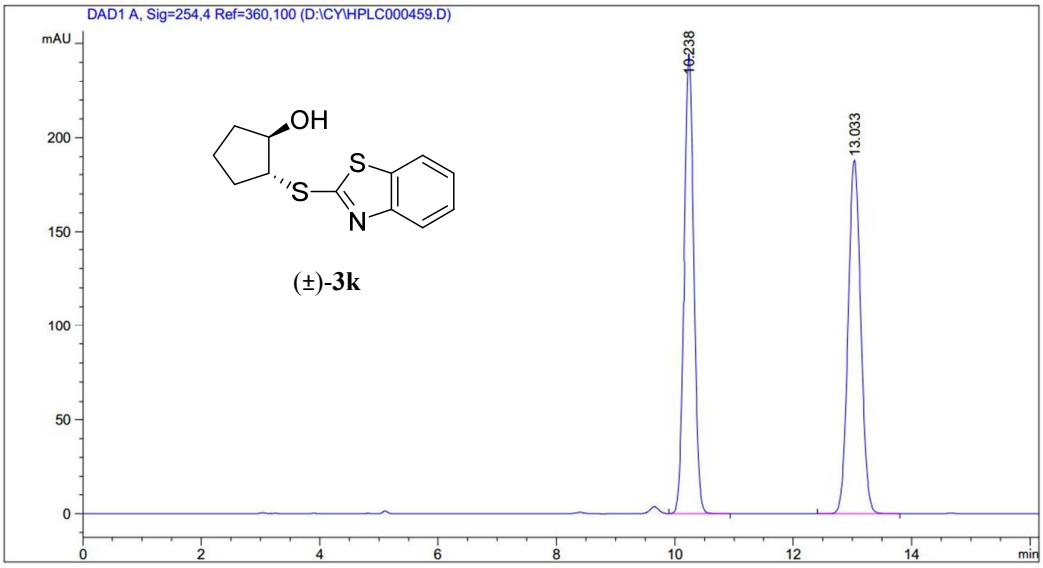
Figure S63. HPLC copies of compound **rac-3j**



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.402	VB	0.3009	2292.77075	118.91279	19.1539
2	17.417	BB	0.5335	9677.49316	266.59525	80.8461

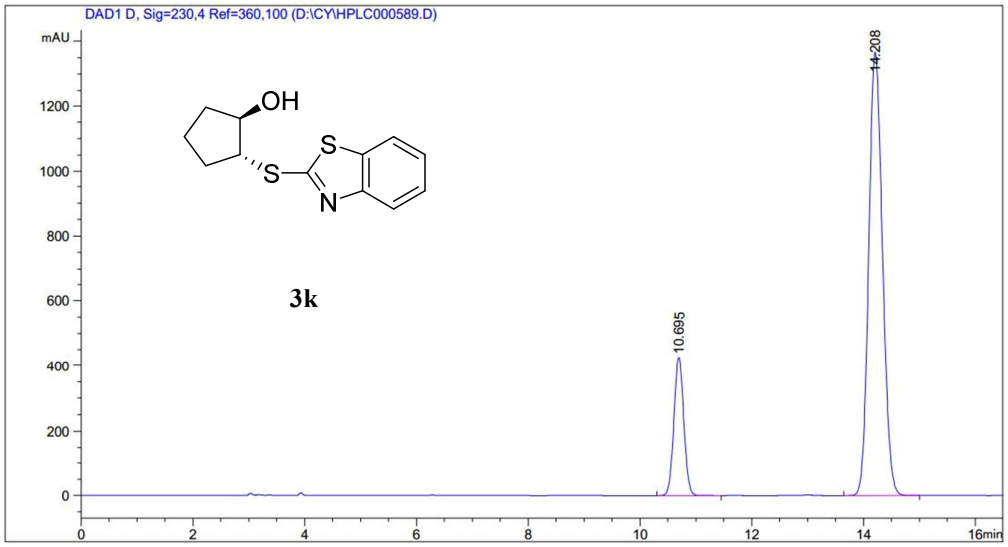
Figure S64. HPLC copies of compound **3j**

AD-H, iPrOH/Hex 10/90, flow rate = 1.0 mL/min



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.238	BB	0.1772	2792.41040	244.51637	49.9766
2	13.033	BB	0.2313	2795.02148	188.19705	50.0234

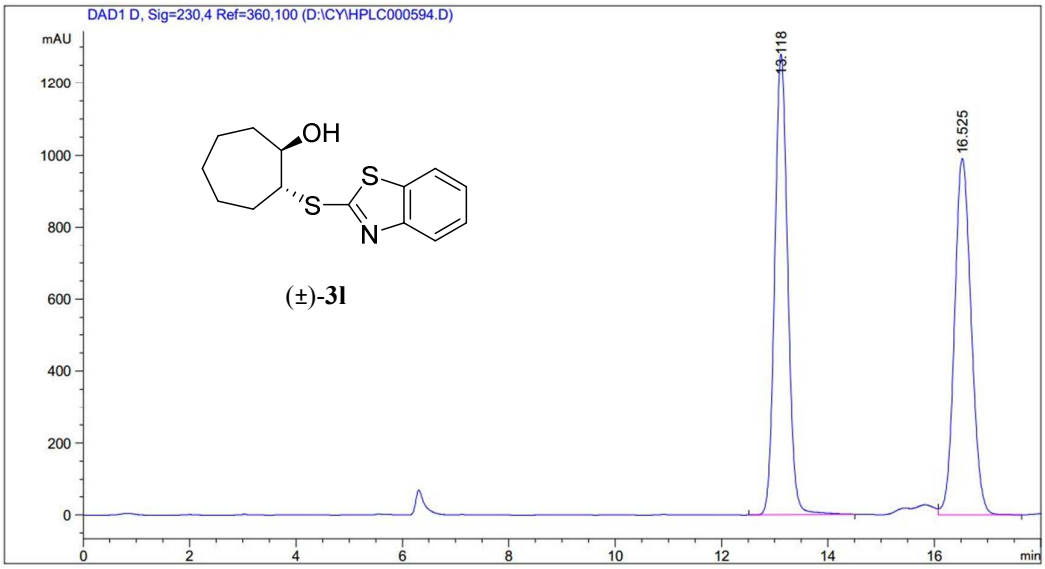
Figure S65. HPLC copies of compound **rac-3k**



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.695	BB	0.1917	5255.42871	426.78342	18.3880
2	14.208	BB	0.2672	2.33253e4	1365.82117	81.6120

Figure S66. HPLC copies of compound **3k**

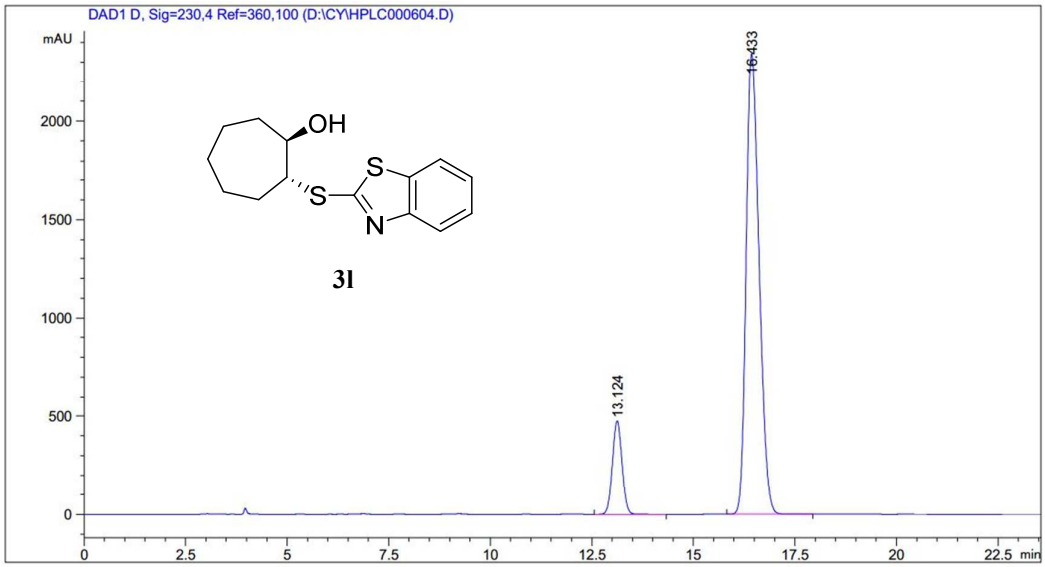
AD-H, iPrOH/Hex 10/90, flow rate = 1.0 mL/min



(±)-**3l**

Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.118	BB	0.2636	2.16858e4	1280.35767	50.1165
2	16.525	VB	0.3380	2.15850e4	991.53900	49.8835

Figure S67. HPLC copies of compound **rac-3l**

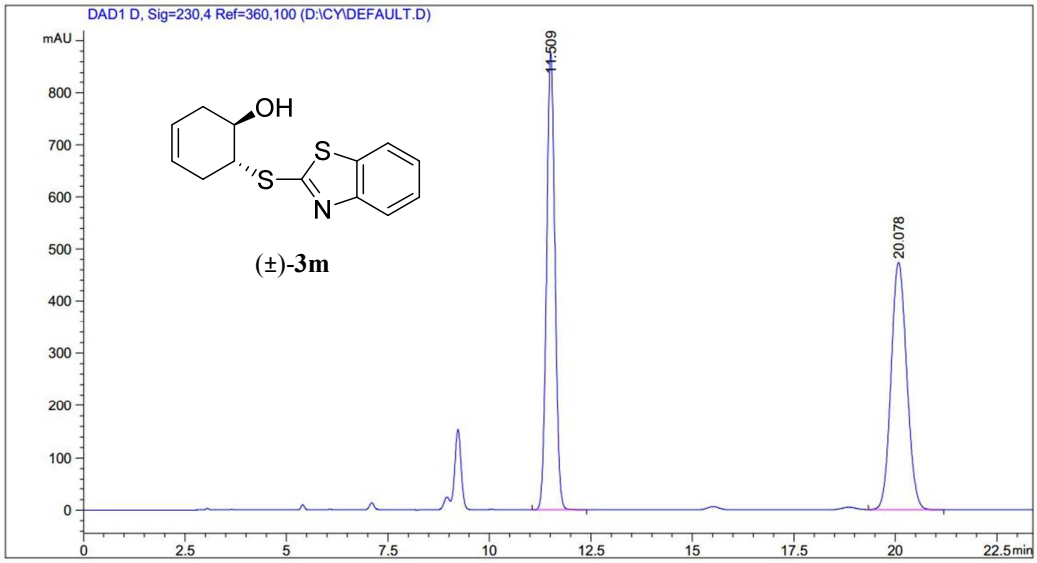


3l

Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.124	BB	0.2570	7846.15723	474.36633	13.0998
2	16.433	BB	0.3454	5.20491e4	2340.95728	86.9002

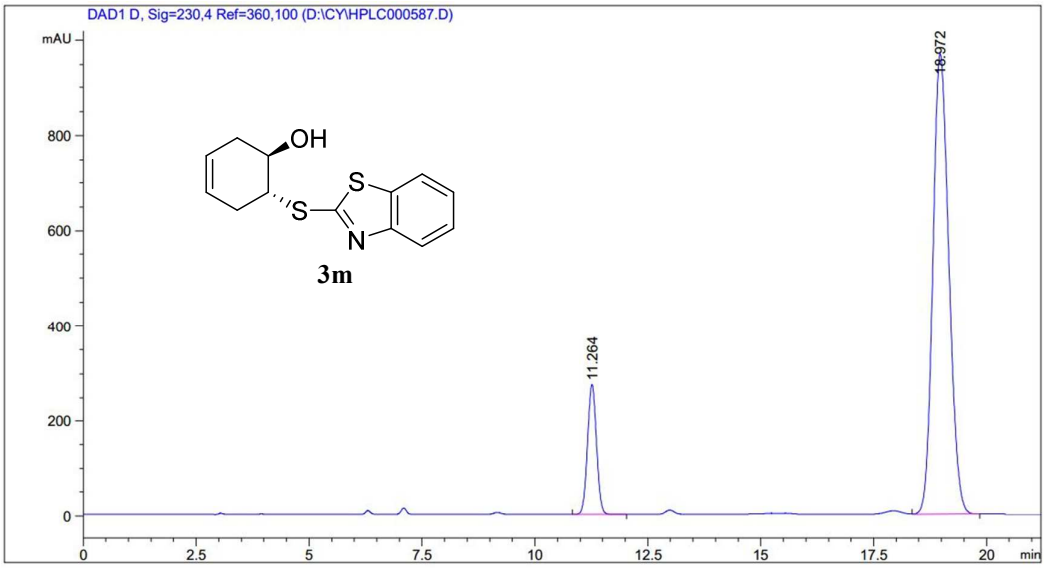
Figure S68. HPLC copies of compound **3l**

AD-H, iPrOH/Hex 10/90, flow rate = 1.0 mL/min



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.509	BB	0.2239	1.26099e4	875.95129	49.8997
2	20.078	BB	0.4158	1.26606e4	473.67377	50.1003

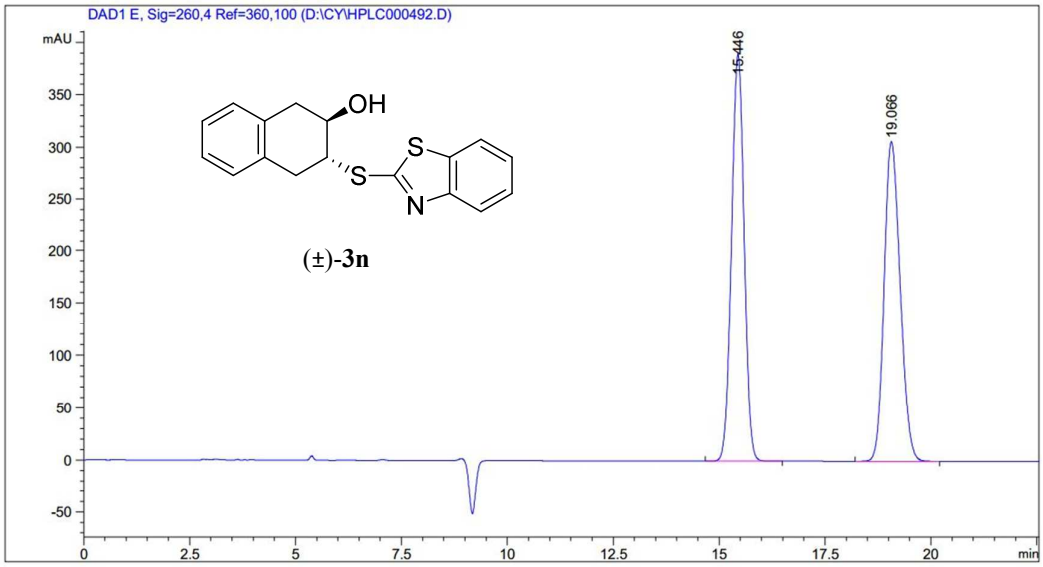
Figure S69. HPLC copies of compound **rac-3m**



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.264	BB	0.2143	3771.51782	274.56259	13.6575
2	18.972	VB	0.3854	2.38434e4	967.75299	86.3425

Figure S70. HPLC copies of compound **3m**

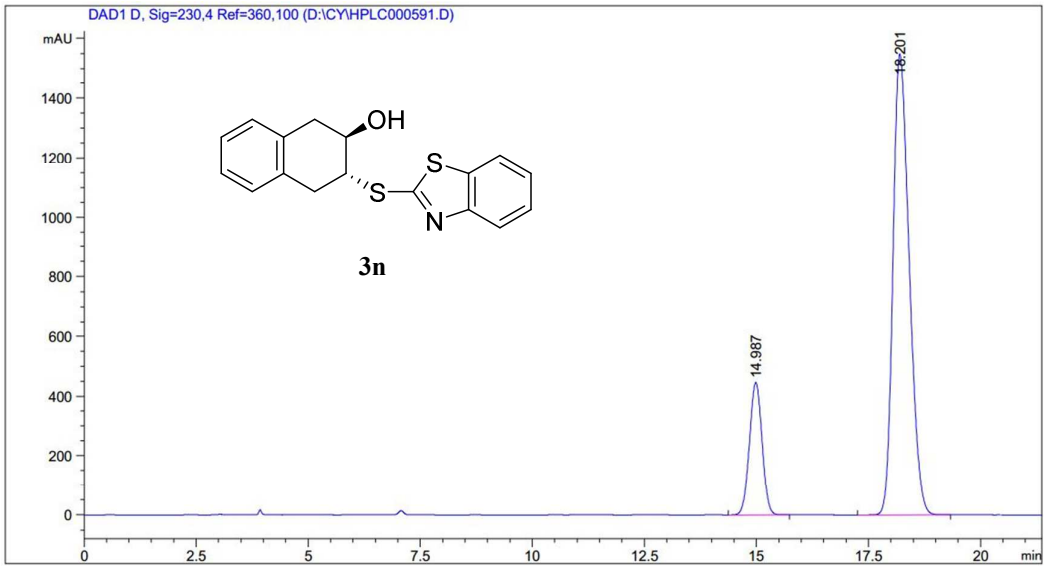
AD-H, iPrOH/Hex 10/90, flow rate = 1.0 mL/min



(±)-**3n**

Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.446	BB	0.3207	8048.61475	390.13434	49.9748
2	19.066	BB	0.4108	8056.73340	306.42227	50.0252

Figure S71. HPLC copies of compound **rac-3n**

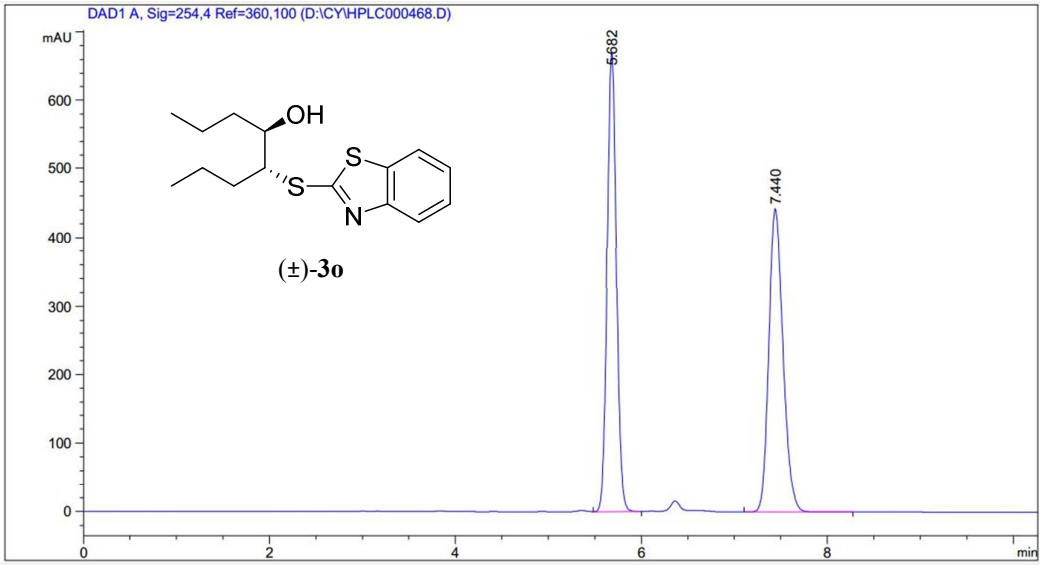


3n

Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.987	BB	0.3057	8728.25195	447.22971	18.2838
2	18.201	BB	0.3921	3.90094e4	1547.55017	81.7162

Figure S72. HPLC copies of compound **3n**

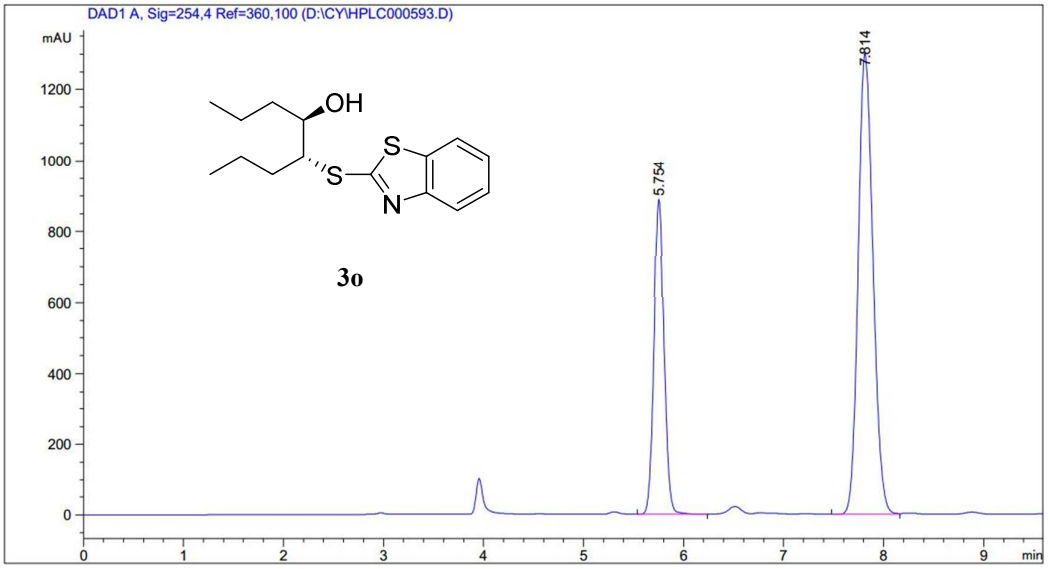
AD-H, iPrOH/Hex 10/90, flow rate = 1.0 mL/min



(±)-**3o**

Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.682	BB	0.1091	4655.03320	669.84845	49.8451
2	7.440	BB	0.1637	4683.96875	441.89224	50.1549

Figure S73. HPLC copies of compound **rac-3o**

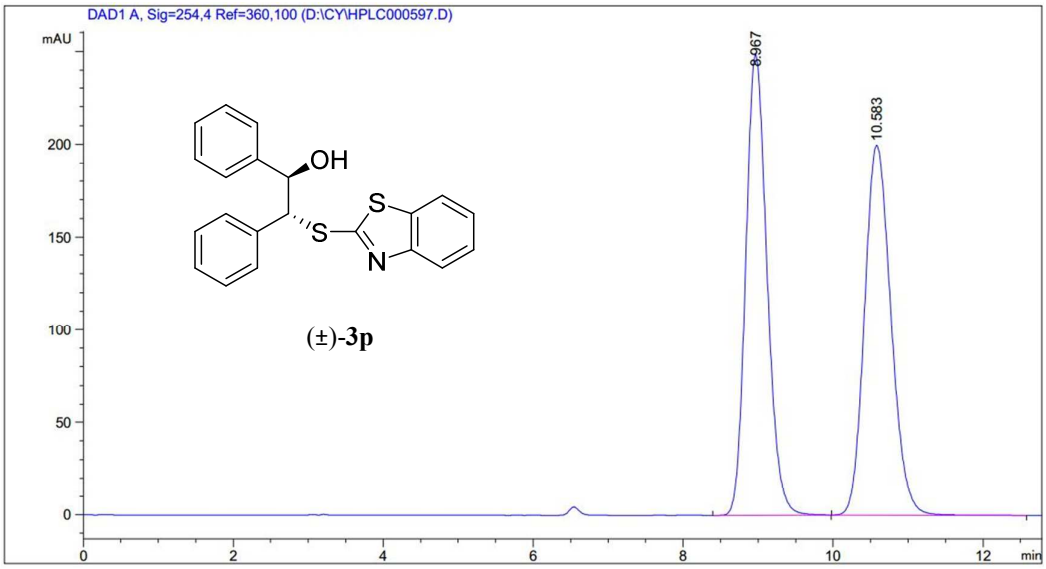


3o

Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.754	VB	0.1085	6279.13574	887.65759	31.8761
2	7.814	BV	0.1604	1.34194e4	1300.30701	68.1239

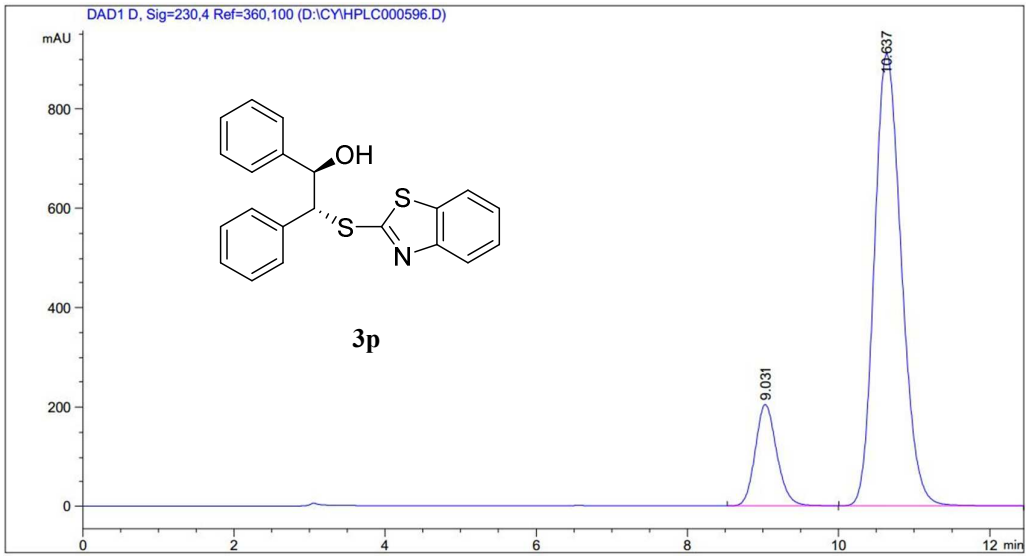
Figure S74. HPLC copies of compound **3o**

Rac-3p, AD-H, iPrOH/Hex 10/90, flow rate = 1.0 mL/min



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.967	BB	0.3035	4892.78857	248.77711	49.9768
2	10.583	BB	0.3820	4897.33447	199.79153	50.0232

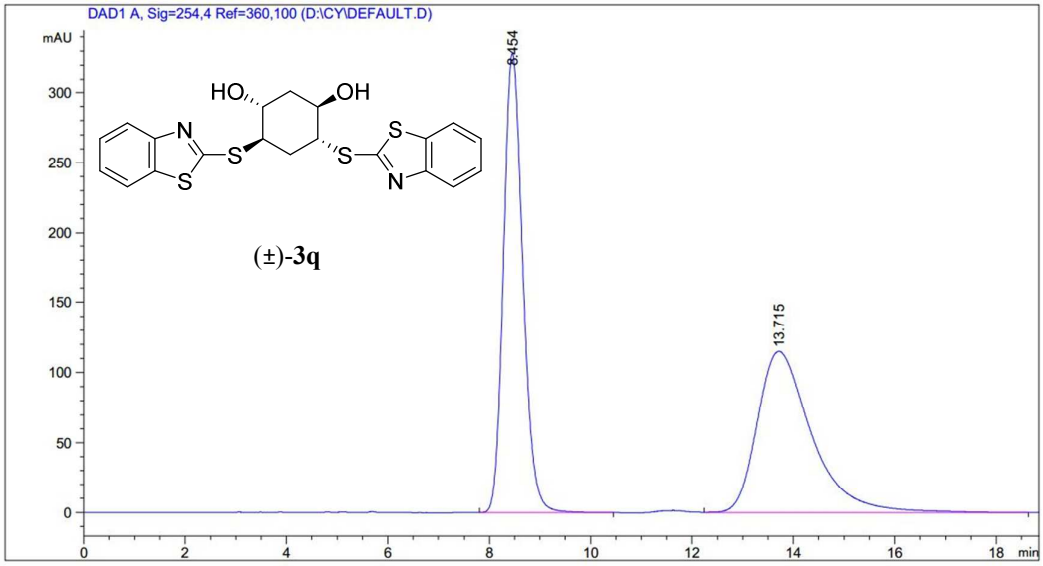
Figure S75. HPLC copies of compound **rac-3p**



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.031	BB	0.3081	4072.34521	204.67598	15.2393
2	10.637	BBA	0.3878	2.26502e4	911.75610	84.7607

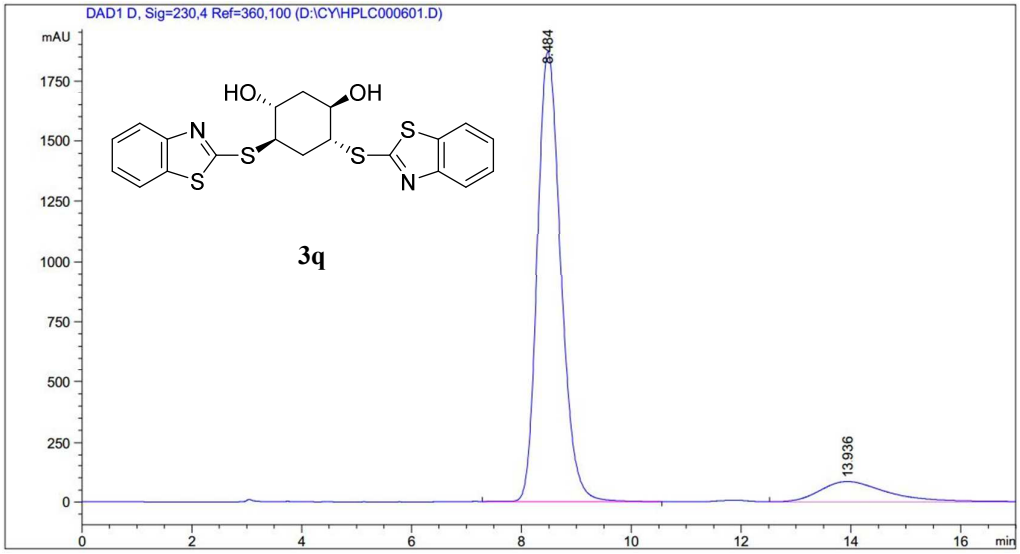
Figure S76. HPLC copies of compound **3p**

AS-H, iPrOH/Hex 20/80, flow rate = 1.0 mL/min



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.454	BB	0.4125	8743.38184	328.47589	50.4028
2	13.715	BB	1.1426	8603.64551	115.03646	49.5972

Figure S77. HPLC copies of compound **rac-3q**



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.484	BB	0.4610	5.55790e4	1868.42163	88.9140
2	13.936	BBA	1.2688	6929.70996	83.28011	11.0860

Figure S78. HPLC copies of compound **3q**