Solid-Phase Synthesis and Chemical Space Analysis of a 190-Membered Library of Alkaloid/Terpenoid-like Small Molecules

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Supporting Information

A. MATERIALS AND METHODS

Reagents were obtained from Aldrich Chemical (www.sigma-aldrich.com) or Acros Organics (www.fishersci.com) and used without further purification. Poly(bromostyrene) resin (150–300 μm) was purchased from Polymer Laboratories (www.polymerlabs.com). Optima grade solvents were obtained from Fisher Scientific (www.fishersci.com), degassed with Ar, and purified on a solvent drying system as described[1] unless otherwise indicated. Solution-phase reactions were performed in flame-dried glassware under positive Ar pressure with magnetic stirring. Solid-phase reactions were performed in flame-dried glassware under positive Ar pressure with magnetic stirring or in a Mettler-Toledo AutoChem MiniBlock XT^{TM} solution-phase synthesizer, or in a Radleys Carousel 12 solution-phase synthesizer. After each reaction, the resin was washed using a standard wash protocol as previously described.[2]

TLC was performed on 0.25 mm E. Merck silica gel 60 F254 plates and visualized under UV light (254 nm) or by staining with potassium permanganate ($KMnO_4$). Silica flash chromatography was performed on E. Merck 230–400 mesh silica gel 60. Parallel chromatography was performed on an ISCO CombiFlash OptiX 10 instrument with RediSep silica gel normal phase columns using a flow rate of 16.0 mL/min and a gradient of 10–100% EtOAc in hexanes over 20 min with UV detection at 254 nm. HPLC analysis was carried out on a Waters analytical HPLC with an XTerra C18 reverse phase column (150 mm x 4.6 mm, 5 μm, 120 Å) using a flow rate of 1.0 mL/min and a gradient of 50–100% CH_3CN in 0.1% aq TFA over 10 min with UV detection at 254 nm. Preparative scale HPLC purification was carried out on a Waters Prep HPLC using an XTerra C18 reverse phase column (150 mm x 19 mm) using a flow rate of 16.0 mL/min and a gradient of 50–100%, 75–100%, or 90–100% CH_3CN in 0.1% aq TFA over 16 min with UV detection at 254 nm. LC–MS analysis was carried out on a Waters 2695 LC system with a 996 diode array detector and a Micromass ZQ4000 mass spectrometer in ESI mode, with an XTerra C18 reverse phase column (150 mm x 4.6 mm) using a flow rate of 1.0 mL/min and a gradient of 50–100% CH_3CN in 0.1% aq TFA over 8 min. Lyophilization of aqueous samples was performed using a GeneVac HT-4X centrifugal evaporator. Lyophilization of larger aqueous samples was performed using a Labconco Freezone 2.5 instrument.

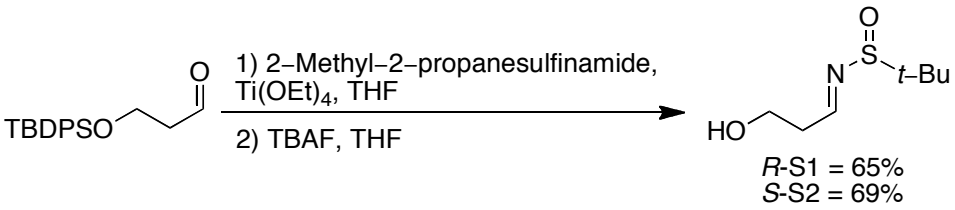
NMR spectra were recorded on Bruker Avance II 500 or Avance II 600 instruments at 24 °C in $CDCl_3$ unless otherwise indicated. Chemical shifts are expressed in ppm relative to TMS (^1H, 0 ppm) or solvent signals: $CDCl_3$ (^{13}C, 77.0 ppm); coupling constants are expressed in Hz. Mass spectra were obtained at the MSKCC Analytical Core Facility on a PE SCIEX API 100 or Waters 2505 mass spectrometer by electrospray (ESI) ionization or atmospheric pressure chemical ionization (AP-CI). Elemental analyses were carried out by Robertson Microlit Laboratories (www.roberston-microlit.com) and are reported in percent atomic abundance.

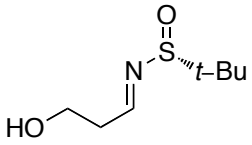
Resin loading levels are expressed in *mequiv/g* (not *mmol/g*), which are the appropriate units for a functionalized polymer. Theoretical maximum loading levels (*LL*) were calculated to account for the expected change in mass per unit of resin after each transformation:

$$LL_2 = \frac{LL_1}{1 + \left(LL_1 \times \left[MW_2 - MW_1\right]\right)}$$

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996,** *15*, 1518 1520.
[2] DiBlasi, C. M.; Macks, D. E.; Tan, D. S. *Org. Lett.* **2005**, *7*, 1777–1780.

B. SYNTHESIS OF SULFINIMINE ALCOHOLS (S1, S2)

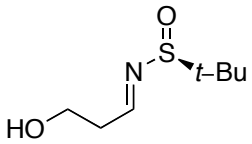




(*R*,*E*)-*N*-(3-Hydroxypropylidene)-2-methylpropane-2-sulfinamide (*R*-S1). In a 250 mL roundbottom flask, 3-(*tert*-butyldiphenylsilyloxy)propanal (16.2 g, 51.9 mmol, 1.0 equiv) was dissolved in 100 mL anhyd THF. $Ti(OEt)_4$ (2.99 mL, 13.0 mmol, 2.5 equiv) was added by syringe and solid (*R*)-*tert*-butylsulfinamide (6.92 g, 57.1 mmol, 1.1 equiv) was then added in one portion. The resulting orange solution was stirred at rt for 75 min. The reaction mixture was poured into 500 mL of vigorously stirred brine, and the flask was rinsed with EtOAc (500 mL). The resulting biphasic mixture was filtered through a pad of celite and transferred to a separatory funnel. The layers were separated and the aq layer was extracted with EtOAc (3 x 300 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated by rotary evaporation. Purification by silica flash chromatography (5:1 hexanes/EtOAc) yielded the *tert*-butylsulfinylimine TBDPS ether[3] (18.2 g, 86%) as a colorless oil.

In a 200 mL roundbottom flask, the (*R*)-*tert*-butylsulfinylimine above (18 g, 50 mmol, 1.0 equiv) was dissolved in 100 mL THF. TBAF (1 M in THF, 75 mL, 1.5 equiv) was added at 0 °C and the resulting solution was stirred for 10 min, then warmed to rt and stirred for 2 h. The reaction was quenched with aqueous NH_4Cl (100 mL), then extracted with EtOAc (3 x 200 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated by rotary evaporation. Purification by silica flash chromatography (1:1 hexanes/EtOAc) yielded the *tert*-butylsulfinylimine alcohol ***R*-S1** (12 g, 80%) as a colorless oil.

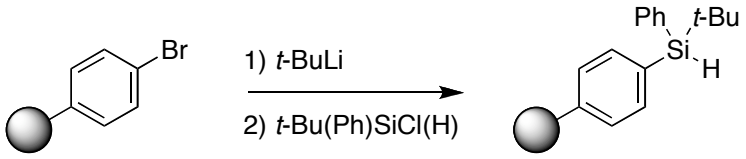
TLC: R_f 0.25 (1:4 hexanes/EtOAc). **^{1}H-NMR** (500 MHz): δ 8.16 (t, 1H, J = 4.7), 3.89 (t, 2H, J = 6.1), 2.74–2.78 (m, 2H), 1.10 (s, 9H). **^{13}C-NMR** (125 MHz): δ 168.2, 62.2, 55.9, 41.2, 25.8. **ESI-MS** *m/z* (rel int): (pos) 200.1 ([M+Na]$^+$, 100).



(*S*,*E*)-*N*-(3-Hydroxypropylidene)-2-methylpropane-2-sulfinamide (*S*-S2). Light yellow oil (12 g, 80%). **TLC**: R_f 0.25 (1:4 hexanes/EtOAc). **^{1}H-NMR** (500 MHz): δ 8.16 (t, 1H, J = 4.7), 3.89 (t, 2H, J = 6.1), 2.74–2.78 (m, 2H), 1.10 (s, 9H). **^{13}C-NMR** (125 MHz): δ 168.2, 62.2, 55.9, 41.2, 25.8. **ESI-MS** *m/z* (rel int): (pos) 200.1 ([M+Na]$^+$, 100).

[3] DiBlasi, C. M.; Macks, D. E.; Tan, D. S. *Org. Lett.* **2005**, *7*, 1777–1780.

C. PREPARATION OF TBDAS POLYSTYRENE RESIN



150–300 μm
2.2 mequiv/g

TBDAS-H
1.52 mequiv/g (81%)
elemental analysis: 4.31% Si

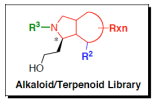
Resin-bound *t*-butyldiarylsilyl hydride (TBDAS-H).[2] Poly(bromostyrene) resin (30.3 g, 2.2 mequiv/g, 66.7 mequiv) was placed in a roundbottom flask with a stirbar under Ar atmosphere. The resin was swelled with anhyd benzene (500 mL) for 15 min at rt. *t*-BuLi (1.5 M in pentane, 202 mL, 303 mmol, 5 equiv) was added by syringe over 10 min, then the reaction was stirred for 1 h. Anhyd benzene (200 mL) was added and the excess *t*-BuLi was drained out under positive Ar pressure. The yellowish resin was rinsed with 2 x 300 mL anhyd benzene and resuspended in 400 mL anhyd benzene. *tert*-Butylchlorophenylsilane (48.1 g, 242 mmol, 4 equiv) was added by syringe and the resulting slurry was stirred at rt for 20 h. The resin was washed thoroughly: THF (2 x 500 mL), 3:1 THF/isopropanol (2 x 500 mL), 3:1 THF/H_2O (2 x 500 mL), 3:1 THF/isopropanol (2 x 500 mL), THF (2 x 500 mL), trimethylorthoformate (2 x 100 mL), CH_2Cl_2 (2 x 50 mL). The resin was then dried under high vacuum for 6 h. The TBDAS loading level was determined to be 1.53 mequiv/g by Si elemental analysis (82% of theoretical maximum 1.86 mequiv/g).

D. SUMMARY OF LIBRARY SYNTHESIS RESULTS

Library members were synthesized, cleaved, and purified as described in the manuscript. Due to the highly diverse nature of the library, the individual compounds exhibited similarly diverse retention properties during HPLC purification. Rather than optimize HPLC methods for each of the 190 library members individually, a series of three general HPLC methods was used, based primarily on the nature of the *N*-substituent, with minor variations based on predicted polarity. This allowed purification of the library in a timely fashion, although at the cost of some material losses.

Purified mass recoveries, overall yields (5–8 steps on solid support from sulfinimine alcohol loading through product cleavage), and average per-step yields are summarized in Table S1 below. The mean overall yield was 20.2% and the mean average per-step yield was 74.0%. All 190 compounds were recovered in sufficient quantities for high-throughput screening at the Rockefeller University High-Throughput Screening Resource Center and 94 compounds were also submitted to the NIH Molecular Libraries Small Molecule Repository under the auspices of the NIH Molecular Libraries Program.

Table S1. Summary of library synthesis results.



LEGEND	
S | R	R^3 = (*S*)- or (*R*)-SOt-Bu
H	R^3 = H
O	R^3 = SO_2t-Bu
E (a)	R^2 = CH_2CH_2OH
P (b)	R^2 = Ph
H (d)	R^2 = H
(S) | (R)	sidechain = (*S*)- or (*R*)-CH_2CH_2OH

a) Molecular weights (g/mol).

R^3	R^2	sidechain	Precursor / Reaction	A (from enynes 3)														P (from diynes 4)											
				K (11–13)		R-R (14–16)		R-S (17–19)		B (20)		G (21–23)		G-M (24)		G-D (25)		P-O-M (30–32)		P-O-O (33–35)		I-B-O (36–38)		I-B-M (39–41)		N-E-M (42–44)		N-E-O (na)		M-W-E (45–47)		M-W-Z (48–50)	
S | R	E (a)	|		315.4	315.4	289.4	289.4	289.4	289.4			287.4	287.4					341.5	341.5			418.6	418.6			384.5	384.5			426.6	426.6	426.6	426.6
	P (b)	|		347.5	347.5	321.5	321.5	321.5	321.5			319.5	319.5					373.5	373.5	373.5	373.5	450.6	450.6			416.5	416.5			458.6	458.6	458.6	458.6
	H (d)	|		271.4	271.4	245.3	245.3					243.3	243.3					297.4	297.4	297.4	297.4	374.5	374.5	374.5	374.5	340.4	340.4			382.6	382.6	382.6	382.6
H	E (a)	|		211.3	211.3	185.3	185.3	185.3	185.3			183.3	183.3					237.3	237.3			314.4	314.4			280.3	280.3			322.4	322.4	322.4	322.4
	P (b)	(S) | (R)		243.3	243.3	217.3	217.3	217.3	217.3			215.3	215.3					269.3	269.3	269.3	269.3	346.4	346.4			312.4	312.4			354.4	354.4	354.4	354.4
	H (d)	|		167.2	167.2	141.2	141.2					139.2	139.2					193.2	193.2	193.2	193.2	270.3	270.3	270.3	270.3	236.3	236.3			278.4	278.4	278.4	278.4
O	E (a)	|		331.4	331.4	305.4	305.4	305.4	305.4	357.5	357.5	303.4	303.4	476.6	476.6	443.5	443.5	357.5	357.5			434.6	434.6			400.5	400.5			442.6	442.6	442.6	442.6
	P (b)	|		363.5	363.5	337.5	337.5	337.5	337.5	389.6	389.6	335.5	335.5	508.6	508.6	475.6	475.6	389.5	389.5	389.5	389.5	466.6	466.6			432.5	432.5			474.6	474.6	474.6	474.6
	H (d)	|		287.4	287.4	261.4	261.4			313.5	313.5	259.4	259.4	432.5	432.5	399.5	399.5	313.4	313.4	313.4	313.4	390.5	390.5	390.5	390.5	356.4	356.4			398.6	398.6	398.6	398.6

b) Theoretical maximum resin loading levels for products (mequiv/g). Calculated based on initial TBDAS linker loading level of 1.53 mequiv/g (Si elemental analysis).

R^3	R^2	sidechain	Precursor / Reaction	A (from enynes 3)														P (from diynes 4)											
				K (11–13)		R-R (14–16)		R-S (17–19)		B (20)		G (21–23)		G-M (24)		G-D (25)		P-O-M (30–32)		P-O-O (33–35)		I-B-O (36–38)		I-B-M (39–41)		N-E-M (42–44)		N-E-O (na)		M-W-E (45–47)		M-W-Z (48–50)	
S | R	E (a)	|		1.04	1.04	1.06	1.06	1.06	1.06			1.07	1.07					1.01	1.01			0.94	0.94			0.97	0.97			0.93	0.93	0.93	0.93
	P (b)	|		1.00	1.00	1.03	1.03	1.03	1.03			1.03	1.03					0.98	0.98	0.98	0.98	0.91	0.91			0.94	0.94			0.90	0.90	0.90	0.90
	H (d)	|		1.09	1.09	1.12	1.12					1.12	1.12					1.06	1.06	1.06	1.06	0.98	0.98	0.98	0.98	1.01	1.01			0.97	0.97	0.97	0.97
H	E (a)	|		1.16	1.16	1.20	1.20	1.20	1.20			1.20	1.20					1.13	1.13			1.04	1.04			1.08	1.08			1.03	1.03	1.03	1.03
	P (b)	(S) | (R)		1.12	1.12	1.15	1.15	1.15	1.15			1.16	1.16					1.09	1.09	1.09	1.09	1.00	1.00			1.04	1.04			1.00	1.00	1.00	1.00
	H (d)	|		1.22	1.22	1.26	1.26					1.27	1.27					1.19	1.19	1.19	1.19	1.09	1.09	1.09	1.09	1.13	1.13			1.08	1.08	1.08	1.08
O	E (a)	|		1.02	1.02	1.05	1.05	1.05	1.05	0.99	0.99	1.05	1.05	0.89	0.89	0.91	0.91	0.99	0.99			0.92	0.92			0.95	0.95			0.92	0.92	0.92	0.92
	P (b)	|		0.99	0.99	1.01	1.01	1.01	1.01	0.96	0.96	1.01	1.01	0.86	0.86	0.89	0.89	0.96	0.96			0.90	0.90			0.92	0.92			0.89	0.89	0.89	0.89
	H (d)	|		1.07	1.07	1.10	1.10			1.04	1.04	1.10	1.10	0.92	0.92	0.95	0.95	1.04	1.04	1.04	1.04	0.96	0.96	0.96	0.96	0.99	0.99			0.95	0.95	0.95	0.95

c) Masses of resin cleaved (mg). Blue cells represent reactions from which two isomers were isolated separately.

R^3	R^2	sidechain	Precursor / Reaction	A (from enynes 3)														P (from diynes 4)														
				K (11–13)		R-R (14–16)		R-S (17–19)		B (20)		G (21–23)		G-M (24)		G-D (25)		P-O-M (30–32)		P-O-O (33–35)		I-B-O (36–38)		I-B-M (39–41)		N-E-M (42–44)		N-E-O (na)		M-W-E (45–47)		M-W-Z (48–50)	
S | R	E (a)	|		75	76	77	74	73	75			75	78					76	78			76	76			76	76			299	301		
	P (b)	|		100	100	100	101	100	104			100	97					200	200			99	100			99	98			398	396		
	H (d)	|		75	75	76	75					73	74					151	148			149	151			78	76			294	298		
H	E (a)	|		73	75	75	77	74	72			75	72					76	76			75	77			74	75			297	299		
	P (b)	(S) | (R)		99	98	100	99	100	97			101	99					201	200			101	102			101	102			402	400		
	H (d)	|		74	75	82	80					75	75					152	154			152	150			76	77			298	300		
O	E (a)	|		76	76	75	76	75	74	76	75	74	75	147	150	152	150	76	75			79	77			74	75			294	298		
	P (b)	|		99	97	101	102	98	99	102	101	99	97	200	200	202	198	201	202			102	101			100	103			401	400		
	H (d)	|		75	73	77	76			73	76	74	73	150	152	149	150	148	152			148	152			75	73			298	294		

d) Masses of purified products recovered (mg). Yields of individual isomers shown separately.

R^3	R^2	sidechain	Precursor / Reaction	A (from enynes 3)														P (from diynes 4)																
				K (11–13)		R-R (14–16)		R-S (17–19)		B (20)		G (21–23)		G-M (24)		G-D (25)		P-O-M (30–32)		P-O-O (33–35)		I-B-O (36–38)		I-B-M (39–41)		N-E-M (42–44)		N-E-O (na)		M-W-E (45–47)		M-W-Z (48–50)		
S | R	E (a)	|		7.0	7.3	8.2	8.3	8.1	8.1			8.8	9.1					8.9	9.1			7.5	7.0			7.4	7.0			1.7	4.4	2.2	3.7	
	P (b)	|		7.5	7.9	8.8	7.9	8.3	7.7			8.6	8.1					8.3	8.0	4.9	3.4	4.3	3.9			4.1	4.0			5.1	3.9	4.2	3.1	
	H (d)	|		7.3	7.1	7.4	7.2					7.8	8.2					7.8	8.1	7.2	7.6	8.1	8.3	8.5	7.0	4.6	4.9			4.9	4.1	4.5	3.3	
H	E (a)	|		3.1	1.7	4.1	5.6	4.0	4.9			0.9	0.8					1.1	1.5			4.9	3.1			3.5	4.1			2.5	2.1	2.1	1.5	
	P (b)	(S) | (R)		1.4	3.3	8.1	7.0	8.0	7.1			1.5	1.1					7.9	7.5	3.5	4.1	7.9	8.1			2.6	2.1			2.1	1.6	1.4	0.6	
	H (d)	|		2.4	3.1	7.5	7.1					1.2	0.7					2.1	1.7	1.0	0.8	3.5	3.9	4.1	2.1	7.1	7.6			1.9	2.0	1.2	0.9	
O	E (a)	|		7.4	7.2	8.3	8.9	7.3	8.1	4.5	3.9	7.7	8.0	8.1	8.6	4.2	2.1	8.8	8.2			7.8	7.0			8.0	7.3			3.9	2.9	3.3	3.1	
	P (b)	|		7.0	7.5	9.2	8.8	8.5	8.2	7.2	7.1	7.6	7.1	5.0	3.5	4.8	4.1	5.0	2.3			3.9	2.1			7.5	8.1			4.5	3.0	3.5	3.3	
	H (d)	|		7.1	7.2	9.1	8.2			7.0	7.5	7.0	7.2	7.5	7.1	8.6	8.0	7.1	7.4	7.3	7.0	3.1	3.5	2.9	1.9	3.1	3.6			4.1	3.3	3.1	2.9	TOTALS
Rockefeller		0.5			18		18		12		6		18		6		6		18		10		18		6		18	0		18		18	190
Rockefeller + NIH		6.0			12		16		10		4		12		4		2		12		4		8		2		8	0		0		0	94

e) Overall yields over 5–8 steps. Blue cells indicate combined yields for the two individual isomers, which were recovered separately.

R^3	R^2	sidechain	Precursor / Reaction	A (from enynes 3)														P (from diynes 4)																
				K (11–13)		R-R (14–16)		R-S (17–19)		B (20)		G (21–23)		G-M (24)		G-D (25)		P-O-M (30–32)		P-O-O (33–35)		I-B-O (36–38)		I-B-M (39–41)		N-E-M (42–44)		N-E-O (na)		M-W-E (45–47)		M-W-Z (48–50)		AVERAGE	
S | R	E (a)	|		29%	29%	35%	36%	36%	35%			38%	38%					34%	34%			25%	24%			26%	25%			3%	7%			28.4%	
	P (b)	|		22%	23%	27%	24%	25%	22%			26%	25%					18%	16%			11%	10%			11%	10%			6%	4%			17.4%	
	H (d)	|		33%	32%	36%	35%					39%	41%					32%	34%			30%	28%			17%	19%			9%	7%			27.9%	24.4%
H	E (a)	|		17%	9%	25%	33%	24%	31%			5%	5%					5%	7%			20%	12%			16%	18%			5%	4%			14.8%	
	P (b)	(S) | (R)		5%	12%	32%	28%	32%	29%			6%	4%					19%	20%			22%	23%			8%	6%			2%	2%			15.8%	
	H (d)	|		16%	20%	51%	50%					9%	5%					9%	7%			17%	14%			35%	37%			3%	3%			19.8%	16.7%
O	E (a)	|		29%	28%	35%	37%	30%	34%	17%	15%	33%	34%	13%	14%	7%	3%	33%	31%			25%	23%			28%	26%			6%	5%			22.9%	
	P (b)	|		20%	22%	27%	25%	25%	24%	19%	19%	23%	21%	6%	4%	6%	5%	7%	3%			9%	5%			19%	20%			5%	4%			14.3%	
	H (d)	|		31%	32%	41%	38%			29%	30%	33%	35%	13%	12%	15%	14%	30%	29%			11%	9%			12%	14%			6%	6%			22.0%	19.7%
		AVERAGE		22%	23%	34%	34%	29%	29%	22%	21%	24%	23%	10%	10%	9%	7%	21%	20%			19%	16%			19%	19%			5%	4%			20.2%	
					23%		34%		29%		21%		23%		10%		8%		20%				18%				19%				5%				

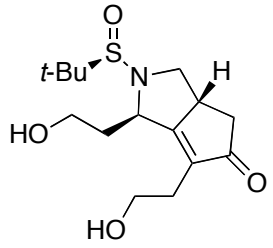
f) Average yields per solid-phase step. Blue cells indicate average yields calculated based on combined overall yields for the two individual isomers in part c above.

R^3	R^2	sidechain	Precursor / Reaction	A (from enynes 3)														P (from diynes 4)															
				K (11–13)		R-R (14–16)		R-S (17–19)		B (20)		G (21–23)		G-M (24)		G-D (25)		P-O-M (30–32)		P-O-O (33–35)		I-B-O (36–38)		I-B-M (39–41)		N-E-M (42–44)		N-E-O (na)		M-W-E (45–47)		M-W-Z (48–50)		AVERAGE	
S | R	E (a)	|		78%	78%	81%	82%	82%	81%			83%	82%					81%	81%			76%	75%			76%	76%			57%	64%			76.9%	
	P (b)	|		74%	74%	77%	75%	76%	74%			76%	76%					71%	69%			64%	62%			64%	64%			62%	59%			69.8%	
	H (d)	|		80%	80%	81%	81%					83%	84%					79%	80%			79%	77%			70%	72%			66%	64%			76.9%	74.4%
H	E (a)	|		75%	67%	79%	83%	79%	82%			62%	61%					62%	65%			76%	71%			73%	75%			65%	62%			71.0%	
	P (b)	(S) | (R)		61%	71%	83%	81%	83%	81%			63%	60%					76%	76%			78%	78%			66%	63%			59%	55%			70.8%	
	H (d)	|		74%	77%	89%	89%					67%	61%					67%	64%			74%	72%			84%	85%			62%	61%			73.3%	71.6%
O	E (a)	|		81%	81%	84%	85%	82%	84%	74%	73%	83%	83%	75%	75%	71%	66%	83%	82%			79%	78%			81%	80%			67%	65%			77.8%	
	P (b)	|		76%	77%	80%	79%	80%	79%	76%	76%	78%	77%	66%	63%	70%	69%	64%	56%			67%	61%			76%	76%			65%	63%			71.5%	
	H (d)	|		82%	83%	86%	85%			82%	82%	83%	84%	74%	74%	79%	78%	82%	81%			69%	68%			70%	72%			67%	66%			77.4%	75.5%
		AVERAGE		76%	76%	82%	82%	80%	80%	77%	77%	75%	74%	72%	71%	73%	71%	74%	73%			74%	71%			73%	74%			63%	62%			74.0%	
					76%		82%		80%		77%		75%		71%		72%		73%				72%				73%				63%				

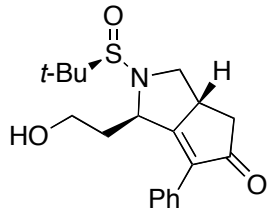
E. ANALYTICAL DATA FOR *R*-SERIES LIBRARY MEMBERS

^{1}H-NMR and mass spectral data are provided for all 190 library members (95 in the (*R*)-*tert*-butylsulfinimine-derived series below). Comprehensive analytical data, including optical rotation, IR, and ^{13}C-NMR data, is provided for a representative subset of 20 compounds from the *R*-series, including at least one compound from each of the 10 scaffold classes: ***R*-11a**, ***R*-14b, *R*-17b**, ***R*-20b**, ***R*-23d**, ***R*-24a**, ***R*-25b**, ***R*-30a**, ***R*-30b**, ***R*-32d**, ***R*-33d**, ***R*-35d**, ***R*-36a**, ***R*-36d**, ***R*-39d**, ***R*-42a**, ***R*-42b**, ***R*-44a**, ***R*-44b**, ***R*-45b**.

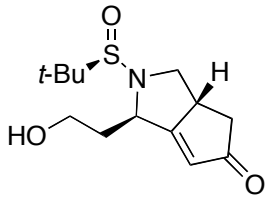
1. PAUSON–KHAND REACTION PRODUCTS (*R*-11–13)



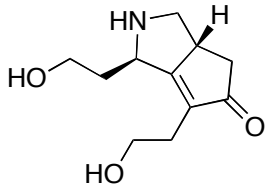
(–)-(1*R*,3a*R*)-2-((*R*)-*tert*-Butylsulfinyl)-1,6-bis(2-hydroxyethyl)-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (*R*-11a). Clear oil (7.3 mg). **TLC**: R_f 0.40 (1:9 hexanes/EtOAc) $[\alpha]_D^{20}$: –18.0° (*c* 0.48, $CHCl_3$). **IR** (NaCl, film): 3388 (O–H st), 3021, 2998, 2882, 1712 (C=O st), 1661, 1452, 1351, 1265, 1131 (S–O st), 910, 836. **^{1}H-NMR** (600 MHz): δ 5.85 (dt, 1H, *J* = 8.8, 6.1), 5.16 (d, 1H, *J* = 10.0), 5.03 (d, 1H, *J* = 8.2), 4.51 (s, 1H), 3.92 (dd, 1H, *J* = 12.5, 8.2), 3.78–3.72 (m, 2H), 3.56–3.52 (m, 2H), 2.48 (t, 1H, *J* = 5.6), 1.83–1.78 (m, 3H), 1.64-1.62 (m, 1H), 1.21 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 208.7, 178.1, 134.6, 60.4, 60.2, 58.2, 57.2, 47.9, 40.2, 40.0, 36.3, 27.9, 25.9. **ESI-MS** *m*/*z* (rel int): (pos) 310.4 ([M–CO+Na]$^+$, 100).



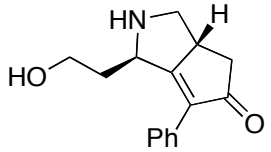
(1*R*,3*R*)-2-((*R*)-*tert*-Butylsulfinyl)-1-(2-hydroxyethyl)-6-phenyl-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (*R*-11b). Clear oil (7.9 mg). **TLC**: R_f 0.24 (1:4 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.39–7.31 (m, 5H), 6.02 (dt, 1H, *J* = 8.4, 2.4), 5.30 (d, 1H, *J* = 14.3), 5.16 (d, 1H, *J* = 8.8), 4.82 (t, 1H, *J* = 8.8), 3.98 (dd, 1H, *J* = 10.2, 4.4), 3.89 (dd, 1H, *J* = 8.8, 3.5), 3.70–3.65 (m, 2H), 2.04–1.98 (m, 2H), 1.31 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 370.5 ([M+Na]$^+$, 100).



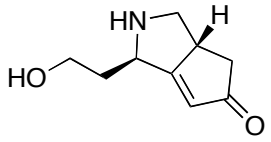
(1*R*,3*R*)-2-((*R*)-*tert*-Butylsulfinyl)-1-(2-hydroxyethyl)-2,3,3a,4-tetrahydrocyclopenta[*c*]-pyrrol-5(1*H*)-one (*R*-11d). Light yellow oil (7.1 mg). **TLC**: R_f 0.27 (1:6 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.92 (dt, 1H, *J* = 5.5, 2.6), 5.16 (d, 1H, *J* = 12.0), 5.03 (d, 1H, *J* = 8.2), 4.59 (t, 1H, *J* = 8.7), 3.98 (s, 1H), 3.96 (dd, 1H, *J* = 10.7, 8.6), 3.85 (dd, 1H, *J* = 9.1, 10.7), 3.54–3.49 (m, 2H), 1.81–1.76 (m, 2H), 1.21 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 240.4 ([M+Na]$^+$, 100).



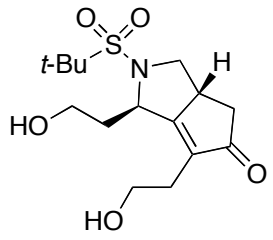
(1*R*,3a*R*)-1,6-Bis(2-hydroxyethyl)-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (*R*-12a). Clear oil (3.3 mg). **TLC**: R_f 0.31 (1:5 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.96 (dt, 1H, *J* = 8.8, 6.2), 5.18 (d, 1H, *J* = 10.0), 5.05 (d, 1H, *J* = 8.2), 4.62 (s, 1H), 4.08 (dd, 1H, *J* = 12.5, 8.2), 3.92–3.88 (m, 1H), 3.76–3.72 (m, 1H), 3.52–3.50 (m, 1H), 2.96–2.92 (m, 1H), 2.48 (t, 1H, *J* = 5.6), 1.89–1.85 (m, 1H), 1.74–1.70 (m, 1H), 1.61–1.58 (m, 2H). **ESI-MS** *m/z* (rel int): (pos) 234.4 ([M+Na]$^+$, 100).



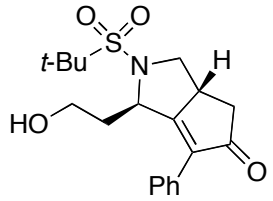
(1*R*,3a*R*)-1-(2-Hydroxyethyl)-6-phenyl-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (R-12b). Clear oil (3.5 mg). **TLC**: R_f 0.48 (1:9 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.34–7.32 (m, 2H), 7.29–7.27 (m, 3H), 6.02 (dt, 1H, *J* = 8.8, 6.2), 5.21 (d, 1H, *J* = 10.0), 5.16 (d, 1H, *J* = 8.2), 4.82 (s, 1H), 4.04 (bs, 1H), 3.98 (dd, 1H, *J* = 12.5, 8.2), 3.88 (dd, 1H, *J* = 10.0, 6.2), 3.67–3.61 (m, 2H), 3.46–3.42 (m, 1H), 2.06–2.02 (m, 1H), 1.70 (bs, 1H). **ESI-MS** *m/z* (rel int): (pos) 267.2 ([M+Na]$^+$, 100).



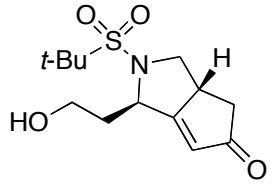
(1*R*,3a*R*)-1-(2-Hydroxyethyl)-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (*R*-12d). Clear oil (3.1 mg). **TLC**: R_f 0.26 (1:5 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.86 (dt, 1H, *J* = 8.8, 6.2), 5.12 (d, 1H, *J* = 10.0), 5.03 (d, 1H, *J* = 8.2), 4.52 (s, 1H), 4.17 (dt, 1H, *J* = 12.5, 8.2), 3.92–3.88 (m, 1H), 3.76–3.72 (m, 1H), 3.52–3.50 (m, 1H), 2.96–2.92 (m, 1H), 2.37 (s, 1H), 1.78–1.74 (m, 2H). **ESI-MS** *m/z* (rel int): (pos) 190.2 ([M+Na]$^+$, 100).



(1*R*,3a*R*)-2-(*tert*-Butylsulfonyl)-1,6-bis(2-hydroxyethyl)-2,3,3a,4-tetrahydrocyclopenta[*c*]-pyrrol-5(1*H*)-one (*R*-13a). Clear oil (7.2 mg). **TLC**: R_f 0.40 (1:6 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.92 (dt, 1H, *J* = 8.8, 6.1), 5.16 (d, 1H, *J* = 10.0), 5.03 (d, 1H, *J* = 8.2), 4.62–4.57 (m, 1H), 4.13–4.04 (m, 1H), 3.92 (dd, 1H, *J* = 14.3, 8.2), 3.68–3.61 (m, 1H), 3.50–3.45 (m, 1H), 2.99 (dd, 1H, *J* = 5.6, 3.5), 1.93–1.87 (m, 1H), 1.81 (dd, 2H, *J* = 7.5, 6.8), 1.61–1.56 (m, 2H), 1.31 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 354.4 ([M+Na]$^+$, 100).

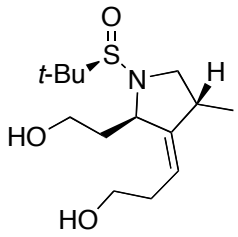


(1*R*,3a*R*)-2-(*tert*-Butylsulfonyl)-1-(2-hydroxyethyl)-6-phenyl-2,3,3a,4-tetrahydrocyclopenta-[*c*]pyrrol-5(1*H*)-one (*R*-13b). Clear oil (7.5 mg). **TLC**: R_f 0.24 (1:6 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.39–7.31 (m, 5H) 5.98 (dt, 1H, *J* = 8.4, 2.4), 5.21 (d, 1H, *J* = 14.3), 5.03 (d, 1H, *J* = 8.8), 4.91 (dd, 1H, *J* = 8.8, 6.1), 4.13 (d, 1H, *J* = 10.2), 4.02 (t, 1H, *J* = 8.0), 3.81–3.76 (m, 1H), 3.56–3.52 (m, 1H), 2.91 (s, 1H), 2.04–1.98 (m, 1H), 1.65 (dt, 1H, *J* = 10.1, 8.8), 1.44 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 386.5 ([M+Na]$^+$, 100).

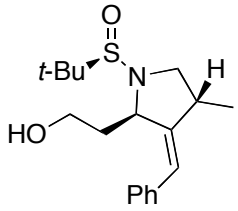


(1*R*,3a*R*)-2-(*tert*-Butylsulfonyl)-1-(2-hydroxyethyl)-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (*R*-13d). Light yellow oil (7.2 mg). **TLC**: R_f 0.27 (1:4 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.92 (dt, 1H, *J* = 5.5, 1.5), 5.16 (d, 1H, *J* = 12.0), 5.03 (d, 1H, *J* = 8.2), 4.69 (dd, 1H, *J* = 5.3, 8.7), 4.13 (d, 1H, *J* = 12.0), 3.96 (dd, 1H, *J* = 10.7, 8.6), 3.68 (dt, 1H, *J* = 9.1, 10.7), 3.50 (dt, 1H, *J* = 6.3, 6.1), 2.80 (s, 1H), 1.98 (dd, 1H, *J* = 7.1, 5.5), 1.81–1.78 (m, 1H), 1.41 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 310.4 ([M+Na]$^+$, 100).

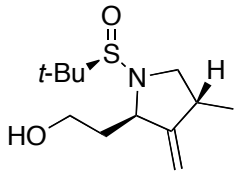
2. KRISCHE REDUCTIVE CYCLIZATION PRODUCTS (*R*-14–19)



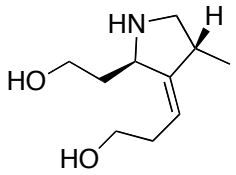
(*Z*)-3-((2*R*,4*R*)-1-((*R*)-*tert*-Butylsulfinyl)-2-(2-hydroxyethyl)-4-methylpyrrolidin-3-ylidene)-propan-1-ol (*R*-14a). Colorless oil (8.3 mg). **TLC**: R_f 0.53 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.02 (t, 1H, *J* = 7.1), 4.49 (t, 1H, *J* = 7.6), 4.09–4.03 (m, 1H), 3.68–3.62 (m, 2H), 3.19 (d, 1H, *J* = 8.8), 3.04–2.98 (m, 2H), 2.78–2.71 (m, 1H), 2.31 (s, 1H), 1.91–1.87 (m, 2H), 1.82–1.76 (m, 2H), 1.21 (s, 9H), 1.05 (d, 3H, *J* = 6.8). **ESI-MS** *m/z* (rel int): (pos) 312.2 ($[M+Na]^+$, 100).



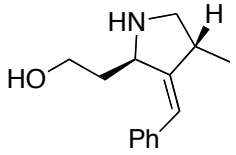
(–)-2-((2*R*,4*R*,*Z*)-3-Benzylidene-1-((*R*)-*tert*-butylsulfinyl)-4-methylpyrrolidin-2-yl)ethanol (*R*-14b). Colorless oil (7.9 mg). **TLC**: R_f 0.40 (1:1 hexanes/EtOAc). $[\alpha]_D^{20}$: –33.2° (*c* 0.35, $CHCl_3$). **IR** (NaCl, film): 3401 (O–H st), 3016, 2990, 2864, 1432, 1351, 1111 (S–O st), 942, 826. **^{1}H-NMR** (600 MHz): δ 7.43–7.40 (m, 2H) 7.36 (d, 1H, *J* = 4.0), 7.23–7.18 (m, 2H), 6.41 (s, 1H), 5.43 (bs, 1H), 4.95 (s, 1H), 3.82–3.79 (m, 1H), 3.76–3.71 (m, 1H), 3.65–3.61 (m, 1H), 3.03 (s, 1H), 2.83 (t, 1H, *J* = 9.5), 1.95–1.89 (m, 1H), 1.87–1.81 (m, 1H) 1.19 (s, 9H), 1.16 (d, 3H, *J* = 6.5). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 149.2, 137.1, 128.5, 128.2, 126.7, 120.9, 65.8, 59.8, 58.3, 48.6, 41.5, 36.4, 23.7, 19.0. **ESI-MS** *m/z* (rel int): (pos) 218.2 ($[M+H]^+$, 100).



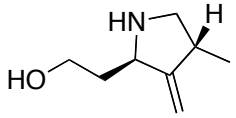
2-((2*R*,4*R*)-1-((*R*)-*tert*-Butylsulfinyl)-4-methyl-3-methylenepyrrolidin-2-yl)ethanol (*R*-14d). Colorless oil (7.2 mg). **TLC:** R_f 0.33 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 4.91 (s, 2H), 4.21 (t, 1H, *J* = 5.5), 3.73–3.69 (m, 2H), 3.11 (t, 1H, *J* = 9.3), 3.00 (t, 1H, *J* = 9.3), 2.76–2.61 (m, 1H), 1.94–1.86 (m, 1H), 1.77–1.72 (m, 1H), 1.16 (s, 9H), 1.08 (d, 3H, *J* = 6.7). **ESI-MS** *m/z* (rel int): (pos) 268.1 ($[M+Na]^+$, 100).



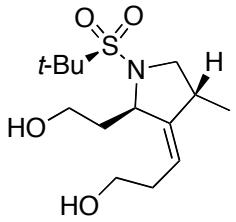
(*Z*)-3-((2*R*,4*R*)-2-(2-Hydroxyethyl)-4-methylpyrrolidin-3-ylidene)propan-1-ol (*R*-15a). Colorless oil (5.6 mg). **TLC**: R_f 0.53 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.11 (t, 1H *J* = 7.1), 4.48 (t, 1H, *J* = 5.8), 3.71–3.63 (m, 2H), 3.61–3.58 (m, 2H), 3.10 (t, 1H, *J* = 9.6), 2.96 (t, 1H, *J* = 8.3), 2.64 (s, 1H), 2.30–2.23 (m, 2H), 1.78 (q, 2H, *J* = 6.5), 1.06 (d, 3H, *J* = 6.7). **ESI-MS** *m/z* (rel int): (pos) 208.2 ([M+Na]+, 100).



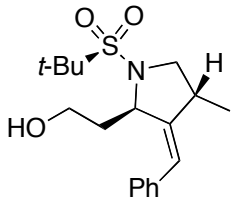
2-((2*R*,4*R*,*Z*)-3-Benzylidene-4-methylpyrrolidin-2-yl)ethanol (*R*-15b). Colorless oil (7.0 mg). **TLC**: R_f 0.40 (1:20 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.31–7.25 (m, 3H) 7.19–7.14 (m, 2H), 6.43 (s, 1H), 4.93 (d, 1H, *J* = 9.2), 3.76 (t, 1H, *J* = 8.6), 3.68–3.54 (m, 2H), 3.05 (t, 1H, *J* = 6.7), 2.78 (t, 1H, *J* = 7.5), 1.92–1.90 (m, 1H), 1.79–1.76 (m, 1H), 1.30 (d, 3H, *J* = 6.5). **ESI-MS** *m/z* (rel int): (pos) 218.0 ([M+H]+, 100).



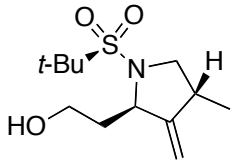
2-((2*R*,4*R*)-4-Methyl-3-methylenepyrrolidin-2-yl)ethanol (*R*-15d). Colorless oil (7.1 mg). **TLC:** R_f 0.33 (1:20 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.10 (d, 1H, *J* = 11.8), 5.03 (d, 1H, *J* = 11.8), 4.24 (t, 1H, *J* = 5.7), 3.90 (t, 1H, *J* = 6.7), 3.78 (t, 1H, *J* = 6.6), 3.58 (t, 1H, *J* = 6.4), 3.30 (bs, 1H), 2.92 (dd, 1H, *J* = 9.5, 7.1), 2.75 (dd, 1H, *J* = 7.1, 5.2), 2.01–1.96 (m, 2H), 1.18 (d, 3H, *J* = 6.7). **ESI-MS** *m/z* (rel int): (pos) 164.1 ($[M+Na]^+$, 100).



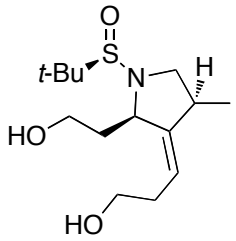
(*Z*)-3-((2*R*,4*R*)-1-(*tert*-Butylsulfonyl)-2-(2-hydroxyethyl)-4-methylpyrrolidin-3-ylidene)-propan-1-ol (*R*-16a). Colorless oil (8.9 mg). **TLC**: R_f 0.53 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 4.89 (t, 1H, *J* = 7.1), 4.51 (d, 1H, *J* = 7.6), 4.22 (t, 2H, *J* = 6.9), 3.72–3.66 (m, 2H), 3.55 (d, 1H, *J* = 8.8), 2.55–2.49 (m, 1H), 2.41–2.38 (m, 1H), 1.98–1.95 (m, 1H), 1.89–1.85 (m, 2H), 1.76 (t, 1H, *J* = 6.5), 1.52 (bs, 1H), 1.21 (s, 12H). **ESI-MS** *m/z* (rel int): (pos) 328.4 ($[M+Na]_+$, 100).



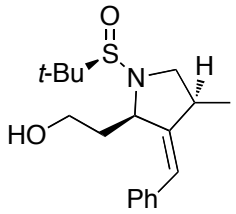
2-((2*R*,4*R*,*Z*)-3-Benzylidene-1-(*tert*-butylsulfonyl)-4-methylpyrrolidin-2-yl)ethanol (*R*-16b). Colorless oil (8.8 mg). **TLC**: R_f 0.40 (3:2 hexnes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.36–7.31 (m, 2H), 7.28–7.23 (m, 2H), 7.20–7.16 (m, 1H), 6.35 (s, 1H), 5.15 (d, 1H, *J* = 10.1), 3.97 (dd, 1H, *J* = 10.1, 7.1), 3.79–3.76 (m, 1H), 3.64–3.61 (m, 1H), 3.11–3.03 (m, 1H), 3.01–2.98 (m, 1H), 2.48 (bs, 1H), 1.88–1.83 (m, 1H), 1.52–1.48 (m, 1H), 1.24 (d, 3H, *J* = 6.9), 1.18 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 360.2 ([M+Na]$^+$, 100).



2-((2*R*,4*R*)-1-(*tert*-Butylsulfonyl)-4-methyl-3-methylenepyrrolidin-2-yl)ethanol (*R*-16d). Colorless oil (8.2 mg, 74%). **TLC:** R_f 0.33 (3:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 4.92 (s, 2H), 4.28 (t, 1H, *J* = 5.5), 3.81–3.69 (bm, 2H), 3.18 (t, 1H, *J* = 6.7), 3.05 (t, 1H, *J* = 7.4), 2.79 (s, 1H), 1.92–1.86 (m, 2H), 1.82–1.78 (m, 1H), 1.25 (s, 9H), 1.11 (d, 3H, *J* = 6.7). **ESI-MS** *m*/*z* (rel int): (pos) 284.4 ([M+Na]$^+$, 100).

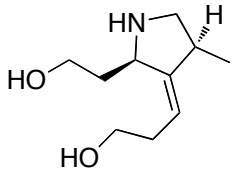


(*Z*)-3-((2*R*,4*S*)-1-((*R*)-*tert*-Butylsulfinyl)-2-(2-hydroxyethyl)-4-methylpyrrolidin-3-ylidene)-propan-1-ol (*R*-17a). Colorless oil (8.1 mg). **TLC**: R_f 0.53 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.21 (t, 1H, *J* = 7.3), 4.47 (d, 1H, *J* = 9.3), 3.91 (t, 1H, *J* = 10.9), 3.71–3.68 (m, 2H), 3.62–3.58 (m, 2H), 2.64–2.61 (m, 1H), 2.51 (dd, 1H, *J* = 9.0, 11.2), 2.31–2.25 (m, 2H), 1.96–1.92 (m, 2H), 1.08 (s, 9H), 1.02 (d, 3H, *J* = 6.9). **ESI-MS** *m*/*z* (rel int): (pos) 312.2 ([M+Na]$^+$, 100).

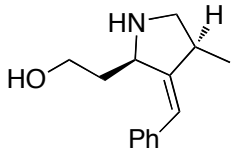


(–)-2-((2*R*,4*S*,*Z*)-3-Benzylidene-1-((*R*)-*tert*-butylsulfinyl)-4-methylpyrrolidin-2-yl)ethanol (*R*-17b). Colorless oil (7.7 mg). **TLC**: R_f 0.40 (1:1 hexanes/EtOAc). $[\alpha]_D^{20}$: –21.1° (*c* 0.32, $CHCl_3$). **IR** (NaCl, film): 3409 (O–H st), 3023, 2988, 1428, 1348, 1101 (S–O st), 950, 817. **^{1}H-NMR** (600 MHz): δ 7.43–7.40 (m, 2H) 7.36 (d, 1H, *J* = 4.2), 7.23–7.18 (m, 2H), 6.44 (s,

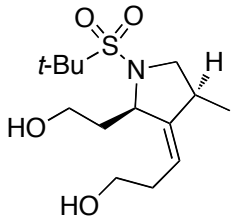
1H), 5.81 (bs, 1H), 4.93 (s, 1H), 3.75–3.73 (m, 1H), 3.71–3.67 (m, 1H), 3.65–3.61 (m, 1H), 3.05 (s, 1H), 2.77 (t, 1H, J = 6.5), 1.95–1.89 (m, 1H), 1.87–1.81 (m, 1H) 1.21 (s, 9H), 1.16 (d, 3H, J = 6.5). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 146.2, 137.0, 128.6, 128.3, 126.8, 120.4, 64.2, 59.4, 57.9, 47.4, 37.9, 37.4, 24.1, 15.5. **ESI-MS** *m/z* (rel int): (pos) 218.2 ($[M+H]^+$, 100).



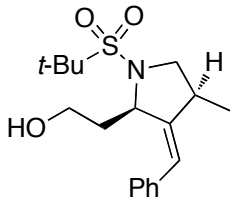
(*Z*)-3-((2*R*,4*S*)-2-(2-Hydroxyethyl)-4-methylpyrrolidin-3-ylidene)propan-1-ol (*R*-18a). Colorless oil (4.9 mg). **TLC**: R_f 0.53 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.21 (t, 1H, J = 7.1), 4.44 (t, 1H, J = 5.8), 3.92 (dt, 1H, J = 9.6, 5.3), 3.71–3.63 (m, 2H), 3.61–3.58 (m, 2H), 2.71 (s, 1H), 2.59 (dd, 1H, J = 8.3, 7.1), 2.30–2.23 (m, 2H), 1.83 (q, 2H, J = 6.5), 1.06 (d, 3H, J = 6.7). **ESI-MS** *m/z* (rel int): (pos) 208.2 ($[M+Na]^+$, 100).



2-((2*R*,4*S*,*Z*)-3-Benzylidene-4-methylpyrrolidin-2-yl)ethanol (*R*-18b). Colorless oil (7.1 mg). **TLC**: R_f 0.40 (1:20 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.30–7.25 (m, 3H) 7.20–7.15 (m, 2H), 6.47 (s, 1H), 4.96 (d, 1H, J = 9.2), 4.01 (br, 1H), 3.76 (t, 1H, J = 8.6), 3.64–3.62 (m, 1H), 3.48 (t, 1H, J = 8.2), 3.04 (t, 1H, J = 6.5), 2.93 (t, 1H, J = 7.2), 1.79–1.73 (m, 1H), 1.69–1.62 (m, 1H), 1.39 (d, 3H, J = 6.5). **ESI-MS** *m/z* (rel int): (pos) 218.1 ([M+H]+, 100).



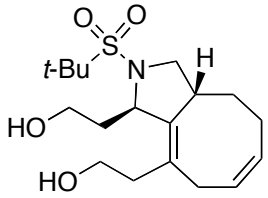
(*Z*)-3-((2*R*,4*S*)-1-(*tert*-Butylsulfonyl)-2-(2-hydroxyethyl)-4-methylpyrrolidin-3-ylidene)-propan-1-ol (*R*-19a). Colorless oil (8.1 mg). **TLC**: R_f 0.53 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.08 (dt, 1H, J = 2.0, 7.1), 4.49 (t, 1H, J = 7.6), 4.97 (t, 1H, J = 6.9), 3.69–3.62 (m, 2H), 3.60–3.55 (m, 2H), 3.08 (dd, 1H, J = 3.1, 8.8), 3.01 (dd, 1H, J = 3.2, 6.5), 2.98–2.93 (m, 1H), 2.76 (bs, 1H), 2.24–2.19 (m, 1H), 2.15 (bs, 1H), 1.88–1.85 (m, 1H), 1.77–1.72 (m, 1H), 1.19 (s, 12H). **ESI-MS** *m/z* (rel int): (pos) 328.4 ($[M+Na]_+$, 100).



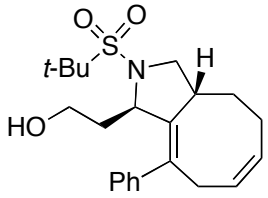
2-((2*R*,4*S*,*Z*)-3-Benzylidene-1-(*tert*-butylsulfonyl)-4-methylpyrrolidin-2-yl)ethanol (*R*-19b). Colorless oil (8.2 mg). **TLC**: R_f 0.40 (3:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.44–7.39

(m, 2H), 7.33–7.28 (m, 2H), 7.22–7.18 (m, 1H), 6.41 (s, 1H), 5.24 (s, 1H), 4.01 (t, 1H, J = 8.0), 3.78–3.65 (m, 1H), 3.10–3.01 (m, 2H), 2.05–1.96 (m, 2H), 1.54–1.51 (m, 1H), 1.36 (d, 3H, J = 6.9), 1.30 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 360.2 ([M+Na]$^+$, 100).

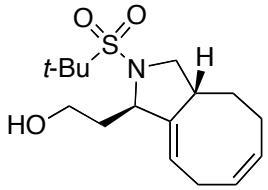
3. EVANS BUTADIENE [4+2+2] CYCLOADDITION PRODUCTS (*R*-20)



2,2'-((1*R*,3a*R*,6*Z*,9*Z*)-2-(*tert*-Butylsulfonyl)-2,3,3a,4,5,8-hexahydro-1*H*-cycloocta[*c*]pyrrole-1,9-diyl)diethanol (*R*-20a). Light yellow oil (3.9 mg). **TLC**: R_f 0.39 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.78–5.74 (m, 1H), 5.67–5.61 (m, 1H), 4.82 (s, 1H), 3.79–3.76 (m, 2H), 3.70 (t, 1H, J = 6.8), 3.67–3.58 (m, 2H), 3.36 (dd, 1H, J = 12.5, 6.8), 3.14 (bs, 1H), 2.93 (dd, 1H, J = 7.9, 14.6), 2.53–2.48 (m, 3H), 2.38 (dd, 1H, J = 6.8, 14.7), 2.31–2.26 (m, 3H), 1.83–1.78 (m, 3H), 1.43 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 358.3 ([M+H]$^+$, 100).

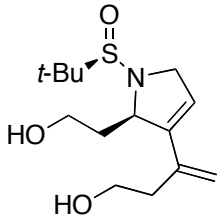


(+)-2-((1*R*,3a*R*,6*Z*,9*Z*)-2-(*tert*-Butylsulfonyl)-9-phenyl-2,3,3a,4,5,8-hexahydro-1*H*-cycloocta-[*c*]pyrrol-1-yl)ethanol (*R*-20b). Light yellow oil (7.1 mg). **TLC**: R_f 0.36 (1:1 hexanes/EtOAc). $[\alpha]_D^{20}$: +35.4° (*c* 0.42, $CHCl_3$). **IR** (NaCl, film): 3373 (O–H st), 3021, 2991, 2856, 1428, 1351 (SO_2 st), 1106 (SO_2 st), 970. **^{1}H-NMR** (600 MHz): δ 7.36–7.31 (m, 3H), 7.18–7.09 (m, 2H), 5.65–5.62 (m, 1H), 5.60–5.56 (m, 1H), 4.91 (s, 1H), 3.50 (s, 1H), 3.44–3.38 (m, 2H), 3.31–3.28 (m, 1H), 2.81 (dd, 1H, J = 6.1, 15.2), 2.47–2.41 (m, 1H), 1.881.69 (m, 2H), 1.65–1.58 (m, 3H), 1.42–1.36 (m, 3H), 1.33 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 143.3, 139.4, 135.5, 133.7, 129.6, 128.3, 127.6, 126.8, 60.4, 60.3, 60.1, 56.5, 44.0, 37.2, 36.4, 26.3, 24.5, 19.0. **ESI-MS** *m/z* (rel int): (pos) 270.2 ([M–SO_2tBu+H]$^+$, 15); 390.2 ([M+H]$^+$, 100).

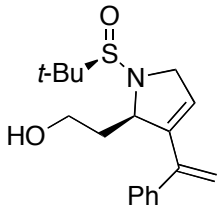


2-((1*R*,3a*R*,6*Z*,9*E*)-2-(*tert*-Butylsulfonyl)-2,3,3a,4,5,8-hexahydro-1*H*-cycloocta[*c*]pyrrol-1-yl)ethanol (*R*-20d). Light yellow oil (7.5 mg). **TLC**: R_f 0.40 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.69–5.61 (m, 1H), 5.58–5.49 (m, 1H), 5.38 (s, 1H), 3.65–3.49 (bm, 2H), 3.73–3.70 (m, 2H), 3.43 (d, 1H, J = 11.1), 3.24 (dd, 1H, J = 6.5, 12.1), 3.19–3.11 (m, 1H), 2.88–2.65 (bm, 2H), 2.40–2.33 (m, 1H), 1.93–1.81 (m, 2H), 1.66–1.61 (m, 1H), 1.55–1.49 (m, 1H), 1.49 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 336.2 ([M+Na]$^+$, 100).

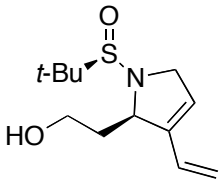
4. ENYNE METATHESIS PRODUCTS (*R*-21–23)



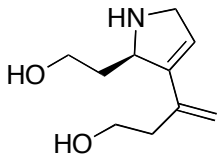
3-((*R*)-1-((*R*)-*tert*-Butylsulfinyl)-2-(2-hydroxyethyl)-2,5-dihydro-1*H*-pyrrol-3-yl)but-3-en-1-ol (*R*-21a). Clear colorless oil (9.1 mg). **TLC**: R_f 0.46 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.79 (s, 1H), 5.06 (s, 1H), 5.01 (s, 1H), 4.91 (t, 1H, *J* = 6.8), 4.50 (d, 2H, *J* = 15.7), 3.61–3.55 (m, 3H), 3.52 (d, 1H, *J* = 12.6) 2.51–2.49 (m, 1H), 2.41–2.37 (m, 1H), 2.01–1.95 (m, 1H), 1.92–1.88 (m, 1H), 1.09 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 310.4 ([M+Na]$^+$, 100).



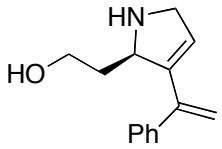
2-((*R*)-1-((*R*)-*tert*-Butylsulfinyl)-3-(1-phenylvinyl)-2,5-dihydro-1*H*-pyrrol-2-yl)ethanol (*R*-21b). Clear oil (8.1 mg). **TLC**: R_f 0.31 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.45–7.34 (m, 3H), 7.32–7.28 (m, 2H), 5.49 (s, 1H), 5.26 (s, 1H), 5.24 (s, 1H), 4.99–4.95 (m, 1H), 4.48 (d, 1H, *J* = 15.2), 4.13 (t, 1H, *J* = 5.3), 3.85–3.78 (m, 1H), 3.75–3.70 (m, 1H), 3.09 (s, 1H), 2.20–2.13 (m, 1H), 1.86–1.77 (m, 1H), 1.07 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 342.5 ([M+Na]$^+$, 100).



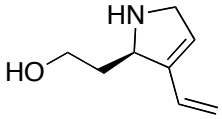
2-((*R*)-1-((*R*)-*tert*-Butylsulfinyl)-3-vinyl-2,5-dihydro-1*H*-pyrrol-2-yl)ethanol (*R*-21d). Yellow oil (8.2 mg). **TLC**: R_f 0.28 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.32 (dd, 1H, J = 17.3, 11.0), 5.71 (s, 1H), 5.20 (d, 1H, J = 17.8), 5.09 (d, 1H, J = 11.0), 4.85 (s, 1H), 4.49 (d, 1H, J = 15.1), 3.72–3.68 (m, 2H), 3.50 (d, 1H, J = 15.3), 1.98–1.89 (m, 2H), 1.12 (s, 9H). **ESI-MS** m/z (rel int): (pos) 266.3 ([M+Na]+, 100).



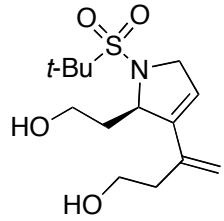
(*R*)-3-(2-(2-Hydroxyethyl)-2,5-dihydro-1*H*-pyrrol-3-yl)but-3-en-1-ol (*R*-22a). Clear colorless oil (0.8 mg). **TLC**: R_f 0.46 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.81 (ddd, 1H, *J* = 10.0, 7.9, 6.8), 5.25 (d, 1H, *J* =11.0), 5.16 (d, 1H, *J* = 8.4), 4.48 (t, 1H, *J* = 9.7), 3.99–3.94 (m, 2H), 3.70–3.66 (m, 2H), 3.41 (dd, 1H, *J* = 10.9, 4.4), 2.15–2.11 (m, 1H) 1.92–1.87 (m, 2H), 1.54–1.47 (m, 2H). **ESI-MS** *m/z* (rel int): (pos) 206.8 ([M+Na]$^+$, 100).



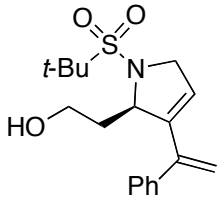
(*R*)-2-(3-(1-Phenylvinyl)-2,5-dihydro-1*H*-pyrrol-2-yl)ethanol (*R*-22b). Clear yellow oil (1.1 mg). **TLC**: R_f 0.31 (1:20 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.45–7.34 (m, 5H), 5.81 (dd, 1H, *J* = 7.1, 6.8), 5.30 (d, 1H, *J* = 14.3), 5.21 (d, 1H, *J* = 10.6), 4.60 (dd, 1H, *J* = 8.8, 7.1), 4.04 (dd, 1H, *J* = 15.2, 7.1), 3.85–3.78 (m, 2H), 3.47 (dd, 1H, *J* = 14.3, 7.1), 2.20–2.13 (m, 1H), 2.04–2.00 (m, 1H), 1.52 (s, 1H). **ESI-MS** *m/z* (rel int): (pos) 216.3 ([M+H]$^+$, 100).



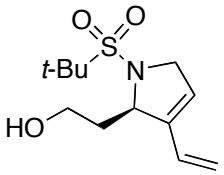
(*R*)-2-(3-Vinyl-2,5-dihydro-1*H*-pyrrol-2-yl)ethanol (*R*-22d). Clear oil (0.7 mg). **TLC**: R_f 0.28 (1:20 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.37 (ddd, 1H, *J* = 17.8, 11.0, 8.0), 5.69 (s, 1H), 5.21 (d, 1H, *J* = 17.8), 5.17 (d, 1H, *J* = 11.0), 4.88 (s, 1H), 4.48 (d, 1H, *J* = 15.9), 3.78–3.74 (m, 1H), 3.73–3.68 (m, 1H), 3.45 (d, 1H, *J* = 15.9), 2.12–2.05 (m, 1H), 1.78–1.71 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 162.3 ([M+Na]$^+$, 100).



(*R*)-3-(1-(*tert*-Butylsulfonyl)-2-(2-hydroxyethyl)-2,5-dihydro-1*H*-pyrrol-3-yl)but-3-en-1-ol (*R*-23a). Clear colorless oil (8.0 mg). **TLC**: *Rf* 0.46 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.65 (t, 1H, *J* =7.1), 5.08 (d, 2H, *J* =11.0), 4.93 (t, 1H, *J* = 4.4), 4.49 (d, 1H, *J* = 8.1), 4.16 (d, 1H, *J* = 7.8), 3.73–3.69 (m, 1H), 3.68–3.61 (m, 2H), 2.99–2.96 (m, 1H), 2.49–2.47 (m, 1H), 2.05–2.01 (m, 1H), 1.68–1.64 (m, 1H), 1.53–1.47 (m, 1H), 1.03 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 326.4 ([M+Na]$^+$, 100).

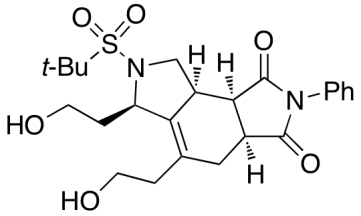


(*R*)-2-(1-(*tert*-Butylsulfonyl)-3-(1-phenylvinyl)-2,5-dihydro-1*H*-pyrrol-2-yl)ethanol (*R*-23b). Clear yellow oil (7.1 mg). **TLC**: R_f 0.31 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.45–7.34 (m, 3H), 7.32–7.28 (m, 2H), 5.49 (s, 1H), 5.19 (s, 1H), 5.12 (s, 1H), 4.98 (s, 1H), 4.40 (d, 1H, *J* = 13.2), 4.07–4.01 (m, 1H), 3.75–3.70 (m, 2H), 3.49 (s, 1H), 2.15–2.08 (m, 2H), 1.25 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 358.5 ([M+Na]$^+$, 100).

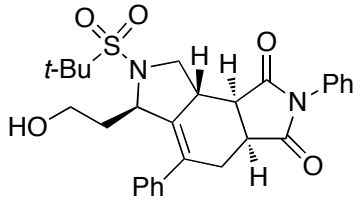


(+)-(*R*)-2-(1-(*tert*-Butylsulfonyl)-3-vinyl-2,5-dihydro-1*H*-pyrrol-2-yl)ethanol (*R*-23d). Yellow oil (7.2 mg). **TLC**: R_f 0.28 (1:1 hexanes/EtOAc). $[\alpha]_D^{20}$: +12.5° (*c* 0.37, $CHCl_3$). **IR** (NaCl, film): 3364 (O–H st), 2998, 2895, 1428, 1351 (SO_2 st), 1265, 1131 (SO_2 st), 910. **^{1}H-NMR** (600 MHz): δ 6.41 (dd, 1H, *J* = 17.8, 11.0), 5.73 (s, 1H), 5.16 (dd, 2H, *J* = 17.8, 11.3), 5.01 (s, 1H), 4.47 (d, 1H, *J* = 15.9), 4.01 (d, 1H, *J* = 12.8), 3.80–3.76 (m, 1H), 3.65–3.61 (m, 1H), 2.05–1.97 (m, 1H), 1.53–1.48 (m, 1H), 1.41 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 135.6, 129.5, 124.1, 116.8, 63.2, 61.3, 59.8, 56.0, 36.5, 26.7. **ESI-MS** *m/z* (rel int): (pos) 282.4 ($[M+Na]^+$, 100).

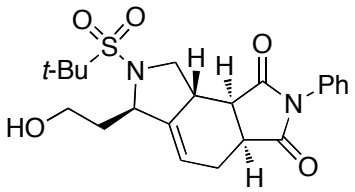
5. Maleimide Diels–Alder products (*R*-24)



(+)-(3a*S*,6*R*,8a*S*,8b*R*)-7-(*tert*-Butylsulfonyl)-5,6-bis(2-hydroxyethyl)-2-phenyl-3a,4,6,7,8,8a-hexahydropyrrolo[3,4-*e*]isoindole-1,3(2*H*,8b*H*)-dione (*R*-24a). Clear oil (8.6 mg). **TLC**: R_f 0.50 (1:2 hexanes/EtOAc). $[\alpha]_D^{20}$: +62.4° (*c* 0.40, $CHCl_3$). **IR** (NaCl, film): 3351 (O–H st), 2992, 2886, 1712 (C=O st), 1445, 1375 (SO_2 st), 1265, 1025 (SO_2 st), 772. **^{1}H-NMR** (600 MHz): δ 7.49–7.36 (m, 5H), 5.92 (t, 1H, *J* = 6.8), 4.51 (d, 1H, *J* = 12.0), 4.49–4.32 (m, 2H), 4.09 (dd, 1H, *J* = 7.9, 13.0), 3.98 (t, 1H, *J* = 10.0), 3.82–3.78 (m, 2H), 3.63–3.59 (m, 1H), 3.40–3.32 (m, 1H), 2.99 (dd, 1H, *J* = 7.4, 12.5), 2.71–2.63 (m, 1H), 1.75–1.70 (m, 2H), 1.66–1.59 (m, 2H), 1.45 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 178.2, 178.0, 138.8, 133.6, 131.6, 129.7, 129.1, 126.4, 61.6, 60.6, 60.5, 58.2, 52.8, 44.4, 39.9, 39.4, 37.5, 36.9, 29.2, 26.0. **ESI-MS** *m/z* (rel int): (pos) 499.6 ([M+Na]+, 100).

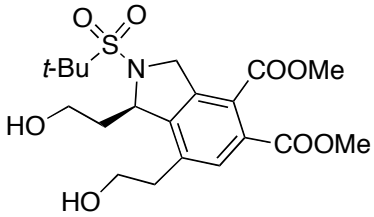


(3a*S*,6*R*,8a*R*,8b*R*)-7-(*tert*-Butylsulfonyl)-6-(2-hydroxyethyl)-2,5-diphenyl-3a,4,6,7,8,8a-hexahydropyrrolo[3,4-*e*]isoindole-1,3(2*H*,8b*H*)-dione (*R*-24b). Light yellow oil (3.5 mg). **TLC**: R_f 0.40 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.49–7.43 (m, 3H), 7.41–7.38 (m, 4H), 7.36–7.34 (m, 3H), 5.83 (s, 1H), 4.91 (dd, 1H, *J* = 13.1, 2.1), 4.13 (d, 1H, *J* = 13.1), 3.74–3.70 (m, 1H), 3.48 (dd, 1H, *J* = 8.0, 9.1), 3.23–3.21 (m, 1H), 3.14–3.12 (m, 2H), 3.05–3.01 (m, 1H), 2.73–2.68 (m, 1H), 2.53–2.48 (m, 1H), 1.62–1.57 (m, 1H), 1.41 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 531.3 ($[M+Na]^+$, 100).

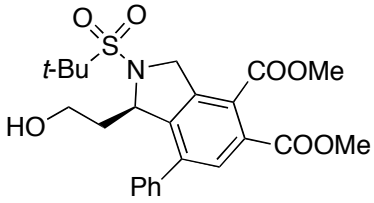


(3a*S*,6*R*,8a*R*,8b*R*)-7-(*tert*-Butylsulfonyl)-6-(2-hydroxyethyl)-2-phenyl-3a,4,6,7,8,8a-hexahydropyrrolo[3,4-*e*]isoindole-1,3(2*H*,8b*H*)-dione (*R*-24d). Clear oil (7.1 mg). **TLC**: R_f 0.32 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.99 (s, 1H), 7.63–7.67 (m, 2H), 7.50–7.37 (m, 3H), 5.98–5.95 (m, 1H), 5.01 (d, 1H, *J* = 11.8), 4.52 (d, 1H, *J* = 12.5), 4.48–4.35 (m, 2H), 3.55–3.49 (m, 2H), 3.29–3.24 (m, 2H), 1.88–1.65 (bm, 2H), 1.64–1.59 (m, 1H), 1.45 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 433.4 ($[M+H]^+$, 100).

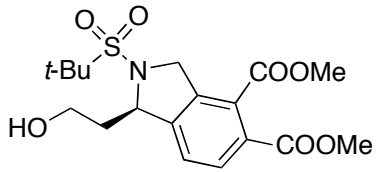
6. DMAD DIELS–ALDER PRODUCTS (*R*-25)



(*R*)-Dimethyl 2-(*tert*-butylsulfonyl)-1,7-bis(2-hydroxyethyl)isoindoline-4,5-dicarboxylate (*R*-25a). Colorless oil (2.1 mg). **TLC**: R_f 0.43 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.63 (s, 1H), 5.62 (s, 1H), 5.03 (d, 1H, *J* = 16.0), 4.51 (d, 1H, *J* = 16.0), 3.88 (s, 6H), 3.85–3.81 (m, 2H), 3.65–3.61 (m, 2H), 2.86–2.79 (m, 2H), 2.11–1.99 (m, 2H), 1.31 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 466.3 $[M+Na]^+$, 100).

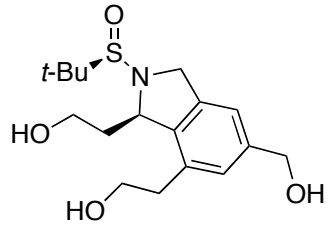


(–)-(*R*)-Dimethyl 2-(*tert*-butylsulfonyl)-1-(2-hydroxyethyl)-7-phenylisoindoline-4,5-dicarboxylate (*R*-25b). Colorless oil (4.1 mg). **TLC**: R_f 0.38 (1:2 hexanes/EtOAc). $[\alpha]_D^{20}$: –8.8° (*c* 0.32, $CHCl_3$). **IR** (NaCl, film): 3388 (O–H st), 3005, 2990, 2881, 1725 (C=O st), 1430, 1393 (SO_2 st), 1265, 1025 (SO_2 st), 968. **^{1}H-NMR** (600 MHz): δ 7.61 (s, 1H), 7.45–7.37 (m, 5H), 5.89 (s, 1H), 5.12 (d, 1H, *J* = 16.4), 4.53 (d, 1H, *J* = 15.8), 3.91 (s, 6H), 3.47–3.43 (m, 1H), 3.39–3.35 (m, 1H), 1.80–1.74 (m, 1H), 1.57–1.51 (m, 1H), 1.38 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 167.4, 166.9, 139.8, 139.1, 138.1, 133.4, 133.3, 131.7, 130.2, 128.3, 127.9, 127.5, 62.8, 62.7, 59.7, 54.6, 52.7 (2 OMe), 36.4, 26.6. **ESI-MS** *m*/*z* (rel int): (pos) 476.5 $[M+H]^+$, 100).

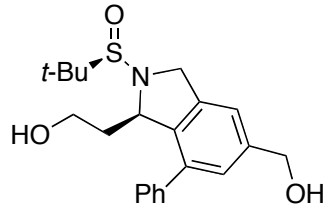


(*R*)-Dimethyl 2-(*tert*-butylsulfonyl)-1-(2-hydroxyethyl)isoindoline-4,5-dicarboxylate (*R*-25d). Colorless oil (8.0 mg). **TLC**: R_f 0.34 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.74 (d, 1H, *J* = 4), 7.42 (d, 1H, *J* = 3.9), 5.49 (s, 1H), 5.08 (d, 1H, *J* =15.1), 4.64 (d, 1H, *J* = 15.2), 3.91 (s, 6H), 3.69–3.62 (m, 1H), 2.40 (s, 1H), 2.05–1.98 (m, 1H), 1.84–1.79 (m, 1H), 1.35 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 422.5 ([M+Na]$^+$, 100).

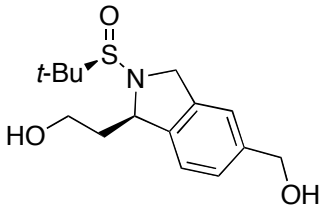
7. ALKYNE [2+2+2] CYCLOTRIMERIZATION PRODUCTS (*R*-30–35)



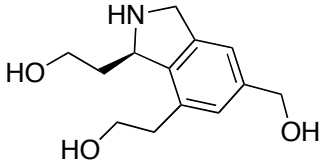
(–)-2,2'-((*R*)-2-((*R*)-*tert*-Butylsulfinyl)-5-(hydroxymethyl)isoindoline-1,7-diyl)diethanol (*R*-30a). Light brown oil (9.1 mg). **TLC**: R_f 0.31 (1:3 hexanes/EtOAc). $[\alpha]_D^{20}$: –7.1° (*c* 0.42, $CHCl_3$). **IR** (NaCl, film): 3409 (O–H st), 2995, 2878, 1408, 1115 (S-O st), 884, 758. **^{1}H-NMR** (600 MHz): δ 7.09 (s, 1H), 7.05 (s, 1H), 5.30 (d, 1H, *J* = 7.9), 4.93 (d, 1H, *J* = 14.3), 4.57 (s, 2H), 3.94 (d, 1H, *J*, 14.3), 3.84 (t, 2H, *J* = 7.0), 3.80–3.72 (m, 1H), 3.63–3.59 (m, 1H), 2.85 (dt, 2H, *J* = 12.5, 6.0), 2.15–2.07 (m, 1H), 1.92–1.84 (m, 1H), 1.15 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 141.3, 139.7, 139.6, 133.1, 127.0 119.0, 69.1, 64.6, 62.7, 58.9, 58.3, 46.8, 39.7, 35.7, 23.9. **ESI-MS** *m/z* (rel int): (pos) 364.5 ([M+Na]$^+$, 100).



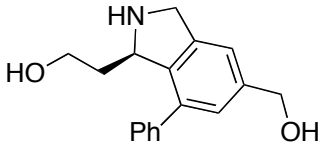
(+)-2-((*R*)-2-((*R*)-*tert*-Butylsulfinyl)-5-(hydroxymethyl)-7-phenylisoindolin-1-yl)ethanol (*R*-30b). Brown oil (8.0 mg). **TLC**: R_f 0.22 (1:3 hexanes/EtOAc). $[\alpha]_D^{20}$: +23.1° (*c* 0.42, $CHCl_3$). **IR** (NaCl, film): 3384 (O–H st), 3079, 2928, 2878, 1455, 1408, 1106 (S-O st), 1063 (S–O st), 1009, 964, 758. **^{1}H-NMR** (600 MHz): δ 7.40–7.34 (m, 5H), 7.18 (s, 1H), 7.16 (s, 1H), 5.58 (d, 1H, *J* = 8.0), 5.08 (d, 1H, *J* = 14.3), 4.69 (d, 2H, *J* = 5.7), 3.99 (dd, 1H, *J* = 14.0, 4.0), 3.61 (ddd, 1H, *J* = 10.0, 8.5, 6.2), 3.38–3.34 (m, 1H), 1.68–1.63 (m, 1H), 1.44–1.38 (m, 1H), 0.91 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 141.4, 140.1, 140.0, 137.3, 137.2, 128.7, 128.2, 127.7, 127.3, 120.1, 69.1, 64.9, 59.1, 58.0, 46.4, 37.6, 23.9. **ESI-MS** *m/z* (rel int): (pos) 374.4 ([M+H]$^+$, 100).



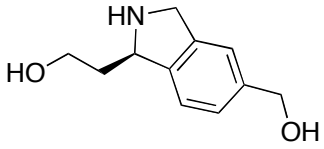
2-((*R*)-2-((*R*)-*tert*-Butylsulfinyl)-5-(hydroxymethyl)isoindolin-1-yl)ethanol (*R*-30d). Light brown oil (8.1 mg). **TLC**: R_f 0.15 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.18 (s, 1H), 7.05 (d, 1H, *J* = 7.0), 6.99 (d, 1H, *J* = 7.0), 5.03 (t, 1H, *J* = 6.0), 4.53 (s, 2H), 3.96 (d, 1H, *J* = 14.9), 3.72 (ddd, 1H, *J* = 10.6, 7.5, 5.5), 3.63 (dt, 1H, *J* = 10.4, 6.6), 2.77 (s, 1H), 1.99–1.93 (m, 2H), 1.26 (t, 1H, *J* = 7.1), 1.21 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 320.4 ([M+Na]$^+$, 100).



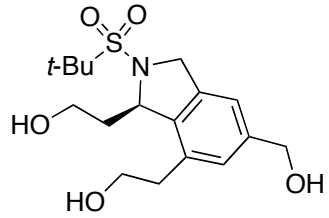
(*R*)-2,2'-(5-(Hydroxymethyl)isoindoline-1,7-diyl)diethanol (*R*-31a). Light brown oil (1.5 mg). **TLC**: R_f 0.31 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.04 (s, 1H), 7.02 (s, 1H), 5.52 (d, 1H, *J* = 14.5), 4.61 (d, 2H, *J* = 7.1), 3.96 (d, 1H, *J* = 14.6), 3.86 (t, 1H, *J* = 7.0), 3.85–3.79 (m, 1H), 3.69–3.64 (m, 1H), 2.85 (dt, 2H, *J* = 12.6, 6.5), 2.15–2.07 (m, 1H), 1.88–1.84 (m, 1H), 1.78–1.76 (m, 2H). **ESI-MS** *m/z* (rel int): (pos) 238.2 ([M+H]$^+$, 100).



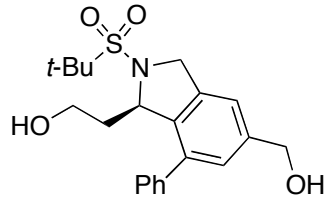
(*R*)-2-(5-(Hydroxymethyl)-7-phenylisoindolin-1-yl)ethanol (*R*-31b). Light brown oil (7.5 mg). **TLC**: R_f 0.22 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.42 (s, 1H), 7.34–7.26 (m, 6H), 5.71 (t, 1H, *J* = 7.1), 5.01 (d, 2H, *J* = 14.1), 4.39 (d, 2H, *J* = 14.0), 4.38–4.34 (m, 2H), 2.20–2.13 (m, 2H). **ESI-MS** *m/z* (rel int): (pos) 292.2 ([M+Na]$^+$, 100).



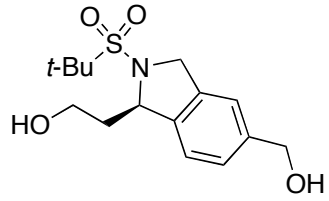
(*R*)-2-(5-(Hydroxymethyl)isoindolin-1-yl)ethanol (*R*-31d). Light brown oil (1.7 mg). **TLC**: R_f 0.15 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.18–7.14 (m, 2H), 7.09 (d, 1H, *J* = 7.2), 5.18 (d, 1H, *J* = 6.0), 4.95 (d, 1H, *J*= 14.0), 4.55–4.51 (m, 3H), 3.96 (d, 1H, *J* = 15.6), 3.81 (ddd, 1H, *J* = 10.7, 7.6, 5.6), 3.72 (ddd, 1H, *J* = 10.7, 7.6, 5.6), 2.07–1.95 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 270.3 ([M+H]$^+$, 100).



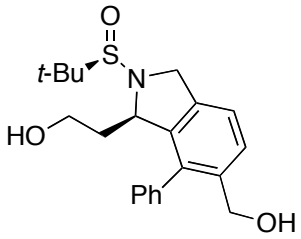
(*R*)-2,2'-(2-(*tert*-Butylsulfonyl)-5-(hydroxymethyl)isoindoline-1,7-diyl)diethanol (*R*-32a). Brown oil (8.2 mg). **TLC**: R_f 0.31 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.99 (s, 1H), 6.93 (s, 1H), 5.17 (d, 1H, *J* = 7.8), 4.83 (d, 1H, *J* = 12.5), 4.51 (s, 2H), 3.91 (d, 1H, *J* = 14.6), 3.79 (t, 2H, *J* = 7.3), 3.78–3.73 (m, 1H), 3.65–3.62 (m, 1H), 2.83 (dt, 2H, *J* = 12.6, 6.5), 2.07–1.99 (m, 1H), 1.78–1.71 (m, 1H), 1.08 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 380.5 ([M+Na]$^+$, 100).



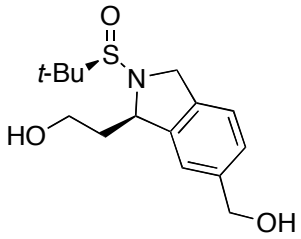
(*R*)-2-(2-(*tert*-Butylsulfonyl)-5-(hydroxymethyl)-7-phenylisoindolin-1-yl)ethanol (*R*-32b). Brown oil (2.3 mg). **TLC**: R_f 0.22 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.38–7.32 (m, 5H), 7.18 (s, 1H), 7.14 (s, 1H), 5.58 (d, 1H, *J* = 8.0), 5.08 (d, 1H, *J* = 14.3), 4.71 (d, 2H, *J* = 6.2), 3.99 (d, 1H, *J* = 14.0), 3.63 (ddd, 1H, *J* = 10.0, 8.5, 6.2), 3.38–3.34 (m, 1H), 1.68 (t, 1H, *J* = 6.0), 1.44–1.38 (m, 1H), 1.19 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 390.3 ([M+H]$^+$, 100).



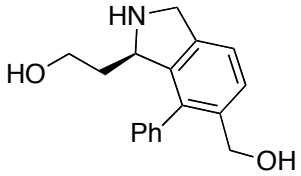
(+)-(*R*)-2-(2-(*tert*-Butylsulfonyl)-5-(hydroxymethyl)isoindolin-1-yl)ethanol (*R*-32d). Light brown oil (7.4 mg). **TLC**: R_f 0.15 (1:1 hexanes/EtOAc). $[\alpha]_D^{20}$: +53.8° (*c* 0.32, $CHCl_3$). **IR** (NaCl, film): 3362 (O–H st), 3067, 2961, 1652, 1403 (SO_2 st), 1180 (SO_2 st), 988, 763. **^{1}H-NMR** (500 MHz): δ 7.01 (d, 1H, *J* = 7.0), 6.94 (d, 1H, *J* = 7.0), 6.89 (s, 1H), 5.01 (t, 1H, *J* = 6.0), 4.78 (d, 1H, *J*= 12.0), 4.46 (s, 2H), 3.79 (d, 1H, *J* = 12.5), 3.64 (ddd, 1H, *J* = 10.1, 7.3, 5.6), 3.56 (dt, 1H, *J* = 10. 0, 6.9), 1.91–1.86 (m, 2H), 1.08 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 141.3, 138.8, 127.0, 122.7, 121.2, 121.1, 65.1, 63.5, 63.4, 60.8, 59.0, 39.6, 25.5. **ESI-MS** *m/z* (rel int): (pos) 336.4 ([M+Na]$^+$, 100).



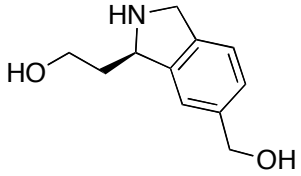
2-((*R*)-2-((*R*)-*tert*-Butylsulfinyl)-6-(hydroxymethyl)-7-phenylisoindolin-1-yl)ethanol (*R*-33b). Light brown oil (3.4 mg). **TLC**: R_f 0.22 (4:6 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.49–7.41 (m, 5H), 7.19 (t, 2H, *J* = 4.0), 5.58 (d, 1H, *J* = 8.0), 5.12 (d, 1H, *J* = 14.3), 4.71 (d, 2H, *J* = 8.8), 4.55 (dd, 1H, *J* = 8.5, 6.2), 4.04 (d, 1H, *J* = 14.0), 3.38–3.34 (m, 1H), 1.99 (s, 1H), 1.80 (s, 1H), 1.68–1.63 (m, 1H), 1.44–1.38 (m, 1H), 1.20 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 396.5 ([M+Na]$^+$, 100).



(+)-2-((*R*)-2-((*R*)-*tert*-Butylsulfinyl)-6-(hydroxymethyl)isoindolin-1-yl)ethanol (*R*-33d). Clear oil (7.6 mg). **TLC**: R_f 0.15 (1:2 hexanes/EtOAc). $[\alpha]_D^{20}$: +4.4° (*c* 0.35, $CHCl_3$). **IR** (NaCl, film): 3401 (O–H st), 3014, 2928, 1652, 1408, 1110 (S–O st), 1065 (S–O st), 964, 758. **^{1}H-NMR** (600 MHz): δ 7.20 (d, 1H, *J* = 7.0), 7.16 (d, 1H, *J* = 7.0), 7.09 (s, 1H), 5.16 (t, 1H, *J* = 6.0), 5.01 (d, 1H, *J*= 14.0), 4.62 (s, 2H), 3.98 (d, 1H, *J* = 14.9), 3.81 (ddd, 1H, *J* = 10.6, 7.9, 5.7), 3.71 (dt, 1H, *J* = 10.2, 6.6), 2.71 (s, 1H), 2.07–2.01 (m, 2H), 1.56 (s, 1H), 1.19 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 140.9, 137.3, 136.2, 126.7, 122.4, 120.9, 64.8, 63.2, 63.0, 60.2, 58.6, 39.3, 22.7. **ESI-MS** *m/z* (rel int): (pos) 320.4 ([M+Na]$^+$, 100).

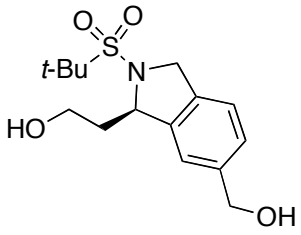


(*R*)-2-(6-(Hydroxymethyl)-7-phenylisoindolin-1-yl)ethanol (*R*-34b). Clear oil (4.1 mg). **TLC**: R_f 0.22 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.42–7.37 (m, 6H), 7.18 (d, 1H, *J* = 7.1), 5.21 (dd, 1H, *J* = 8.0, 6.4), 4.88 (d, 1H, *J* = 14.3), 4.62 (d, 2H, *J* = 3.9), 3.92 (d, 1H, *J* = 14.0), 3.79 (ddd, 1H, *J* = 10.0, 8.5, 6.2), 3.68–3.64 (m, 1H), 2.11–2.08 (m, 1H), 1.83–1.81 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 269.6 ([M+Na]$^+$, 100).



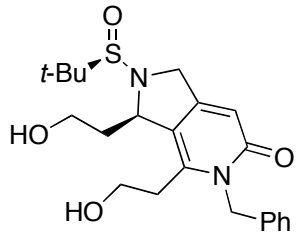
(*R*)-2-(6-(hydroxymethyl)isoindolin-1-yl)ethanol (*R*-34d). Light brown oil (0.8 mg). **TLC**: R_f 0.15 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.21 (d, 1H, *J* = 7.2), 7.09 (d, 1H, *J* =

7.2), 7.11 (s, 1H), 5.18 (t, 1H, *J* = 6.0), 4.98 (d, 1H, *J*= 14.0), 4.55–4.51 (m, 3H), 3.96 (d, 1H, *J* = 15.6), 3.81 (ddd, 1H, *J* = 10.7, 7.6, 5.6), 3.72 (ddd, 1H, *J* = 10.7, 7.6, 5.6), 2.07–1.95 (m, 2H), 1.26 (tt, 1H, *J* = 7.1, 6.2). **ESI-MS** *m/z* (rel int): (pos) 270.3 ([M+H]$^+$, 100).

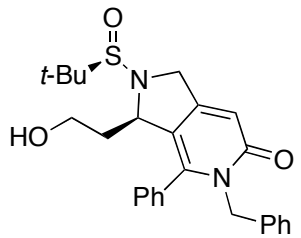


(+)-(*R*)-2-(2-(*tert*-Butylsulfonyl)-6-(hydroxymethyl)isoindolin-1-yl)ethanol (*R*-35d). Light brown oil (7.0 mg). **TLC**: R_f 0.15 (1:1 hexanes/EtOAc). $[\alpha]_D^{20}$: +29.1° (*c* 0.35, $CHCl_3$). **IR** (NaCl, film): 3388 (O–H st), 3023, 2989, 1643, 1221 (SO_2 st), 1095 (SO_2 st), 992, 842. **^{1}H-NMR** (600 MHz): δ 7.08 (s, 2H), 6.99 (d, 1H, *J* = 7.2), 5.08 (t, 1H, *J* = 6.2), 4.93 (d, 1H, *J*= 14.0), 4.52 (d, 2H, *J* = 13.5), 3.90 (dd, 1H, *J* = 14.9, 6.7), 3.80 (ddd, 1H, *J* = 10.7, 7.6, 5.6), 3.73 (dt, 1H, *J* = 10. 4, 6.6), 1.96–1.83 (m, 2H), 1.26 (t, 1H, *J* = 7.1), 1.08 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 141.0, 137.1, 136.2, 126.7, 122.5, 120.9, 64.9, 63.3, 63.2, 60.4, 59.6, 39.4, 25.2. **ESI-MS** *m/z* (rel int): (pos) 336.4 ([M+Na]$^+$, 100).

8. ISOCYANATE [2+2+2] CYCLOTRIMERIZATION PRODUCTS (*R*-36–41)

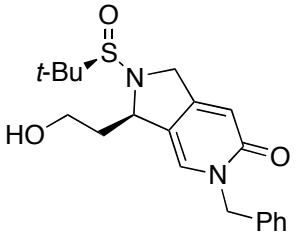


(+)-(*R*)-5-Benzyl-2-((*R*)-*tert*-butylsulfinyl)-3,4-bis(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo-[3,4-*c*]pyridin-6(5*H*)-one (*R*-36a). Clear brown oil (7.0 mg). **TLC**: R_f 0.44 (1:5 MeOH/EtOAc). $[\alpha]_D^{20}$: +52.0° (*c* 0.48, $CHCl_3$). **IR** (NaCl, film): 3390 (O–H st), 2999, 2864, 1670 (C=O st), 1566, 1221, 1099 (S–O st), 990, 862. **^{1}H-NMR** (600 MHz): δ 7.48–7.45 (m, 1H), 7.39–7.35 (m, 2H), 7.30–7.22 (m, 2H), 6.39 (s, 1H), 5.68–5.65 (bs, 1H), 5.37–5.31 (bs, 1H), 5.03 (dd, 1H, *J* = 8.0, 2.8), 4.82 (d, 1H, *J* = 16.0), 3.81–3.78 (m, 3H), 3.69–3.64 (m, 1H), 2.81–2.73 (m, 2H), 1.91–1.88 (m, 1H), 1.88–1.84 (m, 2H), 1.38–1.34 (m, 2H), 1.10 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 163.7, 153.9, 140.3, 136.5, 128.8, 127.3, 126.1, 122.5, 110.2, 67.7, 65.9, 60.5, 58.5, 50.8, 46.9, 45.6, 39.5, 23.6. **ESI-MS** *m/z* (rel int): (pos) 441.6 ([M+Na]$^+$, 100).

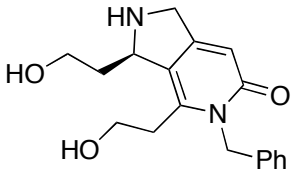


(*R*)-5-Benzyl-2-((*R*)-*tert*-butylsulfinyl)-3-(2-hydroxyethyl)-4-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridin-6(5*H*)-one (*R*-36b). Light brown oil (3.9 mg). **TLC**: R_f 0.19 (1:10

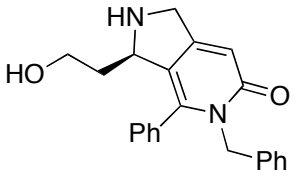
MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.49–7.47 (m, 2H), 7.41–7.38 (m, 4H), 7.36–7.32 (m, 4H), 6.55 (s, 1H), 5.71 (s, 1H), 4.91 (dd, 2H, *J* = 16.3, 8.2), 4.82 (d, 1H, *J* = 7.6), 3.83 (d, 1H, *J* = 16.0), 3.58–3.54 (m, 1H), 3.47–3.41 (m, 1H), 1.52–1.49 (m, 1H), 1.35–1.25 (m, 2H), 0.91 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 473.3 ([M+Na]$^+$, 100).



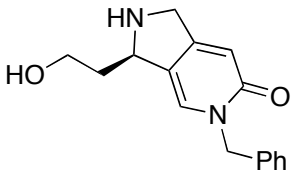
(–)-(*R*)-5-Benzyl-2-((*R*)-*tert*-butylsulfinyl)-3-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo-[3,4-*c*]pyridin-6(5*H*)-one (*R*-36d). Light brown oil (8.3 mg). **TLC**: R_f 0.18 (1:10 MeOH/EtOAc). $[\alpha]_D^{20}$: −14.8° (*c* 0.48, $CHCl_3$). **IR** (NaCl, film): 3399 (O–H st), 3050, 2965, 2853, 1682 (C=O st), 1520, 1403, 1106 (S–O st), 934, 792. **^{1}H-NMR** (600 MHz): δ 7.45–7.40 (m, 2H), 7.39–7.35 (m, 3H), 7.19 (s, 1H), 6.41 (s, 1H), 5.16 (d, 1H, *J* = 7.6), 4.78 (d, 2H, *J* = 14.3), 3.82 (dd, 2H, *J* = 16.0, 1.4), 3.79–3.73 (m, 2H), 1.89–1.86 (m, 1H), 1.82–1.78 (m, 1H), 1.11 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 162.4, 156.4, 136.4, 131.0, 129.0, 128.14, 128.10, 121.2, 112.8, 66.0, 58.6, 58.2, 52.4, 42.7, 40.2, 23.8. **ESI-MS** *m/z* (rel int): (pos) 397.5 ([M+Na]$^+$, 100).



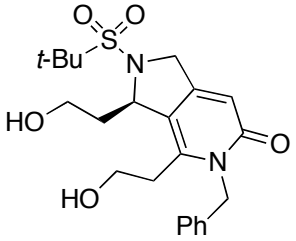
(*R*)-5-Benzyl-3,4-bis(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridin-6(5*H*)-one (*R*-37a). Light brown oil (3.1 mg). **TLC**: R_f 0.44 (1:3 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.32–7.25 (m, 5H), 6.37 (s, 1H), 5.50 (bs, 1H), 5.40–5.32 (bm, 2H), 4.61 (d, 1H, *J* = 8.0), 4.40–4.37 (m, 2H), 4.28 (d, 1H, *J* = 12.0), 3.76–3.72 (m, 2H), 3.63–3.56 (m, 2H), 2.81–2.73 (m, 2H), 2.06–2.00 (m, 1H), 1.87–1.80 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 315.3 ([M+H)$^+$, 100).



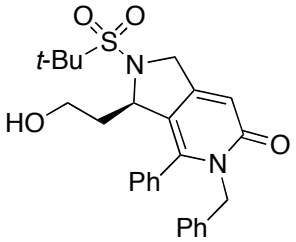
(*R*)-5-Benzyl-3-(2-hydroxyethyl)-4-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridin-6(5*H*)-one (*R*-37b). Clear oil (8.1 mg). **TLC**: R_f 0.19 (1:5 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.66–7.62 (m, 5H), 7.45–7.39 (m, 2H), 7.37–7.33 (m, 3H), 6.48 (s, 1H), 5.41–5.23 (m, 2H), 5.18 (t, 1H, *J* = 6.7), 4.78 (d, 2H, *J* = 15.3), 3.85–3.81 (m, 1H), 3.79–3.73 (m, 1H), 1.94–1.88 (m, 1H), 1.81–1.75 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 369.4 ([M+Na]$^+$, 100).



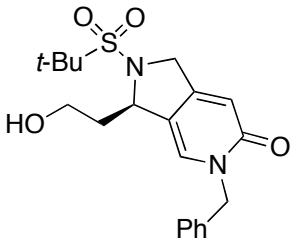
(*R*)-5-Benzyl-3-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridin-6(5*H*)-one (*R*-37d). Light brown oil (3.9 mg). **TLC**: R_f 0.18 (1:5 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.39–7.35 (m, 5H), 7.18 (s, 1H), 6.48 (s, 1H), 5.25 (s, 1H), 5.16 (dd, 1H, *J* = 12.5, 6.3), 4.53 (d, 1H, *J* = 14.6), 4.48 (d, 2H, *J* = 1.4), 4.40 (d, 1H, *J* = 8.8), 3.72–3.67 (m, 2H), 2.00–1.94 (m, 1H), 1.73–1.66 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 293.1 ([M+Na]$^+$, 100).



(*R*)-5-Benzyl-2-(*tert*-butylsulfonyl)-3,4-bis(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]-pyridin-6(5*H*)-one (*R*-38a). Brown oil (7.0 mg). **TLC**: R_f 0.44 (1:6 MeOH/EtOAc). **^{1}H-NMR** (500 MHz): δ 7.39–7.22 (m, 5H), 6.39 (s, 1H), 5.61 (br s, 1H), 5.42 (br s, 1H), 5.03 (dd, 1H, *J* = 2.4, 6.5), 4.84 (d, 1H, *J* = 4.5), 4.80 (d, 2H, *J* = 16.3), 3.85–3.76 (m, 3H), 3.68 (ddd, 2H, *J* = 10.3, 6.0, 4.1), 2.79–2.65 (m, 2H), 1.93–1.88 (m, 1H), 1.87–1.80 (m, 1H), 1.16 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 457.6 ([M+Na]$^+$, 100).

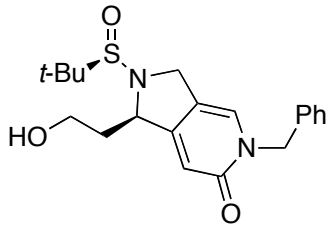


(*R*)-5-Benzyl-2-(*tert*-butylsulfonyl)-3-(2-hydroxyethyl)-4-phenyl-2,3-dihydro-1*H*-pyrrolo-[3,4-*c*]pyridin-6(5*H*)-one (*R*-38b). Light brown oil (2.1 mg). **TLC**: R_f 0.19 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.45–7.41 (m, 10H), 6.55 (d, 1H, *J* = 5.5), 5.26–5.20 (m, 1H), 4.93 (dd, 1H, *J* = 7.6, 3.1), 4.53 (t, 1H, *J* = 8.2), 4.40 (s, 2H), 3.61–3.58 (m, 2H), 1.74–1.70 (m, 2H), 1.52 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 489.3 ([M+Na]$^+$, 100).

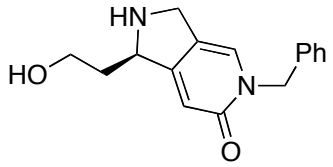


(*R*)-5-Benzyl-2-(*tert*-butylsulfonyl)-3-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]-pyridin-6(5*H*)-one (*R*-38d). Light brown oil (3.5 mg). **TLC**: R_f 0.18 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.41–7.35 (m, 5H), 7.19 (s, 1H), 6.42 (s, 1H), 5.12 (d, 1H, *J* = 14.6),

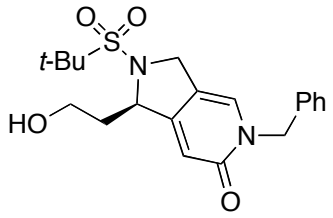
4.99 (t, 1H, *J* = 6.3), 4.93 (t, 1H, *J* = 10.7), 4.71 (dd, 1H, *J* = 16.0, 1.4), 3.81–3.78 (m, 2H), 3.69–3.64 (m, 1H), 1.99–1.84 (m, 1H), 1.69–1.66 (m, 1H), 1.17 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 413.4 ([M+Na]$^+$, 100).



(–)-(*R*)-5-Benzyl-2-((*R*)-*tert*-butylsulfinyl)-1-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo-[3,4-*c*]pyridin-6(5*H*)-one (*R*-39d). Brown oil (7.0 mg). **TLC**: R_f 0.18 (1:10 MeOH/EtOAc). $[\alpha]_D^{20}$: −64.8° (*c* 0.44, $CHCl_3$). **IR** (NaCl, film): 3393 (O–H st), 3087, 2991, 2853, 1676 (C=O st), 1526, 1409, 1106 (S–O st), 934, 792. **^{1}H-NMR** (600 MHz): δ 7.45–7.41 (m, 2H), 7.38–7.32 (m, 3H), 6.94 (s, 1H), 6.51 (s, 1H), 4.91–4.88 (m, 3H), 4.81 (t, 1H, *J* = 6.3), 4.82 (dd, 1H, *J* = 15.2, 1.4), 3.58–3.54 (m, 1H), 3.44–3.40 (m, 1H), 1.32–1.25 (m, 2H), 0.93 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 162.3, 154.0, 136.3, 130.9, 128.9, 128.0, 127.9, 121.1, 112.7, 65.9, 58.5, 58.2, 52.3, 44.8, 40.1, 23.7. **ESI-MS** *m/z* (rel int): (pos) 397.5 ([M+H)$^+$, 100).

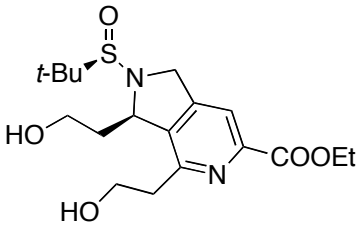


(*R*)-5-Benzyl-1-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridin-6(5*H*)-one (*R*-40d). Light brown oil (2.1 mg). **TLC**: R_f 0.17 (1:5 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.39–7.35 (m, 5H), 7.18 (s, 1H), 6.59 (s, 1H), 5.21 (s, 1H), 5.03 (dd, 1H, *J* = 12.5, 6.3), 4.71 (d, 1H, *J* = 14.6), 4.48–4.40 (m, 3H), 3.41–3.38 (m, 1H), 3.23–3.18 (m, 1H), 2.90 (s, 1H), 1.49–1.43 (m, 1H), 1.25–1.21 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 293.1 ([M+Na]$^+$, 100).

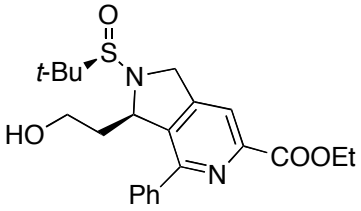


(*R*)-5-Benzyl-2-(*tert*-butylsulfonyl)-1-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]-pyridin-6(5*H*)-one (*R*-41d). Light brown oil (1.9 mg). **TLC**: R_f 0.16 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.38–7.32 (m, 5H), 7.07 (d, 1H, *J* = 14.0), 6.42 (s, 1H), 5.12–5.08 (m, 3H), 4.99 (t, 1H, *J* = 6.3), 4.93 (t, 1H, *J* = 8.8), 4.71 (dd, 1H, *J* = 16.0, 1.4), 3.78–3.72 (m, 2H), 3.69–3.64 (m, 1H), 1.99–1.84 (m, 1H), 1.69–1.66 (m, 1H), 1.17 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 413.4 ([M+Na]$^+$, 100).

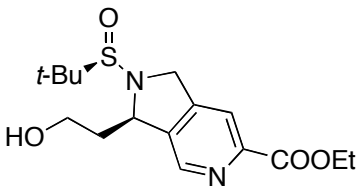
9. NITRILE [2+2+2] CYCLOTRIMERIZATION PRODUCTS (*R*-42–44)



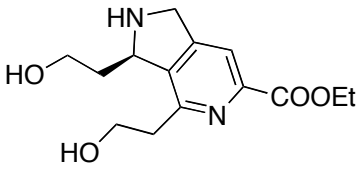
(+)-(*R*)-Ethyl 2-((*R*)-*tert*-butylsulfinyl)-3,4-bis(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridine-6-carboxylate (*R*-42a). Light brown oil (7.0 mg). **TLC**: R_f 0.37 (1:6 hexanes/EtOAc). $[\alpha]_D^{20}$: +23.1° (*c* 0.40, $CHCl_3$). **IR** (NaCl, film): 3344 (O–H st), 3023, 2952, 2835, 1722 (C=O st), 1250, 1106 (S–O st), 913, 758 **^{1}H-NMR** (600 MHz): δ 7.79 (s, 1H), 5.38 (d, 1H, *J* = 8.2), 5.03 (d, 1H, *J* = 16.4), 4.40 (q, 2H, *J* = 10.6), 4.22 (dt, 1H, *J* = 9.8, 6.4), 4.12–4.08 (m, 1H), 3.97 (d, 1H, *J* = 15.2), 3.82–3.78 (m, 1H), 3.72 (ddd, 1H, *J* = 10.2, 6.2, 4.4), 3.12–3.08 (m, 2H), 2.24–2.20 (m, 1H), 1.80 (ddd, 1H, *J* = 18.9, 8.8, 4.4), 1.43 (t, 3H, *J* = 7.1), 1.12 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 165.4, 164.8, 154.8, 150.5, 140.1, 139.8, 117.6, 68.5, 65.9, 61.9, 61.1, 58.4, 52.9, 46.2, 38.7, 23.7, 14.2; 2 peaks observed in ester carbonyl region. **ESI-MS** *m/z* (rel int): (pos) 407.5 ($[M+Na]^+$, 100).



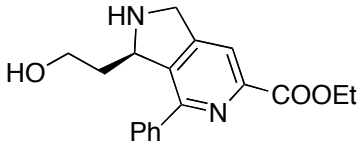
(+)-(*R*)-Ethyl 2-((*R*)-*tert*-butylsulfinyl)-3-(2-hydroxyethyl)-4-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridine-6-carboxylate (*R*-42b). Clear oil (4.0 mg). **TLC**: R_f 0.20 (1:3 hexanes/EtOAc). $[\alpha]_D^{20}$: +12.1° (*c* 0.48, $CHCl_3$). **IR** (NaCl, film): 3401 (O–H st), 3067, 2992, 2918, 2835, 1716 (C=O st), 1267, 1120 (S–O st), 1067 (S–O st), 958. **^{1}H-NMR** (600 MHz): δ 7.93 (s, 1H), 7.44–7.35 (m, 5H), 5.80 (d, 1H, *J* = 7.9), 5.18 (d, 1H, *J* = 15.7), 4.55–4.47 (m, 1H), 4.47–4.39 (m, 1H), 3.99 (d, 1H, *J* = 12.6), 3.66 (td, 1H, *J* = 9.5, 5.0), 3.48–3.40 (m, 1H), 1.72–1.65 (m, 1H), 1.61–1.54 (m, 1H), 1.43 (t, 3H, *J* = 7.1), 0.99 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 165.2, 154.2, 149.6, 148.4, 138.1, 129.7, 129.4, 129.2, 128.4, 117.9, 62.9, 62.8, 62.3, 58.5, 51.0, 36.1, 22.9, 14.5. **ESI-MS** *m/z* (rel int): (pos) 417.2 ($[M+H]^+$, 100).



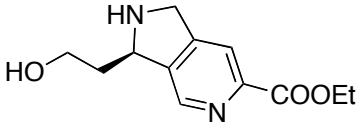
(*R*)-Ethyl 2-((*R*)-*tert*-butylsulfinyl)-3-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]-pyridine-6-carboxylate (*R*-42d). Clear oil (4.9 mg). **TLC**: R_f 0.12 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 8.62 (s, 1H), 8.00 (s, 1H), 5.33 (t, 1H, *J* = 6.0), 5.09 (d, 1H, *J* = 15.6), 4.48 (q, 2H, *J* = 7.5), 3.99 (d, 1H, *J* = 15.6), 3.83–3.76 (m, 2H), 2.11–2.01 (m, 1H), 1.96–1.87 (m, 1H), 1.44 (t, 3H, *J* = 7.1), 1.07 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 340.1 ($[M+H]^+$, 100).



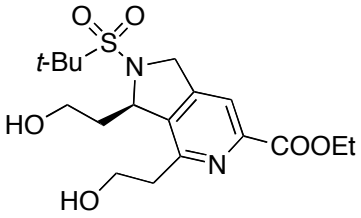
(*R*)-Ethyl 3,4-bis(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridine-6-carboxylate (*R*-43a). Clear oil (4.1 mg). **TLC**: R_f 0.37 (1:6 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.88 (s, 1H), 5.39 (s, 1H), 5.07 (d, 1H, *J* = 16.8), 4.40 (q, 2H, *J* = 10.8), 4.18 (dt, 1H, *J* = 9.8, 6.4), 4.08 (dt, 1H, *J* = 9.8, 6.1), 3.75–3.68 (m, 1H), 3.65–3.62 (m, 1H), 3.08 (dd, 1H, *J* = 13.8, 6.1), 2.91–2.88 (m, 2H), 2.06–1.98 (m, 2H), 1.41 (t, 3H, *J* = 7.1). **ESI-MS** *m/z* (rel int): (pos) 281.3 ([M+H]$^+$, 100).



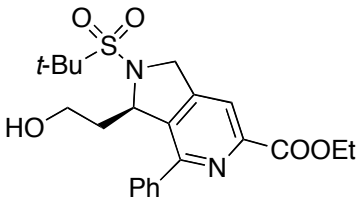
(*R*)-Ethyl 3-(2-hydroxyethyl)-4-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridine-6-carboxylate (*R*-43b). Clear oil (2.1 mg). **TLC**: R_f 0.20 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.93 (s, 1H), 7.44–7.35 (m, 5H), 5.41 (s, 1H), 5.12 (d, 1H, *J* = 15.7), 5.07 (d, 1H, *J* = 15.7), 4.48–4.44 (m, 2H), 3.99 (t, 1H, *J* = 10.6), 3.78–3.72 (m, 2H), 2.04–1.98 (m, 1H), 1.43 (t, 3H, *J* = 7.1). **ESI-MS** *m/z* (rel int): (pos) 313.2 ([M+H]$^+$, 100).



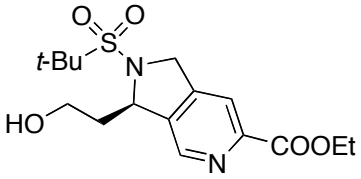
(*R*)-Ethyl 3-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridine-6-carboxylate (*R*-43d). Clear oil (7.5 mg). **TLC**: R_f 0.12 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 8.73 (s, 1H), 8.06 (s, 1H), 5.33 (bt, 1H, *J* = 6.0), 5.06 (d, 1H, *J* = 12.4), 4.66 (d, 1H, *J* = 12.8), 4.50 (q, 2H, *J* = 7.5), 3.97–3.93 (m, 1H), 3.79–3.74 (m, 1H), 2.08–2.01 (m, 2H), 1.49 (t, 3H, *J* = 7.2). **ESI-MS** *m/z* (rel int): (pos) 259.3 ([M+Na]+, 100).



(+)-(*R*)-Ethyl 2-(*tert*-butylsulfonyl)-3,4-bis(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]-pyridine-6-carboxylate (*R*-44a). Brown oil (7.3 mg). **TLC**: R_f 0.37 (1:3 hexanes/EtOAc). $[\alpha]_D^{20}$: +63.3° (*c* 0.37, $CHCl_3$). **IR** (NaCl, film): 3335 (O–H st), 3042, 2971, 2942, 2835, 1735 (C=O st), 1250 (SO_2 st), 1143 (SO_2 st), 968. **^{1}H-NMR** (600 MHz): δ 7.81 (s, 1H), 5.40 (d, 1H, *J* = 8.5), 5.01 (d, 1H, *J* = 15.3), 4.48 (q, 2H, *J* = 10.5, 7.1), 4.21 (dt, 1H, *J* = 9.8, 6.3), 4.05 (dt, 1H, *J* = 9.8, 6.5), 3.97 (d, 1H, *J* = 13.9), 3.82–3.78 (m, 1H), 3.73–3.68 (m, 2H), 3.12–3.06 (m, 2H), 2.31–2.24 (m, 1H), 1.48 (t, 3H, *J* = 7.3), 1.16 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 165.5, 164.9, 155.0, 150.6, 146.7, 146.4, 117.7, 68.6, 66.2, 62.0, 61.1, 58.4, 52.9, 50.9, 38.8, 25.5, 14.3; 2 peaks observed in ester carbonyl region. **ESI-MS** *m/z* (rel int): (pos) 423.5 ([M+Na]$^+$, 100).

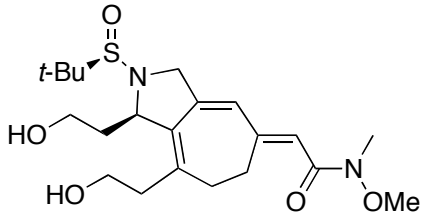


(+)-(*R*)-Ethyl 2-(*tert*-butylsulfonyl)-3-(2-hydroxyethyl)-4-phenyl-2,3-dihydro-1*H*-pyrrolo-[3,4-*c*]pyridine-6-carboxylate (*R*-44b). Clear oil (8.1 mg). **TLC**: R_f 0.20 (1:2 hexanes/EtOAc). $[\alpha]_D^{20}$: +71.0° (*c* 0.42, $CHCl_3$). **IR** (NaCl, film): 3362 (O–H st), 3029, 2999, 2905, 2881, 1721 (C=O st), 1221 (SO_2 st), 1088 (SO_2 st), 968, 798. **^{1}H-NMR** (600 MHz): δ 7.91 (s, 1H), 7.43–7.39 (m, 5H), 5.80 (d, 1H, *J* = 7.7), 5.20 (d, 1H, *J* = 15.2), 4.51–4.48 (m, 1H), 4.42–4.38 (m, 1H), 4.00 (d, 1H, *J* = 12.6), 3.68 (td, 1H, *J* = 9.5, 5.3), 3.47–3.41 (m, 1H), 1.79–1.72 (m, 1H), 1.68–1.63 (m, 1H), 1.46 (t, 3H, *J* = 7.1), 1.25 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 165.0, 154.1, 149.5, 148.2, 137.9, 129.63, 129.60, 129.0, 128.2, 117.7, 62.7, 62.2, 58.3, 50.9, 50.8, 36.0, 25.1, 14.3. **ESI-MS** *m/z* (rel int): (pos) 455.5 ($[M+Na]^+$, 100).

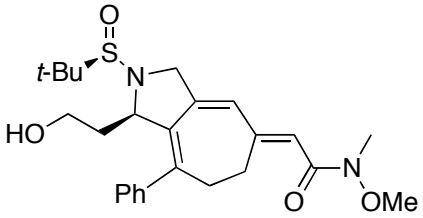


(*R*)-Ethyl 2-(*tert*-butylsulfonyl)-3-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridine-6-carboxylate (*R*-44d). Clear oil (3.6 mg). **TLC**: R_f 0.11 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 8.66 (s, 1H), 8.02 (s, 1H), 5.58 (d, 1H, *J* = 6.0), 5.03 (d, 1H, *J* = 15.6), 4.59 (t, 1H, *J* = 12.5), 4.48 (q, 2H, *J* = 7.5), 3.87 (t, 1H, *J* = 6.4), 3.63–3.61 (m, 1H), 2.11–2.01 (m, 1H), 1.96–1.87 (m, 1H), 1.44 (t, 3H, *J* = 7.1), 1.41 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 357.3 ($[M+H]^+$, 100).

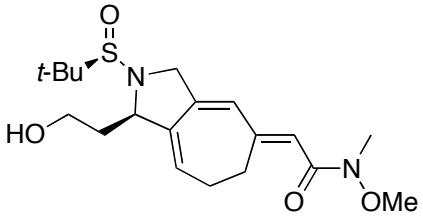
10. SAITO [3+2+2] CYCLOADDITION PRODUCTS (*R*-45–50)



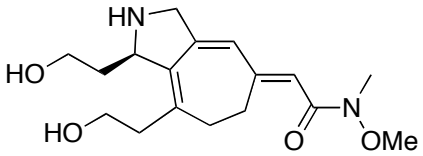
(*E*)-2-((*R*)-2-((*R*)-*tert*-Butylsulfinyl)-1,8-bis(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta-[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-45a). Yellow oil (4.4 mg). **TLC**: R_f 0.44 (1:4 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.28 (s, 1H), 5.96 (s, 1H), 4.68–4.64 (m, 1H), 4.59 (dt, 1H, *J* = 12.5, 5.5), 3.94 (d, 1H, *J* = 16.0), 3.69 (s, 3H), 3.61–3.56 (m, 2H), 3.47–3.41 (m, 2H), 3.21 (s, 3H), 2.60 (t, 1H, *J* = 8.8), 2.49–2.42 (m, 1H), 1.65–1.58 (m, 1H), 1.52–1.47 (m, 2H), 1.22–1.20 (m, 3H), 0.93 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 449.4 ($[M+Na]^+$, 100).



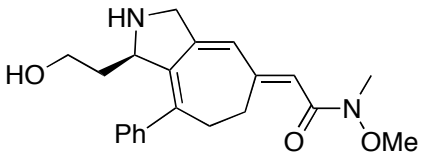
(–)-(*E*)-2-((*R*)-2-((*R*)-*tert*-Butylsulfinyl)-1-(2-hydroxyethyl)-8-phenyl-2,3,6,7-tetrahydrocyclohepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-45b). Light red oil (3.9 mg). **TLC**: R_f 0.25 (1:3 hexanes/EtOAc). $[\alpha]_D^{20}$: –24.4° (*c* 0.35, $CHCl_3$). **IR** (NaCl, film): 3320 (O–H st), 3050, 2990, 2881, 1639 (C=O st), 1520, 1087 (S–O st), 968. **^{1}H-NMR** (600 MHz): δ 7.63 (s, 1H), 7.34–7.27 (m, 5H), 5.73 (s, 1H), 4.66 (dd, 1H, *J* = 9.0, 4.2), 4.51 (dd, 1H, *J* = 10.2, 7.1), 3.69–3.65 (m, 4H), 3.58–3.54 (m, 1H), 3.45–3.41 (m, 1H), 3.23 (s, 3H), 2.64–2.60 (m, 2H), 1.63–1.58 (m, 1H), 1.53–1.49 (m, 2H), 0.91 (s, 9H). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 162.3, 154.0, 141.2, 139.8, 136.3, 130.9, 128.9, 128.0, 127.9, 121.1, 112.7, 67.7, 65.9, 60.4, 58.5, 50.8, 46.9, 45.6, 39.5, 33.9, 23.6. **ESI-MS** *m/z* (rel int): (pos) 459.2 ($[M+H]^+$, 100).



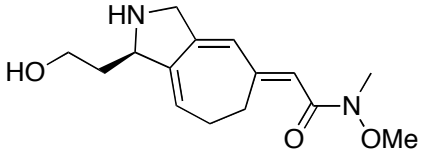
(*E*)-2-((*R*)-2-((*R*)-*tert*-Butylsulfinyl)-1-(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]-pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-45d). Light yellow oil (4.1 mg). **TLC**: R_f 0.41 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.21 (s, 1H), 6.02 (s, 1H), 5.83 (d, 1H, *J* = 16.0), 4.62 (dd, 1H, *J* = 8.0, 3.5), 4.48 (d, 1H, *J* = 16.9), 3.83 (dd, 1H, *J* = 15.2, 6.4), 3.75–3.73 (m, 2H), 3.69 (s, 3H), 3.49 (d, 1H, *J* = 16.0), 3.20 (s, 3H), 2.53 (dd, 1H, *J* = 16.0, 8.0), 2.10–2.02 (m, 2H), 1.83–1.81 (m, 1H), 1.79–1.69 (m, 1H), 102 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 383.2 ($[M+H]^+$, 100).



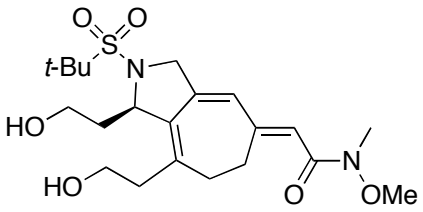
(*R*,*E*)-2-(1,8-Bis(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-46a). Light yellow oil (2.1 mg). **TLC**: R_f 0.44 (1:5 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.29 (s, 1H), 5.91 (s, 1H), 4.68 (dd, 1H, *J* = 9.1, 2.4), 4.19–4.13 (m, 1H), 3.94 (d, 1H, *J* = 16.5), 3.68–3.65 (m, 4H), 3.64–3.61 (m, 1H), 3.46 (t, 2H, *J* = 6.4), 3.21 (s, 3H), 2.61 (t, 2H, *J* = 8.8), 2.49–2.41 (m, 2H), 1.62–1.59 (m, 1H), 1.52–1.47 (m, 2H), 1.22–1.20 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 323.4 ($[M+H]^+$, 100).



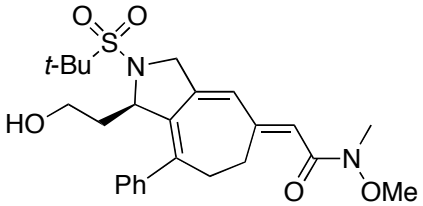
(*R*,*E*)-2-(1-(2-Hydroxyethyl)-8-phenyl-2,3,6,7-tetrahydrocyclohepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-46b). Light red oil (1.6 mg). **TLC**: R_f 0.25 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.68 (s, 1H), 7.38–7.25 (m, 5H), 6.08 (s, 1H), 4.82 (dd, 1H, *J* = 9.0, 4.2), 4.48 (dd, 1H, *J* = 10.2, 7.1), 3.71–3.68 (m, 4H), 3.63–3.58 (m, 1H), 3.49–3.45 (m, 1H), 3.23 (s, 3H), 2.64–2.60 (bm, 2H), 1.63–1.58 (m, 2H), 1.53–1.49 (m, 2H). **ESI-MS** *m/z* (rel int): (pos) 355.2 ([M+H]$^+$, 100).



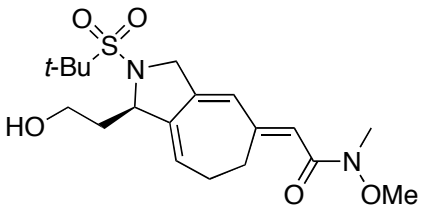
(*R*,*E*)-2-(1-(2-Hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-46d). Light yellow oil (2.0 mg). **TLC**: R_f 0.41 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.21 (s, 1H), 6.03 (s, 1H), 5.80 (d, 1H, *J* = 16.8), 4.59 (dd, 1H, *J* = 8.8, 3.5), 4.50 (d, 1H, *J* = 17.1), 3.85 (dd, 1H, *J* = 15.3, 6.4), 3.75–3.73 (m, 2H), 3.67 (s, 3H), 3.49 (d, 1H, *J* = 16.0), 3.20 (s, 3H), 2.51 (dd, 1H, *J* = 16.0, 8.0), 2.10–2.02 (m, 2H), 1.83–1.81 (m, 1H), 1.79–1.69 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 279.0 ([M+H]$^+$, 100).



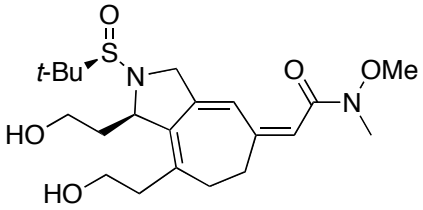
(*R*,*E*)-2-(2-(*tert*-Butylsulfonyl)-1,8-bis(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]-pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-47a). Clear oil (2.9 mg). **TLC**: R_f 0.44 (1:8 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.39 (s, 1H), 6.10 (s, 1H), 4.66–4.63 (m, 1H), 4.59 (dt, 1H, *J* = 12.0, 5.5), 3.94 (d, 1H, *J* = 16.0), 3.69 (s, 3H), 3.61–3.56 (m, 1H), 3.47–3.41 (m, 2H), 3.21 (s, 3H), 2.57 (t, 1H, *J* = 8.8), 2.49–2.42 (m, 2H), 1.65–1.58 (m, 2H), 1.52–1.47 (m, 2H), 1.22–1.20 (m, 2H), 1.2 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 465.2 ([M+Na]$^+$, 100).



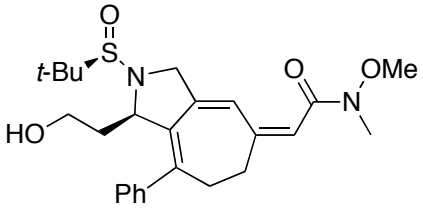
(*R*,*E*)-2-(2-(*tert*-Butylsulfonyl)-1-(2-hydroxyethyl)-8-phenyl-2,3,6,7-tetrahydrocyclohepta[*c*]-pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-47b). Brown oil (3.0 mg). **TLC**: R_f 0.25 (1:15 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.67 (s, 1H), 7.32–7.23 (m, 5H), 5.49 (s, 1H), 4.68 (dd, 1H, *J* = 9.0, 4.2), 4.53 (dd, 1H, *J* = 10.6, 7.1), 3.72–3.67 (m, 4H), 3.58–3.54 (m, 1H), 3.45–3.41 (m, 1H), 3.25 (s, 3H), 2.64–2.60 (m, 2H), 1.63–1.58 (m, 3H), 1.53–1.49 (m, 3H), 1.09 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 475.2 ([M+H]$^+$, 100).



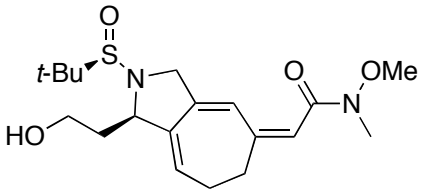
(*R*,*E*)-2-(2-(*tert*-Butylsulfonyl)-1-(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-47d). Light yellow oil (3.3 mg). **TLC**: R_f 0.41 (1:15 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.31 (s, 1H), 6.11 (s, 1H), 5.98 (t, 1H, *J* = 8.0), 4.68–4.62 (m, 2H), 4.00 (dd, 1H, *J* = 12.0, 3.5), 3.72–3.69 (m, 4H), 3.52–3.47 (m, 1H), 3.23 (s, 3H), 3.18–3.14 (m, 2H), 2.70–2.60 (m, 1H), 2.57–2.51 (m, 1H), 1.62–1.52 (m, 2H), 1.19 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 399.2 ([M+H]$^+$, 100).



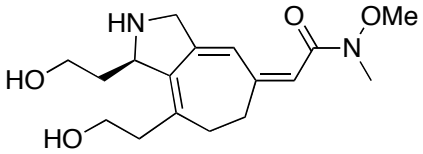
(*Z*)-2-((*R*)-2-((*R*)-*tert*-Butylsulfinyl)-1,8-bis(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta-[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-48a). Yellow oil (3.7 mg). **TLC**: *Rf* 0.44 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.16 (s, 1H), 6.01 (s, 1H), 4.64–4.62 (m, 1H), 4.53 (dt, 1H, *J* = 12.5, 5.9), 3.94 (d, 1H, *J* = 10.0), 3.65–3.61 (m, 3H), 3.59 (s, 3H), 3.52 (dd, 1H, *J* = 12.5, 6.2), 3.23 (s, 3H), 2.49–2.42 (m, 2H), 2.35–2.31 (m, 1H), 2.24–2.20 (m, 1H), 2.17–2.13 (m, 1H), 1.92–1.87 (m, 1H), 1.72–1.67 (m, 2H), 0.88 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 449.4 ([M+Na]$^+$, 100).



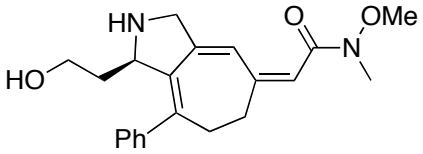
(*Z*)-2-((*R*)-2-((*R*)-*tert*-Butylsulfinyl)-1-(2-hydroxyethyl)-8-phenyl-2,3,6,7-tetrahydrocyclo-hepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-48b). Light red oil (3.1 mg). **TLC**: R_f 0.25 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.69 (s, 1H), 7.34–7.27 (m, 5H), 5.92 (s, 1H), 4.68 (dd, 1H, *J* = 8.8, 4.2), 4.53 (dd, 1H, *J* = 14.2, 7.1), 3.72–3.69 (m, 4H), 3.58–3.54 (m, 1H), 3.45–3.41 (m, 1H), 3.23 (s, 3H), 2.64–2.60 (m, 2H), 1.61–1.56 (m, 2H), 1.53–1.49 (m, 2H), 0.93 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 459.2 ([M+H]$^+$, 100).



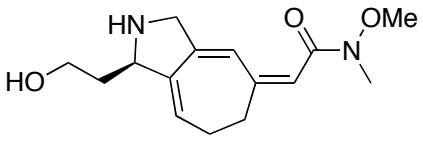
(*Z*)-2-((*R*)-2-((*R*)-*tert*-Butylsulfinyl)-1-(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]-pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-48d). Clear oil (3.3 mg). **TLC**: R_f 0.41 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.21 (s, 1H), 6.11 (s, 1H), 6.00 (s, 1H), 4.59 (dd, 1H, *J* = 8.0, 3.5), 4.48 (d, 1H, *J* = 15.0), 3.83 (dd, 1H, *J* = 15.2, 5.7), 3.75–3.73 (m, 2H), 3.69 (s, 3H), 3.49 (d, 1H, *J* = 14.3), 3.20 (s, 3H), 2.51 (dd, 1H, *J* = 15.2, 6.2), 2.10–2.02 (m, 2H), 1.83–1.81 (m, 1H), 1.79–1.69 (m, 1H), 1.01 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 383.2 ([M+H]$^+$, 100).



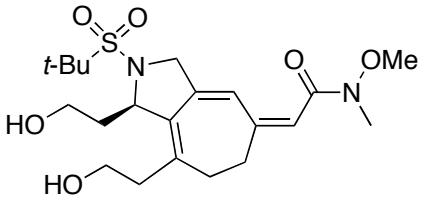
(*R*,*Z*)-2-(1,8-Bis(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-49a). Light yellow oil (1.5 mg). **TLC**: R_f 0.44 (1:5 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.29 (s, 1H), 6.11 (s, 1H), 4.88 (dd, 1H, *J* = 9.0, 2.4), 4.21–4.18 (m, 1H), 3.94 (d, 1H, *J* = 16.0), 3.69 (s, 3H), 3.67–3.63 (m, 2H), 3.48 (t, 2H, *J* = 6.4), 3.21 (s, 3H), 2.61 (t, 2H, *J* = 8.8), 2.49–2.42 (m, 2H), 1.62–1.59 (m, 1H), 1.56–1.52 (m, 3H). **ESI-MS** *m/z* (rel int): (pos) 323.4 ([M+H]$^+$, 100).



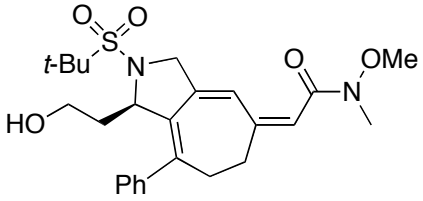
(*R*,*Z*)-2-(1-(2-Hydroxyethyl)-8-phenyl-2,3,6,7-tetrahydrocyclohepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-49b). Light orange oil (0.6 mg). **TLC**: R_f 0.25 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.65 (s, 1H), 7.36–7.23 (m, 5H), 5.92 (s, 1H), 4.68 (dd, 1H, *J* = 9.0, 4.8), 4.42 (dd, 1H, *J* = 12.2, 7.1), 3.69–3.65 (m, 4H), 3.61–3.54 (m, 1H), 3.41–3.38 (m, 1H), 3.21 (s, 3H), 2.64–2.60 (bm, 2H), 1.61–1.52 (m, 2H), 1.50–1.47 (m, 2H). **ESI-MS** *m/z* (rel int): (pos) 355.2 ([M+H]$^+$, 100).



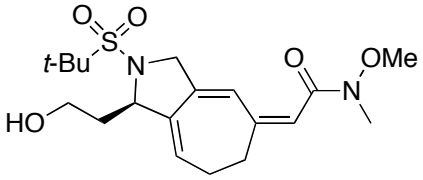
(*R*,*Z*)-2-(1-(2-Hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-49d). Light yellow oil (0.9 mg). **TLC**: R_f 0.41 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.22 (s, 1H), 6.01 (s, 1H), 5.92 (s, 1H), 4.59 (dd, 1H, *J* = 8.8, 3.5), 4.49 (d, 1H, *J* = 17.1), 3.83 (dd, 1H, *J* = 12.4, 6.4), 3.73–3.70 (m, 2H), 3.67 (s, 3H), 3.49 (d, 1H, *J* = 16.0), 3.21 (s, 3H), 2.51 (dd, 1H, *J* = 16.0, 8.0), 2.13–2.04 (m, 2H), 1.81–1.78 (m, 1H), 1.74–1.65 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 279.0 ([M+H]$^+$, 100).



(*R*,*Z*)-2-(2-(*tert*-Butylsulfonyl)-1,8-bis(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]-pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-50a). Clear oil (3.3 mg). **TLC**: R_f 0.44 (1:8 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.26 (s, 1H), 6.03 (s, 1H), 4.62–4.57 (m, 1H), 4.50 (dd, 2H, *J* = 12.0, 5.5), 3.84 (d, 1H, *J* = 11.0), 3.73 (t, 1H, *J* = 12.0), 3.67 (s, 3H), 3.50 (dd, 2H, *J* = 12.0, 6.2), 3.23 (s, 3H), 2.53 (dd, 2H, *J* = 9.1, 8.8), 2.11–1.98 (m, 2H), 1.83–1.78 (m, 2H), 1.72–1.67 (m, 2H), 1.18 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 465.2 ([M+Na]$^+$, 100).



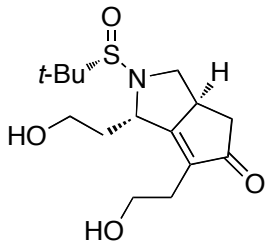
(*R*,*Z*)-2-(2-(*tert*-Butylsulfonyl)-1-(2-hydroxyethyl)-8-phenyl-2,3,6,7-tetrahydrocyclohepta[*c*]-pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-50b). Brown oil (3.3 mg). **TLC**: R_f 0.25 (1:15 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.67 (s, 1H), 7.32–7.23 (m, 5H), 5.93 (s, 1H), 4.68 (dd, 1H, *J* = 9.0, 4.8), 4.53 (dd, 1H, *J* = 10.7, 7.1), 3.72–3.67 (m, 4H), 3.61–3.58 (m, 1H), 3.47–3.43 (m, 1H), 3.23 (s, 3H), 2.64–2.60 (m, 2H), 1.63–1.58 (m, 2H), 1.53–1.49 (m, 2H), 1.10 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 475.3 ([M+H]$^+$, 100).



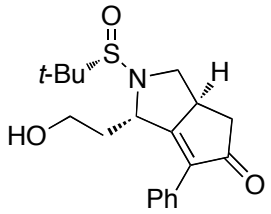
(*R*,*Z*)-2-(2-(*tert*-Butylsulfonyl)-1-(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*R*-50d). Light yellow oil (2.9 mg). **TLC**: R_f 0.41 (1:15 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.27 (t, 1H, *J* = 8.0), 6.13 (s, 1H), 6.02 (s, 1H), 4.73 (dd, 1H, *J* = 14.0, 4.0), 4.52 (dd, 1H, *J* = 16.0, 4.0), 3.92–3.89 (m, 1H), 3.76–3.70 (m, 2H), 3.56 (s, 3H), 3.21 (s, 3H), 2.48–2.44 (m, 2H), 2.39–2.35 (m, 1H), 2.24–2.20 (m, 1H), 1.94–1.87 (m, 1H), 1.70–1.65 (m, 1H), 1.07 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 399.2 ([M+H]$^+$, 100).

F. ANALYTICAL DATA FOR *S*-SERIES LIBRARY MEMBERS

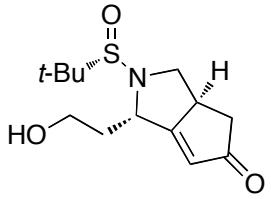
1. PAUSON–KHAND REACTION PRODUCTS (*S*-11–13)



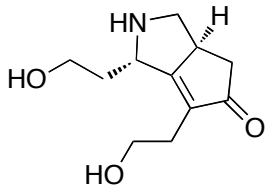
(1*S*,3a*S*)-2-((*S*)-*tert*-Butylsulfinyl)-1,6-bis(2-hydroxyethyl)-2,3,3a,4-tetrahydrocyclopenta[*c*]-pyrrol-5(1*H*)-one (*S*-11a). Clear oil (7.0 mg). **TLC**: R_f 0.40 (1:9 hexanes/EtOAc) **^{1}H-NMR** (600 MHz): δ 5.85 (dt, 1H, *J* = 8.8, 6.1), 5.16 (d, 1H, *J* = 10.0), 5.03 (d, 1H, *J* = 8.2), 4.51 (s, 1H), 3.92 (dd, 1H, *J* = 12.5, 8.2), 3.78–3.72 (m, 2H), 3.56–3.52 (m, 2H), 2.48 (t, 1H, *J* = 5.6), 1.83–1.78 (m, 3H), 1.64–1.61 (m, 1H), 1.21 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 310.4 ([M–CO+Na]$^+$, 100).



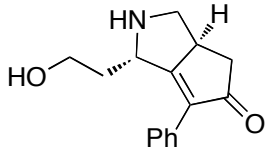
(1*S*,3*S*)-2-((*S*)-*tert*-Butylsulfinyl)-1-(2-hydroxyethyl)-6-phenyl-2,3,3a,4-tetrahydrocyclo-penta[*c*]pyrrol-5(1*H*)-one (*S*-11b). Clear oil (7.5 mg). **TLC**: R_f 0.24 (1:4 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.39–7.31 (m, 5H) 6.02 (dt, 1H, *J* = 8.4, 2.4), 5.30 (d, 1H, *J* = 14.3), 5.16 (d, 1H, *J* = 8.8), 4.82 (t, 1H, *J* = 8.8), 3.98 (dd, 1H, *J* = 10.2, 4.4), 3.89 (dd, 1H, *J* = 8.8, 3.5), 3.70–3.65 (m, 2H), 2.04–1.98 (m, 2H), 1.31 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 370.5 ([M+Na]$^+$, 100).



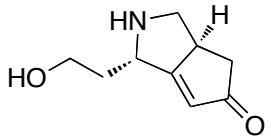
(1*S*,3*S*)-2-((*S*)-*tert*-Butylsulfinyl)-1-(2-hydroxyethyl)-2,3,3a,4-tetrahydrocyclopenta[*c*]-pyrrol-5(1*H*)-one (*S*-11d). Light yellow oil (7.3 mg). **TLC**: R_f 0.27 (1:6 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.92 (dt, 1H, *J* = 5.5, 2.6), 5.16 (d, 1H, *J* = 12.0), 5.03 (d, 1H, *J* = 8.2), 4.59 (t, 1H, *J* = 8.7), 3.98 (s, 1H), 3.96 (dd, 1H, *J* = 10.7, 8.6), 3.85 (dd, 1H, *J* = 9.1, 10.7), 3.54–3.49 (m, 2H), 1.81–1.74 (m, 2H), 1.21 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 240.4 ([M+Na]$^+$, 100).



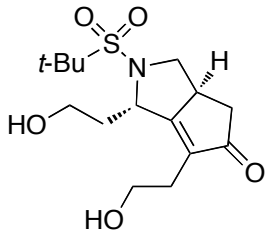
(1*S*,3a*S*)-1,6-Bis(2-hydroxyethyl)-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (*S*-12a). Clear oil (2.6 mg). **TLC**: R_f 0.31 (1:5 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.96 (dt, 1H, *J* = 8.8, 6.2), 5.18 (d, 1H, *J* = 10.0), 5.05 (d, 1H, *J* = 8.2), 4.62 (s, 1H), 4.08 (dd, 1H, *J* = 12.5, 8.2), 3.92–3.88 (m, 1H), 3.76–3.72 (m, 1H), 3.52–3.50 (m, 1H), 2.96–2.92 (m, 1H), 2.48 (t, 1H, *J* = 5.6), 1.89–1.85 (m, 1H), 1.74–1.70 (m, 1H), 1.61–1.58 (m, 2H). **ESI-MS** *m*/*z* (rel int): (pos) 234.4 ([M+Na]$^+$, 100).



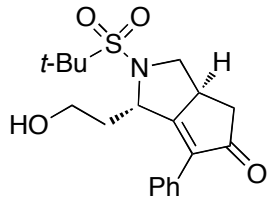
(1*S*,3a*S*)-1-(2-Hydroxyethyl)-6-phenyl-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (S-12b). Clear oil (2.8 mg). **TLC**: R_f 0.48 (1:9 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.34–7.32 (m, 2H), 7.29–7.27 (m, 3H), 6.02 (dt, 1H, *J* = 8.8, 6.2), 5.21 (d, 1H, *J* = 10.0), 5.16 (d, 1H, *J* = 8.2), 4.82 (s, 1H), 4.04 (bs, 1H), 3.98 (dd, 1H, *J* = 12.5, 8.2), 3.88 (dd, 1H, *J* = 10.0, 6.2), 3.67–3.61 (m, 2H), 3.46–3.42 (m, 1H), 2.06–2.02 (m, 2H), 1.70 (bs, 1H). **ESI-MS** *m*/*z* (rel int): (pos) 267.2 ([M+Na]$^+$, 100).



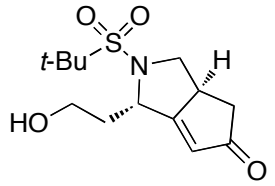
(1*S*,3a*S*)-1-(2-Hydroxyethyl)-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (*S*-12d). Clear oil (3.7 mg). **TLC**: R_f 0.26 (1:5 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.86 (dt, 1H, *J* = 8.8, 6.2), 5.12 (d, 1H, *J* = 10.0), 5.03 (d, 1H, *J* = 8.2), 4.52 (s, 1H), 4.17 (dt, 1H, *J* = 12.5, 8.2), 3.92–3.88 (m, 1H), 3.76–3.72 (m, 1H), 3.52–3.50 (m, 1H), 2.96–2.92 (m, 1H), 2.37 (s, 1H), 1.78–1.74 (m, 2H). **ESI-MS** *m*/*z* (rel int): (pos) 190.2 ([M+Na]$^+$, 100).



(1*S*,3a*S*)-2-(*tert*-Butylsulfonyl)-1,6-bis(2-hydroxyethyl)-2,3,3a,4-tetrahydrocyclopenta[*c*]-pyrrol-5(1*H*)-one (*S*-13a). Clear oil (7.4 mg). **TLC**: R_f 0.40 (1:6 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.92 (dt, 1H, *J* = 8.8, 6.1), 5.16 (d, 1H, *J* = 10.0), 5.03 (d, 1H, *J* = 8.2), 4.62–4.57 (m, 1H), 4.13–4.04 (m, 1H), 3.92 (dd, 1H, *J* = 14.3, 8.2), 3.68–3.61 (m, 1H), 3.50–3.45 (m, 1H), 2.99 (dd, 1H, *J* = 5.6, 3.5), 1.93–1.87 (m, 1H), 1.81 (dd, 2H, *J* = 7.5, 6.8), 1.61–1.56 (m, 2H), 1.31 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 354.4 ([M+Na]$^+$, 100).

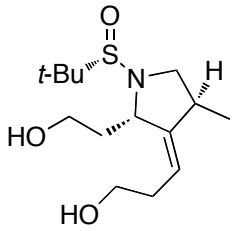


(1*S*,3a*S*)-2-(*tert*-Butylsulfonyl)-1-(2-hydroxyethyl)-6-phenyl-2,3,3a,4-tetrahydrocyclopenta-[*c*]pyrrol-5(1*H*)-one (*S*-13b). Clear oil (7.0 mg). **TLC**: R_f 0.24 (1:6 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.39–7.31 (m, 5H) 5.98 (dt, 1H, *J* = 8.4, 2.4), 5.21 (d, 1H, *J* = 14.3), 5.03 (d, 1H, *J* = 8.8), 4.91 (d, 1H, *J* = 8.8, 6.1), 4.13 (d, 1H, *J* = 10.2), 4.02 (t, 1H, *J* = 8.0), 3.81–3.76 (m, 1H), 3.56–3.52 (m, 1H), 2.91 (s, 1H), 2.04–1.98 (m, 1H), 2.48 (dt, 1H, *J* = 10.1, 8.8), 1.44 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 386.5 ([M+Na]$^+$, 100).

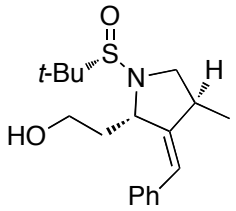


(1*S*,3a*S*)-2-(*tert*-Butylsulfonyl)-1-(2-hydroxyethyl)-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (*S*-13d). Light yellow oil (7.1 mg). **TLC**: R_f 0.27 (1:4 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.92 (dt, 1H, *J* = 5.5, 1.5), 5.16 (d, 1H, *J* = 12.0), 5.03 (d, 1H, *J* = 8.2), 4.69 (dd, 1H, *J* = 5.3, 8.7), 4.13 (d, 1H, *J* = 12.0), 3.96 (dd, 1H, *J* = 10.7, 8.6), 3.68 (dt, 1H, *J* = 9.1, 10.7), 3.50 (dt, 1H, *J* = 6.3, 6.1), 2.80 (s, 1H), 1.98 (dd, 1H, *J* = 7.1, 5.5), 1.81–1.78 (m, 1H), 1.41 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 310.4 ([M+Na]$^+$, 100).

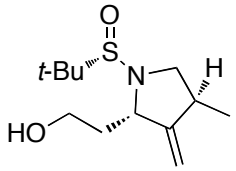
2. KRISCHE REDUCTIVE CYCLIZATION PRODUCTS (*S*-14–19)



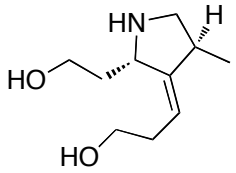
(*Z*)-3-((2*S*,4*S*)-1-((*S*)-*tert*-Butylsulfinyl)-2-(2-hydroxyethyl)-4-methylpyrrolidin-3-ylidene)-propan-1-ol (*S*-14a). Colorless oil (8.2 mg). **TLC**: R_f 0.53 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.02 (t, 1H, *J* = 7.1), 4.49 (t, 1H, *J* = 7.6), 4.09–4.03 (m, 1H), 3.68–3.62 (m, 2H), 3.19 (d, 1H, *J* = 8.8), 3.04–2.98 (m, 2H), 2.78–2.71 (m, 1H), 2.31 (s, 1H), 1.91–1.87 (m, 2H), 1.82–1.76 (m, 2H), 1.21 (s, 9H), 1.05 (d, 3H, *J* = 6.8). **ESI-MS** *m*/*z* (rel int): (pos) 312.2 ([M+Na]$^+$, 100).



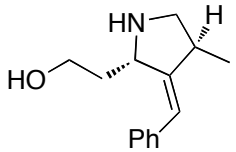
2-((2*S*,4*S*,*Z*)-3-Benzylidene-1-((*S*)-*tert*-butylsulfinyl)-4-methylpyrrolidin-2-yl)ethanol (S-14b). Colorless oil (8.8 mg). **TLC**: R_f 0.40 (1:1 hexanes/EtOAc). **^{1}H-NMR**(600 MHz): δ 7.43–7.40 (m, 2H) 7.36 (d, 1H, *J* = 4.0), 7.23–7.18 (m, 2H), 6.41 (s, 1H), 5.43 (bs, 1H), 4.95 (s, 1H), 3.82–3.79 (m, 1H), 3.76–3.71 (m, 1H), 3.65–3.61 (m, 1H), 3.03 (s, 1H), 2.83 (t, 1H, *J* = 9.5), 1.95–1.89 (m, 1H), 1.87–1.81 (m, 1H) 1.19 (s, 9H), 1.16 (d, 3H, *J* = 6.5). **ESI-MS** *m/z* (rel int): (pos) 218.2 ([M+H]$^+$, 100).



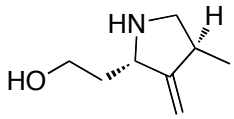
2-((2*S*,4*S*)-1-((*S*)-*tert*-Butylsulfinyl)-4-methyl-3-methylenepyrrolidin-2-yl)ethanol (*S*-14d). Colorless oil (7.4 mg). **TLC:** R_f 0.33 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 4.91 (s, 2H), 4.21 (t, 1H, *J* = 5.5), 3.73–3.69 (m, 2H), 3.11 (t, 1H, *J* = 9.3), 3.00 (t, 1H, *J* = 9.3), 2.76–2.61 (m, 1H), 1.94–1.86 (m, 1H), 1.77–1.72 (m, 1H), 1.16 (s, 9H), 1.08 (d, 3H, *J* = 6.7). **ESI-MS** *m/z* (rel int): (pos) 268.1 ([M+Na]$^+$, 100).



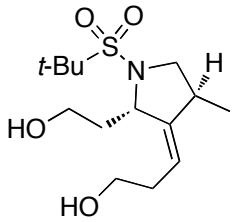
(*Z*)-3-((2*S*,4*S*)-2-(2-Hydroxyethyl)-4-methylpyrrolidin-3-ylidene)propan-1-ol (*S*-15a). Colorless oil (4.1 mg). **TLC**: R_f 0.53 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.11 (t, 1H *J* = 7.1), 4.48 (t, 1H, *J* = 5.8), 3.71–3.63 (m, 2H), 3.61–3.58 (m, 2H), 3.10 (t, 1H, *J* = 9.6), 2.96 (t, 1H, *J* = 8.3), 2.64 (s, 1H), 2.30–2.23 (m, 2H), 1.78 (q, 2H, *J* = 6.5), 1.06 (d, 3H, *J* = 6.7). **ESI-MS** *m/z* (rel int): (pos) 208.2 ([M+Na]$^+$, 100).



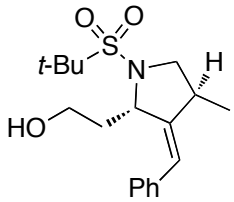
2-((2*S*,4*S*,*Z*)-3-Benzylidene-4-methylpyrrolidin-2-yl)ethanol (*S*-15b). Colorless oil (8.1 mg). **TLC**: R_f 0.40 (1:20 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.31–7.25 (m, 3H) 7.19–7.14 (m, 2H), 6.43 (s, 1H), 4.93 (d, 1H, *J* = 9.2), 3.76 (t, 1H, *J* = 8.6), 3.68–3.54 (m, 2H), 3.05 (t, 1H, *J* = 6.7), 2.78 (t, 1H, *J* = 7.5), 1.92–1.90 (m, 1H), 1.79–1.76 (m, 1H), 1.30 (d, 3H, *J* = 6.5). **ESI-MS** *m/z* (rel int): (pos) 218.0 ([M+H]$^+$, 100).



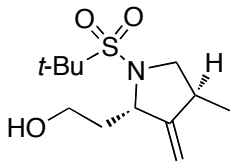
2-((2*S*,4*S*)-4-Methyl-3-methylenepyrrolidin-2-yl)ethanol (*S*-15d). Colorless oil (7.5 mg). **TLC:** R_f 0.33 (1:20 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.10 (d, 1H, *J* = 11.8), 5.03 (d, 1H, *J* = 11.8), 4.24 (t, 1H, *J* = 5.7), 3.90 (t, 1H, *J* = 6.7), 3.78 (t, 1H, *J* = 6.6), 3.58 (t, 1H, *J* = 6.4), 3.30 (bs, 1H), 2.92 (dd, 1H, *J* = 9.5, 7.1), 2.75 (dd, 1H, *J* = 7.1, 5.2), 2.01–1.96 (m, 2H), 1.18 (d, 3H, *J* = 6.7). **ESI-MS***m*/*z* (rel int): (pos) 164.1 ([M+Na]$^+$, 100).



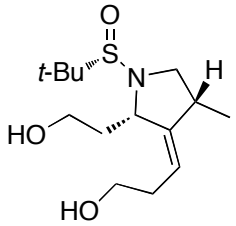
(*Z*)-3-((2*S*,4*S*)-1-(*tert*-Butylsulfonyl)-2-(2-hydroxyethyl)-4-methylpyrrolidin-3-ylidene)-propan-1-ol (*S*-16a). Colorless oil (8.3 mg). **TLC**: R_f 0.53 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 4.89 (t, 1H, *J* = 7.1), 4.51 (d, 1H, *J* = 7.6), 4.22 (t, 2H, *J* = 6.9), 3.72–3.66 (m, 2H), 3.55 (d, 1H, *J* = 8.8), 2.55–2.49 (m, 1H), 2.41–2.38 (m, 1H), 1.98–1.95 (m, 1H), 1.89–1.85 (m, 2H), 1.76 (t, 1H, *J* = 6.5), 1.52 (bs, 1H), 1.21 (s, 12H). **ESI-MS** *m*/*z* (rel int): (pos) 328.4 ([M+Na]$^+$, 100).



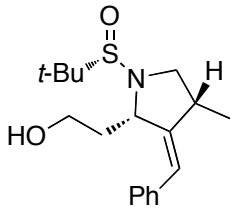
2-((2*S*,4*S*,*Z*)-3-Benzylidene-1-(*tert*-butylsulfonyl)-4-methylpyrrolidin-2-yl)ethanol (*S*-16b). Colorless oil (9.2 mg). **TLC**: R_f 0.40 (3:2 hexnes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.36–7.31 (m, 2H), 7.28–7.23 (m, 2H), 7.20–7.16 (m, 1H), 6.35 (s, 1H), 5.15 (d, 1H, *J* = 10.1), 3.97 (dd, 1H, *J* = 10.1, 7.1), 3.79–3.76 (m, 1H), 3.64–3.61 (m, 1H), 3.11–3.03 (m, 1H), 3.01–2.98 (m, 1H), 2.48 (bs, 1H), 1.88–1.83 (m, 1H), 1.52–1.48 (m, 1H), 1.24 (d, 3H, *J* = 6.9), 1.18 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 360.2 ([M+Na]$^+$, 100).



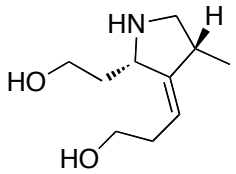
2-((2*S*,4*S*)-1-(*tert*-Butylsulfonyl)-4-methyl-3-methylenepyrrolidin-2-yl)ethanol (*S*-16d). Colorless oil (9.1 mg). **TLC:** R_f 0.33 (3:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7 4.92 (s, 2H), 4.28 (t, 1H, *J* = 5.5), 3.81–3.69 (bm, 2H), 3.18 (t, 1H, *J* = 6.7), 3.05 (t, 1H, *J* = 7.4), 2.79 (s, 1H), 1.92–1.86 (m, 2H), 1.82–1.78 (m, 1H), 1.25 (s, 9H), 1.11 (d, 3H, *J* = 6.7). **ESI-MS** *m*/*z* (rel int): (pos) 284.4 ([M+Na]$^+$, 100).



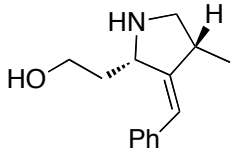
(*Z*)-3-((2*S*,4*R*)-1-((*S*)-*tert*-Butylsulfinyl)-2-(2-hydroxyethyl)-4-methylpyrrolidin-3-ylidene)-propan-1-ol (*S*-17a). Colorless oil (8.1 mg). **TLC**: R_f 0.53 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.21 (t, 1H, *J* = 7.3), 4.47 (d, 1H, *J* = 9.3), 3.91 (t, 1H, *J* = 10.9), 3.71–3.68 (m, 2H), 3.62–3.58 (m, 2H), 2.64–2.61 (m, 1H), 2.51 (dd, 1H, *J* = 9.0, 11.2), 2.31–2.25 (m, 2H), 2.31–2.25 (m, 2H), 1.08 (s, 9H), 1.02 (d, 3H, *J* = 6.9). **ESI-MS** *m/z* (rel int): (pos) 642.5 ([M+H]+,25); 312.2 ([M+Na]$^+$, 100).



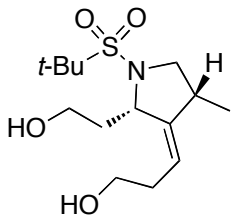
2-((2*S*,4*R*,*Z*)-3-Benzylidene-1-((*S*)-*tert*-butylsulfinyl)-4-methylpyrrolidin-2-yl)ethanol (*S*-17b). Colorless oil (8.3 mg). **TLC**: R_f 0.40 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.43–7.40 (m, 2H) 7.36 (d, 1H, *J* = 4.2), 7.23–7.18 (m, 2H), 6.44 (s, 1H), 5.81 (bs, 1H), 4.93 (s, 1H), 3.75–3.73 (m, 1H), 3.71–3.67 (m, 1H), 3.65–3.61 (m, 1H), 3.05 (s, 1H), 2.77 (t, 1H, *J* = 6.5), 1.95–1.89 (m, 1H), 1.87–1.81 (m, 1H) 1.21 (s, 9H), 1.16 (d, 3H, *J* = 6.5). **ESI-MS** *m/z* (rel int): (pos) 218.2 ([M+H]$^+$, 100).



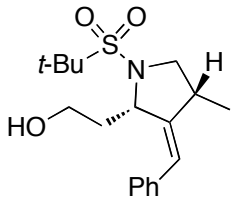
(*Z*)-3-((2*S*,4*R*)-2-(2-Hydroxyethyl)-4-methylpyrrolidin-3-ylidene)propan-1-ol (*S*-18a). Colorless oil (4.0 mg). **TLC**: R_f 0.53 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.21 (t, 1H *J* = 7.1), 4.44 (t, 1H, *J* = 5.8), 3.92 (dt, 1H, *J* = 9.6, 5.3), 3.71–3.63 (m, 2H), 3.61–3.58 (m, 2H), 2.71 (s, 1H), 2.59 (dd, 1H, *J* = 8.3, 7.1), 2.30–2.23 (m, 2H), 1.83 (q, 2H, *J* = 6.5), 1.06 (d, 3H, *J* = 6.7). **ESI-MS** *m/z* (rel int): (pos) 208.2 ([M+Na]$^+$, 100).



2-((2*S*,4*R*,*Z*)-3-Benzylidene-4-methylpyrrolidin-2-yl)ethanol (*S*-18b). Colorless oil (8.0 mg). **TLC**: R_f 0.40 (1:20 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ δ 7.30–7.25 (m, 3H) 7.20–7.15 (m, 2H), 6.47 (s, 1H), 4.96 (d, 1H, *J* = 9.2), 4.01 (br, 1H), 3.76 (t, 1H, *J* = 8.6), 3.64–3.62 (m, 1H), 3.48 (t, 1H, *J* = 8.2), 3.04 (t, 1H, *J* = 6.5), 2.93 (t, 1H, *J* = 7.2), 1.79–1.73 (m, 1H), 1.69–1.62 (m, 1H), 1.39 (d, 3H, *J* = 6.5). **ESI-MS** *m/z* (rel int): (pos) 218.1 ([M+H]$^+$, 100).

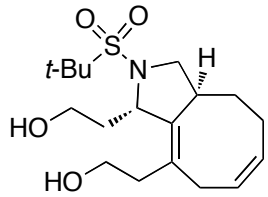


(*Z*)-3-((2*S*,4*R*)-1-(*tert*-Butylsulfonyl)-2-(2-hydroxyethyl)-4-methylpyrrolidin-3-ylidene)-propan-1-ol (*S*-19a). Colorless oil (7.3 mg). **TLC**: R_f 0.53 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.08 (dt, 1H, *J* = 2.0, 7.1), 4.49 (t, 1H, *J* = 7.6), 4.97 (t, 1H, *J* = 6.9), 3.69–3.62 (m, 2H), 3.60–3.55 (m, 2H), 3.08 (dd, 1H, *J* = 3.1, 8.8), 3.01 (dd, 1H, *J* = 3.2, 6.5), 2.98–2.93 (m, 1H), 2.76 (bs, 1H), 2.24–2.19 (m, 1H), 2.15 (bs, 1H), 1.88–1.85 (m, 1H), 1.77–1.72 (m, 1H), 1.61–1.54 (m, 1H), 1.19 (s, 12H). **ESI-MS** *m*/*z* (rel int): (pos) 328.4 ([M+Na]$_+$, 100).

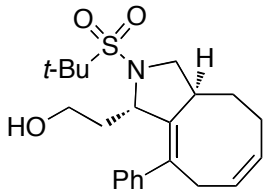


2-((2*S*,4*R*,*Z*)-3-Benzylidene-1-(*tert*-butylsulfonyl)-4-methylpyrrolidin-2-yl)ethanol (*S*-19b). Colorless oil (8.5 mg). **TLC**: R_f 0.40 (3:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.44–7.39 (m, 2H), 7.33–7.28 (m, 2H), 7.22–7.18 (m, 1H), 6.41 (s, 1H), 5.24 (s, 1H), 4.01 (t, 1H, *J* = 8.0), 3.78–3.65 (m, 1H), 3.10–3.01 (m, 2H), 2.05–1.96 (m, 2H), 1.54–1.51 (m, 1H), 1.36 (d, 3H, *J* = 6.9), 1.30 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) ([M+Na]$^+$, 100).

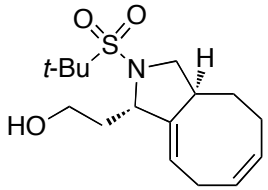
3. EVANS BUTADIENE [4+2+2] CYCLOADDITION PRODUCTS (*S*-20)



2,2'-((1*S*,3a*S*,6*Z*,9*Z*)-2-(*tert*-Butylsulfonyl)-2,3,3a,4,5,8-hexahydro-1*H*-cycloocta[*c*]pyrrole-1,9-diyl)diethanol (*S*-20a). Light yellow oil (4.5 mg). **TLC**: R_f 0.39 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.78–5.74 (m, 1H), 5.67–5.61 (m, 1H), 4.82 (s, 1H), 3.79–3.76 (m, 2H), 3.70 (t, 1H, *J* = 6.8), 3.67–3.58 (m, 2H), 3.36 (dd, 1H, *J* = 12.5, 6.8), 3.14 (bs, 1H), 2.93 (dd, 1H, *J* = 7.9, 14.6), 2.53–2.48 (m, 3H), 2.38 (dd, 1H, *J* = 6.8, 14.7), 2.31–2.26 (m, 3H), 1.83–1.78 (m, 3H), 1.43 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 358.3 ([M+H]$^+$, 100).

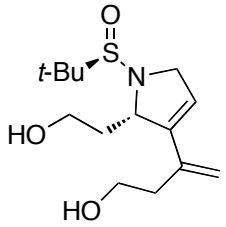


2-((1*S*,3a*S*,6*Z*,9*Z*)-2-(*tert*-Butylsulfonyl)-9-phenyl-2,3,3a,4,5,8-hexahydro-1*H*-cycloocta[*c*]-pyrrol-1-yl)ethanol (*S*-20b). Light yellow oil (7.2 mg). **TLC**: R_f 0.36 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.36–7.31 (m, 3H), 7.8–7.09 (m, 2H), 5.65–5.62 (m, 1H), 5.60–5.56 (m, 1H), 4.91 (s, 1H), 3.50 (s, 1H), 3.44–3.38 (m, 2H), 3.31–3.28 (m, 1H), 2.81 (dd, 1H, *J* = 6.1, 15.2), 2.47–2.41 (m, 1H), 1.881.69 (m, 2H), 1.65–1.58 (m, 3H), 1.42–1.36 (m, 3H), 1.33 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 270.2 ([M–SO_2tBu+H]$^+$, 15); 390.2 ([M+H]$^+$, 100).

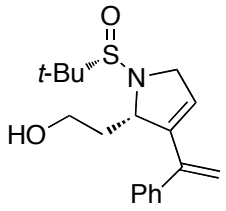


2-((1*S*,3a*S*,6*Z*,9*E*)-2-(*tert*-Butylsulfonyl)-2,3,3a,4,5,8-hexahydro-1*H*-cycloocta[*c*]pyrrol-1-yl)-ethanol (*S*-20d). Light yellow oil (7.0 mg). **TLC**: R_f 0.40 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.69–5.61 (m, 1H), 5.58–5.49 (m, 1H), 5.38 (s, 1H), 3.65–3.49 (bm, 2H), 3.73–3.70 (m, 2H), 3.43 (d, 1H, *J* = 11.1), 3.24 (dd, 1H, *J* = 6.5, 12.1), 3.19–3.11 (m, 1H), 2.88–2.65 (bm, 2H), 2.40–2.33 (m, 1H), 1.93–1.81 (m, 2H), 1.66–1.61 (m, 1H), 1.55–1.49 (m, 1H), 1.49 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 336.2 ([M+Na]$^+$, 100).

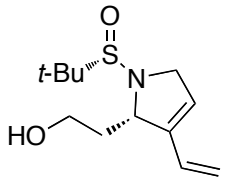
4. ENYNE METATHESIS PRODUCTS (*S*-21–23)



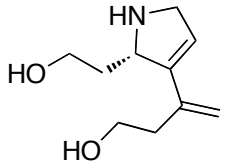
3-((*S*)-1-((*S*)-*tert*-Butylsulfinyl)-2-(2-hydroxyethyl)-2,5-dihydro-1*H*-pyrrol-3-yl)but-3-en-1-ol (*S*-21a). Clear oil (8.8 mg). **TLC**: R_f 0.46 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.79 (s, 1H), 5.06 (s, 1H), 5.01 (s, 1H), 4.91 (t, 1H, *J* = 6.8), 4.50 (d, 2H, *J* = 15.7), 3.61–3.55 (m, 3H), 3.52 (d, 1H, *J* = 12.6) 2.51–2.49 (m, 1H), 2.41–2.37 (m, 1H), 2.01– 1.95 (m, 1H), 1.92–1.88 (m, 1H), 1.09 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 310.4 ([M+Na]$^+$, 100).



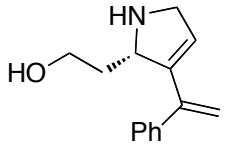
2-((*S*)-1-((*S*)-*tert*-Butylsulfinyl)-3-(1-phenylvinyl)-2,5-dihydro-1*H*-pyrrol-2-yl)ethanol (*S*-21b). Clear oil (8.6 mg). **TLC**: R_f 0.31 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.45–7.34 (m, 3H), 7.32–7.28 (m, 2H), 5.49 (s, 1H), 5.26 (s, 1H), 5.24 (s, 1H), 4.99–4.95 (m, 1H), 4.48 (d, 1H, *J* = 15.2), 4.13 (t, 1H, *J* = 5.3), 3.85–3.78 (m, 1H), 3.75–3.70 (m, 1H), 3.09 (s, 1H), 2.20–2.13 (m, 1H), 1.86–1.77 (m, 1H), 1.07 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 342.5 ([M+Na]$^+$, 100).



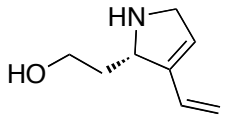
2-((*S*)-1-((*S*)-*tert*-Butylsulfinyl)-3-vinyl-2,5-dihydro-1*H*-pyrrol-2-yl)ethanol (*S*-21d). Yellow oil (7.8 mg). **TLC**: R_f 0.28 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.32 (dd, 1H, *J* = 17.3, 11.0), 5.71 (s, 1H), 5.20 (d, 1H, *J* = 17.8), 5.09 (d, 1H, *J* = 11.0), 4.85 (s, 1H), 4.49 (d, 1H, *J* = 15.1), 3.72–3.68 (m, 2H), 3.50 (d, 1H, *J* = 15.3), 1.98–1.89 (m, 2H), 1.12 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 266.3 ([M+Na]$^+$, 100).



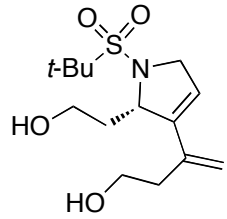
(*S*)-3-(2-(2-Hydroxyethyl)-2,5-dihydro-1*H*-pyrrol-3-yl)but-3-en-1-ol (*S*-22a). Clear colorless oil (1.2 mg). **TLC**: R_f 0.46 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 5.81 (ddd, 1H, *J* = 10.0, 7.9, 6.8), 5.25 (d, 1H, *J* =11.0), 5.16 (d, 1H, *J* = 8.4), 4.48 (t, 1H, *J* = 9.7), 3.99–3.94 (m, 2H), 3.70–3.66 (m, 2H), 3.41 (dd, 1H, *J* = 10.9, 4.4), 2.15–2.11 (m, 1H) 1.92– 1.87 (m, 2H), 1.54–1.47 (m, 2H). **ESI-MS** *m/z* (rel int): (pos) 206.8 ([M+Na]$^+$, 100).



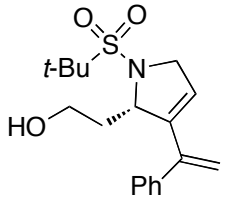
(*S*)-2-(3-(1-Phenylvinyl)-2,5-dihydro-1*H*-pyrrol-2-yl)ethanol (*S*-22b). Clear yellow oil (1.5 mg). **TLC**: R_f 0.31 (1:20 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.45–7.34 (m, 5H), 5.81 (dd, 1H, *J* = 7.1, 6.8), 5.30 (d, 1H, *J* = 14.3), 5.21 (d, 1H, *J* = 10.6), 4.60 (dd, 1H, *J* = 8.8, 7.1), 4.04 (dd, 1H, *J* = 15.2, 7.1), 3.85–3.78 (m, 2H), 3.47 (dd, 1H, *J* = 14.3, 7.1), 2.20–2.13 (m, 1H), 2.04–2.00 (m, 1H), 1.52 (s, 1H). **ESI-MS** *m/z* (rel int): (pos) 216.3 ([M+H]$^+$, 100).



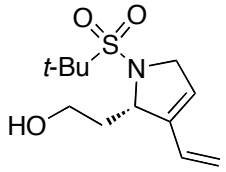
(*S*)-2-(3-Vinyl-2,5-dihydro-1*H*-pyrrol-2-yl)ethanol (*S*-22d). Clear oil (0.9 mg). **TLC**: R_f 0.28 (1:20 MeOH/EtOAc). ^{1}**H-NMR** (600 MHz): δ 6.37 (ddd, 1H, *J* = 17.8, 11.0, 8.0), 5.69 (s, 1H), 5.21 (d, 1H, *J* = 17.8), 5.17 (d, 1H, *J* = 11.0), 4.88 (s, 1H), 4.48 (d, 1H, *J* = 15.9), 3.78–3.74 (m, 1H), 3.73–3.68 (m, 1H), 3.45 (d, 1H, *J* = 15.9), 2.12–2.05 (m, 1H), 1.78–1.71 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 162.3 ([M+Na]$^+$, 100).



(*S*)-3-(1-(*tert*-Butylsulfonyl)-2-(2-hydroxyethyl)-2,5-dihydro-1*H*-pyrrol-3-yl)but-3-en-1-ol (*S*-23a). Colorless oil (7.7 mg). **TLC**: R_f 0.46 (1:2 hexanes/EtOAc). ^{1}**H-NMR** (600 MHz): δ 5.65 (t, 1H, *J* =7.1), 5.08 (d, 2H, *J* =11.0), 4.93 (t, 1H, *J* = 4.4), 4.49 (d, 1H, *J* = 8.1), 4.16 (d, 1H, *J* = 7.8), 3.73–3.69 (m, 1H), 3.68–3.61 (m, 2H), 2.99–2.96 (m, 1H), 2.49–2.47 (m, 1H), 2.05–2.01 (m, 1H), 1.68–1.64 (m, 1H), 1.53–1.47 (m, 1H), 1.03 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 326.4 ([M+Na]$^+$, 100).

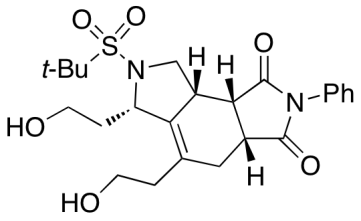


(*S*)-2-(1-(*tert*-Butylsulfonyl)-3-(1-phenylvinyl)-2,5-dihydro-1*H*-pyrrol-2-yl)ethanol (*S*-23b). Clear yellow oil (7.6 mg). **TLC**: R_f 0.31 (1:1 hexanes/EtOAc). ^{1}**H-NMR** (600 MHz): δ 7.45–7.34 (m, 3H), 7.32–7.28 (m, 2H), 5.49 (s, 1H), 5.19 (s, 1H), 5.12 (s, 1H), 4.98 (s, 1H), 4.40 (d, 1H, *J* = 13.2), 4.07–4.01 (m, 1H), 3.75–3.70 (m, 2H), 3.49 (s, 1H), 2.15–2.08 (m, 2H), 1.25 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 358.5 ([M+Na]$^+$, 100).

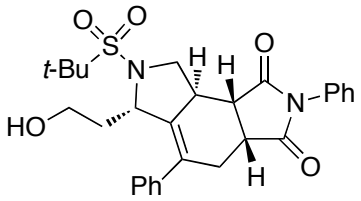


(*S*)-2-(1-(*tert*-Butylsulfonyl)-3-vinyl-2,5-dihydro-1*H*-pyrrol-2-yl)ethanol (*S*-23d). Yellow oil (7.0 mg). **TLC**: R_f 0.28 (1:1 hexanes/EtOAc). ^{1}**H-NMR** (600 MHz): δ 6.41 (dd, 1H, *J* = 17.8, 11.0), 5.73 (s, 1H), 5.16 (dd, 2H, *J* = 17.8, 11.3), 5.01 (s, 1H), 4.47 (d, 1H, *J* = 15.9), 4.01 (d, 1H, *J* = 12.8), 3.80–3.76 (m, 1H), 3.65–3.61 (m, 1H), 2.05–1.97 (m, 1H), 1.53–1.48 (m, 1H), 1.41 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 282.4 ([M+Na]$^+$, 100).

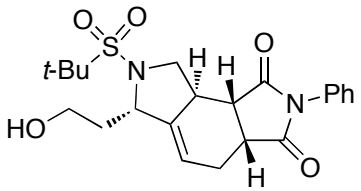
5. MALEIMIDE DIELS–ALDER PRODUCTS (*S*-24)



(3a*R*,6*S*,8a*R*,8b*S*)-7-(*tert*-Butylsulfonyl)-5,6-bis(2-hydroxyethyl)-2-phenyl-3a,4,6,7,8,8a-hexahydropyrrolo[3,4-*e*]isoindole-1,3(2*H*,8b*H*)-dione (*S*-24a). Clear oil (8.1 mg). **TLC**: R_f 0.50 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.49–7.36 (m, 5H), 5.92 (t, 1H, *J* = 6.8), 4.51 (d, 1H, *J* = 12.0), 4.49–4.32 (m, 2H), 4.09 (dd, 1H, *J* = 7.9, 13.0), 3.98 (t, 1H, *J* = 10.0), 3.82–3.78 (m, 2H), 3.63–3.59 (m, 1H), 3.40–3.32 (m, 1H), 2.99 (dd, 1H, *J* = 7.4, 12.5), 2.71–2.63 (m, 1H), 1.75–1.70 (m, 2H), 1.66–1.59 (m, 2H), 1.45 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 499.6 ([M+Na]$^+$, 100).

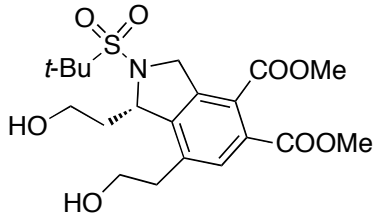


(3a*R*,6*S*,8a*S*,8b*S*)-7-(*tert*-Butylsulfonyl)-6-(2-hydroxyethyl)-2,5-diphenyl-3a,4,6,7,8,8a-hexahydropyrrolo[3,4-*e*]isoindole-1,3(2*H*,8b*H*)-dione (*S*-24b). Light yellow oil (5.0 mg). **TLC**: R_f 0.40 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.49–7.43 (m, 3H), 7.41–7.38 (m, 4H), 7.36–7.34 (m, 3H), 5.83 (s, 1H), 4.91 (dd, 1H, *J* = 13.1, 2.1), 4.13 (d, 1H, *J* = 13.1), 3.74–3.70 (m, 1H), 3.48 (dd, 1H, *J* = 8.0, 9.1), 3.23–3.21 (m, 1H), 3.14–3.12 (m, 2H), 3.05–3.01 (m, 1H), 2.73–2.68 (m, 1H), 2.53–2.48 (m, 1H), 1.62–1.57 (m, 1H), 1.41 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 531.3 ([M+Na]$^+$, 100).

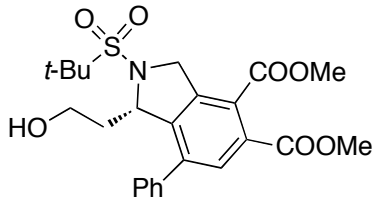


(3a*R*,6*S*,8a*S*,8b*S*)-7-(*tert*-Butylsulfonyl)-6-(2-hydroxyethyl)-2-phenyl-3a,4,6,7,8,8a-hexahydropyrrolo[3,4-*e*]isoindole-1,3(2*H*,8b*H*)-dione (*S*-24d). Clear oil (7.5 mg). **TLC**: R_f 0.32 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.99 (s, 1H), 7.63–7.67 (m, 2H), 7.50–7.37 (m, 3H), 5.98–5.95 (m, 1H), 5.01 (d, 1H, *J* = 11.8), 4.52 (d, 1H, *J* = 12.5), 4.48–4.35 (m, 2H), 3.55–3.49 (m, 2H), 3.29–3.24 (m, 2H), 1.88–1.65 (bm, 2H), 1.64–1.59 (m, 1H), 1.45 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 433.4 ([M+H]$^+$, 100).

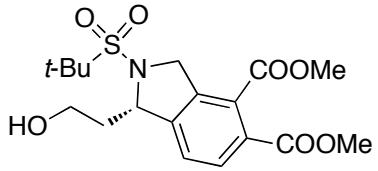
6. DMAD DIELS–ALDER PRODUCTS (*S*-25)



(*S*)-Dimethyl 2-(*tert*-butylsulfonyl)-1,7-bis(2-hydroxyethyl)isoindoline-4,5-dicarboxylate (*S*-25a). Colorless oil (4.2 mg). **TLC**: R_f 0.43 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.63 (s, 1H), 5.62 (s, 1H), 5.03 (d, 1H, *J* = 16.0), 4.51 (d, 1H, *J* = 16.0), 3.88 (s, 6H), 3.85–3.81 (m, 2H), 3.65–3.61 (m, 2H), 2.86–2.79 (m, 2H), 2.11–1.99 (m, 2H), 1.31 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 466.3 $[M+Na]^+$, 100).

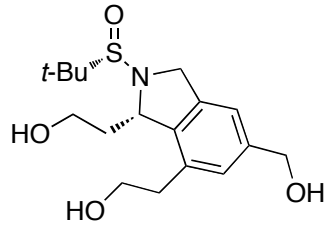


(*S*)-Dimethyl 2-(*tert*-butylsulfonyl)-1-(2-hydroxyethyl)-7-phenylisoindoline-4,5-dicarboxylate (*S*-25b). Colorless oil (4.8 mg). **TLC**: R_f 0.38 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.61 (s, 1H), 7.45–7.37 (m, 5H), 5.89 (s, 1H), 5.12 (d, 1H, *J* = 16.4), 4.53 (d, 1H, *J* = 15.8), 3.91 (s, 6H), 3.47–3.43 (m, 1H), 3.39–3.35 (m, 1H), 1.80–1.74 (m, 1H), 1.57–1.51 (m, 1H), 1.38 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 476.5 $[M+H]^+$, 100).



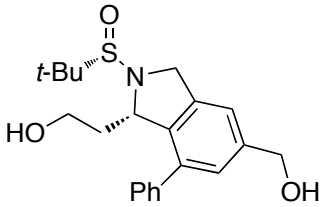
(*S*)-Dimethyl 2-(*tert*-butylsulfonyl)-1-(2-hydroxyethyl)isoindoline-4,5-dicarboxylate (*S*-25d). Colorless oil (8.6 mg). **TLC**: R_f 0.34 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.74 (d, 1H, *J* = 4), 7.42 (d, 1H, *J* = 3.9), 5.49 (s, 1H), 5.08 (d, 1H, *J* =15.1), 4.64 (d, 1H, *J* = 15.2), 3.91 (s, 6H), 3.69–3.62 (m, 1H), 2.40 (s, 1H), 2.05–1.98 (m, 1H), 1.84–1.79 (m, 1H), 1.35 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 422.5 ($[M+Na]^+$, 100).

7. ALKYNE [2+2+2] CYCLOTRIMERIZATION PRODUCTS (*S*-30–35)

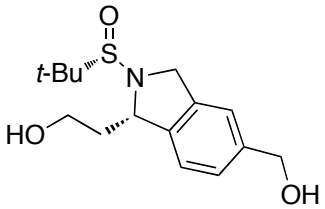


2,2'-((*S*)-2-((*S*)-*tert*-Butylsulfinyl)-5-(hydroxymethyl)isoindoline-1,7-diyl)diethanol (*S*-30a). Light brown oil (8.9 mg). **TLC**: R_f 0.31 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.09 (s,

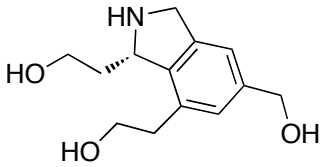
1H), 7.05 (s, 1H), 5.30 (d, 1H, *J* = 7.9), 4.93 (d, 1H, *J* = 14.3), 4.57 (s, 2H), 3.94 (d, 1H, *J* 14.3), 3.84 (t, 2H, *J* = 7.0), 3.80–3.72 (m, 1H), 3.63–3.59 (m, 1H), 2.85 (dt, 2H, *J* = 12.5, 6.0), 2.15–2.07 (m, 1H), 1.92–1.84 (m, 1H), 1.15 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 364.5 ($[M+Na]^+$, 100).



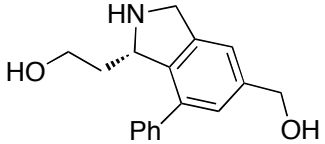
2-((*S*)-2-((*S*)-*tert*-Butylsulfinyl)-5-(hydroxymethyl)-7-phenylisoindolin-1-yl)ethanol (*S*-30b). Brown oil (8.3 mg). **TLC**: R_f 0.22 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.40–7.34 (m, 5H), 7.18 (s, 1H), 7.16 (s, 1H), 5.58 (d, 1H, *J* = 8.0), 5.08 (d, 1H, *J* = 14.3), 4.69 (d, 2H, *J* = 5.7), 3.99 (dd, 1H, *J* = 14.0, 4.0), 3.61 (ddd, 1H, *J* = 10.0, 8.5, 6.2), 3.38–3.34 (m, 1H), 1.68–1.63 (m, 1H), 1.44–1.38 (m, 1H), 0.91 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 374.4 ($[M+H]^+$, 100).



2-((*S*)-2-((*S*)-*tert*-Butylsulfinyl)-5-(hydroxymethyl)isoindolin-1-yl)ethanol (*S*-30d). Light brown oil (7.8 mg). **TLC**: R_f 0.15 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.18 (s, 1H), 7.05 (d, 1H, *J* = 7.0), 6.99 (d, 1H, *J* = 7.0), 5.03 (t, 1H, *J* = 6.0), 4.53 (s, 2H), 3.96 (d, 1H, *J* = 14.9), 3.72 (ddd, 1H, *J* = 10.6, 7.5, 5.5), 3.63 (dt, 1H, *J* = 10.4, 6.6), 2.77 (s, 1H), 1.99–1.93 (m, 2H), 1.26 (t, 1H, *J* = 7.1), 1.21 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 320.4 ($[M+Na]^+$, 100).

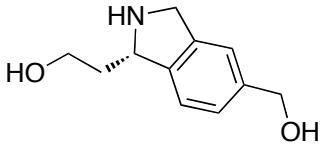


(*S*)-2,2'-(5-(Hydroxymethyl)isoindoline-1,7-diyl)diethanol (*S*-31a). Light brown oil (1.1 mg). **TLC**: R_f 0.31 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.04 (s, 1H), 7.02 (s, 1H), 5.52 (d, 1H, *J* = 14.5), 4.61 (d, 2H, *J* = 7.1), 3.96 (d, 1H, *J* = 14.6), 3.86 (t, 1H, *J* = 7.0), 3.85–3.79 (m, 1H), 3.69–3.64 (m, 1H), 2.85 (dt, 2H, *J* = 12.6, 6.5), 2.15–2.07 (m, 1H), 1.88–1.84 (m, 1H), 1.78–1.76 (m, 2H). **ESI-MS** *m/z* (rel int): (pos) 238.2 ($[M+H]^+$, 100).

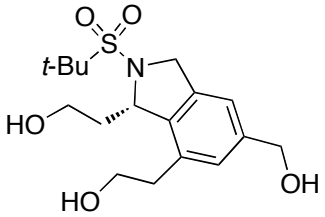


(*S*)-2-(5-(Hydroxymethyl)-7-phenylisoindolin-1-yl)ethanol (*S*-31b). Light brown oil (7.9 mg). **TLC**: R_f 0.22 (1:2 hexanes/EtOAc). **^{1}H-NMR** (500 MHz): δ 7.42 (s, 1H), 7.34–7.26 (m, 6H),

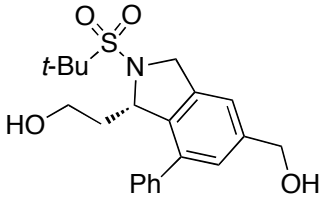
5.71 (t, 1H, *J* = 7.1), 5.01 (d, 2H, *J* = 14.1), 4.39 (d, 2H, *J* = 14.0), 4.38–4.34 (m, 2H), 2.20–2.13 (m, 2H). **ESI-MS** *m/z* (rel int): (pos) 292.2 ([M+Na]$^+$, 100).



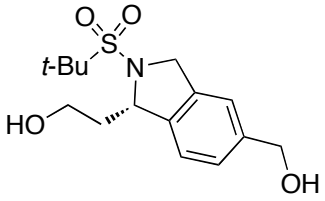
(*S*)-2-(5-(Hydroxymethyl)isoindolin-1-yl)ethanol (*S*-31d). Light brown oil (2.1 mg). **TLC**: R_f 0.15 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.18–7.14 (m, 2H), 7.09 (d, 1H, *J* = 7.2), 5.18 (d, 1H, *J* = 6.0), 4.95 (d, 1H, *J*= 14.0), 4.55–4.51 (m, 3H), 3.96 (d, 1H, *J* = 15.6), 3.81 (ddd, 1H, *J* = 10.7, 7.6, 5.6), 3.72 (ddd, 1H, *J* = 10.7, 7.6, 5.6), 2.07–1.95 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 270.3 ([M+H]$^+$, 100).



(*S*)-2,2'-(2-(*tert*-Butylsulfonyl)-5-(hydroxymethyl)isoindoline-1,7-diyl)diethanol (*S*-32a). Brown oil (8.8 mg). **TLC**: R_f 0.31 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.99 (s, 1H), 6.93 (s, 1H), 5.17 (d, 1H, *J* = 7.8), 4.83 (d, 1H, *J* = 12.5), 4.51 (S, 2H), 3.91 (d, 1H, *J* = 14.6), 3.79 (t, 2H, *J* = 7.3), 3.78–3.73 (m, 1H), 3.65–3.62 (m, 1H), 2.83 (dt, 2H, *J* = 12.6, 6.5), 2.07–1.99 (m, 1H), 1.78–1.71 (m, 1H), 1.08 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 380.5 ([M+Na]$^+$, 100).

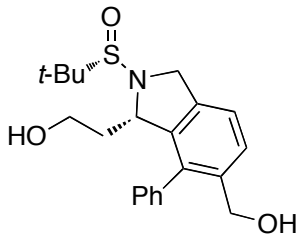


(*S*)-2-(2-(*tert*-Butylsulfonyl)-5-(hydroxymethyl)-7-phenylisoindolin-1-yl)ethanol (*S*-32b). Brown oil (5.0 mg). **TLC**: R_f 0.22 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.38–7.32 (m, 5H), 7.18 (s, 1H), 7.14 (s, 1H), 5.58 (d, 1H, *J* = 8.0), 5.08 (d, 1H, *J* = 14.3), 4.71 (d, 2H, *J* = 6.2), 3.99 (d, 1H, *J* = 14.0), 3.63 (ddd, 1H, *J* = 10.0, 8.5, 6.2), 3.38–3.34 (m, 1H), 1.68 (t, 1H, *J* = 6.0), 1.44–1.38 (m, 1H), 1.19 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 390.3 ([M+H]$^+$, 100).

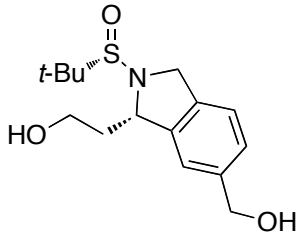


(*S*)-2-(2-(*tert*-Butylsulfonyl)-5-(hydroxymethyl)isoindolin-1-yl)ethanol (*S*-32d). Light brown oil (7.1 mg). **TLC**: R_f 0.15 (1:1 hexanes/EtOAc). **^{1}H-NMR** (500 MHz): δ 7.01 (d, 1H, *J* = 7.0), 6.94 (d, 1H, *J* = 7.0), 6.89 (s, 1H), 5.01 (t, 1H, *J* = 6.0), 4.78 (d, 1H, *J*= 12.0), 4.46 (s, 2H), 3.79

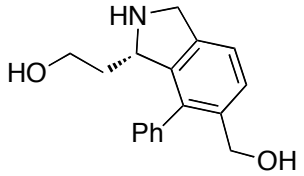
(d, 1H, *J* = 12.5), 3.64 (ddd, 1H, *J* = 10.1, 7.3, 5.6), 3.56 (dt, 1H, *J* = 10. 0, 6.9), 1.91–1.86 (m, 2H), 1.08 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 336.4 ([M+Na]$^+$, 100).



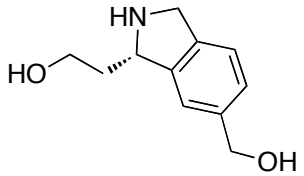
2-((*S*)-2-((*S*)-*tert*-Butylsulfinyl)-6-(hydroxymethyl)-7-phenylisoindolin-1-yl)ethanol (*S*-33b). Light brown oil (4.9 mg). **TLC**: R_f 0.22 (4:6 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.49–7.41 (m, 5H), 7.19 (t, 2H, *J* = 4.0), 5.58 (d, 1H, *J* = 8.0), 5.12 (d, 1H, *J* = 14.3), 4.71 (d, 2H, *J* = 8.8), 4.55 (dd, 1H, *J* = 8.5, 6.2), 4.04 (d, 1H, *J* = 14.0), 3.38–3.34 (m, 1H), 3.28 (dd, 1H, *J* = 8.5, 6.2), 1.99 (s, 1H), 1.80 (s, 1H), 1.68–1.63 (m, 1H), 1.44–1.38 (m, 1H), 1.20 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 396.5 ([M+Na]$^+$, 100).



2-((*S*)-2-((*S*)-*tert*-Butylsulfinyl)-6-(hydroxymethyl)isoindolin-1-yl)ethanol (*S*-33d). Clear oil (7.2 mg). **TLC**: R_f 0.15 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.20 (d, 1H, *J* = 7.0), 7.16 (d, 1H, *J* = 7.0), 7.09 (s, 1H), 5.16 (t, 1H, *J* = 6.0), 5.01 (d, 1H, *J*= 14.0), 4.62 (s, 2H), 3.98 (d, 1H, *J* = 14.9), 3.81 (ddd, 1H, *J* = 10.6, 7.9, 5.7), 3.71 (dt, 1H, *J* = 10.2, 6.6), 2.71 (s, 1H), 2.07–2.01 (m, 2H), 1.56 (s, 1H), 1.19 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 320.4 ([M+Na]$^+$, 100).

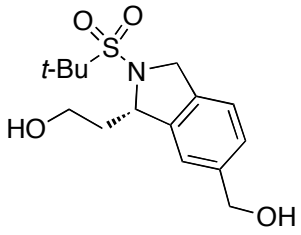


(*S*)-2-(6-(Hydroxymethyl)-7-phenylisoindolin-1-yl)ethanol (*S*-34b). Clear oil (3.5 mg). **TLC**: R_f 0.22 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.42–7.37 (m, 6H), 7.18 (d, 1H, *J* = 7.1), 5.21 (dd, 1H, *J* = 8.0, 6.4), 4.88 (d, 1H, *J* = 14.3), 4.62 (d, 2H, *J* = 3.9), 3.92 (d, 1H, *J* = 14.0), 3.79 (ddd, 1H, *J* = 10.0, 8.5, 6.2), 3.68–3.64 (m, 1H), 2.11–2.08 (m, 1H), 1.83–1.81 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 269.6 ([M+Na]$^+$, 100).



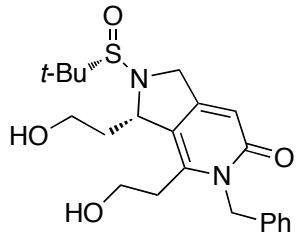
(*S*)-2-(6-(Hydroxymethyl)isoindolin-1-yl)ethanol (*S*-34d). Light brown oil (1.0 mg). **TLC**: R_f 0.15 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.21 (d, 1H, *J* = 7.2), 7.09 (d, 1H, *J* =

7.2), 7.11 (s, 1H), 5.18 (t, 1H, *J* = 6.0), 4.98 (d, 1H, *J*= 14.0), 4.55–4.51 (m, 3H), 3.96 (d, 1H, *J* = 15.6), 3.81 (ddd, 1H, *J* = 10.7, 7.6, 5.6), 3.72 (ddd, 1H, *J* = 10.7, 7.6, 5.6), 2.07–1.95 (m, 2H), 1.26 (tt, 1H, *J* = 7.1, 6.2). **ESI-MS** *m/z* (rel int): (pos) 270.3 ([M+H]$^+$, 100).

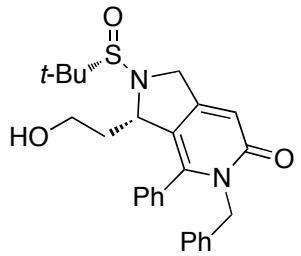


(*S*)-2-(2-(*tert*-Butylsulfonyl)-6-(hydroxymethyl)isoindolin-1-yl)ethanol (*S*-35d). Light brown oil (7.3 mg). **TLC**: R_f 0.15 (1:1 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.08 (s, 2H), 6.99 (d, 1H, *J* = 7.2), 5.08 (t, 1H, *J* = 6.2), 4.93 (d, 1H, *J*= 14.0), 4.52 (d, 2H), 3.90 (dd, 1H, *J* = 14.9, 6.7), 3.80 (ddd, 1H, *J* = 10.7, 7.6, 5.6), 3.73 (dt, 1H, *J* = 10.4, 6.6), 1.96–1.83 (m, 2H), 1.26 (t, 1H, *J* = 7.1), 1.08 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 336.4 ([M+Na]$^+$, 100).

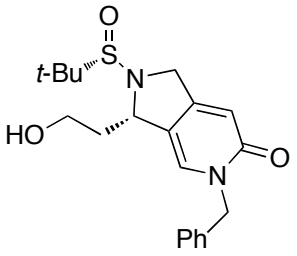
8. ISOCYANATE [2+2+2] CYCLOTRIMERIZATION PRODUCTS (*S*-36–41)



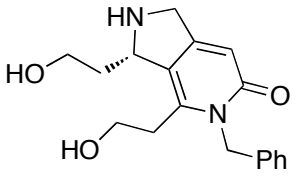
(*S*)-5-Benzyl-2-((*S*)-*tert*-butylsulfinyl)-3,4-bis(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo-[3,4-*c*]pyridin-6(5*H*)-one (*S*-36a). Clear brown oil (7.5 mg). **TLC**: R_f 0.44 (1:5 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.48–7.45 (m, 1H), 7.39–7.35 (m, 2H), 7.30–7.22 (m, 2H), 6.39 (s, 1H), 5.66 (bs, 1H), 5.35 (bs, 1H), 5.03 (dd, 1H, *J* = 8.0, 2.8), 4.82 (d, 1H, *J* = 16.0), 3.81–3.78 (m, 3H), 3.69–3.64 (m, 1H), 2.81–2.73 (m, 2H), 1.91–1.88 (m, 1H), 1.88–1.84 (m, 2H), 1.38–1.34 (m, 2H), 1.10 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 441.6 ([M+Na]$^+$, 100).



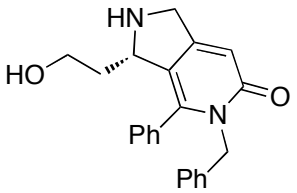
(*S*)-5-Benzyl-2-((*S*)-*tert*-butylsulfinyl)-3-(2-hydroxyethyl)-4-phenyl-2,3-dihydro-1*H*-pyrrolo-[3,4-*c*]pyridin-6(5*H*)-one (*S*-36b). Light brown oil (4.3 mg). **TLC**: R_f 0.19 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.49–7.47 (m, 2H), 7.41–7.38 (m, 4H), 7.36–7.32 (m, 4H), 6.55 (s, 1H), 5.71 (s, 1H), 4.91 (dd, 2H, *J* = 16.3, 8.2), 4.82 (d, 1H, *J* = 7.6), 3.83 (d, 1H, *J* = 16.0), 3.58–3.54 (m, 1H), 3.47–3.41 (m, 1H), 1.52–1.49 (m, 1H), 1.35–1.25 (m, 2H), 0.91 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 473.3 ([M+Na]$^+$, 100).



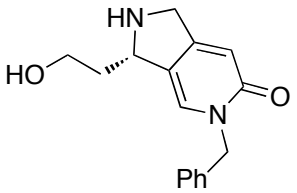
(*S*)-5-Benzyl-2-((*S*)-*tert*-butylsulfinyl)-3-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]-pyridin-6(5*H*)-one (*S*-36d). Light brown oil (8.1 mg). **TLC**: R_f 0.18 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.45–7.40 (m, 2H), 7.39–7.35 (m, 3H), 7.19 (s, 1H), 6.41 (s, 1H), 5.16 (d, 1H, *J* = 7.6), 4.78 (d, 2H, *J* = 14.3), 3.82 (dd, 2H, *J* = 16.0, 1.4), 3.79–3.73 (m, 2H), 1.89–1.86 (m, 1H), 1.82–1.78 (m, 1H), 1.11 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 397.5 ([M+Na]$^+$, 100).



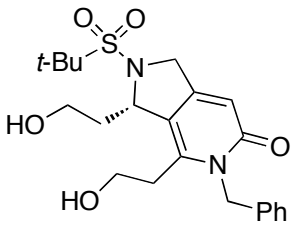
(*S*)-5-Benzyl-3,4-bis(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridin-6(5*H*)-one (*S*-37a). Light brown oil (4.9 mg). **TLC**: R_f 0.44 (1:3 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.32–7.25 (m, 5H), 6.37 (s, 1H), 5.50 (bs, 1H), 5.40–5.32 (bm, 2H), 4.61 (d, 1H, *J* = 8.0), 4.40–4.37 (m, 2H), 4.28 (d, 1H, *J* = 12.0), 3.76–3.72 (m, 2H), 3.63–3.56 (m, 2H), 2.81–2.73 (m, 2H), 2.06–2.00 (m, 1H), 1.87–1.80 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 315.3 ([M+H)$^+$, 100).



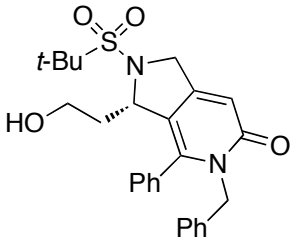
(*S*)-5-Benzyl-3-(2-hydroxyethyl)-4-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridin-6(5*H*)-one (*S*-37b). Clear oil (7.9 mg). **TLC**: R_f 0.19 (1:5 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.66–7.62 (m, 5H), 7.45–7.39 (m, 2H), 7.37–7.33 (m, 3H), 6.48 (s, 1H), 5.41–5.23 (m, 2H), 5.18 (t, 1H, *J* = 6.7), 4.78 (d, 2H, *J* = 15.3), 3.85–3.81 (m, 1H), 3.79–3.73 (m, 1H), 1.94–1.88 (m, 1H), 1.81–1.75 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 369.4 ([M+Na]$^+$, 100).



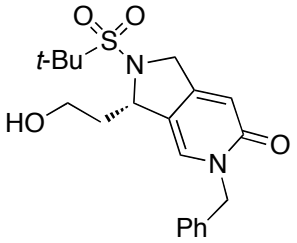
(*S*)-5-Benzyl-3-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridin-6(5*H*)-one (*S*-37d). Light brown oil (3.5 mg). **TLC**: R_f 0.18 (1:5 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.39–7.35 (m, 5H), 7.18 (s, 1H), 6.48 (s, 1H), 5.25 (s, 1H), 5.16 (dd, 1H, *J* = 12.5, 6.3), 4.53 (d, 1H, *J* = 14.6), 4.48 (d, 2H, *J* = 1.4), 4.40 (d, 1H, *J* = 8.8), 3.72–3.67 (m, 2H), 2.00–1.94 (m, 1H), 1.73–1.66 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 293.1 ([M+Na]$^+$, 100).



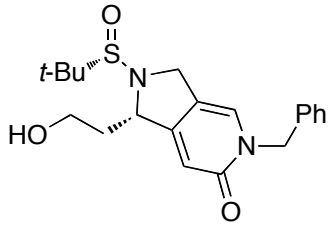
(*S*)-5-Benzyl-2-(*tert*-butylsulfonyl)-3,4-bis(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]-pyridin-6(5*H*)-one (*S*-38a). Brown oil (7.8 mg). **TLC**: R_f 0.44 (1:6 MeOH/EtOAc). **^{1}H-NMR** (500 MHz): δ 7.39–7.22 (m, 5H), 6.39 (s, 1H), 5.61 (bs, 1H), 5.42 (bs, 1H), 5.03 (dd, 1H, *J* = 2.4, 6.5), 4.84 (d, 1H, *J* = 4.5), 4.80 (d, 2H, *J* = 16.3), 3.85–3.76 (m, 3H), 3.68 (ddd, 2H, *J* = 10.3, 6.0, 4.1), 2.79–2.65 (m, 2H), 1.93–1.88 (m, 1H), 1.87–1.80 (m, 1H), 1.16 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 457.6 ([M+Na]$^+$, 100).



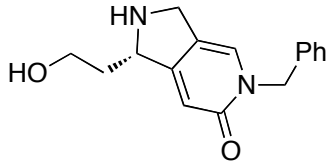
(*S*)-5-Benzyl-2-(*tert*-butylsulfonyl)-3-(2-hydroxyethyl)-4-phenyl-2,3-dihydro-1*H*-pyrrolo-[3,4-*c*]pyridin-6(5*H*)-one (*S*-38b). Light brown oil (3.9 mg). **TLC**: R_f 0.19 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.45–7.41 (m, 10H), 6.55 (d, 1H, *J* = 5.5), 5.26–5.20 (m, 1H), 4.93 (dd, 1H, *J* = 7.6, 3.1), 4.53 (t, 1H, *J* = 8.2), 4.40 (s, 2H), 3.61–3.58 (m, 2H), 1.74–1.70 (m, 2H), 1.52 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 489.3 ([M+Na]$^+$, 100).



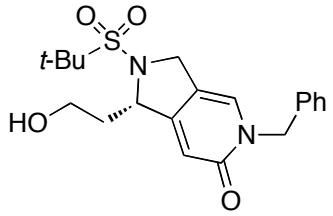
(*S*)-5-Benzyl-2-(*tert*-butylsulfonyl)-3-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]-pyridin-6(5*H*)-one (*S*-38d). Light brown oil (3.1 mg). **TLC**: R_f 0.18 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.41–7.35 (m, 5H), 7.19 (s, 1H), 6.42 (s, 1H), 5.12 (d, 1H, *J* = 14.6), 4.99 (t, 1H, *J* = 6.3), 4.93 (t, 1H, *J* = 10.7), 4.71 (dd, 1H, *J* = 16.0, 1.4), 3.81–3.78 (m, 2H), 3.69–3.64 (m, 1H), 1.99–1.84 (m, 1H), 1.69–1.66 (m, 1H), 1.17 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 413.4 ([M+Na]$^+$, 100).



(*S*)-5-Benzyl-2-((*S*)-*tert*-butylsulfinyl)-1-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]-pyridin-6(5*H*)-one (*S*-39d). Brown oil (8.5 mg). **TLC**: R_f 0.18 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.45–7.41 (m, 2H), 7.38–7.32 (m, 3H), 6.94 (s, 1H), 6.51 (s, 1H), 4.91–4.88 (m, 3H), 4.81 (t, 1H, *J* = 6.3), 4.82 (dd, 1H, *J* = 15.2, 1.4), 3.58–3.54 (m, 1H), 3.44–3.40 (m, 1H), 1.32–1.25 (m, 2H), 0.93 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 397.5 ([M+H]$^+$, 100).

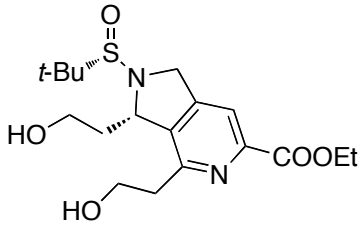


(*S*)-5-Benzyl-1-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridin-6(5*H*)-one (*S*-40d). Light brown oil (4.1 mg). **TLC**: R_f 0.17 (1:5 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.39–7.35 (m, 5H), 7.18 (s, 1H), 6.59 (s, 1H), 5.21 (s, 1H), 5.03 (dd, 1H, *J* = 12.5, 6.3), 4.71 (d, 1H, *J* = 14.6), 4.48–4.40 (m, 3H), 3.41–3.38 (m, 1H), 3.23–3.18 (m, 1H), 2.90 (s, 1H), 1.49–1.43 (m, 1H), 1.25–1.21 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 293.1 ([M+Na]$^+$, 100).



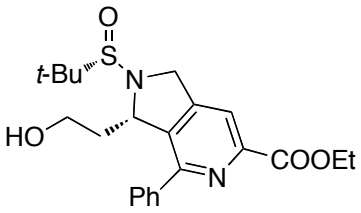
(*S*)-5-Benzyl-2-(*tert*-butylsulfonyl)-1-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]-pyridin-6(5*H*)-one (*S*-41d). Light brown oil (2.9 mg). **TLC**: R_f 0.16 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.38–7.32 (m, 5H), 7.07 (d, 1H, *J* = 14.0), 6.42 (s, 1H), 5.12–5.08 (m, 3H), 4.99 (t, 1H, *J* = 6.3), 4.93 (t, 1H, *J* = 8.8), 4.71 (dd, 1H, *J* = 16.0, 1.4), 3.78–3.72 (m, 2H), 3.69–3.64 (m, 1H), 1.99–1.84 (m, 1H), 1.69–1.66 (m, 1H), 1.17 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 413.4 ([M+Na]$^+$, 100).

9. NITRILE [2+2+2] CYCLOTRIMERIZATION PRODUCTS (*S*-42–44)

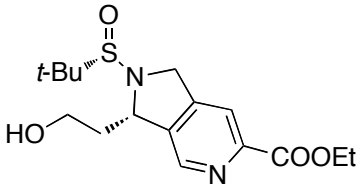


(*S*)-Ethyl 2-((*S*)-*tert*-butylsulfinyl)-3,4-bis(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]-pyridine-6-carboxylate (*S*-42a). Light brown oil (7.4 mg). **TLC**: R_f 0.37 (1:6 hexanes/EtOAc).

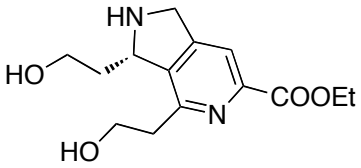
^{1}H-NMR (600 MHz): δ 7.79 (s, 1H), 5.38 (d, 1H, *J* = 8.2), 5.03 (d, 1H, *J* = 16.4), 4.40 (q, 2H, *J* = 10.6), 4.22 (dt, 1H, *J* = 9.8, 6.4), 4.12–4.08 (m, 1H), 3.97 (d, 1H, *J* = 15.2), 3.82–3.78 (m, 1H), 3.72 (ddd, 1H, *J* = 10.2, 6.2, 4.4), 3.12–3.08 (m, 2H), 2.24–2.20 (m, 1H), 1.80 (ddd, 1H, *J* = 18.9, 8.8, 4.4), 1.43 (t, 3H, *J* = 7.1), 1.12 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 407.5 ([M+Na]$^+$, 100).



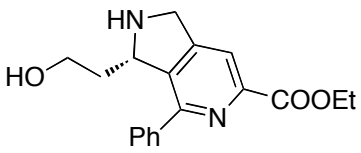
(*S*)-Ethyl 2-((*S*)-*tert*-butylsulfinyl)-3-(2-hydroxyethyl)-4-phenyl-2,3-dihydro-1*H*-pyrrolo-[3,4-*c*]pyridine-6-carboxylate (*S*-42b). Clear oil (4.1 mg). **TLC**: R_f 0.20 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.93 (s, 1H), 7.44–7.35 (m, 5H), 5.80 (d, 1H, *J* = 7.9), 5.18 (d, 1H, *J* = 15.7), 4.55–4.47 (m, 1H), 4.47–4.39 (m, 1H), 3.99 (d, 1H, *J* = 12.6), 3.66 (td, 1H, *J* = 9.5, 5.0), 3.48–3.40 (m, 1H), 1.72–1.65 (m, 1H), 1.61–1.54 (m, 1H), 1.43 (t, 3H, *J* = 7.1), 0.99 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 417.2 ([M+H]$^+$, 100).



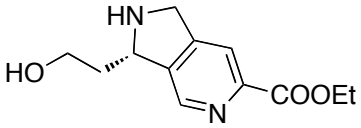
(*S*)-Ethyl 2-((*S*)-*tert*-butylsulfinyl)-3-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridine-6-carboxylate (*S*-42d). Clear oil (4.6 mg). **TLC**: R_f 0.12 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 8.62 (s, 1H), 8.00 (s, 1H), 5.33 (t, 1H, *J* = 6.0), 5.09 (d, 1H, *J* = 15.6), 4.48 (q, 2H, *J* = 7.5), 3.99 (d, 1H, *J* = 15.6), 3.83–3.76 (m, 2H), 2.11–2.01 (m, 1H), 1.96–1.87 (m, 1H), 1.44 (t, 3H, *J* = 7.1), 1.07 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 340.1 ([M+H]$^+$, 100).



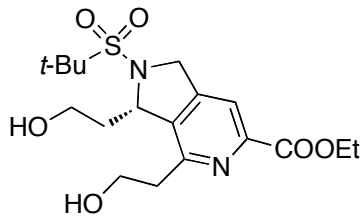
(*S*)-Ethyl 3,4-bis(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridine-6-carboxylate (*S*-43a). Clear oil (3.5 mg). **TLC**: R_f 0.37 (1:6 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.88 (s, 1H), 5.39 (s, 1H), 5.07 (d, 1H, *J* = 16.8), 4.40 (qq, 2H, *J* = 10.8, 7.1), 4.18 (dt, 1H, *J* = 9.8, 6.4), 4.08 (dt, 1H, *J* = 9.8, 6.1), 3.75–3.68 (m, 1H), 3.65–3.62 (m, 1H), 3.08 (dd, 1H, *J* = 13.8, 6.1), 2.91–2.88 (m, 2H), 2.06–1.98 (m, 2H), 1.41 (t, 3H, *J* = 7.1). **ESI-MS** *m/z* (rel int): (pos) 281.3 ([M+H]$^+$, 100).



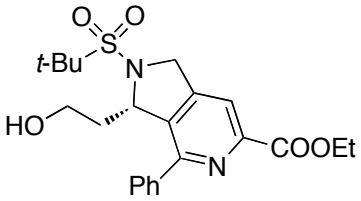
(*S*)-Ethyl 3-(2-hydroxyethyl)-4-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridine-6-carboxylate (*S*-43b). Clear oil (2.6 mg). **TLC**: R_f 0.20 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.93 (s, 1H), 7.44–7.35 (m, 5H), 5.41 (s, 1H), 5.12 (d, 1H, *J* = 15.7), 5.07 (d, 1H, *J* = 15.7), 4.48–4.44 (m, 2H), 3.99 (t, 1H, *J* = 10.6), 3.78–3.72 (m, 2H), 2.04–1.98 (m, 1H), 1.43 (t, 3H, *J* = 7.1). **ESI-MS** *m/z* (rel int): (pos) 313.2 ([M+H]$^+$, 100).



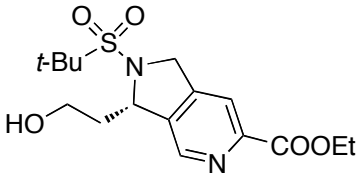
(*S*)-Ethyl 3-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridine-6-carboxylate (*S*-43d). Clear oil (7.1 mg). **TLC**: R_f 0.12 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 8.73 (s, 1H), 8.06 (s, 1H), 5.33 (bt, 1H, *J* = 6.0), 5.06 (d, 1H, *J* = 12.4), 4.66 (d, 1H, *J* = 12.8), 4.50 (q, 2H, *J* = 7.5), 3.97–3.93 (m, 1H), 3.79–3.74 (m, 1H), 2.08–2.01 (m, 2H), 1.49 (t, 3H, *J* = 7.2). **ESI-MS** *m/z* (rel int): (pos) 259.3 ([M+Na]+, 100).



(*S*)-Ethyl 2-(*tert*-butylsulfonyl)-3,4-bis(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridine-6-carboxylate (*S*-44a). Brown oil (8.0 mg). **TLC**: R_f 0.37 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.81 (s, 1H), 5.40 (d, 1H, *J* = 8.5), 5.01 (d, 1H, *J* = 15.3), 4.48 (q, 2H, *J* = 10.5, 7.1), 4.21 (dt, 1H, *J* = 9.8, 6.3), 4.05 (dt, 1H, *J* = 9.8, 6.5), 3.97 (d, 1H, *J* = 13.9), 3.82–3.78 (m, 1H), 3.73–3.68 (m, 2H), 3.12–3.06 (m, 2H), 2.31–2.24 (m, 1H), 1.48 (t, 3H, *J* = 7.3), 1.16 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 423.5 ([M+Na]$^+$, 100).

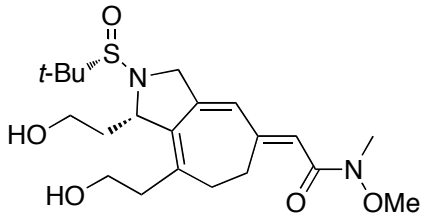


(*S*)-Ethyl 2-(*tert*-butylsulfonyl)-3-(2-hydroxyethyl)-4-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]-pyridine-6-carboxylate (*S*-44b). Clear oil (7.5 mg). **TLC**: R_f 0.20 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.91 (s, 1H), 7.43–7.39 (m, 5H), 5.80 (d, 1H, *J* = 7.7), 5.20 (d, 1H, *J* = 15.2), 4.51–4.48 (m, 1H), 4.42–4.38 (m, 1H), 4.00 (d, 1H, *J* = 12.6), 3.68 (td, 1H, *J* = 9.5, 5.3), 3.47–3.41 (m, 1H), 1.79–1.72 (m, 1H), 1.68–1.63 (m, 1H), 1.46 (t, 3H, *J* = 7.1), 1.25 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 455.5 ([M+Na]$^+$, 100).

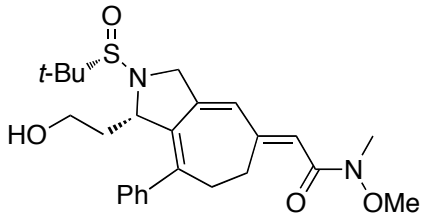


(*S*)-Ethyl 2-(*tert*-butylsulfonyl)-3-(2-hydroxyethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]pyridine-6-carboxylate (*S*-44d). Clear oil (3.1 mg). **TLC**: R_f 0.11 (1:2 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 8.66 (s, 1H), 8.02 (s, 1H), 5.58 (d, 1H, *J* = 6.0), 5.03 (d, 1H, *J* = 15.6), 4.59 (t, 1H, *J* = 12.5), 4.48 (q, 2H, *J* = 7.5), 3.87 (t, 1H, *J* = 6.4), 3.63–3.61 (m, 1H), 2.11–2.01 (m, 1H), 1.96–1.87 (m, 1H), 1.44 (t, 3H, *J* = 7.1), 1.41 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 357.3 ([M+H]$^+$, 100).

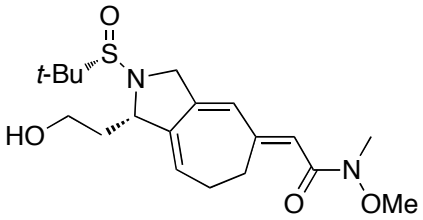
10. SAITO [3+2+2] CYCLOADDITION PRODUCTS (*S*-45–50)



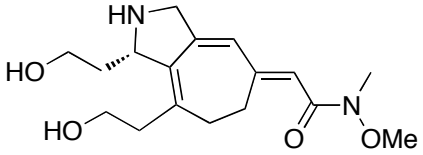
(*E*)-2-((*S*)-2-((*S*)-*tert*-Butylsulfinyl)-1,8-bis(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]-pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-45a). Yellow oil (1.7 mg). **TLC**: R_f 0.44 (1:4 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.28 (s, 1H), 5.96 (s, 1H), 4.68–4.64 (m, 1H), 4.59 (dt, 1H, *J* = 12.5, 5.5), 3.94 (d, 1H, *J* = 16.0), 3.69 (s, 3H), 3.61–3.56 (m, 2H), 3.47–3.41 (m, 2H), 3.21 (s, 3H), 2.60 (t, 1H, *J* = 8.8), 2.49–2.42 (m, 1H), 1.65–1.58 (m, 1H), 1.52–1.47 (m, 2H), 1.22–1.20 (m, 3H), 0.93 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 449.4 ([M+Na]$^+$, 100).



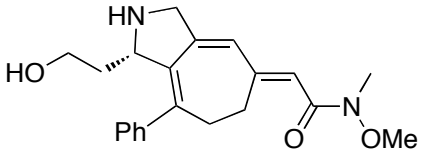
(*E*)-2-((*S*)-2-((*S*)-*tert*-Butylsulfinyl)-1-(2-hydroxyethyl)-8-phenyl-2,3,6,7-tetrahydrocyclo-hepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-45b). Light red oil (5.1 mg). **TLC**: R_f 0.25 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.63 (s, 1H), 7.34–7.27 (m, 5H), 5.73 (s, 1H), 4.66 (dd, 1H, *J* = 9.0, 4.2), 4.51 (dd, 1H, *J* = 10.2, 7.1), 3.69–3.65 (m, 4H), 3.58–3.54 (m, 1H), 3.45–3.41 (m, 1H), 3.23 (s, 3H), 2.64–2.60 (m, 2H), 1.63–1.58 (m, 1H), 1.53–1.49 (m, 2H), 0.91 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 459.2 ([M+H]$^+$, 100).



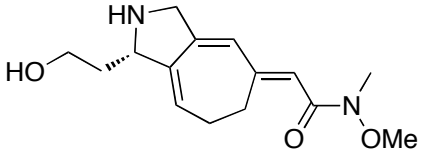
(*E*)-2-((*S*)-2-((*S*)-*tert*-Butylsulfinyl)-1-(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]-pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-45d). Light yellow oil (4.9 mg). **TLC**: R_f 0.41 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.21 (s, 1H), 6.02 (s, 1H), 5.83 (d, 1H, *J* = 16.0), 4.62 (dd, 1H, *J* = 8.0, 3.5), 4.48 (d, 1H, *J* = 16.9), 3.83 (dd, 1H, *J* = 15.2, 6.4), 3.75–3.73 (m, 2H), 3.69 (s, 3H), 3.49 (d, 1H, *J* = 16.0), 3.20 (s, 3H), 2.53 (dd, 1H, *J* = 16.0, 8.0), 2.10–2.02 (m, 2H), 1.83–1.81 (m, 1H), 1.79–1.69 (m, 1H), 102 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 383.2 ([M+H]$^+$, 100).



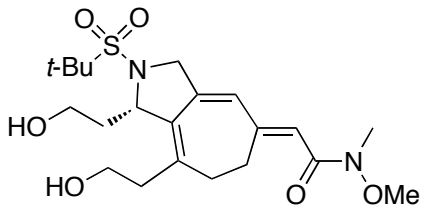
(*S*,*E*)-2-(1,8-Bis(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-46a). Light yellow oil (2.5 mg). **TLC**: R_f 0.44 (1:5 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.29 (s, 1H), 5.91 (s, 1H), 4.68 (dd, 1H, *J* = 9.1, 2.4), 4.19–4.13 (m, 1H), 3.94 (d, 1H, *J* = 16.5), 3.68–3.65 (m, 4H), 3.64–3.61 (m, 1H), 3.46 (t, 2H, *J* = 6.4), 3.21 (s, 3H), 2.61 (t, 2H, *J* = 8.8), 2.49–2.41 (m, 2H), 1.62–1.59 (m, 1H), 1.52–1.47 (m, 2H), 1.22–1.20 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 323.4 ([M+H]$^+$, 100).



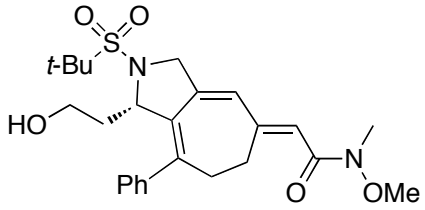
(*S*,*E*)-2-(1-(2-Hydroxyethyl)-8-phenyl-2,3,6,7-tetrahydrocyclohepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-46b). Light red oil (2.1 mg). **TLC**: R_f 0.25 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.68 (s, 1H), 7.38–7.25 (m, 5H), 6.08 (s, 1H), 4.82 (dd, 1H, *J* = 9.0, 4.2), 4.48 (dd, 1H, *J* = 10.2, 7.1), 3.71–3.68 (m, 4H), 3.63–3.58 (m, 1H), 3.49–3.45 (m, 1H), 3.23 (s, 3H), 2.64–2.60 (bm, 2H), 1.63–1.58 (m, 2H), 1.53–1.49 (m, 2H). **ESI-MS** *m/z* (rel int): (pos) 355.2 ([M+H]$^+$, 100).



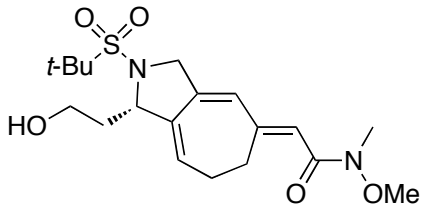
(*S*,*E*)-2-(1-(2-Hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-46d). Light yellow oil (1.9 mg). **TLC**: R_f 0.41 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.21 (s, 1H), 6.03 (s, 1H), 5.80 (d, 1H, *J* = 16.8), 4.59 (dd, 1H, *J* = 8.8, 3.5), 4.50 (d, 1H, *J* = 17.1), 3.85 (dd, 1H, *J* = 15.3, 6.4), 3.75–3.73 (m, 2H), 3.67 (s, 3H), 3.49 (d, 1H, *J* = 16.0), 3.20 (s, 3H), 2.51 (dd, 1H, *J* = 16.0, 8.0), 2.10–2.02 (m, 2H), 1.83–1.81 (m, 1H), 1.79–1.69 (m, 1H). **ESI-MS** *m/z* (rel int): (pos) 279.0 ([M+H]$^+$, 100).



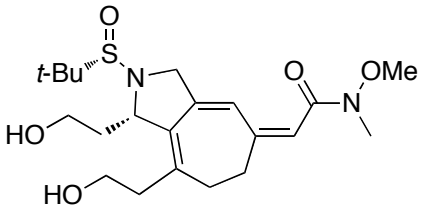
(*S*,*E*)-2-(2-(*tert*-Butylsulfonyl)-1,8-bis(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]-pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-47a). Clear oil (3.9 mg). **TLC**: R_f 0.44 (1:8 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.39 (s, 1H), 6.10 (s, 1H), 4.66–4.63 (m, 1H), 4.59 (dt, 1H, *J* = 12.0, 5.5), 3.94 (d, 1H, *J* = 16.0), 3.69 (s, 3H), 3.61–3.56 (m, 1H), 3.47–3.41 (m, 2H), 3.21 (s, 3H), 2.57 (t, 1H, *J* = 8.8), 2.49–2.42 (m, 2H), 1.65–1.58 (m, 2H), 1.52–1.47 (m, 2H), 1.22–1.20 (m, 2H), 1.2 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 465.2 ([M+Na]$^+$, 100).



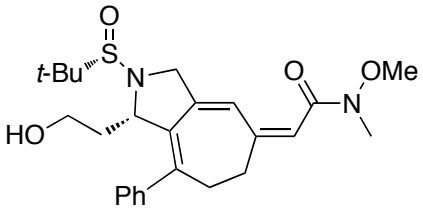
(*S*,*E*)-2-(2-(*tert*-Butylsulfonyl)-1-(2-hydroxyethyl)-8-phenyl-2,3,6,7-tetrahydrocyclohepta[*c*]-pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-47b). Brown oil (4.5 mg). **TLC**: R_f 0.25 (1:15 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.67 (s, 1H), 7.32–7.23 (m, 5H), 5.49 (s, 1H), 4.68 (dd, 1H, *J* = 9.0, 4.2), 4.53 (dd, 1H, *J* = 10.6, 7.1), 3.72–3.67 (m, 4H), 3.58–3.54 (m, 1H), 3.45–3.41 (m, 1H), 3.25 (s, 3H), 2.64–2.60 (m, 2H), 1.63–1.58 (m, 1H), 1.53–1.49 (m, 3H), 1.09 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 475.2 ([M+H]$^+$, 100).



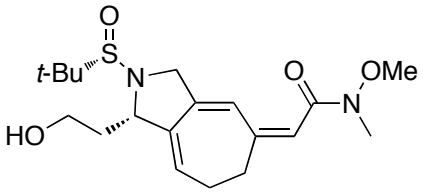
(*S*,*E*)-2-(2-(*tert*-Butylsulfonyl)-1-(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-47d). Light yellow oil (4.1 mg). **TLC**: R_f 0.41 (1:15 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.31 (s, 1H), 6.11 (s, 1H), 5.98 (t, 1H, *J* = 8.0), 4.68–4.62 (m, 2H), 4.00 (dd, 1H, *J* = 12.0, 3.5), 3.72–3.69 (m, 4H), 3.52–3.47 (m, 1H), 3.23 (s, 3H), 3.18–3.14 (m, 2H), 2.70–2.60 (m, 1H), 2.57–2.51 (m, 1H), 1.62–1.52 (m, 2H), 1.19 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 399.2 ([M+H]$^+$, 100).



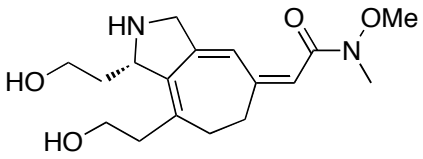
(*Z*)-2-((*S*)-2-((*S*)-*tert*-Butylsulfinyl)-1,8-bis(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]-pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-48a). Yellow oil (2.2 mg). **TLC**: R_f 0.44 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.16 (s, 1H), 6.01 (s, 1H), 4.64–4.62 (m, 1H), 4.53 (dt, 1H, *J* = 12.5, 5.9), 3.94 (d, 1H, *J* = 10.0), 3.65–3.61 (m, 3H), 3.59 (s, 3H), 3.52 (dd, 1H, *J* = 12.5, 6.2), 3.23 (s, 3H), 2.49–2.42 (m, 2H), 2.35–2.31 (m, 1H), 2.24–2.20 (m, 1H), 2.17–2.13 (m, 1H), 1.92–1.87 (m, 1H), 1.72–1.67 (m, 2H), 0.88 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 449.4 ([M+Na]$^+$, 100).



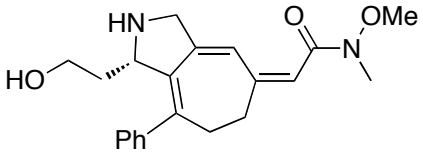
(*Z*)-2-((*S*)-2-((*S*)-*tert*-Butylsulfinyl)-1-(2-hydroxyethyl)-8-phenyl-2,3,6,7-tetrahydrocyclo-hepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-48b). Light red oil (4.2 mg). **TLC**: R_f 0.25 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.69 (s, 1H), 7.34–7.27 (m, 5H), 5.92 (s, 1H), 4.68 (dd, 1H, *J* = 8.8, 4.2), 4.53 (dd, 1H, *J* = 14.2, 7.1), 3.72–3.69 (m, 4H), 3.58–3.54 (m, 1H), 3.45–3.41 (m, 1H), 3.23 (s, 3H), 2.64–2.60 (m, 2H), 1.61–1.56 (m, 2H), 1.53–1.49 (m, 2H), 0.93 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 459.2 ([M+H]$^+$, 100).



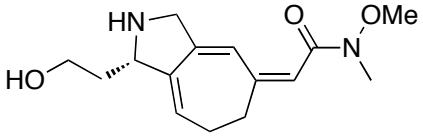
(*Z*)-2-((*S*)-2-((*S*)-*tert*-Butylsulfinyl)-1-(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]-pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-48d). Clear oil (4.5 mg). **TLC**: R_f 0.41 (1:3 hexanes/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.21 (s, 1H), 6.11 (s, 1H), 6.00 (s, 1H), 4.59 (dd, 1H, *J* = 8.0, 3.5), 4.48 (d, 1H, *J* = 15.0), 3.83 (dd, 1H, *J* = 15.2, 5.7), 3.75–3.73 (m, 2H), 3.69 (s, 3H), 3.49 (d, 1H, *J* = 14.3), 3.20 (s, 3H), 2.51 (dd, 1H, *J* = 15.2, 6.2), 2.10–2.02 (m, 2H), 1.83–1.81 (m, 1H), 1.79–1.69 (m, 1H), 1.01 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 383.2 ([M+H]$^+$, 100).



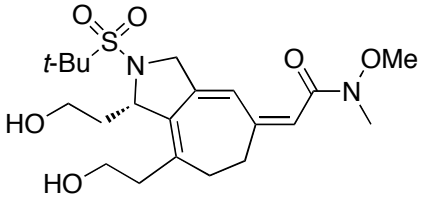
(*S*,*Z*)-2-(1,8-Bis(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-49a). Light yellow oil (2.1 mg). **TLC**: R_f 0.44 (1:5 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.29 (s, 1H), 6.11 (s, 1H), 4.88 (dd, 1H, *J* = 9.0, 2.4), 4.21–4.18 (m, 1H), 3.94 (d, 1H, *J* = 16.0), 3.69 (s, 3H), 3.67–3.63 (m, 2H), 3.48 (t, 2H, *J* = 6.4), 3.21 (s, 3H), 2.61 (t, 2H, *J* = 8.8), 2.49–2.42 (m, 2H), 1.62–1.59 (m, 1H), 1.56–1.52 (m, 3H). **ESI-MS** *m*/*z* (rel int): (pos) 323.4 ([M+H]$^+$, 100).



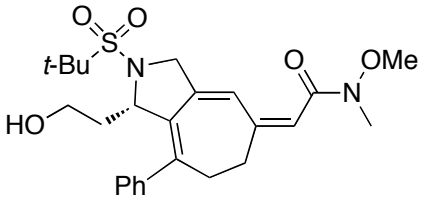
(*S*,*Z*)-2-(1-(2-Hydroxyethyl)-8-phenyl-2,3,6,7-tetrahydrocyclohepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-49b). Light orange oil (1.4 mg). **TLC**: R_f 0.25 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.65 (s, 1H), 7.36–7.23 (m, 5H), 5.92 (s, 1H), 4.68 (dd, 1H, *J* = 9.0, 4.8), 4.42 (dd, 1H, *J* = 12.2, 7.1), 3.69–3.65 (m, 4H), 3.61–3.54 (m, 1H), 3.41–3.38 (m, 1H), 3.21 (s, 3H), 2.64–2.60 (bm, 2H), 1.61–1.52 (m, 2H), 1.50–1.47 (m, 2H). **ESI-MS** *m*/*z* (rel int): (pos) 355.2 ([M+H]$^+$, 100).



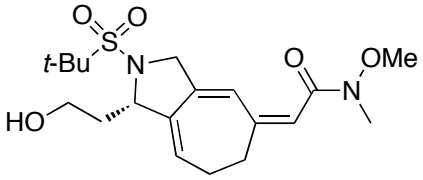
(*S*,*Z*)-2-(1-(2-Hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-49d). Light yellow oil (1.2 mg). **TLC**: R_f 0.41 (1:10 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.22 (s, 1H), 6.01 (s, 1H), 5.92 (s, 1H), 4.59 (dd, 1H, *J* = 8.8, 3.5), 4.49 (d, 1H, *J* = 17.1), 3.83 (dd, 1H, *J* = 12.4, 6.4), 3.73–3.70 (m, 2H), 3.67 (s, 3H), 3.49 (d, 1H, *J* = 16.0), 3.21 (s, 3H), 2.51 (dd, 1H, *J* = 16.0, 8.0), 2.13–2.04 (m, 2H), 1.81–1.78 (m, 1H), 1.74–1.65 (m, 1H). **ESI-MS** *m*/*z* (rel int): (pos) 279.0 ([M+H]$^+$, 100).



(*S*,*Z*)-2-(2-(*tert*-Butylsulfonyl)-1,8-bis(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]-pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-50a). Clear oil (3.3 mg). **TLC**: R_f 0.44 (1:8 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.26 (s, 1H), 6.03 (s, 1H), 4.62–4.57 (m, 1H), 4.50 (dd, 2H, *J* = 12.0, 5.5), 3.84 (d, 1H, *J* = 11.0), 3.73 (t, 1H, *J* = 12.0), 3.67 (s, 3H), 3.50 (dd, 2H, *J* = 12.0, 6.2), 3.23 (s, 3H), 2.53 (dd, 2H, *J* = 9.1, 8.8), 2.11–1.98 (m, 2H), 1.83–1.78 (m, 2H), 1.72–1.67 (m, 2H), 1.18 (s, 9H). **ESI-MS** *m*/*z* (rel int): (pos) 465.2 ([M+Na]$^+$, 100).



(*S*,*Z*)-2-(2-(*tert*-Butylsulfonyl)-1-(2-hydroxyethyl)-8-phenyl-2,3,6,7-tetrahydrocyclohepta[*c*]-pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-50b). Brown oil (3.5 mg). **TLC**: R_f 0.25 (1:15 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 7.67 (s, 1H), 7.32–7.23 (m, 5H), 5.93 (s, 1H), 4.68 (dd, 1H, *J* = 9.0, 4.8), 4.53 (dd, 1H, *J* = 10.7, 7.1), 3.72–3.67 (m, 4H), 3.61–3.58 (m, 1H), 3.47–3.43 (m, 1H), 3.23 (s, 3H), 2.64–2.60 (m, 2H), 1.63–1.58 (m, 2H), 1.53–1.49 (m, 2H), 1.10 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 475.3 ([M+H]$^+$, 100).



(*S*,*Z*)-2-(2-(*tert*-Butylsulfonyl)-1-(2-hydroxyethyl)-2,3,6,7-tetrahydrocyclohepta[*c*]pyrrol-5(1*H*)-ylidene)-*N*-methoxy-*N*-methylacetamide (*S*-50d). Light yellow oil (3.1 mg). **TLC**: R_f 0.41 (1:15 MeOH/EtOAc). **^{1}H-NMR** (600 MHz): δ 6.27 (t, 1H, *J* = 8.0), 6.13 (s, 1H), 6.02 (s, 1H), 4.73 (dd, 1H, *J* = 14.0, 4.0), 4.52 (dd, 1H, *J* = 16.0, 4.0), 3.92–3.89 (m, 1H), 3.76–3.70 (m, 2H), 3.56 (s, 3H), 3.21 (s, 3H), 2.48–2.44 (m, 2H), 2.39–2.35 (m, 1H), 2.24–2.20 (m, 1H), 1.94–1.87 (m, 1H), 1.70–1.65 (m, 1H), 1.07 (s, 9H). **ESI-MS** *m/z* (rel int): (pos) 399.2 ([M+H]$^+$, 100).

G. PRINCIPAL COMPONENT ANALYSIS (PCA)

A total of 330 compounds were compared by principal component analysis:[4]

- 40 top selling brand-name small molecule drugs by revenue in 2006.[4,5]
- 60 natural products with diverse structures[4]
- 20 polycyclic alkaloid and terpenoid natural products (Figure S1)[4b]
- 10 drug-like pyrrazolecarboxamides in the MLSMR from ChemBridge[4]
- 10 drug-like dihydrotriazolopyrimidines in the MLSMR from Chem Div[4]
- 190 alkaloid/terpenoid-like library members synthesized herein

PCA was performed using 20 structural and physicochemical parameters as previously described.[4] Complete data and results are included as an Excel spreadsheet file attached to this Supporting Information. Average values for each parameter by compound class are shown in Table S2 below. A total of 81% of the variance in the overall dataset is represented in the first two principal components (Table S3). Component loadings are shown graphically in Figure S2 below. High-resolution versions of Figure 1a–d from the manuscript are reproduced below as Figures S3, S4, S5, and S6.

Table S2. Average structural and physicochemical parameters by compound series. † = nStereo ÷ MW × 1000 for clarity.

AVGs	Drug	NP	AlkTerp	ChBr	ChDv	Multi
MW	361	629	267	381	446	333
N	2.2	2.6	0.6	4.3	4.7	1.4
O	2.9	9.7	3.3	3.1	3.4	3.5
XLogP	2.7	1.5	1.6	2.9	1.8	0.8
HBD	1.5	4.9	1.9	1.1	1.9	1.8
HBA	5.4	10.8	3.8	5.9	7.7	5.0
RotB	6.3	9.7	2.2	5.3	6.1	5.7
tPSA	69	183	63	103	94	71
ALOGPs	2.8	2.1	1.8	3.3	2.7	1.3
ALOGpS	-3.9	-3.8	-2.6	-4.0	-3.8	-2.5
nStereo	1.4	9.1	3.6	0.0	1.0	1.7
R	0.6	4.1	1.3	0.0	0.5	0.9
S	0.8	5.0	2.3	0.0	0.5	0.8
nStMW†	3.7	13.9	12.7	0.0	2.2	5.4
RSdelta	-0.2	-0.9	-1.0	0.0	0.0	0.0
Rings	2.9	3.8	2.7	3.2	4.2	2.3
RngAr	2.1	1.0	0.5	2.9	2.9	0.8
RngSys	2.1	2.0	1.3	3.1	3.1	1.5
RngLg	8.4	15.8	10.2	6.3	9.4	8.3
RRSys	1.4	2.3	2.3	1.0	1.4	1.6

[4] (a) Bauer, R. A.; Wurst, J. M.; Tan, D. S. *Curr. Opin. Chem. Biol.* **2010**, *14*, 308–314. (b) Bauer, R. A.; DiBlasi, C. M.; Tan, D. S. *Org. Lett.* **2010**, *12*, 2084–2087.

[5] Drug Topics Website – "Top 200 brand-name drugs by retail dollars in 2006": http://drugtopics.modernmedicine.com/drugtopics/Pharmacy+Facts+%26+Figures/Top-200-brand-name-drugs-by-retail dollars-in-2006/ArticleStandard/Article/detail/405100?contextCategoryId=7604

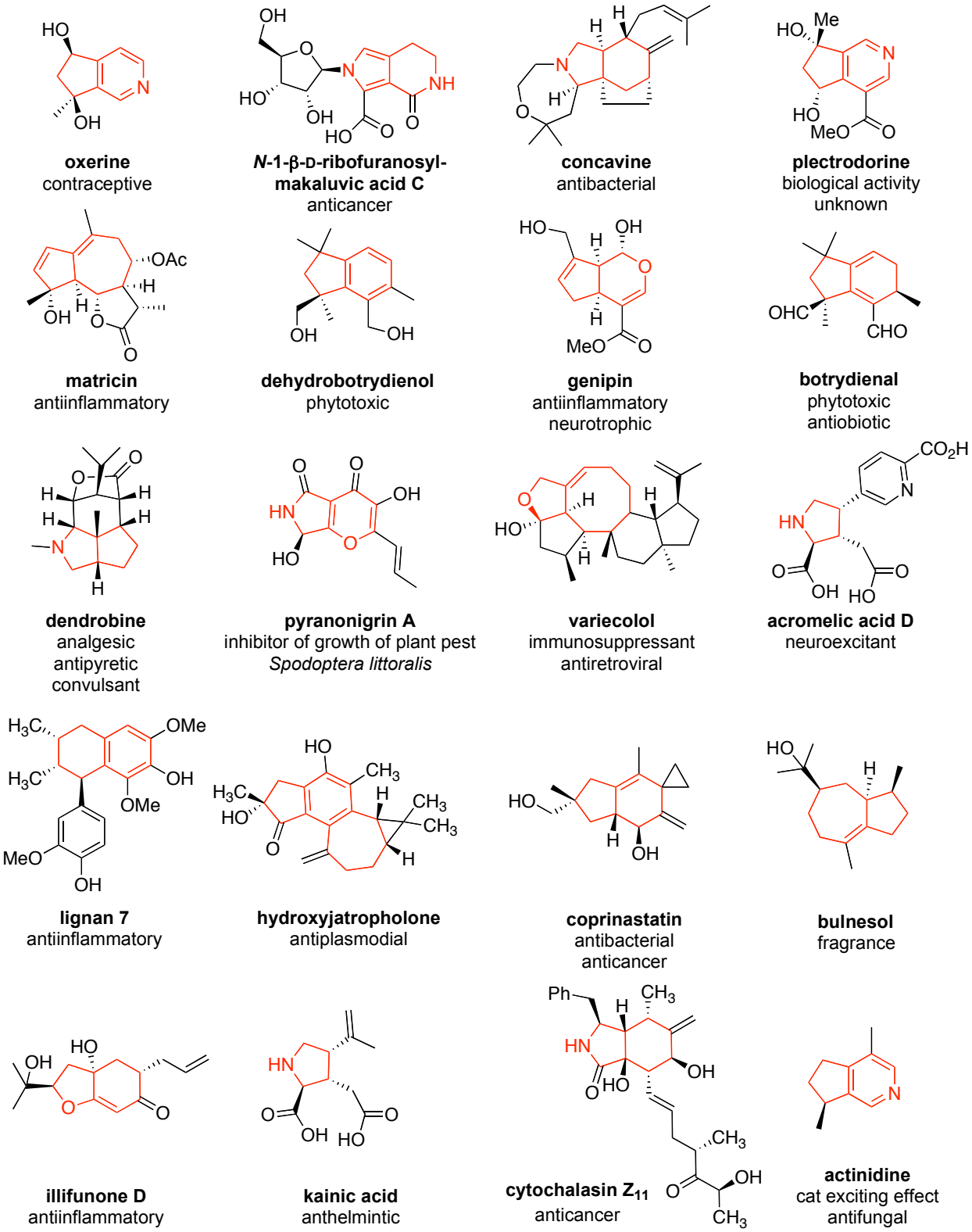


Figure S1. Collection of 20 polycyclic alkaloid and terpenoid natural products having scaffolds related to those synthesized herein.

Table S3. Standard deviation and percent contribution for each principal component (R summary).

	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9	PC10
Standard deviation	3.303	1.232	1.021	0.727	0.614	0.560	0.484	0.284	0.275	0.239
Proportion of Variance	0.714	0.099	0.068	0.035	0.025	0.021	0.015	0.005	0.005	0.004
Cumulative Proportion	0.714	0.813	0.882	0.916	0.941	0.961	0.977	0.982	0.987	0.991

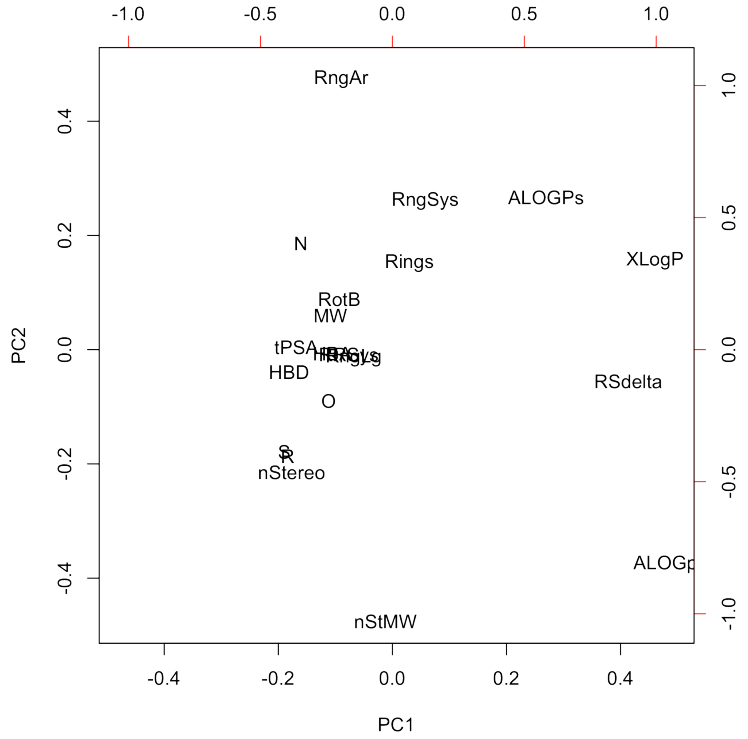


Figure S2. Plot of PCA component loadings generated using the biplot function of R.

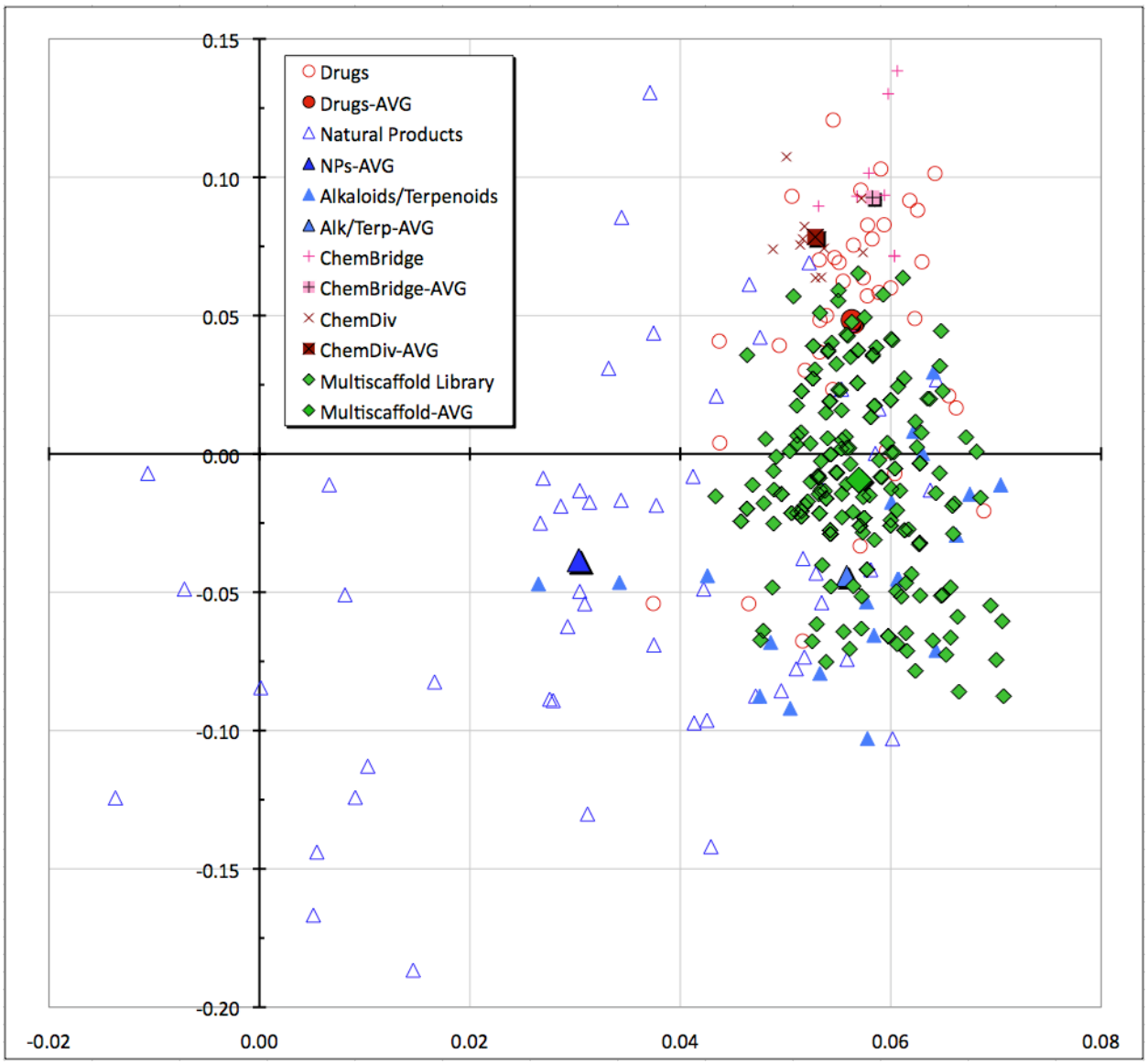


Figure S3. High-resolution version of Figure 1a from the manuscript. Principal component analysis of 20 structural and physicochemical descriptors of the 40 top-selling drugs (red circles), 60 diverse natural products (open blue triangles), 20 polycyclic alkaloids and terpenoids (filled blue triangles), 20 ChemBridge and Chem Div library members (crosses), and 190 multiscaffold library members (green diamonds).

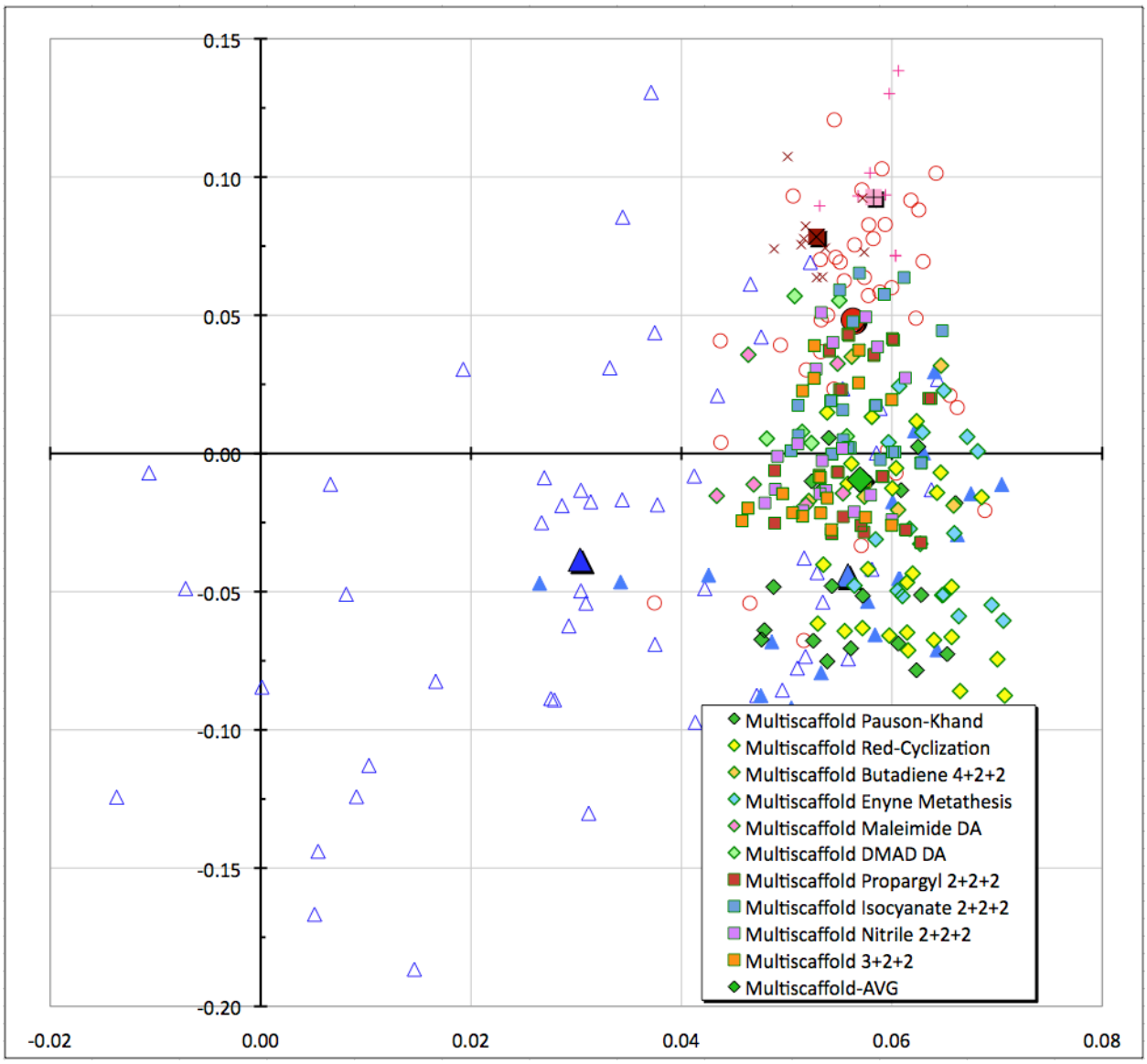


Figure S4. High-resolution version of Figure 1b from the manuscript. Influence of the scaffold: enyne-derived scaffolds (filled diamonds), diyne-derived scaffolds (filled squares).

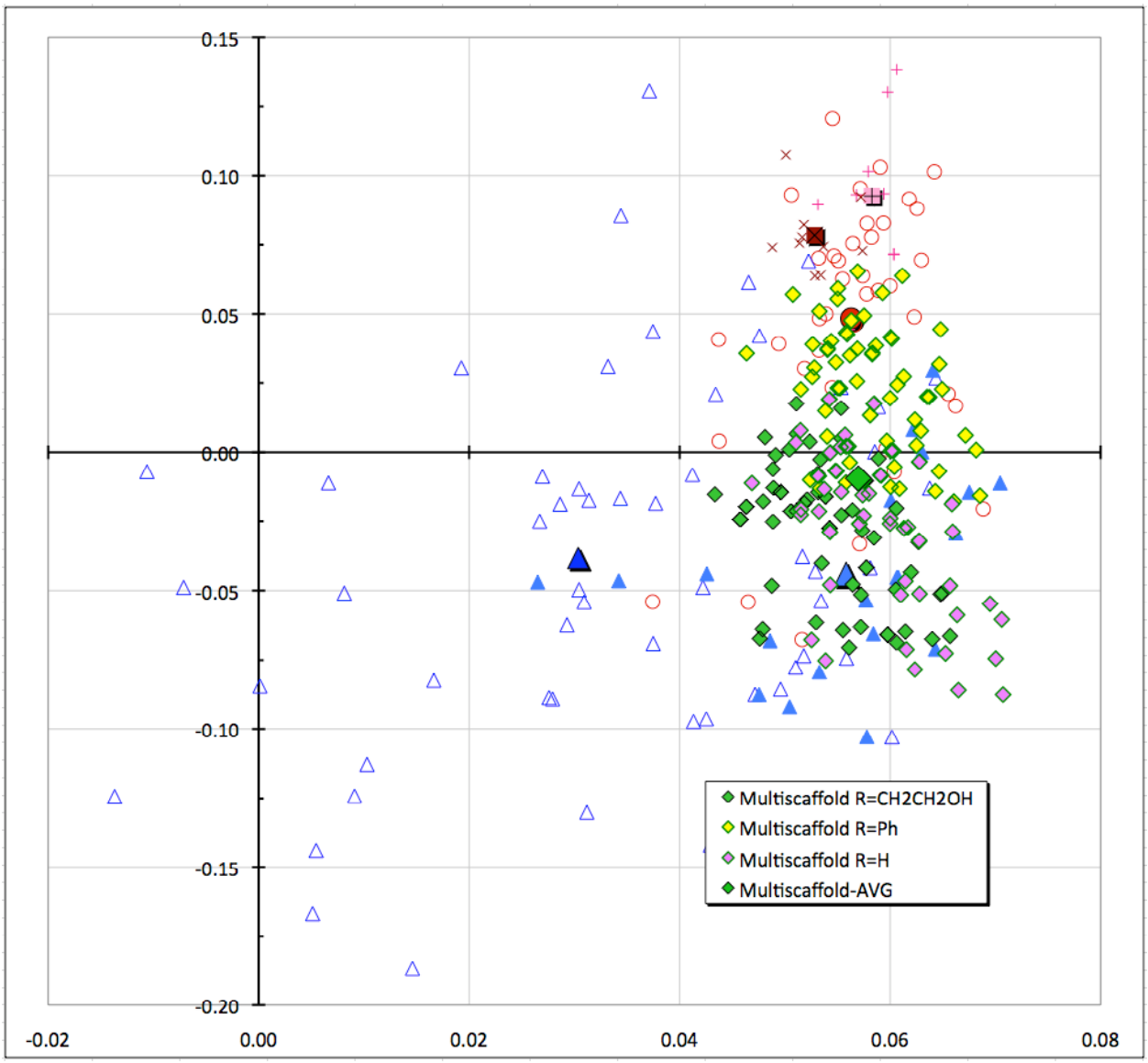


Figure S5. High-resolution version of Figure 1c from the manuscript. Influence of the R^2 substituent: CH_2CH_2OH (green fill), Ph (yellow fill), H (pink fill).

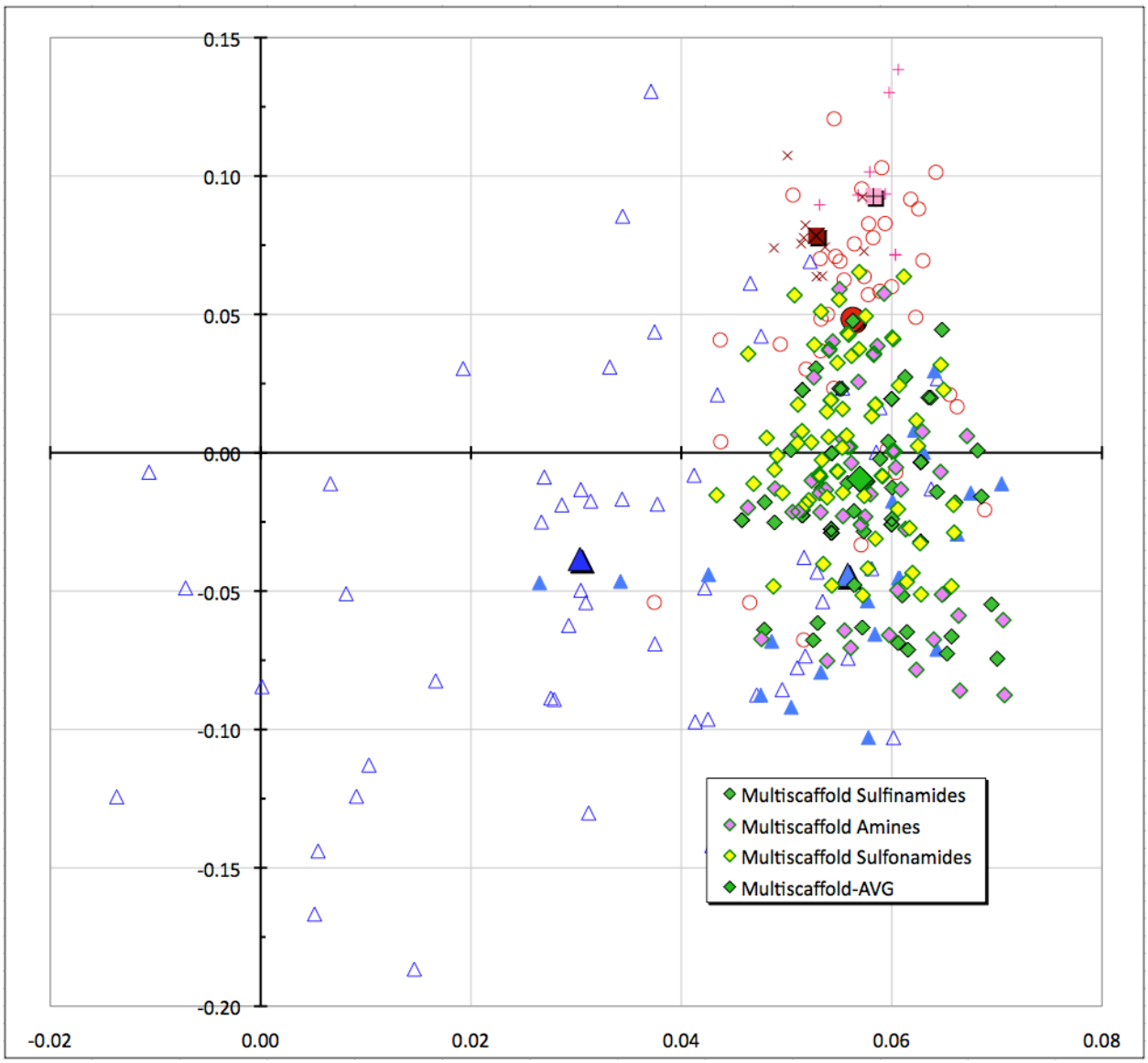


Figure S6. High-resolution version of Figure 1d from the manuscript. Influence of the R^3 *N*-capping group: sulfinamides (green fill), free amines (pink fill), sulfonamides (yellow fill).

H. PRINCIPAL MOMENT OF INERTIA (PMI) ANALYSIS

Normalized principal moments of inertia were calculated for the 95 *R*-series library members by Dr. Lakshmi B. Akella (Broad Institute) as previously described.[6] Enantiomers are not distinguished in this analysis. Briefly, low energy conformations were calculated using MOE (Molecular Operating Environment; http://www.chemcomp.com/software.htm), resulting in a total of 97 structures (two low-energy conformations were identified for Saito [3+2+2] cycloaddition products **45a** and **47a**). Principal moment of inertia ratios were calculated, then normalized. The results were plotted using Spotfire (http://spotfire.tibco.com/), with the boundary triangle added manually at coordinates {0,1} (rod), {1,1} (sphere), and {0.5,0.5} (disc).

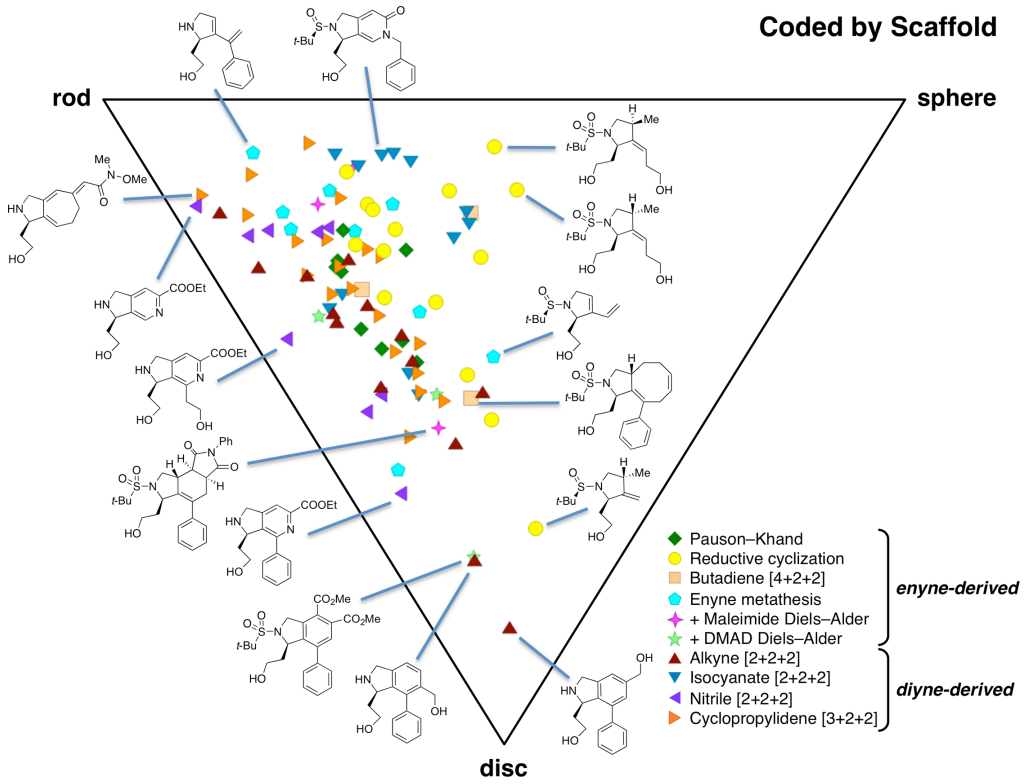


Figure S7. PMI analysis of *R*-series library members, coded by scaffold. Products derived from reductive cyclization (yellow circles), enyne metathesis (cyan pentagons), and isocyanate [2+2+2] cyclotrimerization (blue triangles) exhibited relatively more sphere-like character.

[6] (a) Sauer, W. H. B.; Schwarz, M. K. *J. Chem. Inf. Comput. Sci.* **2003**, *43*, 987–1003. (b) Akella, L. B.; DeCaprio, D. *Curr. Opin. Chem. Biol.* **2010**, *14*, 325–330.

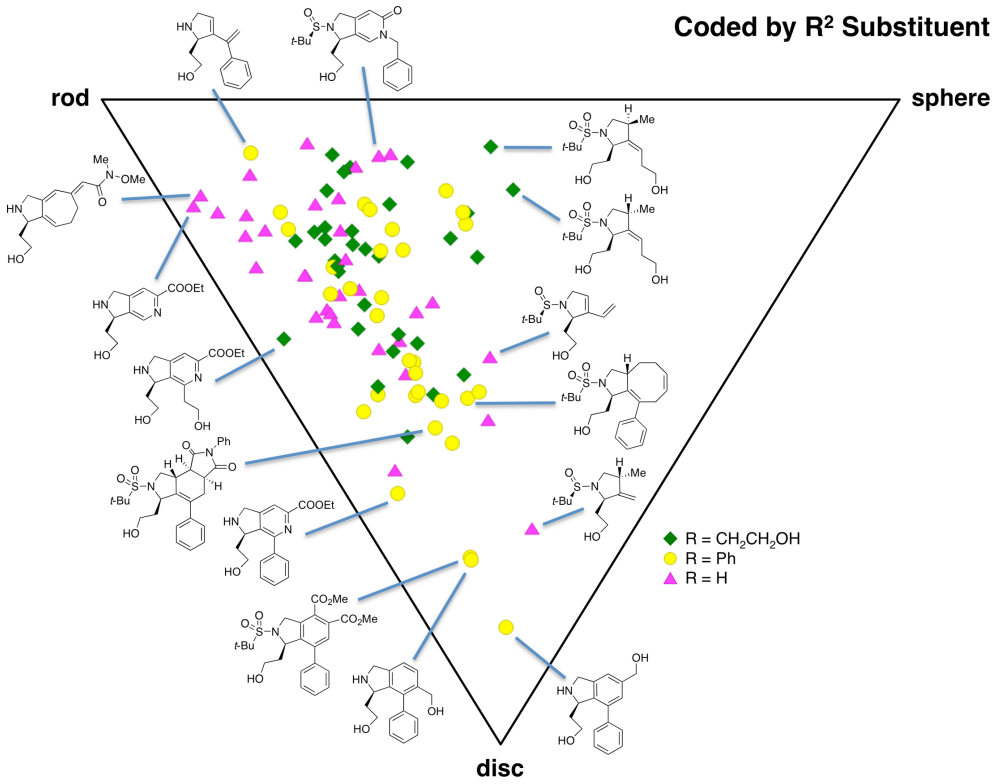


Figure S8. PMI analysis of *R*-series library members, coded by R^2 substituent.

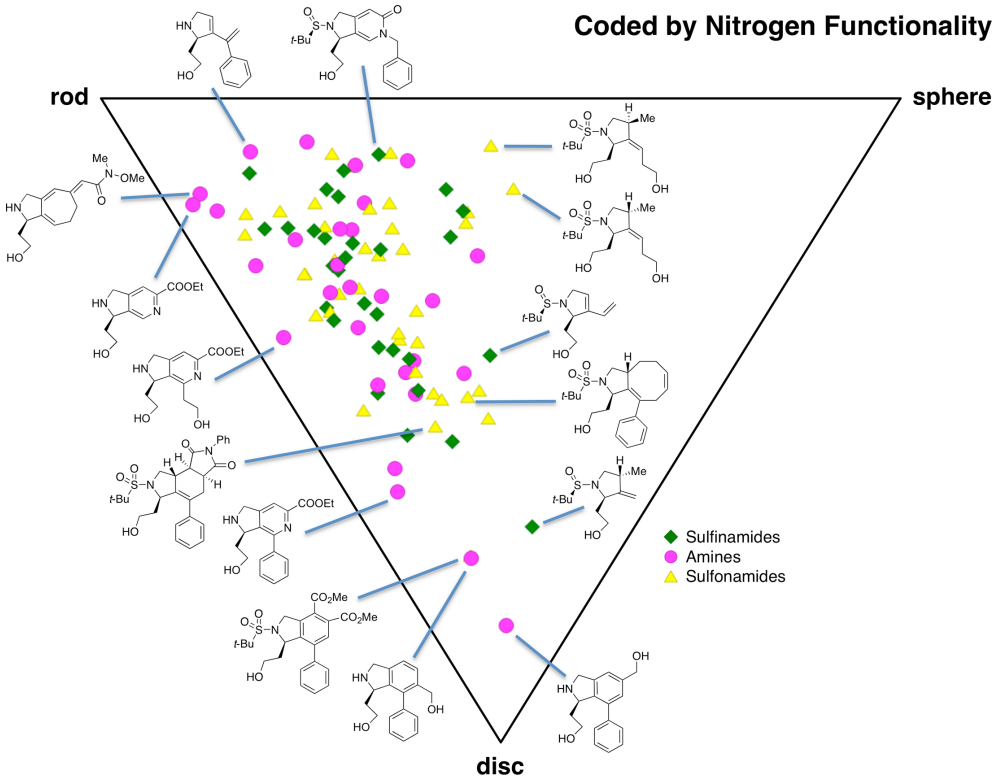
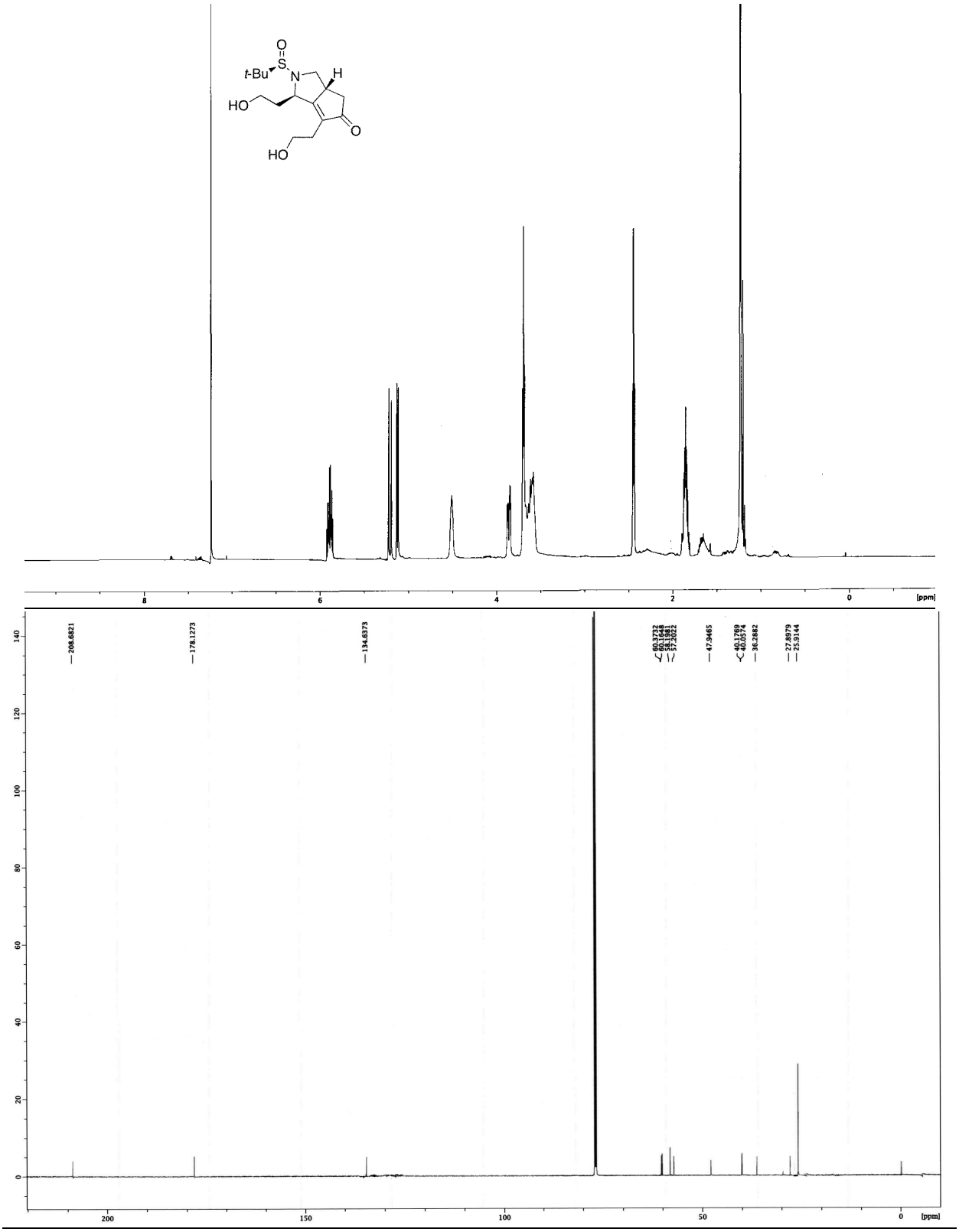


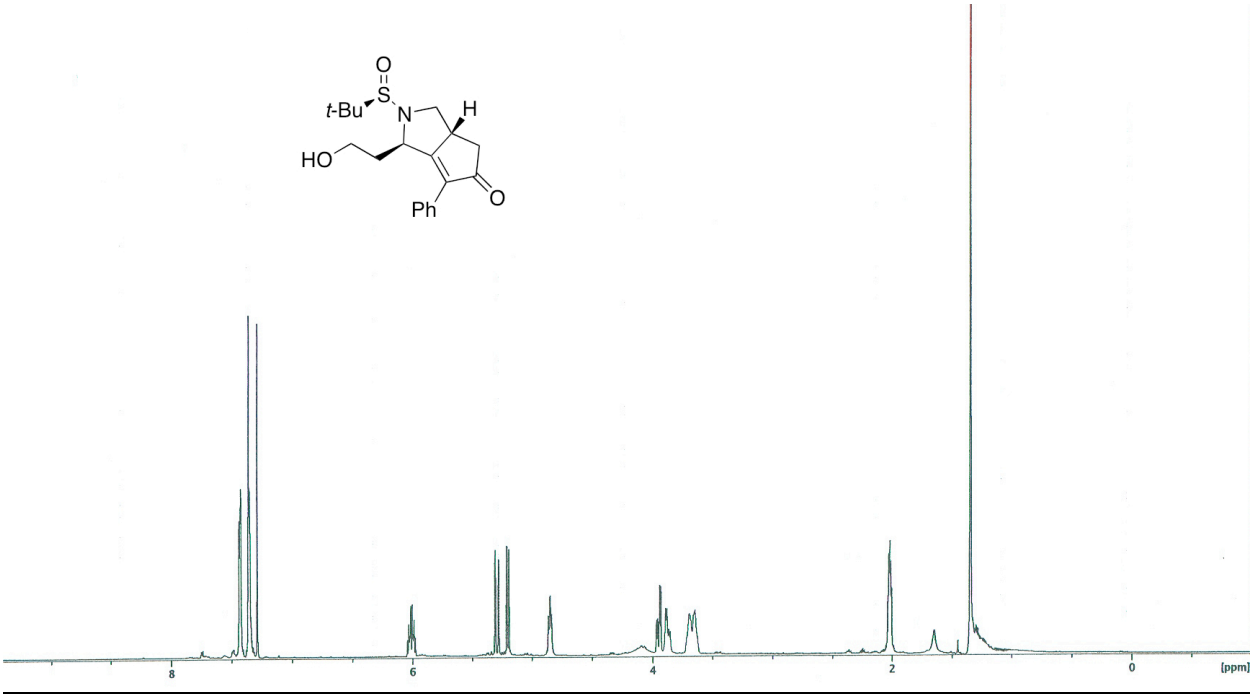
Figure S9. PMI analysis of *R*-series library members, coded by R^3 *N*-capping group.

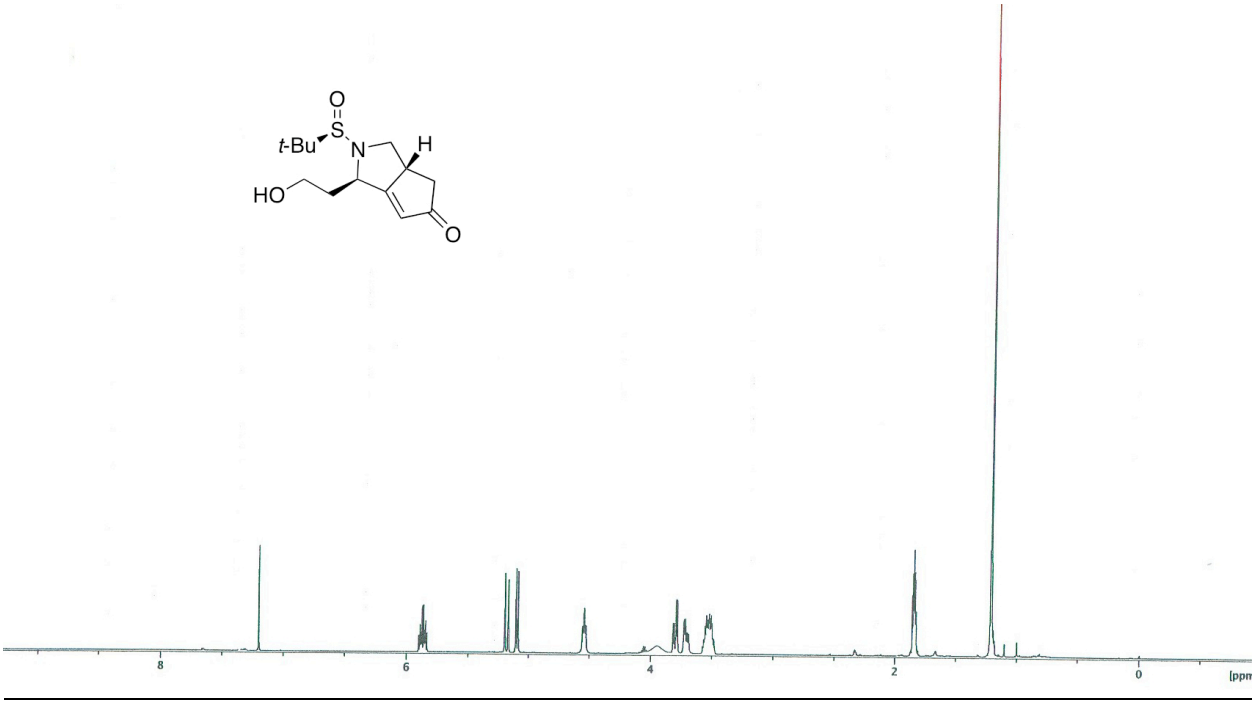
I. ^{1}H-NMR AND SELECTED ^{13}C-NMR SPECTRA

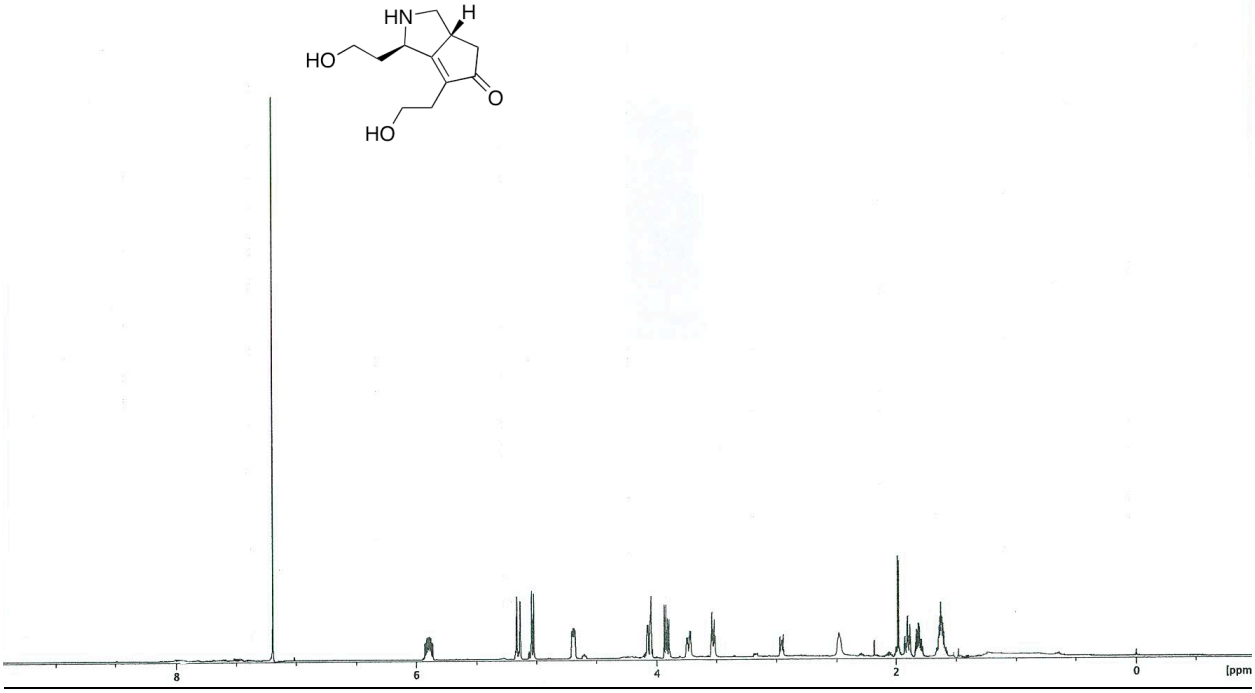
1. ^{1}H-NMR AND SELECTED 13C-NMR SPECTRA FOR *R*-SERIES LIBRARY MEMBERS

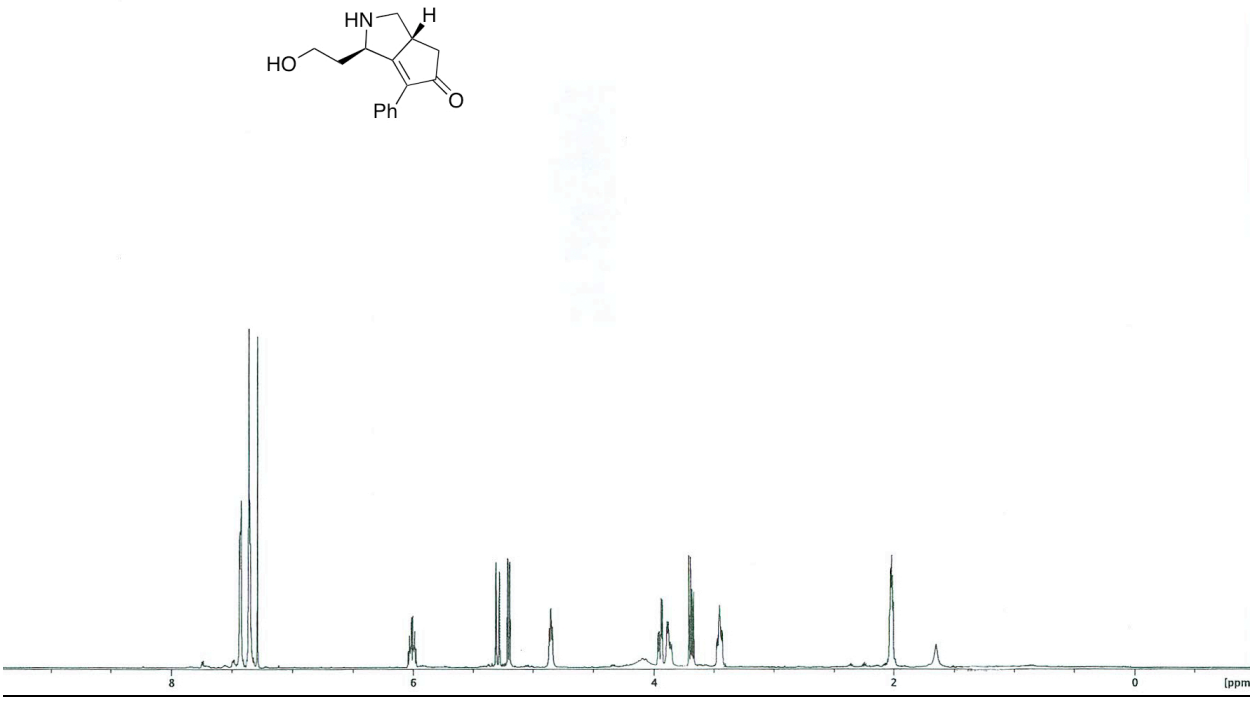
a. Pauson–Khand reaction products (*R*-11–13)

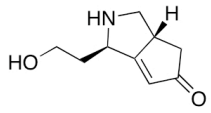


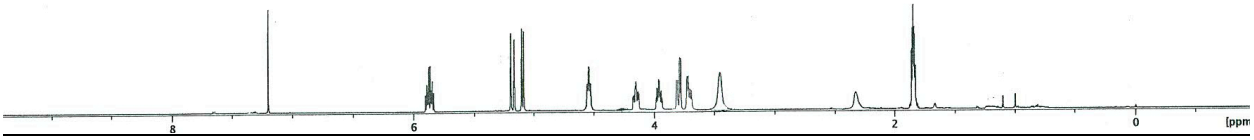

O
S
t-Bu
N
H
HO
Ph
O
8
6
4
2
0
[ppm]

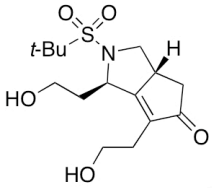

O
S
t-Bu
N
H
HO
O
8
6
4
2
0


HN
H
HO
O
HO
8
6
4
2
0
[ppm

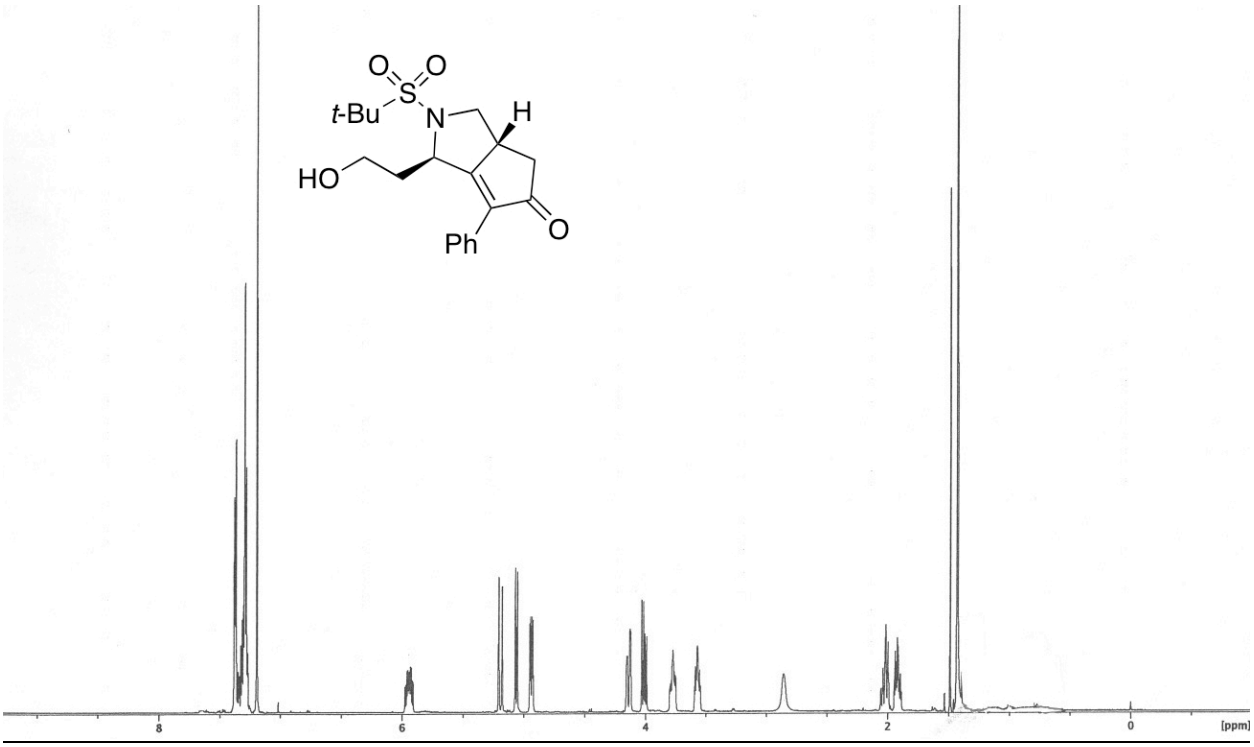

HN
H
HO
Ph
O
8
6
4
2
0
[ppm

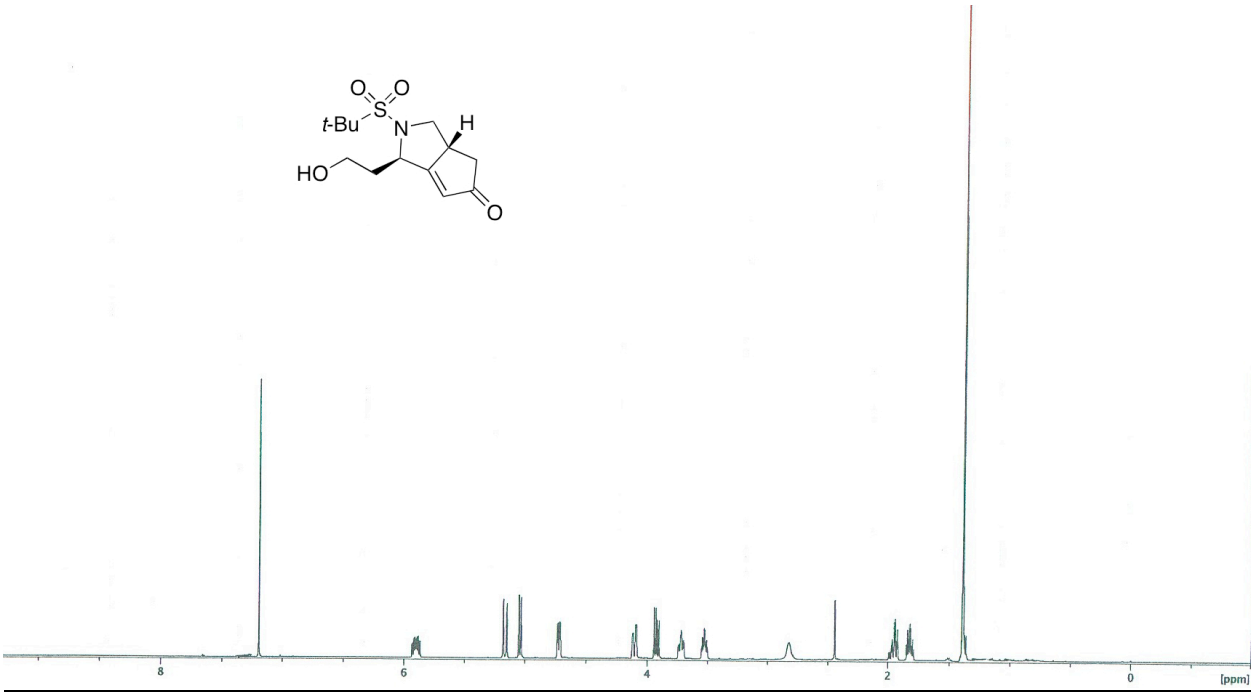

HN
H
HO
O


8
6
4
2
0
[ppm

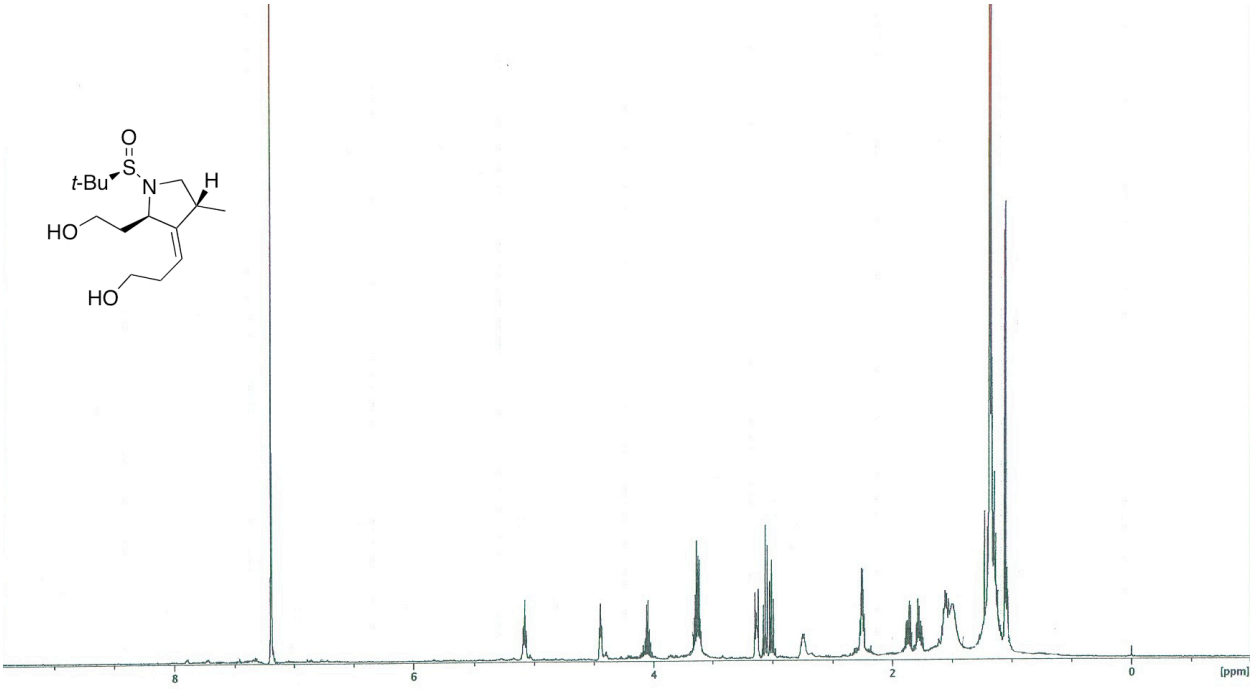

O
O
S
t-Bu
N
H
HO
O
HO

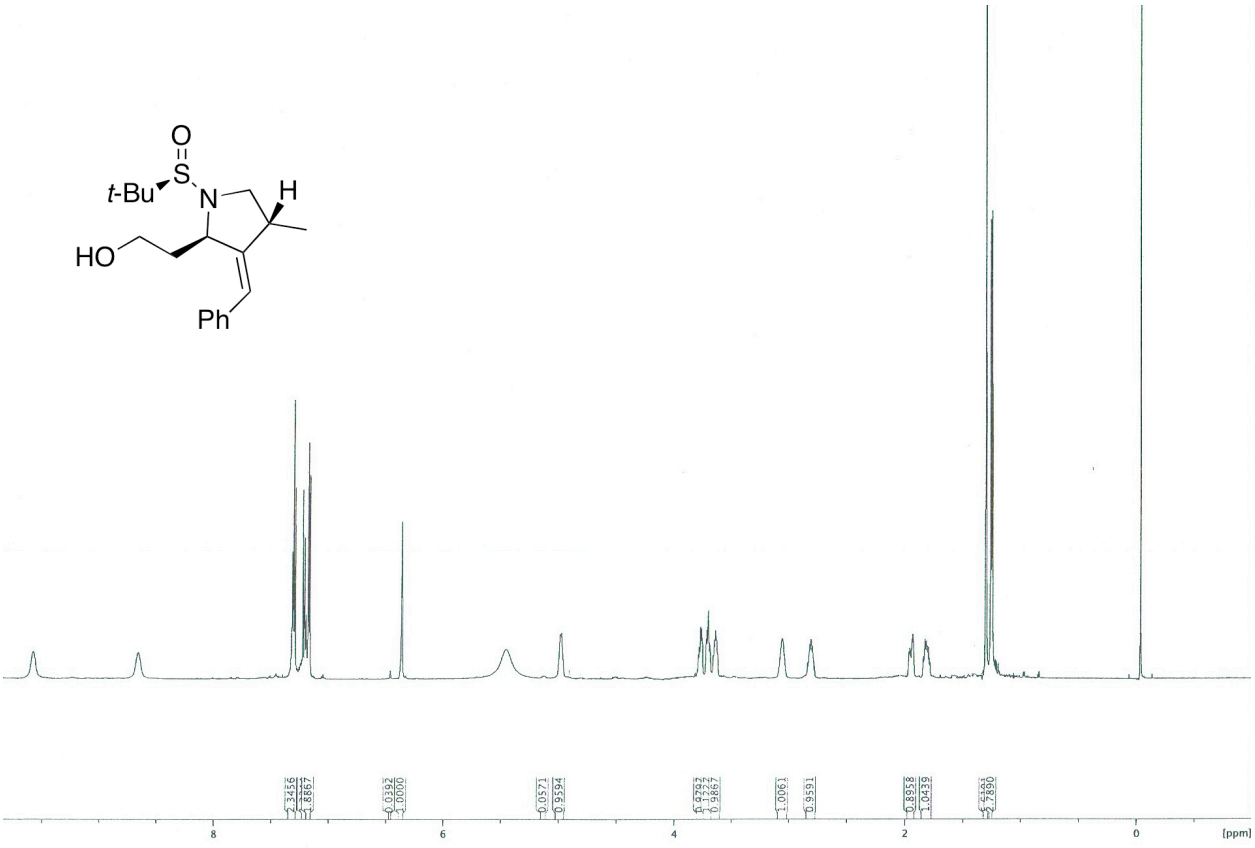
8
6
4
2
0
[ppm

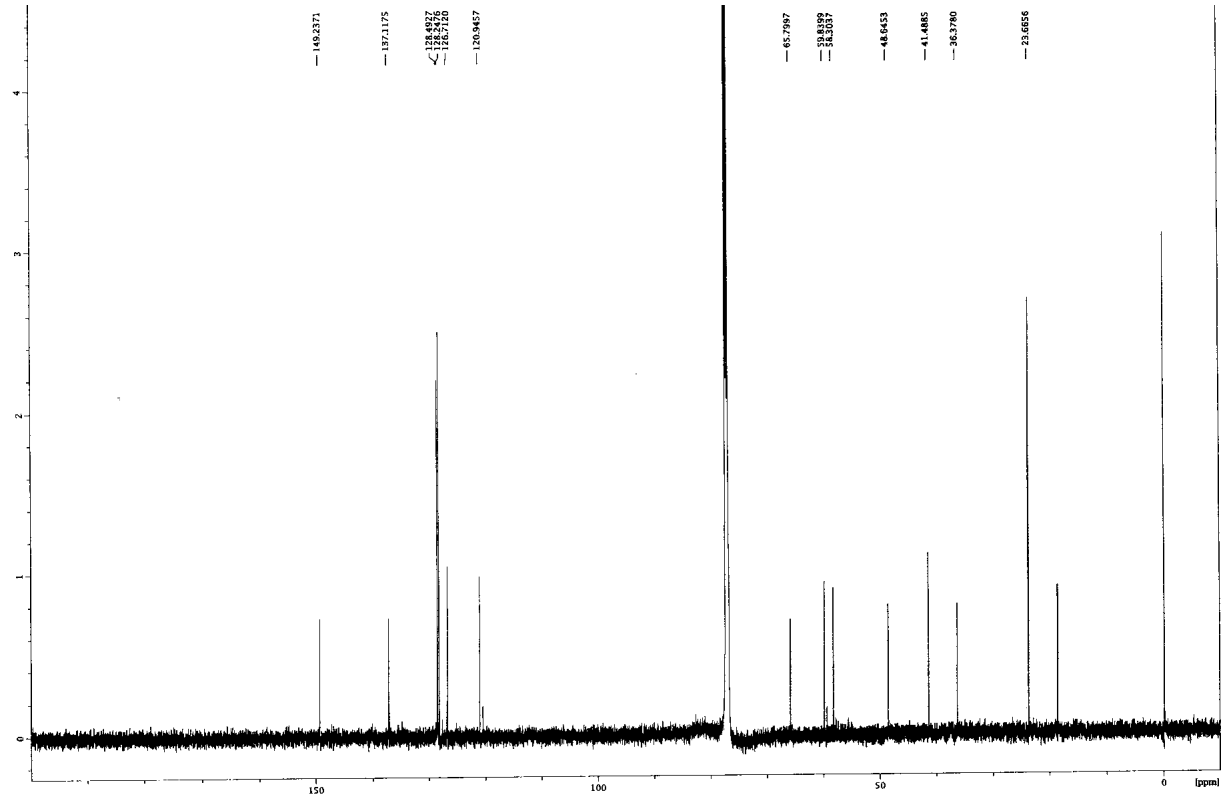

O
O
S
t-Bu
N
H
HO
Ph
O
8
6
4
2
0
[ppm]

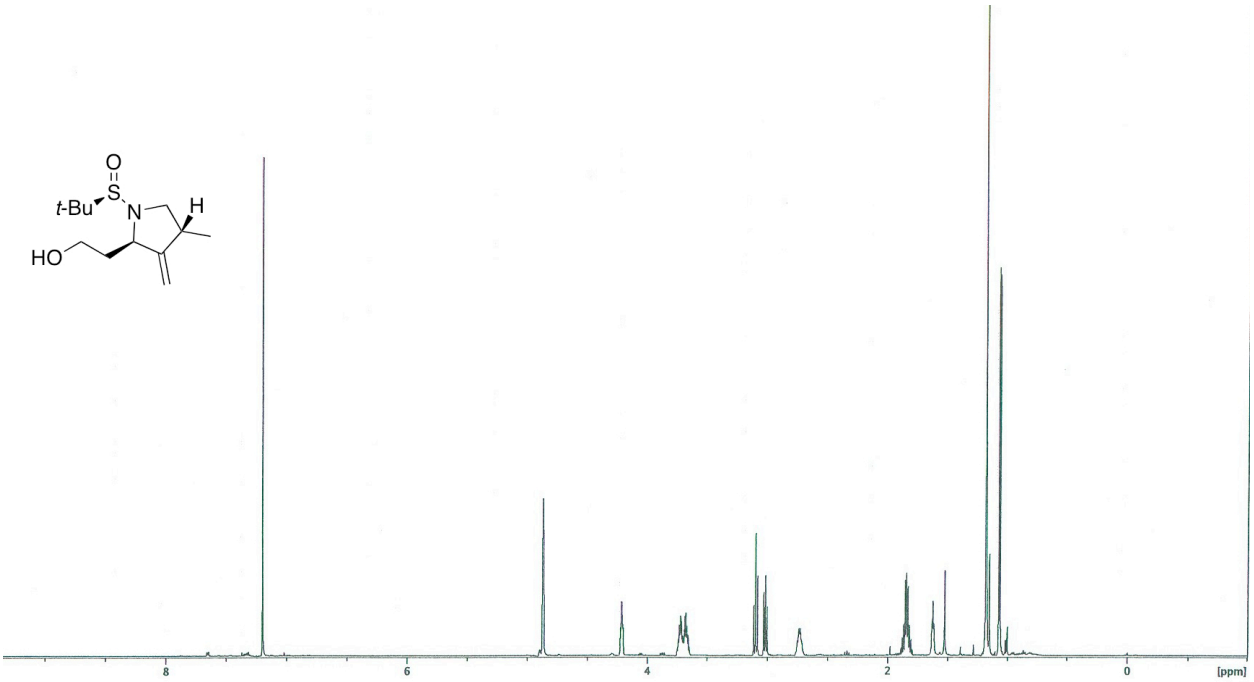

O
O
S
t-Bu
N
H
HO
O
8
6
4
2
0
[ppm]

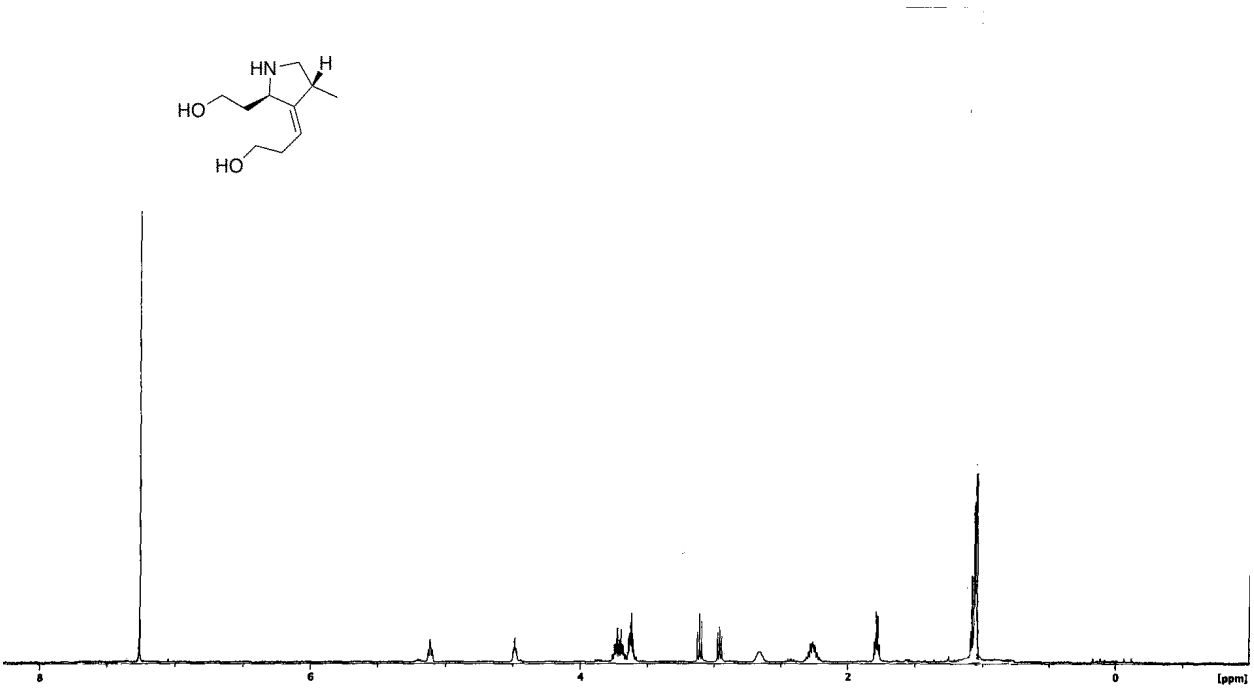
b. Krische reductive cyclization products (*R*-14–19)

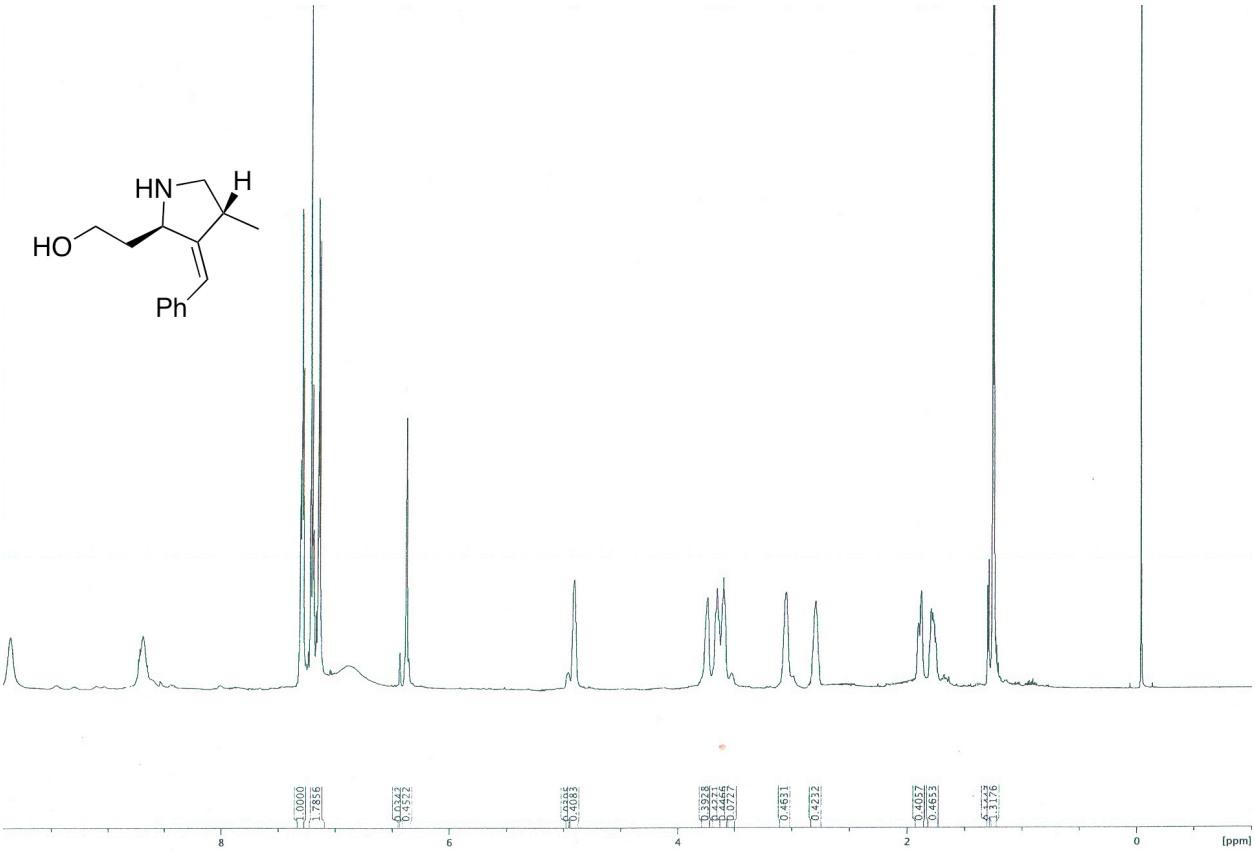


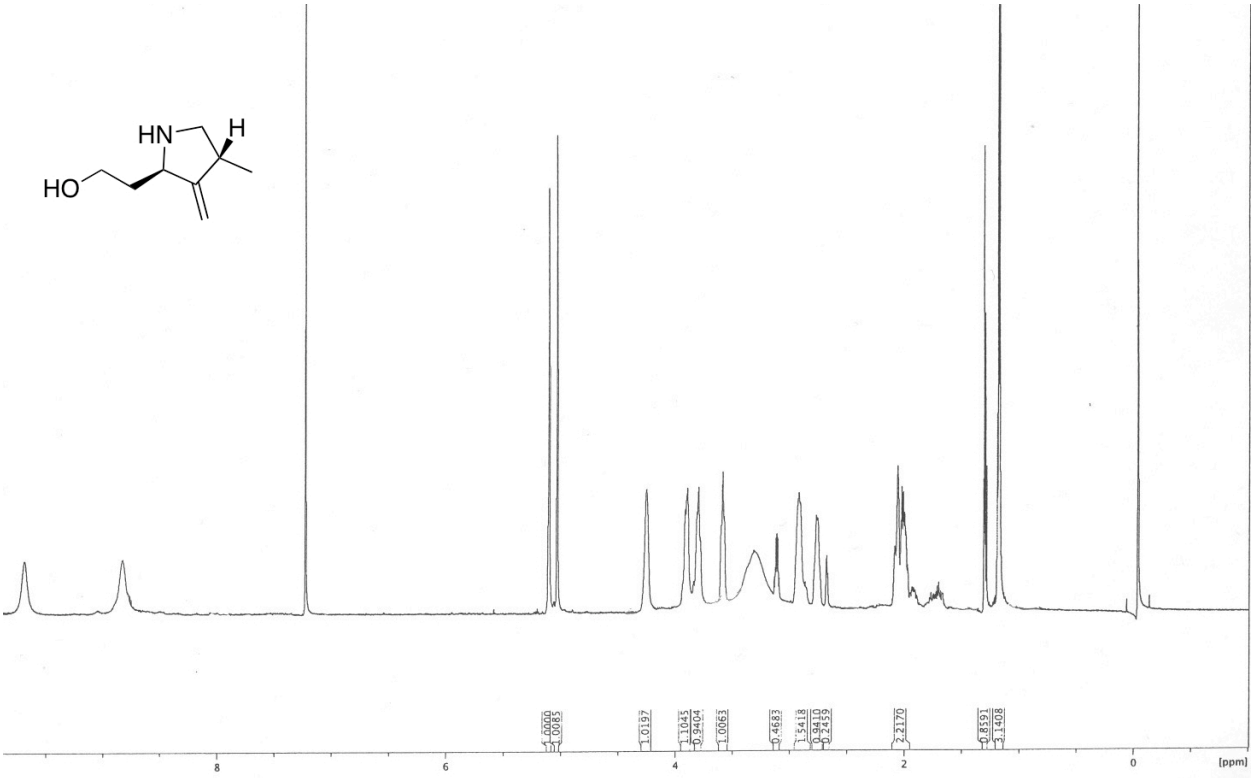

O
S
t-Bu
N
H
HO
Ph
2.3456
2.2424
2.8867
0.0352
1.0000
0.0571
0.9594
0.9792
0.9867
1.0063
0.9591
0.8958
1.0439
6.6261
2.7890
8
6
4
2
0
[ppm]

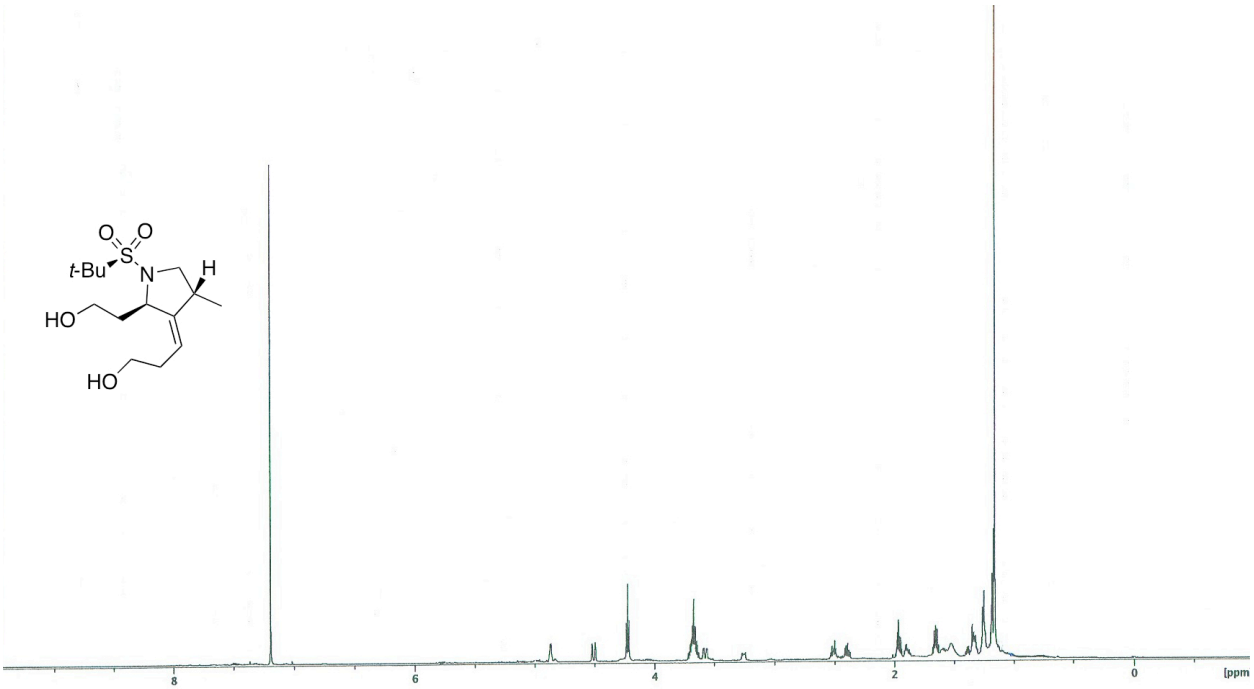

149.2371
137.1175
128.6927
128.5476
128.7120
120.9457
65.7997
59.8199
58.3037
48.6453
41.4885
36.3780
23.6656
150
100
50
0
[ppm]

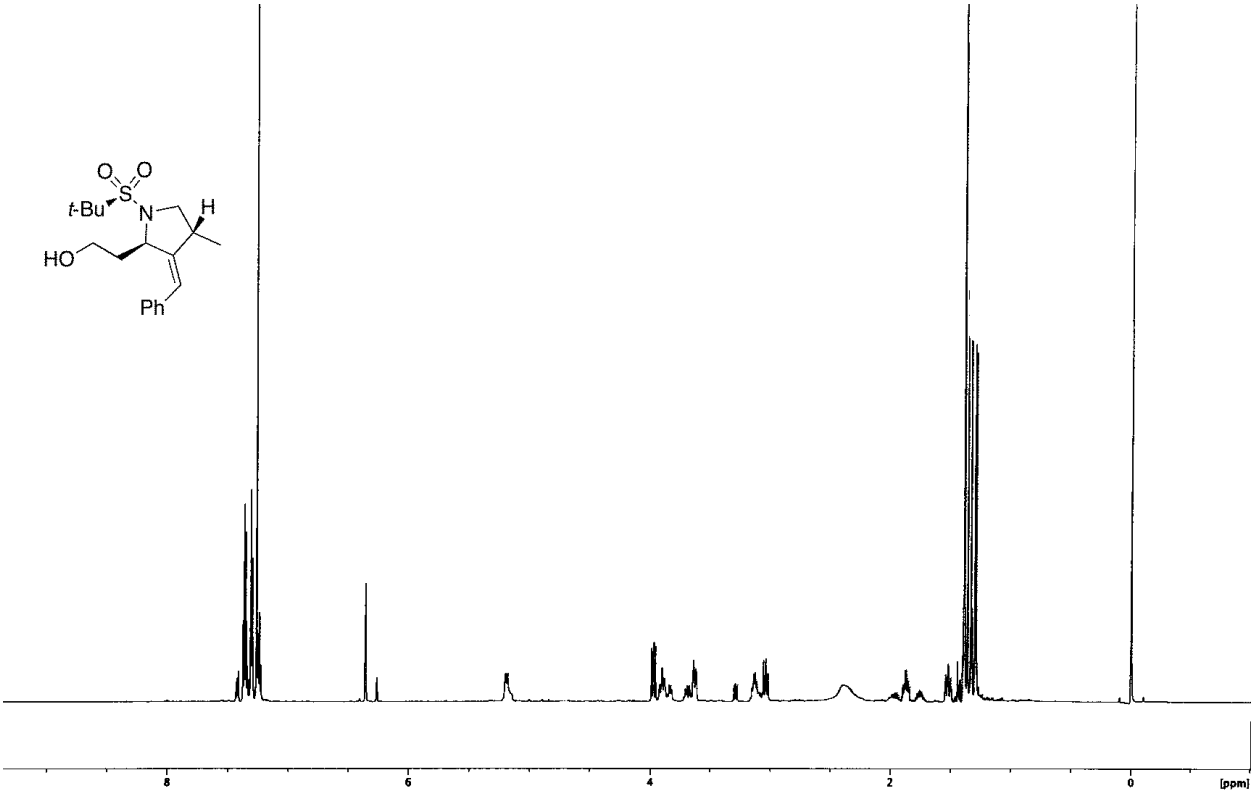

O
S
t-Bu
N
H
HO
8
6
4
2
0
[ppm]

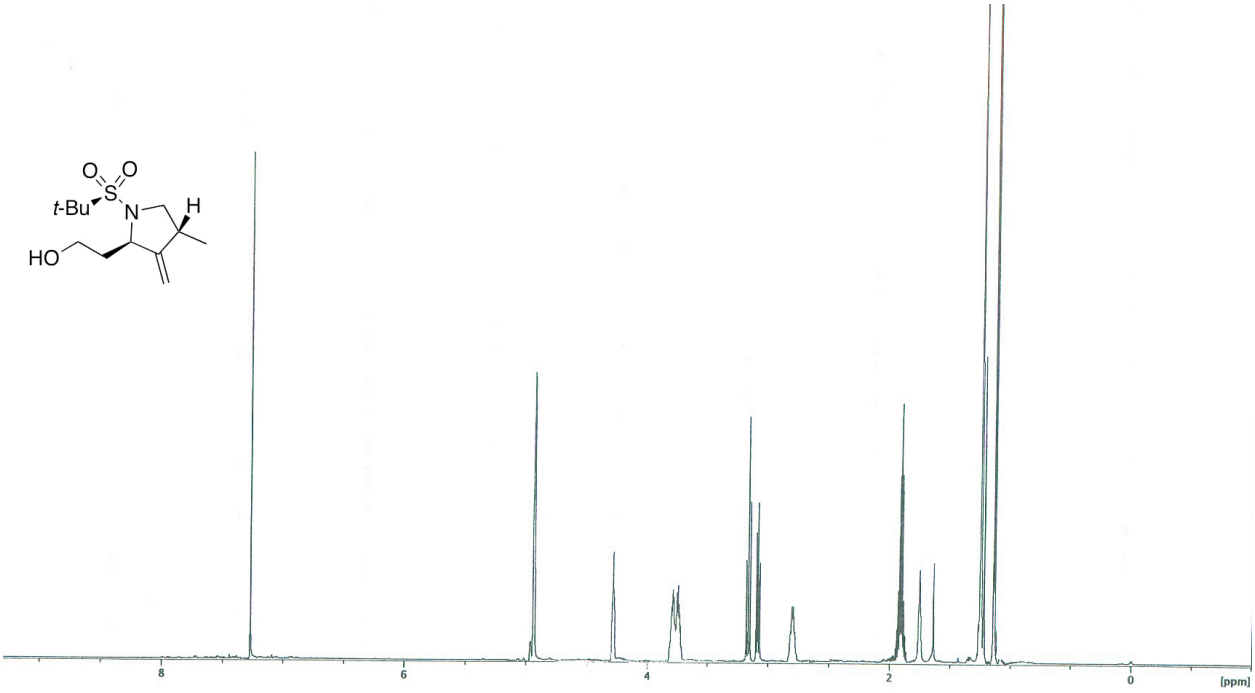

HN
H
HO
HO
8
6
4
2
0
[ppm]

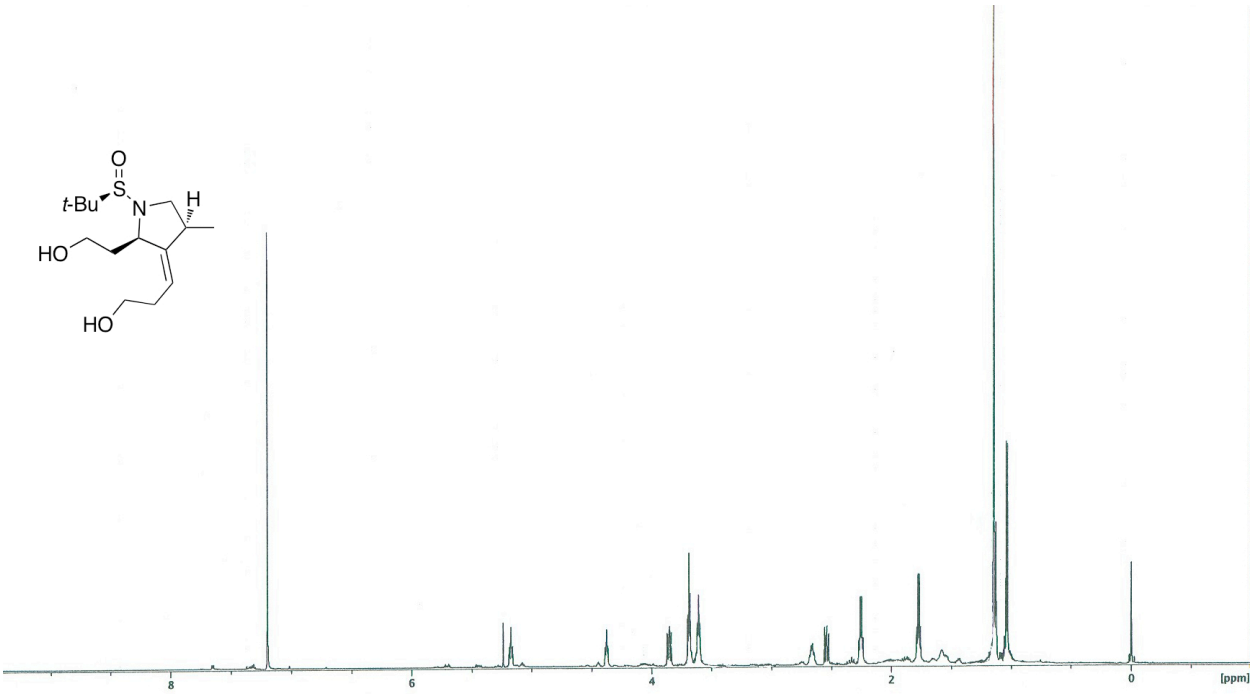

HN
H
HO
Ph
1.0000
1.7856
6.0343
6.4522
6.0305
6.4083
6.3928
6.4221
6.0767
6.0767
6.4631
6.4232
6.4057
6.4653
6.4449
6.3176
8
6
4
2
0
[ppm]

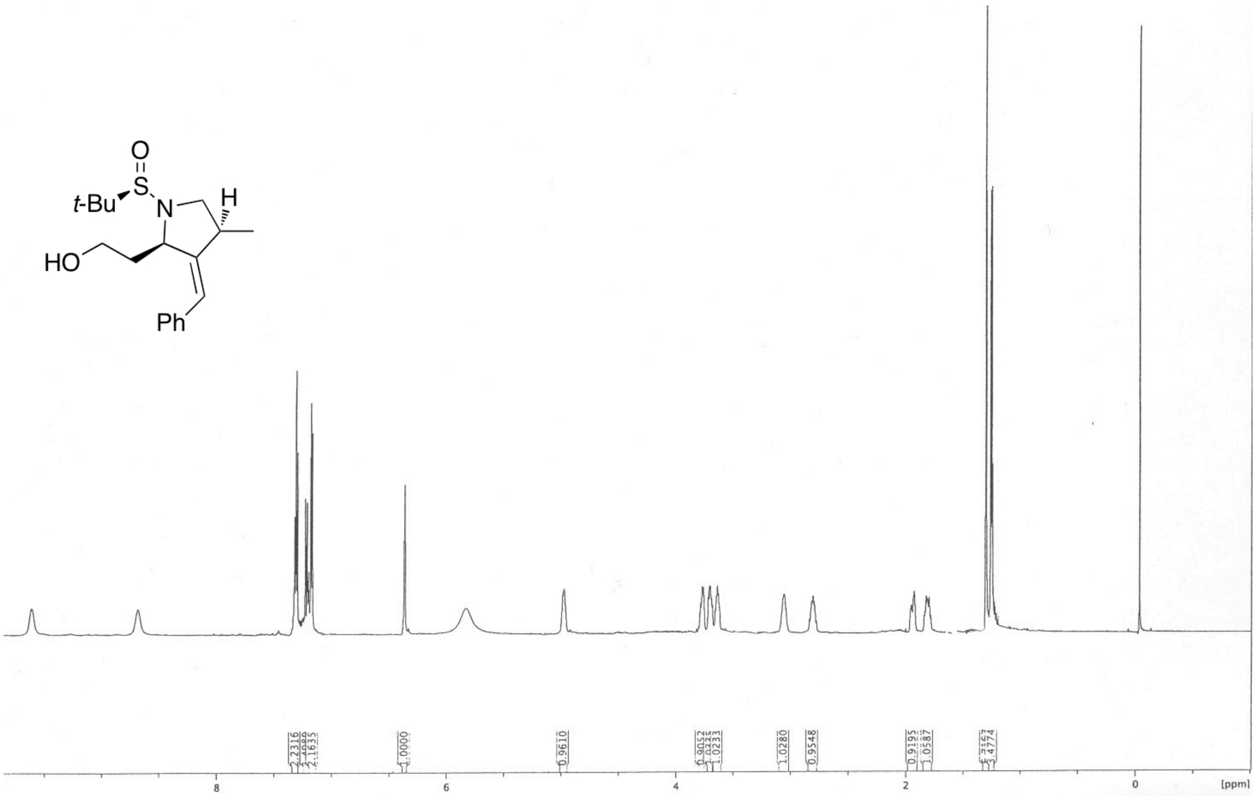

HN
H
HO
1.0000
1.0085
1.0197
1.1045
0.9404
1.0063
0.4683
1.5418
0.9410
0.2459
2.2170
0.8591
1.1408
8
6
4
2
0
[ppm]

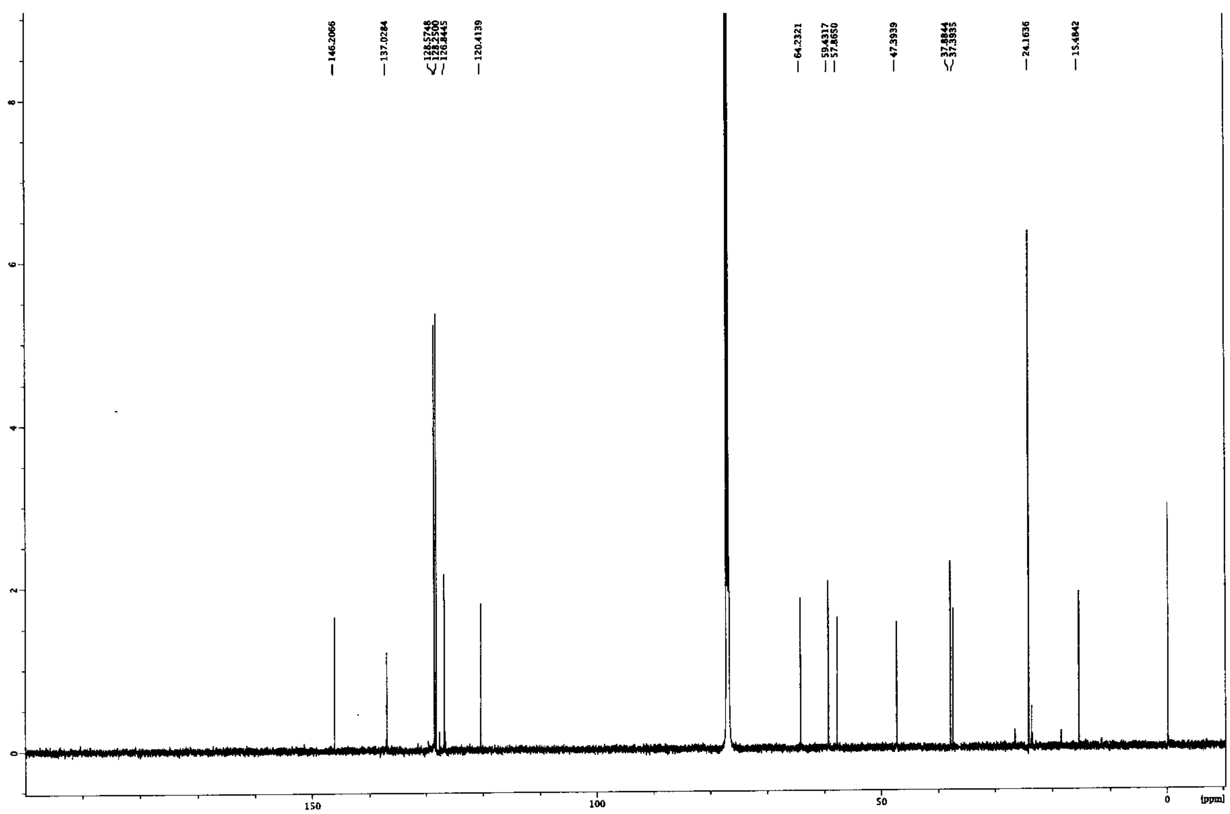

O
O
S
t-Bu
N
H
HO
HO
8
6
4
2
0
[ppm

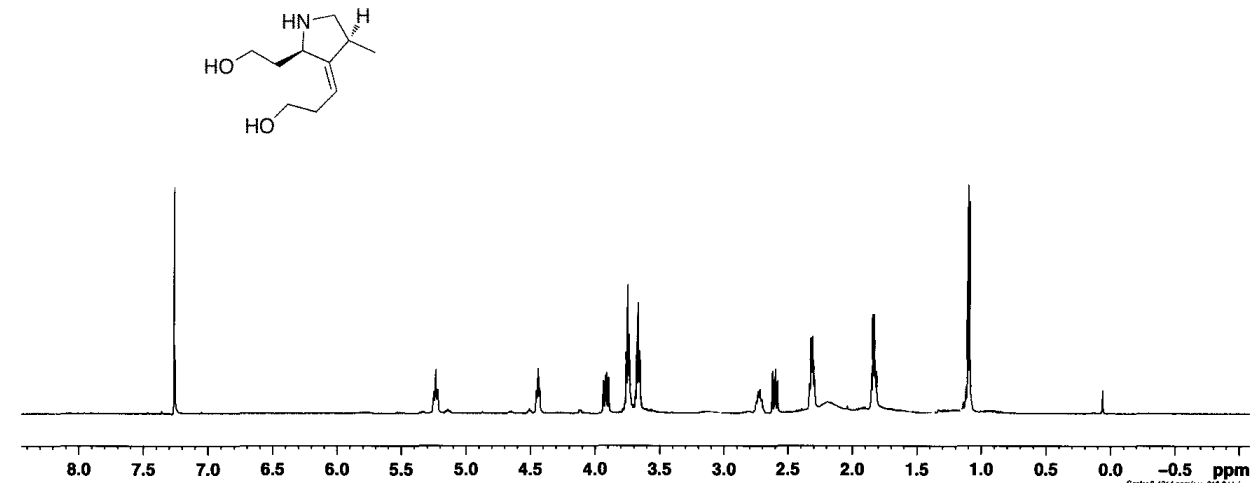

O
O
S
t-Bu
N
H
HO
Ph
8
6
4
2
0
[ppm]

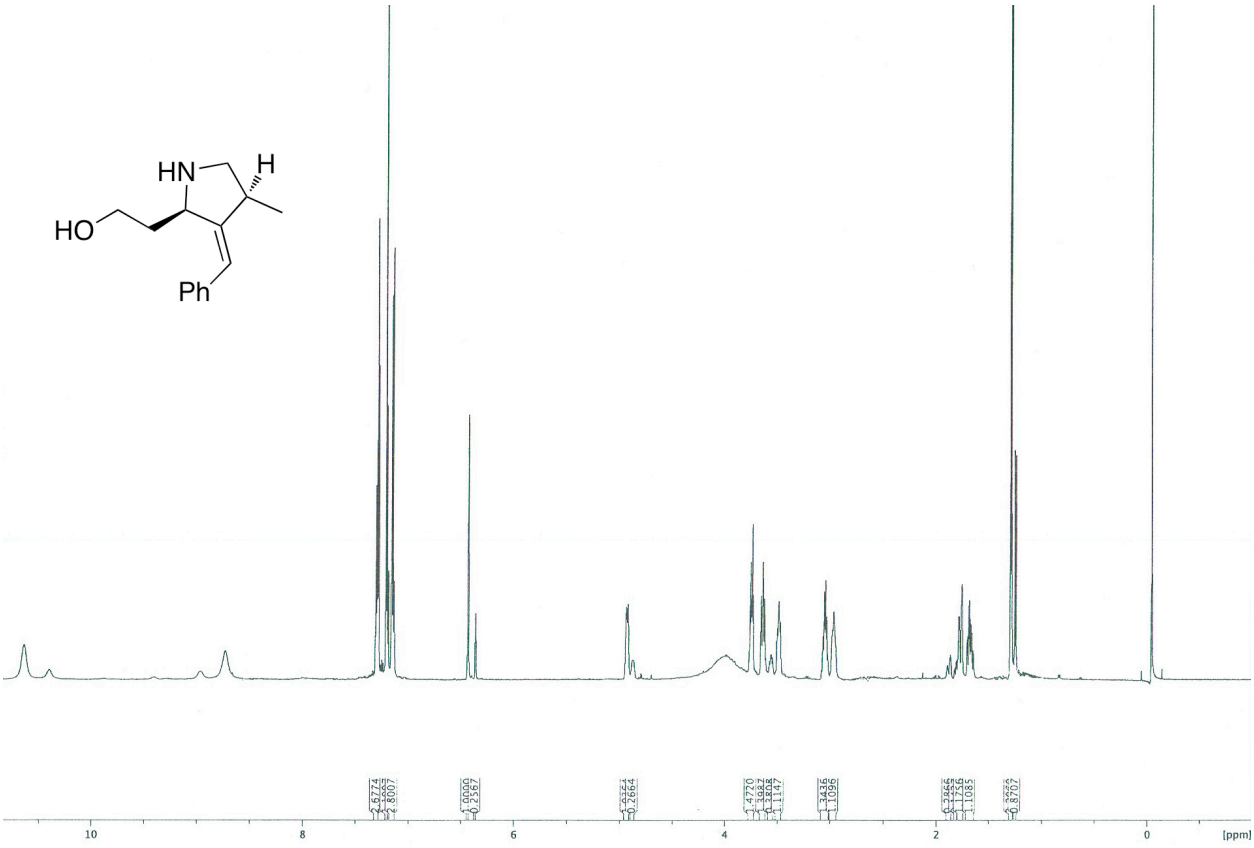

O
O
S
t-Bu
N
H
HO
8
6
4
2
0
[ppm]

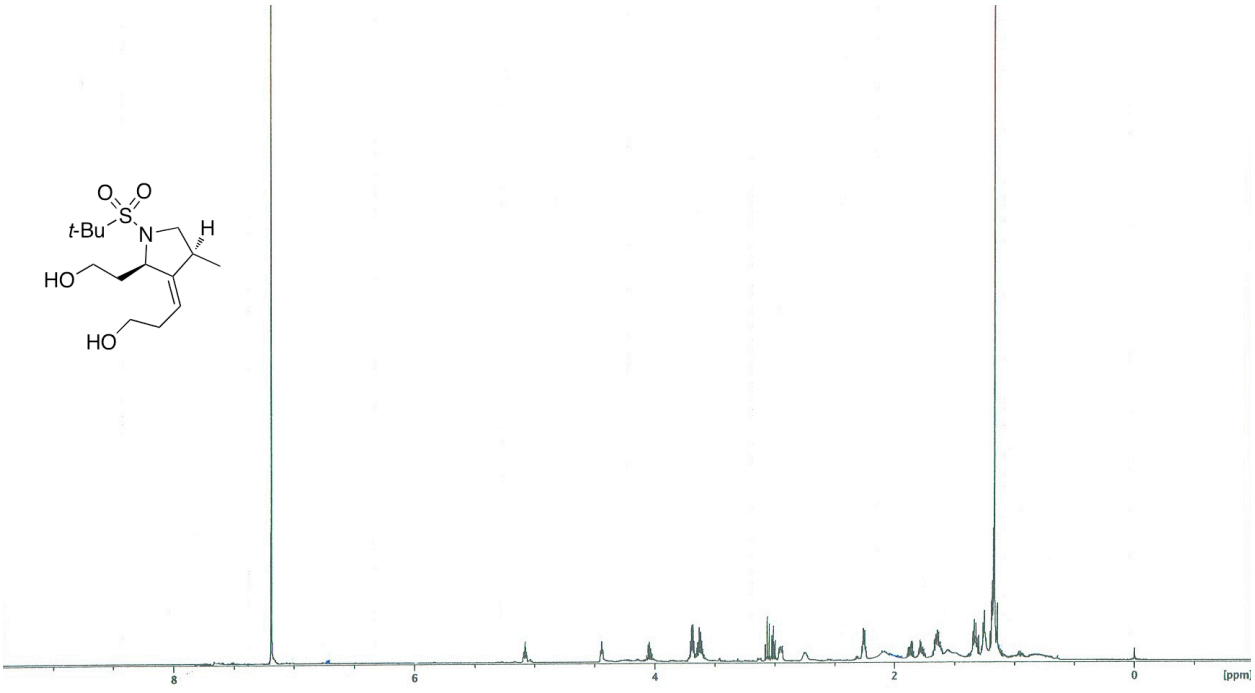

O
S
t-Bu
N
H
HO
HO
8
6
4
2
0
[ppm]

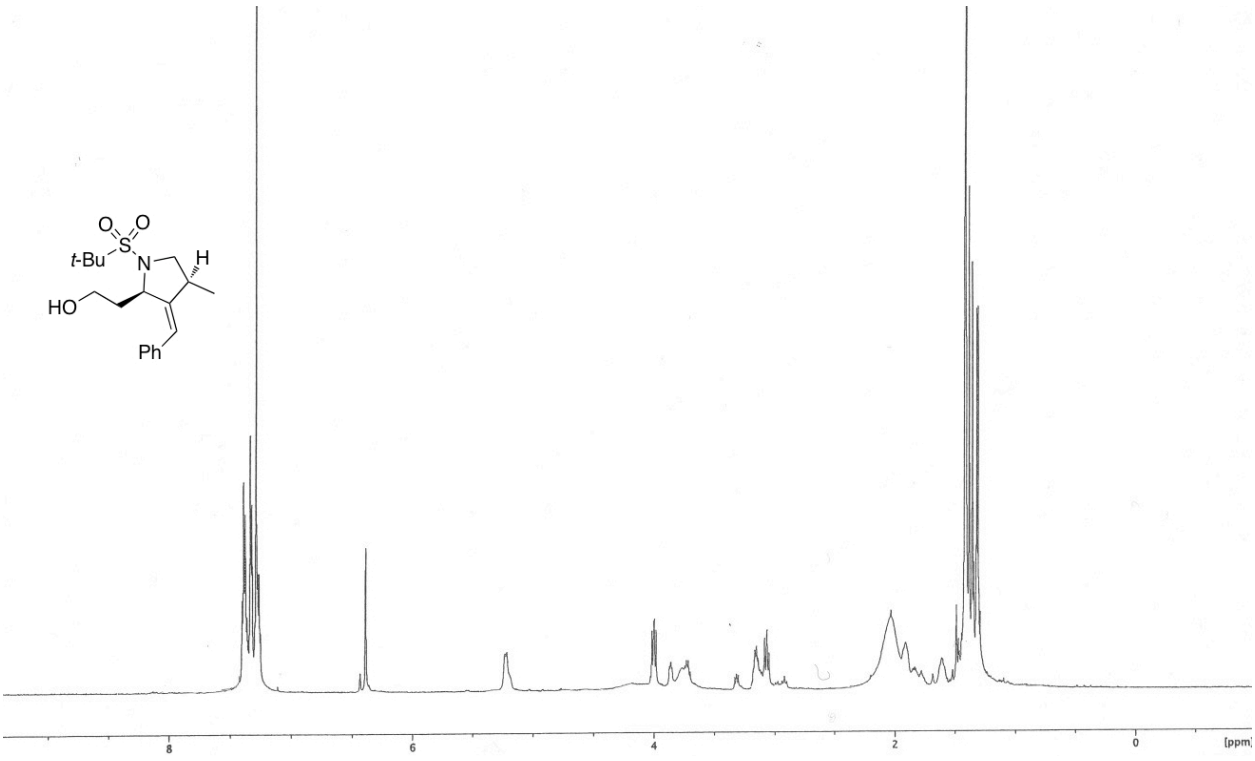

O
S
t-Bu
N
H
HO
Ph
[ppm]


146.2066
137.0284
120.4139
64.2321
47.3939
24.1636
15.4842
150
100
50
0
[ppm]

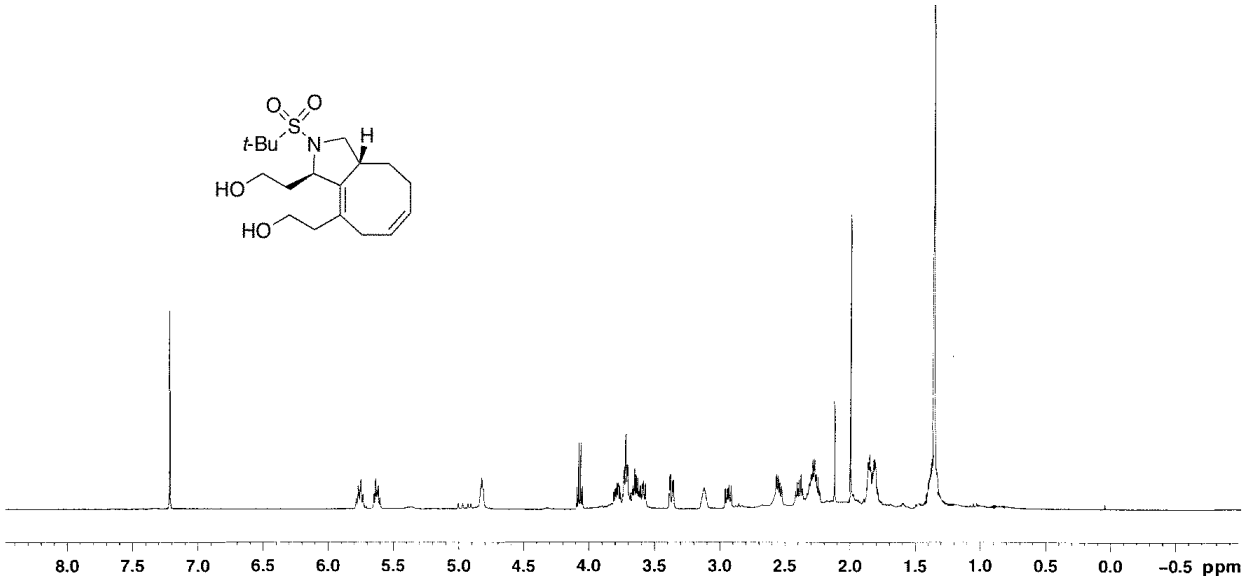

HN
H
HO
HO
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
ppm

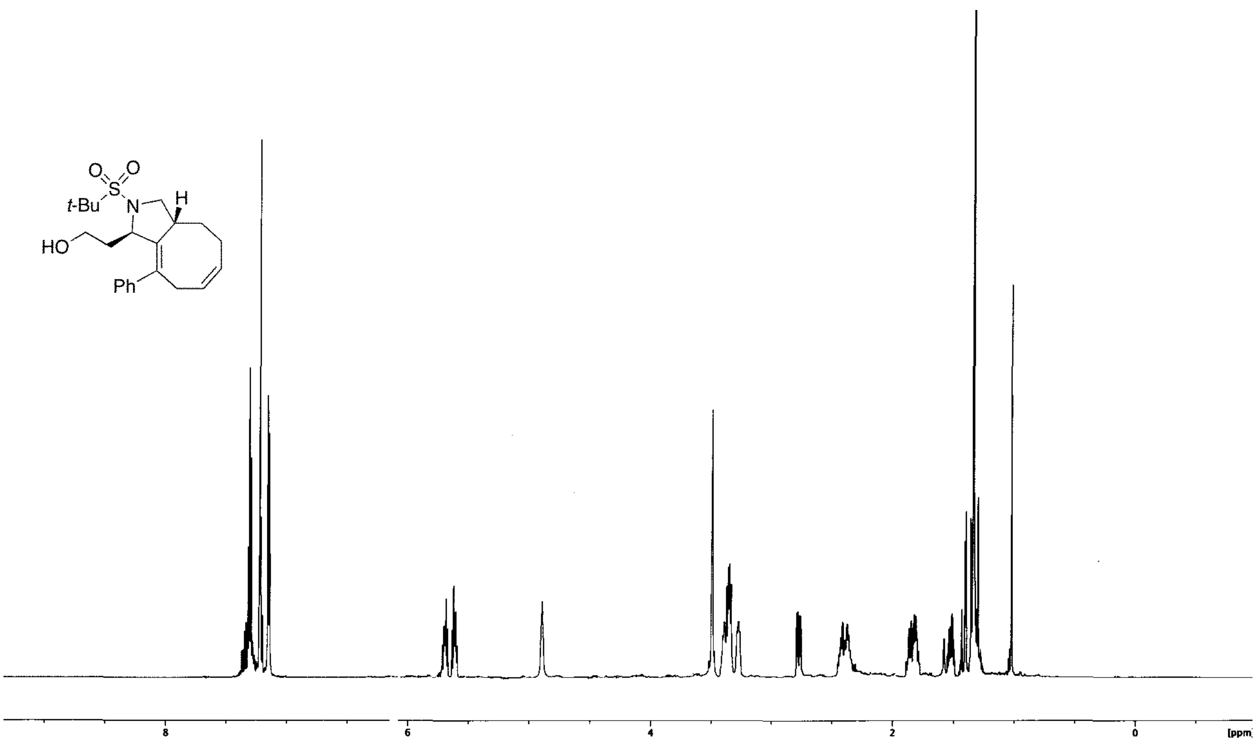

HN
H
HO
Ph
10
8
6
4
2
0
[ppm]

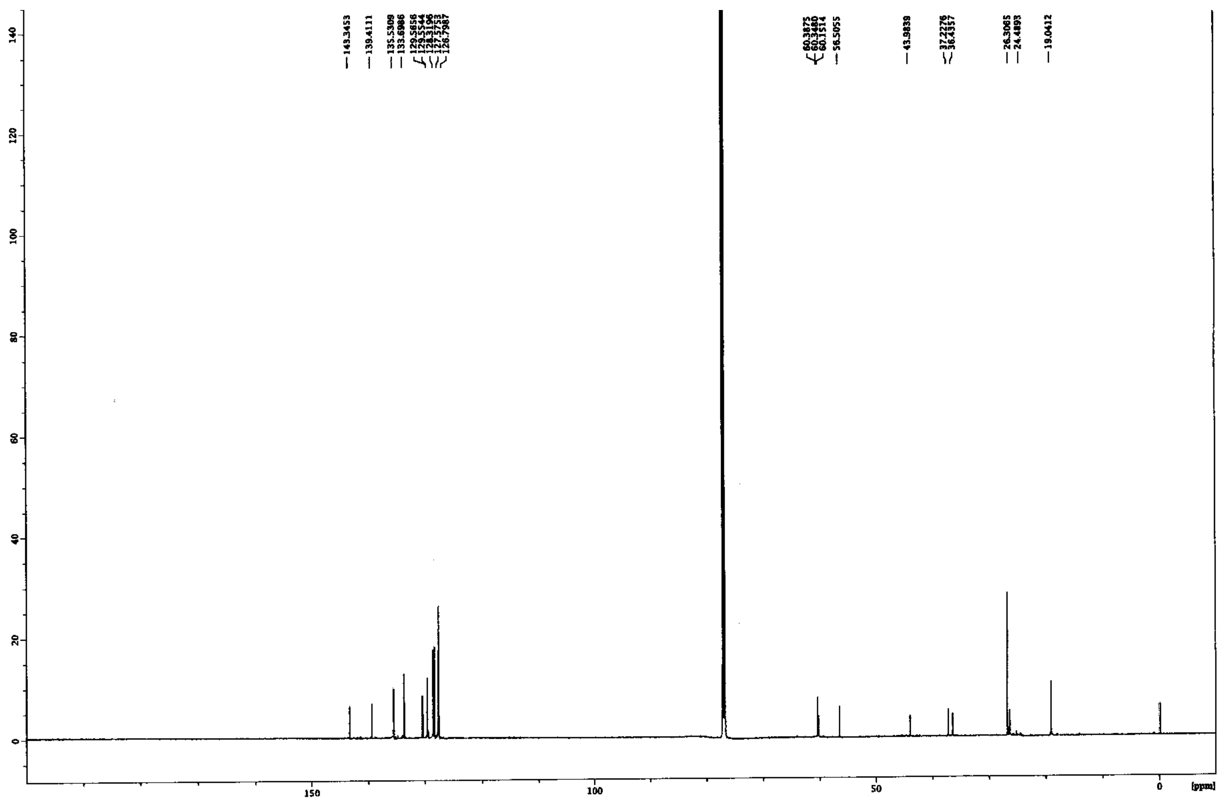

O
O
S
t-Bu
N
H
HO
HO
8
6
4
2
0
[ppm]

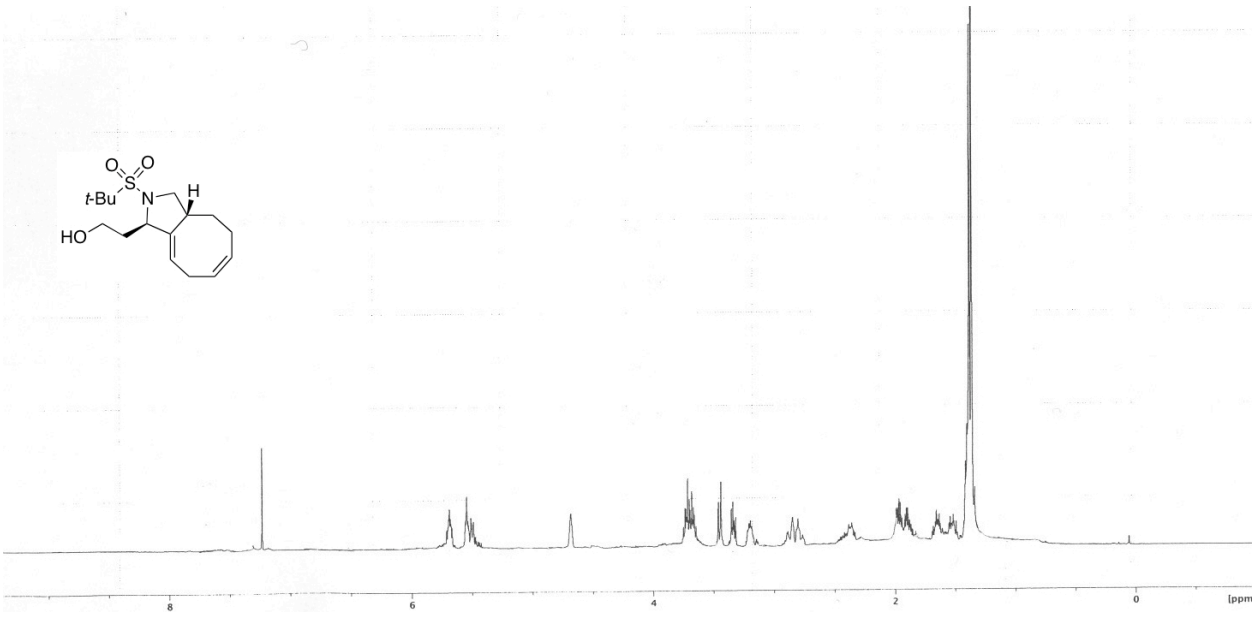

O
O
S
t-Bu
N
H
HO
Ph
8
6
4
2
0
[ppm]

c. Evans butadiene [4+2+2] cycloaddition products (*R*-20)

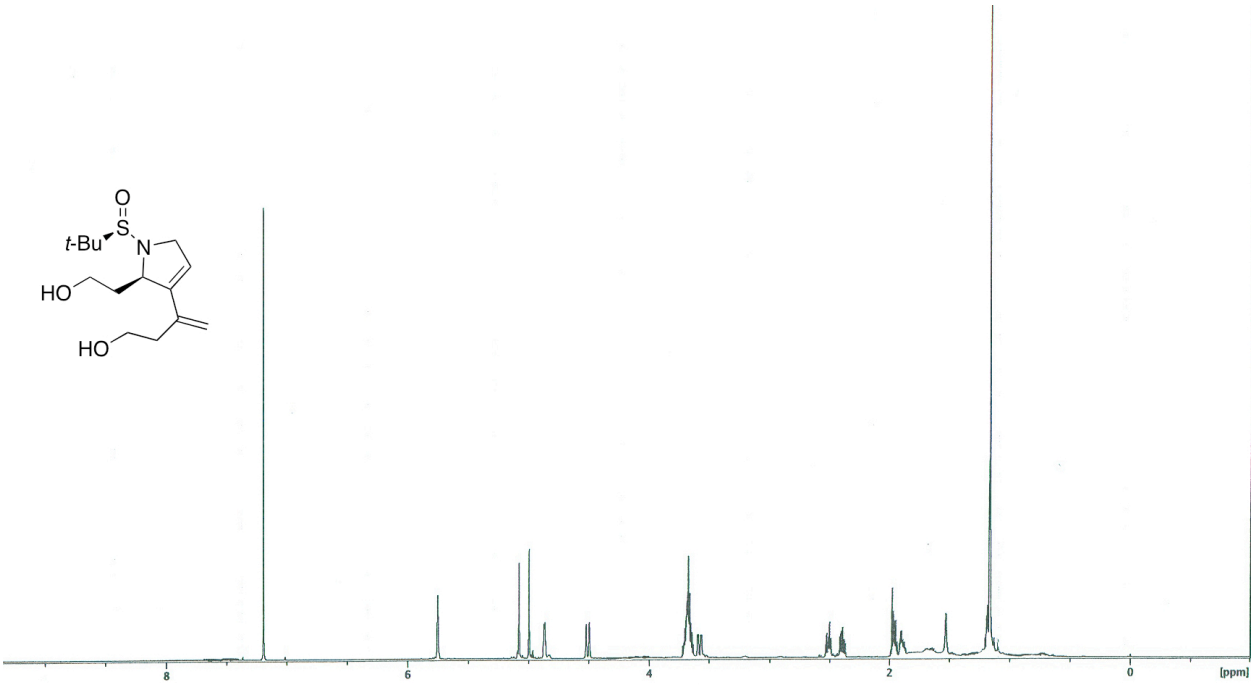


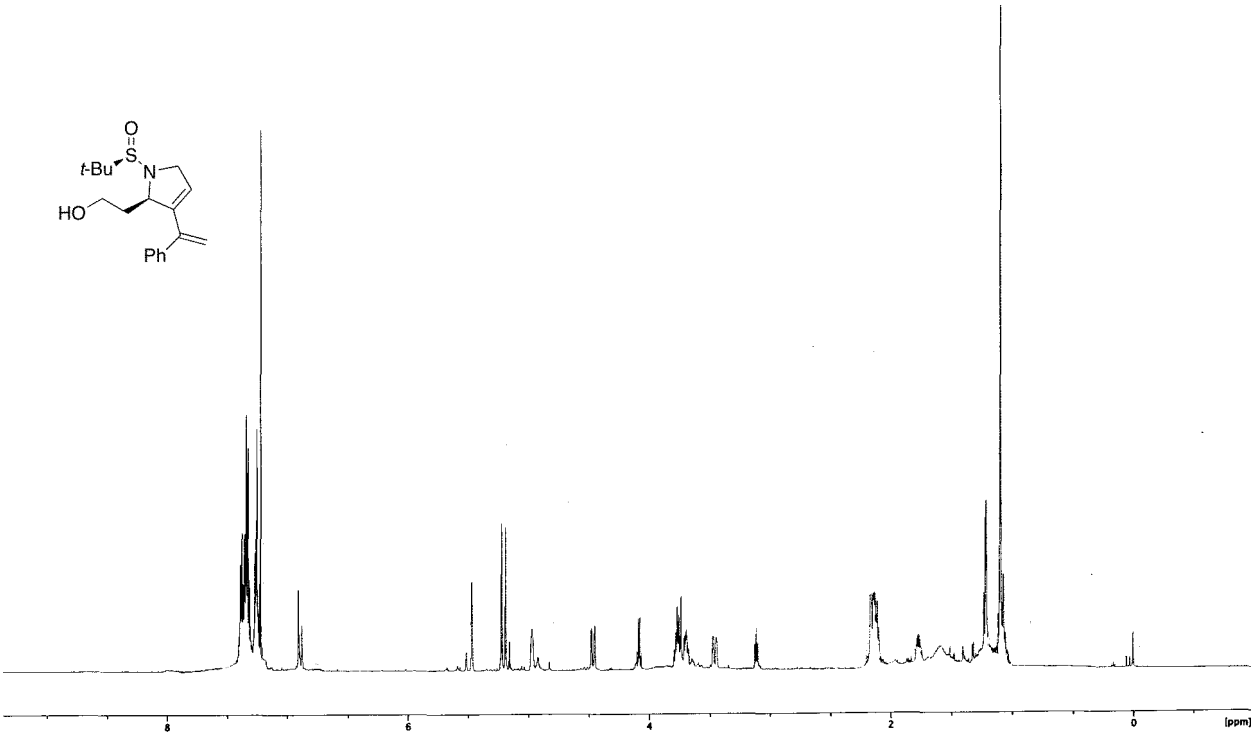

O
O
S
t-Bu
N
H
HO
Ph
[ppm]

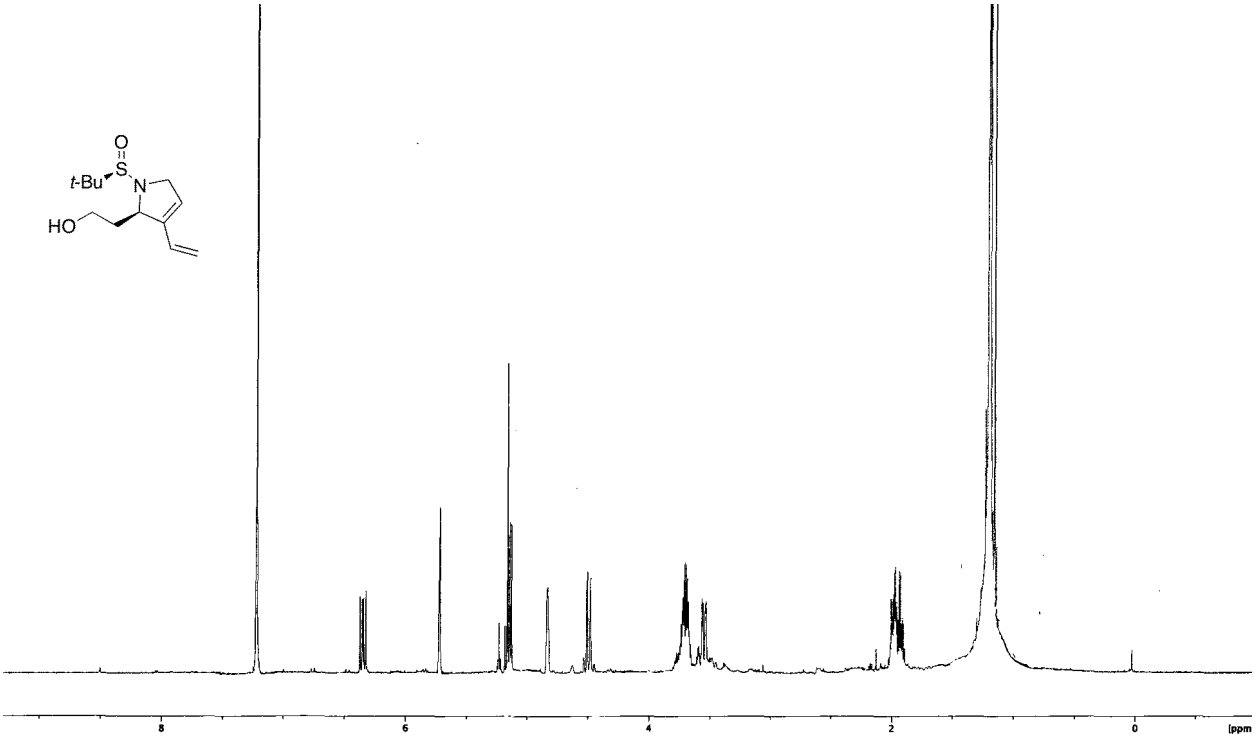

[ppm]

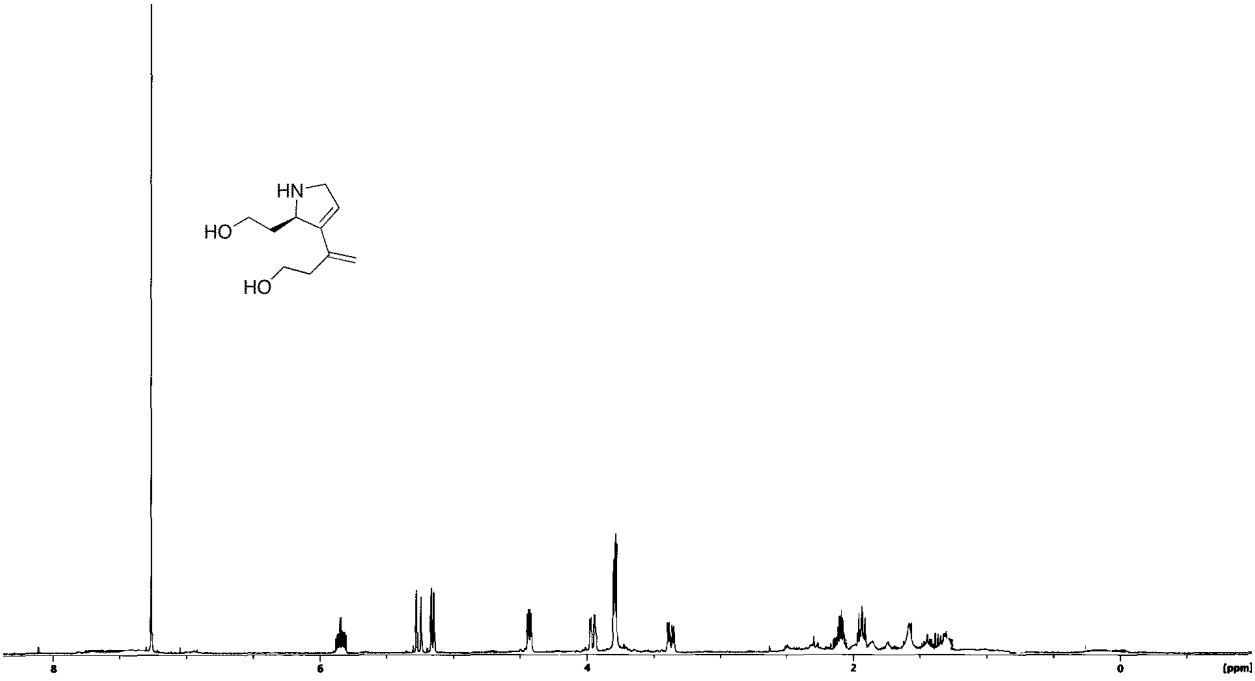

O
O
S
t-Bu
N
H
HO
8
6
4
2
0
[ppm

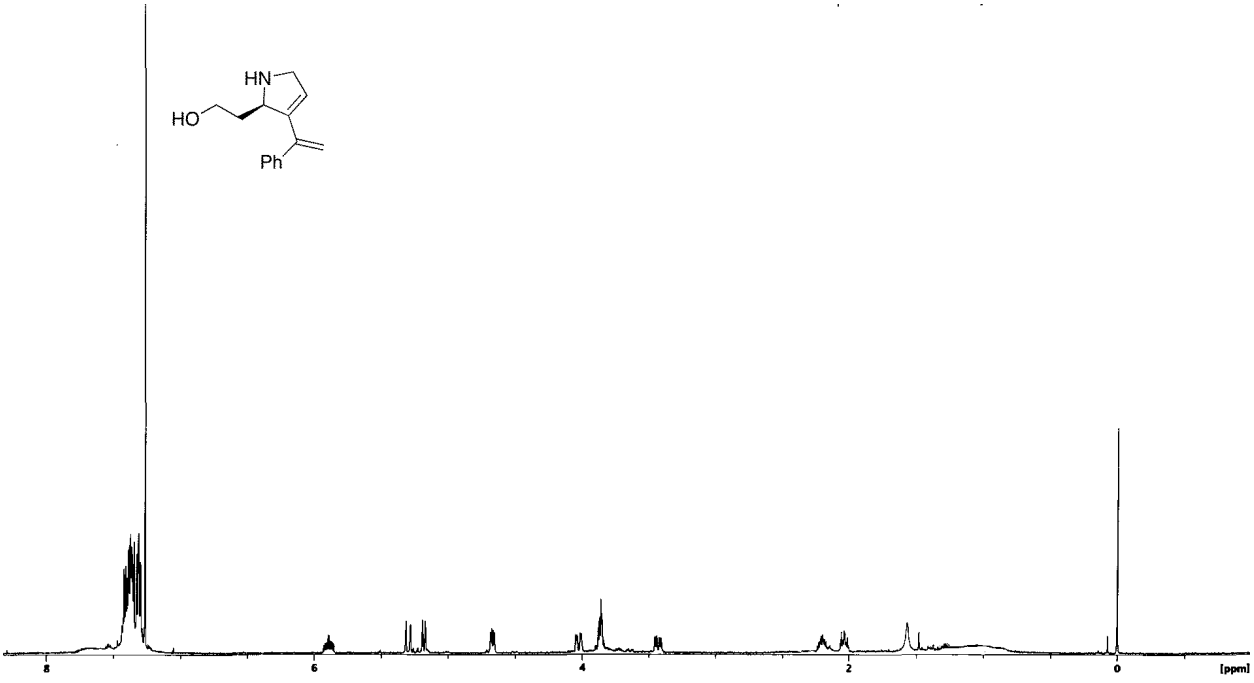
d. Enyne metathesis products (*R*-21–23)

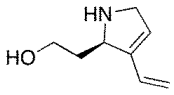


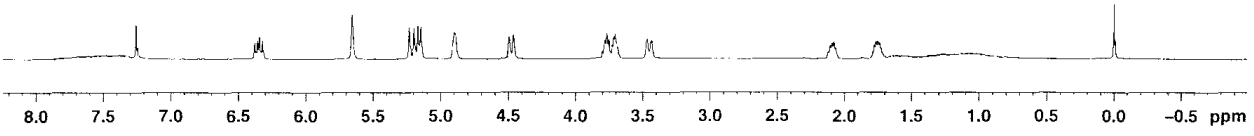


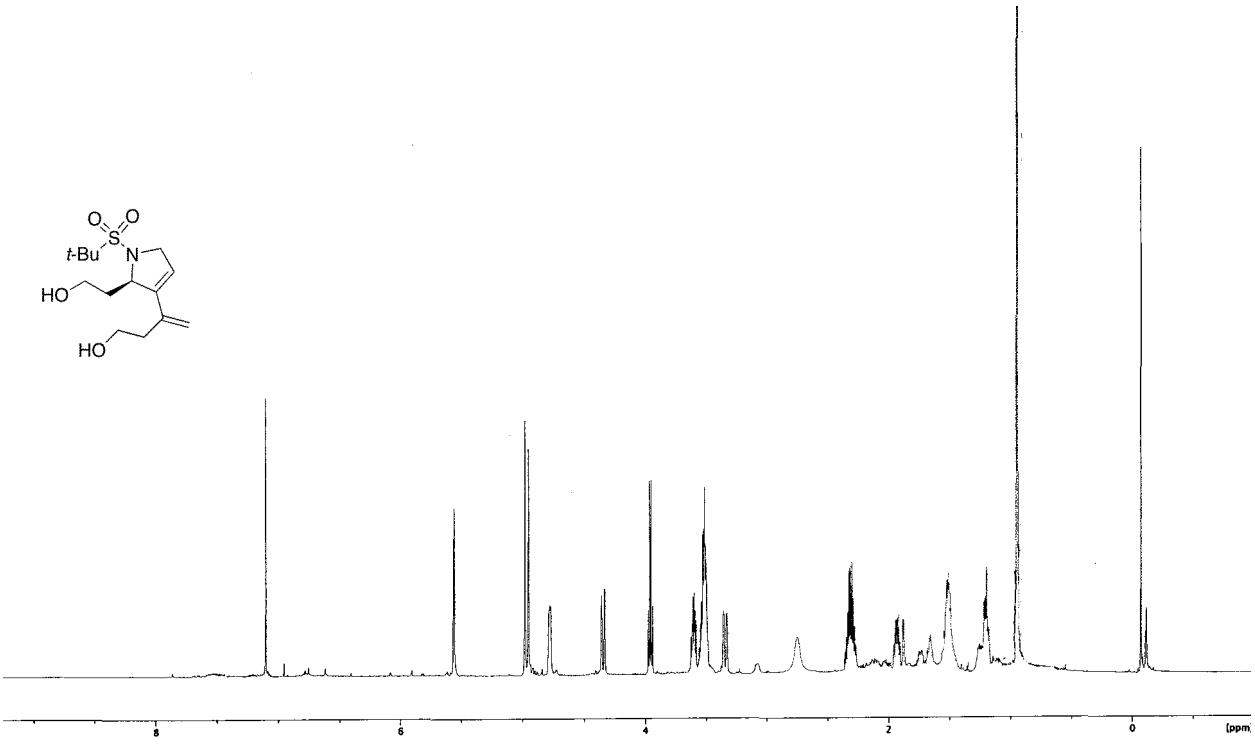

O
S
t-Bu
N
HO
8
6
4
2
0
(ppm

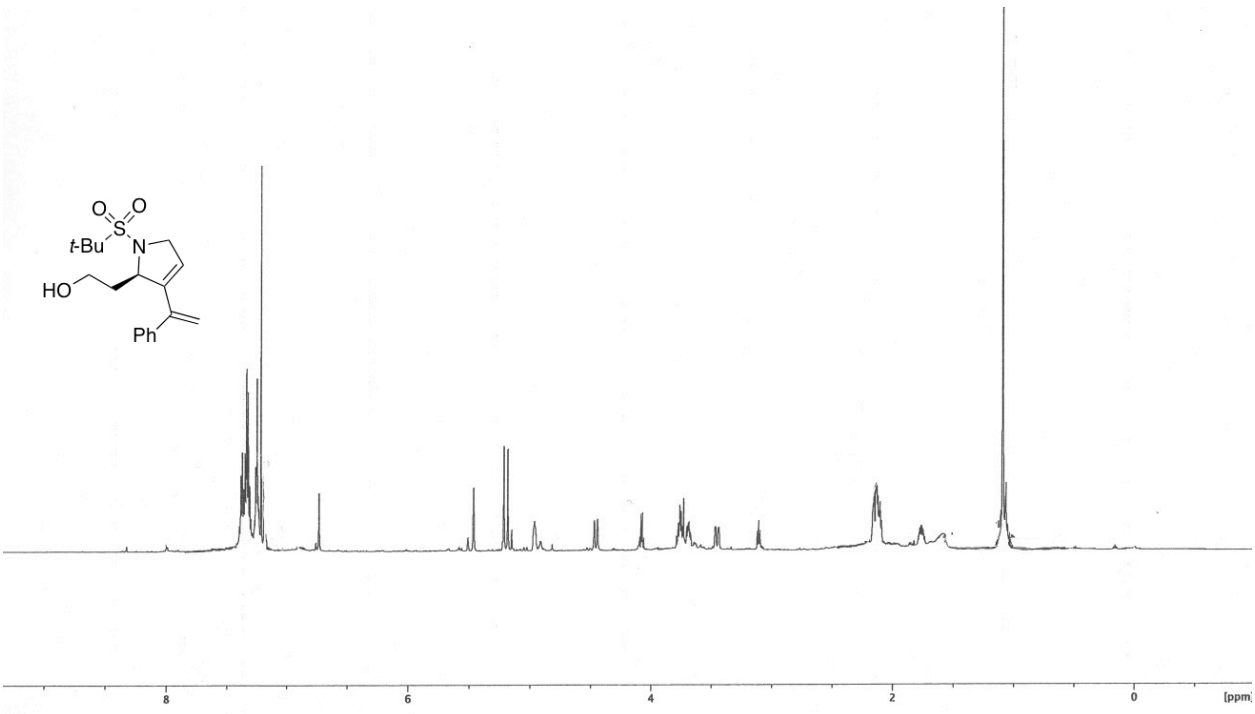

HN
HO
HO
8
6
4
2
0
(ppm)

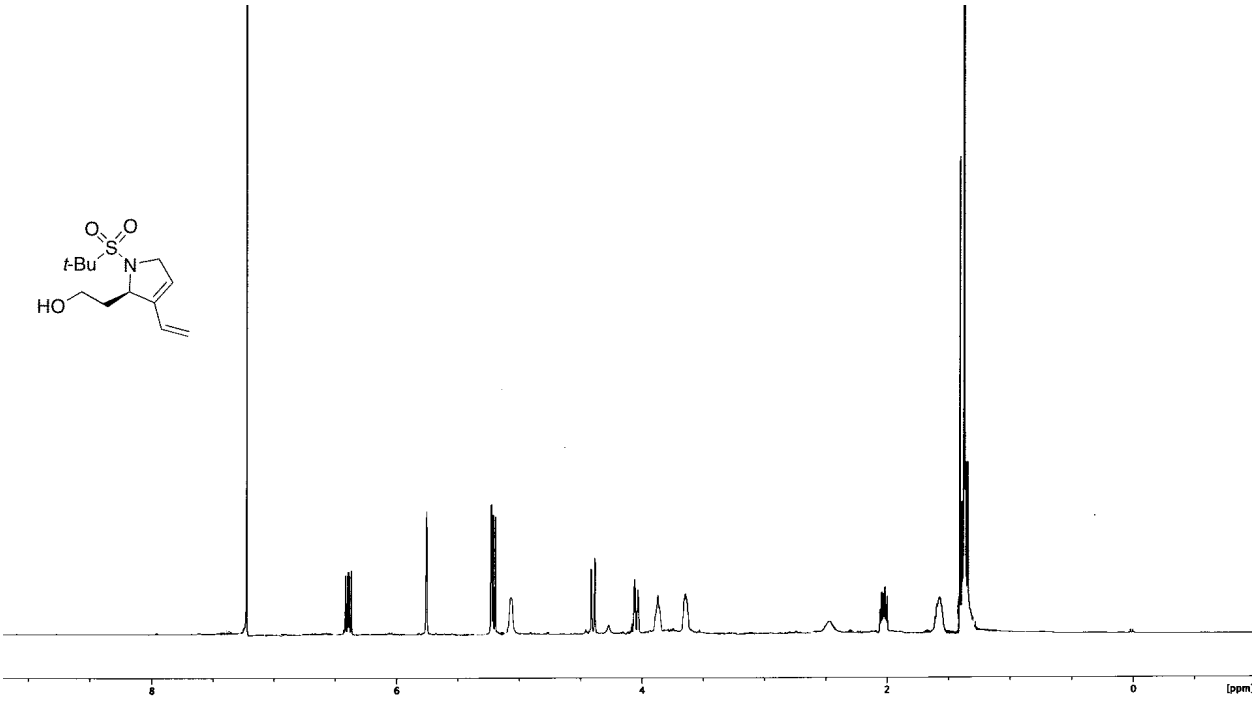

HN
HO
Ph
8
6
4
2
0
[ppm]

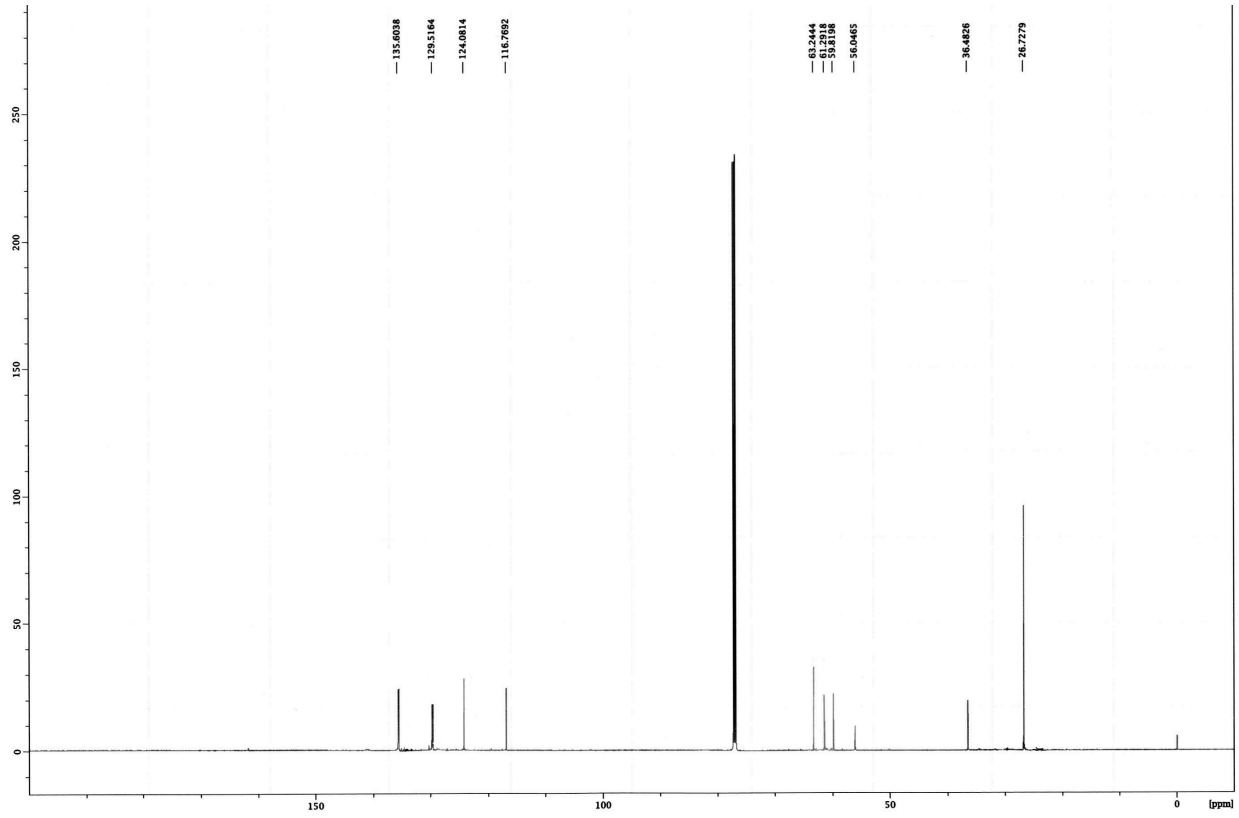

HN
HO


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
−0.5 ppm

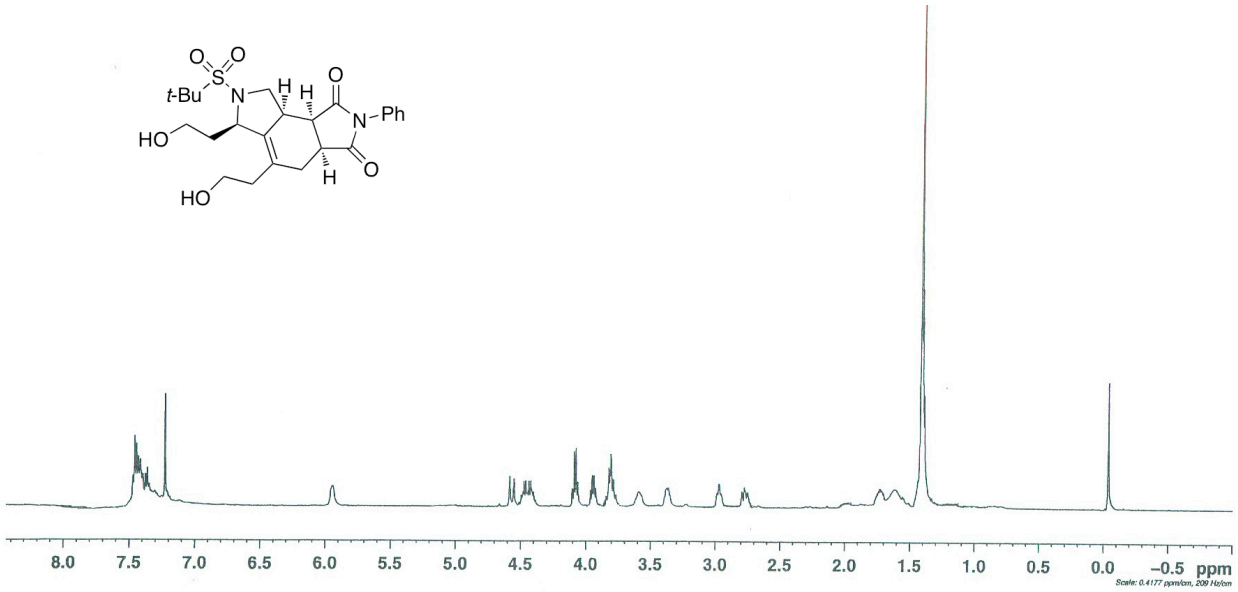

O
O
S
t-Bu
N
HO
HO
8
6
4
2
0
[ppm]

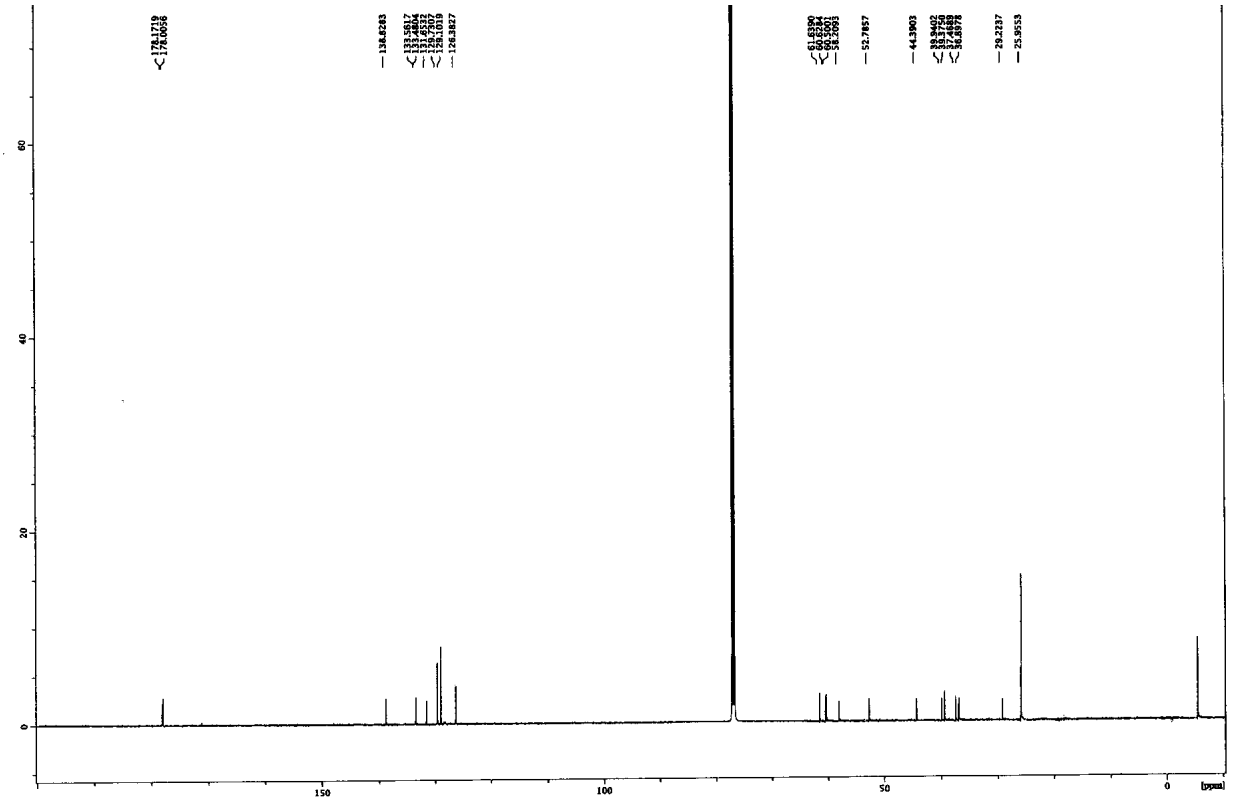

O
O
S
t-Bu
N
HO
Ph
8
6
4
2
0
[ppm]

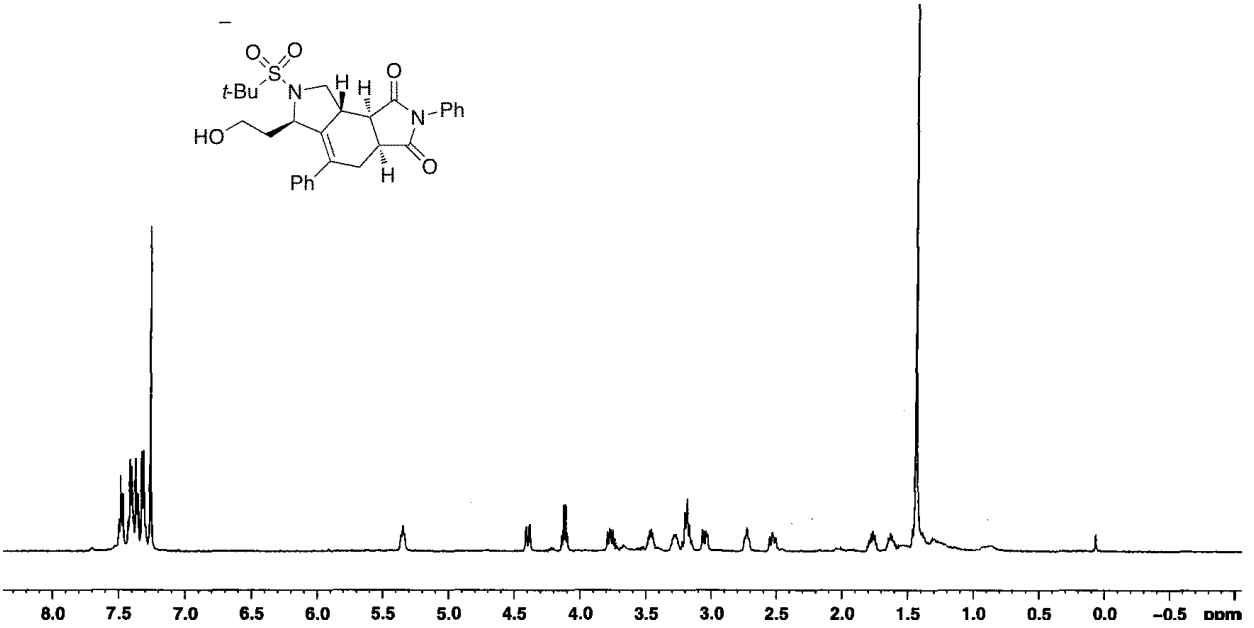

O
O
S
t-Bu
N
HO
8
6
4
2
0
[ppm]

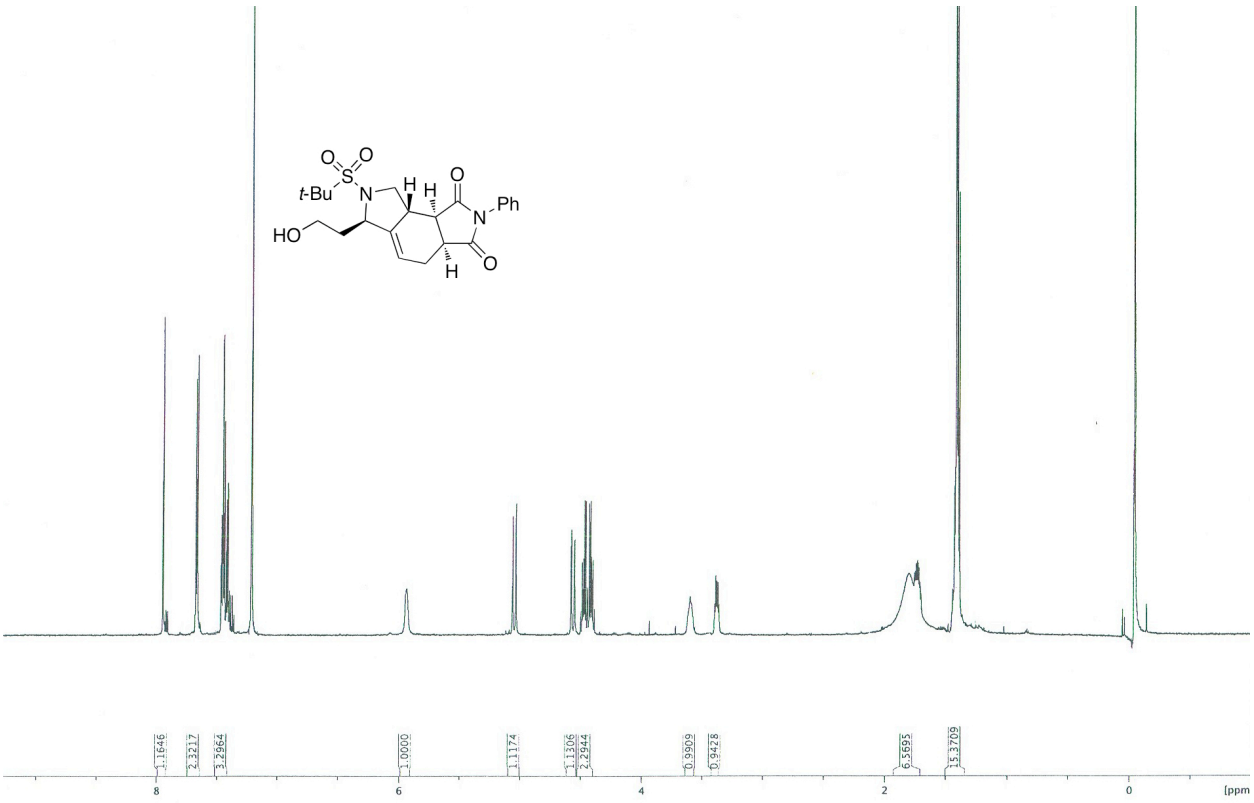

135.6038
129.5164
124.0814
116.7692
63.2444
61.2318
59.8198
56.0465
36.4826
26.7279
250
200
150
100
50
0
150
100
50
0
[ppm]

e. Maleimide Diels–Alder products (*R*-24)

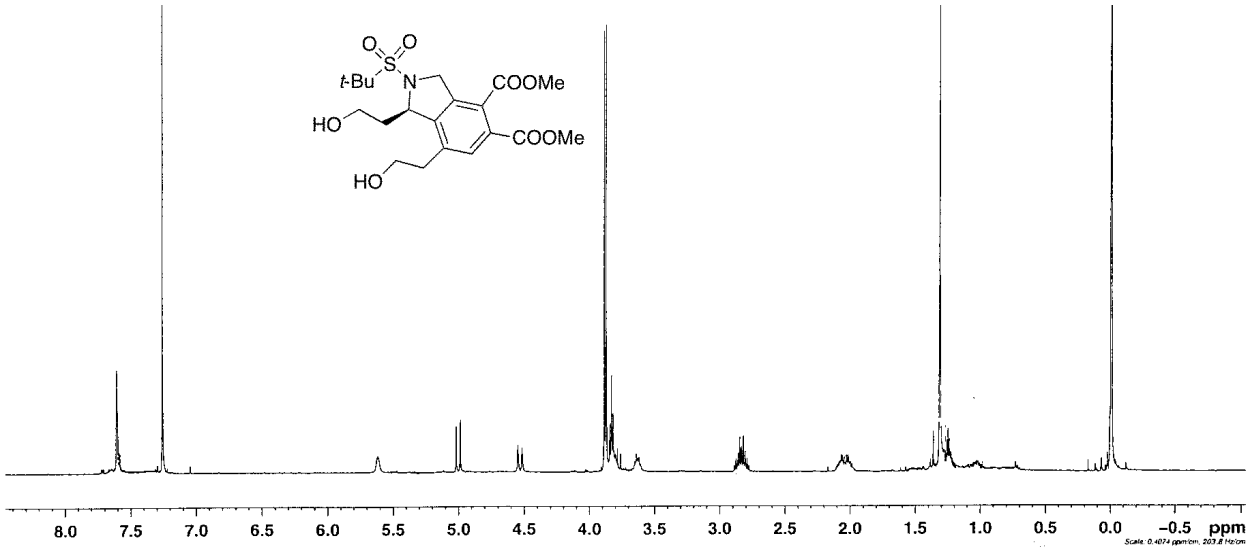


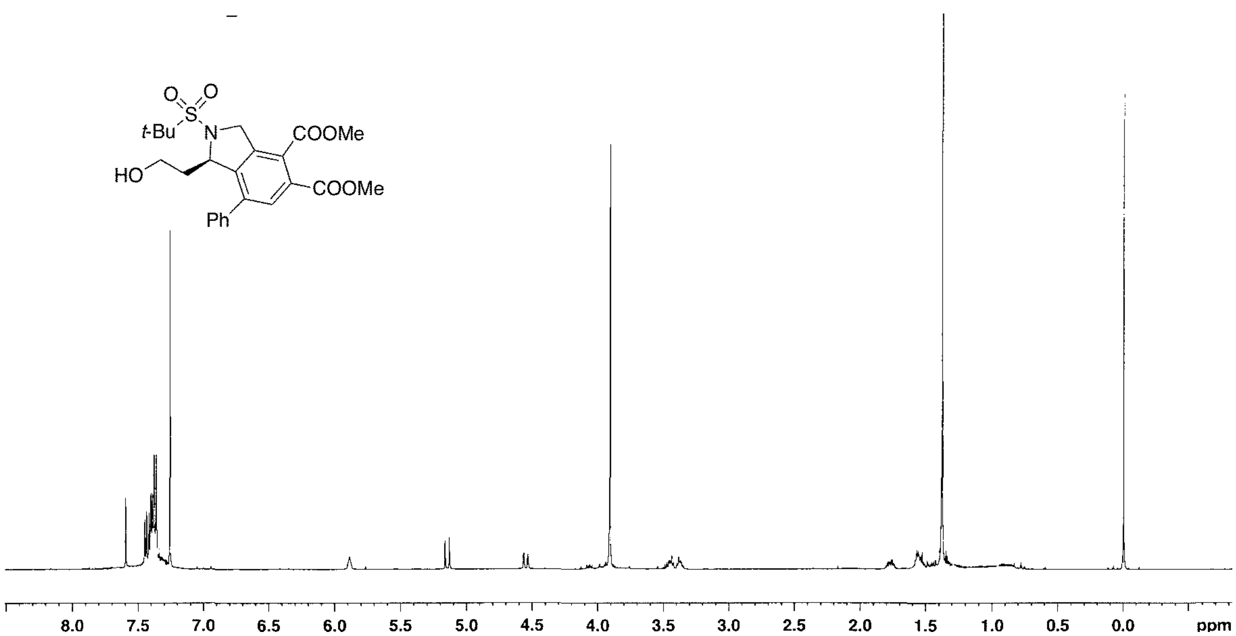


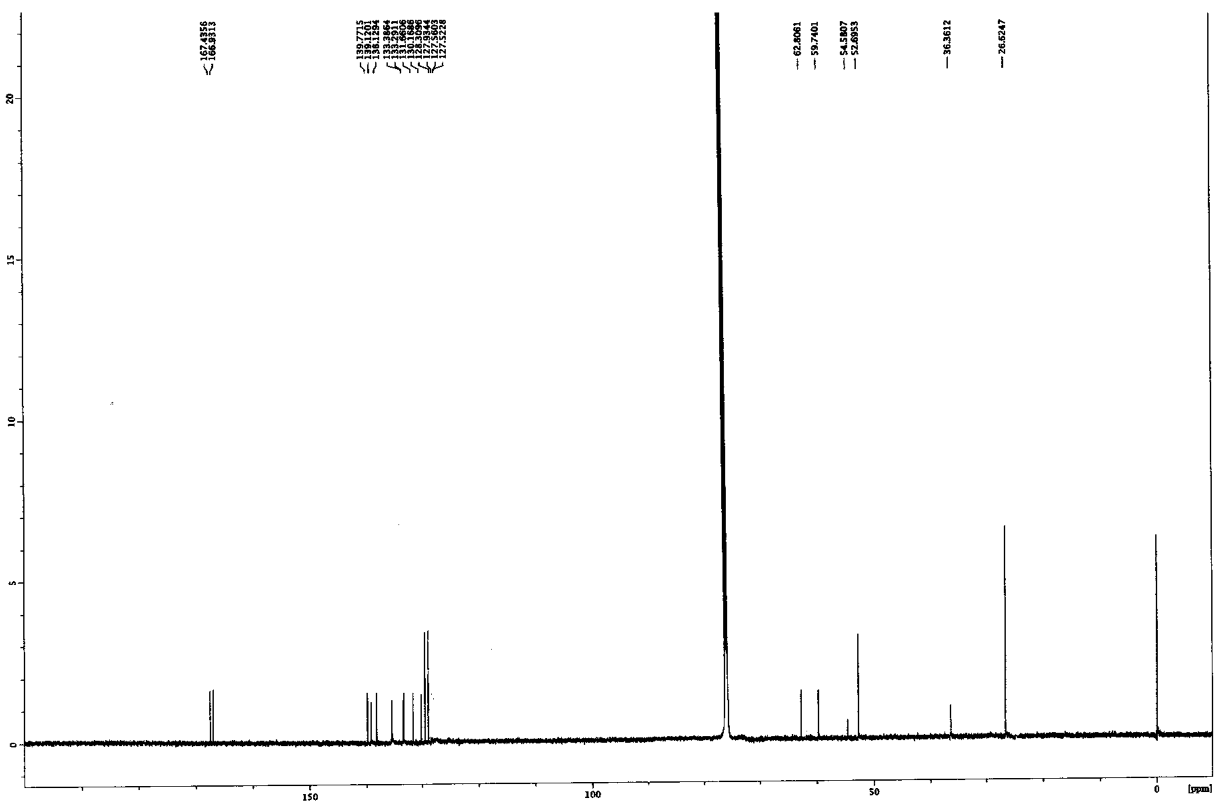

t-Bu
HO
Ph
N-Ph
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

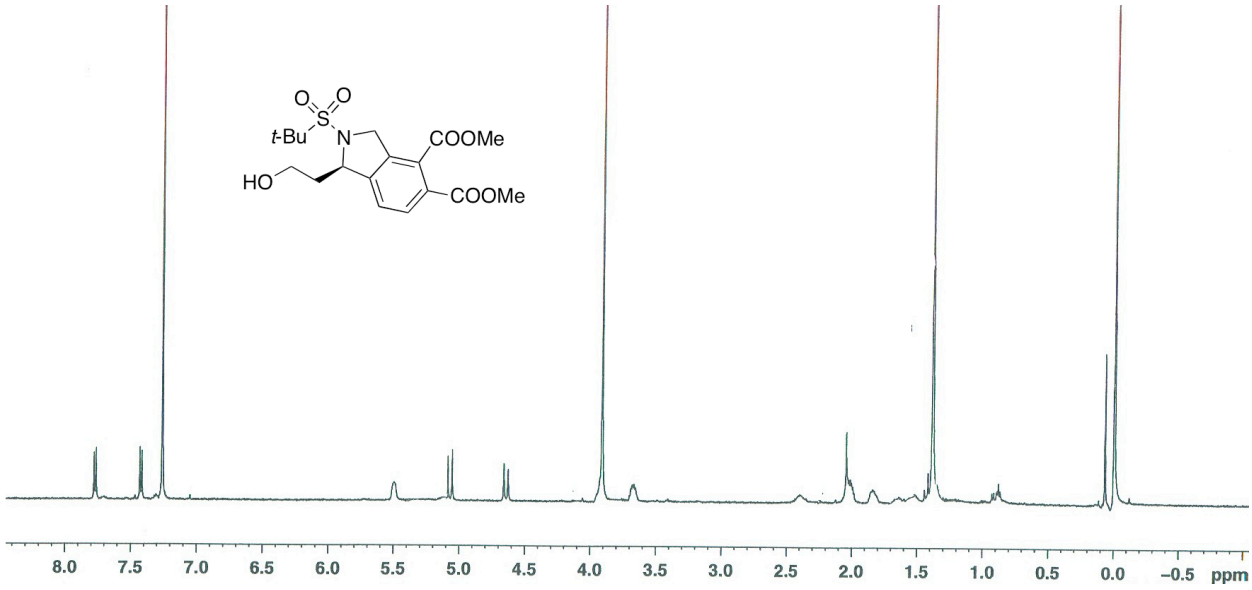

t-Bu
HO
Ph
1.1646
2.3217
3.2964
1.0000
1.1174
1.1306
2.2944
0.9909
0.9428
6.5695
15.3709
8
6
4
2
0
[ppm]

f. DMAD Diels–Alder products (*R*-25)

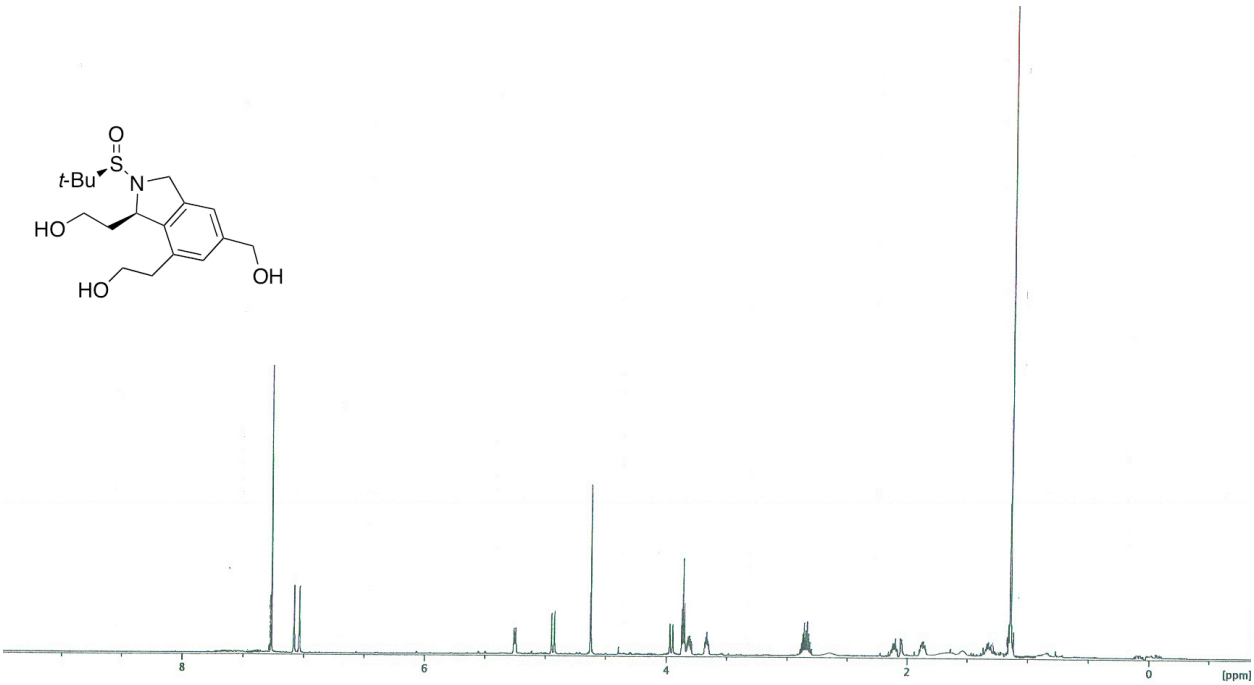


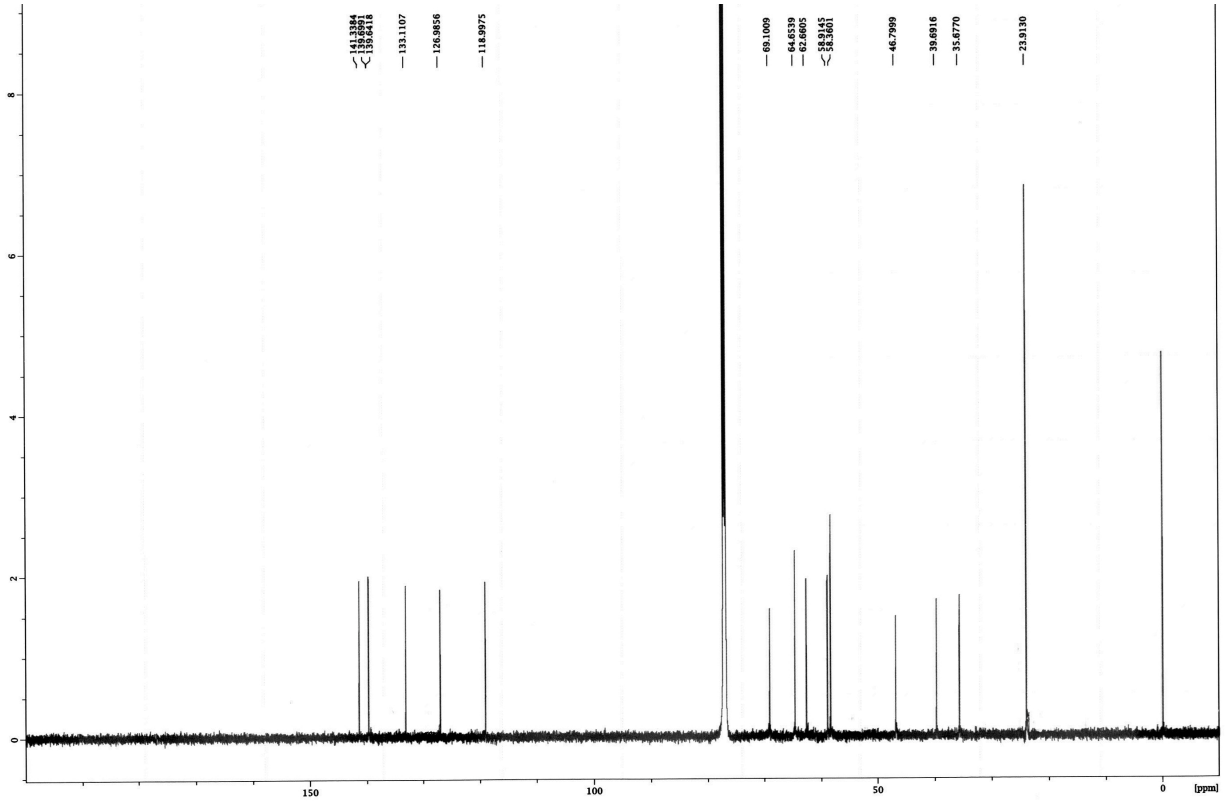

O
O
S
t-Bu
N
COOMe
HO
COOMe
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

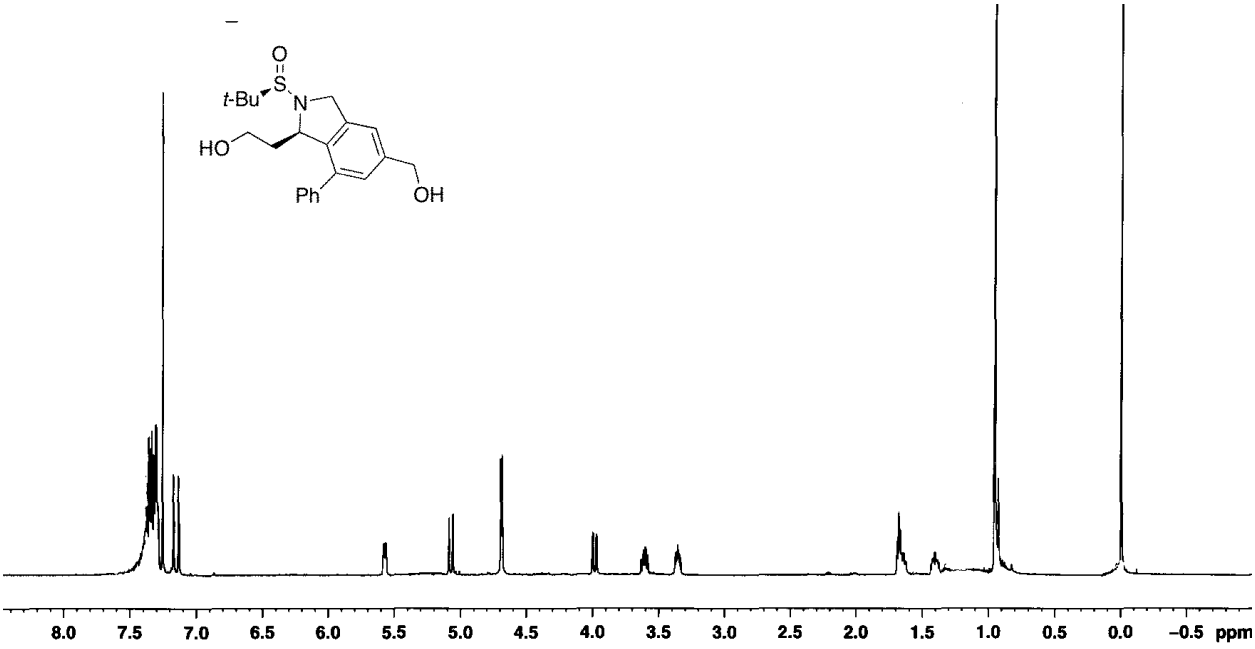

150
100
50
0
[ppm]

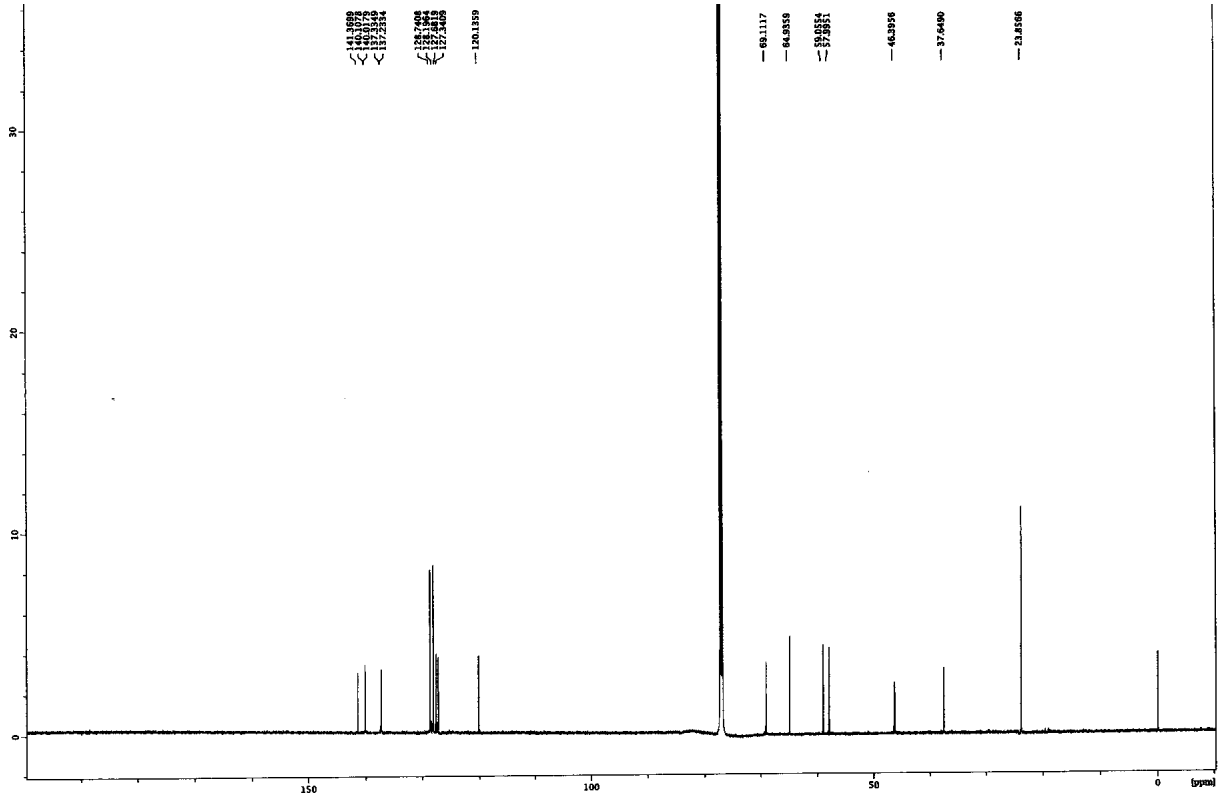

O
O
S
t-Bu
N
COOMe
HO
COOMe
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
ppm

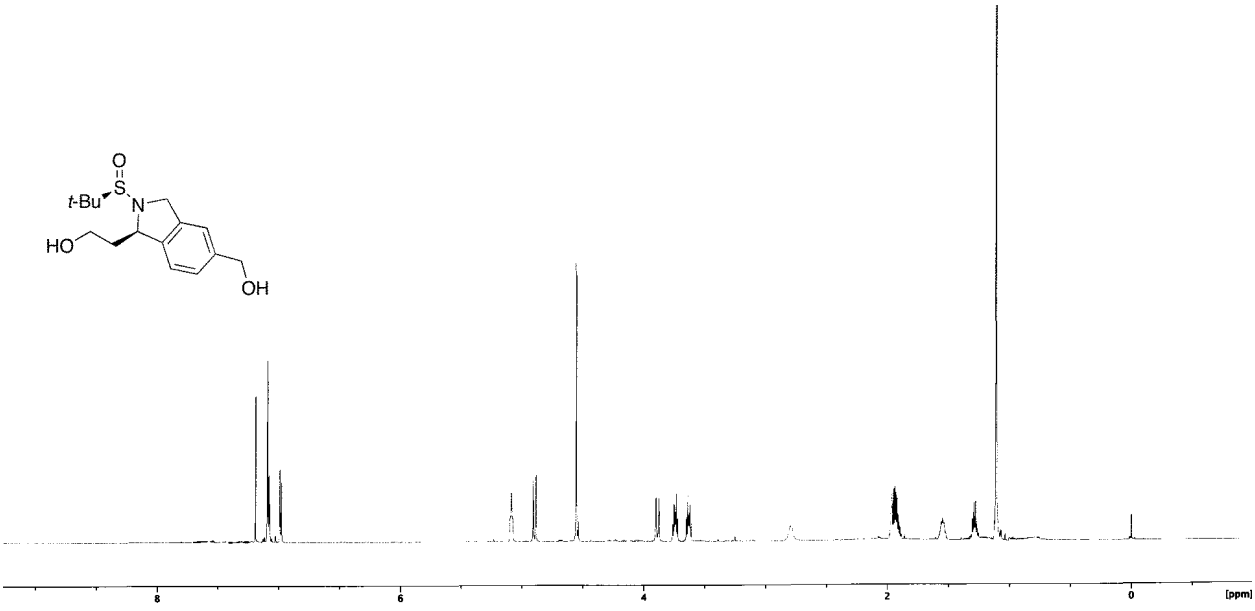
g. Alkyne [2+2+2] cyclotrimerization products (*R*-30–35)

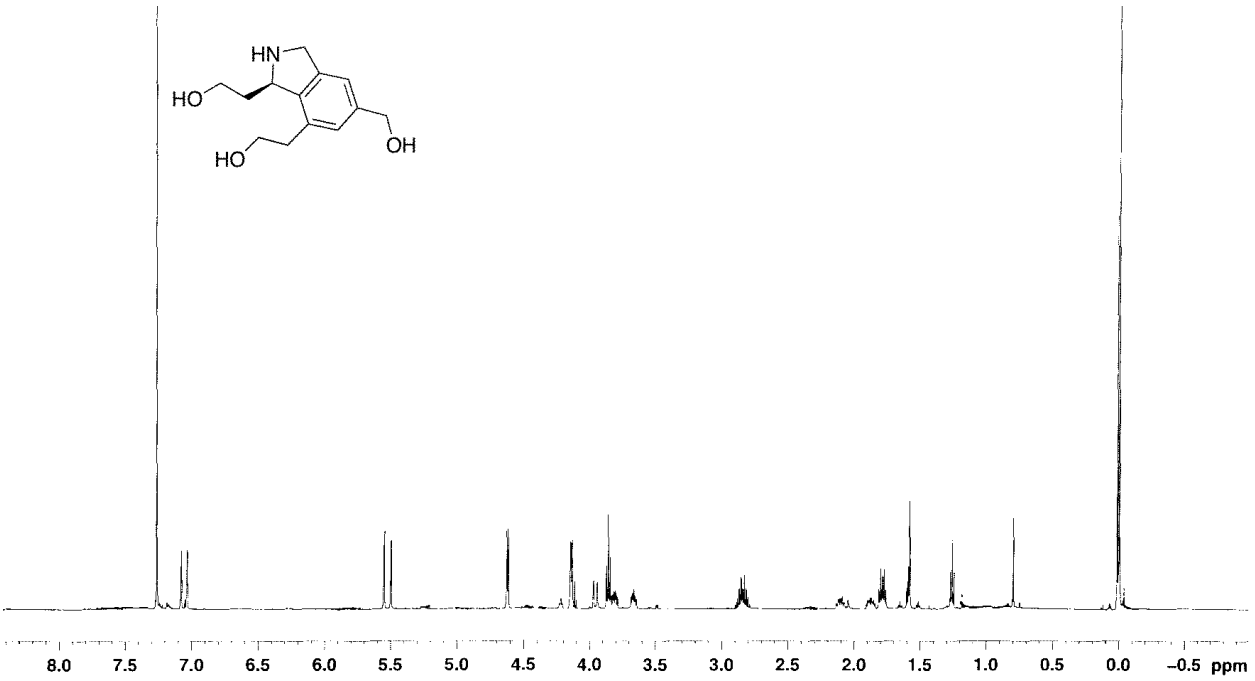


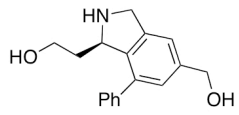


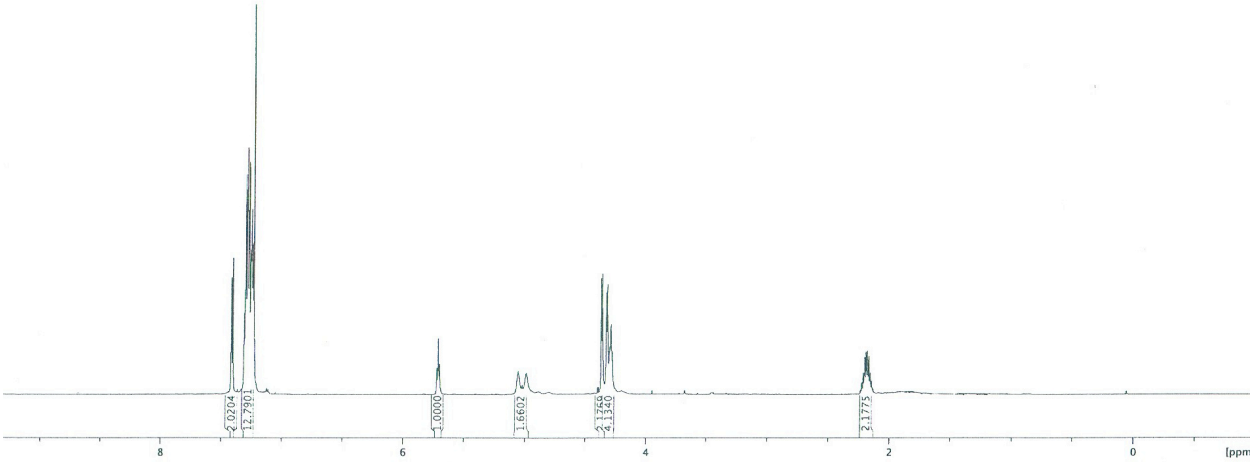

O
S
t-Bu
N
HO
Ph
OH
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
ppm

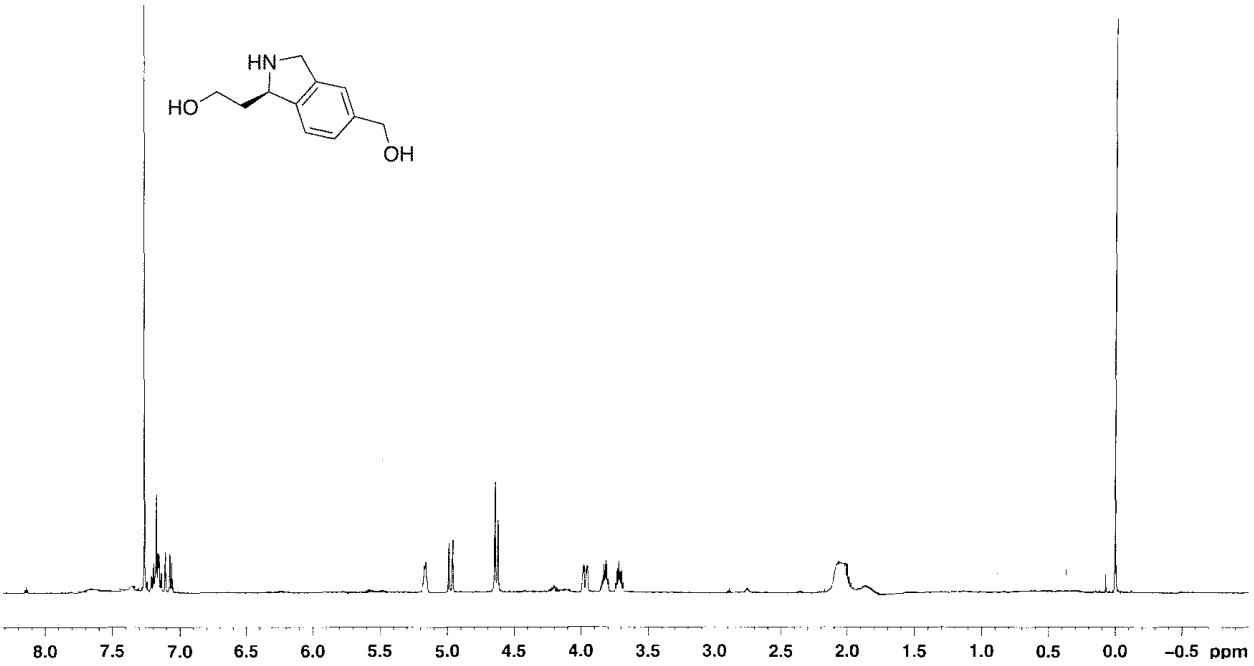

141.3689
140.0179
137.2354
128.7408
127.4819
127.3409
120.1359
69.1117
64.9359
59.0554
57.5951
46.3956
37.6490
23.8566
30
20
10
0
150
100
50
0
(ppm)

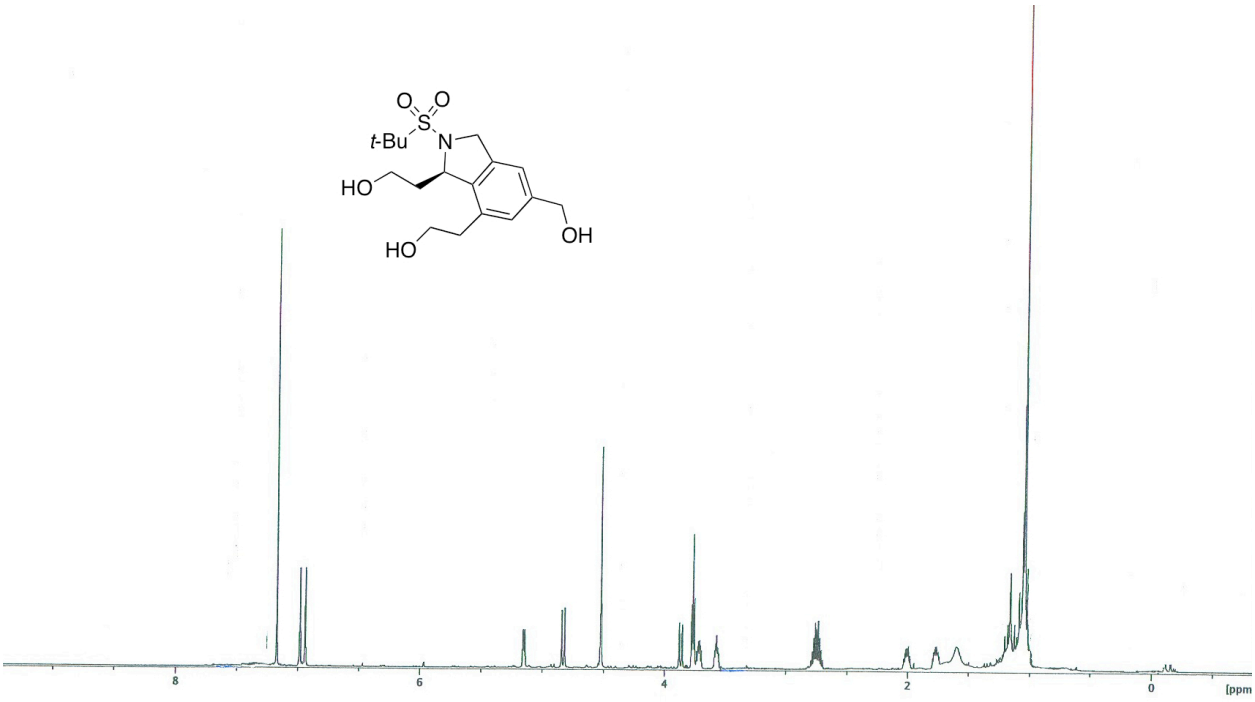

O
S
t-Bu
N
HO
OH
8
6
4
2
0
[ppm]

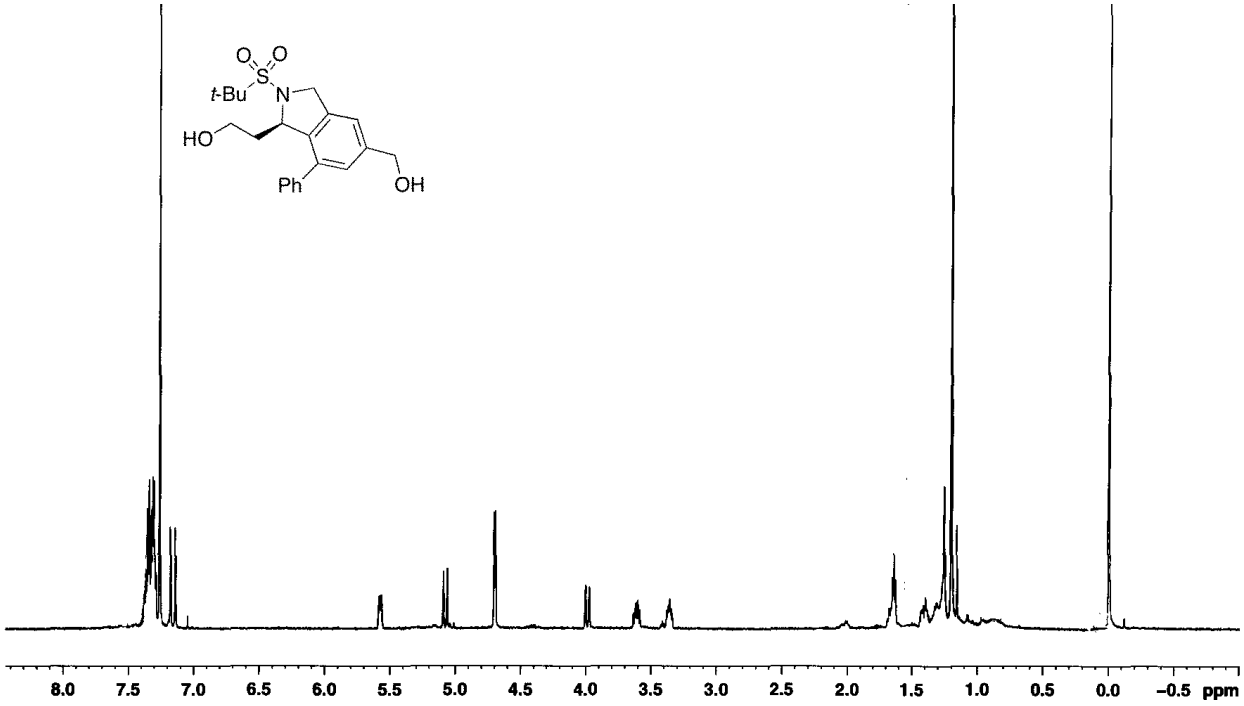

HN
HO
HO
OH
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5 ppm

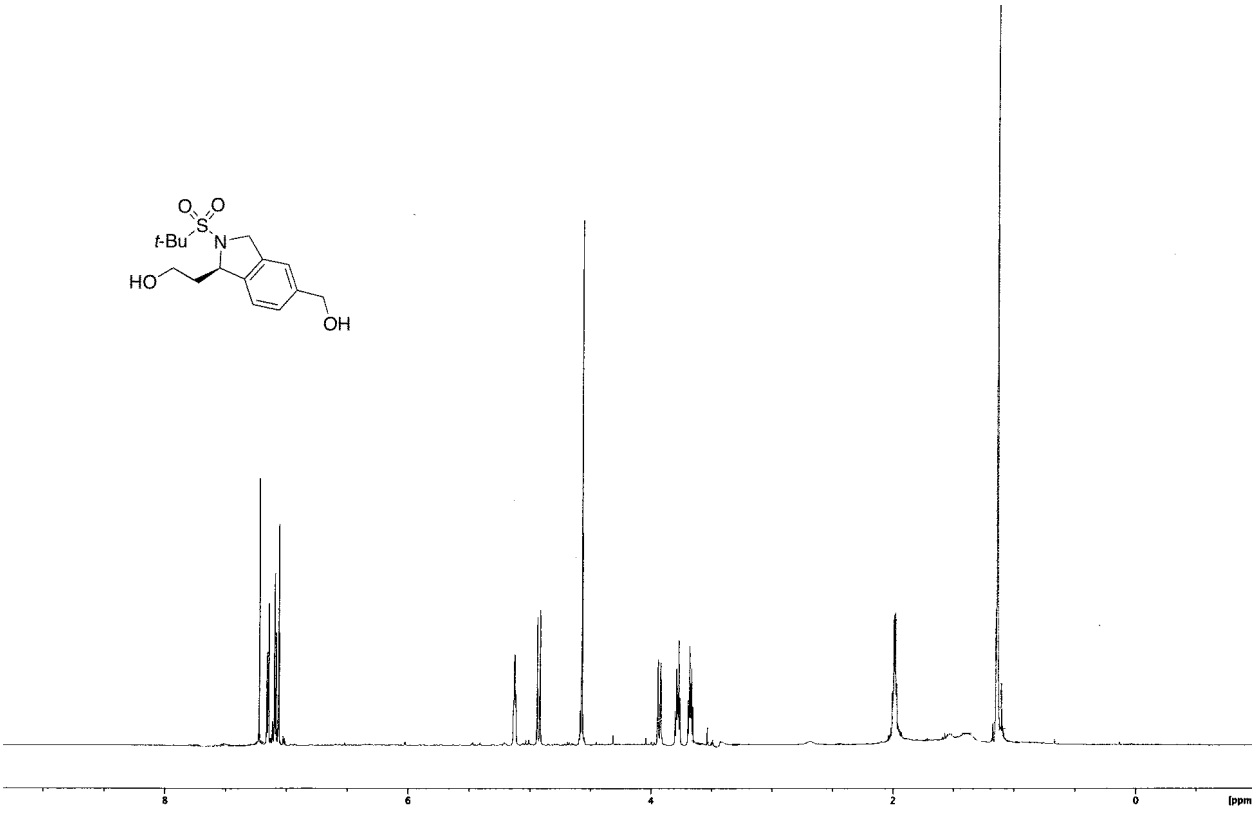

HN
HO
Ph
OH

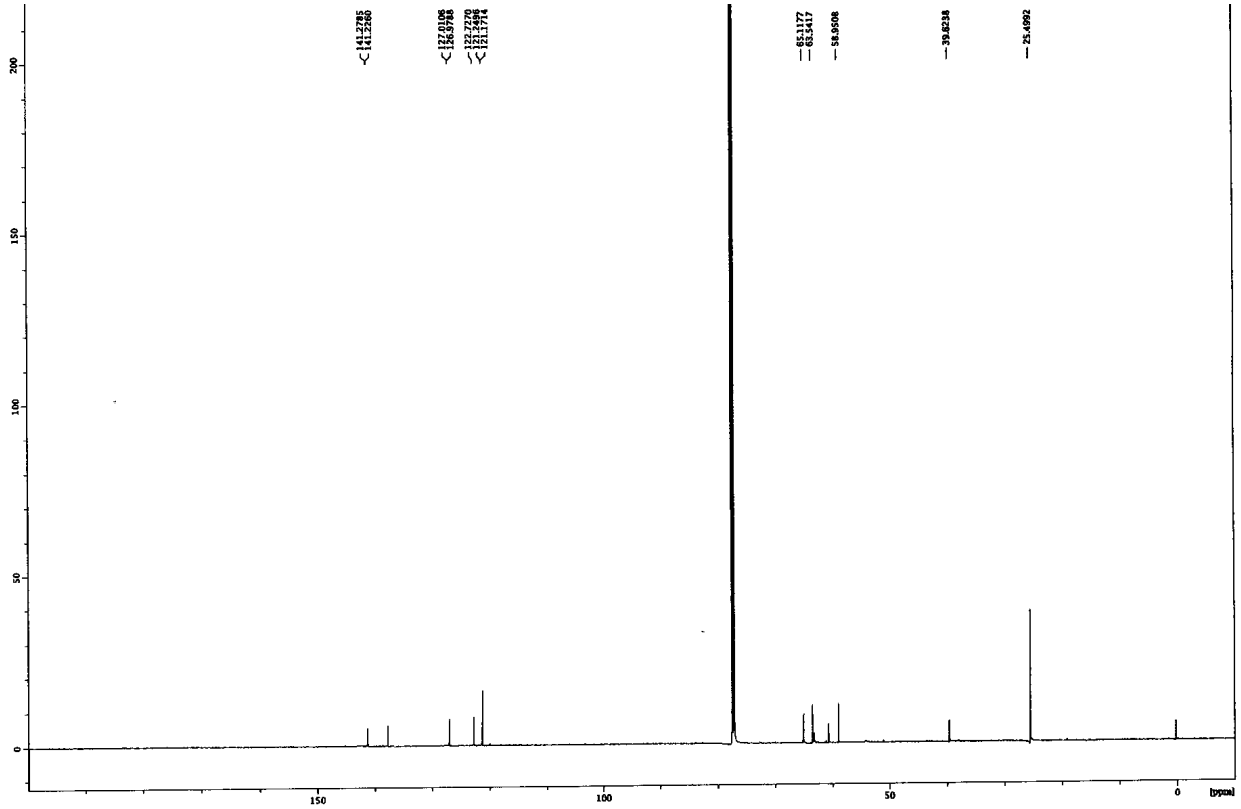

2.0204
12.7901
1.0000
1.6602
2.1769
4.1349
2.1775
8
6
4
2
0
[ppm

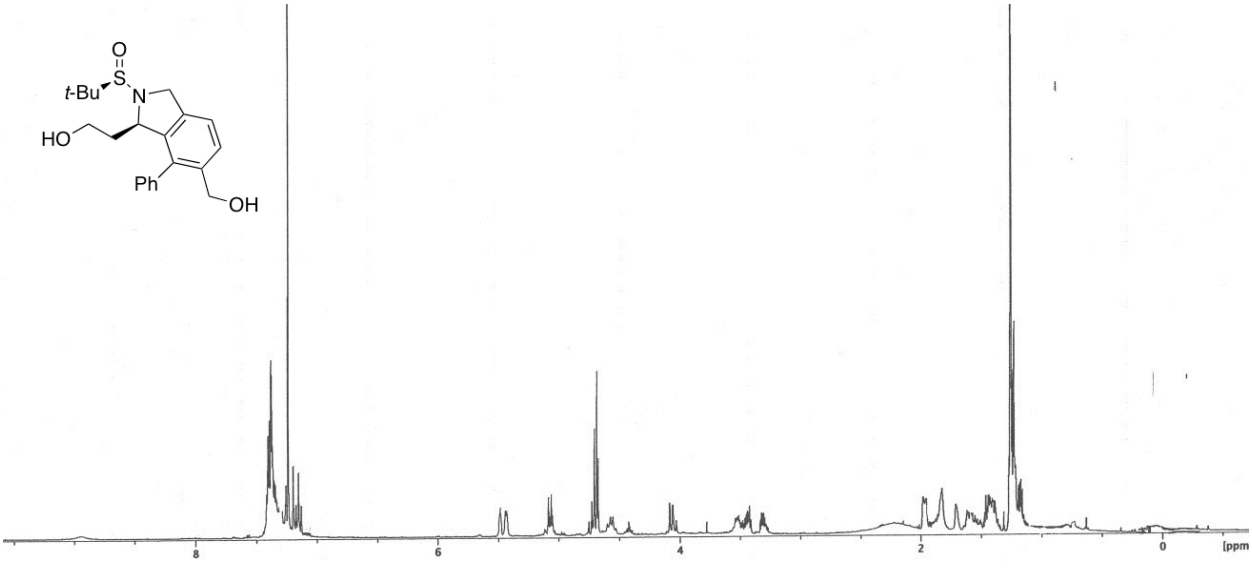

HN
HO
OH
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5 ppm

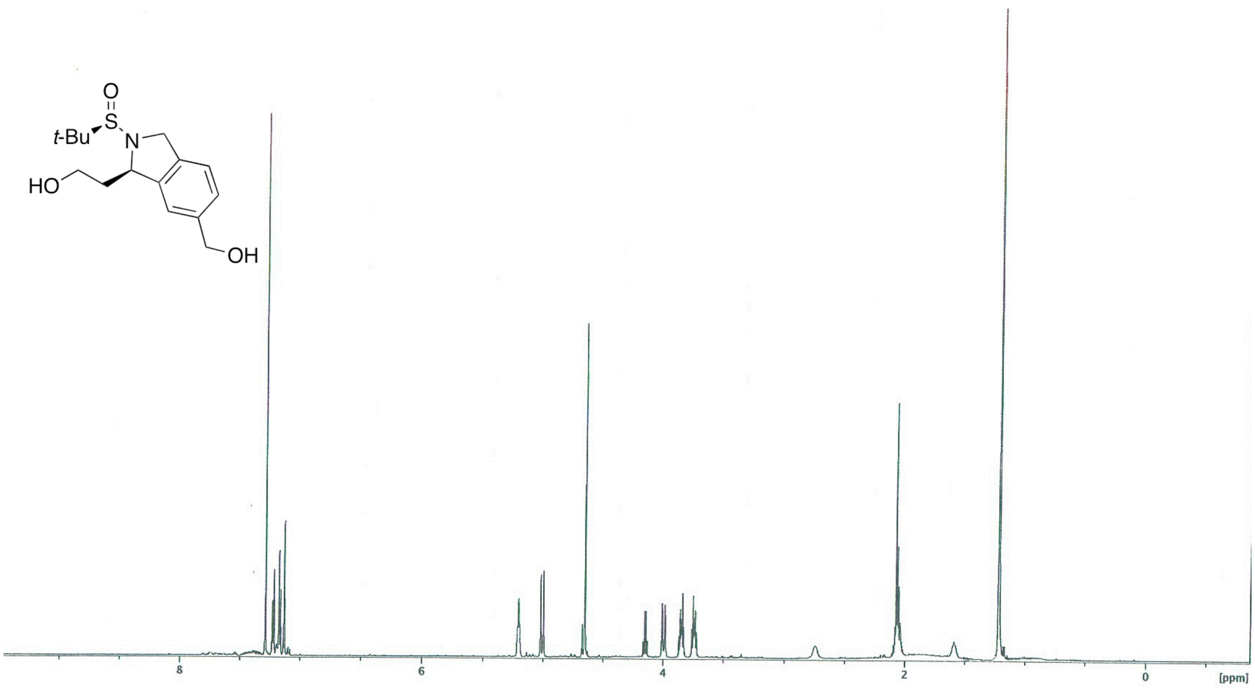

O
O
S
t-Bu
N
HO
HO
OH
8
6
4
2
0
(ppm

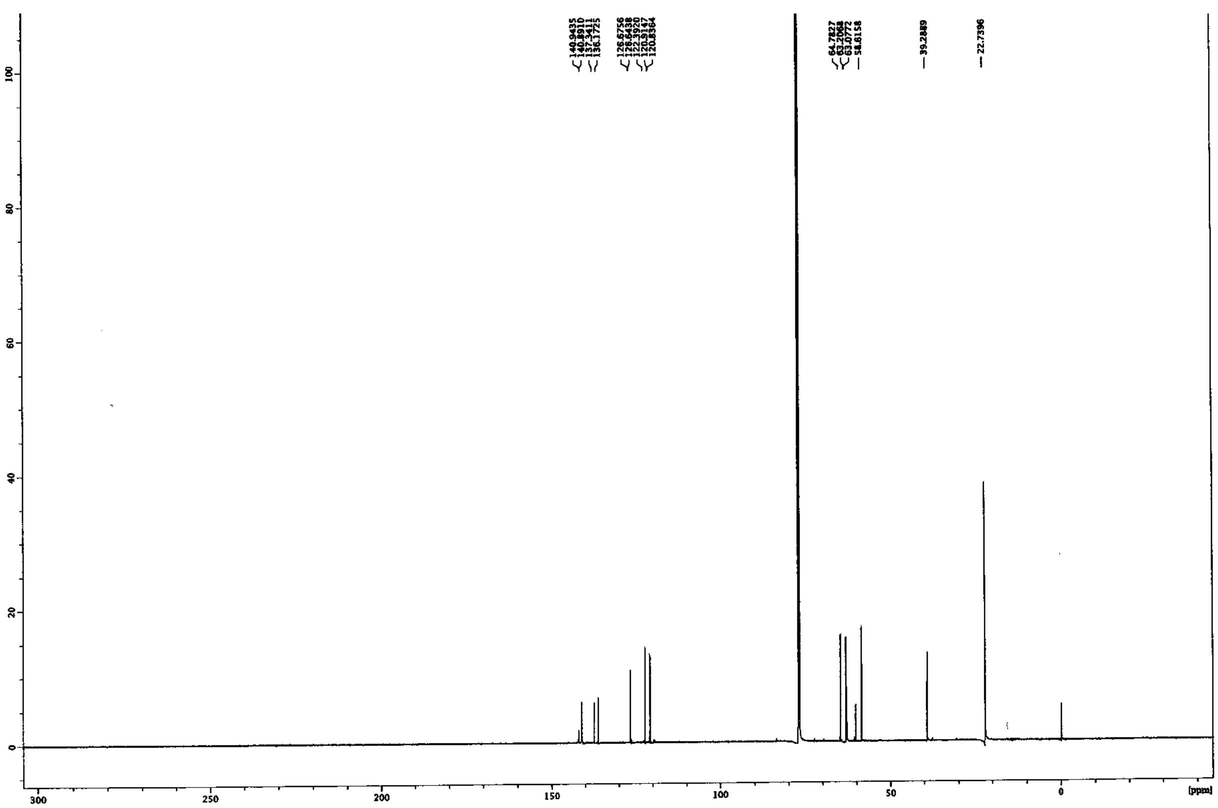

O
O
S
t-Bu
N
HO
Ph
OH
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5 ppm

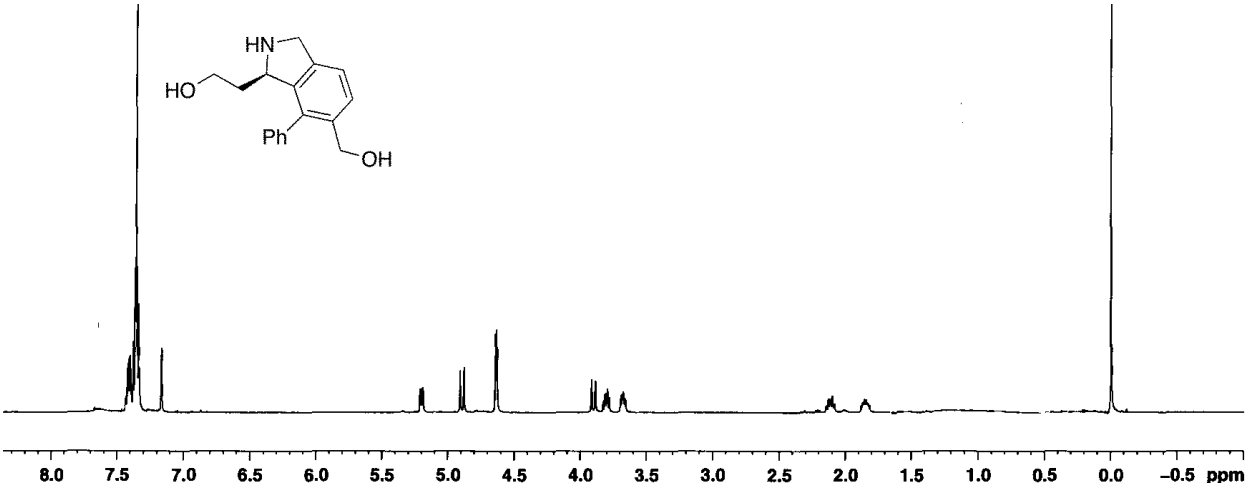

O
O
S
N
t-Bu
HO
OH
8
6
4
2
0
[ppm]

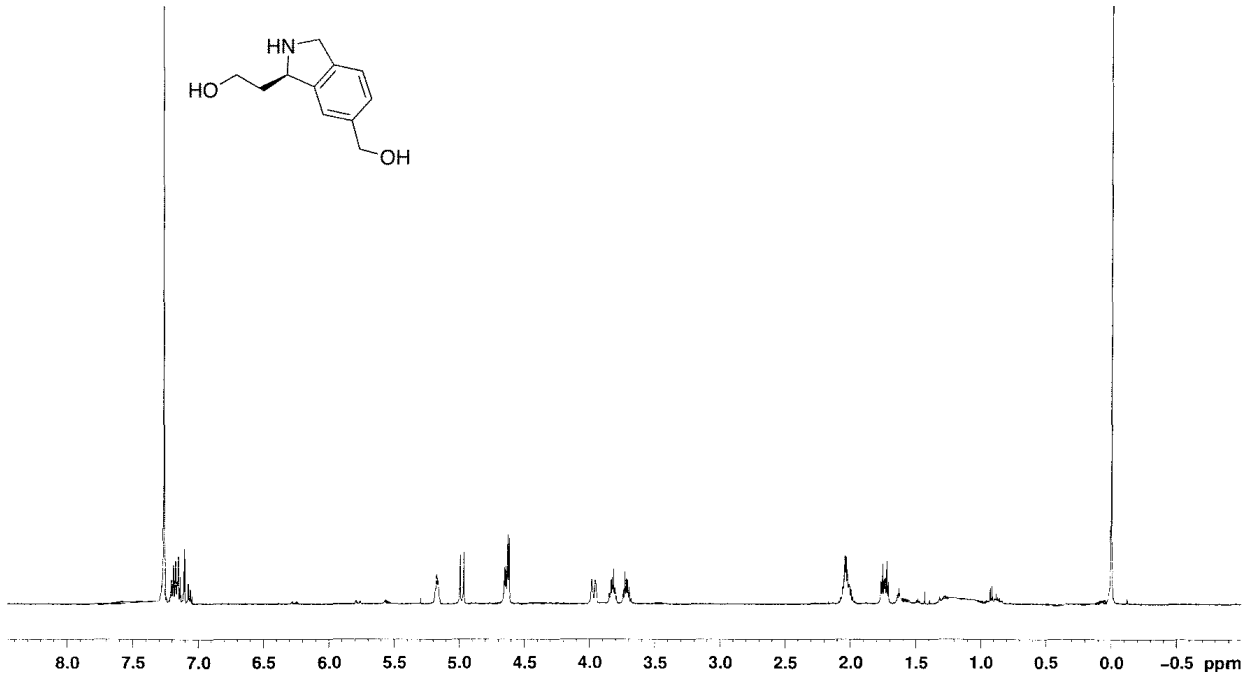

141.2785
141.2580
127.0106
126.9788
123.7270
121.2496
121.1714
65.1177
63.5417
58.9508
39.6238
25.4092
200
150
100
50
0
150
100
50
0
[ppm]

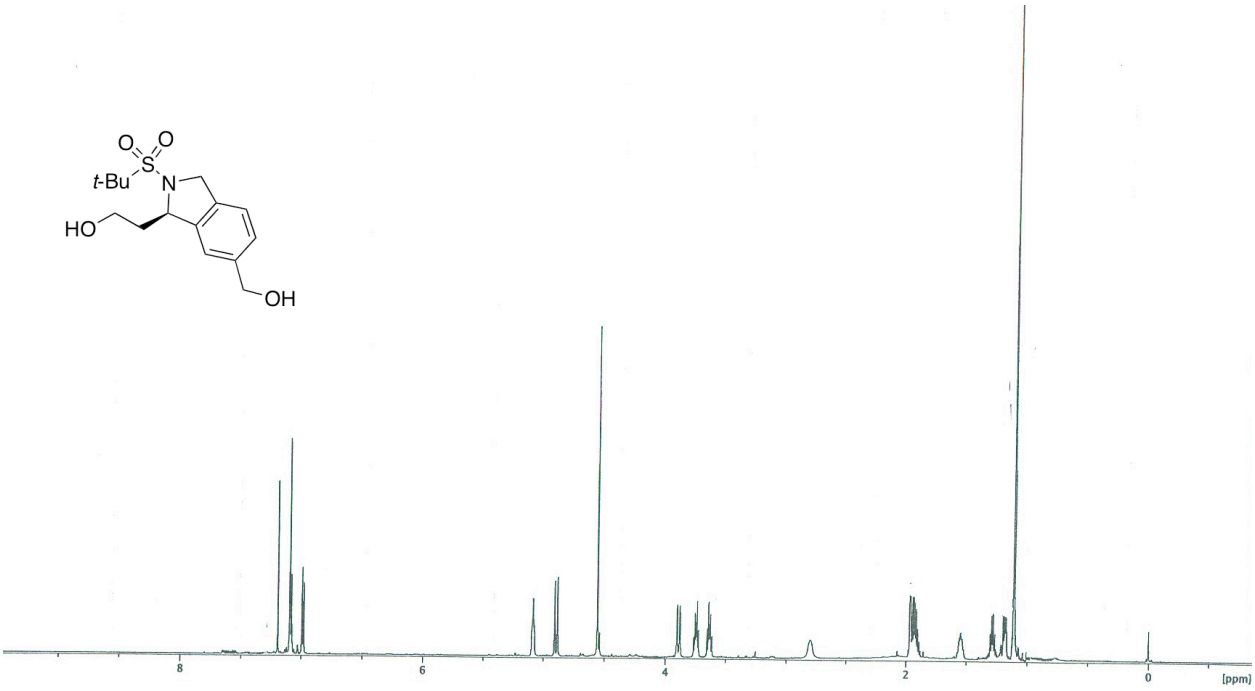

O
S
t-Bu
N
HO
Ph
OH
8
6
4
2
0
[ppm

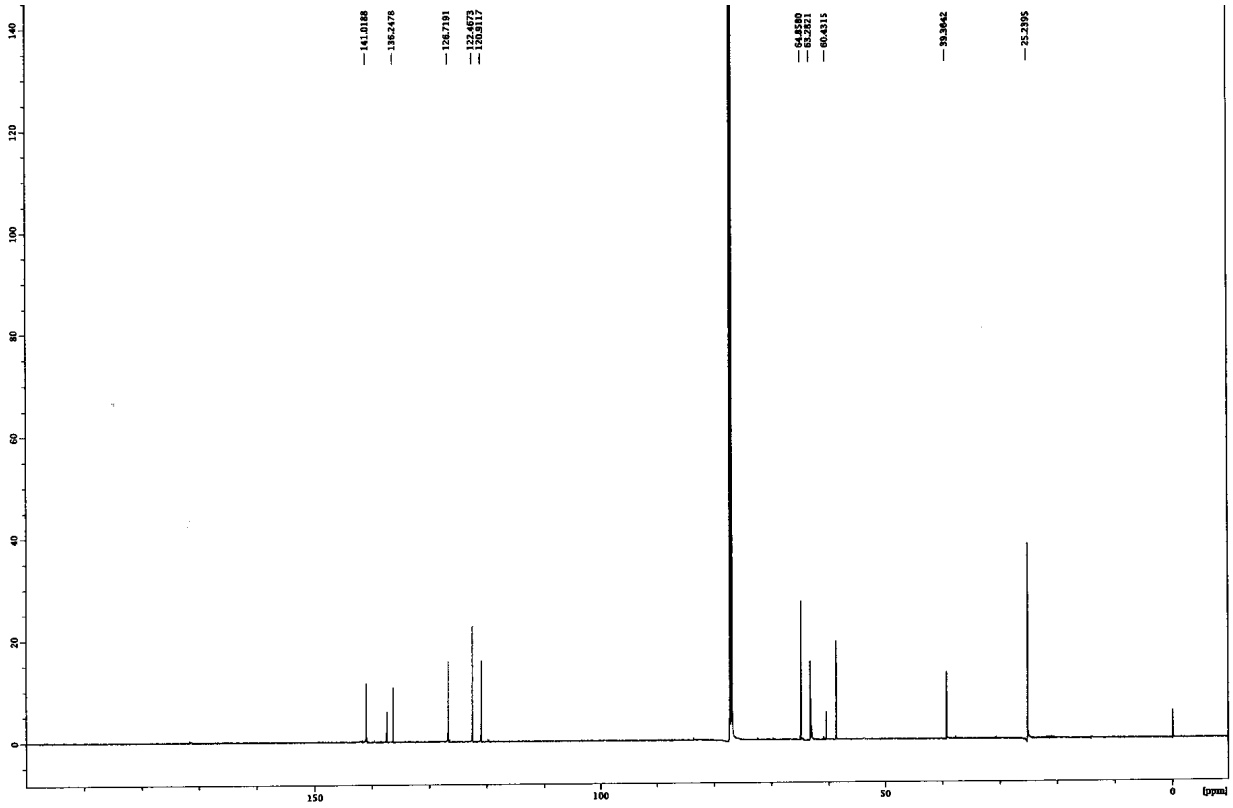

O
S
N
t-Bu
HO
OH
8
6
4
2
0
[ppm]


140.9435
140.8910
137.3411
136.1725
126.6756
126.6438
122.3920
120.9147
120.8364
64.7827
63.2068
63.0772
58.8158
39.2889
22.7396
100
80
60
40
20
0
300
250
200
150
100
50
0
[ppm]

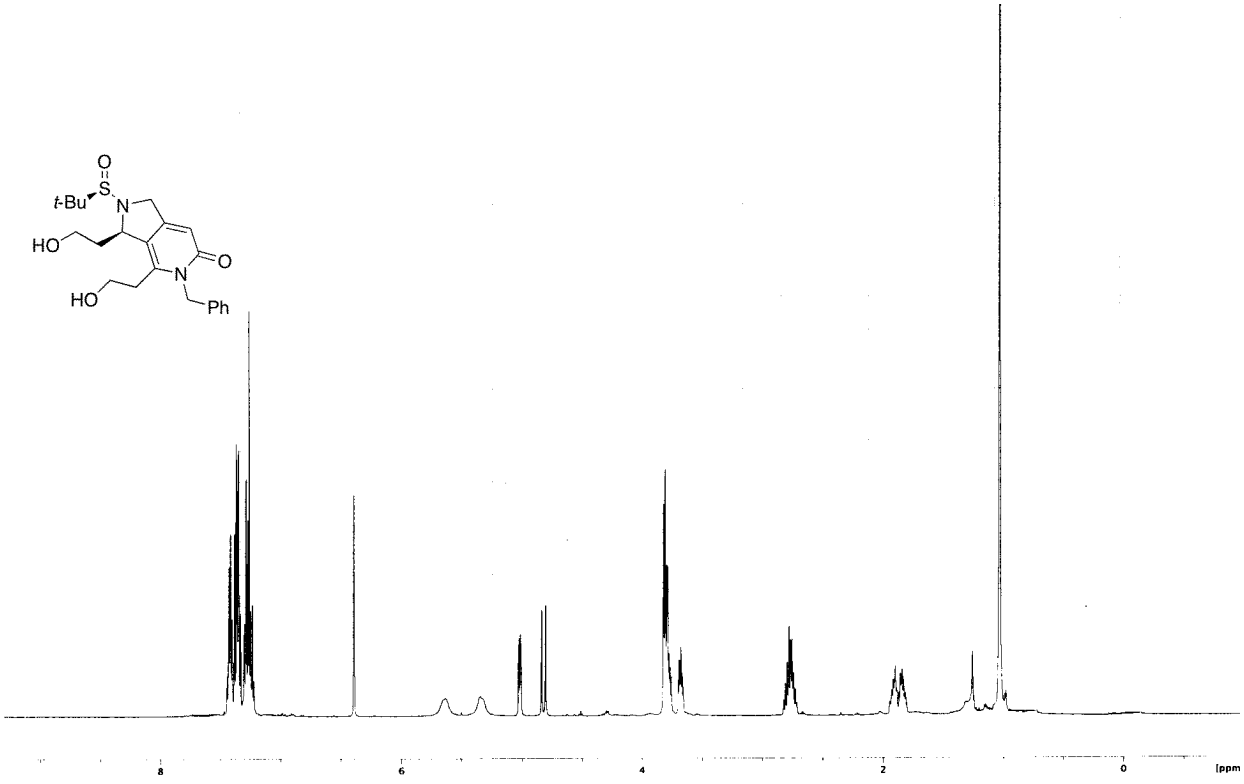

HN
HO
Ph
OH
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 –0.5 ppm

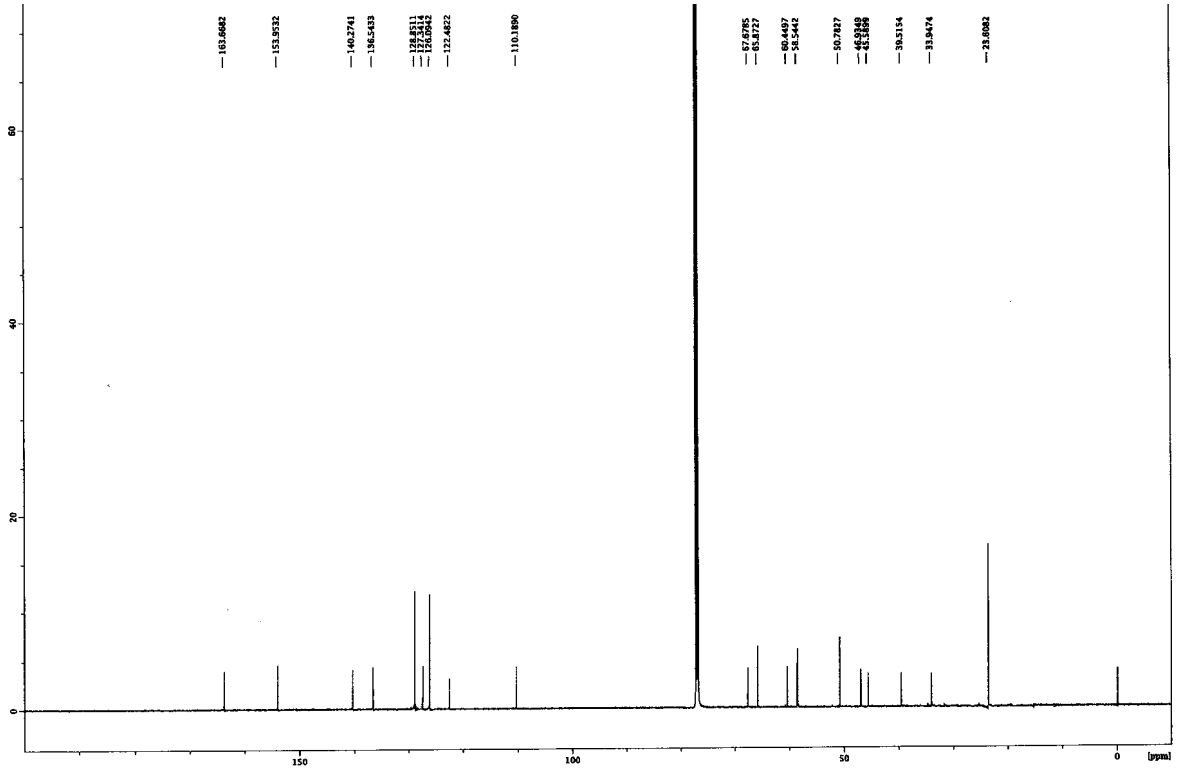

HN
HO
OH
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 –0.5 ppm

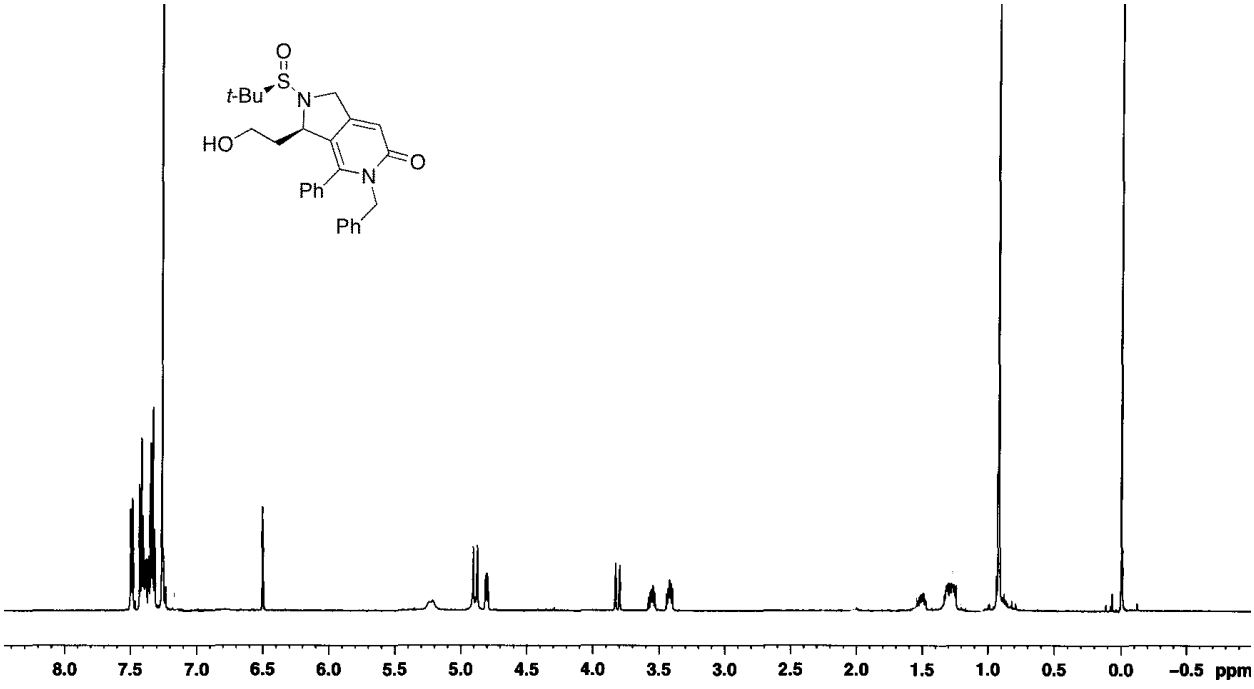

O
O
S
N
t-Bu
HO
OH
8
6
4
2
0
[ppm]

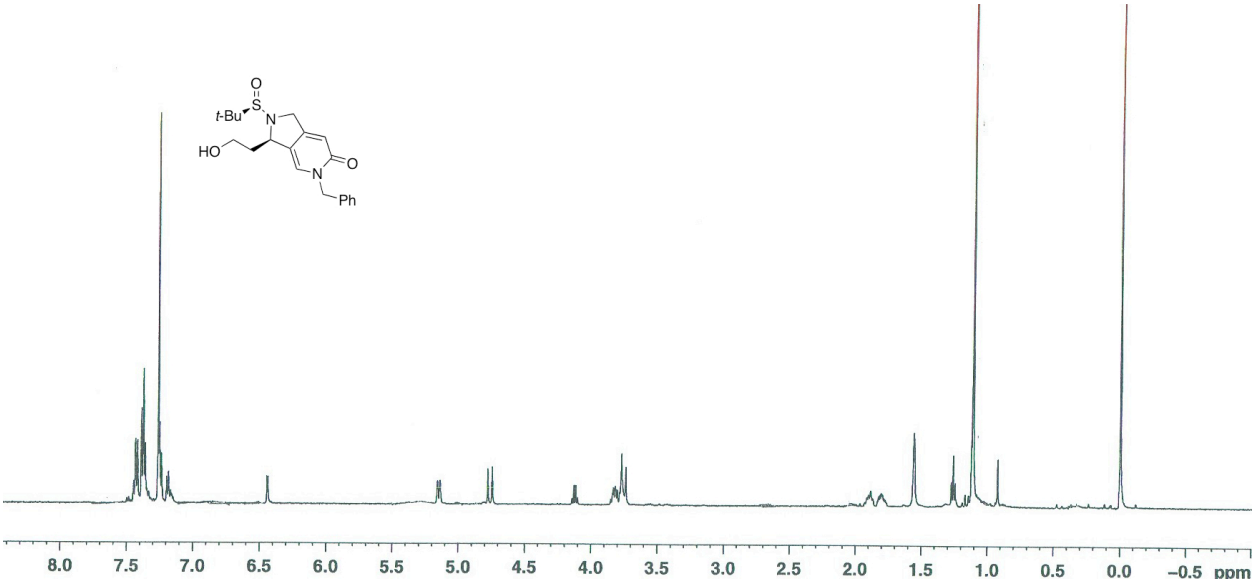

141.0188
136.2478
126.7191
122.4673
120.9117
64.8580
63.2821
60.4315
39.3642
25.2395
140
120
100
80
60
40
20
0
150
100
50
0
[ppm]

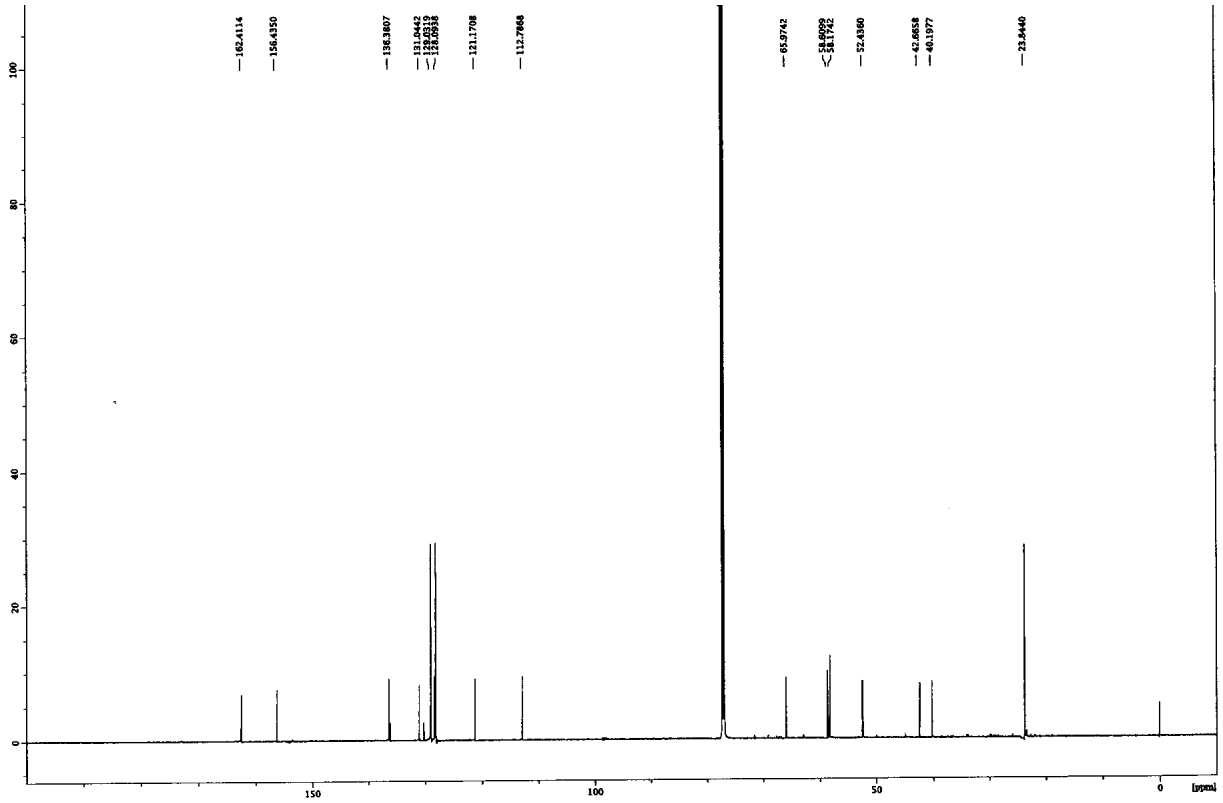
h. Isocyanate [2+2+2] cyclotrimerization products (*R*-36–41)

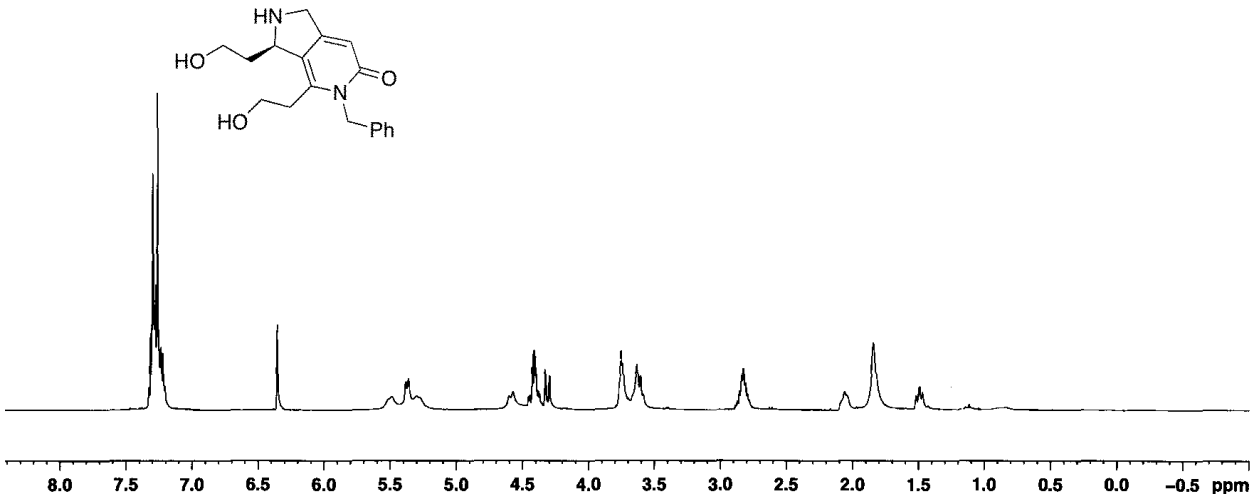


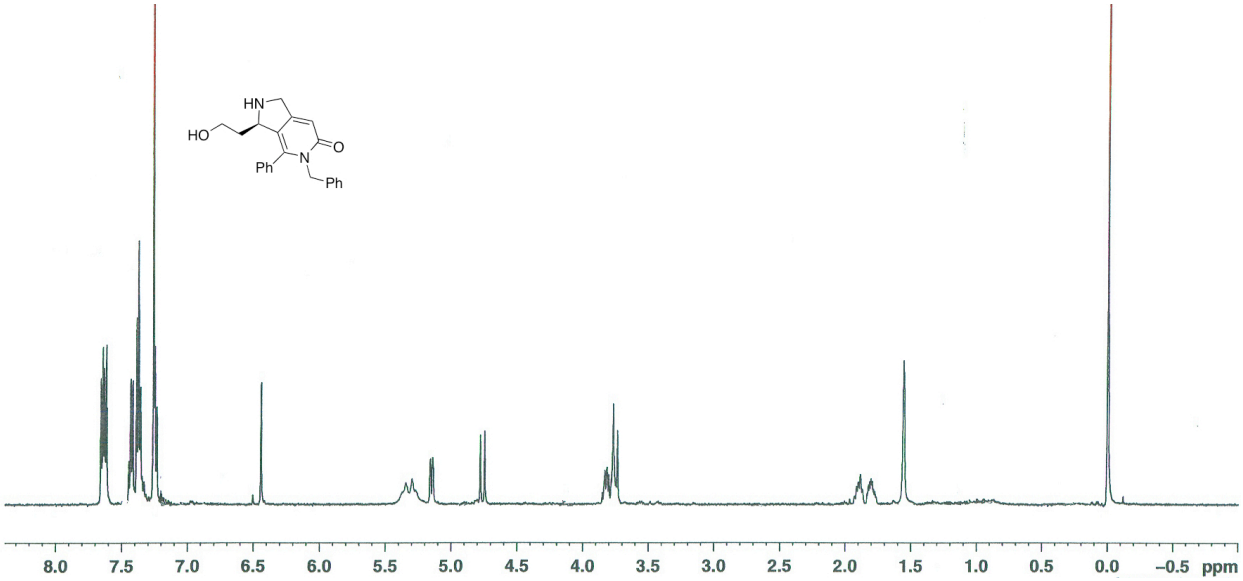


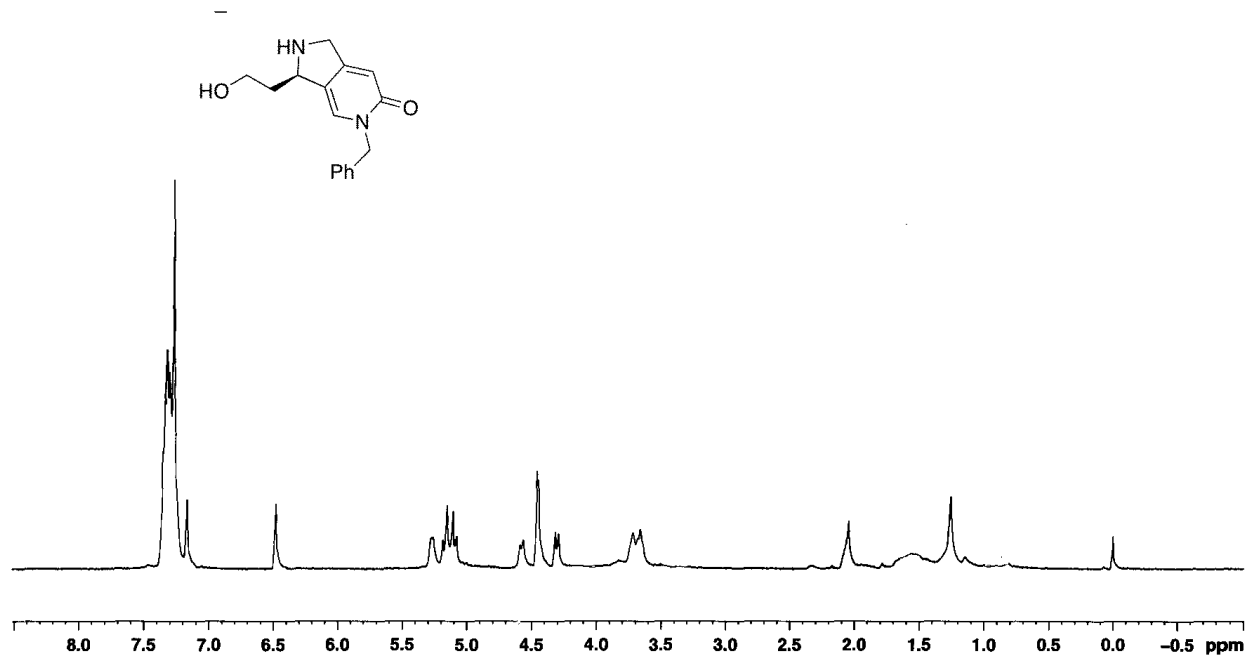

O
S
t-Bu
N
HO
O
N
Ph
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
ppm

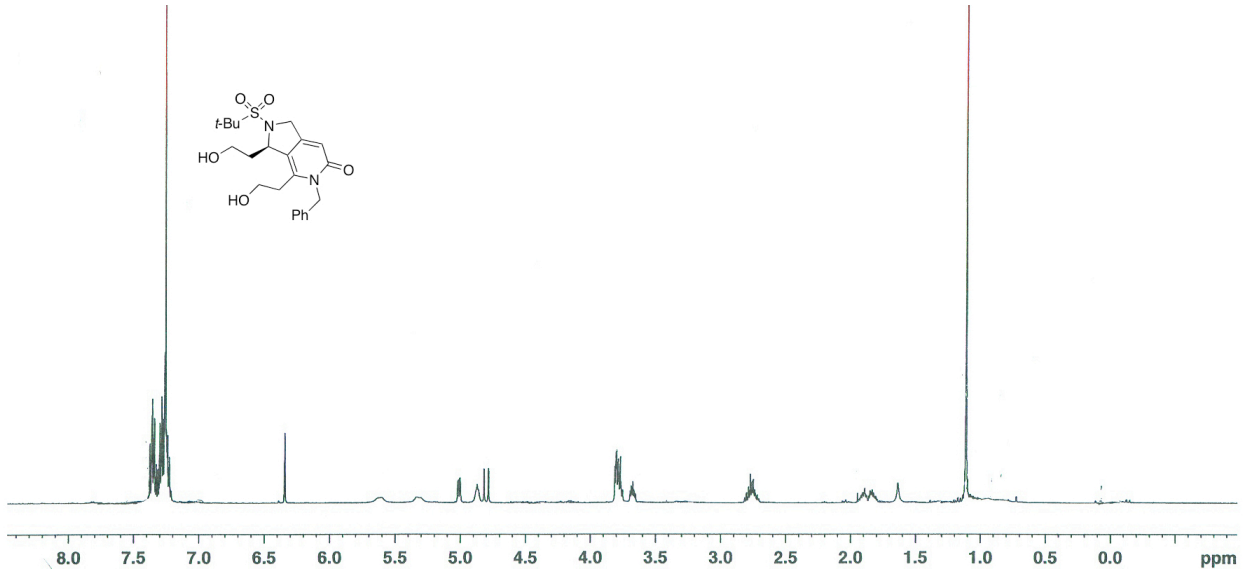

O
S
t-Bu
N
HO
O
N
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5 ppm

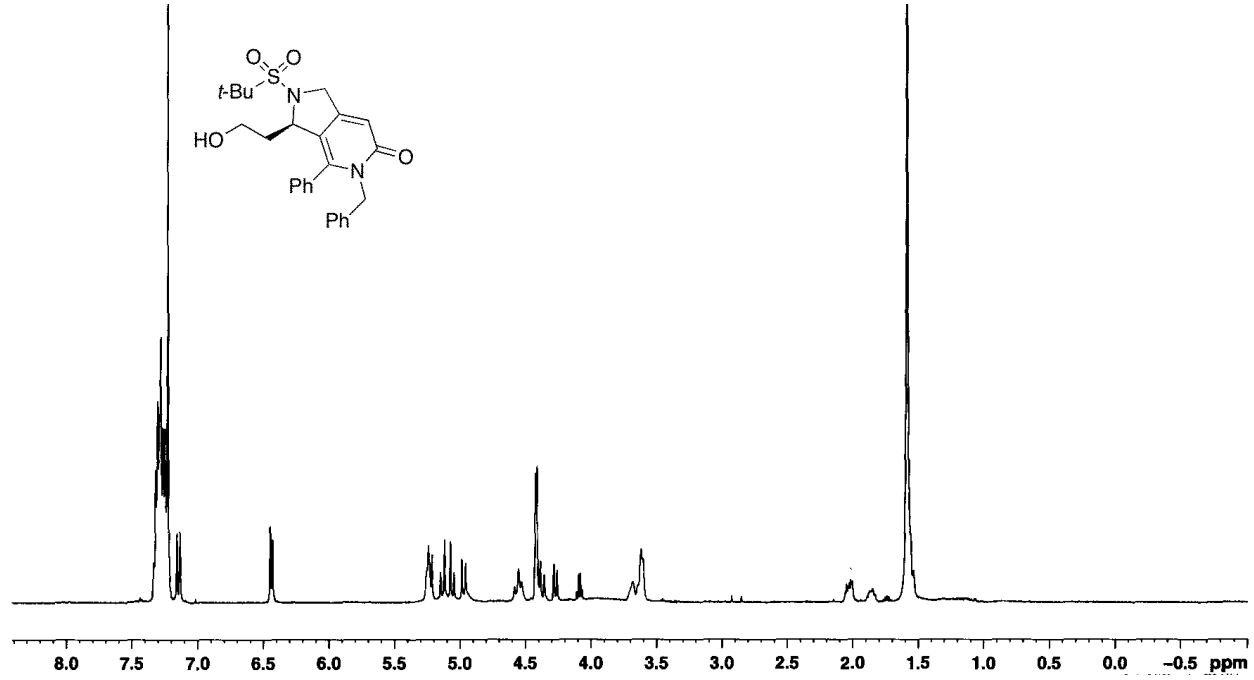

162.4114
156.4350
136.3607
131.0442
128.0819
128.0538
128.0938
121.1708
112.7866
65.9742
58.6099
58.1742
52.4360
42.6658
40.1977
23.8440
100
80
60
40
20
0
150
100
50
0
[ppm]

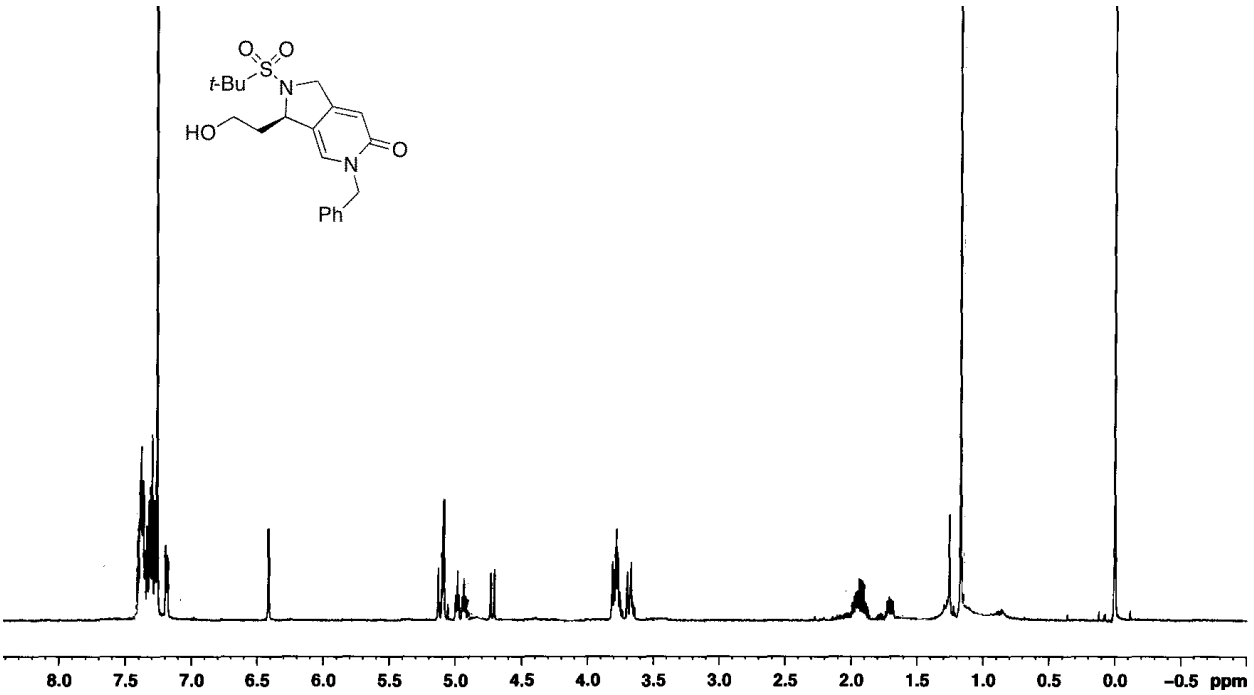

HN
HO
O
N
HO
Ph
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

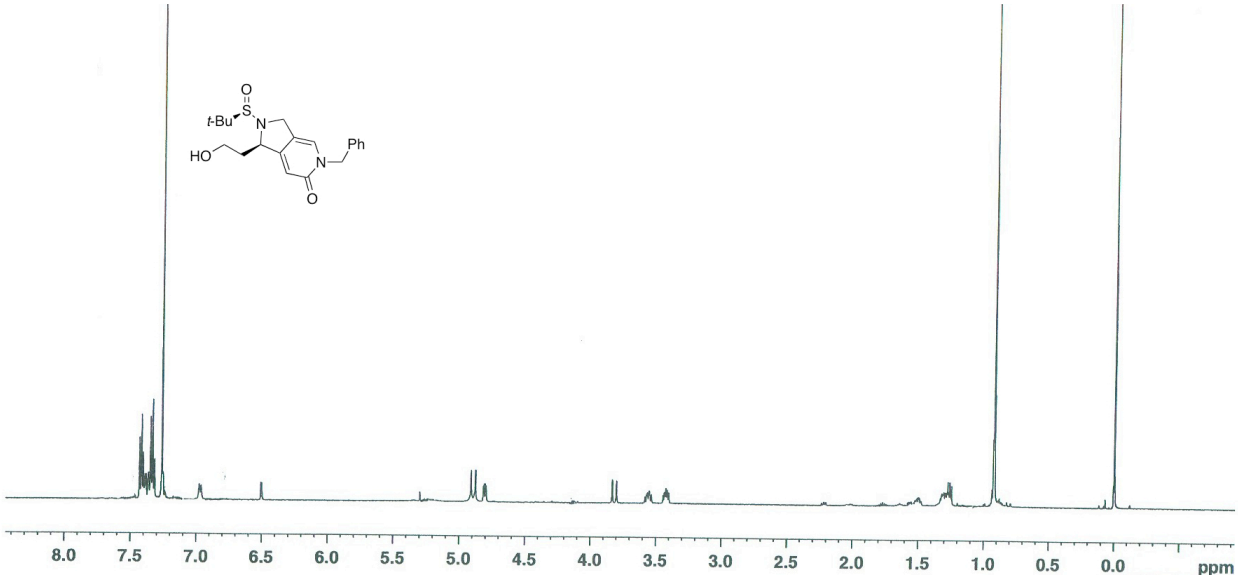

HN
HO
O
Ph
N
Ph
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

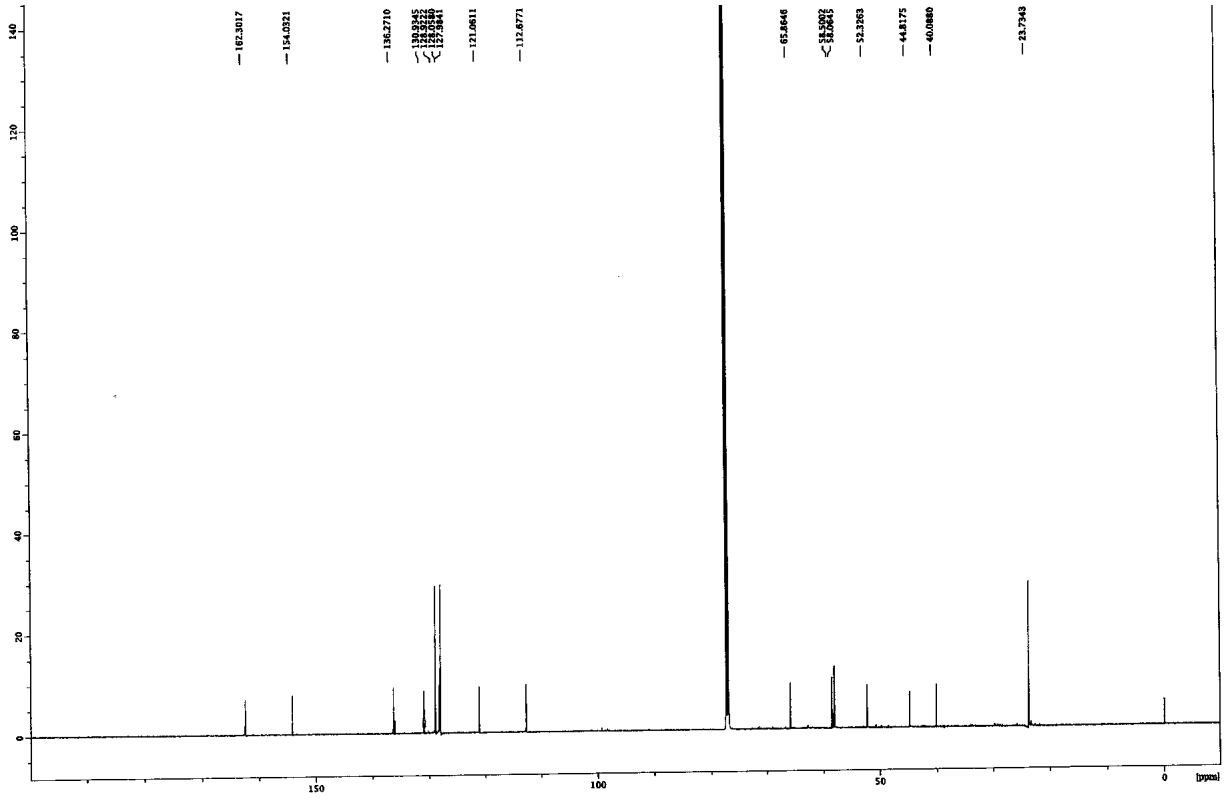

HN
HO
O
N
Ph
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 –0.5 ppm

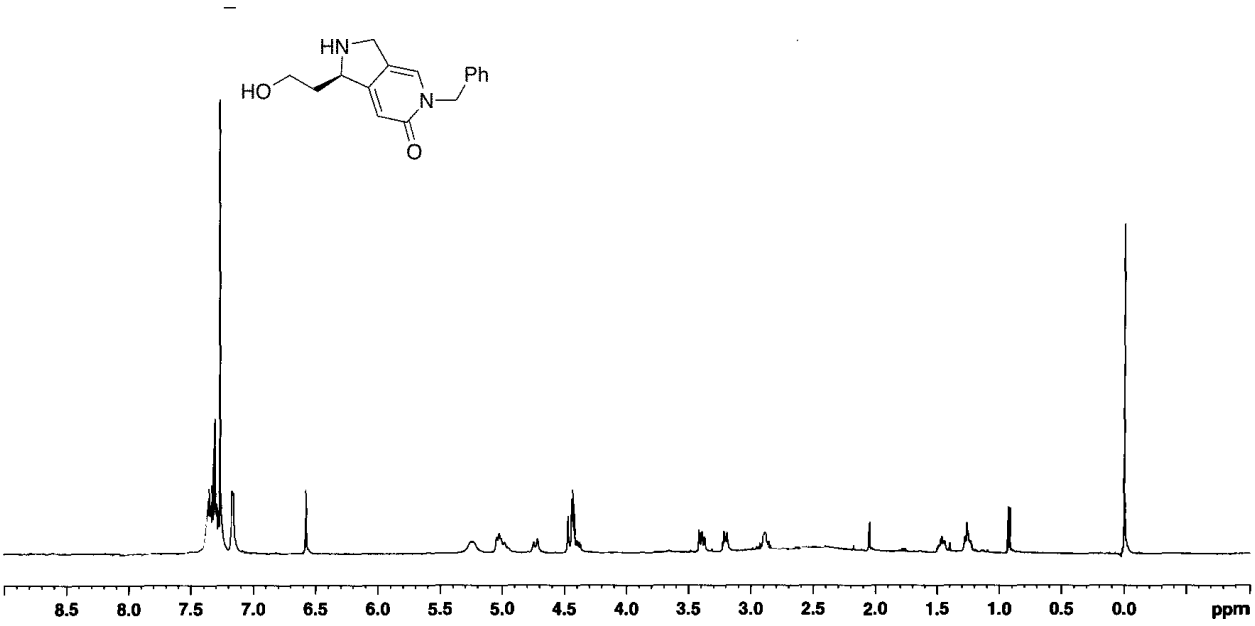

O
O
S
t-Bu
N
HO
HO
N
O
Ph
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

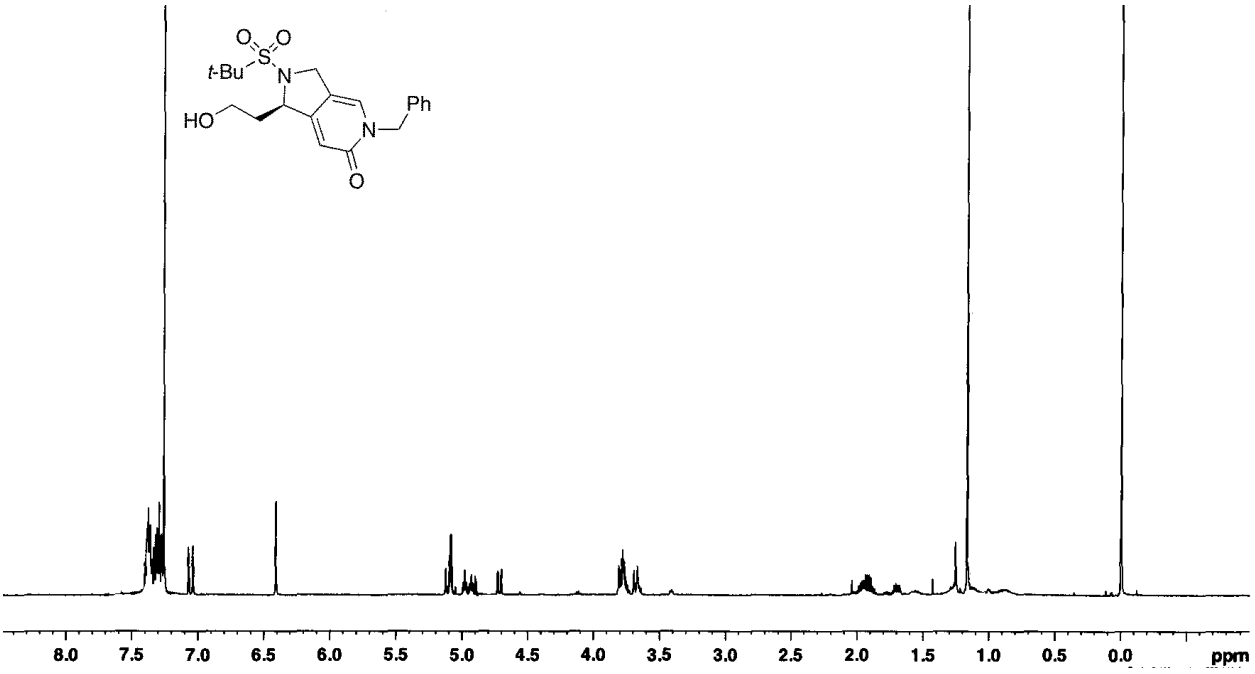

t-Bu
HO
Ph
Ph
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm


t-Bu
HO
Ph
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 −0.5 ppm

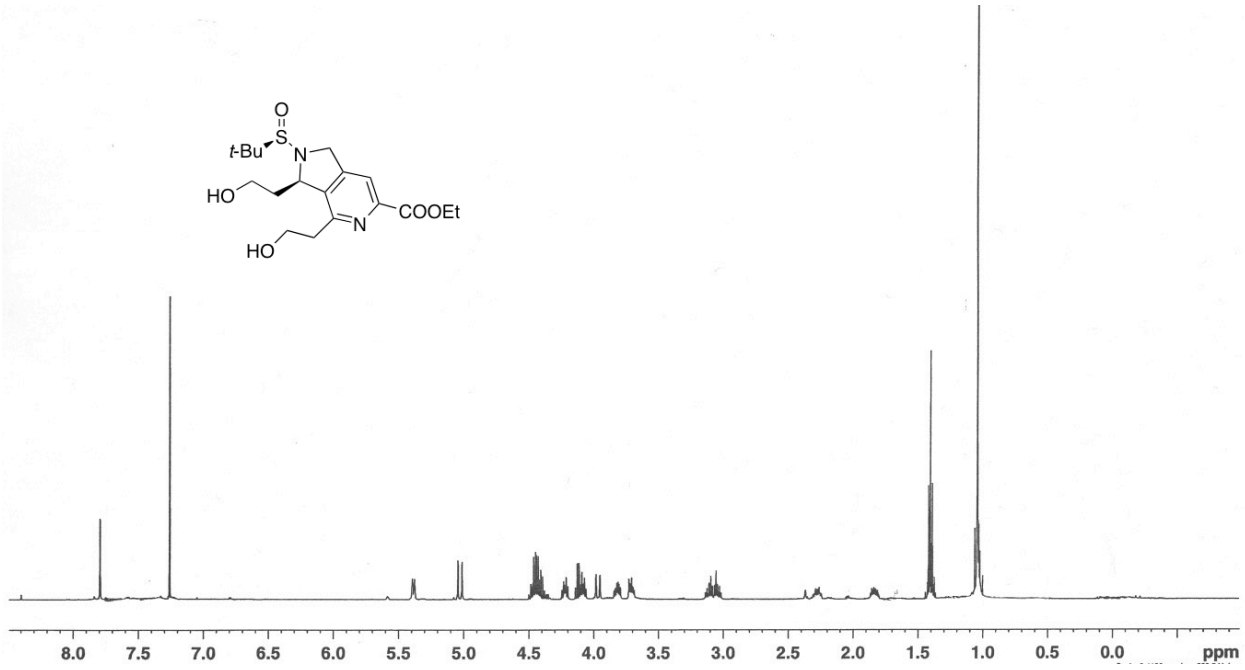

t-Bu
HO
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

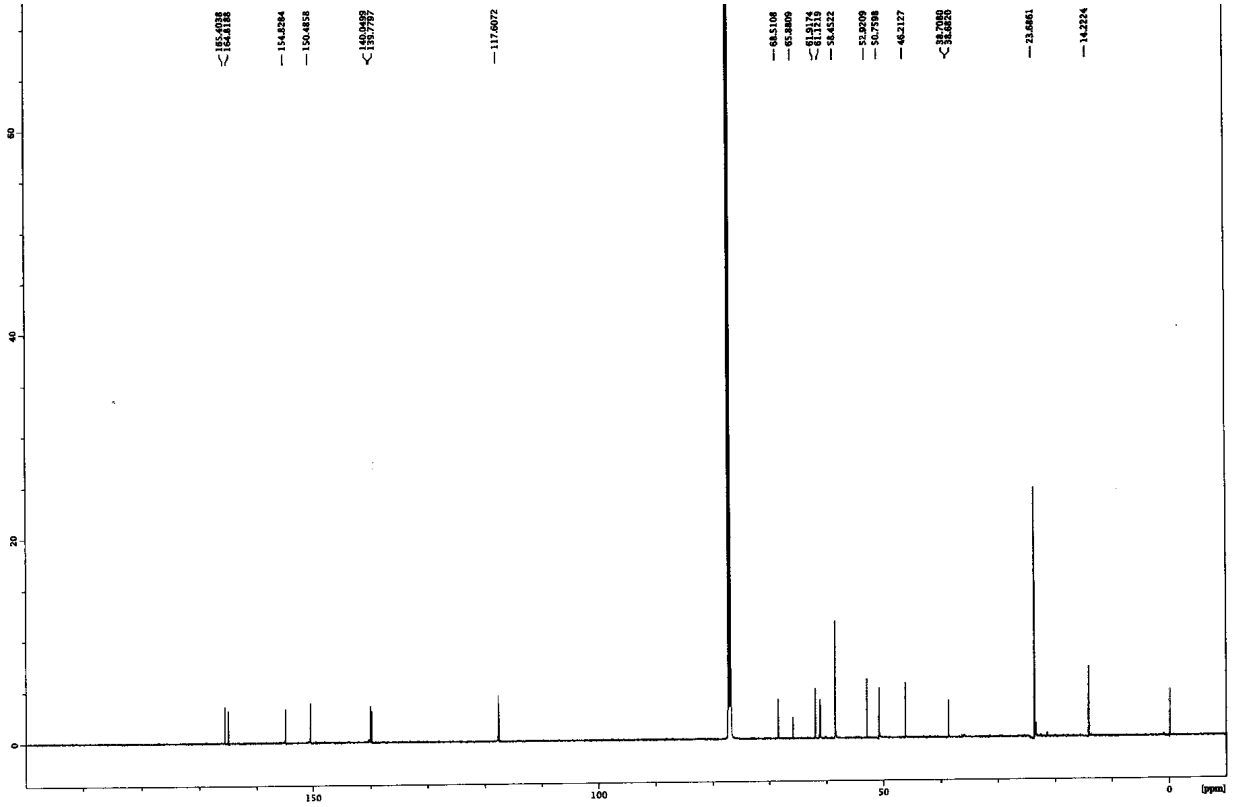

162.3017
154.0321
136.2710
121.0611
112.6771
65.8646
58.5092
52.3263
44.8175
40.0880
23.7343
150
100
50
0
[ppm]

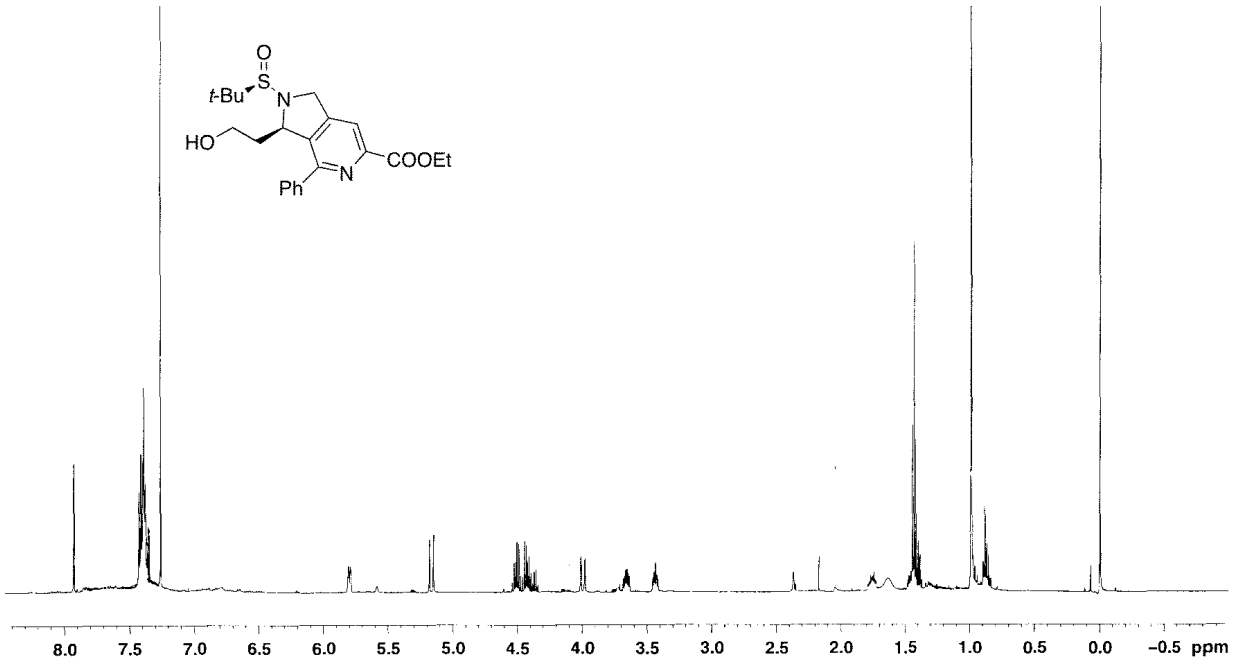

HN
HO
Ph
N
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

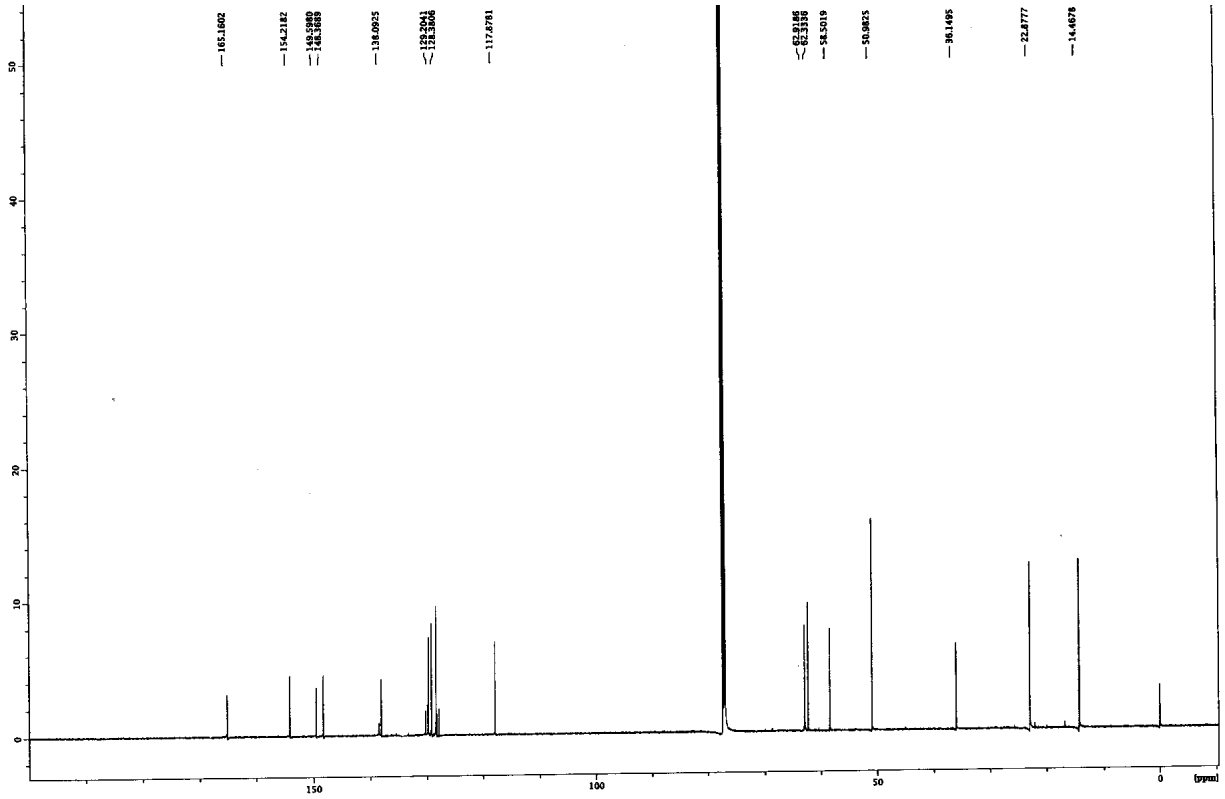

O
O
S
t-Bu
N
HO
Ph
N
O
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

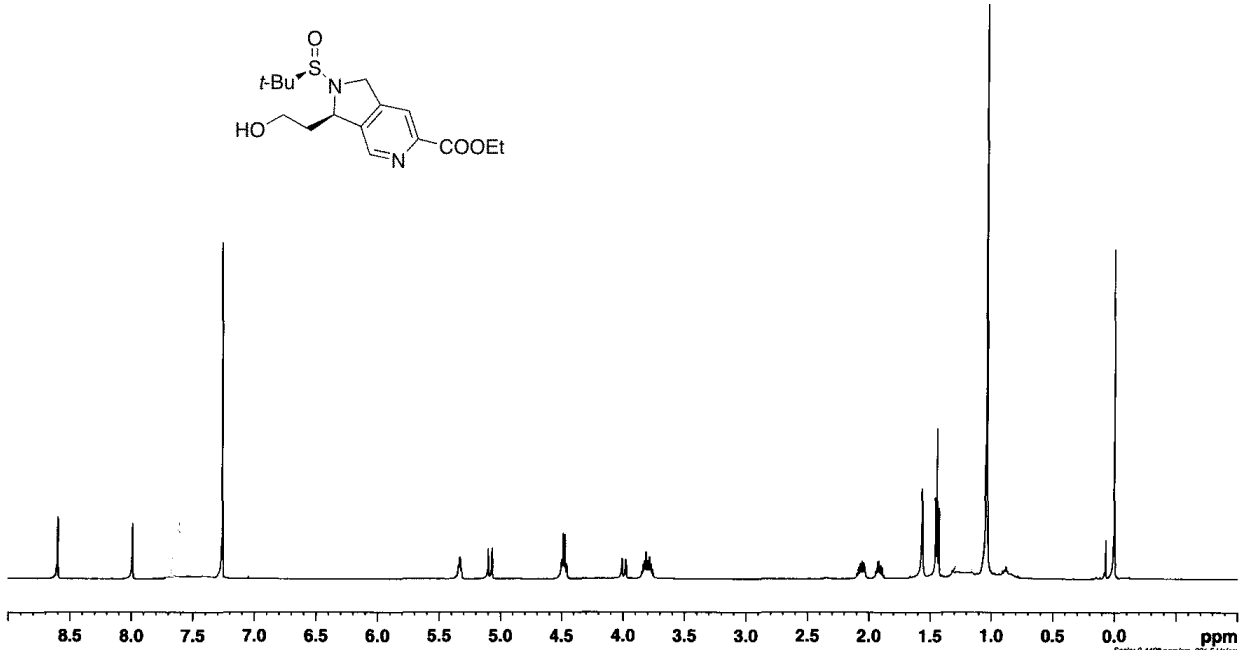
i. Nitrile [2+2+2] cyclotrimerization products (*R*-42–44)

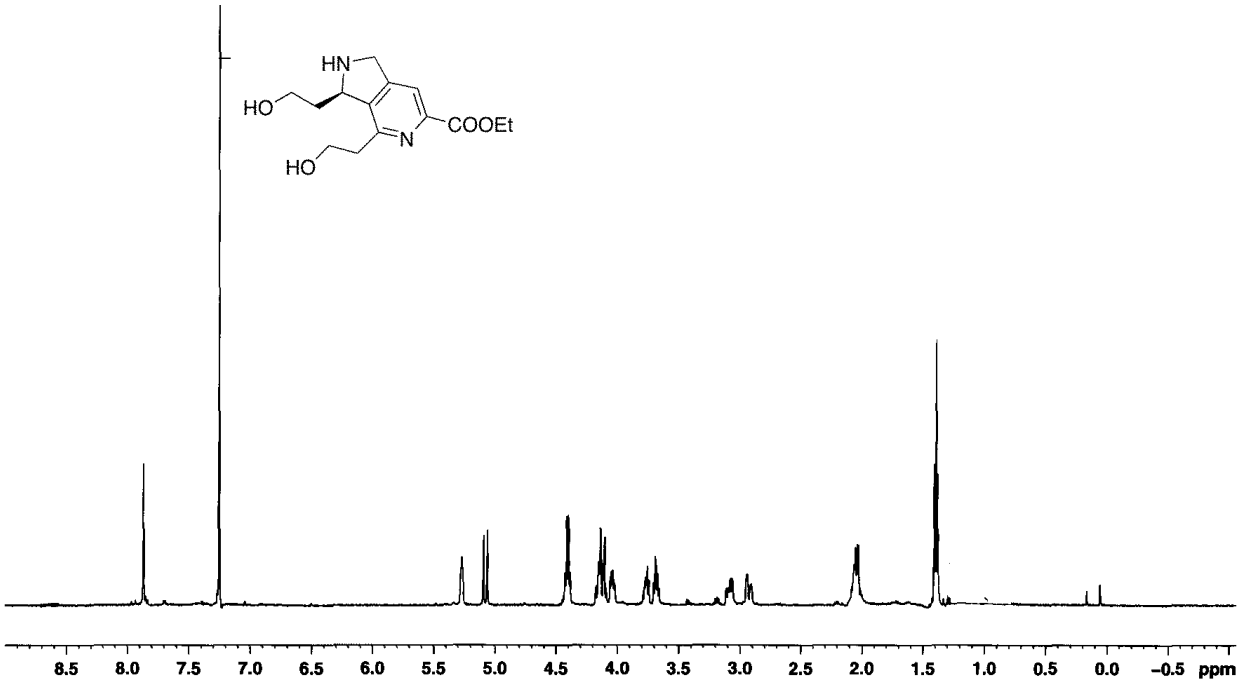


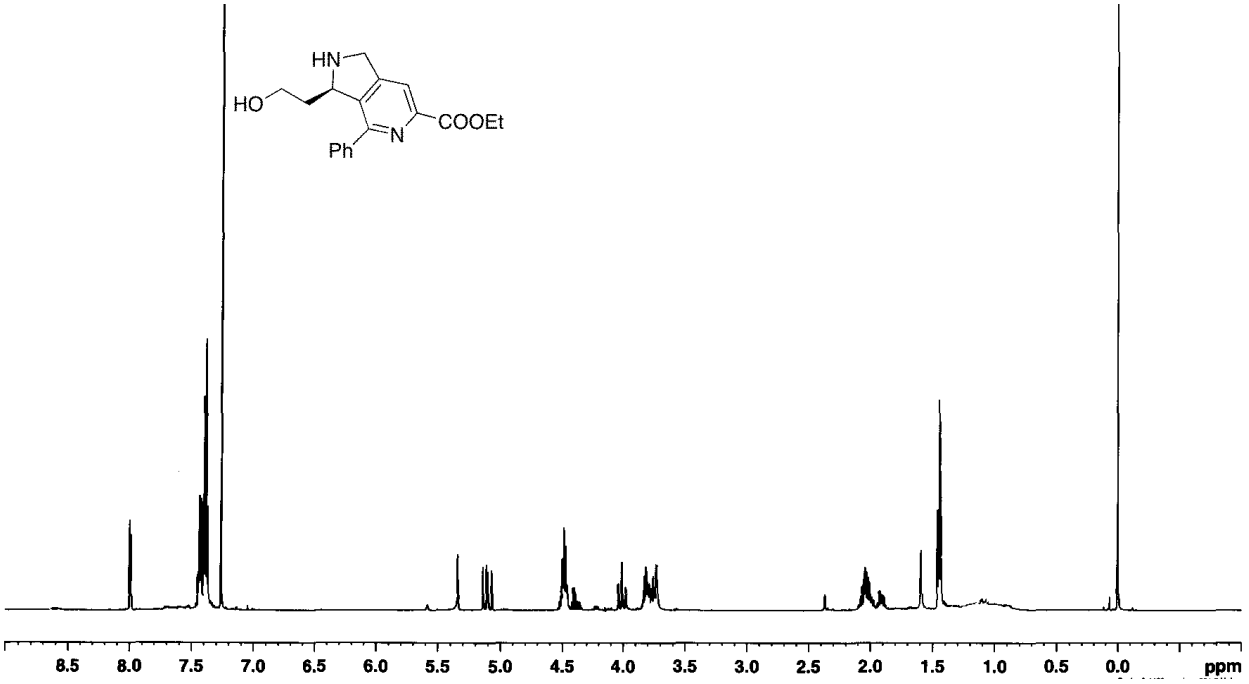


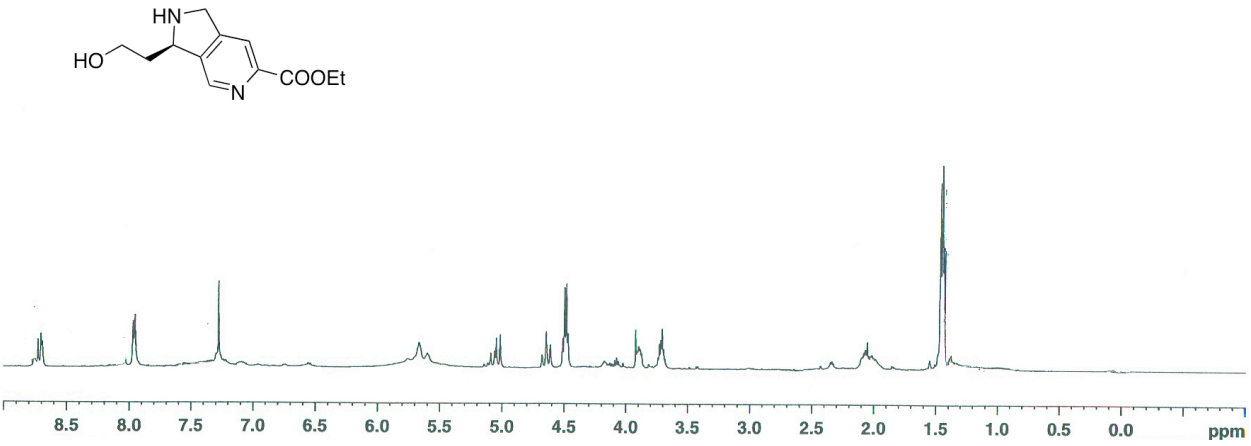

O
S
t-Bu
N
HO
COOEt
N
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5 ppm

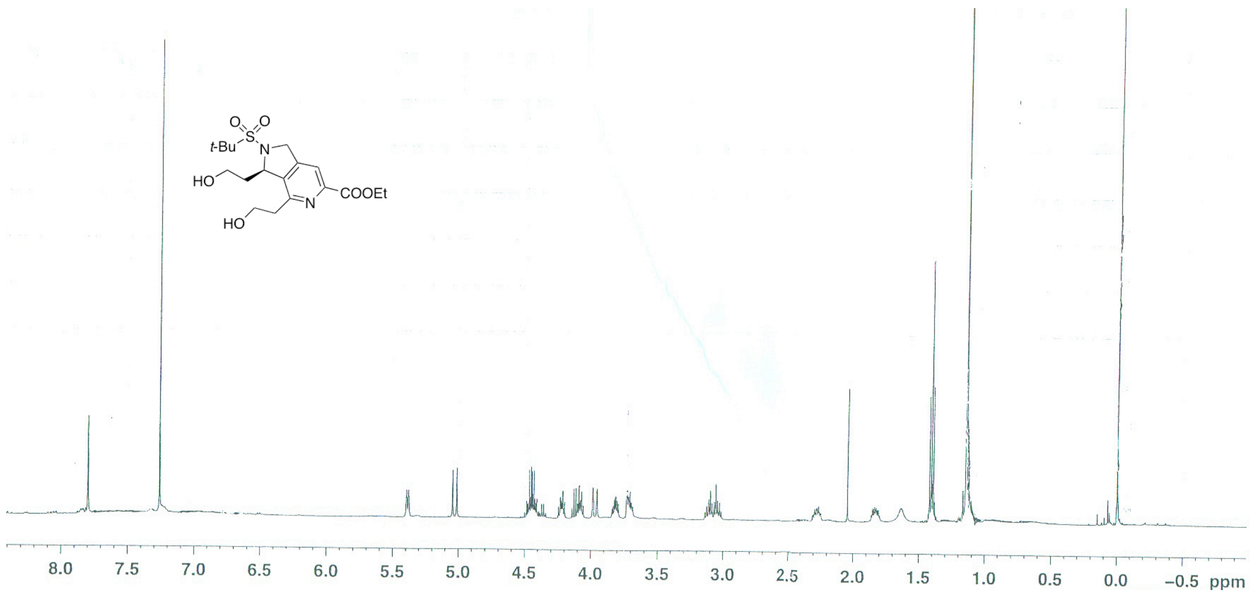

165.1602
154.2182
149.5880
148.3889
138.0925
129.2041
128.3806
117.8781
68.2186
67.3358
58.5019
50.9825
36.1495
22.8777
14.4678
50
40
30
20
10
0
150
100
50
0
(ppm)

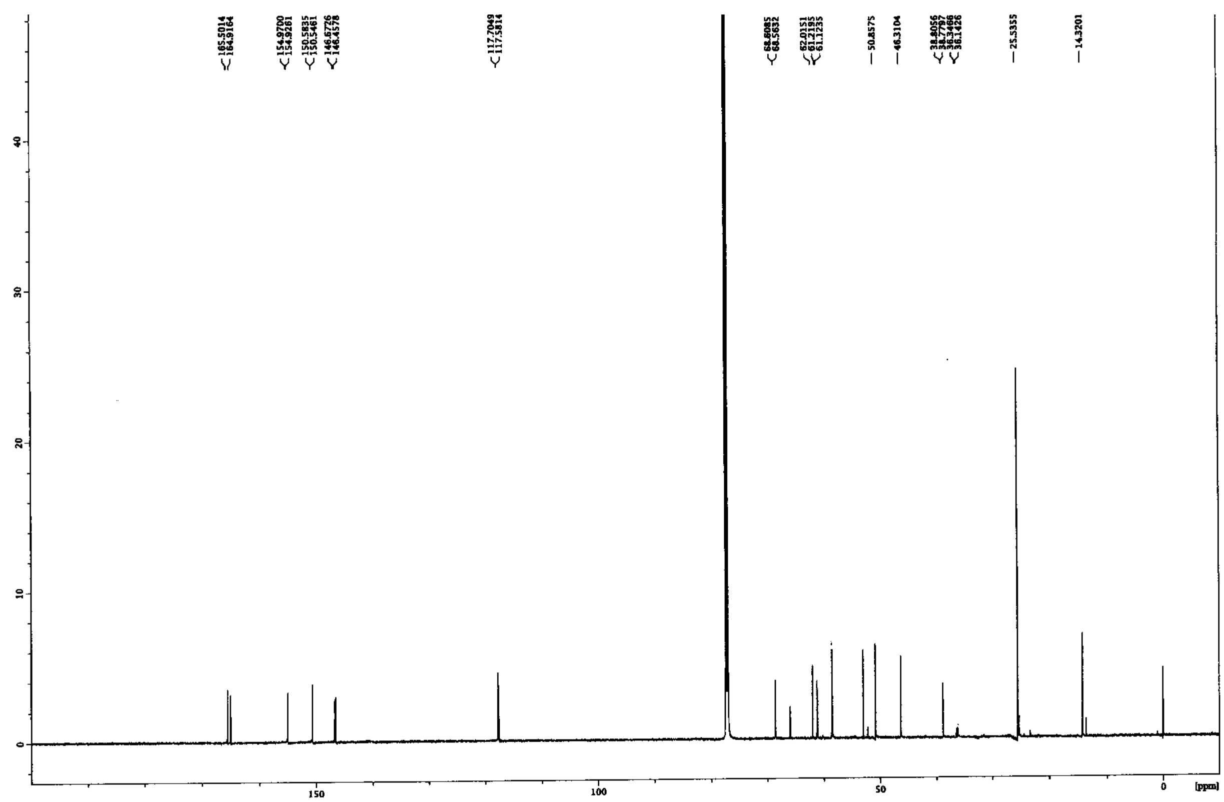

O
S
t-Bu
N
HO
COOEt
N
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

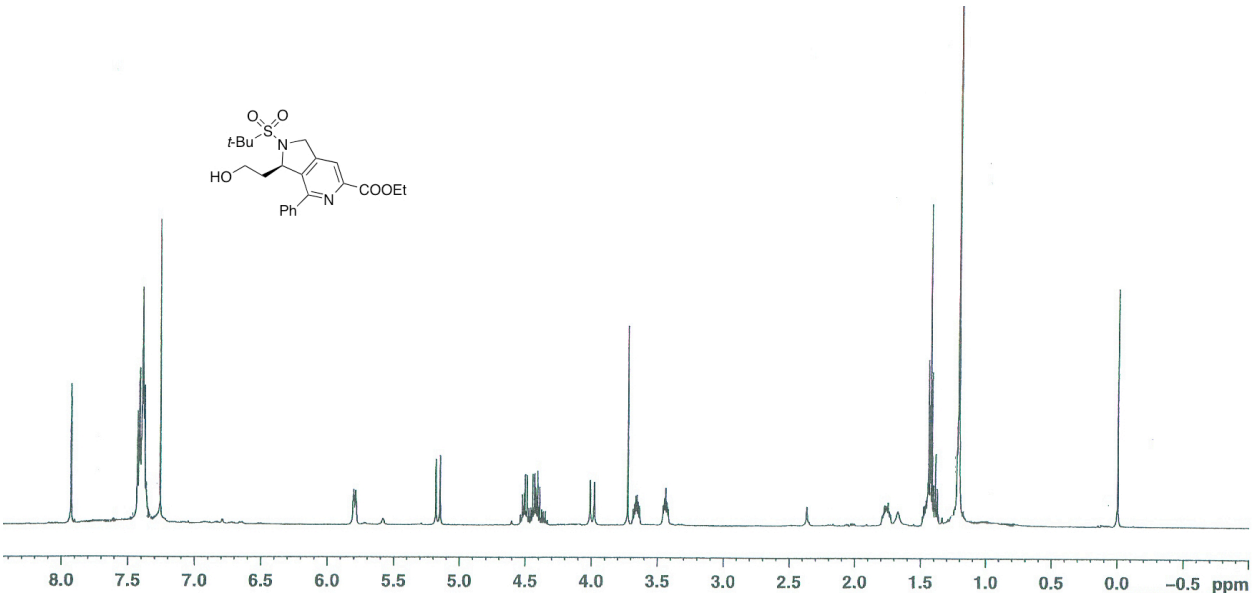

HN
HO
COOEt
N
HO
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm

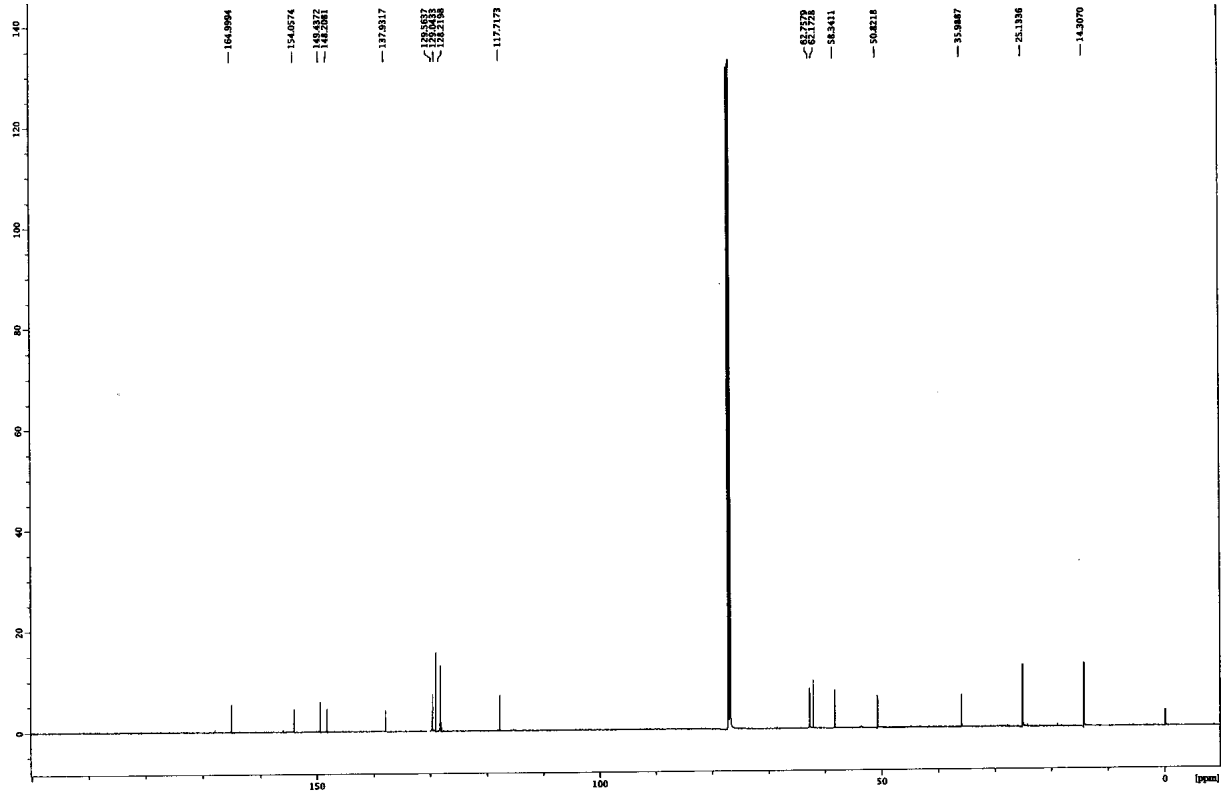

HN
HO
COOEt
Ph
N
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

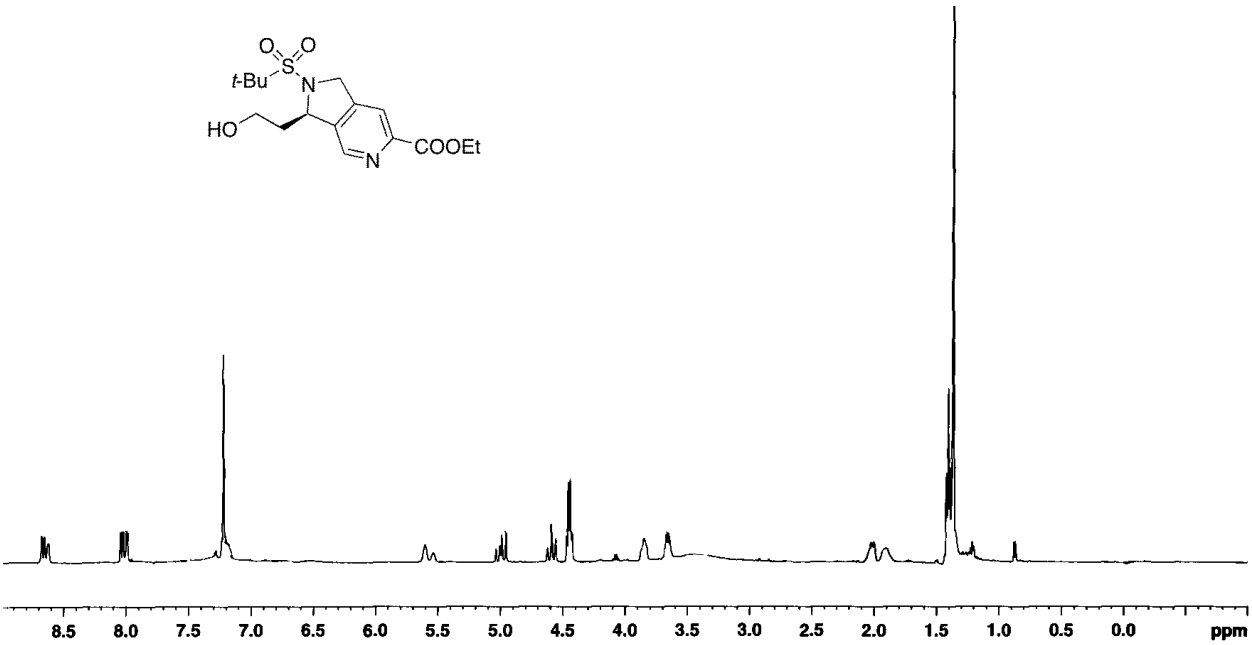

HN
HO
COOEt
N
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm


t-Bu
HO
COOEt
N
HO
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 −0.5 ppm

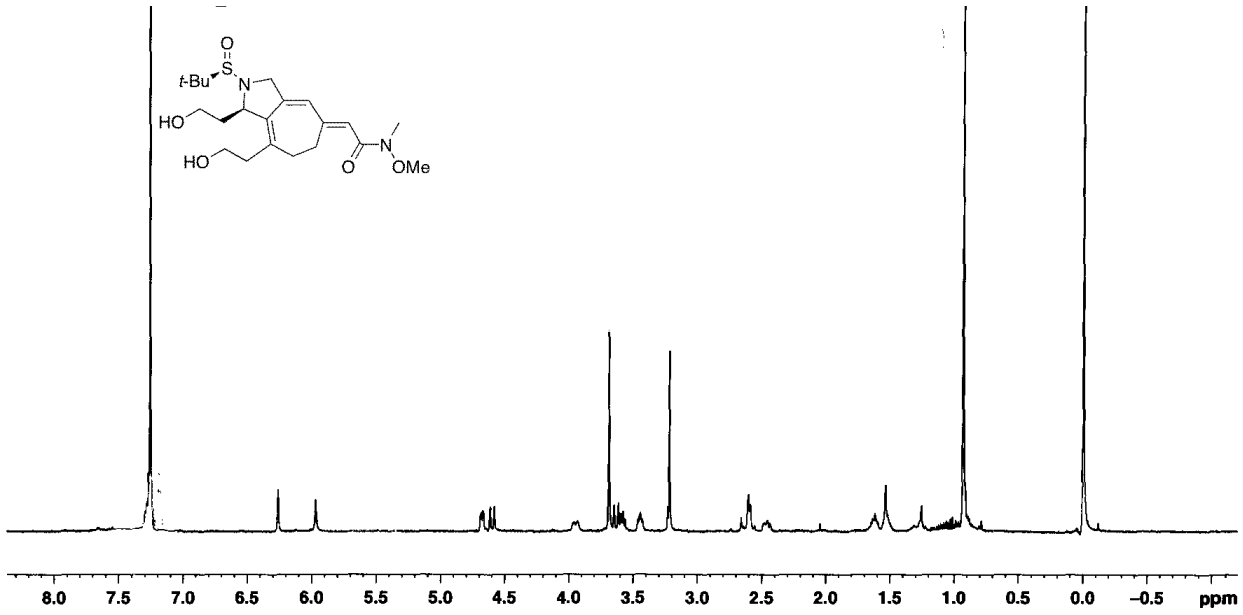

150
100
50
0
[ppm]

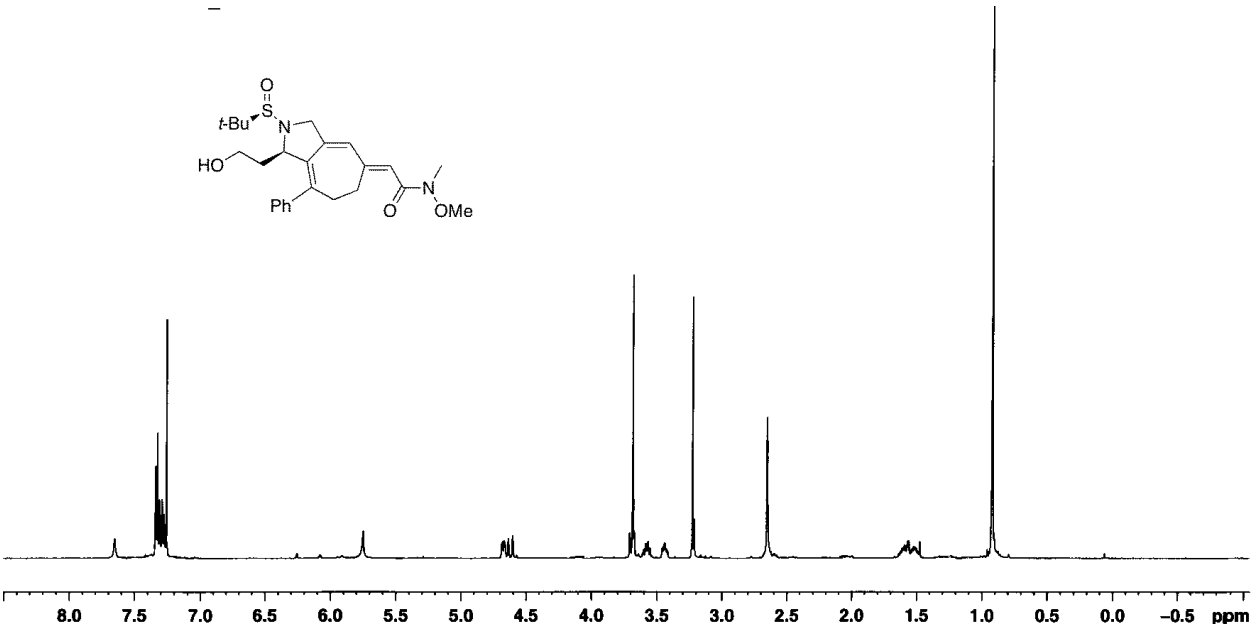

O
O
S
t-Bu
N
HO
COOEt
N
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5 ppm

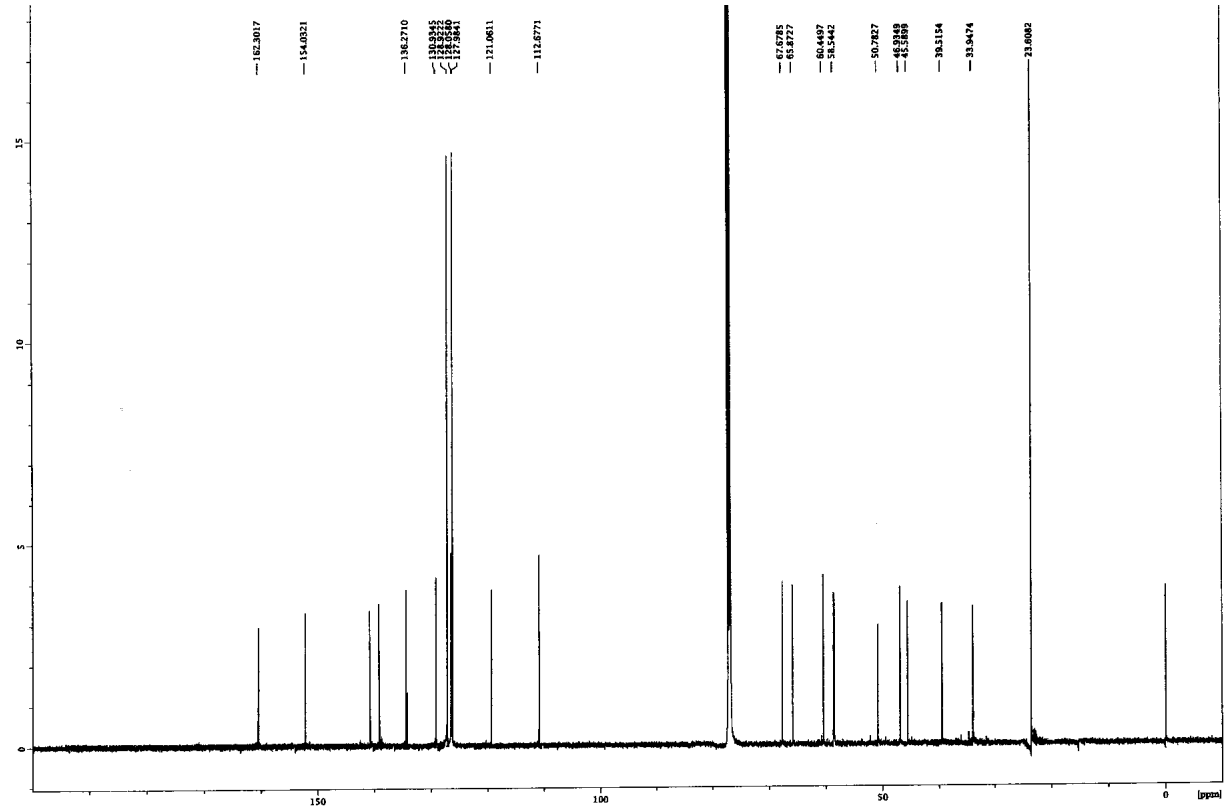

164.9994
154.0574
149.4377
142.2061
137.9517
117.7173
83.7579
82.1728
58.3411
50.8218
35.9887
25.1336
14.3070
140
120
100
80
60
40
20
0
150
100
50
0
[ppm]

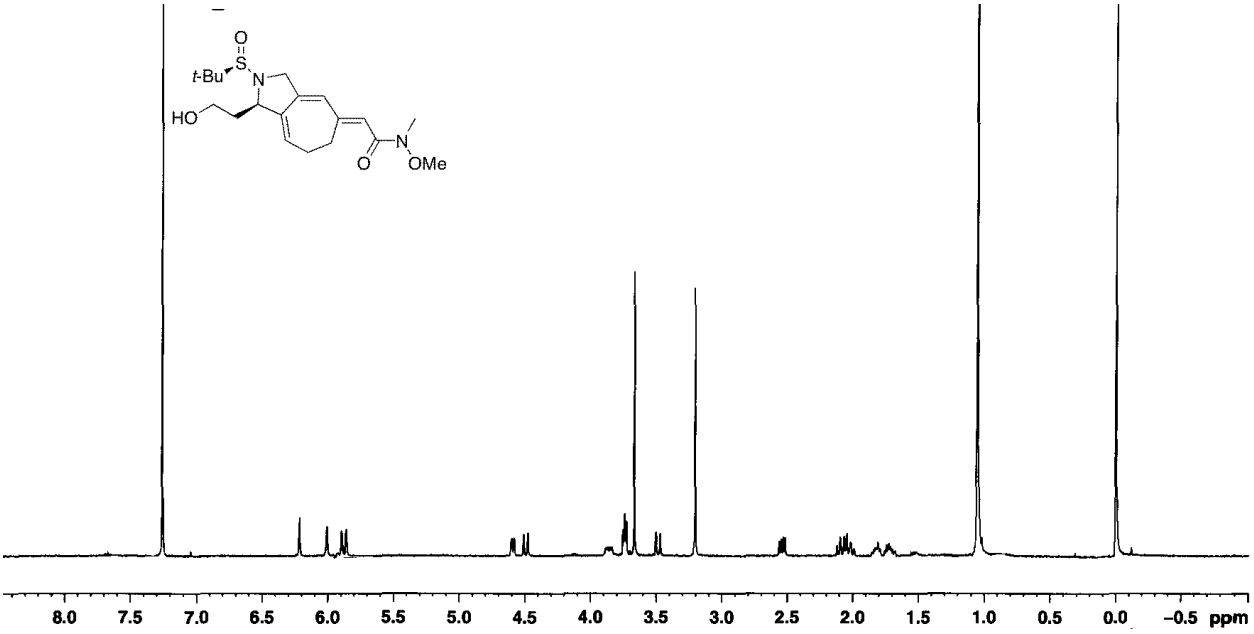

O
O
S
t-Bu
N
HO
COOEt
N
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

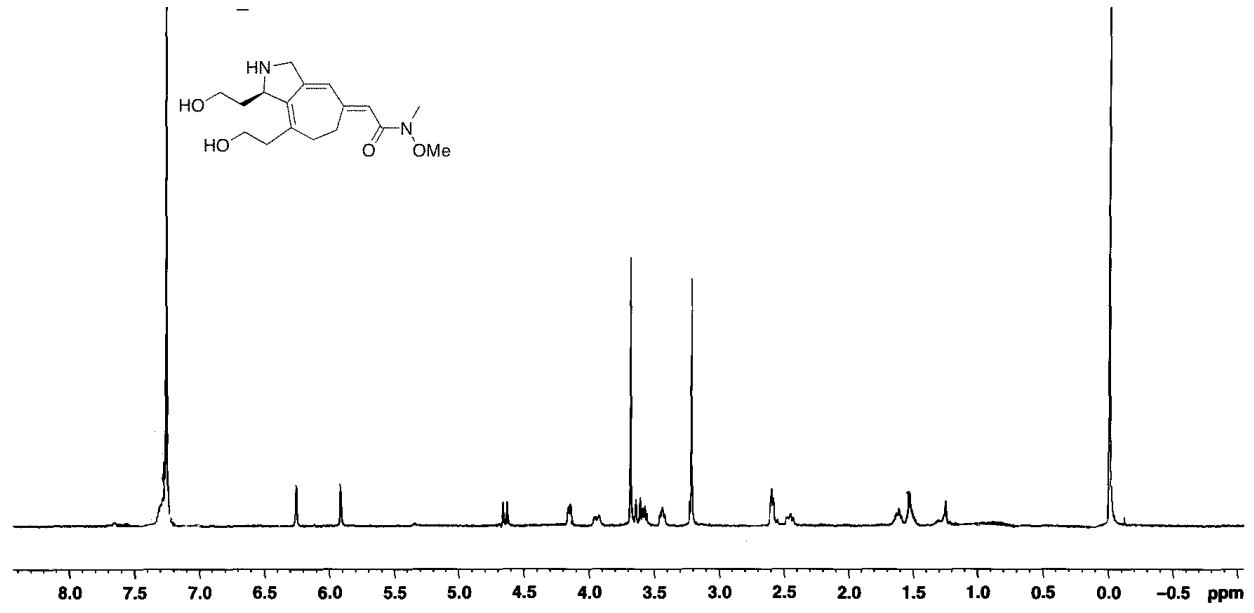
j. Saito [3+2+2] cycloaddition products (*R*-45–50)

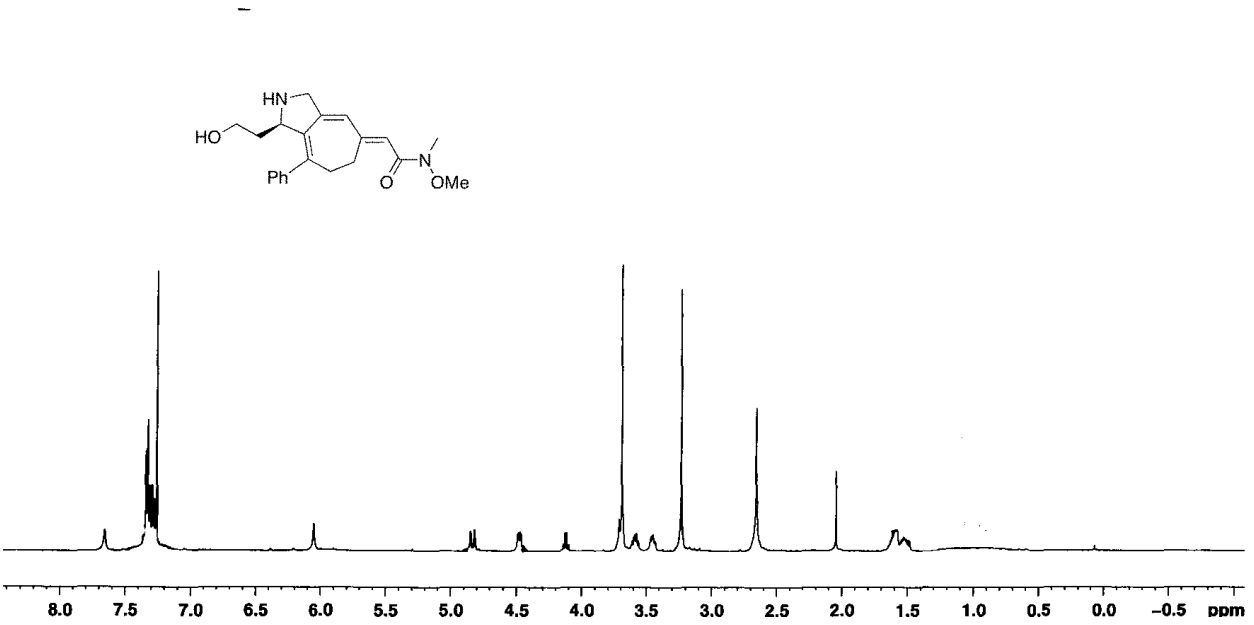


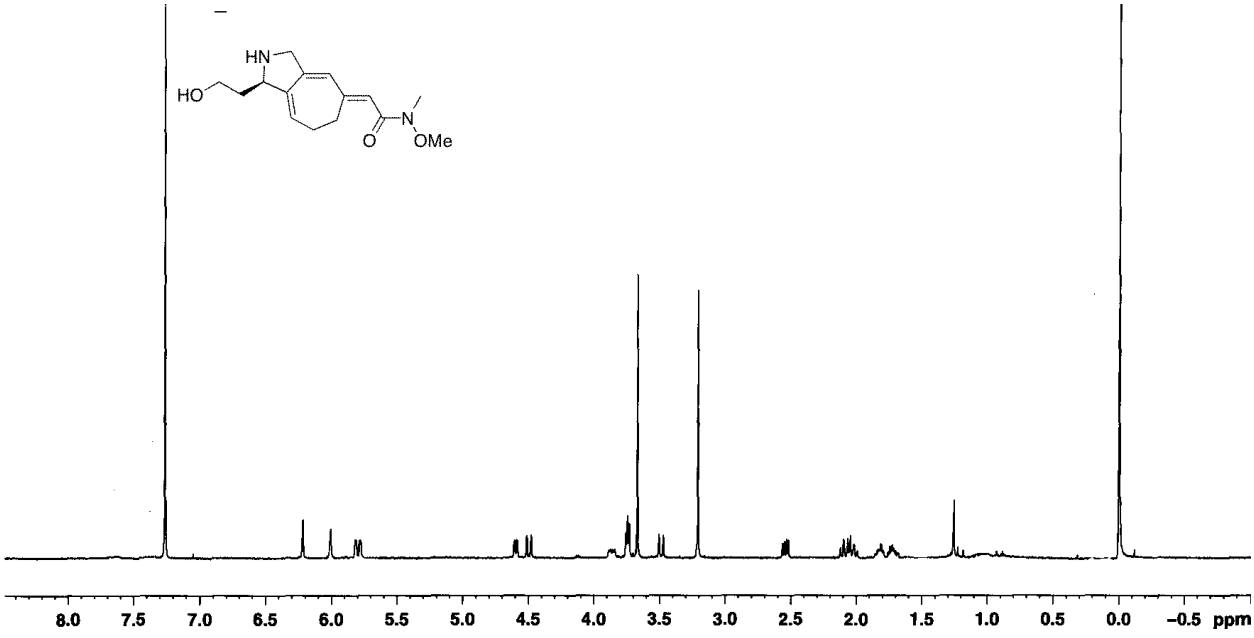

t-Bu
S
O
N
HO
Ph
O
N
OMe
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

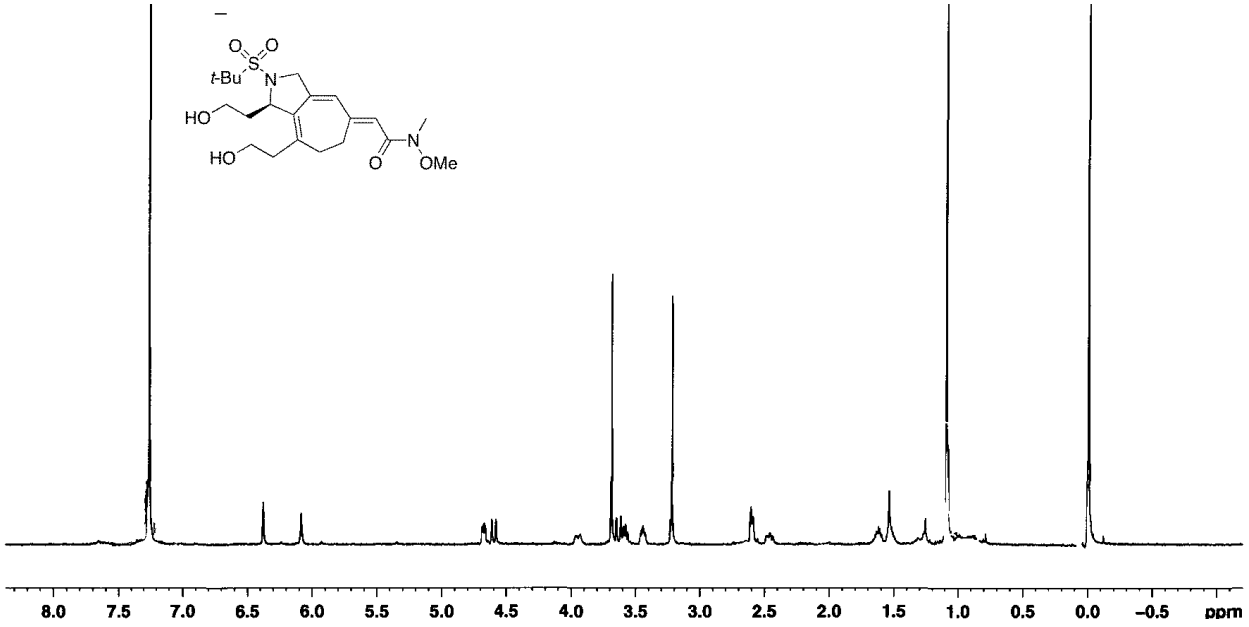

162.3017
154.0321
136.2710
121.0611
112.6771
67.6785
65.8727
60.4497
38.5442
50.7827
45.9348
45.5899
39.5154
33.9474
23.6082
150
100
50
0
[ppm]

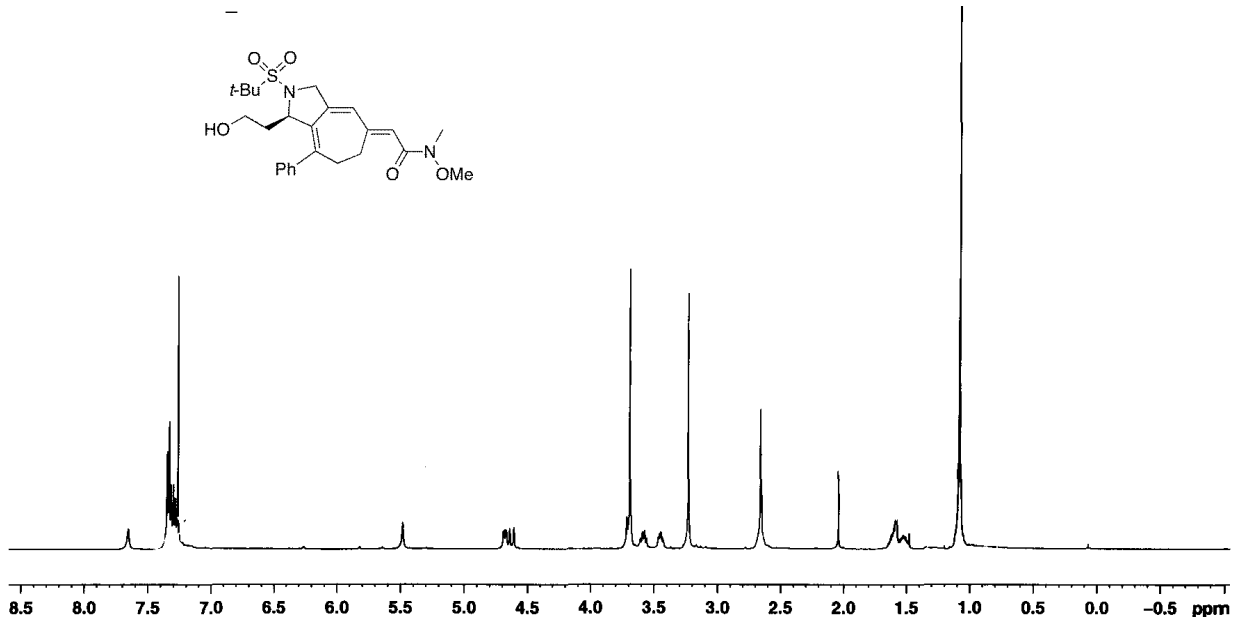

t-Bu
HO
OMe
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

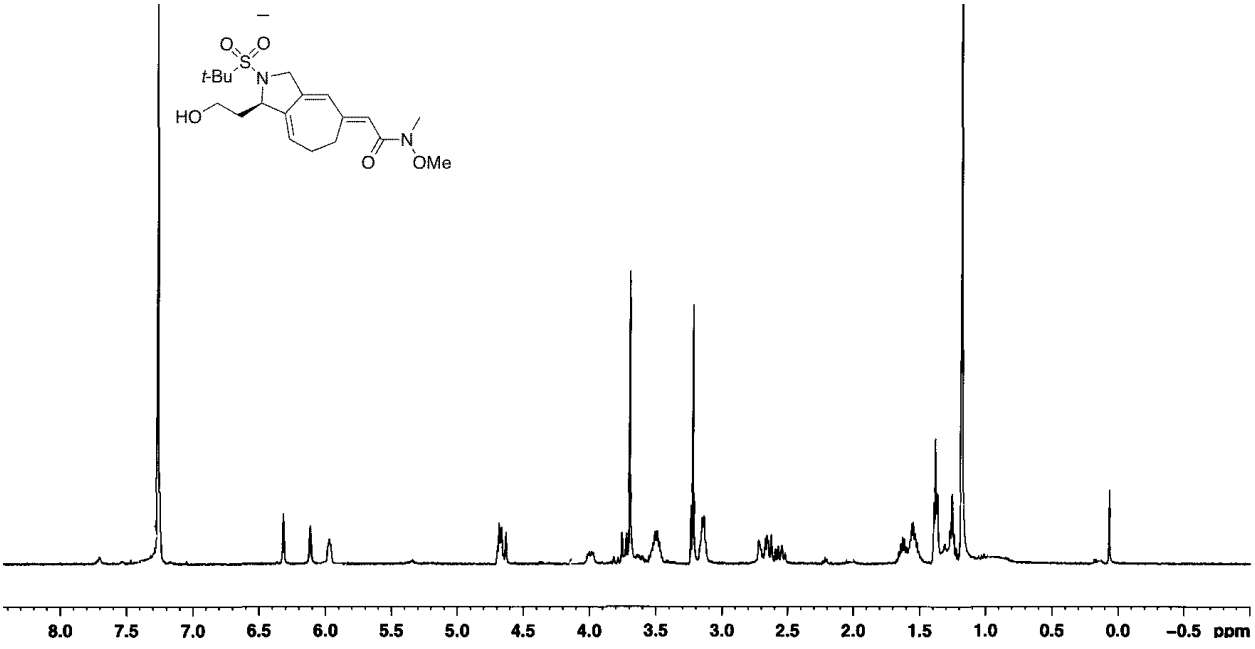

HN
HO
HO
OMe
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

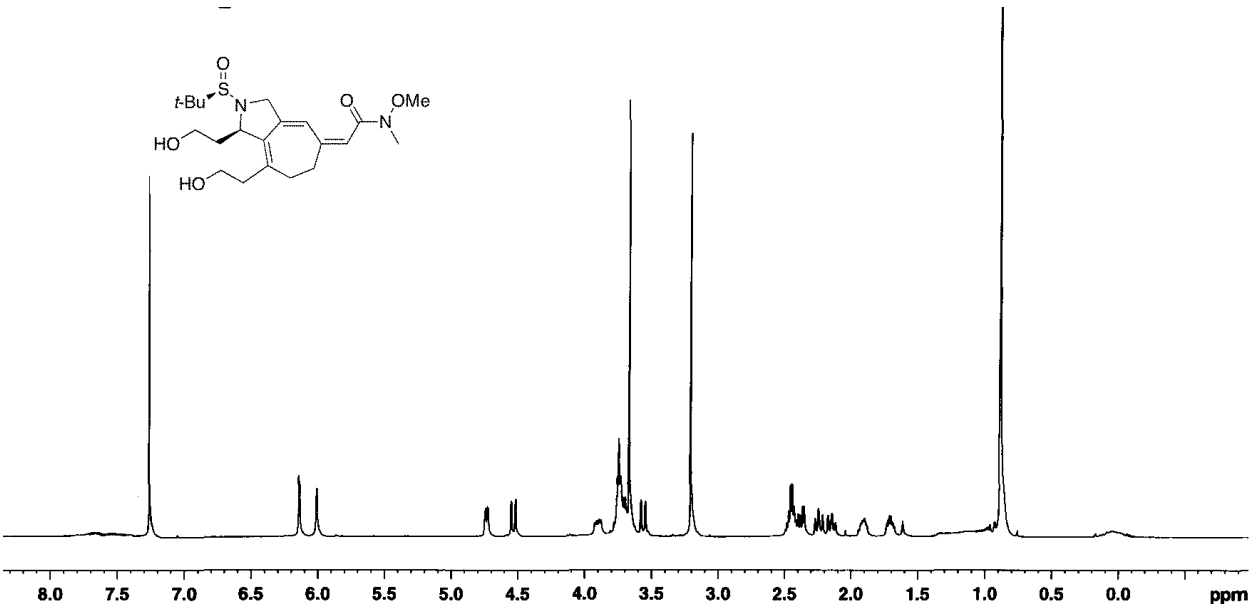

HN
HO
Ph
O
N
OMe
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

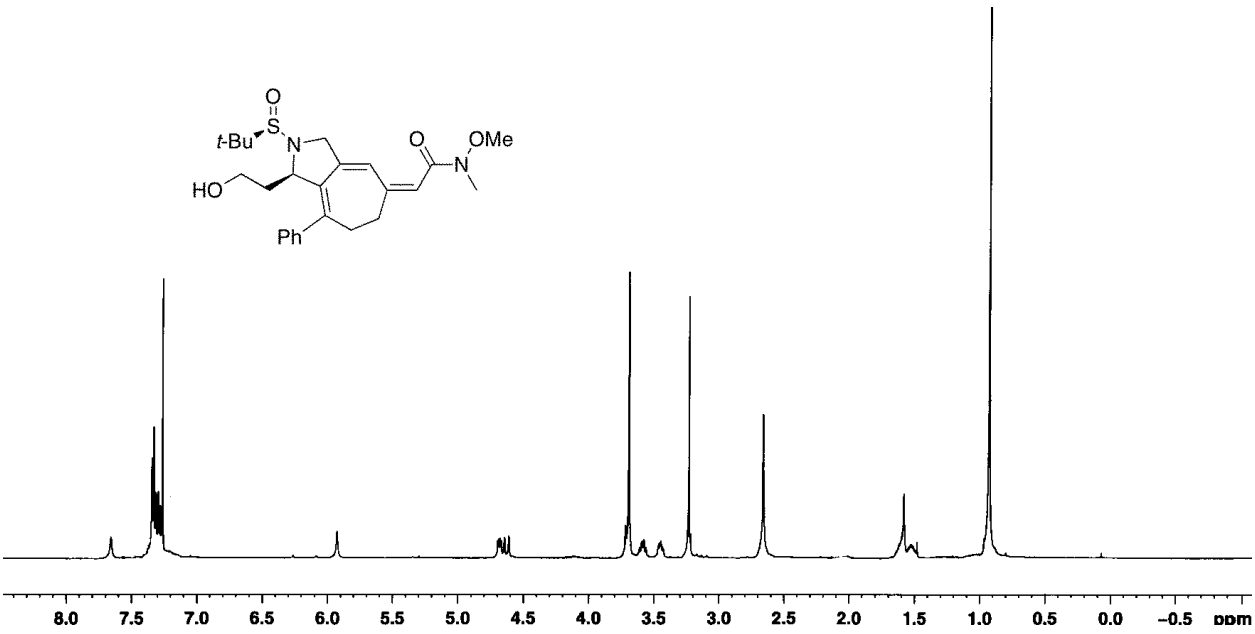

HN
HO
O
N
OMe
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

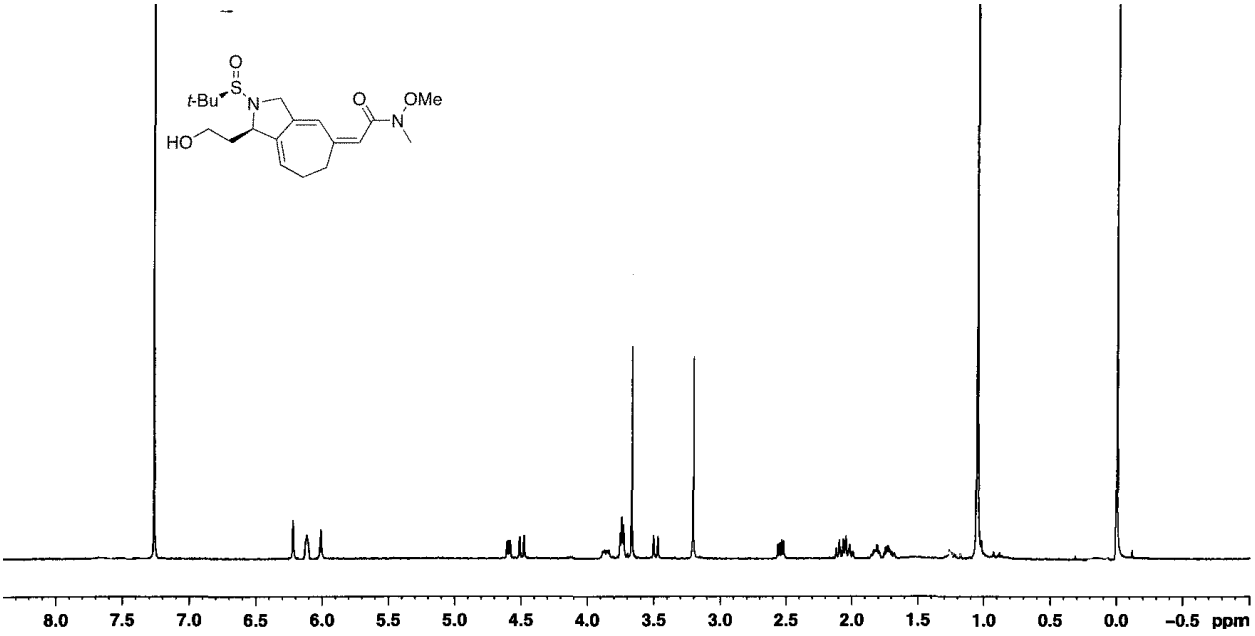

t-Bu
HO
HO
OMe
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

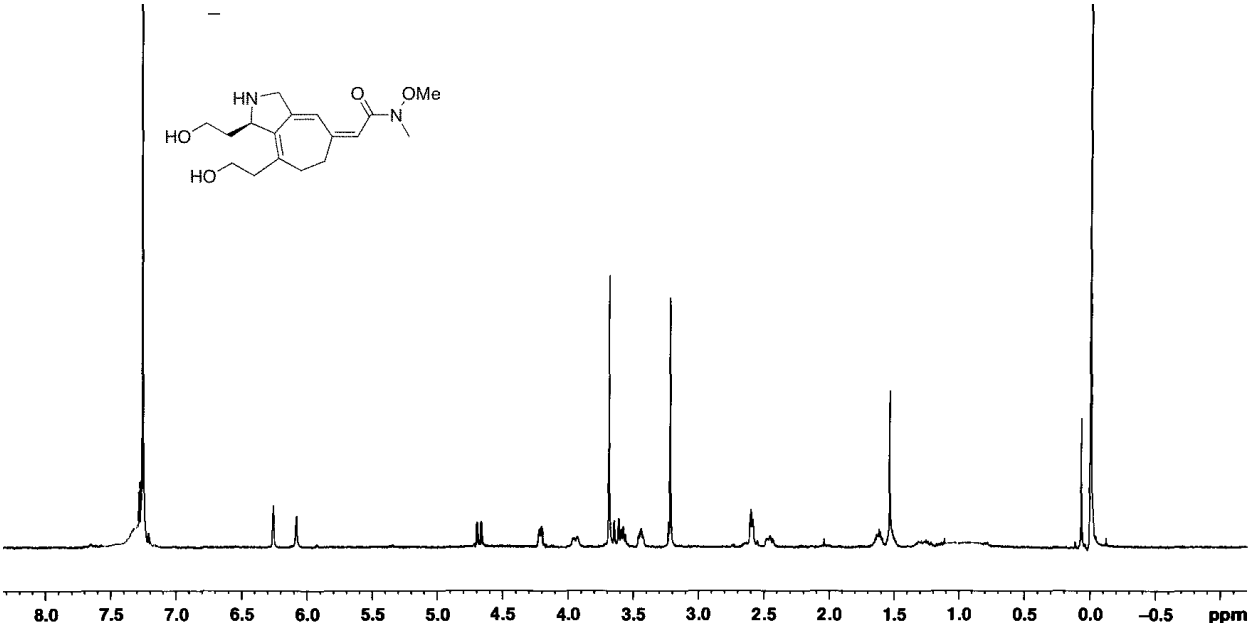

t-Bu
HO
Ph
OMe
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

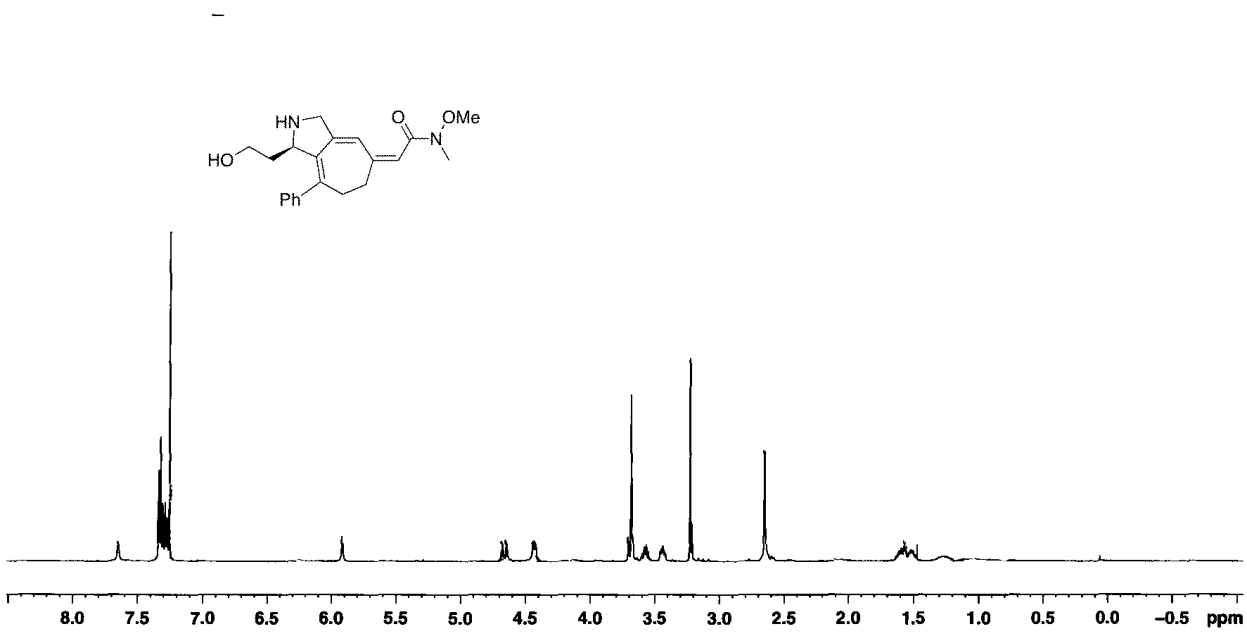

t-Bu
HO
OMe
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5 ppm

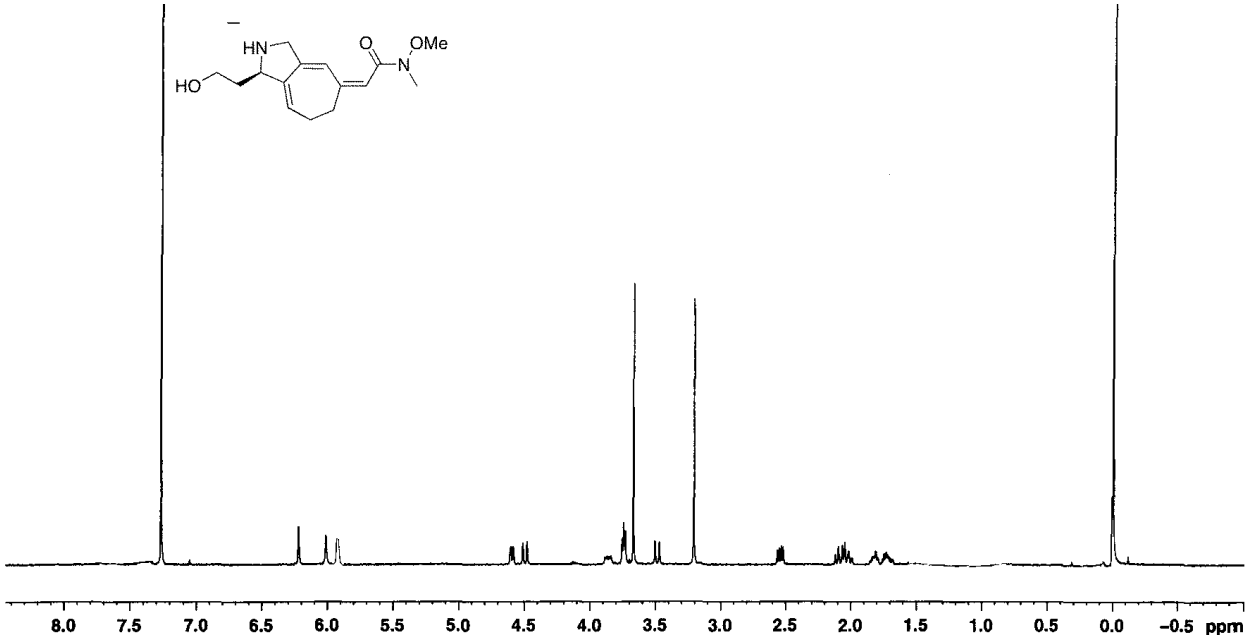

t-Bu
O
S
N
O
N
OMe
HO
HO
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

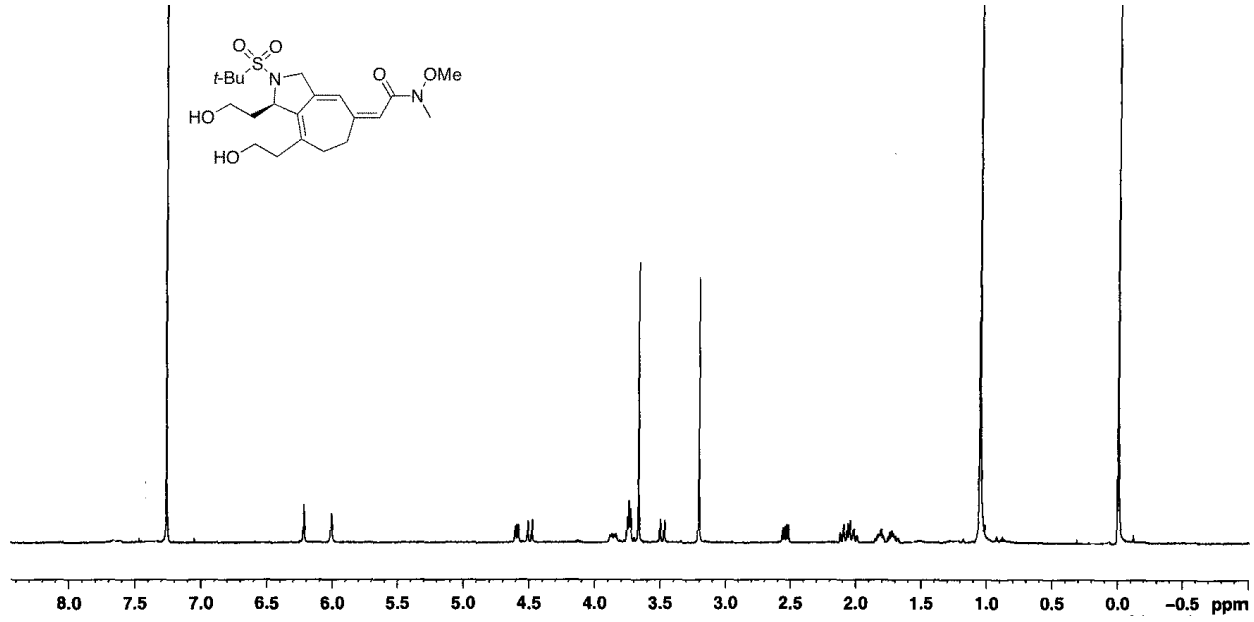

t-Bu
O
S
N
O
N
OMe
HO
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
ppm

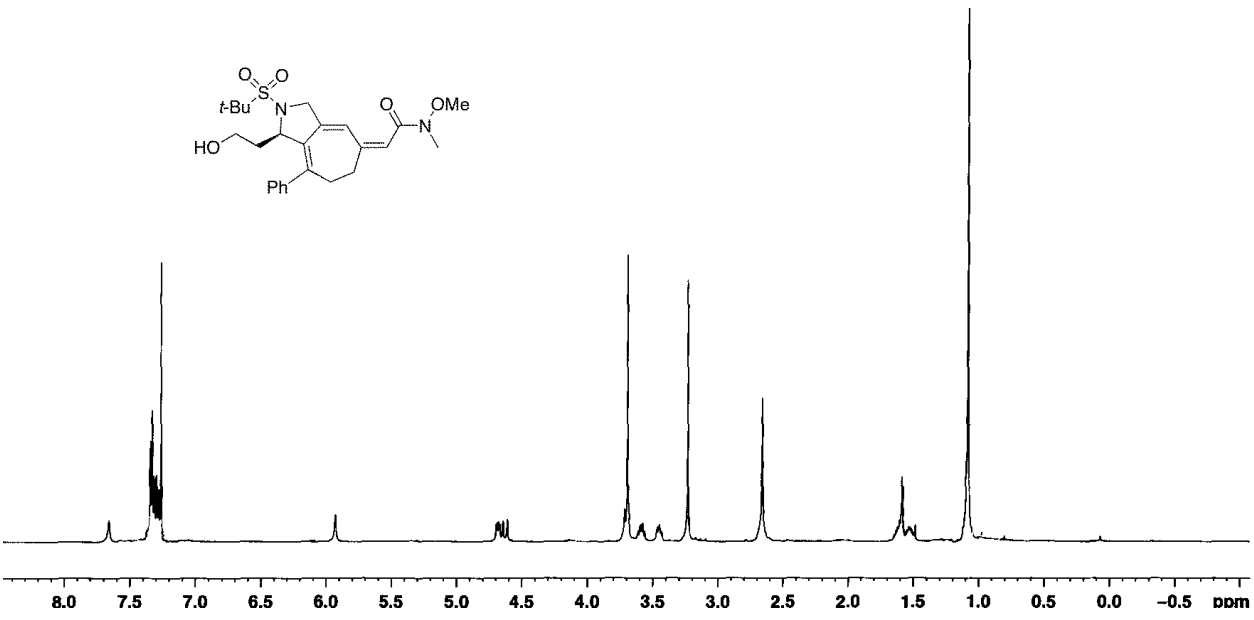

t-Bu
S
O
N
HO
O
N
OMe
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

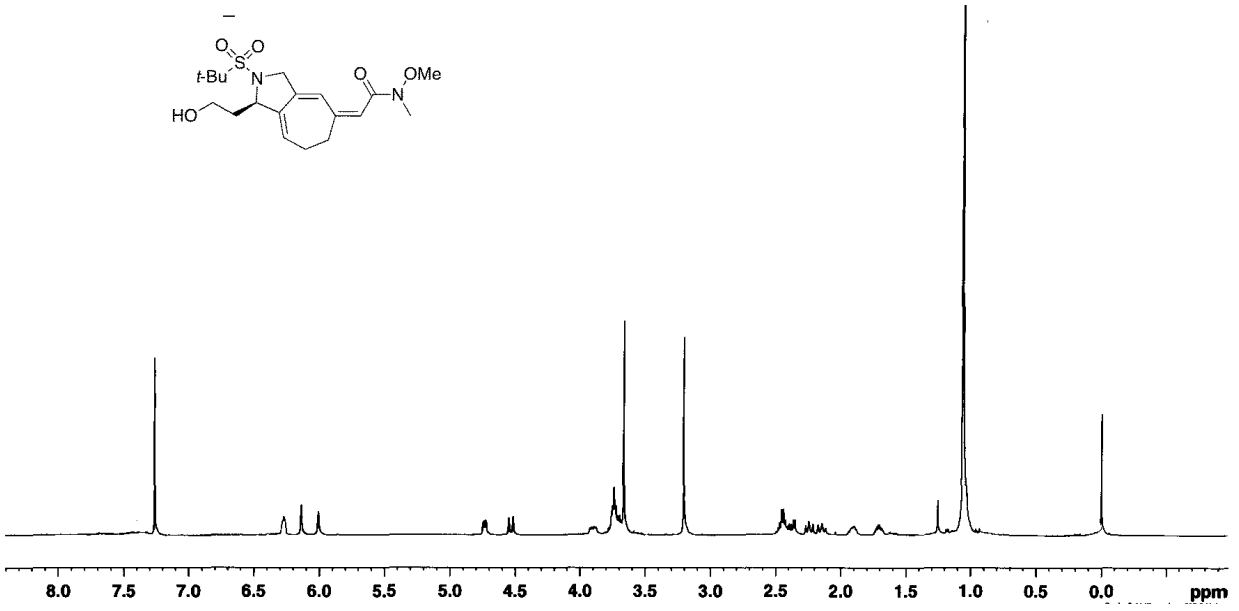

HN
HO
HO
O
N
OMe
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm


HN
O
OMe
N
HO
Ph
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 −0.5 ppm


HN
O
OMe
N
HO
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 −0.5 ppm

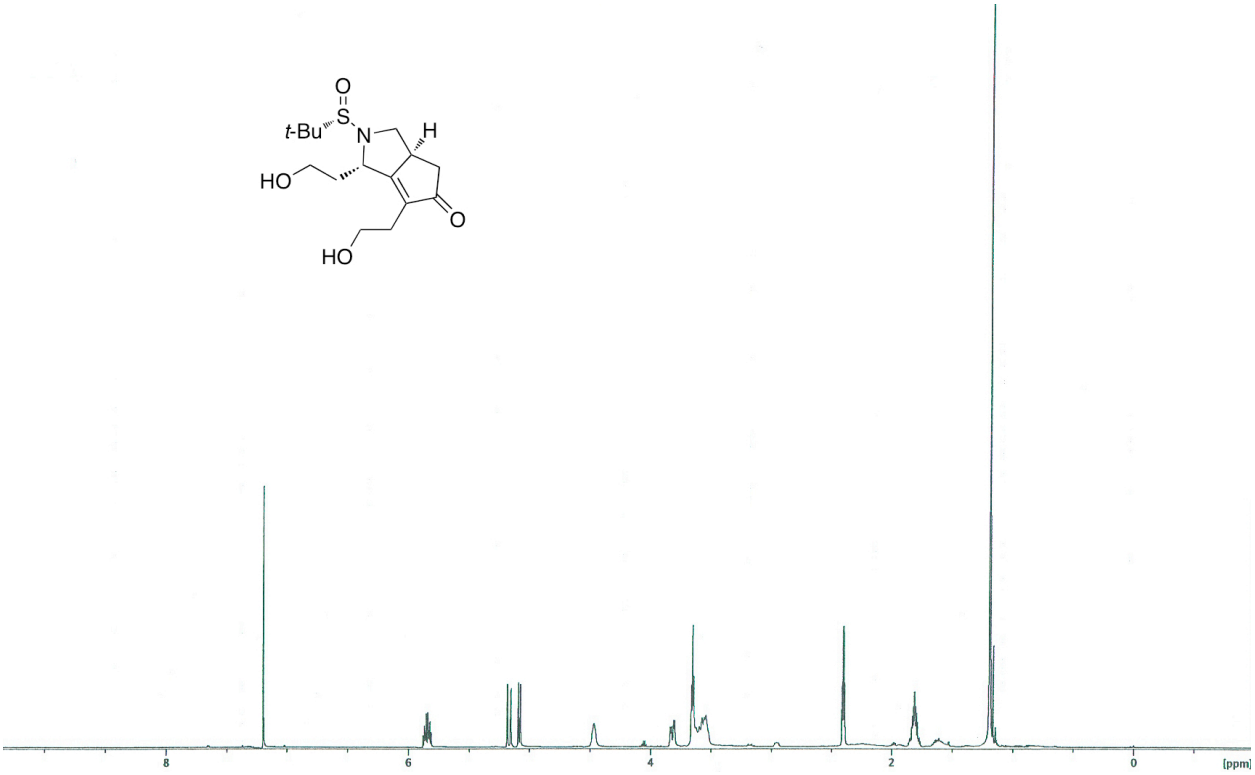

t-Bu
HO
HO
OMe
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

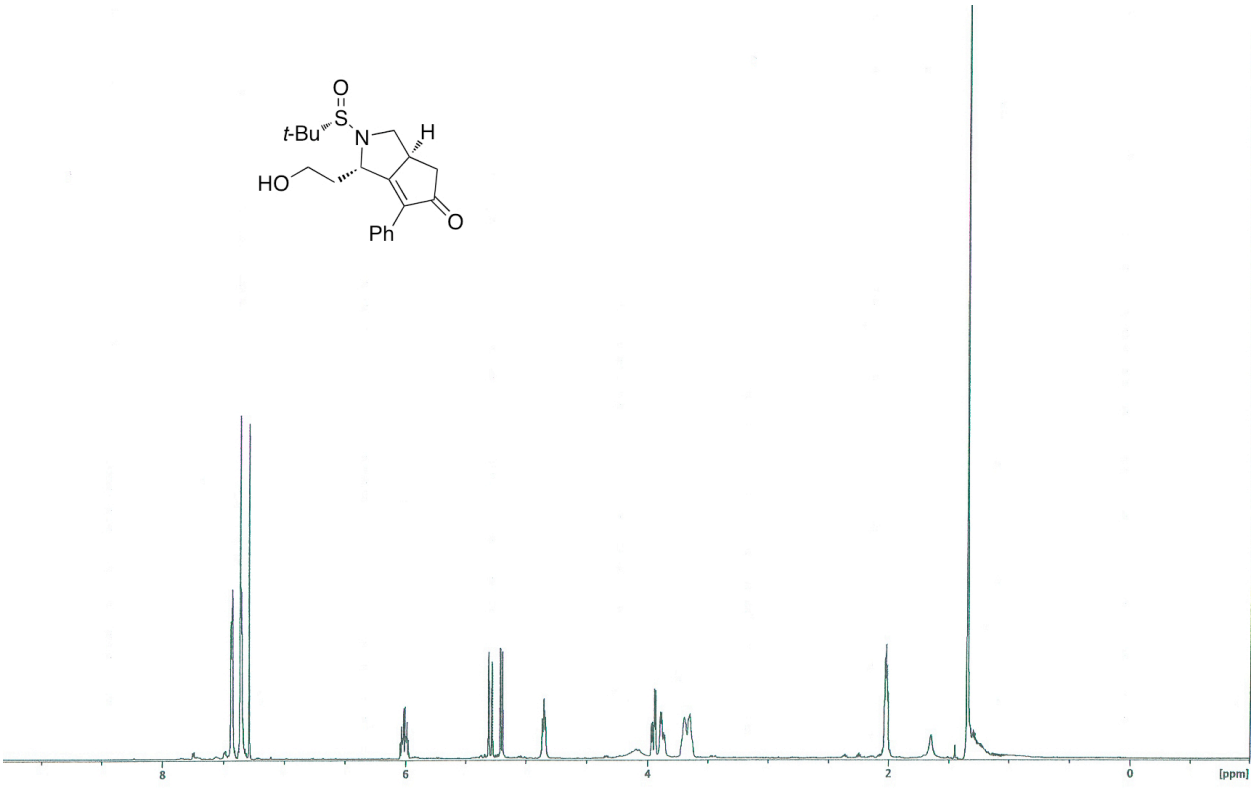

t-Bu
HO
Ph
OMe
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

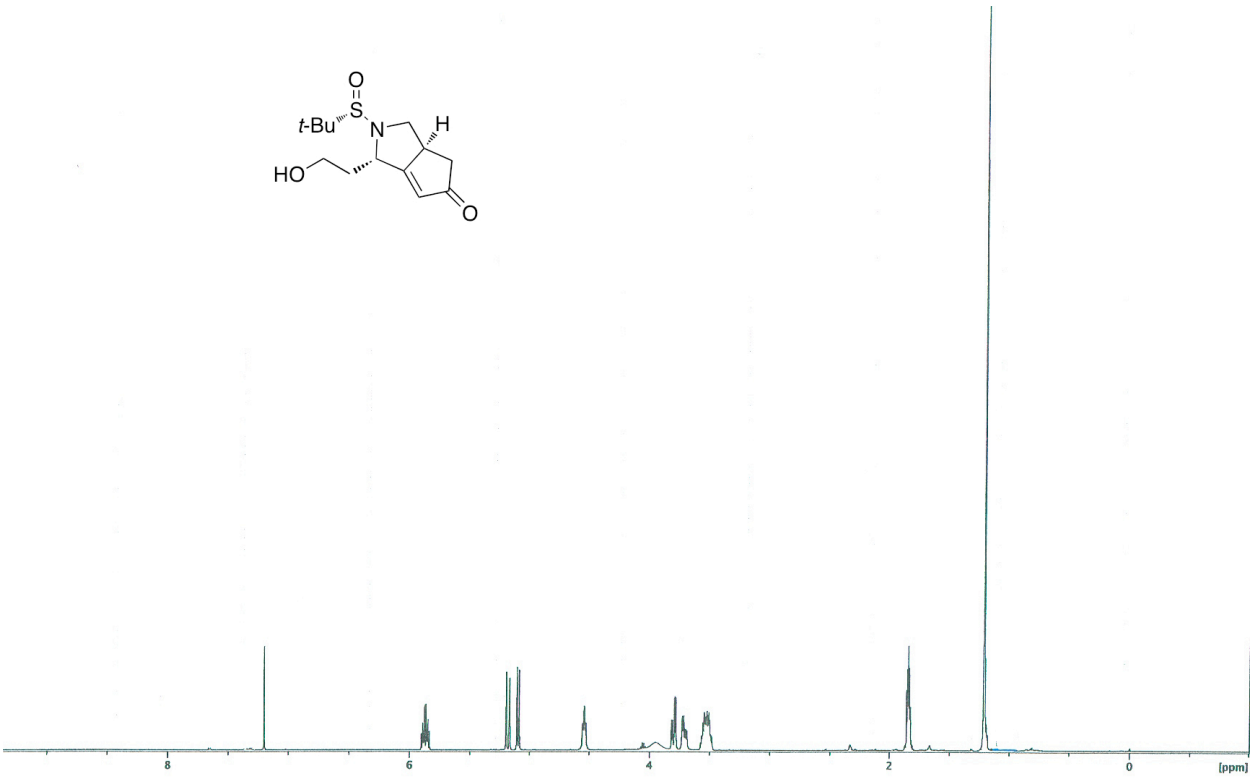

t-Bu
HO
OMe
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

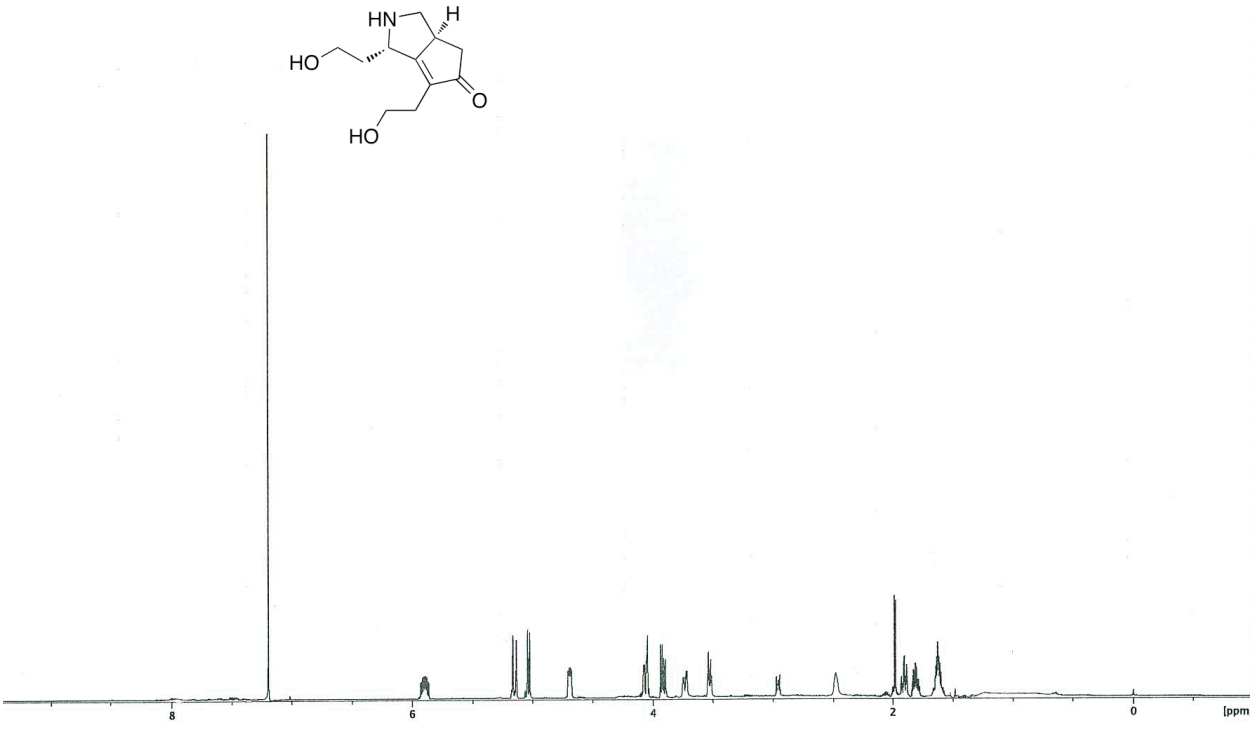
2. ^{1}H-NMR SPECTRA FOR *S*-SERIES LIBRARY MEMBERS

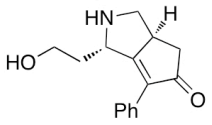
a. Pauson–Khand reaction products (*S*-11–13)

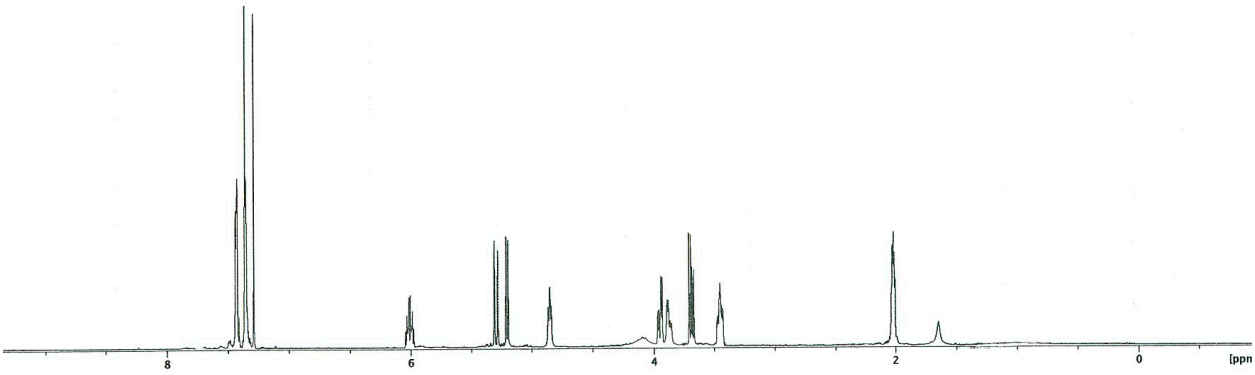


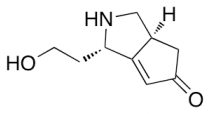


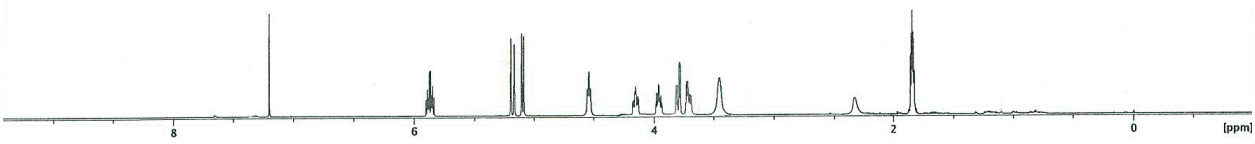

O
S
t-Bu
N
H
HO
O
8
6
4
2
0
[ppm]

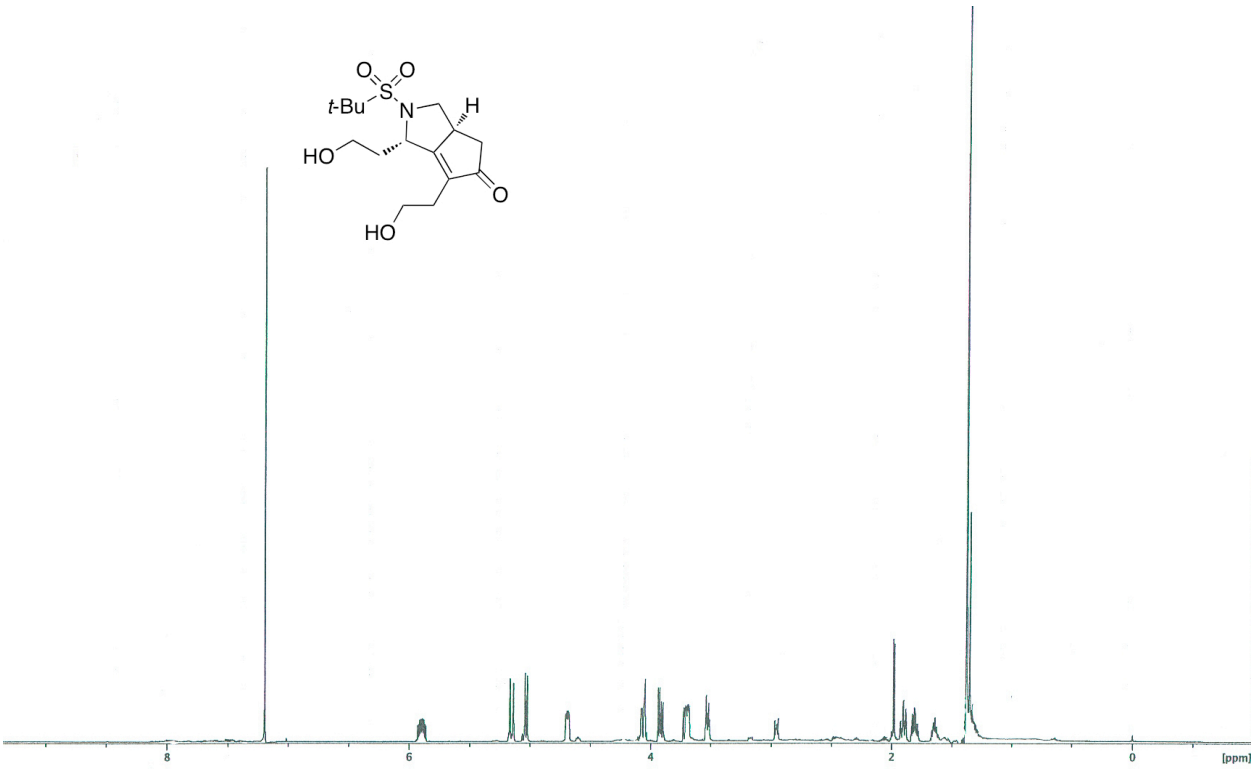

HN
H
HO
O
HO
8
6
4
2
0
[ppm

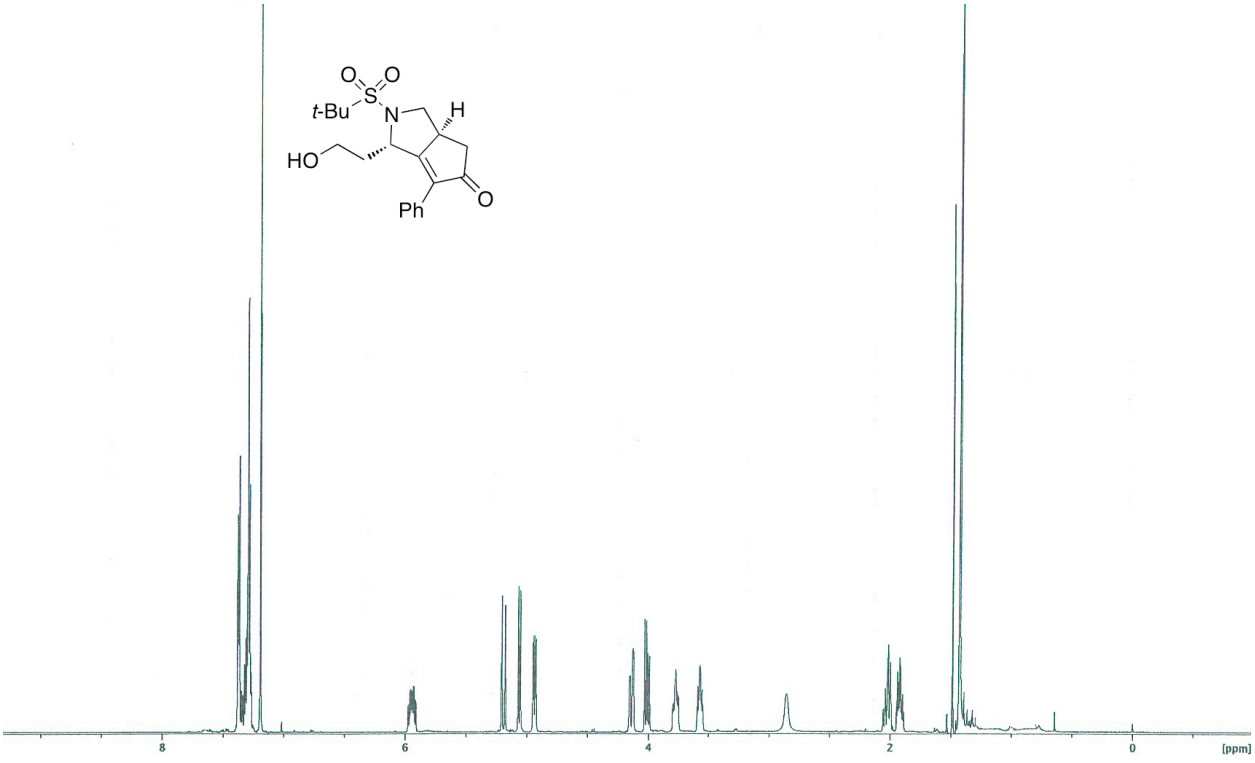

HN
H
HO
Ph
O

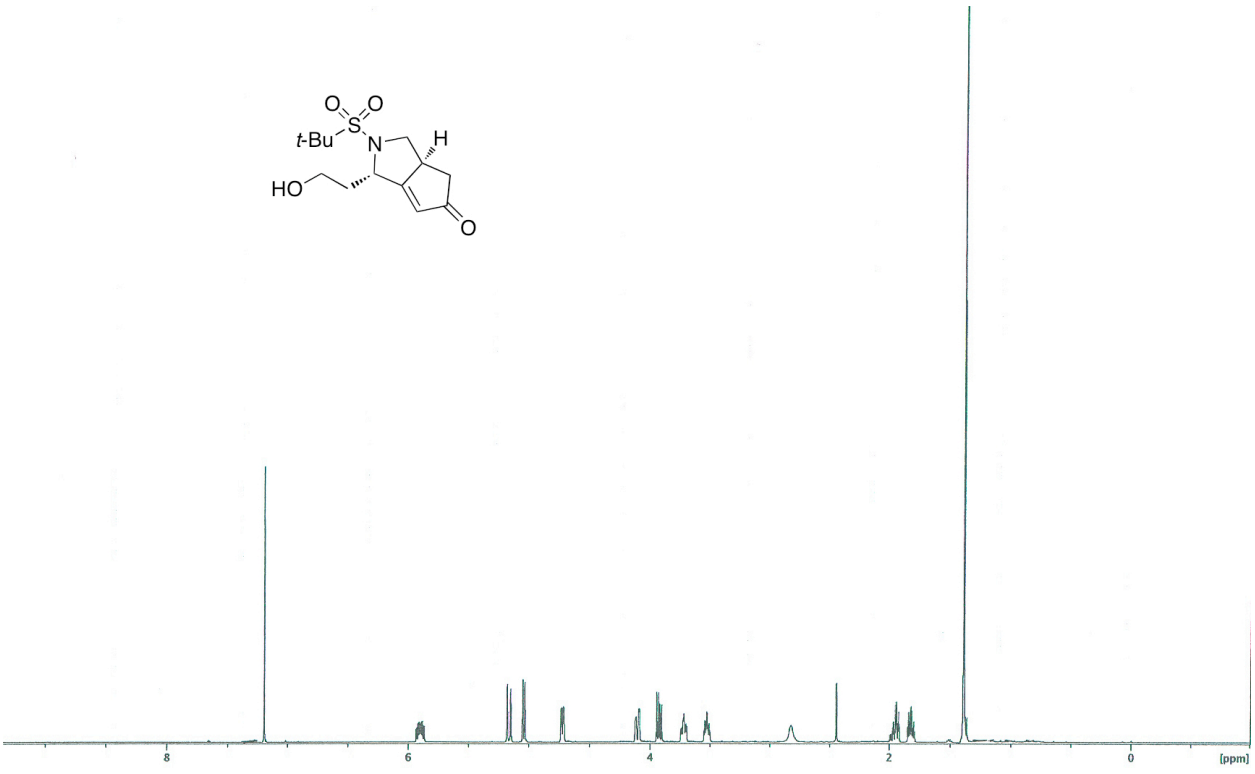

8
6
4
2
0
[ppm]


HN
H
HO
O

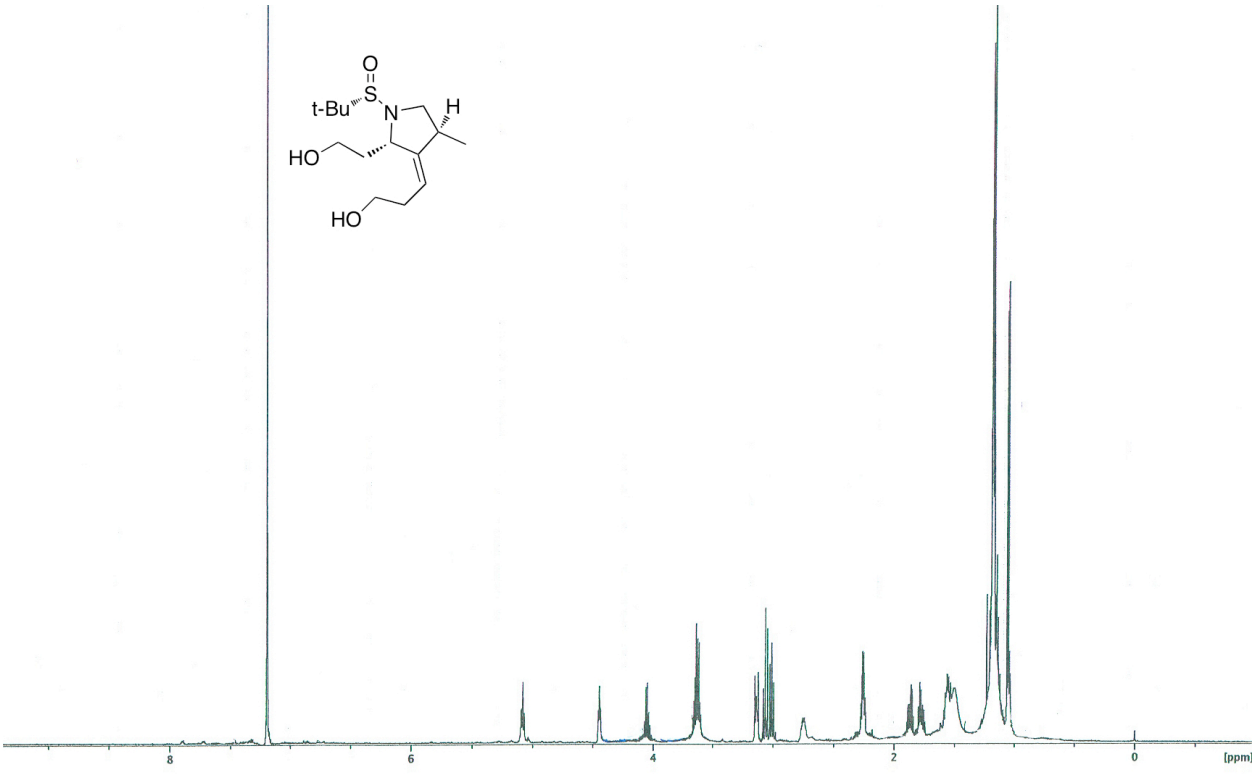

8
6
4
2
0
[ppm]

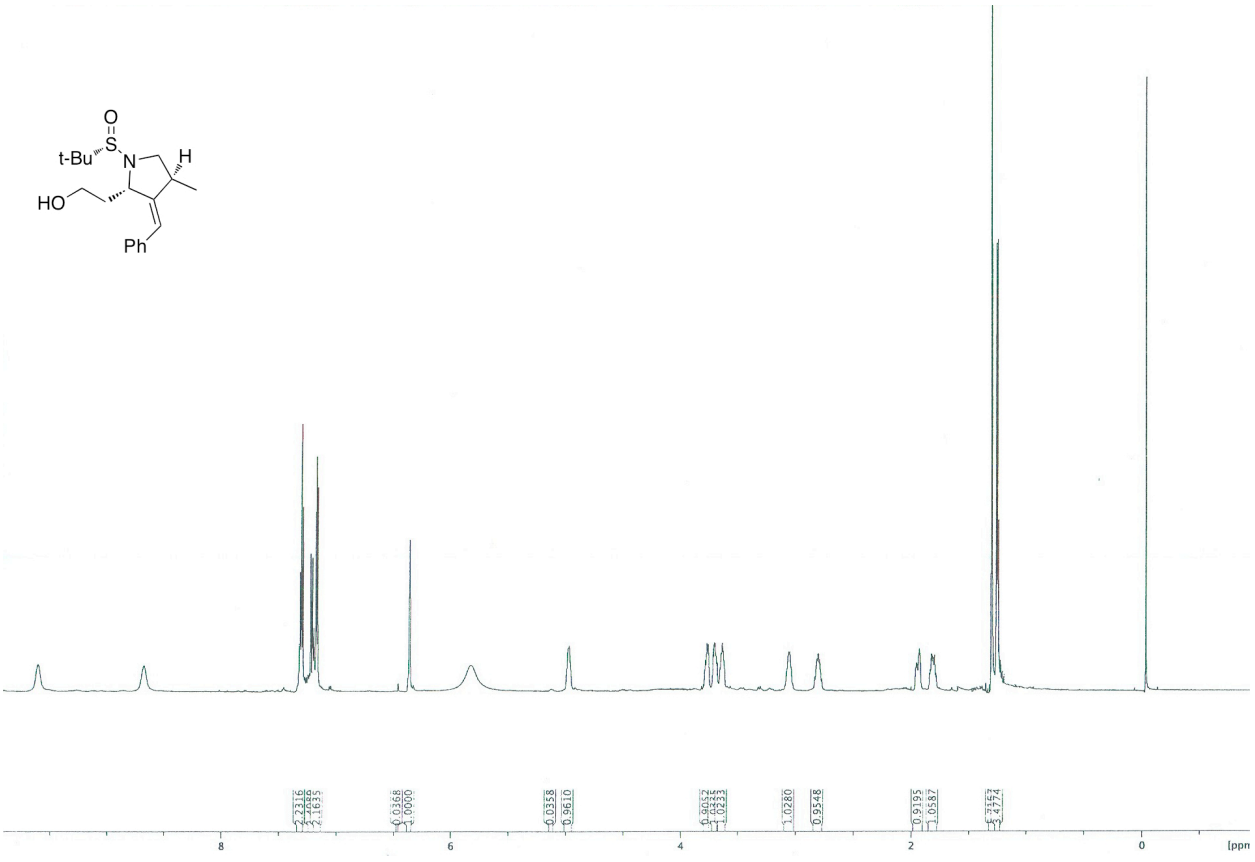

O
S
O
t-Bu
N
H
HO
O
HO
8
6
4
2
0
[ppm]

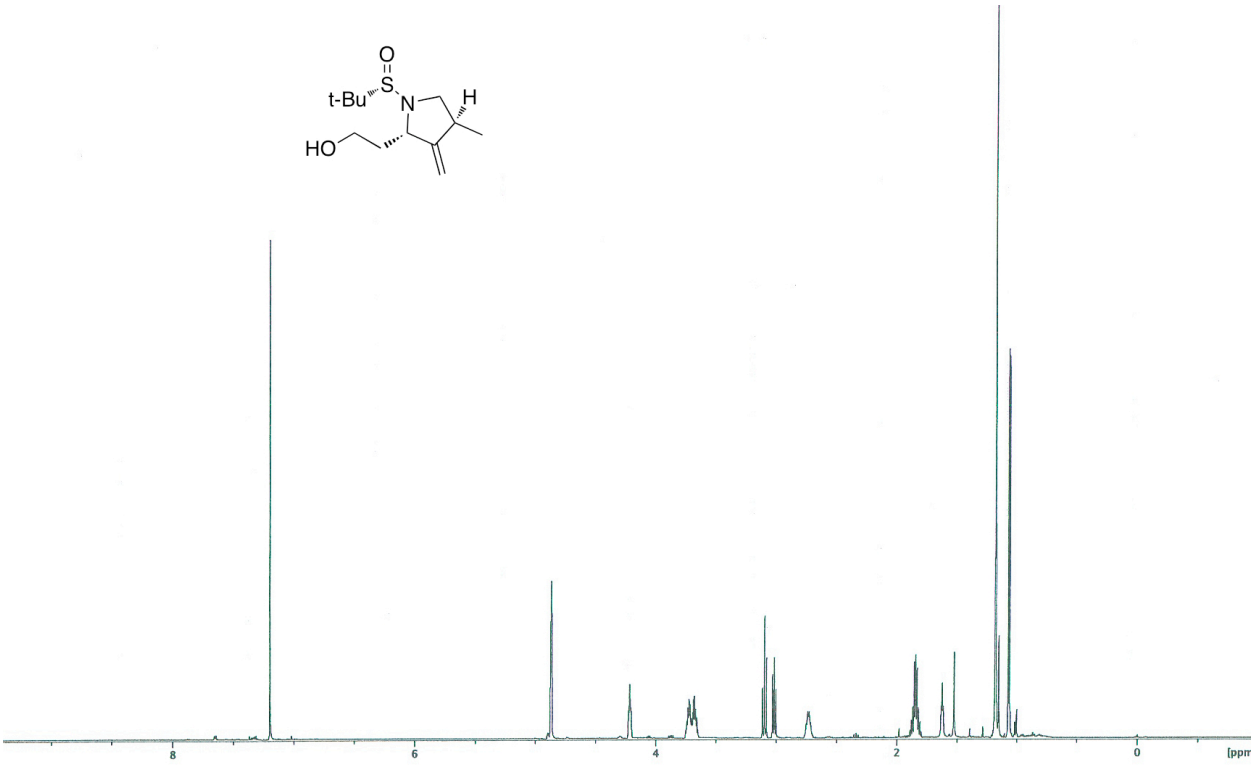

O
S
O
t-Bu
N
H
HO
Ph
O
8
6
4
2
0
[ppm]


O
O
S
t-Bu
N
H
HO
O
8
6
4
2
0
[ppm]

b. Krische reductive cyclization products (*S*-14–19)






O
S
t-Bu
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H
HO
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4
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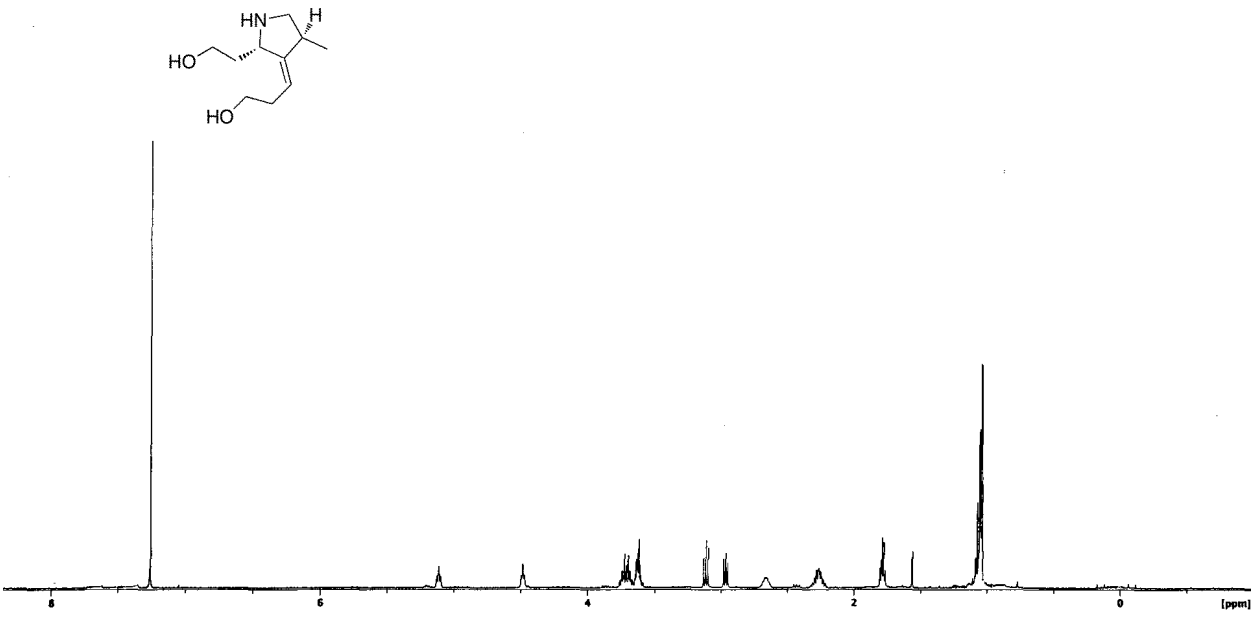
0
[ppm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HO
HO
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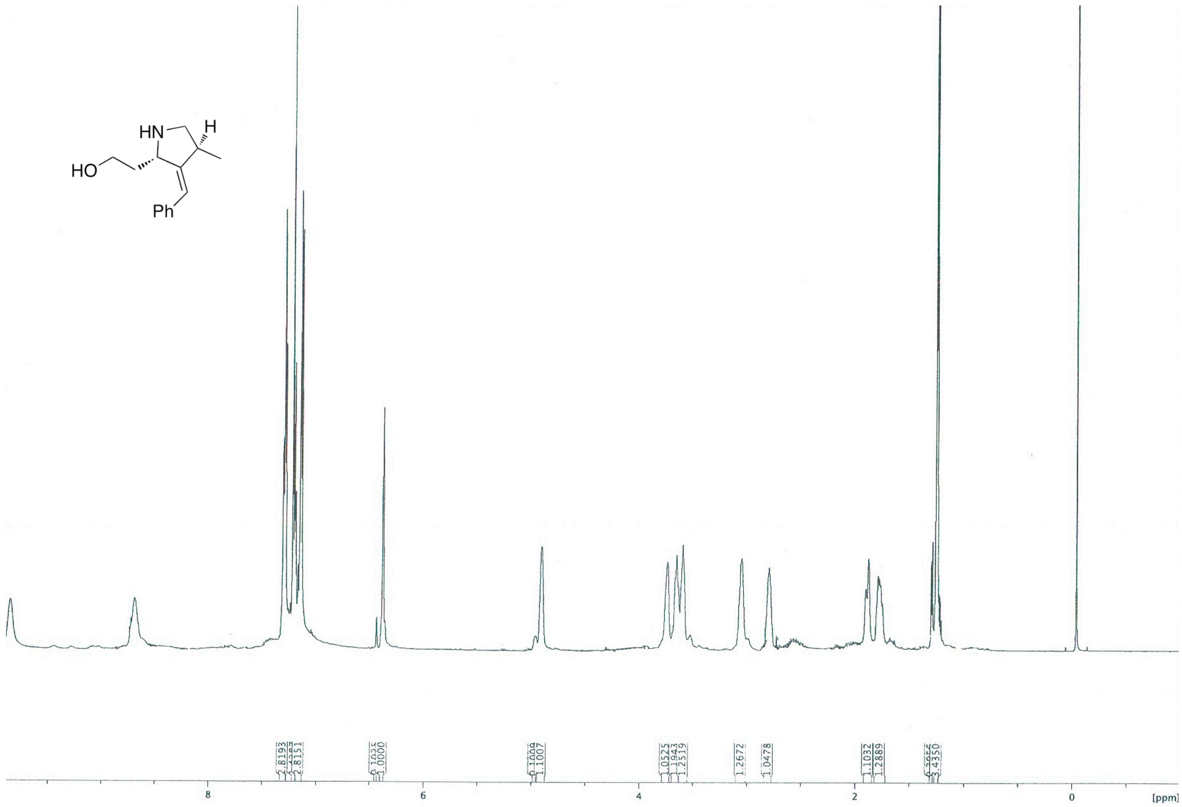
4
2
0
[ppm]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HO
Ph
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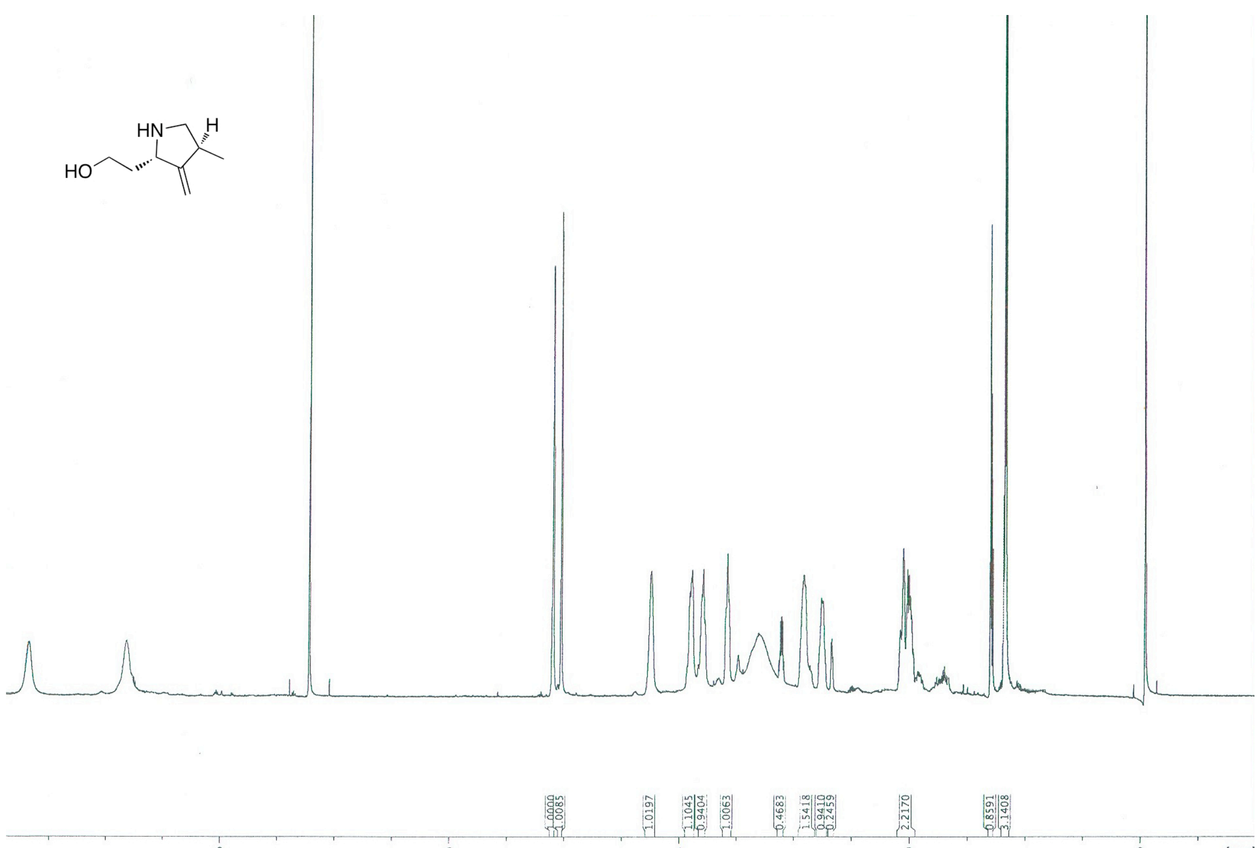
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H
HO
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4
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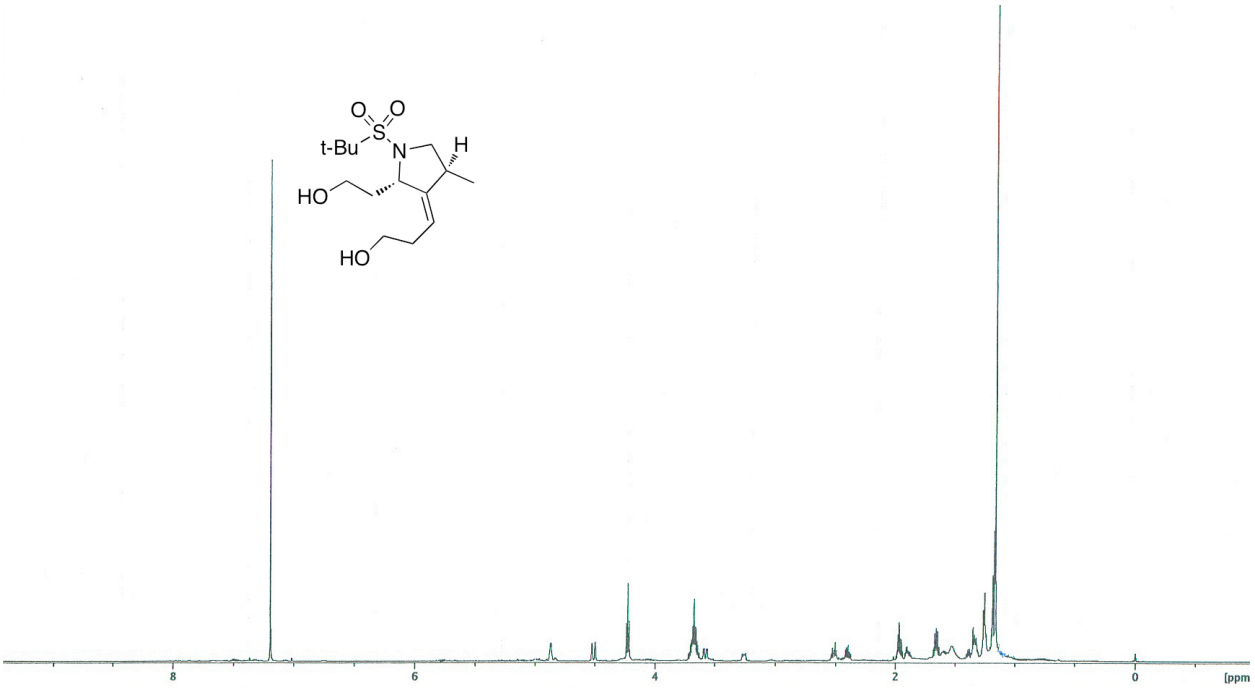
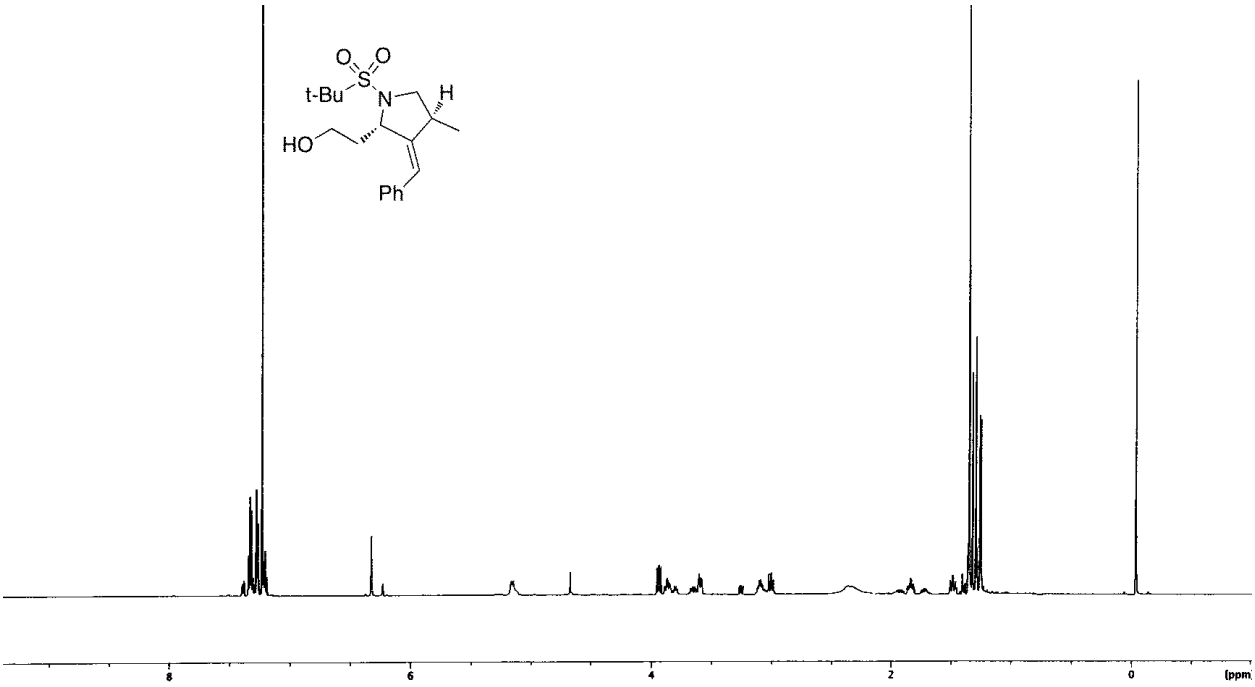
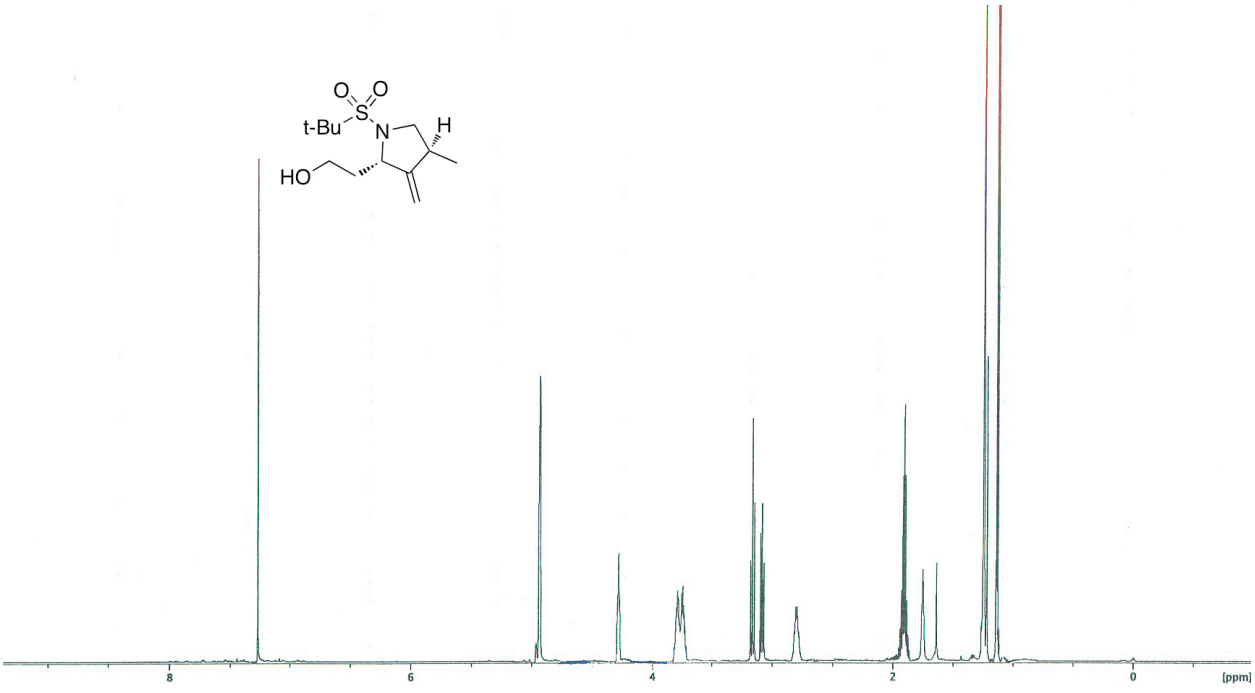
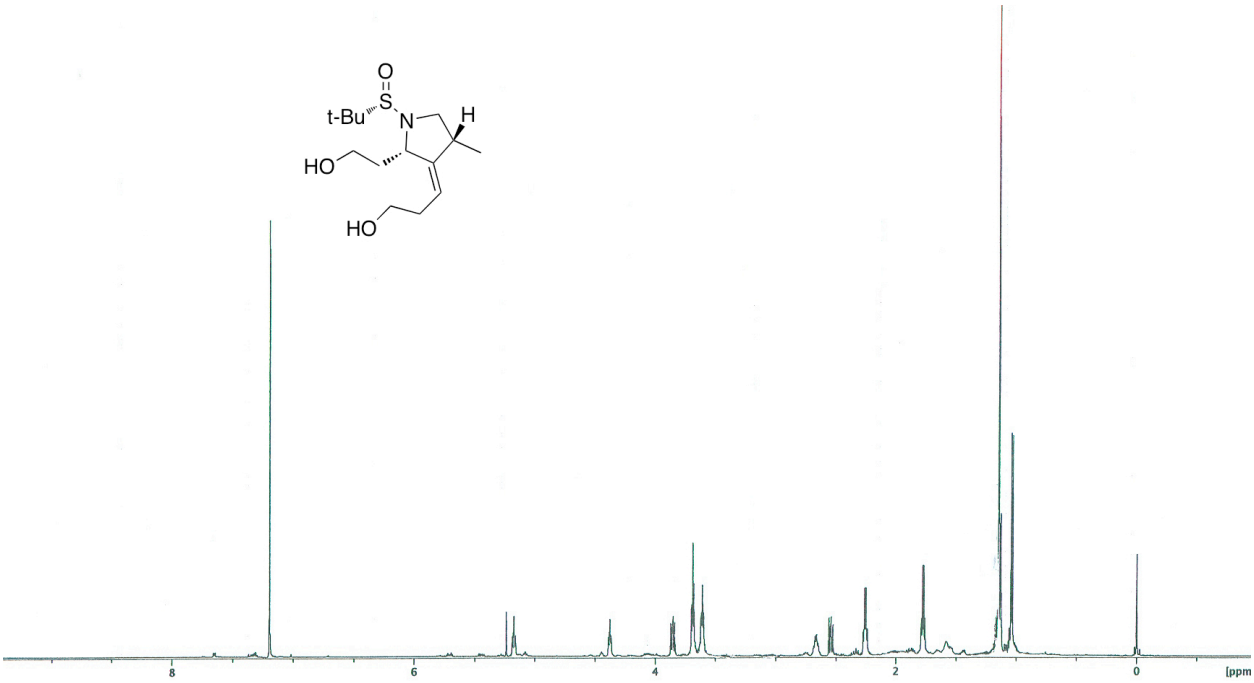
[ppm]


t-Bu
HO
HO
8
6
4
2
0
(ppm


t-Bu
HO
Ph
8
6
4
2
0
(ppm


O
O
S
t-Bu
N
H
HO
8
6
4
2
0
[ppm]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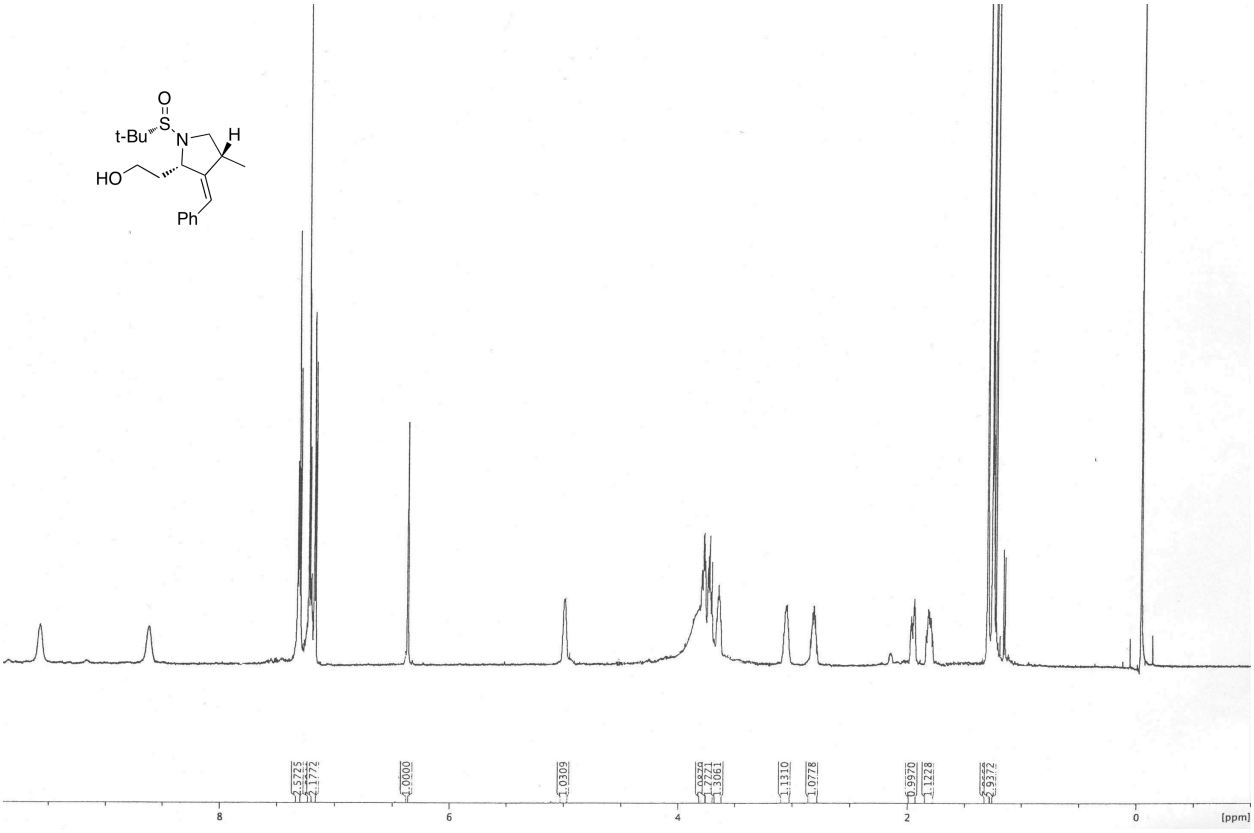
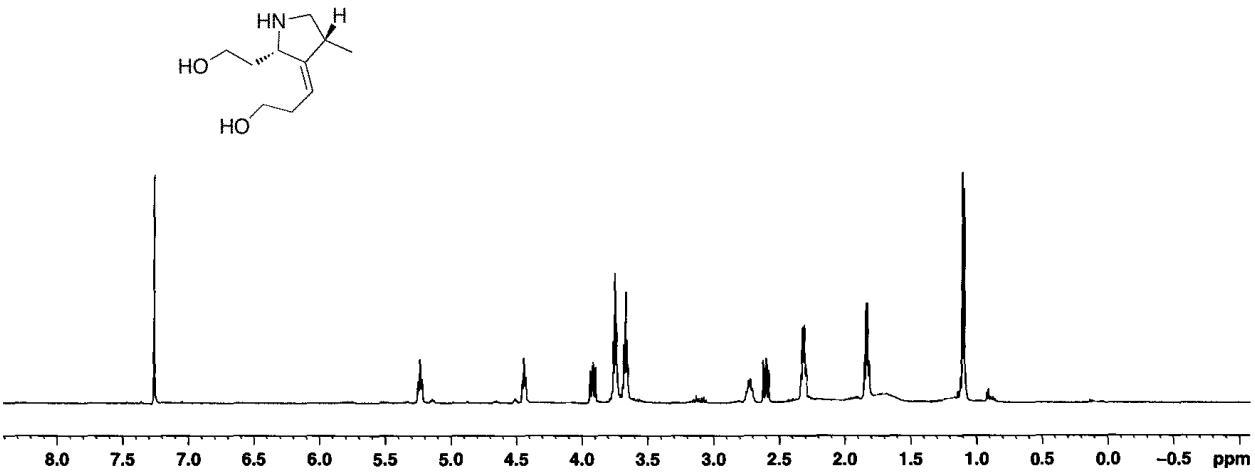
S
t-Bu
N
H
HO
HO
8
6
4
2
0
[ppm


O
S
t-Bu
N
H
HO
Ph
2.5725
2.1772
1.0000
1.0309
1.0826
1.0661
1.1310
1.0778
0.9970
1.1228
2.9372
8
6
4
2
0
[ppm]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H
HO
HO
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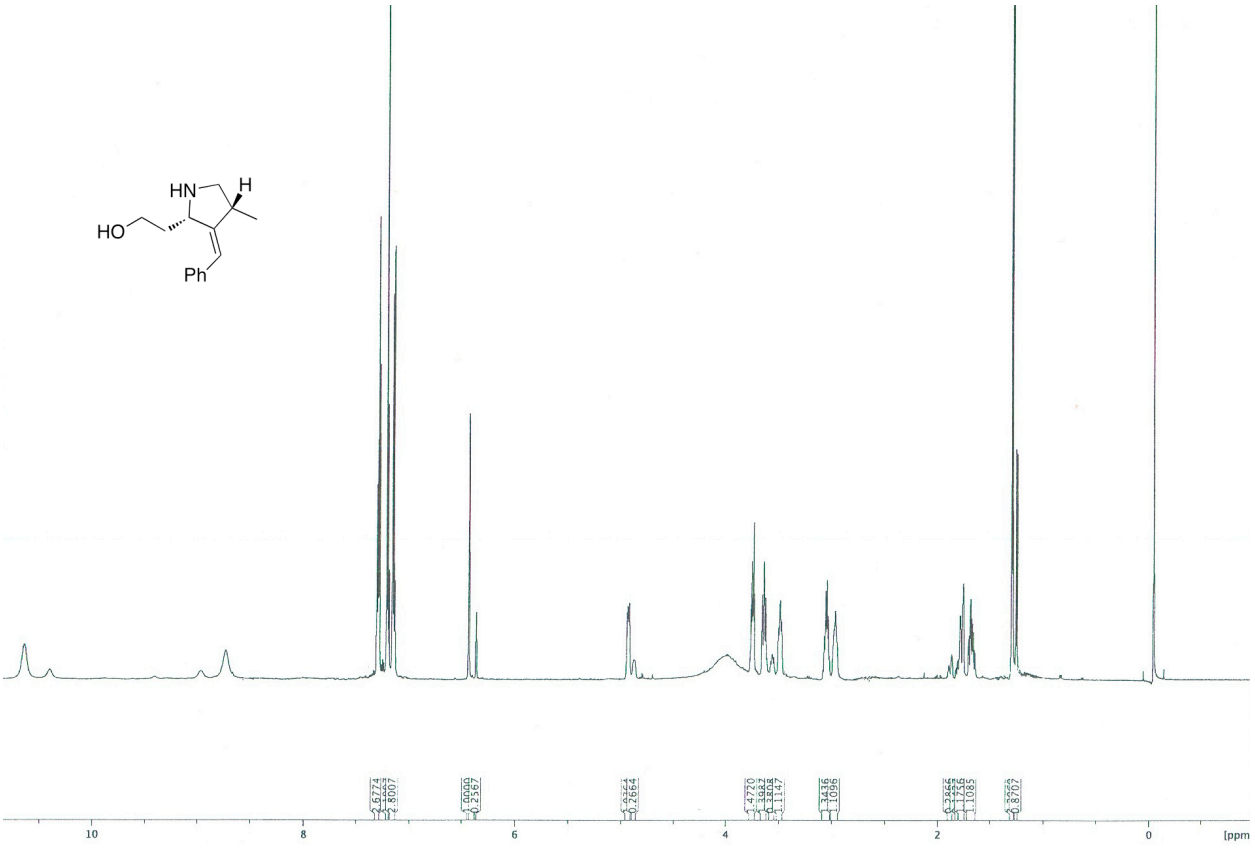
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
ppm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H
HO
Ph
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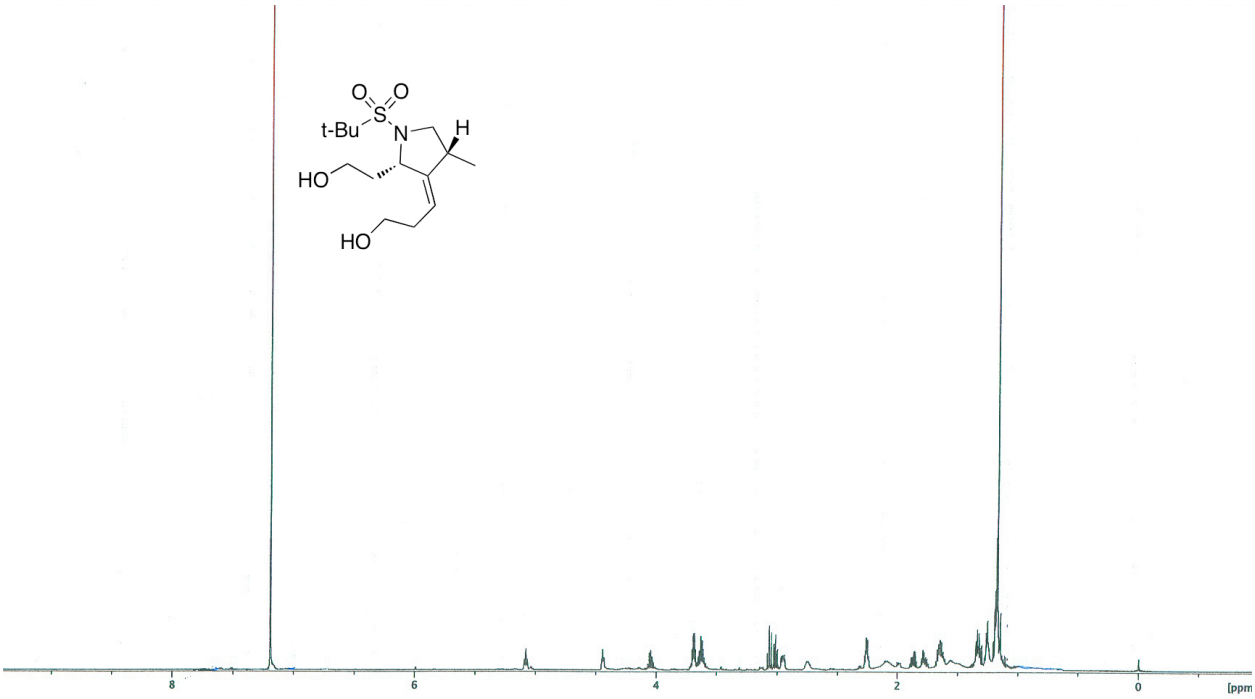
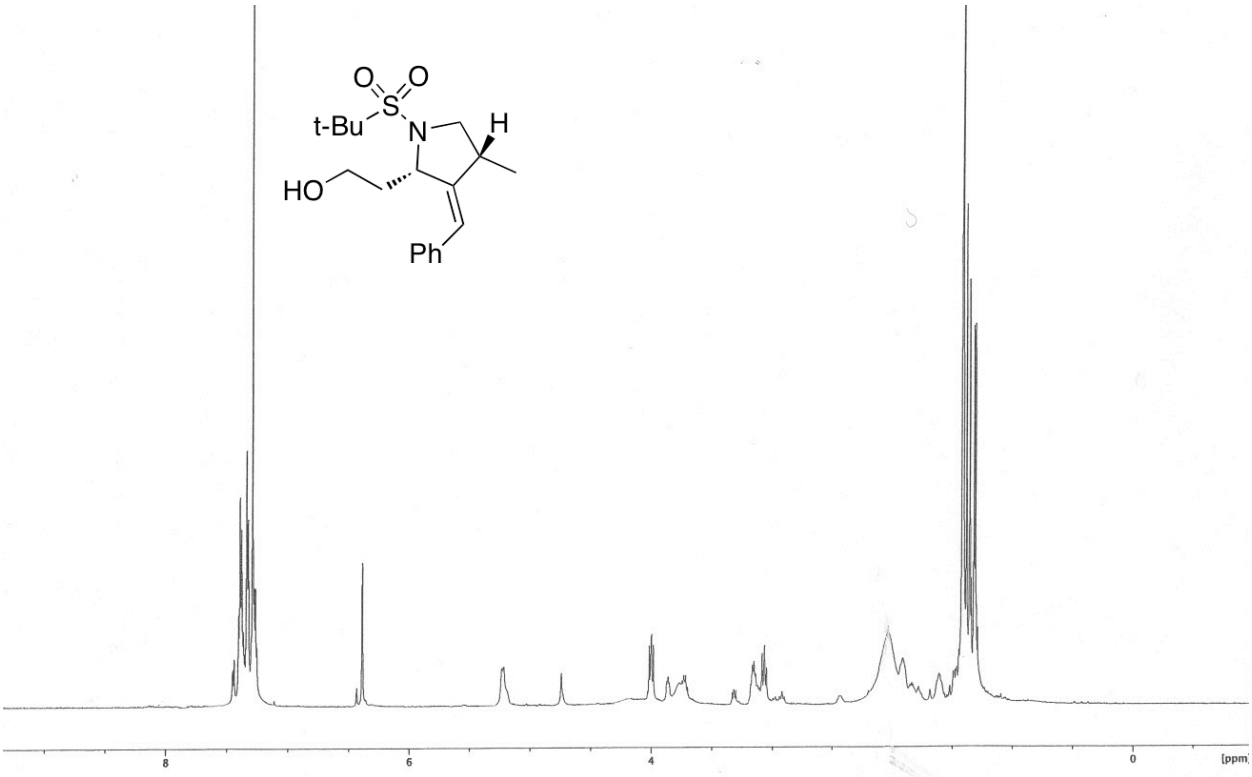
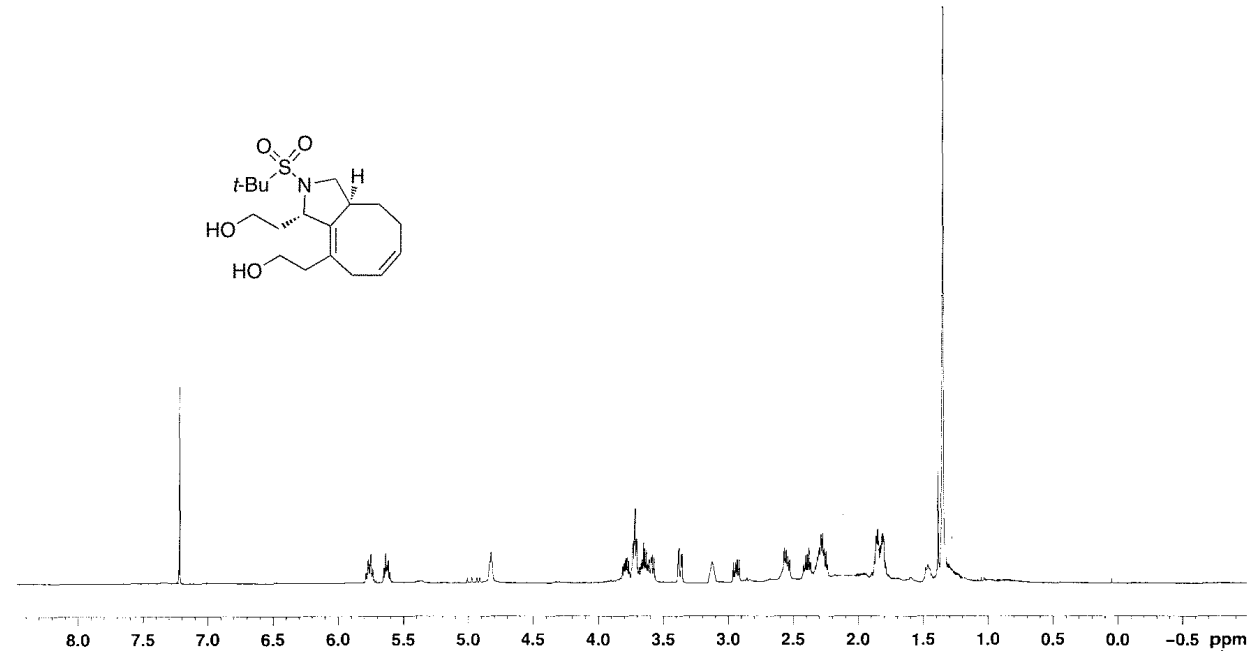
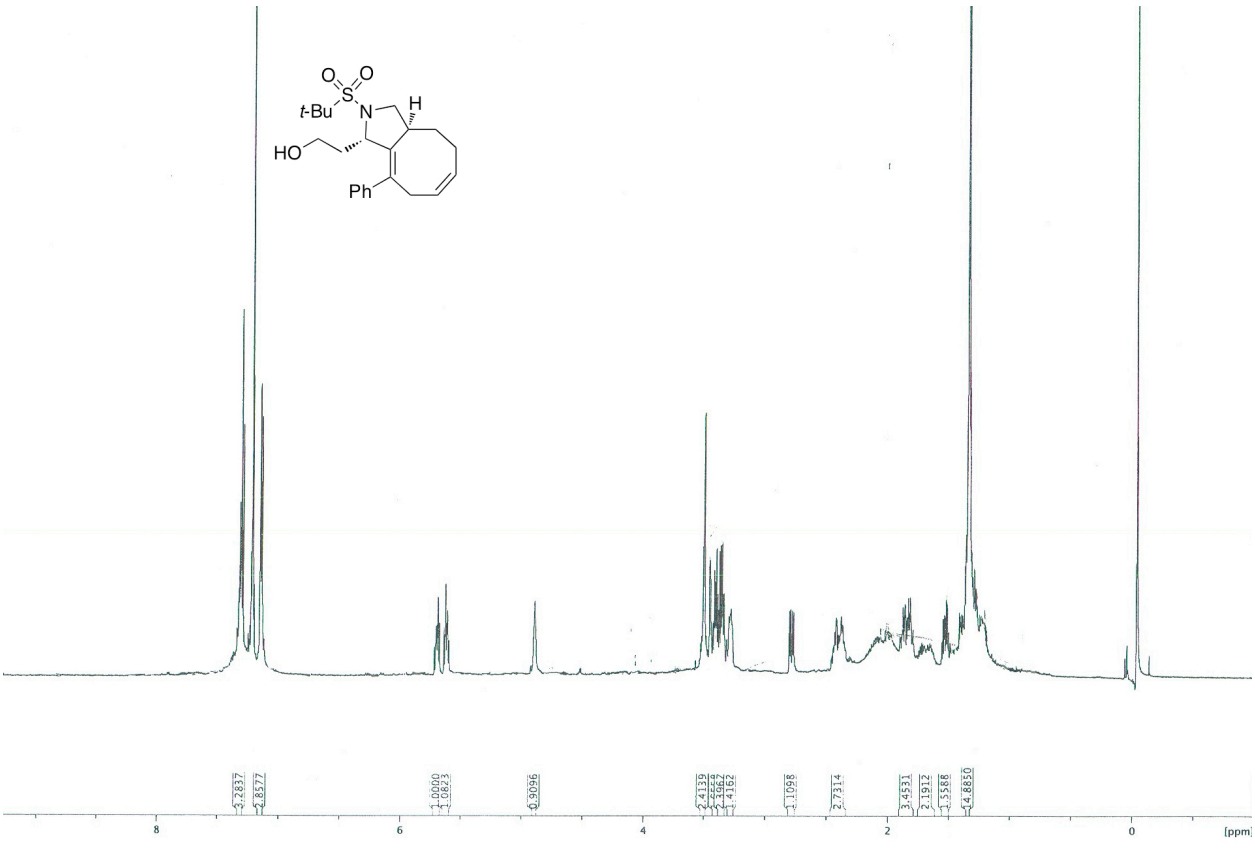
8
6
4
2
0
[ppm]

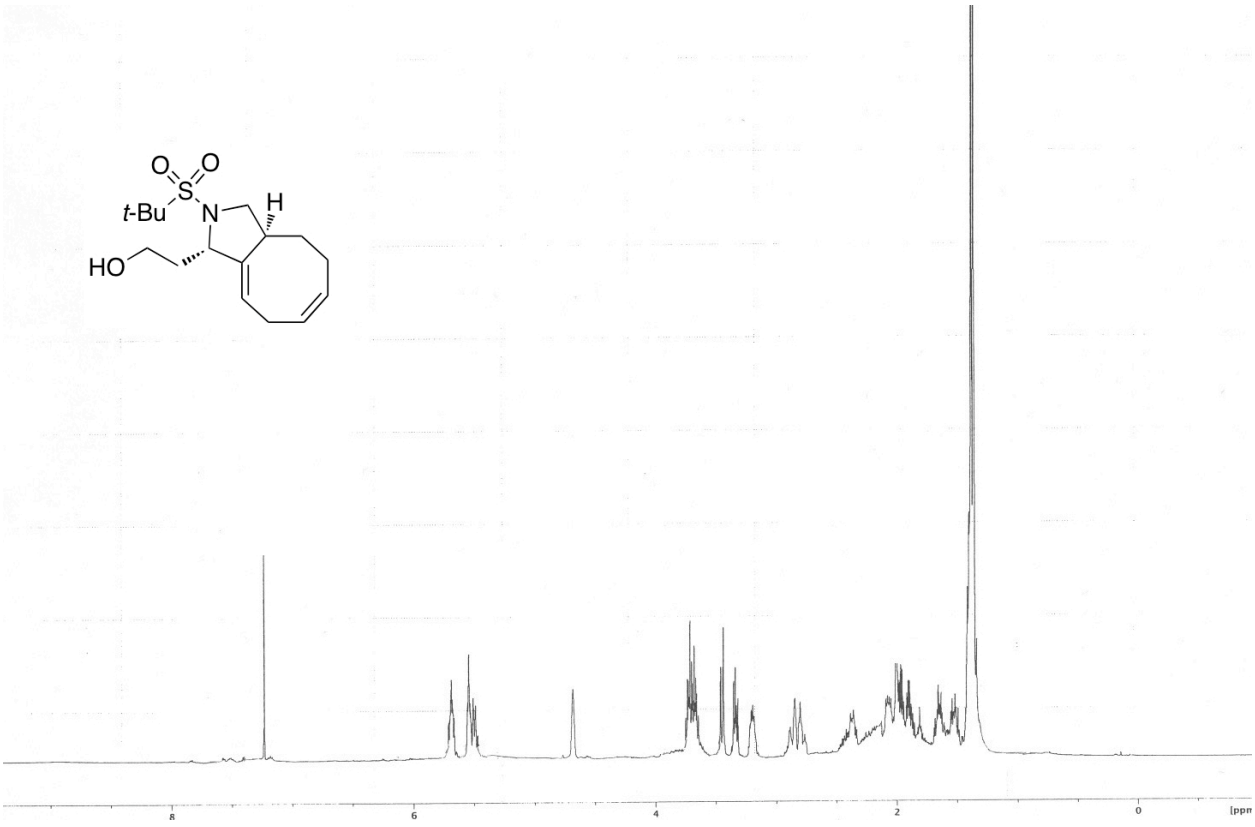

O
O
S
t-Bu
N
H
HO
HO
8
6
4
2
0
[ppm


O
O
S
t-Bu
N
H
HO
Ph
8
6
4
0
[ppm

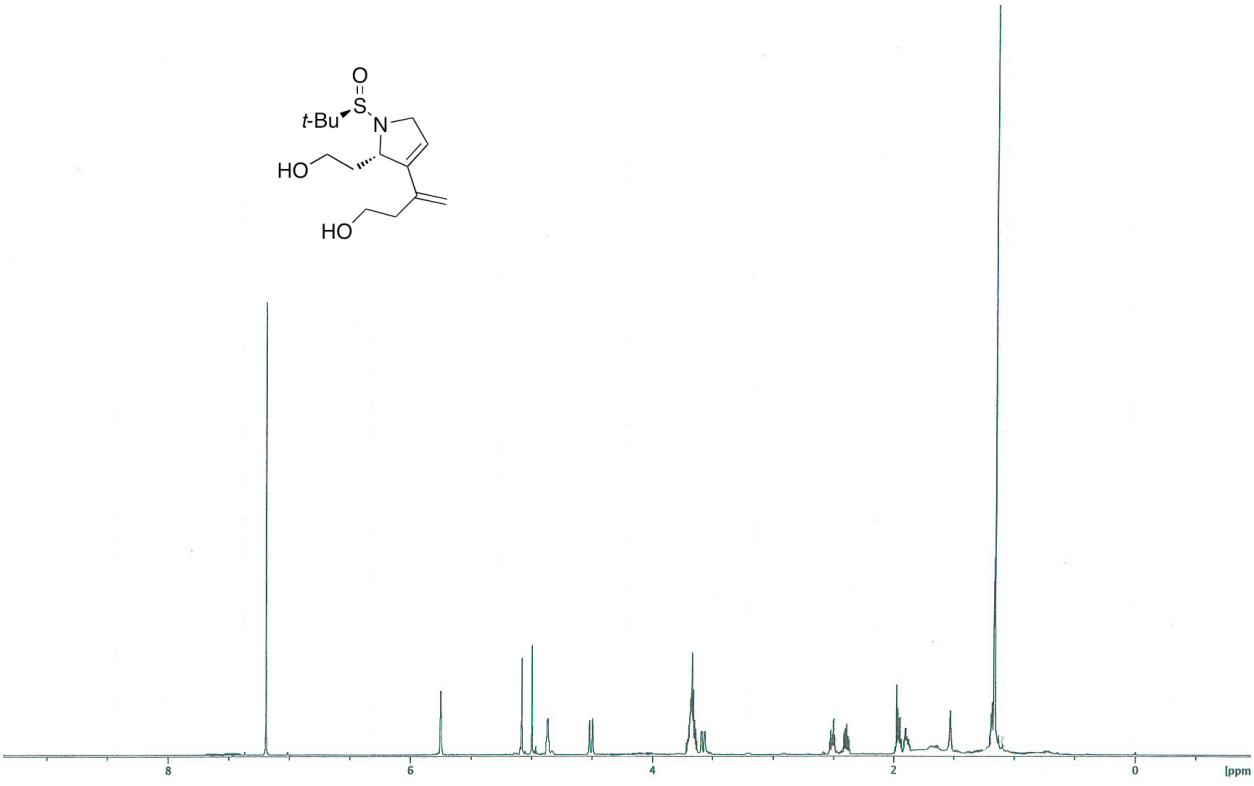
c. Evans butadiene [4+2+2] cycloaddition products (*S*-20)

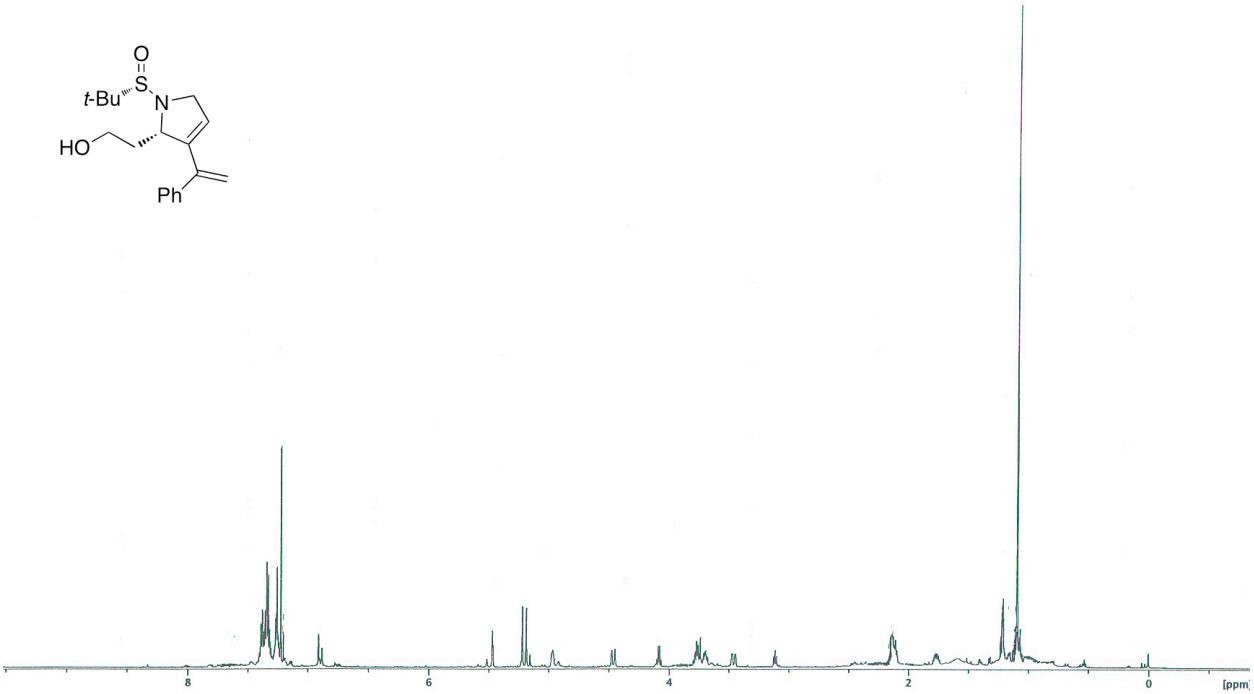


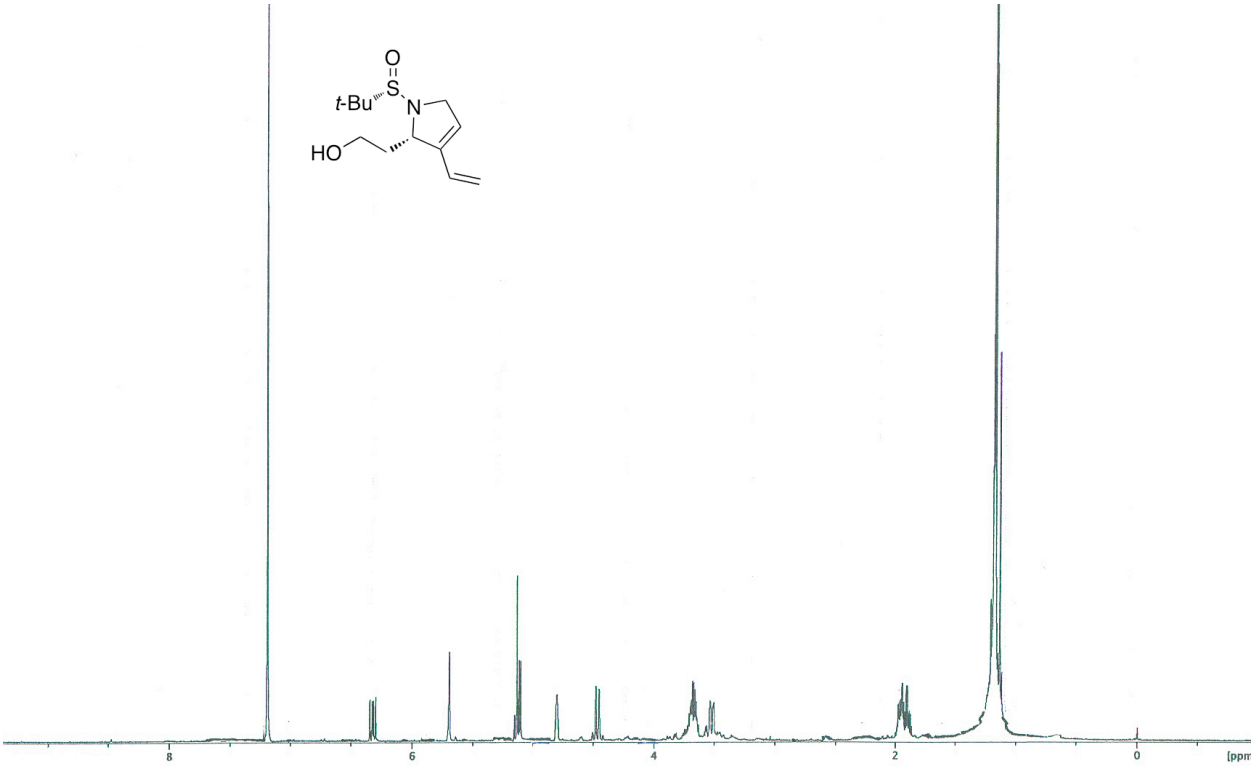


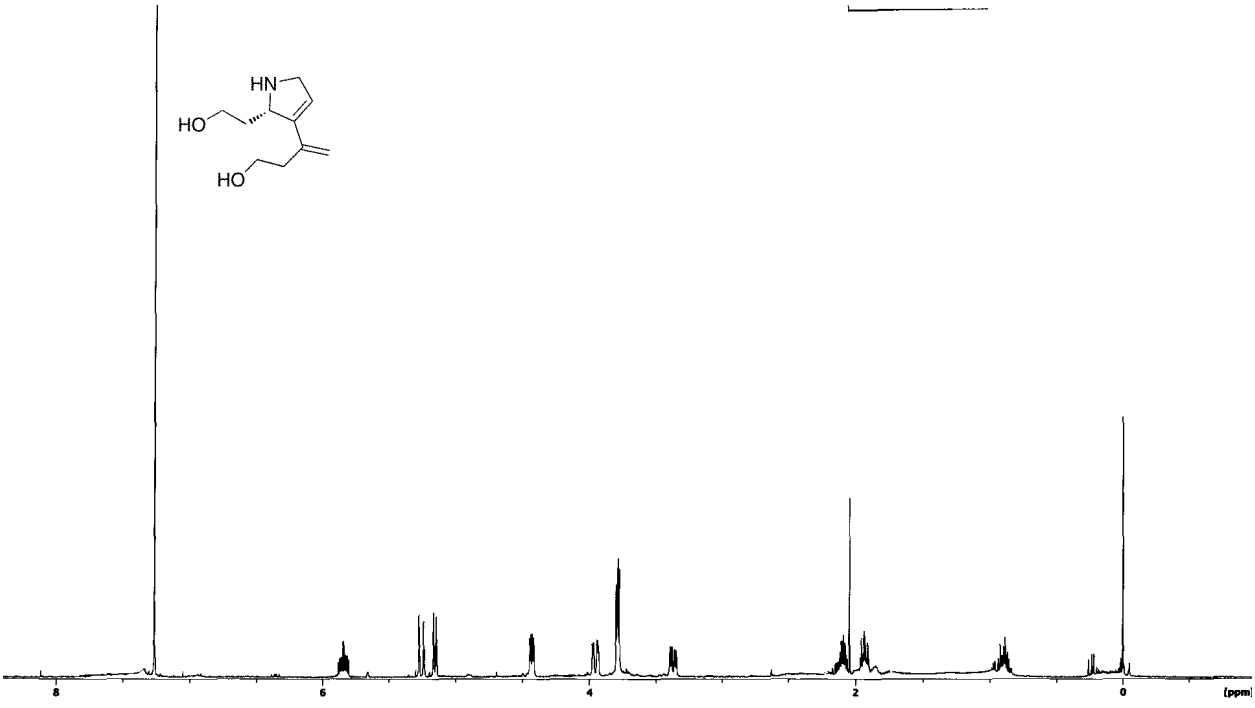

O
O
S
t-Bu
N
H
HO
8
6
4
2
0
[ppm

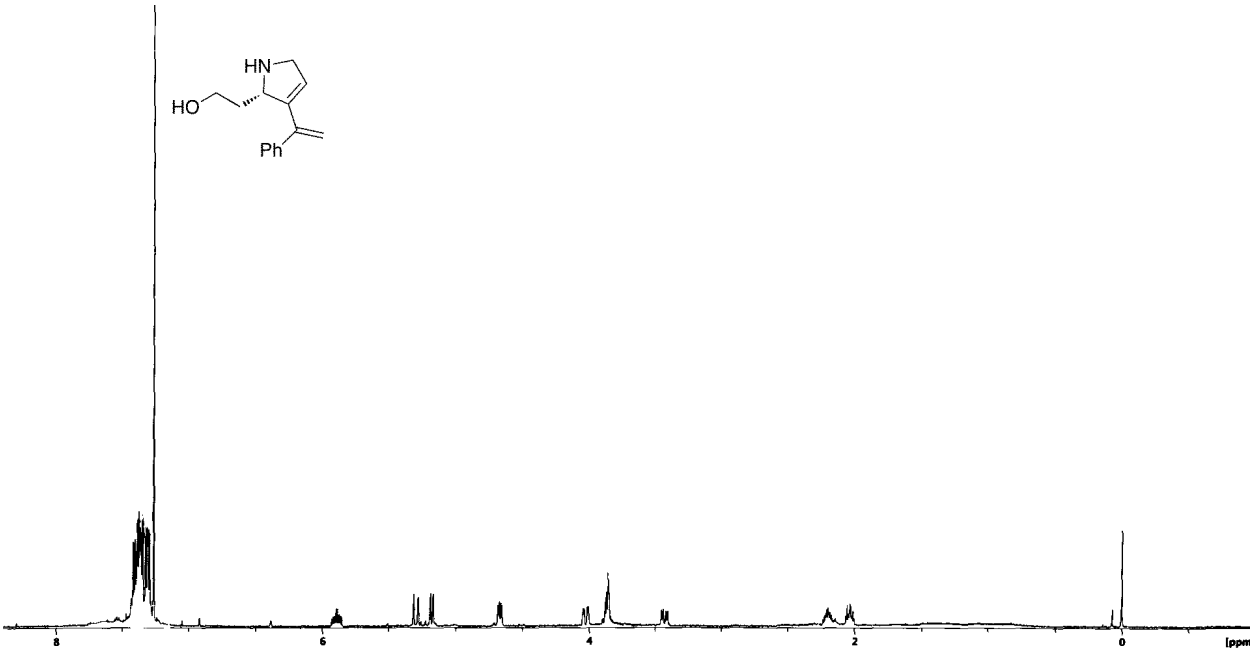
d. Enyne metathesis products (*S*-21–23)

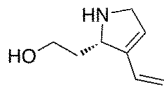


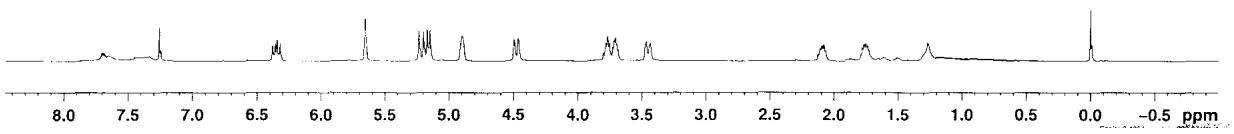


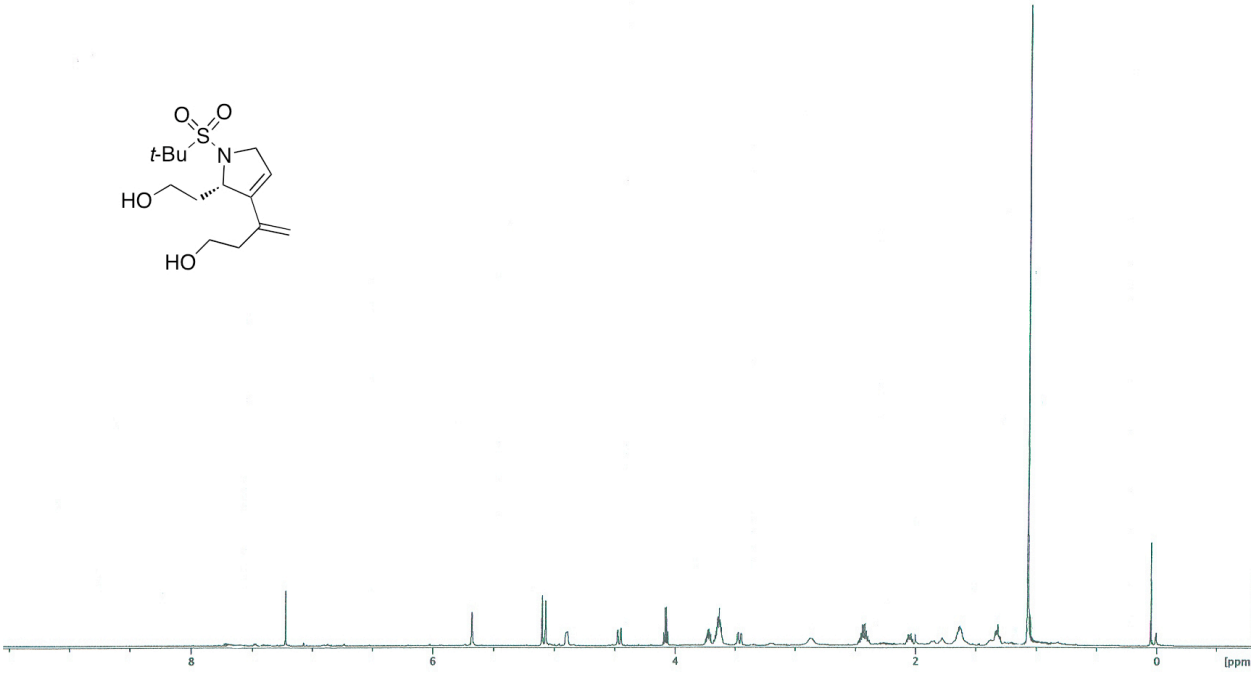

O
S
N
t-Bu
HO
8
6
4
2
0
[ppm

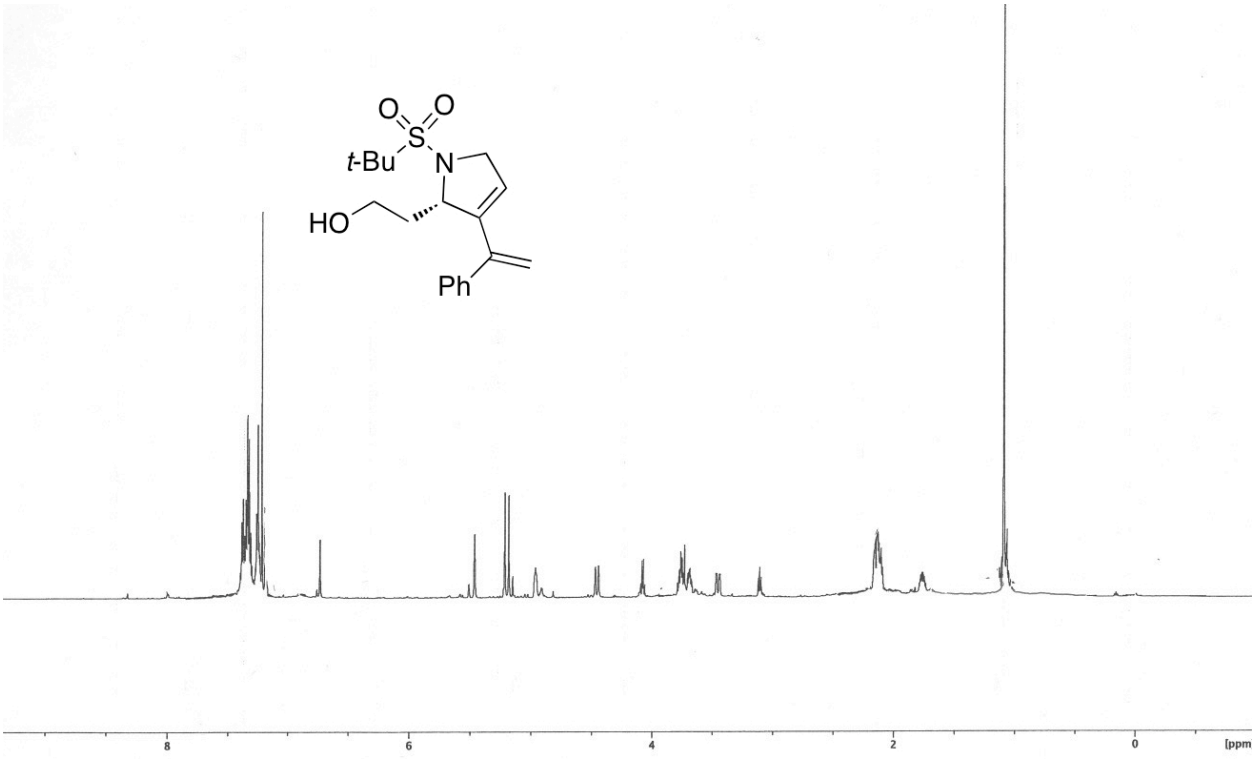

HN
HO
HO
8
6
4
2
0
(ppm)

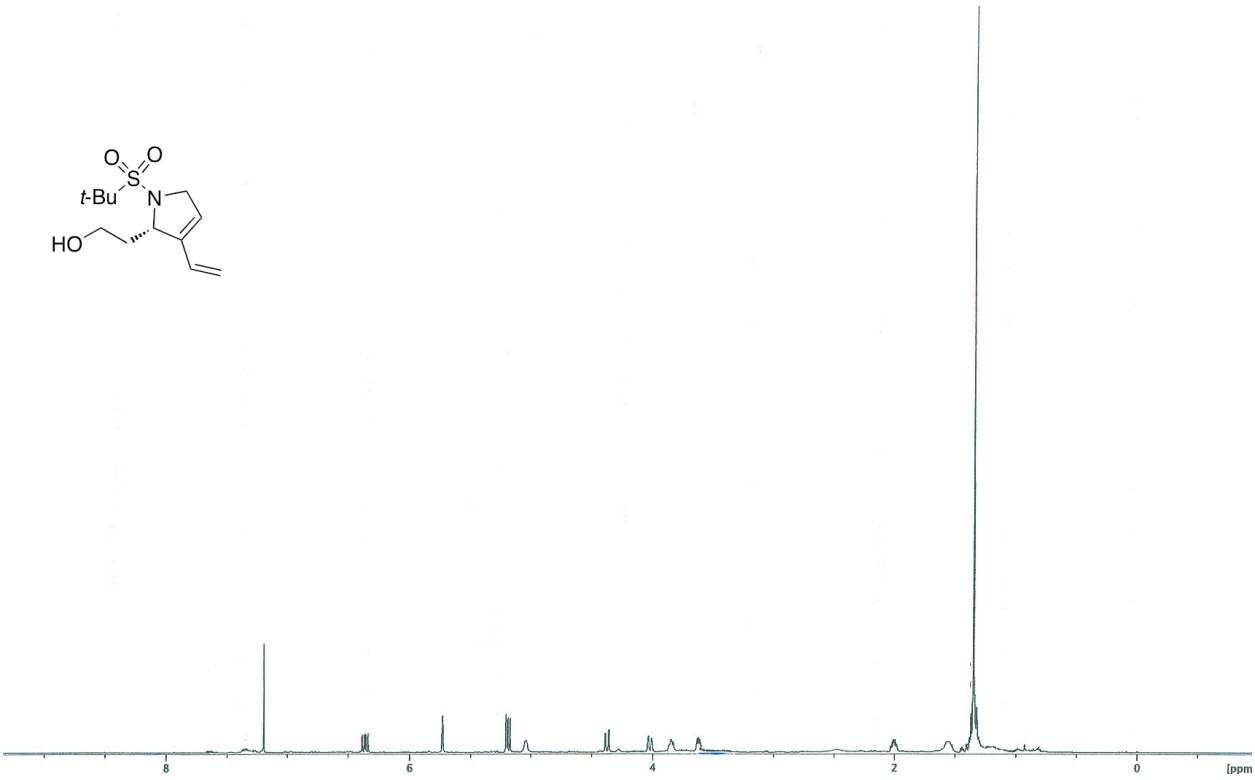

HN
HO
Ph
8
6
4
2
0
[ppm


HN
HO

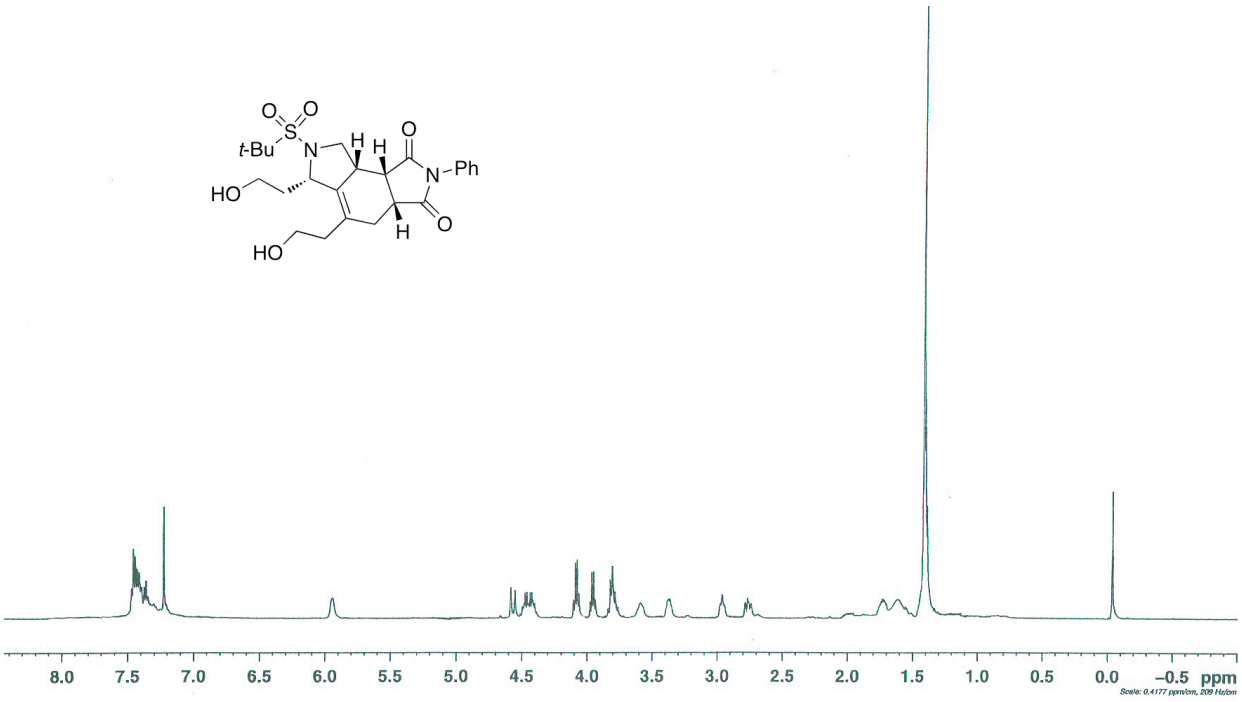

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5 ppm

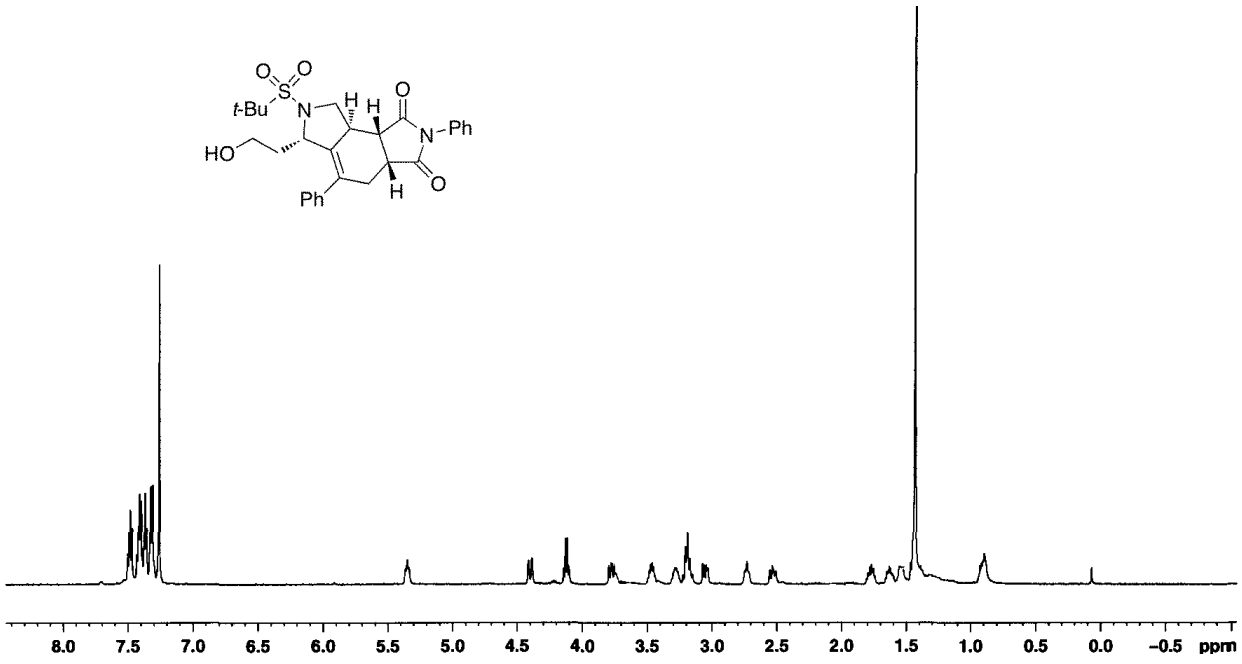

O
O
S
t-Bu
N
HO
HO
8
6
4
2
0
[ppm

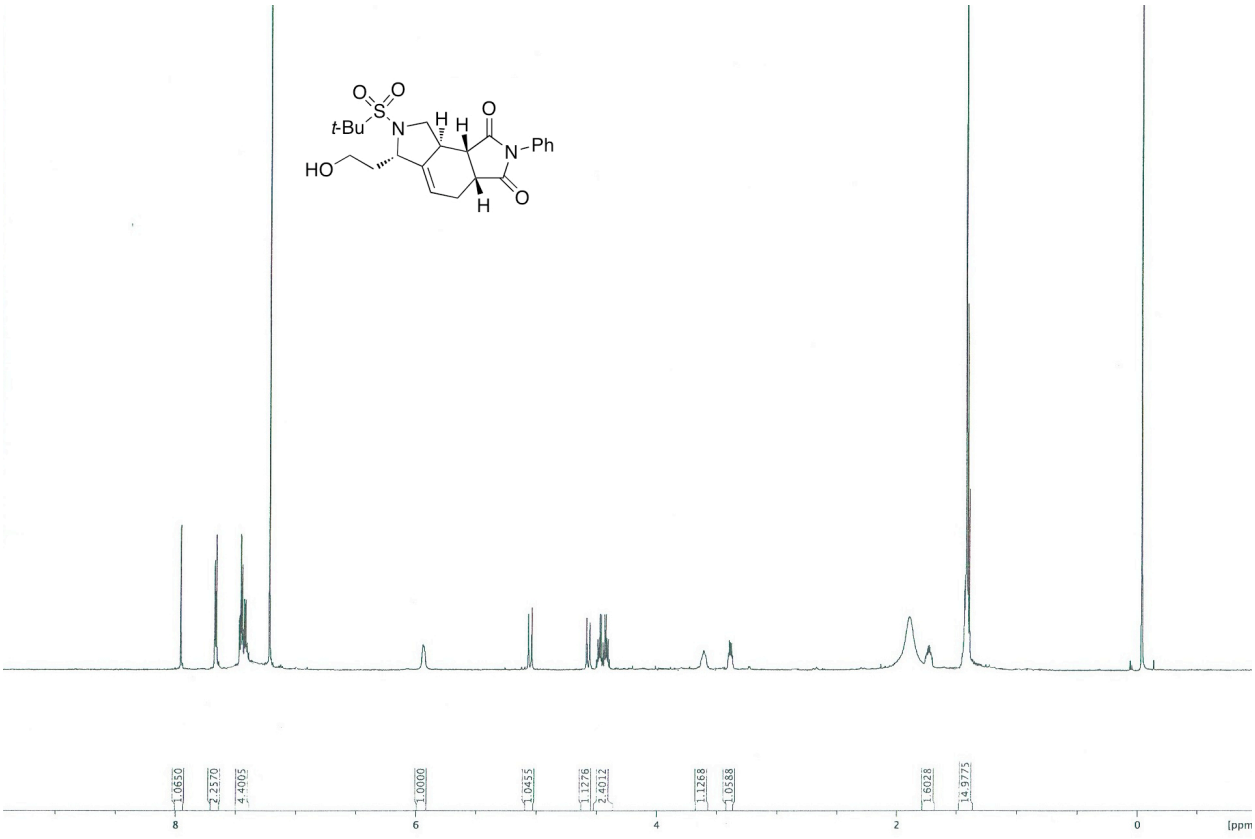

O
O
S
t-Bu
N
HO
Ph
8
6
4
2
0
[ppm


O
O
S
t-Bu
N
HO
8
6
4
2
0
[ppm

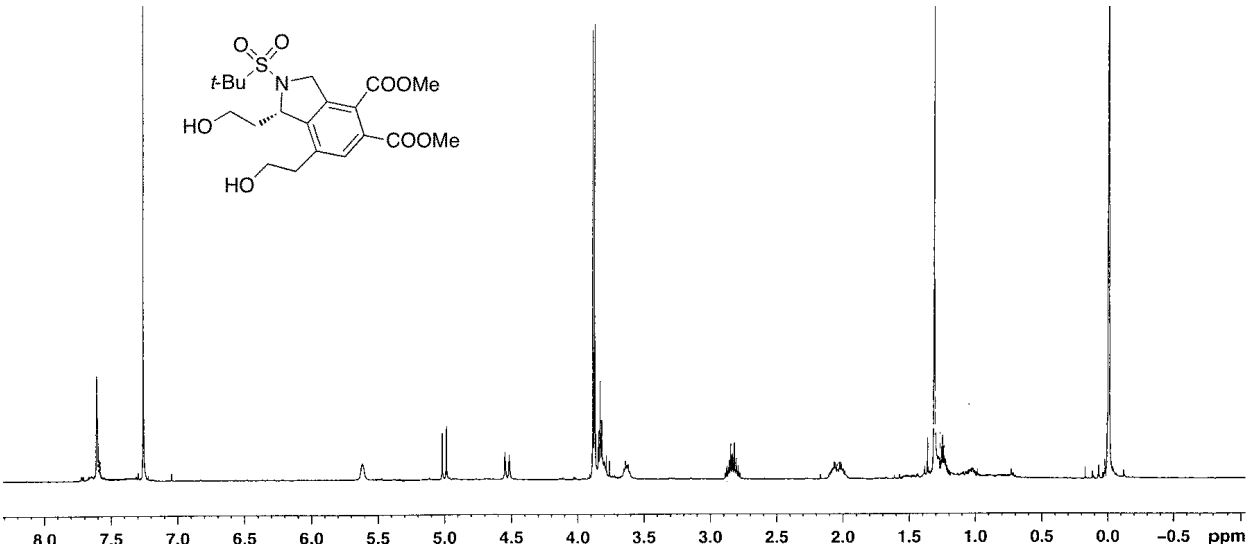
e. Maleimide Diels–Alder products (*S*-24)

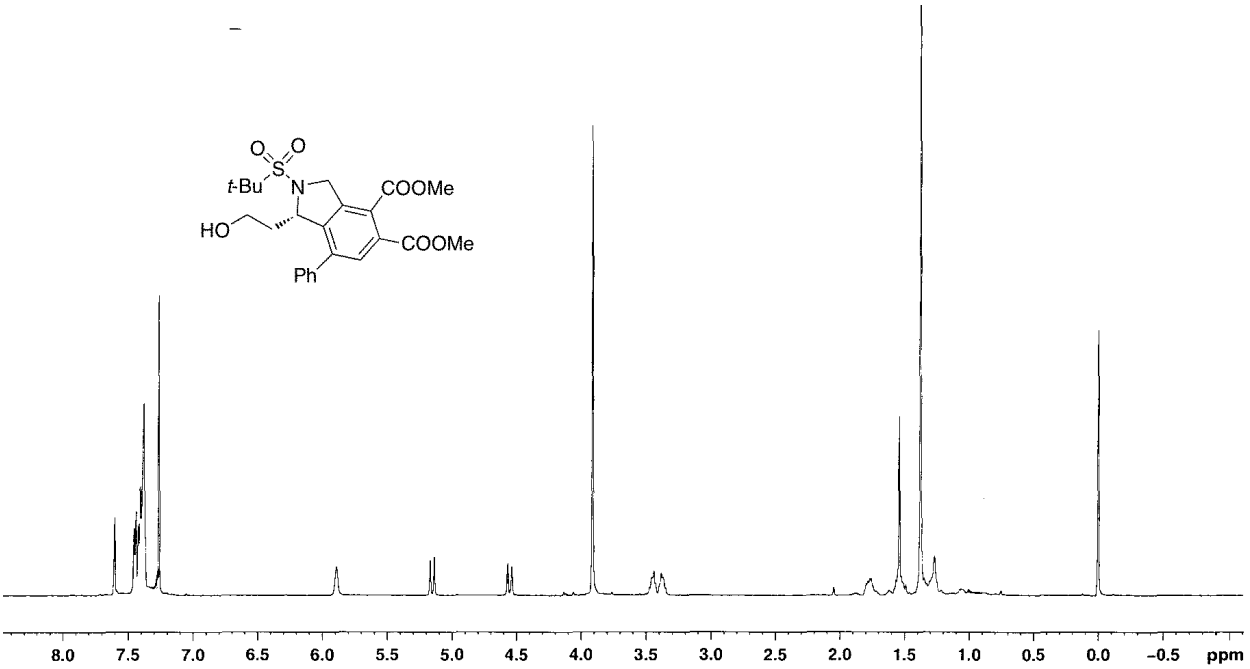


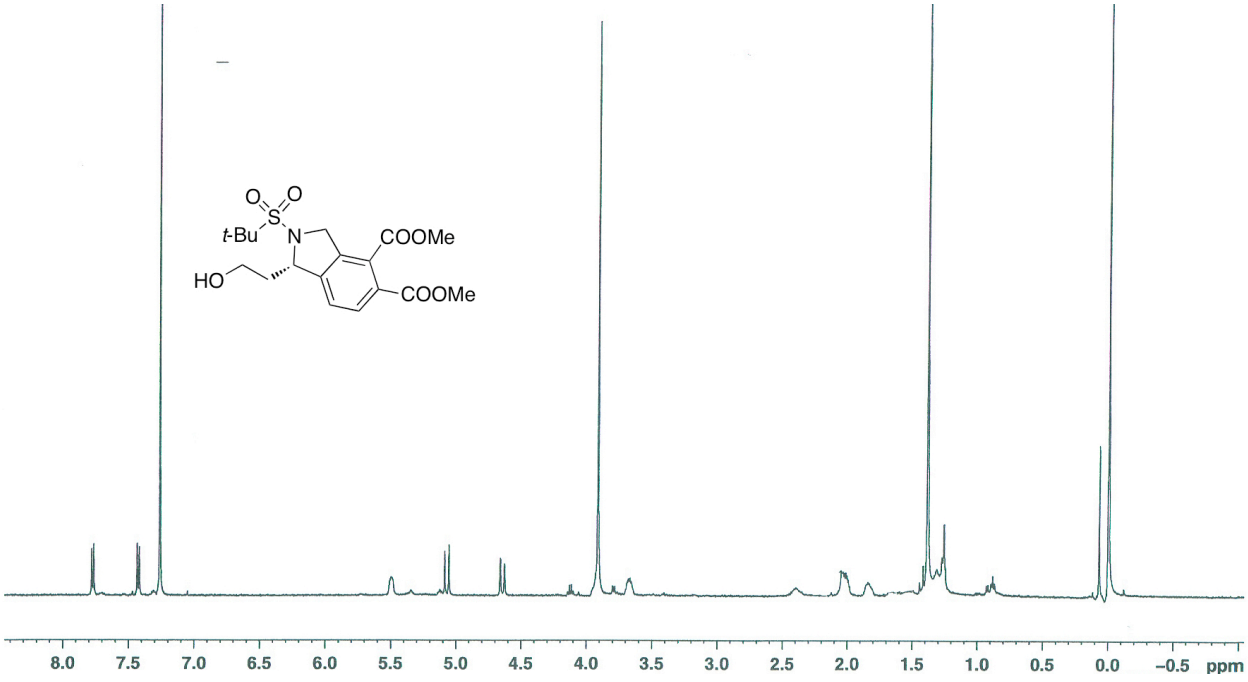



O
O
S
t-Bu
N
H
H
O
N-Ph
HO
O
H
1.0650
2.2570
4.4005
1.0000
1.0455
1.1276
2.4012
1.1268
1.0588
1.6028
14.9775
8
6
4
2
0
[ppm]

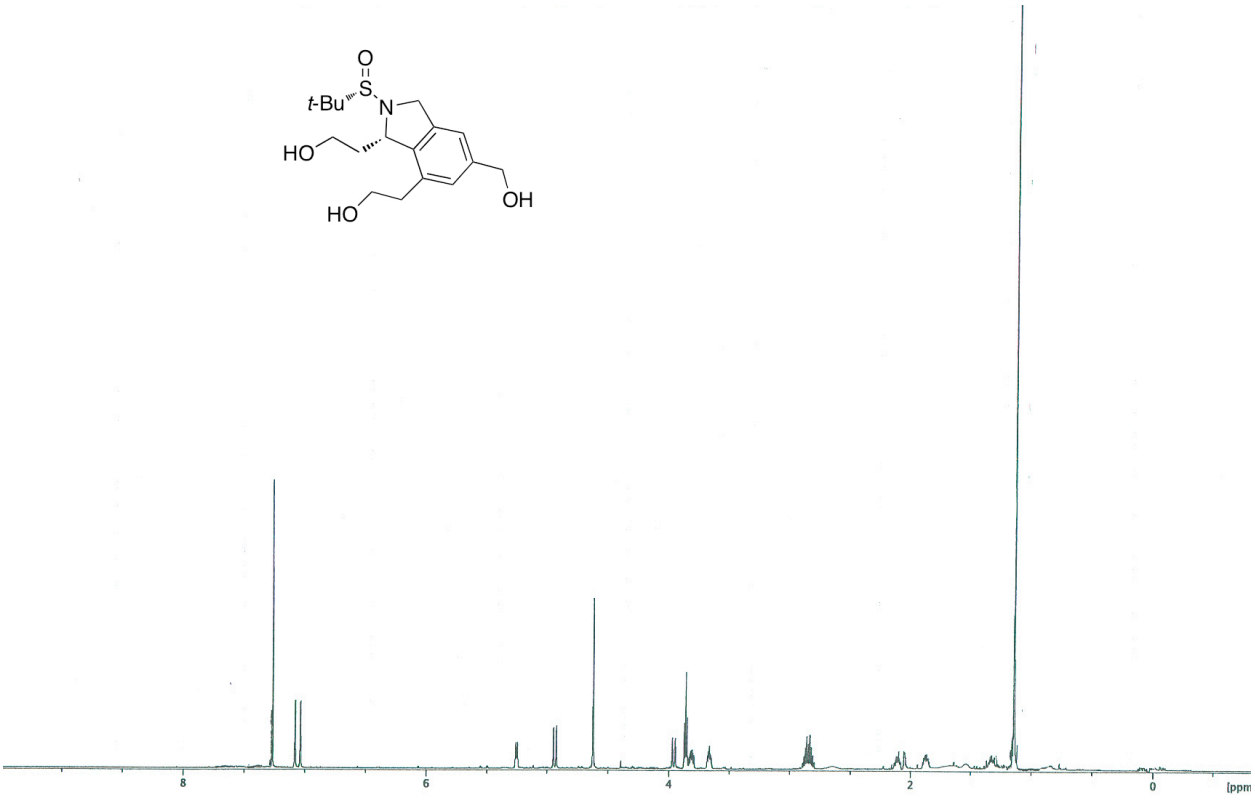
f. DMAD Diels–Alder products (*S*-25)

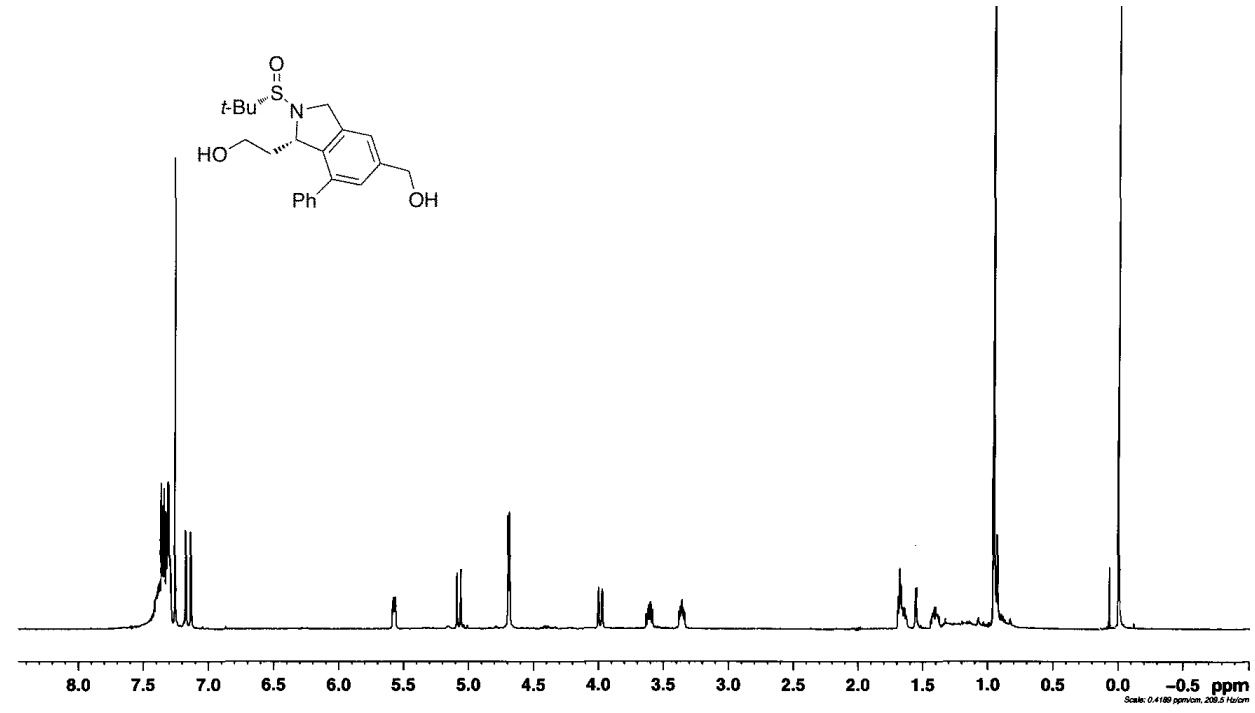


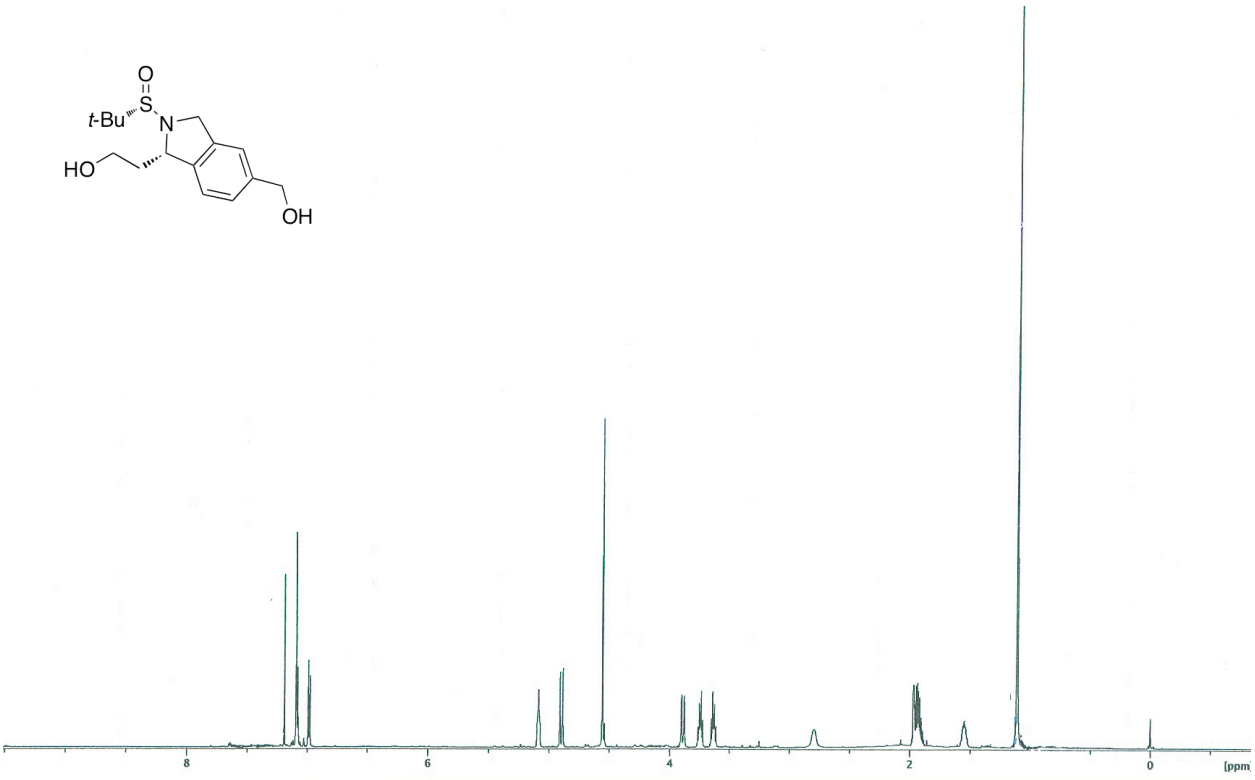


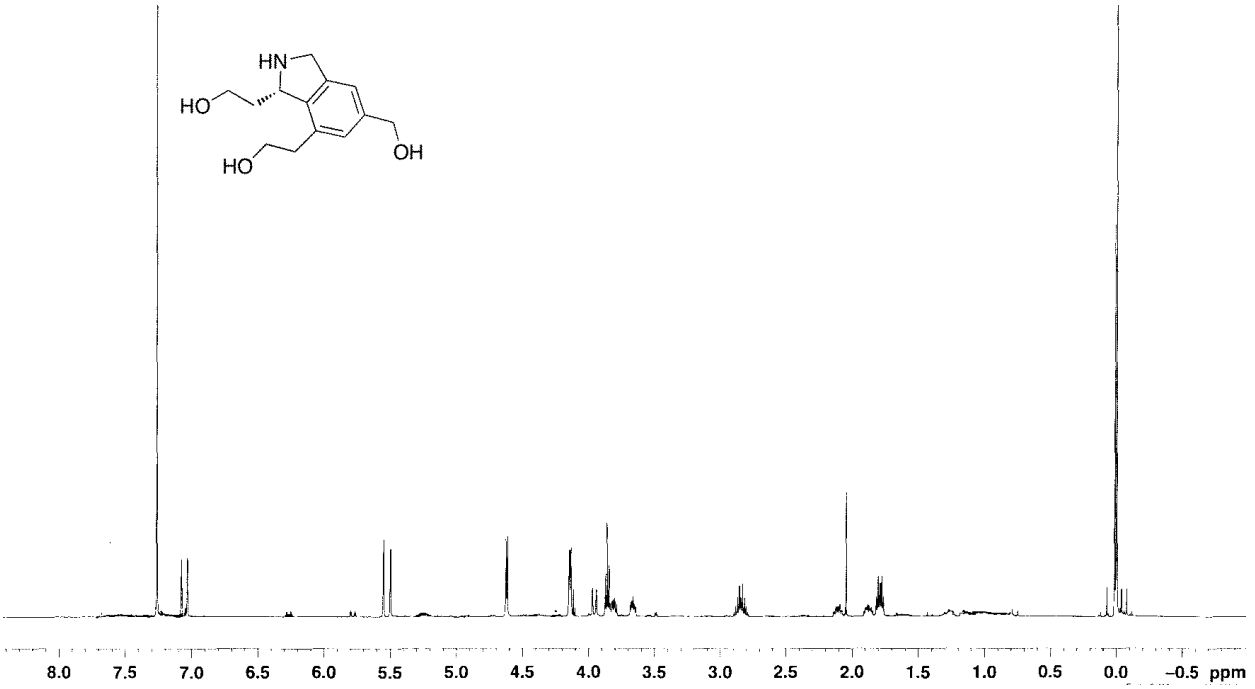

O
O
S
t-Bu
N
COOMe
HO
COOMe
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
ppm

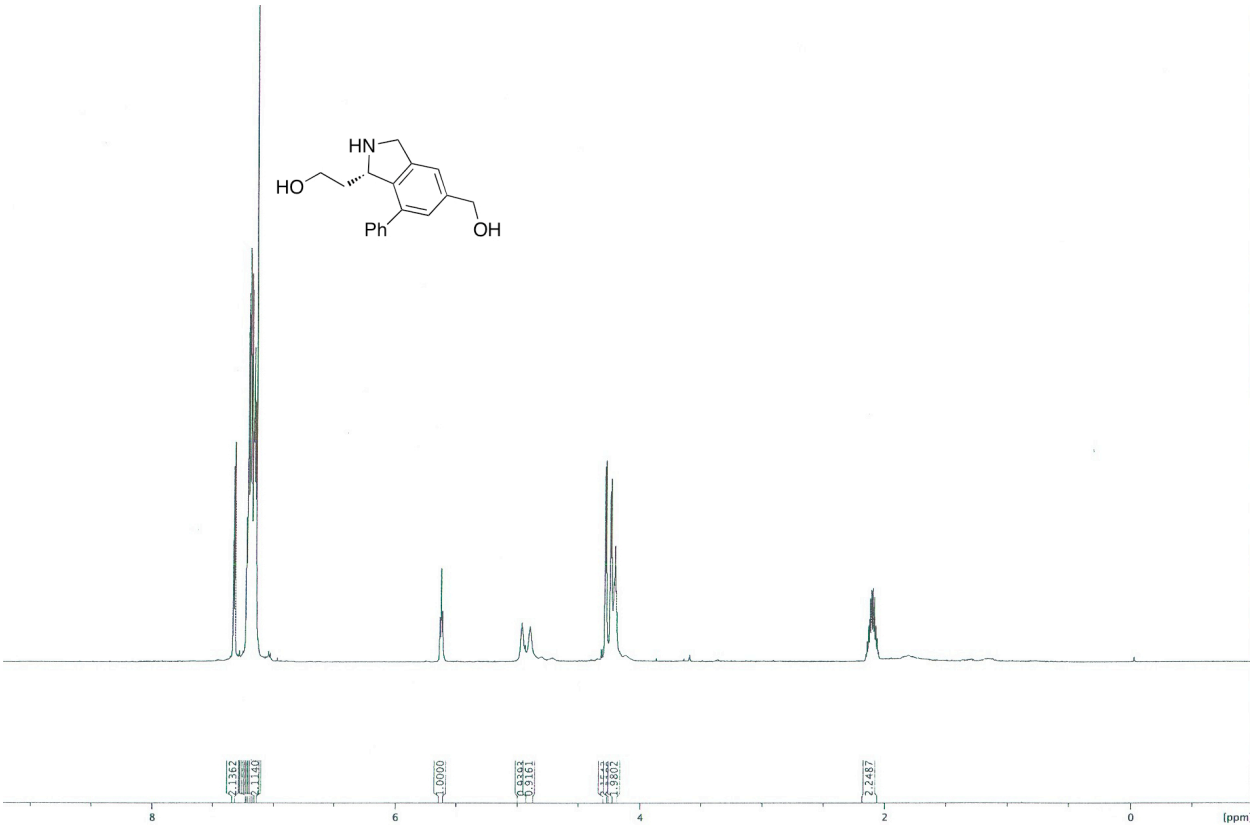
g. Alkyne [2+2+2] cyclotrimerization products (*S*-30–35)






O
S
t-Bu
N
HO
OH
8
6
4
2
0
(ppm


HN
HO
HO
OH
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
–0.5 ppm


HN
HO
Ph
OH
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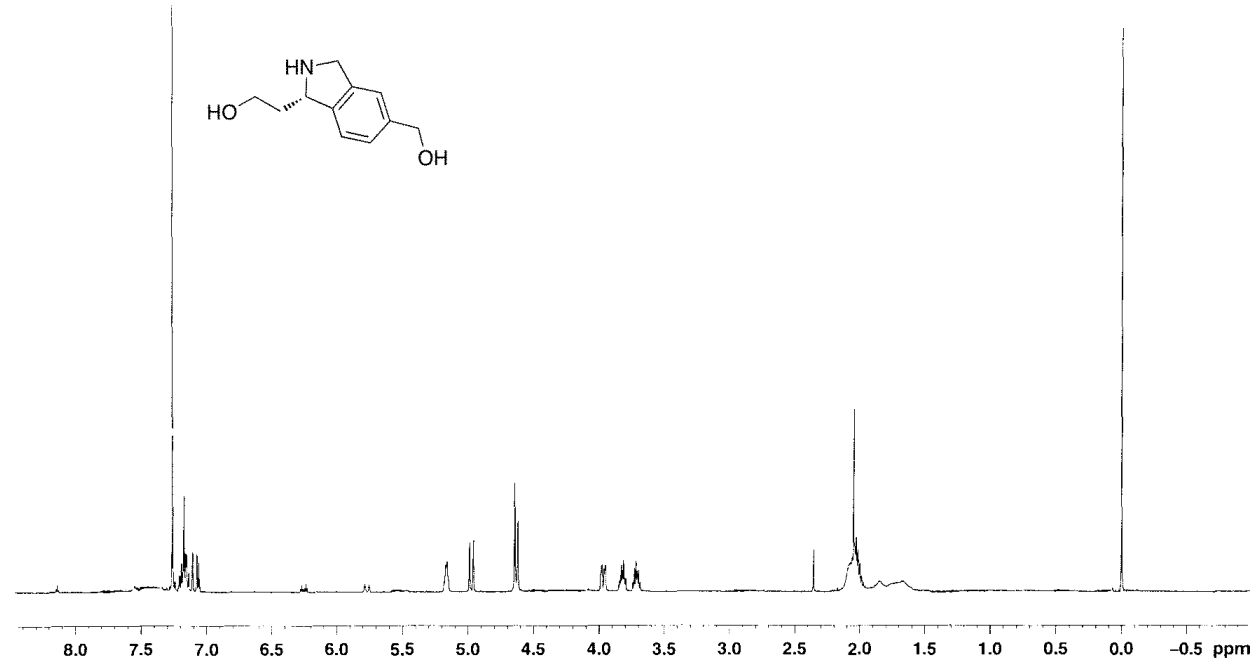
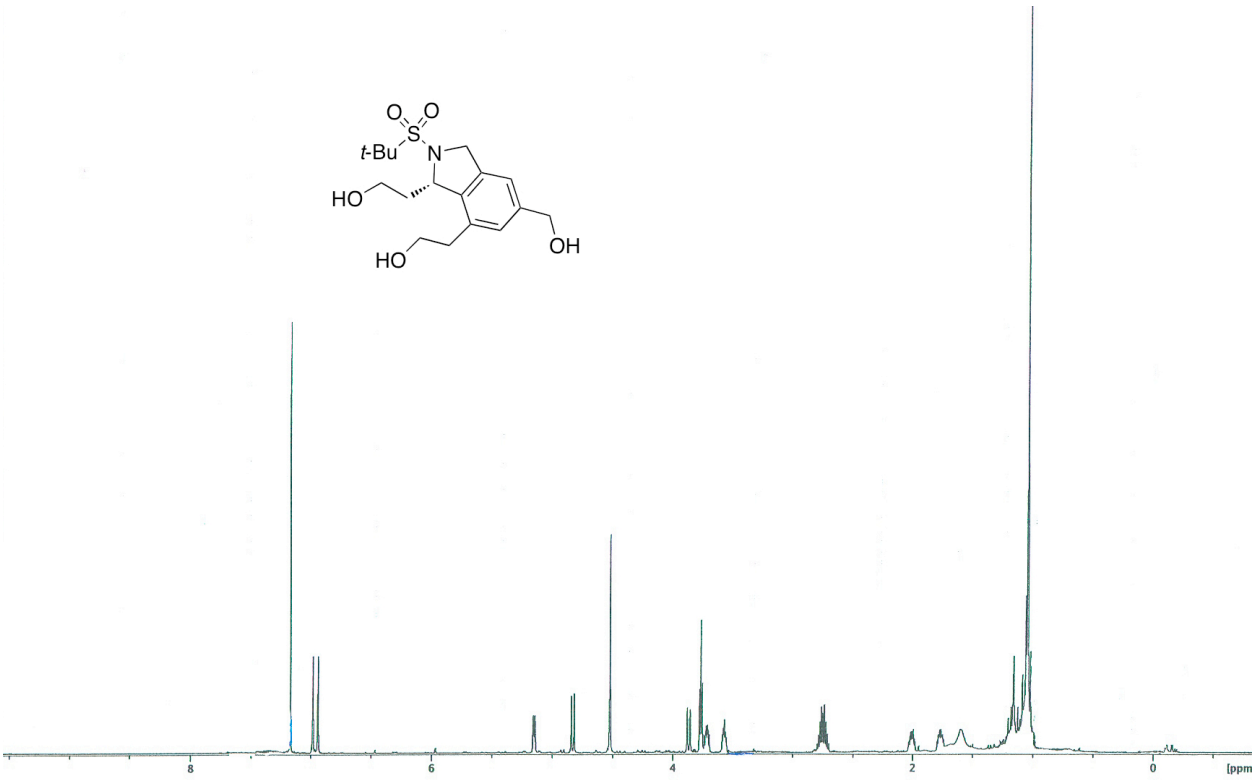
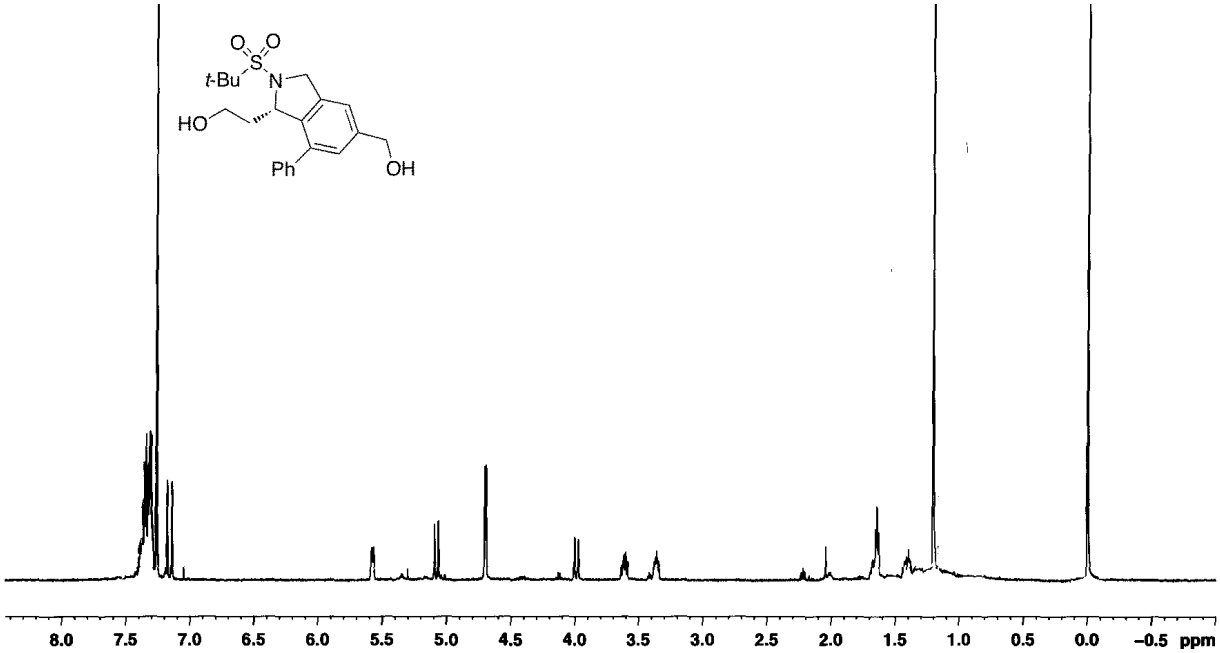
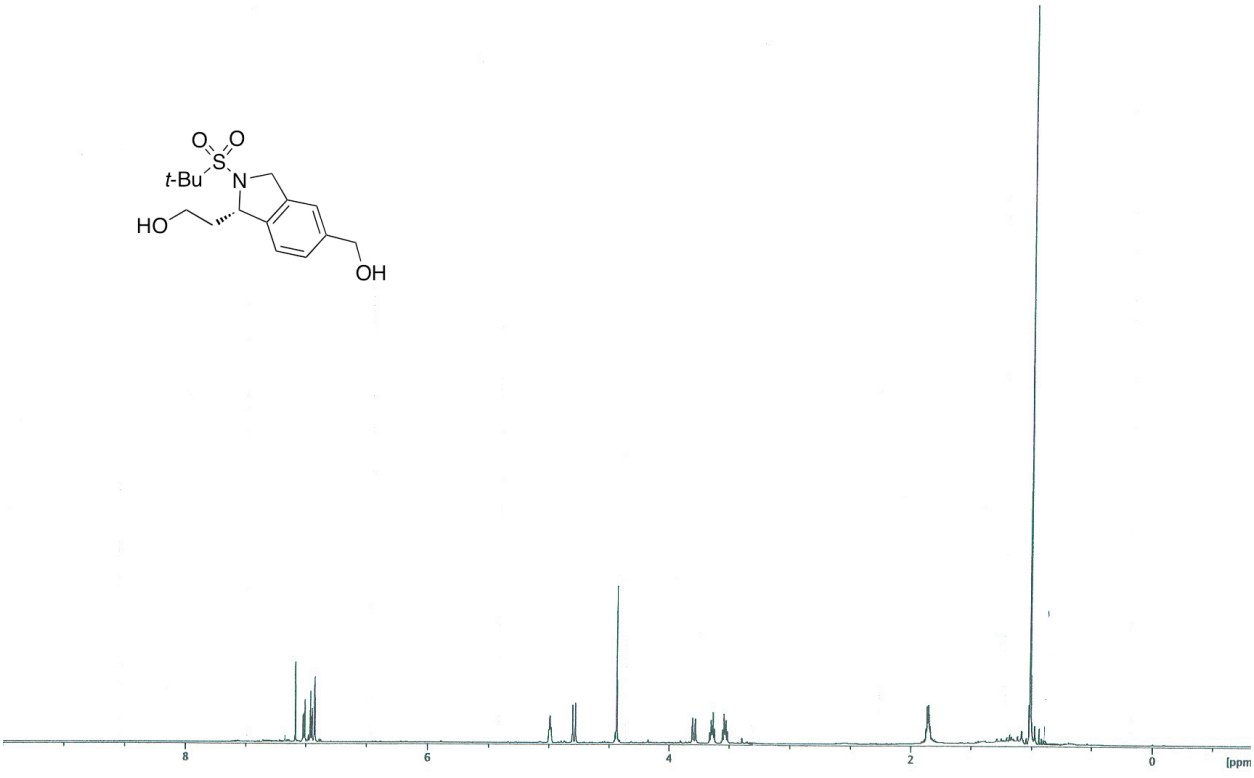
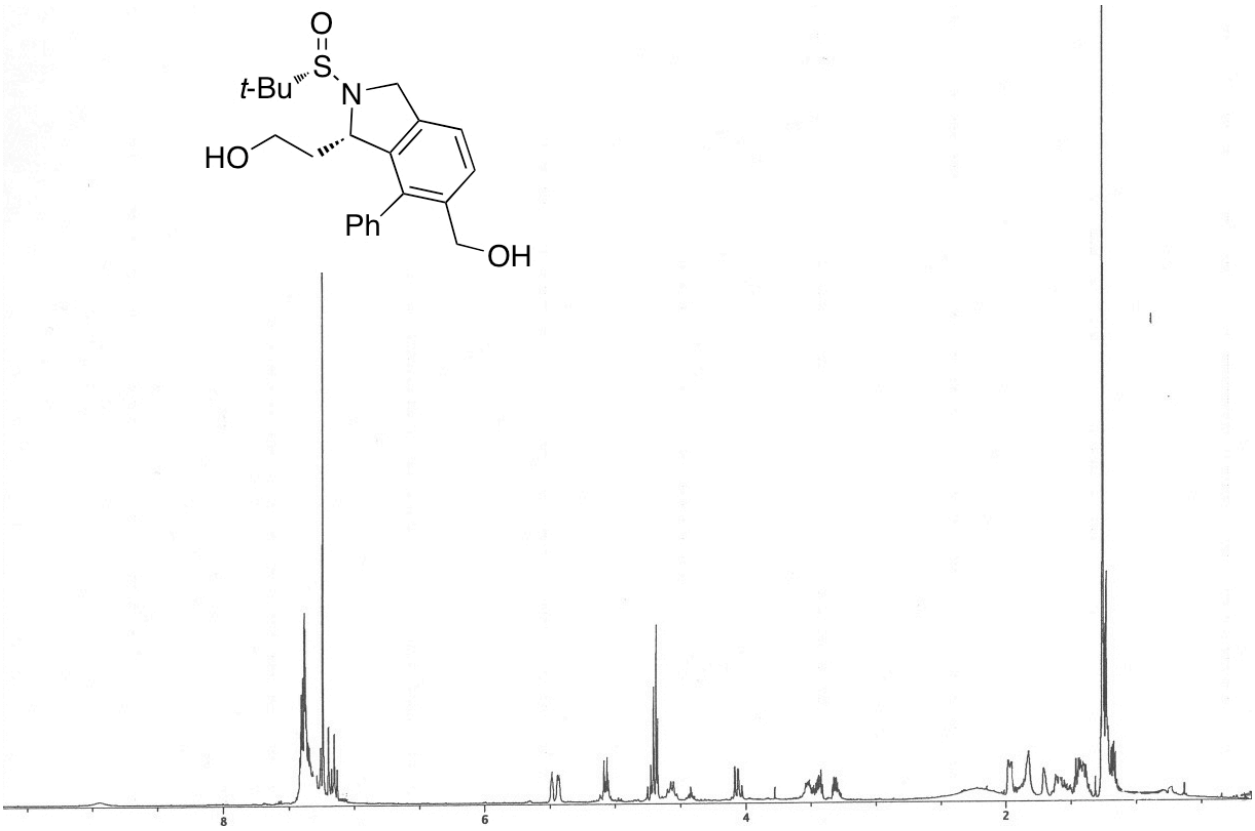
1.0000
0.9393
0.9161
1.9802
2.2487
8
6
4
2
0
[ppm]

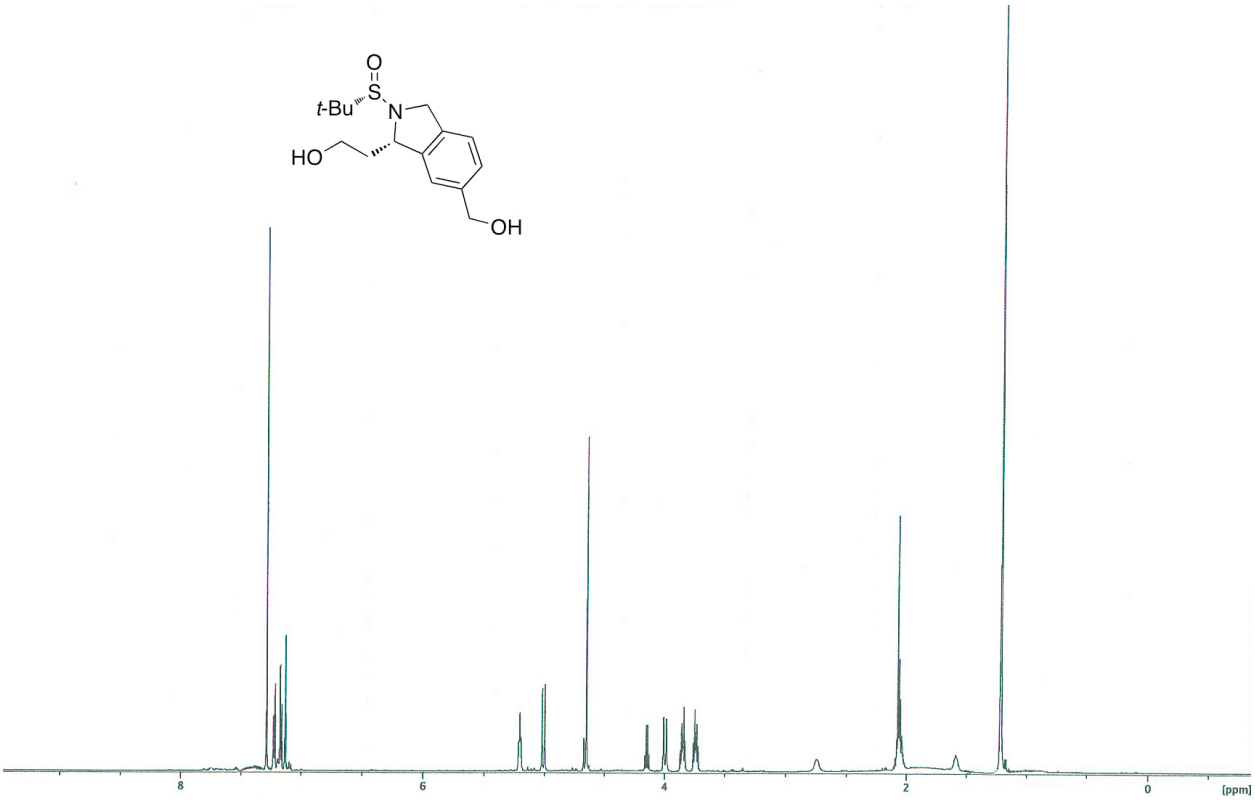

HN
HO
OH
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5 ppm

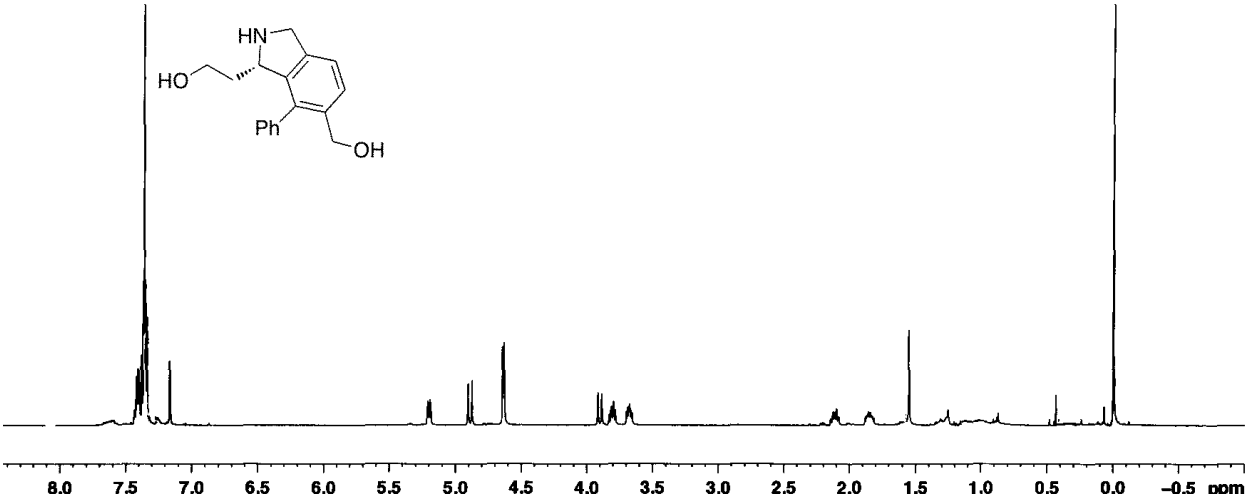

O
O
S
t-Bu
N
HO
HO
OH
8
6
4
2
0
[ppm

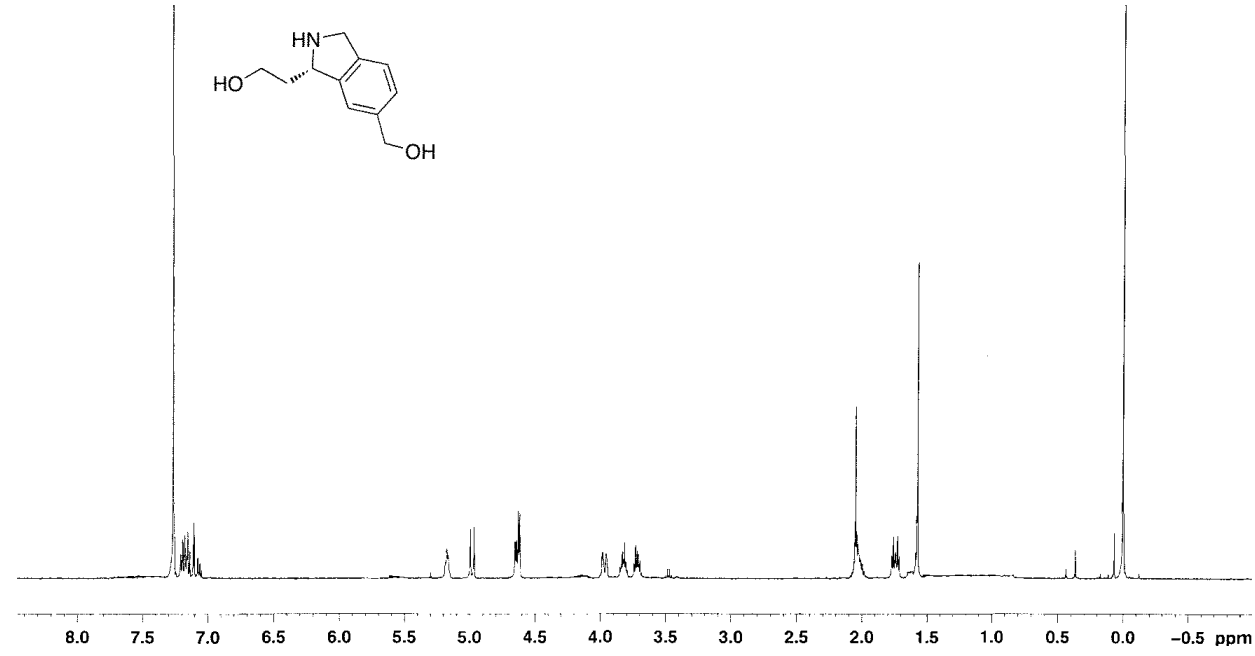

O
O
S
t-Bu
N
HO
Ph
OH
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5 ppm

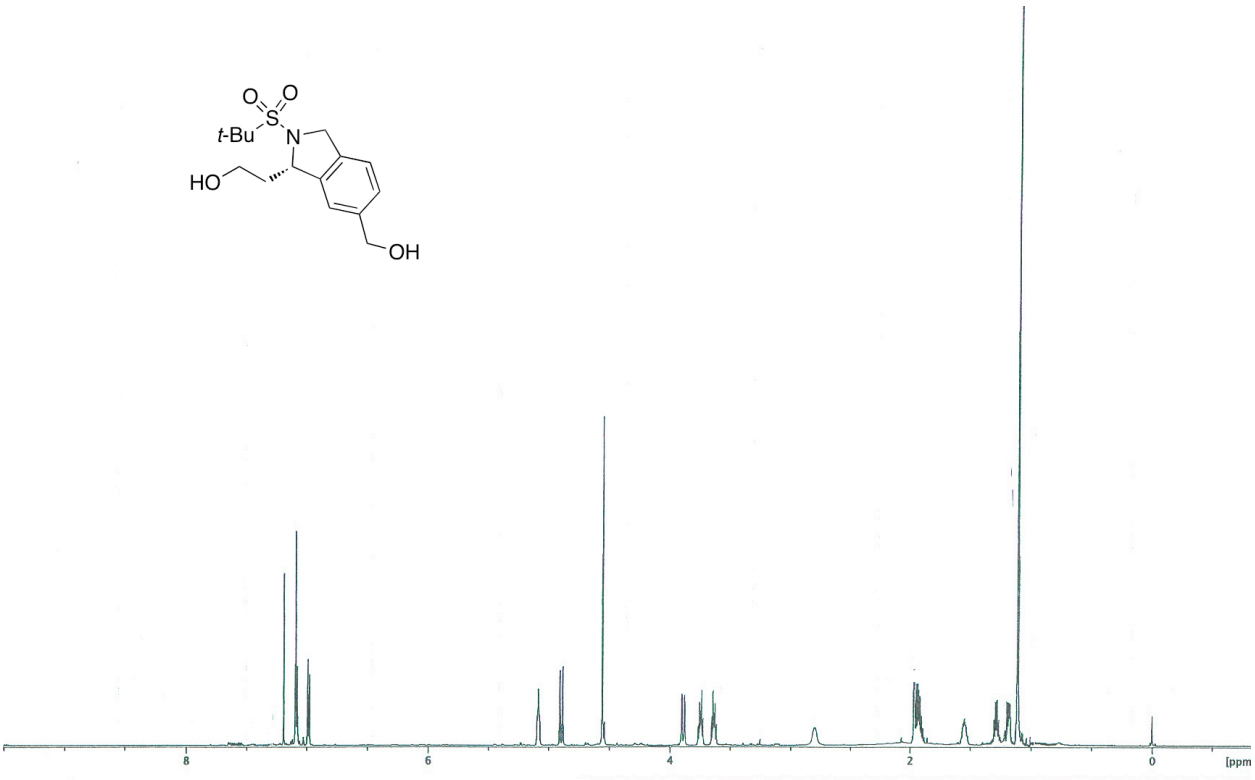

O
O
S
t-Bu
N
HO
OH
8
6
4
2
0
[ppm


O
S
t-Bu
N
HO
Ph
OH
8
6
4
2

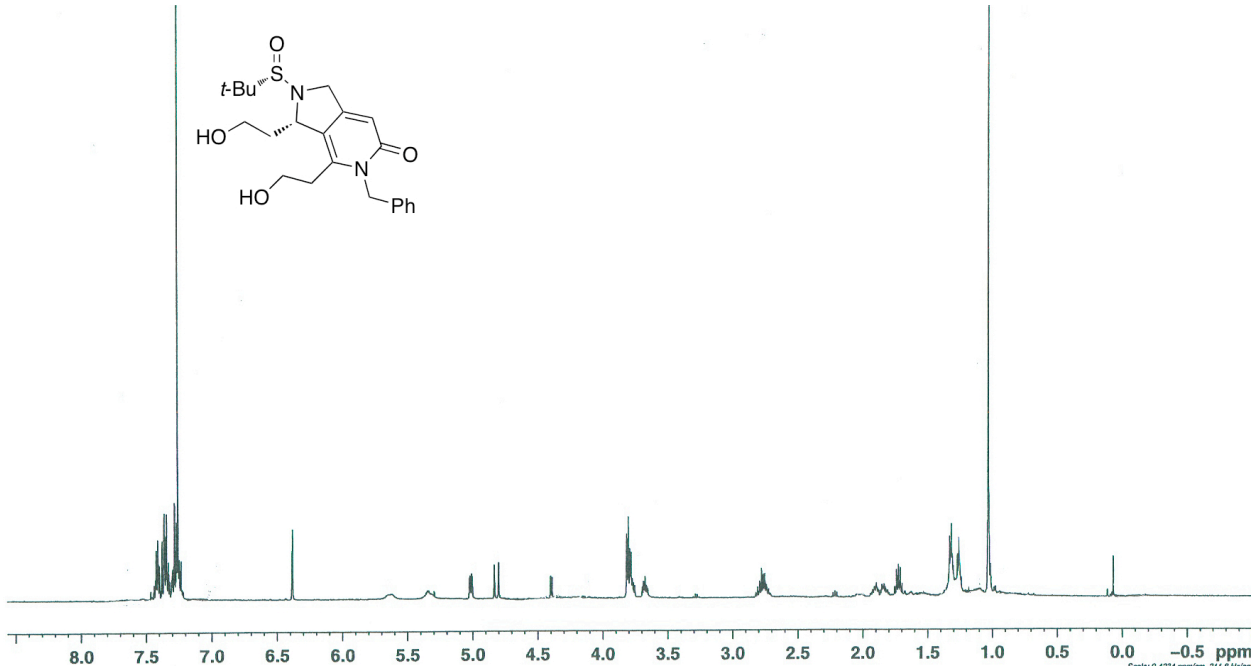

O
S
t-Bu
N
HO
OH
8
6
4
2
0
[ppm]

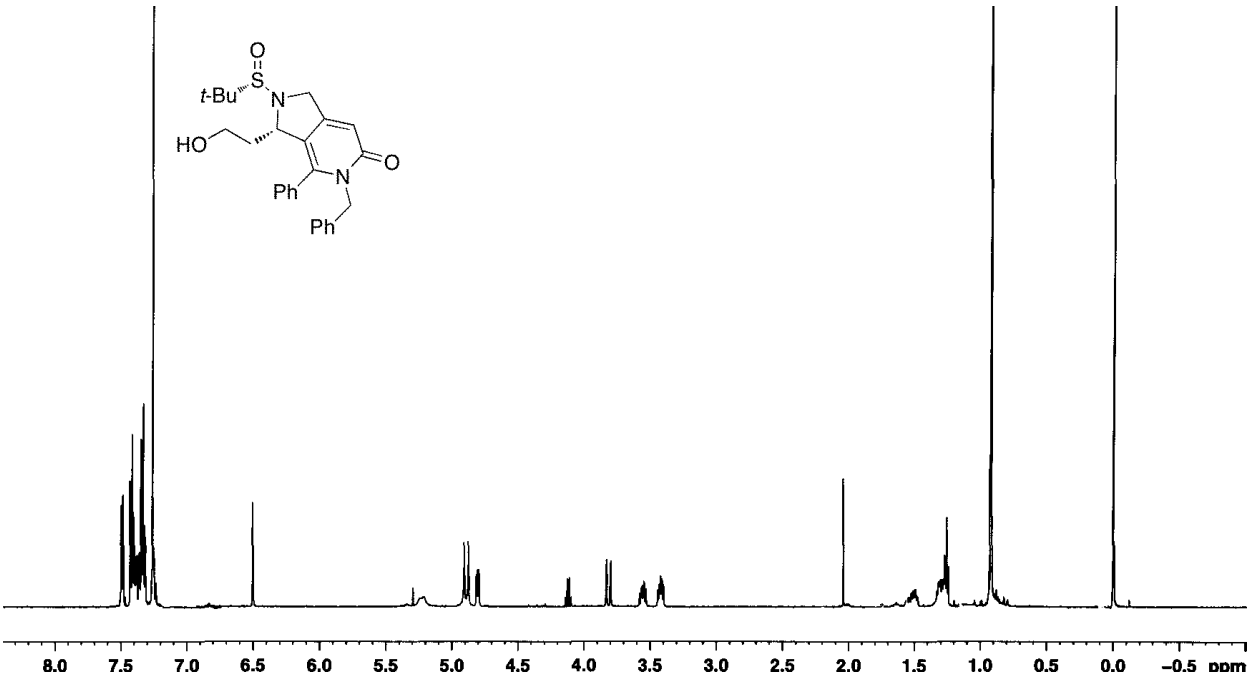

HN
HO
Ph
OH
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

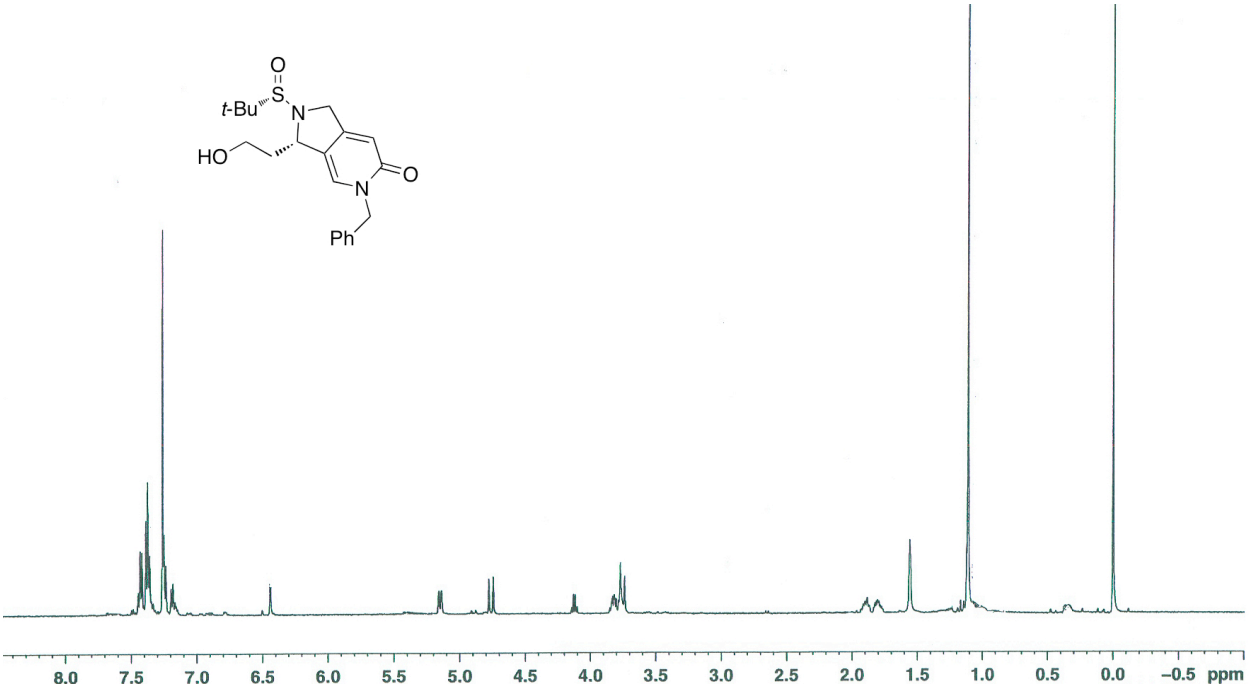

HN
HO
OH
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

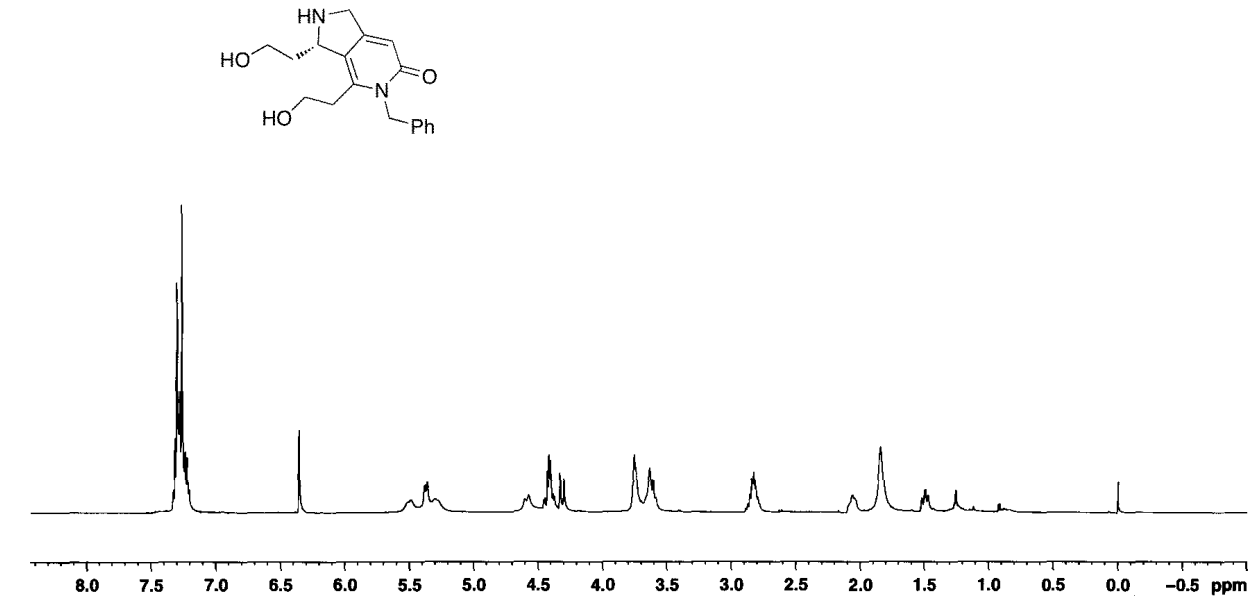

O
O
S
t-Bu
N
HO
OH
8
6
4
2
0
[ppm

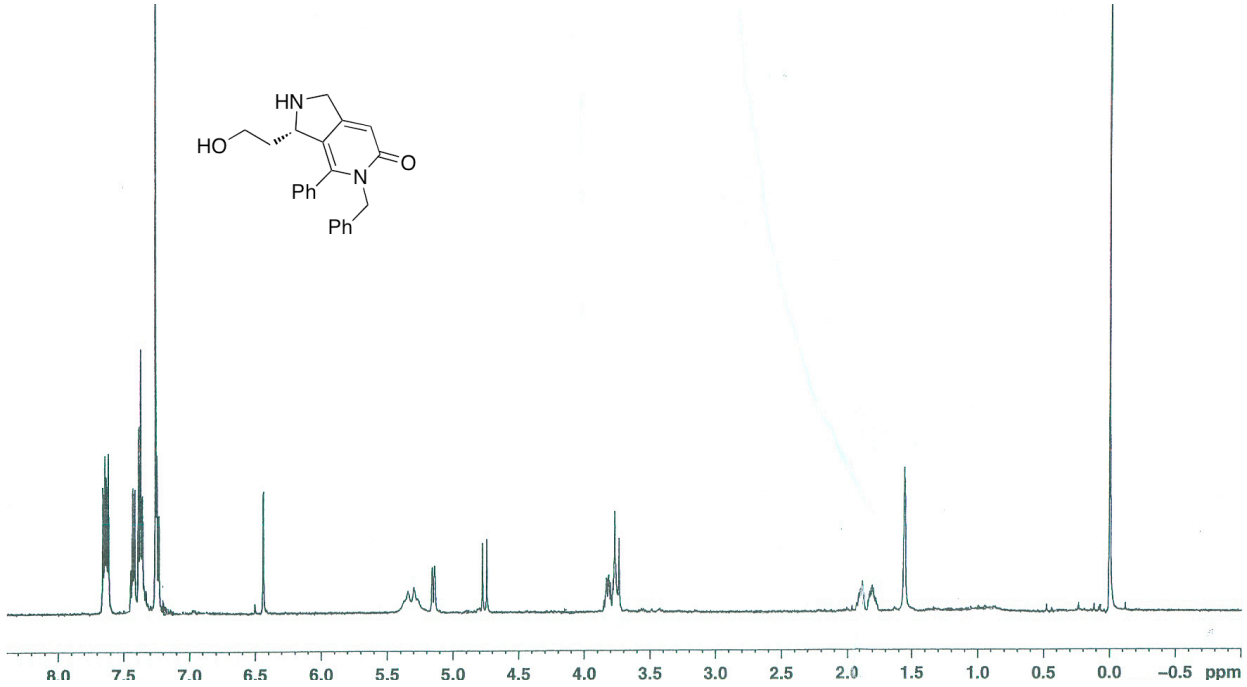
h. Isocyanate [2+2+2] cyclotrimerization products (*S*-36–41)

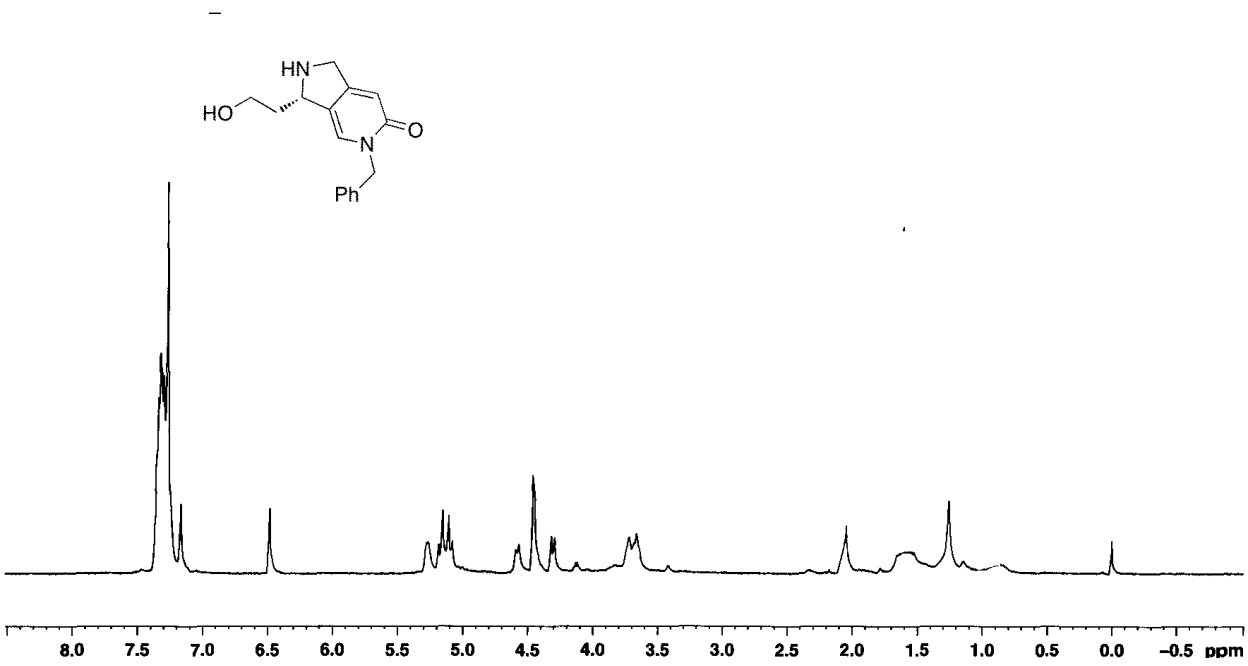


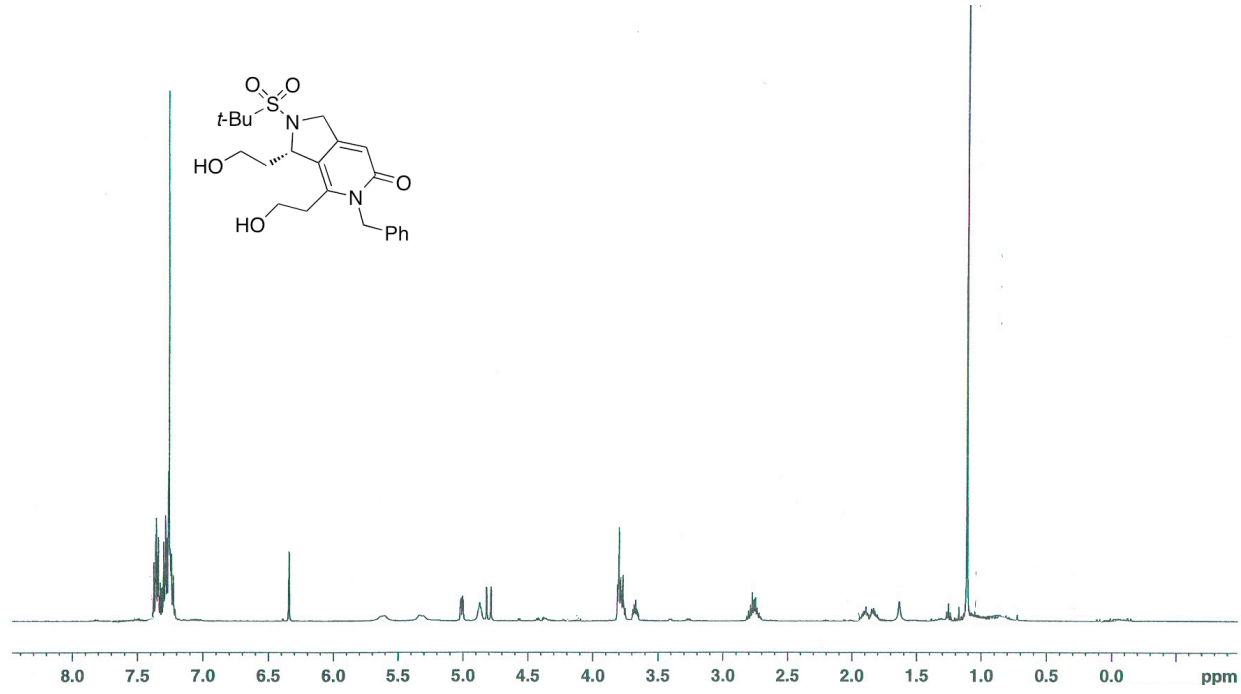


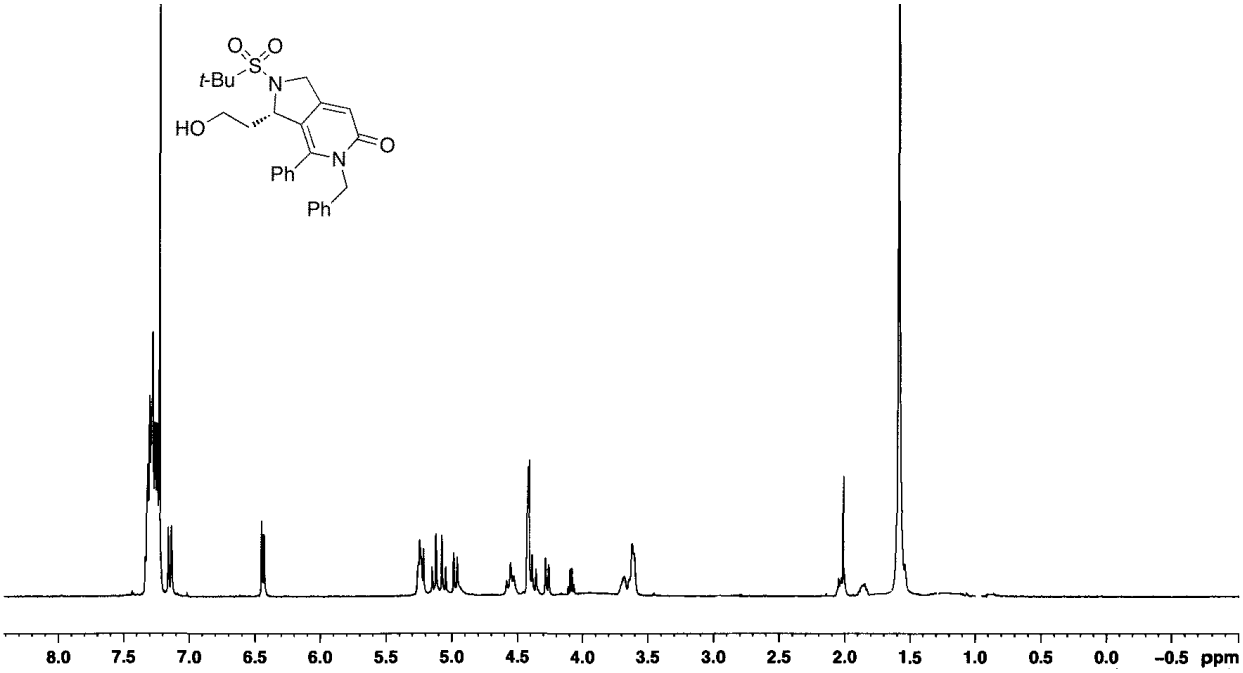

O
S
t-Bu
N
HO
O
N
Ph
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

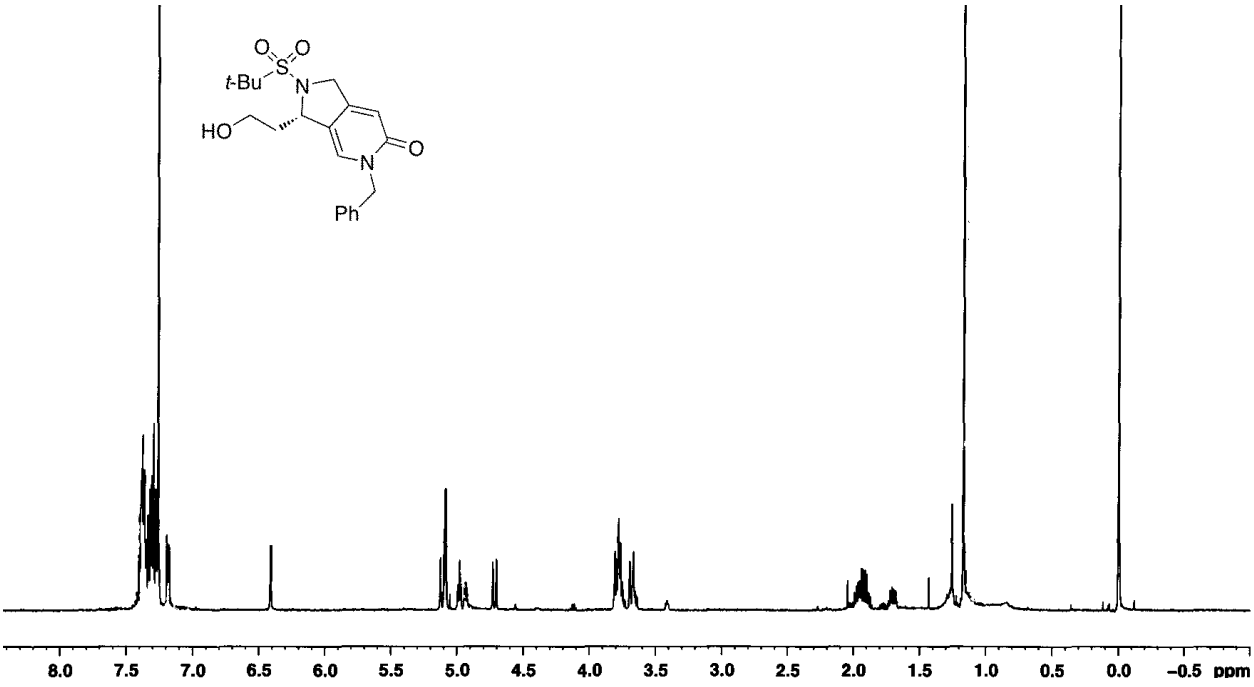

HN
HO
O
N
HO
Ph
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

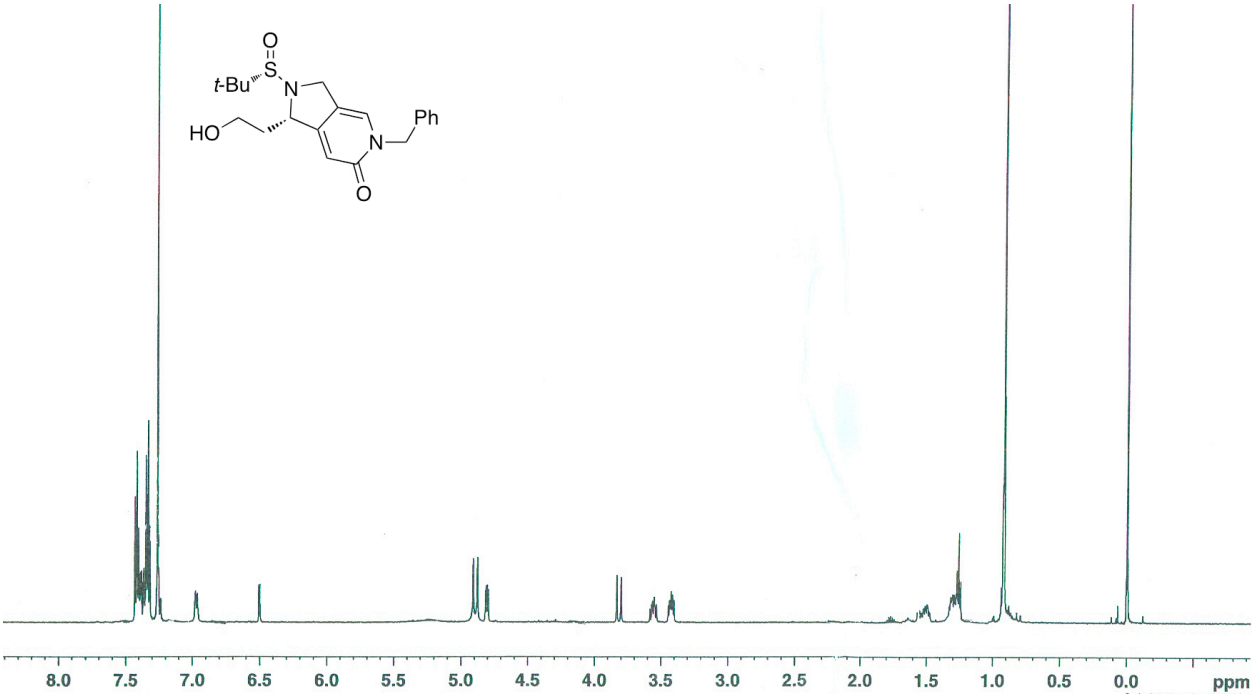

HN
HO
O
N
Ph
Ph
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

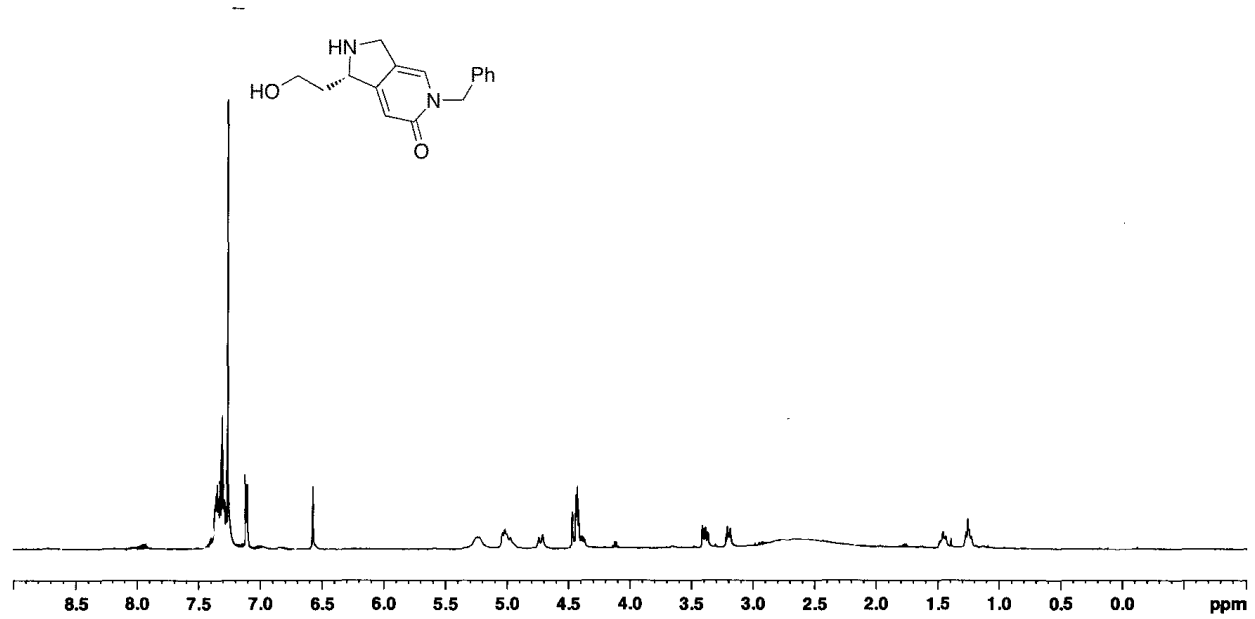

HN
HO
O
N
Ph
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

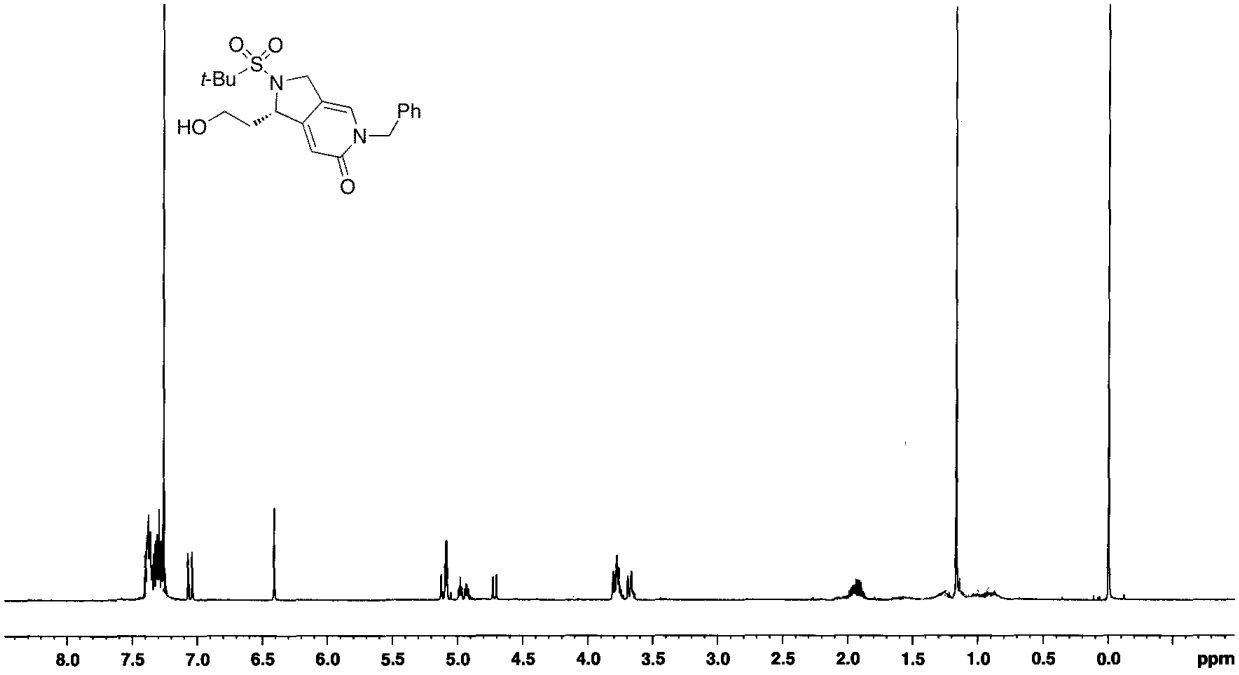

t-Bu
HO
HO
Ph
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm


t-Bu
HO
Ph
Ph
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 −0.5 ppm

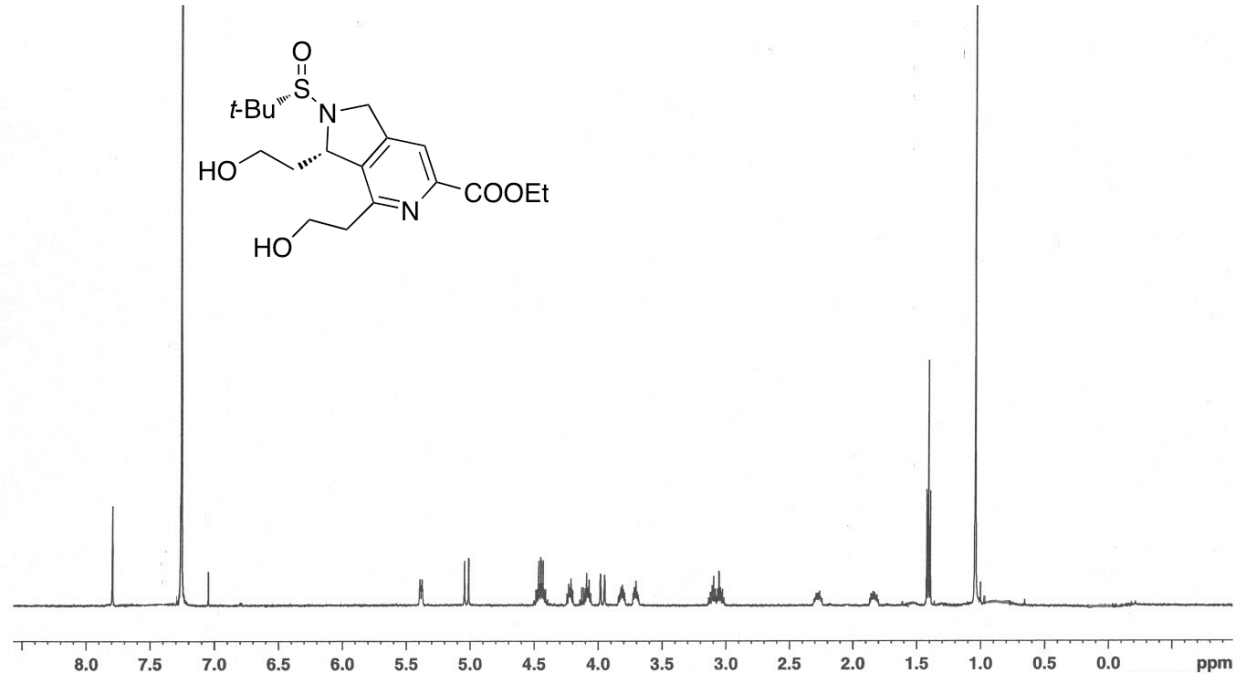

O
O
S
t-Bu
N
HO
O
N
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5 ppm

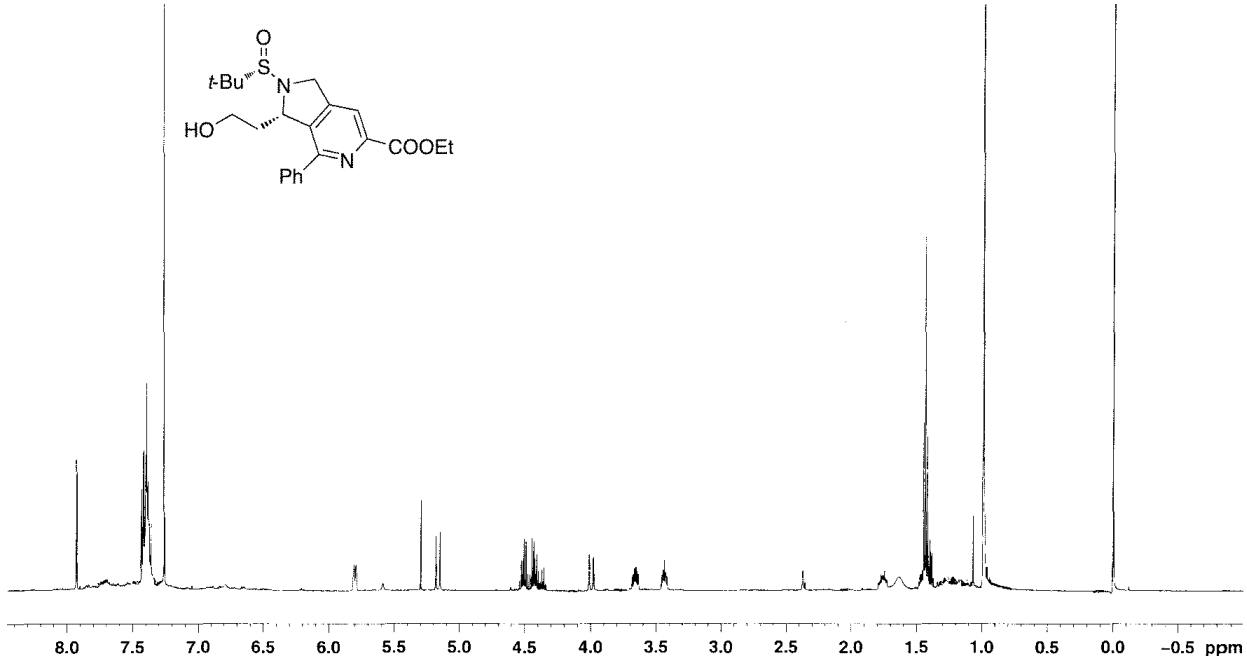

O
S
t-Bu
N
HO
N
Ph
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

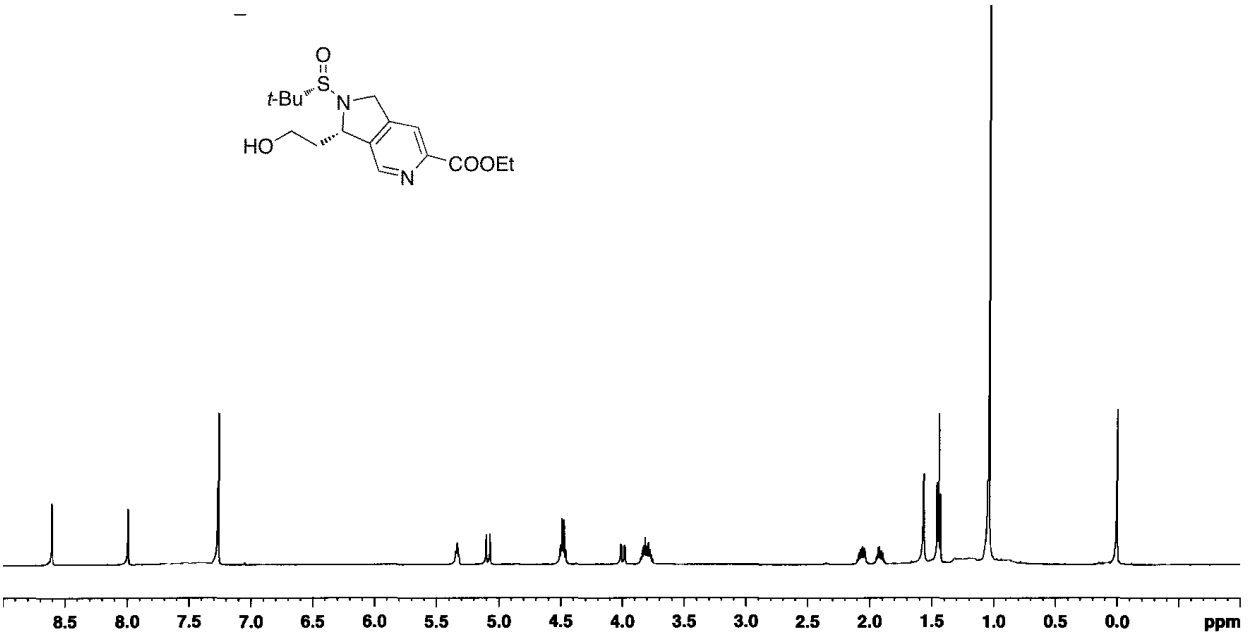

HN
HO
Ph
N
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

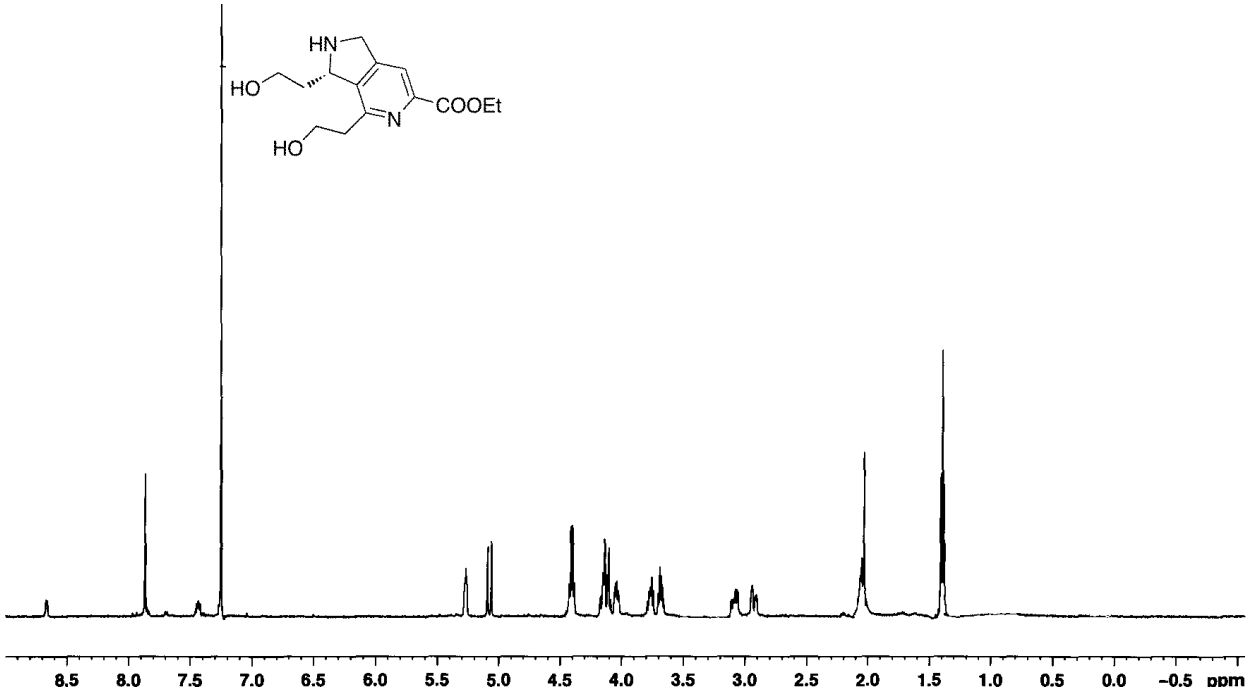

t-Bu
HO
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

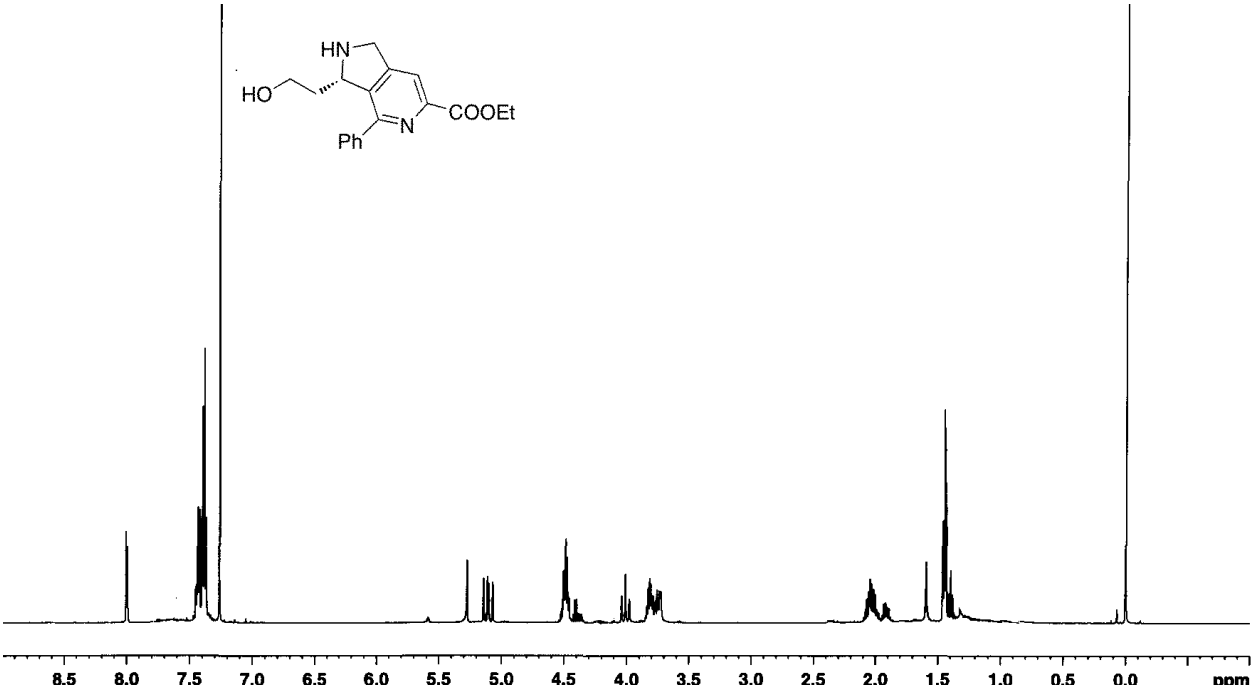
i. Nitrile [2+2+2] cyclotrimerization products (*S*-42–44)

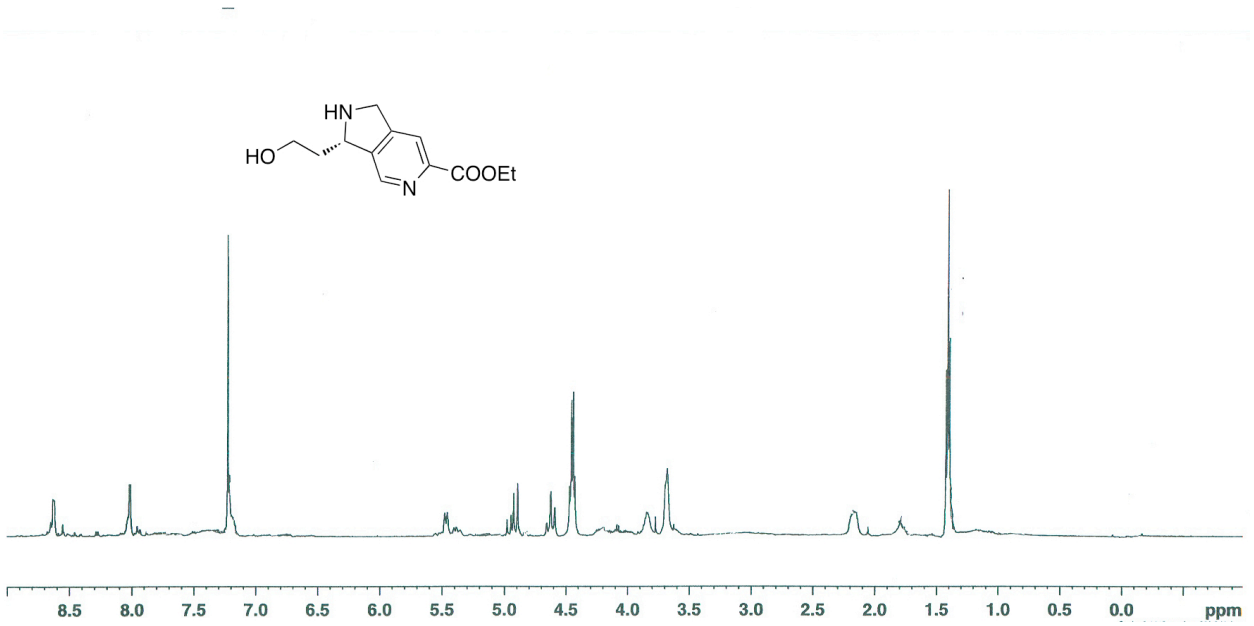


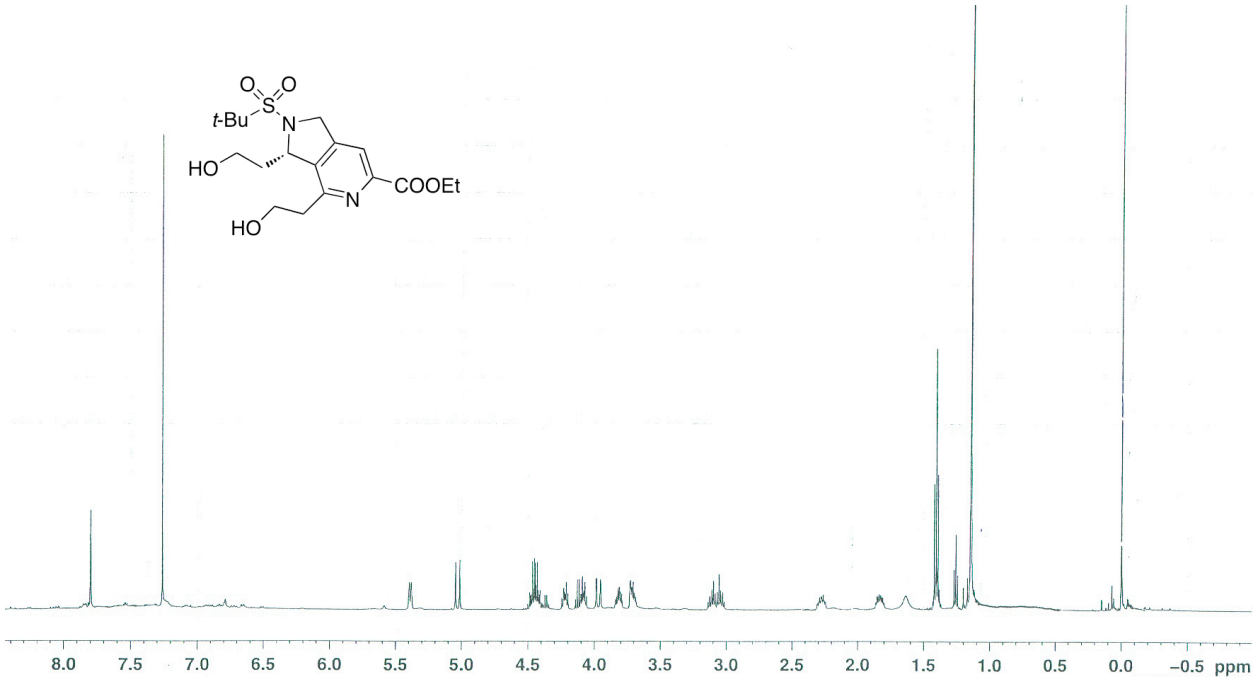


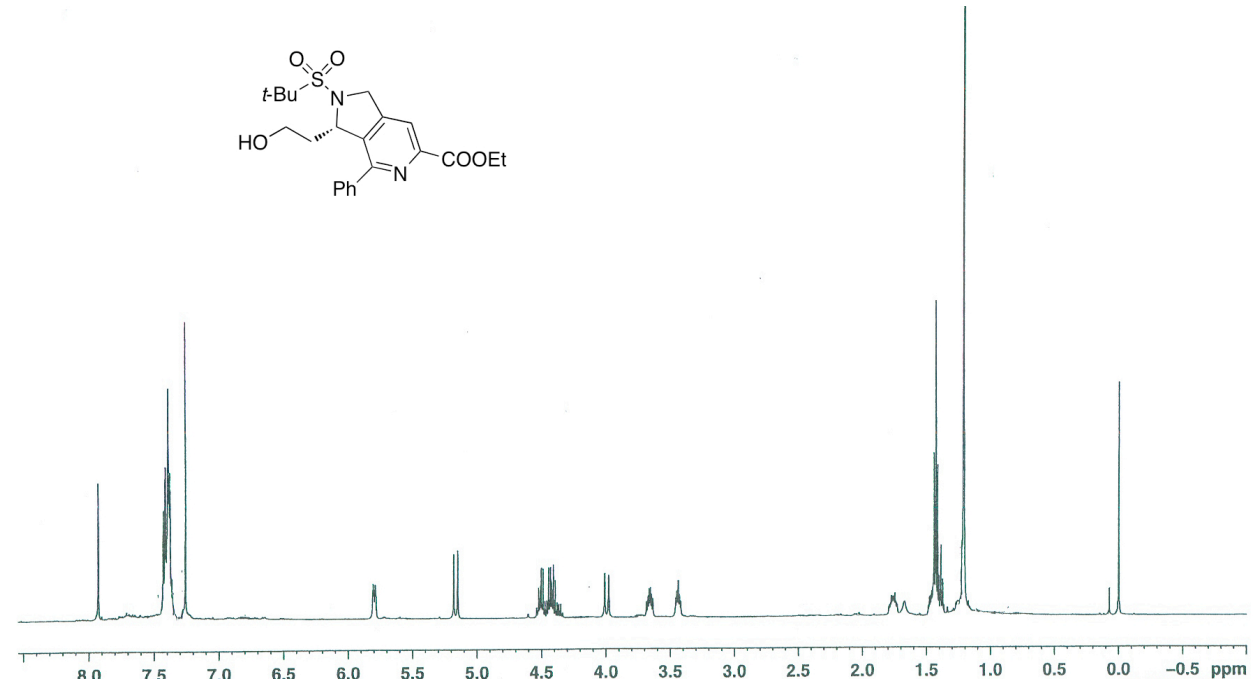

t-Bu
O
S
N
HO
N
COOEt
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

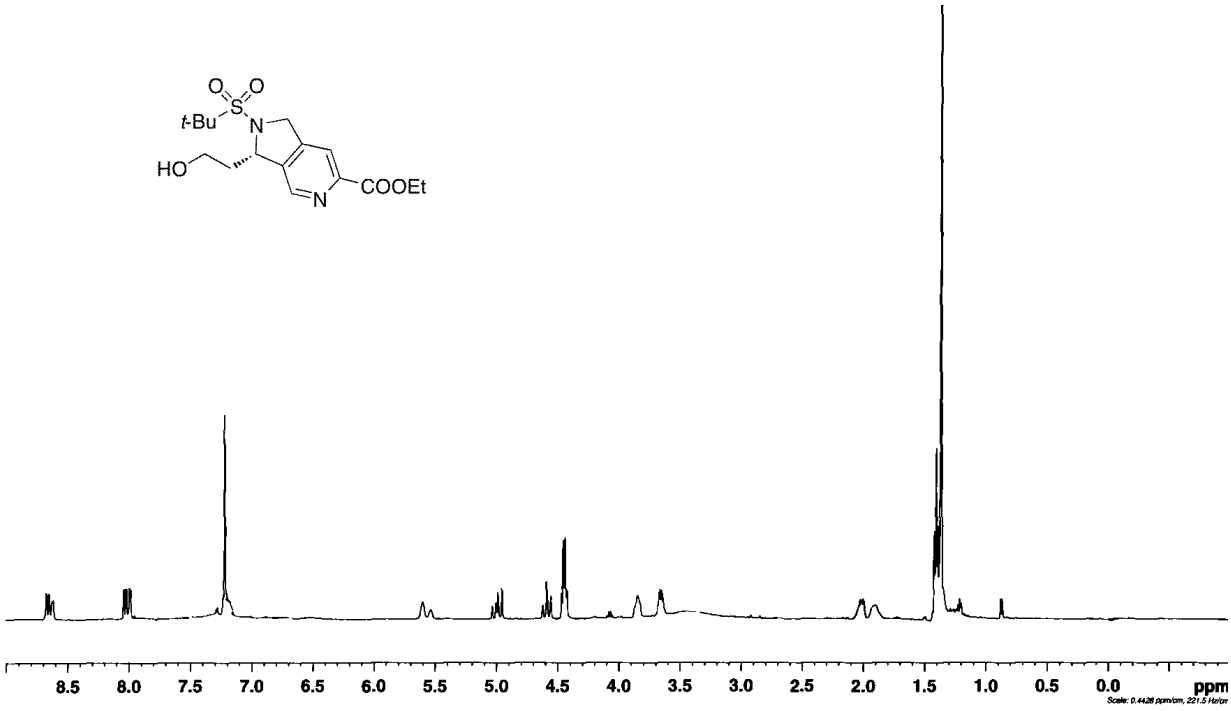

HN
HO
N
COOEt
HO
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm


HN
HO
COOEt
N
Ph
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

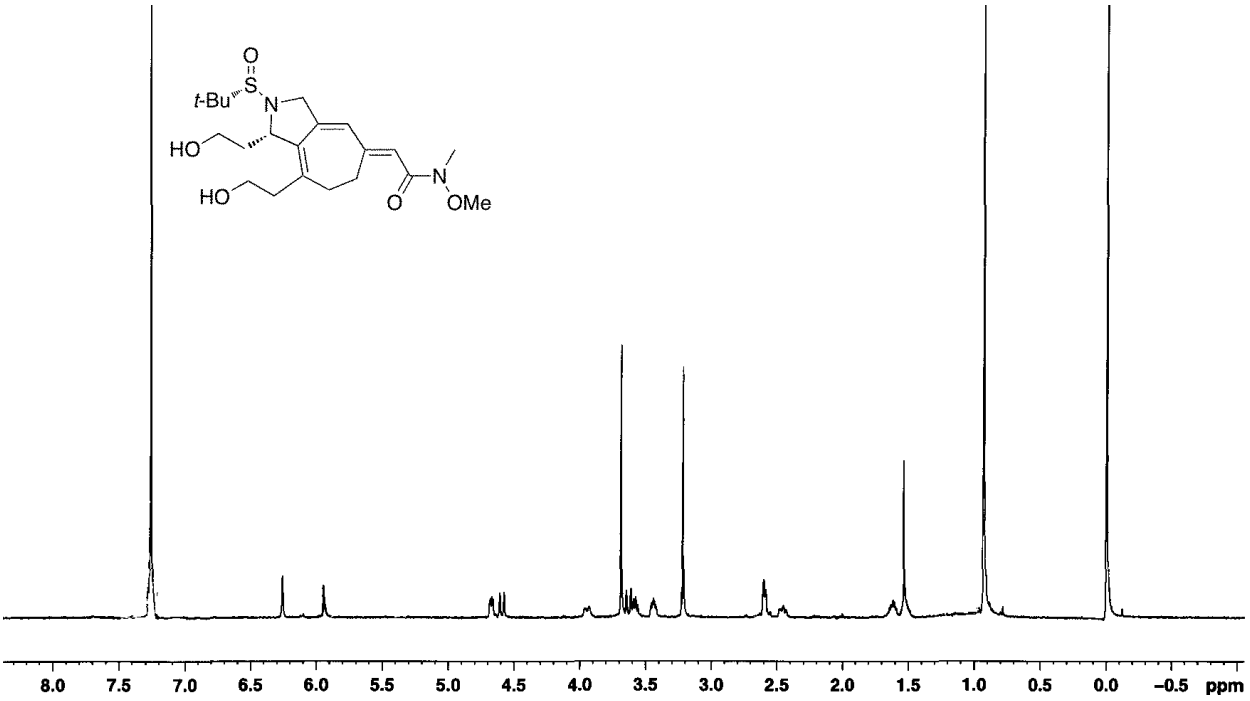

HN
HO
COOEt
N
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

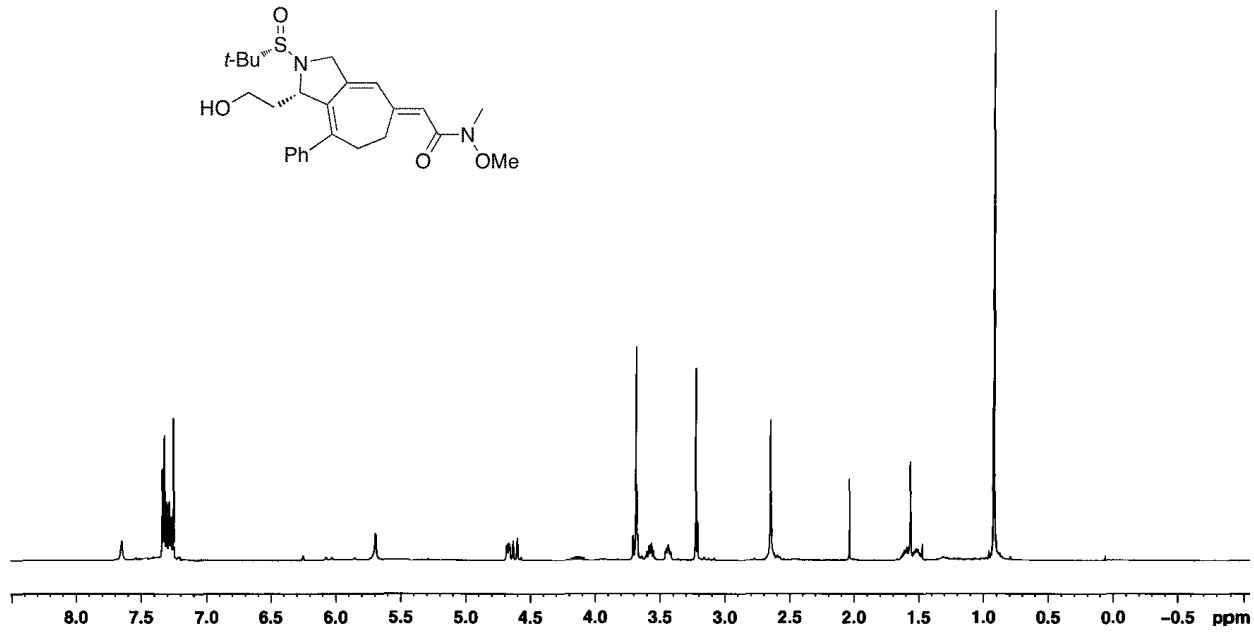

O
O
S
t-Bu
N
HO
COOEt
N
HO
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

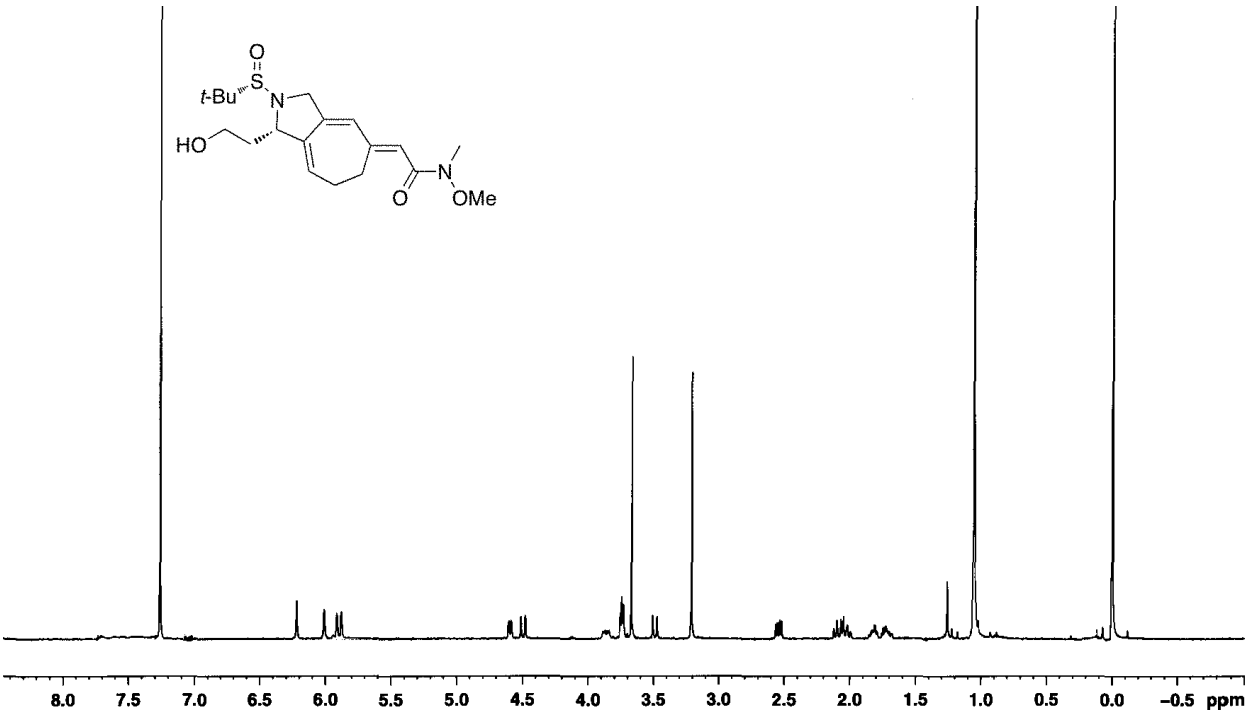

O
O
S
t-Bu
N
HO
COOEt
Ph
N
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

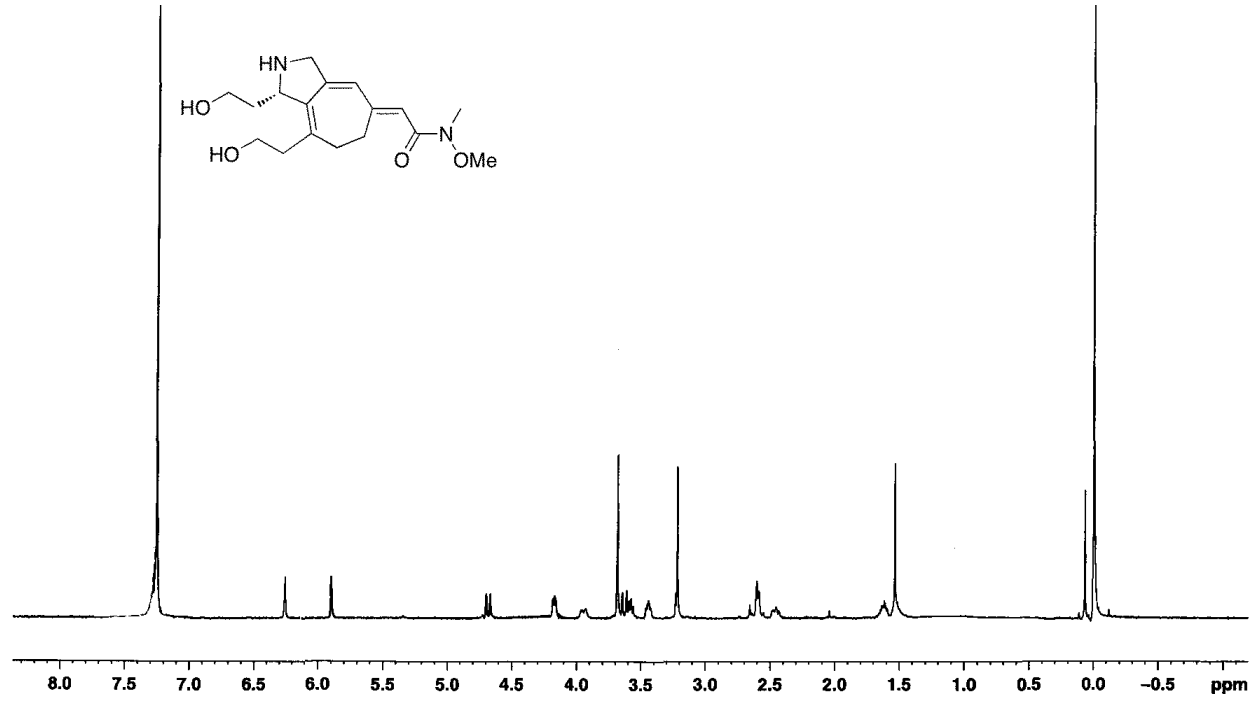

O
O
S
t-Bu
N
HO
COOEt
N
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

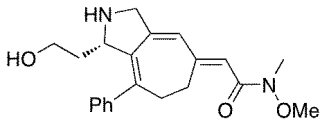
j. Saito [3+2+2] cycloaddition products (*S*-45–50)

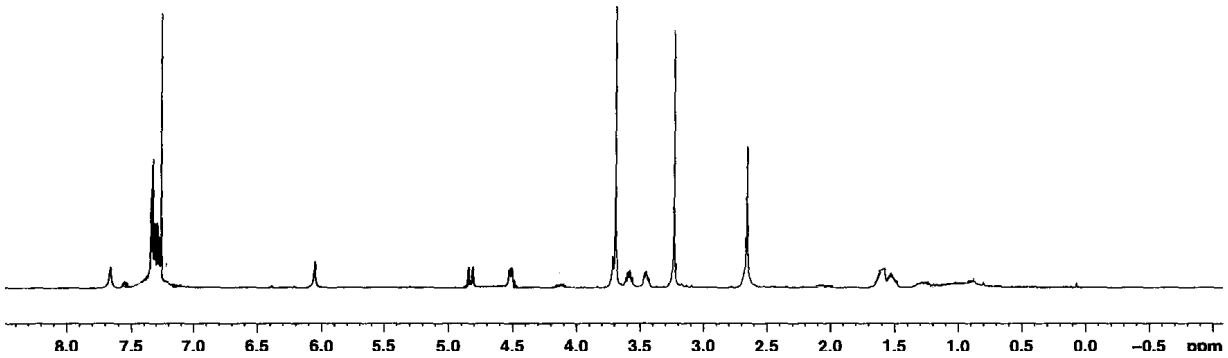


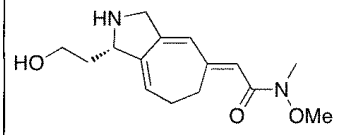



O
S
t-Bu
N
HO
N
O
OMe
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

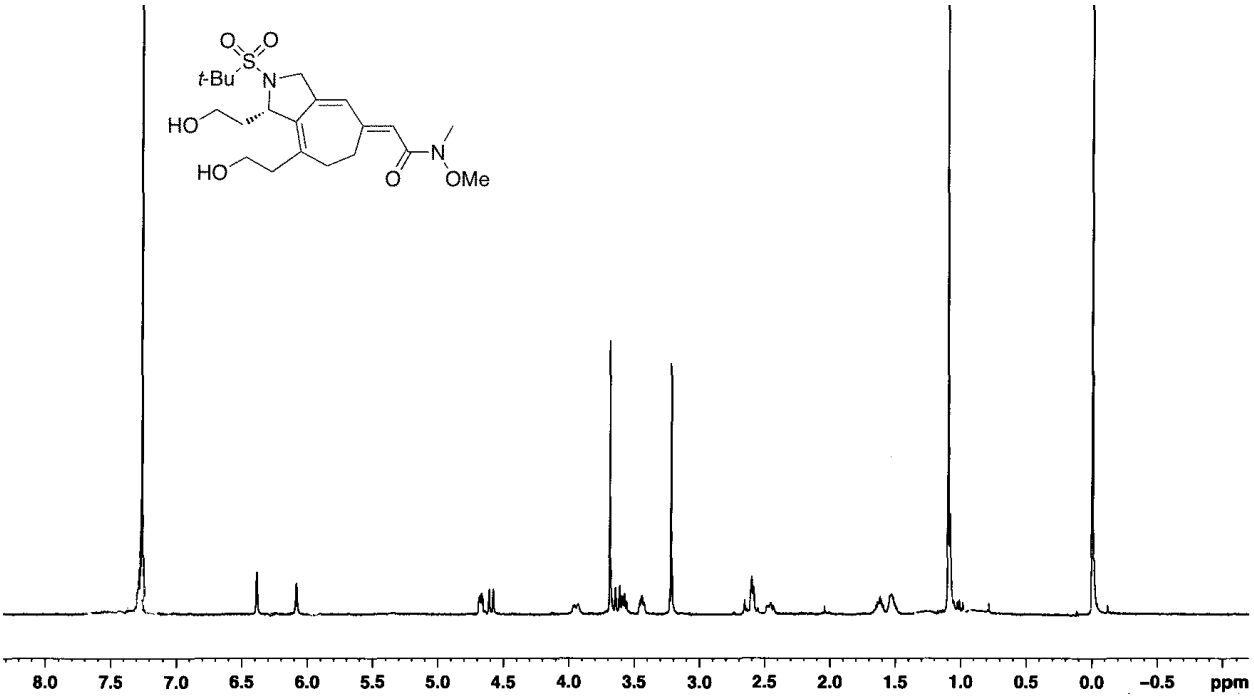

HN
HO
HO
N
O
OMe
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

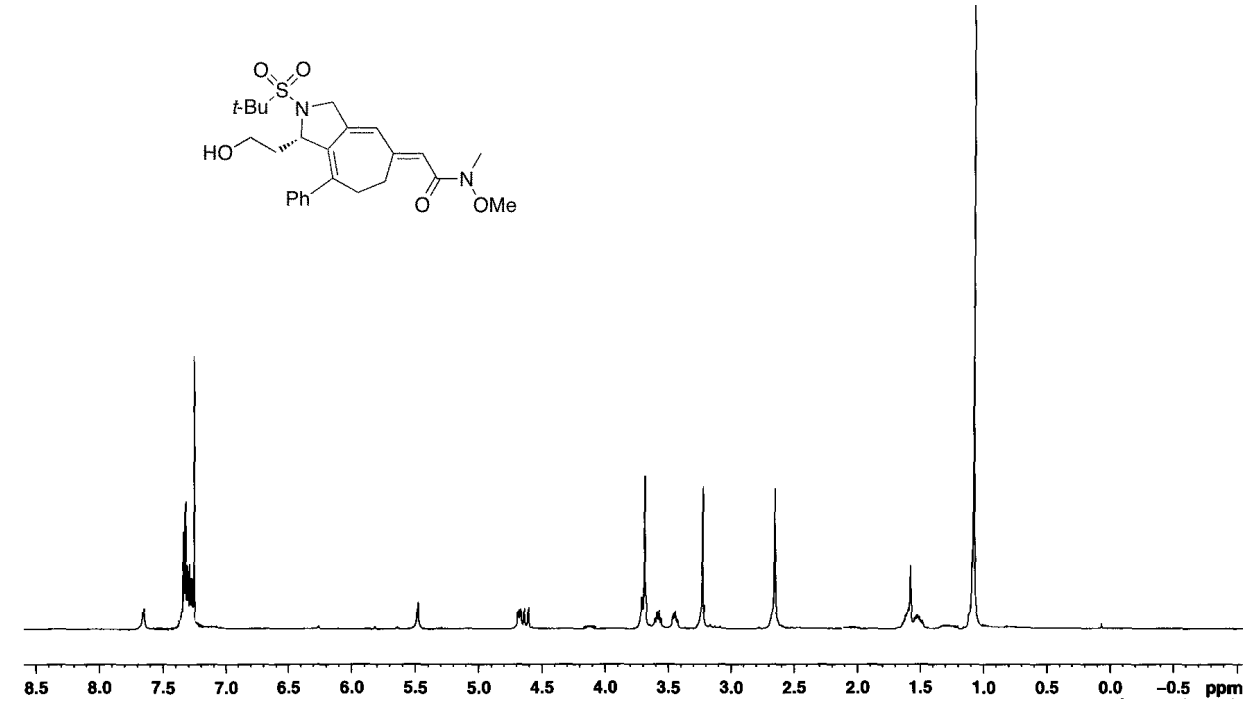

HN
HO
Ph
N
O
OMe

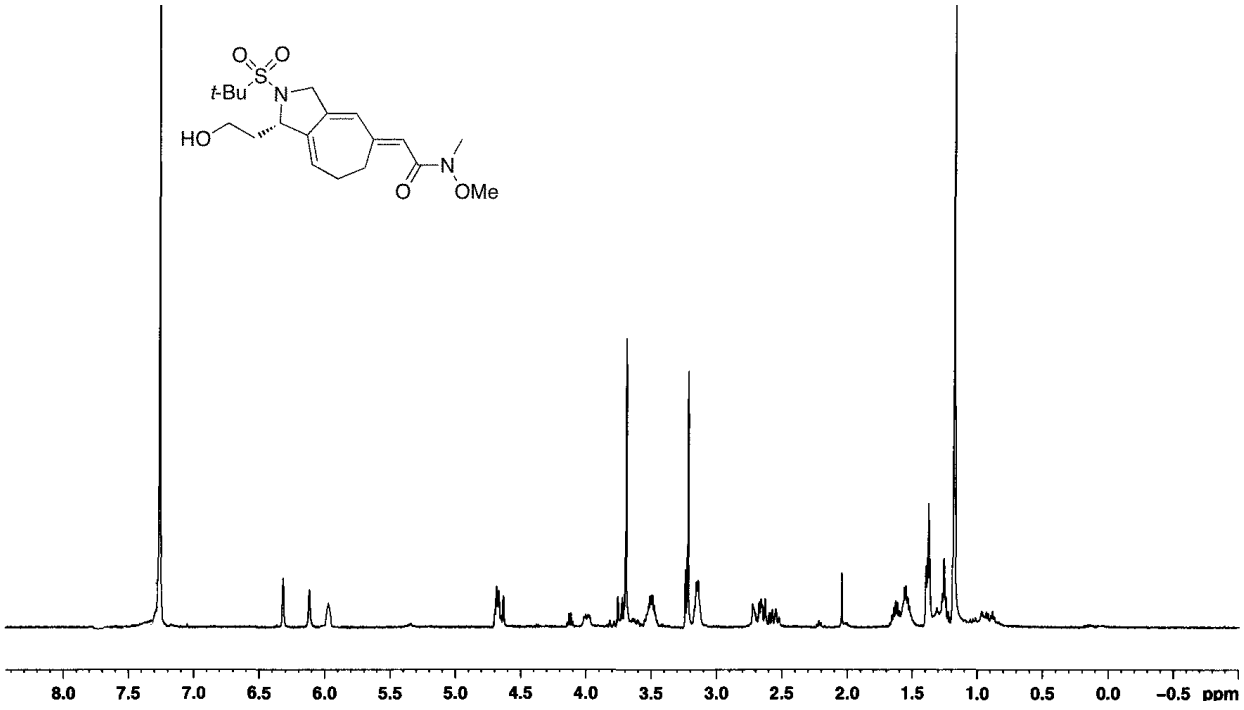

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

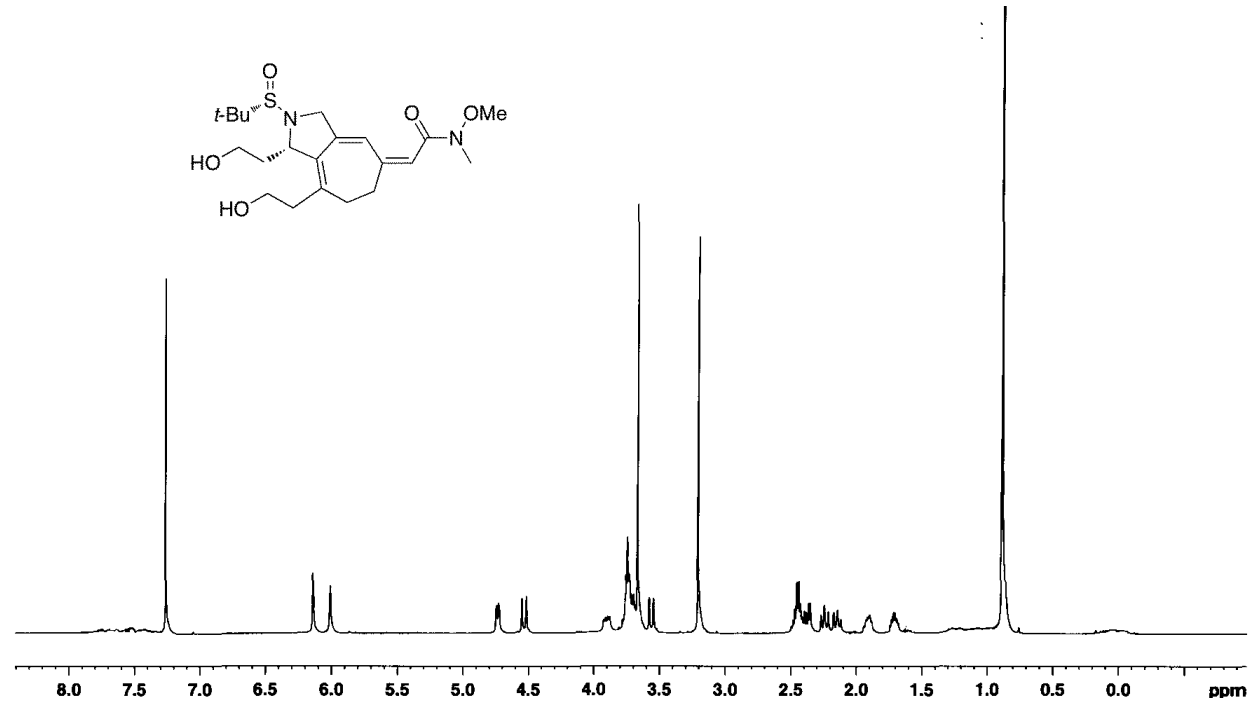

HN
HO
N
O
OMe

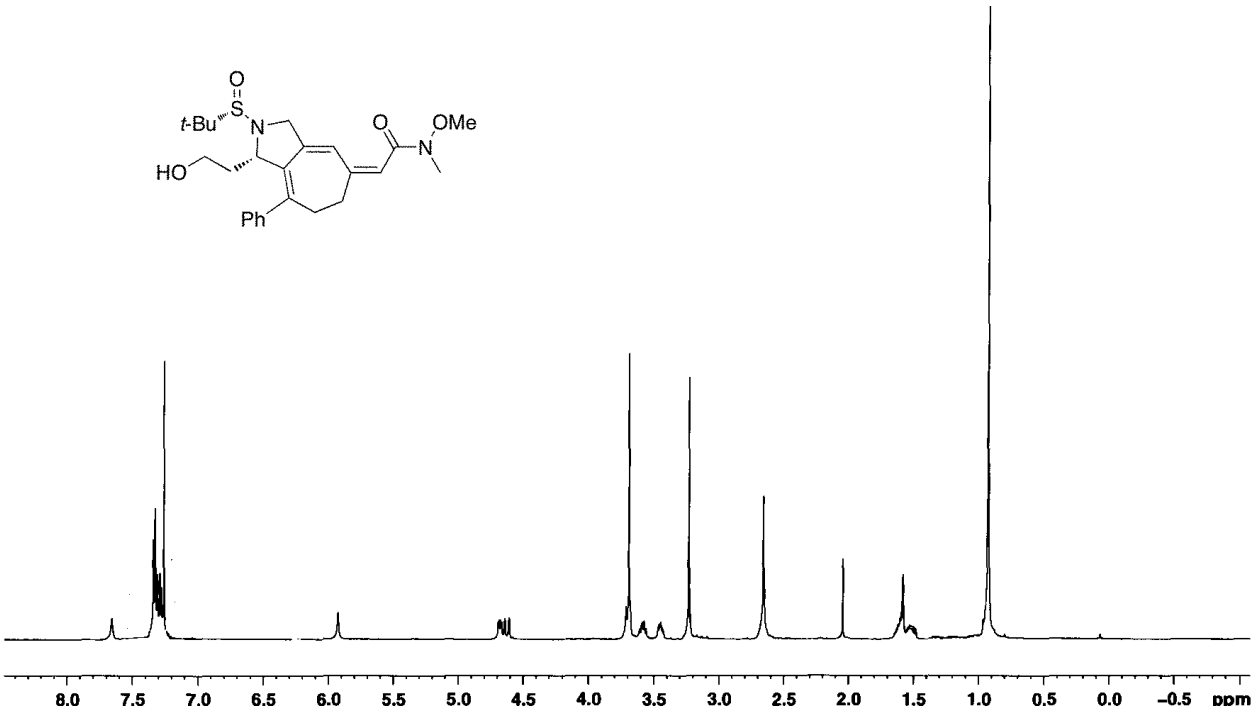
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

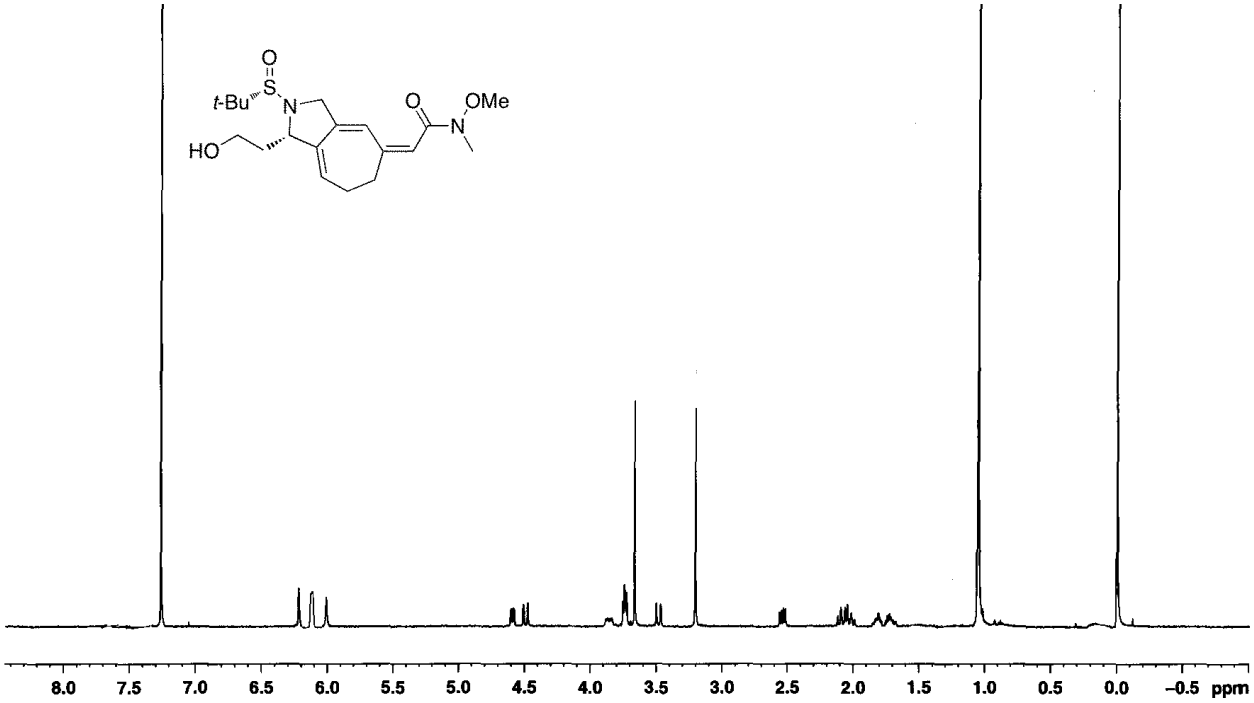

t-Bu
HO
HO
OMe
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

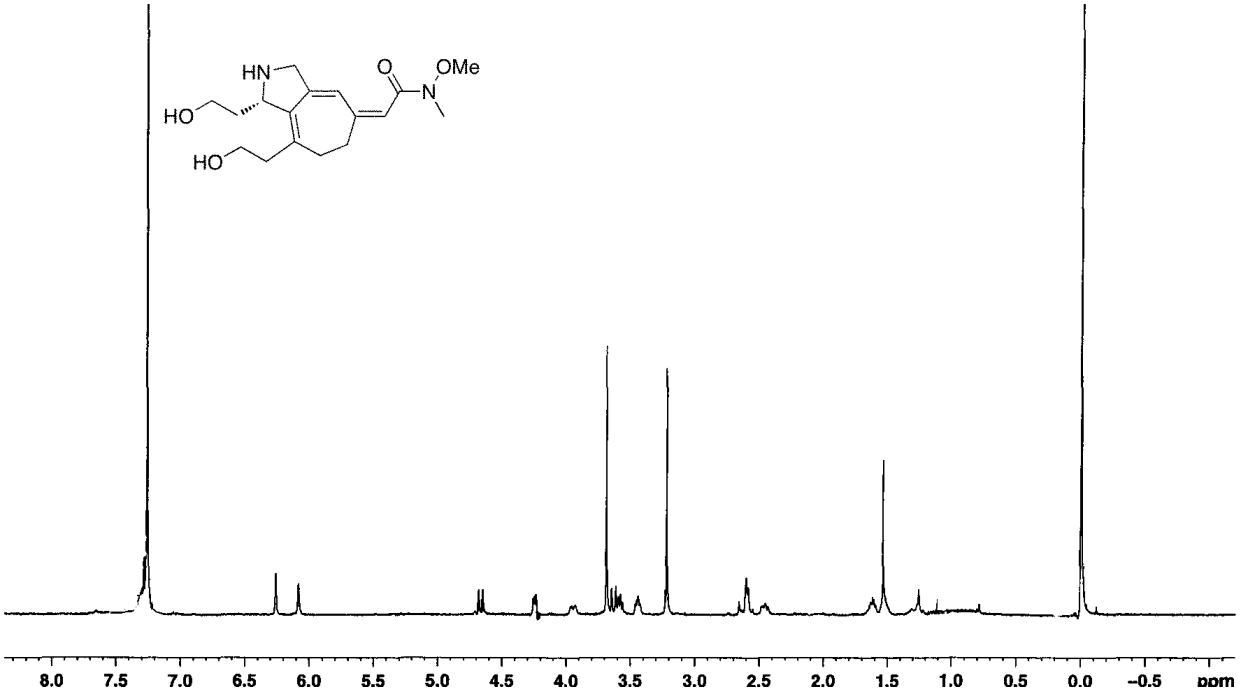

t-Bu
HO
Ph
OMe
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

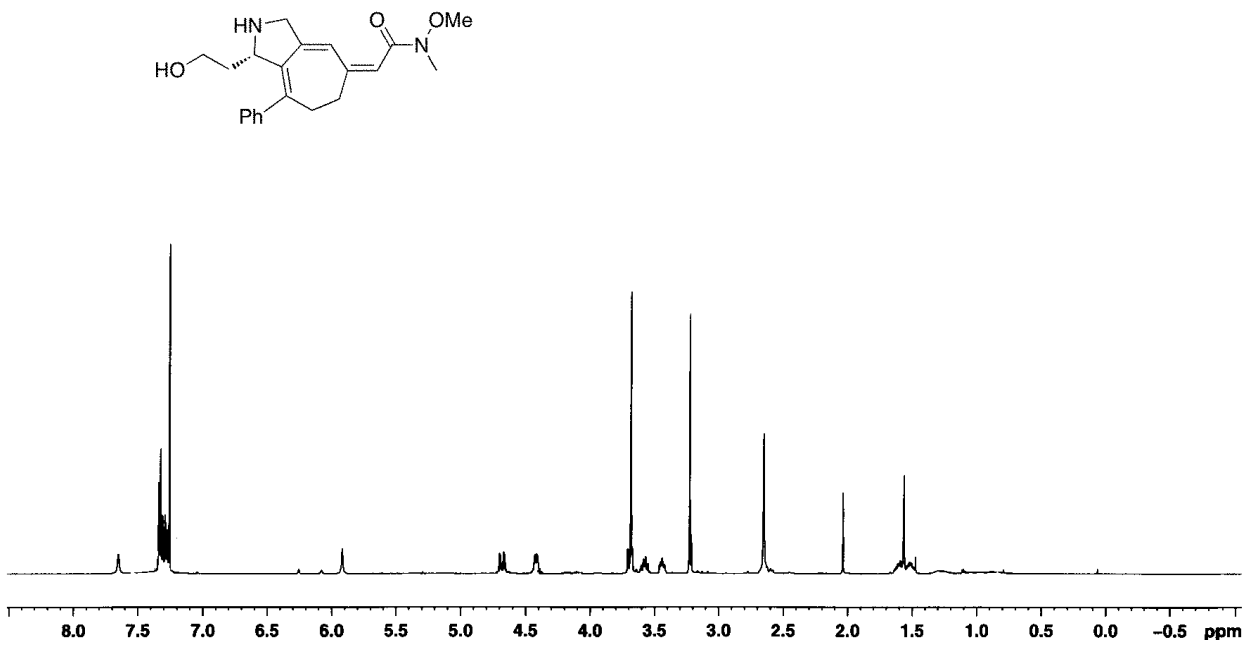

O
O
S
t-Bu
N
HO
N
O
OMe
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5 ppm

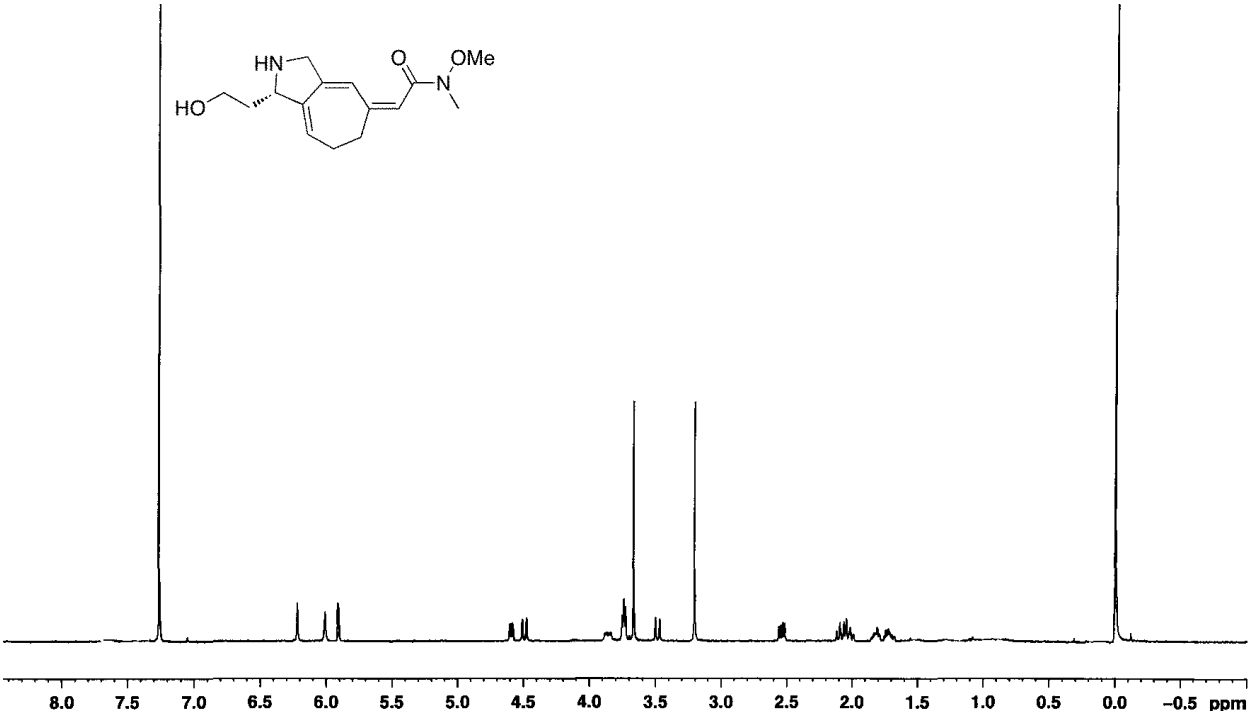

t-Bu
S
O
N
O
OMe
N
HO
HO
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

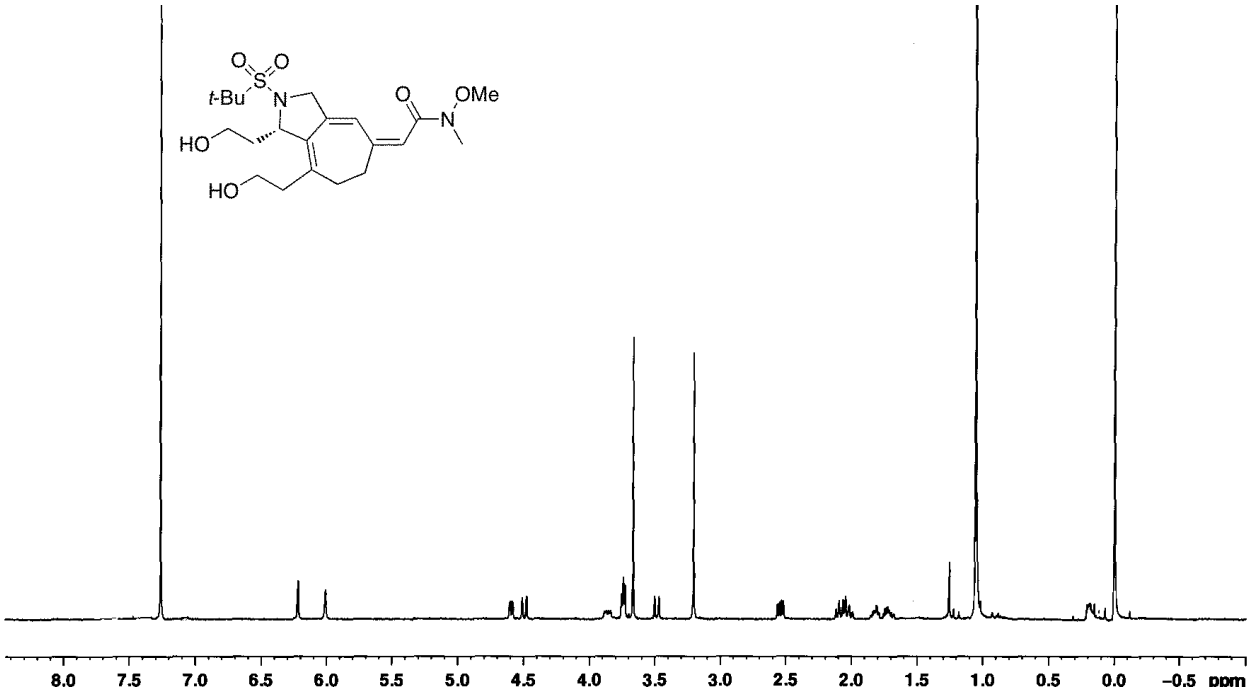

t-Bu
S
O
N
O
OMe
N
HO
Ph
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm

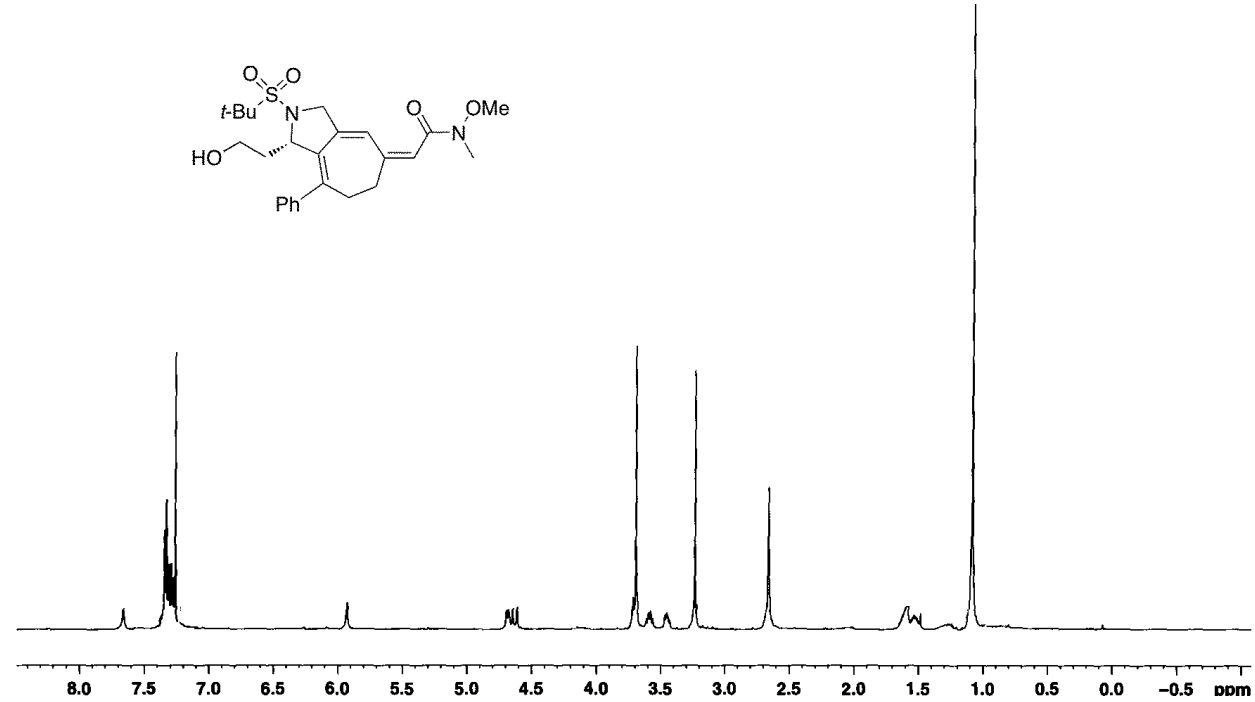

O
t-Bu
S
N
HO
O
OMe
N
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm

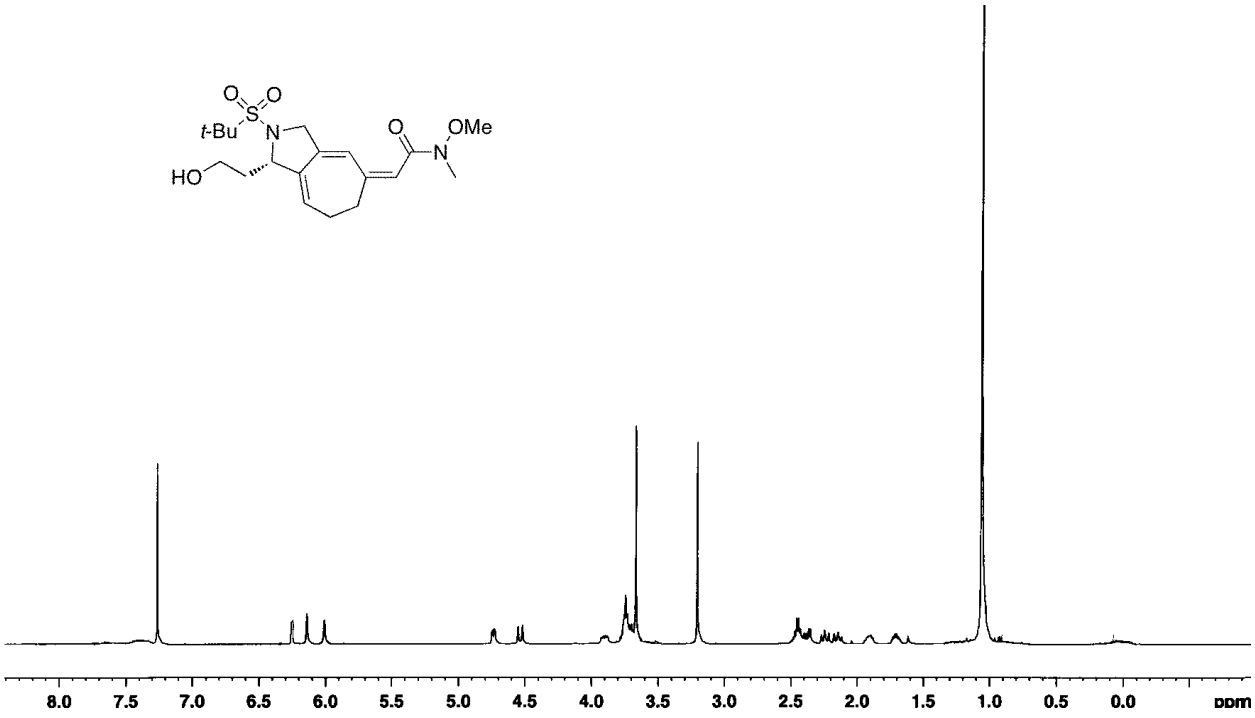

HN
HO
HO
O
OMe
N
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm


HN
O
OMe
N
HO
Ph
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
−0.5
ppm


HN
O
OMe
N
HO
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
−0.5
ppm


t-Bu
HO
HO
OMe
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 −0.5 ppm


t-Bu
HO
Ph
OMe
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 −0.5 ppm


O
O
S
t-Bu
N
HO
O
OMe
N
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm