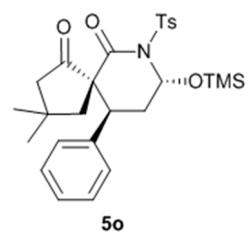
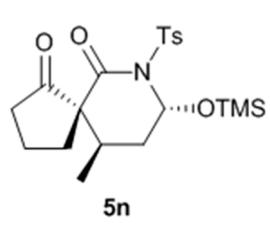
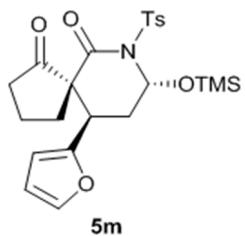
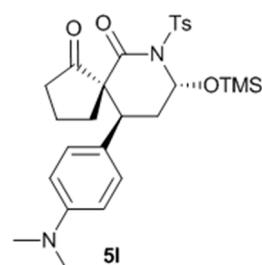
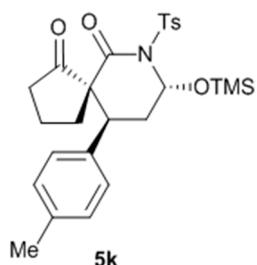
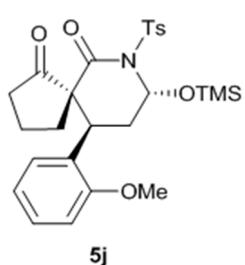
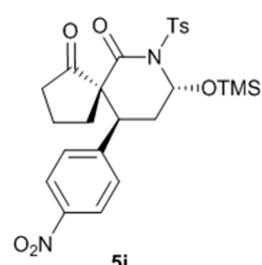
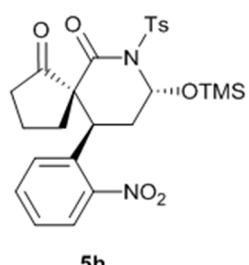
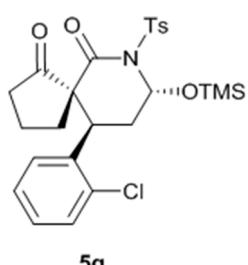
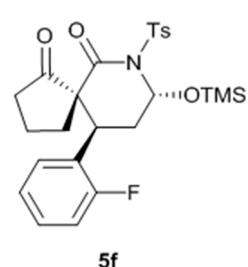
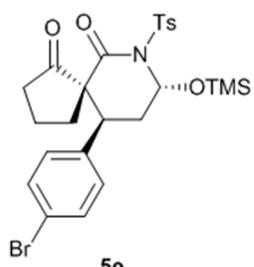
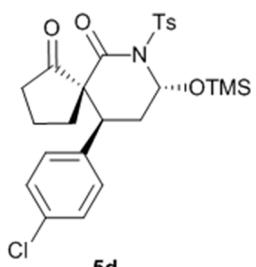
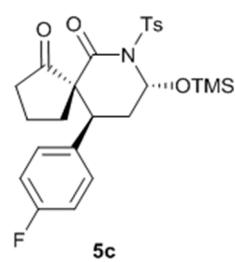
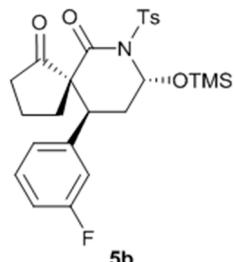
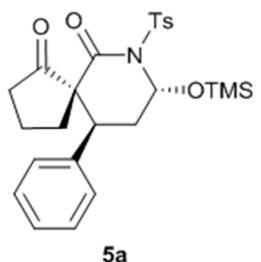
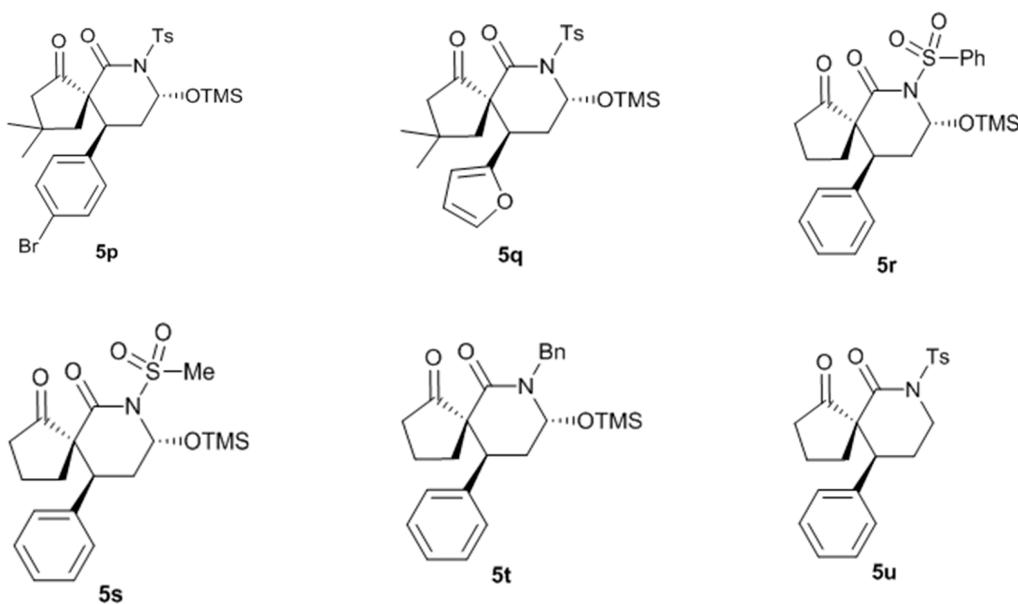


Supplementary Materials: One-Pot Two-Step Organocatalytic Asymmetric Synthesis of Spirocyclic Piperidones via Wolff Rearrangement–Amidation–Michael–Hemiaminalization Sequence

Yanqing Liu, Liang Ouyang, Ying Tan, Xue Tang, Jingwen Kang, Chunting Wang, Yaning Zhu, Cheng Peng and Wei Huang



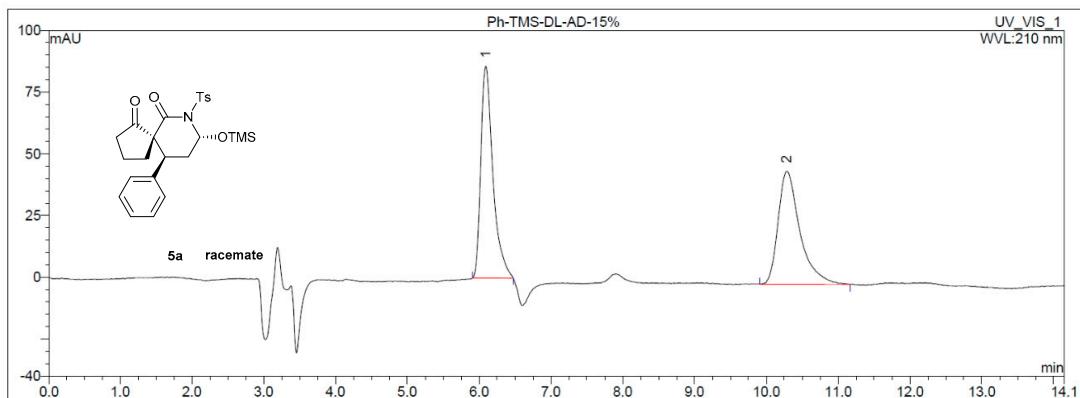
**Figure S1.** Structure of compounds **5a–5u**.**Crystal Data of 5m**

Empirical formula: C₂₃H₂₉NO₆SSi; Formula weight: 475.62; Temperature: 296 K; Wavelength: 0.71073 Å; Crystal system: Orthorhombic; Space group: P 21 21 2; Unit cell dimensions: $a = 11.1118 \text{ \AA}$; $\alpha = 90^\circ$; $b = 21.4220 \text{ \AA}$; $\beta = 90^\circ$; $c = 10.2188 \text{ \AA}$; $\gamma = 90^\circ$; Volume: 2432.5 Å³; Z: 4; Density (calculated): 1.299 mg/m³; Absorption coefficient: 0.220 mm⁻¹; $F(000)$: 1008; Crystal size: 0.407 × 0.198 × 0.155 mm³; Theta range for data collection: 3.310° to 27.535°; Index ranges: -14 ≤ h ≤ 14, -27 ≤ k ≤ 27, -13 ≤ l ≤ 13; Reflections collected: 50,554; Independent reflections: 5596 [$R(\text{int}) = 0.0574$]; Completeness to theta = 25.242°: 99.7%; Absorption correction: Semi-empirical from equivalents; Max. and min. transmission: 0.966 and 0.914; Refinement method: Full-matrix least-squares on F^2 ; Data/restraints/parameters: 5596/24/293; Goodness-of-fit on F^2 : 1.022; Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0445$, $wR_2 = 0.0704$; R indices (all data): $R_1 = 0.0744$, $wR_2 = 0.0788$; Absolute structure parameter: 0.00; Extinction coefficient: n/a; Largest diff. peak and hole: 0.198 and -0.222 e·Å⁻³.

HPLC Chromatograms and NMR Spectra

Peak Analysis Report

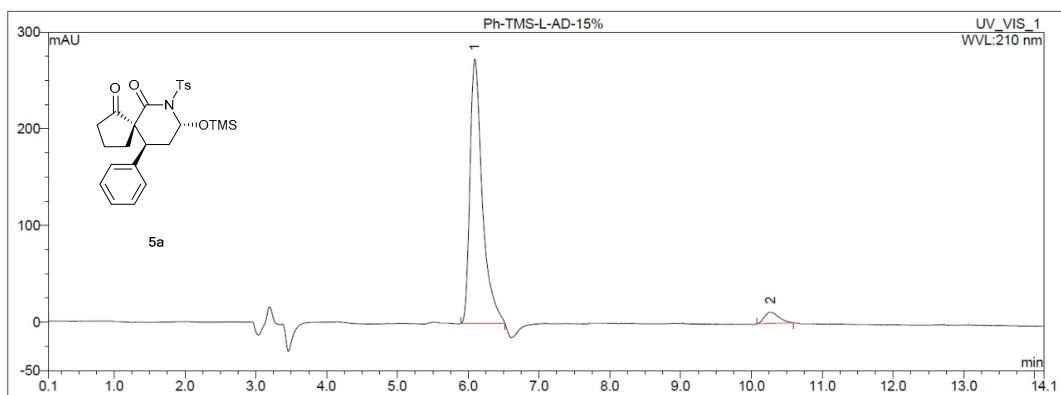
No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
		min	mAU*min	%	mAU	
1	n.a.	6.09	16.738	50.88	85.814	n.a.
2	n.a.	10.28	16.157	49.12	45.841	n.a.



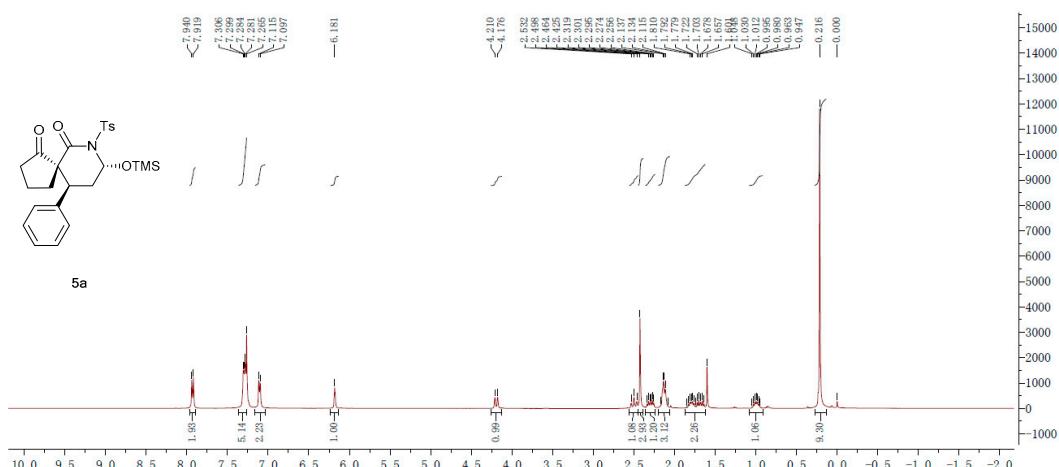
(a)

Peak Analysis Report

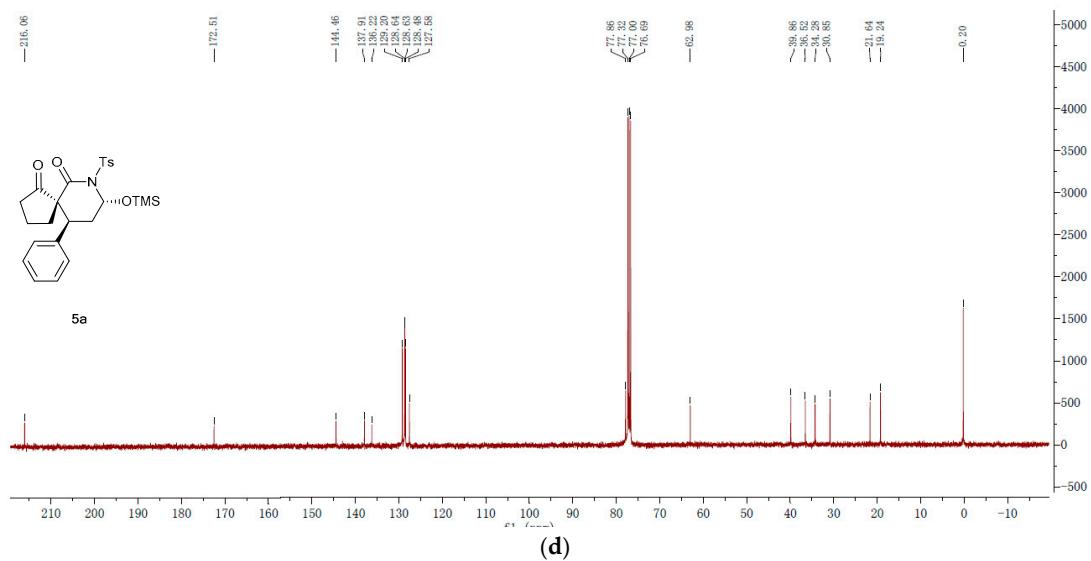
No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
		min	mAU*min	%	mAU	
1	n.a.	6.09	55.283	95.10	273.460	n.a.
2	n.a.	10.29	2.848	4.90	11.898	n.a.



(b)



(c)

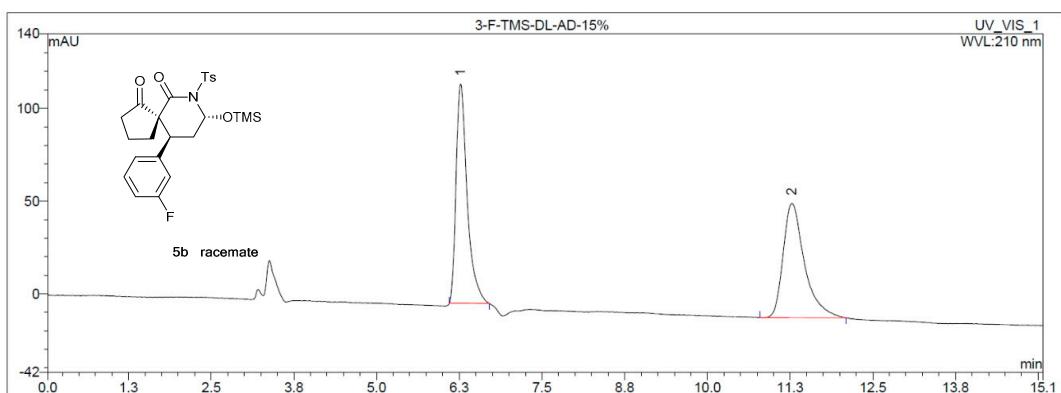


(d)

Figure S2. (a) HPLC chromatogram of racemic **5a**; (b) HPLC chromatogram of chiral **5a**; (c) ¹H-NMR spectrum (CDCl_3 , 400 MHz) of **5a**; (d) ¹³C-NMR spectrum (CDCl_3 , 100 MHz) of **5a**.

Peak Analysis Report

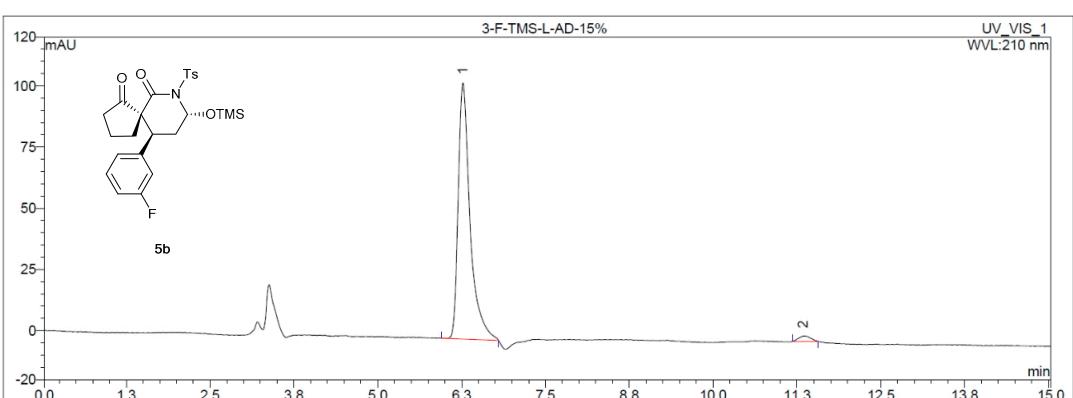
No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
1	n.a.	6.27	23.019	50.01	118.203	n.a.
2	n.a.	11.28	23.012	49.99	61.651	n.a.



(a)

Peak Analysis Report

No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
1	n.a.	6.27	21.484	96.45	104.673	n.a.
2	n.a.	11.28	0.791	3.55	5.056	n.a.



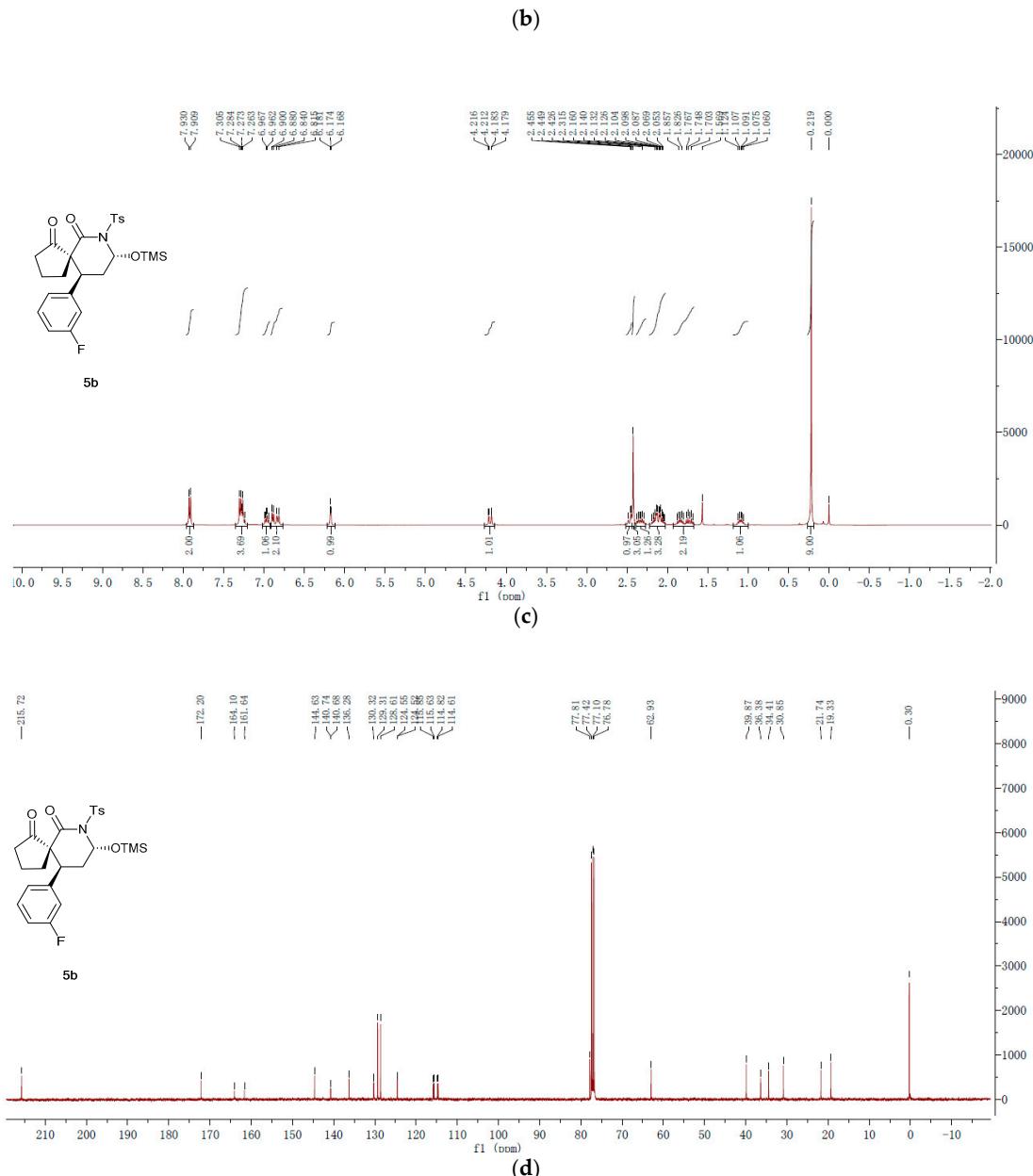
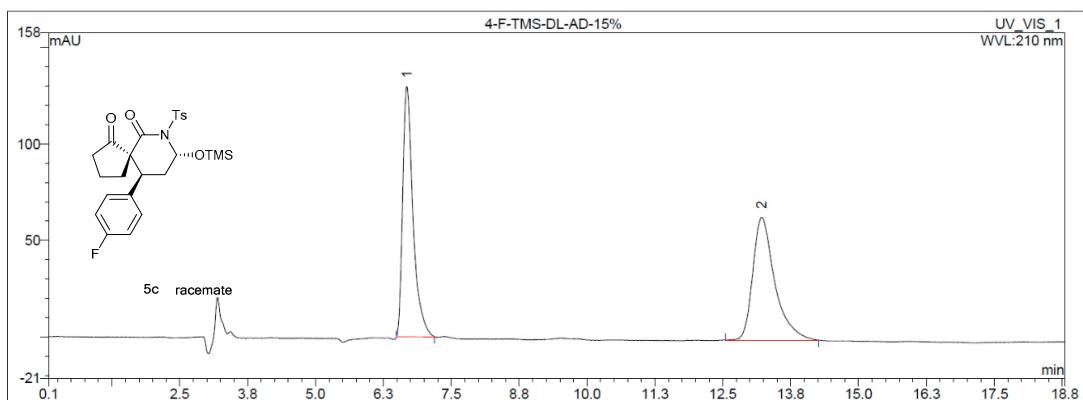


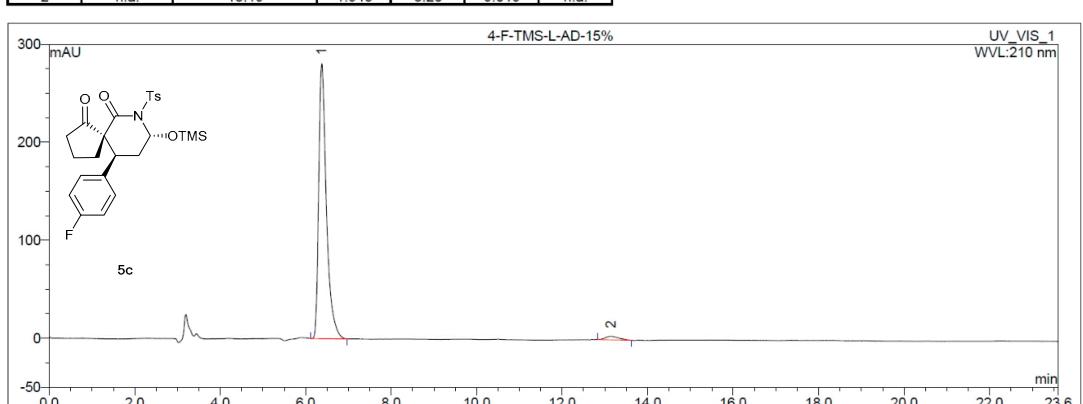
Figure S3. (a) HPLC chromatogram of racemic **5b**; (b) HPLC chromatogram of chiral **5b**; (c) ^1H -NMR spectrum (CDCl_3 , 400 MHz) of **5b**; (d) ^{13}C -NMR spectrum (CDCl_3 , 100 MHz) of **5b**.

Peak Analysis Report

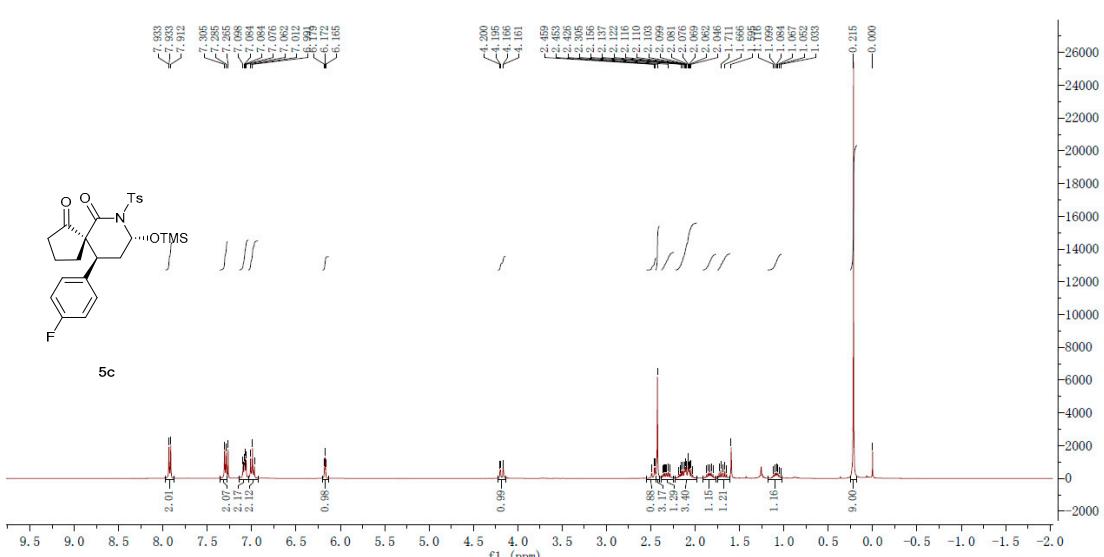
No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
		min	mAU*min	%	mAU	
1	n.a.	6.68	28.483	48.79	129.763	n.a.
2	n.a.	13.22	29.896	51.21	63.692	n.a.

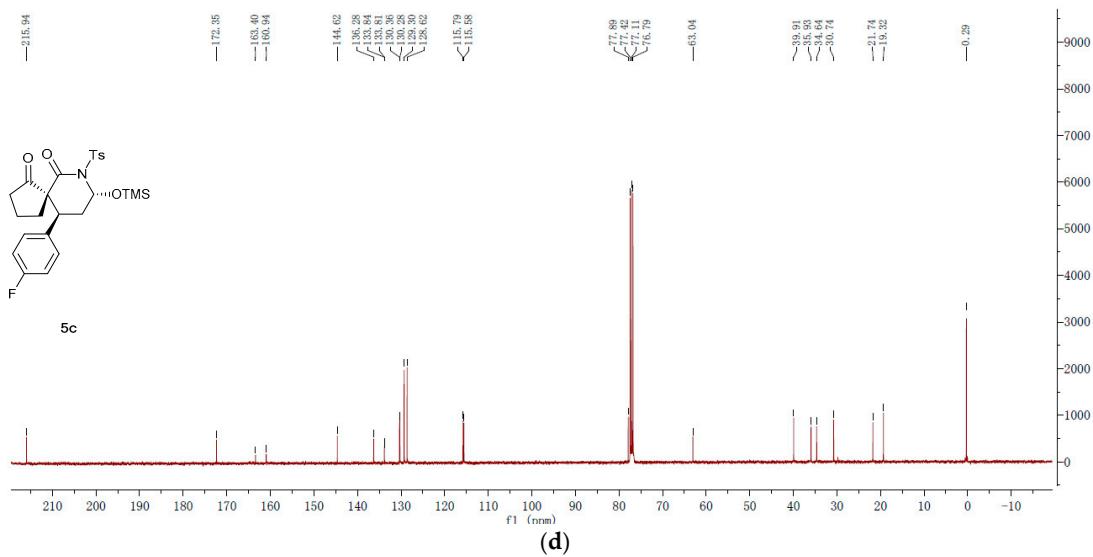
**Peak Analysis Report**

No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
		min	mAU*min	%	mAU	
1	n.a.	6.38	58.862	96.80	280.651	n.a.
2	n.a.	13.19	1.945	3.20	9.019	n.a.



(b)



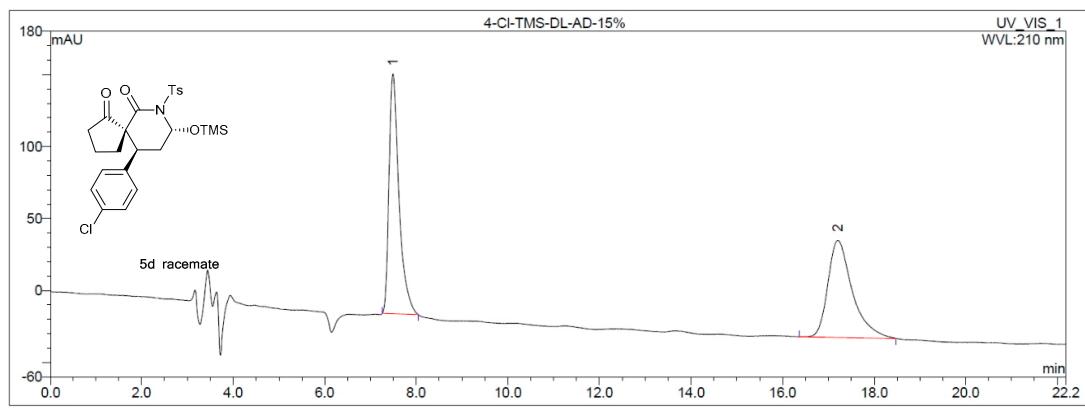


(d)

Figure S4. (a) HPLC chromatogram of racemic **5c**; (b) HPLC chromatogram of chiral **5c**; (c) ^1H -NMR spectrum (CDCl_3 , 400 MHz) of **5c**; (d) ^{13}C -NMR spectrum (CDCl_3 , 100 MHz) of **5c**.

Peak Analysis Report

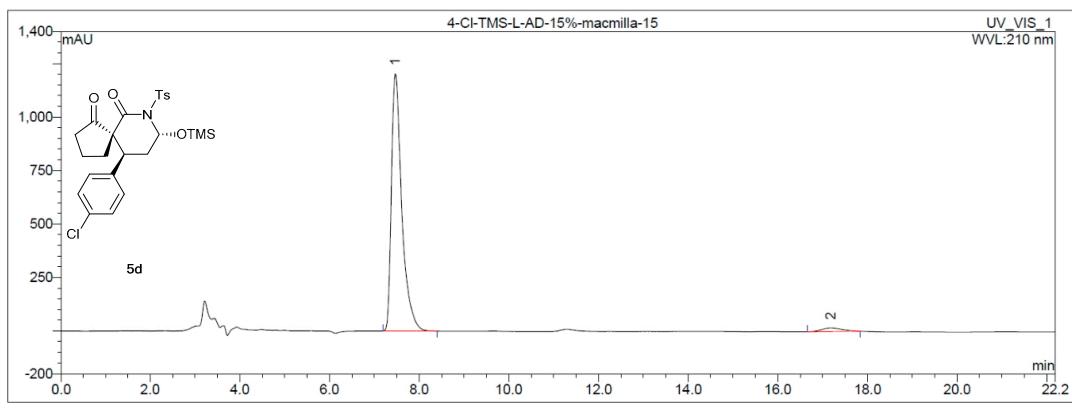
No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
1	n.a.	7.49	42.175	50.35	166.793	n.a.
2	n.a.	17.21	41.584	49.65	67.495	n.a.



(a)

Peak Analysis Report

No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
1	n.a.	7.47	322.490	97.44	1201.652	n.a.
2	n.a.	17.18	8.461	2.56	16.325	n.a.



(b)

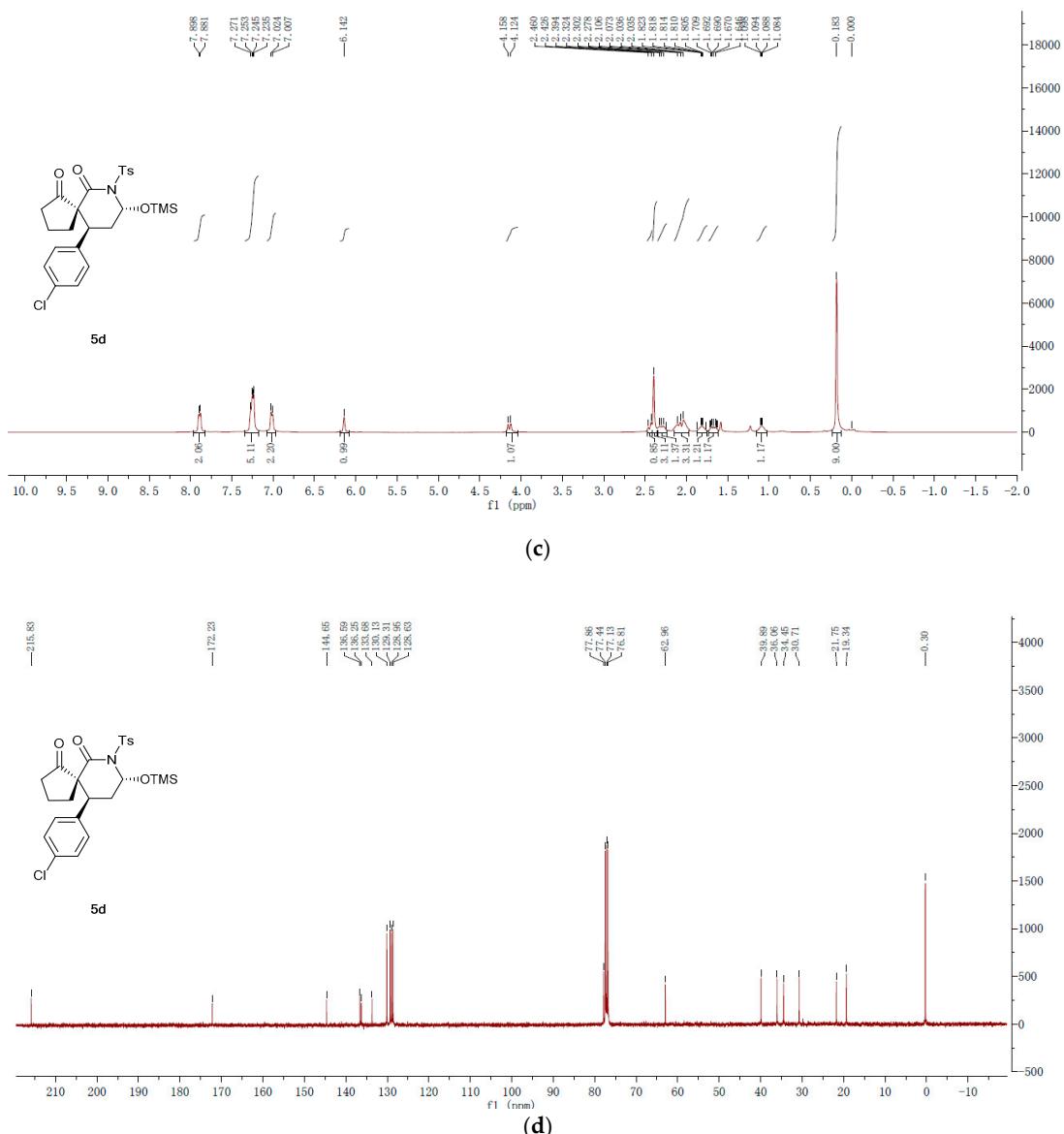
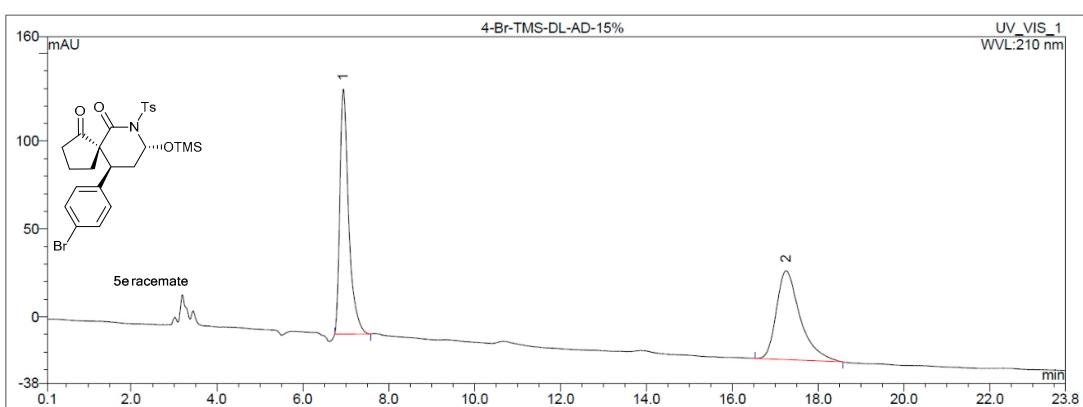


Figure S5. (a) HPLC chromatogram of racemic **5d**; (b) HPLC chromatogram of chiral **5d**; (c) ¹H-NMR spectrum (CDCl_3 , 400 MHz) of **5d**; (d) ¹³C-NMR spectrum (CDCl_3 , 100 MHz) of **5d**.

Peak Analysis Report

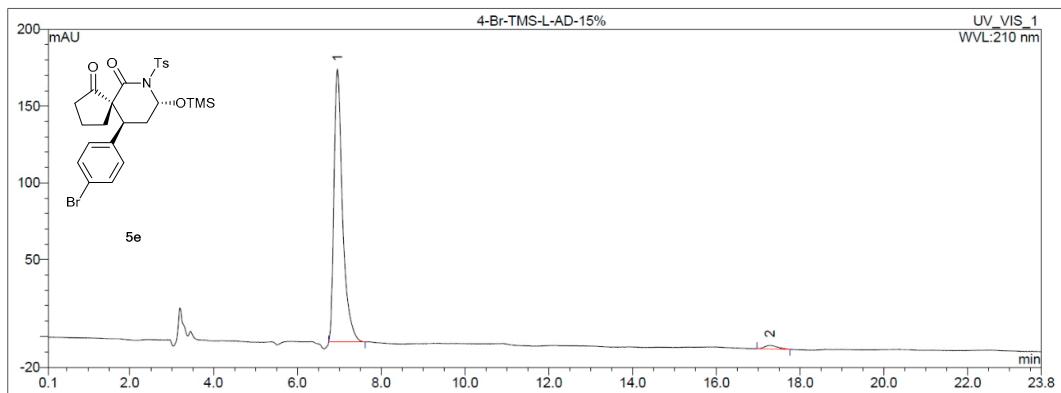
No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
		min	mAU*min	%	mAU	
1	n.a.	6.94	33.165	50.59	139.214	n.a.
2	n.a.	17.25	32.386	49.41	50.620	n.a.



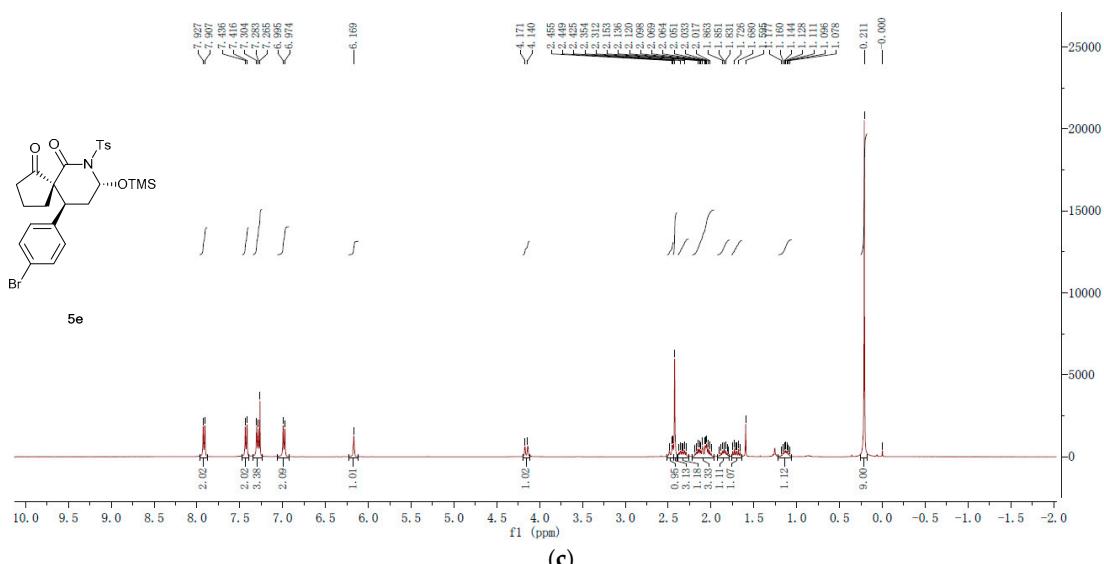
(a)

Peak Analysis Report

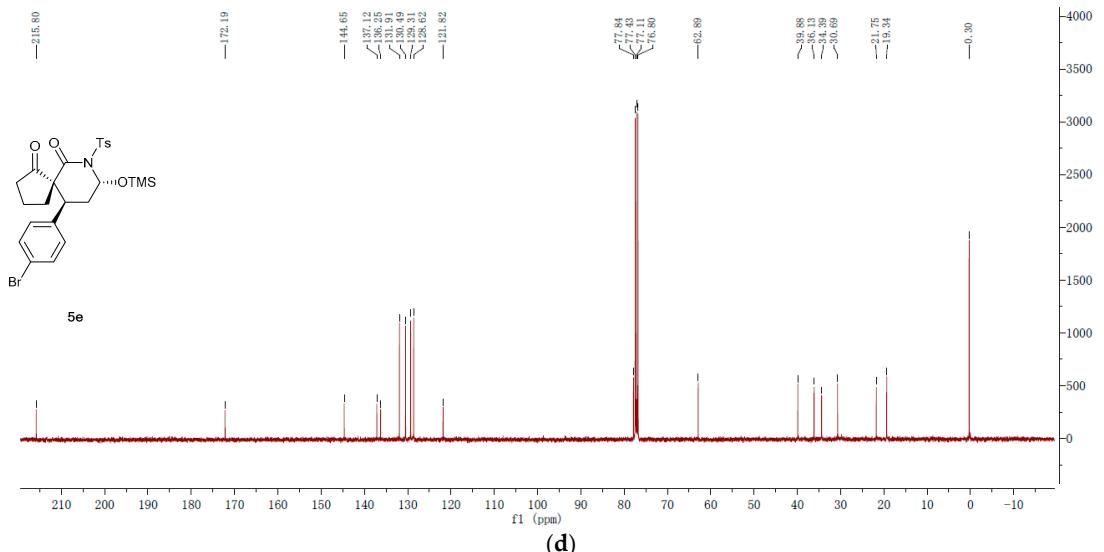
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel Area %	Height mAU	Amount
1	n.a.	6.96	42.207	98.08	177.584	n.a.
2	n.a.	17.26	0.825	1.92	2.253	n.a.



(b)



(c)

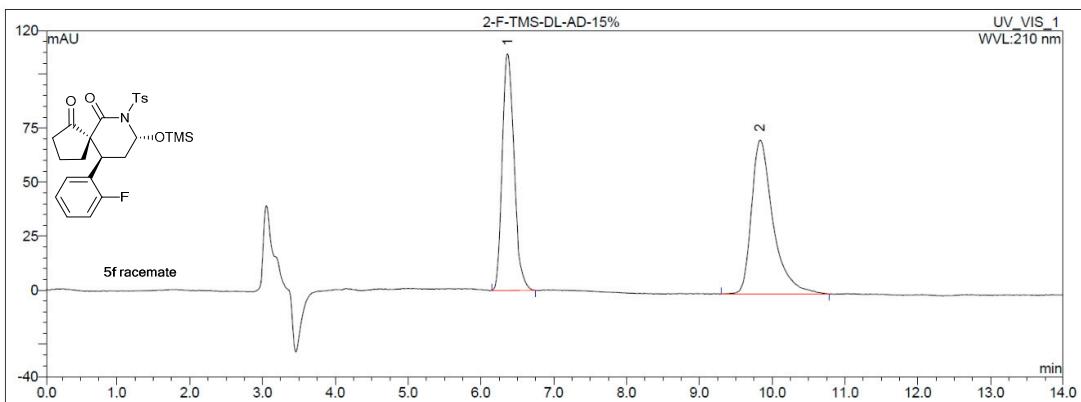


(d)

Figure S6. (a) HPLC chromatogram of racemic **5e**; (b) HPLC chromatogram of chiral **5e**; (c) ¹H-NMR spectrum (CDCl_3 , 400 MHz) of **5e**; (d) ¹³C-NMR spectrum (CDCl_3 , 100 MHz) of **5e**.

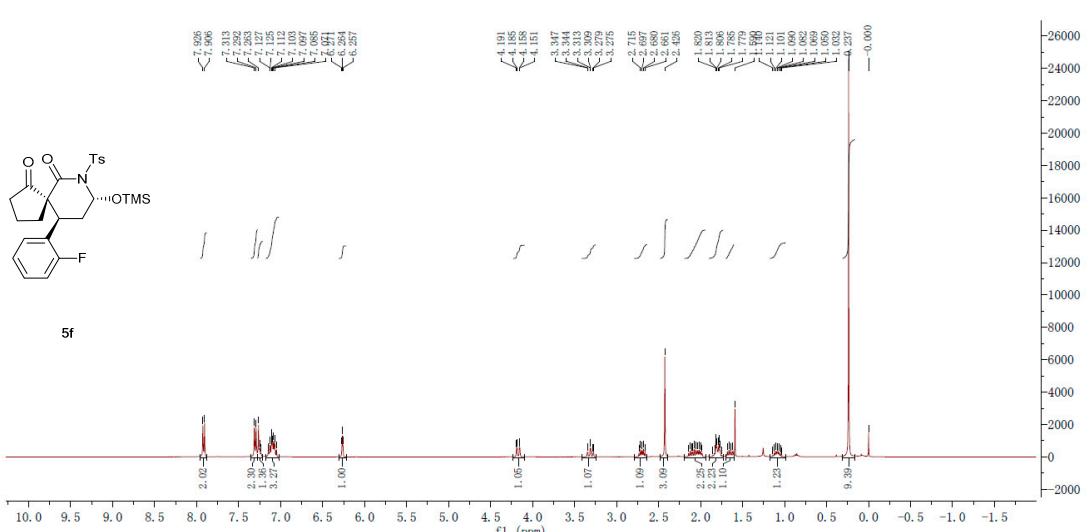
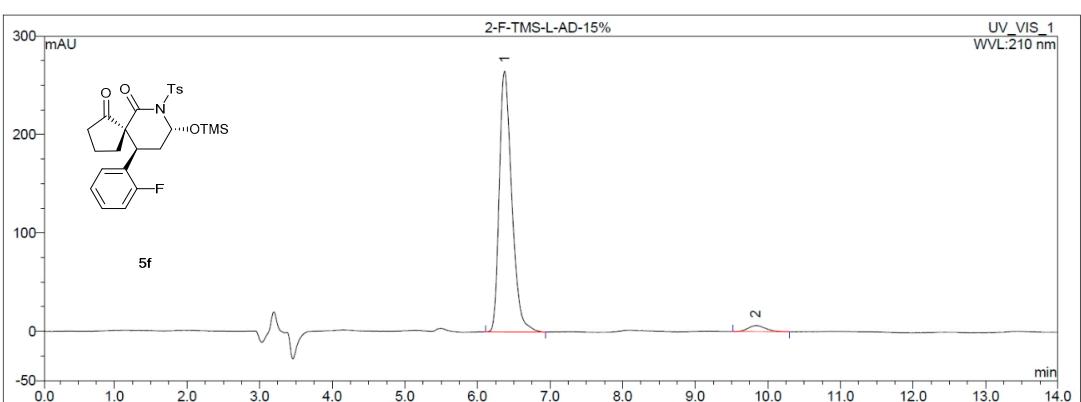
Peak Analysis Report

No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
1	n.a.	6.37	24.922	50.38	122.367	n.a.
2	n.a.	9.83	24.543	49.62	71.175	n.a.



Peak Analysis Report

No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
1	n.a.	6.38	52.956	96.90	265.076	n.a.
2	n.a.	9.83	1.695	3.10	6.025	n.a.



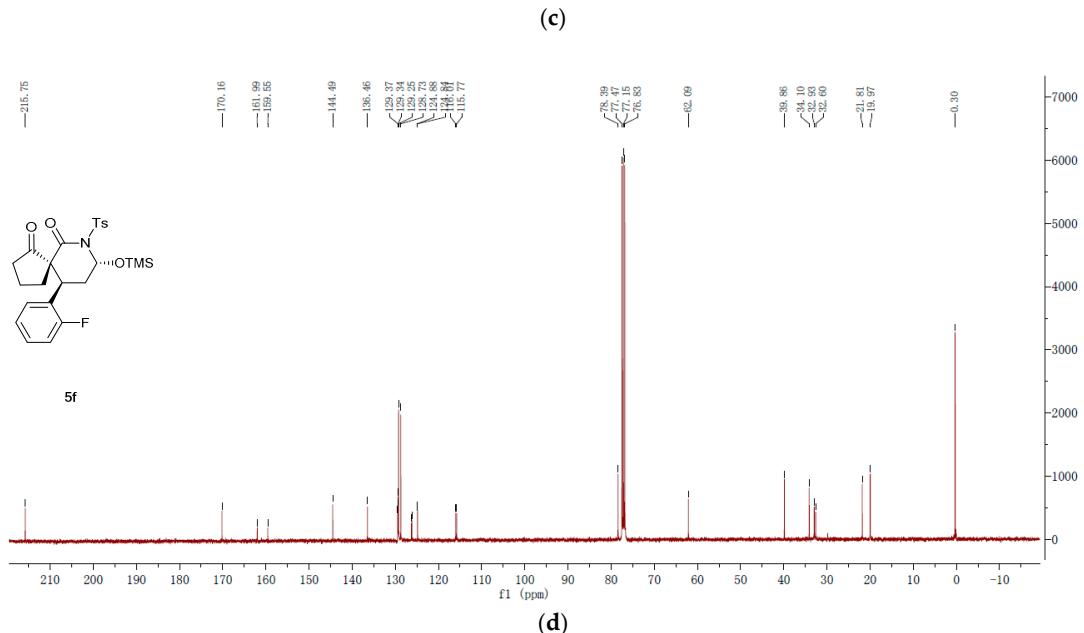
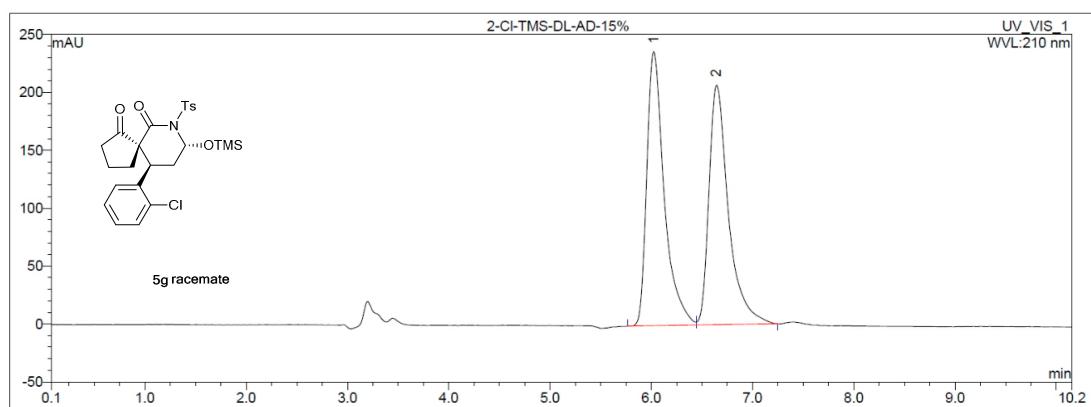


Figure S7. (a) HPLC chromatogram of racemic **5f**; (b) HPLC chromatogram of chiral **5f**; (c) ¹H-NMR spectrum (CDCl_3 , 400 MHz) of **5f**; (d) ¹³C-NMR spectrum (CDCl_3 , 100 MHz) of **5f**.

Peak Analysis Report

No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area %	Height mAU	Amount
1	n.a.	6.03	47.205	50.62	236.847	n.a.
2	n.a.	6.64	46.044	49.38	206.802	n.a.



Peak Analysis Report

No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area %	Height mAU	Amount
1	n.a.	6.02	24.451	95.49	125.077	n.a.
2	n.a.	6.63	1.154	4.51	7.587	n.a.

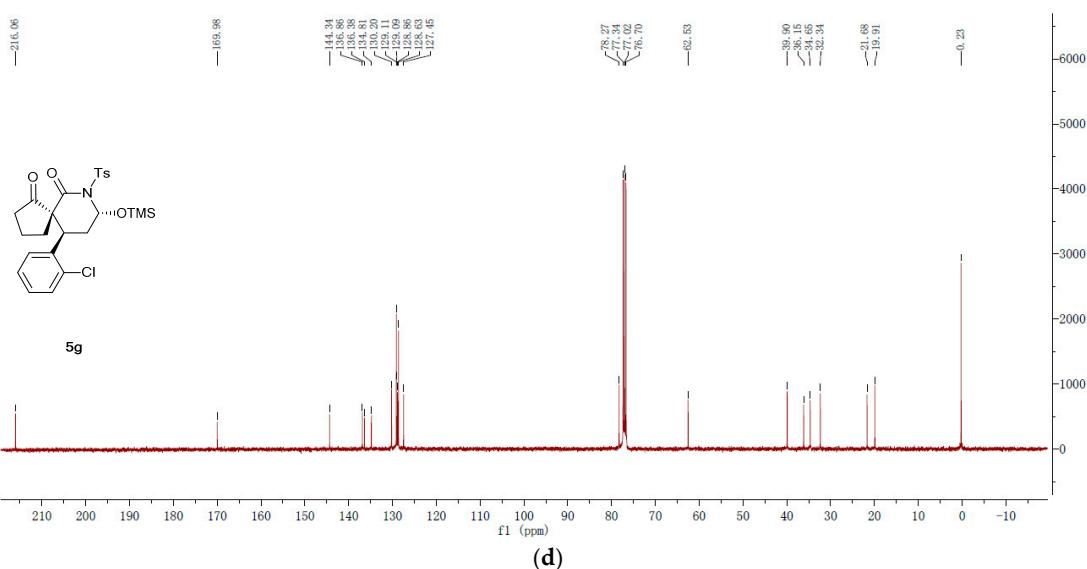
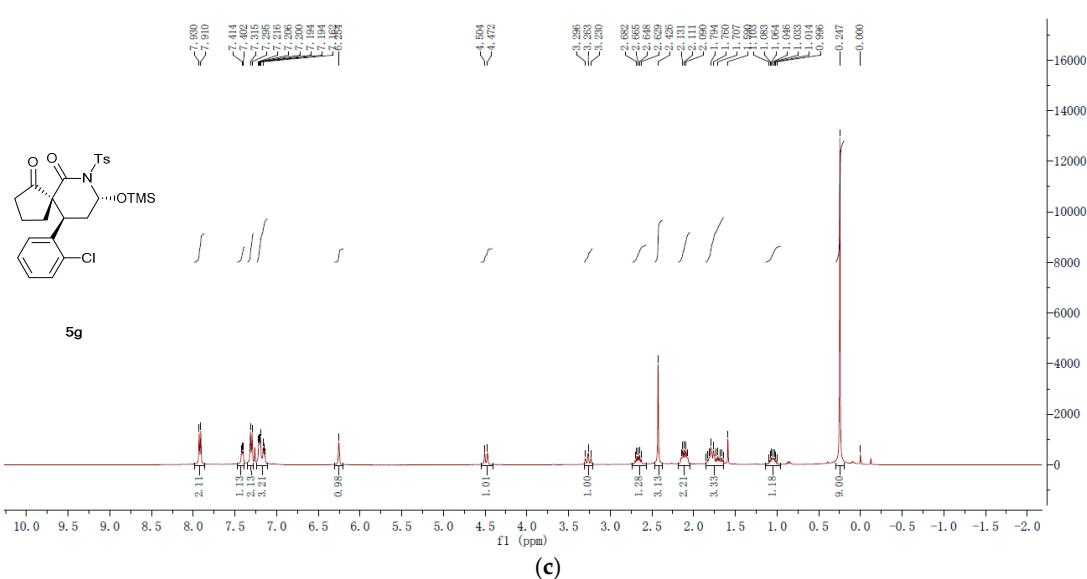
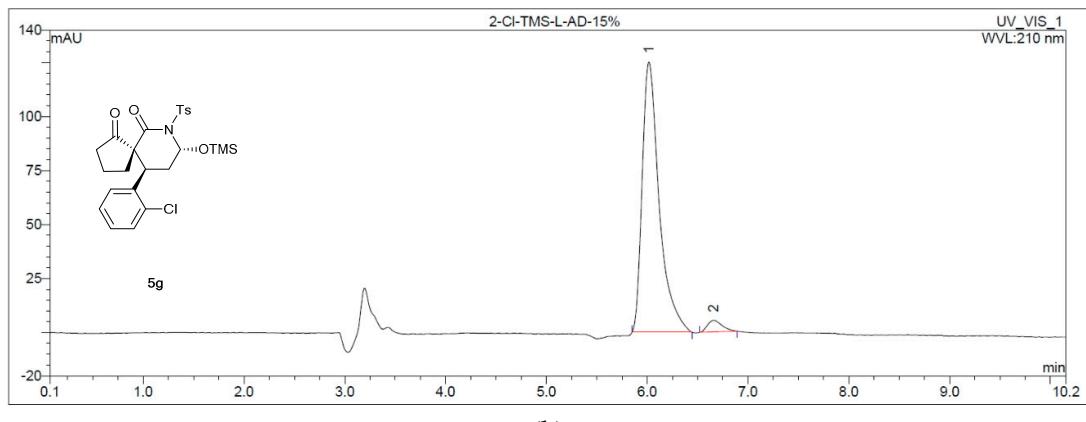
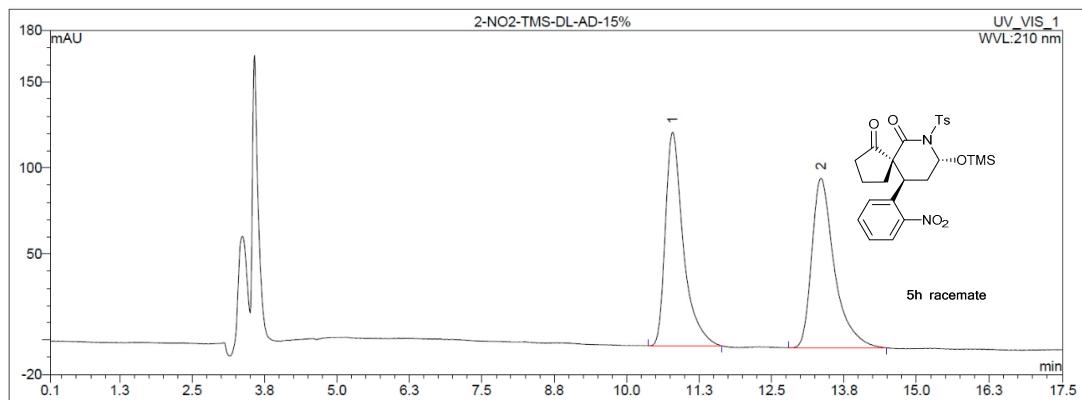


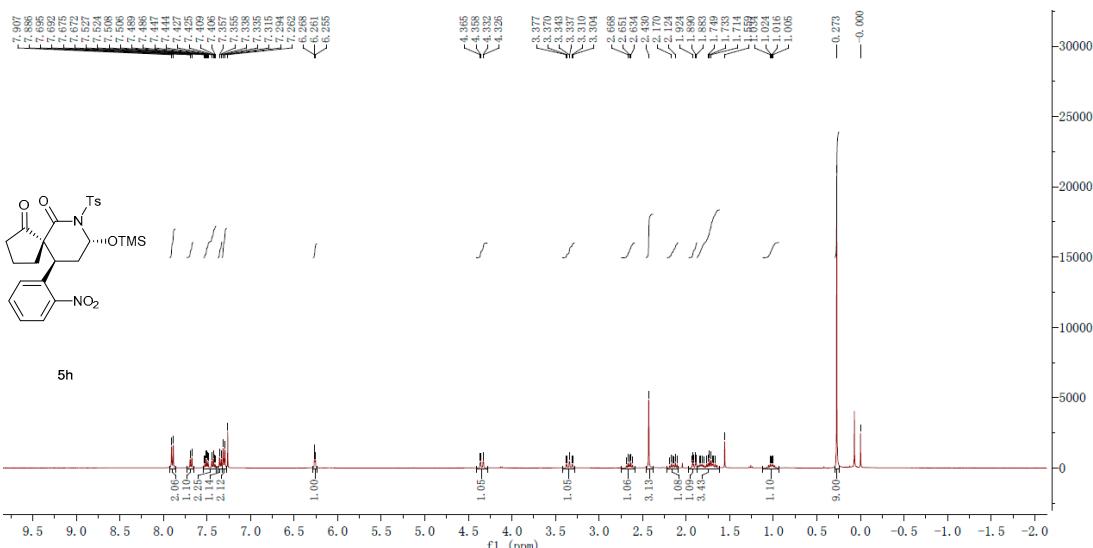
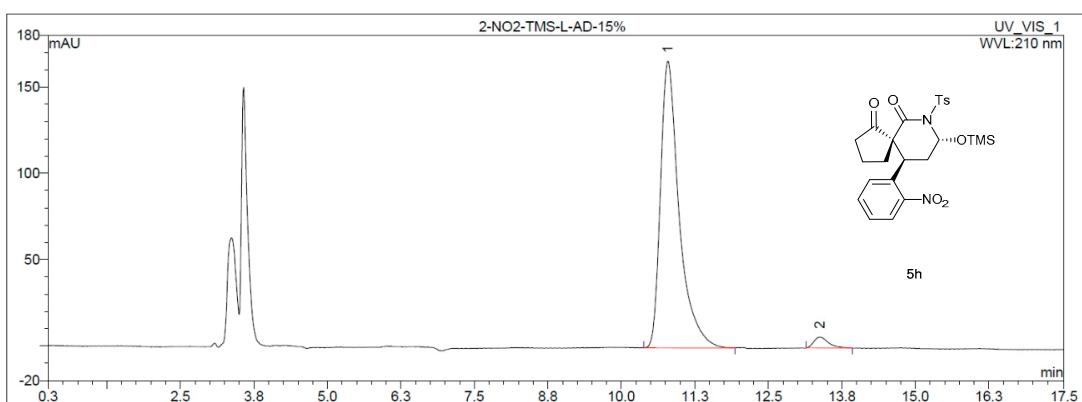
Figure S8. (a) HPLC chromatogram of racemic **5g**; (b) HPLC chromatogram of chiral **5g**; (c) ^1H -NMR spectrum (CDCl_3 , 400 MHz) of **5g**; (d) ^{13}C -NMR spectrum (CDCl_3 , 100 MHz) of **5g**.

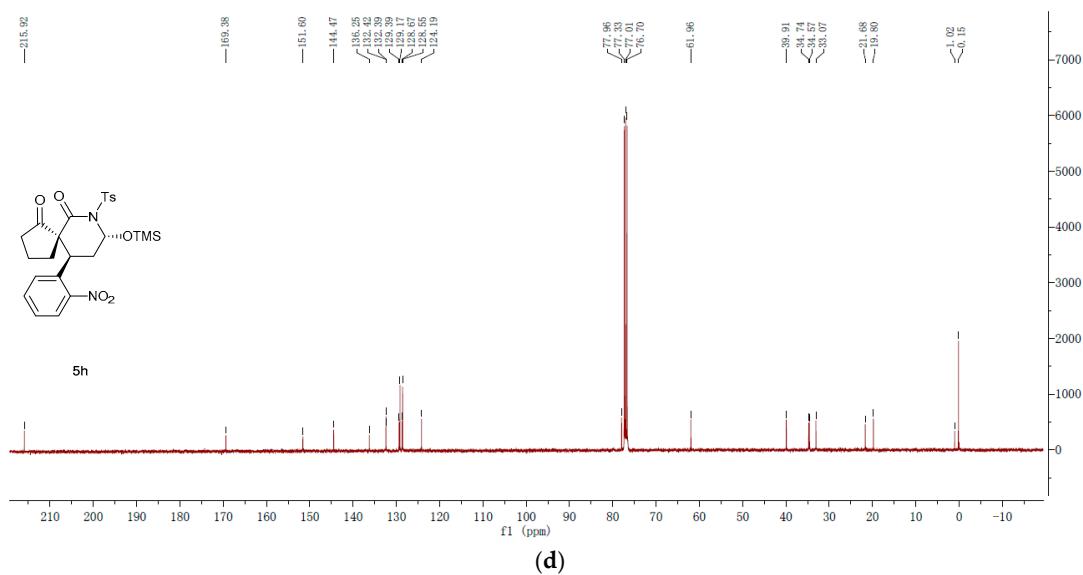
Peak Analysis Report

No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
		min	mAU*min	%	mAU	
1	n.a.	10.79	44.627	49.98	124.083	n.a.
2	n.a.	13.36	44.661	50.02	98.507	n.a.

**Peak Analysis Report**

No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
		min	mAU*min	%	mAU	
1	n.a.	10.79	61.185	96.36	166.004	n.a.
2	n.a.	13.35	2.311	3.64	19.339	n.a.



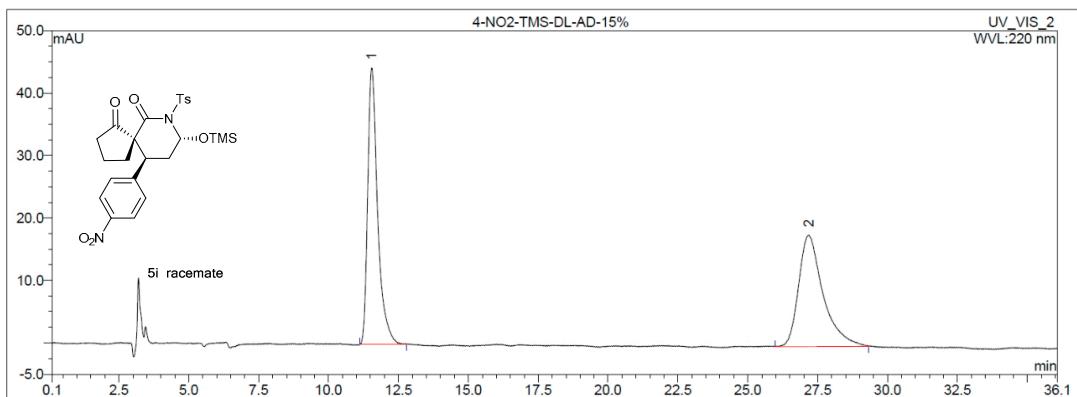


(d)

Figure S9. (a) HPLC chromatogram of racemic **5h**; (b) HPLC chromatogram of chiral **5h**; (c) ¹H-NMR spectrum (CDCl₃, 400 MHz) of **5h**; (d) ¹³C-NMR spectrum (CDCl₃, 100 MHz) of **5h**.

Peak Analysis Report

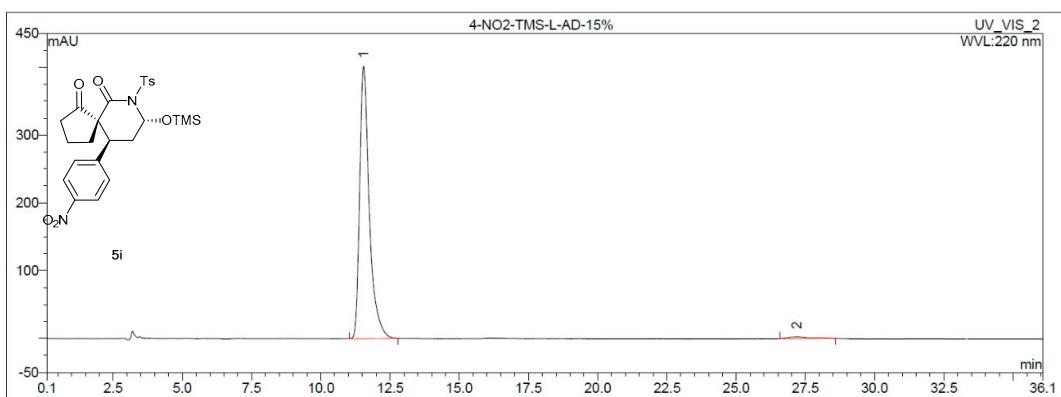
No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
		min	mAU*min	%	mAU	
1	n.a.	11.54	18.236	50.28	44.241	n.a.
2	n.a.	27.19	18.030	49.72	17.854	n.a.



(a)

Peak Analysis Report

No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
		min	mAU*min	%	mAU	
1	n.a.	11.54	162.221	98.65	401.441	n.a.
2	n.a.	27.19	2.219	1.35	2.447	n.a.



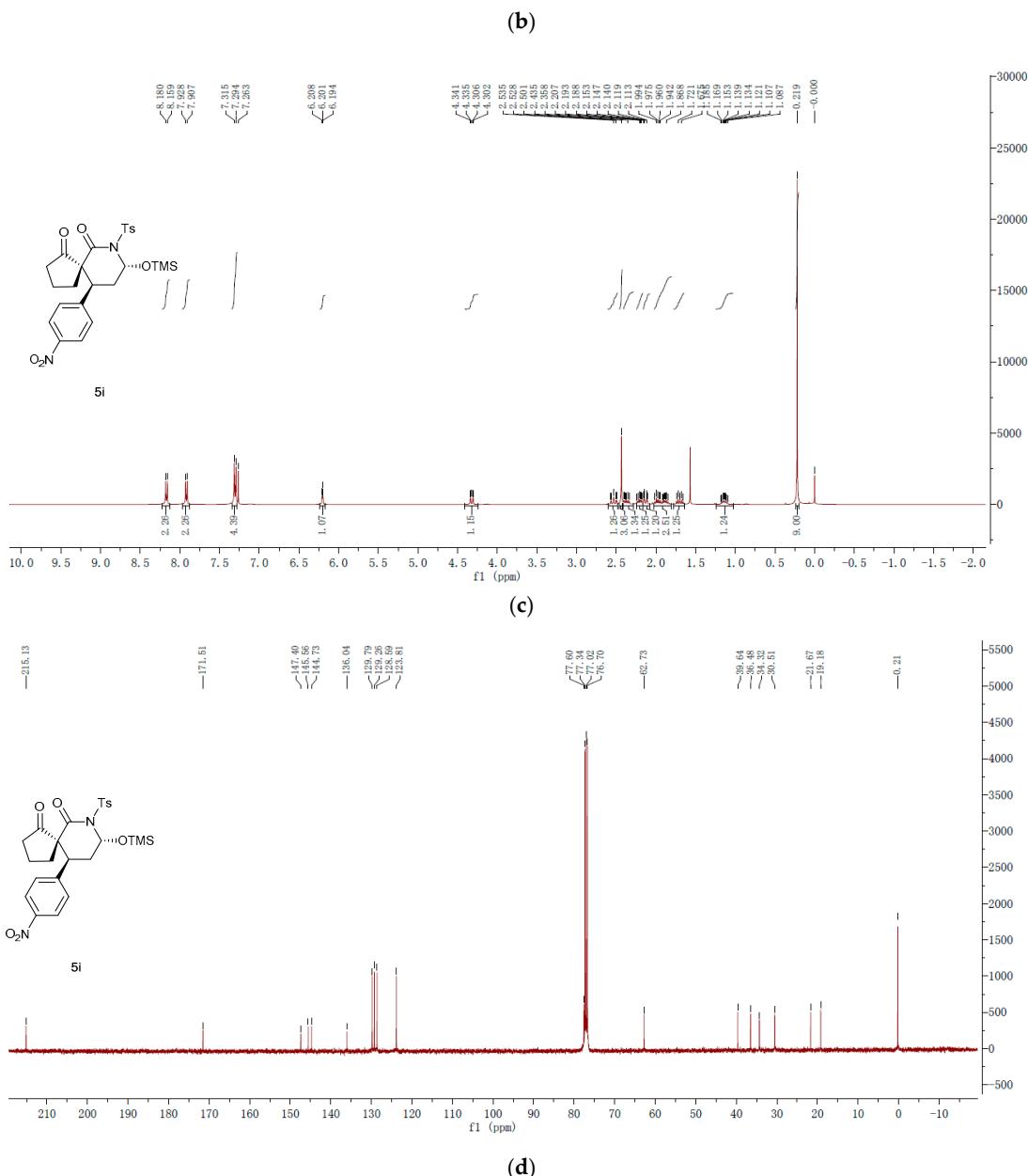
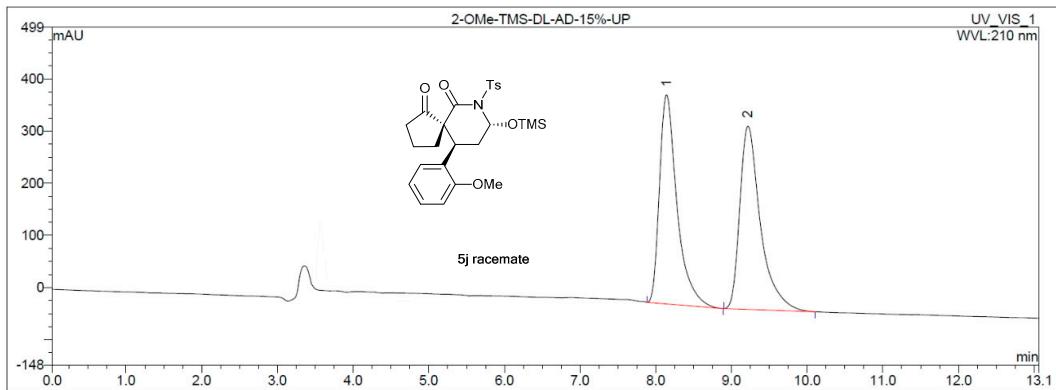


Figure S10. (a) HPLC chromatogram of racemic **5i**; (b) HPLC chromatogram of chiral **5i**; (c) ¹H-NMR spectrum (CDCl_3 , 400 MHz) of **5i**; (d) ¹³C-NMR spectrum (CDCl_3 , 100 MHz) of **5i**.

Peak Analysis Report

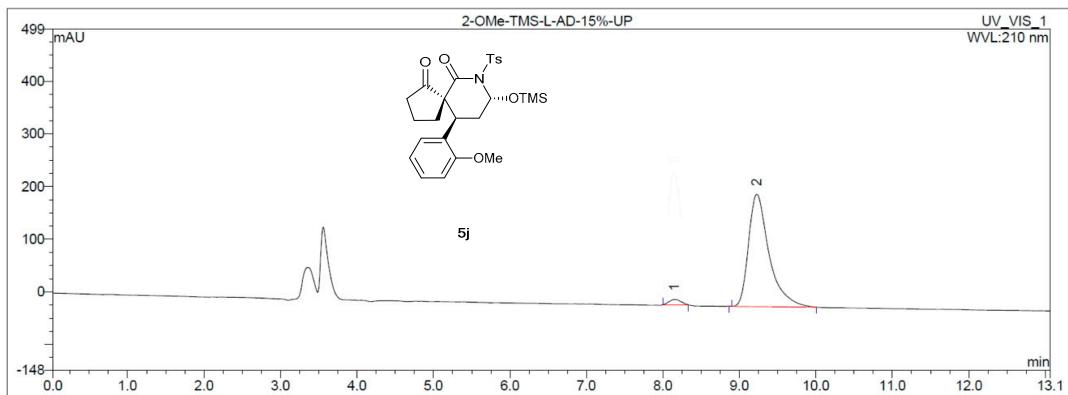
No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
		min	mAU*min	%	mAU	
1	n.a.	8.14	107.521	49.25	401.190	n.a.
2	n.a.	9.22	110.799	50.75	351.608	n.a.



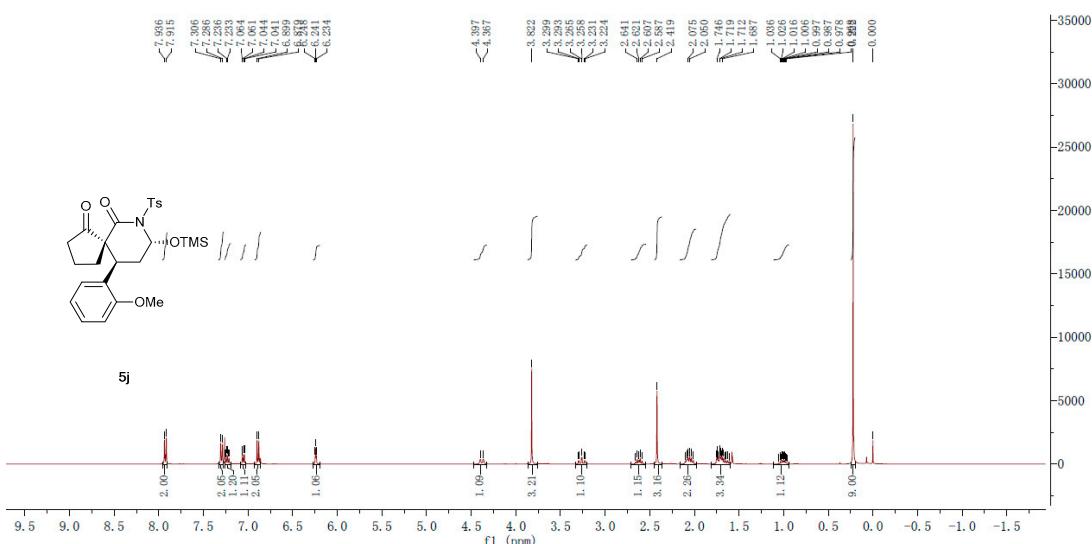
(a)

Peak Analysis Report

No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
		min	mAU*min	%	mAU	
1	n.a.	8.14	3.277	4.69	32,787	n.a.
2	n.a.	9.23	66.523	95.31	213,385	n.a.



(b)



(c)

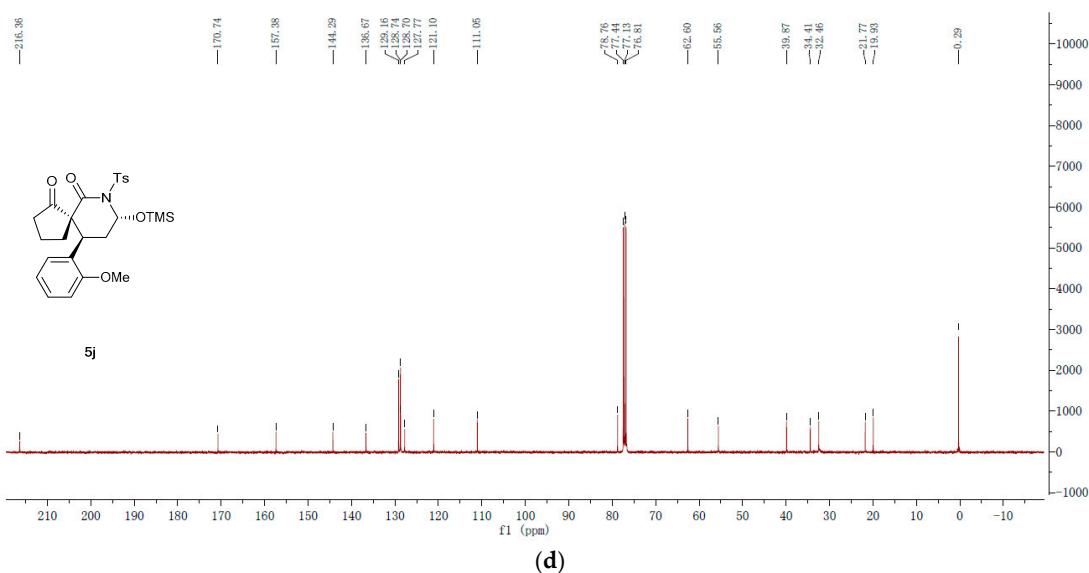
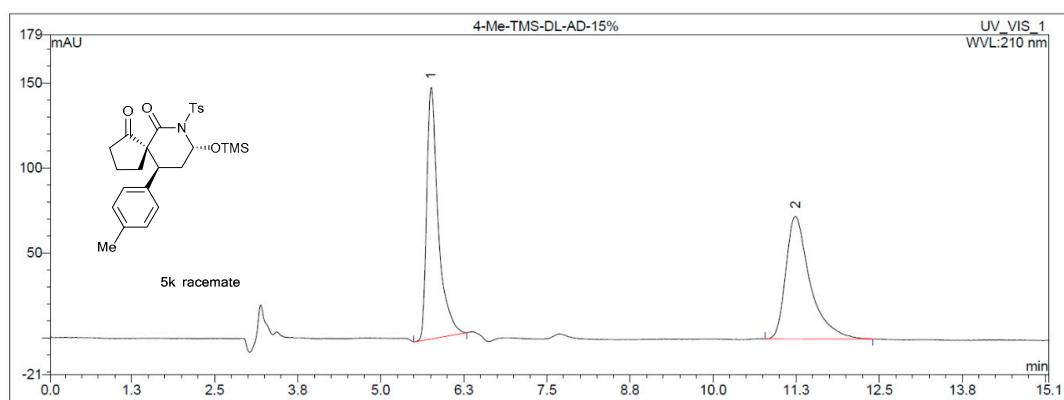


Figure S11. (a) HPLC chromatogram of racemic **5j**; (b) HPLC chromatogram of chiral **5j**; (c) ¹H-NMR spectrum (CDCl_3 , 400 MHz) of **5j**; (d) ¹³C-NMR spectrum (CDCl_3 , 100 MHz) of **5j**.

Peak Analysis Report

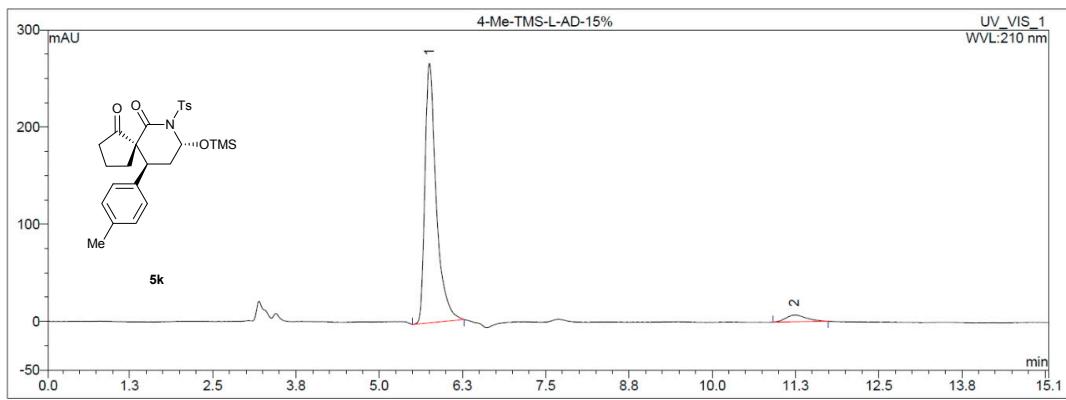
No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
1	n.a.	5.76	29.726	49.27	148.168	n.a.
2	n.a.	11.24	30.608	50.73	72.134	n.a.



(a)

Peak Analysis Report

No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
1	n.a.	5.75	52.582	95.46	266.899	n.a.
2	n.a.	11.23	2.502	4.54	6.954	n.a.



(b)

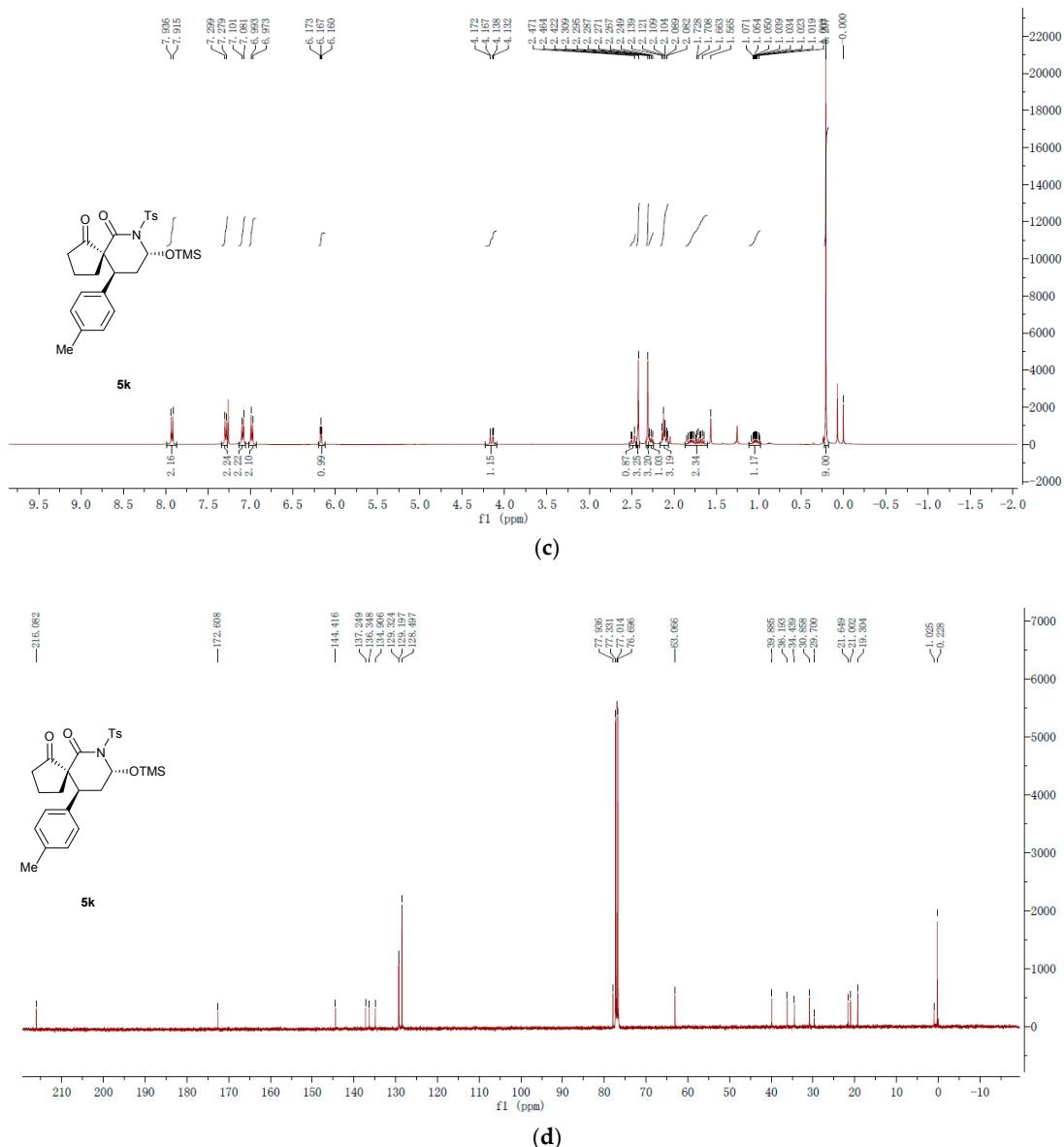
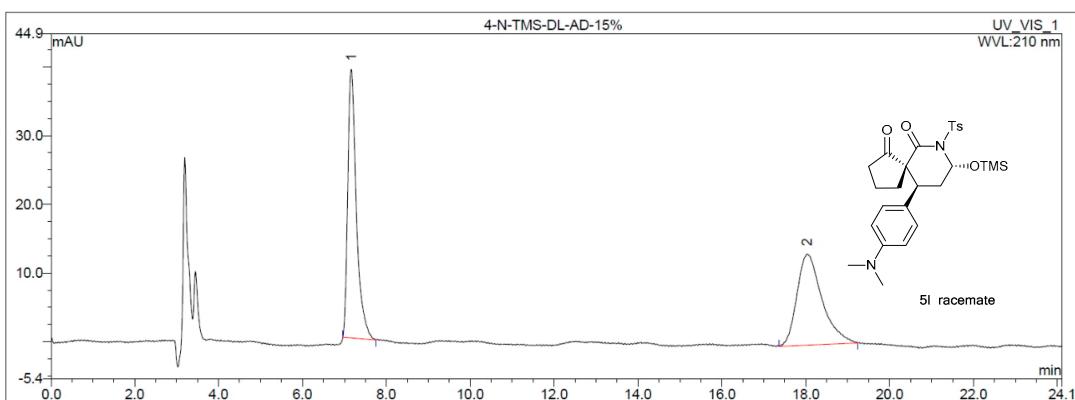


Figure S12. (a) HPLC chromatogram of racemic **5k**; (b) HPLC chromatogram of chiral **5k**; (c) ¹H-NMR spectrum (CDCl₃, 400 MHz) of **5k**; (d) ¹³C-NMR spectrum (CDCl₃, 100 MHz) of **5k**.

Peak Analysis Report

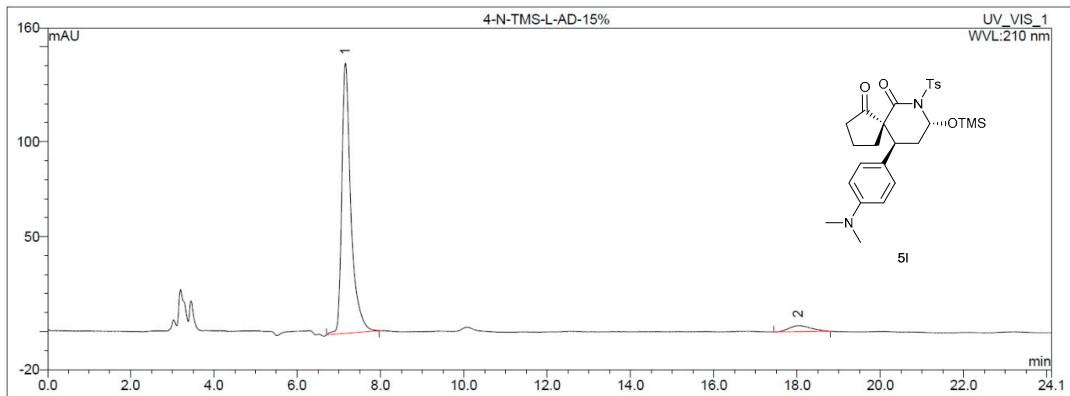
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area %	Height mAU	Amount
1	n.a.	7.17	9.281	50.34	39.096	n.a.
2	n.a.	18.03	9.157	49.66	13.284	n.a.



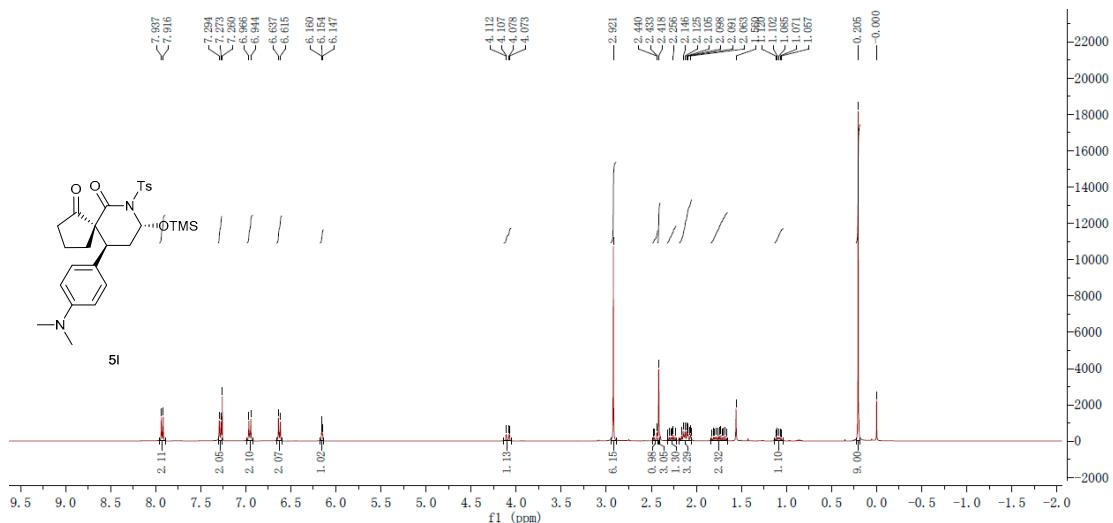
(a)

Peak Analysis Report

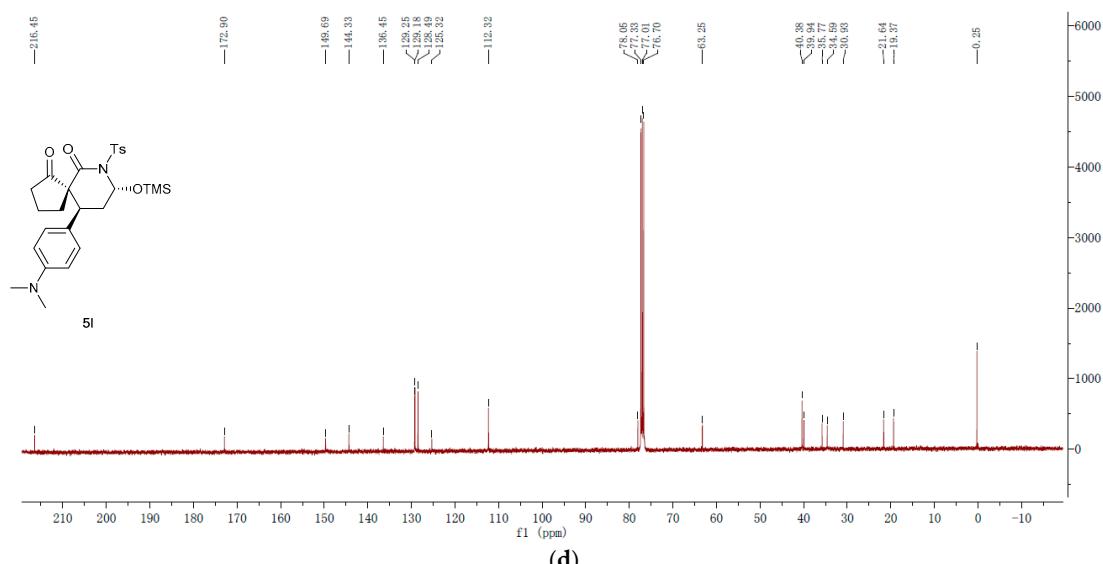
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area %	Height mAU	Amount
1	n.a.	7.16	36.269	94.94	142.330	n.a.
2	n.a.	18.03	1.932	5.06	3.192	n.a.



(b)



(c)

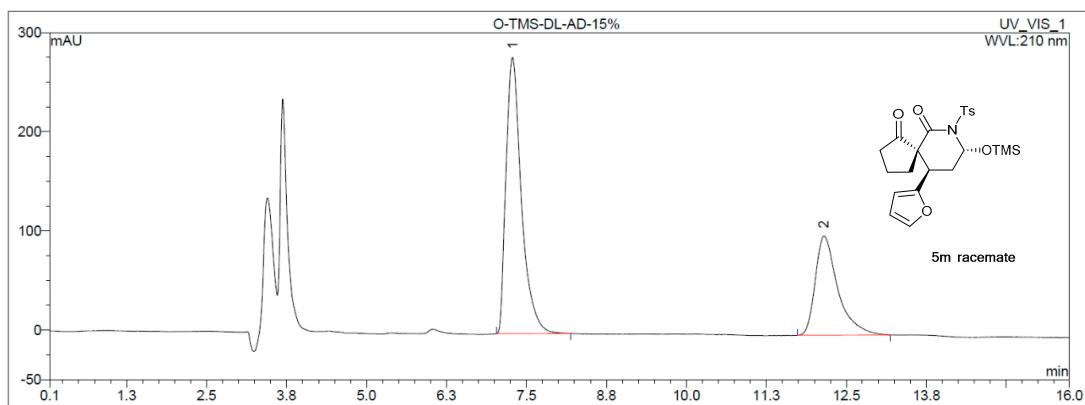


(d)

Figure S13. (a) HPLC chromatogram of racemic **5l**; (b) HPLC chromatogram of chiral **5l**; (c) ¹H-NMR spectrum (CDCl_3 , 400 MHz) of **5l**; (d) ¹³C-NMR spectrum (CDCl_3 , 100 MHz) of **5l**.

Peak Analysis Report

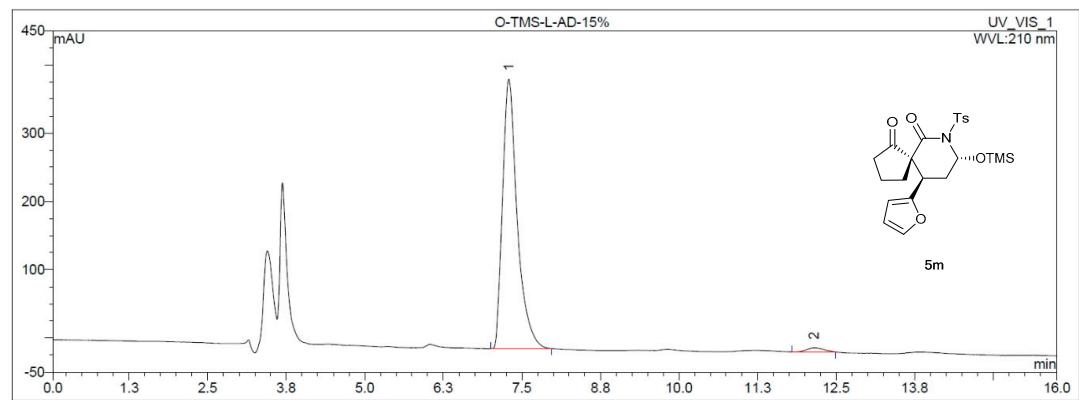
No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
1	n.a.	7.28	42.031	50.65	209.085	n.a.
2	n.a.	12.15	40.948	49.35	99.987	n.a.



(a)

Peak Analysis Report

No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
1	n.a.	7.29	106.729	98.20	394.759	n.a.
2	n.a.	12.15	1.951	1.80	6.098	n.a.



(b)

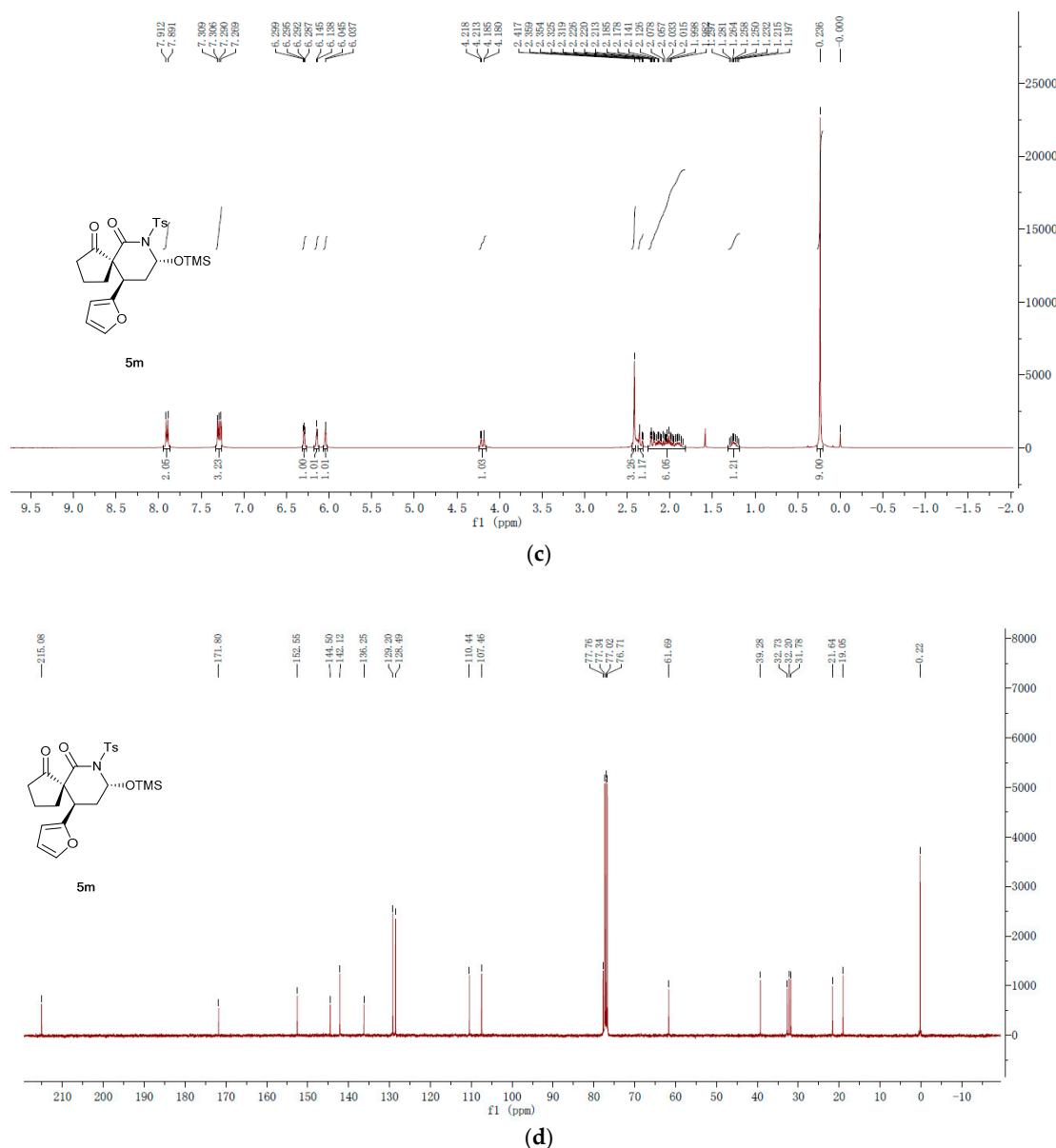
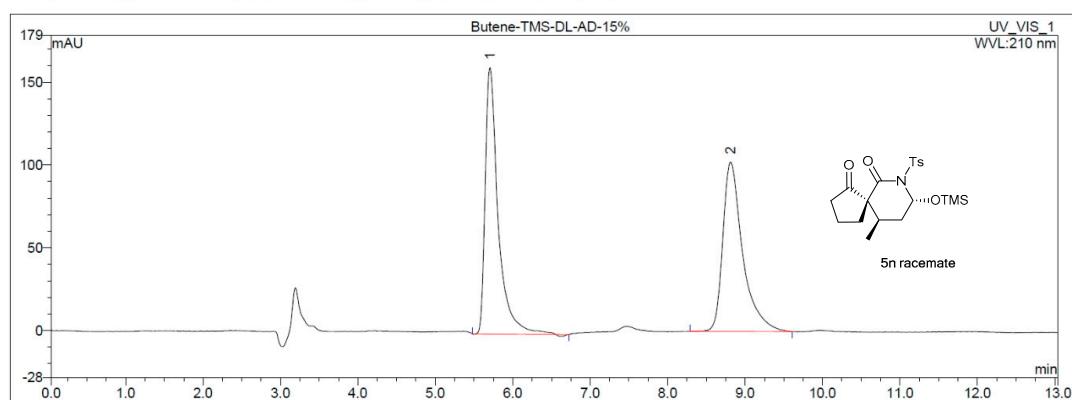


Figure S14. (a) HPLC chromatogram of racemic **5m**; (b) HPLC chromatogram of chiral **5m**; (c) ¹H-NMR spectrum (CDCl₃, 400 MHz) of **5m**; (d) ¹³C-NMR spectrum (CDCl₃, 100 MHz) of **5m**.

Peak Analysis Report

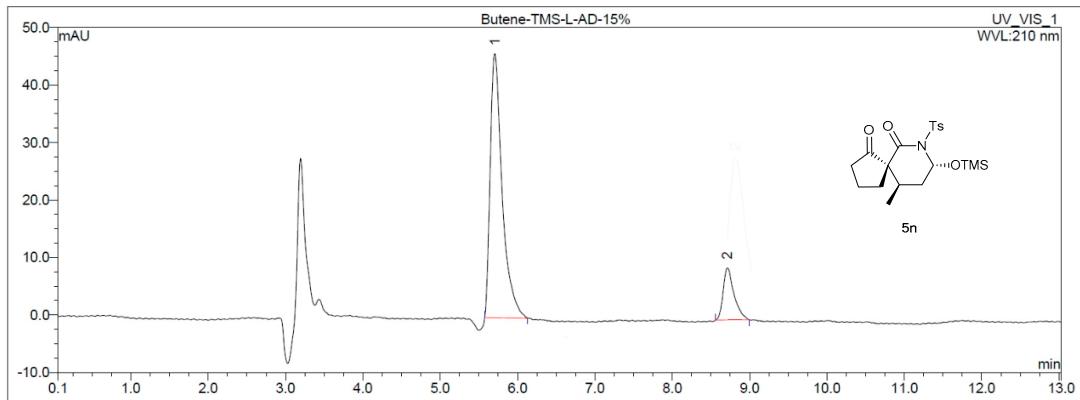
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area %	Height mAU	Amount
1	n.a.	5.71	31.064	50.51	161.036	n.a.
2	n.a.	8.82	30.440	49.49	102.262	n.a.



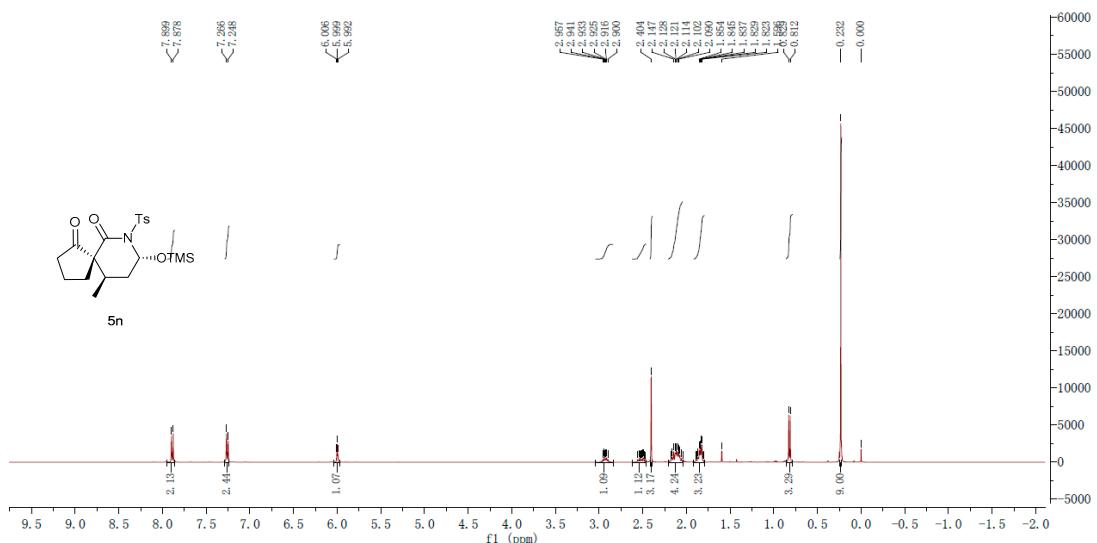
(a)

Peak Analysis Report

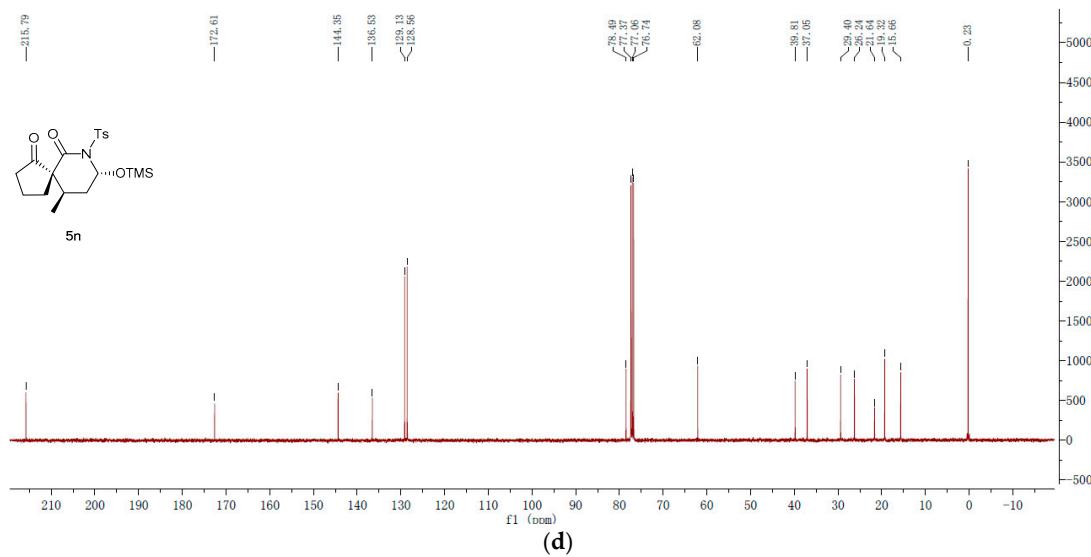
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area %	Height mAU	Amount
1	n.a.	5.71	8.255	75.04	46.000	n.a.
2	n.a.	8.82	2.746	24.96	16.414	n.a.



(b)



(c)

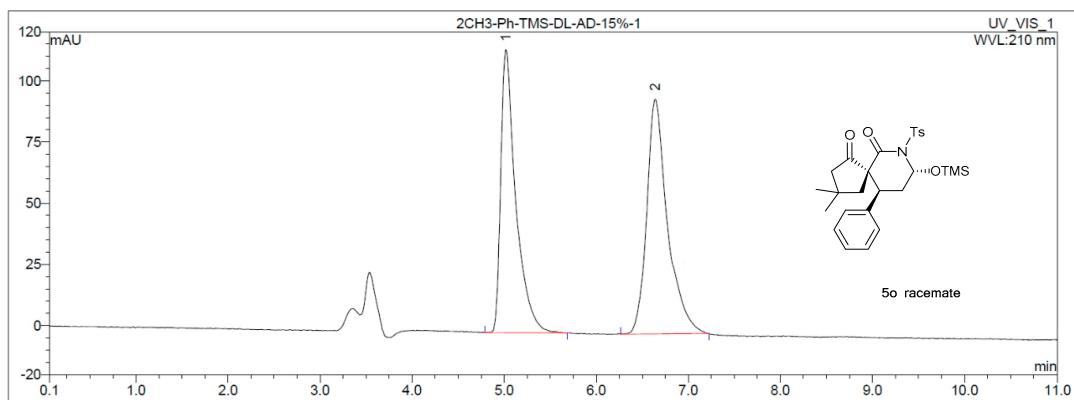


(d)

Figure S15. (a) HPLC chromatogram of racemic **5n**; (b) HPLC chromatogram of chiral **5n**; (c) ¹H-NMR spectrum (CDCl_3 , 400 MHz) of **5n**; (d) ¹³C-NMR spectrum (CDCl_3 , 100 MHz) of **5n**.

Peak Analysis Report

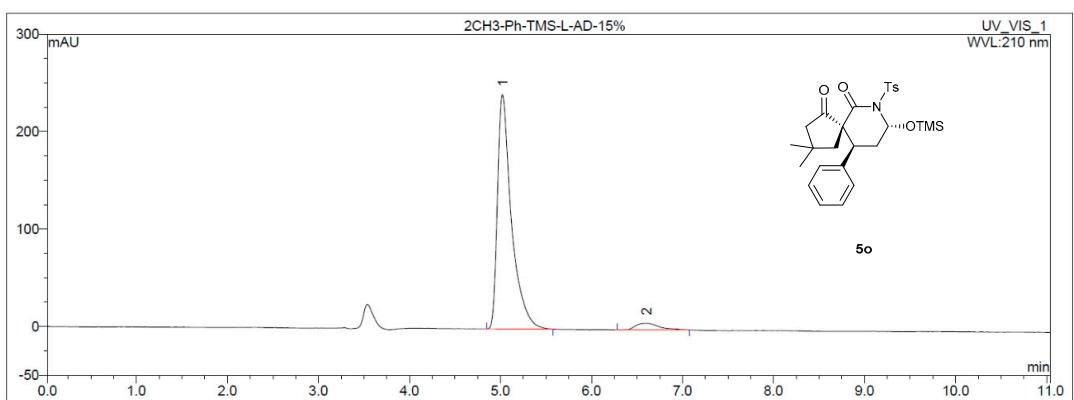
No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
1	n.a.	5.02	21.856	49.12	115.710	n.a.
2	n.a.	6.64	22.636	50.88	87.250	n.a.



(a)

Peak Analysis Report

No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
1	n.a.	5.03	42.783	95.35	240.558	n.a.
2	n.a.	6.61	2.086	4.65	6.901	n.a.



(b)

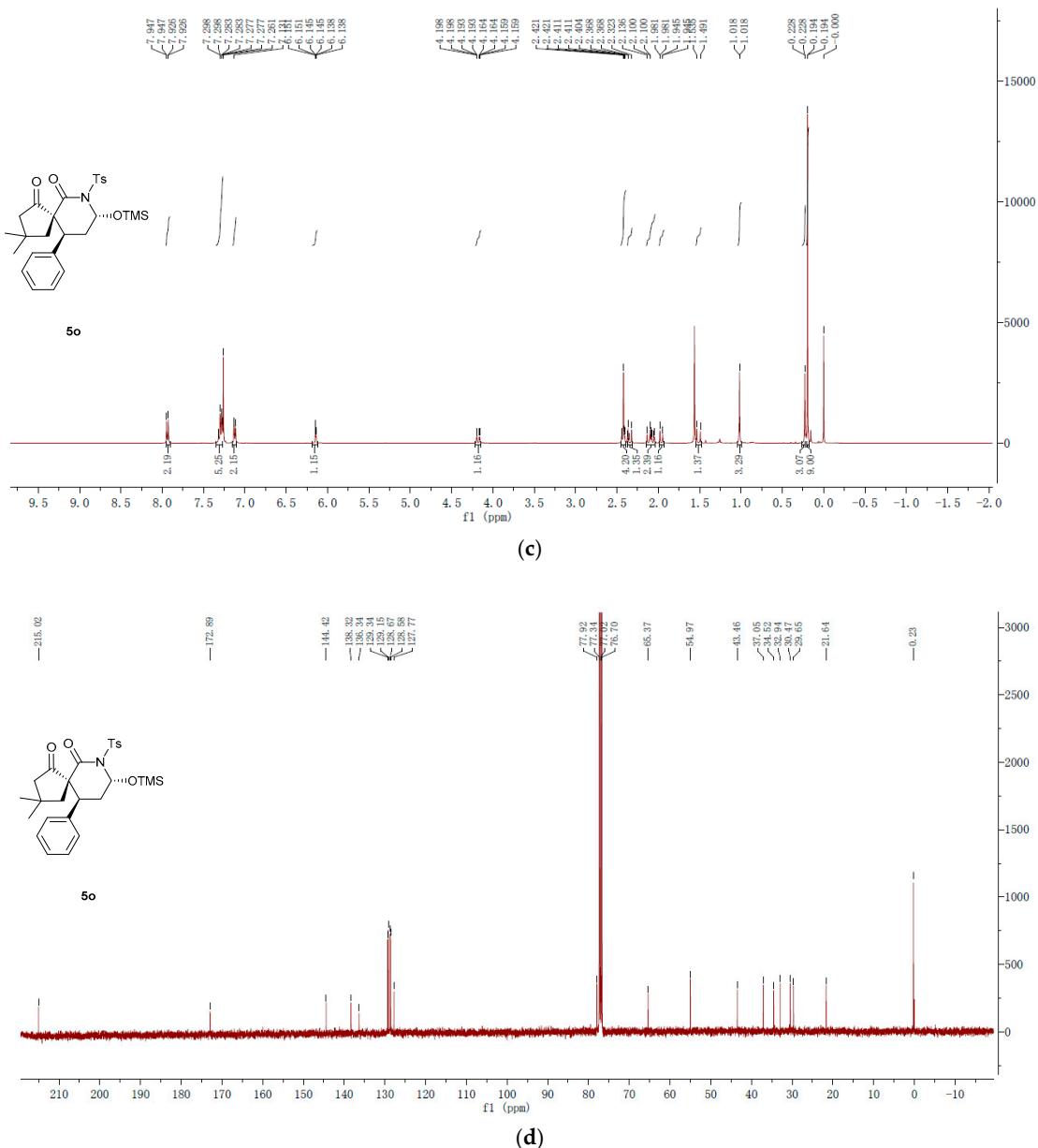
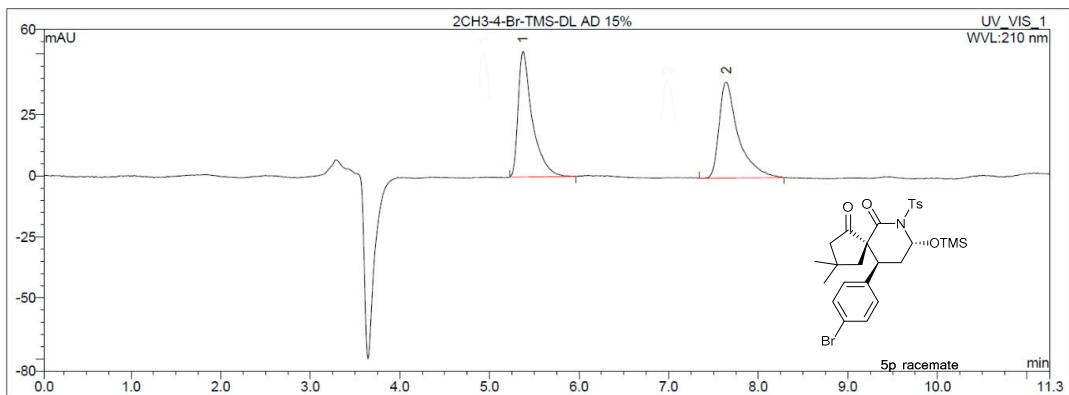


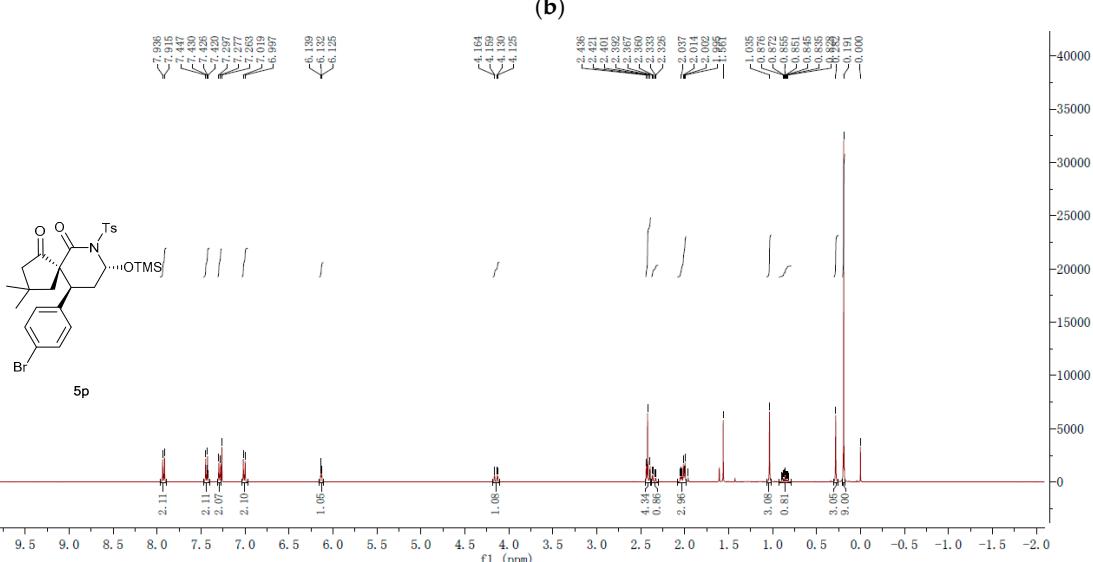
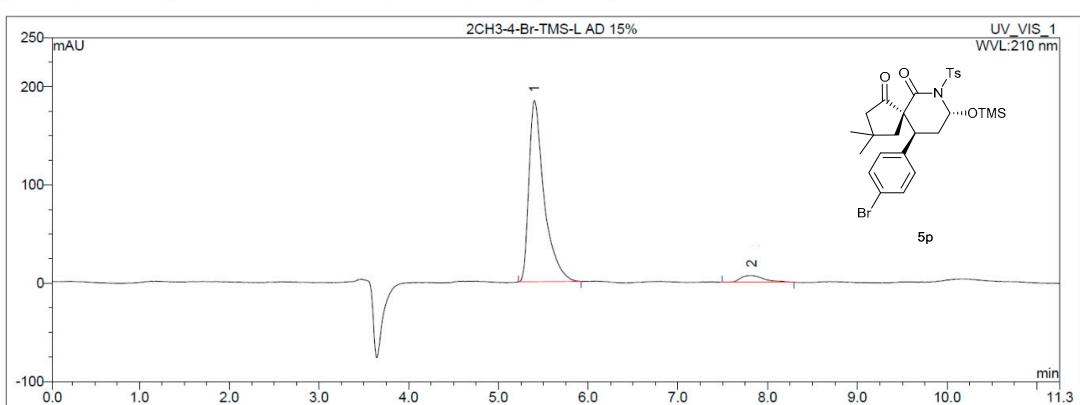
Figure S16. (a) HPLC chromatogram of racemic **5o**; (b) HPLC chromatogram of chiral **5o**; (c) ¹H-NMR spectrum (CDCl₃, 400 MHz) of **5o**; (d) ¹³C-NMR spectrum (CDCl₃, 100 MHz) of **5o**.

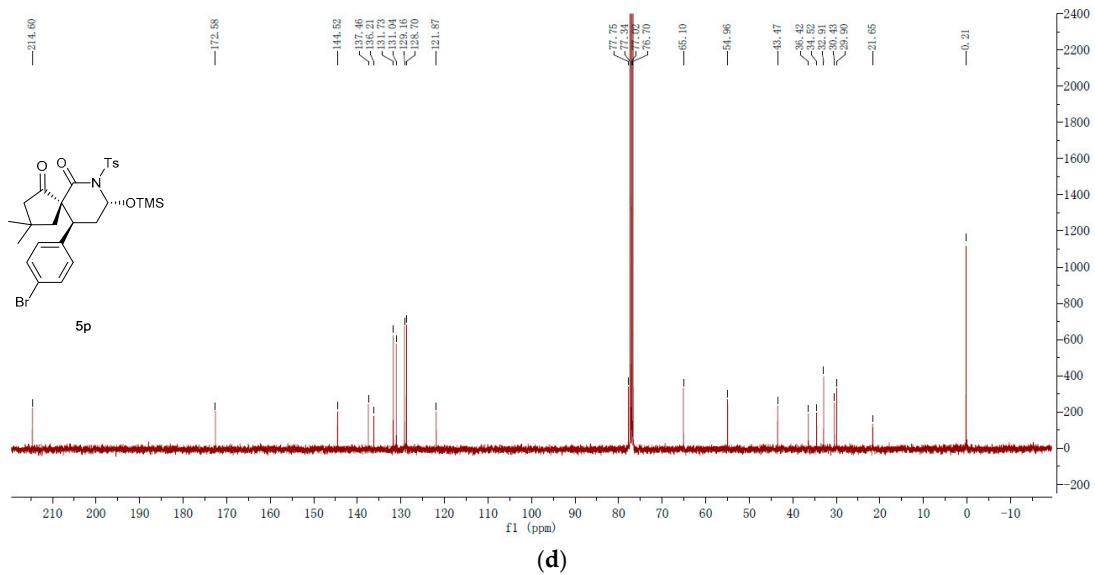
Peak Analysis Report

No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
		min	mAU·min	%	mAU	
1	n.a.	5.40	9.456	49.21	51.561	n.a.
2	n.a.	7.89	9.758	50.79	39.391	n.a.

**Peak Analysis Report**

No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
		min	mAU·min	%	mAU	
1	n.a.	5.40	36.065	95.39	184.558	n.a.
2	n.a.	7.86	1.742	4.61	9.974	n.a.



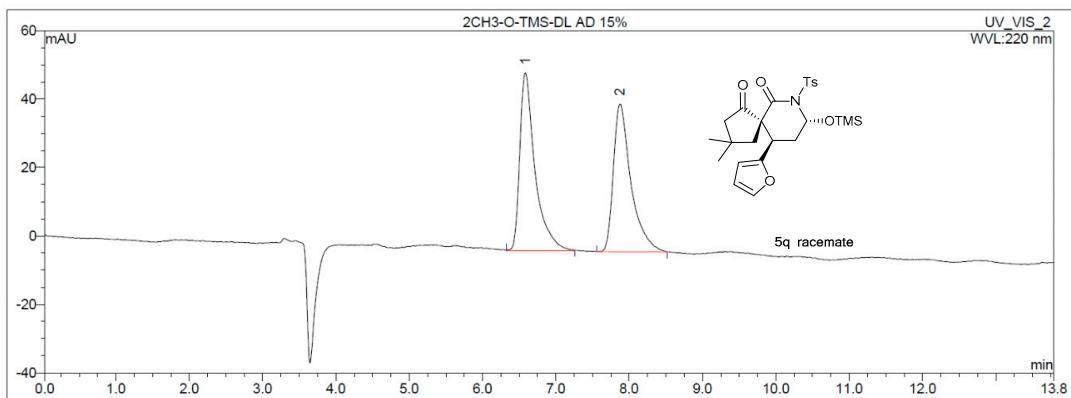


(d)

Figure S17. (a) HPLC chromatogram of racemic **5p**; (b) HPLC chromatogram of chiral **5p**; (c) ¹H-NMR spectrum (CDCl₃, 400 MHz) of **5p**; (d) ¹³C-NMR spectrum (CDCl₃, 100 MHz) of **5p**.

Peak Analysis Report

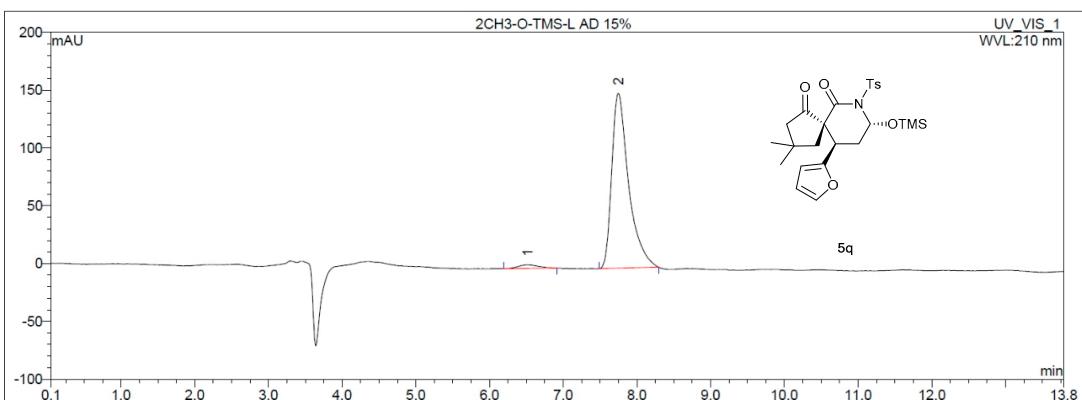
No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
1	n.a.	6.58	12.413	50.86	51.907	n.a.
2	n.a.	7.88	11.993	49.14	43.213	n.a.



(a)

Peak Analysis Report

No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
1	n.a.	6.50	1.083	2.63	7.489	n.a.
2	n.a.	7.75	40.104	97.37	151.249	n.a.



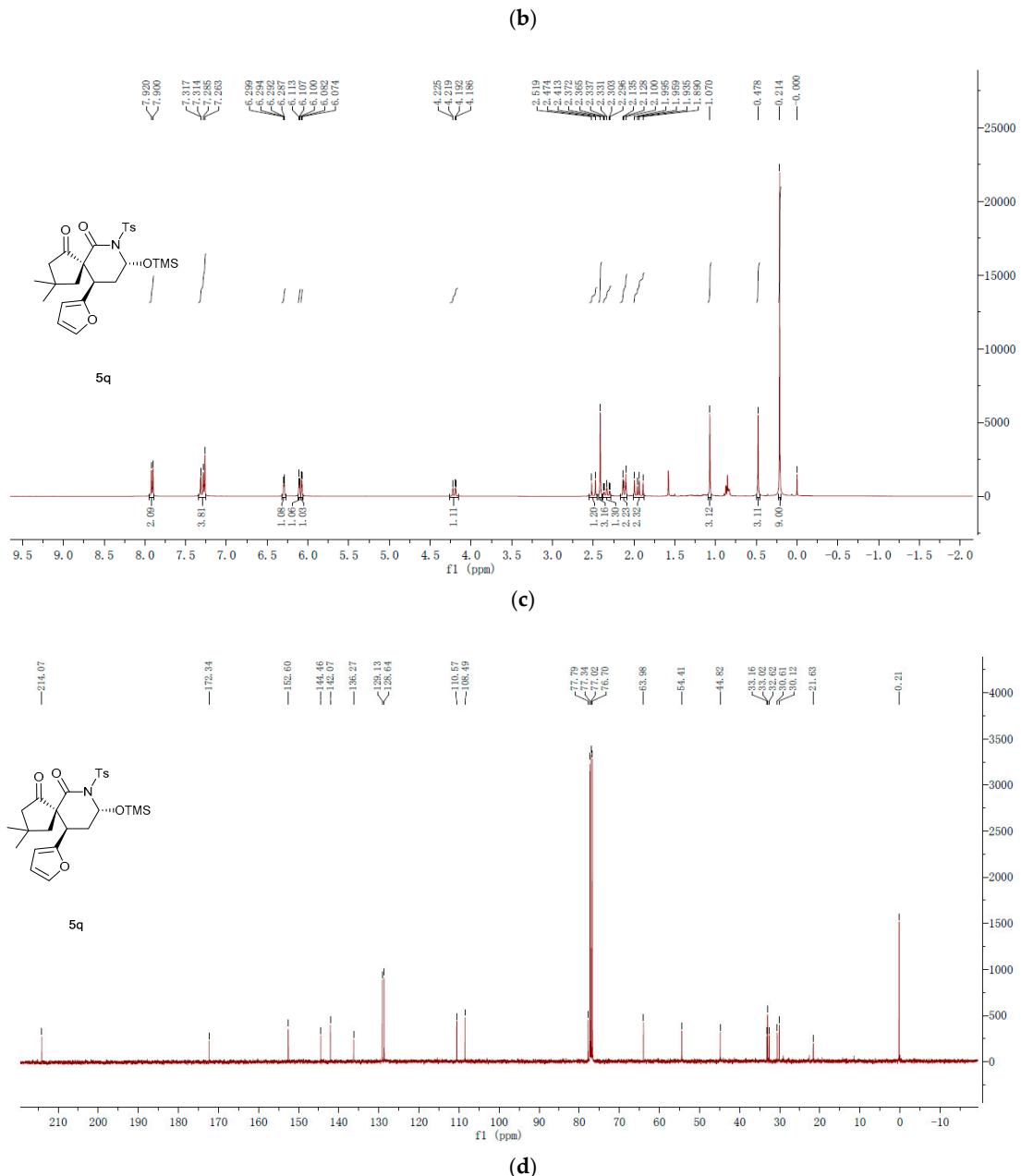
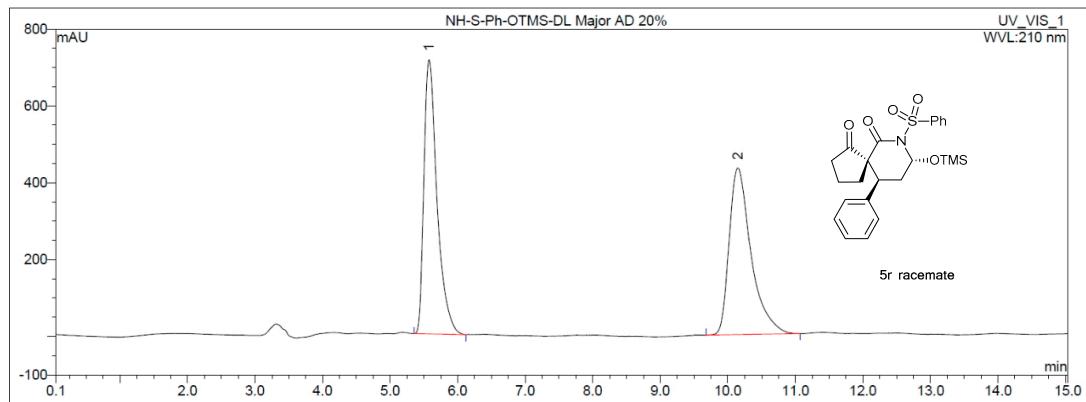


Figure S18. (a) HPLC chromatogram of racemic **5q**; (b) HPLC chromatogram of chiral **5q**; (c) ^1H -NMR spectrum (CDCl_3 , 400 MHz) of **5q**; (d) ^{13}C -NMR spectrum (CDCl_3 , 100 MHz) of **5q**.

Peak Analysis Report

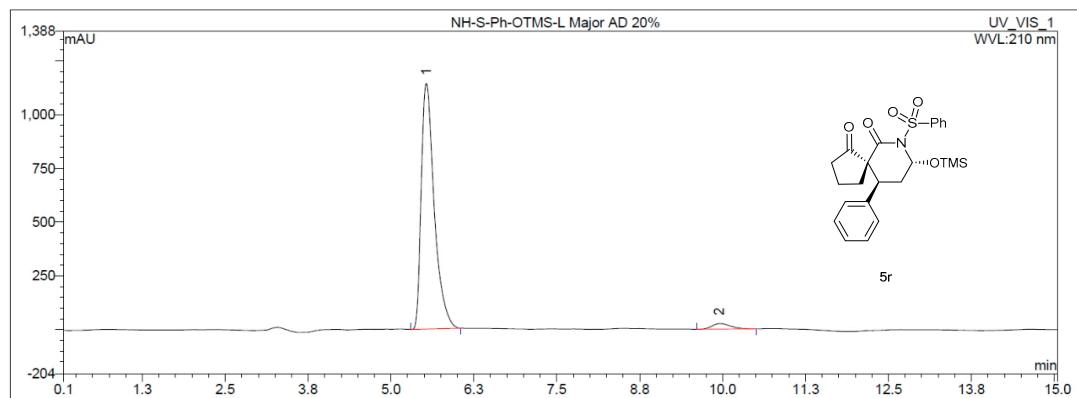
No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
		min	mAU*min	%	mAU	
1	n.a.	5.58	160.838	49.66	714.518	n.a.
2	n.a.	10.15	163.036	50.34	433.719	n.a.



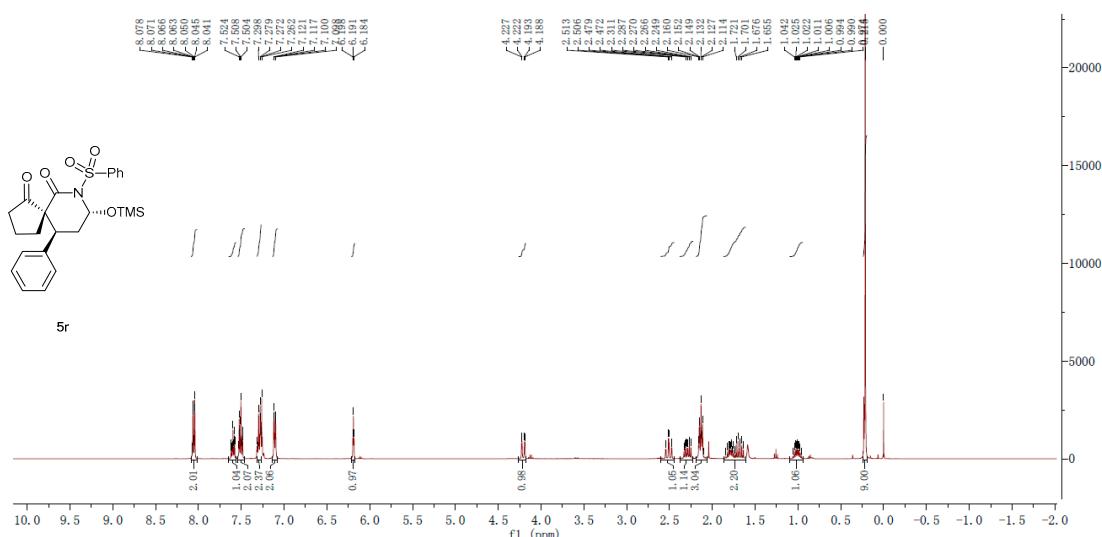
(a)

Peak Analysis Report

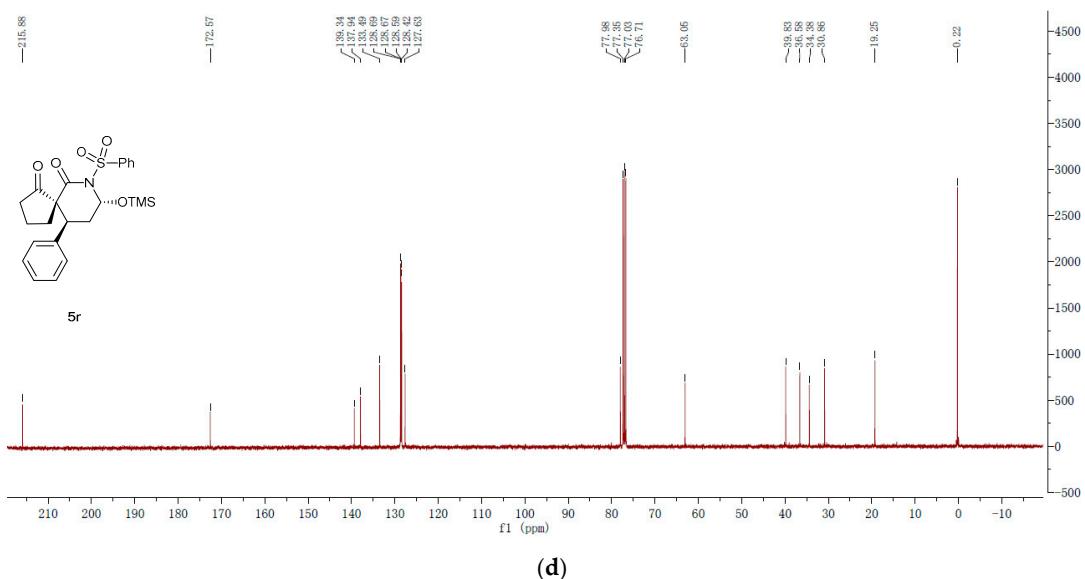
No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
		min	mAU*min	%	mAU	
1	n.a.	5.53	259.250	96.89	1141.990	n.a.
2	n.a.	9.95	8.311	3.11	25.827	n.a.



(b)



(c)

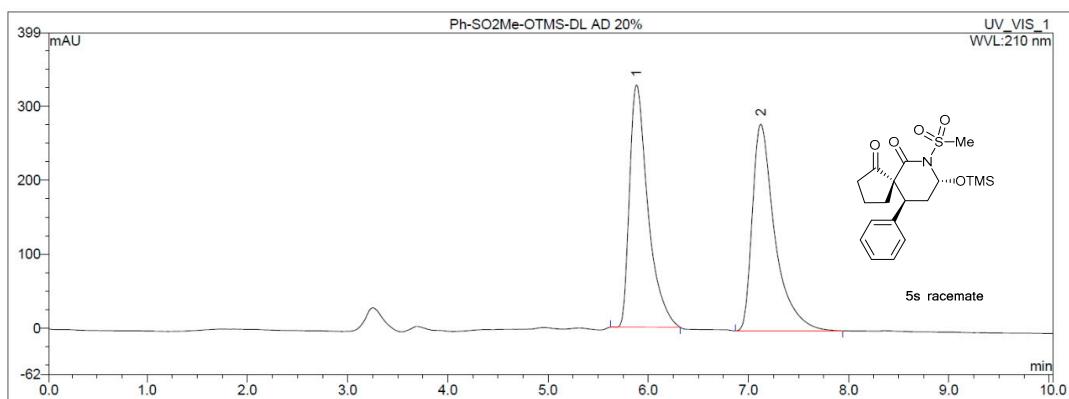


(d)

Figure S19. (a) HPLC chromatogram of racemic **5r**; (b) HPLC chromatogram of chiral **5r**; (c) ^1H -NMR spectrum (CDCl_3 , 400 MHz) of **5r**; (d) ^{13}C -NMR spectrum (CDCl_3 , 100 MHz) of **5r**.

Peak Analysis Report

No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area %	Height mAU	Amount
1	n.a.	5.88	69.662	48.92	326.868	n.a.
2	n.a.	7.13	72.747	51.08	279.134	n.a.



(a)

Peak Analysis Report

No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
		min	mAU*min	%	mAU	
1	n.a.	5.90	132.947	97.44	564.053	n.a.
2	n.a.	7.17	3.486	2.56	10.534	n.a.

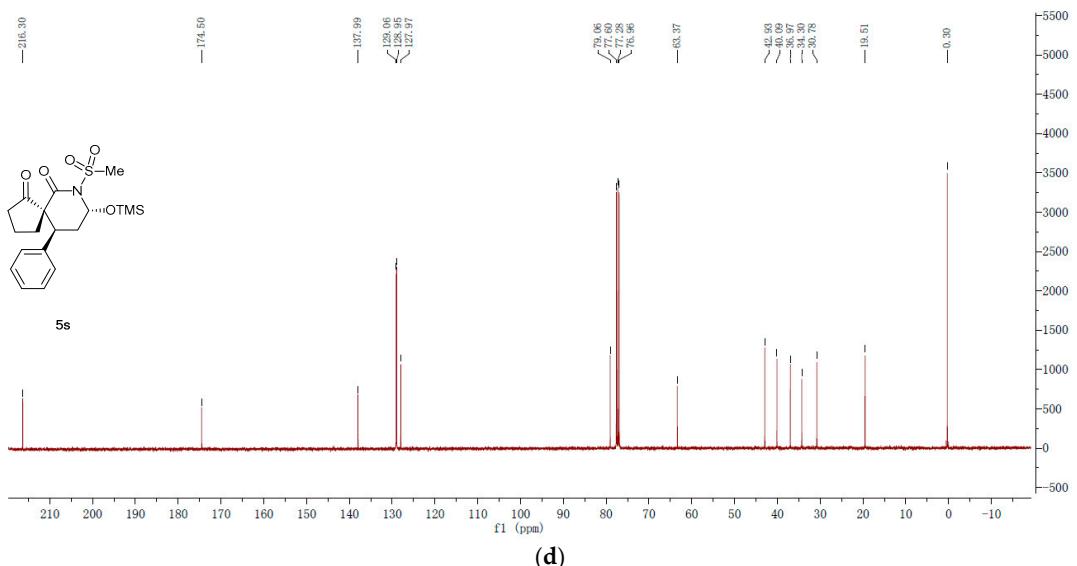
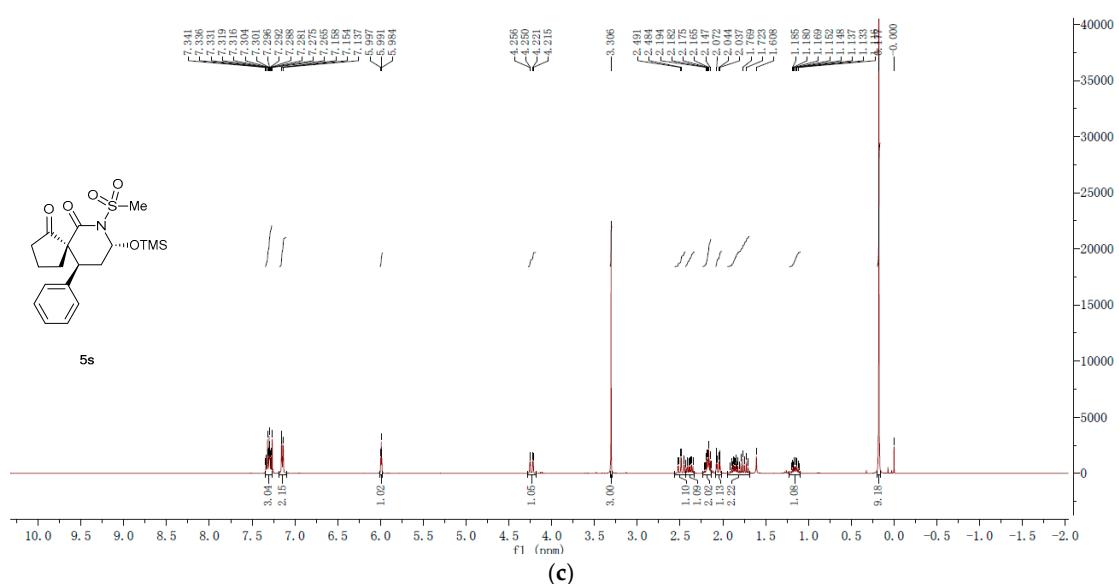
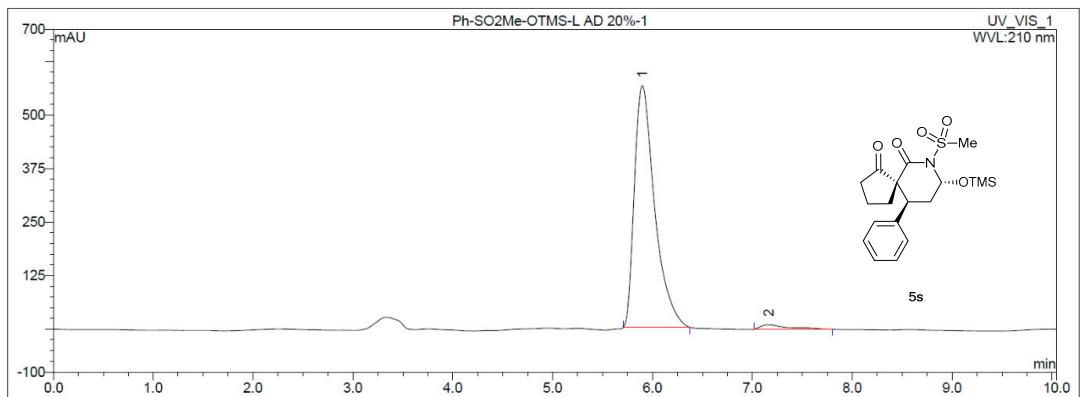
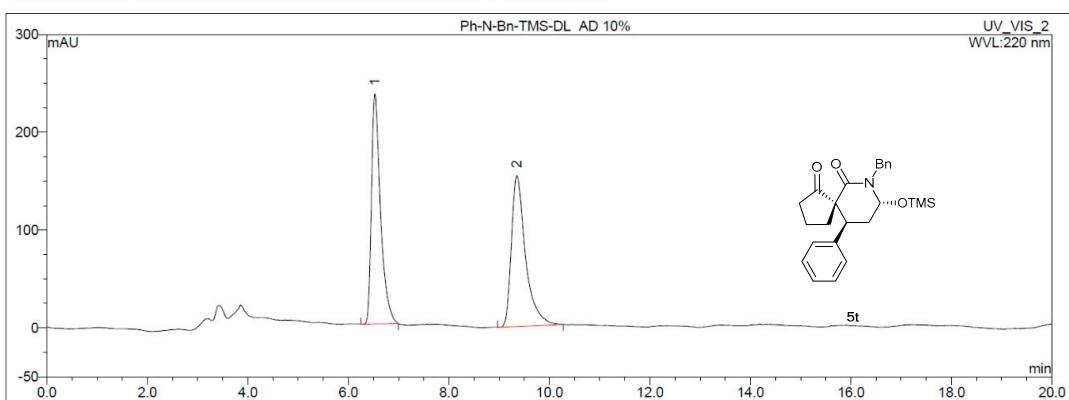


Figure S20. (a) HPLC chromatogram of racemic **5s**; (b) HPLC chromatogram of chiral **5s**; (c) $^1\text{H-NMR}$ spectrum (CDCl_3 , 400 MHz) of **5s**; (d) $^{13}\text{C-NMR}$ spectrum (CDCl_3 , 100 MHz) of **5s**.

Peak Analysis Report

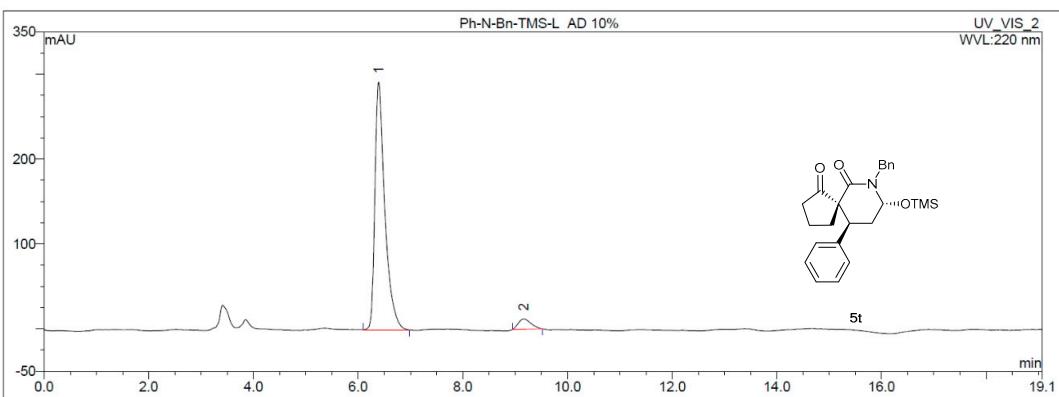
No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
		min	mAU·min	%	mAU	
1	n.a.	6.53	49.183	49.53	235.425	n.a.
2	n.a.	9.35	50.114	50.47	154.154	n.a.



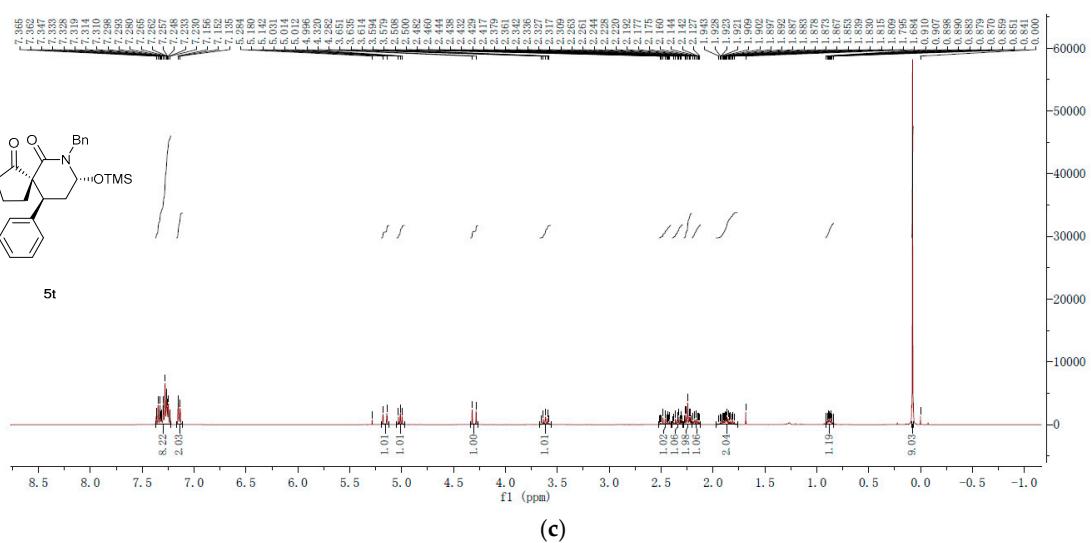
(a)

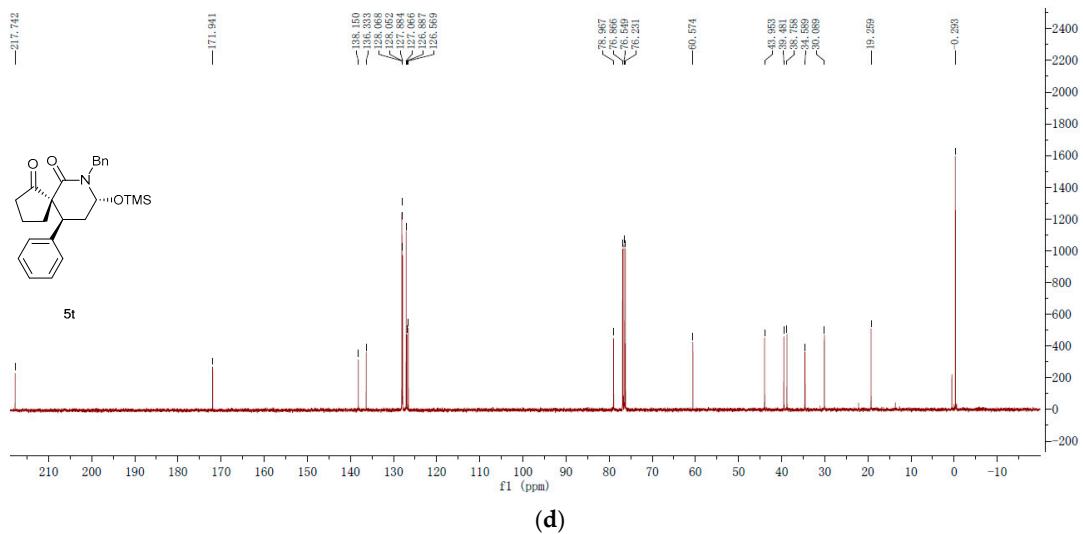
Peak Analysis Report

No.	Peak Name	Ret. Time (detected)	Area	Rel. Area	Height	Amount
		min	mAU·min	%	mAU	
1	n.a.	6.39	64.507	94.92	292.006	n.a.
2	n.a.	9.17	3.453	5.08	20.971	n.a.



(b)



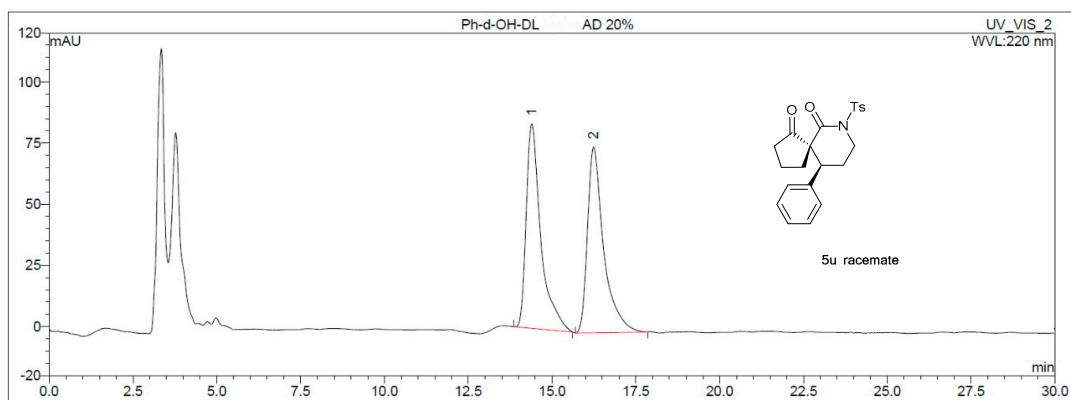


(d)

Figure S21. (a) HPLC chromatogram of racemic **5t**; (b) HPLC chromatogram of chiral **5t**; (c) ¹H-NMR spectrum (CDCl_3 , 400 MHz) of **5t**; (d) ¹³C-NMR spectrum (CDCl_3 , 100 MHz) of **5t**.

Peak Analysis Report

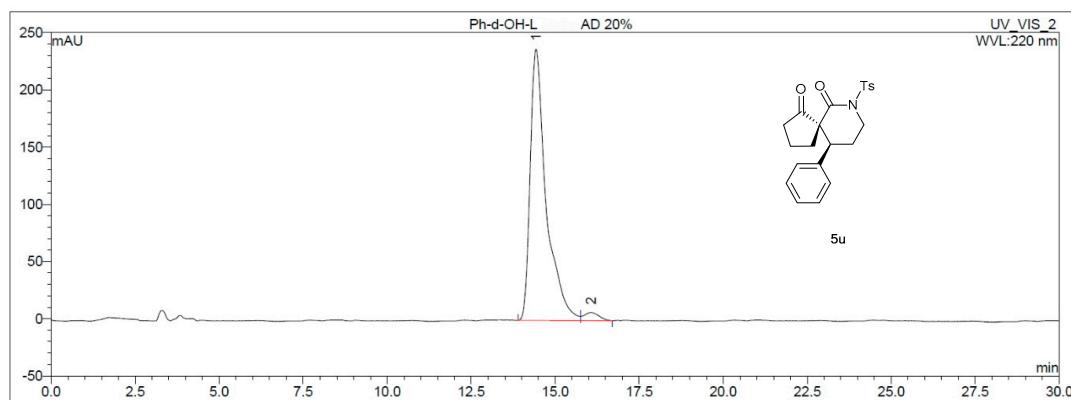
No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
1	n.a.	14.39	42.188	49.79	83.583	n.a.
2	n.a.	16.23	42.537	50.21	75.880	n.a.



(a)

Peak Analysis Report

No.	Peak Name	Ret.Time (detected)	Area	Rel.Area	Height	Amount
1	n.a.	14.43	140.816	97.49	237.120	n.a.
2	n.a.	16.23	3.628	2.51	7.103	n.a.



(b)

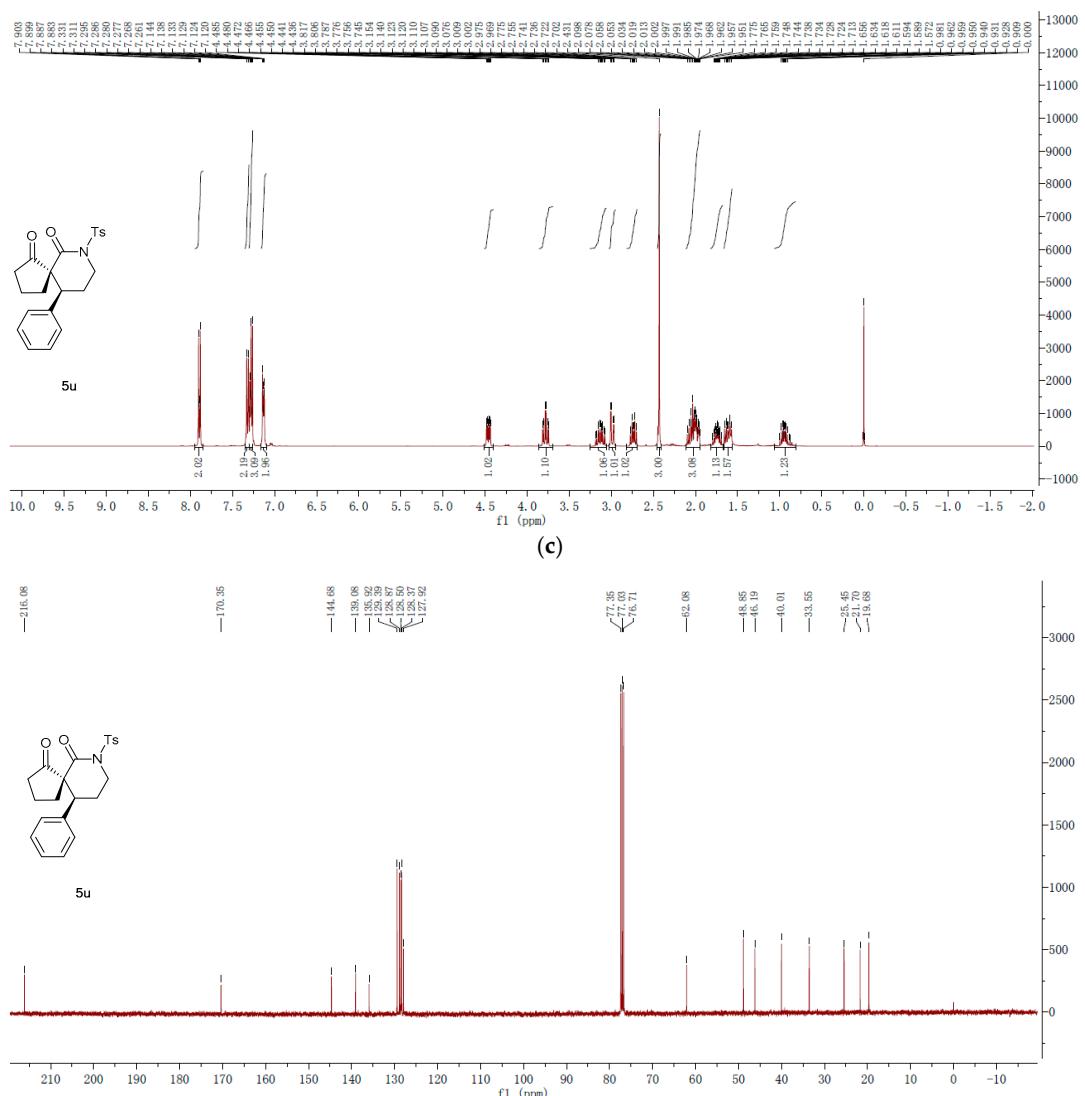


Figure S22. (a) HPLC chromatogram of racemic **5u**; (b) HPLC chromatogram of chiral **5u**; (c) ^1H -NMR spectrum (CDCl_3 , 400 MHz) of **5u**; (d) ^{13}C -NMR spectrum (CDCl_3 , 100 MHz) of **5u**.