

Supplementary Information

Synthesis of *N,O*-Type Inherently Chiral Calix[4]arenes Substituted on the Lower Rim and Their Organocatalysis Properties

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^1H NMR and ^{13}C NMR spectra of new compounds

Compound **2a**

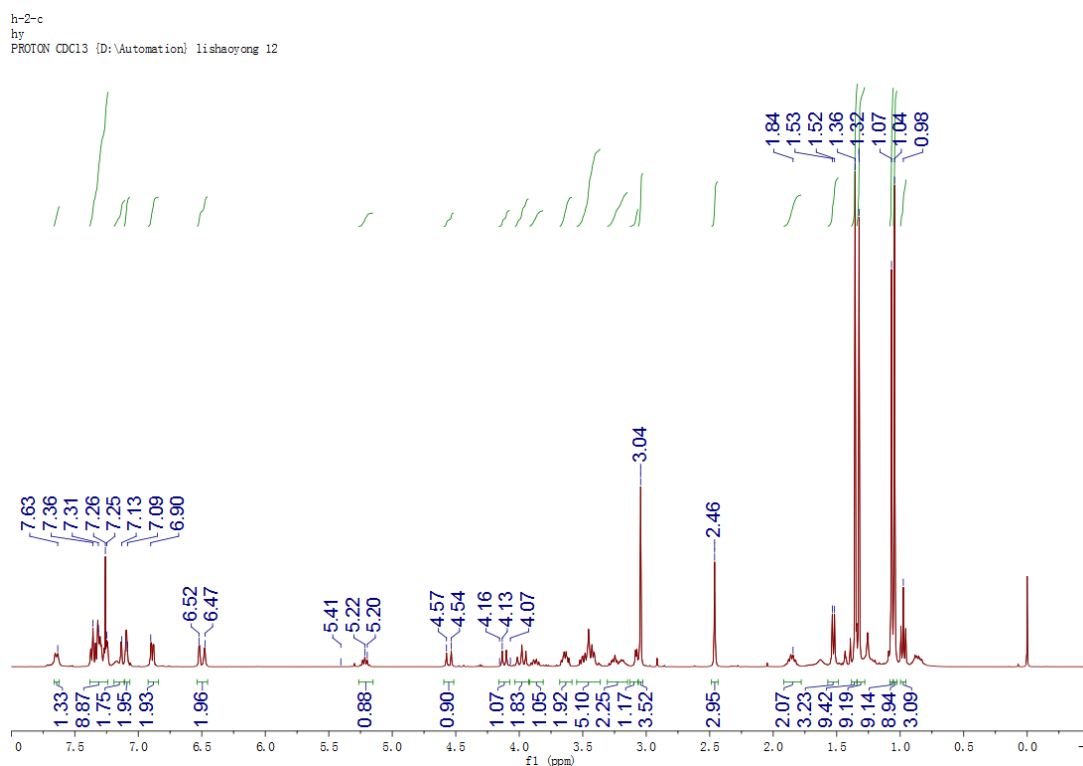


Figure S1. ^1H NMR (400 MHz, CDCl_3 , 298 K) spectrum of compound **2a**.

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t-c-a-m
cml
C13CPD CDCl3 (D:\Automation) lishaoyong 51

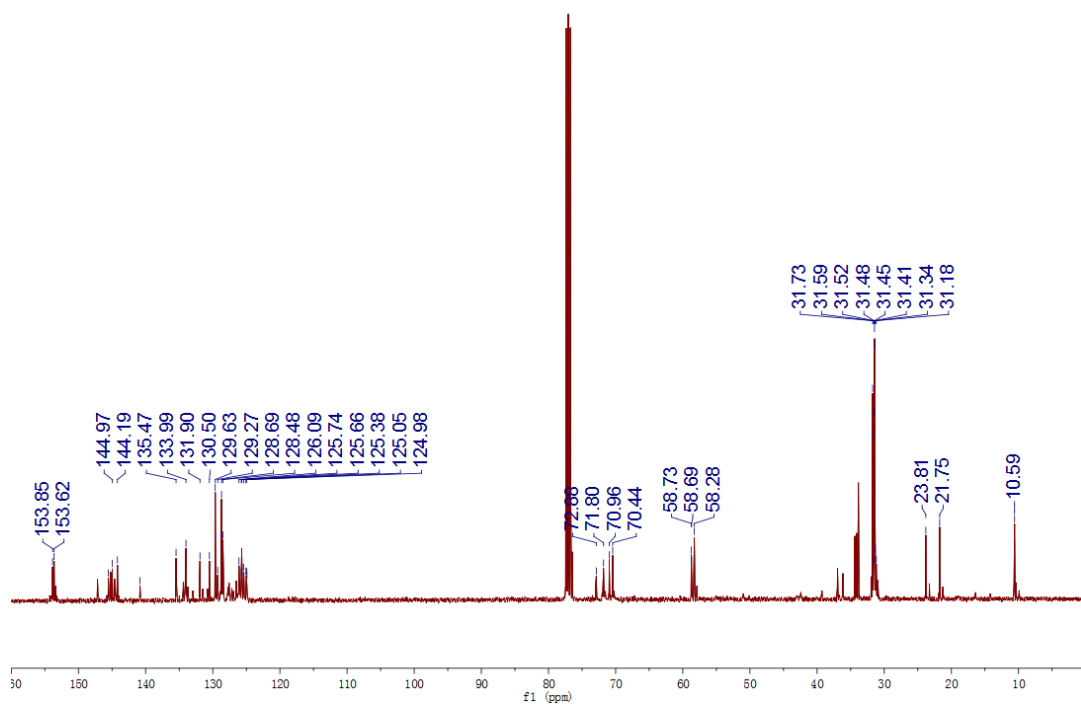


Figure S2. ^{13}C NMR (101 MHz, CDCl_3 , 298 K) spectrum of compound **2a**.

Compound **2b**

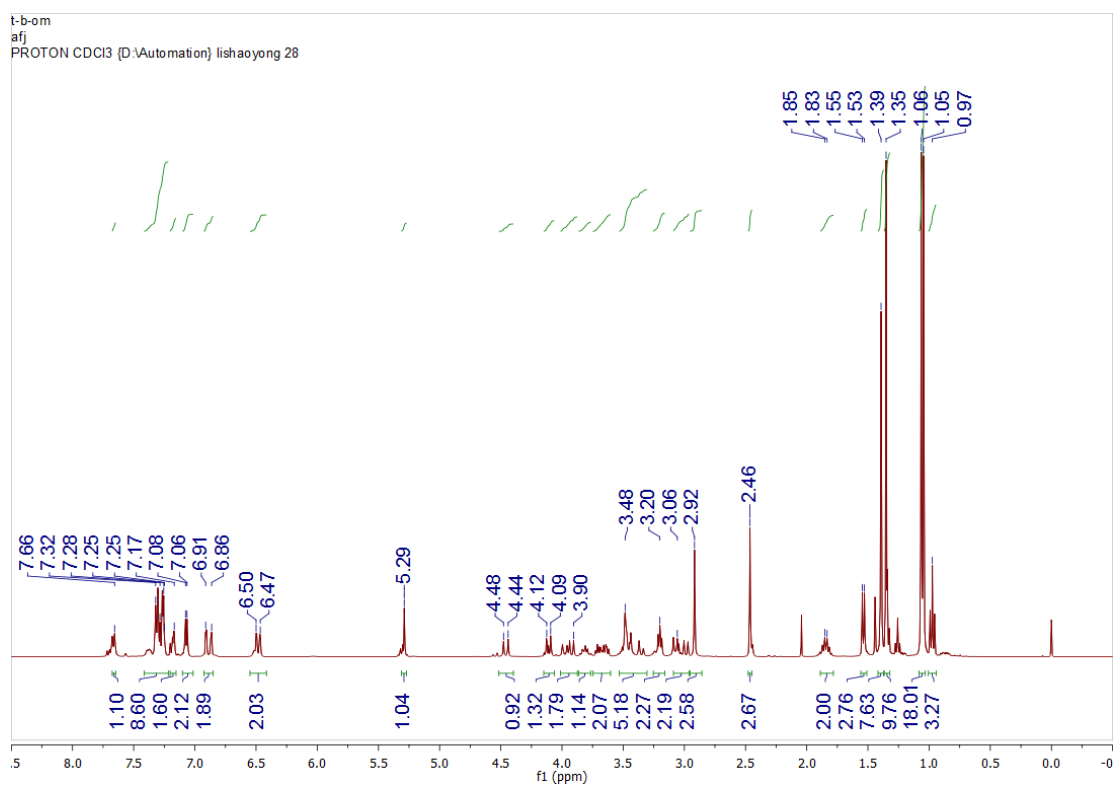


Figure S3. ^1H NMR (400 MHz, CDCl_3 , 298 K) spectrum of compound **2b**.

t-b-om
cml
C13CPD CDCB {D:\Automation\} lishaoyong 30

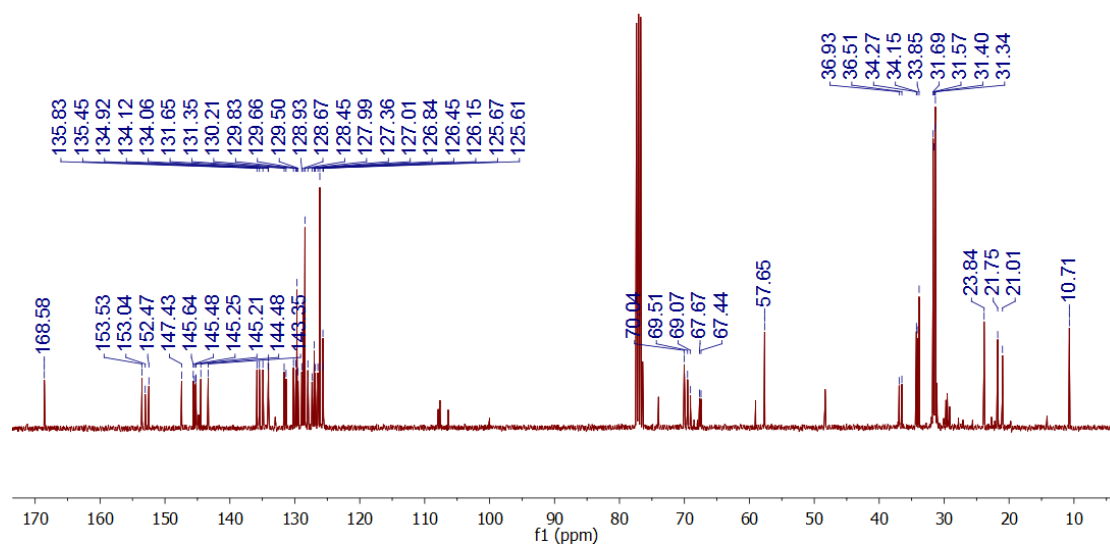


Figure S4. ^{13}C NMR (101 MHz, CDCl_3 , 298 K) spectrum of compound **2b**.

Compounds **3a** and **3b**

t-a-om-ac
cml
PROTON CDC13 {D:\Automation\} lishaoyong 20

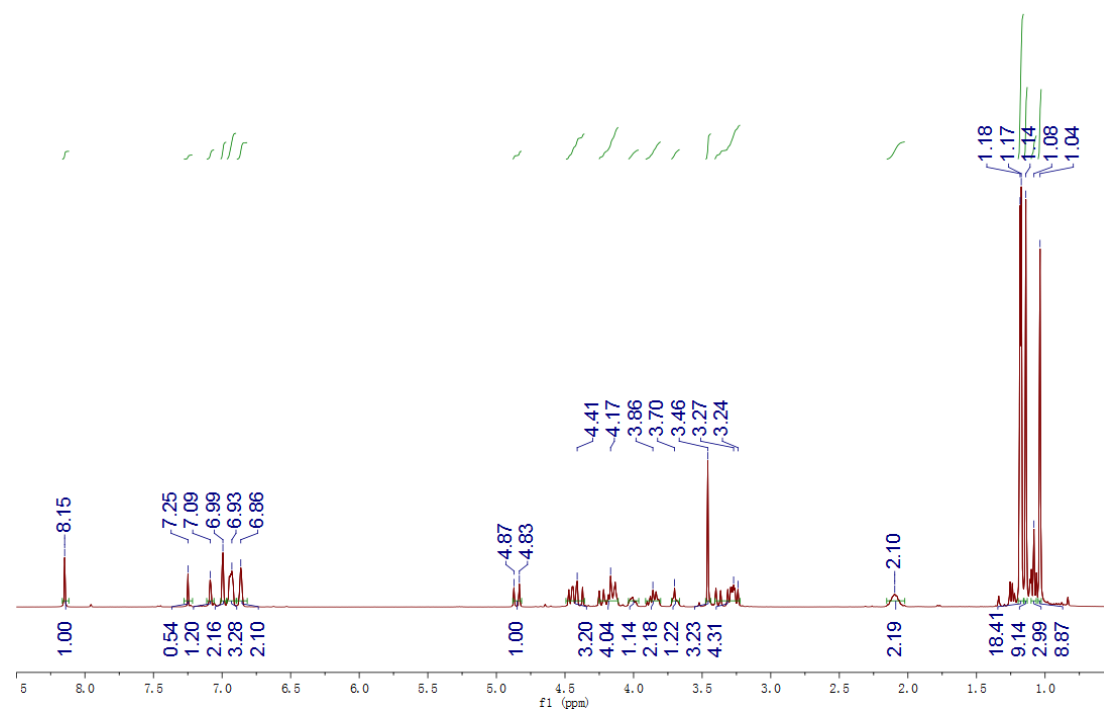


Figure S5. ^1H NMR (400 MHz, CDCl_3 , 298 K) spectrum of compound **3a** (or **3b**).

t-g-om-ac
cm
C13CPD CDCl3 {D:\Automation} chengxianchao 13

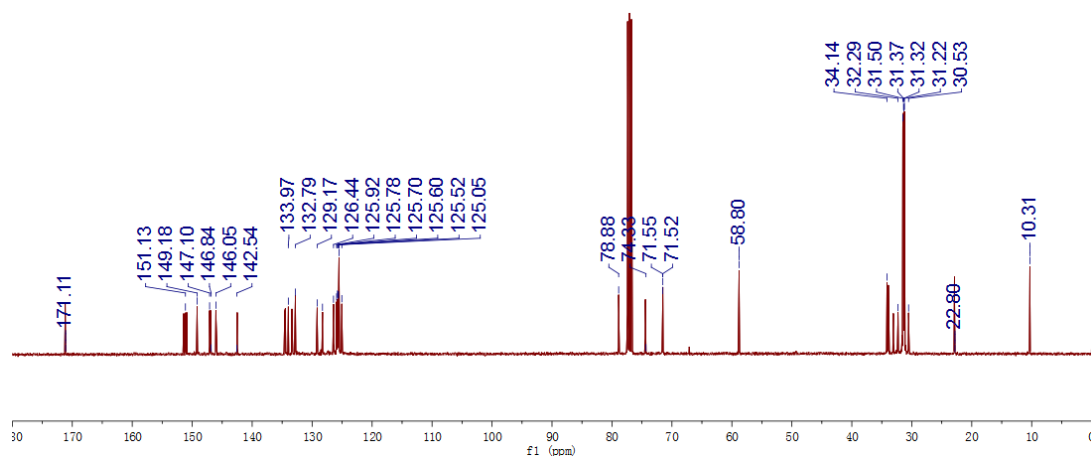


Figure S6. ^{13}C NMR (101 MHz, CDCl_3 , 298 K) spectrum of compound **3a** (or **3b**).

Compounds **4a** and **4b**

T-A-AME
CML
PROTON CDCl3 {D:\Automation} lishayong 4

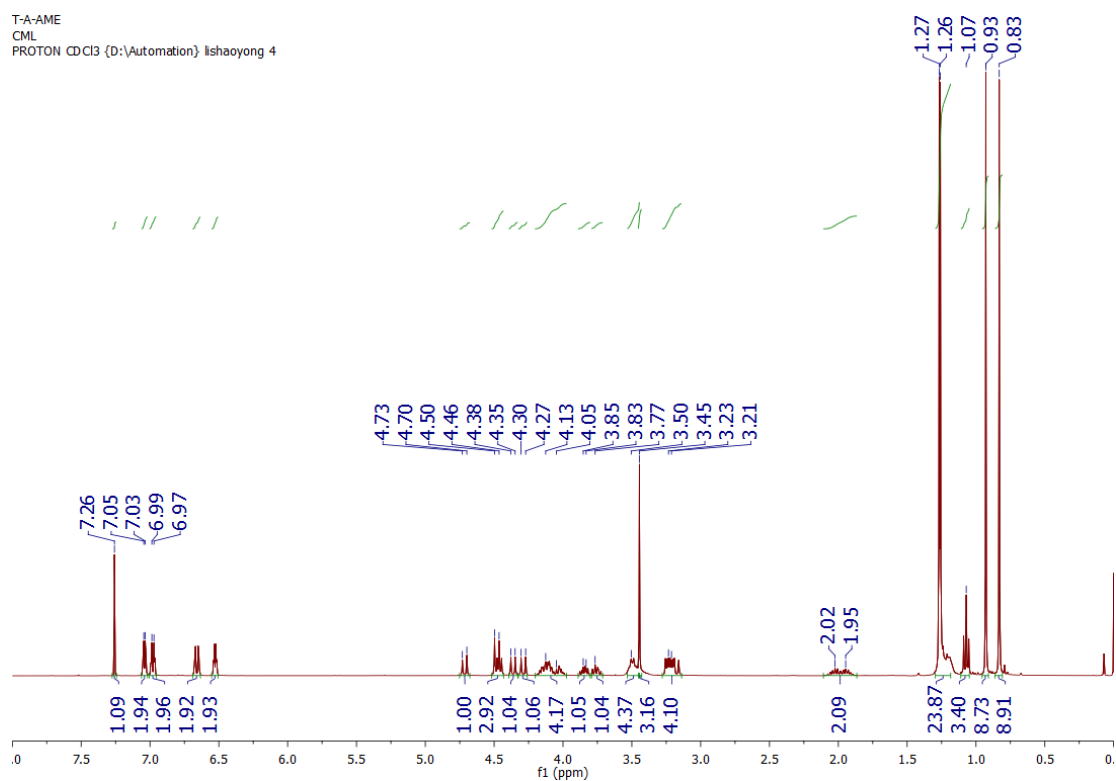


Figure S7. ^1H NMR (400 MHz, CDCl_3 , 298 K) spectrum of compound **4a** (or **4b**).

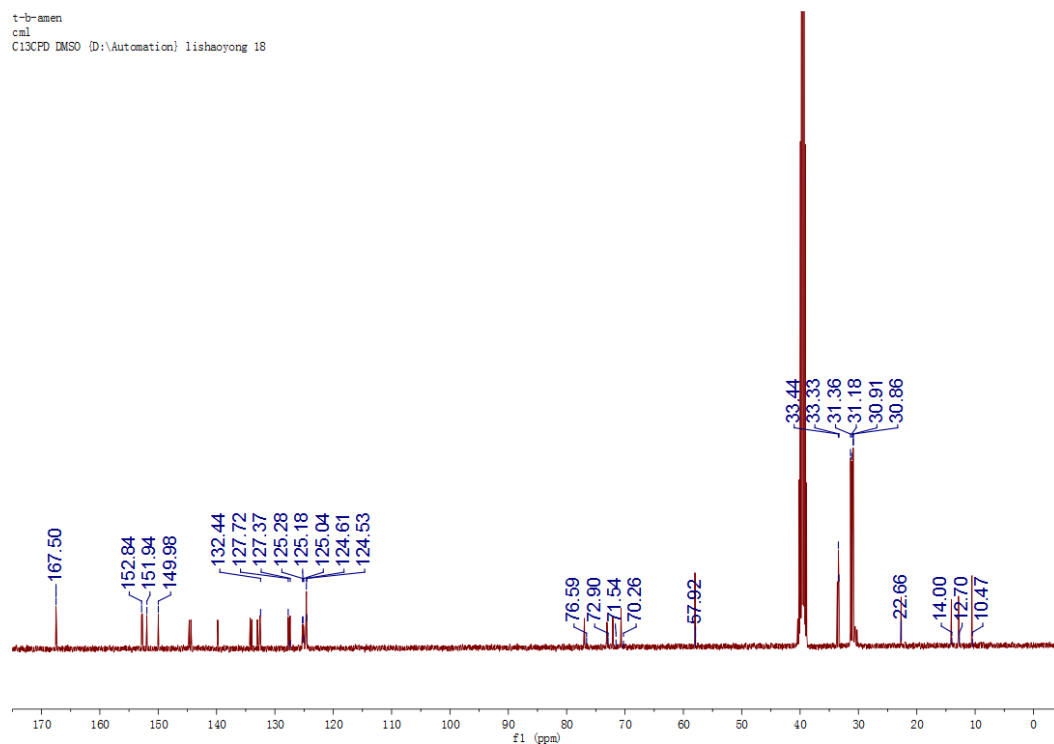


Figure S8. ^{13}C NMR (101 MHz, CDCl_3 , 298 K) spectrum of compound **4a** (or **4b**).

Compounds **5a** and **5b**

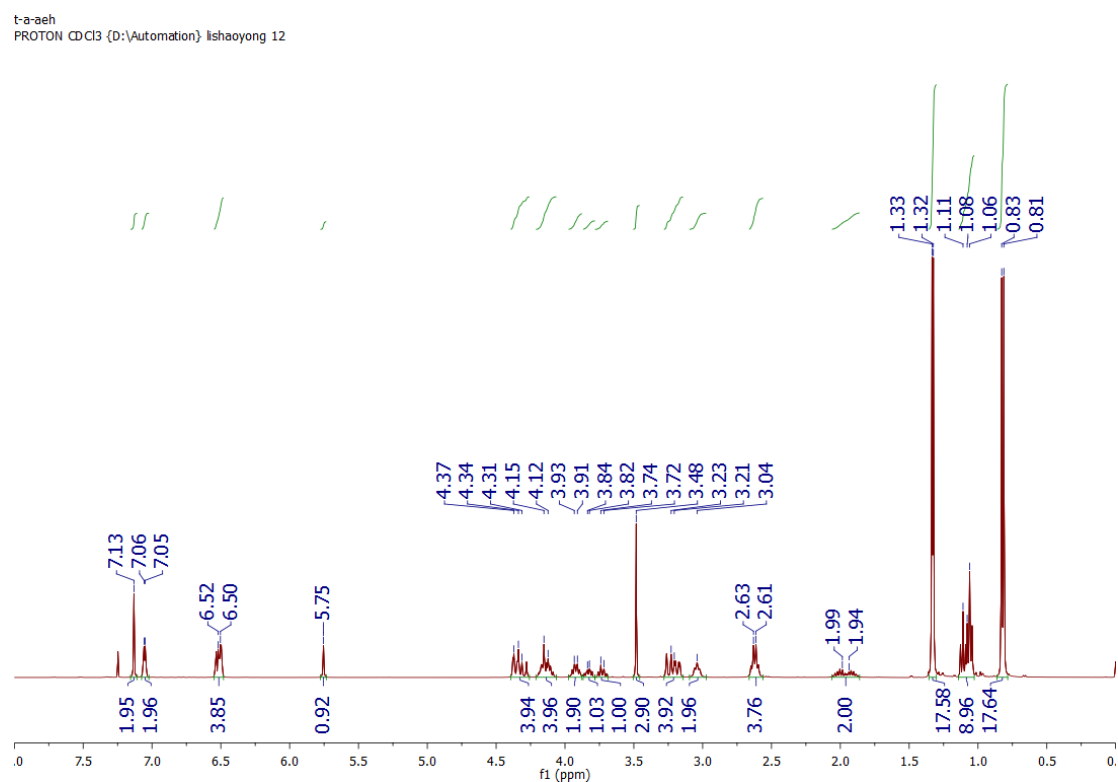


Figure S9. ^1H NMR (400 MHz, CDCl_3 , 298 K) spectrum of compound **5a** (or **5b**).

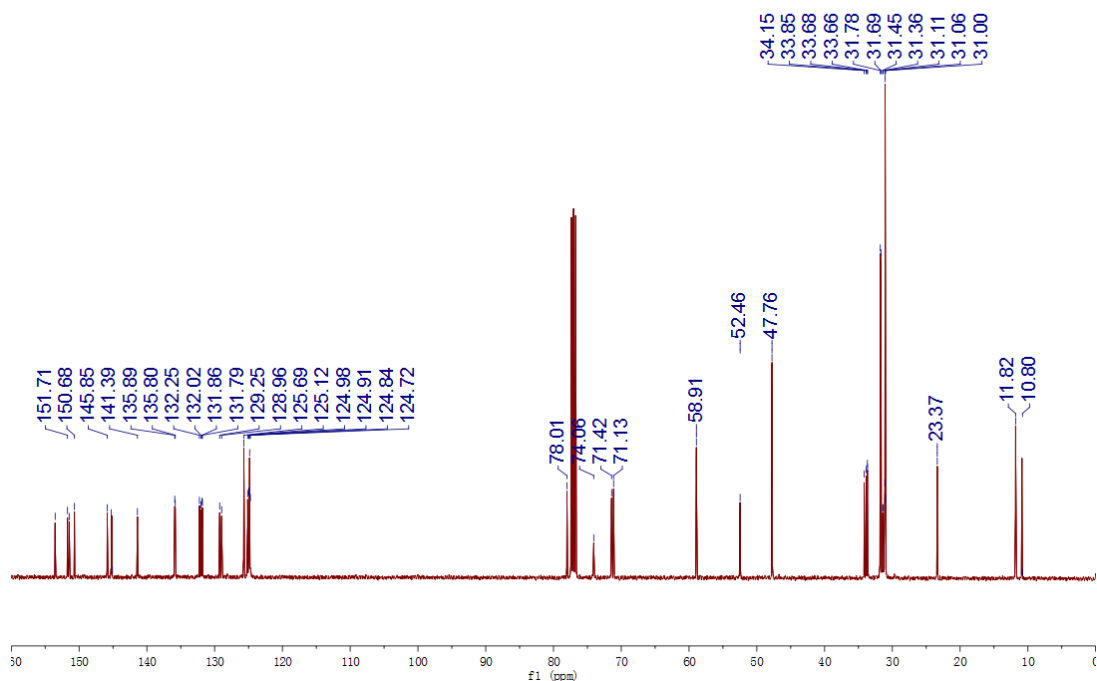
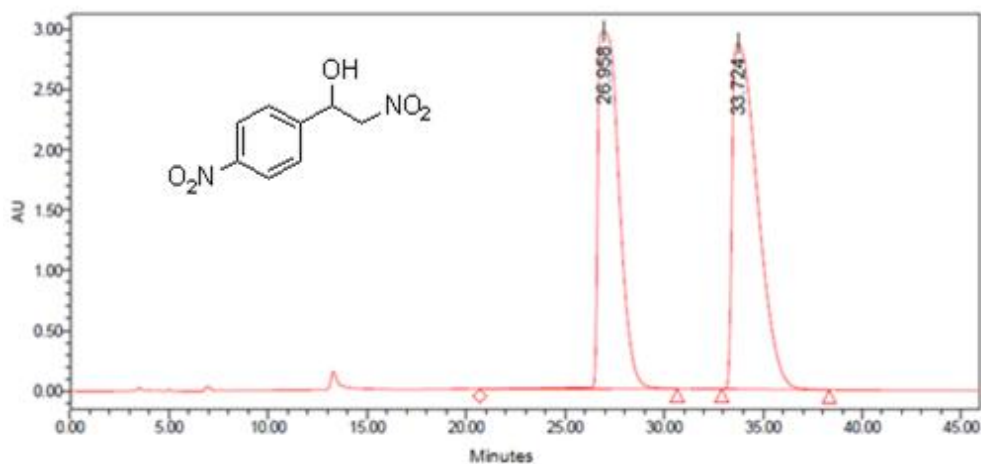


Figure S10. ^{13}C NMR (CDCl_3 , 298 K, 101 MHz) spectrum of compound **5a** (or **5b**).

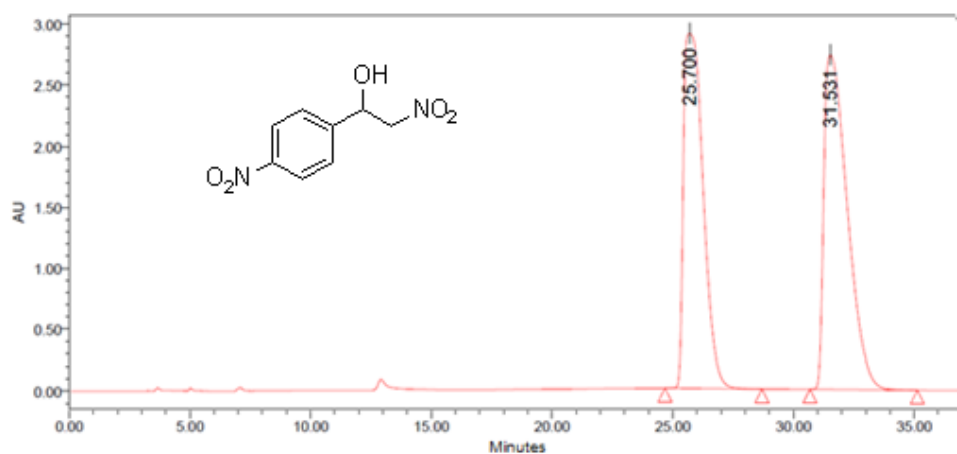
HPLC spectra



Peak results:

Index name	time / min	Height / ($\mu\text{V S}$)	Area / μV	Area / %
1	26.958	2958463	218832274	46.37
2	33.724	2865240	253123270	53.63
Total		5823703	471955544	100.00

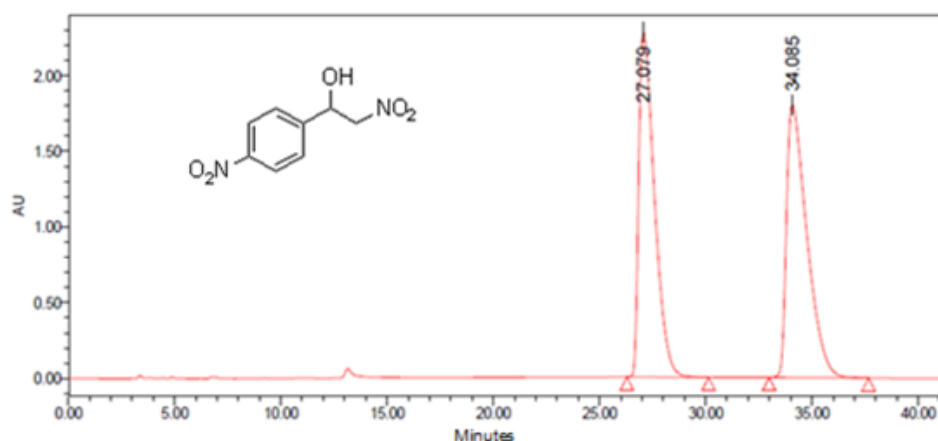
HPLC trace (**5a**; $\text{CH}_3\text{CN}/\text{H}_2\text{O}$, 3:1, v/v; rt). Chiralcel OD-H column 10% isopropyl alcohol in *n*-hexane, 1 mL min^{-1} .



Peak results:

Index name	time / min	Height / ($\mu\text{V S}$)	Area / μV	Area / %
1	25.700	2898031	164209983	47.33
2	31.531	2730877	183483196	52.77
Total		5628908	347693179	100.00

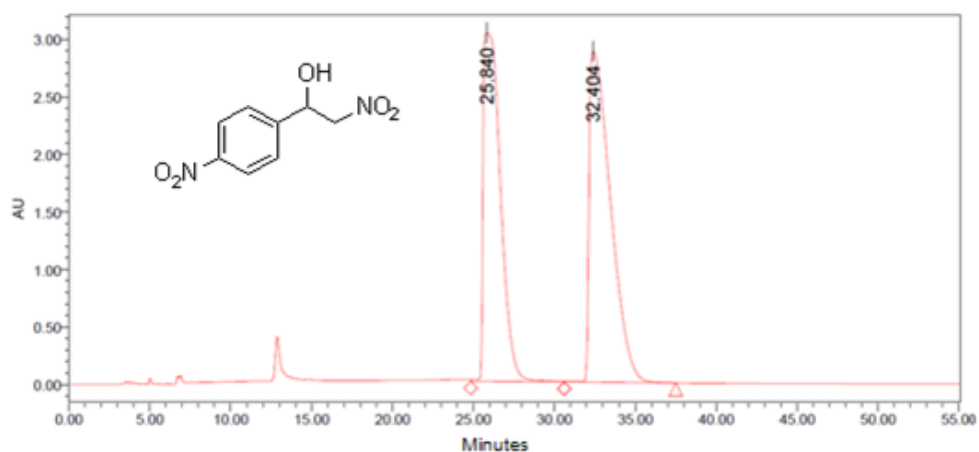
HPLC trace (**5b**; $\text{CH}_3\text{CN}/\text{H}_2\text{O}$, 3:1, v/v; rt). Chiralcel OD-H column 10% isopropyl alcohol in *n*-hexane, 1 mL min^{-1} .



Peak results:

Index name	time / min	Height / ($\mu\text{V S}$)	Area / μV	Area / %
1	27.079	2274481	116734092	49.38
2	34.085	1802617	119665148	50.62
Total		4077098	236399240	100.00

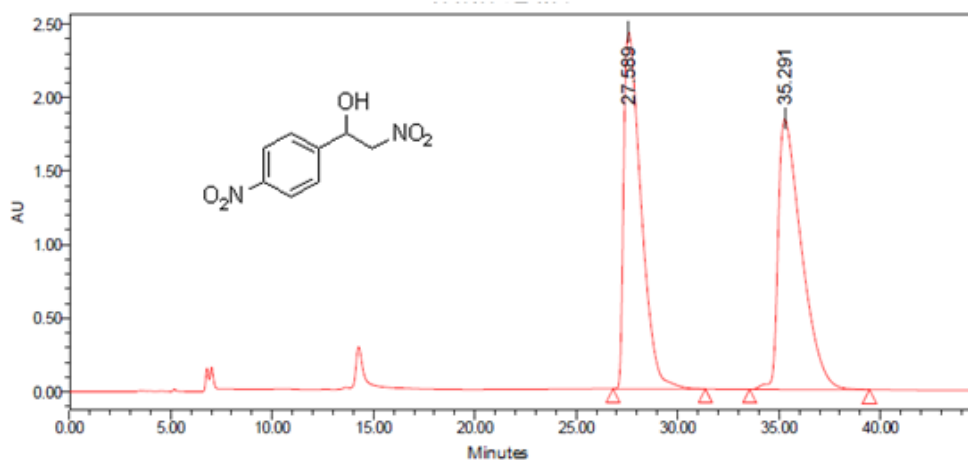
HPLC trace (**5a**; $\text{THF}/\text{H}_2\text{O}$, 3:1, v/v; rt). Chiralcel OD-H column 10% isopropyl alcohol in *n*-hexane, 1 mL min^{-1} .



Peak results:

Index name	time / min	Height / ($\mu\text{V S}$)	Area / μV	Area / %
1	25.840	3030268	226317455	46.24
2	32.404	2878871	263160996	53.76
Total		5909139	489478451	100.00

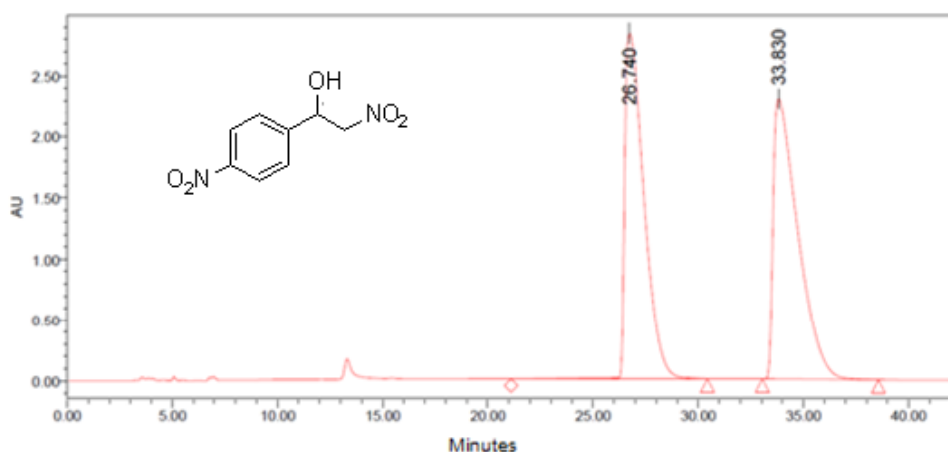
HPLC trace (**5a**; EtOH/H₂O, 3:1, v/v; rt). Chiralcel OD-H column 10% isopropyl alcohol in *n*-hexane, 1 mL min⁻¹.



Peak results:

Index name	time / min	Height / ($\mu\text{V S}$)	Area / μV	Area / %
1	27.589	2424685	147203587	50.54
2	35.291	1840205	144097946	49.46
Total		4264890	291301533	100.00

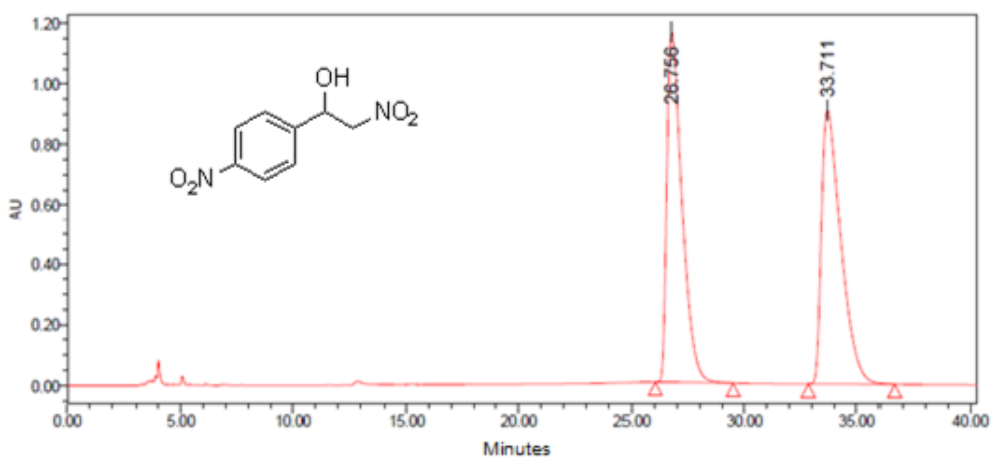
HPLC trace (**5b**; EtOH/H₂O, 3:1, v/v; rt). Chiralcel OD-H column 10% isopropyl alcohol in *n*-hexane, 1 mL min⁻¹.



Peak results:

Index name	time / min	Height / ($\mu\text{V S}$)	Area / μV	Area / %
1	26.740	2829750	178298720	48.84
2	33.830	2301216	186803382	51.16
Total		5130966	365102102	100.00

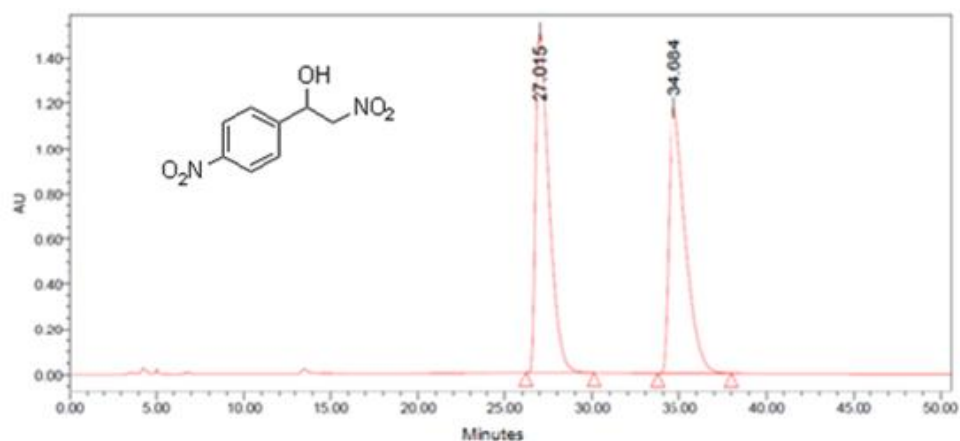
HPLC trace (**5a**; EtOH; rt). Chiralcel OD-H column 10% isopropyl alcohol in *n*-hexane, 1 mL min⁻¹.



Peak results:

Index name	time / min	Height / ($\mu\text{V S}$)	Area / μV	Area / %
1	26.756	1159138	54439826	50.03
2	33.711	907889	54390788	49.97
Total		2067027	108830614	100.00

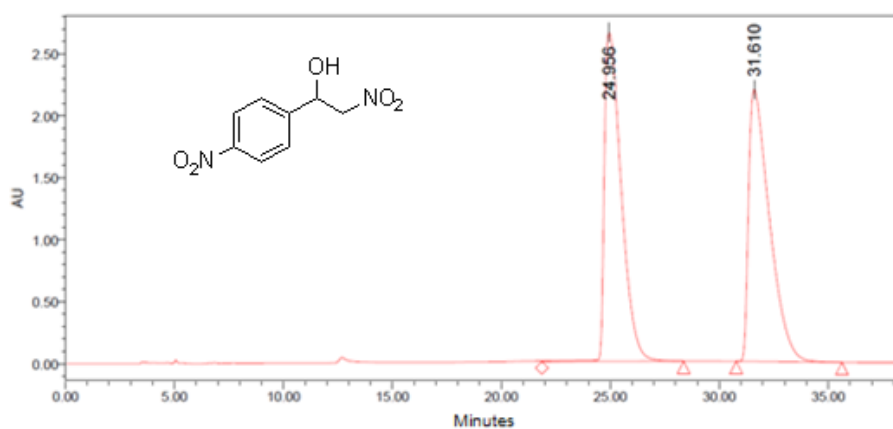
HPLC trace (**5b**; EtOH; rt). Chiralcel OD-H column 10% isopropyl alcohol in *n*-hexane, 1 mL min⁻¹.



Peak results:

Index name	time / min	Height / ($\mu\text{V S}$)	Area / μV	Area / %
1	27.015	1506871	80213760	49.93
2	34.684	1173089	80444733	50.07
Total		2679960	160658493	100.00

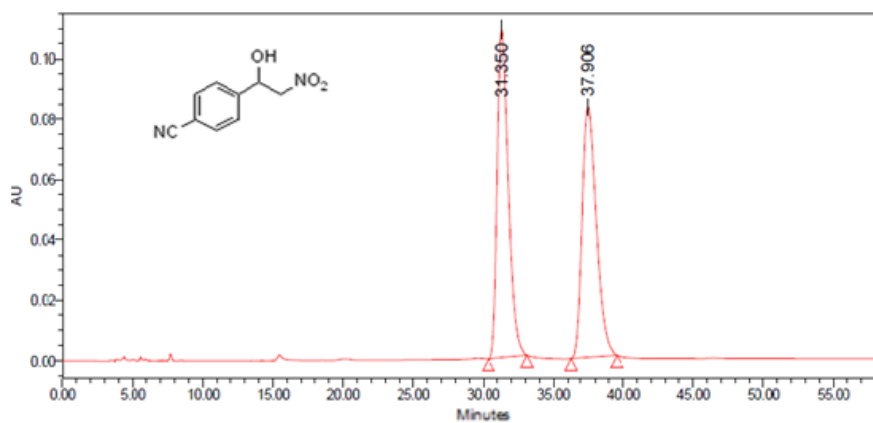
HPLC trace (**5a**; EtOH/H₂O, 3:1, v/v; $-10\text{ }^{\circ}\text{C}$). Chiralcel OD-H column 10% isopropyl alcohol in *n*-hexane, 1 mL/min⁻¹.



Peak results:

Index name	time / min	Height / ($\mu\text{V S}$)	Area / μV	Area / %
1	24.956	2651952	142817074	49.42
2	31.610	2194852	146156287	50.58
Total		4846804	288973361	100.00

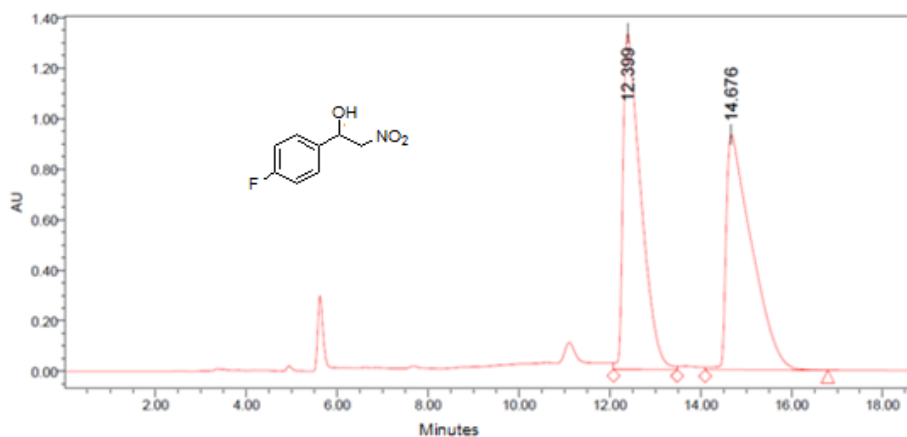
HPLC trace (**5b**; EtOH/H₂O, 3:1, v/v; $-10\text{ }^{\circ}\text{C}$). Chiralcel OD-H column 10% isopropyl alcohol in *n*-hexane, 1 mL min⁻¹.



Peak results:

Index name	time / min	Height / ($\mu\text{V S}$)	Area / μV	Area / %
1	31.350	108348	5741089	48.96
2	37.906	82945	5986061	51.04
Total		191293	11727150	100.00

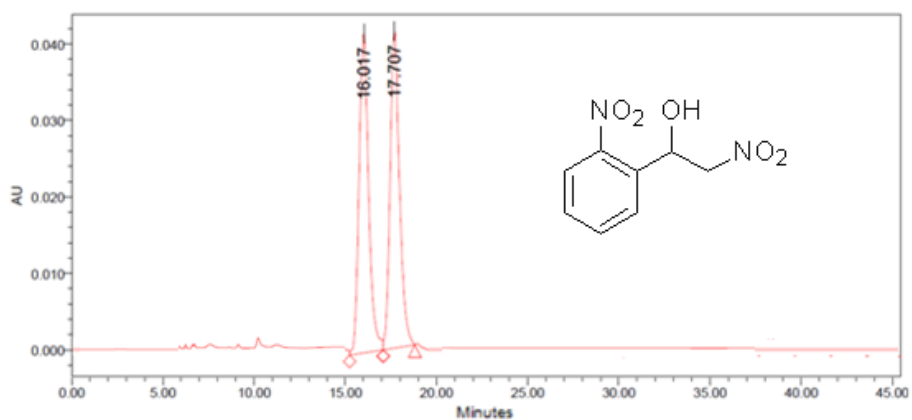
HPLC trace (5a; EtOH/H₂O, 3:1, v/v; rt). Chiralcel OD-H column 10% isopropyl alcohol in *n*-hexane, 0.8 mL min⁻¹.



Peak results:

Index name	time / min	Height / ($\mu\text{V S}$)	Area / μV	Area / %
1	12.399	1330713	36278363	49.92
2	14.676	934061	36397901	50.08
Total		2264774	72676264	100.00

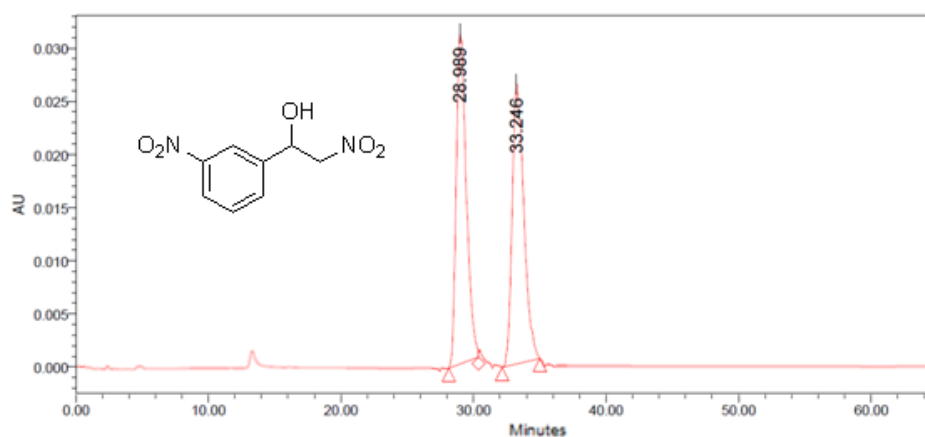
HPLC trace (5a; EtOH/H₂O, 3:1, v/v; rt). Chiralcel OD-H column 10% isopropyl alcohol in *n*-hexane, 0.8 mL min⁻¹.



Peak results:

Index name	time / min	Height / ($\mu\text{V S}$)	Area / μV	Area / %
1	16.017	41794	1480259	49.36
2	17.707	41468	1518734	50.64
Total		83262	2998993	100.00

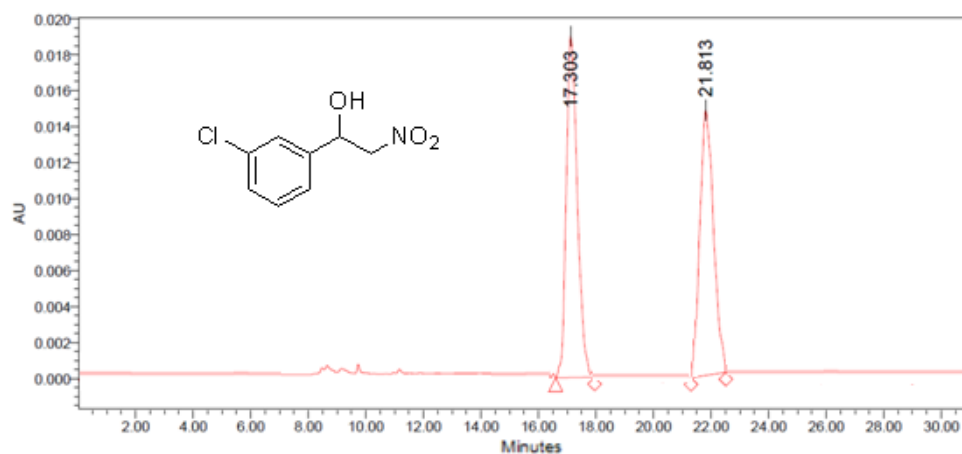
HPLC trace (5a; EtOH/H₂O, 3:1, v/v; rt). Chiralcel OD-H column 10% isopropyl alcohol in *n*-hexane, 0.9 mL min⁻¹.



Peak results:

Index name	time / min	Height / ($\mu\text{V S}$)	Area / μV	Area / %
1	28.989	31142	1609818	49.40
2	33.246	26371	1649028	50.60
Total		57513	3258846	100.00

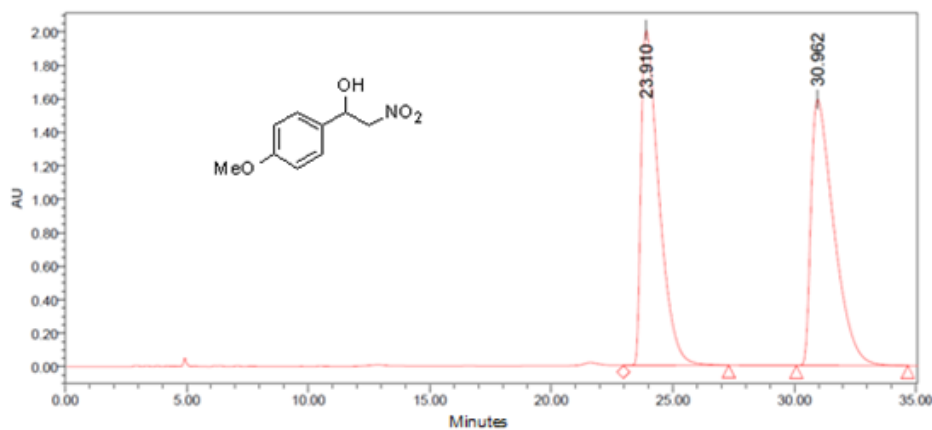
HPLC trace (5a; EtOH/H₂O, 3:1, v/v; rt). Chiralcel OD-H column 10% isopropyl alcohol in *n*-hexane, 1 mL min⁻¹.



Peak results:

Index name	time / min	Height / (μV S)	Area / μV	Area / %
1	17.303	18988	482310	48.67
2	21.813	14747	508642	51.33
Total		33735	990952	100.00

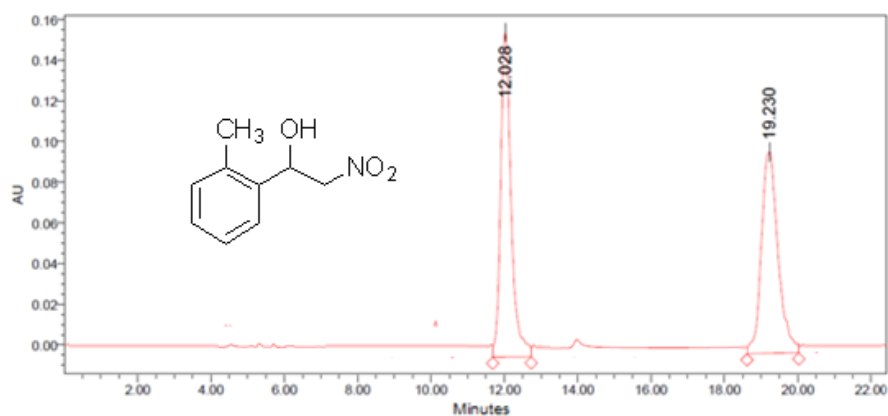
HPLC trace (5a; EtOH/H₂O, 3:1, v/v; rt). Chiralcel OD-H column 15% isopropyl alcohol in *n*-hexane, 0.6 mL min⁻¹.



Peak results:

Index name	time / min	Height / (μV S)	Area / μV	Area / %
1	23.910	2003763	43090455	49.49
2	30.962	1590036	43979274	50.51
Total		3593799	97069729	100.00

HPLC trace (5a; EtOH/H₂O, 3:1, v/v; rt). Chiralcel OD-H column 10% isopropyl alcohol in *n*-hexane, 0.8 mL min⁻¹.



Peak results:

Index name	time / min	Height / ($\mu\text{V S}$)	Area / μV	Area / %
1	12.028	159842	3127355	49.75
2	19.230	99143	3158666	50.25
Total		258985	6286021	100.00

HPLC trace (**5a**; EtOH/H₂O, 3:1, v/v; rt). Chiralcel OD-H column 15% isopropyl alcohol in *n*-hexane, 0.8 mL min⁻¹.