Supporting Information

When Chirality Breaks: Mechanochemical Degradation of Biaryl Atropisomers

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1.1. Ball milling of *(S)*-BINOL.

Table S1. Degradation study of *(S)*-BINOL under ball milling conditions, as seen in Figure 1: **1a** (100 mg, 0.35 mmol) and base were added to a zirconium oxide milling vessel (10 mL) with two zirconium oxide balls (diameter: 10 mm) and milled in an MM400 ball mill at 30 Hz.

Entry	Base	Base / eq.	*t* / h	Additive	$V_{toluene}$ / µL	Yield of **1b** / %[a]	Yield of **1** / %[b]
1	Pyrrolidine	0.1	1.5	-	-	1.88	94.1
2	Pyrrolidine	0.1	4.5	-	-	4.97	93.6
3	Pyrrolidine	1.0	4.5	-	-	1.35	77.9
4	Pyrrolidine	0.1	4.5	NaCl	-	0	97.8
5	Pyrrolidine	0.1	4.5	NaCl	350	1.27	76.5
6	Pyrrolidine	0.1	24	-	-	20.2	84.7
7	Pyrrolidine	0.1	24	NaCl		0.49	36.1
8[c]	Pyrrolidine	0.1	24	NaCl	350	2.38	57.0
9	DBU	0.1	1.5	-	-	0	90.1
10	DBU	0.1	4.5	-	-	2.48	81.1
11	DBU	1.0	4.5	-	-	0	20.3
12	DBU	0.1	4.5	NaCl	-	0	66.2
13	DBU	0.1	4.5	NaCl	350	0	97.0
14	DBU	0.1	24	-	-	3.14	25.0
15	DBU	0.1	24	NaCl	-	10.97	51.4
16	DBU	0.1	24	NaCl	350	5.71	66.2
17	K_2CO_3	1.0	4.5	-	-	2.82	71.5
18	K_2CO_3	1.0	4.5		20	1.48	87.9
19	K_2CO_3	1.0	24	-	-	2.75	10.1
20	K_2CO_3	1.0	24		20	3.45	69.5
21	K_2CO_3	1.0	4.5	NaCl	-	0	82.2
22	K_2CO_3	1.0	4.5	NaCl	350	0	80.6
23	K_2CO_3	1.0	4.5	NaCl	-	4.51	57.4
24	K_2CO_3	1.0	4.5	NaCl	350	7.65	79.4
25	K_2CO_3	25	4.5	-	-	0	92.9
26	K_2CO_3	25	4.5	-	200	0.40	96.7
27[c]	K_2CO_3	25	24	-	-	2.76	77.1
28	K_2CO_3	25	24	-	200	14.04	91.5
29	Cs_2CO_3	1.0	4.5	-	-	2.47	90.8
30	Cs_2CO_3	1.0	4.5	-	20	1.27	81.2
31	Cs_2CO_3	1.0	24	-	-	1.31	34.8
32	Cs_2CO_3	1.0	24	-	20	1.68	26.2
33	Cs_2CO_3	1.0	4.5	NaCl	-	0	66.5
34	Cs_2CO_3	1.0	4.5	NaCl	350	0	78.2
35	Cs_2CO_3	1.0	24	NaCl	-	0.67	11.1
36	Cs_2CO_3	1.0	24	NaCl	350	20.4	56.0
37	Cs_2CO_3	25	4.5	-	-	0	92.0
38	Cs_2CO_3	25	4.5	-	300	0	85.4
39	Cs_2CO_3	25	24	-	-	0.57	86.8
40	Cs_2CO_3	25	24	-	300	0.31	73.6
41	-	-	4.5	NaCl	-	0.15	90.3
42	-	-	4.5	NaCl	350	4.00	92.3
43	-	-	24	NaCl	-	2.39	93.0
44[c]	-	-	24	NaCl	350	6.03	88.4
45	-	-	1.5	-	-	0	98.1
46	-	-	4.5	-	-	0	84.1
47	-	-	24	-	-	5.00	55.6

[a]Determined by chiral HPLC analysis and adjusted according to the total yield. [b]Determined by chiral HPLC analysis, given as the sum of **1a** and **1b** and calculated according to a calibration curve. [c]Given as an average of 3 independent measurements.

Ball milling of *(S)*-BINOL in the presence of various bases, NaCl as an additive, and milling conditions revealed three primary degradation pathways: racemisation, cyclisation and oligomerisation. Pyrrolidine and DBU promoted degradation, similarly, favouring side reactions with racemisation occurring in smaller extents. Longer milling times increased degradation, with mechanical forces being the driving force behind degradation. NaCl as an additive initially reduced degradation but lost effectiveness over time, while liquid-assisted grinding (LAG, e.g., toluene) generally increased degradation by enhancing molecular mobility. Solid bases such as K_2CO_3 and Cs_2CO_3 showed varying effects depending on base quantity and milling conditions, with Cs_2CO_3 often causing severe degradation. Base-free milling maintained high yields but still showed time-dependent racemisation, particularly under LAG. Overall, base presence and physical form, milling duration, and an additive strongly influenced the balance between racemisation and side reaction pathways.

1.2. Ball milling of *(S)*-BINAM

Table S2. Degradation study of *(S)*-BINAM under ball milling conditions, as seen in Figure 2: **2a** (100 mg, 0.35 mmol) and base were added to a zirconium oxide milling vessel (10 mL) with two zirconium oxide balls (diameter: 10 mm) and milled in an MM400 ball mill at 30 Hz.

Entry	Base	Base / eq.	*t* / h	Additive	$V_{toluene}$ / µL	Yield of **2b** / %[a]	Yield of **2** / %[a,b]
1	Pyrrolidine	0.1	24	NaCl	350	0.59	45.1
2	-	-	24	NaCl	350	0.28	10.7
3	K_2CO_3	1.0	24	-	-	0.25	59.9
4	K_2CO_3	25	24	-	-	0	73.2
5	Cs_2CO_3	1.0	24	NaCl	-	0.19	74.7
6	Cs_2CO_3	1.0	24	NaCl	350	1.04	90.4
7	-	-	1.5	-	-	0	89.2
8	-	-	4.5	-	-	0.41	41.8
9	-	-	24	-	-	1.56	22.3

[a]Determined by chiral HPLC analysis and adjusted according to the total yield. [b]Determined by chiral HPLC analysis, given as the sum of **2a** and **2b** and calculated according to a calibration curve.

Degradation of *(S)*-BINAM under ball milling varies significantly with base type, base quantity, and presence of an additive. K_2CO_3 at high loading (50 eq.) achieved the highest yield (97.0 %), with racemisation as the main degradation pathway, while using smaller quantities increased degradation via side product formation, seen in smaller yield. LAG mitigated degradation in comparison to NG with Cs_2CO_3, with 90.3 % yield compared to 74.7 % yield. Using only additive significantly increased degradation, with a yield of only 10.7 %, indicating an important base role in the system, since the experiment with pyrrolidine showed higher yield of 45.7 %. No racemisation was occurring, indicating that in these conditions, degradation via side product formation is the main degradation pathway.

1.3. Ball milling of *(S)*-NOBIN

Table S3. Optimization study of degradation of *(S)*-NOBIN under ball milling conditions, as seen in Figure 2: **3a** (50 mg, 0.18 mmol) and base were added to a zirconium oxide milling vessel (10 mL) with two zirconium oxide balls (diameter: 10 mm) and milled in an MM400 ball mill at 30 Hz for 24 h.

Entry	Base	Base / eq.	*t* / h	Additive	$V_{toluene}$ / µL	Yield of **3b** / %[a]	Yield of **3** / %[a,b]
1	Pyrrolidine	0.1	24	NaCl	350	12.53	85.1

2	-	-	24	NaCl	350	9.16	44.8
3	K_2CO_3	1.0	24	-	-	10.31	45.8
4	K_2CO_3	25	24	-	-	2.02	82.7
5	Cs_2CO_3	1.0	24	NaCl	-	2.73	32.2
6*	Cs_2CO_3	1.0	24	NaCl	350	12.24	60.6
7	-	-	1.5	-	-	2.23	99.1
8	-	-	4.5	-	-	2.23	97.2
9	-	-	24	-	-	5.6	62.5

[a]Determined by chiral HPLC analysis and adjusted according to the total yield. [b]Determined by chiral HPLC analysis, given as the sum of **3a** and **3b** and calculated according to a calibration curve. *Due to lack of **3a** as starting material, experiment 6 was done with **3b** as starting material, and the yield column indicates yield of **3a**.

The results indicate that *(S)*-NOBIN stability under ball milling is strongly influenced by base type, amount, and the presence of additive. Pyrrolidine (0.1 eq.) with NaCl gave the highest yield (85.1 %), while Cs_2CO_3 with NaCl also performed moderately well (60.6 %). In contrast, Cs_2CO_3 without additive resulted in the lowest yield (32.2 %), indicating substantial degradation. Increasing K_2CO_3 loading from 1 eq. to 50 eq. improved product retention (45.8 % to 77.2 %), suggesting that higher loadings can mitigate degradation. Overall, NaCl additive generally improves yields, while stronger bases without additive promote more extensive side reactions.

1.4. Study of milling frequency

Table S4. Degradation study of *(S)*-BINOL under ball milling conditions: **1a** (100 mg, 0.35 mmol) and pyrrolidine were added to a zirconium oxide milling vessel (10 mL) with two zirconium oxide balls (diameter: 10 mm) and milled in an MM400 ball mill for 4.5 h.

Entry	Base / eq.	*f* / Hz	Yield of **1b** / %[a]	Yield of **1** / %[a,b]
1	0.1	30	4.97	93.6
2	0.1	20	0	53.6
3	0.1	10	0	88.0
4	0.1	5	0	94.6
5	0.2	30	2.03	75.6
6	0.2	20	0	58.3
7	0.2	10	0	90.3
8	0.2	5	0	95.9

[a]Determined by chiral HPLC analysis and adjusted according to the total yield. [b]Determined by chiral HPLC analysis, given as the sum of **1a** and **1b** and calculated according to a calibration curve.

The data shows that milling frequency and base loading significantly impact *(S)*-BINOL degradation over 4.5 h. At 0.1 eq. pyrrolidine, high frequency (30 Hz) resulted in moderate degradation, with 4.97 % racemisation and 93.6 % yield, whereas lower frequencies (5–10 Hz) maintained yields above 88 %, indicating little degradation. Increasing the base to 0.2 eq. generally reduced yields, particularly at 20 Hz (58.3 %), though low frequency milling (5 Hz) showed least degradation (95.9 % yield). Overall, lower milling frequencies and reduced base loading improve product retention.

1.5. Study of milling vessel effect

Table S5. Degradation study of *(S)*-BINOL under ball milling conditions: **1a** (140 mg, 0.49 mmol) and base were added to a polytetrafluoroethylene (PTFE) milling vessel (14 mL) with three zirconium oxide balls (diameter: 10 mm) and milled in an MM400 ball mill at 30 Hz for 24 h.

Entry	Base	Base / eq.	Additive	$V_{toluene}$ / µL	Yield of **1b** / %[a]	Yield of **1** / %[a,b]
1	Pyrrolidine	0.1	NaCl	350	3.08	88.4
2	-	-	NaCl	350	0.52	47.8
3	K_2CO_3	1.0	-	-	2.20	11.7
4	K_2CO_3	50	-	-	0	47.8
5	Cs_2CO_3	1.0	NaCl	-	0	85.5
6	Cs_2CO_3	1.0	NaCl	350	0	89.5

[a]Determined by chiral HPLC analysis and adjusted according to the total yield. [b]Determined by chiral HPLC analysis, given as the sum of **1a** and **1b** and calculated according to a calibration curve.

Changing the milling vessel material did not significantly influence the degradation of *(S)*-BINOL over 24 h compared to ZrO_2 jars. The predominant degradation pathway was side-product formation, most pronounced in the experiment with 1.0 equiv. K_2CO_3, which afforded only 11.7 % yield. Increasing the amount of material in the vessel, either by adding additive or additional base, reduced degradation to some extent, though levels remained high. Racemisation was identified as a secondary degradation pathway in three experiments, with the highest observed value of 3.08 % in the presence of pyrrolidine.

1.6. Reproducibility assessment

Table S6. Reproducibility assessment: *(S)*-BINOL (**1a)** (100 mg, 0.35 mmol) and base were added to a zirconium oxide milling vessel (10 mL) with two zirconium oxide balls (diameter: 10 mm) and milled in an MM400 ball mill at 30 Hz for 24 h.

Entry	Base	Base / eq.	Additive	$V_{toluene}$ / µL	Yield of **1b** / %[a]	Yield of **1** / %[b]
1	-	-	NaCl	350	6.33	87.0
2	-	-	NaCl	350	5.61	90.0
3	-	-	NaCl	350	6.14	88.2
4	Pyrrolidine	0.1	NaCl	350	2.32	59.2
5	Pyrrolidine	0.1	NaCl	350	2.27	58.1
6	Pyrrolidine	0.1	NaCl	350	2.55	53.8
7	K_2CO_3	25	-	-	3.18	73.9
8	K_2CO_3	25	-	-	2.22	79.7
9	K_2CO_3	25	-	-	2.87	77.7

[a]Determined by chiral HPLC analysis and adjusted according to the total yield. [b]Determined by chiral HPLC analysis, given as the sum of **1a** and **1b** and calculated according to a calibration curve.

The reproducibility of the reaction was evaluated by performing independent experiments under identical milling conditions. For the standard conditions (NaCl additive, no base), three separate experiments gave comparable yields of compound **1b** (5.61–6.33%) and consistently high yields of **1** (87.0–90.0%). Similarly, reactions conducted with pyrrolidine (0.1 eq.) or K_2CO_3 (25 eq.) showed good reproducibility, with only minor variations. These results demonstrate that the mechanochemical protocol provides reliable and reproducible outcomes.

2. Experimental Section

2.1. General Information

2.1.1. Materials

Unless otherwise stated, all chemicals were obtained from commercial sources and used without further purification.

BLDPharm: *(S)*-BINOL (99.79 %), *(S)*-BINAM (98 %), *(S)*-NOBIN (98 %), *(R)*-NOBIN (97 %), caesium carbonate (99 %)

Carl Roth: sodium chloride (>99.8 %), sodium bicarbonate (>99 %)

VWR: hydrochloric acid (37 %, $d = 1.18\ g \cdot mL^{-1}$), potassium carbonate (99.2 %), ethyl acetate (>99.8 %), toluene (100 %)

TCI Chemicals: 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) (>98 %) and pyrrolidine (>98 %)

Thermo Fisher Scientific: sodium sulphate (99 %)

2.1.2. Devices

^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Jeol JNM-EZCL400 R series spectrometer operating at 400 MHz. Measurements were carried out in deuterated solvents ($CDCl_3$, DMSO-d_6), using the residual solvent peaks as internal references. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS). Signal multiplicities are denoted as follows: s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, and m = multiplet. Minor residual solvent signals corresponding to ethyl acetate from the reaction workup and acetone arising from tube cleaning are observed in some spectra.

Chiral high-performance liquid chromatography (cHPLC) analysis were performed on a Waters ARC HPLC system. Daicel Chiralpak IA column was employed, with dimensions of 5 µm, 4.6 x 250 mm. The mobile phase was isocratic with different mixtures for respective derivative, as stated below. Detection was conducted using a Waters PDA 2998 at 224 nm. Minor variations in elution time are likely due to small fluctuations in temperature and pressure, since the column was inserted manually and the setup was not thermostated.

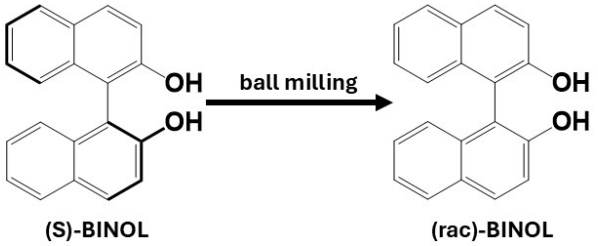
- BINOL: The mobile phase for cHPLC was the mixture of isohexane (A) and 2-propanol (B) at a ratio of 90 % (A) – 10 % (B) for 30 minutes at 1 mL/min with an injection volume of 5 µL.
- BINAM: The mobile phase for cHPLC was the mixture of isohexane (A) and ethanol (B) at a ratio of 70 % (A) – 30 % (B) for 20 minutes at 1 mL/min with an injection volume of 5 µL.
- NOBIN: The mobile phase for cHPLC was the mixture of isohexane (A) and 2-propanol (B) at a ratio of 85 % (A) – 15 % (B) for 40 minutes at 1 mL/min with an injection volume of 5 µL.

Ball milling experiments were performed using a Retsch Mixer Mill MM400. The zirconium oxide (ZrO_2) milling jar and the polytetrafluoroethylene (PTFE) milling jar have lengths of 70 mm and inner jar diameters of 20 mm. The average mass of one ZrO_2 ball is 1941.92 mg and is given as an average of 5 measurements of randomly selected balls available. In all experiments, two balls were used. Milling frequency is 30 Hz unless specified otherwise. The vibration amplitude is determined as per [1] and is calculated to be 35 mm.

High resolution mass spectrometry measurements (HRMS) were performed using infusion on Waters Synapt XS instrument, with atmospheric pressure chemical ionisation (APCI) in positive mode as an ionisation source. Detection was done using time-of-flight (TOF).

2.2. Experimental protocols

2.2.1. Ball milling of *(S)*-BINOL

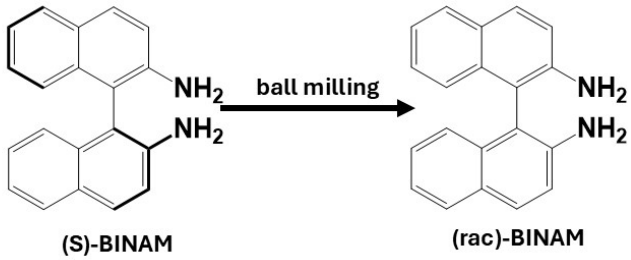


In a typical reaction, a ZrO_2 jar (10 mL) was filled with, in this order, two ZrO_2 milling balls (diameter = 10 mm), *(S)*-BINOL (100 mg, 0.35 mmol, 1.0 eq.), NaCl as additive (3.5 g), pyrrolidine (2.8 µL, 0.1 eq.) as base and toluene (350 µL) as LAG additive. The reaction was milled for 24 h at 30 Hz in an MM400 mixer mill. The crude mixture was washed with H_2O and HCl (c = 1 mol L^{-1}). The pH was adjusted to 7 using $NaHCO_3$ (aq., sat.). The aqueous phase was extracted using 3 x 20 mL of ethyl acetate. The combined organic fractions were dried over anhydrous sodium sulphate, filtered and the organic solvents were removed under reduced pressure. The thus obtained product was analysed via quantitative cHPLC. The absolute amount of recovered BINOL was determined by converting chromatographic peak areas into concentrations using the BINOL calibration curve (see Figure S1); the resulting concentration was then compared to the theoretical value based on the weighed sample during HPLC sample preparation.

HPLC retention times: *(S)*-BINOL elutes at 22.5 min, *(R)*-BINOL elutes at 24.8 min (see Figure S4).

^{1}H-NMR spectrum peaks (400 MHz, CHLOROFORM-D): δ 7.99 (d, 2H), 7.90 (d, 2H), 7.42 – 7.27 (m, 6H), 7.16 (d, 2H), 5.05 (s, 2H). The experimental spectrum is in accordance with the literature.[2,3]

2.2.2. Ball milling of *(S)*-BINAM

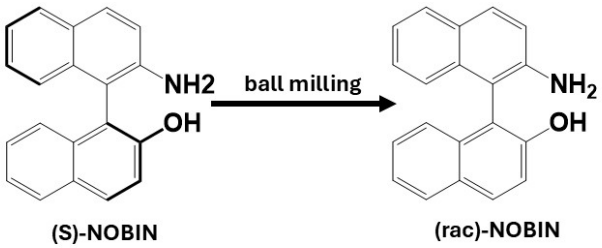


In a typical reaction, a ZrO_2 jar (10 mL) was filled with, in this order, two ZrO_2 milling balls (diameter = 10 mm), *(S)*-BINAM (100 mg, 0.35 mmol, 1.0 eq.), NaCl as additive (3.5 g), pyrrolidine (2.8 µL, 0.1 eq.) as base and toluene (350 µL) as LAG additive. The reaction was milled for 24 h at 30 Hz in an MM400 mixer mill. The crude mixture was washed with H_2O and HCl (c = 1 mol L^{-1}). The pH was adjusted to 7 using $NaHCO_3$ (aq., sat.). The aqueous phase was extracted using 3 x 20 mL of ethyl acetate. The combined organic fractions were dried over anhydrous sodium sulphate, filtered, and the organic solvents were removed under reduced pressure. The thus obtained product was analysed via quantitative cHPLC. The absolute amount of recovered BINAM was determined by converting chromatographic peak areas into concentrations using the BINAM calibration curve (see Figure S2); the resulting concentration was then compared to the theoretical value based on the weighed sample during HPLC sample preparation.

HPLC retention times: 8.5 min for *(R)*-BINAM, 11.5 min for *(S)*-BINAM (see Figure S5).

^{1}H NMR spectrum peaks (400 MHz, CHLOROFORM-*D*): δ 7.83 – 7.78 (m, 5H), 7.25 – 7.13 (m, 7H), 7.08 (m, 2H), 3.69 (s, 2H). The experimental spectrum is in accordance with the literature.[4]

2.2.3. Ball milling of *(S)*-NOBIN



In a typical reaction, a ZrO_2 jar (10 mL) was filled with, in this order, two ZrO_2 milling balls (diameter = 10 mm), *(S)*-NOBIN (50 mg, 0.18 mmol, 1.0 eq.), NaCl as additive (3.5 g), pyrrolidine (2.8 µL, 0.1 eq.) as base and toluene (350 µL) as LAG additive. The reaction was milled for 24 h at 30 Hz in an MM400 mixer mill. The crude mixture was washed with H_2O and HCl (c = 1 mol L^{-1}). The pH was adjusted to 7 using $NaHCO_3$ (aq., sat.). The aqueous phase was extracted using 3 x 20 mL of ethyl acetate. The combined organic fractions were dried over anhydrous sodium sulphate, filtered, and the organic solvents were removed under reduced pressure. The thus obtained product was analysed via quantitative cHPLC. The absolute amount of recovered NOBIN was determined by converting chromatographic peak areas into concentrations using the NOBIN calibration curve (see Figure S3); the resulting concentration was then compared to the theoretical value based on the weighed sample during HPLC sample preparation.

HPLC retention times: 12.1 min for *(R)*-NOBIN, 17.9 min for *(S)*-NOBIN (see Figure S6).

^{1}H NMR spectrum peaks (400 MHz, CHLOROFORM-*D*): δ 7.95 – 7.79 (m, 4H), 7.40 – 7.27 (m, 3H), 7.25 – 7.13 (m, 4H), 7.07 – 7.02 (m, 1H), 5.14 (s, 1H), 3.75 (s, 2H). The experimental spectrum is in accordance with the literature.[5]

2.3. Other

2.3.1. Calibration curve for BINOL

To create a calibration curve for BINOL, 3.07 mg of *(S)*-BINOL was weighed and dissolved in 3 mL of cHPLC solvent (isohexane:ethanol = 90:10, v/v). The solution was ultrasonicated for 10 minutes to ensure complete dissolution and then diluted to obtain a concentration series. Each solution was analysed by cHPLC, and the number of counts was plotted against concentration. A linear calibration curve was obtained with the equation $y = 108227.45\,x + 1698197.03$ and an R^2 value of 0.9990.

Table S6. Calibration data for BINOL obtained by chiral HPLC.

Entry	*c*(*(S)*-BINOL, calc.) / ppm	Number of counts
1	50.67	7322571
2	50.67	7451720
3	50.67	7649594
4	101.33	12024158
5	101.33	12249150
6	202.67	23389023
7	202.67	23793130
8	304.00	34704172
9	304.00	34755412

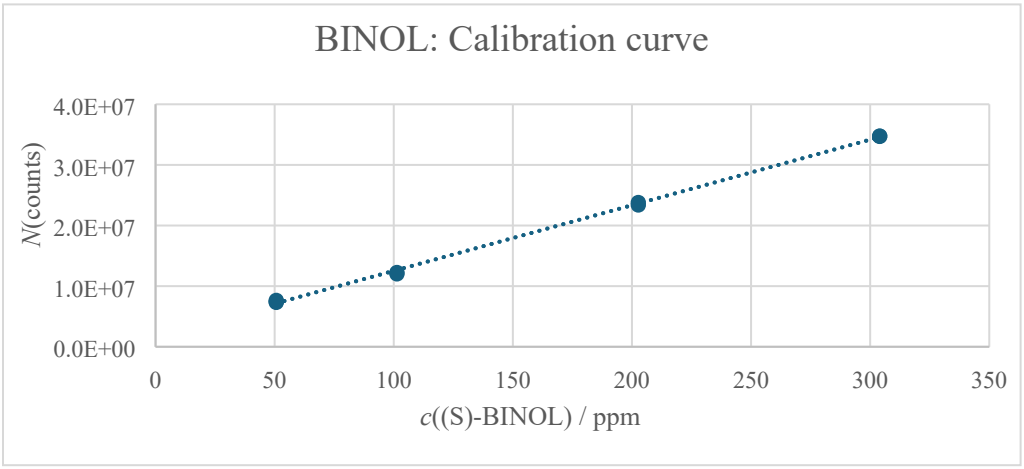


Figure S1. Calibration curve for BINOL obtained by chiral HPLC. Detector response (counts) is plotted against concentration to generate the calibration curve used for quantification.

2.3.2. Calibration curve for BINAM

To create a calibration curve for BINAM, 3.12 mg of *(S)*-BINAM was weighed and dissolved in 3 mL of cHPLC solvent (isohexane:ethanol = 90:10, v/v). The solution was ultrasonicated for 10 minutes to ensure complete dissolution and then diluted to obtain a concentration series. Each solution was analysed by cHPLC, and the number of counts was plotted against concentration. A linear calibration curve was obtained with the equation $y = 58818.63x + 4535884.0_0$ and an R^2 value of 0.9834.

Table S7. Calibration data for BINAM obtained by chiral HPLC. Detector response (counts) is plotted against concentration to generate the calibration curve used for quantification.

Entry	*c*((*S*)-BINAM, calc.) / ppm	Number of counts
1	104.00	10180547
2	104.00	9847240
3	104.00	10055752
4	208.00	19785946
5	312.00	22114663
6	520.00	34087758
7	520.00	35787751
8	520.00	41292026

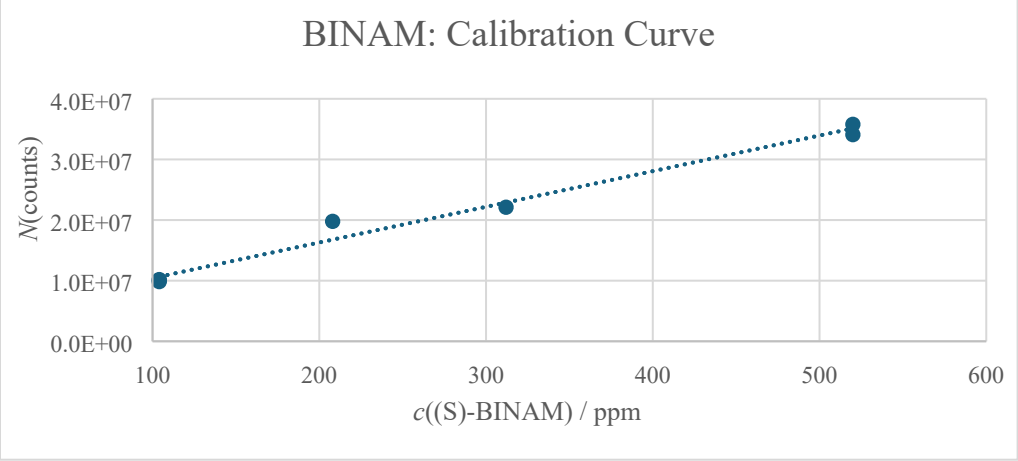


Figure S2. Calibration curve for BINAM obtained by chiral HPLC. Detector response (counts) is plotted against concentration to generate the calibration curve used for quantification.

2.3.3. Calibration curve for NOBIN

To create a calibration curve for NOBIN, 3.04 mg of *(S)*-NOBIN was weighed and dissolved in 3 mL of cHPLC solvent (isohexane:ethanol = 90:10, v/v). The solution was ultrasonicated for 10 minutes to ensure complete dissolution and then diluted to obtain a concentration series. Each solution was analysed by cHPLC, and the number of counts was plotted against concentration. A linear calibration curve was obtained with the equation $y = 79143.29x + 1440155.55$ and an R^2 value of 0.9994.

Table S8. Calibration data for NOBIN obtained by chiral HPLC. Detector response (counts) is plotted against concentration to generate the calibration curve used for quantification.

Entry	*c*(*(S)*-NOBIN, calc.) / ppm	Number of counts
1	101.33	9404388
2	101.33	9651464
3	202.67	17246841
4	304.00	25577582
5	506.67	42176846
6	506.67	41414782
7	506.67	41045966

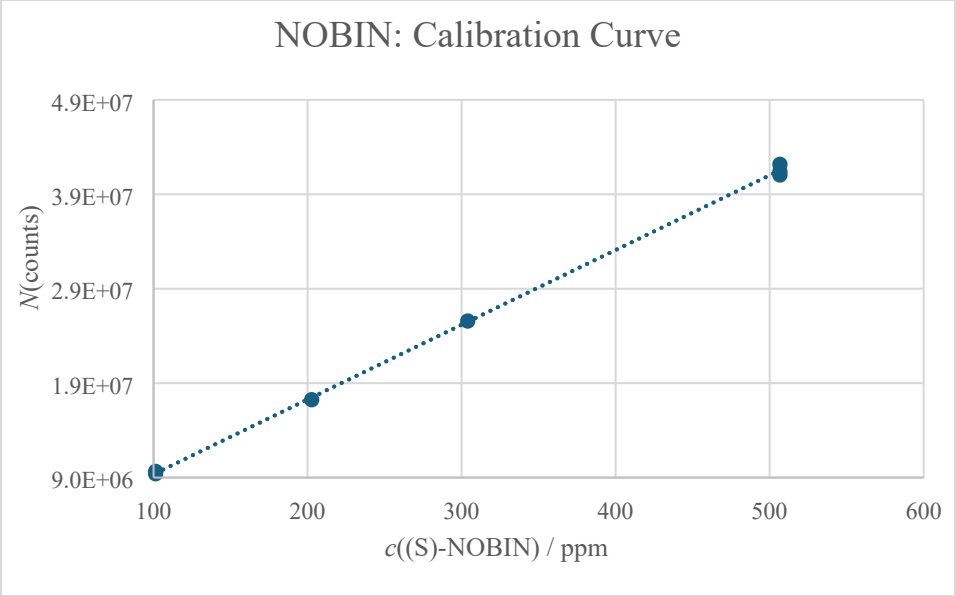
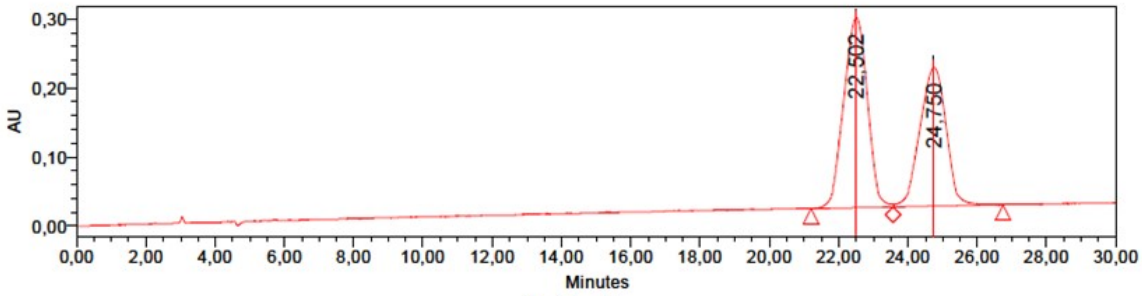


Figure S3. Calibration curve for NOBIN obtained by chiral HPLC. Detector response (counts) is plotted against concentration to generate the calibration curve used for quantification.

3. Characterization

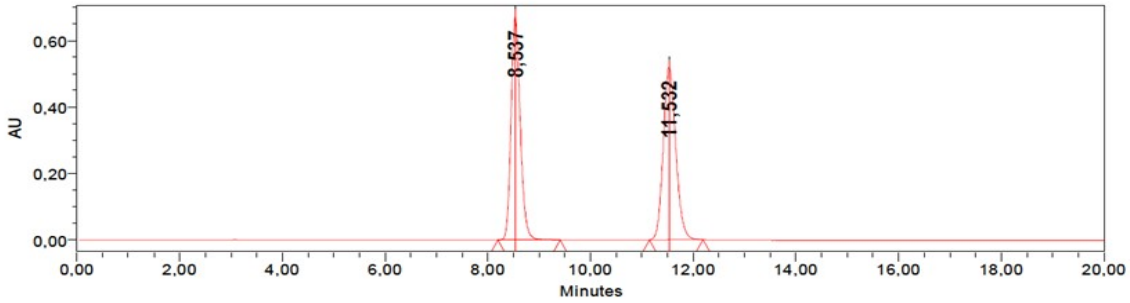
3.1. HPLC analysis



Peak Results

	Name	RT	Area	% Area
1		22,502	13095366	55,32
2		24,750	10578357	44,68

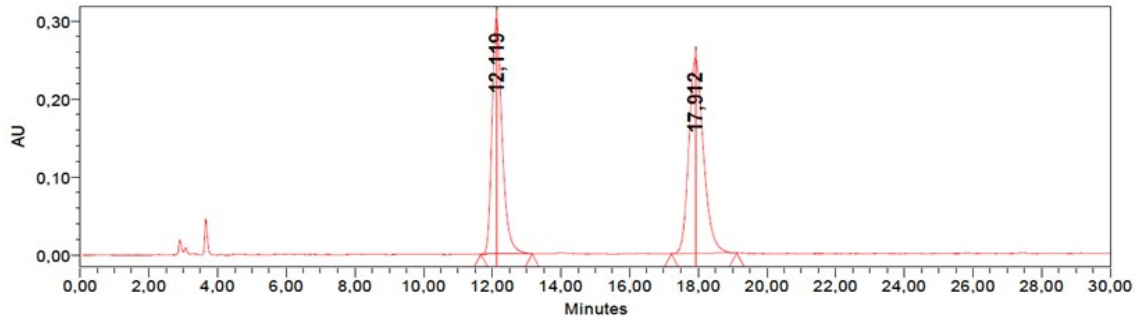
Figure S4. HPLC analysis for the mixture of *(S)*- and *(R)*-BINOL. *(S)*-BINOL elutes at 22.5 min, *(R)*-BINOL elutes at 24.8 min.



Peak Results

	Name	RT	Area	% Area
1		8,537	8337627	48,97
2		11,532	8689326	51,03

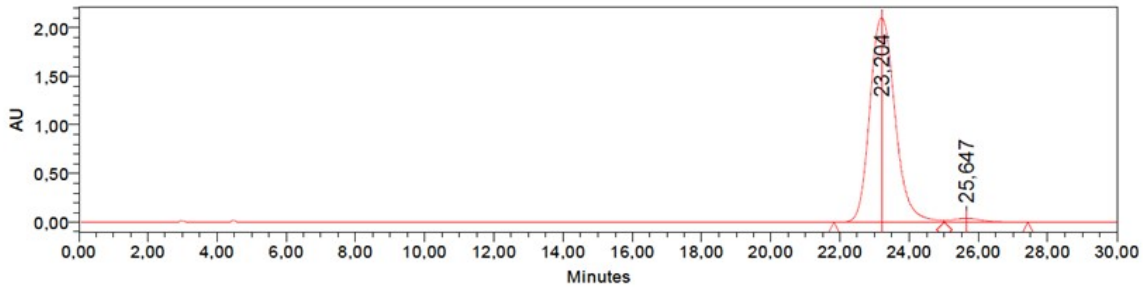
Figure S5. HPLC analysis for rac-BINAM. *(R)*-BINAM elutes at 8.5 min, *(S)*-BINAM elutes at 11.5 min.



Peak Results

	Name	RT	Area	% Area
1		12,119	6233318	45,53
2		17,912	7457696	54,47

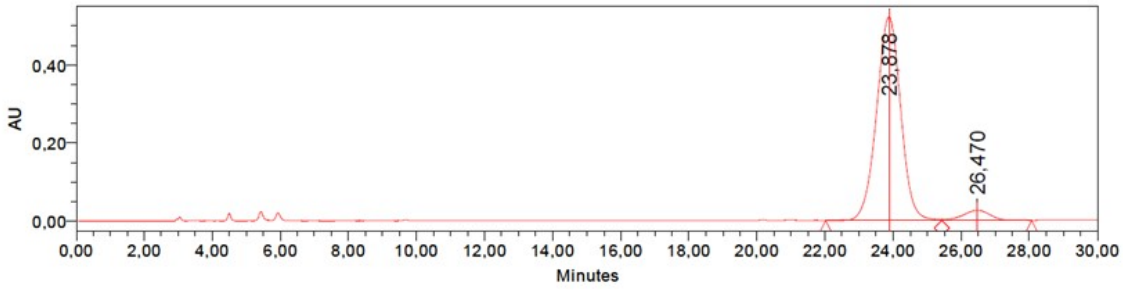
Figure S6. HPLC analysis for the mixture of *(S)*- and *(R)*-NOBIN. *(R)*-NOBIN elutes at 12.1 min, *(S)*-NOBIN elutes at 17.9 min.



Peak Results

	Name	RT	Area	% Area
1		23,204	106458688	98,01
2		25,647	2166915	1,99

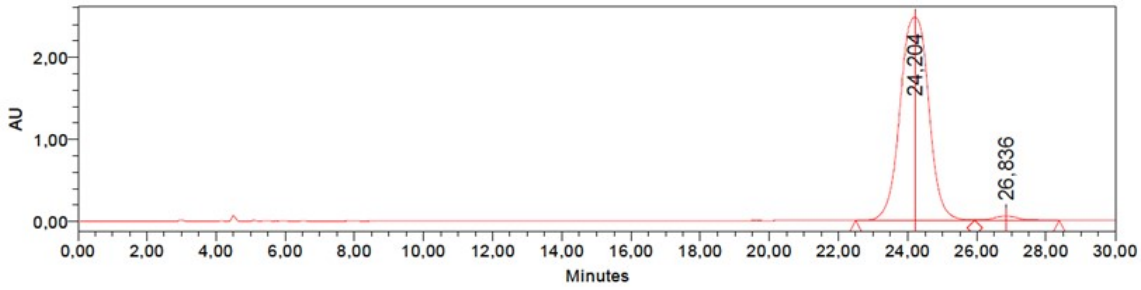
Figure S7. HPLC analysis for Table S1, entry 1: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG, 1.5 h.



Peak Results

	Name	RT	Area	% Area
1		23,878	25429831	94,69
2		26,470	1425061	5,31

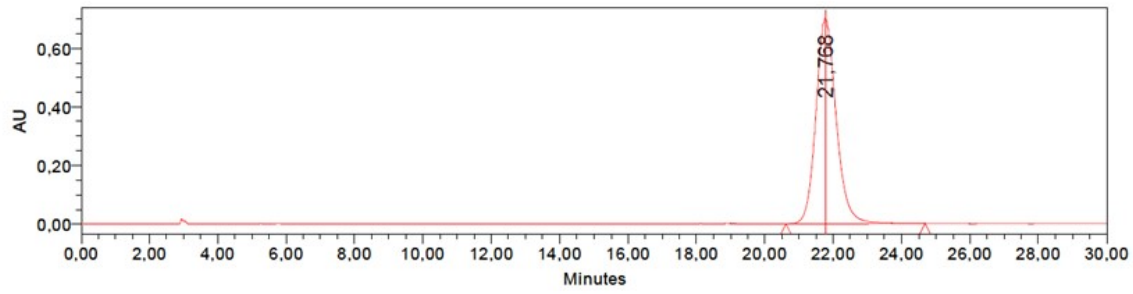
Figure S8. HPLC analysis Table S1, entry 2: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		24,204	142176904	98,26
2		26,836	2516980	1,74

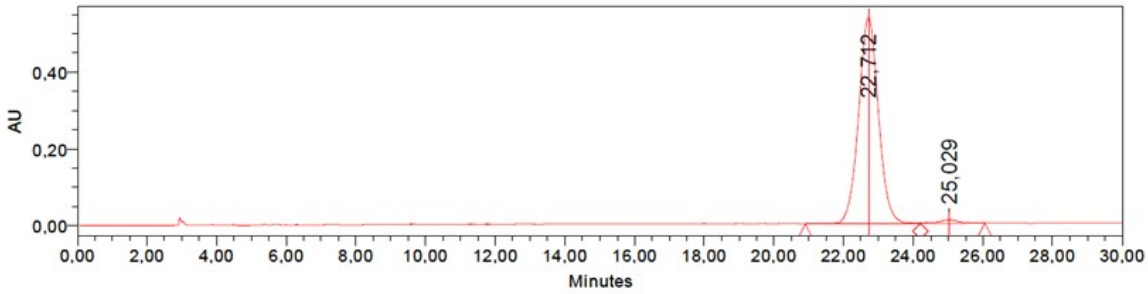
Figure S9. HPLC analysis for Table S1, entry 3: *(S)*-BINOL with 1.0 eq. pyrrolidine, NG, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		21,768	28576568	100,00

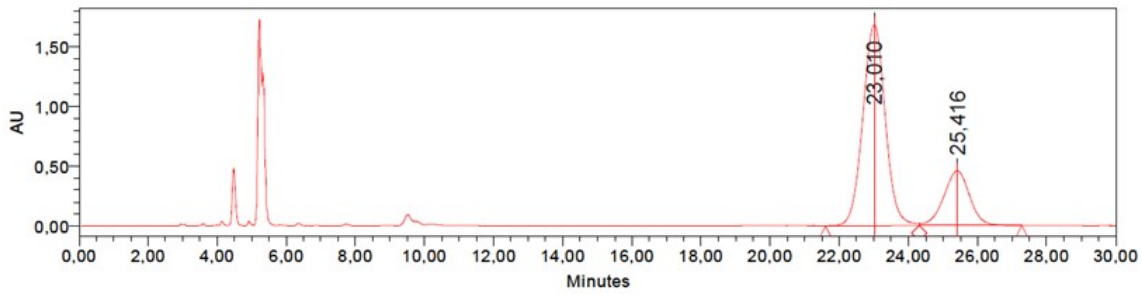
Figure S10. HPLC analysis for Table S1, entry 4: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG with NaCl, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		22,712	21331544	98,34
2		25,029	360514	1,66

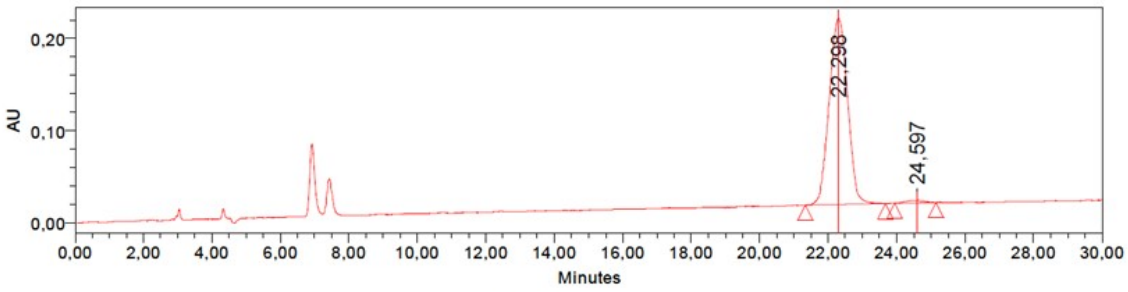
Figure S11. HPLC analysis for Table S1, entry 5: *(S)*-BINOL with 0.1 eq. pyrrolidine, LAG with NaCl, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		23,010	76059586	76,18
2		25,416	23777120	23,82

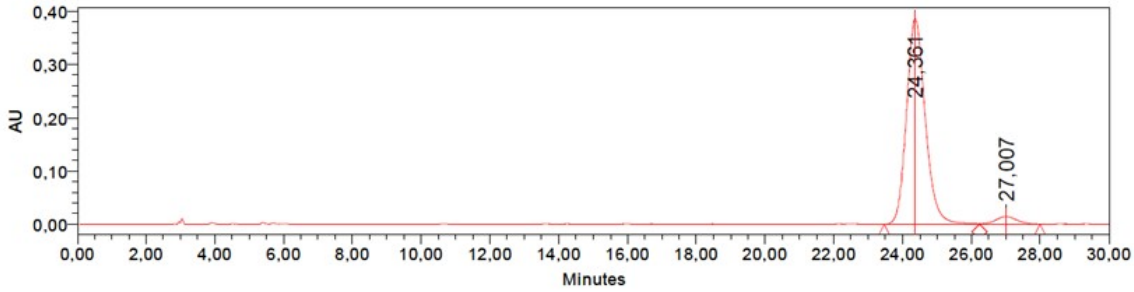
Figure S12. HPLC analysis for Table S1, entry 6: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG, 24 h. Peak at ~5.5 min corresponds to side reaction products and does not impact main analyte quantification.



Peak Results

	Name	RT	Area	% Area
1		22,298	7535945	98,64
2		24,597	104279	1,36

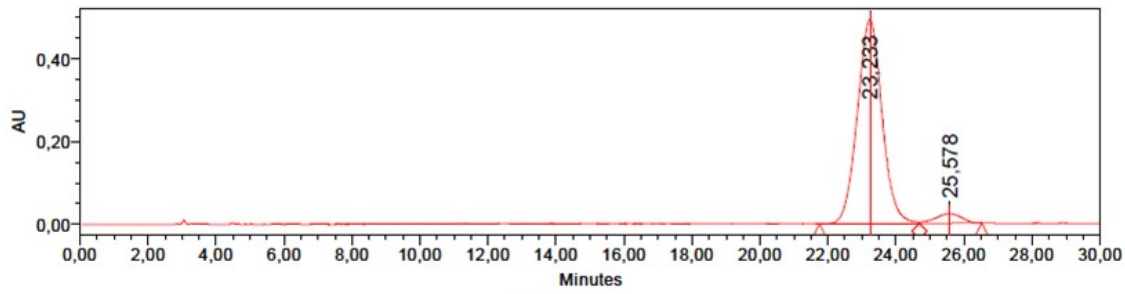
Figure S13. HPLC analysis for Table S1, entry 7: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG with NaCl, 24 h. Peaks at ~7 min correspond to side reaction products and do not impact main analyte quantification.



Peak Results

	Name	RT	Area	% Area
1		24,361	14645924	96,08
2		27,007	597958	3,92

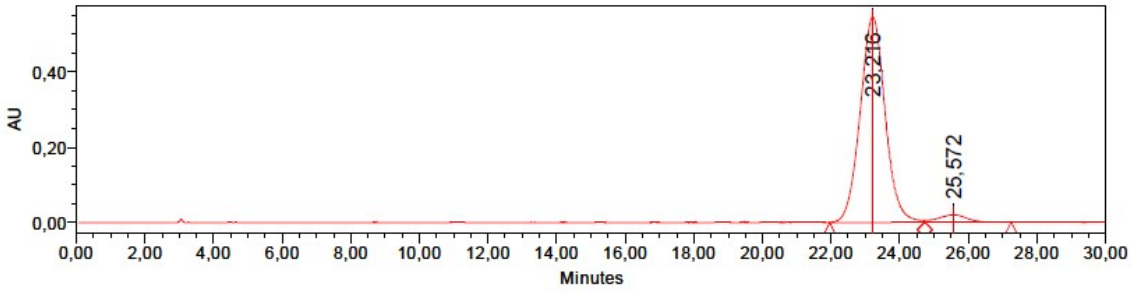
Figure S14. HPLC analysis for Table S1, entry 8: *(S)*-BINOL with 0.1 eq. pyrrolidine, LAG with NaCl, 24 h, sample #1.



Peak Results

	Name	RT	Area	% Area
1		23,233	24747324	95,25
2		25,578	1233288	4,75

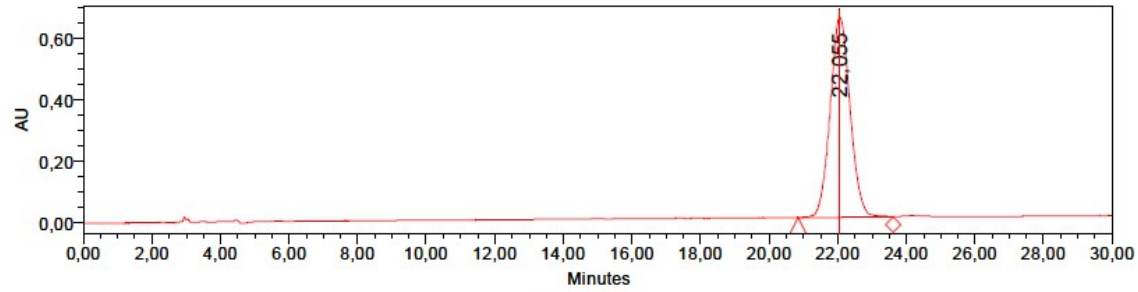
Figure S15. HPLC analysis for Table S1, entry 8: *(S)*-BINOL with 0.1 eq. pyrrolidine, LAG with NaCl, 24 h, sample #2.



Peak Results

	Name	RT	Area	% Area
1		23,216	27590272	96,09
2		25,572	1122305	3,91

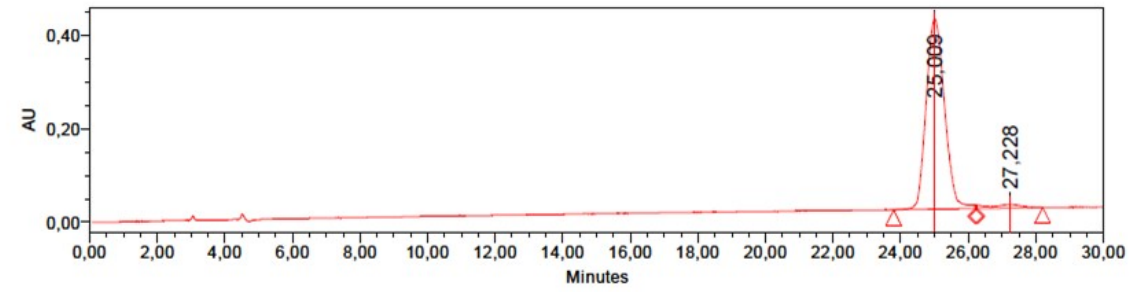
Figure S16. HPLC analysis for Table S1, entry 8: *(S)*-BINOL with 0.1 eq. pyrrolidine, LAG with NaCl, 24 h, sample #3.



Peak Results

	Name	RT	Area	% Area
1		22,055	26243865	100,00

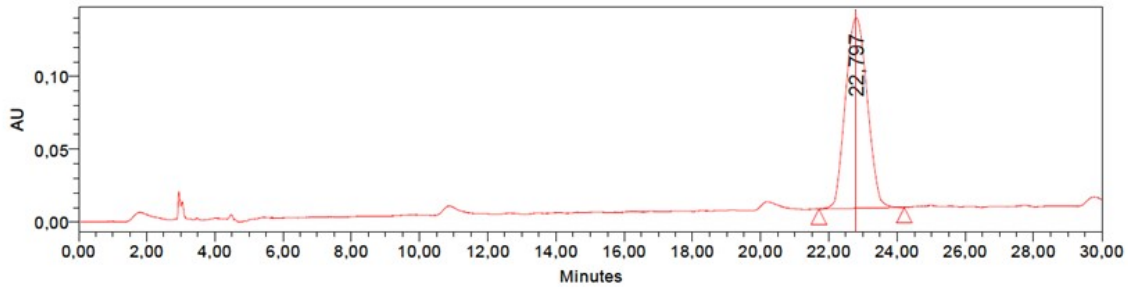
Figure S17. HPLC analysis for Table S1, entry 9: *(S)*-BINOL with 0.1 eq. DBU, 1.5 h.



Peak Results

	Name	RT	Area	% Area
1		25,009	15423295	96,94
2		27,228	487315	3,06

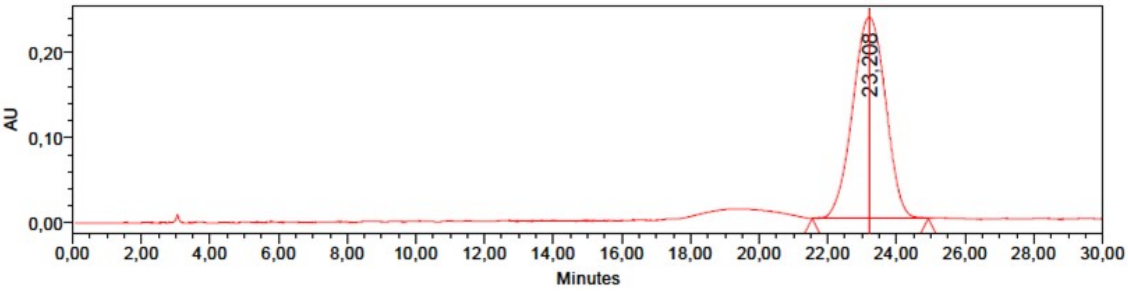
Figure S18. HPLC analysis for Table S1, entry 10: *(S)*-BINOL with 0.1 eq. DBU, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		22,797	5856286	100,00

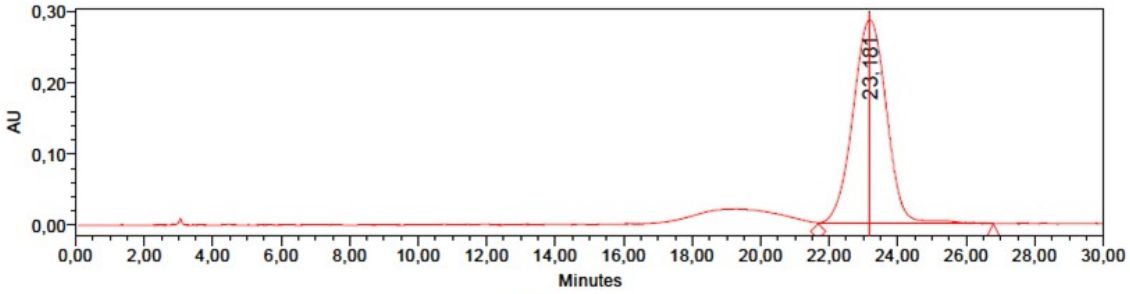
Figure S19. HPLC analysis for Table S1, entry 11: *(S)*-BINOL with 1.0 eq. DBU, NG, 4.5 h. Peaks at ~11 min and ~20 min correspond to side reaction products and do not impact main analyte quantification.



Peak Results

	Name	RT	Area	% Area
1		23,208	15717700	100,00

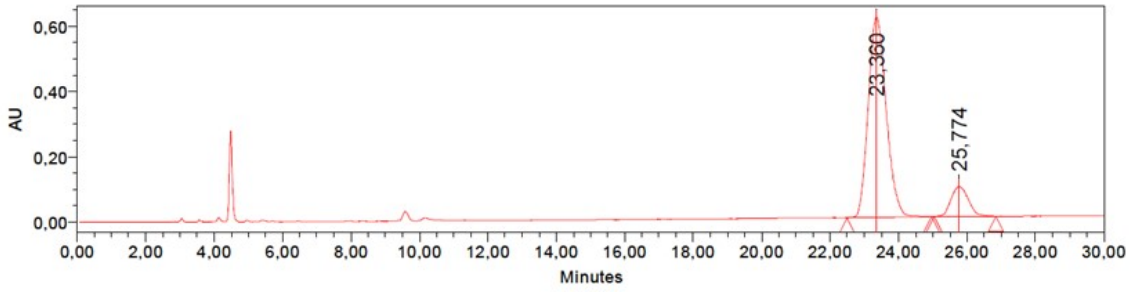
Figure S20. HPLC analysis for Table S1, entry 12: *(S)*-BINOL with 0.1 eq. DBU, NG with NaCl, 4.5 h. Peak at and ~20 min corresponds to side reaction products and do not impact main analyte quantification.



Peak Results

	Name	RT	Area	% Area
1		23,181	19653961	100,00

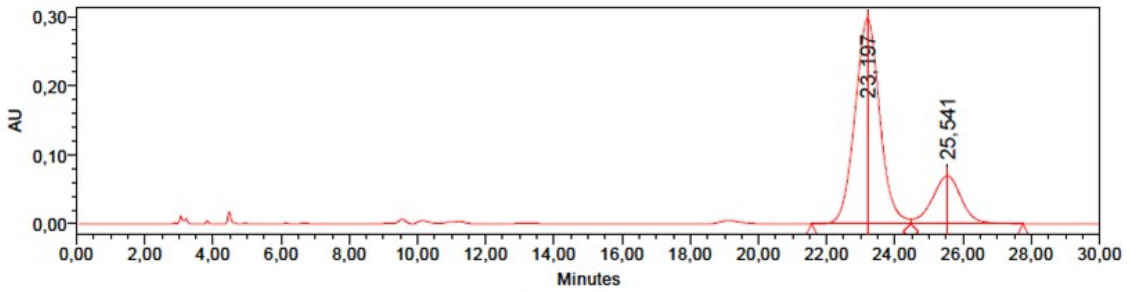
Figure S21. HPLC analysis for Table S1, entry 13: *(S)*-BINOL with 0.1 eq. DBU, LAG with NaCl, 4.5 h. Peak at and ~20 min corresponds to side reaction products and do not impact main analyte quantification.



Peak Results

	Name	RT	Area	% Area
1		23,360	22367706	87,42
2		25,774	3218003	12,58

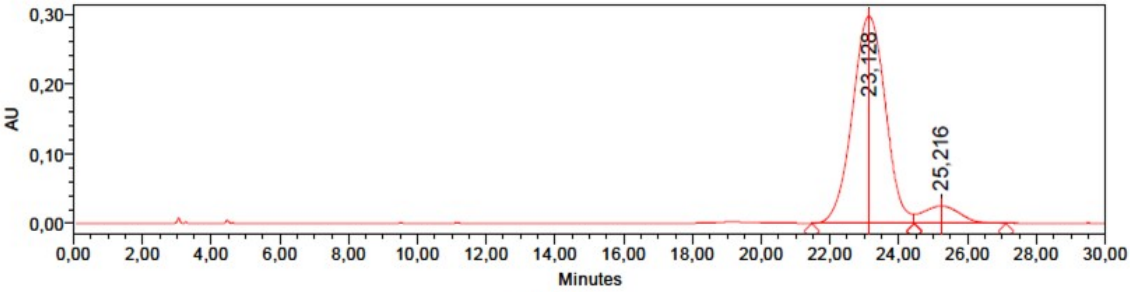
Figure S22. HPLC analysis for Table S1, entry 14: *(S)*-BINOL with 0.1 eq. DBU, 24 h.



Peak Results

	Name	RT	Area	% Area
1		23,197	15022348	78,66
2		25,541	4074436	21,34

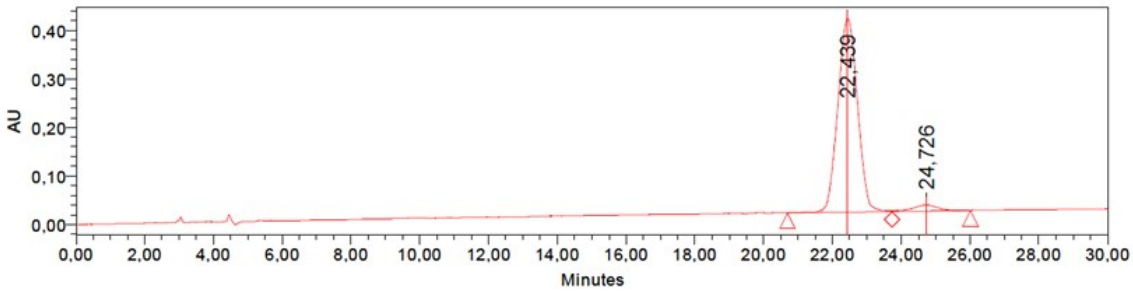
Figure S23. HPLC analysis for Table S1, entry 15: *(S)*-BINOL with 0.1 eq. DBU, NG with NaCl, 24 h.



Peak Results

	Name	RT	Area	% Area
1		23,128	19914705	91,37
2		25,216	1880209	8,63

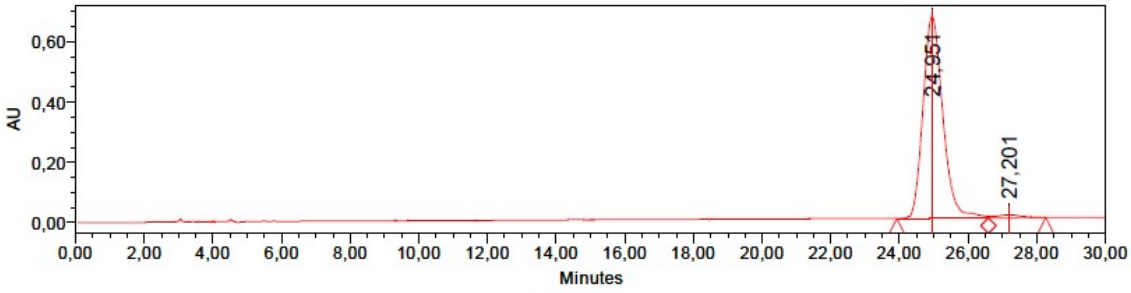
Figure S24. HPLC analysis for Table S1, entry 16: *(S)*-BINOL with 0.1 eq. DBU, LAG with NaCl, 24 h.



Peak Results

	Name	RT	Area	% Area
1		22,439	15868010	96,05
2		24,726	652783	3,95

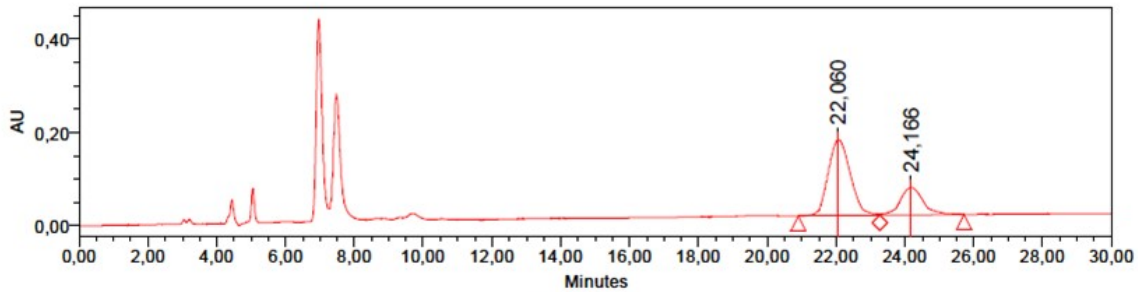
Figure S25. HPLC analysis for Table S1, entry 17: *(S)*-BINOL with 1.0 eq. K_2CO_3, NG, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		24,951	26909751	98,31
2		27,201	463868	1,69

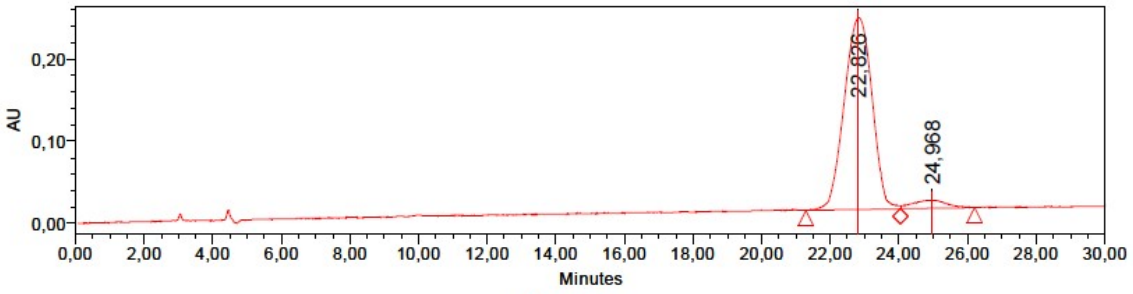
Figure S26. HPLC analysis for Table S1, entry 18: *(S)*-BINOL with 1 eq. K_2CO_3, LAG, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		22,060	7233544	72,74
2		24,166	2710494	27,26

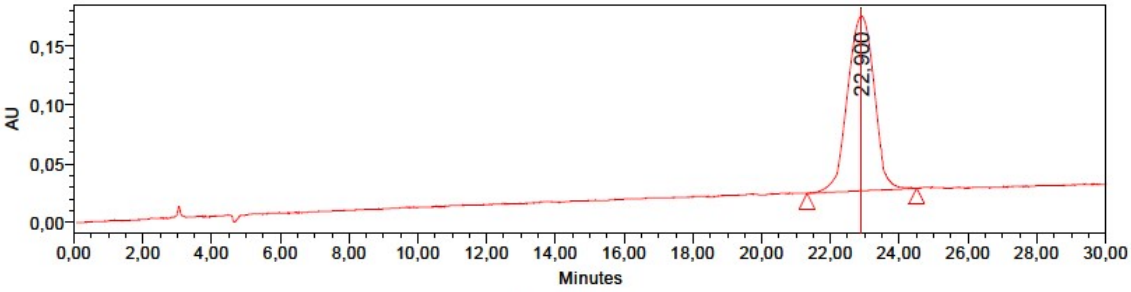
Figure S27. HPLC analysis for Table S1, entry 19: *(S)*-BINOL with 1.0 eq. K_2CO_3, NG, 24 h. Peaks at ~5.5 min and at ~7 min correspond to side reaction products and do not impact main analyte quantification.



Peak Results

	Name	RT	Area	% Area
1		22,826	13237765	95,04
2		24,968	691179	4,96

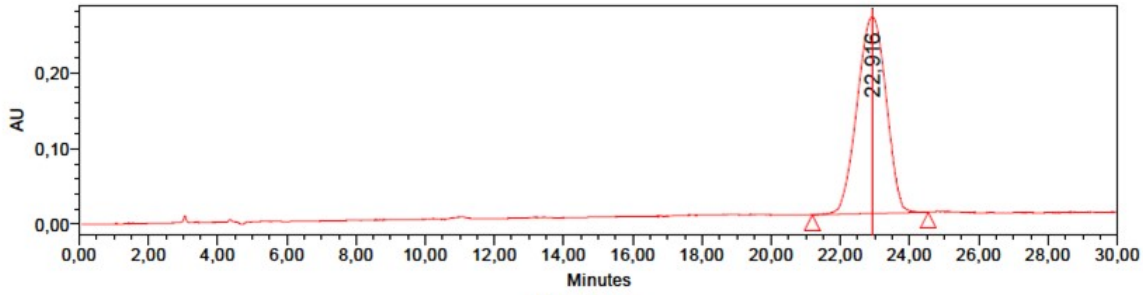
Figure S28. HPLC analysis for Table S1, entry 20: *(S)*-BINOL with 1 eq. K_2CO_3, LAG, 24 h.



Peak Results

	Name	RT	Area	% Area
1		22,900	8031553	100,00

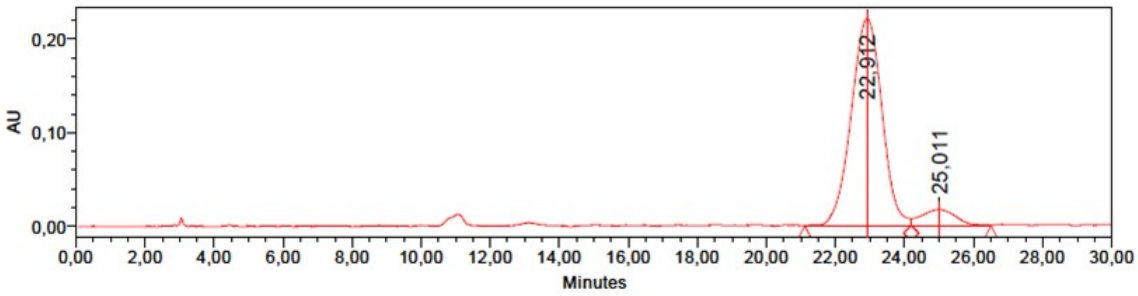
Figure S29. HPLC analysis for Table S1, entry 21: *(S)*-BINOL with 1 eq. K_2CO_3, NG with NaCl, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		22,916	15152734	100,00

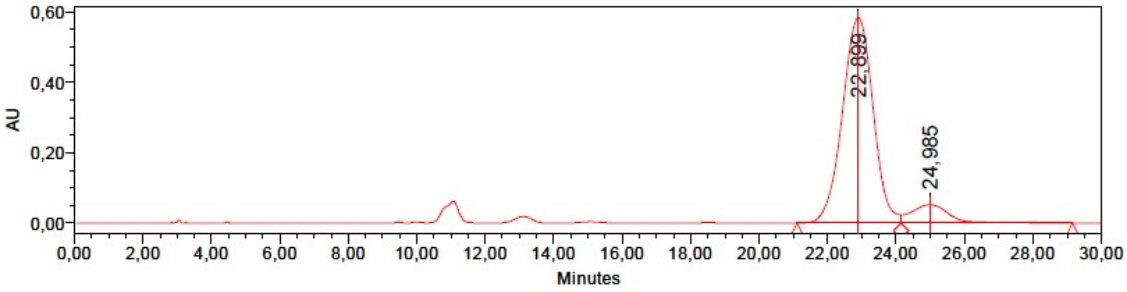
Figure S30. HPLC analysis for Table S1, entry 22: *(S)*-BINOL with 1 eq. K_2CO_3, LAG with NaCl, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		22,912	13680916	92,15
2		25,011	1165217	7,85

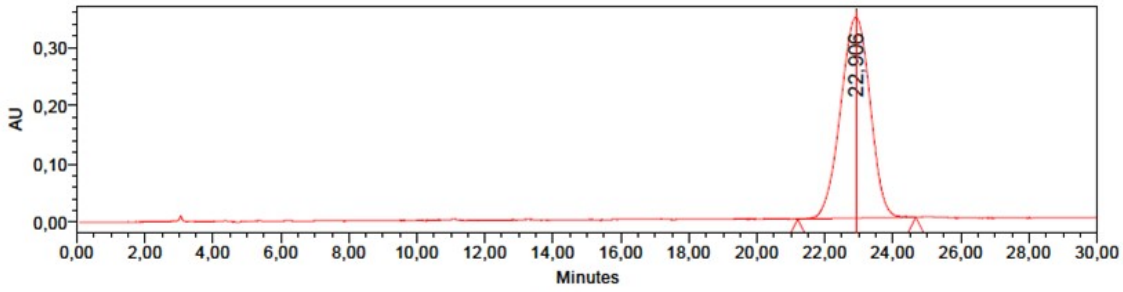
Figure S31. HPLC analysis for Table S1, entry 23: *(S)*-BINOL with 1 eq. K_2CO_3, NG with NaCl, 24 h.



Peak Results

	Name	RT	Area	% Area
1		22,899	36477953	90,36
2		24,985	3889475	9,64

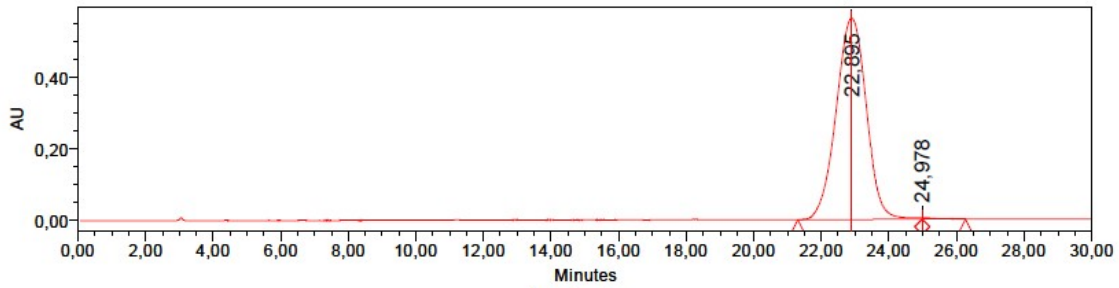
Figure S32. HPLC analysis for Table S1, entry 24: *(S)*-BINOL with 1 eq. K_2CO_3, LAG with NaCl, 24 h.



Peak Results

	Name	RT	Area	% Area
1		22,906	20847341	100,00

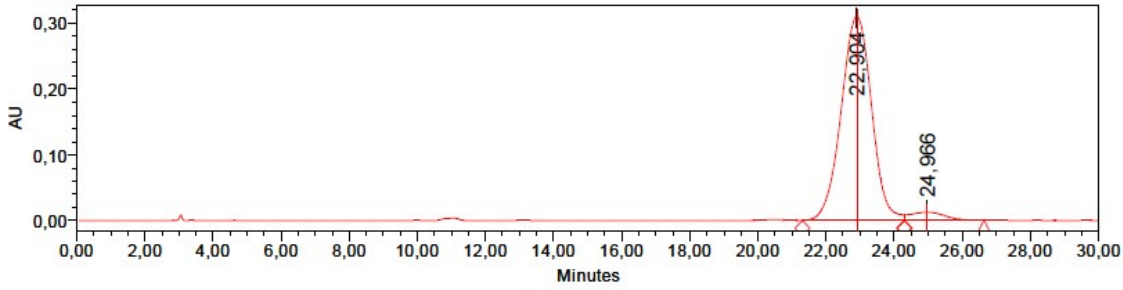
Figure S33. HPLC analysis for Table S1, entry 25: *(S)*-BINOL with 25 eq. K_2CO_3, NG, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		22,895	35023296	99,59
2		24,978	145593	0,41

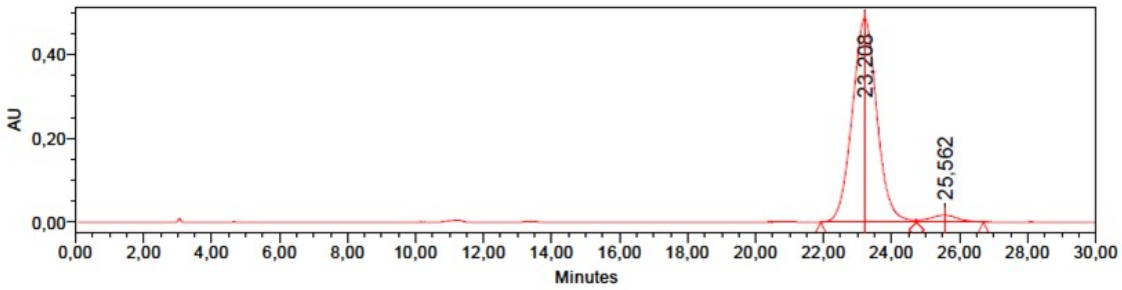
Figure S34. HPLC analysis for Table S1, entry 26: *(S)*-BINOL with 25 eq. K_2CO_3, LAG, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		22,904	19319983	95,69
2		24,966	869272	4,31

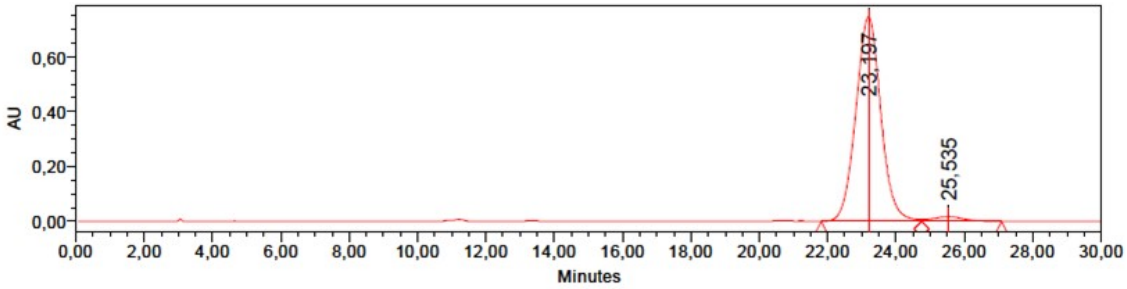
Figure S35. HPLC analysis for Table S1, entry 27: *(S)*-BINOL with 25 eq. K_2CO_3, NG, 24 h, sample #1.



Peak Results

	Name	RT	Area	% Area
1		23,208	24457087	96,30
2		25,562	939123	3,70

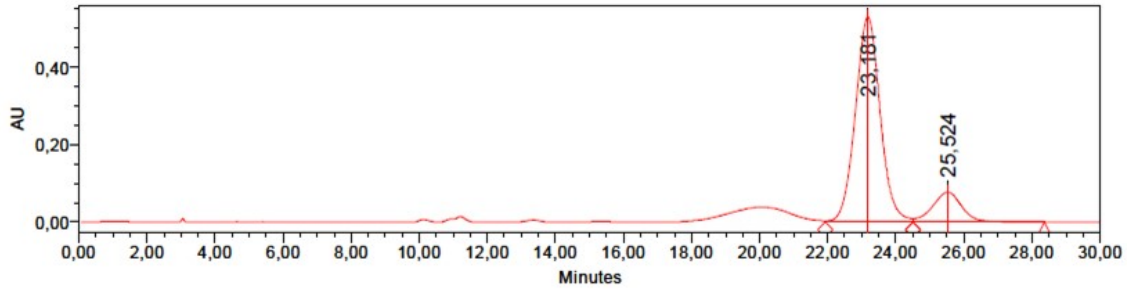
Figure S36. HPLC analysis for Table S1, entry 27: *(S)*-BINOL with 25 eq. K_2CO_3, NG, 24 h, sample #2.



Peak Results

	Name	RT	Area	% Area
1		23,197	37911524	97,22
2		25,535	1083276	2,78

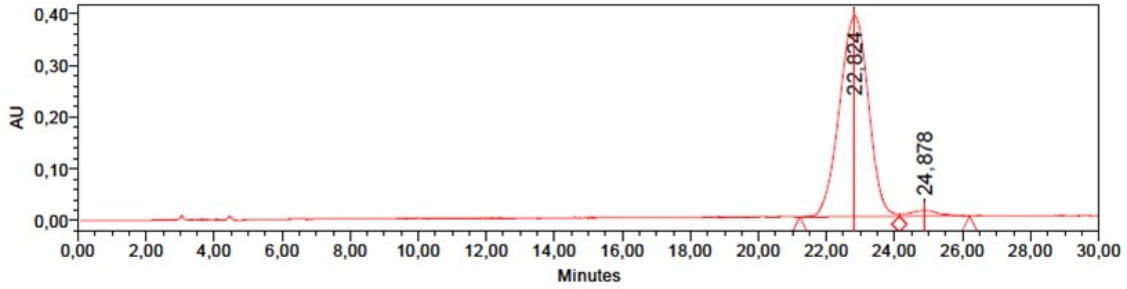
Figure S37. HPLC analysis for Table S1, entry 27: *(S)*-BINOL with 25 eq. K_2CO_3, NG, 24 h, sample #3.



Peak Results

	Name	RT	Area	% Area
1		23,181	26787705	85,39
2		25,524	4583915	14,61

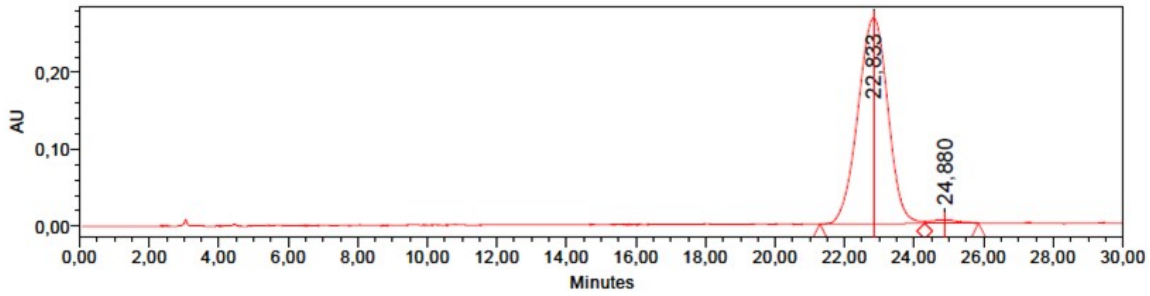
Figure S38. HPLC analysis for Table S1, entry 28: *(S)*-BINOL with 25 eq. K_2CO_3, LAG, 24 h.



Peak Results

	Name	RT	Area	% Area
1		22,824	22994331	97,28
2		24,878	644045	2,72

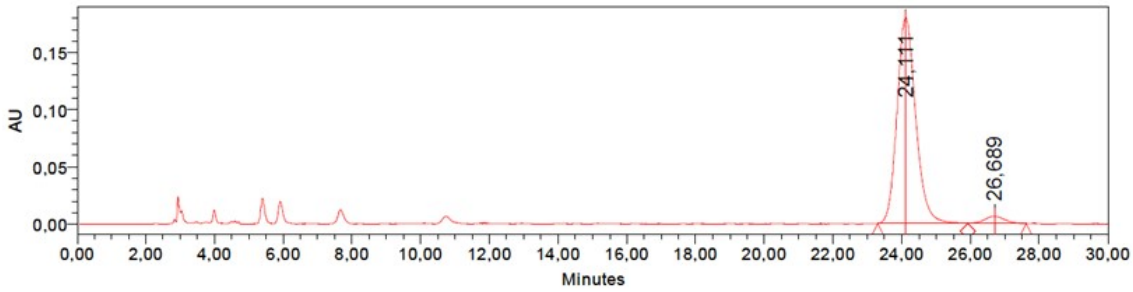
Figure S39. HPLC analysis for Table S1, entry 29: *(S)*-BINOL with 1 eq. Cs_2CO_3, NG, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		22,833	16006886	98,43
2		24,880	255756	1,57

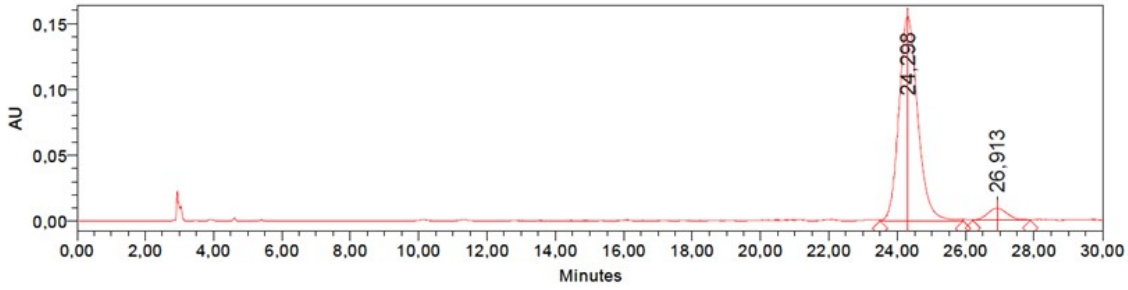
Figure S40. HPLC analysis for Table S1, entry 30: *(S)*-BINOL with 1 eq. Cs_2CO_3, LAG, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		24,111	6770520	96,24
2		26,689	264455	3,76

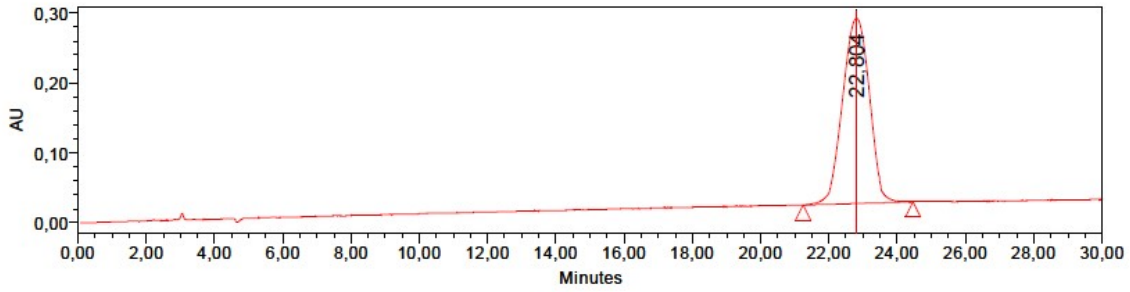
Figure S41. HPLC analysis for Table S1, entry 31: *(S)*-BINOL with 1.0 eq. Cs_2CO_3, NG, 24 h. Peaks in the range from 3 min to 11 min correspond to side reaction products and do not impact main analyte quantification.



Peak Results

	Name	RT	Area	% Area
1		24,298	5905625	93,86
2		26,913	386210	6,14

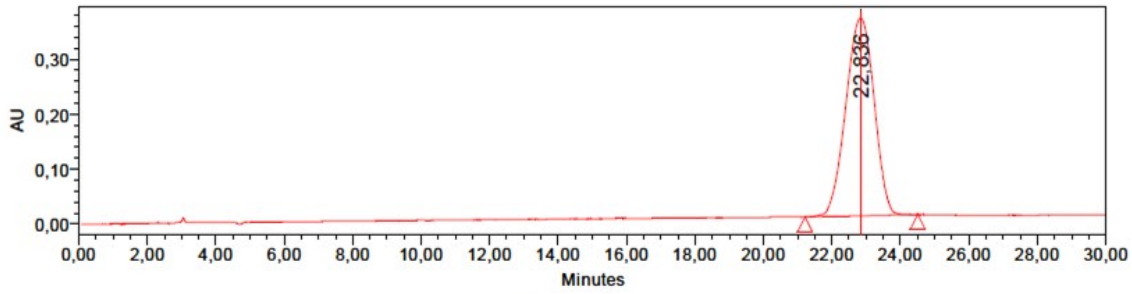
Figure S42. HPLC analysis for Table S1, entry 32: *(S)*-BINOL with 1.0 eq. Cs_2CO_3, LAG, 24 h.



Peak Results

	Name	RT	Area	% Area
1		22,804	14530385	100,00

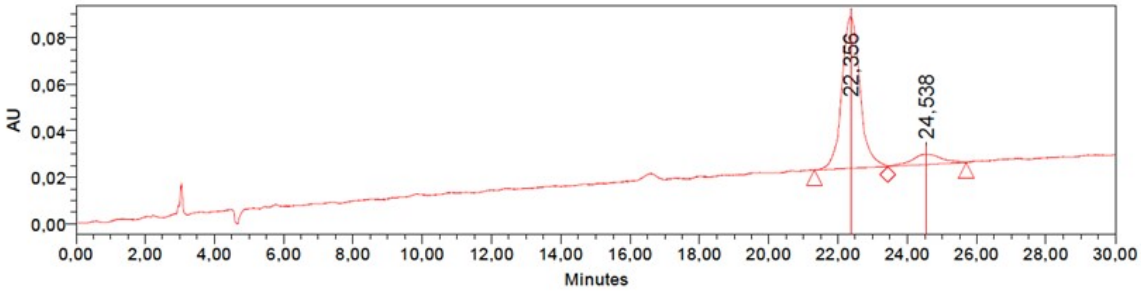
Figure S43. HPLC analysis for Table S1, entry 33: *(S)*-BINOL with 1 eq. Cs_2CO_3, NG with NaCl, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		22,836	20813832	100,00

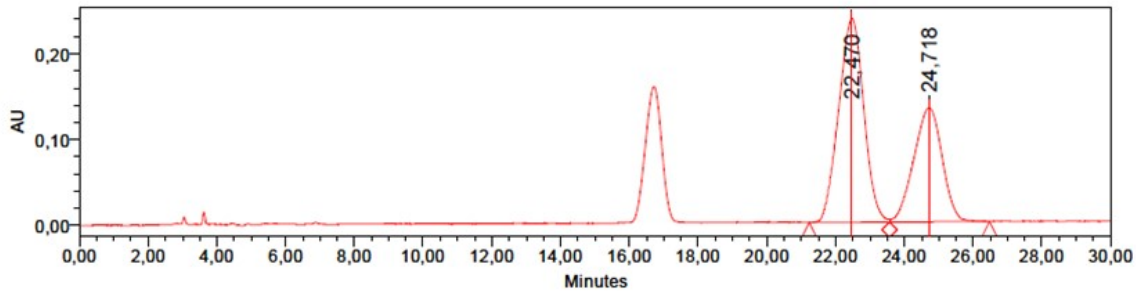
Figure S44. HPLC analysis for Table S1, entry 34: *(S)*-BINOL with 1 eq. Cs_2CO_3, LAG with NaCl, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		22,356	2384063	89,94
2		24,538	266571	10,06

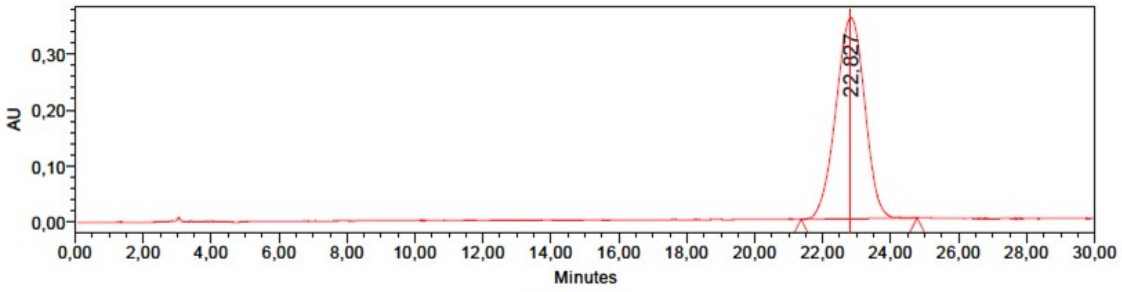
Figure S45. HPLC analysis for Table S1, entry 35: *(S)*-BINOL with 1.0 eq. Cs_2CO_3, NG with NaCl, 24 h. Due to small concentration of the analyte, baseline is increasing, which does not affect the main analyte quantification.



Peak Results

	Name	RT	Area	% Area
1		22,470	12056709	61,27
2		24,718	7621560	38,73

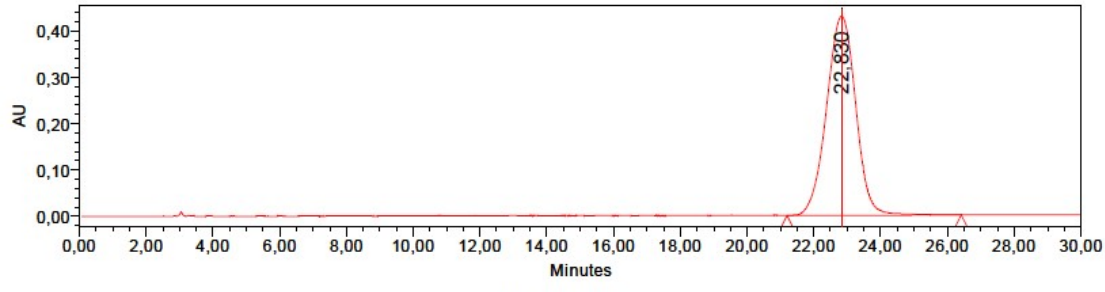
Figure S46. HPLC analysis for Table S1, entry 36: *(S)*-BINOL with 1.0 eq. Cs_2CO_3, LAG with NaCl, 24 h. Peak at ~17 min corresponds to side reaction product and does not impact main analyte quantification.



Peak Results

	Name	RT	Area	% Area
1		22,827	21249211	100,00

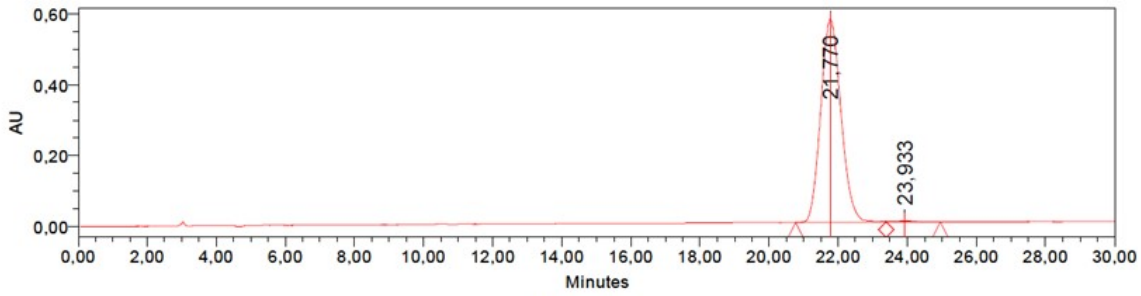
Figure S47. HPLC analysis for Table S1, entry 37: *(S)*-BINOL with 25 eq. Cs_2CO_3, NG, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		22,830	26280101	100,00

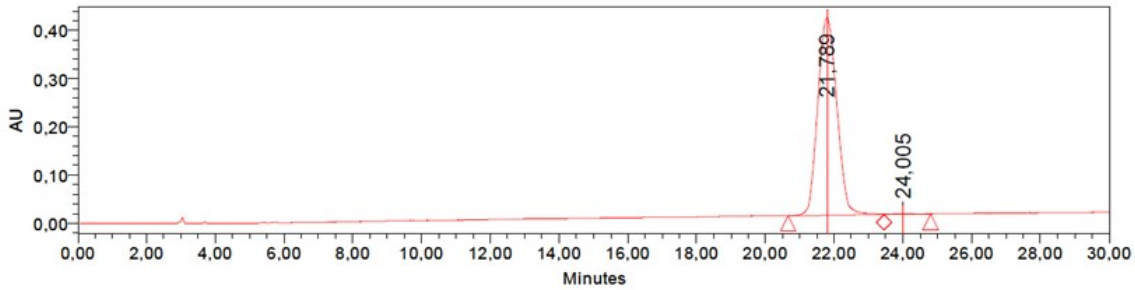
Figure S48. HPLC analysis for Table S1, entry 38: *(S)*-BINOL with 25 eq. Cs_2CO_3, LAG, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		21,770	23091278	99,34
2		23,933	152906	0,66

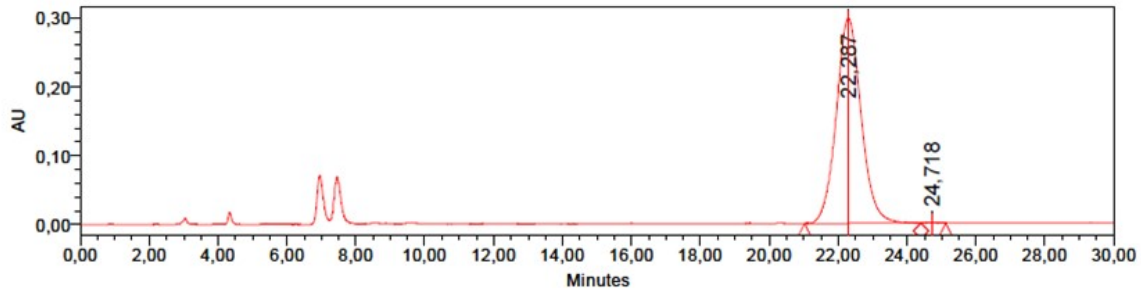
Figure S49. HPLC analysis for Table S1, entry 39: *(S)*-BINOL with 25 eq. Cs_2CO_3, NG, 24 h.



Peak Results

	Name	RT	Area	% Area
1		21,789	15638422	99,58
2		24,005	65247	0,42

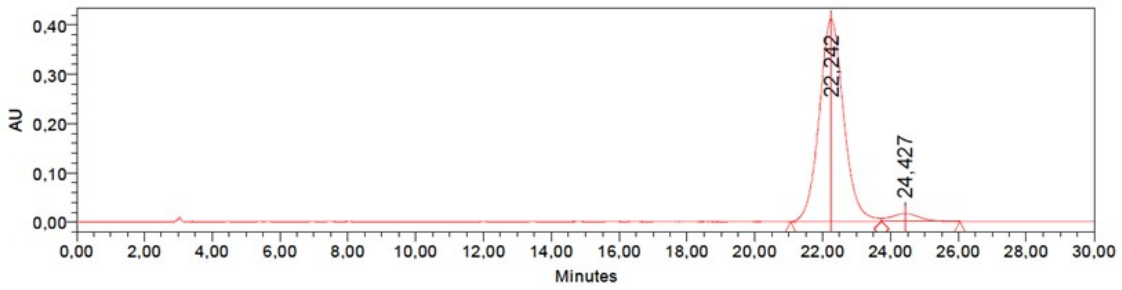
Figure S50. HPLC analysis for Table S1, entry 40: *(S)*-BINOL with 25 eq. Cs_2CO_3, LAG, 24 h.



Peak Results

	Name	RT	Area	% Area
1		22,287	14979189	99,83
2		24,718	26067	0,17

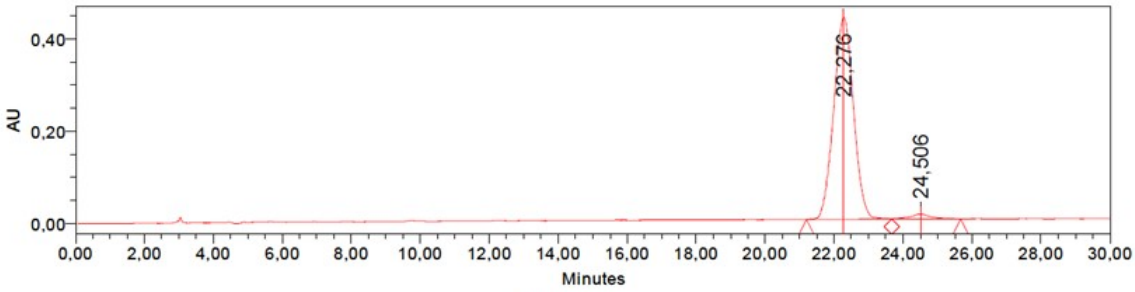
Figure S51. HPLC analysis for Table S1, entry 41: *(S)*-BINOL without base, NG with NaCl, 4.5 h. Peaks at ~17 min correspond to side reaction product and do not impact main analyte quantification.



Peak Results

	Name	RT	Area	% Area
1		22,242	20574362	95,66
2		24,427	933692	4,34

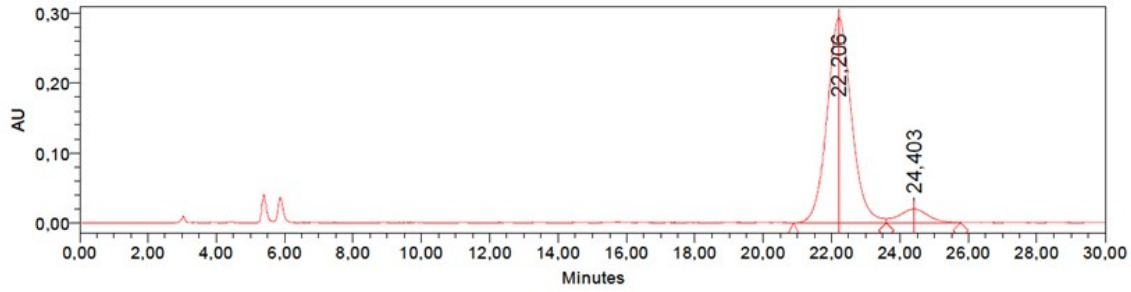
Figure S52. HPLC analysis for Table S1, entry 42: *(S)*-BINOL without base, LAG with NaCl, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		22,276	17494112	97,43
2		24,506	461150	2,57

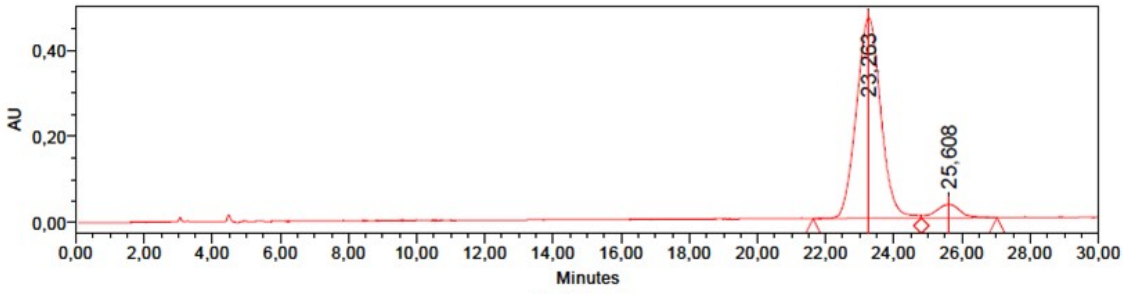
Figure S53. HPLC analysis for Table S1, entry 43: *(S)*-BINOL without base, NG with NaCl, 24 h.



Peak Results

	Name	RT	Area	% Area
1		22,206	14514878	92,72
2		24,403	1139058	7,28

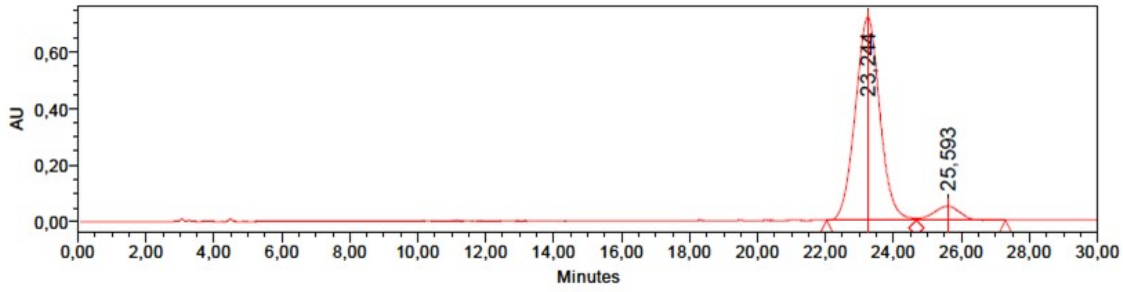
Figure S54. HPLC analysis for Table S1, entry 44: *(S)*-BINOL without base, LAG with NaCl, 24 h, sample #1. Peak at ~5.5 min corresponds to side reaction products and does not impact main analyte quantification.



Peak Results

	Name	RT	Area	% Area
1		23,263	23047202	93,76
2		25,608	1534895	6,24

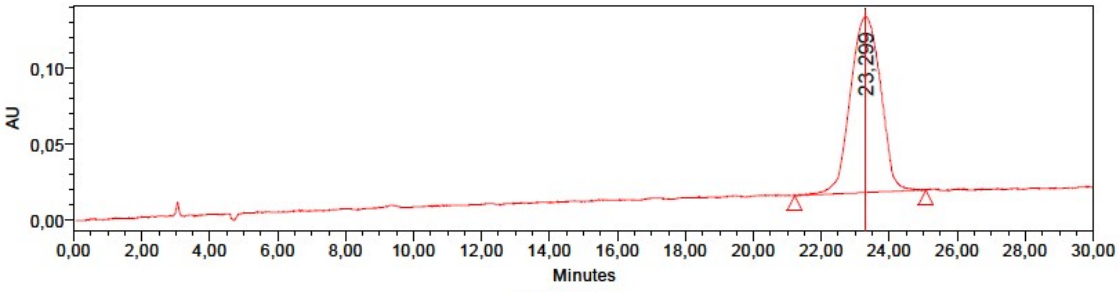
Figure S55. HPLC analysis for Table S1, entry 44: *(S)*-BINOL without base, LAG with NaCl, 24 h, sample #2.



Peak Results

	Name	RT	Area	% Area
1		23,244	35988890	93,04
2		25,593	2690250	6,96

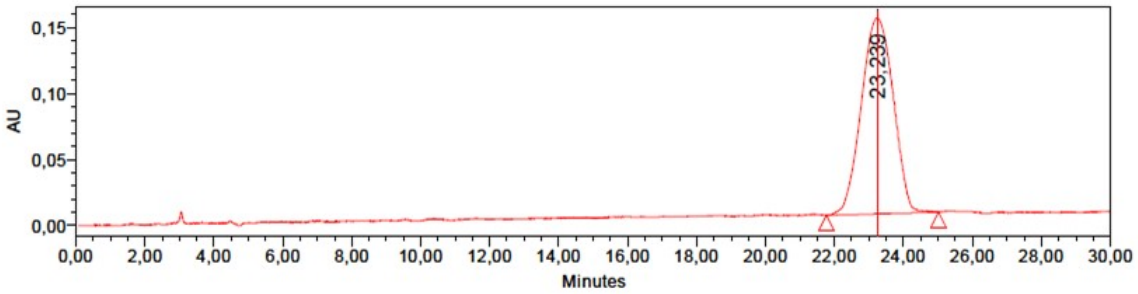
Figure S56. HPLC analysis for Table S1, entry 44: *(S)*-BINOL without base, LAG with NaCl, 24 h, sample #3.



Peak Results

	Name	RT	Area	% Area
1		23,299	7145022	100,00

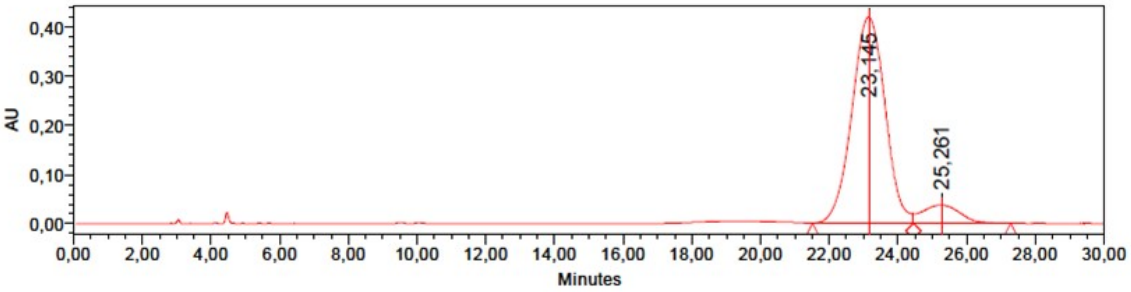
Figure S57. HPLC analysis for Table S1, entry 45: *(S)*-BINOL, 1.5 h.



Peak Results

	Name	RT	Area	% Area
1		23,239	9578540	100,00

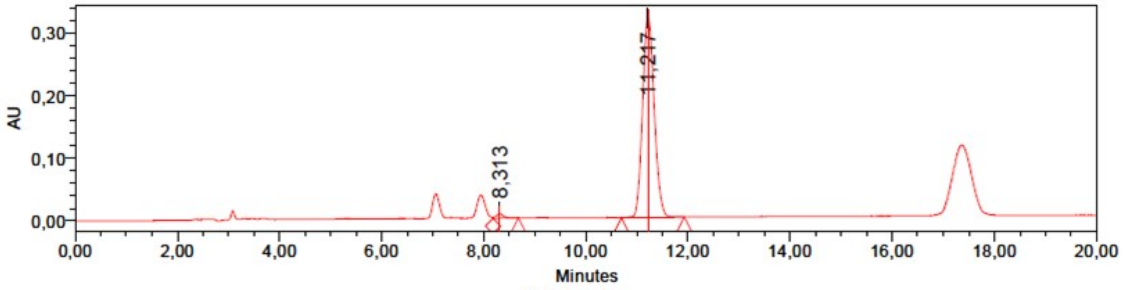
Figure S58. HPLC analysis for Table S1, entry 46: *(S)*-BINOL, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		23,145	28258295	90,99
2		25,261	2798073	9,01

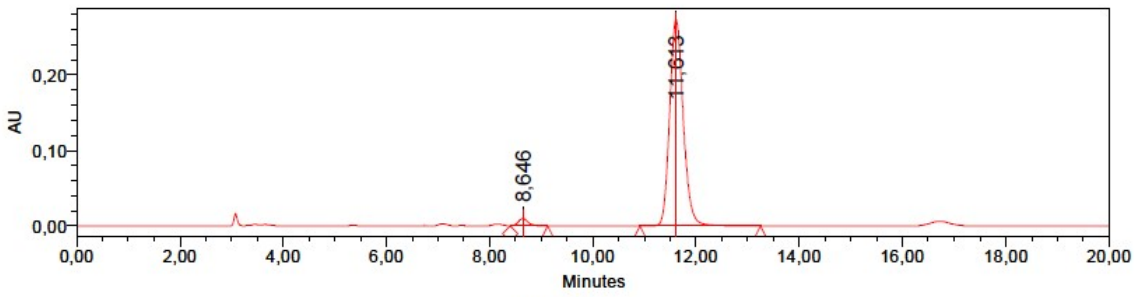
Figure S59. HPLC analysis for Table S1, entry 47: *(S)*-BINOL, 24 h.



Peak Results

	Name	RT	Area	% Area
1		8,313	67860	1,31
2		11,217	5100895	98,69

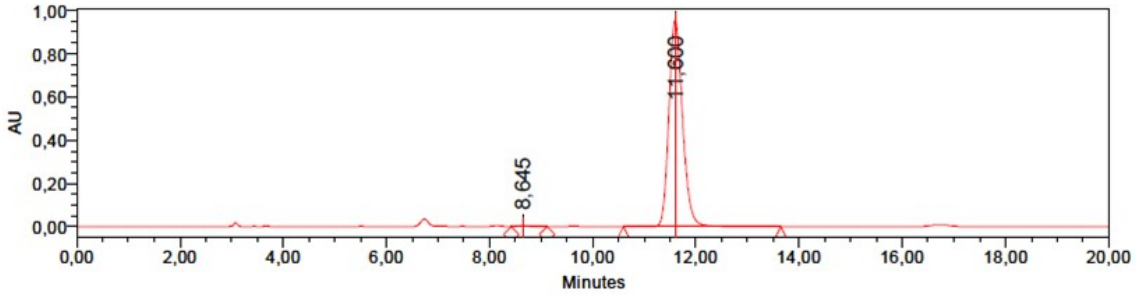
Figure S60. HPLC analysis for Table S2, entry 1: *(S)*-BINAM with 0.1 eq. pyrrolidine, LAG with NaCl, 24 h. Peaks at ~7 min and ~17 min correspond to side reaction products and do not impact main analyte quantification.



Peak Results

	Name	RT	Area	% Area
1		8,646	129504	2,54
2		11,613	4976312	97,46

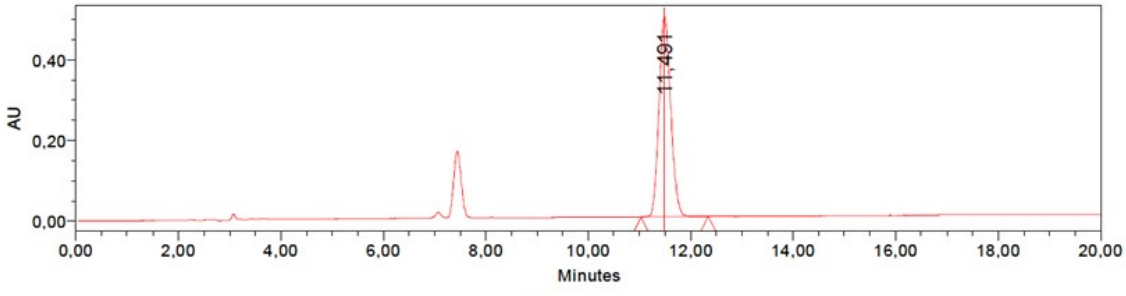
Figure S61. HPLC analysis for Table S2, entry 2. *(S)*-BINAM without base, LAG with NaCl, 24 h.



Peak Results

	Name	RT	Area	% Area
1		8,645	73956	0,42
2		11,600	17529330	99,58

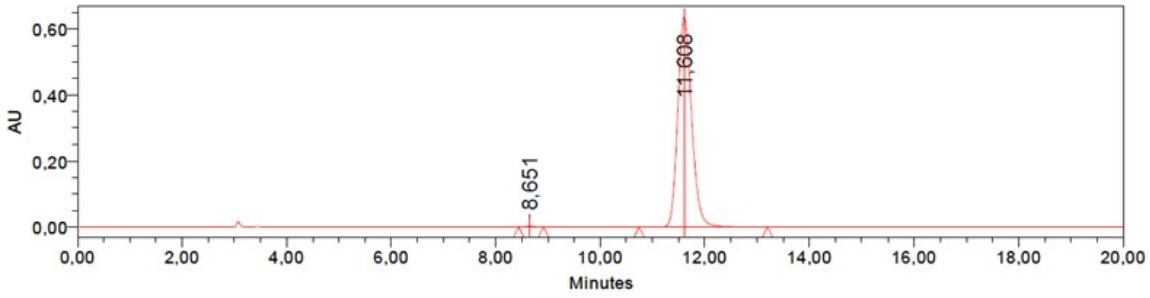
Figure S62. HPLC analysis for Table S2, entry 3: *(S)*-BINAM with 1.0 eq. K_2CO_3, NG, 24 h.



Peak Results

	Name	RT	Area	% Area
1		11,491	7882484	100,00

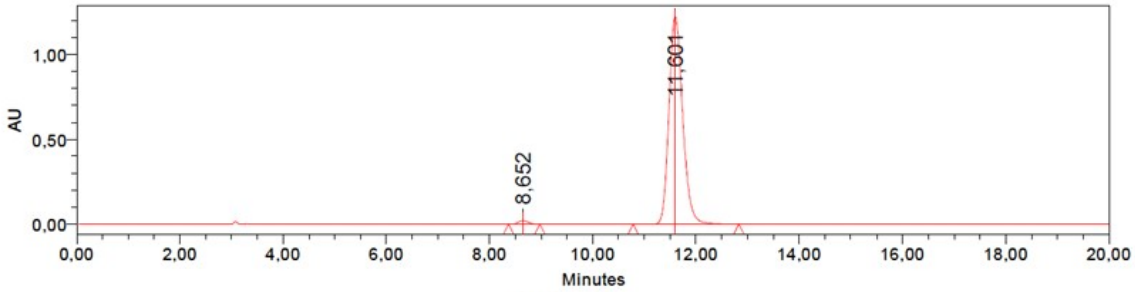
Figure S63. HPLC analysis for Table S2, entry 4: *(S)*-BINAM with 25 eq. K_2CO_3, NG, 24 h.



Peak Results

	Name	RT	Area	% Area
1		8,651	30229	0,26
2		11,608	11619111	99,74

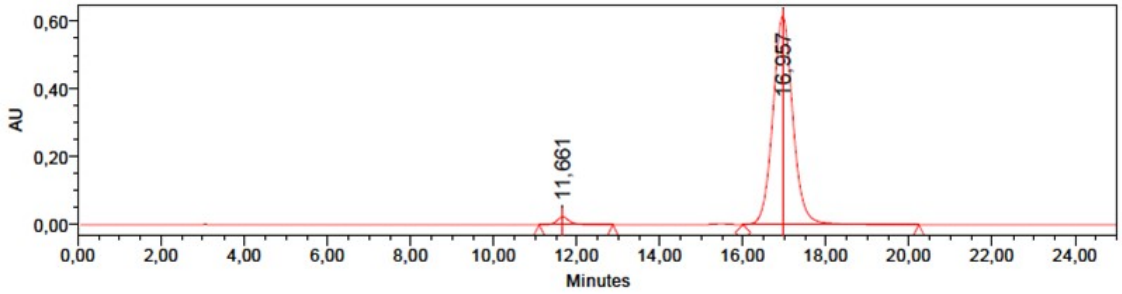
Figure S64. HPLC analysis for Table S2, entry 5: *(S)*-BINAM with 1.0 eq. Cs_2CO_3, NG with NaCl, 24 h.



Peak Results

	Name	RT	Area	% Area
1		8,652	261969	1,15
2		11,601	22460140	98,85

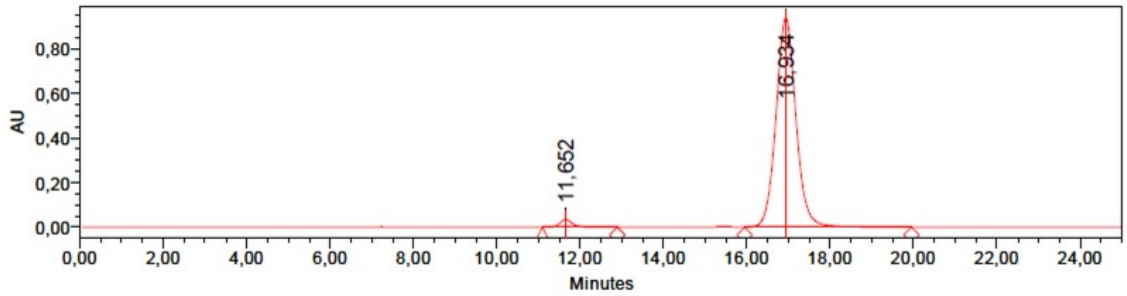
Figure S65. HPLC analysis for Table S2, entry 6: *(S)*-BINAM with 1.0 eq. Cs_2CO_3, NG with NaCl, 24 h.



Peak Results

	Name	RT	Area	% Area
1		11,661	477813	2,25
2		16,957	20719438	97,75

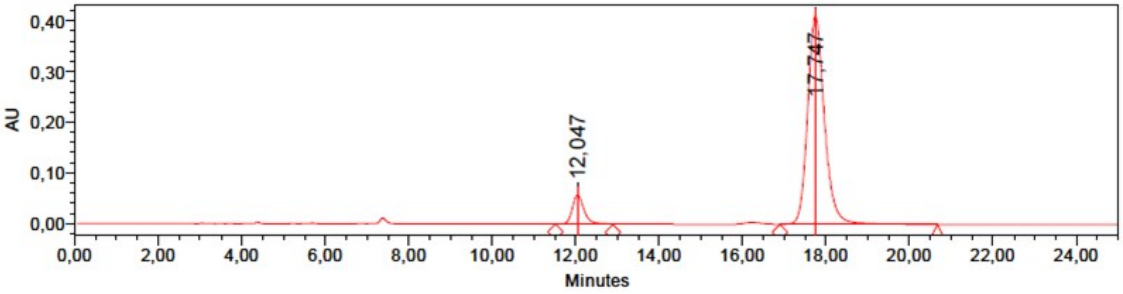
Figure S66. HPLC analysis for Table S2, entry 7: *(S)*-BINAM, 1.5 h.



Peak Results

	Name	RT	Area	% Area
1		11,652	739185	2,29
2		16,934	31470399	97,71

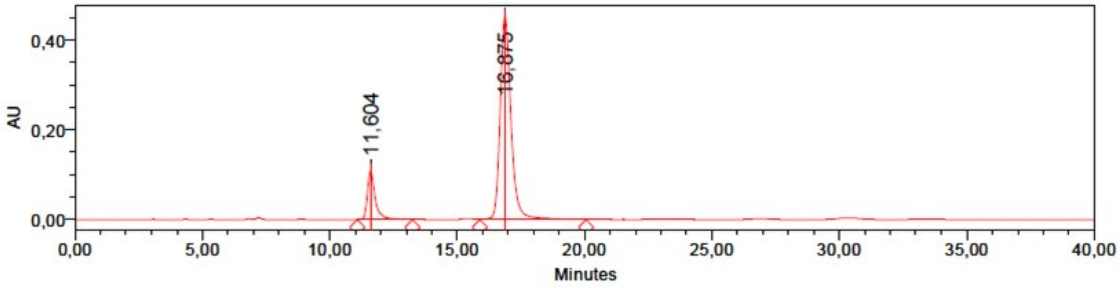
Figure S67. HPLC analysis for Table S2, entry 8: *(S)*-BINAM, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		12,047	1131152	8,96
2		17,747	11495163	91,04

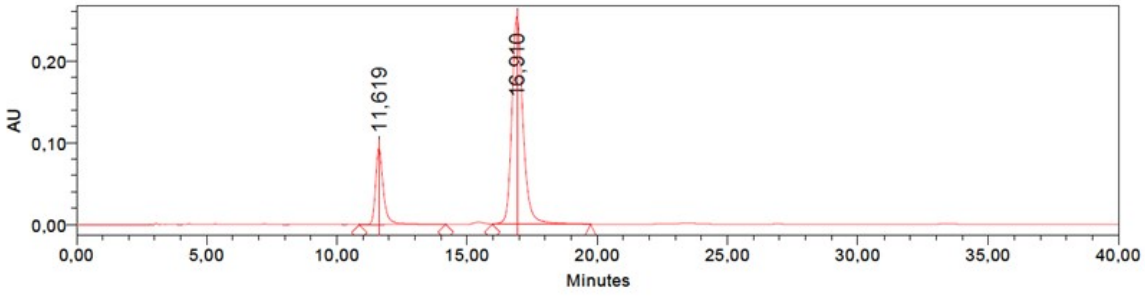
Figure S68. HPLC analysis for Table S2, entry 9: *(S)*-BINAM, 24 h.



Peak Results

	Name	RT	Area	% Area
1		11,604	2313047	14,72
2		16,875	13397654	85,28

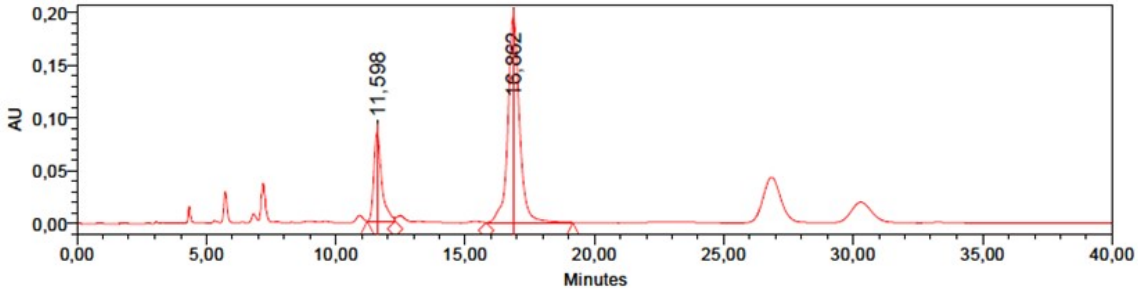
Figure S69. HPLC analysis for Table S3, entry 1: *(S)*-NOBIN with 0.1 eq. pyrrolidine, LAG with NaCl, 24 h.



Peak Results

	Name	RT	Area	% Area
1		11,619	1961897	20,46
2		16,910	7625310	79,54

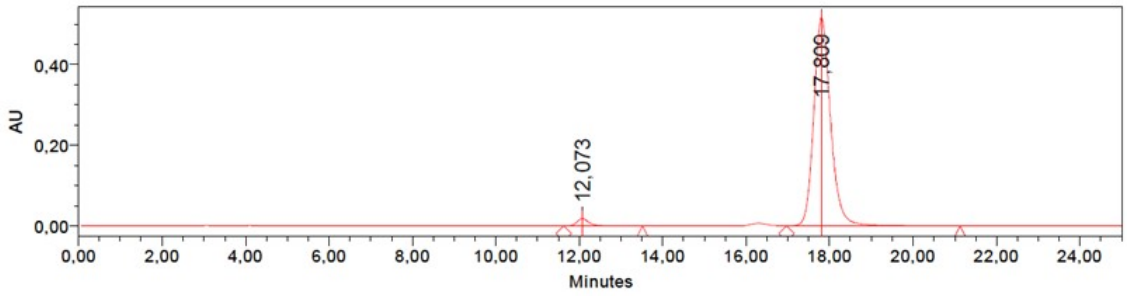
Figure S70. HPLC analysis for Table S3, entry 2: *(S)*-NOBIN without base, LAG with NaCl, 24 h.



Peak Results

	Name	RT	Area	% Area
1		11,598	1786278	22,52
2		16,862	6144624	77,48

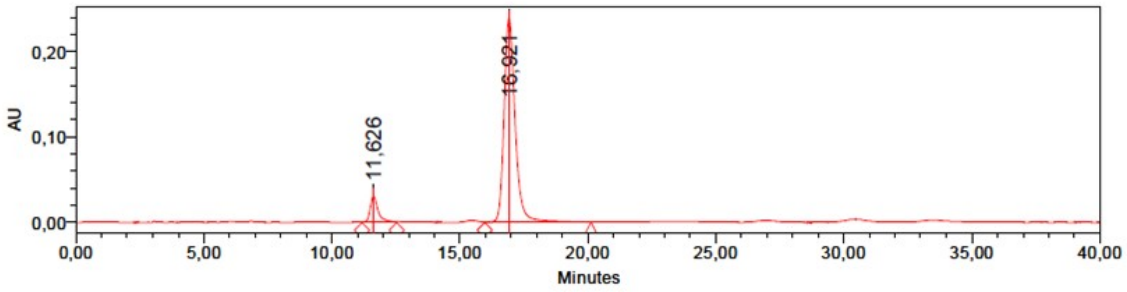
Figure S71. HPLC analysis for Table S3, entry 3: *(S)*-NOBIN with 1.0 eq. K_2CO_3, NG, 24 h. Peaks at ~7 min, ~8 min, ~26 min and ~30 min correspond to side reaction products and do not impact main analyte quantification.



Peak Results

	Name	RT	Area	% Area
1		12,073	360882	2,44
2		17,809	14443405	97,56

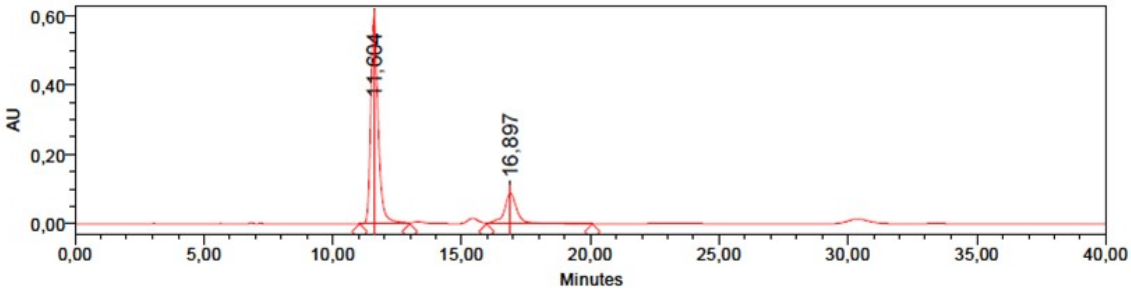
Figure S72. HPLC analysis for Table S3, entry 4: *(S)*-NOBIN with 25 eq. K_2CO_3, NG, 24 h.



Peak Results

	Name	RT	Area	% Area
1		11,626	664937	8,47
2		16,921	7189092	91,53

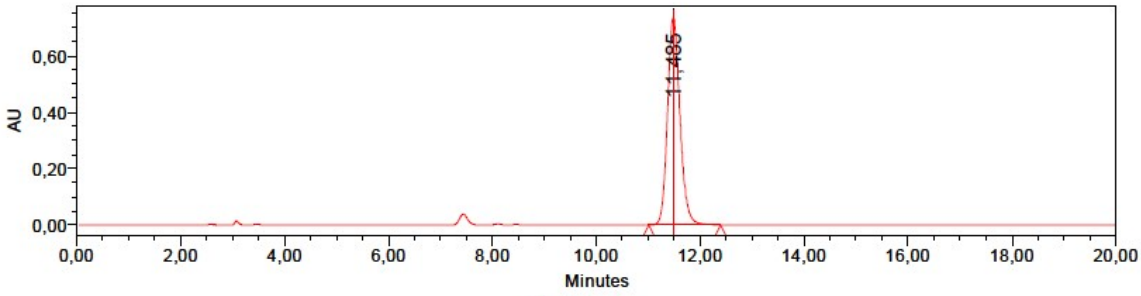
Figure S73. HPLC analysis for Table S3, entry 5: *(S)*-NOBIN with 1.0 eq. Cs_2CO_3, NG with NaCl, 24 h.



Peak Results

	Name	RT	Area	% Area
1		11,604	12019750	79,81
2		16,897	3040056	20,19

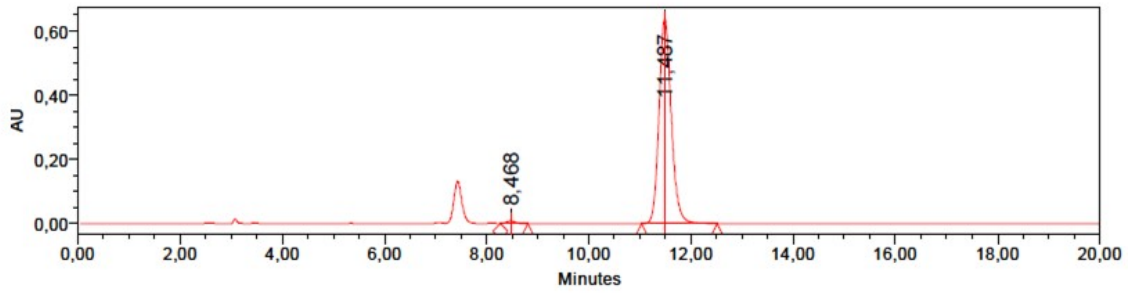
Figure S74. HPLC analysis for Table S3, entry 6: *(R)*-NOBIN with 1.0 eq. Cs_2CO_3, LAG with NaCl, 24 h.



Peak Results

	Name	RT	Area	% Area
1		11,485	12194267	100,00

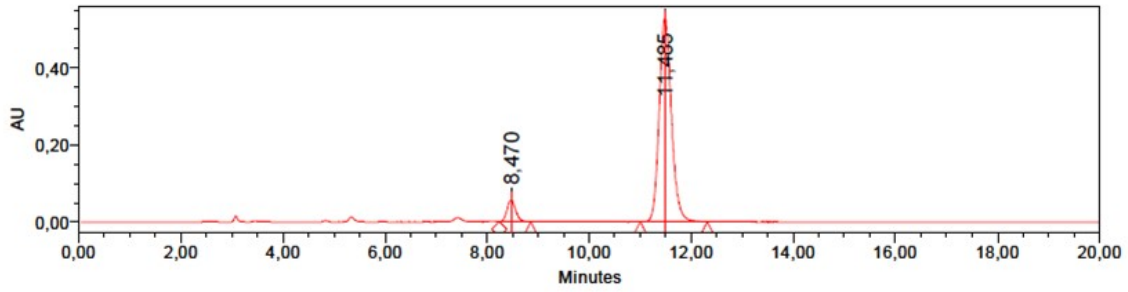
Figure S75. HPLC analysis for Table S3, entry 7: *(S)*-NOBIN, 1.5 h.



Peak Results

	Name	RT	Area	% Area
1		8,468	103106	0,96
2		11,487	10585122	99,04

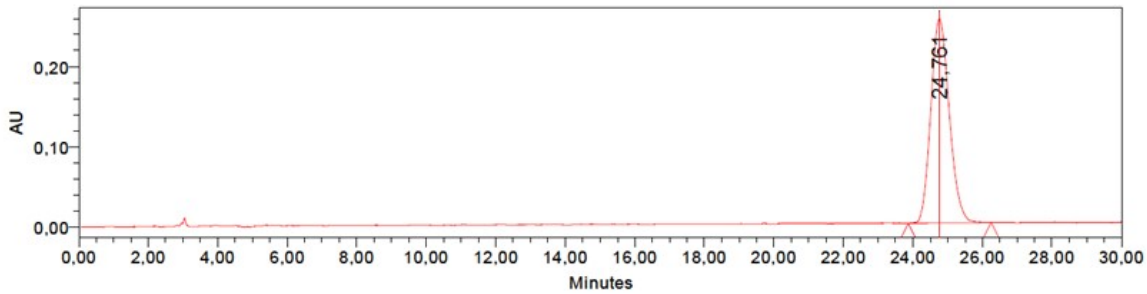
Figure S76. HPLC analysis for Table S3, entry 8: *(S)*-NOBIN, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		8,470	660528	7,02
2		11,485	8753239	92,98

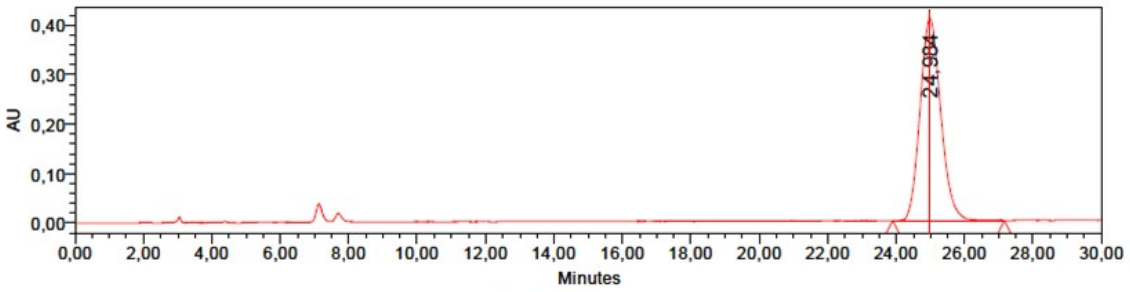
Figure S77. HPLC analysis for Table S3, entry 9: *(S)*-NOBIN, 24 h.



Peak Results

	Name	RT	Area	% Area
1		24,761	9463984	100,00

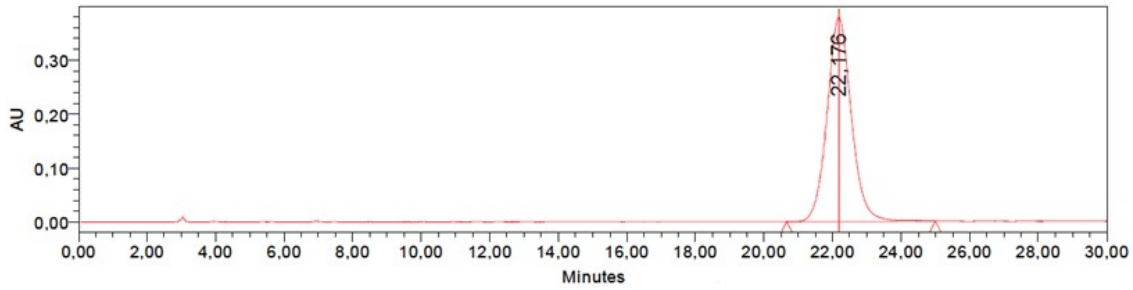
Figure S78. HPLC analysis for Table S4, entry 2: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG, 20 Hz, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		24,984	17303410	100,00

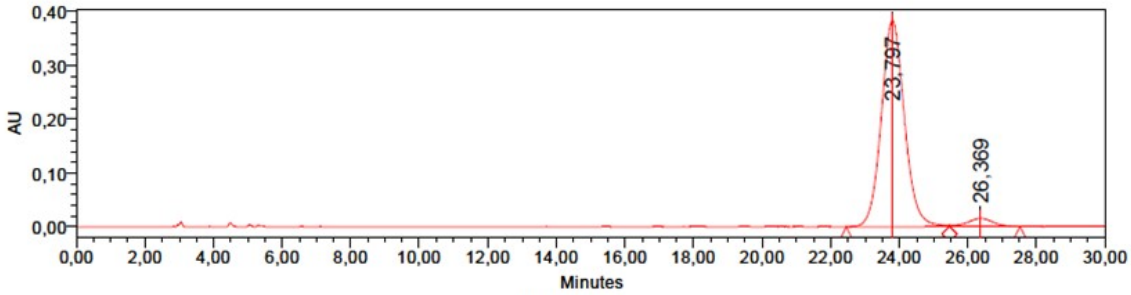
Figure S79. HPLC analysis for Table S4, entry 3: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG, 10 Hz, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		22,176	18524368	100,00

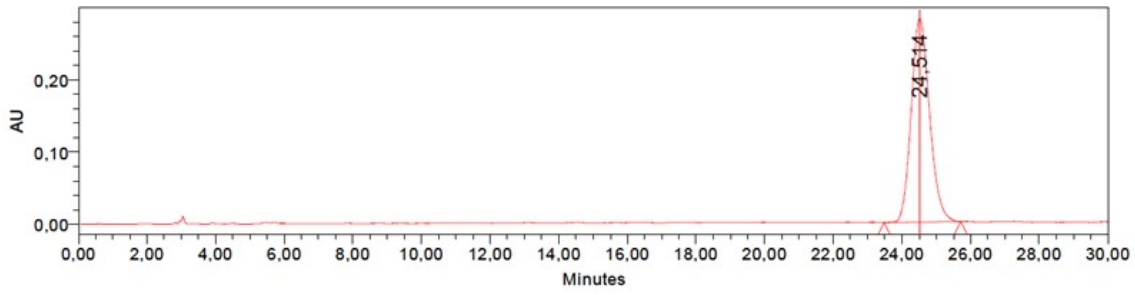
Figure S80. HPLC analysis for Table S4, entry 4: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG, 5 Hz, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		23,797	17751235	95,82
2		26,369	773976	4,18

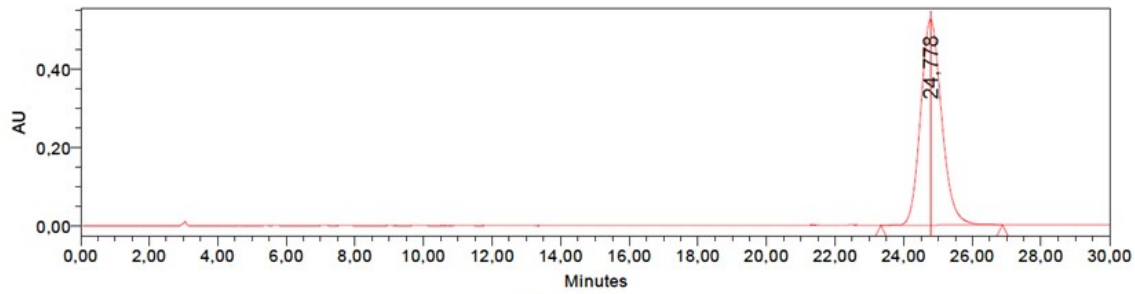
Figure S81. HPLC analysis for Table S4, entry 5: *(S)*-BINOL with 0.2 eq. pyrrolidine, NG, 30 Hz, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		24,514	10519696	100,00

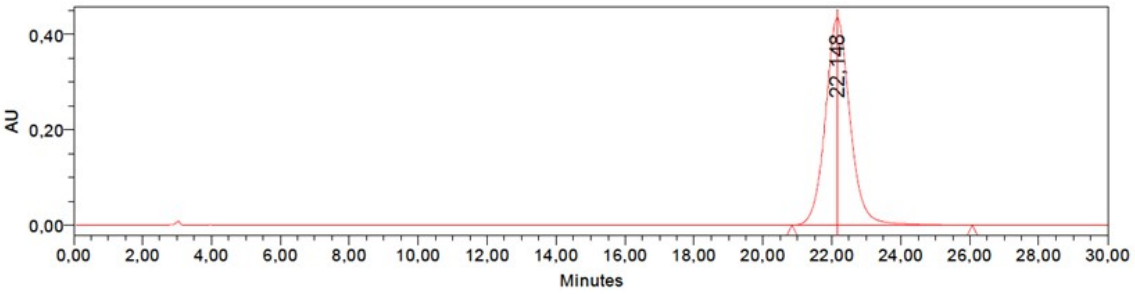
Figure S82. HPLC analysis for Table S4, entry 6: *(S)*-BINOL with 0.2 eq. pyrrolidine, NG, 20 Hz, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		24,778	22422904	100,00

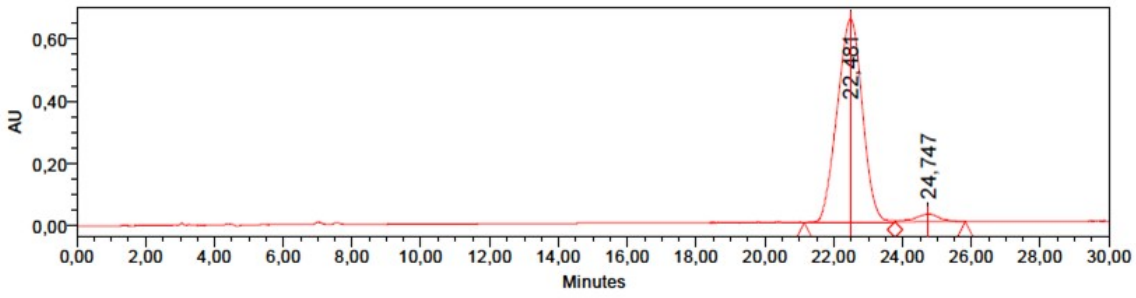
Figure S83. HPLC analysis for Table S4, entry 7: *(S)*-BINOL with 0.2 eq. pyrrolidine, NG, 10 Hz, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		22,148	21466130	100,00

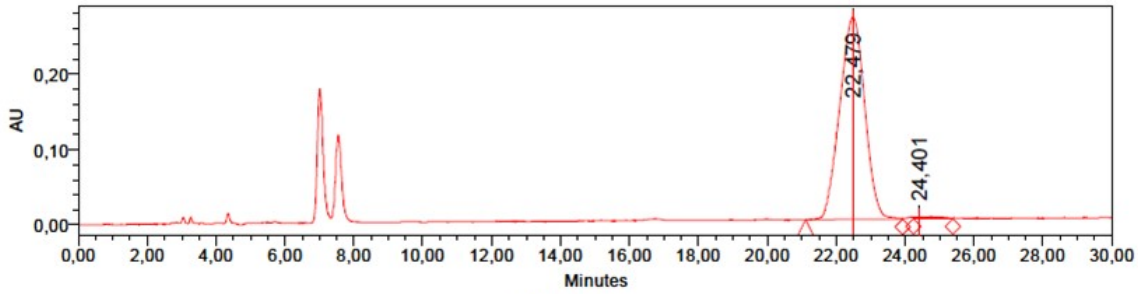
Figure S84. HPLC analysis for Table S4, entry 8: *(S)*-BINOL with 0.2 eq. pyrrolidine, NG, 5 Hz, 4.5 h.



Peak Results

	Name	RT	Area	% Area
1		22,481	33159822	96,52
2		24,747	1195111	3,48

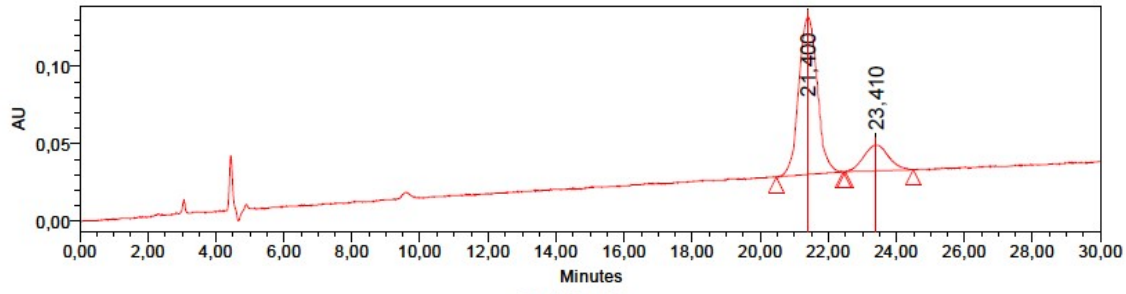
Figure S85. HPLC analysis for Table S5, entry 1: *(S)*-BINOL with 0.1 eq. pyrrolidine, LAG with NaCl, 24 h, PTFE milling vessel.



Peak Results

	Name	RT	Area	% Area
1		22,479	13560414	98,92
2		24,401	147590	1,08

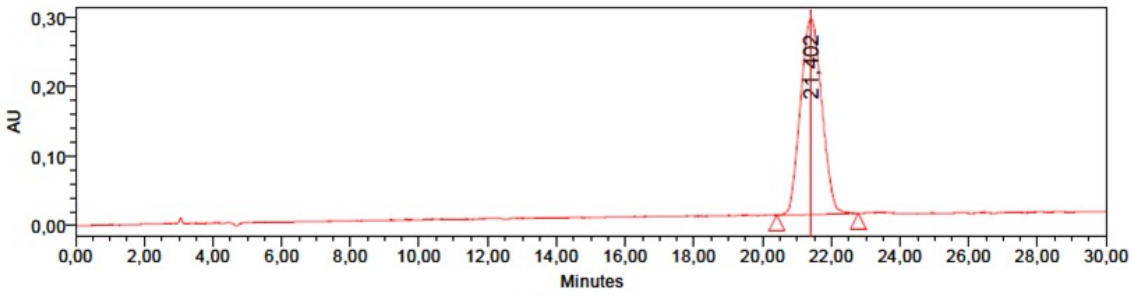
Figure S86. HPLC analysis for Table S5, entry 2: *(S)*-BINOL without base, LAG with NaCl, 24 h, PTFE milling vessel. Peaks at ~7 min correspond to side reaction products and do not impact main analyte quantification.



Peak Results

	Name	RT	Area	% Area
1		21,400	3801551	81,88
2		23,410	841305	18,12

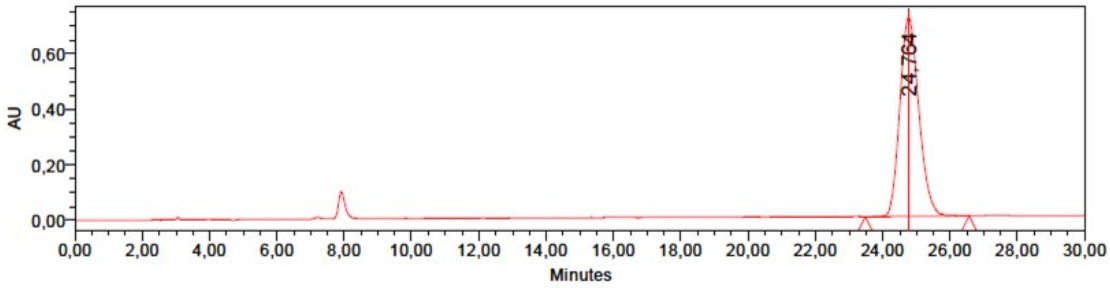
Figure S87. HPLC analysis for Table S5, entry 3: *(S)*-BINOL with 1.0 eq. K_2CO_3, NG, 24 h., PTFE milling vessel. Due to small concentration of the analyte, baseline is increasing, which does not affect the main analyte quantification.



Peak Results

	Name	RT	Area	% Area
1		21,402	12103668	100,00

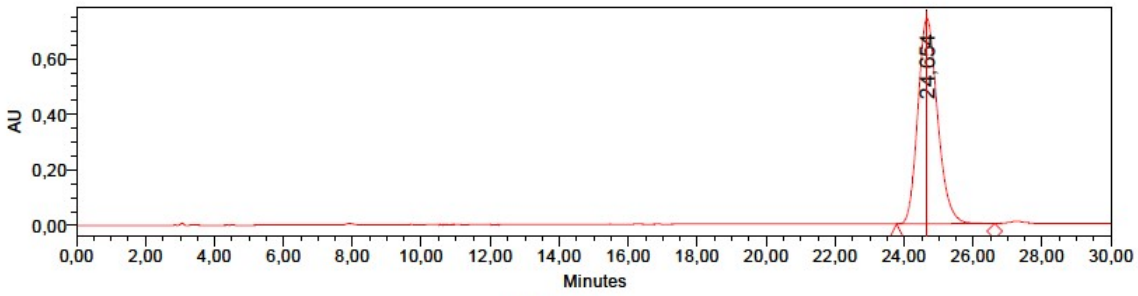
Figure S88. HPLC analysis for Table S5, entry 4: *(S)*-BINOL with 50 eq. K_2CO_3, NG, 24 h, PTFE milling vessel.



Peak Results

	Name	RT	Area	% Area
1		24,764	28268006	100,00

Figure S89. HPLC analysis for Table S5, entry 5: *(S)*-BINOL with 1.0 eq. Cs_2CO_3, NG with NaCl, 24 h, PTFE milling vessel. Peak at ~8min corresponds to side reaction product and do not impact main analyte quantification.



Peak Results

	Name	RT	Area	% Area
1		24,654	29523474	100,00

Figure S90. HPLC analysis for Table S5, entry 6: *(S)*-BINOL with 1.0 eq. Cs_2CO_3, LAG with NaCl, 24 h PTFE milling vessel.

3.2. NMR analysis

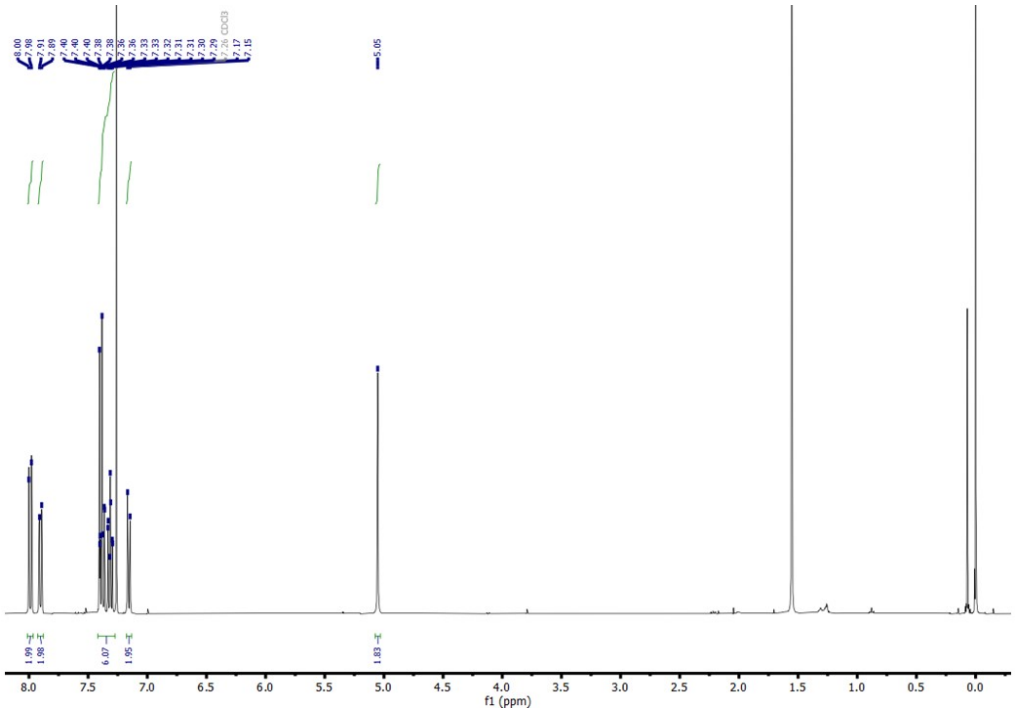


Figure S91. ^{1}H-NMR spectrum in $CDCl_3$ of *(S)*-BINOL as starting material.

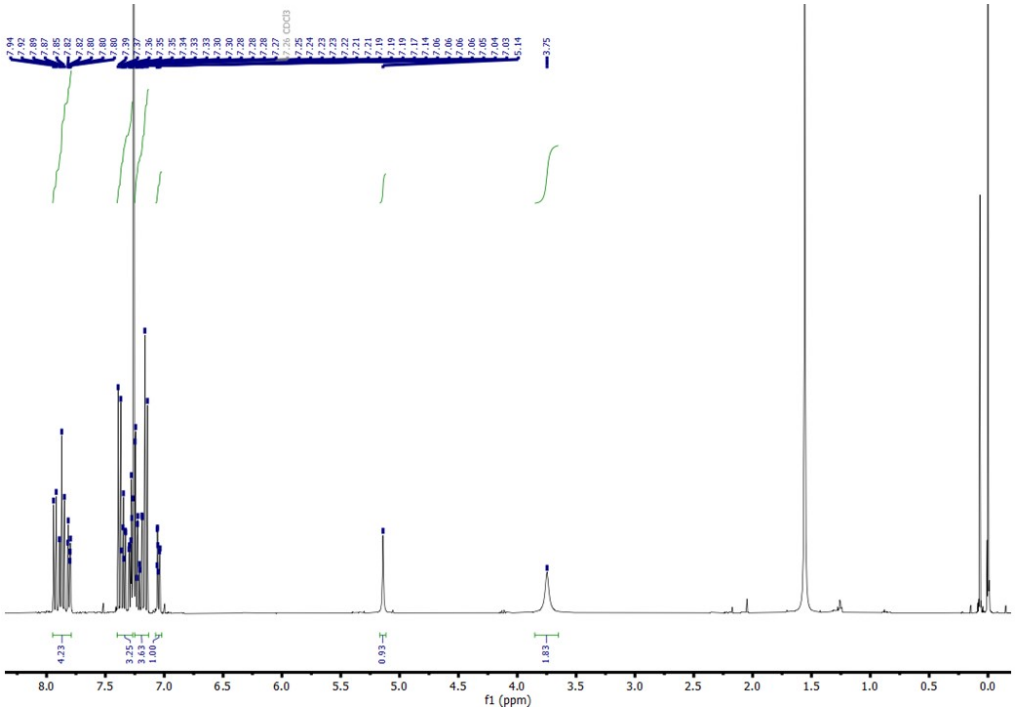


Figure S92. ^{1}H-NMR spectrum in $CDCl_3$ of *(S)*-NOBIN as starting material.

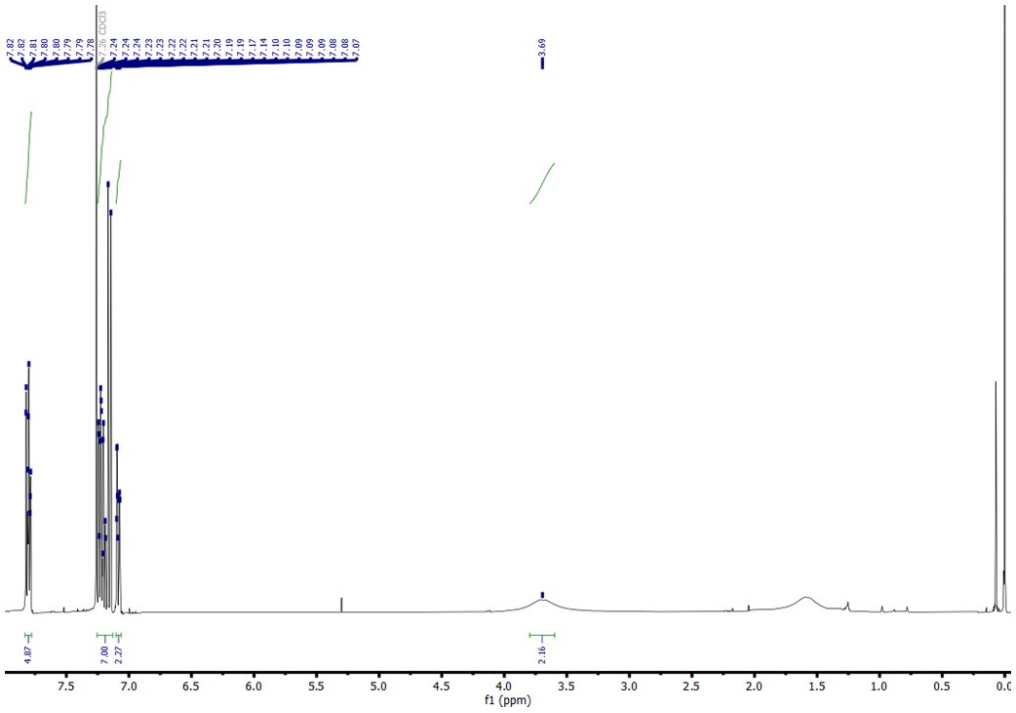


Figure S93. ^{1}H-NMR spectrum in $CDCl_3$ of *(S)*-BINAM as starting material.

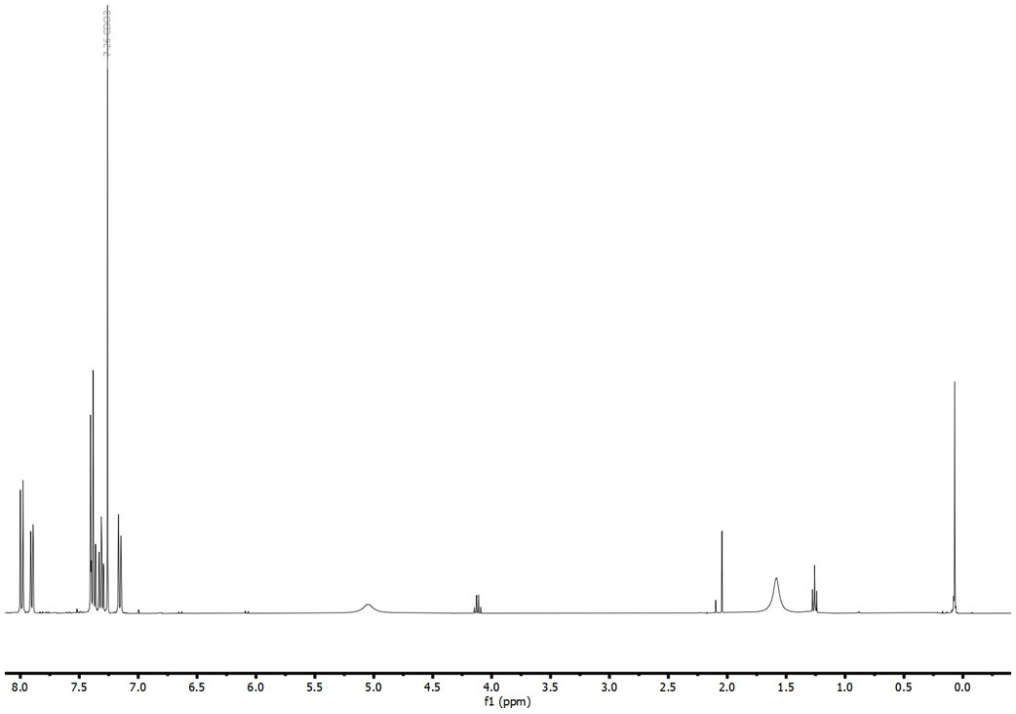


Figure S94. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 1:*(S)*-BINOL with 0.1 eq. pyrrolidine, NG, 1.5 h.

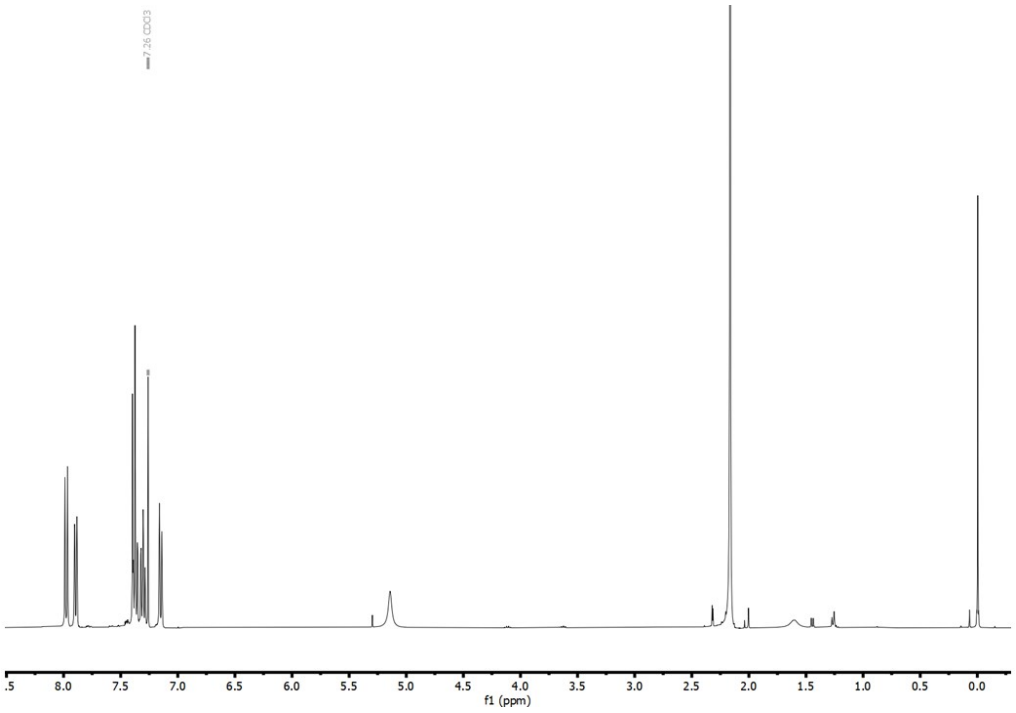


Figure S95. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 2: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG, 4.5 h.

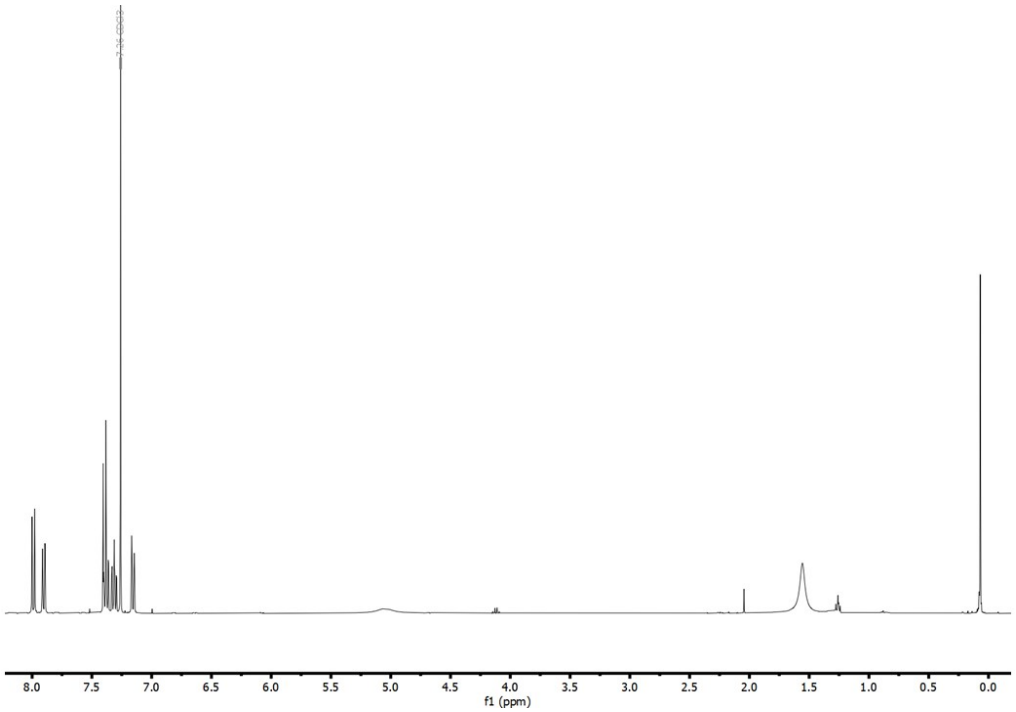


Figure S96. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 3: *(S)*-BINOL with 1.0 eq. pyrrolidine, NG, 4.5 h.

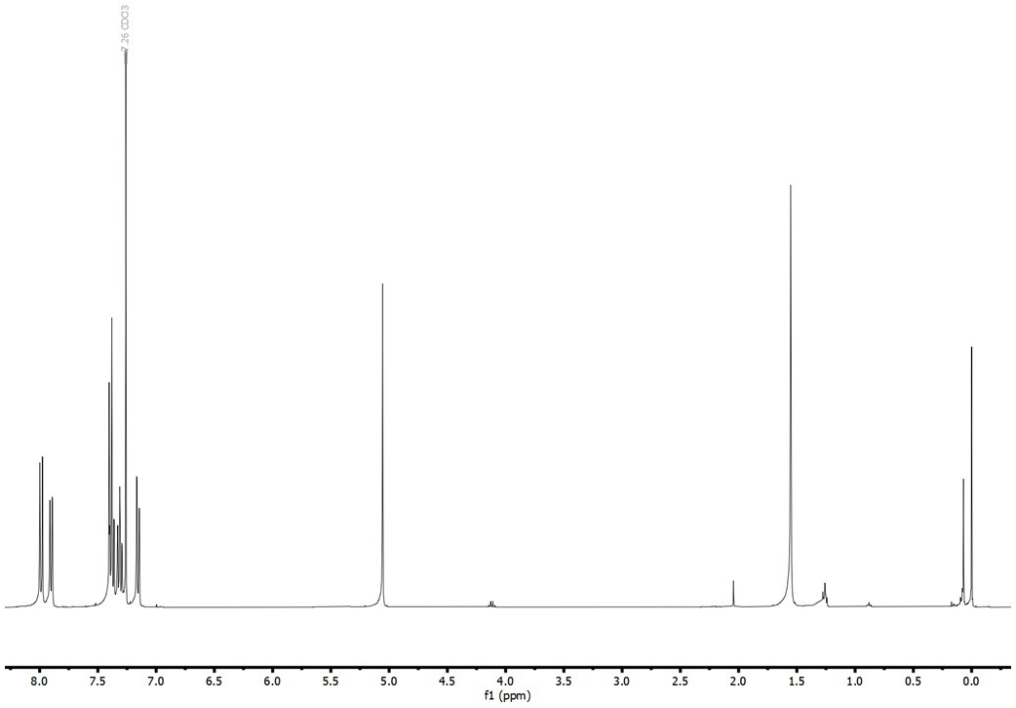


Figure S97. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 4: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG with NaCl, 4.5 h.

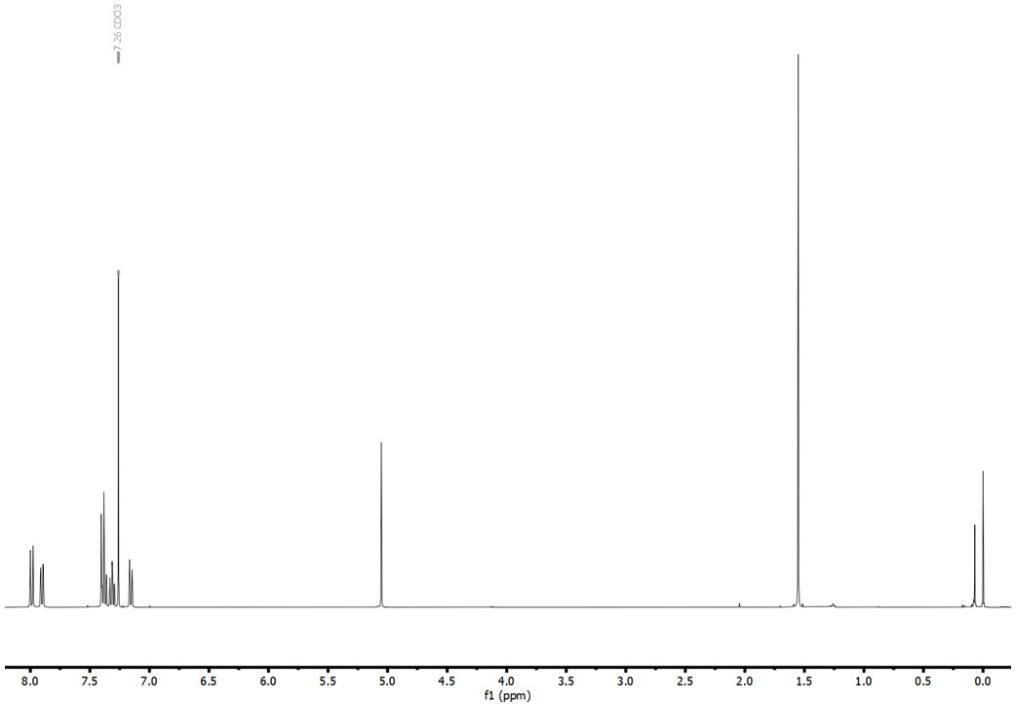


Figure S98. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 5: *(S)*-BINOL with 0.1 eq. pyrrolidine, LAG with NaCl, 4.5 h.

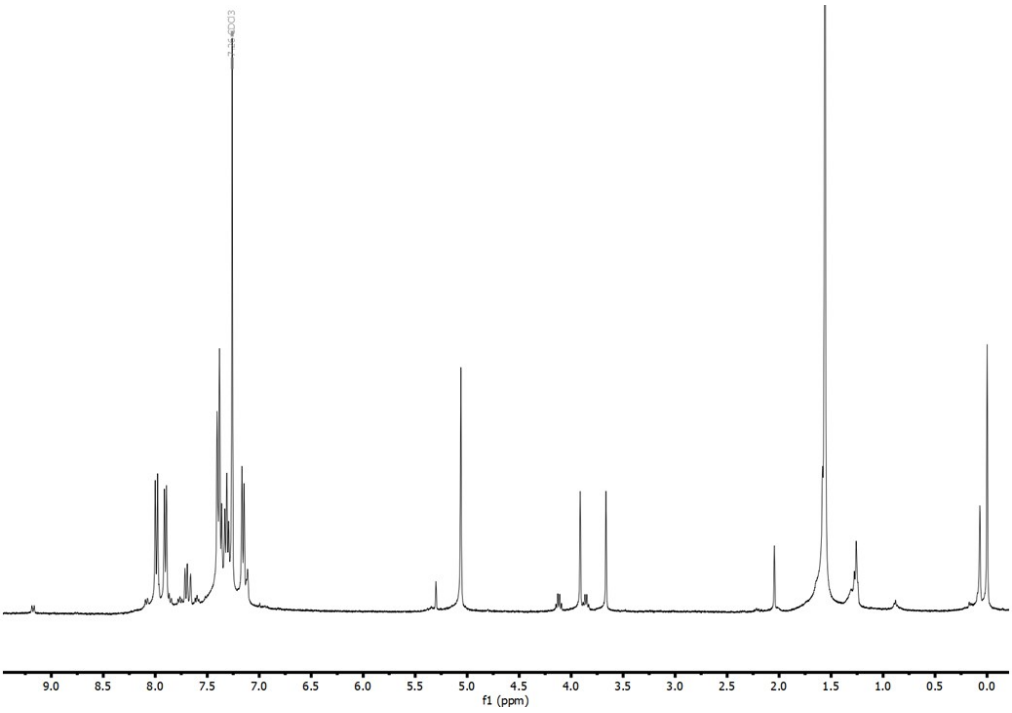


Figure S99. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 6: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG, 24 h. Signals at 4 and 3.5 likely correspond to side-products.

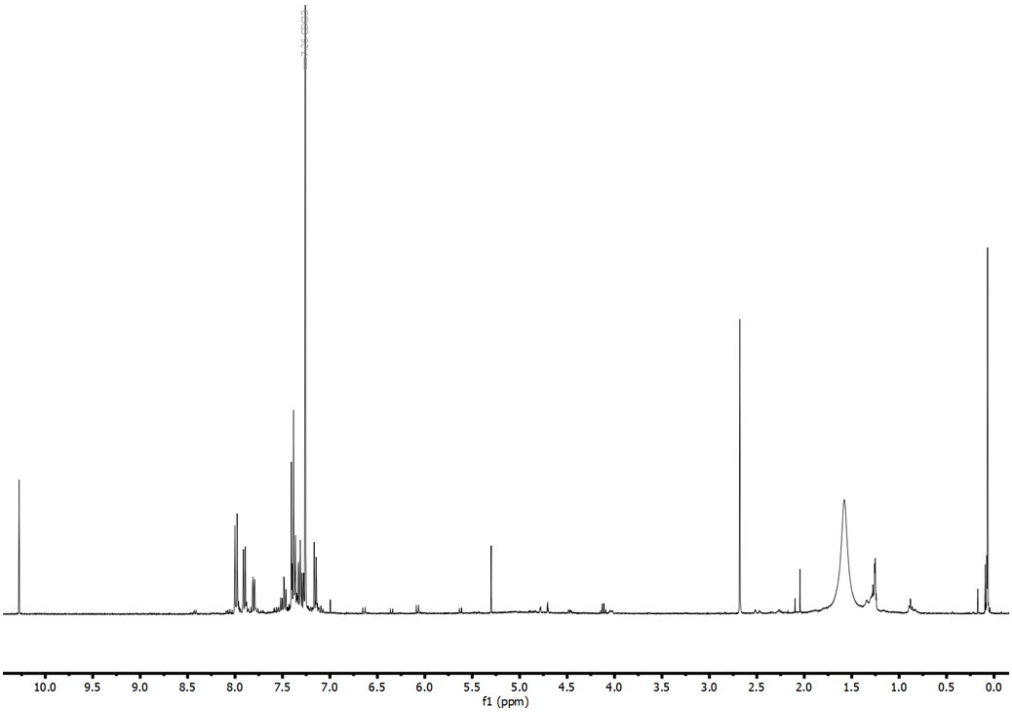


Figure S100. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 7: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG with NaCl, 24 h.

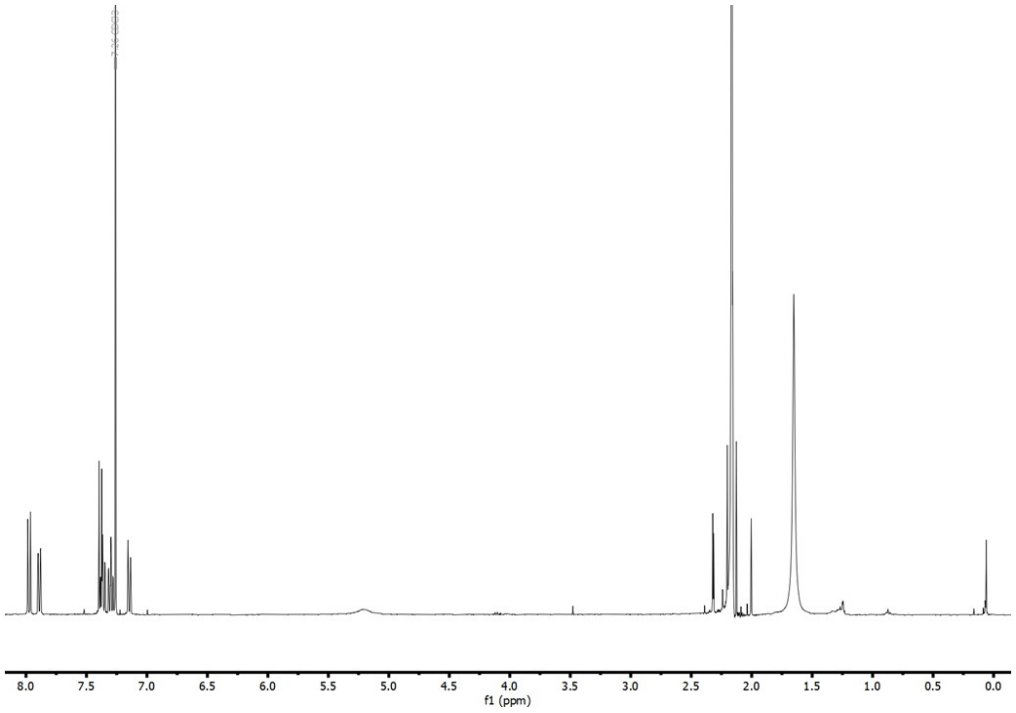


Figure S101. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 8: *(S)*-BINOL with 0.1 eq. pyrrolidine, LAG with NaCl, 24 h.

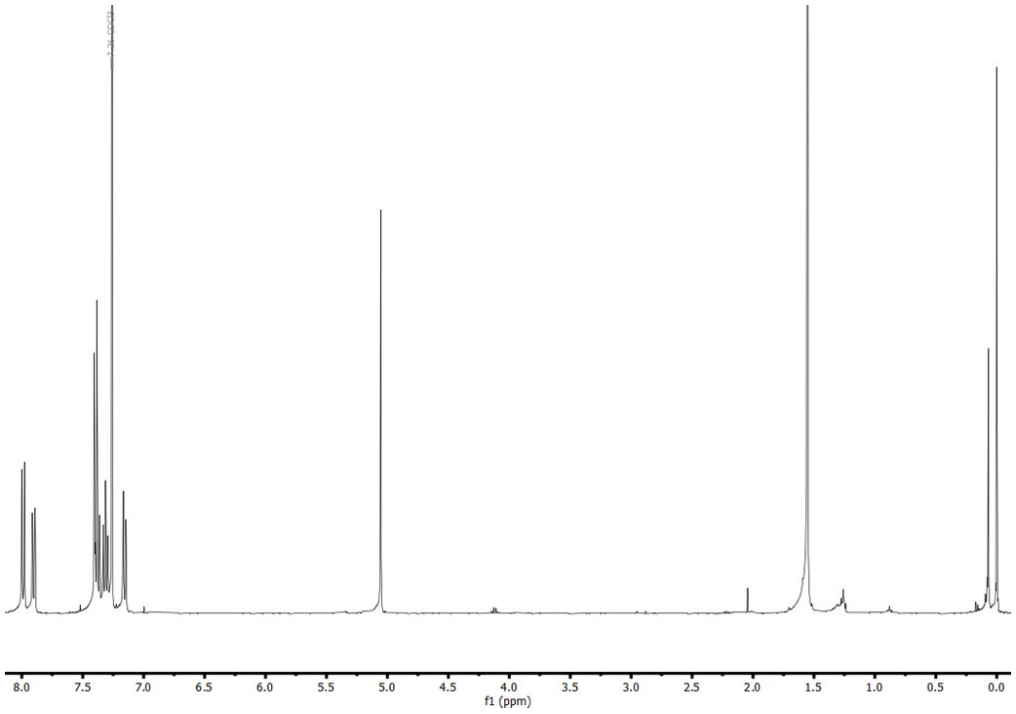


Figure S102. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 9: *(S)*-BINOL with 0.1 eq. DBU, 1.5 h.

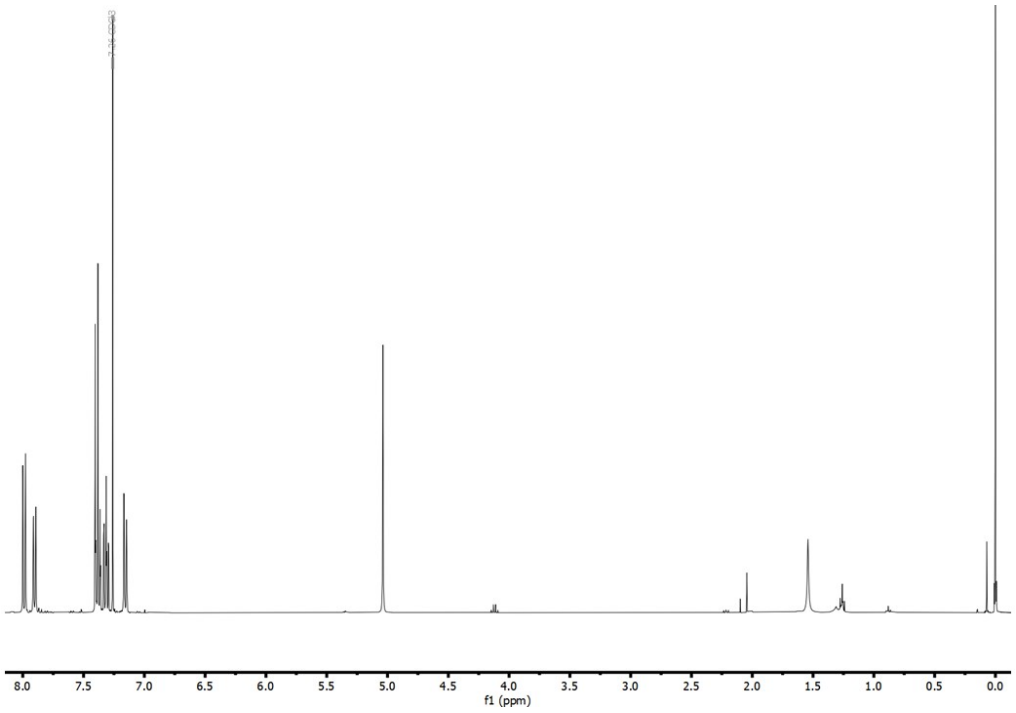


Figure S103. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 10: *(S)*-BINOL with 0.1 eq. DBU, 4.5 h.

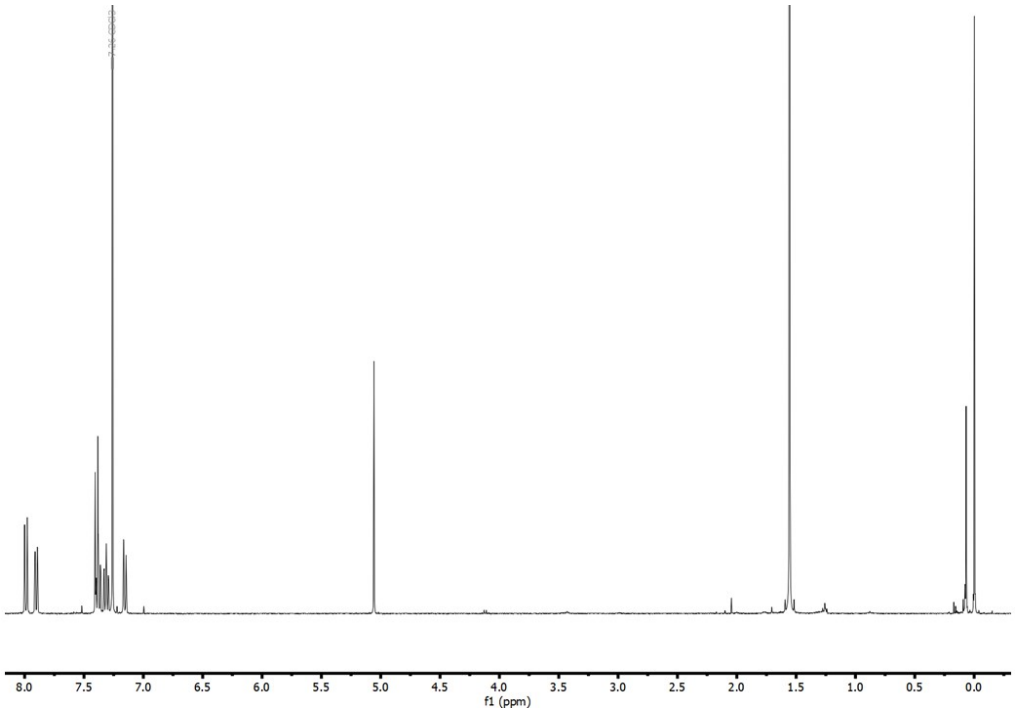


Figure S104. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 11: *(S)*-BINOL with 1.0 eq. DBU, NG, 4.5 h.

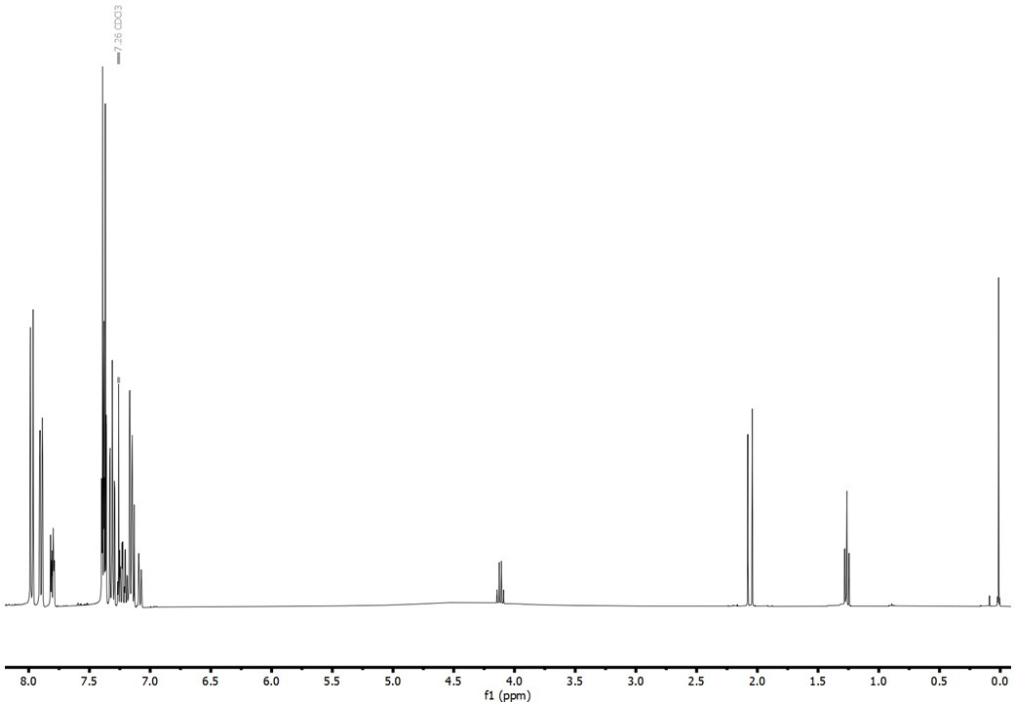


Figure S105. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 12: *(S)*-BINOL with 0.1 eq. DBU, NG with NaCl, 4.5 h.

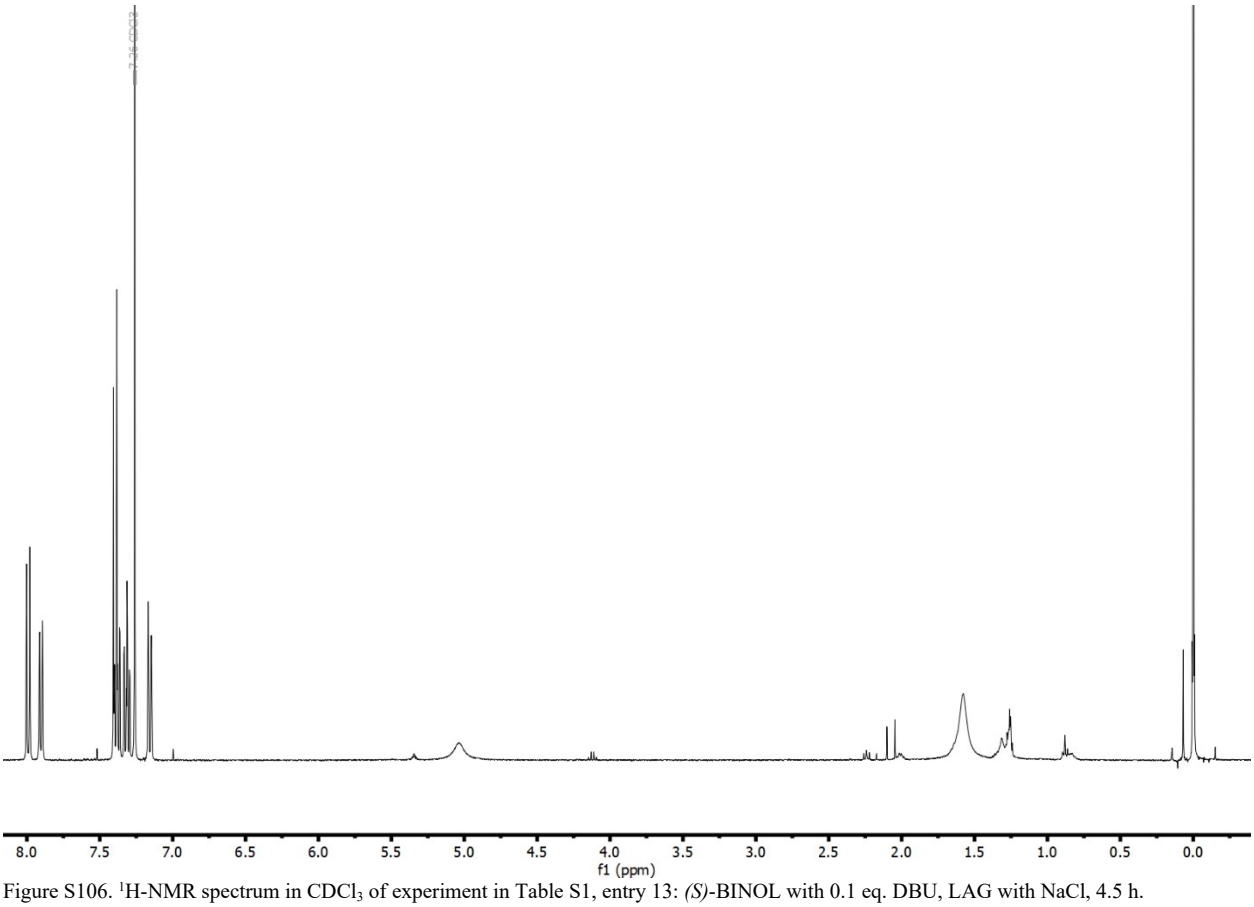


Figure S106. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 13: *(S)*-BINOL with 0.1 eq. DBU, LAG with NaCl, 4.5 h.

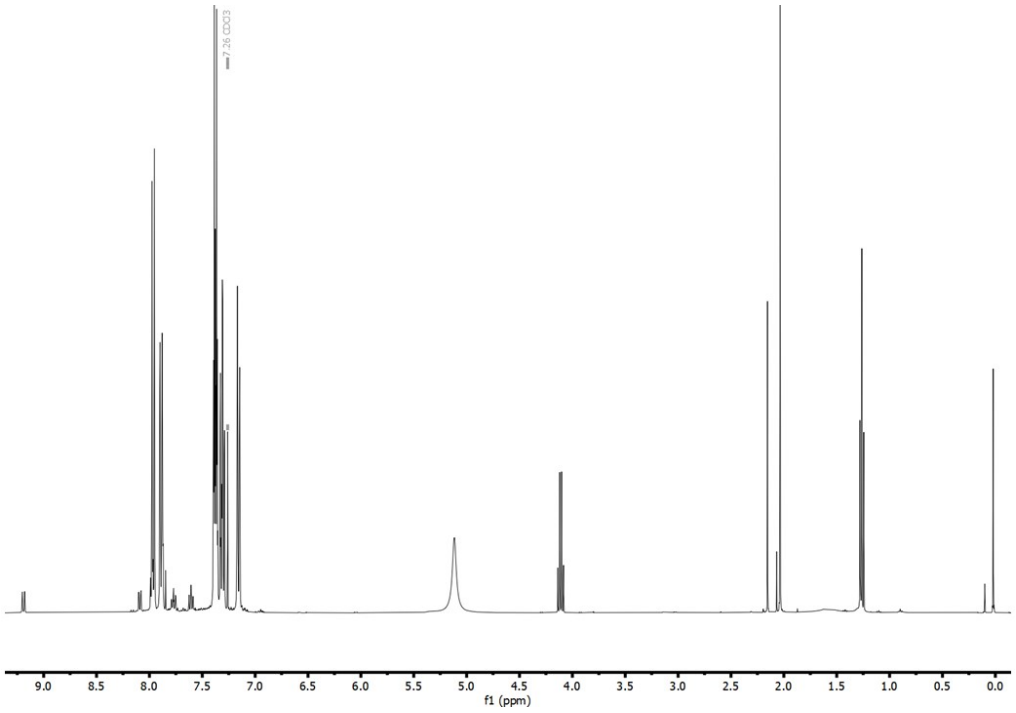


Figure S107. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 14: *(S)*-BINOL with 0.1 eq. DBU, 24 h.

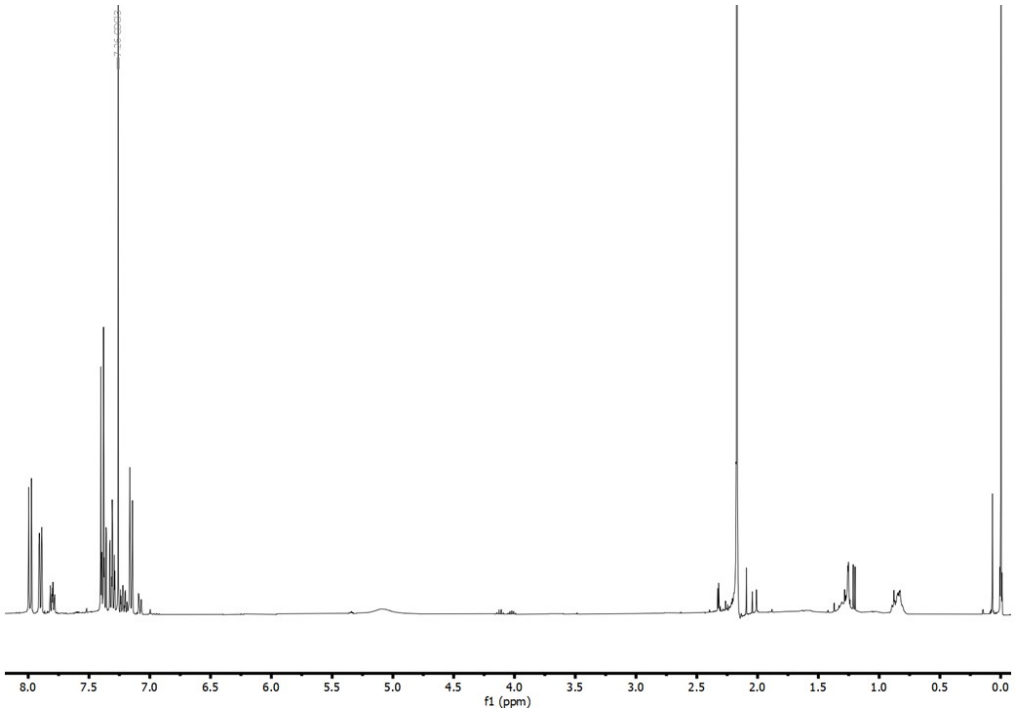


Figure S108. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 15: *(S)*-BINOL with 0.1 eq. DBU, NG with NaCl, 24 h.

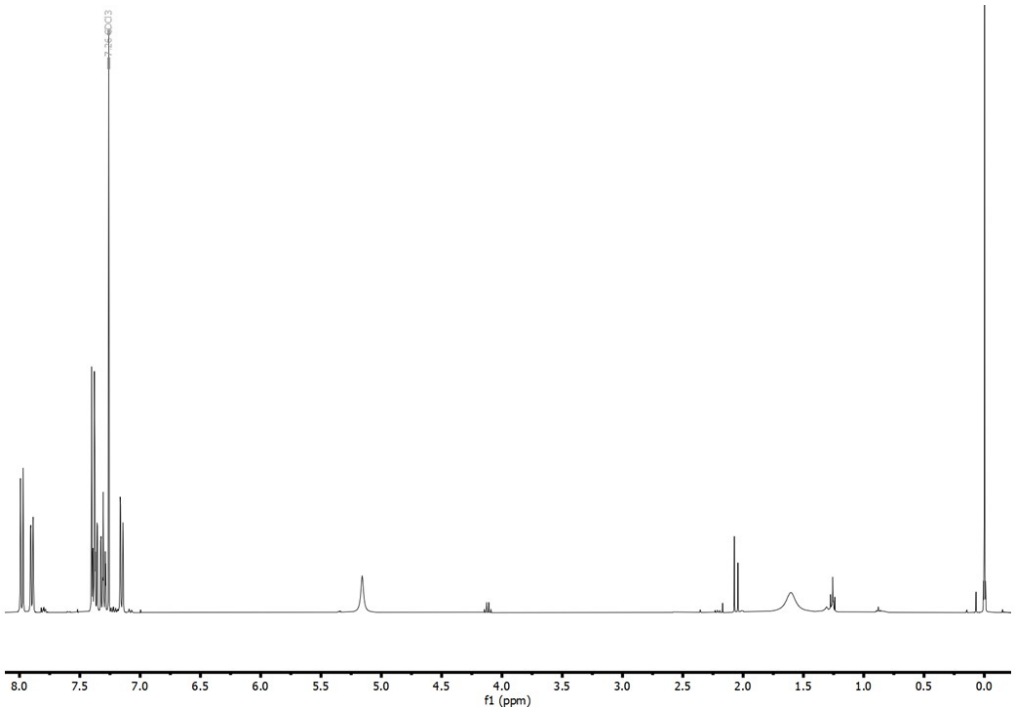


Figure S109. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 16: *(S)*-BINOL with 0.1 eq. DBU, LAG with NaCl, 24 h.

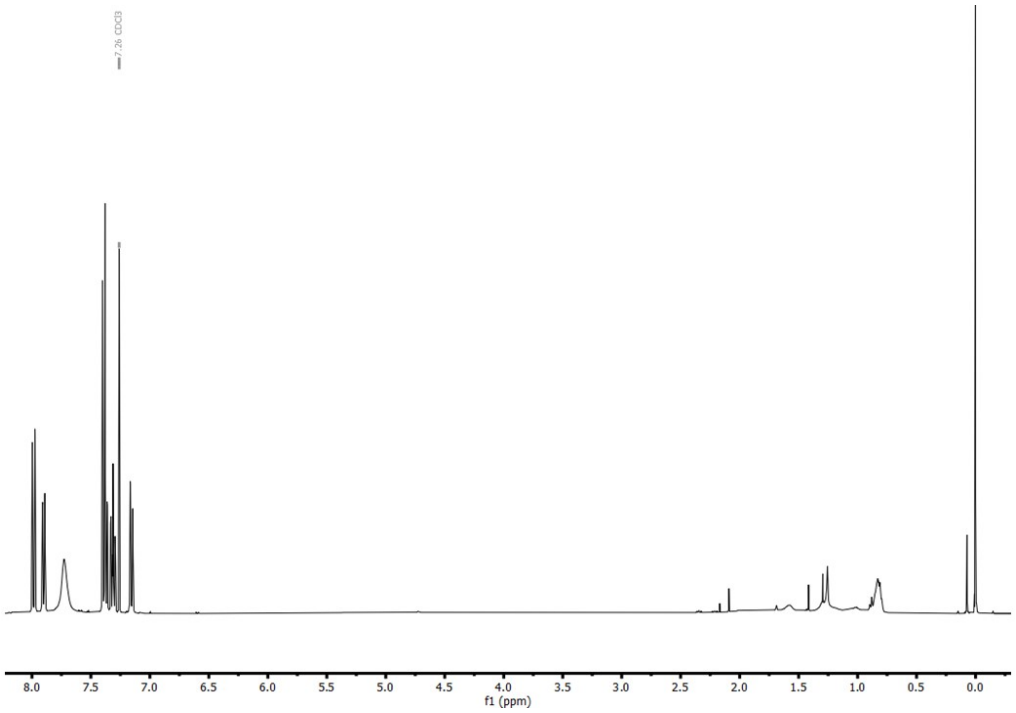


Figure S110. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 17: *(S)*-BINOL with 1.0 eq. K_2CO_3, NG, 4.5 h.

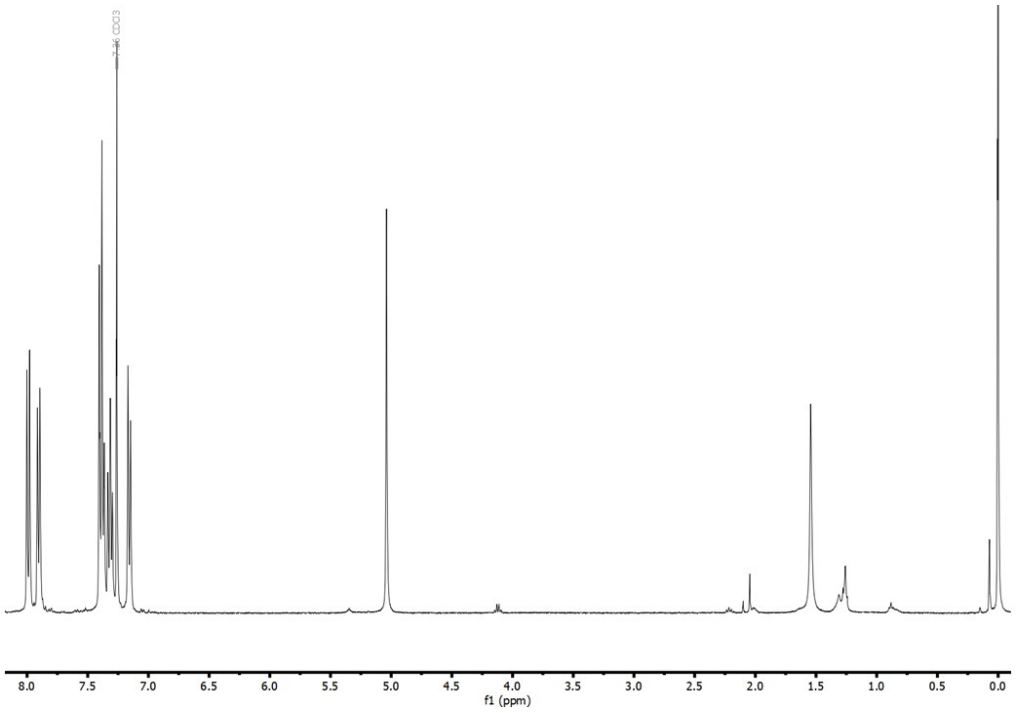


Figure S111. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 18: *(S)*-BINOL with 1.0 eq. K_2CO_3, LAG, 4.5 h.

Figure S112. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 19: *(S)*-BINOL with 1.0 eq. K_2CO_3, NG, 24 h.

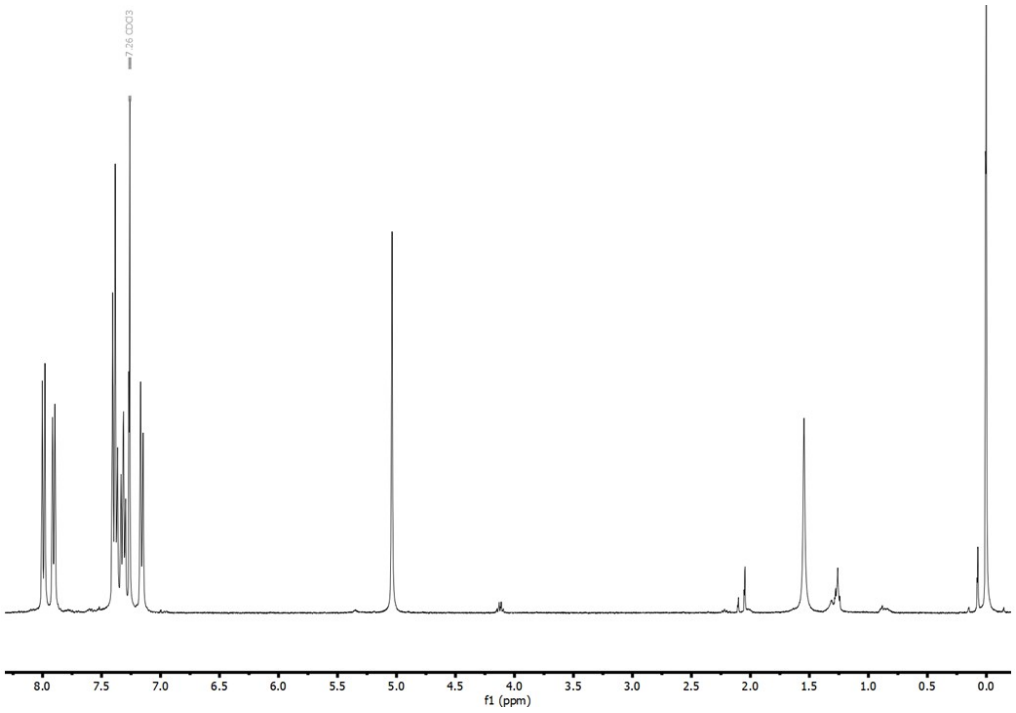


Figure S113. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 20: *(S)*-BINOL with 1.0 eq. K_2CO_3, LAG, 24 h.

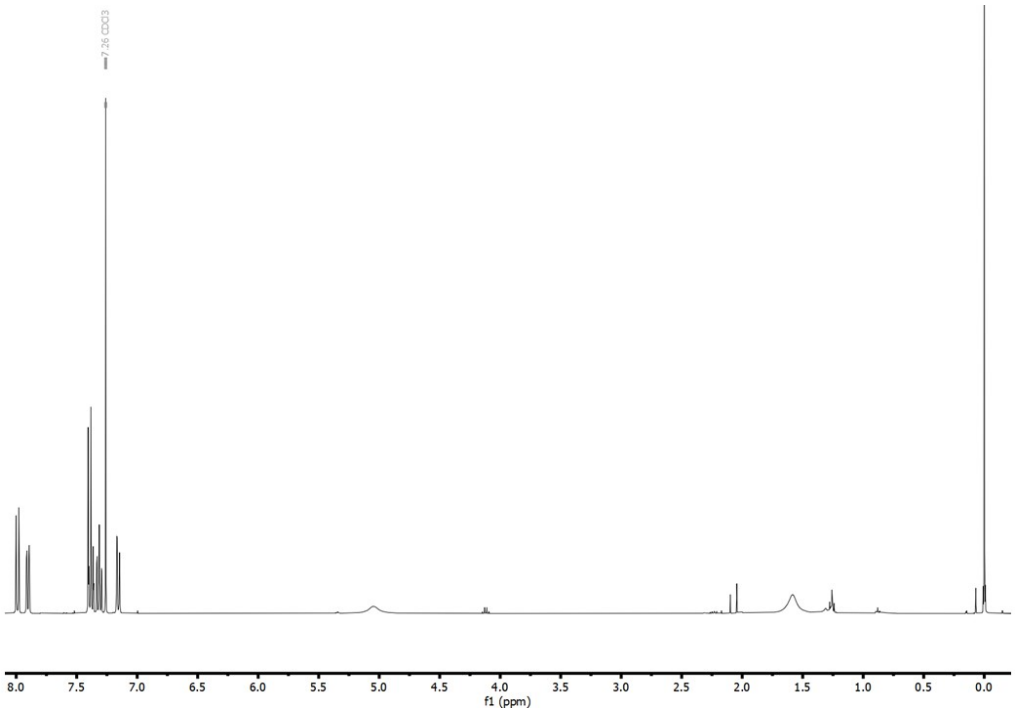


Figure S114. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 21: *(S)*-BINOL with 1.0 eq. K_2CO_3, NG with NaCl, 4.5 h.

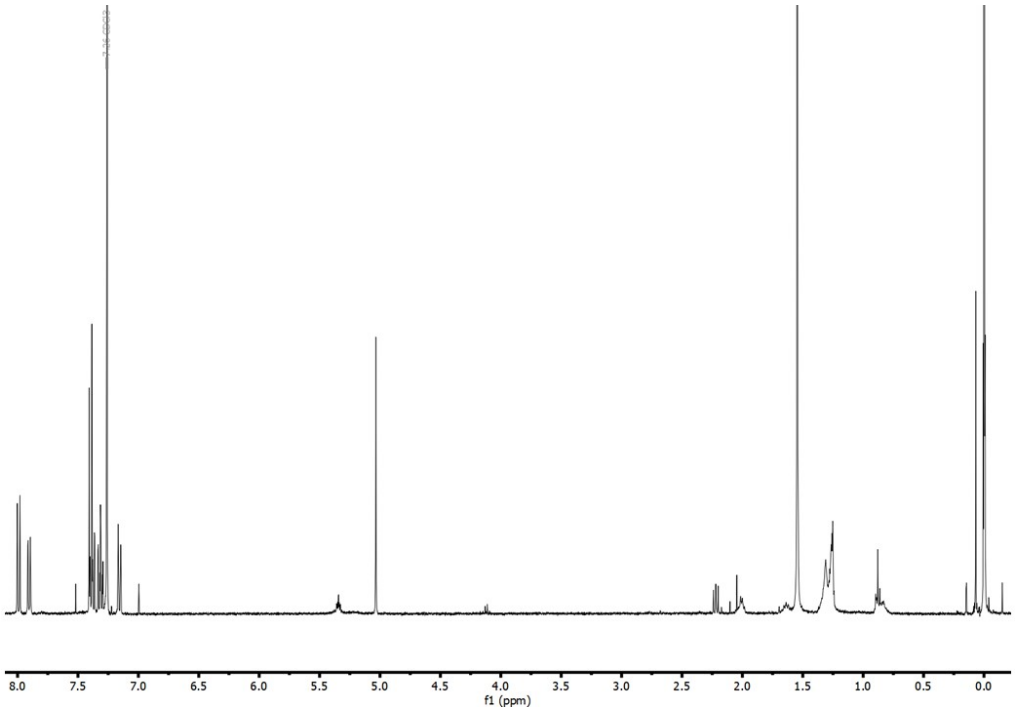


Figure S115. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 22: *(S)*-BINOL with 1.0 eq. K_2CO_3, LAG with NaCl, 4.5 h.

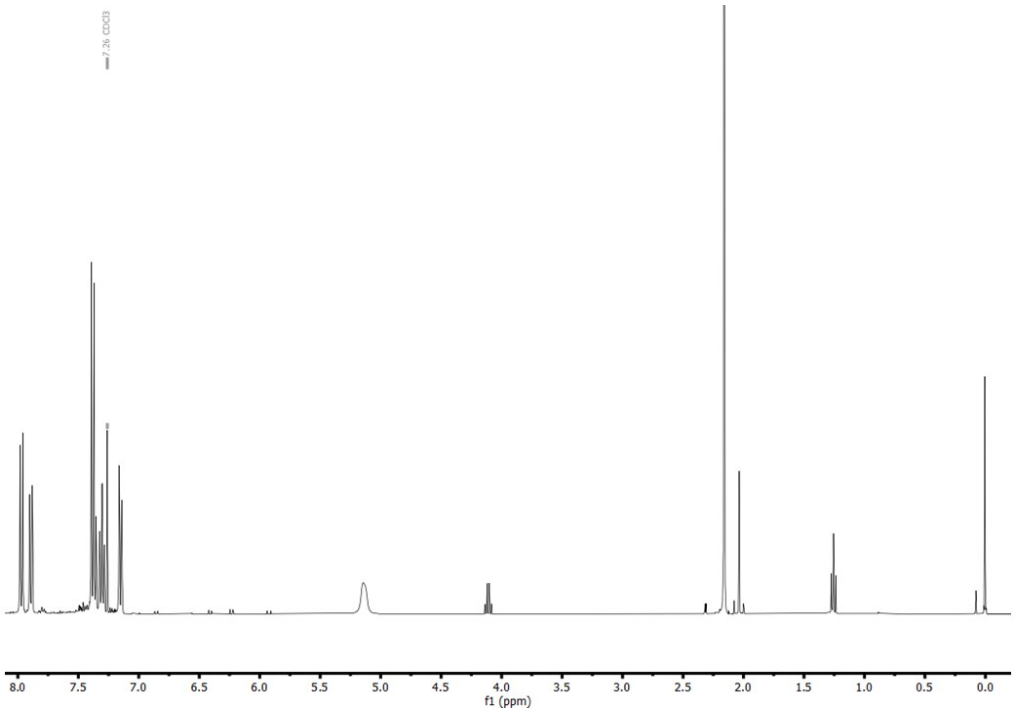


Figure S116. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 23: *(S)*-BINOL with 1.0 eq. K_2CO_3, NG with NaCl, 24 h.

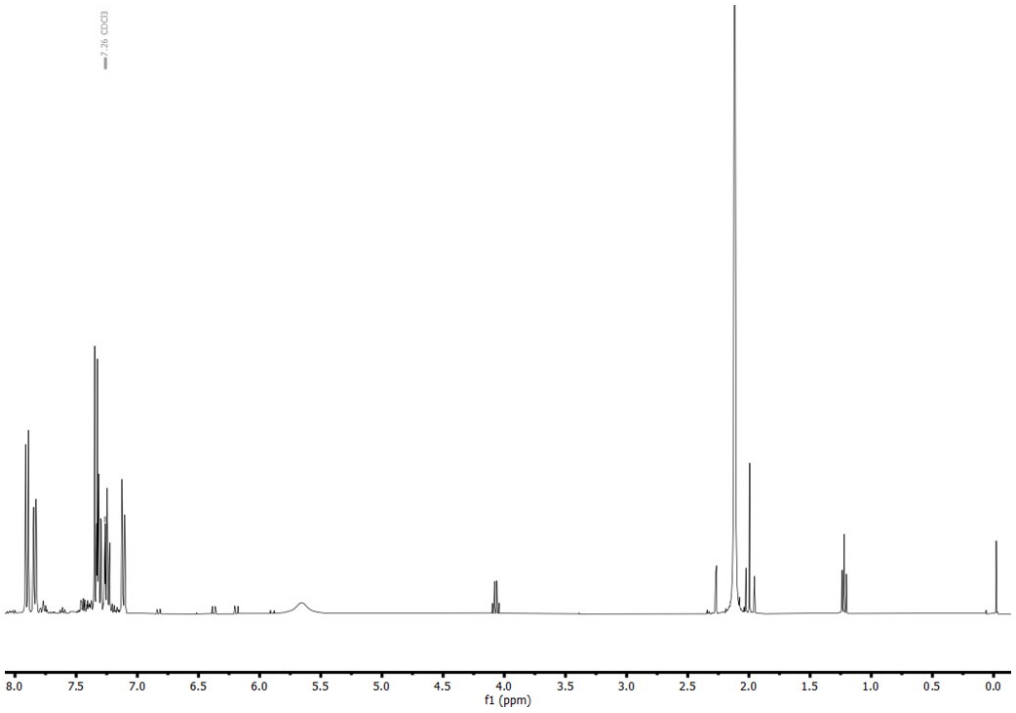


Figure S117. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 24: *(S)*-BINOL with 1.0 eq. K_2CO_3, LAG with NaCl, 24 h.

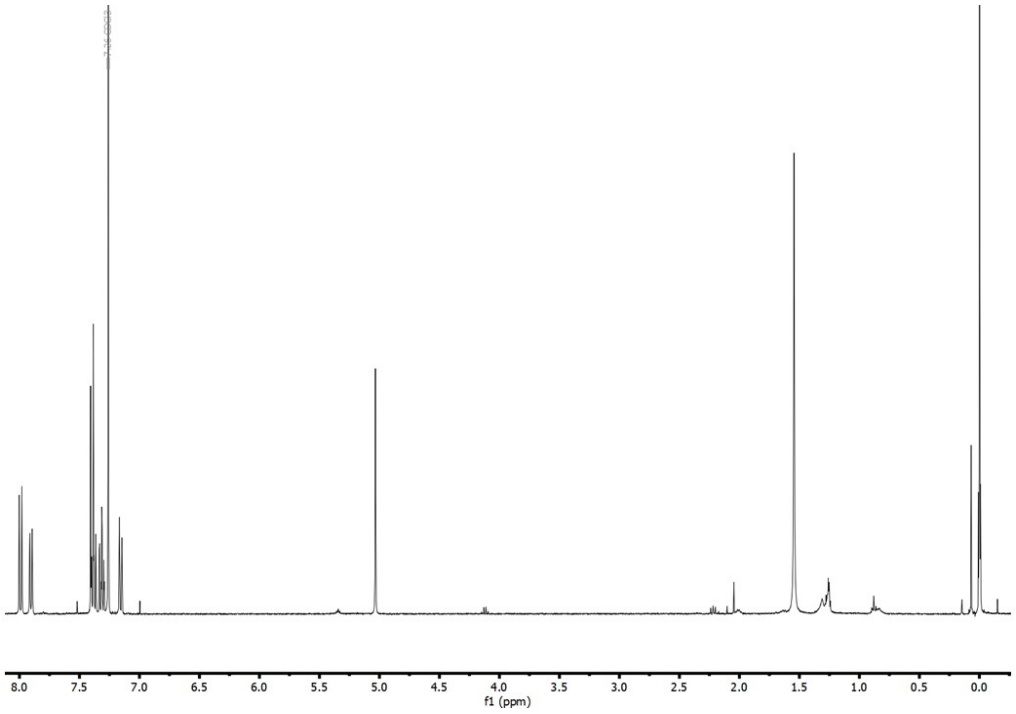


Figure S118. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 25: *(S)*-BINOL with 25 eq. K_2CO_3, NG, 4.5 h.

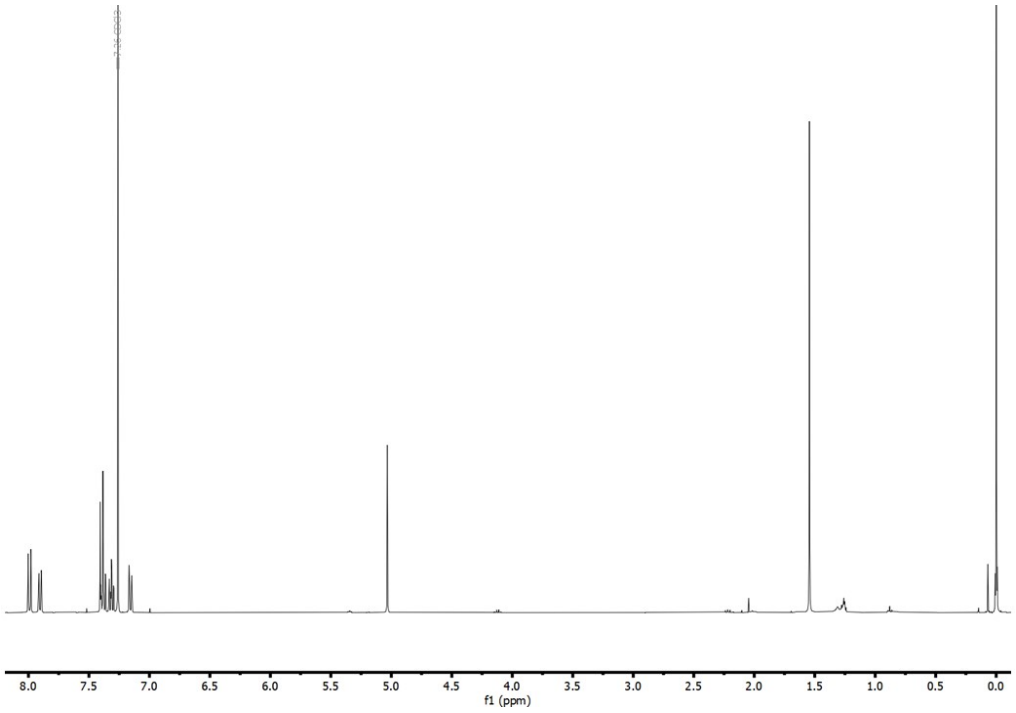


Figure S119. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 26: *(S)*-BINOL with 25 eq. K_2CO_3, LAG, 4.5 h.

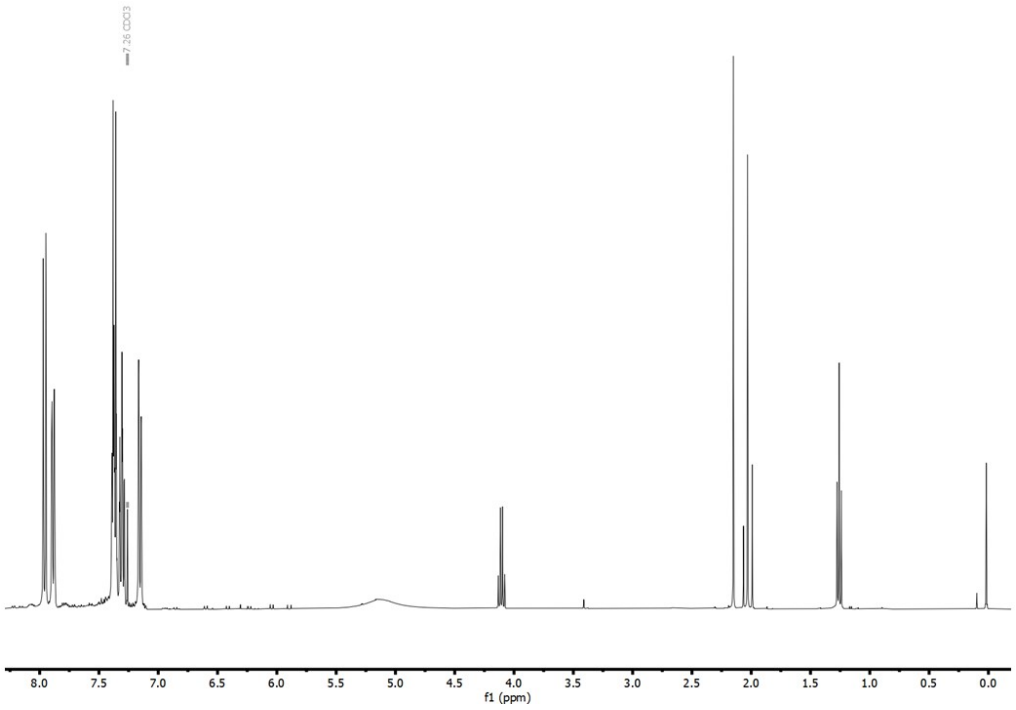


Figure S120. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 27: *(S)*-BINOL with 25 eq. K_2CO_3, NG, 24 h.

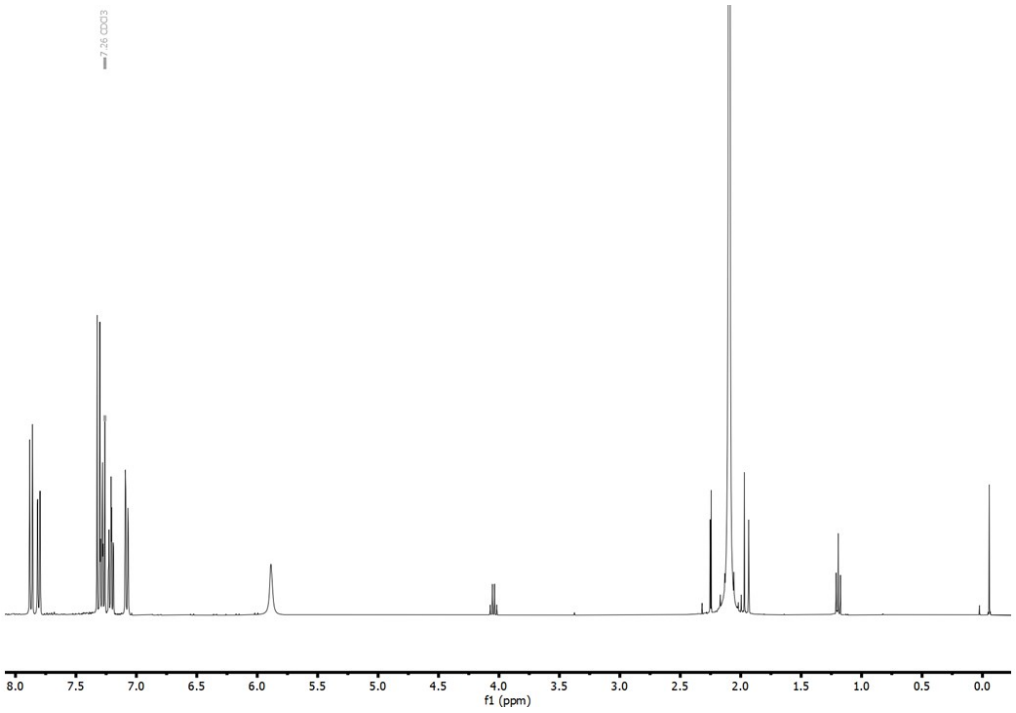


Figure S121. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 28: *(S)*-BINOL with 25 eq. K_2CO_3, LAG, 24 h.

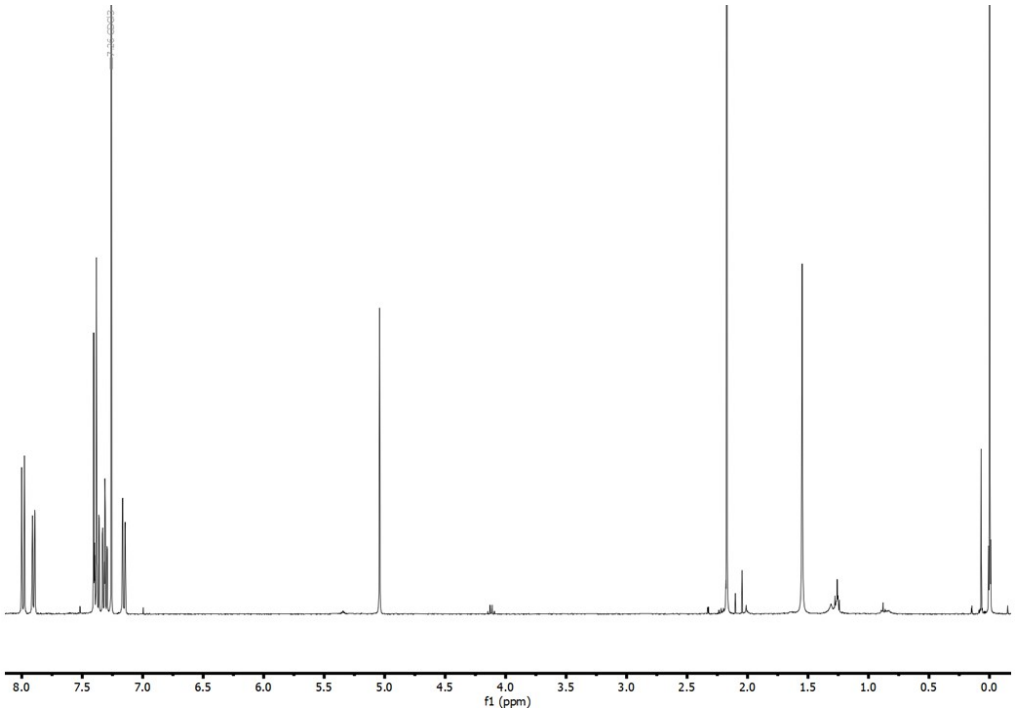


Figure S122. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 29: *(S)*-BINOL with 1 eq. Cs_2CO_3, NG, 4.5 h.

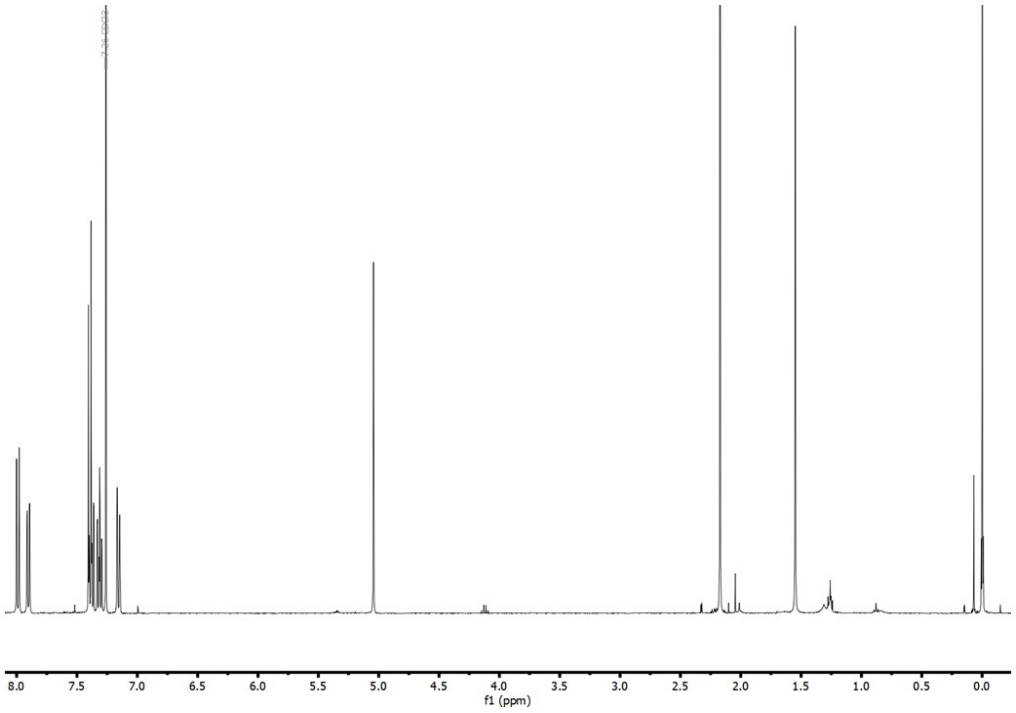


Figure S122. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 30: *(S)*-BINOL with 1 eq. Cs_2CO_3, LAG, 4.5 h.

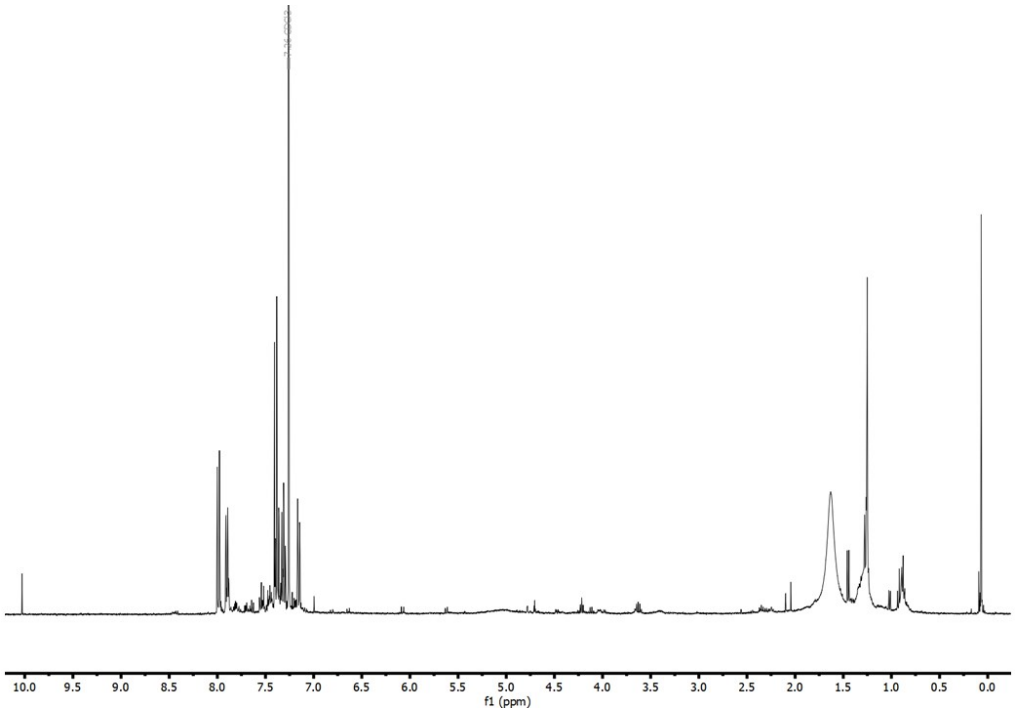


Figure S123. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 31: *(S)*-BINOL with 1.0 eq. Cs_2CO_3, NG, 24 h.

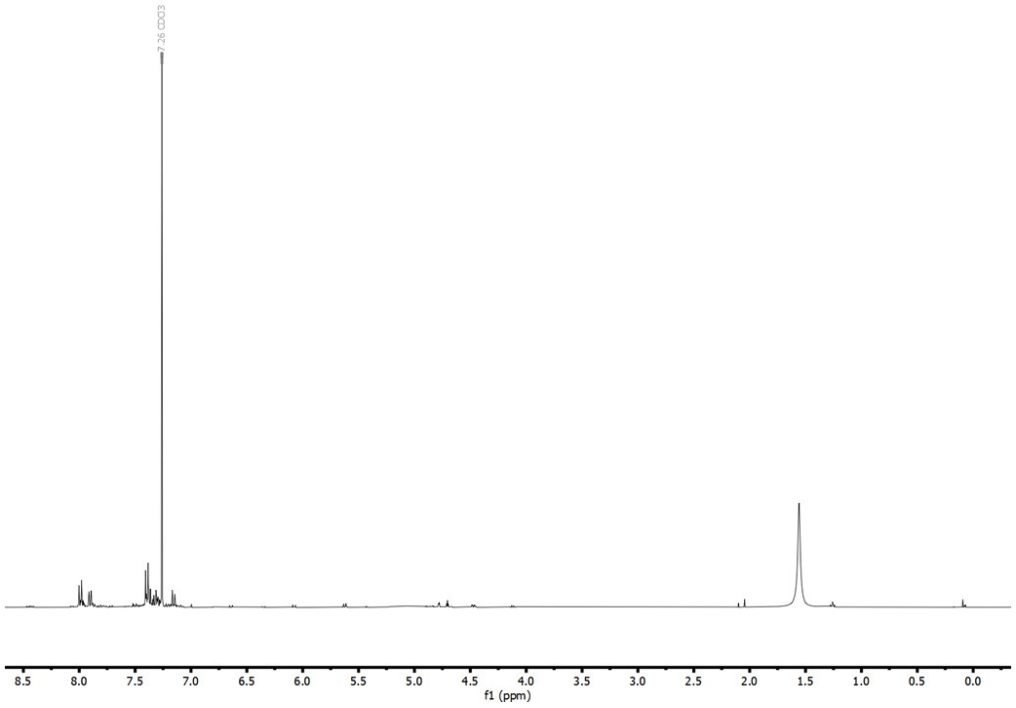


Figure S124. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 32: *(S)*-BINOL with 1.0 eq. Cs_2CO_3, LAG, 24 h.

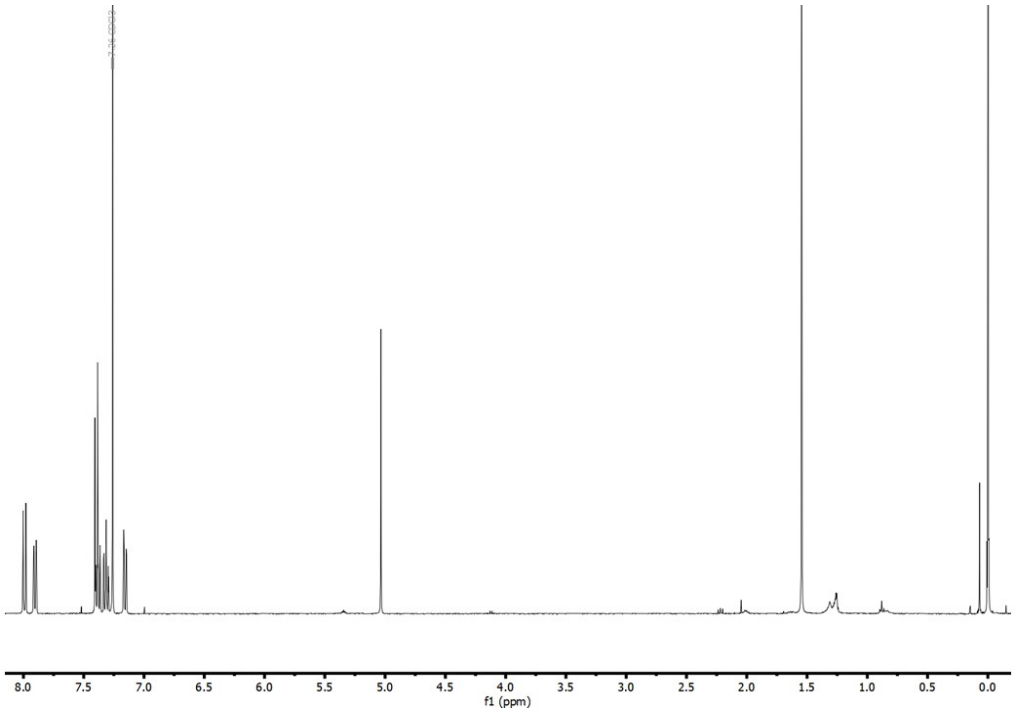


Figure S125. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 33: *(S)*-BINOL with 1 eq. Cs_2CO_3, NG with NaCl, 4.5 h.

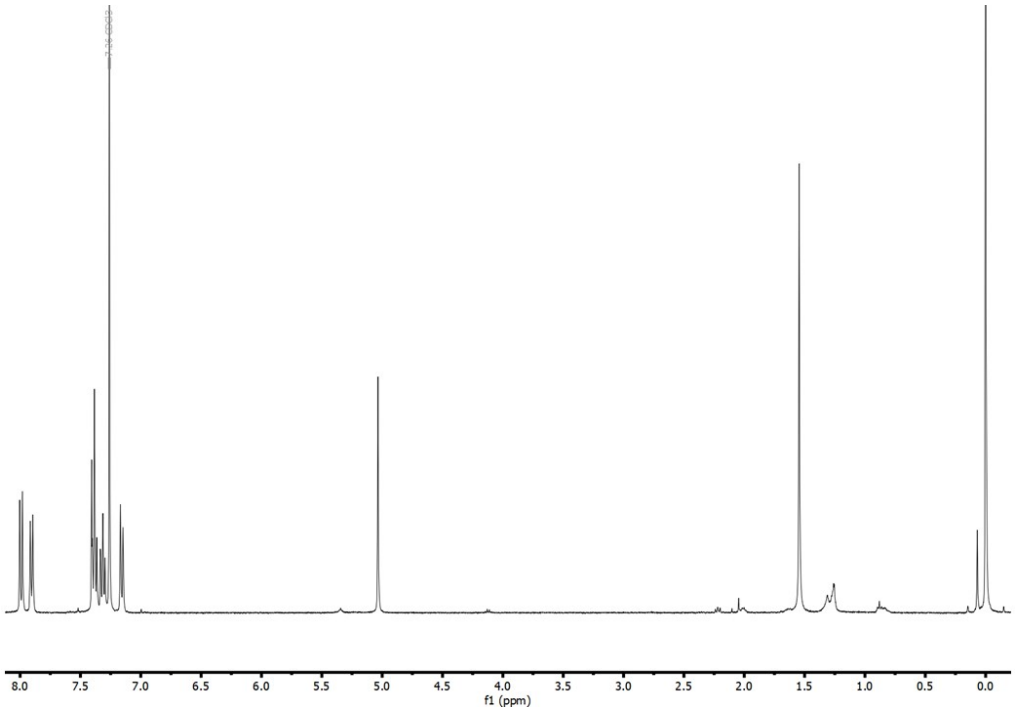


Figure S126. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 34: *(S)*-BINOL with 1 eq. Cs_2CO_3, LAG with NaCl, 4.5 h.

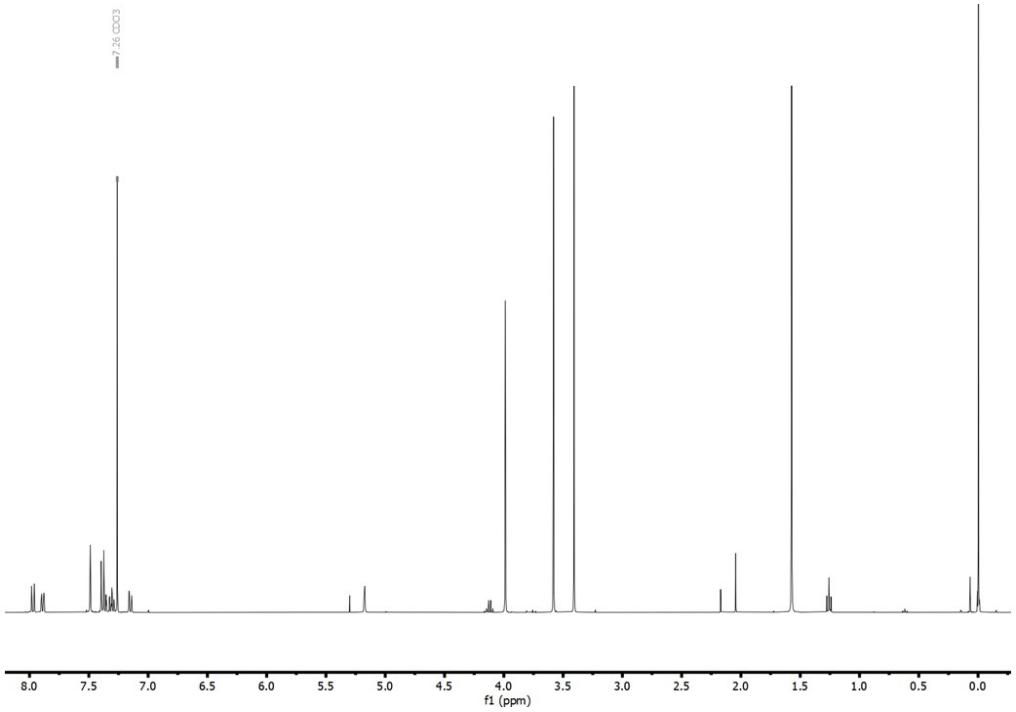


Figure S127. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 35: *(S)*-BINOL with 1.0 eq. Cs_2CO_3, NG with NaCl, 24 h. Signals at 4 and 3.5 likely correspond to side-products.

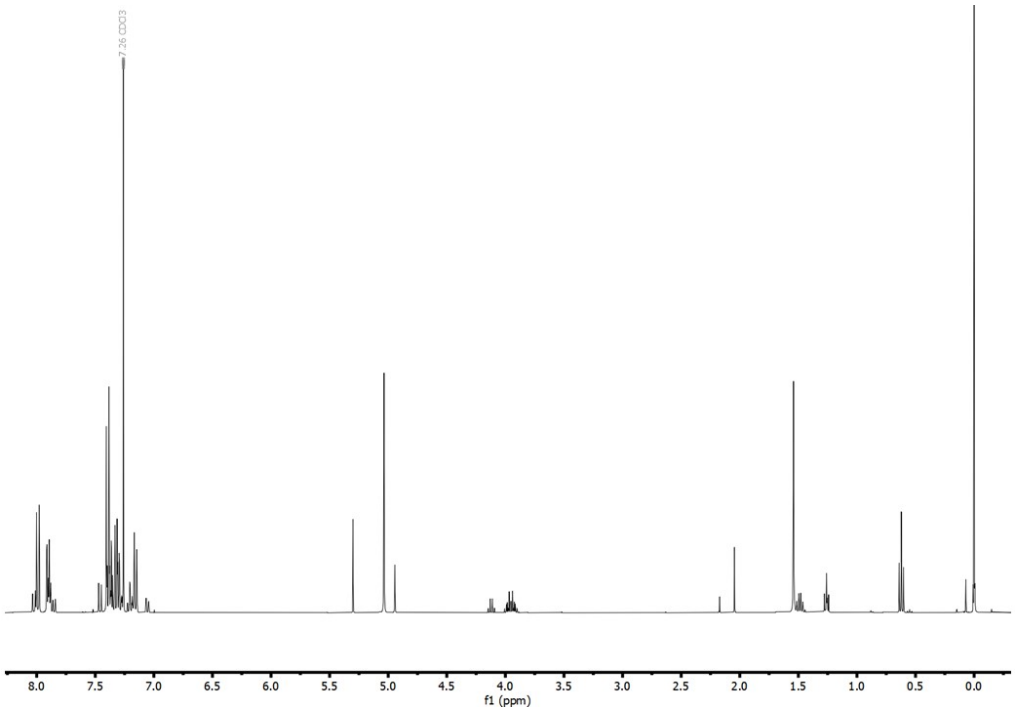


Figure S128. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 36: *(S)*-BINOL with 1.0 eq. Cs_2CO_3, LAG with NaCl, 24 h.

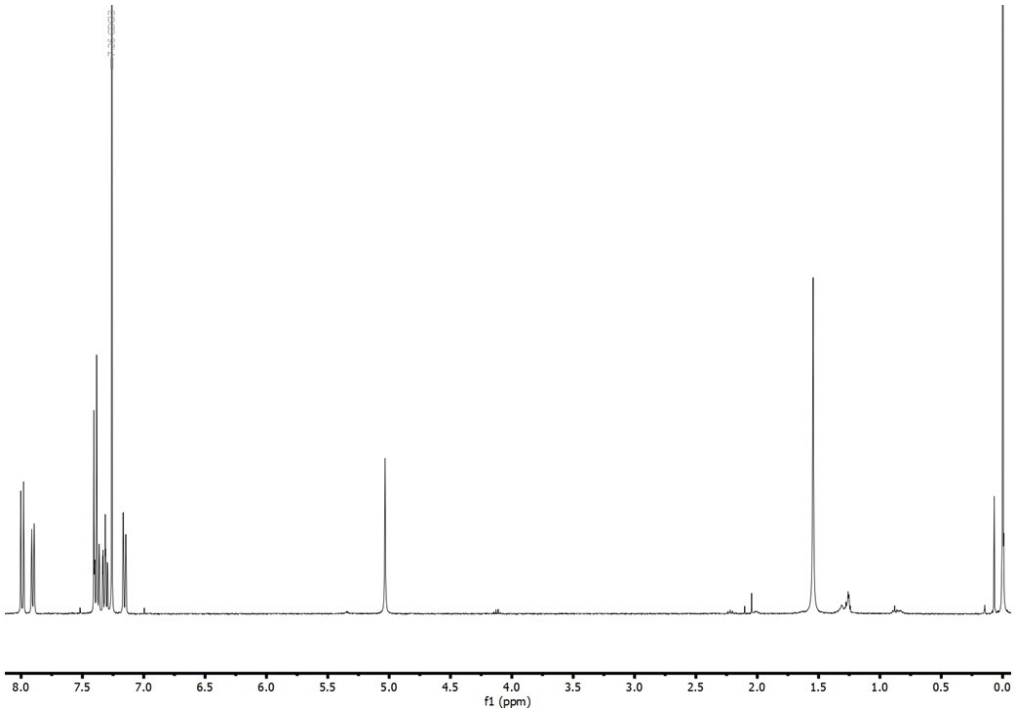


Figure S129. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 37: *(S)*-BINOL with 25 eq. Cs_2CO_3, NG 4.5 h.

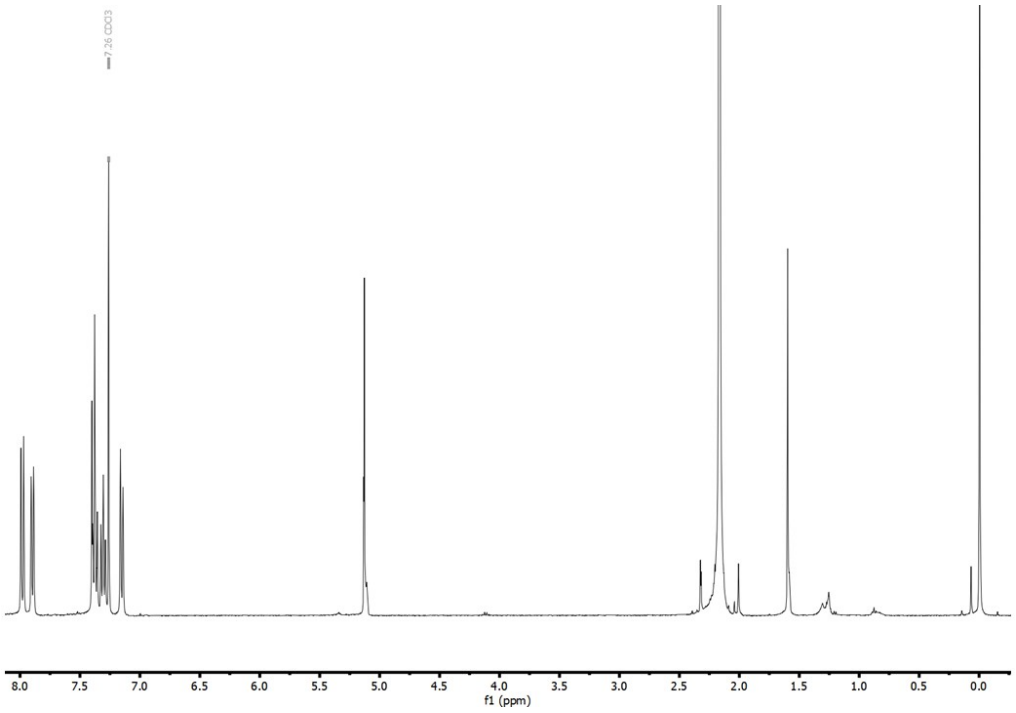


Figure S130. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 38: *(S)*-BINOL with 25 eq. Cs_2CO_3, LAG 4.5 h.

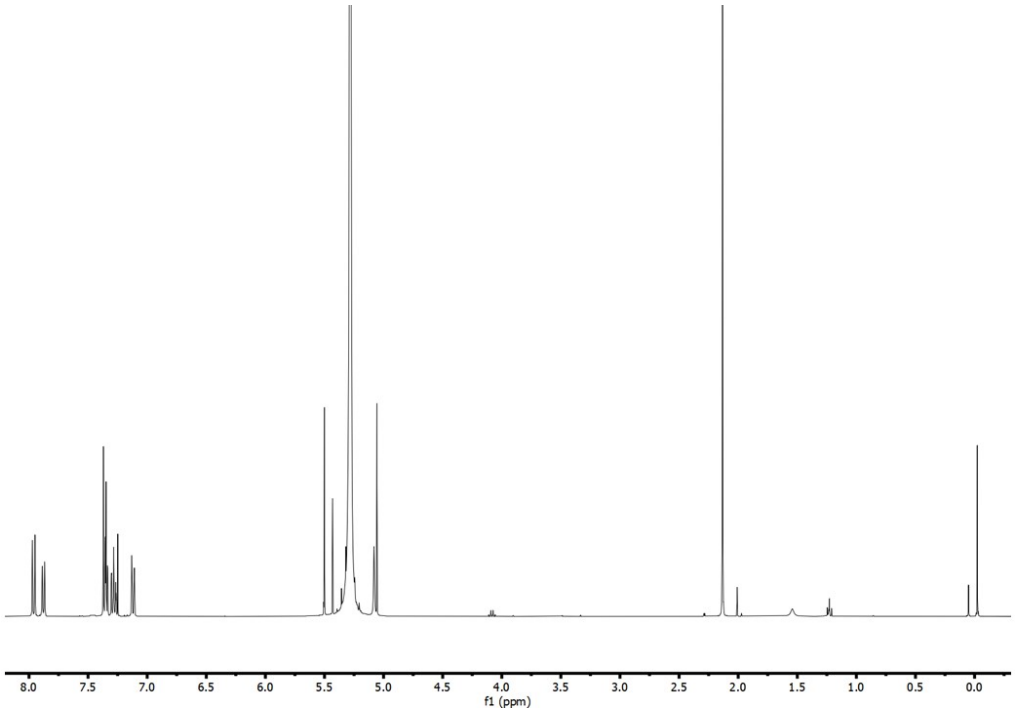


Figure S131. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 39: *(S)*-BINOL with 25 eq. Cs_2CO_3, NG, 24 h.

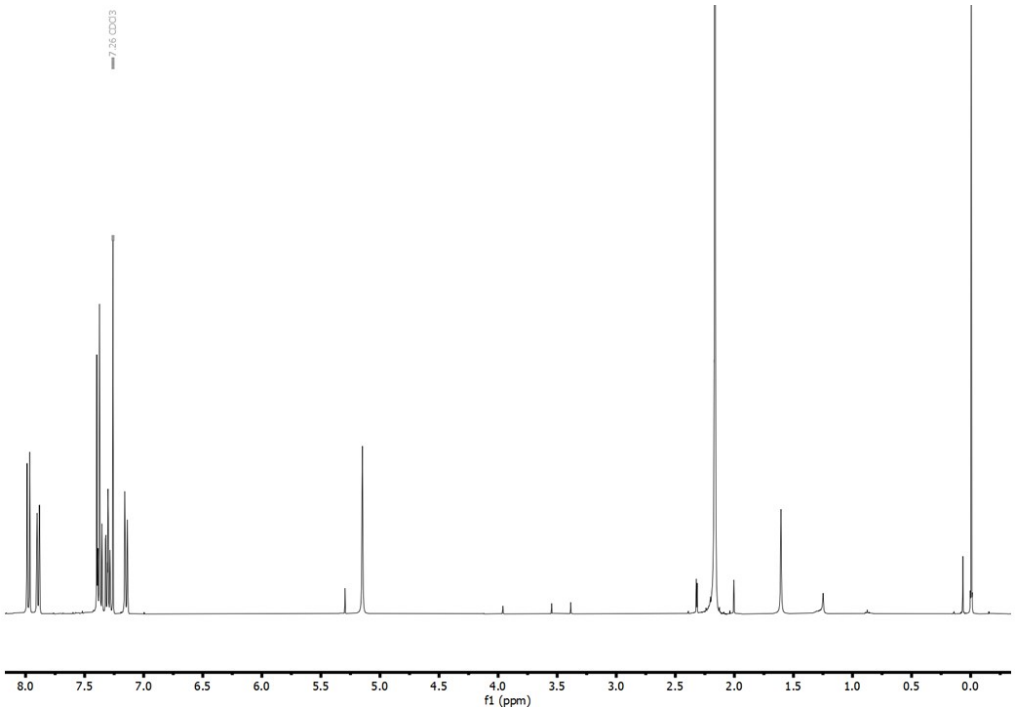


Figure S132. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 40: *(S)*-BINOL with 25 eq. Cs_2CO_3, LAG, 24 h.

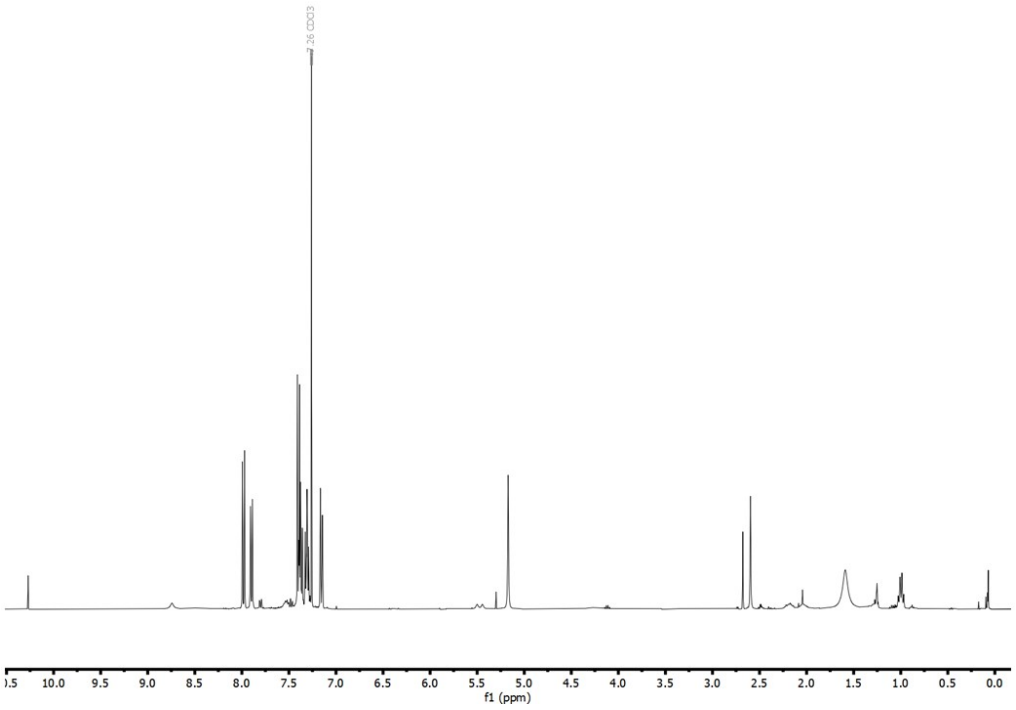


Figure S133. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 41: *(S)*-BINOL without base, NG with NaCl, 4.5 h.

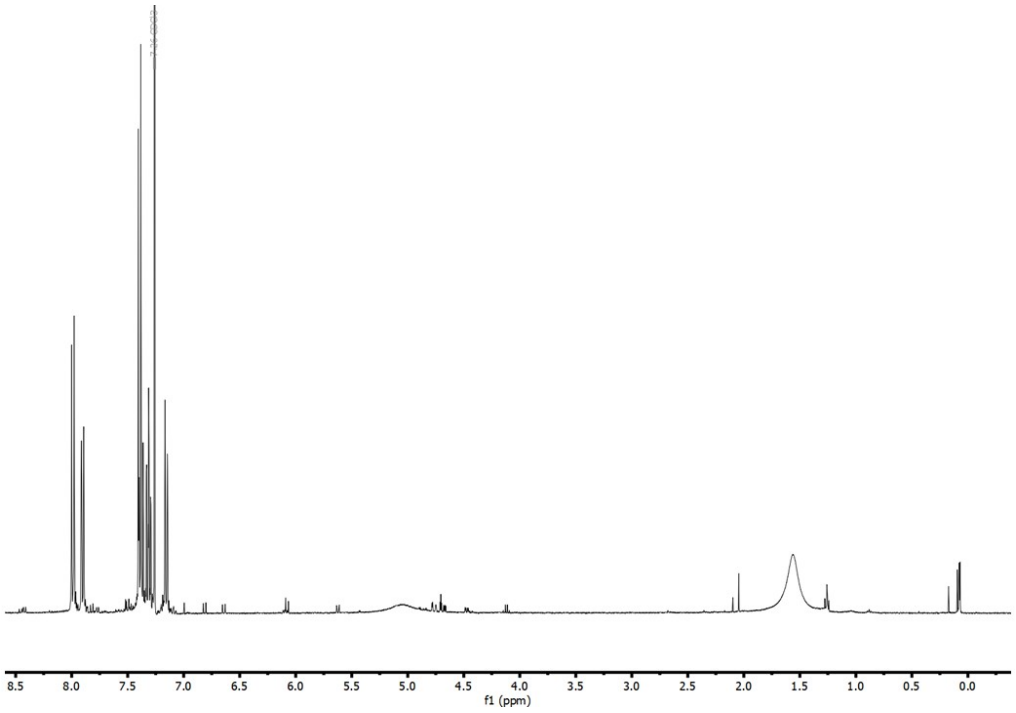


Figure S134. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 42: *(S)*-BINOL without base, LAG with NaCl, 4.5 h.

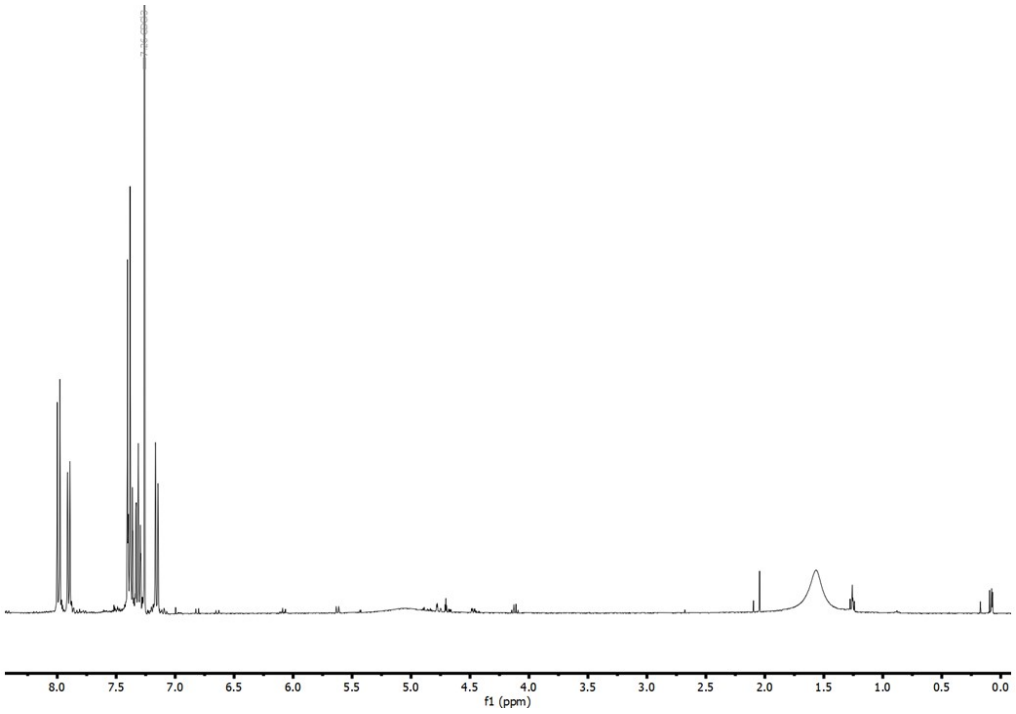


Figure S135. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 43: *(S)*-BINOL without base, NG with NaCl, 24 h.

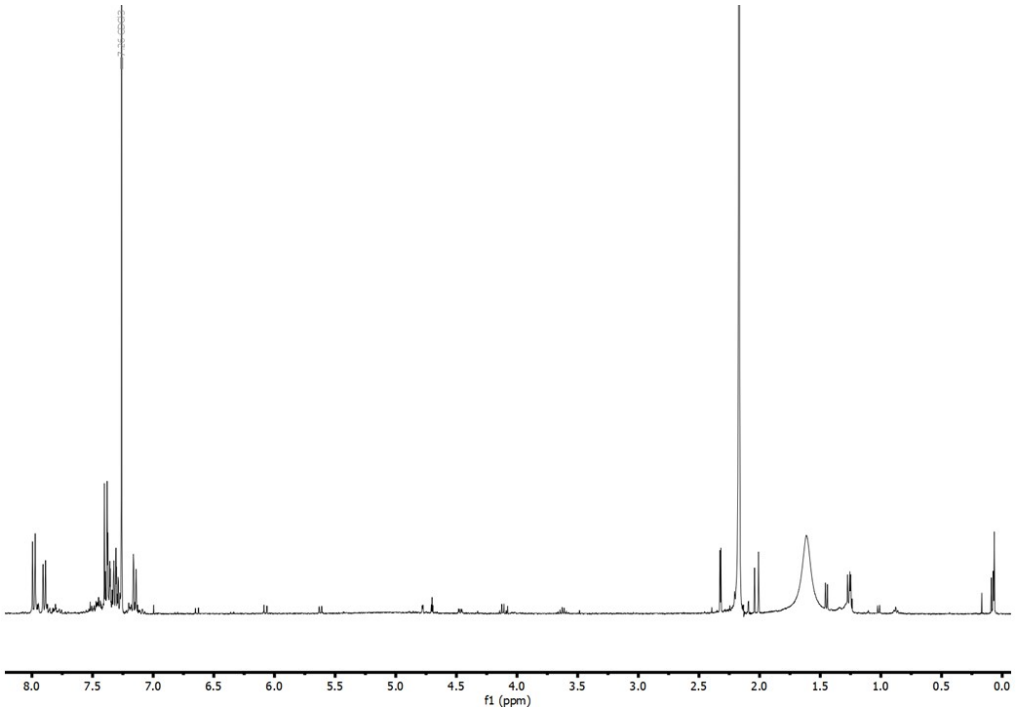


Figure S136. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 44: *(S)*-BINOL without base, LAG with NaCl, 24 h.

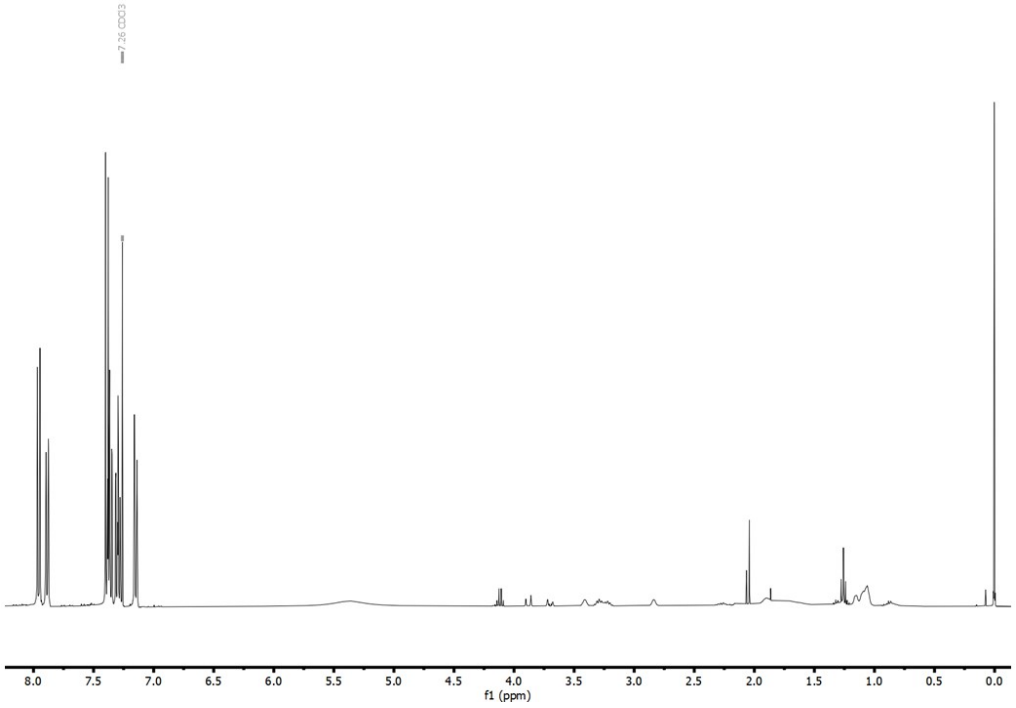


Figure S137. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 45: *(S)*-BINOL, 1.5 h.

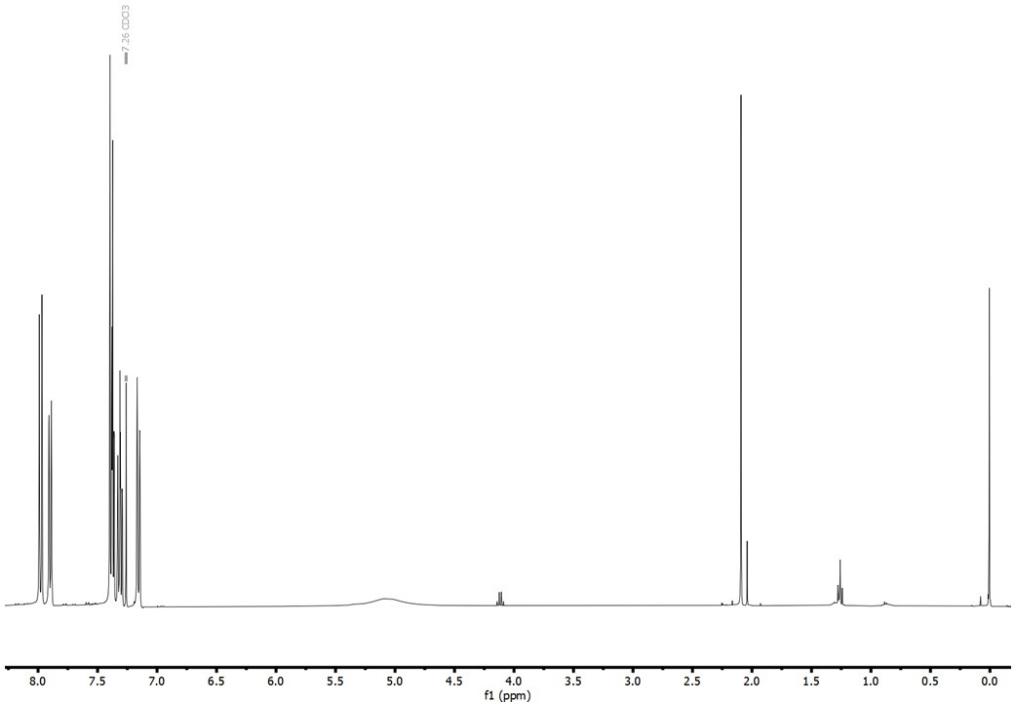


Figure S138. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 46: *(S)*-BINOL, 4.5 h.

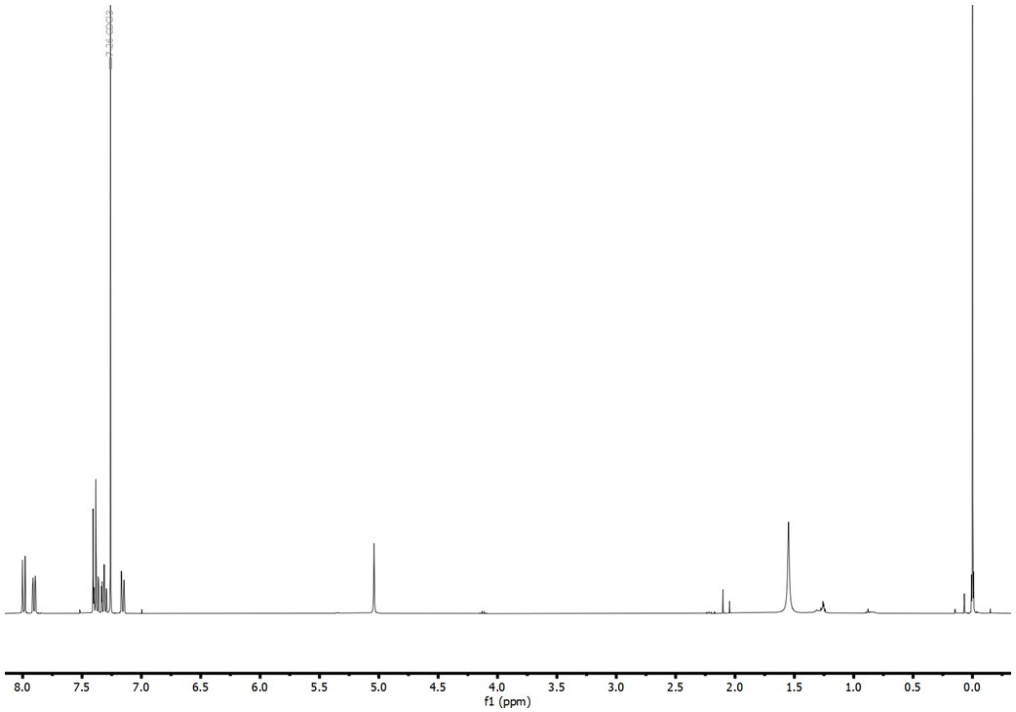


Figure S139. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S1, entry 47: *(S)*-BINOL, 24 h.

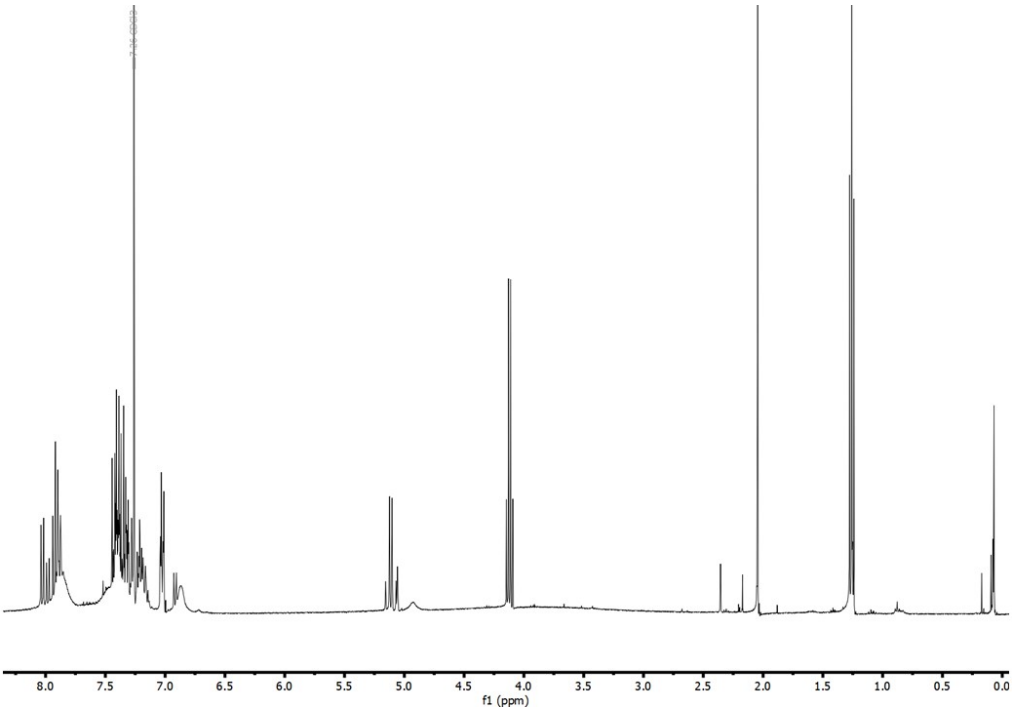


Figure S140. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S2, entry 1: *(S)*-BINAM with 0.1 eq. pyrrolidine, LAG with NaCl, 24 h.

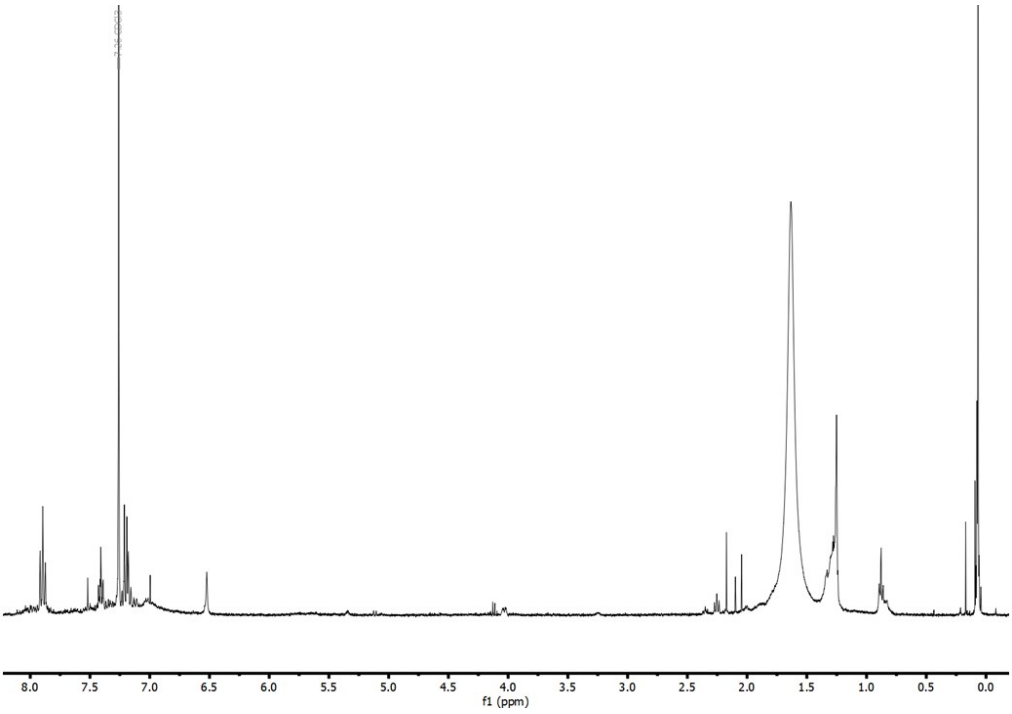


Figure S141. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S2, entry 2: *(S)*-BINAM without base, LAG with NaCl, 24 h.

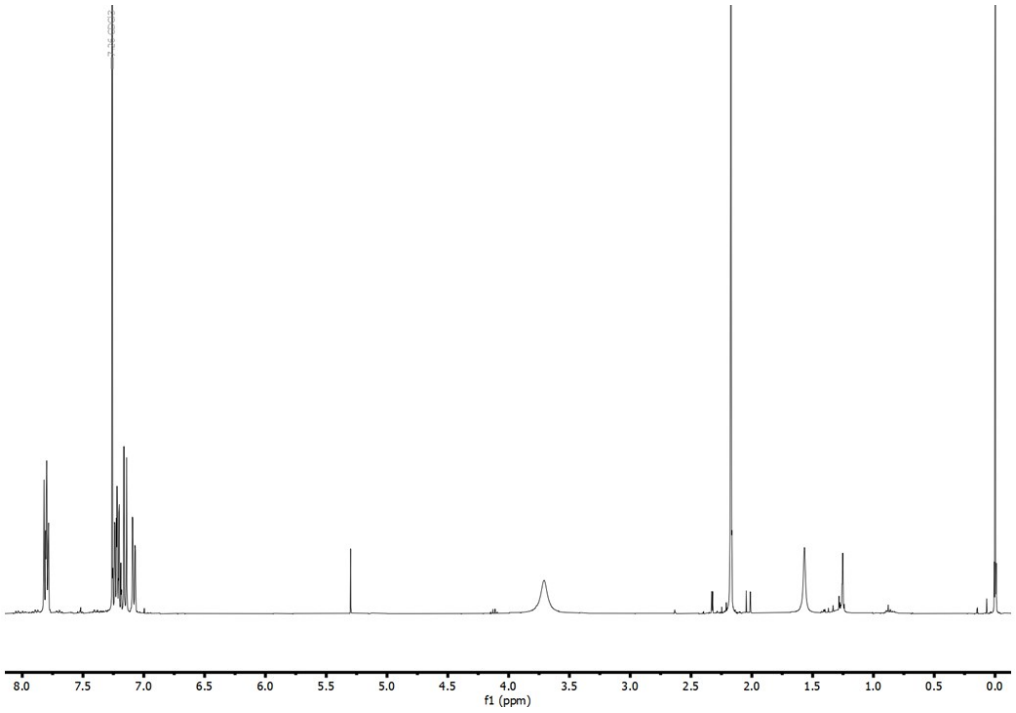


Figure S142. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S2, entry 3: *(S)*-BINAM with 1.0 eq. K_2CO_3, NG, 24 h.

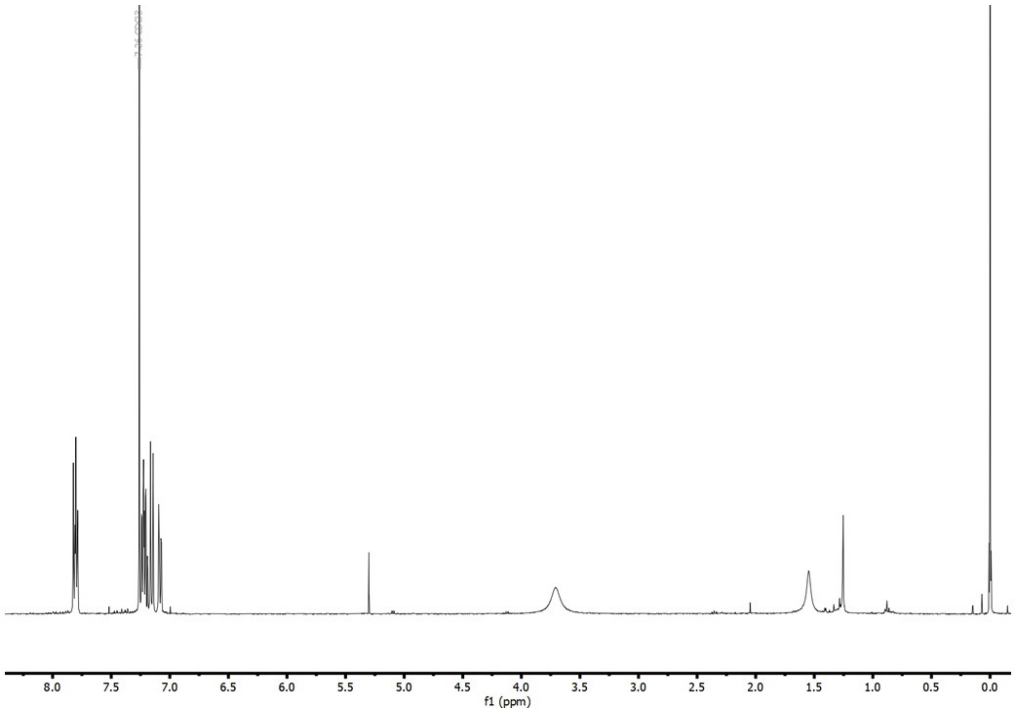


Figure S143. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S2, entry 4: *(S)*-BINAM with 1.0 eq. K_2CO_3, LAG, 24 h.

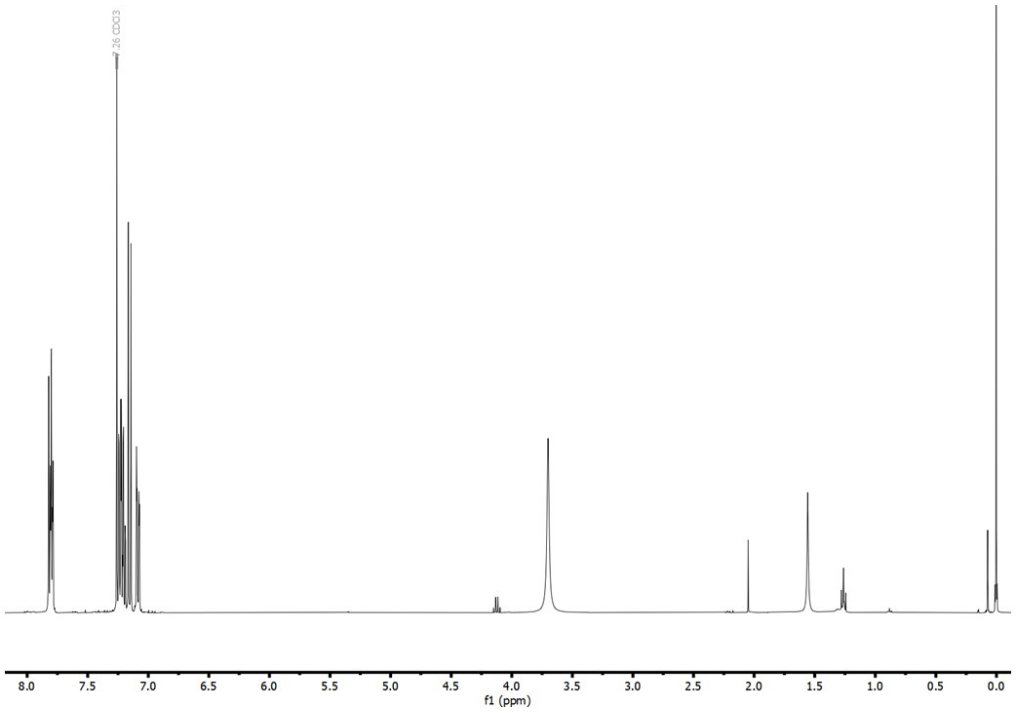


Figure S144. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S2, entry 5: *(S)*-BINAM with 1.0 eq. Cs_2CO_3, NG with NaCl, 24 h.

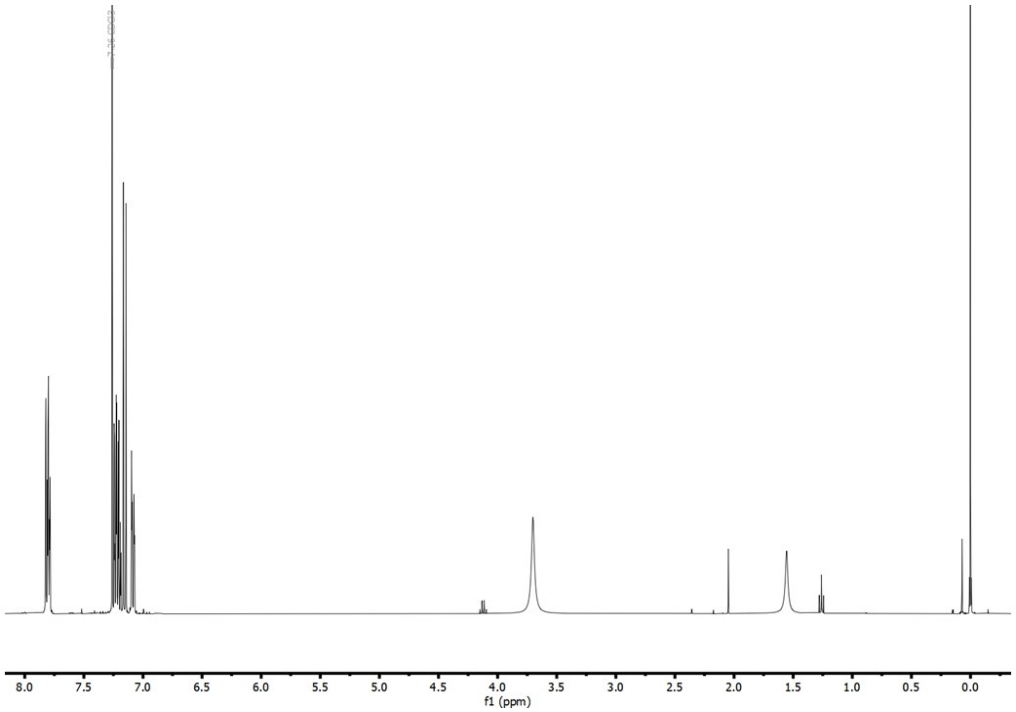


Figure S145. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S2, entry 6: *(S)*-BINAM with 1.0 eq. Cs_2CO_3, LAG with NaCl, 24 h.

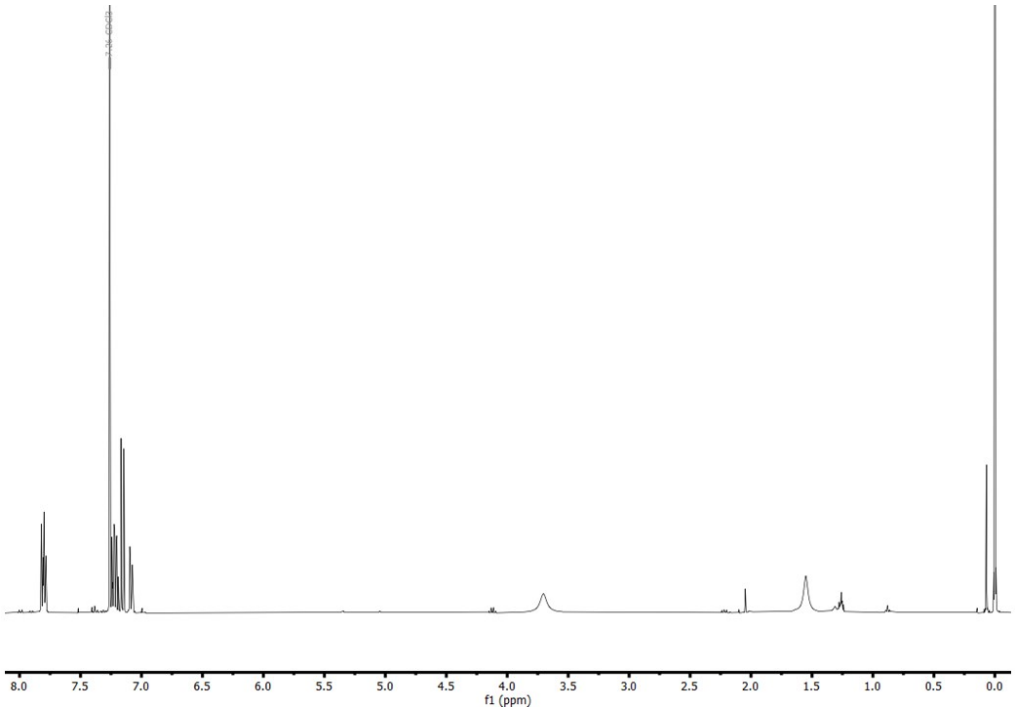


Figure S146. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S2, entry 7: *(S)*-BINAM, 1.5 h.

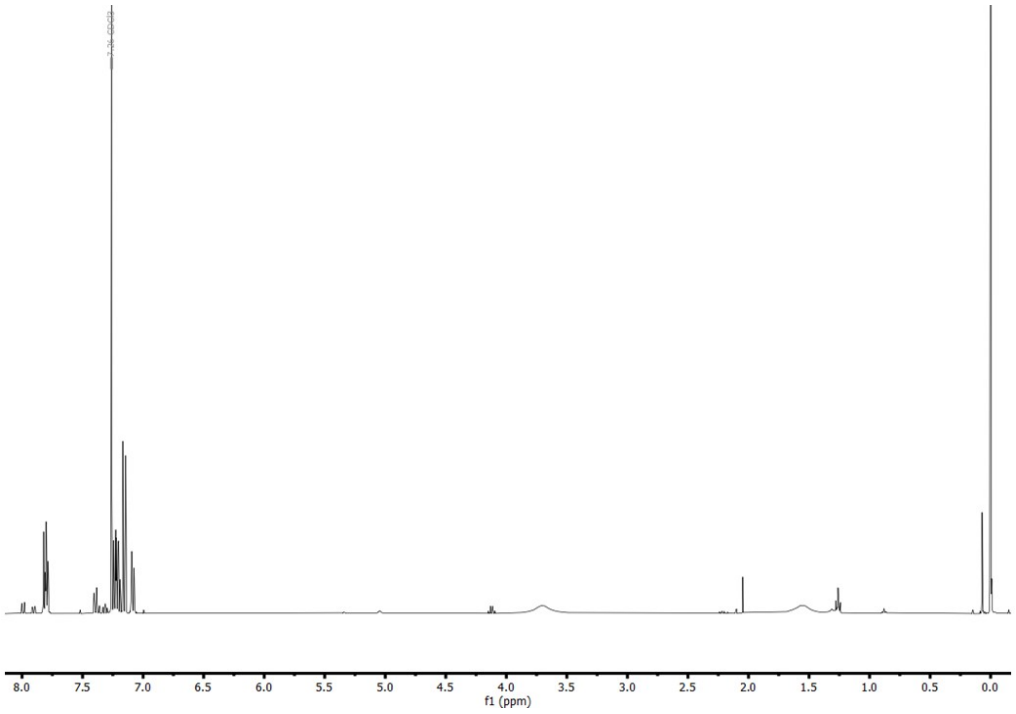


Figure S147. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S2, entry 8: *(S)*-BINAM, 4.5 h.

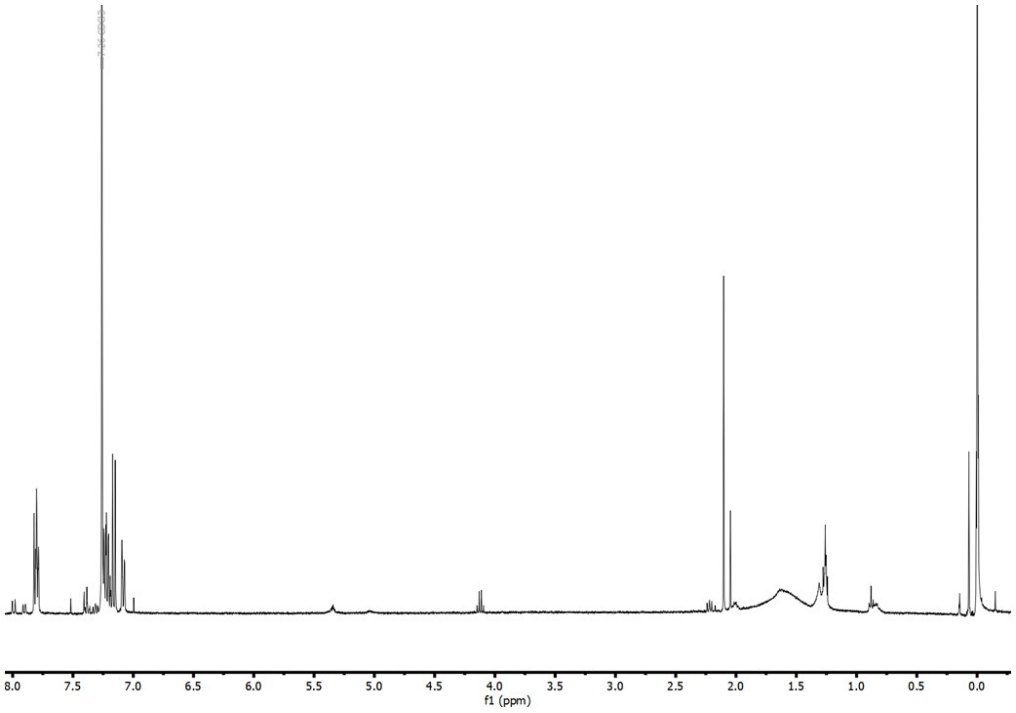


Figure S148. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S2, entry 9: *(S)*-BINAM, 24 h.

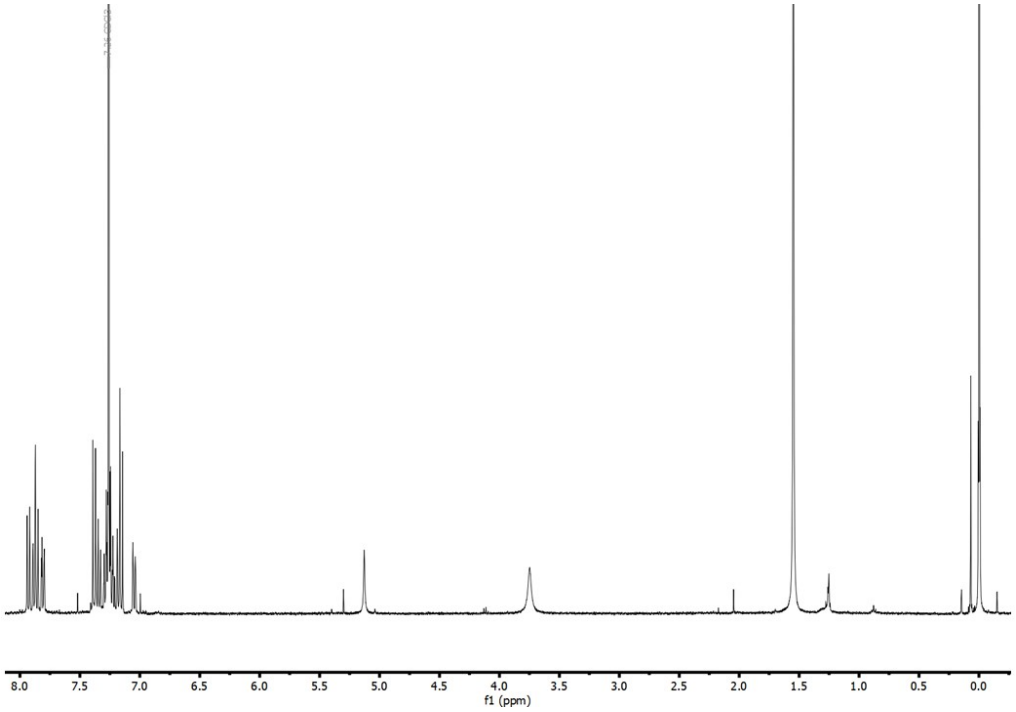


Figure S149. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S3, entry 1: *(S)*-NOBIN with 0.1 eq. pyrrolidine, LAG with NaCl, 24 h.

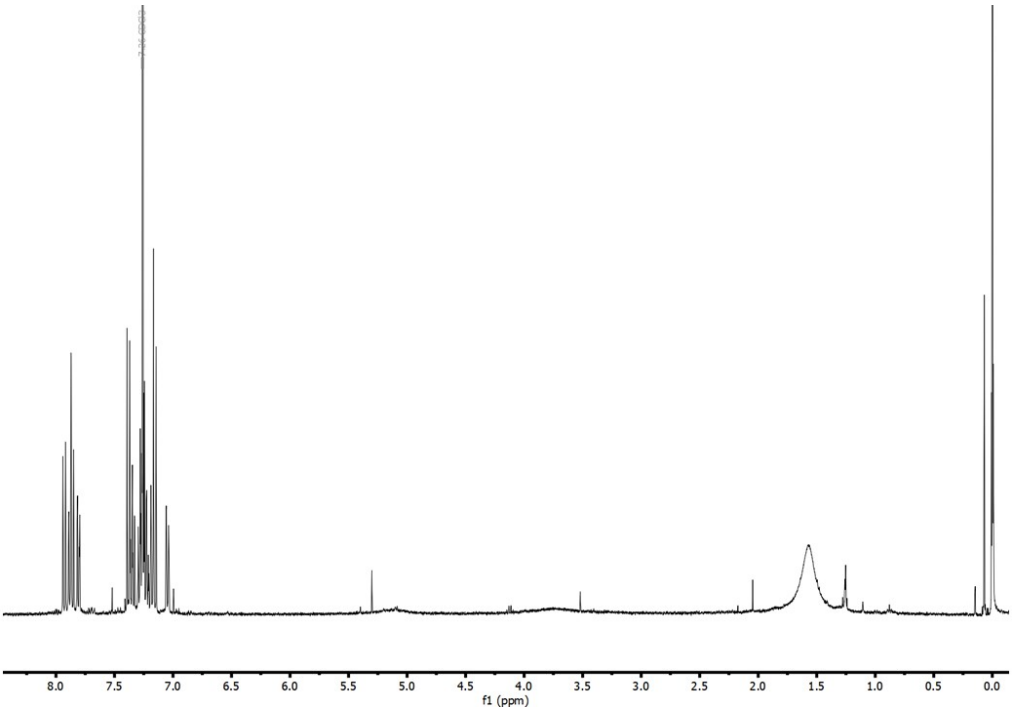


Figure S150. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S3, entry 2: *(S)*-NOBIN without base, LAG with NaCl, 24 h.

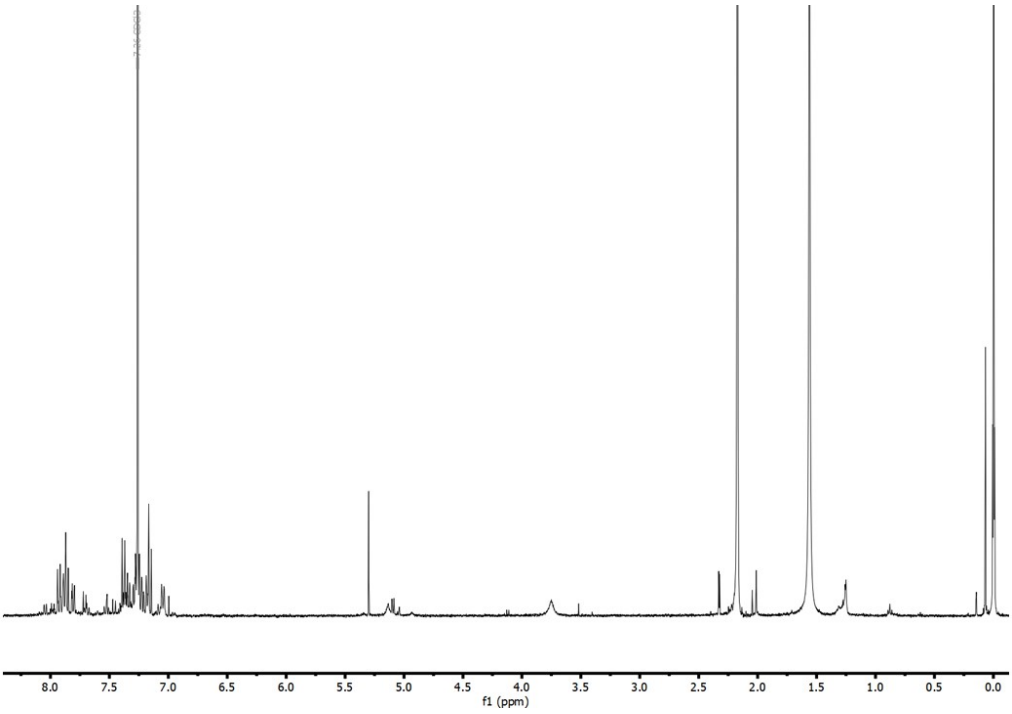


Figure S151. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S3, entry 3: *(S)*-NOBIN with 1.0 eq. K_2CO_3, NG, 24 h.

Figure S152. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S3, entry 4: *(S)*-NOBIN with 50 eq. K_2CO_3, NG, 24 h.

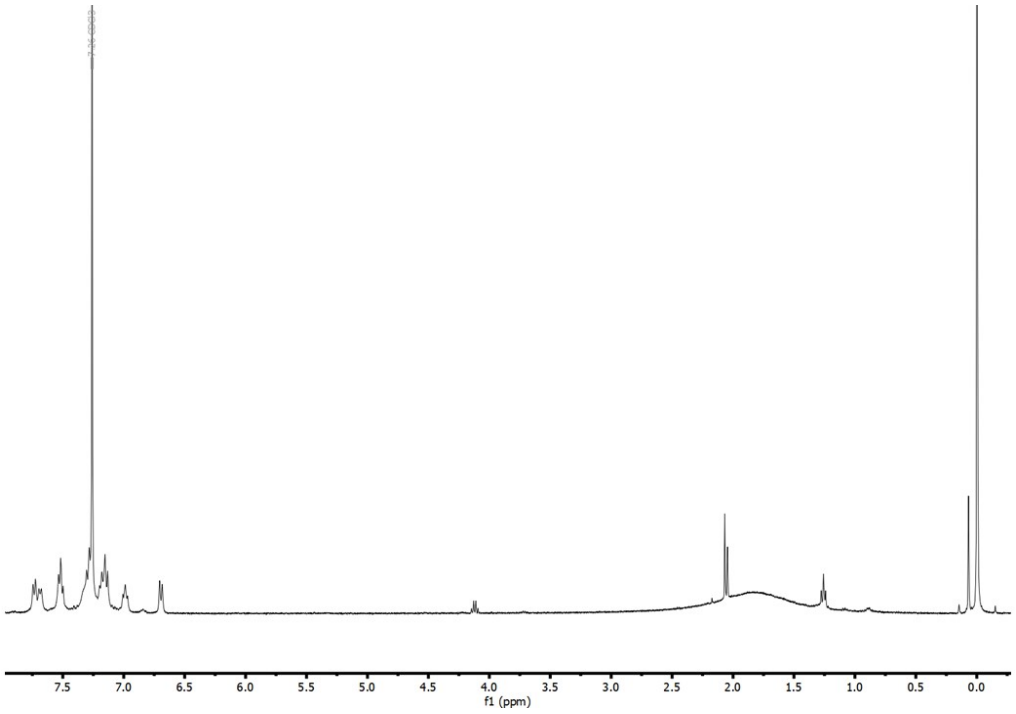


Figure S153. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S3, entry 5: *(S)*-NOBIN with 1.0 eq. Cs_2CO_3, NG with NaCl, 24 h.

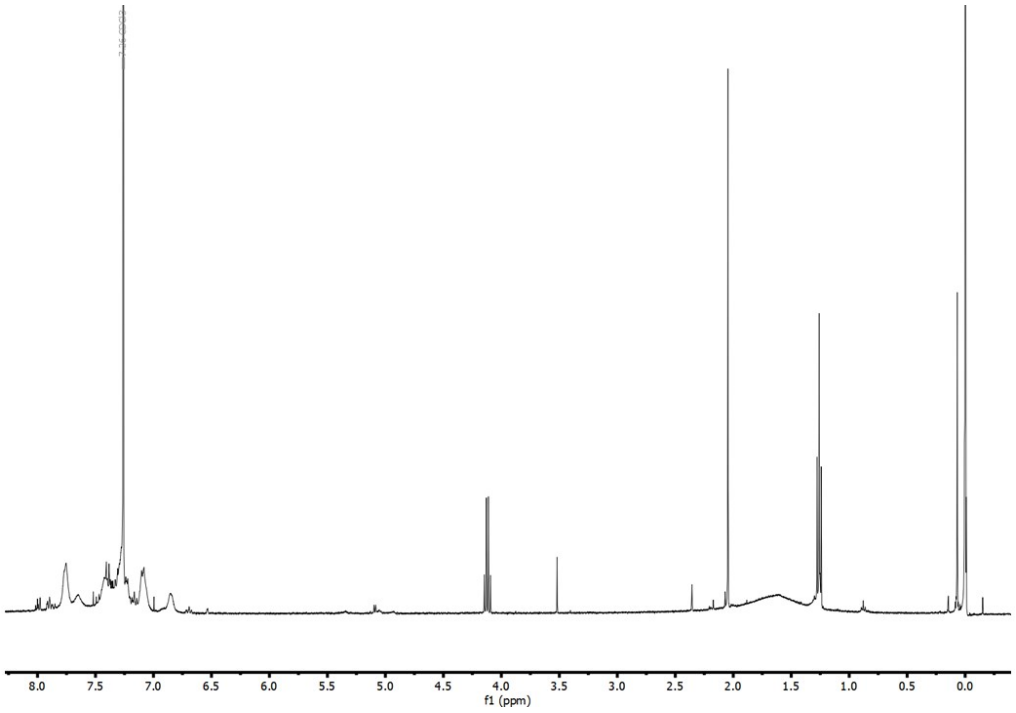


Figure S154. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S3, entry 6: *(R)*-NOBIN with 1.0 eq. Cs_2CO_3, LAG with NaCl, 24 h.

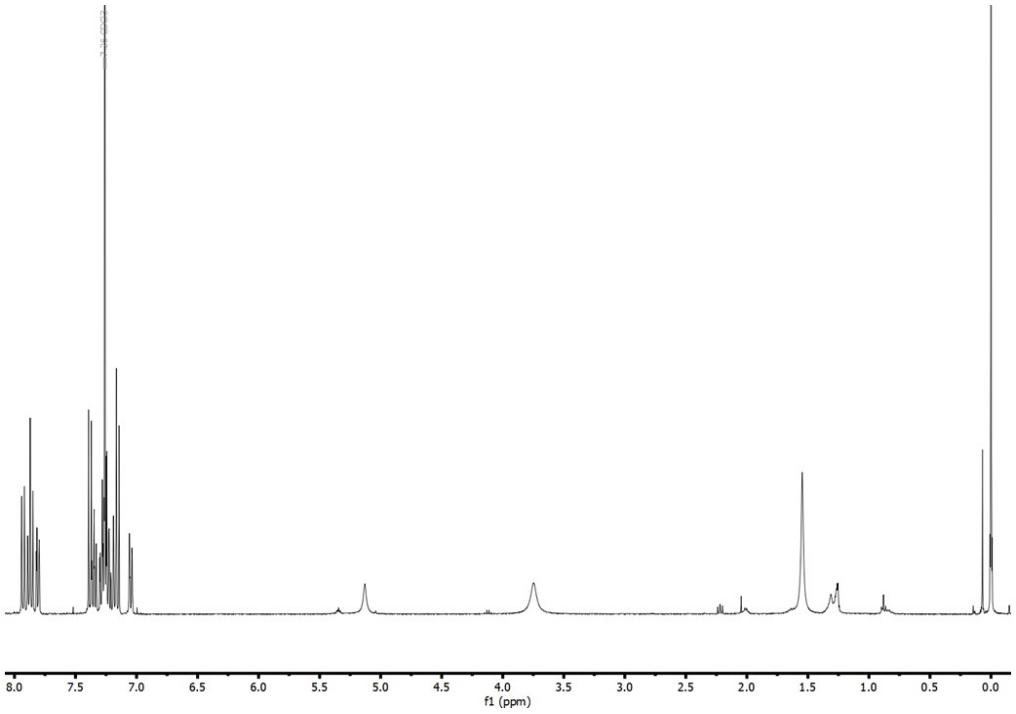


Figure S155. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S3, entry 7: *(S)*-NOBIN, 1.5 h.

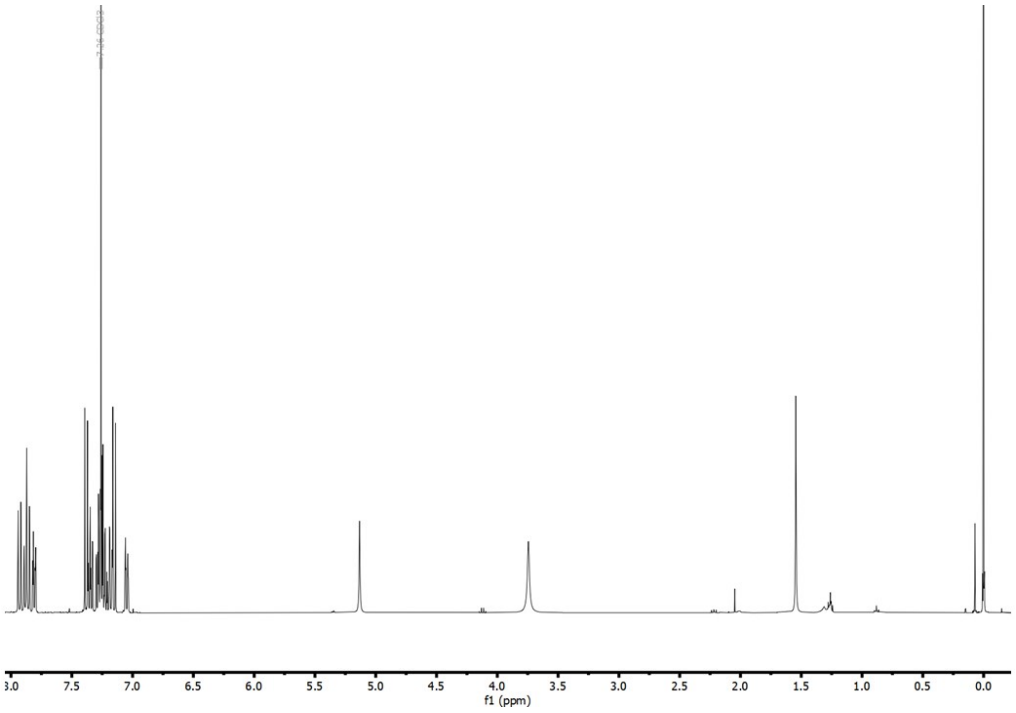


Figure S156. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S3, entry 8: *(S)*-NOBIN, 4.5 h.

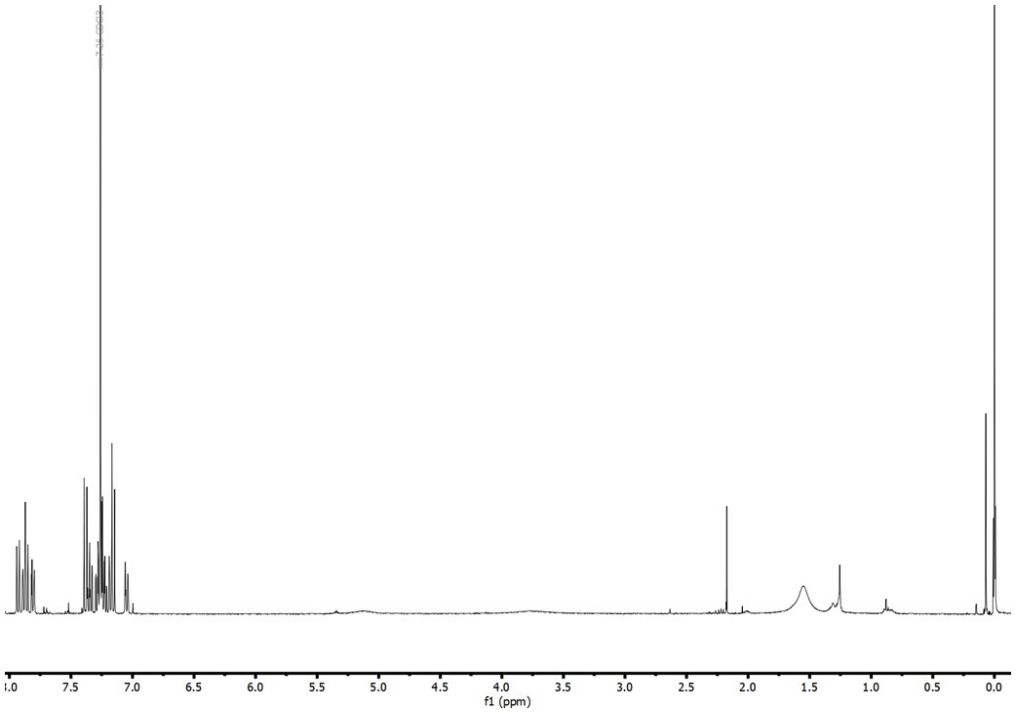


Figure S157. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S3, entry 9: *(S)*-NOBIN, 24 h.

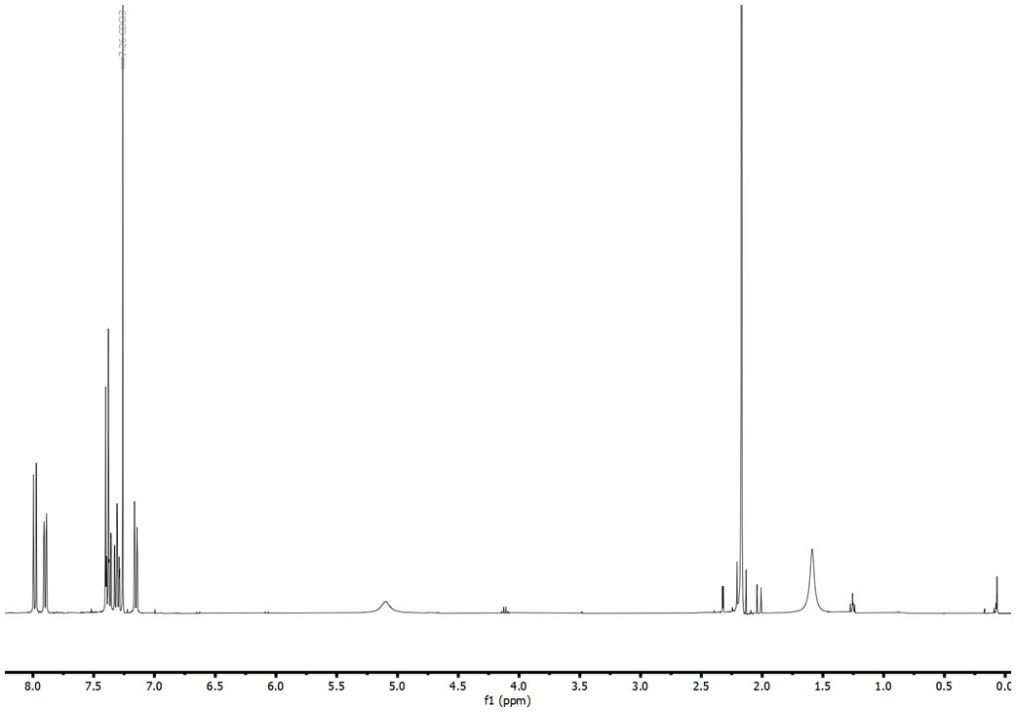


Figure S158. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S4, entry 2: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG, 20 Hz, 4.5 h.

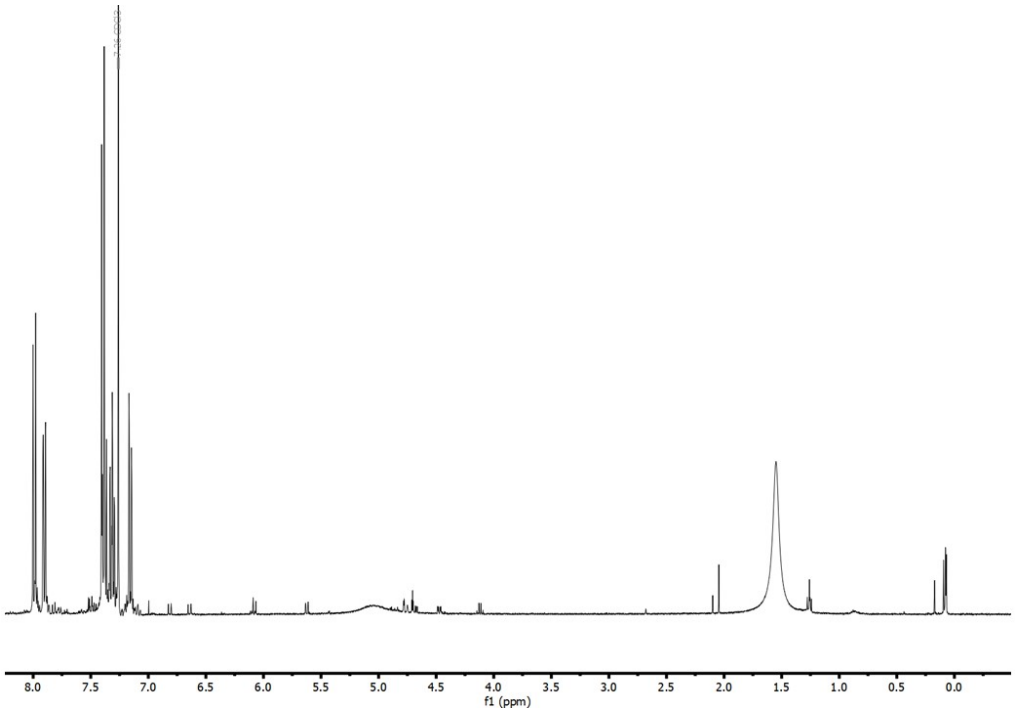


Figure S159. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S4, entry 3: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG, 10 Hz, 4.5 h.

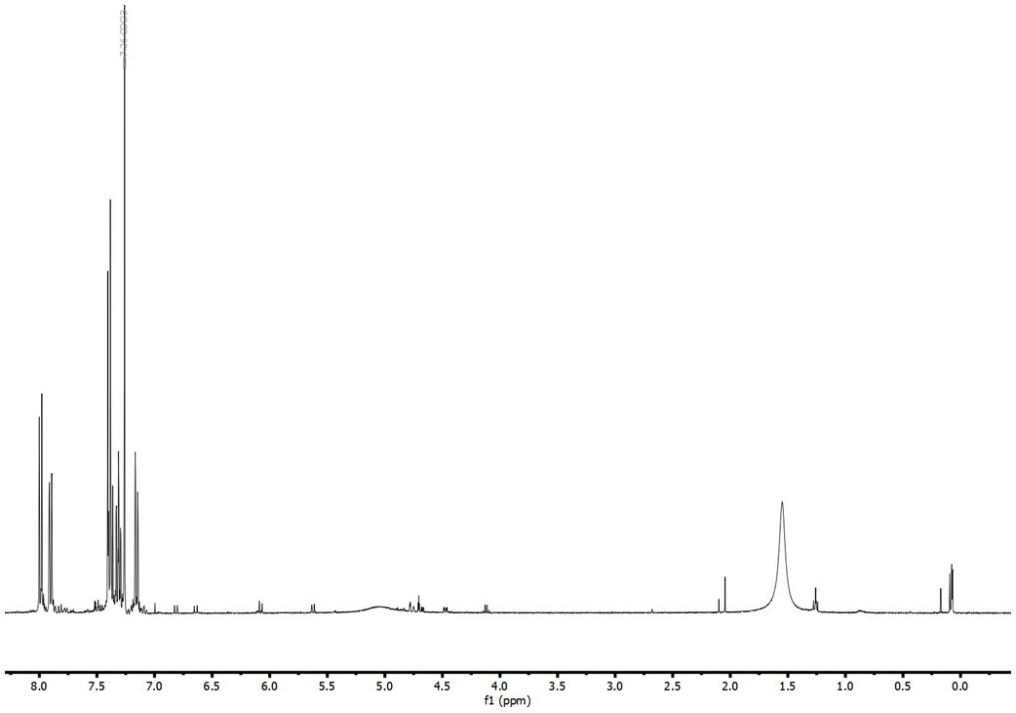


Figure S160. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S4, entry 4: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG, 5 Hz, 4.5 h.

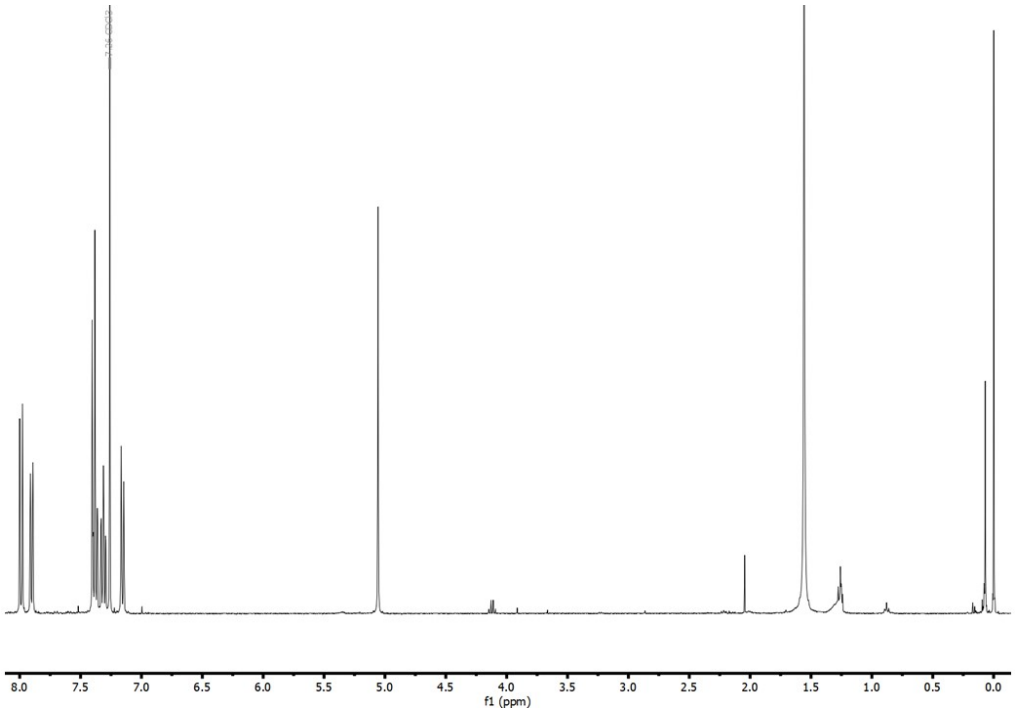


Figure S161. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S4, entry 5: *(S)*-BINOL with 0.2 eq. pyrrolidine, NG, 30 Hz, 4.5 h.

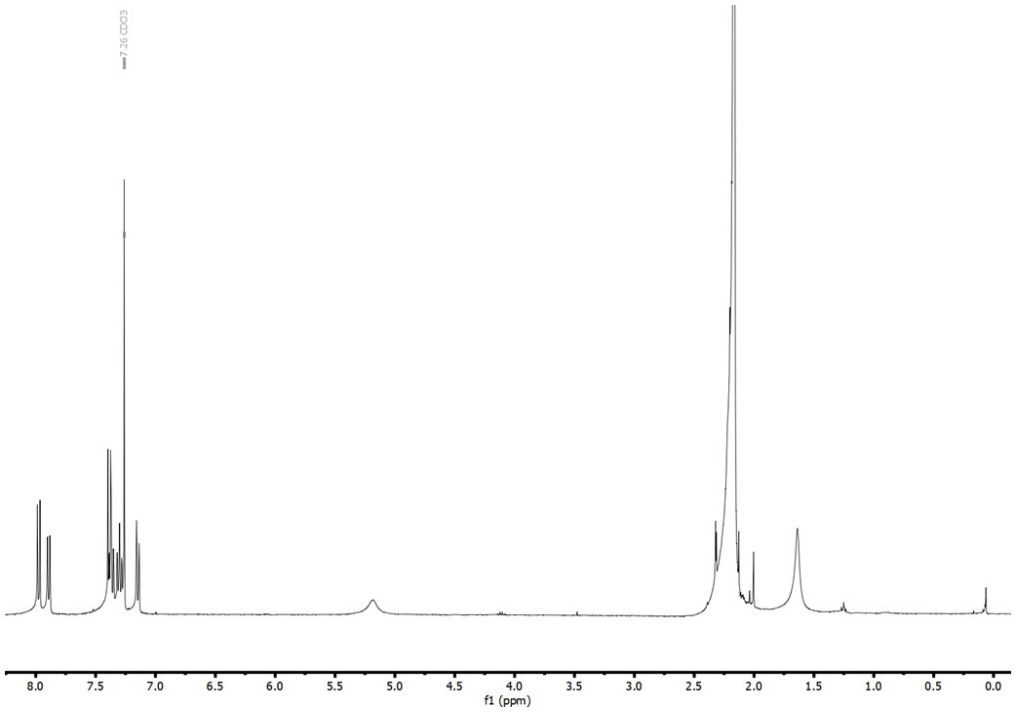


Figure S162. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S4, entry 6: *(S)*-BINOL with 0.2 eq. pyrrolidine, NG, 20 Hz, 4.5 h.

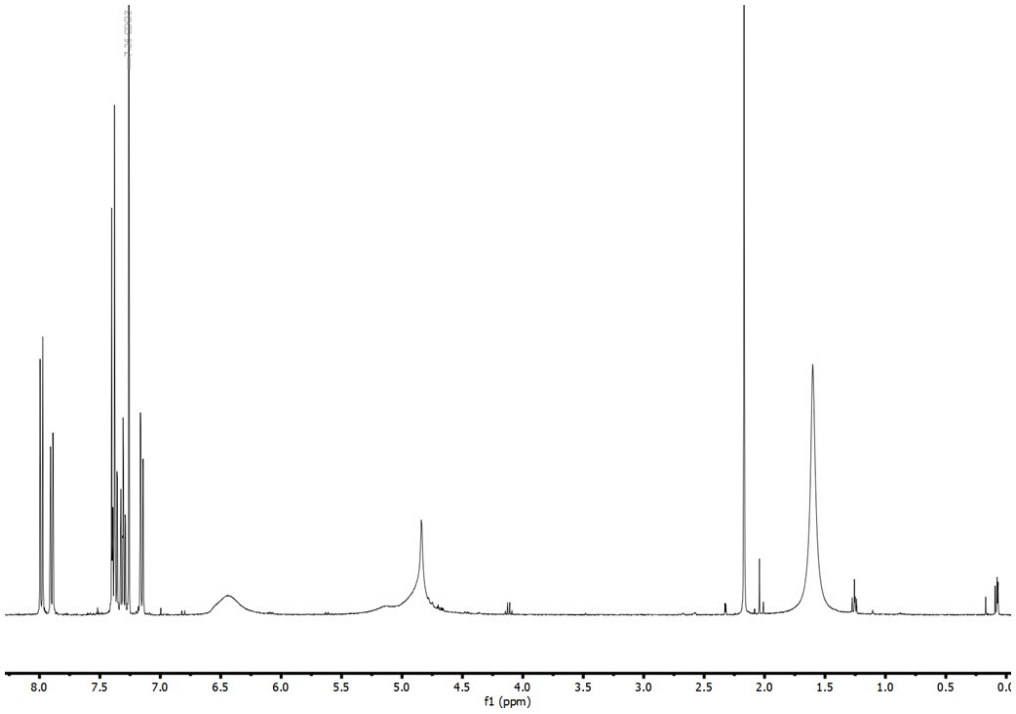


Figure S163. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S4, entry 7: *(S)*-BINOL with 0.2 eq. pyrrolidine, NG, 10 Hz, 4.5 h.

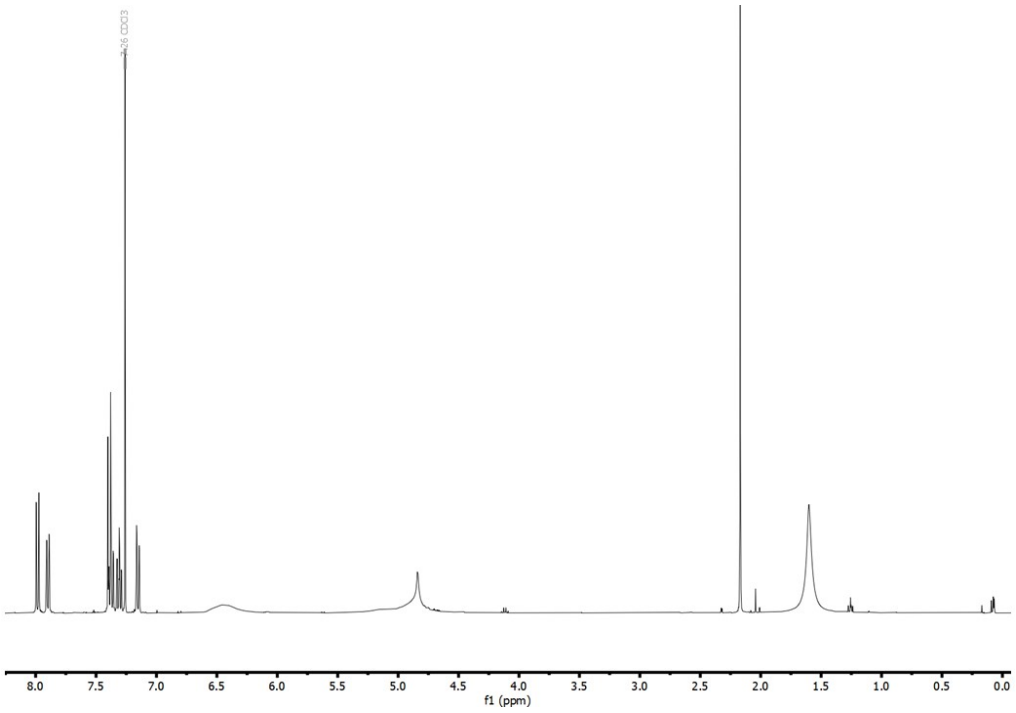


Figure S164. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S4, entry 8: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG, 5 Hz, 4.5 h.

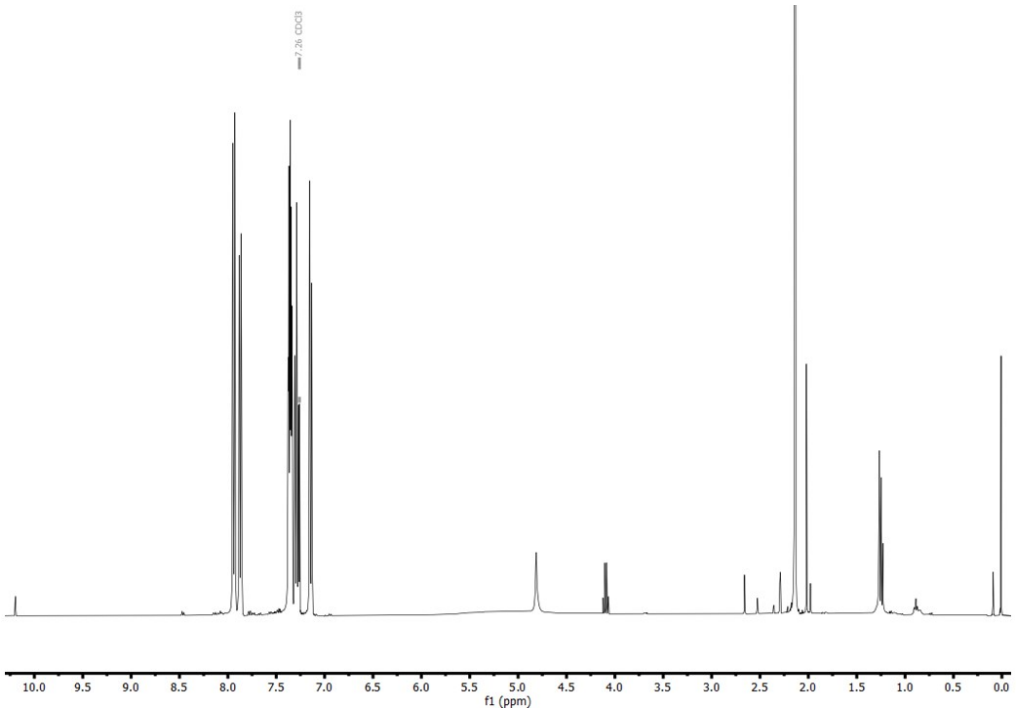


Figure S165. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S5, entry 1: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG, 24 h, PTFE milling vessel.

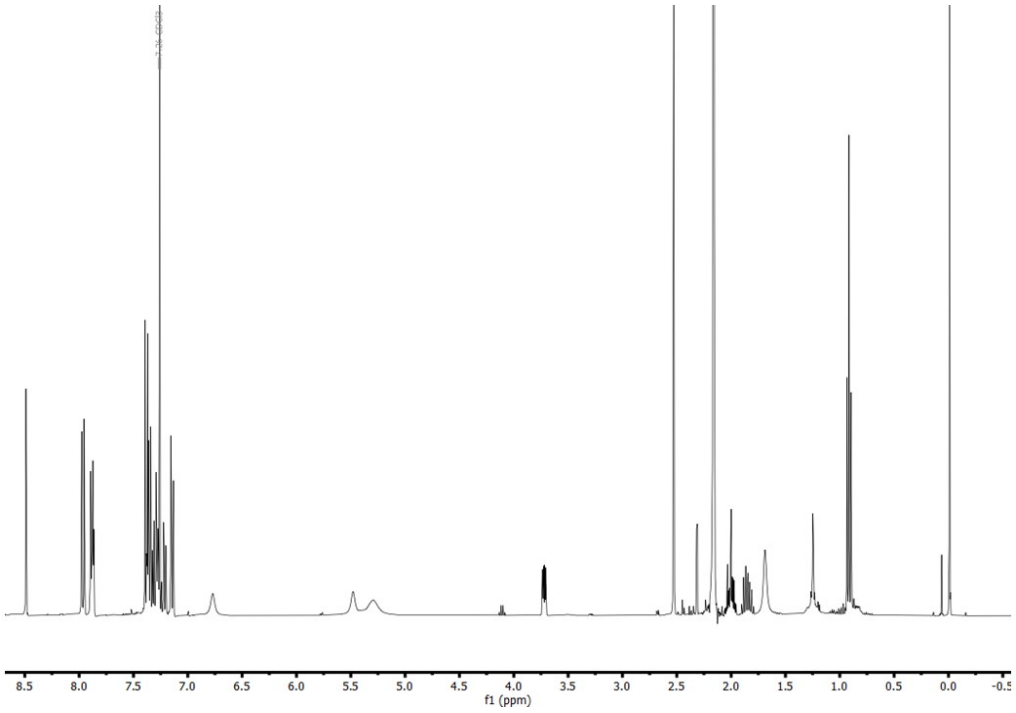


Figure S166. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S5, entry 2: *(S)*-BINOL without base, LAG with NaCl, 24 h, PTFE milling vessel.

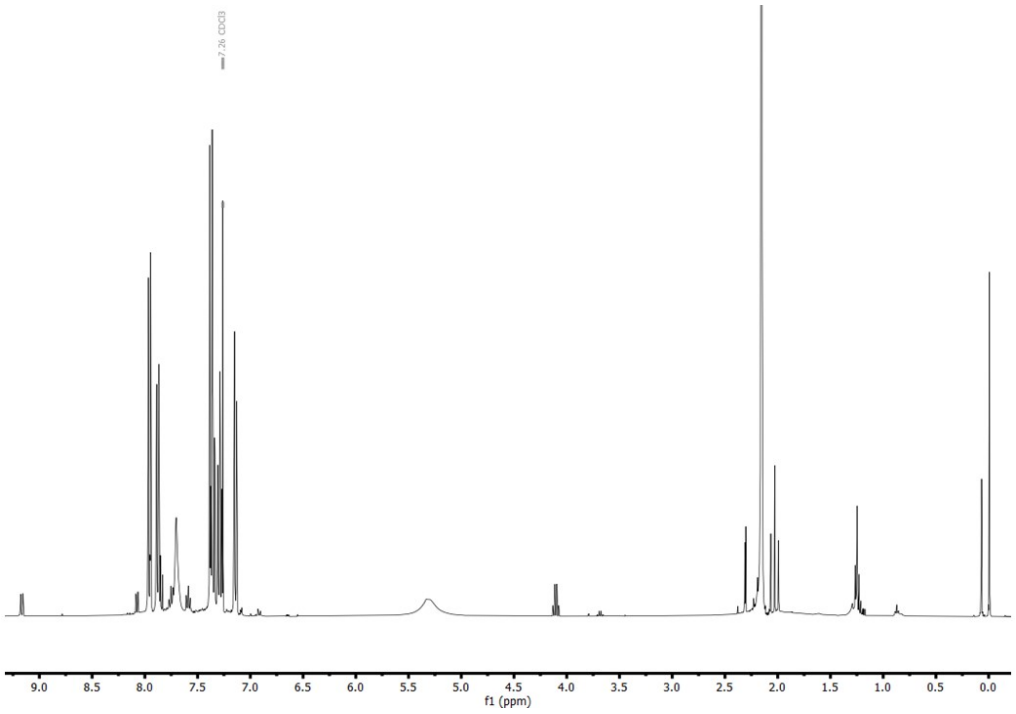


Figure S167. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S5, entry 3: *(S)*-BINOL with 1.0 eq. K_2CO_3, NG, 24 h, PTFE milling vessel.

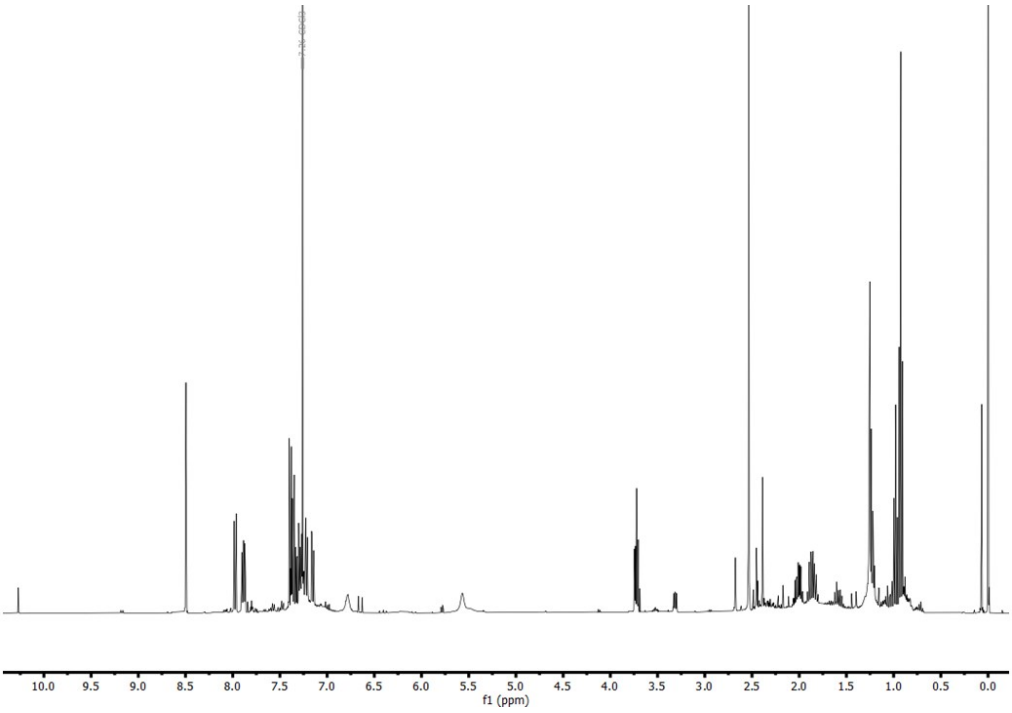


Figure S168. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S5, entry 4: *(S)*-BINOL with 50 eq. K_2CO_3, NG, 24 h, PTFE milling vessel.

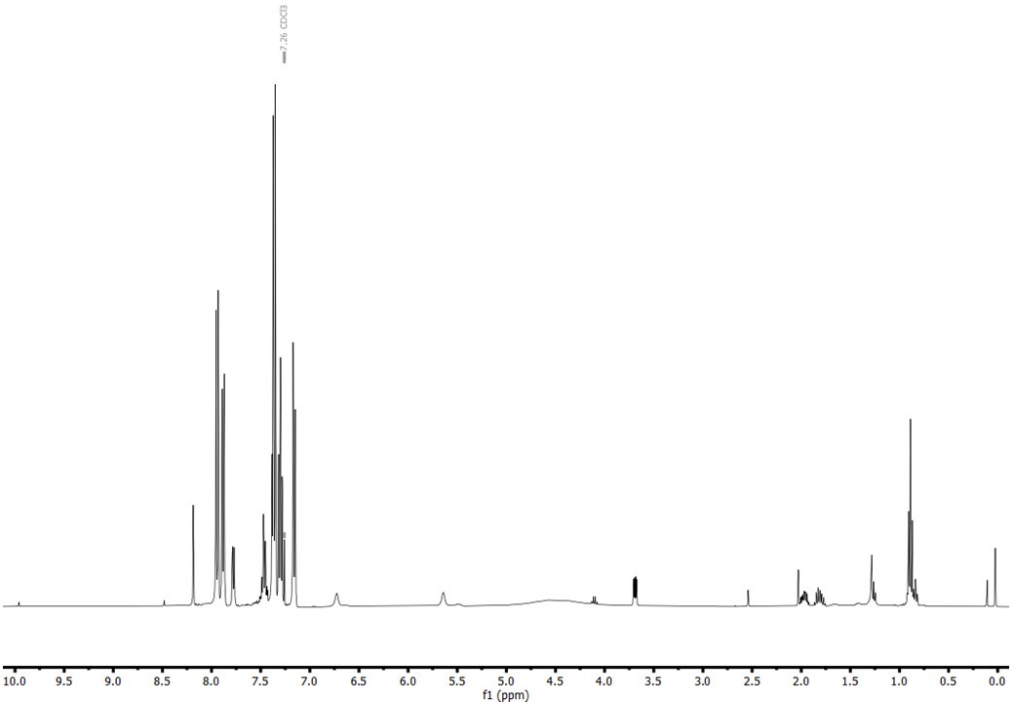


Figure S169. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S5, entry 5: *(S)*-BINOL with 1.0 eq. Cs_2CO_3, NG with NaCl, 24 h, PTFE milling vessel.

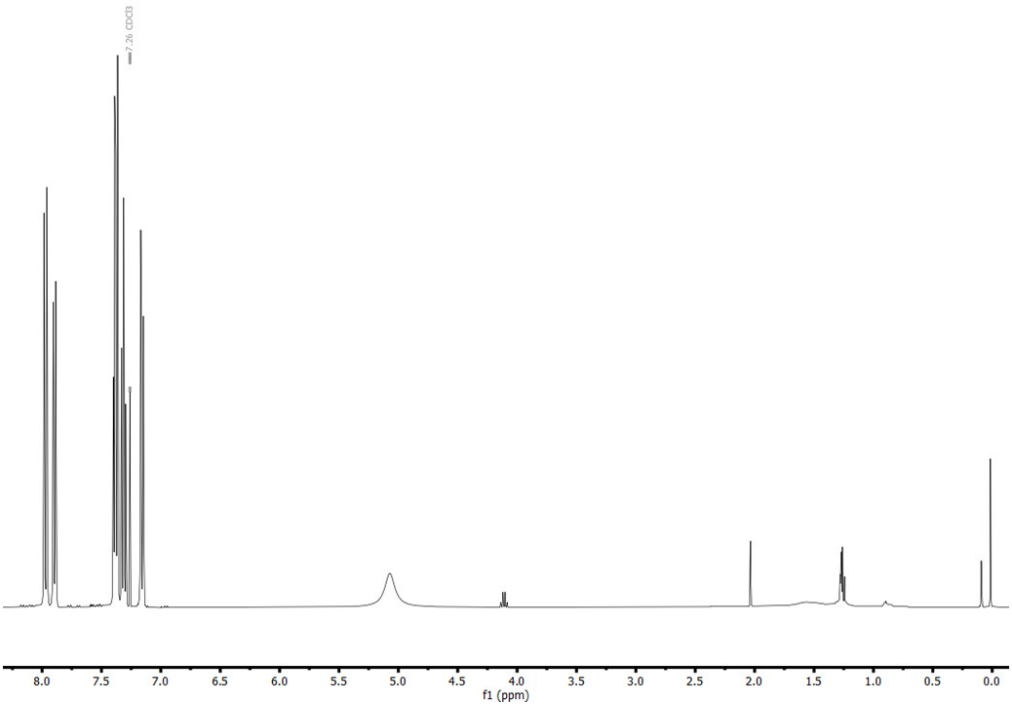


Figure S170. ^{1}H-NMR spectrum in $CDCl_3$ of experiment in Table S5, entry 6: *(S)*-BINOL with 1.0 eq. Cs_2CO_3, LAG with NaCl, 24 h, PTFE milling vessel.

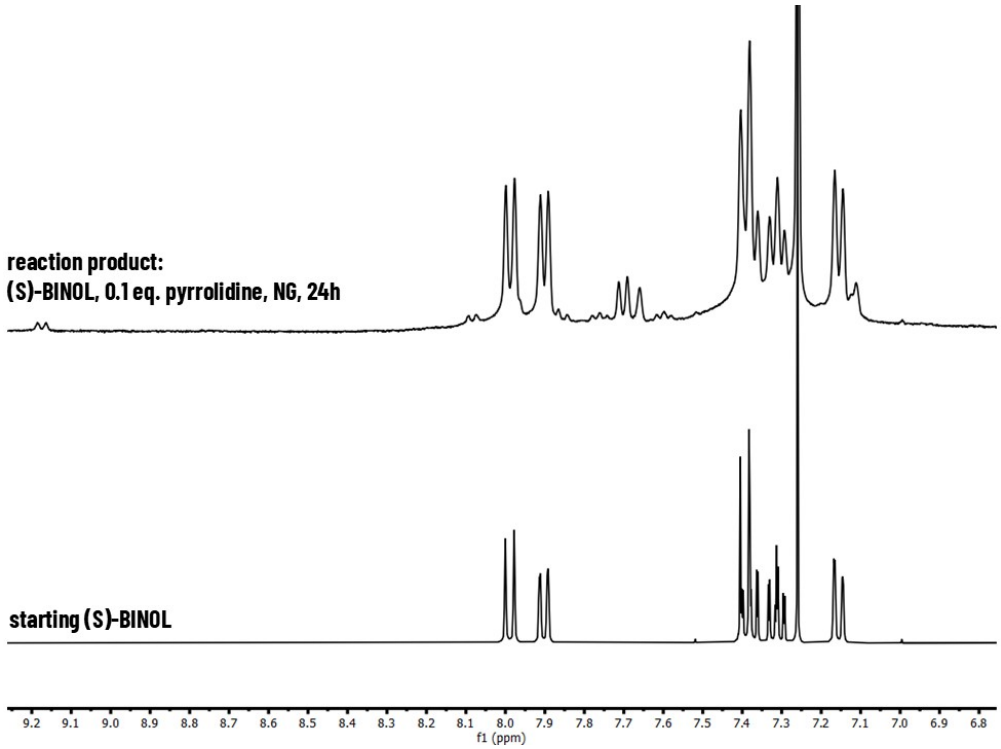


Figure S171. Comparison of ^{1}H-NMR spectra in $CDCl_3$ of extracted product from experiment in Table S1, entry 6: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG, 24 h (top) and starting material for the reaction, *(S)*-BINOL (bottom), in the range from 6.8 ppm to 9.2 ppm. The comparison reveals that, following the reaction, new peaks appear in the mixture at approximately 9.2 ppm, 8.1 ppm, 7.7 ppm, and 7.1 ppm, indicating the formation of additional products. Quantification of these products is not feasible due to peak overlap.

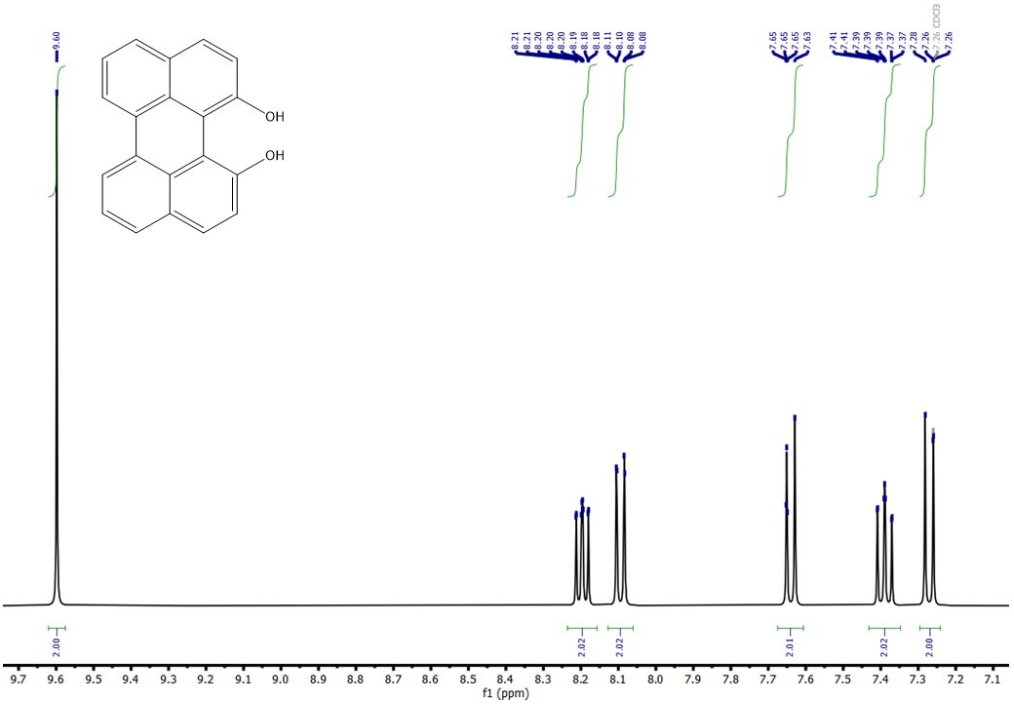


Figure S172. Simulated ^{1}H-NMR spectrum in $CDCl_3$ of BINOL C-C side product. The predicted spectrum was done using MestReNova software at the frequency of 400.13 Hz and at 32 K number of points. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.60 (s, 2H), 8.20 (ddd, 2H), 8.09 (dd, 2H), 7.67 – 7.61 (m, 2H), 7.39 (ddd, 2H), 7.30 – 7.24 (m, 2H).

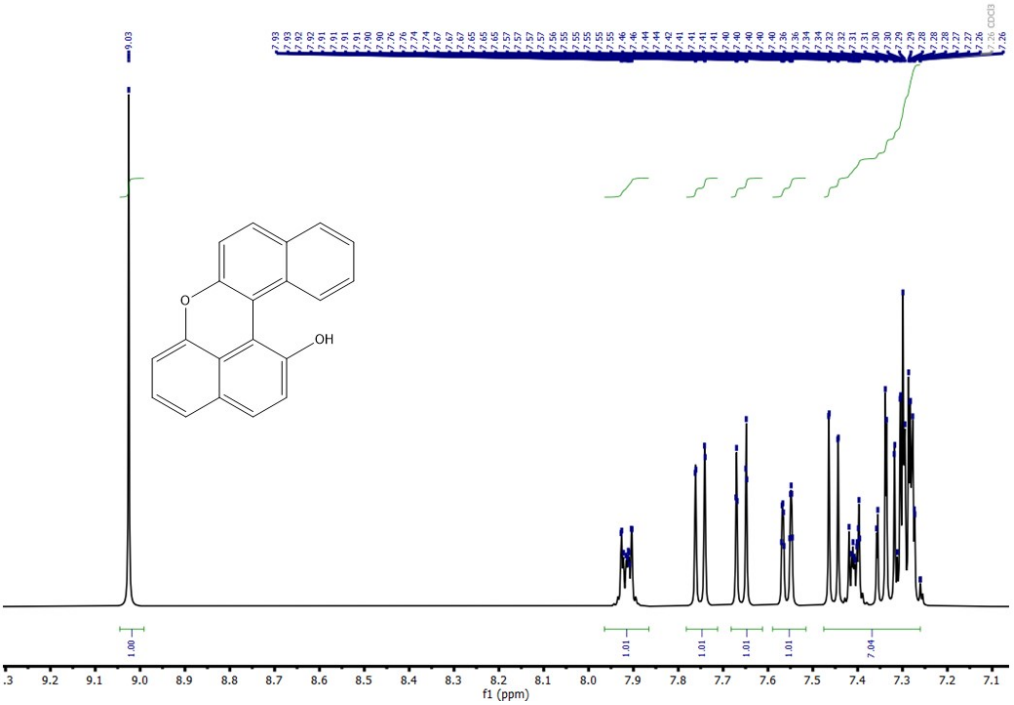


Figure S173. Simulated ^{1}H-NMR spectrum in $CDCl_3$ of BINOL C-O side product. The predicted spectrum was done using MestReNova software at the frequency of 400.13 Hz and at 32 K number of points. ^{1}H NMR (400 MHz, Chloroform-d) δ 9.03 (s, 1H), 7.96 – 7.87 (m, 1H), 7.75 (dd, 1H), 7.66 (dt, 1H), 7.56 (ddt, 1H), 7.48 – 7.26 (m, 7H).

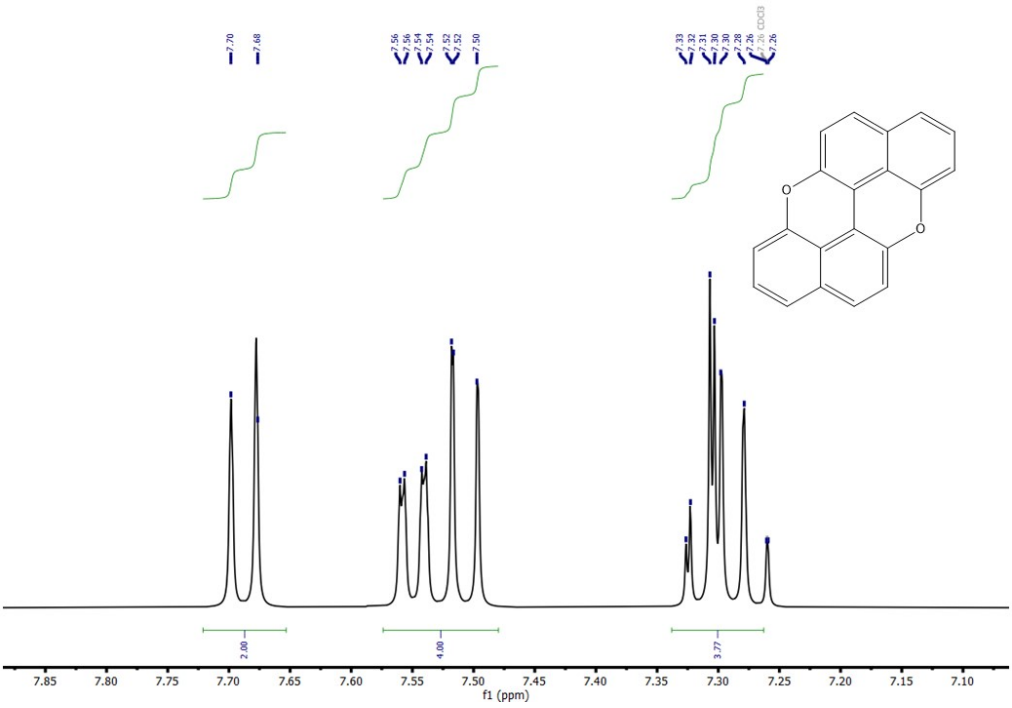


Figure S174. Simulated ^{1}H-NMR spectrum in $CDCl_3$ of BINOL 2(C-O) side product. The predicted spectrum was done using MestReNova software at the frequency of 400.13 Hz and at 32 K number of points. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.57 – 7.48 (m, 4H), 7.34 – 7.26 (m, 4H).

3.3. MS analysis

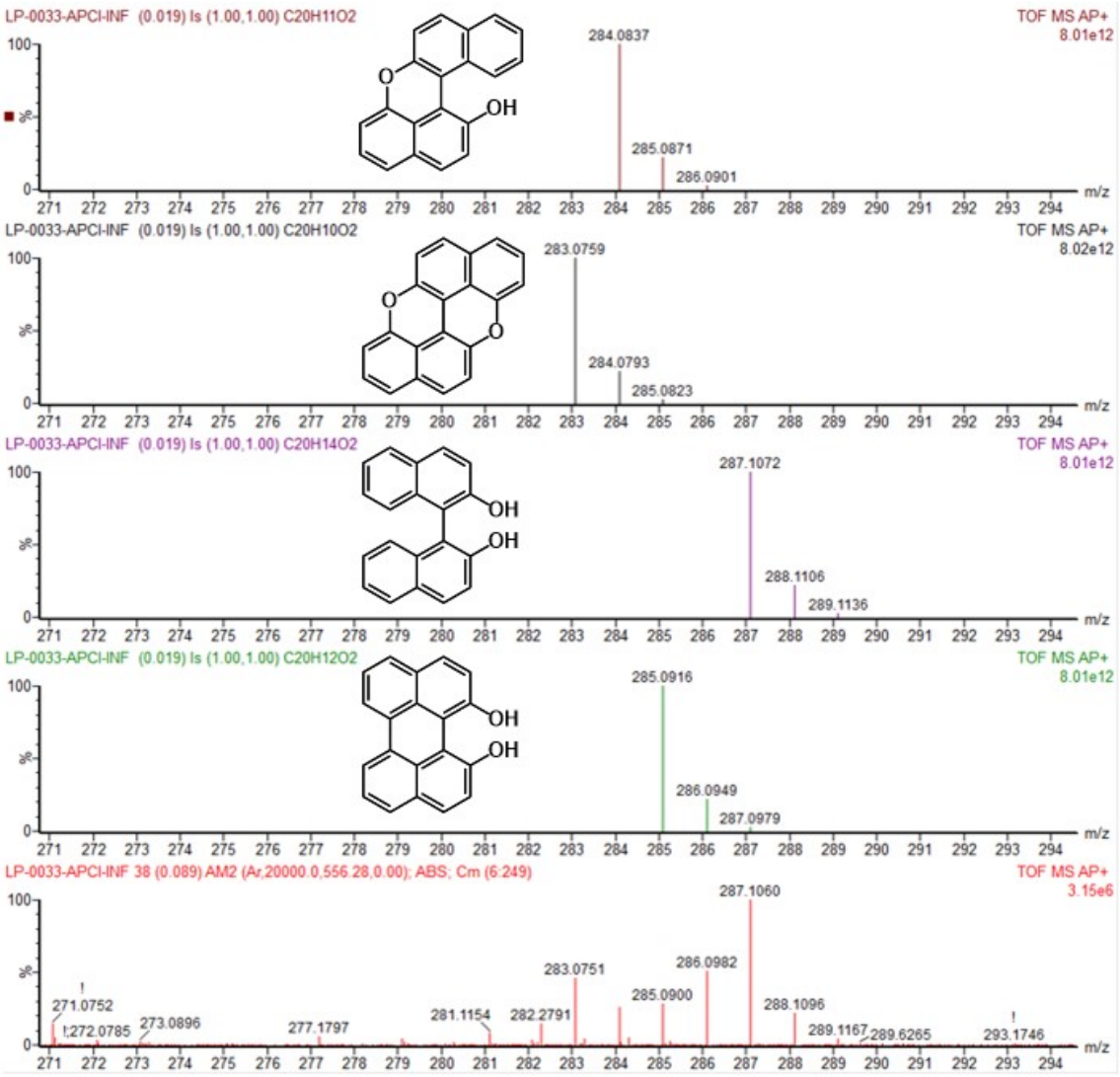


Figure S175. MS analysis of the sample from the experiment in Table S1, entry 6: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG, 24 h. The bottom trace shows the experimental MS spectrum, displayed as a zoomed-in region corresponding to the detected products. Calculated exact masses are provided for reference. The upper traces show theoretical isotope patterns for the proposed species (C–O product, 2(C–O) product, starting BINOL, and C–C product) and are included solely for comparison. Based on fragmentation analysis and comparison with the experimental spectrum, the proposed side products are detected in varying abundances.

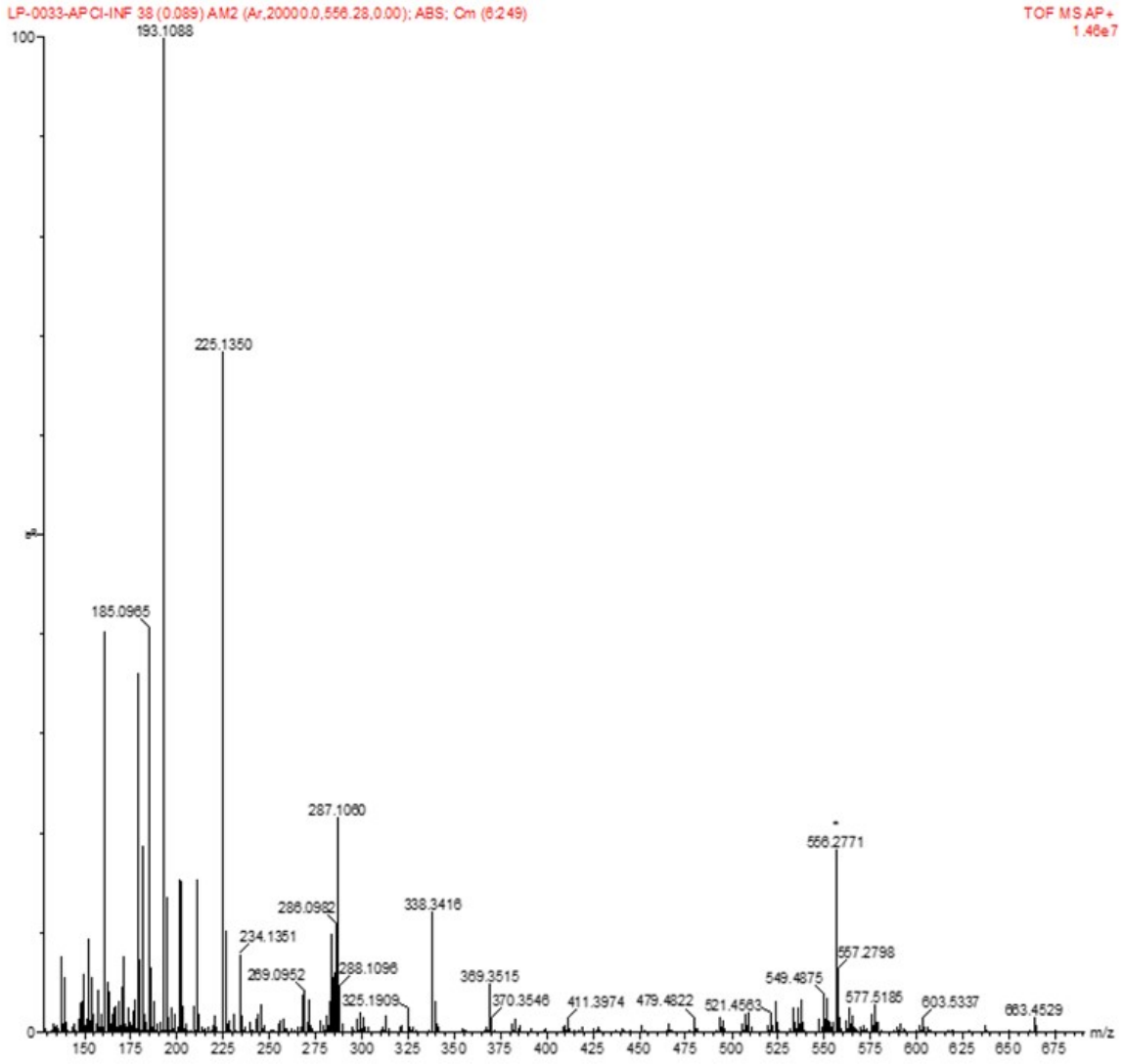


Figure S176. Full MS spectra of the sample of experiment in Table S1, entry 6: *(S)*-BINOL with 0.1 eq. pyrrolidine, NG, 24 h. The observed higher molecular weights suggest the formation of oligomeric products, which could account for the colour change and observed insoluble material during workup.

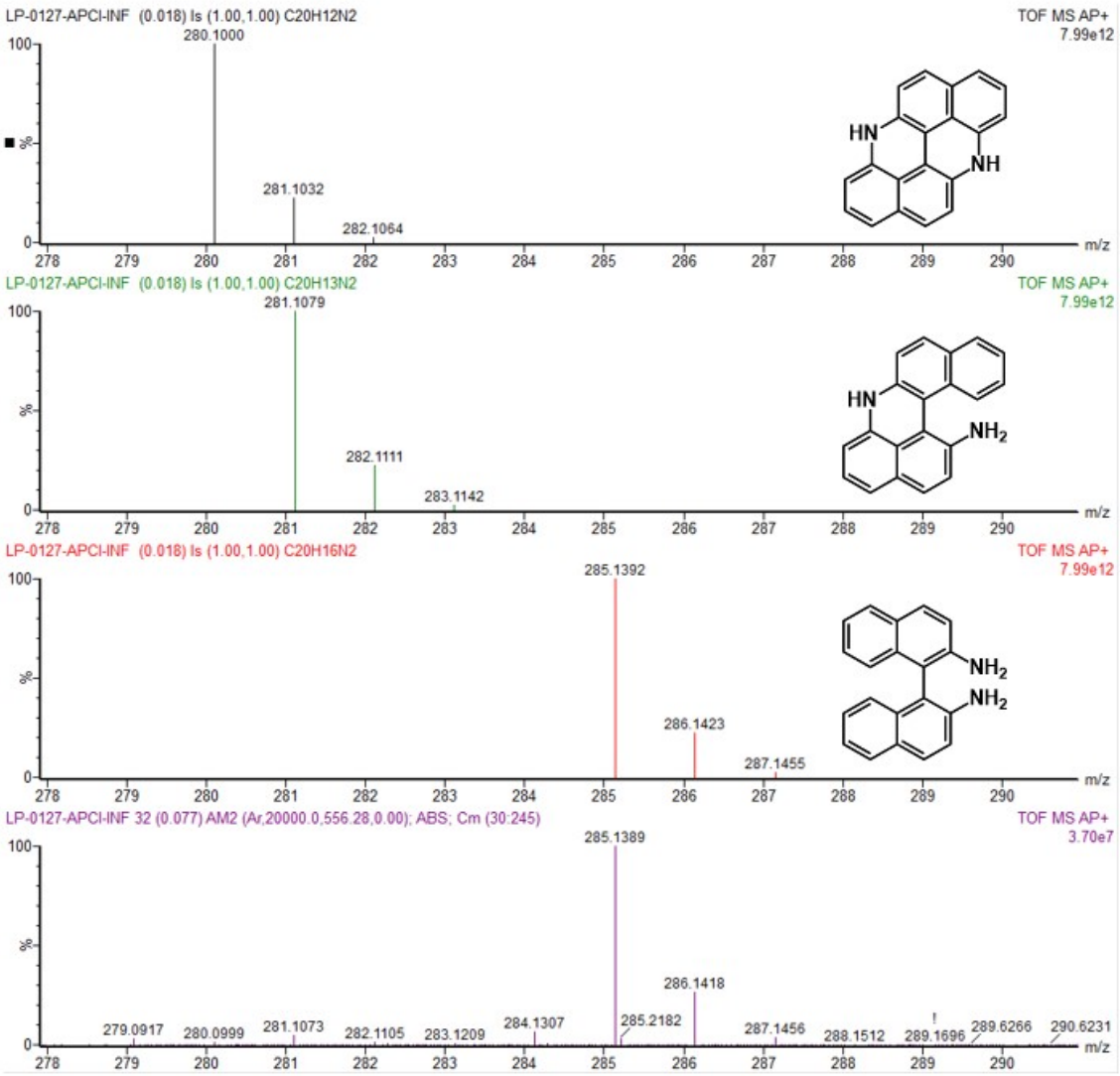


Figure S177. MS analysis of the sample from the experiment in Table S2, entry 3: *(S)*-BINAM with 1.0 eq. K_2CO_3, NG, 24 h. The bottom trace shows the experimental MS spectrum, displayed as a zoomed-in region corresponding to the detected products. Calculated exact masses are provided for reference. The upper traces show theoretical isotope patterns for the proposed species (di(C–N) product, C–N product, and starting BINAM) and are included solely for comparison. Based on fragmentation analysis and comparison with the experimental spectrum, all proposed side products are detected in low abundance.

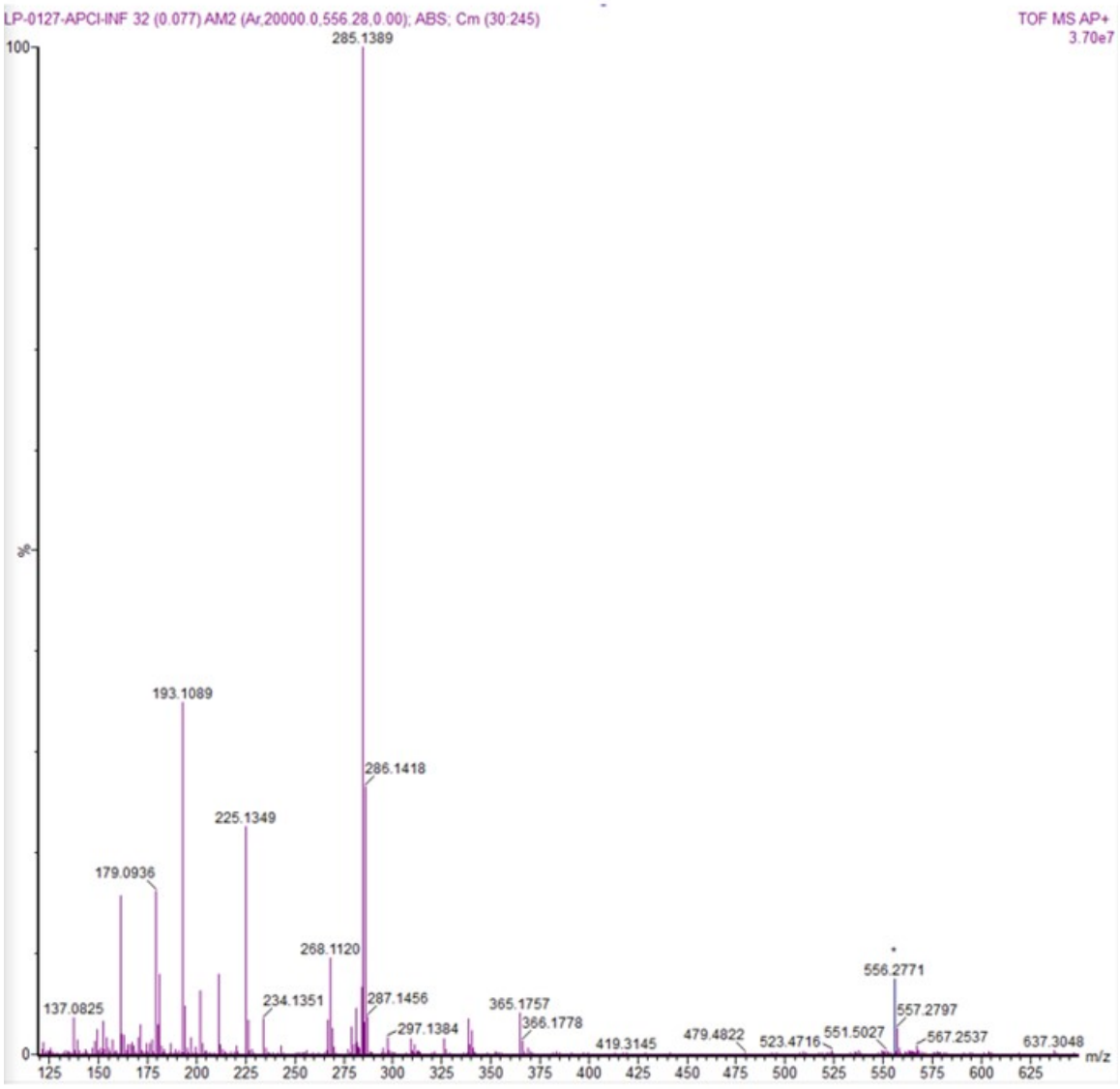


Figure S178. Full MS spectra of the sample of experiment in Table S2, entry 3: *(S)*-BINAM with 1.0 eq. K_2CO_3, NG, 24 h. The observed higher molecular weights suggest the formation of oligomeric products, which could account for the colour change and observed insoluble material during workup.

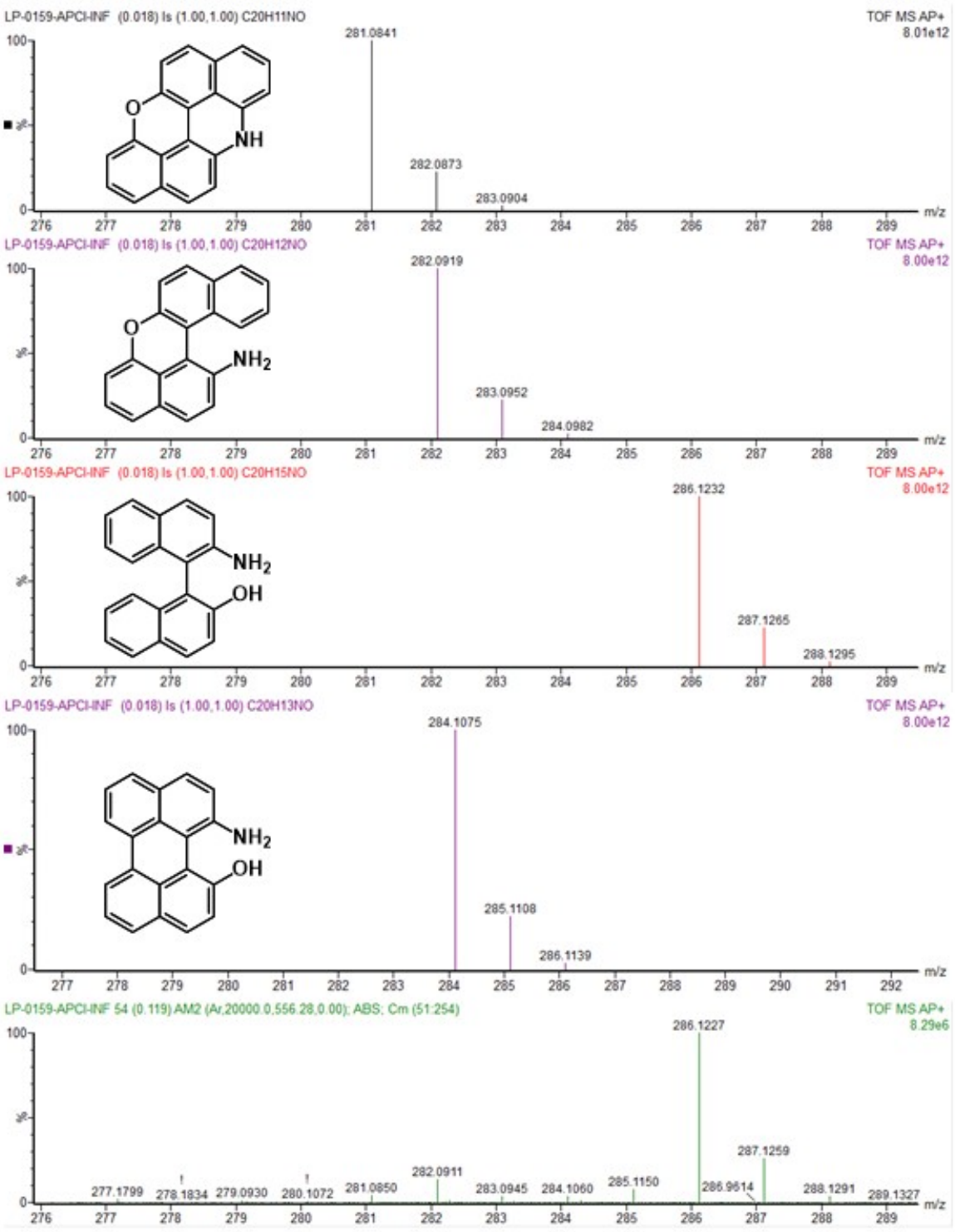


Figure S179. MS analysis of the sample from the experiment in Table S3, entry 3: *(S)*-NOBIN with 1.0 eq. K_2CO_3, NG, 24 h. The bottom trace shows the experimental MS spectrum, displayed as a zoomed-in region corresponding to the detected products. Calculated exact masses are provided for reference. The upper traces show theoretical isotope patterns for the proposed species ((C–N)(C–O) product, C–O product, starting NOBIN, and C–C product) and are included solely for comparison. Based on fragmentation analysis and comparison with the experimental spectrum, all proposed side products are detected in low abundance.

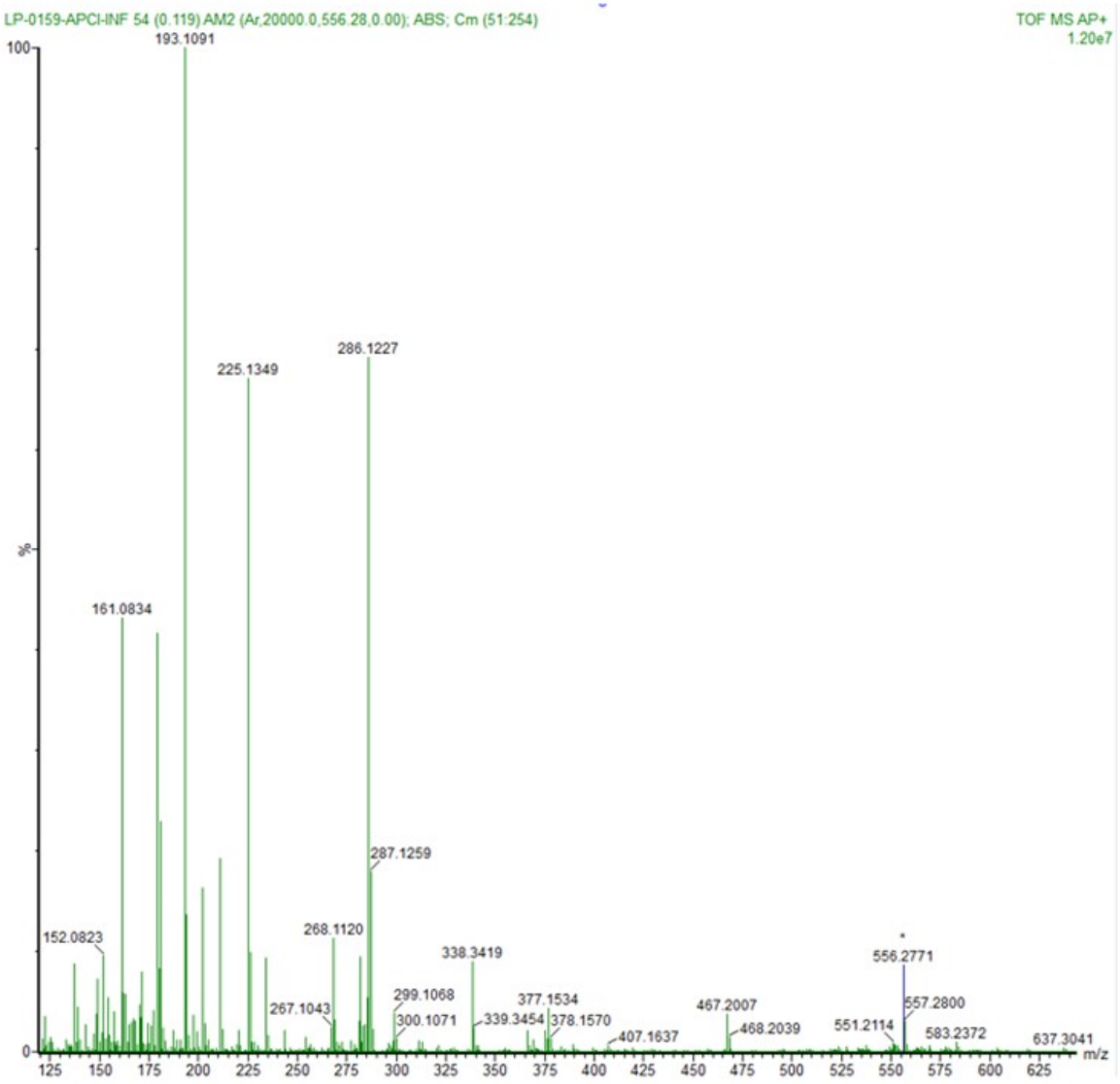


Figure S180. Full MS spectra of the sample of experiment in Table S3, entry 3: *(S)*-NOBIN with 1.0 eq. K_2CO_3, NG, 24 h. The observed higher molecular weights suggest the formation of oligomeric products, which could account for the colour change and observed insoluble material during workup.

4. References

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