ADMET Polymerization of Dimeric Cinchona Squaramides for the Preparation of a Highly Enantioselective Polymeric Organocatalyst

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Polymer **P1**

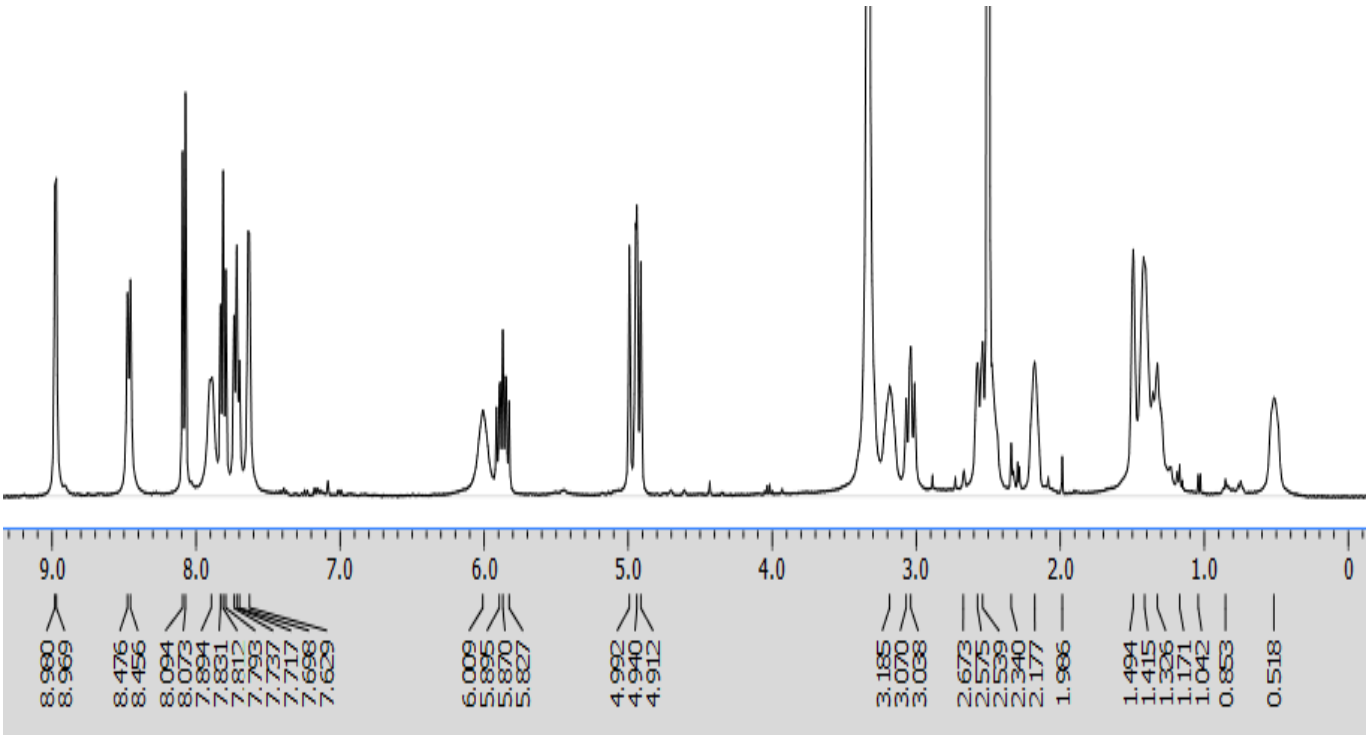


Figure S1: ^{1}H NMR spectrum of polymer P2Q in DMSO-d$_6$

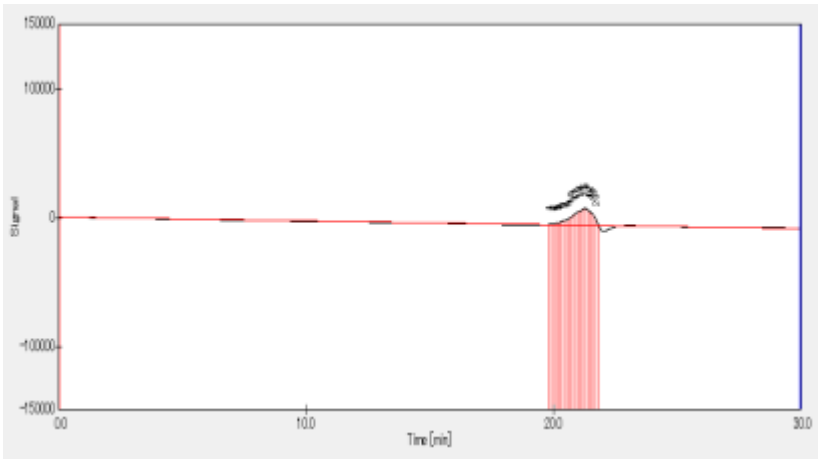
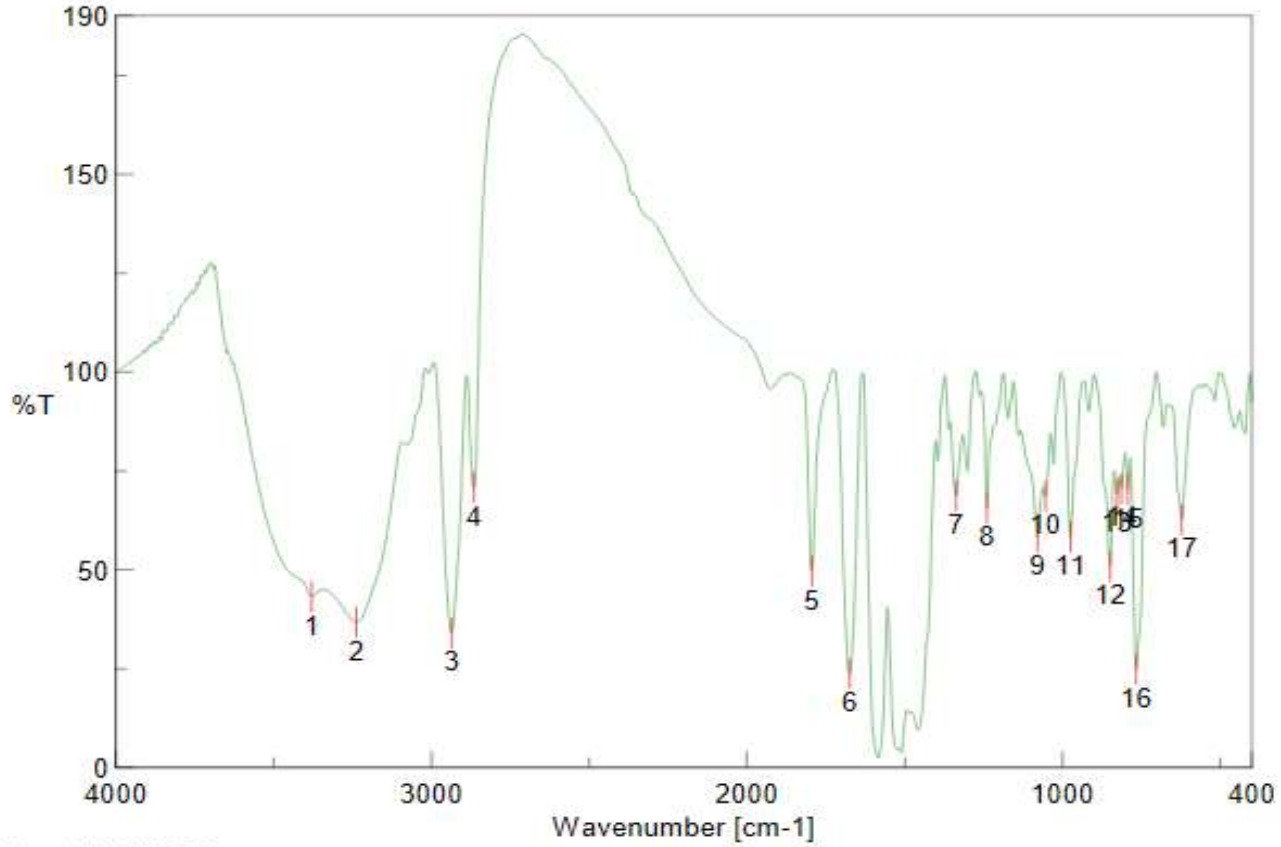


Figure S2: SEC trace of P1 M_n: 47000, M_w: 49000, M_w/M_n: 1.04



[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	3379.64	43.1594	2	3236.93	36.695
3	2936.09	33.9734	4	2865.7	70.7693
5	1794.44	49.6407	6	1674.87	23.6632
7	1337.39	68.7085	8	1240	65.5555
9	1078.98	58.2615	10	1053.91	68.5649
11	974.84	58.219	12	849.49	50.9021
13	827.312	69.0001	14	812.849	70.3912
15	792.6	70.1161	16	766.566	24.7736
17	621.931	62.6525			

Figure S3: IR spectrum of polymer P1

Polymer **P2C**

Squaramide **2C** (133.0 mg, 0.200 mmol), **HG$_2$A** (6.26 mg, 0.010 mmol), and toluene (0.5 mL) were collected in a dried Schlenk tube, after which they were set in an oil bath with a condenser. The Schlenk tube was connected to continuous N_2 gas flow. After setting the desired reaction temperature (100 °C), the reaction mixture was stirred for 9 h. Thereafter the reaction mixture was cooled to room temperature and poured into diethyl ether (50 mL). Next, the solid polymer product was purified by reprecipitation in diethyl ether (70–80 mL) three times. The precipitate was filtered out and vacuum-dried at 40 °C for 3 h to afford the desired polymer (**P2C** with 93% yield as a brownish solid), which is an ADMET polymeric organocatalyst. $[\alpha]^{25}_{D}$ = −109.30 (*c* 0.175 g/dL in DMF at 26.1 ℃).

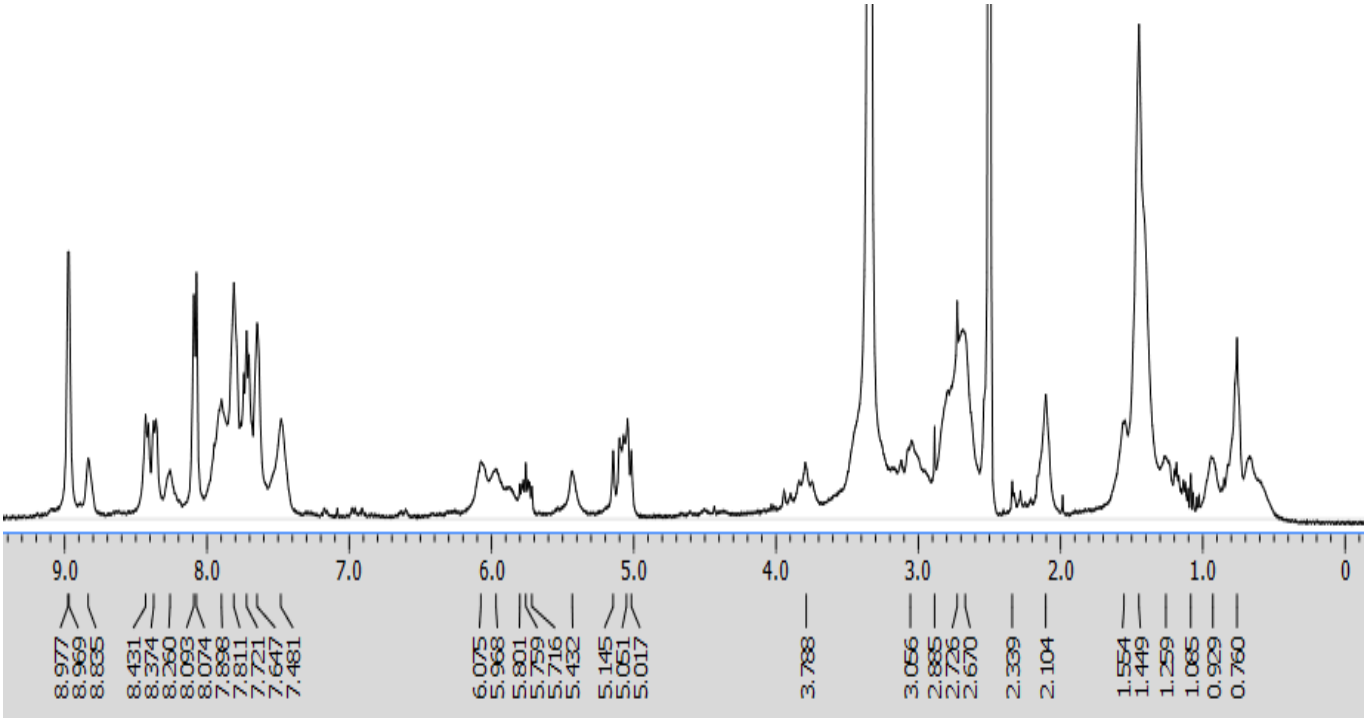


Figure S4: ^{1}H NMR spectrum of polymer P2C in DMSO-d$_6$

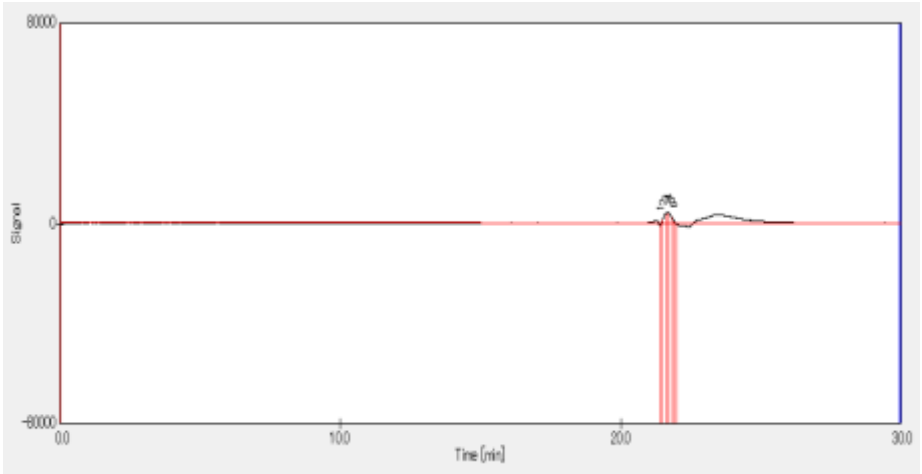
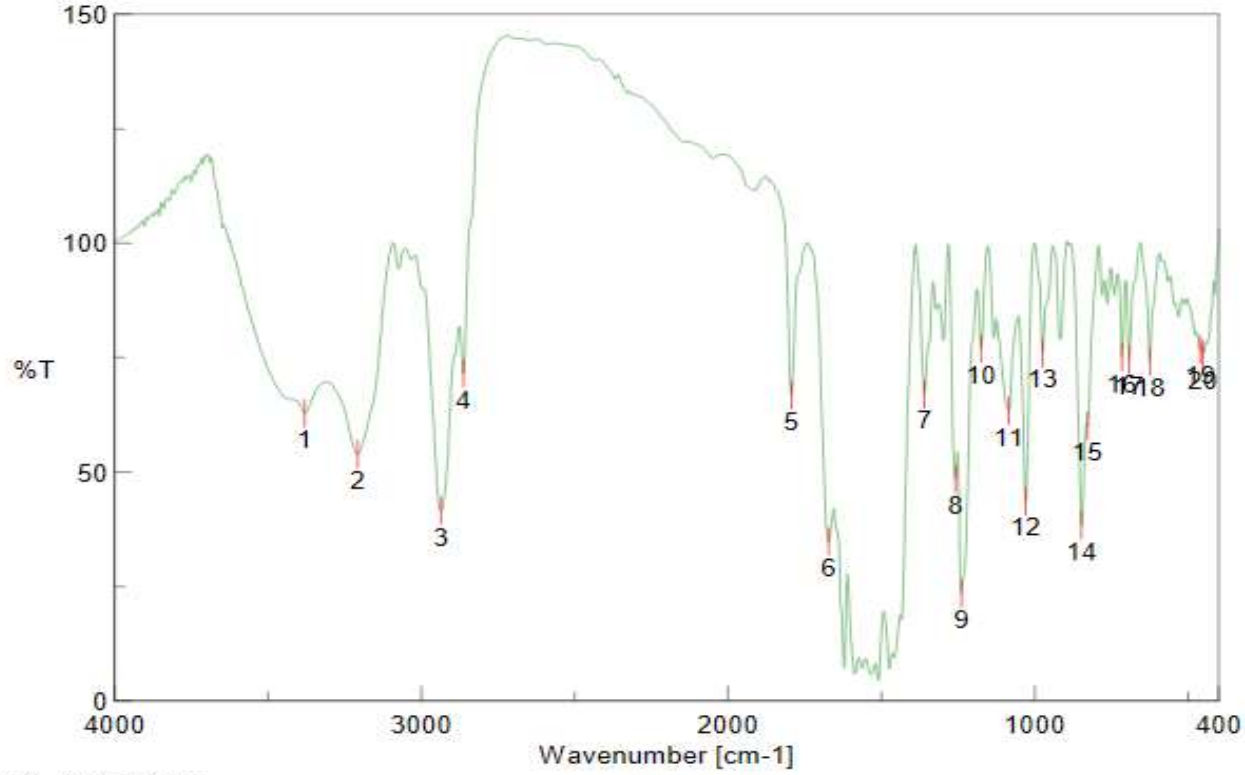


Figure S5: SEC trace of P2C M_n: 54000, M_w: 55000, M_w/M$_n$: 1.02



[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	3380.6	62.8279	2	3208	53.9169
3	2936.09	41.502	4	2862.81	71.5161
5	1793.47	66.7422	6	1671.98	34.7941
7	1359.57	66.9221	8	1258.32	48.3685
9	1239.04	23.4191	10	1174.44	76.9319
11	1084.76	63.3131	12	1029.8	43.5066
13	974.84	75.9144	14	847.561	38.3649
15	828.277	59.9847	16	715.461	75.0475
17	692.32	74.5336	18	624.823	74.0939
19	460.904	76.67	20	451.261	75.7662

Figure S6: IR spectrum of polymer P2C

Polymer **P3**

Squaramide **3** (72.0 mg, 0.075 mmol), **HG_2A** (2.50 mg, 0.004 mmol), and toluene (0.5 mL) were collected in a dried Schlenk tube, after which they were set in an oil bath with a condenser. The Schlenk tube was connected to continuous N_2 gas flow. After setting the desired reaction temperature (100 °C), the reaction mixture was stirred for 9 h. Thereafter the reaction mixture was cooled to room temperature and poured into diethyl ether (50 mL). Next, the solid polymer product was purified by reprecipitation in diethyl ether (50 mL) three times. The precipitate was filtered out and vacuum-dried at 40 °C for 3 h to afford the desired polymer (**P3** with 86% yield as a brownish solid), which is an ADMET polymeric organocatalyst. $[\alpha]^{25}_{D}$=– 77.81 (*c* 0.075 g/dL in DMF at 26.8 ℃).

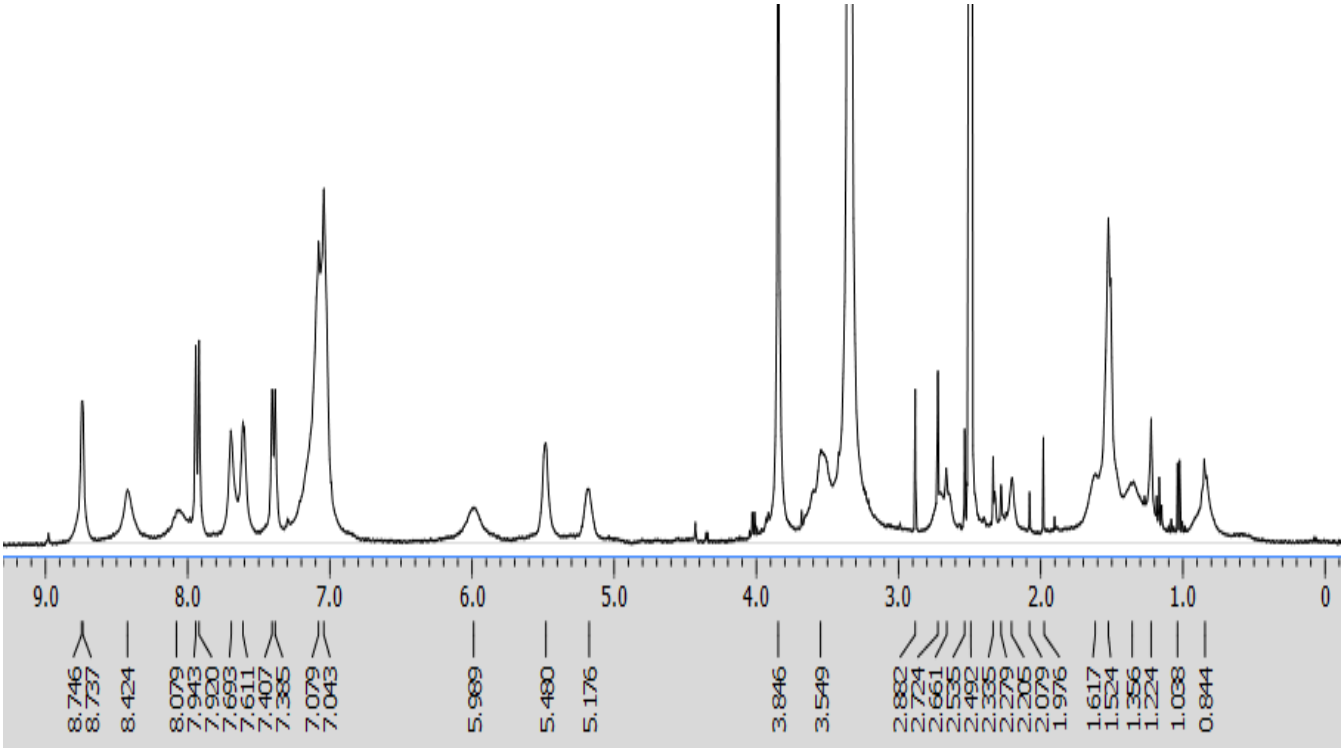


Figure S7: ^{1}H NMR spectrum of polymer P3 in DMSO-d$_6$

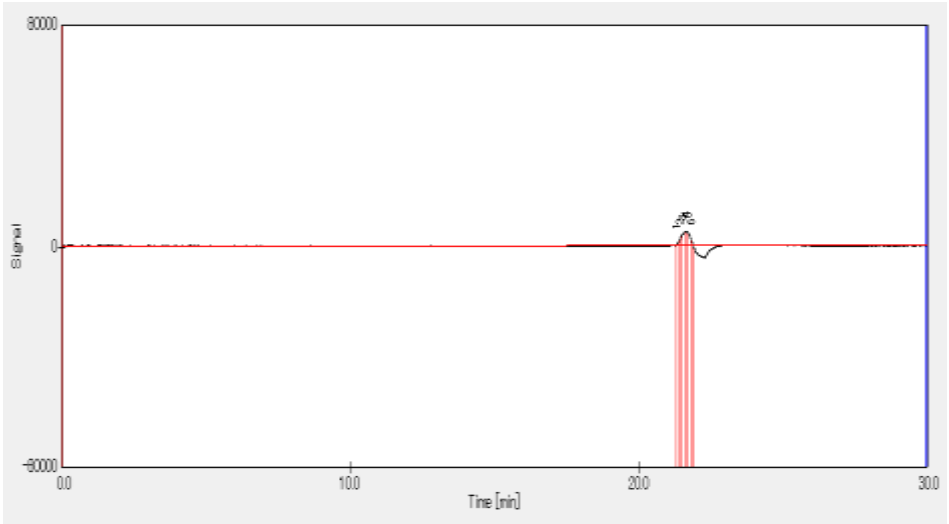
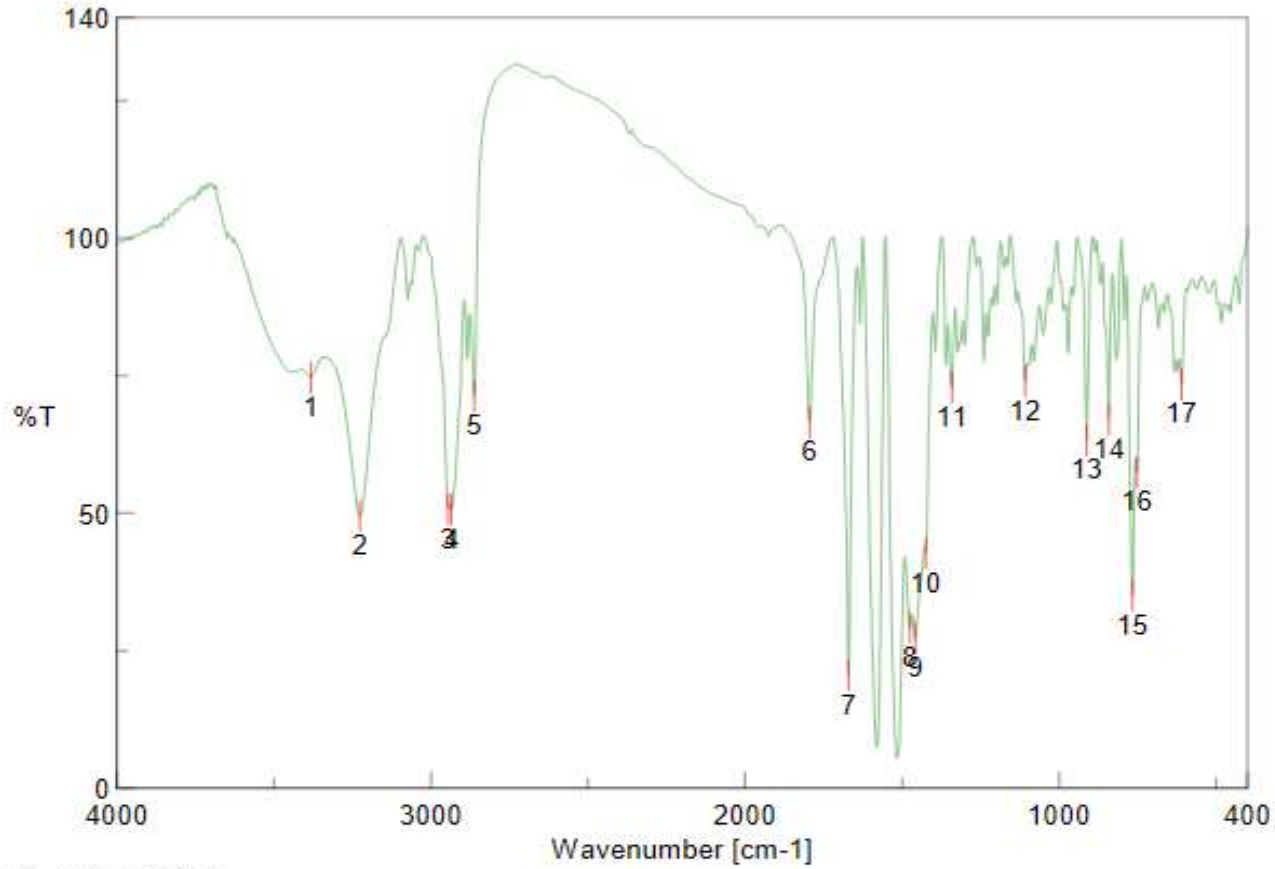


Figure S8: SEC trace of P3 M_n: 74000, M_w: 75000, M_w/M$_n$: 1.01



[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	3382.53	74.5495	2	3226.33	49.4192
3	2945.73	50.6771	4	2934.16	50.6647
5	2861.84	71.167	6	1794.44	66.4468
7	1670.05	20.4988	8	1475.28	29.2195
9	1457.92	27.1092	10	1425.14	42.6482
11	1341.25	72.8182	12	1107.9	73.9321
13	912.165	63.1877	14	841.776	67.0274
15	766.566	35.0399	16	752.102	57.4023
17	610.36	73.3235			

Figure S9: IR spectrum of polymer P3

Triallyl ether **4**

50 mL round bottom flask fitted with reflux condenser is charged with 2.5 mmol tris(4-hydroxy phenyl)methane **14**, 7.8 mmol of allyl bromide **15**, 8 mmol of dry KOH and 5 mL of acetone. Reaction mixture was refluxed for 8 hrs. After cooling, distill water was added and mixture was extracted with ether. Extract was washed with 10% NaOH solution to remove unreacted phenol, with a little amount of distill water and dried over K_2CO_3. Ether is removed by evaporation and crude product is purified by column chromatography. Yellow oil, 900mg (87%); R_f:0.49 (hexane/CH_2Cl_2=5:/5) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (d, J=8.8 Hz, 6H), 6.81 (d, *J*=8.4 Hz, 6H), 5.99-6.10 (m, 3H), 5.41(d, *J*=15.6 Hz, 4H), 5.27 (d, *J*=10.4 Hz, 3H), 4.50 (d, *J*=6.0 Hz, 6H), ^{13}C NMR (400 MHz, $CDCl_3$): δ 157.09, 137.06, 133.55, 130.34, 117.74, 114.55, 69.94, 54.50. HRMS (ESI) *m/z* for $C_{28}H_{28}O_3Na$ [M^+Na^+] calcd. 435.1936, found 435.1931.

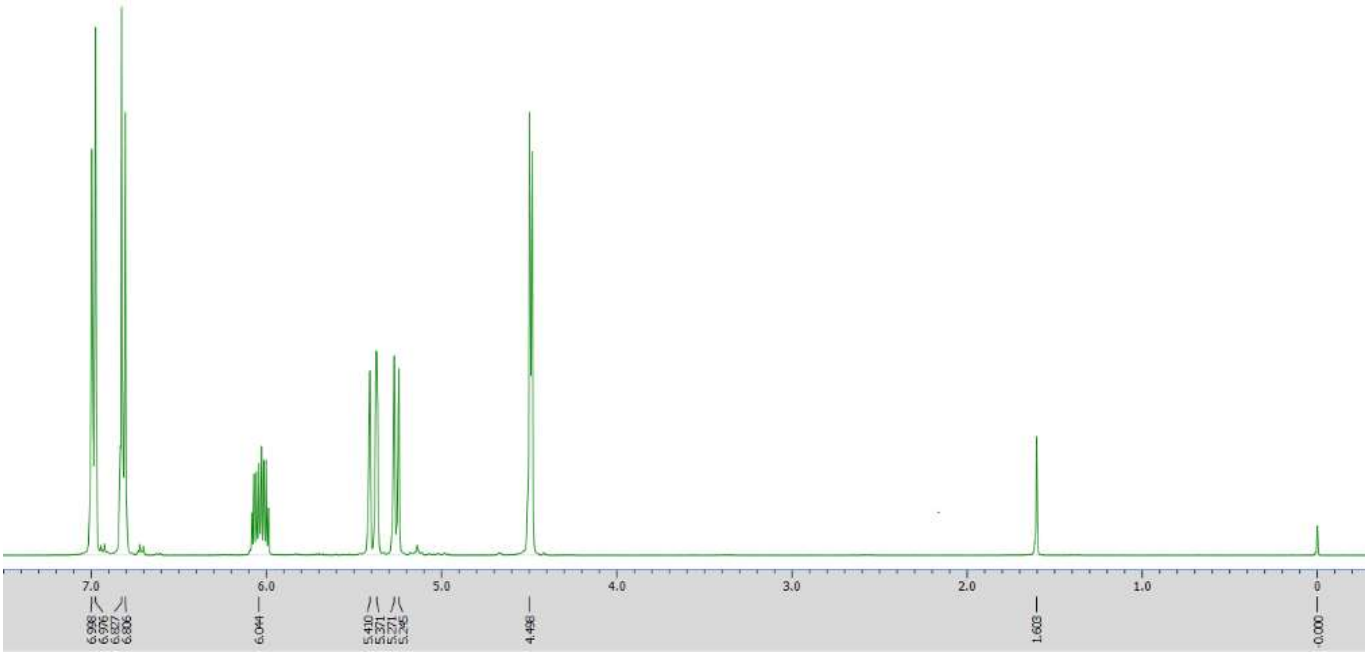


Figure S10: ^{1}H NMR spectrum of compound 4 in $CDCl_3$

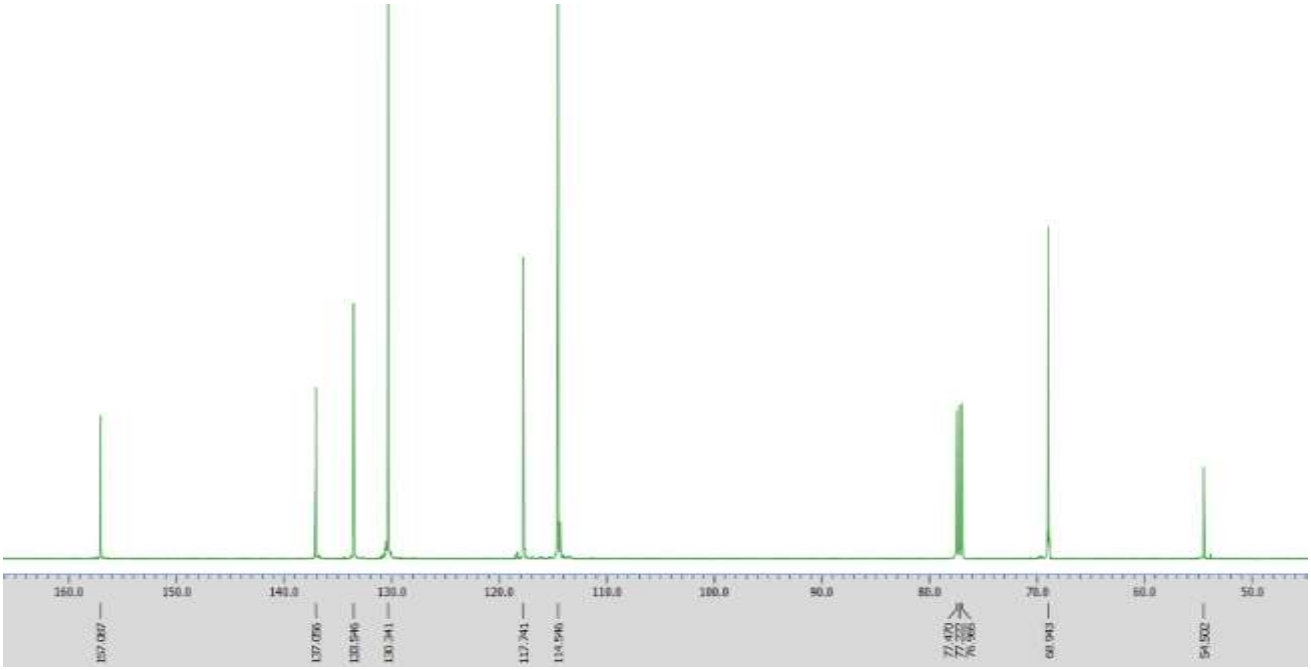


Figure S11: ^{13}C NMR spectrum of compound 4 in $CDCl_3$

Polymer **P4**

Squaramide **2C** (133.0 mg, 0.20 mmol), tris 4-allyloxy phenyl methane **4** (82.05 mg, 0.20 mmol), **HG_2A** (6.26 mg, 0.010 mmol) were taken in a dried Schlenk tube, after which they were set in an oil bath with a condenser. The Schlenk tube was connected to continuous N_2 gas flow. After setting the desired reaction temperature (100 °C), the reaction mixture was stirred for 24 h. Thereafter the reaction mixture was cooled to room temperature and poured into diethyl ether (50 mL). Next, the solid polymer product was purified by reprecipitation in diethyl ether (70 mL) three times. The precipitate was filtered out and vacuum-dried at 40 °C for 3 h to afford the desired polymer (**P4** with 70% yield as a brownish solid), which is an ADMET polymeric organocatalyst.

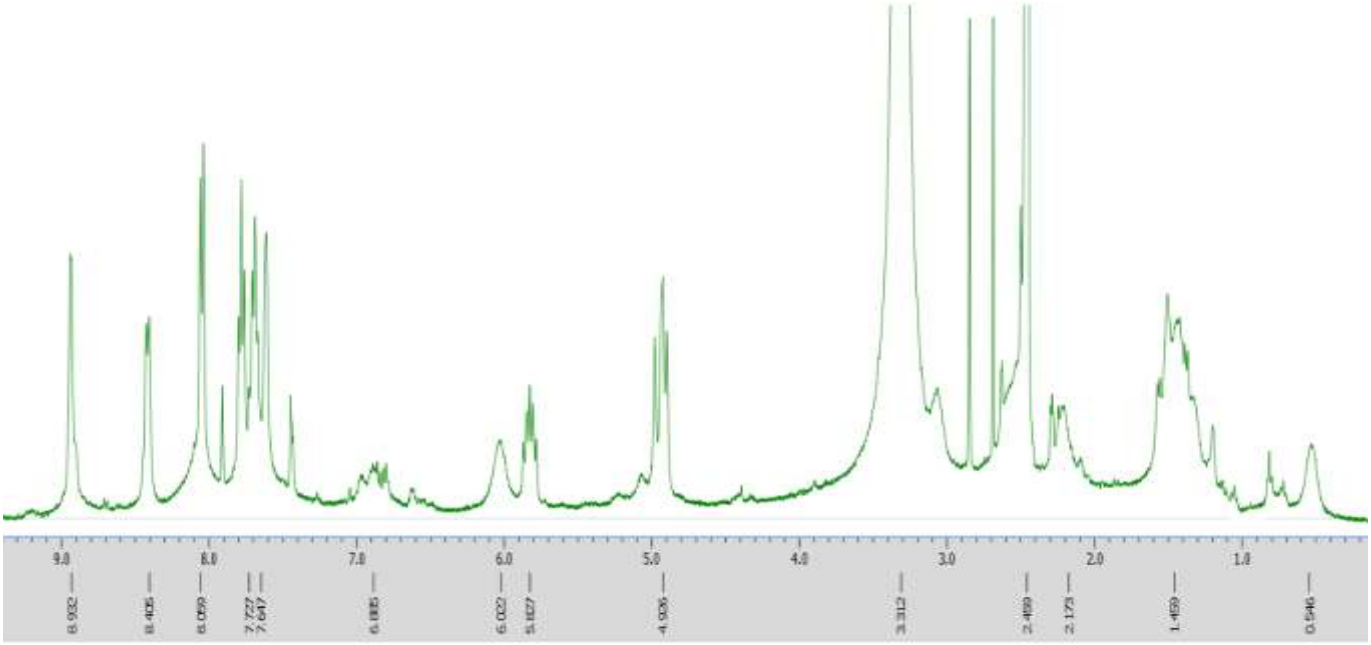
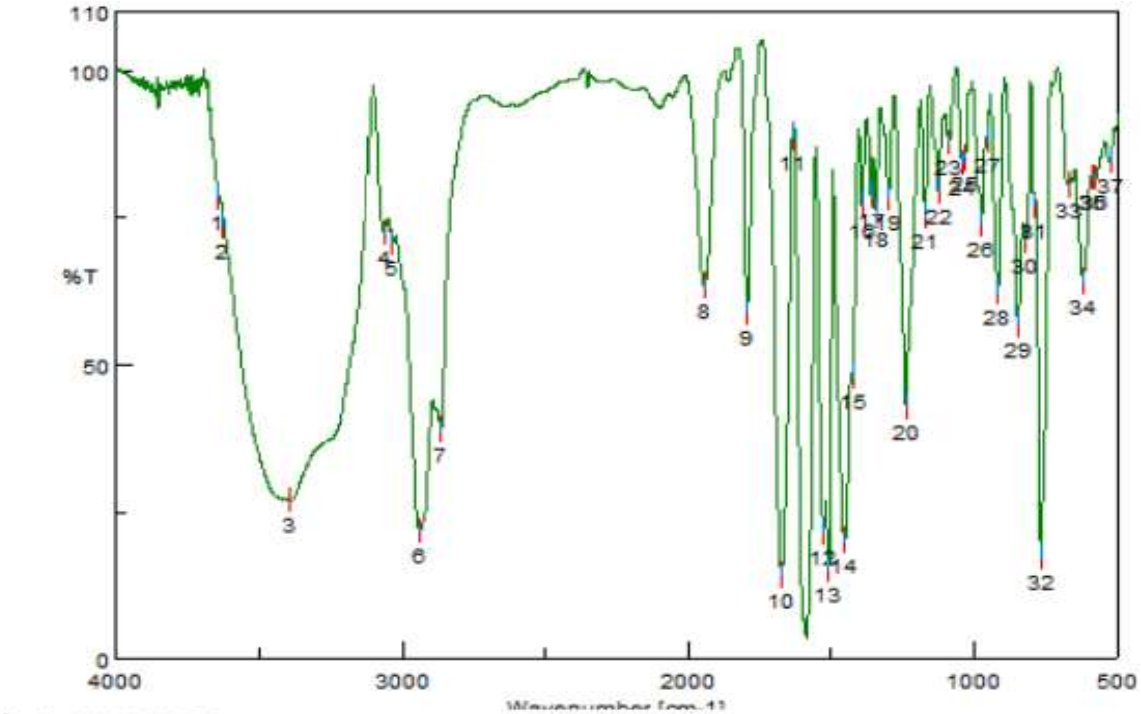


Figure S12: ^{1}H NMR spectrum of polymer P4 in DMSO-d_6



[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3646.73	78.3493	2	3626.48	73.5595	27	955.555	88.0065
3	3389.28	26.8702	4	3062.41	72.2231	28	918.914	62.1959
5	3033.48	70.6882	6	2938.98	21.7034	29	847.561	56.8252
7	2864.74	38.8914	8	1942.93	63.3326	30	821.527	71.0372
9	1794.44	58.8437	10	1673.91	14.2573	31	791.636	77.0054
11	1634.38	88.4704	12	1529.27	21.4433	32	766.566	17.1404
13	1509.99	14.9855	14	1455.03	20.0687	33	667.25	80.3676
15	1427.07	47.8016	16	1393.32	76.946	34	620.002	63.948
17	1361.5	78.6328	18	1344.14	75.4704	35	586.254	81.6914
19	1300.75	78.1702	20	1240	42.7814	36	575.647	81.7267
21	1172.51	74.9787	22	1126.22	79.4481	37	525.507	84.4844
23	1089.58	87.6091	24	1043.3	84.1553			
25	1032.69	85.069	26	973.876	73.8557			

Figure S13: IR spectrum of polymer P4

[HPLC data of the products obtained from enantioselective Michael addition of methyl 2-oxocyclopentanecarboxylate (**5**) to *trans*-β-nitrostyrene (**6**)]

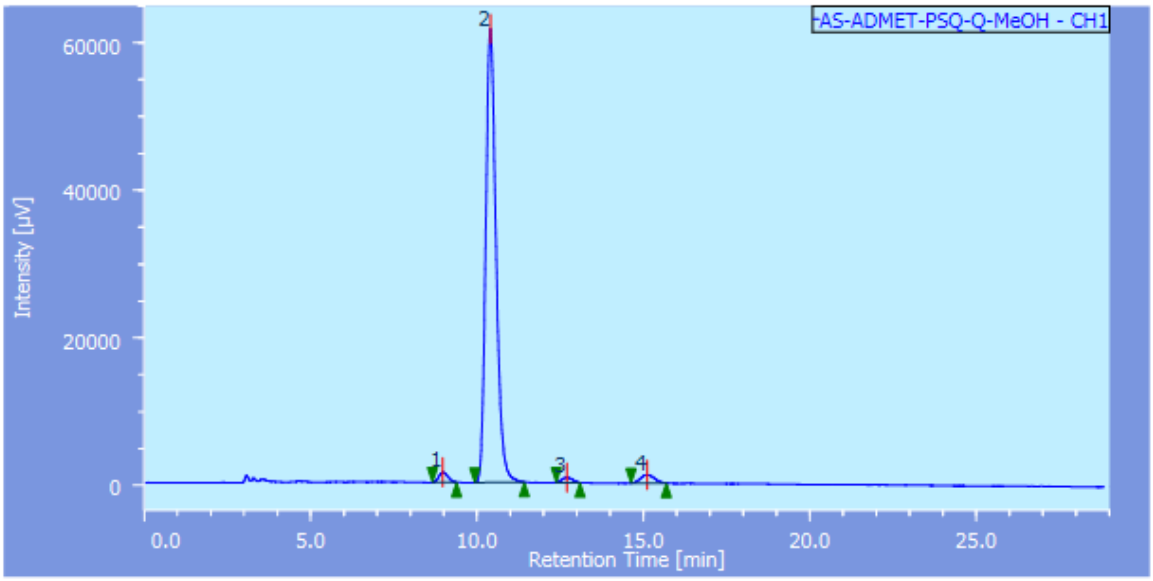


Figure S14: HPLC chromatogram of 7
Table 2, entry 2
87% ee

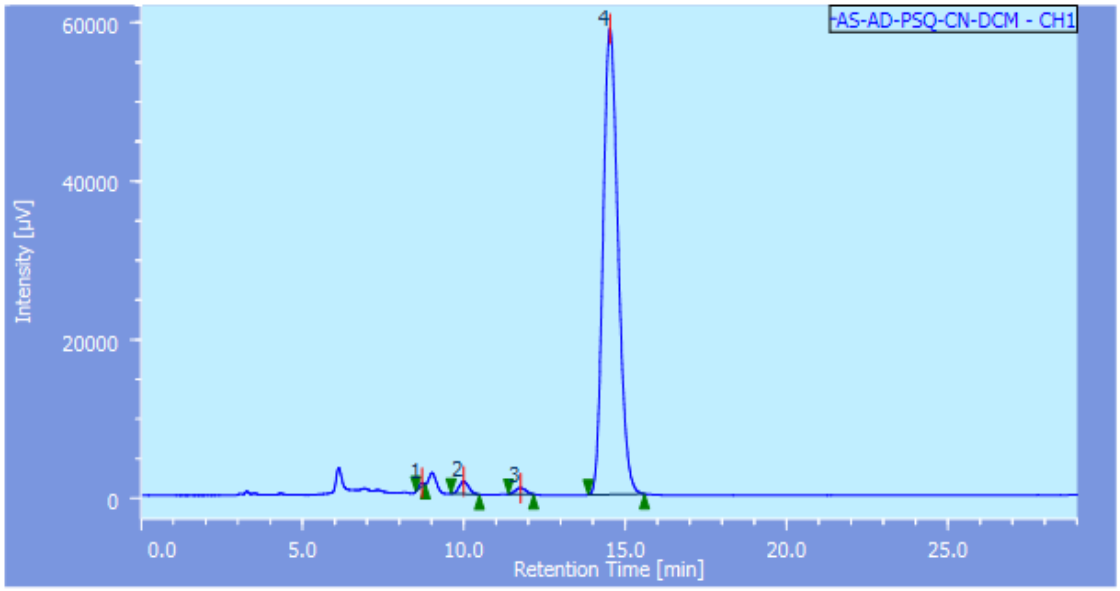


Figure S15: HPLC chromatogram of 7
Table 2, entry 3
97% ee

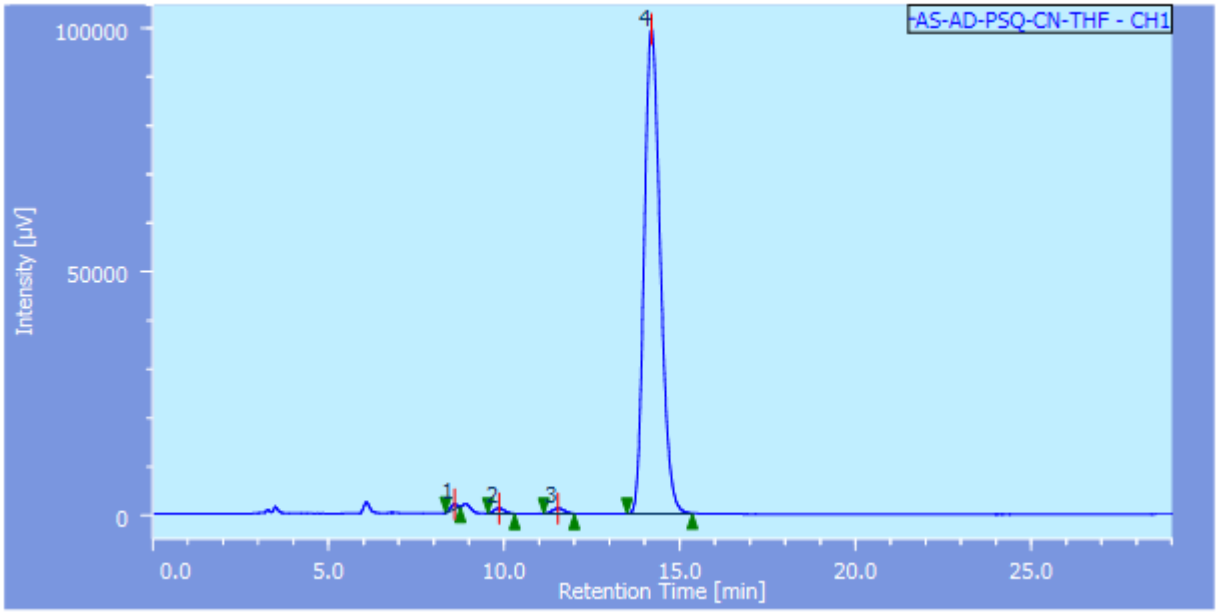


Figure S16: HPLC chromatogram of 7
Table 2, entry 4
99% ee

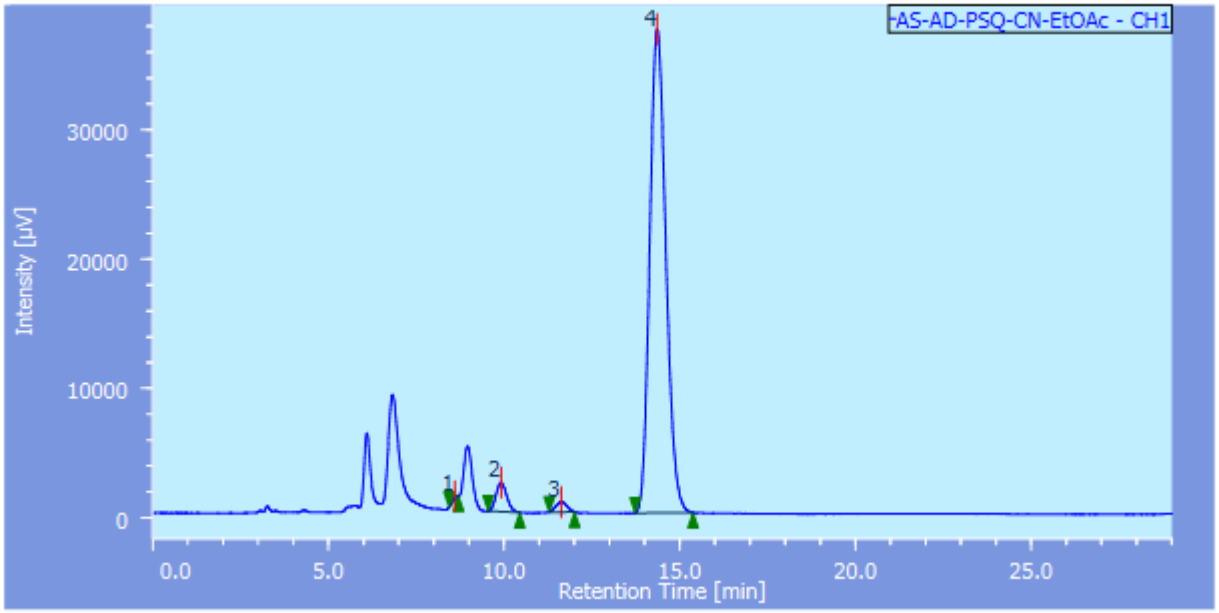


Figure S17: HPLC chromatogram of 7
Table 2, entry 5
92% ee

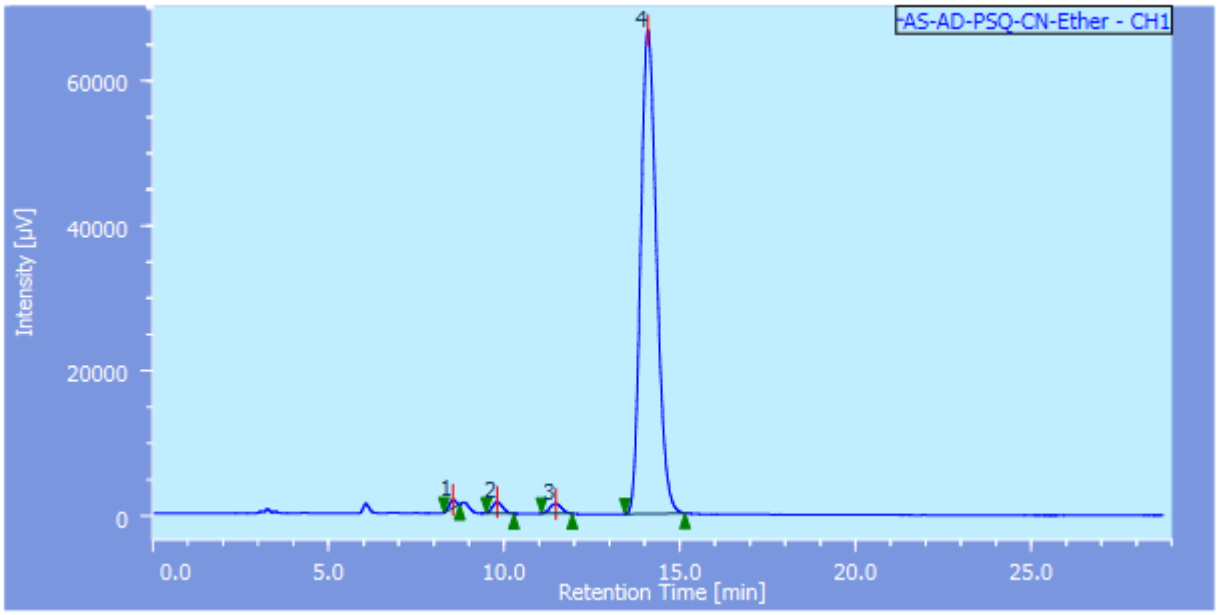


Figure S18: HPLC chromatogram of 7
Table 2, entry 6
97% ee

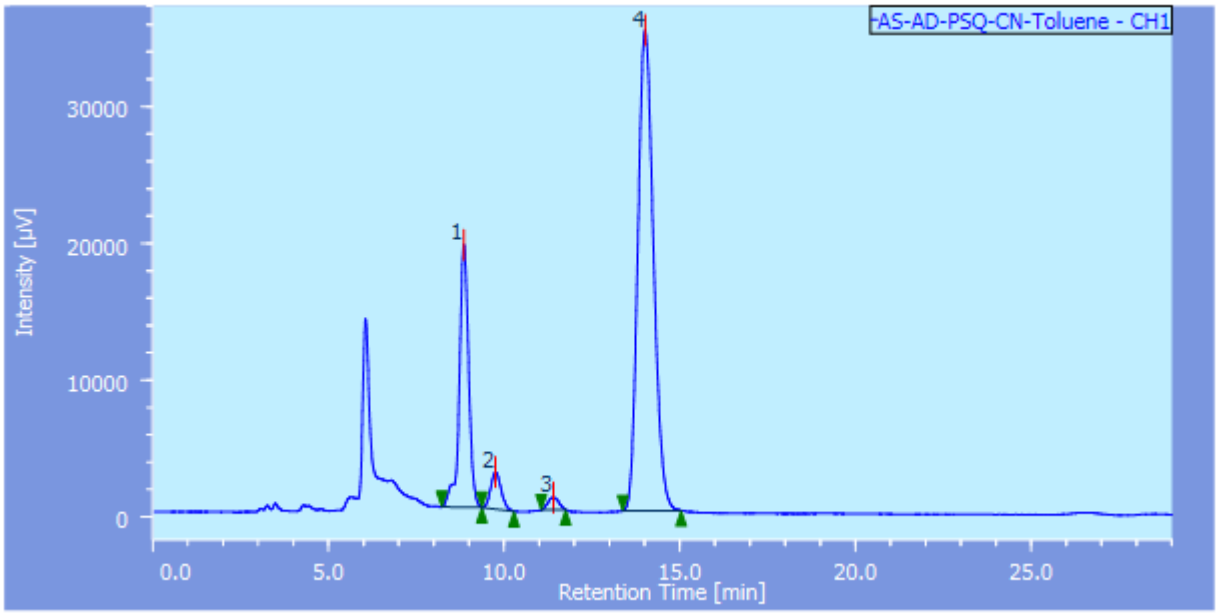


Figure S19: HPLC chromatogram of 7

Table 2, entry 7
90% ee

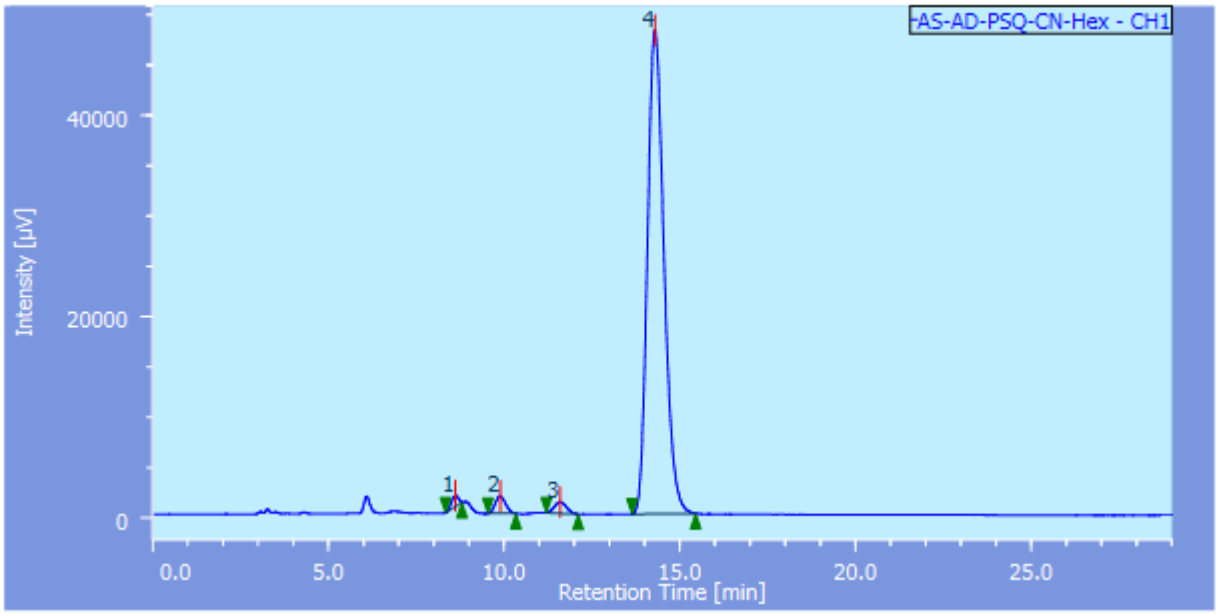


Figure S20: HPLC chromatogram of 7
Table 2, entry 8
96% ee

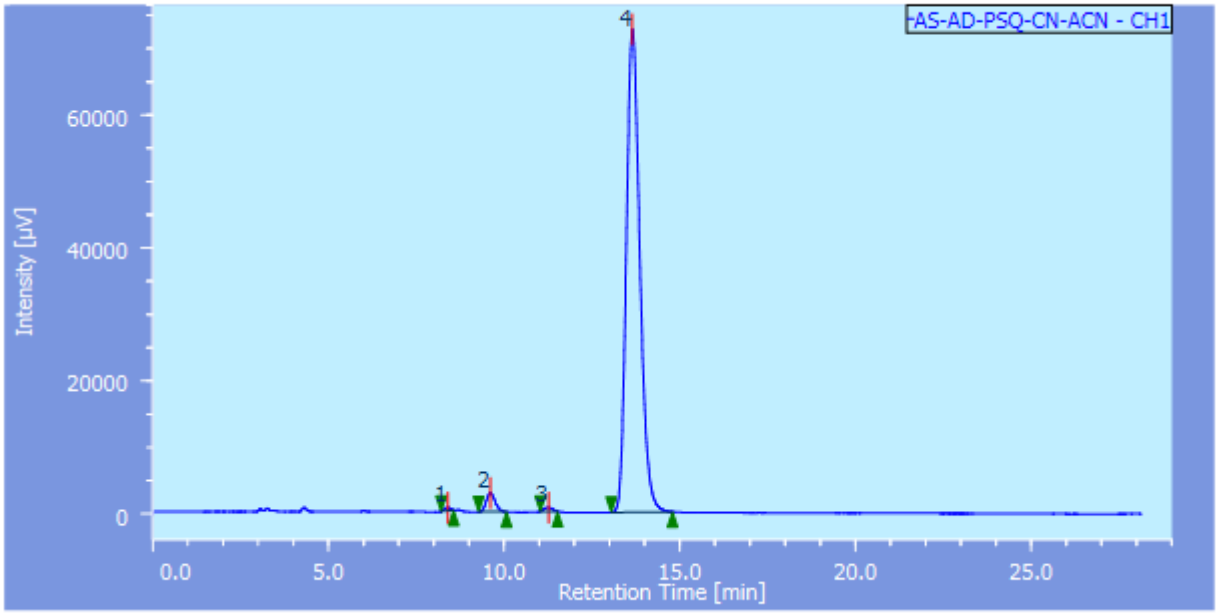


Figure S21: HPLC chromatogram of 7
Table 2, entry 9
95% ee

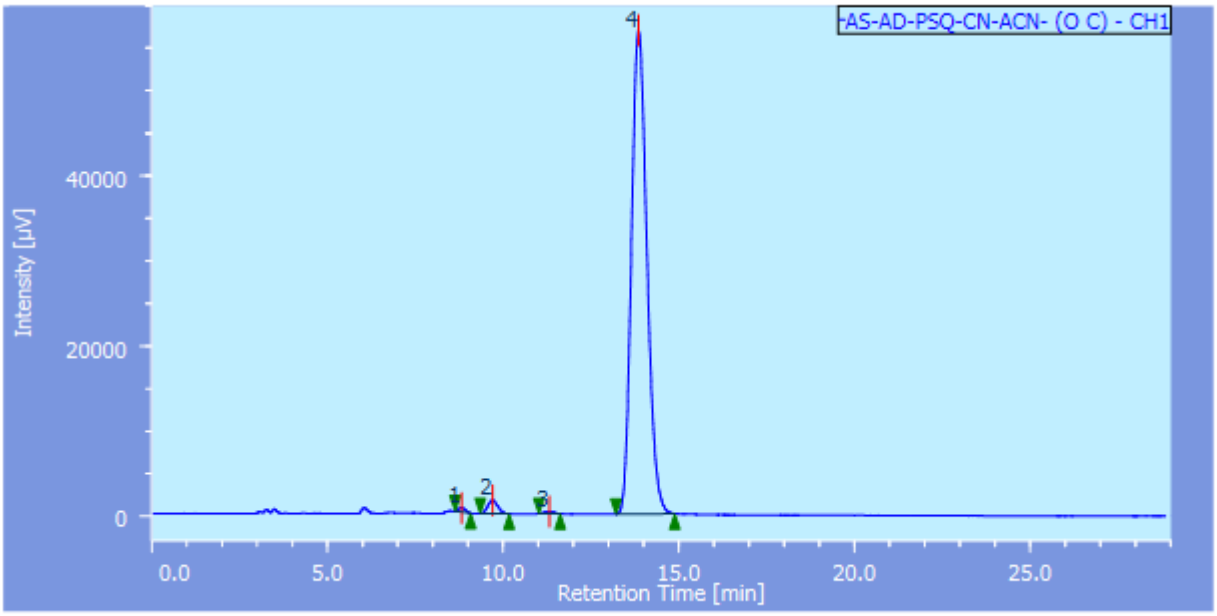


Figure S22: HPLC chromatogram of 7
Table 2, entry 10
96% ee

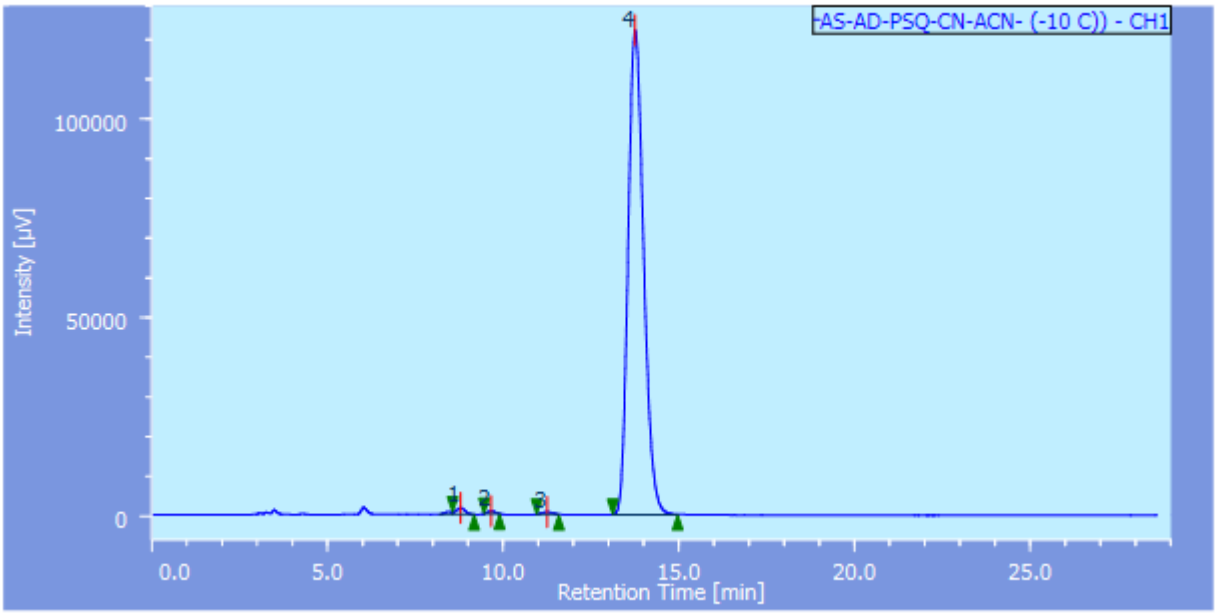


Figure S23: HPLC chromatogram of 7
Table 2, entry 11
99% ee

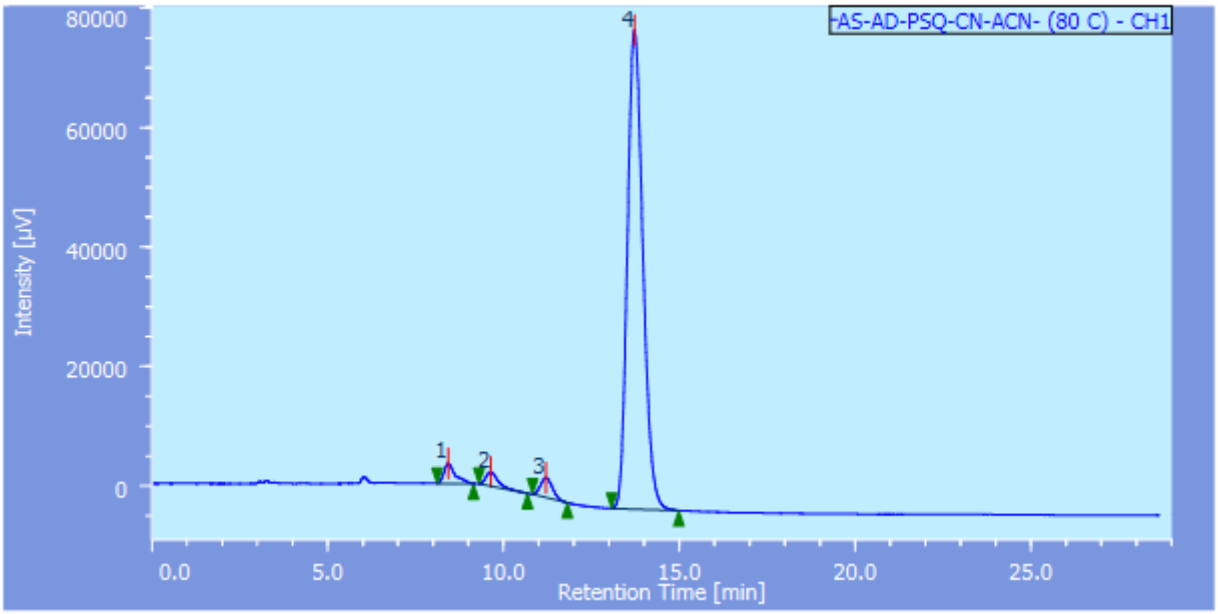


Figure S24: HPLC chromatogram of 7
Table 2, entry 12
95% ee

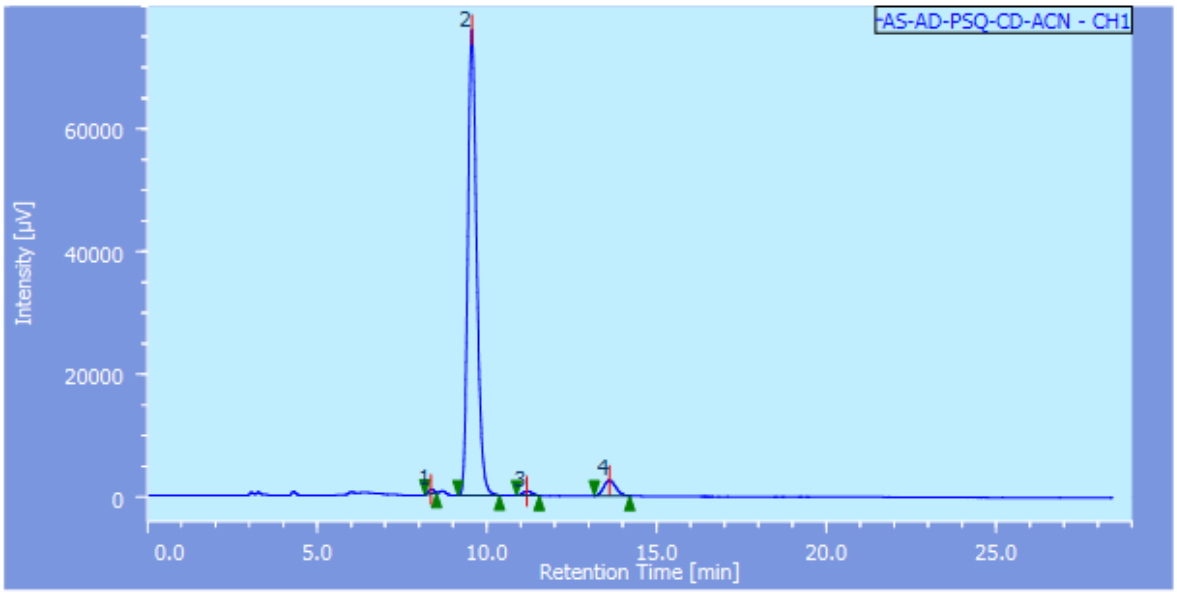


Figure S25: HPLC chromatogram of 7
Table 2, entry 14
91% ee

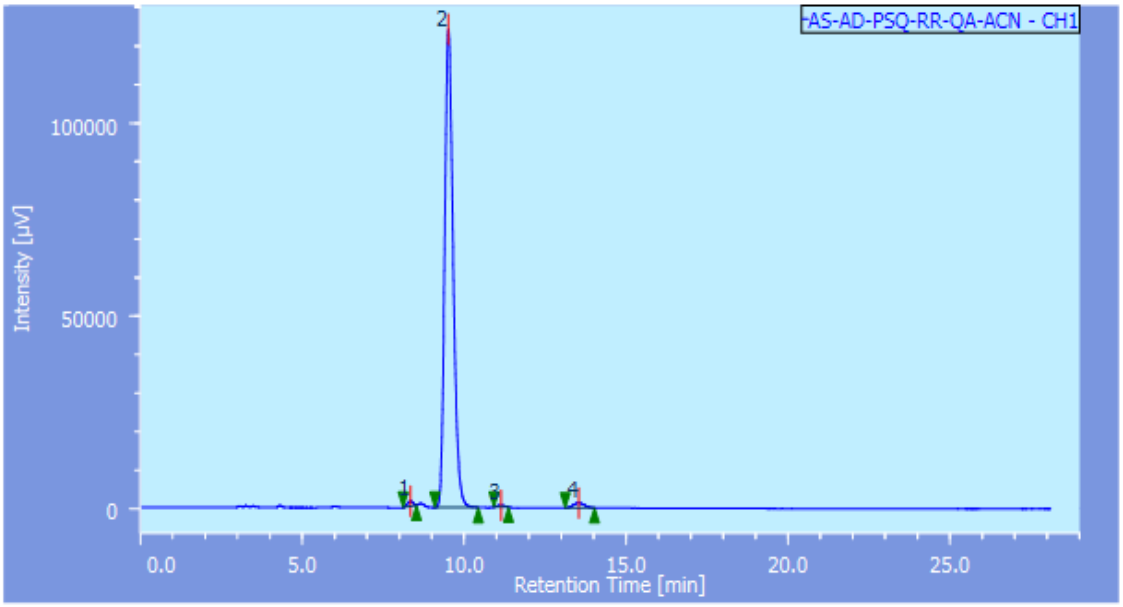


Figure S26: HPLC chromatogram of 7
Table 2, entry 17
97% ee

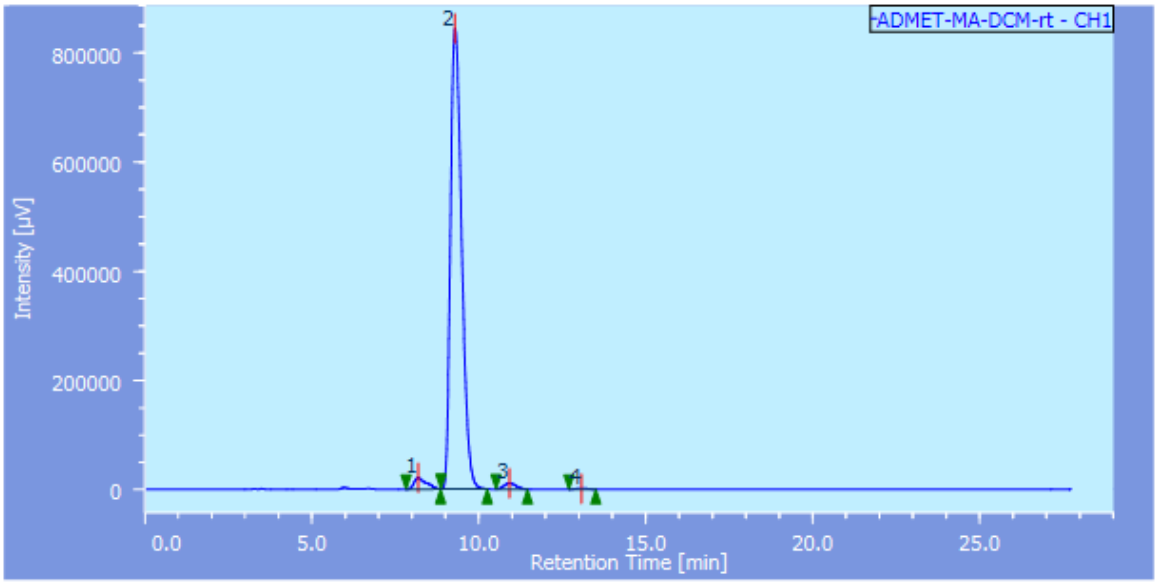


Figure S27: HPLC chromatogram of 7
Table 2, entry 18
99% ee

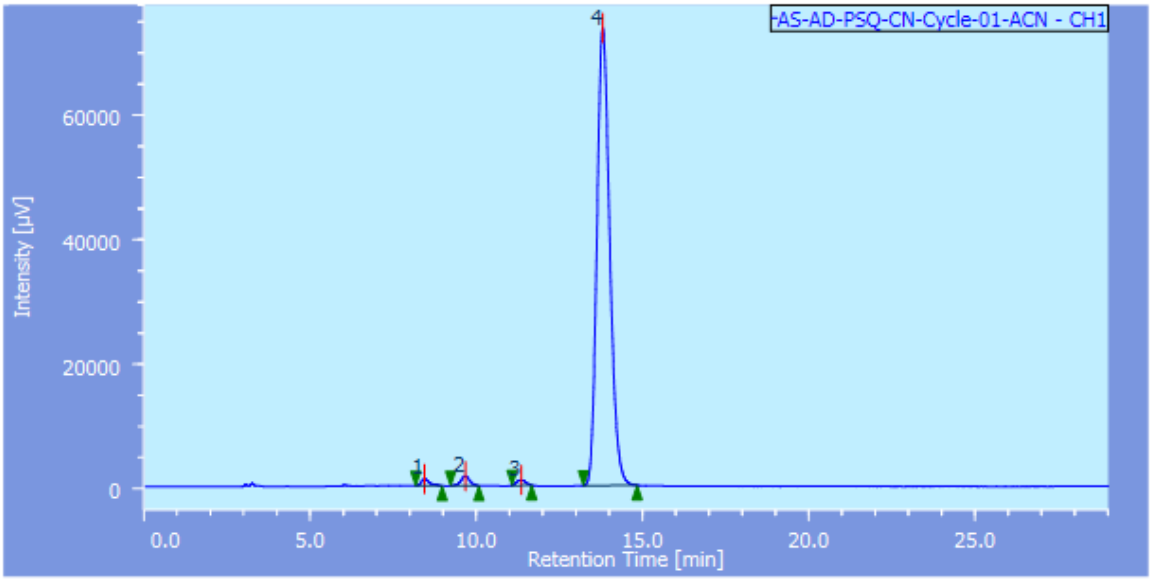


Figure S28: HPLC chromatogram of 7
Table 3, cycle 1
97% ee

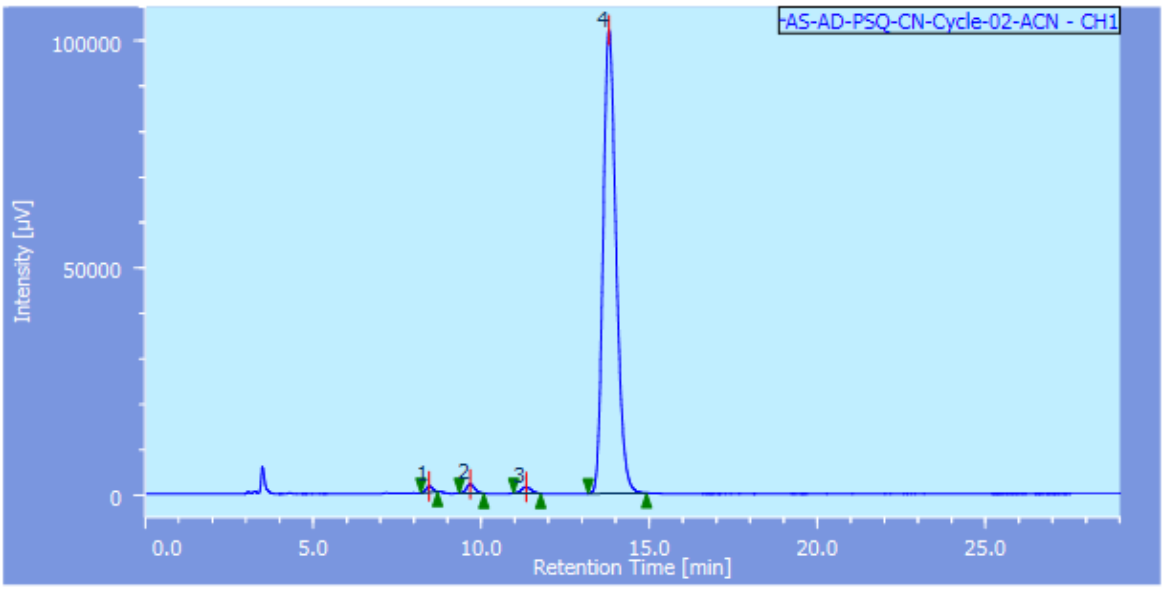


Figure S29: HPLC chromatogram of 7

Table 3, cycle 2
97% ee

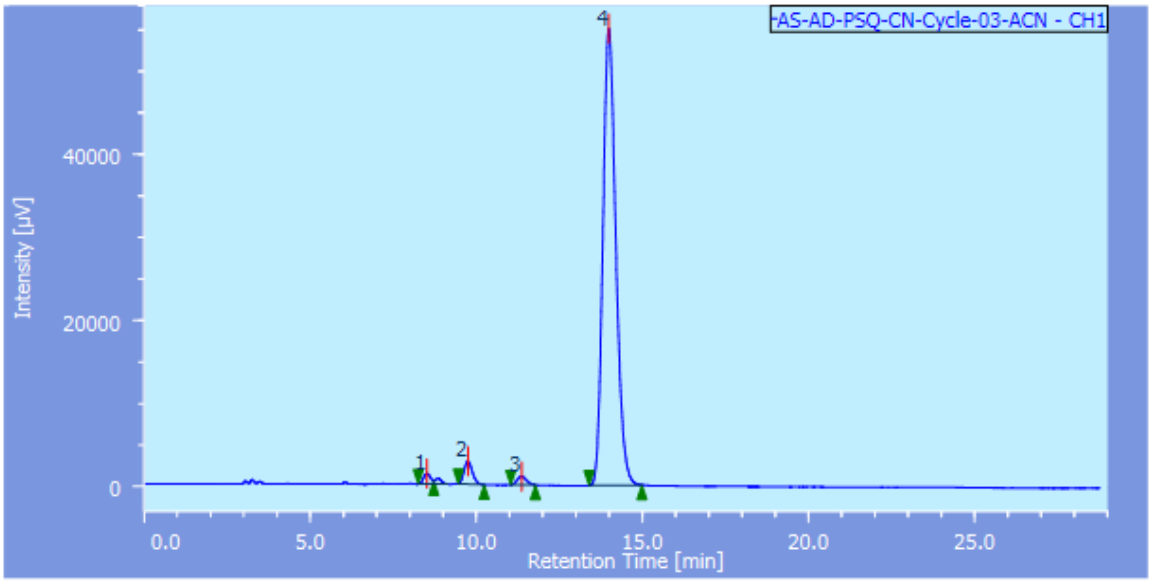


Figure S30: HPLC chromatogram of 7

Table 3, cycle 3
94% ee

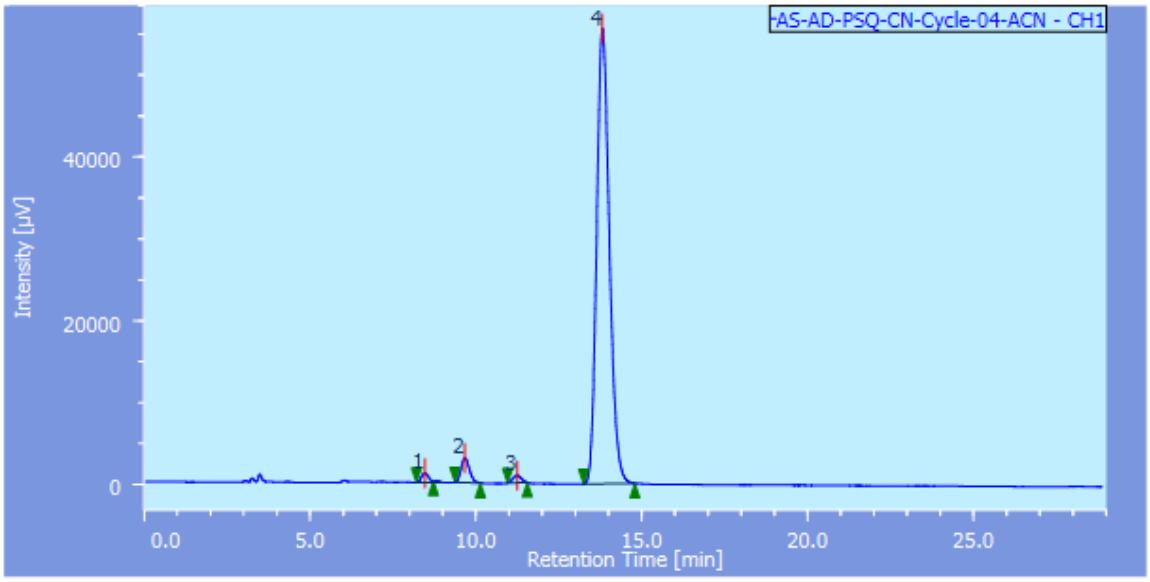


Figure S31: HPLC chromatogram of 7
Table 3, cycle 4
93% ee

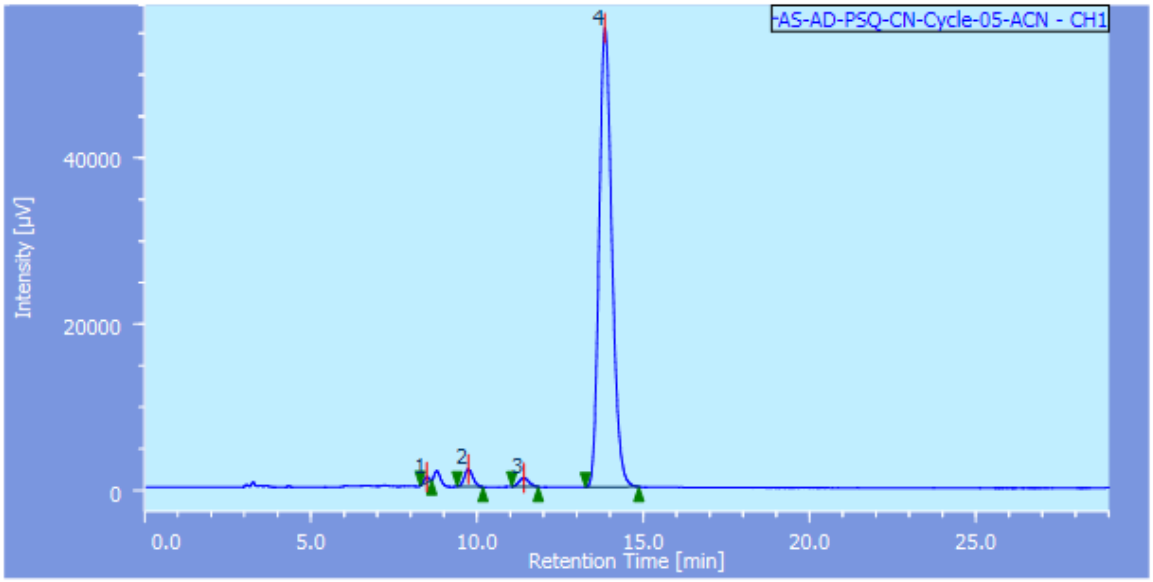


Figure S32: HPLC chromatogram of 7
Table 3, cycle 5
95% ee

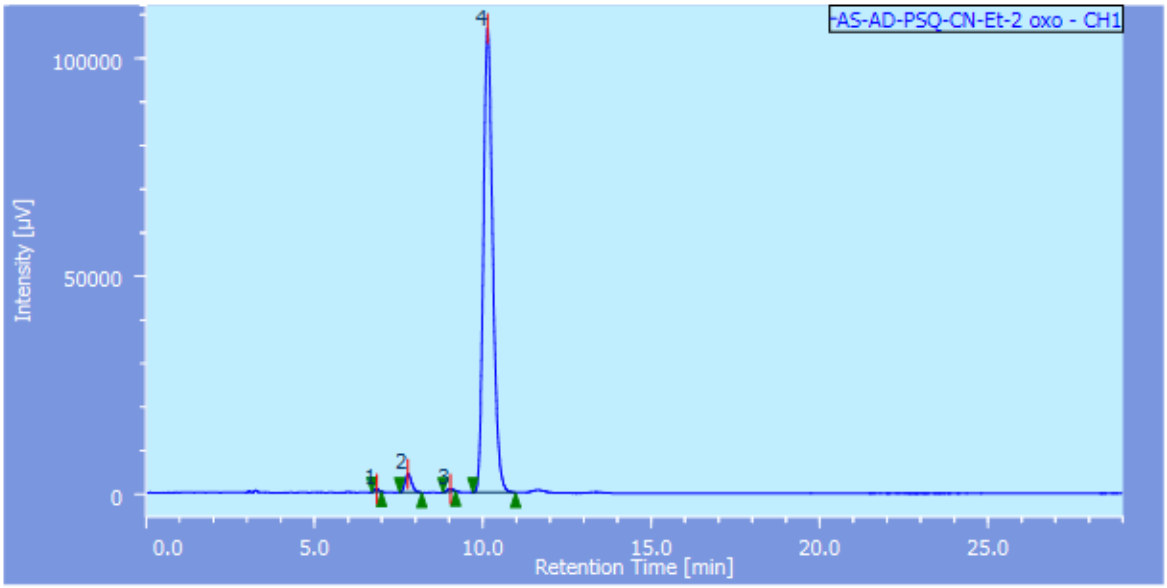


Figure S33: HPLC chromatogram of 8
Scheme 3
94% ee

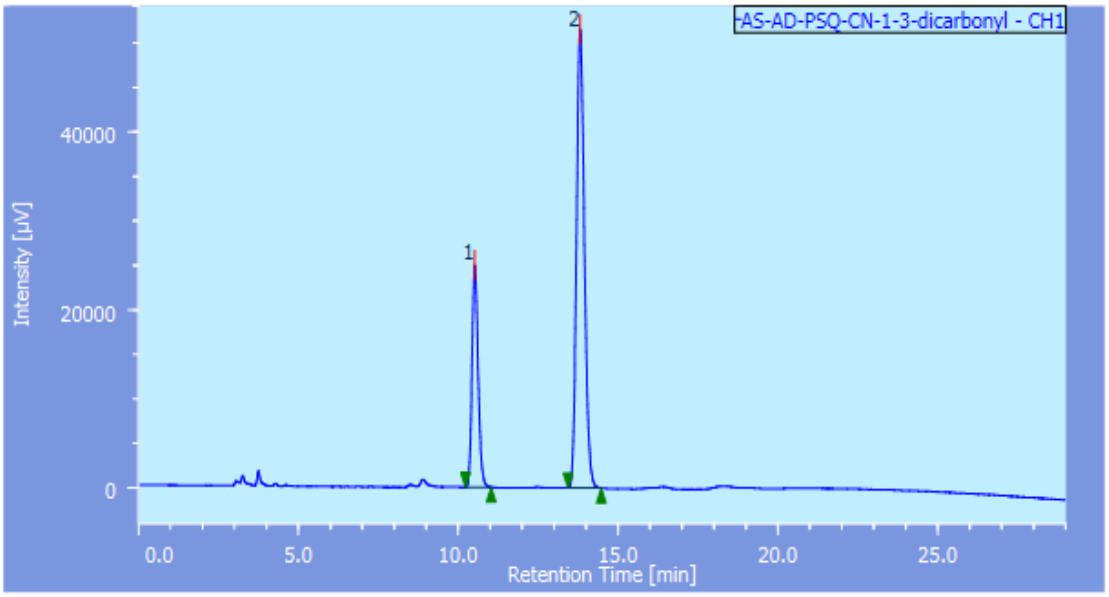


Figure S34: HPLC chromatogram of 9
Scheme 3
45% ee

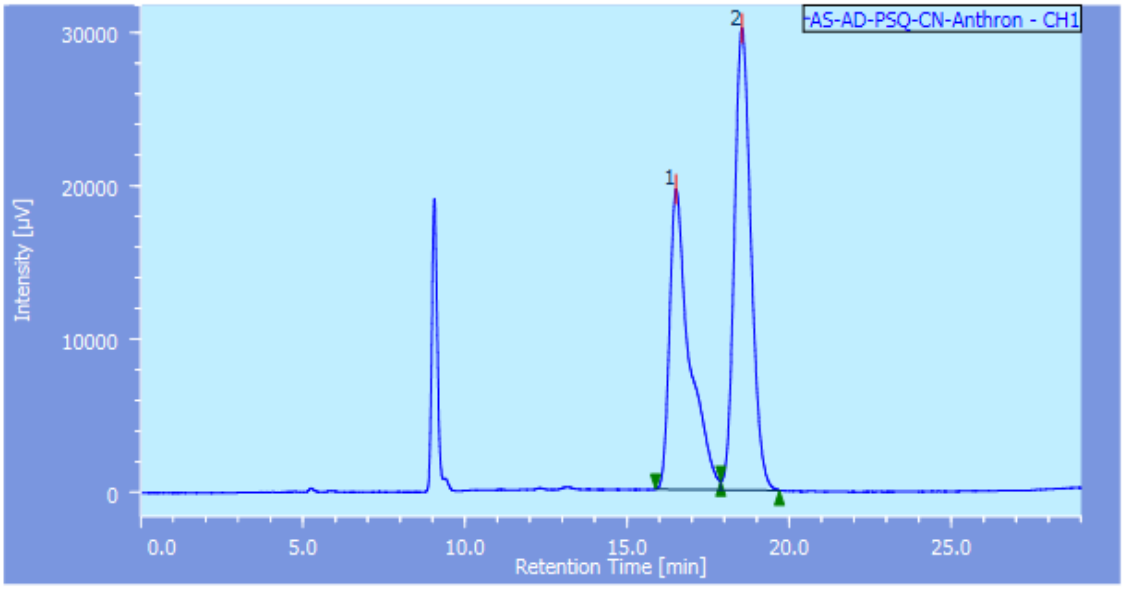


Figure S35: HPLC chromatogram of 10
Scheme 3
12% ee

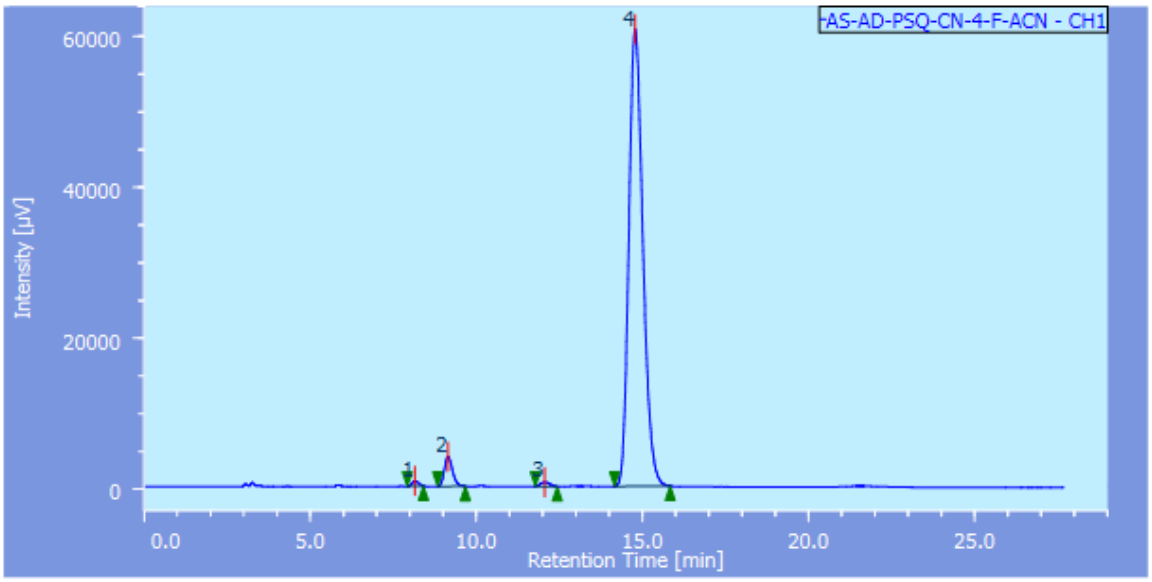


Figure S36: HPLC chromatogram of 11
Scheme 3
93% ee

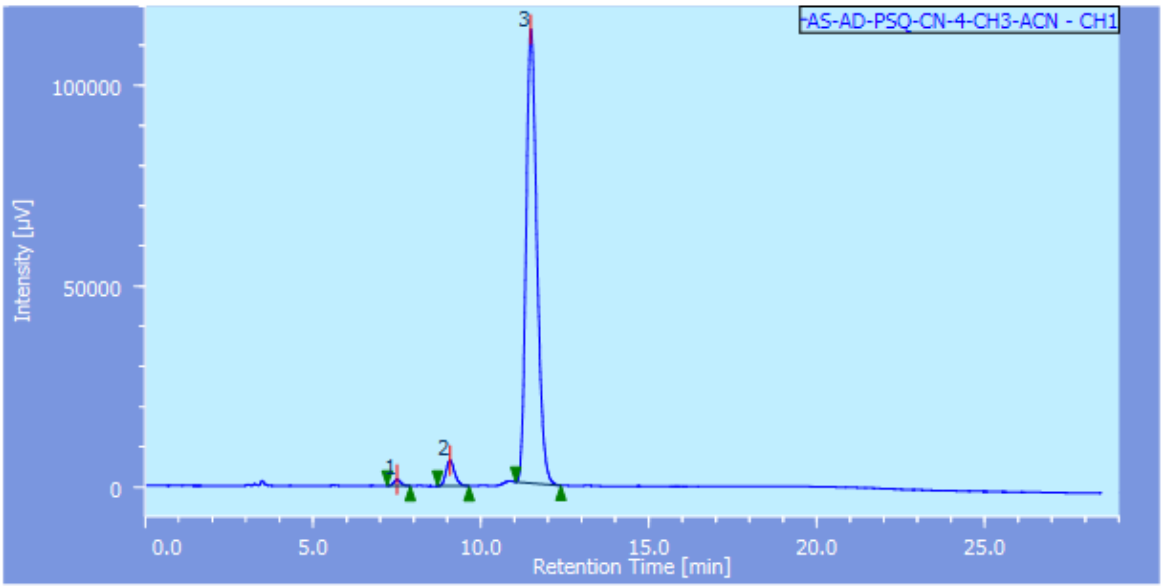


Figure S37: HPLC chromatogram of 12
Scheme 3
91% ee

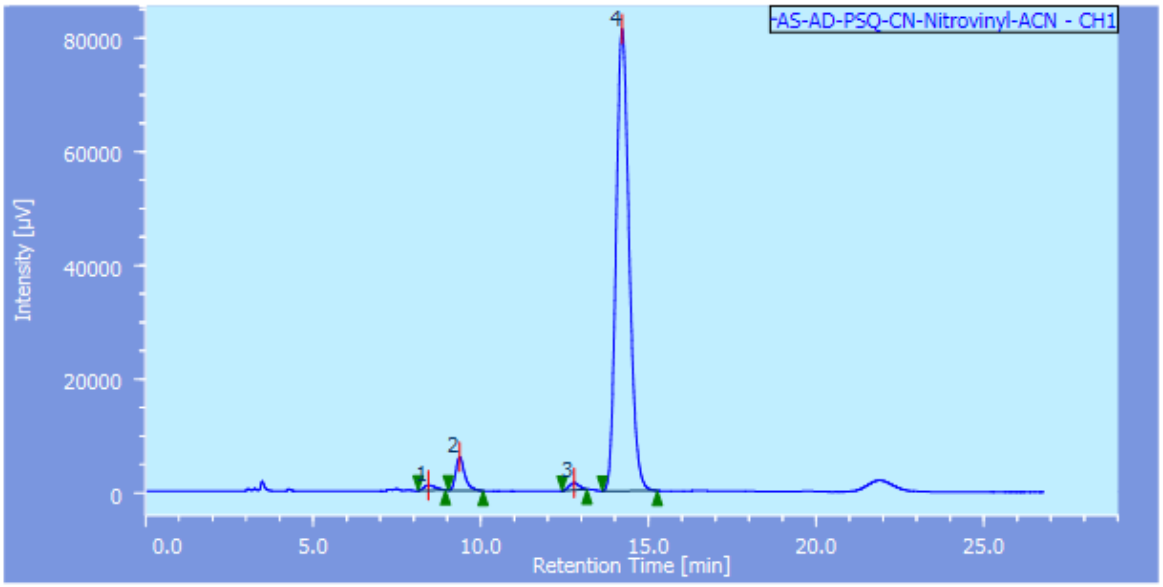


Figure S38: HPLC chromatogram of 13
Scheme 3
96% ee