Electronic Supplementary Material (ESI) for New Journal of Chemistry.

New Series of Bipyridine Based Chiral Organocatalyst for Enantioselective Henry Reaction

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Supporting Information

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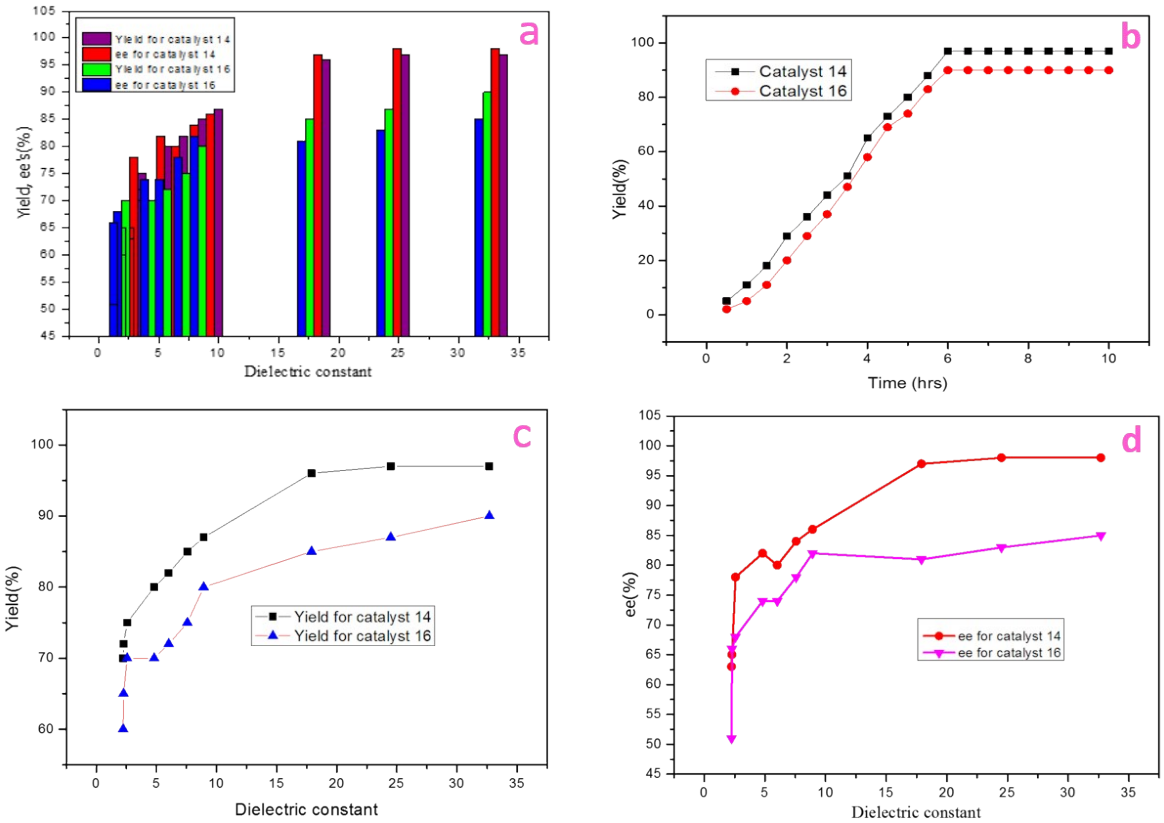


Fig. F1 The effect of solvent on enantioselective Henry reaction. (**a**) Dielectric constant *vs* yield and ee's for catalysts **14** and **16**. (**b**) Time *vs* yield for catalysts **14** and **16**. (**c**) Dielectric constant *vs* yield for catalysts **14** and **16**. (**d**) Dielectric constant *vs* ee's for catalysts **14** and **16**.

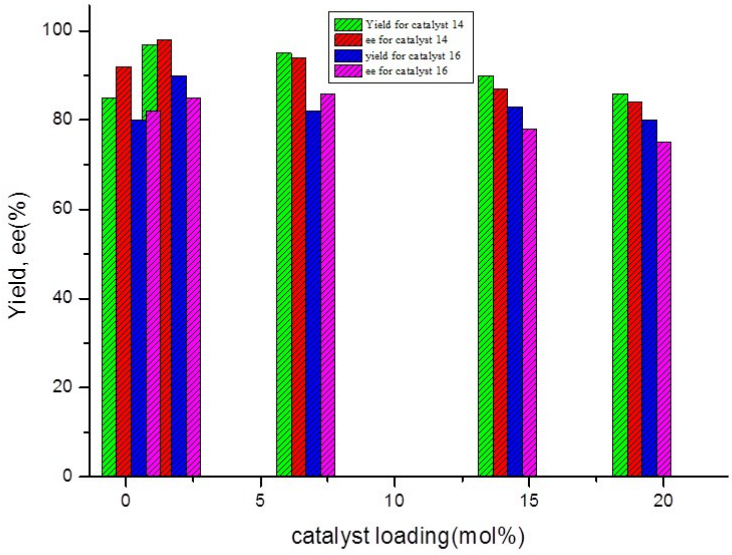
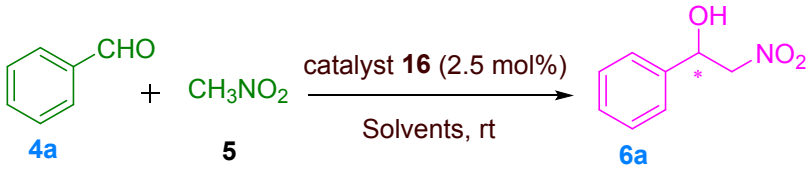


Fig. F2 Catalyst loading *vs* yield and ee's for organocatalysts **14** & **16**.

Table S1: Effect of solvents in enantioselective Henry reaction.

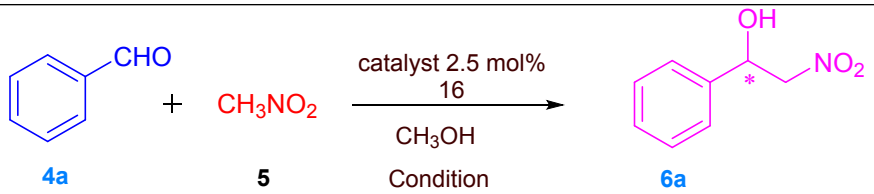


4a 5 6a

Entry	solvents	Time (h) [a]	Yield % [b]	ee % [c]	Abs. Conf.[d]
1	CH_3OH	6	86	85	*S*
2	C_2H_5OH	6	87	84	*S*
3	i-PrOH	6	85	81	*S*
4	DCM	7	80	82	*S*
5	THF	7	75	78	*S*
6	EtOAc	8	72	73	*S*
7	$CHCl_3$	8	70	71	*S*
8	o-Xylene	10	70	67	*S*
9	Benzene	10	65	48	*S*
10	CCl_4	10	60	41	*S*

[a] The enantioselective Henry reaction of aldehyde **4a** (0.1 mmol), nitromethane **5** (1.0 mmol), organocatalyst **16** (2.5 mol%) with 1.5 ml of various solvents at room temperature with different time. [b] Isolated yield of purified material. [c] Enantiopurity was determined by HPLC analysis of the Henry product **6a** using a chiral column (Chiralcel OD-H) with hexane–IPA as an eluent. [d] Absolute configuration was determined by comparison of the HPLC retention time using known literature data.[1]

Table S2: The optimization of enantioselective Henry reaction under various temperature conditions.



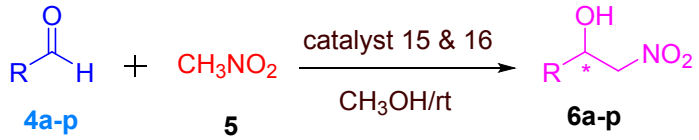
4a 5 6a

Entry	Condition	Time (h) [a]	Yield % [b]	ee % [c]	Abs. Conf.[d]
1	60˚C	6	60	59	S
2	50˚C	6	70	63	S
3	30˚C RT)	6	86	85	S
4	25˚C	7	78	75	S
5	20˚C	7	73	71	S
6	15˚C	7	70	62	S
7	10˚C	7	65	56	S
8	05˚C	6	60	59	R
9	0˚C	8	80	65	R
10	−10˚C	9	82	71	R
11	−20˚C	10	83	79	R

[a] The enantioselective Henry reaction of aldehyde **4a** (0.1 mmol), nitromethane **5** (1.0 mmol), organocatalyst **16** (2.5 mol%) with 1.5 ml of methanol at various temperature condition with different

time. [b] Isolated yield of purified material. [c] Enantiopurity was determined by HPLC analysis of the Henry product **6a** using a chiral column (Chiralcel OD-H) with hexane–IPA as an eluent. [d] Absolute configuration was determined by comparison of the HPLC retention time using known literature data.[1]

Table S3: Enantioselective Henry reaction of nitromethane with various aromatic/aliphatic aldehydes.



Entry	R	Product	Catalyst	Time (h) [a]	Yield % [b]	ee % [c]	Abs Conf. [d]
1	Ph	6a	15	6.0	95	97	S
2	Ph	6a	16	6.0	86	85	S
3	4Cl-Ph	6b	15	6.5	92	92	S
4	4Cl-Ph	6b	16	6.5	81	83	S
5	4Br-Ph	6c	15	6.5	92	90	S
6	4Br-Ph	6c	16	6.5	82	82	S
7	$4CH_3$-Ph	6d	15	7.0	90	91	S
8	$4CH_3$-Ph	6d	16	7.0	80	77	S
9	$4OCH_3$-Ph	6e	15	7.0	90	94	S
10	$4OCH_3$-Ph	6e	16	7.0	84	71	S
11	$2OCH_3$-Ph	6f	15	10.0	86	90	S
12	$2OCH_3$-Ph	6f	16	10.0	72	74	S
13	$3OCH_3$-Ph	6g	15	12.0	88	92	S
14	$3OCH_3$-Ph	6g	16	12.0	75	78	S
15	$4NO_2$-Ph	6h	15	6.0	97	98	S
16	$4NO_2$-Ph	6h	16	6.0	85	84	S
17	4CN-Ph	6i	15	6.0	97	99	S
18	4CN-Ph	6i	16	6.0	86	82	S
19	2-naphthyl	6j	15	8.0	94	97	S
20	2-naphthyl	6j	16	8.0	80	81	S
21	Furfuryl	6k	15	8.0	91	94	S
22	Furfuryl	6k	16	8.0	72	79	S
23	E-cinnamyl	6l	15	8.0	80	93	S
24	E-cinnamyl	6l	16	8.0	70	73	S
25	$-(CH_3)_2CH$	6m	15	8.0	90	90	R
26	$-(CH_3)_2CH$	6m	16	8.0	75	65	R
27	$-C_2H_5)_2CH$	6n	15	8.0	89	92	R
28	$-C_2H_5)_2CH$	6n	16	8.0	72	63	R
29	$-CH_3(CH_2)_4$	6o	15	8.0	90	91	R
30	$-CH_3(CH_2)_4$	6o	16	8.0	70	41	R
31	Cyclohexyl	6p	15	8.0	96	97	R
32	Cyclohexyl	6p	16	8.0	65	71	R

[a] The enantioselective Henry reaction of aldehyde **4a-p** (0.1 mmol), nitromethane **5** (1.0 mmol), organocatalyst **15** & **16**, (2.5 mol%) and 1.5 ml of methnol at room temperature condition with different time intervels. [b] Isolated yield of purified material. [c] Enantiopurity was determined by HPLC analysis of the Henry product **6a-p** using a chiral column (Chiralcel OD-H) with hexane–IPA as an eluent. [d] Absolute configuration was determined by comparison of the HPLC retention time using known literature data.[1]

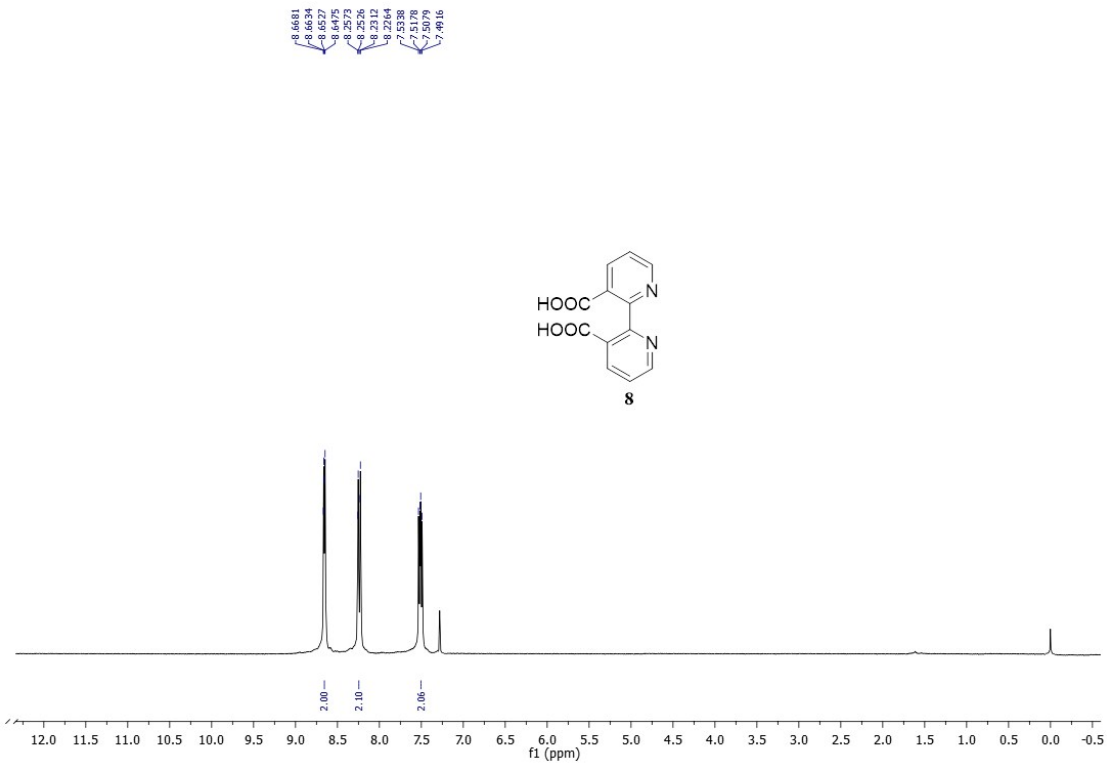


Figure S1: ^{1}H NMR Spectrum of compound **8**.

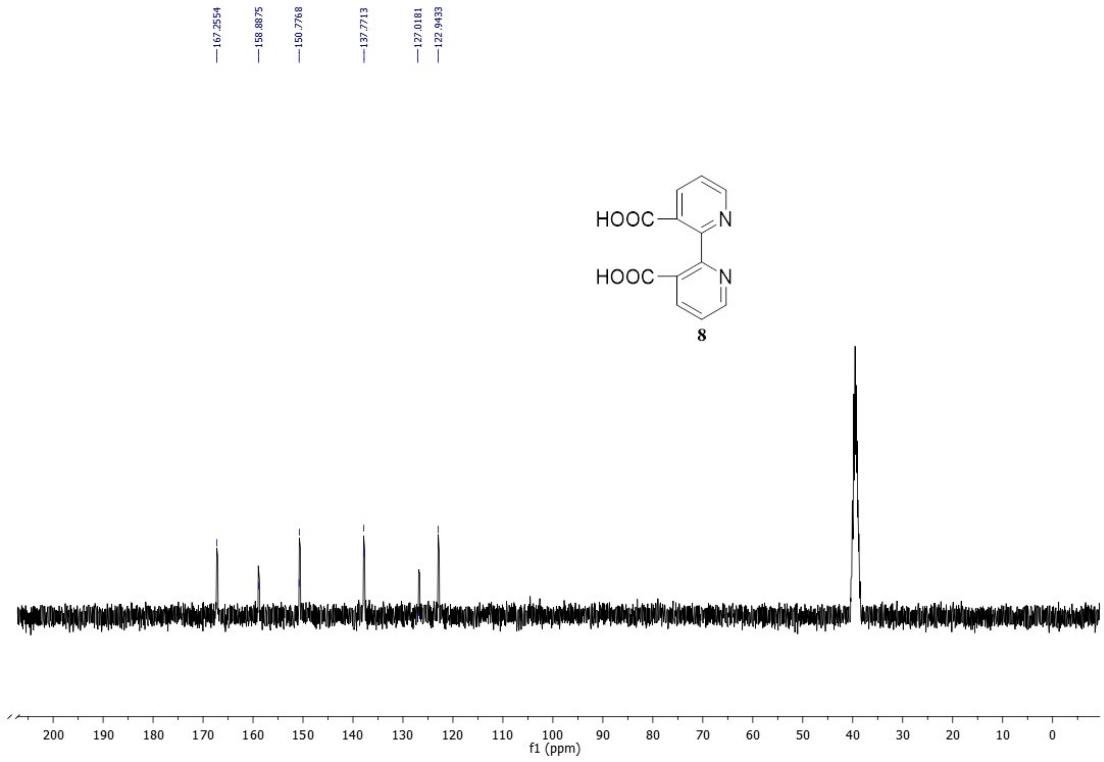


Figure S2: ^{13}C NMR Spectrum of compound **8**.

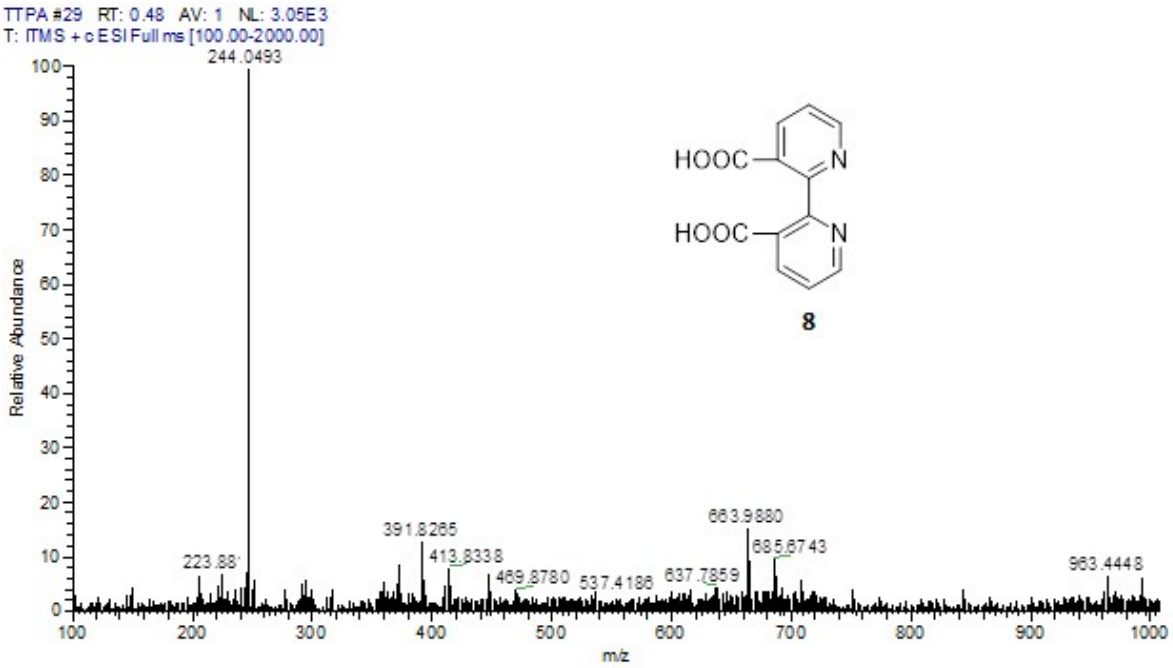


Figure S3: ESI-Mass Spectrum of compound **8**.

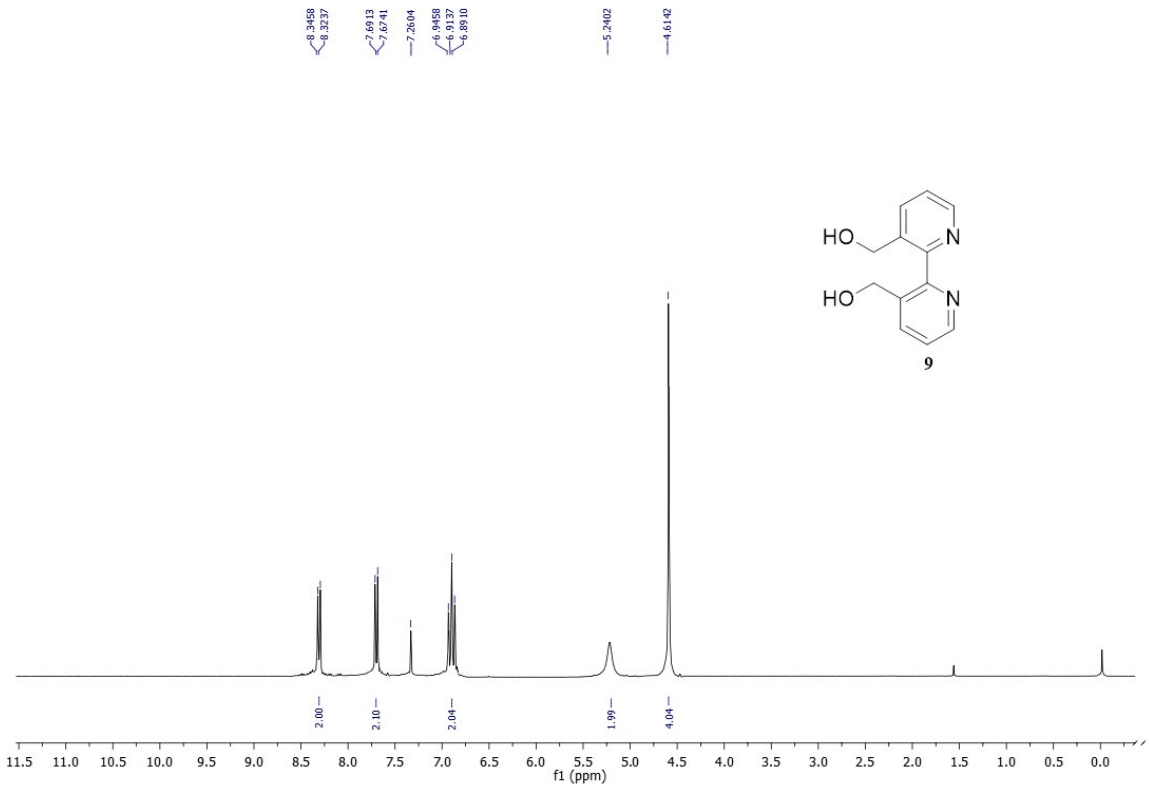


Figure S4: ^{1}H NMR Spectrum of compound **9**.

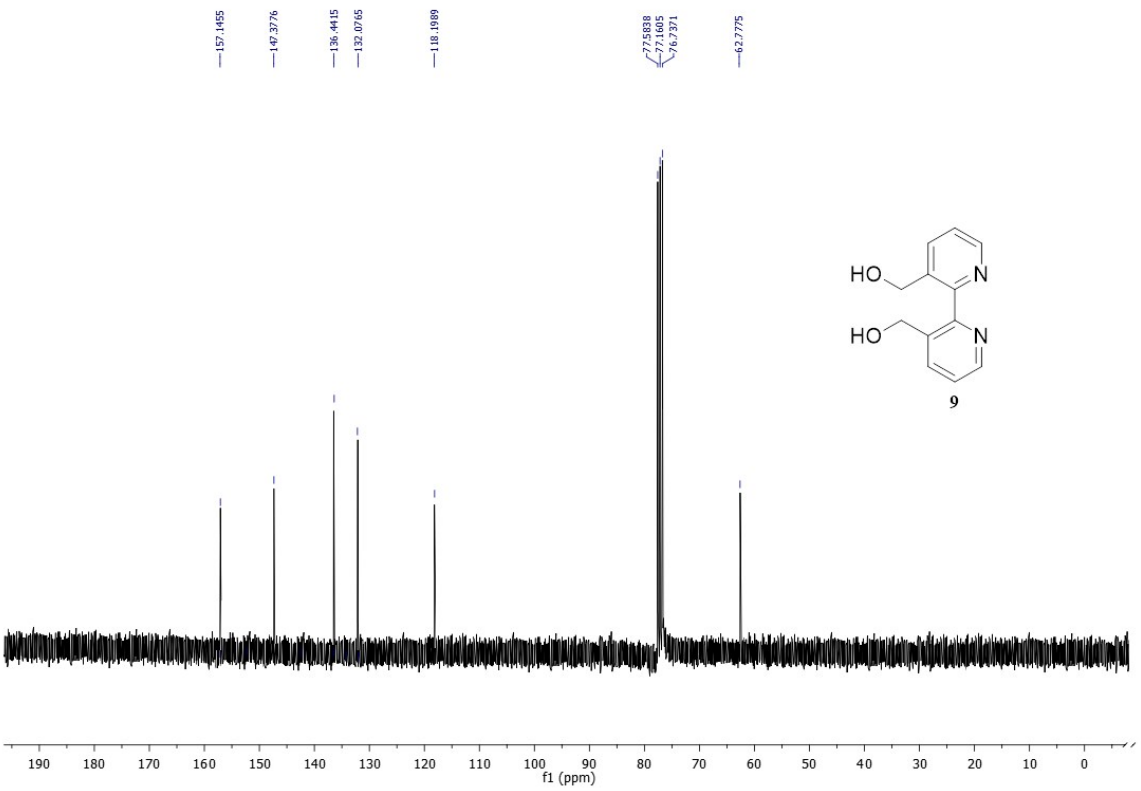


Figure S5: ^{13}C NMR Spectrum of compound **9**.

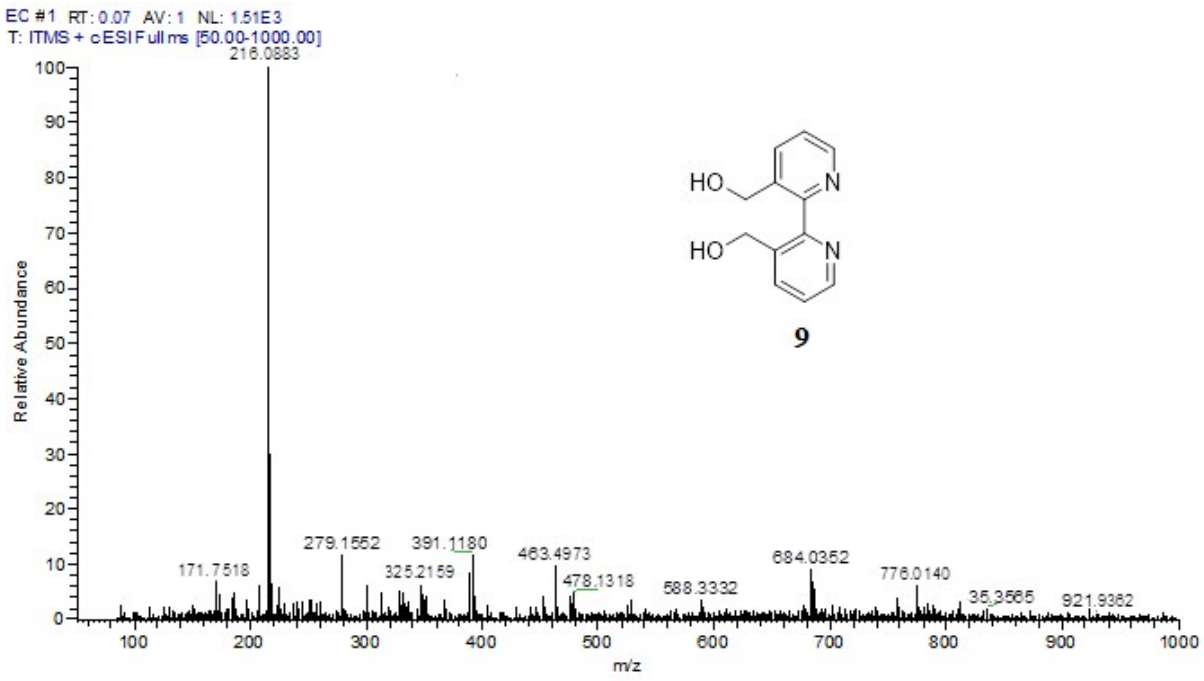


Figure S6: ESI-Mass Spectrum of compound **9**.

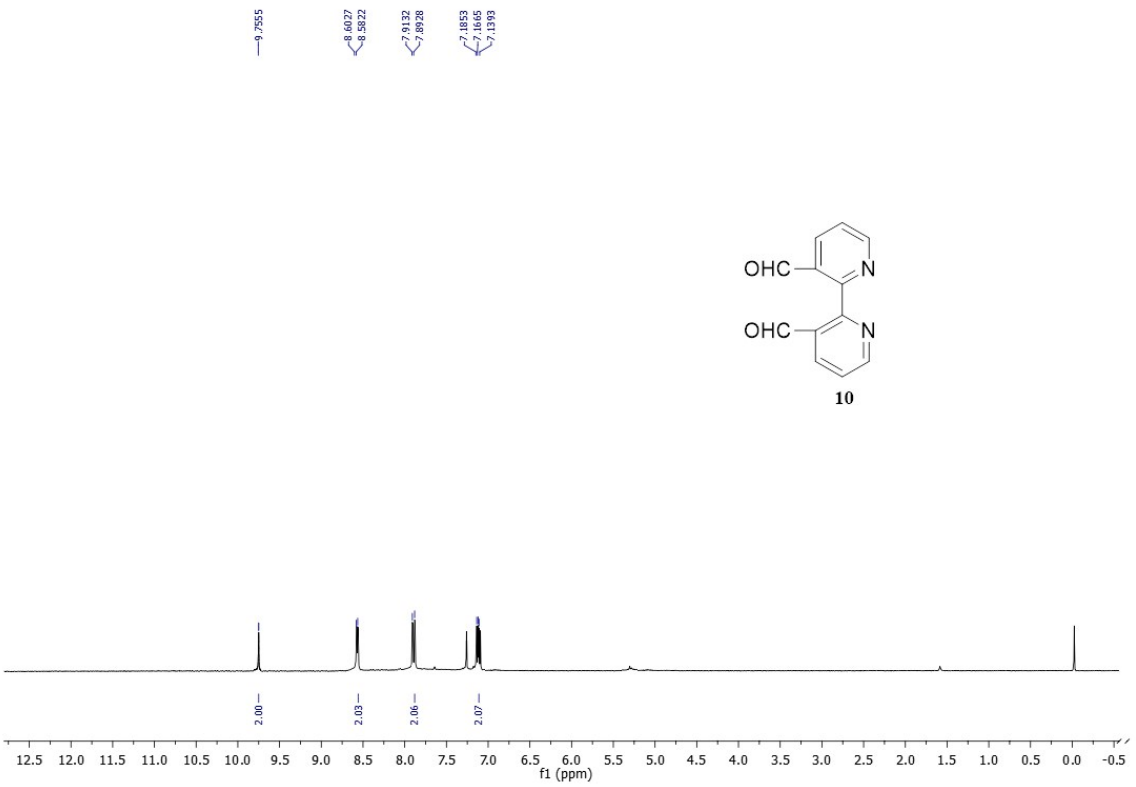


Figure S7: ^{1}H NMR Spectrum of compound **10**.

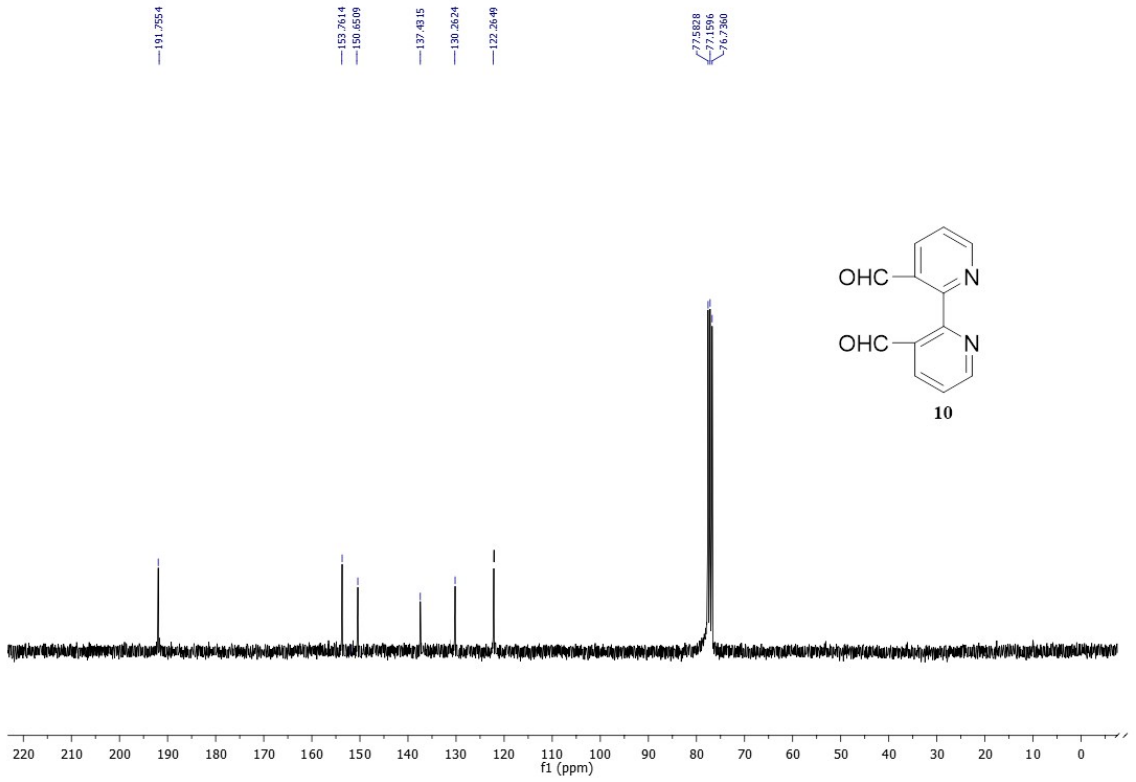


Figure S8: ^{13}C NMR Spectrum of compound **10**.

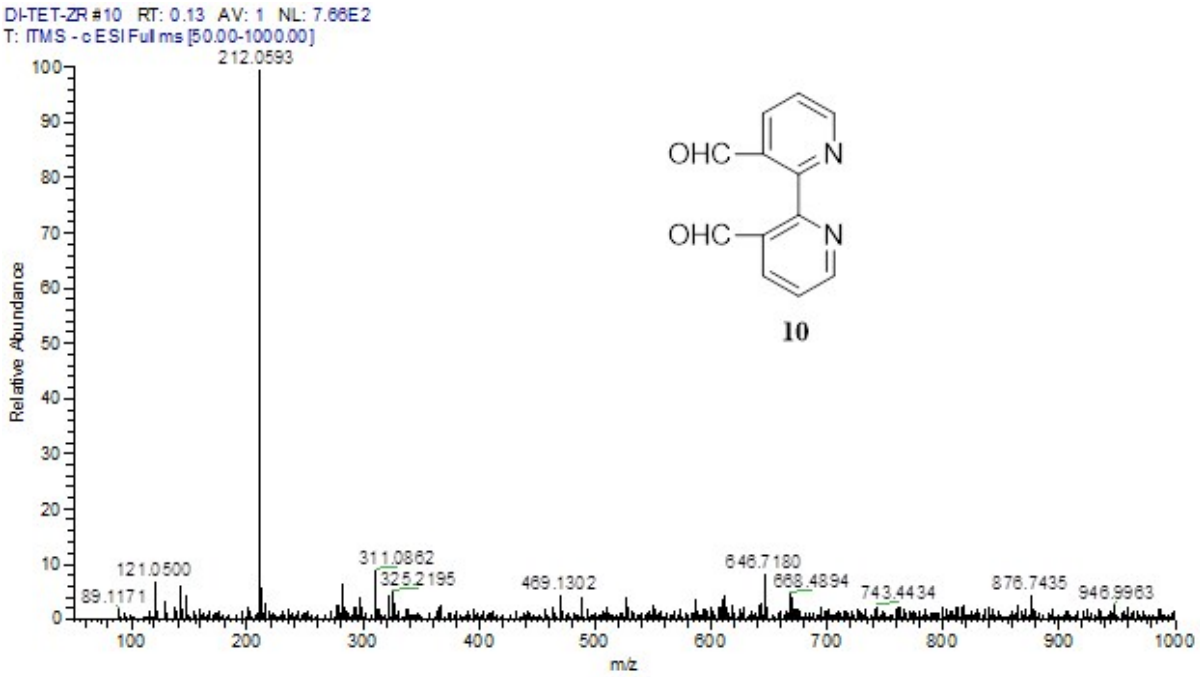


Figure S9: ESI-Mass Spectrum of compound **10**.

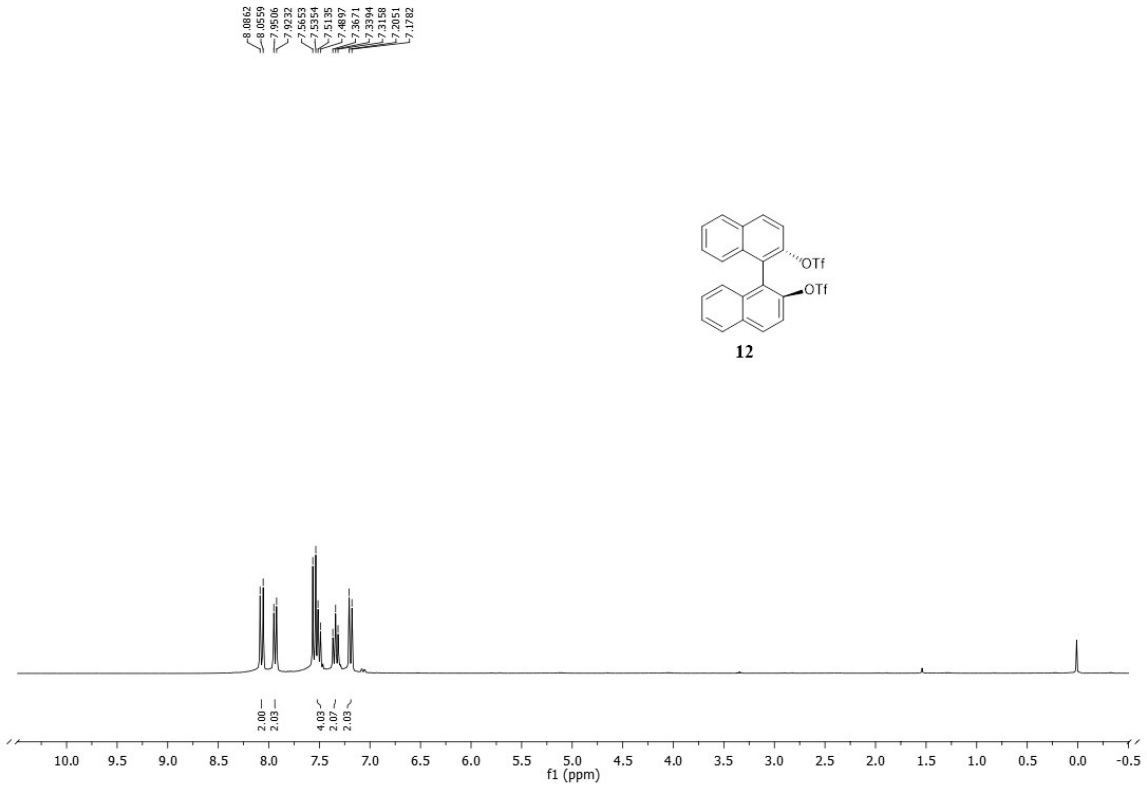


Figure S10: ^{1}H NMR Spectrum of compound **12**.

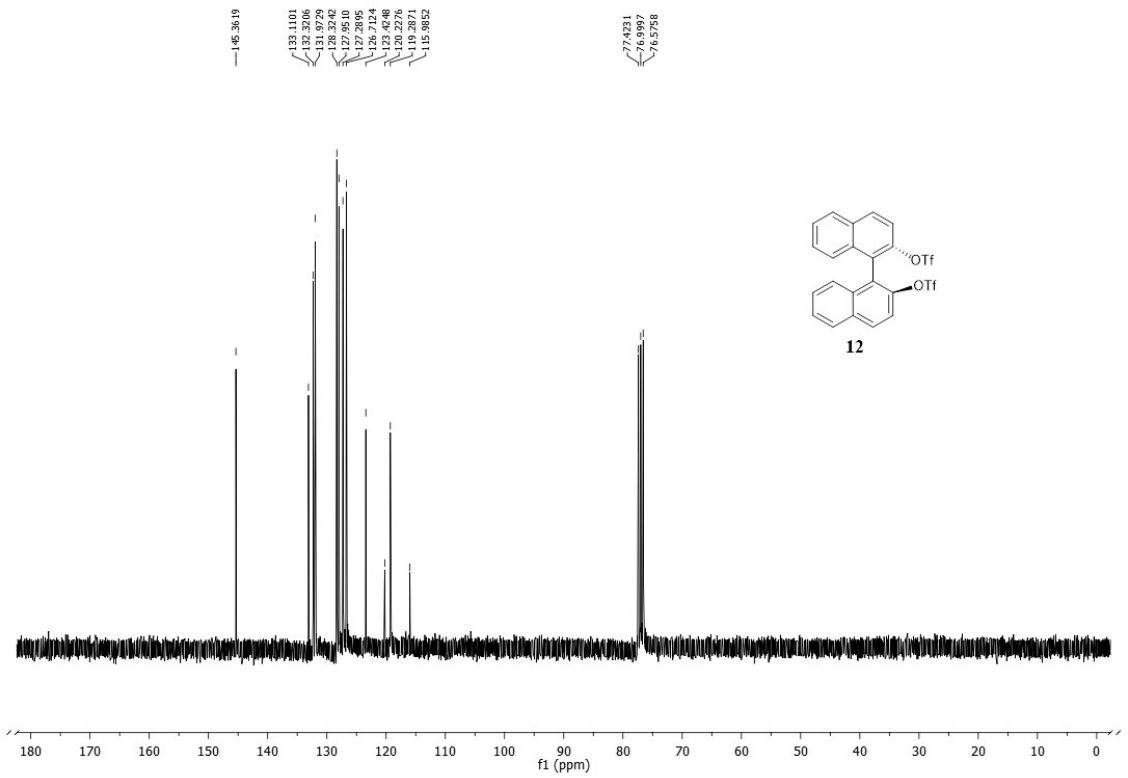


Figure S11: ^{13}C NMR Spectrum of compound **12**.

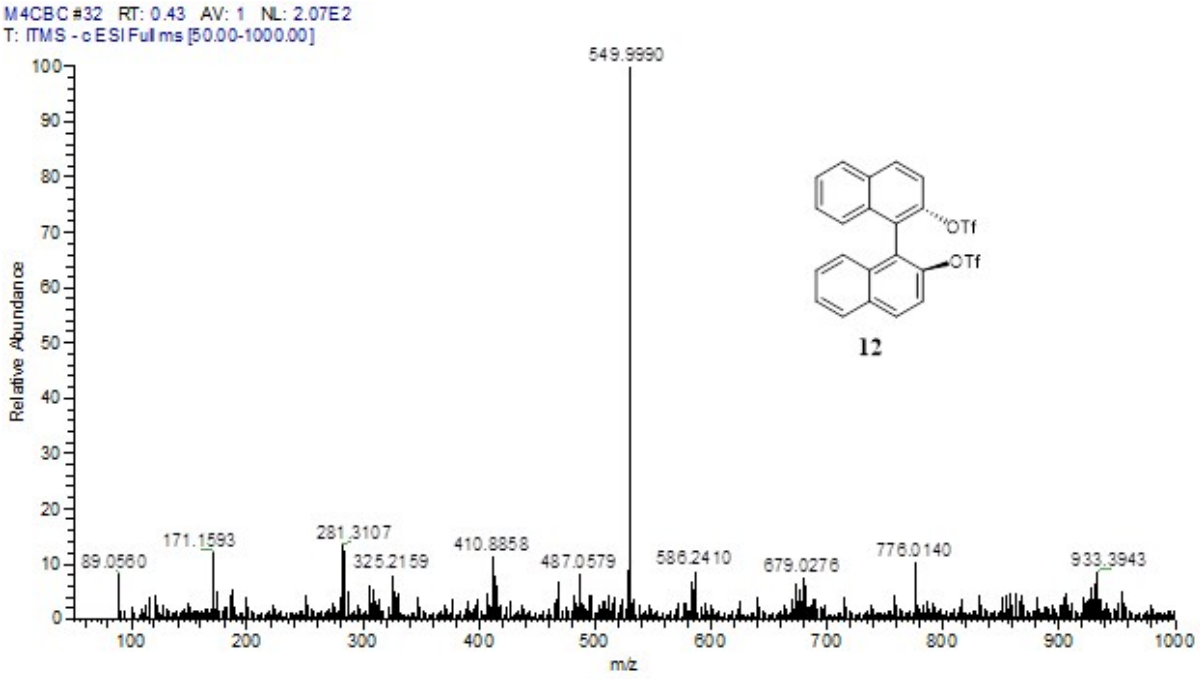


Figure S12: ESI-Mass Spectrum of compound **12**.

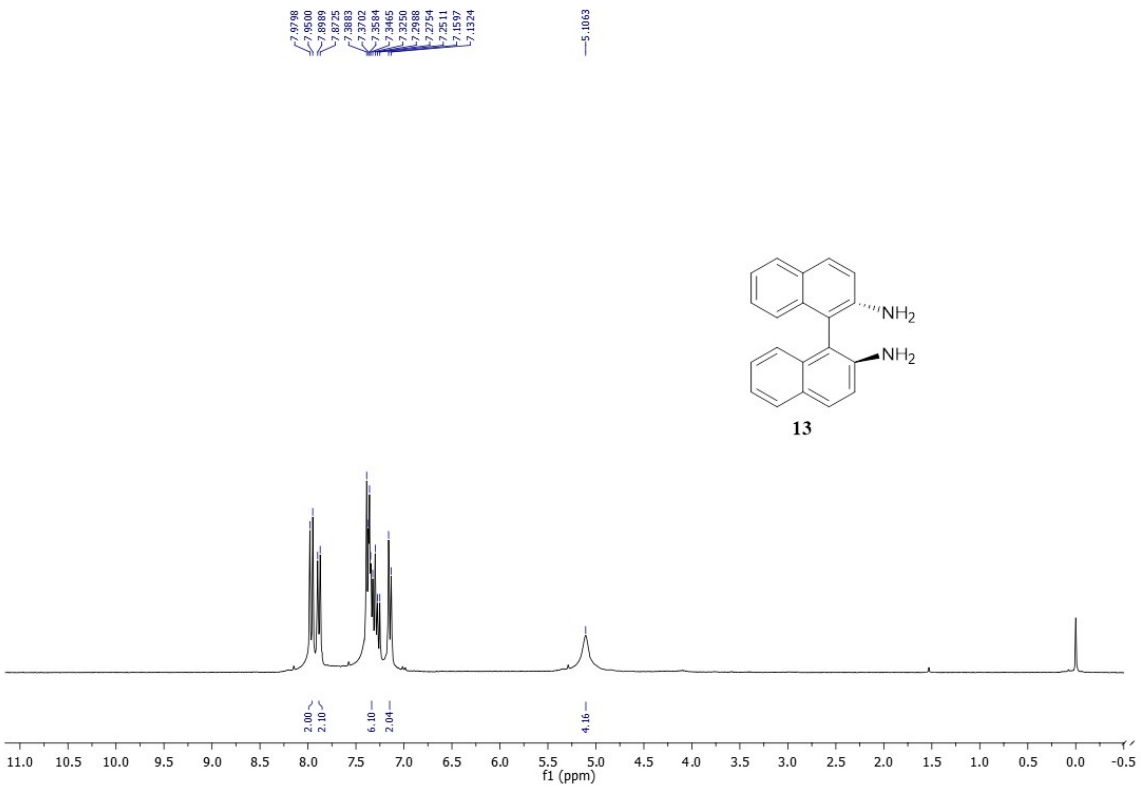


Figure S13: ^{1}H NMR Spectrum of compound **13**.

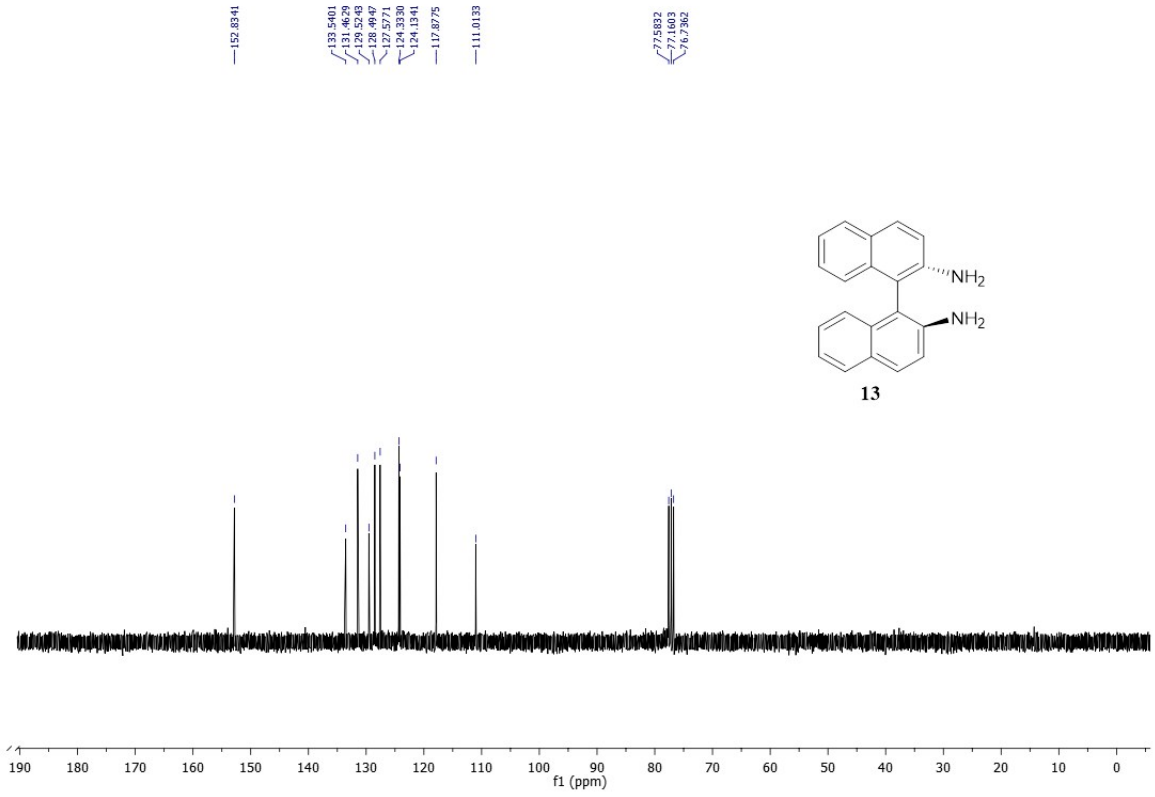


Figure S14: ^{13}C NMR Spectrum of compound **13**.

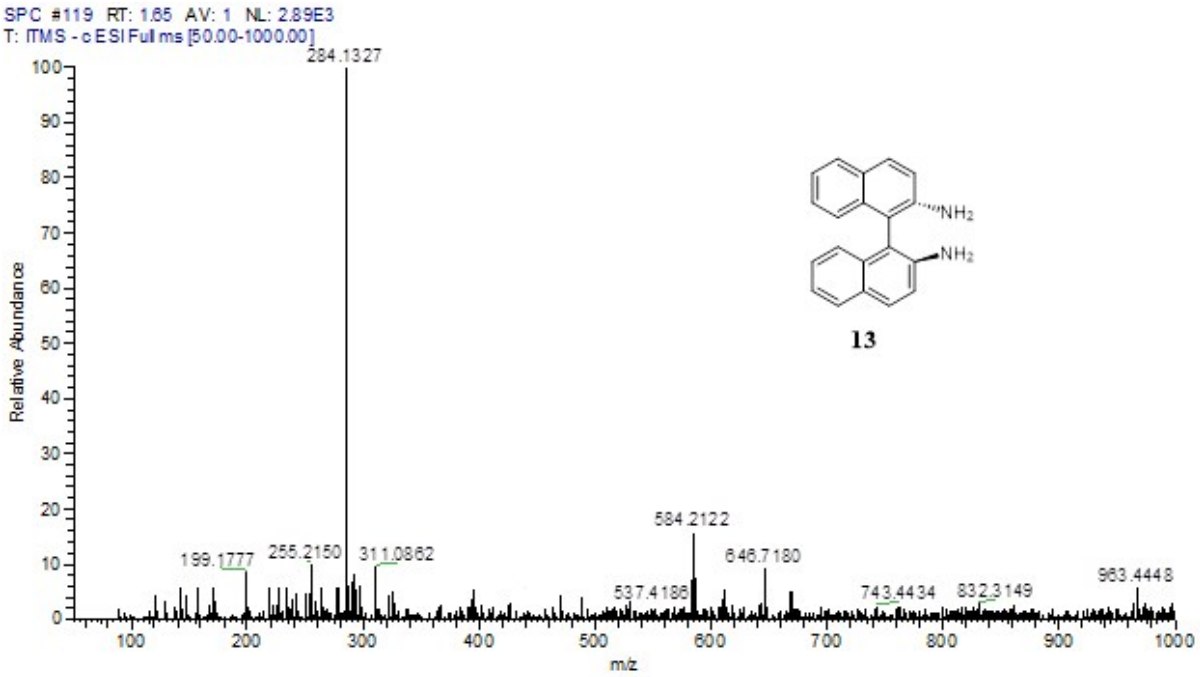


Figure S15: ESI-Mass Spectrum of compound **13**.

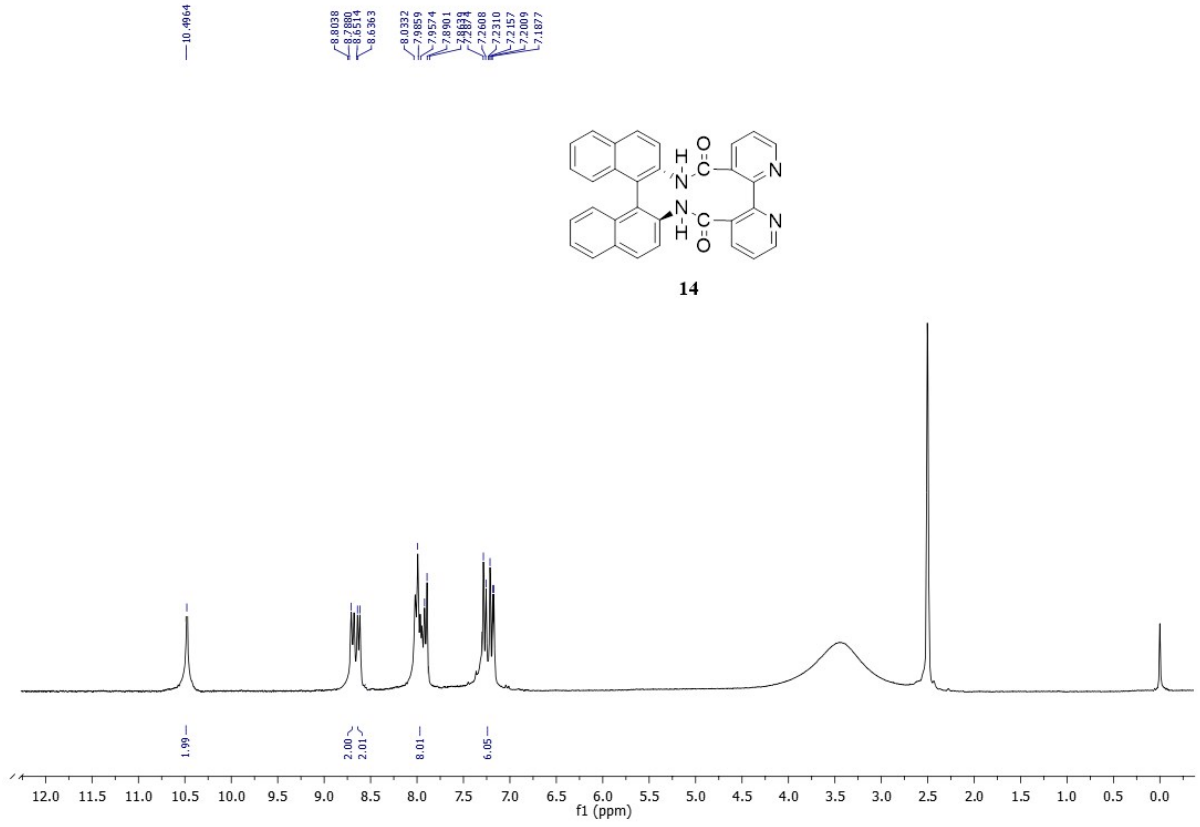


Figure S16: ^{1}H NMR Spectrum of organocatalyst **14**.

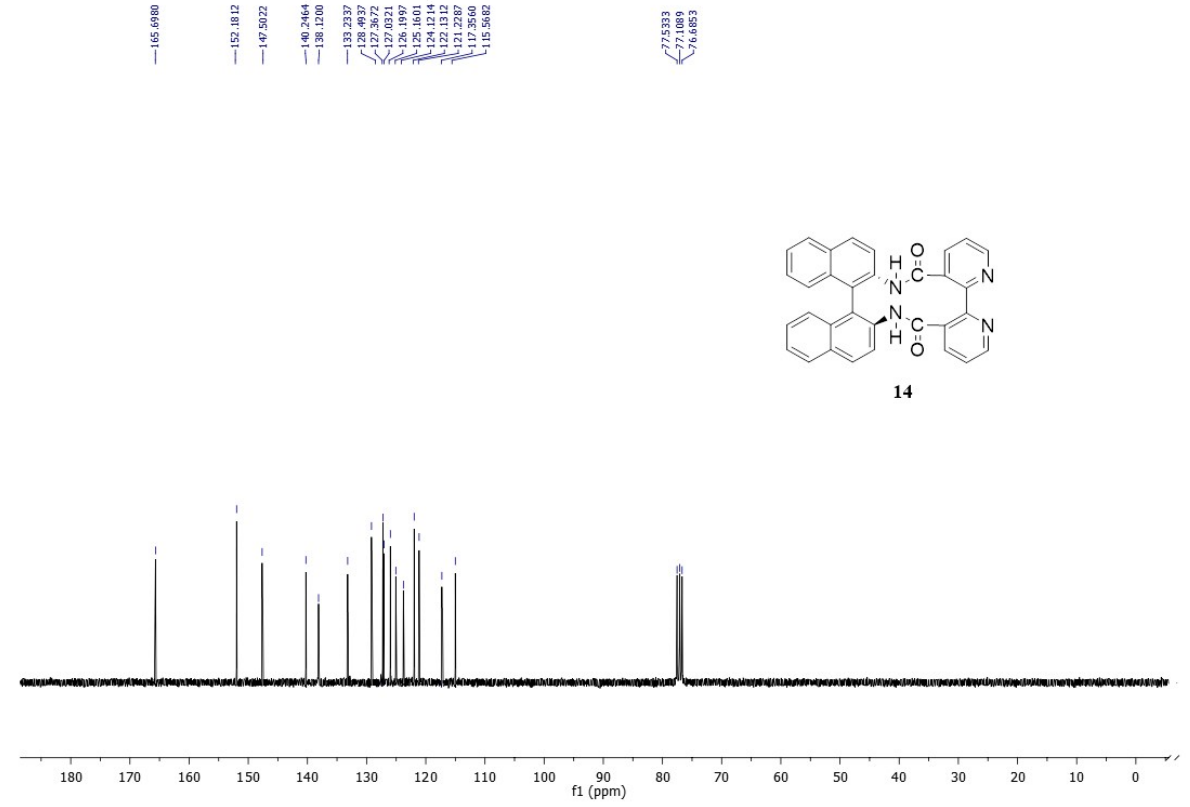


Figure S17: ^{13}C NMR Spectrum of organocatalyst **14**.

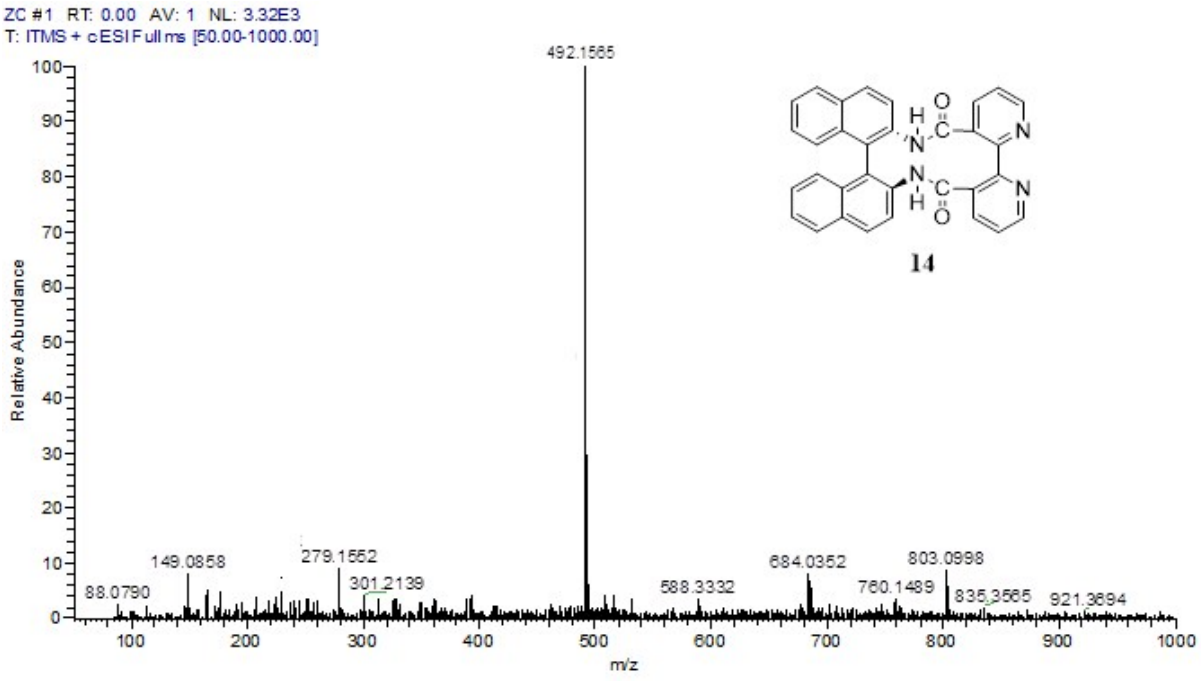


Figure S18: ESI-Mass Spectrum organocatalyst **14**.

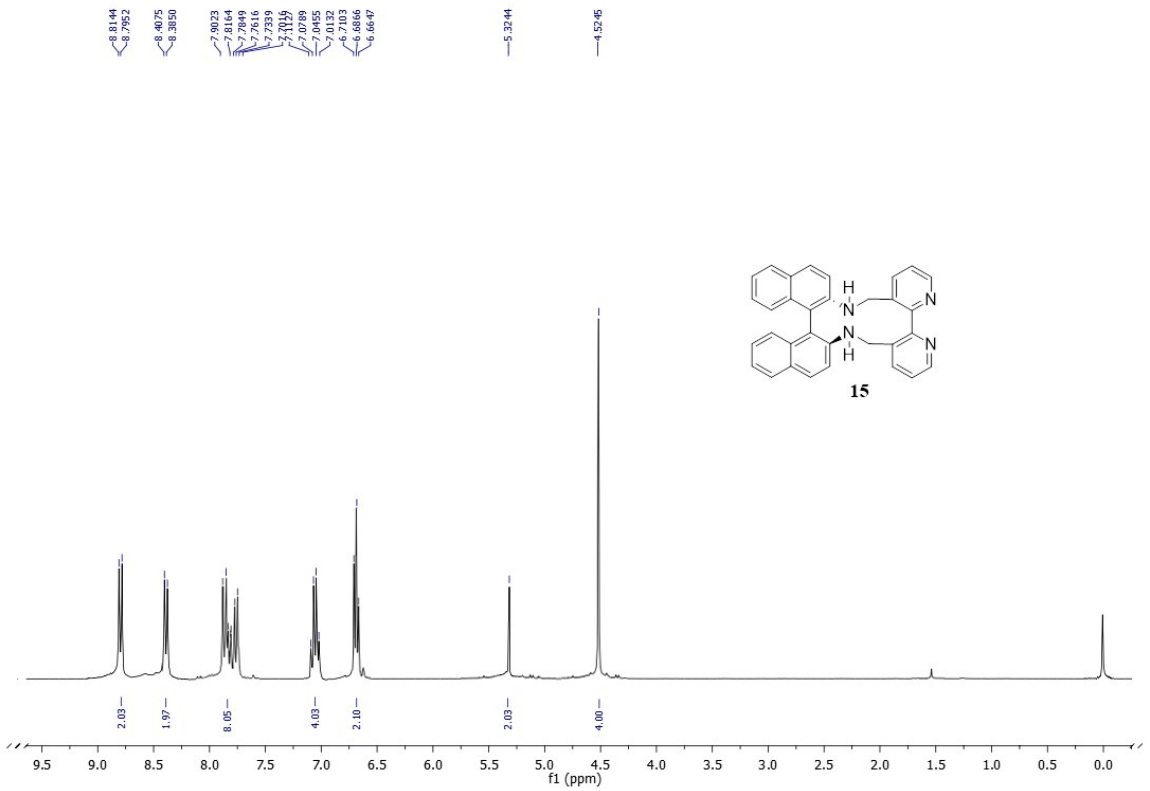


Figure S19: ^{1}H NMR Spectrum of organocatalyst **15**.

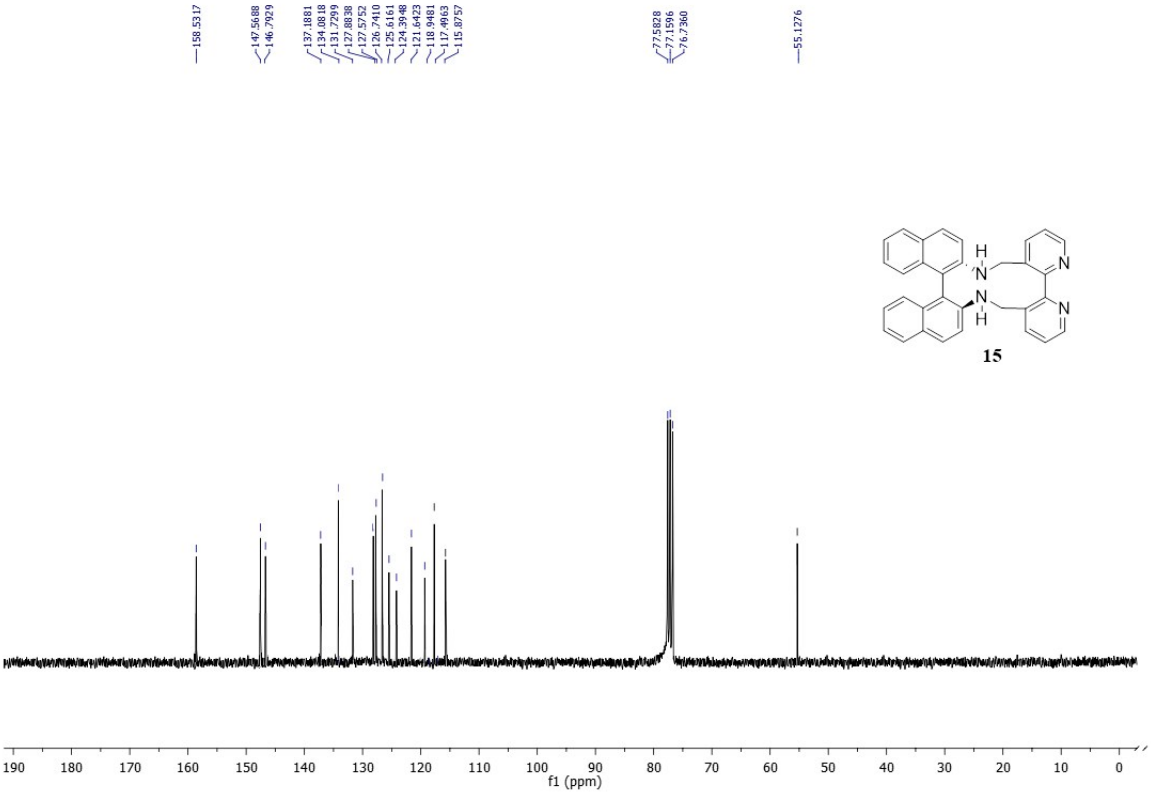


Figure S20: ^{13}C NMR Spectrum of organocatalyst **15**.

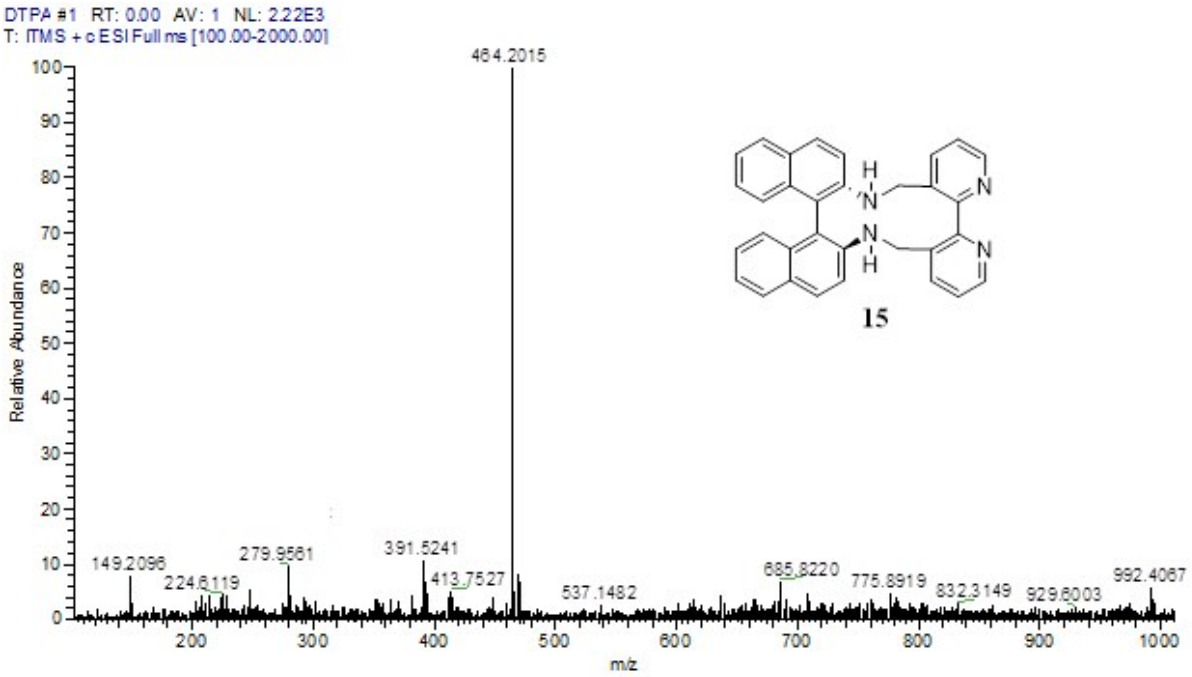


Figure S21: ESI-Mass Spectrum organocatalyst **15**.

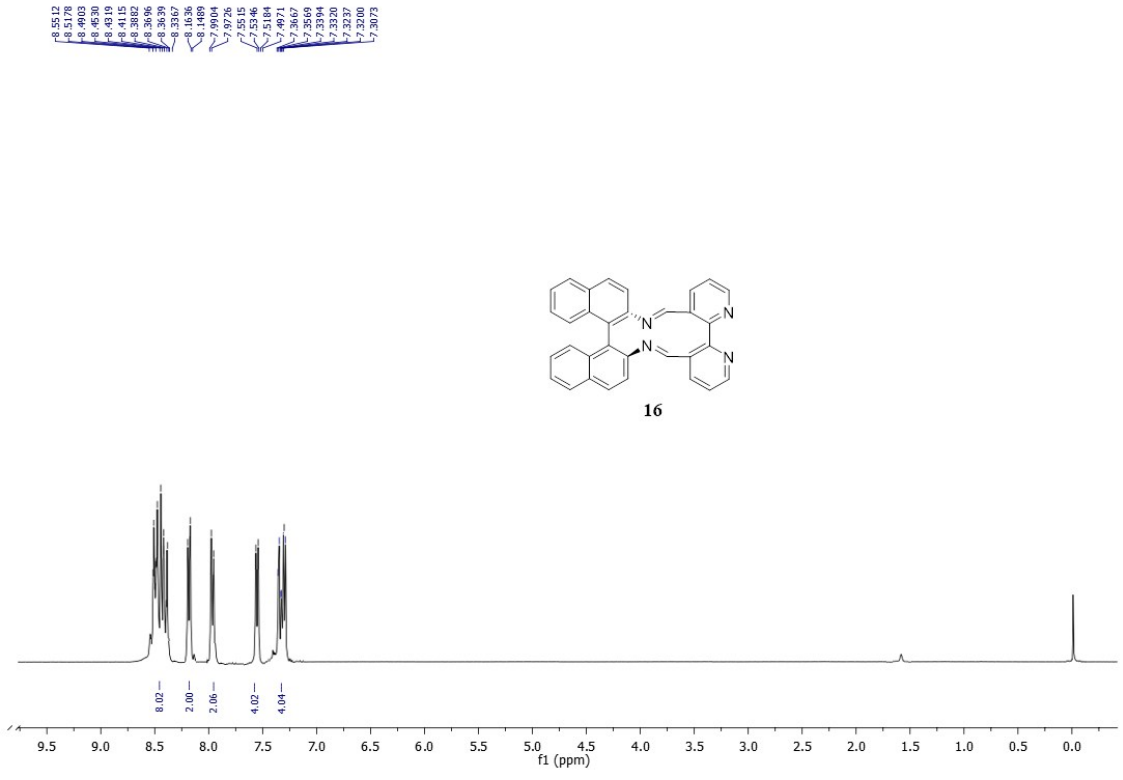


Figure S22: ^{1}H NMR Spectrum of organocatalyst **16**.

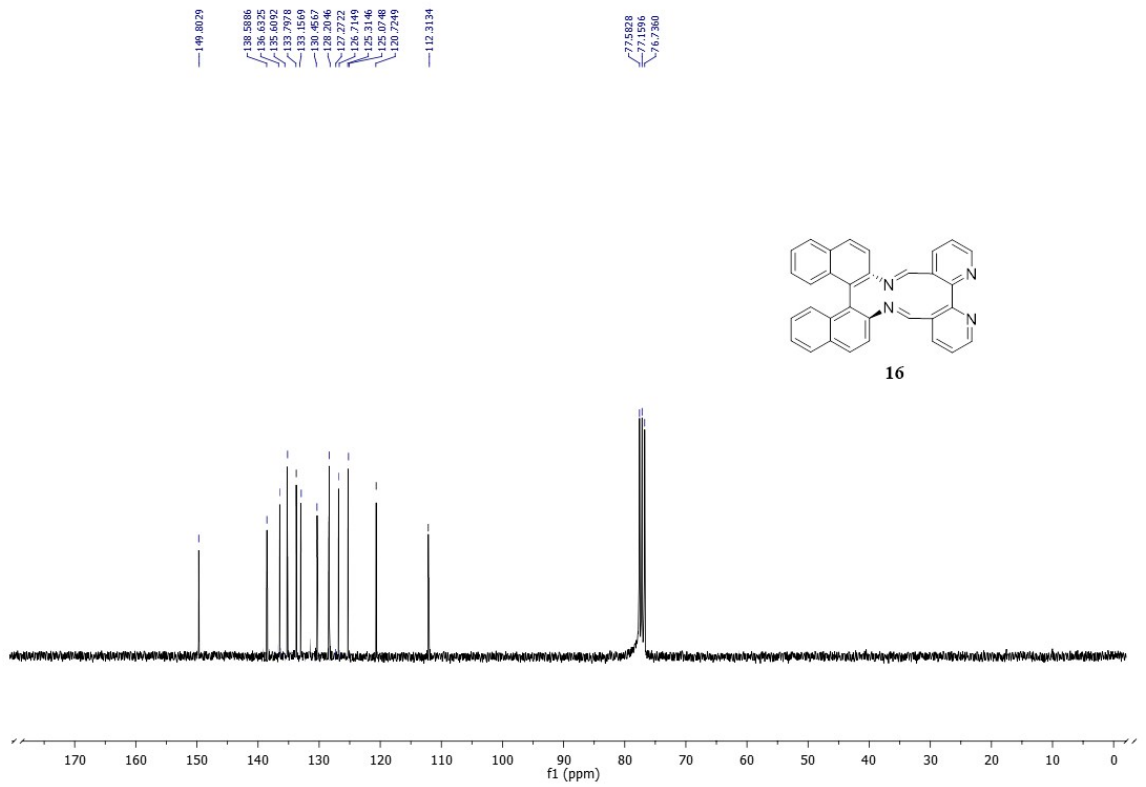


Figure S23: ^{13}C NMR Spectrum of organocatalyst **16**.

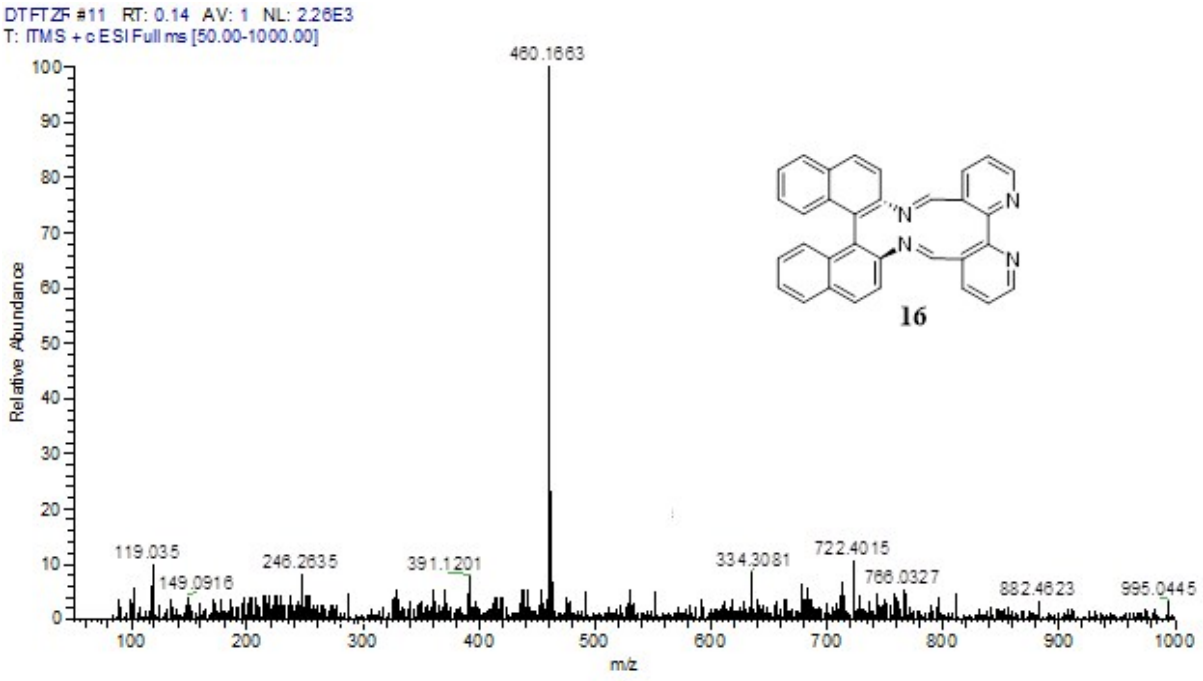


Figure S24: ESI-Mass Spectrum organocatalyst **16**.

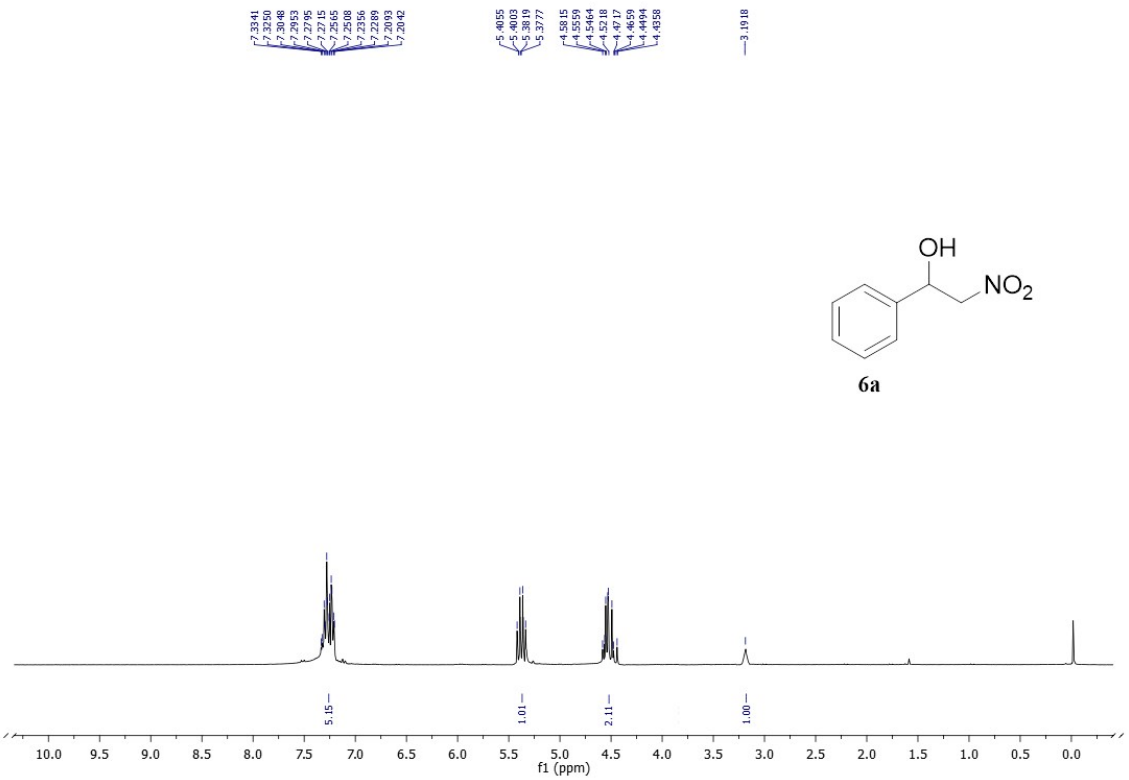


Figure S25: ^{1}H NMR Spectrum of Henry product **6a**.

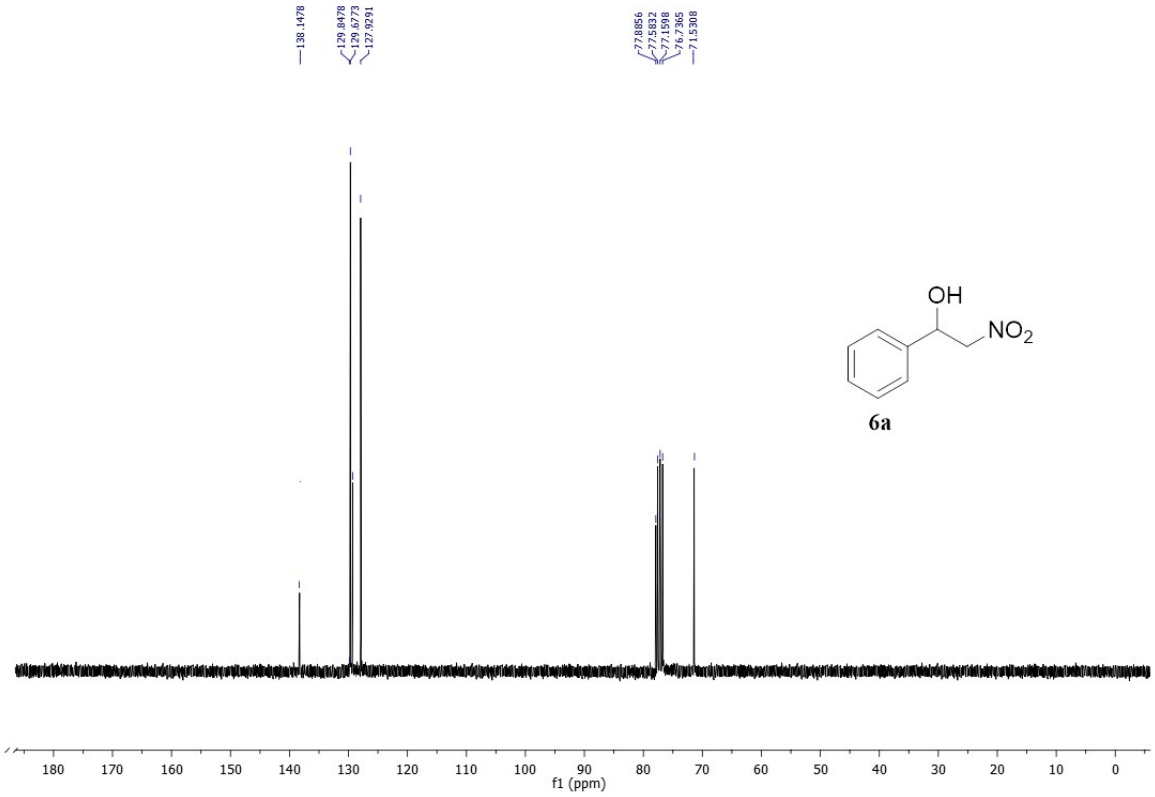


Figure S26: ^{13}C NMR Spectrum of Henry product **6a**.

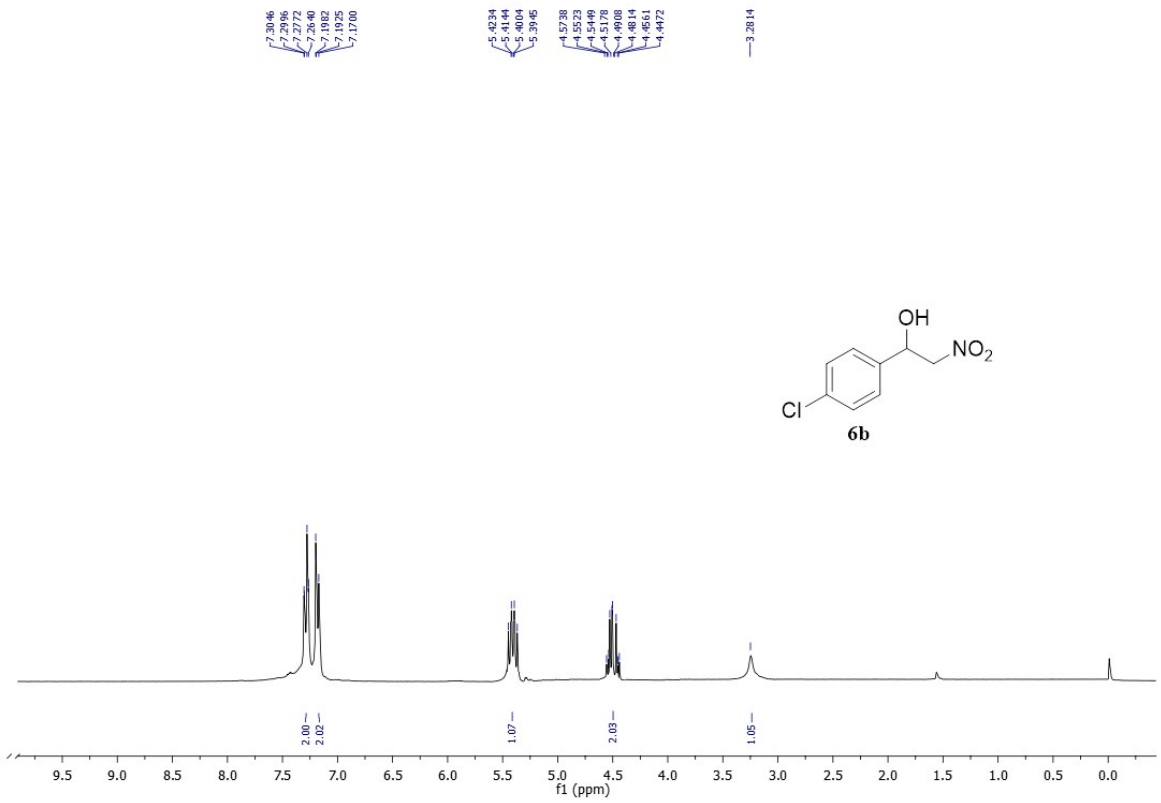


Figure S27: ^{1}H NMR Spectrum of Henry product **6b**.

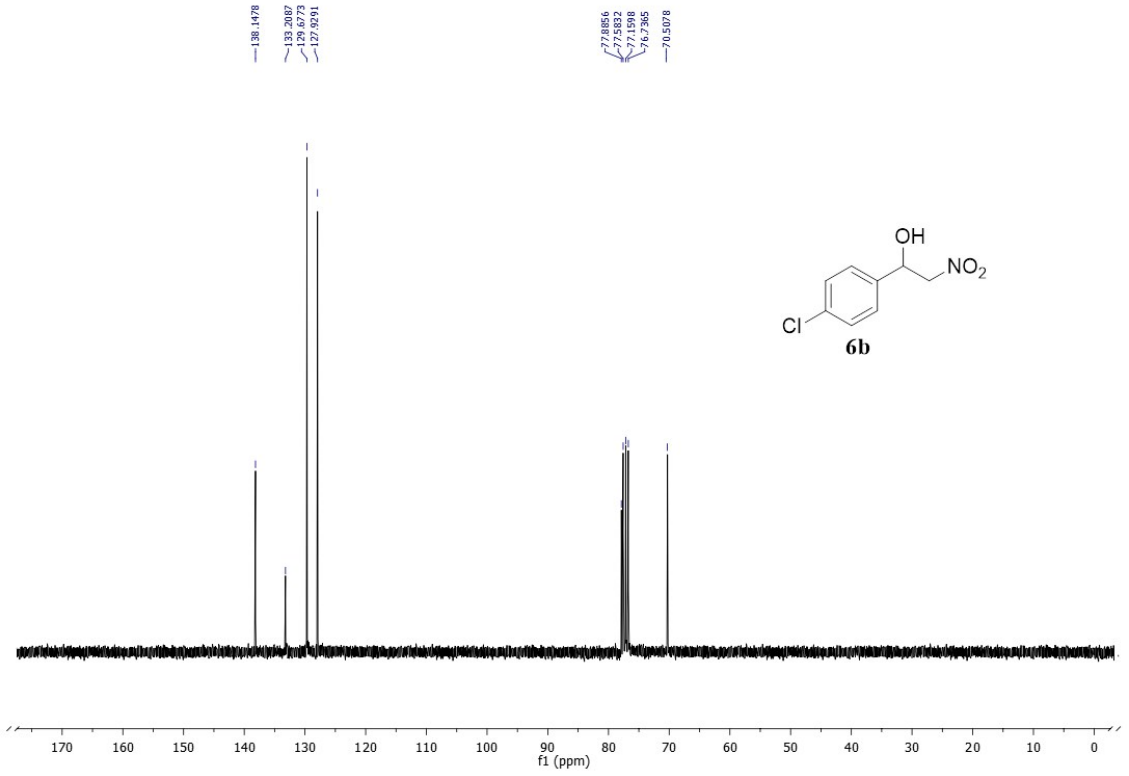


Figure S28: ^{13}C NMR Spectrum of Henry product **6b**.

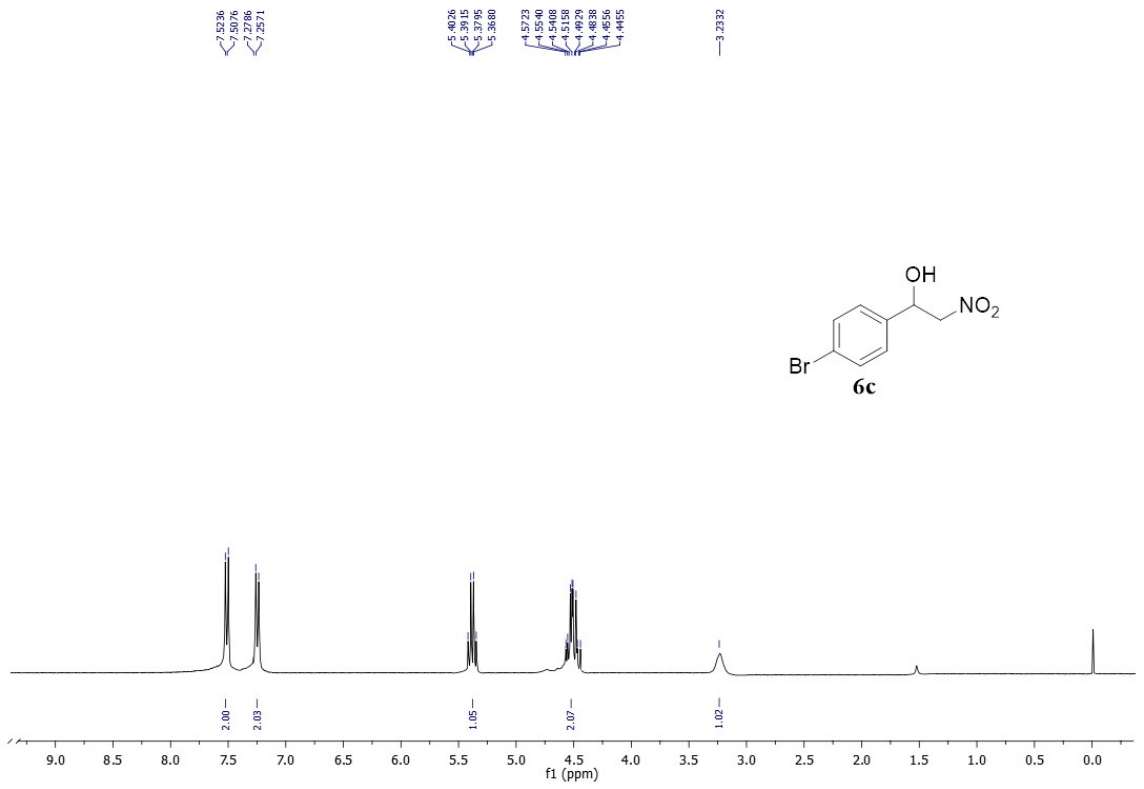


Figure S29: ^{1}H NMR Spectrum of Henry product **6c**.

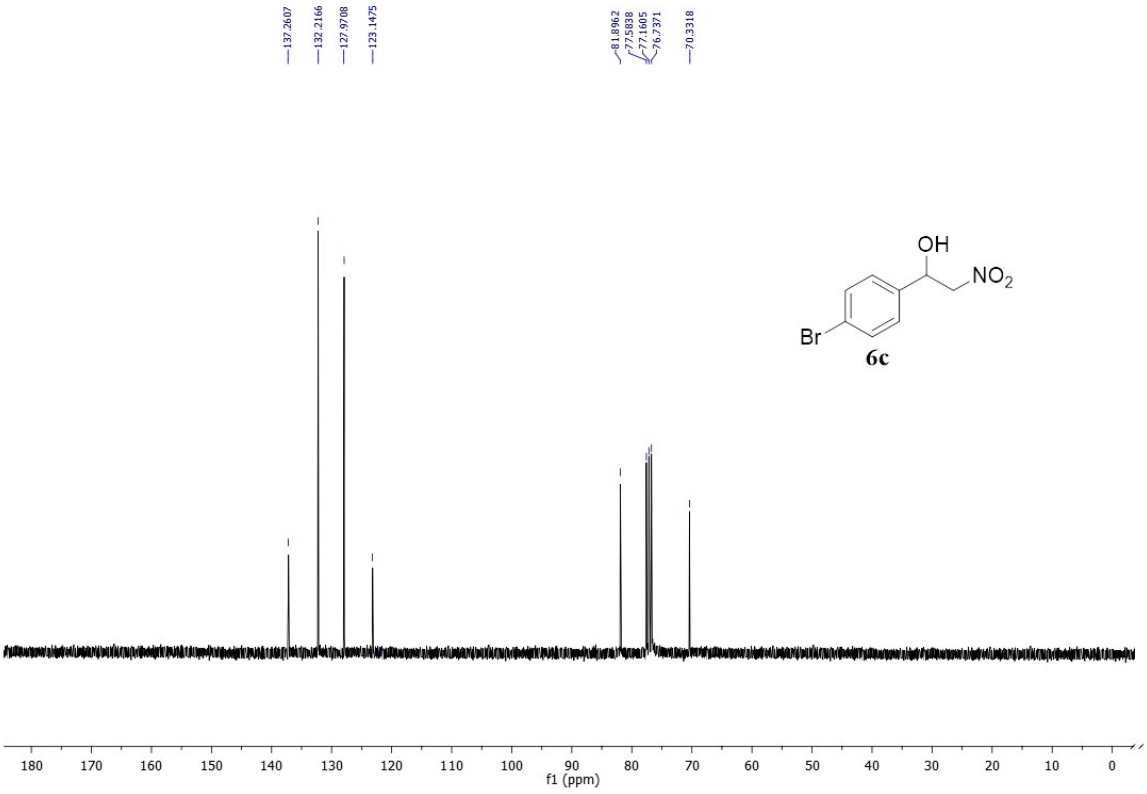


Figure S30: ^{13}C NMR Spectrum of Henry product **6c**.

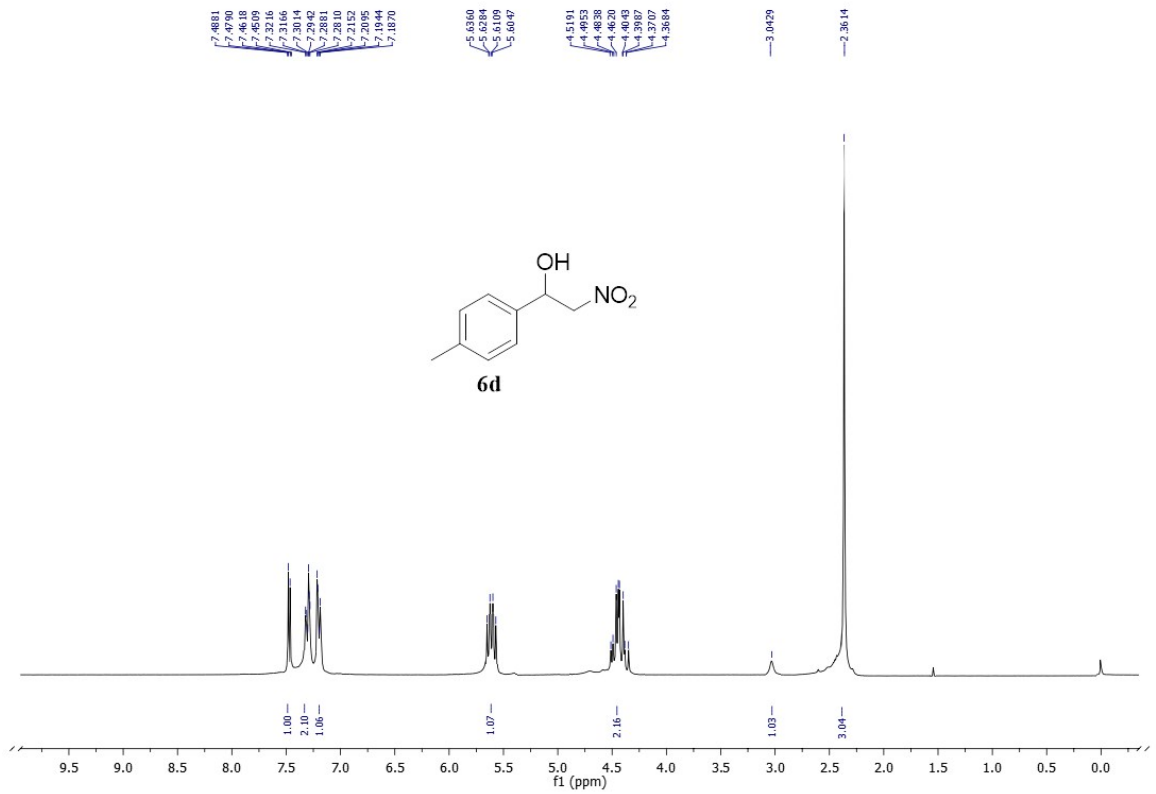


Figure S31: ^{1}H NMR Spectrum of Henry product **6d**.

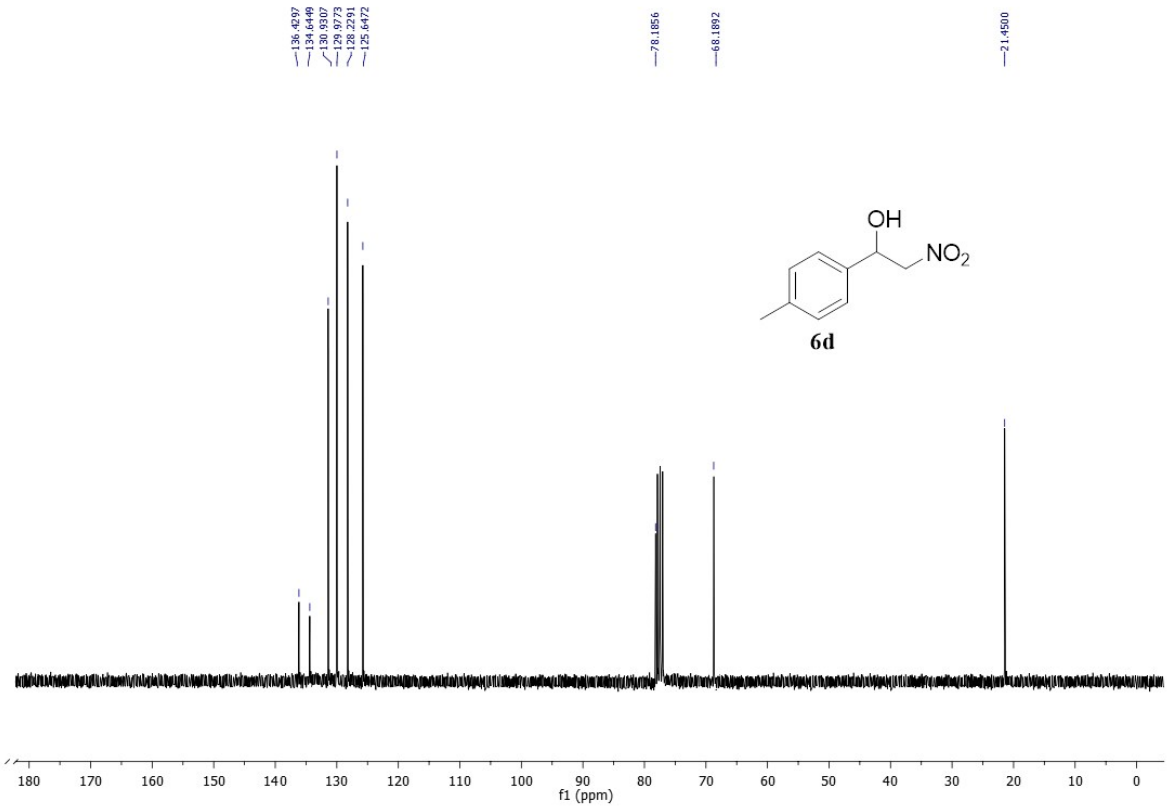


Figure S32: ^{13}C NMR Spectrum of Henry product **6d**.

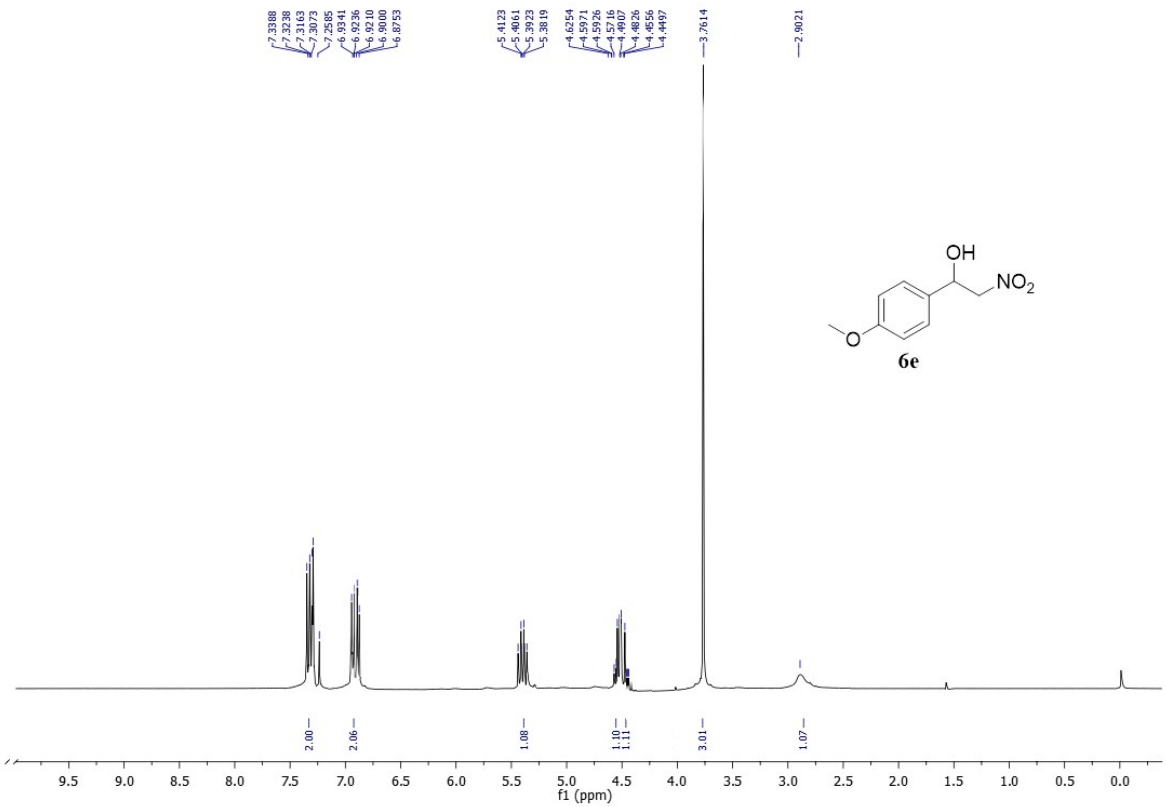


Figure S33: ^{1}H NMR Spectrum of Henry product **6e**.

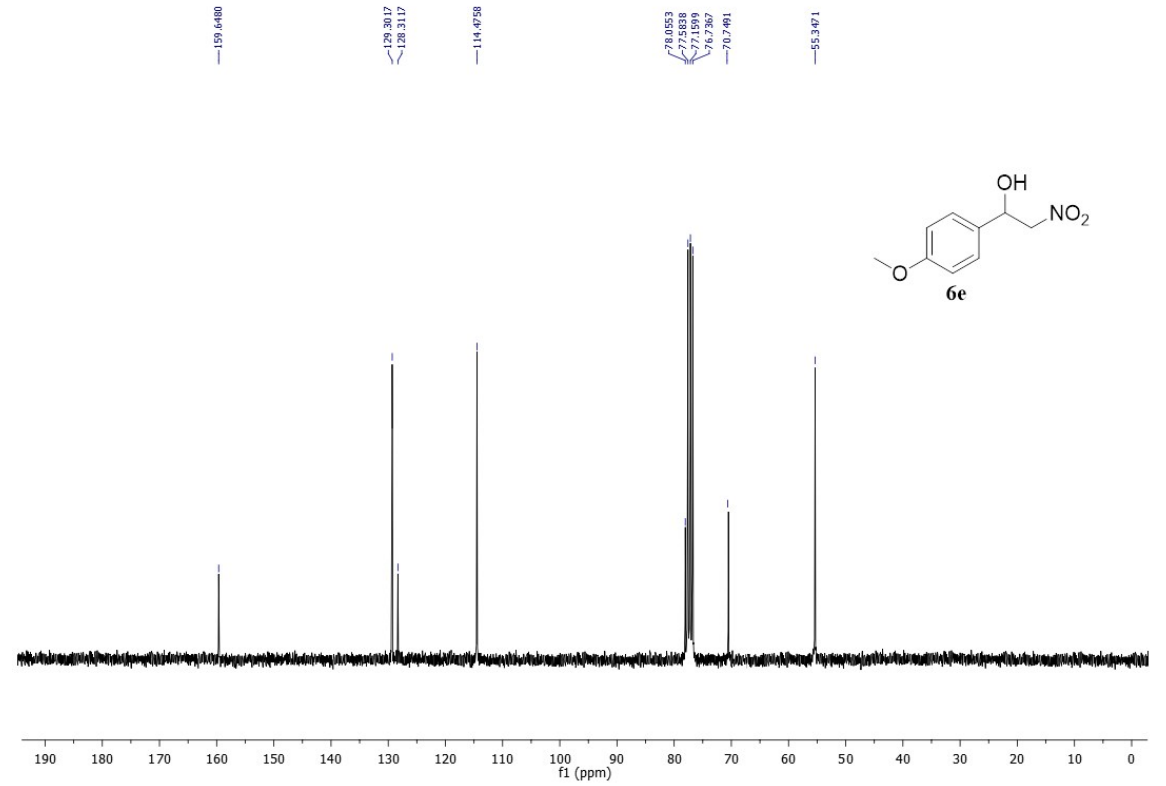


Figure S34: ^{13}C NMR Spectrum of Henry product **6e**.

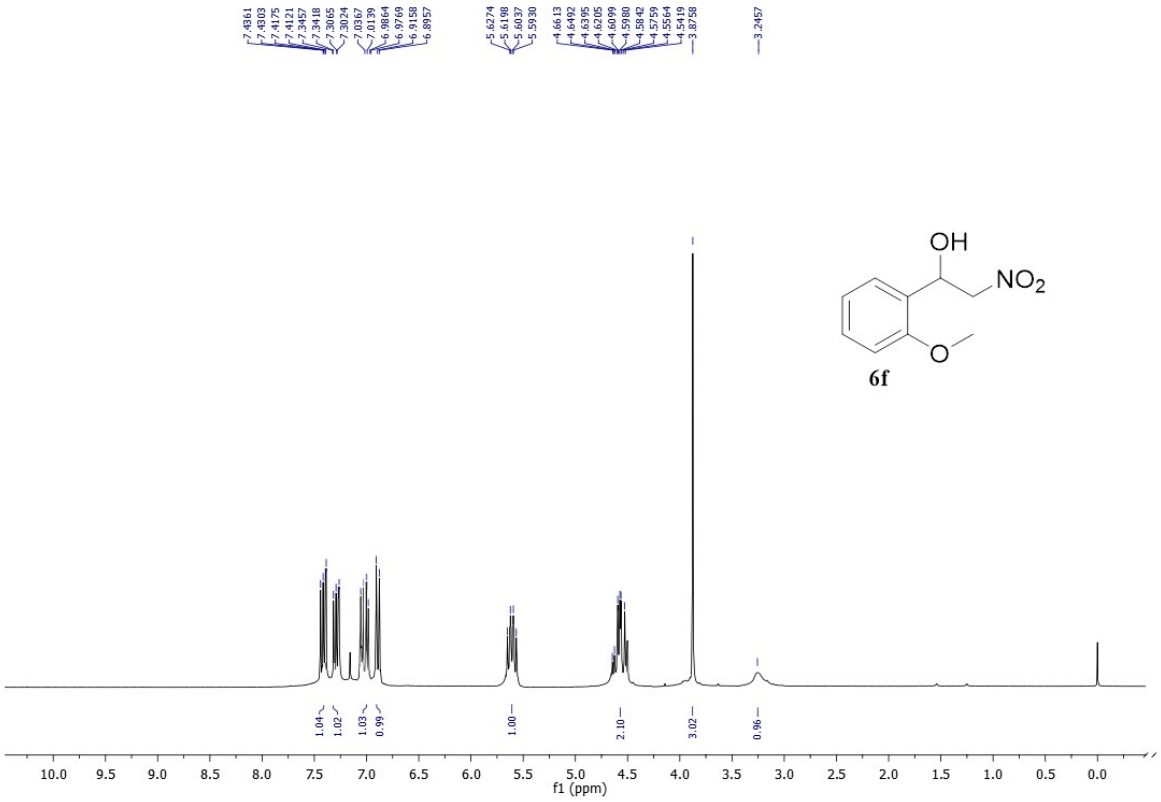


Figure S35: ^{1}H NMR Spectrum of Henry product **6f**.

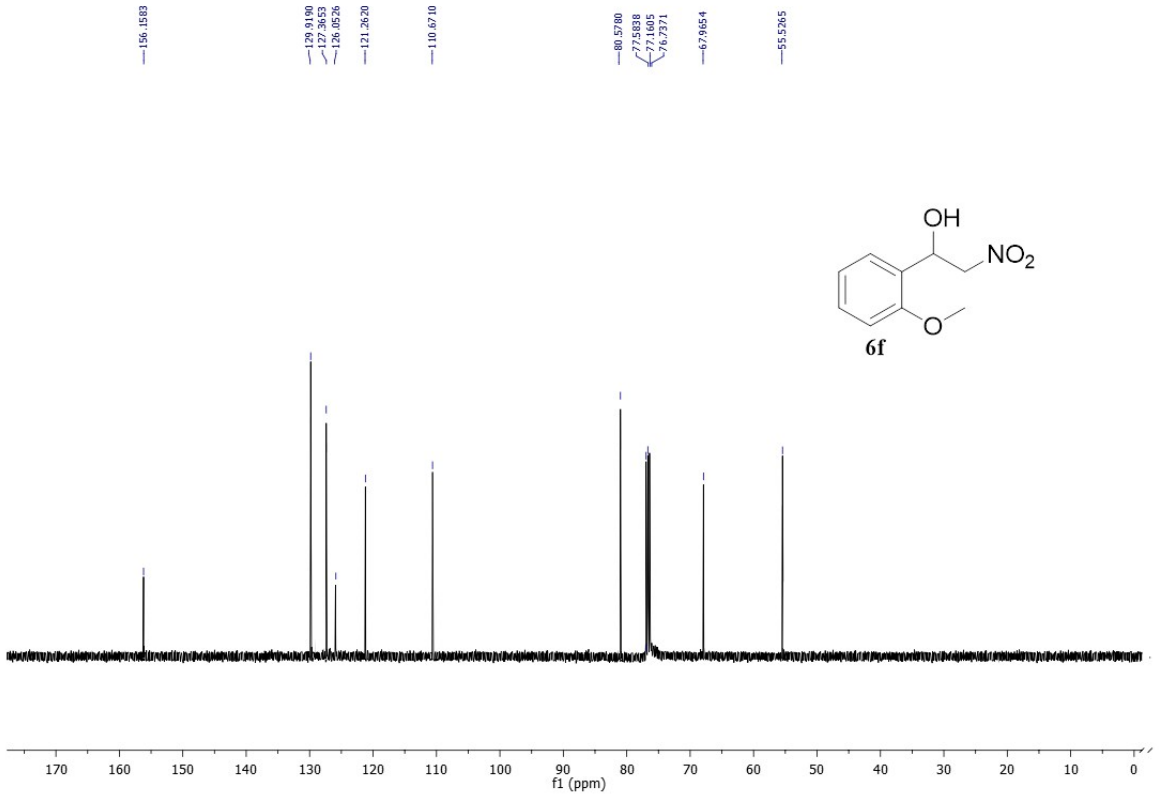


Figure S36: ^{13}C NMR Spectrum of Henry product **6f**.

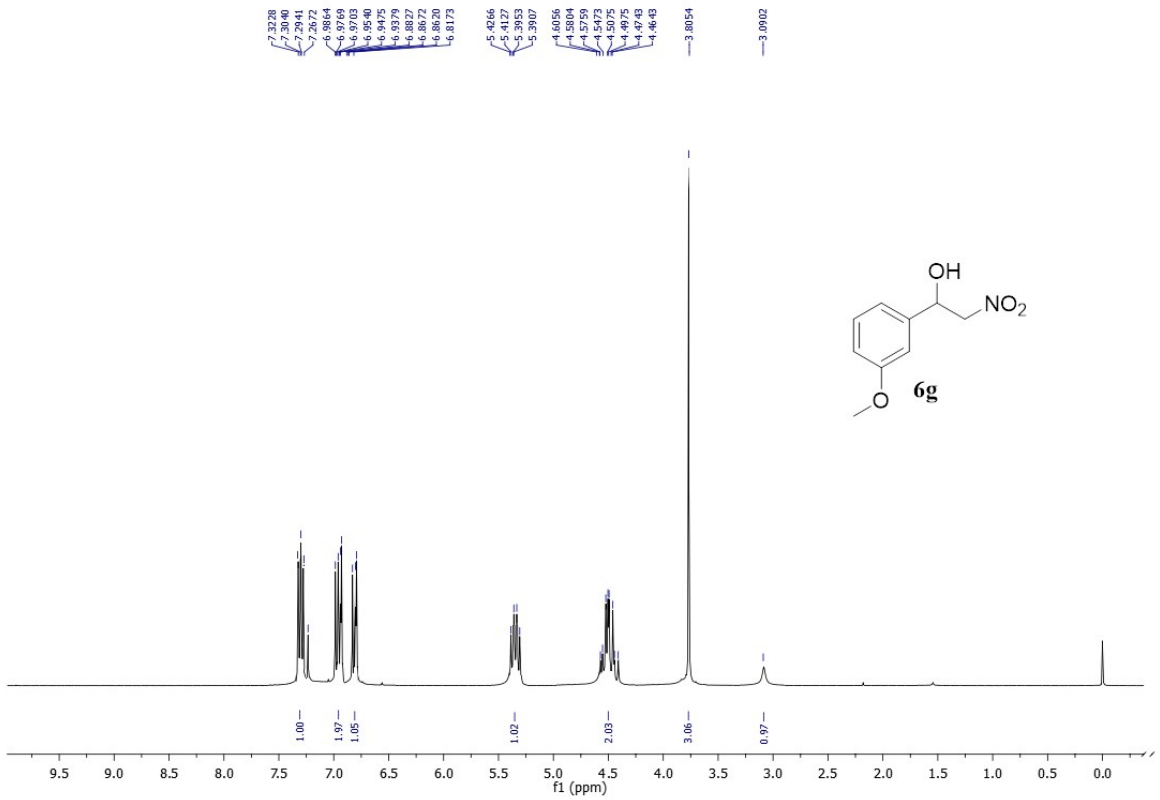


Figure S37: ^{1}H NMR Spectrum of Henry product **6g**.

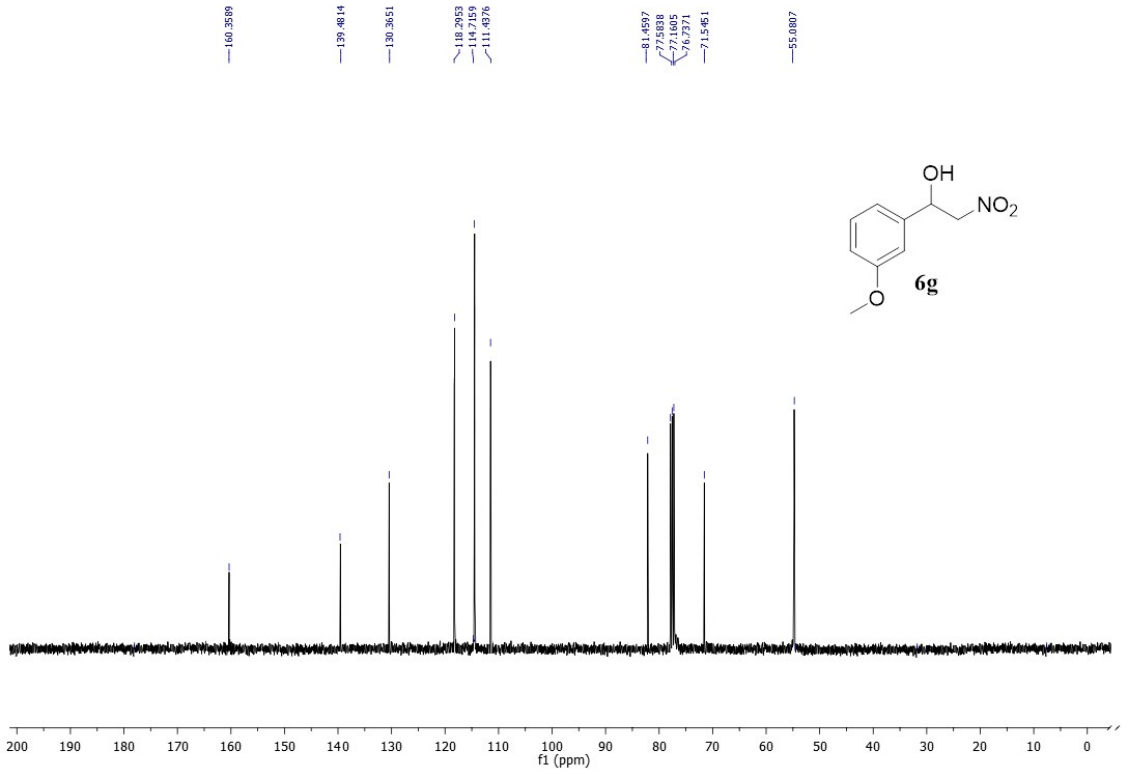


Figure S38: ^{13}C NMR Spectrum of Henry product **6g**.

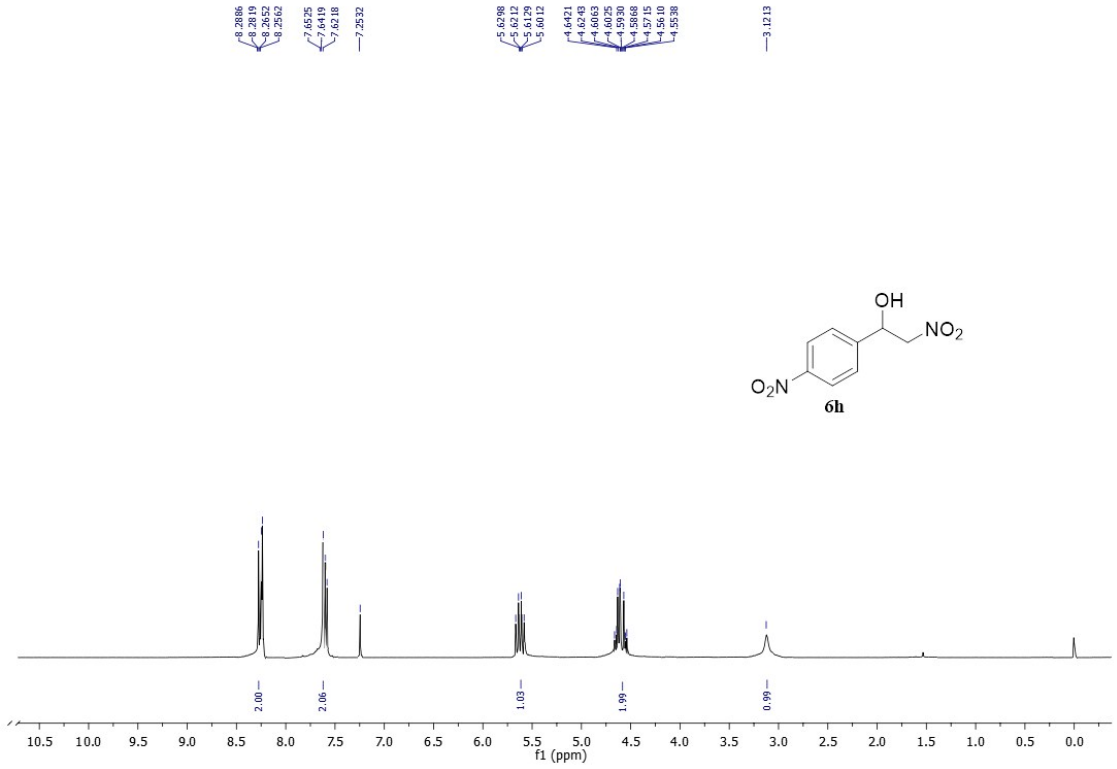


Figure S39: ^{1}H NMR Spectrum of Henry product **6h**.

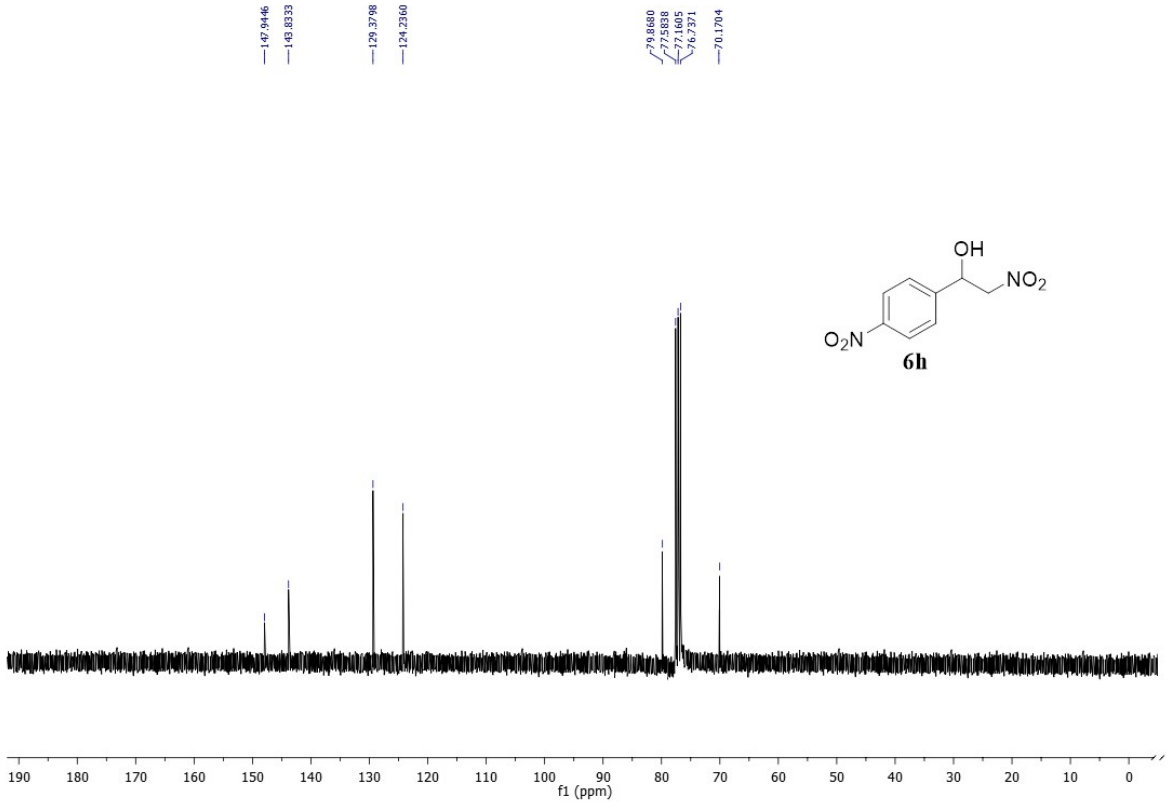


Figure S40: ^{13}C NMR Spectrum of Henry product **6h**.

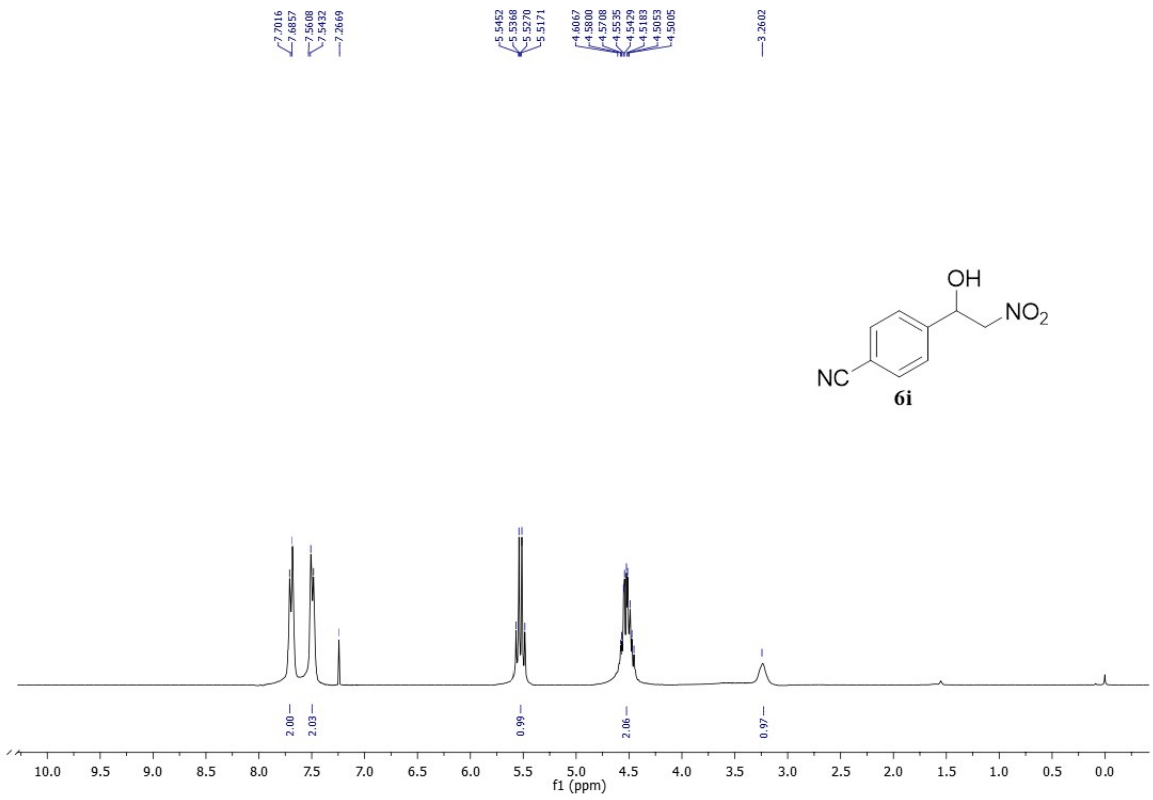


Figure S41: ^{1}H NMR Spectrum of Henry product **6i**.

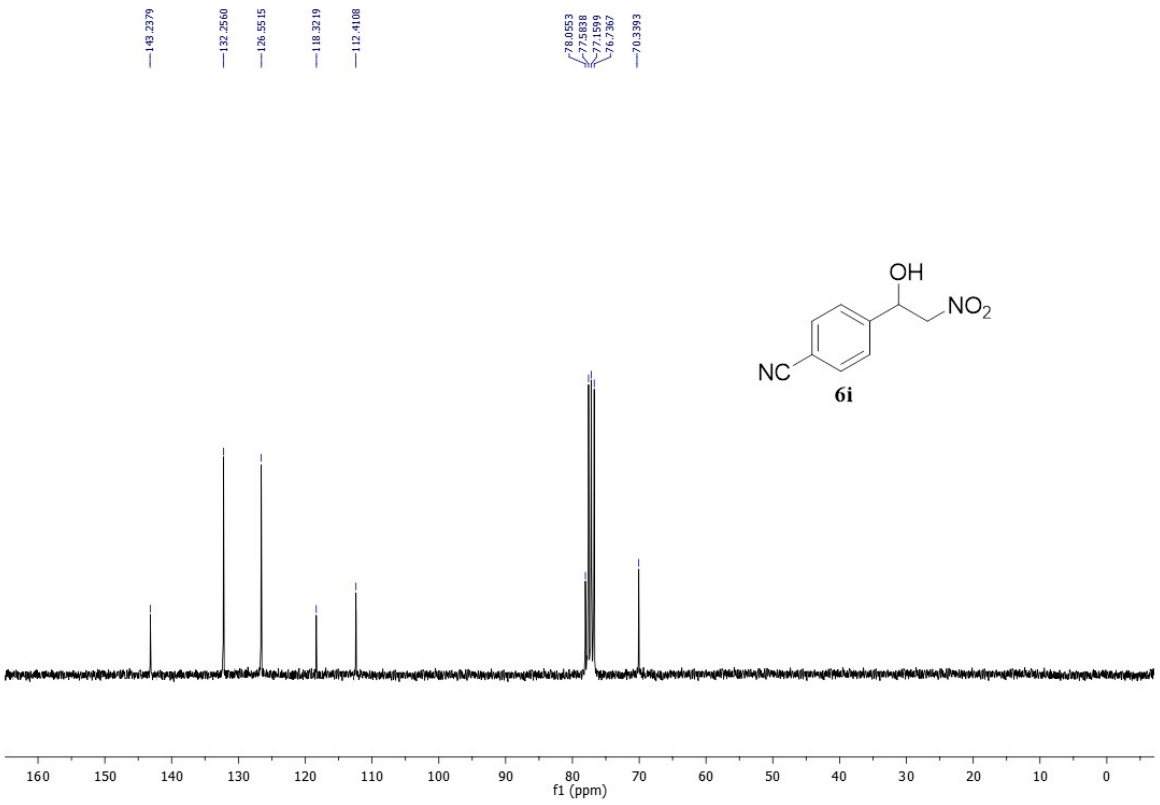


Figure S42: ^{13}C NMR Spectrum of Henry product **6i**.

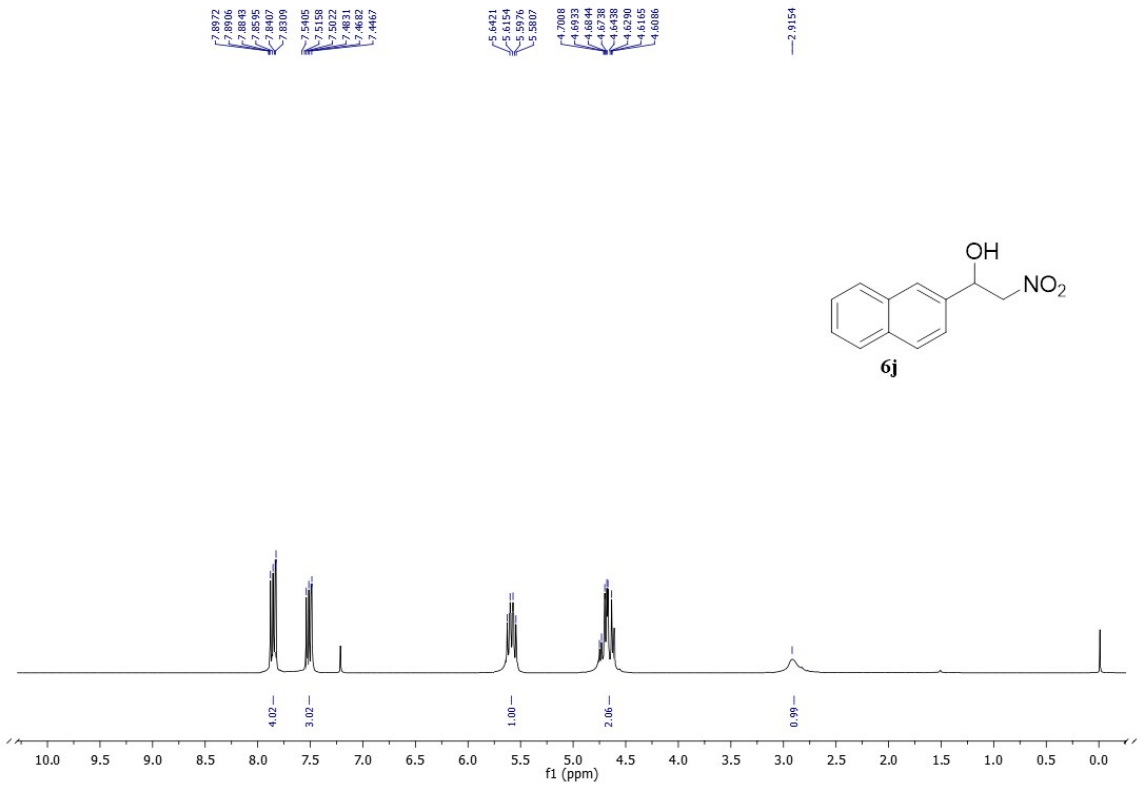


Figure S43: ^{1}H NMR Spectrum of Henry product **6j**.

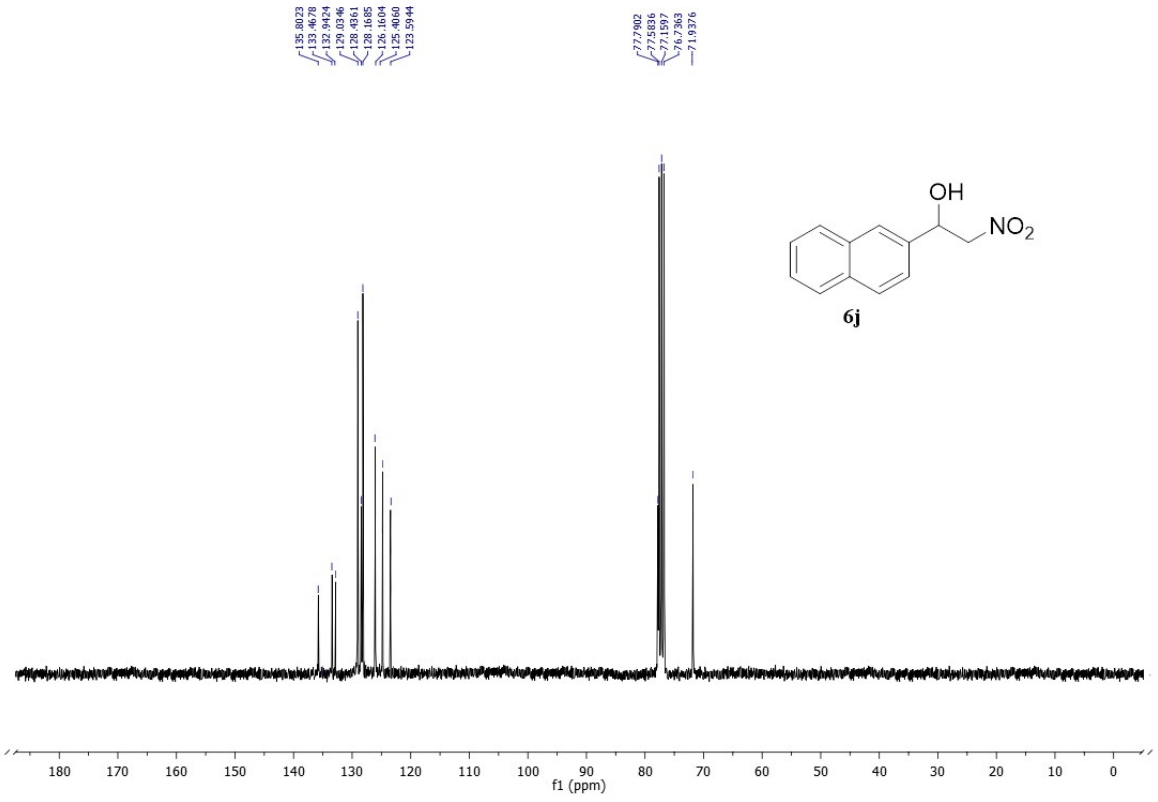


Figure S44: ^{13}C NMR Spectrum of Henry product **6j**.

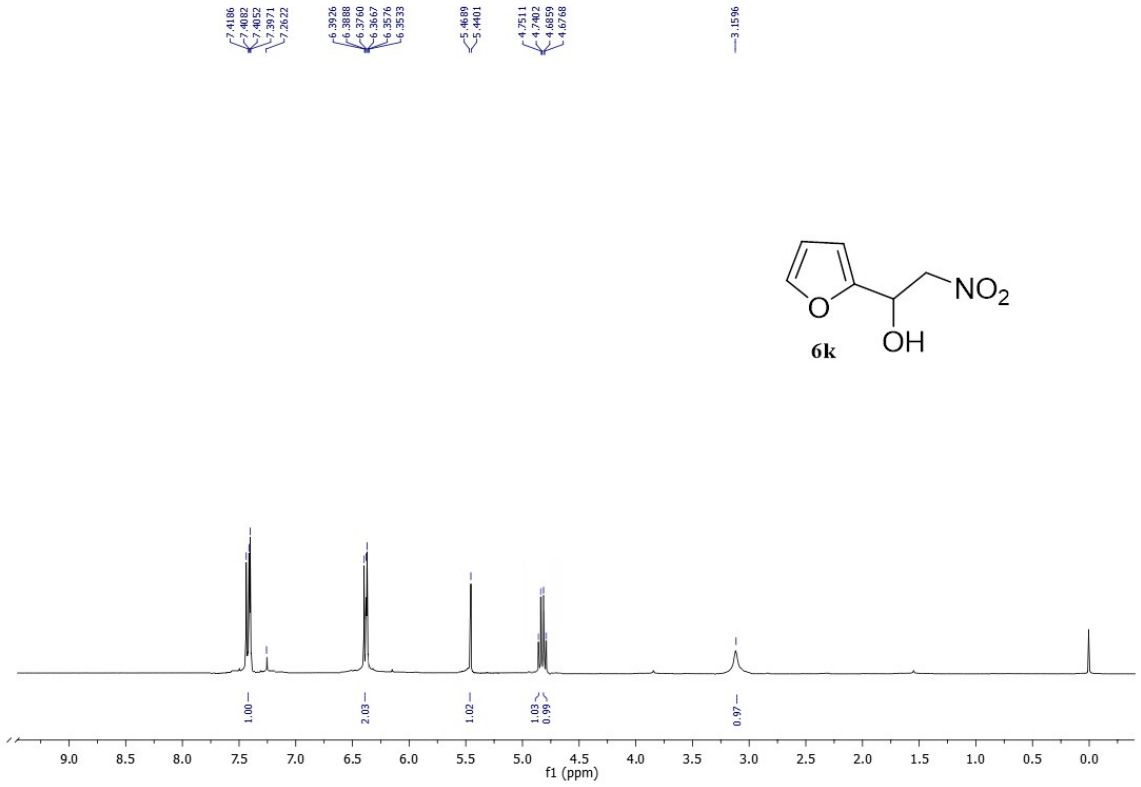


Figure S45: [1]H NMR Spectrum of Henry product **6k**.

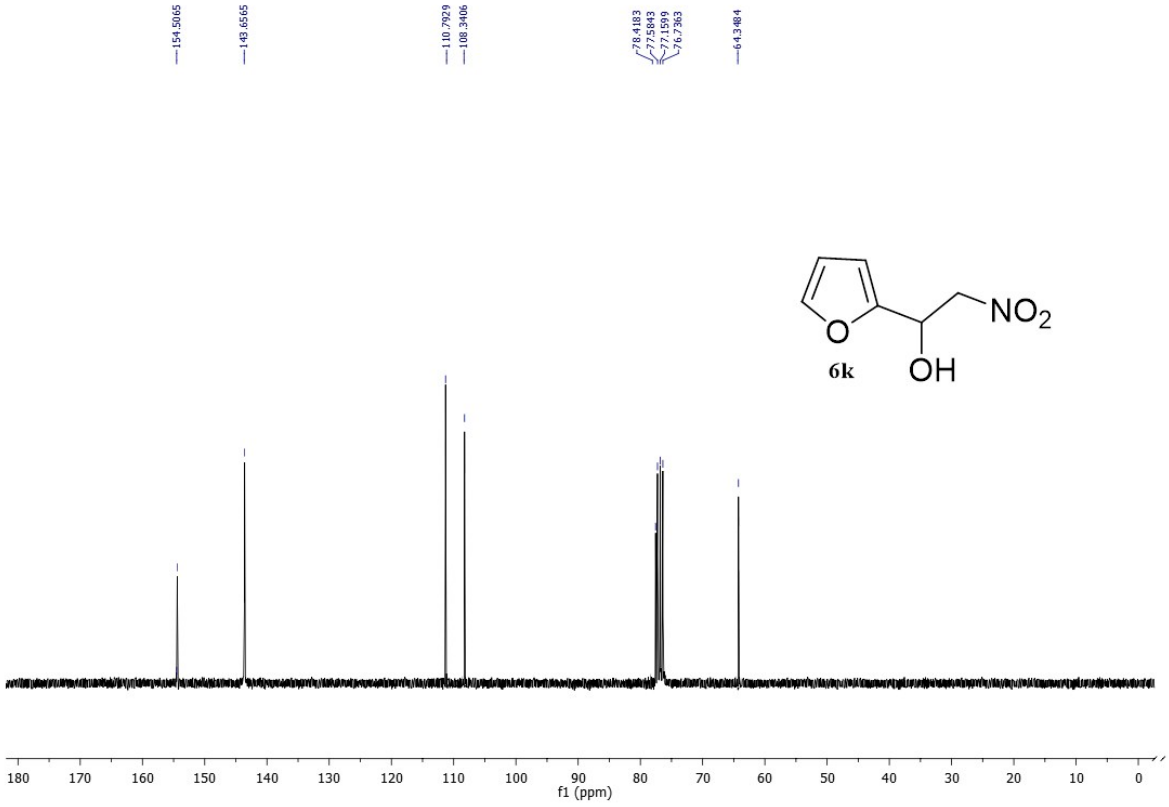


Figure S46: [13]C NMR Spectrum of Henry product **6k**.

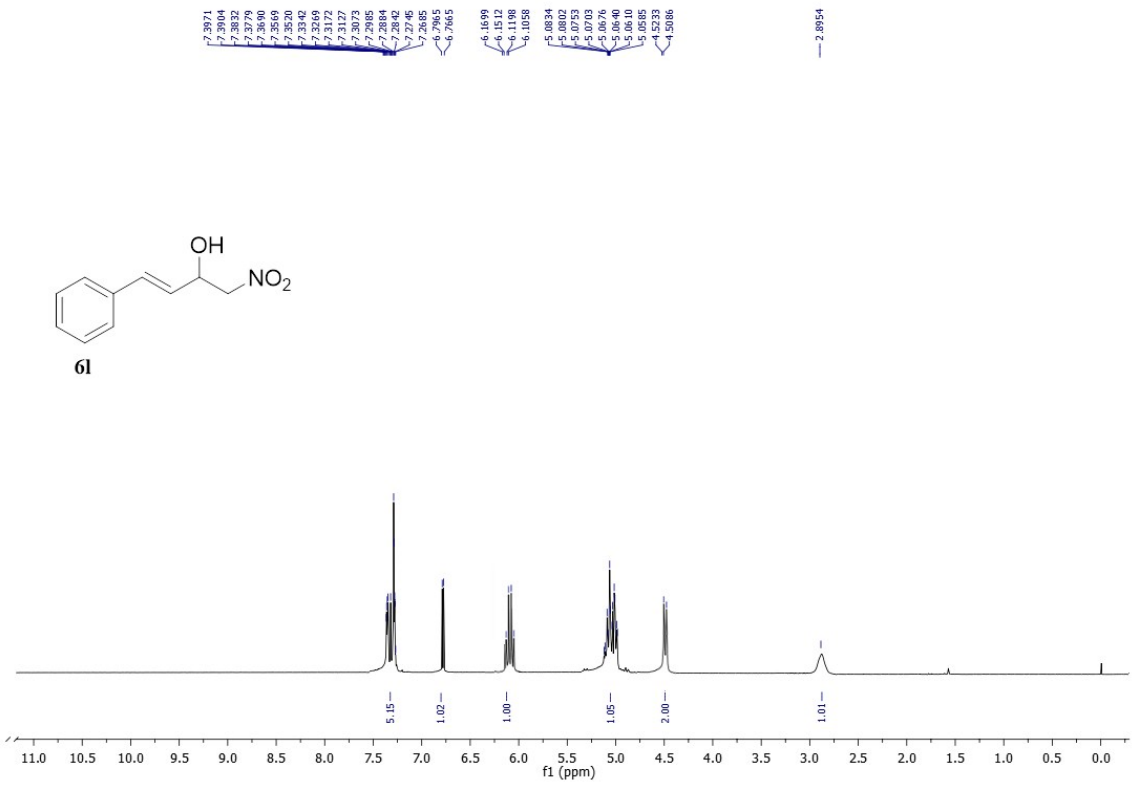


Figure S47: ^{1}H NMR Spectrum of Henry product **6l**.

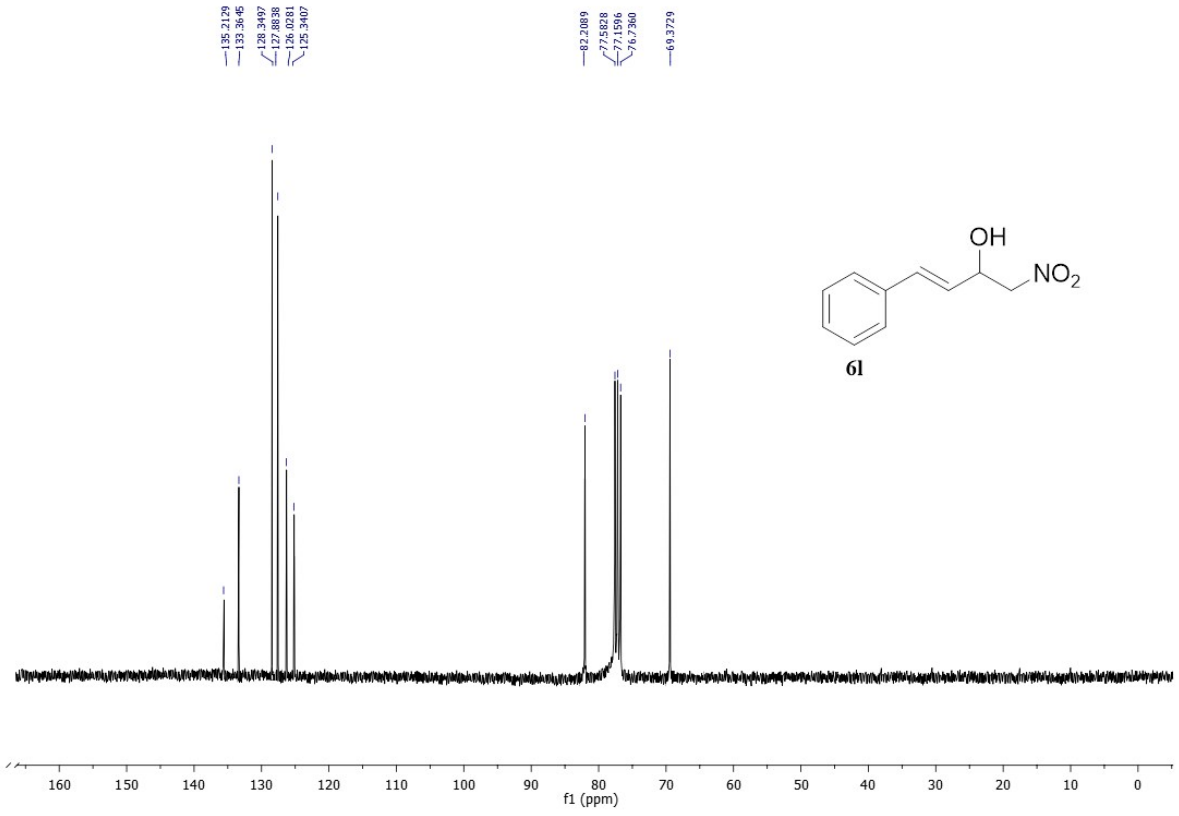


Figure S48: ^{13}C NMR Spectrum of Henry product **6l**.

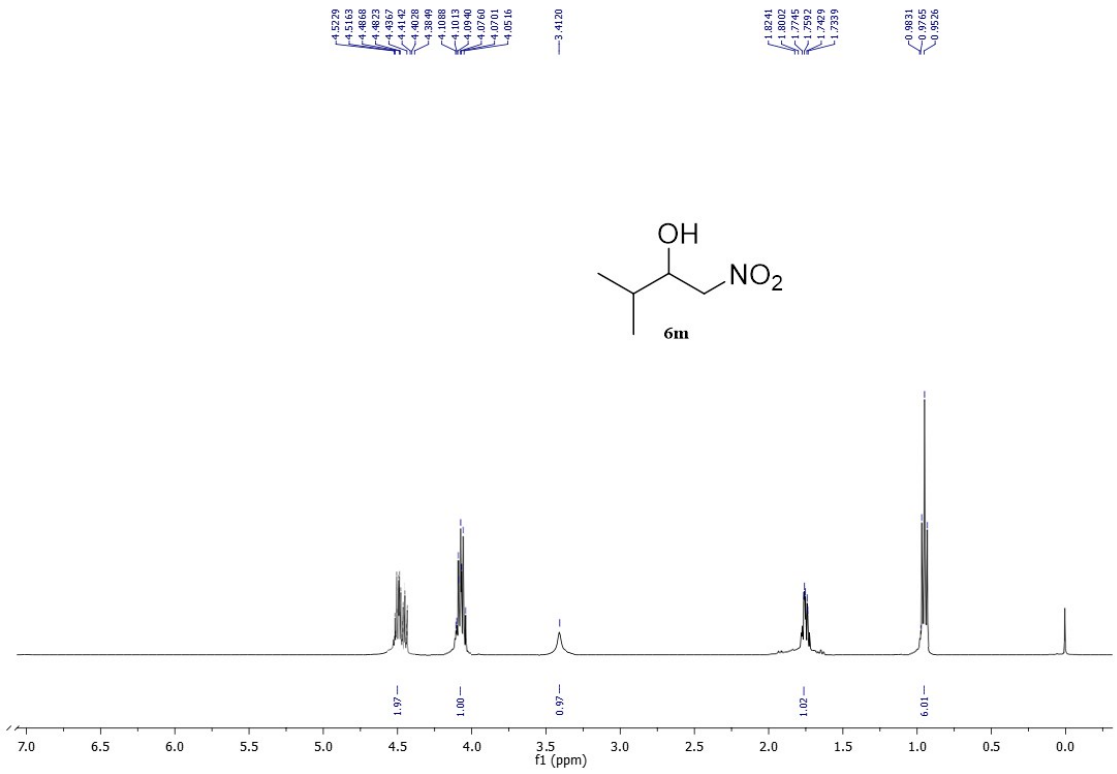


Figure S49: ^{1}H NMR Spectrum of Henry product **6m**.

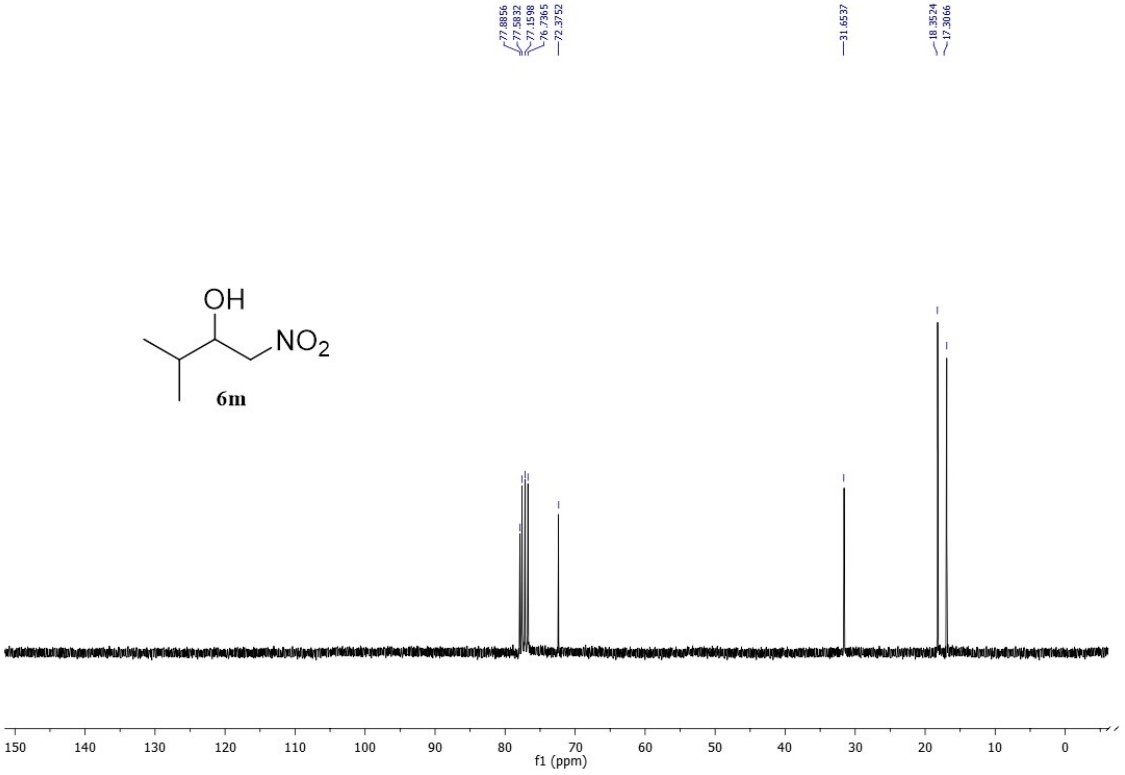


Figure S50: ^{13}C NMR Spectrum of Henry product **6m**.

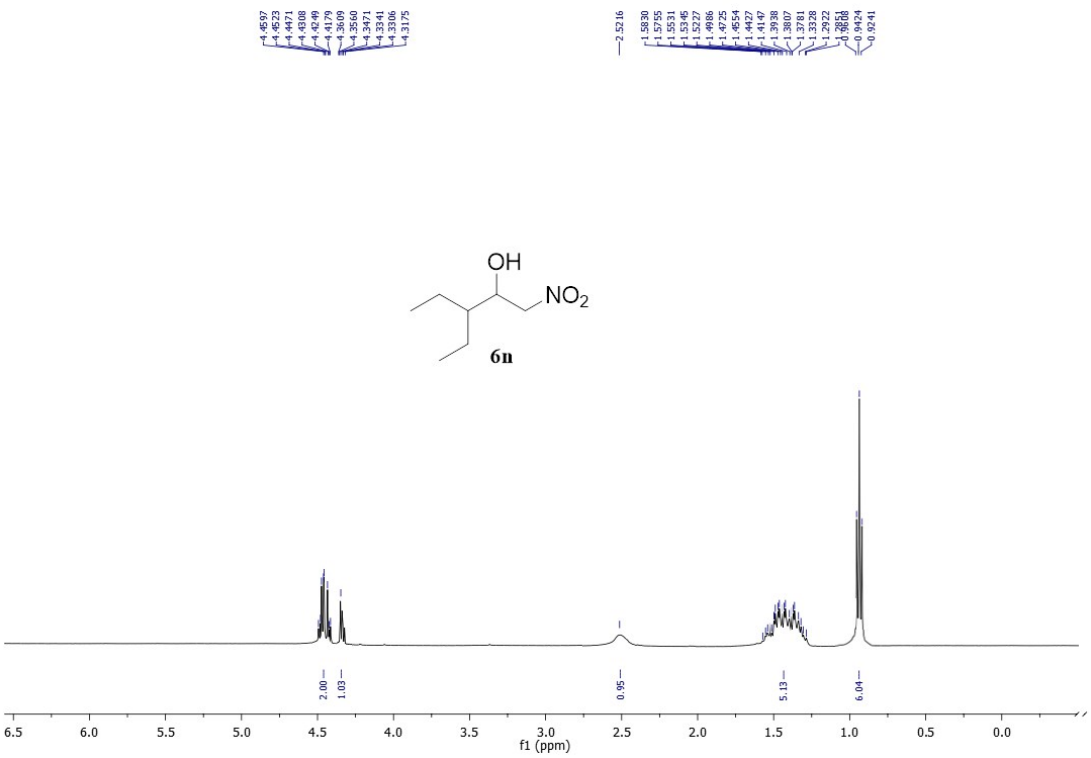


Figure S51: ^{1}H NMR Spectrum of Henry product **6n**.

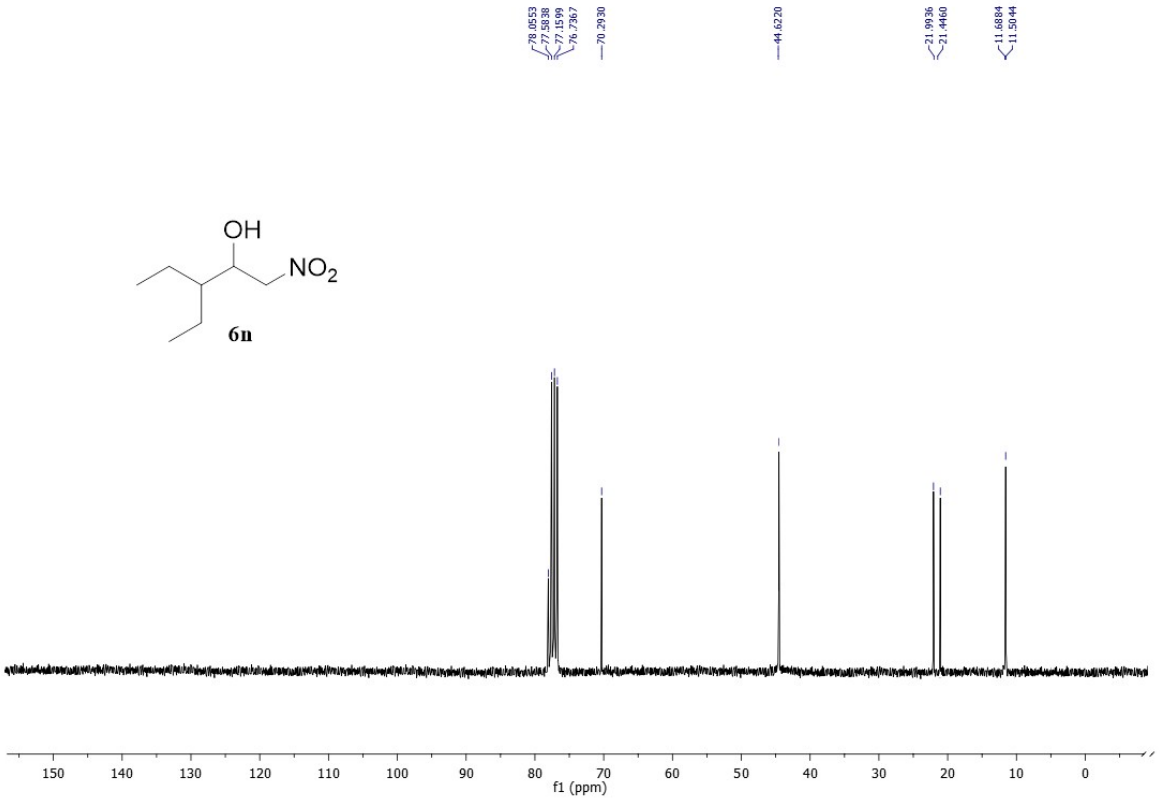


Figure S52: ^{13}C NMR Spectrum of Henry product **6n**.

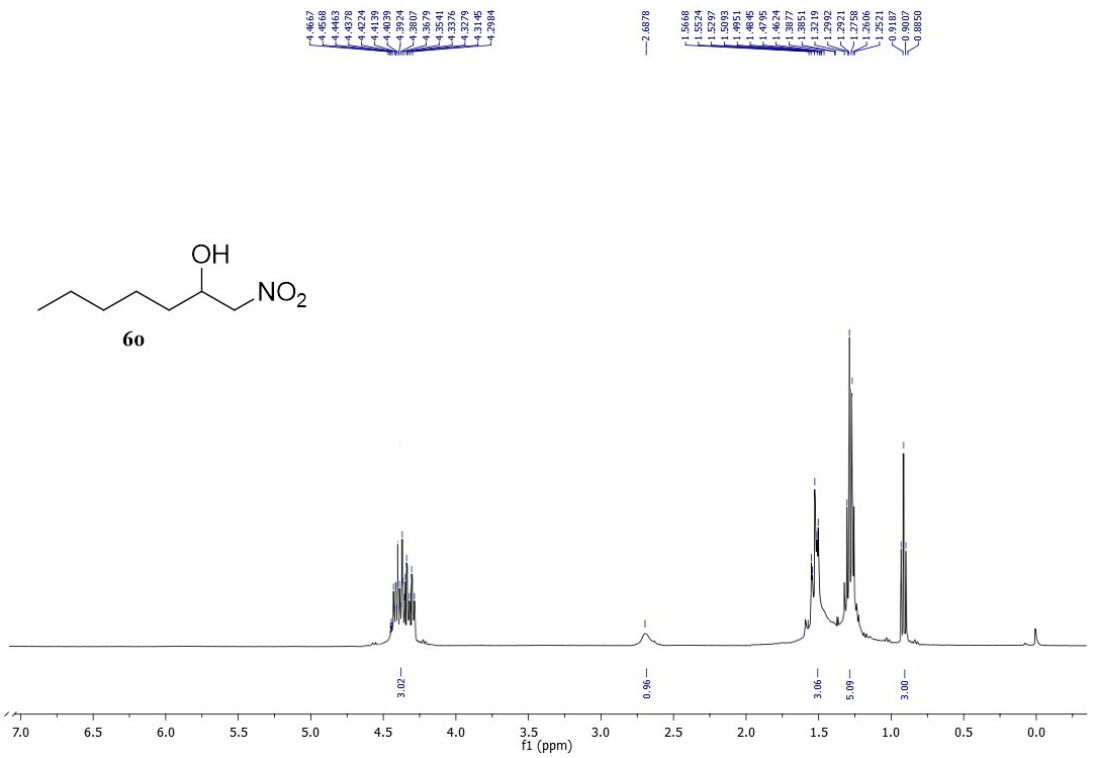


Figure S53: ^{1}H NMR Spectrum of Henry product **6o**.

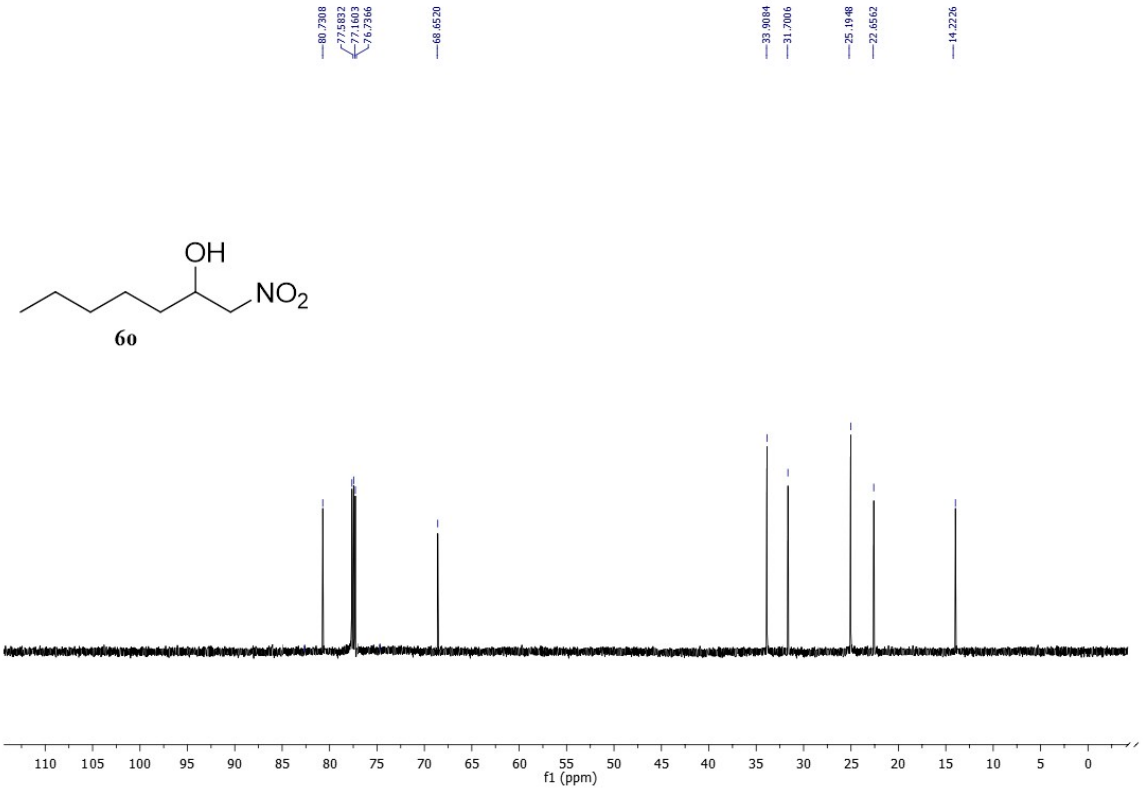


Figure S54: ^{13}C NMR Spectrum of Henry product **6n**.

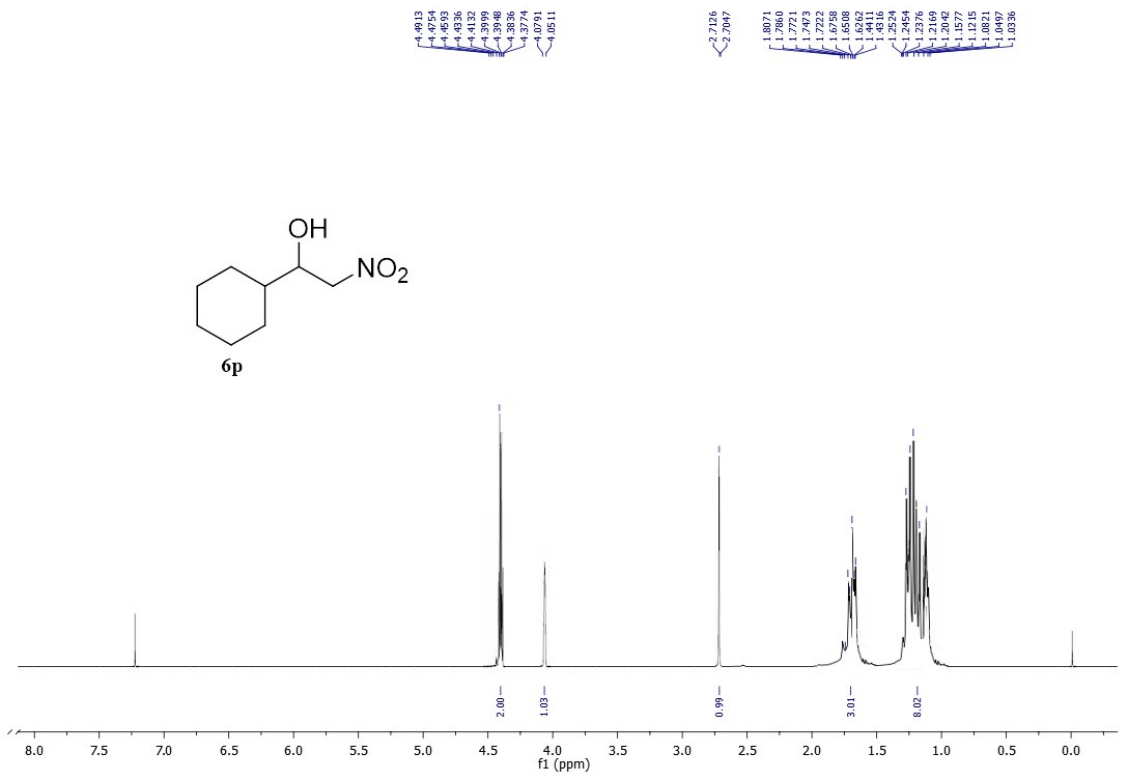


Figure S55: ^{1}H NMR Spectrum of Henry product **6p**.

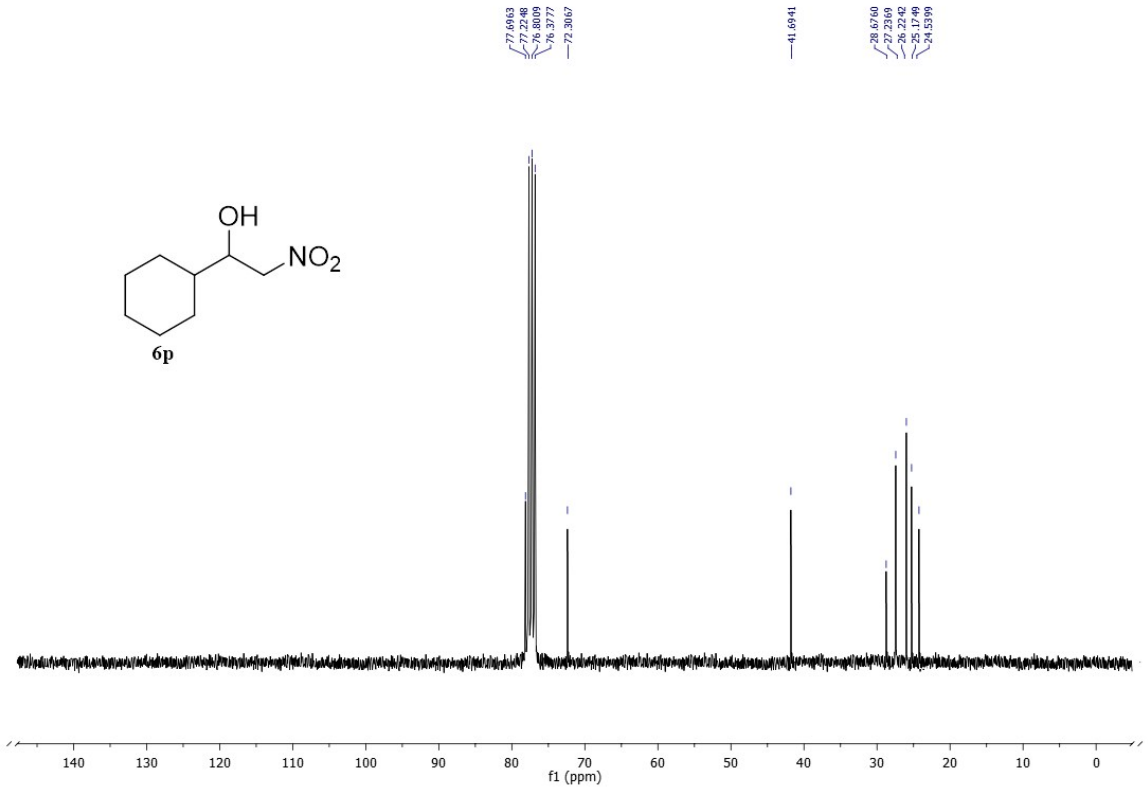
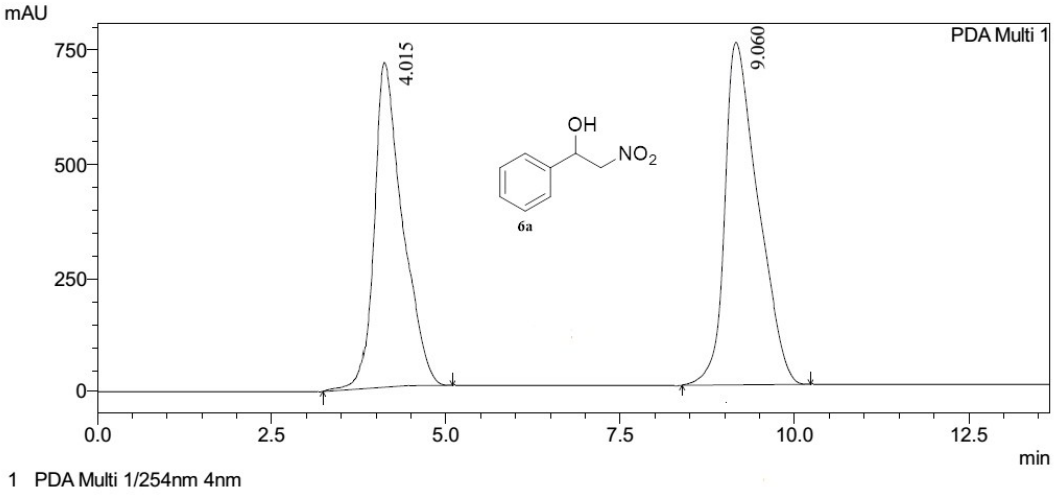


Figure S56: ^{13}C NMR Spectrum of Henry product **6p**.

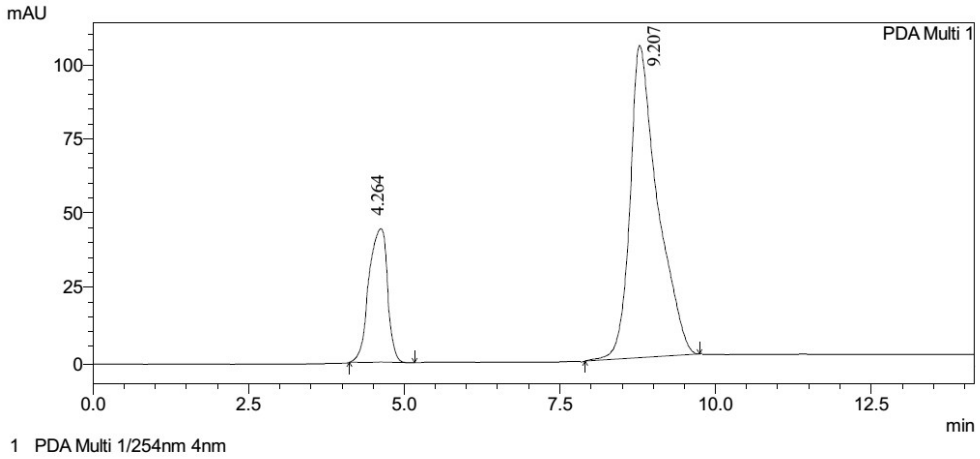


PeakTable

PDA Ch1 240nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.015	68652226	2277315	49.400	47.400
2	9.060	70184317	2339861	50.600	52.600
Total		138836543	4517176	100.000	100.000

Figure S57: HPLC chromatogram of (**6a**) Racemic mixture.

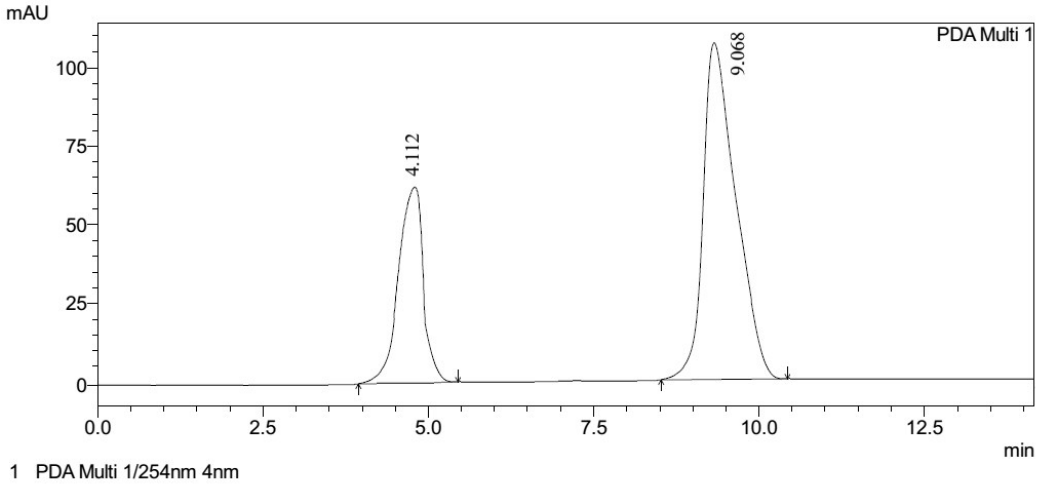


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.264	1647576	36770	16.279	25.283
2	9.207	8473498	108659	83.721	74.717
Total		10121074	145429	100.000	100.000

Figure S58: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and CH_3OH in 60 °C condition.



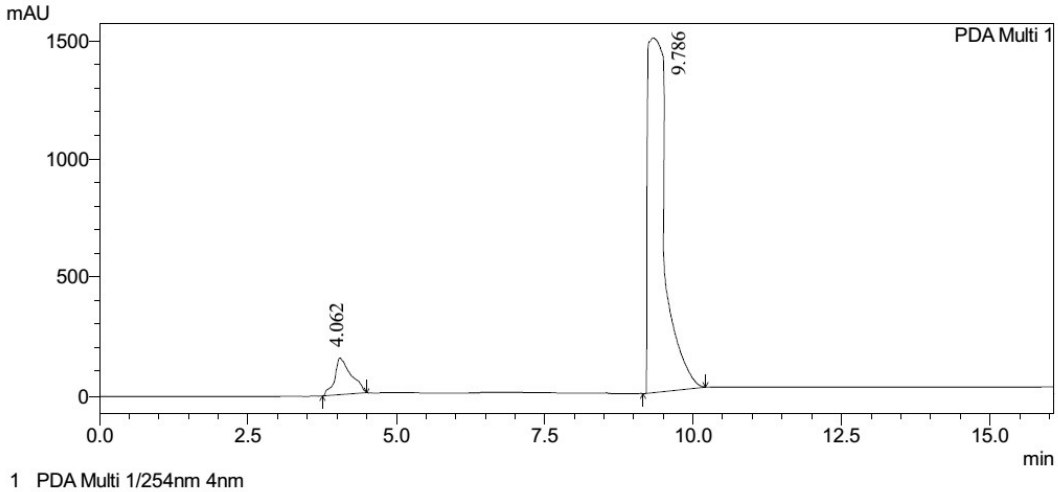
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.112	3643082	70856	20.621	40.104
2	9.068	14023952	105826	79.379	59.896
Total		17667034	176683	100.000	100.000

Figure S59: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and CH_3OH in 60 °C condition.



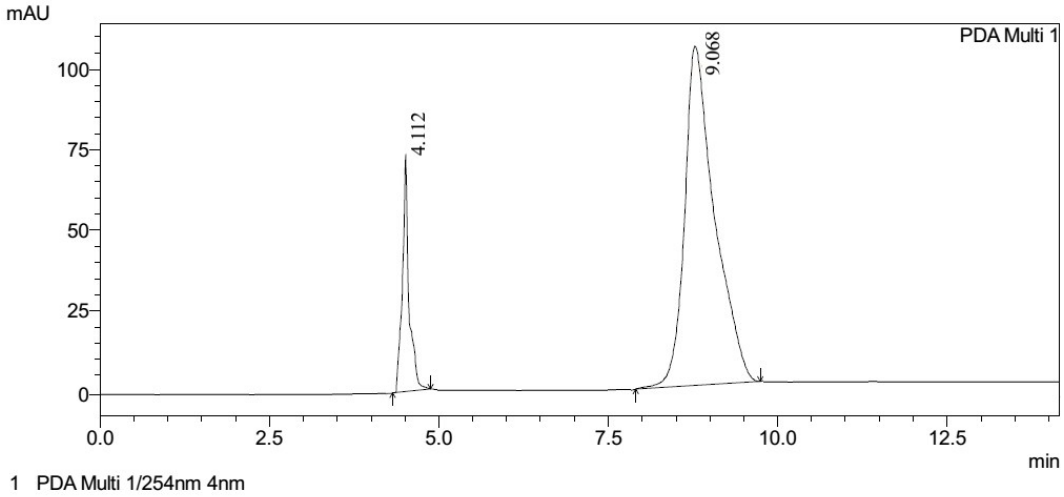
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.062	1741162	50817	7.786	16.630
2	9.786	20622334	254758	92.214	83.370
Total		22363496	305575	100.000	100.000

Figure S60: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and CH_3OH in 50 °C condition.

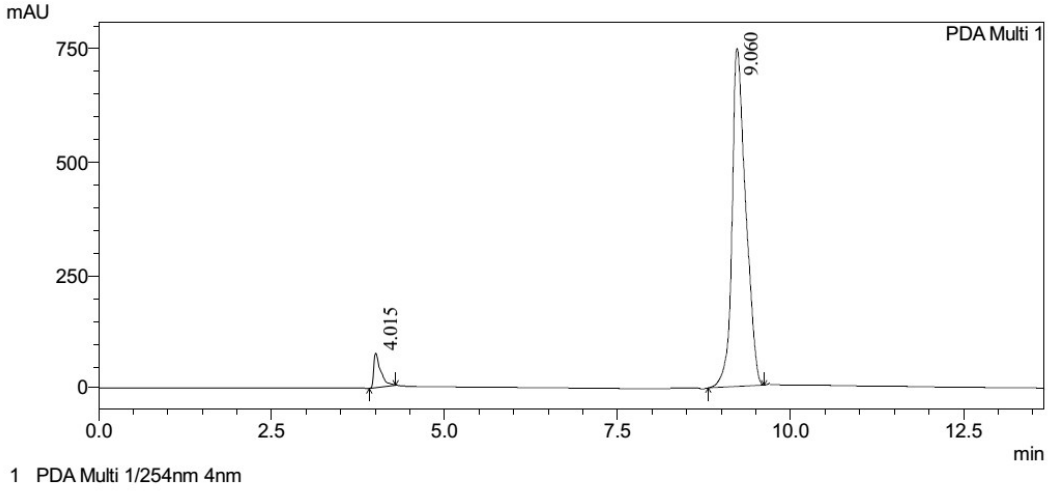


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.112	2142474	37487	18.517	26.448
2	9.068	9427796	104252	81.483	73.552
Total		11570271	141740	100.000	100.000

Figure S61: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and CH_3OH in 50 °C condition.

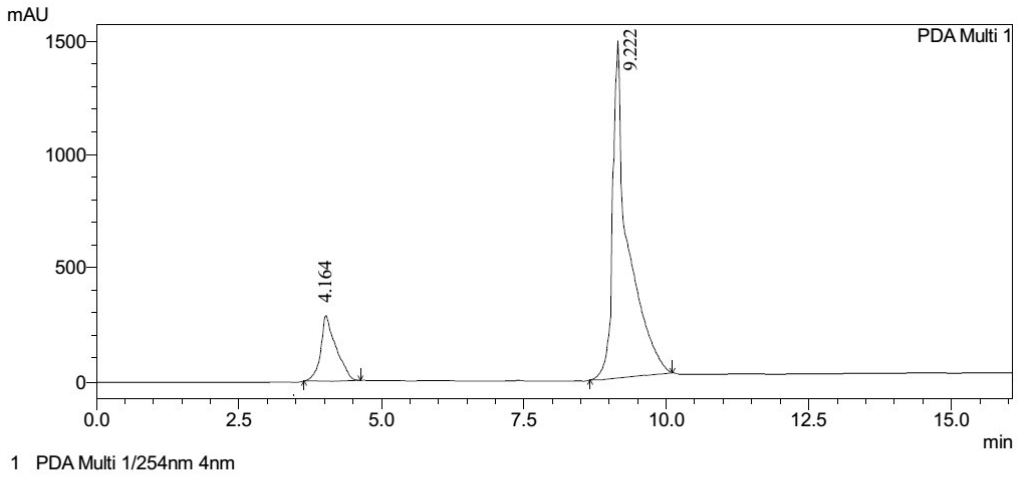


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.015	751420	46813	1.182	5.836
2	9.060	62830428	755323	98.818	94.164
Total		63581847	802136	100.000	100.000

Figure S62: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and CH_3OH in room temperature (30 ºC) condition.

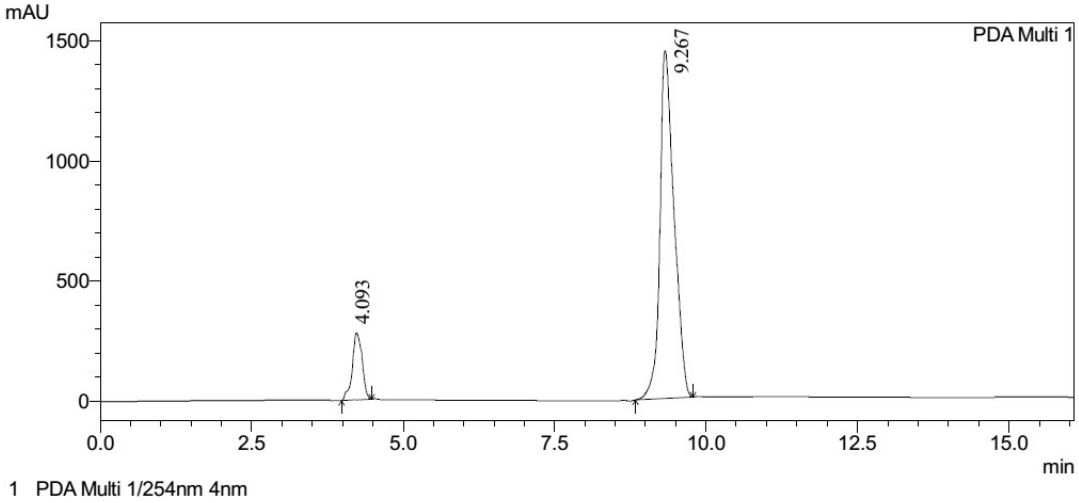


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.164	3721829	71448	9.247	15.174
2	9.222	36525852	399404	90.753	84.826
Total		40247681	470851	100.000	100.000

Figure S63: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and CH_3OH in room temperature (30 ºC) condition.

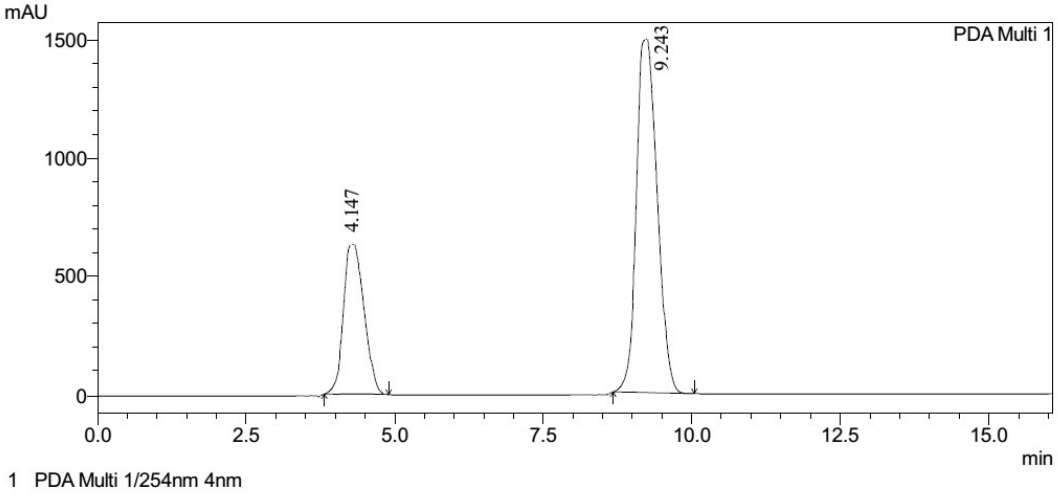


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.093	7602045	86041	5.193	5.555
2	9.267	138778209	1462970	94.807	94.445
Total		146380254	1549011	100.000	100.000

Figure S64: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and CH_3OH in 25 ºC condition.

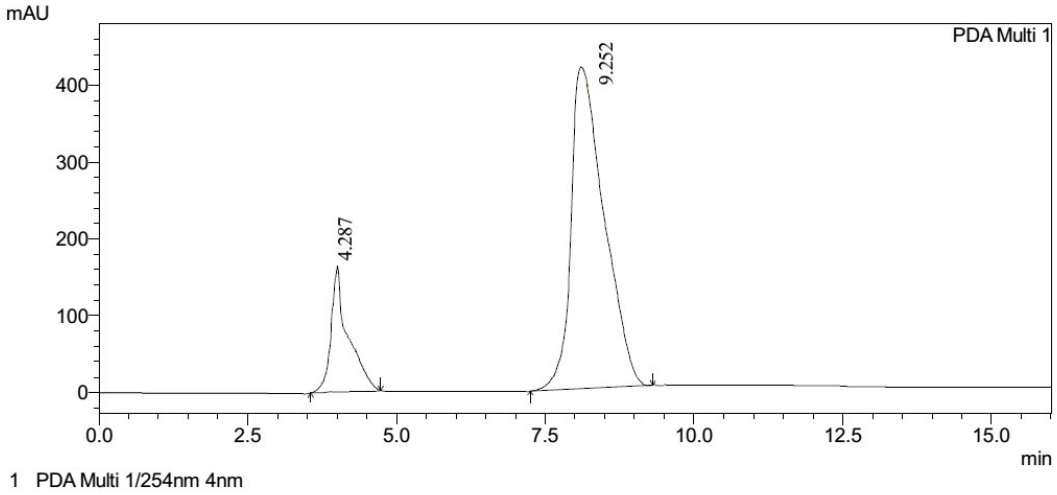


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.147	3717500	71316	14.777	17.401
2	9.243	34306874	338531	90.223	82.599
Total		38024374	409847	100.000	100.000

Figure S65: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and CH_3OH in 25 ºC condition.

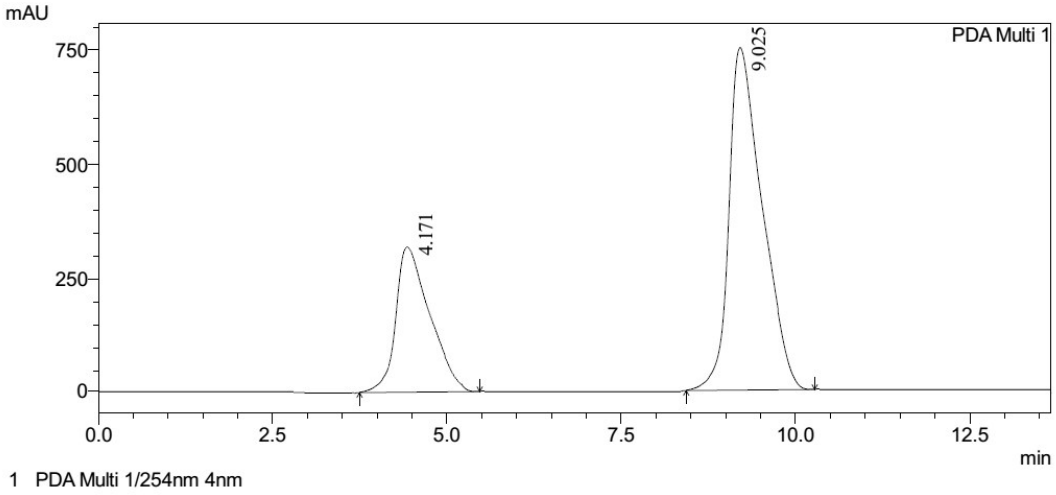


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.287	968610	33250	9.661	22.642
2	9.252	9057877	113602	90.339	77.358
Total		10026487	146852	100.000	100.000

Figure S66: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and CH_3OH in 20 ºC condition.

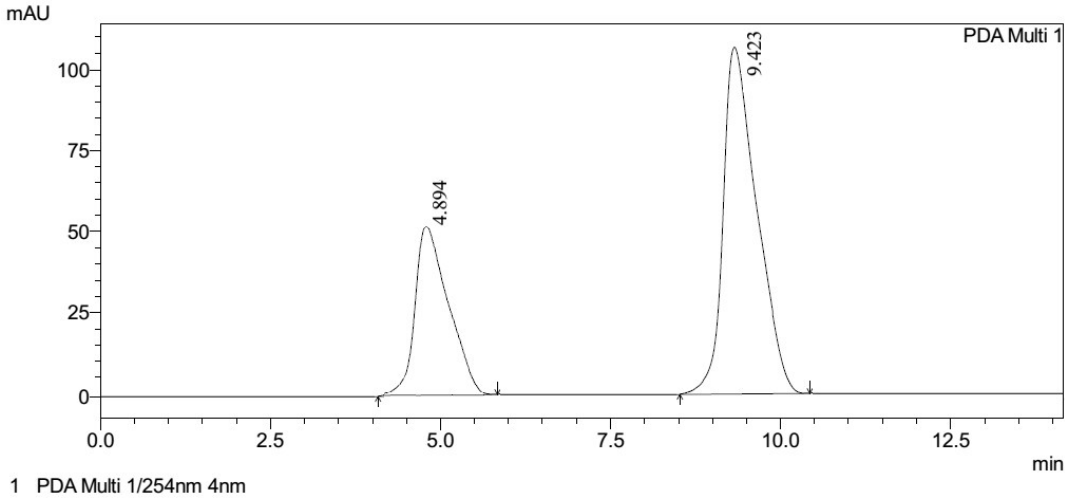


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.171	1565393	35255	15.606	25.680
2	9.025	9151863	102571	84.394	74.320
Total		10717256	137826	100.000	100.000

Figure S67: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and CH_3OH in 20 ºC condition.

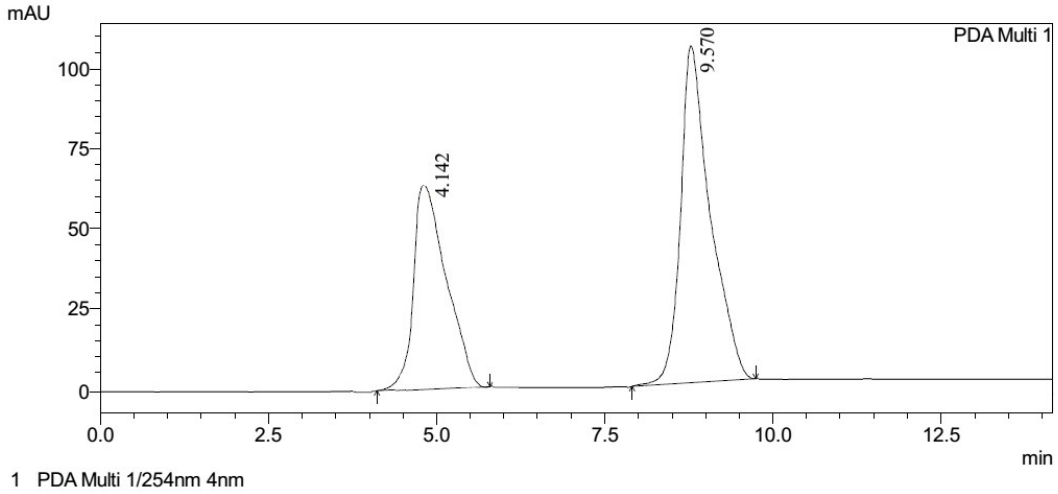


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.894	1168886	54431	20.546	29.024
2	9.423	6550055	84239	90.454	70.976
Total		7718940	138670	100.000	100.000

Figure S68: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and CH_3OH in 15 ºC condition.

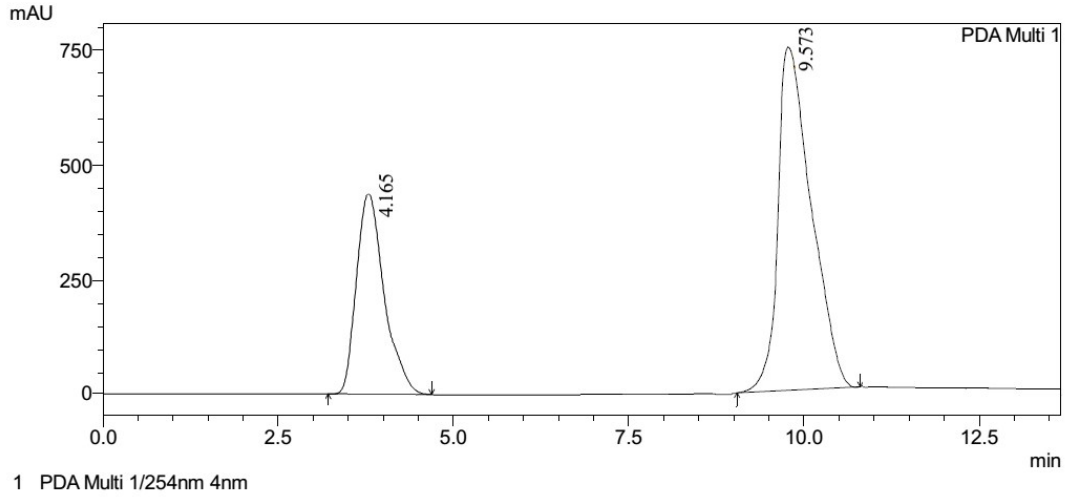


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.142	2042474	36487	17.517	26.448
2	9.570	9227796	104252	79.483	73.552
Total		11370271	141740	100.000	100.000

Figure S69: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and CH_3OH in 15 ºC condition.

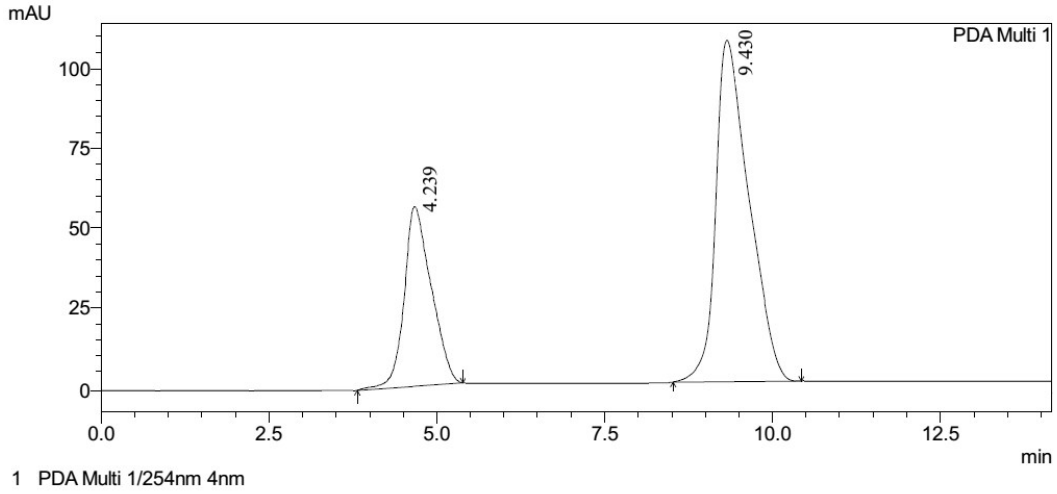


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.165	957358	39159	23.205	27.684
2	9.573	6292723	84006	86.795	72.316
Total		7250081	123165	100.000	100.000

Figure S70: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and CH_3OH in 10 ºC condition.

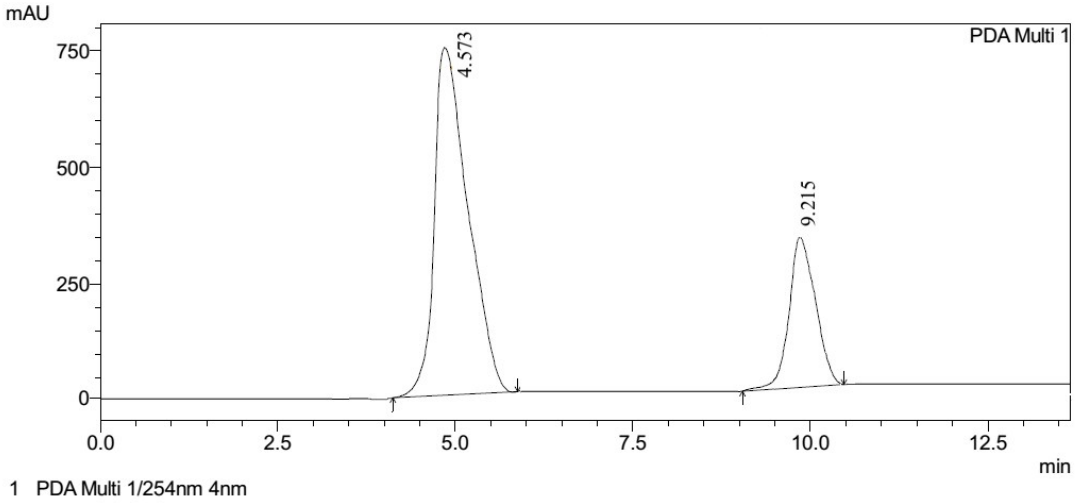


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.239	3643082	70856	20.621	40.204
2	9.430	16023952	101826	76.379	59.796
Total		19667034	172683	100.000	100.000

Figure S71: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and CH_3OH in 10 ºC condition.

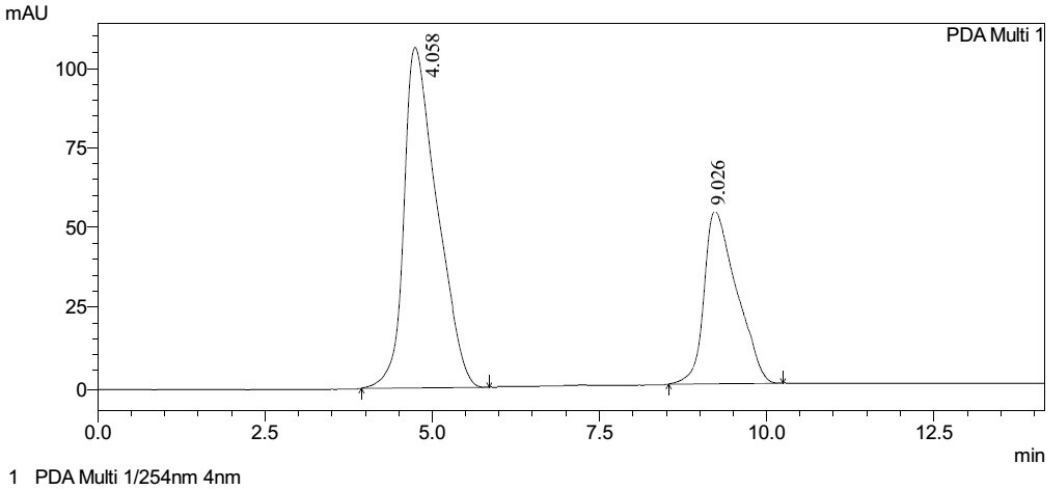


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.573	6292723	84006	86.795	72.316
2	9.215	957358	32159	12.205	27.684
Total		7250081	116165	100.000	100.000

Figure S72: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and CH_3OH in 5 ºC condition.

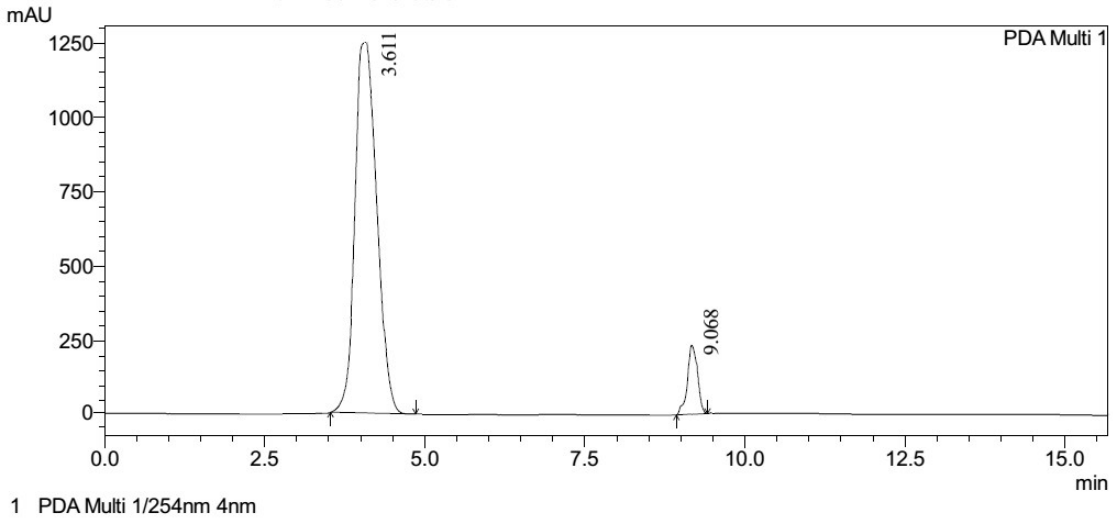


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.058	14023952	105826	79.379	59.896
2	9.026	3643082	70856	20.621	40.104
Total		17667034	176683	100.000	100.000

Figure S73: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and CH_3OH in 5 ºC condition.

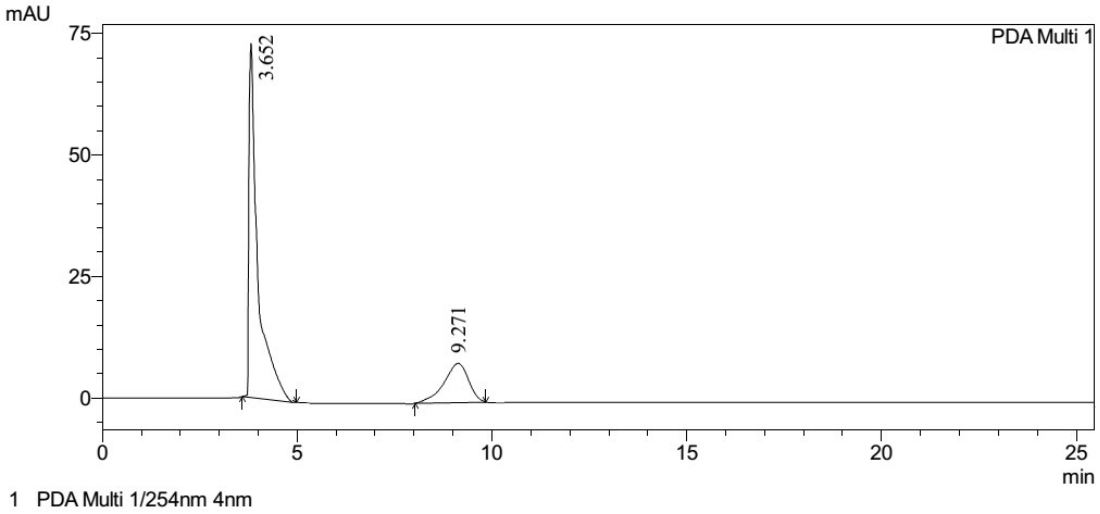


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.611	2753234	112968	95.961	98.933
2	9.068	115892	1219	4.039	1.067
Total		2869127	114187	100.000	100.000

Figure S74: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and CH_3OH in 0 °C condition.

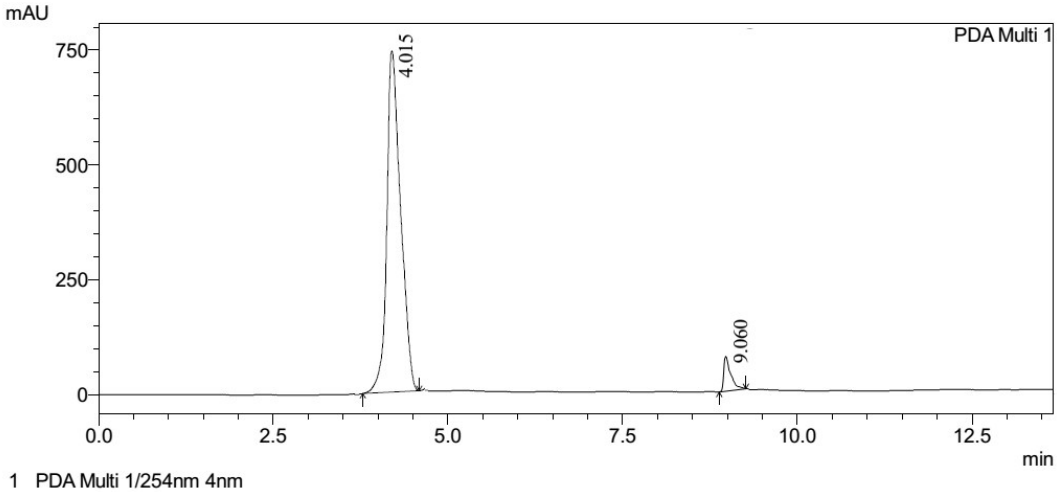


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.652	1677846	72754	82.584	90.046
2	9.271	353831	8042	17.416	9.954
Total		2031677	80797	100.000	100.000

Figure S75: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and CH_3OH in 0 °C condition.

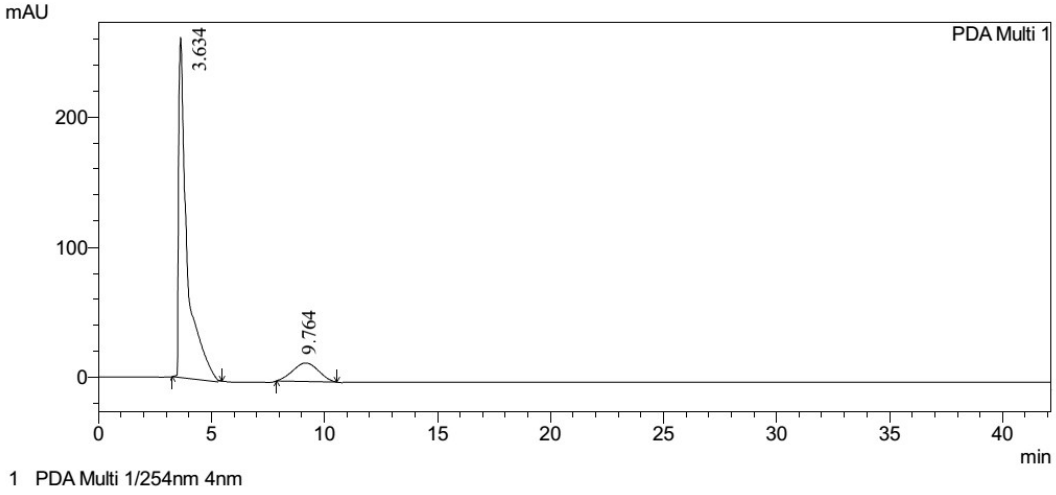


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.015	3904352	75789	96.378	95.441
2	9.060	146742	3620	3.622	4.559
Total		4051094	79409	100.000	100.000

Figure S76: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and CH_3OH in −10 °C condition.

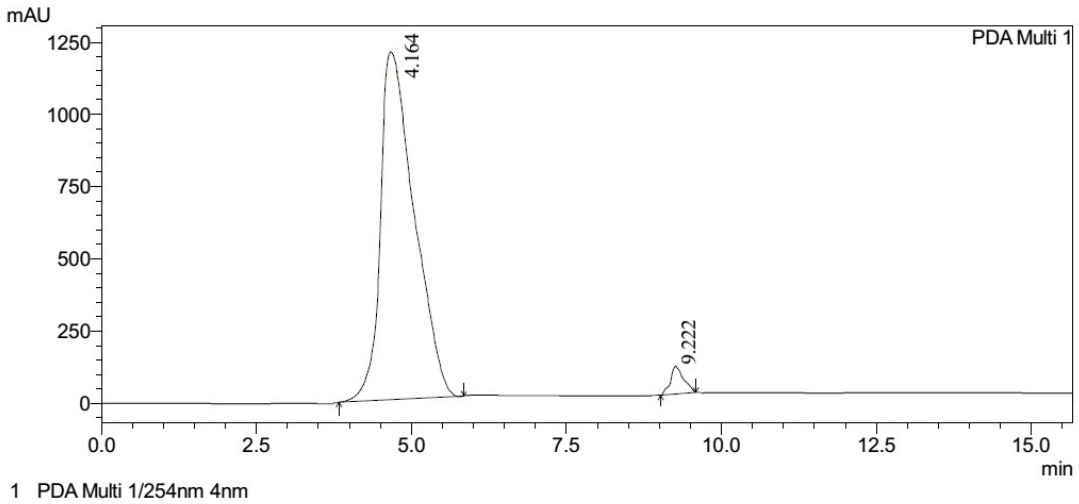


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.634	6770649	261063	85.713	94.819
2	9.764	1128573	14265	14.287	5.181
Total		7899222	275328	100.000	100.000

Figure S77: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and CH_3OH in −10 °C condition.

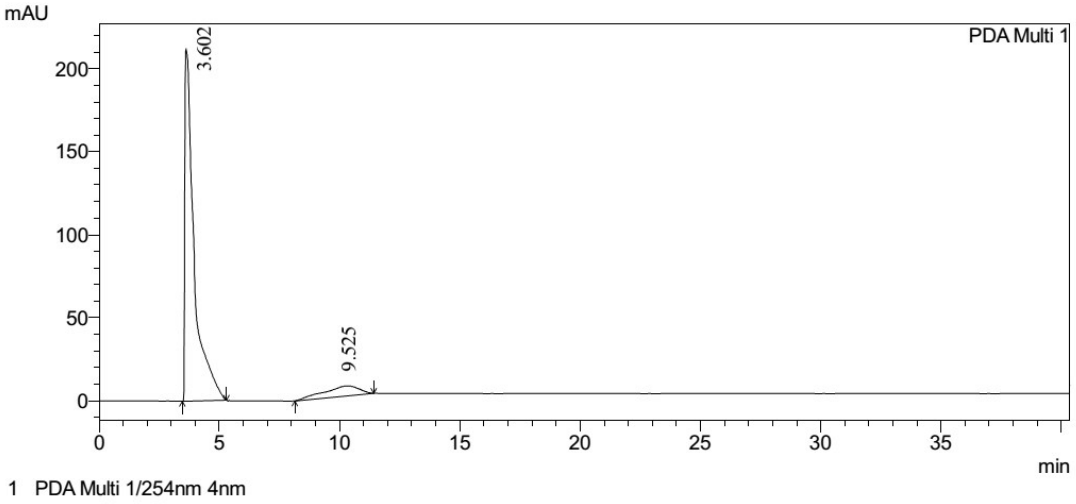


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.164	62251896	752263	98.445	93.889
2	9.222	983580	48963	1.555	6.111
Total		63235475	801226	100.000	100.000

Figure S78: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and CH_3OH in −20 °C condition.



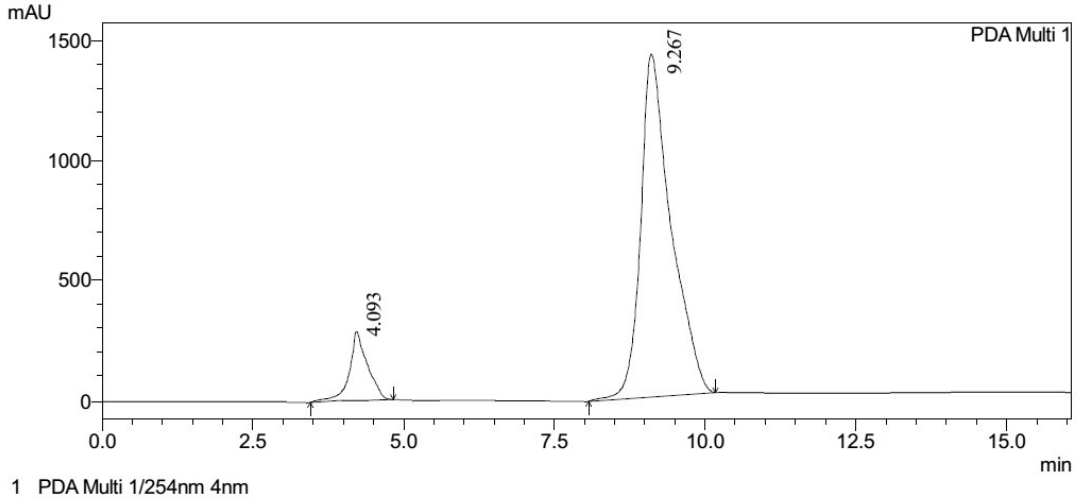
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.602	5687279	212415	89.975	97.258
2	9.525	633682	5989	10.025	2.742
Total		6320961	218404	100.000	100.000

Figure S79: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and CH_3OH in −20 °C condition.

Figure S80: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and CH_3OH/room temperature condition.

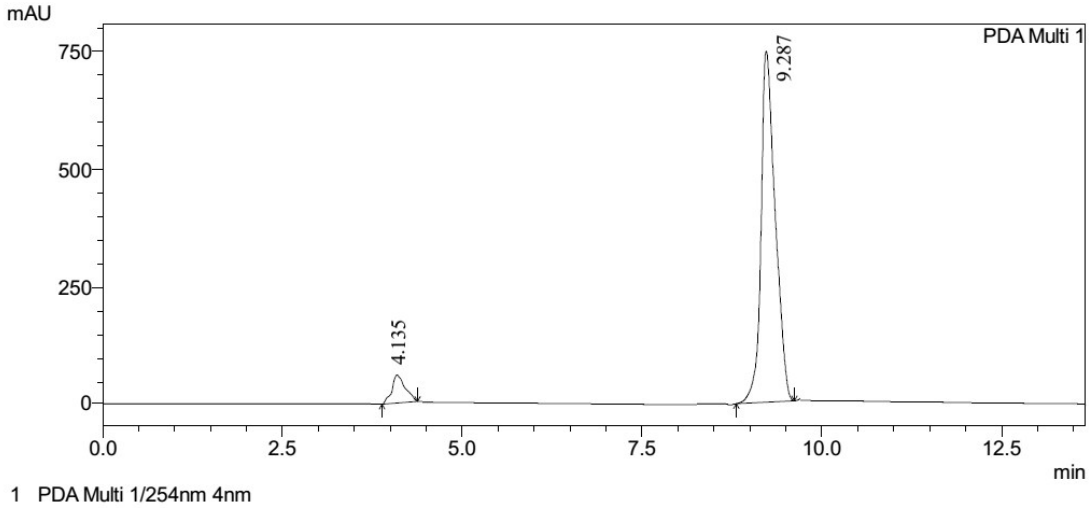


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.093	11972419	110813	7.683	6.949
2	9.267	143863194	1483918	92.317	93.051
Total		155835613	1594731	100.000	100.000

Figure S81: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and CH_3OH/room temperature condition.



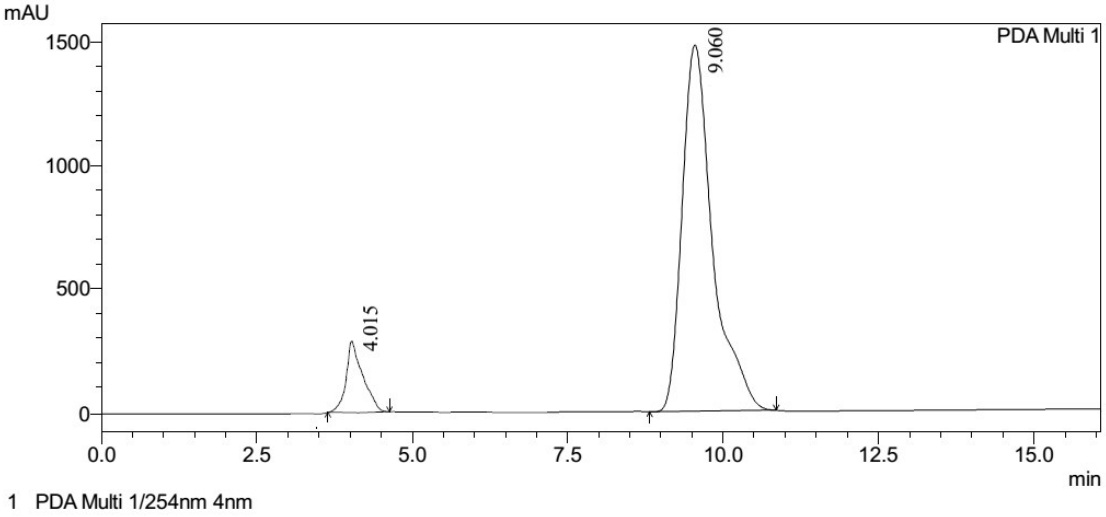
135

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.135	427069	21110	1.511	5.023
2	9.287	27835219	399135	98.489	94.977
Total		28262287	420246	100.000	100.000

Figure S82: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and C_2H_5OH/room temperature condition.

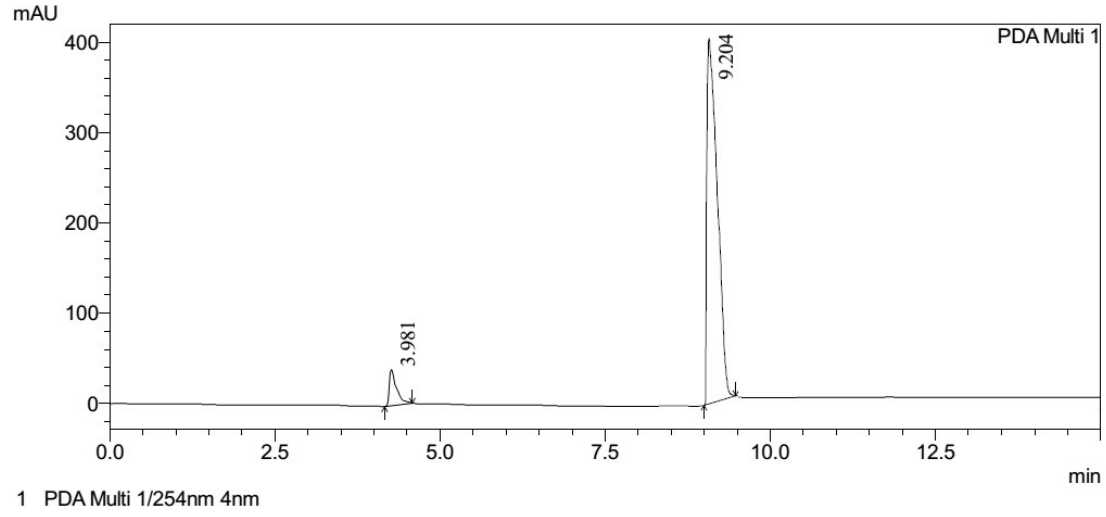


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.015	1741162	50817	7.786	16.630
2	9.060	20622334	254758	92.214	83.370
Total		22363496	305575	100.000	100.000

Figure S83: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and C_2H_5OH/room temperature condition.

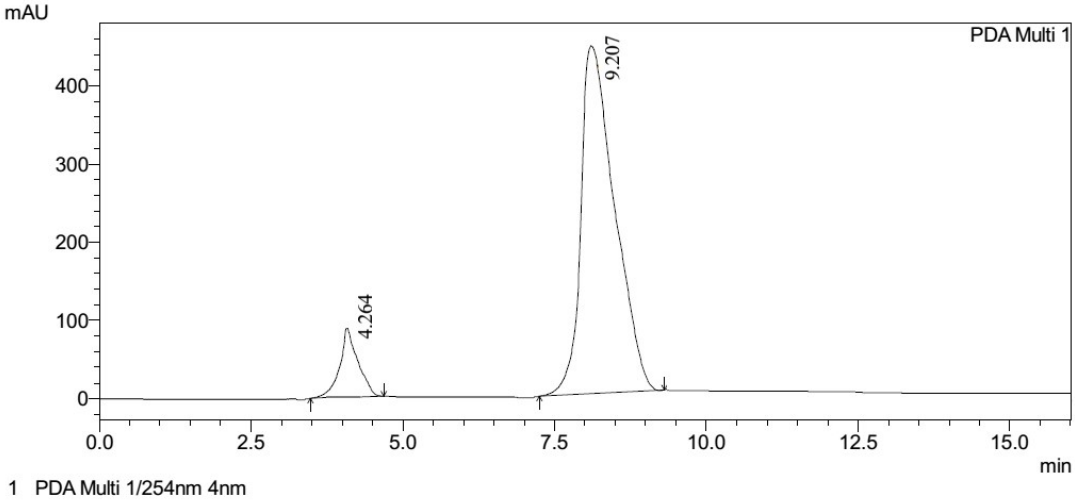


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.981	427069	21110	1.511	5.023
2	9.204	27835219	399135	98.489	94.977
Total		28262287	420246	100.000	100.000

Figure S84: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and i-PrOH/room temperature condition.

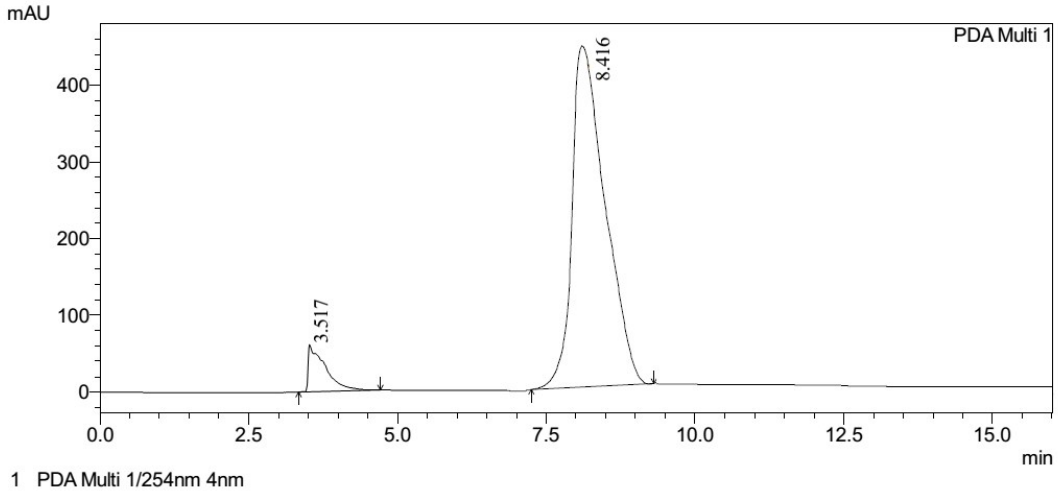


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.264	968610	33250	9.661	22.642
2	9.207	9057877	113602	90.339	77.358
Total		10026487	146852	100.000	100.000

Figure S85: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and i-PrOH/room temperature condition.



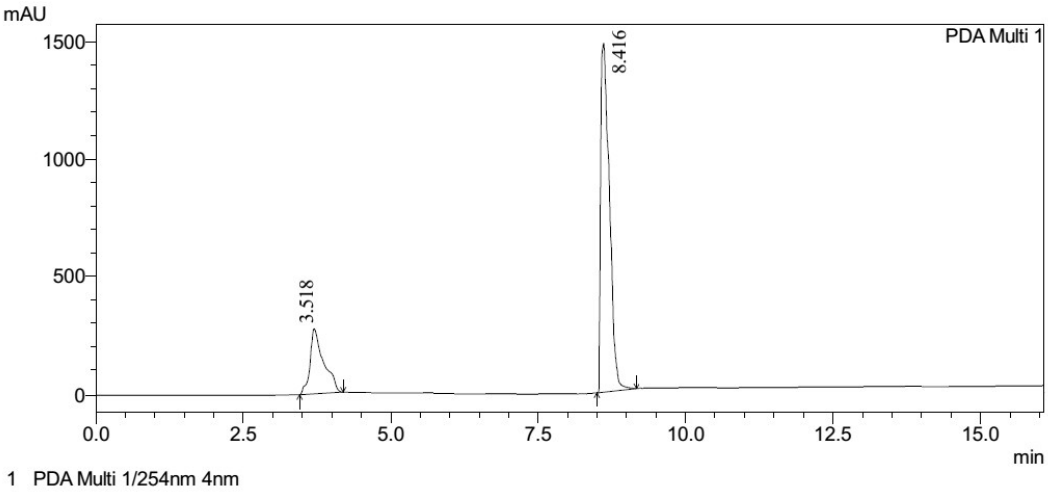
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.517	1217689	61815	6.956	11.991
2	8.416	16288090	453694	93.044	88.009
Total		17505779	515509	100.000	100.000

Figure S86: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and DCM/room temperature condition.

Figure S87: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and DCM/room temperature condition.



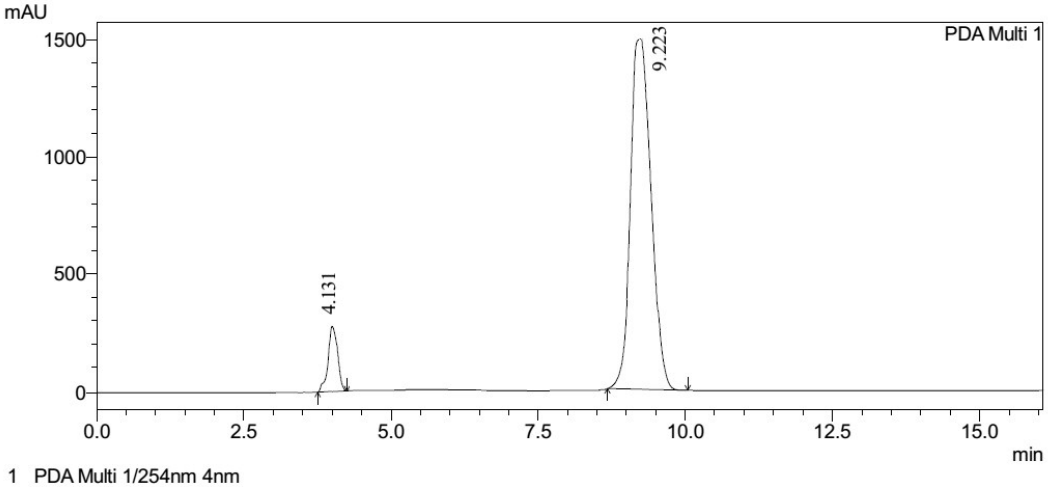
PeakTable

PDA Ch1 250nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.518	1521312	83958	8.041	14.663
2	8.416	17397702	488633	91.959	85.337
Total		18919015	572591	100.000	100.000

Figure S88: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and THF/room temperature condition.

Figure S89: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and THF/room temperature condition.



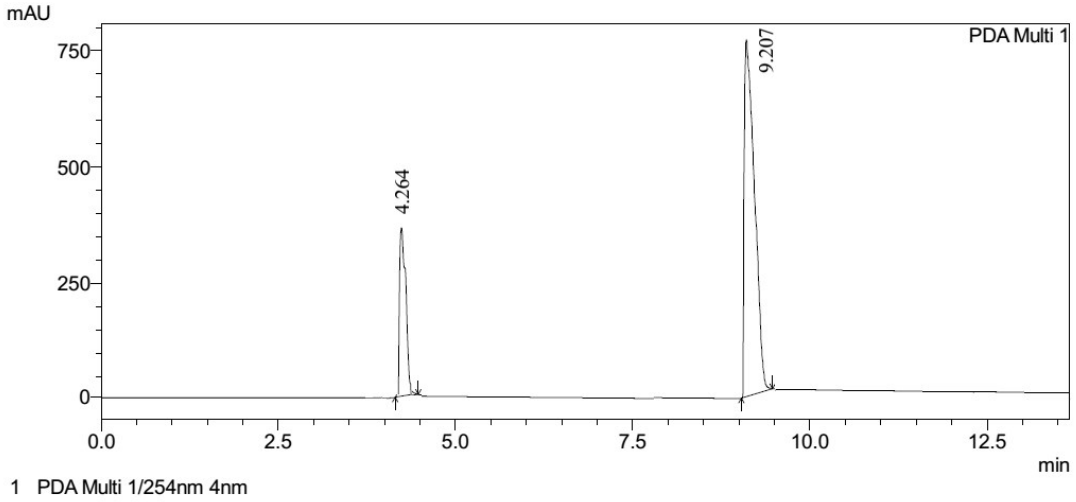
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.131	3717500	71316	9.777	17.401
2	9.223	34306874	338531	90.223	82.599
Total		38024374	409847	100.000	100.000

Figure S90: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and Ethyl acetate/room temperature condition.

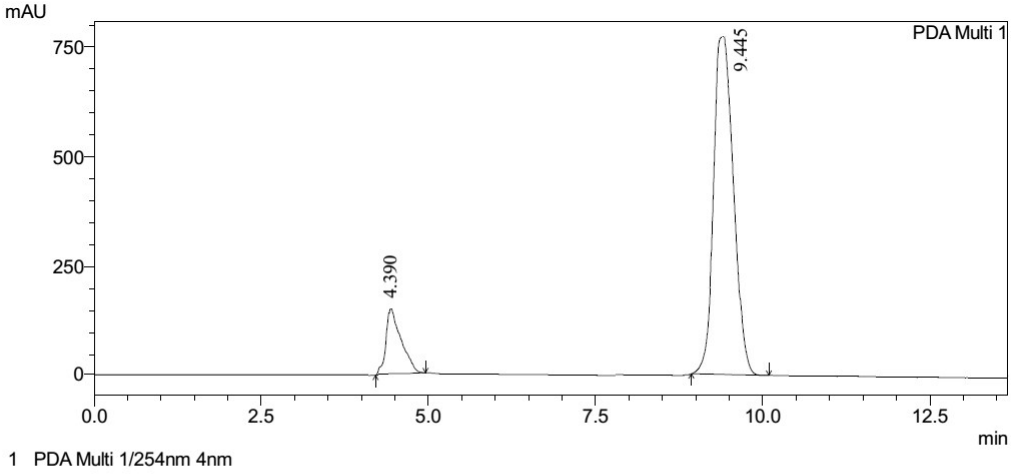


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.264	957358	32159	13.205	27.684
2	9.207	6292723	84006	86.795	72.316
Total		7250081	116165	100.000	100.000

Figure S91: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and Ethyl acetate/room temperature condition.

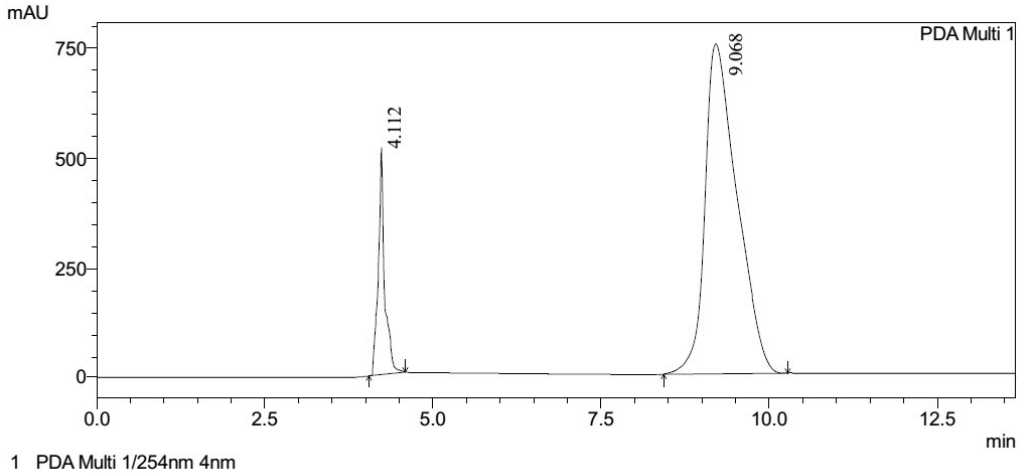


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.390	3721829	71448	9.247	15.174
2	9.445	36525852	399404	90.753	84.826
Total		40247681	470851	100.000	100.000

Figure S92: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and $CHCl_3$/room temperature condition.

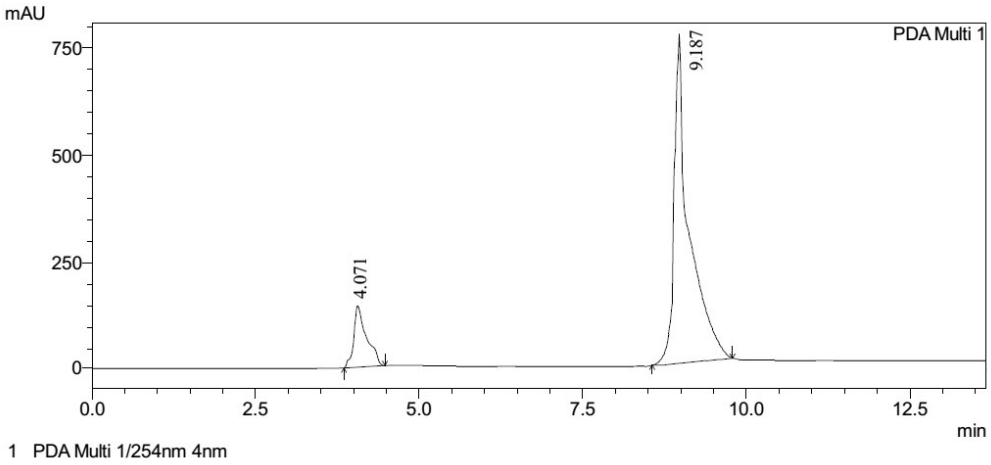


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.112	1565393	35256	14.606	25.580
2	9.068	9151863	102571	85.394	74.420
Total		10717256	137826	100.000	100.000

Figure S93: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and $CHCl_3$/room temperature condition.



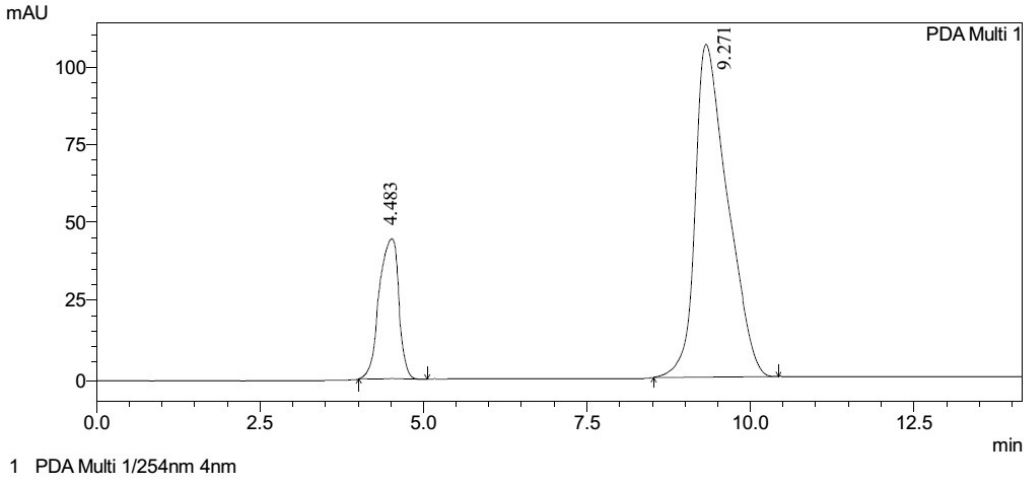
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.071	738383	30187	10.326	26.090
2	9.187	6412071	85516	89.674	73.910
Total		7150455	115703	100.000	100.000

Figure S94: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and *O*-Xylene/room temperature condition.

Figure S95: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and *O*-Xylene/room temperature condition.

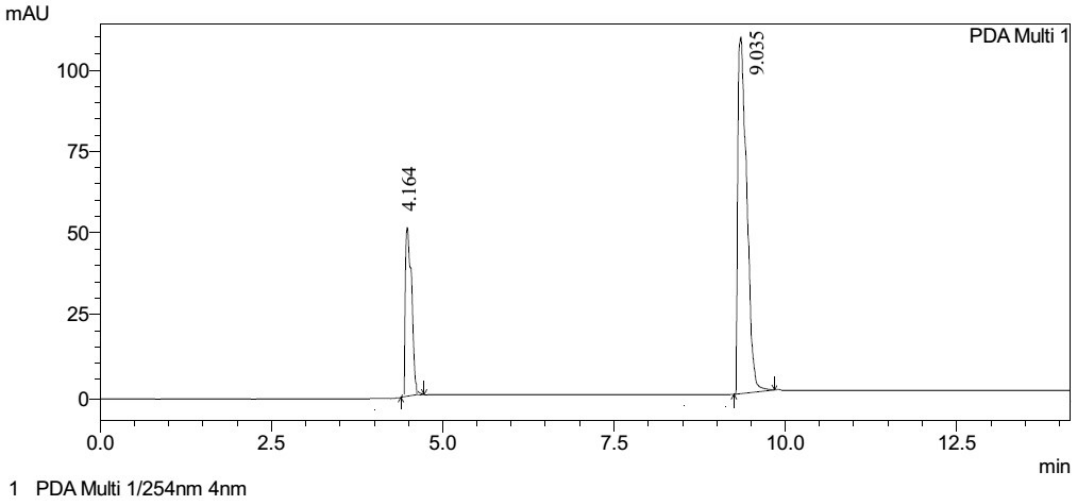


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.483	1168886	34431	15.546	29.014
2	9.271	6350055	84239	84.454	70.986
Total		7518940	118670	100.000	100.000

Figure S96: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and benzene/room temperature condition.



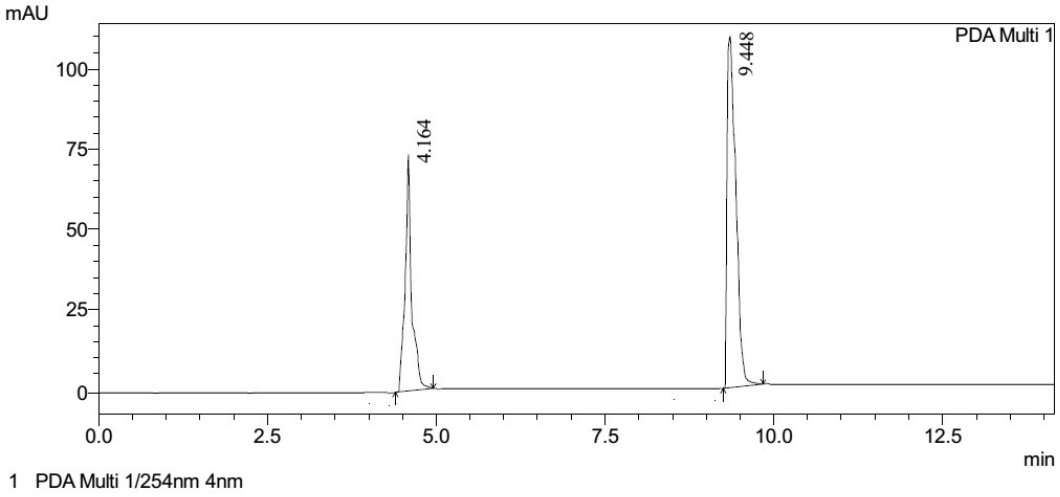
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.164	3658295	71215	26.111	99.309
2	9.035	10352322	496	73.889	0.691
Total		14010617	71711	100.000	100.000

Figure S97: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and benzene/room temperature condition.

Figure S98: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and CCl_4/room temperature condition.



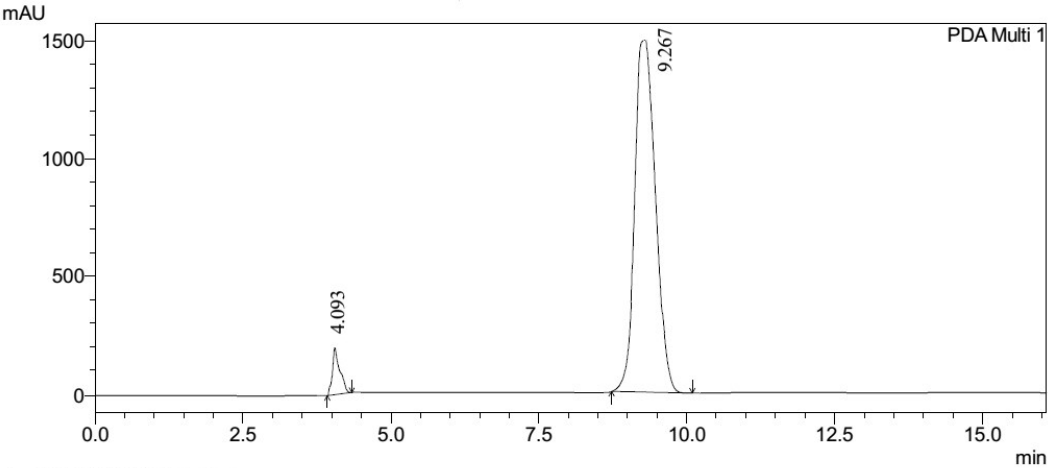
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.164	1659166	16403	29.389	14.421
2	9.448	3986453	97339	70.611	85.579
Total		5645619	113742	100.000	100.000

Figure S99: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and CCl_4/room temperature condition.



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

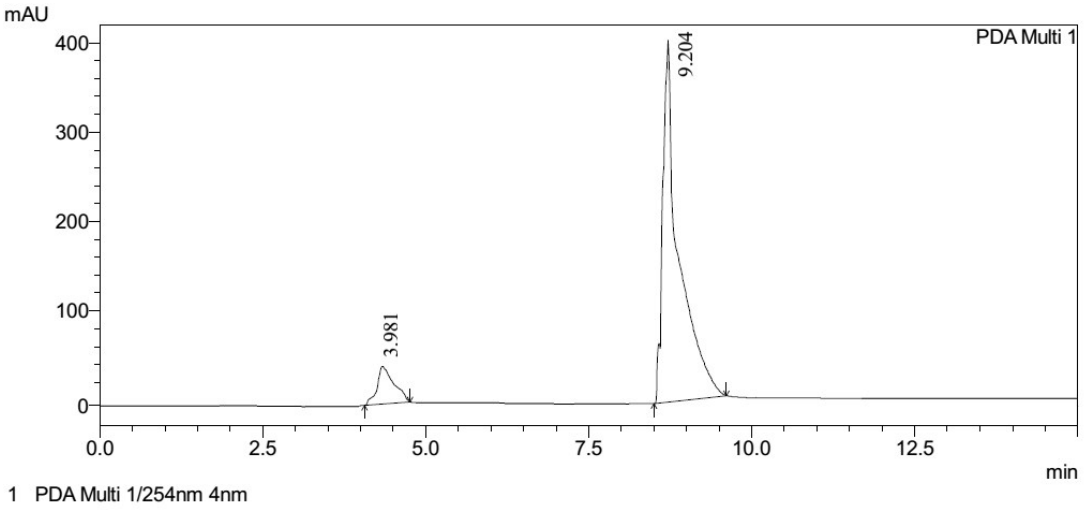
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.093	4838897	65126	3.259	4.206
2	9.267	143622513	1483220	96.741	95.794
Total		148461409	1548346	100.000	100.000

Figure S100: HPLC chromatogram of (**6a**) in the presence 1 mol% of organocatalyst (**14**) and CH_3OH/room temperature condition.

Figure S101: HPLC chromatogram of (**6a**) in the presence 1 mol% of organocatalyst (**16**) and CH_3OH/room temperature condition.

Figure S102: HPLC chromatogram of (**6a**) in the presence 2.5 mol% of organocatalyst (**14**) and CH_3OH/room temperature condition.

Figure S103: HPLC chromatogram of (**6a**) in the presence 2.5 mol% of organocatalyst (**16**) and CH_3OH/room temperature condition.



PeakTable

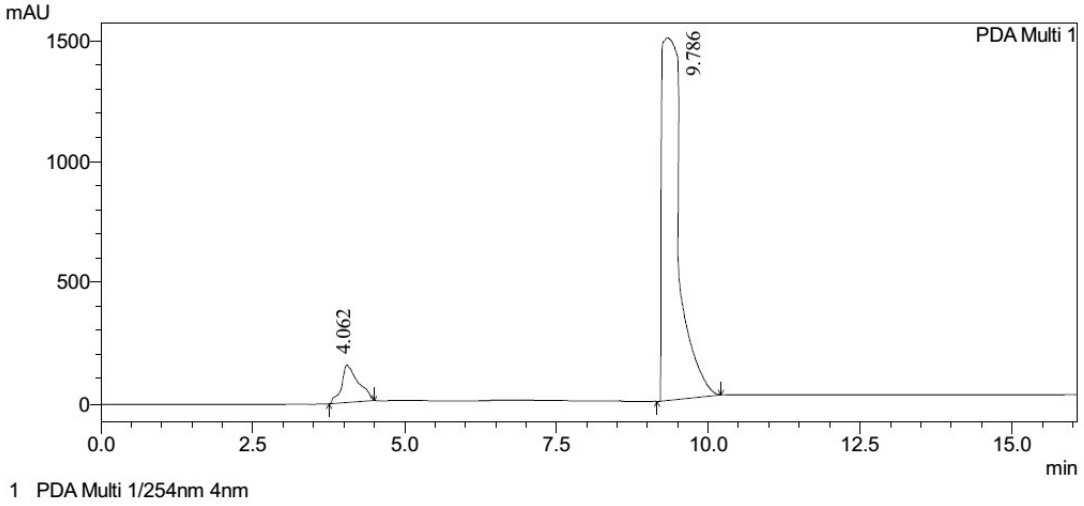
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.981	838351	21549	2.999	5.171
2	9.204	27112859	395206	97.001	94.829
Total		27951210	416755	100.000	100.000

Figure S104: HPLC chromatogram of (**6a**) in the presence 7.5 mol% of organocatalyst (**14**) and CH_3OH/room temperature condition.

Figure S105: HPLC chromatogram of (**6a**) in the presence 7.5 mol% of organocatalyst (**16**) and CH_3OH/room temperature condition.

Figure S106: HPLC chromatogram of (**6a**) in the presence 15 mol% of organocatalyst (**14**) and CH_3OH/room temperature condition.



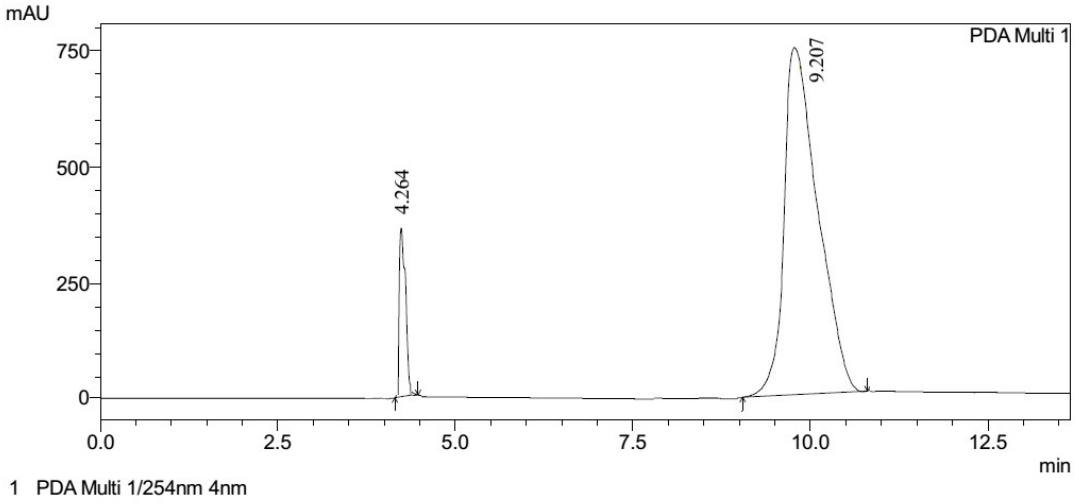
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.062	957358	32159	13.205	27.684
2	9.786	6292723	84006	86.795	72.316
Total		7250081	116165	100.000	100.000

Figure S107: HPLC chromatogram of (**6a**) in the presence 15 mol% of organocatalyst (**16**) and CH_3OH/room temperature condition.

Figure S108: HPLC chromatogram of (**6a**) in the presence 20 mol% of organocatalyst (**14**) and CH_3OH/room temperature condition.



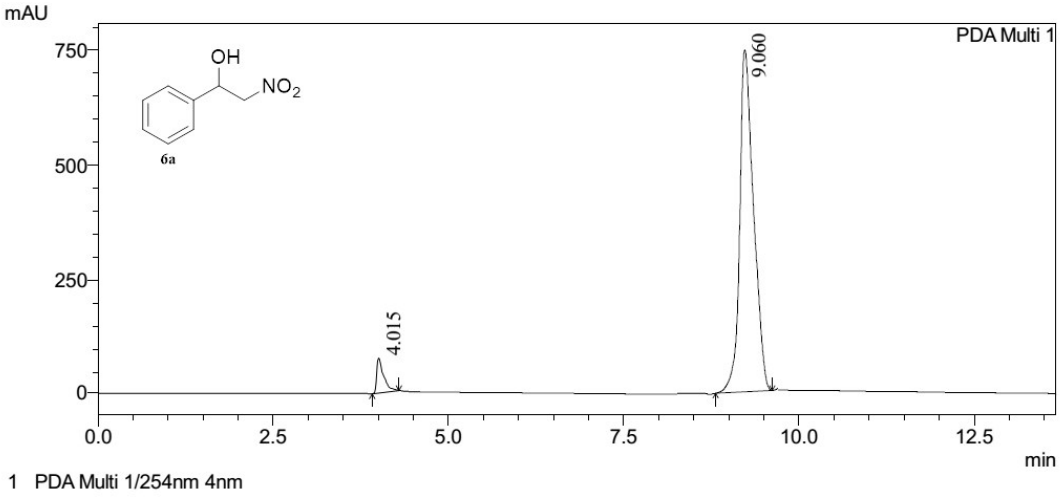
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.264	1565393	35256	14.606	25.580
2	9.207	9151863	102571	85.394	74.420
Total		10717256	137826	100.000	100.000

Figure S109: HPLC chromatogram of (**6a**) in the presence 20 mol% of organocatalyst (**16**) and CH_3OH/room temperature condition.

Figure S110: HPLC chromatogram of (**6a**) Racemic mixture.

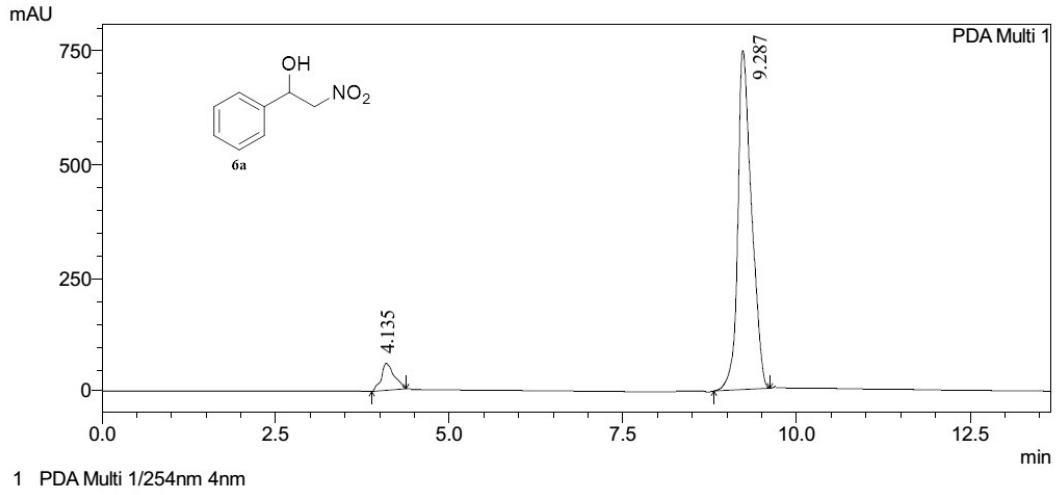


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.015	751420	46813	1.182	5.836
2	9.060	62830428	755323	98.818	94.164
Total		63581847	802136	100.000	100.000

Figure S111: HPLC chromatogram of (**6a**) in the presence organocatalyst (**14**) and CH_3OH/room temperature condition.



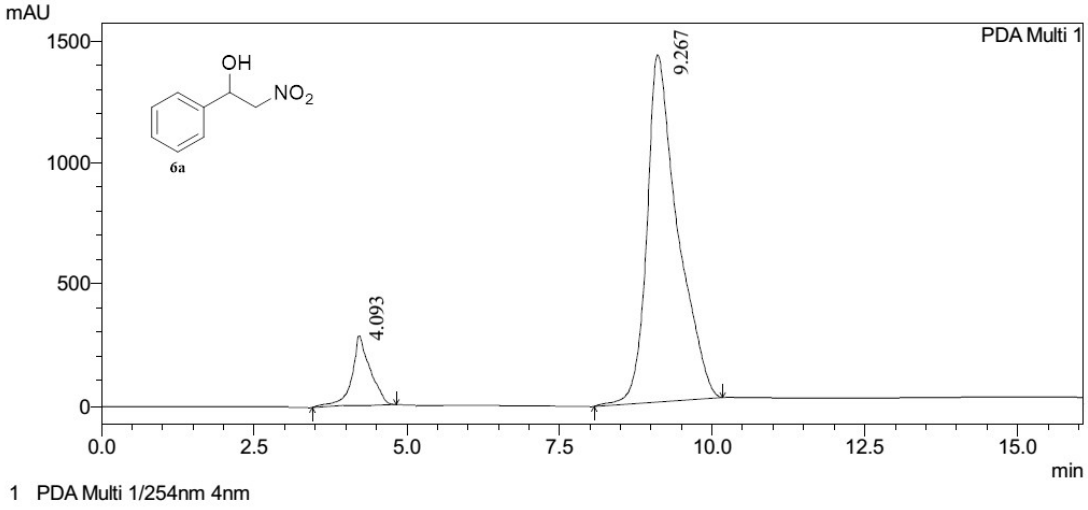
135

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.135	427069	21110	1.511	5.023
2	9.287	27835219	399135	98.489	94.977
Total		28262287	420246	100.000	100.000

Figure S112: HPLC chromatogram of (**6a**) in the presence organocatalyst (**15**) and CH_3OH/room temperature condition.

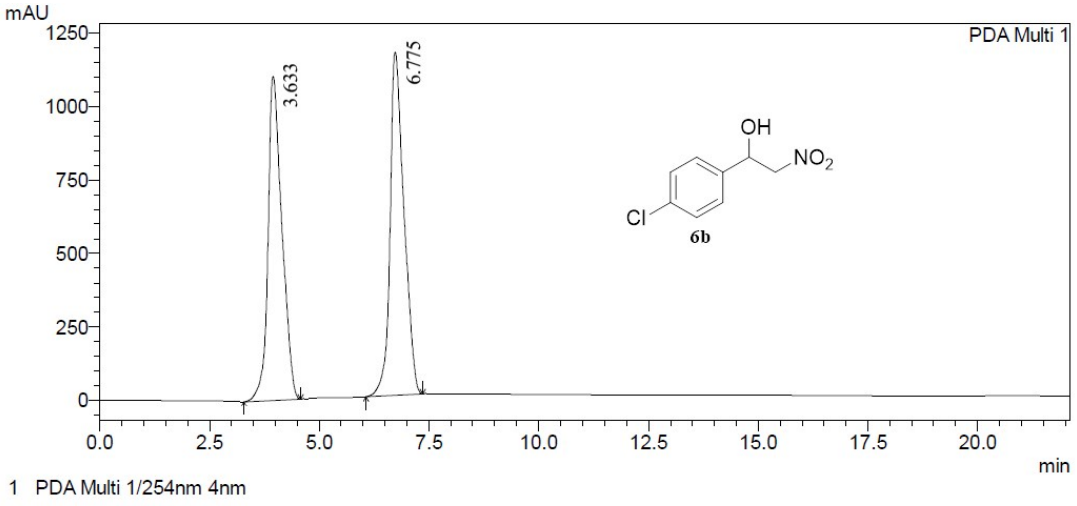


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.093	11972419	110813	7.683	6.949
2	9.267	143863194	1483918	92.317	93.051
Total		155835613	1594731	100.000	100.000

Figure S113: HPLC chromatogram of (**6a**) in the presence organocatalyst (**16**) and CH_3OH/room temperature condition.

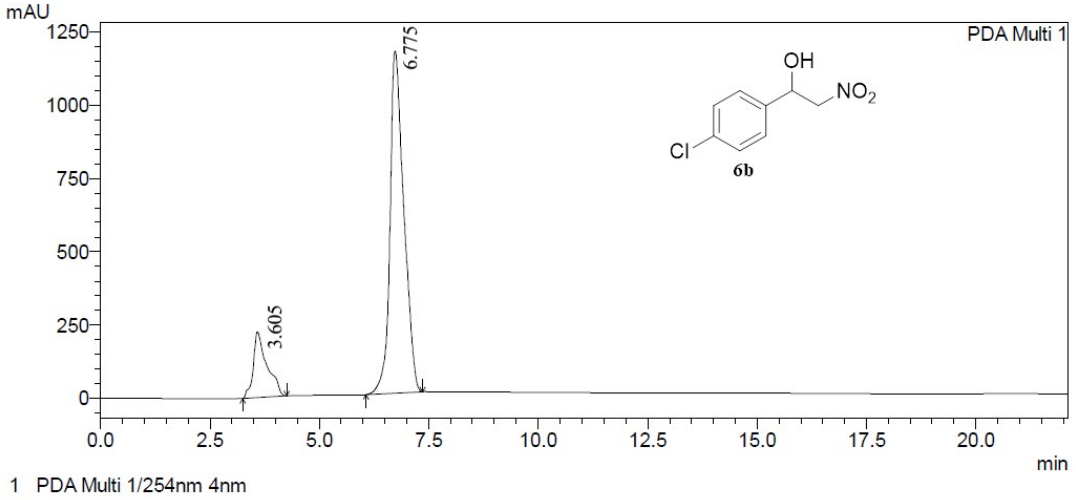


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.633	1877623	8633	49.784	48.360
2	6.775	1973568	8839	50.216	51.640
Total		3851191	17472	100.000	100.000

Figure S114: HPLC chromatogram of (**6b**) Racemic mixture.

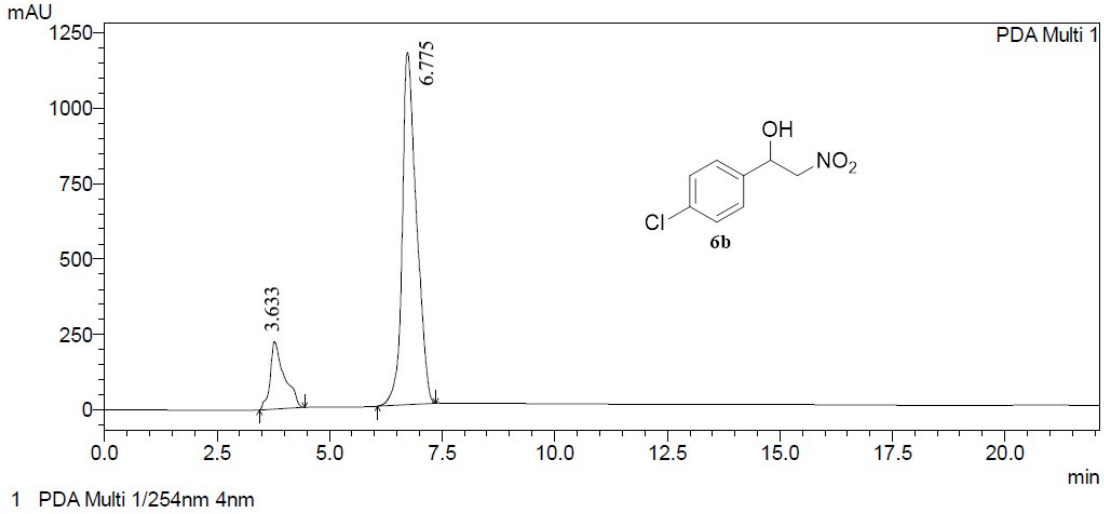


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.605	148617	5305	3.481	2.623
2	6.775	4120354	196930	96.519	97.377
Total		4268971	202235	100.000	100.000

Figure S115: HPLC chromatogram of (**6b**) in the presence organocatalyst (**14**) and CH_3OH/room temperature condition.

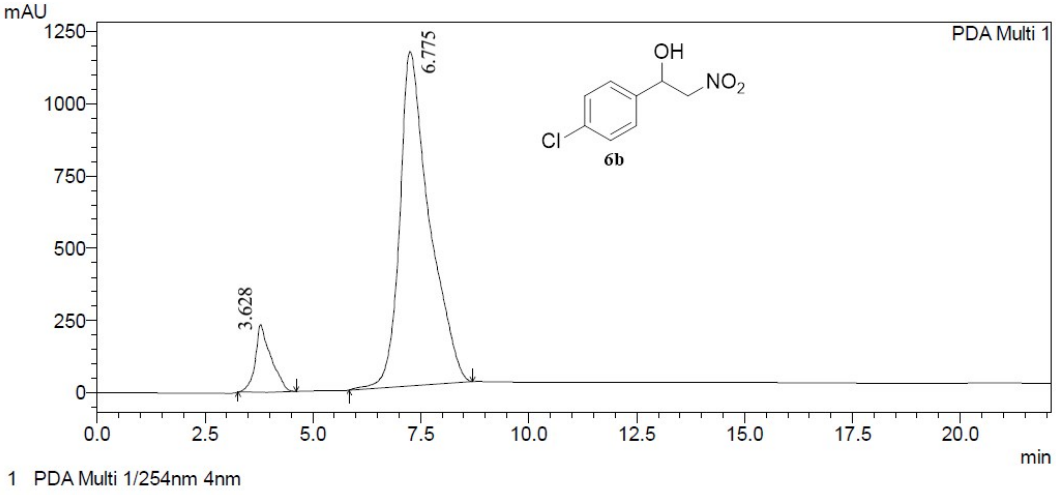


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.633	77623	1133	3.784	11.360
2	6.775	1973568	8839	96.216	88.640
Total		2051191	9971	100.000	100.000

Figure S116: HPLC chromatogram of (**6b**) in the presence organocatalyst (**15**) and CH_3OH/room temperature condition.

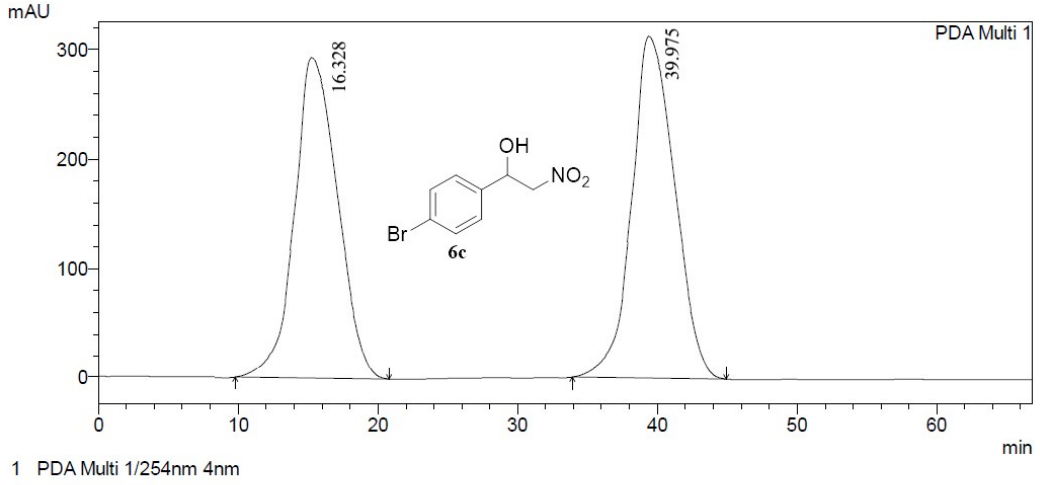


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.628	102253	2798	8.634	46.168
2	6.775	1082036	3263	91.366	53.832
Total		1184289	6061	100.000	100.000

Figure S117: HPLC chromatogram of (**6b**) in the presence organocatalyst (**16**) and CH_3OH/room temperature condition.

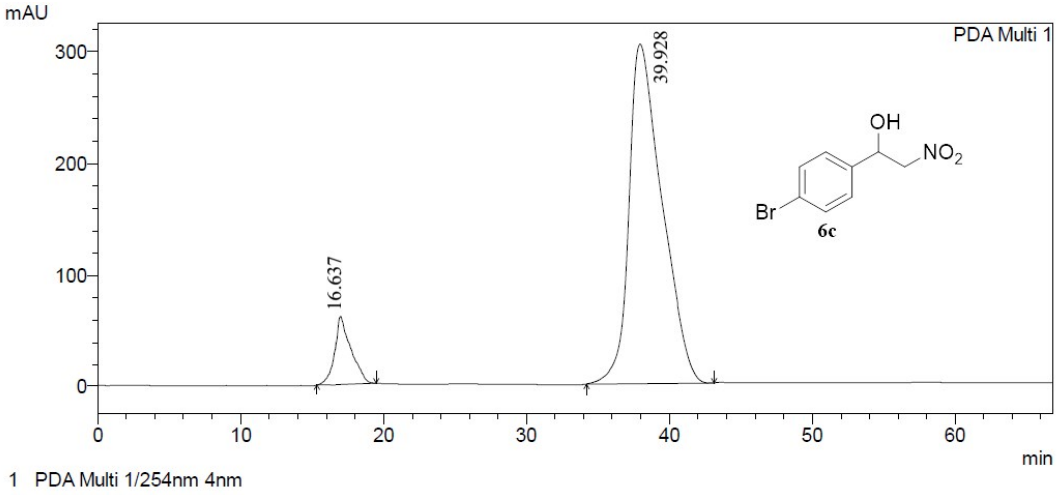


PeakTable

PDA Ch1 244nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.328	4011796	185535	49.086	47.286
2	39.975	4120354	196930	50.914	52.714
Total		8132150	382465	100.000	100.000

Figure S118: HPLC chromatogram of (**6c**) Racemic mixture.

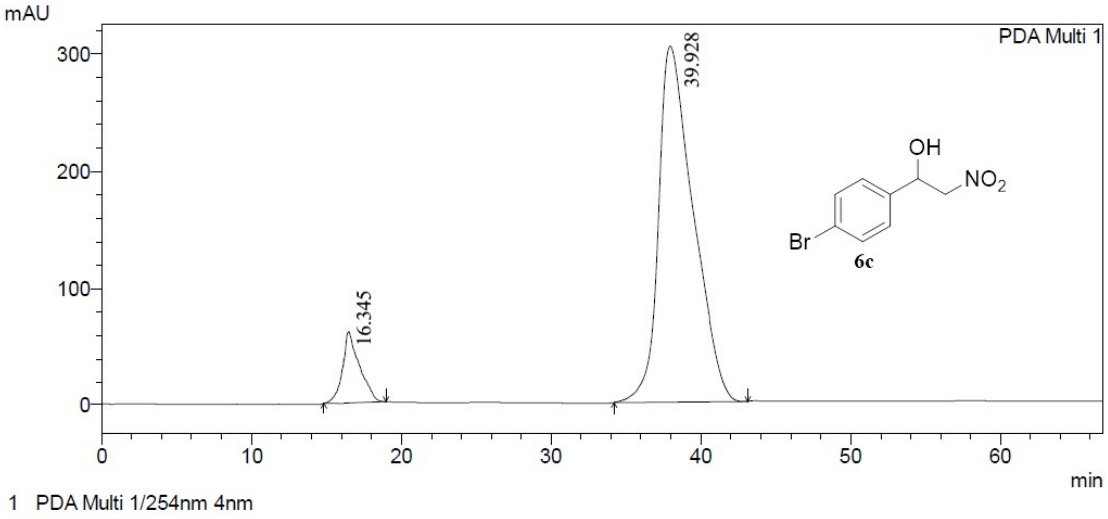


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.637	42124	15	4.347	0.476
2	39.928	926878	3162	95.653	99.524
Total		969002	3177	100.000	100.000

Figure S119: HPLC chromatogram of (**6c**) in the presence organocatalyst (**14**) and CH_3OH/room temperature condition.

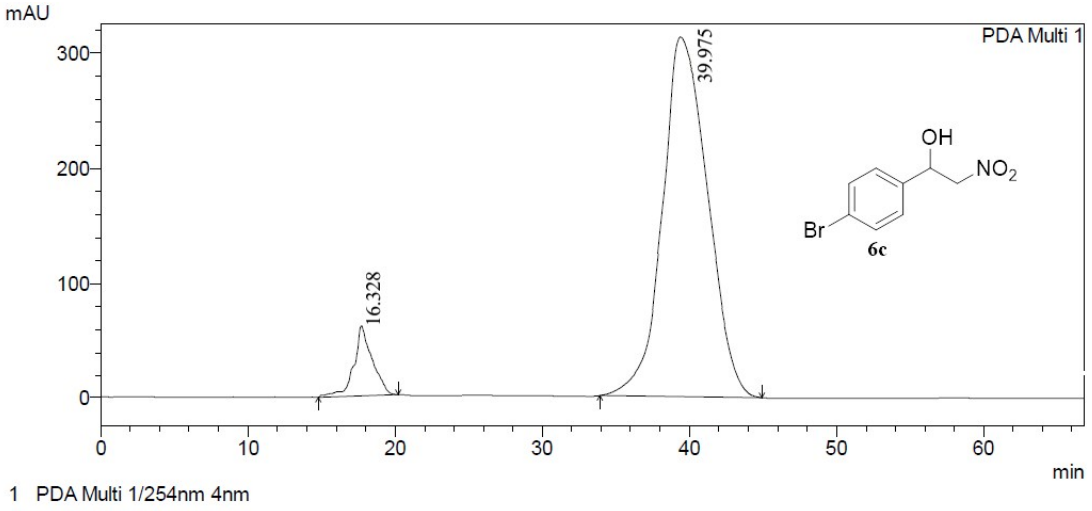


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.345	54454	605	4.791	15.650
2	39.928	1082036	3263	95.209	84.350
Total		1136491	3868	100.000	100.000

Figure S120: HPLC chromatogram of (**6c**) in the presence organocatalyst (**15**) and CH_3OH/room temperature condition.

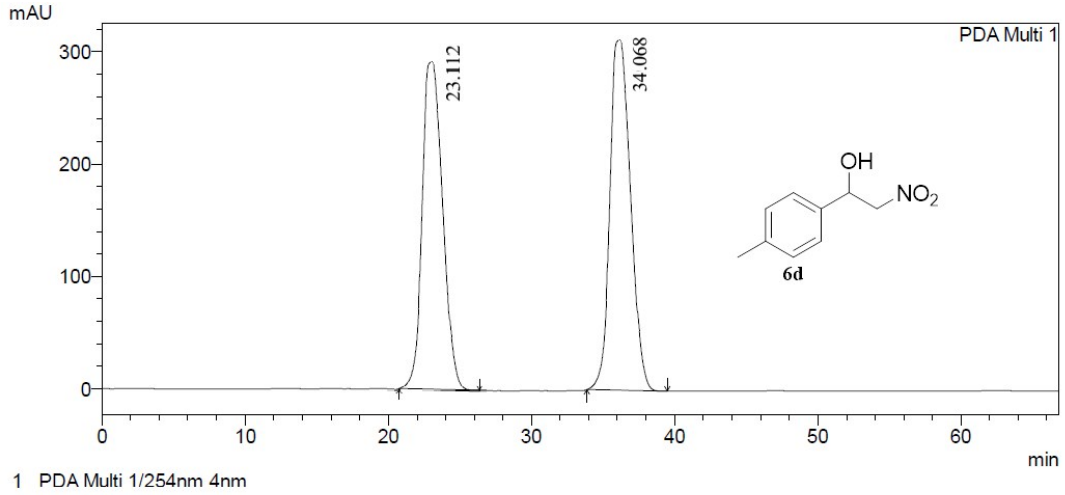


PeakTable

PDA Ch1 244nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.328	411796	35535	9.086	15.286
2	39.975	4120354	196930	90.914	84.714
Total		4532150	232465	100.000	100.000

Figure S121: HPLC chromatogram of (**6c**) in the presence organocatalyst (**16**) and CH_3OH/room temperature condition.

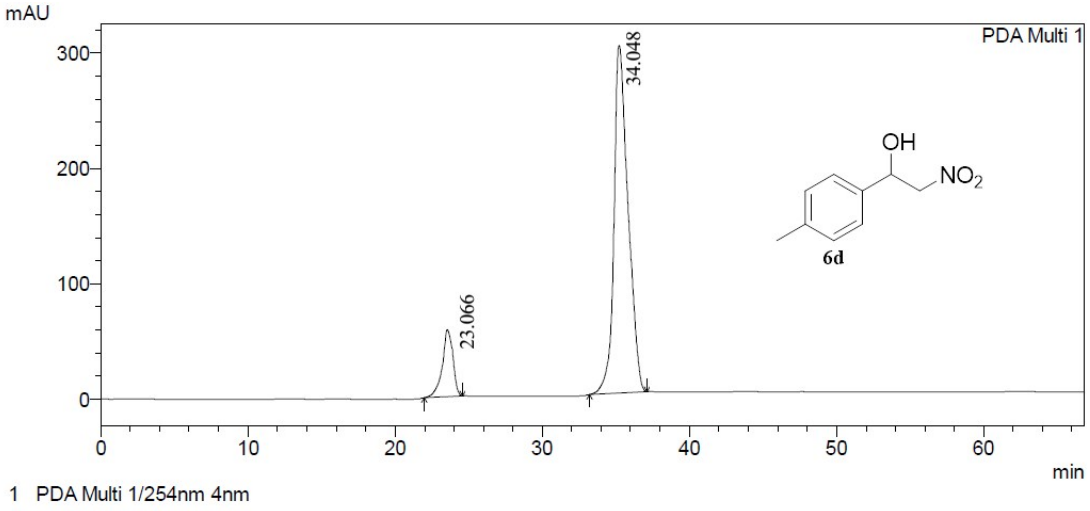


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.112	9187611	102591	49.393	48.999
2	34.068	9236738	103209	50.607	51.001
Total		18424349	205800	100.000	100.000

Figure S122: HPLC chromatogram of (**6d**) Racemic mixture.

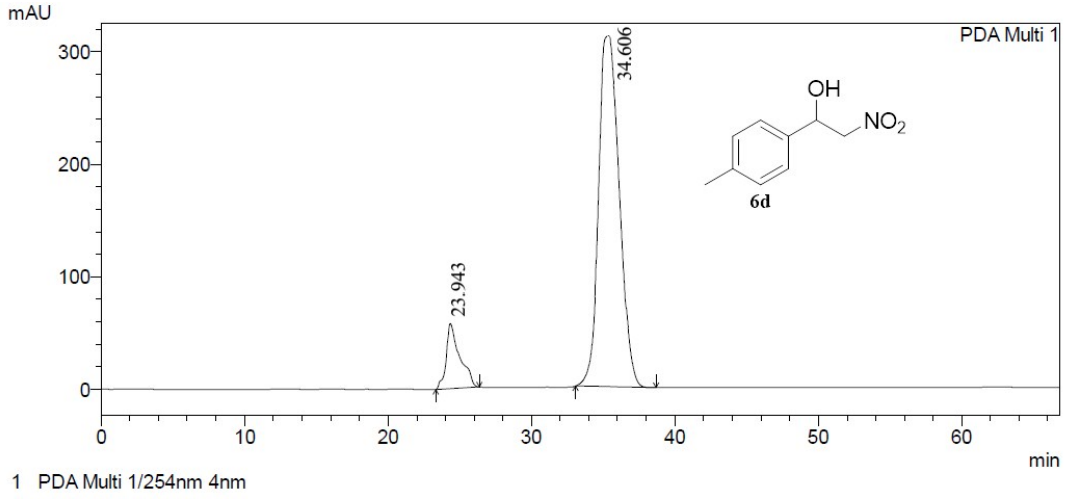


PeakTable

PDA Ch1 240nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.066	251466	807	3.258	3.919
2	34.048	7466737	19786	96.742	96.081
Total		7718203	20593	100.000	100.000

Figure S123: HPLC chromatogram of (**6d**) in the presence organocatalyst (**14**) and CH_3OH/room temperature condition.

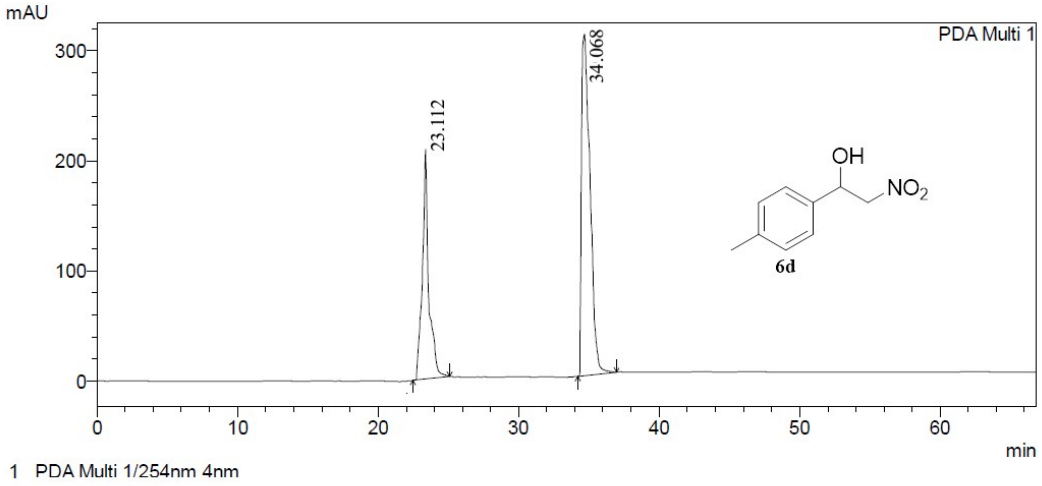


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.943	42124	15	4.347	0.476
2	34.606	926878	3162	95.653	99.524
Total		969002	3177	100.000	100.000

Figure S124: HPLC chromatogram of (**6d**) in the presence organocatalyst (**15**) and CH_3OH/room temperature condition.

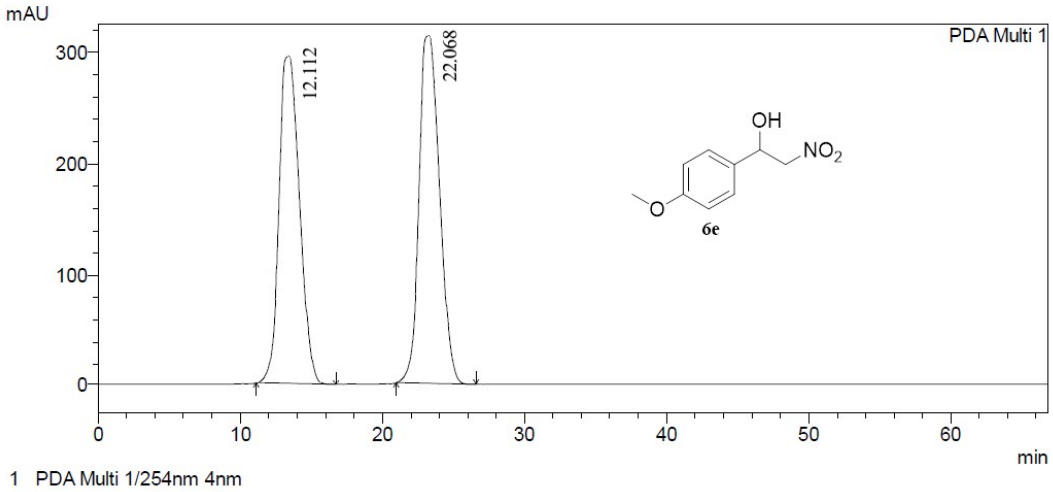


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.112	1187611	32591	11.393	23.999
2	34.068	9236738	103209	88.607	76.001
Total		10424349	135800	100.000	100.000

Figure S125: HPLC chromatogram of (**6d**) in the presence organocatalyst (**16**) and CH_3OH/room temperature condition.

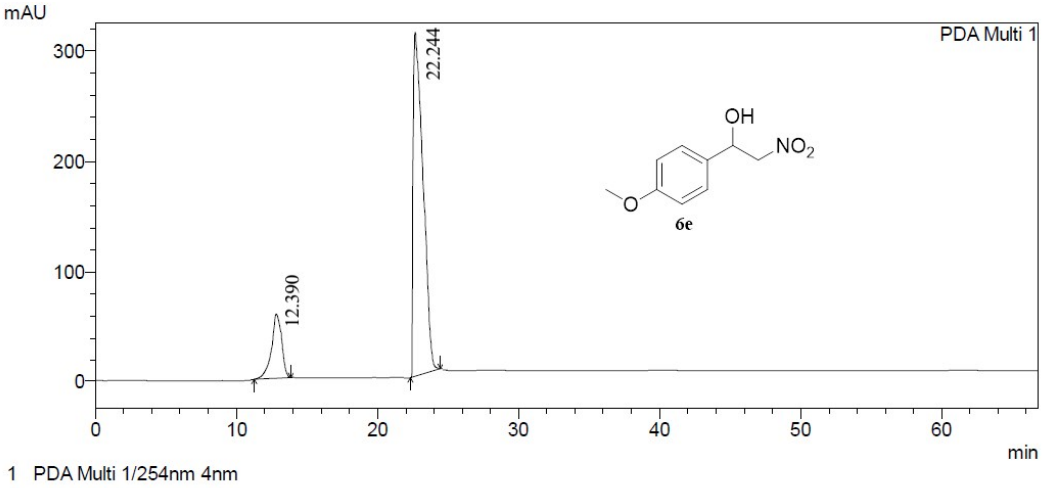


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.112	9065393	95256	49.606	48.580
2	22.068	9151863	102571	50.394	51.420
Total		18217256	197826	100.000	100.000

Figure S126: HPLC chromatogram of (**6e**) Racemic mixture.

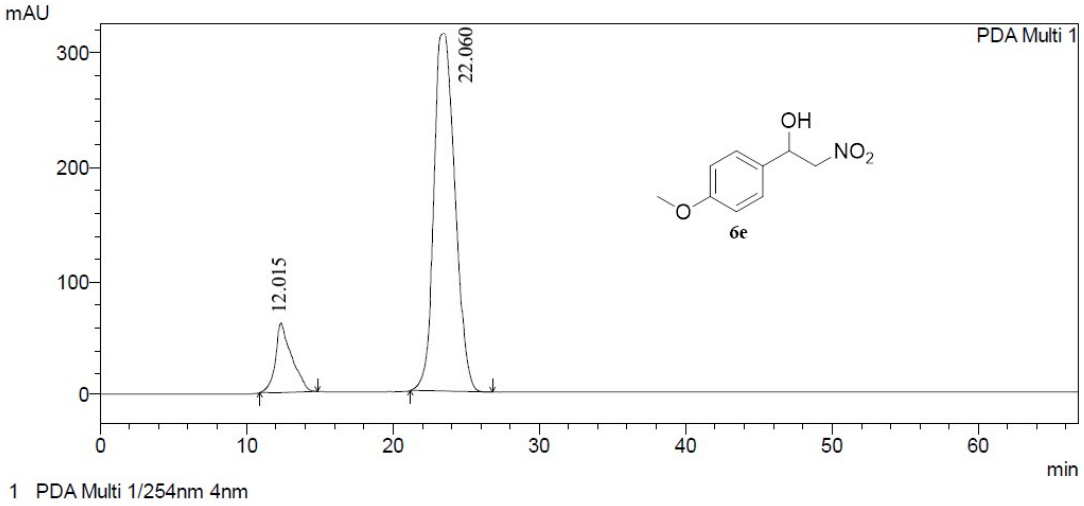


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.390	983580	48963	2.555	6.111
2	22.244	62251896	752263	98.445	93.889
Total		63235475	801226	100.000	100.000

Figure S127: HPLC chromatogram of (**6e**) in the presence organocatalyst (**14**) and CH_3OH/room temperature condition.

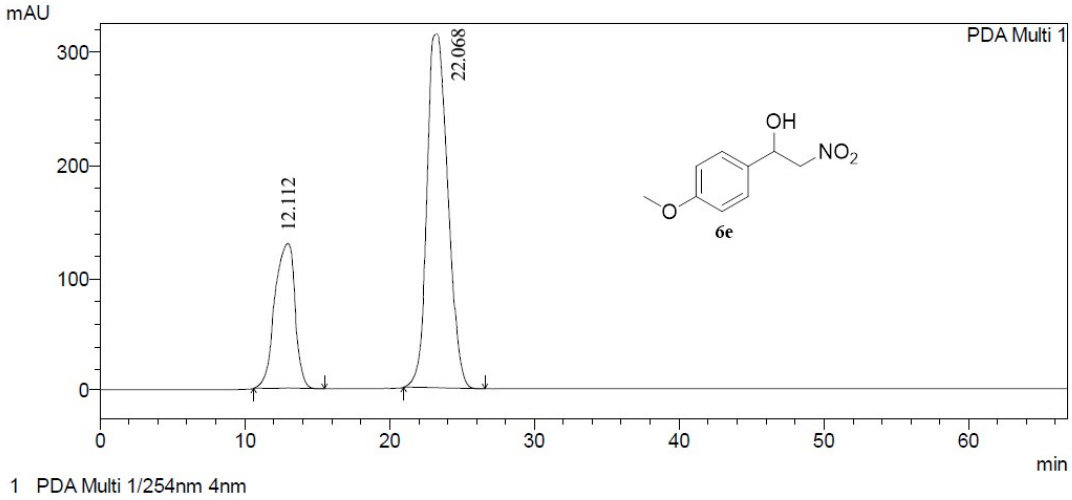


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.015	1860393	50970	2.943	6.394
2	22.060	61357098	746211	97.057	93.606
Total		63217491	797180	100.000	100.000

Figure S128: HPLC chromatogram of (**6e**) in the presence organocatalyst (**15**) and CH_3OH/room temperature condition.

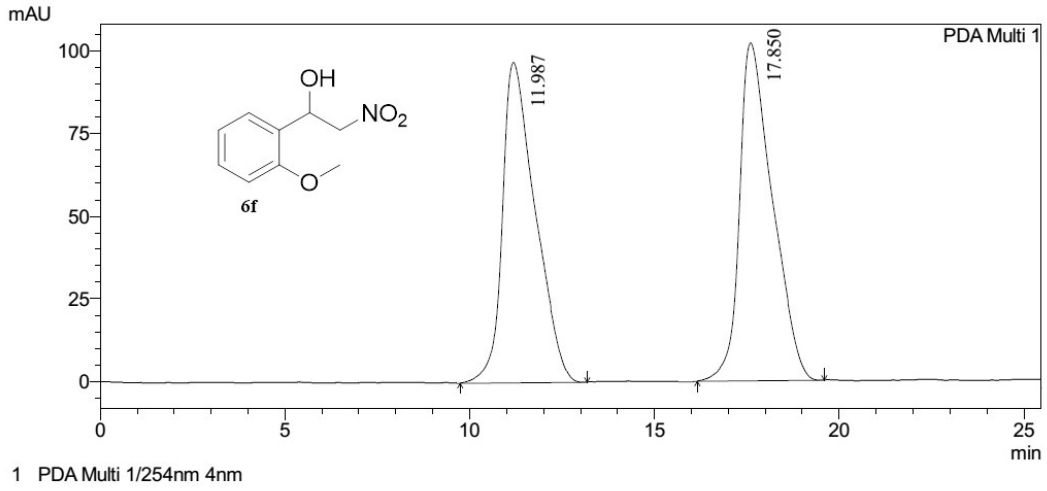


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.112	1565393	35256	14.606	25.580
2	22.068	9151863	102571	85.394	74.420
Total		10717256	137826	100.000	100.000

Figure S129: HPLC chromatogram of (**6e**) in the presence organocatalyst (**16**) and CH_3OH/room temperature condition.

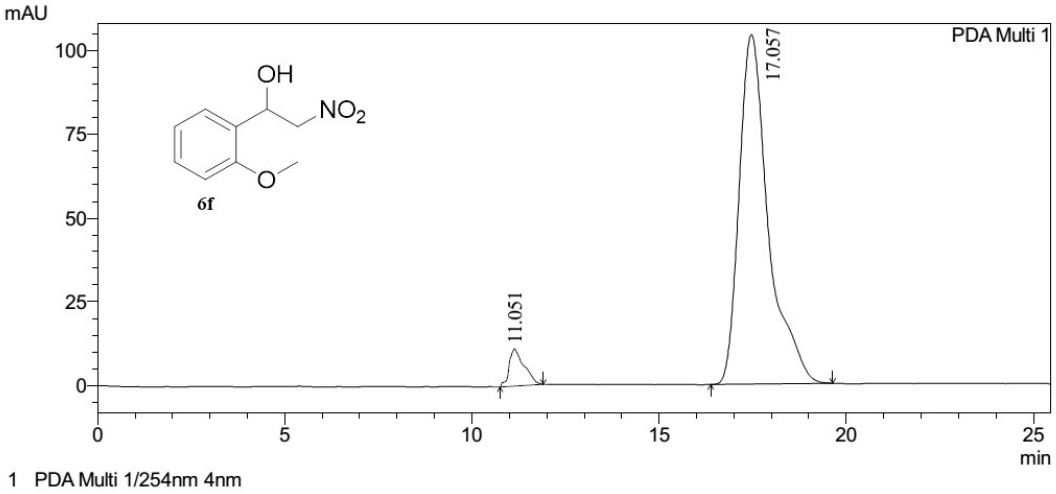


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.987	5517457	97410	49.838	48.631
2	17.850	5653681	104342	50.162	51.369
Total		11171138	201752	100.000	100.000

Figure S130: HPLC chromatogram of (**6f**) Racemic mixture.

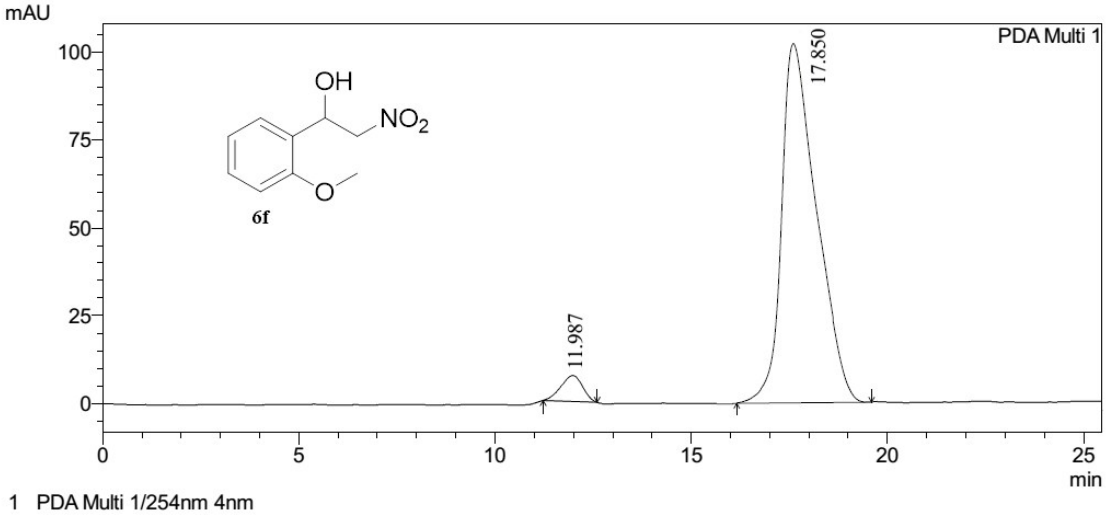


PeakTable

PDA Ch1 265nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.051	13297	583	4.443	17.362
2	17.057	286006	2776	95.557	82.638
Total		299303	3360	100.000	100.000

Figure S131: HPLC chromatogram of (**6f**) in the presence organocatalyst (**14**) and CH_3OH/room temperature condition.

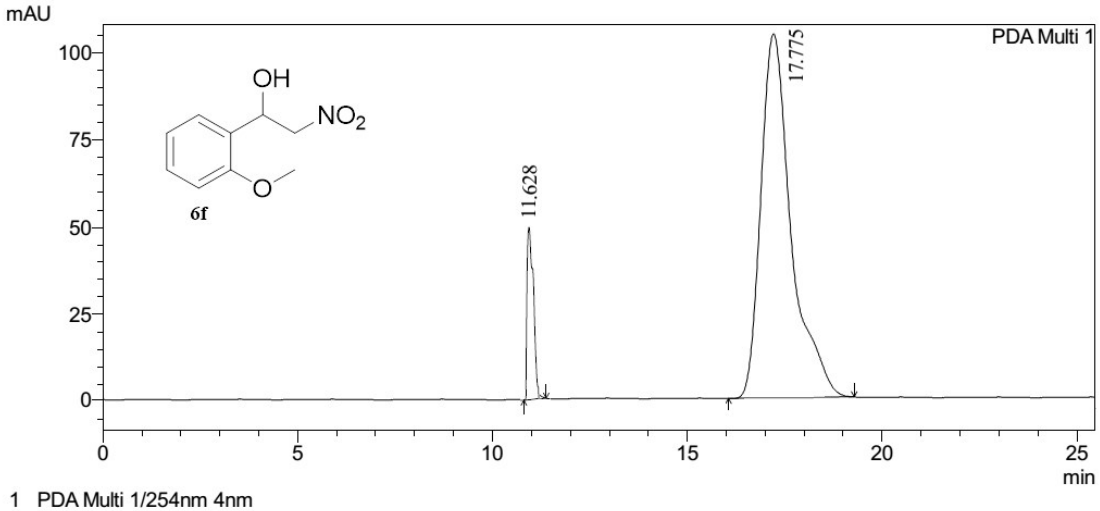


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.987	287457	7410	4.838	6.631
2	17.850	5653681	104342	95.162	93.369
Total		5941138	111752	100.000	100.000

Figure S132: HPLC chromatogram of (**6f**) in the presence organocatalyst (**15**) and CH_3OH/room temperature condition.



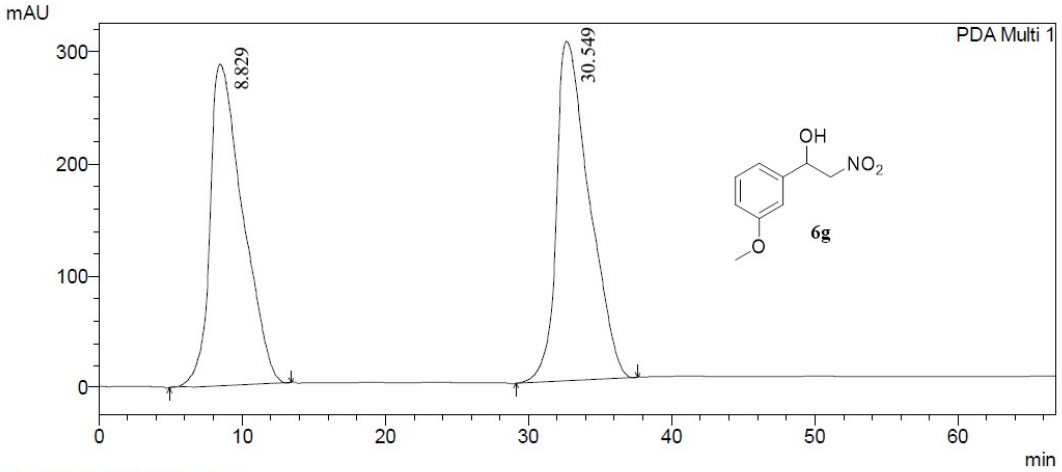
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 244nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.628	605497	51109	12.812	20.605
2	17.775	4120354	196930	87.188	79.395
Total		4725851	248039	100.000	100.000

Figure S133: HPLC chromatogram of (**6f**) in the presence organocatalyst (**16**) and CH_3OH/room temperature condition.



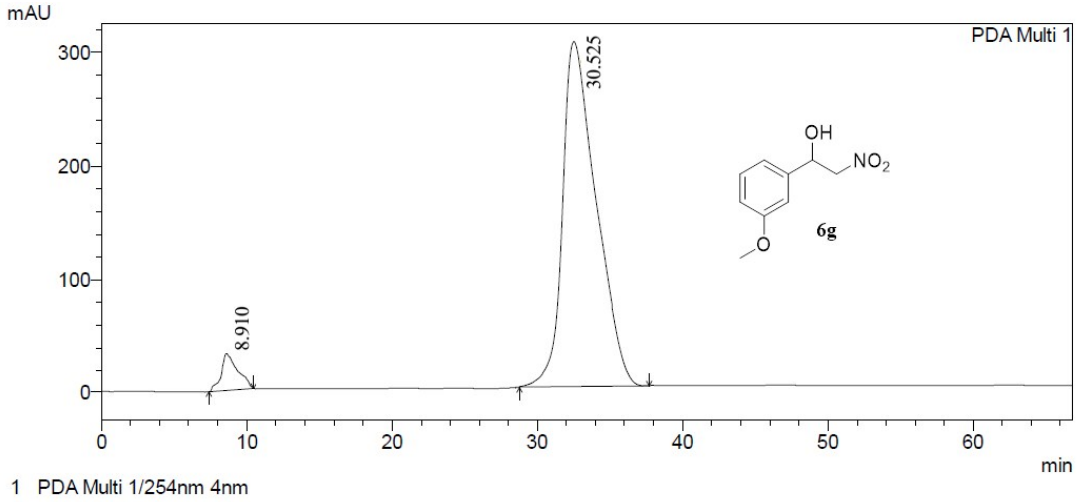
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.829	1877623	8433	49.784	48.360
2	30.549	1973568	8839	50.216	51.640
Total		3851191	17272	100.000	100.000

Figure S134: HPLC chromatogram of (**6g**) Racemic mixture.

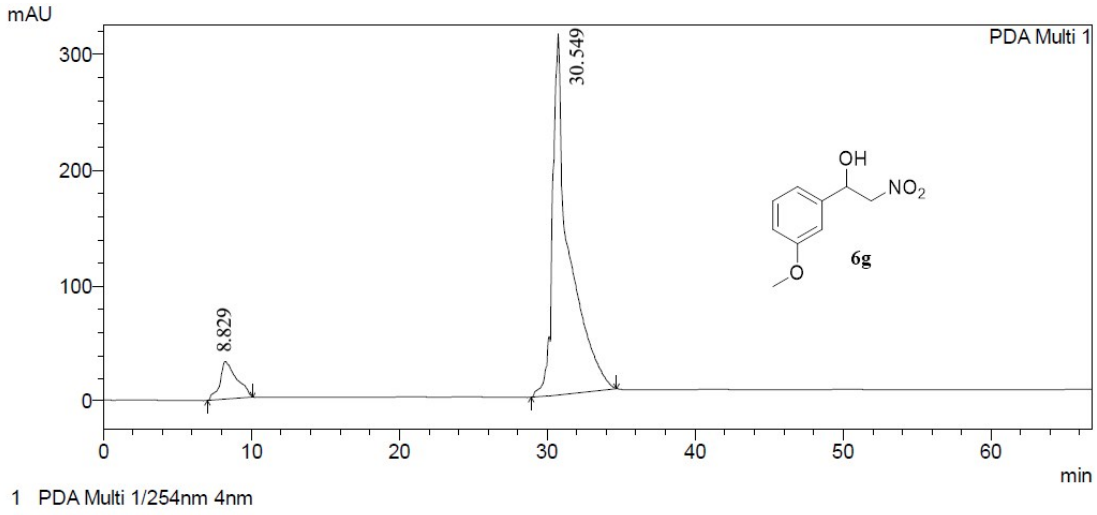


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.910	77623	1133	3.784	11.360
2	30.525	1973568	8839	96.216	88.640
Total		2051191	9971	100.000	100.000

Figure S135: HPLC chromatogram of (**6g**) in the presence organocatalyst (**14**) and CH_3OH/room temperature condition.

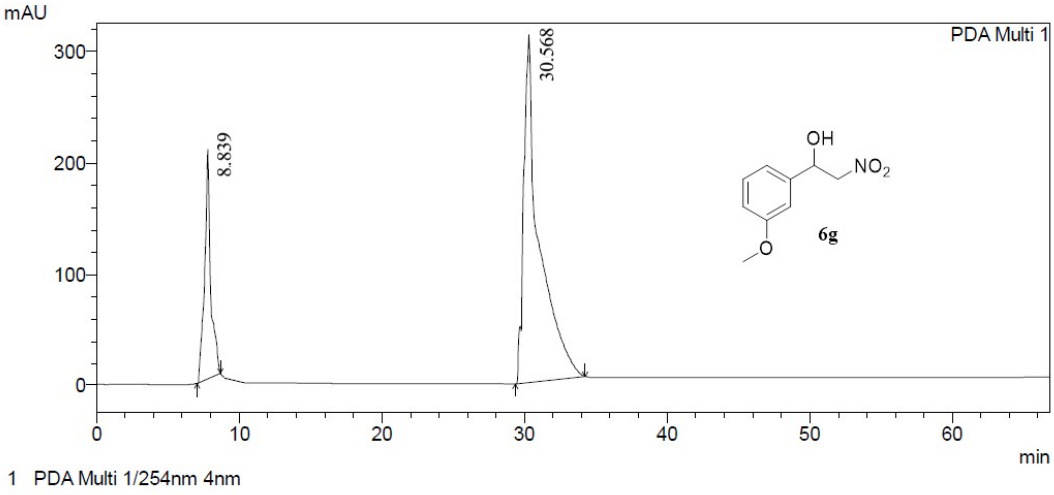


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.829	77623	1133	3.784	11.360
2	30.549	1973568	8839	96.216	88.640
Total		2051191	9971	100.000	100.000

Figure S136: HPLC chromatogram of (**6g**) in the presence organocatalyst (**15**) and CH_3OH/room temperature condition.

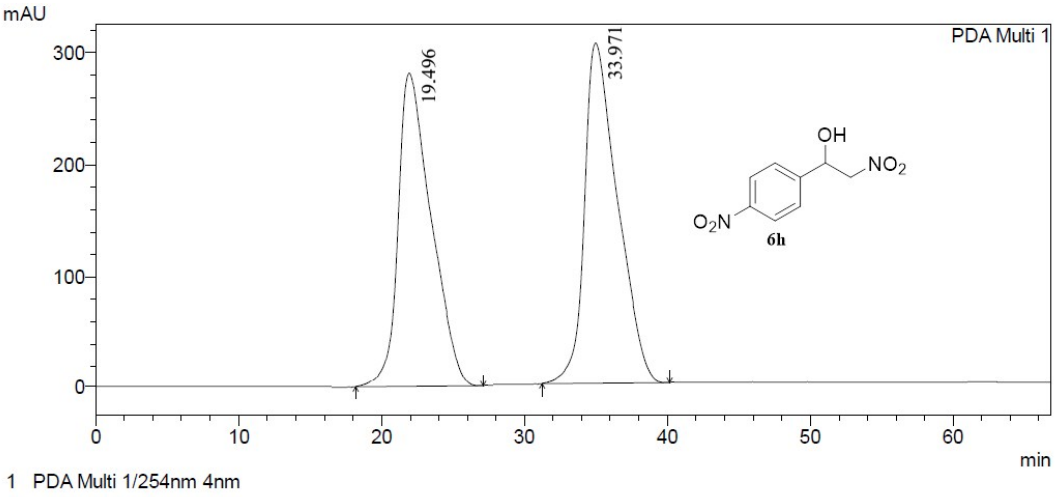


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.839	1977554	49261	10.877	20.371
2	30.568	16202761	192554	89.123	79.629
Total		18180315	241814	100.000	100.000

Figure S137: HPLC chromatogram of (**6g**) in the presence organocatalyst (**16**) and CH_3OH/room temperature condition.

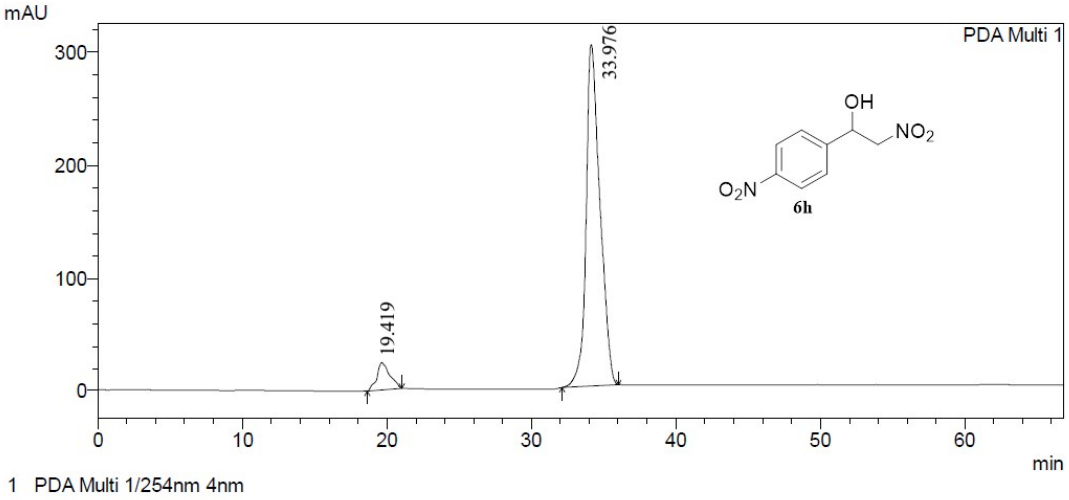


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.496	19741162	230817	49.786	48.630
2	33.971	20622334	254758	50.214	51.370
Total		40363496	485575	100.000	100.000

Figure S138: HPLC chromatogram of (**6h**) Racemic mixture.

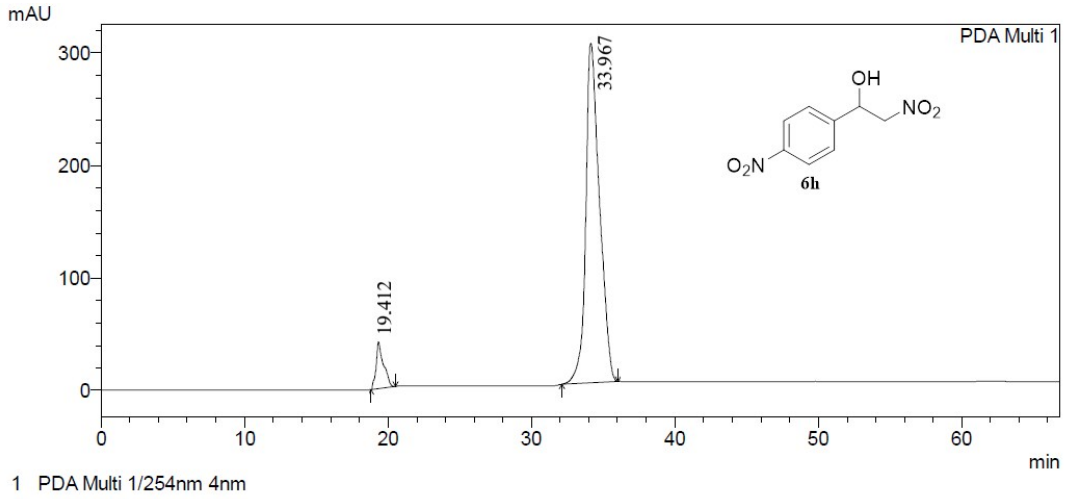


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.419	19096	450	0.588	4.057
2	33.976	3228770	10643	99.412	95.943
Total		3247867	11093	100.000	100.000

Figure S139: HPLC chromatogram of (**6h**) in the presence organocatalyst (**14**) and CH_3OH/room temperature condition.

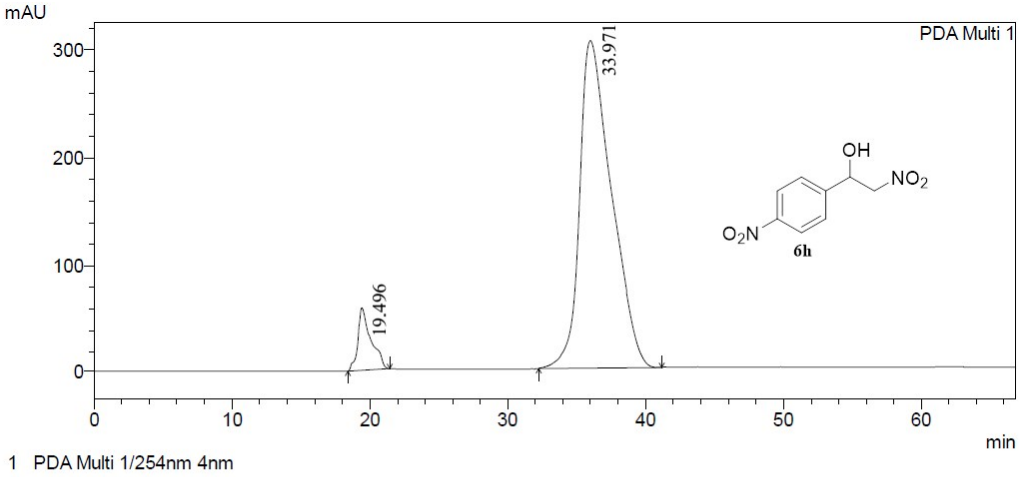


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.412	51471	1896	1.178	14.083
2	33.967	4317152	11569	98.822	85.917
Total		4368624	13465	100.000	100.000

Figure S140: HPLC chromatogram of (**6h**) in the presence organocatalyst (**15**) and CH_3OH/room temperature condition.

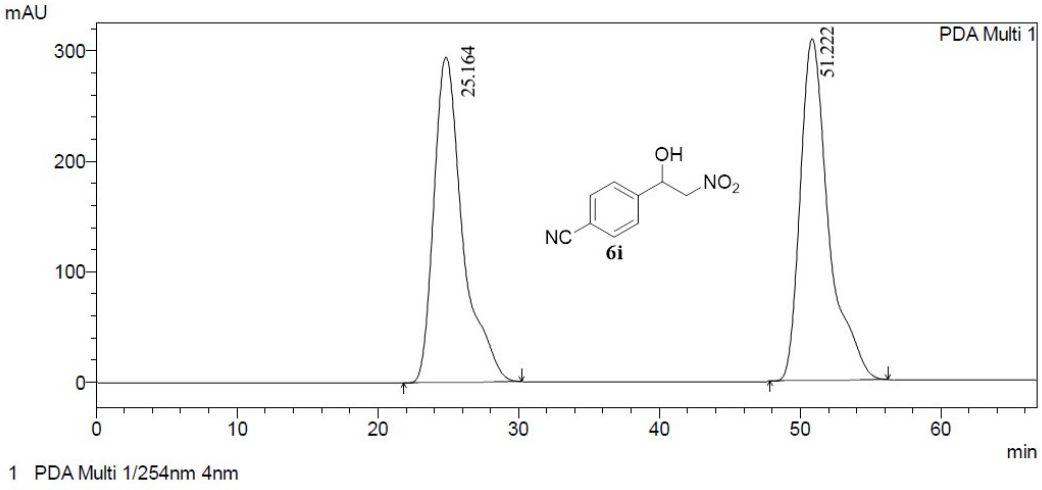


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.496	1741162	50817	7.786	16.630
2	33.971	20622334	254758	92.214	83.370
Total		22363496	305575	100.000	100.000

Figure S141: HPLC chromatogram of (**6h**) in the presence organocatalyst (**16**) and CH_3OH/room temperature condition.

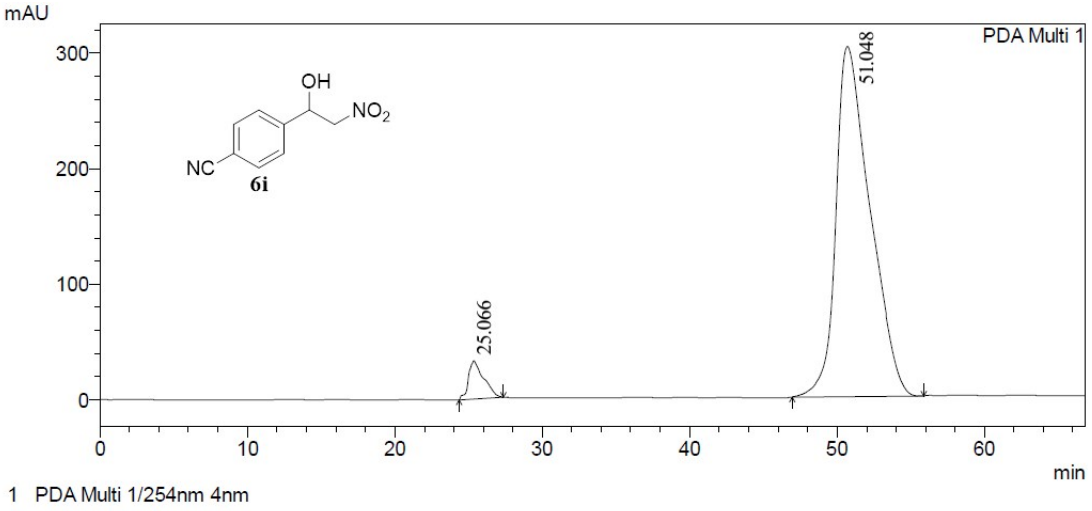


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.164	35721829	371448	49.247	48.174
2	51.222	36525852	399404	50.753	51.826
Total		72247681	770851	100.000	100.000

Figure S142: HPLC chromatogram of (**6i**) Racemic mixture.

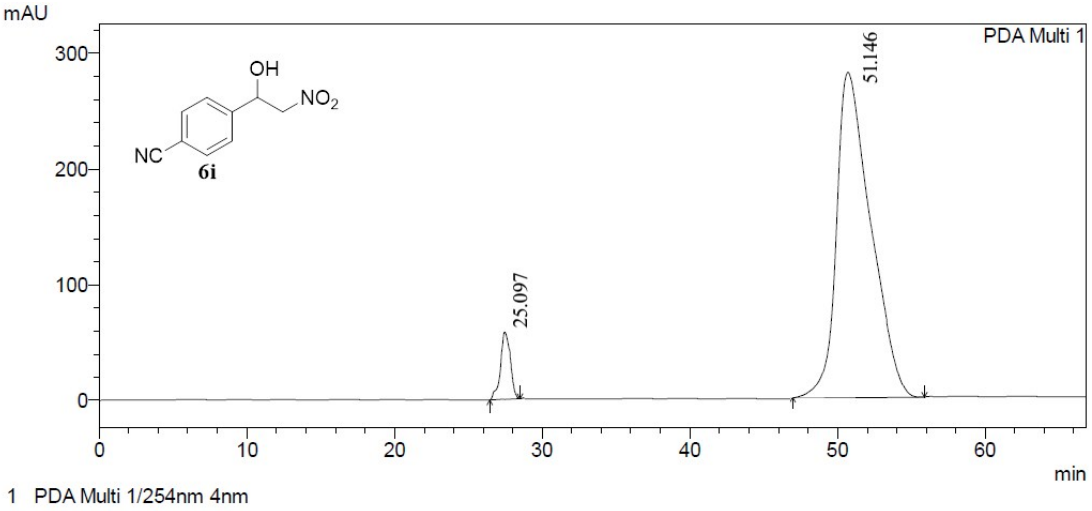


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.066	1896787	228145	0.457	9.206
2	51.048	412999376	2250170	99.543	90.794
Total		414896163	2478314	100.000	100.000

Figure S143: HPLC chromatogram of (**6i**) in the presence organocatalyst (**14**) and CH_3OH/room temperature condition.

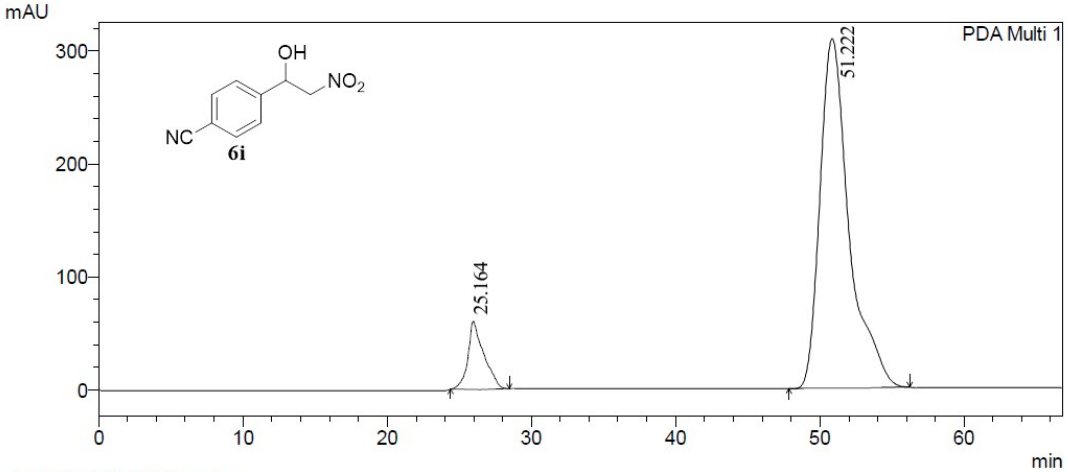


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.097	751420	46813	1.182	5.836
2	51.146	62830428	755323	98.818	94.164
Total		63581847	802136	100.000	100.000

Figure S144: HPLC chromatogram of (**6i**) in the presence organocatalyst (**15**) and CH_3OH/room temperature condition.

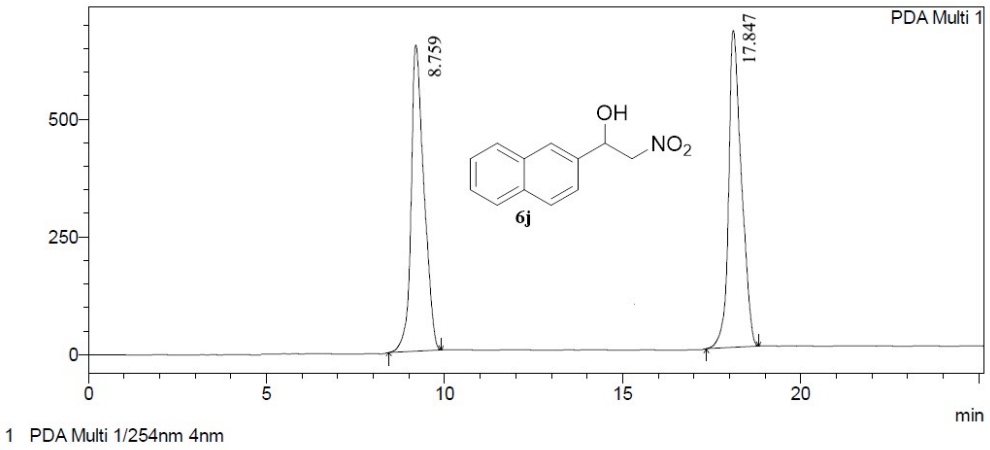


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.164	3721829	71448	9.247	15.174
2	51.222	36525852	399404	90.753	84.826
Total		40247681	470851	100.000	100.000

Figure S145: HPLC chromatogram of (**6i**) in the presence organocatalyst (**16**) and CH_3OH/room temperature condition.

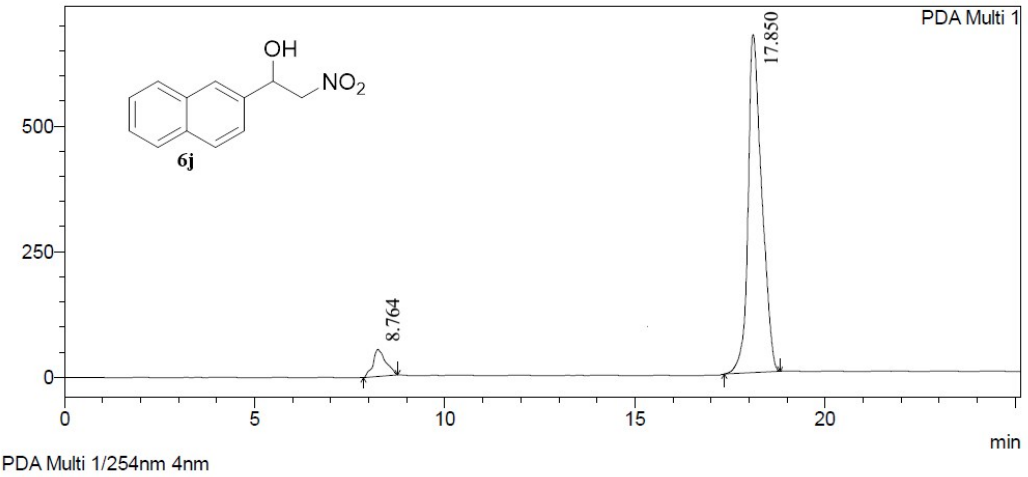


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.759	1222762	8981	49.643	48.704
2	17.847	1362622	9131	50.357	51.296
Total		2585384	18112	100.000	100.000

Figure S146: HPLC chromatogram of (**6j**) Racemic mixture.



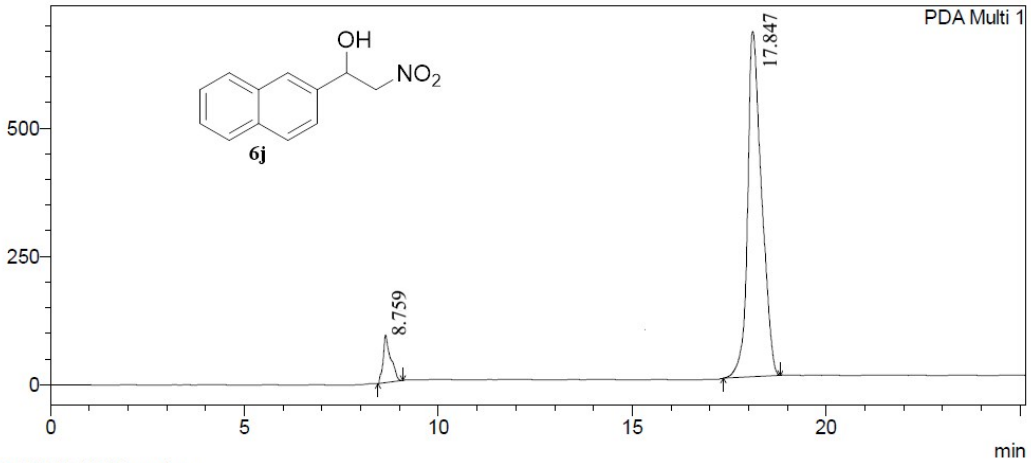
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.764	84159	819	1.470	0.779
2	17.850	5641798	104287	98.530	99.221
Total		5725958	105106	100.000	100.000

Figure S147: HPLC chromatogram of (**6j**) in the presence organocatalyst (**14**) and CH_3OH/room temperature condition.



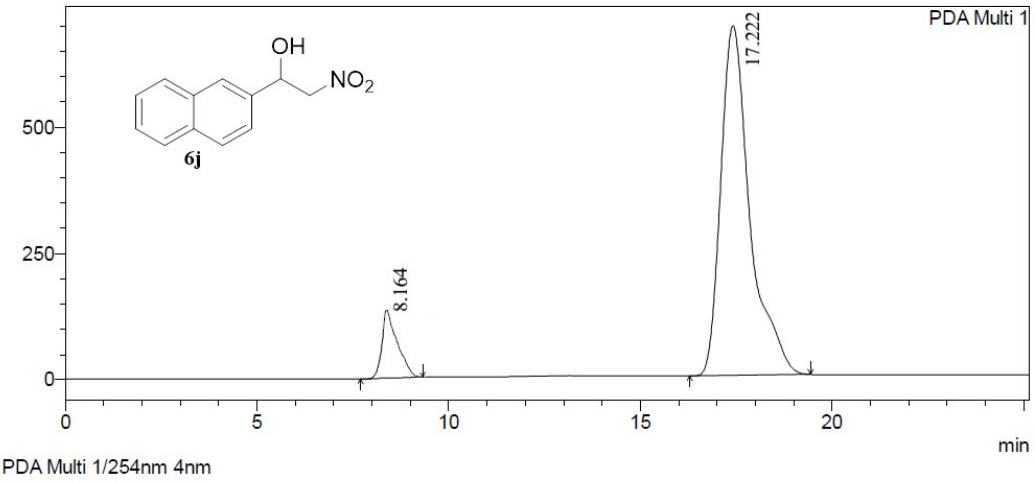
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.759	22762	981	1.643	9.704
2	17.847	1362622	9131	98.357	90.296
Total		1385384	10112	100.000	100.000

Figure S148: HPLC chromatogram of (**6j**) in the presence organocatalyst (**15**) and CH_3OH/room temperature condition.



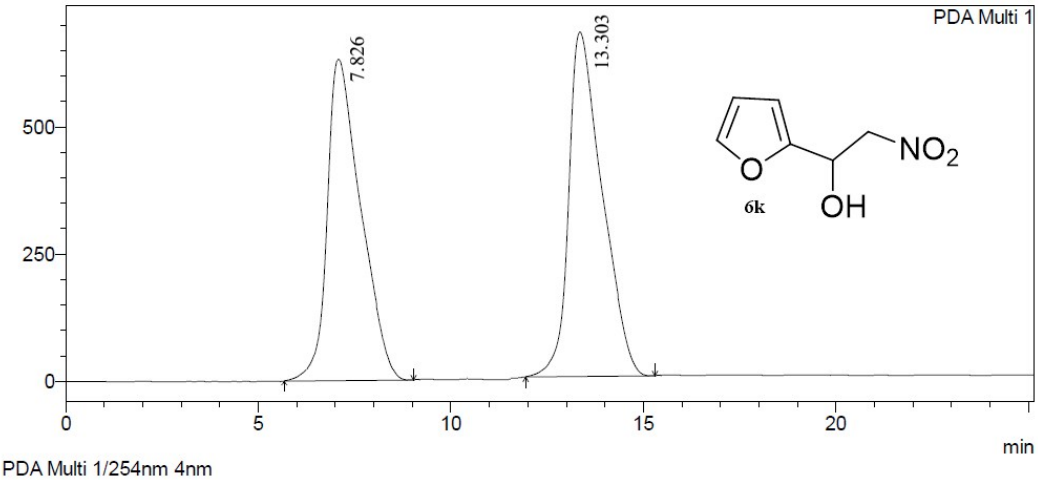
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.164	3721829	71448	9.247	15.174
2	17.222	36525852	399404	90.753	84.826
Total		40247681	470851	100.000	100.000

Figure S149: HPLC chromatogram of (**6j**) in the presence organocatalyst (**16**) and CH_3OH/room temperature condition.



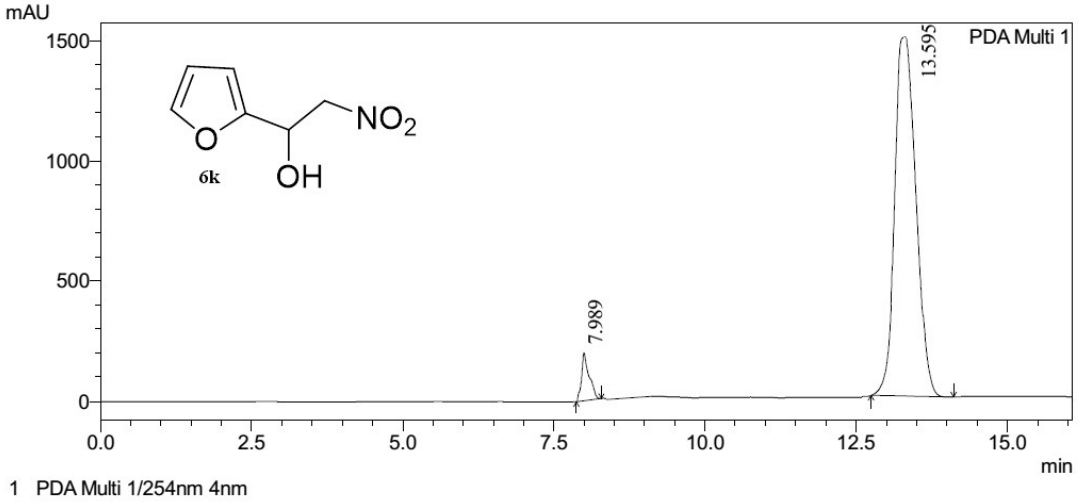
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.826	6338383	83187	49.326	48.090
2	13.303	6412071	85516	50.674	51.910
Total		12750455	168703	100.000	100.000

Figure S150: HPLC chromatogram of (**6k**) Racemic mixture.

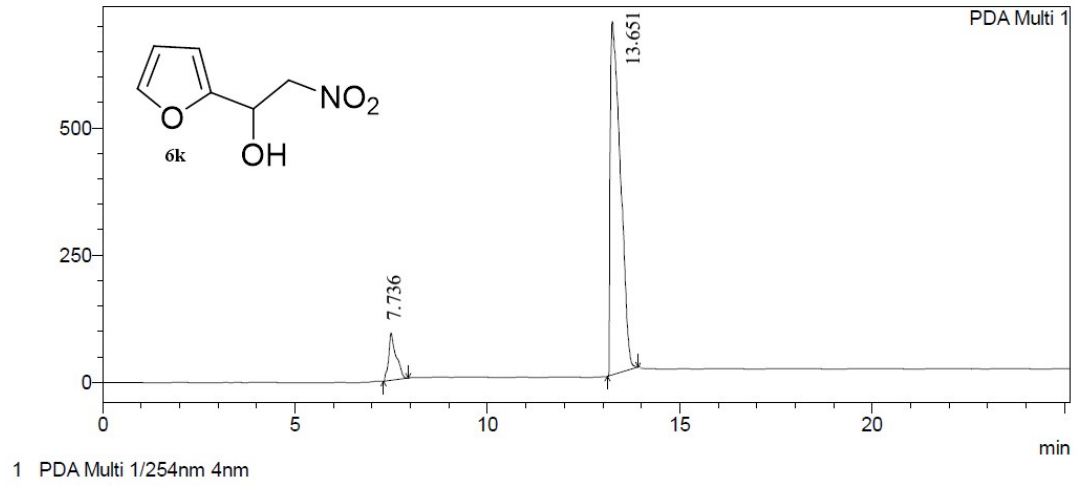


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.989	1860393	50970	2.943	6.394
2	13.595	61357098	746211	97.057	93.606
Total		63217491	797180	100.000	100.000

Figure S151: HPLC chromatogram of (**6k**) in the presence organocatalyst (**14**) and CH_3OH/room temperature condition.

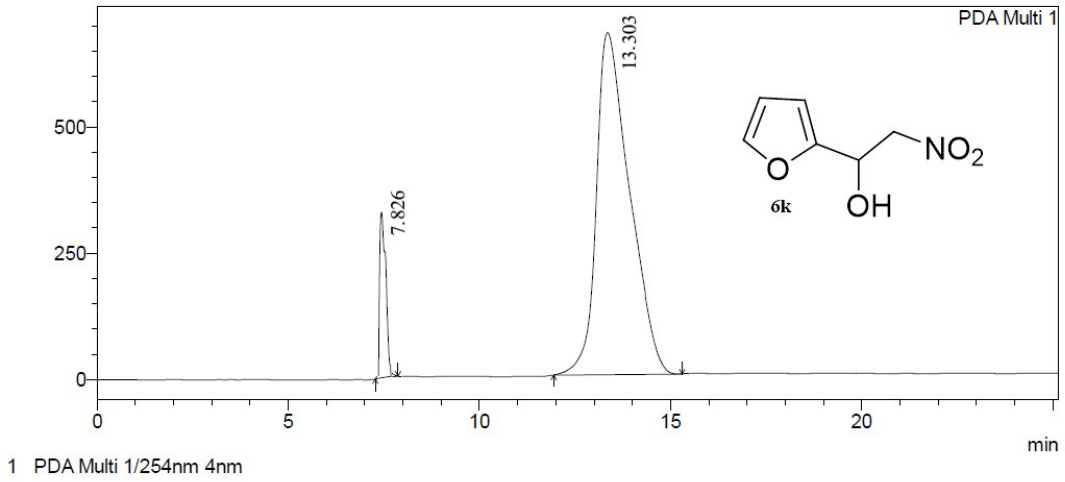


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.736	838351	21549	2.999	5.171
2	13.651	27112859	395206	97.001	94.829
Total		27951210	416755	100.000	100.000

Figure S152: HPLC chromatogram of (**6k**) in the presence organocatalyst (**15**) and CH_3OH/room temperature condition.



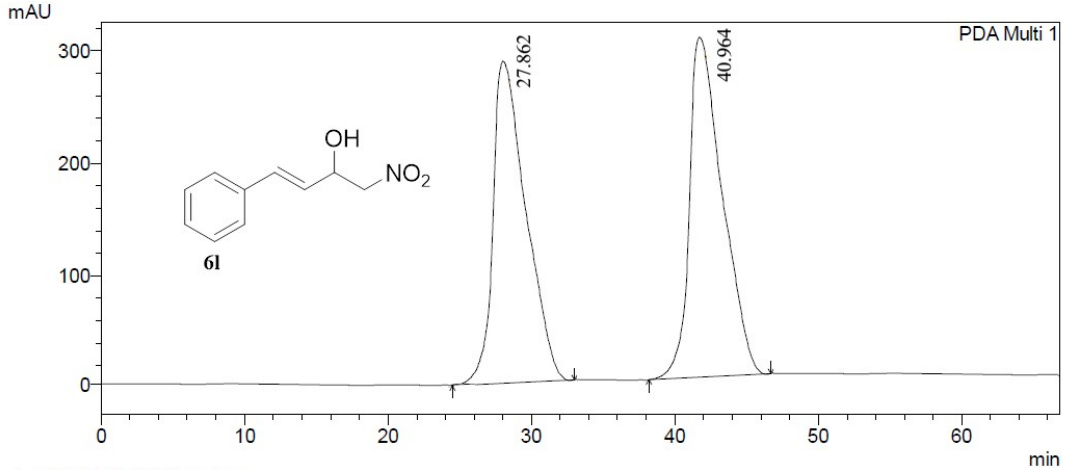
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.826	738383	30187	10.326	26.090
2	13.303	6412071	85516	89.674	73.910
Total		7150455	115703	100.000	100.000

Figure S153: HPLC chromatogram of (**6k**) in the presence organocatalyst (**16**) and CH_3OH/room temperature condition.



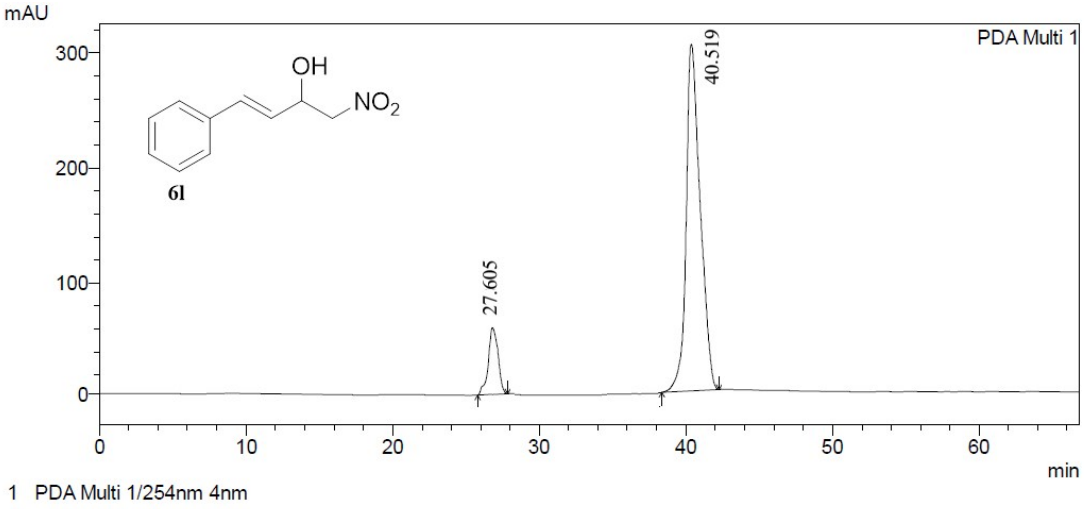
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.862	142638897	1365126	49.259	48.206
2	40.964	143622513	1483220	50.741	51.794
Total		286261409	2848346	100.000	100.000

Figure S154: HPLC chromatogram of (**6l**) Racemic mixture.

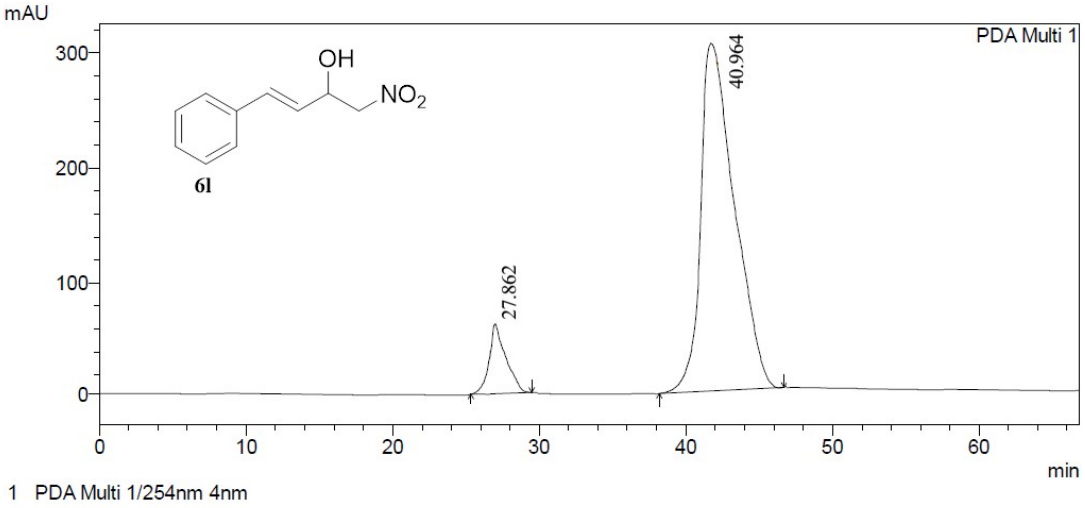


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.605	2066695	115427	2.129	27.502
2	40.519	95011537	304278	97.871	72.498
Total		97078231	419705	100.000	100.000

Figure S155: HPLC chromatogram of (**6l**) in the presence organocatalyst (**14**) and CH_3OH/room temperature condition.

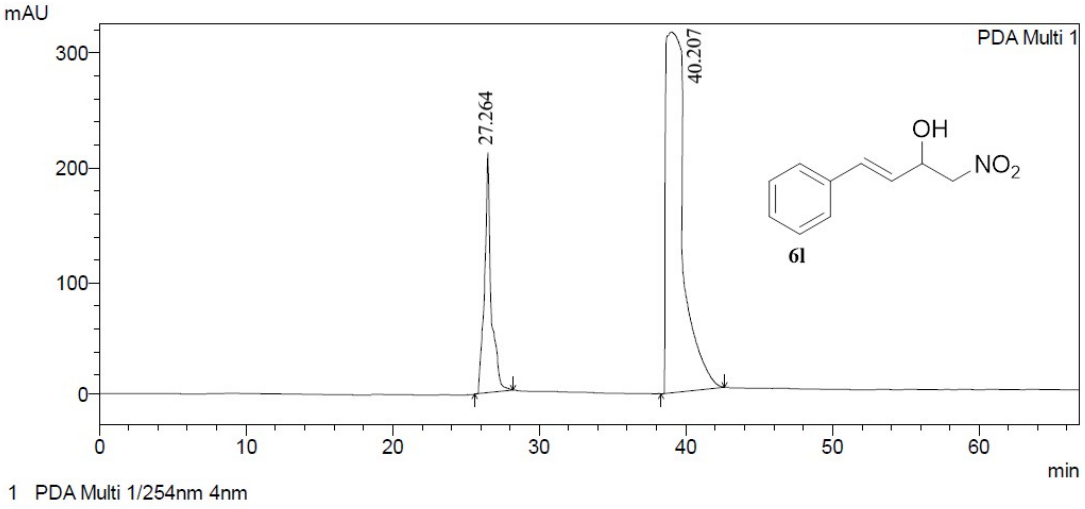


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.862	4838897	65126	3.259	4.206
2	40.964	143622513	1483220	96.741	95.794
Total		148461409	1548346	100.000	100.000

Figure S156: HPLC chromatogram of (**6l**) in the presence organocatalyst (**15**) and CH_3OH/room temperature condition.

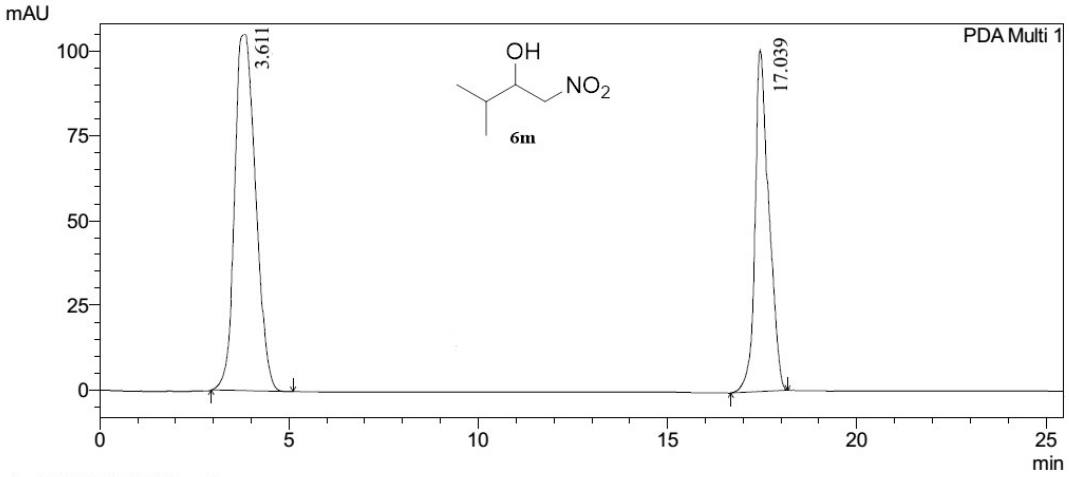


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.264	957358	32159	13.205	27.684
2	40.207	6292723	84006	86.795	72.316
Total		7250081	116165	100.000	100.000

Figure S157: HPLC chromatogram of (**6l**) in the presence organocatalyst (**16**) and CH_3OH/room temperature condition.

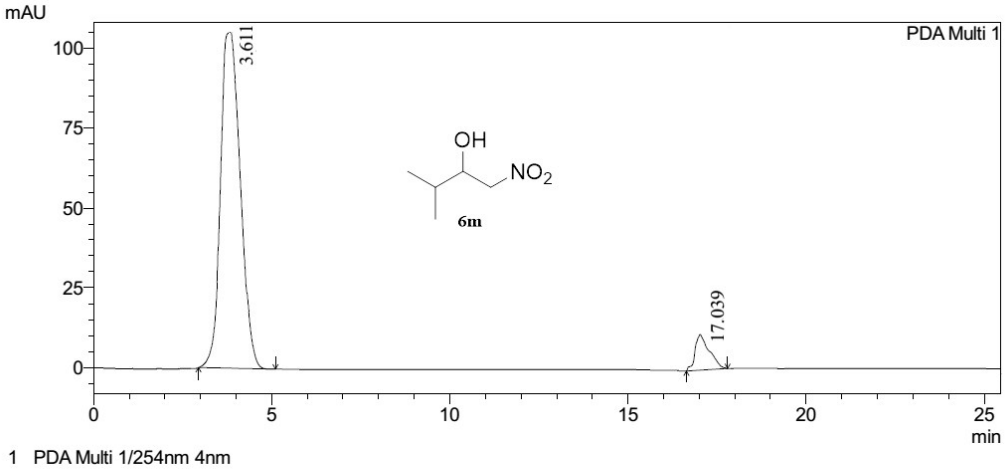


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.611	2753234	112968	50.961	51.633
2	17.039	2615892	111219	49.039	48.367
Total		5369127	224187	100.000	100.000

Figure S158: HPLC chromatogram of (**6m**) Racemic mixture.

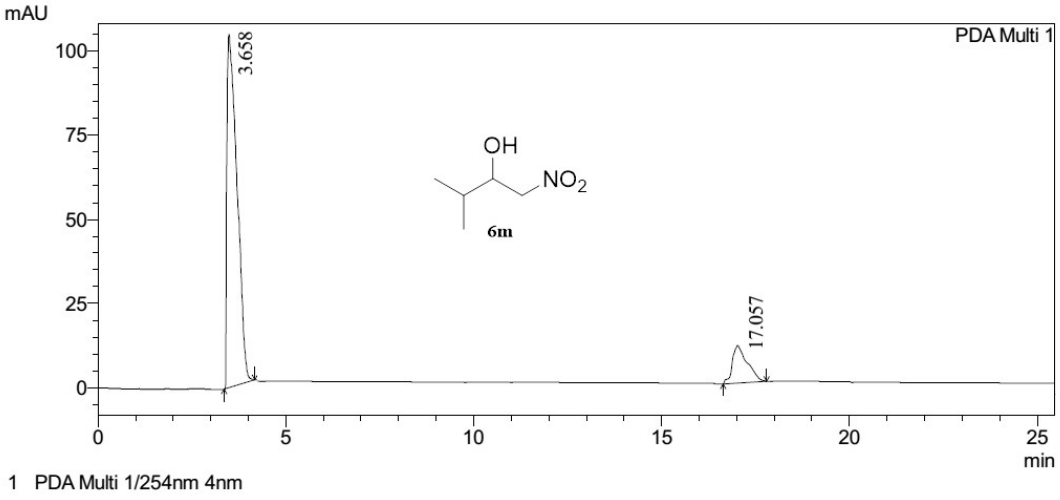


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.611	2753234	112968	95.961	98.933
2	17.039	115892	1219	4.039	1.067
Total		2869127	114187	100.000	100.000

Figure S159: HPLC chromatogram of (**6m**) in the presence organocatalyst (**14**) and CH_3OH/room temperature condition.

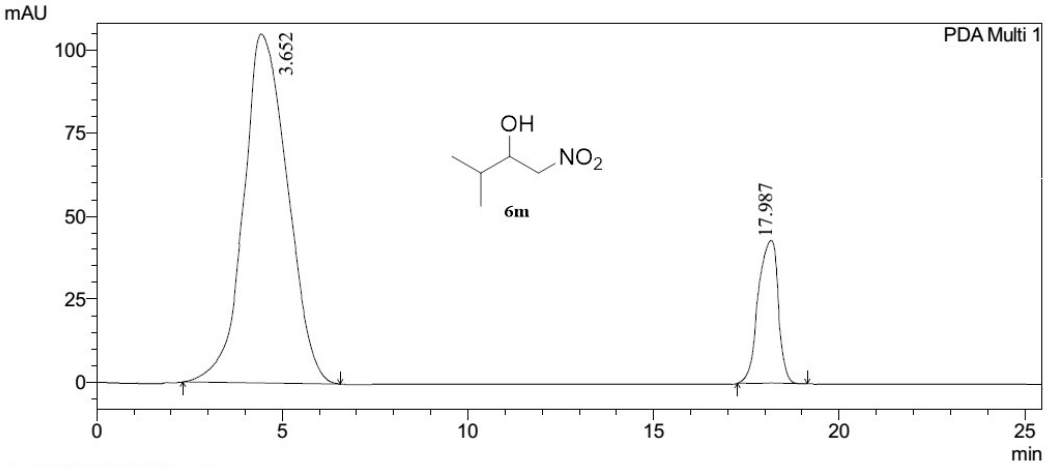


PeakTable

PDA Ch1 265nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.658	1762884	75448	94.944	97.470
2	17.057	93869	1958	5.056	2.530
Total		1856754	77407	100.000	100.000

Figure S160: HPLC chromatogram of (**6m**) in the presence organocatalyst (**15**) and CH_3OH/room temperature condition.



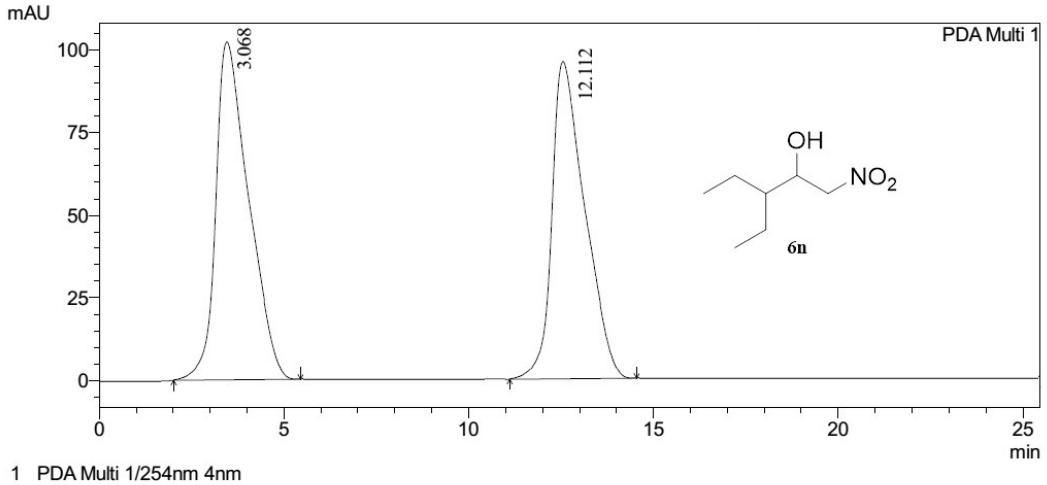
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.652	1677846	72754	82.584	90.046
2	17.987	353831	8042	17.416	9.954
Total		2031677	80797	100.000	100.000

Figure S161: HPLC chromatogram of (**6m**) in the presence organocatalyst (**16**) and CH_3OH/room temperature condition.



1 PDA Multi 1/254nm 4nm

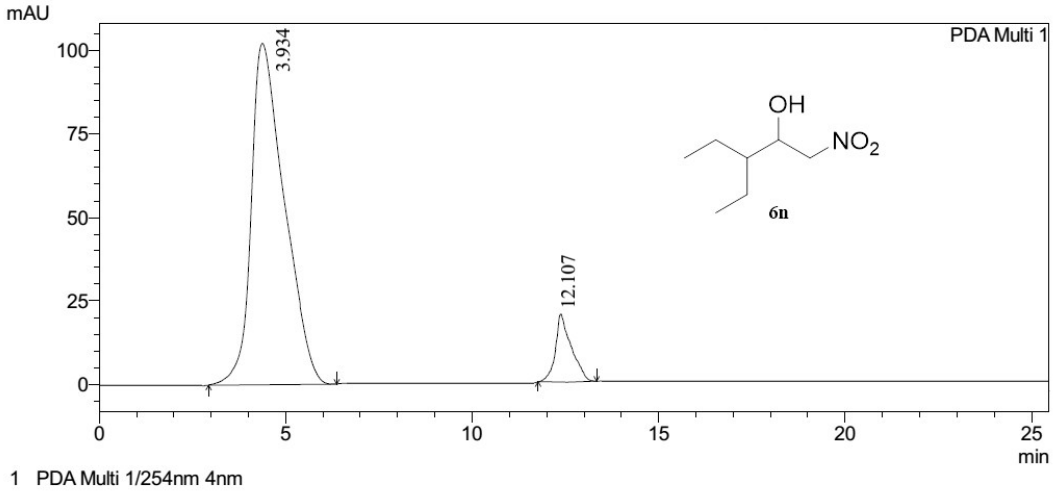
51

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.068	9427796	104252	50.483	51.552
2	12.112	9342474	97487	49.517	48.448
Total		18770271	201740	100.000	100.000

Figure S162: HPLC chromatogram of (**6n**) Racemic mixture.

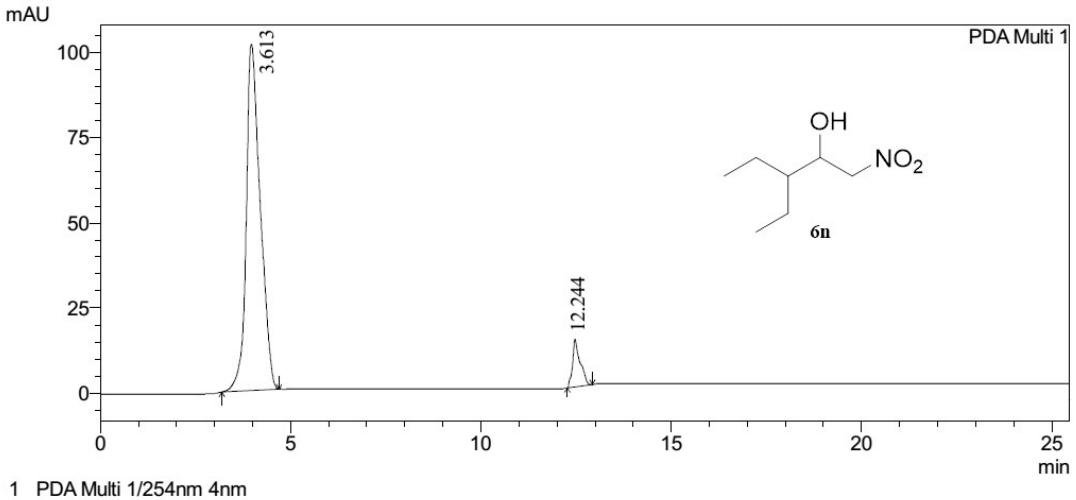


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.934	3904352	75789	96.378	95.441
2	12.107	146742	3620	3.622	4.559
Total		4051094	79409	100.000	100.000

Figure S163: HPLC chromatogram of (**6n**) in the presence organocatalyst (**14**) and CH_3OH/room temperature condition.

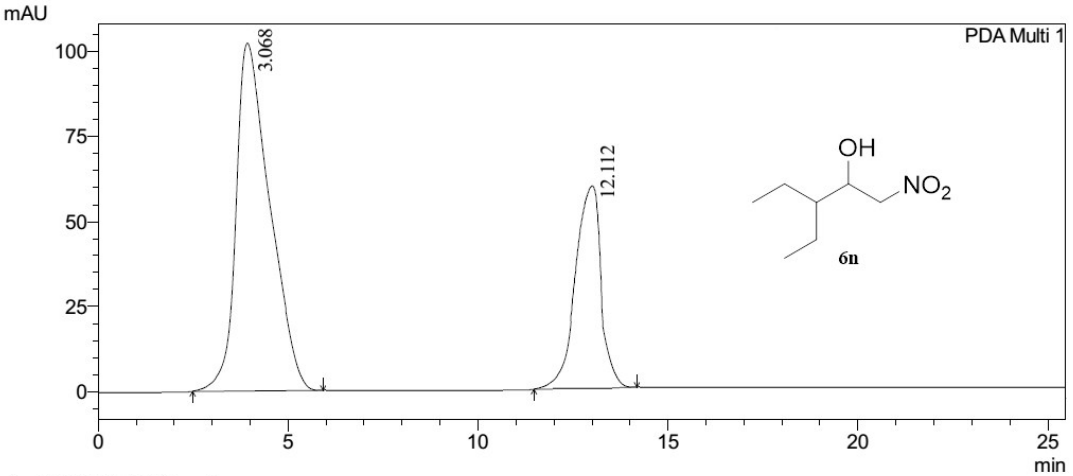


PeakTable

PDA Ch1 259nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.613	2838323	120455	96.039	98.991
2	12.244	117063	1228	3.961	1.009
Total		2955386	121683	100.000	100.000

Figure S164: HPLC chromatogram of (**6n**) in the presence organocatalyst (**15**) and CH_3OH/room temperature condition.



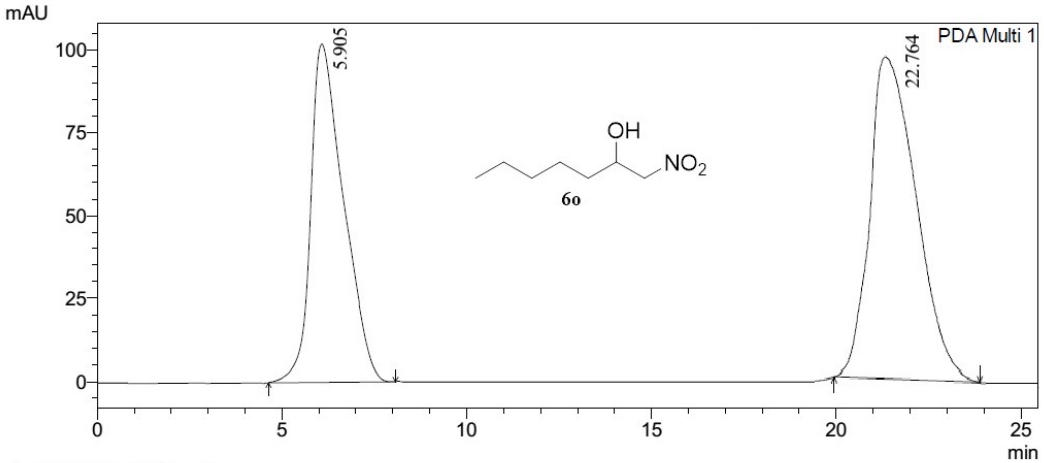
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.068	9427796	104252	81.483	73.552
2	12.112	2142474	37487	18.517	26.448
Total		11570271	141740	100.000	100.000

Figure S165: HPLC chromatogram of (**6n**) in the presence organocatalyst (**16**) and CH_3OH/room temperature condition.



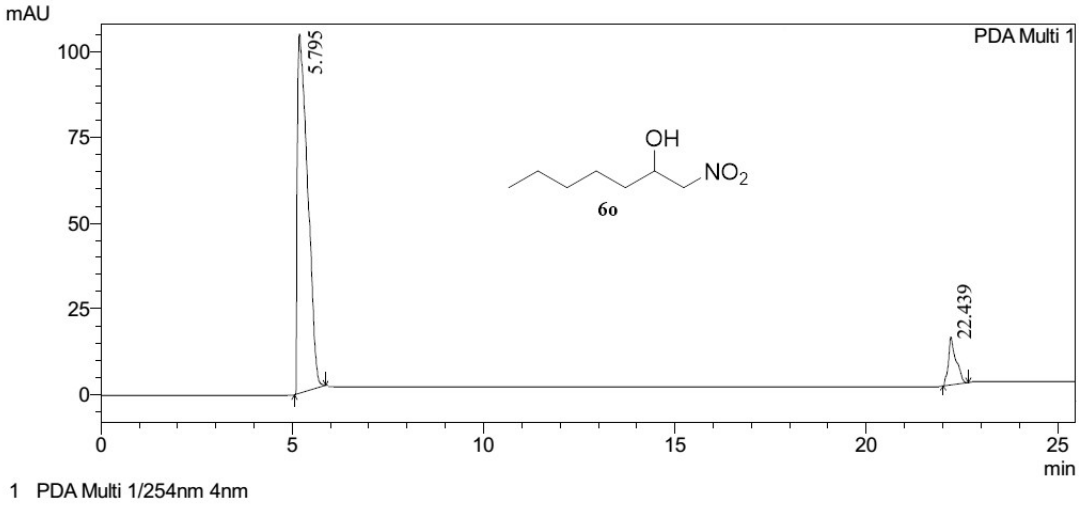
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.905	3986453	97339	50.611	51.579
2	22.764	3859166	95403	49.389	48.421
Total		7845619	192742	100.000	100.000

Figure S166: HPLC chromatogram of (**6o**) Racemic mixture.

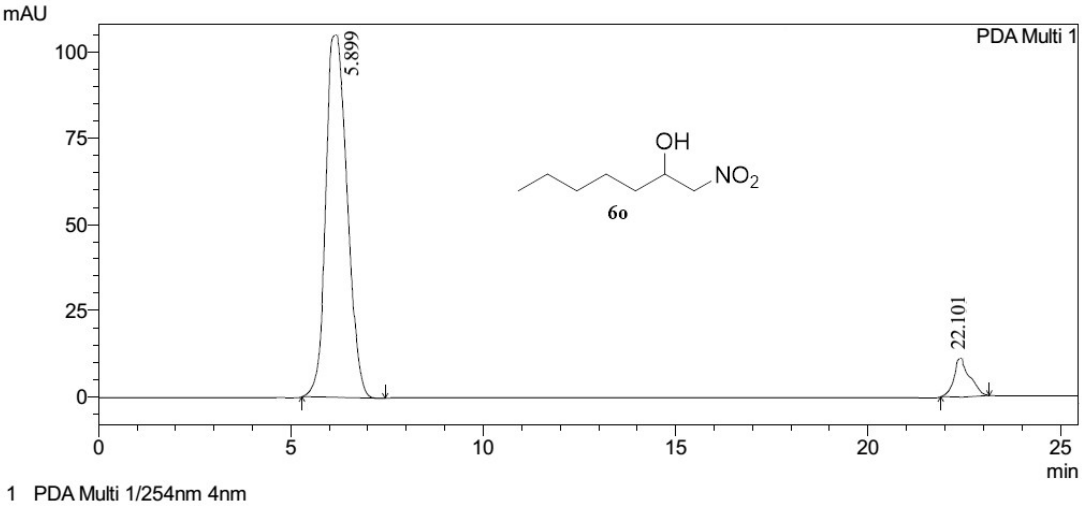


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.795	1044211	5204	95.899	72.340
2	22.439	44650	1990	4.101	27.660
Total		1088862	7194	100.000	100.000

Figure S167: HPLC chromatogram of (**6o**) in the presence organocatalyst (**14**) and CH_3OH/room temperature condition.

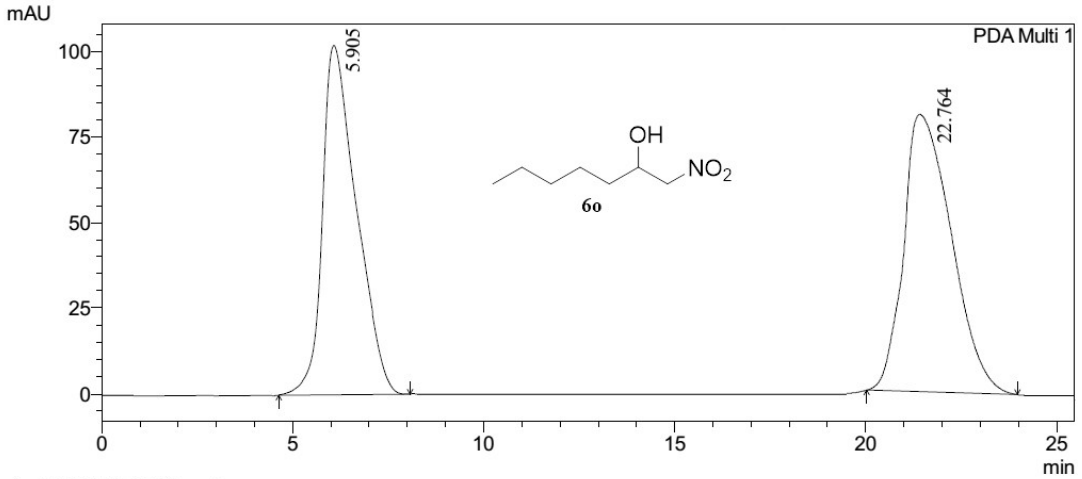


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.899	237472	2587	95.575	81.550
2	22.101	10994	585	4.425	18.450
Total		248466	3173	100.000	100.000

Figure S168: HPLC chromatogram of (**6o**) in the presence organocatalyst (**15**) and CH_3OH/room temperature condition.



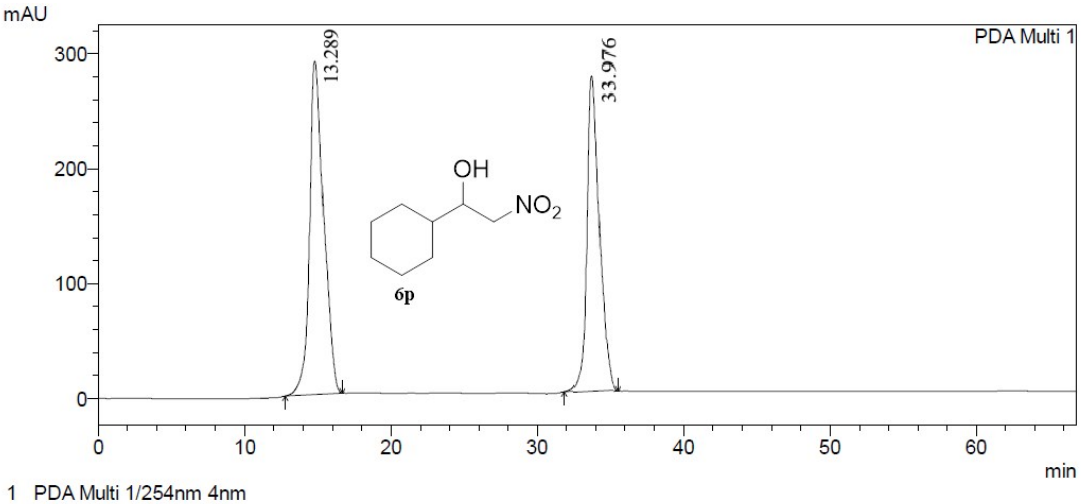
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.905	3986453	97339	70.611	85.579
2	22.764	1659166	16403	29.389	14.421
Total		5645619	113742	100.000	100.000

Figure S169: HPLC chromatogram of (**6o**) in the presence organocatalyst (**16**) and CH_3OH/room temperature condition.



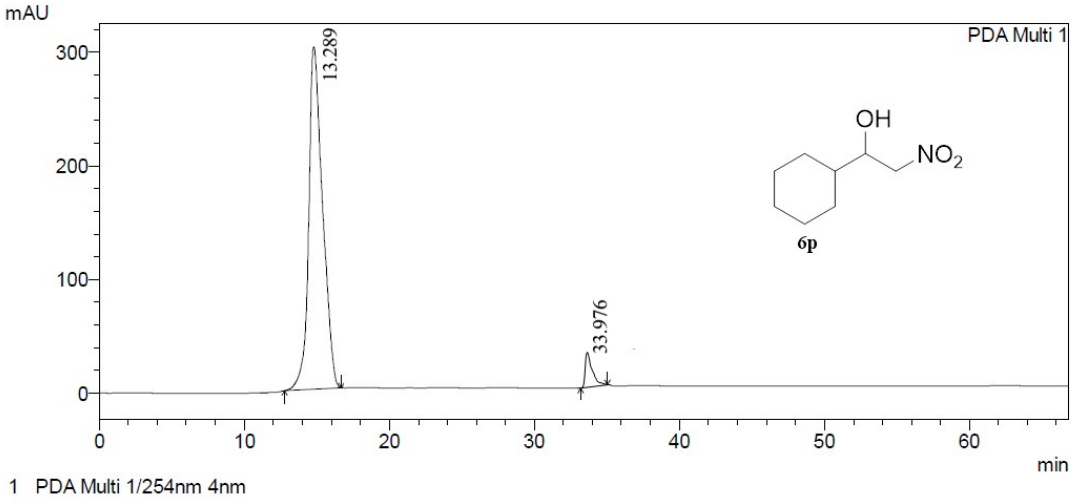
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.289	2317152	11569	50.713	52.819
2	33.976	2151471	10896	49.287	47.181
Total		4468624	22465	100.000	100.000

Figure S170: HPLC chromatogram of (**6p**) Racemic mixture.

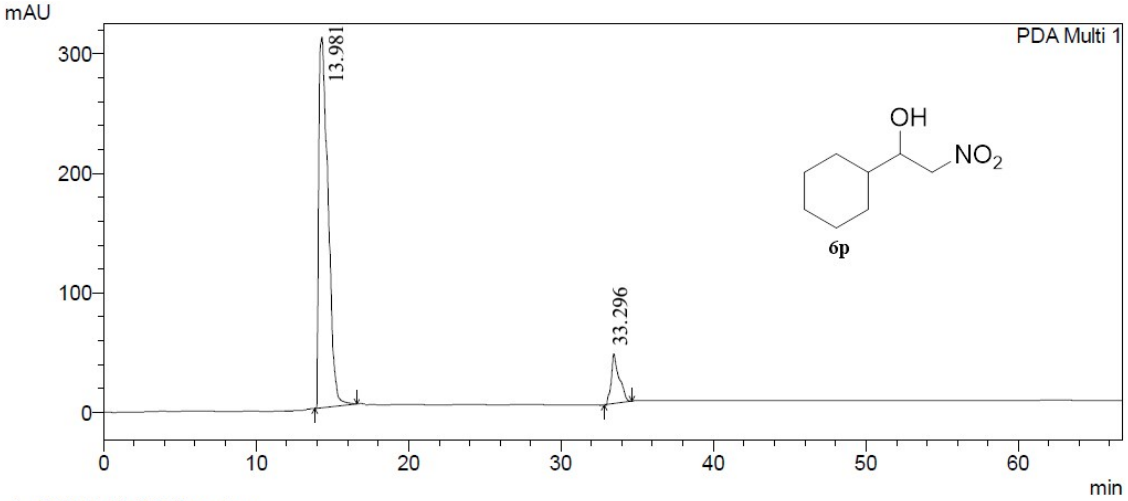


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.289	4317152	11569	98.822	85.917
2	33.976	51471	1896	1.178	14.083
Total		4368624	13465	100.000	100.000

Figure S171: HPLC chromatogram of (**6p**) in the presence organocatalyst (**14**) and CH_3OH/room temperature condition.

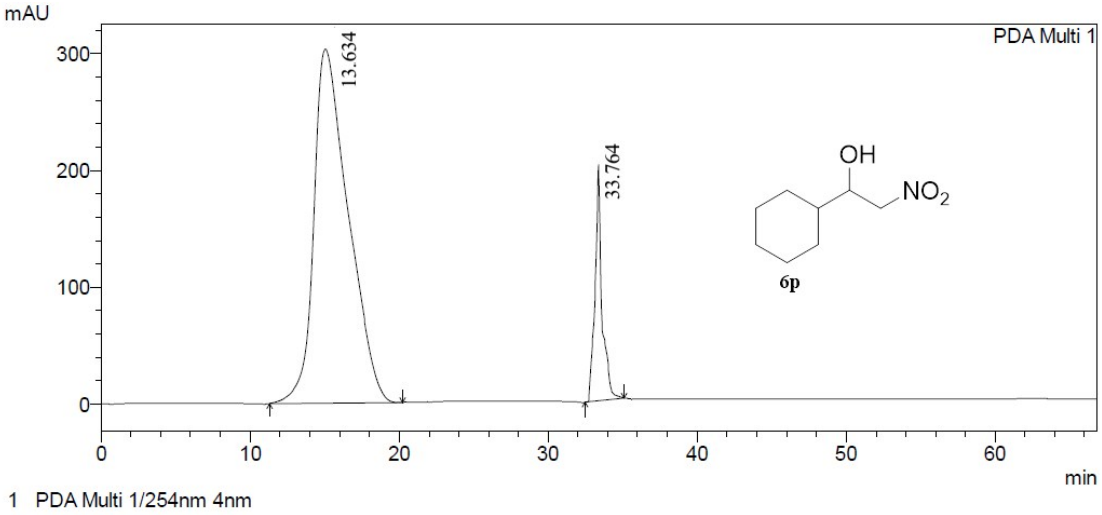


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.981	27835219	399135	98.489	94.977
2	33.296	427069	21110	1.511	5.023
Total		28262287	420246	100.000	100.000

Figure S172: HPLC chromatogram of (**6p**) in the presence organocatalyst (**15**) and CH_3OH/room temperature condition.

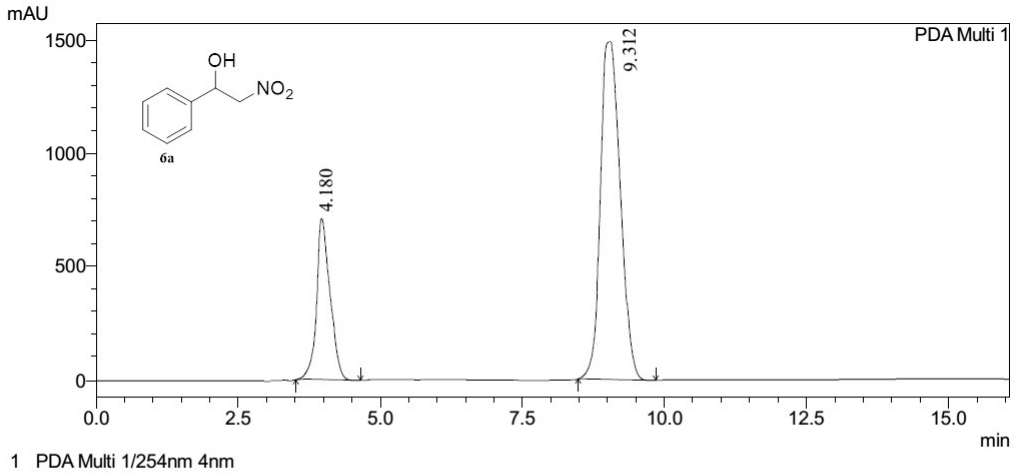


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.634	6770649	261063	85.713	94.819
2	33.764	1128573	14265	14.287	5.181
Total		7899222	275328	100.000	100.000

Figure S173: HPLC chromatogram of (**6p**) in the presence organocatalyst (**16**) and CH_3OH/room temperature condition.

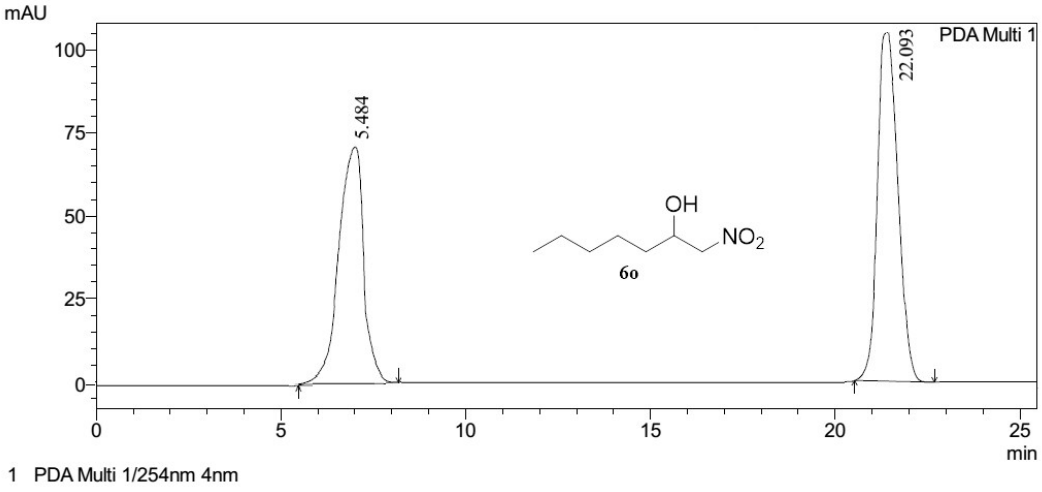


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.180	91972419	210813	16.683	26.949
2	9.312	143863194	1483918	83.317	73.051
Total		234835613	1694731	100.000	100.000

Figure S174: HPLC chromatogram of (**6a**) in the presence organocatalyst (**13**) and CH_3OH/room temperature condition.



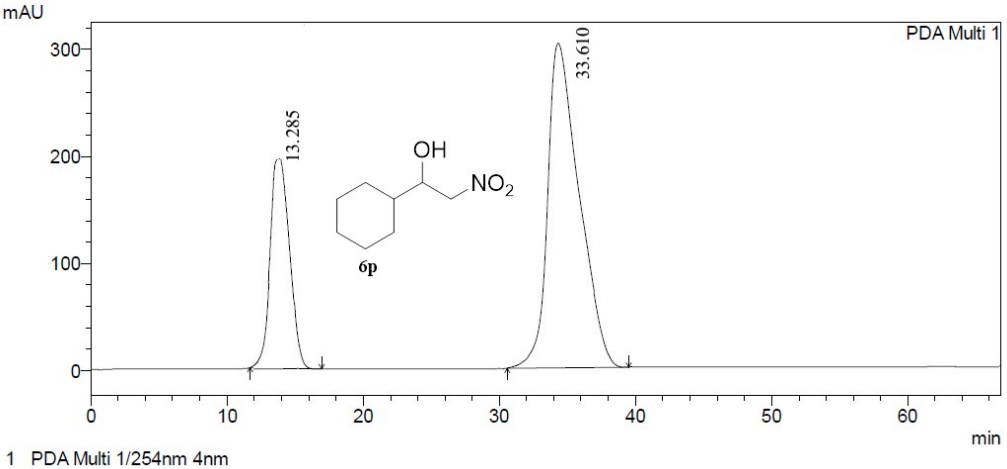
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.484	1542474	67487	26.111	26.448
2	22.093	9427796	104252	73.889	73.552
Total		10970271	161740	100.000	100.000

Figure S175: HPLC chromatogram of (**6o**) in the presence organocatalyst (**13**) and CH_3OH/room temperature condition.



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.285	3643082	70856	20.621	40.104
2	33.610	14023952	105826	79.379	59.896
Total		17667034	176683	100.000	100.000

Figure S176: HPLC chromatogram of (**6p**) in the presence organocatalyst (**13**) and CH_3OH/room temperature condition.

References

1. (a) R. Boobalan, G. H. Lee, C. Chen, *Adv. Synth. Catal*., 2012, **354**, 2511 – 2520; (b) H. A. Semaa, G. Beza, S. Karmakarb, *Appl. Organometal. Chem.,* 2014, **28**, 290–297; (c) W. Jin, X. Li, B. Wan, *J. Org. Chem*., 2011, **76**, 484–491; (d) G. Lai, F. Guo, Y. Zheng, Y. Fang, H. Song, K. Xu, S. Wang, Z. Zha, Z. Wang, *Chem. Eur. J*., 2011, **17**, 1114 – 1117.