Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Synthesis of chiral fluorescence active probe and its application as an efficient catalyst in asymmetric Friedel-Crafts alkylation of indole derivatives with nitroalkenes

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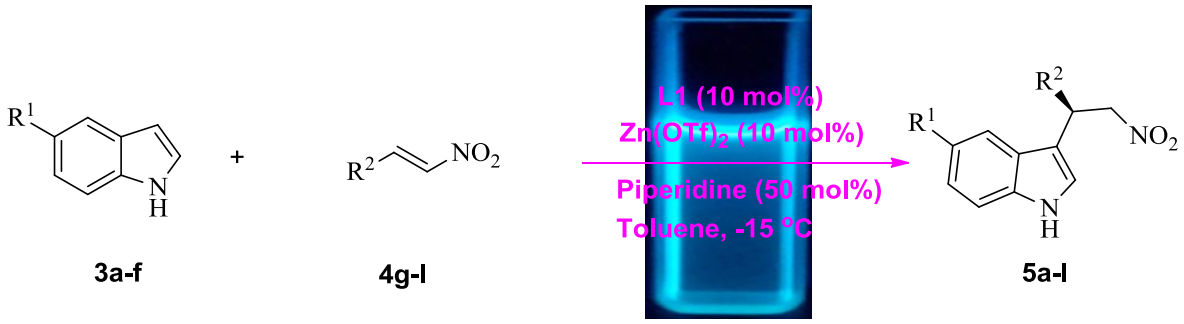
General Methods: All chemicals and solvents were purchased from M/S Sigma Aldrich, S. D. Fine Chemicals, and commercial suppliers. The progress of the reaction was monitored by thin layer chromatography (TLC) using Merck silica gel 60 F254 plates. Products were purified by column chromatography on silica gel (60–120 mesh). The ^{1}H and ^{13}C NMR spectroscopic data were analysed with a 500 MHz spectrometer in either $CDCl_3$. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as the internal standard. The coupling constants (J) are reported in Hz, and the splitting patterns of the proton signals are described as s (singlet), d (doublet), t (triplet), and m (multiplet). Optical rotations were measured by using a Rudolph Autopol IV Polarimeter. The enantiomeric excess values (*ee*) of the products were determined by HPLC analysis with an Agilent 1260 Infinity-HPLC on Daicel Chiralcel OD-H chiral columns using propan-2-ol/*n*-hexane as the eluent.

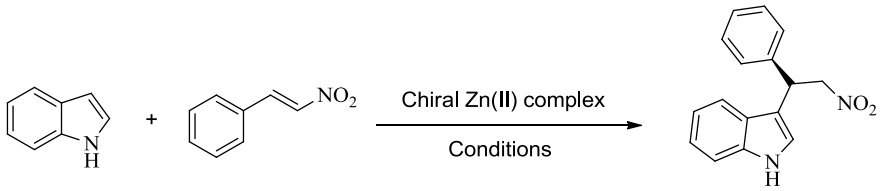
General procedure for asymmetric Friedel-Crafts alkylation reaction of indole derivative with nitroalkenes



In general procedure, the ligand **L1** (10 mol %), $Zn(OTf)_2$ (10 mol %) were added to the 10 ml round bottom flask under nitrogen atmosphere, followed by addition of toluene (3 mL).

The mixture was stirred for 10 minutes and add piperidine (50 mol %), then the reaction mixture stirred for another 30 minutes. The reaction mixture was cooled to -15 °C and add nitrostyrene (1 mmol), indole (1.2 mmol). After completion of the addition, the mixture was stirred at the -15 °C temperature until nitrostyrene has disappeared. The reaction solvent was removed under reduced pressure and the obtained residue was purified by silica gel column chromatography with petroleum ether-ethyl as a eluent. The enantiomeric excess was determined by HPLC analysis using a Daicel Chiralcel OD-H column.

Table 1 Effect of acid additives on the asymmetric Friedel- Crafts alkylation of indole.[a]



3a **4a** **5a**

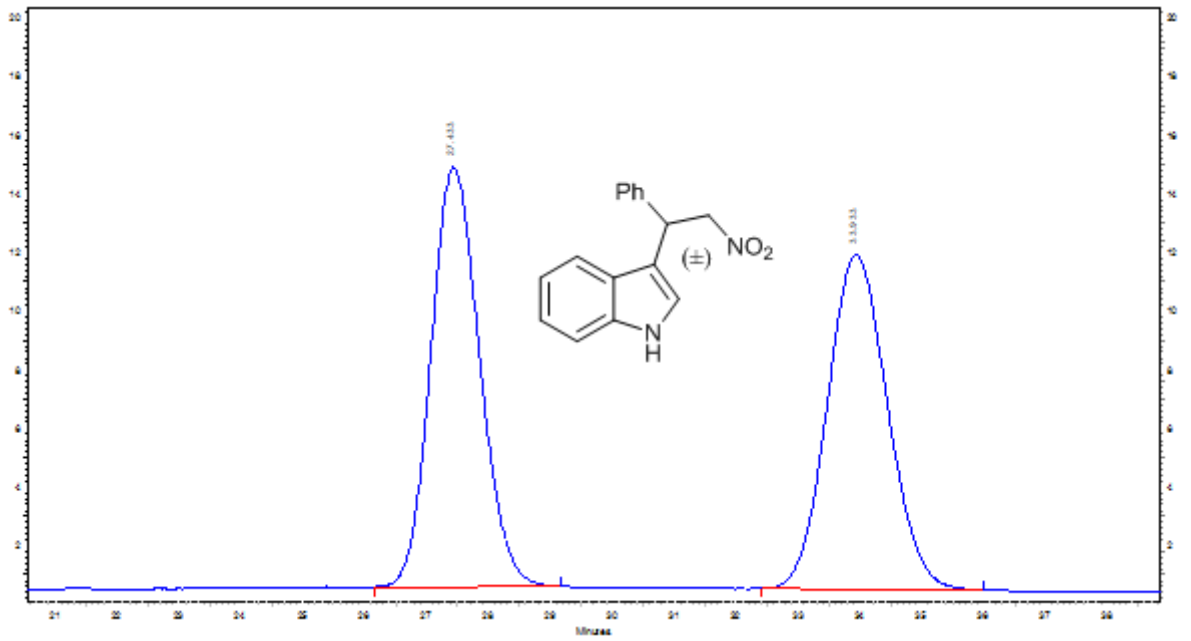
Sr.No.	Acid additives	Yield	% ee
1	---	92	64
2	Para-trifluoro benzoic acid	90	16
3	D- Camphor sulphonic acid	91	48
4	N-boc Proline	85	19
5	L- Lactic acid	93	5
6	Triflic acid	95	62
7	(*R*)-tetrahydrofuran-2-carboxylic acid	87	62
8	Tartaric acid	70	38

[a] Reaction conditions: nitrostyrene-0.5 mmol, indole-0.6 mmol, toluene-3mL, **L1**-0.05 mmol, $Zn(OTf)_2$-0.05 mmol, time-48 h, temperature-RT, [b] Isolated yield, [c] Determined by chiral HPLC analysis on a Chiralcel OD-H column.

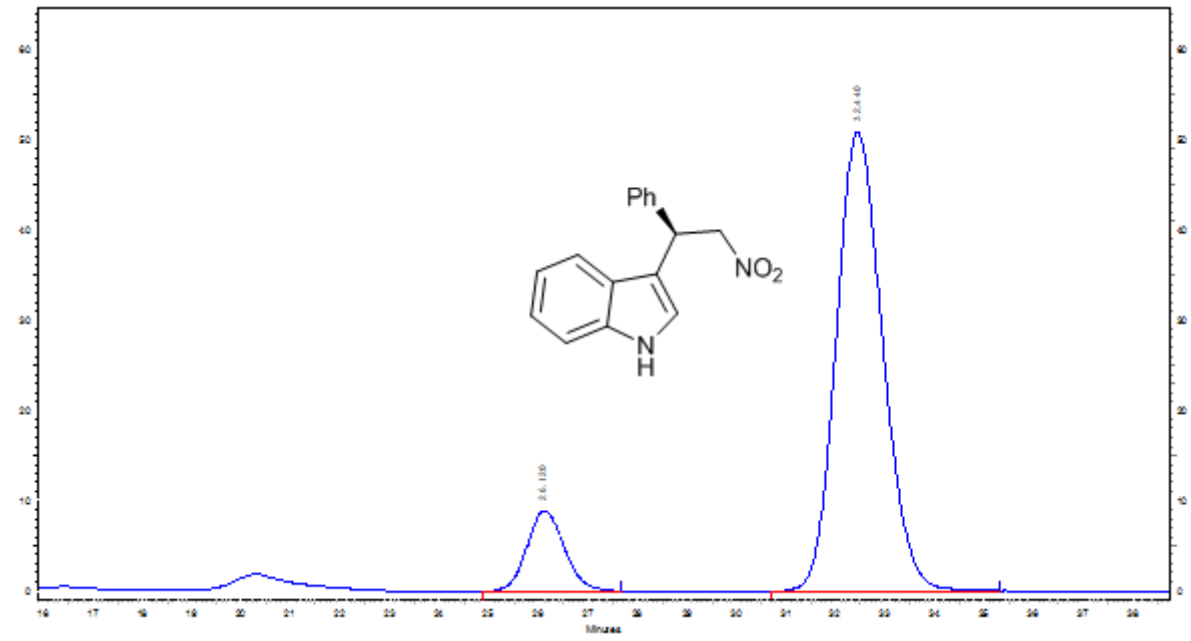
(*R*)-3-(2-nitro-1-phenylethyl)-1H-indole (5a); (Table 3, entry1)

The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **5a** in 92% yield. The ee was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ i-PrOH = 75/25, flow rate = 0.9 mL/min, 254nm; t_R = 26.1 min (minor), t_R = 32.4 min (major); 76% ee; ^{1}H NMR (500 MHz, $CDCl_3$):δ 8.12 (s, 3H), 7.45 (d, *J*= 8Hz, 1H), 7.37-7.26 (m, 6H), 7.22-7.18(m, 1H), 7.10-7.06 (m ,1H), 7.03 (d, *J*= 2.5 Hz, 1H), 5.20 (t, *J*= 8 Hz, 1H), 5.07 (dd, *J*= 7.5Hz, 2.5Hz, 1H), 4.95 (dd, *J*=

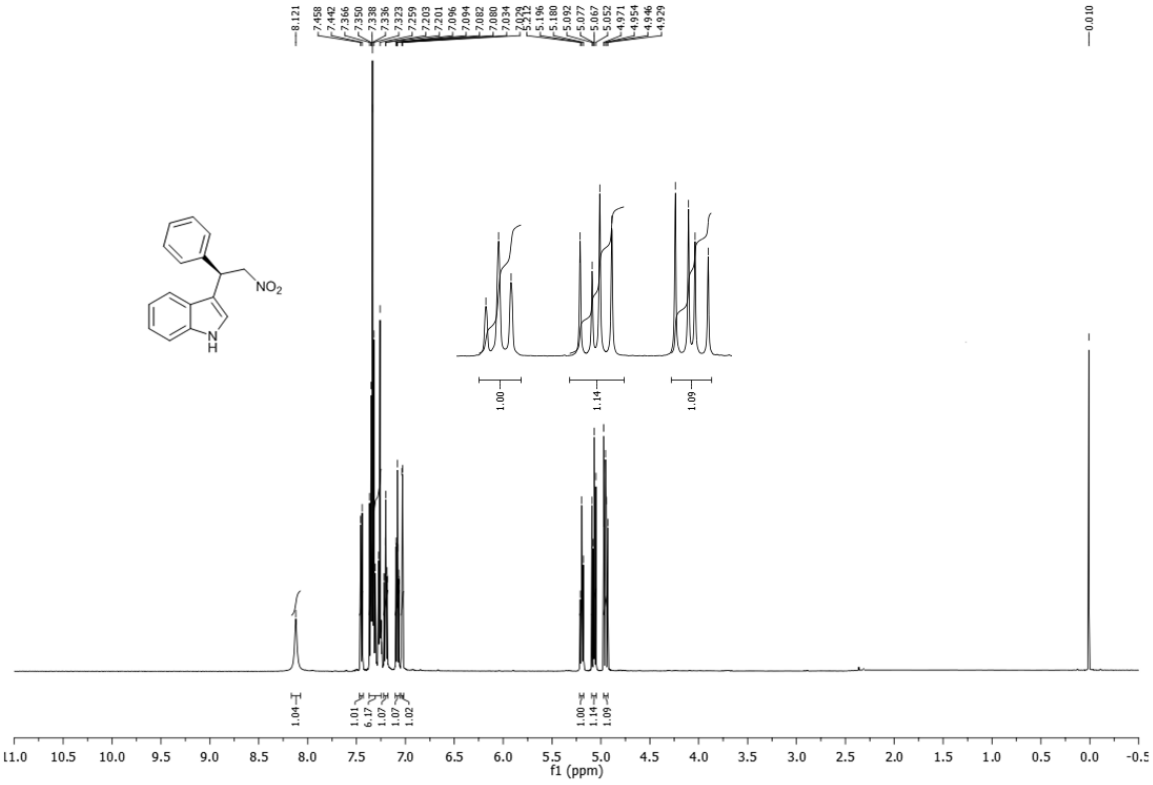
8.5Hz, 8.5Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$):139.17, 136.48, 128.89, 127.74, 127.54, 126.09, 122.68, 121.58, 119.95, 118.91, 114.44, 111.35, 79.51, 41.54.

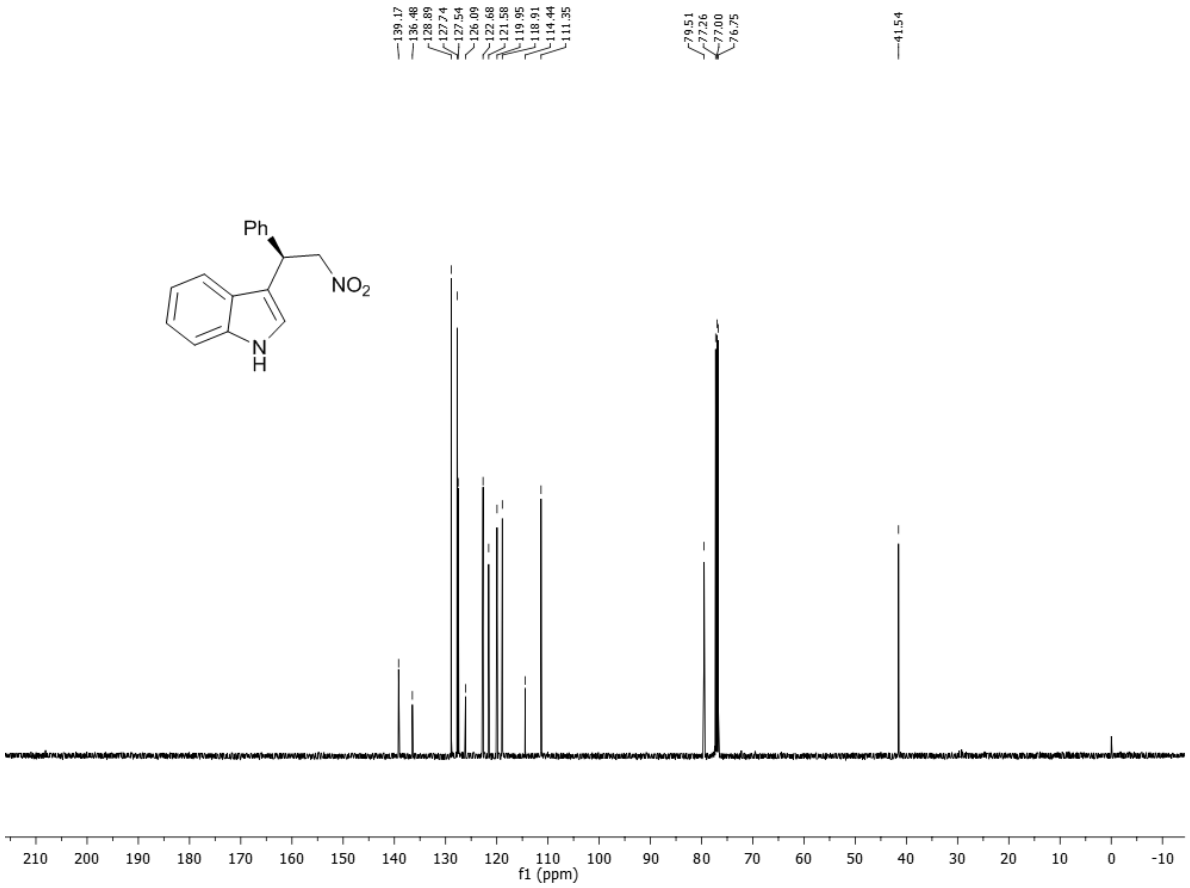


Retention Time	Area	Area %	Height	Height %
27.433	1641596	50.35	30055	55.64
33.933	1618644	49.65	23960	44.36
Totals	3260240	100.00	54015	100.00



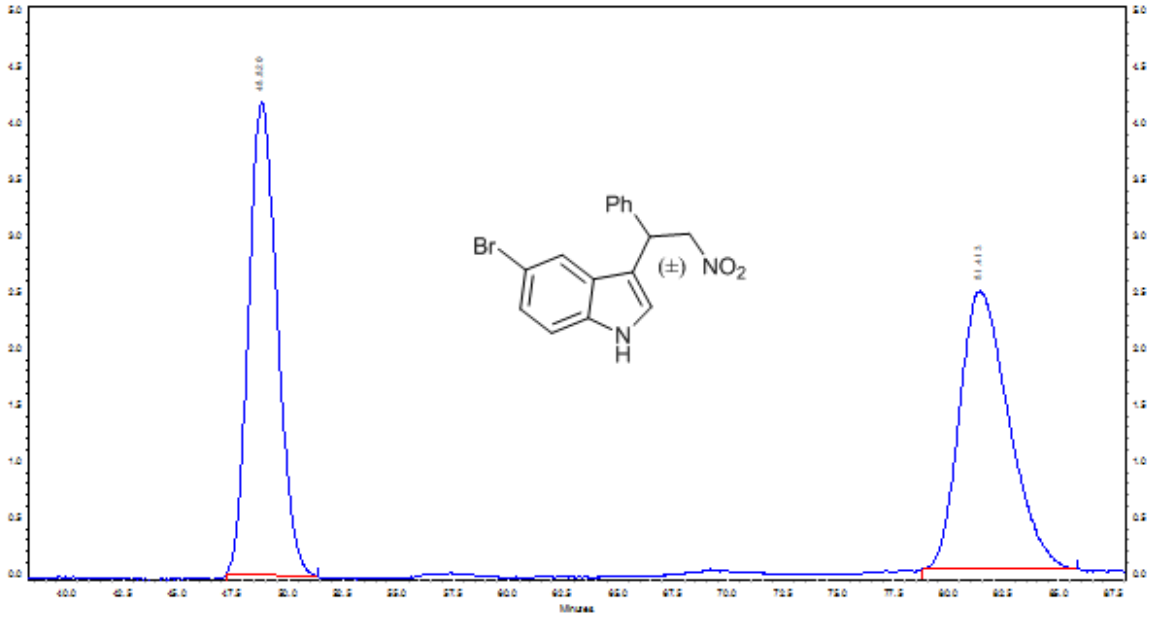
Retention Time	Area	Area %	Height	Height %
26.120	635792	11.96	12619	14.55
32.440	4678350	88.04	74122	85.45
Totals	7870533	100.00	125161	100.00



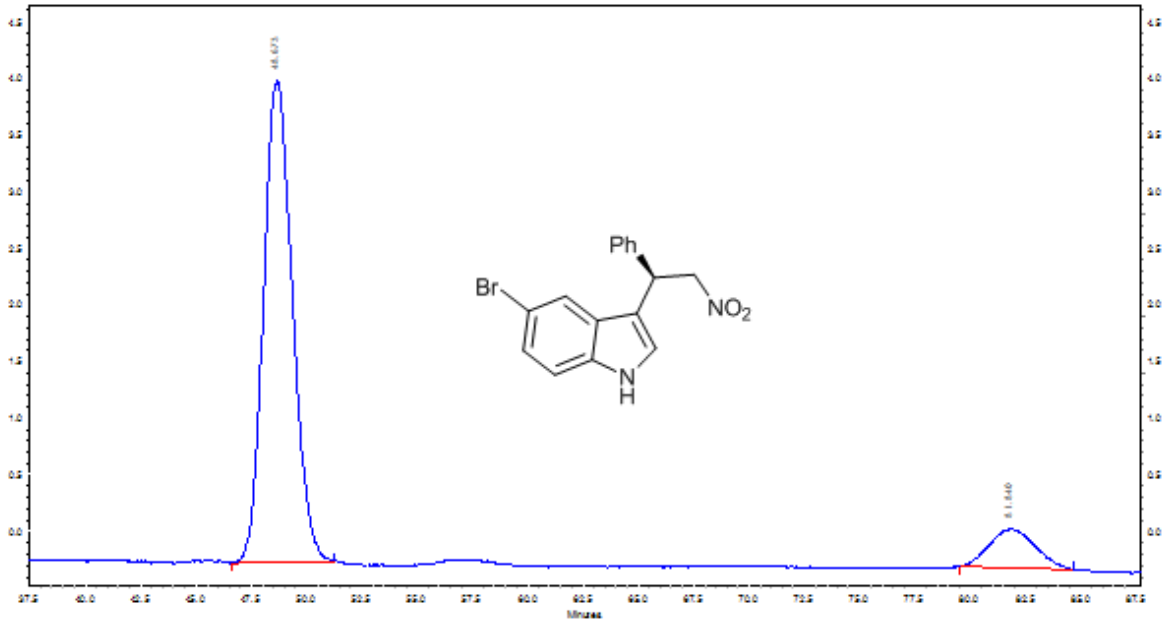


(*R*)-5-bromo-3-(2-nitro-1-phenylethyl)-1H-indole (5b); (Table 3, entry2)

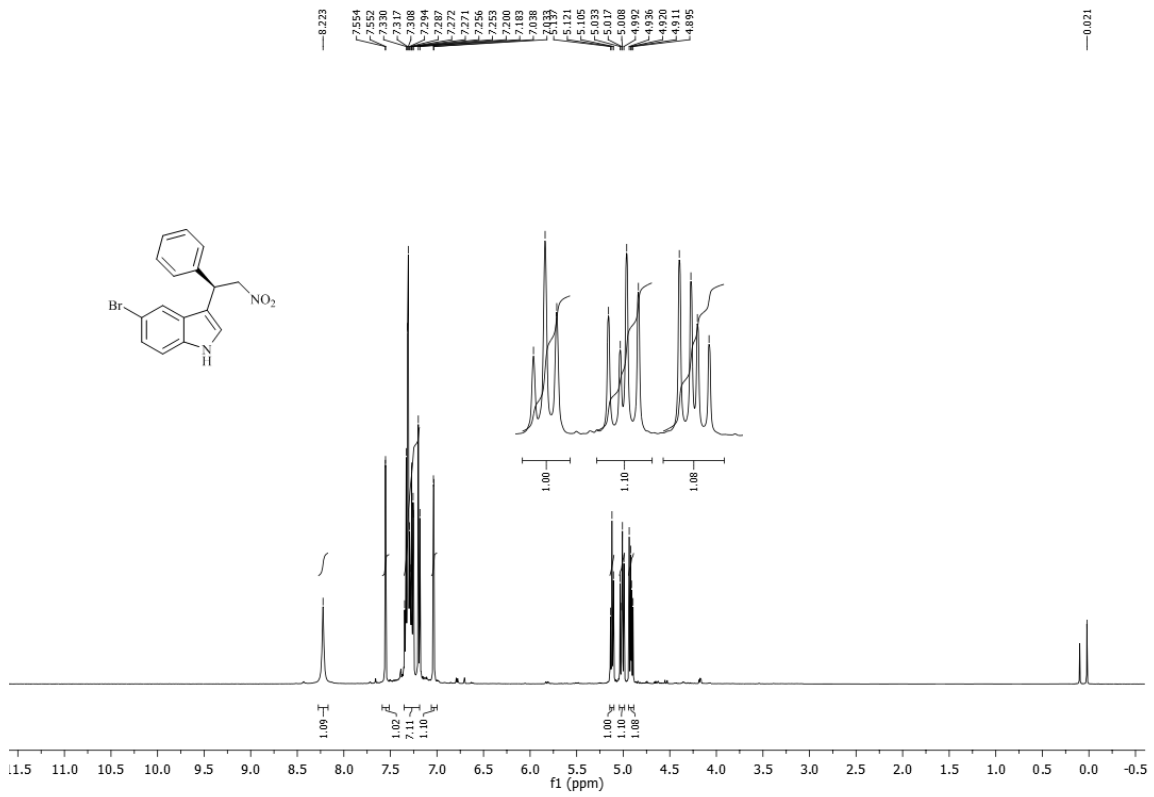
The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **5b** in 85% yield. The ee was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ i-PrOH = 90/10, flow rate = 1mL/min, 254nm; t_R = 48.6 min (major), t_R = 81.8 min (minor); 78% ee; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.6 (d, *J*=1Hz, 1H), 7.33-7.18 (m ,7H), 7.03 (d, *J*=2.5 Hz, 1H), 5.12 (t, *J*=8Hz, 1H), 5.01 (dd, *J*=8Hz, 8Hz, 1H), 4.91(dd, *J*=8Hz, 8Hz, 1H) ; ^{13}C NMR (126 MHz, $CDCl_3$): δ 138.72, 135.09, 129.04, 127.85, 127.75, 127.65, 125.61, 122.78, 121.42, 113.95, 113.20, 112.90, 79.41, 41.30.



Retention Time	Area	Area %	Height	Height %
48.820	791679	49.53	8797	62.94
81.413	806756	50.47	5179	37.06
Totals	1598435	100.00	13976	100.00



Retention Time	Area	Area %	Height	Height %
48.673	805773	88.76	8903	92.53
81.840	102024	11.24	719	7.47
Totals	907797	100.00	9622	100.00


8.223
7.554
7.552
7.330
7.317
7.308
7.294
7.287
7.272
7.271
7.256
7.253
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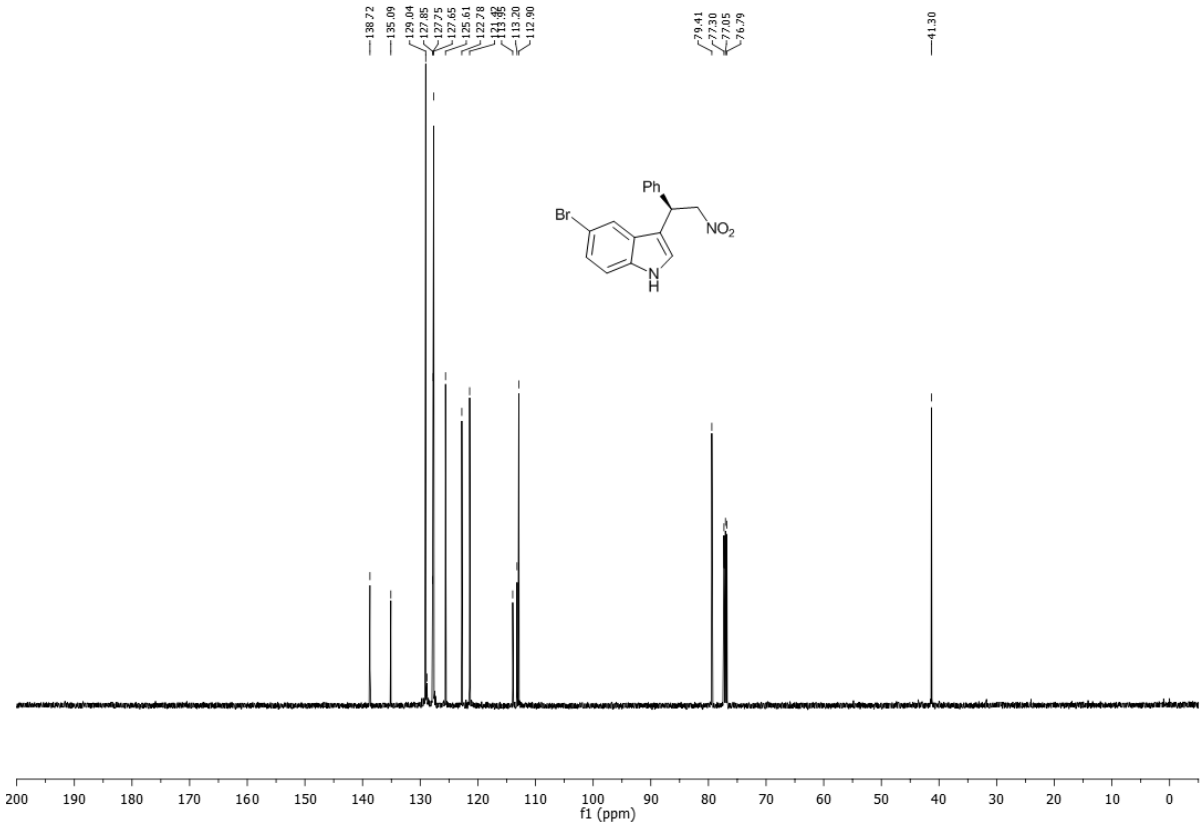
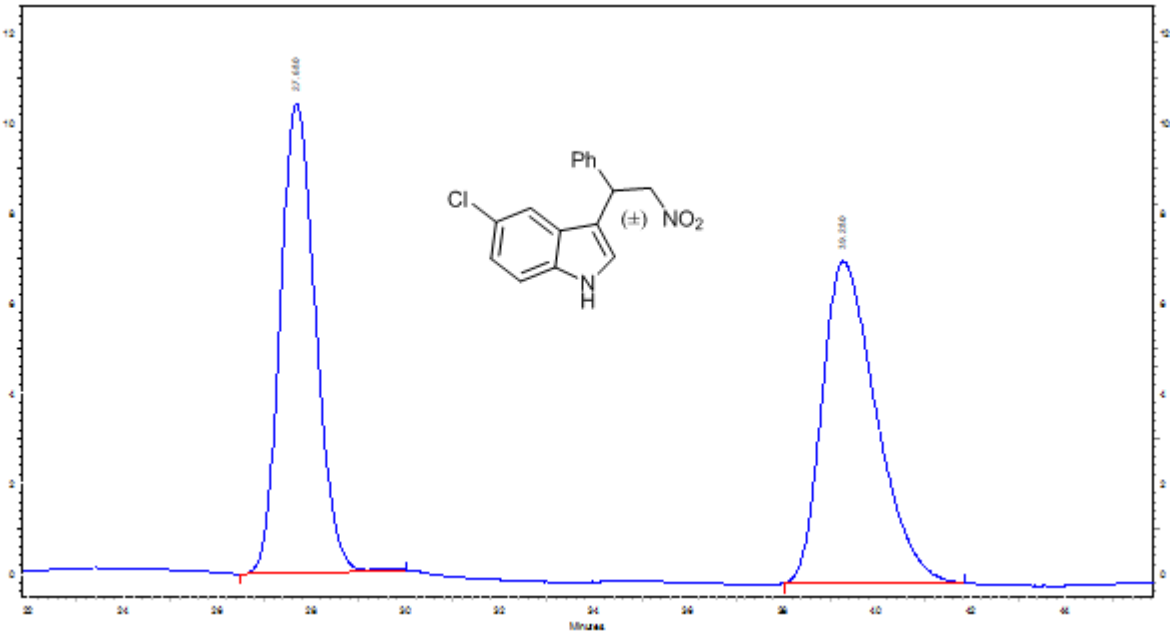
7.183
7.038
5.137
5.121
5.105
5.033
5.017
5.008
4.992
4.936
4.920
4.911
4.895
0.021
Br
NO2
N
H
1.00
1.10
1.08
1.09
1.02
1.11
1.10
1.00
1.10
1.08
f1 (ppm)

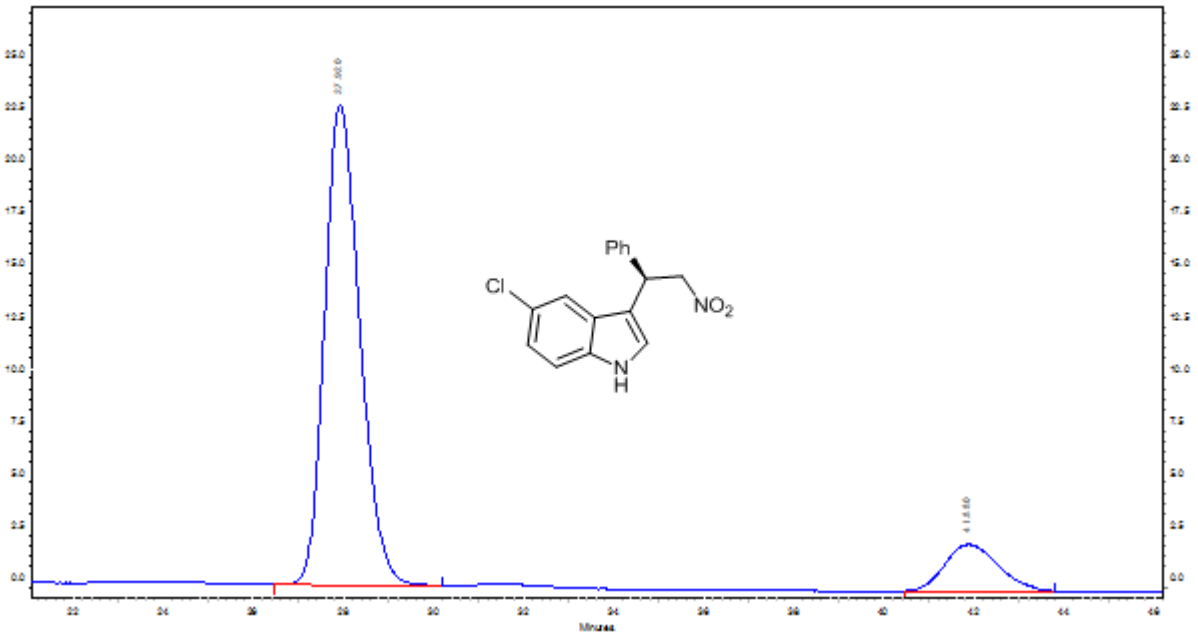

138.72
135.09
129.04
127.85
127.75
127.65
125.61
122.78
113.20
112.90
79.41
77.30
77.05
76.79
41.30
Ph
Br
NO2
N
H
f1 (ppm)

(*R*)-5-chloro-3-(2-nitro-1-phenylethyl)-1H-indole (5c); (Table 3, entry 3)

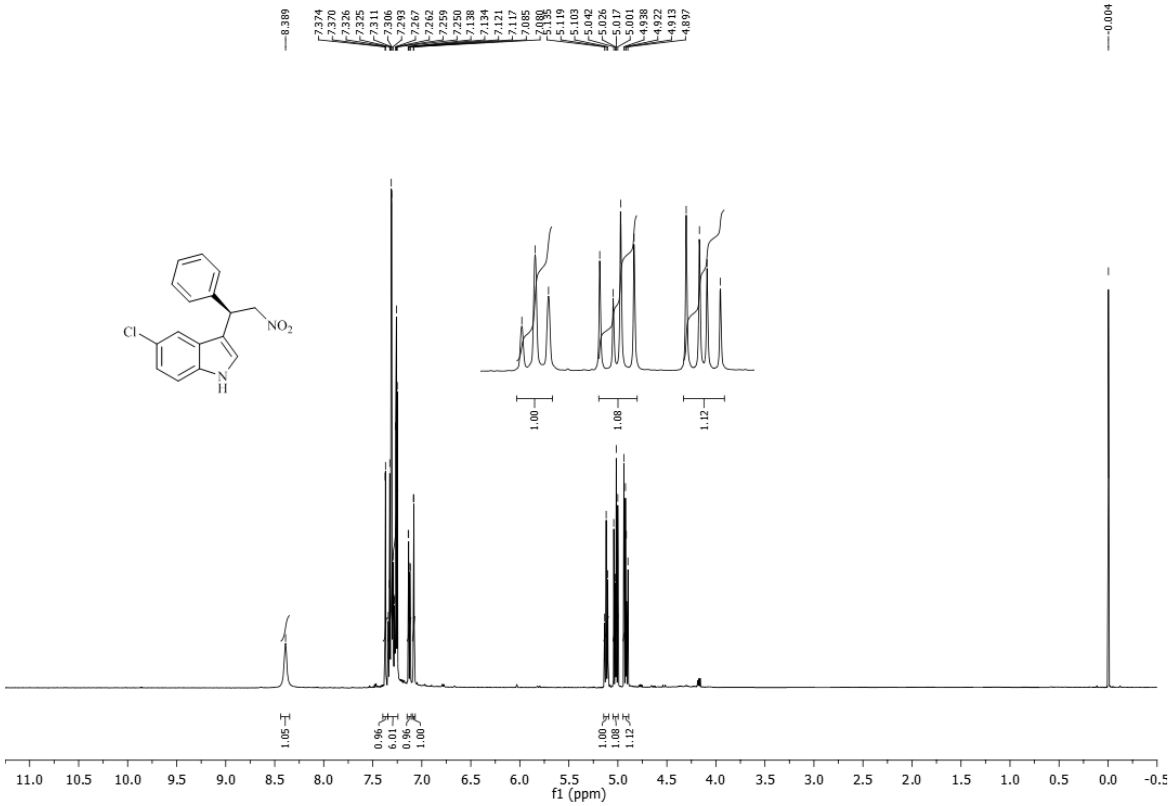
The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **5c** in 87% yield. The ee was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ i-PrOH = 85/15, flow rate = 1mL/min, 254nm; t_R = 27.9 min (major), t_R = 41.8 min (minor); 75% ee; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (s, 3H), 7.37 (d, *J*=2Hz, 1H), 7.32-7.25 (m, 6H), 7.14-7.12 (m, 1H), 7.08 (d, *J*=2.5 Hz, 1H), 5.12(t, *J*=8Hz, 1H), 5.02(dd, *J*=8Hz, 8Hz, 1H), 4.91(dd, *J*=8Hz, 8Hz, 1H) ; ^{13}C NMR (126 MHz, $CDCl_3$): δ 138.26, 134.84, 129.01, 127.71, 127.64, 127.20, 125.64, 123.03, 122.89, 118.37, 114.06, 112.41, 79.40, 41.32.

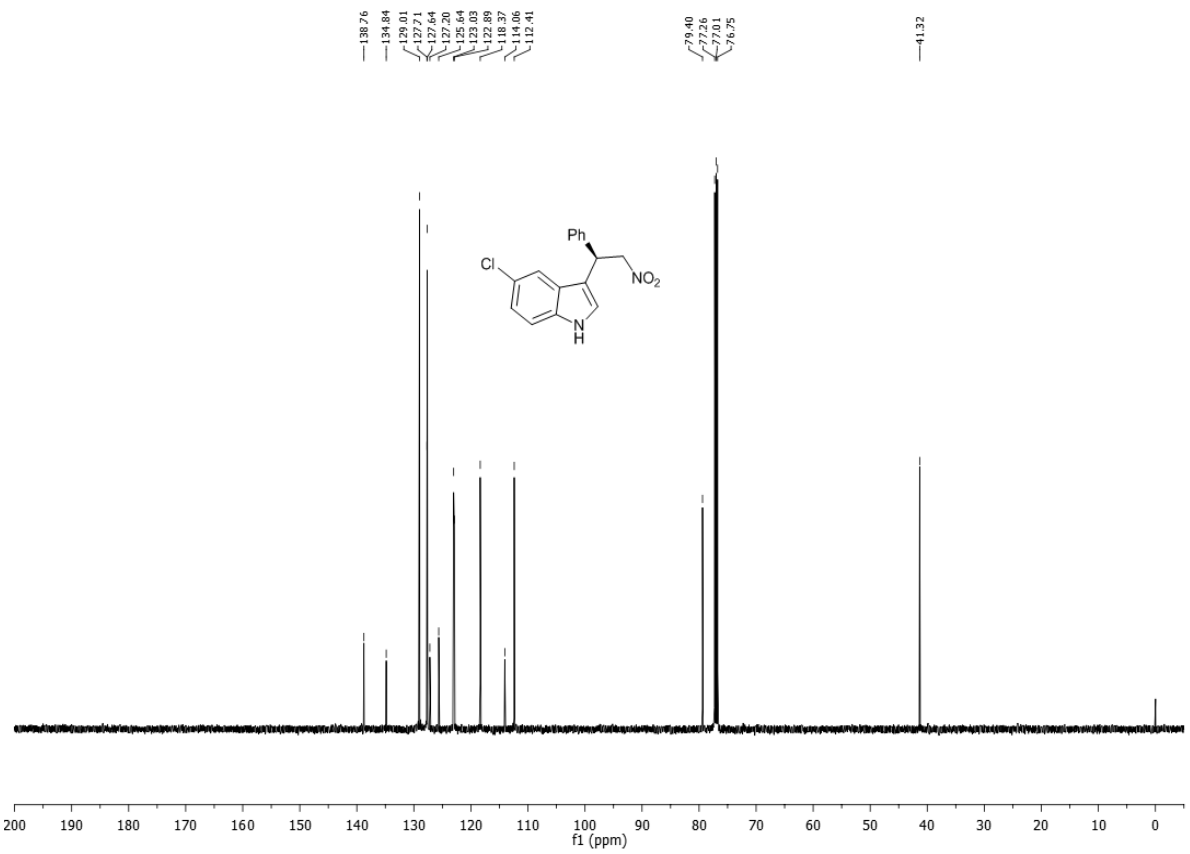


Retention Time	Area	Area %	Height	Height %
27.680	1134313	48.63	21873	59.34
39.280	1198378	51.37	14986	40.66
Totals	2332691	100.00	36859	100.00



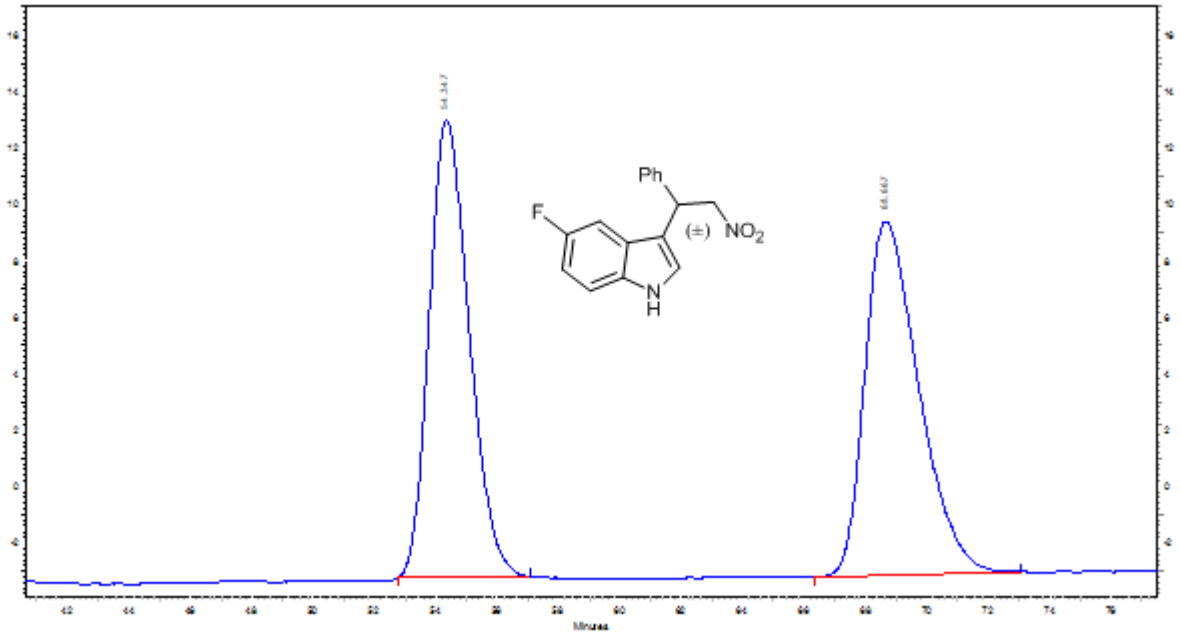
Retention Time	Area	Area %	Height	Height %
27.920	2619250	87.29	48204	91.16
41.880	381336	12.71	4672	8.84
Totals	3000586	100.00	52876	100.00



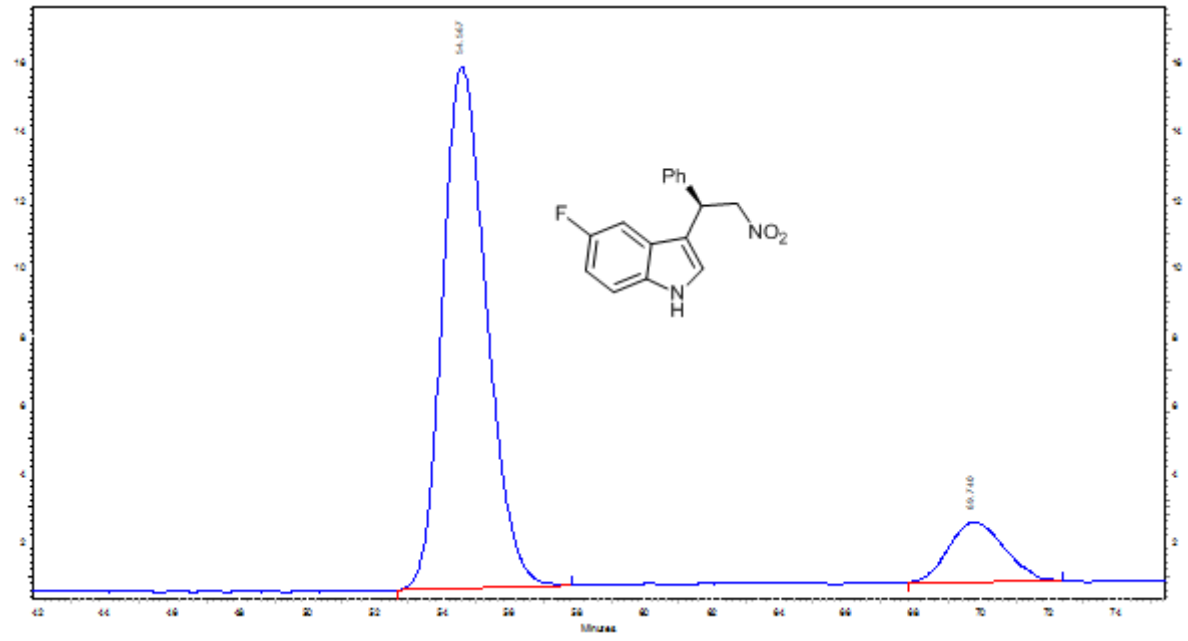


(*R*)-5-fluoro-3-(2-nitro-1-phenylethyl)-1H-indole (5d); (Table 3, entry 4)

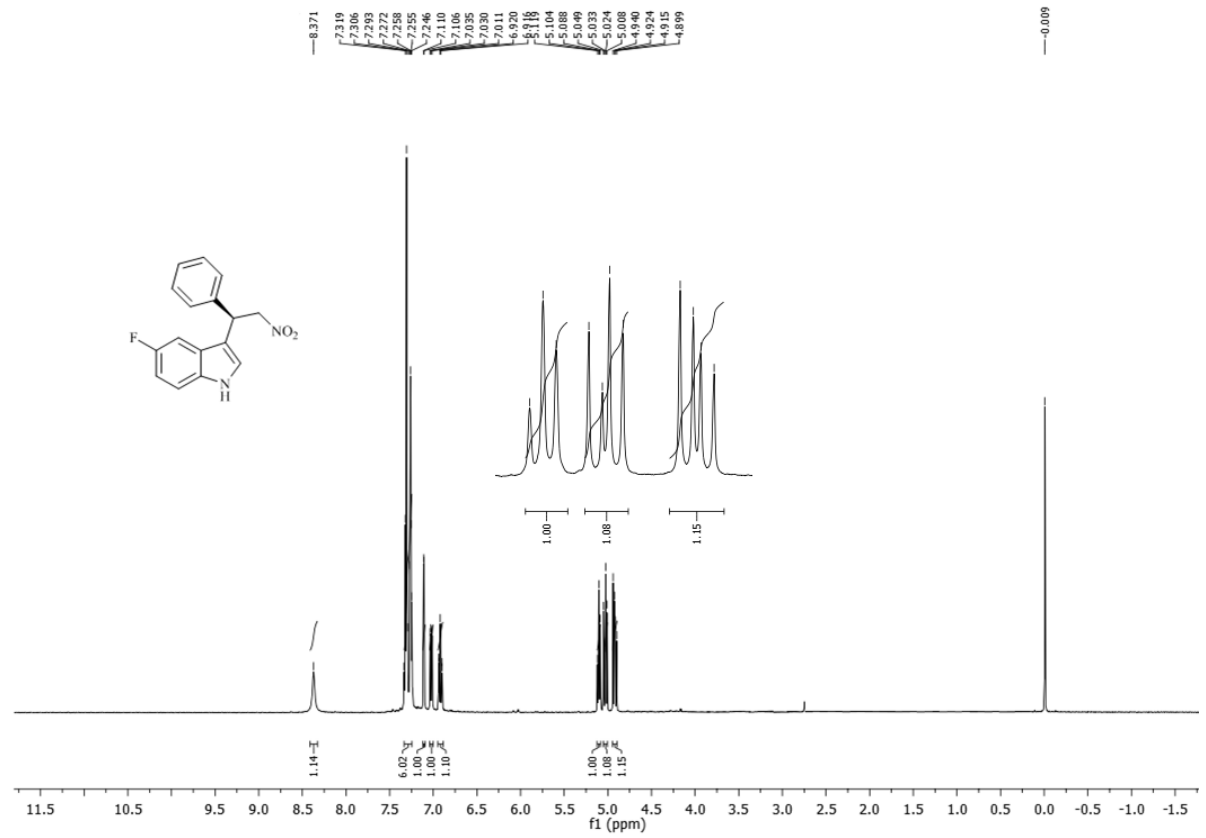
The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **5d** in 91% yield. The ee was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ i-PrOH = 90/10, flow rate = 0.9 mL/min, 254nm; t_R = 54.5 min (major), t_R = 69.7 min (minor); 74% ee; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37(s, 3H), 7.32-7.26 (m 6H), 7.11 (d, *J*= 2Hz, 1H), 7.04 (dd, *J*= 2.5Hz, 2.5Hz, 1H), 6.92 (td, *J*= 2.5 Hz, 2Hz, 2.5 Hz, 1H), 5.10 (t, *J*=7.5Hz, 1H), 5.02 (dd, *J*=8Hz, 8Hz, 1H), 4.92 (dd, *J*=8Hz 8Hz, 1H) ; ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.75, 138.86, 132.98, 128.97, 127.66, 126.49, 123.19, 114.41, 112.05, 111.10, 103.92, 79.40, 41.46.



Retention Time	Area	Area %	Height	Height %
54.347	3078372	49.03	33986	56.34
68.667	3200604	50.97	26339	43.66
Totals	6278976	100.00	60325	100.00



Retention Time	Area	Area %	Height	Height %
54.567	2905959	87.38	32024	89.73
69.740	419671	12.62	3666	10.27
Totals	3325630	100.00	35690	100.00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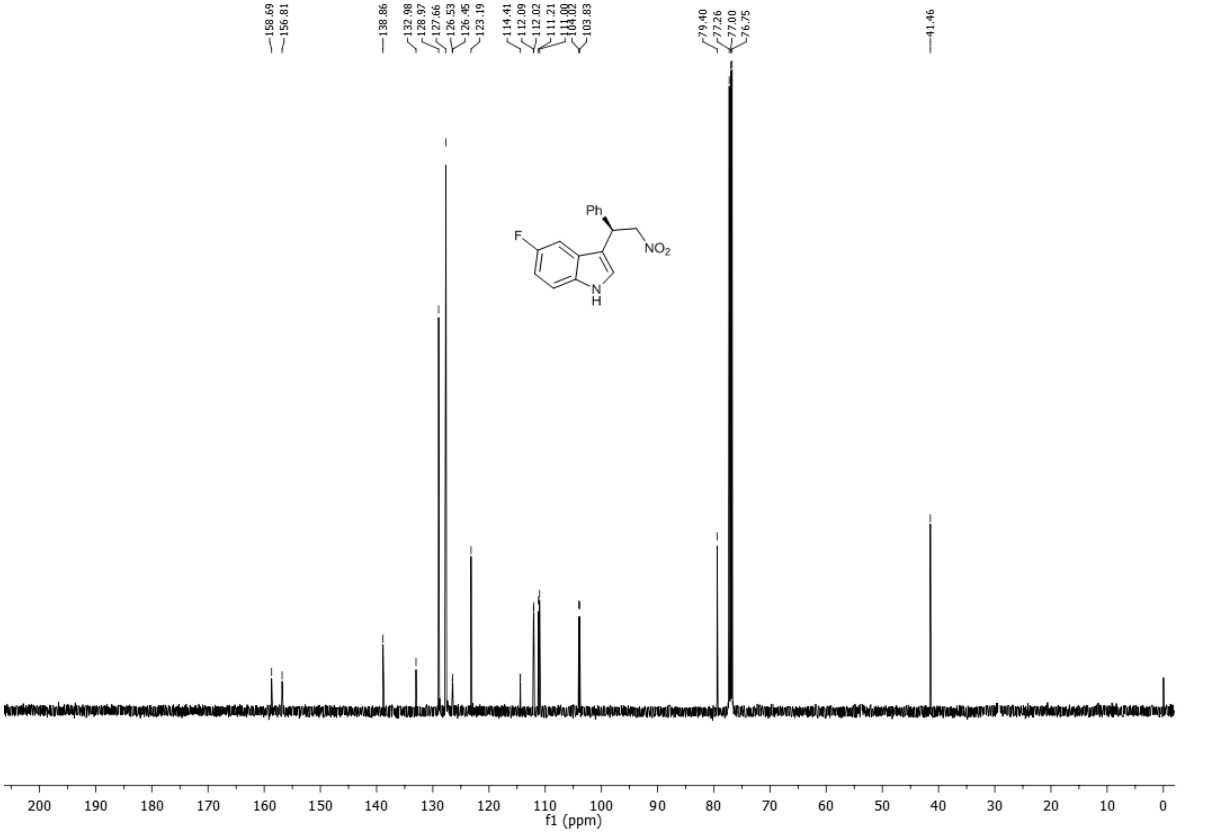
7.293
7.272
7.258
7.255
7.246
7.110
7.106
7.035
7.030
7.011
6.920
5.104
5.088
5.049
5.033
5.024
5.008
4.940
4.924
4.915
4.899
0.009
F
NO2
N
H
1.00
1.08
1.15
1.14
6.02
1.00
1.00
1.10
1.00
1.08
1.15
f1 (ppm)


158.69
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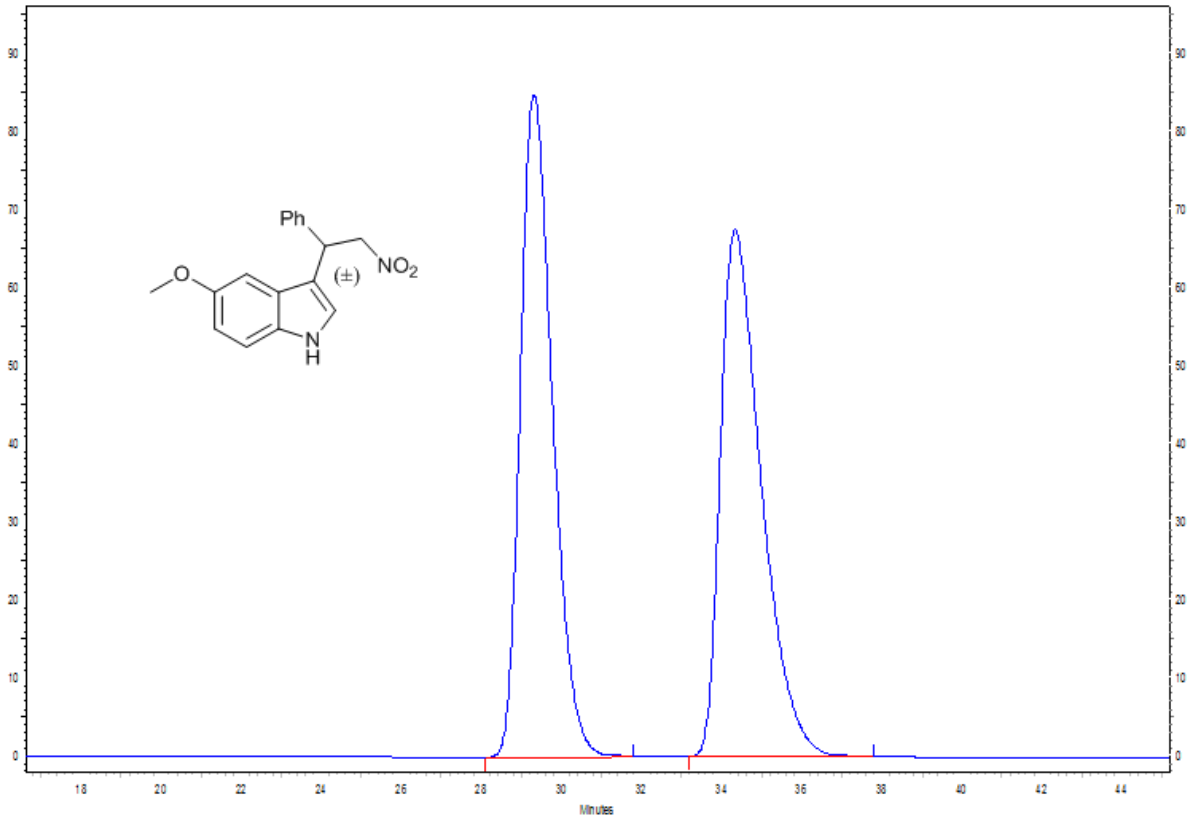
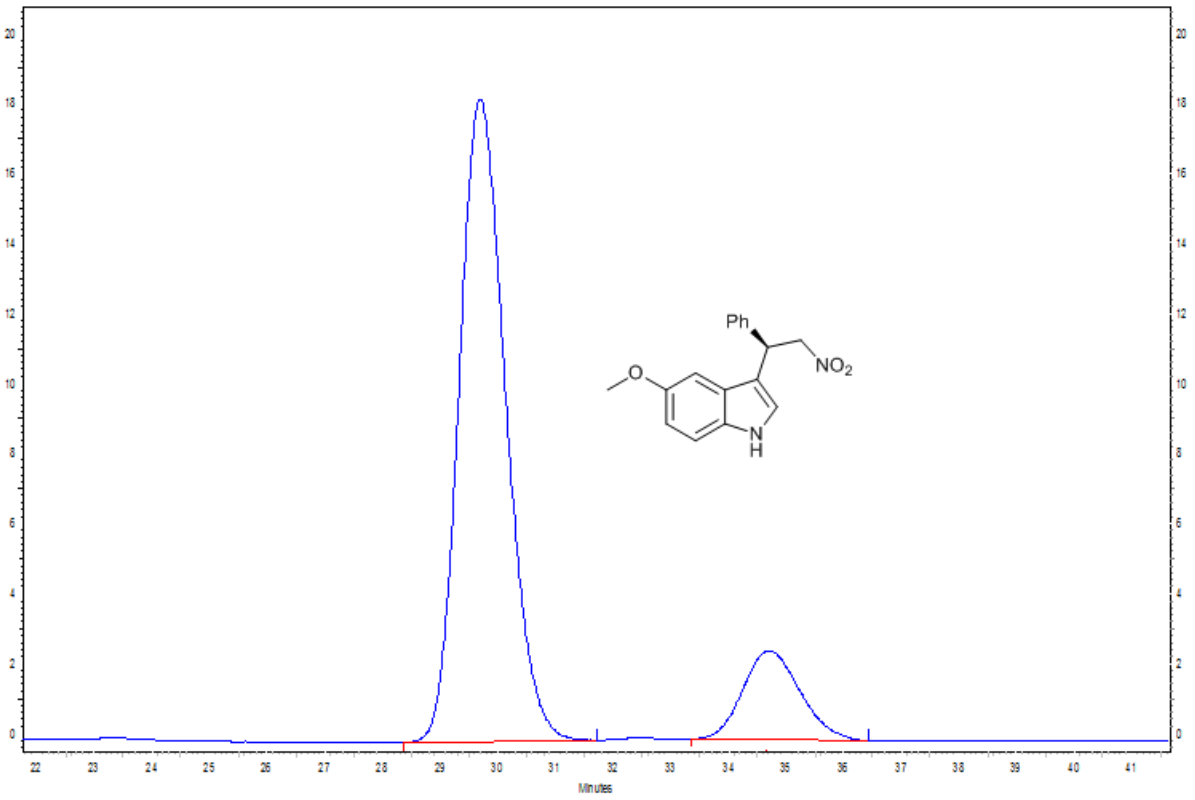
132.98
128.97
127.66
126.53
126.45
123.19
114.41
112.09
112.02
111.21
103.83
79.40
77.26
77.00
76.75
41.46
Ph
F
NO2
N
H
f1 (ppm)

(*R*)-5-methoxy-3-(2-nitro-1-phenylethyl)-1H-indole (5e); (Table 3, entry 5)

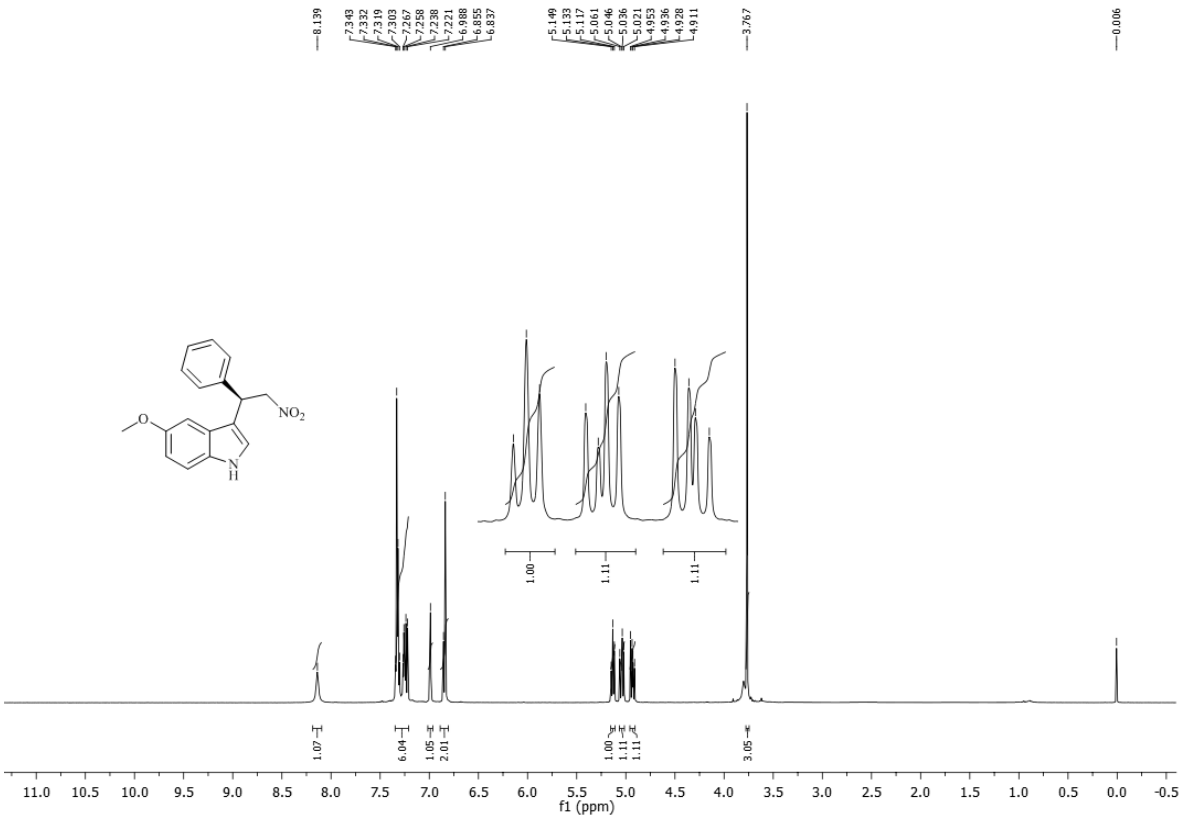
The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **5e** in 90% yield. The ee was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ i-PrOH = 85/15, flow rate = 1 mL/min, 254nm; t_R = 29.6 min (major), t_R = 34.8 min (minor); 70% ee; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.34-7.24 (m, 6H), 5.22(d, *J*=2.5Hz, 1H), 6.99-6.84(m, 2H), 5.13 (t, *J*=8Hz, 1H), 5.04 (dd, *J*=7.5Hz, 7.5Hz, 1H), 4.93(dd, *J*=8.5Hz, 8Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 154.15, 139.16, 131.61, 128.89, 127.74, 127.53, 126.55, 122.28, 114.02, 112.68, 112.09, 100.85, 79.48, 55.83, 41.52.

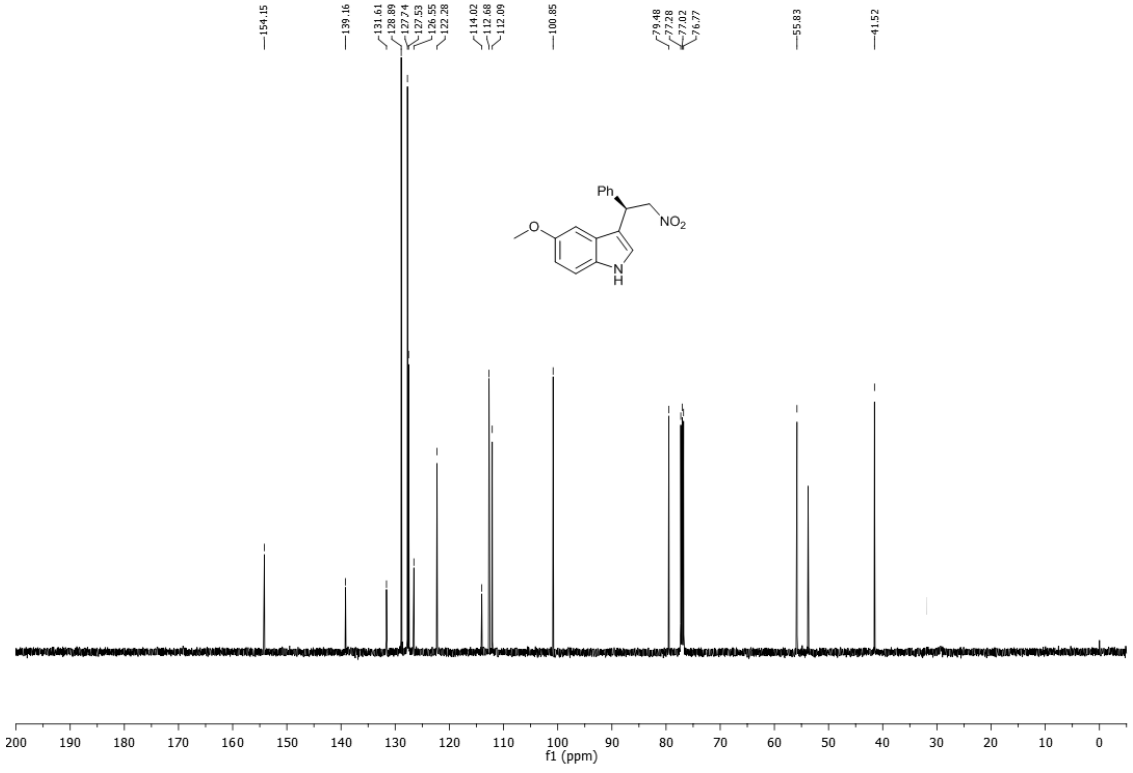


Retention Time	Area	Area %	Height	Height %
29.307	9961001	49.78	178023	55.70
34.333	10050400	50.22	141581	44.30
Totals	20011401	100.00	319604	100.00



Retention Time	Area	Area %	Height	Height %
29.693	2155463	85.45	38528	87.84
34.813	366920	14.55	5334	12.16
Totals	2522383	100.00	43862	100.00

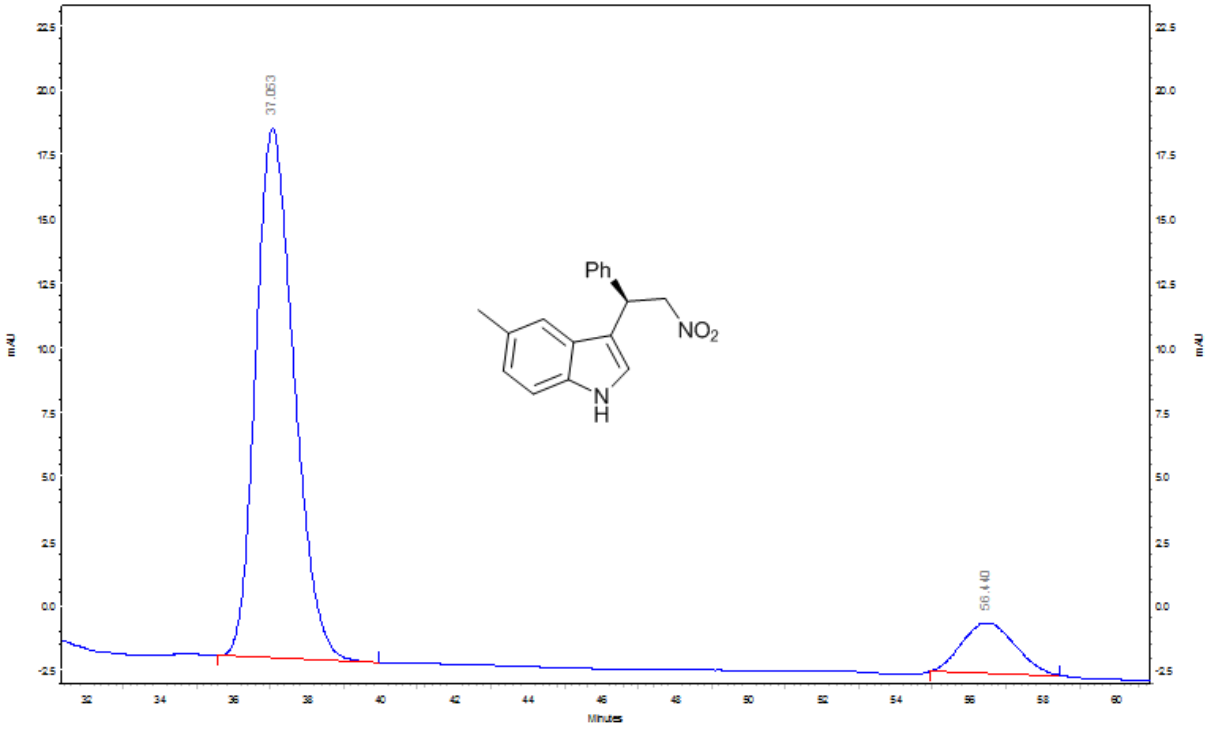




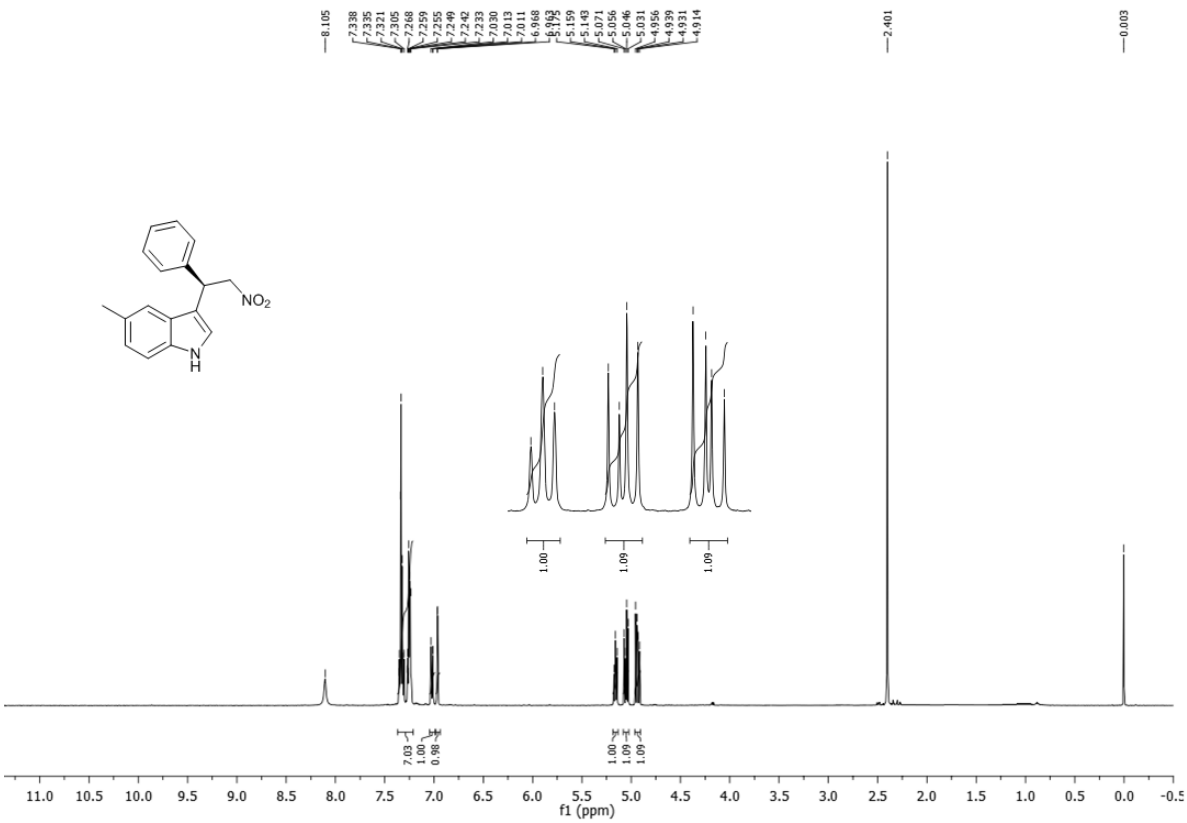
(*R*)-5-methyl-3-(2-nitro-1-phenylethyl)-1H-indole (5f); (Table 3, entry 6)

The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **5f** in 89% yield. The ee was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ i-PrOH = 85/15, flow rate = 1 mL/min,

254nm; t_R = 37.0min (major), t_R = 56.4 min (minor); 76% ee; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (s, 3H), 7.34-7.23(m, 7H), 7.02(d, *J*=8.5Hz, 1H), 6.10(d, *J*=2.5Hz, 1H), 5.16 (t, *J*=8Hz, 1H), 5.06 (dd, *J*=2.5Hz, 7.5Hz, 1H), 4.93(dd, *J*=8.5Hz, 8.5Hz, 1H), 2.40 (s, 3H).

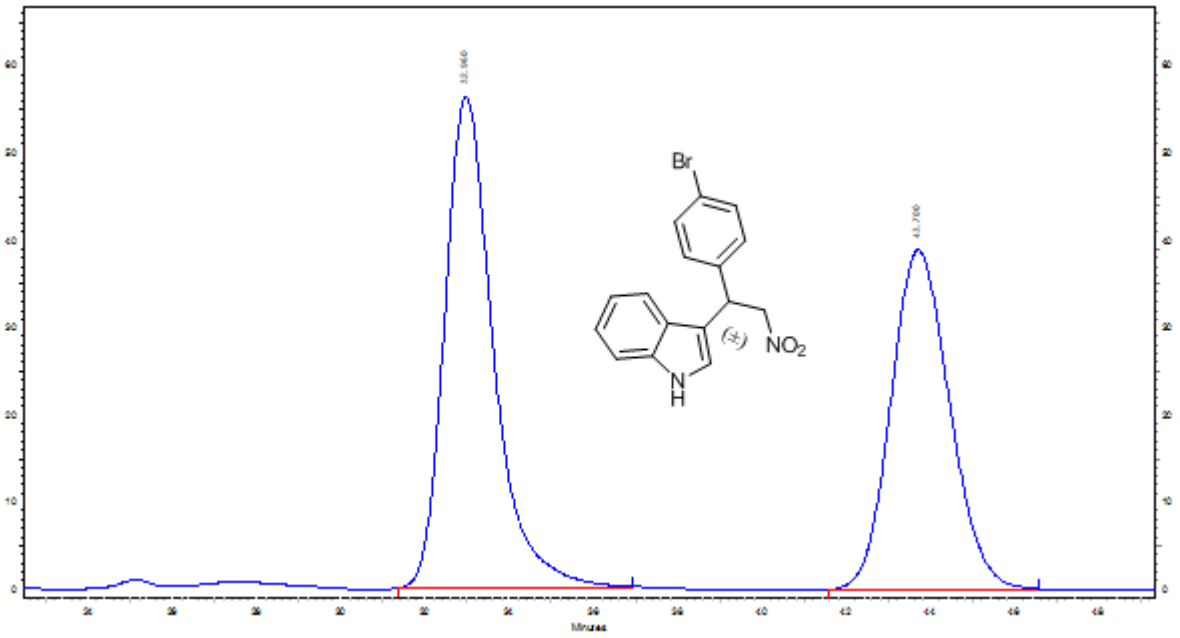


Retention Time	Area	Area %	Height	Height %
37.053	3110782	88.29	43036	91.28
56.440	412499	11.71	4111	8.72
Totals	3523281	100.00	47147	100.00

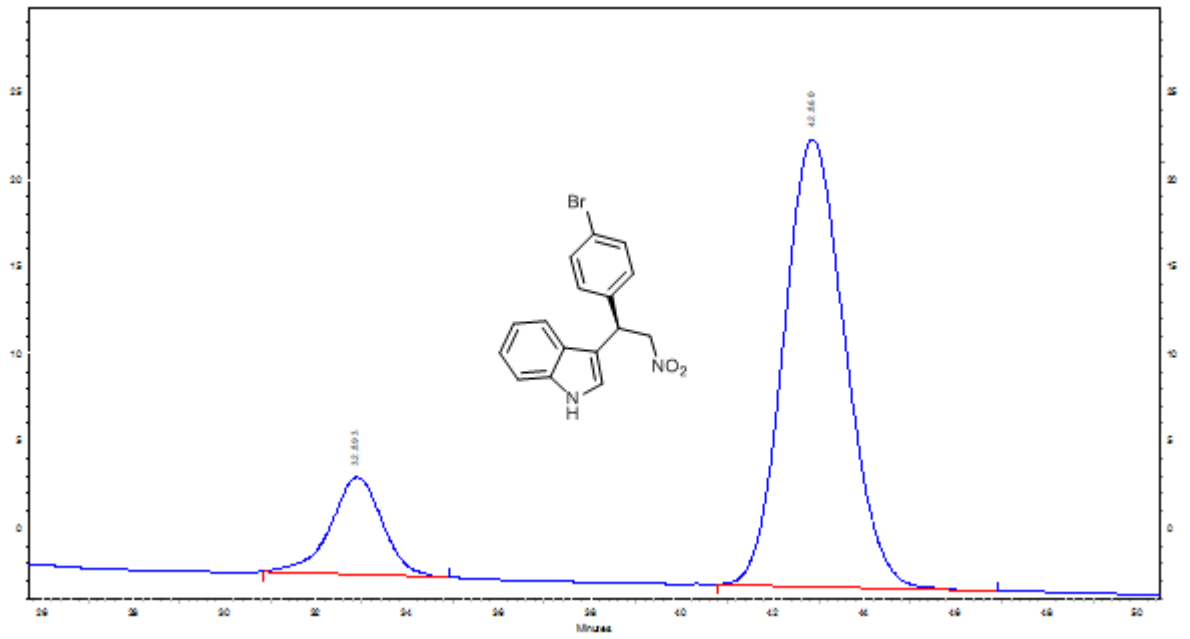


(*R*)-3-(1-(4-bromophenyl)-2-nitroethyl)-1H-indole (5g); (Table 3, entry 7)

The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **5g** in 87% yield. The ee was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ i-PrOH = 75/25, flow rate = 1 mL/min, 254nm; t_R = 32.8 min (minor), t_R = 42.8 min (major); 69% ee.



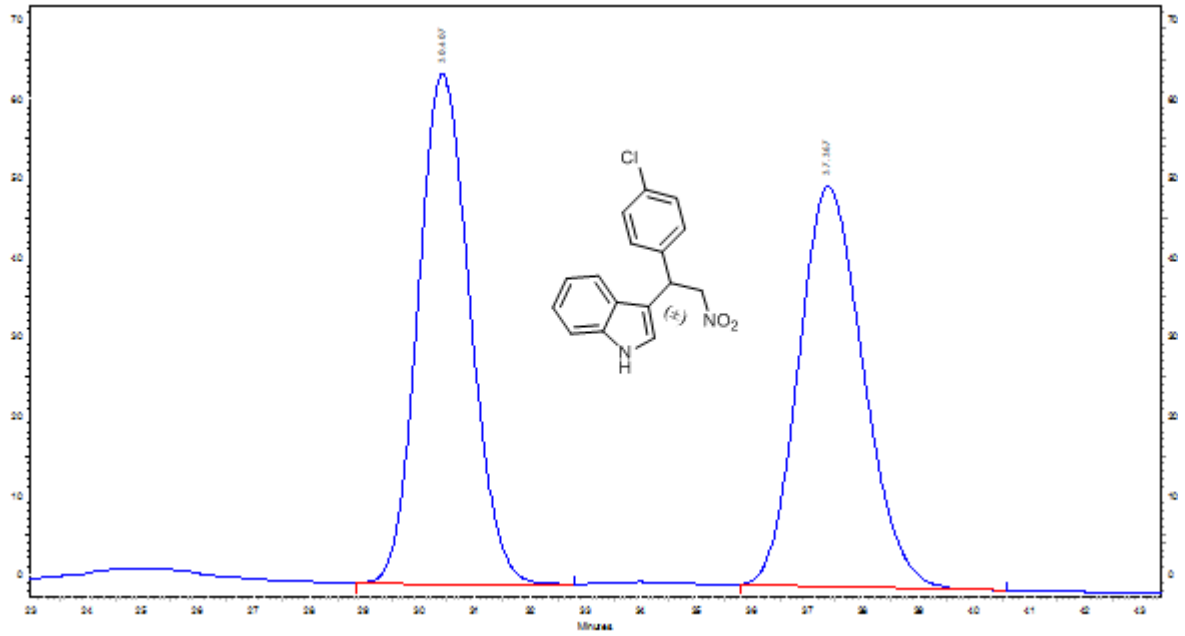
Retention Time	Area	Area %	Height	Height %
32.960	8985177	53.20	116717	58.87
43.700	7904908	46.80	81544	41.13
Totals	16890085	100.00	198261	100.00



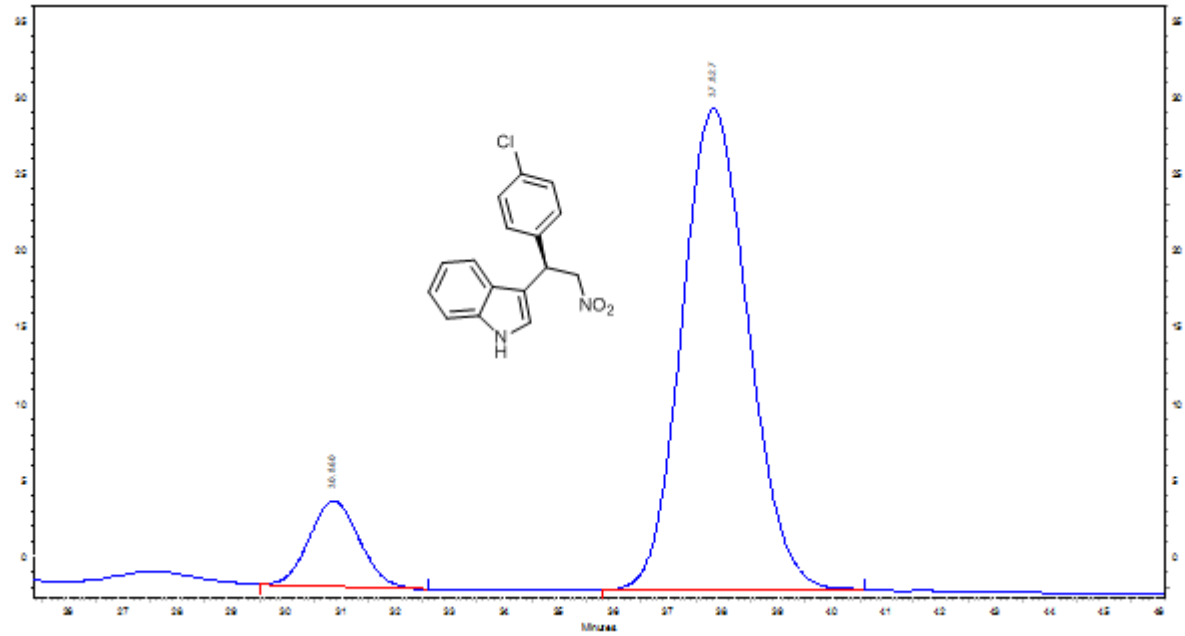
Retention Time	Area	Area %	Height	Height %
32.893	912147	15.41	11636	17.78
42.860	5007833	84.59	53812	82.22
Totals	5919980	100.00	65448	100.00

(*R*)-3-(1-(4-chlorophenyl)-2-nitroethyl)-1H-indole (5h); (Table 3, entry 8)

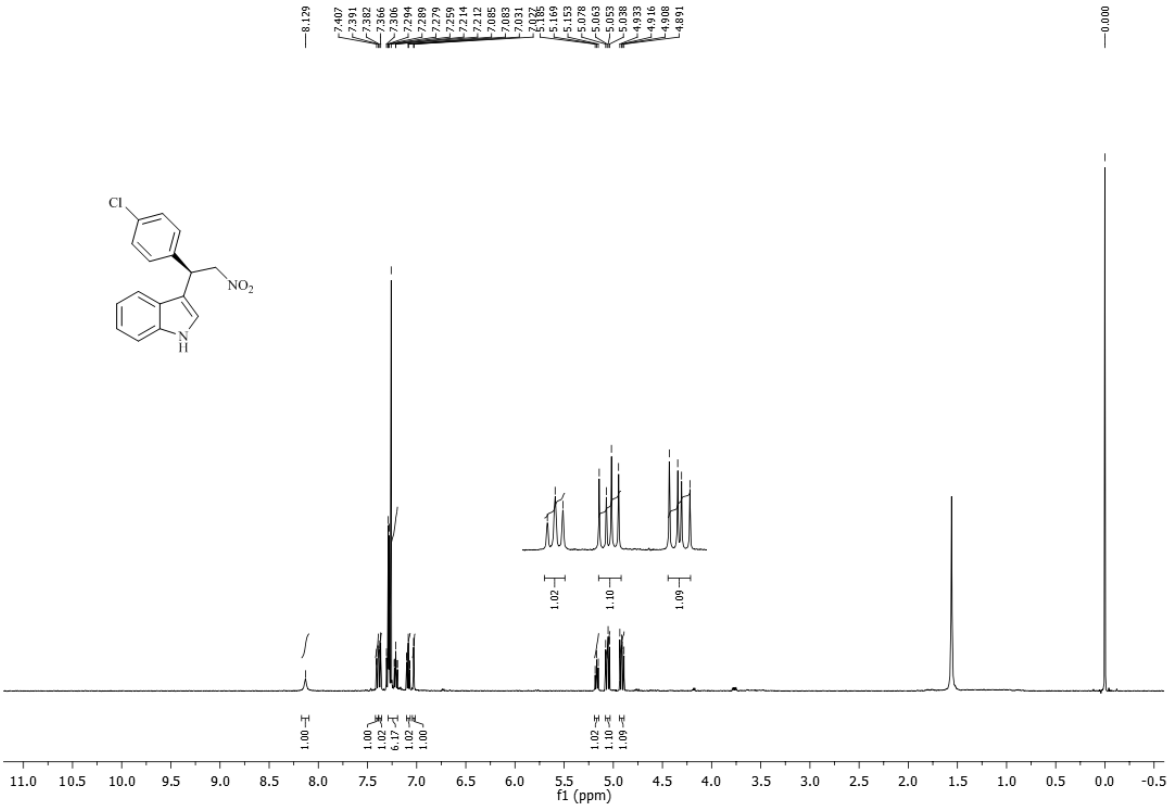
The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **5h** in 91% yield. The ee was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ i-PrOH = 75/25, flow rate = 1 mL/min, 254nm; t_R = 30.8 min (minor), t_R = 37.8 min (major); 76% ee; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (s, 3H), 7.34 (d, *J*=8Hz, 1H), 7.37 (d, *J*=8Hz, 1H), 7.04-7.19 (m, 6H), 7.08(td, *J*= 1Hz, 1H), 7.029 (d, *J*=2Hz, 1H), 6.17 (t, *J*=8Hz, 1H), 5.09(dd, *J*=7.5Hz, 7.5Hz, 1H), 4.91(dd, *J*=8.5Hz, 8.5Hz, 1H).



Retention Time	Area	Area %	Height	Height %
30.407	8761098	50.53	135043	56.04
37.367	8576719	49.47	105920	43.96
Totals	17337817	100.00	240963	100.00

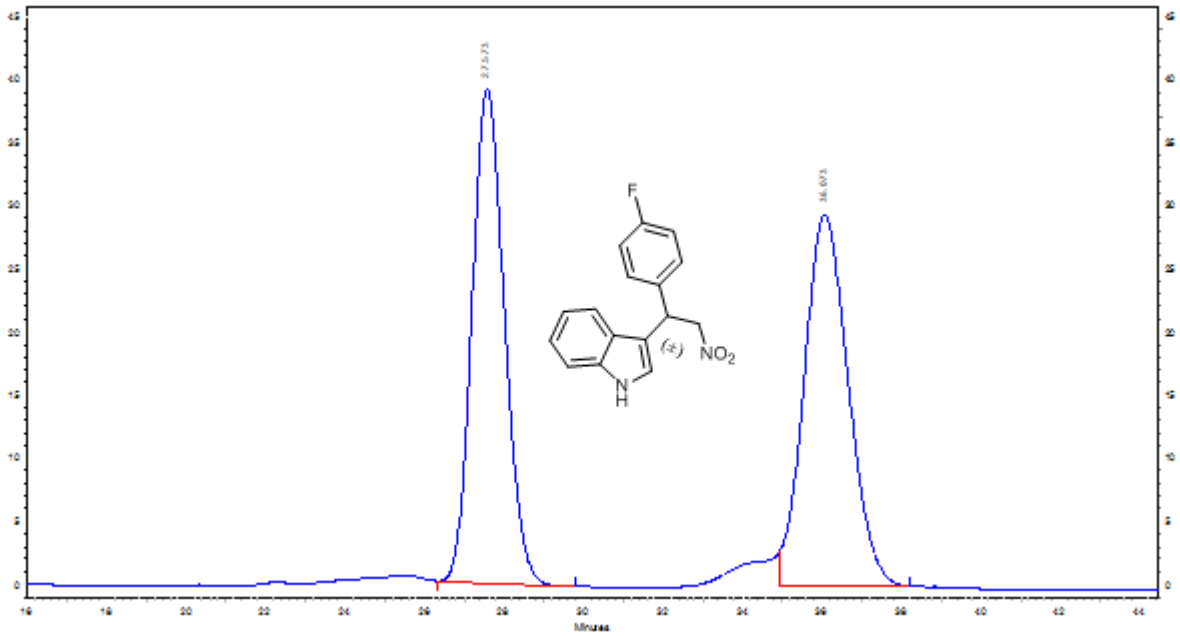


Retention Time	Area	Area %	Height	Height %
30.860	745992	11.78	11707	15.08
37.827	5584235	88.22	65934	84.92
Totals	6330227	100.00	77641	100.00

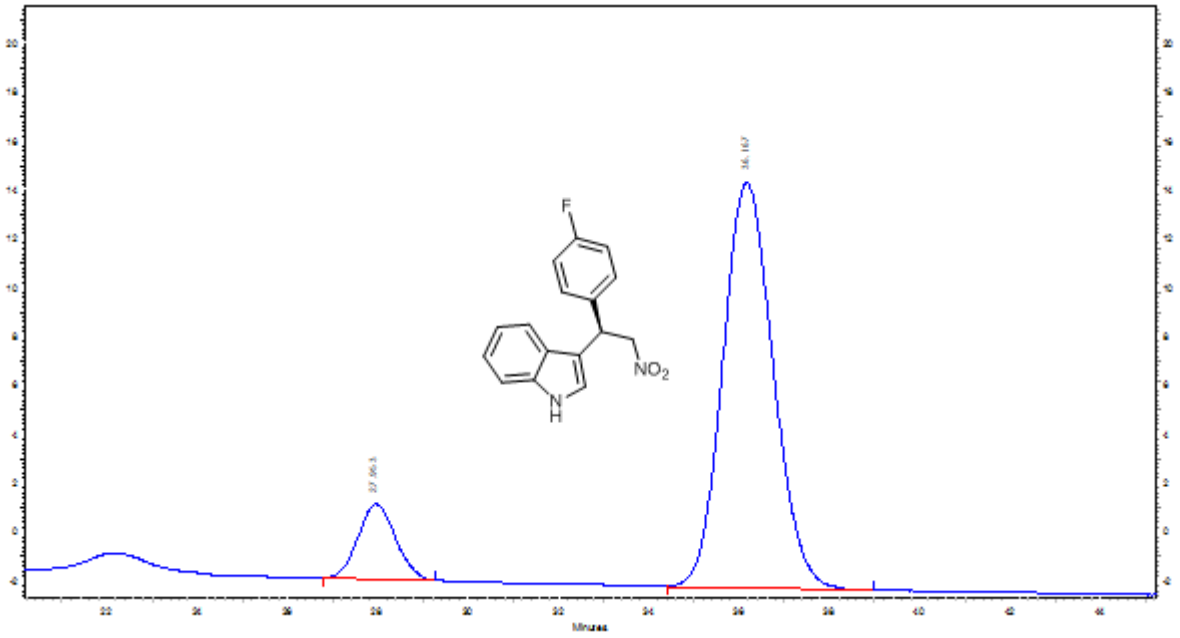


(*R*)-3-(1-(4-fluorophenyl)-2-nitroethyl)-1H-indole (5i); (Table 3, entry 8)

The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **5i** in 93% yield. The ee was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ i-PrOH = 75/25, flow rate = 1 mL/min, 254nm; t_R = 27.9 min (minor), t_R = 36.1 min (major); 76% ee.



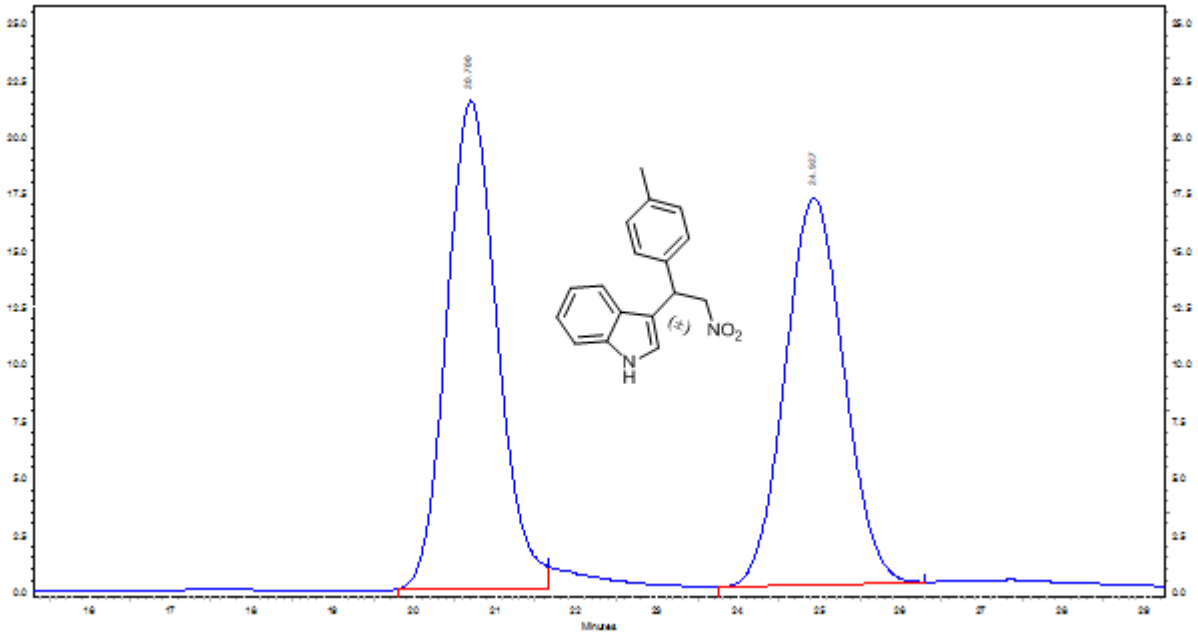
Retention Time	Area	Area %	Height	Height %
27.573	4643556	49.32	82112	57.09
36.073	4770944	50.68	61706	42.91
Totals	9414500	100.00	143818	100.00



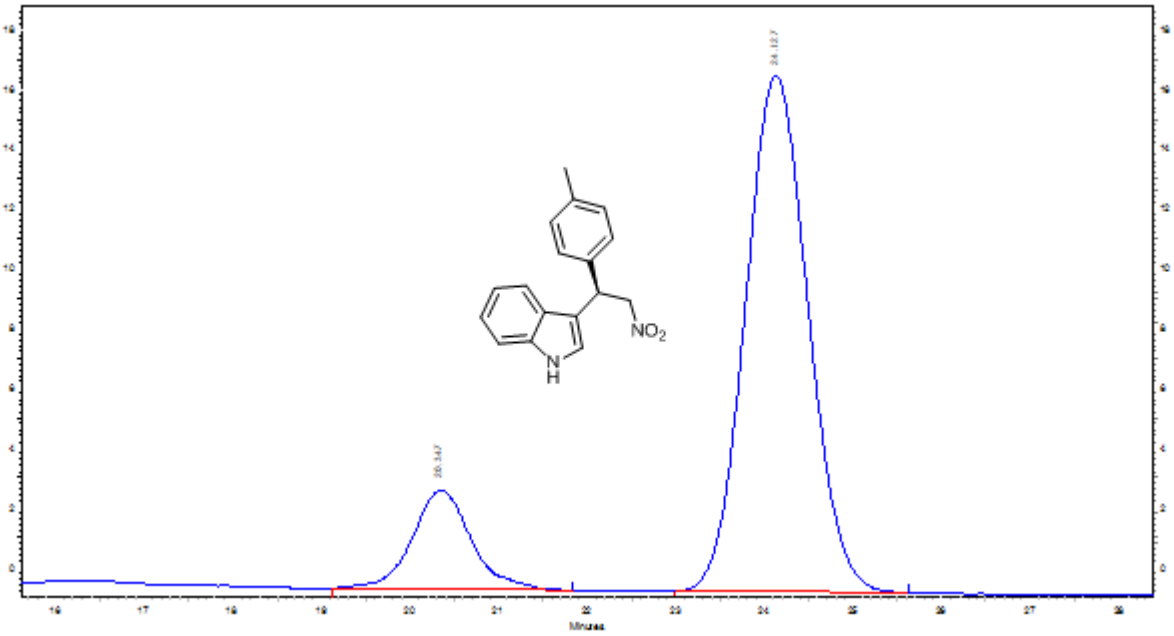
Retention Time	Area	Area %	Height	Height %
27.953	371212	12.09	6419	15.57
36.167	2698029	87.91	34799	84.43
Totals	3069241	100.00	41218	100.00

(*R*)-3-(2-nitro-1-(p-tolyl)ethyl)-1H-indole (5j); (Table 3, entry 10)

The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **5j** in 88% yield. The ee was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ i-PrOH = 75/25, flow rate = 1 mL/min, 254nm; t_R = 27.9 min (minor), t_R = 36.1 min (major); 70% ee.



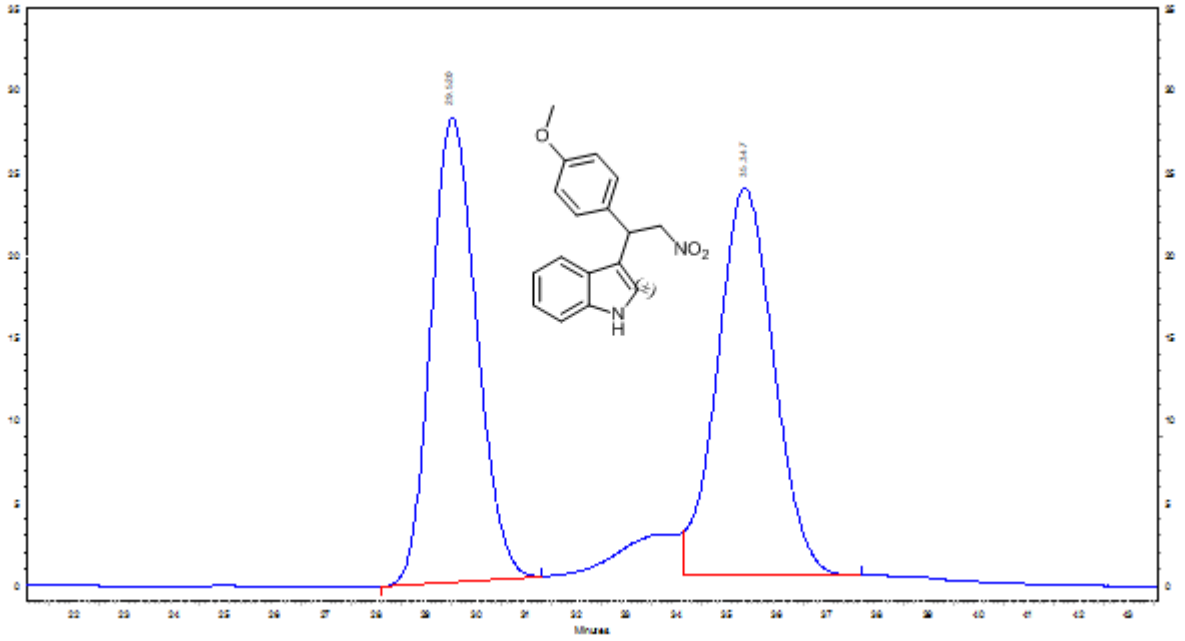
Retention Time	Area	Area %	Height	Height %
20.700	1930994	51.67	44987	55.77
24.927	1806177	48.33	35681	44.23
Totals	3737171	100.00	80668	100.00



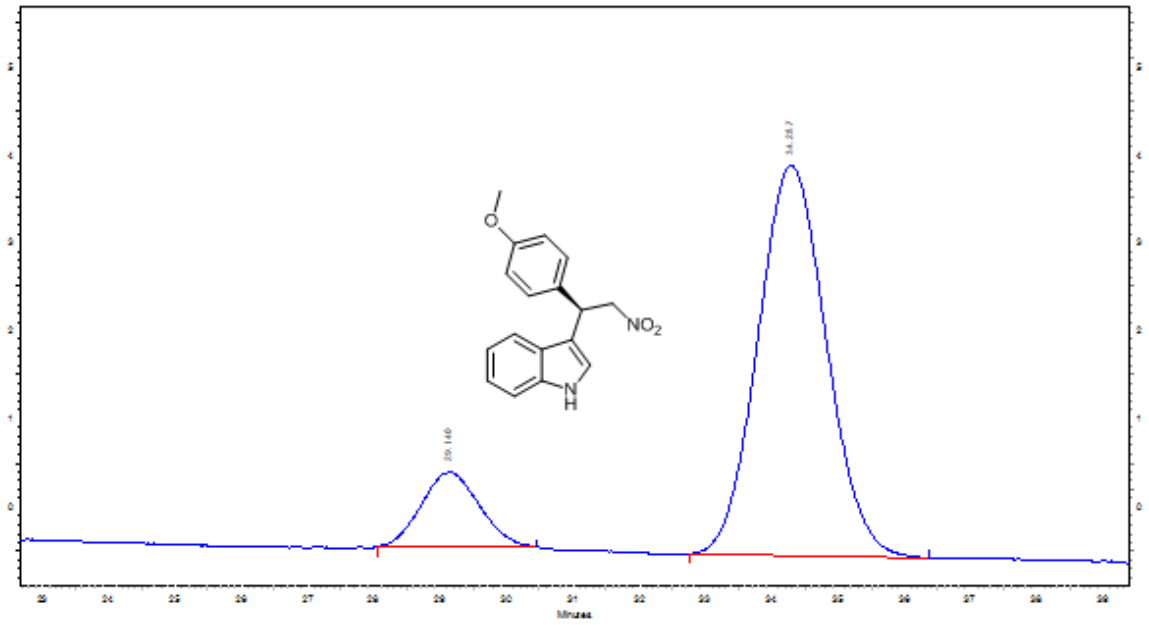
Retention Time	Area	Area %	Height	Height %
20.347	318060	15.19	6921	16.04
24.127	1775904	84.81	36229	83.96
Totals	2093964	100.00	43150	100.00

(*R*)-3-(1-(4-methoxyphenyl)-2-nitroethyl)-1H-indole (5k); (Table 3, entry 11)

The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **5k** in 85% yield. The ee was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ i-PrOH = 75/25, flow rate = 1 mL/min, 254nm; t_R = 29.1 min (minor), t_R = 34.2 min (major); 72% ee.



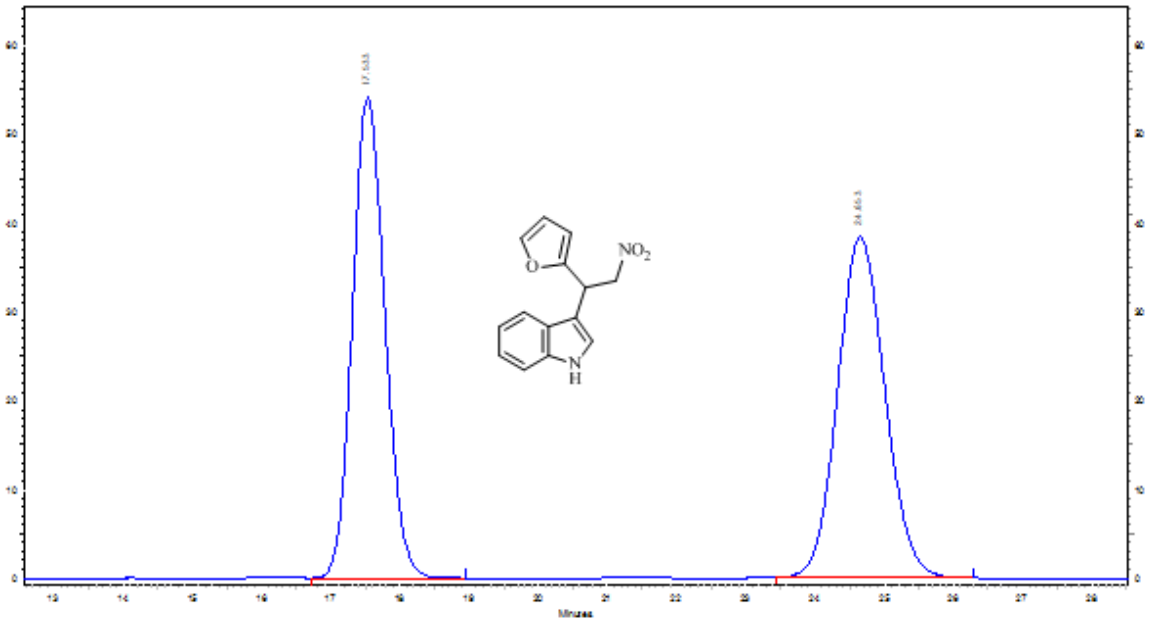
Retention Time	Area	Area %	Height	Height %
29.520	3728146	49.10	59108	54.53
35.347	3864050	50.90	49278	45.47
Totals	7592196	100.00	108386	100.00



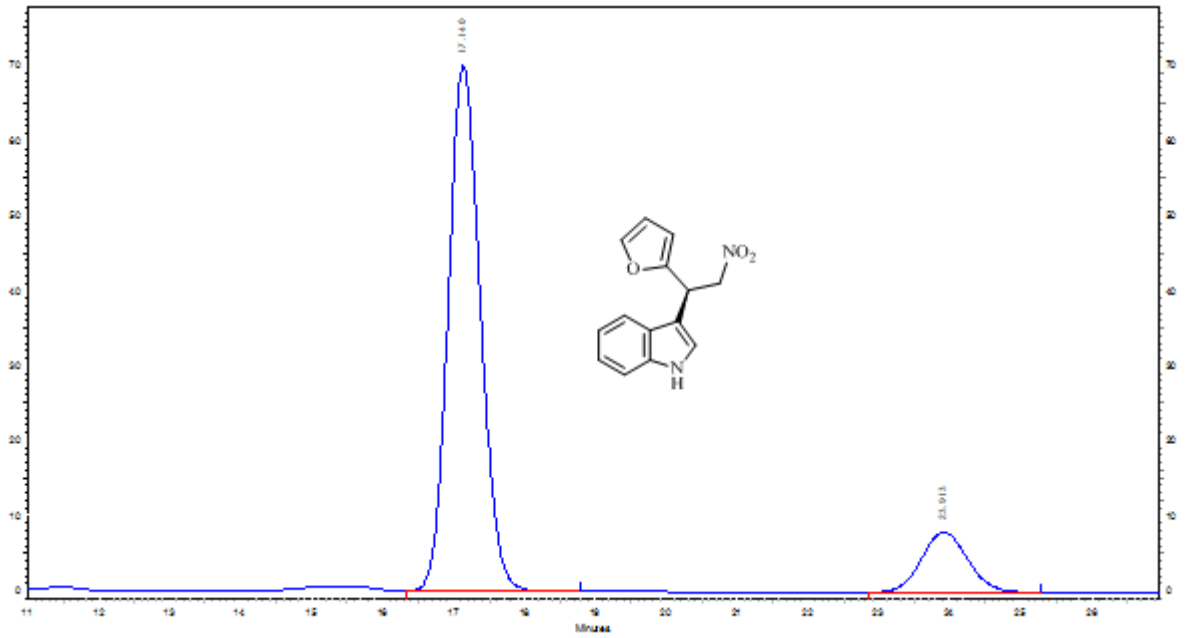
Retention Time	Area	Area %	Height	Height %
29.140	109378	14.10	1787	16.15
34.287	666471	85.90	9276	83.85
Totals	775849	100.00	11063	100.00

(*R*)-3-(1-(furan-2-yl)-2-nitroethyl)-1H-indole (5l); (Table 3, entry 12)

The crude product was purified by column chromatography with silica (20% ethyl acetate in hexanes) to afford the title compound **5l** in 94% yield. The ee was determined by HPLC using a Daicel Chiralcel OD-H column, *n*-hexane/ i-PrOH = 75/25, flow rate = 1 mL/min, 254nm; t_R = 17.1 min (major), t_R = 23.9 min (minor); 72% ee.



Retention Time	Area	Area %	Height	Height %
17.533	3696882	49.21	113370	58.51
24.653	3815137	50.79	80390	41.49
Totals	7512019	100.00	193760	100.00



Retention Time	Area	Area %	Height	Height %
17.140	4607174	85.92	146871	89.75
23.913	754785	14.08	16767	10.25
Totals	5361959	100.00	163638	100.00