Supplementary Information

Highly Efficient Asymmetric Organocatalytic Friedel-Crafts Alkylation of Indoles with *α,β*-Unsaturated Aldehydes

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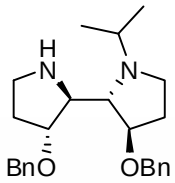
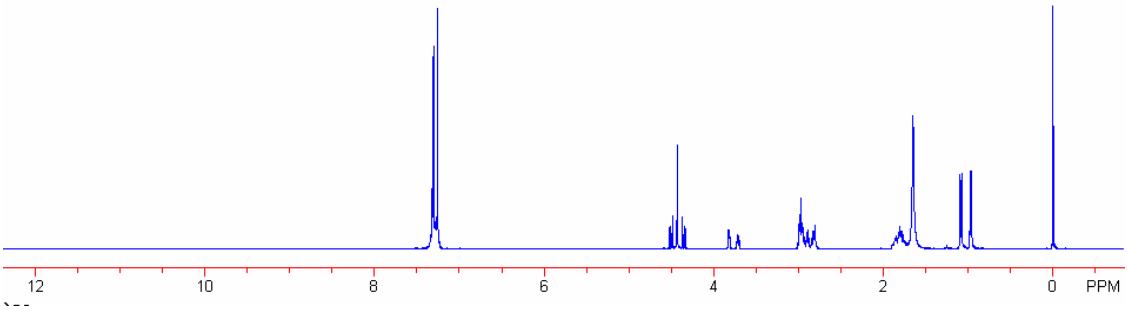
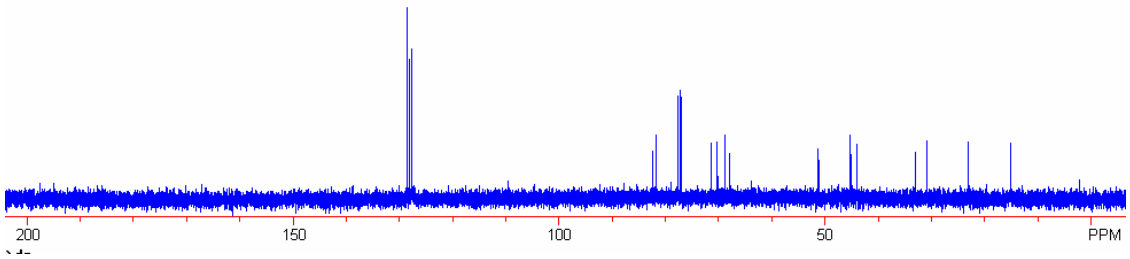
(2*S*,2'*S*,3*R*,3'*R*)-3,3'-bis(benzyloxy)-1-isopropyl-2,2'-bipyrrolidine (2a)

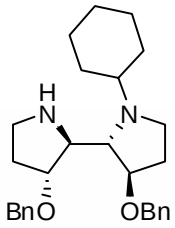


2a





(2*S*,2'*S*,3*R*,3'*R*)-3, 3'-bis(benzyloxy)-1-cyclohexyl-2,2'-bipyrrolidine (2b)



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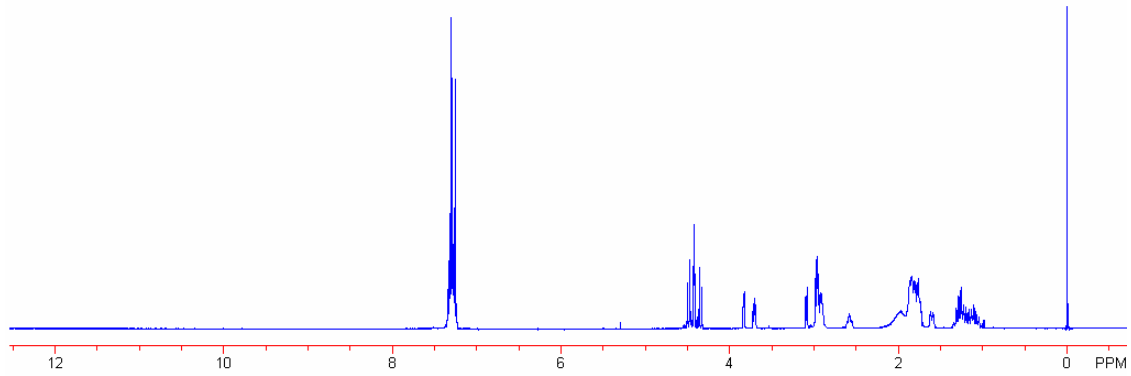
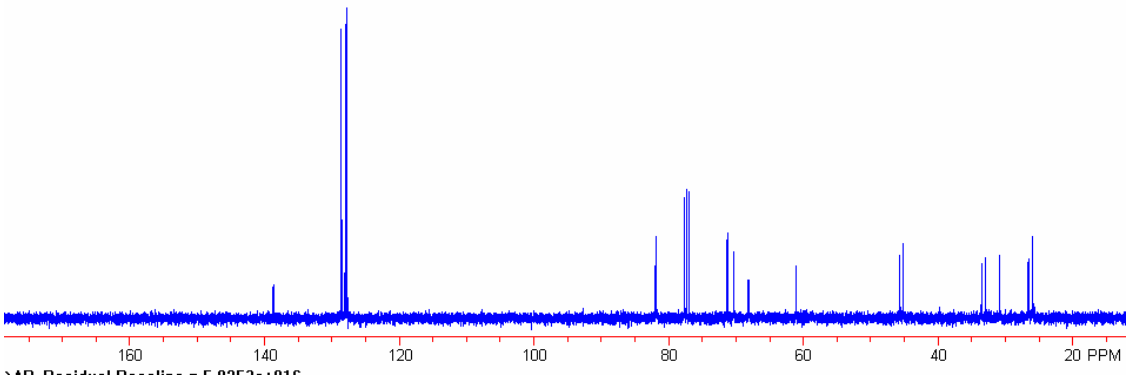
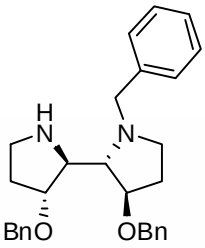




(2*S*,2'*S*,3*R*,3'*R*)-1-benzyl-3, 3'-bis(benzyloxy)-2,2'-bipyrrolidine(2c)



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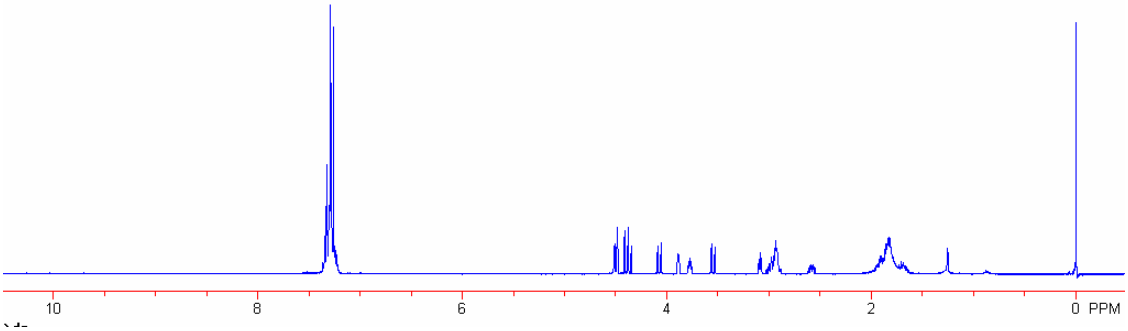
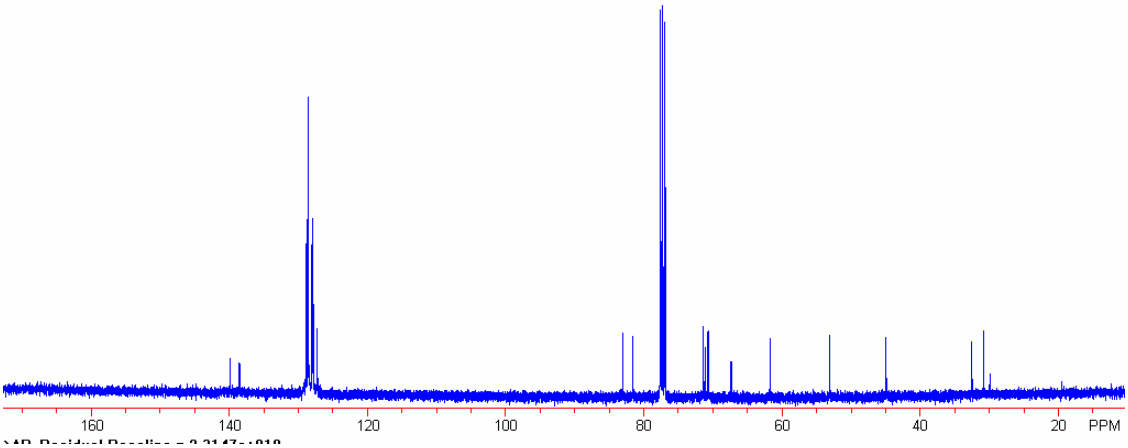
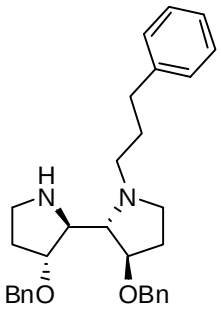
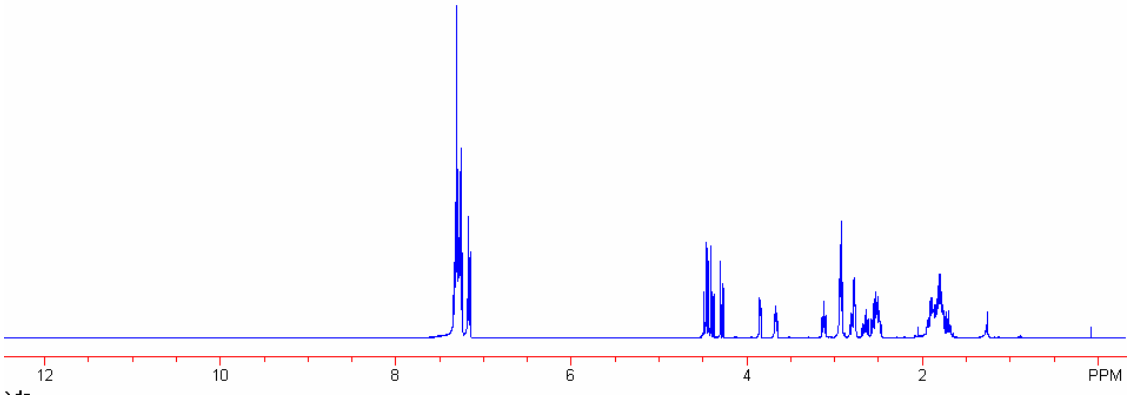


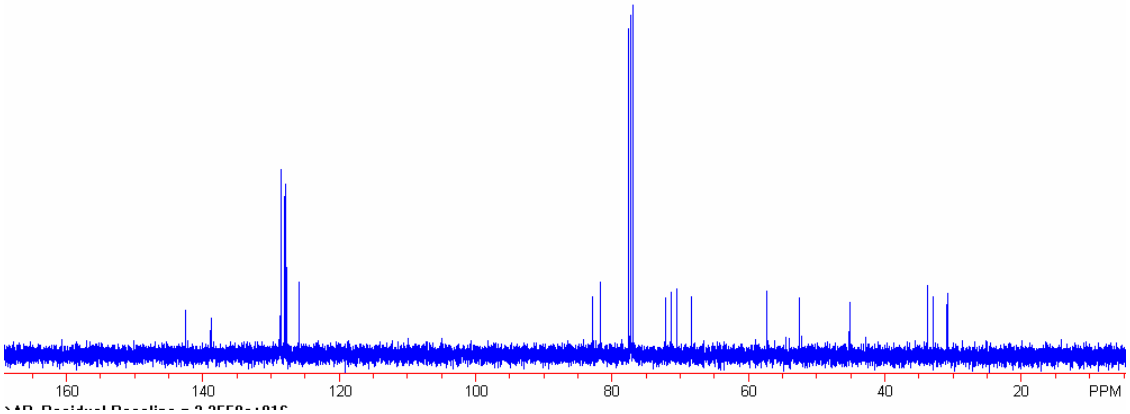


(2*S*,2'*S*,3*R*,3'*R*)-3,3'-bis(benzyloxy)-1-(3-phenylpropyl)-2,2'-bipyrrolidine(2d)

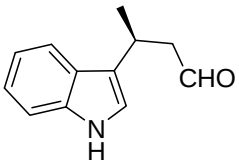


2d





(S)-3-(1H-indol-3-yl)-butanal (5a)[1]



5a

In accordance with the general procedures, the product was isolated by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:4) to afford title compound **5a** (80.5 mg, 86% yield) as a yellowish oil. $[\alpha]_D^{25}$ = + 8.0 (*c* = 0.60, $CHCl_3$).

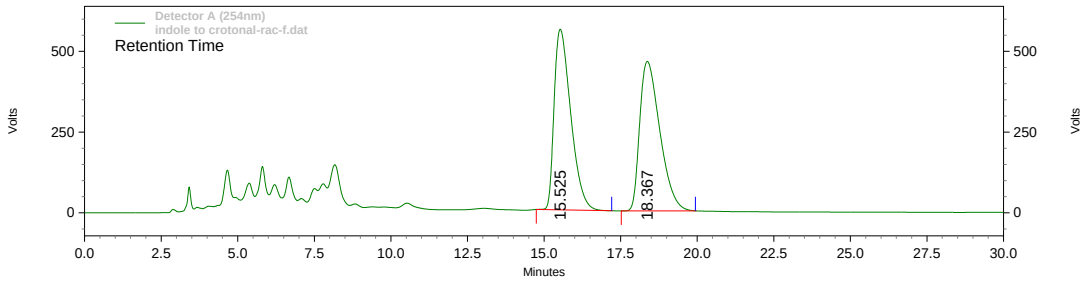
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (t, *J* = 2.0 Hz, 1H), 8.04 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.24–7.10 (m, 2H), 6.98 (d, *J* = 2.2 Hz, 1H), 3.70 (m, 1H), 2.94–2.84 (m, 1H), 2.77–2.67 (m, 1H),1.45 (d, *J* = 7.2 Hz, 3H);

HPLC The product was converted to the corresponding alcohol with $NaBH_4$ in MeOH and enantiomeric excess was determined by HPLC using a Chiracel OD-H column (85/15 hexane/*i*-PrOH; flow rate 1.0 ml/min); *R* isomer t_r = 15.85 min (minor), *S* isomer t_r = 18.35 min (major), 80% ee.

[1] L. Hong, L. Wang, C. Chen, B. Zhang and R. Wang, *Adv. Synth. Catal.*, 2009, **351**, 772.

(rac)-3-(1H-indol-3-yl)-butanal (5a)

Chiral HPLC : Chiracel OD-H, 85/15 hexane/*i*PrOH, 1 ml/min, 254 nm

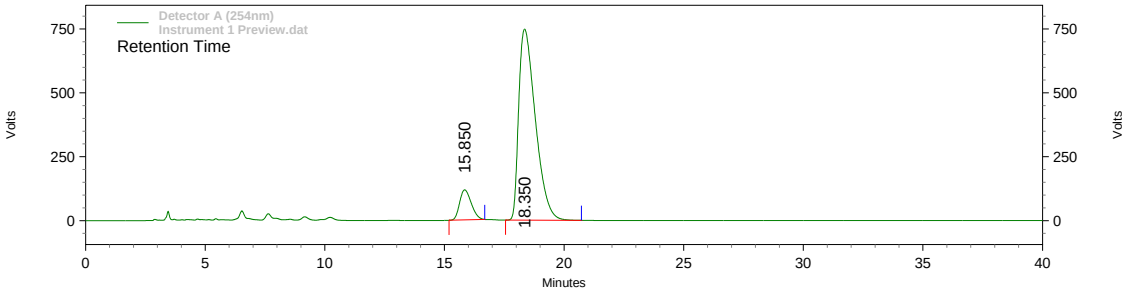


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	15.525	21099414	49.916	559430	54.728
2	18.367	21170213	50.084	462769	45.272
Totals		42269627	100.000	1022199	100.000

(S)-3-(1H-indol-3-yl)-butanal (5a)

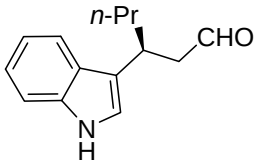
Chiral HPLC : Chiracel OD-H, 85/15 hexane/*i*PrOH, 1 ml/min, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	15.850	3980021	9.920	117552	13.587
2	18.350	36140198	90.080	747601	86.413
Totals		40120219	100.000	865153	100.000

(*S*)-3-(1H-indol-3-yl)-hexanal (5b)[1]



5b

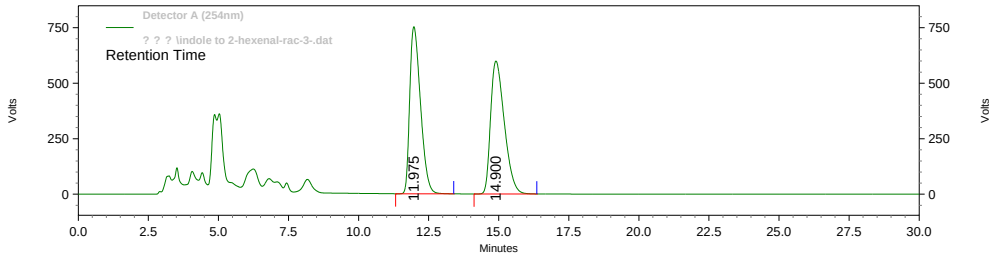
In accordance with the general procedures, the product was isolated by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:6) to afford title compound **5b** (94.0 mg, 88% yield) as a yellowish oil, $[\alpha]_D^{25} = +65.2$ ($c = 0.18$, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (t, $J = 2.4$ Hz, 1H), 8.01 (s, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.23–7.07 (m, 2H), 6.98 (d, $J = 2.4$ Hz, 1H), 3.58–3.48 (m, 1H), 2,89–2.73 (m, 2H), 1.88–1.66 (m, 2H), 1.36–1.26 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H).

HPLC The product was converted to the corresponding alcohol with $NaBH_4$ in MeOH and enantiomeric excess was determined by HPLC using a Chiracel OD-H column (85/15 hexane/*i*-PrOH; flow rate 1.0 ml/min); *R* isomer $t_r = 12.56$ min (minor), *S* isomer $t_r = 15.69$ min (major), 92% ee.

(*rac*)-3-(1H-indol-3-yl)-hexanal (5b)

Chiracel OD-H, 85/15 hexane/*i*PrOH, 1 ml/min, 254 nm

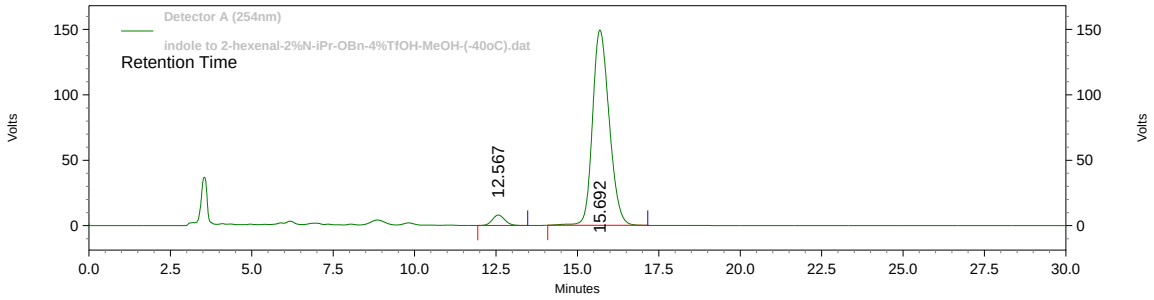


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	11.975	20063719	49.547	752492	55.688
2	14.900	20430202	50.453	598783	44.312
Totals		40493921	100.000	1351275	100.000

(*S*)-3-(1H-indol-3-yl)-hexanal (5b)

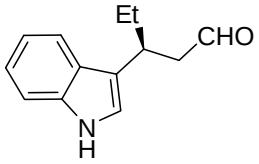
Chiracel OD-H, 85/15 hexane/*i*PrOH, 1 ml/min, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	12.567	210405	3.802	7943	5.053
2	15.692	5323221	96.198	149262	94.947
Totals		5533626	100.000	157205	100.000

(*S*)-3-(1H-indol-3-yl)-pentanal (5c)[1]



5c

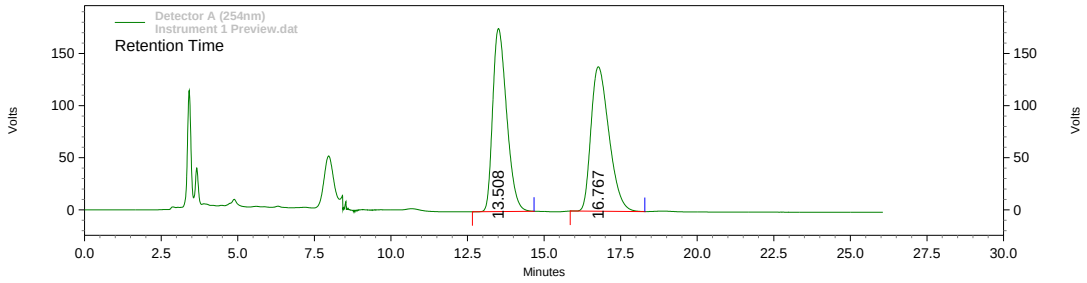
In accordance with the general procedures, the product was isolated by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:6) to afford title compound **5c** (90.1 mg, 89% yield) as yellowish oil, $[\alpha]_D^{25} = +3.6$ (*c* = 0.90, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (t, *J* = 2.4 Hz, 1H), 8.12 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.24–7.11 (m, 2H), 6.95 (d, *J* = 2.4 Hz, 1H), 3.52–3.42 (m, 1H), 2.91–2.74 (m, 2H), 1.93–1.73 (m, 2H), 0.90 (t, *J* = 9.6 Hz, 3H).

HPLC The product was converted to the corresponding alcohol with $NaBH_4$ in MeOH and enantiomeric excess was determined by HPLC using a Chiracel OD-H column (85/15, hexane/*i*-PrOH; flow rate 1.0 ml/min); *R* isomer t_r = 13.59 min (minor), *S* isomer t_r = 16.32 min (major), 92% ee.

(*rac*)-3-(1H-indol-3-yl)-pentanal (5c)

Chiracel OD-H, 85/15 hexane/*i*PrOH, 1 ml/min, 254 nm

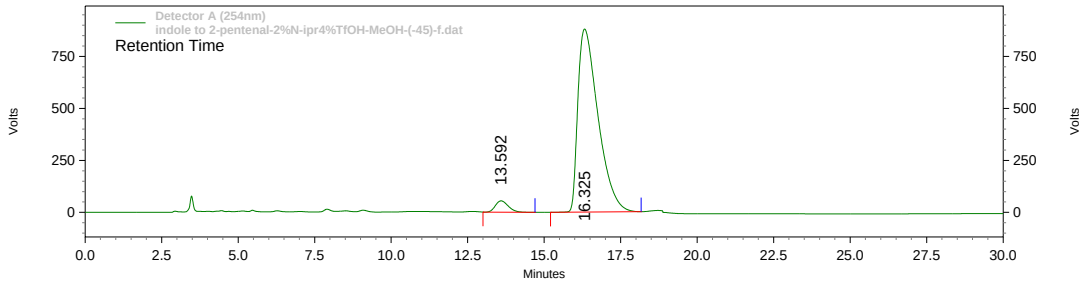


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	13.508	5560542	49.582	175548	55.889
2	16.767	5654281	50.418	138554	44.111
Totals		11214823	100.000	314102	100.000

(*S*)-3-(1H-indol-3-yl)-pentanal (5c)

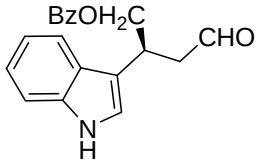
Chiracel OD-H, 85/15 hexane/*i*PrOH, 1 ml/min, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	13.592	1583866	3.782	54292	5.812
2	16.325	40292091	96.218	879906	94.188
Totals		41875957	100.000	934198	100.000

(*S*)-2-(1H-indol-3-yl)-4-oxobutyl-benzoate (5d)



5d

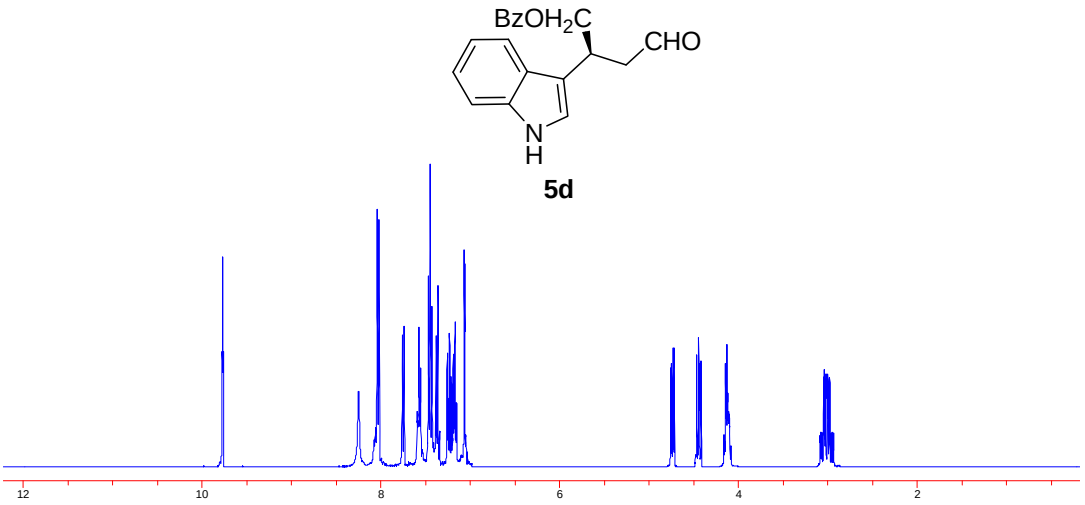
In accordance with the general procedures, the product was isolated by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:4) to afford title compound **5d** (154 mg, 71% yield) as yellowish oil. $[\alpha]_D^{25}$ = +66.0 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (t, *J* = 2.4 Hz, 1H), 8.25 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.57 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.45 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.26–7.14 (m, 2H), 7.06 (d, *J* = 3.2 Hz, 1H), 4.74 (dd, *J* = 5.2, 10.8 Hz, 1H), 4.44 (dd, *J* = 8.8, 10.8 Hz, 1H), 4.17–4.08 (m, 1H), 3.09–2.92 (m, 2H).

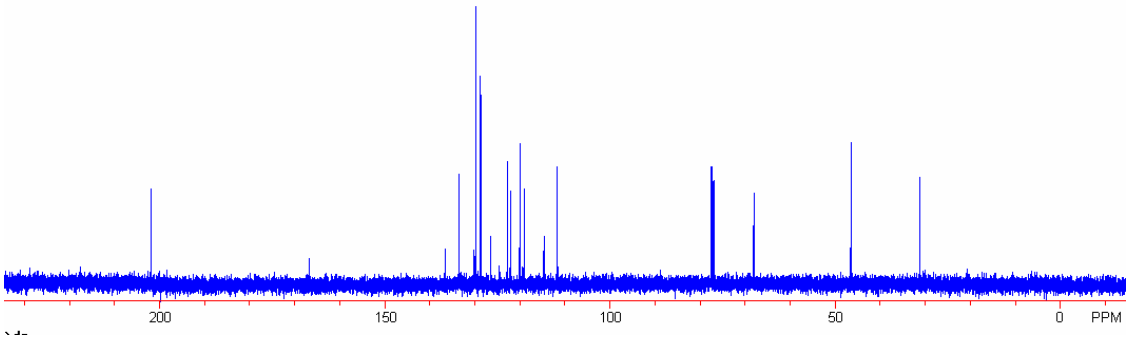
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 166.7, 126.6, 133.4, 130.2, 129.9, 128.7, 126.6, 122.7, 122.0, 120.0, 119.1, 114.7, 111.7, 68.1, 46.5, 31.2.

HRMS(EI-TOF) Calcd. for $C_{14}H_{15}NO_3$ 307.1208, Found: 302.1205.

HPLC The product was converted to the corresponding alcohol with $NaBH_4$ in MeOH and enantiomeric excess was determined by HPLC using a Chiracel AD-H column (85/15 hexane/*i*-PrOH; flow rate 1.0 ml/min); *R* isomer t_r = 19.53 min (major), *S* isomer t_r = 22.02 min (minor), 87% ee.

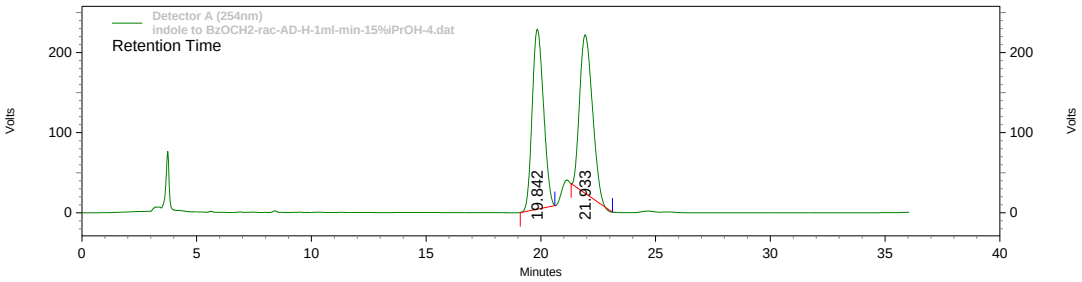


5d



(*rac*)-2-(1H-indol-3-yl)-4-oxobutyl-benzoate (5d)

Chiracel AD-H, 85/15 hexane/*i*-PrOH, 1.0 ml/min, 254 nm

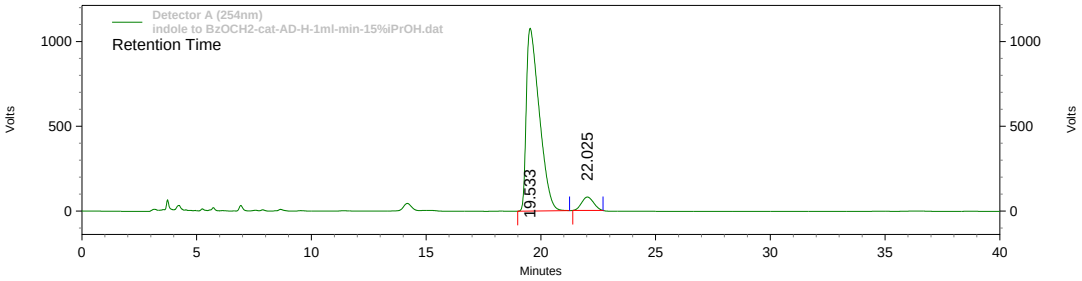


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	19.842	7716346	50.206	224629	53.148
2	21.933	7652898	49.794	198020	46.852
Totals		15369244	100.000	422649	100.000

(*S*)-2-(1H-indol-3-yl)-4-oxobutyl-benzoate (5d)

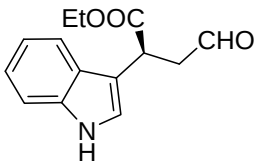
Chiracel AD-H, 85/15 hexane/*i*-PrOH; 1.0 ml/min, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	19.533	42376141	93.648	1077873	93.162
2	22.025	2874423	6.352	79116	6.838
Totals		45250564	100.000	1156989	100.000

(*S*)-ethyl 2-(1H-indol-3-yl)-4-oxobutanoate (5e)



5e

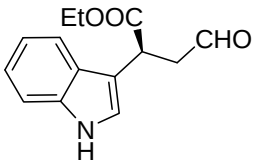
In Accordance with the general procedures, the product was isolated by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:4) to afford title compound **5e** (107 mg, 88 % yield) as yellowish oil. $[\alpha]_D^{25} = +44.4$ (*c* = 0.7, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 8.22 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.24–7.12 (m, 2H), 7.11 (d, *J* = 2.4 Hz, 1H), 4.43 (dd, *J* = 4.8, 9.6 Hz, 1H), 4.24–4.04 (m, 2H), 3.46 (dd, *J* = 9.6, 18.0 Hz, 1H), 2.94 (dd, *J* = 4.8, 18.0, 1H), 1.20 (t, *J* = 7.2 Hz, 3H).

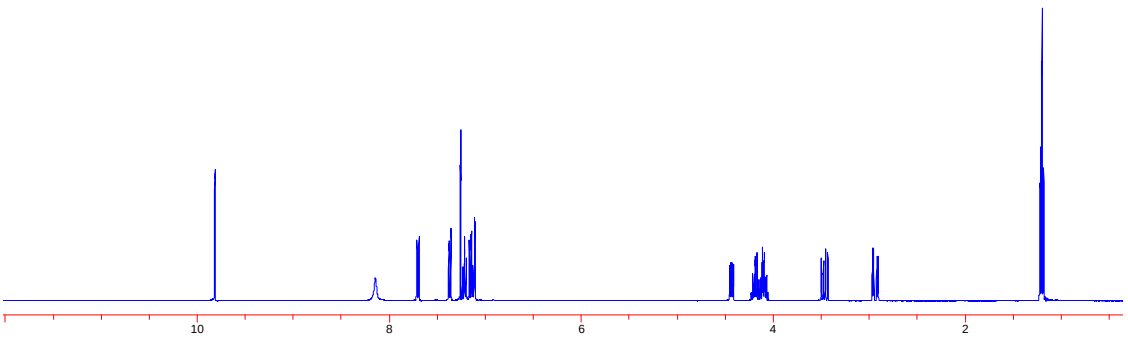
^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 173.5, 136.5, 126.3, 122.7, 122.4, 120.1, 119.4, 112.7, 111.6, 61.5, 46.6, 36.9, 14.3.

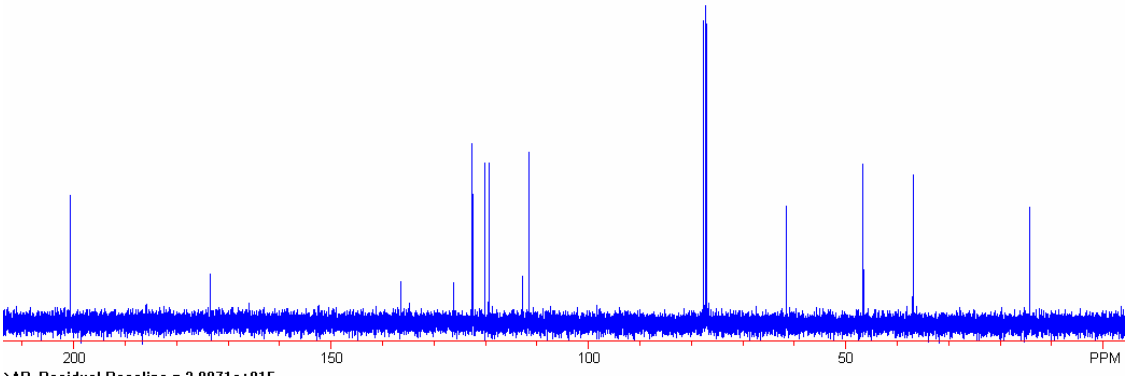
HRMS(EI-TOF) Calcd. for $C_{14}H_{15}NO_3$ 245.1052, Found: 245.1055.

HPLC The product was converted to the corresponding alcohol with $NaBH_4$ and enantiomeric excess was determined by HPLC using a Chiracel OD-H column (85/15 hexane/*i*-PrOH; flow rate 1.0 ml/min), *R* isomer t_r = 14.50 min (minor), *S* isomer t_r = 18.83 min (major), 90% ee.



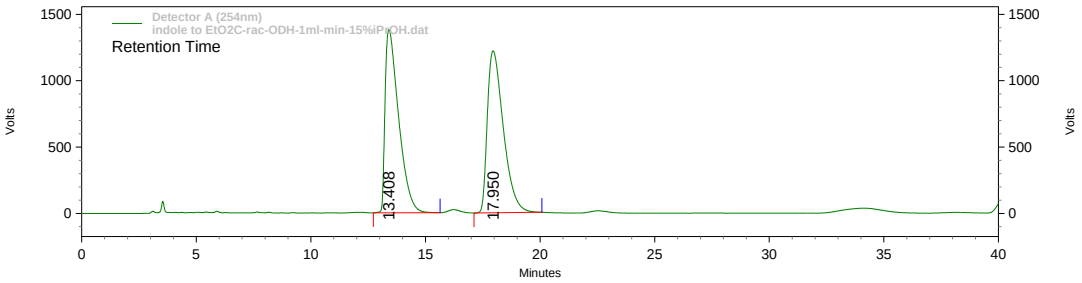
5e





(*rac*)-ethyl 2-(1H-indol-3-yl)-4-oxobutanoate (5e)

Chiracel OD-H, 85/15 hexane/*i*-PrOH, 1.0 ml/min, 254 nm

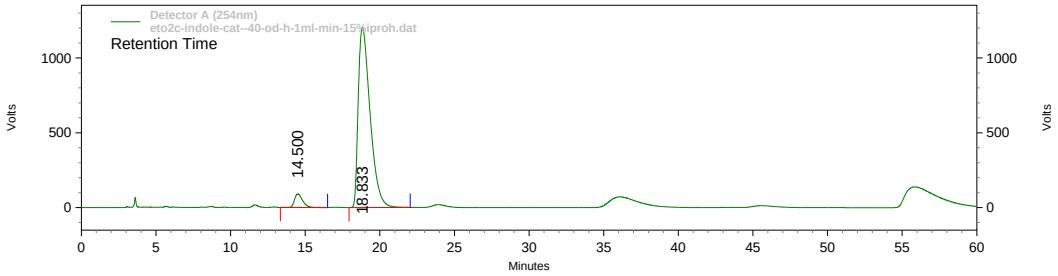


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	13.408	56719840	48.912	1380463	53.073
2	17.950	59242709	51.088	1220610	46.927
Totals		115962549	100.000	2601073	100.000

(*S*)-ethyl 2-(1H-indol-3-yl)-4-oxobutanoate (5e)

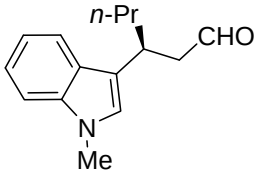
Chiracel OD-H, 85/15 hexane/*i*-PrOH, 1.0 ml/min, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	14.500	3340174	4.796	90041	6.971
2	18.833	66310774	95.204	1201586	93.029
Totals		69650948	100.000	1291627	100.000

(*S*)-3-(1-methyl-1H-indol-3-yl)-hexanal (5f)[2]



5f

In Accordance with the general procedures, the product was isolated by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:40) to afford title compound **5f** (102 mg, 88% yield) as yellowish oil, $[\alpha]_D^{25} = +20.0$ ($c = 0.20$, $CHCl_3$).

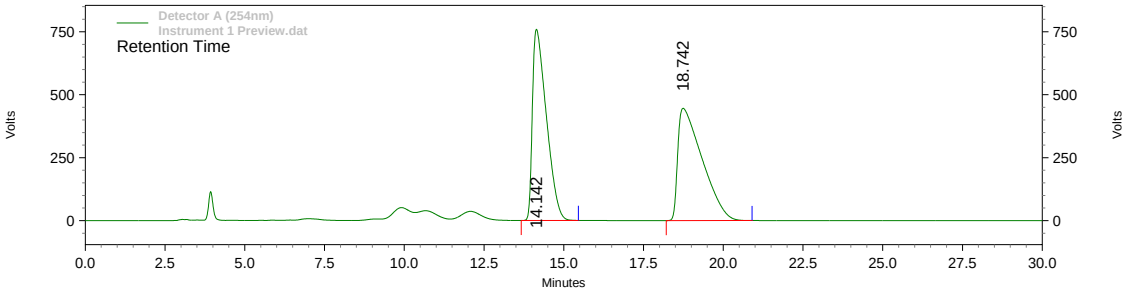
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (t, J = 2.0 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.33–7.20 (m, 2H), 7.15–7.08 (m, 1H), 6.84 (s, 1H), 3.74 (s, 3H), 3.58–3.48 (m, 1H), 2.88–2.72 (m, 2H), 1.87–1.56 (m, 2H), 1.38–1.22 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H).

HPLC The product was converted to the corresponding alcohol with $NaBH_4$ in MeOH and enantiomeric excess was determined by HPLC using a Chiracel AS-H column (95/5 hexane/*i*-PrOH; flow rate 1.0 ml/min); *S* isomer t_r =14.80 min (major), *R* isomer t_r = 20.19 min (minor), 89% ee.

[2] J. F. Austin and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2002, **124**, 1172.

(*rac*)-3-(1-methyl-1H-indol-3-yl)-hexanal (5f)

Chiracel AS-H, 95/5 hexane/*i*PrOH, 1 ml/min, 254 nm

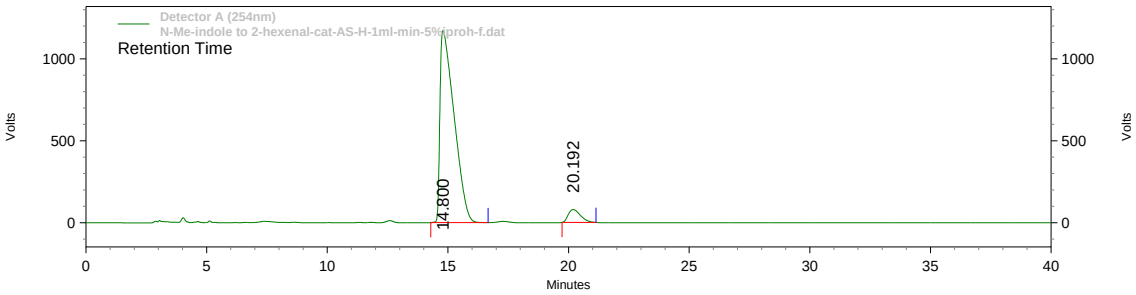


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	14.142	23130962	49.435	759297	62.995
2	18.742	23659849	50.565	446023	37.005
Totals		46790811	100.000	1205320	100.000

(*S*)-3-(1-methyl-1H-indol-3-yl)-hexanal (5f)

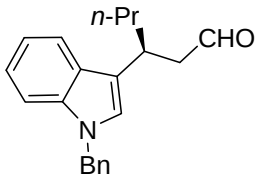
Chiracel AS-H, 95/5 hexane/*i*PrOH, 1 ml/min, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	14.800	47584392	94.438	1173153	93.706
2	20.192	2802564	5.562	78799	6.294
Totals		50386956	100.000	1251952	100.000

(*S*)-3-(1-benzyl-1H-indol-3-yl)-hexanal (5g)[3]



5g

In Accordance with the general procedures, the product was isolated by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:40) to afford title compound **5g** (128 mg, 84% yield) as yellowish oil, $[\alpha]_D^{25}$ = +20.2 (*c* = 0.21, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (t, *J* = 2.4 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.35–7.24 (m, 4H), 7.22–7.05 (m, 2H), 7.08 (d, *J* = 6.8 Hz, 2H), 6.94 (s, 1H), 5.29 (s, 2H), 3.60–3.50 (m, 1H), 2.90–2.75 (m, 2H), 1.90–1.60 (m, 2H), 1.40–1.26 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H).

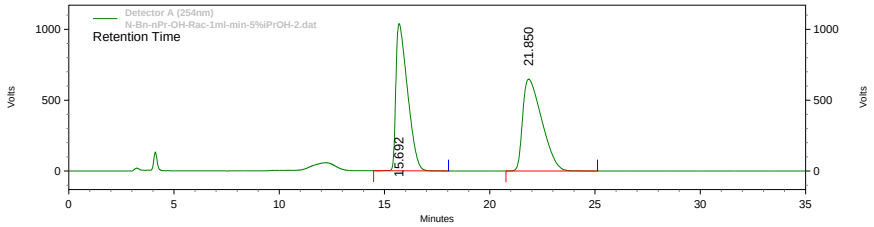
^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 137.8, 137.1, 129.0, 127.7, 127.4, 126.8, 125.7, 122.1, 119.6, 119.3, 117.9, 110.2, 77.6, 77.2, 76.9, 50.1, 49.7, 38.5, 31.5, 20.9, 14.3.

HPLC The product was converted to the corresponding alcohol with $NaBH_4$ in MeOH and enantiomeric excess was determined by HPLC using a Chiracel AS-H column (95/5 hexane/*i*-PrOH; flow rate 1.0 ml/min); *S* isomer t_r =16.30 min (major), *R* isomer t_r = 24.20 min (minor), 90% ee.

[3] T. Tian, B.-J. Pei, Q.-H. Li, H. He, L.-Y. Chen, X. Zhou, W.-H. Chan and A. W. M. Lee. *Synlett.*, 2009, 2115.

(*rac*)-3-(1-benzyl-1H-indol-3-yl)-hexanal (5g)

Chiracel AS-H, 95/5 hexane/*i*PrOH, 1 ml/min, 254 nm

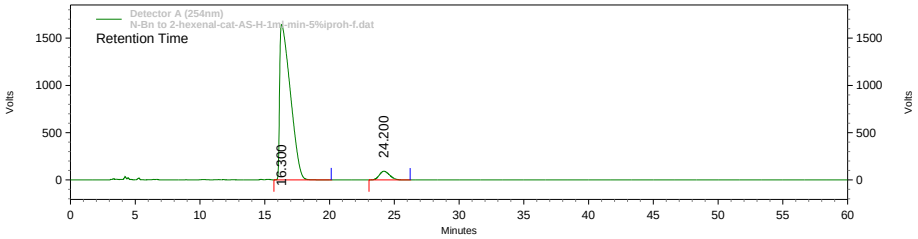


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	15.692	39936584	49.428	1038760	61.583
2	21.850	40860773	50.572	648005	38.417
Totals		80797357	100.000	1686765	100.000

(*S*)-3-(1-benzyl-1H-indol-3-yl)-hexanal (5g)

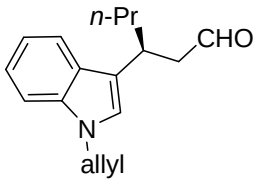
Chiracel AS-H, 95/5 hexane/*i*PrOH, 1 ml/min, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	16.300	93985272	94.889	1644390	94.727
2	24.200	5062223	5.111	91531	5.273
Totals		99047495	100.000	1735921	100.000

(*S*)-3-(1-allyl-1H-indol-3-yl)-hexanal (5h)



5h

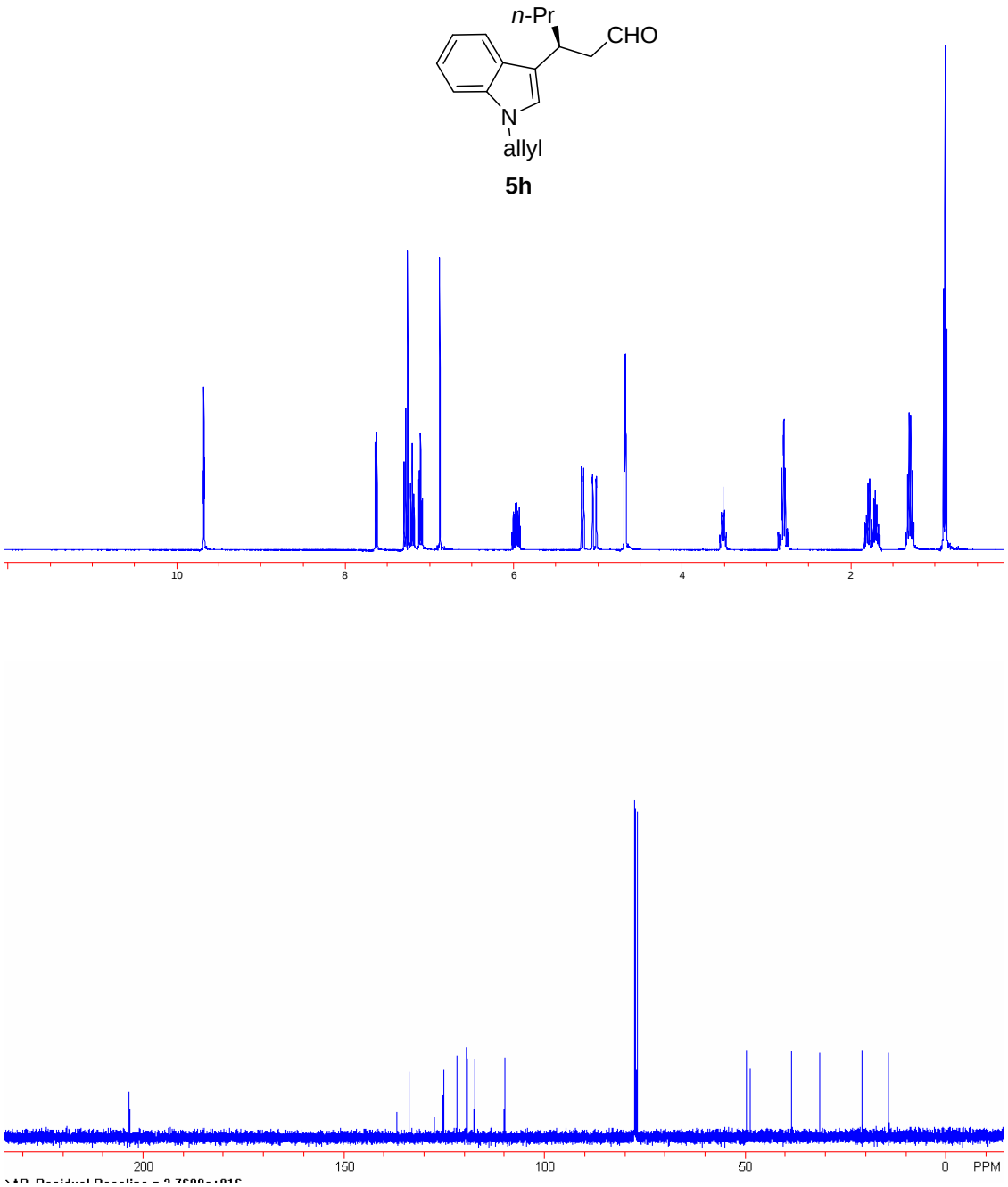
In Accordance with the general procedures, the product was isolated by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:40) to afford title compound **5h** (105 mg, 82% yield) as yellowish oil, $[\alpha]_D^{25} = +16.2$ ($c = 0.20$, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (t, J = 2.4 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.20 (dd, J = 7.6, 8.4 Hz, 1H), 7.10 (ddd, J = 0.8, 7.6, 7.6 Hz, 1H), 6.88 (s, 1H), 6.03–5.92 (m, 1H), 5.18 (dd, J = 1.2, 10.4 Hz, 1H), 5.04 (dd, J = 1.2, 16.8 Hz, 1H), 4.68 (d, J = 4.8 Hz, 1H), 3.56–3.47 (m, 1H), 2.87–2.73 (m, 2H), 1.86–1.64 (m, 2H), 1.36–1.22 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 203.4, 136.9, 133.7, 127.3, 125.2, 121.9, 119.5, 119.1, 117.6, 117.4, 109.9, 49.7, 48.9, 38.4, 31.5, 20.8, 20.7, 14.3.

HRMS(EI-TOF) Calcd. for $C_{17}H_{21}NO$: 255.1623, Found: 255.1631.

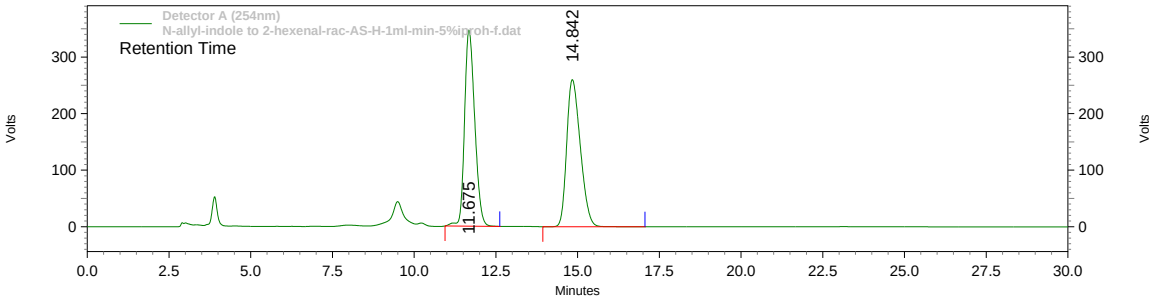
HPLC The product was converted to the corresponding alcohol with $NaBH_4$ in MeOH and enantiomeric excess was determined by HPLC using a Chiracel AS-H (95/5 hexane/*i*-PrOH; flow rate 1.0 ml/min); *S* isomer t_r = 12.22 min (major), *R* isomer t_r = 16.22 min (minor), 90% ee.



5h

(*rac*)-3-(1-allyl-1H-indol-3-yl)-hexanal (5h)

Chiracel AS-H, 95/5 hexane/*i*PrOH, 1 ml/min, 254 nm

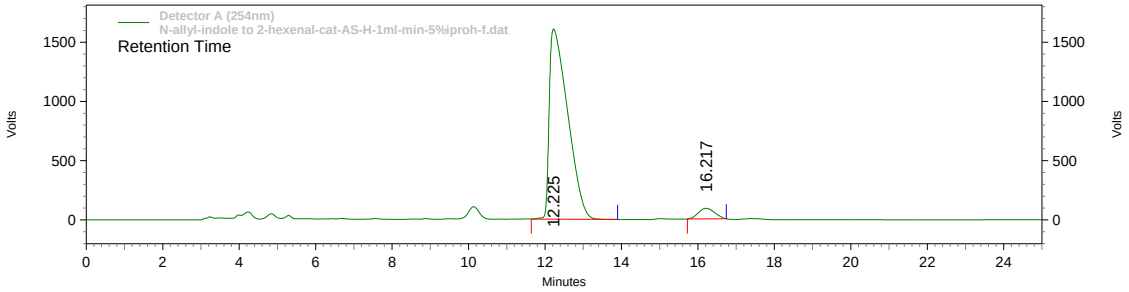


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	11.675	7521626	49.964	346378	57.117
2	14.842	7532429	50.036	260057	42.883
Totals		15054055	100.000	606435	100.000

(*S*)-3-(1-allyl-1H-indol-3-yl)-hexanal (5h)

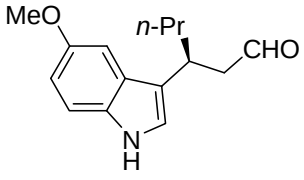
Chiracel AS-H, 95/5 hexane/*i*PrOH, 1 ml/min, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	12.225	53693999	95.282	1606736	94.734
2	16.217	2658553	4.718	89318	5.266
Totals		56352552	100.000	1696054	100.000

(*S*)-3-(5-methoxy-1H-indol-3-yl)-hexanal (5i)



5i

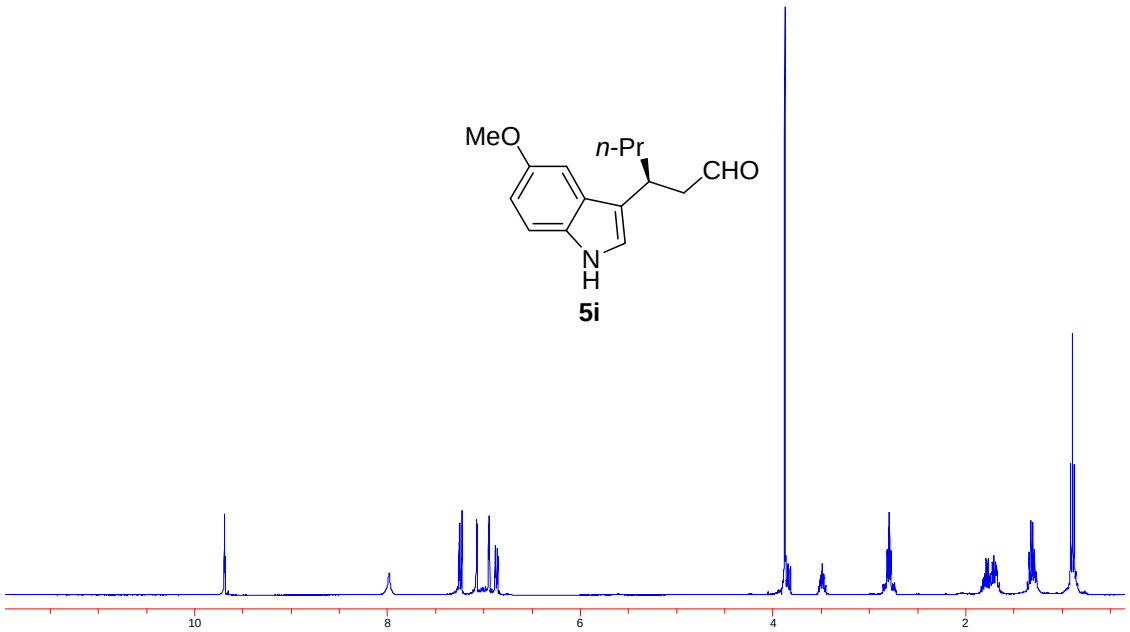
In Accordance with the general procedures, the product was isolated by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:6) to afford title compound **5e** (85.0 mg, 70% yield) as a yellowish oil, $[\alpha]_D^{25}$ = +16.0 (*c* = 0.30, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (t, *J* = 2.4, 1H), 7.98 (s, 1H), 7.25 (d, *J* = 3.2 Hz, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 6.94 (d, *J* = 2.4 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 6.85 (d, *J* = 2.4 Hz, 1H), 3.87 (s, 3H), 3.55–3.44 (m, 1H), 2.90–2.71 (m, 2H), 1.87–1.61 (m, 2H), 1.38–1.20 (m, 2H), 0.89 (t, *J* = 3.2 Hz, 3H).

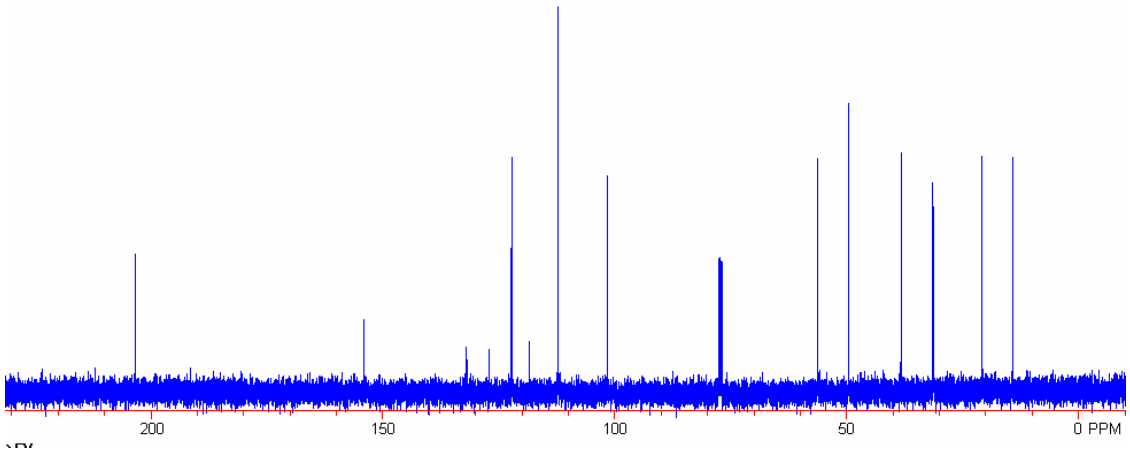
^{13}C NMR (100 MHz, $CDCl_3$) δ 203.4, 154.0, 131.9, 127.2, 122.3, 118.5, 112.2, 101.5, 56.2, 56.2, 49.6, 38.3, 31.4, 20.8, 14.3.

HRMS(EI-TOF) Calcd. for $C_{15}H_{19}NO_2$: 245.1416, Found: 245.1420.

HPLC The product was converted to the corresponding alcohol with $NaBH_4$ in MeOH and enantiomeric excess was determined by HPLC using a Chiracel OD-H, 85/15 hexane/*i*PrOH, 1 ml/min, 254 nm, *R* isomer t_r = 13.63 min (minor), *S* isomer t_r = 15.32 min (major), 93% ee.

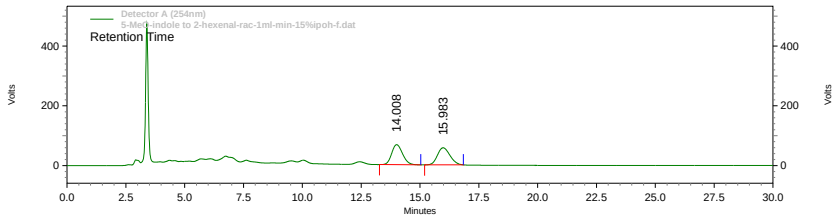


5i



(*rac*)-3-(5-methoxy-1H-indol-3-yl)-hexanal (5i)

Chiracel OD-H, 85/15 hexane/*i*PrOH, 1 ml/min, 254 nm

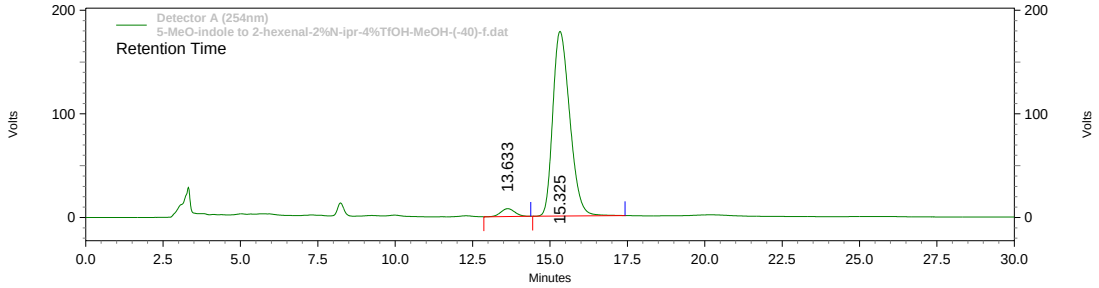


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	14.008	2162147	50.571	67051	53.957
2	15.983	2113304	49.429	57217	46.043
Totals		4275451	100.000	124268	100.000

(*S*)-3-(5-methoxy-1H-indol-3-yl)-hexanal (5i)

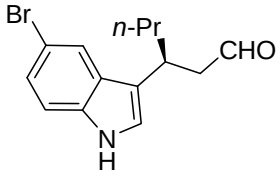
Chiracel OD-H, 85/15 hexane/*i*PrOH, 1 ml/min, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	13.633	237259	3.385	7582	4.082
2	15.325	6771875	96.615	178148	95.918
Totals		9134	100.000	185730	100.000

(*S*)-3-(5-bromo-1H-indol-3-yl)-hexanal (5j)



5j

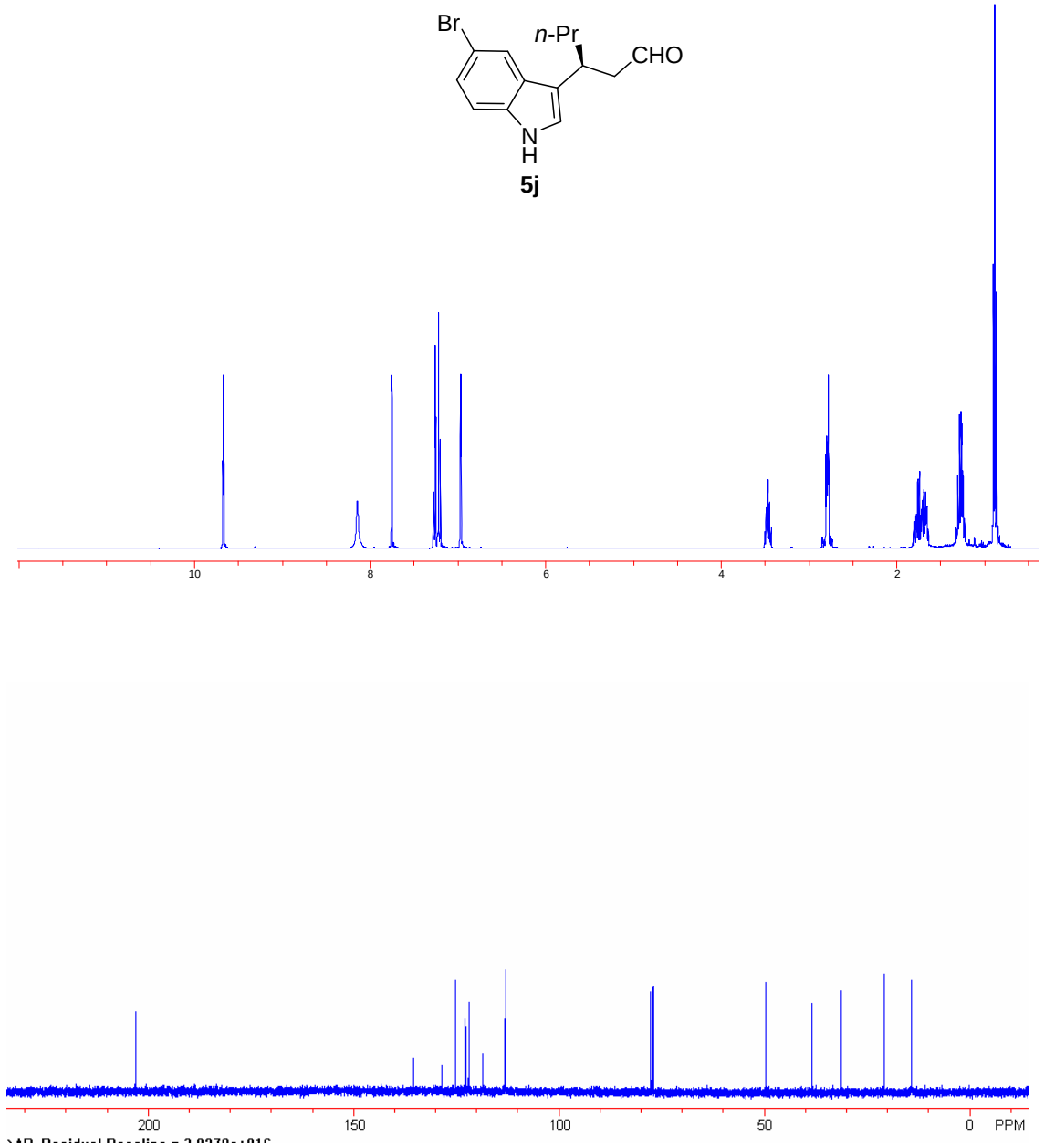
In Accordance with the general procedures, the product was isolated by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:6) to afford title compound **5j** (90.0 mg, 62% yield) as yellowish oil, $[\alpha]_D^{25}$ = -12.6 (*c* = 0.63, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (t, *J* = 2.4 Hz, 1H), 8.07 (bs, 1H), 7.77 (s, 1H), 7.30–7.19 (m, 2H), 6.98 (d, *J* = 2.4 Hz, 1H), 3.52–3.43 (m, 1H), 2.82–2.77 (m, 2H), 1.84–1.63 (m, 2H), 1.34–1.21 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 135.3, 128.4, 125.2, 122.8, 121.9, 118.4, 113.1, 112.8, 49.6, 38.3, 31.3, 20.8, 14.2.

HRMS(EI-TOF) Calcd. for $C_{14}H_{16}BrNO$: 293.0415, Found: 293.0437.

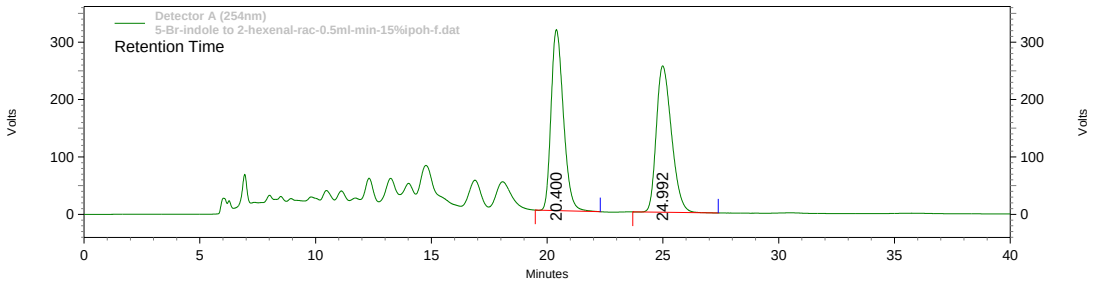
HPLC The product was converted to the corresponding alcohol with $NaBH_4$ in MeOH and enantiomeric excess was determined by HPLC using a Chiracel OD-H, 85/15 hexane/*i*PrOH, 0.5 ml/min, 254 nm, *R* isomer t_r = 20.12 min (minor), *S* isomer t_r = 23.74 min (major), 90% ee.



5j

(*rac*)-3-(5-bromo-1H-indol-3-yl)-hexanal (5j)

Chiracel OD-H, 85/15 hexane/*i*PrOH, 0.5 ml/min, 254 nm

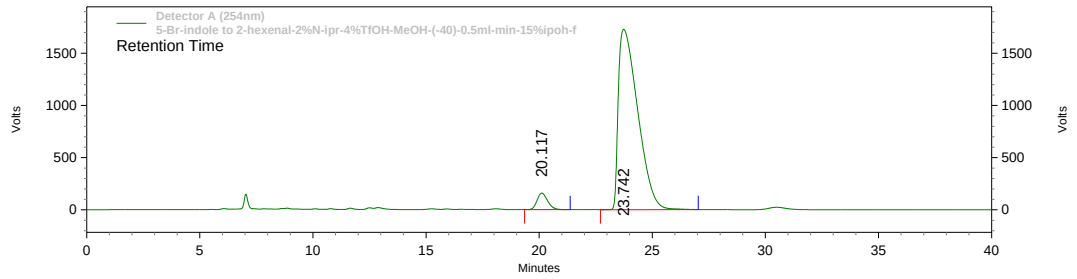


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	20.400	11684447	50.055	315454	55.302
2	24.992	11658858	49.945	254970	44.698
Totals		23343305	100.000	570424	100.000

(*S*)-3-(5-bromo-1H-indol-3-yl)-hexanal (5j)

Chiracel OD-H, 85/15 hexane/*i*PrOH, 0.5 ml/min, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	20.117	5130944	4.752	157854	8.368
2	23.742	102846617	95.248	1728601	91.632
Totals		107977561	100.000	1886455	100.000