Supporting Information for

Ir-Catalyzed Regio- and Enantio-selective Friedel-Crafts Type Allylic Alkylation of Indoles

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General: All manipulations were carried out under the argon atmosphere using standard Schlenk techniques. All glassware was oven or flame dried immediately prior to use. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise.

All reagents were obtained from commercial sources and used without further purification except indole (chemical pure) was purified by vacuum distillation. ^{1}H NMR spectra were obtained at 300 MHz and recorded relative to tetramethylsilane signal (0 ppm) or residual protio-solvent. ^{13}C NMR spectra were obtained at 75 MHz, and chemical shifts were recorded relative to the solvent resonance ($CDCl_3$, 77.0 ppm). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

The phosphoramidite ligands[1] and the substituted allylic carbonates[2] were prepared according to known procedures.

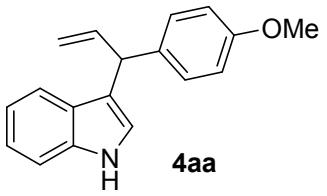
Reference:

1. (a) Alexakis, A.; Rosset, S.; Allamand, J.; March, S.; Guillen, F.; Benhaim, C. *Synlett* **2001**, *9*, 1375-1378. (b) Naasz, R.; Arnold, L. A.; Minnaard, A. J.; Feringa, B. L. *Angew. Chem. Int. Ed.* **2001**, *40*, 927-930. (c) Polet, D.; Alexakis, A. *Synthesis* **2004**, *15*, 2586-2590.

2. Wuts, P. G. M.; Ashford, S. W.; Anderson, A. M.; Atkins, J. R. *Org. Lett.* **2003**, *5*, 1483-1485.

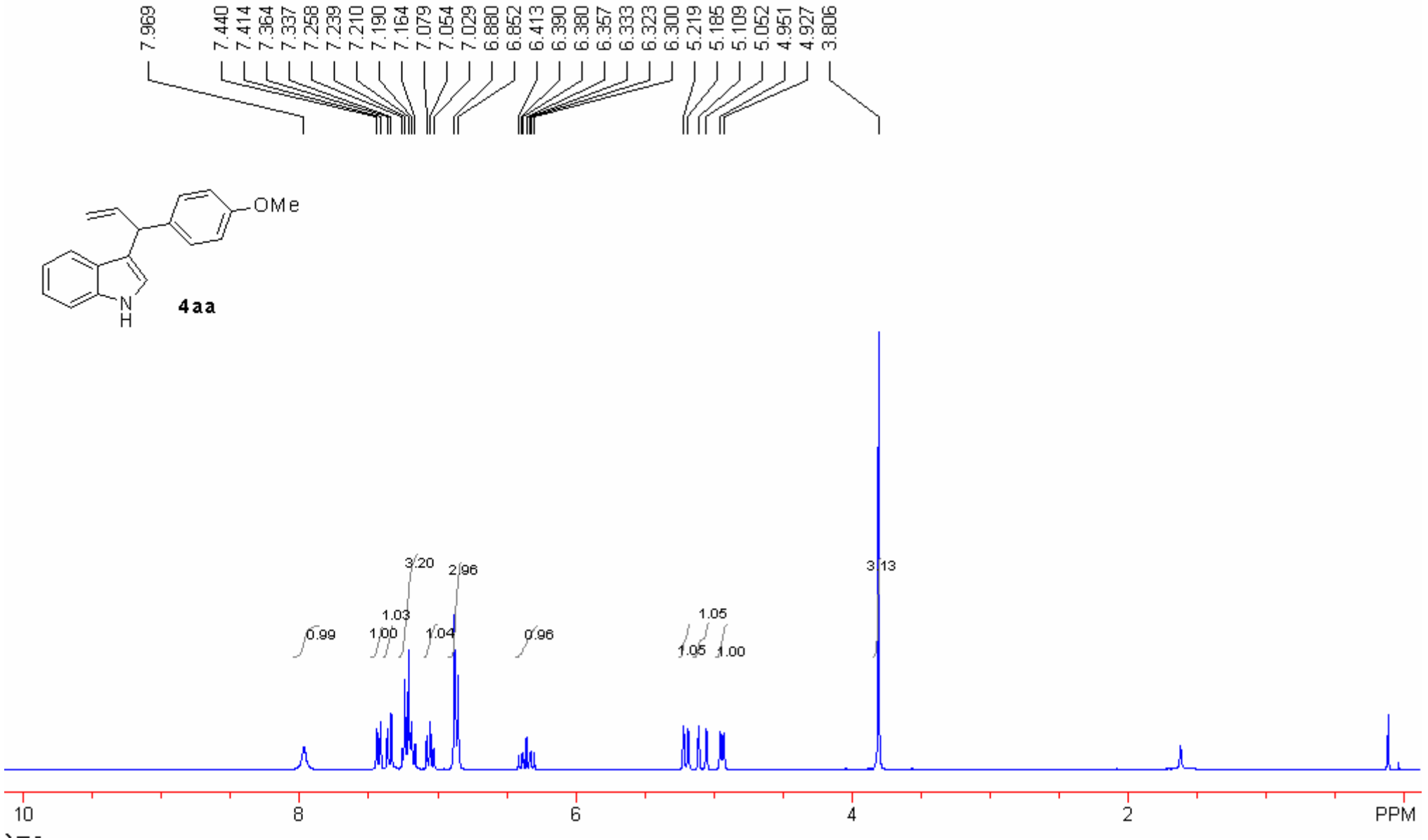
General Procedure for the Iridium(I)-Catalyzed Enantioselective Allylic Alkylation of Indoles:

$[Ir(COD)Cl]_2$ (0.004 mmol, 2 mol%), phosphoramidite ligand **1** [O,O'-(*S*)-(1,1'-Dinaphthyl-2,2'-diyl)-N,N'-di-(*S,S*)-[Phenylethylphosphoramidite] (0.008 mmol, 4 mol%) were dissolved in THF (0.5 mL) and propylamine (0.3 mL) in a dry Schlenk tube filled with argon. The reaction mixture was heated at 50°C for 30 min and then the volatile solvents were removed under vacuum to give a yellow solid. After that, allylic carbonate **2** (0.20 mmol), indole **3** (0.40 mmol, 200 mol%), cesium carbonate (0.20 mmol, 100 mol%), and 1,4-dioxane (1.0 mL) were added. The reaction was refluxed until the carbonate was fully consumed, monitored by TLC or ^{1}H NMR. Then the crude reaction mixture was filtrated with celite and the solvent was removed under reduced pressure. The ratio of regioisomers (branched to linear b/l) was determined by ^{1}H NMR of the crude reaction mixture. The crude residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to give the desired products.



4aa

The general procedure was followed with the methyl carbonate **2a** (44.5 mg, 0.20 mmol) derived from (E)-3-(4-methoxyphenyl)prop-2-en-1-ol, indole **3a** (46.9 mg, 0.40 mmol) and cesium carbonate (65.2 mg, 0.20 mmol) in 1,4-dioxane (1.0 mL). The reaction was conducted at reflux for 4 h. ^{1}H NMR analysis of the crude reaction mixture indicated that the ratio of regioisomers (b/l) was >99/1. The crude reaction mixture was purified by column chromatography (petroleum ether/ethyl acetate: 30/1) to give the product **4aa** (43.1 mg, 82% yield) as a yellow oil. HPLC analysis indicated that the enantiomeric excess of the product was 92% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 230 nm; t_R = 13.46 (minor), 13.89 (major) min]. $[\alpha]_D^{20}$ = -2.8°(c 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.97 (br s, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.26-7.16 (m, 3H), 7.05 (t, J = 7.5 Hz, 1H), 6.88-6.85(m, 3H), 6.36 (ddd, J = 6.9, 9.9, 17.1 Hz, 1H), 5.20(d, J = 10.2 Hz, 1H), 5.08(d, J = 17.1 Hz, 1H), 4.94 (d, J = 7.2 Hz, 1H), 3.81(s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 140.7, 136.6, 135.3, 129.3, 126.7, 122.4, 121.9, 119.8, 119.2, 118.7, 115.1, 113.6, 111.0, 55.2, 46.1. IR (liquid film): ν_{max} (cm^{-1}) = 3420, 3058, 2957, 2836, 1664, 1637, 1608, 1510, 1457, 1247, 1178, 1034, 823, 743. MS (EI, *m/z*, rel. intensity) 263 (M^+, 100); HRMS (EI) calcd for $C_{18}H_{17}NO$ (M^+): 263.1310, Found: 263.1322.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6.300
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5.185
5.109
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4.927
3.806
OMe
N
H
4aa
0.99
1.00
1.03
3.20
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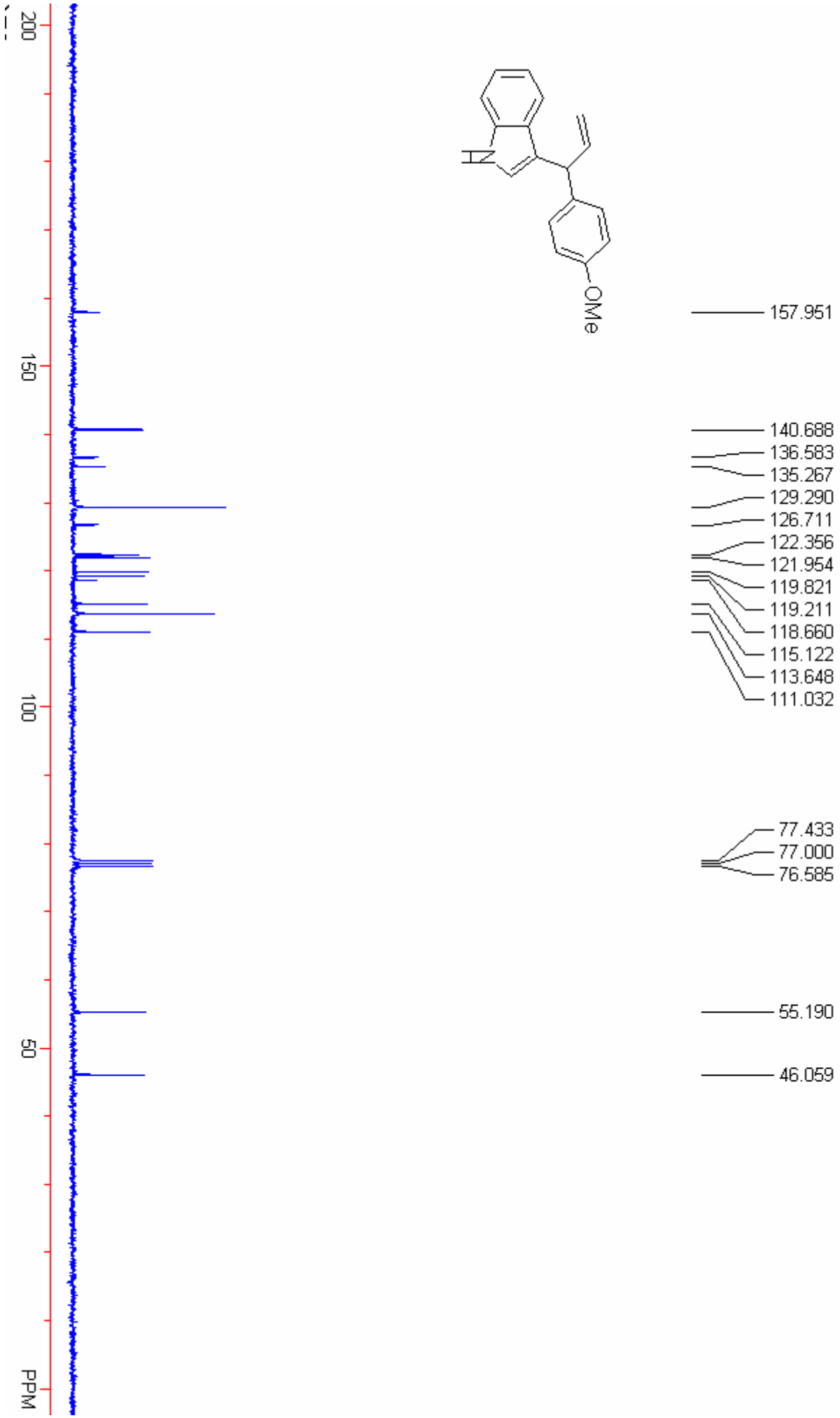
0.96
1.05
1.05
1.00
3.13
10
8
6
4
2
PPM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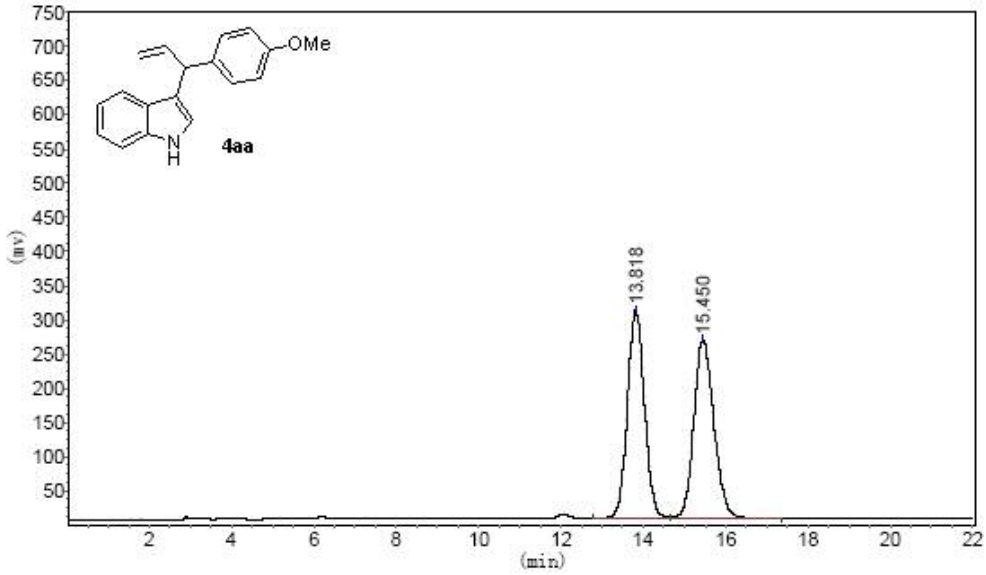

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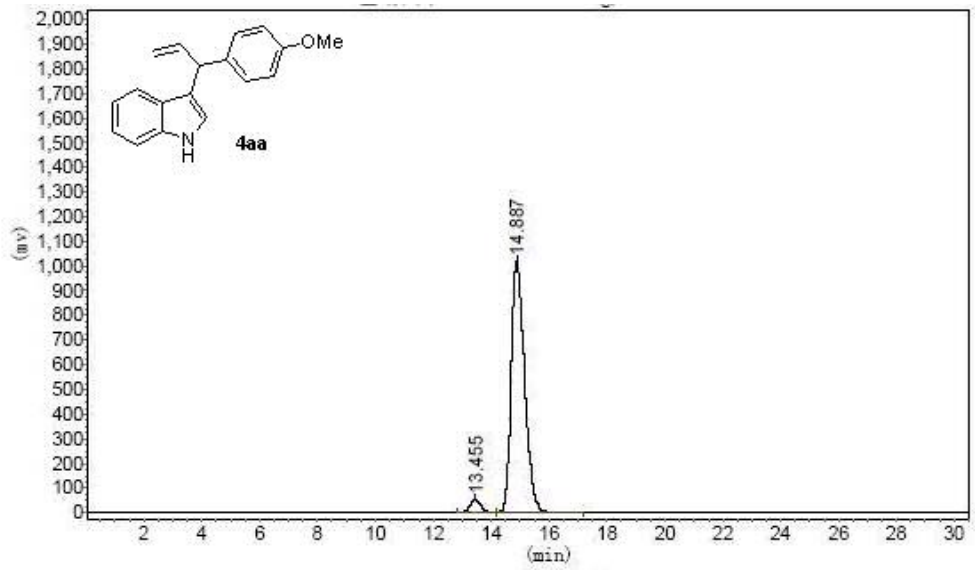

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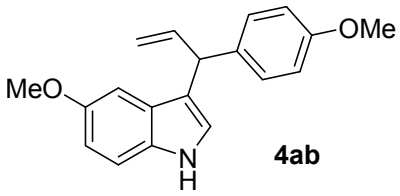
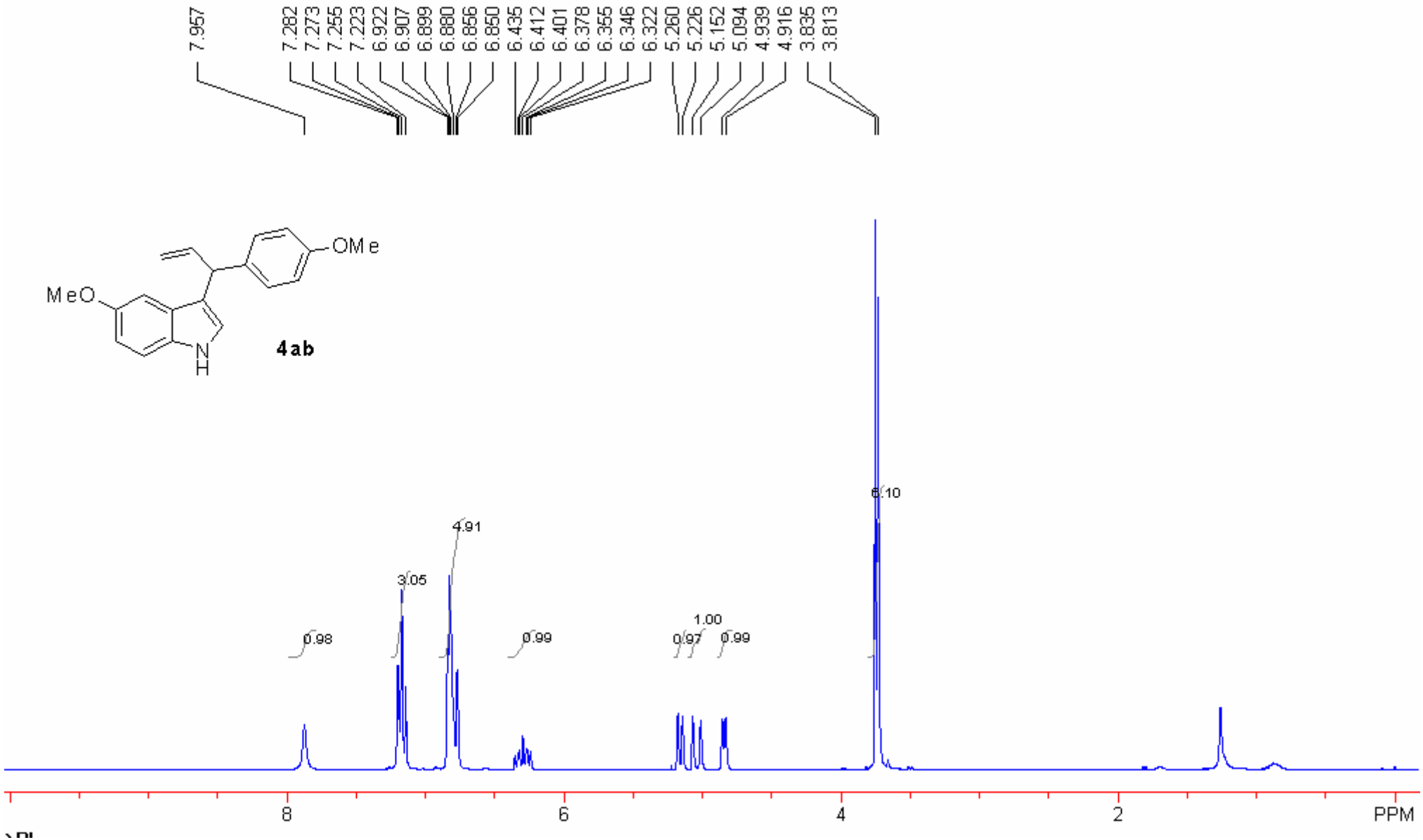


4ab

The general procedure was followed with the methyl carbonate **2a** (45.1 mg, 0.20 mmol), 5-methoxyindole **3b** (58.9 mg, 0.40 mmol) and cesium carbonate (65.0 mg, 0.20 mmol) in 1,4-dioxane (1.0 mL). The reaction was conducted at reflux for 8 h. ^{1}H NMR analysis of the crude reaction mixture indicated that the ratio of regioisomers (b/l) was >99/1. The crude reaction mixture was purified by column chromatography (petroleum ether/ethyl acetate: 30/1) to give the product **4ab** (49.8mg, 85%) as a yellow oil. HPLC analysis indicated that the enantiomeric excess of the product was 89% [Diacel CHIRALCEL AD-H (0.46 cm x 25 cm); hexanes/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 230 nm; t_R = 20.64 (minor), 33.39 (major) min]. $[\alpha]_D^{20}$ = -20.8°(c 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.90 (br s, 1H), 7.25-7.17 (m, 3H), 6.86-6.80 (m, 5H), 6.31 (ddd, J = 6.9, 10.2, 17.1 Hz, 1H), 5.17(d, J = 10.2 Hz, 1H), 5.05(d, J = 17.1 Hz, 1H), 4.86 (d, J = 7.2 Hz, 1H), 3.79(s, 3H), 3.75 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 157.9, 153.5, 140.6, 135.2, 131.7, 129.3, 127.1, 123.2, 118.2, 115.1, 113.6, 111.9, 111.7, 101.7, 55.7, 55.2, 46.0. IR(liquid film): ν_{max} (cm^{-1}) = 3419, 3075, 3001, 2954, 2934, 2835, 1625, 1610, 1583, 1510, 1484, 1455, 1440, 1300, 1247, 1211, 1176, 1034, 923, 829, 800. MS (EI, *m/z*, rel. intensity) 293 (M^+, 100); HRMS (EI) calcd for $C_{18}H_{17}NO$ (M^+): 293.1416, Found: 293.1417.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3.835
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H
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0.99
0.97
0.99
8
6
4
2
PPM

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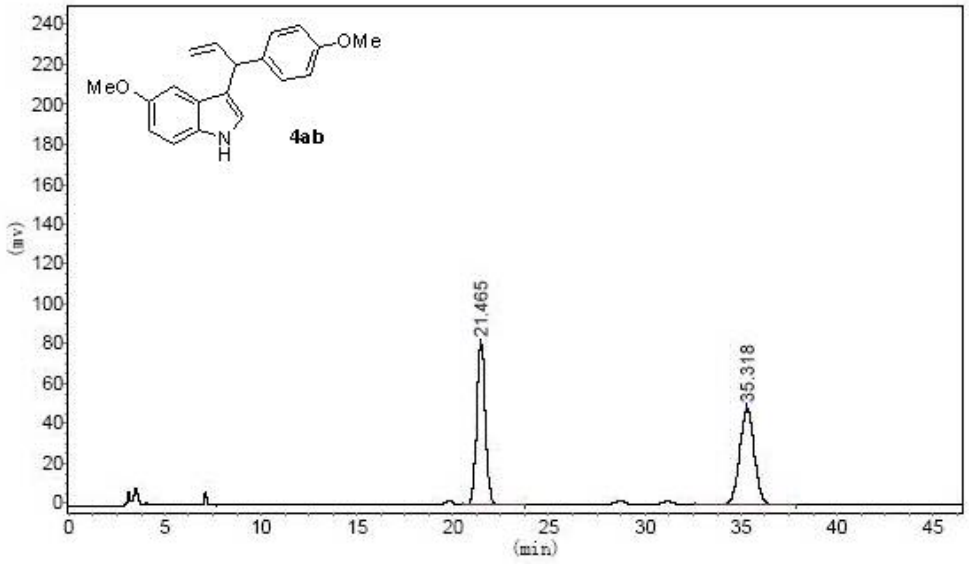

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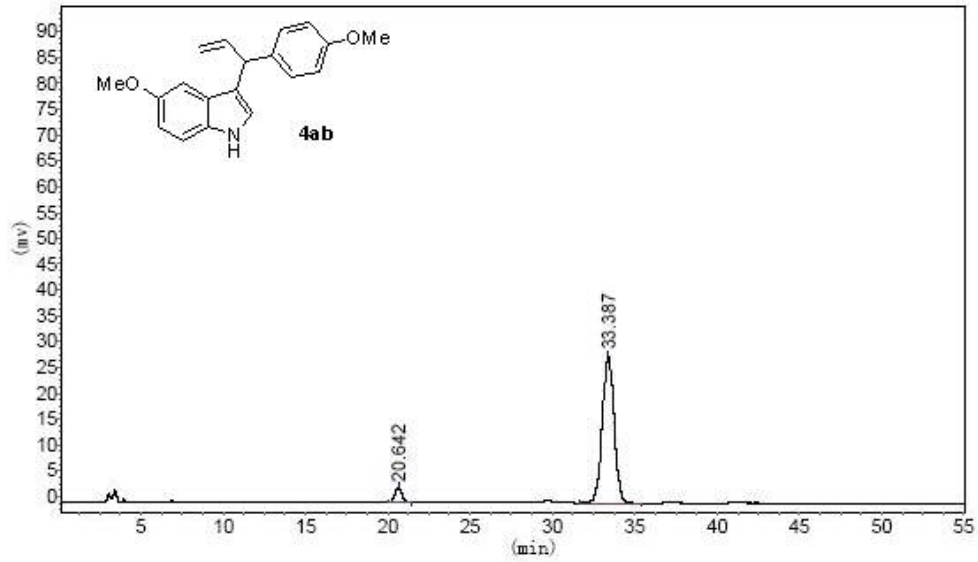

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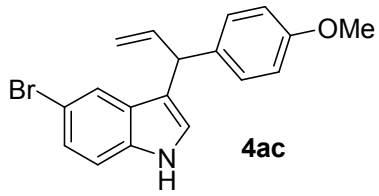
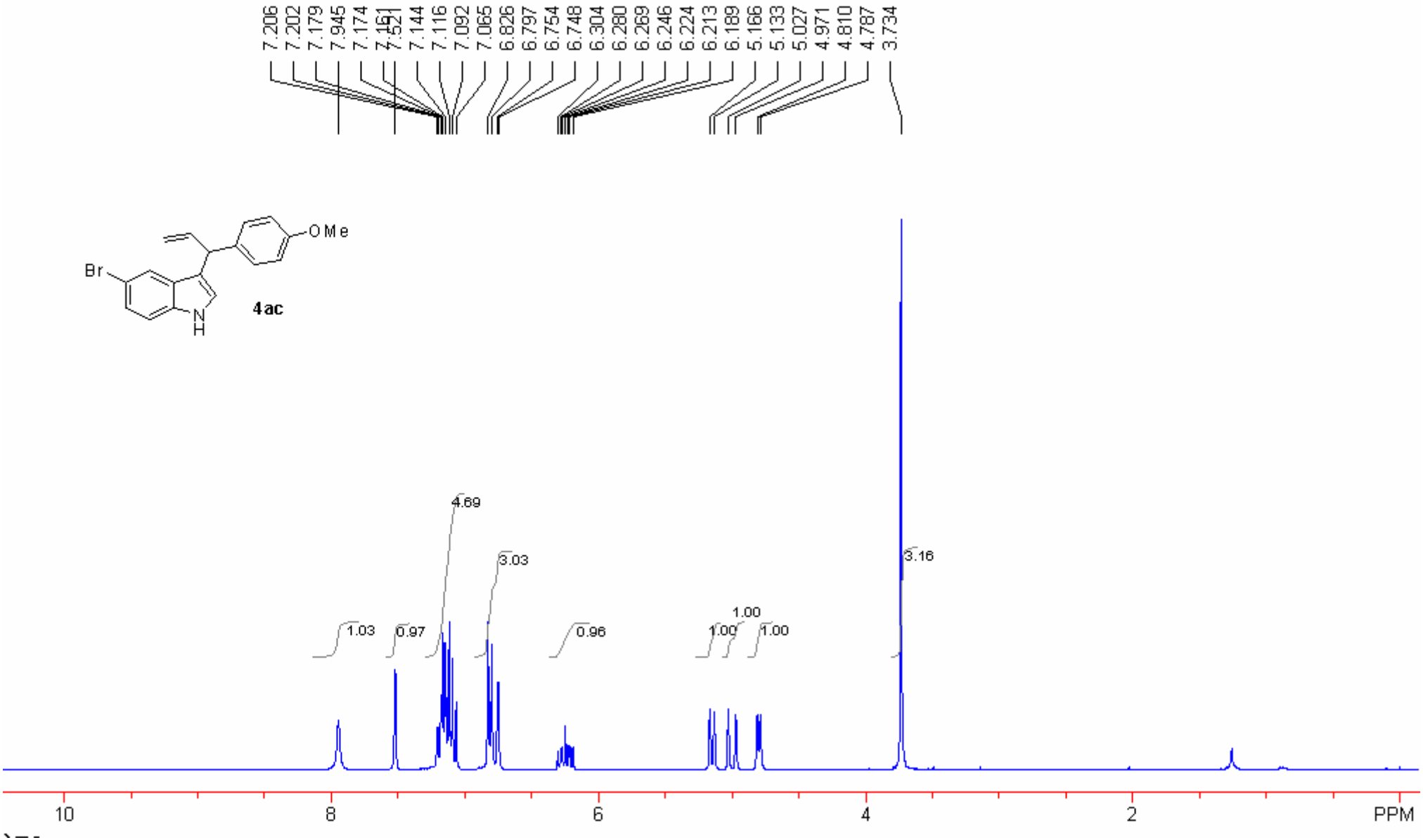


4ac

The general procedure was followed with the methyl carbonate **2a** (90.1 mg, 0.40 mmol), 5-bromoindole **3c** (156.2 mg, 0.80 mmol) and cesium carbonate (130.4 mg, 0.40 mmol) in 1,4-dioxane (2.0 mL). The reaction was conducted at reflux for 2 h. ^{1}H NMR analysis of the crude reaction mixture indicated that the ratio of regioisomers (b/l) was >99/1. The crude reaction mixture was purified by column chromatography (petroleum ether/ethyl acetate: 30/1) to give the product **4ac** (99.1 mg, 73%) as a yellow oil. HPLC analysis indicated that the enantiomeric excess of the product was 91% [Diacel CHIRALCEL AD-H (0.46 cm x 25 cm); hexanes/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 230 nm; t_R = 12.54 (minor), 14.54 (major) min]. $[\alpha]_D^{20}$ = -46.7 (c 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.95 (br s, 1H), 7.52 (s, 1H), 7.21-7.06 (m, 4H), 6.83-6.75 (m, 3H), 6.25 (ddd, J = 7.2, 10.5, 17.1 Hz, 1H), 5.15 (d, J = 9.6 Hz, 1H), 5.00 (d, J = 17.1 Hz, 1H), 4.80 (d, J = 6.9 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 157.9, 140.2, 135.1, 134.7, 129.2, 128.4, 124.7, 123.6, 122.1, 118.2, 115.4, 113.7, 112.5, 112.4, 55.1, 45.7. IR (liquid film): ν_{max} (cm^{-1}) = 3426, 3078, 3003, 2955, 2930, 2858, 2837, 1637, 1610, 1510, 1459, 1443, 1247, 1177, 1097, 1035, 796. MS (EI, *m/z*, rel. intensity) 341 (M^+, 100); HRMS (EI) calcd for $C_{18}H_{16}NOBr$ (M^+): 341.0415, Found: 341.0422.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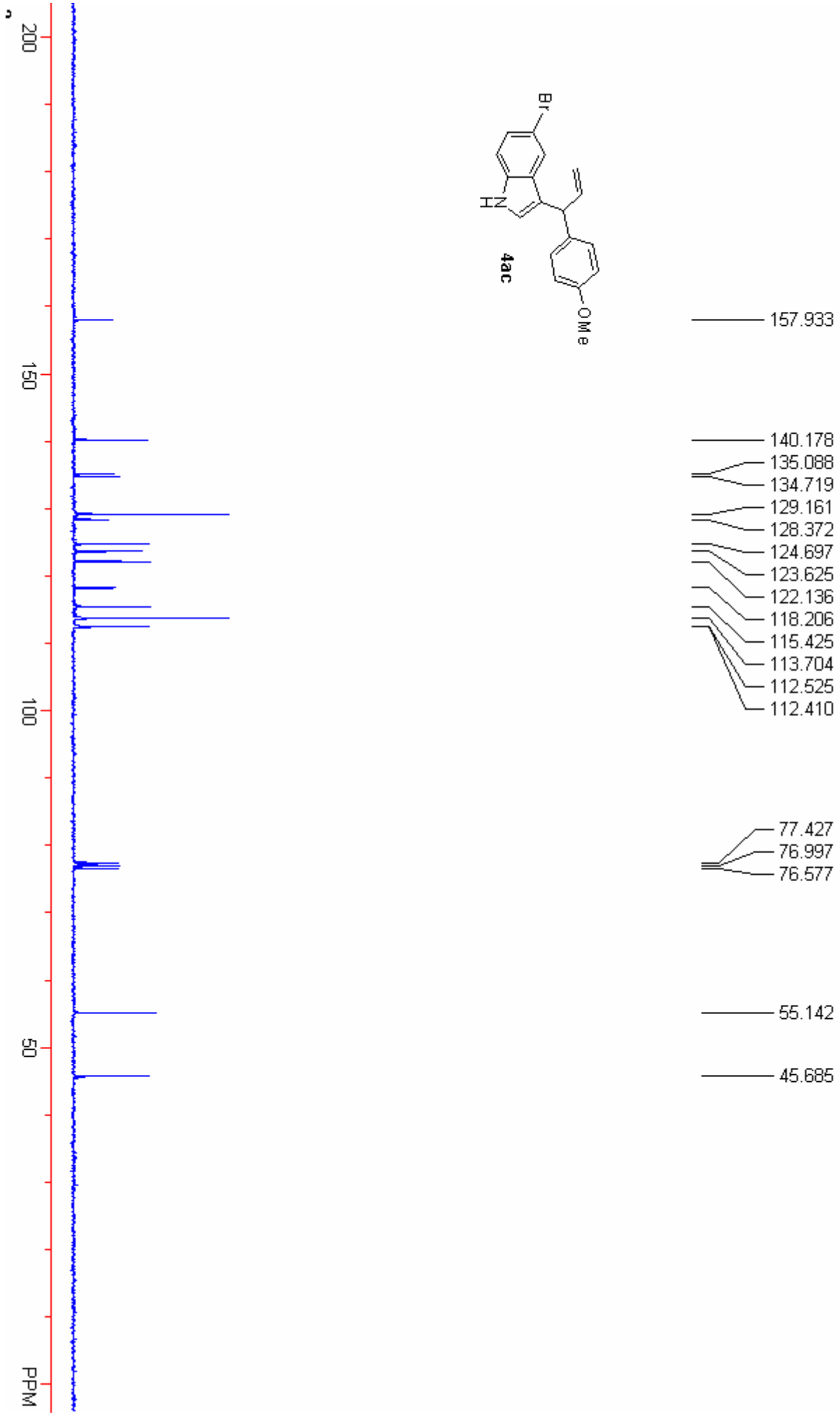
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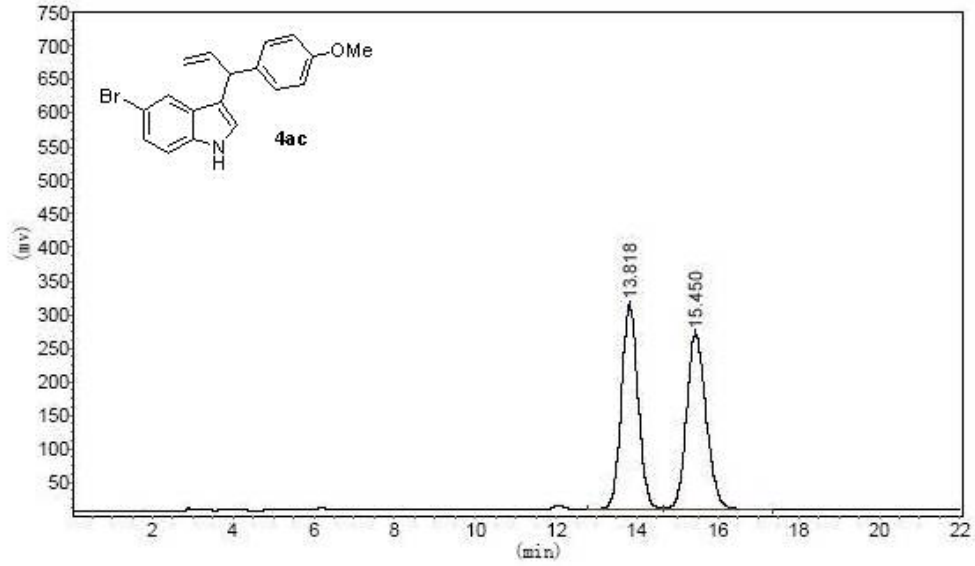
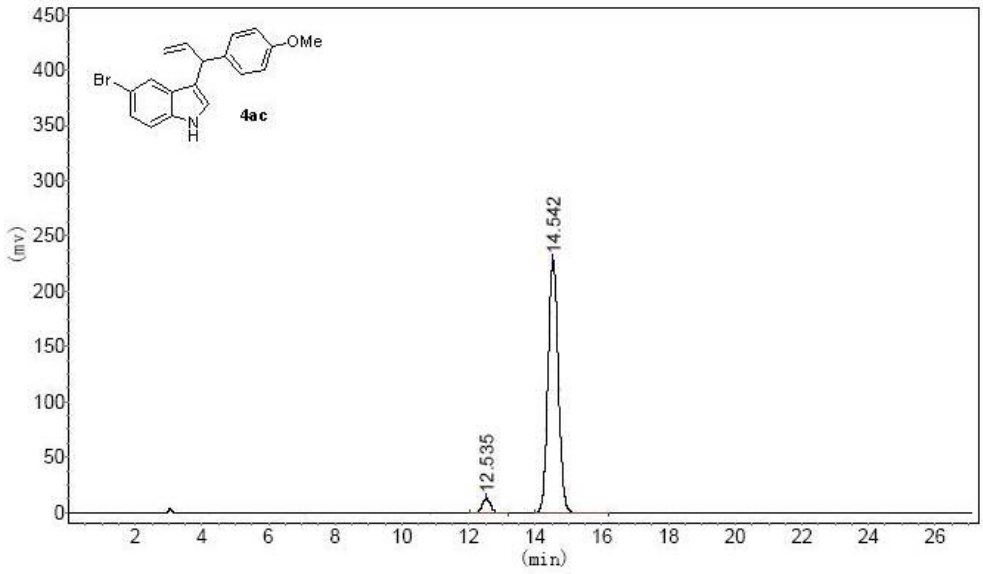


PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	13.818	304521.594	8792842.000	49.8834
2	15.450	261393.625	8833949.000	50.1166
Total		565915.219	17626791.000	100.0000



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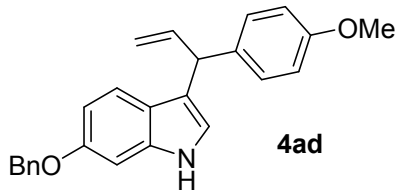
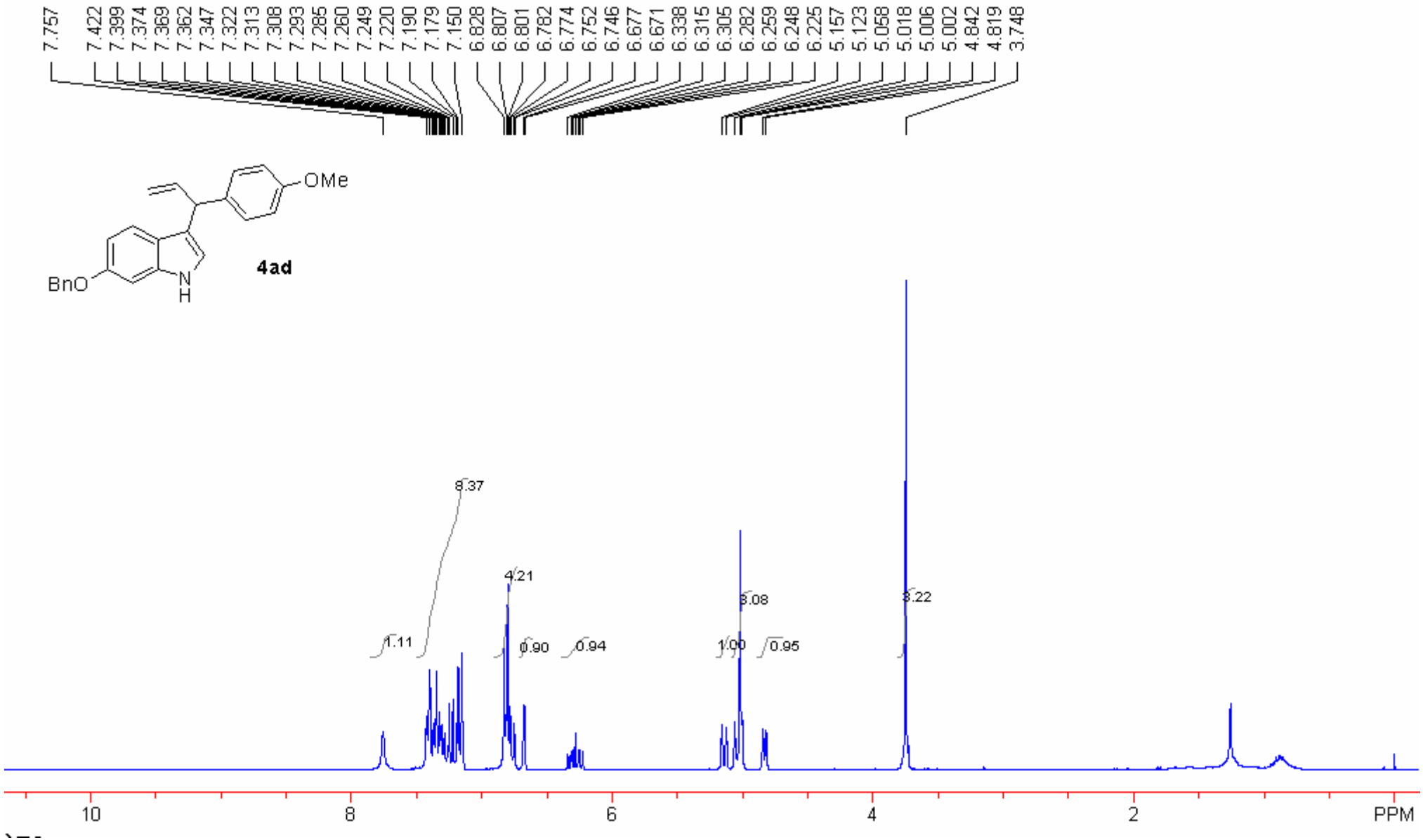
Total		242905.021	5188345.781	100.0000



4ad

The general procedure was followed with the methyl carbonate **2a** (44.9 mg, 0.20 mmol), 6-benzyloxyindole **3d** (89.3 mg, 0.40 mmol) and cesium carbonate (65.4 mg, 0.20 mmol) in 1,4-dioxane (1.0 mL). The reaction was conducted at reflux for 6 h. ^{1}H NMR analysis of the crude reaction mixture indicated that the ratio of regioisomers (b/l) was >99/1. The crude reaction mixture was purified by column chromatography (petroleum ether/ethyl acetate: 30/1) to give the product **4ad** (61.3 mg, 83%) as a yellow oil. HPLC analysis indicated that the enantiomeric excess of the product was 85% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 230 nm; t_R = 45.24 (minor), 51.99 (major) min]. $[\alpha]_D^{20}$ = +0.8 (c 2.0, $CHCl_3$). ^{1}H NMR (300 MHz, CDCl3) δ = 7.75 (br s, 1H), 7.42-7.15 (m, 8H), 6.83-6.66 (m, 5H), 6.28 (ddd, J = 7.2, 10.2, 16.8 Hz, 1H), 5.14 (d, J = 9.9, 1H), 5.03 (d, J = 14.7 Hz, 1H), 5.01 (s, 2H), 4.83 (d, J = 6.9 Hz, 1H) , 3.74 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 157.9, 155.4, 140.7, 137.3, 137.2, 135.2, 129.2, 128.5, 127.8, 127.4, 121.31, 121.28, 120.4, 118.5, 115.0, 113.6, 109.8, 95.9, 70.4, 55.1, 46.1. IR (liquid film): ν_{max} (cm^{-1}) = 3423, 3065, 3033, 3004, 2955, 2929, 2858, 2836, 1628, 1610, 1583, 1549, 1510, 1455, 1400, 1380, 1340, 1301, 1249, 1166, 1034, 917, 807, 740, 698. MS (EI, *m/*z, rel. intensity) 369 (M^+, 32), 278 (100); HRMS (EI) calcd for $C_{25}H_{23}NO_2$ (M^+): 369.1729, Found: 369.1733.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8
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4
2
PPM

4ad

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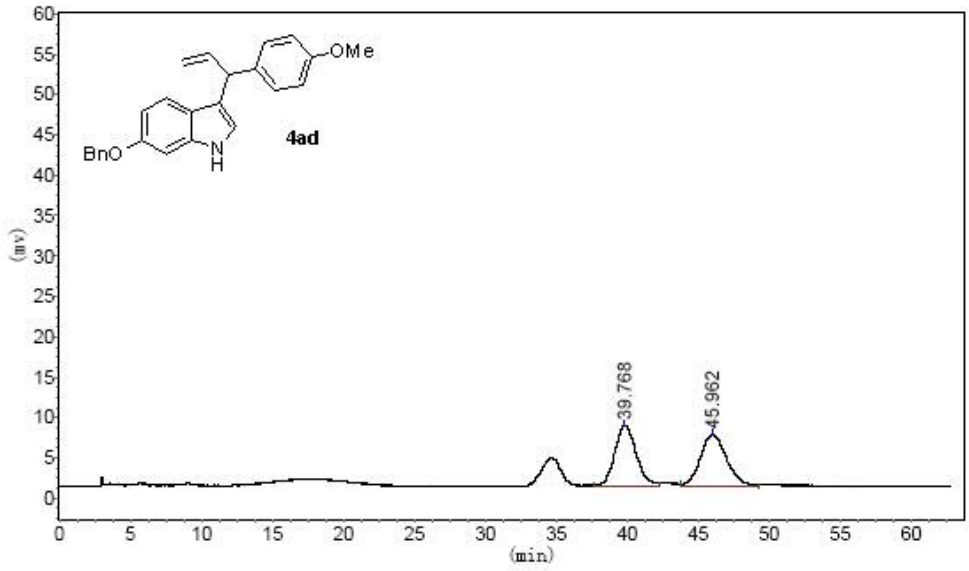

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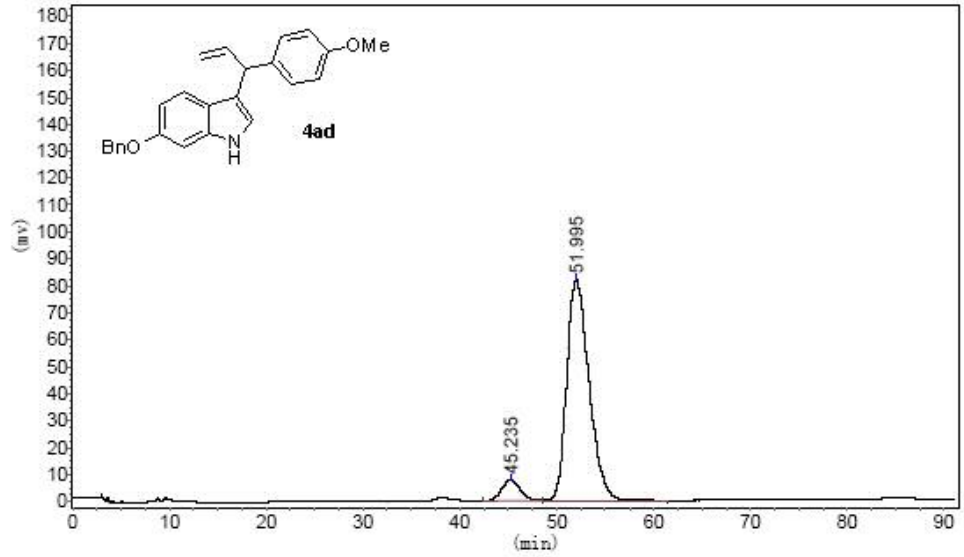

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1	45.235	7973.070	1057370.250	7.4603
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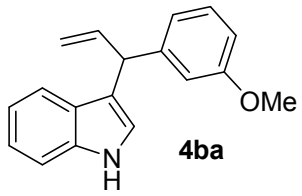
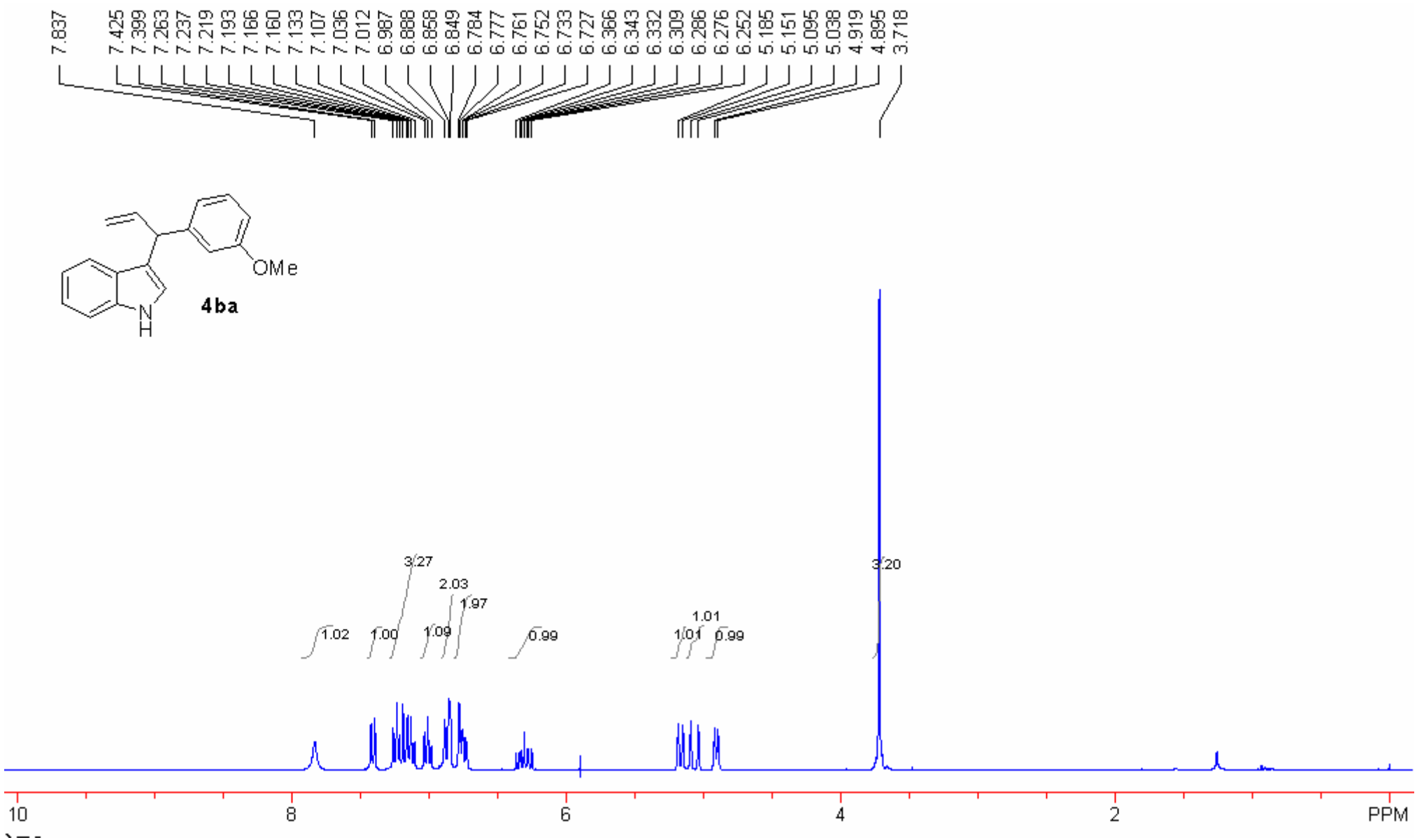


4ba

The general procedure was followed with the methyl carbonate **2b** (89.3 mg, 0.40 mmol) derived from (E)-3-(3-methoxyphenyl)prop-2-en-1-ol, indole **3a** (93.4 mg, 0.80 mmol) and cesium carbonate (130.4 mg, 0.40 mmol) in 1,4-dioxane (2.0 mL). The reaction was conducted at reflux for 3 h. ^{1}H NMR analysis of the crude reaction mixture indicated that the ratio of regioisomers (b/l) was >99/1. The crude reaction mixture was purified by column chromatography (petroleum ether/ethyl acetate: 30/1) to give the product **4ba** (76.6 mg, 73%) as a yellow oil. HPLC analysis indicated that the enantiomeric excess of the product was 91% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 98/2; flow rate = 1.0 mL/min; detection wavelength = 230 nm; t_R = 51.94 (minor), 59.23 (major) min]. $[\alpha]_D^{20}$ = -2.2 (c 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.84 (br s, 1H), 7.43-6.73 (m, 9H), 6.31 (ddd, J = 7.2, 10.2, 17.1 Hz, 1H), 5.17 (d, J = 10.2, 1H), 5.07 (d, J = 17.1 Hz, 1H), 4.91 (d, J = 7.5 Hz, 1H) , 3.72 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.5, 144.9, 140.2, 136.5, 129.2, 126.7, 122.4, 121.9, 120.8, 119.7, 119.2, 118.0, 115.5, 114.3, 111.3, 111.0, 55.1, 46.9. IR (liquid film): ν_{max} (cm^{-1}) = 3420, 3079, 3057, 3003, 2957, 2935, 2836, 1637, 1606, 1599, 1585, 1488, 1457, 1436, 1419, 1263, 1151, 1047, 773, 759, 743, 700. MS (EI, *m/z*, rel. intensity) 263 (M^+, 100); HRMS (EI) calcd for $C_{18}H_{17}NO$ (M^+): 263.1310, Found: 263.1320.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6.987
6.888
6.858
6.849
6.784
6.777
6.761
6.752
6.733
6.727
6.366
6.343
6.332
6.309
6.286
6.276
6.252
5.185
5.151
5.095
5.038
4.919
4.895
3.718
OMe
4ba
3.27
2.03
1.97
1.02
1.00
1.09
0.99
1.01
1.01
0.99
3.20
10
8
6
4
2
PPM

200
150
100
50
PPM
4ba
OMe
159.489
144.860
140.169
136.471
129.233
126.651
122.418
121.926
120.841
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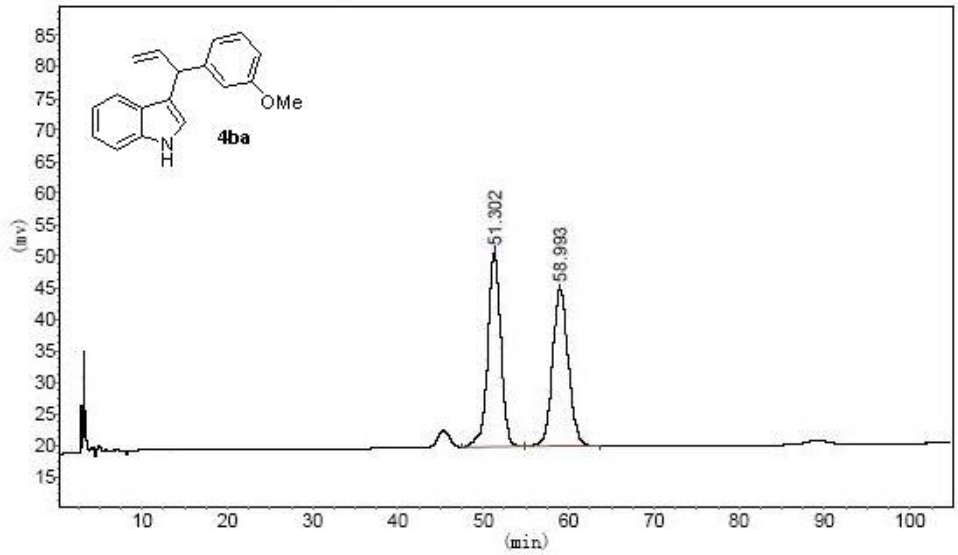
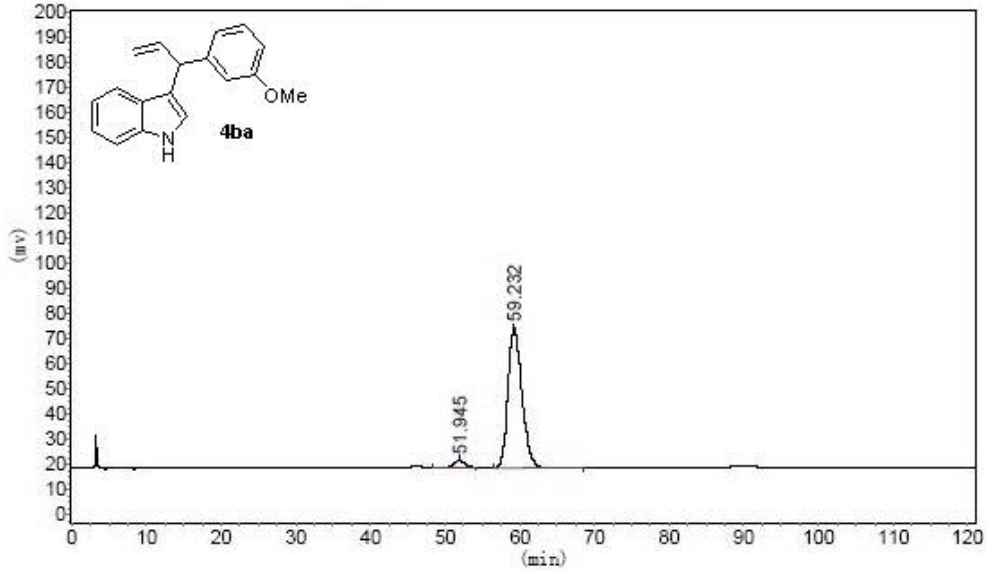
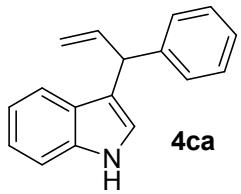
111.322
111.033
77.421
77.000
76.570
55.053
46.882



PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	51.302	30941.063	3291627.500	50.6766
2	58.993	24973.420	3203730.250	49.3234
Total		55914.482	6495357.750	100.0000

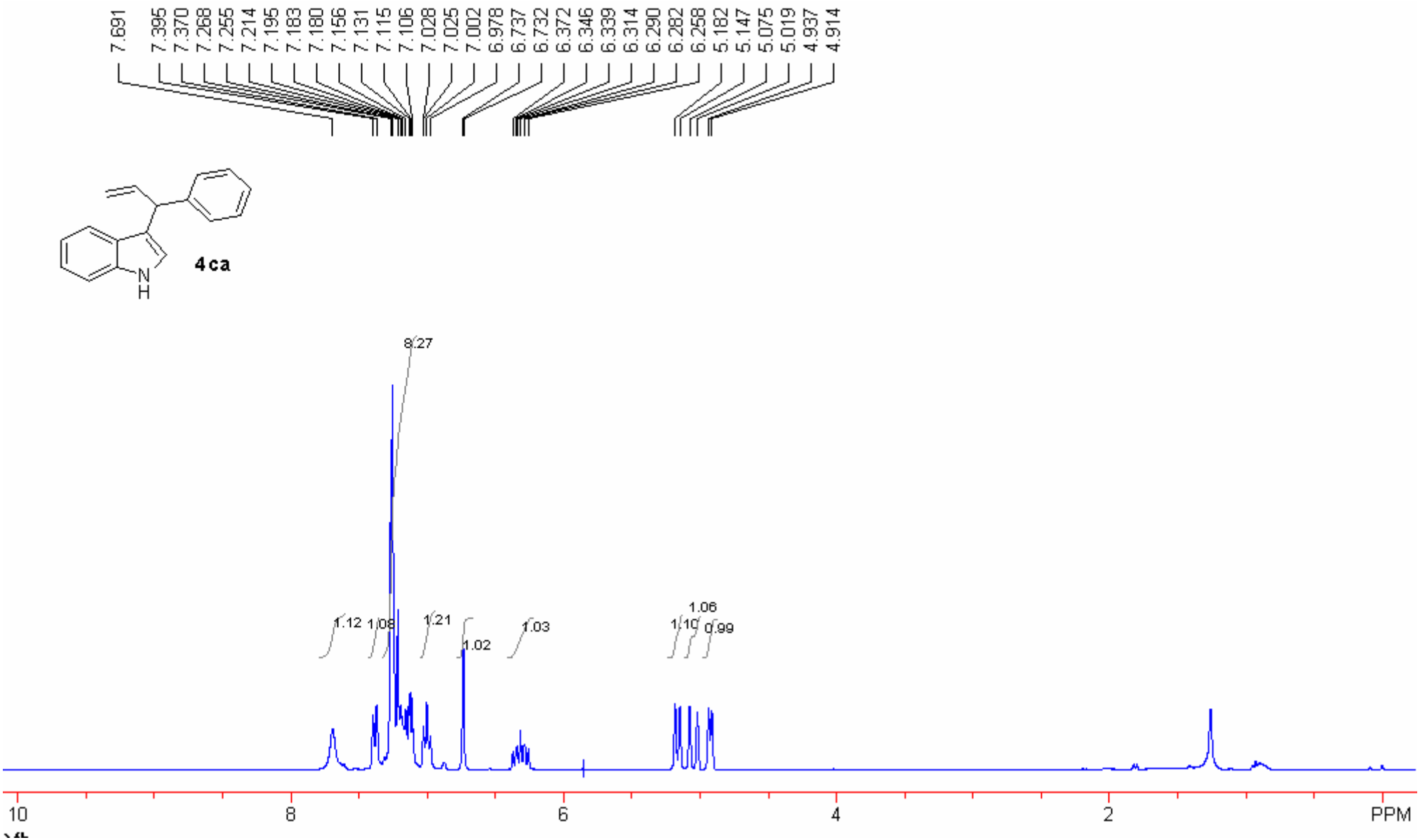


PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	51.945	3011.588	347181.563	4.5609
2	59.232	55701.371	7264926.500	95.4391
Total		58712.959	7612108.063	100.0000



4ca

The general procedure was followed with the methyl carbonate **2c** (76.9 mg, 0.40 mmol) derived from cinnamyl alcohol, indole **3a** (94.0 mg, 0.80 mmol) and cesium carbonate (131.6 mg, 0.40 mmol) in 1,4-dioxane (2.0 mL). The reaction was conducted at reflux for 3 h. ^{1}H NMR analysis of the crude reaction mixture indicated that the ratio of regioisomers (b/l) was 99/1. The crude reaction mixture was purified by column chromatography (petroleum ether/ethyl acetate: 50/1) to give the mixture of **3a** and product **4ca** (114.0 mg), then indole was removed by vacuum distillation to give the product (45.8 mg, 49%) as a yellow oil. $[\alpha]_D^{20}$ = -0.7 (c 2.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.94 (br s, 1H), 7.42-6.86 (m, 10H), 6.35 (ddd, J = 7.2, 9.9, 16.8 Hz, 1H), 5.17 (d, J = 10.5, 1H), 5.05 (d, J = 16.8 Hz, 1H), 4.93 (d, J = 6.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.1, 140.4, 136.5, 128.4, 128.3, 126.7, 126.2, 122.5, 121.9, 119.7, 119.2, 118.2, 115.4, 111.1, 46.9. IR (liquid film): ν_{max} (cm^{-1}) = 3420, 3081, 3059, 3004, 2926, 1637,1600, 1491, 1456, 1419, 1338, 1220, 1095, 919, 742, 701. MS (EI, *m/z*, rel. intensity) 233 (M^+, 100); HRMS (EI) calcd for $C_{17}H_{15}N$ (M^+): 233.1204, Found: 233.1208.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7.156
7.131
7.115
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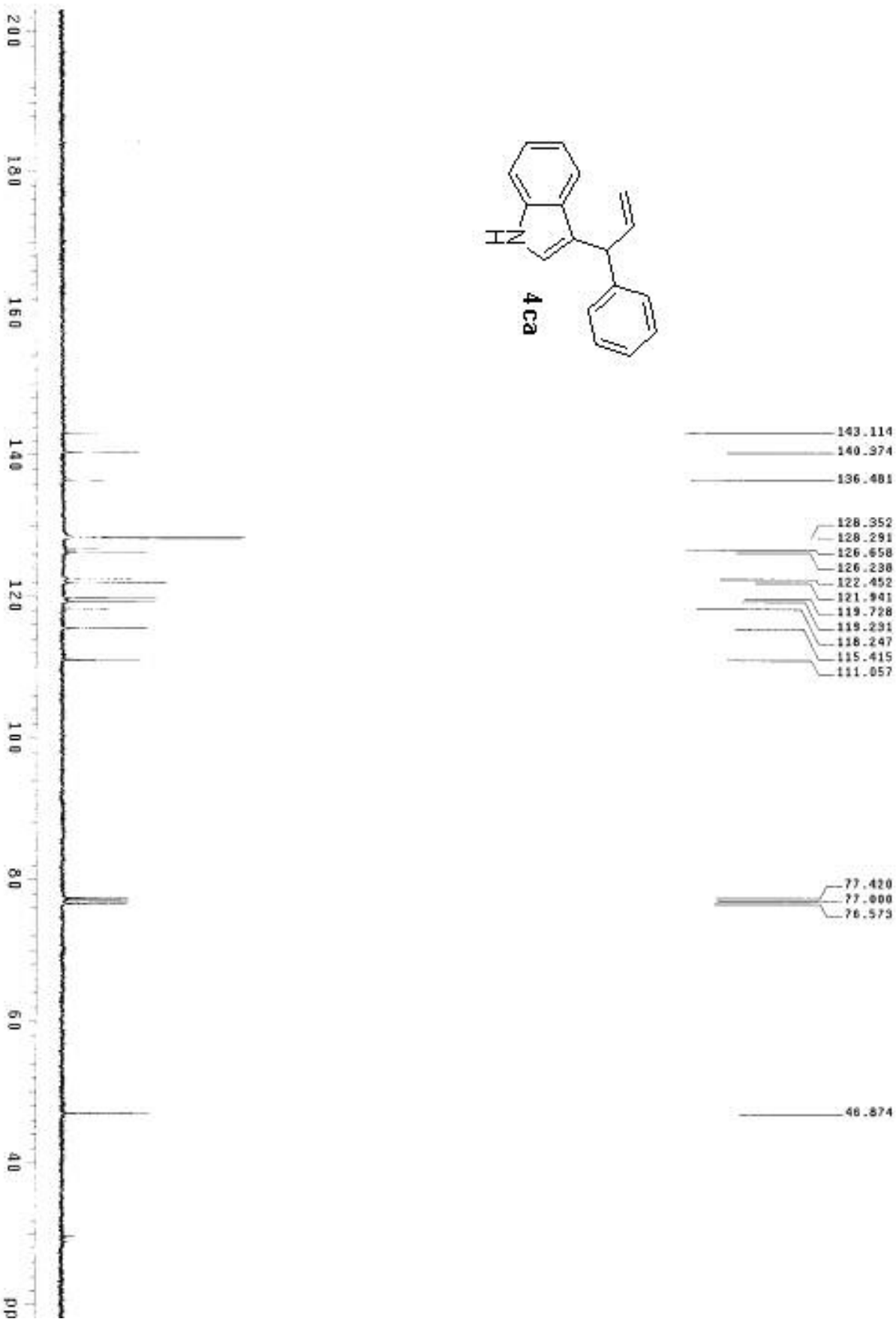
7.025
7.002
6.978
6.737
6.732
6.372
6.346
6.339
6.314
6.290
6.282
6.258
5.182
5.147
5.075
5.019
4.937
4.914
4ca
8.27
1.12
1.08
1.21
1.02
1.03
1.06
1.10
0.99
10
8
6
4
2
PPM


4ca
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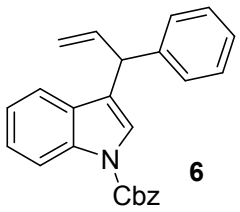
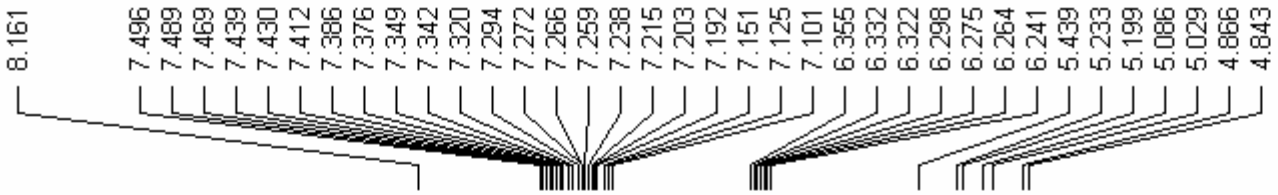
128.352
128.291
126.658
126.238
122.452
121.941
119.728
119.231
118.247
115.415
111.057
77.420
77.000
76.579
46.874



6

The substrate **4ca** (65.4 mg, 0.28 mmol), NaH (10.1 mg, 0.42 mmol) were added into a flask containing DMF (3 mL). After stirring for 10 min at room temperature, benzyl carbonochloridate (0.08 mL, 0.42 mmol) was added. The reaction was stirred for 1 h and quenched with water, extracted with Et_2O, dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (petroleum ether/ethyl acetate: 200/1) to afford the product **6** (77.3 mg, 75%) as a colorless oil. HPLC analysis indicated that the enantiomeric excess of the product was 85% [Diacel CHIRALCEL AD-H (0.46 cm x 25 cm); hexanes/2-propanol = 95/5; flow rate = 0.6 mL/min; detection wavelength = 230 nm; t_R = 10.15 (minor), 10.84 (major) min]. $[\alpha]_D^{20}$ = +21.8 (c 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.16 (br s, 1H), 7.50-7.10 (m, 15H), 6.30 (ddd, J = 6.9, 10.2, 17.1 Hz, 1H), 5.44 (s, 2H), 5.21 (d, J = 10.2, 1H), 5.06 (d, J = 17.1 Hz, 1H), 4.85 (d, J = 6.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 150.8, 141.5, 139.1, 135.8, 135.1, 129.8, 128.7, 128.6, 128.4, 128.3, 126.6, 124.6, 123.7, 123.2, 122.7, 120.1, 116.3, 115.2, 68.5, 46.6. IR (liquid film): ν_{max} (cm^{-1}) = 3063, 3032, 1734, 1638, 1602, 1455, 1397, 1356, 1307, 1241, 1216, 1067, 1027, 1010, 917, 746, 699. MS (EI, *m/z*, rel. intensity) 367 (M^+, 7.7), 91 (100); HRMS (EI) calcd for $C_{25}H_{21}NO_2$ (M^+): 367.1572, Found: 367.1575.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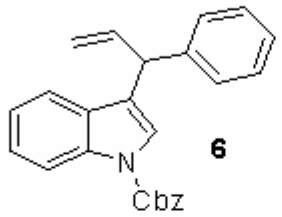
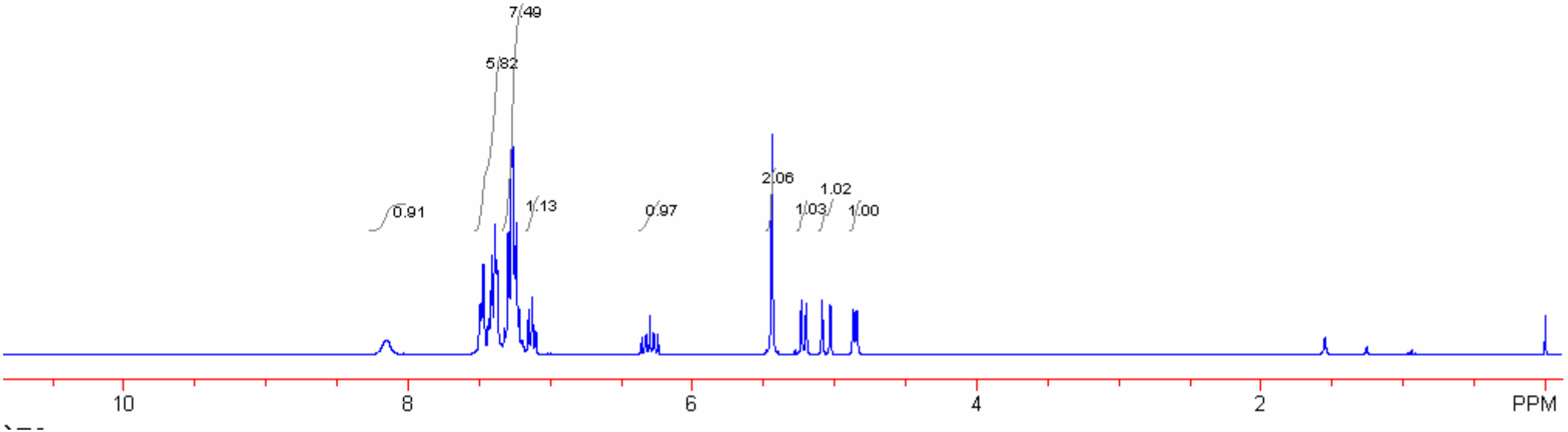
4.843


N
Cbz

6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1.02
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10
8
6
4
2
PPM

N
Cbz
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139.132
135.849
135.126
129.787
128.673
128.616
128.447
128.277
128.134
126.604
124.589
123.683
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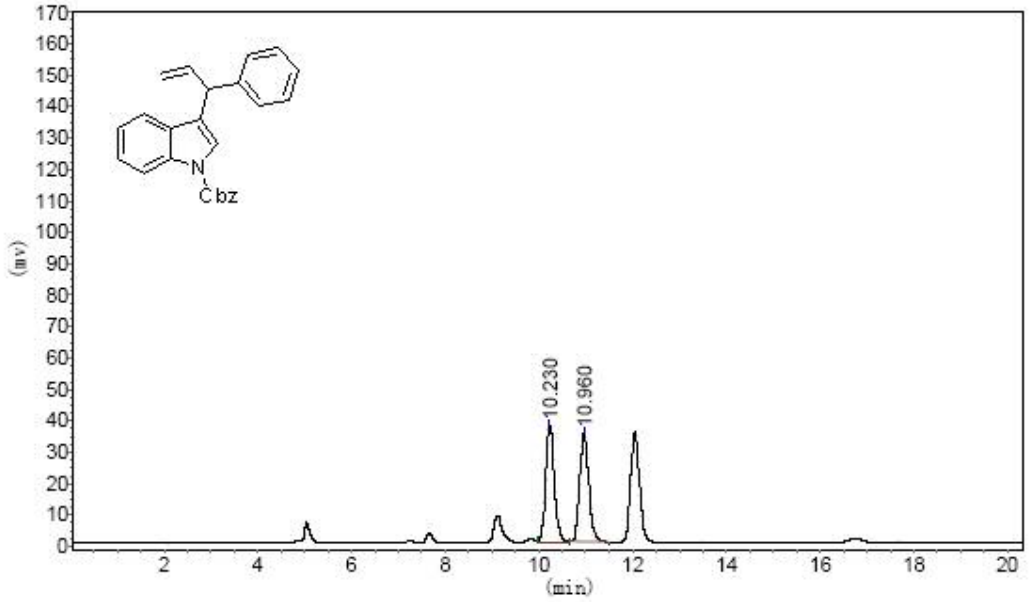
50
PPM



PeakNo	R. Time	PeakHeight	PeakArea	PerCent
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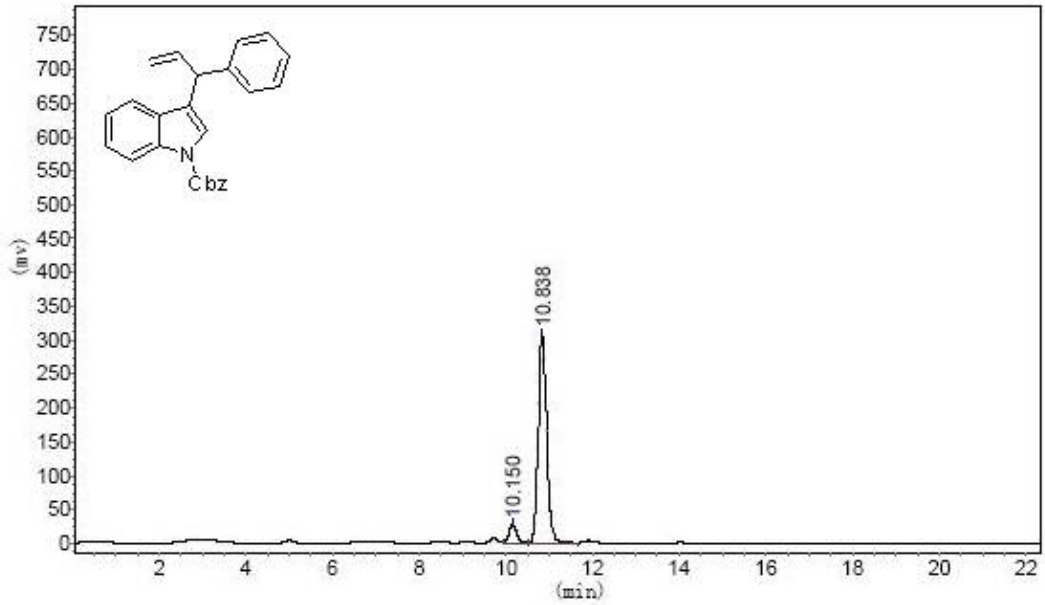
Total		72060.262	956026.188	100.0000



PeakNo	R. Time	PeakHeight	PeakArea	PerCent
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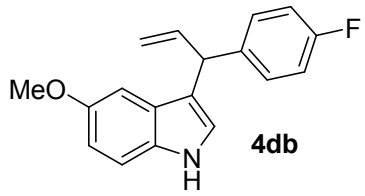
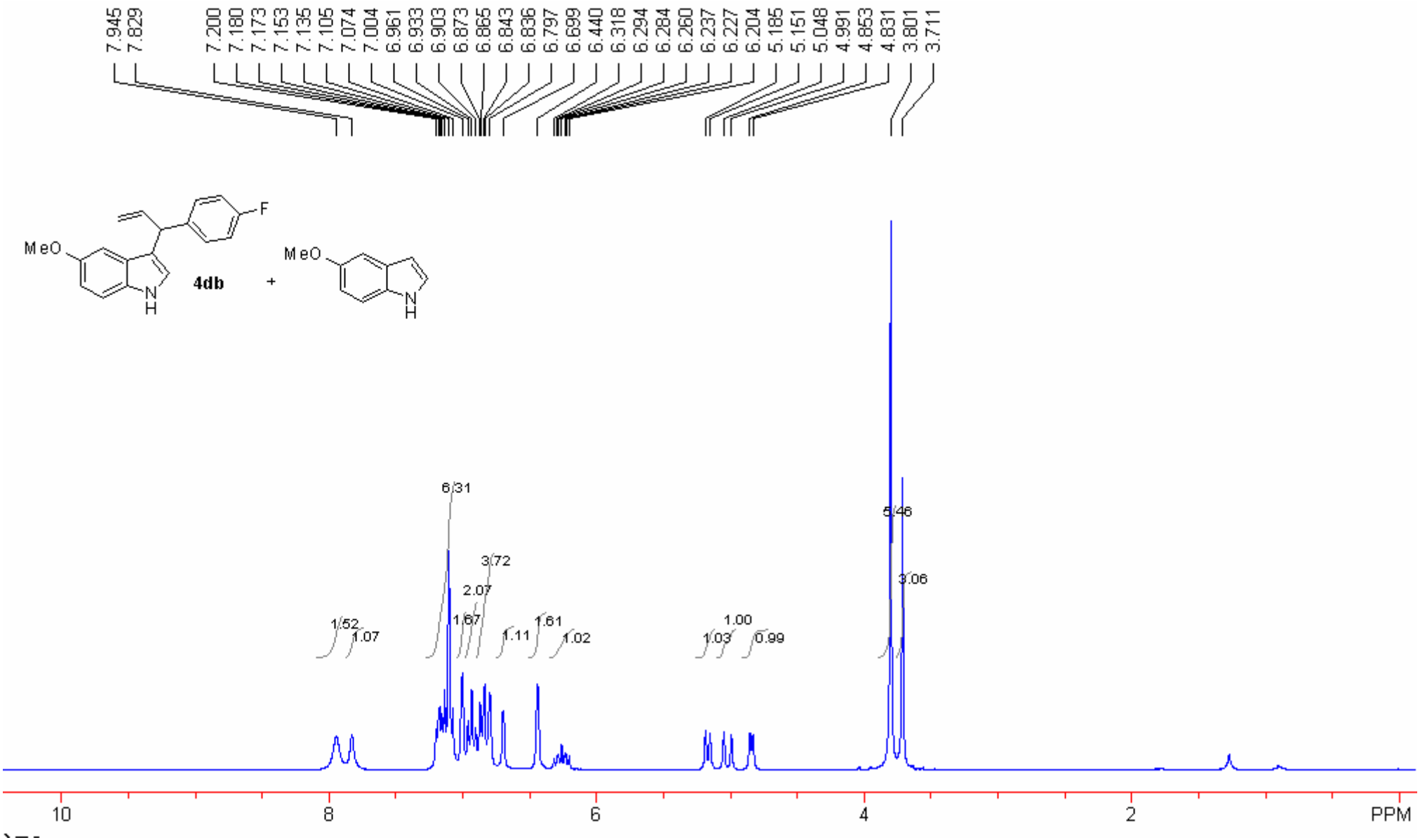
Total		335712.043	4506855.375	100.0000



4db

The general procedure was followed with the methyl carbonate **2d** (83.1 mg, 0.40 mmol) derived from (E)-3-(4-fluorophenyl)prop-2-en-1-ol, 5-methoxyindole **3b** (117.9 mg, 0.80 mmol) and cesium carbonate (130.7 mg, 0.40 mmol) in 1,4-dioxane (2.0 mL). The reaction was conducted at reflux for 4 h. ^{1}H NMR analysis of the crude reaction mixture indicated that the ratio of regioisomers (b/l) was >99/1. The reaction mixture was purified by column chromatography (petroleum ether/ethyl acetate: 50/1) to give the mixture (148.7 mg) of **3b** and **4db** (52.5 mg, 47%). Because **4db** was inseparable from **3b,** the yield was determined by ^{1}H NMR of the isolated mixture. HPLC analysis indicated that the enantiomeric excess of the product was 92% [Diacel CHIRALCEL AD-H (0.46 cm x 25 cm); hexanes/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 230 nm; t_R = 11.89 (minor), 18.44 (major) min]. $[\alpha]_D^{20}$ = -21.5 (c 0.37, $CHCl_3$). ^{1}H NMR (300 MHz, CDCl3) δ = 7.83 (br s, 1H), 7.18-6.80 (m, 7H), 6.70 (s, 1H), 6.26 (ddd, J = 6.9, 10.2, 17.4 Hz, 1H), 5.17 (d, J = 10.2, 1H), 5.02 (d, J = 17.1 Hz, 1H), 4.84 (d, J = 6.6 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.9, 159.7, 153.5, 140.1, 138.6, 138.6, 131.7, 129.8, 129.6, 126.4, 123.3, 117.5, 115.5, 115.1, 114.8, 111.9, 111.8, 101.6, 55.7, 46.0. IR (liquid film): ν_{max} (cm^{-1}) = 3417, 3070, 2997, 2938, 2833, 1625,1602, 1583, 1507, 1483, 1455, 1440, 1287, 1224, 1153, 1029, 799, 757, 725. MS (EI, *m/*z, rel. intensity) 281 (M^+, 100); HRMS (EI) calcd for $C_{18}H_{16}NOF$ (M^+): 281.1216, Found: 281.1223.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3.801
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+
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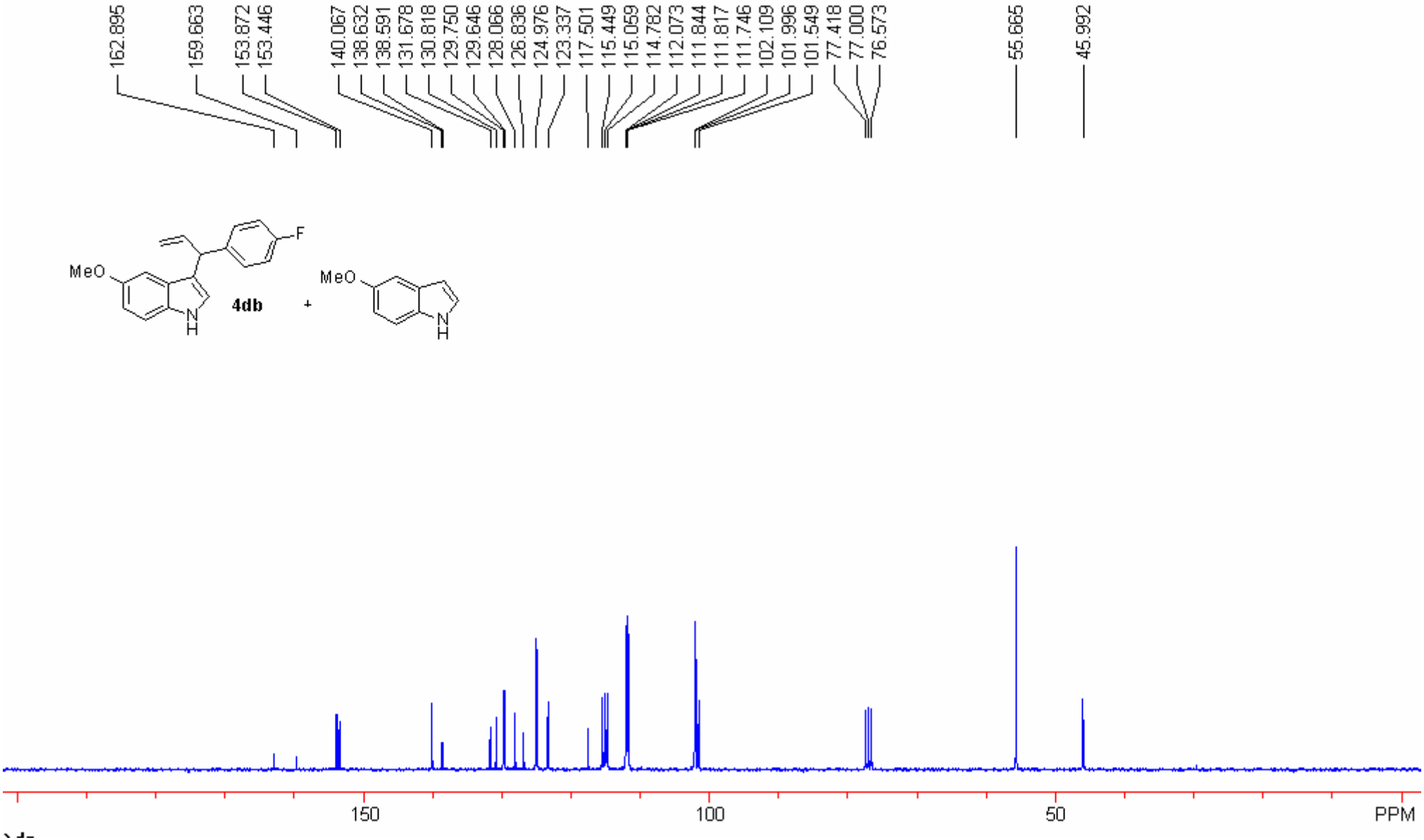
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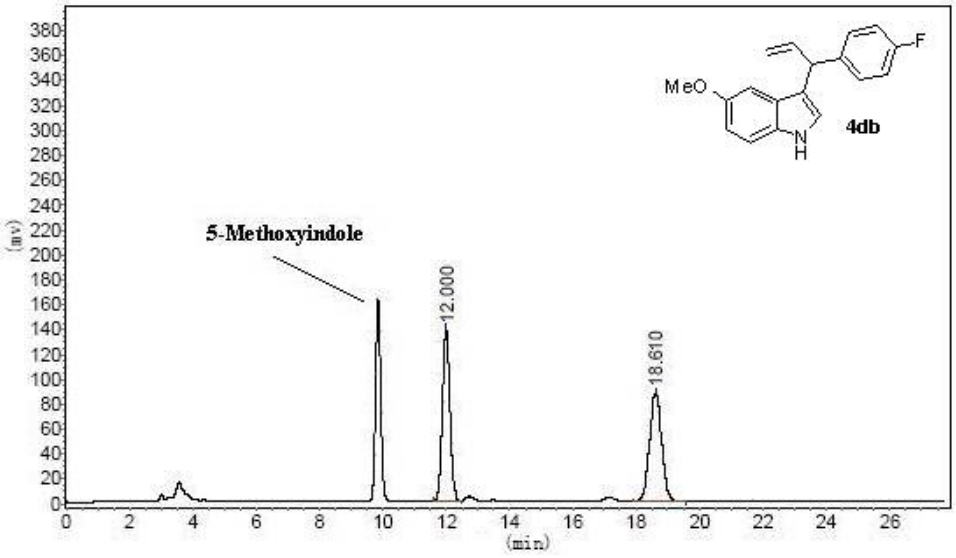
PPM



PeakNo	R. Time	PeakHeight	PeakArea	PerCent
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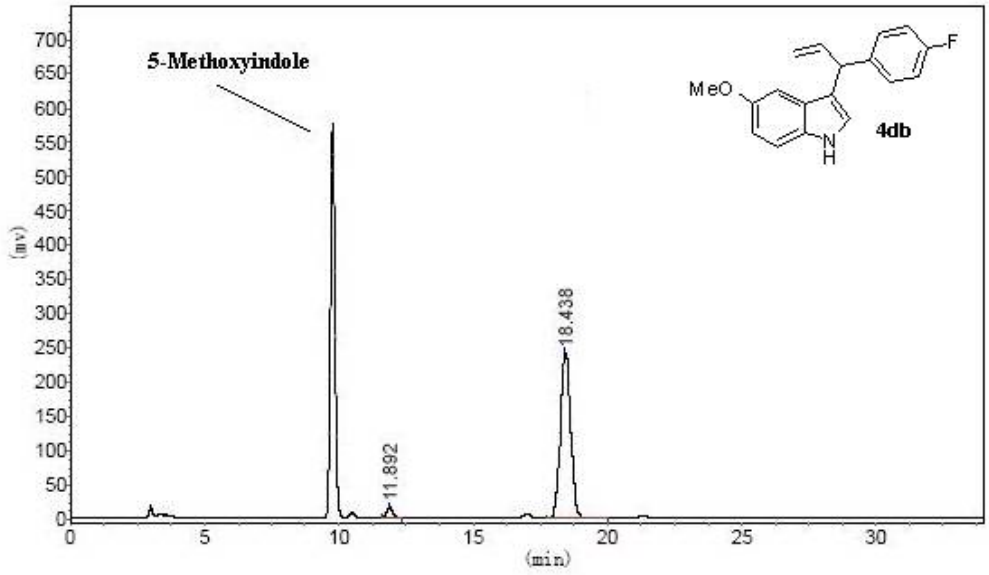
2	18.610	87412.570	2324767.750	50.1806
Total		225935.117	4632797.500	100.0000



PeakNo	R. Time	PeakHeight	PeakArea	PerCent
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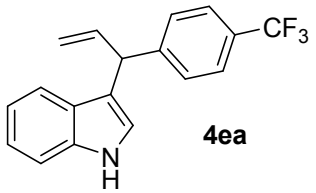
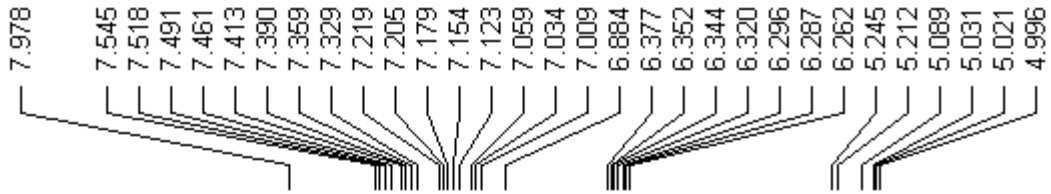
2	18.438	241939.125	6429940.500	95.9704
Total		257902.958	6699917.469	100.0000



4ea

The general procedure was followed with the methyl carbonate **2e** (108.3 mg, 0.41 mmol) derived from (E)-3-(4-trifluoromethylphenyl)prop-2-en-1-ol, indole **3a** (95.9 mg, 0.82 mmol) and cesium carbonate (133.1 mg, 0.41 mmol) in 1,4-dioxane (2.0 mL). The reaction was conducted at reflux for 3 h. ^{1}H NMR analysis of the crude reaction mixture indicated that the ratio of regioisomers (b/l) was >99/1. The crude reaction mixture was purified by column chromatography (petroleum ether/ethyl ether: 30/1) to give the product **4ea** (76.0, 63%) as a yellow oil. HPLC analysis indicated that the enantiomeric excess of the product was 87% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 98/2; flow rate = 1.0 mL/min; detection wavelength = 230 nm; t_R = 35.50 (major), 38.16 (minor) min]. $[\alpha]_D^{20}$ = -21.5 (c 0.37, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.98 (br s, 1H), 7.55-7.01 (m, 8H), 6.89 (s, 1H), 6.32 (ddd, J = 7.2, 9.6, 17.1 Hz, 1H), 5.23 (d, J = 9.6, 1H), 5.06 (d, J = 17.1 Hz, 1H), 5.01 (d, J = 7.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.2, 139.5, 136.6, 128.7, 128.3, 126.4, 125.3, 125.2, 122.5, 122.3, 119.5, 119.5, 117.5, 116.3, 111.2, 46.7. IR (liqiud film): ν_{max} (cm^{-1}) = 3415, 3061, 2903, 2933, 2874, 1714, 1639, 1618, 1488, 1457, 1419, 1327, 1162, 1110, 1068, 1018, 923, 856, 826, 797, 744. MS (EI, *m/*z, rel. intensity) 301 (M^+, 100), 156 (88); HRMS (EI) calcd for $C_{18}H_{14}F_3N$ (M^+): 301.1078, Found: 301.1085.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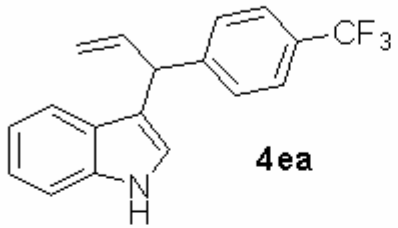
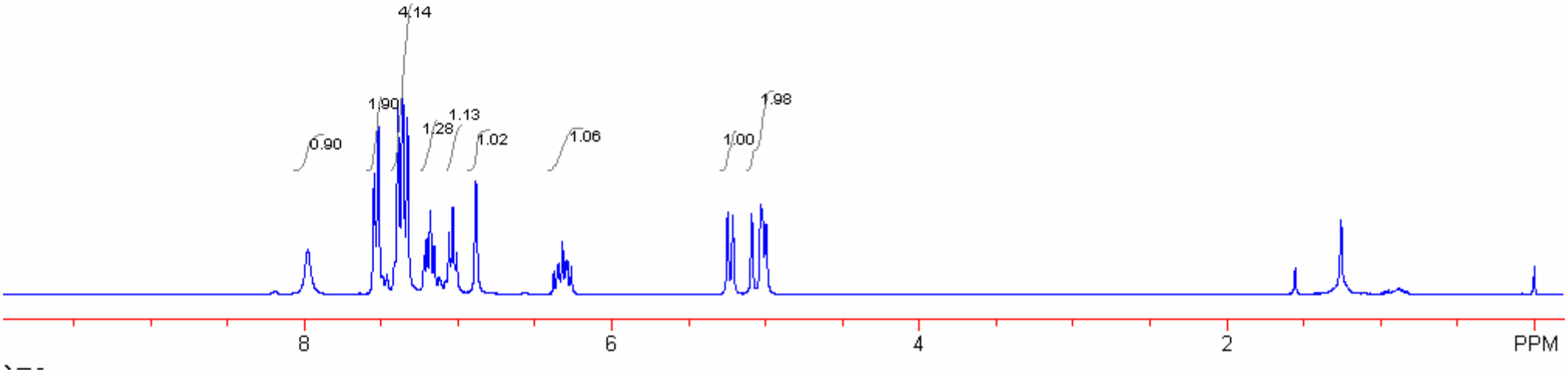
4.996


CF3
NH

4ea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1.28
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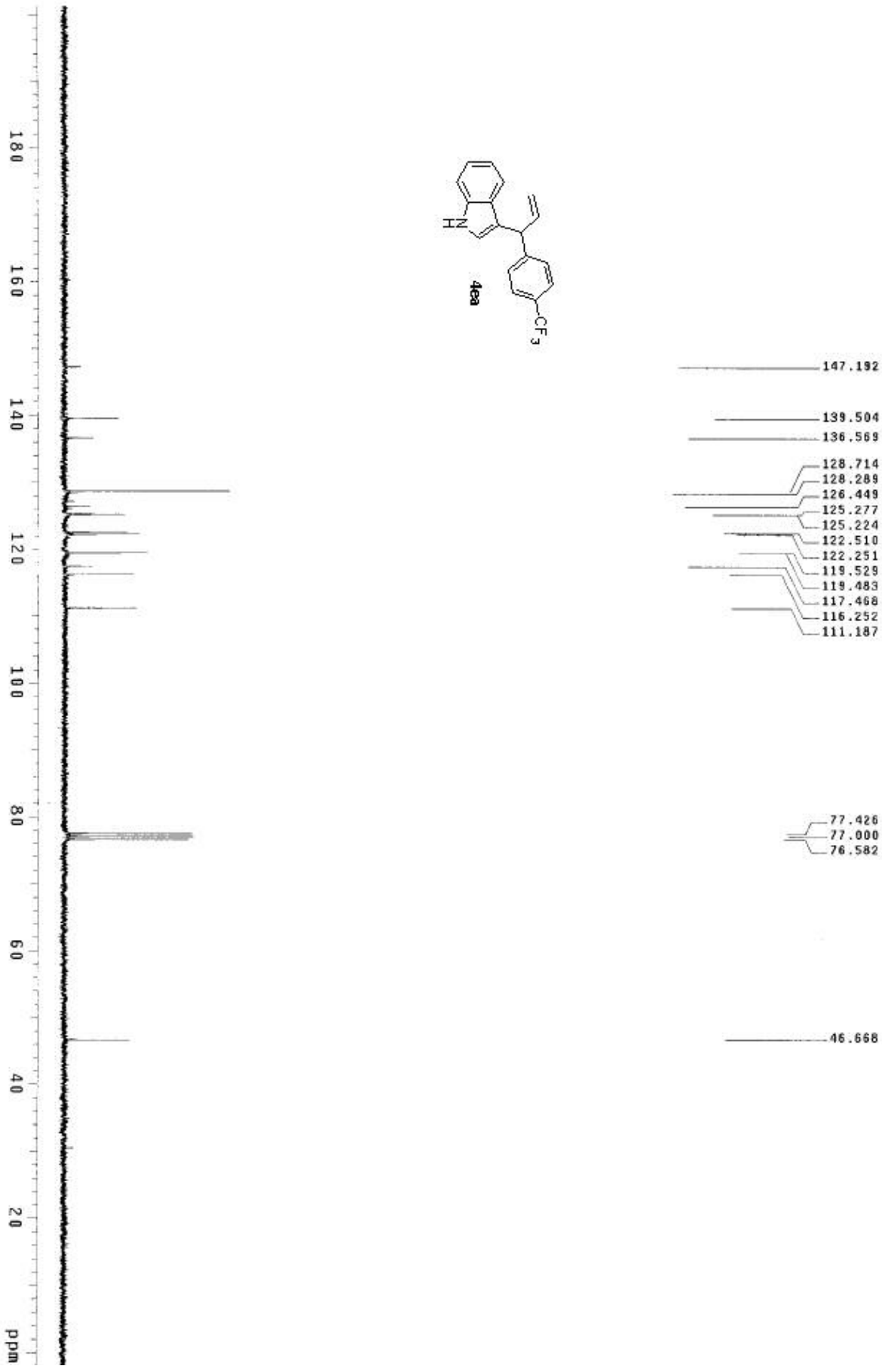
0.90
1.06
1.00
1.98
8
6
4
2
PPM


4ea
CF3
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122.510
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119.529
119.483
117.468
116.252
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77.000
76.582
46.668
180
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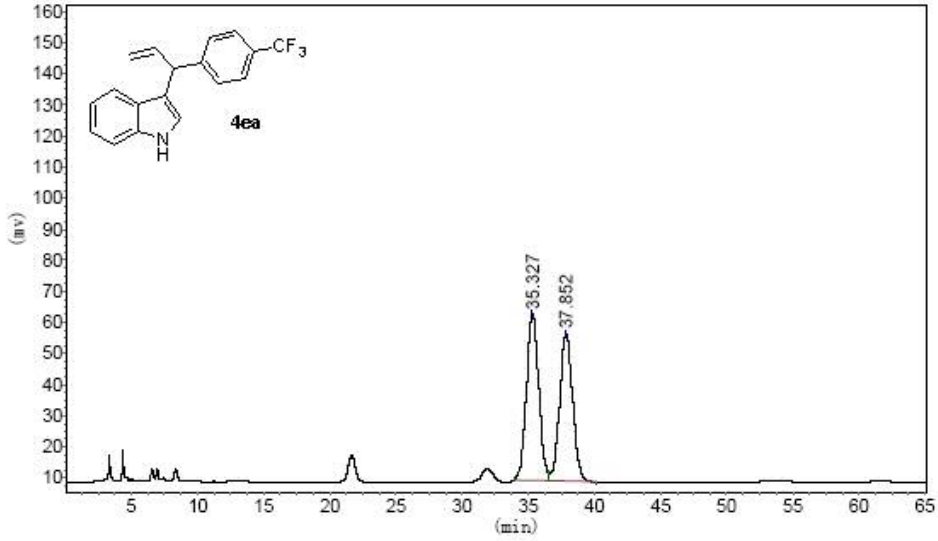
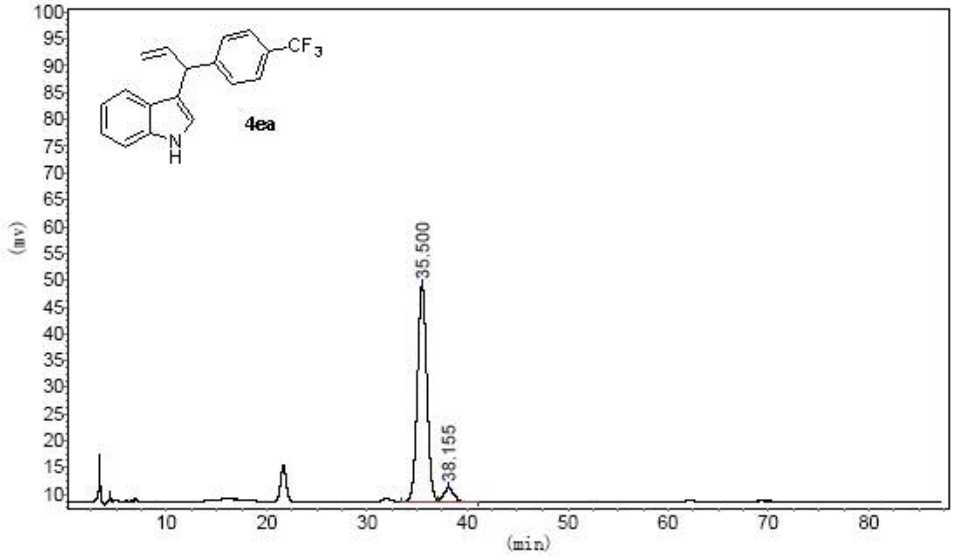
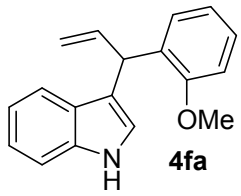
140
120
100
80
60
40
20
ppm



PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	35.327	53305.805	3438461.000	51.4739
2	37.852	47109.434	3241545.000	48.5261
Total		100415.238	6680006.000	100.0000

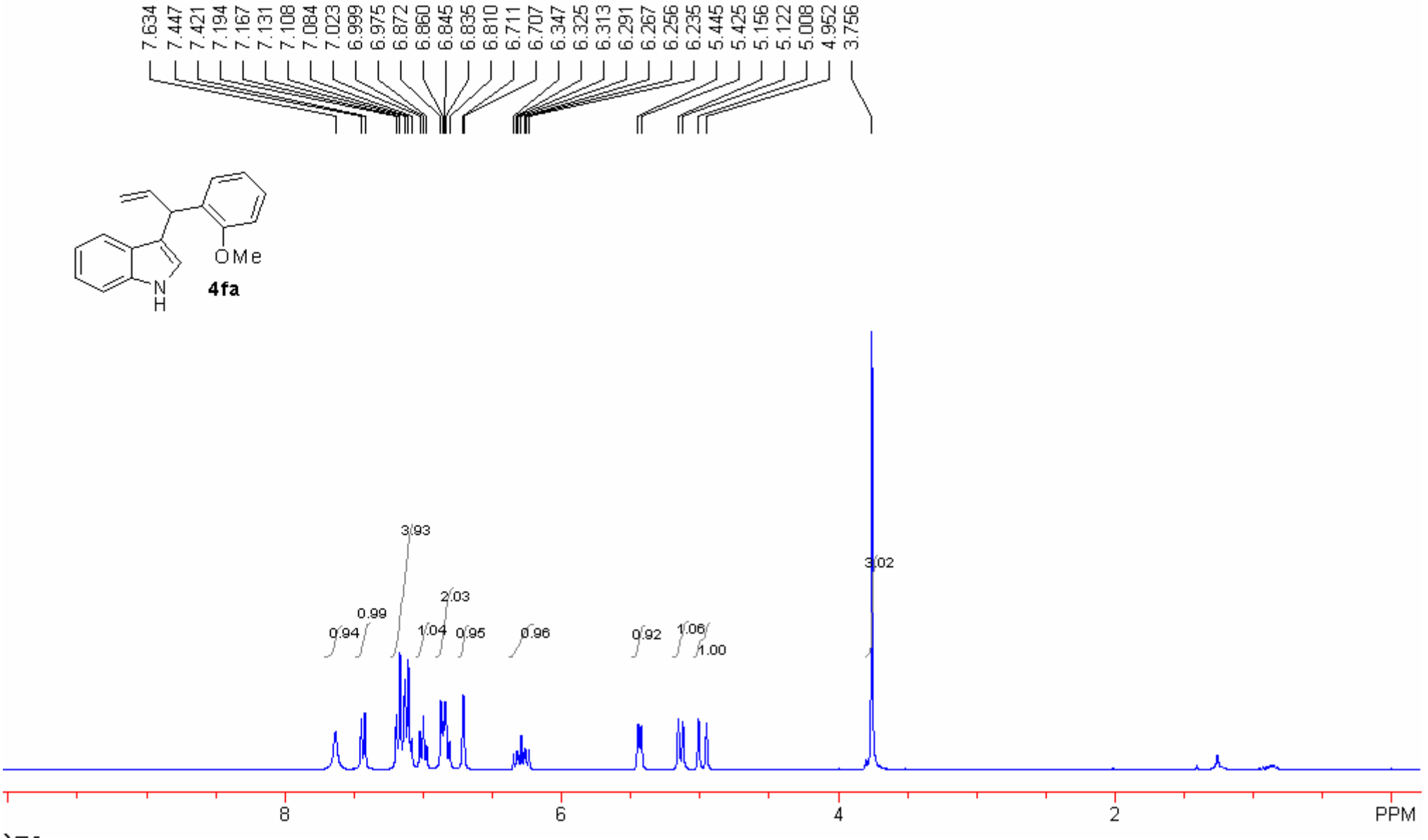


PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	35.500	40641.656	2675309.000	93.5162
2	38.155	2573.029	185487.500	6.4838
Total		43214.686	2860796.500	100.0000



4fa

The general procedure was followed with the methyl carbonate **2f** (91.8 mg, 0.40 mmol) derived from (E)-3-(2-methoxyphenyl)prop-2-en-1-ol, indole **3a** (93.6 mg, 0.80 mmol) and cesium carbonate (130.5 mg, 0.40 mmol) in 1,4-dioxane (2.0 mL). The reaction was conducted at reflux for 3 h. ^{1}H NMR analysis of the crude reaction mixture indicated that the ratio of regioisomers (b/l) was >99/1. The crude reaction mixture was purified by column chromatography (petroleum ether/ethyl acetate: 30/1) to give the product **4fa** (88.2 mg, 84%) as a yellow oil. HPLC analysis indicated that the enantiomeric excess of the product was 70% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 98/2; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R = 24.46 (minor), 28.32 (major) min]. $[\alpha]_D^{20}$ = +6.2 (c 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, CDCl3) δ = 7.63 (br s, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.19-7.08 (m, 4H), 7.00 (t, J = 7.2 Hz, 1H), 6.87-6.81 (m, 2H), 6.71 (d, J = 1.2 Hz, 1H), 6.29 (ddd, J =6.3, 10.2, 16.8 Hz, 1H), 5.43 (d, J = 6.0 Hz, 1 H), 5.14 (d, J = 10.2 Hz, 1 H), 4.98 (d, J = 16.8 Hz, 1 H), 3.76 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 156.7, 140.0, 136.4, 131.4, 129.2, 127.3, 126.9, 122.5, 121.7, 120.4, 119.7, 119.0, 118.0, 115.0, 110.9, 110.6, 55.5, 38.7. IR (liquid film): ν_{max} (cm^{-1}) = 3418, 3078, 3059, 3003, 2955, 2934, 2837, 1637, 1619, 1599, 1587, 1548, 1490, 1457, 1438, 1419, 1244, 1105, 1029, 917, 743. MS (EI, *m/z*, rel. intensity) 263 (M^+, 89), 130 (100); HRMS (EI) calcd for $C_{18}H_{17}NO$ (M^+): 263.1310, Found: 263.1319.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7.131
7.108
7.084
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6.975
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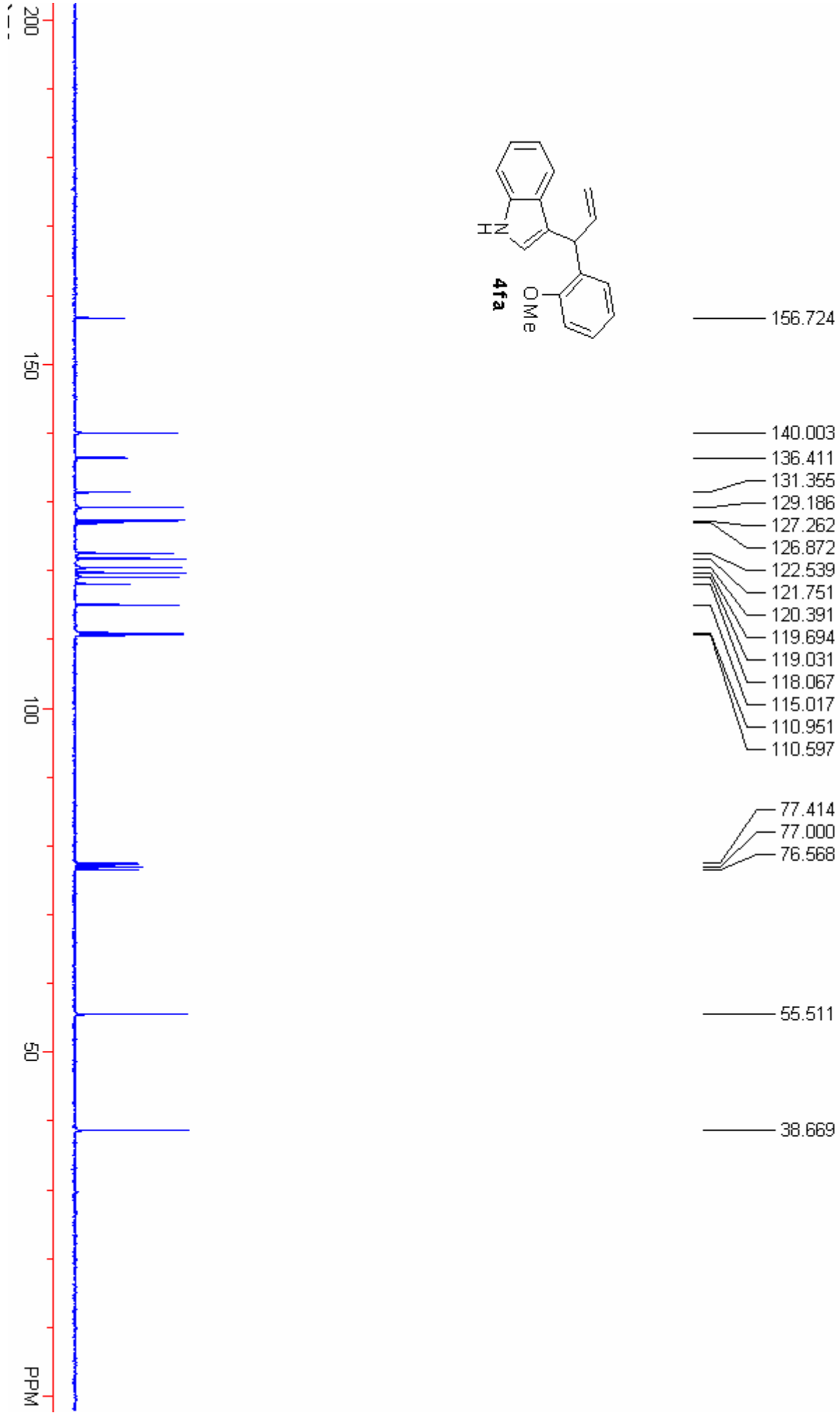
6.845
6.835
6.810
6.711
6.707
6.347
6.325
6.313
6.291
6.267
6.256
6.235
5.445
5.425
5.156
5.122
5.008
4.952
3.756
OMe
N
H
4fa
3.93
2.03
0.99
0.94
1.04
0.95
0.96
0.92
1.06
1.00
3.02
8
6
4
2
PPM


200
150
100
50
PPM
N
H
OMe
4fa
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140.003
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131.355
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126.872
122.539
121.751
120.391
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118.067
115.017
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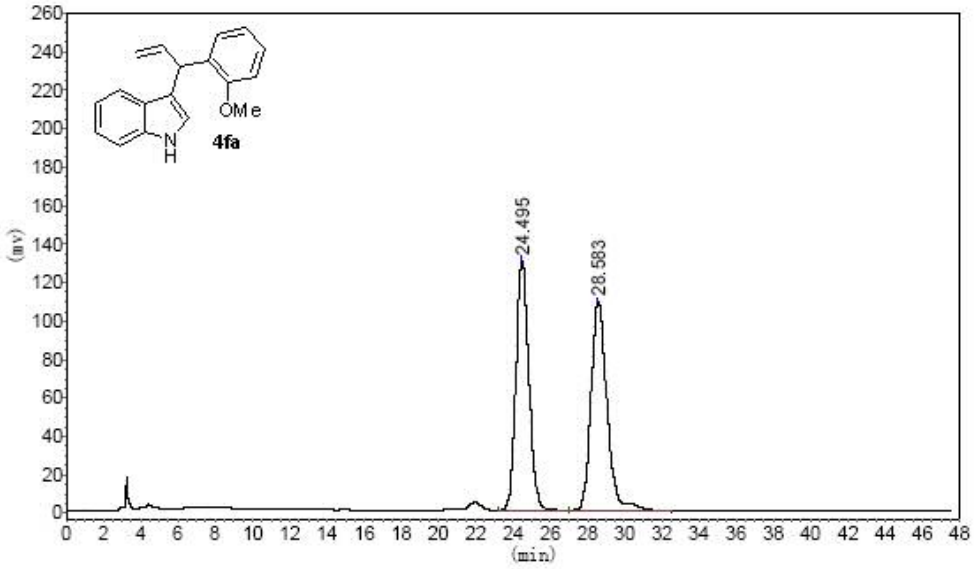
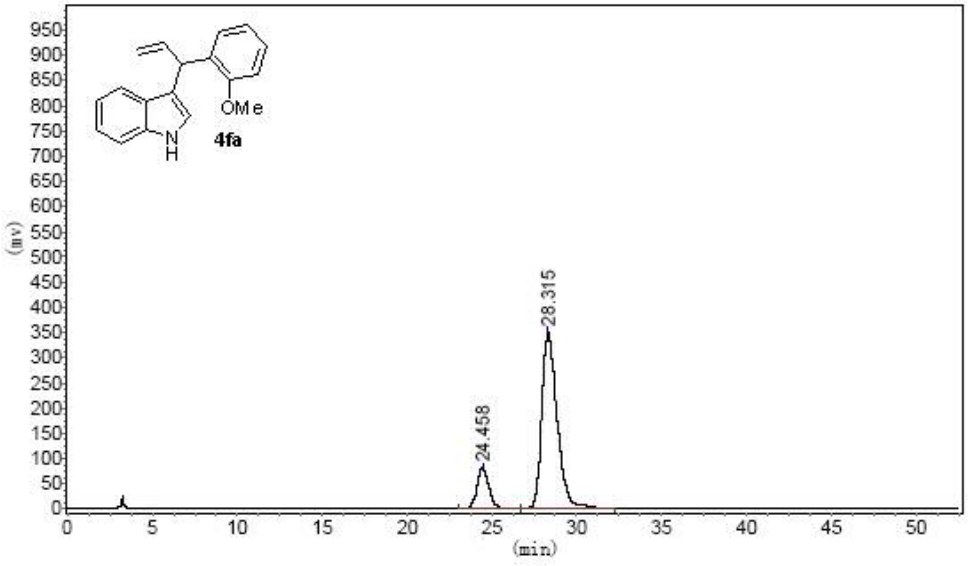
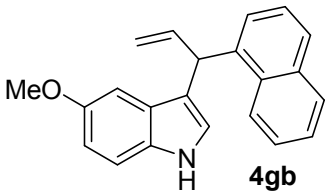
77.000
76.568
55.511
38.669



PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	24.495	130014.422	6252501.000	49.1631
2	28.583	108201.742	6465363.500	50.8369
Total		238216.164	12717864.500	100.0000

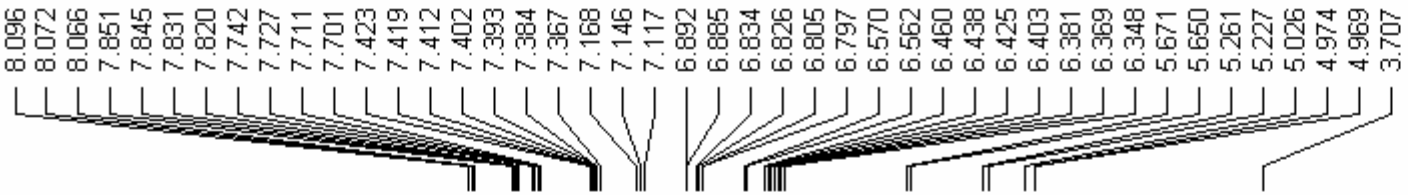


PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	24.458	80136.281	3842759.000	15.0800
2	28.315	348232.375	21639716.000	84.9200
Total		428368.656	25482475.000	100.0000



4gb

The general procedure was followed with the methyl carbonate **2g** (97.3 mg, 0.40 mmol) derived from (E)-3-(naphthalen-1-yl)prop-2-en-1-ol, 5-methoxyindole **3b** (117.6 mg, 0.80 mmol) and cesium carbonate (130.5 mg, 0.40 mmol) in 1,4-dioxane (2.0 mL). The reaction was conducted at reflux for 5 h. ^{1}H NMR analysis of the crude reaction mixture indicated that the ratio of regioisomers (b/l) was >99/1. The crude reaction mixture was purified by column chromatography (petroleum ether/ethyl ether: 30/1) to give the product **4gb** (48.3 mg, 39%) as a yellow oil. HPLC analysis indicated that the enantiomeric excess of the product was 31% [Diacel CHIRALCEL AD-H (0.46 cm x 25 cm); hexanes/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R = 15.60 (minor), 26.46 (major) min]. $[\alpha]_D^{20}$ = -24.2 (c 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.08 (d, J = 7.5 Hz, 1H), 7.85-7.70 (m, 3H), 7.44-7.37 (m, 4H), 7.17-7.12 (m, 1H), 6.89 (d, J = 2.4 Hz, 1H), 6.82 (dd, J = 2.7, 8.7 Hz, 1H), 6.57 (d, J = 2.1 Hz, 1H), 6.40 (ddd, J = 6.0, 9.9, 16.8), 5.66 (d, J = 6.3 Hz, 1H), 5.24 (d, J = 10.2 Hz, 1H), 5.00 (d, J = 16.8 Hz, 1 H), 3.71 (s, 3H),. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 153.6, 139.7, 138.7, 133.9, 131.7, 131.6, 128.6, 127.2, 127.0, 125.8, 125.7, 125.4, 125.3, 124.2, 124.1, 117.5, 116.2, 111.8, 111.7, 101.5, 55.7, 42.1. IR (liquid film) : ν_{max} (cm^{-1}) = 3424, 3051, 3001, 2934, 2830, 1718, 1636, 1625, 1596, 1583, 1508, 1484, 1456, 1438, 1209, 1172, 1045, 1027, 921, 800, 781. MS (EI, *m/*z, rel. intensity) 313 (M^+, 100); HRMS (EI) calcd for $C_{22}H_{19}NO$ (M^+): 313.1467, Found: 313.1472.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7.831
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7.742
7.727
7.711
7.701
7.423
7.419
7.412
7.402
7.393
7.384
7.367
7.168
7.146
7.117
6.892
6.885
6.834
6.826
6.805
6.797
6.570
6.562
6.460
6.438
6.425
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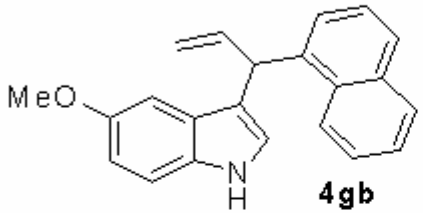
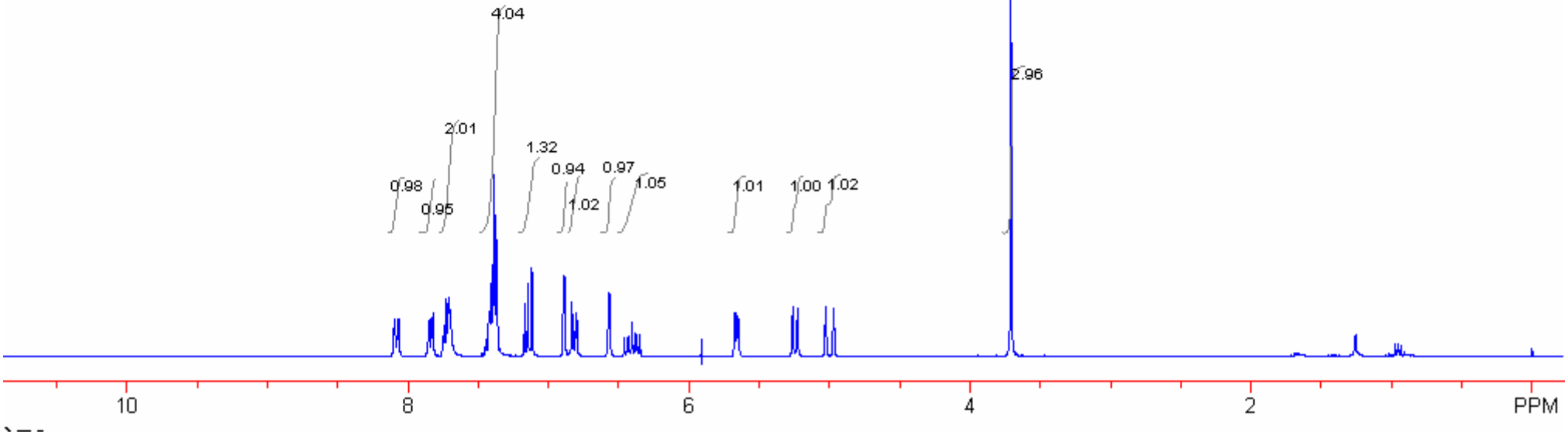
5.227
5.026
4.974
4.969
3.707


MeO
N
H

4gb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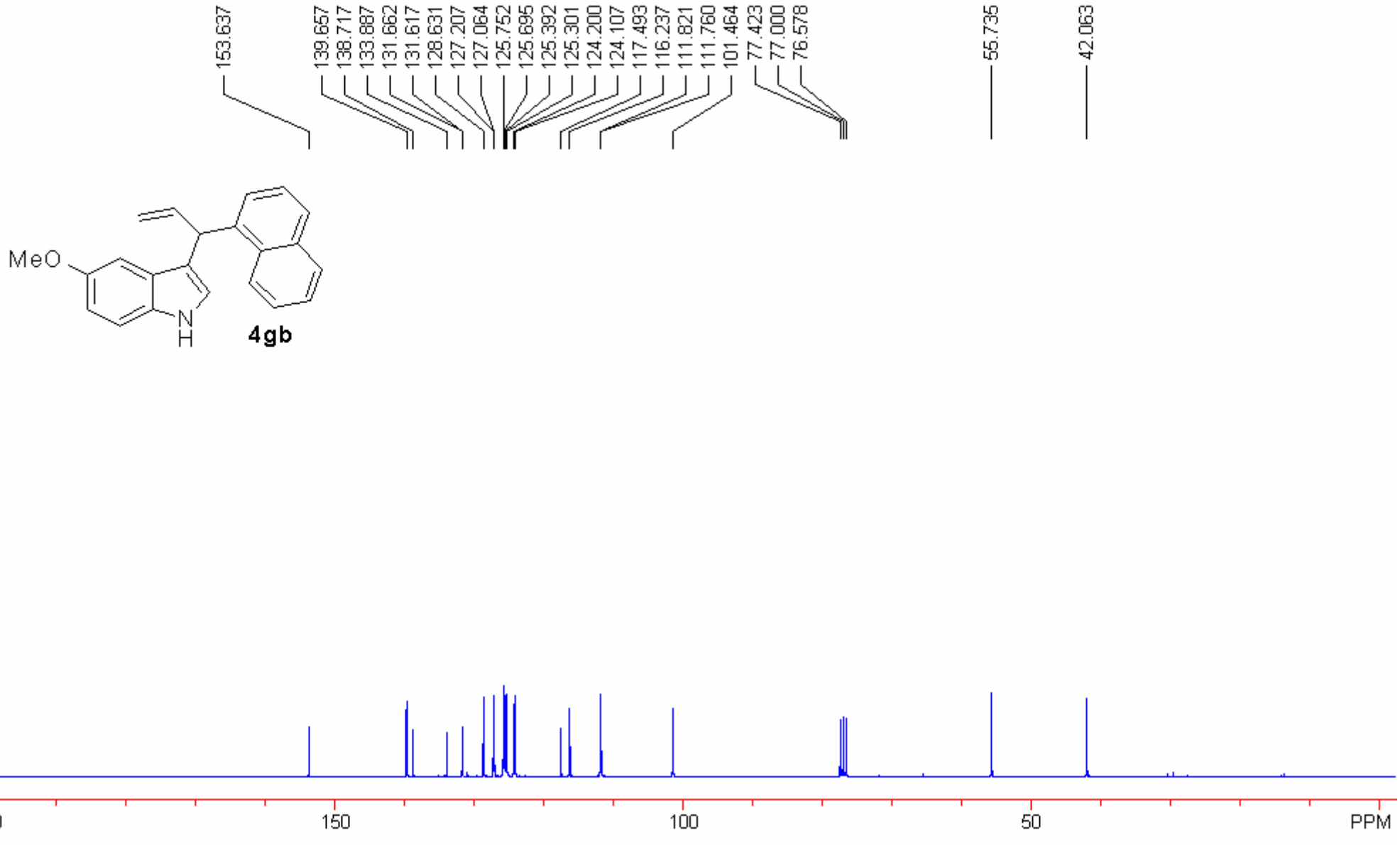
1.00
1.02
2.96
10
8
6
4
2
PPM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125.752
125.695
125.392
125.301
124.200
124.107
117.493
116.237
111.821
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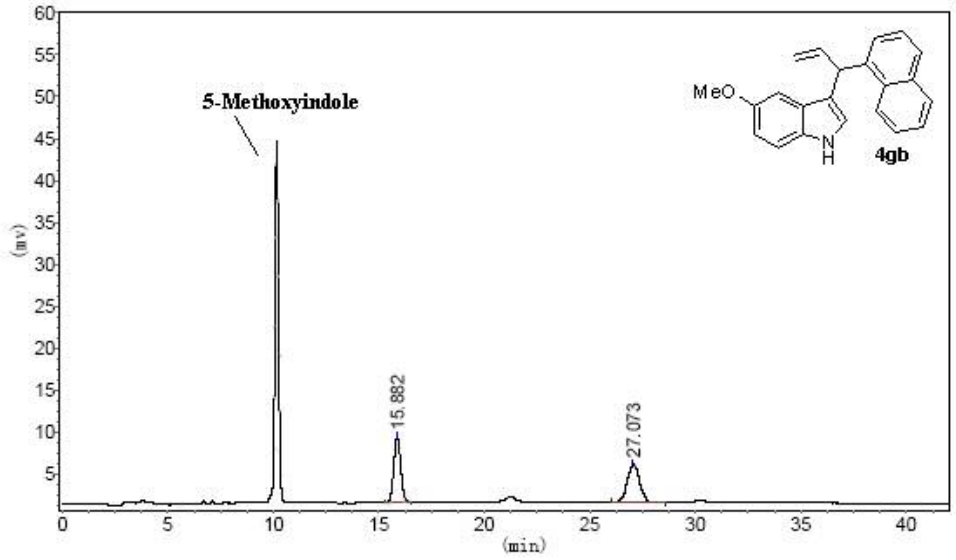
MeO
NH
4gb
200
150
100
50
PPM



PeakNo	R. Time	PeakHeight	PeakArea	PerCent
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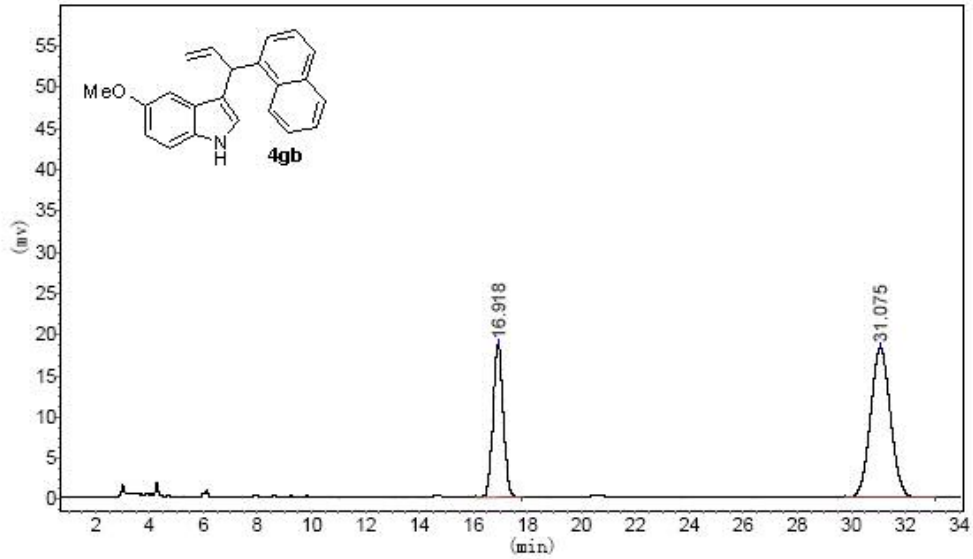
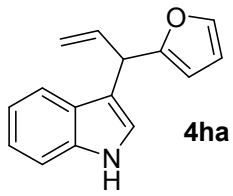
2	27.073	4507.892	179949.672	50.4600
Total		12326.606	356618.125	100.0000

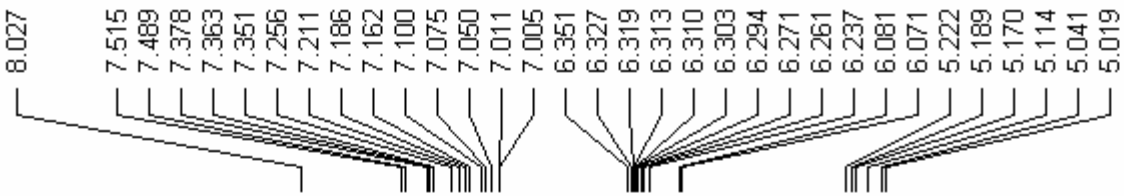


PeakNo				
1	16.918	18404.182	489667.094	34.5083
2	31.075	18120.854	929318.000	65.4917
Total		36525.035	1418985.094	100.0000



4ha

The general procedure was followed with the methyl carbonate **2h** (77.1 mg, 0.42 mmol) derived from (E)-3-(furan-2-yl)prop-2-en-1-ol, indole **3a** (95.2 mg, 0.81 mmol) and cesium carbonate (133.7 mg, 0.41 mmol) in 1,4-dioxane (2.0 mL). The reaction was conducted at reflux for 3 h. ^{1}H NMR analysis of the crude reaction mixture indicated that the ratio of regioisomers (b/l) was >99/1. The crude reaction mixture was purified by column chromatography (petroleum ether/ethyl acetate: 50/1) to give the product **4ha** (75.3, 80%) as a red oil. HPLC analysis indicated that the enantiomeric excess of the product was 89% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 254 nm; t_R = 10.73 (major), 12.94 (minor) min]. $[\alpha]_D^{20}$ = -3.0 (c 0.25, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.03 (br s, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.38-7.35 (m, 2H), 7.19 (t, J = 7.2 Hz, 1H), 7.08 (t, J = 7.2 Hz, 1H), 7.01 (d, J = 2.7 Hz, 1H), 6.35-6.24 (m, 2H), 6.08 (d, J = 3.0 Hz, 1H), 5.21 (d, J = 10.2 Hz, 1H), 5.14 (d, J = 16.8 Hz, 1 H), 5.03 (d, J = 6.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 156.1, 141.4, 137.7, 136.3, 126.3, 122.3, 119.4, 119.3, 115.9, 115.5, 111.2, 110.1, 106.1, 40.6. IR (liquid film): ν_{max} (cm^{-1}) = 3415, 2955, 2925, 2855, 1504, 1457, 1419, 1378, 1338, 1148, 1095, 1010, 918, 799, 738. MS (EI, *m/z*, rel. intensity) 223 (M^+, 9.9), 43 (100); HRMS (EI) calcd for $C_{15}H_{13}NO$ (M^+): 223.0997, Found: 223.1003.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7.351
7.256
7.211
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7.162
7.100
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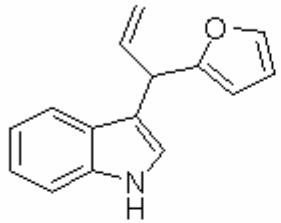
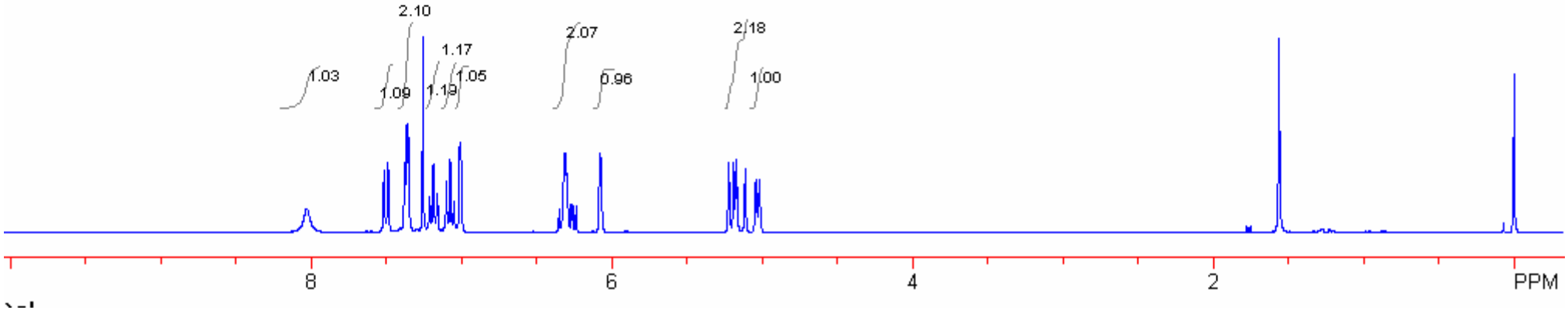
7.050
7.011
7.005
6.351
6.327
6.319
6.313
6.310
6.303
6.294
6.271
6.261
6.237
6.081
6.071
5.222
5.189
5.170
5.114
5.041
5.019


O
N
H


2.10
2.07
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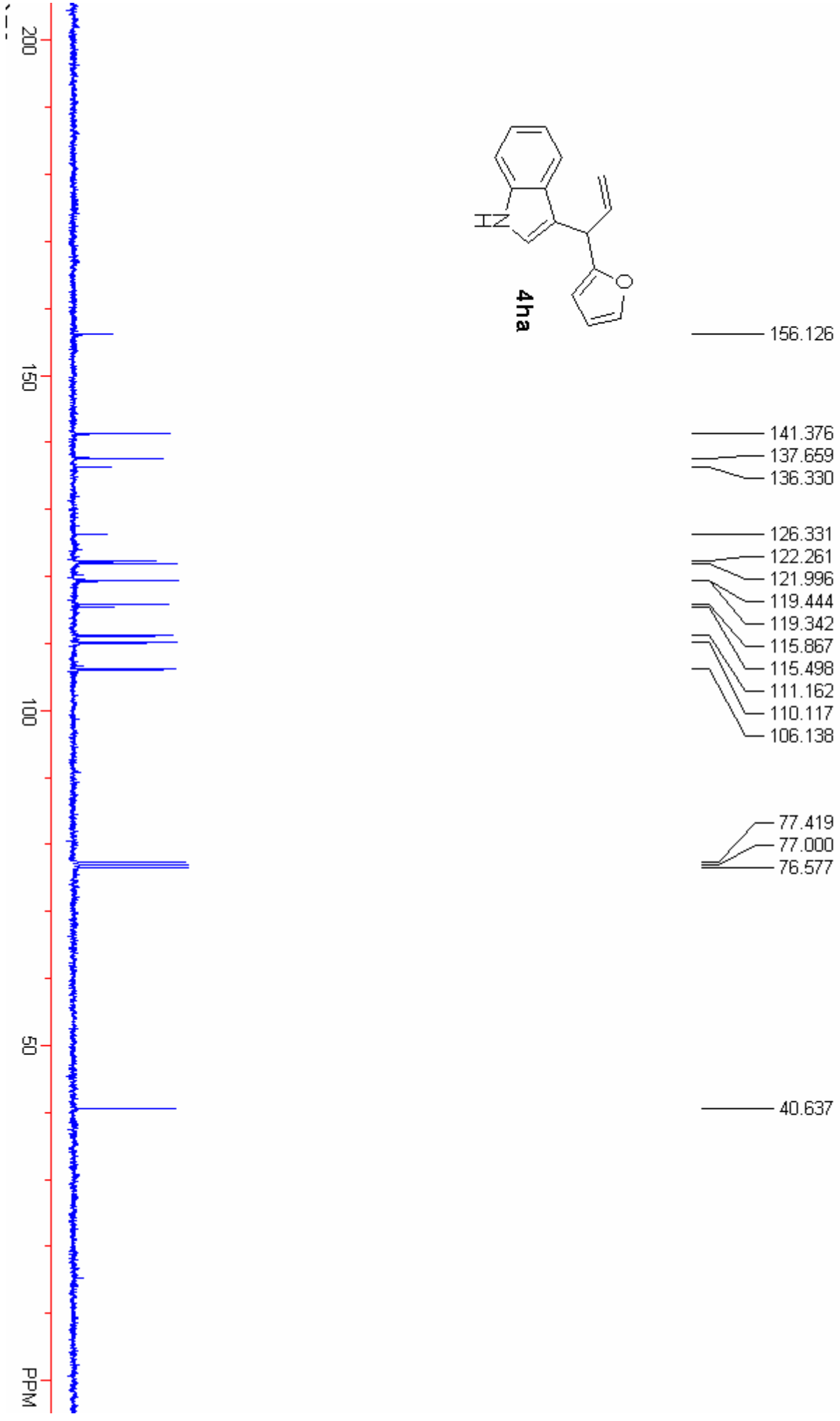
1.03
1.09
1.19
1.05
0.96
1.00
8
6
4
2
PPM


200
150
100
50
PPM
4ha
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126.331
122.261
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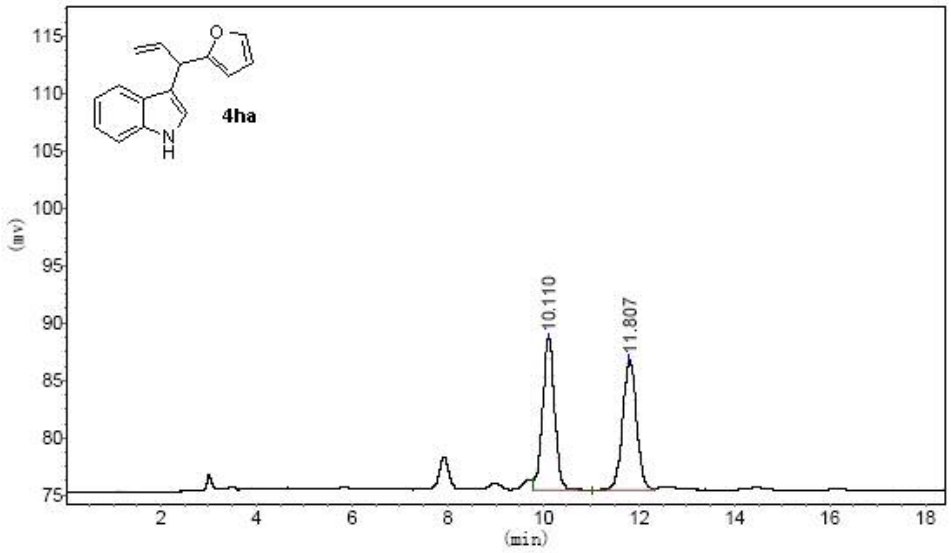
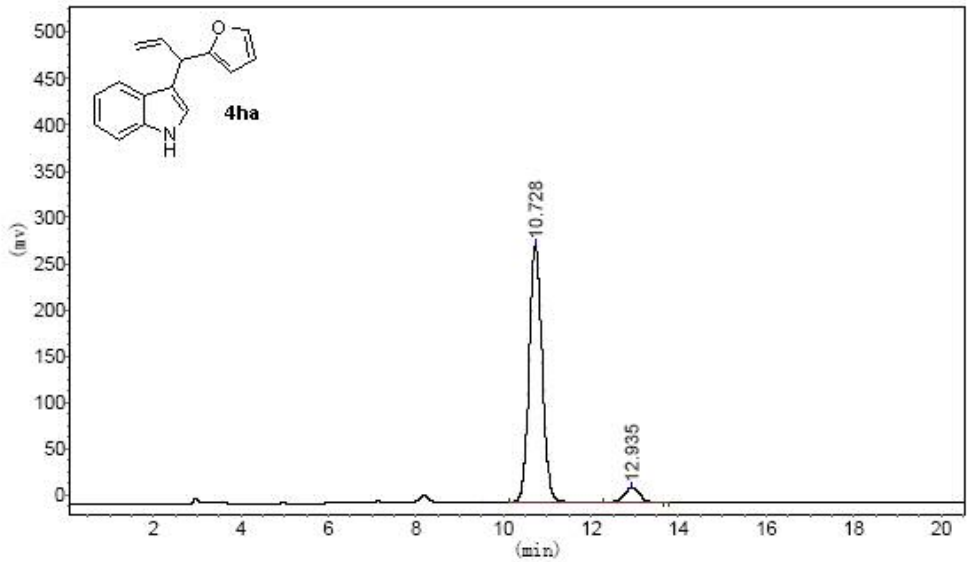
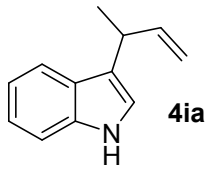
119.342
115.867
115.498
111.162
110.117
106.138
77.419
77.000
76.577
40.637



PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	10.110	13303.327	231974.406	49.9889
2	11.807	11419.335	232077.734	50.0111
Total		24722.662	464052.141	100.0000

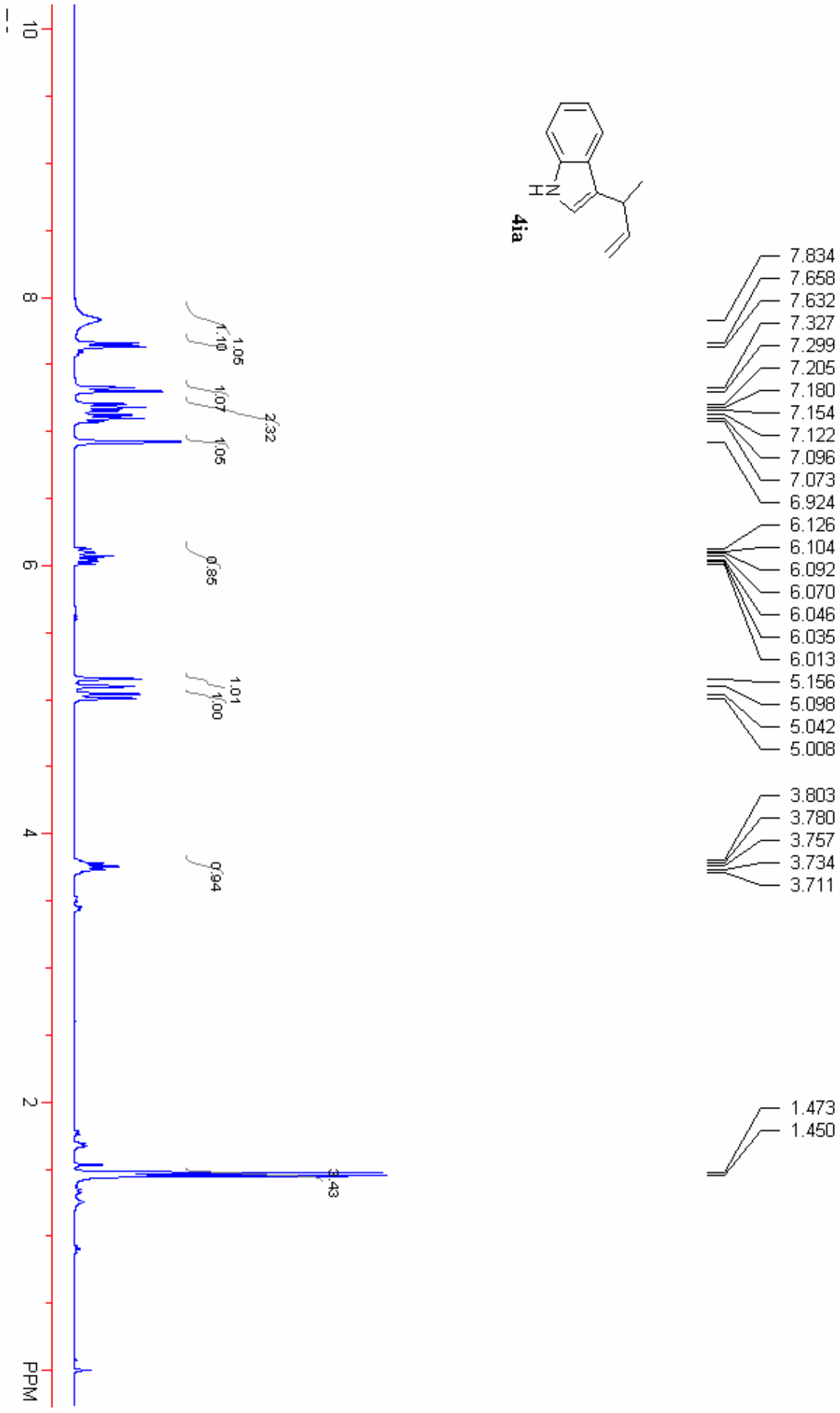


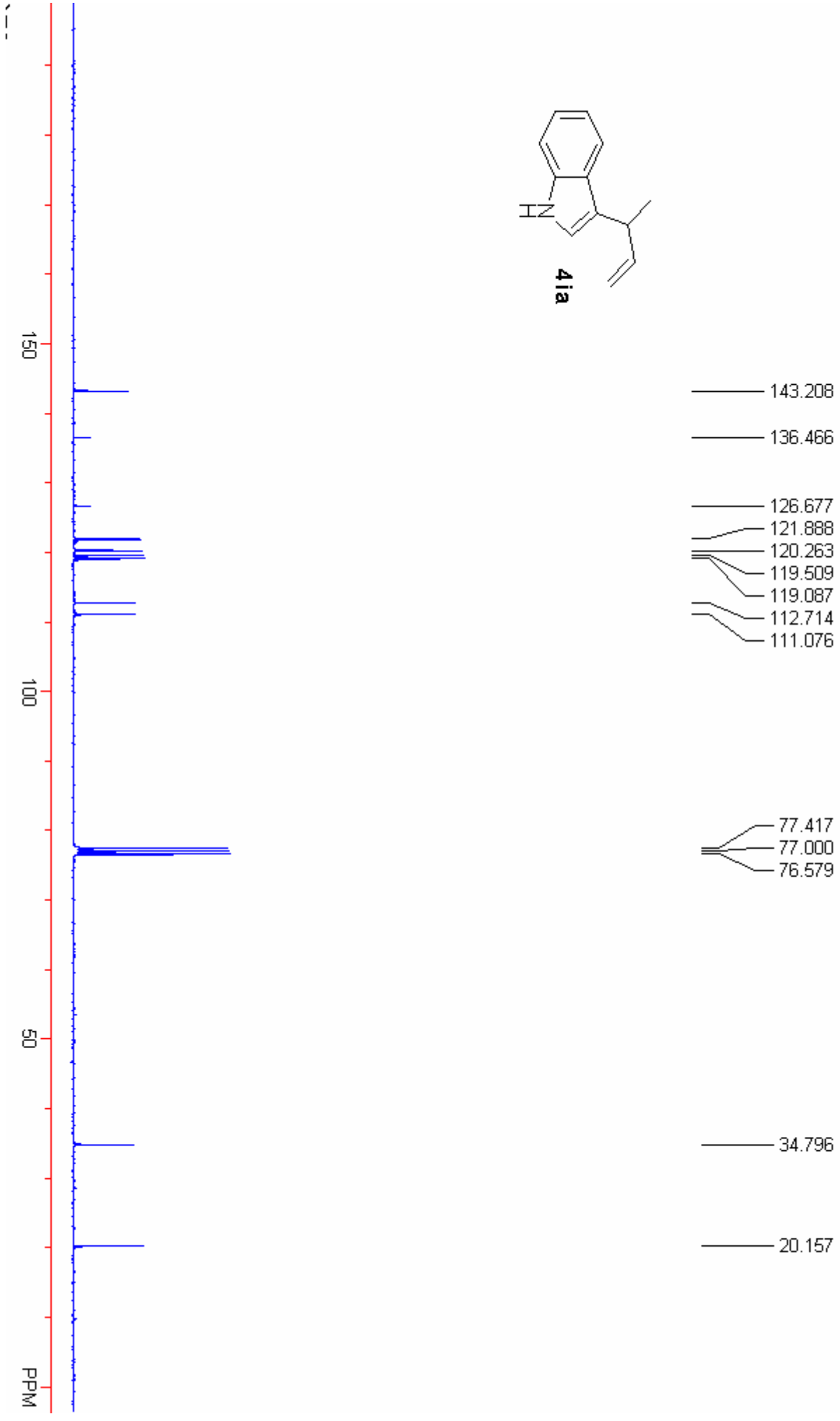
PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	10.728	280059.719	6191818.500	94.2005
2	12.935	15695.875	381205.250	5.7995
Total		295755.594	6573023.750	100.0000

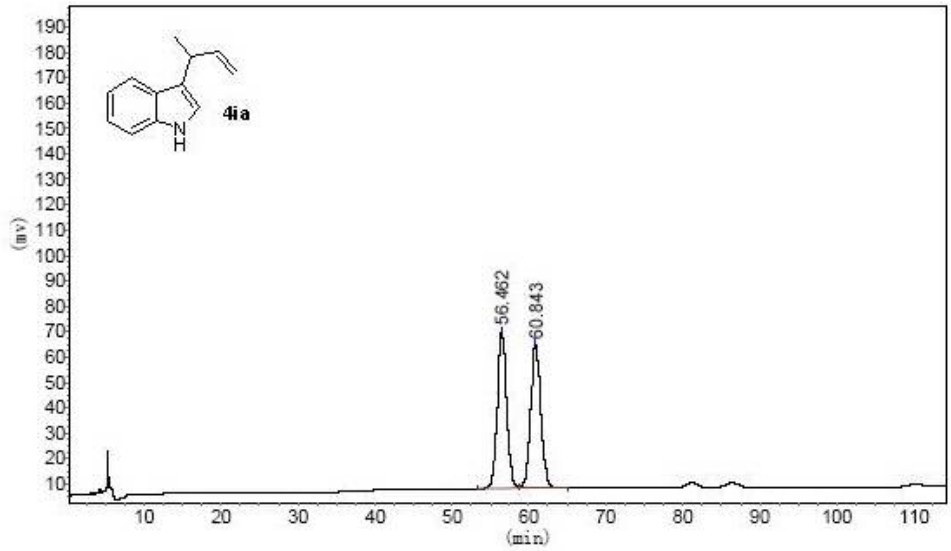


4ia

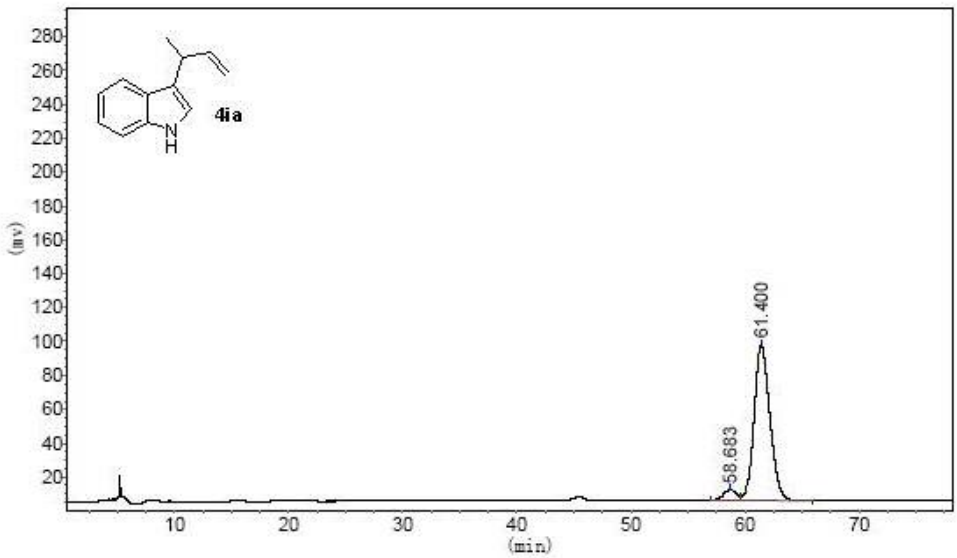
The general procedure was followed with the methyl carbonate **2i** (53.2 mg, 0.40 mmol) derived from (E)-but-2-en-1-ol, indole **3a** (95.3 mg, 0.80 mmol) and cesium carbonate (130.5 mg, 0.40 mmol) in 1,4-dioxane (2.0 mL). The reaction was conducted at reflux for 4 h. ^{1}H NMR analysis of the crude reaction mixture indicated that the ratio of regioisomers (b/l) was 93/7. The crude reaction mixture was purified by column chromatography (petroleum ether/ethyl acetate: 100/1) to give the product **4ia** (29.6 mg, 43%) as a colorless oil [Known compound: Patterson, J. M.; Wu, A.; Kook, C. S.; Smith, Jr. W. T. *J. Org. Chem*., **1974**, *39*, 486-488]. HPLC analysis indicated that the enantiomeric excess of the product was 88% [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 99.5/0.5; flow rate = 1.0 mL/min; detection wavelength = 230 nm; t_R = 58.68 (minor), 61.40 (major) min]. $[\alpha]_D^{20}$ = -10.2 (c 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.83 (br s, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 7.10 (t, J = 7.8 Hz, 1H), 6.92 (s, 1 H), 6.07 (ddd, J = 6.6, 9.9, 17.1 Hz, 1H), 5.13 (d, J = 17.4 Hz, 1H), 5.03 (d, J = 9.9 Hz, 1H), 3.76 (quint, J = 6.9 Hz, 1H), 1.46 (d, J = 6.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.2, 136.5, 126.7, 121.9, 120.3, 119.5, 119.1, 112.7, 111.1, 34.8, 20.2.


4ia
7.834
7.658
7.632
7.327
7.299
7.205
7.180
7.154
7.122
7.096
7.073
6.924
6.126
6.104
6.092
6.070
6.046
6.035
6.013
5.156
5.098
5.042
5.008
3.803
3.780
3.757
3.734
3.711
1.473
1.450
1.10
1.05
1.07
2.32
1.05
0.85
1.01
1.00
0.94
3.43
PPM

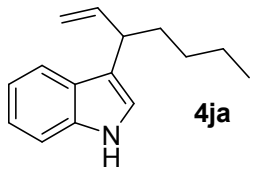

4ia
143.208
136.466
126.677
121.888
120.263
119.509
119.087
112.714
111.076
77.417
77.000
76.579
34.796
20.157
150
100
50
PPM



PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	56.462	61858.539	5236570.000	50.0378
2	60.843	56814.387	5228649.500	49.9622
Total		118672.926	10465219.500	100.0000

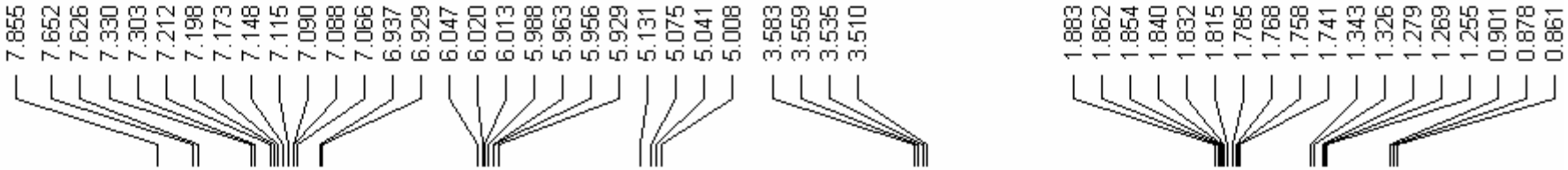


PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	58.683	6435.732	522853.344	5.5680
2	61.400	92115.250	8867509.000	94.4320
Total		98550.982	9390362.344	100.0000



4ja

The general procedure was followed with the methyl carbonate **2j** (67.2 mg, 0.39 mmol) derived from (E)-hept-2-en-1-ol, indole **3a** (95.0 mg, 0.80 mmol) and cesium carbonate (129.3 mg, 0.40 mmol) in 1,4-dioxane (2.0 mL). The reaction was conducted at reflux for 4 h. ^{1}H NMR analysis of the crude reaction mixture indicated that the ratio of regioisomers (b/l) was 87/13. The crude reaction mixture was purified by column chromatography (petroleum ether/ethyl acetate; 100/1) to give the product **4ja** (45.7 mg, 55%) as a colorless oil. HPLC analysis indicated that the enantiomeric excess of the product was 85 % [Diacel CHIRALCEL OD-H (0.46 cm x 25 cm); hexanes/2-propanol = 95/5; flow rate = 1.0 mL/min; detection wavelength = 230 nm; t_R = 10.74 (minor), 11.63 (major) min]. $[\alpha]_D^{20}$ = -22.8 (c 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.85 (br s, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.21-7.07 (m, 2H), 6.93 (d, J = 2.1 Hz, 1H), 5.99 (ddd, J = 7.8, 9.9, 16.8 Hz, 1H), 5.10 (d, J = 16.8 Hz, 1H), 5.02 (d, J = 9.9 Hz, 1 H), 3.55 (q, J = 7.5 Hz, 1H), 1.88-1.74 (m, 2 H), 1.34-1.25 (m, 4H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 142.3, 136.4, 126.8, 121.8, 120.5, 119.5, 119.2, 119.0, 113.6, 111.1, 41.1, 34.4, 29.9, 22.7, 14.1. IR (liquid film): ν_{max} (cm^{-1}) = 3420, 3059, 2958, 2930, 2872, 2859, 1735, 1637, 1619, 1457, 1419, 1353, 1338, 1271, 1224, 1095, 1011, 994, 912, 765, 741. MS (EI, *m/*z, rel. intensity) 213 (M^+, 20.2), 156 (100); HRMS (EI) calcd for $C_{15}H_{19}N$ (M^+): 213.1517, Found: 213.1510.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7.212
7.198
7.173
7.148
7.115
7.090
7.088
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6.937
6.929
6.047
6.020
6.013
5.988
5.963
5.956
5.929
5.131
5.075
5.041
5.008
3.583
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1.862
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1.832
1.815
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1.741
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1.326
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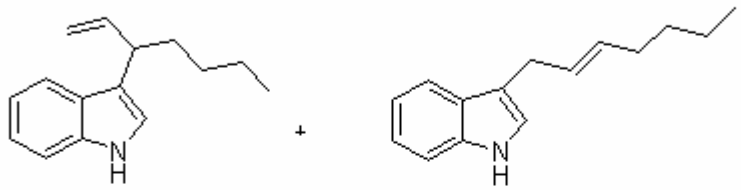
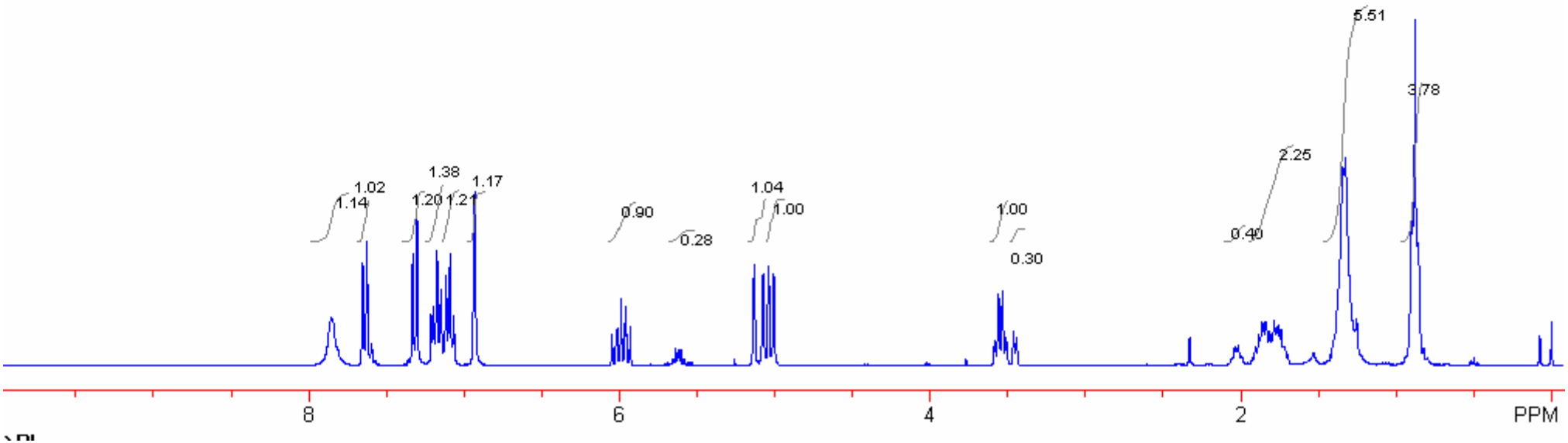
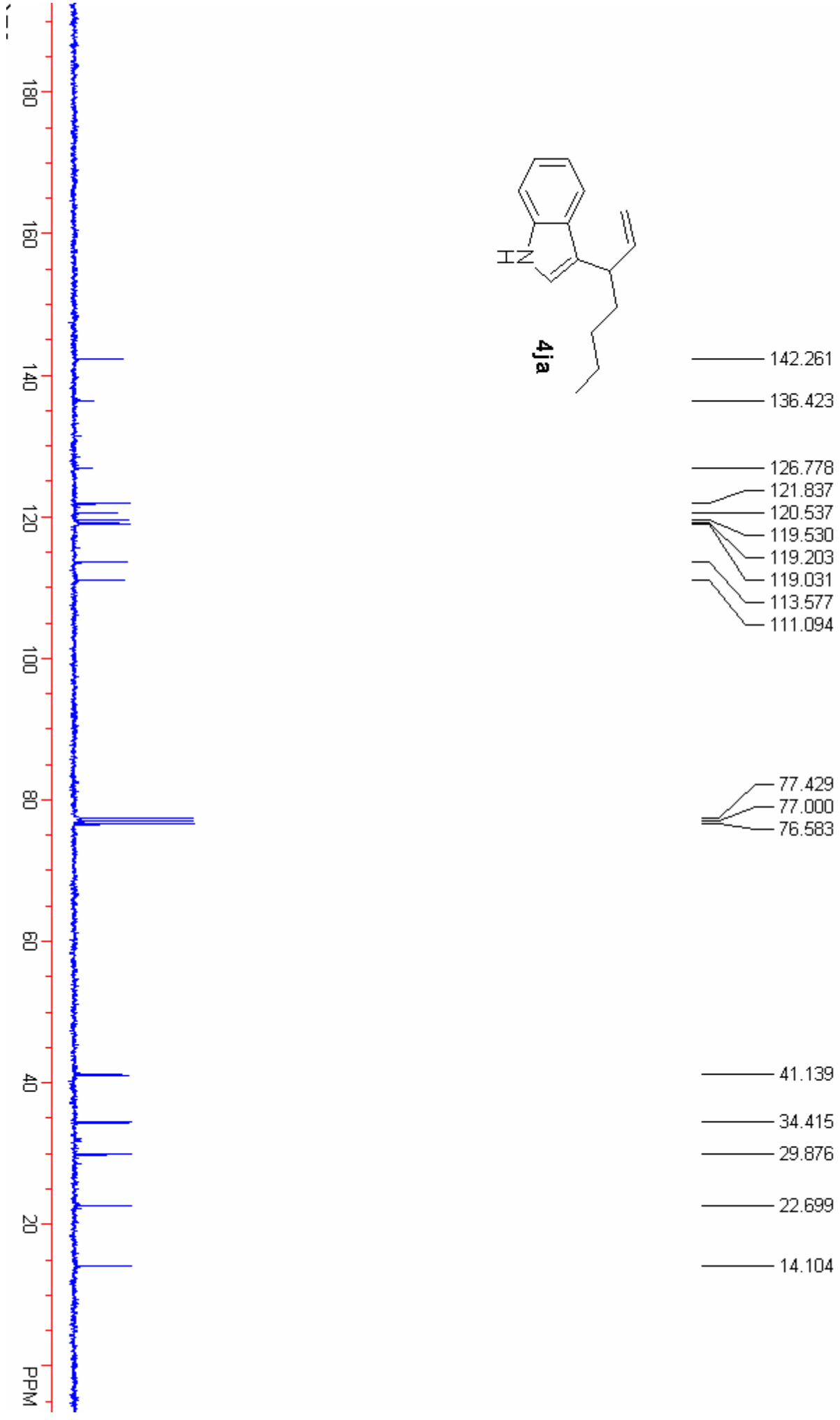
1.269
1.255
0.901
0.878
0.861

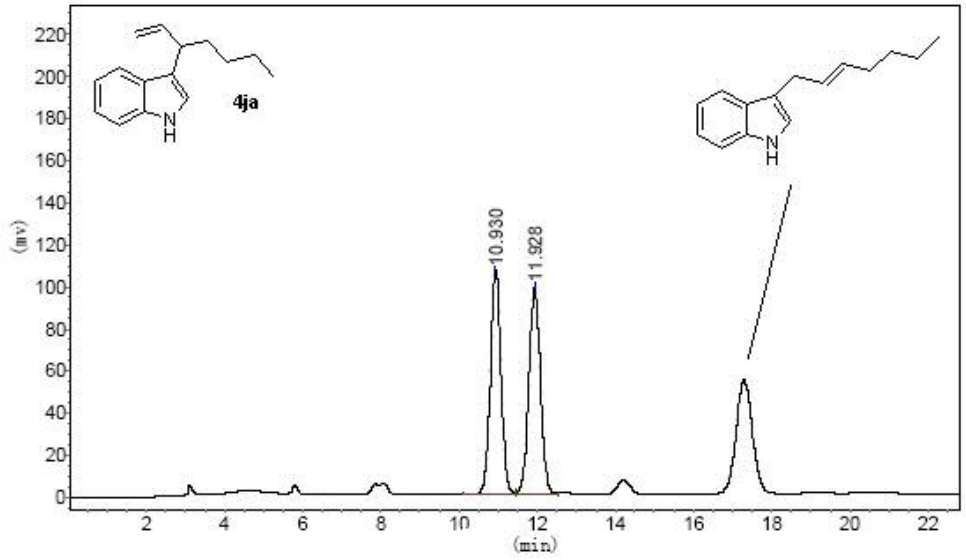


4ja 87%

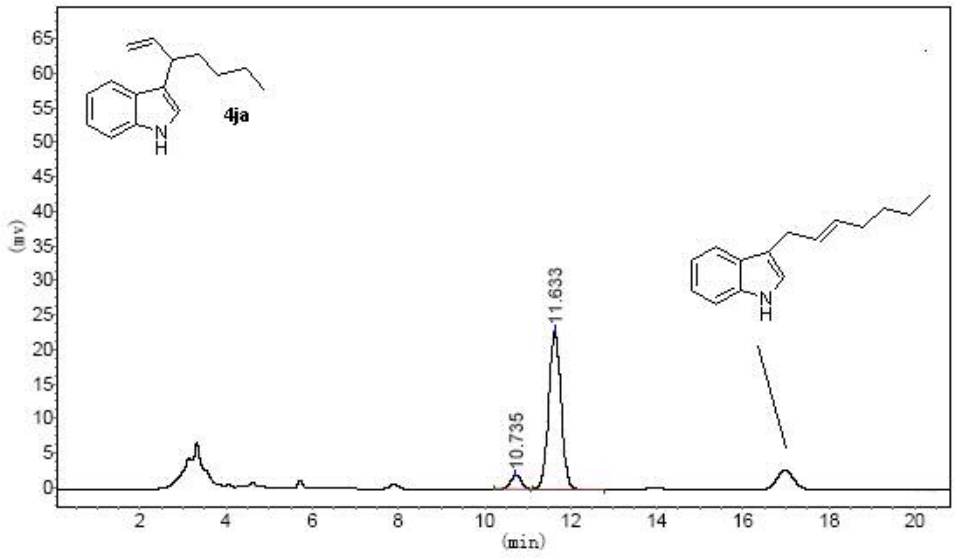
13%


1.02
1.14
1.38
1.20
1.21
1.17
0.90
0.28
1.04
1.00
1.00
0.30
0.40
2.25
5.51
3.78
8
6
4
2
PPM


180
160
140
120
100
80
60
40
20
PPM
4ja
142.261
136.423
126.778
121.837
120.537
119.530
119.203
119.031
113.577
111.094
77.429
77.000
76.583
41.139
34.415
29.876
22.699
14.104



PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	10.930	106413.313	2022493.000	49.7358
2	11.928	98220.836	2043978.375	50.2642
Total		204634.148	4066471.375	100.0000



PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	10.735	2026.879	36035.637	7.3170
2	11.633	23043.195	456453.719	92.6830
Total		25070.074	492489.355	100.0000