Supporting Information

For

Olefin Isomerization/Asymmetric Pictet-Spengler Cascade *via* Sequential Catalysis of Ruthenium Alkylidene and Chiral Phosphoric Acid

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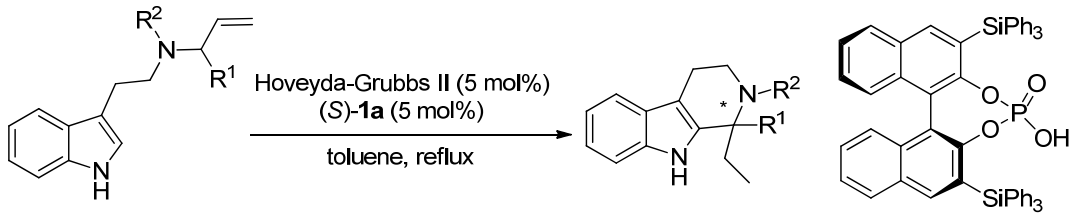
1. **General Methods**. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Varian instrument (300 MHz and 75 MHz) and internally referenced to tetramethylsilane signal or residual protio solvent signals. 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 protected *N*-allyltryptamines **2a**-**2n** were prepared according to the references.[1, 2]

2. Experimental Section.

2.1 The Screening of the Substituents on the Side Chain of Tryptamines.

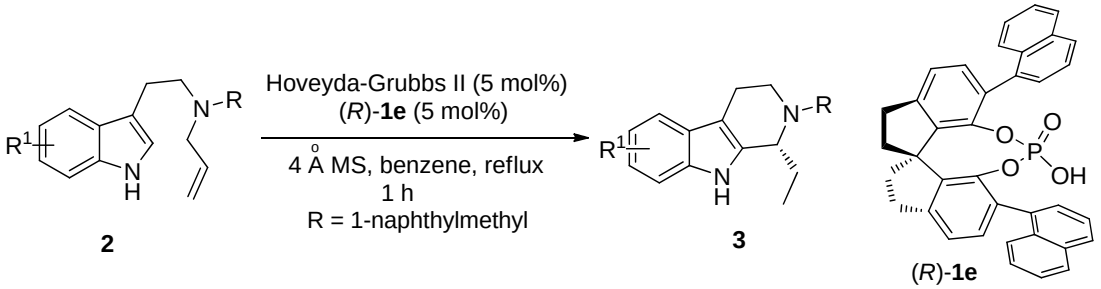


2 **3** (*S*)-**1a**

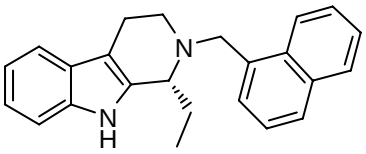
Entry[a]	R^1	R^2	time (h)	**3**, yield (%)[b]	ee (%)[c]
1	Ph	Ac	10	no product	n.d
2	Ph	Bn	5	no reaction	n.d.
3	H	Bn	0.5	70	58
4	H	Boc	6	44	36
5	H	Bz	8	42	7
6	H	Ts	3	73	6
7	H	1-naphthylmethyl	0.1	88	71
8	H	9-anthylmethyl	4	46	56

[a] Reaction conditions: 5 mol% (*S*)-**1a**, 5 mol% Hoveyda-Grubbs II, 0.1 mol/L of **2** in toluene, reflux. [b] Isolated yield of **3**. [c] Determined by HPLC analysis.

2.2 Olefin Isomerization/Asymmetric Pictet-Spengler Cascade Reaction of *N*-Allyltryptamines.

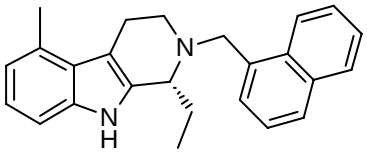


In a dry Schlenk tube, substrate **2** (0.2 mmol) and 4 Å molecular sieves (100 mg) were dissolved in benzene (2 mL) under argon. The solution was heated to reflux, and then the chiral phosphoric acid (*R*)-**1e** (5.7 mg, 0.01 mmol) and Hoveyda-Grubbs II (6.3 mg, 0.01 mmol) were added in one portion. After the reaction was complete (monitored by TLC), the solvent was removed and the residue was purified by flash chromatography to afford the product **3**.



(*R*)-1-ethyl-2-(naphthalen-1-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3a)

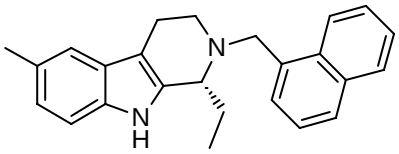
Viscous oil (95% yield, 90% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 30/1/1, v/v). Analytical data for **3a**: $[\alpha]_D^{20}$ = +62.1 (*c* = 1.04, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.82 (t, *J* = 7.5 Hz, 3H), 1.67-1.77 (m, 2H), 2.56 (dd, *J* = 4.2, 7.5 Hz, 1H), 2.94-3.05 (m, 2H), 3.17-3.26 (m, 1H), 3.58 (t, *J* = 6.9 Hz, 1H), 4.16 (s, 2H), 7.09-7.20 (m, 2H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.36-7.58 (m, 6H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.82-7.85 (m, 1H), 8.31 (d, *J* = 8.7 Hz, 1H); The enantiomeric excess was determined by Daicel Chiralcel OD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 9.69 min, t (minor) = 7.98 min.



(*R*)-1-ethyl-5-methyl-2-(naphthalen-1-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3b)

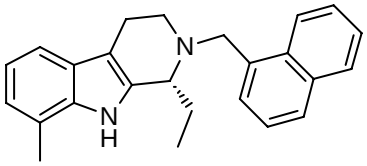
Viscous oil (92% yield, 85% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 30/1/1, v/v). Analytical data for **3b**: $[\alpha]_D^{20}$ = +60.2 (*c* = 0.5, acetone); ^1H NMR (300 MHz, $CDCl_3$) δ 0.79 (t, *J* = 7.5 Hz, 3H), 1.65-1.71 (m, 2H), 2.66 (s, 3H), 2.80-2.95 (m, 2H), 3.18-3.20 (m, 2H), 3.48 (t, *J* = 6.3 Hz, 1H), 4.13 (s, 2H), 6.82 (d, *J* = 6.6 Hz, 1H), 6.97-7.07 (m, 2H), 7.37-7.47 (m, 5H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 8.31 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.0, 19.7, 20.3, 27.6, 44.4, 55.5, 58.2, 108.0,

108.4, 120.4, 121.2, 125.0, 125.1, 125.5, 125.5, 126.2, 127.1, 127.7, 128.3, 130.3, 132.6, 133.8, 134.9, 135.3, 135.6; IR (film) 3409, 3046, 2922, 1508, 1332, 1310, 1193, 1077, 1001, 827, 790, 772, 734, 647 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{25}H_{26}N_2$ requires *m/z* 354.2096, found *m/z* 354.2090. The enantiomeric excess was determined by Daicel Chiralcel OD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 9.35 min, t (minor) = 7.67 min.



(*R*)-1-ethyl-6-methyl-2-(naphthalen-1-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3c)

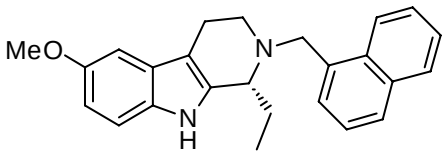
Viscous oil (84% yield, 85% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 30/1/1, v/v). Analytical data for **3c**: $[\alpha]_D^{20}$ = +53.9 (*c* = 0.5, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.80 (t, *J* = 7.5 Hz, 3H), 1.63-1.71 (m, 2H), 2.45 (s, 3H), 2.48-2.54 (m, 1H), 2.92-3.00 (m, 2H), 3.14-3.21 (m, 1H), 3.53 (t, *J* = 6.6 Hz, 1H), 4.14 (s, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 7.31 (s, 1H), 7.35-7.48 (m, 5H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.81-7.84 (m, 1H), 8.30-8.33 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.1, 17.6, 21.5, 27.7, 44.2, 55.6, 58.2, 107.2, 110.3, 117.8, 122.7, 125.0, 125.1, 125.5, 125.5, 127.2, 127.6, 127.8, 128.3, 128.4, 132.6, 133.8, 134.0, 135.3, 135.7; IR (film) 3407, 3042, 2929, 1946, 1715, 1594, 1509, 1461, 1360, 1300, 1188, 1128, 791, 776 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{25}H_{26}N_2$ requires *m/z* 354.2096, found *m/z* 354.2091. The enantiomeric excess was determined by Daicel Chiralcel OD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 9.42 min, t (minor) = 7.30 min.



(*R*)-1-ethyl-8-methyl-2-(naphthalen-1-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3d)

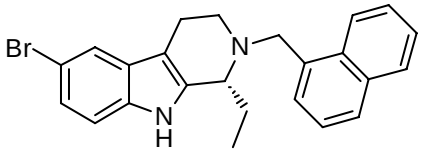
Viscous oil (94% yield, 87% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 30/1/1, v/v). Analytical data for **3d**: $[\alpha]_D^{20}$ = +34.0 (*c* = 0.5, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (t, *J* = 7.5 Hz, 3H), 1.68-1.75 (m, 2H), 2.44 (s, 3H), 2.51-2.57 (m, 1H), 2.96-3.03 (m, 2H), 3.18-3.22 (m, 1H), 3.60 (t, *J* = 6.6 Hz, 1H), 4.15 (s, 2H), 6.96 (d, *J* = 6.6 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 7.34-7.50 (m, 5H), 7.58 (s, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 8.32 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.1, 16.7, 17.6, 27.8, 44.0, 55.5, 58.2, 108.2, 115.8, 119.4, 119.8, 122.0, 125.0, 125.1, 125.5, 126.9, 127.2, 127.8, 128.3, 132.6, 133.8, 135.2, 135.3; IR (film) 3422, 3315, 2926, 1509, 1461, 1338, 1297, 1163, 1123,

1081, 1058, 997, 947, 863, 792, 776, 744 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{25}H_{26}N_2$ requires *m/z* 354.2096, found *m/z* 354.2086. The enantiomeric excess was determined by Daicel Chiralcel OD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 7.59 min, t (minor) = 5.70 min.



(*R*)-1-ethyl-6-methoxy-2-(naphthalen-1-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3e)

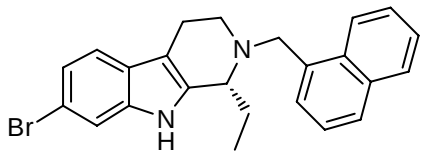
Viscous oil (84% yield, 85% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 30/1/1, v/v). Analytical data for **3e**: $[\alpha]_D^{20}$ = +68.5 (*c* = 0.5, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.80 (t, *J* = 5.7 Hz, 3H), 1.66-1.71 (m, 2H), 2.48-2.53 (m, 1H), 2.94-2.97 (m, 2H), 3.15-3.22 (m, 1H), 3.54 (t, *J* = 4.8 Hz, 1H), 3.85 (s, 3H), 4.14 (s, 2H), 6.80 (dd, *J* = 1.5, 6.9 Hz, 1H), 6.99 (s, 1H), 7.14 (d, *J* = 6.6 Hz, 1H), 7.37-7.47 (m, 4H), 7.57 (s, 1H), 7.75 (d, *J* = 6.0 Hz, 1H), 7.83 (d, *J* = 5.1 Hz, 1H), 8.31 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.0, 17.7, 27.6, 44.1, 55.6, 56.0, 58.3, 100.4, 107.5, 110.9, 111.3, 125.0, 125.1, 125.5, 125.5, 127.1, 127.7, 127.7, 128.3, 130.8, 132.6, 133.8, 135.3, 136.5, 153.9; IR (film) 3402, 2930, 1722, 1590, 1543, 1510, 1453, 1276, 1213, 1135, 1027, 791, 776 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{25}H_{26}N_2O$ requires *m/z* 370.2045, found *m/z* 370.2035. The enantiomeric excess was determined by Daicel Chiralcel OD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 19.63 min, t (minor) = 11.44 min.



(*R*)-6-bromo-1-ethyl-2-(naphthalen-1-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3f)

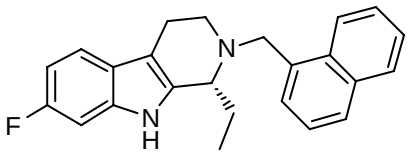
Viscous oil (63% yield, 85% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 30/1/1, v/v). Analytical data for **3f**: $[\alpha]_D^{20}$ = +46.2 (*c* = 0.5, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.80 (t, *J* = 7.2 Hz, 3H), 1.68-1.73 (m, 2H), 2.46-2.51 (m, 1H), 2.92-2.98 (m, 2H), 3.14-3.23 (m, 1H), 3.56 (t, *J* = 6.6 Hz, 1H), 4.13 (s, 2H), 7.13 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.38-7.49 (m, 4H), 7.64 (br, 2H), 7.76-7.86 (m, 2H), 8.29-8.32 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.1, 17.5, 27.6, 44.1, 55.6, 58.1, 107.6, 112.1, 112.5, 120.8, 124.0, 125.0, 125.1, 125.6, 127.2, 127.9, 128.4, 129.2, 132.6, 133.9, 134.4, 135.1, 137.0; IR (film) 3426, 2955, 2921, 2852, 1463, 1436, 1360, 1297, 1149, 1042, 986, 909, 861, 791, 778, 736 cm^{-1};

HRMS (ESI): Exact mass calcd for $C_{24}H_{23}N_2Br$ requires *m/z* 418.1045, found *m/z* 418.1036. The enantiomeric excess was determined by Daicel Chiralcel OD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 10.66 min, t (minor) = 8.20 min.



(*R*)-7-bromo-1-ethyl-2-(naphthalen-1-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3g)

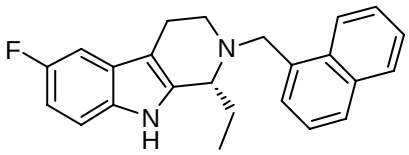
Viscous oil (71% yield, 83% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 30/1/1, v/v). Analytical data for **3g**: $[\alpha]_D^{20}$ = +57.8 (*c* = 0.5, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (t, *J* = 7.5 Hz, 3H), 1.66-1.74 (m, 2H), 2.50-2.56 (m, 1H), 2.96-3.02 (m, 2H), 3.15-3.22 (m, 1H), 3.57 (t, *J* = 6.6 Hz, 1H), 4.15 (s, 2H), 7.21 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.35-7.50 (m, 6H), 7.58 (s, 1H), 7.77-7.87 (m, 2H), 8.30-8.33 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.0, 17.5, 27.6, 44.0, 55.6, 58.1, 108.0, 113.6, 114.6, 119.2, 122.4, 125.0, 125.1, 125.6, 126.3, 127.2, 127.9, 128.4, 132.6, 133.8, 135.1, 136.2, 136.5; IR (film) 3426, 3042, 2924, 2838, 1611, 1461, 1435, 1359, 1292, 1151, 1134, 1121, 1063, 909, 799, 780, 734, 653 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{24}H_{23}N_2Br$ requires *m/z* 418.1045, found *m/z* 418.1038. The enantiomeric excess was determined by Daicel Chiralcel OJ-H (25 cm), Hexanes / IPA = 75 / 25, 0.4 mL/min, λ = 254 nm, t (major) = 30.18 min, t (minor) = 35.91 min.



(*R*)-1-ethyl-7-fluoro-2-(naphthalen-1-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3h)

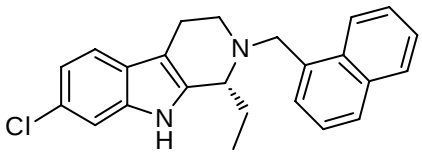
Viscous oil (71% yield, 87% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 30/1/1, v/v). Analytical data for **3h**: $[\alpha]_D^{20}$ = +44.3 (*c* = 0.5, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (t, *J* = 6.9 Hz, 3H), 1.68-1.70 (m, 2H), 2.46-2.50 (m, 1H), 2.89-2.98 (m, 2H), 3.14-3.19 (m, 1H), 3.55 (t, *J* = 6.0 Hz, 1H), 4.14 (s, 2H), 6.88 (t, *J* = 9.0 Hz, 1 H), 7.15 (d, *J* = 8.7 Hz, 2H), 7.36-7.57 (m, 5H), 7.75-7.85 (m, 2H), 8.31 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.1, 17.6, 27.6, 44.0, 55.6, 58.2, 103.2 (*J* = 23.5 Hz), 108.0 (*J* = 3.7 Hz), 109.2 (*J* = 26.2 Hz), 111.1 (*J* = 10.3 Hz), 125.0, 125.1, 125.6, 127.2, 127.8, 128.4, 132.4 (*J* = 28.1 Hz), 133.8, 135.1, 137.6, 157.8 (*J* = 233.2 Hz); IR (film) 3435, 2958, 2925, 2846, 1716, 1584, 1509, 1484, 1445, 1358, 1322, 1293, 1173, 1128, 999, 876, 802, 777, 621 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{24}H_{23}FN_2$ requires *m/z* 358.1845, found *m/z* 358.1838. The enantiomeric excess was

determined by Daicel Chiralcel OD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 9.29 min, t (minor) = 7.27 min.



(*R*)-1-ethyl-6-fluoro-2-(naphthalen-1-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3i)

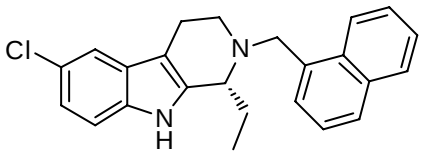
Viscous oil (85% yield, 87% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 30/1/1, v/v). Analytical data for **3i**: $[\alpha]_D^{20}$ = +44.4 (*c* = 0.5, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (t, *J* = 6.9 Hz, 3H), 1.65-1.73 (m, 2H), 2.49-2.55 (m, 1H), 2.92-3.01 (m, 2H), 3.15-3.21 (m, 1H), 3.56 (t, *J* = 6.0 Hz, 1H), 4.15 (s, 2H), 6.84-6.98 (m, 2H), 7.38-7.50 (m, 5H), 7.57 (s, 1H), 7.76-7.86 (m, 2H), 8.30-8.33 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.1, 17.6, 27.6, 44.1, 55.6, 58.2, 97.3 (*J* = 26.0 Hz), 107.6 (*J* = 20.6 Hz), 118.5 (*J* = 9.8 Hz), 123.9, 125.0, 125.1, 125.6, 127.2, 127.8, 128.3, 132.6, 133.8, 135.2, 135.5, 135.7, 135.8, 159.6 (*J* = 236.5 Hz); IR (film) 3444, 3043, 2967, 2839, 1621, 1571, 1493, 1464, 1335, 1226, 1192, 1129, 836, 792, 778, 739, 694, 658, 613 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{24}H_{23}FN_2$ requires *m/z* 358.1845, found *m/z* 358.1838. The enantiomeric excess was determined by Daicel Chiralcel OJ-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 32.27 min, t (minor) = 47.32 min.



(*R*)-7-chloro-1-ethyl-2-(naphthalen-1-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3j)

Viscous oil (64% yield, 87% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 30/1/1, v/v). Analytical data for **3j**: $[\alpha]_D^{20}$ = +55.7 (*c* = 0.5, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, *J* = 7.2 Hz, 3H), 1.71-1.75 (m, 2H), 2.52-2.56 (m, 1H), 2.97-3.01 (m, 2H), 3.20-3.21 (m, 1H), 3.60 (t, *J* = 6.4 Hz, 1H), 4.16 (s, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.28 (s, 1H), 7.38-7.49 (m, 5H), 7.62 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.84-7.86 (m, 1H), 8.31 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.0, 17.6, 27.6, 44.1, 55.6, 58.2, 108.0, 110.7, 118.8, 119.9, 125.0, 125.1, 125.6, 125.6, 126.0, 127.1, 127.2, 127.9, 128.4, 132.6, 133.8, 135.1, 136.1, 136.2; IR (film) 3435, 2962, 2924, 2855, 1614, 1463, 1359, 1331, 1293, 1150, 1120, 1062, 910, 809, 799, 780, 737, 657 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{24}H_{23}N_2Cl$ requires *m/z* 374.1550, found *m/z* 374.1540. The enantiomeric excess was determined by Daicel Chiralcel OJ-H (25 cm),

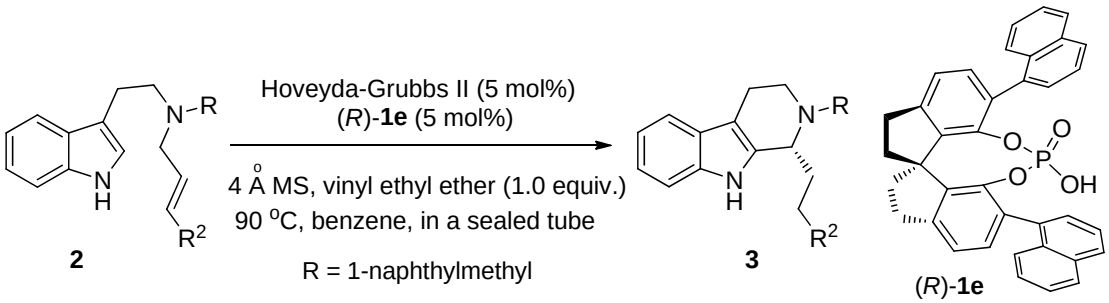
Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 33.46 min, t (minor) = 46.51 min.



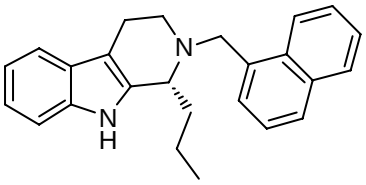
(*R*)-6-chloro-1-ethyl-2-(naphthalen-1-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3k)

Viscous oil (57% yield, 85% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 30/1/1, v/v). Analytical data for **3k**: $[\alpha]_D^{20}$ = +55.3 (*c* = 0.5, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, *J* = 7.6 Hz, 3H), 1.67-1.72 (m, 2H), 2.46-2.50 (m, 1H), 2.94-2.97 (m, 2H), 3.16-3.21 (m, 1H), 3.55 (t, *J* = 6.4 Hz, 1H), 4.13 (s, 2H), 7.07-7.16 (m, 2H), 7.38-7.47 (m, 5H), 7.60 (s 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.83-7.85 (m, 1H), 8.29-8.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.0, 17.5, 27.5, 44.0, 55.6, 58.1, 107.6, 111.5, 117.6, 121.4, 124.9, 124.9, 125.1, 125.6, 125.6, 127.2, 127.9, 128.3, 128.5, 132.5, 133.8, 134.1, 135.1, 137.1; IR (film) 3421, 3042, 2951, 2930, 2848, 1579, 1510, 1440, 1359, 1298, 1120, 1062, 988, 861, 791, 775, 644 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{24}H_{23}N_2Cl$ requires *m/z* 374.1550, found *m/z* 374.1545. The enantiomeric excess was determined by Daicel Chiralcel OD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 12.90 min, t (minor) = 9.76 min.

2.2 Olefin Isomerization/Asymmetric Pictet-Spengler Cascade Reaction of Internal Olefin Substrates.

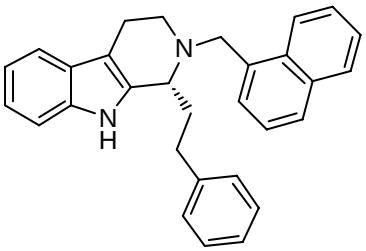


In a dry sealed tube, substrate **2** (0.2 mmol), vinyl ethyl ether (0.2 mmol), 4 Å molecular sieves (100 mg) were dissolved in benzene (2 mL) under argon. Then the chiral phosphoric acid (*R*)-**1e** (5.7 mg, 0.01 mmol) and Hoveyda-Grubbs II (6.3 mg, 0.01 mmol) were added in one portion. The reaction was sealed and heated at 90 °C. After the reaction was complete (monitored by TLC), the solvent was removed and the residue was purified by flash chromatography to afford the product **3**.



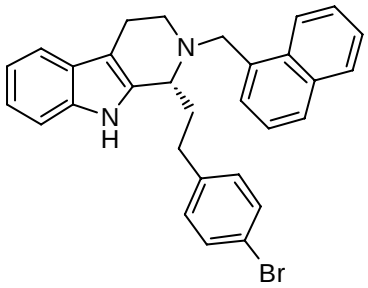
(*R*)-2-(naphthalen-1-ylmethyl)-1-propyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3l)

Viscous oil (72% yield, 85% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 30/1/1, v/v). Analytical data for **3l**: $[\alpha]_D^{20}$ = +65.6 (*c* = 0.5, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.68 (t, *J* = 7.5 Hz, 3H), 1.20-1.38 (m, 2H), 1.55-1.63 (m, 1H), 1.73-1.78 (m, 1H), 2.54-2.61 (m, 1H), 2.99-3.08 (m, 2H), 3.21-3.30 (m, 1H), 3.71 (dd, *J* = 4.8, 9.0 Hz, 1H), 4.18 (AB, J_{AB} = 13.2 Hz, J_{BA} = 13.2 Hz, 2H), 7.09-7.19 (m, 2H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.36-7.55 (m, 5H), 7.61 (s 1H), 7.76-7.79 (m, 1H), 7.83-7.86 (m, 1H), 8.30-8.33 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 17.5, 19.5, 37.2, 44.0, 55.5, 56.1, 107.6, 110.6, 118.1, 119.3, 121.3, 125.1, 125.5, 127.3, 127.4, 127.8, 128.3, 132.6, 133.8, 135.3, 135.7; IR (film) 3054, 2963, 2931, 2871, 2844, 1596, 1509, 1464, 1378, 1300, 1156, 949, 787, 774, 740 cm^{-1}; HRMS (MALDI/DHB): Exact mass calcd for $C_{25}H_{27}N_2^{+1}$ requires *m/z* 355.2169, found *m/z* 355.2160. The enantiomeric excess was determined by Daicel Chiralcel OD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 5.72 min, t (minor) = 7.59 min.



(*R*)-2-(naphthalen-1-ylmethyl)-1-phenethyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3m)

Viscous oil (75% yield, 85% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 30/1/1, v/v). Analytical data for **3m**: $[\alpha]_D^{20}$ = +17.4 (*c* = 0.5, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.81-1.90 (m, 1H), 1.98-2.09 (m, 1H), 2.30-2.40 (m, 1H), 2.54-2.67 (m, 2H), 2.97-3.14 (m, 2H), 3.26-3.36 (m, 1H), 3.66 (dd, *J* = 3.9, 9.3 Hz, 1H), 4.16 (AB, J_{AB} = 13.5 Hz, J_{BA} = 13.5 Hz, 2H), 6.76 (d, *J* = 6.3 Hz, 2H), 7.05-7.23 (m, 6H), 7.34-7.47 (m, 3H), 7.47-7.53 (m, 3H), 7.78-7.87 (m, 2H), 8.37 (d, *J* = 7.5 Hz, 1H),; ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.4, 32.3, 36.6, 44.3, 55.2, 55.6, 107.7, 110.7, 118.0, 119.3, 121.4, 125.1, 125.6, 125.7, 127.3, 127.5, 128.0, 128.2, 128.4, 132.7, 133.9, 135.1, 135.7, 142.4; IR (film) 3568, 3408, 3054, 2927, 2844, 1946, 1597, 1495, 1454, 1300, 1104, 1073, 1010, 946, 790, 777, 740, 699 cm^{-1}; HRMS (MALDI/DHB): Exact mass calcd for $C_{30}H_{29}N_2^{+1}$ requires *m/z* 417.2325, found *m/z* 417.2320. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (major) = 21.21 min, t (minor) = 24.94 min.



(*R*)-1-(4-bromophenethyl)-2-(naphthalen-1-ylmethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3n)

Viscous oil (74% yield, 87% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 30/1/1, v/v). Analytical data for **3m**: $[\alpha]_D^{20}$ = -3.2 (*c* = 0.5, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.71-1.82 (m, 1H), 1.96-2.05 (m, 1H), 2.20-2.30 (m, 1H), 2.45-2.63 (m, 2H), 2.99-3.20 (m, 2H), 3.28-3.38 (m, 1H), 3.61 (dd, *J* = 3.3, 9.6 Hz, 1H), 4.15 (AB, J_{AB} = 12.9 Hz, J_{BA} = 12.9 Hz, 2H), 6.48 (d, *J* = 8.4 Hz, 2H), 7.08-7.19 (m, 4H), 7.24-7.39 (m, 3H), 7.45-7.54 (m, 4H), 7.79-7.88 (m, 2H), 8.34 (d, *J* = 7.5 Hz, 1H),; ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.4, 31.4, 36.4, 44.6, 54.5, 55.6, 107.8, 110.7, 118.1, 119.1, 119.3, 121.5, 125.1, 125.7, 127.3, 127.7, 128.0, 128.4, 130.0, 131.1, 132.7, 133.9, 134.8, 135.0, 135.8, 141.2; IR (film) 3577, 3424, 3049, 2936, 1921, 1595, 1509, 1486, 1462, 1300, 1235, 1154, 1107, 1071, 1010, 945, 790, 738, 667 cm^{-1}; HRMS (MALDI/DHB): Exact mass calcd for $C_{30}H_{28}N_2Br^{+1}$ requires *m/z* 495.1430, found *m/z* 495.1431. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 10.81 min, t (minor) = 12.10 min.

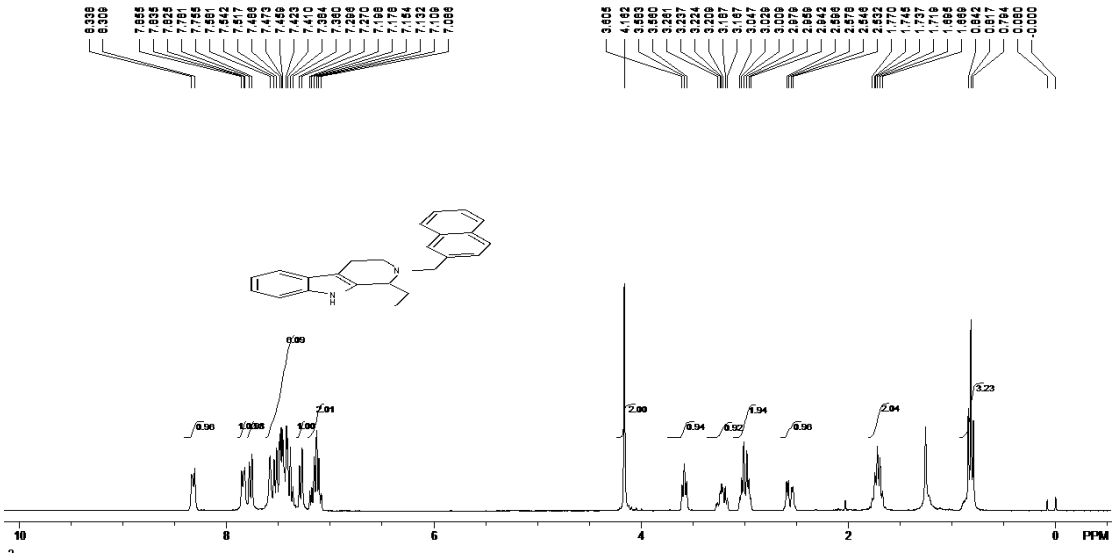
3. References

1. D. Huang, F. Xu, X. Lin, Y. Wang, *Chem. Eur. J.* **2012**, 18, 3148.

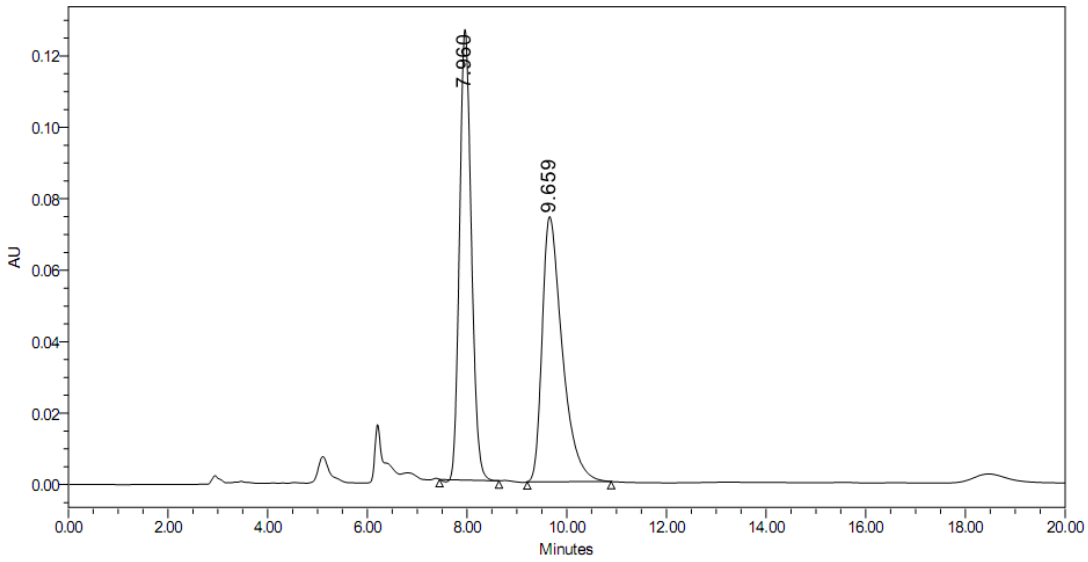
2. E. Ascic, C. L. Hansen, S. T. Le Quement, T. E. Nielsen, *Chem. Commun.* **2012**, *48*, 3345.

4. Copies of ^{1}H NMR, ^{13}C NMR Spectra and HPLC Analysis of the Compounds

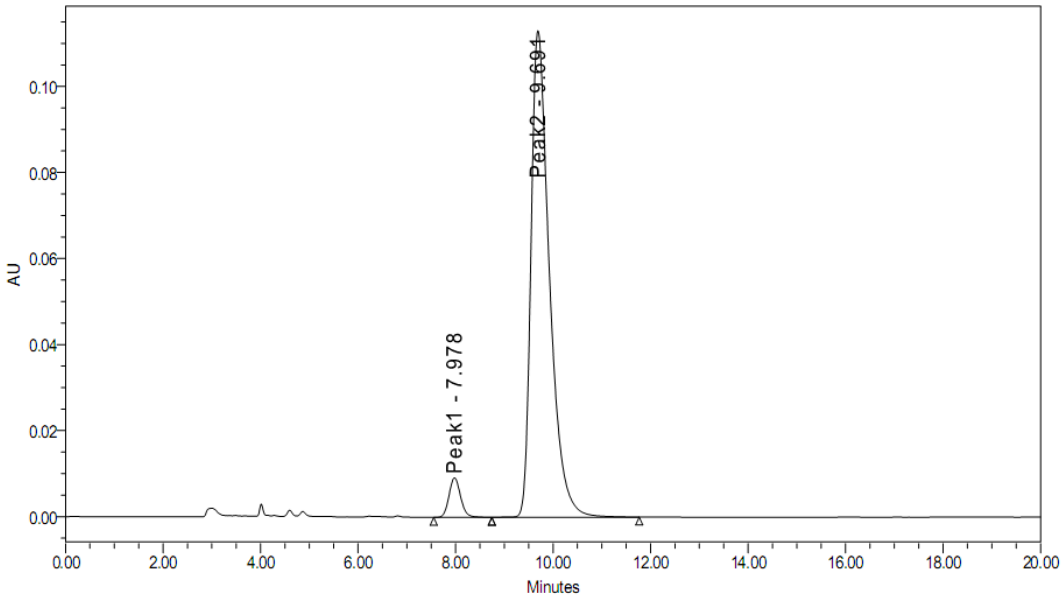
Compound **3a**'s ^{1}H NMR spectra



Compound **3a**'s HPLC spectra

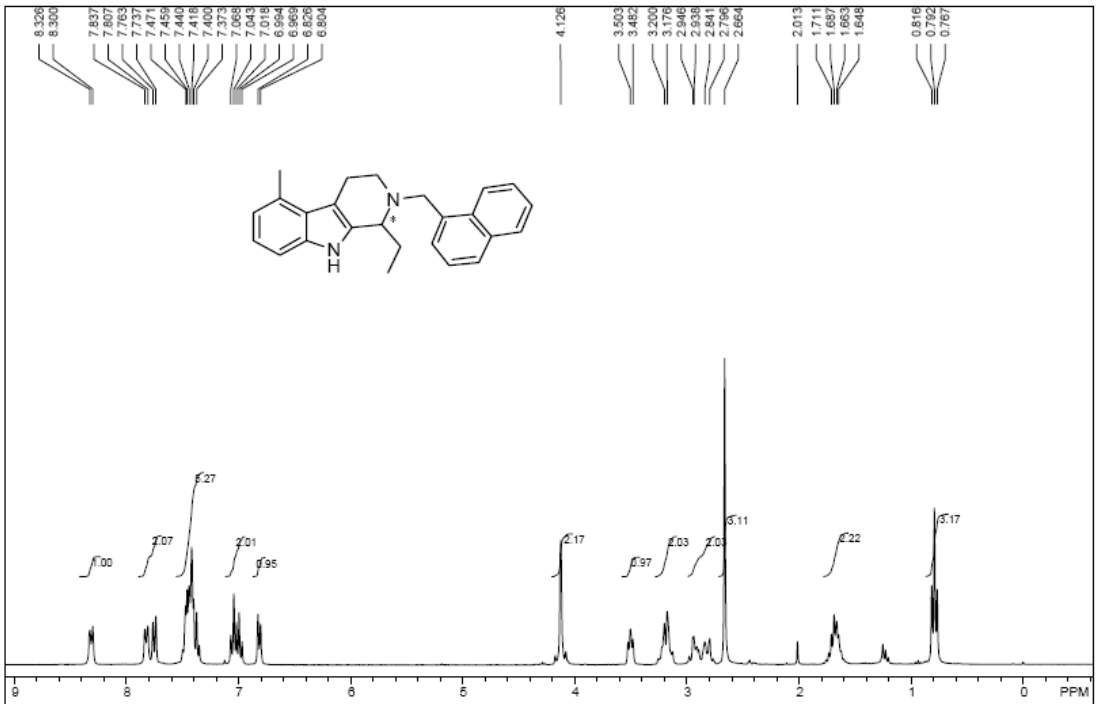


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	7.960	2078626	49.99	126115	62.96
2	9.659	2079834	50.01	74210	37.04

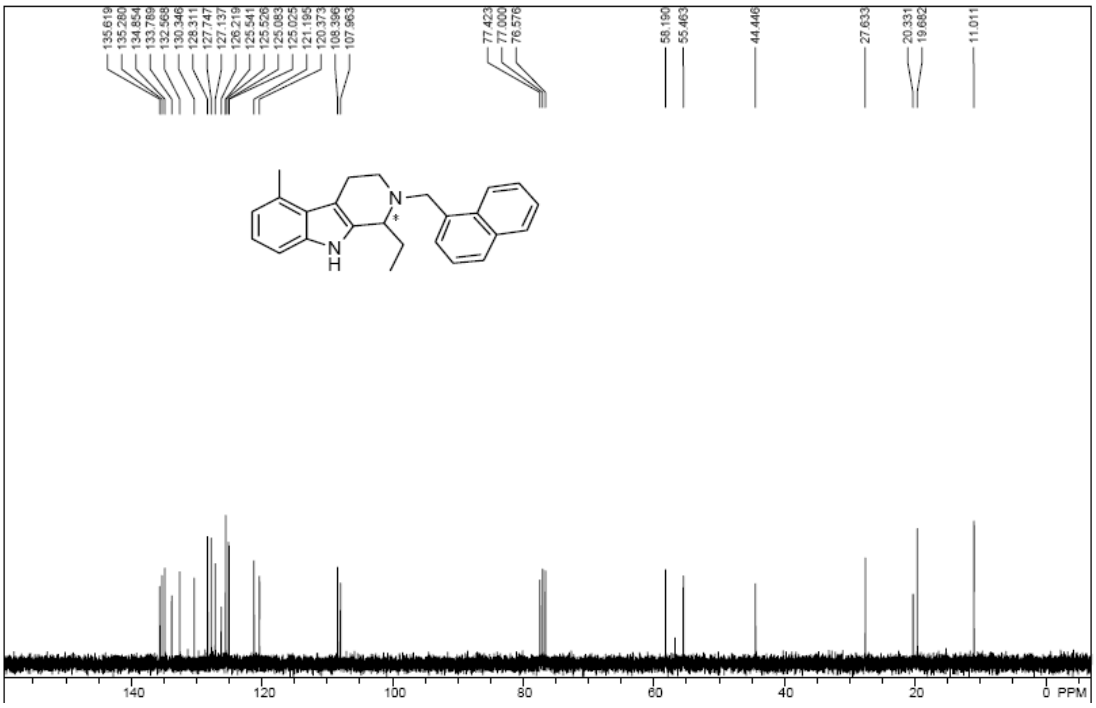


	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	7.978	152859	4.90	9205	7.53
2	Peak2	9.691	2964859	95.10	113097	92.47

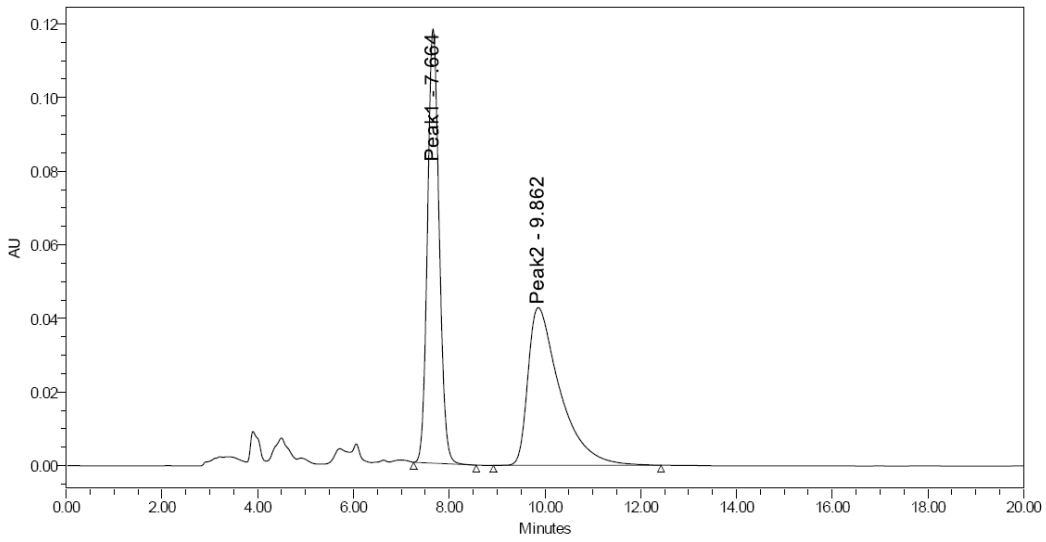
Compound **3b**'s ^{1}H NMR spectra



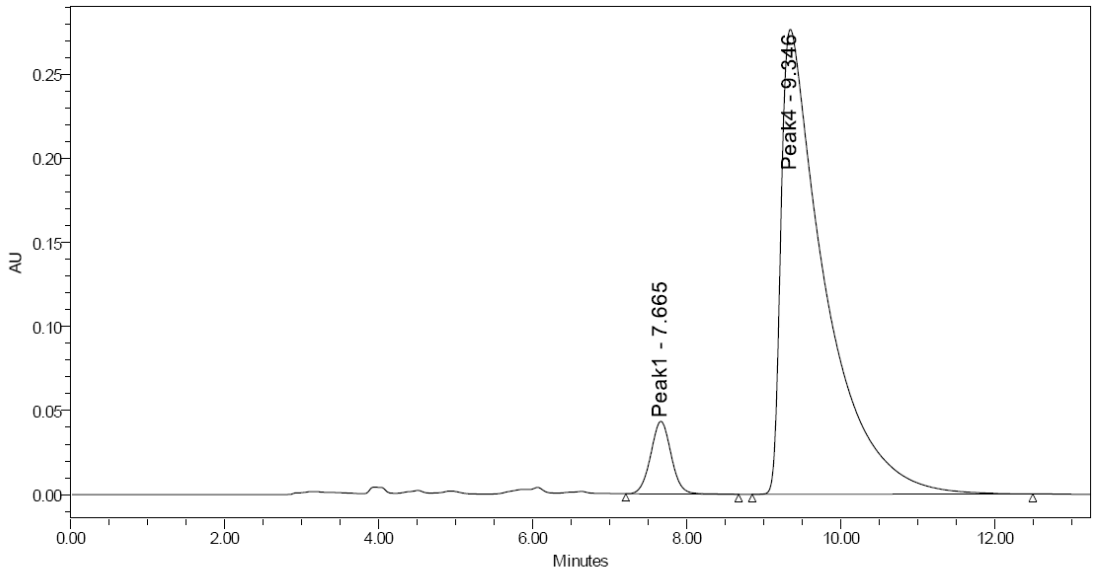
Compound **3b**'s ^{13}C NMR spectra



Compound **3b**'s HPLC spectra

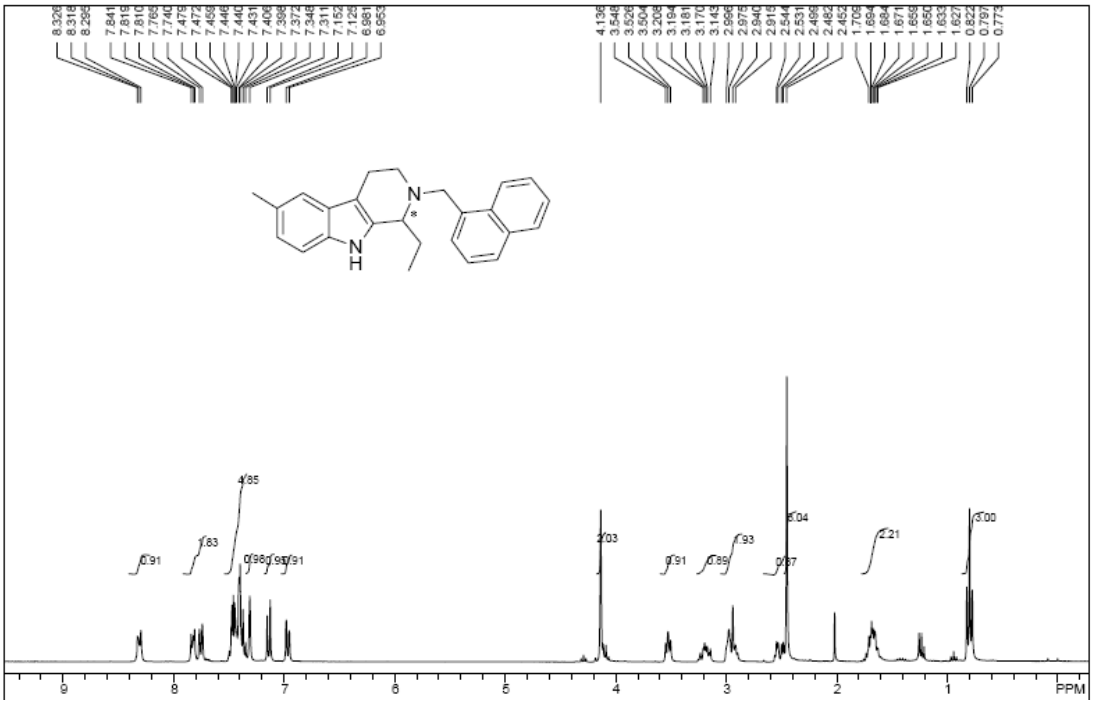


	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak3	7.267				
2	Peak1	7.664	1990774	50.11	118010	73.36
3	Peak4	9.336				
4	Peak2	9.862	1981875	49.89	42846	26.64

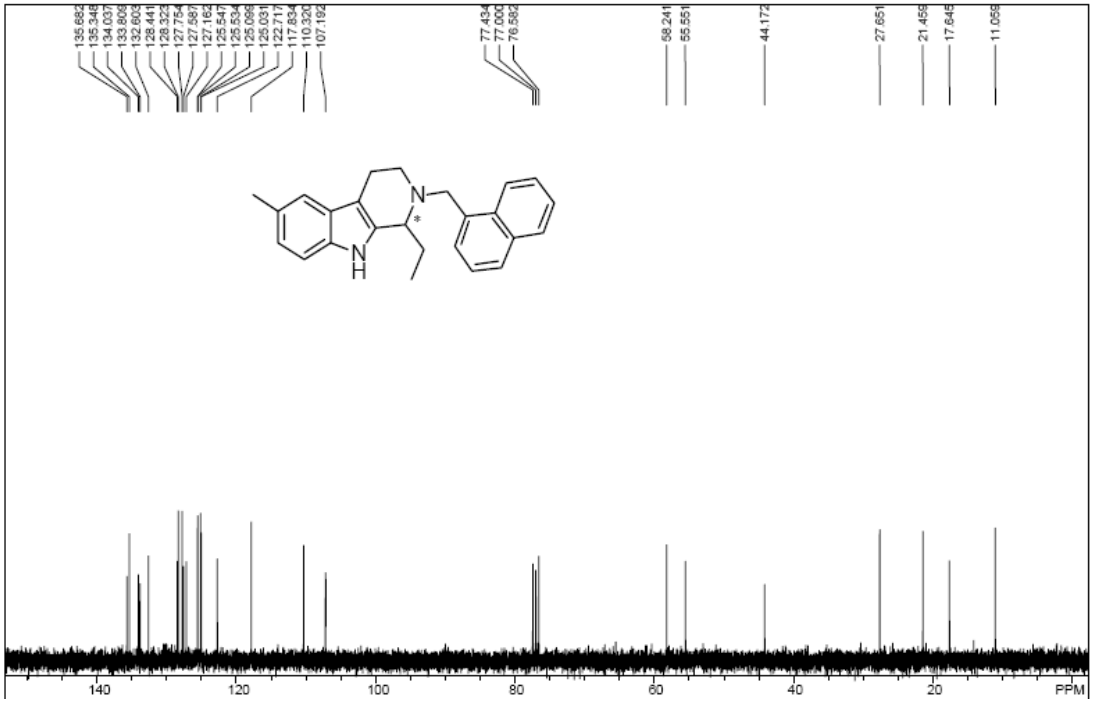


	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak3	7.267				
2	Peak1	7.665	795413	6.82	43148	13.50
3	Peak4	9.346	10869666	93.18	276517	86.50
4	Peak2	9.743				

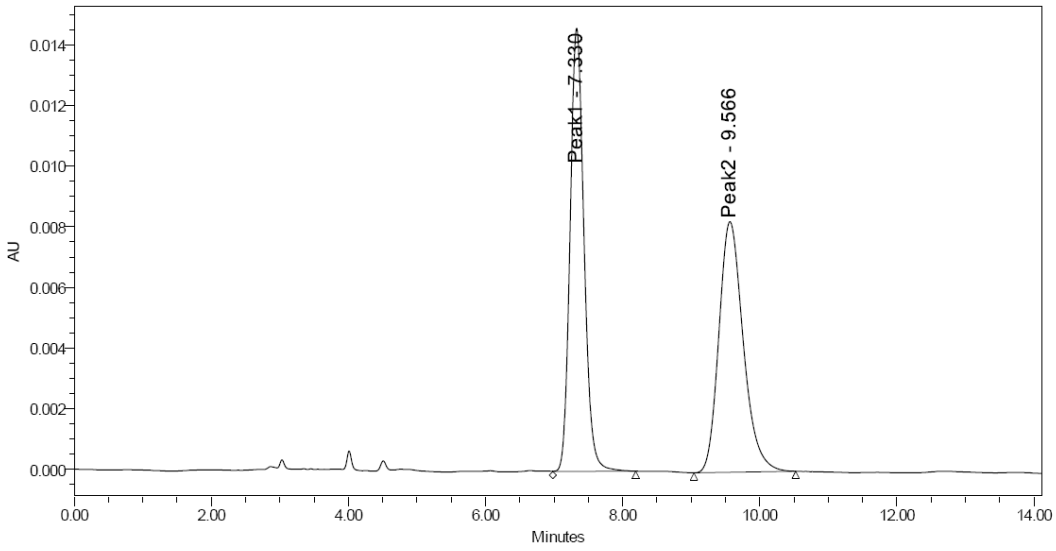
Compound **3c**'s ^{1}H NMR spectra



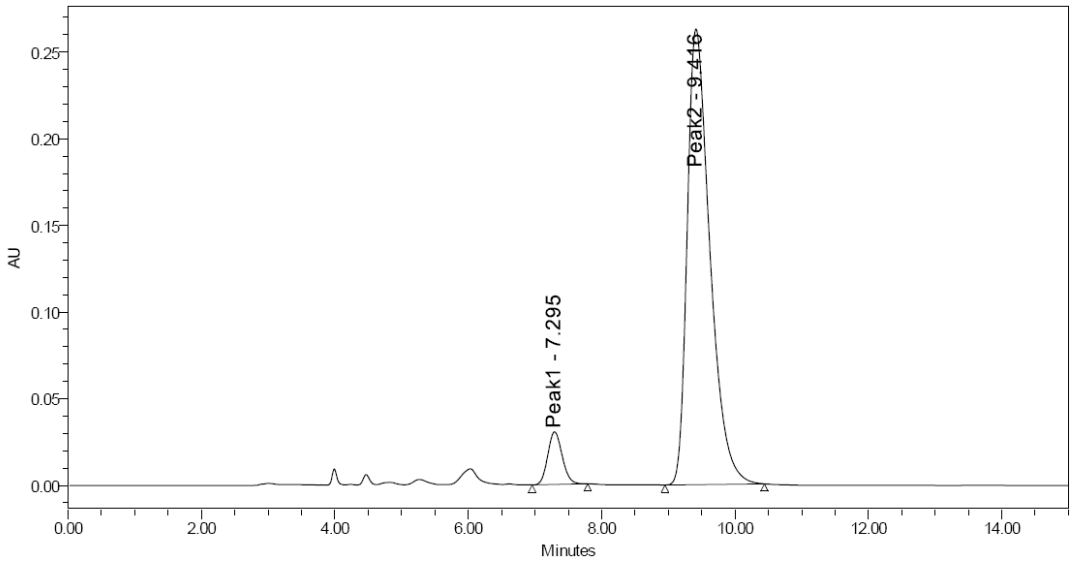
Compound **3c**'s ^{13}C NMR spectra



Compound **3c**'s HPLC spectra

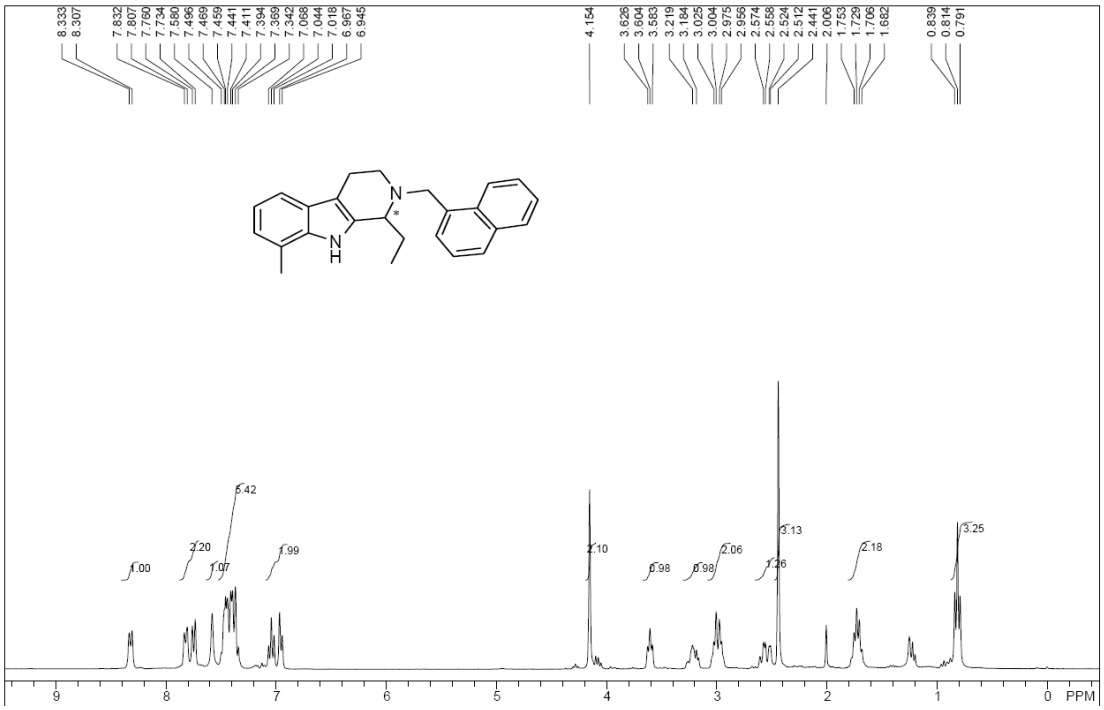


	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	7.330	205782	50.20	14619	63.88
2	Peak2	9.566	204125	49.80	8266	36.12

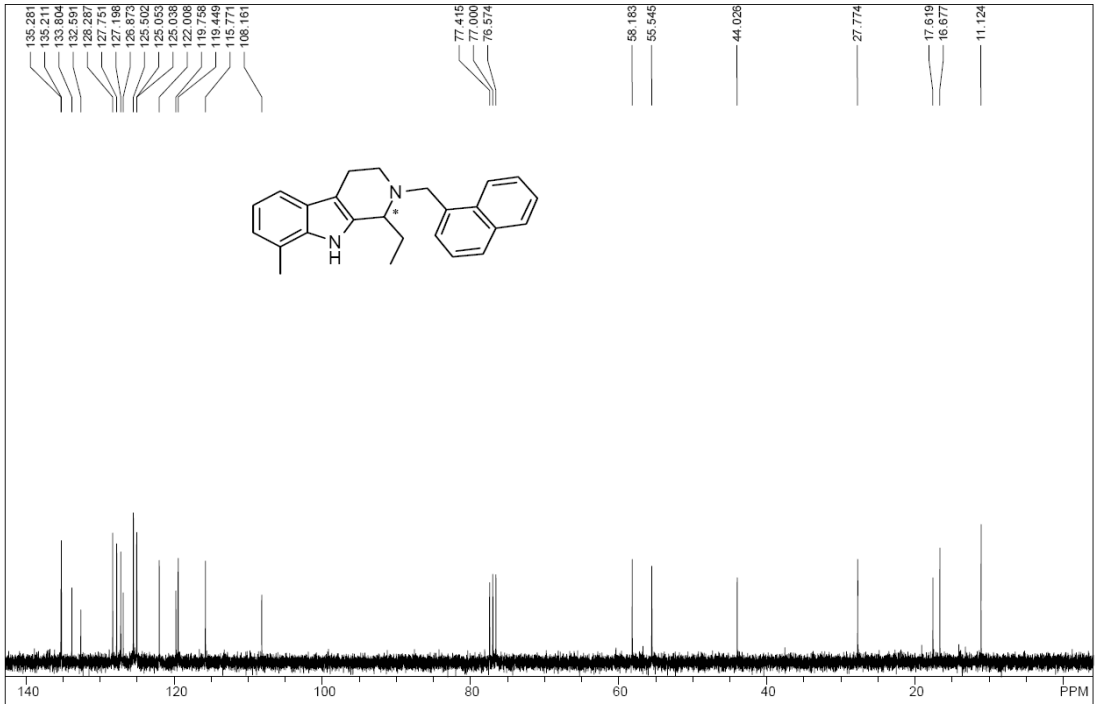


	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	7.295	456758	6.85	30372	10.35
2	Peak2	9.416	6209474	93.15	262953	89.65

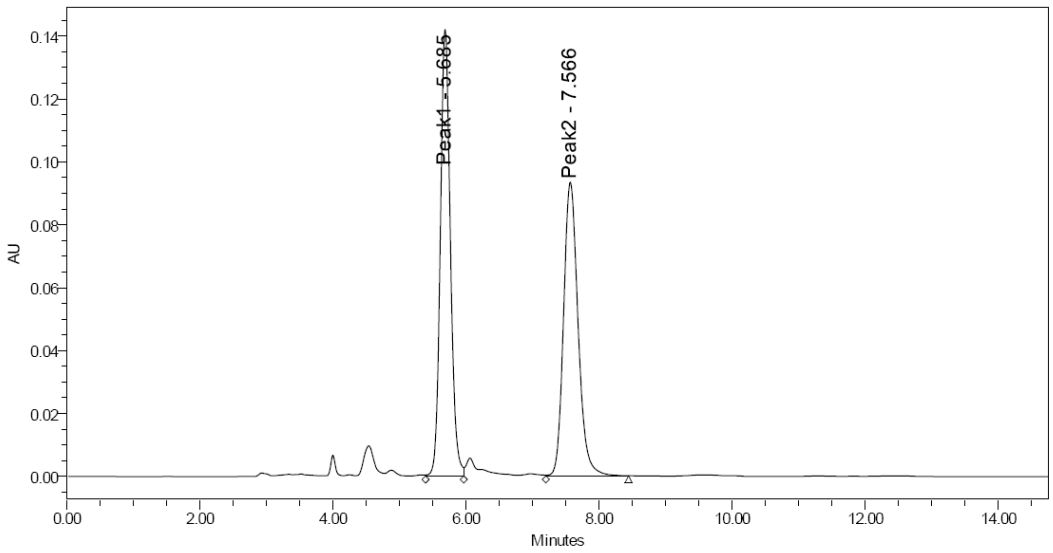
Compound **3d**'s ^{1}H NMR spectra



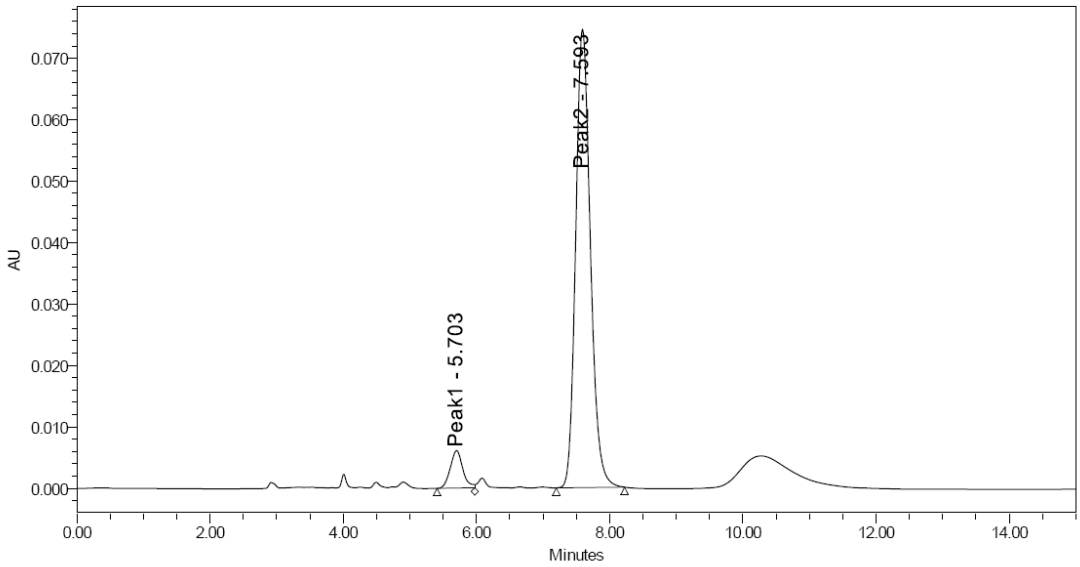
Compound **3d**'s ^{13}C NMR spectra



Compound **3d**'s HPLC spectra

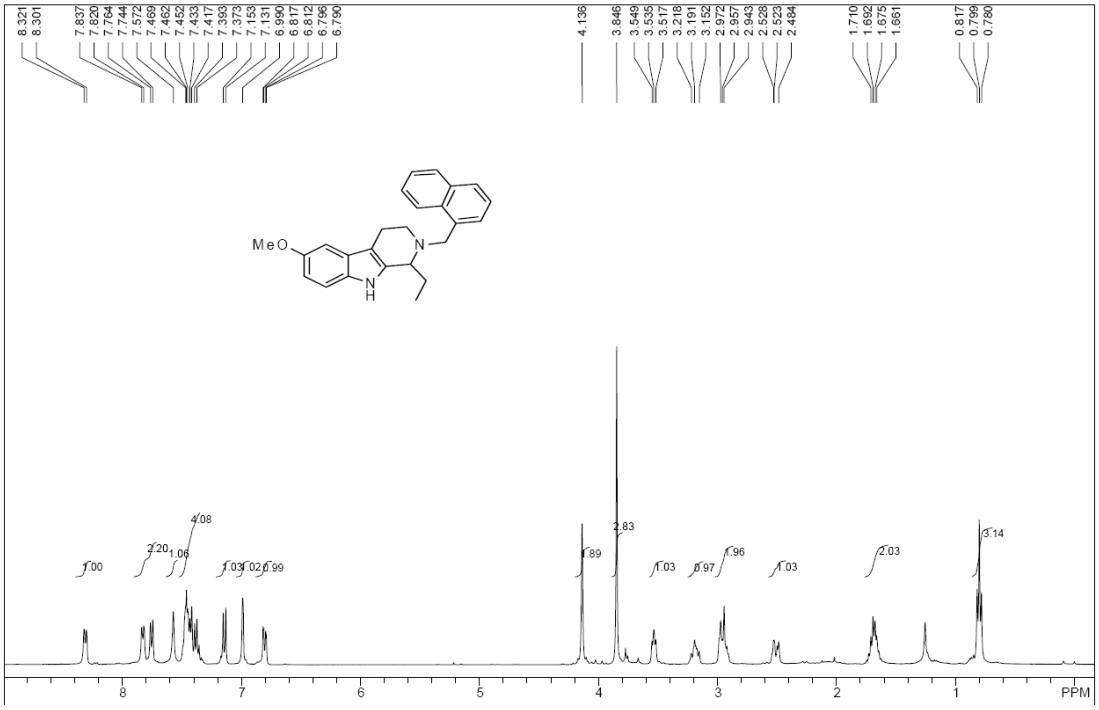


	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	5.685	1483724	51.26	141937	60.33
2	Peak2	7.566	1410652	48.74	93318	39.67

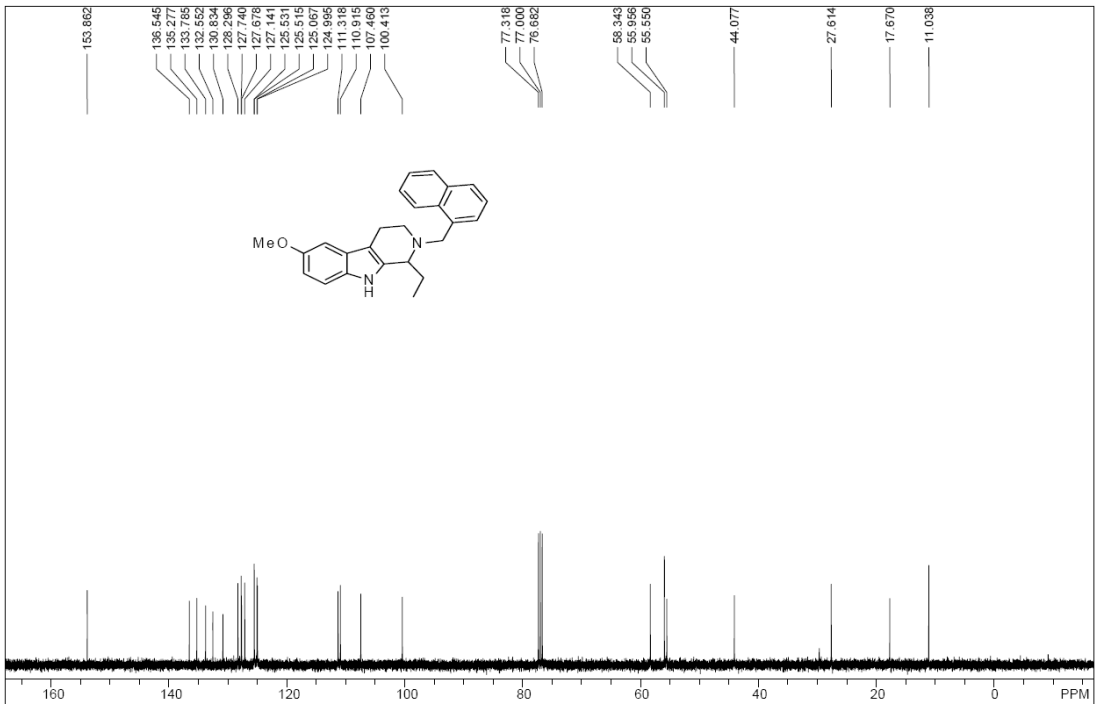


	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	5.703	79611	6.51	6099	7.55
2	Peak2	7.593	1143442	93.49	74638	92.45

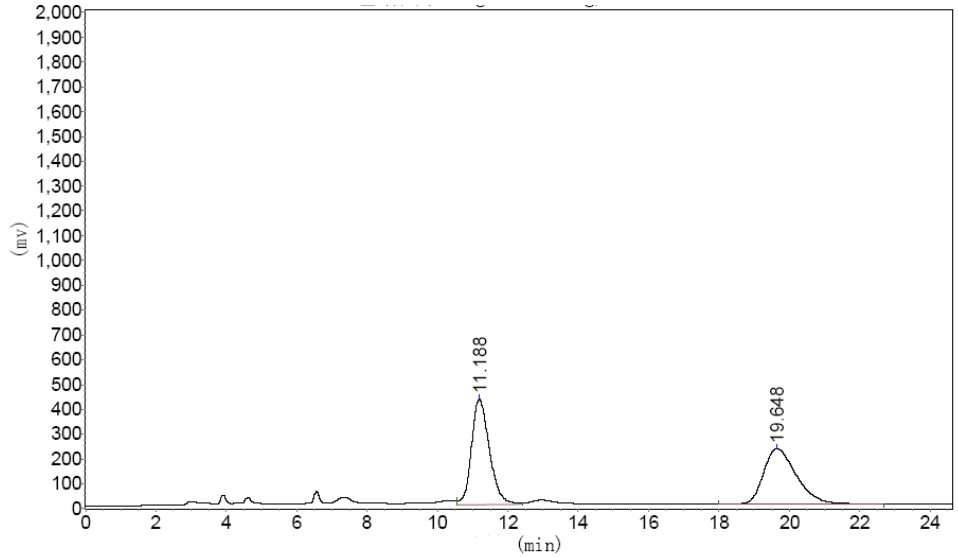
Compound **3e**'s ^{1}H NMR spectra



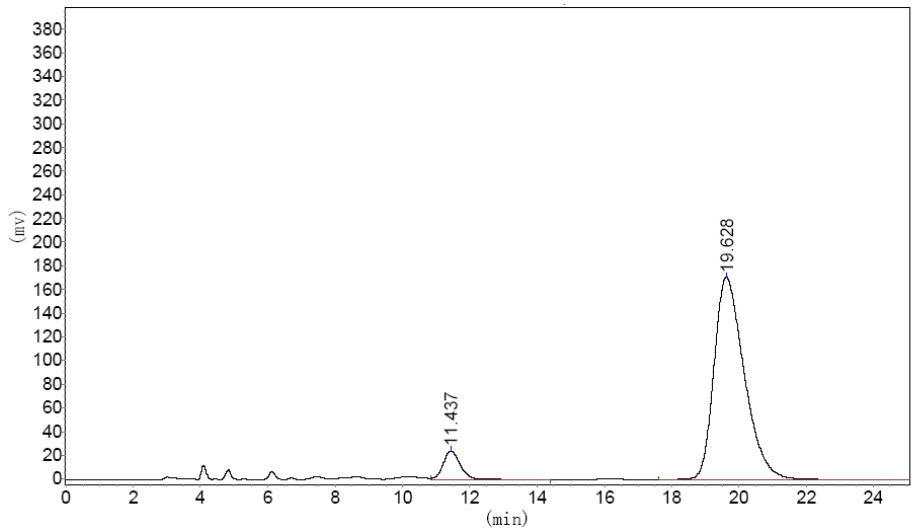
Compound **3e**'s ^{13}C NMR spectra



Compound **3e**'s HPLC spectra

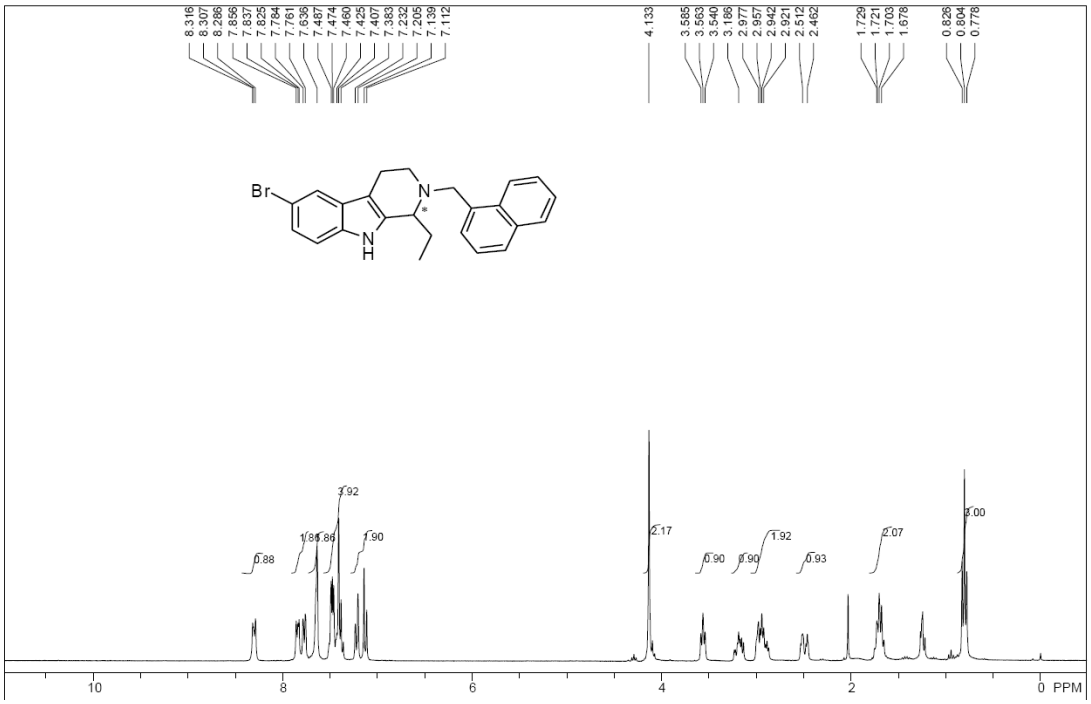


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11.188	425064.531	15057853.000	51.4184
2	19.648	222503.859	14227109.000	48.5816
Total		647568.391	29284962.000	100.0000

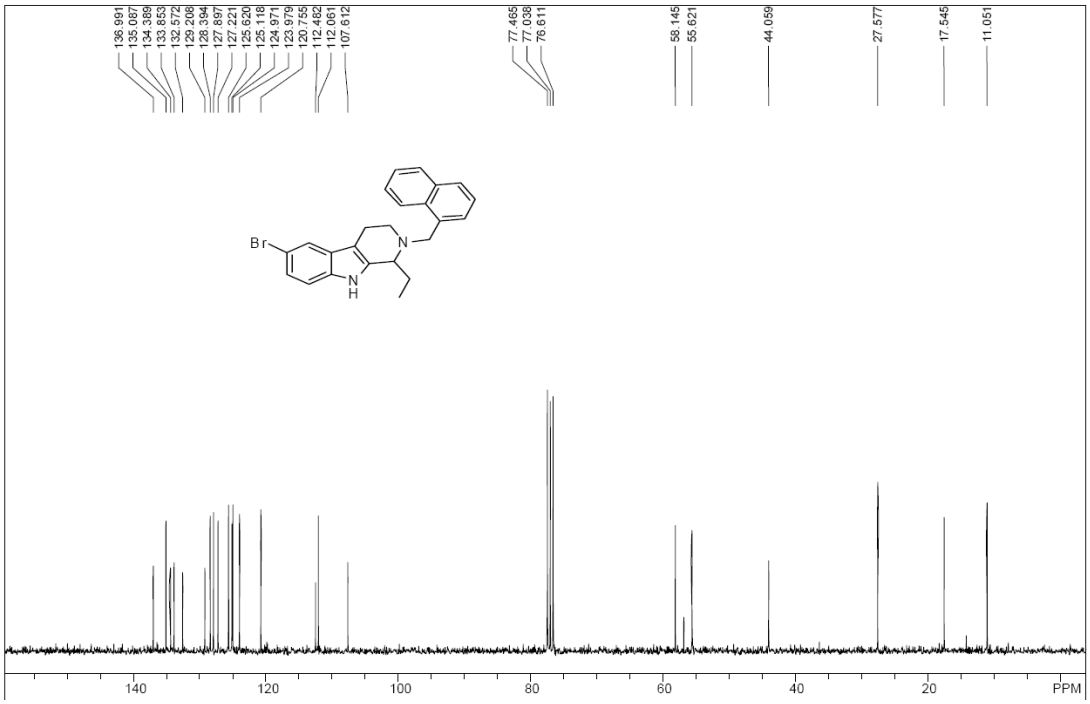


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11.437	23993.258	852782.625	7.3612
2	19.628	170887.453	10732071.000	92.6388
Total		194880.711	11584853.625	100.0000

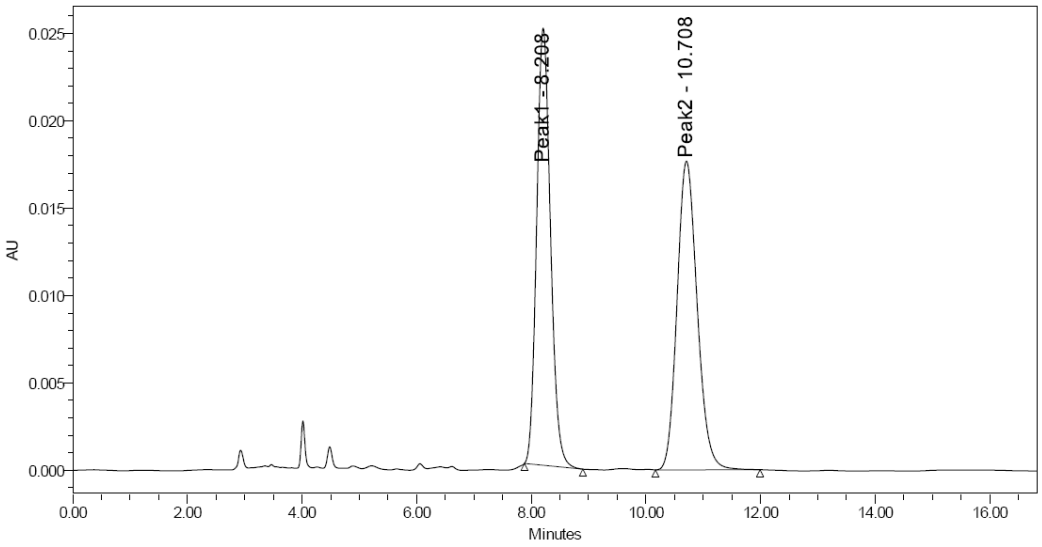
Compound **3f**'s ^{1}H NMR spectra



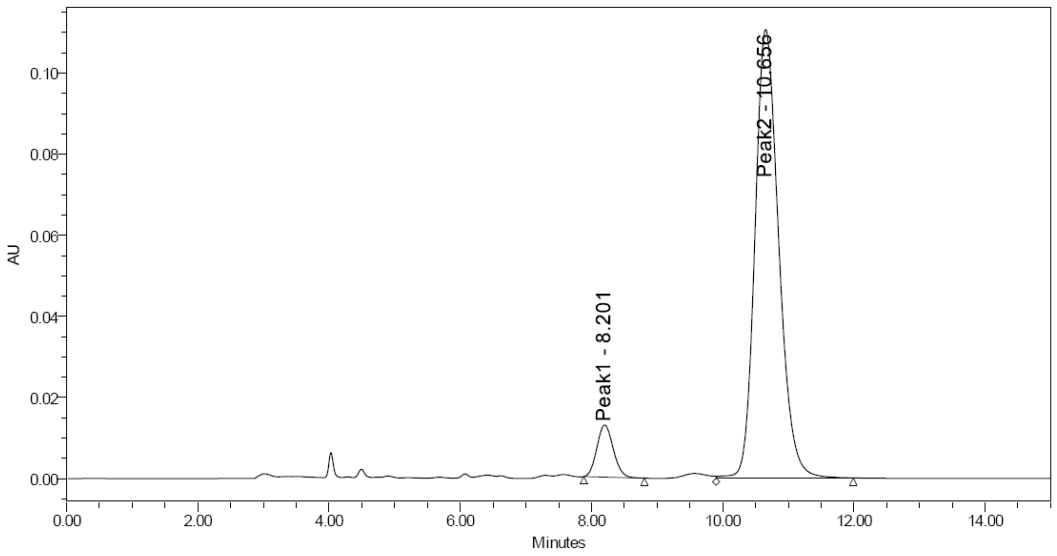
Compound **3f**'s ^{13}C NMR spectra



Compound **3f**'s HPLC spectra

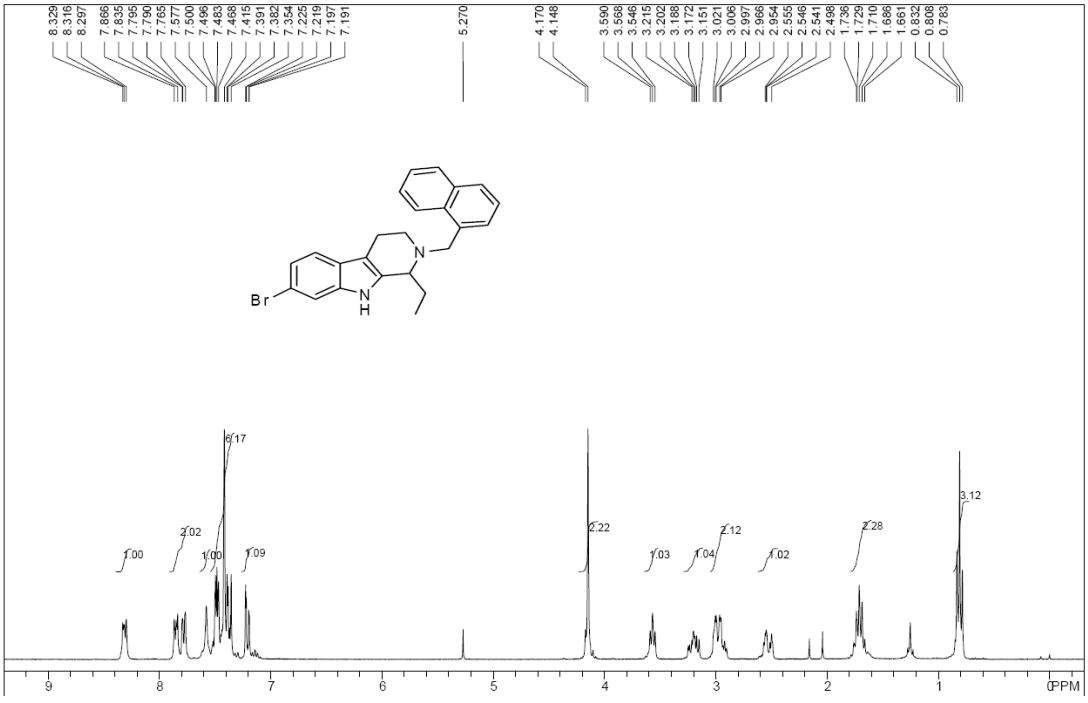


	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	8.208	419215	49.34	25013	58.61
2	Peak2	10.708	430356	50.66	17664	41.39

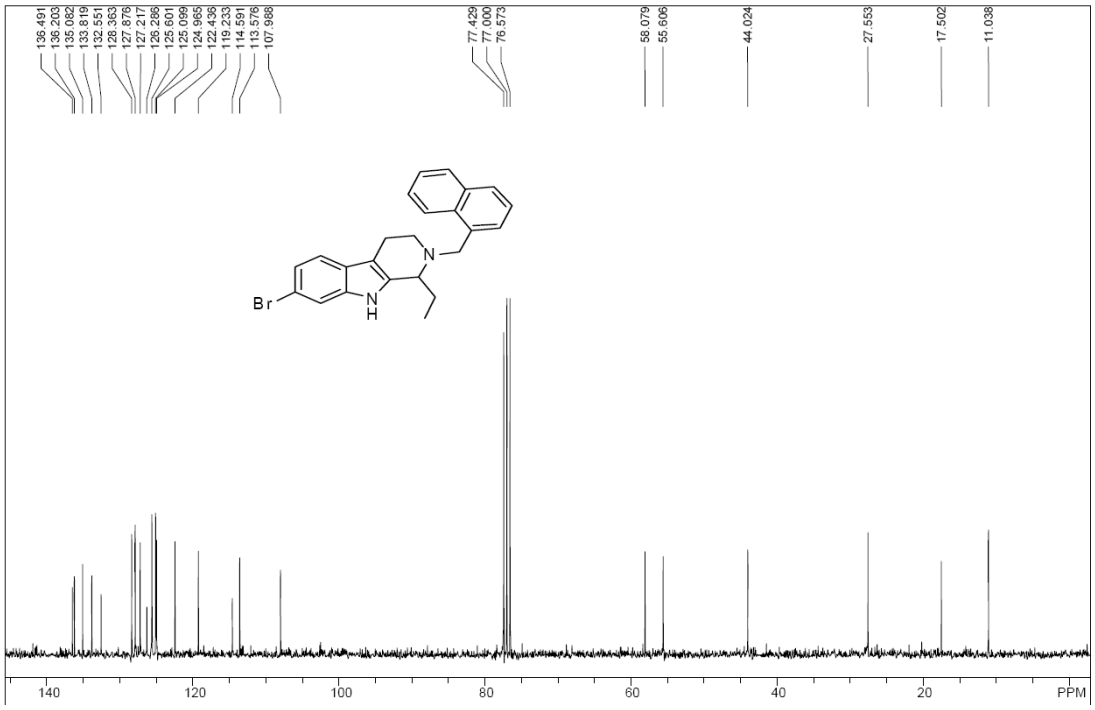


	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	8.201	223489	7.45	12849	10.40
2	Peak2	10.656	2777833	92.55	110641	89.60

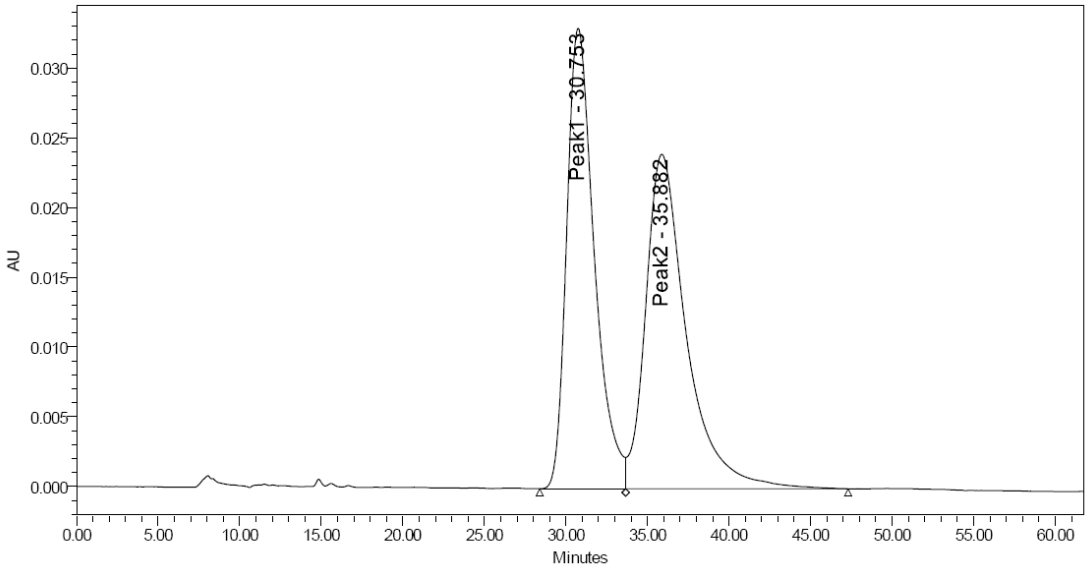
Compound **3g**'s ^{1}H NMR spectra



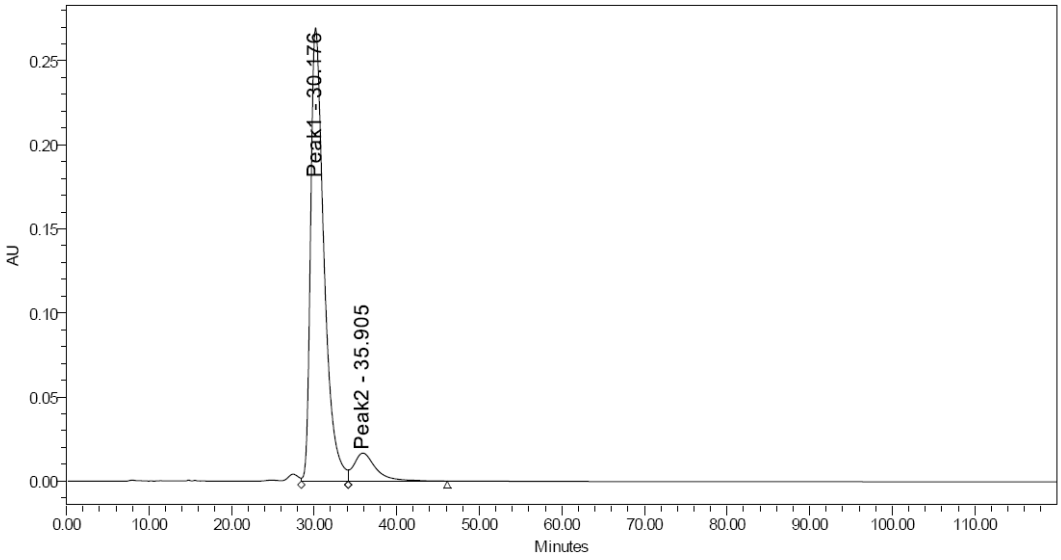
Compound **3g**'s ^{13}C NMR spectra



Compound **5f**'s HPLC spectra

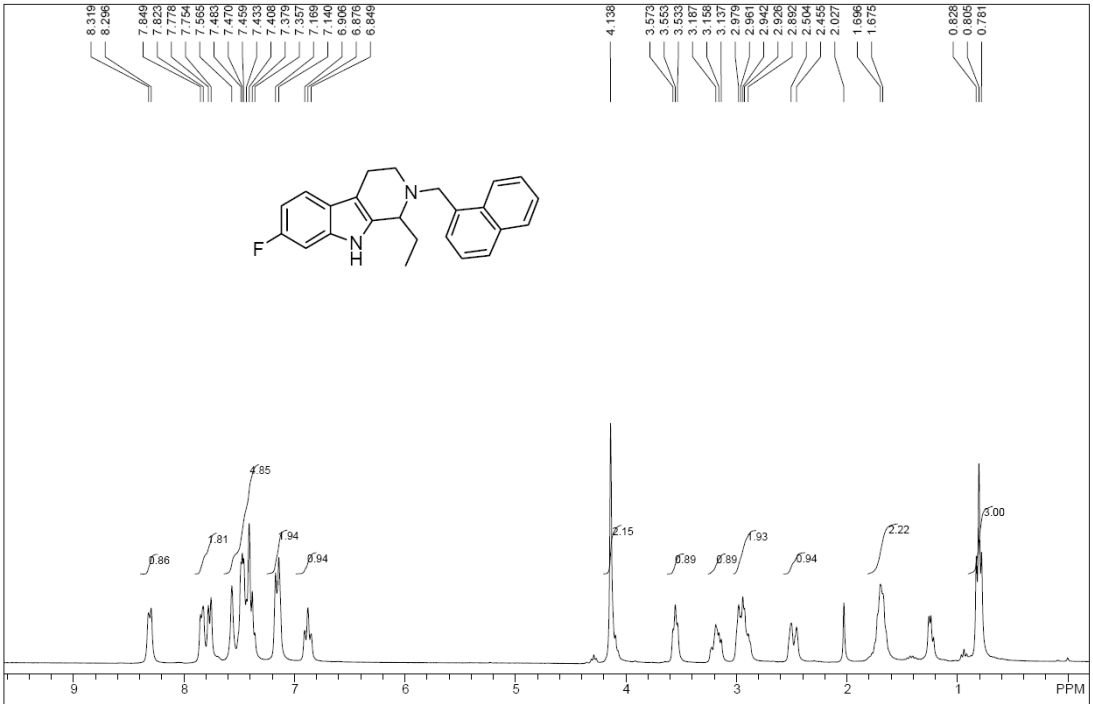


	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	30.753	3890428	48.27	33022	57.92
2	Peak2	35.882	4170102	51.73	23992	42.08

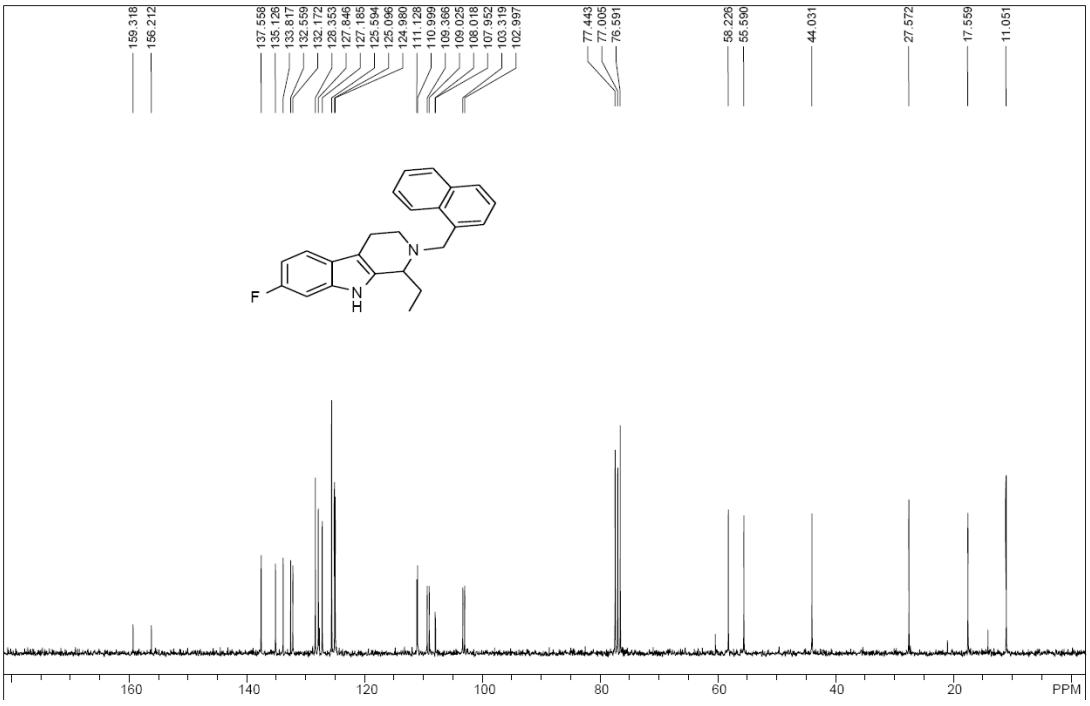


	Peak Name	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	Peak1	30.176	30283148	90.74	269515	94.18
2	Peak2	35.905	3090351	9.26	16652	5.82

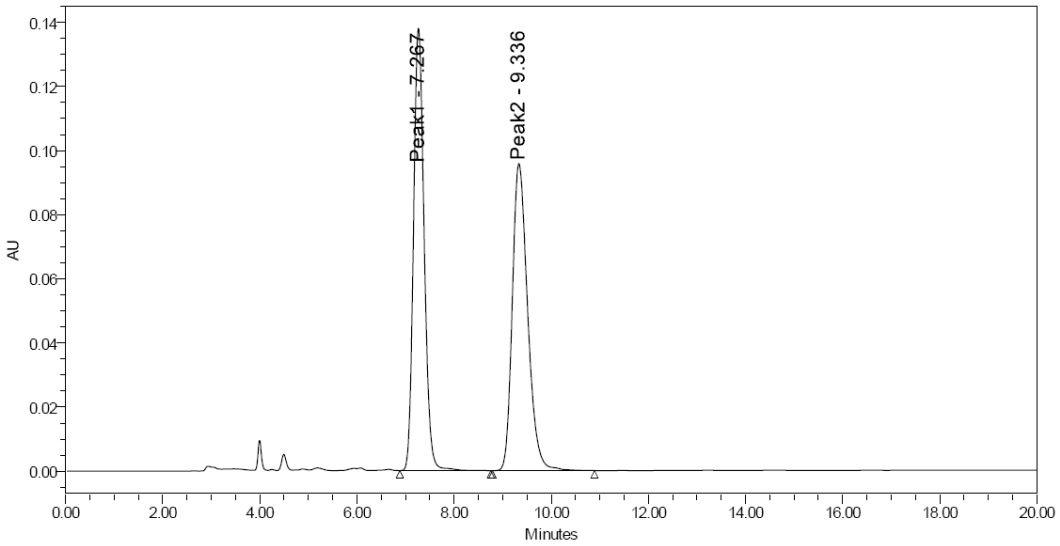
Compound **3h**'s ^{1}H NMR spectra



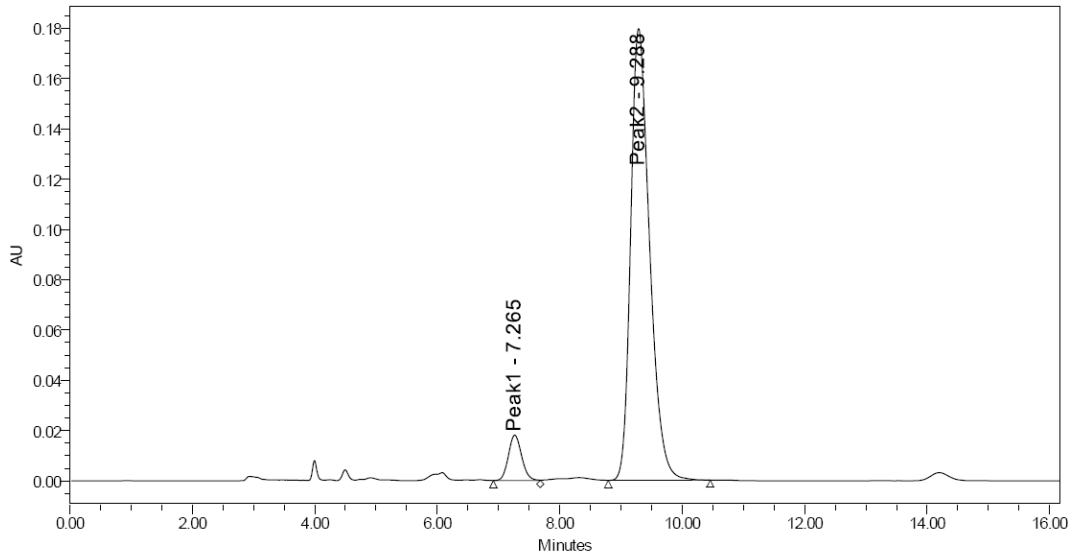
Compound **3h**'s ^{13}C NMR spectra



Compound **3h**'s HPLC spectra

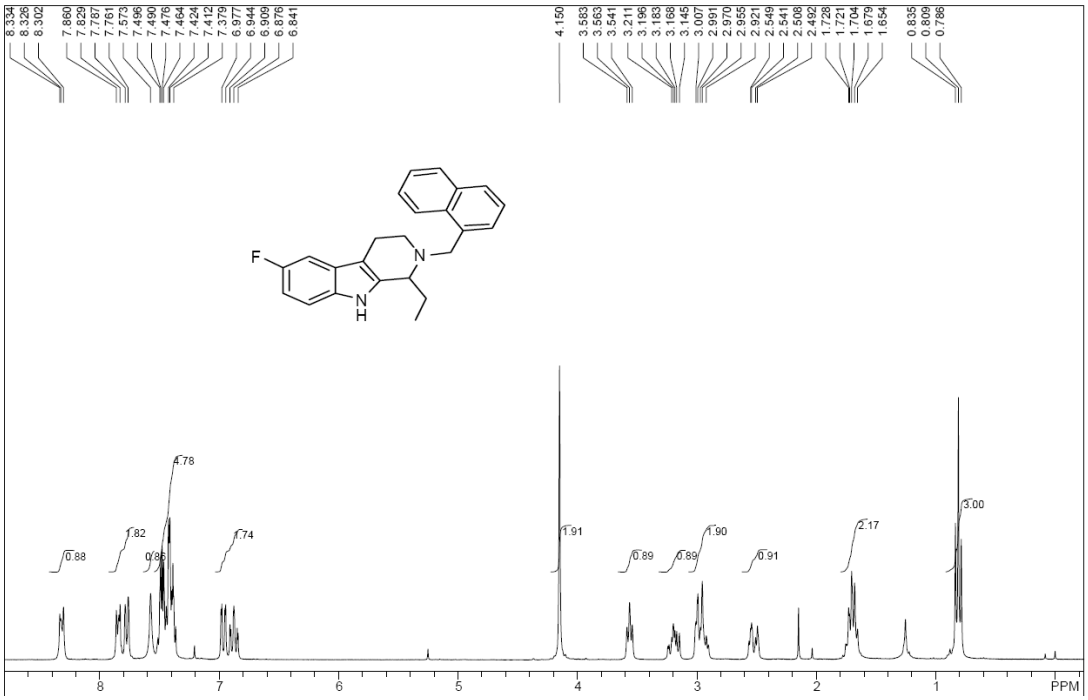


	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	7.267	2095902	49.92	138038	59.03
2	Peak2	9.336	2102892	50.08	95819	40.97

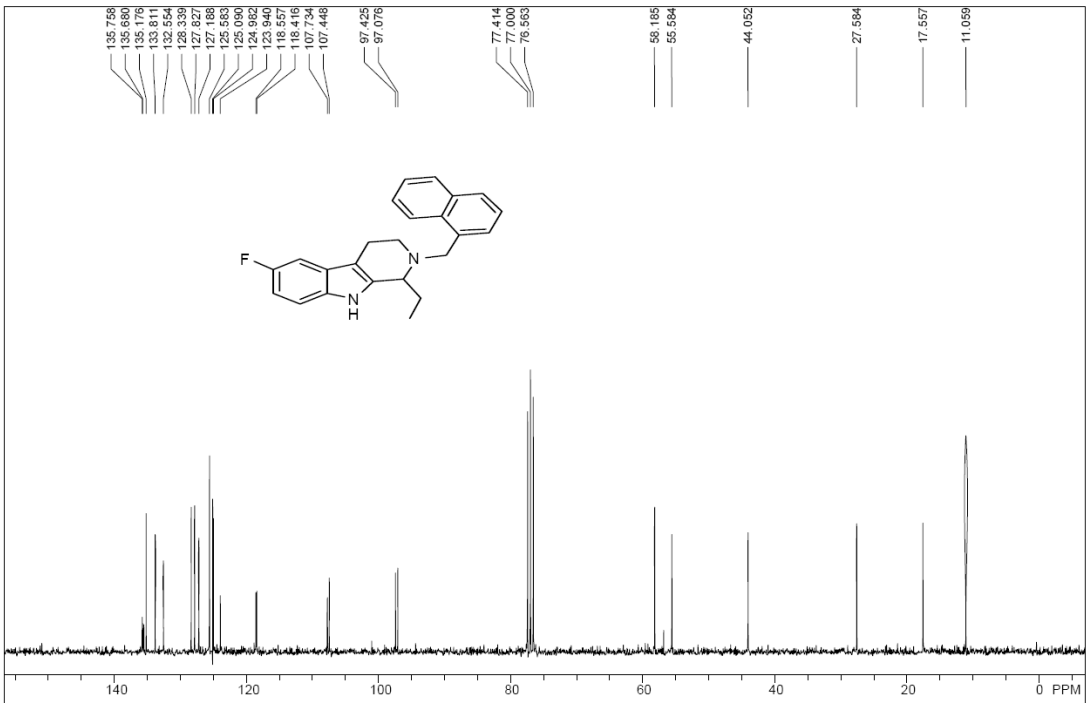


	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	7.265	269632	6.56	18033	9.12
2	Peak2	9.288	3842954	93.44	179719	90.88

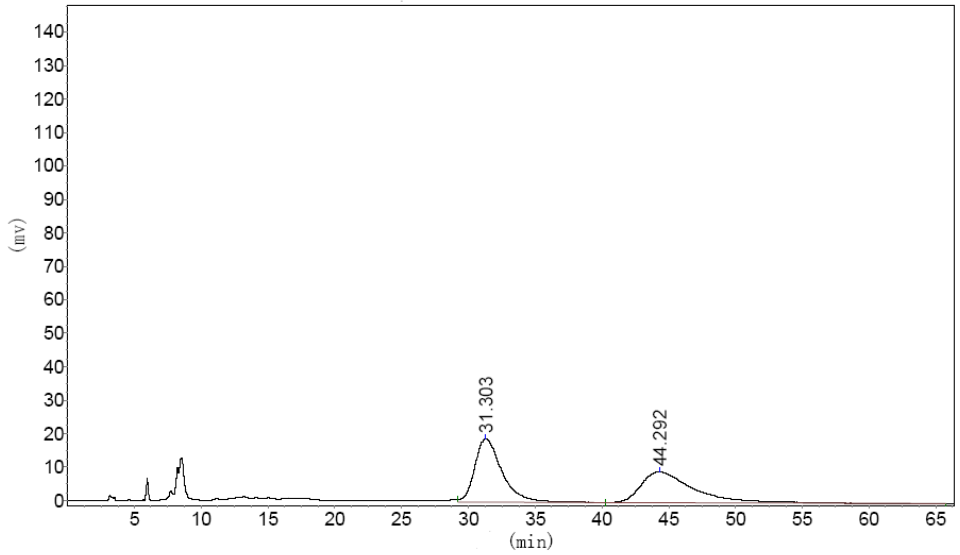
Compound **3i**'s ^{1}H NMR spectra



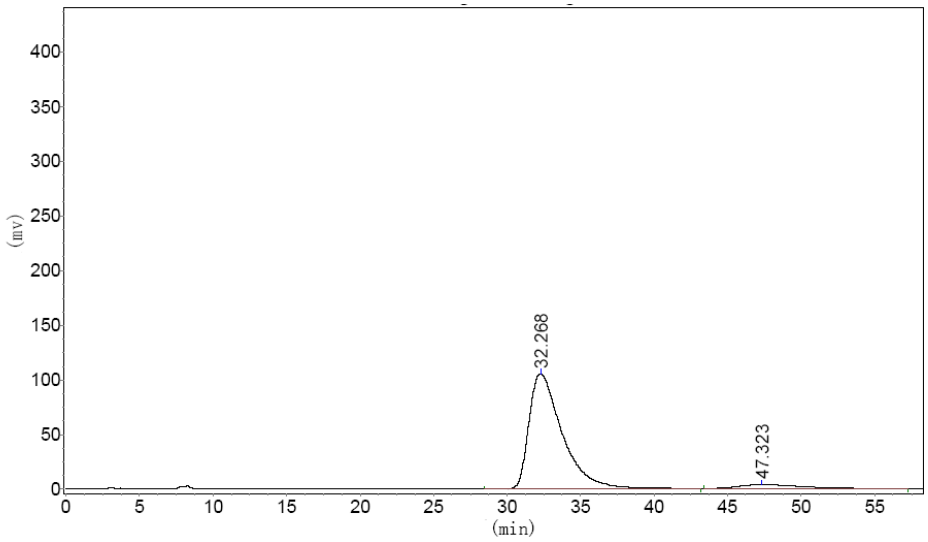
Compound **3i**'s ^{13}C NMR spectra



Compound **3i**'s HPLC spectra

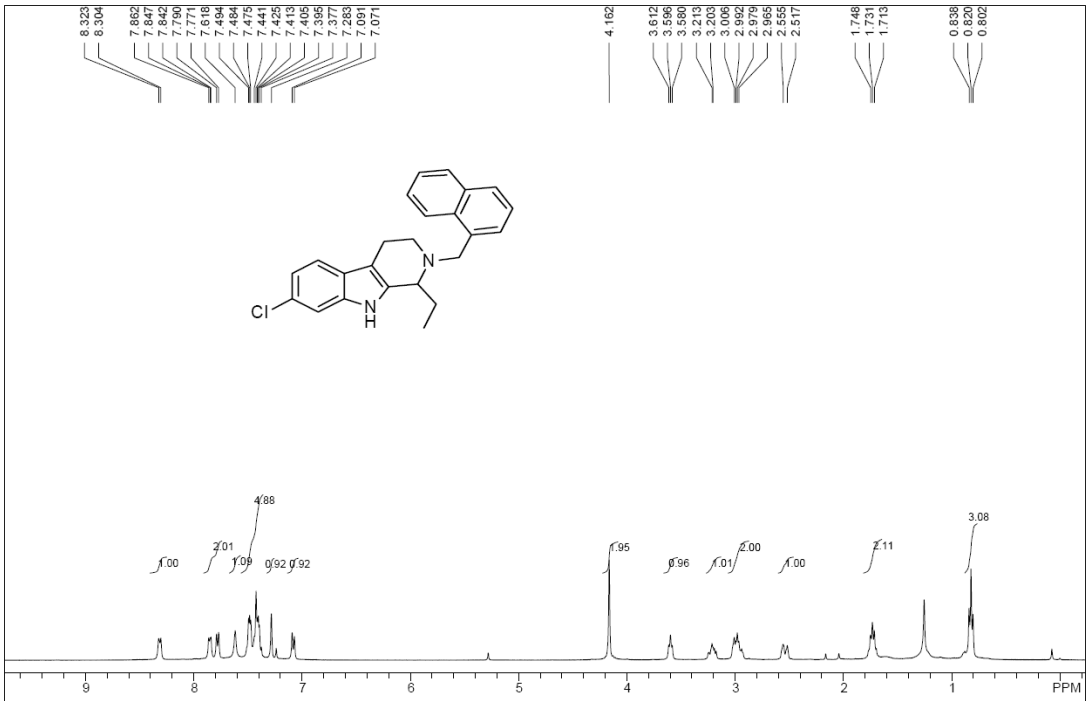


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	31.303	18907.240	2684776.750	51.3162
2	44.292	9156.021	2547056.500	48.6838
Total		28063.262	5231833.250	100.0000

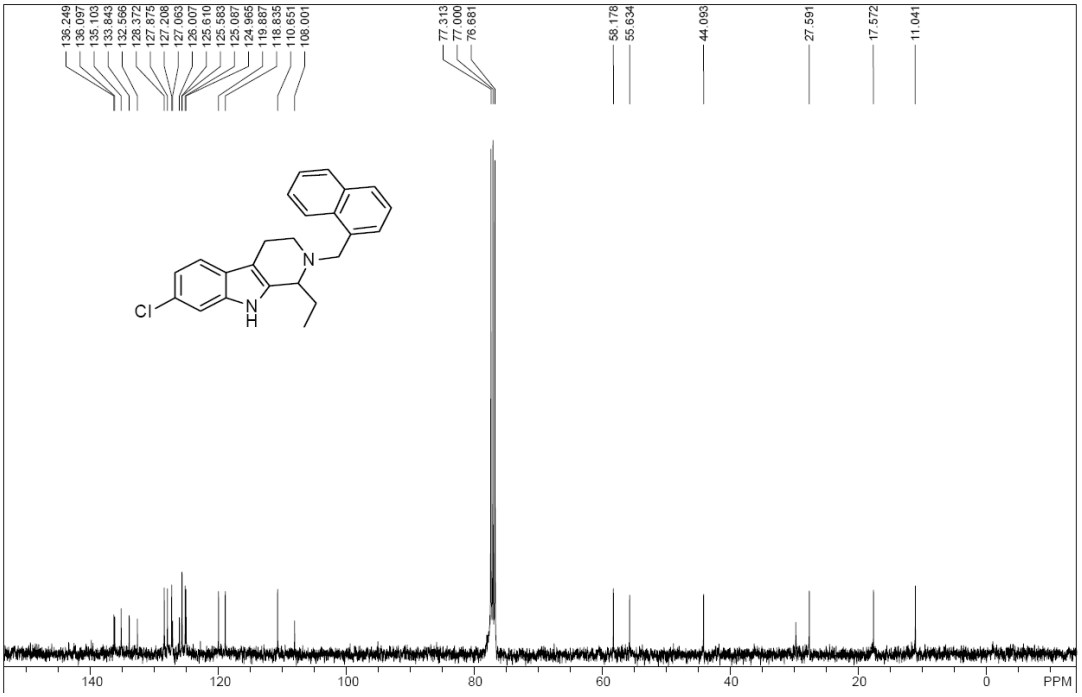


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	32.268	105591.313	16696643.000	93.3932
2	47.323	3955.678	1181143.125	6.6068
Total		109546.991	17877786.125	100.0000

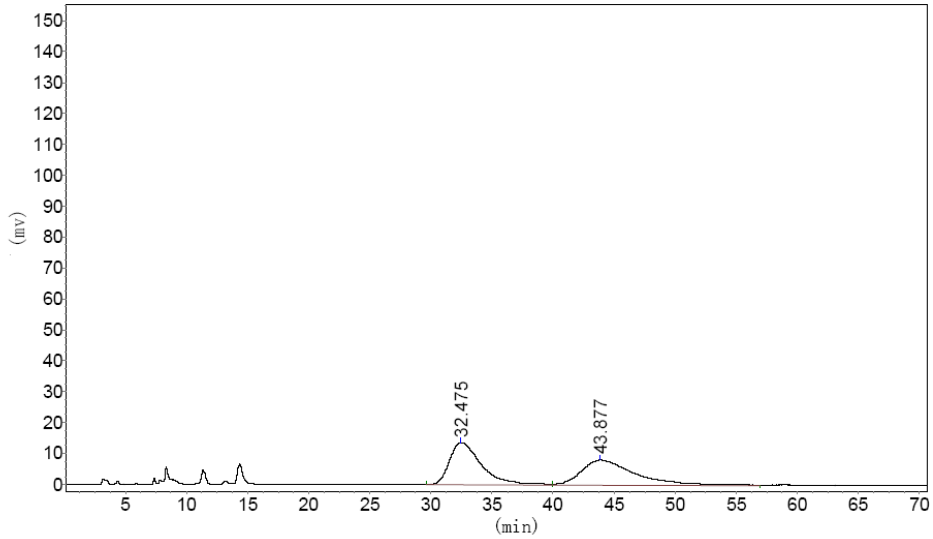
Compound **3j**'s ^{1}H NMR spectra



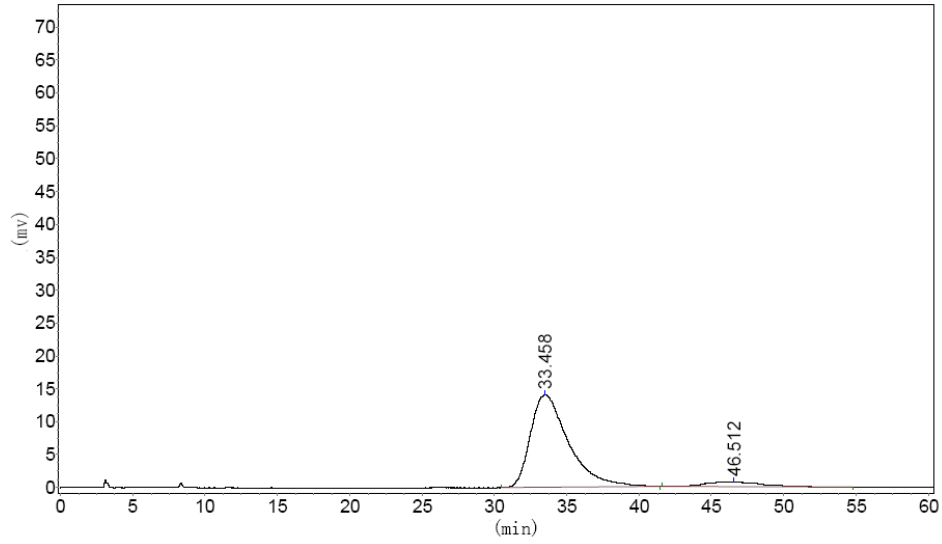
Compound **3j**'s ^{13}C NMR spectra



Compound **3j**'s HPLC spectra

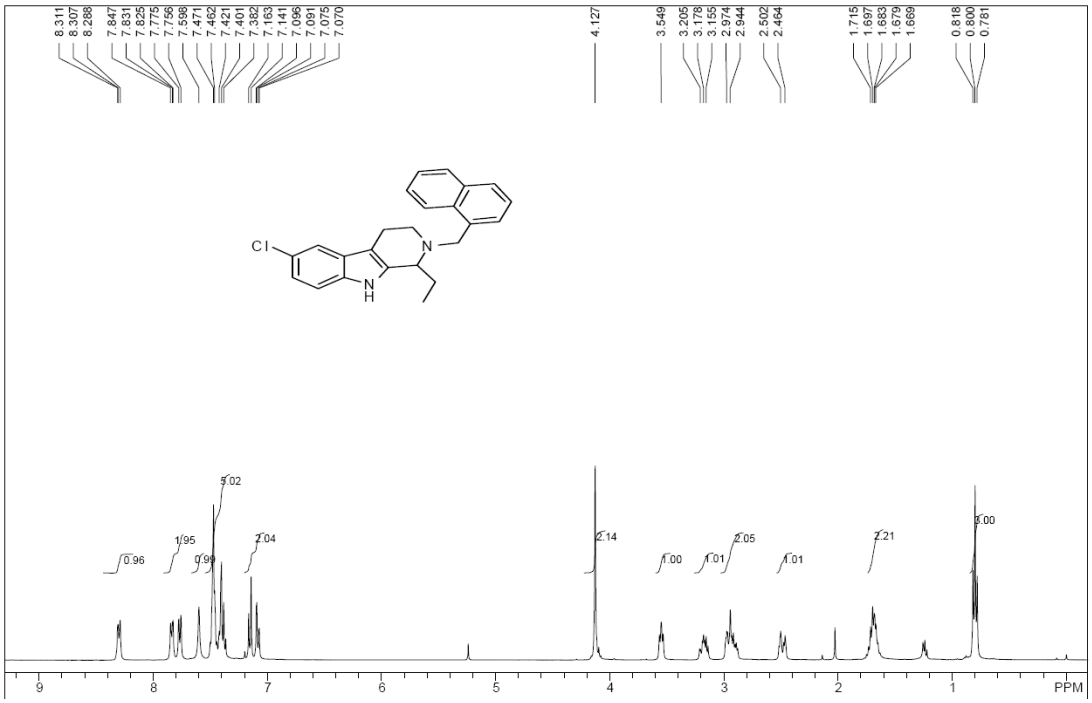


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	32.475	13768.727	2534536.500	50.0531
2	43.877	8047.895	2529161.500	49.9469
Total		21816.621	5063698.000	100.0000

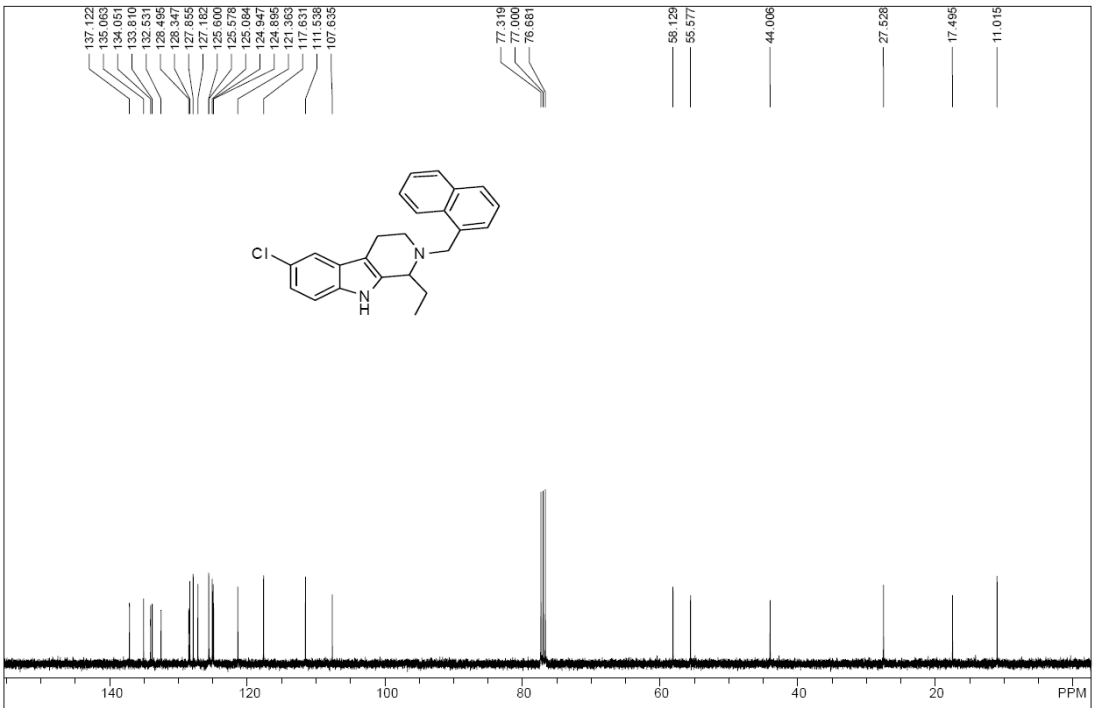


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	33.458	14031.124	2569907.250	93.3128
2	46.512	669.846	184169.609	6.6872
Total		14700.971	2754076.859	100.0000

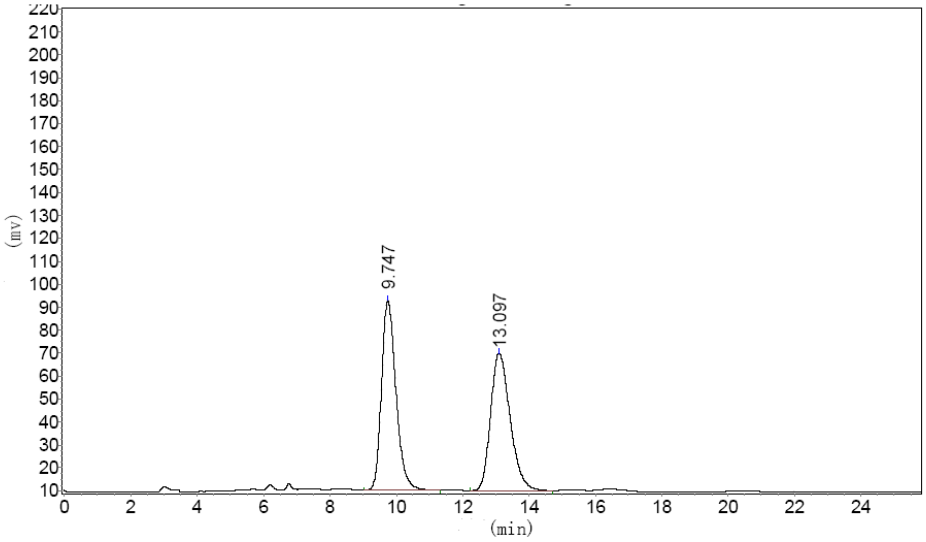
Compound **3k**'s ^{1}H NMR spectra



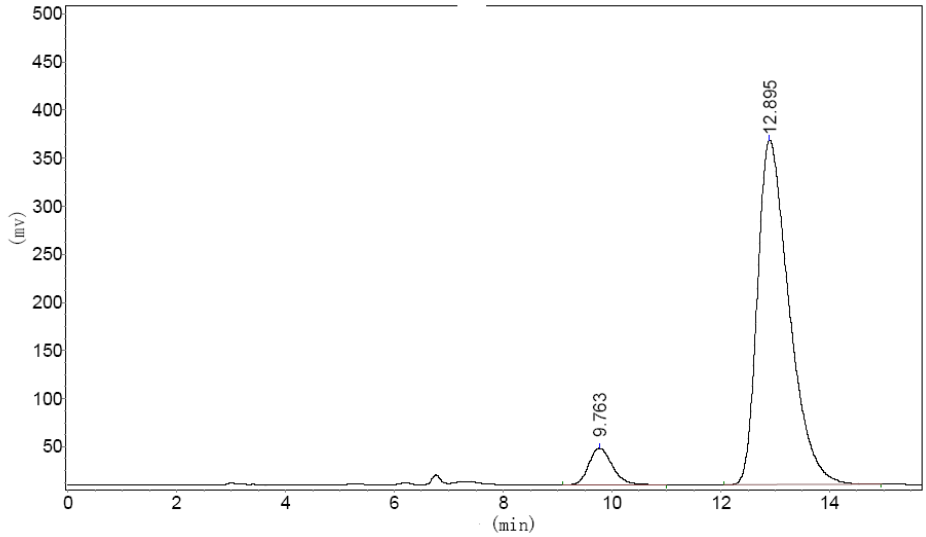
Compound **3k**'s ^{13}C NMR spectra



Compound **3k**'s HPLC spectra

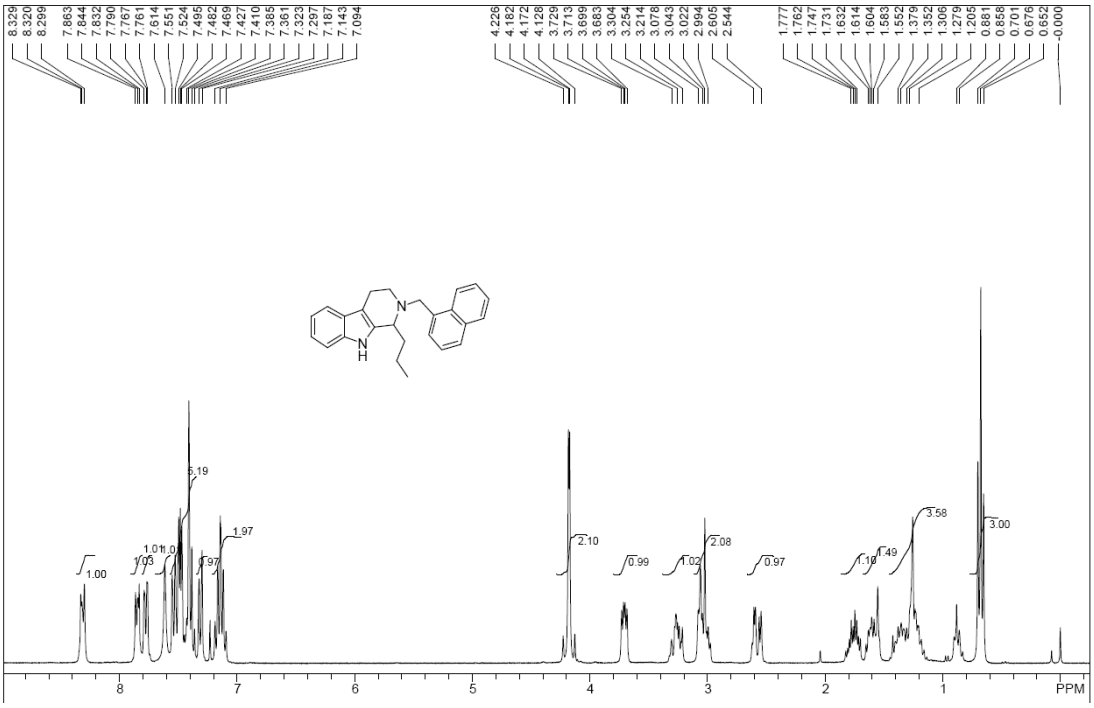


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	9.747	82798.055	2497063.750	50.4406
2	13.097	59918.137	2453437.250	49.5594
Total		142716.191	4950501.000	100.0000

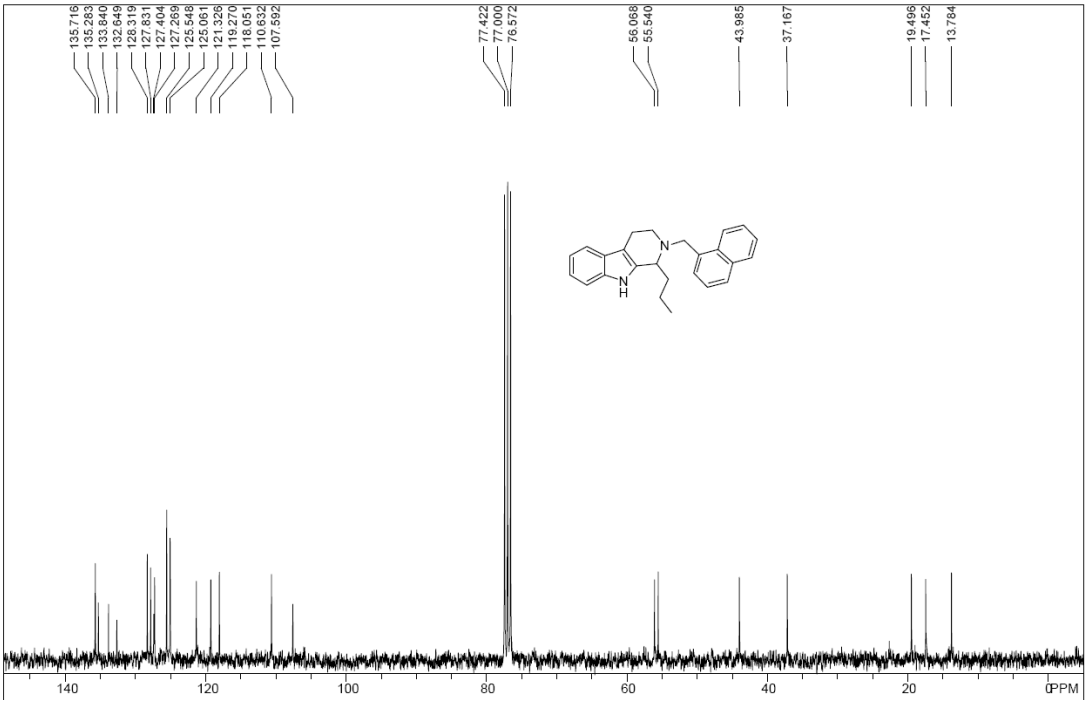


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	9.763	38398.828	1159138.250	7.3745
2	12.895	358552.781	14558983.000	92.6255
Total		396951.609	15718121.250	100.0000

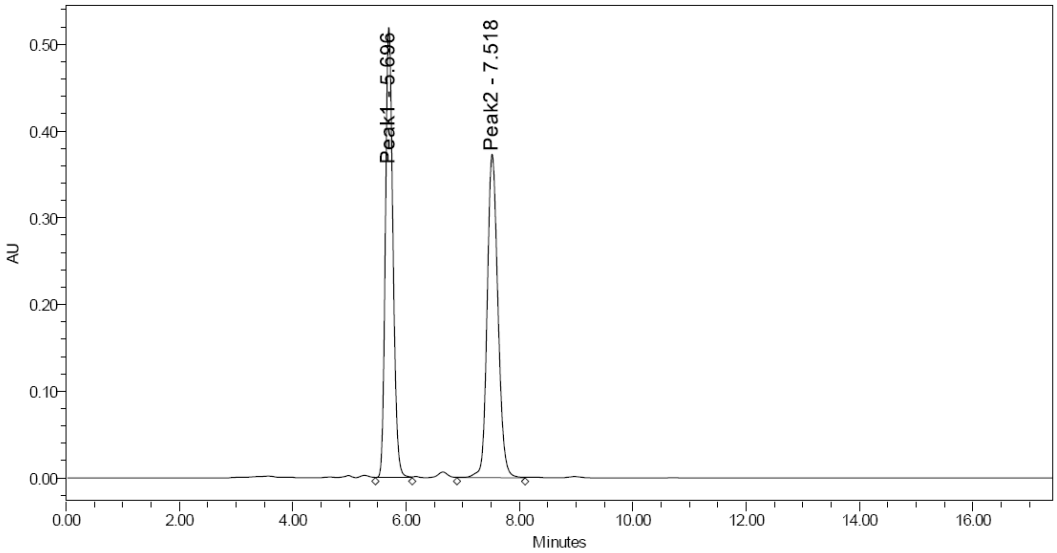
Compound **3l**'s ^{1}H NMR spectra



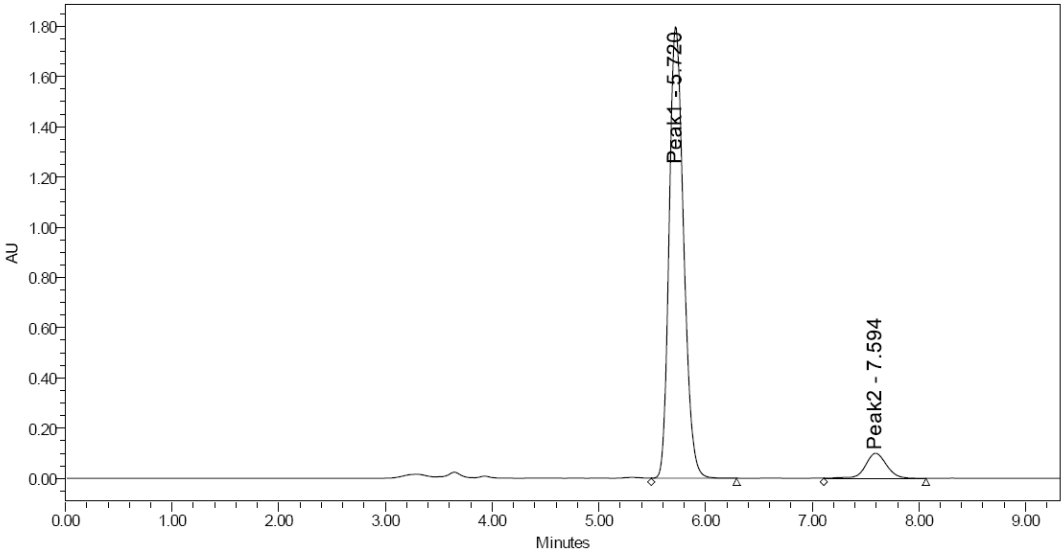
Compound **3l**'s ^{13}C NMR spectra



Compound **3l**'s HPLC spectra

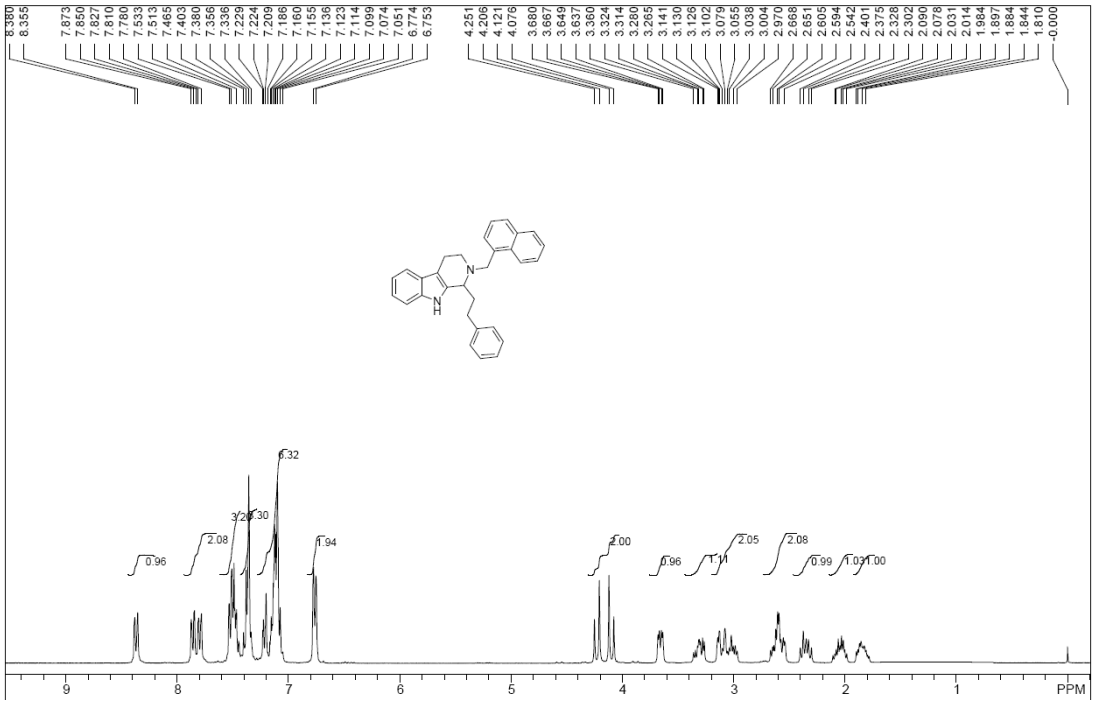


	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	5.696	4804092	49.38	520094	58.24
2	Peak2	7.518	4923969	50.62	372979	41.76

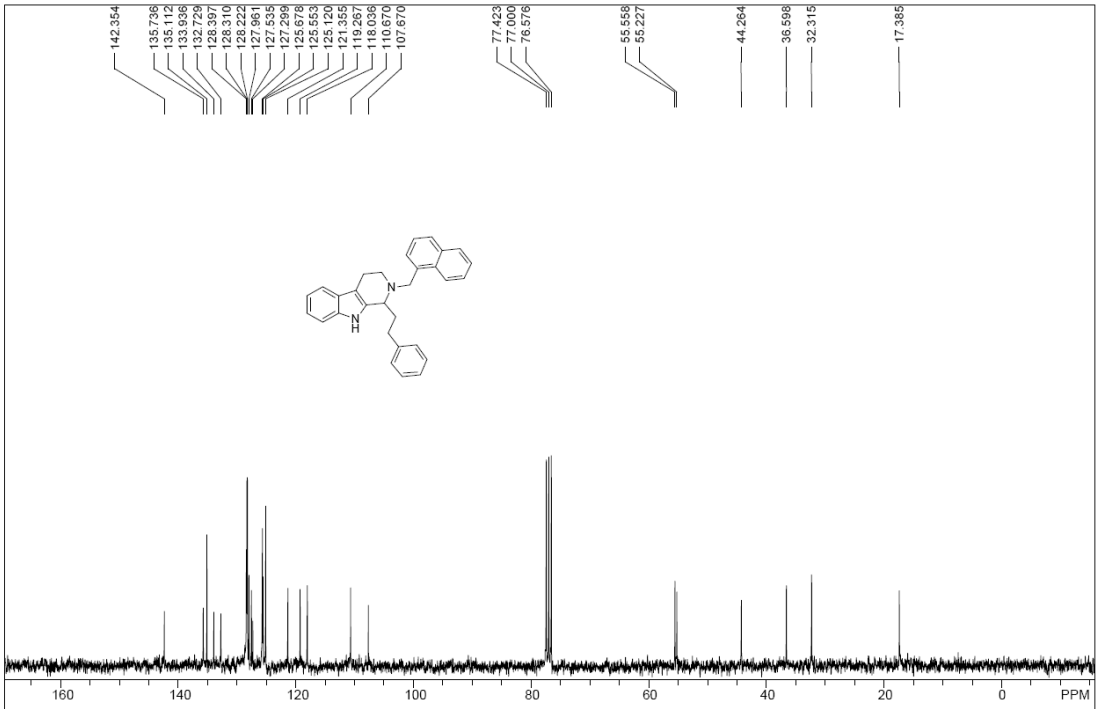


	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	5.720	16941940	92.53	1800184	94.75
2	Peak2	7.594	1367672	7.47	99654	5.25

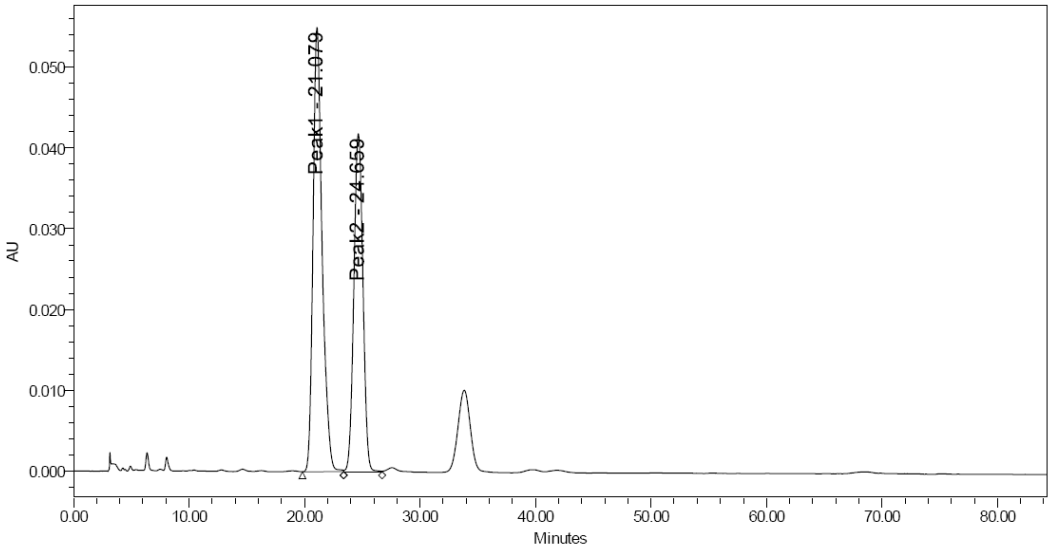
Compound **3m**'s ^{1}H NMR spectra



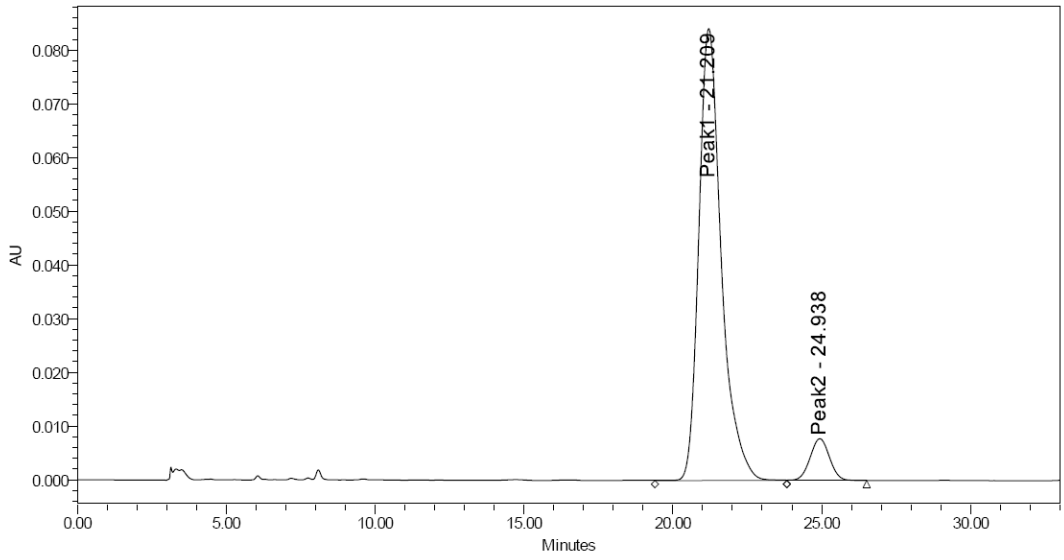
Compound **3m**'s ^{13}C NMR spectra



Compound **3m**'s HPLC spectra

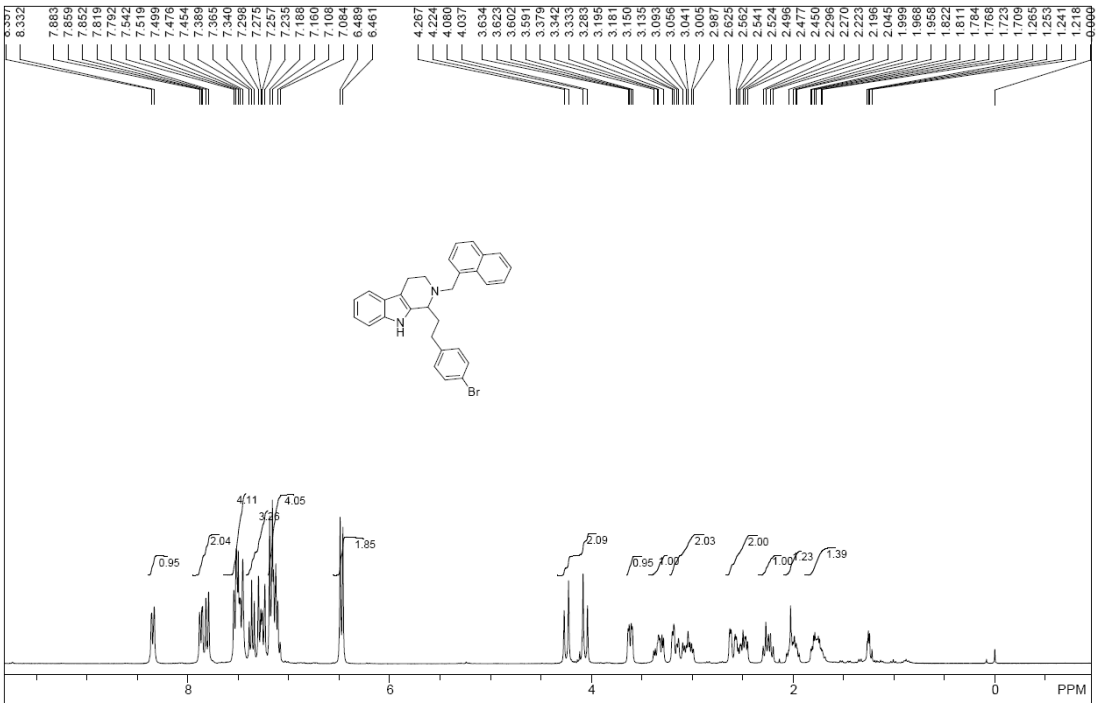


	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	21.079	3006651	56.94	54985	56.80
2	Peak2	24.659	2273554	43.06	41814	43.20

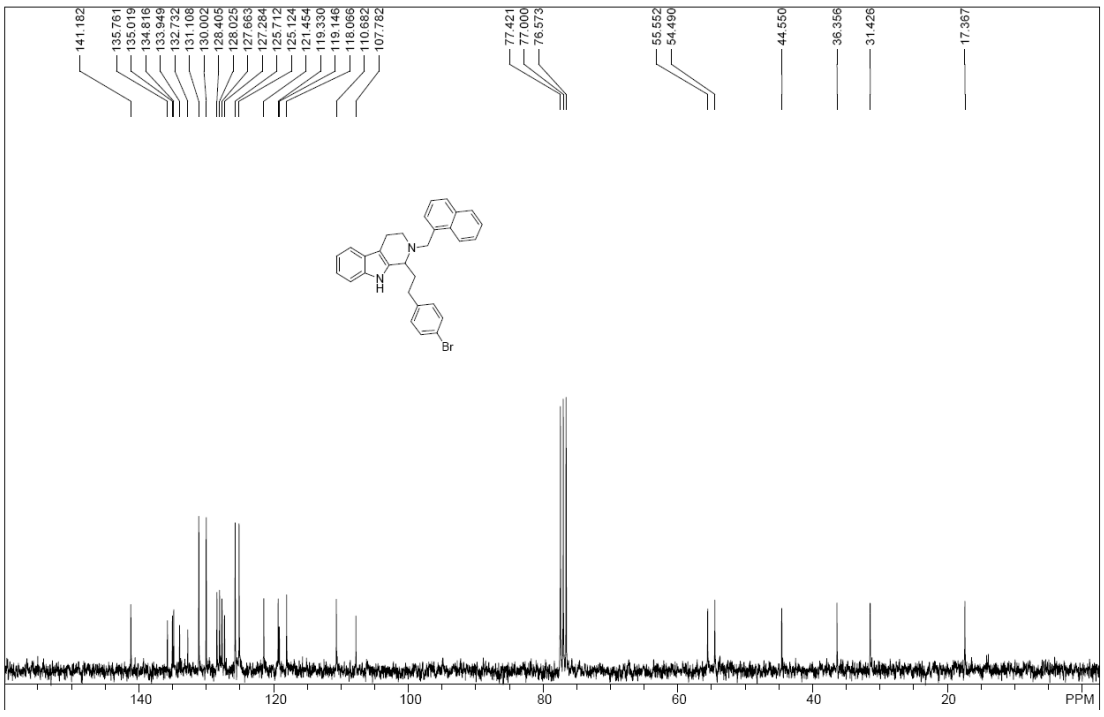


	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	21.209	4406135	92.60	84140	91.54
2	Peak2	24.938	352231	7.40	7778	8.46

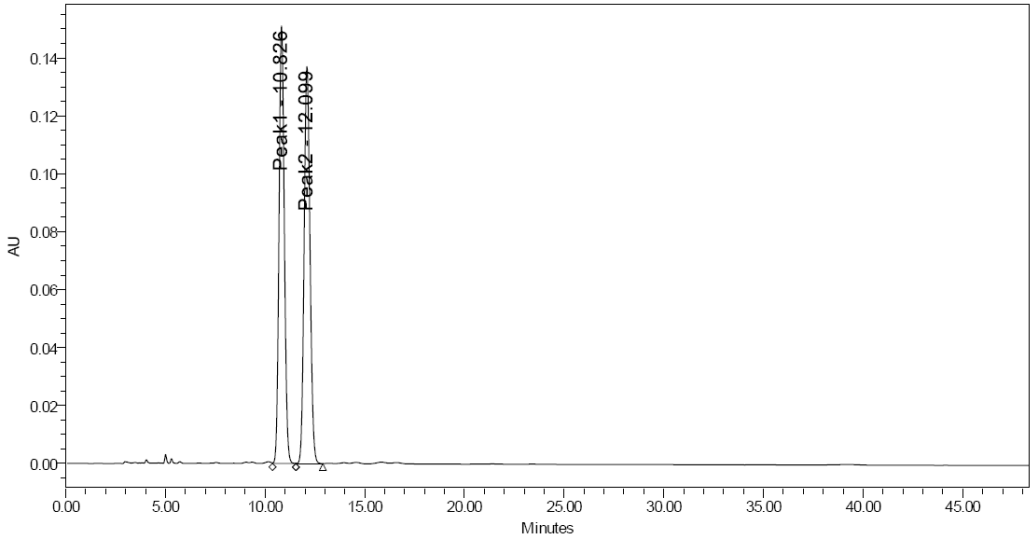
Compound **3n**'s ^{1}H NMR spectra



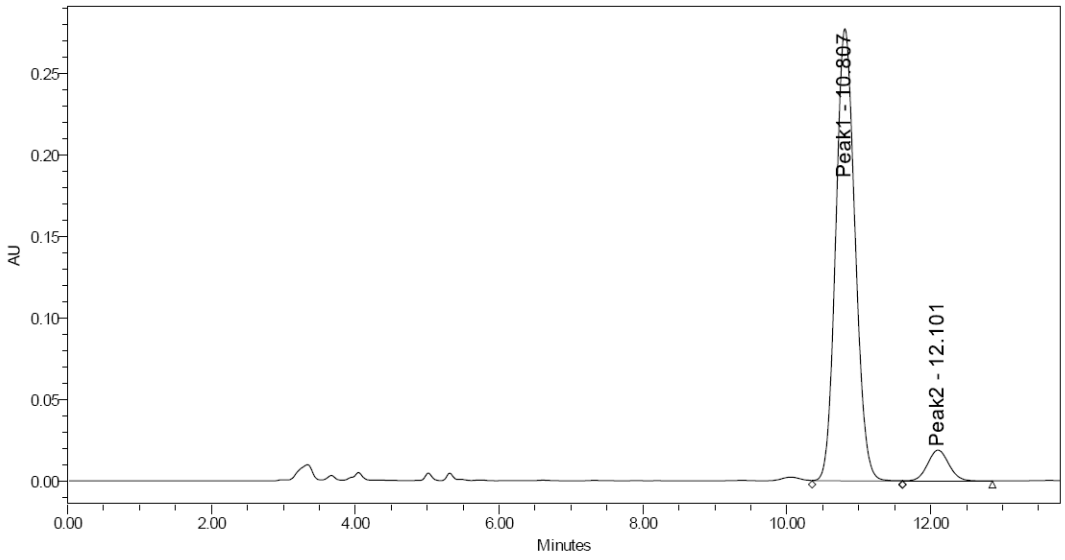
Compound **3n**'s ^{13}C NMR spectra



Compound **3n**'s HPLC spectra



	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	10.826	2792828	49.77	151054	52.42
2	Peak2	12.099	2818774	50.23	137119	47.58



	Peak Name	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	Peak1	10.807	5163232	93.02	277535	93.62
2	Peak2	12.101	387596	6.98	18908	6.38