

## Supporting Information for

# Diversity Oriented Synthesis of Indole-based Peri-annulated Compounds *via* Allylic Alkylation Reactions

Qing-Long Xu, Li-Xin Dai, and Shu-Li You\*

State Key Laboratory of Organometallic Chemistry  
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences  
345 Lingling Lu, Shanghai 200032, China

E-mail: [slyou@sioac.ac.cn](mailto:slyou@sioac.ac.cn)

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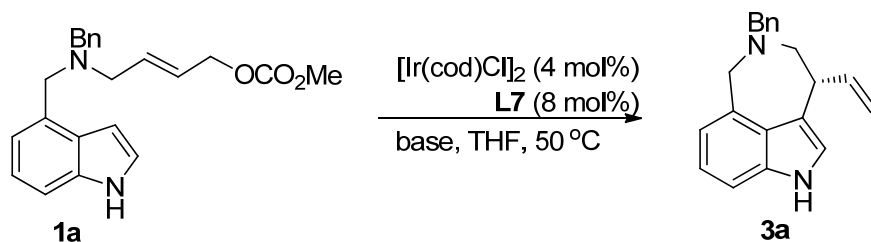
**Table S1.** Screening of bases and solvents in Pd-catalyzed Friedel-Crafts type allylic alkylation reaction of indole fused through C4-C3.

Reaction scheme: **1a** (indole with a benzyl group and a prop-1-en-2-yl ester side chain) reacts with  $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$  (5 mol%), **L6** (11 mol%),  $\text{Cs}_2\text{CO}_3$  (100 mol%) in THF at 50 °C to yield **2a** (indole with a benzyl group and a 7-membered ring fused to the indole system) and **3a** (indole with a benzyl group and a 7-membered ring fused to the indole system, with an allyl group at the 3-position).

entry	base	solvent	time (h)	<b>2a</b> / <b>3a</b> <sup>a</sup>	yield (%) <sup>b</sup>
1	$\text{Cs}_2\text{CO}_3$	THF	10	>97/3	32
2	$\text{K}_3\text{PO}_4$	THF	6	>97/3	54
3	$\text{Li}_2\text{CO}_3$	THF	16	>97/3	54
4	BSA	THF	16	>97/3	56
5	KOAc	THF	2	>97/3	70
6	$\text{K}_2\text{CO}_3$	THF	2	>97/3	55
7	$\text{Et}_3\text{N}$	THF	16	>97/3	39
8	DBU	THF	2	-	complex
9	NaOAc	THF	0.5	>97/3	48
10	DIEA	THF	22	-	NR
11	DABCO	THF	6	-	52
12 <sup>c</sup>	$\text{K}_3\text{PO}_4$	THF	4	>97/3	52
13 <sup>d</sup>	KOAc	THF	12	-	55
14 <sup>e</sup>	KOAc	THF	0.5	>97/3	68
15 <sup>f</sup>	KOAc	THF	12	-	41
16	KOAc	dioxane	0.5	>97/3	65
17	KOAc	DCM	5	>97/3	52
18	KOAc	DME	6	>97/3	50
19	KOAc	DCE	6	>97/3	41
20	KOAc	$\text{CH}_3\text{CN}$	28	>97/3	21
21	KOAc	toluene	2	>97/3	40

<sup>a</sup> Determined by  $^1\text{H}$  NMR of the crude reaction mixture. <sup>b</sup> Isolated yield of **2a**. <sup>c</sup> Reaction concentration: 0.02 mol/L. <sup>d</sup> 50 mol% of KOAc was used. <sup>e</sup> 200 mol% of KOAc was used. <sup>f</sup> At room temperature.

**Table S2.** Screening of bases and solvents in Ir-catalyzed Friedel-Crafts type allylic alkylation reaction of indole fused through C4-C3.<sup>a</sup>



entry	base	solvent	time (h)	conv (%) <sup>b</sup>	yield (%) <sup>c</sup>	ee (%) <sup>d</sup>
1	DBU	THF	20	-	-	-
2	Cs <sub>2</sub> CO <sub>3</sub>	THF	20	54	32	98
3	K <sub>3</sub> PO <sub>4</sub>	THF	24	45	20	99
4	BSA	THF	24	17	10	99
5	<sup>t</sup> BuONa	THF	8	100	8	96
6	KOAc	THF	28	-	17	99
7	Cs <sub>2</sub> CO <sub>3</sub>	DCM	18	95	56	90
8	Cs <sub>2</sub> CO <sub>3</sub>	dioxane	8	95	28	99
9 <sup>e</sup>	Cs <sub>2</sub> CO <sub>3</sub>	dioxane	8	90	32	94
10	Cs <sub>2</sub> CO <sub>3</sub>	toluene	42	50	27	99
11	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	44	42	18	93
12	Cs <sub>2</sub> CO <sub>3</sub>	DME	44	28	15	99
13	Cs <sub>2</sub> CO <sub>3</sub>	DCE	28	95	42	94
14 <sup>f</sup>	Cs <sub>2</sub> CO <sub>3</sub>	DCM	18	95	60	94

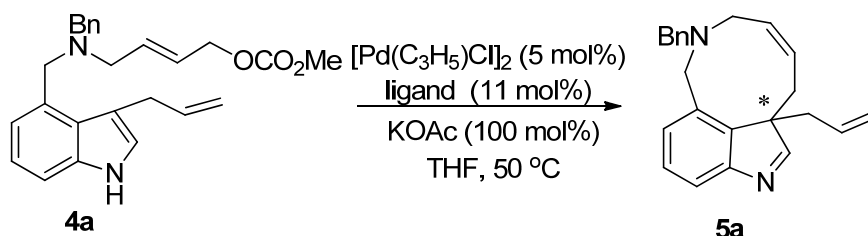
<sup>a</sup> Reaction conditions: 4 mol% of  $[\text{Ir}(\text{cod})\text{Cl}]_2$ , 8 mol% of L7, 0.2 mmol of **1a**, and 100 mol% of base in solvent (2 mL). <sup>b</sup> Determined by <sup>1</sup>H NMR of the crude reaction mixture. <sup>c</sup> Isolated yield of **3a**. <sup>d</sup> Determined by HPLC analysis. <sup>e</sup> Reaction at 100 °C. <sup>f</sup> 0.04 mol/L of substrate.

**Table S3.** Screening of bases and solvents in Ir-catalyzed Friedel-Crafts type allylic alkylation reaction of indole fused through C4-C3.<sup>a</sup>

entry	ligand	additives	con. (mol/L)	conv (%) <sup>b</sup>	yield (%) <sup>c</sup>	ee (%) <sup>d</sup>
1	<b>L7</b>	-	0.1	95	56	90
2	<b>L8</b>	-	0.1	100	44	83
3	<b>L9</b>	-	0.1	20	-	-
4	<b>L10</b>	-	0.1	80	24	53
5	<b>L7</b>	CuI	0.1	-	26	88
6	<b>L7</b>	LiCl	0.1	-	10	88
7	<b>L7</b>	-	0.04	95	60	94
8	<b>L7</b>	-	0.02	95	51	95

<sup>a</sup> Reactions were conducted under the conditions of entry 7, Table S2. <sup>b</sup> Determined by <sup>1</sup>H NMR of the crude reaction mixture. <sup>c</sup> Isolated yield of **3a**. <sup>d</sup> Determined by HPLC analysis.

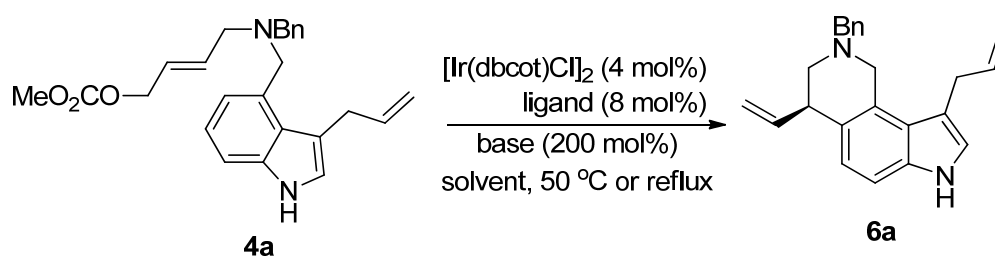
**Table S4.** Screening Different Ligands in Pd-catalyzed allylic dearomatization of indole fused through C4-C3.<sup>a</sup>



entry	ligand	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	( <i>S</i> )- <b>L1</b>	54	19
2	( <i>R,R</i> )- <b>L2</b>	N.R.	/
3	( <i>S,S<sub>a</sub></i> )- <b>L11</b>	complex	/
4	( <i>S</i> )-Tol-BINAP	complex	/
5	( <i>S,S<sub>p</sub></i> )- <b>L12a</b>	40	62
6	( <i>R,R<sub>p</sub></i> )- <b>L12b</b>	72	75
7	( <i>S,S<sub>p</sub></i> )- <b>L12c</b>	74	78
8	( <i>S,S<sub>p</sub></i> )- <b>L12d</b>	52	21
9	( <i>S,R<sub>p</sub></i> )- <b>L12e</b>	32	3
10	( <i>S,S<sub>p</sub></i> )- <b>L12f</b>	44	76
11	( <i>S,S<sub>p</sub></i> )- <b>L12g</b>	22	66

<sup>a</sup> Reaction conditions: 5 mol% of [Pd(C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub>, 11 mol% of ligand, 0.2 mmol of **4a**, and 100 mol% KOAc in THF (2 mL). <sup>b</sup> Isolated yield of **5a**. *N.R.* = no reaction. <sup>c</sup> Determined by HPLC analysis.

**Table S5.** Condition optimization in Ir-catalyzed Friedel-Crafts type allylic alkylation reaction of indole fused through C4-C5. <sup>a</sup>



entry	solvent	base	ligand	conv (%) <sup>b</sup>	yield (%) <sup>c</sup>	ee (%) <sup>d</sup>
1	DCM	Cs <sub>2</sub> CO <sub>3</sub>	<b>L8</b>	75	45	66
2	THF	Cs <sub>2</sub> CO <sub>3</sub>	<b>L8</b>	>95	40	83
3	dioxane	Cs <sub>2</sub> CO <sub>3</sub>	<b>L8</b>	92	33	67
4	DCE	Cs <sub>2</sub> CO <sub>3</sub>	<b>L8</b>	64	27	76
5	DME	Cs <sub>2</sub> CO <sub>3</sub>	<b>L8</b>	72	20	91
6	DMF	Cs <sub>2</sub> CO <sub>3</sub>	<b>L8</b>	65	14	76
7	toluene	Cs <sub>2</sub> CO <sub>3</sub>	<b>L8</b>	95	48	83
8	Et <sub>2</sub> O	Cs <sub>2</sub> CO <sub>3</sub>	<b>L8</b>	85	30	87
9	MeCN	Cs <sub>2</sub> CO <sub>3</sub>	<b>L8</b>	>95	35	84
10	toluene	Li <sub>2</sub> CO <sub>3</sub>	<b>L8</b>	15	/	/
11	toluene	K <sub>3</sub> PO <sub>4</sub>	<b>L8</b>	95	38	88
12	toluene	DBU	<b>L8</b>	complex	8	/
13	toluene	BSA	<b>L8</b>	85	45	81
14	toluene	NaH	<b>L8</b>	30	/	/
15	toluene	<sup>t</sup> BuONa	<b>L8</b>	complex	/	/
16	toluene	KHMDS	<b>L8</b>	100	/	/
17	toluene	Cs <sub>2</sub> CO <sub>3</sub>	<b>L7</b>	15	/	/
18	toluene	Cs <sub>2</sub> CO <sub>3</sub>	<b>L9</b>	40	/	/
19	toluene	Cs <sub>2</sub> CO <sub>3</sub>	<b>L10</b>	/	14	6

<sup>a</sup> Reaction conditions: 4 mol% of [Ir(dbcot)Cl]<sub>2</sub>, 8 mol% of **L8**, 0.2 mmol of **4a**, and 200 mol% Cs<sub>2</sub>CO<sub>3</sub> in solvent (2 mL). <sup>b</sup> Determined by <sup>1</sup>H NMR of the crude reaction mixture. <sup>c</sup> Isolated yield of **6a**. <sup>d</sup> Determined by HPLC analysis.

**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.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian instrument (300, 400 MHz and 75, 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for  $^1\text{H}$  NMR are recorded as follows: chemical shift ( $\delta$ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for  $^{13}\text{C}$  NMR are reported in terms of chemical shift ( $\delta$ , ppm).

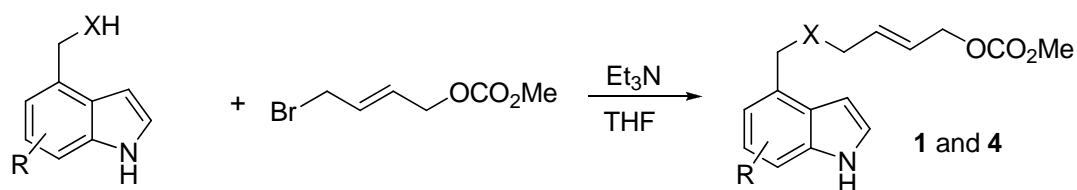
The phosphoramidite ligands<sup>1</sup>, the amine<sup>2</sup> and (*E*)-4-bromo-but-2-enyl methyl ester<sup>3</sup> were prepared according to the reported procedures.

(1) Alexakis, A.; Rosset, S.; Allamand, J.; March, S.; Guillen, F.; Benhaim, C. *Synlett* **2001**, 1375.

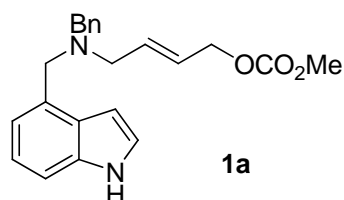
(2) (a) Yang, S.-D.; Sun, C.-L.; Fang, Z.; Li, B.-J.; Li, Y.-Z.; Shi, Z.-J. *Angew. Chem., Int. Ed.* **2008**, *47*, 1473. (b) Gagnon, D.; Spino, C. *J. Org. Chem.* **2009**, *74*, 6035. (c) Engler, T. A.; Henry, J. R.; Malhotra, S.; Cunningham, B.; Furness, K.; Brozinick, J. Burkholder, T. P.; Clay, M. P.; Clayton, J.; Diefenbacher, C.; Hawkins, E.; Iversen, P. W.; Li, Y. H.; Lindstrom, T. D.; Marquart, A. L.; McLean, J.; Mendel, D.; Misener, E.; Briere, D.; C. O'Toole, J.; Porter, W. J.; Queener, S.; Reel, J. K.; Owens, R. A.; Brier, R. A.; Eessalu, T. E.; Wagner, J. R.; Campbell, R. M. Vaughn, R. *J. Med. Chem.* **2004**, *47*, 3934.

(3) Trost, B. M.; Sacchi, K. L.; Schroeder, G. M.; Asakawa, N. *Org. Lett.* **2002**, *4*, 3427.

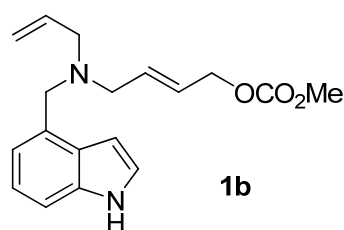
### General Procedure for Synthesis of the Substituted Allylic Carbonates:



To a solution of the amine<sup>[2]</sup> (2 mmol, 1.0 equiv) and Et<sub>3</sub>N (1.2 equiv) in dry THF (25 mL), carbonic acid (*E*)-4-bromo-but-2-enyl methyl ester (2.0 equiv) was added at 0 °C. The ice bath was then removed and the reaction mixture was stirred at rt for 6-12 h. After the reaction was complete (monitored by TLC), the crude reaction mixture was filtrated through a pad of celite and washed with EtOAc. The solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (PE/EA = 8/1) to afford the desired product **1** and **4**.

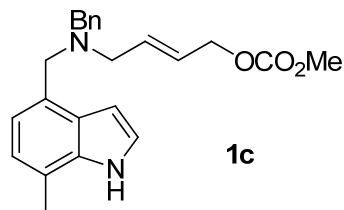


Viscous yellow oil, yield 85%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.18 (br s, 1H), 7.38-7.12 (m, 9H), 6.67 (m, 1H), 5.93 (dt, *J* = 6.0, 15.3 Hz, 1H), 5.75 (dt, *J* = 6.0, 15.3 Hz, 1H), 4.59 (d, *J* = 6.0 Hz, 2H), 3.84 (s, 2H), 3.76 (s, 3H), 3.59 (s, 2H), 3.10 (d, *J* = 6.0 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 155.6, 139.6, 135.8, 134.1, 131.3, 128.9, 128.1, 127.4, 126.7, 125.9, 123.6, 121.7, 119.9, 109.8, 101.5, 68.1, 58.3, 56.4, 55.1, 54.7; IR (film): ν<sub>max</sub> (cm<sup>-1</sup>) = 3413, 3027, 2954, 2794, 1744, 1495, 1344, 1258, 1115, 939, 753, 698; EI-MS (*m/z*): 364 (M<sup>+</sup>, 2), 288 (25), 234 (7), 130 (100), 91 (34), 77 (7), 65 (5); HRMS (EI): Exact mass calcd. for C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub> [M]<sup>+</sup>: 364.1787. Found: 364.1777.

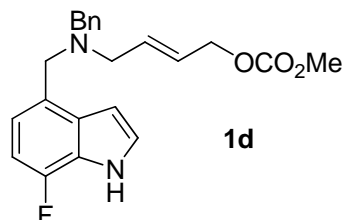


Viscous yellow oil, yield 83%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.30 (br s, 1H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.23-7.10 (m, 3H), 6.69 (m, 1H), 5.99-5.85 (m, 2H), 5.75 (dt, *J* = 6.0, 15.6 Hz, 1H), 5.19 (d, *J* = 18.9 Hz, 1H), 5.13 (d, *J* = 10.2 Hz, 1H), 4.59 (d, *J* = 6.0 Hz, 2H), 3.83 (s, 2H), 3.76 (s, 3H), 3.11 (d, *J* = 6.0 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

$\delta$  155.6, 135.9, 135.8, 133.9, 131.1, 127.5, 125.8, 123.7, 121.6, 119.9, 117.4, 109.8, 101.3, 68.1, 56.9, 55.9, 55.0, 54.7; IR (film):  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 3409, 2799, 1745, 1440, 1258, 938, 753; EI-MS ( $m/z$ ): 314 ( $M^+$ , 0.8), 238 (8), 130 (100), 103 (10), 41 (16); HRMS (EI): Exact mass calcd. for  $C_{18}H_{22}N_2O_3$  [ $M$ ] $^+$ : 314.1630. Found: 314.1635.

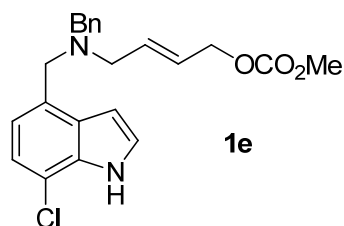


Viscous yellow oil, yield 87%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (br s, 1H), 7.37-7.13 (m, 6H), 7.05 (d,  $J = 7.2$  Hz, 1H), 6.93 (d,  $J = 7.2$  Hz, 1H), 6.67 (m, 1H), 5.94 (dt,  $J = 6.0, 15.6$  Hz, 1H), 5.75 (dt,  $J = 6.0, 15.6$  Hz, 1H), 4.58 (d,  $J = 6.0$  Hz, 2H), 3.81 (s, 2H), 3.75 (s, 3H), 3.58 (s, 2H), 3.08 (d,  $J = 6.0$  Hz, 2H), 2.44 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 139.7, 135.4, 134.1, 128.9, 128.4, 128.1, 127.0, 126.7, 125.8, 123.3, 122.2, 120.2, 118.9, 102.1, 68.1, 58.2, 56.3, 55.0, 54.7, 16.5; IR (film):  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 3412, 2955, 2923, 2707, 1745, 1442, 1259, 941, 811, 731, 698; EI-MS ( $m/z$ ): 378 ( $M^+$ , 2), 302 (14), 144 (100), 91 (52), 43 (34); HRMS (EI): Exact mass calcd. for  $C_{23}H_{26}N_2O_3$  [ $M$ ] $^+$ : 378.1943. Found: 348.1937.

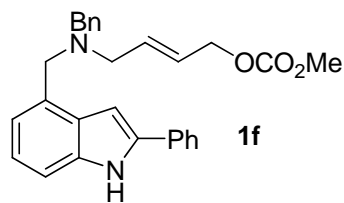


Viscous yellow oil, yield 72%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.45 (br s, 1H), 7.35-7.15 (m, 6H), 7.00 (dd,  $J = 4.8, 8.0$  Hz, 1H), 6.81 (dd,  $J = 8.0, 10.8$  Hz, 1H), 6.68 (m, 1H), 5.92 (dt,  $J = 6.0, 15.2$  Hz, 1H), 5.75 (dt,  $J = 6.0, 15.2$  Hz, 1H), 4.59 (d,  $J = 6.0$  Hz, 2H), 3.77 (s, 2H), 3.76 (s, 3H), 3.56 (s, 2H), 3.07 (d,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 152.1 (d,  $J = 240.9$  Hz), 139.5, 133.9, 130.8 (d,  $J = 5.2$  Hz), 126.9 (d,  $J = 3.1$  Hz), 126.8, 126.0, 124.3, 124.0 (d,  $J = 13.4$  Hz), 120.0 (d,  $J = 6.0$  Hz), 106.2 (d,  $J = 15.6$  Hz), 102.5, 68.1, 58.2, 55.9, 55.0, 54.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -137.4 (m); IR (film):  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 3422, 2798, 1745, 1442, 1345, 1260, 940, 805, 698; EI-MS ( $m/z$ ): 382 ( $M^+$ , 4), 306 (28), 148 (100), 91 (61); HRMS (EI): Exact mass calcd. for  $C_{22}H_{23}N_2O_3\text{F}$  [ $M$ ] $^+$ : 382.1693. Found: 382.1691.

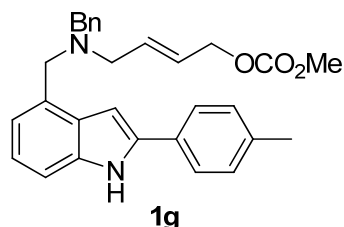




Viscous yellow oil, yield 75%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.45 (br s, 1H), 7.34-7.05 (m, 8H), 6.68 (m, 1H), 5.90 (dt,  $J = 6.0, 15.3$  Hz, 1H), 5.73 (dt,  $J = 6.0, 15.3$  Hz, 1H), 4.59 (d,  $J = 6.0$  Hz, 2H), 3.78 (s, 2H), 3.75 (s, 3H), 3.56 (s, 2H), 3.06 (d,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 139.4, 133.7, 132.9, 130.2, 128.84, 128.76, 128.1, 126.8, 126.0, 124.3, 120.9, 120.7, 115.1, 102.6, 68.0, 58.2, 55.9, 54.9, 54.7; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3419, 3027, 2921, 2797, 1744, 1498, 1442, 1337, 1295, 1123, 935, 791, 698; EI-MS ( $m/z$ ): 398 ( $\text{M}^+$ , 4), 322 (34), 234 (12), 164 (100), 91 (84); HRMS (EI): Exact mass calcd. for  $\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}_3\text{Cl}$  [ $\text{M}$ ] $^+$ : 398.1397. Found: 398.1407.

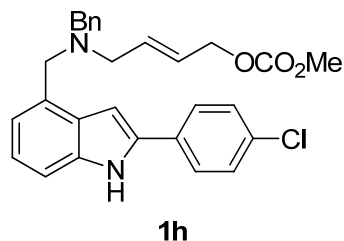


Viscous yellow oil, yield 70%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.43 (br s, 1H), 7.60 (d,  $J = 7.5$  Hz, 2H), 7.41-7.36 (m, 4H), 7.31-7.18 (m, 5H), 7.14-7.09 (m, 2H), 6.88 (s, 1H), 5.92 (dt,  $J = 6.0, 15.3$  Hz, 1H), 5.75 (dt,  $J = 6.0, 15.3$  Hz, 1H), 4.58 (d,  $J = 6.0$  Hz, 2H), 3.83 (s, 2H), 3.71 (s, 3H), 3.59 (s, 2H), 3.10 (d,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 139.6, 137.2, 136.9, 133.9, 132.4, 131.1, 129.0, 128.8, 128.1, 127.4, 126.8, 125.9, 125.0, 122.0, 120.3, 109.7, 98.9, 68.1, 58.2, 56.1, 55.0, 54.7; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3401, 3027, 2923, 2793, 1745, 1730, 1450, 1259, 972, 757, 737, 692; EI-MS ( $m/z$ ): 440 (1), 365 (6), 206 (100), 91(24); HRMS (EI): Exact mass calcd. for  $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_3$  [ $\text{M}$ ] $^+$ : 440.2100. Found: 440.2099.

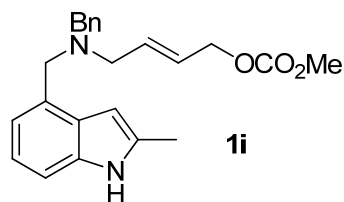


Viscous yellow oil, yield 72%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.33 (br s, 1H), 7.52 (d,  $J = 8.1$  Hz, 2H), 7.40-7.37 (m, 2H), 7.30 (t,  $J = 7.2$  Hz, 2H), 7.24-7.21 (m, 4H), 7.12-7.09 (m, 2H), 6.84 (s, 1H), 5.94 (dt,  $J = 6.0, 15.3$  Hz, 1H), 5.75 (dt,  $J = 6.0, 15.3$

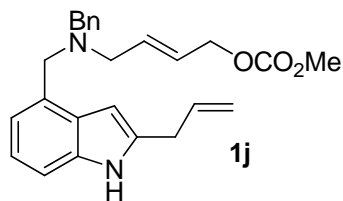
Hz, 1H), 4.59 (d,  $J = 6.0$  Hz, 2H), 3.83 (s, 2H), 3.73 (s, 3H), 3.60 (s, 2H), 3.12 (d,  $J = 6.0$  Hz, 2H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 139.7, 137.44, 137.39, 136.8, 134.0, 131.1, 129.6, 129.0, 128.9, 128.1, 126.8, 125.9, 125.0, 121.8, 120.3, 109.6, 98.4, 68.1, 58.3, 56.1, 55.1, 54.7, 21.2; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3406, 3025, 2953, 2792, 1745, 1441, 1260, 772, 731, 698; EI-MS ( $m/z$ ): 454 ( $\text{M}^+$ , 1), 378 (23), 220 (100), 91 (34); HRMS (EI): Exact mass calcd. for  $\text{C}_{29}\text{H}_{30}\text{N}_2\text{O}_3$  [ $\text{M}$ ] $^+$ : 454.2256. Found: 454.2257.



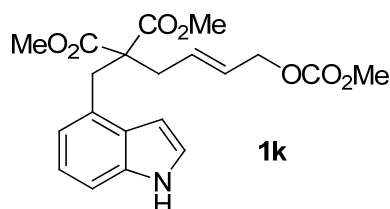
Viscous yellow oil, yield 70%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.34 (br s, 1H), 7.54 (d,  $J = 8.4$  Hz, 2H), 7.38 (d,  $J = 8.1$  Hz, 4H), 7.30 (t,  $J = 7.2$  Hz, 2H), 7.25-7.22 (m, 2H), 7.13-7.11 (m, 2H), 6.85 (s, 1H), 5.94 (dt,  $J = 6.3, 15.3$  Hz, 1H), 5.77 (dt,  $J = 6.3, 15.9$  Hz, 1H), 4.60 (d,  $J = 6.0$  Hz, 2H), 3.83 (s, 2H), 3.74 (s, 3H), 3.60 (s, 2H), 3.12 (d,  $J = 6.3$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 139.6, 137.0, 136.1, 133.9, 133.2, 131.4, 130.9, 129.1, 129.0, 128.8, 128.1, 126.8, 126.2, 126.0, 122.4, 120.6, 109.8, 99.5, 68.1, 58.3, 56.1, 55.1, 54.7; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3399, 3027, 2955, 2794, 1737, 1442, 1262, 906, 776, 728, 699; EI-MS ( $m/z$ ): 474 ( $\text{M}^+$ , 1), 398 (39), 240 (100), 91 (58); HRMS (EI): Exact mass calcd. for  $\text{C}_{28}\text{H}_{27}\text{N}_2\text{O}_3\text{Cl}$  [ $\text{M}$ ] $^+$ : 474.1710. Found: 474.1714.



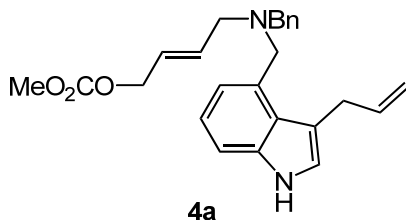
Viscous yellow oil, yield 80%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (br s, 1H), 7.37-7.01 (m, 8H), 6.29 (s, 1H), 5.93 (dt,  $J = 6.3, 15.6$  Hz, 1H), 5.75 (dt,  $J = 6.3, 15.3$  Hz, 1H), 4.59 (d,  $J = 6.6$  Hz, 2H), 3.78 (s, 2H), 3.75 (s, 3H), 3.58 (s, 2H), 3.09 (d,  $J = 6.3$  Hz, 2H), 2.39 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 139.6, 136.0, 134.5, 134.1, 130.0, 128.9, 128.6, 128.0, 126.7, 125.8, 120.6, 119.8, 109.0, 99.2, 68.1, 58.2, 56.2, 55.0, 54.7, 13.7; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3399, 3026, 2953, 2792, 1745, 1439, 1258, 940, 791, 738, 698; EI-MS ( $m/z$ ): 302 ( $\text{M}^+$ , 41), 144 (100), 91 (30); HRMS (EI): Exact mass calcd. for  $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_3$  [ $\text{M}$ ] $^+$ : 378.1943. Found: 378.1940.



Viscous yellow oil, yield 65%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (br s, 1H), 7.37-7.03 (m, 8H), 6.35 (s, 1H), 6.06-5.88 (m, 2H), 5.75 (dt,  $J = 6.0, 15.3$  Hz, 1H), 5.20 (d,  $J = 14.4$  Hz, 1H), 5.16 (d,  $J = 8.7$  Hz, 1H), 4.59 (d,  $J = 6.0$  Hz, 2H), 3.79 (s, 2H), 3.75 (s, 3H), 3.58 (s, 2H), 3.50 (d,  $J = 6.6$  Hz, 2H), 3.09 (d,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 139.7, 136.4, 136.1, 134.9, 134.1, 130.5, 128.9, 128.3, 128.0, 126.7, 125.8, 121.0, 119.8, 117.1, 109.2, 99.1, 68.1, 58.2, 56.2, 55.0, 54.7, 32.8; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3399, 3026, 2954, 2791, 1746, 1439, 1259, 940, 791, 738, 698; EI-MS ( $m/z$ ): 328 (44), 170 (100), 130 (19), 91 (28); HRMS (EI): Exact mass calcd. for  $\text{C}_{25}\text{H}_{28}\text{N}_2\text{O}_3$   $[\text{M}]^+$ : 404.2100. Found: 404.2101.

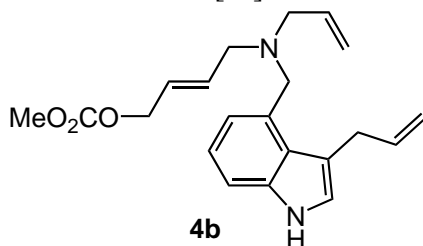


Viscous yellow oil, yield 74%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (br s, 1H), 7.24 (d,  $J = 8.1$  Hz, 1H), 7.15-7.05 (m, 2H), 6.83 (d,  $J = 7.5$  Hz, 1H), 6.50 (m, 1H), 5.85 (dt,  $J = 7.2, 15.6$  Hz, 1H), 5.75 (dt,  $J = 6.3, 15.6$  Hz, 1H), 4.57 (d,  $J = 6.3$  Hz, 2H), 3.78 (s, 3H), 3.67 (s, 6H), 3.57 (s, 2H), 2.62 (d,  $J = 7.2$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.4, 155.5, 135.7, 131.1, 128.5, 127.6, 123.9, 121.7, 120.8, 110.0, 101.1, 68.0, 59.2, 54.7, 52.3, 35.8, 35.7; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3383, 2954, 1750, 1720, 1448, 1273, 1199, 939, 755; EI-MS ( $m/z$ ): 389 ( $\text{M}^+$ , 22), 282 (9), 254 (16), 130 (100); HRMS (EI): Exact mass calcd. for  $\text{C}_{20}\text{H}_{23}\text{NO}_7$   $[\text{M}]^+$ : 389.1475. Found: 389.1476.

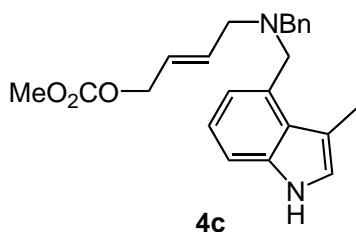


Viscous yellow oil, 65% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (br s, 1H), 7.31-7.06 (m, 8H), 6.87 (d,  $J = 2.1$  Hz, 1H), 6.07 (ddd,  $J = 6.0, 9.9, 16.2$  Hz, 1H), 5.90 (dt,  $J = 6.3, 15.6$  Hz, 1H), 5.70 (dt,  $J = 6.6, 15.3$  Hz, 1H), 5.04 (d,  $J = 9.9$  Hz, 1H), 4.97 (d,  $J = 17.1$  Hz, 1H), 4.57 (d,  $J = 6.3$  Hz, 2H), 3.96 (s, 2H), 3.75 (s, 3H),

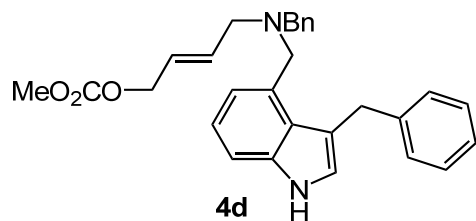
3.73 (d,  $J = 6.0$  Hz, 2H), 3.59 (s, 2H), 3.09 (d,  $J = 6.3$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 139.3, 138.5, 137.1, 133.4, 132.0, 128.9, 128.0, 126.7, 125.9, 125.7, 122.5, 121.5, 120.8, 115.1, 114.9, 110.2, 68.1, 57.8, 56.6, 54.7, 54.6, 31.5; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3415, 3027, 2954, 2794, 1745, 1441, 1259, 940, 741, 698; EI-MS ( $m/z$ ): 404 ( $\text{M}^+$ , 2), 209 (41), 168 (100), 154 (65), 91 (89); HRMS (EI): Exact mass calcd. for  $\text{C}_{25}\text{H}_{28}\text{N}_2\text{O}_3$  [ $\text{M}$ ] $^+$ : 404.2100. Found: 404.2095.



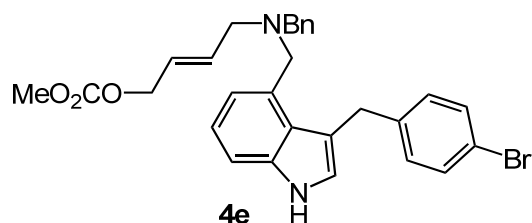
Viscous colorless oil, 72% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (br s, 1H), 7.21-7.17 (m, 1H), 7.09-7.07 (m, 2H), 6.87 (s, 1H), 6.17-6.04 (m, 1H), 5.93-5.82 (m, 2H), 5.72 (dt,  $J = 6.0, 15.6$  Hz, 1H), 5.19-4.97 (m, 4H), 4.57 (d,  $J = 6.0$  Hz, 2H), 3.91 (s, 2H), 3.76 (s, 3H), 3.74 (d,  $J = 8.1$  Hz, 2H), 3.12 (d,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 138.5, 137.1, 135.5, 133.6, 131.9, 125.8, 125.7, 122.5, 121.4, 120.9, 117.4, 115.0, 114.9, 110.2, 68.1, 56.4, 56.3, 54.7, 54.4, 31.5; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3411, 2955, 2810, 1748, 1442, 1269, 1113, 942, 792; ESI-MS ( $m/z$ ): 355 ( $\text{M}+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $\text{C}_{21}\text{H}_{27}\text{N}_2\text{O}_3$  [ $\text{M}+1$ ] $^+$ : 355.2016. Found: 355.2016.



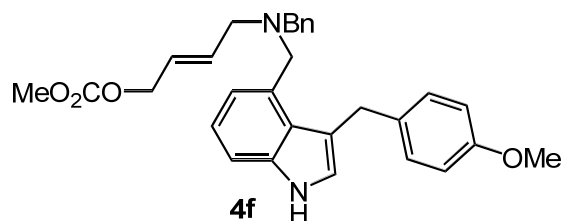
Viscous yellow oil, 45% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (br s, 1H), 7.32-7.05 (m, 8H), 6.86 (s, 1H), 5.92 (dt,  $J = 6.3, 15.6$  Hz, 1H), 5.72 (dt,  $J = 6.3, 15.6$  Hz, 1H), 4.57 (d,  $J = 6.0$  Hz, 2H), 4.01 (s, 2H), 3.75 (s, 3H), 3.62 (s, 2H), 3.11 (d,  $J = 6.0$  Hz, 2H), 2.49 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 139.4, 137.2, 133.5, 132.3, 128.8, 128.0, 126.6, 126.4, 125.9, 122.3, 121.5, 120.5, 112.1, 110.1, 68.1, 57.8, 56.3, 54.7, 13.3; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3412, 3027, 2952, 2795, 1745, 1441, 1259, 940, 736, 698; EI-MS ( $m/z$ ): 378 ( $\text{M}^+$ , 14), 302 (14), 236 (20), 144 (100), 91 (38); HRMS (EI): Exact mass calcd. for  $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_3$  [ $\text{M}$ ] $^+$ : 378.1943. Found: 378.1945.



Viscous colorless oil, 70% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (br s, 1H), 7.24-7.09 (m, 13H), 6.73 (m, 1H), 5.81 (dt,  $J = 6.0, 15.2$  Hz, 1H), 5.62 (dt,  $J = 6.0, 15.2$  Hz, 1H), 4.50 (d,  $J = 6.0$  Hz, 2H), 4.36 (s, 2H), 3.82 (s, 2H), 3.75 (s, 3H), 3.46 (s, 2H), 2.98 (d,  $J = 6.4$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 142.1, 139.4, 137.3, 133.4, 132.2, 128.8, 128.6, 128.3, 128.0, 126.6, 125.9, 125.7, 123.7, 121.8, 120.7, 115.6, 110.2, 68.1, 57.6, 56.5, 54.7, 54.5, 33.3; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3419, 3058, 3025, 2954, 2795, 1746, 1441, 1260, 940, 740, 698; ESI-MS ( $m/z$ ): 455 ( $\text{M}+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $\text{C}_{29}\text{H}_{31}\text{N}_2\text{O}_3$  [ $\text{M}+1$ ] $^+$ : 455.2329. Found: 455.2337.

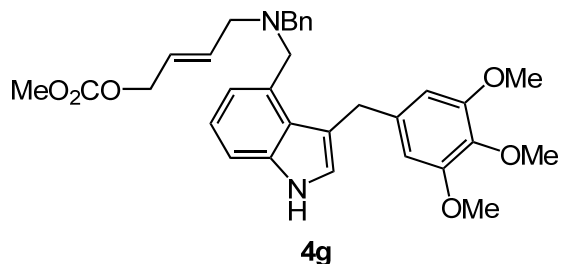


Viscous yellow oil, 40% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (br s, 1H), 7.33 (d,  $J = 8.1$  Hz, 2H), 7.23-7.06 (m, 8H), 6.97 (d,  $J = 8.1$  Hz, 2H), 6.66 (s, 1H), 5.80 (dt,  $J = 6.0, 15.3$  Hz, 1H), 5.62 (dt,  $J = 6.0, 15.3$  Hz, 1H), 4.51 (d,  $J = 5.7$  Hz, 2H), 4.26 (s, 2H), 3.76 (s, 2H), 3.73 (s, 3H), 3.44 (s, 2H), 2.97 (d,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 141.2, 139.2, 137.2, 133.1, 131.9, 131.2, 130.3, 128.8, 128.0, 126.6, 125.9, 125.6, 123.7, 121.7, 120.7, 119.3, 114.8, 110.2, 67.9, 57.6, 56.5, 54.6, 54.4, 32.6; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3416, 3026, 2954, 2798, 1744, 1486, 1441, 1260, 941, 791, 740, 698; ESI-MS ( $m/z$ ): 533 ( $\text{M}+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $\text{C}_{29}\text{H}_{30}\text{N}_2\text{O}_3\text{Br}$  [ $\text{M}+1$ ] $^+$ : 533.1434. Found: 533.1430.

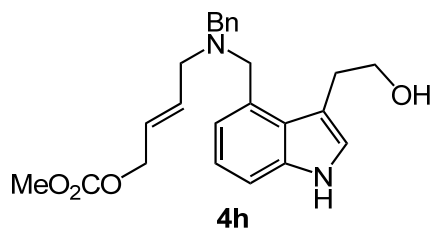


Viscous yellow oil, 60% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (br s, 1H), 7.26-7.06 (m, 10H), 6.81 (d,  $J = 8.7$  Hz, 2H), 6.75 (m, 1H), 5.83 (dt,  $J = 6.0, 15.3$  Hz,

1H), 5.65 (dt,  $J = 6.0, 15.3$  Hz, 1H), 4.52 (d,  $J = 6.0$  Hz, 2H), 4.30 (s, 2H), 3.83 (s, 2H), 3.78 (s, 3H), 3.76 (s, 3H), 3.48 (s, 2H), 3.01 (d,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  157.7, 155.6, 139.5, 137.3, 134.1, 133.4, 132.3, 129.5, 128.8, 128.0, 126.6, 125.9, 125.8, 123.5, 121.8, 120.6, 116.2, 113.6, 110.1, 68.1, 57.6, 56.5, 55.2, 54.7, 54.5, 32.5; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3418, 3027, 2951, 2833, 1745, 1509, 1441, 1244, 940, 740, 699; ESI-MS ( $m/z$ ): 485 ( $\text{M}+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $\text{C}_{30}\text{H}_{33}\text{N}_2\text{O}_4$  [ $\text{M}+1$ ] $^+$ : 485.2435. Found: 485.2450.

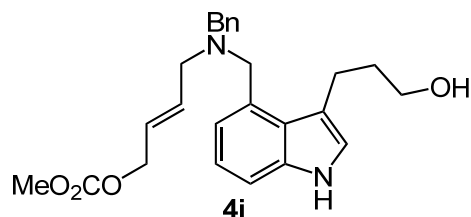


Viscous yellow oil, 74% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (br s, 1H), 7.29-7.09 (m, 8H), 6.75 (s, 1H), 6.45 (s, 2H), 5.86 (dt,  $J = 6.0, 15.6$  Hz, 1H), 5.66 (dt,  $J = 6.0, 15.3$  Hz, 1H), 4.54 (d,  $J = 6.3$  Hz, 2H), 4.33 (s, 2H), 3.90 (s, 2H), 3.85 (s, 3H), 3.76 (s, 9H), 3.53 (s, 2H), 3.05 (d,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 153.1, 139.4, 137.8, 137.3, 136.0, 133.3, 132.1, 128.8, 128.0, 126.7, 126.0, 125.8, 123.5, 121.7, 120.9, 115.9, 110.3, 105.7, 68.0, 60.9, 57.6, 56.7, 56.0, 54.7, 54.5, 33.9; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3373, 2937, 2835, 1748, 1589, 1505, 1455, 1266, 1125, 943, 745; ESI-MS ( $m/z$ ): 545 ( $\text{M}+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $\text{C}_{32}\text{H}_{37}\text{N}_2\text{O}_6$  [ $\text{M}+1$ ] $^+$ : 545.2646. Found: 545.2649.

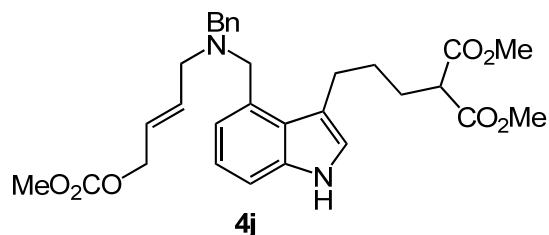


Viscous colorless oil, 72% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.45 (br s, 1H), 7.37-7.25 (m, 5H), 7.19 (d,  $J = 7.8$  Hz, 1H), 7.07-6.98 (m, 2H), 6.84 (d,  $J = 1.8$  Hz, 1H), 5.94 (dt,  $J = 6.6, 15.0$  Hz, 1H), 5.75 (dt,  $J = 6.3, 15.3$  Hz, 1H), 4.63 (br s, 1H), 4.58 (d,  $J = 6.3$  Hz, 2H), 3.91 (s, 2H), 3.76 (s, 3H), 3.73 (t,  $J = 6.0$  Hz, 2H), 3.61 (s, 2H), 3.09 (d,  $J = 6.6$  Hz, 2H), 2.81 (t,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 137.5, 137.0, 132.4, 130.0, 129.6, 128.2, 127.4, 127.3, 126.4, 123.1, 123.0, 121.1, 113.7, 111.2, 67.9, 64.8, 58.9, 57.4, 55.0, 54.7, 29.2; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) =

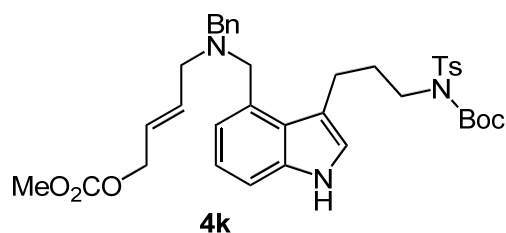
3406, 2954, 2827, 1748, 1443, 1269, 942, 748; ESI-MS ( $m/z$ ): 409 ( $M+1^+$ ); HRMS (ESI): Exact mass calcd. for  $C_{24}H_{29}N_2O_4$  [ $M+1$ ] $^+$ : 409.2122. Found: 409.2140.



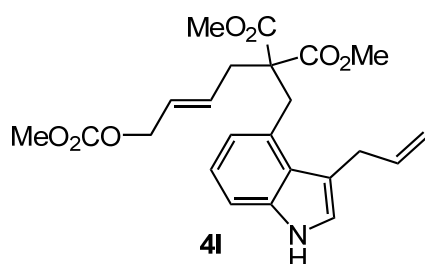
Viscous yellow oil, 62% yield.  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  8.12 (br s, 1H), 7.33-7.17 (m, 7H), 7.11 (d,  $J = 7.8$  Hz, 1H), 6.92 (d,  $J = 1.8$  Hz, 1H), 5.95 (dt,  $J = 6.3$ , 15.6 Hz, 1H), 5.73 (dt,  $J = 6.0$ , 15.6 Hz, 1H), 4.58 (d,  $J = 6.0$  Hz, 2H), 3.98 (s, 2H), 3.76 (s, 3H), 3.68 (t,  $J = 6.0$  Hz, 2H), 3.61 (s, 2H), 3.11 (d,  $J = 6.3$  Hz, 2H), 3.00 (t,  $J = 7.2$  Hz, 2H), 2.07 (br s, 1H), 1.94-1.85 (m, 2H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  155.6, 139.0, 137.0, 133.4, 131.7, 129.1, 128.0, 126.8, 126.2, 125.7, 121.8, 121.5, 121.2, 116.4, 110.3, 68.1, 62.1, 58.0, 56.8, 54.9, 54.8, 33.8, 22.9; IR (film):  $\nu_{max}$  ( $cm^{-1}$ ) = 3410, 2937, 2863, 1747, 1443, 1268, 941, 747; ESI-MS ( $m/z$ ): 423 ( $M+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $C_{25}H_{31}N_2O_4$  [ $M+1$ ] $^+$ : 423.2278. Found: 423.2294.



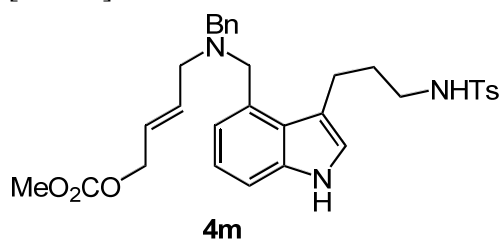
Viscous yellow oil, 30% yield.  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  8.17 (br s, 1H), 7.32-7.06 (m, 8H), 6.90 (d,  $J = 1.8$  Hz, 1H), 5.92 (dt,  $J = 6.3$ , 15.6 Hz, 1H), 5.74 (dt,  $J = 6.3$ , 15.6 Hz, 1H), 4.58 (d,  $J = 6.3$  Hz, 2H), 3.96 (s, 2H), 3.76 (s, 3H), 3.71 (s, 6H), 3.61 (s, 2H), 3.40 (t,  $J = 7.2$  Hz, 2H), 3.11 (d,  $J = 6.0$  Hz, 2H), 2.98 (t,  $J = 7.2$  Hz, 2H), 2.06-1.98 (m, 2H), 1.71-1.63 (m, 2H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  169.8, 155.5, 139.3, 137.0, 133.4, 131.9, 128.8, 128.0, 126.6, 125.9, 125.5, 121.7, 121.4, 120.6, 116.2, 110.2, 68.0, 57.7, 56.6, 54.6, 52.4, 51.6, 28.6, 28.5, 26.8; IR (film):  $\nu_{max}$  ( $cm^{-1}$ ) = 3406, 2953, 1748, 1439, 1267, 1155, 943; ESI-MS ( $m/z$ ): 537 ( $M+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $C_{30}H_{37}N_2O_7$  [ $M+1$ ] $^+$ : 537.2595. Found: 537.2601.



Viscous yellow oil, 58% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (br s, 1H), 7.76 (d,  $J = 8.4$  Hz, 2H), 7.34-7.18 (m, 9H), 7.11-7.05 (m, 1H), 7.01 (d,  $J = 2.1$  Hz, 1H), 5.93 (dt,  $J = 6.0, 15.0$  Hz, 1H), 5.73 (dt,  $J = 6.0, 15.3$  Hz, 1H), 4.58 (d,  $J = 6.0$  Hz, 2H), 4.01 (s, 2H), 3.96 (t,  $J = 7.8$  Hz, 2H), 3.74 (s, 3H), 3.64 (s, 2H), 3.13 (d,  $J = 6.0$  Hz, 2H), 3.04 (t,  $J = 7.5$  Hz, 2H), 2.38 (s, 3H), 2.21-2.11 (m, 2H), 1.29 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.4, 150.8, 143.9, 139.3, 137.3, 137.0, 133.3, 131.9, 129.1, 128.8, 127.9, 127.5, 126.5, 125.8, 125.6, 121.7, 121.3, 120.4, 115.7, 110.2, 83.9, 68.0, 57.6, 56.5, 54.6, 54.4, 46.9, 30.9, 27.7, 24.3, 21.4; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3405, 2954, 1747, 1728, 1441, 1351, 1267, 1155, 944, 751; ESI-MS ( $m/z$ ): 676 ( $\text{M}+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $\text{C}_{37}\text{H}_{46}\text{N}_3\text{O}_7\text{S}$  [ $\text{M}+1$ ] $^+$ : 676.3051. Found: 676.3052.



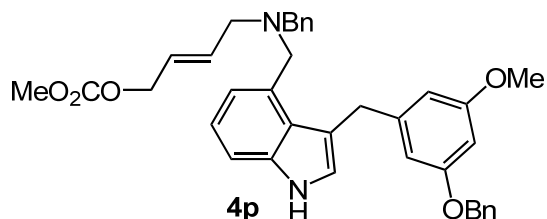
Viscous colorless oil, 72% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 (br s, 1H), 7.20 (d,  $J = 8.4$  Hz, 1H), 7.05 (dd,  $J = 7.2, 8.1$  Hz, 1H), 6.94 (d,  $J = 1.8$  Hz, 1H), 6.78 (d,  $J = 7.2$  Hz, 1H), 6.08 (ddd,  $J = 6.3, 12.0, 16.5$  Hz, 1H), 5.75 (dt,  $J = 6.9, 15.0$  Hz, 1H), 5.55 (dt,  $J = 6.3, 15.0$  Hz, 1H), 5.10-5.04 (m, 2H), 4.50 (d,  $J = 6.0$  Hz, 2H), 3.76 (s, 3H), 3.74 (s, 2H), 3.69 (d,  $J = 6.0$  Hz, 2H), 3.62 (s, 6H), 3.64 (d,  $J = 7.2$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  171.6, 155.5, 137.9, 137.3, 131.1, 128.8, 127.3, 126.1, 123.2, 121.7, 120.2, 115.6, 114.2, 110.0, 67.9, 59.2, 54.7, 52.3, 36.4, 34.6, 31.8; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3408, 2953, 1732, 1439, 1270, 1205, 1060, 942, 793; ESI-MS ( $m/z$ ): 447 ( $\text{M}+\text{H}_2\text{O}^+$ ); HRMS (MALDI): Exact mass calcd. for  $\text{C}_{23}\text{H}_{27}\text{NO}_7\text{Na}$  [ $\text{M}+\text{Na}$ ] $^+$ : 452.1680. Found: 452.1688.



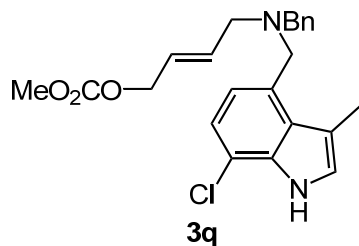
Viscous yellow oil, 65% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (br s, 1H), 7.68 (d,  $J = 8.1$  Hz, 2H), 7.27-7.15 (m, 9H), 7.09-7.03 (m, 1H), 6.80 (d,  $J = 1.5$  Hz, 1H), 5.86 (dt,  $J = 6.3, 15.6$  Hz, 1H), 5.68 (dt,  $J = 6.0, 15.6$  Hz, 1H), 5.09 (t,  $J = 6.0$  Hz, 1H), 4.54 (d,  $J = 6.0$  Hz, 2H), 3.86 (s, 2H), 3.74 (s, 3H), 3.54 (s, 2H), 3.04 (d,  $J = 6.3$  Hz,



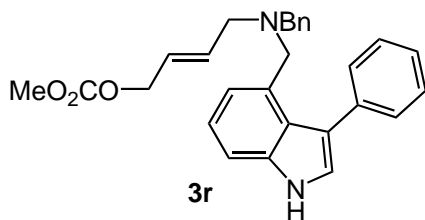
2H), 2.98-2.86 (m, 4H), 2.32 (s, 3H), 1.76-1.67 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 143.1, 139.1, 137.0, 136.8, 133.2, 131.5, 129.5, 128.8, 127.9, 126.8, 126.6, 126.0, 125.4, 122.1, 121.3, 120.7, 115.2, 110.3, 67.9, 57.7, 56.6, 54.7, 54.6, 42.5, 30.4, 23.6, 21.3; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3407, 2923, 1747, 1443, 1268, 1157, 943, 750; ESI-MS ( $m/z$ ): 576 ( $\text{M}+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $\text{C}_{32}\text{H}_{38}\text{N}_3\text{O}_5\text{S}$  [ $\text{M}+1$ ] $^+$ : 576.2527. Found: 576.2519.



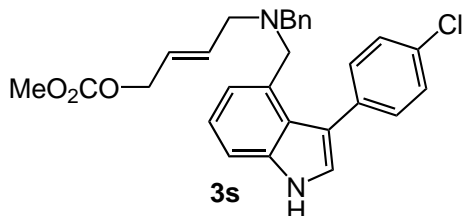
Viscous yellow oil, 42% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (br s, 1H), 7.44-7.06 (m, 13H), 6.79-6.76 (m, 2H), 6.66-6.60 (m, 2H), 5.84 (dt,  $J = 6.3, 15.6$  Hz, 1H), 5.65 (dt,  $J = 6.3, 15.6$  Hz, 1H), 5.10 (s, 2H), 4.52 (d,  $J = 6.0$  Hz, 2H), 4.29 (s, 2H), 3.85 (s, 2H), 3.77 (s, 3H), 3.73 (s, 3H), 3.49 (s, 2H), 3.01 (d,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 149.4, 146.2, 139.3, 137.3, 135.3, 133.3, 132.1, 128.7, 128.4, 128.0, 127.7, 127.2, 126.6, 125.9, 125.8, 123.5, 121.6, 120.6, 120.5, 115.9, 113.9, 112.5, 110.2, 71.0, 68.0, 57.5, 56.5, 55.8, 54.6, 54.4, 33.0; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3394, 3030, 2953, 2798, 1745, 1509, 1449, 1257, 1153, 941, 739, 697; ESI-MS ( $m/z$ ): 591 ( $\text{M}+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $\text{C}_{37}\text{H}_{39}\text{N}_2\text{O}_5$  [ $\text{M}+1$ ] $^+$ : 591.2854. Found: 591.2867.



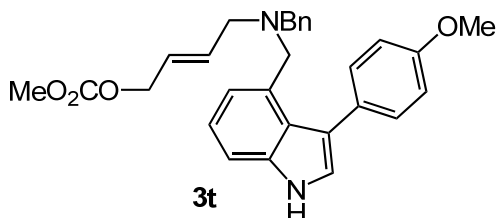
Viscous colorless oil, 50% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 (br s, 1H), 7.27-7.07 (m, 7H), 6.92 (s, 1H), 5.90 (dt,  $J = 6.0, 15.6$  Hz, 1H), 5.72 (dt,  $J = 6.0, 15.6$  Hz, 1H), 4.57 (d,  $J = 6.0$  Hz, 2H), 3.95 (s, 2H), 3.76 (s, 3H), 3.59 (s, 2H), 3.10 (d,  $J = 6.0$  Hz, 2H), 2.47 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 139.2, 134.1, 133.3, 131.3, 128.8, 128.1, 127.8, 126.7, 126.1, 123.0, 121.2, 120.7, 115.3, 113.4, 68.0, 57.7, 55.7, 54.7, 13.1; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3424, 2953, 2924, 2796, 1745, 1441, 1259, 1082, 940, 792, 698; EI-MS ( $m/z$ ): 412 ( $\text{M}^+$ , 13), 336 (13), 321 (18), 236 (27), 178 (100), 115 (30), 91 (92); HRMS (EI): Exact mass calcd. for  $\text{C}_{23}\text{H}_{25}\text{N}_2\text{O}_3\text{Cl}$  [ $\text{M}$ ] $^+$ : 412.1554. Found: 412.1557.



Viscous yellow oil, 52% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30 (br s, 1H), 7.38-7.29 (m, 6H), 7.21-7.13 (m, 7H), 6.96 (d,  $J = 2.4$  Hz, 1H), 5.67-5.53 (m, 2H), 4.50 (d,  $J = 5.4$  Hz, 2H), 3.73 (s, 3H), 3.64 (s, 2H), 3.31 (s, 2H), 2.78 (d,  $J = 5.1$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 139.3, 137.4, 136.3, 133.6, 132.5, 130.4, 128.6, 127.9, 127.5, 126.5, 126.3, 125.4, 124.6, 123.4, 122.0, 119.8, 118.9, 109.9, 68.1, 57.1, 55.6, 54.6, 54.2; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3416, 3056, 3027, 2954, 2797, 1745, 1442, 1260, 940, 750, 700; ESI-MS ( $m/z$ ): 441 ( $\text{M}+1^+$ ); HRMS (ESI): Exact mass calcd. for  $\text{C}_{28}\text{H}_{29}\text{N}_2\text{O}_3$  [ $\text{M}+1$ ] $^+$ : 441.2173. Found: 441.2169.



Viscous yellow oil, 64% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 (br s, 1H), 7.40-7.16 (m, 12H), 7.01 (d,  $J = 2.4$  Hz, 1H), 5.70-5.56 (m, 2H), 4.54 (d,  $J = 4.8$  Hz, 2H), 3.76 (s, 3H), 3.62 (s, 2H), 3.36 (s, 2H), 2.81 (d,  $J = 4.5$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 139.2, 136.3, 135.9, 133.6, 132.5, 131.5, 128.7, 128.0, 127.7, 126.6, 125.6, 124.5, 123.5, 122.3, 120.1, 117.8, 110.0, 68.1, 57.2, 55.7, 54.7, 54.3; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3406, 3027, 2955, 2797, 1744, 1442, 1260, 1112, 941, 750, 699; ESI-MS ( $m/z$ ): 475 ( $\text{M}+1^+$ ); HRMS (ESI): Exact mass calcd. for  $\text{C}_{28}\text{H}_{28}\text{ClN}_2\text{O}_3$  [ $\text{M}+1$ ] $^+$ : 475.1783. Found: 475.1782.

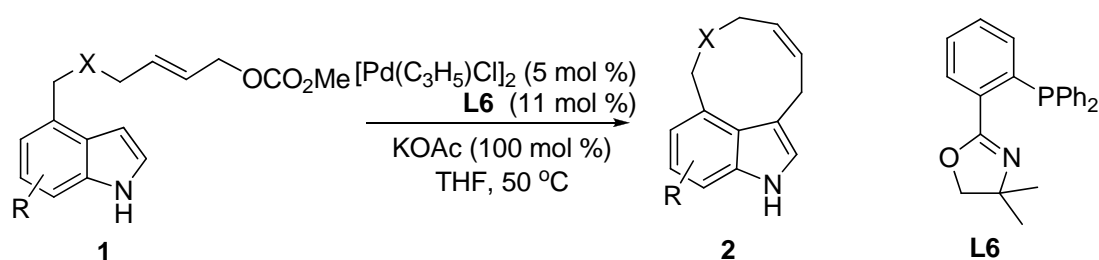


Viscous yellow oil, 68% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (br s, 1H), 7.40-7.16 (m, 10H), 7.04 (d,  $J = 2.1$  Hz, 1H), 6.92 (d,  $J = 8.4$  Hz, 2H), 5.74-5.56 (m, 2H), 4.53 (d,  $J = 5.7$  Hz, 2H), 3.86 (s, 3H), 3.76 (s, 3H), 3.63 (s, 2H), 3.37 (s, 2H), 2.83 (d,  $J = 5.1$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 155.6, 139.5, 136.3,

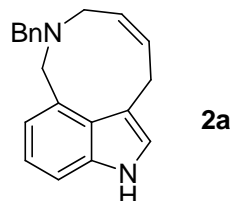
133.8, 132.8, 131.5, 129.7, 128.7, 128.0, 126.6, 125.5, 125.0, 123.2, 122.2, 119.8, 118.6, 113.0, 109.8, 68.2, 57.4, 55.4, 55.3, 54.7, 54.4; IR (film):  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 3414, 3027, 2955, 2796, 1745, 1549, 1442, 1261, 940, 750, 699; ESI-MS ( $m/z$ ): 471 ( $M+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_4$  [ $M+1$ ] $^+$ : 471.2278. Found: 471.2295.

### General Procedure for Palladium-Catalyzed Friedel-Crafts Type Allylic

#### Alkylation Reaction of Indole Fused through C3-C4:

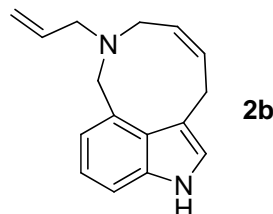


A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added  $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$  (3.7 mg, 0.010 mmol, 5 mol%), ligand **L6** (8.0 mg, 0.022 mmol, 11 mol%), THF (1 mL). The reaction mixture was stirred at rt for 30 min and then allyl carbonate **1** (0.20 mmol, dissolved in 1.0 mL THF), and KOAc (19.6 mg, 0.20 mmol, 100 mol%) were added. The reaction mixture was stirred at 50 °C for 1 h. After the reaction was complete (monitored by TLC), the crude reaction mixture was filtrated through a pad of celite and washed with EtOAc. The solvents were removed under reduced pressure. Then the residue was purified by silica gel column chromatography (PE/EA = 10/1) to afford the desired product **2**.

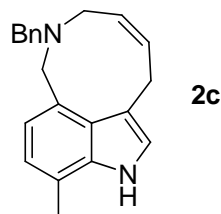


Colorless oil, yield 70%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (br s, 1H), 7.26-7.23 (m, 6H), 7.07 (t,  $J = 6.9$  Hz, 1H), 7.00 (s, 1H), 6.85 (d,  $J = 6.9$  Hz, 1H), 5.95 (dt,  $J = 7.2, 10.5$  Hz, 1H), 5.62 (dt,  $J = 5.7, 10.8$  Hz, 1H), 3.97 (s, 2H), 3.72 (d,  $J = 7.5$  Hz, 2H), 3.67 (s, 2H), 3.14 (d,  $J = 5.7$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  139.3, 137.8, 135.6, 133.5, 129.4, 128.3, 128.0, 126.8, 126.7, 123.4, 121.4, 120.4, 115.7, 110.2,

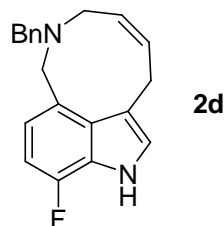
59.4, 56.4, 49.6, 30.0; IR (film):  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 3411, 3140, 2993, 2926, 1642, 1442, 1333, 1124, 740, 697; EI-MS ( $m/z$ ): 288 ( $M^+$ , 82), 197 (100), 183 (80), 181 (67), 154 (39), 130 (30), 91 (73); HRMS (EI): Exact mass calcd. for  $C_{20}H_{20}N_2$  [ $M$ ] $^+$ : 288.1626. Found: 288.1623.



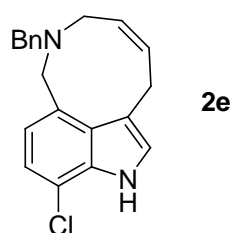
Colorless oil, yield 40%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (br s, 1H), 7.23 (d,  $J$  = 4.0 Hz, 1H), 7.07 (t,  $J$  = 7.8 Hz, 1H), 6.96 (d,  $J$  = 1.5 Hz, 1H), 6.86 (d,  $J$  = 7.2 Hz, 1H), 5.99-5.85 (m, 2H), 5.64 (dt,  $J$  = 6.4, 11.2 Hz, 1H), 5.17 (d,  $J$  = 17.2 Hz, 1H), 5.09 (d,  $J$  = 10.4 Hz, 1H), 3.94 (s, 2H), 3.74 (d,  $J$  = 6.8 Hz, 2H), 3.19-3.15 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  137.6, 136.6, 135.1, 132.6, 128.2, 126.2, 123.5, 121.5, 120.8, 117.2, 115.3, 110.3, 58.0, 55.5, 48.8, 30.1; IR (film):  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 3138, 2872, 2826, 1614, 1424, 1331, 1055, 1018, 925, 759, 707; EI-MS ( $m/z$ ): 238 ( $M^+$ , 100), 197 (60), 180 (96), 168 (88), 154 (90), 130 (94), 91 (39), 44 (66); HRMS (EI): Exact mass calcd. for  $C_{16}H_{18}N_2$  [ $M$ ] $^+$ : 238.1470. Found: 238.1476.



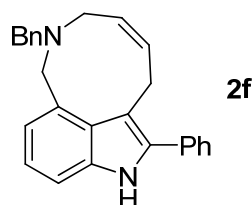
Colorless oil, yield 68%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (br s, 1H), 7.27-7.20 (m, 5H), 7.01 (d,  $J$  = 1.8 Hz, 1H), 6.89 (d,  $J$  = 6.9 Hz, 2H), 6.79 (d,  $J$  = 7.2 Hz, 2H), 5.94 (dt,  $J$  = 7.2, 10.8 Hz, 1H), 5.60 (dt,  $J$  = 6.0, 11.7 Hz, 1H), 3.96 (s, 2H), 3.72 (d,  $J$  = 7.2 Hz, 2H), 3.67 (s, 2H), 3.13 (d,  $J$  = 5.7 Hz, 2H), 2.45 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.4, 137.3, 135.5, 131.1, 129.4, 128.0, 127.8, 126.7, 123.1, 121.9, 120.6, 119.1, 116.3, 59.3, 56.2, 49.4, 30.0, 16.4; IR (film):  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 3418, 3021, 2920, 1609, 1493, 1349, 1260, 1109, 1034, 737, 699; ESI-MS ( $m/z$ ): 303 ( $[M+1]^+$ ); HRMS (ESI): Exact mass calcd. for  $C_{21}H_{23}N_2$  [ $M+1$ ] $^+$ : 303.1856. Found: 303.1852.



Colorless oil, yield 57%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (br s, 1H), 7.23-7.19 (m, 5H), 7.02 (s, 1H), 6.78-6.69 (m, 2H), 5.93 (dt,  $J = 7.2, 12.8$  Hz, 1H), 5.61 (dt,  $J = 5.6, 11.2$  Hz, 1H), 3.90 (s, 2H), 3.70 (d,  $J = 7.2$  Hz, 2H), 3.66 (s, 2H), 3.15 (d,  $J = 5.2$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.0 (d,  $J = 240.5$  Hz), 139.2, 135.4, 131.5 (d,  $J = 3.9$  Hz), 129.5 (d,  $J = 2.6$  Hz), 129.4, 128.0, 127.1, 126.8, 126.1 (d,  $J = 13.3$  Hz), 123.9, 119.7 (d,  $J = 6.0$  Hz), 116.8, 105.6 (d,  $J = 15.5$  Hz), 59.4, 56.0, 49.8, 29.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -138.6 (m); IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3108, 2846, 2815, 1576, 1452, 1335, 1240, 1156, 1022, 791, 736, 696; EI-MS ( $m/z$ ): 306 ( $\text{M}^+$ , 19), 215 (22), 199 (23), 186 (22), 172 (30), 148 (12), 91 (54), 84 (100); HRMS (EI): Exact mass calcd. for  $\text{C}_{20}\text{H}_{19}\text{N}_2\text{F}$  [ $\text{M}$ ] $^+$ : 306.1532. Found: 306.1534.

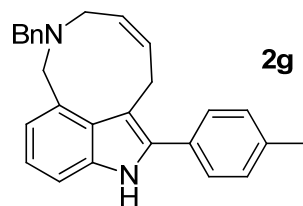


Colorless oil, yield 60%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 (br s, 1H), 7.22-7.20 (m, 5H), 7.06-7.04 (m, 2H), 6.75 (d,  $J = 7.6$  Hz, 2H), 5.93 (dt,  $J = 7.6, 12.8$  Hz, 1H), 5.61 (dt,  $J = 5.6, 10.8$  Hz, 1H), 3.91 (s, 2H), 3.69 (d,  $J = 7.6$  Hz, 2H), 3.65 (s, 2H), 3.14 (d,  $J = 5.6$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  139.1, 135.4, 134.8, 132.9, 129.4, 128.2, 128.0, 127.2, 126.8, 123.9, 120.7, 120.5, 117.1, 115.4, 59.5, 56.2, 49.9, 29.9; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3421, 3022, 2788, 1614, 1415, 1294, 1121, 1074, 786, 698; EI-MS ( $m/z$ ): 322 ( $\text{M}^+$ , 33), 231 (47), 217 (44), 190 (36), 180 (31), 164 (29), 91 (100), 84 (76); HRMS (EI): Exact mass calcd. for  $\text{C}_{20}\text{H}_{19}\text{N}_2\text{Cl}$  [ $\text{M}$ ] $^+$ : 322.1237. Found: 322.1241.

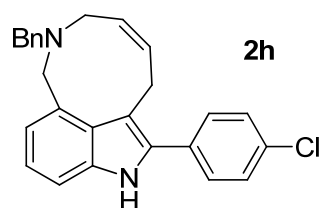


Colorless oil, yield 64%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (br s, 1H), 7.53-7.08 (m, 12H), 7.11 (t,  $J = 6.9$  Hz, 1H), 6.87 (d,  $J = 6.9$  Hz, 1H), 6.03 (dt,  $J = 6.9, 11.7$  Hz, 1H), 5.69 (dt,  $J = 5.7, 11.1$  Hz, 1H), 4.06 (s, 2H), 3.83 (d,  $J = 6.9$  Hz, 2H), 3.69 (s, 2H), 3.18 (d,  $J = 6.3$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  139.3, 136.7, 136.2, 134.9, 133.2, 132.7, 130.4, 129.3, 128.74, 128.68, 128.1, 127.8, 127.1, 126.8, 121.8, 121.6, 111.8, 110.0, 59.3, 55.8, 49.0, 28.4; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3414, 2920, 2787, 1603, 1489, 1449, 1331, 906, 730, 697; EI-MS ( $m/z$ ): 364 ( $\text{M}^+$ , 3), 273 (4), 230 (7), 91 (15),

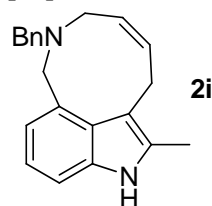
84 (100); HRMS (EI): Exact mass calcd. for  $C_{26}H_{24}N_2$   $[M]^+$ : 364.1939. Found: 364.1943.



Colorless oil, yield 68%.  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.98 (br s, 1H), 7.40 (d,  $J = 8.4$  Hz, 2H), 7.31-7.19 (m, 8H), 7.08 (t,  $J = 7.2$  Hz, 1H), 6.85 (d,  $J = 7.2$  Hz, 1H), 6.02 (dt,  $J = 6.6, 11.4$  Hz, 1H), 5.68 (dt,  $J = 6.3, 11.4$  Hz, 1H), 4.05 (s, 2H), 3.82 (d,  $J = 6.9$  Hz, 2H), 3.79 (s, 2H), 3.18 (d,  $J = 6.3$  Hz, 2H), 2.41 (s, 3H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  139.4, 137.6, 136.6, 136.3, 135.0, 132.7, 130.4, 130.3, 129.4, 129.3, 128.6, 128.0, 127.1, 126.7, 121.7, 121.5, 111.5, 109.9, 59.3, 55.8, 49.1, 28.5, 21.2; IR (film):  $\nu_{max}$  ( $cm^{-1}$ ) = 3412, 2918, 2785, 1497, 1430, 1332, 821, 740, 698; EI-MS ( $m/z$ ): 378 ( $M^+$ , 100), 337 (52), 287 (67), 271 (80), 244 (64), 220 (60), 91 (96); HRMS (EI): Exact mass calcd. for  $C_{27}H_{26}N_2$   $[M]^+$ : 378.2096. Found: 378.2100.

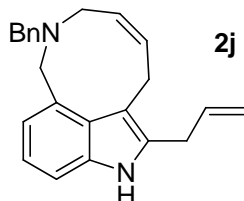


Colorless oil, yield 68%.  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.80 (br s, 1H), 7.41-7.07 (m, 10H), 7.10 (t,  $J = 7.2$  Hz, 1H), 6.86 (d,  $J = 7.2$  Hz, 1H), 5.98 (dt,  $J = 6.9, 11.4$  Hz, 1H), 5.68 (dt,  $J = 6.3, 11.4$  Hz, 1H), 4.03 (s, 2H), 3.79 (d,  $J = 6.9$  Hz, 2H), 3.67 (s, 2H), 3.16 (d,  $J = 6.0$  Hz, 2H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  139.3, 136.8, 134.9, 134.6, 133.7, 133.0, 131.6, 129.9, 129.2, 128.9, 128.4, 128.0, 127.4, 126.8, 122.1, 121.6, 112.3, 110.0, 59.4, 55.8, 49.1, 28.4; IR (film):  $\nu_{max}$  ( $cm^{-1}$ ) = 3403, 3023, 2922, 2789, 1484, 1429, 1091, 831, 739, 698; EI-MS ( $m/z$ ): 398 ( $M^+$ , 32), 357 (14), 307 (29), 293 (42), 264 (32), 240 (27), 91 (100); HRMS (EI): Exact mass calcd. for  $C_{26}H_{23}N_2Cl$   $[M]^+$ : 398.1550. Found: 398.1553.

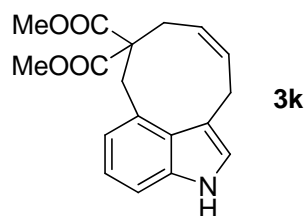


Colorless oil, yield 40%.  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.72 (br s, 1H), 7.28-7.14 (m, 6H), 7.00 (t,  $J = 7.5$  Hz, 1H), 6.80 (d,  $J = 7.2$  Hz, 1H), 5.93 (dt,  $J = 6.9, 11.1$  Hz, 1H), 5.60 (dt,  $J = 6.3, 11.4$  Hz, 1H), 3.99 (s, 2H), 3.67 (d,  $J = 6.9$  Hz, 2H), 3.66 (s, 2H),

3.13 (d,  $J = 6.0$  Hz, 2H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  139.5, 135.9, 135.1, 131.9, 131.4, 129.6, 129.3, 128.0, 126.7, 126.6, 121.0, 120.5, 110.7, 109.3, 59.2, 56.1, 49.1, 27.8, 12.0; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3357, 3013, 2911, 2795, 1609, 1381, 1253, 1062, 739, 699; EI-MS ( $m/z$ ): 302 ( $\text{M}^+$ , 55), 261 (21), 211 (51), 195 (49), 168 (56), 144 (35), 91 (100); HRMS (EI): Exact mass calcd. for  $\text{C}_{21}\text{H}_{22}\text{N}_2$  [ $\text{M}$ ] $^+$ : 302.1783. Found: 302.1782.

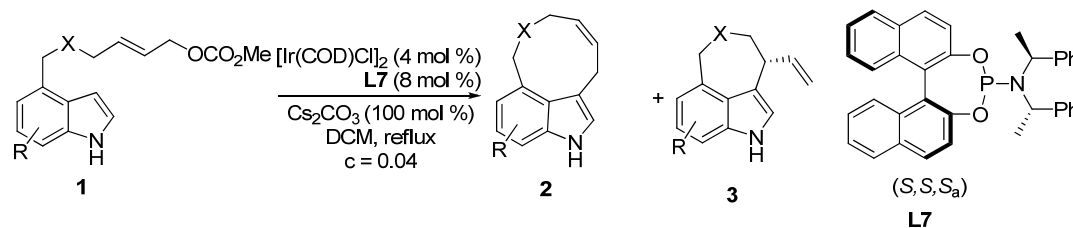


Colorless oil, yield 50%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (br s, 1H), 7.27-7.15 (m, 6H), 7.01 (t,  $J = 7.5$  Hz, 1H), 6.81 (d,  $J = 7.2$  Hz, 1H), 6.03-5.86 (m, 2H), 5.60 (dt,  $J = 6.3, 11.4$  Hz, 1H), 5.16 (d,  $J = 11.1$  Hz, 1H), 5.15 (d,  $J = 15.9$  Hz, 1H), 3.99 (s, 2H), 3.68 (d,  $J = 6.6$  Hz, 2H), 3.67 (s, 2H), 3.52 (d,  $J = 6.6$  Hz, 2H), 3.15 (d,  $J = 5.7$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  139.4, 136.1, 135.1, 132.7, 132.6, 129.6, 129.3, 128.0, 126.7, 120.9, 120.7, 117.0, 111.1, 109.5, 59.2, 56.3, 49.4, 30.8, 27.7; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3393, 2878, 2824, 1639, 1428, 1377, 1205, 1066, 978, 918, 741, 700; EI-MS ( $m/z$ ): 328 ( $\text{M}^+$ , 53), 287 (34), 237 (50), 223 (50), 180 (54), 167 (41), 91 (100); HRMS (EI): Exact mass calcd. for  $\text{C}_{23}\text{H}_{24}\text{N}_2$  [ $\text{M}$ ] $^+$ : 328.1939. Found: 328.1941.

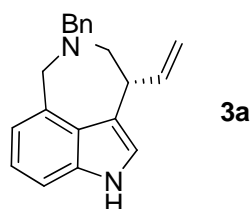


Colorless oil, yield 70%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (br s, 1H), 7.15 (d,  $J = 8.4$  Hz, 1H), 7.02 (t,  $J = 7.5$  Hz, 1H), 6.93 (s, 1H), 6.69 (d,  $J = 6.9$  Hz, 1H), 5.85-5.80 (m, 1H), 5.41-5.30 (m, 1H), 3.89-3.70 (m, 3H), 3.76 (s, 3H), 3.64 (s, 3H), 3.46-3.89 (m, 1H), 2.87 (dd,  $J = 11.1, 12.6$  Hz, 1H), 2.26 (dd,  $J = 7.5, 13.2$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  171.3, 171.2, 137.0, 132.8, 128.8, 128.1, 124.4, 122.7, 121.9, 120.6, 112.5, 110.5, 61.4, 52.4, 52.1, 34.8, 29.7, 27.6; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3409, 2952, 1726, 1430, 1287, 1193, 1177, 756, 746; EI-MS ( $m/z$ ): 313 ( $\text{M}^+$ , 100), 194 (39), 168 (33), 130 (55); HRMS (EI): Exact mass calcd. for  $\text{C}_{18}\text{H}_{19}\text{NO}_4$  [ $\text{M}$ ] $^+$ : 313.1314. Found: 313.1317.

### General Procedure for Iridium-Catalyzed Friedel-Crafts Type Allylic Alkylation Reaction of Indole Fused through C3-C4:



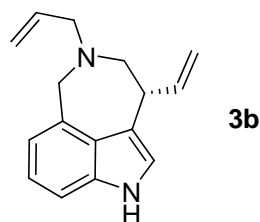
A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added  $[\text{Ir}(\text{COD})\text{Cl}]_2$  (5.4 mg, 0.008 mmol, 4 mol %), phosphoramidite ligand **L7** (8.6 mg, 0.016 mmol, 8 mol %), THF (1 mL) and propylamine (0.7 mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed *in vacuo* to give a pale yellow solid. After that, allyl carbonate **1** (0.20 mmol, dissolved in 5.0 mL DCM), and cesium carbonate (65 mg, 0.20 mmol, 100 mol %) were added. The reaction mixture was refluxed for 24 h. After the reaction was complete (monitored by TLC), the crude reaction mixture was filtrated through a pad of celite and washed with EtOAc. The solvents were removed under reduced pressure. The **2/3** ratio was determined by  $^1\text{H}$  NMR of the crude reaction mixture. Then the residue was purified by silica gel column chromatography (PE/EA = 10/1) to afford the desired product **3**.



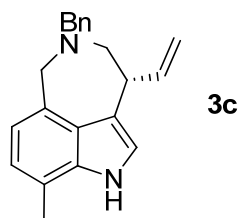
Yellow oil, 60% yield, **2a/3a**: 2/98, 94% ee. [Daicel CHIRALCEL OJ-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 80/20; flow rate = 0.7 mL/min; detection wavelength = 214 nm;  $t_{\text{R}}$  = 18.15 (minor), 22.10 (major) min].  $[\alpha]_{\text{D}}^{20} = -47.1$  ( $c$  0.5,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (br s, 1H), 7.36-7.18 (m, 6H), 7.09 (t,  $J = 7.2$  Hz, 1H), 6.91 (s, 1H), 6.78 (d,  $J = 6.9$  Hz, 1H), 5.83 (ddd,  $J = 9.0, 17.1, 18.6$  Hz, 1H), 5.10 (d,  $J = 17.1$  Hz, 1H), 5.05 (d,  $J = 10.2$  Hz, 1H), 4.26 (AB,  $J_{\text{AB}} = 16.5$  Hz, 1H), 4.17 (BA,  $J_{\text{BA}} = 16.5$  Hz, 1H), 3.97-3.82 (m, 3H), 3.30 (dd,  $J = 4.2, 13.5$  Hz, 1H), 3.08 (dd,  $J = 11.1, 13.5$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 139.4, 136.5, 134.5, 128.9, 128.2, 126.9, 125.0, 122.8, 121.8, 118.1, 117.5, 114.8, 109.1, 61.1, 60.9, 58.1, 43.4;



IR (film):  $\nu_{\max}$  (cm<sup>-1</sup>) = 3382, 2921, 1634, 1495, 1432, 1353, 1332, 1108, 1009, 905, 753, 695; EI-MS (m/z): 288 (M<sup>+</sup>, 7), 197 (69), 168 (100), 154 (52), 91 (54); HRMS (EI): Exact mass calcd. for C<sub>20</sub>H<sub>20</sub>N<sub>2</sub> [M]<sup>+</sup>: 288.1626. Found: 288.1622.

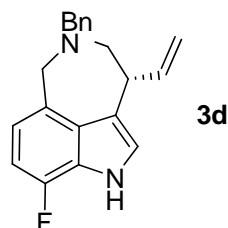


Yellow oil, 51% yield, **2b/3b**: 1/99, 94% ee. [Daicel CHIRALCEL OJ-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 80/20; flow rate = 0.7 mL/min; detection wavelength = 214 nm;  $t_R$  = 10.99 (minor), 13.30 (major) min].  $[\alpha]_D^{20}$  = -19.5 (c 0.5, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.25 (br s, 1H), 7.19 (d,  $J$  = 7.8 Hz, 1H), 7.09 (t,  $J$  = 7.2 Hz, 1H), 6.90 (s, 1H), 6.84 (d,  $J$  = 7.2 Hz, 1H), 6.05-5.79 (m, 2H), 5.22-5.07 (m, 4H), 4.26 (AB,  $J_{AB}$  = 16.5 Hz, 1H), 4.20 (BA,  $J_{BA}$  = 16.5 Hz, 1H), 3.83-3.77 (m, 1H), 3.44 (dd,  $J$  = 6.0, 13.5 Hz, 1H), 3.35 (dd,  $J$  = 6.6, 13.5 Hz, 1H), 3.27 (dd,  $J$  = 4.5, 13.5 Hz, 1H), 2.98 (dd,  $J$  = 10.5, 13.5 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.1, 136.7, 136.1, 134.0, 124.9, 122.8, 121.7, 118.0, 117.45, 117.40, 114.8, 109.0, 61.7, 61.0, 58.4, 43.5; IR (film):  $\nu_{\max}$  (cm<sup>-1</sup>) = 3136, 2894, 2736, 1642, 1440, 1358, 1112, 1021, 926, 744; EI-MS (m/z): 238 (M<sup>+</sup>, 10), 197 (43), 168 (100), 154 (62), 127 (19), 115 (31); HRMS (EI): Exact mass calcd. for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub> [M]<sup>+</sup>: 238.1470. Found: 238.1472.

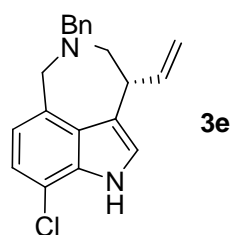


Yellow oil, 46% yield, **2c/3c**: 1/99, 94% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 90/10; flow rate = 0.7 mL/min; detection wavelength = 254 nm;  $t_R$  = 12.56 (minor), 10.40 (major) min].  $[\alpha]_D^{20}$  = -52.7 (c 0.5, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 (br s, 1H), 7.36-7.21 (m, 5H), 6.94-6.89 (m, 2H), 6.71 (d,  $J$  = 7.2 Hz, 1H), 5.82 (ddd,  $J$  = 9.3, 16.8, 19.2 Hz, 1H), 5.11 (dd,  $J$  = 1.2, 17.1 Hz, 1H), 5.04 (dd,  $J$  = 1.8, 11.2 Hz, 1H), 4.24 (AB,  $J_{AB}$  = 16.2 Hz, 1H), 4.14 (BA,  $J_{BA}$  = 16.2 Hz, 1H), 3.96-3.82 (m, 3H), 3.29 (dd,  $J$  = 4.5, 13.8 Hz, 1H), 3.08 (dd,  $J$  = 10.8, 13.8 Hz, 1H), 2.45 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.1, 139.5, 136.0, 132.2, 128.9, 128.2, 126.9, 124.6, 122.5, 122.3, 118.8, 118.0, 117.6, 114.8, 61.3, 60.7, 58.0, 43.3, 16.3; IR (film):  $\nu_{\max}$  (cm<sup>-1</sup>) = 3411, 2846, 1635, 1453, 1331, 1147, 1126, 913,

757, 694; ESI-MS ( $m/z$ ): 303 ( $[M+1]^+$ ); HRMS (ESI): Exact mass calcd. for  $C_{21}H_{23}N_2$   $[M]^+$ : 303.1856. Found: 303.1851.

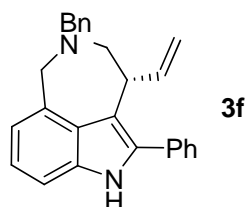


Yellow oil, 64% yield, **2d/3d**: 4/96, 93% ee. [Daicel CHIRALCEL IC (0.46 cm x 25 cm); *n*-hexane/2-propanol = 95/5; flow rate = 0.3 mL/min; detection wavelength = 214 nm;  $t_R$  = 15.93 (minor), 17.28 (major) min].  $[\alpha]_D^{20}$  = -32.4 (c 0.5,  $CHCl_3$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  8.39 (br s, 1H), 7.35-7.21 (m, 5H), 6.92 (s, 1H), 6.87-5.75 (m, 1H), 6.64 (dd,  $J$  = 4.8, 7.8 Hz, 1H), 5.81 (ddd,  $J$  = 6.6, 16.8, 18.3 Hz, 1H), 5.12 (d,  $J$  = 18.3 Hz, 1H), 5.06 (d,  $J$  = 10.5 Hz, 1H), 4.19 (AB,  $J_{AB}$  = 16.2 Hz, 1H), 4.12 (BA,  $J_{BA}$  = 16.2 Hz, 1H), 3.95-3.81 (m, 3H), 3.28 (dd,  $J$  = 4.2, 13.8 Hz, 1H), 3.06 (dd,  $J$  = 10.8, 13.8 Hz, 1H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  148.2 (d,  $J$  = 240.3 Hz), 139.7, 139.3, 130.1 (d,  $J$  = 3.5 Hz), 128.9, 128.4 (d,  $J$  = 4.7 Hz), 128.2, 127.0, 124.6 (d,  $J$  = 13.4 Hz), 123.5, 119.1, 117.2 (d,  $J$  = 5.8 Hz), 115.1, 106.2 (d,  $J$  = 16.2 Hz), 61.2, 60.3, 58.2, 43.3;  $^{19}F$  NMR (282 MHz,  $CDCl_3$ )  $\delta$  -139.6 (m); IR (film):  $\nu_{max}$  ( $cm^{-1}$ ) = 3121, 2845, 1633, 1583, 1441, 1237, 1142, 1082, 904, 742, 698; EI-MS ( $m/z$ ): 306 ( $M^+$ , 10), 215 (68), 186 (100), 172 (63), 91 (69); HRMS (EI): Exact mass calcd. for  $C_{20}H_{19}N_2F$   $[M]^+$ : 306.1532. Found: 306.1530.

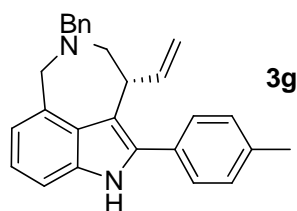


Yellow oil, 62% yield, **2e/3e**: 6/94, 93% ee. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 90/10; flow rate = 0.7 mL/min; detection wavelength = 214 nm;  $t_R$  = 9.81 (minor), 11.92 (major) min].  $[\alpha]_D^{20}$  = -50.7 (c 0.5,  $CHCl_3$ ).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.34 (br s, 1H), 7.35-7.08 (m, 5H), 7.08 (d,  $J$  = 8.0 Hz, 1H), 6.98 (t,  $J$  = 1.5 Hz, 1H), 6.70 (d,  $J$  = 7.6 Hz, 1H), 5.81 (ddd,  $J$  = 8.4, 10.0, 17.2 Hz, 1H), 5.12 (d,  $J$  = 17.2 Hz, 1H), 5.06 (d,  $J$  = 10.0 Hz, 1H), 4.20 (AB,  $J_{AB}$  = 16.0 Hz, 1H), 4.12 (BA,  $J_{BA}$  = 16.0 Hz, 1H), 3.94-3.81 (m, 3H), 3.28 (dd,  $J$  = 4.4, 14.0 Hz, 1H), 3.08 (dd,  $J$  = 10.0, 14.0 Hz, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  139.7, 139.3, 135.2, 133.6, 128.9, 128.2, 127.0, 126.5, 125.0, 123.4, 121.0, 119.5, 118.2, 115.2,

114.3, 61.2, 60.4, 58.3, 43.5; IR (film):  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 3147, 2773, 1638, 1447, 1330, 1129, 1073, 1033, 915, 740, 698; EI-MS ( $m/z$ ): 322 ( $M^+$ , 9), 231 (75), 202 (60), 188 (44), 168 (55), 91 (100); HRMS (EI): Exact mass calcd. for  $\text{C}_{20}\text{H}_{19}\text{N}_2\text{Cl}$  [ $M$ ] $^+$ : 322.1237. Found: 322.1240.

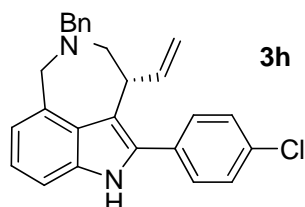


Yellow oil, 78% yield, **2f/3f**: 2/98, 94% ee. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 99/1; flow rate = 0.7 mL/min; detection wavelength = 214 nm;  $t_R$  = 67.72 (minor), 62.29 (major) min].  $[\alpha]_D^{20}$  = -73.2 (c 0.1,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 (br s, 1H), 7.54 (d,  $J$  = 7.2 Hz, 2H), 7.41-7.17 (m, 9H), 7.07 (t,  $J$  = 7.8 Hz, 1H), 6.77 (d,  $J$  = 6.9 Hz, 1H), 5.92 (ddd,  $J$  = 6.6, 10.5, 17.4 Hz, 1H), 4.83 (d,  $J$  = 10.2 Hz, 1H), 4.66 (d,  $J$  = 17.4 Hz, 1H), 4.30 (d,  $J$  = 15.9 Hz, 1H), 3.98-3.79 (m, 4H), 3.25 (dd,  $J$  = 5.4, 13.5 Hz, 1H), 3.11 (dd,  $J$  = 3.0, 13.5 Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  142.0, 139.6, 136.1, 134.5, 133.8, 133.5, 129.1, 128.4, 128.2, 128.1, 127.5, 126.9, 121.8, 117.9, 114.2, 114.1, 108.5, 63.1, 62.4, 61.7, 42.8; IR (film):  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 3406, 3057, 2849, 1633, 1491, 1449, 1334, 1260, 1047, 749, 696; EI-MS ( $m/z$ ): 364 ( $M^+$ , 3), 273 (85), 244 (100), 230 (41), 91 (28); HRMS (EI): Exact mass calcd. for  $\text{C}_{26}\text{H}_{24}\text{N}_2$  [ $M$ ] $^+$ : 364.1939. Found: 364.1930.

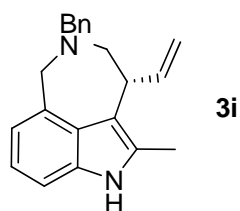


Yellow oil, 76% yield, **2g/3g**: 1/99, 91% ee. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 95/5; flow rate = 0.5 mL/min; detection wavelength = 230 nm;  $t_R$  = 27.79 (minor), 30.21 (major) min].  $[\alpha]_D^{20}$  = +24.2 (c 0.5,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (br s, 1H), 7.46-7.38 (m, 4H), 7.31-7.16 (m, 6H), 7.05 (t,  $J$  = 8.1 Hz, 1H), 6.76 (d,  $J$  = 7.2 Hz, 1H), 5.93 (ddd,  $J$  = 6.6, 10.2, 16.8 Hz, 1H), 4.85 (d,  $J$  = 9.9 Hz, 1H), 4.68 (d,  $J$  = 17.1 Hz, 1H), 4.30 (d,  $J$  = 15.9 Hz, 1H), 3.98-3.84 (m, 4H), 3.25 (dd,  $J$  = 5.4, 12.9 Hz, 1H), 3.13 (dd,  $J$  = 5.7, 13.2 Hz, 1H), 2.36 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  142.2, 139.7, 137.3, 136.0, 134.6, 133.7, 130.5, 129.2, 129.1, 128.1, 128.0, 127.0, 126.9, 121.7, 117.8, 114.2, 113.7, 108.4,

63.1, 62.4, 61.7, 42.8, 21.2; IR (film):  $\nu_{\max}$  (cm<sup>-1</sup>) = 3410, 3057, 2925, 1723, 1501, 1442, 1256, 1089, 820, 779, 698; EI-MS (m/z): 378 (M<sup>+</sup>, 7), 287 (100), 258 (80), 244 (34), 91 (28); HRMS (EI): Exact mass calcd. for C<sub>27</sub>H<sub>26</sub>N<sub>2</sub> [M]<sup>+</sup>: 378.2096. Found: 378.2098.

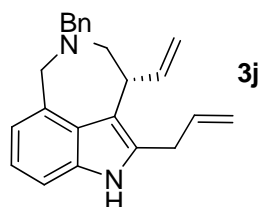


Yellow oil, 68% yield, **2h/3h**: 2/98, 91% ee. [Sino-Chiral OD (0.46 cm x 25 cm); *n*-hexane/ethanol = 98/2; flow rate = 1.0 mL/min; detection wavelength = 214 nm;  $t_R$  = 20.15 (minor), 22.92 (major) min].  $[\alpha]_D^{20}$  = +24.8 (c 0.4, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.12 (br s, 1H), 7.48-7.05 (m, 11H), 6.77 (d,  $J$  = 7.5 Hz, 1H), 5.89 (ddd,  $J$  = 6.6, 10.2, 16.8 Hz, 1H), 4.85 (d,  $J$  = 9.9 Hz, 1H), 4.65 (d,  $J$  = 17.1 Hz, 1H), 4.28 (d,  $J$  = 16.2 Hz, 1H), 3.98-3.84 (m, 4H), 3.24 (dd,  $J$  = 5.7, 13.2 Hz, 1H), 3.11 (dd,  $J$  = 3.3, 13.5 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  141.9, 139.6, 136.3, 134.0, 133.4, 133.3, 131.9, 129.4, 129.1, 128.6, 128.1, 126.9, 126.8, 122.1, 118.0, 114.6, 114.5, 108.6, 63.1, 62.4, 61.7, 42.9; IR (film):  $\nu_{\max}$  (cm<sup>-1</sup>) = 3400, 3047, 2925, 1736, 1482, 1450, 1088, 1014, 917, 829, 763, 702; EI-MS (m/z): 398 (M<sup>+</sup>, 4), 307 (82), 278 (100), 91 (79); HRMS (EI): Exact mass calcd. for C<sub>26</sub>H<sub>23</sub>N<sub>2</sub>Cl [M]<sup>+</sup>: 398.1550. Found: 398.1548.



Yellow oil, 40% yield, **2i/3i**: 1/99, 95% ee. [Daicel CHIRALCEL OJ-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 90/10; flow rate = 0.5 mL/min; detection wavelength = 230 nm;  $t_R$  = 23.63 (major), 27.96 (minor) min].  $[\alpha]_D^{20}$  = -64.0 (c 0.5, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (br s, 1H), 7.36 (d,  $J$  = 7.2 Hz, 2H), 7.30-7.20 (m, 3H), 7.10 (d,  $J$  = 8.4 Hz, 1H), 6.98 (t,  $J$  = 7.2 Hz, 1H), 6.71 (d,  $J$  = 7.2 Hz, 1H), 5.93 (ddd,  $J$  = 8.0, 10.4, 17.2 Hz, 1H), 4.93 (d,  $J$  = 10.0 Hz, 1H), 4.92 (d,  $J$  = 17.2 Hz, 1H), 4.23 (d,  $J$  = 16.0 Hz, 1H), 3.99 (d,  $J$  = 16.0 Hz, 1H), 3.85 (s, 2H), 3.65-3.60 (m, 1H), 3.25-3.15 (m, 2H), 2.28 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.6, 139.7, 135.3, 132.9, 131.8, 129.0, 128.1, 126.8, 126.2, 120.4, 117.3, 113.2, 112.0, 107.9, 62.7, 62.4,

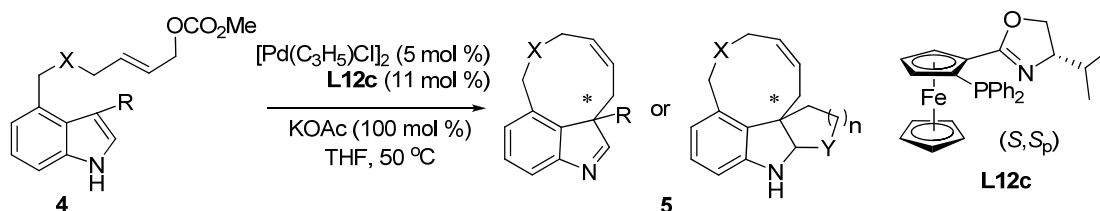
62.1, 43.6, 12.6; IR (film):  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 3396, 3059, 2930, 1632, 1450, 1329, 1144, 1062, 994, 907, 732, 697; EI-MS ( $m/z$ ): 302 ( $M^+$ , 7), 211 (89), 182 (84), 168 (88), 91 (54), 57 (100); HRMS (EI): Exact mass calcd. for  $C_{21}H_{22}N_2$  [ $M$ ] $^+$ : 302.1783. Found: 302.1781.



Yellow oil, 60% yield, **2i/3i**: 1/99, 97% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 90/10; flow rate = 0.5 mL/min; detection wavelength = 230 nm;  $t_R$  = 14.19 (major), 21.05 (minor) min].  $[\alpha]_D^{20}$  = -47.6 (c 0.5,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (br s, 1H), 7.38-7.21 (m, 5H), 7.12 (d,  $J$  = 7.8 Hz, 1H), 7.00 (t,  $J$  = 7.5 Hz, 1H), 6.72 (d,  $J$  = 7.2 Hz, 1H), 6.02-5.85 (m, 2H), 5.17 (d,  $J$  = 17.7 Hz, 1H), 5.15 (d,  $J$  = 9.9 Hz, 1H), 4.94 (d,  $J$  = 11.1 Hz, 1H), 4.93 (d,  $J$  = 16.2 Hz, 1H), 4.25 (d,  $J$  = 16.2 Hz, 1H), 4.00 (d,  $J$  = 16.2 Hz, 1H), 3.85 (s, 2H), 3.70-3.64 (m, 1H), 3.45 (d,  $J$  = 6.3 Hz, 2H), 3.21-3.18 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  141.9, 139.8, 135.5, 134.7, 133.3, 133.1, 129.0, 128.1, 126.9, 126.1, 120.7, 117.33, 117.25, 113.3, 112.2, 108.1, 62.7, 62.4, 62.1, 43.4, 31.3; IR (film):  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 3373, 3059, 3027, 2929, 1639, 1625, 1447, 1431, 1347, 1140, 1061, 1026, 913, 748, 697; EI-MS ( $m/z$ ): 328 ( $M^+$ , 8), 237 (100), 208 (40), 168 (36), 91 (45); HRMS (EI): Exact mass calcd. for  $C_{23}H_{24}N_2$  [ $M$ ] $^+$ : 328.1939. Found: 328.1943.

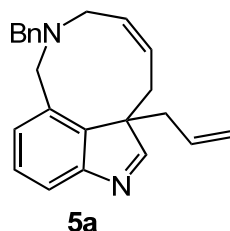
## General Procedure for Palladium-Catalyzed Allylic Dearomatization of Indole

### Fused through C3-C4:

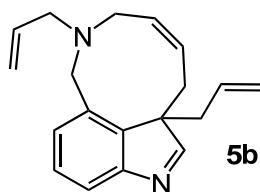


A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added  $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$  (3.7 mg, 0.010 mmol, 5 mol%), ligand **L12c** (11.2 mg, 0.022 mmol, 11 mol%), and THF (1 mL). The reaction mixture was stirred at rt for 30 min and then allyl carbonate **4** (0.20 mmol, dissolved in 1.0 mL THF), and

KOAc (19.6 mg, 0.20 mmol, 100 mol%) were added. The reaction mixture was stirred at 50 °C. After the reaction was complete (monitored by TLC), the crude reaction mixture was filtrated through a pad of celite and washed with EtOAc. The solvents were removed under reduced pressure. Then the residue was purified by silica gel column chromatography (PE/EA = 4/1) to afford the desired product **5**.

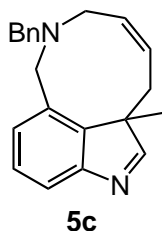


Colorless oil, 74% yield, 78% ee. [Daicel CHIRALPAK IC (0.46 cm x 25 cm); *n*-hexane/2-propanol = 95/5; flow rate = 0.5 mL/min; detection wavelength = 230nm;  $t_R$  = 31.54 (major), 29.29 (minor) min].  $[\alpha]_D^{20} = -57.1$  (c 0.5, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (s, 1H), 7.55 (d,  $J$  = 7.2 Hz, 1H), 7.47-7.25 (m, 6H), 7.08 (d,  $J$  = 7.5 Hz, 1H), 6.01-5.90 (m, 2H), 5.37-5.23 (m, 1H), 5.97 (d,  $J$  = 17.1 Hz, 1H), 4.87 (d,  $J$  = 9.9 Hz, 1H), 4.03 (d,  $J$  = 13.5 Hz, 1H), 3.69-3.56 (m, 3H), 2.98-2.95 (m, 1H), 2.84-2.76 (m, 2H), 2.66-2.58 (m, 2H), 2.10-2.00 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  178.9, 155.4, 140.7, 139.4, 133.1, 132.4, 130.0, 129.8, 128.8, 128.3, 127.7, 127.1, 120.5, 118.1, 63.4, 58.9, 51.5, 46.6, 35.9, 28.0; IR (film):  $\nu_{max}$  (cm<sup>-1</sup>) = 3019, 2923, 2833, 1567, 1474, 1262, 1113, 915, 738; EI-MS (*m/z*): 328 (27, M<sup>+</sup>), 287 (47), 223 (59), 180 (27), 167 (27), 115 (21), 91 (100); HRMS (EI): Exact mass calcd. for C<sub>23</sub>H<sub>24</sub>N<sub>2</sub> [M]<sup>+</sup>: 328.1939. Found: 328.1933.

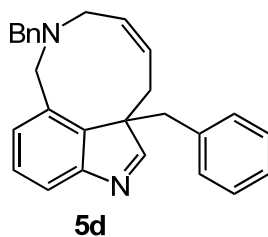


Colorless oil, 56% yield, 76% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 95/5; flow rate = 0.5 mL/min; detection wavelength = 230nm;  $t_R$  = 14.38 (major), 10.87 (minor) min].  $[\alpha]_D^{20} = -98.8$  (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.94 (s, 1H), 7.56 (d,  $J$  = 7.6 Hz, 1H), 7.33 (t,  $J$  = 8.0 Hz, 1H), 7.16 (d,  $J$  = 7.6 Hz, 1H), 6.04-5.86 (m, 3H), 5.35-5.21 (m, 3H), 4.99 (d,  $J$  = 18.0 Hz, 1H), 4.88 (d,  $J$  = 10.0 Hz, 1H), 3.66 (AB,  $J_{AB}$  = 12.8 Hz, 1H), 3.61 (BA,  $J_{BA}$  = 12.8 Hz, 1H), 3.49 (dd,  $J$  = 5.6, 13.2 Hz, 1H), 3.16 (dd,  $J$  = 6.8, 13.2 Hz, 1H), 3.04-3.01 (m, 1H), 2.82-2.58 (m, 4H), 2.08-1.00 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  178.9, 155.5,

140.7, 136.5, 132.9, 132.5, 129.9, 129.8, 128.5, 127.8, 120.5, 118.2, 117.7, 63.4, 57.9, 51.6, 46.5, 35.9, 28.0; IR (film):  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 3073, 2921, 2850, 1640, 1568, 1457, 1443, 1120, 992, 918, 753; EI-MS ( $m/z$ ): 278 ( $M^+$ , 30), 237 (81), 180 (91), 167 (100), 154 (68), 115 (72); HRMS (EI): Exact mass calcd. for  $C_{19}H_{22}N_2$  [ $M$ ] $^+$ : 278.1783. Found: 278.1782.

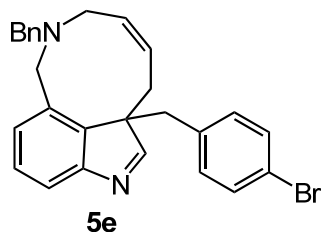


Colorless oil, 62% yield, 74% ee. [Daicel CHIRALCEL OJ-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 90/10; flow rate = 0.5 mL/min; detection wavelength = 214nm;  $t_R$  = 12.62 (major), 20.41 (minor) min].  $[\alpha]_D^{20}$  = -17.3 (c 0.5,  $CHCl_3$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.88 (s, 1H), 7.57 (d,  $J$  = 7.8 Hz, 1H), 7.47-7.26 (m, 6H), 7.10 (d,  $J$  = 7.8 Hz, 1H), 6.03-5.90 (m, 2H), 4.04 (d,  $J$  = 12.9 Hz, 1H), 3.74-3.58 (m, 3H), 2.98-2.95 (m, 1H), 2.84-2.76 (m, 1H), 2.63-2.55 (m, 1H), 2.10-2.00 (m, 1H), 1.39 (s, 3H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  180.4, 154.9, 142.6, 139.4, 133.0, 129.9, 129.7, 128.9, 128.7, 128.4, 127.6, 127.1, 120.5, 59.2, 59.0, 51.4, 46.5, 28.9, 16.6; IR (film):  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 3004, 2925, 2852, 2788, 1571, 1455, 1358, 1071, 873, 756; ESI-MS ( $m/z$ ): 303 ( $M+1^+$ ); HRMS (ESI): Exact mass calcd. for  $C_{21}H_{23}N_2$  [ $M$ ] $^+$ : 303.1856. Found: 303.1852.

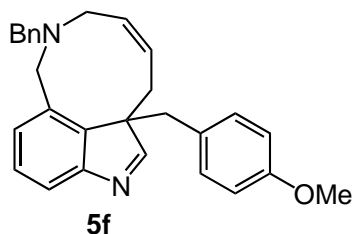


Colorless oil, 68% yield, 74% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 90/10; flow rate = 0.5 mL/min; detection wavelength = 214nm;  $t_R$  = 17.53 (major), 18.58 (minor) min].  $[\alpha]_D^{20}$  = -147.6 (c 0.5,  $CHCl_3$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.94 (s, 1H), 7.52-7.21 (m, 7H), 7.09-7.01 (m, 4H), 6.80 (s, 2H), 6.18-6.00 (m, 2H), 4.08-4.00 (m, 1H), 3.90-3.85 (m, 1H), 2.73-2.67 (m, 2H), 3.29 (s, 2H), 2.90-2.73 (m, 3H), 2.15-2.00 (m, 1H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  178.6, 155.4, 140.3, 139.4, 136.0, 133.0, 130.0, 129.7, 128.9, 128.8, 128.6, 128.4, 127.7, 127.1, 126.4, 120.4, 64.7, 58.8, 51.4, 46.5, 37.9, 28.6; IR (film):  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 3023,

2833, 2799, 1565, 1492, 1451, 1027, 830, 741, 705; ESI-MS ( $m/z$ ): 379 ( $M+1^+$ ); HRMS (ESI): Exact mass calcd. for  $C_{27}H_{27}N_2$  [ $M$ ] $^+$ : 379.2169. Found: 379.2167.

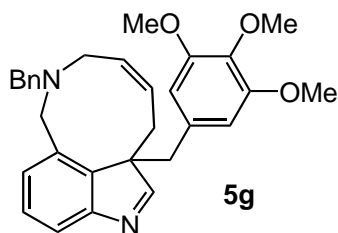


Colorless oil, 56% yield, 35% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 90/10; flow rate = 0.5 mL/min; detection wavelength = 214nm;  $t_R$  = 23.38 (major), 28.23 (minor) min].  $[\alpha]_D^{20}$  = -67.9 (c 0.5,  $CHCl_3$ ).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.92 (s, 1H), 7.49 (d,  $J$  = 7.6 Hz, 2H), 7.42-7.22 (m, 5H), 7.10-7.07 (m, 3H), 6.63 (d,  $J$  = 8.0 Hz, 2H), 6.17-5.98 (m, 2H), 4.05 (d,  $J$  = 13.6 Hz, 1H), 3.84 (d,  $J$  = 12.4 Hz, 1H), 3.70 (d,  $J$  = 13.2 Hz, 2H), 3.32-3.21 (m, 2H), 3.02-2.72 (m, 3H), 2.18-1.05 (m, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  178.2, 155.5, 139.8, 139.4, 135.0, 133.1, 130.8, 130.6, 130.2, 129.9, 128.9, 128.4, 128.3, 127.9, 127.2, 120.6, 120.5, 64.6, 58.6, 51.5, 46.6, 37.4, 28.9; IR (film):  $\nu_{max}$  ( $cm^{-1}$ ) = 3019, 2925, 2850, 1588, 1567, 1487, 1452, 1071, 1010, 740, 698; ESI-MS ( $m/z$ ): 457 ( $M+1^+$ ); HRMS (ESI): Exact mass calcd. for  $C_{27}H_{26}BrN_2$  [ $M$ ] $^+$ : 457.1274. Found: 457.1270.

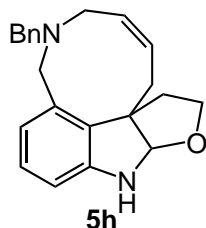


Colorless oil, 65% yield, 78% ee. [Daicel CHIRALPAK AS-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 95/5; flow rate = 0.5 mL/min; detection wavelength = 214nm;  $t_R$  = 28.23 (major), 23.96 (minor) min].  $[\alpha]_D^{20}$  = -189.5 (c 0.5,  $CHCl_3$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.94 (s, 1H), 7.50 (d,  $J$  = 7.2 Hz, 2H), 7.42-7.22 (m, 5H), 7.09-7.06 (m, 1H), 6.72 (d,  $J$  = 8.4 Hz, 2H), 6.55 (d,  $J$  = 9.0 Hz, 2H), 6.17-5.99 (m, 2H), 4.07 (d,  $J$  = 12.6 Hz, 1H), 3.86 (d,  $J$  = 12.9 Hz, 1H), 3.75-3.67 (m, 2H), 3.65 (s, 3H), 3.24 (s, 2H), 3.02-2.82 (m, 3H), 2.20-2.00 (m, 1H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  178.9, 158.0, 155.5, 140.5, 139.5, 133.1, 130.0, 129.7, 129.6, 128.9, 128.7, 128.4, 128.2, 127.7, 127.1, 120.4, 113.1, 64.9, 58.8, 55.0, 51.5, 46.6, 37.1, 28.7; IR (film):  $\nu_{max}$  ( $cm^{-1}$ ) = 2961, 1511, 1300, 1026, 799, 731, 698; ESI-MS ( $m/z$ ): 409 ( $M+1^+$ ); HRMS (ESI): Exact mass calcd. for  $C_{28}H_{29}N_2O$  [ $M$ ] $^+$ : 409.2274. Found: 409.2271.

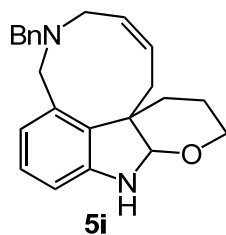




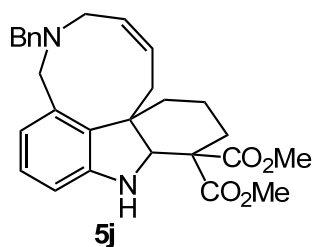
Colorless oil, 60% yield, 60% ee. [Daicel CHIRALPAK OD-H (0.46 cm x 15 cm); *n*-hexane/2-propanol = 80/20; flow rate = 0.6 mL/min; detection wavelength = 214nm;  $t_R$  = 23.33 (major), 27.63 (minor) min].  $[\alpha]_D^{20} = -117.5$  (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (s, 1H), 7.49-7.12 (m, 7H), 7.10 (d,  $J = 7.5$  Hz, 1H), 6.14-5.94 (m, 2H), 5.94 (s, 2H), 4.06 (d,  $J = 12.3$  Hz, 1H), 3.90 (d,  $J = 12.9$  Hz, 1H), 3.70 (s, 3H), 3.72-3.65 (m, 2H), 3.57 (s, 6H), 3.33-3.18 (m, 2H), 2.99-2.66 (m, 3H), 2.20-2.02 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  178.8, 155.7, 152.3, 140.6, 139.3, 136.4, 132.9, 131.8, 130.2, 129.7, 128.8, 128.4, 127.8, 127.1, 120.6, 105.8, 64.5, 60.7, 58.9, 55.7, 51.6, 46.4, 38.1, 28.9; IR (film):  $\nu_{\max}$  (cm<sup>-1</sup>) = 3012, 2935, 1590, 1507, 1457, 1420, 1332, 1241, 1127, 751; ESI-MS (*m/z*): 469 ( $M+1^+$ ); HRMS (MALDI): Exact mass calcd. for C<sub>30</sub>H<sub>33</sub>N<sub>2</sub>O<sub>3</sub> [ $M$ ]<sup>+</sup>: 469.2486. Found: 469.2479.



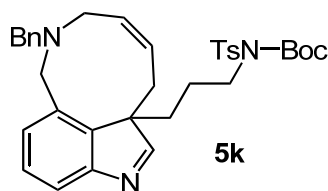
Colorless oil, 56% yield, 63% ee. [Daicel CHIRALPAK IC (0.46 cm x 25 cm); *n*-hexane/2-propanol = 90/10; flow rate = 0.5 mL/min; detection wavelength = 230 nm;  $t_R$  = 23.13 (major), 20.38 (minor) min].  $[\alpha]_D^{20} = -46.0$  (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 (d,  $J = 7.5$  Hz, 2H), 7.35 (t,  $J = 7.8$  Hz, 2H), 7.29-7.24 (m, 1H), 7.04 (t,  $J = 7.5$  Hz, 1H), 6.61 (d,  $J = 7.5$  Hz, 1H), 6.51 (d,  $J = 7.5$  Hz, 1H), 6.04-6.02 (m, 1H), 5.82-5.73 (m, 1H), 5.24 (s, 1H), 4.61 (br s, 1H), 4.02-3.91 (m, 2H), 3.62 (d,  $J = 12.9$  Hz, 2H), 3.55-3.45 (m, 2H), 3.03-3.29 (m, 2H), 2.63 (dd,  $J = 8.7, 13.2$  Hz, 1H), 2.41 (m, 1H), 2.22-2.17 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  149.4, 139.7, 134.5, 131.7, 130.4, 128.9, 128.3, 127.8, 127.0, 122.9, 107.3, 101.9, 67.6, 59.5, 51.3, 47.4, 37.6, 35.6; IR (film):  $\nu_{\max}$  (cm<sup>-1</sup>) = 3332, 2937, 2860, 1605, 1588, 1455, 1262, 1057, 1026, 744, 698; ESI-MS (*m/z*): 333 ( $M+1^+$ ); HRMS (ESI): Exact mass calcd. for C<sub>22</sub>H<sub>25</sub>N<sub>2</sub>O [ $M$ ]<sup>+</sup>: 333.1961. Found: 333.1975.



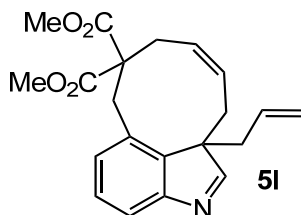
Colorless oil, 72% yield, 35% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 0.5 mL/min; detection wavelength = 214 nm;  $t_R$  = 14.83 (major), 12.48 (minor) min].  $[\alpha]_D^{20} = -20.5$  (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 (d,  $J$  = 7.5 Hz, 2H), 7.34 (t,  $J$  = 8.1 Hz, 2H), 7.31-7.25 (m, 1H), 7.03 (t,  $J$  = 7.5 Hz, 1H), 6.62 (t,  $J$  = 7.2 Hz, 2H), 5.95-5.76 (m, 2H), 4.76 (s, 1H), 4.32 (br s, 1H), 3.92 (AB,  $J_{AB}$  = 13.2 Hz, 1H), 3.81-3.73 (m, 1H), 3.67 (BA,  $J_{BA}$  = 13.2 Hz, 1H), 3.60-3.51 (m, 2H), 3.44 (d,  $J$  = 12.0 Hz, 1H), 2.92 (dd,  $J$  = 5.7, 12.6 Hz, 1H), 2.80 (dd,  $J$  = 9.6, 13.2 Hz, 1H), 2.58 (dd,  $J$  = 8.4, 13.2 Hz, 1H), 2.37-2.18 (m, 2H), 1.89-1.80 (m, 1H), 1.62-1.55 (m, 1H), 1.47-1.35 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  148.5, 139.7, 135.6, 133.2, 130.4, 128.8, 128.5, 128.2, 127.2, 126.9, 122.8, 108.5, 96.2, 61.4, 59.3, 52.0, 50.2, 47.9, 35.7, 27.6, 20.9; IR (film):  $\nu_{max}$  (cm<sup>-1</sup>) = 3299, 3008, 2906, 1603, 1582, 1457, 1262, 1079, 1020, 949, 739, 698; ESI-MS (*m/z*): 347 ( $M+1^+$ ); HRMS (MALDI): Exact mass calcd. for C<sub>23</sub>H<sub>26</sub>N<sub>2</sub>O [ $M$ ]<sup>+</sup>: 347.2118. Found: 347.2122.



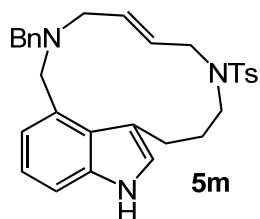
Colorless oil, 48% yield, 47% ee. [Daicel CHIRALPAK IC (0.46 cm x 15 cm); *n*-hexane/2-propanol = 95/5; flow rate = 0.5 mL/min; detection wavelength = 230nm;  $t_R$  = 10.73 (major), 9.08 (minor) min].  $[\alpha]_D^{20} = -14.0$  (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.40-7.27 (m, 5H), 6.95-6.90 (m, 1H), 6.54-6.45 (m, 2H), 5.73-5.65 (m, 1H), 4.46 (br s, 2H), 3.82-3.65 (m, 4H), 3.77 (s, 3H), 3.75 (s, 3H), 3.60-3.40 (m, 1H), 3.22-3.09 (m, 2H), 2.64-2.44 (m, 2H), 1.96-1.88 (m, 1H), 1.76-1.55 (m, 4H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  171.3, 170.9, 148.7, 139.4, 135.3, 130.7, 129.2, 128.2, 127.9, 127.0, 126.9, 123.2, 108.8, 60.8, 56.9, 54.8, 53.0, 52.8, 51.5, 50.9, 34.2, 29.7, 25.2, 17.9; IR (film):  $\nu_{max}$  (cm<sup>-1</sup>) = 3393, 2950, 1731, 1589, 1454, 1434, 1246, 745; ESI-MS (*m/z*): 461 ( $M+1^+$ ); HRMS (MALDI): Exact mass calcd. for C<sub>28</sub>H<sub>33</sub>N<sub>2</sub>O<sub>4</sub> [ $M$ ]<sup>+</sup>: 461.2435. Found: 461.2428.



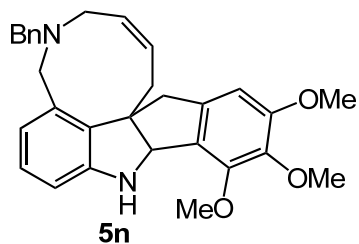
White solid, 62% yield, 75% ee. [Daicel CHIRALPAK IC (0.46 cm x 15 cm); *n*-hexane/2-propanol = 60/40; flow rate = 0.6 mL/min; detection wavelength = 214nm;  $t_R$  = 31.88 (major), 36.58 (minor) min].  $[\alpha]_D^{20} = -45.6$  (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (s, 1H), 7.65 (d,  $J$  = 8.4 Hz, 2H), 7.57 (d,  $J$  = 7.5 Hz, 1H), 7.46 (d,  $J$  = 7.2 Hz, 2H), 7.39-7.22 (m, 6H), 7.09 (d,  $J$  = 7.2 Hz, 1H), 5.92 (m, 2H), 4.02 (d,  $J$  = 13.2 Hz, 1H), 3.70-3.54 (m, 5H), 2.98-2.65 (m, 3H), 2.40 (s, 3H), 2.12-2.06 (m, 2H), 1.29 (s, 9H), 1.33-1.22 (s, 2H), 0.91-0.87 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  179.1, 155.3, 150.7, 144.1, 140.5, 139.3, 137.1, 133.4, 129.9, 129.7, 129.1, 128.8, 128.5, 128.3, 127.70, 127.66, 127.0, 120.5, 112.4, 84.1, 63.4, 58.8, 51.1, 46.8, 46.5, 36.6, 28.5, 27.7, 24.8, 21.5; IR (film):  $\nu_{max}$  (cm<sup>-1</sup>) = 3022, 2931, 1727, 1455, 1356, 1280, 1155, 1087, 752; ESI-MS (*m/z*): 600 ( $M+1^+$ ); HRMS (MALDI): Exact mass calcd. for C<sub>35</sub>H<sub>42</sub>N<sub>3</sub>O<sub>4</sub>S [ $M$ ]<sup>+</sup>: 600.2891. Found: 600.2905.



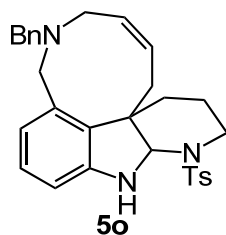
Colorless oil, 78% yield, 42% ee. [Phenomenex Lux 5u Cellulose-2 (0.46 cm x 25 cm); *n*-hexane/2-propanol/gxs = 80/20; flow rate = 0.5 mL/min; detection wavelength = 230nm;  $t_R$  = 22.88 (major), 33.29 (minor) min].  $[\alpha]_D^{20} = -68.8$  (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (s, 1H), 7.52 (d,  $J$  = 7.2 Hz, 1H), 7.23 (t,  $J$  = 8.0 Hz, 1H), 6.78 (d,  $J$  = 7.6 Hz, 1H), 6.01-5.94 (m, 1H), 5.57-5.50 (m, 1H), 5.31-5.22 (m, 1H), 5.01 (d,  $J$  = 16.8 Hz, 1H), 4.87 (d,  $J$  = 10.0 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.31 (AB,  $J_{AB}$  = 14.0 Hz, 1H), 3.11 (BA,  $J_{BA}$  = 14.0 Hz, 1H), 2.76 (dd,  $J$  = 7.2, 14.4 Hz, 1H), 2.67 (dd,  $J$  = 8.0, 13.6 Hz, 1H), 2.60 (dd,  $J$  = 7.2, 14.4 Hz, 1H), 2.49 (dd,  $J$  = 4.8, 13.2 Hz, 1H), 2.34 (dd,  $J$  = 13.2, 13.2 Hz, 1H), 2.07 (dd,  $J$  = 8.8, 13.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  179.2, 171.2, 170.7, 156.0, 140.9, 132.2, 129.6, 128.5, 128.04, 127.95, 120.5, 118.3, 63.8, 61.6, 52.8, 52.4, 34.7, 34.6, 29.2, 28.4; IR (film):  $\nu_{max}$  (cm<sup>-1</sup>) = 2951, 1735, 1450, 1289, 1200, 924, 752; ESI-MS (*m/z*): 354 ( $M+1^+$ ); HRMS (MALDI): Exact mass calcd. for C<sub>21</sub>H<sub>24</sub>NO<sub>4</sub> [ $M$ ]<sup>+</sup>: 354.1700. Found: 354.1709.



White solid, 82% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (br s, 1H), 7.70 (d,  $J = 8.1$  Hz, 2H), 7.31-7.04 (m, 10H), 6.91 (d,  $J = 1.8$  Hz, 1H), 6.07 (dt,  $J = 7.5, 15.3$  Hz, 1H), 5.68 (dt,  $J = 5.7, 15.3$  Hz, 1H), 3.87 (s, 2H), 3.63 (d,  $J = 5.7$  Hz, 2H), 3.60 (s, 2H), 3.23 (t,  $J = 6.6$  Hz, 2H), 3.06-3.00 (m, 4H), 2.40 (s, 3H), 1.95-1.85 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  143.2, 140.2, 137.3, 135.9, 131.2, 130.2, 129.7, 128.5, 128.1, 127.0, 126.6, 125.7, 122.3, 122.0, 121.1, 117.2, 110.5, 58.0, 55.9, 54.8, 51.9, 51.2, 33.8, 25.5, 21.4; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3406, 2923, 2791, 1598, 1450, 1334, 1157, 1100, 975, 753; ESI-MS ( $m/z$ ): 500 ( $\text{M}+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $\text{C}_{30}\text{H}_{34}\text{N}_3\text{O}_2\text{S}$  [ $\text{M}$ ] $^+$ : 500.2366. Found: 500.2384. m.p. 152-153  $^\circ\text{C}$ .

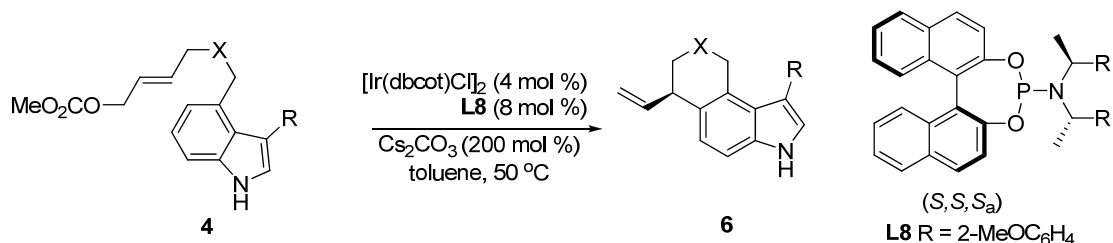


Colorless oil, 60% yield, 54% ee. [Daicel CHIRALPAK IC (0.46 cm x 15 cm); *n*-hexane/2-propanol = 60/40; flow rate = 0.7 mL/min; detection wavelength = 214nm;  $t_{\text{R}} = 31.63$  (major), 14.18 (minor) min].  $[\alpha]_{\text{D}}^{20} = -70.1$  (c 1.0,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 7.2$  Hz, 2H), 7.36 (t,  $J = 7.2$  Hz, 2H), 7.28 (d,  $J = 7.2$  Hz, 1H), 6.99 (t,  $J = 7.5$  Hz, 1H), 6.59 (d,  $J = 7.5$  Hz, 1H), 6.54 (d,  $J = 7.5$  Hz, 1H), 6.39 (s, 1H), 6.17-6.08 (m, 1H), 5.85-5.75 (m, 1H), 4.94 (s, 1H), 4.02 (d,  $J = 11.1$  Hz, 1H), 4.00 (s, 3H), 3.79 (s, 3H), 3.77 (s, 3H), 3.69 (d,  $J = 12.0$  Hz, 1H), 3.64 (d,  $J = 13.2$  Hz, 1H), 3.49 (d,  $J = 12.6$  Hz, 1H), 3.35 (AB,  $J_{\text{AB}} = 16.8$  Hz, 1H), 3.27 (BA,  $J_{\text{BA}} = 16.8$  Hz, 1H), 3.04-2.83 (m, 3H), 2.49-2.45 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  154.4, 149.9, 149.6, 140.2, 139.8, 137.4, 134.9, 134.7, 131.1, 128.9, 128.3, 127.7, 127.4, 127.0, 122.8, 109.0, 102.9, 76.3, 60.9, 60.6, 59.7, 59.3, 56.0, 51.4, 47.2, 43.5, 37.7; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3358, 2929, 1601, 1485, 1456, 1340, 1260, 1120, 1037, 749; ESI-MS ( $m/z$ ): 469 ( $\text{M}+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $\text{C}_{30}\text{H}_{33}\text{N}_2\text{O}_3$  [ $\text{M}$ ] $^+$ : 469.2486. Found: 469.2502.



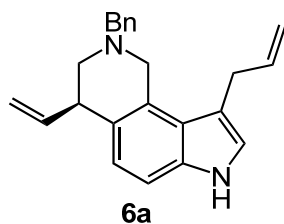
Colorless oil, 80% yield, 73% ee. [Daicel CHIRALPAK IC (0.46 cm x 15 cm); *n*-hexane/2-propanol = 60/40; flow rate = 0.7 mL/min; detection wavelength = 214nm;  $t_R$  = 18.63 (major), 15.48 (minor) min].  $[\alpha]_D^{20} = -54.3$  (c 0.5, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.77 (d,  $J$  = 8.4 Hz, 2H), 7.36-7.21 (m, 7H), 6.94 (t,  $J$  = 7.5 Hz, 1H), 6.53 (d,  $J$  = 6.9 Hz, 1H), 6.48 (d,  $J$  = 7.5 Hz, 1H), 5.69-5.66 (m, 2H), 5.18 (s, 1H), 3.89 (s, 1H), 3.77-3.66 (m, 4H), 3.29-3.03 (m, 4H), 2.48 (s, 3H), 1.87-1.82 (m, 1H), 1.60-1.54 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  147.3, 143.7, 139.3, 137.3, 135.5, 130.0, 129.5, 129.1, 128.2, 127.1, 126.9, 123.3, 109.1, 59.8, 54.3, 50.9, 48.6, 40.1, 33.2, 29.8, 29.3, 21.6, 20.0; IR (film):  $\nu_{max}$  (cm<sup>-1</sup>) = 3361, 2918, 2849, 1595, 1456, 1338, 1261, 1155, 798, 747; ESI-MS (*m/z*): 500 ( $M+1^+$ ); HRMS (MALDI): Exact mass calcd. for C<sub>30</sub>H<sub>34</sub>N<sub>3</sub>O<sub>2</sub>S [ $M$ ]<sup>+</sup>: 500.2366. Found: 500.2379.

### General Procedure for Iridium-Catalyzed Friedel-Crafts Type Allylic Alkylation Reaction of Indole Fused through C4-C5:

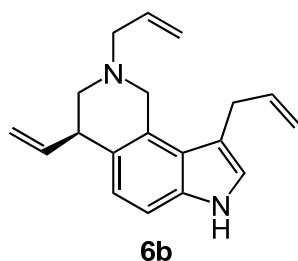


A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added [Ir(dbcot)Cl]<sub>2</sub> (6.9 mg, 0.008 mmol, 4 mol %), phosphoramidite ligand **L8** (9.6 mg, 0.016 mmol, 8 mol %), THF (1 mL) and *n*-propylamine (0.7 mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed *in vacuo* to give a pale yellow solid. After that, allyl carbonate **4** (0.20 mmol, dissolved in 2.0 mL toluene), cesium carbonate (130 mg, 0.40 mmol, 200 mol %) were added. The reaction mixture was heated at 50 °C. After the reaction was complete (monitored by TLC), the crude reaction mixture was filtrated through a pad of celite and washed with EtOAc. The solvents were removed under reduced pressure. Then the residue was purified by silica gel column chromatography (PE/EA = 10/1) to

afford the desired product **6**.

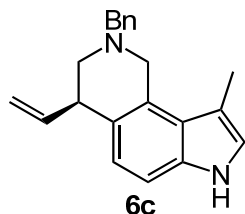


Colorless oil, 48% yield, 83% ee. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 90/10; flow rate = 0.7 mL/min; detection wavelength = 230 nm;  $t_R$  = 12.18 (major), 13.97 (minor) min].  $[\alpha]_D^{20} = -81.9$  (c 0.5, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (br s, 1H), 7.42-7.23 (m, 5H), 7.12 (d,  $J = 8.1$  Hz, 1H), 6.98 (d,  $J = 8.4$  Hz, 1H), 6.84 (s, 1H), 6.02-5.86 (m, 2H), 5.16 (d,  $J = 17.1$  Hz, 1H), 5.06 (d,  $J = 9.9$  Hz, 1H), 4.95 (d,  $J = 9.9$  Hz, 1H), 4.88 (d,  $J = 17.7$  Hz, 1H), 4.13 (AB,  $J_{AB} = 15.3$  Hz, 1H), 4.05 (BA,  $J_{BA} = 15.3$  Hz, 1H), 3.79-3.65 (m, 3H), 3.47 (d,  $J = 6.0$  Hz, 2H), 2.90 (dd,  $J = 5.1, 11.4$  Hz, 1H), 2.61 (dd,  $J = 6.9, 11.1$  Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  142.0, 138.3, 138.2, 135.3, 129.1, 128.2, 127.4, 127.0, 126.4, 123.7, 123.2, 122.6, 115.3, 114.9, 114.3, 109.6, 62.8, 56.2, 54.4, 44.4, 31.6; IR (film):  $\nu_{max}$  (cm<sup>-1</sup>) = 3412, 3074, 2970, 2792, 1636, 1602, 1492, 1453, 1349, 1025, 911, 801, 734, 698; ESI-MS (*m/z*): 329 ( $M+1^+$ ); HRMS (ESI): Exact mass calcd. for C<sub>23</sub>H<sub>25</sub>N<sub>2</sub> [ $M+1$ ]<sup>+</sup>: 329.2012. Found: 329.2008.

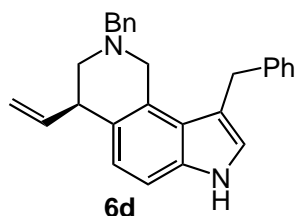


Colorless oil, 40% yield, 90% ee. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 80/20; flow rate = 0.5 mL/min; detection wavelength = 230 nm;  $t_R$  = 10.27 (major), 12.46 (minor) min].  $[\alpha]_D^{20} = -60.8$  (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 (br s, 1H), 7.13 (d,  $J = 8.4$  Hz, 1H), 6.98 (d,  $J = 8.4$  Hz, 1H), 6.87 (s, 1H), 6.11-5.87 (m, 3H), 5.30-5.00 (m, 6H), 4.20 (AB,  $J_{AB} = 15.2$  Hz, 1H), 4.02 (BA,  $J_{BA} = 15.2$  Hz, 1H), 3.72-3.66 (m, 1H), 3.58 (d,  $J = 6.0$  Hz, 2H), 3.26 (dd,  $J = 6.4, 13.2$  Hz, 1H), 3.19 (dd,  $J = 6.8, 13.2$  Hz, 1H), 2.91 (dd,  $J = 5.2, 11.4$  Hz, 1H), 2.58 (dd,  $J = 7.6, 11.4$  Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.9, 138.3, 135.44, 135.36, 127.4, 126.5, 123.8, 123.3, 122.5, 117.8, 115.5, 115.2, 114.7, 109.5, 61.5, 56.2, 54.4, 44.3, 31.8; IR (film):  $\nu_{max}$  (cm<sup>-1</sup>) = 3405, 2921, 1748, 1637, 1441, 1265,

994, 917, 754; EI-MS ( $m/z$ ): 278 ( $M^+$ , 7), 209 (84), 194 (44), 180 (65), 168 (100), 154 (6); HRMS (EI): Exact mass calcd. for  $C_{19}H_{22}N_2$  [ $M$ ] $^+$ : 278.1783. Found: 278.1779.

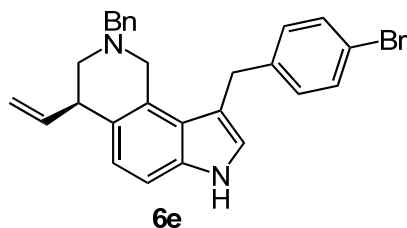


Colorless oil, 56% yield, 79% ee. [Daicel CHIRALPAK IC (0.46 cm x 25 cm); *n*-hexane/2-propanol = 95/5; flow rate = 0.5 mL/min; detection wavelength = 214 nm;  $t_R$  = 17.50 (major), 22.61 (minor) min].  $[\alpha]_D^{20}$  = -69.8 (c 0.5,  $CHCl_3$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.81 (br s, 1H), 7.43-7.22 (m, 5H), 7.09 (d,  $J$  = 8.4 Hz, 1H), 6.95 (d,  $J$  = 8.4 Hz, 1H), 6.80 (s, 1H), 5.96 (ddd,  $J$  = 8.7, 9.9, 17.1 Hz, 1H), 5.14 (d,  $J$  = 17.1 Hz, 1H), 5.06 (d,  $J$  = 9.9 Hz, 1H), 4.19 (AB,  $J_{AB}$  = 16.2 Hz, 1H), 4.14 (BA,  $J_{BA}$  = 16.2 Hz, 1H), 3.78 (AB,  $J_{AB}$  = 13.2 Hz, 1H), 3.71 (BA,  $J_{BA}$  = 13.2 Hz, 1H), 3.68-3.61 (m, 1H), 2.87 (dd,  $J$  = 5.1, 11.1 Hz, 1H), 2.60 (dd,  $J$  = 6.6, 11.1 Hz, 1H), 2.34 (s, 3H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  142.1, 138.4, 135.3, 129.1, 128.2, 127.7, 127.0, 126.4, 124.3, 123.3, 122.2, 114.8, 111.9, 109.5, 62.8, 56.0, 54.6, 44.3, 13.1; IR (film):  $\nu_{max}$  ( $cm^{-1}$ ) = 3414, 3028, 2858, 1637, 1459, 1216, 1092, 914, 797, 760, 699; ESI-MS ( $m/z$ ): 303 ( $M+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $C_{21}H_{23}N_2$  [ $M$ ] $^+$ : 303.1856. Found: 303.1849.

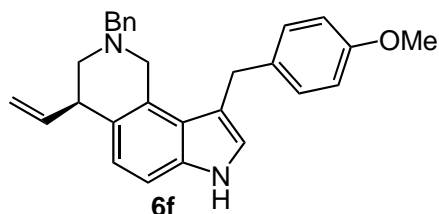


Colorless oil, 63% yield, 86% ee. [Daicel CHIRALPAK IC (0.46 cm x 25 cm); *n*-hexane/2-propanol = 95/5; flow rate = 0.5 mL/min; detection wavelength = 230 nm;  $t_R$  = 14.78 (major), 19.58 (minor) min].  $[\alpha]_D^{20}$  = -76.0 (c 0.5,  $CHCl_3$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.92 (br s, 1H), 7.32-7.07 (m, 11H), 6.98 (d,  $J$  = 8.1 Hz, 1H), 6.70 (s, 1H), 5.94 (ddd,  $J$  = 7.2, 9.9, 17.1 Hz, 1H), 5.14 (d,  $J$  = 17.1 Hz, 1H), 5.04 (d,  $J$  = 9.9 Hz, 1H), 4.08 (s, 2H), 3.96 (AB,  $J_{AB}$  = 15.6 Hz, 1H), 3.89 (BA,  $J_{BA}$  = 15.6 Hz, 1H), 3.66-3.55 (m, 3H), 2.82 (dd,  $J$  = 5.1, 11.1 Hz, 1H), 2.54 (dd,  $J$  = 6.9, 11.1 Hz, 1H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  142.1, 141.6, 138.3, 135.5, 129.0, 128.6, 128.3, 128.2, 127.6, 127.0, 126.7, 125.8, 123.7, 123.6, 123.5, 115.4, 114.9, 109.5, 62.8, 56.0, 54.5, 44.4, 33.6; IR (film):  $\nu_{max}$  ( $cm^{-1}$ ) = 3649, 3415, 3026, 2970, 1634, 1601, 1492, 1453,

1126, 1028, 914, 697; ESI-MS ( $m/z$ ): 379 ( $M+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $C_{27}H_{27}N_2$  [ $M$ ] $^+$ : 379.2169. Found: 379.2176.



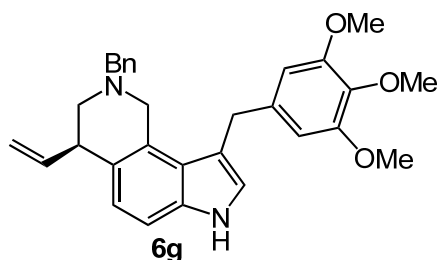
Colorless oil, 64% yield, 81% ee. [Daicel CHIRALPAK IC (0.46 cm x 25 cm); *n*-hexane/2-propanol = 95/5; flow rate = 0.5 mL/min; detection wavelength = 214 nm;  $t_R$  = 14.16 (major), 18.52 (minor) min].  $[\alpha]_D^{20}$  = -60.4 (c = 0.5,  $CHCl_3$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  8.03 (br s, 1H), 7.31-7.27 (m, 7H), 7.12 (d,  $J$  = 8.4 Hz, 1H), 6.98 (d,  $J$  = 8.7 Hz, 1H), 6.88 (d,  $J$  = 8.1 Hz, 2H), 6.69 (s, 1H), 5.94 (ddd,  $J$  = 7.8, 9.9, 17.1 Hz, 1H), 5.15 (d,  $J$  = 17.1 Hz, 1H), 5.06 (d,  $J$  = 9.9 Hz, 1H), 3.99 (s, 2H), 3.88 (AB,  $J_{AB}$  = 15.6 Hz, 1H), 3.82 (BA,  $J_{BA}$  = 15.6 Hz, 1H), 3.80-3.56 (m, 3H), 2.85 (dd,  $J$  = 5.1, 11.1 Hz, 1H), 2.56 (dd,  $J$  = 6.9, 11.1 Hz, 1H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  141.9, 140.6, 138.2, 135.5, 131.3, 130.1, 128.9, 128.5, 128.2, 127.4, 127.1, 127.0, 126.8, 123.7, 123.6, 119.5, 115.0, 114.5, 109.6, 62.9, 56.2, 54.3, 44.4, 32.8; IR (film):  $\nu_{max}$  ( $cm^{-1}$ ) = 3412, 3028, 2957, 1635, 1487, 1455, 1260, 1089, 1071, 1012, 799, 761; ESI-MS ( $m/z$ ): 457 ( $M+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $C_{27}H_{26}N_2Br$  [ $M$ ] $^+$ : 457.1274. Found: 457.1278.



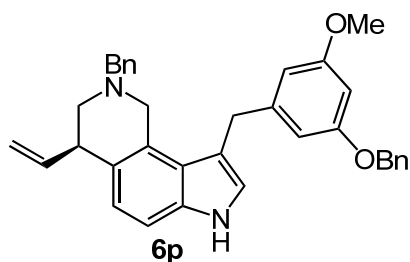
Colorless oil, 54% yield, 85% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 0.7 mL/min; detection wavelength = 230 nm;  $t_R$  = 16.33 (major), 14.78 (minor) min].  $[\alpha]_D^{20}$  = -45.8 (c 1.0,  $CHCl_3$ ).  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.96 (br s, 1H), 7.35-7.11 (m, 5H), 7.11 (d,  $J$  = 8.1 Hz, 1H), 7.00-6.96 (m, 3H), 6.77 (d,  $J$  = 8.7 Hz, 2H), 6.66 (d,  $J$  = 2.4 Hz, 1H), 5.94 (ddd,  $J$  = 7.2, 9.9, 17.1 Hz, 1H), 5.13 (d,  $J$  = 17.1 Hz, 1H), 5.04 (d,  $J$  = 9.9 Hz, 1H), 4.01 (s, 2H), 3.96 (AB,  $J_{AB}$  = 15.6 Hz, 1H), 3.91 (BA,  $J_{BA}$  = 15.6 Hz, 1H), 3.77 (s, 3H), 3.66-3.60 (m, 3H), 2.82 (dd,  $J$  = 5.1, 11.1 Hz, 1H), 2.55 (dd,  $J$  = 7.2, 11.1 Hz, 1H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  157.7, 142.0, 138.3, 135.5, 133.7, 129.4, 129.0, 128.2, 127.6, 127.0, 126.6, 123.7, 123.5, 123.4, 115.9, 114.9, 113.7, 109.5, 62.8, 56.0, 55.2,



54.5, 44.4, 32.6; IR (film):  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 3413, 2927, 1610, 1510, 1459, 1245, 1028, 799, 761; ESI-MS ( $m/z$ ): 409 ( $M+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $\text{C}_{28}\text{H}_{29}\text{N}_2\text{O}$  [ $M$ ] $^+$ : 409.2274. Found: 409.2282.

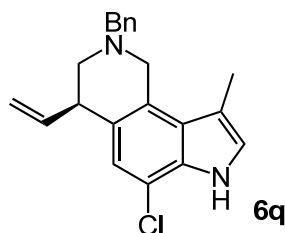


Colorless oil, 50% yield, 85% ee. [Phenomenex Lux 5u Cellulose-4 (0.46 cm x 25 cm); *n*-hexane/2-propanol = 80/20; flow rate = 0.4 mL/min; detection wavelength = 214 nm;  $t_R$  = 22.63 (major), 25.13 (minor) min].  $[\alpha]_D^{20}$  = -43.5 (c 1.0,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (br s, 1H), 7.35-7.24 (m, 5H), 7.15 (d,  $J$  = 8.4 Hz, 1H), 6.98 (d,  $J$  = 8.4 Hz, 1H), 6.68 (s, 1H), 6.39 (s, 2H), 5.93 (ddd,  $J$  = 7.5, 9.9, 17.4 Hz, 1H), 5.14 (d,  $J$  = 17.1 Hz, 1H), 5.05 (d,  $J$  = 9.9 Hz, 1H), 4.05 (d,  $J$  = 7.5 Hz, 1H), 3.84 (s, 3H), 3.76 (s, 6H), 3.62-3.60 (m, 3H), 2.84 (dd,  $J$  = 5.1, 11.1 Hz, 1H), 2.57 (dd,  $J$  = 6.9, 11.4 Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  153.1, 142.0, 138.2, 137.3, 136.0, 135.5, 129.0, 128.2, 127.5, 127.0, 126.7, 123.7, 123.6, 123.5, 115.4, 114.9, 109.6, 105.6, 62.7, 60.9, 56.0, 55.8, 54.7, 44.3, 34.0; IR (film):  $\nu_{\max}$  ( $\text{cm}^{-1}$ ) = 3364, 2935, 2835, 1590, 1506, 1456, 1419, 1329, 1233, 1125, 1005; ESI-MS ( $m/z$ ): 469 ( $M+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $\text{C}_{30}\text{H}_{33}\text{N}_2\text{O}_3$  [ $M+1$ ] $^+$ : 469.2486. Found: 469.2490.

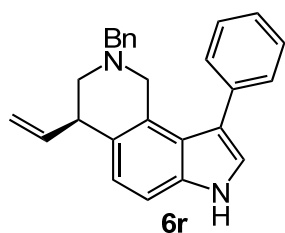


Colorless oil, 56% yield, 80% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 70/30; flow rate = 0.5 mL/min; detection wavelength = 230 nm;  $t_R$  = 28.53 (major), 31.18 (minor) min].  $[\alpha]_D^{20}$  = -87.3 (c 0.5,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (br s, 1H), 7.44-7.22 (m, 11H), 7.10 (d,  $J$  = 8.4 Hz, 1H), 6.96 (d,  $J$  = 8.4 Hz, 1H), 6.73-6.69 (m, 2H), 6.63 (d,  $J$  = 2.1 Hz, 1H), 6.50 (dd,  $J$  = 2.1, 8.4 Hz, 1H), 5.93 (ddd,  $J$  = 7.2, 9.9, 17.1 Hz, 1H), 5.13 (d,  $J$  = 17.1 Hz, 1H), 5.10 (s, 2H), 5.04 (d,  $J$  = 9.9 Hz, 1H), 4.02 (s, 2H), 3.95 (s, 2H), 3.78 (s, 3H), 3.64-3.60 (m,

3H), 2.82 (dd,  $J = 5.1, 11.1$  Hz, 1H), 2.55 (dd,  $J = 7.2, 11.1$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  149.4, 146.2, 142.0, 138.2, 137.3, 135.5, 134.8, 128.9, 128.5, 128.1, 127.7, 127.5, 127.2, 127.1, 127.0, 126.6, 123.7, 123.5, 123.4, 120.4, 115.6, 114.9, 114.0, 112.3, 109.5, 71.0, 62.7, 56.0, 55.8, 54.5, 44.4, 33.2; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3402, 3029, 2929, 2858, 1509, 1455, 1259, 1218, 1136, 1024, 799, 760; ESI-MS ( $m/z$ ): 515 ( $M+1^+$ ); HRMS (MALDI): Exact mass calcd. for  $\text{C}_{35}\text{H}_{35}\text{N}_2\text{O}_2$  [ $M$ ] $^+$ : 515.2693. Found: 515.2695.

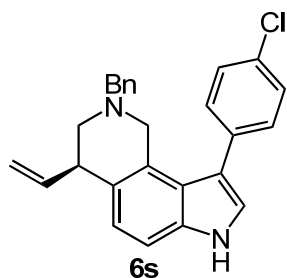


Colorless oil, 40% yield, 97% ee. [Daicel CHIRALPAK AD (0.46 cm x 25 cm);  $n$ -hexane/2-propanol = 95/5; flow rate = 0.5 mL/min; detection wavelength = 230 nm;  $t_{\text{R}} = 22.73$  (major), 40.78 (minor) min].  $[\alpha]_{\text{D}}^{20} = -40$  (c 0.25,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (br s, 1H), 7.42-7.24 (m, 5H), 6.98 (s, 1H), 6.89 (s, 1H), 5.92 (ddd,  $J = 8.7, 10.2, 17.4$  Hz, 1H), 5.17 (d,  $J = 17.7$  Hz, 1H), 5.09 (d,  $J = 9.9$  Hz, 1H), 4.16 (AB,  $J_{\text{AB}} = 14.7$  Hz, 1H), 4.07 (BA,  $J_{\text{BA}} = 16.2$  Hz, 1H), 3.78 (AB,  $J_{\text{AB}} = 13.2$  Hz, 1H), 3.72 (BA,  $J_{\text{BA}} = 13.2$  Hz, 1H), 3.65-3.58 (m, 1H), 2.88 (dd,  $J = 5.7, 11.1$  Hz, 1H), 2.58 (dd,  $J = 6.0, 11.1$  Hz, 1H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  141.4, 138.2, 132.4, 129.1, 128.3, 127.7, 127.1, 126.7, 125.8, 122.7, 122.2, 115.6, 114.7, 113.1, 62.7, 55.8, 54.2, 44.3, 13.0; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3207, 2925, 1634, 1455, 1273, 1085, 923, 754; ESI-MS ( $m/z$ ): 337 ( $M+1^+$ ); HRMS (ESI): Exact mass calcd. for  $\text{C}_{21}\text{H}_{21}\text{N}_2\text{Cl}$  [ $M$ ] $^+$ : 337.1466. Found: 337.1476.

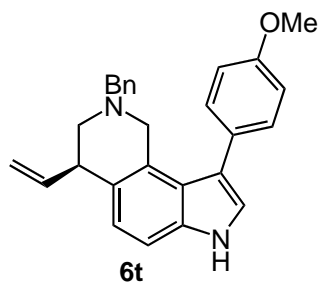


Colorless oil, 78% yield [4.3:(3.2/1)], 85% ee. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm);  $n$ -hexane/2-propanol = 80/20; flow rate = 0.5 mL/min; detection wavelength = 230 nm;  $t_{\text{R}} = 12.29$  (major), 13.98 (minor) min].  $[\alpha]_{\text{D}}^{20} = -38.2$  (c 1.0,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (br s, 1H), 7.31-7.19 (m, 9H), 7.12-7.02 (m, 4H), 5.94 (ddd,  $J = 7.5, 10.2, 17.1$  Hz, 1H), 5.18 (dd,  $J = 1.8, 17.1$  Hz, 1H), 5.07 (dd,  $J = 2.1, 10.2$  Hz, 1H), 3.67 (q,  $J = 7.2$  Hz, 1H), 3.53-3.42 (m, 4H), 2.87 (dd,  $J =$

5.1, 11.1 Hz, 1H), 2.56 (dd,  $J = 6.9, 11.1$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  142.0, 137.7, 136.9, 134.4, 130.5, 129.2, 128.0, 127.6, 127.5, 127.1, 126.8, 126.5, 123.7, 123.1, 122.9, 119.1, 115.0, 109.6, 62.7, 56.5, 55.2, 44.5; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3413, 2927, 2855, 1602, 1510, 1490, 1457, 12165, 1026, 801, 763; ESI-MS ( $m/z$ ): 365 ( $\text{M}+1^+$ ); HRMS (ESI): Exact mass calcd. for  $\text{C}_{26}\text{H}_{25}\text{N}_2$  [ $\text{M}$ ] $^+$ : 365.2012. Found: 365.2020.

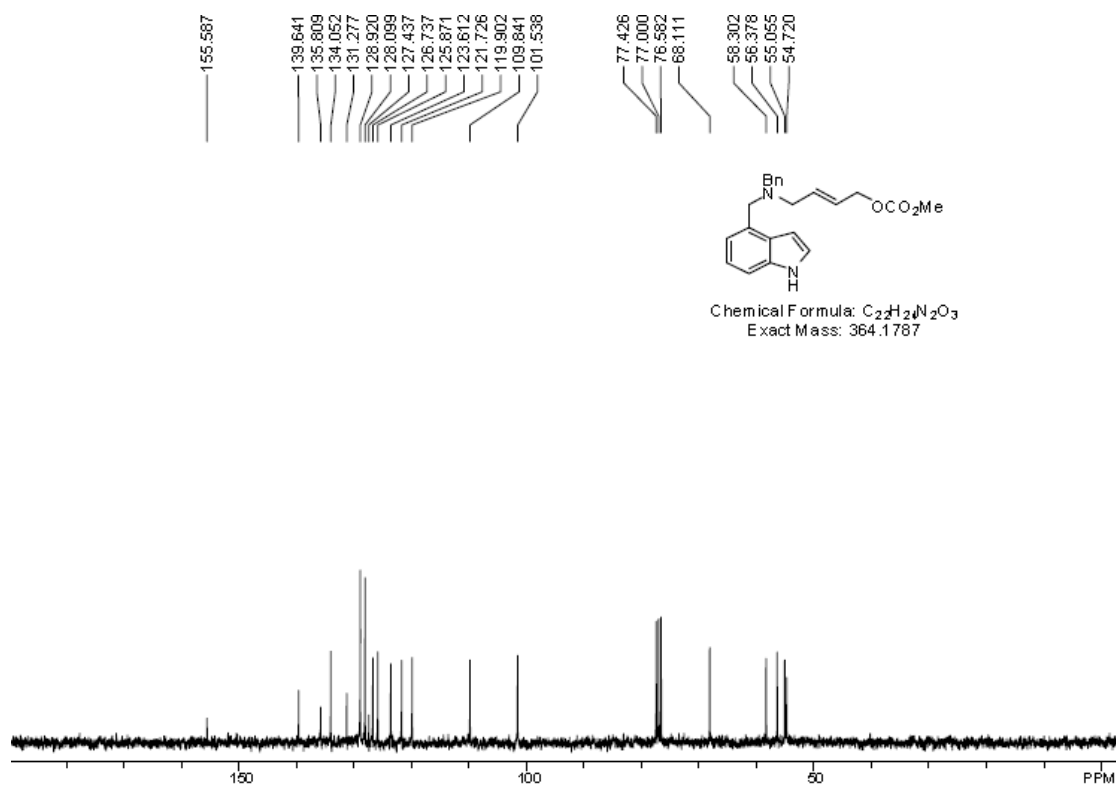
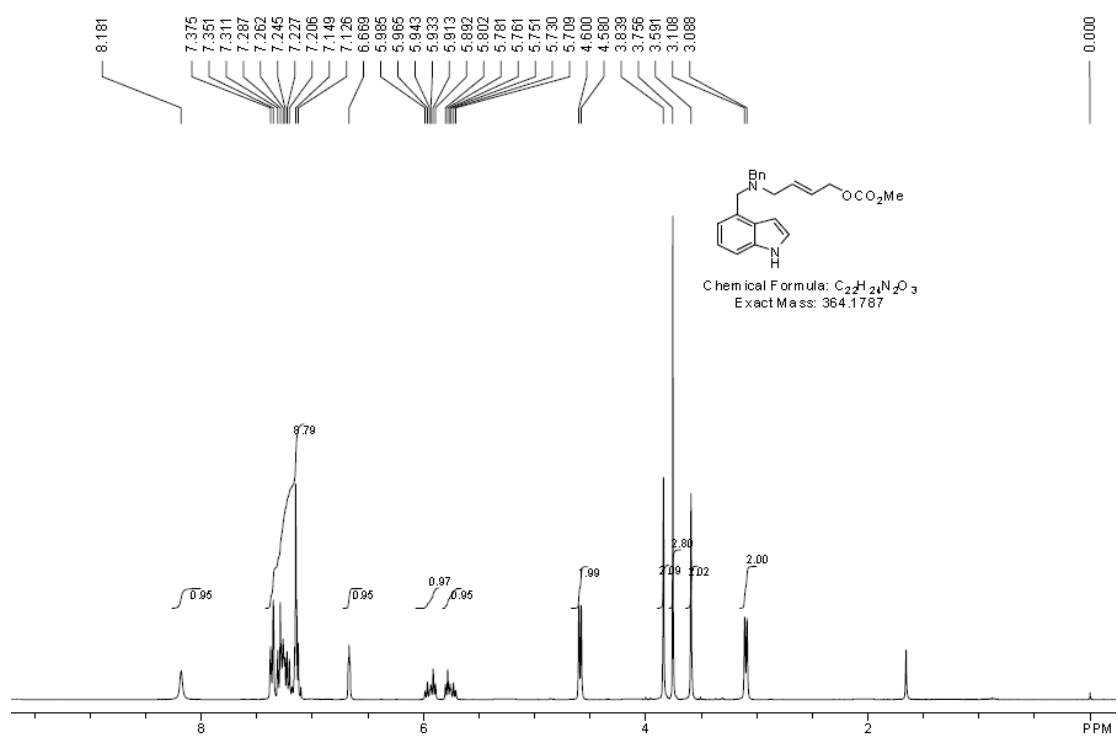


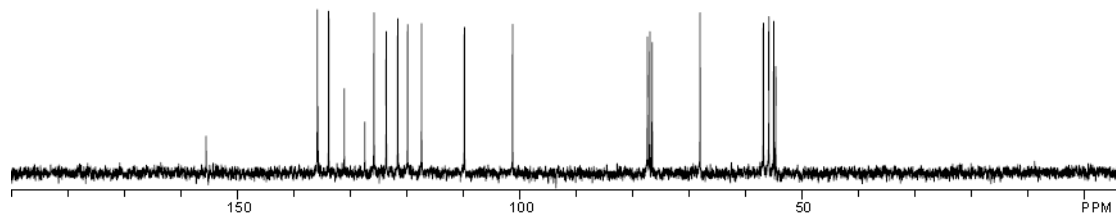
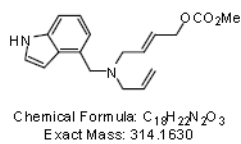
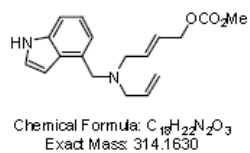
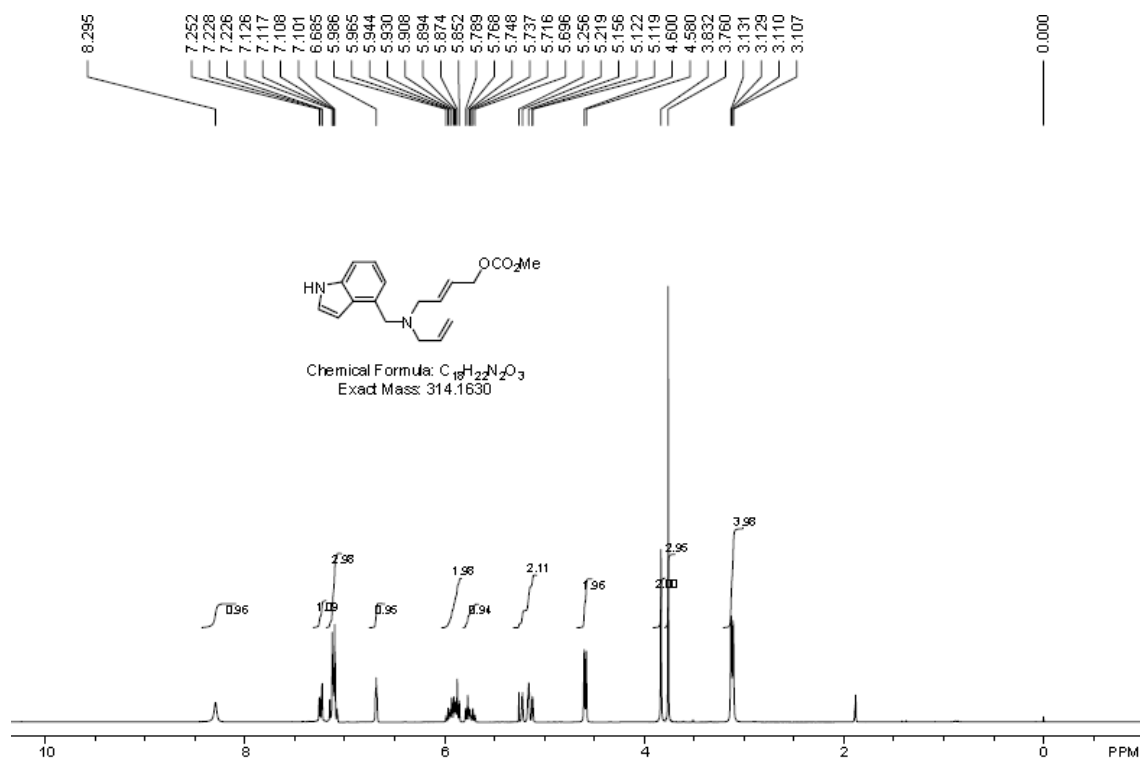
Colorless oil, 52% yield, 56% ee. [Daicel CHIRALPAK AD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 85/15; flow rate = 0.5 mL/min; detection wavelength = 214 nm;  $t_{\text{R}} = 10.13$  (major), 12.43 (minor) min].  $[\alpha]_{\text{D}}^{20} = -43.7$  (c 0.5,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20 (br s, 1H), 7.23-7.04 (m, 11H), 6.94 (d,  $J = 2.4$  Hz, 1H), 5.96 (ddd,  $J = 7.5, 9.6, 17.1$  Hz, 1H), 5.20 (d,  $J = 17.1$  Hz, 1H), 5.08 (d,  $J = 9.9$  Hz, 1H), 3.69 (q,  $J = 6.9$  Hz, 1H), 3.54 (AB,  $J_{\text{AB}} = 12.9$  Hz, 1H), 3.44 (BA,  $J_{\text{BA}} = 12.9$  Hz, 1H), 4.42-4.36 (m, 2H), 2.92 (dd,  $J = 5.4, 11.1$  Hz, 1H), 2.60 (dd,  $J = 6.9, 11.1$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  141.9, 137.6, 135.3, 135.2, 134.4, 132.4, 131.6, 129.2, 128.1, 127.6, 127.4, 127.3, 126.9, 123.8, 123.0, 117.7, 115.1, 109.7, 63.1, 57.0, 55.0, 44.6; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3416, 2926, 1483, 1458, 1216, 1089, 1015, 801, 762; ESI-MS ( $m/z$ ): 399 ( $\text{M}+1^+$ ); HRMS (ESI): Exact mass calcd. for  $\text{C}_{29}\text{H}_{24}\text{ClN}_2$  [ $\text{M}$ ] $^+$ : 399.1623. Found: 399.1636.

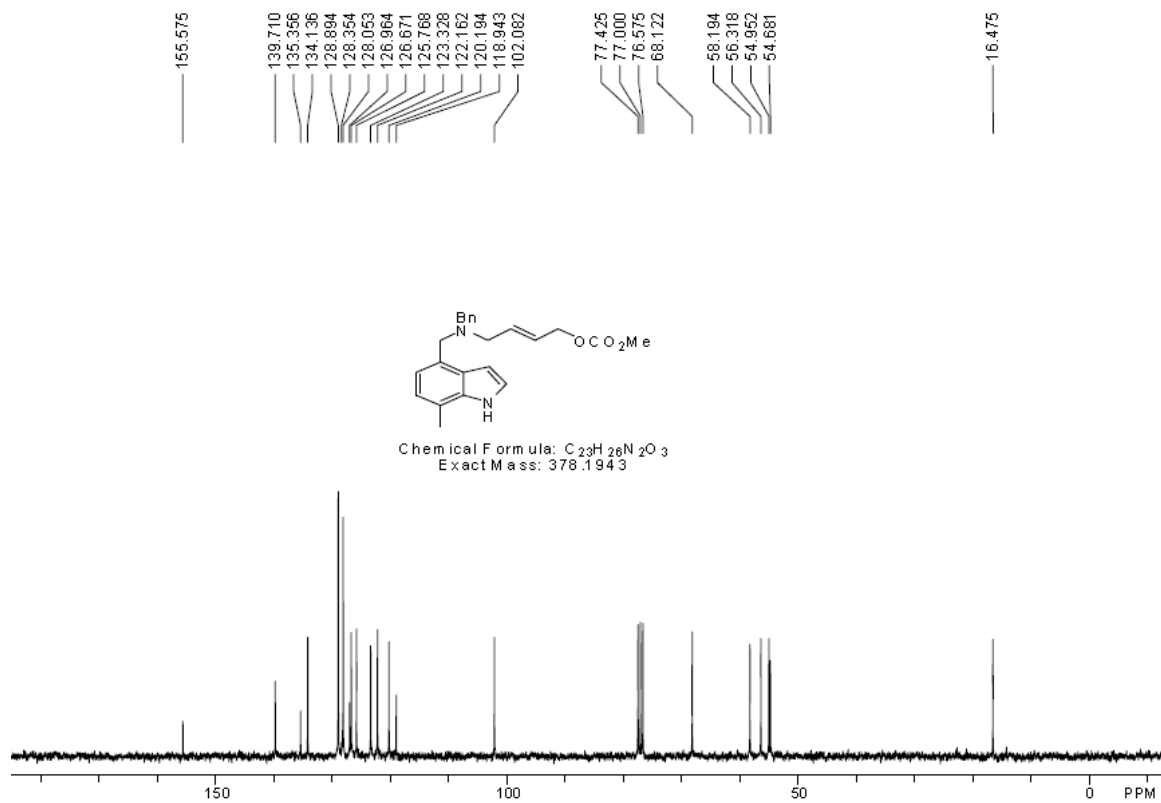
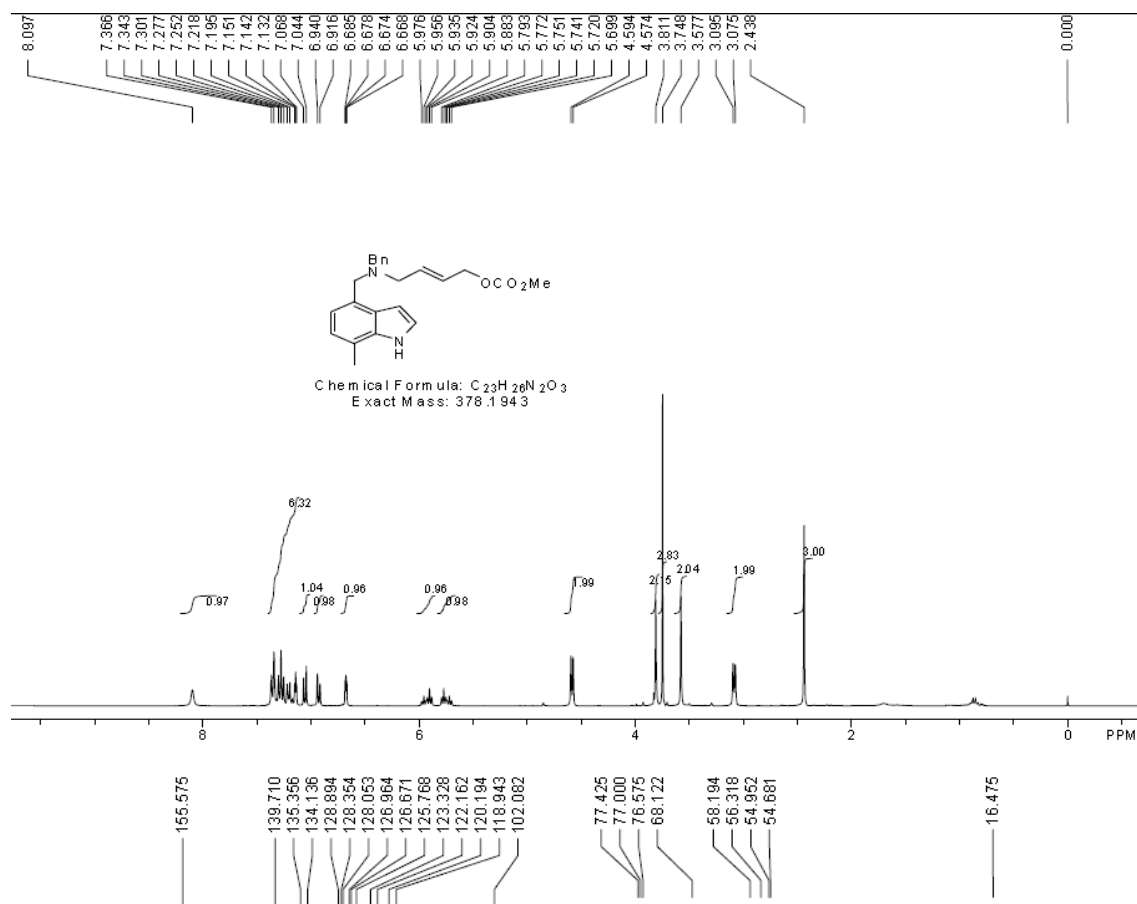


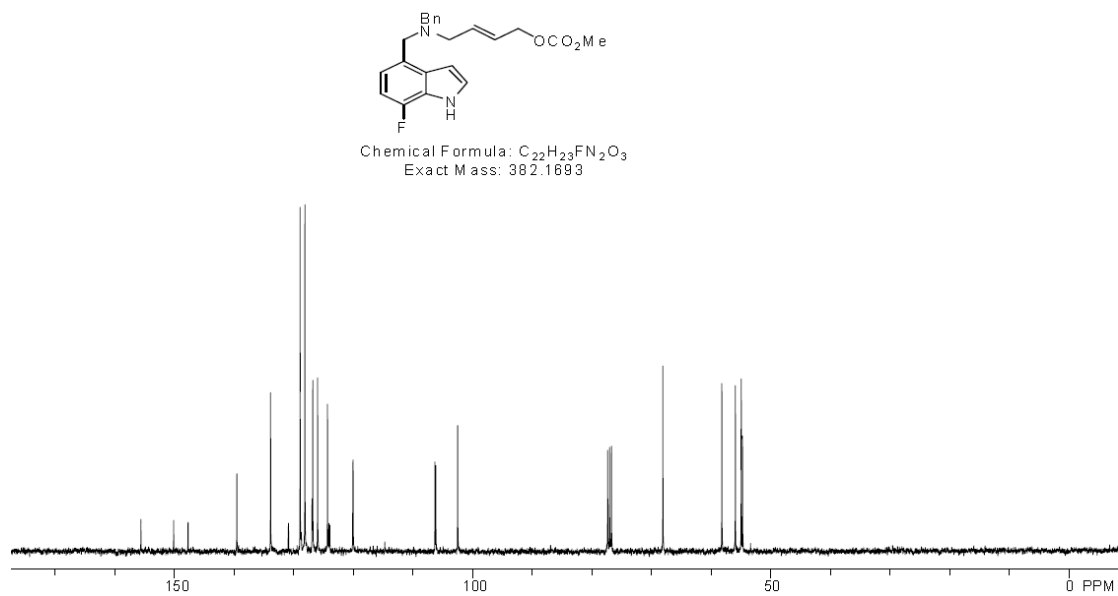
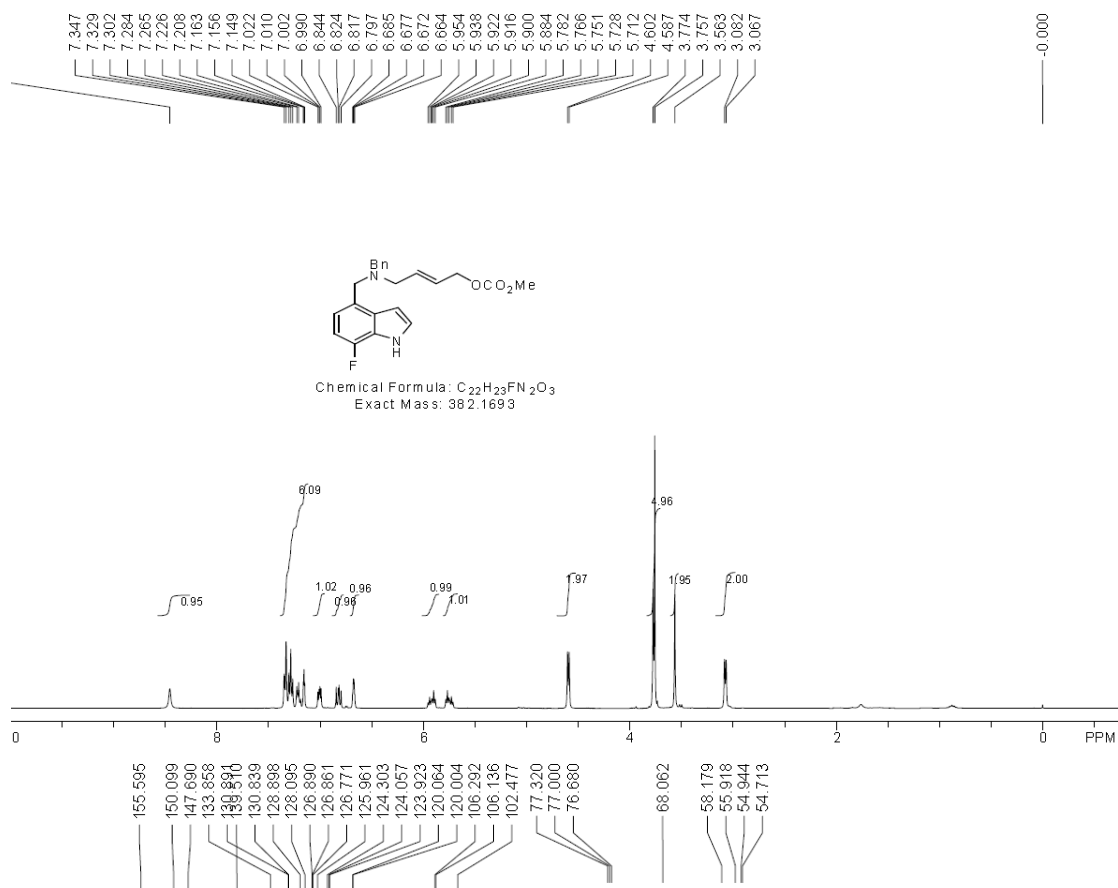
Colorless oil, 80% yield [4.4:(2.7/1)], 78% ee. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); *n*-hexane/2-propanol = 80/20; flow rate = 0.5 mL/min; detection wavelength = 230 nm;  $t_{\text{R}} = 17.96$  (major), 16.13 (minor) min].  $[\alpha]_{\text{D}}^{20} = -64.6$  (c 0.5,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (br s, 1H), 7.24-7.11 (m, 8H), 7.03 (d,  $J = 8.4$  Hz, 1H), 6.95 (d,  $J = 2.7$  Hz, 1H), 6.82 (d,  $J = 12.0$  Hz, 2H), 5.95 (ddd,  $J = 7.2,$

9.9, 17.1 Hz, 1H), 5.18 (d,  $J = 17.1$  Hz, 1H), 5.07 (dd,  $J = 2.1, 10.2$  Hz, 1H), 3.87 (s, 3H), 3.68 (q,  $J = 7.2$  Hz, 1H), 3.56-3.40 (m, 4H), 2.91 (dd,  $J = 5.4, 11.1$  Hz, 1H), 2.57 (dd,  $J = 7.2, 11.1$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 141.9, 137.6, 134.4, 131.5, 129.2, 129.1, 128.0, 127.4, 126.9, 126.8, 123.5, 123.3, 122.9, 118.5, 115.0, 112.9, 109.6, 62.8, 56.6, 55.2, 55.0, 44.4; IR (film):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) = 3419, 2958, 1549, 1501, 1284, 1259, 1025, 797, 758; ESI-MS ( $m/z$ ): 395 ( $\text{M}+1^+$ ); HRMS (ESI): Exact mass calcd. for  $\text{C}_{27}\text{H}_{27}\text{N}_2\text{O}$  [ $\text{M}$ ] $^+$ : 395.2118. Found: 395.2129.

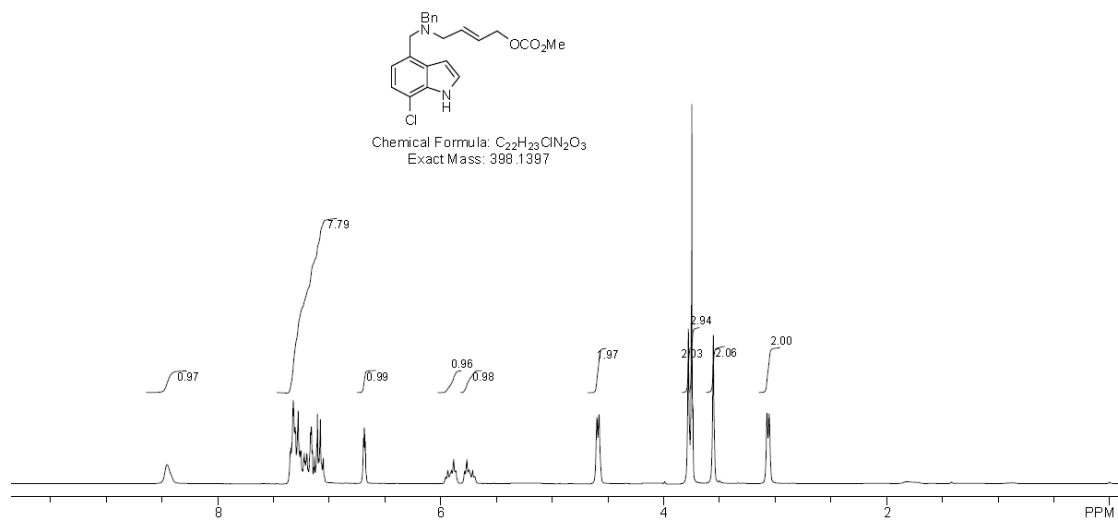
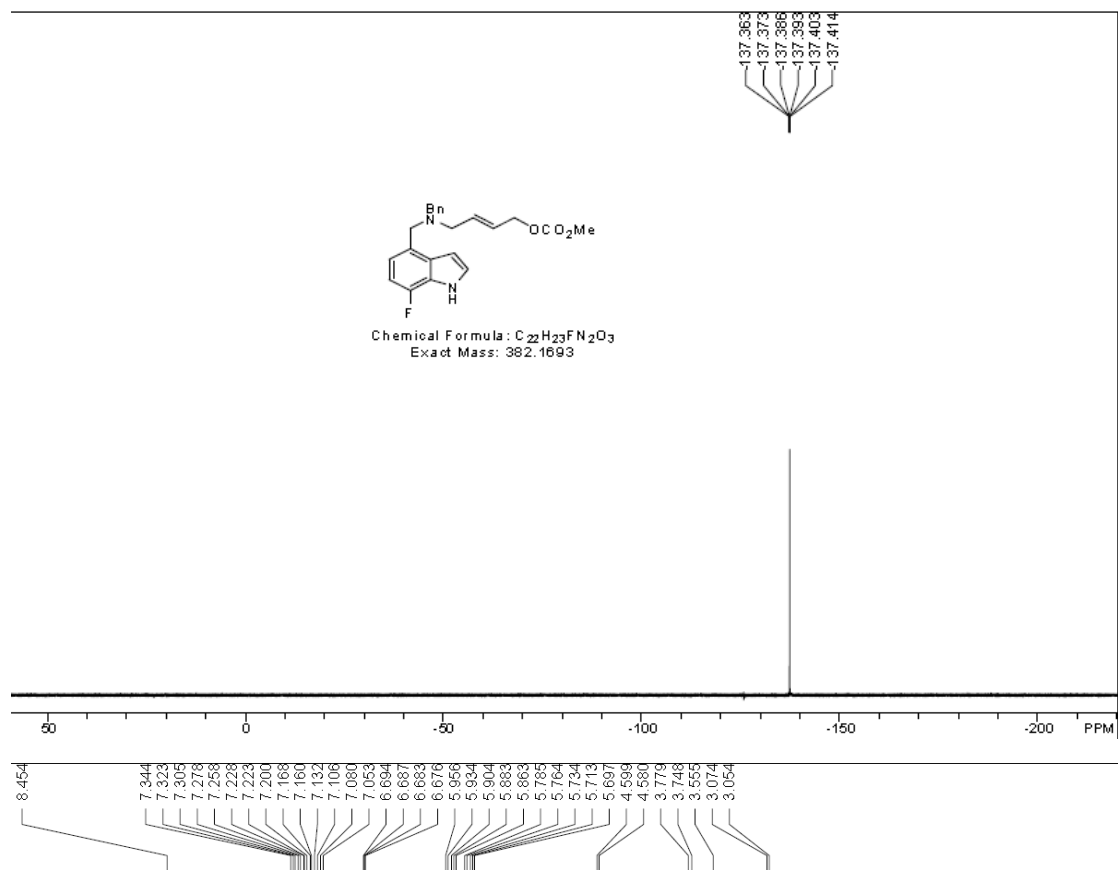


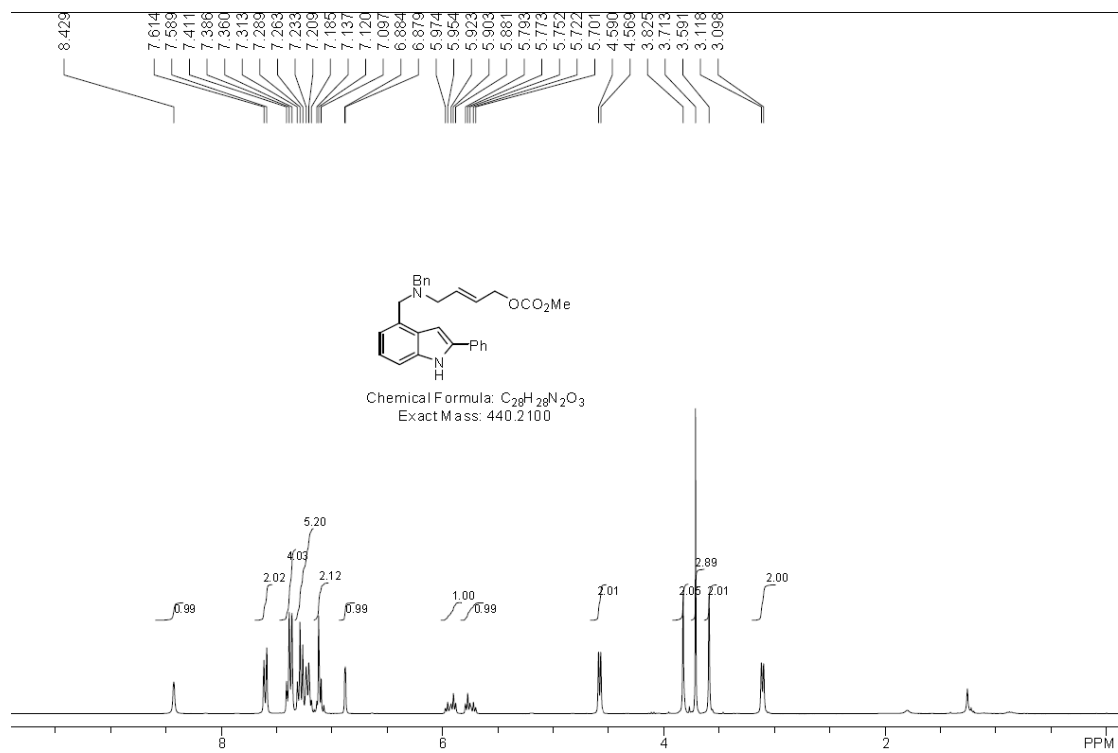
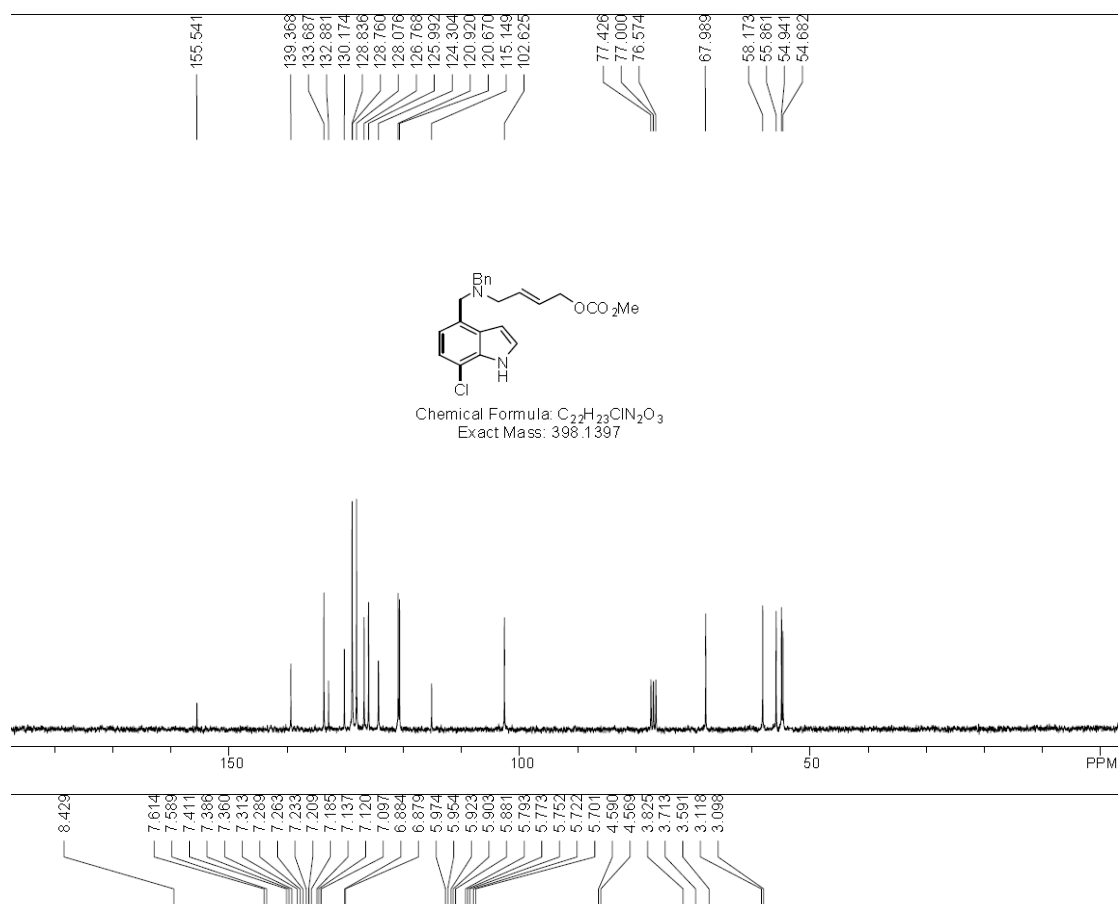


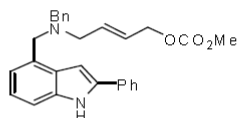
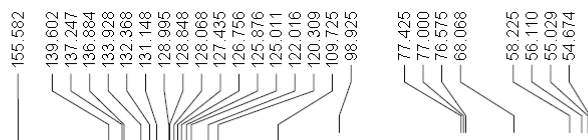




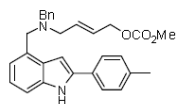
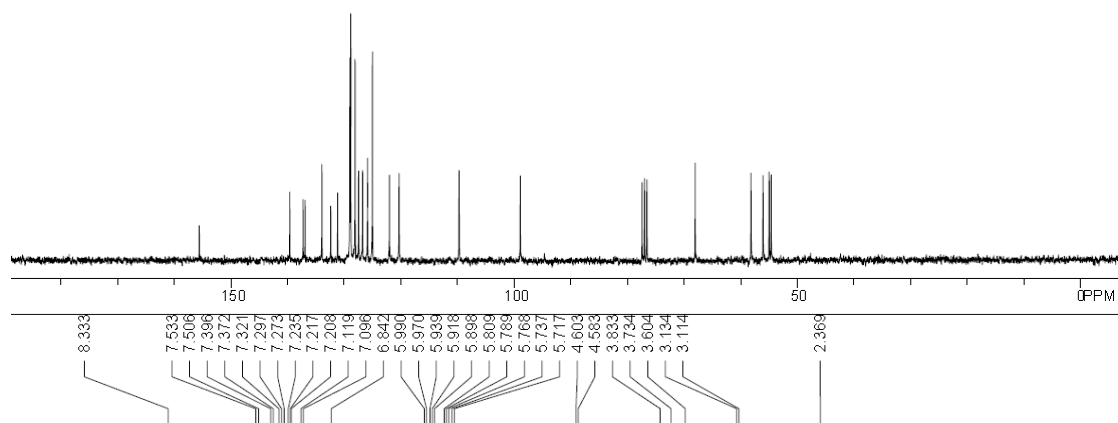




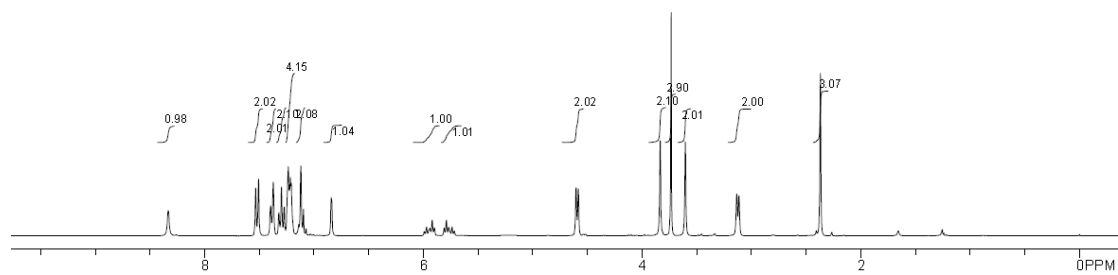


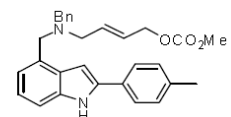
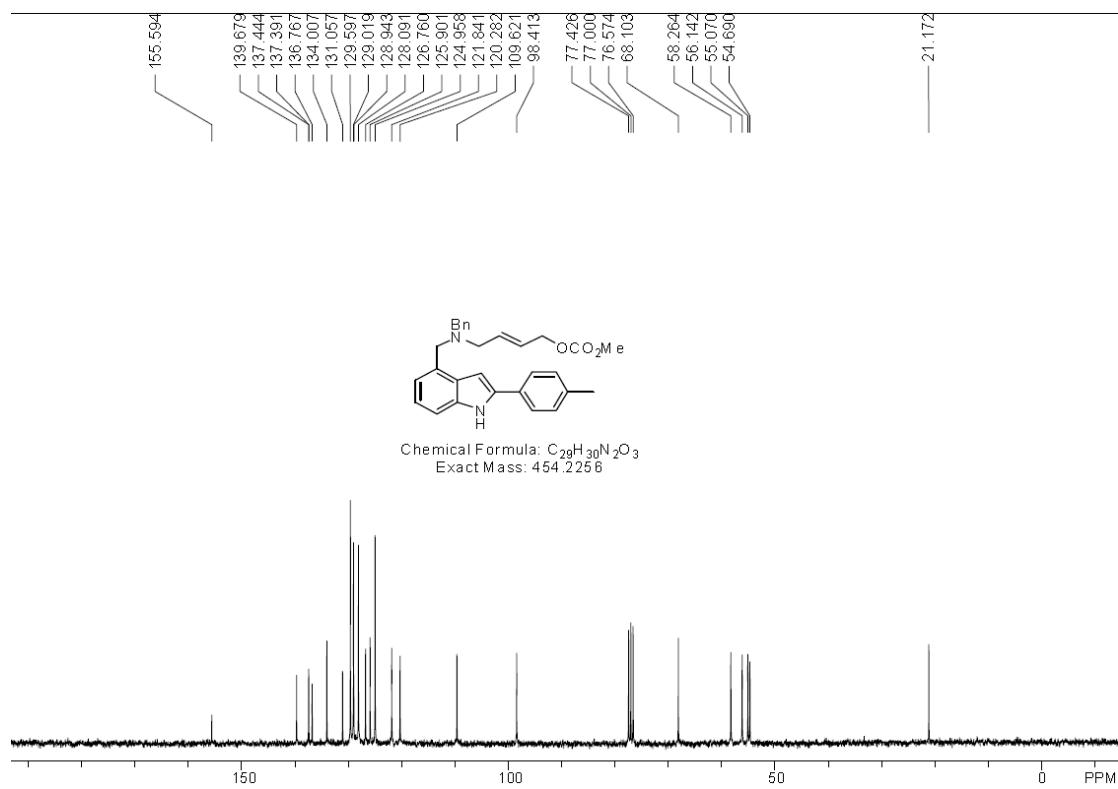


Chemical Formula:  $C_{28}H_{28}N_2O_3$   
Exact Mass: 440.2100

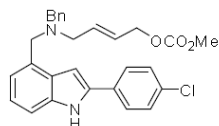
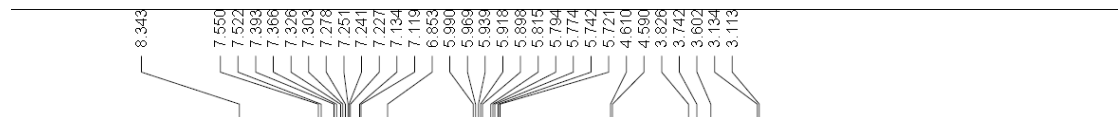


Chemical Formula:  $C_{29}H_{29}N_2O_3$   
Exact Mass: 454.2256

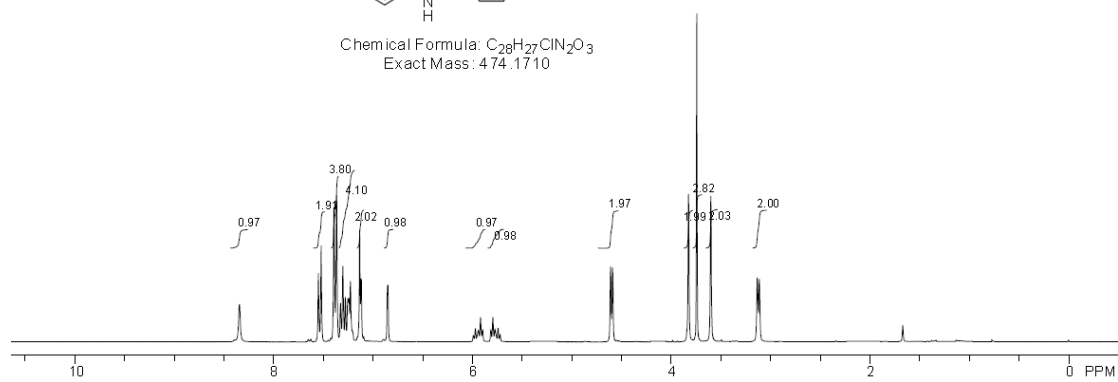


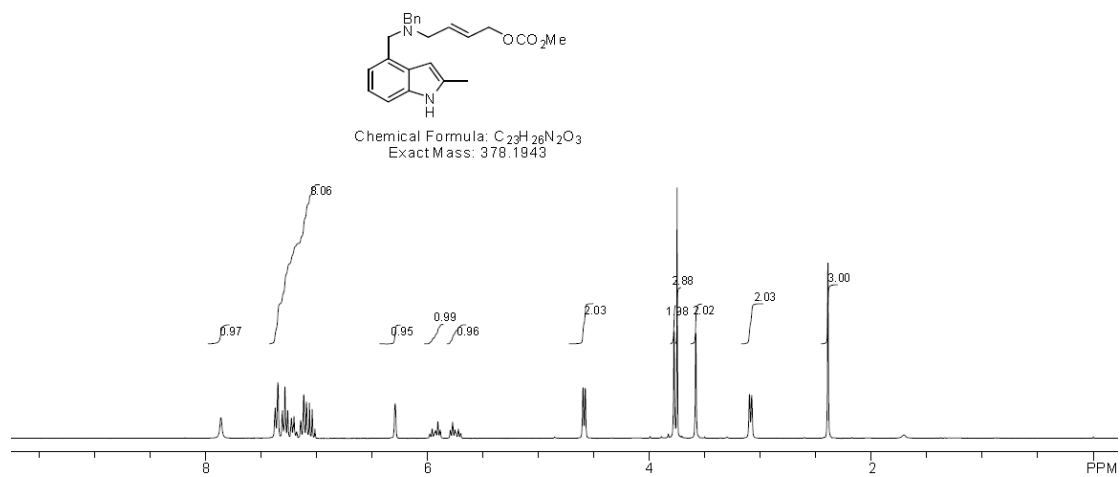
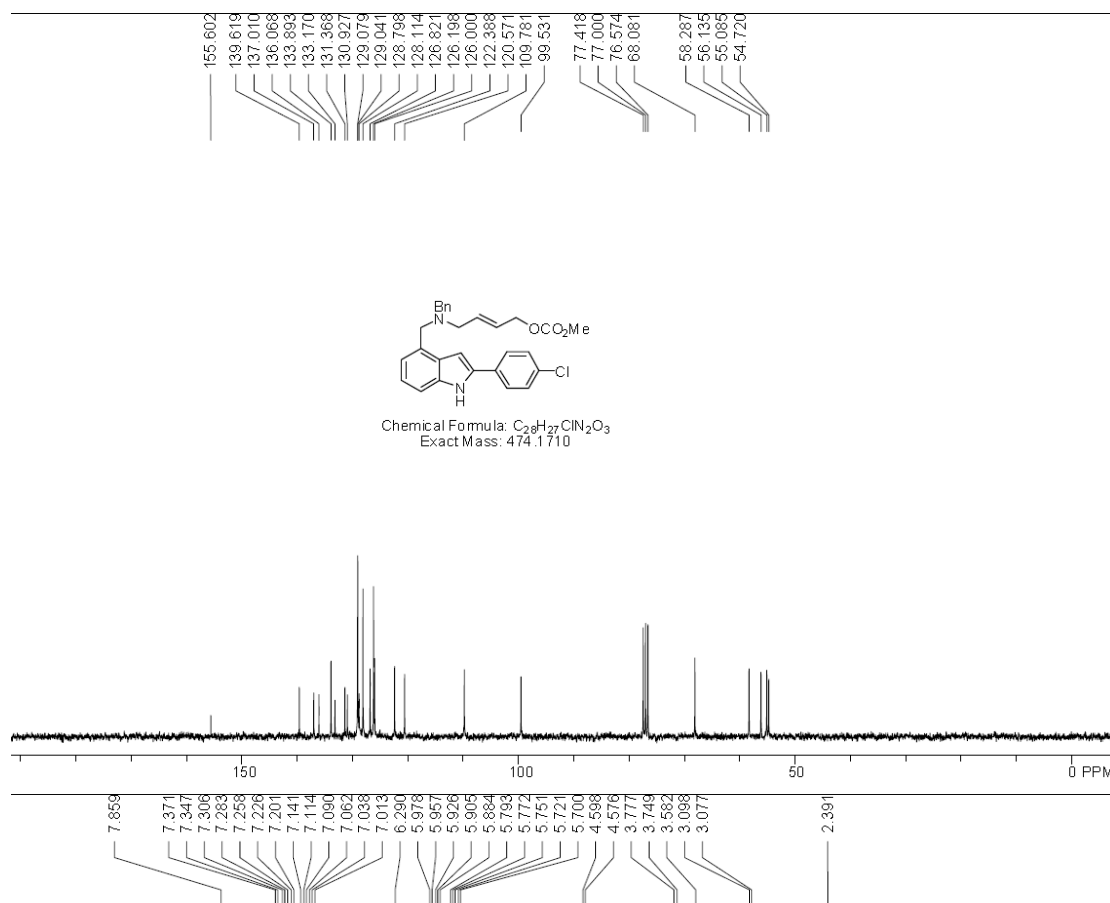


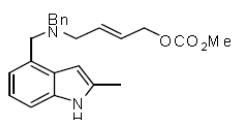
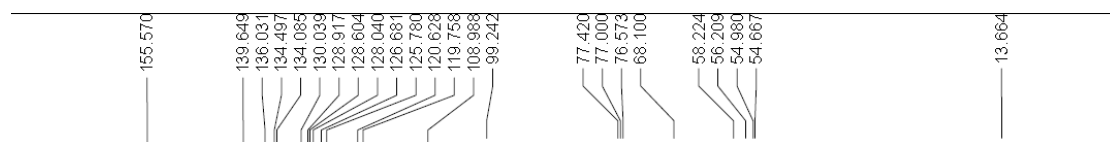
Chemical Formula:  $C_{29}H_{30}N_2O_3$   
Exact Mass: 454.2256



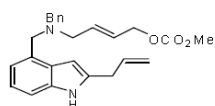
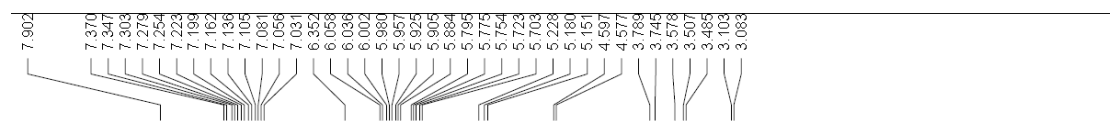
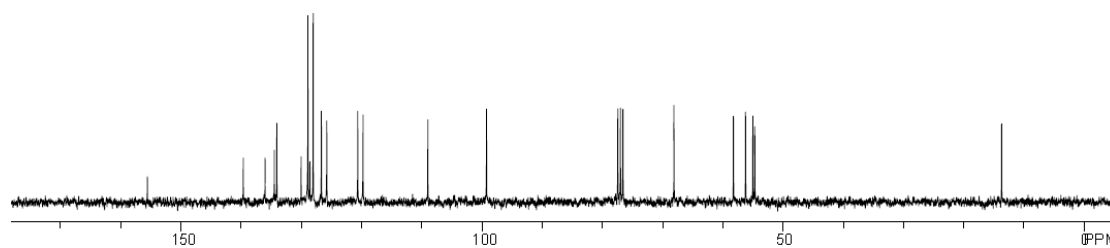
Chemical Formula:  $C_{29}H_{27}ClN_2O_3$   
Exact Mass: 474.1710



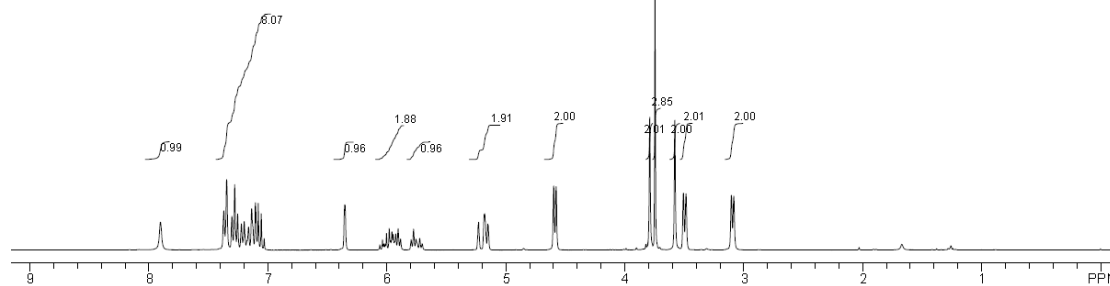


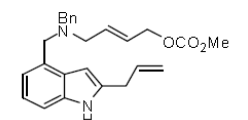
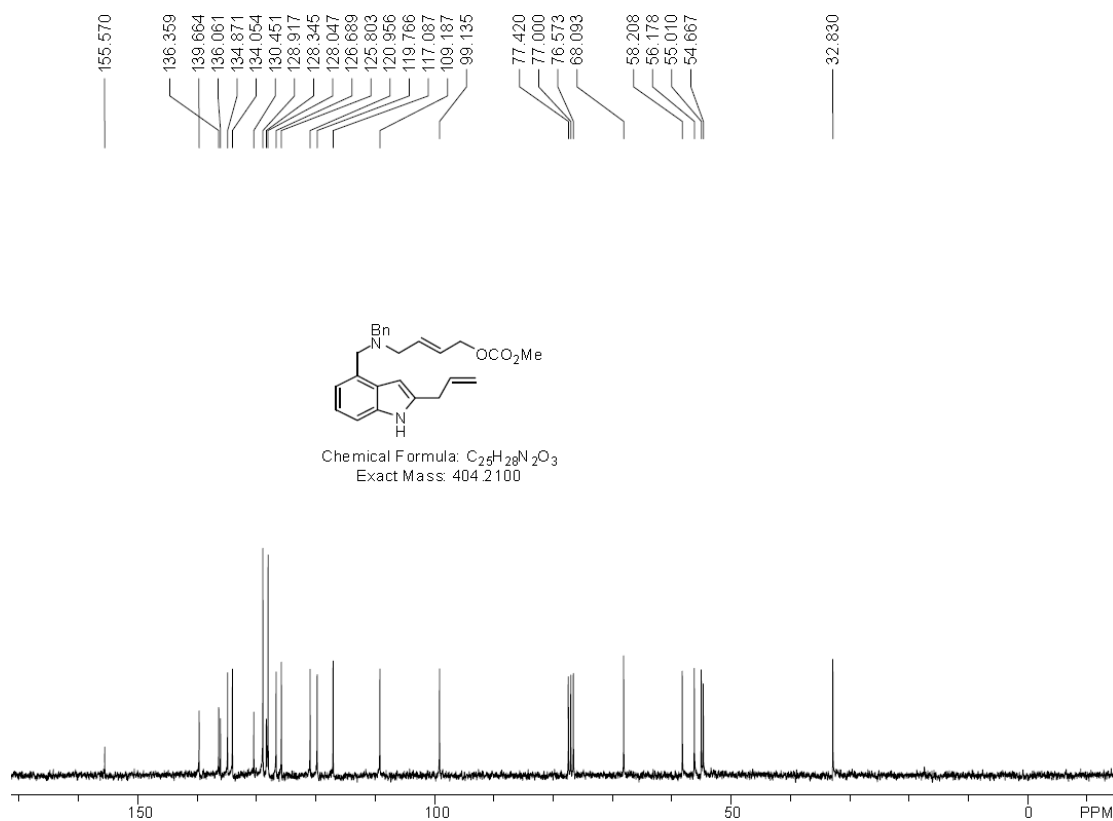


Chemical Formula:  $C_{23}H_{28}N_2O_3$   
Exact Mass: 378.1943

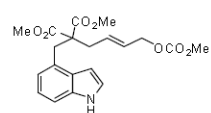
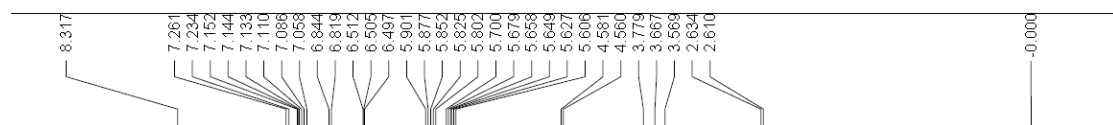


Chemical Formula:  $C_{25}H_{28}N_2O_3$   
Exact Mass: 404.2100

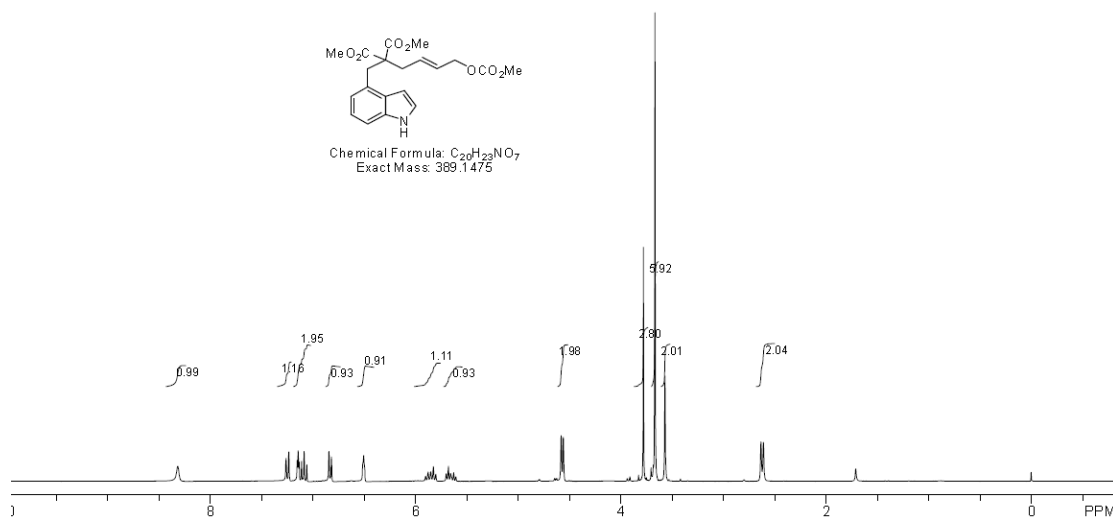


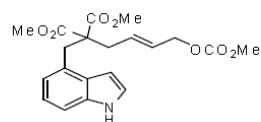
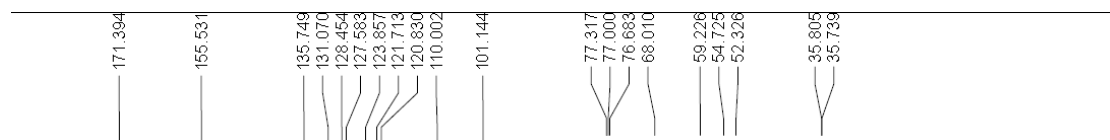


Chemical Formula:  $C_{25}H_{28}N_2O_3$   
 Exact Mass: 404.2100

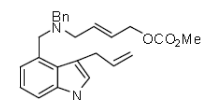
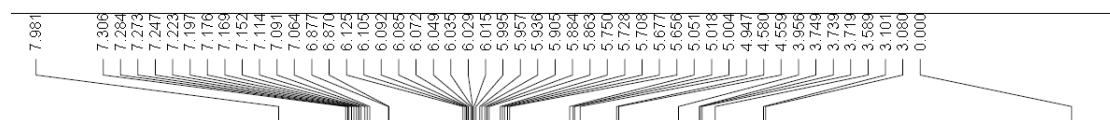
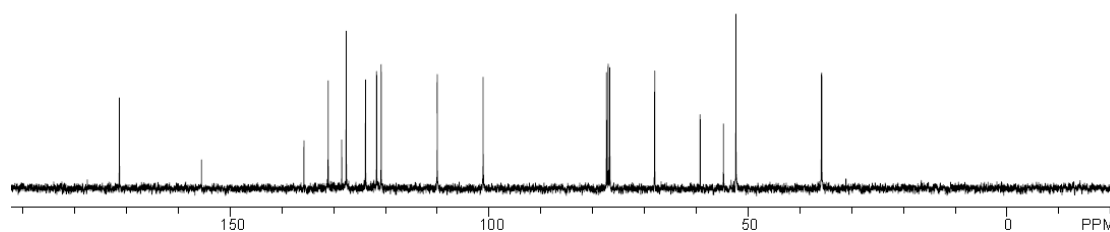


Chemical Formula:  $C_{20}H_{23}NO_7$   
 Exact Mass: 389.1475

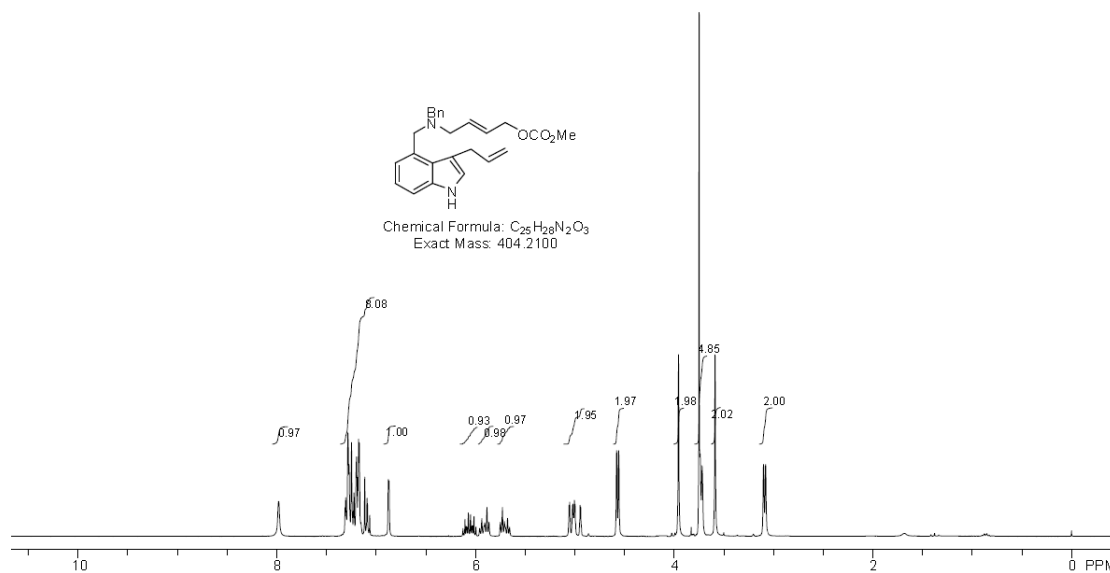




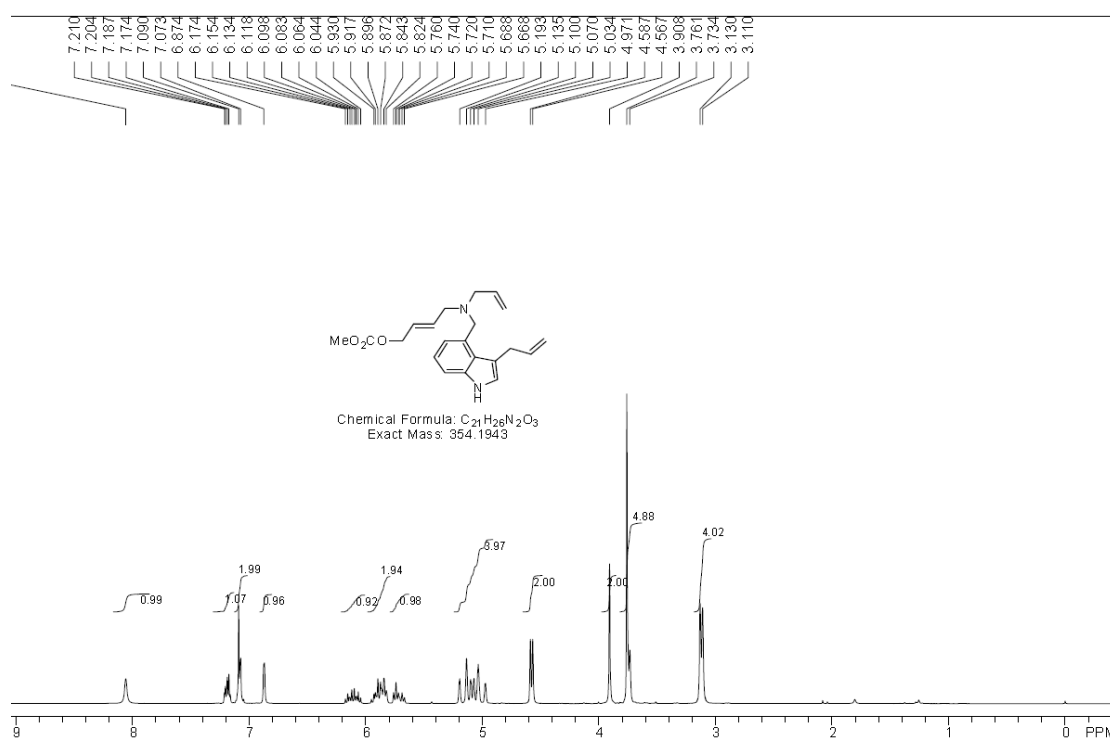
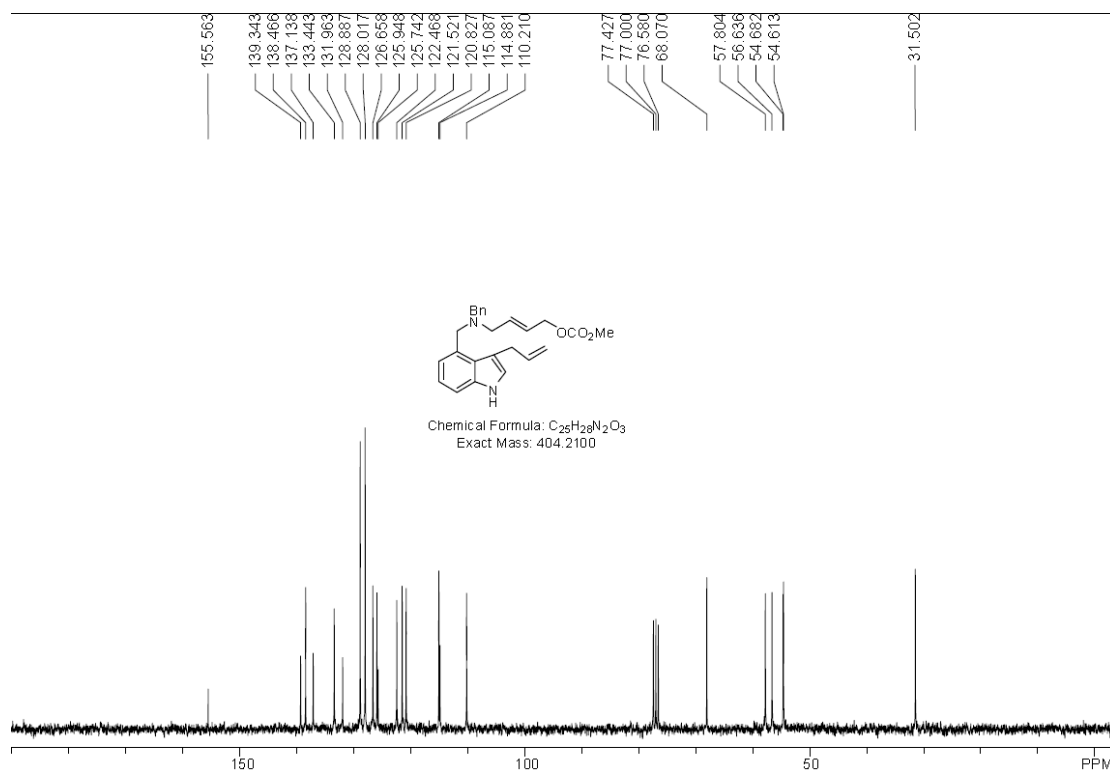
Chemical Formula: C<sub>20</sub>H<sub>23</sub>N O<sub>7</sub>  
Exact Mass: 389.1475

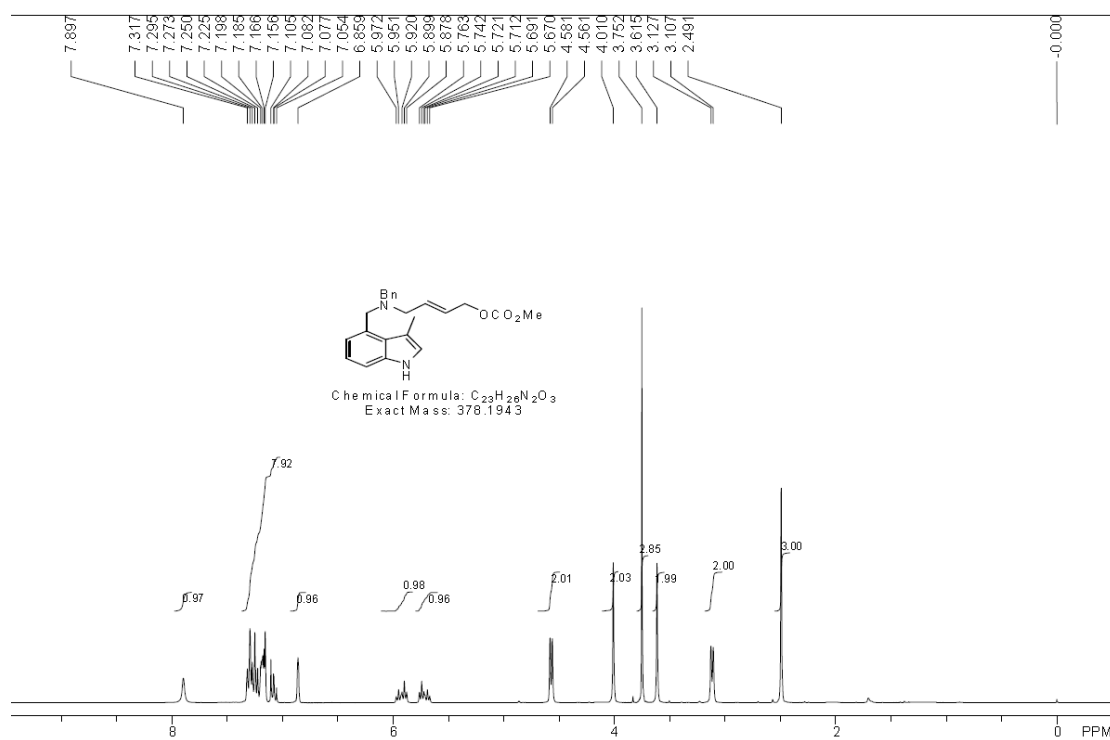
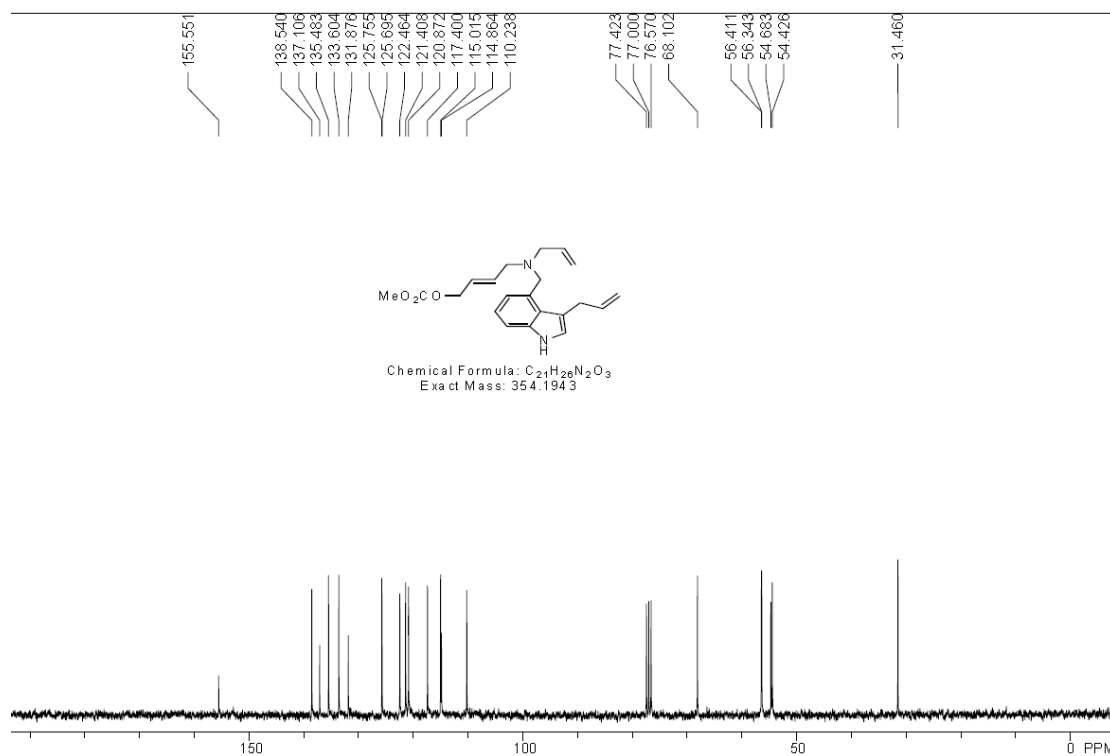


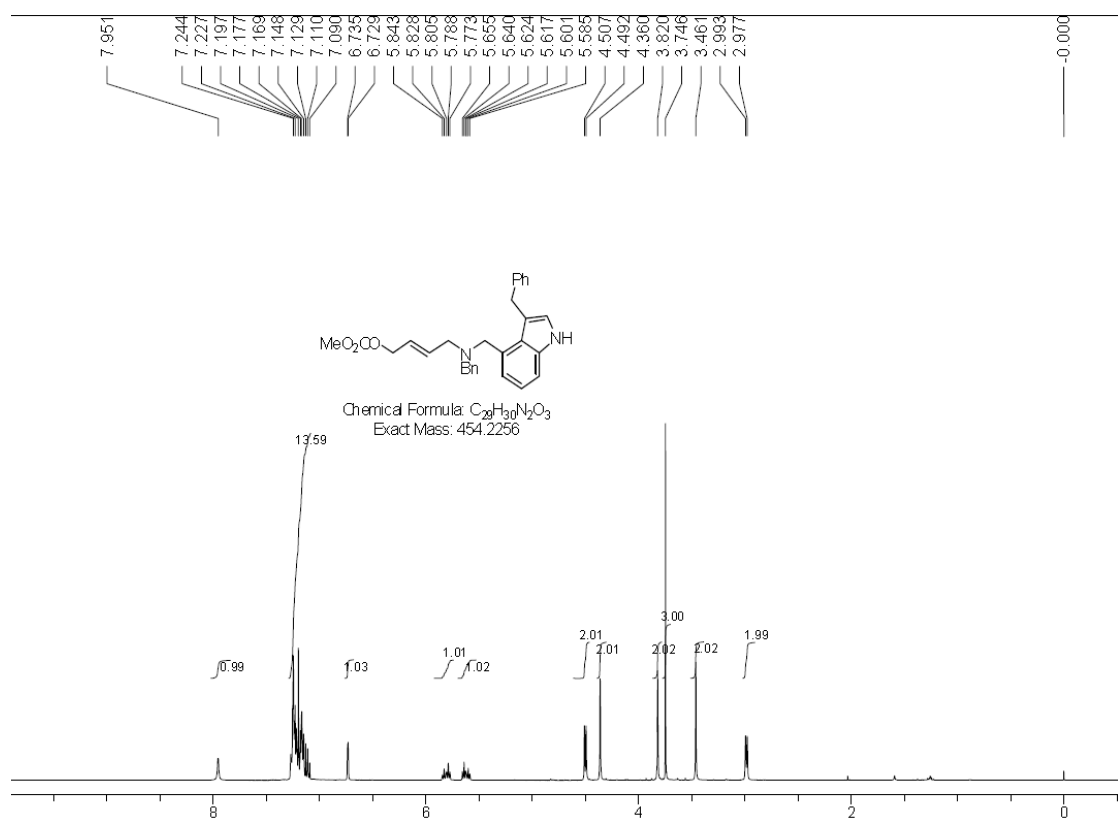
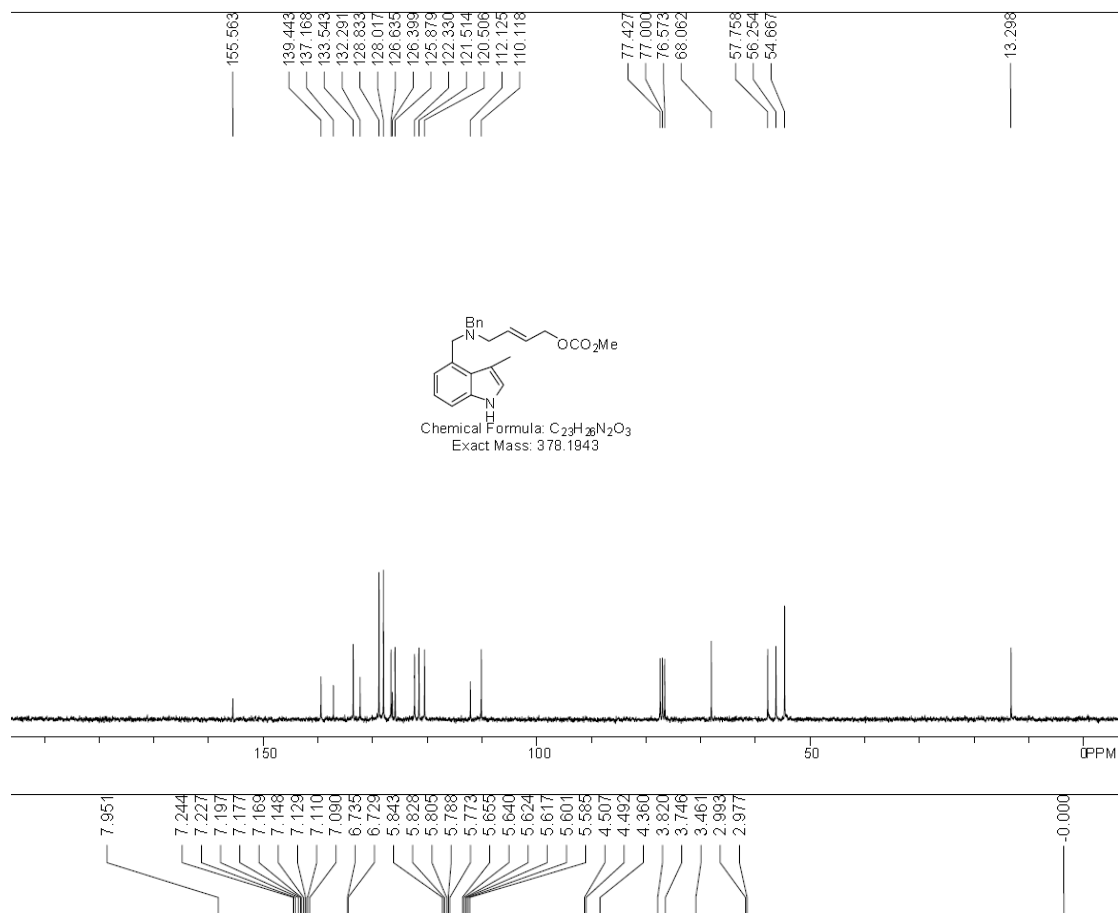
Chemical Formula: C<sub>25</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub>  
Exact Mass: 404.2100

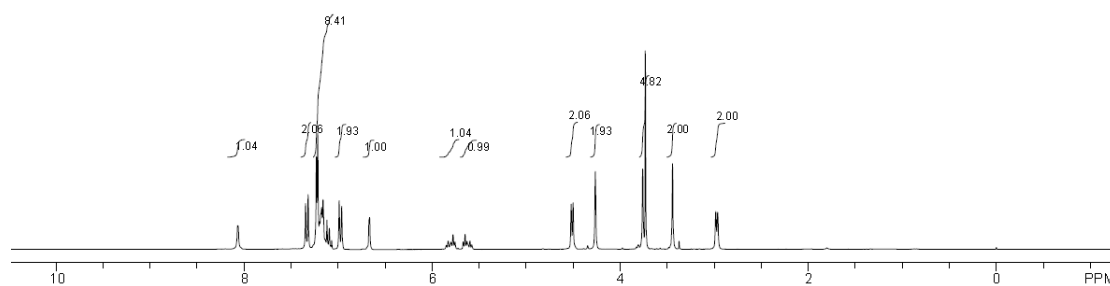
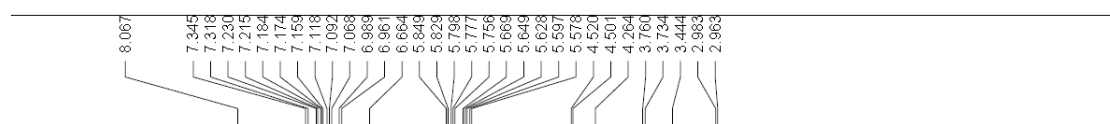
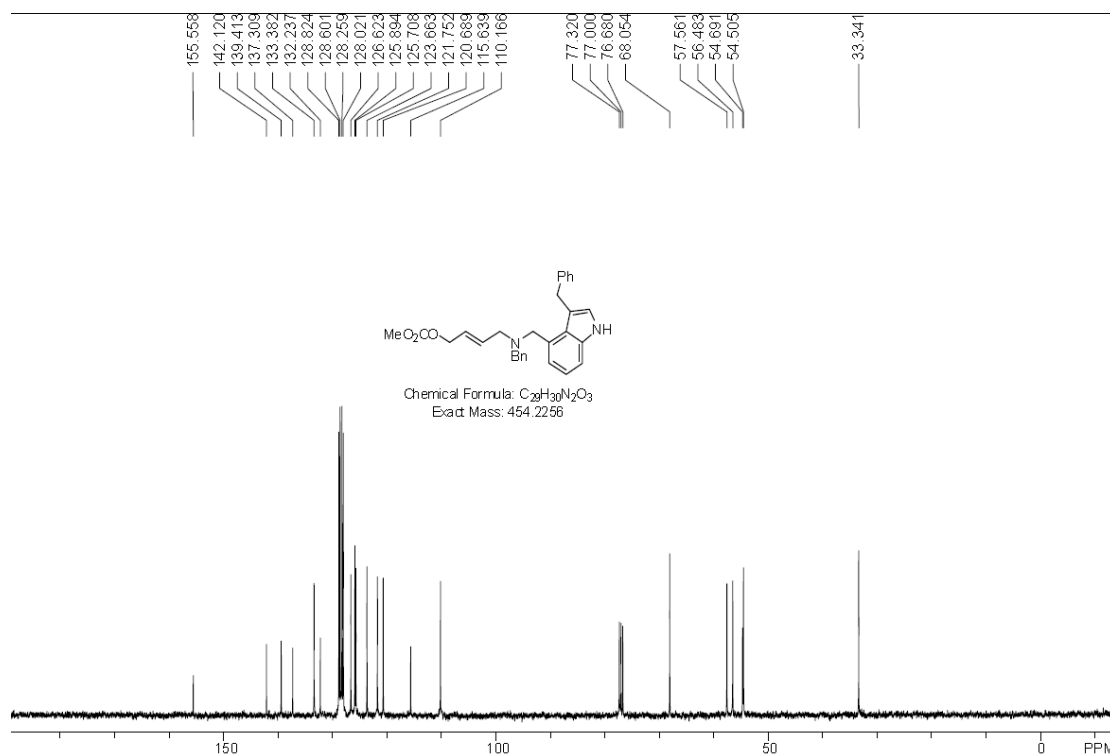


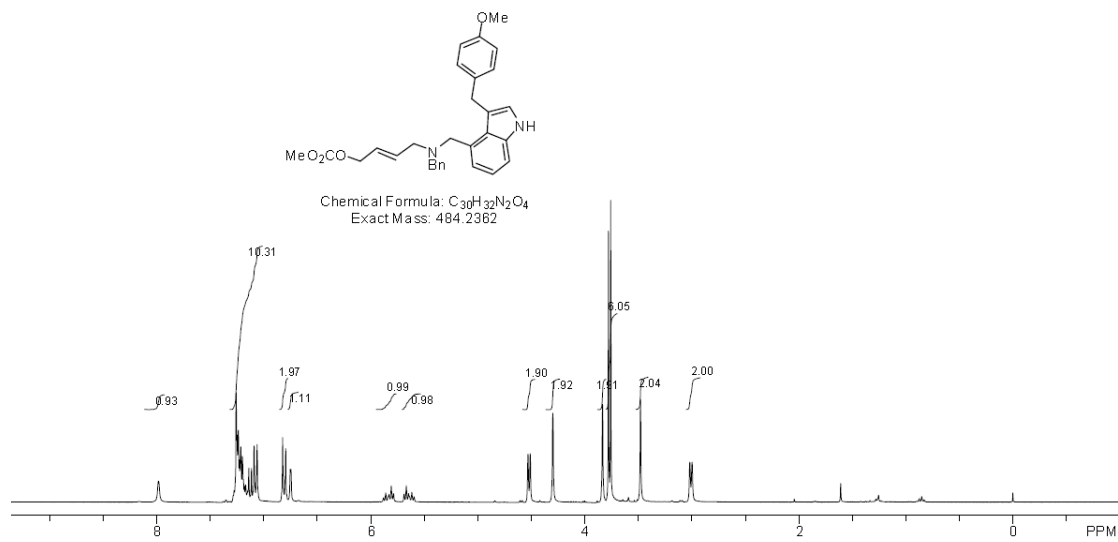
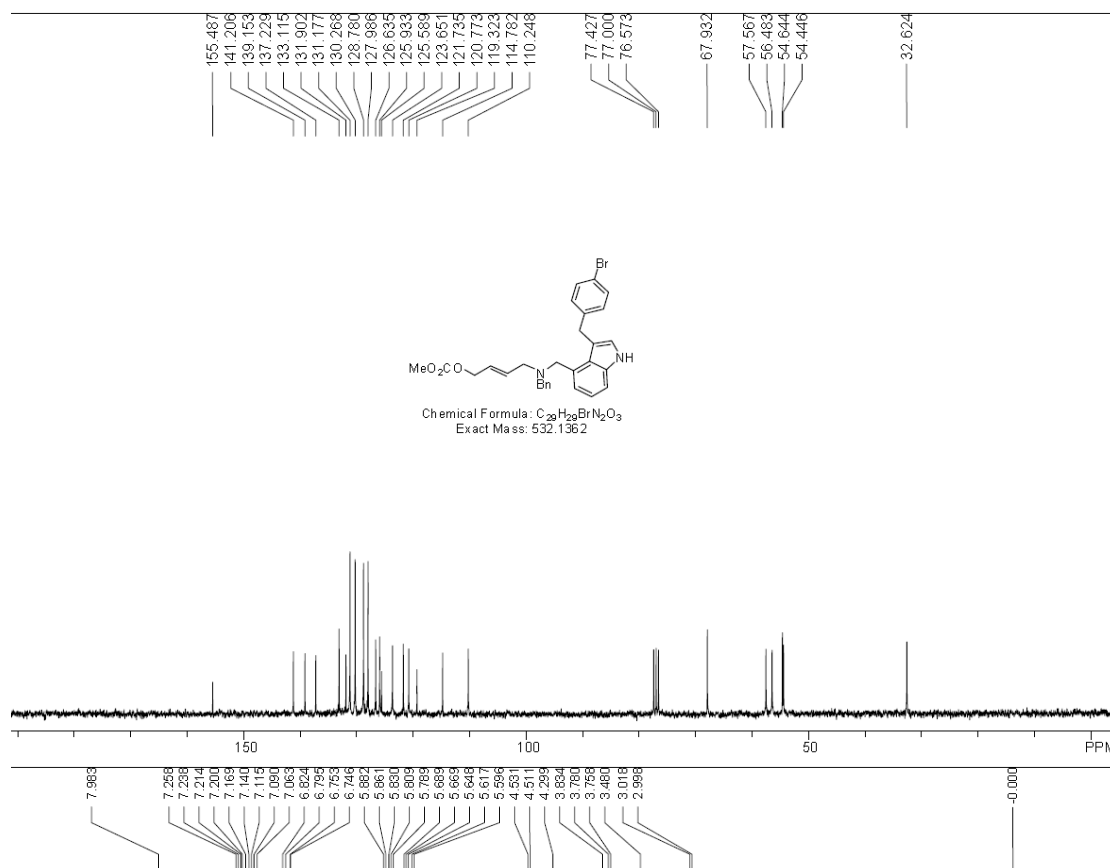


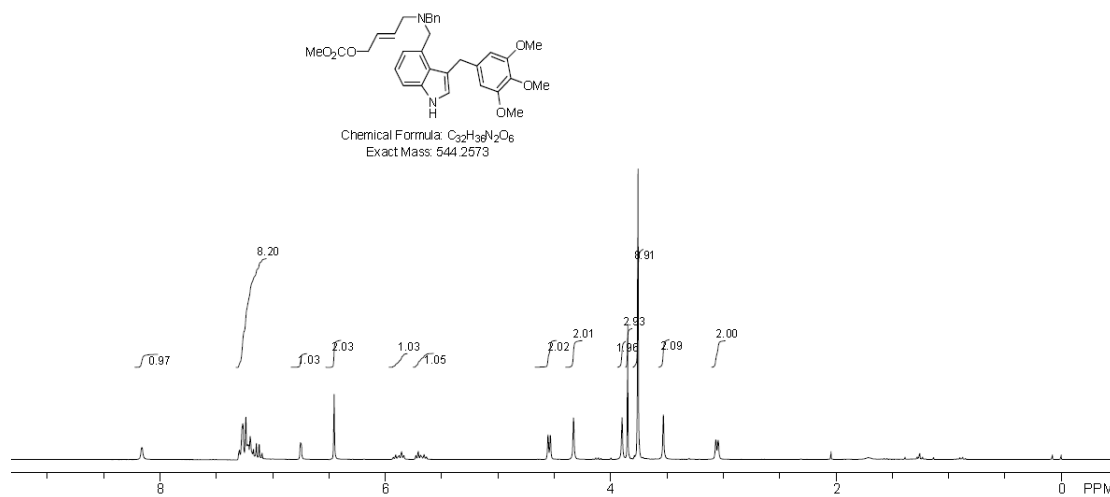
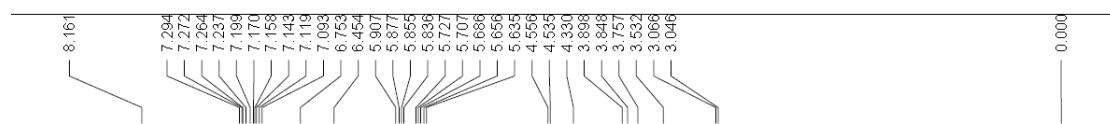
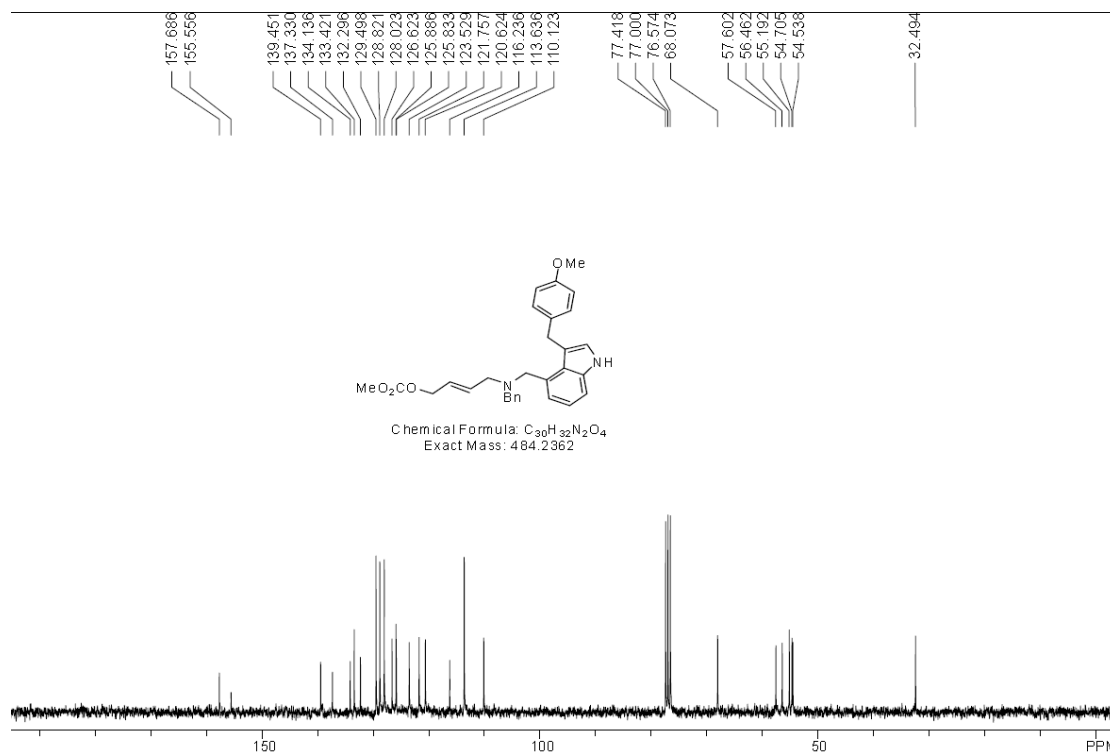


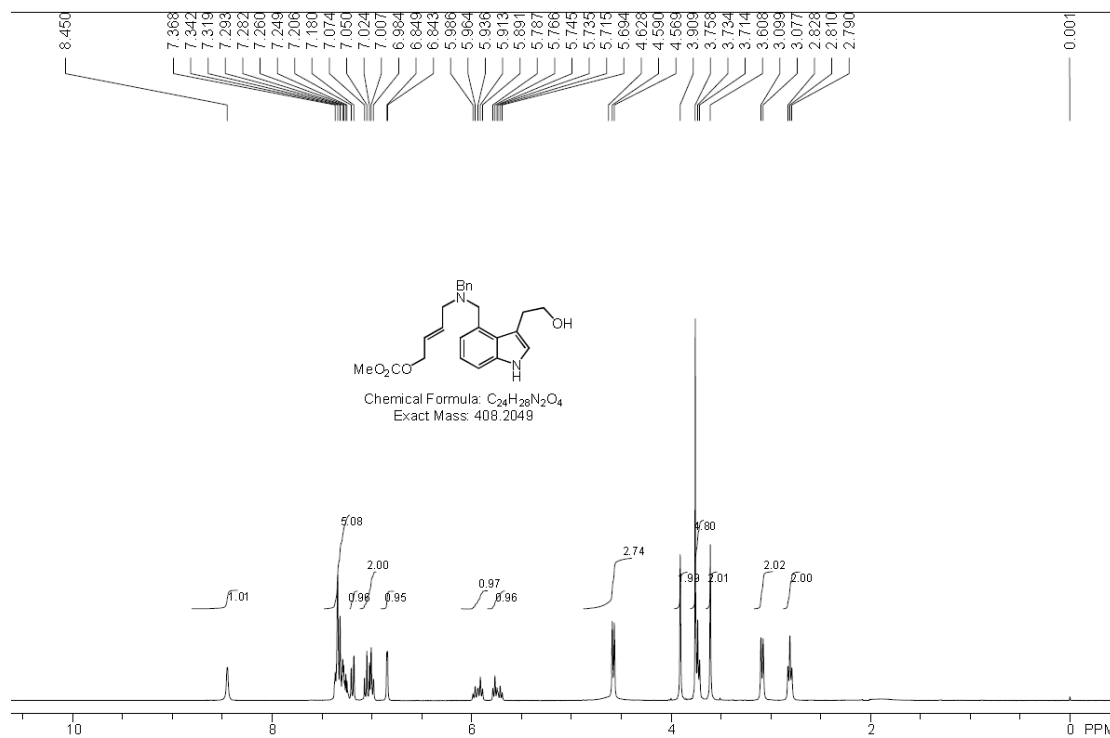
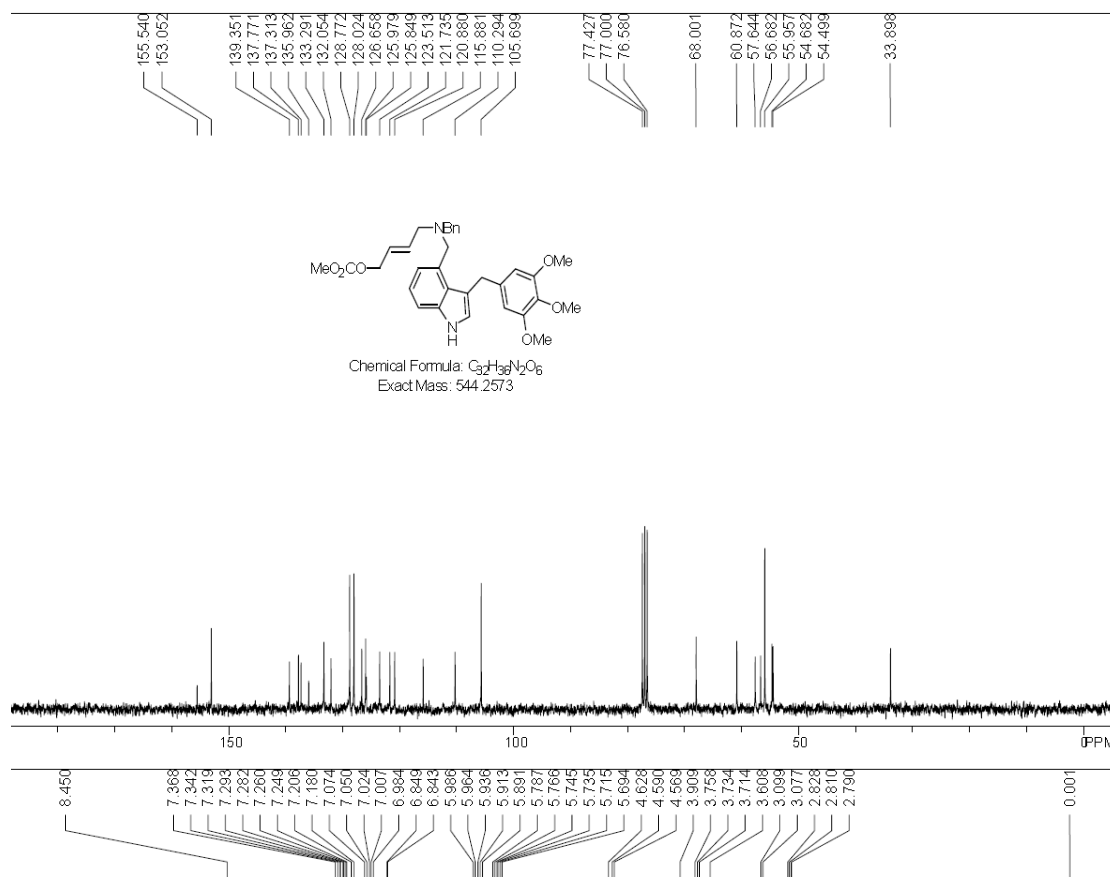


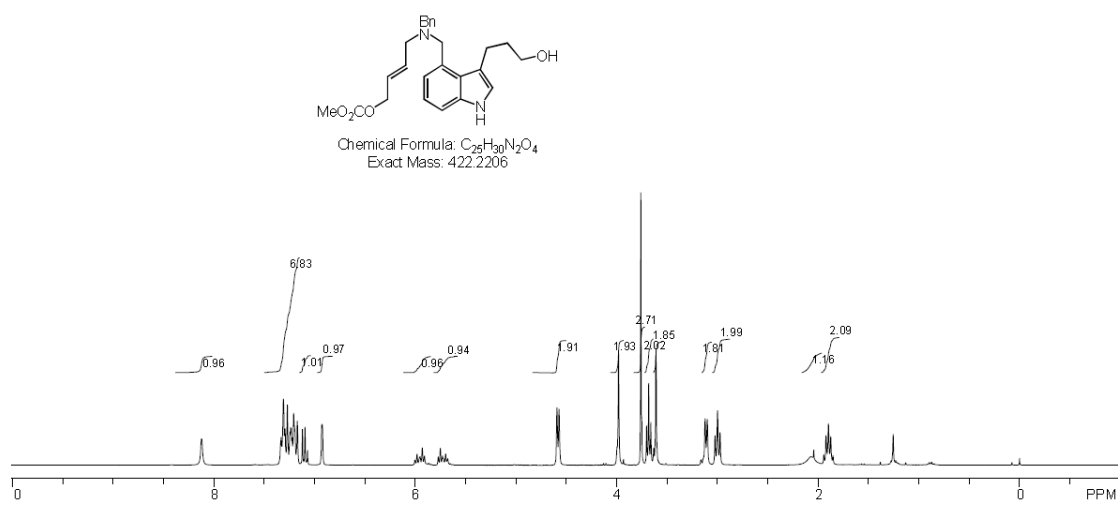
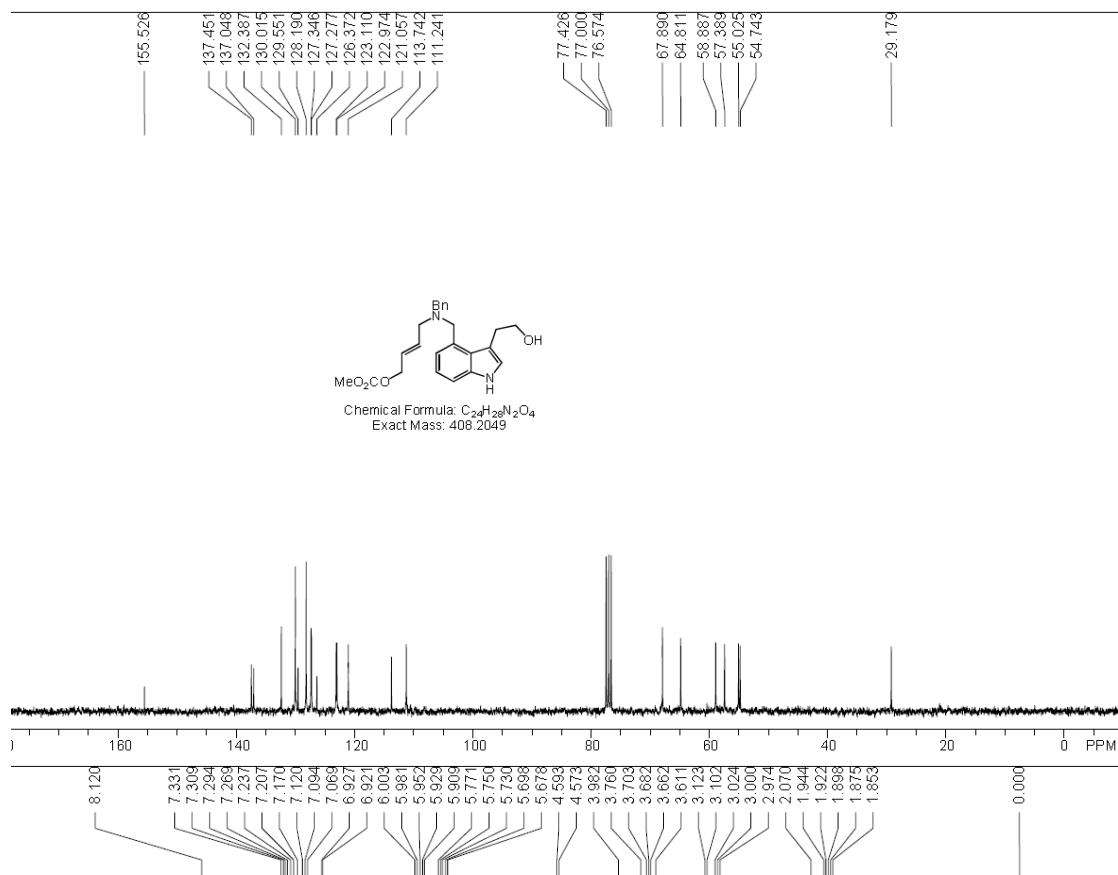




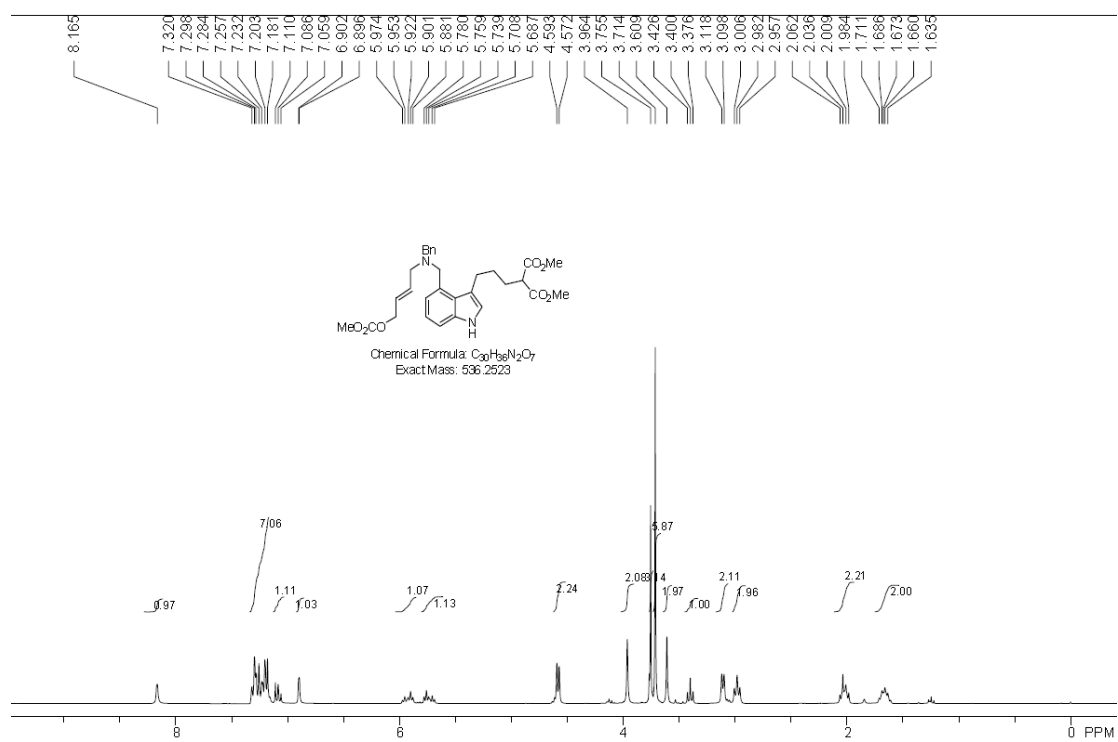
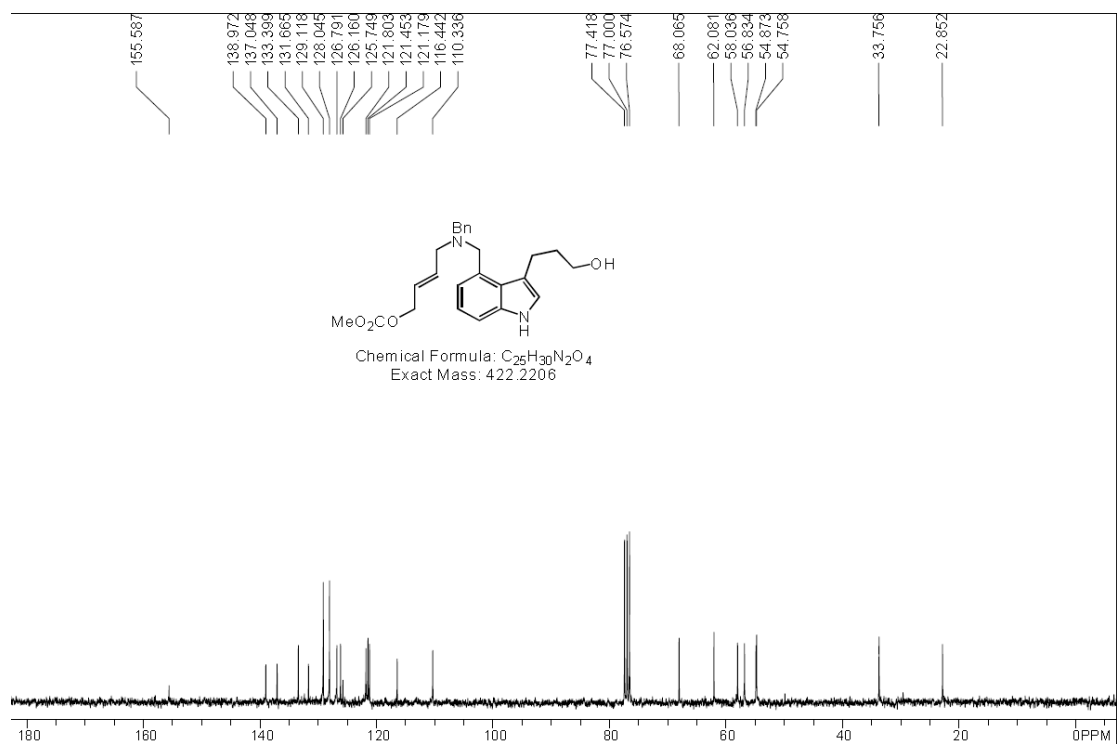


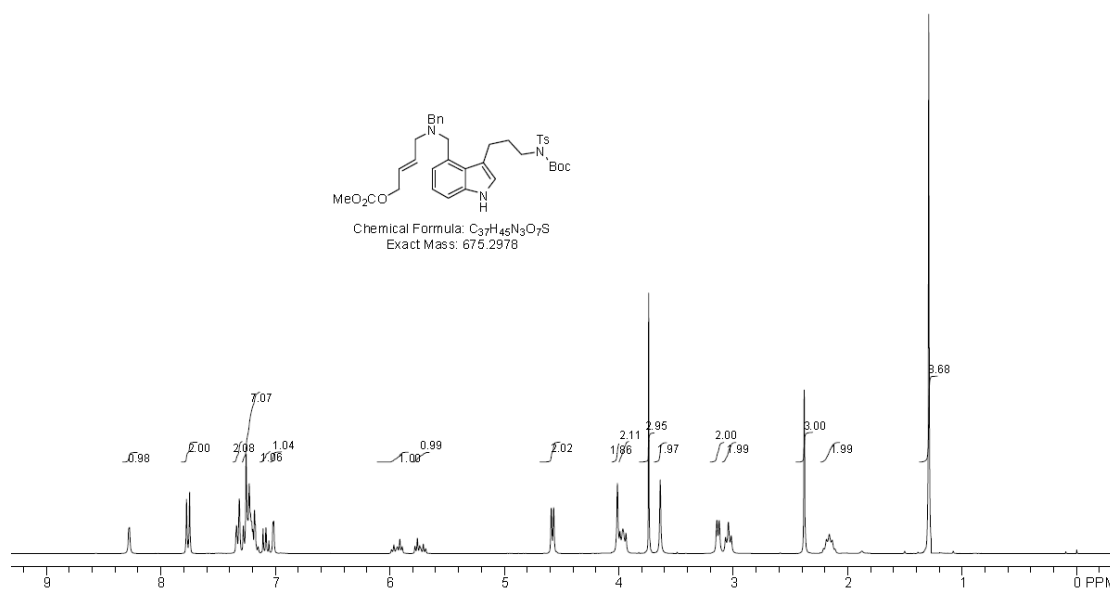
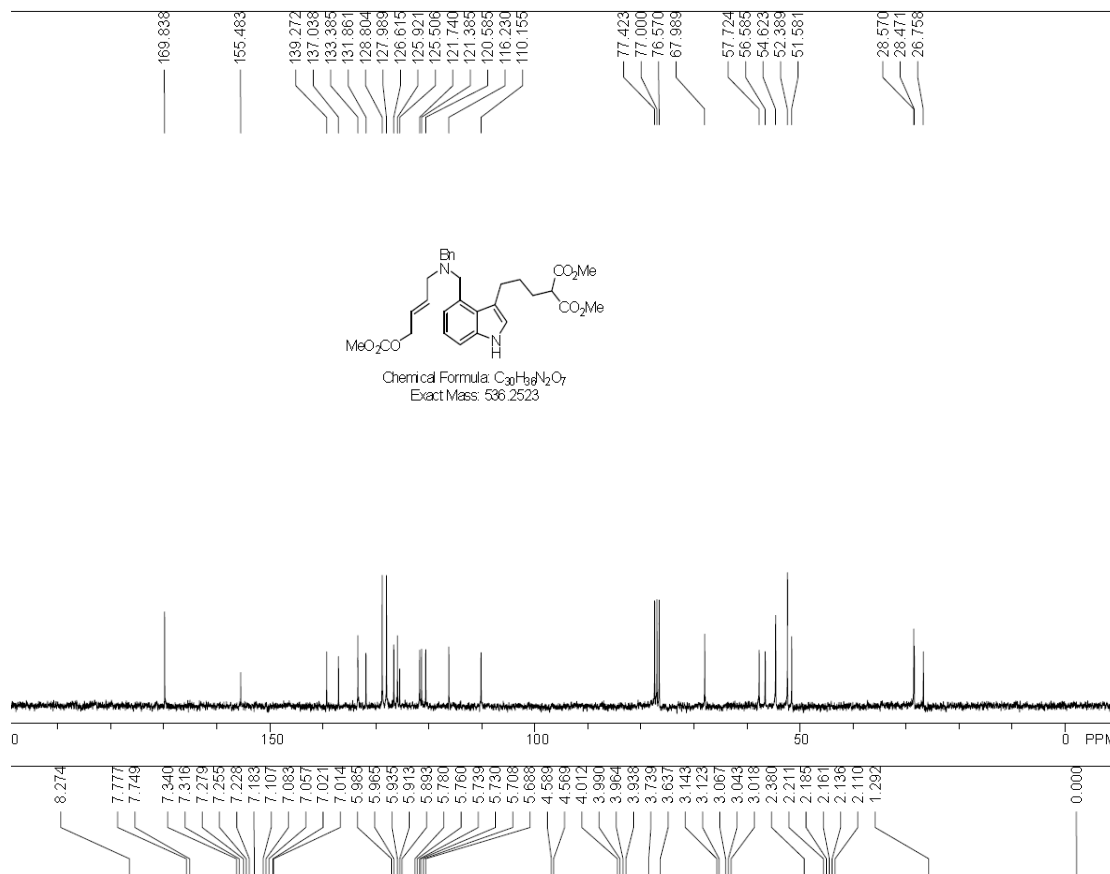


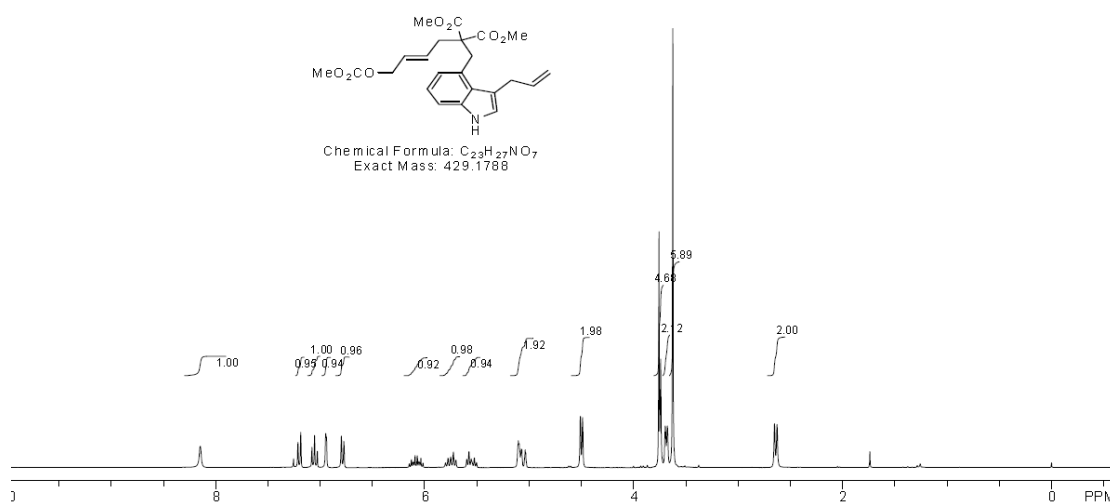
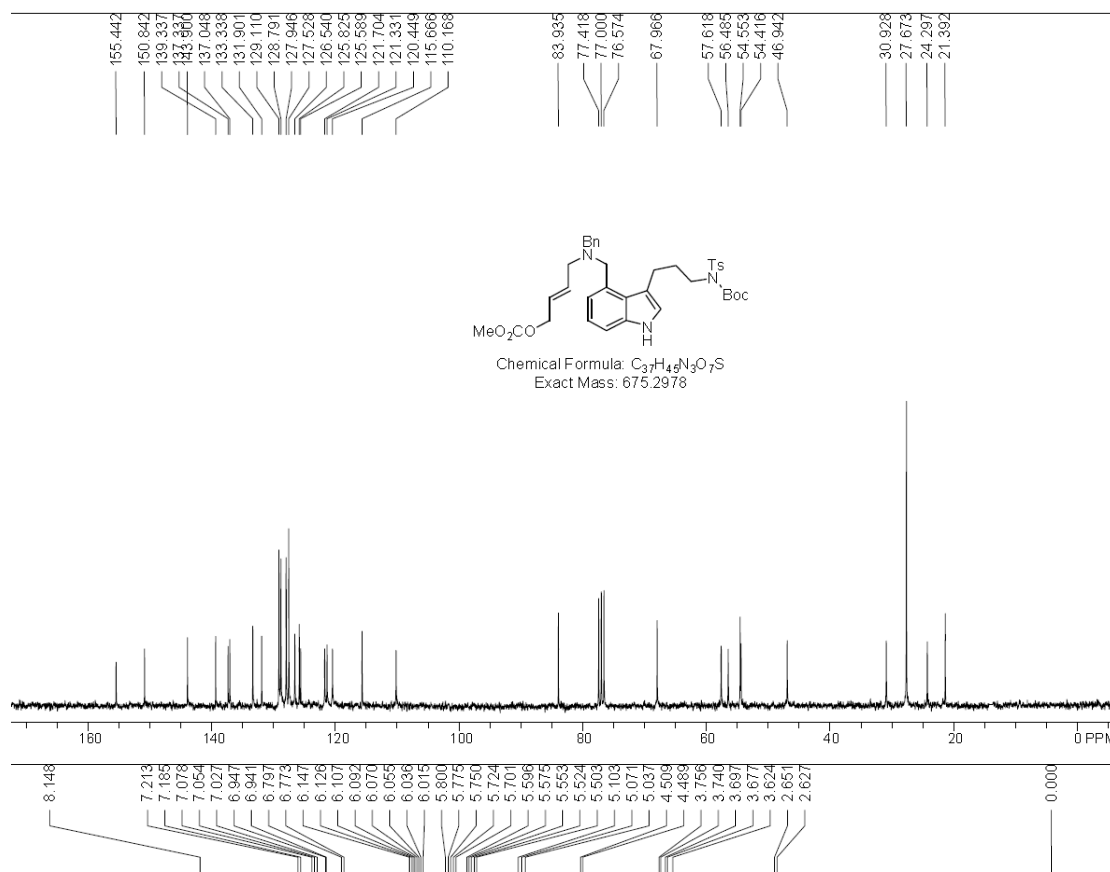


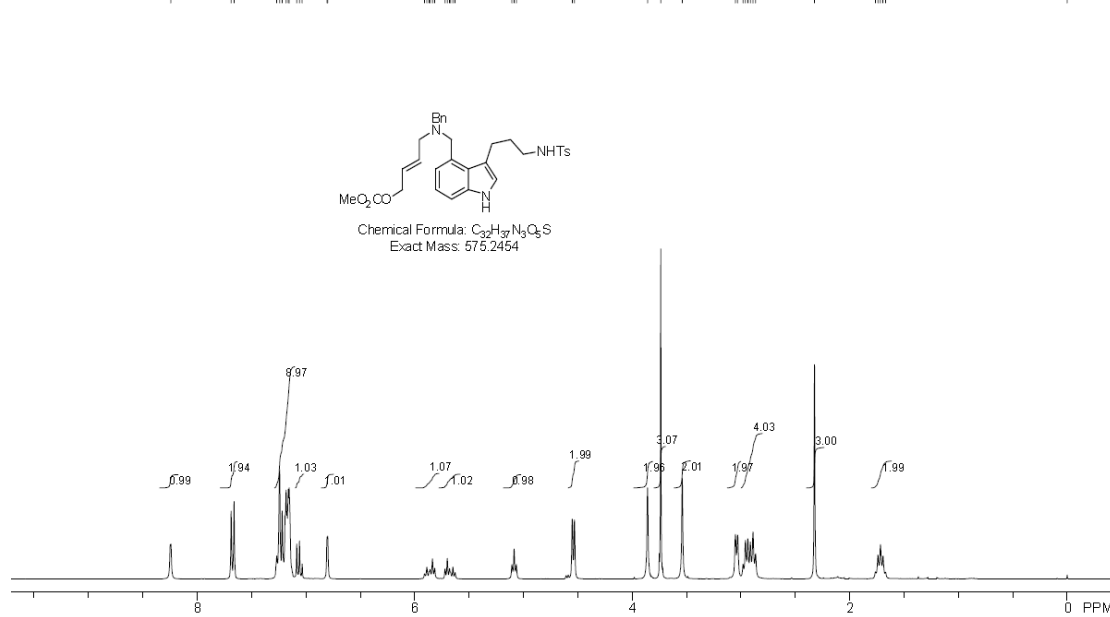
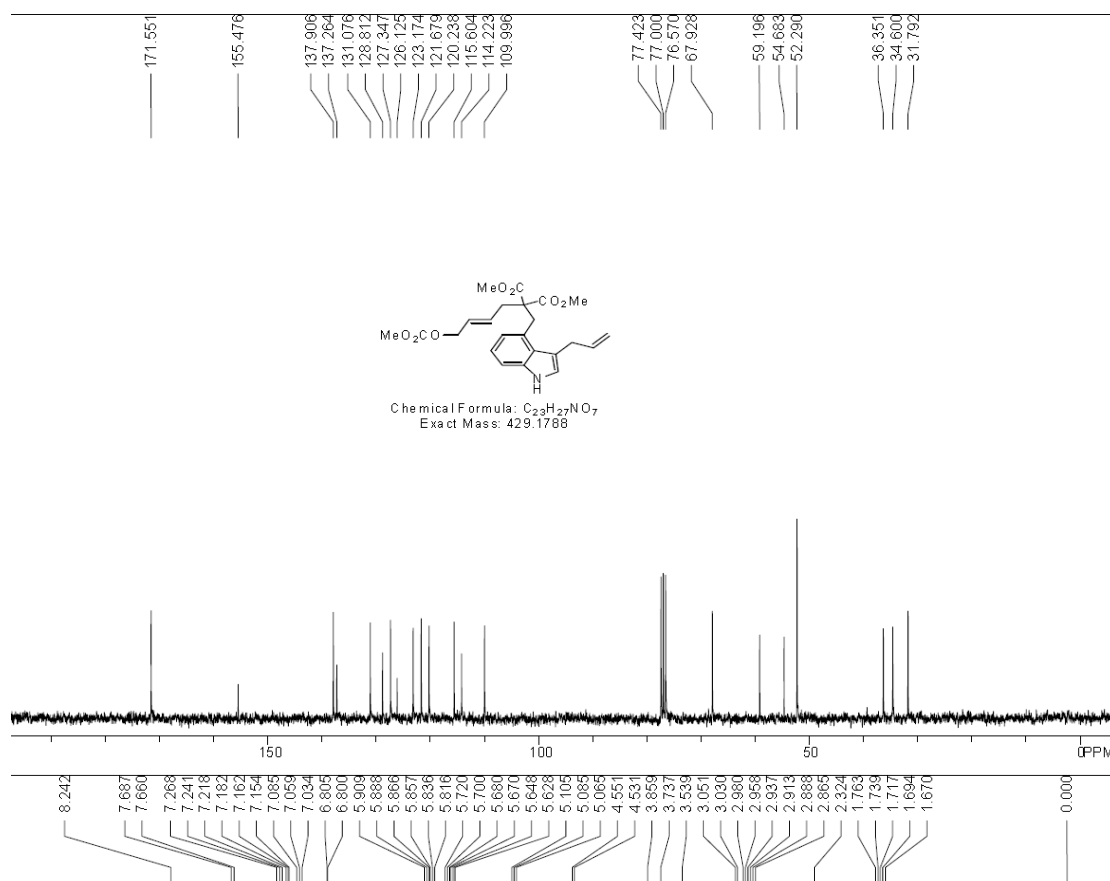


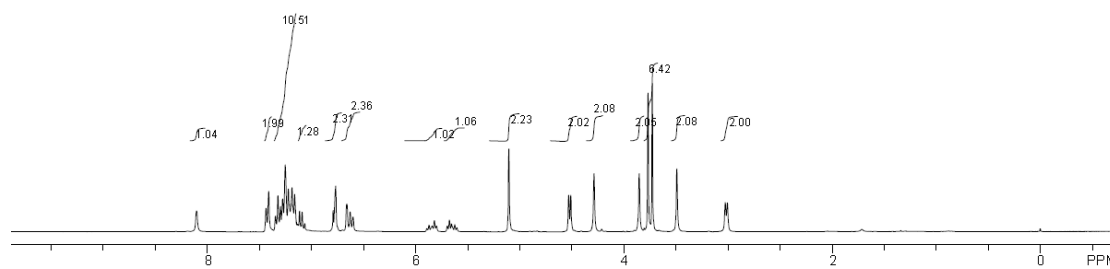
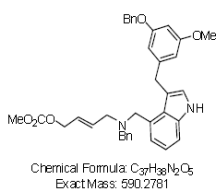
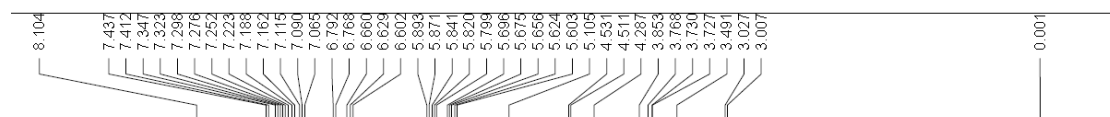
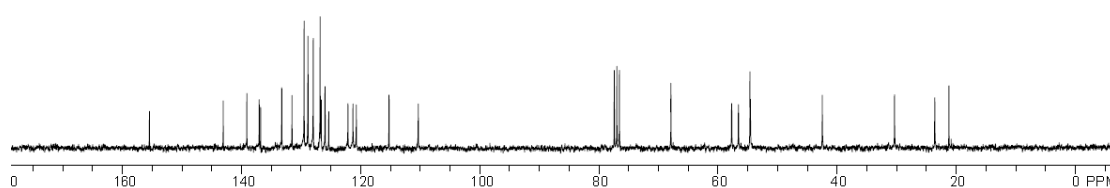
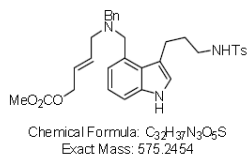
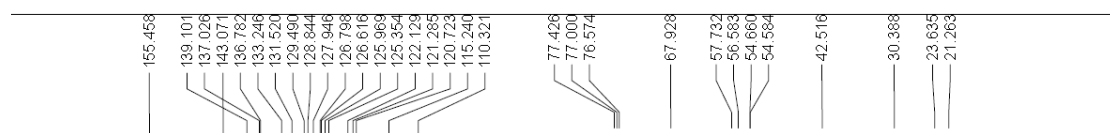


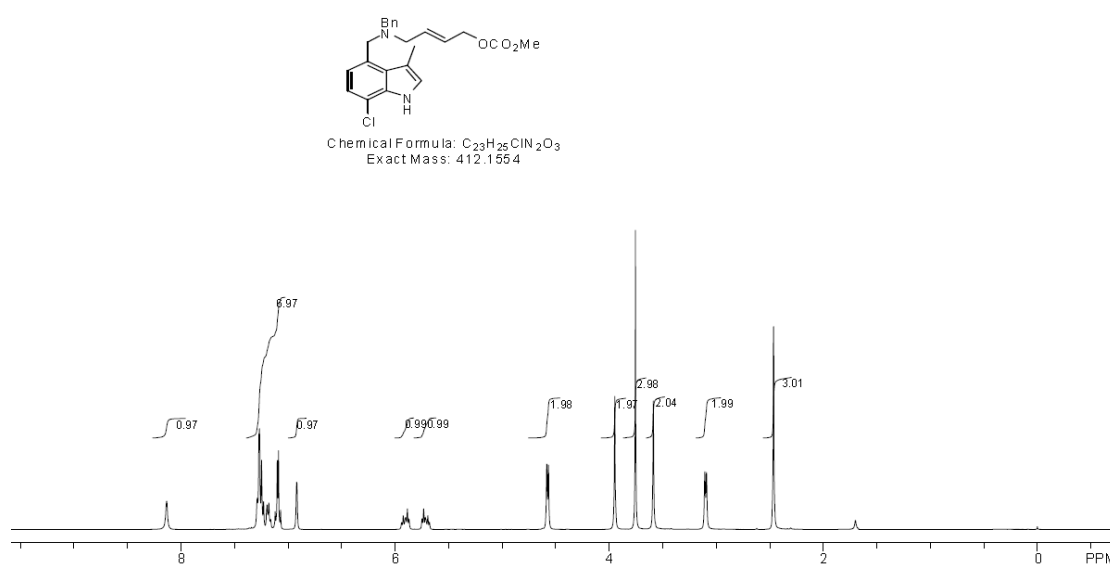
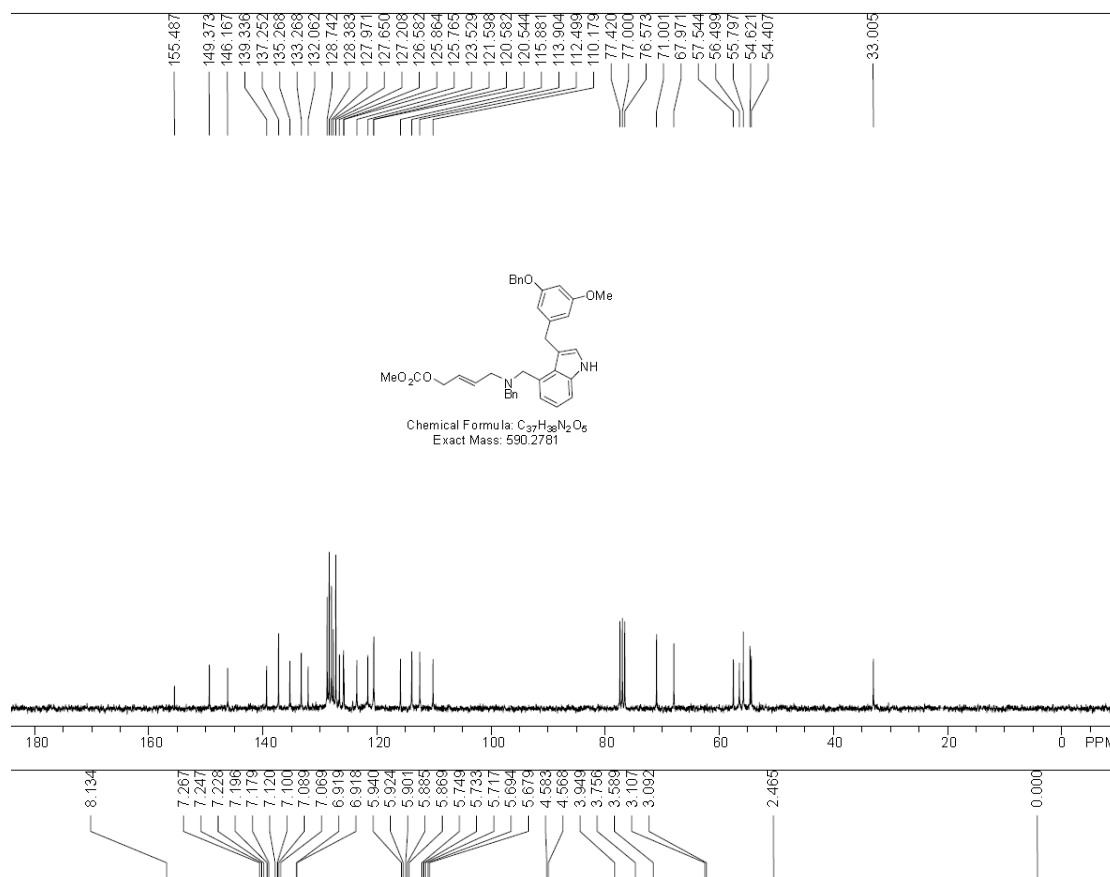


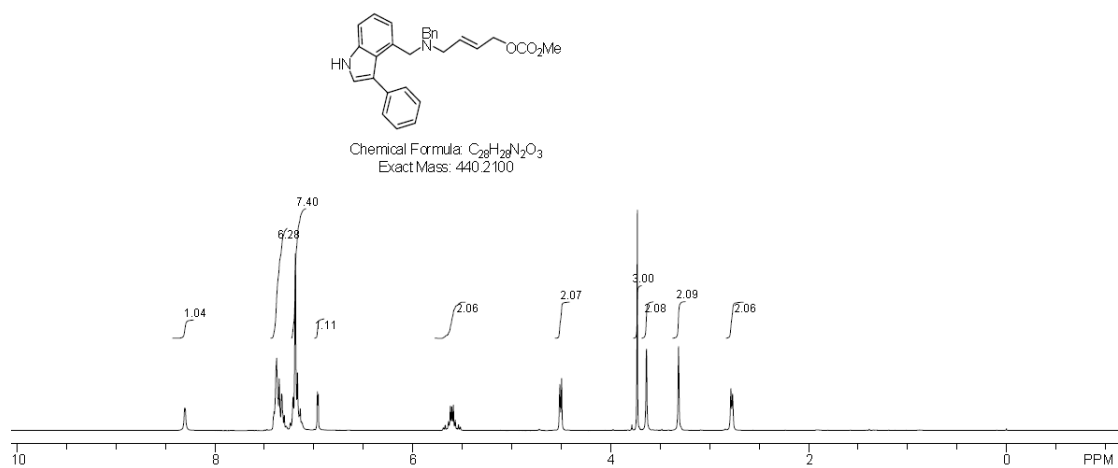
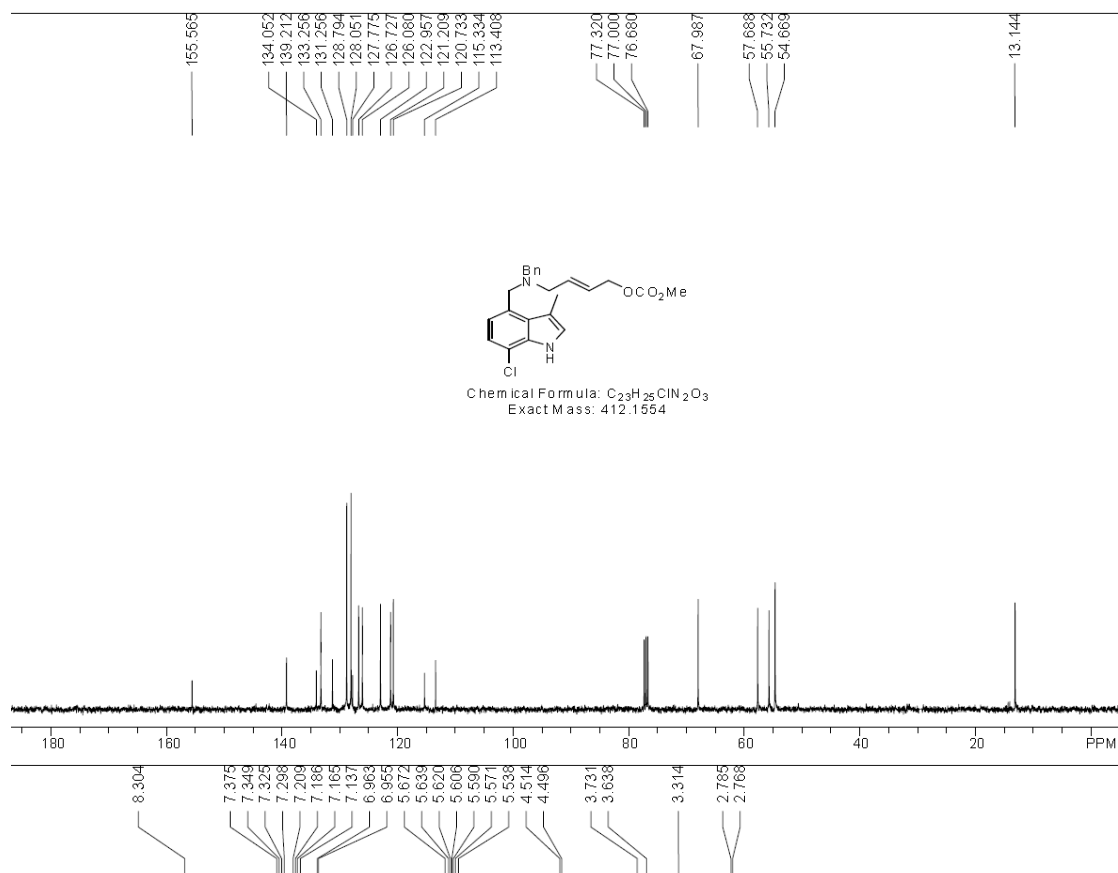


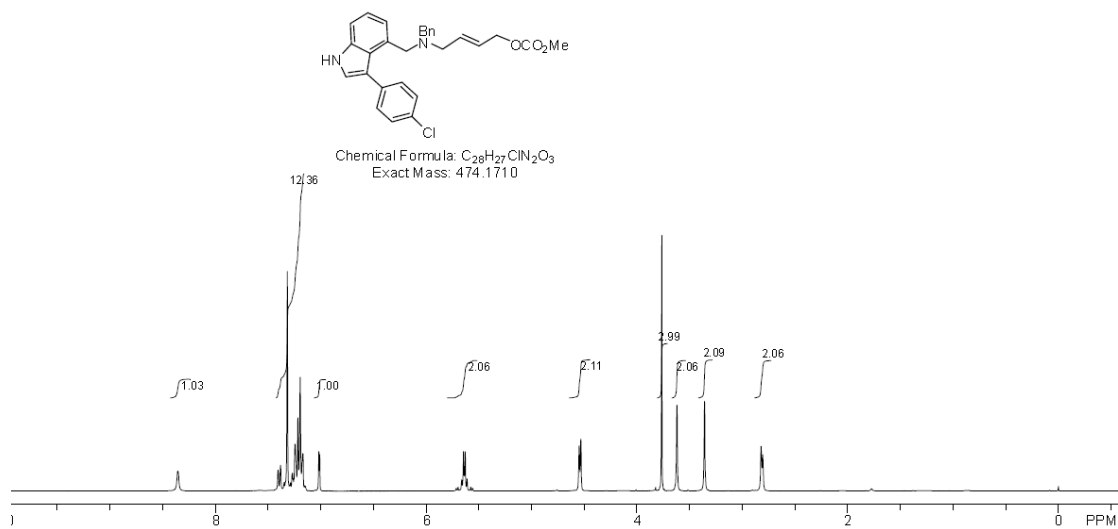
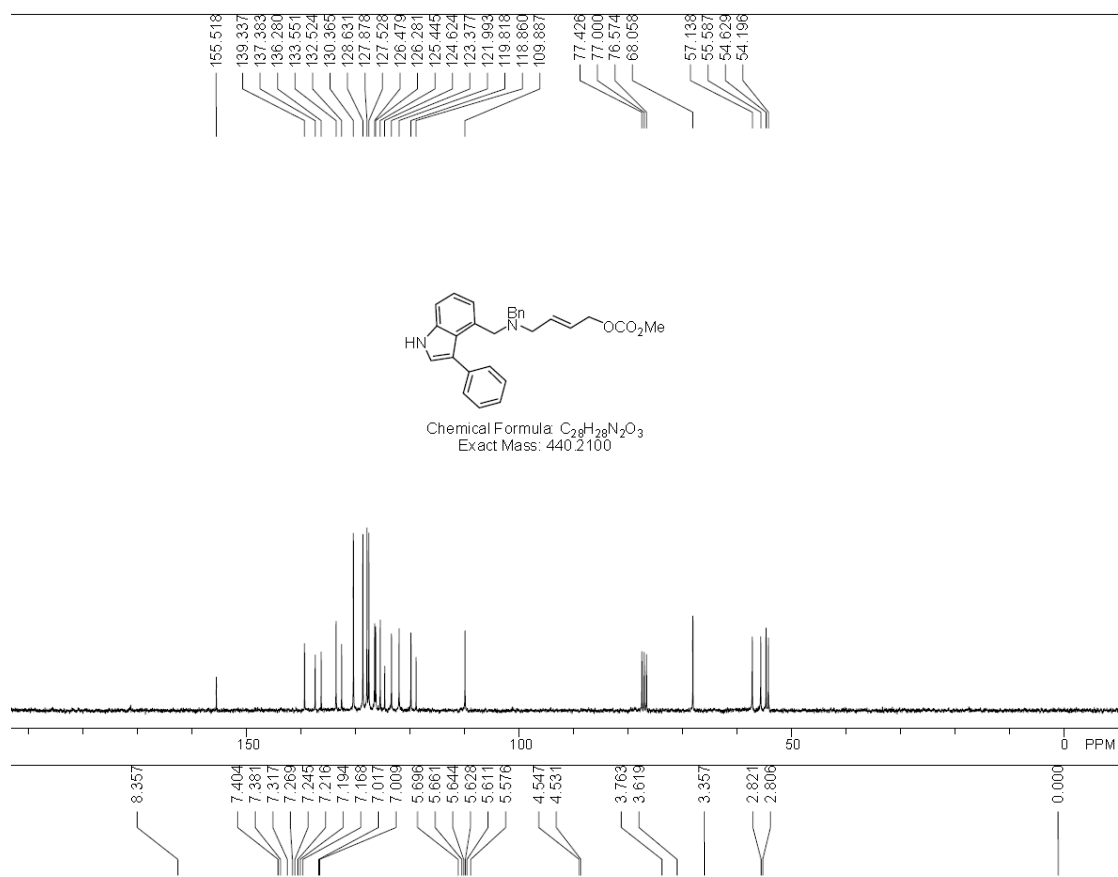




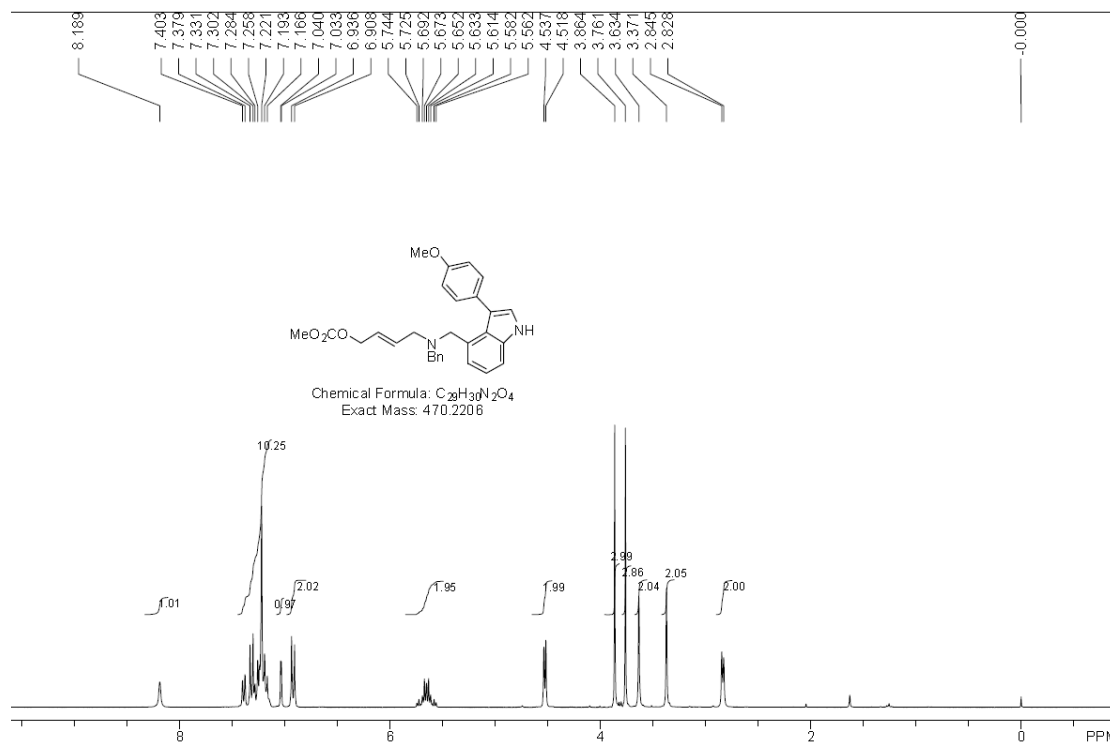
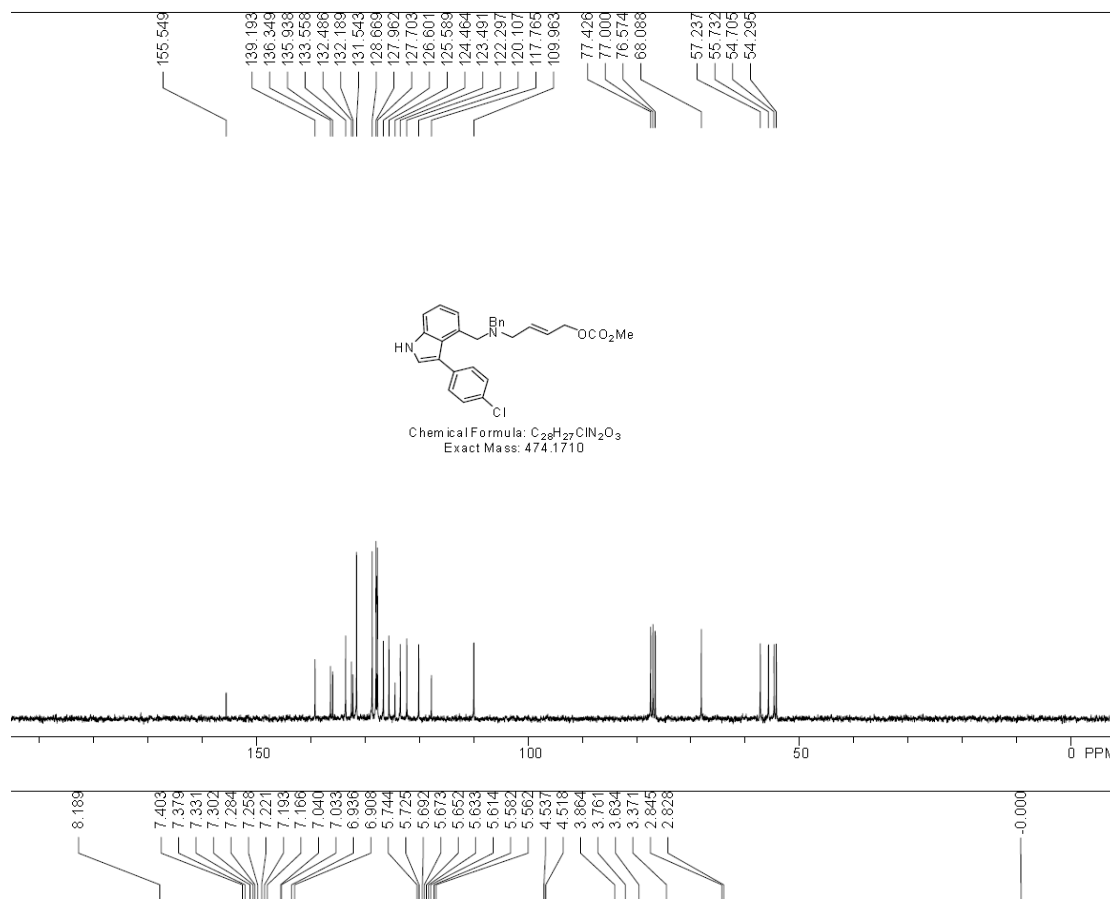


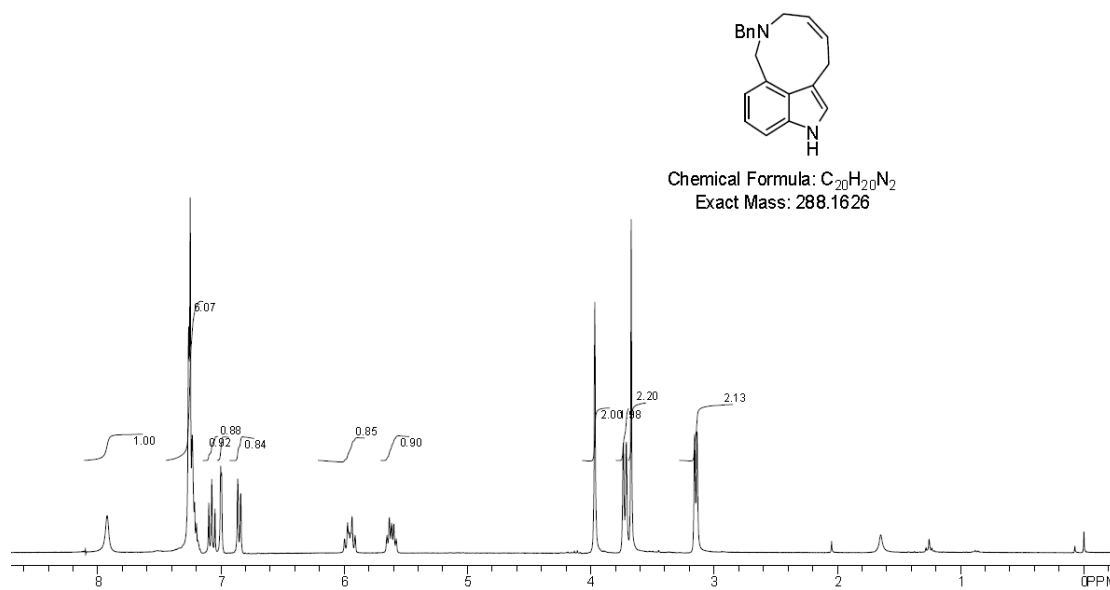
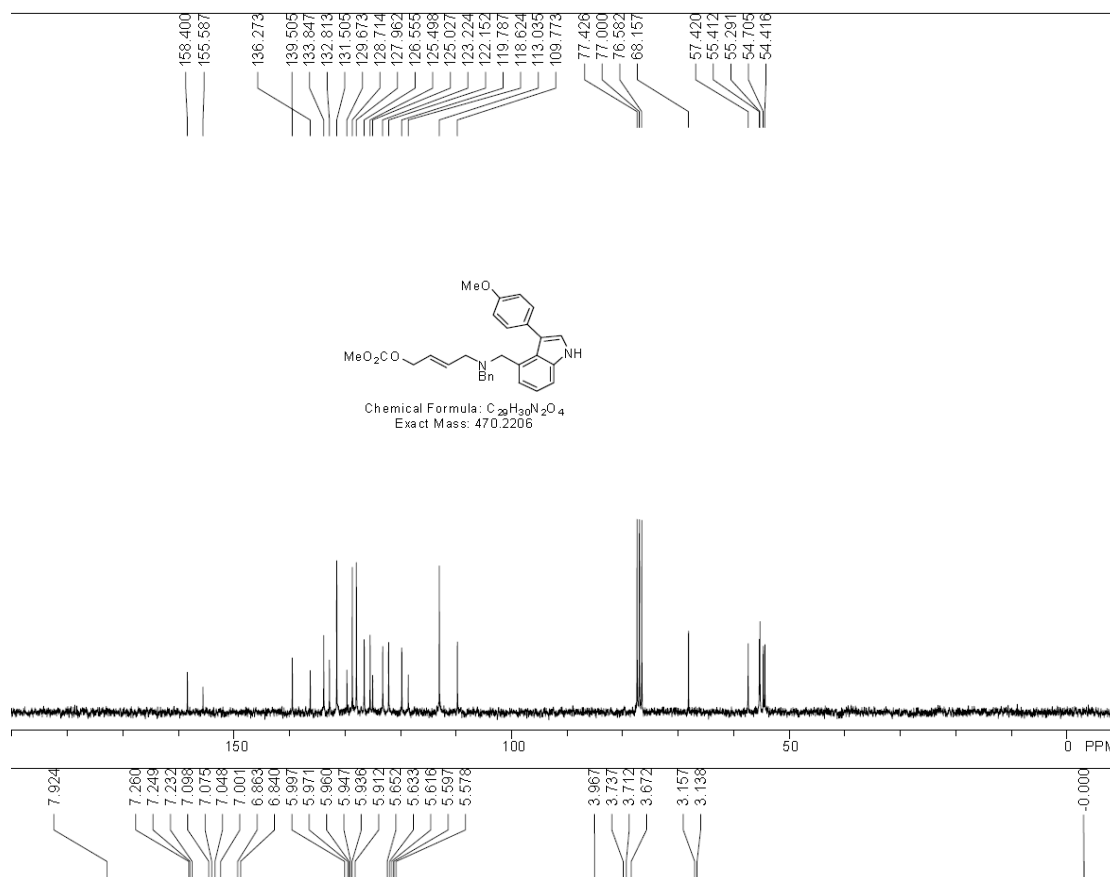


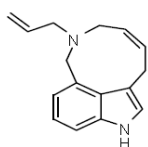
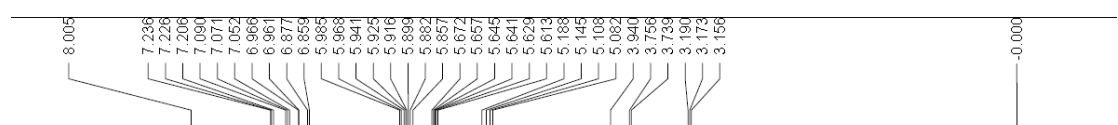
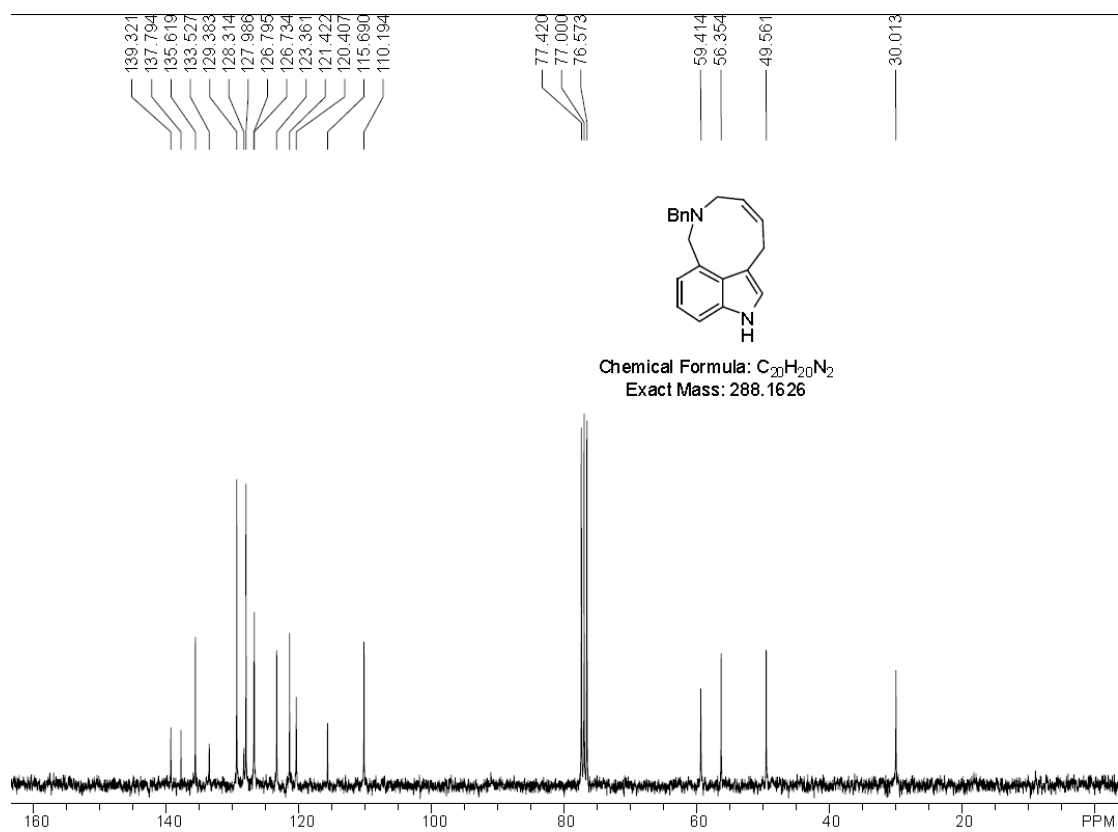




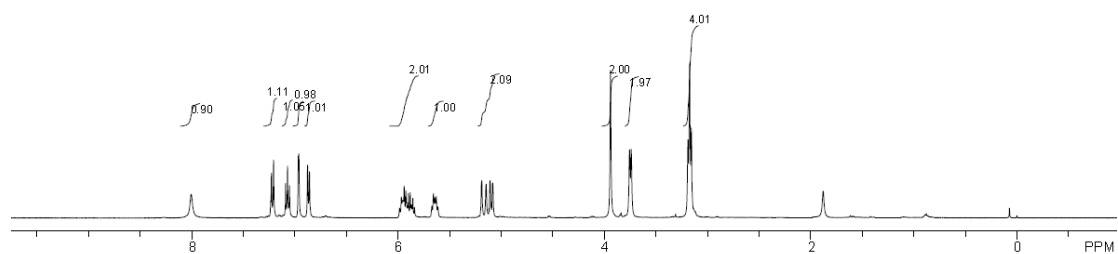


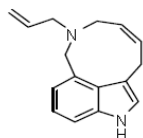
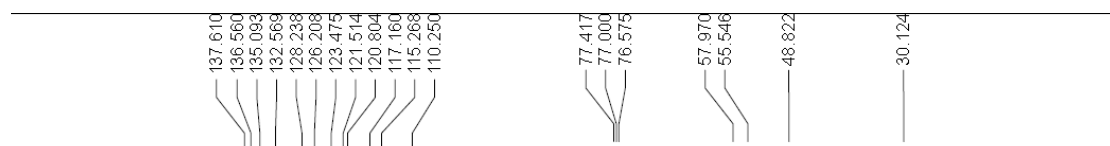




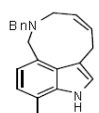
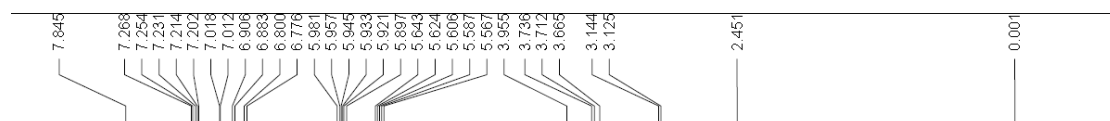
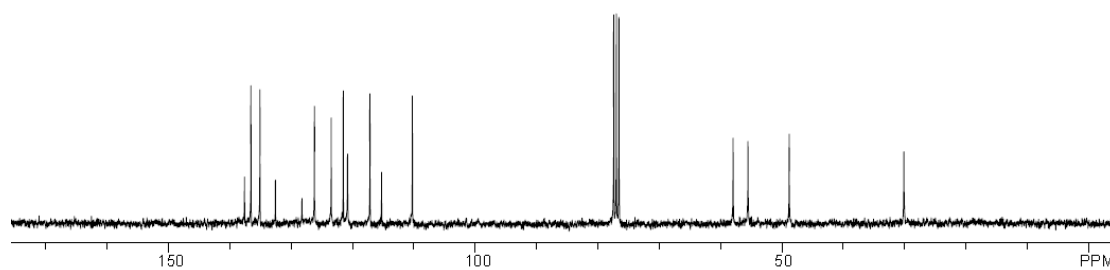


Chemical Formula:  $C_{16}H_{16}N_2$   
Exact Mass: 238.1470

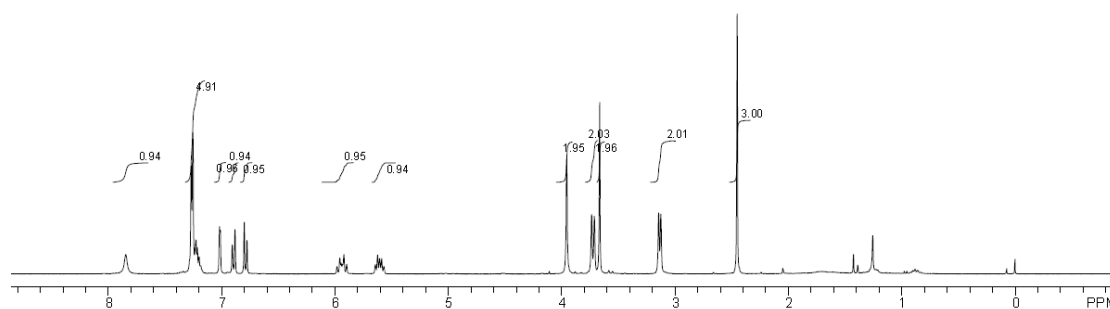


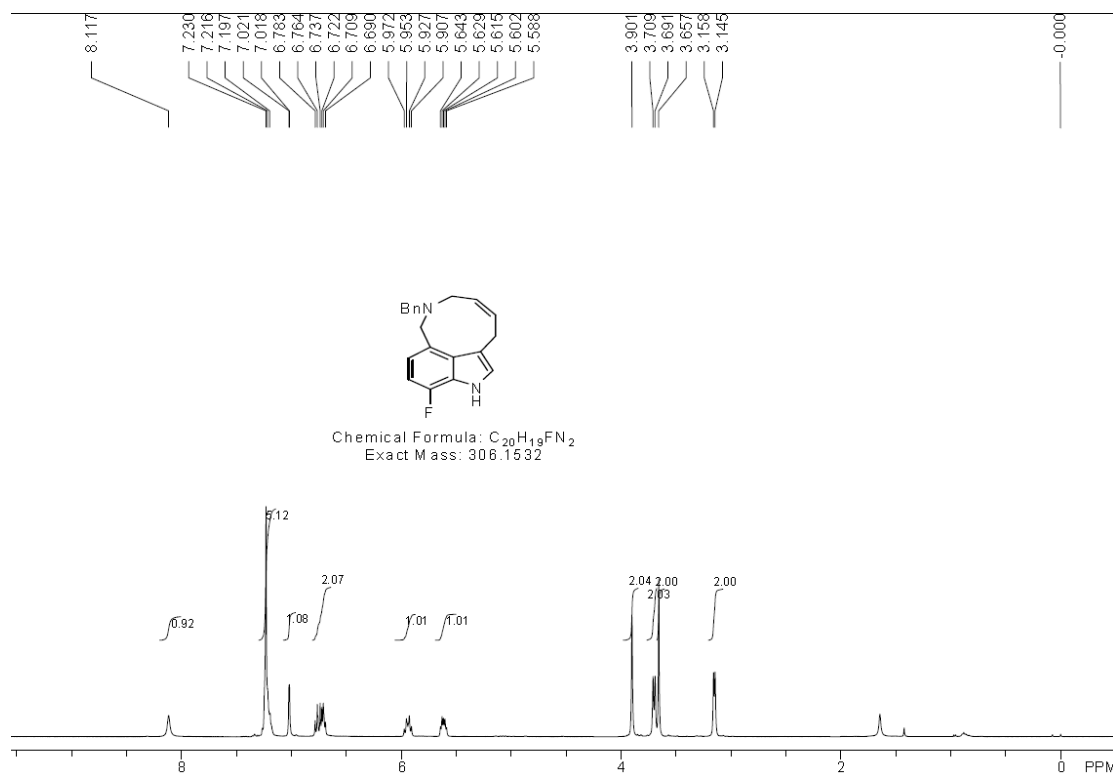
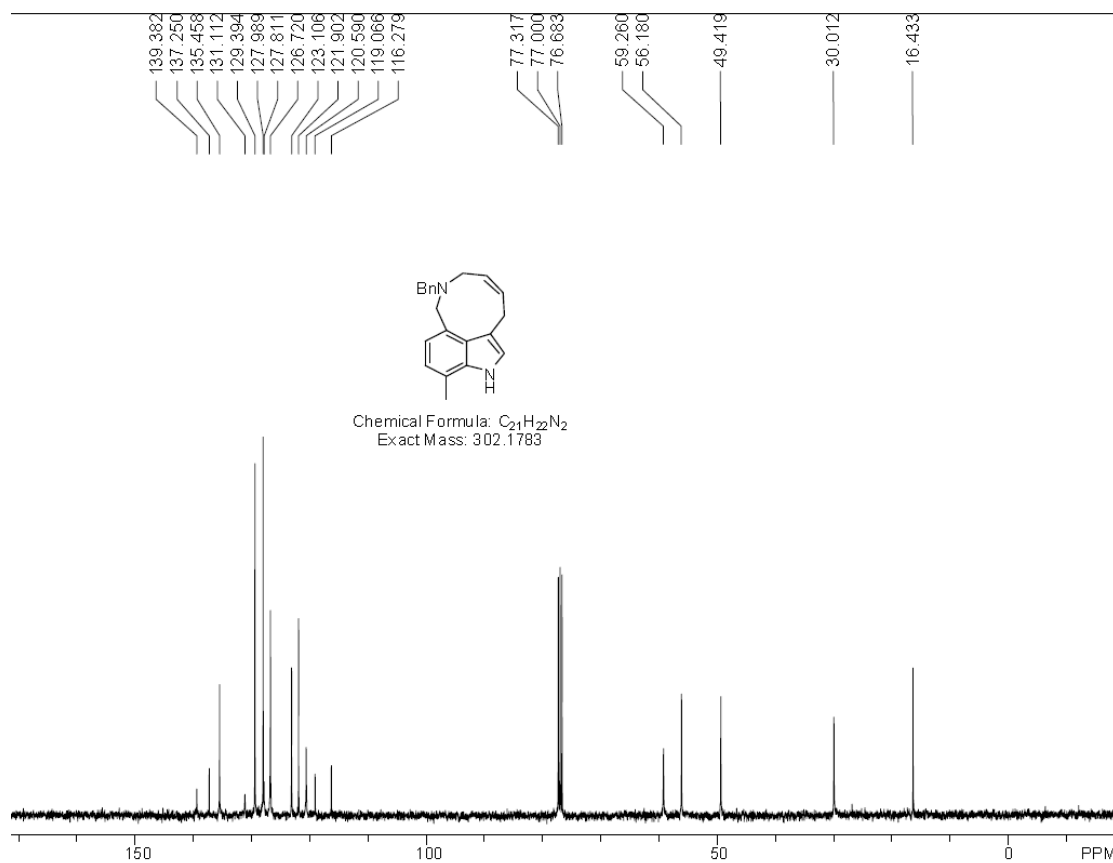


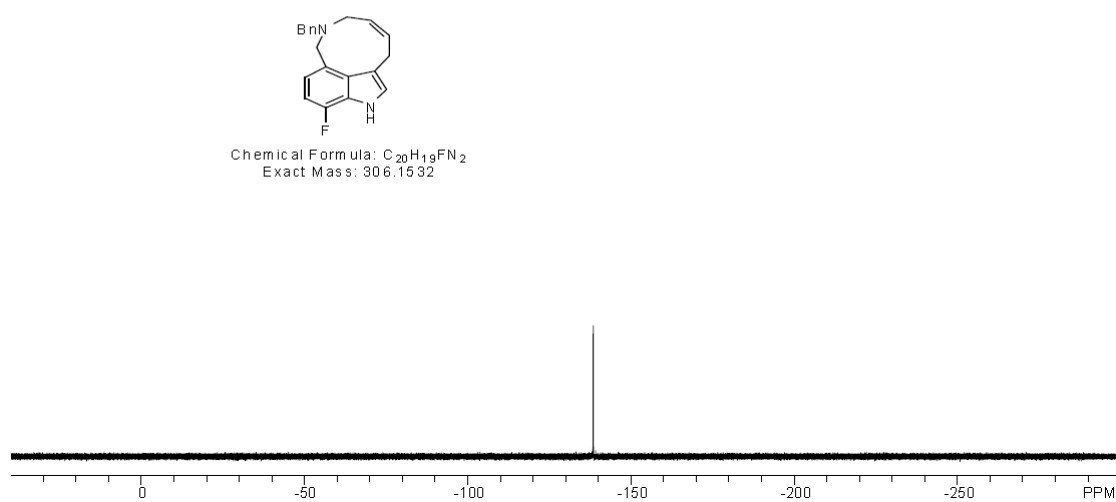
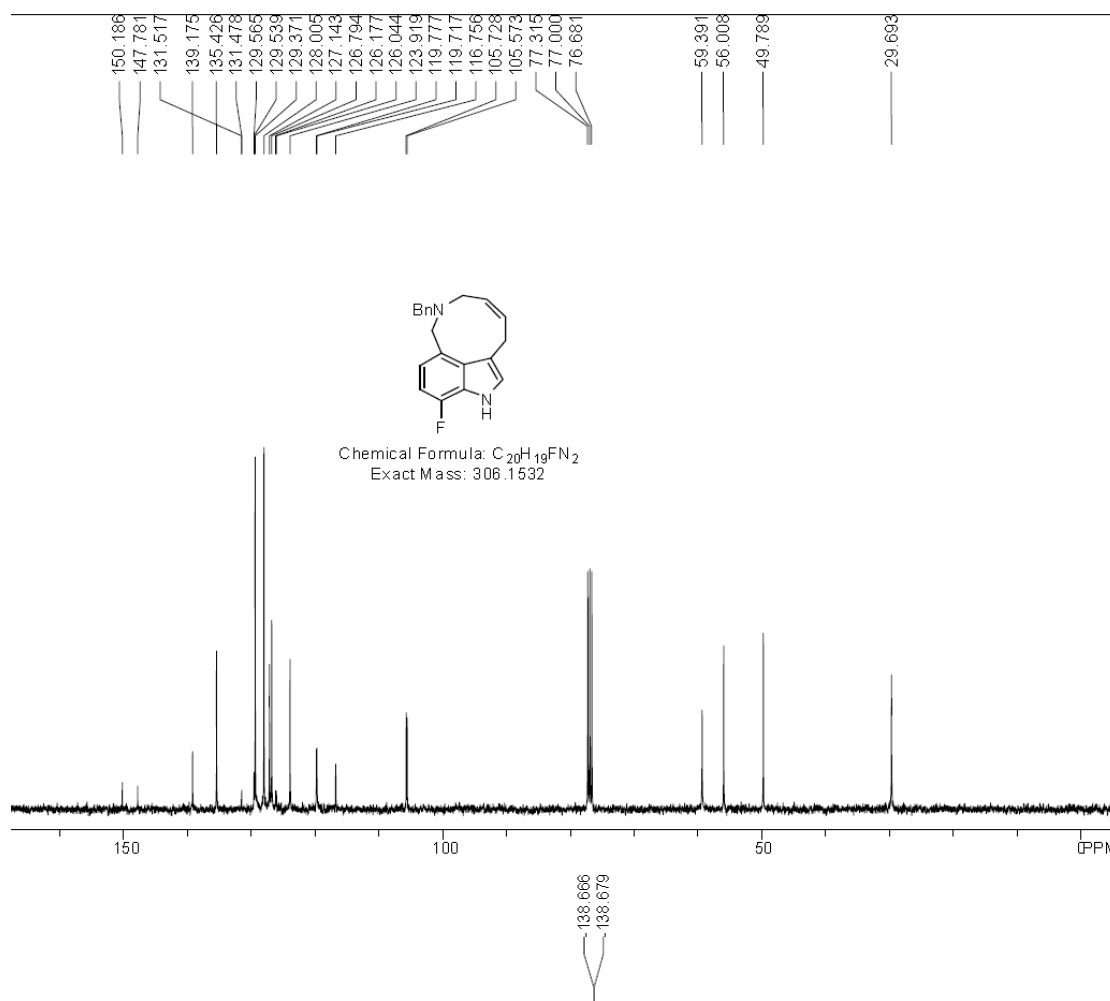
Chemical Formula: C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>  
Exact Mass: 238.1470

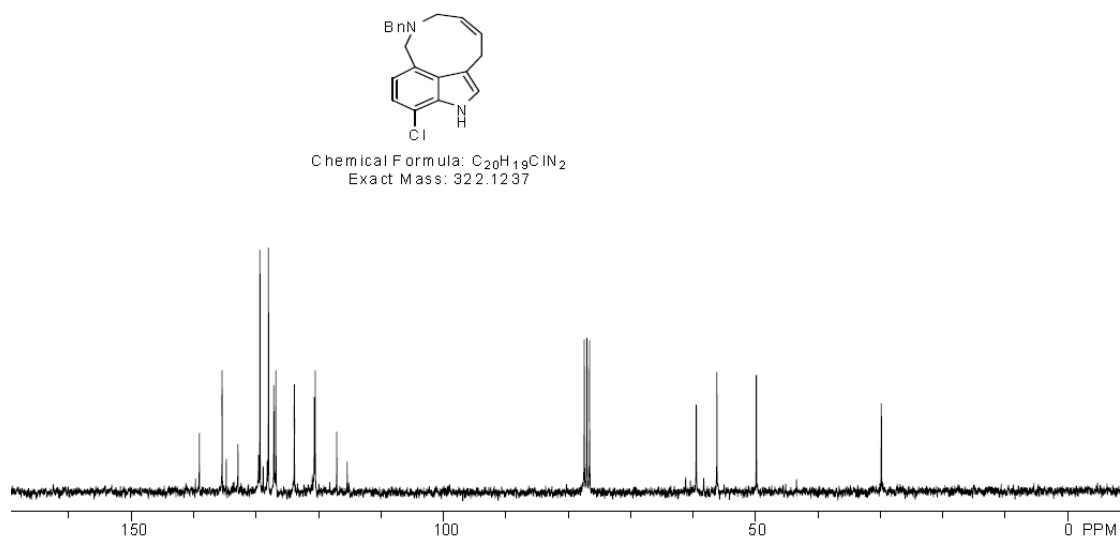
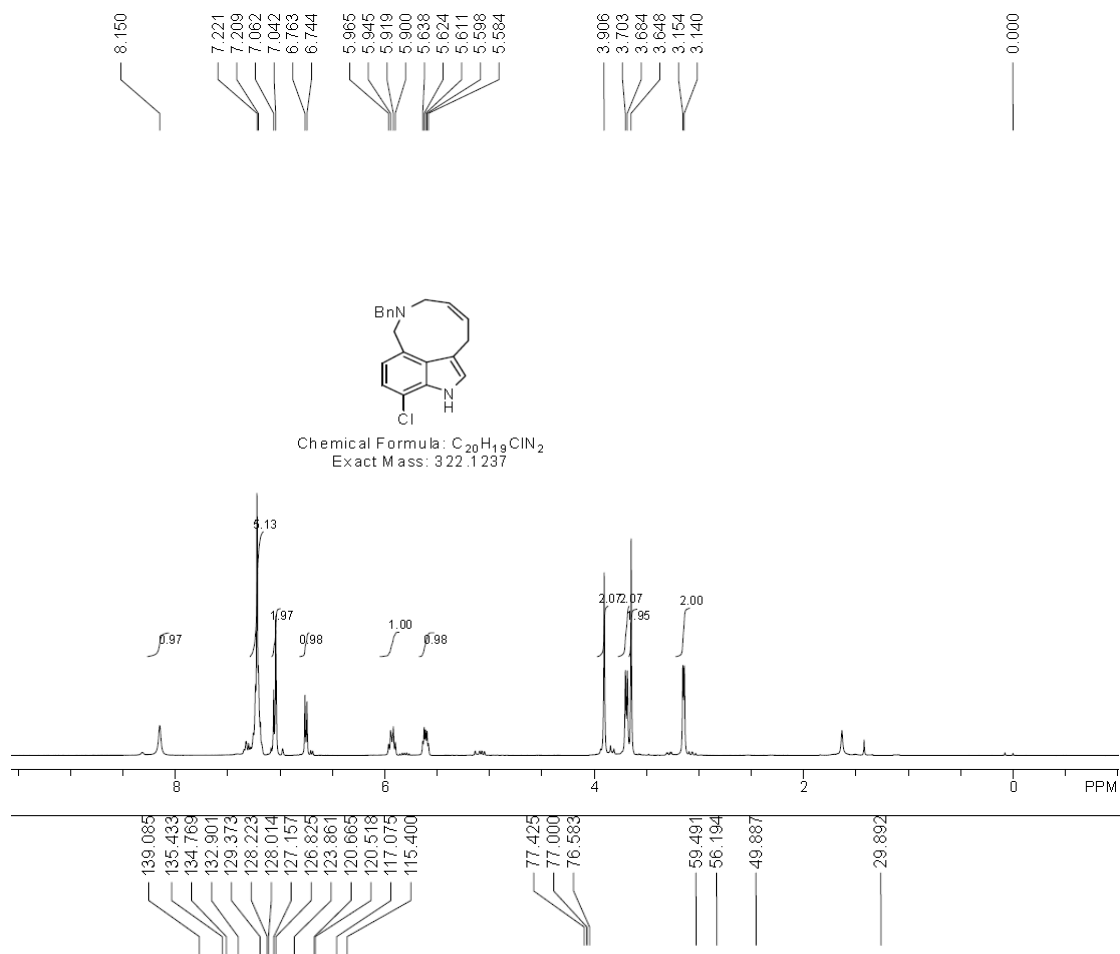


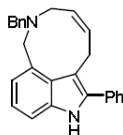
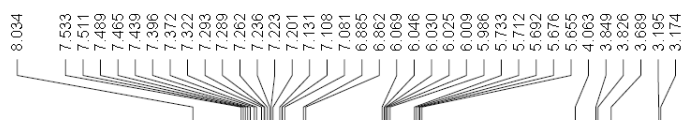
Chemical Formula: C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>  
Exact Mass: 302.1783



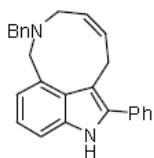
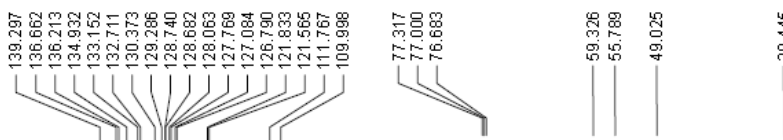
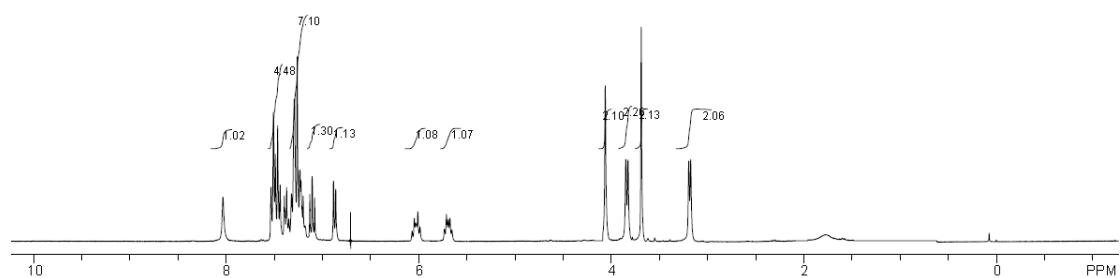




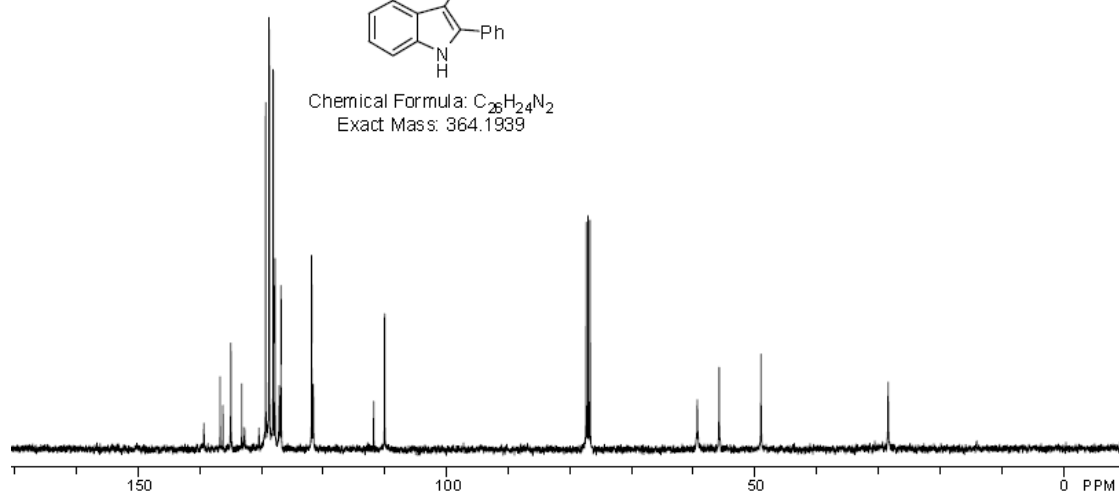




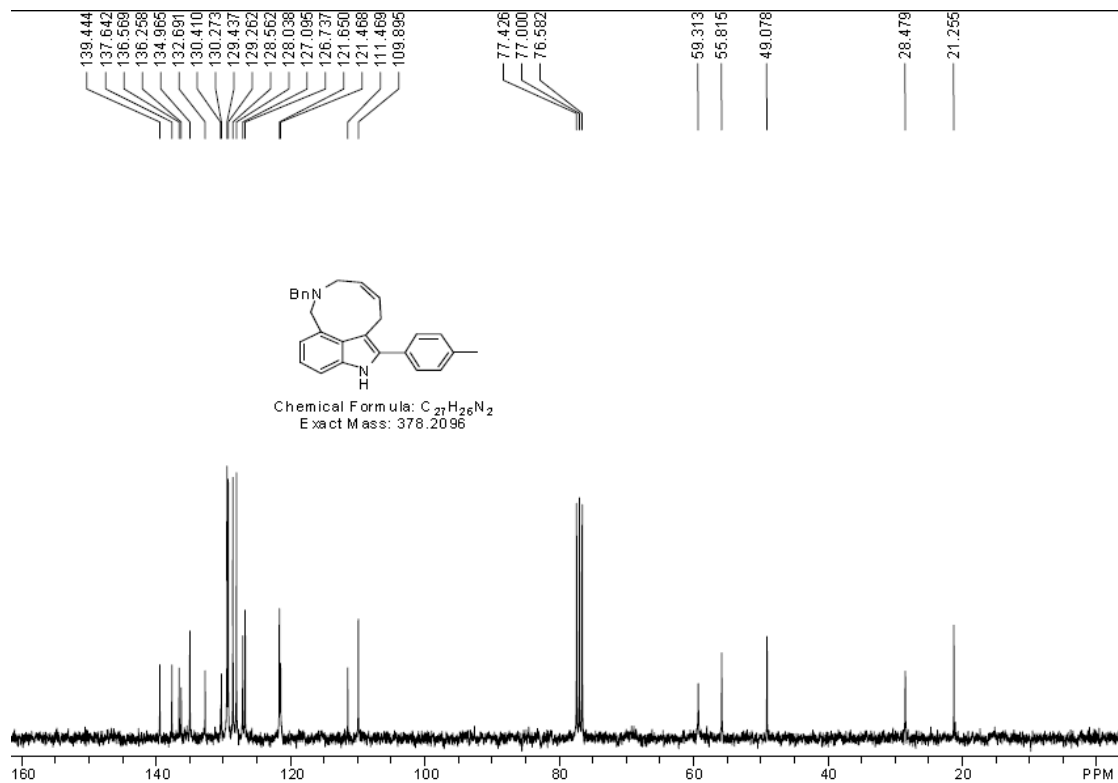
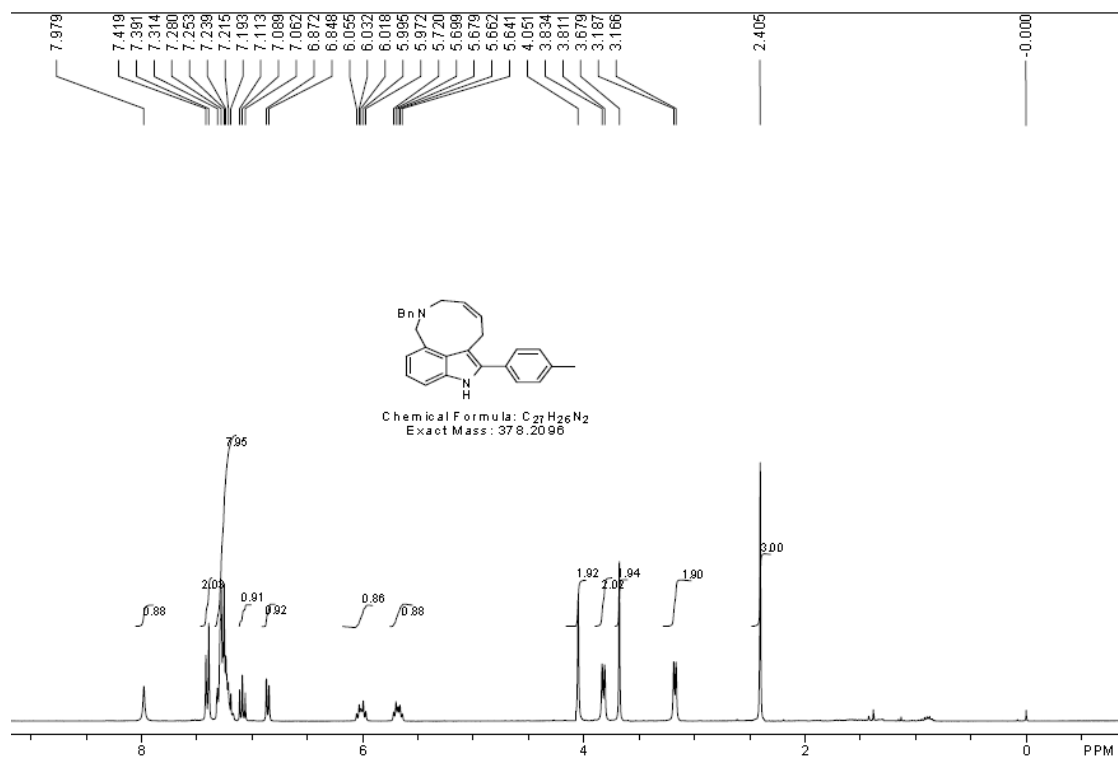
Chemical Formula:  $C_{26}H_{24}N_2$   
Exact Mass: 364.1939

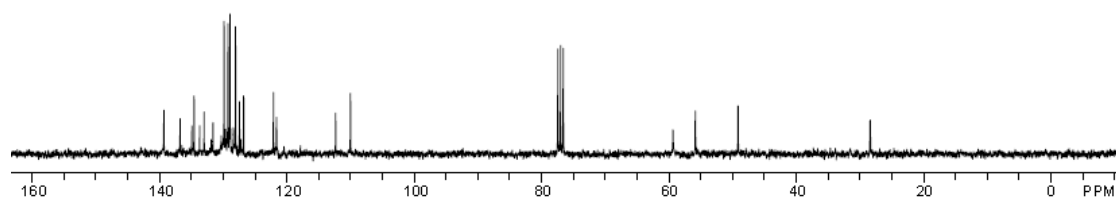
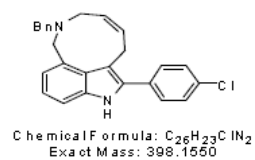
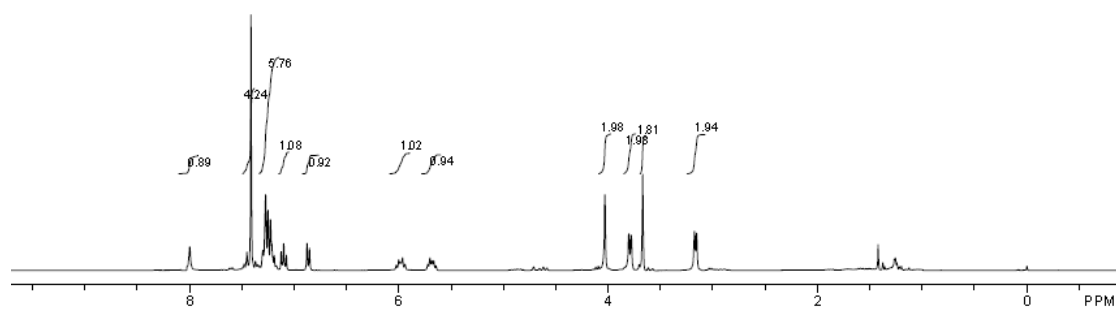
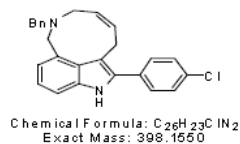
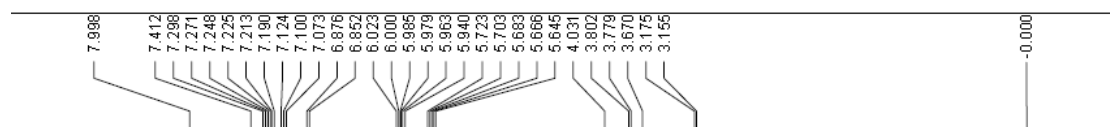


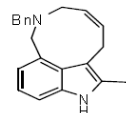
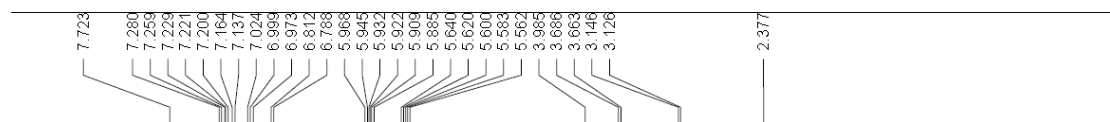
Chemical Formula:  $C_{26}H_{24}N_2$   
Exact Mass: 364.1939



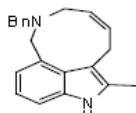
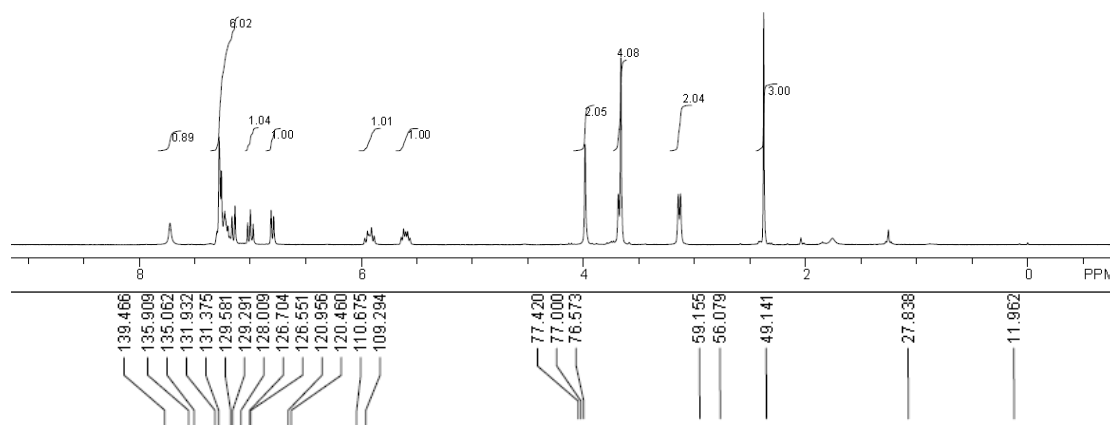




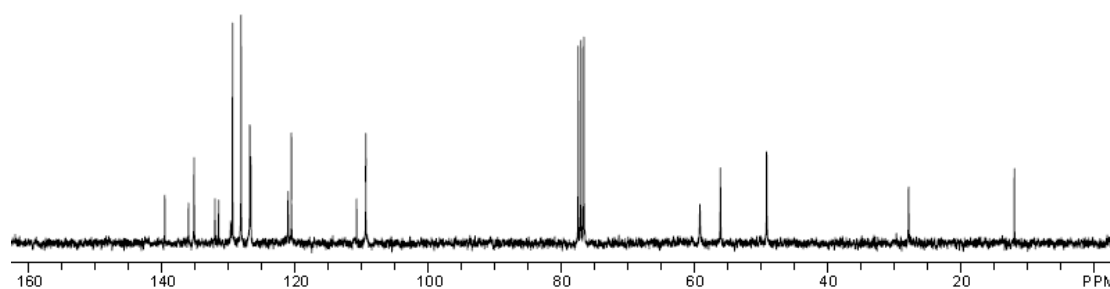


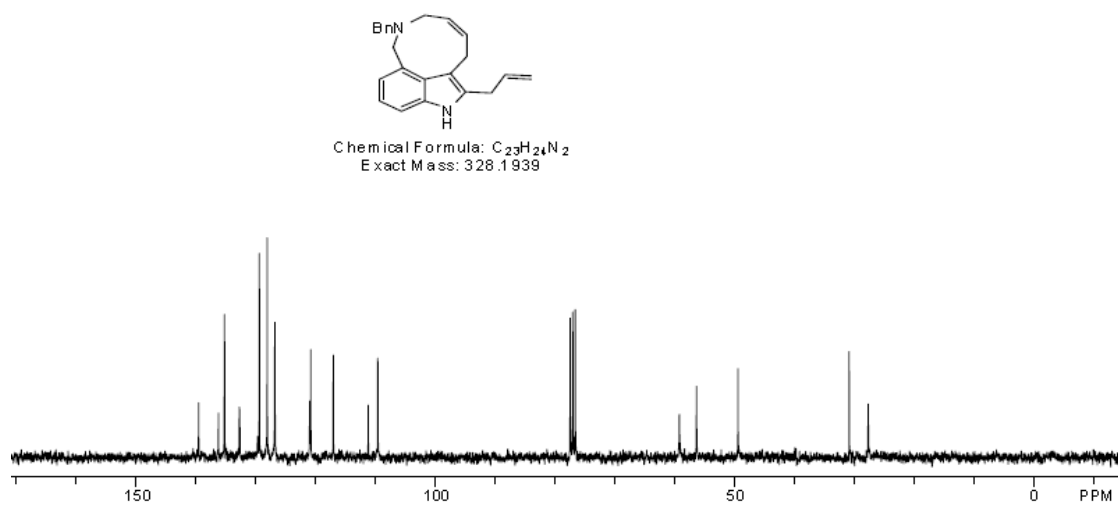
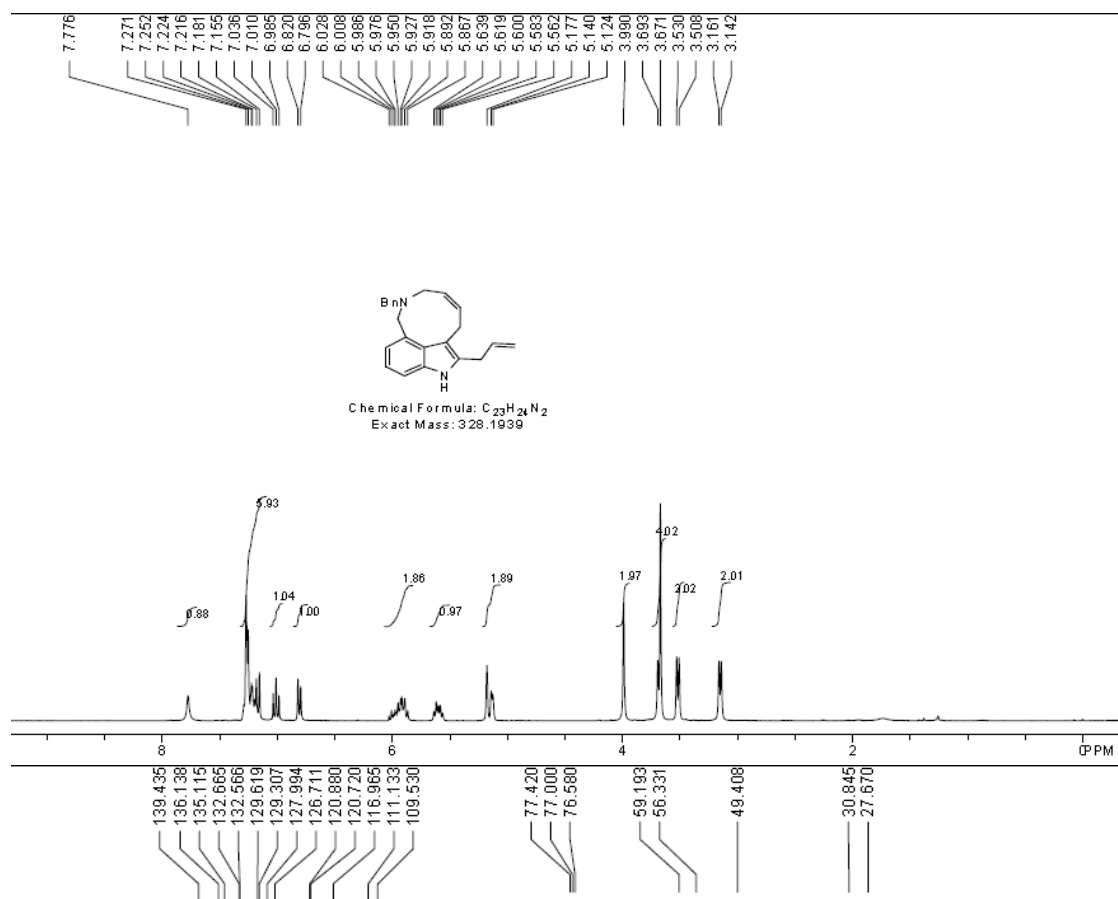


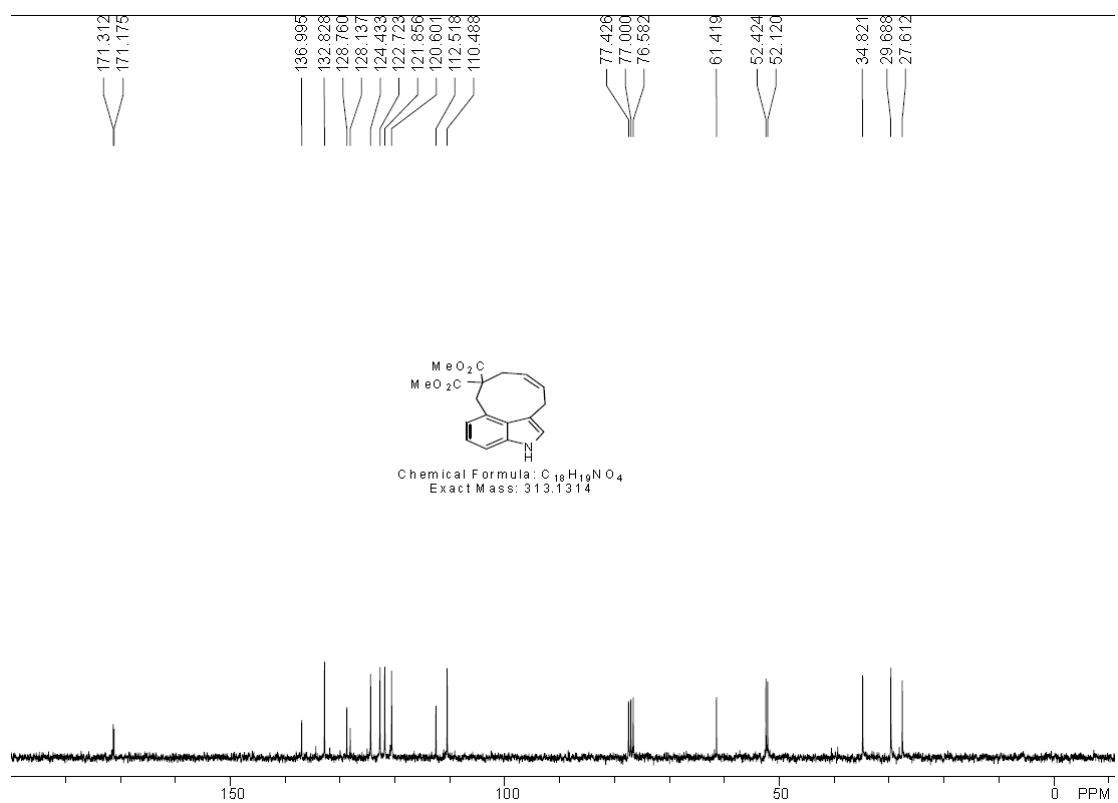
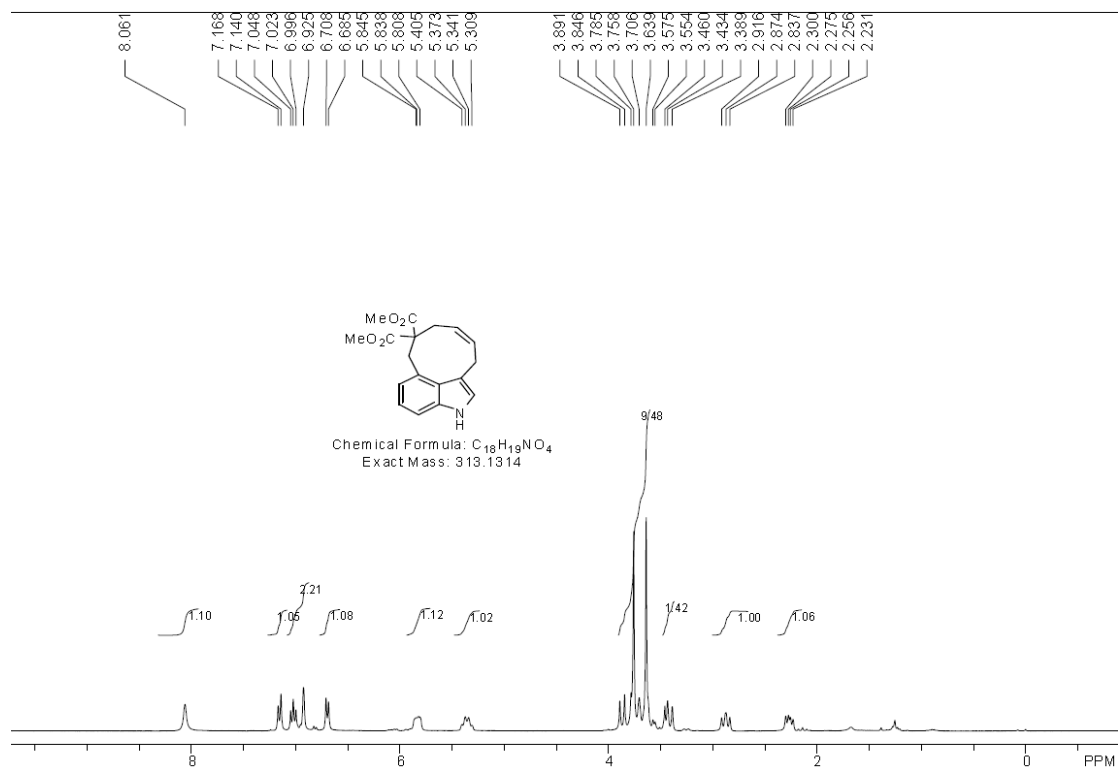
Chemical Formula:  $C_{21}H_{22}N_2$   
Exact Mass: 302.1783

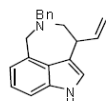
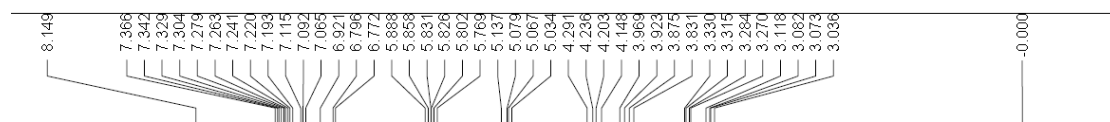


Chemical Formula:  $C_{21}H_{22}N_2$   
Exact Mass: 302.1783

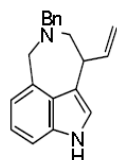
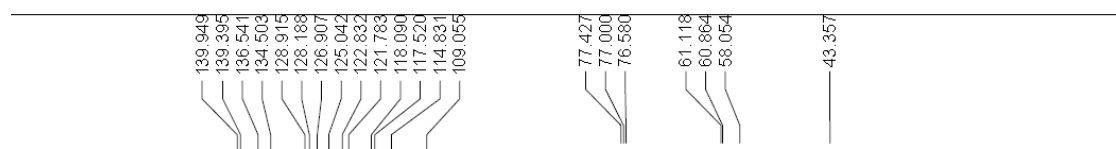
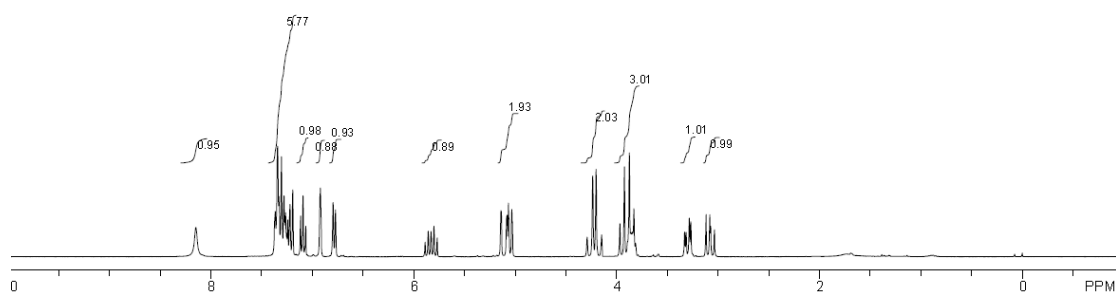




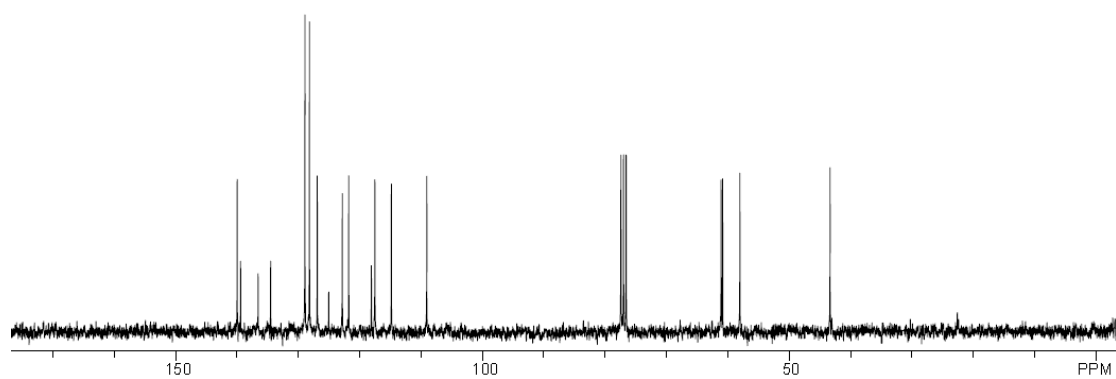


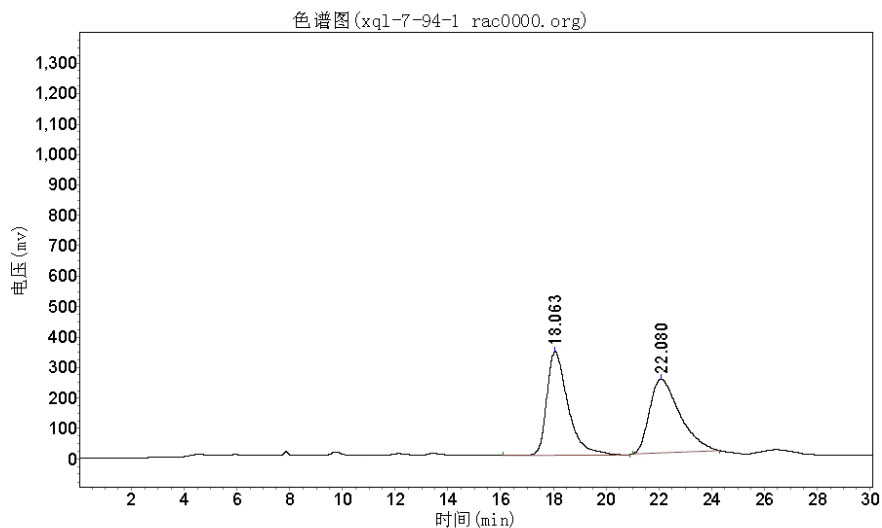


Chemical Formula: C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>  
Molecular Weight: 288.3862



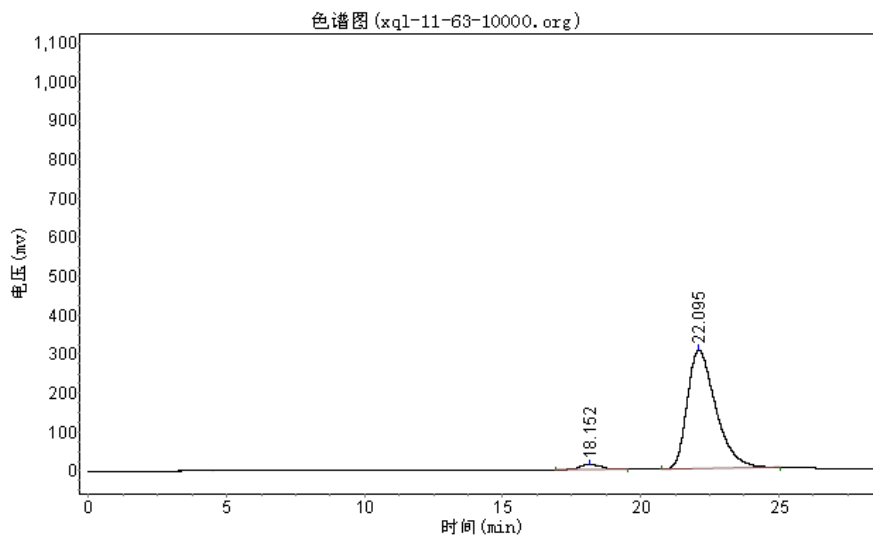
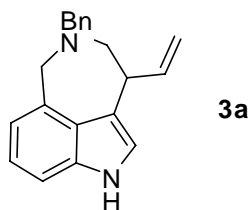
Chemical Formula: C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>  
Exact Mass: 288.1626





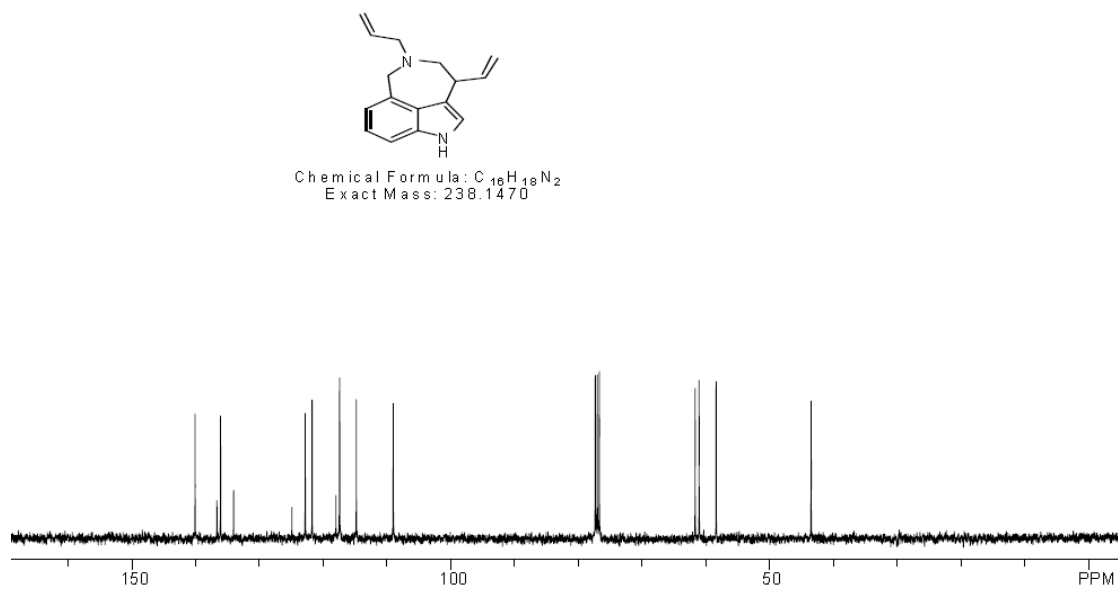
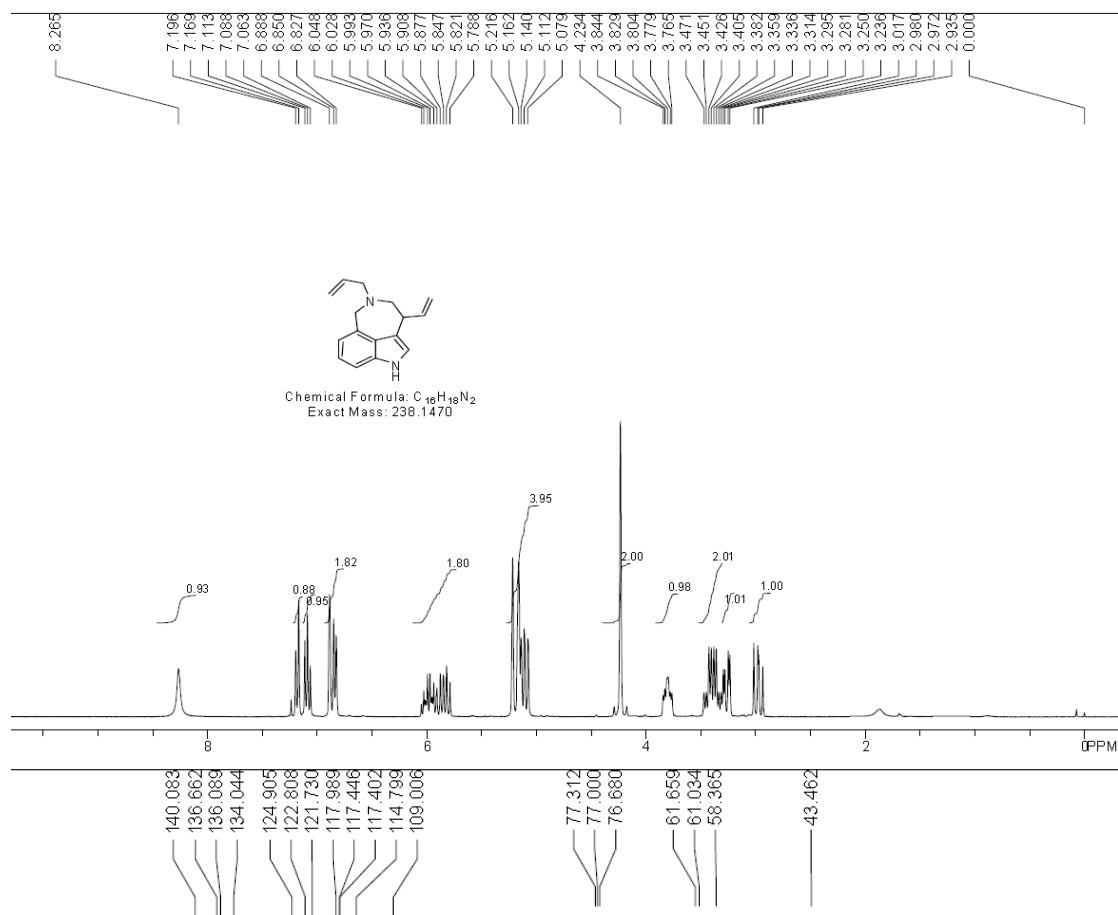
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		18.063	339819.531	18839492.000	49.3247
2		22.080	242114.000	19355380.000	50.6753
总计			581933.531	38194872.000	100.0000

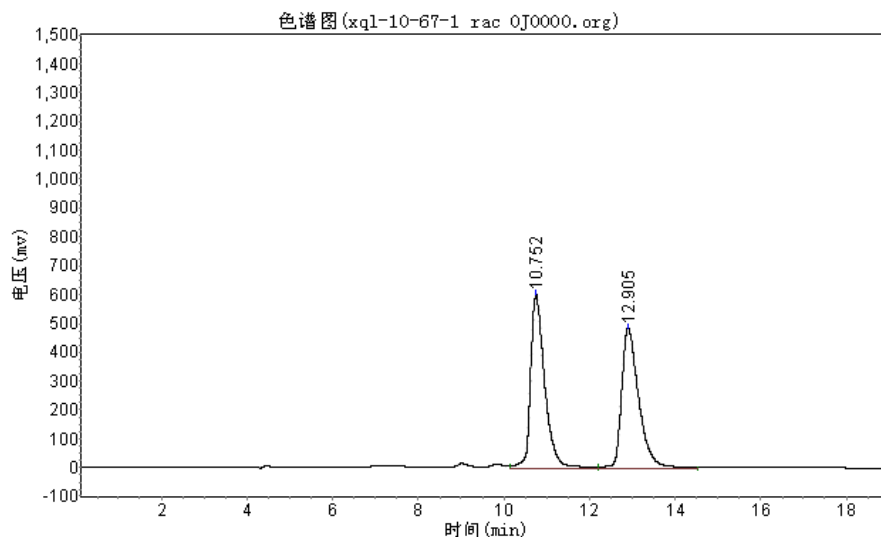


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		18.152	13152.357	657963.938	2.9281
2		22.095	304637.813	21812996.000	97.0719
总计			317790.170	22470959.938	100.0000

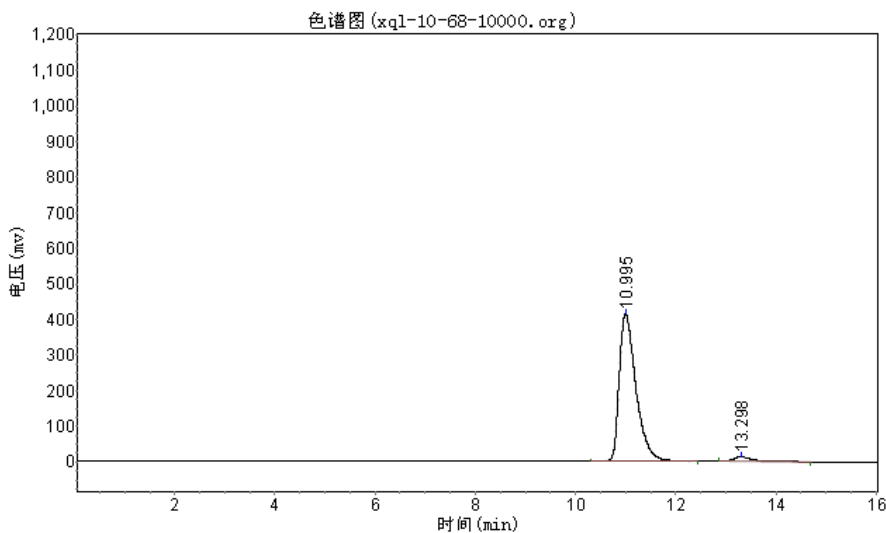
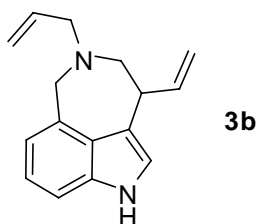






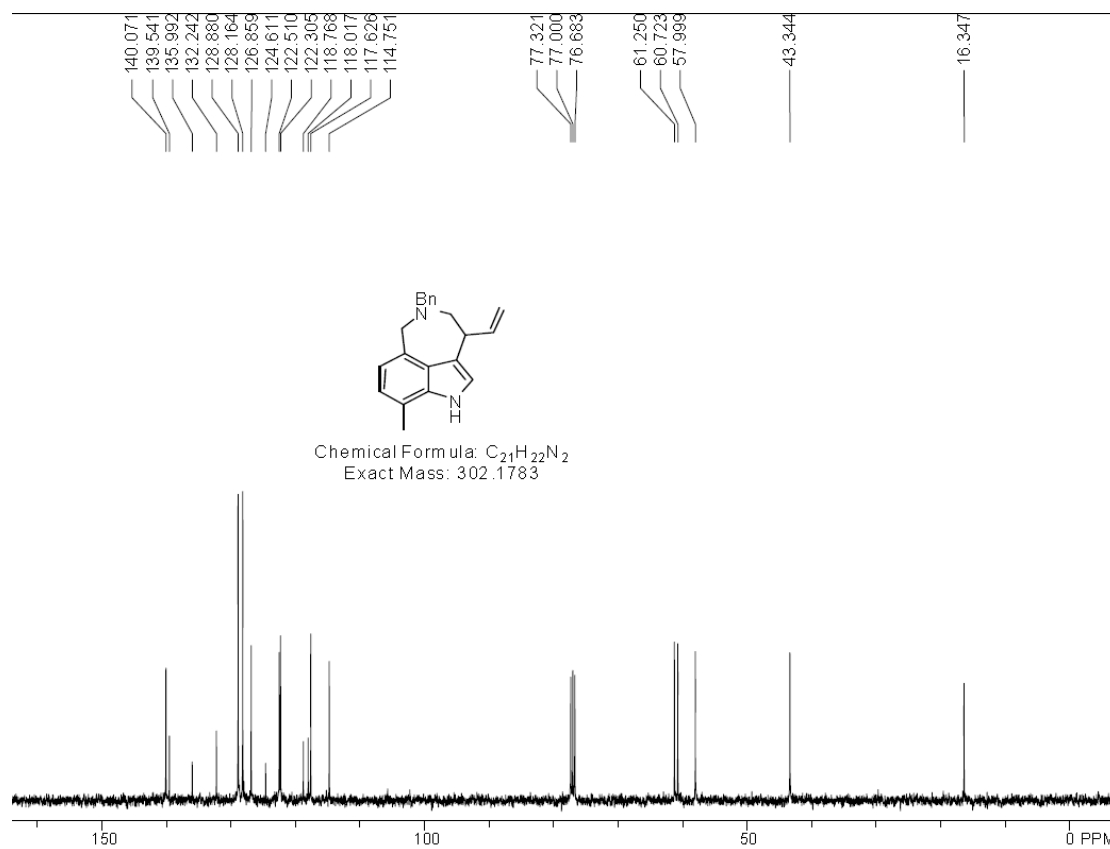
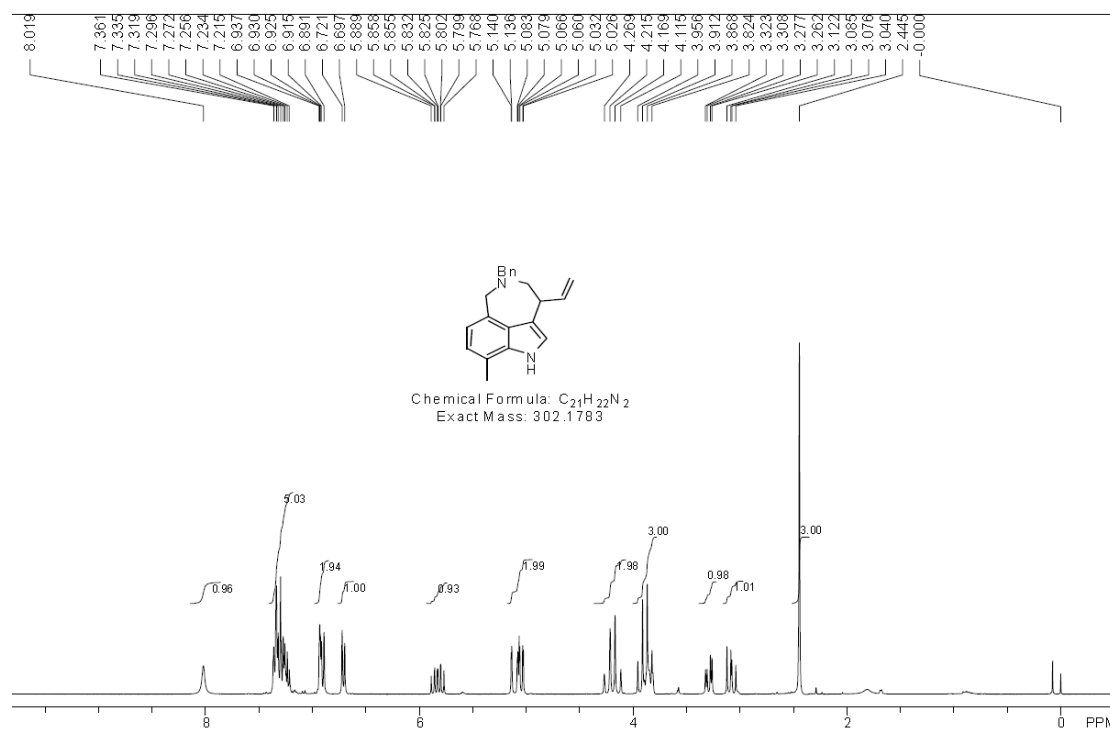
分析结果表

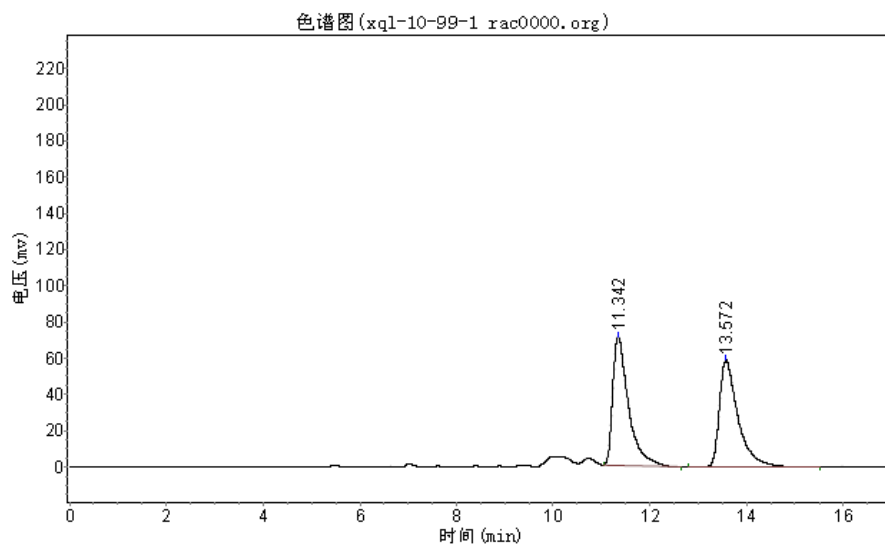
峰号	峰名	保留时间	峰高	峰面积	含量
1		10.752	600759.250	13679254.000	50.5576
2		12.905	483554.563	13377512.000	49.4424
总计			1084313.813	27056766.000	100.0000



分析结果表

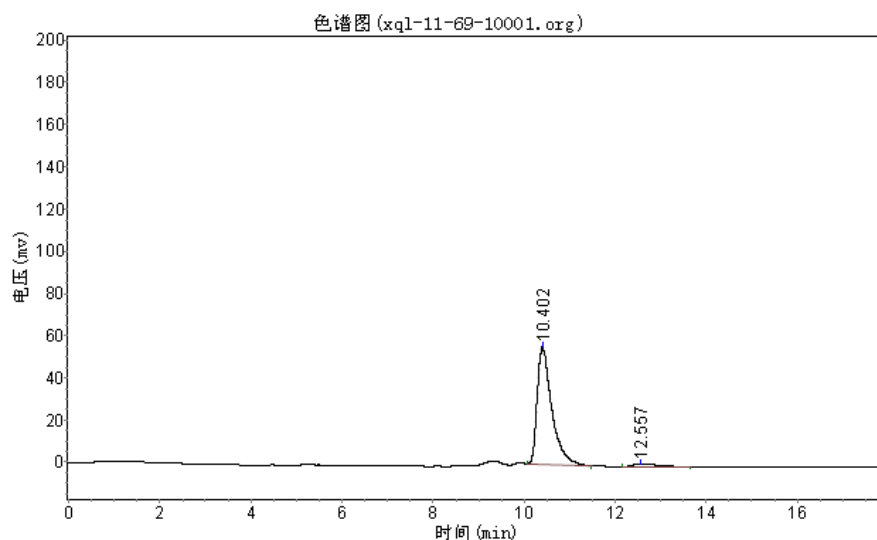
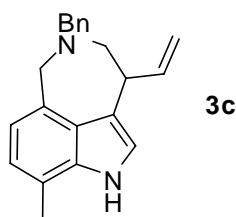
峰号	峰名	保留时间	峰高	峰面积	含量
1		10.995	415693.344	9662115.000	96.8388
2		13.298	12005.385	315411.281	3.1612
总计			427698.729	9977526.281	100.0000





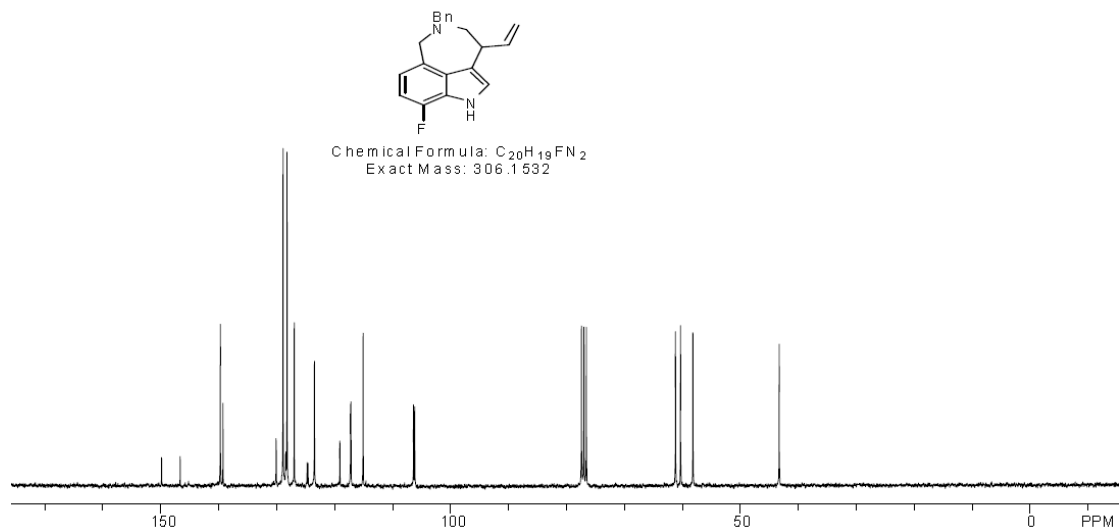
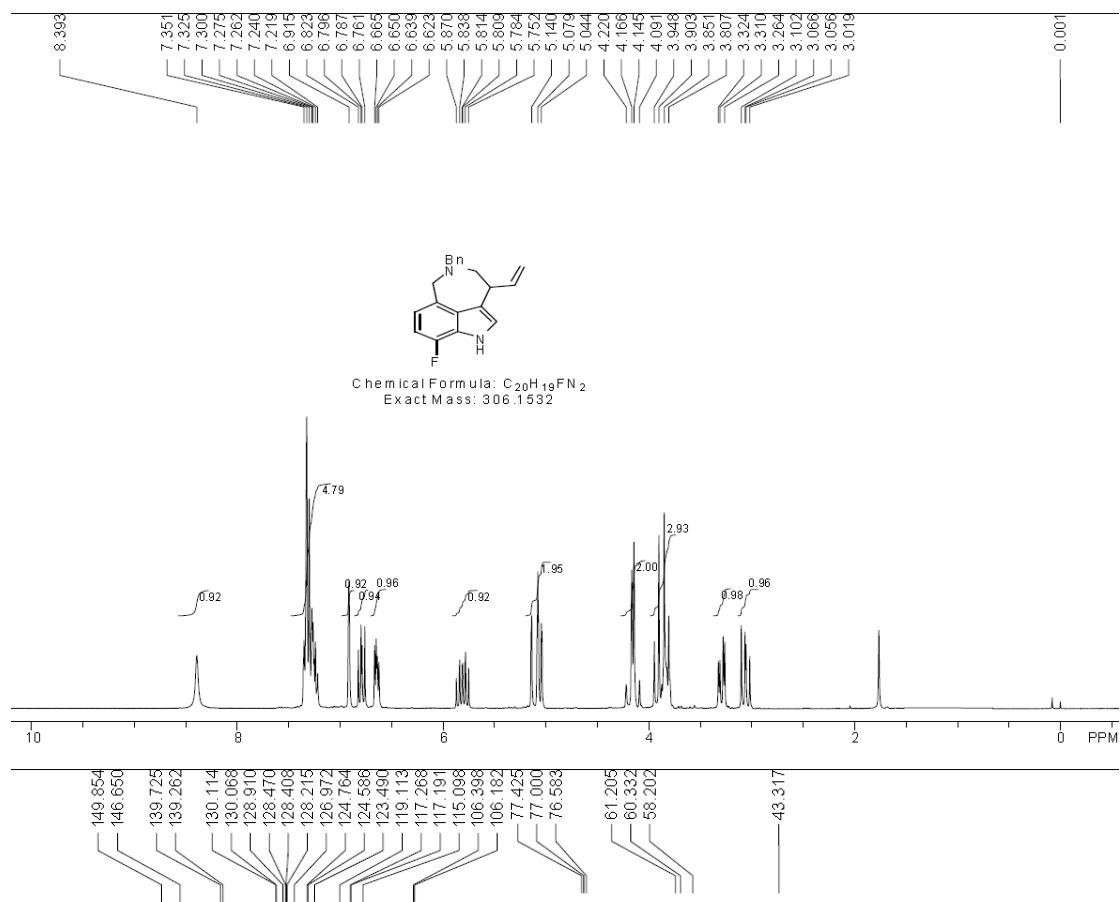
分析结果表

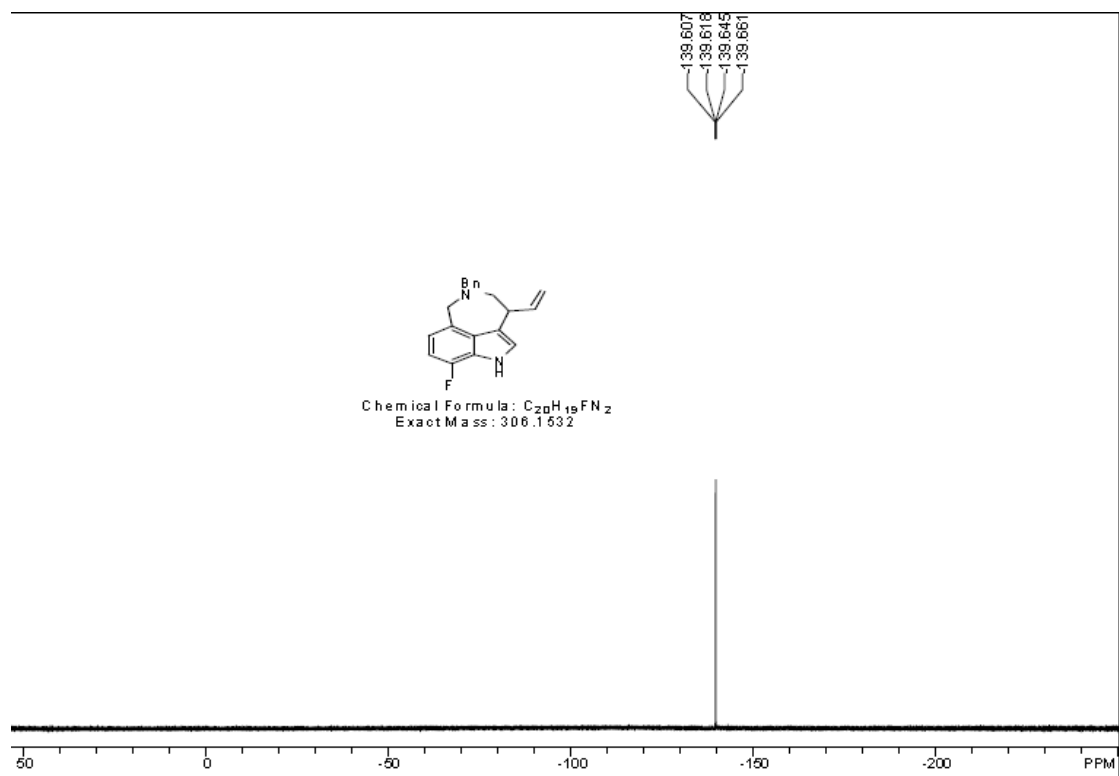
峰号	峰名	保留时间	峰高	峰面积	含量
1		11.342	71220.000	1604813.250	50.6945
2		13.572	58969.840	1560843.000	49.3055
总计			130189.840	3165656.250	100.0000

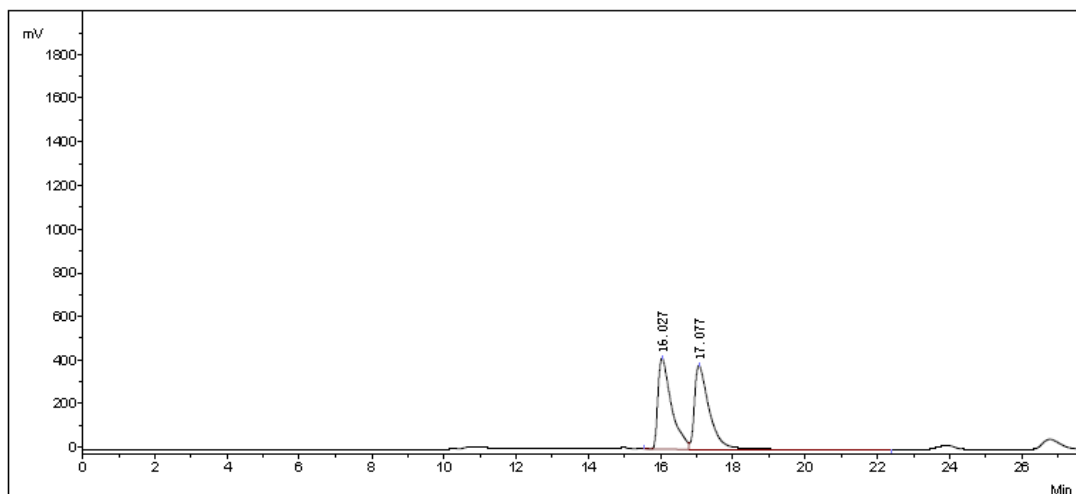


分析结果表

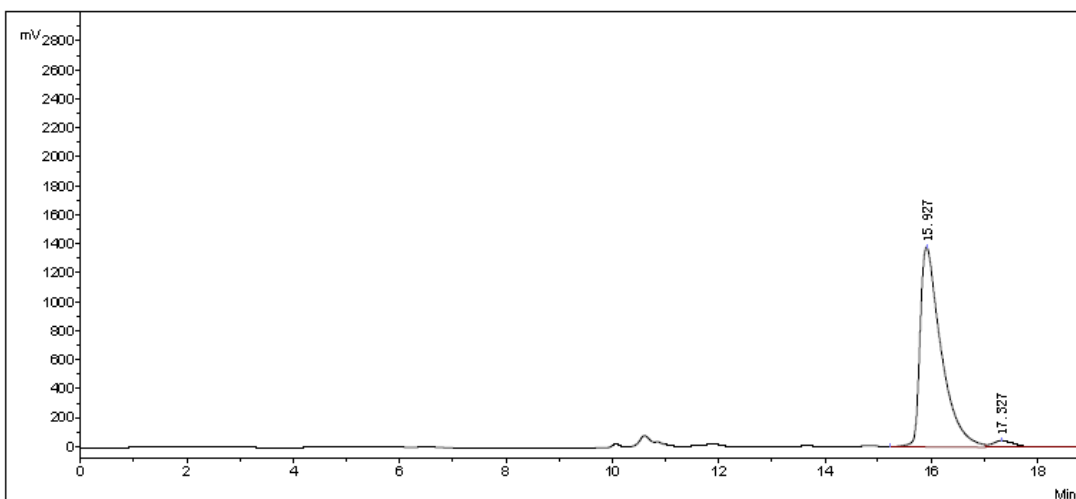
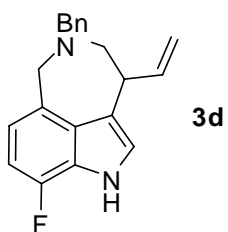
峰号	峰名	保留时间	峰高	峰面积	含量
1		10.402	55616.652	1237930.375	97.2768
2		12.557	943.889	34654.695	2.7232
总计			56560.542	1272585.070	100.0000



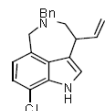
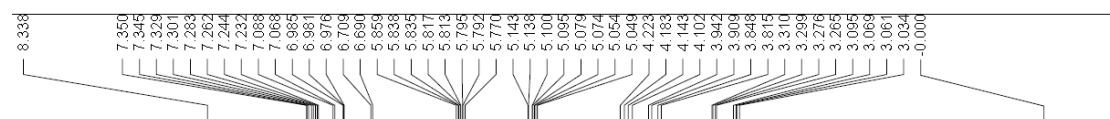




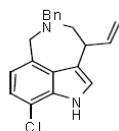
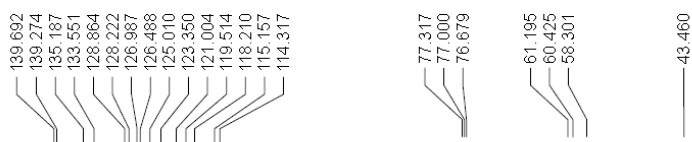
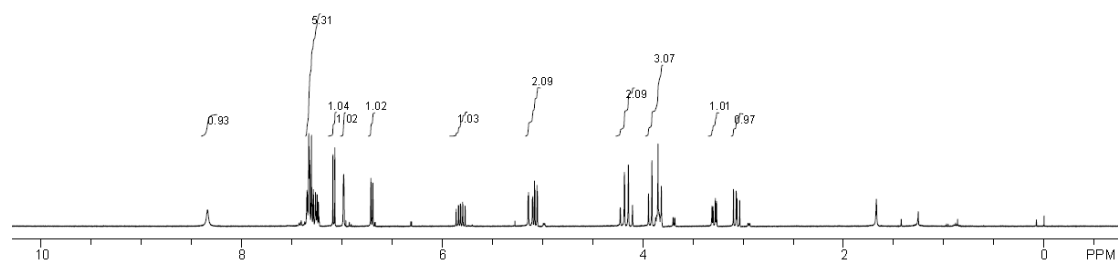
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	16.027	415265.4	10812085.4	50.0554
2	2	17.077	382474.7	10788172.6	49.9446
Total			797740.1	21600258.0	100.0000



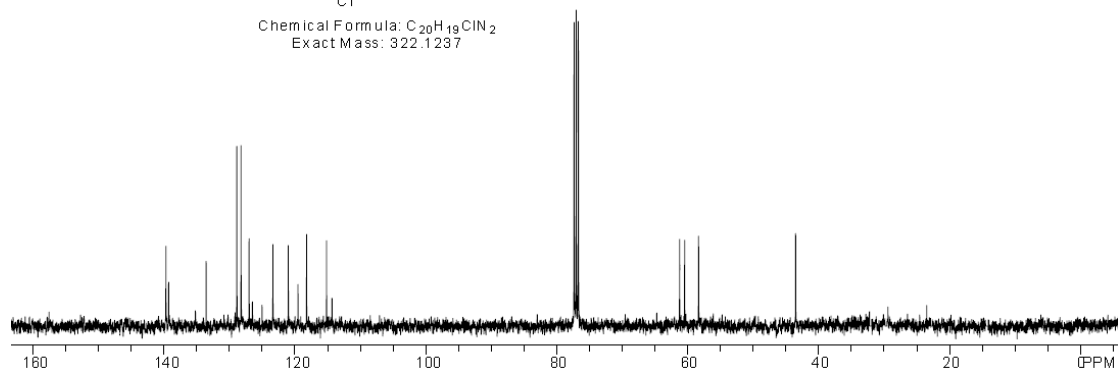
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	15.927	1374934.9	37856120.4	96.4347
2	2	17.327	45877.1	1399564.1	3.5653
Total			1420812.1	39255684.5	100.0000

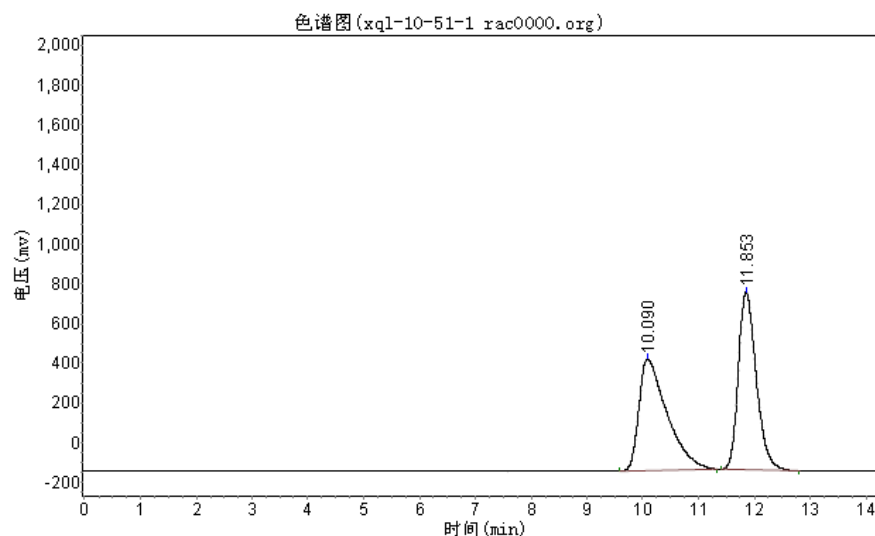


Chemical Formula: C<sub>20</sub>H<sub>19</sub>ClN<sub>2</sub>  
Exact Mass: 322.1237



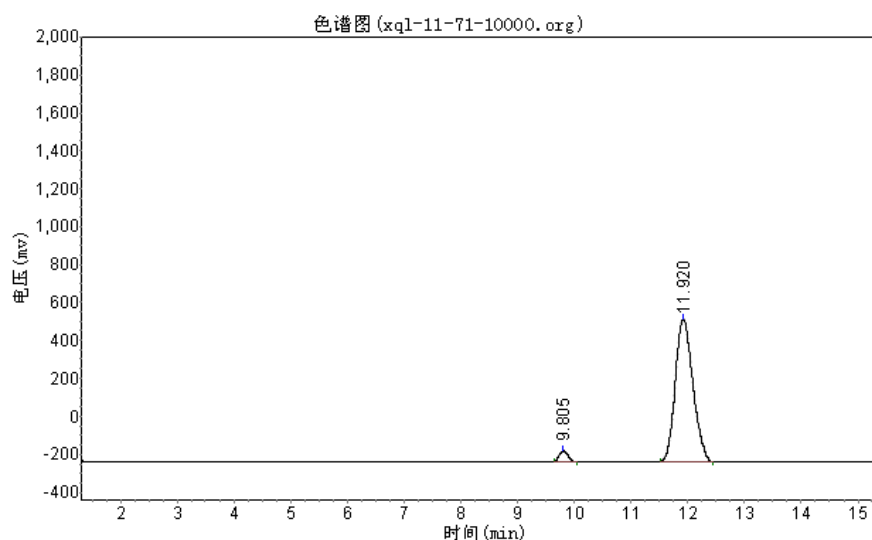
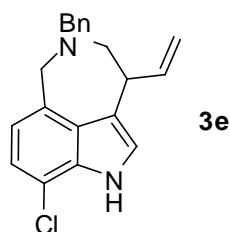
Chemical Formula: C<sub>20</sub>H<sub>19</sub>ClN<sub>2</sub>  
Exact Mass: 322.1237





分析结果表

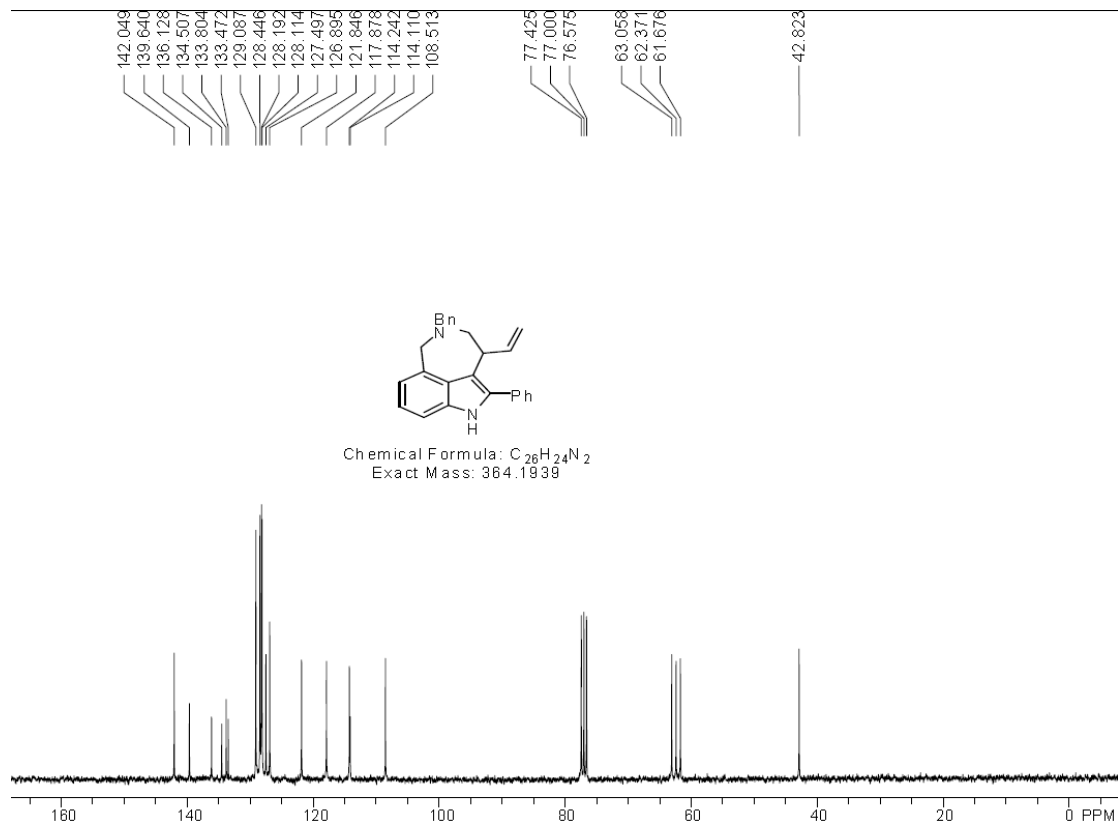
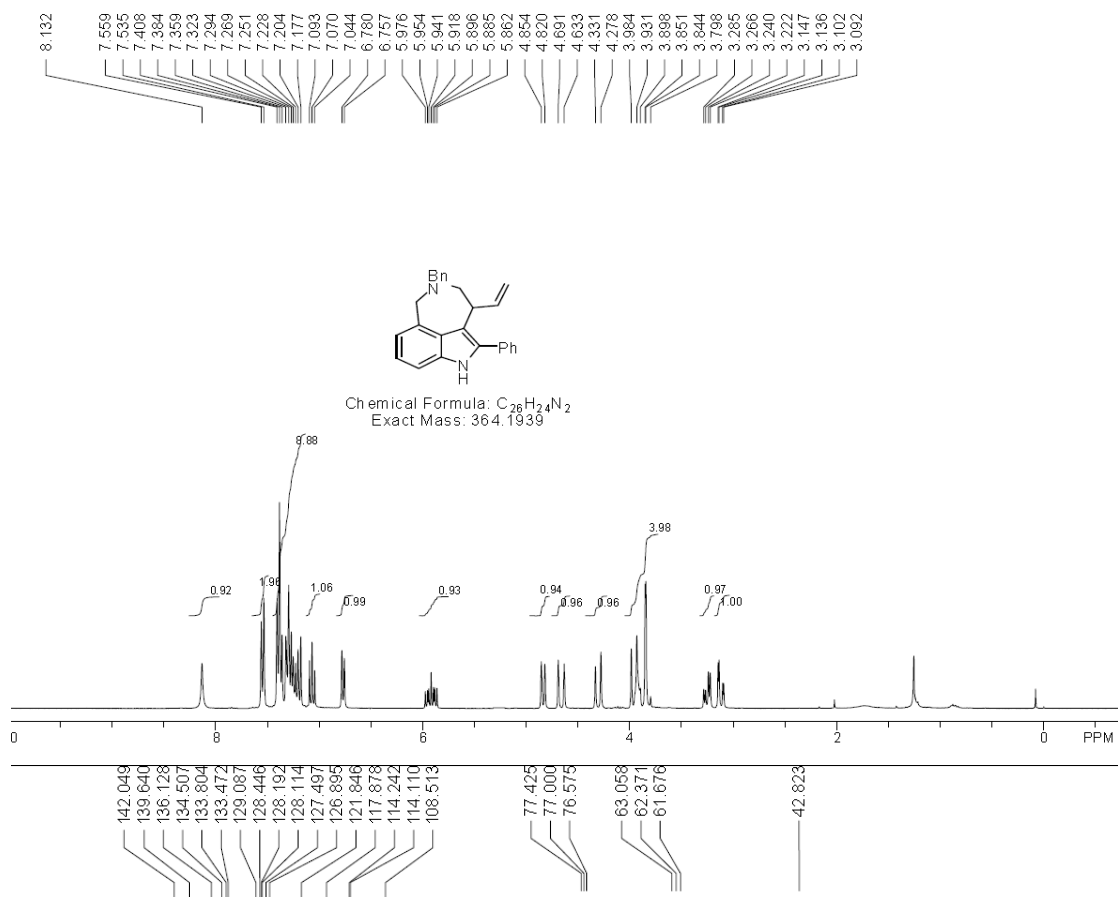
峰号	峰名	保留时间	峰高	峰面积	含量
1		10.090	561018.000	19589972.000	49.5605
2		11.853	896424.875	19937412.000	50.4395
总计			1457442.875	39527384.000	100.0000

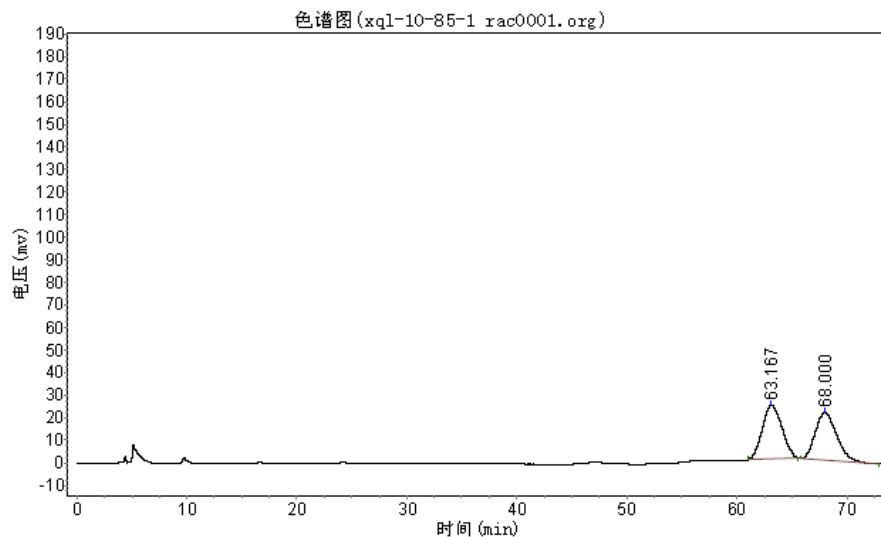


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		9.805	53383.957	570191.938	3.4194
2		11.920	752163.875	16104878.000	96.5806
总计			805547.832	16675069.938	100.0000

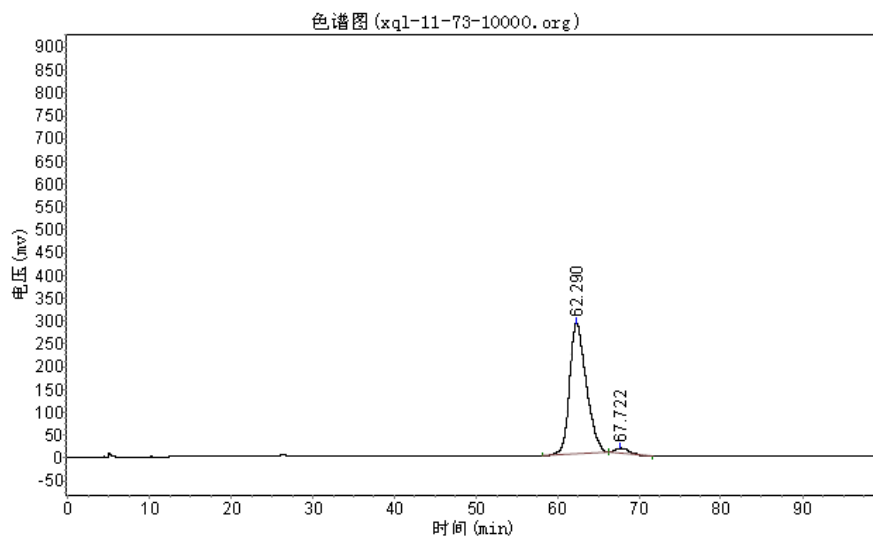
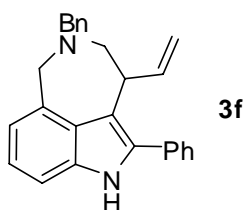






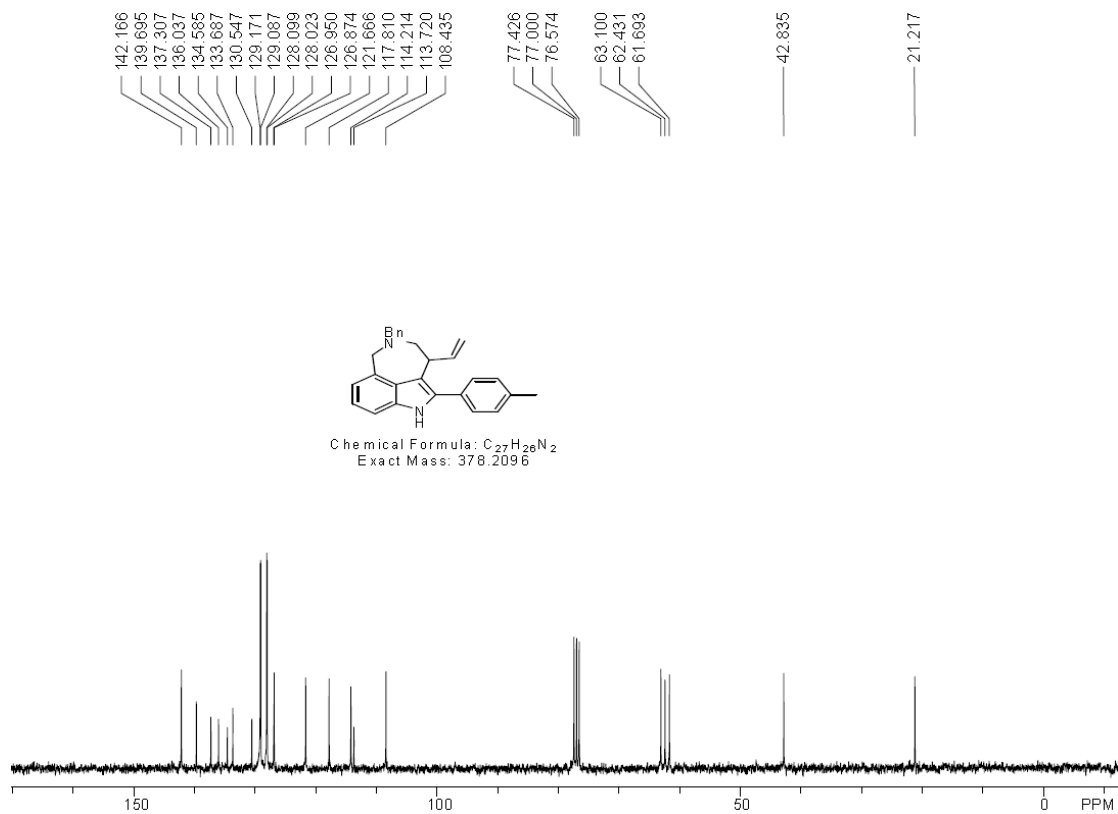
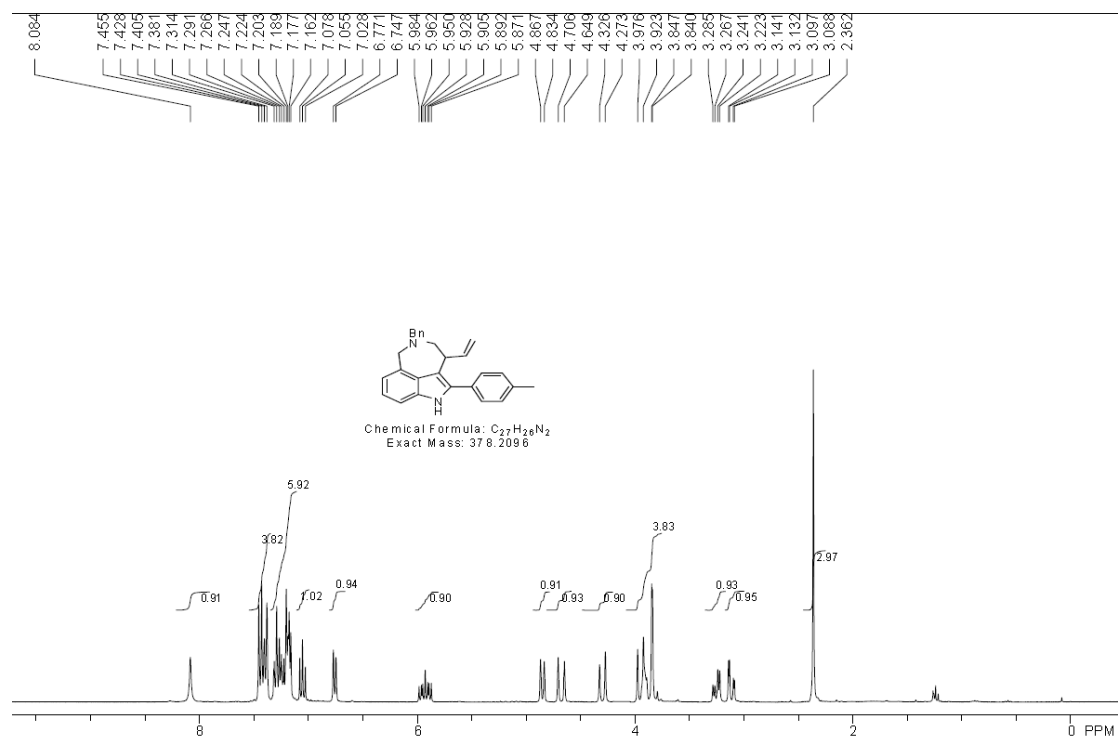
分析结果表

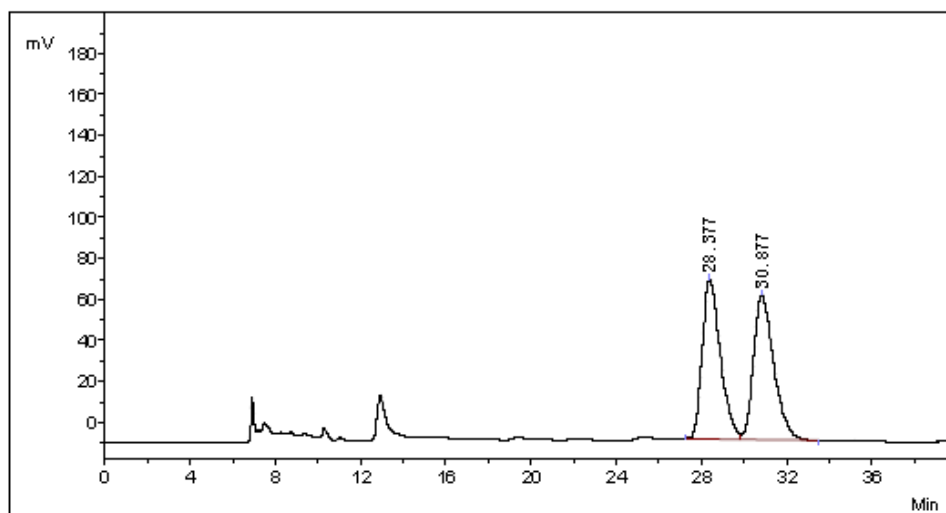
峰号	峰名	保留时间	峰高	峰面积	含量
1		63.167	23819.764	2955090.000	51.0597
2		68.000	20936.752	2832431.000	48.9403
总计			44756.516	5787521.000	100.0000



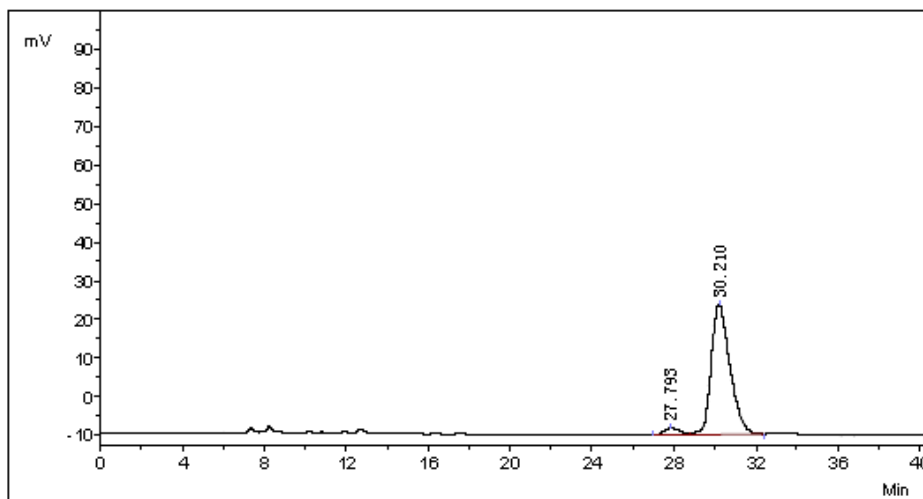
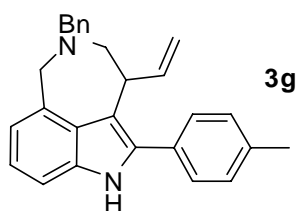
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		62.290	287195.219	40565372.000	97.1373
2		67.722	11122.245	1195492.125	2.8627
总计			298317.464	41760864.125	100.0000

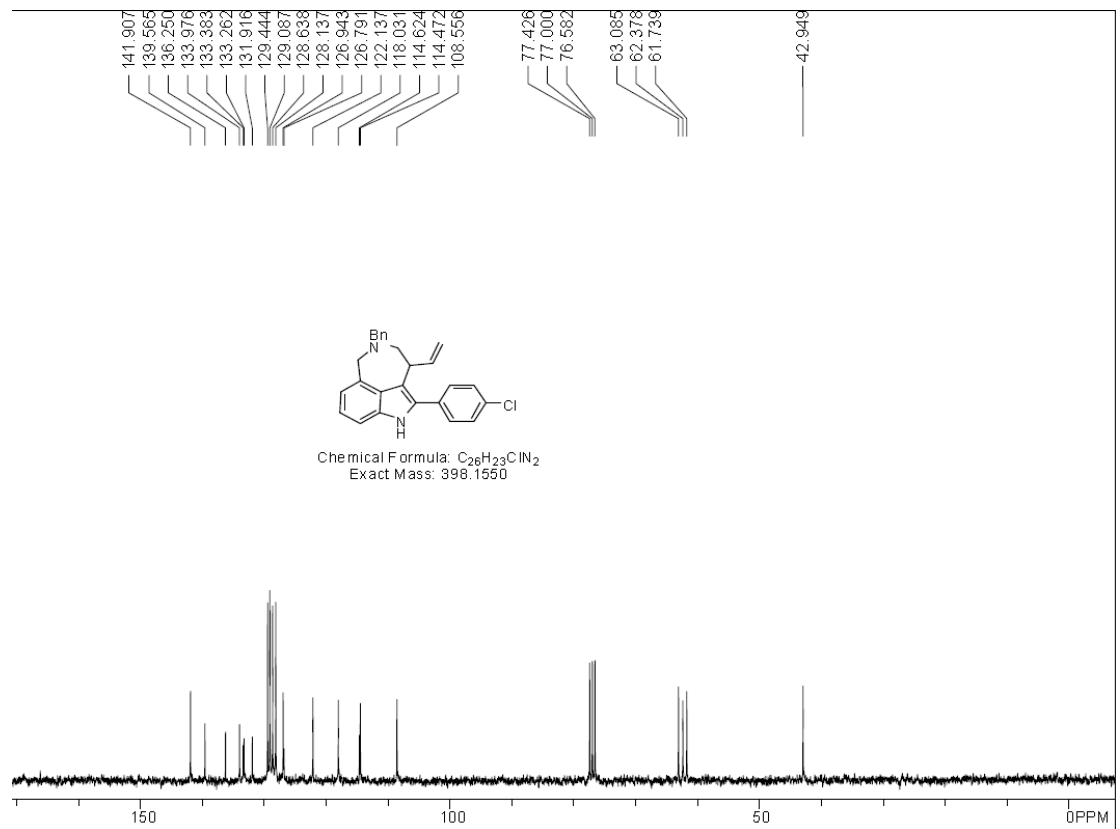
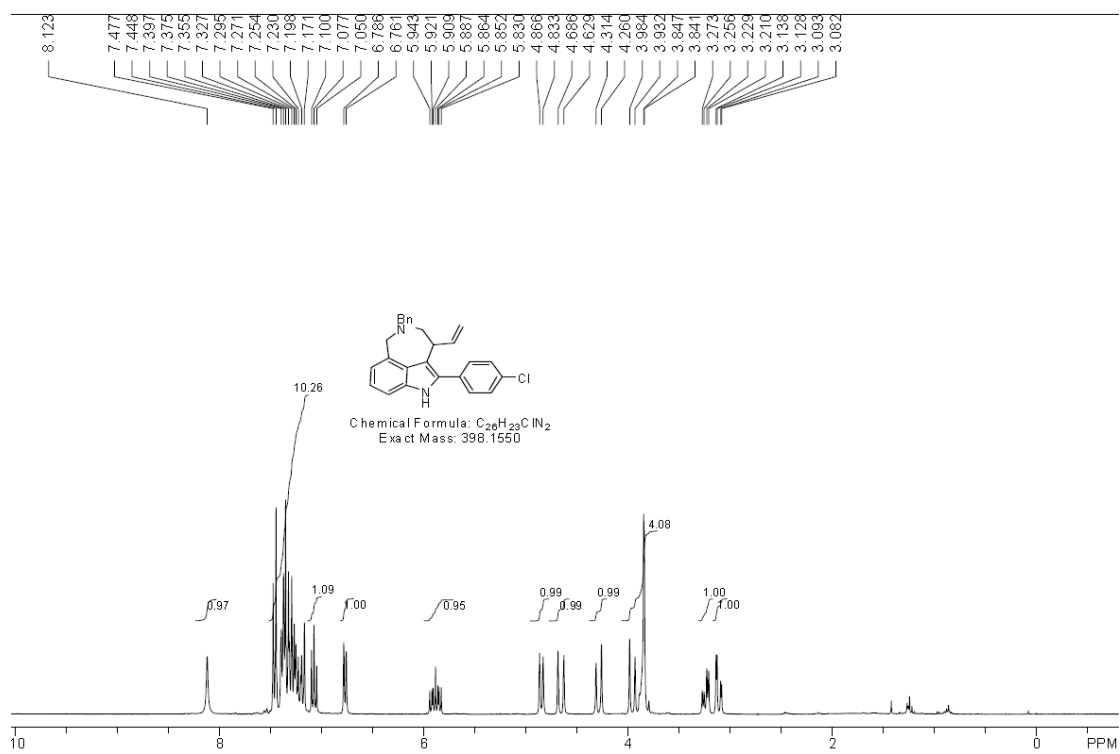


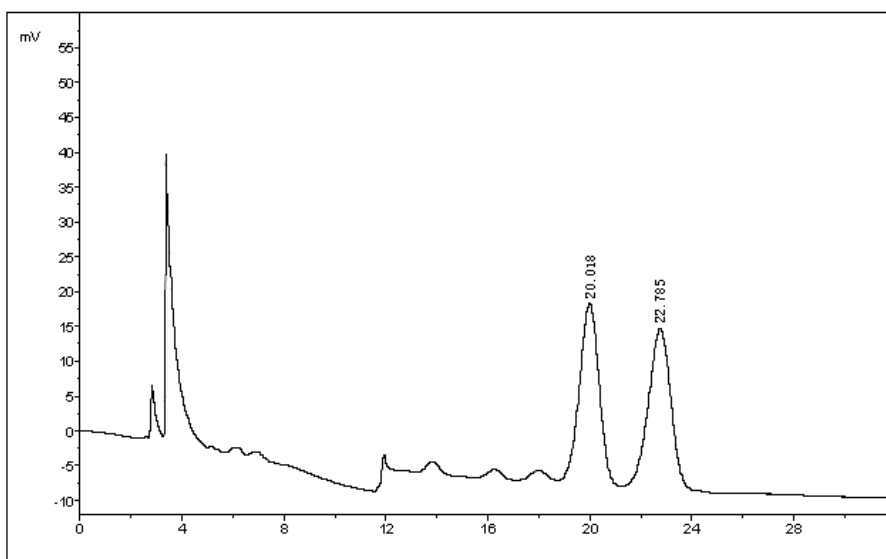


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	28.377	77909.4	4610799.6	49.8926
2	2	Unknown	30.877	70626.5	4630658.7	50.1074
Total				148535.9	9241458.3	100.0000

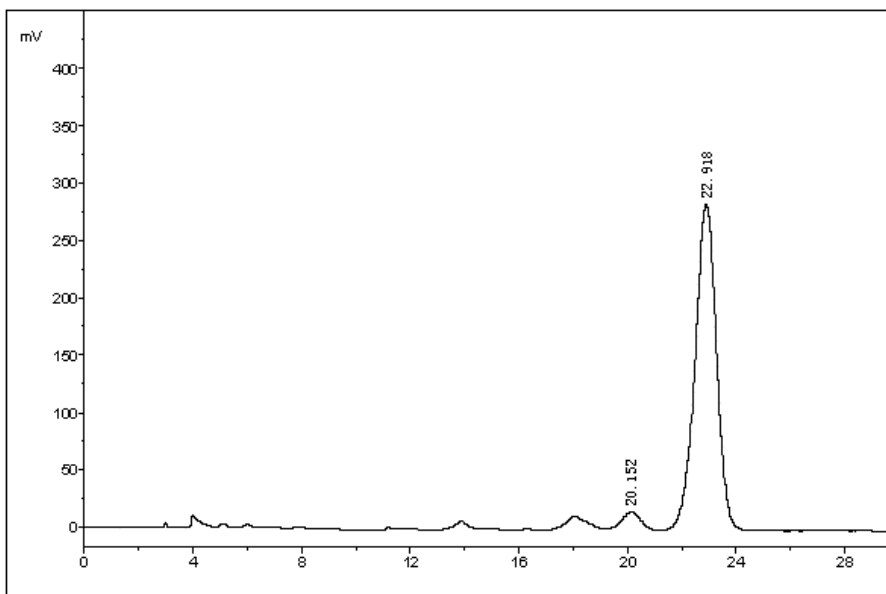
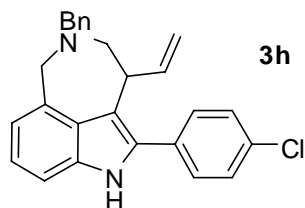


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	27.793	1765.1	98448.5	4.4071
2	2	Unknown	30.210	33703.9	2135437.0	95.5929
Total				35469.0	2233885.5	100.0000

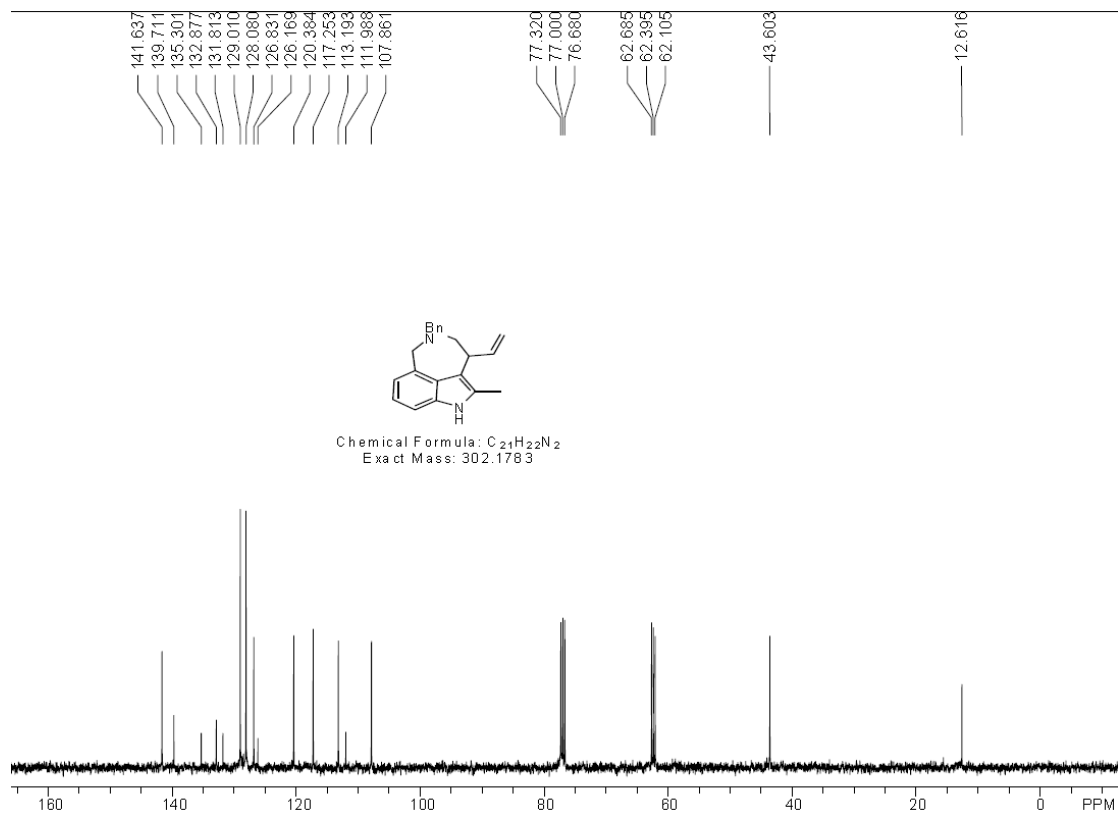
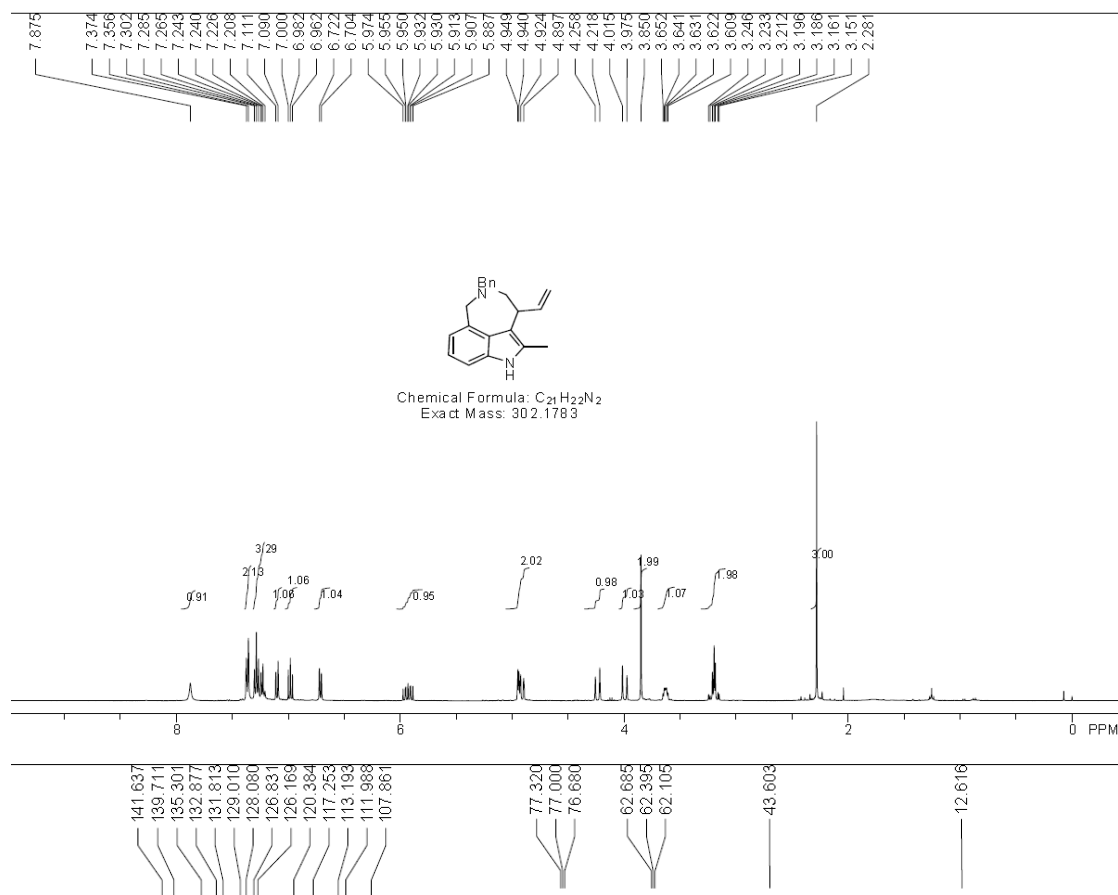


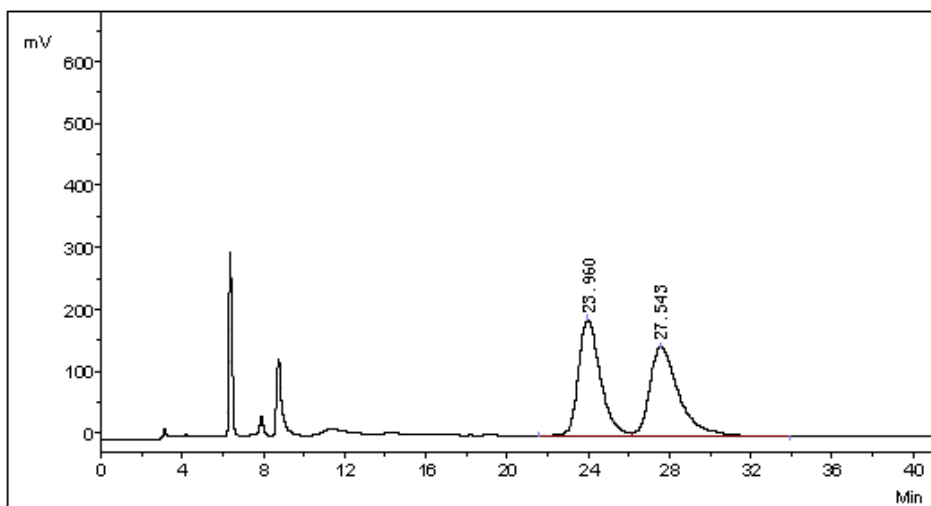


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		20.018	25833.9	1371504.5	49.5657
2	2		22.785	22936.3	1395536.3	50.4343
Total				48770.2	2767040.8	100.0000

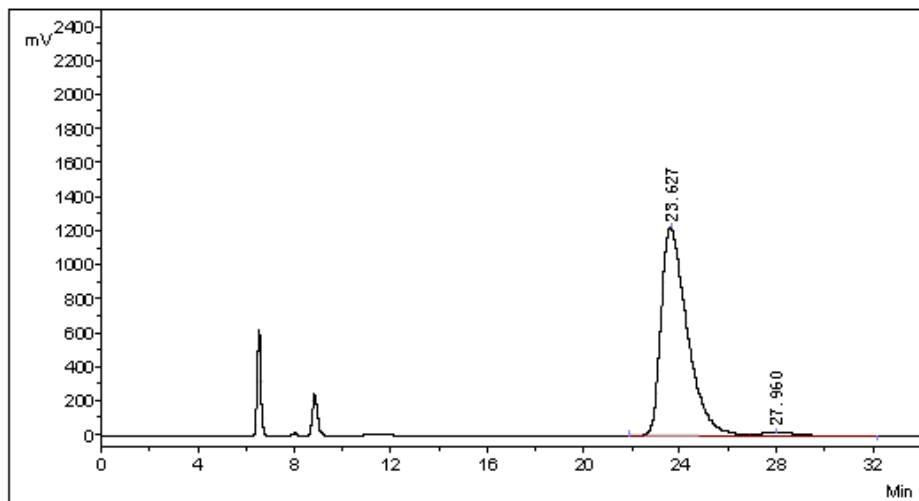
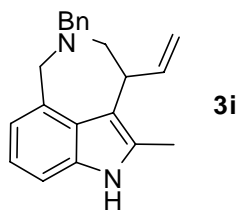


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		20.152	15731.4	728063.2	4.4604
2	2		22.918	284963.5	15594799.6	95.5396
Total				300694.9	16322862.8	100.0000



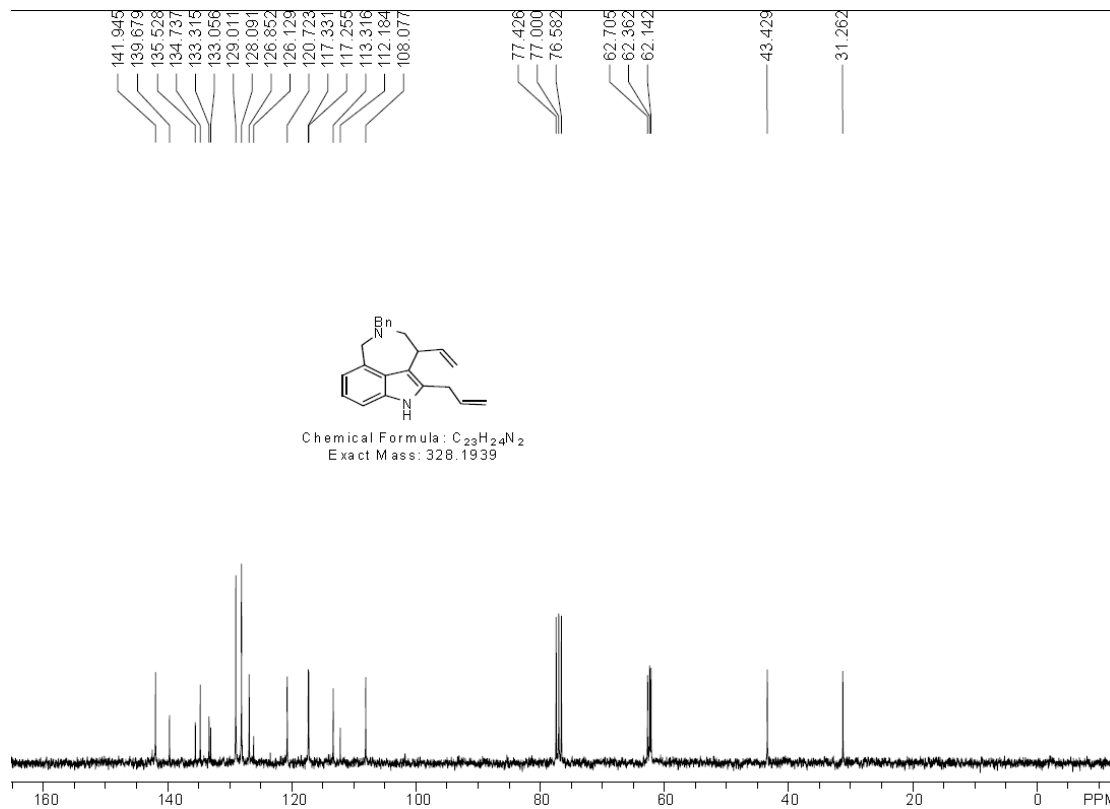
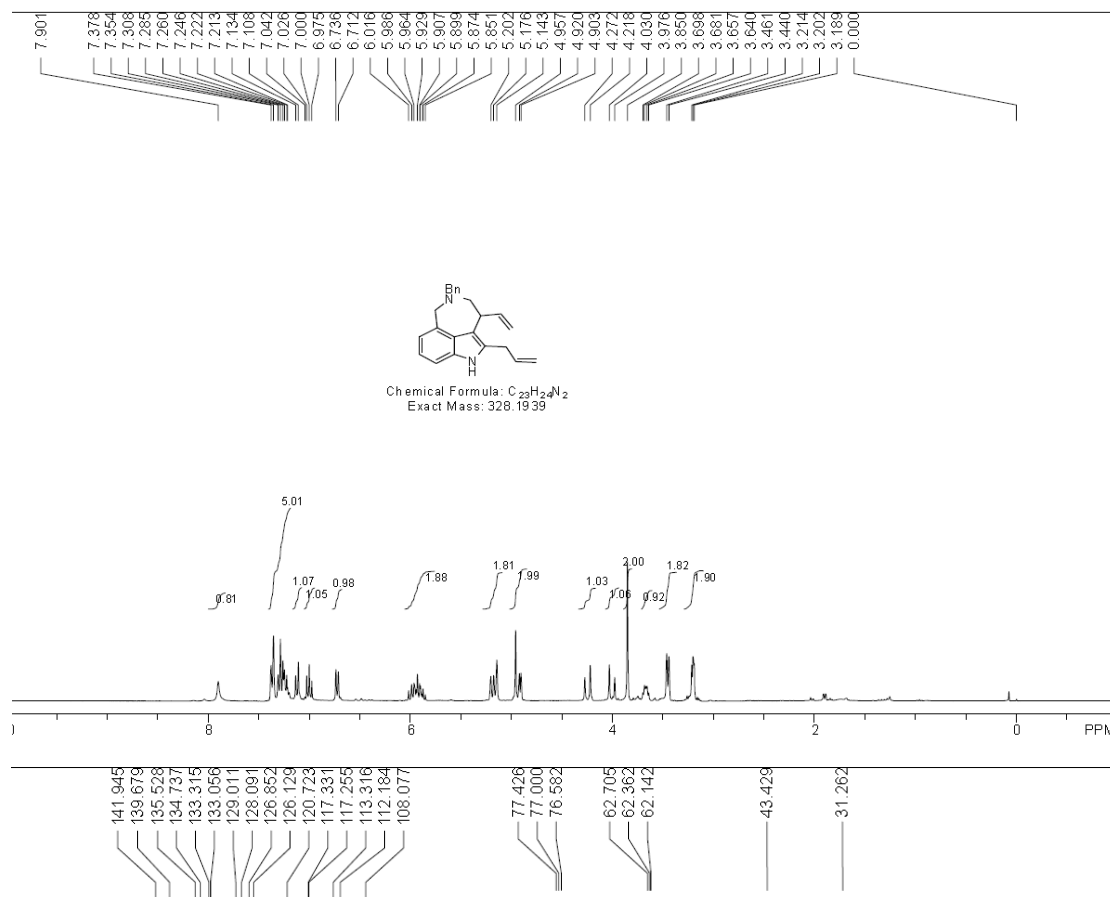


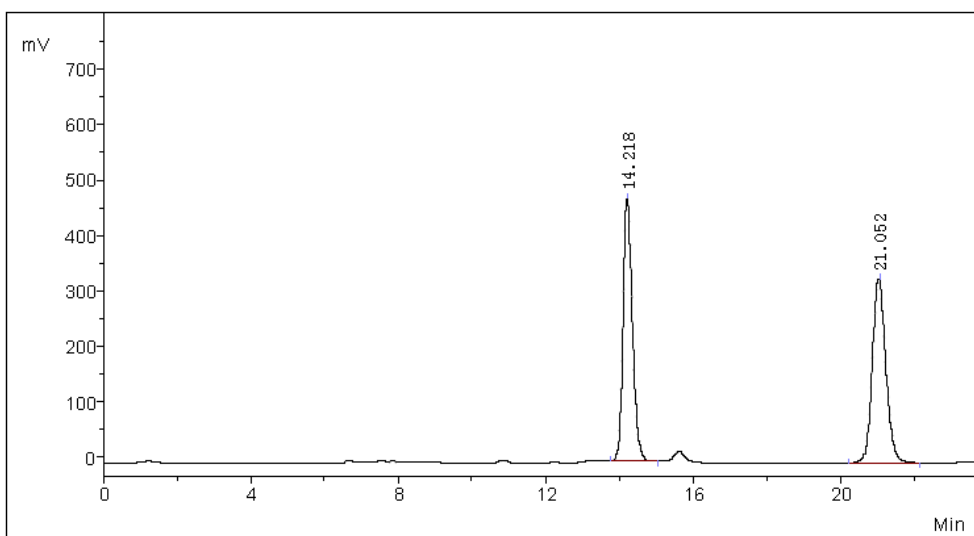
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	23.960	188246.7	14133496.5	49.3820
2	2	Unknown	27.543	144421.6	14487226.4	50.6180
Total				332668.3	28620722.9	100.0000



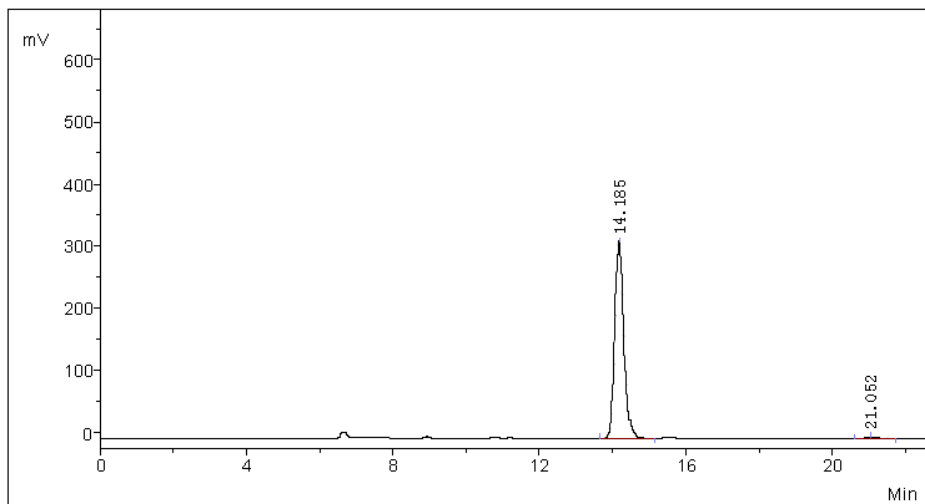
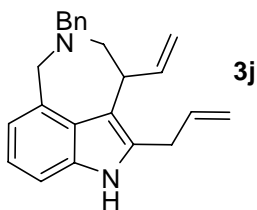
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	23.627	1224702.8	92556358.7	97.5431
2	2	Unknown	27.960	21038.8	2331300.2	2.4569
Total				1245741.5	94887658.9	100.0000



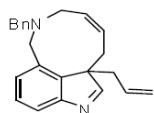
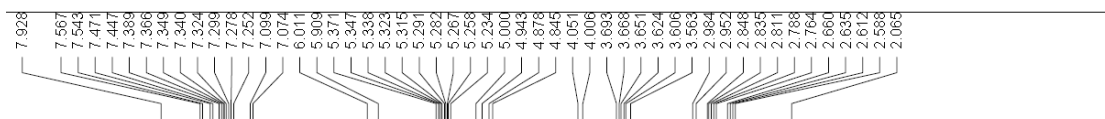




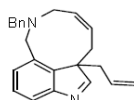
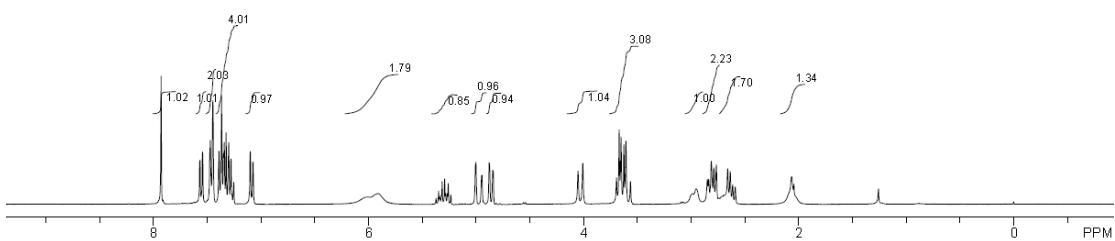
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	14.218	475372.8	8476402.3	50.1882
2	2	Unknown	21.052	330887.6	8412839.8	49.8118
Total				806260.4	16889242.1	100.0000



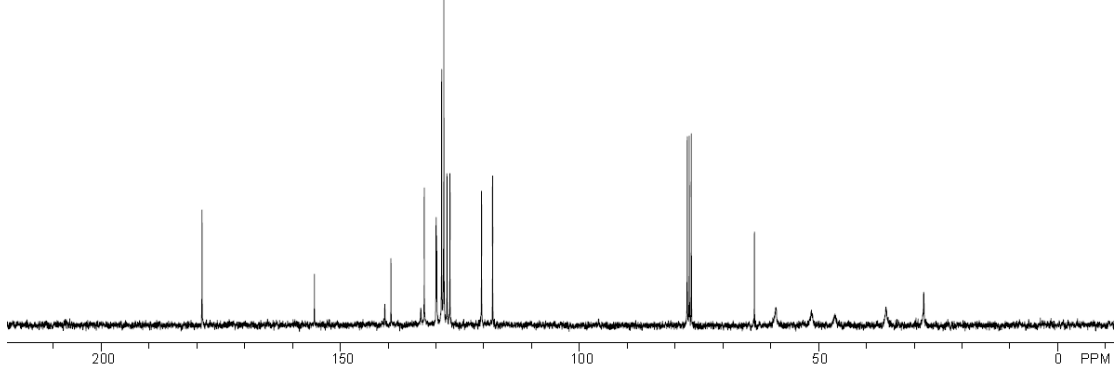
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	14.185	316024.8	5456199.6	98.7307
2	2	Unknown	21.052	2886.7	70147.6	1.2693
Total				318911.5	5526347.2	100.0000

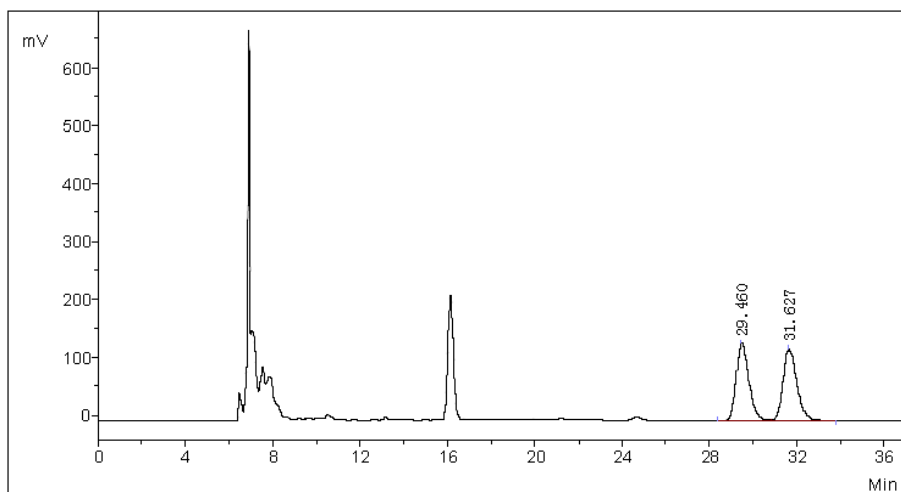


Chemical Formula: C<sub>23</sub>H<sub>24</sub>N<sub>2</sub>  
Exact Mass: 328.1939

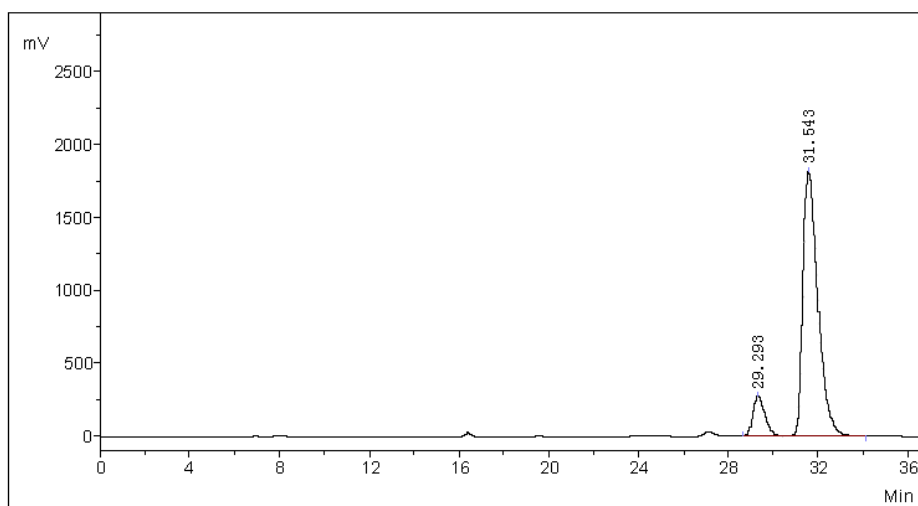
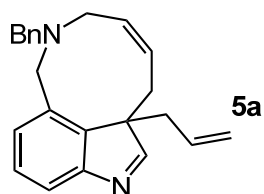


Chemical Formula: C<sub>23</sub>H<sub>24</sub>N<sub>2</sub>  
Exact Mass: 328.1939

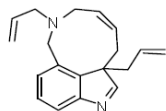
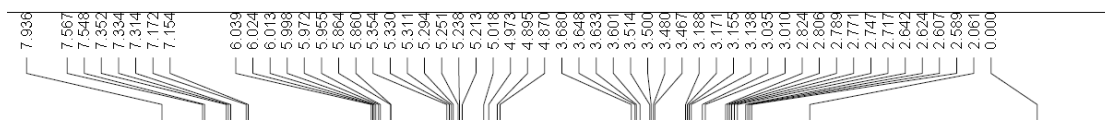




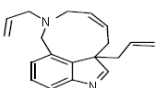
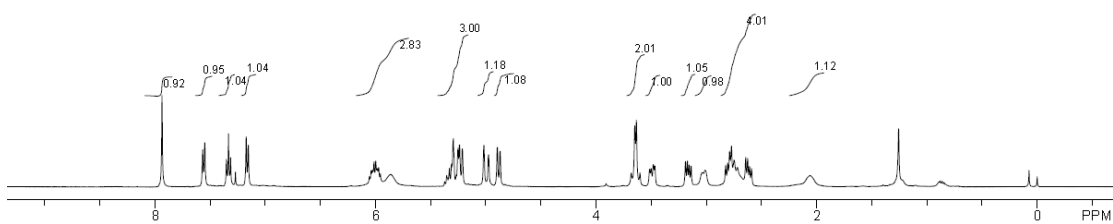
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	29.460	132733.8	5413683.5	49.9009
2	2	Unknown	31.627	123291.1	5435187.6	50.0991
Total				256024.8	10848871.1	100.0000



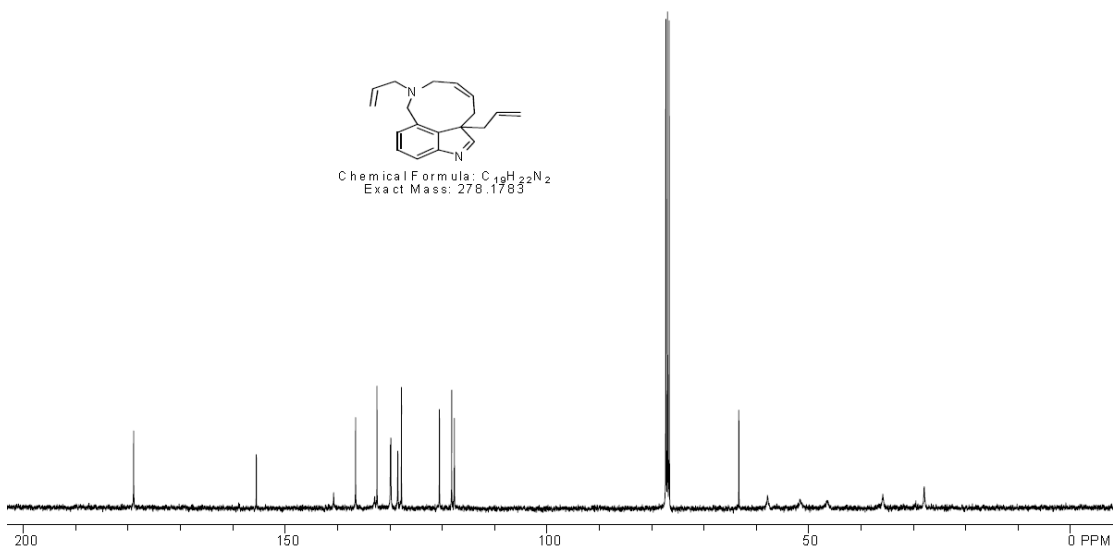
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	29.293	274648.6	10538701.2	11.0298
2	2	Unknown	31.543	1824882.8	85009256.2	88.9702
Total				2099531.5	95547957.4	100.0000

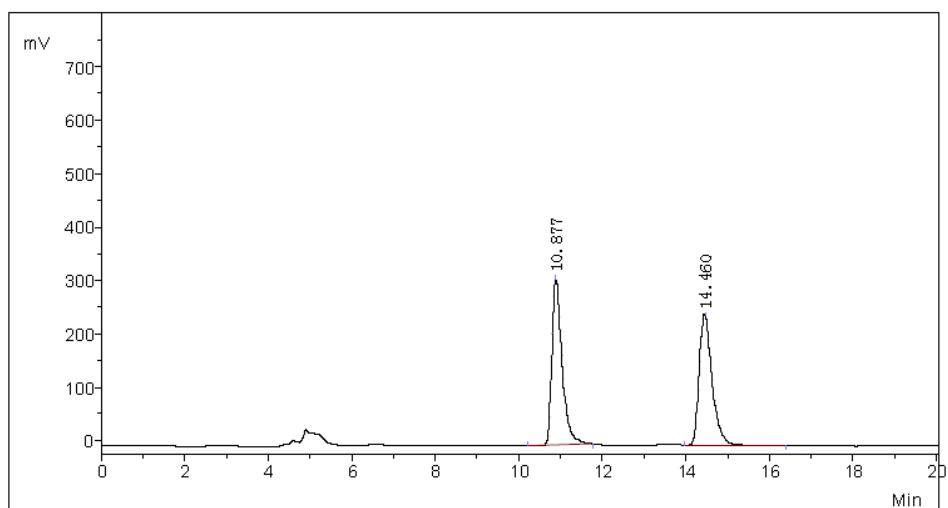


Chemical Formula:  $C_{19}H_{22}N_2$   
Exact Mass: 278.1783

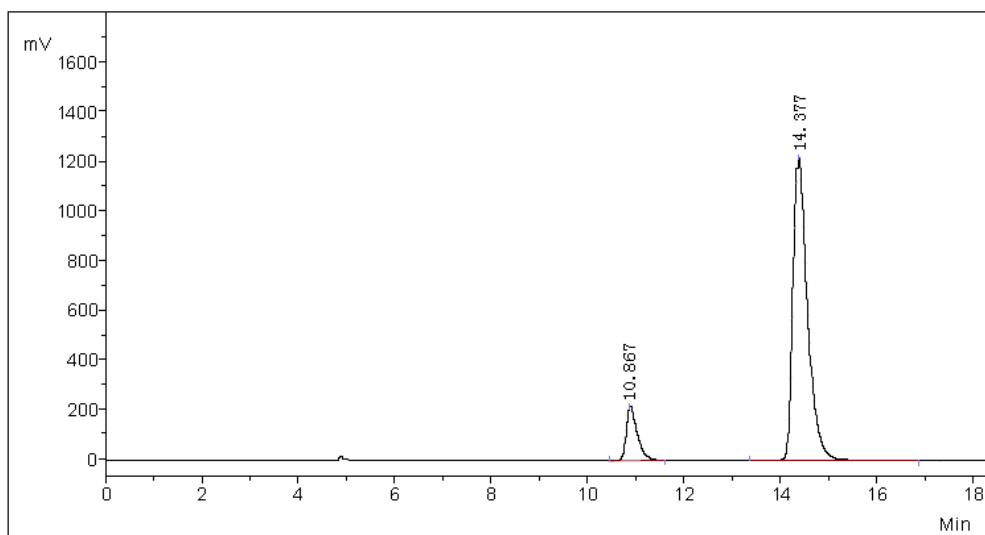
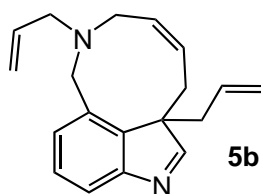


Chemical Formula:  $C_{19}H_{22}N_2$   
Exact Mass: 278.1783

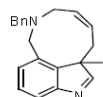
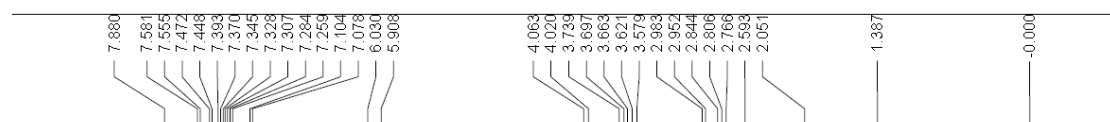




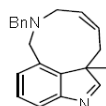
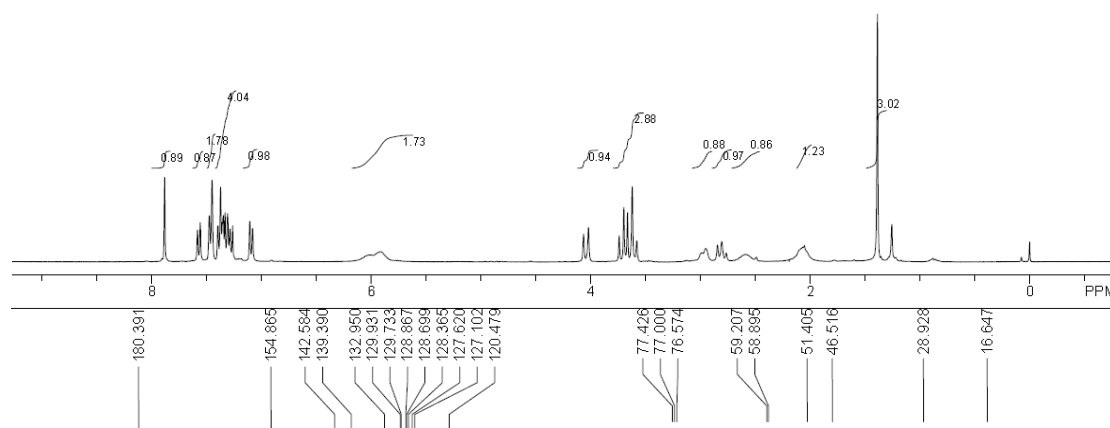
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	10.877	310240.6	5348661.0	50.2856
2	2	Unknown	14.460	242547.7	5287908.8	49.7144
Total				552788.3	10636569.8	100.0000



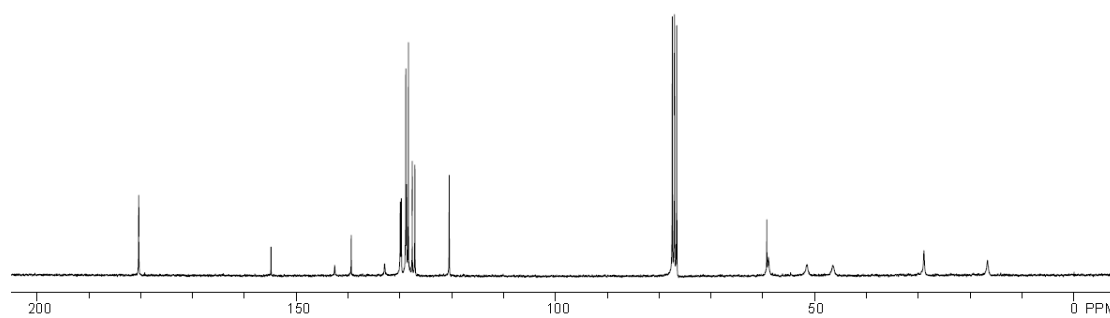
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	10.867	211271.2	3533114.8	12.0663
2	2	Unknown	14.377	1217766.7	25747662.9	87.9337
Total				1429038.0	29280777.7	100.0000

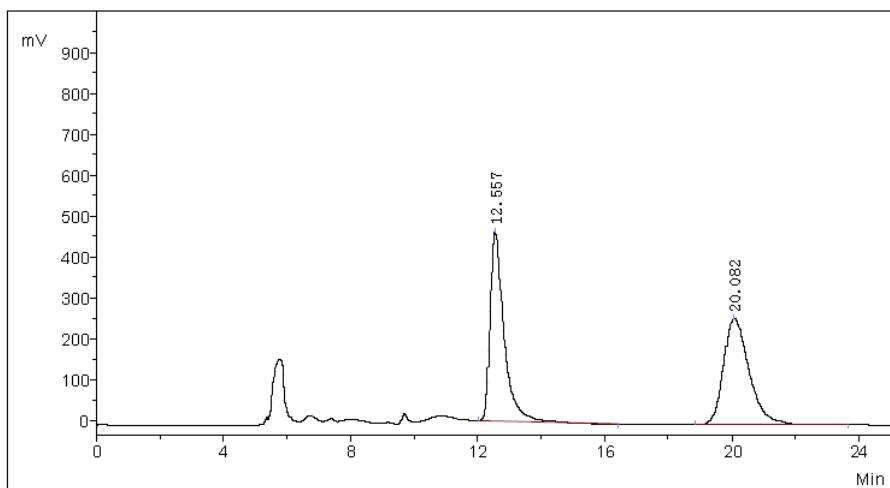


Chemical Formula: C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>  
Exact Mass: 302.1783

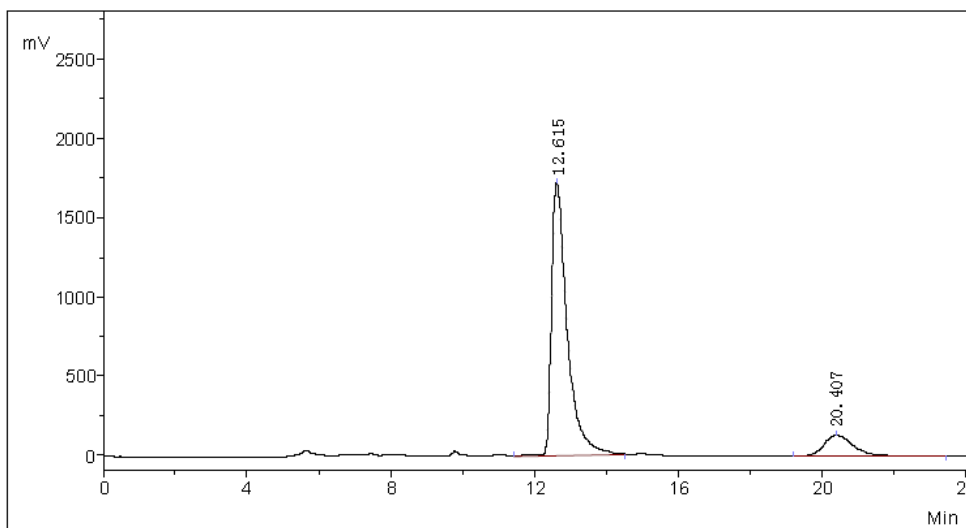
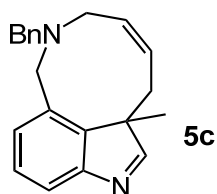


Chemical Formula: C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>  
Exact Mass: 302.1783



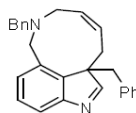
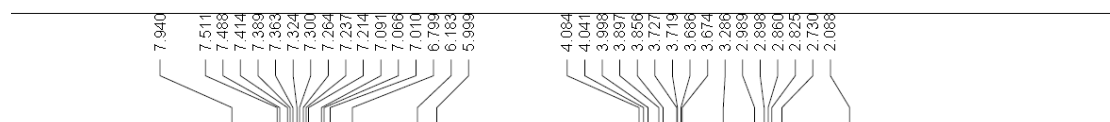


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	12.557	463084.9	14198169.9	49.6002
2	2	Unknown	20.082	258085.4	14427047.1	50.3998
Total				721170.3	28625217.0	100.0000

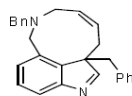
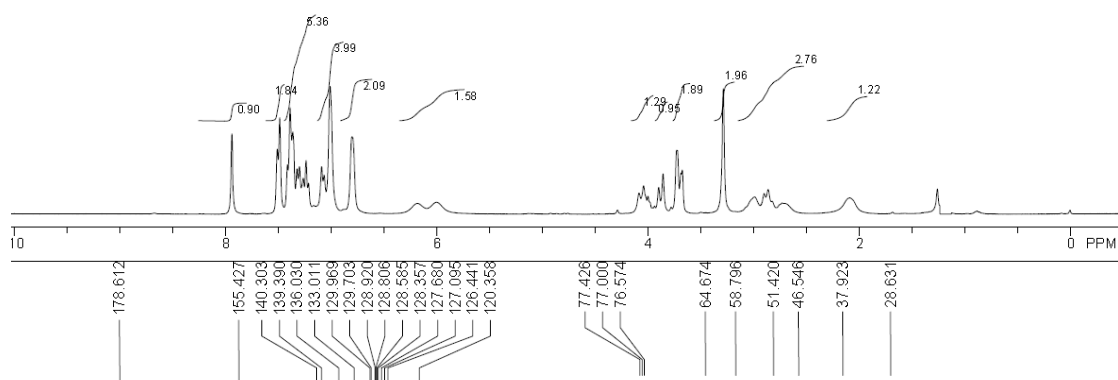


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	12.615	1716434.4	51419730.9	86.8883
2	2	Unknown	20.407	134804.9	7759394.9	13.1117
Total				1851239.4	59179125.8	100.0000

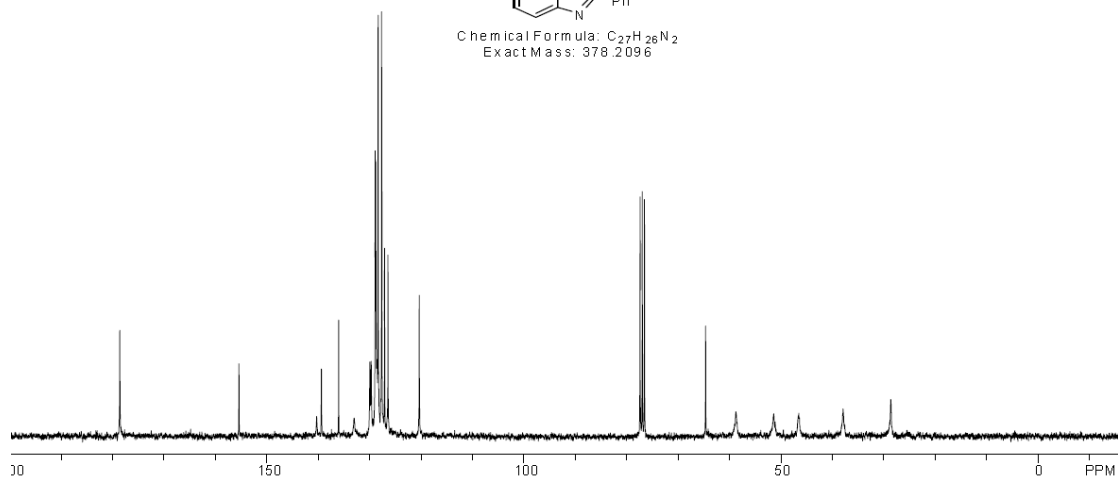


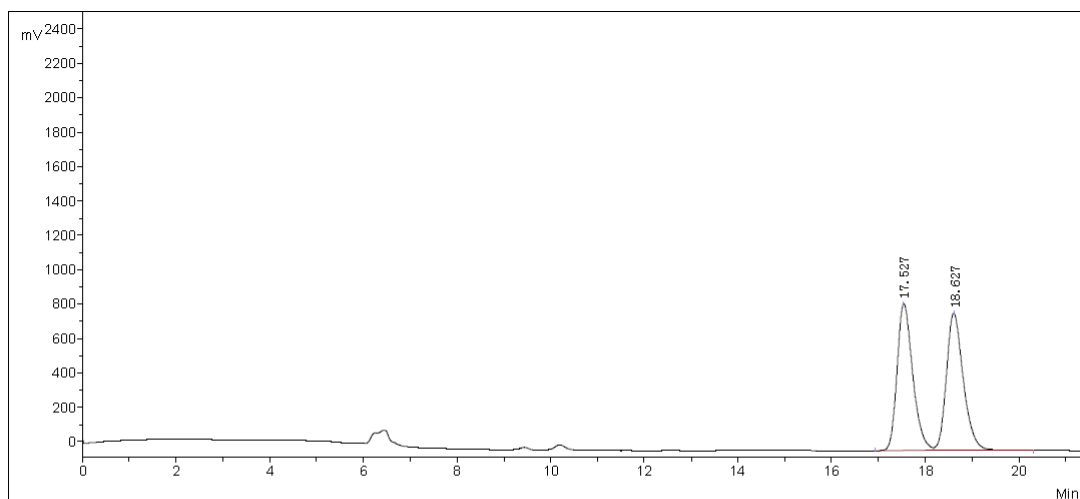


Chemical Formula:  $C_{27}H_{26}N_2$   
Exact Mass: 378.2096

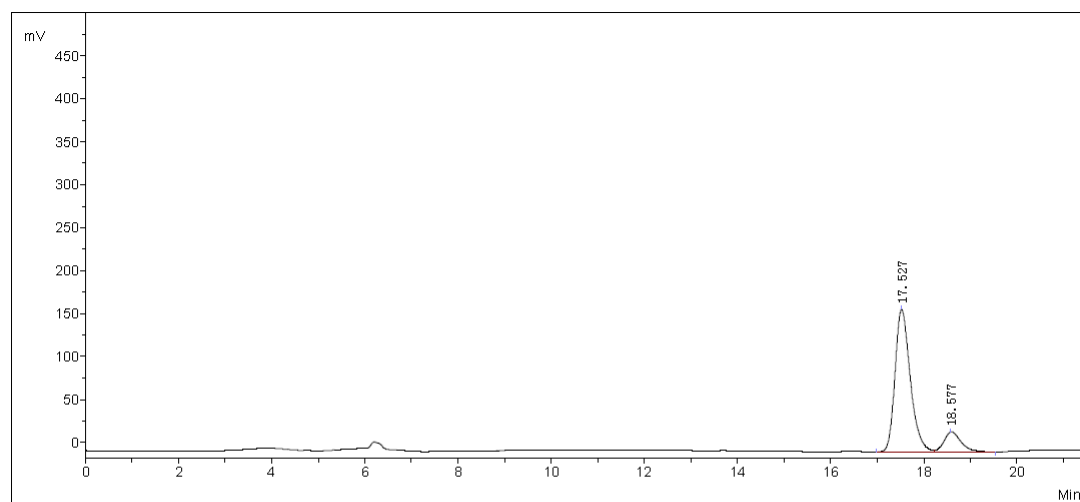
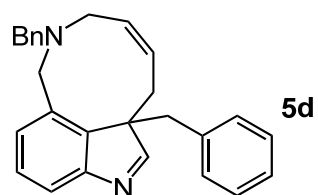


Chemical Formula:  $C_{27}H_{26}N_2$   
Exact Mass: 378.2096

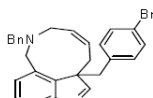
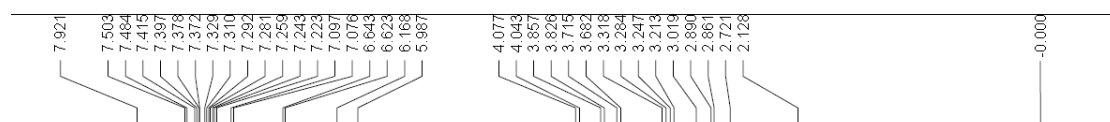




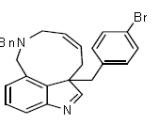
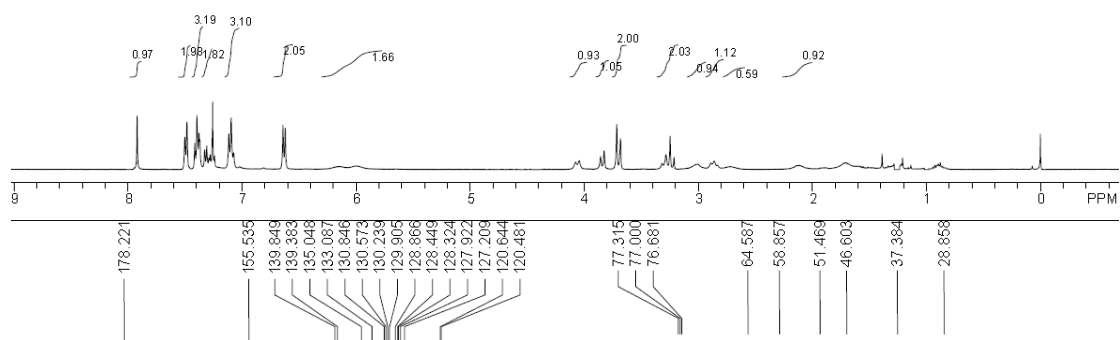
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	17.527	848738.4	19776223.7	49.8354
2	2	18.627	792823.7	19906884.0	50.1646
Total			1641562.1	39683107.7	100.0000



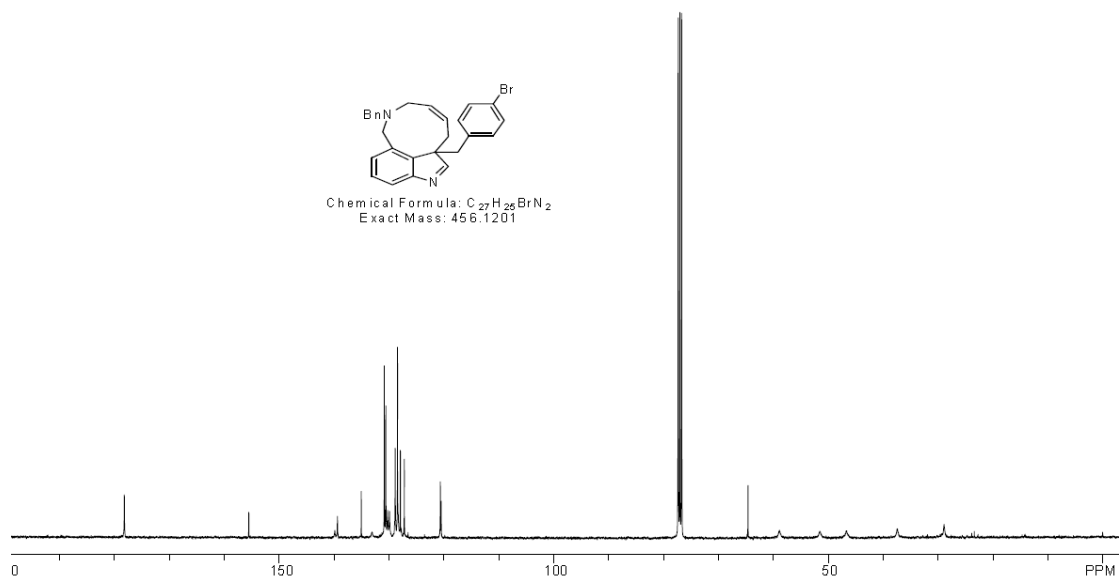
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	17.527	165483.5	3761975.6	86.9566
2	2	18.577	22982.2	564294.5	13.0434
Total			188465.7	4326270.1	100.0000

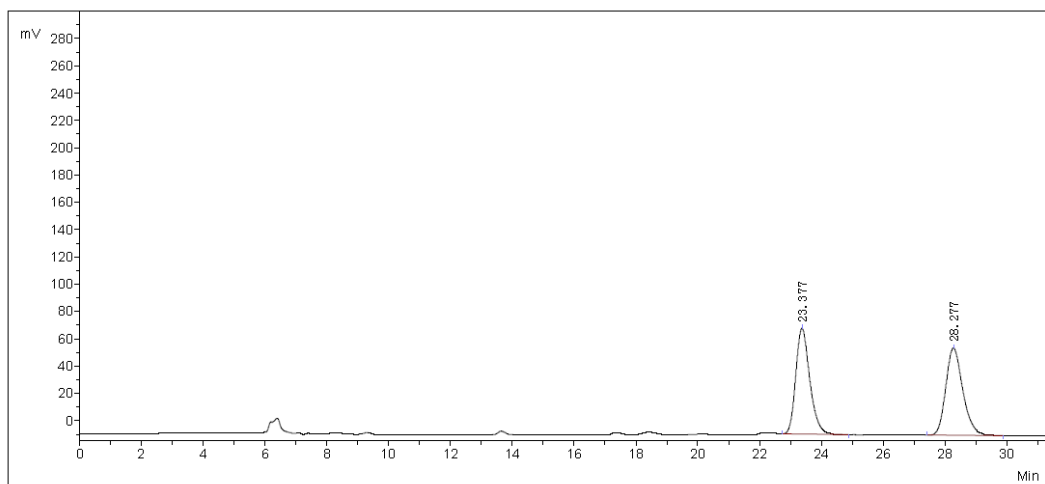


Chemical Formula:  $C_{27}H_{25}BrN_2$   
Exact Mass: 456.1201

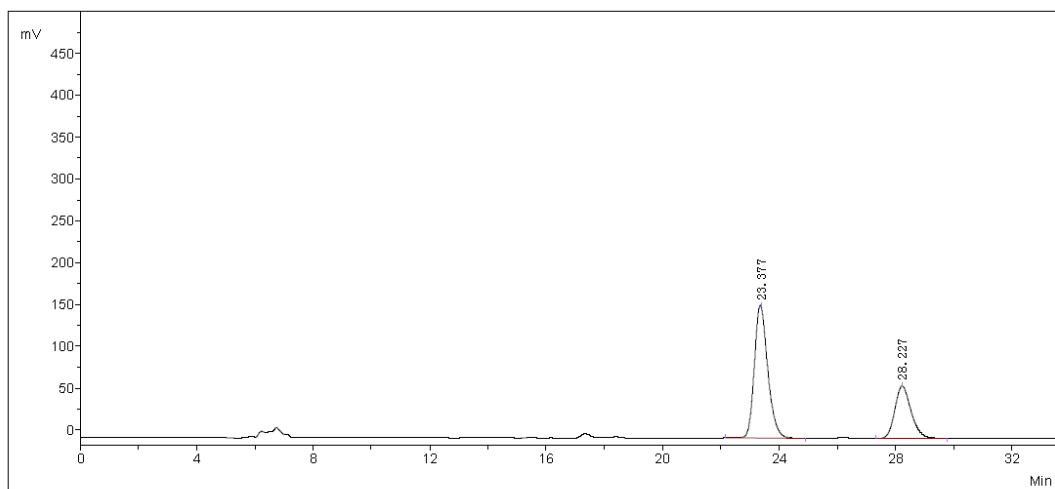
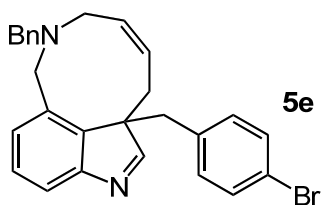


Chemical Formula:  $C_{27}H_{25}BrN_2$   
Exact Mass: 456.1201

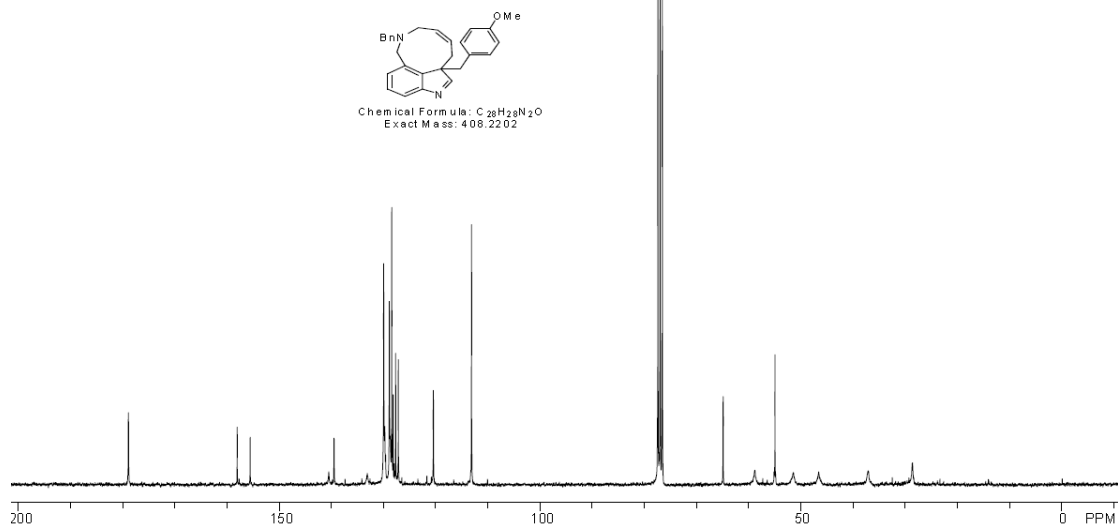
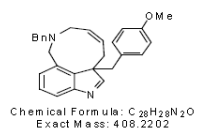
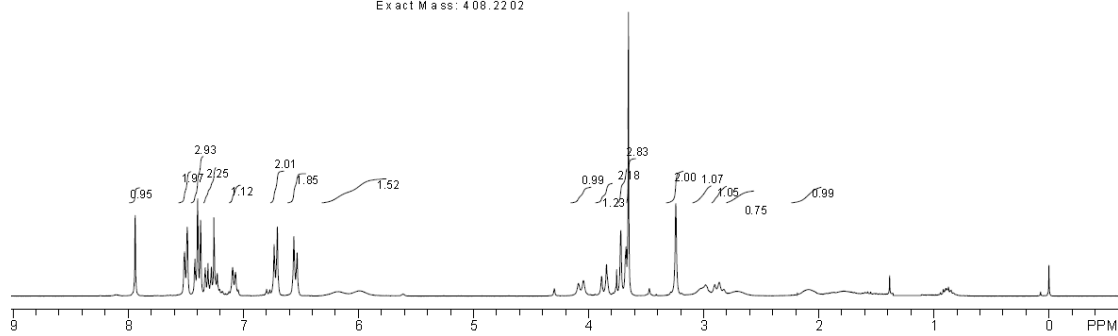
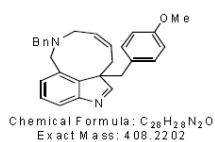
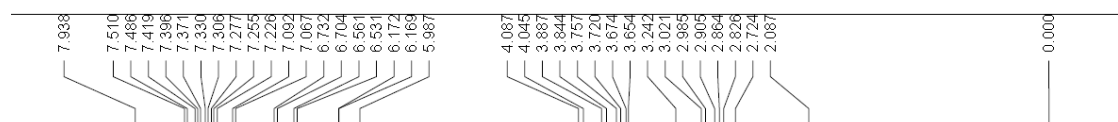


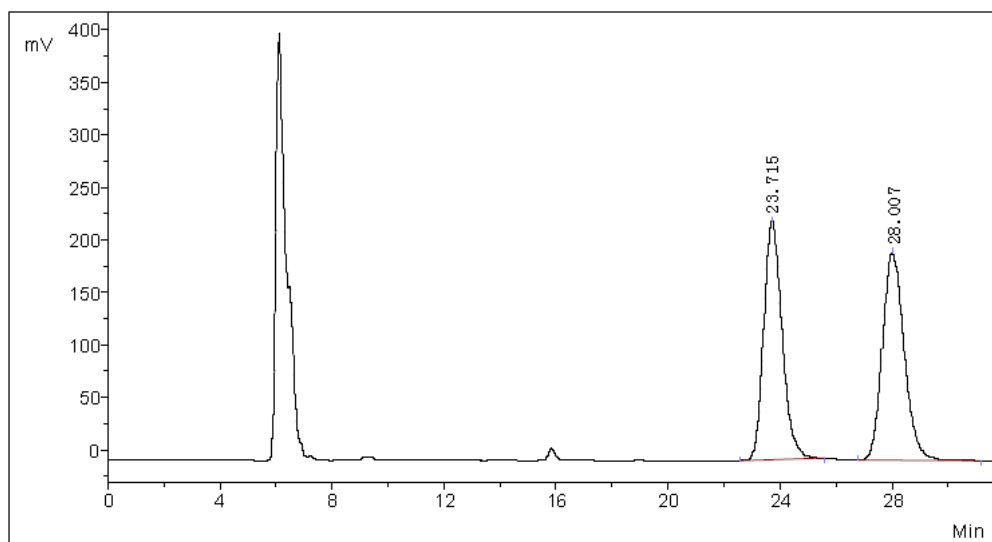


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	23.377	77568.7	2437525.5	49.8683
2	2	28.277	64027.4	2450403.1	50.1317
Total			141596.1	4887928.6	100.0000

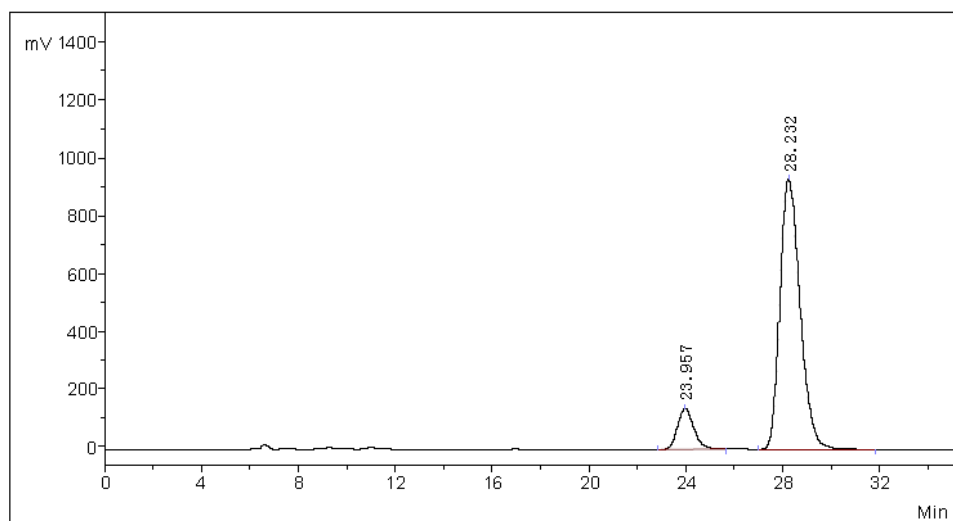
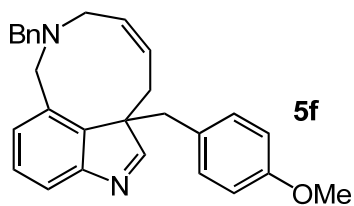


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	23.377	157836.8	5099483.7	67.6830
2	2	28.227	62892.5	2434880.3	32.3170
Total			220729.4	7534364.0	100.0000

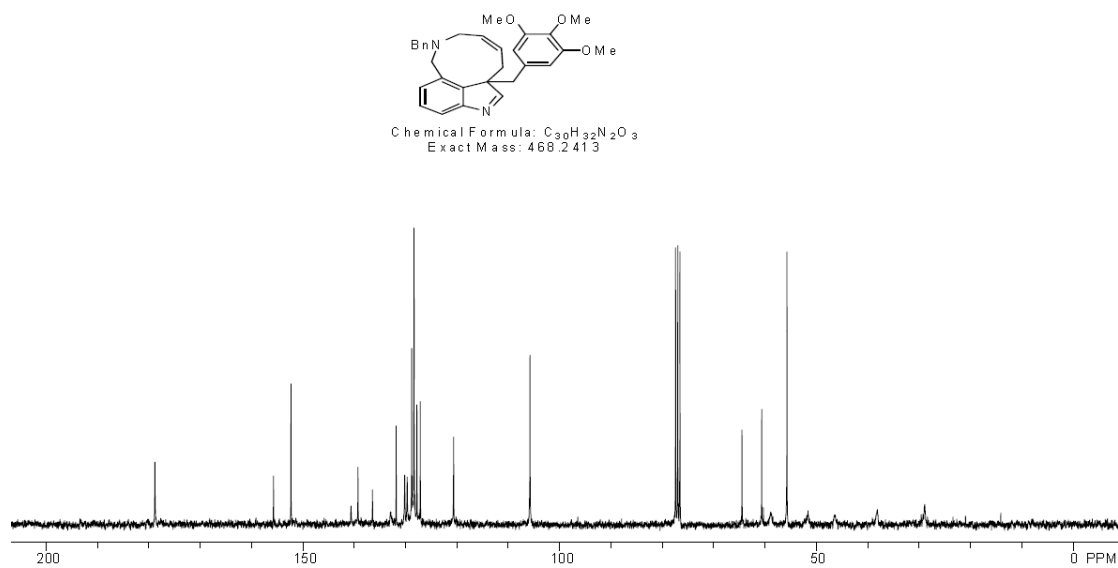
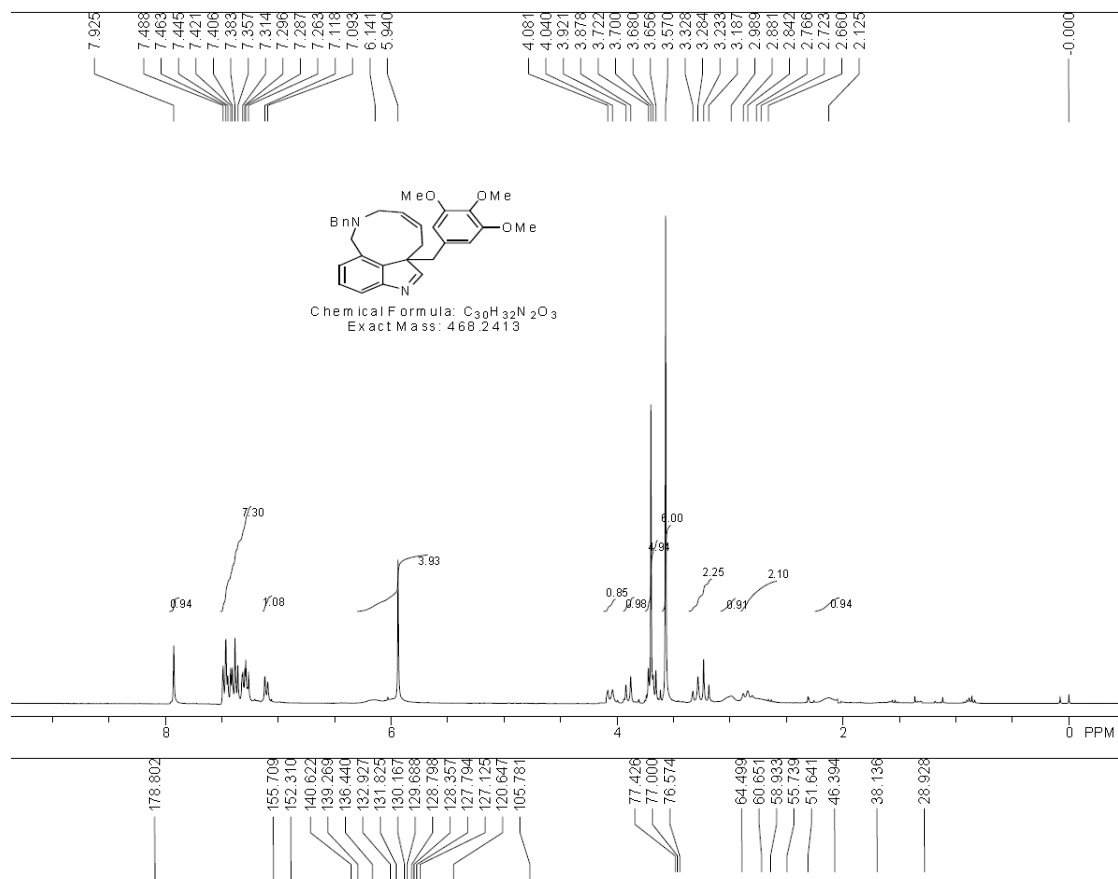


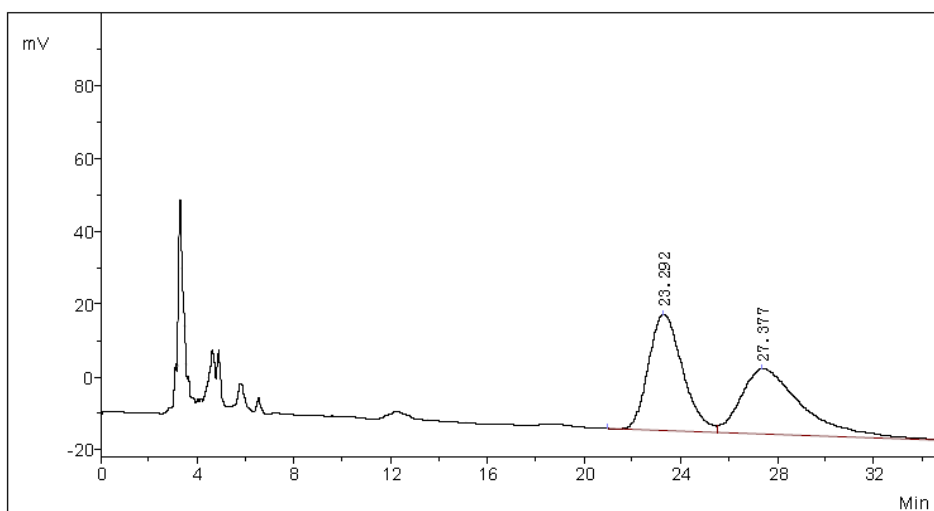


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	23.715	226785.8	10340060.1	49.0852
2	2	Unknown	28.007	197244.1	10725487.9	50.9148
Total				424029.9	21065548.0	100.0000

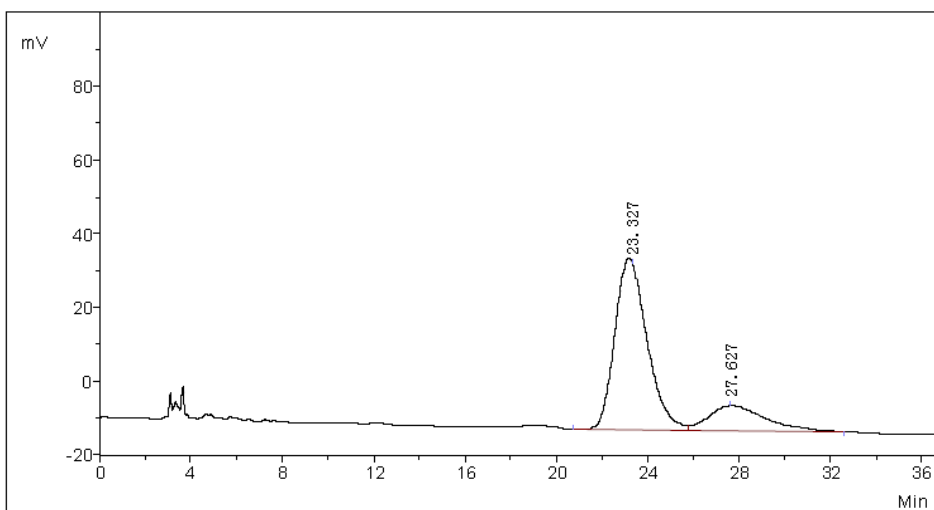
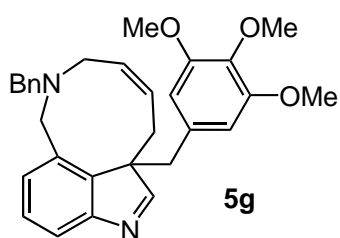


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	23.957	143289.1	6728964.4	11.0601
2	2	Unknown	28.232	934951.1	54110945.8	88.9399
Total				1078240.2	60839910.2	100.0000



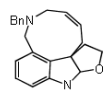
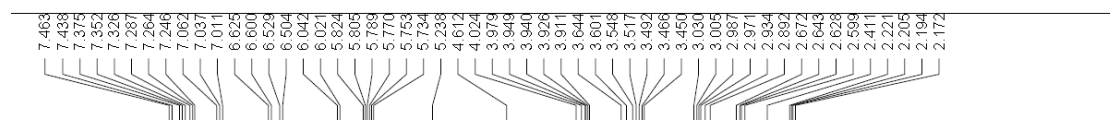


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	23.292	32049.4	3149986.2	50.2665
2	2	Unknown	27.377	17836.6	3116581.6	49.7335
Total				49886.0	6266567.8	100.0000

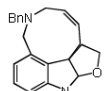
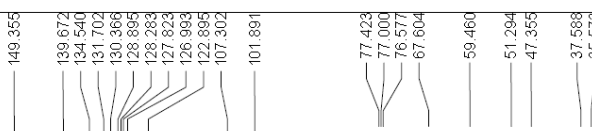
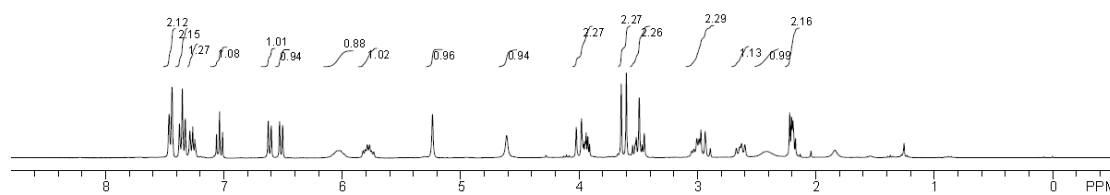


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	23.327	45183.8	4532878.5	79.7110
2	2	Unknown	27.627	6705.7	1153763.8	20.2890
Total				51889.5	5686642.3	100.0000

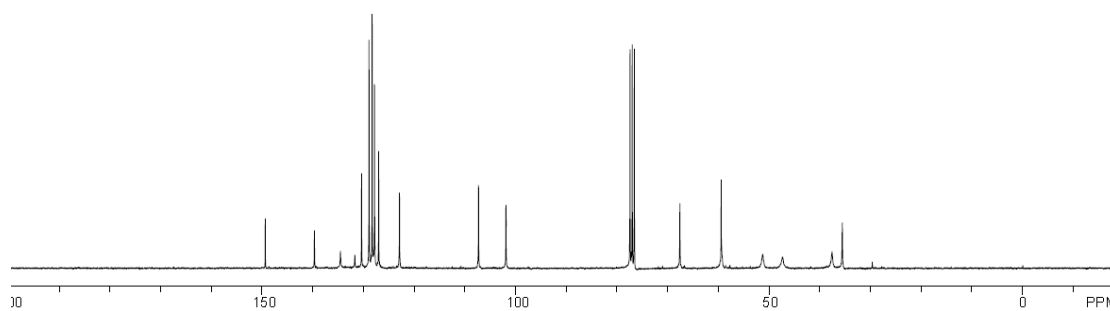


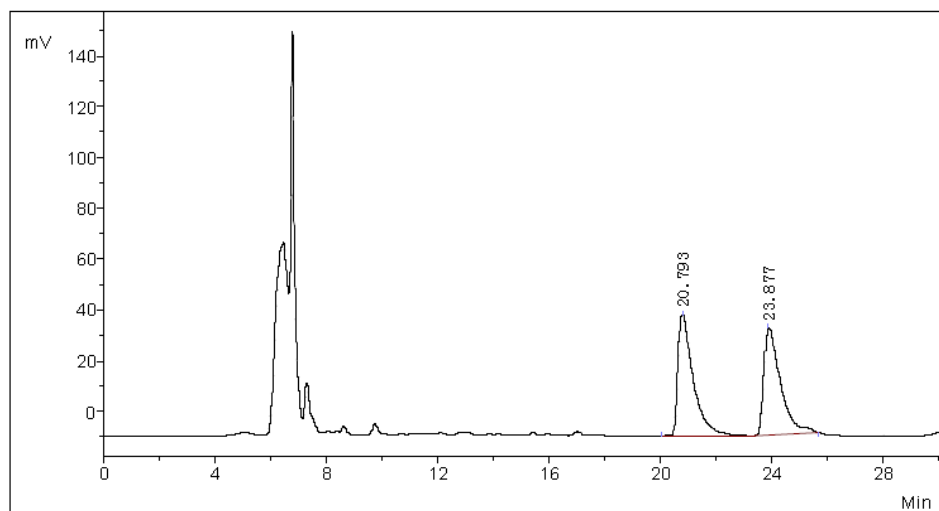


Chemical Formula: C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O  
Exact Mass: 332.1869

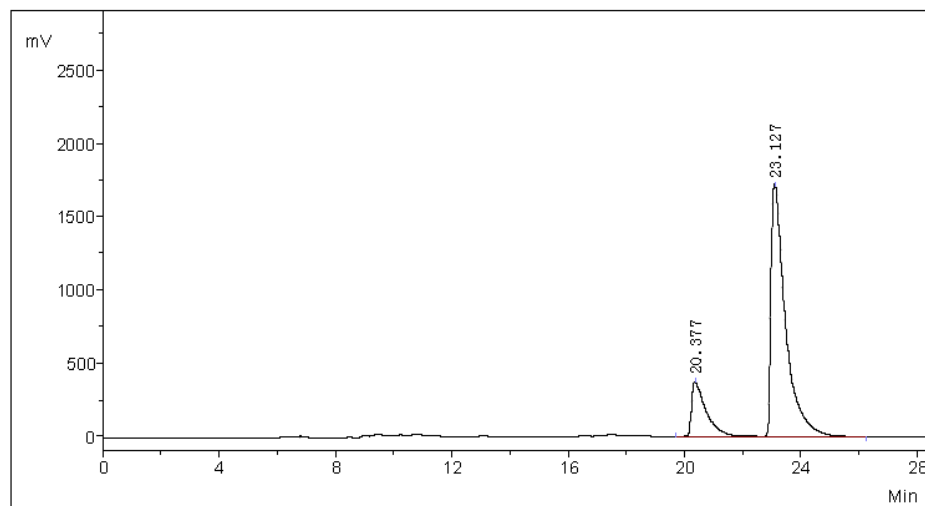
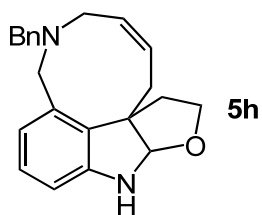


Chemical Formula: C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O  
Exact Mass: 332.1869

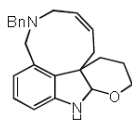
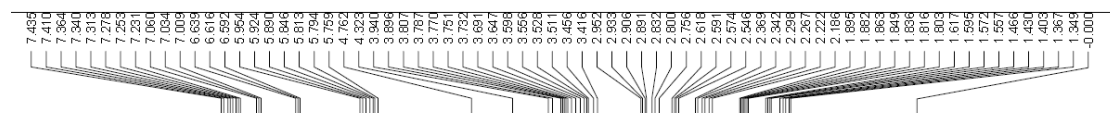




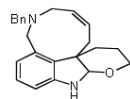
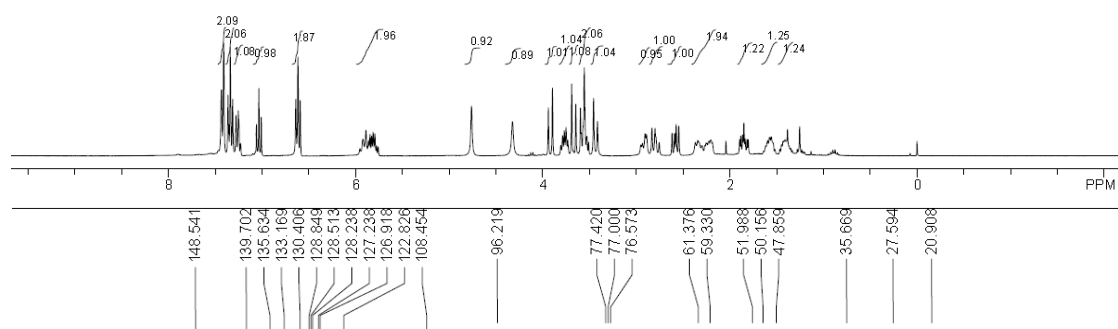
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	20.793	47389.8	1817628.9	51.1710
2	2	Unknown	23.877	42001.0	1734437.8	48.8290
Total				89390.8	3552066.7	100.0000



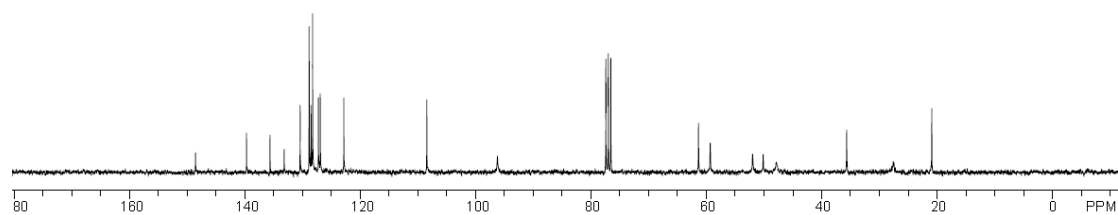
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	20.377	377802.2	13507256.5	18.2563
2	2	Unknown	23.127	1714611.9	60479467.6	81.7437
Total				2092414.1	73986724.1	100.0000

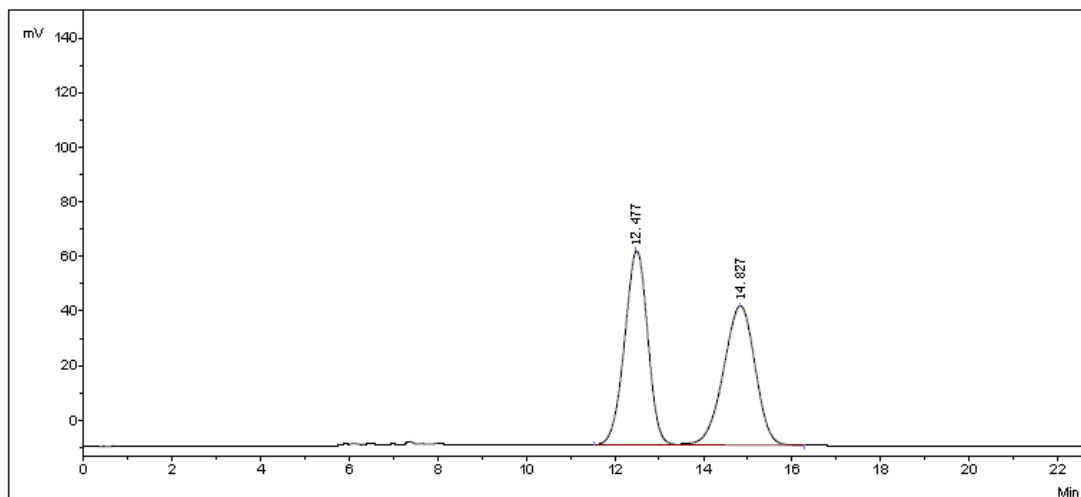


Chemical Formula: C<sub>23</sub>H<sub>26</sub>N<sub>2</sub>O  
Exact Mass: 346.2045

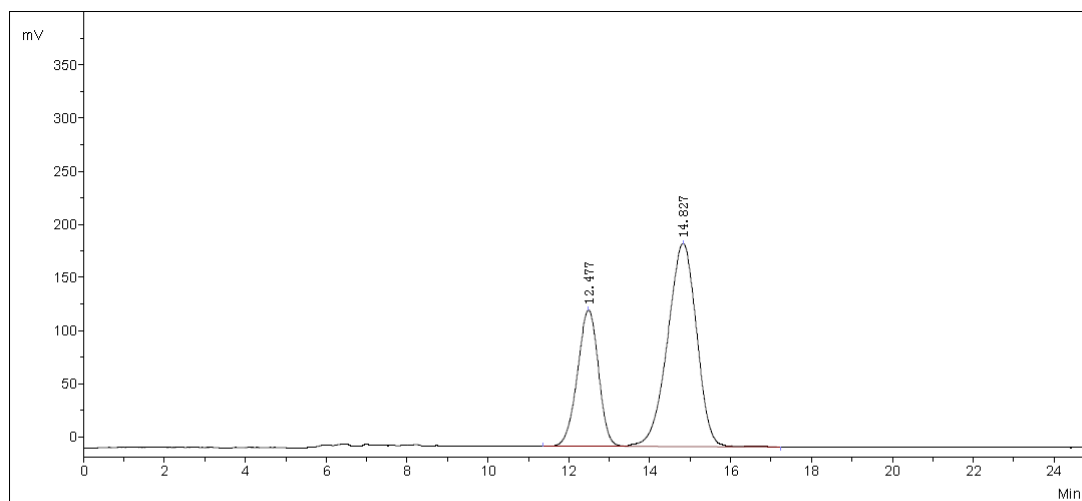
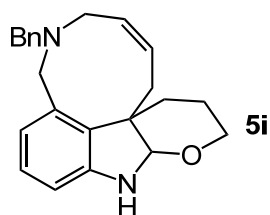


Chemical Formula: C<sub>23</sub>H<sub>26</sub>N<sub>2</sub>O  
Exact Mass: 346.2045

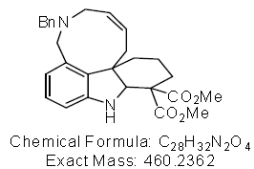
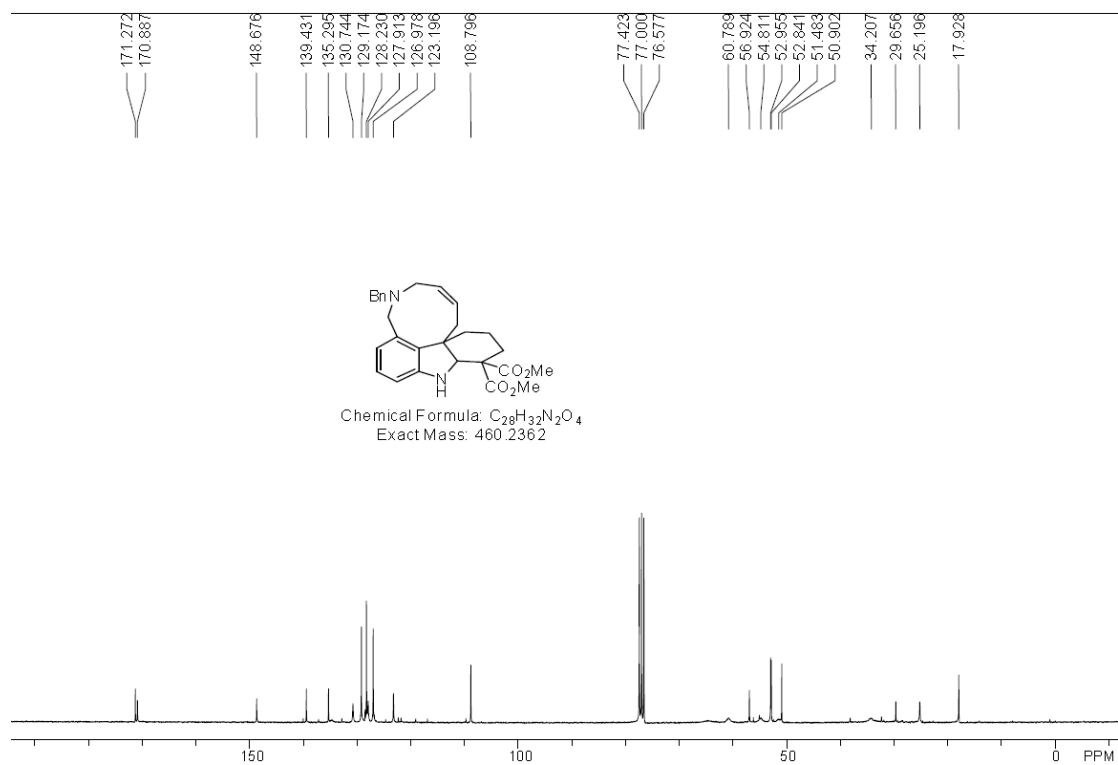
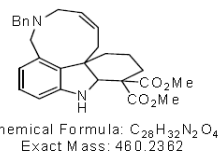
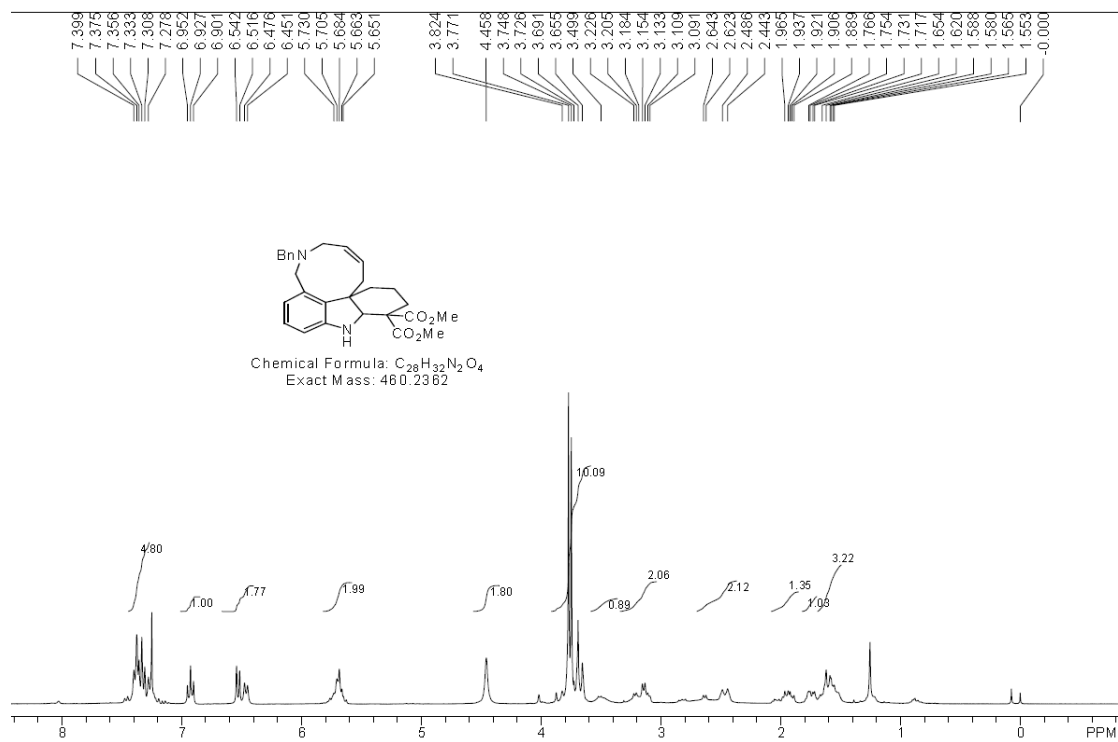


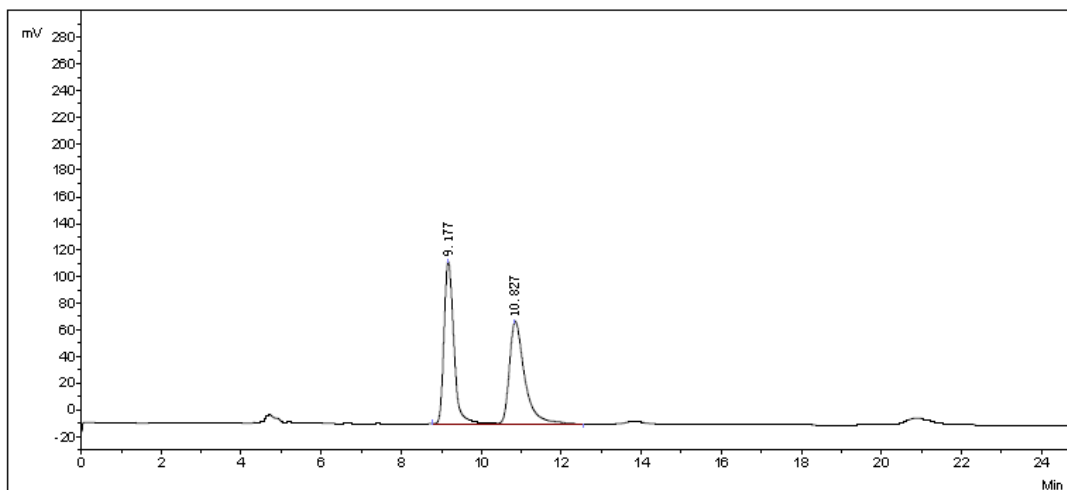


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	12.477	70889.0	2570938.9	50.2667
2	2	14.827	51039.8	2543656.9	49.7333
Total			121928.8	5114595.8	100.0000

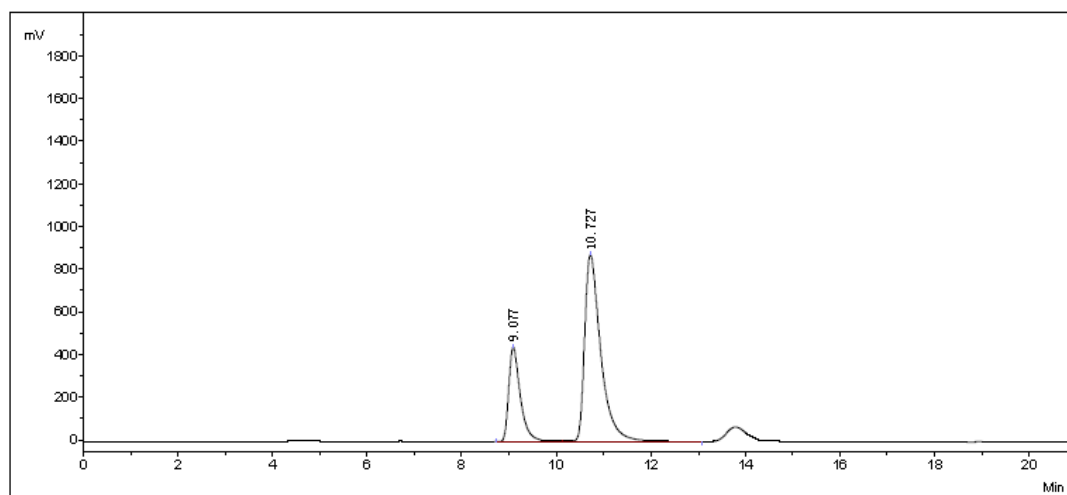
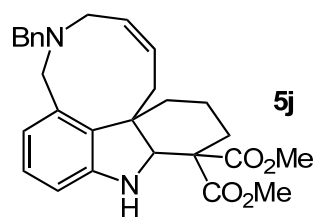


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	12.477	128197.6	4657182.6	32.7704
2	2	14.827	191116.5	9554387.5	67.2296
Total			319314.1	14211570.1	100.0000

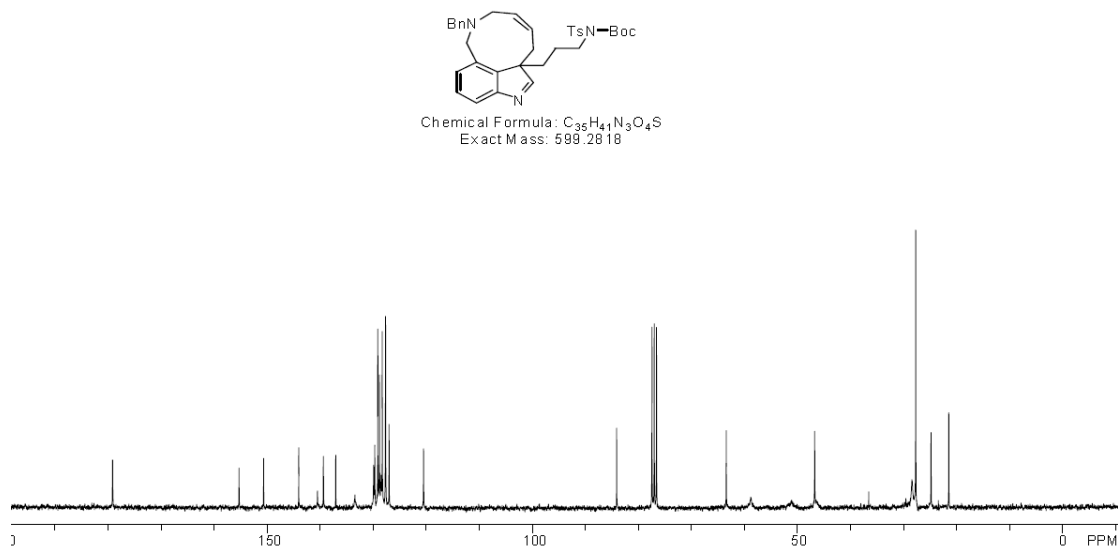
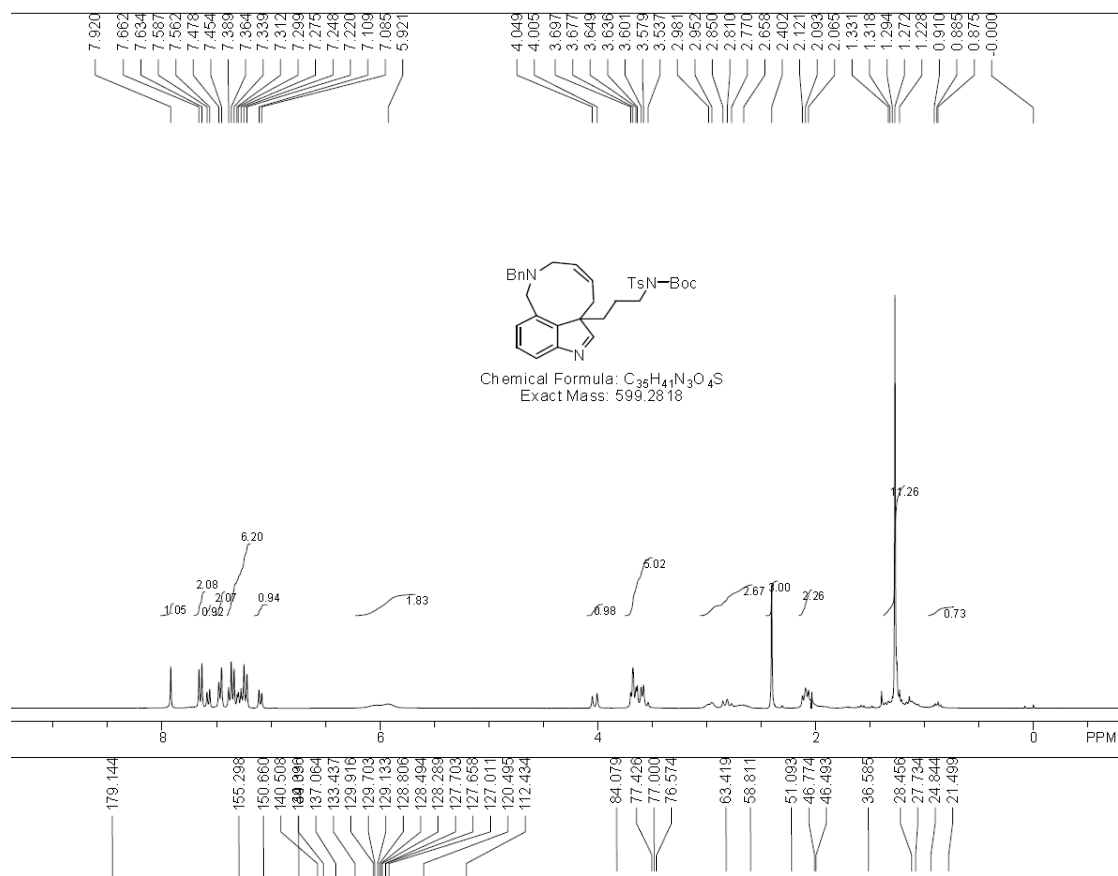


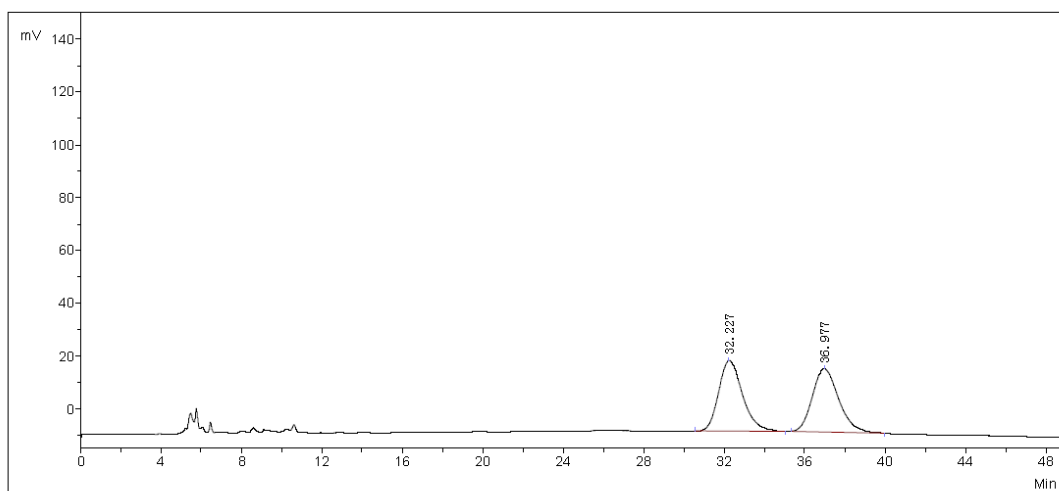


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	9.177	121652.8	2072717.8	50.7356
2	2	10.827	75819.0	2012610.7	49.2644
Total			197471.7	4085328.5	100.0000

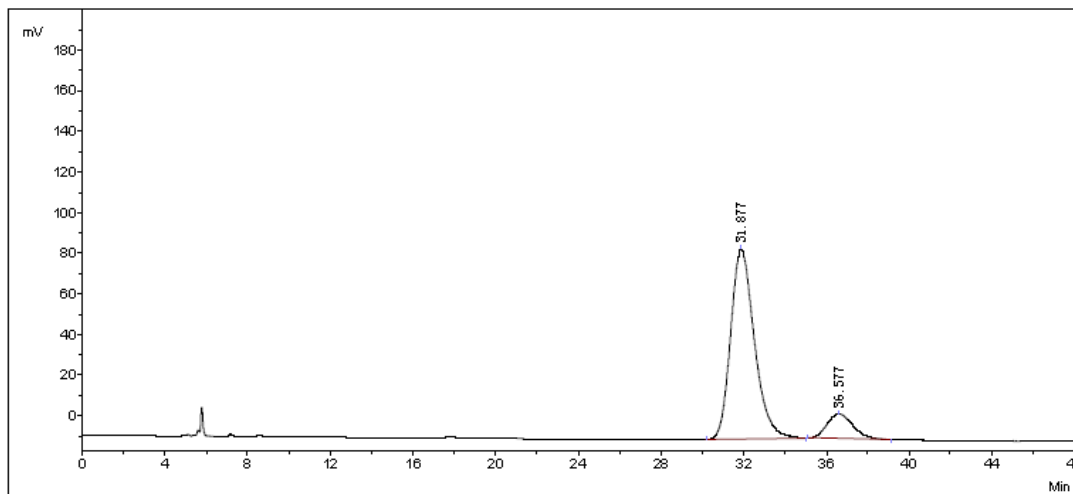
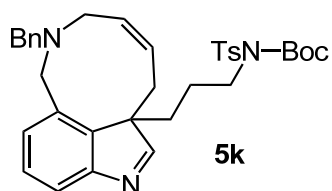


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	9.077	441634.0	7636223.4	26.8046
2	2	10.727	875259.3	20852219.1	73.1954
Total			1316893.3	28488442.5	100.0000



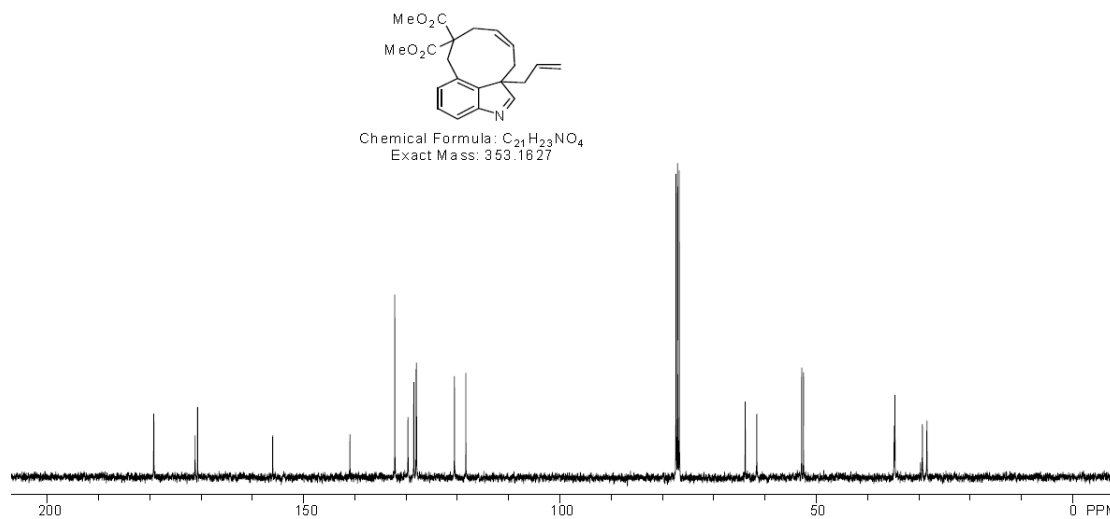
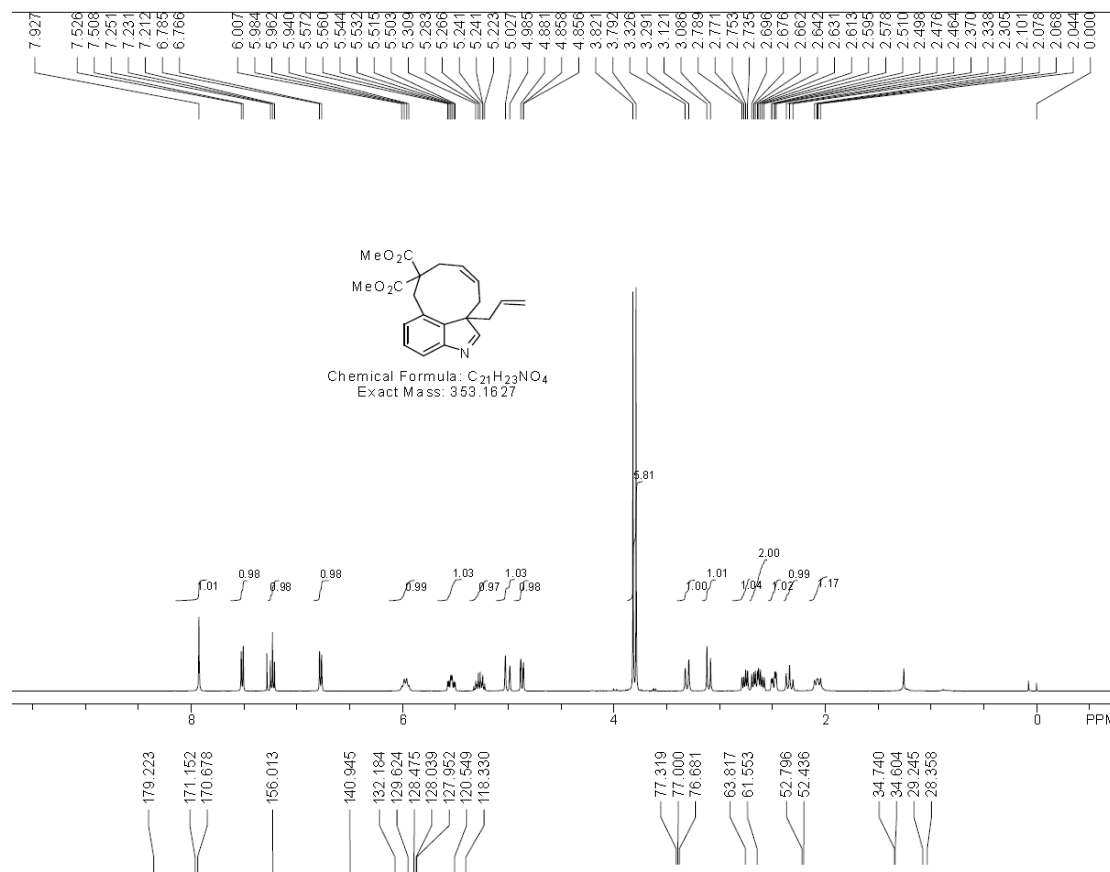


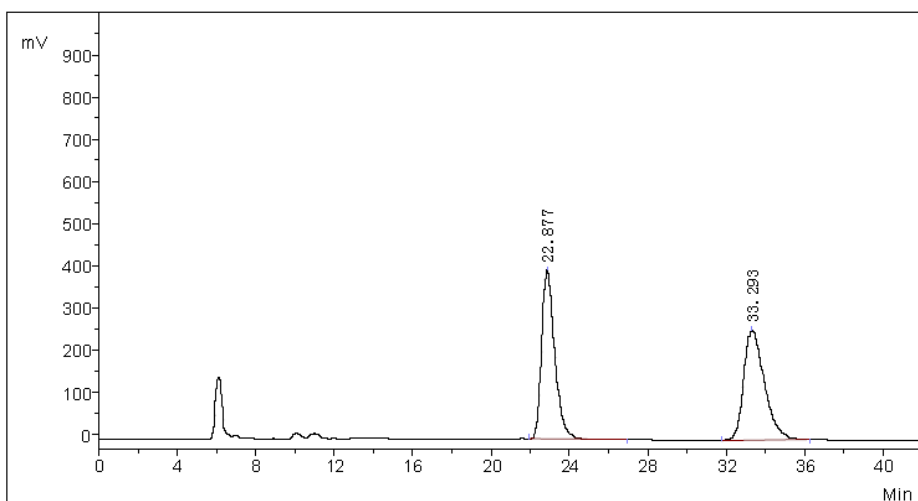
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	32.227	26714.0	2199488.0	50.3118
2	2	36.977	23864.6	2172226.4	49.6882
Total			50578.6	4371714.4	100.0000



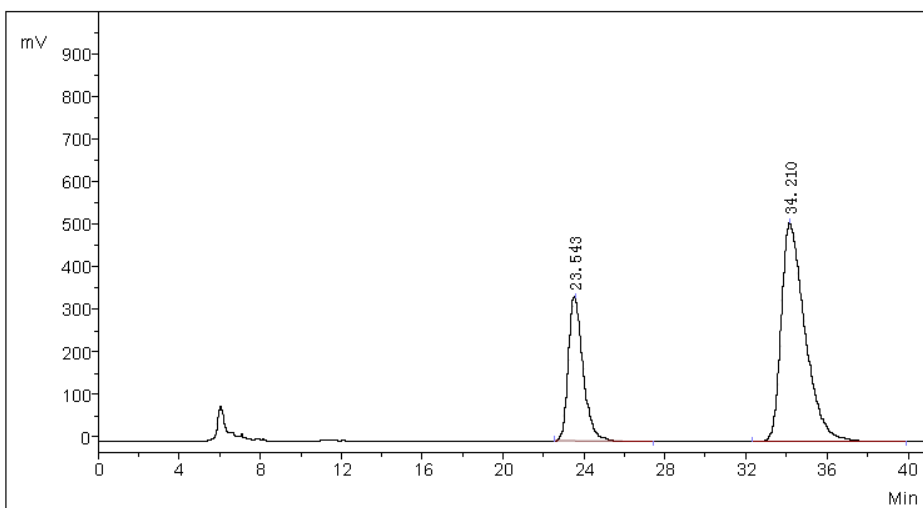
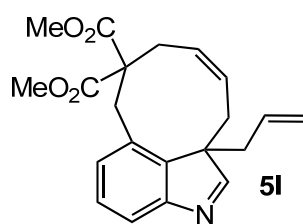
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	31.877	93436.7	7484621.8	87.5585
2	2	36.577	12098.1	1063518.2	12.4415
Total			105534.8	8548140.0	100.0000



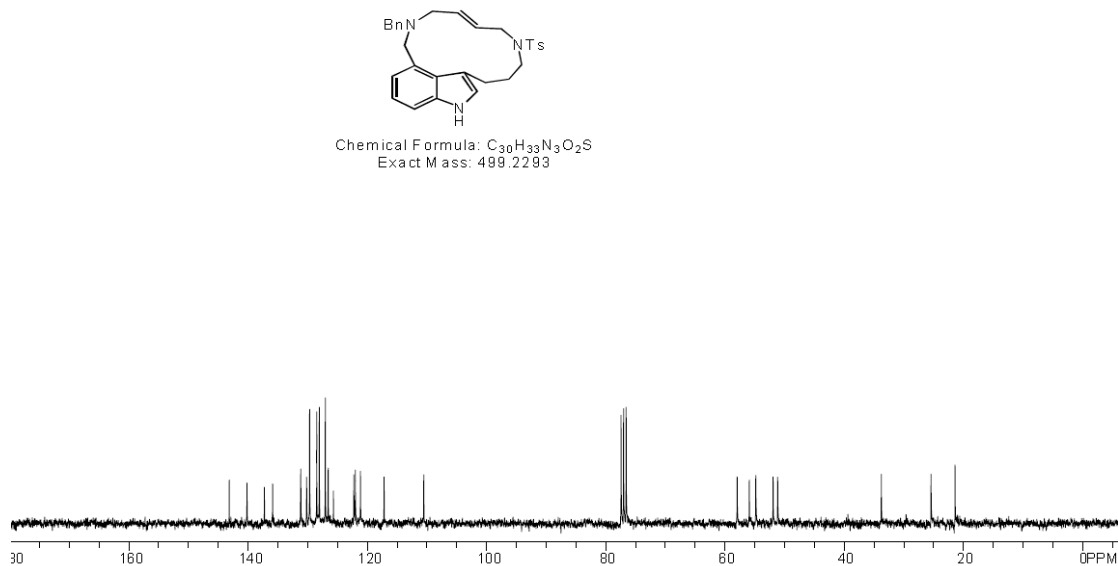
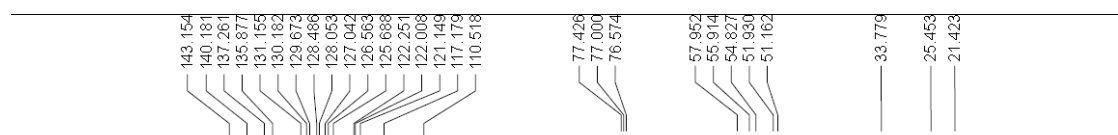
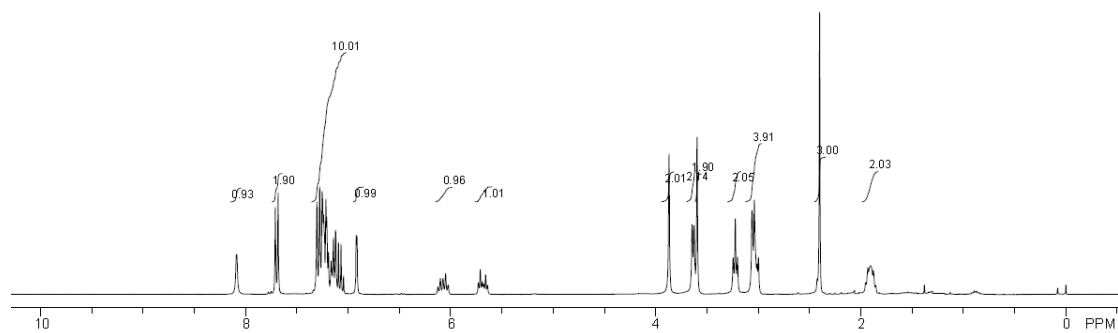
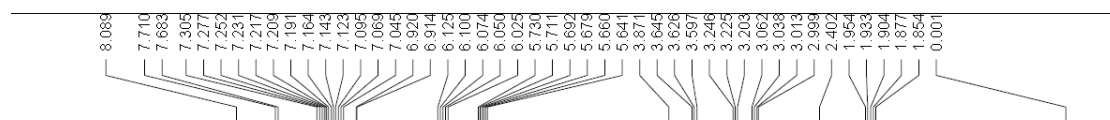


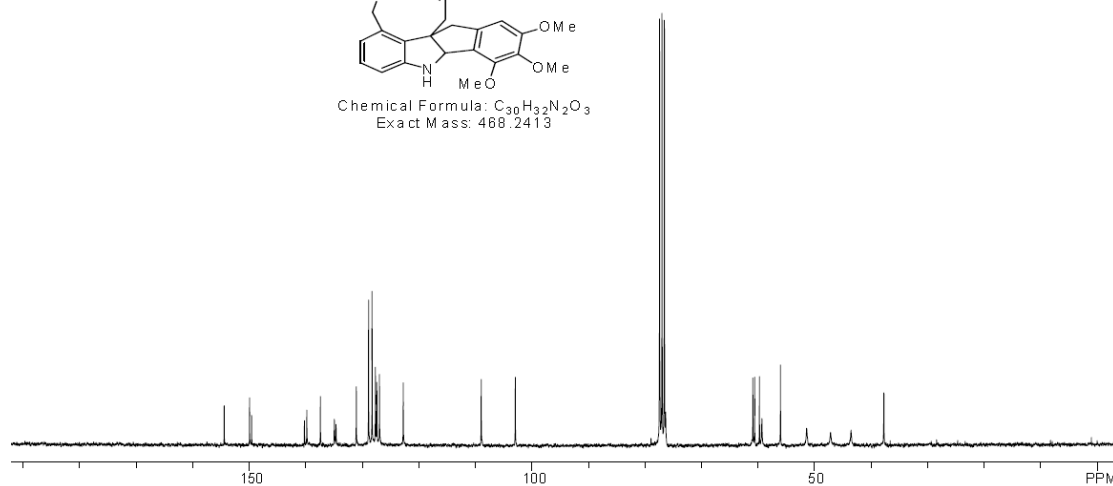
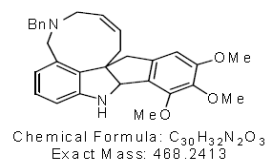
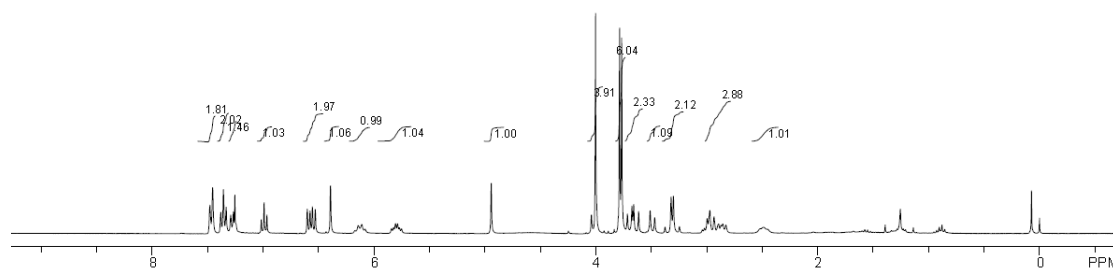
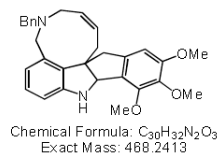
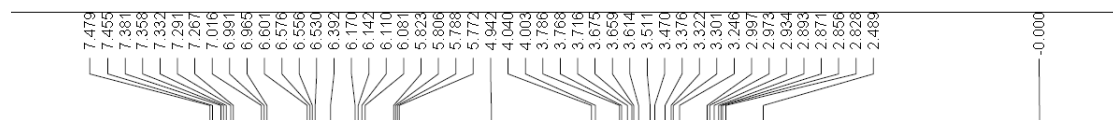


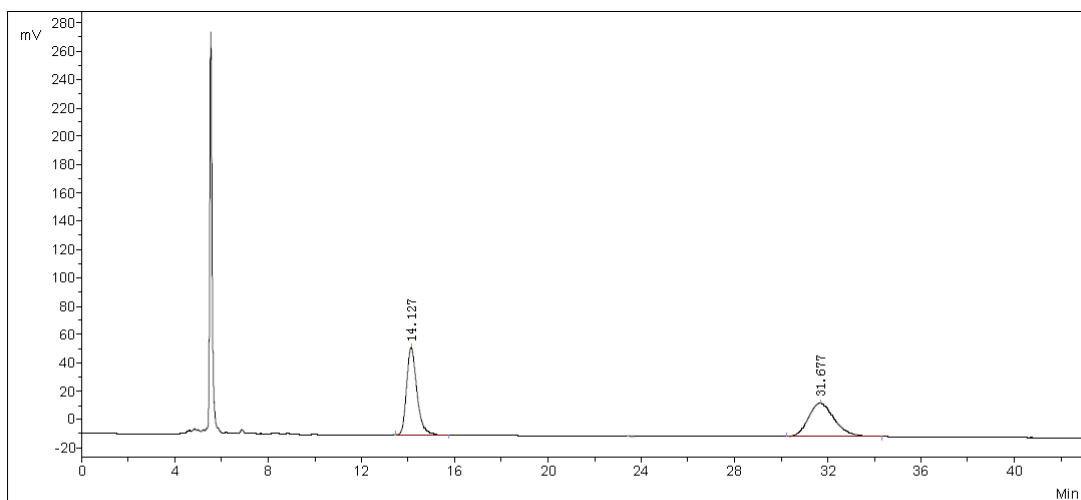
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	22.877	400442.9	18830800.4	49.6801
2	2	Unknown	33.293	259851.6	19073284.6	50.3199
Total				660294.5	37904085.0	100.0000



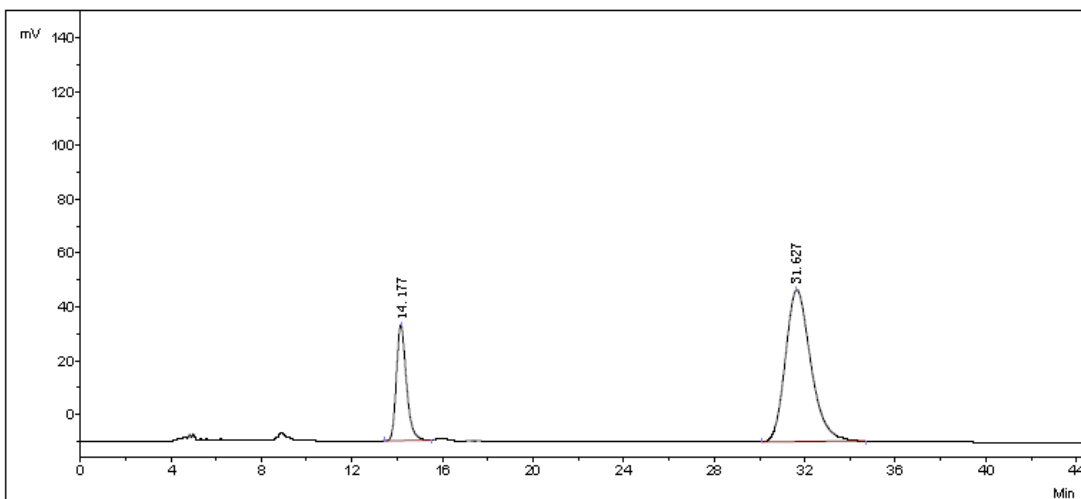
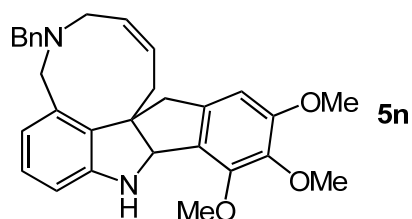
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	23.543	337970.0	17148775.0	28.9771
2	2	Unknown	34.210	513962.4	42031761.2	71.0229
Total				851932.5	59180536.2	100.0000



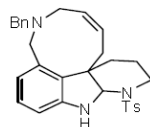
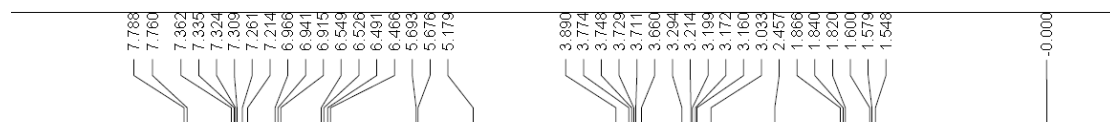




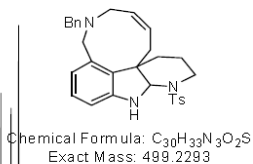
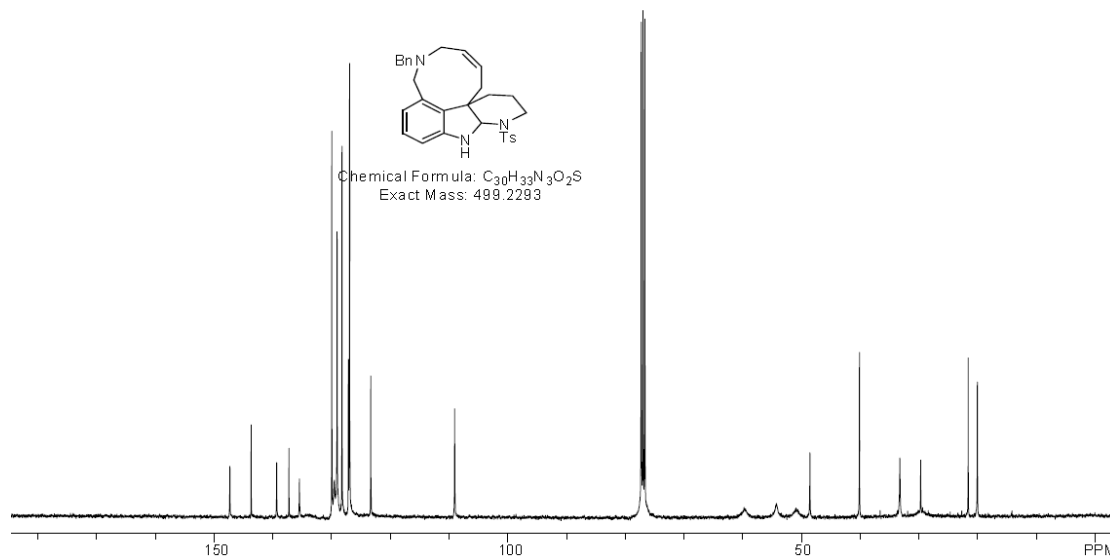
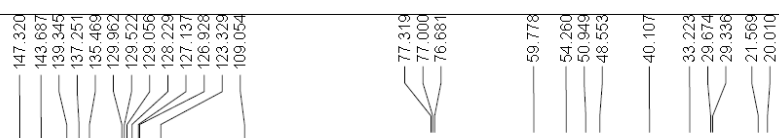
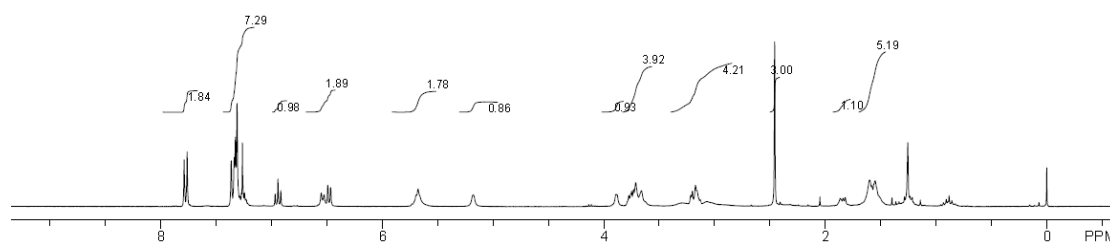
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	14.127	61619.1	1885489.9	50.5095
2	2	31.677	23720.1	1847453.8	49.4905
Total			85339.2	3732943.7	100.0000



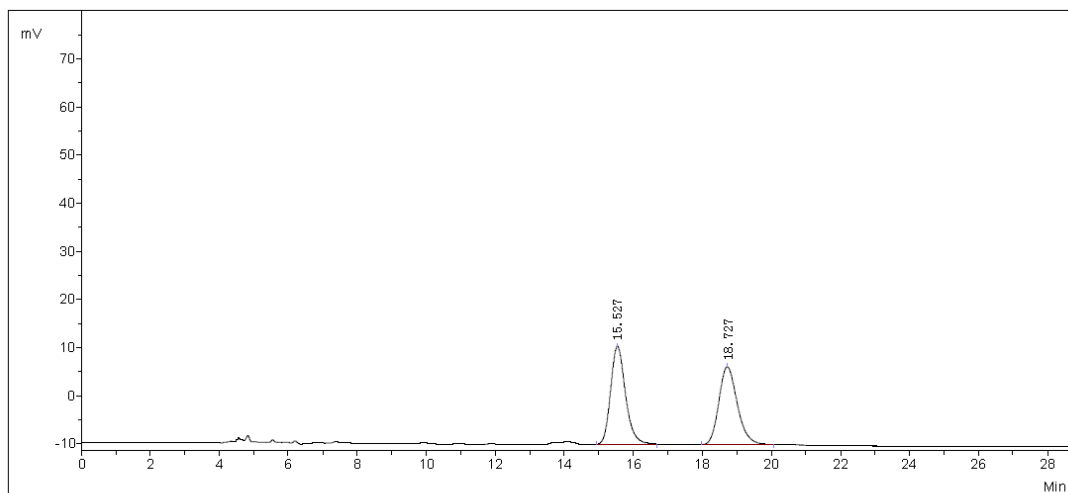
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	14.177	42673.7	1319785.9	23.1070
2	2	31.627	56285.5	4391830.3	76.8930
Total			98959.2	5711616.2	100.0000



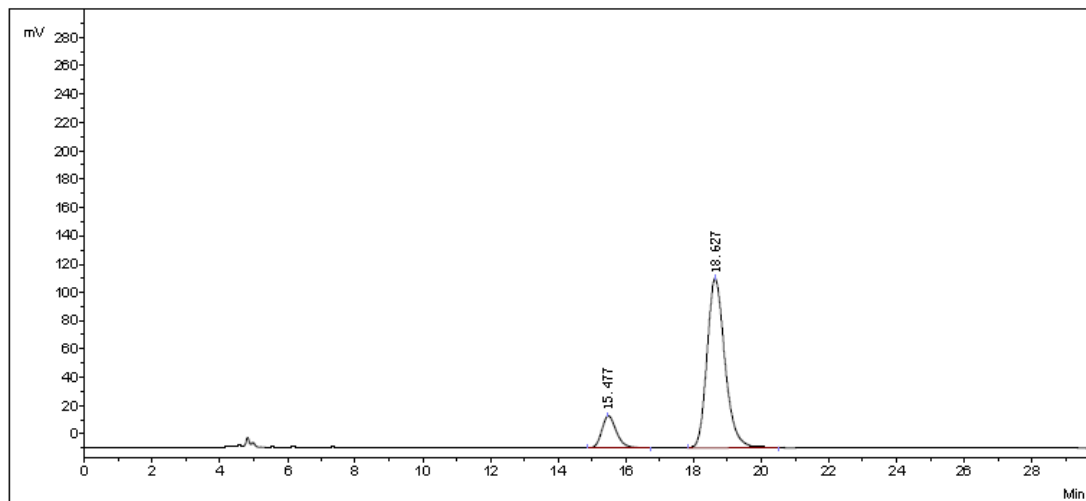
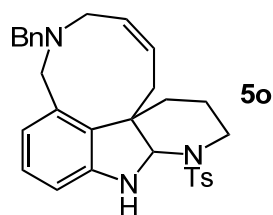
Chemical Formula: C<sub>30</sub>H<sub>33</sub>N<sub>3</sub>O<sub>2</sub>S  
Exact Mass: 499.2293



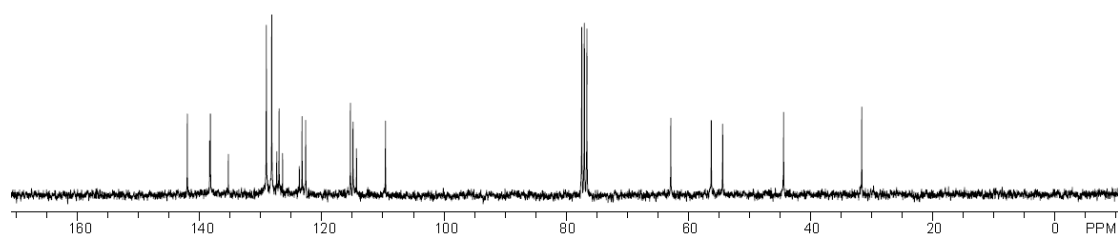
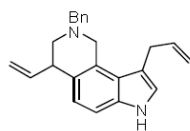
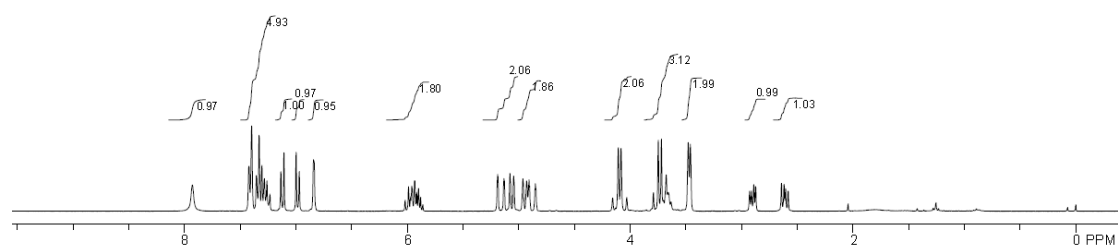
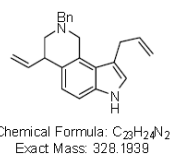
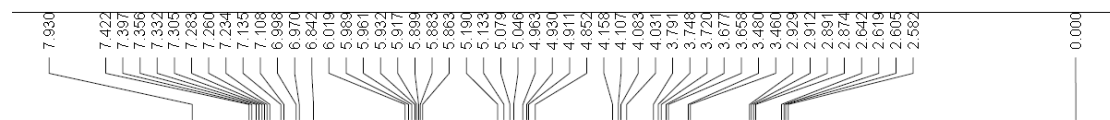
Chemical Formula: C<sub>30</sub>H<sub>33</sub>N<sub>3</sub>O<sub>2</sub>S  
Exact Mass: 499.2293



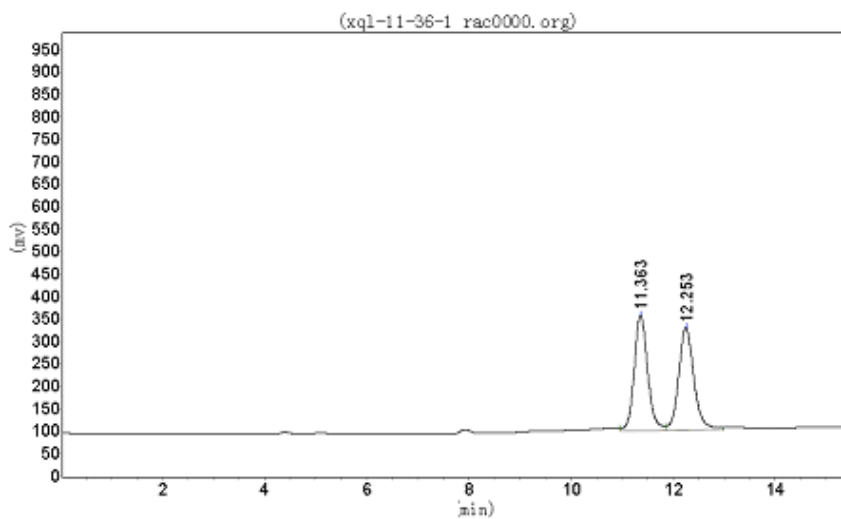
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	15.527	20370.0	605571.2	50.2650
2	2	18.727	16167.6	599184.8	49.7350
Total			36537.6	1204756.0	100.0000



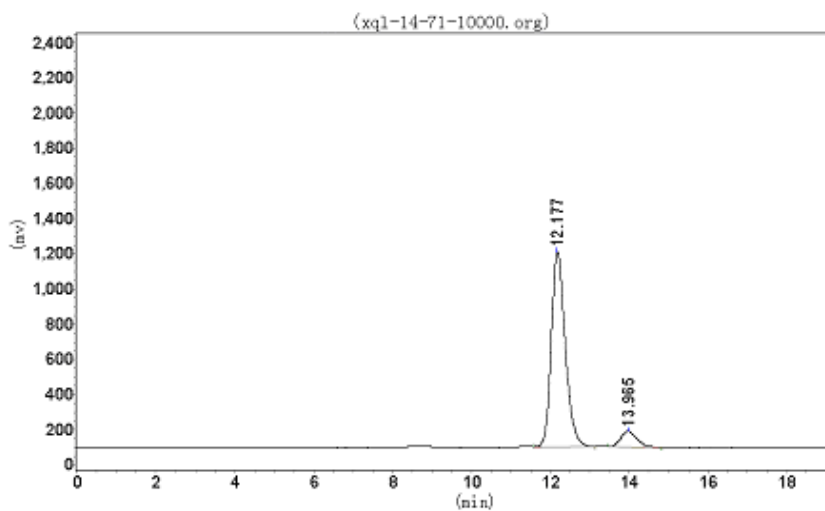
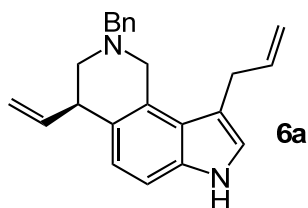
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	15.477	22728.8	675373.0	13.3194
2	2	18.627	119585.0	4395232.5	86.6806
Total			142313.8	5070605.5	100.0000



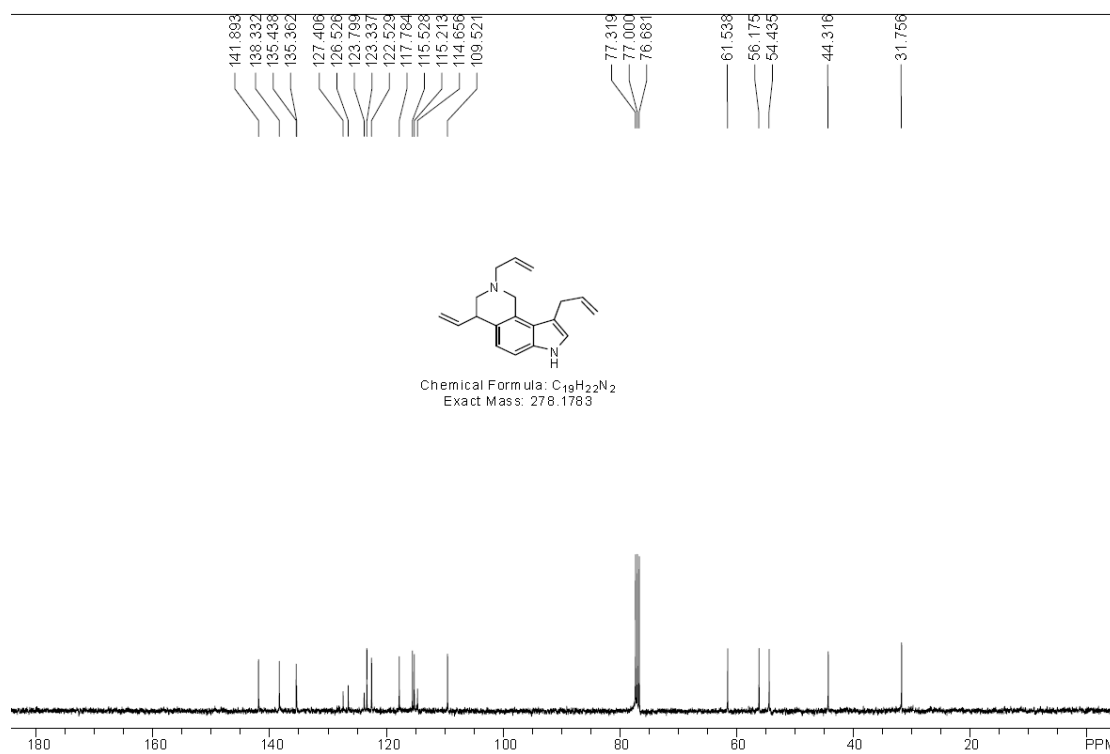
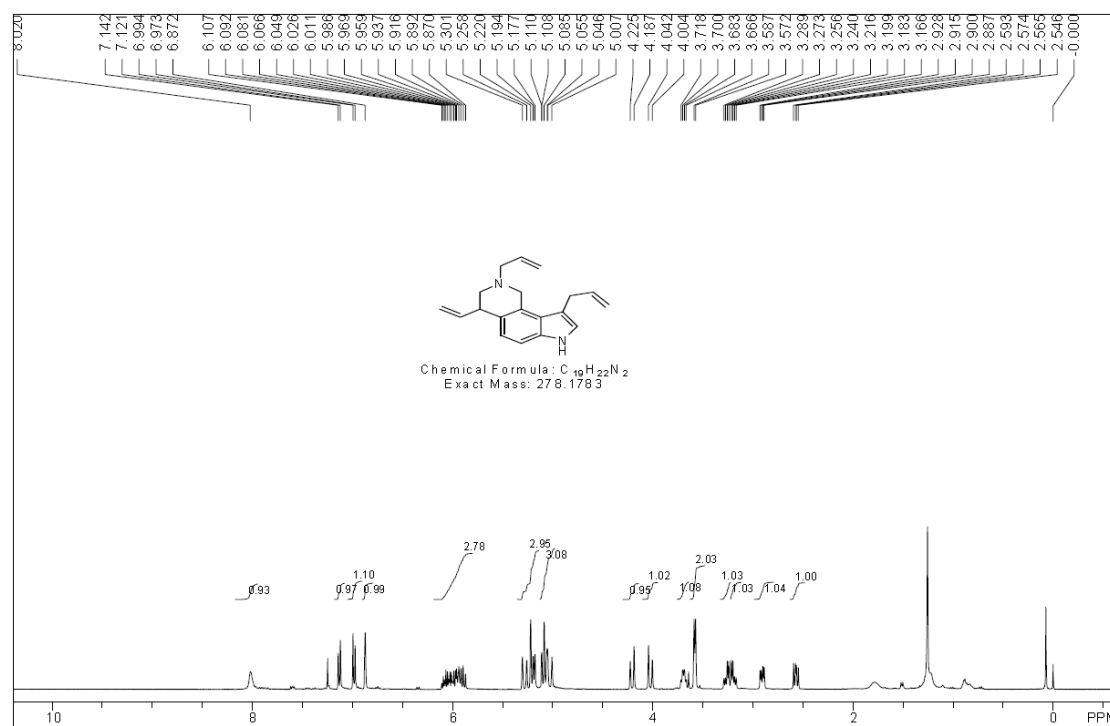


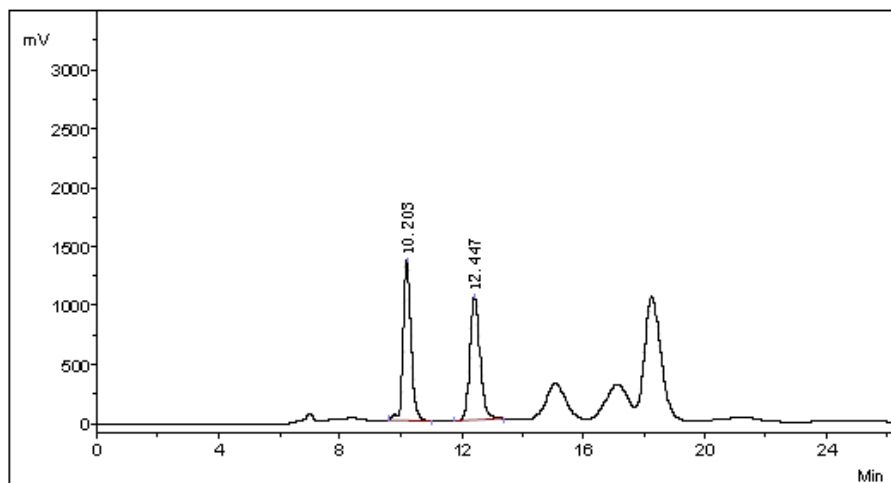


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11.363	257604.000	4691478.000	49.7362
2	12.253	227601.094	4741239.500	50.2638
<b>Total</b>		485205.094	9432717.500	100.0000

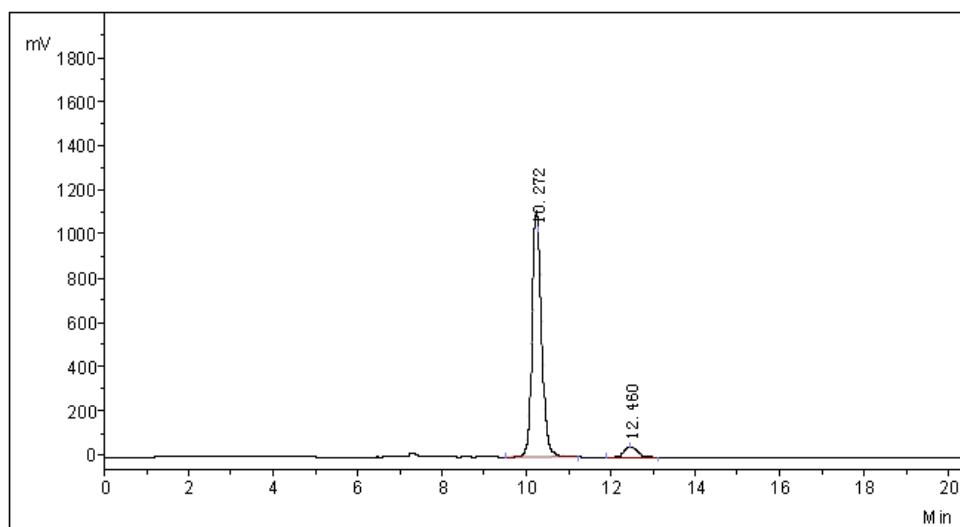
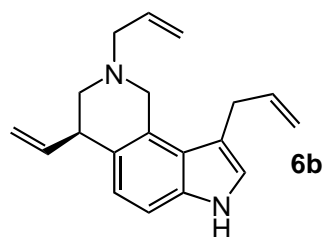


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12.177	1107453.000	26944264.000	91.6936
2	13.965	86927.250	2440859.750	8.3064
<b>Total</b>		1194380.250	29385123.750	100.0000

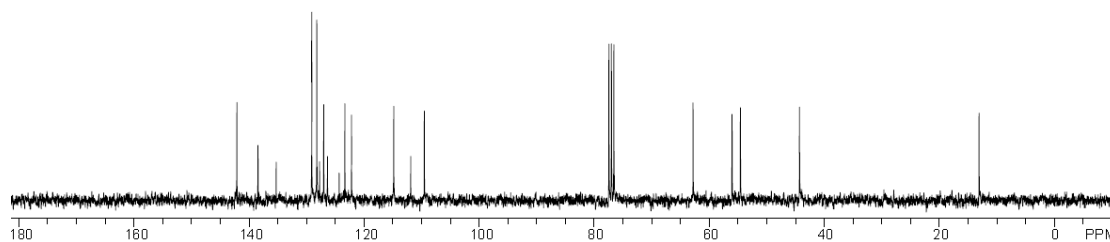
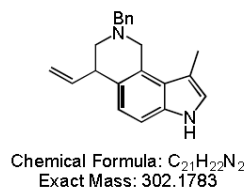
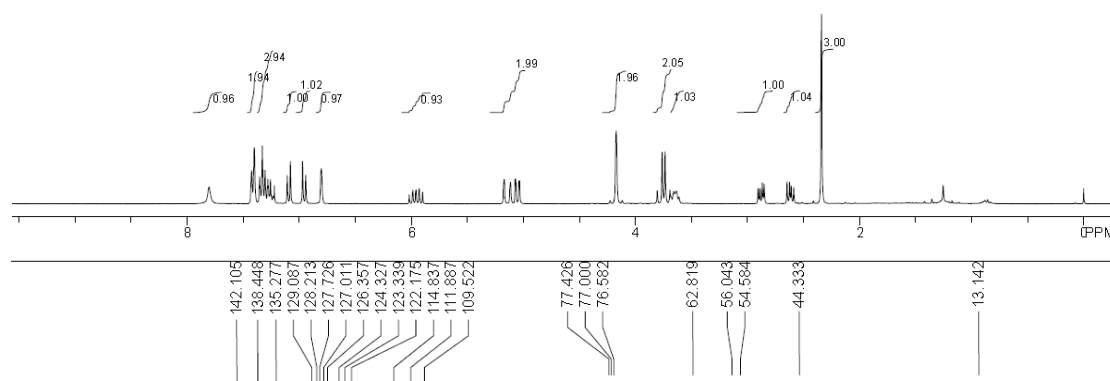
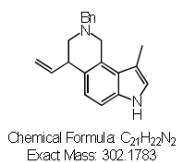


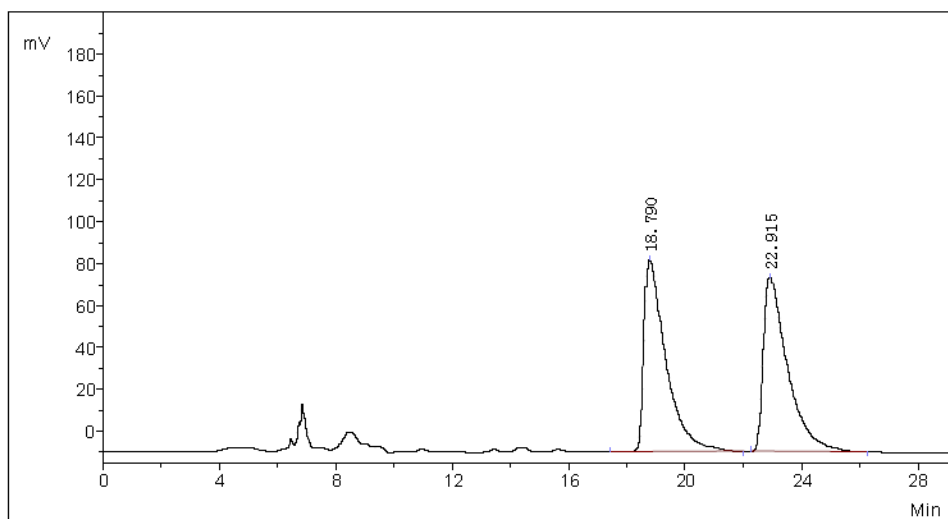


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	10.203	1349703.4	24173137.0	50.2185
2	2	Unknown	12.447	1037314.2	23962789.2	49.7815
Total				2387017.6	48135926.2	100.0000

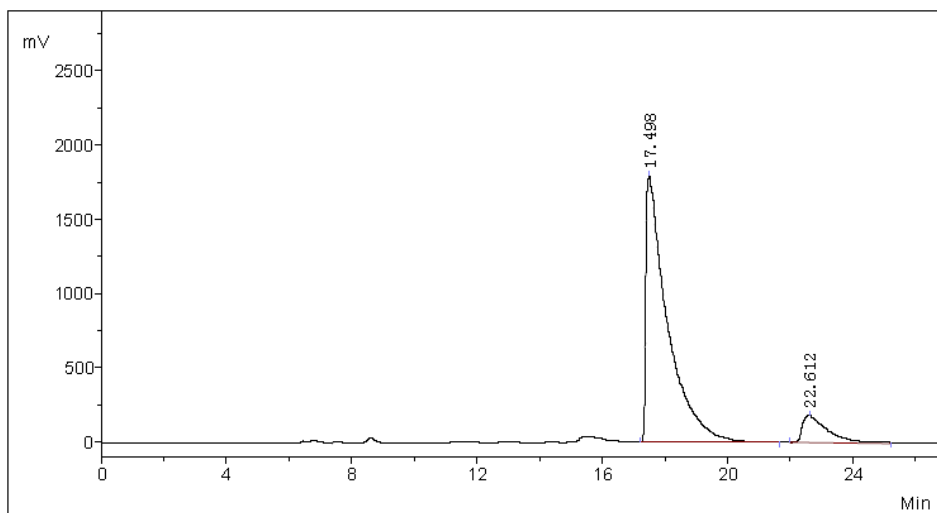
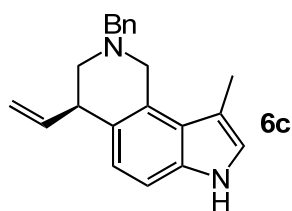


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	10.272	1025241.4	17246387.1	94.7905
2	2	Unknown	12.460	46701.1	947818.8	5.2095
Total				1071942.5	18194205.9	100.0000

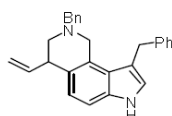
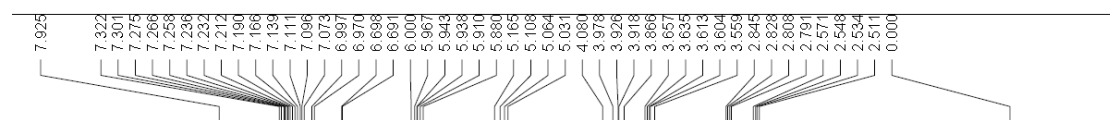




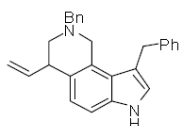
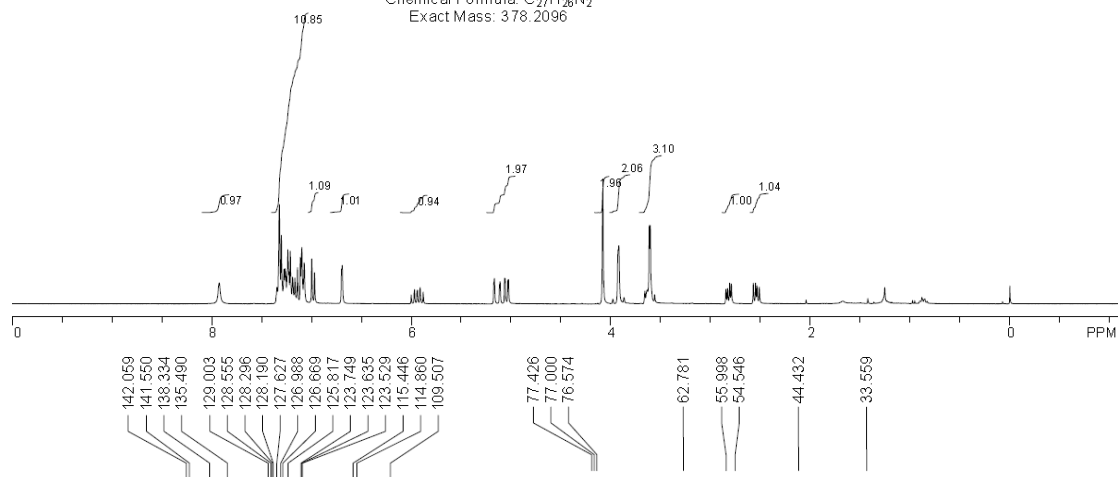
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	18.790	91351.1	4806953.0	49.9907
2	2	Unknown	22.915	82987.5	4808735.6	50.0093
Total				174338.6	9615688.6	100.0000



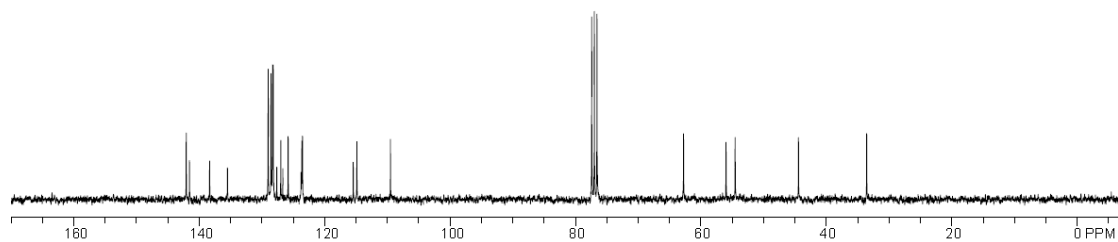
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	17.498	179992.4	85861685.9	89.4676
2	2	Unknown	22.612	181917.9	10107900.6	10.5324
Total				1981910.2	95969586.5	100.0000

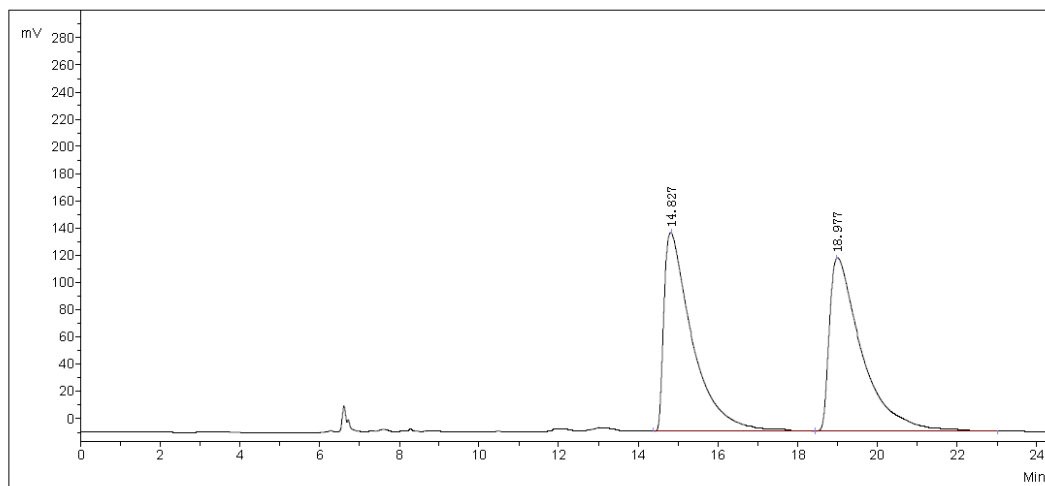


Chemical Formula: C<sub>27</sub>H<sub>26</sub>N<sub>2</sub>  
Exact Mass: 378.2096

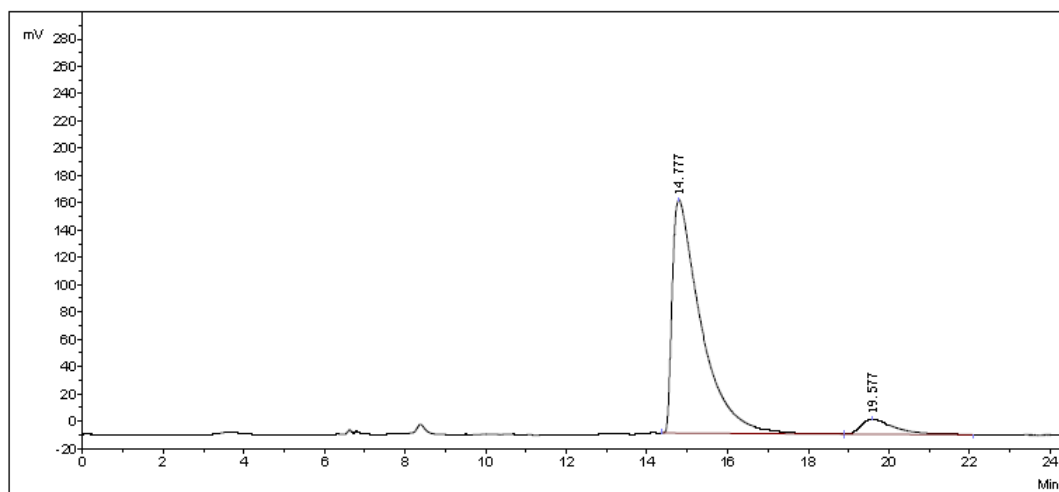
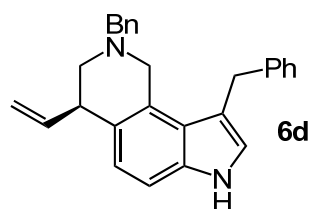


Chemical Formula: C<sub>27</sub>H<sub>26</sub>N<sub>2</sub>  
Exact Mass: 378.2096

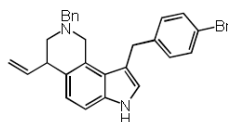
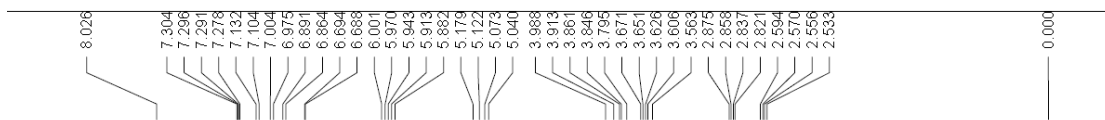




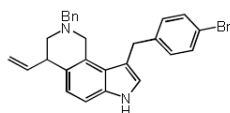
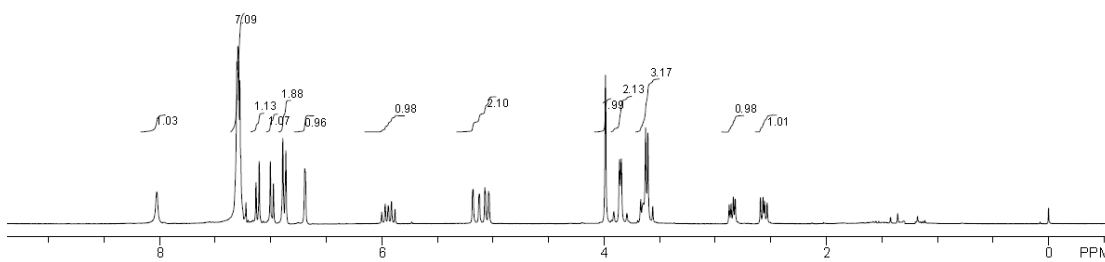
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	14.827	145969.4	7204330.1	50.1791
2	2	18.977	127149.0	7152888.5	49.8209
Total			273118.4	14357218.6	100.0000



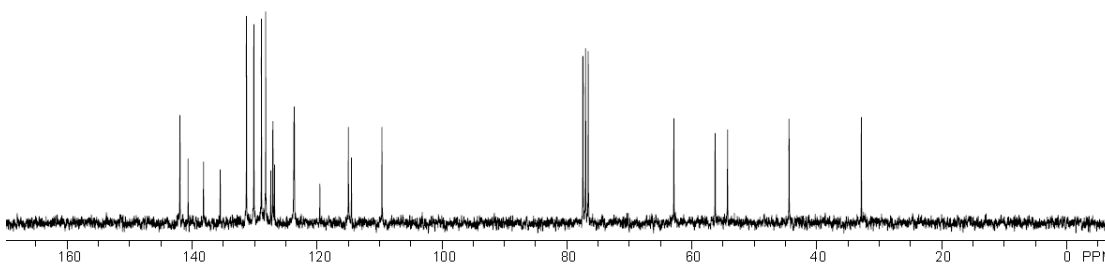
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	14.777	170553.6	8463867.2	92.9145
2	2	19.577	11079.9	645441.2	7.0855
Total			181633.5	9109308.4	100.0000



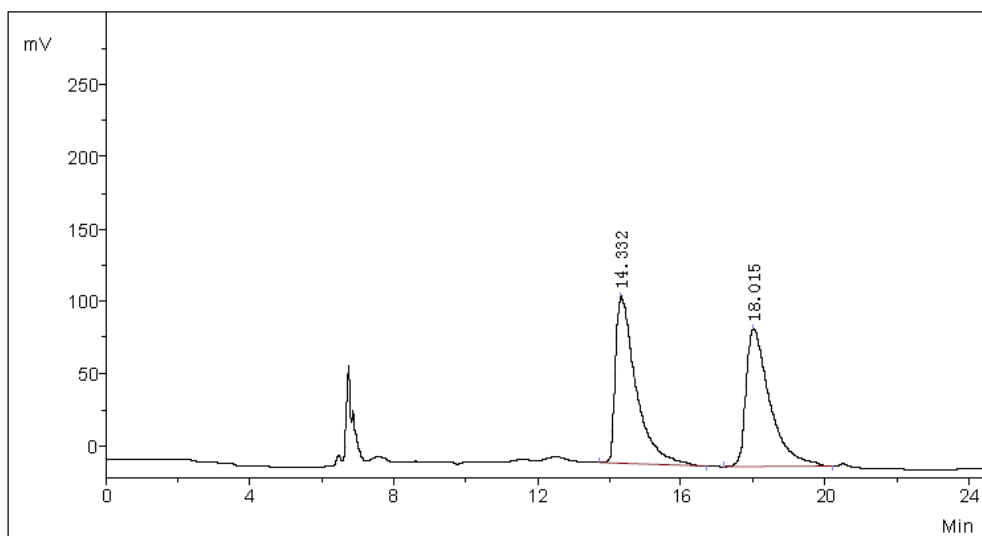
Chemical Formula: C<sub>27</sub>H<sub>25</sub>BrN<sub>2</sub>  
Exact Mass: 456.1201



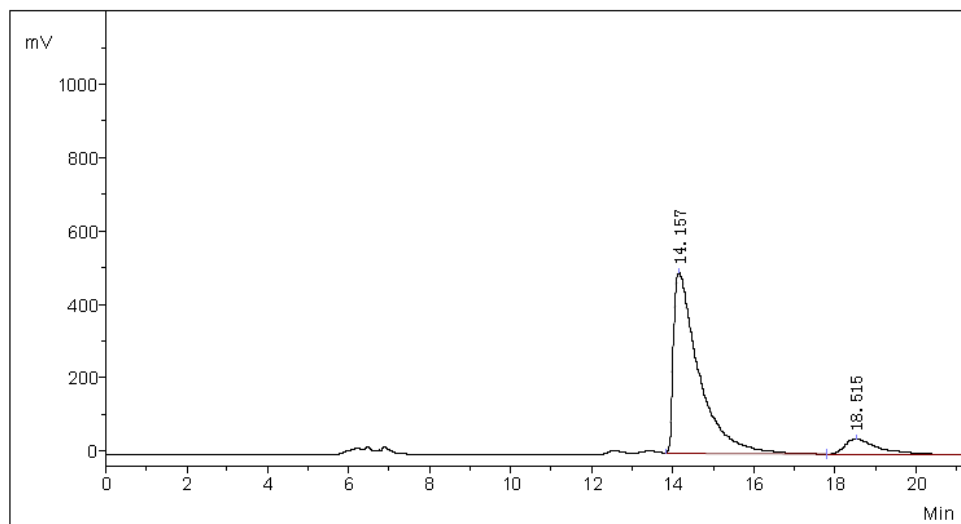
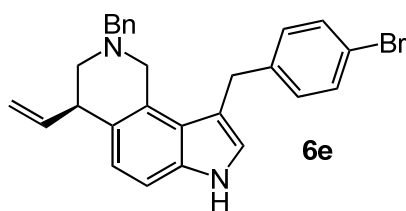
Chemical Formula: C<sub>27</sub>H<sub>25</sub>BrN<sub>2</sub>  
Exact Mass: 456.1201



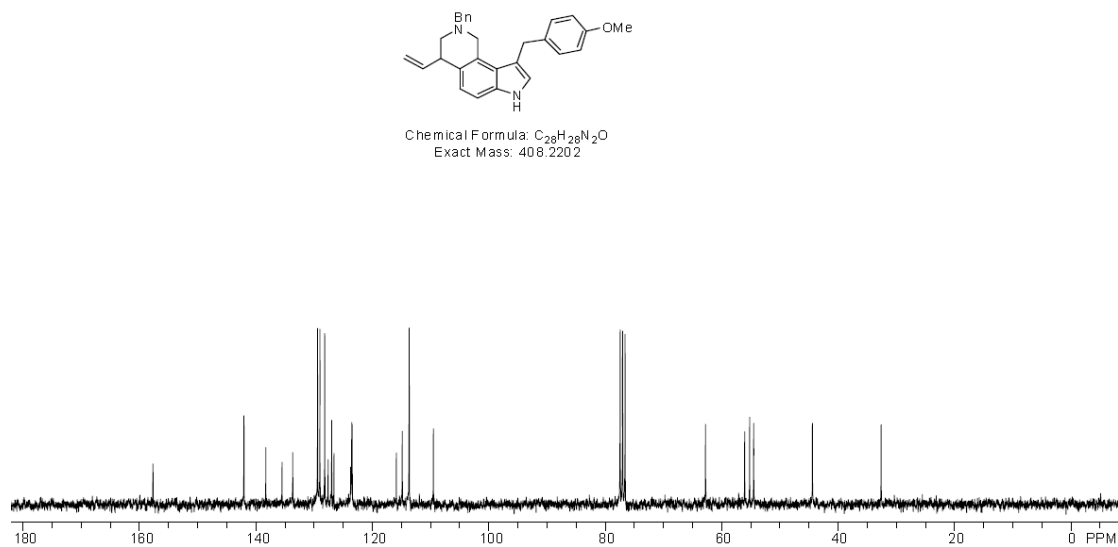
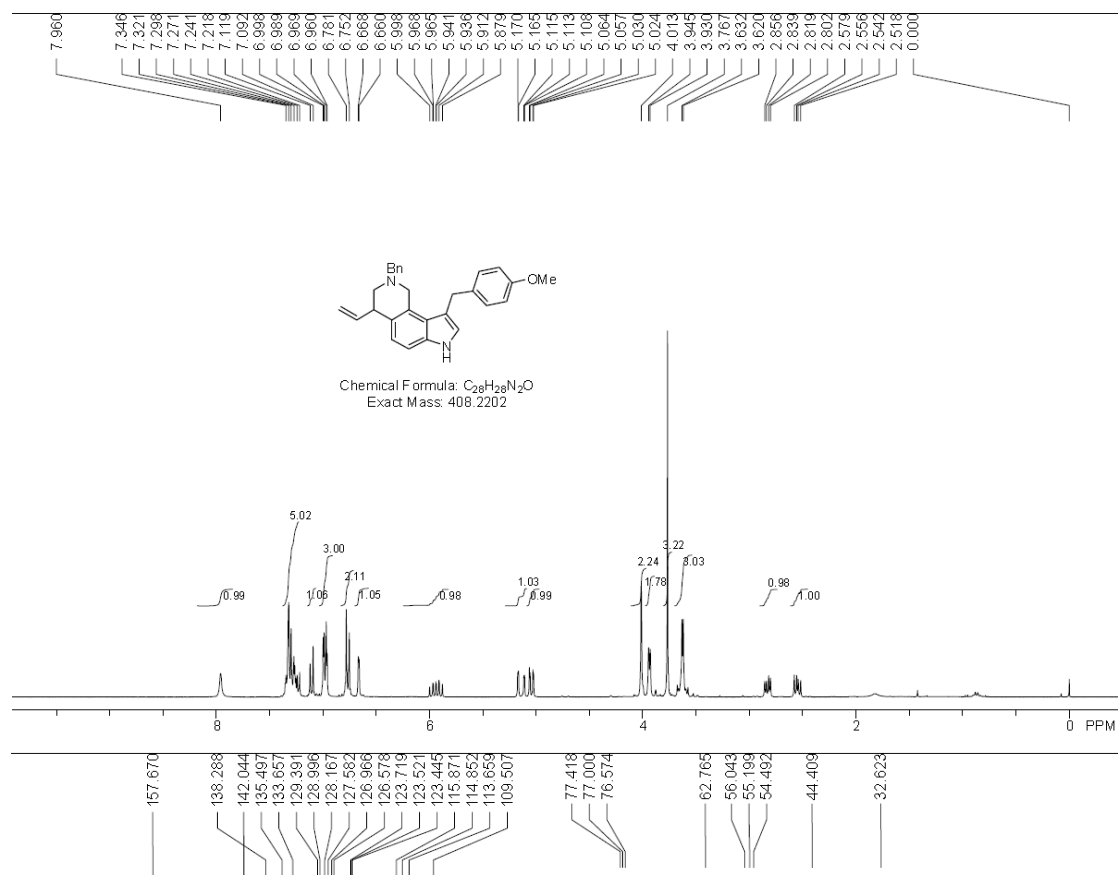


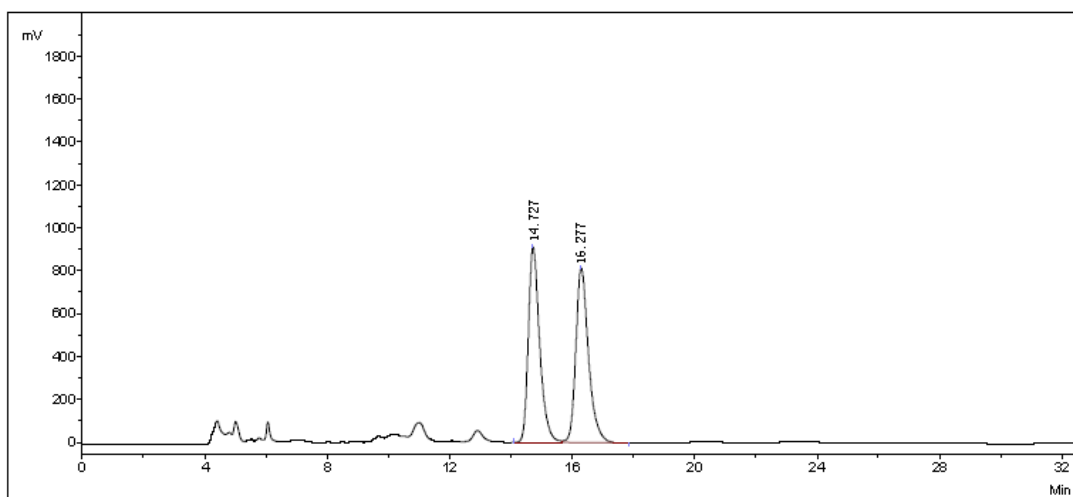


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	14.332	115691.8	4641019.5	51.2587
2	2	Unknown	18.015	95307.0	4413098.2	48.7413
Total				210998.7	9054117.8	100.0000

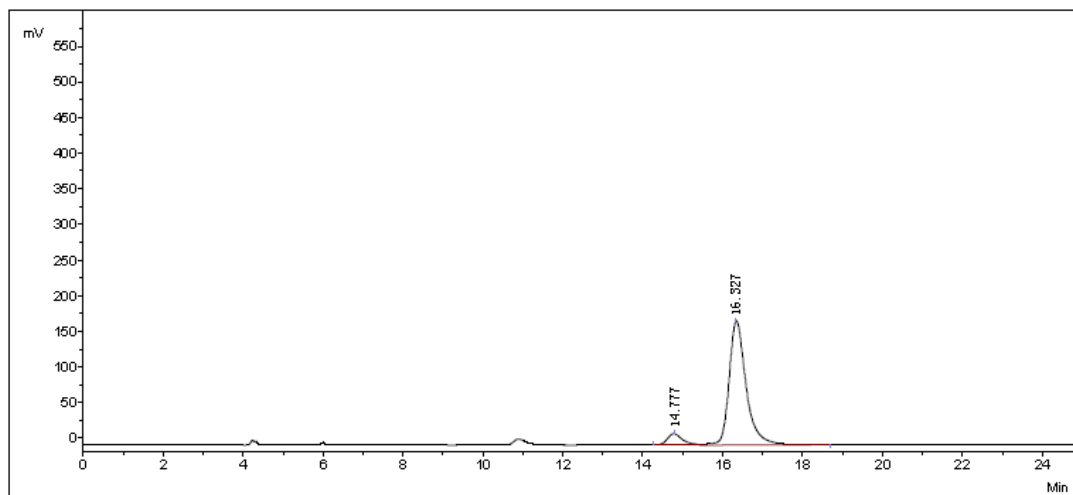
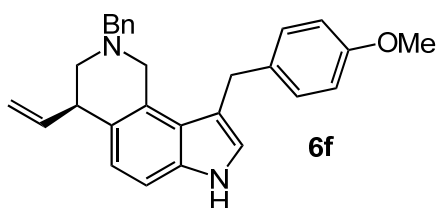


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	14.157	492805.6	21174049.4	90.5421
2	2	Unknown	18.515	41842.7	2211812.2	9.4579
Total				534648.3	23385861.6	100.0000

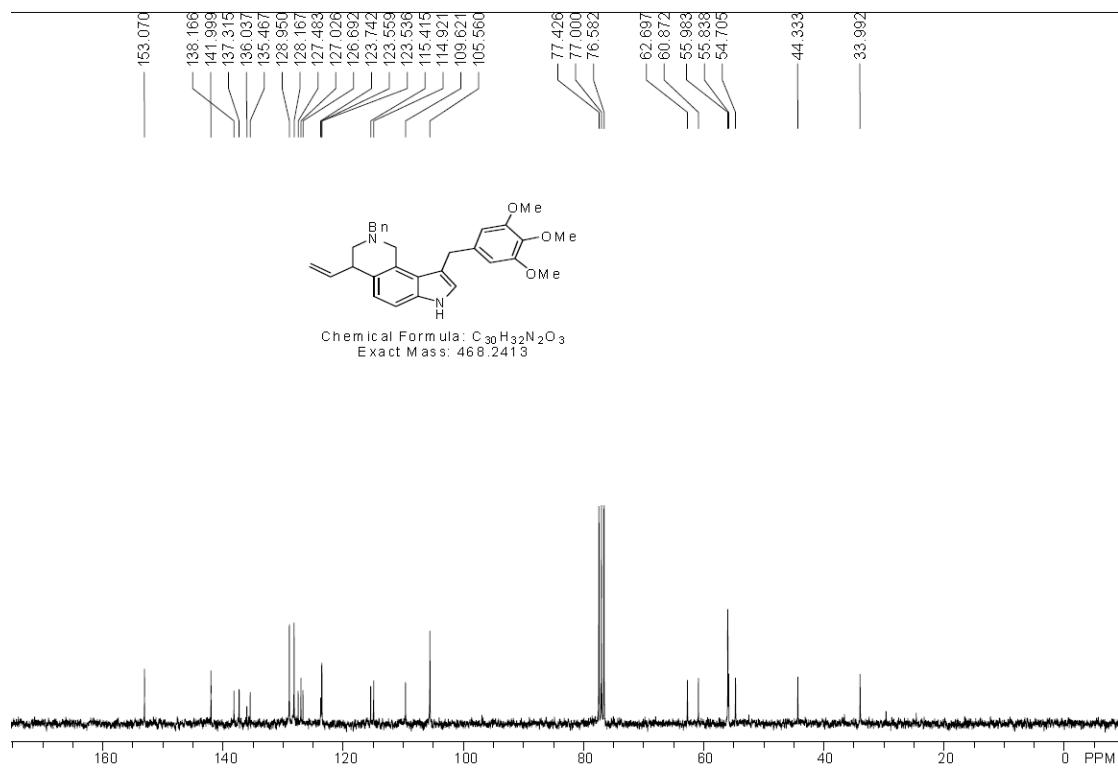
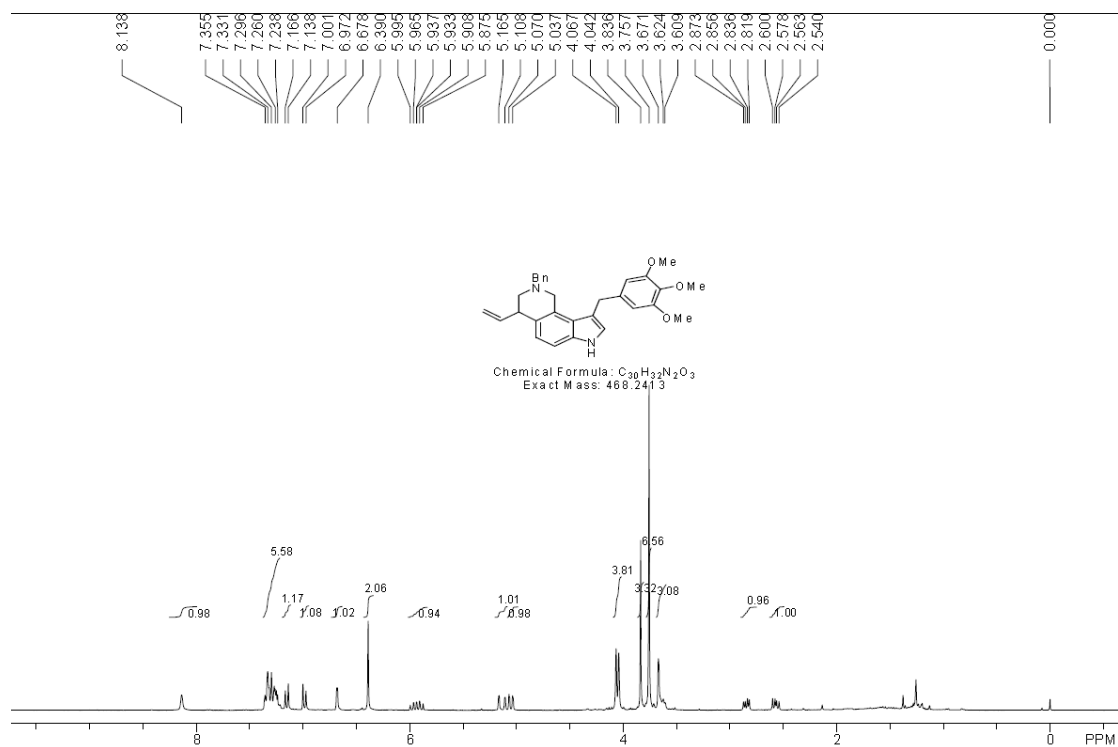


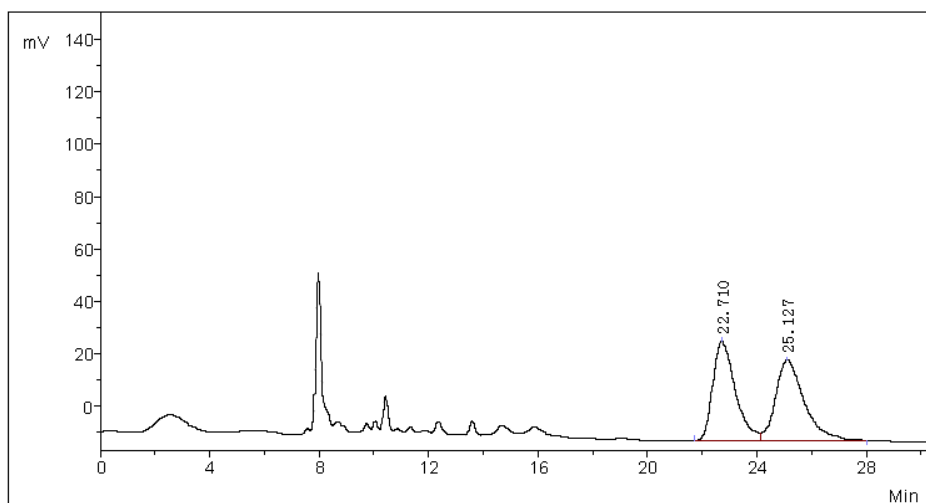


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	14.727	909519.2	23410913.5	49.9328
2	2	16.277	806337.7	23473918.5	50.0672
Total			1715856.9	46884832.0	100.0000

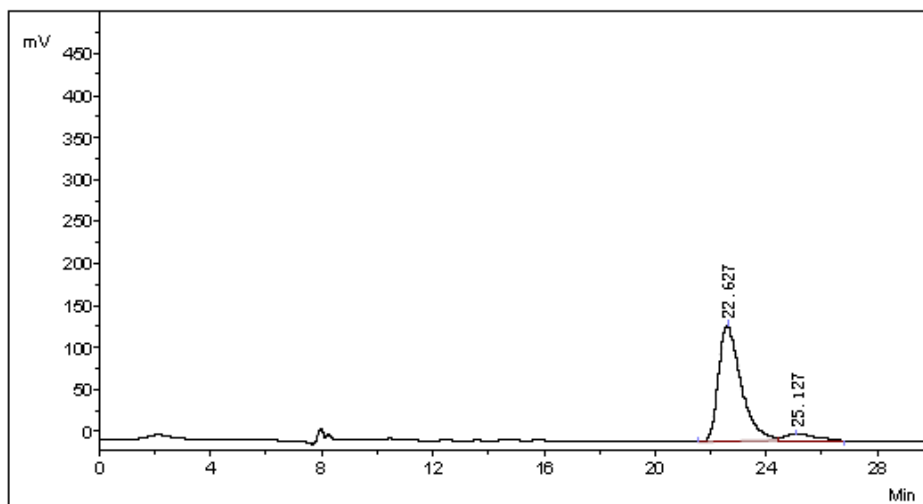
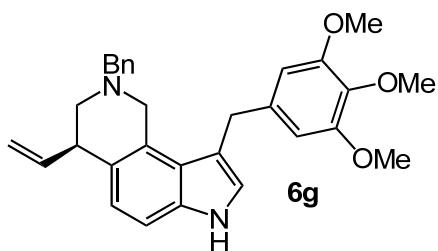


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	14.777	15783.6	414348.9	7.3986
2	2	16.327	173309.9	5185984.0	92.6014
Total			189093.5	5600332.9	100.0000

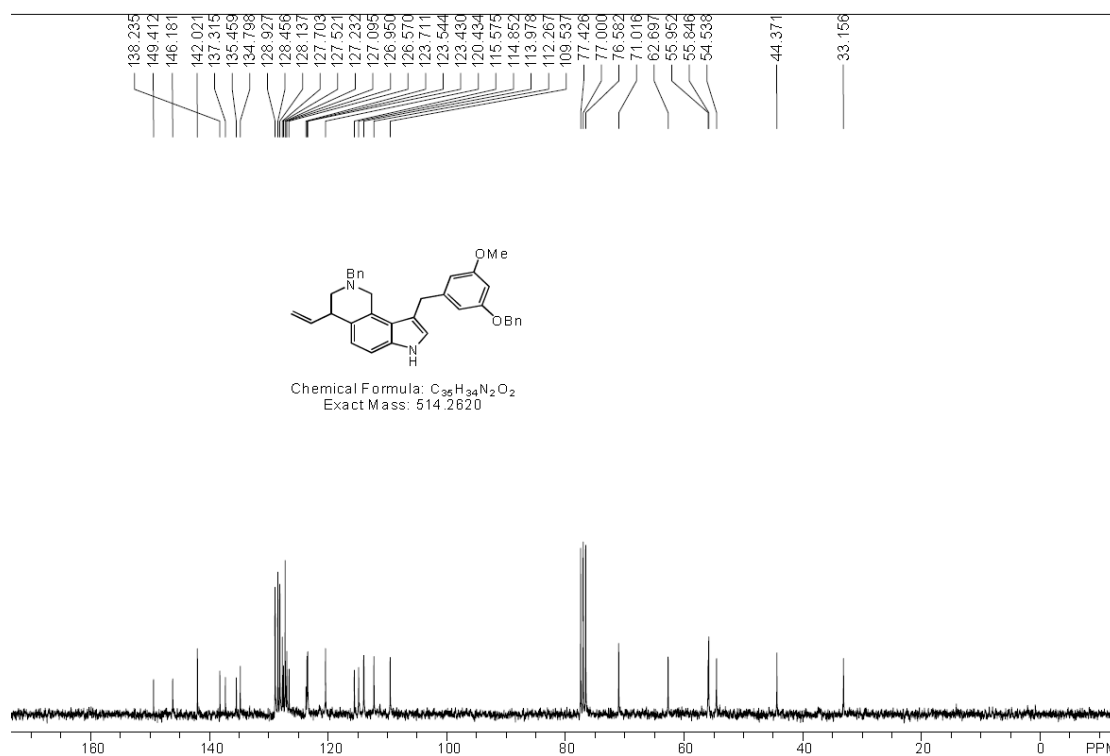
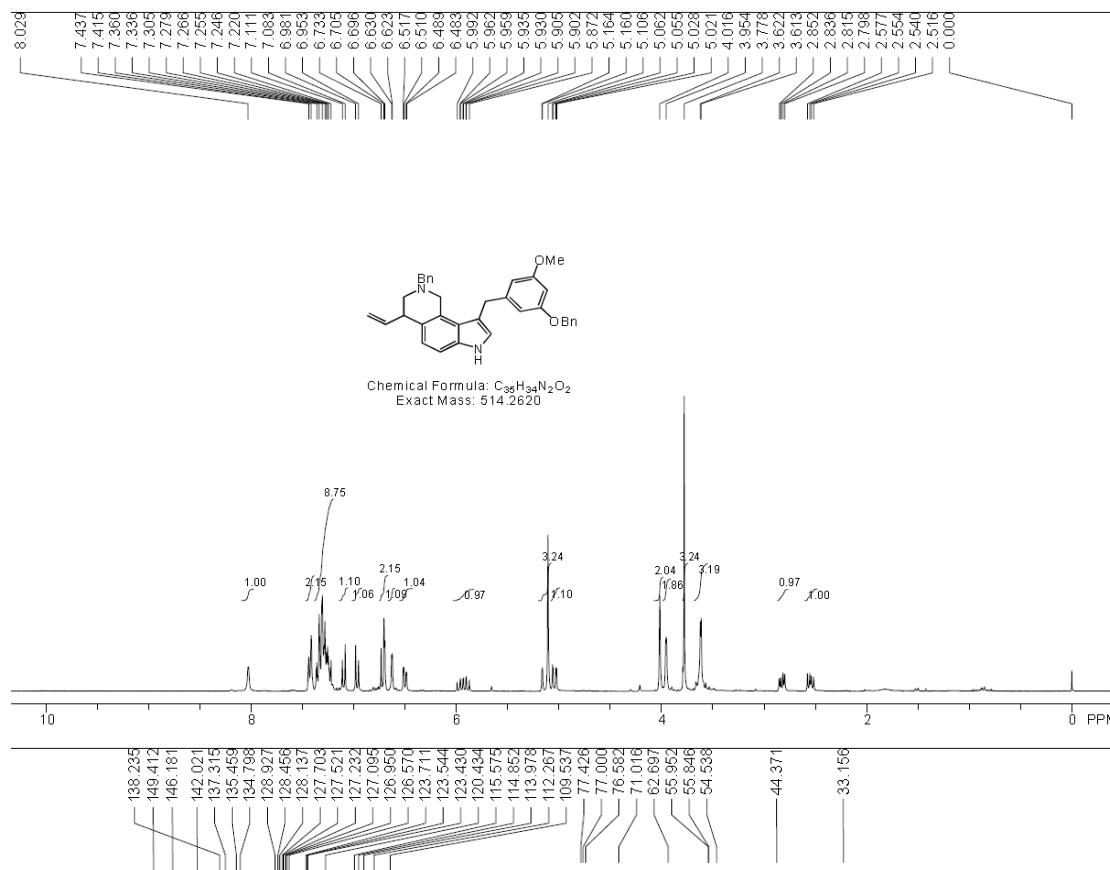


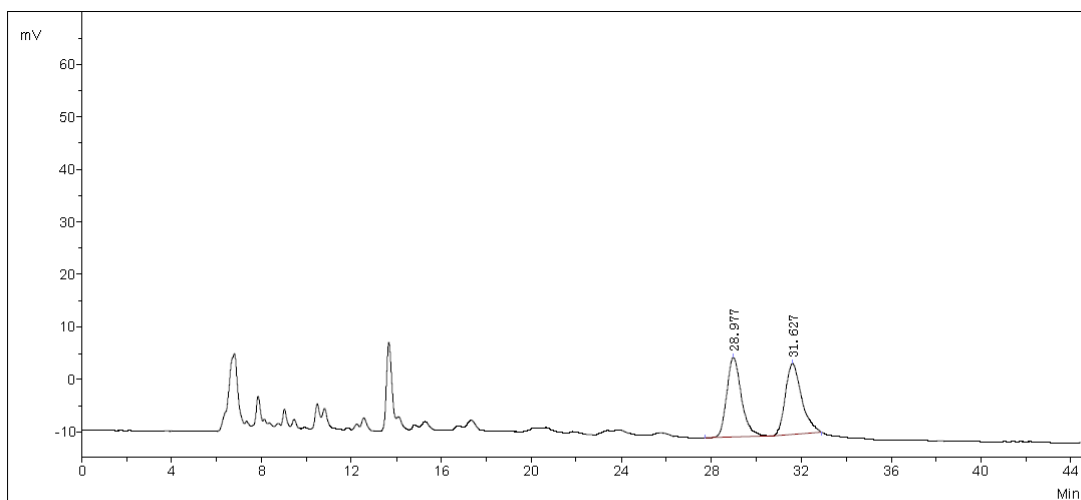


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	22.710	37567.2	2146381.4	49.3224
2	2	Unknown	25.127	30538.9	2205352.7	50.6776
Total				68106.1	4351734.1	100.0000

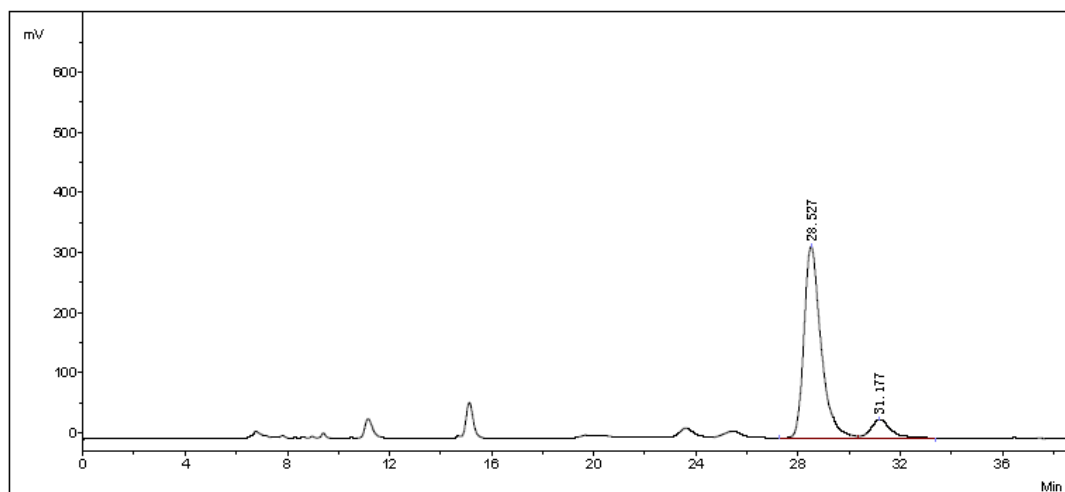
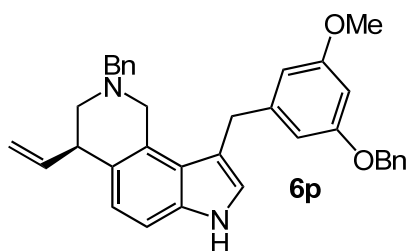


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	22.627	137912.4	7906489.5	92.2572
2	2	Unknown	25.127	8507.0	663558.7	7.7428
Total				146419.4	8570048.2	100.0000

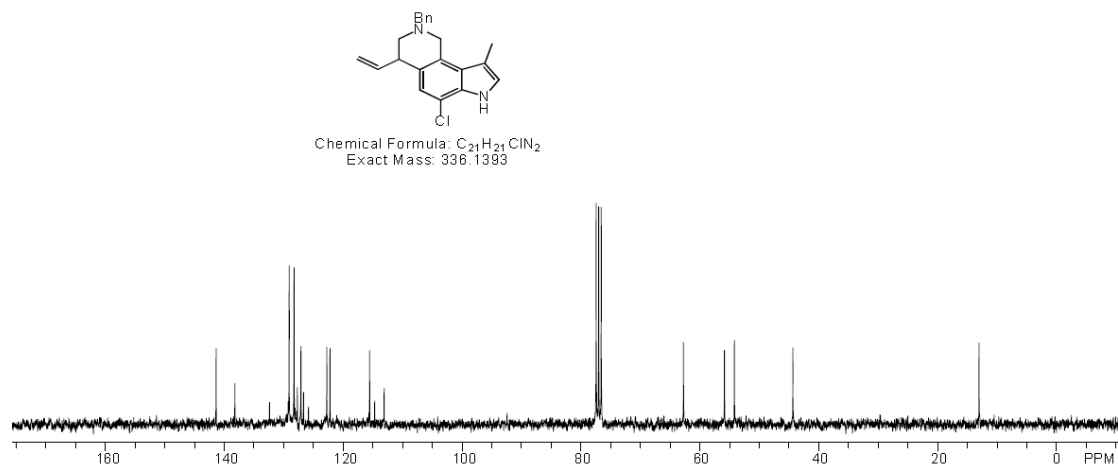
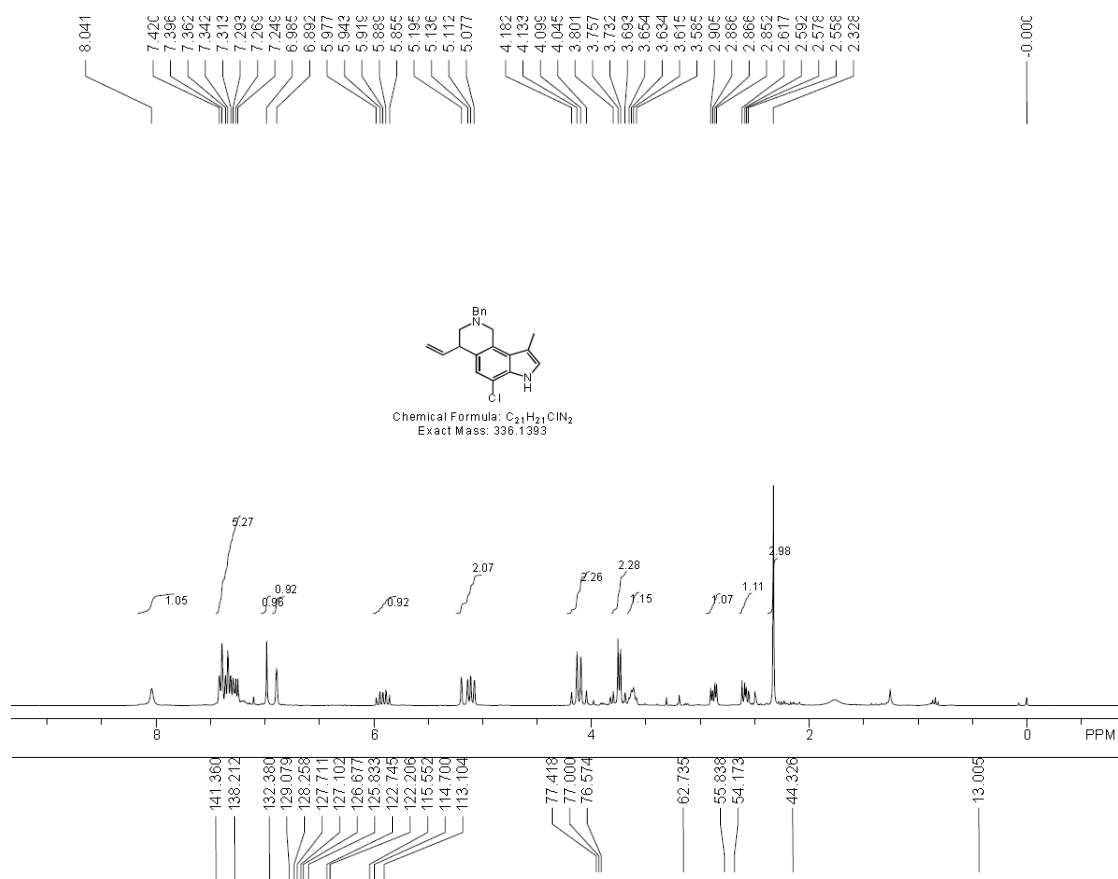




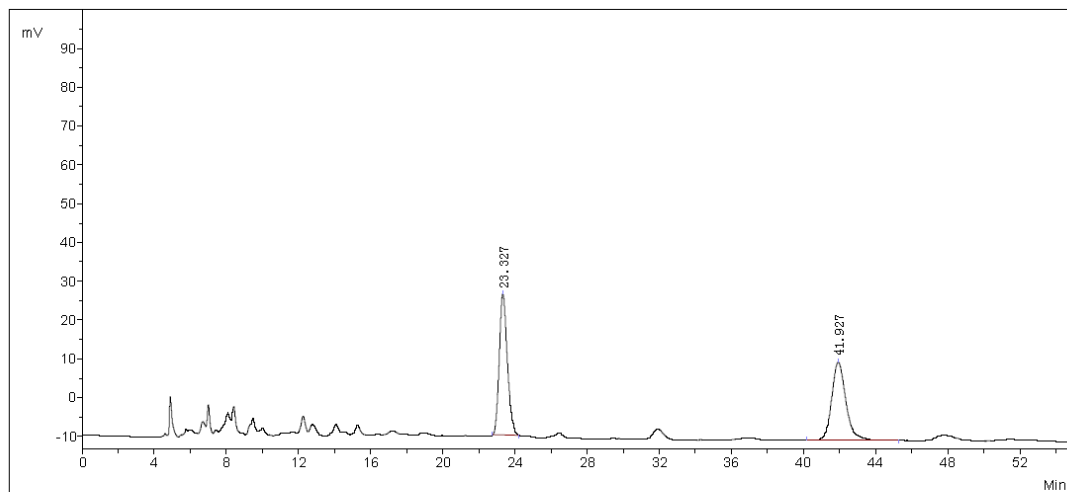
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	28.977	15122.1	680245.2	50.0924
2	2	31.627	13484.7	677735.3	49.9076
Total			28606.8	1357980.5	100.0000



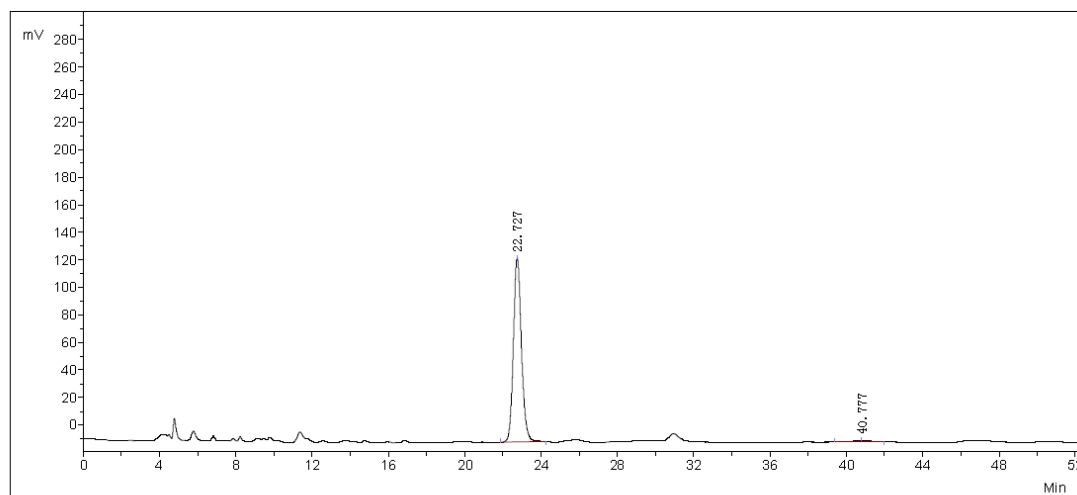
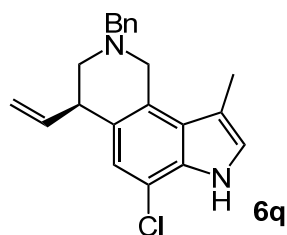
No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	28.527	318089.9	14786503.2	90.0348
2	2	31.177	30763.0	1636588.2	9.9652
Total			348852.9	16423091.4	100.0000



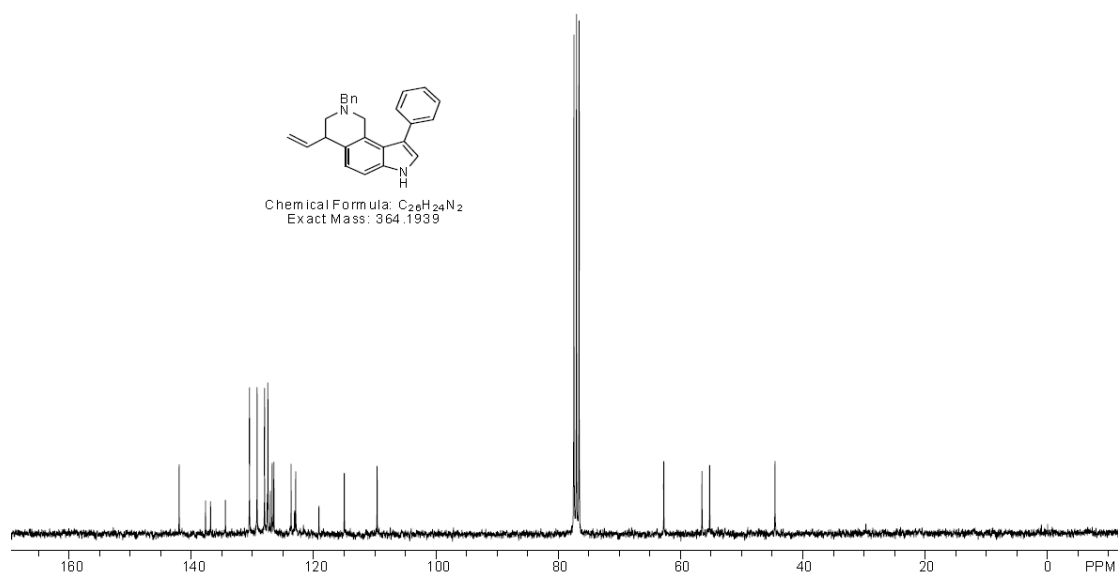
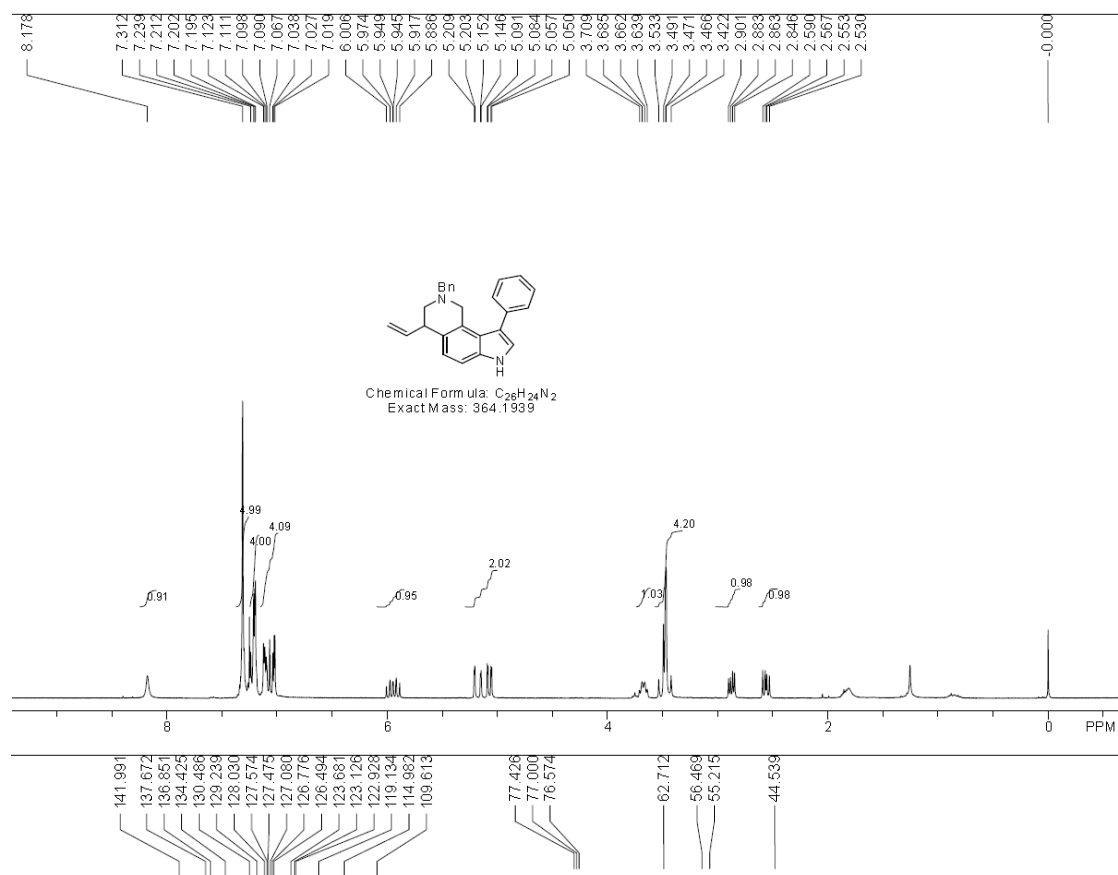


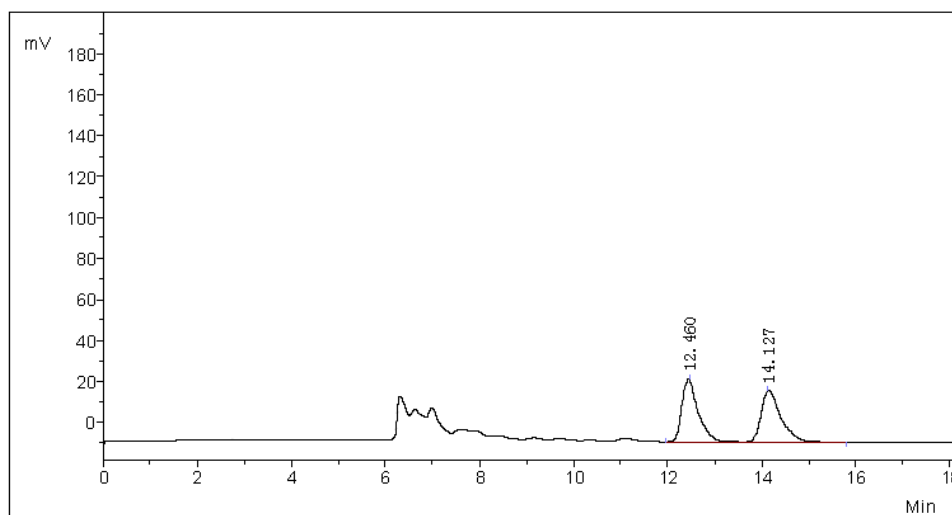


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	23.327	36355.7	1134447.7	50.5992
2	2	41.927	20142.9	1107579.2	49.4008
Total			56498.6	2242026.9	100.0000

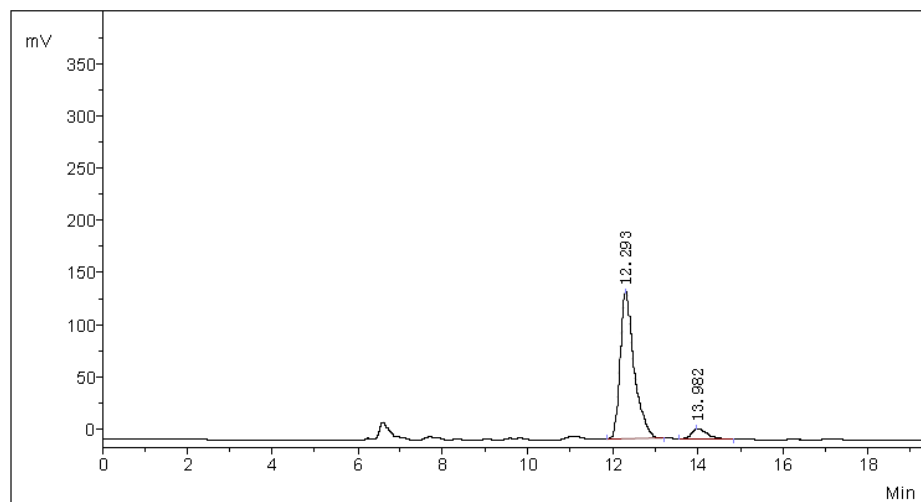
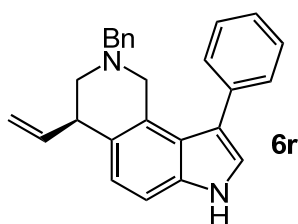


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	22.727	133059.4	3905006.0	98.7913
2	2	40.777	837.5	47775.5	1.2087
Total			133896.9	3952781.5	100.0000

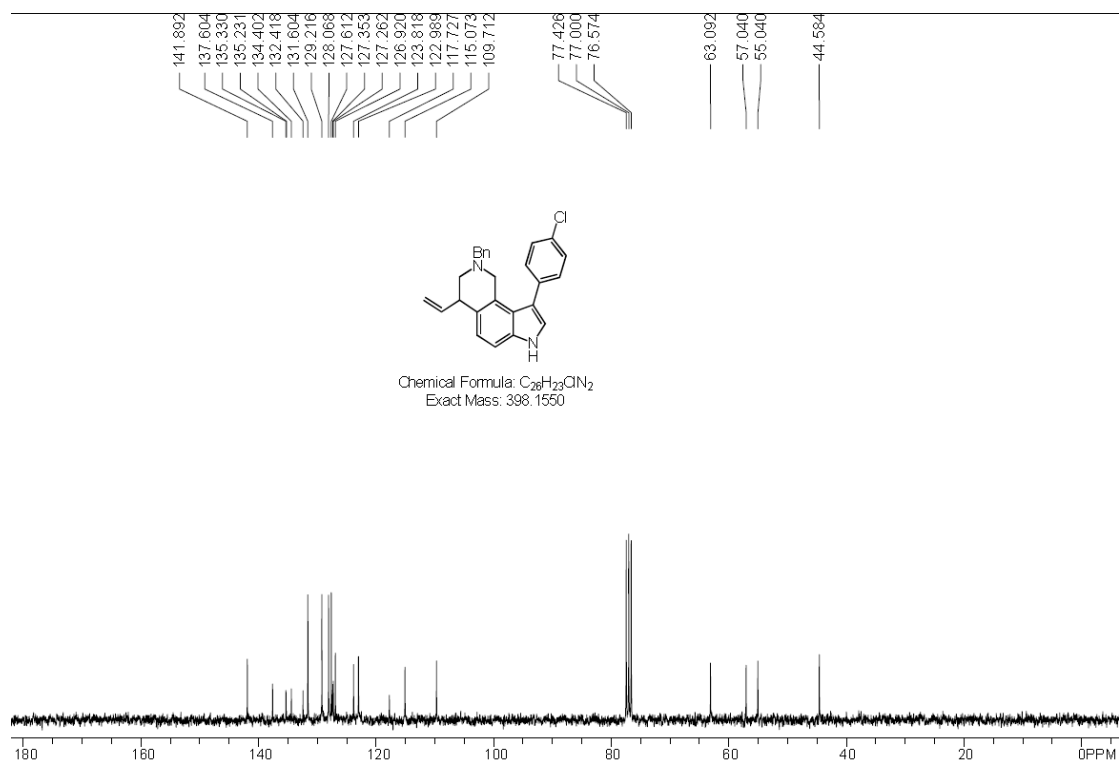
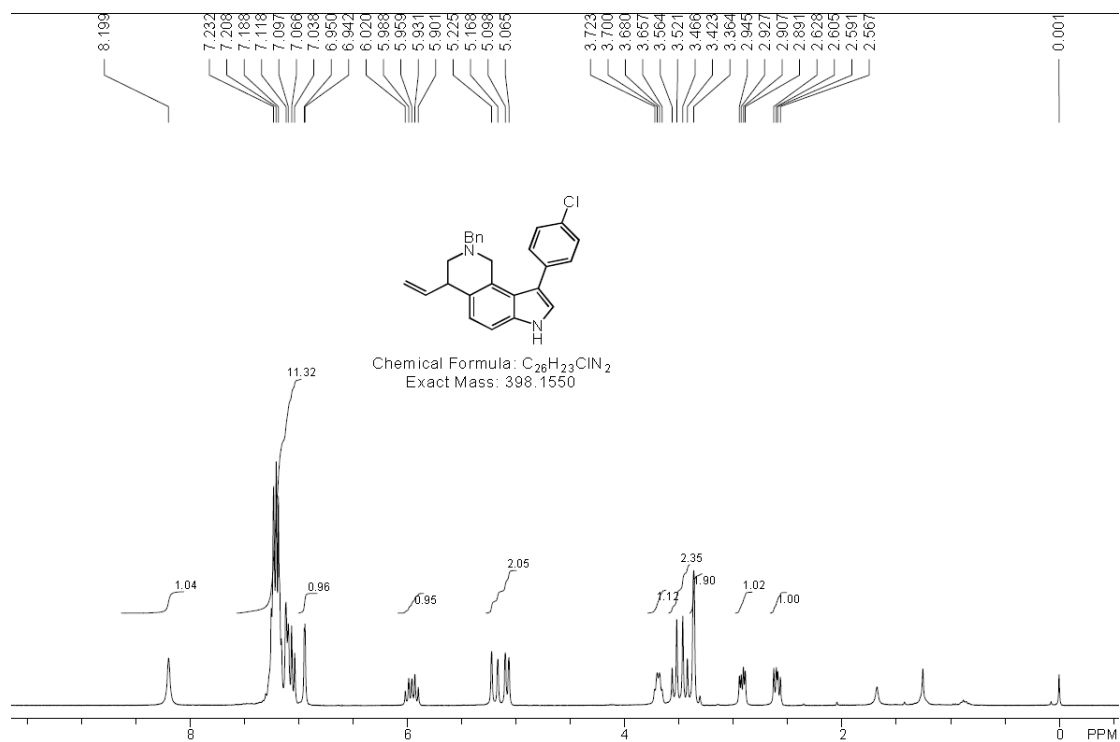


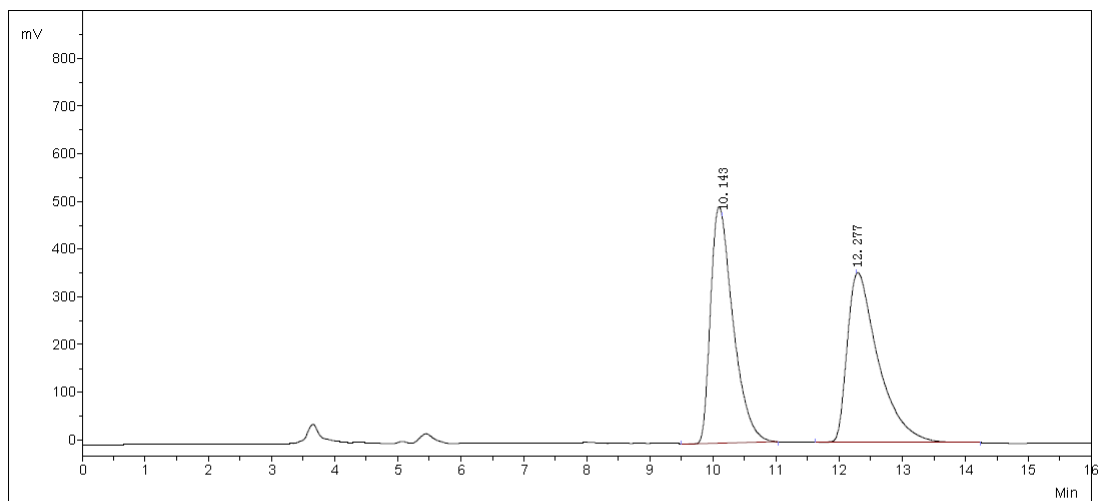


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	12.460	30892.2	745798.9	50.1396
2	2	Unknown	14.127	25097.6	741646.1	49.8604
Total				55989.8	1487445.0	100.0000

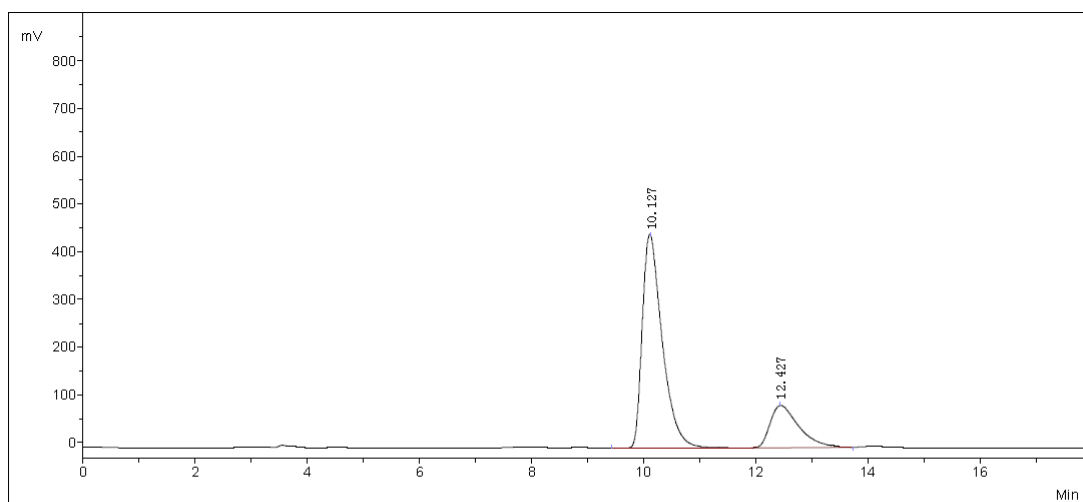
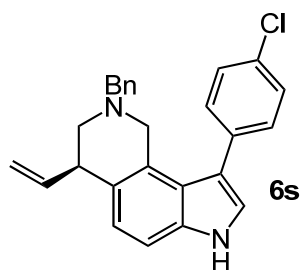


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	12.293	139971.4	3225210.0	92.7406
2	2	Unknown	13.982	9521.6	252458.9	7.2594
Total				149493.1	3477668.9	100.0000

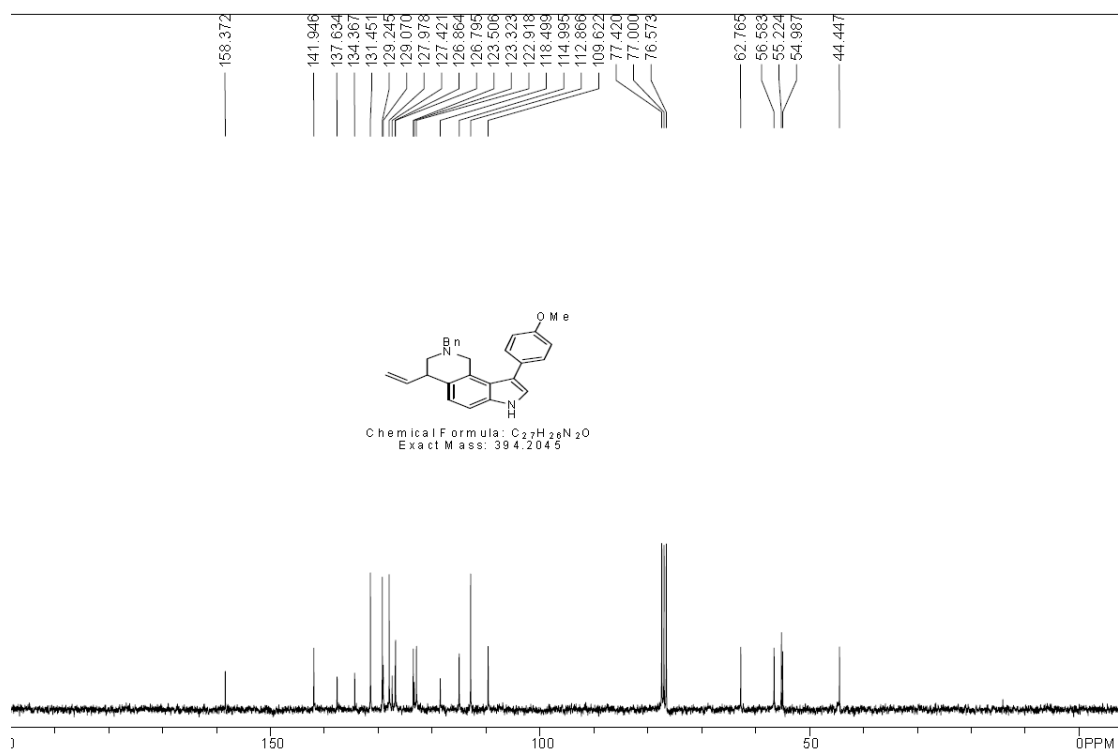
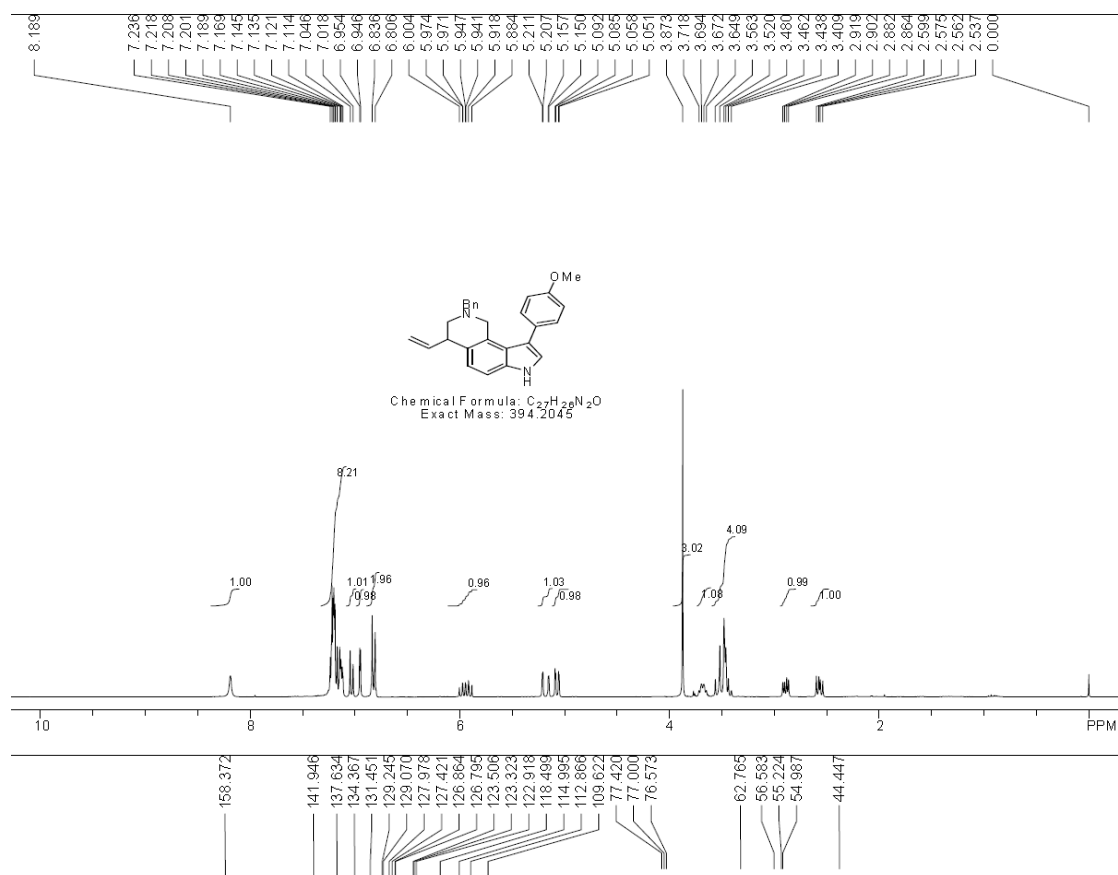


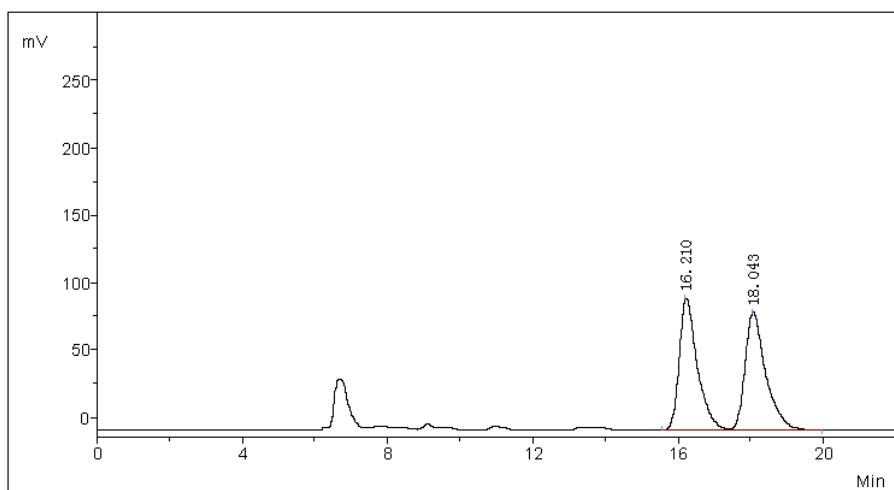


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	10.143	475807.0	12250444.2	50.1814
2	2	12.277	354594.0	12161860.7	49.8186
Total			830401.0	24412304.9	100.0000

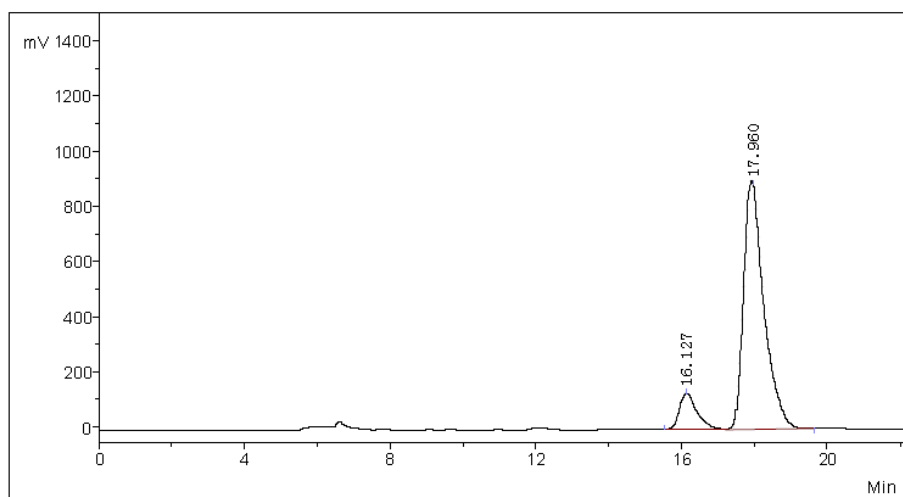
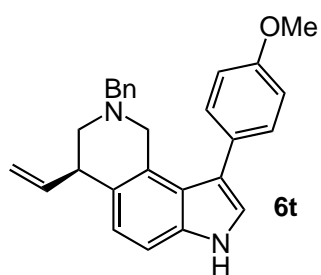


No.	PeakNo	R. Time	PeakHeight	PeakArea	PerCent
1	1	10.127	445597.4	11057270.2	77.9268
2	2	12.427	88162.5	3132042.4	22.0732
Total			533759.9	14189312.6	100.0000





No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	16.210	96641.7	3329551.6	49.4923
2	2	Unknown	18.043	86016.2	3397858.7	50.5077
Total				182657.9	6727410.3	100.0000



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	16.127	132579.4	4417942.4	11.2793
2	2	Unknown	17.960	890454.1	34750500.9	88.7207
Total				1023033.5	39168443.3	100.0000